Supporting Information

Rhodium-Catalyzed Selective C-H Activation/Olefination of Phenol Carbamates
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I. General Remark:
All solvents were obtained from commercial suppliers and used without further purification. Phenols and Alkenes were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. \([\text{RhCp}^*\text{Cl}_2]_2, \text{AgSbF}_6, \text{Cu(OAc)}_2\) was obtained from commercial suppliers. Analytical TLC was done on pre-coated silica gel plates. Column chromatography was conducted with 300-400 mesh silica gel. \(^1\)H NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts of \(^1\)H NMR spectra were reported in parts per million relative to tetramethylsilane \((\delta = 0)\). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, \(J\), were reported in hertz unit \((\text{Hz})\). \(^19\)F NMR spectra were recorded on 400 MHz spectrometers. \(^{13}\)C NMR spectra were recorded on 101 MHz spectrometers. Chemical shifts were reported in parts per million relative to tetramethylsilane \((\delta = 0)\). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI mode unless otherwise stated.

II. General Procedure For The Synthesis of phenol cambamates
Phenol cambamate were readily prepared by corresponding phenol unless otherwise noted: phenol was dissolved in 10 mL dry CHCl\(_3\), Et\(_3\)N was added. The solution was cool to 0\(^\circ\)C and dimethylcarbamic chloride was added dropwise. The reaction was allowed to rise to room temperature and stirred over night. 0.1 M aq.Na\(_2\)CO\(_3\) was added and stirred for anther 30 min, then the organic layer was separated and washed with water/aq HCl/water, dried with MgSO\(_4\), concentrated and dried \textit{in vacuo} to give the phenol cambamate.
Synthesis of 3-(thiophen-3-yl)phenyl dimethylcarbamate

3-bromothiophene (1 mmol), 3-Hydroxyphenylboronic acid (1.1 mmol, 152 mg), Pd(Ph₃P)₄ (0.05 mmol, 57.8 mg) and K₂CO₃ (2 mmol, 276 mg) was placed in a vial under Ar, then a mixed solvent of toluene/ EtOH / H₂O (1 ml/1 ml/1 ml) was added. The mixture was violently stirred at 80 °C for 4h, then cooled to room temperature. The organic phase was purified by flash chromatography to give the 3-(thiophen-3-yl)phenol.

The 3-(thiophen-3-yl)phenyl dimethylcarbamate was simply obtained by the reaction of 3-(thiophen-3-yl)phenol and dimethylcarbamic chloride in presence of Et₃N and purified by reduced pressure distillation or flash chromatography.

Synthesis of 4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl dimethylcarbamate

2,5-Hexanedione (50 mmol), 4-aminophenol (52 mmol) and p-toluene-sulfonic acid (50 mg) in toluene (50 mL) was refluxed for 6 h. The reaction mixture was cooled, filtered, and concentrated. The crude mixture was purified by flash chromatography to give pure product 4-(2,5-dimethyl-1H-pyrrol-1-yl)phenol as white solid.

The 4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl dimethylcarbamate was simply obtained by the reaction of 4-(2,5-dimethyl-1H-pyrrol-1-yl)phenol and dimethylcarbamic chloride in presence of Et₃N and purified by flash chromatography.

Synthesis of 2-deuterio 4-methylphenol Cambamate

A solution of 2-bromo-4-methylphenol in 1 mL toluene was slowly added to excess nBuLi (3 mL, 1.6 M in THF) at -10 °C under Ar. The temperature was allowed to rise to 10 °C and stirred for 4h, then 2 mL D₂O was carefully added. After violent stirred overnight, the mixture was extracted with Et₂O (3 x 5 mL), organic layer was dried with MgSO₄, concentrated, and the mixture was purified by flash chromatography to give 2-deuterio 4-methylphenol.

2-deuterio 4-methylphenol cambamate was readily prepared by corresponding 2-deuterio 4-methylphenol and dimethylcarbamic chloride in presence of Et₃N and...
purified by flash chromatography to give 2-deuterio 4-methylphenol Cambamate as a white solid in quantitative yield.

III. General Procedure for Experiments and NMR Spectra of Compounds.

In a nitrogen-filled inert atmosphere box, to a vial was combined [Cp*RhCl2]2, AgSbF6, Phenol Carbamate (0.25 mmol), Alkene (0.5 mmol), Cu(OAc)2, solvent (1 mL) was added under Ar atmosphere (1 atm). After addition of all substrates, the reaction mixture was heated to the desired temperature with stirring for 24 h. After the desired reaction time, the vial was cooled to rt, the crude product was purified by flash chromatography.
(E)-butyl 3-(2-(dimethylcarbamoyloxy)-4-methylphenyl)acrylate(1a)
Colorless oil 74%
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J$ = 16.1, 1H), 7.50 (d, $J$ = 8.0, 1H), 7.02 (d, $J$ = 8.1, 1H), 6.99 (s, 1H), 6.39 (d, $J$ = 16.1, 1H), 4.19 (t, $J$ = 6.6, 2H), 3.16 (s, 3H), 3.02 (s, 3H), 2.35 (s, 3H), 1.68 (m, 2H), 1.43 (m, 2H), 0.96 (t, $J$ = 7.4, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.08, 153.37, 148.98, 140.86, 137.22, 125.99, 125.69, 123.44, 122.85, 117.62, 63.28, 35.79, 35.45, 29.73, 20.37, 18.18, 12.73. HRMS calcd for C$_{17}$H$_{23}$NO$_4$: 305.1627; found: 305.1629.
(E)-butyl 3-(2-(diethylcarbamoyloxy)-4-methylphenyl)acrylate (1b)

Colorless oil (58% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 16.1$, 1H), 7.51 (d, $J = 8.0$, 1H), 7.02 (d, $J = 8.1$, 1H), 6.99 (s, 1H), 6.38 (d, $J = 16.1$, 1H), 4.18 (t, $J = 6.6$, 2H), 3.59 – 3.45 (m, 2H), 3.40 (m, 2H), 2.35 (s, 3H), 1.73 – 1.59 (m, 2H), 1.50 – 1.36 (m, 2H), 1.32 (t, $J = 6.8$, 3H), 1.22 (t, $J = 6.8$, 3H), 0.95 (t, $J = 7.4$, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.05, 153.75, 150.10, 141.85, 138.32, 127.00, 126.62, 124.65, 123.82, 118.69, 64.30, 42.35, 41.97, 30.80, 21.39, 19.22, 14.34, 13.74, 13.34.

HRMS calcd for C$_{19}$H$_{27}$NO$_4$: 333.1940; found: 333.1943.
(E)-butyl 3-(2-(dimethylcarbamoyloxy)phenyl)acrylate (1c)

Colorless oil  (70% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 16.1$, 1H), 7.63 (d, $J = 7.8$, 1H), 7.38 (dt, $J = 7.8$, 1H), 7.22 (t, $J = 7.6$, 1H), 7.17 (d, $J = 8.1$, 1H), 6.44 (d, $J = 16.1$, 1H), 4.20 (t, $J = 6.5$, 2H), 3.18 (s, 3H), 3.03 (s, 3H), 1.68 (m, 2H), 1.51 – 1.36 (m, 2H), 0.97 (t, $J = 7.3$, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.93, 154.30, 150.14, 138.29, 130.99, 127.39, 127.27, 125.70, 123.43, 119.87, 77.36, 77.04, 76.72, 64.43, 36.88, 36.53, 30.77, 19.22, 13.75. HRMS calcd for C$_{16}$H$_{21}$NO$_4$: 291.1471; found: 291.1472.
(E)-butyl 3-(2-(dimethylcarbamoyloxy)-4-methoxyphenyl)acrylate and (E)-butyl 3-(2-(dimethylcarbamoyloxy)-6-methoxyphenyl)acrylate (1d) mixture. Colorless oil (58%)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 16.3$, 0.5H), 7.76 (d, $J = 16.1$, 1H), 7.55 (d, $J = 8.8$, 1H), 7.29 (t, $J = 8.3$, 0.5H), 6.78 (ddd, $J = 7.5$, 5.2, 2.5, 2.5H), 6.75 (d, $J = 8.9$, 1H), 6.72 (d, $J = 2.5$, 1H), 6.32 (d, $J = 16.0$, 1H), 4.19 (dd, $J = 8.1$, 5.1, 3H), 3.90 (s, 1.5H), 3.81 (s, 3H), 3.17 (s, 4.5H), 3.02 (d, $J = 5.4$, 4.5H), 3.02 (s, 2H), 1.68 (tdd, $J = 8.7$, 6.8, 3.5, 3H), 1.49 – 1.37 (m, 3H), 0.96 (t, $J = 7.4$, 4.5H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.95, 167.30, 161.93, 154.18, 154.14, 151.42, 151.33, 138.05, 134.78, 130.45, 128.15, 122.38, 119.97, 117.17, 116.94, 115.62, 112.63, 108.42, 108.06, 64.24, 64.22, 55.86, 55.58, 36.88, 36.54, 30.83, 30.81, 19.23, 13.75.

HRMS calcd for C$_{17}$H$_{23}$NO$_5$: 321.1576; found: 321.1578.
(E)-butyl 3-(4-bromo-2-(dimethylcarbamoyloxy)phenyl)acrylate (1e)
Colorless oil (53% yield)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 16.1, 1H), 7.47 (d, $J$ = 8.4, 1H), 7.35 (m, 2H), 6.42 (d, $J$ = 16.1, 1H), 4.20 (t, $J$ = 6.6, 2H), 3.16 (s, 3H), 3.03 (s, 3H), 1.68 (m, 2H), 1.43 (m, 2H), 0.96 (t, $J$ = 7.4, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.70, 153.74, 150.34, 137.25, 129.03, 128.17, 126.81, 126.50, 124.09, 120.31, 64.54, 36.94, 36.55, 30.74, 19.21, 13.74. HRMS calcd for C$_{16}$H$_{20}$BrNO$_4$: 369.0576; found: 369.0578.
(E)-butyl 3-(2-(dimethylcarbamoyloxy)-4-iodophenyl)acrylate (If)

Colorless oil  (49% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J$ = 16.1, 1H), 7.60 – 7.53 (m, 2H), 7.32 (d, $J$ = 8.7, 1H), 6.43 (d, $J$ = 16.1, 1H), 4.20 (t, $J$ = 6.6, 2H), 3.15 (s, 3H), 3.03 (s, 3H), 1.68 (m, 2H), 1.44 (m, 2H), 0.96 (t, $J$ = 7.4, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.69, 153.78, 150.05, 137.36, 134.94, 132.60, 128.24, 127.18, 120.38, 95.52, 64.55, 36.94, 36.54, 30.74, 19.21, 13.74. HRMS calcd for C$_{16}$H$_{20}$INO$_4$: 417.0437; found: 417.0441
(E)-butyl 3-(3-(dimethylcarbamoyloxy)biphenyl-4-yl)acrylate (1g)
White solid. (67% yield)
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J = 16.1, 1H), 7.68 (d, J = 8.2, 1H), 7.62 – 7.57 (m, 2H), 7.48 – 7.39 (m, 4H), 7.38 – 7.32 (m, 1H), 6.47 (d, J = 16.1, 1H), 4.21 (t, J = 6.6, 2H), 3.19 (s, 3H), 3.04 (s, 3H), 1.80 – 1.63 (m, 2H), 1.53 – 1.38 (m, 2H), 0.97 (t, J = 7.4, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.98, 154.28, 150.48, 144.13, 139.46, 137.94, 128.83, 128.05, 127.63, 127.08, 126.14, 124.33, 121.93, 119.53, 64.42, 36.90, 36.55, 30.78, 19.23, 13.75. HRMS calcd for C$_{22}$H$_{25}$NO$_4$: 367.1784; found: 367.1785
(E)-butyl 3-(5-tert-butyl-2-(dimethylcarbamoyloxy)phenyl)acrylate (1h)
White solid. (61% yield)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, $J$ = 16.1, 1H), 7.61 (s, 1H), 7.41 (d, $J$ = 8.4, 1H), 7.09 (d, $J$ = 8.5, 1H), 6.45 (d, $J$ = 16.1, 1H), 4.21 (t, $J$ = 6.5, 2H), 3.17 (s, 3H), 3.03 (s, 3H), 1.84 – 1.55 (m, 2H), 1.56 – 1.36 (m, 2H), 1.33 (s, 9H), 0.97 (t, $J$ = 7.3, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.04, 154.45, 148.40, 147.89, 138.93, 128.45, 126.39, 124.01, 122.81, 119.30, 64.38, 36.84, 36.48, 34.53, 31.31, 30.76, 19.22, 13.76. HRMS caled for C$_{20}$H$_{29}$NO$_4$: 347.2097; found: 347.2096
(E)-butyl 3-(2-(dimethylcarbamoyloxy)-3,4-dimethylphenyl)acrylate (1i)

Colorless oil (50% yield)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, $J = 16.0$, 1H), 7.38 (d, $J = 7.9$, 1H), 7.03 (d, $J = 8.0$, 1H), 6.38 (d, $J = 16.0$, 1H), 4.18 (s, 2H), 3.21 (s, 3H), 3.03 (s, 3H), 2.30 (s, 3H), 2.09 (s, 3H), 1.73 – 1.60 (m, 2H), 1.51 – 1.36 (m, 2H), 0.96 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.15, 154.12, 148.70, 140.82, 138.96, 130.44, 127.46, 125.58, 124.09, 118.76, 64.27, 36.91, 36.50, 30.80, 20.33, 19.24, 13.76, 12.58. HRMS calcd for C$_{18}$H$_{25}$NO$_4$: 319.1784; found: 319.1786
(E)-butyl 3-(3-chloro-2-(dimethylcarbamoyloxy)phenyl)acrylate (1j)

Colorless oil (67% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 16.1$, 1H), 7.52 (dd, $J = 7.9$, 1.3, 1H), 7.44 (dd, $J = 8.0$, 1.4, 1H), $\delta$ 7.18 (t, $J = 7.8$, 1H), 7.04 (d, $J = 8.0$, 1H), 6.44 (d, $J = 6.6$, 2H), 4.20 (t, $J = 6.6$, 2H), 3.21 (s, 3H), 3.05 (s, 3H), 1.68 (m, 2H), 1.52 – 1.37 (m, 2H), 0.97 (t, $J = 7.4$, 3H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.57, 153.11, 146.59, 137.68, 131.40, 130.39, 128.88, 126.51, 125.69, 121.23, 64.57, 37.03, 36.66, 30.73, 19.21, 13.74. HRMS calcd for C$_{16}$H$_{20}$ClNO$_4$: 325.1081; found: 325.1080
(E)-butyl 3-(3-(dimethylcarbamoyloxy)naphthalen-2-yl)acrylate (1k)

White solid. (80% yield)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (s, 1H), 7.93 (d, $J = 16.1$, 1H), 7.83 (d, $J = 7.7$, 1H), 7.76 (d, $J = 7.9$, 1H), 7.62 (s, 1H), 7.51 – 7.41 (m, 2H), 6.59 (d, $J = 16.0$, 1H), 4.23 (t, $J = 6.6$, 2H), 3.22 (s, 3H), 3.06 (s, 3H), 1.78 – 1.65 (m, 2H), 1.52 – 1.32 (m, 2H), 0.98 (t, $J = 7.4$, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.90, 154.50, 147.35, 138.93, 134.50, 131.08, 128.23, 128.03, 127.47, 127.41, 127.12, 126.10, 120.39, 120.30, 64.45, 36.94, 36.58, 30.79, 19.24, 13.76. HRMS calcd for C$_{20}$H$_{23}$NO$_4$: 341.1627; found: 341.1626
(E)-butyl 3-(7-bromo-3-(dimethylcarbamoyloxy)naphthalen-2-yl)acrylate(II)

White solid. (58% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (s, 2H), 7.90 (d, $J = 16.1$, 1H), 7.63 (d, $J = 8.9$, 1H), 7.60 (s, 1H), 7.55 (d, $J = 8.7$, 1H), 6.57 (d, $J = 16.1$, 1H), 4.23 (t, $J = 6.6$, 2H), 3.22 (s, 3H), 3.06 (s, 3H), 1.77 – 1.64 (m, 2H), 1.51 – 1.38 (m, 2H), 0.98 (t, $J = 7.4$, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.69, 154.25, 147.61, 138.39, 132.81, 132.07, 130.78, 130.12, 129.01, 128.26, 126.86, 121.18, 120.38, 119.97, 64.56, 36.97, 36.58, 30.77, 19.23, 13.76. HRMS calcd for C$_{20}$H$_{22}$BrNO$_4$: 419.0732; found: 419.0735.
(2E,2'E)-dibutyl 3,3'-(4-acetyl-6-(dimethylcarbamoyloxy)-1,3-phenylene)diacrylate (1m)
White solid. (62% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 15.9$, 1H), 7.80 (t, $J = 15.9$, 1H), 7.79 (s, 1H), 7.61 (s, 1H), 6.55 (d, $J = 16.1$, 1H), 6.29 (d, $J = 15.8$, 1H), 4.23 (t, $J = 6.6$, 4H), 3.20 (s, 3H), 3.06 (s, 3H), 2.60 (s, 3H), 1.70 (m, 4H), 1.50 – 1.39 (m, 4H), 0.97 (m, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$
199.13, 166.38, 166.31, 153.65, 150.22, 142.90, 139.21, 136.51, 132.43, 130.75, 127.34, 124.48, 122.53, 121.50, 64.77, 64.60, 37.00, 36.62, 30.74, 30.69, 29.14, 19.20, 13.76, 13.74. HRMS calcd for C$_{25}$H$_{33}$NO$_7$: 459.2257; found: 459.2256
(E)-butyl 3-(2-(dimethylcarbamoyloxy)-4-((E)-3-methoxy-3-oxoprop-1-enyl)phenyl)acrylate (1n)

White solid. (61% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, J = 16.1, 1H), 7.63 (m, 2H), 7.36 (m, 2H), 6.46 (dd, J = 16.1, 6.0, 2H), 4.21 (t, J = 6.6, 2H), 3.80 (s, 3H), 3.18 (s, 3H), 3.04 (s, 3H), 1.69 (m, 2H), 1.51 – 1.36 (m, 2H), 0.97 (t, J = 7.4, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.97, 166.68, 154.00, 150.38, 143.07, 137.32, 137.21, 129.05, 127.66, 125.30, 122.75, 120.75, 119.61, 64.55, 51.81, 36.93, 36.55, 30.75, 19.21, 13.74. HRMS calcd for C$_{20}$H$_{25}$NO$_6$: 375.1682; found: 375.1686
(E)-butyl 3-(6-(dimethylcarbamoyloxy)-4-methyl-2-oxo-2H-chromen-7-yl) acrylate (I0)

White solid. (64% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 16.4$, 1H), 7.60 (d, $J = 8.8$, 1H), 7.18 (d, $J = 8.8$, 1H), 6.98 (d, $J = 16.4$, 1H), 6.30 (d, $J = 0.9$, 1H), 4.22 (t, $J = 6.7$, 2H), 3.20 (s, 3H), 3.04 (s, 3H), 2.44 (d, $J = 0.9$, 3H), 1.81 – 1.52 (m, 2H), 1.55 – 1.35 (m, 2H), 0.97 (t, $J = 7.4$, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.16, 159.67, 153.44, 152.72, 152.62, 152.23, 132.26, 125.54, 125.46, 119.33, 117.61, 116.59, 114.27, 64.62, 37.01, 36.62, 30.73, 19.20, 19.05, 13.76. HRMS calcd for C$_{20}$H$_{23}$NO$_6$: 373.1525; found: 373.1526
(E)-butyl 3-(2-(dimethylcarbamoyloxy)-4-(thiophen-3-yl)phenyl)acrylate (1p)

White solid. (56% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 16.1$, 1H), 7.63 (d, $J = 8.2$, 1H), 7.54 – 7.47 (m, 1H), 7.44 (dd, $J = 8.1$, 1.4, 1H), 7.39 (t, $J = 3.5$, 1H), 7.39 – 7.34 (m, 2H), 6.44 (d, $J = 16.1$, 1H), 4.21 (t, $J = 6.6$, 2H), 3.19 (s, 3H), 3.04 (s, 3H), 1.85 – 1.59 (m, 2H), 1.56 – 1.29 (m, 2H), 0.97 (t, $J = 7.4$, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.98, 154.24, 150.54, 140.76, 138.67, 137.85, 127.66, 126.49, 126.10, 125.92, 123.66, 121.60, 121.14, 119.28, 64.40, 36.89, 36.54, 30.77, 19.22, 13.75.

HRMS calcd for C$_{20}$H$_{23}$NO$_4$S: 373.1348; found: 373.1345.
(2E,2′E)-dibutyl 3,3′-((S)-2,2′-bis(dimethylcarbamoyloxy)-1,1′-binaphthyl-3,3′-diyl) Diacrylate (1q) White solid. (82% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28 (s, 2H), 7.92 (dd, $J$ = 12.2, 3.9, 4H), 7.50 – 7.43 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 (d, $J$ = 9.3, 2H), 6.66 (d, $J$ = 16.0, 2H), 4.22 (t, $J$ = 6.7, 4H), 2.52 (s, 6H), 2.29 (s, 6H), 1.69 (m, 4H), 1.54 – 1.36 (m, 4H), 0.96 (t, $J$ = 7.4, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.88, 153.41, 146.37, 139.48, 133.92, 131.16, 128.42, 128.30, 128.02, 127.56, 126.30, 125.56, 120.25, 64.44, 36.32, 35.73, 30.78, 19.23, 13.75. HRMS calcd for C$_{40}$H$_{44}$N$_2$O$_8$: 680.3098; found: 680.3098
(E)-butyl 3-((8R,9S,13S,14S)-3-(dimethylcarbamoyloxy)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)acrylate (1r)

White solid. (65% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 16.1$, 1H), 7.53 (s, 1H), 6.90 (s, 1H), 6.40 (d, $J = 16.1$, 1H), 4.19 (t, $J = 6.6$, 2H), 3.16 (s, 3H), 3.02 (s, 3H), 2.91 (dd, $J = 8.6$, 4.0, 2H), 2.48 (m, 12.2, 5.9, 2H), 2.28 (td, $J = 10.7$, 3.9, 1H), 2.21 – 1.94 (m, 4H), 1.74 – 1.35 (m, 10H), 0.96 (t, $J = 7.4$, 3H), 0.92 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.12, 154.55, 148.06, 140.60, 138.65, 137.44, 124.58, 124.28, 123.31, 118.63, 64.33, 50.44, 47.89, 44.00, 37.90, 36.85, 36.50, 35.83, 31.50, 30.78, 29.39, 26.22, 25.78, 21.59, 19.22, 13.82, 13.75. HRMS calcd for C$_{28}$H$_{37}$NO$_5$: 467.2672; found: 467.2672.
(E)-butyl 3-(5-(2,5-dimethyl-1H-pyrrol-1-yl)-2-(dimethylcarbamoyloxy)phenyl)acrylate (1s)

White solid. (34% yield)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J = 16.1$, 1H), 7.46 (d, $J = 2.4$, 1H), 7.29 (d, $J = 8.6$, 1H), 7.23 (dd, $J = 8.6$, 2.4, 1H), 6.41 (d, $J = 16.1$, 1H), 5.90 (s, 2H), 4.20 (t, $J = 6.6$, 2H), 3.20 (s, 3H), 3.06 (s, 3H), 2.04 (s, 6H), 1.68 (m, 2H), 1.43 (m, 2H), 0.96 (t, $J = 7.4$, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.61, 153.98, 149.20, 137.39, 136.38, 130.43, 128.82, 128.14, 126.71, 124.10, 120.90, 106.07, 64.57, 36.95, 36.57, 30.72, 19.20, 13.73, 13.06. HRMS calcd for C$_{22}$H$_{28}$N$_2$O$_4$: 384.2049; found: 384.2047.
(E)-butyl 3-(1-(4-(dimethylcarbamoyloxy)phenyl)-2,5-dimethyl-1H-pyrrol-3-yl)acrylate

White solid. (59% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J = 15.6$, 1H), 7.26 – 7.22 (m, 2H), 7.20 – 7.13 (m, 2H), 6.18 (s, 1H), 6.04 (d, $J = 15.5$, 1H), 4.17 (t, $J = 6.7$, 2H), 3.13 (s, 3H), 3.04 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.72 – 1.62 (m, 2H), 1.50 – 1.38 (m, 2H), 0.96 (t, $J = 7.4$, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.52, 154.40, 151.33, 137.91, 134.71, 133.06, 130.95, 128.87, 122.63, 116.80, 111.55, 103.95, 63.79, 36.77, 36.49, 30.96, 19.26, 13.80, 12.79, 10.90. HRMS calcd for C$_{22}$H$_{28}$N$_2$O$_4$: 384.2049; found: 384.2046.
(E)-3-styrylnaphthalen-2-yl dimethylcarbamate(2a)

White solid. (72% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (s, 1H), 7.87 – 7.80 (m, 1H), 7.78 – 7.71 (m, 1H), 7.60 (s, 1H), 7.56 – 7.49 (m, 2H), 7.46 – 7.19 (m, 7H), 3.23 (s, 3H), 3.06 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.76, 147.25, 137.50, 133.28, 131.51, 131.22, 130.03, 128.72, 127.85, 127.76, 127.69, 126.69, 126.25, 125.80, 125.74, 122.87, 119.88, 36.92, 36.60. HRMS calcd for C$_{21}$H$_{19}$NO$_2$: 317.1416; found: 317.1416.
(E)-3-(4-fluorostyryl)naphthalen-2-yl dimethylcarbamate (2b)

White solid. (55% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (s, 1H), 7.83 (m, 1H), 7.79 – 7.72 (m, 1H), 7.59 (s, 1H), 7.51 – 7.46 (m, 2H), 7.45 – 7.40 (m, 2H), 7.20 (d, $J$ = 2.8, 2H), 7.06 (dd, $J$ = 9.6, 7.8, 2H), 3.23 (s, 3H), 3.06 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.48 ($J$ = 247.6), 154.77, 147.21, 133.70, 133.67, 133.29, 131.50, 129.99, 129.90, 128.18 ($J$ = 8.0), 127.74, 127.34, 126.30, 125.78, 125.73, 122.65 ($J$ = 2.3), 119.89, 115.68 ($J$ = 21.7), 36.93, 36.61.

$^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -113.81.

HRMS calcd for C$_{21}$H$_{18}$FNO$_2$: 335.1322; found: 335.1325.
(E)-3-(4-chlorostyryl)naphthalen-2-yl dimethylcarbamate (2c)

White solid. (63% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (s, 1H), 7.88 – 7.81 (m, 1H), 7.75 (dd, $J = 5.9, 3.6$, 1H), 7.59 (s, 1H), 7.48 – 7.41 (m, 4H), 7.34 (d, $J = 8.5$, 2H), 7.28 (d, 1H), 7.17 (d, $J = 16.3$, 1H), 3.23 (s, 3H), 3.07 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.76, 136.02, 133.46, 133.39, 131.49, 129.89, 129.74, 128.92, 127.83, 127.79, 127.36, 126.41, 125.91, 125.83, 123.55, 119.94, 36.94. HRMS calcd for C$_{21}$H$_{18}$ClNO$_2$: 351.1026; found: 351.1026.
(E)-3-(4-bromostyryl)naphthalen-2-yl dimethylcarbamate(2d)

White solid. (53% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (s, 1H), 7.86 – 7.80 (m, 1H), 7.75 (m, 1H), 7.59 (s, 1H), 7.49 (d, $J$ = 8.5, 2H), 7.46 – 7.41 (m, 2H), 7.37 (d, $J$ = 8.5, 2H), 7.28 (d, $J$ = 16.4, 1H), 7.15 (d, $J$ = 16.3, 1H), 3.22 (s, 3H), 3.06 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.73, 147.18, 136.43, 133.38, 131.84, 131.46, 129.91, 129.69, 128.13, 127.78, 127.35, 126.42, 125.91, 125.83, 123.63, 121.59, 119.94, 36.93, 36.61. HRMS calcd for C$_{21}$H$_{18}$BrNO$_2$: 395.0521; found: 395.0524.
(E)-tert-butyl 3-(3-(dimethylcarbamoyloxy)naphthalen-2-yl)acrylate(2e)

White solid. (62% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (s, 1H), 7.88 – 7.81 (d, 1H), 7.82 (t, $J = 3.7$, 1H), 7.75 (d, $J = 7.7$, 1H), 7.61 (s, 1H), 7.46 (m, 2H), 6.54 (d, 1H), 3.22 (s, 3H), 3.06 (s, 3H), 1.55 (s, 9H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.07, 154.54, 137.72, 134.40, 131.10, 128.18, 127.72, 127.40, 127.33, 127.23, 126.03, 122.24, 120.23, 80.52, 36.93, 36.59, 28.23. HRMS calcd for C$_{20}$H$_{23}$NO$_4$: 341.1627; found: 341.1627.
(E)-methyl 3-(3-(dimethylcarbamoyloxy)naphthalen-2-yl)acrylate(2f)

White solid.  (73% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (s, 1H), 7.94 (d, $J$ = 16.1, 1H), 7.84 (d, $J$ = 7.7, 1H), 7.76 (d, $J$ = 7.8, 1H), 7.62 (s, 1H), 7.47 (m, 2H), 6.59 (d, $J$ = 16.1, 1H), 3.82 (s, 3H), 3.23 (s, 3H), 3.07 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.32, 154.50, 147.33, 139.39, 134.51, 131.05, 128.25, 127.53, 127.40, 127.03, 126.12, 120.34, 119.88, 51.77, 36.96, 36.62. HRMS calcd for C$_{17}$H$_{17}$NO$_4$: 299.1158; found: 299.1160.
(E)-3-(2-(methylsulfonyl)vinyl)naphthalen-2-yl dimethylcarbamate(2g)

White solid. (54% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (s, 1H), 7.87 (d, $J$ = 15.6, 1H), 7.84 (d, $J$ = 10.1, 1H), 7.77 (d, $J$ = 8.1, 1H), 7.65 (s, 1H), 7.50 (m, 2H), 7.06 (d, $J$ = 15.5, 1H), 3.21 (s, 3H), 3.06 (s, 3H), 3.05 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.25, 147.13, 138.79, 134.93, 130.79, 129.16, 128.35, 128.14, 128.01, 127.46, 126.42, 124.68, 120.56, 43.25, 36.99, 36.67. HRMS calcd for C$_{16}$H$_{17}$NO$_4$S: 319.0878; found: 319.0878
(E)-3-(2-(diethoxyphosphoryl)vinyl)naphthalen-2-yl dimethylcarbamate(2h)

White solid. (48% yield)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (s, 1H), 7.88 – 7.67 (m, 3H), 7.62 (s, 1H), 7.47 (p, $J$ = 6.9, 2H), 6.42 (t, $J$ = 17.9, 1H), 4.15 (p, $J$ = 7.2, 4H), 3.21 (s, 3H), 3.05 (s, 3H), 1.37 (t, $J$ = 7.0, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.43, 147.08, 143.06, 142.99, 134.41, 130.98, 128.21, 127.67, 127.45, 127.37, 126.10, 120.24, 117.47, 115.58, 61.91, 61.86, 36.90, 36.62, 16.46, 16.39. HRMS calcd for C$_{19}$H$_{24}$NO$_5$P: 377.1392; found: 377.1396
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 – 7.10 (m, 2H), 6.98 (d, $J = 8.9$, 1H), 3.08 (s, 3H), 3.00 (s, 3H), 2.32 (s, 3H).

White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 16.1$, 1H), 7.41 (d, $J = 2.0$, 1H), 7.18 (t, $J = 3.3$, 1H), 7.04 (d, $J = 8.3$, 0.24H), 6.42 (d, $J = 16.1$, 1H), 4.20 (t, $J = 6.6$, 2H), 3.09 (d, $J = 57.1$, 6H), 2.34 (s, 3H), 1.76 – 1.61 (m, 2H), 1.50 – 1.36 (m, 3H), 0.96 (t, $J = 7.4$, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.01, 154.52, 147.98, 138.44, 135.27, 131.70, 127.58, 126.92, 123.15, 119.55, 64.38, 36.87, 36.51, 30.78, 20.88, 19.23, 13.75.
HPLC e.e. Determination of (S)-1q.
SAMPLE INFORMATION

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Injection #: 4
Injection Volume: 20.00 ul
Run Time: 60.00 Minutes

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Date Processed: 3/29/2011 5:35:03 PM
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