Expeditious Synthesis of 1-Aminoindane Derivatives by [1,4]-Hydride Shift Mediated C(sp^3)–H Bond Functionalization

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Supporting Information

General experimental procedures

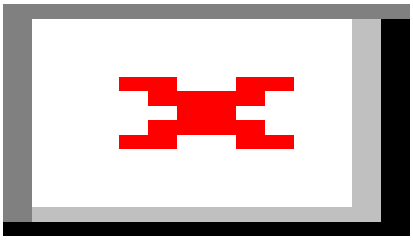
All reactions utilizing air- and moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry nitrogen. Ethereal solvents (THF, Et_2O) were distilled from benzophenone ketyl. Dichloromethane and 1,2-dichloroethane were distilled over CaH_2. Benzene and toluene were distilled over CaH_2, and stored over 4A molecular sieves. *N*,*N*-Dimethylformamide (DMF) was distilled over CaH_2, and stored over 4A molecular sieves.

For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. Column chromatography and preparative TLC (PTLC) were performed on PSQ 60B, Fuji Silysia Chemical Ltd. and Wakogel B-5F, Wako Pure Chemical Industries, respectively.

Melting point (mp) determinations were performed by using a AS ONE ATM-01 instrument and are uncorrected. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR were measured on a varian-400 MR (Varian Ltd., 400 MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane for ^{1}H, C_6F_6 for ^{19}F, and H_3PO_4 for ^{31}P NMR, 0.00 ppm), and coupling constants are reported as hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet. Infrared (IR) spectra were recorded on a FTIR-8600PC instrument (Shimadzu Co.). Elemental analysis (EA) was carried out on Flash2000 instrument (Amco Inc.).

1. Preparation of starting materials.

Scheme 1. General synthetic route to benzylidene malonate.[1] Preparation of **3a** is shown as a representative example.



Synthesis of 2-((diisopropylamino)methyl)benzaldehyde (s3):

To a solution of commercially available **s1** (1.25 g, 5.00 mmol) in toluene (10.0 mL) were successively added *i*-Pr_2NEt (1.00 mL, 5.74 mmol), and *i*-Pr_2NH (0.770 mL, 5.49 mmol). After the mixture was heated to reflux for 16 h, the reaction was quenched by addition of H_2O. The crude mixture was extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 40/1) to give **s2** (1.10 g) as a brown oil. At this moment, s5 could not be isolated as a pure compound, so this crude material was used for next reaction without further purification.

To a solution of **s2** in THF (20.0 mL) was added *n*-BuLi (1.60 M in hexane, 3.10 mL, 4.90 mmol) at –78 °C. The reaction mixture was stirred for 10 min at –78 °C, to which DMF (0.50 mL, 6.1 mmol) was added. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ at –78 °C. The crude mixture was extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 8/1) to afford aldehyde **s3** (748 mg, 68% from **s1**) as red oil.

IR (neat) 3065, 3028, 2965, 2931, 2871, 2729, 1764, 1693, 1599, 1572, 1465, 1383, 1364, 1324, 1287, 1202, 1174, 1158, 1139, 1119, 1049, 960, 887, 858, 759, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (d, 12H, J = 6.8 Hz), 3.01 (sept, 2H, J = 6.8 Hz), 4.03 (s, 2H), 7.36 (dd, 1H, J = 7.6, 7.6 Hz), 7.51 (ddd, 1H, J = 1.6, 7.6, 7.6 Hz), 7.67 (d, 1H, J = 7.6 Hz), 7.81 (dd, 1H, J = 1.6, 7.6 Hz), 10.46 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 46.4, 47.7, 126.6, 129.7, 130.0, 133.0, 134.4, 145.0, 192.5

Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.51; H, 9.45; N, 6.17.

Synthesis of dimethyl 2-(2-((diisopropylamino)methyl)benzylidene)malonate (3a):

To a solution of **s3** (1.01 g, 3.85 mmol) in benzene (23.0 mL) were successively added dimethyl malonate (0.500 mL, 4.40 mmol), piperidine (0.500 mL, 5.10 mmol), and AcOH (0.320 mL, 5.57 mmol) at room temperature. The reaction mixture was heated to reflux for 1.5 h. The crude mixture was concentrated in vacuo, and the residue was purified by column chromatography (silica gel, hexane/EtOAc = 8/1) to give **3a** (1.13 g, 73%) as a yellow solid.

Mp. 79–82 °C.

IR (KBr) 2968, 2878, 1730, 1699, 1618, 1601, 1439, 1384, 1303, 1265, 1235, 1205, 1192, 1173, 1122, 1107, 1069, 1019, 985, 954, 926, 890, 847, 819, 787, 766, 701 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (d, 12H, J = 6.4 Hz), 2.98 (sept, 2H, J = 6.8 Hz), 3.68 (s, 3H), 3.71 (s, 2H), 3.84 (s, 3H), 7.19 (ddd, 1H, J = 1.2, 7.6, 7.6 Hz), 7.23-7.27 (m, 1H), 7.30 (ddd, 1H, J = 1.2, 7.6, 7.6 Hz), 7.44 (d, 1H, J = 7.6 Hz), 8.37 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 47.3, 47.8, 52.2, 52.4, 125.6, 126.7, 127.8, 129.6, 129.8, 133.1, 141.1, 144.1, 164.5, 167.0.

Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16; N, 4.20. Found: C, 68.56; H, 8.28; N, 3.91.

2-((diethylamino)methyl)benzaldehyde(**5**).

Yellow oil.

Yield: 85%.

IR (neat) 2970, 2934, 2873, 2805, 1694, 1600, 1574, 1455, 1386, 1290, 1209, 1165, 1120, 1059, 984, 849, 810, 753, 637 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, 6H, *J* = 7.2 Hz), 2.52 (q, 4H, *J* = 7.2 Hz), 3.87 (s, 2H), 7.37–7.49 (m, 2H), 7.49 (ddd, 1H, *J* = 1.2, 7.6, 7.6 Hz), 7.85 (dd, 1H, *J* = 1.2, 7.6 Hz), 10.47 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 46.2, 55.1, 127.3, 129.0, 130.2, 133.0, 135.0, 142.8, 192.3.

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.35; H, 9.18; N, 7.28.

Dimethyl 2-(2-((diethylamino)methyl)benzylidene)malonate (**3b**).

Yellow oil.

Yield: 75%.

IR (neat) 3064, 3023, 2969, 2952, 2937, 2900, 2874, 2800, 2756, 1735, 1627, 1601, 1484, 1436, 1385, 1371, 1294, 1261, 1214, 1188, 1166, 1122, 1068, 987, 944, 767 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, 6H, *J* = 7.2 Hz), 2.48 (q, 4H, *J* = 7.2 Hz), 3.59 (s, 2H), 3.69 (s, 3H), 3.85 (s, 3H), 7.18–7.38 (m, 4H), 8.40 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 46.5, 52.1, 52.2, 56.2, 125.3, 126.9, 127.7, 129.4, 129.9, 133.3, 139.4, 143.8, 164.4, 166.8.

Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 66.62; H, 7.61; N, 4.66.

2-((dibenzylamino)methyl)benzaldehyde (**s4**).

White solid.

Mp. 91–92 °C.

Yield: 94%.

IR (KBr) 2924, 2880, 2790, 2359, 1688, 1598, 1494, 1453, 1400, 1362, 1322, 1287, 1234, 1210, 1111, 1075, 1028, 984, 959, 916, 883, 869, 851, 811, 755, 639 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ3.51 (s, 4H), 3.89 (s, 2H), 7.22–7.53 (m, 14H), 7.84 (d, 1H, J = 7.6 Hz), 10.20 (s, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 58.2, 127.2, 127.7, 128.3, 129.0, 129.2, 130.7, 133.2, 135.0, 138.6, 141.9, 192.6.

Anal. Calcd for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.93; H, 6.85; N, 4.18.

Dimethyl 2-(2-((dibenzylamino)methyl)benzylidene)malonate (**3c**).

White solid.

Mp. 119–121 °C.

Yield: 47%.

IR (KBr) 3059, 3034, 2947, 2931, 2889, 2805, 2787, 2710, 1730, 1724, 1621, 1599, 1495, 1452, 1439, 1382, 1361, 1272, 1240, 1219, 1187, 1161, 1127, 1105, 1068, 1028, 993, 972, 951, 931, 879, 861, 828, 770, 751, 741, 703 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 4H), 3.60 (s, 2H), 3.64 (s, 3H), 3.90 (s, 3H), 7.18–7.39 (m, 13H), 7.50 (d, 1H, J = 7.2 Hz), 8.28 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 52.5, 56.8, 58.2, 126.5, 126.9, 127.2, 128.0, 128.2, 128.9, 129.8, 130.3, 133.3, 138.7, 138.8, 143.5, 164.4, 166.8.

Anal. Calcd for $C_{27}H_{27}NO_4$: C, 75.50; H, 6.34; N, 3.26. Found: C, 75.68; H, 6.53; N, 3.31.

2-((Diphenylamino)methyl)benzaldehyde (**s5**).

White solid.

Mp. 157–159 °C.

Yield: 80%.

IR (KBr) 3057, 2832, 2741, 1690, 1589, 1500, 1448, 1415, 1399, 1374, 1347, 1299, 1256, 1230, 1195, 1109, 1091, 1071, 989, 851, 776, 753, 695, 657 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) □ 5.44 (s, 2H), 6.93 (dd, 2H, *J* = 7.2, 7.2 Hz), 7.00-–7.08 (m, 4H), 7.19–7.28 (m, 4H), 7.43 (dd, 1H, *J* = 7.2, 7.2 Hz), 7.51 (ddd, 1H, *J* = 1.2, 7.6, 7.6 Hz), 7.67 (d, 1H, *J* = 7.6 Hz), 7.84 (dd, 1H, *J* = 1.2, 7.2 Hz), 10.18 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) □ 54.7, 120.4, 121.5, 127.1, 127.7, 129.3, 133.3, 134.0, 135.3, 141.8, 147.7, 193.7.

Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.72; H, 5.89; N, 4.90.

Dimethyl 2-(2-((diphenylamino)methyl)benzylidene)malonate (**3d**).

White solid.

Mp. 100–102 °C.

Yield: 86%.

IR (KBr) 3033, 2945, 1721, 1632, 1590, 1497, 1434, 1371, 1263, 1235, 1188, 1106, 1074, 1004, 988, 974, 950, 936, 876, 836, 773, 753, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) □ 3.70 (s, 3H), 3.84 (s, 3H), 4.99 (s, 2H), 6.92–6.98 (m, 2H), 7.00–7.07 (m, 4H), 7.17–7.33 (m, 7H), 7.48 (d, 1H, *J* = 7.6 Hz), 8.04 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) □ 52.5, 52.7, 54.4, 120.8, 121.7, 127.0, 128.1, 128.2, 129.3, 130.2, 131.6, 137.8, 141.5, 147.8, 164.1, 166.4.

Anal. Calcd for $C_{25}H_{23}NO_4$: C, 74.79; H, 5.77; N, 3.49. Found: C, 74.83; H, 5.52; N, 3.37.

2-((Diallylamino)methyl)benzaldehyde (**s6**).

Colorless oil.

Yield: 98%.

IR (neat) 3074, 3006, 2978, 2809, 1693, 1643, 1599, 1574, 1446, 1418, 1397, 1353, 1286, 1256, 1210, 1189, 1157, 1115, 996, 921, 847, 808, 756 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.06 (d, 4H, J = 6.4 Hz), 3.88 (brs, 2H), 5.10–5.23 (m, 4H), 5.76–5.92 (m, 2H), 7.33–7.55 (m, 2H), 7.50 (ddd, 1H, J = 1.2, 7.6, 7.6 Hz), 7.86 (dd, 1H, J = 1.6, 7.6 Hz), 10.43 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 54.8, 56.4, 118.0, 127.6, 129.3, 130.5, 133.1, 135.0, 135.1, 142.2, 192.4.

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.36; H, 7.73; N, 6.35.

Dimethyl 2-(2-((diallylamino)methyl)benzylidene)malonate (**3e**).

Pale red oil.

Yield: 95%.

IR (neat) 3073, 3005, 2952, 2804, 1735, 1627, 1436, 1366, 1261, 1213, 1119, 1068, 987, 922, 836, 766 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.02 (d, 4H, J = 6.8 Hz), 3.58 (s, 2H), 3.69 (s, 3H), 3.86 (s, 3H), 5.08–5.20 (m, 4H), 5.63–5.95 (m, 2H), 7.17–7.39 (m, 4H), 8.33 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 52.4, 56.1, 56.5, 115.6, 125.6, 127.2, 127.9, 129.6, 130.3, 133.5, 135.6, 139.1, 143.9, 164.5, 167.0.

Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.11; H, 7.25; N, 3.98.

2-(Piperidin-1-ylmethyl)benzaldehyde (**s7**).

Colorless oil.

Yield: 83%.

IR (neat) 2935, 28252, 2799, 2756, 1695, 1600, 1454, 1396, 1368, 1344, 1288, 1246, 1211, 1154, 1112, 1038, 994, 860, 806, 788, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35–1.58 (m, 6H), 2.38 (brs, 4H), 3.74 (s, 2H), 7.30–7.44 (m, 2H), 7.48 (ddd, 1H, J = 1.2, 7.6, 7.6 Hz), 7.86 (d, 1H, J = 1.2, 7.6 Hz) 10.45 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 24.3, 25.9, 54.2, 60.6, 127.5, 128.9, 130.4, 133.0, 135.2, 141.8, 192.3.

Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.87; H, 8.37; N, 6.98.

Dimethyl 2-(2-(piperidin-1-ylmethyl)benzylidene)malonate (**3f**).

Colorless oil.

Yield: quant.

IR (neat) 2935, 2852, 2798, 2756, 1734, 1627, 1436, 1367, 1296, 1259, 1214, 1155, 1115, 1068, 1038, 992, 944, 860, 835, 785, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37–1.60 (m, 6H), 2.37 (brs, 2H), 3.48 (s, 2H), 3.69 (s, 3H), 3.86 (s, 3H), 7.18–7.38 (m, 4H), 8.37 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 25.7, 52.0, 52.2, 54.0, 61.6, 124.8, 127.0, 127.6, 129.3, 129.7, 133.4, 138.5, 143.9, 164.4, 166.8

Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41. Found: 67.94; H, 7.54; N, 4.21.

2-((2,2,6,6-Tetramethylpiperidin-1-yl)methyl)benzaldehyde (**s8**).

Colorless oil.

Yield: quant.

IR (neat) 3066, 2965, 2928, 2724, 1696, 1601, 1571, 1477, 1458, 1402, 1381, 1367, 1350, 1298, 1263, 1237, 1188, 1154, 1133, 1080, 1043, 1026, 975, 948, 919, 904, 860, 832, 760, 690, 659 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (brs, 12H), 1.51–1.74 (brm, 6H), 4.23 (s, 2H), 7.35 (dd, 1H, J = 7.6, 7.6 Hz), 7.56 (ddd, 1H, J = 1.2, 7.6, 7.6 Hz), 7.74 (dd, 1H, J = 1.2, 7.6 Hz), 8.25 (d, 1H, J = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 41.2, 15.6, 54.7, 125.7, 129.4, 132.4, 133.1, 133.7, 149.3, 193.6.

Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 78.55; H, 9.62; N, 5.70.

Dimethyl 2-(2-((2,2,6,6-tetramethylpiperidin-1-yl)methyl)benzylidene)malonate (**3g**).

White solid.

Mp. 60–62 °C.

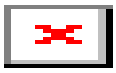
Yield: 80%.

IR (KBr) 3060, 2977, 2921, 2844, 1740, 1719, 1634, 1601, 1454, 1442, 1433, 1380, 1294, 1265, 1215, 1133, 1087, 1065, 1025, 984, 955, 938, 912, 903, 870, 849, 834, 812, 797, 785, 758, 721, 709, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (brs, 12H), 1.51–1.68 (brm, 6H), 3.66 (s, 3H), 3.74 (s, 2H), 3.88 (s, 3H), 7.12 (dd, 1H, J = 8.0, 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.34 (dd, 1H, J = 8.0, 8.0 Hz), 7.96 (d, 1H, J = 8.0 Hz), 8.12 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 41.2, 45.5, 52.3, 52.5, 54.8, 125.5, 126.8, 127.3, 128.3, 129.4, 130.5, 142.6, 144.4, 164.3, 166.6.

Anal. Calcd for $C_{22}H_{31}NO_4$: C, 70.75; H, 8.37; N, 3.75. Found: C, 70.96; H, 8.46; N, 3.79.



2-((3,4-Dihydroisoquinolin-2(1*H*)-yl)methyl)benzaldehyde (**s9**).

Yellow solid.

Mp. 98–99 °C.

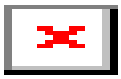
Yield: 90%.

IR (KBr) 3093, 3062, 3028, 2892, 2859, 2827, 2734, 1691, 1599, 1573, 1506, 1450, 1418, 1401, 1373, 1346, 1297, 1253, 1215, 1194, 1159, 1119, 1033, 997, 986, 957, 932, 856, 829, 748, 691, 658 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (t, 2H, J = 5.6 Hz), 2.85 (t, 2H, J = 5.6 Hz), 3.67 (s, 2H), 4.00 (s, 2H), 6.90–7.18 (m, 4H), 7.38–7.60 (m, 3H), 7.89 (d, 1H, J = 7.6 Hz), 10.45 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 29.1, 50.4, 55.8, 59.4, 125.6, 126.1, 126.4, 127.8, 128.6, 129.8, 130.4, 133.3, 134.3, 134.5, 135.0, 141.0, 192.1.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.35; H, 6.98; N, 5.63.



Dimethyl 2-(2-((3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)benzylidene)malonate (**3i**).

Pale yellow oil.

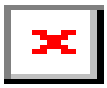
Yield: quant.

IR (neat) 3066, 3023, 2950, 2924, 2803, 2760, 1732, 1627, 1483, 1435, 1366, 1261, 1215, 1068, 987, 934, 835, 750 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.77 (d, 2H, J = 5.6 Hz), 2.89 (d, 2H, J = 5.6 Hz), 3.62 (s, 2H), 3.69 (s, 3H), 3.72 (s, 2H), 3.78 (s, 3H), 6.96 (d, 1H, J = 7.2 Hz), 7.03–7.19 (m, 3H), 7.20–7.38 (m, 3H), 7.42 (d, 1H, J = 7.2 Hz), 8.36 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0, 50.5, 52.1, 52.3, 55.5, 60.5, 125.4, 125.9, 126.0, 126.3, 127.3, 127.8, 128.5, 129.6, 129.9, 133.5, 134.2, 134.6, 137.8, 143.4, 164.3, 166.6.

Anal. Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.57; H, 6.27; N, 3.56.



2-((Dibenzylamino)methyl)-5-methylbenzaldehyde (**s10**).

Brown solid

Mp. 99–101 °C.

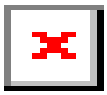
Yield: 91% (synthesized from 2-bromo-1-(bromomethyl)-4-methylbenzene[2]).

IR (KBr) 3085, 3061, 3026, 2922, 2799, 1686, 1609, 1570, 1495, 1453, 1398, 1364, 1302, 1282, 1246, 1224, 1205, 1156, 1106, 1071, 1028, 989, 967, 939, 910, 871, 839, 805, 745, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.49 (s, 4H), 3.83 (s, 2H), 7.19–7.40 (m, 10H), 7.66 (s, 1H), 10.18 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 55.1, 58.0, 127.0, 128.2, 128.9, 129.2, 130.7, 133.8, 134.7, 137.4, 138.6, 138.9, 192.6.

Anal. Calcd for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25. Found: C, 83.93; H, 6.84; N, 4.42.



Dimethyl 2-(2-((dibenzylamino)methyl)-5-methylbenzylidene)malonate (**3j**).

Colorless oil.

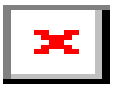
Yield: 90%.

IR(neat) 3085, 3061, 3027, 3003, 2950, 2925, 2796, 2711, 1733, 1626, 1607, 1495, 1453, 1436, 1365, 1268, 1225, 1164, 1122, 1108, 1070, 1028, 996, 971, 912, 874, 836, 818, 795, 747, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.50 (s, 4H), 3.56 (s, 2H), 3.65 (s, 3H), 3.90 (s, 3H), 7.09 (s, 1H), 7.13 (d, 1H, J = 8.0 Hz), 7.18–7.38 (m, 11H), 8.27 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 52.1, 52.4, 56.6, 58.1, 126.2, 126.8, 128.1, 128.5, 128.8, 130.4, 120.5, 133.1, 135.7, 136.8, 138.8, 143.5, 164.4, 166.8.

Anal. Calcd for $C_{28}H_{29}NO_4$: C, 75.82; H, 6.59; N, 3.16. Found: C, 75.55; H, 6.32; N, 3.29.



2-((Dibenzylamino)methyl)-5-methoxybenzaldehyde (**s11**).

Yellow solid.

Mp. 62–64 °C.

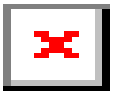
Yield: 87% (synthesized from 2-bromo-1-(bromomethyl)- 4-methoxybenzene[3]).

IR (KBr) 3082, 3060, 3026, 2962, 2927, 2902, 2830, 2794, 2736, 2709, 1688, 1677, 1604, 1575, 1496, 1451, 1427, 1404, 1358, 1325, 1288, 1262, 1250, 1223, 1199, 1161, 1103, 1075, 1038, 1003, 984, 962, 937, 906, 866, 837, 810, 743, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47 (s, 4H), 3.80 (s, 2H), 3.82 (s, 3H), 7.03 (dd, 1H, J = 2.8, 8.4 Hz), 7.21–7.40 (m, 12H), 10.18 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 54.9, 55.4, 58.1, 111.8, 120.1, 127.2, 128.3, 129.1, 132.4, 134.3, 135.9. 138.7, 159.2, 192.2.

Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05. Found: C, 80.15; H, 6.91; N, 3.83.



Dimethyl 2-(2-((dibenzylamino)methyl)-5-methoxybenzylidene)malonate (**3k**).

Yellow oil.

Yield: 85%.

IR(neat) 3060, 3027, 2950, 2795, 1731, 1624, 1605, 1573, 1494, 1453, 1435, 1365, 1229, 1206, 1168, 1120, 1070, 1038, 992, 916, 813, 747, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 4H), 3.53 (s, 2H), 3.68 (s, 3H), 3.74 (s, 3H), 3.90 (s, 3H), 6.83–6.91 (m, 2H), 7.18–7.40 (m, 11H), 8.25 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 52.5, 55.2, 56.3, 58.1, 112.9, 115.8, 126.7, 126.8, 128.2, 128.9, 130.9, 131.7, 134.2, 139.0, 143.1, 158.6, 164.4, 166.8.

Anal. Calcd for $C_{28}H_{29}NO_5$: C, 73.18; H, 6.36; N, 3.05. Found: C, 73.16; H, 6.38; N, 3.25.

2-((Dibenzylamino)methyl)-5-fluorobenzaldehyde (**s12**).

Yellow solid.

Mp. 46–48 °C.

Yield: 85% (synthesized from 2-bromo-1-(bromomethyl)-4-fluorobenzene[4]).

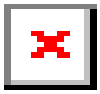
IR (KBr) 3086, 3063, 3029, 2884, 2802, 2713, 1689, 1608, 1587, 1494, 1453, 1422, 1399, 1364, 1307, 1251, 1223, 1148, 1108, 1072, 1028, 992, 971, 910, 886, 838, 810, 746, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 4H), 3.83 (s, 2H), 7.14–7.36 (m, 11H), 7.43 (dd, 1H, J = 5.2, 8.4 Hz), 7.52 (dd, 1H, J = 2.4, 8.8 Hz), 10.13 (d, 1H, J = 2.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 54.8, 58.1, 114.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 119.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 127.2, 128.3, 129.0, 132.7 (d, $J_{C\text{-}F}$ = 6.7 Hz), 136.6 (d, $J_{C\text{-}F}$ = 5.9 Hz), 137.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 138.3, 162.1 (d, $J_{C\text{-}F}$ = 247.0 Hz), 191.0 (d, $J_{C\text{-}F}$ = 1.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ 48.0–48.3 (m, 1F).

Anal. Calcd for $C_{22}H_{20}FNO$: C, 79.26; H, 6.05; N, 4.20. Found: C, 79.52; H, 6.48; N, 4.02.



Dimethyl 2-(2-((dibenzylamino)methyl)-5-fluorobenzylidene)malonate (**3l**).

Yellow oil.

Yield: quant.

IR (neat) 3062, 3029, 2952, 2797, 2712, 1732, 1628, 1609, 1584, 1491, 1453, 1436, 1366, 1276, 1225, 1190, 1162, 1120, 1070, 1028, 998, 973, 935, 914, 878, 836, 816, 796, 747, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (s, 4H), 3.55 (s, 2H), 3.69 (s, 3H), 3.90 (s, 3H), 6.97-7.06 (m, 2H), 7.18-7.38 (m, 10H), 7.45 (dd, 1H, J = 5.6, 8.4 Hz), 8.18 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 52.5, 56.1, 58.1, 114.7 (d, J_{C-F} = 22.3 Hz), 116.4 (d, J_{C-F} = 20.8 Hz), 126.9, 127.6, 128.1, 128.8, 131.9 (d, J_{C-F} = 8.2 Hz), 134.5 (d, J_{C-F} = 3.0 Hz), 134.9 (d, J_{C-F} = 7.4 Hz), 138.6, 141.7, 161.4 (d, J_{C-F} = 244.8 Hz), 164.0, 166.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ 46.9 (dd, J_{H-F} = 8.3, 14.3 Hz).

Anal. Calcd for $C_{27}H_{26}FNO_4$: C, 72.47; H, 5.86; N, 3.13. Found: C, 72.19; H, 6.11; N, 3.25.

2-((Dibenzylamino)methyl)-3-methylbenzaldehyde (**s13**).

Pale yellow solid.

Mp. 58–60 °C.

Yield: 72%.

IR (KBr) 3061, 3021, 2925, 2898, 2852, 2787, 2736, 2710, 1685, 1589, 1494, 1466, 1453, 1397, 1362, 1322, 1304, 1258, 1232, 1206, 1108, 1087, 1073, 7028, 989, 957, 916, 898, 867, 833, 793, 765, 744, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.46 (s, 4H), 3.86 (s, 2H), 7.16–7.37 (m, 12H), 7.67 (d, 1H, J = 7.6 Hz), 10.11 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 49.9, 57.9, 126.3, 127.2, 127.3, 128.2, 129.2, 134.9, 135.8, 138.0, 138.4, 139.3, 192.9.

Anal. Calcd for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25. Found: C, 83.56; H, 7.03; N, 4.28.

Dimethyl 2-(2-((dibenzylamino)methyl)-3-methylbenzylidene)malonate (**3m**).

Colorless solid.

Mp. 90–92 °C.

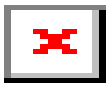
Yield: 90%.

IR (KBr) 3085, 3059, 3028, 2987, 2945, 2928, 2897, 2850, 2831, 2801, 2786, 2710, 1735, 1723, 1622, 1602, 1590, 1495, 1453, 1439, 1368, 1355, 1305, 1281, 1265, 1243, 1232, 1217, 1183, 1153, 1124, 1097, 1070, 1042, 1026, 969, 957, 933, 915, 896, 876, 821, 796, 767, 747, 701 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 3.48 (s, 4H), 3.59 (s, 5H), 3.91 (s, 3H), 7.04–7.34 (m, 13H), 8.35 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 52.1, 52.4, 52.9, 58.2, 125.9, 126.5, 126.8, 127.0, 128.0, 129.1, 132.1, 134.6, 136.0, 138.6, 138.9, 145.1, 164.4, 166.7.

Anal. Calcd for $C_{28}H_{29}NO_4$: C, 75.82; H, 6.59; N, 3.16. Found: C, 75.55; H, 6.62; N, 3.39.



3-((Dibenzylamino)methyl)-2-naphthaldehyde (**s14**).

Mp. 99–101 °C.

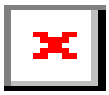
Yield: 90% (synthesized from 2-bromomethyl-3-iodo-naphthalene[5]).

IR (KBr) 3060, 3027, 2882, 2799, 1688, 1628, 1596, 1495, 1450, 1365, 1332, 1227, 1173, 1148, 1110, 1086, 1028, 968, 895, 844, 749, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.47 (s, 4H), 3.95 (s, 2H), 7.11–7.29 (m, 10H), 7.42 (ddd, 1H, J = 1.2, 8.4, 8.4 Hz), 7.50 (ddd, 1H, J = 1.2, 8.4, 8.4 Hz), 7.75 (d, 1H, J = 8.4 Hz), 7.83 (s, 1H), 7.85 (d, 1H, J = 8.4 Hz), 10.15 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1, 58.2, 126.6, 127.2, 127.5, 128.3, 128.7, 129.1, 129.5, 131.4, 132.0, 133.1, 135.3, 136.7, 138.6, 192.8.

Anal. Calcd for $C_{26}H_{23}NO$: C, 85.45; H, 6.34; N, 3.83. Found: C, 85.36; H, 6.60; N, 4.11.



Dimethyl 2-((3-((dibenzylamino)methyl)naphthalen-2-yl)methylene)malonate (**3n**).

Colorless oil.

Yield: 95%.

IR (neat) 3060, 3028, 2950, 2797, 1731, 1619, 1495, 1452, 1435, 1365, 1335, 1265, 1218, 1182, 1154, 1117, 1093, 1070, 28, 973, 908, 895, 875, 839, 749, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 4H), 3.62 (s, 3H), 3.76 (s, 2H), 3.93 (s, 3H), 7.21 (dd, 2H, *J* = 7.2, 7.2 Hz), 7.29 (dd, 4H, *J* = 7.2, 7.2 Hz), 7.37 (d, 4H, *J* = 7.2 Hz), 7.42–7.53 (m, 2H), 7.74–7.88 (m, 4H), 8.43 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 52.4, 57.8, 58.1, 126.2, 126.5, 126.8, 127.2, 127.7, 128.0, 128.1, 128.2, 128.9, 129.2, 131.7, 132.2, 133.5, 135.3, 138.5, 143.5, 164.3, 166.9.

Anal. Calcd for $C_{31}H_{29}NO_4$: C, 77.64; H, 6.10; N, 2.92. Found: C, 77.69; H, 5.89; N, 2.89.

2-((Methyl(phenyl)amino)methyl)benzaldehyde (**s15**).

Yellow oil.

Yield: 82%.

IR (neat) 2827, 2734, 1691, 1599, 1573, 1506, 1450, 1373, 1346, 1297, 1253, 1215, 1194, 1159, 1119, 1033, 997, 957, 932, 856, 748, 691, 658 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.08 (s, 3H), 4.99 (s, 2H), 6.61–6.76 (m, 3H), 7.19–7.24 (m, 2H), 7.36 (dd, 1H, *J* = 0.8, 7.2 Hz), 7.45–7.54 (m, 2H), 7.89 (dd, 1H, *J* = 1.6, 7.2 Hz) 10.22 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 38.7, 55.0, 111.9, 116.5, 127.1, 127.3, 129.2, 133.6, 134.0, 134.9, 141.8, 149.3, 193.6.

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.23; H, 6.55; N, 6.25.

Dimethyl 2-(2-((methyl(phenyl)amino)methyl)benzylidene)malonate (**3o**).

Yellow solid.

Mp. 94–96 °C.

Yield: 85%.

IR (KBr) 3066, 3034, 2996, 2950, 2893, 2845, 1729, 1627, 1603, 1571, 1510, 1474, 1439, 1422, 1363, 1350, 1258, 1232, 1202, 1158, 1124, 1094, 1068, 1032, 1002, 986, 952, 922, 882, 866, 835, 815, 757, 723, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (s, 3H), 3.71 (s, 3H), 3.80 (s, 3H), 4.54 (s, 2H), 6.69–6.77 (m, 3H), 7.18–7.35 (m, 6H), 8.01 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 38.4, 52.4, 52.6, 54.9, 112.5, 117.0, 127.1, 127.2, 127.6, 127.9, 129.1, 130.0, 132.1, 138.0, 142.0, 149.4, 164.1, 166.4.

Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.89; H, 6.28; N, 4.05.

3. Synthesis of indane derivatives.

General Procedure of [1,4]-hydride shift for the formation of indane derivatives.

To a solution of dimethyl malonate **3** (0.10 mmol) in 1,2-dichloroethane (1.0 mL) was added $Yb(OTf)_3$ (5–30 mol%) at room temperature, then the reaction mixture was heated at reflux. After completion of the reaction, the reaction was stopped by adding saturated aqueous $NaHCO_3$. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (or preparative TLC) to give indane derivative **4**.

Dimethyl 1-(diisopropylamino)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4a**).

Colorless crystal (crystallized from hexane), which is subjected to X-ray crystal analysis.

Mp. 109–111 °C.

Yield: quant.

IR (KBr) 3076, 3025, 2987, 2968, 2949, 2870, 2834, 1736, 1460, 1429, 1397, 1386, 1365, 1346, 1281, 1256, 1212, 1181, 1153, 1139, 1119, 1080, 1046, 1011, 969, 947, 938, 910, 876, 850, 827, 784, 759, 734, 717 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.20–1.60 (brm, 12H), 2.63 (brs, 1H), 3.12 (brs, 1H), 3.27 (d, 1H, J = 17.2 Hz), 3.65 (s, 3H), 3.73 (s, 3H), 4.14 (d, 1H, J = 17.2 Hz), 5.46 (s, 1H), 7.12–7.24 (m, 3H), 7.43 (d, 1H, J = 7.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 24.0, 39.8, 44.4, 48.9, 52.1, 52.6, 66.3, 66.7, 124.4, 126.5, 126.7, 127.8, 140.4, 141.9, 169.8, 172.4.

Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16; N, 4.20. Found: C, 68.48; H, 8.22; N, 4.13.

Dimethyl 1-(diethylamino)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4b**).

Colorless oil.

Yield: 54%.

IR (neat) 3071, 3025, 2970, 2871, 2817, 1736, 1483, 1458, 1434, 1383, 1282, 1250, 1218, 1193, 1156, 1117, 1081, 1049, 997, 966, 946, 890, 871, 811, 790, 760, 740 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, 6H, J = 6.8 Hz), 2.32 (brs, 4H), 3.23 (d, 1H, J = 17.6 Hz), 3.70 (s, 3H), 3.75 (s, 3H), 4.03 (d, 1H, J = 17.6 Hz), 5.26 (s, 1H), 7.15-7.31 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 39.5, 45.4, 52.2, 52.7, 65.7, 71.0, 124.6, 125.2, 126.7, 128.0, 140.3, 140.4, 169.8, 172.5.

Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 66.77; H, 7.64; N, 4.31.

Dimethyl 1-(dibenzylamino)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4c**).

Colorless crystal (crystallized from hexane/CH_2Cl_2), which is subjected to X-ray crystal analysis.

Mp. 159–161 °C.

Yield: 98%.

IR (KBr) 3088, 3065, 3038, 3029, 3008, 2951, 2857, 2822, 2805, 1740, 1716, 1497, 1481, 1452, 1433, 1379, 1358, 1281, 1252, 1243, 1220, 1194, 1162, 1109, 1094, 1068, 1046, 1031, 957, 944, 922, 848, 819, 753, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.18–3.38 (brm, 2H), 3.30 (d, 1H, J = 17.2 Hz), 3.58–3.67 (brm, 2H), 3.61 (s, 3H), 3.86 (s, 3H), 4.08 (d, 1H, J = 17.2 Hz), 5.32 (s, 1H), 7.13 (d, 1H, J = 6.8 Hz), 7.17–7.34 (m, 13H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 52.5, 52.7, 55.2, 65.1, 68.2, 124.8, 125.6, 126.9, 127.0, 128.1, 128.3, 129.2, 139.1, 139.8, 140.3, 169.8, 171.8.

Anal. Calcd for $C_{27}H_{27}NO_4$: C, 75.50; H, 6.34; N, 3.26. Found: C, 75.68; H, 6.14; N, 3.32.

Dimethyl 1-(diphenylamino)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4d**).

White solid.

Mp. 127–129 °C.

Yield: 92%.

IR (KBr) 3037, 2950, 1742, 1724, 1589, 1496, 1447, 1427, 1380, 1347, 1292, 1255, 1217, 1190, 1164, 1093, 1076, 1051, 954, 931, 885, 869, 820, 797, 768, 748, 703 cm^{-1}

^1H NMR (400 MHz, $CDCl_3$) δ 3.32 (d, 1H, J = 17.2 Hz), 3.38 (s, 3H), 3.73 (s, 3H), 3.86 (d, 1H, J = 17.2 Hz), 6.78 (s, 1H), 6.83-6.90 (m, 6H), 7.03–7.15 (m, 7H), 7.21 (d, 1H, J = 7.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.5, 52.3, 53.1, 64.4, 69.2, 121.9, 123.1, 124.4, 126.3, 126.9, 128.5, 128.6, 139.8, 139.9, 147.0, 169.4, 171.9.

Anal. Calcd for $C_{25}H_{23}NO_4$: C, 74.79; H, 5.77; N, 3.49. Found: C, 74.94; H, 5.57; N, 3.46.

Dimethyl 1-(diallylamino)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4e**).

Colorless oil.

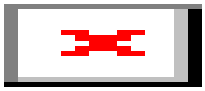
Yield: 64%.

IR (neat) 3074, 3008, 2952, 2928, 2817, 1736, 1642, 1481, 1459, 1434, 1418, 1355, 1285, 1251, 1219, 1193, 1156, 1116, 1080, 1052, 997, 978, 921, 863, 830 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.70–2.86 (brm, 2H), 2.95–3.10 (brm, 2H), 3.25 (d, 1H, J = 17.6 Hz), 3.69 (s, 3H), 3.78 (s, 3H), 4.04 (d, 1H, J = 17.6 Hz), 5.05–5.20 (m, 4H), 5.32 (s, 1H), 5.62–5.85 (m, 2H), 7.15–7.36 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.6, 52.3, 52.7, 54.7, 65.6, 69.3, 117.0, 124.7, 125.4, 126.8, 128.3, 136.9, 139.8, 140.4, 169.8, 172.2.

Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.37; H, 6.79; N, 3.99.



Dimethyl 1-(2,2,6,6-tetramethylpiperidin-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4g**) and dimethyl 1-(2,6-dimethylhept-5-en-2-ylamino)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4h**).

Yield: quant. (**4g**:**4h** = 2.3:1, * shows the peaks of **4h**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15–1.78 (m, 5H+4H*), 0.84 (s, 3H), 1.09* (s, 3H), 1.20* (s, 3H), 1.01 (s, 3H), 1.40 (s, 3H), 1.51 (s, 3H), 1.57* (s, 3H), 1.66* (s, 3H), 1.87–2.03 (m, 1H), 3.18 (d, 1H, *J* = 17.2 Hz), 3.23* (d, 1H, *J* = 16.8 Hz), 3.67 (s, 3H), 3.70* (s, 3H), 3.71* (s, 3H), 3.80 (s, 3H), 3.90* (d, 1H, *J* = 16.8 Hz), 4.23 (d, 1H, *J* = 17.2 Hz), 5.01–5.12* (m, 1H), 5.17* (s, 1H), 6.09 (s, 1H), 7.05–7.38 (m, 3H+4H*), 7.49 (d, 1H, *J* = 8.0 Hz).

Dimethyl 1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4i**).

Colorless amorphous.

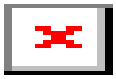
Yield: 61%.

IR (neat) 3023, 2949, 2912, 2803, 2764, 1725, 1494, 1454, 1433, 1369, 1339, 1293, 1256, 1223, 1204, 1173, 1149, 1112, 1098, 1054, 943, 896, 870, 816, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52–2.72 (m, 2H), 2.86–3.24 (m, 3H), 3.05 (s, 3H), 3.67 (s, 3H), 4.09 (d, 1H, *J* = 15.2 Hz), 4.47 (d, 1H, *J* = 15.2 Hz), 4.57 (brs, 1H), 4.87 (s, 1H), 6.95 (d, 1H, *J* = 7.6 Hz), 7.00–7.23 (m, 6H), 7.36–7.46 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 30.3, 39.3, 50.5, 51.5, 52.1, 62.9, 63.5, 125.6, 126.5, 126.6, 127.1, 127.5, 127.5, 129.0, 130.4, 134.9, 134.9, 137.2, 137.6, 170.1, 171.8.

Anal. Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.56; H, 6.37; N, 3.61.



Dimethyl 1-(dibenzylamino)-5-methyl-1*H*-indene-2,2(3*H*)-dicarboxylate (**4j**).

Colorless oil.

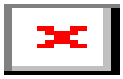
Yield: 92%.

IR (neat) 3086, 3061, 6027, 3006, 2951, 2839, 1735, 1494, 1453, 1434, 1371, 1282, 1254, 1219, 1156, 1098, 1077, 1048, 1029, 973, 911, 869, 847, 799, 738, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 3.08–3.32 (brm, 2H), 3.18 (d, 1H, J = 17.6 Hz), 3.47–3.59 (brm, 2H), 3.53 (s, 3H), 3.79 (s, 3H), 3.97 (d, 1H, J = 17.6 Hz), 5.20 (s, 1H), 6.91–6.97 (m, 3H), 7.10–7.27 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 39.9, 52.4, 52.7, 55.2, 65.3, 68.0, 125.3, 125.4, 126.9, 127.8, 128.1, 129.2, 136.8, 138.1, 139.2, 140.5, 169.8, 171.9.

Anal. Calcd for $C_{28}H_{29}NO_4$: C, 75.82; H, 6.59; N, 3.16. Found: C, 75.92; H, 6.29; N, 3.36.



Dimethyl 1-(dibenzylamino)-5-methoxy-1*H*-indene-2,2(3*H*)-dicarboxylate (**4k**).

Colorless oil.

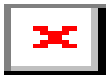
Yield: 86%.

IR (neat) 3086, 3060, 3026, 3002, 2951, 2904, 2835, 2808, 1734, 1607, 1493, 1453, 1434, 1370, 1283, 1246, 1219, 1155, 1122, 1077, 1048, 1029, 972, 913, 804, 742, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.26 (d, 1H, J = 17.6 Hz), 3.32 (brs, 2H), 3.50–3.80 (m, 2H), 3.61 (s, 3H), 3.78 (s, 3H), 3.85 (s, 3H), 4.04 (d, 1H, J = 17.6 Hz), 5.28 (s, 1H), 6.71 (s, 1H), 6.75 (d, 1H, J = 8.8 Hz), 7.00 (d, 1H, J = 8.8 Hz), 7.15-7.35 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 40.1, 52.4, 52.7, 55.2, 55.2, 65.6, 67.7, 109.6, 113.2, 126.3, 126.9, 128.1, 129.1, 131.9, 139.2, 142.0, 160.1, 169.7, 171.8.

Anal. Calcd for $C_{28}H_{29}NO_5$: C, 73.18; H, 6.36; N, 3.05. Found: C, 73.15; H, 6.28; N, 3.18.



Dimethyl 1-(dibenzylamino)-5-fluoro-1*H*-indene-2,2(3*H*)-dicarboxylate (**4l**).

Amorphous solid.

Yield: 80%.

IR (neat) 3087, 3062, 3028, 2952, 2839, 1735, 1612, 1600, 1487, 1454, 1434, 1372, 1321, 1283, 1244, 1217, 1158, 1097, 1077, 1049, 1029, 972, 945, 910, 868, 803, 740, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.16–3.44 (brm, 2H), 3.28 (d, 1H, J = 17.6 Hz), 3.54–3.72 (brm, 2H), 3.63 (s, 3H), 3.87 (s, 3H), 4.06 (d, 1H, J = 17.6 Hz), 5.28 (s, 1H), 6.86–6.94 (m, 2H), 7.00 (dd, 1H, J = 5.6, 8.0 Hz), 7.19–7.36 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 52.2, 52.8, 55.1, 65.5, 67.5, 111.7 (d, J_{C-F} = 22.4 Hz), 114.1 (d, J_{C-F} = 22.4 Hz), 126.7 (d, J_{C-F} = 8.9 Hz), 127.0, 128.1, 129.1, 135.4 (d, J_{C-F} = 3.0 Hz), 138.9, 142.6 (d, J_{C-F} = 8.2 Hz), 163.1 (d, J_{C-F} = 244.8 Hz), 169.4, 171.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ 47.4 (dd, J_{H-F} = 8.3, 14.3 Hz).

Anal. Calcd for $C_{27}H_{26}FNO_4$: C, 72.47; H, 5.86; N, 3.13. Found: C, 72.61; H, 5.78; N, 3.28.

Dimethyl 1-(dibenzylamino)-7-methyl-1*H*-indene-2,2(3*H*)-dicarboxylate (**4m**).

Colorless oil.

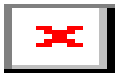
Yield: 94%.

IR(neat) 3087, 3061, 3028, 2951, 2853, 1733, 1602, 1495, 1454, 1434, 1375, 1278, 1245, 1211, 1158, 1135, 1075, 1029, 967, 919, 847, 827, 749, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 3.37 (d, 1H, J = 16.8 Hz), 3.45–3.75 (m, 7H), 3.84 (s, 3H), 3.94 (d, 1H, J = 16.8 Hz), 5.40 (s, 1H), 6.94 (d, 1H, J = 7.6 Hz), 6.98 (d, 1H, J = 7.2 Hz), 7.06–7.31 (m, 11H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 39.8, 52.5, 52.7, 54.7, 64.3, 69.0, 121.6, 126.9, 127.9, 128.5, 128.8, 129.5, 135.6, 139.6, 140.6, 170.7, 171.7.

Anal. Calcd for $C_{28}H_{29}NO_4$: C, 75.82; H, 6.59; N, 3.16. Found: C, 75.62; H, 6.48; N, 3.00.



Dimethyl 1-(dibenzylamino)-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (**4n**).

Yield: 98%.

IR(neat) 3086, 3060, 3028, 3003, 2951, 2839, 2810, 1734, 1603, 1496, 1453, 1434, 1371, 1338, 1287, 1258, 1222, 1193, 1156, 1091, 1067, 1047, 1029, 972, 909, 837, 811, 774, 735, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 3.20–3.45 (m, 2H), 3.61 (s, 3H), 3.46 (d, 1H, J = 17.6 Hz), 3.55–3.78 (m, 2H), 3.89 (s, 3H), 4.25 (d, 1H, J = 17.6 Hz), 5.44 (s, 1H), 7.20–7.52 (m, 13H), 7.64 (s, 1H), 7.75–7.85 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 52.3, 52.7, 55.2, 65.6, 67.6, 123.1, 124.3, 125.4, 125.8, 127.0, 127.5, 128.2, 129.2, 132.8, 133.8, 138.5, 138.8, 139.0, 169.6, 171.7.

Anal. Calcd for $C_{31}H_{29}NO_4$: C, 77.64; H, 6.10; N, 2.92. Found: C, 77.65; H, 6.00; N, 2.82.

Dimethyl 1-(methyl(phenyl)amino)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4o**).

White solid.

Mp. 151–153 °C.

Yield: quant.

IR (KBr) 3066, 3027, 2998, 2952, 2889, 2820, 1732, 1598, 1504, 1434, 1379, 1315, 1253, 1216, 1161, 1108, 1080, 1057, 1034, 991, 969, 865, 798, 748, 693 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.37 (s, 3H), 3.43 (d, 1H, J = 17.6 Hz), 3.77 (s, 3H), 4.16 (d, 1H, J = 17.6 Hz), 6.45 (s, 1H), 6.77 (dd, 1H, J = 7.6 Hz), 6.99 (d, 2H, J = 8.0 Hz), 7.12 (d, 1H, J = 7.6 Hz), 7.18–7.33 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 33.3, 39.8, 52.3, 53.0, 63.9, 70.1, 113.5, 117.4, 124.7, 125.5, 127.5, 128.8, 128.9, 139.0, 140.0, 149.9, 169.6, 172.0.

Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.68; H, 6.31; N, 4.28.

Zwitter ionic compounds **7**.

Colorless crystal (crystallized from hexane/CH_2Cl_2), which is subjected to X-ray crystal analysis.

Mp. 158–159 °C

IR (KBr) 3475, 2982, 2950, 2236, 1678, 1594, 1432, 1390, 922, 795 cm^{-1}.

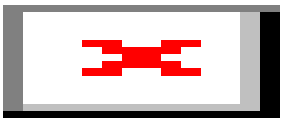
^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (brs, 6H), 3.15 (s, 3H), 3.25 (brs, 4H), 3.37 (s, 3H), 4.67 (brs, 2H), 6.55 (s, 1H), 7.16–7.25 (m, 2H), 7.28–7.36 (m, 2H).

Anal. Calcd for $C_{18}H_{23}N_3O_3$: C, 65.63; H, 7.04; N, 12.76. Found: C, 65.42; H, 6.85; N, 12.97.

4. Examination of the reaction conditions.

Table 1 illustrates the screening of the catalyst and reaction conditions. When the solution of **3a** in $ClCH_2CH_2Cl$ was treated with 5 mol% of $Sc(OTf)_3$ at refluxing temperature for 24 h, the desired reaction proceeded smoothly to give indane **4a** in 86% (entry 1). Other lanthanoid triflates, such as $Gd(OTf)_3$ and $Yb(OTf)_3$, were more effectively catalyzed the reaction, and the reaction time could be reduced to less than 2.5 h (Entries 2 and 3). Especially, the reaction finished within 30 min with $Yb(OTf)_3$ (80%, entry 3). Various strong Brønsted acids ($TsOH•H_2O$, TfOH, Tf_2NH) also promoted the reaction, although, the chemical yield was moderate (Entries 4–6). Finally, we found that the purification method was the key to achieve excellent chemical yield, *i.e.*, the use of Et_3N (2%) containing eluent in the purification by column chromatography afforded **4a** in quantitative yield (Entry 7). The examination of solvent system (toluene, CH_3CN, and EtOH) suggested that $ClCH_2CH_2Cl$ was the solvent of choice.

Table 1. Examination of the reaction conditions.[a]



Entry	catalyst	solvent	Time (h)	Yield (%)
1[b]	$Sc(OTf)_3$	$ClCH_2CH_2Cl$	24	86
2[b]	$Gd(OTf)_3$	$ClCH_2CH_2Cl$	2.5	78
3[b]	$Yb(OTf)_3$	$ClCH_2CH_2Cl$	0.5	80
4[b]	$TsOH•H_2O$	$ClCH_2CH_2Cl$	24	48
5[b]	TfOH	$ClCH_2CH_2Cl$	24	63
6[b]	Tf_2NH	$ClCH_2CH_2Cl$	24	76
7[c]	$Yb(OTf)_3$	$ClCH_2CH_2Cl$	0.5	Quant.
8[c]	$Yb(OTf)_3$	toluene	2.5	63
9[c]	$Yb(OTf)_3$	CH_3CN	0.5	68
10[c]	$Yb(OTf)_3$	EtOH	24	76

[a] Unless otherwise noted, all reactions were conducted with 0.1 mmol of **3a** and 5 mol% of catalyst in 1.0 mL of solvent at reflux [b] Purified by preparative TLC. [c] Purified by column chromatography (eluent with 2% of Et_3N was used).

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