Palladium-Catalyzed Intramolecular Coupling between Aryl Iodides and Allyl Moieties *via* Thermal and Microwave-Assisted Conditions

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Supporting Information

General. Infrared (IR) spectra were recorded on a Perkin Elmer FT-IR spectrometer, SPECTRUM 1000. ^1H and ^{13}C NMR spectra were measured on Mercury 300, Mercury 400 and Unity 500 spectrometers. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF₂₅₄ on aluminium sheet) were used. The products were purified by preparative column chromatography on silica gel (60Å, ultrapure silica gel, SILICYCLE). The high-resolution mass spectra (HRMS) analysis was accomplished at the Department of Chemistry, University of Toronto (EI and ESI). Reactions were conducted in round-bottomed flasks with magnetic stirbars under an atmosphere of dry nitrogen for conventional thermal conditions. Microwave-assisted reactions were performed in Emrys Liberator model from Personal Chemistry. Reactants were filled into appropriate microwave process vials. $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ was prepared according to the literature.¹ $\text{Pd}(\text{OAc})_2$, $\text{Pd}(\text{PPh}_3)_4$, $\text{PdCl}_2(\text{tri-}o\text{-tolylphosphine})_2$ and $\text{Sc}(\text{OTf})_3$, were purchased from Strem Chemicals, Inc. 2-Methyl-2-vinyloxirane **1** was purchased from Sigma-Aldrich Canada Ltd.

2-iodoaniline and 4-Chloro-2-iodoaniline: purchased from Aldrich.
2-Iodo-4,6-dimethylaniline: prepared according to a procedure described in the literature.²

2-Iodo-6-methoxyaniline: *N*-(*tert*-Butoxycarbonyl)-2-iodo-6-methoxyaniline³ (1.03 g, 2.95 mmol) was dissolved in CH₂Cl₂ (5.9 mL) and treated with trifluoroacetic acid (1.4 mL, 18 mmol) at 0 °C and the solution was stirred for 4.5 h at room temperature. The volatiles were removed by evaporation and the residue was treated with saturated NaHCO₃. The mixture was extracted with Et₂O and the combined extracts were washed with brine, dried over Na₂SO₄ and concentrated. The residue was used without purification in next step (preparation of aldimine).

Preparation of aromatic aldimine.

General procedure: To a solution of aldehyde (1.0 equiv), aniline (1.0 equiv) and Et₃N (3.0 equiv) in CH₂Cl₂ (0.3 M) was added a 1.0 M TiCl₄ solution in CH₂Cl₂ (0.6 equiv) at 0 °C. After stirring for 30 min at the same temperature, the mixture was allowed to warm to room temperature and stirred for a few hours. Removal of TiO₂ by Celite filtration and the filtrate was concentrated. To the residue was added toluene again and Et₃N·HCl was removed by Celite filtration. The volatiles were removed by evaporation and the residue was purified by chromatography on silica gel (hexane/Et₂O as eluent) and/or recrystallization from hexane or hexane-benzene and/or Kugelrohr distillation in vacuo to afford the corresponding aldimine. The yields are noted in Table 1.

Table 1. Preparation of Aldimines.

entry	Ar	R ²	R ³		Yield (%) ^{a,b}
1	Ph	H	H	a	87
2	4-Me-Ph	H	H	b	49
3	4-Cl-Ph	H	H	c	78
4	4-Br-Ph	H	H	d	68
5	Ph	Me	Me	e	66
6	Ph	H	Cl	f	69
7	Ph	OMe	H	g	77

^a Isolated yield.

^b The yields were determined after recrystallization.

Benzylidene(2-iodophenyl)amine:⁴ pale yellow crystal, mp = 56-57 °C, purified by recrystallization from hexane; ¹H NMR (300 MHz, CDCl₃) δ 8.31 (1H, s, CH=N), 7.99-7.96 (2H, m, Ar-H), 7.90 (1H, dd, *J* = 7.8, 1.5 Hz, Ar-H), 7.53-7.46 (3H, m, Ar-H), 7.37 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 7.01 (1H, dd, *J* = 7.8, 1.5 Hz, Ar-H), 6.93 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ 161.0, 153.1, 139.1, 135.9, 131.8, 129.4, 129.2, 128.9, 127.1, 118.4, 94.8; IR (film) 3051, 2881, 1626, 1572, 1460, 1429, 1310, 1195, 1167, 1015, 974, 879, 760 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₃H₁₀IN 306.9858, Found: 306.9862.

4-Methylbenzylidene(2-iodophenyl)amine: pale yellow crystal, mp = 33-35 °C, purified by chromatography on silica gel (hexane/Et₂O = 15:1 to 10:1 as eluent) and then recrystallized from hexane; ¹H NMR (300 MHz, CDCl₃) δ 8.25 (1H, s, CH=N), 7.90-7.84 (3H, m, Ar-H), 7.35 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 7.29 (2H, d, *J* = 7.8 Hz, Ar-H), 6.99 (1H, dd, *J* = 7.8, 1.5 Hz, Ar-H), 6.90 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 2.42 (3H, s, Me); ¹³C NMR (75 MHz, CDCl₃) δ 160.8, 153.2, 142.3, 139.0, 133.3, 129.6, 129.3, 129.1, 126.8, 118.4, 94.8, 21.7; IR (film) 3051, 2881, 1623, 1568, 1460, 1365, 1307, 1195, 1171, 1015, 977, 882, 814, 750 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₄H₁₂IN 321.0015, Found: 321.0029.

4-Chlorobenzylidene(2-iodophenyl)amine:⁴ pale yellow crystal, mp = 43-44 °C, purified by chromatography on silica gel (hexane/Et₂O = 15:1 to 10:1 as eluent) and then recrystallized from hexane; ¹H NMR (300 MHz, CDCl₃) δ 8.26 (1H, s, CH=N), 7.92-7.88 (3H, m, Ar-H), 7.46 (2H, dt, *J* = 8.4, 2.1 Hz, Ar-H), 7.36 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 6.99 (1H, dd, *J* = 7.8, 1.5 Hz, Ar-H), 6.93 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ 159.4, 152.6, 139.1, 137.8, 134.3, 130.2, 129.3, 129.2, 127.2, 118.2, 94.9; IR (film) 3051, 2990, 2874, 1623, 1592, 1562, 1483, 1460, 1361, 1191, 1086, 1015, 882, 821, 753 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₃H₉ClIN 340.9468, Found: 340.9472.

4-Bromobenzylidene(2-iodophenyl)amine: pale yellow crystal, mp = 50-52 °C, purified by recrystallization from hexane; ¹H NMR (300 MHz, CDCl₃) δ 8.26 (1H, s, CH=N), 7.90 (1H, dd, *J* = 7.8, 1.5 Hz, Ar-H), 7.84 (2H, dt, *J* = 8.4, 2.1 Hz, Ar-H), 7.63 (2H, dt, *J* = 8.4, 2.1

Hz, Ar-H), 7.37 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 7.00 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 6.94 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.5, 152.6, 139.1, 134.7, 132.1, 130.4, 129.3, 127.3, 126.4, 118.2, 94.8; IR (film) 3058, 2990, 2881, 1623, 1565, 1483, 1460, 1191, 1167, 1066, 1008, 882, 817, 753 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{13}\text{H}_9\text{BrIN}$ 384.8963, Found: 384.8968.

Benzylidene(2,4-dimethyl-6-iodophenyl)amine: pale yellow crystal, mp = 67-68 °C, purified by chromatography on silica gel (hexane/ Et_2O = 15:1 as eluent) and then recrystallized from hexane; ^1H NMR (300 MHz, CDCl_3) δ 8.19 (1H, s, $\text{CH}=\text{N}$), 7.96-7.92 (2H, m, Ar-H), 7.55-7.47 (4H, m, Ar-H), 6.99 (1H, s, Ar-H), 2.27 (3H, s, Me), 2.16 (3H, s, Me); ^{13}C NMR (75 MHz, CDCl_3) δ 164.8, 150.7, 137.0, 135.6, 135.2, 131.8, 131.4, 128.8, 128.2, 89.4, 20.2, 19.1; IR (film) 3024, 2908, 1636, 1579, 1463, 1310, 1195, 1113, 977, 875, 848, 753 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{15}\text{H}_{14}\text{IN}$ 335.0171, Found: 335.0167.

Benzylidene(4-chloro-2-iodophenyl)amine: pale yellow crystal, mp = 52-53 °C, purified by chromatography on silica gel (hexane/ Et_2O = 15:1 to 10:1 as eluent) and then recrystallized from hexane; ^1H NMR (300 MHz, CDCl_3) δ 8.28 (1H, s, $\text{CH}=\text{N}$), 7.97-7.94 (2H, m, Ar-H), 7.88 (1H, d, $J = 2.4$ Hz, Ar-H), 7.56-7.46 (3H, m, Ar-H), 7.34 (1H, dd, $J = 8.4, 2.4$ Hz, Ar-H), 6.93 (1H, d, $J = 8.4$ Hz, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ 161.3, 151.7, 138.3, 135.6, 132.0, 131.4, 129.3, 129.2, 128.9, 118.7, 95.1; IR (film) 3065, 3024, 2881, 1626, 1575, 1453, 1368, 1310, 1191, 1093, 1032, 970, 872, 811, 753 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{13}\text{H}_9\text{ClIN}$ 340.9468, Found: 340.9465.

Benzylidene(2-iodo-6-methoxyphenyl)amine: yellow crystal, mp = 70-71 °C, purified by chromatography on silica gel (hexane/ Et_2O = 15:1 to 10:1 as eluent) and then recrystallized from hexane; ^1H NMR (300 MHz, CDCl_3) δ 8.38 (1H, s, $\text{CH}=\text{N}$), 8.00-7.96 (2H, m, Ar-H), 7.53-7.46 (4H, m, Ar-H), 6.94 (1H, dd, $J = 8.1, 0.9$ Hz, Ar-H), 6.82 (1H, t, $J = 8.1$ Hz, Ar-H), 3.77 (3H, s, OCH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 165.4, 149.7, 142.8, 136.0, 131.7, 130.9, 128.9, 128.7, 126.2, 112.0, 93.7, 56.1; IR (film) 3058, 3003, 2935, 2826, 1630, 1575, 1558, 1456, 1426, 1310, 1252, 1191, 1028, 872, 753 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{14}\text{H}_{12}\text{INO}$ 336.9964, Found: 336.9966.

Preparation of 2,4-dimethyl-6-iodoiminoacetic acid cyclohexyl ester: A mixture of

L-tartalic acid (3.0 g, 20 mmol), cyclohexanol (6.3 mL, 60 mmol) and *p*-TsOH·H₂O (0.19 g, 1.0 mmol) in benzene (20 mL) was refluxed for 15 h while removing H₂O by Dean-Stark trap. The resulting mixture was cooled to room temperature and concentrated. The residue was purified by Kugelrohr distillation to give dicyclohexyl tartrate as a viscous colorless oil (6.05 g, 19.2 mmol, 96% yield). The spectroscopic data was assigned with a literature.⁵ To a solution of dicyclohexyl tartrate (943 mg, 3.0 mmol) in THF (15 mL) was added H₅IO₆ (684 mg, 3.0 mmol) at 0 °C and the mixture was stirred for 2 h at room temperature. The resulting white suspension was filtered through a pad of Celite and the filtrate was concentrated to obtain a crude cyclohexyl glyoxalate.⁵ The crude product was used without purification in next step. To the solution of crude cyclohexyl glyoxalate (~6.0 mmol) and 2,4-dimethyl-6-iodoaniline² (1.24 g, 5.0 mmol) in CH₂Cl₂ (10 mL) was added MgSO₄ (3.0 g, 25 mmol) at room temperature. After stirring for 20 h, the resulting mixture was filtered and the volatiles were removed by evaporation. Purification of the residue by chromatography on silica gel (hexane/Et₂O = 10:1 to 6:1 as eluent) and then, recrystallization from hexane gave 2,4-dimethyl-6-iodoiminoacetic acid cyclohexyl ester as pale yellow crystals (1.22 g, 3.17 mmol, 63% yield). mp = 73-74 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.66 (1H, s, CH=N), 7.53 (1H, s, Ar-H), 6.98 (1H, s, Ar-H), 5.05 (1H, tt, *J* = 9.6, 4.2 Hz, OCH), 2.26 (3H, s, Me), 2.14 (3H, s, Me), 2.04-1.97 (2H, m, *c*-Hex), 1.85-1.77 (2H, m, *c*-Hex), 1.67-1.55 (3H, m, *c*-Hex), 1.50-1.24 (3H, m, *c*-Hex); ¹³C NMR (75 MHz, CDCl₃) δ 162.0, 157.5, 148.6, 137.3, 136.6, 131.6, 127.5, 87.5, 75.0, 31.5, 25.3, 23.8, 20.2, 19.0; IR (film) 2935, 2853, 1742, 1718, 1446, 1290, 1201, 1120, 1008, 981, 851, 780 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₆H₂₀INO₂ 385.0539, Found: 385.0540.

^a Isolated yield.

^b The yield was determined after recrystallization.

Scheme 1. Preparation of α -Imino Cyclohexyl Ester.

Preparation of amino aldehyde 2 by direct vinylogous Mannich-type reaction: To a solution of imine (0.50 mmol) and vinyloxirane (74 μ L, 0.75 mmol) in THF (1.0 mL) was added $\text{Sc}(\text{OTf})_3$ (25 mg, 0.050 mmol, 10 mol%) at 0 $^\circ\text{C}$ and the mixture was stirred for the time noted in Table 2. The resulting mixture was quenched by addition of saturated NaHCO_3 and extracted with Et_2O . The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the residue by column chromatography on silica gel gave the corresponding amino aldehydes **2**. The reaction time, temperature and yields were noted in Table 2.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-phenylpent-2-en-1-al
: colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 9.42 (1H, s, CHO), 7.64 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 7.39-7.24 (5H, m, Ar-H), 7.03 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.51 (1H, tq, $J = 7.2, 1.2$ Hz, 3-CH), 6.41 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.33 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 4.63-4.58 (2H, m, NH and 5-CH), 2.92 (2H, dd, $J = 7.2, 6.6$ Hz, 4- CH_2), 1.78 (3H, d, $J = 1.2$ Hz, 2- CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 194.7, 148.5, 145.7, 141.8, 141.7, 138.9, 129.3, 128.9, 127.7, 126.1, 119.3, 112.1, 85.9, 57.7, 38.0, 9.6; IR (film) 3379, 3058, 3024, 2819, 2710, 1687, 1585, 1504, 1450, 1317, 1004, 926, 865, 743 cm^{-1} ; HRMS-EI (m/z): [M^+] calcd for $\text{C}_{18}\text{H}_{18}\text{INO}$ 391.0433, Found: 391.0429.

Table 2. Preparation of α,β -Conjugated Aldehydes **2** by Direct Vinylogous Mannich-type Reaction.

entry	R ¹	R ²	R ³		temp ($^\circ\text{C}$)	time (h)	Yield ^a (%)
1	Ph	H	H	a	0	1	91
2	4-Me-Ph	H	H	b	0	1	88
3	4-Cl-Ph	H	H	c	0	1	85
4	4-Br-Ph	H	H	d	0	1	87
5	Ph	Me	Me	e	0	1	91
6	Ph	H	Cl	f	0	1	87
7	Ph	OMe	H	g	0	1	88
8	COO-c-Hex	Me	Me	h	0 addition to 50	0.5	80

^a Isolated yield.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-(4-methylphenyl)pent-2-en-1-al: colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 9.41 (1H, s, CHO), 7.64 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 7.23 (2H, d, $J = 8.1$ Hz, Ar-H), 7.15 (2H, d, $J = 8.1$ Hz, Ar-H), 7.03 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.51 (1H, tq, $J = 7.5, 1.2$ Hz, 3-CH), 6.41 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.34 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 4.61-4.55 (2H, m, NH and 5-CH), 2.90 (2H, dd, $J = 7.5, 6.6$ Hz, 4- CH_2), 2.33 (3H, s, Ar- CH_3), 1.78 (3H, d, $J = 1.2$ Hz, 2- CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 194.8, 148.8, 148.7, 145.8, 141.7, 139 (m), 138.6, 137.3, 129.6, 129.3, 126.0, 119 (m), 112 (m), 85.9, 57.3, 38.0, 21.1, 21.0, 9.6; IR (film) 3379, 3010, 2915, 2710, 1684, 1582, 1504, 1450, 1314, 1079, 1004, 923, 814, 743 cm^{-1} ; HRMS-EI (m/z): [M^+] calcd for $\text{C}_{19}\text{H}_{20}\text{INO}$ 405.0590, Found: 405.0586.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-(4-chlorophenyl)pent-2-en-1-al: colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 9.42 (1H, s, CHO), 7.65 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 7.33 (2H, dt, $J = 6.5, 2.1$ Hz, Ar-H), 7.28 (2H, dt, $J = 6.5, 2.1$ Hz, Ar-H), 7.04 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.49 (1H, tq, $J = 7.5, 0.9$ Hz, 3-CH), 6.43 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.27 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 4.61-4.55 (2H, m, NH and 5-CH), 2.90 (2H, dd, $J = 7.5, 6.9$ Hz, 4- CH_2), 1.80 (3H, d, $J = 0.9$ Hz, 2- CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 194.6, 147.8, 145.4, 142.1, 140.3, 139.0, 133.4, 129.3, 129.1, 127.5, 119.6, 112.1, 85.9, 57.2, 37.8, 9.7; IR (film) 3379, 3058, 2826, 2710, 1684, 1585, 1500, 1450, 1314, 1086, 1004, 923, 824, 743 cm^{-1} ; HRMS-ESI (m/z): [$\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{18}\text{ClINO}$ 426.0116, Found: 426.0130.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-(4-bromophenyl)pent-2-en-1-al: yellow viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 9.42 (1H, s, CHO), 7.65 (1H, dd, $J = 7.8, 1.2$ Hz, Ar-H), 7.48 (2H, dt, $J = 8.7, 2.4$ Hz, Ar-H), 7.23 (2H, dt, $J = 8.7, 2.4$ Hz, Ar-H), 7.03 (1H, td, $J = 7.8, 1.2$ Hz, Ar-H), 6.48 (1H, tq, $J = 7.5, 1.2$ Hz, 3-CH), 6.43 (1H, td, $J = 7.8, 1.2$ Hz, Ar-H), 6.26 (1H, dd, $J = 7.8, 1.2$ Hz, Ar-H), 4.61-4.53 (2H, m, NH and 5-CH), 2.88-2.81 (2H, m, 4- CH_2), 1.80 (3H, d, $J = 1.2$ Hz, 2- CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 194.5, 147.7, 145.4, 142.1, 140.8, 139.0, 132.1, 129.3, 127.9, 121.4, 119.6, 112.0, 85.9, 57.2, 37.8, 9.7; IR (film) 3386, 3058, 2819, 2710, 1681, 1585, 1500, 1453, 1314, 1072, 1008, 926, 821, 743 cm^{-1} ; HRMS-EI (m/z): [M^+] calcd for $\text{C}_{18}\text{H}_{17}\text{BrINO}$ 468.9538, Found: 468.9537.

(2E)-N-(2,4-Dimethyl-6-iodophenyl)-5-amino-2-methyl-5-phenylpent-2-en-1-al: colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 9.28 (1H, s, CHO), 7.41 (1H, d, $J = 0.9$ Hz, Ar-H), 7.35-7.23 (5H, m, Ar-H), 6.85 (1H, d, $J = 0.9$ Hz, Ar-H), 6.42 (1H, tq, $J = 7.2, 1.2$ Hz, 3-CH), 4.51 (1H, t, $J = 6.9$ Hz, 5-CH), 3.78 (1H, s, NH), 3.03-2.86 (2H, m, 4-CH₂), 2.20 (3H, s, Ar-CH₃), 2.18 (3H, s, Ar-CH₃), 1.68 (3H, d, $J = 1.2$ Hz, 2-CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 195.0, 150.3, 143.3, 141.7, 140.5, 137.5, 133.6, 132.8, 130.3, 128.6, 127.7, 126.9, 95.9, 61.1, 36.2, 20.1, 19.9, 9.4; IR (film) 3338, 3024, 2915, 2710, 1684, 1640, 1473, 1436, 1266, 1232, 1055, 1025, 851, 760 cm^{-1} ; HRMS-EI (m/z): [M^+] calcd for $\text{C}_{20}\text{H}_{22}\text{INO}$ 419.0746, Found: 419.0755.

(2E)-N-(4-Chloro-4-iodophenyl)-5-amino-2-methyl-5-chlorophenylpent-2-en-1-al: colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 9.42 (1H, s, CHO), 7.61 (1H, d, $J = 2.1$ Hz, Ar-H), 7.39-7.26 (5H, m, Ar-H), 6.99 (1H, dd, $J = 8.7, 2.4$ Hz, Ar-H), 6.49 (1H, tq, $J = 7.5, 1.2$ Hz, 3-CH), 6.21 (1H, d, $J = 8.7$ Hz, Ar-H), 4.62-4.54 (2H, m, NH and 5-CH), 3.00-2.84 (2H, m, 4-CH₂), 1.78 (3H, d, $J = 1.2$ Hz, 2-CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 194.65, 194.60, 148.1, 148.0, 144.5, 142.0, 141.2, 137.9, 137.7, 129 (m), 128 (m), 126 (m), 122.7, 112.4, 112.2, 85.2, 57.8, 37.9, 9.7; IR (film) 3386, 3058, 3024, 2819, 2710, 1687, 1582, 1494, 1453, 1385, 1310, 1103, 1021, 868, 800, 756 cm^{-1} ; HRMS-ESI (m/z): [$\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{18}\text{ClINO}$ 426.0116, Found: 426.0128.

(2E)-N-(2-Iodo-6-methoxyphenyl)-5-amino-2-methyl-5-phenylpent-2-en-1-al: pale yellow viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 9.33 (1H, s, CHO), 7.32-7.18 (6H, m, Ar-H), 6.71 (1H, dd, $J = 8.1, 1.2$ Hz, Ar-H), 6.58-6.52 (2H, m, Ar-H and 3-CH), 5.07 (1H, br, 5-CH), 4.21 (1H, s, NH), 3.71 (3H, s, OCH_3), 2.94 (1H, dddd, $J = 15.0, 15.0, 7.2, 0.9$ Hz, 4-CH₂), 2.87 (1H, dddd, $J = 15.0, 15.0, 7.2, 0.9$ Hz, 4-CH₂), 1.71 (3H, d, $J = 1.2$ Hz, 2-CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 195.1, 150.7, 150.6, 142.3, 140.6, 137.2, 131.5, 128.4, 127.4, 126.7, 123.0, 111.7, 92.1, 59.9, 55.7, 36.9, 9.4; IR (film) 3338, 3024, 2935, 2826, 2710, 1684, 1575, 1463, 1229, 1086, 1025, 865, 760 cm^{-1} ; HRMS-ESI (m/z): [$\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{INO}_2$ 422.0611, Found: 422.0614.

(2E)-N-(2,4-Dimethyl-6-iodophenyl)-5-amino-5-cyclohexylcarbonyl-2-methylpent-2-en-1-ol: colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 9.39 (1H, s, CHO), 7.44 (1H, s, Ar-H), 6.89 (1H, s, Ar-H), 6.50 (1H, tq, $J = 7.2, 1.2$ Hz, 3-CH), 4.84-4.75 (1H, m, OCH), 4.29 (1H, dt, $J = 10.5, 6.3$ Hz, 5-CH), 4.18 (1H, d, $J = 10.5$ Hz, NH), 2.88-2.72 (2H, m, 4- CH_2), 2.30 (3H, s, Ar- CH_3), 2.20 (3H, s, Ar- CH_3), 1.82-1.20 (10H, m, *c*-Hex), 1.69 (3H, d, $J = 1.2$ Hz, 2- CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 194.7, 172.1, 148.0, 142.6, 141.3, 137.8, 133.7, 132.7, 129.8, 94.4, 74.1, 58.7, 32.7, 31.5, 25.2, 23.6, 19.9, 19.8, 9.4; IR (film) 3331, 2928, 2853, 2710, 1732, 1687, 1473, 1446, 1337, 1273, 1195, 1123, 1011, 855, 783 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{INO}_3$ 470.1186, Found: 470.1190.

Preparation of allyl alcohol or allylic ester 1 from amino aldehyde : A amino aldehyde (1.0 equiv) was dissolved in MeOH (0.2 M) and treated with NaBH_4 (1.0 equiv) at 0°C . The mixture was stirred for 30 min at the same temperature and for over 1 h at room temperature. The reactant was diluted with water and extracted with Et_2O . The combined extracts were washed with brine, dried over MgSO_4 and concentrated. The crude allyl alcohol was used without purification if required allyl acetate. Pure allyl alcohol could be obtained in quantitative yield as a colorless viscous oil after purification by chromatography on silica gel (hexane/ $\text{Et}_2\text{O} = 2:1$ to $1:2$). The crude allyl alcohol was dissolved in CH_2Cl_2 (0.2 M) and treated with Ac_2O (1.5 equiv), pyridine (1.5 equiv) and DMAP (0.05 equiv) at room temperature. After stirring for several hours, the volatiles were removed by evaporation and the residue was purified by chromatography on silica gel (hexane/ Et_2O as eluent) to give the corresponding allylic ester **1**. The yields of all compounds were noted in Table 3.

Table 3. Preparation of Allyl Alcohols and Allylic Acetates **1**.

entry	R ¹	R ²	R ³	Yield (%) ^a
1	Ph	H	H	a 93
2	4-Me-Ph	H	H	b 98
3	4-Cl-Ph	H	H	c 97
4	4-Br-Ph	H	H	d 92
5	Ph	Me	Me	e 97
6	Ph	H	Cl	f 99
7	Ph	OMe	H	g 97
8	COO-c-Hex	Me	Me	h 98

^a Isolated yield.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-phenyl-2-penten-1-ol:

colorless crystal, mp = 64-66 °C, purified by chromatography on silica gel (hexane/Et₂O = 3:1 to 1.5:1); ¹H NMR (300 MHz, CDCl₃) δ 7.62 (1H, dd, *J* = 8.1, 1.2 Hz, Ar-H), 7.34-7.20 (6H, m, Ar-H), 6.98 (1H, td, *J* = 7.5, 1.2 Hz, Ar-H), 6.36 (1H, td, *J* = 7.5, 1.2 Hz, Ar-H), 5.47 (1H, td, *J* = 7.2, 1.2 Hz, 3-CH), 4.68 (1H, d, *J* = 5.1 Hz, NH), 4.40 (1H, td, *J* = 7.5, 5.1 Hz, 5-CH), 4.03 (2H, s, 1-CH₂), 2.68-2.52 (2H, m, 4-CH₂), 1.74 (3H, s, 2-CH₃), 1.45 (1H, s, OH); ¹³C NMR (75 MHz, CDCl₃) δ 146.2, 142.8, 139.0, 138.7, 129.2, 128.6, 127.1, 126.1, 120.9, 118.7, 112.1, 85.5, 68.6, 58.2, 37.1, 14.1; IR (film) 3372, 3058, 3024, 2915, 2853, 1585, 1500, 1446, 1310, 1066, 1001, 919, 739 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₈H₂₀INO 393.0590, Found: 393.0594.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-phenyl-2-pentenyl

acetate (1a): colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ

7.63 (1H, dd, *J* = 7.8, 1.5 Hz, Ar-H), 7.33-7.21 (5H, m, Ar-H), 6.99 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 6.37 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 6.25 (1H, dd, *J* = 7.8, 1.5 Hz, Ar-H), 5.50 (1H, t, *J* = 7.5 Hz, 3-CH), 4.68 (1H, d, *J* = 5.1 Hz, NH), 4.49 (2H, s, 1-CH₂), 4.42 (1H, td, *J* = 7.5, 5.1 Hz, 5-CH), 2.69-2.53 (2H, m, 4-CH₂), 2.07 (3H, s, OCOCH₃), 1.73 (3H, s, 2-CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 146.1, 142.5, 138.8, 134.1, 129.2, 128.6, 127.1, 126.1, 124.0, 118.7, 112.1, 85.5, 69.6, 57.9, 37.0, 21.0, 14.4; IR (film) 3386, 3058, 3024, 2928, 1738, 1585, 1504, 1446,

1314, 1225, 1021, 1004, 919, 739 cm^{-1} ; HRMS-EI (m/z): [M^+] calcd for $\text{C}_{20}\text{H}_{22}\text{INO}_2$ 435.0695, Found: 435.0711.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-(4-methylphenyl)-2-pentenyl acetate (1b): colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 7.62 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 7.20 (2H, d, $J = 7.8$ Hz, Ar-H), 7.12 (2H, d, $J = 7.8$ Hz, Ar-H), 6.99 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.36 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.27 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 5.50 (1H, td, $J = 7.5, 1.2$ Hz, 3-CH), 4.66 (1H, d, $J = 5.4$ Hz, NH), 4.49 (2H, s, 1- CH_2), 4.39 (1H, td, $J = 7.2, 5.4$ Hz, 5-CH), 2.67-2.51 (2H, m, 4- CH_2), 2.32 (3H, s, Ar- CH_3), 2.07 (3H, s, OCOCH_3), 1.73 (3H, s, 2- CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 170.8, 146.3, 139.6, 139 (m), 136.7, 134.0, 129 (m), 126 (m), 124.34, 124.28, 119 (m), 112 (m), 85.5, 69.7 (t, $J = 4$ Hz), 57.7, 37.1, 21 (m), 14.4; IR (film) 3379, 3010, 2976, 2915, 2860, 1738, 1585, 1504, 1450, 1314, 1225, 1018, 1001, 814, 743 cm^{-1} ; HRMS-EI (m/z): [M^+] calcd for $\text{C}_{21}\text{H}_{24}\text{INO}_2$ (449.0852, Found: 449.0843.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-(4-chlorophenyl)-2-pentenyl acetate (1c): colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 7.64 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 7.31-7.23 (4H, m, Ar-H), 7.00 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.39 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.19 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 5.47 (1H, td, $J = 7.5, 1.5$ Hz, 3-CH), 4.66 (1H, d, $J = 5.1$ Hz, NH), 4.49 (2H, s, 1- CH_2), 4.39 (1H, td, $J = 7.2, 5.1$ Hz, 5-CH), 2.67-2.50 (2H, m, 4- CH_2), 2.07 (3H, s, OCOCH_3), 1.72 (3H, s, 2- CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 170.8, 145.9, 141.2, 138.9, 134.6, 132.8, 129.2, 128.8, 127.6, 123.5, 119.0, 112.1, 85.6, 69.5, 57.5, 36.9, 21.0, 14.4; IR (film) 3379, 3058, 2976, 2922, 1735, 1585, 1500, 1450, 1314, 1225, 1086, 1004, 824, 743 cm^{-1} ; HRMS-EI (m/z): [M^+] calcd for $\text{C}_{20}\text{H}_{21}\text{INO}_2$ 469.0306, Found: 469.0313.

(2E)-N-(2-Iodophenyl)-5-amino-2-methyl-5-(4-bromophenyl)-2-pentenyl acetate (1d): colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 7.64 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 7.44 (2H, dt, $J = 8.1, 1.8$ Hz, Ar-H), 7.20 (2H, dt, $J = 8.1, 1.8$ Hz, Ar-H), 7.00 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.39 (1H, td, $J = 7.8, 1.5$ Hz, Ar-H), 6.19 (1H, dd, $J = 7.8, 1.5$ Hz, Ar-H), 5.47 (1H, td, $J = 7.5, 0.9$ Hz, 3-CH), 4.66 (1H, d, $J = 5.1$ Hz, NH), 4.49 (2H, s, 1- CH_2), 4.37

(1H, td, $J = 7.2, 5.1$ Hz, 5-CH), 2.66-2.50 (2H, m, 4-CH₂), 2.07 (3H, s, OCOCH₃), 1.73 (3H, s, 2-CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 145.8, 141.7, 138.9, 134.6, 131.7, 129.2, 128.0, 123.5, 120.8, 119.0, 112.1, 85.6, 69.5, 57.5, 36.9, 21.0, 14.4; IR (film) 3379, 3058, 2922, 1735, 1585, 1500, 1453, 1314, 1225, 1072, 1008, 821, 743 cm⁻¹; HRMS-EI (m/z): [M^+] calcd for C₂₀H₂₁BrINO₂ 512.9800, Found: 512.9795.

(2E)-N-(2,4-Dimethyl-6-iodophenyl)-5-amino-2-methyl-5-phenyl-2-pentenyl acetate (1e): colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.39 (1H, d, $J = 1.2$ Hz, Ar-H), 7.31-7.18 (5H, m, Ar-H), 6.81 (1H, d, $J = 1.2$ Hz, Ar-H), 5.40 (1H, td, $J = 7.2, 0.9$ Hz, 3-CH), 4.42-4.34 (1H, m, 5-CH), 4.38 (2H, s, 1-CH₂), 3.82 (1H, s, NH), 2.72-2.56 (2H, m, 4-CH₂), 2.18 (3H, s, Ar-CH₃), 2.16 (3H, s, Ar-CH₃), 2.02 (3H, s, OCOCH₃), 1.58 (3H, s, 2-CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 143.8, 142.7, 137.3, 132.8, 132.7, 132.4, 129.7, 128.3, 127.13, 127.11, 125.4, 95.4, 69.8, 61.7, 35.4, 20.9, 20.3, 19.9, 14.2; IR (film) 3338, 3024, 2922, 2853, 1735, 1470, 1439, 1371, 1225, 1021, 848, 753 cm⁻¹; HRMS-EI (m/z): [M^+] calcd for C₂₂H₂₆INO₂ 464.1087, Found: 464.1093.

(2E)-N-(4-Chloro-2-Iodophenyl)-5-amino-2-methyl-5-phenyl-2-pentenyl acetate (1f): colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.60 (1H, d, $J = 2.4$ Hz, Ar-H), 7.35-7.21 (5H, m, Ar-H), 6.95 (1H, dd, $J = 8.7, 2.4$ Hz, Ar-H), 6.14 (1H, d, $J = 8.7$ Hz, Ar-H), 5.48 (1H, td, $J = 7.5, 1.2$ Hz, 3-CH), 4.67 (1H, d, $J = 5.4$ Hz, NH), 4.49 (2H, s, 1-CH₂), 4.38 (1H, td, $J = 7.2, 5.4$ Hz, 5-CH), 2.69-2.52 (2H, m, 4-CH₂), 2.07 (3H, s, OCOCH₃), 1.72 (3H, s, 2-CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 144.9, 142.1, 137.7, 134.4, 129.0, 128.7, 127.3, 126.1, 123.7, 122.1, 112.3, 84.9, 69.5, 58.1, 37.0, 21.0, 14.4; IR (film) 3372, 3058, 3024, 2922, 1735, 1582, 1490, 1450, 1385, 1310, 1225, 1021, 868, 797, 753 cm⁻¹; HRMS-ESI (m/z): [$M+H$]⁺ calcd for C₂₀H₂₂INO₂ 470.0378, Found: 470.0385.

(2E)-N-(2-Iodo-6-methoxyphenyl)-5-amino-2-methyl-5-phenyl-2-pentenyl acetate (1g): colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.12 (6H, m, Ar-H), 6.66 (1H, dd, $J = 8.1, 1.2$ Hz, Ar-H), 6.48 (1H, t, $J = 8.1$ Hz, Ar-H), 5.47 (1H, td, $J = 7.2, 1.2$ Hz, 3-CH), 4.97 (1H, br, NH), 4.42 (2H, s, 1-CH₂), 4.24 (1H, br, 5-CH), 3.67 (3H, s, Ar-OCH₃), 2.68-2.53 (2H, m, 4-CH₂), 2.03 (3H, s, OCOCH₃), 1.61 (3H, s, 2-CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 150.2, 143.2, 137.7, 132.5, 131.5, 128.0, 126.9,

126.8, 125.3, 122.1, 111.8, 91.5, 69.9, 60.4, 55.6, 35.9, 21.0, 14.2; IR (film) 3338, 3058, 3024, 2935, 2826, 1735, 1568, 1463, 1371, 1225, 1025, 851, 753 cm^{-1} ; HRMS-ESI (m/z): $[M+H]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{INO}_2$ 466.0873, Found: 466.0875.

(2E)-N-(2,4-Dimethyl-6-iodophenyl)-5-amino-5-cyclohexylcarbonyl-2-methyl-2-pentenyl acetate (1h):

colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 7.43 (1H, s, Ar-H), 6.87 (1H, s, Ar-H), 5.46 (1H, td, $J = 7.2, 1.2$ Hz, 3-CH), 4.80-4.71 (1H, m, OCH), 4.44 (2H, s, 1- CH_2), 4.20-4.11 (2H, m, NH and 5-CH), 2.62-2.47 (2H, m, 4- CH_2), 2.28 (3H, s, Ar- CH_3), 2.18 (3H, s, Ar- CH_3), 2.06 (3H, s, OCOCH_3), 1.81-1.47 (5H, m), 1.60 (3H, s, 2- CH_3), 1.42-1.20 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 172.7, 170.8, 143.2, 137.7, 133.4, 133.1, 132.6, 129.4, 123.2, 94.0, 73.6, 69.7, 59.3, 31.6, 31.48, 31.45, 25.3, 23.6, 20.9, 19.9, 14.1; IR (film) 3324, 2928, 2853, 1732, 1470, 1446, 1375, 1225, 1120, 1015, 851, 783 cm^{-1} ; HRMS-ESI (m/z): $[M+H]^+$ calcd for $\text{C}_{23}\text{H}_{33}\text{INO}_4$ 514.1448, Found: 514.1428.

General procedure of palladium catalyzed cross-coupling reactions between an aryl iodide and allyl acetate: To a mixture of **1** (1.0 equiv), (*o*-tolyl) $_3\text{P}$ (22 mol%) and *n*-BuNMe $_2$ (2.0 equiv) in $\text{CH}_3\text{CN-H}_2\text{O}$ (10:1, 0.1 M) was added $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (5 mol%). The mixture was degassed and filled with a N_2 gas quickly and refluxed for 6 h under a N_2 atmosphere. The resulting mixture was cooled to room temperature and treated with saturated NH_4Cl . Extractive workup and purification of the residue by column chromatography on silica gel (hexane/Et $_2\text{O}$ = 40:1 to 20:1 as eluent) gave 2,4-disubstituted-1,2,3,4-tetrahydroquinoline **2**. The yields of all compounds are noted in Table 4.

Table 4. Intramolecular Cross-Coupling Reactions between Aryl Iodide and Allyl Acetate.

entry	R ¹	R ²	R ³		Yield (%) ^b
1	Ph	H	H	a	76
2	4-Me-Ph	H	H	b	80
3	4-Cl-Ph	H	H	c	81
4	4-Br-Ph	H	H	d	73
5	Ph	Me	Me	e	79
6	Ph	H	Cl	f	88
7	Ph	OMe	H	g	77
8	COO- <i>c</i> -Hex	Me	Me	h	84 ^c

^a CHCl₃ adduct was used.

^b Isolated yield.

^c *cis* isomer was isolated in 2% yield.

***trans*-4-Isopropenyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2a):**

colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.26 (5H, m, Ar-H), 7.04 (1H, td, *J* = 7.8, 1.2 Hz, Ar-H), 6.97 (1H, d, *J* = 7.8 Hz, Ar-H), 6.65 (1H, td, *J* = 7.8, 1.2 Hz, Ar-H), 6.57 (1H, dd, *J* = 7.8, 1.2 Hz, Ar-H), 5.01 (1H, s, C=CH₂), 4.43 (1H, s, C=CH₂), 4.40 (1H, dd, *J* = 9.6, 3.3 Hz, 2-CH), 4.07 (1H, s, NH), 3.41 (1H, dd, *J* = 5.4, 3.6 Hz, 4-CH), 2.11 (1H, ddd, *J* = 13.2, 3.6, 3.3 Hz, 3-CH₂), 2.00 (1H, ddd, *J* = 13.2, 9.6, 5.4 Hz, 3-CH₂), 1.83 (3H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 149.1, 144.62, 144.57, 130.3, 128.6, 127.4, 127.3, 126.7, 122.0, 117.0, 114.7, 113.9, 52.4, 43.4, 34.2, 21.1; IR (film) 3392, 3024, 2956, 2915, 2853, 1606, 1483, 1314, 1256, 1113, 1025, 896, 746 cm⁻¹; HRMS-EI (*m/z*): [M⁺] calcd for C₁₈H₁₉N 249.1518, Found: 249.1519.

***trans*-4-Isopropenyl-2-(4-methylphenyl)-1,2,3,4-tetrahydroquinoline (2b):**

colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.27 (2H, d, *J* = 8.1 Hz, Ar-H), 7.15 (2H, d, *J* = 8.1 Hz, Ar-H), 7.03 (1H, td, *J* = 7.5, 1.2 Hz, Ar-H), 6.96 (1H, d, *J* = 7.5 Hz, Ar-H), 6.64 (1H, td, *J* = 7.5, 1.2 Hz, Ar-H), 6.55 (1H, d, *J* = 7.5 Hz, Ar-H), 5.00 (1H, s, C=CH₂), 4.42 (1H, d, *J* = 0.9 Hz, C=CH₂), 4.35 (1H, dd, *J* = 9.9, 3.3 Hz, 4-CH), 4.02 (1H, s,

NH), 3.41 (1H, dd, $J = 5.7, 3.6$ Hz, 2-CH), 2.35 (3H, s, Ar-CH₃), 2.08 (1H, ddd, $J = 13.2, 3.6, 3.3$ Hz, 3-CH₂), 1.98 (1H, ddd, $J = 13.2, 9.9, 5.7$ Hz, 3-CH₂), 1.83 (3H, d, $J = 0.9$ Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 149.1, 144.7, 141.6, 137.1, 130.3, 129.2, 127.3, 126.6, 122.0, 116.9, 114.7, 113.9, 52.0, 43.4, 34.2, 21.2, 21.1; IR (film) 3392, 3010, 2922, 2853, 1606, 1480, 1443, 1310, 1256, 1174, 1103, 1018, 896, 817, 746 cm⁻¹; HRMS-EI (m/z): [M^+] calcd for C₁₉H₂₁N 263.1674, Found: 263.1679.

***trans*-2-(4-Chlorophenyl)-4-isopropenyl-1,2,3,4-tetrahydroquinoline (2c):**

colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.31 (4H, s, Ar-H), 7.04 (1H, t, $J = 7.8$ Hz, Ar-H), 6.97 (1H, d, $J = 7.8$ Hz, Ar-H), 6.67 (1H, t, $J = 7.8$ Hz, Ar-H), 6.57 (1H, d, $J = 7.8$ Hz, Ar-H), 5.01 (1H, s, C=CH₂), 4.42 (1H, s, C=CH₂), 4.38 (1H, dd, $J = 9.6, 3.3$ Hz, 2-CH), 4.03 (1H, s, NH), 3.39 (1H, dd, $J = 5.4, 3.9$ Hz, 4-CH),

2.07 (1H, ddd, $J = 13.2, 3.9, 3.3$ Hz, 3-CH₂), 1.95 (1H, ddd, $J = 13.2, 9.6, 5.4$ Hz, 3-CH₂), 1.82 (3H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 148.9, 144.3, 143.1, 133.0, 130.2, 128.7, 128.0, 127.4, 122.0, 117.2, 114.9, 114.0, 51.8, 43.2, 34.3, 21.1; IR (film) 3392, 3044, 3010, 2922, 2853, 1602, 1483, 1310, 1252, 1089, 1011, 902, 824, 743 cm⁻¹; HRMS-EI (m/z): [M^+] calcd for C₁₈H₁₈N 283.1123, Found: 283.1124.

***trans*-2-(4-Bromophenyl)-4-isopropenyl-1,2,3,4-tetrahydroquinoline (2d):**

colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.46 (2H, dt, $J = 8.4, 2.4$ Hz, Ar-H), 7.25 (2H, dt, $J = 8.4, 2.4$ Hz, Ar-H), 7.04 (1H, td, $J = 7.5, 1.2$ Hz, Ar-H), 6.96 (1H, dd, $J = 7.5, 1.2$ Hz, Ar-H), 6.67 (1H, td, $J = 7.5, 1.2$ Hz, Ar-H), 6.57 (1H, dd, $J = 7.5, 1.2$ Hz, Ar-H), 5.01 (1H, s, C=CH₂), 4.41 (1H, s, C=CH₂),

4.37 (1H, dd, $J = 9.6, 3.3$ Hz, 2-CH), 4.03 (1H, s, NH), 3.38 (1H, dd, $J = 5.4, 3.9$ Hz, 4-CH), 2.07 (1H, ddd, $J = 13.2, 3.9, 3.3$ Hz, 3-CH₂), 1.94 (1H, ddd, $J = 13.2, 9.6, 5.4$ Hz, 3-CH₂), 1.82 (3H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 148.8, 144.3, 143.6, 132 (m), 131 (m), 130 (m), 129 (m), 128 (m), 127 (m), 121.9, 121.0, 117 (m), 115.1, 114.7, 114.1, 113.9, 51.8 (d, $J = 6$ Hz), 43.1 (d, $J = 10$ Hz), 34.2 (t, $J = 10$ Hz), 21.1; IR (film) 3392, 3044, 2956, 2922, 2853, 1602, 1483, 1314, 1256, 1117, 1069, 1004, 899, 821, 746 cm⁻¹; HRMS-EI (m/z): [M^+] calcd for C₁₈H₁₈BrN 327.0623, Found: 327.0614.

***trans*-6,8-Dimethyl-4-isopropenyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2e):**

colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.25 (5H, m, Ar-H), 6.79 (1H, s, Ar-H), 6.69 (1H, s, Ar-H), 5.01 (1H, s,

C=CH₂), 4.44-4.39 (1H, m, 2-CH), 4.42 (1H, s, C=CH₂), 3.77 (1H, s, NH), 3.39 (1H, dd, *J* = 5.4, 3.6 Hz, 4-CH), 2.21 (3H, s, Ar-CH₃), 2.12-2.06 (1H, m, 3-CH₂), 2.10 (3H, s, Ar-CH₃), 1.98 (1H, ddd, *J* = 13.2, 9.9, 5.4 Hz, 3-CH₂), 1.84 (3H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 149.3, 145.1, 140.3, 129.2, 128.6, 128.5, 128.5 (d, *J* = 8 Hz), 127.4, 126.7, 125.4, 121.5, 120.9, 114.6 (d, *J* = 8 Hz), 52.6, 43.7 (d, *J* = 3 Hz), 34.4, 21.2, 20.4 (d, *J* = 3 Hz), 17.3; IR (film) 3413, 3031, 2962, 2915, 2853, 1643, 1487, 1450, 1310, 1259, 1062, 1028, 896, 858, 756 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₂₀H₂₃N 277.1831, Found: 277.1832.

***trans*-6-Chloro-4-isopropenyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2f):**

colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.26 (5H, m, Ar-H), 6.98 (1H, dd, *J* = 8.4, 2.4 Hz, Ar-H), 6.94 (1H, d, *J* = 2.4 Hz, Ar-H), 6.49 (1H, d, *J* = 8.4 Hz, Ar-H), 5.02 (1H, s, C=CH₂), 4.44 (1H, s, C=CH₂), 4.38 (1H, dd, *J* = 9.6, 3.3 Hz, 2-CH), 4.09 (1H, s, NH), 3.36 (1H, dd, *J* = 5.4, 3.6 Hz, 4-CH), 2.10 (1H, ddd, *J* = 13.2, 3.6, 3.3 Hz, 3-CH₂), 1.96 (1H, ddd, *J* = 13.2, 9.6, 5.4 Hz, 3-CH₂), 1.81 (3H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 148.2, 144.1, 143.2, 129.7, 128.6, 127.6, 127.2, 126.6, 123.5, 121.4, 115.1, 114.9, 52.4, 43.2, 33.8, 21.0; IR (film) 3399, 3024, 2956, 2922, 2853, 1599, 1490, 1303, 1252, 1086, 896, 807, 756 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₈H₁₈N 283.1128, Found: 283.1129.

***trans*-4-Isopropenyl-8-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline (2g):**

colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.23 (5H, m, Ar-H), 6.68-6.58 (3H, m, Ar-H), 4.99 (1H, s, C=CH₂), 4.55 (1H, s, NH), 4.43 (1H, s, C=CH₂), 4.39 (1H, dd, *J* = 9.6, 3.3 Hz, 2-CH), 3.83 (3H, s, OCH₃), 3.43 (1H, dd, *J* = 5.7, 3.6 Hz, 4-CH), 2.11 (1H, ddd, *J* = 13.2, 3.6, 3.3 Hz, 3-CH₂), 2.01 (1H, ddd, *J* = 13.2, 9.6, 5.7 Hz, 3-CH₂), 1.82 (3H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 149.1, 145.9, 144.7, 134.6, 128.5, 127.3, 126.7, 122.3, 121.8, 115.6, 114.5, 107.5, 55.3, 51.9, 43.2, 34.3, 21.1; IR (film) 3413, 3058, 3024, 2949, 2853, 1585, 1494, 1450, 1337, 1246, 1100, 1045, 896, 729 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₉H₂₁N 279.1623, Found: 279.1628.

***trans*-6,8-Dimethyl-4-isopropenyl-1,2,3,4-tetrahydroquinoline-2-carboxylic acid cyclohexyl ester (2h):**

pale yellow viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 6.77 (1H, s, Ar-H), 6.64 (1H, s, Ar-H), 4.99 (1H, s, C=CH₂), 4.86 (1H, tt, *J* = 8.7, 3.9 Hz, OCH), 4.45 (1H, s, C=CH₂), 4.13 (1H, s, NH), 3.99 (1H, dd, *J* = 9.9, 3.3 Hz, 2-CH), 3.43 (1H, dd, *J* = 5.4, 3.6 Hz, 4-CH), 2.28 (1H, ddd, *J* = 13.2, 3.6, 3.3

Hz, 3-CH₂), 2.19 (3H, s, Ar-CH₃), 2.15 (3H, s, Ar-CH₃), 1.91 (1H, ddd, $J = 13.2, 9.9, 5.4$ Hz, 3-CH₂), 1.87-1.78 (2H, m), 1.82 (3H, s, CH₃), 1.76-1.66 (2H, m), 1.57-1.24 (6H, m); ¹³C NMR (75 MHz, CDCl₃) δ 173.3, 147.9, 138.8, 129.3, 127.9, 125.9, 121.7, 121.5, 114.9, 73.4, 51.4, 43.4, 31.4, 28.3, 25.3, 23.5, 20.7, 20.4, 17.2; IR (film) 3406, 3072, 2928, 2853, 1732, 1490, 1446, 1215, 1035, 1011, 896, 858, 743 cm⁻¹; HRMS-EI (m/z): [M^+] calcd for C₂₁H₂₉N 327.2198, Found: 327.2203.

***cis*-6,8-Dimethyl-4-isopropenyl-1,2,3,4-tetrahydroquinoline-2-carboxylic acid cyclohexyl ester (*cis*-2h):** This compound was assigned by only ¹H NMR and HRMS because little amount was obtained as a side product; pale yellow viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 6.76 (1H, s, Ar-H), 6.69 (1H, s, Ar-H),

4.99-4.96 (2H, m, NH and C=CH₂), 4.88 (1H, tt, $J = 8.7, 3.6$ Hz, OCH), 4.10 (1H, s, C=CH₂), 4.10-4.03 (1H, m, 2-CH), 3.73 (1H, dd, $J = 11.7, 5.4$ Hz, 4-CH), 2.31-2.24 (1H, m), 2.19 (3H, s, Ar-CH₃), 2.14 (3H, s, Ar-CH₃), 1.93 (1H, ddd, $J = 12.3, 11.7, 11.7$ Hz, 3-CH₂), 1.91-1.84 (2H, m), 1.78-1.69 (2H, m), 1.59 (3H, s, CH₃), 1.59-1.24 (6H, m); HRMS-EI (m/z): [M^+] calcd for C₂₁H₂₉N 327.2198, Found: 327.2201.

Determination of configuration of 2,4-disubstituted-1,2,3,4-tetrahydro-quinoline 2:

The configuration was determined by preparation of *trans*- and *cis*-4-isopropyl-2-phenyl-1,2,3,4-tetrahydroquinoline **2i** respectively (Scheme 2 and 3).

(1) ***trans*-4-isopropyl-2-phenyl-1,2,3,4-tetrahydroquinoline:** To a solution of *trans*-4-isopropenyl-2-phenyl-1,2,3,4-tetrahydroquinoline **2a** (49.3 mg, 0.198 mmol, *trans* only) in MeOH (2.0 mL) was added Pd-C (10%, 10 mg) and the mixture was stirred for 48 h at room temperature under a H₂ atmosphere. The resulting mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was purified by chromatography on silica gel (hexane/Et₂O = 40:1 to 15:1 as eluent) to give *trans*-4-isopropyl-2-phenyl-1,2,3,4-tetrahydroquinoline as a pale yellow viscous oil (45.5 mg, 0.181 mmol, 91 % yield, *trans/cis* = 8:1 determined by ¹H NMR analysis). ¹H NMR (300 MHz, CDCl₃) δ 7.46-7.23 (5H, m, Ar-H), 7.05-6.99 (2H, m, Ar-H), 6.62 (1H, td, $J = 7.5, 1.2$ Hz, Ar-H), 6.53 (1H, d, $J = 8.4$ Hz, Ar-H), 4.50 (1H, dd, $J = 11.2, 3.6$ Hz, 2-CH), 4.02 (1H, br, NH), 2.44-2.38 (1H, m, 4-CH), 2.17 (1H, ddd, $J = 13.5, 3.9, 3.6$ Hz, 3-CH₂), 2.05-1.92 (1H, m, CH(CH₃)₂), 1.82 (1H, ddd, $J = 13.5, 11.1, 4.5$ Hz, 3-CH₂), 1.02 (3H, d, $J = 6.6$ Hz, CH(CH₃)₂), 0.98 (3H, d, $J = 6.6$ Hz, CH(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 145.4, 143.9, 130.1, 128.6, 127.4, 127.0, 126.5, 123.6, 116.0, 113.6, 53.1, 42.8, 33.1, 31.4, 21.6, 19.7; IR

(film) 3399, 3051, 3017, 2956, 2860, 1606, 1483, 1310, 1256, 1117, 1021, 913, 743 cm^{-1} ;
HRMS-EI (m/z): [M^+] calcd for $\text{C}_{18}\text{H}_{21}\text{N}$ 251.1674, Found: 251.1671.

^a The selectivity was determined by ^1H NMR analysis.

Scheme 2. Reduction of Isopropenyl by Hydrogenation.

(2) ***cis*-4-isopropenyl-2-phenyl-1,2,3,4-tetrahydroquinoline:** (i) To a mixture of 2-phenyl-4-quinolinecarboxylic acid (1.25 g, 5.00 mmol), MeOH (0.61 mL, 15 mmol) and DMAP (31 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) was added a solution of DCC (1.03 g, 5.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C and for 12 h at room temperature. The resulting mixture was filtered and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (hexane/ Et_2O = 10:1 to 5:1 as eluent) to obtain the corresponding methyl ester as colorless crystals (1.30 g, 4.94 mmol, 99% yield). (ii) To a solution of methyl ester (263 mg, 1.00 mmol) in Et_2O (2.0 mL) was added a 1 M MeMgI solution in Et_2O (5.0 mL, 5.0 mmol) at 0 °C. After stirring for 36 h at room temperature, the resulting mixture was quenched with saturated NH_4Cl at 0 °C and extracted with Et_2O . The combined extracts were washed with saturated NaHCO_3 and brine, dried over Na_2SO_4 and concentrated. The crude *tert*-alcohol was obtained as colorless crystals (251 mg, 0.953 mmol, 95% yield) and it was used without purification in next step. The crude *tert*-alcohol (79 mg, 0.30 mmol) was dissolved in pyridine (1.0 mL) and treated with SOCl_2 (2.0 mL) at 0 °C and the mixture was stirred for 2 h at room temperature. The volatiles were removed in vacuo (high-vacuum with heating) and saturated NaHCO_3 was added to the residue. The mixture was extracted with Et_2O and the combined extracts were washed with brine and dried over Na_2SO_4 . Removal of the solvents and purification of the residue by column chromatography on silica gel (hexane/ Et_2O = 20:1 to 10:1 as eluent) gave 4-isopropenyl-2-phenylquinoline as a colorless viscous oil (43.9 mg, 0.179 mmol, 60% yield). (iii) A mixture of 4-isopropenyl-2-phenylquinoline (112 mg, 0.446 mmol) and PtO_2 (5.0 mg, 0.022 mmol) in MeOH (4.5 mL) was stirred for 16 h under a H_2 atmosphere. After removal of the catalyst by Celite filtration, the volatiles were removed by evaporation. The

residue was purified by column chromatography on silica gel (hexane/Et₂O = 40:1 to 20:1) to afford *cis*-4-isopropyl-2-phenyl-1,2,3,4-tetrahydroquinoline as a colorless viscous oil (66.1 mg, 0.263 mmol, 59 % yield, *trans/cis* = 1:>20 determined by ¹H NMR analysis). Similar selectivities have been previously observed in PtO₂ catalyzed hydrogenations of substituted quinolines.⁶

^a The selectivity was determined by ¹H NMR analysis.

Scheme 3. Determination of Configuration of 2,4-Disubstituted-1,2,3,4-Tetrahydroquinoline.

2-Phenyl-4-quinolinecarboxylic acid methyl ester⁷: colorless crystal, mp = 60-61 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.74 (1H, dd, *J* = 8.4, 0.6 Hz, Ar-H), 8.40 (1H, s, Ar-H), 8.24-8.19 (3H, m, Ar-H), 7.76 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 7.62 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 7.57-7.45 (3H, m, Ar-H), 4.06 (3H, s, COOCH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.8, 156.7, 149.2, 138.8, 135.5, 130.3, 129.9, 129.7, 128.9, 127.8, 127.4, 125.4, 124.0, 120.3, 52.7 (d, *J* = 3 Hz); IR (film) 3058, 2949, 1725, 1589, 1548, 1433, 1344, 1249, 1198, 1147, 1028, 1015, 947, 899, 767 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₇H₁₃NO₂ 263.0946, Found: 263.0954.

4-Isopropenyl-2-phenylquinoline: colorless viscous oil; ¹H NMR (300 MHz, CDCl₃) δ 8.20-8.14 (3H, m, Ar-H), 8.04 (1H, dd, *J* = 8.4, 0.9 Hz, Ar-H), 7.71 (1H, td, *J* = 7.8, 1.5 Hz, Ar-H), 7.69 (1H, s, Ar-H), 7.55-7.43 (4H, m, Ar-H), 5.51 (1H, dq, *J* = 1.8, 1.5 Hz, C=CH₂), 5.18 (1H, dd, *J* = 1.8, 0.9 Hz, C=CH₂), 2.26 (3H, dd, *J* = 1.5, 0.9 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 157.0, 151.3, 148.7, 142.5, 139.8, 130.2, 129.4, 129.2, 128.8, 127.5, 126.1, 125.3, 125.1, 117.3,

117.2, 24.6; IR (film) 3058, 2962, 1585, 1545, 1494, 1443, 1351, 1232, 1076, 1028, 906, 882, 770 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{18}\text{H}_{15}\text{N}$ 245.1205, Found: 245.1199.

***cis*-4-isopropyl-2-phenyl-1,2,3,4-tetrahydroquinoline:**

colorless viscous oil; ^1H NMR (300 MHz, CDCl_3) δ 7.46-7.42 (2H, m, Ar-H), 7.37 (2H, tt, $J = 7.5, 1.2$ Hz, Ar-H), 7.30 (1H, tt, $J = 7.5, 1.2$ Hz, Ar-H), 7.18 (1H, d, $J = 7.2$ Hz, Ar-H), 6.99 (1H, tt, $J = 7.5, 1.2$ Hz, Ar-H), 6.72 (1H, td, $J = 7.5, 1.2$ Hz, Ar-H), 6.54 (1H, dd, $J = 7.5, 1.2$ Hz, Ar-H), 4.37 (1H, dd, $J = 11.4, 2.7$ Hz, 2-CH), 3.89 (1H, br, NH), 3.12-3.05 (1H, m, 4-CH), 2.51 (1H, qqd, $J = 6.9, 6.9, 3.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.01 (1H, ddd, $J = 12.9, 5.7, 2.7$ Hz, 3- CH_2), 1.76 (1H, dd, $J = 12.9, 11.4$ Hz, 3- CH_2), 1.05 (3H, d, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.73 (3H, d, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 146.2, 144.8, 128.6, 127.6, 127.0, 126.6, 126.5, 124.6, 117.9, 114.7, 57.2, 41.6, 32.1, 29.3, 20.9, 15.5; IR (film) 3365, 3024, 2949, 2867, 1602, 1477, 1334, 1310, 1252, 1184, 1113, 919, 845, 746 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{18}\text{H}_{21}\text{N}$ 251.1674, Found: 251.1666.

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Preparation of iodophenols derivatives

Iodophenols derivatives (1-iodonaphthol, 2-iodo-5-trifluoromethylphenol and 3-hydroxy-4-iodo-benzoic acid methyl ester) were prepared according to procedures

described in the literature.¹ The iodinated compounds were purified by chromatography over silica gel using mixtures of hexanes/ethyl acetate as eluent: (1-iodonaphthol : 74%, Hexanes:EtOAc, 95:5); (2-iodo-5-trifluoromethylphenol : 75%, Hexanes:EtOAc, 9:1); (3-hydroxy-4-iodo-benzoic acid methyl ester : 75%, Hexanes:EtOAc, 9:1). *N*-(2-Iodo-phenyl)-4-methyl-benzenesulfonamide and 2-(2-iodophenyl)-malonic acid diethyl ester were prepared according to procedures described in the literature.²

To a solution of the aromatic substrate (iodophenol derivative or tosylated aniline derivative) (1 eq.) in dry CH₃CN (C=0.06 M) were added K₂CO₃ (1.2 eq.) and (Z)-BrCH₂CH=CHCH₂OCO₂Et (1.1 eq.). The reaction mixture was stirred at room temperature for 3-24h depending on the starting material (see table below). The reaction was quenched with water and extracted with diethyl ether. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography over silica gel with mixtures of hexanes/EtOAc.

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IR (film) 2982, 2931, 2906, 1743, 1621, 1592, 1501, 1460, 1370, 1349, 1255, 1149, 1049, 1018, 873 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{O}_4\text{INa}$ 435.0063, found 435.0077.

Carbonic acid ethyl ester 4-(2-iodo-5-trifluoromethyl-phenoxy)-but-2-enyl ester (3b): colorless viscous oil, purified by chromatography over

silica gel (81%, Hexanes:EtOAc, 95:5, R_f = 0.3); ^1H NMR (CDCl_3 , 400 MHz) 7.89 (d, J = 8.1 Hz, 1H), 7.01 (s, 1H), 6.97 (d, J = 8.8 Hz, 1H), 6.00-5.95 (m, 1H), 5.89-5.83 (m, 1H), 4.79 (m, 4H), 4.21 (q, J = 7.3 Hz, 2H), 1.31 (t, J = 7.3 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) 157.19, 154.86, 139.99, 131.77 (q, J = 32.8 Hz), 128.55, 127.42, 123.59 (q, J = 272.7 Hz), 119.18 (q, J = 3.8 Hz), 108.52 (q, J = 3.8 Hz), 91.03 (q, J = 1.5 Hz), 65.28, 64.08, 63.23, 14.11; IR (film) 2985, 2931, 2869, 1745, 1595, 1580, 1481, 1416, 1377, 1327, 1261, 1170, 1128, 1083, 1017, 874, 791 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{O}_4\text{F}_3\text{INa}$ 452.9781, found 452.9770.

3-(4-Ethoxycarbonyloxy-but-2-enyloxy)-4-iodo-benzoic acid methyl ester (3c): white solid, purified by chromatography over silica gel (91%, Hexanes:EtOAc,

9:1, R_f = 0.2); M.p. 57-59 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) 7.79 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 1.5 Hz, 1H), 7.31 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H), 5.97-5.91 (m, 1H), 5.83-5.76 (m, 1H), 4.76 (d, J = 6.6 Hz, 2H), 4.71 (d, J = 6.0 Hz, 2H), 4.15 (q, J = 7.3 Hz, 2H), 3.85 (s, 3H), 1.25 (t, J = 7.3 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) 166.14, 156.87, 154.78, 139.47, 131.36, 128.57, 127.28, 123.47, 112.23, 93.03, 65.05, 63.98, 63.32, 52.17, 14.11; IR (film) 2984, 2952, 2906, 1745, 1723, 1585, 1571, 1475, 1436, 1406, 1377, 1291, 1257, 1109, 1017, 874, 791, 759 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_6\text{INa}$ 442.9962, found 442.9963.

Carbonic acid ethyl ester 4-[(2-iodo-phenyl)-(toluene-4-sulfonyl)-amino]-but-2-enyl ester (3d): white solid, purified by chromatography over silica

gel (95%, Hexanes:EtOAc, 85:15, R_f = 0.2); M.p. 76-78 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) 7.89 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.31-7.25 (m, 3H), 7.02 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 5.80-5.74 (m,

1H), 5.65-5.59 (m, 1H), 4.42-4.18 (m, 4H), 4.14 (q, $J = 7.3$ Hz, 2H), 2.44 (s, 3H), 1.27 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 154.71, 143.83, 140.98, 140.36, 136.10, 130.62, 129.97, 129.54, 128.71, 128.45, 128.08, 127.45, 103.00, 64.00, 62.41, 48.05, 21.53, 14.17; IR (film) 3053, 3022, 2983, 2924, 2869, 1745, 1597, 1466, 1440, 1375, 1352, 1258, 1164, 1092, 1018, 873, 715, 658 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_5\text{SiNa}$ 538.0155, found 538.0137.

To a solution of 2-(2-iodophenyl)-malonic acid diethyl ester (1 eq.) in dry THF ($C = 0.05$ M) were added potassium *tert*-butoxide (1.2 eq.) and (Z)- $\text{BrCH}_2\text{CH}=\text{CHCH}_2\text{OCO}_2\text{Et}$ (1.1 eq.). The reaction mixture was stirred at room temperature for 48h. The reaction was quenched with water and extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography over silica gel (Hexanes:EtOAc, 9:1) to give **3e** as a colorless viscous oil.

1-(4-Ethoxycarbonyloxybut-2-enyl)-2-(2-iodo-phenyl)-malonic acid diethyl ester (3e): colorless viscous oil, purified by chromatography over silica gel (87%, Hexanes:EtOAc, 9:1, $R_f = 0.2$); ^1H NMR (CDCl_3 , 400 MHz) 7.91 (dd, $J = 8.1$ Hz, $J = 1.5$ Hz, 1H), 7.29 (td, $J = 8.1$ Hz, $J = 1.5$ Hz, 1H), 7.05 (dd, $J = 8.1$ Hz, $J = 1.5$ Hz, 1H), 6.93 (td, $J = 8.1$ Hz, $J = 1.5$ Hz, 1H), 5.57-5.46 (m, 2H), 4.64 (d, $J = 5.9$ Hz, 2H), 4.35-4.19 (m, 4H), 4.16 (q, $J = 7.3$ Hz, 2H), 3.30 (d, $J = 5.9$ Hz, 2H), 1.29-1.24 (m, 9H); ^{13}C NMR (CDCl_3 , 100 MHz) 169.31, 154.93, 142.16, 139.45, 130.10, 129.63, 128.81, 127.80, 125.52, 97.49, 66.15, 63.76, 63.59, 62.16, 32.55, 14.16, 13.71; IR (film) 2982, 2937, 2900, 1744, 1466, 1440, 1388, 1374, 1255, 1201, 1095, 1060, 1013, 872, 792, 743; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{O}_7\text{INa}$ 527.0537, found 527.0519.

substrates	R	X	Reaction time (h)	Yield (%)
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3a	H, naphthalene	O	3	76
3b	CF ₃	O	24	81
3c	CO ₂ Me	O	3	91
3d	H	NTs	24	95
3e	H	C(CO ₂ Et) ₂	48	87

To a suspension of NaH (1.3 eq.) in DMF (C = 0.15 M) was added 1-iodonaphthol (1 eq.) at room temperature. After 10 minutes were added *n*Bu₄NI (10 mol%) and 4-bromo-1-butene or 5-bromo-1-pentene (1.2 eq.). After stirring at room temperature for 2h, the mixture was poured into water (100 mL). The aqueous layer was extracted with Et₂O. The organic layer was washed with water and brine, and dried over Na₂SO₄. After concentration under reduced pressure, the residue was purified by chromatography over silica gel (Hexanes:EtOAc, 98:2) to give the alkylated products with 4-bromo-1-butene or 5-bromo-1-pentene as colorless viscous oils in 54% and 91% yields respectively.

2-But-3-enyloxy-1-iodo-naphthalene: colorless viscous oil, purified by chromatography over silica gel (54%, Hexanes:EtOAc, 95:5, R_f = 0.46); ¹H NMR (CDCl₃, 400 MHz) 8.17 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.54 (ddd, *J* = 8.4 Hz, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.39 (ddd, *J* = 8.0 Hz, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.10-5.99 (tdd, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 7.0 Hz, 1H), 5.28-5.23 (tdd, *J* = 17.2 Hz, *J* = 1.8 Hz, *J* = 1.4 Hz, 1H), 5.19-5.16 (tdd, *J* = 10.2 Hz, *J* = 1.8 Hz, *J* = 1.4 Hz, 1H), 4.20 (m, 2H), 2.67 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) 155.99, 135.62, 134.32, 131.24, 130.16, 129.92, 128.10, 127.96, 124.32, 117.31, 114.28, 88.73, 69.68, 33.91; IR (film) 3064.6, 2931.1, 2869.5, 1638.7, 1621.5, 1593.0, 1501.2, 1457.9, 1426.6, 1345.4, 1328.4, 1266.5, 1241.5, 1148.5, 1056.6, 1023.8, 917.6, 801.2, 762.9, 745.2 cm⁻¹; HRMS-EI (*m/z*): [M⁺] calcd for C₁₄H₁₃OI 324.001117, found 324.001091.

1-Iodo-2-pent-4-enyloxy-naphthalene: colorless viscous oil, purified by chromatography over silica gel (91%, Hexanes:EtOAc, 95:5, $R_f = 0.5$); ^1H NMR (CDCl_3 , 400 MHz) 8.13 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.1$ Hz, 1H), 7.51 (t, $J = 8.4$ Hz, 1H), 7.35 (t, $J = 8.1$ Hz, 1H), 7.12 (d, $J = 8.8$ Hz, 1H), 5.93-5.83 (m, 1H), 5.10 (d, $J = 17.2$ Hz, 1H), 5.01 (d, $J = 10.2$ Hz, 1H), 4.15 (t, $J = 6.2$ Hz, 2H), 2.39-2.34 (m, 2H), 2.93-1.93 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) 156.07, 137.70, 135.63, 131.19, 130.15, 129.87, 128.10, 127.95, 124.25, 115.33, 114.20, 88.51, 69.31, 30.19, 28.58; IR (film) 3060.6, 2939.2, 2873.1, 2843.8, 1621.6, 1593.6, 1500.5, 1457.8, 1426.6, 1345.7, 1328.4, 1265.4, 1242.0, 1148.5, 1131.7, 1060.3, 1021.1, 912.5, 802.3, 762.8, 745.2 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{15}\text{H}_{15}\text{OI}$ 338.016767, found 338.016410.

To a solution of tosylated 2-iodoaniline (1 eq.) in CH_3CN were added K_2CO_3 (3 eq.) and 5-bromo-1-pentene (1.2 eq.). After stirring at reflux for 24h, the mixture was quenched with water. The aqueous layer was extracted with Et_2O . The organic layer was washed with water and brine, and dried over Na_2SO_4 . After concentration under reduced pressure, the residue was purified by chromatography over silica gel (Hexanes:EtOAc, 9:1) to give the desired compound (79%) as a colorless viscous oil.

N-(2-Iodo-phenyl)-4-methyl-N-pent-4-enyl-benzenesulfonamide: colorless viscous oil, purified by chromatography over silica gel (79%, Hexanes:EtOAc, 9:1, $R_f = 0.3$); ^1H NMR (CDCl_3 , 400 MHz) 7.90 (dd, $J = 8.1$ Hz, $J = 1.5$ Hz, 1H), 7.61 (d, $J = 8.1$ Hz, 2H), 7.28-7.25 (m, 3H), 7.01 (dt, $J = 7.3$ Hz, $J = 1.5$ Hz, 1H), 6.88 (dd, $J = 8.1$ Hz, $J = 1.5$ Hz, 1H), 5.75-5.64 (tdd, $J = 17.2$ Hz, $J = 10.2$ Hz, $J = 7.0$ Hz, 1H), 4.98-4.90 (m, 2H), 3.71-3.64 (m, 1H), 3.38-3.30 (m, 1H), 2.41 (s, 3H), 2.13-1.97 (m, 2H), 1.71-1.44 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) 143.43, 141.48, 140.19, 137.06, 135.68, 129.74, 129.63, 129.27, 128.62, 127.84, 115.05, 103.19, 51.20, 30.66, 27.09, 21.35; IR (film) 3061.4, 2924.6,

2858.1, 1639.8, 1596.8, 1493.9, 1466.1, 1436.0, 1350.9, 1164.4, 1091.0, 1018.5, 916.4, 815.1, 767.5, 715.0, 657.8 cm^{-1} ; HRMS-ESI (m/z): $[M+H]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{SI}$ 442.0332, found 442.0339.

To a solution of 2-(2-iodophenyl)-malonic acid diethyl ester (1 eq.) in THF (15 mL) were added potassium *tert*-butoxide (1.3 eq.) and 5-iodo-1-pentene (1.2 eq.) (5-iodo-1-pentene was prepared from 5-bromo-1-pentene according to a procedure described in the literature³). After stirring at room temperature for 20h, the mixture was quenched with water. The aqueous layer was extracted with Et_2O . The organic layer was washed with water and brine and dried over Na_2SO_4 . After concentration under reduced pressure, the residue was purified by chromatography over silica gel (Hexanes: EtOAc , 9:1) to give the desired compound (81%) as a colorless oil.

2-(2-Iodo-phenyl)-2-pent-4-enyl-malonic acid diethyl ester:

colorless viscous oil, purified by chromatography over silica gel (81%, Hexanes: EtOAc , 9:1, R_f = 0.4); ^1H NMR (CDCl_3 , 400 MHz) 7.92 (d, J = 7.7 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 6.93 (t, J = 7.3 Hz, 1H), 5.79 (tdd, J = 16.8 Hz, J = 10.2 Hz, J = 6.6 Hz, 1H), 4.97 (d, J = 16.8 Hz, 1H), 4.91 (d, J = 10.2 Hz, 1H), 4.33-4.17 (m, 4H), 2.49-2.45 (m, 2H), 2.07-2.01 (m, 2H), 1.29-1.20 (m, 8H); ^{13}C NMR (CDCl_3 , 100 MHz) 170.13, 142.01, 140.19, 138.31, 129.95, 128.63, 127.80, 114.79, 98.00, 66.38, 61.99, 33.98, 33.74, 24.74, 13.85; IR (film) 2979.2, 2932.0, 2902.7, 2867.5, 1744.8, 1731.2, 1465.4, 1439.2, 1363.2, 1296.1, 1254.2, 1196.5, 1135.4, 1095.7, 1009.8, 912.7, 857.9, 744.5 cm^{-1} ; HRMS-ESI (m/z): $[M+H]^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4\text{I}$ 431.0724, found 431.0712.

³ Shi, B.; Hawryluk, N. A.; Snider B. B. *J. Org. Chem.* **2003**, 68, 1030.

To a solution of substrate (1 eq.) and methyl acrylate (20 eq.) in CH_2Cl_2 (2 mL/1 mmol of substrate) was added Grubb's 2nd generation catalyst (5 mol%). The resulting mixture was stirred at room temperature for 20h and DMSO (50 eq. relative to the Grubb's catalyst) was added and the mixture was stirred for further 15h. Evaporation of the volatiles gave residue that was purified over silica gel using mixtures of Hexanes:EtOAc as eluent.

5-(1-Iodo-naphthalen-2-yloxy)-pent-2-enoic acid

methyl ester: white solid, purified by chromatography over silica gel (67%, Hexanes:EtOAc, 9:1, $R_f = 0.2$); M.p. 61-63 °C; ^1H NMR (CDCl_3 , 400 MHz) 8.13 (d, $J = 8.4$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.1$ Hz, 1H), 7.51 (dd, $J = 8.1$ Hz, 1H), 7.36 (t, $J = 8.1$ Hz, 1H), 7.14 (td, $J = 15.7$ Hz, $J = 7.0$ Hz, 1H), 7.04 (d, $J = 8.8$ Hz, 1H), 6.04 (d, $J = 15.7$ Hz, 1H), 4.16 (t, $J = 6.6$ Hz, 2H), 3.74 (s, 3H), 2.73-2.71 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) 166.48, 155.47, 144.56, 135.41, 131.09, 130.12, 129.85, 128.00, 127.92, 124.35, 123.25, 113.98, 88.69, 68.14, 51.36, 32.12; IR (film) 2943.7, 2873.4, 2832.3, 1721.9, 1620.3, 1591.0, 1503.5, 1456.7, 1433.3, 1346.3, 1325.3, 1266.0, 1237.6, 1167.5, 1056.0, 802.5 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{I}$ 383.0138, found 383.0158.

6-(1-Iodo-naphthalen-2-yloxy)-hex-2-enoic acid

methyl ester: colorless viscous oil, purified by chromatography over silica gel (62%, Hexanes:EtOAc, 9:1, $R_f = 0.2$); ^1H NMR (CDCl_3 , 400 MHz) 8.13 (d, $J = 8.4$ Hz, 1H), 7.70 (m, 2H), 7.51 (ddd, $J = 8.4$ Hz, $J = 7.0$ Hz, $J = 1.1$ Hz, 1H), 7.35 (ddd, $J = 8.1$ Hz, $J = 7.0$ Hz, $J = 1.1$ Hz, 1H), 7.05 (td, $J = 15.8$ Hz, $J = 7.0$ Hz, 1H), 7.03 (d, $J = 8.8$ Hz, 1H), 5.92 (td, $J = 15.8$ Hz, $J = 1.5$ Hz, 1H), 4.05 (t, $J = 5.9$ Hz, 2H), 3.72 (s, 3H), 2.53-2.47 (m, 2H), 1.99-1.93 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) 166.61, 155.55, 148.04, 135.33, 130.90, 130.02, 129.67, 127.94,

127.83, 124.13, 121.43, 113.76, 88.24, 68.57, 51.18, 28.60, 27.62; IR (film) 2947.6, 2879.0, 2845.0, 1721.1, 1658.8, 1621.4, 1593.2, 1555.5, 1501.5, 1458.1, 1434.6, 1346.0, 1327.8, 1266.0, 1242.0, 1206.7, 1166.8, 1061.4, 978.8, 803.3, 764.0, 747.0 cm^{-1} ; HRMS-EI (m/z): [M^+] calcd for $C_{17}H_{17}O_3I$ 396.022247, found 396.022800.

6-[(2-Iodo-phenyl)-(toluene-4-sulfonyl)-amino]-hex-2-

enoic acid methyl ester: colorless viscous oil, purified by

chromatography over silica gel (80%, Hexanes:EtOAc,

8:2, R_f = 0.3); ^1H NMR (CDCl_3 , 400 MHz) 7.92 (dd, J =

7.9 Hz, J = 1.5 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.32-7.26

(m, 3H), 7.03 (dt, J = 7.9 Hz, J = 1.5 Hz, 1H), 6.89 (dd, J = 7.9 Hz, J = 1.8 Hz, 1H), 6.86 (td,

J = 15.5 Hz, J = 7.0 Hz, 1H), 5.77 (td, J = 15.5 Hz, J = 1.5 Hz, 1H), 3.73-3.64 (m, 1H), 3.70

(s, 3H), 3.40-3.31 (m, 1H), 2.43 (s, 3H), 2.36-2.18 (m, 2H), 1.77-1.52 (m, 2H); ^{13}C NMR

(CDCl_3 , 100 MHz) 166.63, 147.61, 143.67, 141.43, 140.40, 135.58, 129.82, 129.39, 128.77,

127.96, 121.40, 103.13, 51.25, 51.17, 29.32, 26.46, 21.41; IR (film) 2941.9, 2860.0, 1720.1,

1656.0, 1592.2, 1466.1, 1435.7, 1349.8, 1273.0, 1201.4, 1160.5, 1089.7, 1037.2, 1019.2,

815.5, 714.7, 657.6 cm^{-1} ; HRMS-ESI (m/z): [$M+\text{Na}$] $^+$ calcd for $C_{20}H_{22}NO_4\text{SiNa}$ 522.0206,

found 522.0181.

7-Ethoxycarbonyl-7-(2-iodo-phenyl)-oct-2-enedioic acid

8-ethyl ester 1-methyl ester: colorless viscous oil, purified

by chromatography over silica gel (65%, Hexanes:EtOAc,

8:2, R_f = 0.45); ^1H NMR (CDCl_3 , 400 MHz) 7.93 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H), 7.31 (td, J

= 7.7 Hz, J = 1.5 Hz, 1H), 7.06 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H), 6.95 (td, J = 7.7 Hz, J = 1.5

Hz, 1H), 6.90 (td, J = 15.8 Hz, J = 7.0 Hz, 1H), 5.79 (td, J = 15.8 Hz, J = 1.5 Hz, 1H),

4.35-4.19 (m, 4H), 3.69 (s, 3H), 2.53-2.49 (m, 2H), 2.22-2.17 (m, 2H), 1.35-1.25 (m, 2H),

1.27 (t, J = 7.3 Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) 169.80, 166.72, 148.63, 141.91, 139.64,

129.84, 128.59, 127.70, 121.01, 97.50, 66.19, 61.87, 51.11, 33.24, 32.16, 23.81, 13.65; IR

(film) 2980.0, 2947.1, 2897.8, 1740.6, 1724.4, 1658.0, 1465.2, 1435.5, 1366.5, 1254.1,

1196.3, 1153.6, 1096.3, 1010.0, 978.9, 859.7, 744.5 cm^{-1} ; HRMS-ESI (m/z): [$M+\text{H}$] $^+$ calcd

for $C_{20}H_{26}O_6I$ 489.0768, found 489.0757.

To a solution of substrate (1 eq.) in THF (C= 0.2 M) cooled at $-78\text{ }^\circ\text{C}$ was added DIBAL-H 1.5M in toluene (2.5 eq.). After stirring at $-78\text{ }^\circ\text{C}$ for 2h, the mixture was allowed to warm at room temperature. The reaction was quenched with a 20% solution of K/Na tartrate and stirred for few minutes before being extracted with Et_2O . The combined organic layers were washed with water, brine and dried over Na_2SO_4 . After concentration under reduced pressure, the residue was purified by chromatography over silica gel using mixtures of hexanes/ EtOAc as eluent to give the desired compounds as colorless viscous oils.

5-(1-Iodo-naphthalen-2-yloxy)-pent-2-en-1-ol: colorless viscous oil, purified by chromatography over silica gel (78%, Hexanes: EtOAc , 8:2, $R_f = 0.2$); ^1H NMR (CDCl_3 , 400 MHz) 8.13 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.71 (d, $J = 8.1$ Hz, 1H), 7.52 (t, $J = 8.1$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.12 (d, $J = 8.8$ Hz, 1H), 5.92-5.79 (m, 2H), 4.18-4.12 (m, 4H), 2.64-2.59 (m, 2H), 1.70 (s, OH); ^{13}C NMR (CDCl_3 , 100 MHz) 155.84, 135.36, 131.91, 131.16, 130.18, 129.89, 128.10, 128.08, 127.99, 124.33, 114.20, 88.66, 69.54, 63.46, 32.32; IR (film) 3363.9, 2927.2, 2873.3, 1621.1, 1592.6, 1500.9, 1457.6, 1426.3, 1345.5, 1328.6, 1266.1, 1241.1, 1148.9, 1057.3, 1022.8, 971.0, 801.8 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{INa}$ 377.0009, found 376.9997.

6-(1-Iodo-naphthalen-2-yloxy)-hex-2-en-1-ol: colorless viscous oil, purified by chromatography over silica gel (95%, Hexanes: EtOAc , 8:2, $R_f = 0.2$); ^1H NMR (CDCl_3 , 400 MHz) 8.13 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.53 (ddd, $J = 8.4$ Hz, $J = 7.0$ Hz, $J = 1.1$ Hz, 1H), 7.37 (ddd, $J = 8.1$ Hz, $J = 7.0$ Hz, $J = 1.1$ Hz, 1H), 7.15 (d, $J = 8.8$ Hz, 1H), 5.82-5.69 (m, 2H), 4.17 (t, $J = 6.2$ Hz, 2H), 4.09 (d, $J = 4.8$ Hz, 2H), 2.40-2.35 (m, 2H), 2.01-1.94 (m, 2H), 1.37 (s, OH); ^{13}C NMR (CDCl_3 , 100 MHz) 155.78, 135.40, 131.41, 130.95, 130.03, 129.72, 129.67,

127.98, 127.83, 124.10, 113.95, 88.28, 69.08, 63.22, 28.64, 28.57; IR (film) 3354.8, 2937.9, 2863.4, 1621.3, 1592.9, 1500.6, 1457.3, 1426.8, 1345.6, 1328.5, 1264.7, 1241.8, 1148.8, 1058.8, 1020.7, 969.4, 802.0, 763.2, 745.8 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{INa}$ 391.0165, found 391.0157.

***N*-(6-Hydroxy-hex-4-enyl)-*N*-(2-iodo-phenyl)-4-methyl-**

benzenesulfonamide: colorless viscous oil, purified by

chromatography over silica gel (88%, Hexanes:EtOAc, 7:3,

$R_f = 0.2$); ^1H NMR (CDCl_3 , 400 MHz) 7.91 (d, $J = 8.1$ Hz,

1H), 7.61 (d, $J = 8.1$ Hz, 2H), 7.29-7.25 (m, 3H), 7.02 (t, $J =$

7.7 Hz, 1H), 6.89 (d, $J = 7.7$ Hz, 1H), 5.62-5.52 (m, 2H),

4.06-3.97 (m, 2H), 3.70-3.63 (m, 1H), 3.37-3.30 (m, 1H), 2.43 (s, 3H), 2.14-1.95 (m, 3H),

1.68-1.58 (m, 1H), 1.53-1.43 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) 143.57, 141.43, 140.32,

135.64, 130.89, 129.85, 129.72, 129.35, 128.68, 127.94, 103.16, 63.14, 51.18, 29.21, 27.39,

21.41; IR (film) 3372.6, 3055.3, 2926.5, 1596.8, 1466.1, 1435.9, 1348.3, 1160.0, 1090.3,

1018.4, 971.2, 815.6, 767.8 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3\text{SiNa}$

494.0257, found 494.0249.

2-(6-Hydroxy-hex-4-enyl)-2-(2-iodo-phenyl)-malonic acid

diethyl ester: colorless viscous oil, purified by

chromatography over silica gel (98%, Hexanes:EtOAc, 7:3,

$R_f = 0.3$); ^1H NMR (CDCl_3 , 400 MHz) 7.88 (d, $J = 7.7$ Hz, 1H), 7.26 (t, $J = 8.1$ Hz, 1H), 7.04

(d, $J = 8.1$ Hz, 1H), 6.89 (t, $J = 7.7$ Hz, 1H), 5.60-5.50 (m, 2H), 4.29-4.13 (m, 4H), 3.98-3.97

(m, 2H), 2.45-2.41 (m, 2H), 2.01-1.97 (m, 2H), 1.89 (s, OH), 1.28-1.15 (m, 2H), 1.22 (t, $J =$

7.3 Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) 169.96, 141.86, 139.93, 132.11, 129.83, 129.38,

128.52, 127.67, 97.76, 66.25, 63.37, 61.86, 33.52, 32.20, 24.80, 13.69; IR (film) 3340.1,

2979.2, 2938.6, 2899.9, 2866.8, 1715.7, 1651.7, 1464.1, 1442.0, 1389.8, 1365.0, 1251.9,

1191.9, 1161.6, 1093.3, 1008.1, 969.2, 856.6 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for

$\text{C}_{19}\text{H}_{26}\text{O}_5\text{I}$ 461.0819, found 461.0842.

To a solution of the substrate (1 eq.) in CH_2Cl_2 ($C = 0.6 \text{ M}$) were successively added pyridine (1.5 eq.) and ethyl chloroformate (1.2 eq.) at 0°C . The resulting mixture was stirred for 1h30 at 0°C . Then, the reaction mixture was diluted with CH_2Cl_2 and washed with 1N HCl, saturated NaHCO_3 and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography over silica gel using mixtures of hexanes/EtOAc as eluent.

Carbonic acid ethyl ester
5-(1-iodo-naphthalen-2-yloxy)-pent-2-enyl ester

(4a): white solid, purified by chromatography over

silica gel (87%, Hexanes:EtOAc, 9:1, $R_f = 0.26$); M.p. $66-68^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) 8.13 (d, $J = 8.4 \text{ Hz}$, 1H), 7.78 (d, $J = 8.8 \text{ Hz}$, 1H), 7.72 (d, $J = 8.1 \text{ Hz}$, 1H), 7.52 (ddd, $J = 8.4 \text{ Hz}$, $J = 7.0 \text{ Hz}$, $J = 1.1 \text{ Hz}$, 1H), 7.37 (ddd, $J = 8.1 \text{ Hz}$, $J = 7.0 \text{ Hz}$, $J = 1.1 \text{ Hz}$, 1H), 7.14 (d, $J = 8.8 \text{ Hz}$, 1H), 6.06-5.99 (m, 1H), 5.85-5.77 (m, 1H), 4.62 (t, $J = 6.2 \text{ Hz}$, 2H), 4.19 (m, 4H), 2.68-2.63 (m, 2H), 1.30 (t, $J = 7.3 \text{ Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) 155.92, 154.86, 135.49, 131.96, 131.11, 130.10, 129.83, 128.02, 127.91, 126.18, 124.27, 114.10, 88.59, 69.14, 67.91, 63.81, 32.29, 14.18; IR (film) 3058.0, 2981.2, 2935.1, 2873.7, 1743.1, 1621.3, 1593.1, 1502.7, 1458.2, 1427.1, 1380.8, 1346.0, 1257.9, 1149.5, 1056.7, 1023.0, 973.7, 871.9, 802.2, 764.0, 747.0 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{O}_4\text{INa}$ 449.0220, found 449.0217.

Carbonic acid ethyl ester
6-(1-iodo-naphthalen-2-yloxy)-hex-2-enyl ester (4b):

white solid, purified by chromatography over silica gel (94%, Hexanes:EtOAc, 9:1, R_f = 0.3); M.p. 40-42 °C; ¹H NMR (CDCl₃, 400 MHz) 8.13 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.52 (ddd, *J* = 8.4 Hz, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 7.36 (ddd, *J* = 8.1 Hz, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 5.93-5.86 (m, 1H), 5.73-5.65 (m, 1H), 4.58 (d, *J* = 6.6 Hz, 2H), 4.18 (q, *J* = 7.7 Hz, 2H), 4.13 (t, *J* = 5.9 Hz, 2H), 2.42-2.36 (m, 2H), 2.00-1.95 (m, 2H), 1.29 (t, *J* = 7.7 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) 155.88, 154.90, 135.68, 135.54, 131.10, 130.11, 129.81, 128.05, 127.92, 124.22, 114.05, 88.41, 69.08, 68.10, 63.80, 28.72, 28.47, 14.19; IR (film) 3051.8, 2977.9, 2942.1, 2875.5, 1743.3, 1621.6, 1593.3, 1502.1, 1458.2, 1346.0, 1259.0, 1149.4, 1060.0, 1017.8, 973.0, 873.6, 802.9, 746.9 cm⁻¹; HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₉H₂₁O₄INa 463.0376, found 463.0353.

Carbonic acid ethyl ester
6-[(2-iodo-phenyl)-(toluene-4-sulfonyl)-amino]-hex-2-enyl ester (4c):

colorless viscous oil, purified by chromatography over silica gel (90%, Hexanes:EtOAc, 8:2, R_f = 0.3); ¹H NMR (CDCl₃, 400 MHz) 7.92 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.30-7.27 (m, 3H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 5.74-5.67 (m, 1H), 5.57-5.50 (m, 1H), 4.52 (d, *J* = 6.2 Hz, 2H), 4.18 (q, *J* = 7.3 Hz, 2H), 3.68-3.61 (m, 1H), 3.38-3.31 (m, 1H), 2.44 (s, 3H), 2.16-2.00 (m, 2H), 1.70-1.45 (m, 2H), 1.30 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) 154.89, 143.62, 141.61, 140.49, 135.24, 135.94, 130.13, 129.80, 129.44, 128.76, 128.12, 124.20, 103.15, 68.02, 63.86, 51.29, 29.41, 27.30, 21.52, 14.22; IR (film) 2978.8, 2939.7, 2862.6, 1742.9, 1466.2, 1380.9, 1351.4, 1256.9, 1162.7, 1091.3, 1018.3, 715.2, 657.7 cm⁻¹; HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₂₂H₂₆NO₅SiNa 566.0468, found 566.0480.

2-(6-Ethoxycarbonyloxy-hex-4-enyl)-2-(2-iodo-phenyl)-malonic acid diethyl ester (4d):

colorless viscous oil, purified by chromatography over silica gel (83%, Hexanes:EtOAc, 8:2, R_f = 0.45); ¹H NMR (CDCl₃, 400 MHz) 7.88 (d, *J* = 8.1 Hz, 1H), 7.27

(t, $J = 7.7$ Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 1H), 6.90 (t, $J = 7.7$ Hz, 1H), 5.70 (td, $J = 15.4$ Hz, $J = 6.6$ Hz, 1H), 5.52 (td, $J = 15.4$ Hz, $J = 6.6$ Hz, 1H), 4.48 (d, $J = 6.2$ Hz, 2H), 4.30-4.17 (m, 4H), 4.13 (q, $J = 7.3$ Hz, 2H), 2.46-2.42 (m, 2H), 2.04-1.99 (m, 2H), 1.26-1.17 (m, 11H); ^{13}C NMR (CDCl_3 , 100 MHz) 169.92, 154.85, 141.92, 139.92, 136.30, 129.86, 128.56, 127.71, 123.59, 97.71, 68.15, 66.25, 63.68, 61.86, 33.50, 32.28, 24.52, 14.14, 13.72; IR (film) 2980.6, 2937.2, 2900.3, 1743.7, 1465.2, 1447.0, 1381.8, 1365.8, 1250.8, 1192.6, 1094.9, 1009.1, 971.4, 871.2, 744.2 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{29}\text{O}_7\text{INa}$ 555.0850, found 555.0825.

To a suspension of NaH 80% in mineral oil (0.12 g) in dry THF (12 mL) was added the benzylic alcohol (0.64 g, 2.7 mmol). After stirring for 10 min at room temperature, (Z)- $\text{BrCH}_2\text{CH}=\text{CHCH}_2\text{OTBS}$ (0.82 g, 2.9 mmol) was added and the resulting mixture was stirred for 3h at room temperature. The reaction was carefully quenched with water. The aqueous layer was extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography over silica gel (Hexanes:EtOAc, 97:3) to give the desired compound (0.82 g, 95 %) as a colorless viscous oil.

***tert*-Butyl-[4-(2-iodo-benzyloxy)-but-2-enyloxy]-dimethyl-sil**

ane: colorless viscous oil, purified by chromatography over silica gel (95%, Hexanes:EtOAc, 97:3, $R_f = 0.4$); ^1H NMR

(CDCl_3 , 400 MHz) 7.82 (d, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 7.7$ Hz, 1H), 7.35 (t, $J = 7.3$ Hz, 1H), 6.99 (t, $J = 7.3$ Hz, 1H), 5.77 (m, 2H), 4.49 (s, 2H), 4.27 (d, $J = 5.5$ Hz, 2H), 4.17 (d, $J = 5.8$ Hz, 2H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) 140.34, 138.99, 132.94, 129.00, 128.60, 128.05, 126.43, 97.70, 75.86, 66.33, 59.52, 25.86, 18.19, 5.21; IR (film) 2927.9, 2855.5, 1697.8, 1565.7, 1462.9, 1435.9, 1253.9, 1200.0, 115.2, 1088.5, 1012.7, 837.3, 778.8, 750.1 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{27}\text{O}_2\text{ISiNa}$ 441.0728, found 441.0751.

To a solution of the substrate (0.76 g, 1.9 mmol) in THF (20 mL) was added a solution of tetrabutylammonium fluoride 1M in THF (2 mL). The mixture was stirred for 30 minutes at room temperature. The reaction was quenched with water. The aqueous layer was extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography over silica gel (Hexanes:EtOAc, 9:1) to give the desired compound (0.57 g, 96 %) as a colorless viscous oil.

4-(2-Iodo-benzyloxy)-but-2-en-1-ol: colorless viscous oil, purified by chromatography over silica gel (96%,), Hexanes:EtOAc, 9:1, $R_f = 0.13$; ^1H NMR (CDCl_3 , 400 MHz) 7.82 (d, $J = 7.7$ Hz, 1H), 7.41 (d, $J = 7.7$ Hz, 1H), 7.34 (t, $J = 7.7$ Hz, 1H), 6.99 (t, $J = 7.7$ Hz, 1H), 5.87-5.73 (m, 2H), 4.51 (s, 2H), 4.21 (d, $J = 6.2$ Hz, 2H), 4.17 (d, $J = 5.8$ Hz, 2H), 2.13 (s br, OH); ^{13}C NMR (CDCl_3 , 100 MHz) 140.08, 139.20, 132.45, 129.31, 128.85, 128.24, 127.97, 97.99, 76.16, 66.16, 58.68; IR (film) 3385.5, 3022.4, 3055.3, 2861.9, 1719.8, 1694.4, 1585.7, 1564.4, 1464.3, 1436.9, 1205.3, 1118.9, 1088.5, 1012.7, 749.7 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_{13}\text{O}_2\text{INa}$ 326.9863, found 326.9860.

To a solution of substrate (0.5 g, 1.65 mmol) in CH_2Cl_2 (5 mL) were added pyridine (0.2 mL, 2.50 mmol) and ethylchloroformate (0.19 mL, 1.98 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1h30, warmed up at room temperature and diluted with CH_2Cl_2 . The organic layer was washed with HCl 1N, with a saturated solution of NaHCO_3 and brine. The

organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography over silica gel (Hexanes:EtOAc, 97:3) to give the desired compound (0.57 g, 92 %) as a colorless viscous oil.

Carbonic acid ethyl ester 4-(2-iodo-benzyloxy)-but-2-enyl

ester (5): colorless viscous oil, purified by chromatography over silica gel (92%, Hexanes:EtOAc, 97:3, R_f = 0.2); ¹H

NMR (CDCl₃, 400 MHz) 7.81 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 5.91-5.72 (m, 2H), 4.72 (d, *J* = 6.6 Hz, 2H), 4.49 (m, 2H), 4.22 (d, *J* = 6.2 Hz, 2H), 4.19 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) 154.71, 139.98, 138.89, 130.79, 128.98, 128.51, 127.97, 126.07, 97.61, 75.91, 66.00, 63.76, 63.10, 14.07; IR (film) 2982.5, 2935.5, 2866.8, 1747.5, 1465.5, 1438.7, 1373.2, 1262.0, 1090.8, 1013.3, 873.6, 752.3 cm⁻¹; HRMS-ESI (*m/z*): [M+H]⁺ calcd for C₁₄H₁₇O₄I 377.0244, found 377.0256.

Conventional thermal conditions: To a mixture of **3a-e** or **4a-d** or **5** (1.0 equiv), (*o*-tolyl)₃P (22 mol%) and *n*BuNMe₂ (2.0 equiv) in CH₃CN:H₂O (10:1, 0.1 M) was added Pd₂(dba)₃·CHCl₃ (5 mol%). The resulting mixture was degassed by Ar bubling and was refluxed for 6 h under N₂ atmosphere. The mixture was cooled at room temperature and treated with H₂O. The aqueous layer was extracted with CH₂Cl₂. The organic layer was washed with water, brine and was dried over Na₂SO₄. After concentration under reduced pressure, the resulting residue was purified over silica gel using mixtures of hexanes or pentane/Et₂O as eluent.

Microwave-assisted reaction: the reactants were filled into an appropriate microwave

process vial sealed with a Teflon septum. The mixture was degassed by Ar bubbling and was heated at 160 °C for 1 minute (pressure ~ 8 bars). After microwave irradiation and subsequent gas jet cooling (down to 40 °C), the reaction mixture was quenched with water. The workup described above for conventional thermal conditions was then realized.

1-Vinyl-1,2-dihydro-naphtho[2,1-*b*]furan (6a): colorless viscous oil, purified by chromatography over silica gel (56% (microwave irradiation), 33% (conventional thermal conditions), Hexanes:Et₂O, 99:1, R_f = 0.4); ¹H NMR (CDCl₃, 400 MHz) 7.80 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 6.06-5.97 (m, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 4.87-4.80 (m, 1H), 4.51-4.43 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) 157.54, 138.66, 130.90, 129.68, 129.38, 128.60, 126.42, 122.68, 122.32, 119.49, 116.08, 112.01, 76.51, 46.38; IR (film) 3067, 2971, 2888, 1630, 1597, 1579, 1519, 1473, 1459, 1372, 1246, 1156, 1058, 989, 950, 921, 810, 745 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₄H₁₂O 196.088815, found 196.089237.

6-Trifluoromethyl-3-vinyl-2,3-dihydro-benzofuran (6b): colorless viscous oil, purified over thin layer chromatography plate of SiO₂ (61% (microwave irradiation), 20% (conventional thermal conditions), Pentane:Et₂O, 99:1, R_f = 0.6); ¹H NMR (CDCl₃, 400 MHz) 7.20-7.13 (m, 2H), 7.02 (s, 1H), 5.89-5.81 (ddd, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 8.1 Hz, 1H), 5.27-5.19 (m, 2H), 4.78 (t, *J* = 9.1 Hz, 1H), 4.31 (t, *J* = 8.8 Hz, 1H), 4.16 (q, *J* = 9.1 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) 160.06, 136.79, 133.41, 131.06 (q, *J* = 32.7 Hz), 125.10, 121.8 (q, *J* = 272 Hz), 117.77 (q, *J* = 3.8 Hz), 117.46, 106.70 (q, *J* = 3.8 Hz), 76.84, 46.62; IR (film) 2959.4, 2922.5, 2848.7, 1728.9, 1693.3, 1625.7, 1597.6, 1503.6, 1435.5, 1320.0, 1170.2, 1126.3, 1052.5, 978.8, 827.6 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₁H₉OF₃ 214.060550, found 214.060721.

3-Vinyl-2,3-dihydro-benzofuran-6-carboxylic acid methyl ester (6c): colorless viscous oil, purified by chromatography over silica gel (66% (microwave irradiation), 36% (conventional thermal conditions), Pentane:Et₂O, 95:5, R_f = 0.3); ¹H NMR (CDCl₃, 400 MHz) 7.59 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 7.41 (d, *J* = 1.4 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 5.88-5.80 (ddd, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 8.1 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 4.75 (t, *J* =

9.1 Hz, 1H), 4.28 (t, $J = 8.8$ Hz, 1H), 4.14 (q, $J = 8.8$ Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) 166.86, 160.02, 136.94, 134.77, 130.83, 124.57, 122.61, 117.34, 110.48, 76.60, 52.10, 46.82; IR (film) 2953, 2895, 1721, 1591, 1493, 1437, 1288, 1262, 1216, 1107, 1080, 989, 802, 762 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3$ 204.078644, found 204.078155.

1-(Toluene-4-sulfonyl)-3-vinyl-2,3-dihydro-1H-indole (6d): white solid, purified by chromatography over silica gel and by subsequent treatment with hydroxylamine hydrochloride and sodium acetate in MeOH to remove traces of dibenzylidene-acetone (74% in both conditions, Hexanes: Et_2O , 95:5, $R_f = 0.16$); M.p. 99-101 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) 7.68-7.64 (m, 3H), 7.24-7.20 (m, 3H), 7.01-7.00 (m, 2H), 5.58-5.49 (m, 1H), 5.10-5.04 (m, 2H), 4.14 (dd, $J = 10.6$ Hz, $J = 9.5$ Hz, 1H), 3.74 (q, $J = 8.4$ Hz, 1H), 3.58 (dd, $J = 10.6$ Hz, $J = 7.7$ Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 144.07, 141.67, 137.34, 133.89, 133.76, 129.62, 128.28, 127.32, 125.04, 123.86, 117.10, 115.07, 55.55, 44.82, 21.51; IR (film) 3064.6, 2924.3, 1638.1, 1598.5, 1476.1, 1459.0, 1355.1, 1234.3, 1168.2, 1101.6, 1091.0, 1047.7, 926.0, 813.9, 754.6 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_2\text{S}$ 299.098001, found 299.098227.

3-Vinyl-indan-1,1-dicarboxylic acid diethyl ester (6e): colorless viscous oil, purified by chromatography over silica gel (67% (microwave irradiation), Hexanes: Et_2O , 95:5, $R_f = 0.27$); ^1H NMR (CDCl_3 , 400 MHz) 7.59-7.56 (m, 1H), 7.32-7.25 (m, 2H), 7.16-7.14 (m, 1H), 5.85-5.76 (ddd, $J = 17.2$ Hz, $J = 10.2$ Hz, $J = 8.4$ Hz, 1H), 5.23 (d, $J = 17.2$ Hz, 1H), 5.15 (d, $J = 10.2$ Hz, 1H), 4.26 (q, $J = 7.3$ Hz, 2H), 4.22-4.11 (m, 2H), 3.93 (q, $J = 8.4$ Hz, 1H), 3.04 (dd, $J = 13.5$ Hz, $J = 7.7$ Hz, 1H), 2.38 (dd, $J = 13.2$ Hz, $J = 8.8$ Hz, 1H), 1.29 (t, $J = 7.3$ Hz, 3H), 1.23 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) 170.59, 170.28, 145.93, 139.82, 138.97, 128.98, 127.14, 126.57, 124.46, 116.29, 64.74, 61.69, 61.65, 47.78, 41.07, 14.07, 13.96; IR (film) 2982.1, 2929.8, 2900.3, 2878.2, 1732.1, 1474.8, 1366.8, 1250.3, 1186.5, 1097.5, 859.8, 761.2 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{17}\text{H}_{20}\text{O}_4$ 288.136159, found 288.136099.

1-Vinyl -2,3-dihydro-1H-benzo[f]chromene (6f): colorless viscous oil, purified by chromatography over silica gel (62% (microwave irradiation),

46% (conventional thermal conditions), Hexanes:Et₂O, 99:1, R_f = 0.4); ¹H NMR (CDCl₃, 400 MHz) 7.80 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.43 (ddd, *J* = 8.4 Hz, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.30 (ddd, *J* = 8.1 Hz, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.05 (d, *J* = 9.1 Hz, 1H), 6.11 (ddd, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 5.5 Hz, 1H), 5.20 (dt, *J* = 10.2 Hz, *J* = 1.5 Hz, 1H), 4.81 (dt, *J* = 17.2 Hz, *J* = 1.5 Hz, 1H), 4.33-4.28 (m, 1H), 4.24-4.18 (m, 1H), 4.07-4.04 (m, 1H), 2.31-2.22 (m, 1H), 2.01-1.96 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) 152.33, 141.01, 133.03, 128.99, 128.51, 128.33, 126.11, 122.91, 122.88, 118.96, 117.65, 114.06, 61.74, 34.12, 27.28; IR (film) 3062.0, 2972.4, 2880.9, 1622.0, 1599.3, 1514.1, 1474.2, 1433.3, 1403.2, 1285.9, 1264.9, 1235.7, 1211.9, 1083.6, 1002.6, 921.6, 812.2 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₅H₁₄O 210.104465, found 210.105084.

1-Vinyl-1,2,3,4-tetrahydro-naphtho[2,1-*b*]oxepine (6g): colorless viscous oil, purified by chromatography over silica gel (72% (microwave irradiation), 49% (conventional thermal conditions), Hexanes:Et₂O, 99:1, R_f = 0.4); ¹H NMR (CDCl₃, 400 MHz) 7.98 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.1

Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.46 (ddd, *J* = 8.4 Hz, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.35 (ddd, *J* = 8.1 Hz, *J* = 7.0 Hz, *J* = 1.1 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.29 (ddd, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 5.9 Hz, 1H), 5.13 (td, *J* = 10.2 Hz, *J* = 1.5 Hz, 1H), 4.93 (td, *J* = 17.2 Hz, *J* = 1.8 Hz, 1H), 4.51-4.44 (m, 1H), 4.42-4.36 (m, 1H), 3.99-3.94 (m, 1H), 2.22-1.94 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) 158.01, 140.23, 133.36, 130.66, 128.49, 128.27, 126.20, 126.09, 123.77, 123.49, 122.51, 115.94, 72.53, 41.37, 29.63, 26.66; IR (film) 3064.8, 2935.8, 2860.0, 1636.4, 1620.3, 1596.8, 1508.8, 1470.0, 1429.5, 1382.4, 1241.5, 1220.1, 1159.4, 1047.9, 952.0, 918.5, 821.1, 748.1 cm⁻¹; HRMS-EI (*m/z*): [*M*⁺] calcd for C₁₆H₁₆O 224.120115, found 224.120409.

1-(Toluene-4-sulfonyl)-5-vinyl-2,3,4,5-tetrahydro-1H-benzo[*b*]azepine (6h): white solid, purified by chromatography over silica gel and by subsequent treatment with hydroxylamine hydrochloride and sodium acetate in MeOH to remove traces of dibenzylidene-acetone (65% (microwave irradiation), Hexanes:Et₂O, 95:5, R_f = 0.15); M.p. 127-129 °C; ¹H NMR (DMSO-*d*₆,

500 MHz, 100 °C) 7.64 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.24-7.20 (m, 1H), 7.19-7.18 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 1H), 6.05 (ddd, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 8.1 Hz,

1H), 5.07 (d, $J = 10.2$ Hz, 1H), 4.87 (d, $J = 17.2$ Hz, 1H), 3.77-3.72 (m, 1H), 3.43-3.38 (m, 1H), 3.21-3.18 (m, 1H), 2.40 (s, 3H), 1.84-1.69 (m, 2H), 1.66-1.59 (m, 1H), 1.50-1.41 (m, 1H); ^{13}C NMR (DMSO- d_6 , 125 MHz, 100 °C) 142.57, 141.27, 139.31, 138.11, 137.73, 129.09, 127.82, 127.02, 126.17, 126.15, 114.21, 48.92, 44.16, 29.93, 25.41, 20.28; IR (film) 3070.9, 2927.0, 2853.9, 1598.1, 1486.0, 1449.9, 1345.4, 1158.8, 1092.4, 1037.8, 917.4, 839.9, 713.7 cm^{-1} ; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2\text{S}$ 328.1365, found 328.1370.

9-Vinyl-6,7,8,9-tetrahydro-benzocycloheptene-5,5-dicarboxylic acid

diethyl ester (6i): colorless viscous oil, purified by chromatography over

silica gel (73% (microwave irradiation), Hexanes: Et_2O , 95:5, $R_f = 0.2$); ^1H

NMR (CDCl_3 , 400 MHz) 7.22-7.21 (m, 2H), 7.18-7.13 (m, 1H), 6.96 (d, $J =$

EtO_2C CO_2Et 7.7 Hz, 1H), 6.12 (ddd, $J = 17.2$ Hz, $J = 10.2$ Hz, $J = 6.9$ Hz, 1H), 5.17 (td, $J = 10.2$ Hz, $J = 1.5$ Hz, 1H), 5.06 (td, $J = 17.2$ Hz, $J = 1.5$ Hz, 1H), 4.37-4.22 (m, 4H), 3.47-3.43 (m, 1H), 2.53-2.47 (m, 1H), 2.28-2.21 (m, 1H), 1.93-1.80 (m, 3H), 1.56-1.48 (m, 1H), 1.30 (t, $J = 7.3$ Hz, 3H), 1.25 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) 172.71, 171.24, 143.45, 141.02, 137.23, 128.90, 128.14, 127.41, 125.99, 114.58, 64.86, 61.75, 61.59, 46.10, 33.38, 31.16, 24.31, 13.98, 13.94; IR (film) 3071.6, 2979.9, 2935.6, 2869.1, 1731.6, 1640.0, 1488.0, 1445.8, 1389.2, 1365.8, 1232.5, 1174.8, 1096.4, 1030.1, 916.6, 750.0 cm^{-1} ; HRMS-EI (m/z): $[\text{M}^+]$ calcd for $\text{C}_{19}\text{H}_{24}\text{O}_4$ 316.167460, found 316.167381.

4-Vinyl-isochroman (6j): colorless viscous oil, purified by chromatography

over silica gel (45% (conventional thermal conditions), Pentane: Et_2O , 95:5, R_f

$= 0.46$); ^1H NMR (CDCl_3 , 400 MHz) 7.23 (m, 3H), 7.03-6.97 (m, 1H),

5.91-5.82 (m, 1H), 5.22-5.18 (m, 2H), 4.84-4.75 (m, 2H), 4.01 (dd, $J = 11.4$ Hz, $J = 5.0$ Hz, 1H), 3.78 (dd, $J = 11.4$ Hz, $J = 6.5$ Hz, 1H), 3.57-3.52 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) 138.66, 135.15, 134.34, 128.93, 126.58, 126.48, 124.27, 117.23, 69.87, 68.33, 42.90; IR (film) 3076.5, 2961.5, 2845.6, 1638.8, 1488.6, 1451.4, 1417.8, 1380.4, 1316.2, 1205.1, 1103.5, 995.5, 922.3, 848.8, 747.4 cm^{-1} .