< Supporting Information >

Unique Photophysical Properties of 9-Styryl-1,2-dihydropyrrolo[3,4-*β*]indolizin-3-one and their Efficient Synthesis via Direct C-H Activation

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I. General Information

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-300 (Bruker Biospin, Germany) and Varian Inova-500 (Varian Assoc, Palo Alto, USA), chemical shifts were measured in ppm downfield from internal tetramethylsilane (TMS) standard. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublet); dt (doublet of triplet); br s (broad singlet), etc. Coupling constants were reported in Hz. Low resolution mass analyses were performed on LC/MS system, Finnigan MSQ plus Surveyer (Thermo) equipped with a reverse phase column (C-18, 50 × 2.1 mm, 5 μm) and photodiode array detector using electron spray ionization (ESI) or performed on 6120 Quadrupole LC/MS (Agilent Technologies). The identity of desired compounds were further confirmed by high-resolution mass spectrometry (HRMS). The HRMS analyses were conducted at the Mass Spectrometry Laboratory of Seoul National University by direct injection on a JEOL JMS AX505WA spectrometer using fast atom bombardment (FAB) method. Absorbance of final fluorescence compounds was measured by UV-VIS spectrophotometer UV-1650PC (Shimatzu, Japan). Excitation and Emission maxima were measured by Cary Eclipse Fluorescence spectrophotometer (Varian Assoc., Palo Alto, USA). Absolute quantum yield was measured by absolute PL quantum yield measurement system QE-1000 (OTSUKA Electronics). *In silico* calculations were performed using the Materials Studio® 4.2 program (Accelrys Software Inc.) A generalized gradient approximation (GAA) for the exchange correlation function of Perdew, Burke, and Ernzerhof (PBE) was used with the double numerical basis set with polarization (DNP) as implemented in DMol3. Internal standard analysis for checking yield of crude reaction was performed on SHIMADZU HPLC equipped with a reverse phase column (XDB C18, 5 μm, 4.6 × 150 mm). Samples were analyzed starting with 5% ACN in H_2O (0.1% TFA) for 5 min after injected 10 μL of sample and solvent was changed from 5% ACN in H_2O (0.1% TFA) to 100% ACN (0.1% TFA) for 30 min with 1.0 mL/min flow. Absorbance was detected by 365 nm.

All chemical reagents including 3-bromopropylamine hydrobromide, di-*tert*-butyl dicarbonate, propargyl amine, triethylamine, 1,3-diazabicyclo[5.4.0]undec-7-ene, diisopropylethylamine, bromoacetyl bromide, pyridine derivatives, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, substituted styrenes, palladium acetate, silver oxide, silver acetate, copper acetate, anhydrous dimethyl formamide were purchased either from Sigma-Aldrich and Tokyo Chemical Industry Co., or Acros, and used without further purification. Progress of reaction was monitored using thin-layer chromatography (silica gel 60 F_{254} 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm) or by treating TLC plates with anisaldehyde or ninhydrin, followed by heating. Solvents were purchased from commercial venders and used without further purification. Distilled water was polished by ion exchange and filtration.

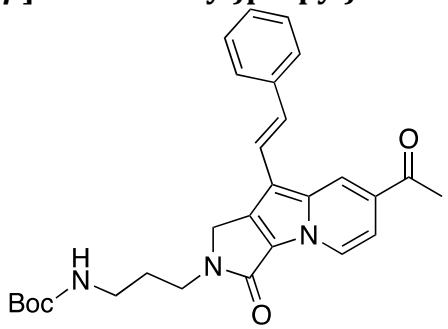
II General Experimental Procedure and Compound Characterization

Preparation of *tert*-butyl (3-(prop-2-yn-1-ylamino)propyl)carbamate (1): *tert*-butyl (3-(prop-2-yn-1-ylamino)propyl)carbamate was synthesized by previously reported method.[1]

Preparation of 1,2-dihydro-3H-pyrrolo[3,4-*β*]indolizin-3-one derivatives (4a-c): 1,2-dihydro-3H-pyrrolo[3,4-b]indolizin-3-one derivatives were synthesized by previously reported method.[1]

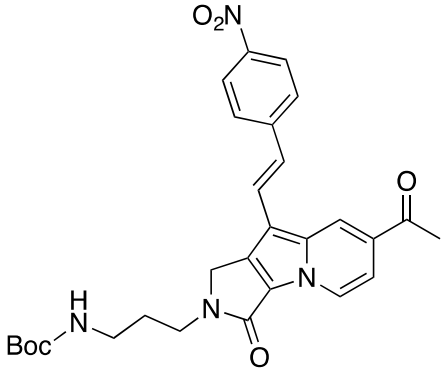
General synthetic procedure of the cross-coupling reaction: To a solution of ɣ-lactam embedded indolizines (**4a**–**c**) in dimethylformamide, 10 volume% acetic acid, styrene derivatives (3 equiv.), palladium acetate (0.1 equiv.) and silver acetate (2 equiv.) were added and stirred at 80°C for overnight (20 h). After the reaction completion as monitored by TLC, reaction mixture was concentrated *in vacuo* after filtration. The residue was purified by silica gel flash column chromatography to afford the desired product (**5**–**18**). In case of *tert*-butyl (*E*)-(3-(7-acetyl-9-(4-aminostyryl)-3-oxo-1,3-dihydro-2*H*-pyrrolo[3,4-*b*]indolizin-2-yl)propyl)carbamate (**12**), 4-nitrostyrene was used as a substrate of cross-coupling reaction and reduced by tin(II) chloride dihydrate in dimethylformamide and 10 volume% acetic acid. In case of *tert*-butyl (*E*)-(3-(7-methyl-3-oxo-9-styryl-1,3-dihydro-2*H*-pyrrolo[3,4-*b*]indolizin-2-yl)propyl)carbamate (**17**), copper(II) acetate (2 equiv.) was used as oxidant instead of silver acetate.

***tert*-Butyl (E)-(3-(7-acetyl-3-oxo-9-styryl-1,3-dihydro-2H-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (5):**



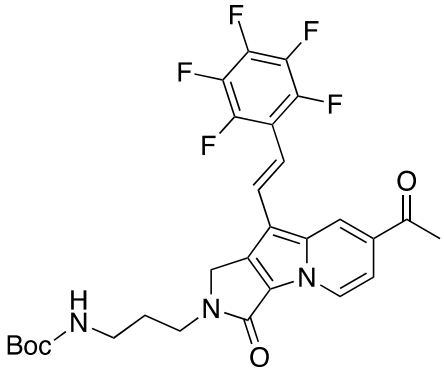
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.2 Hz, 1H), 8.30 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.43-7.32 (m, 4H), 7.25 (d, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 15.9 Hz, 1H), 5.36 (br s, 1H), 4.57 (s, 2H), 3.73 (t, *J* = 6.0 Hz, 2H), 3.21 (d, *J* = 5.1 Hz, 2H), 2.68 (s, 3H), 1.92–1.88 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 161.7, 156.2, 137.3, 136.0, 133.1, 128.8, 128.7, 128.5, 127.9, 127.5, 126.0, 124.6, 123.4, 120.0, 117.8, 112.0, 109.7, 79.2, 47.2, 40.2, 37.4, 28.8, 28.4, 26.2; HRMS (FAB+) m/z calcd. for $C_{28}H_{31}N_3O_4$ $[M]^+$ 473.23; found : 473.2315.

***tert*-Butyl (E)-(3-(7-acetyl-9-(4-nitrostyryl)-3-oxo-1,3-dihydro-2H-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (6):**



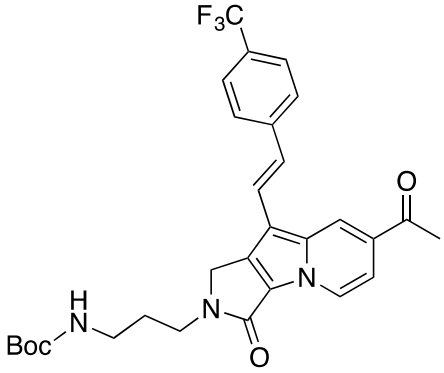
^{1}H NMR (300 MHz, DMSO) δ 8.79 (s, 1H) 8.42 (d, *J* = 7.2 Hz, 1H), 8.21 (d, *J* = 8.7 Hz, 2H), 8.05 (d, *J* = 15.9 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 16.2 Hz, 1H), 4.69 (s, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 3.01 (dd, *J* = 11.0, 5.0 Hz, 2H), 2.66 (s, 3H), 1.81–1.76 (m, 2H), 1.38 (s, 9H); HRMS (FAB+) m/z calcd. for $C_{28}H_{30}N_4O_6$ $[M]^+$ 518.22; found : 518.2165.

***tert*-Butyl (*E*)-(3-(7-acetyl-3-oxo-9-(2-(perfluorophenyl)vinyl)-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (7):**



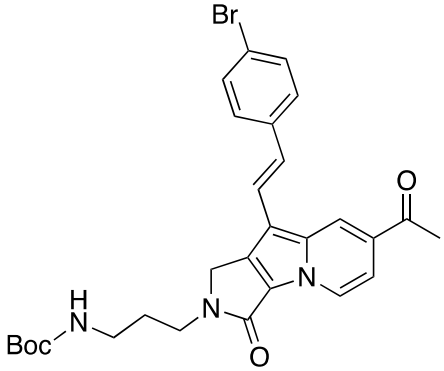
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.2 Hz, 1H), 8.27 (s, 1H), 7.73 (d, *J* = 16.5 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 16.5 Hz, 1H), 5.30 (br s, 1H), 4.59 (s, 2H), 3.74 (t, *J* = 6.5 Hz, 2H), 3.21 (dd, *J* = 12.3, 6.0 Hz, 2H), 2.69 (s, 3H), 1.95–1.86 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.2, 161.4, 156.1, 136.8, 133.6, 129.8, 126.3 (t, $^2J_{C,F}$ = 9.4 Hz), 126.2, 124.9, 124.0, 119.5, 112.6, 112.5, 111.4, 111.38, 111.33, 111.2, 110.2, 79.2, 47.0, 40.3, 37.3, 29.7, 28.8, 28.4, 26.2; HRMS (FAB+) m/z calcd. for $C_{28}H_{26}F_5N_3O_4$ $[M+H]^+$ 564.19; found : 564.1922.

***tert*-Butyl (*E*)-(3-(7-acetyl-3-oxo-9-(4-(trifluoromethyl)styryl)-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (8):**



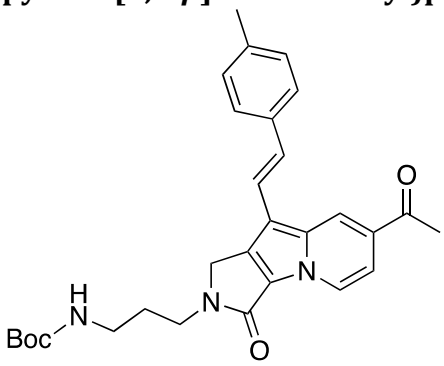
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.2 Hz, 1H), δ 8.32 (s, 1H), 7.64 (s, 4H), 7.48 (d, *J* = 16.2 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 16.2 Hz, 1H), 5.31 (br s, 1H), 4.60 (s, 2H), 3.73 (t, *J* = 6.3 Hz, 2H), 3.21 (dd, *J* = 12.3, 6.0 Hz, 2H), 2.69 (s, 3H), 1.95–1.86 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 161.5, 156.1, 140.8, 139.8, 136.4, 133.5, 129.2, 129.0 (q, $^2J_{C,F}$ = 31.5 Hz), 126.0, 125.7 (q, $^3J_{C,F}$ = 3.8 Hz), 125.7 (q, $^1J_{C,F}$ = 143 Hz), 123.7, 120.3, 119.6, 111.3, 110.0, 79.2, 47.1, 40.2, 37.4, 29.7, 28.8, 28.4, 26.3; HRMS (FAB+) m/z calcd. for $C_{29}H_{30}F_3N_3O_4$ $[M]^+$ 541.22; found : 541.2188.

***tert*-Butyl (*E*)-(3-(7-acetyl-9-(4-bromostyryl)-3-oxo-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (9):**



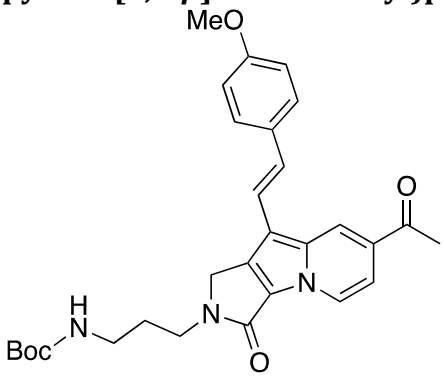
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, *J* = 6.6 Hz, 1H), 8.31 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.36 (s, 1H), 7.27 (s, 1H), 6.62(d, *J* = 15.9 Hz, 1H), 5.32 (br s, 1H), 4.58 (s, 2H), 3.75–3.65 (m, 2H), 3.21 (dd, *J* = 11.4, 5.7 Hz, 2H), 2.69 (s, 3H), 1.92–1.82 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 161.6, 156.1, 138.0, 136.3, 133.2, 131.9, 128.9, 127.4, 127.1, 124.7, 123.6, 122.1, 121.1, 119.8, 118.6, 111.6, 109.8, 79.2, 47.1, 40.2, 37.4, 29.7, 28.4, 26.3; HRMS (FAB+) m/z calcd. for $C_{28}H_{30}BrN_3O_4$ $[M]^+$ 551.14; found : 551.1420.

***tert*-Butyl (*E*)-(3-(7-acetyl-9-(4-methylstyryl)-3-oxo-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (10):**



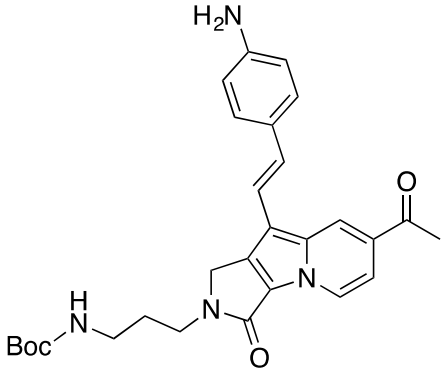
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.8 Hz, 1H), 8.28 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.34 (s, 1H), 7.24–7.19 (m, 3H), 6.65 (d, *J* = 15.9 Hz, 1H), 5.36 (br s, 1H), 4.55 (s, 2H), 3.71 (t, *J*= 6.5 Hz, 2H), 3.20 (dd, *J* = 12.2, 6.2 Hz, 2H), 2.66 (s, 3H), 2.39 (s, 3H), 1.93–1.84 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 161.7, 156.1, 137.5, 135.8, 134.5, 133.0, 129.5, 128.5, 125.9, 124.5, 123.4, 120.0, 116.8, 112.2, 109.6, 79.1, 47.1, 40.2, 37.3, 29.7, 28.8, 28.4, 26.2, 21.3; HRMS (FAB+) m/z calcd. for $C_{29}H_{33}N_3O_4$ $[M]^+$ 487.25; found : 487.2471.

***tert*-Butyl (*E*)-(3-(7-acetyl-9-(4-methoxystyryl)-3-oxo-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (11):**



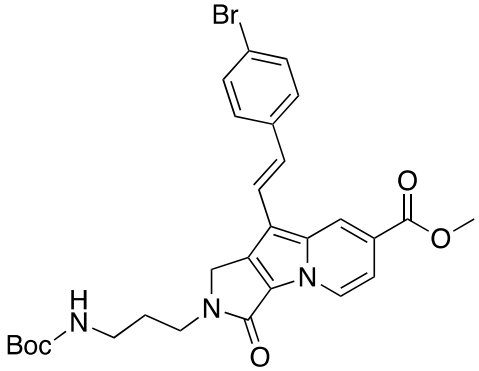
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.2 Hz, 1H), 8.30 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.25 (dd, *J* = 11.7, 5.0 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 16.2 Hz, 1H), 5.36 (br s, 1H), 4.57 (s, 2H), 3.87 (s, 3H), 3.72 (t, *J* = 6.3 Hz, 2H), 3.21 (dd, *J*= 12.6, 6.0 Hz, 2H), 2.67 (s, 3H), 1.93–1.87 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 161.7, 159.3, 156.1, 135.7, 132.8, 130.1, 128.4, 128.3, 127.2, 124.5, 123.3, 120.1, 115.8, 114.3, 112.4, 109.5, 79.1, 55.4, 47.1, 40.2, 37.4, 31.9, 29.7, 28.4, 26.2; HRMS (FAB+) m/z calcd. for $C_{29}H_{33}N_3O_5$ $[M]^+$ 503.24; found : 503.2420.

***tert*-Butyl (*E*)-(3-(7-acetyl-9-(4-aminostyryl)-3-oxo-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (12):**



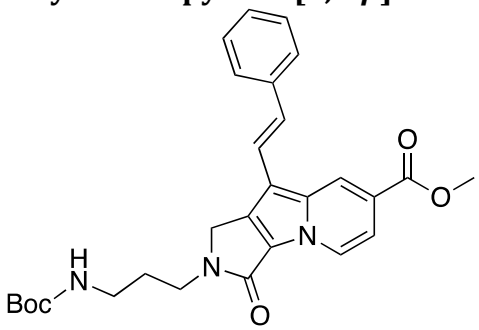
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 6.9 Hz, 1H), 8.24 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.21–7.12 (m, 2H), 6.72 (d, *J* = 7.8 Hz, 2H), 6.58 (d, *J* = 16.2 Hz, 1H), 5.39 (br s, 1H), 4.51 (s, 2H), 3.70 (t, *J* = 5.9 Hz, 2H), 3.20 (d, *J* = 5.1 Hz, 2H), 2.65 (s, 3H), 1.90–1.86 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 161.7, 156.1, 146.2, 135.4, 132.6, 128.9, 128.1, 127.9, 127.3, 124.4, 123.2, 120.2, 115.3, 114.2, 112.7, 109.4, 79.1, 47.1, 40.1, 37.3, 29.7, 28.8, 28.4, 26.2; HRMS (FAB+) m/z calcd. for $C_{28}H_{32}N_4O_4$ $[M]^+$ 488.24; found : 488.2424.

Methyl (*E*)-9-(4-bromostyryl)-2-(3-((*tert*-butoxycarbonyl)amino)propyl)-3-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*β*]indolizine-7-carboxylate (13):



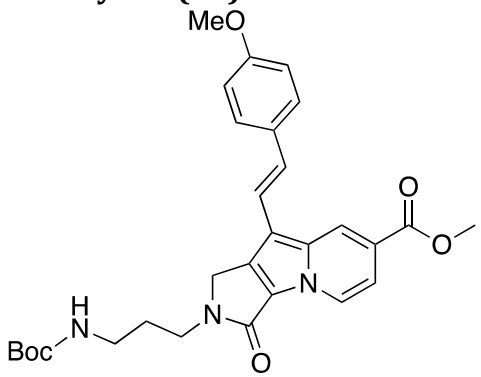
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.5 Hz, 1H), 8.43 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 16.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 5.34 (br s, 1H), 4.55 (s, 2H), 3.98 (s, 3H), 3.71 (t, *J* = 6.5 Hz, 2H), 3.19 (dd, *J* = 11.3, 5.8 Hz, 2H), 1.91–1.86 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 161.7, 156.2, 136.4, 133.3, 131.9, 127.4, 126.8, 124.6, 123.3, 122.1, 121.0, 118.7, 111.0, 79.3, 52.6, 47.2, 40.3, 37.4, 29.8, 28.8, 28.5; HRMS (FAB+) m/z calcd. for $C_{28}H_{30}BrN_3O_5$ $[M]^+$ 567.14; found : 567.1369.

Methyl (*E*)-2-(3-((*tert*-butoxycarbonyl)amino)propyl)-3-oxo-9-styryl-2,3-dihydro-1*H*-pyrrolo[3,4-*β*]indolizine-7-carboxylate (14):



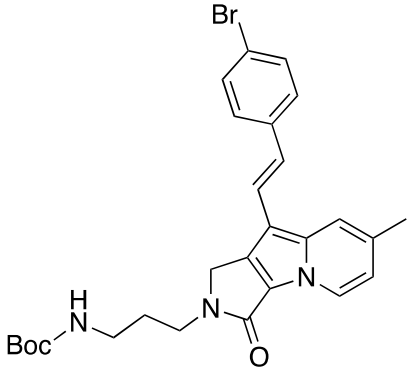
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.2 Hz, 1H), 8.37 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.41–7.34 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 16.2 Hz, 1H), 5.41 (br s, 1H), 4.50 (s, 2H), 3.96 (s, 3H), 3.69 (t, *J* = 6.5 Hz, 2H), 3.20 (br s, 2H), 1.90-1.86 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 161.7, 156.2, 140.8, 137.3, 136.2, 133.1, 128.8, 128.5, 128.2, 127.7, 127.4, 125.9, 124.3, 123.0, 121.7, 120.9, 117.8, 79.2, 52.4, 47.1, 40.2, 37.4, 31.1, 28.8, 28.4; HRMS (FAB+) m/z calcd. for $C_{28}H_{31}N_3O_5$ $[M]^+$ 489.23; found : 489.2264.

Methyl (*E*)-2-(3-((*tert*-butoxycarbonyl)amino)propyl)-9-(4-methoxystyryl)-3-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*β*]indolizine-7-carboxylate (15):



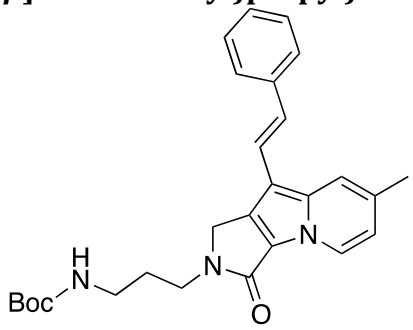
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, *J* = 6.0 Hz, 1H), 8.35 (s, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.20–7.13 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 16.5 Hz, 1H), 5.42 (br s, 1H), 4.48 (s, 2H), 3.95 (s, 3H), 3.85 (s, 3H), 3.68 (t, *J* = 5.0 Hz, 2H), 3.19 (br s, 2H), 1.89-1.85 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 161.8, 159.2, 156.3, 135.9, 132.8, 130.2, 127.9, 127.2, 124.3, 122.8, 121.4, 121.0, 115.8, 114.2, 111.6, 110.6, 79.3, 55.3, 52.4, 47.1, 40.2, 37.4, 31.1, 28.8, 28.4; HRMS (FAB+) m/z calcd. for $C_{29}H_{33}N_3O_6$ $[M]^+$ 519.24; found : 519.2369.

***tert*-Butyl (*E*)-(3-(9-(4-bromostyryl)-7-methyl-3-oxo-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (16):**



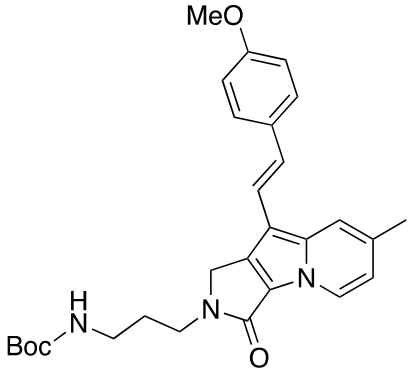
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.9 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43–7.32 (m, 3H), 7.27 (s, 1H), 6.62 (d, *J* = 6.9 Hz, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 5.42 (br s, 1H), 4.52 (s, 2H), 3.70 (t, *J* = 6.3 Hz, 2H), 3.20 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.90–1.86 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 138.7, 137.0, 133.9, 132.8, 131.7, 127.0, 124.9, 124.0, 120.2, 120.1, 119.5, 115.8, 114.9, 105.7, 79.4, 42.3, 40.2, 29.7, 28.9, 28.4, 21.6; HRMS (FAB+) m/z calcd. for $C_{27}H_{30}BrN_3O_3$ $[M]^+$ 523.15; found : 523.1471.

***tert*-Butyl (*E*)-(3-(7-methyl-3-oxo-9-styryl-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (17):**



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.9 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.44–7.34 (m, 4H), 7.25 (d, *J* = 7.2 Hz, 1H), 6.61-6.53 (m, 2H), 5.48 (br s, 1H), 4.53 (s, 2H), 3.70 (t, *J* = 6.5 Hz, 2H), 3.20 (t, *J*= 5.4 Hz, 2H), 2.42 (s, 3H), 1.90-1.86 (m, 2H), 1.46 (s, 9H); HRMS (FAB+) m/z calcd. for $C_{27}H_{31}N_3O_3$ $[M]^+$ 445.24; found : 445.2365.

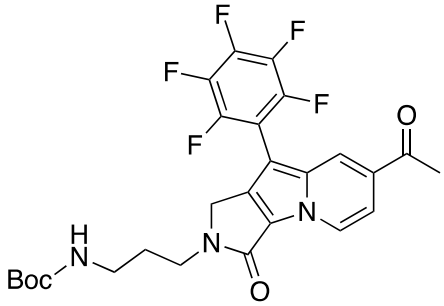
***tert*-Butyl (*E*)-(3-(9-(4-methoxystyryl)-7-methyl-3-oxo-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate (18):**



^{1}H NMR (300 MHz, CD_3OD) δ 8.36 (d, *J* = 6.9 Hz, 1H), 7.56 (s, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 16.2 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 6.9 Hz, 1H), 6.58 (d, *J* = 16.2 Hz, 1H), 5.35 (br s, 1H), 4.58 (s, 2H), 3.82 (s, 3H), 3.65 (t, *J* = 8.4 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.91-1.87 (m, 2H), 1.43 (s, 9H); HRMS (FAB+) m/z calcd. for $C_{28}H_{33}N_3O_4$ $[M]^+$ 475.25; found : 475.2471.

Preparation of *tert*-butyl (3-(7-acetyl-3-oxo-9-(perfluorophenyl)-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate: *tert*-Butyl (3-(7-acetyl-3-oxo-9-(perfluorophenyl)-1,3-dihydro-2*H*-pyrrolo[3,4-*b*]indolizin-2-yl)propyl)carbamate was synthesized by previously reported method.[1]

***tert*-Butyl (3-(7-acetyl-3-oxo-9-(perfluorophenyl)-1,3-dihydro-2*H*-pyrrolo[3,4-*β*]indolizin-2-yl)propyl)carbamate :**

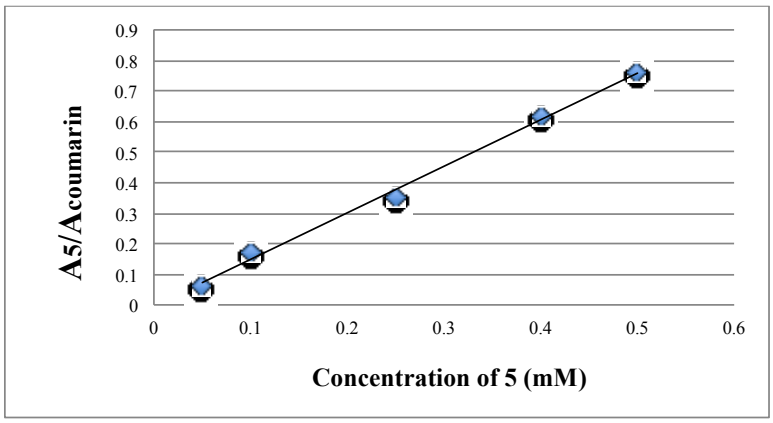


^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 7.2 Hz, 1H), 7.99 (s, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 5.30 (br s, 1H), 4.40 (s, 2H), 3.70 (t, *J* = 6.3 Hz, 2H), 3.20 (dd, *J*= 12.3, 6.3 Hz, 2H), 2.65 (s, 3H), 1.88–1.83 (m, 2H), 1.45 (s, 9H); HRMS (FAB+) m/z calcd. for $C_{26}H_{24}F_5N_3O_4$ $[M+H]^+$ 538.18; found : 538.1765.

III Internal standard method and HPLC spectra

1. Calibration curve of styryl SF 5 using 7-hydroxycoumarin as the internal standard.

To measure the reaction yields with HPLC, we plotted the calibration curve of styryl SF **5** with different concentration using 7-hydroxycoumarin at the fixed concentration (15 mM) as the internal standard. As shown in Graph S1, we obtained the estimated yield of this transformation by measuring the absorbance ratio between **5** and 7-hydroxycoumarin. Each solution was prepared by serial dilution with ACN. Data showed the excellent linearity of absorbance ratio ($A_5/A_{coumarin}$) with the concentration of styryl SF **5**.



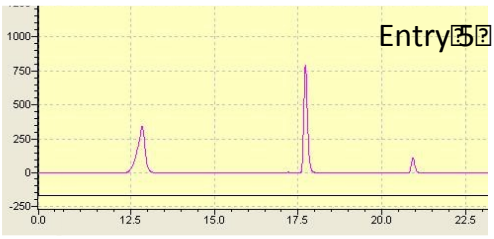
Graph S1. Calibration curve of absorbance ratio ($A_5/A_{coumarin}$) between **5** and 7-hydroxycoumarin under the different concentration of **5**.

2. Optimization of reaction condition by HPLC Analysis.

A 4-mL vial was charged with **4a** (0.027 mmol) and styrene (0.081 mmol) in the presence of various catalysts (10 mol%), oxidants (2 equiv.), and solvent (total volue of 400 μL). The vial was closed with cap, and heated at 80 °C for 20 h. The reaction mixture was cooled down to ambient temperature, followed by the addition of 7-hydroxycoumarin as the internal standard. The crude mixtures were analyzed by HPLC. Retention times of internal standard, starting compound (**4a**), and product (**5**) were as follows: t_R of 7-hydroxycoumarin; 12.9 ± 0.2 min, t_R of **4a**; 17.7 ± 0.1 min; t_R of **5**; 20.9 ± 0.1 min.


Entry 3


Entry 4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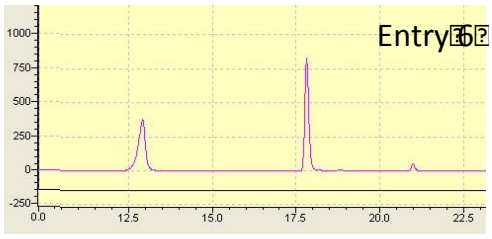
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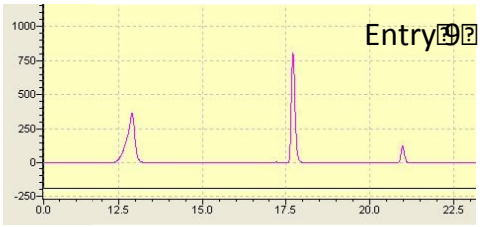
Entry 7


Entry 8


Entry 9

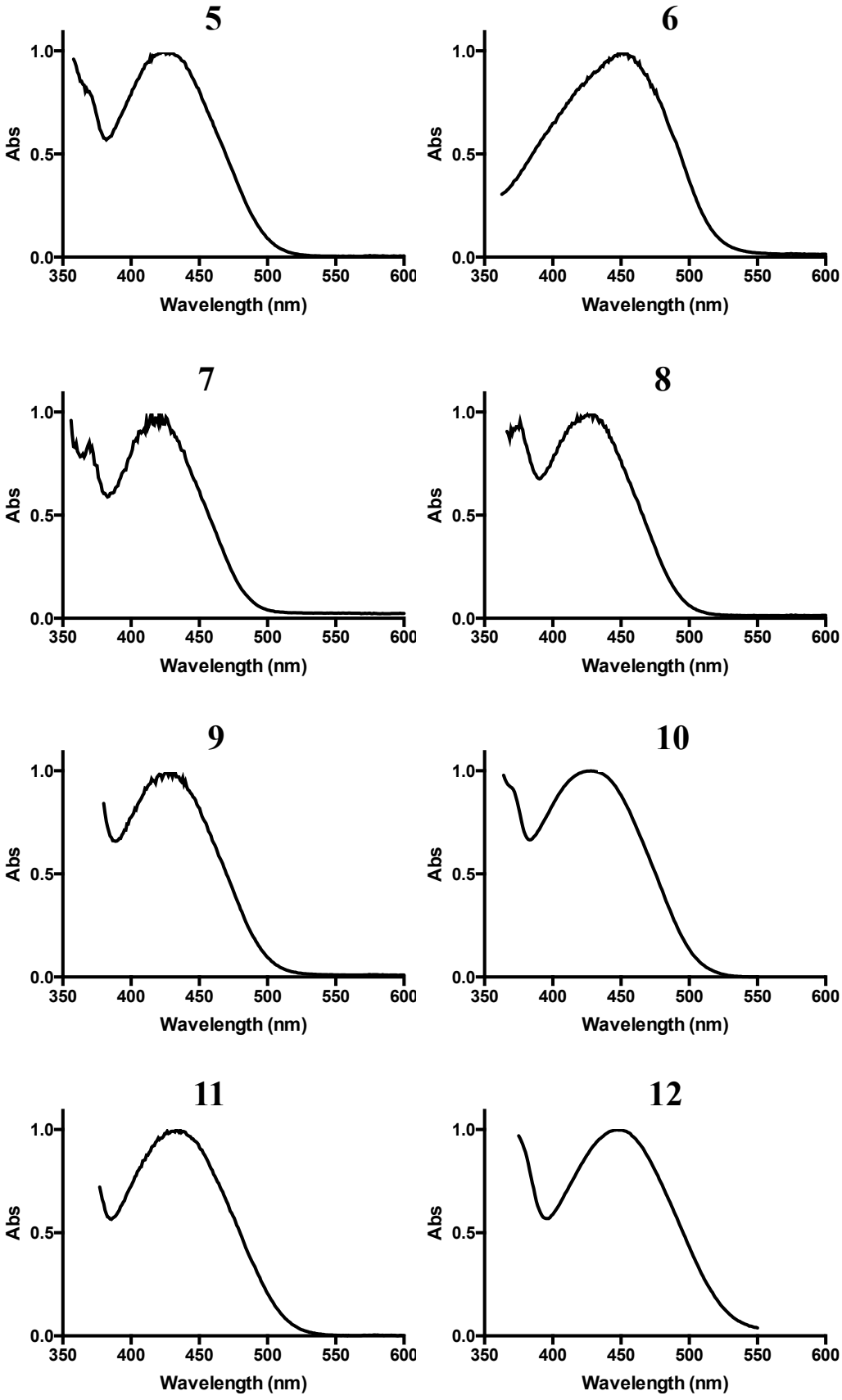

Entry 10

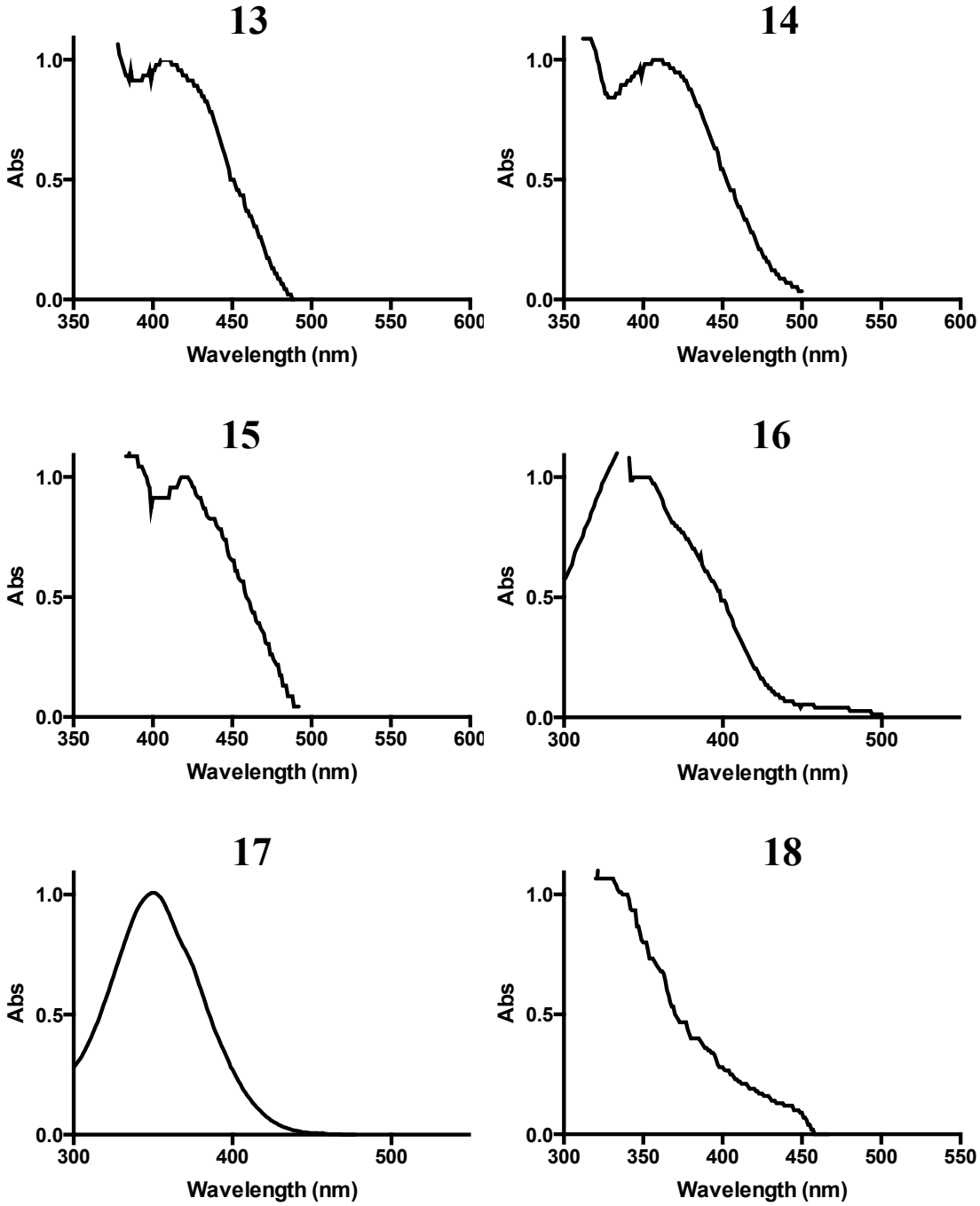

Entry 11


Entry 12

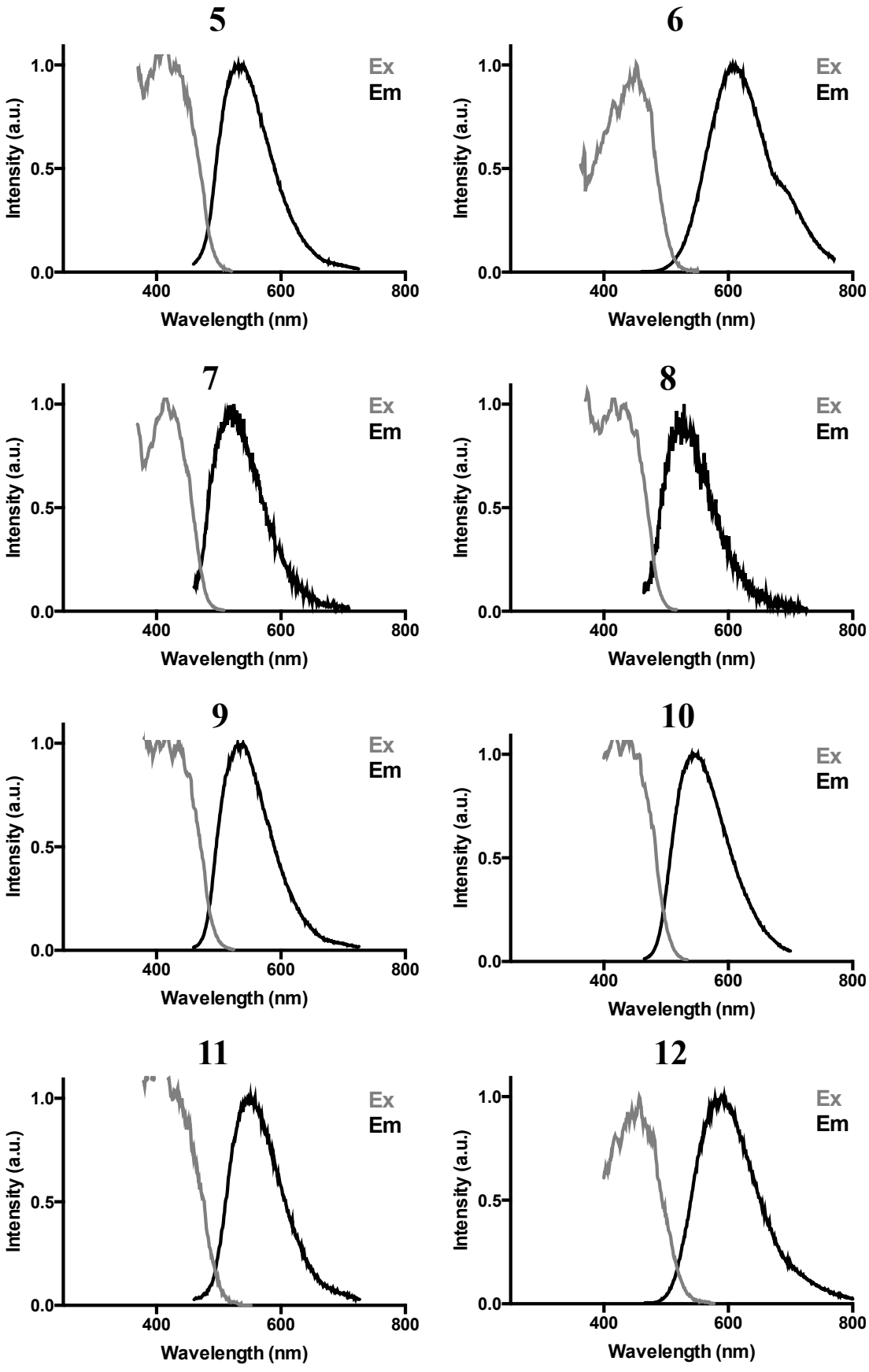
VI Absorption and excitation/emission spectra of each compound

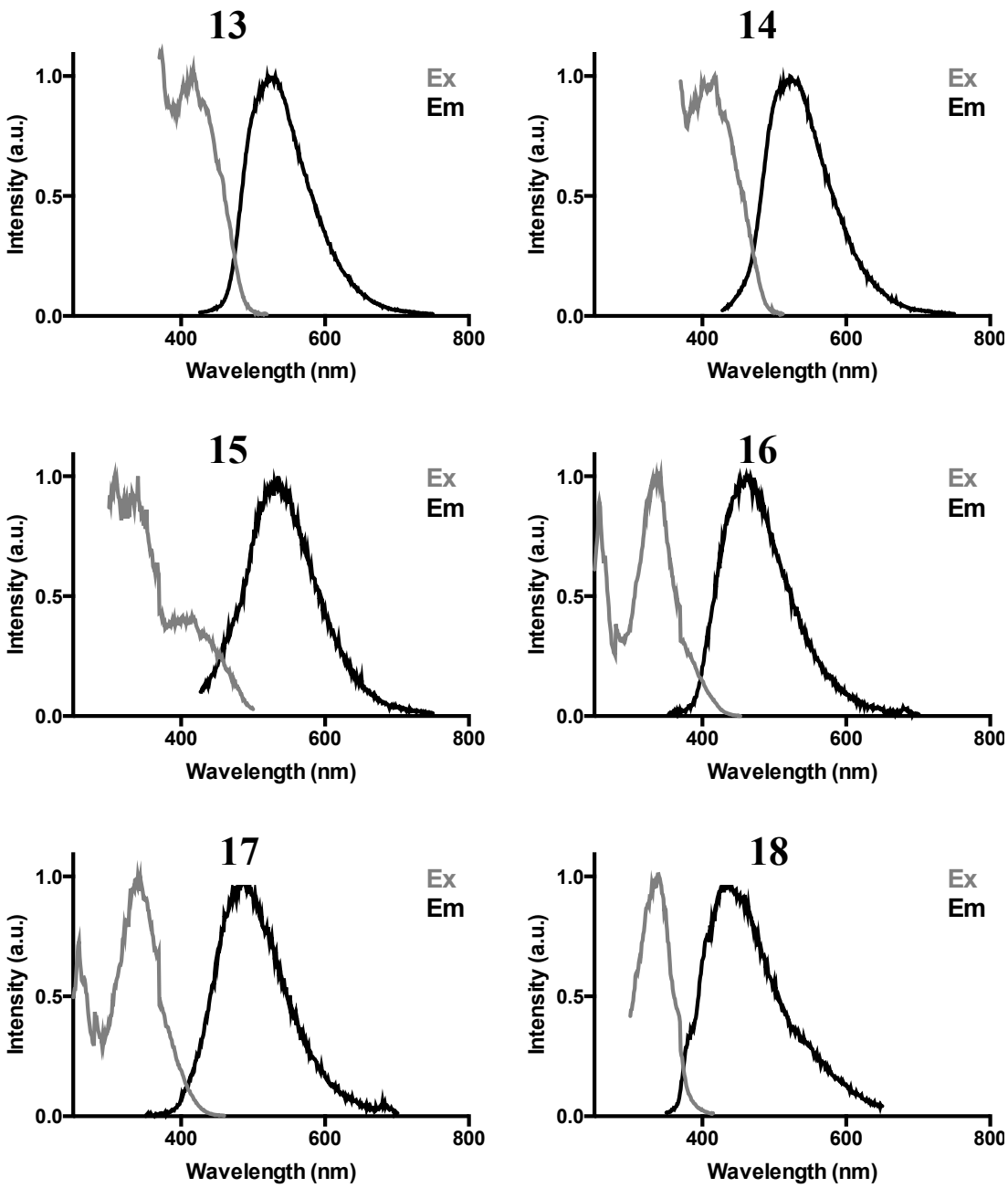
<Absorption Spectra of Styryl Seoul-Fluor Analogs (5–18)>



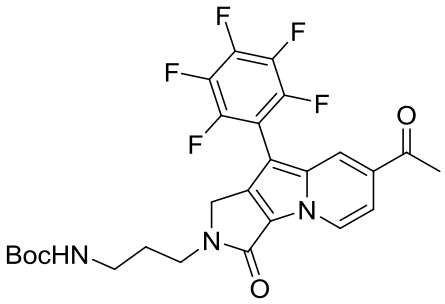

13
14
15
16
17
18
Abs
Wavelength (nm)

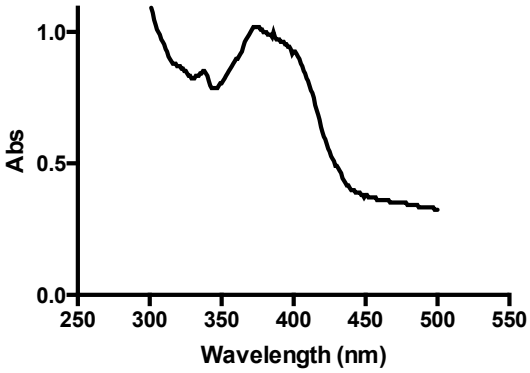
<Excitation/Emission Spectra of Styryl Seoul-Fluor Analogs (5–18)>

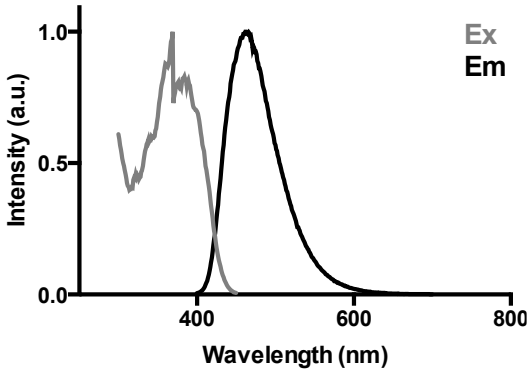



13
14
15
16
17
18
Ex
Em
Intensity (a.u.)
Wavelength (nm)
0.0
0.5
1.0
400
600
800

<Absorption/Excitation/Emission Spectra of *tert*-butyl (3-(7-acetyl-3-oxo-9-(perfluorophenyl)-1,3-dihydro-2*H*-pyrrolo[3,4-*b*]indolizin-2-yl)propyl)carbamate>







V Supporting figures

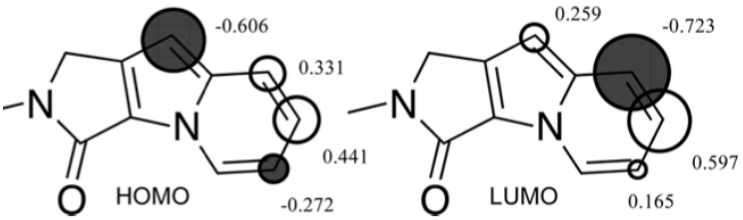


Figure S1. Schematic figure of the atomic coefficients of the HOMO and LUMO in lactam-embedded indolizine core. The sizes and colors of the circles indicate the π-electron density and phase difference of the orbitals, respectively.[1]

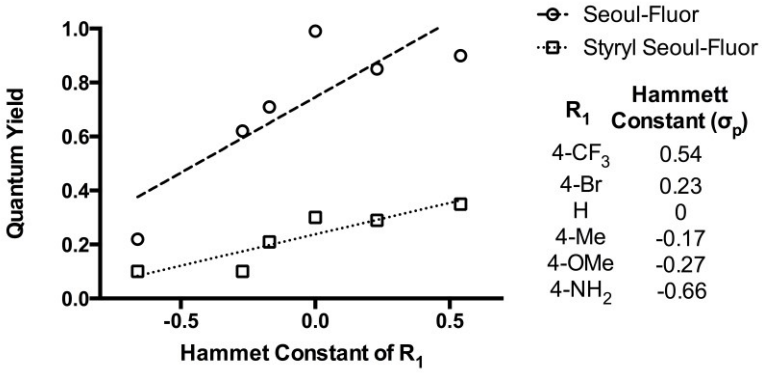
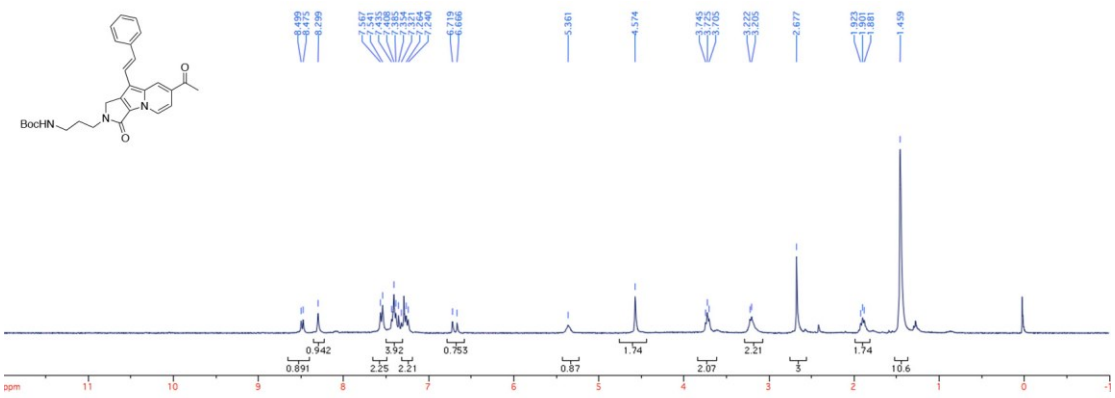
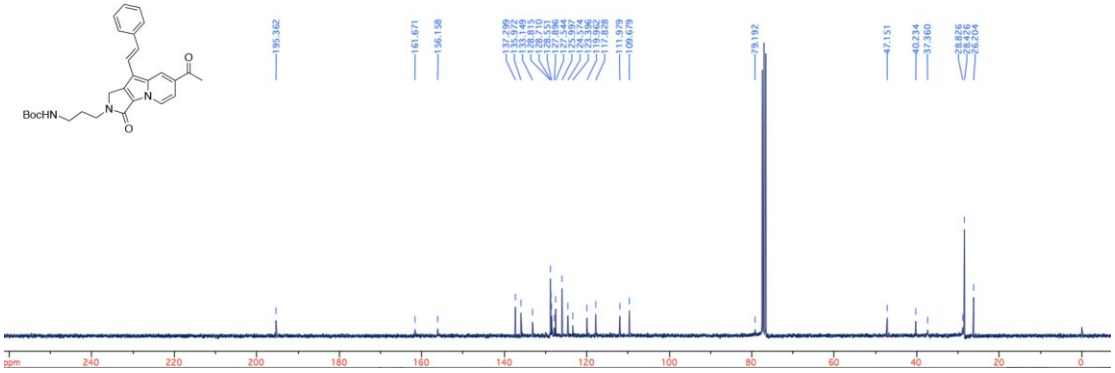
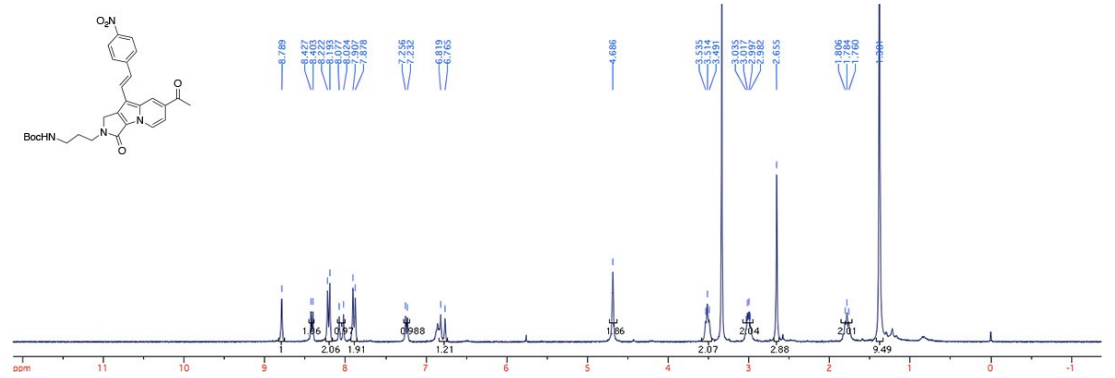


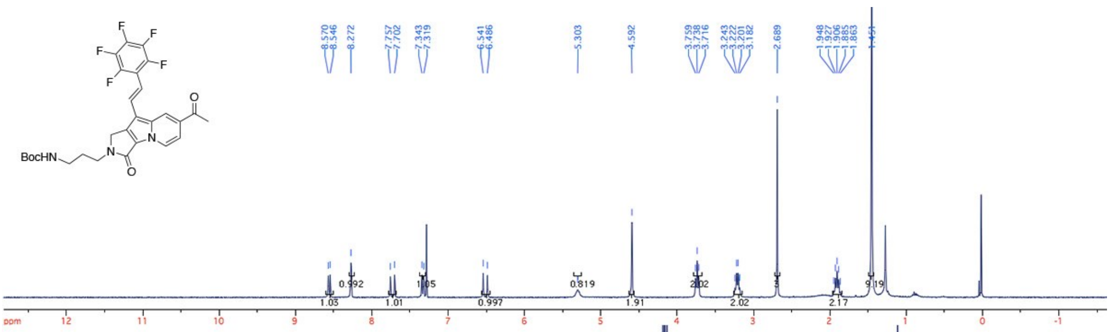
Figure S2. Relationships between the Hammett substituent constant (σ_p) of R_1 and the quantum yield of SF and styryl SF analogs measured in dichloromethane.

VI Copies of NMR spectra of all new compounds





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6.486
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3.759
3.738
3.716
3.243
3.222
3.201
3.182
2.689
1.948
1.927
1.906
1.885
1.863
1.451
1.03
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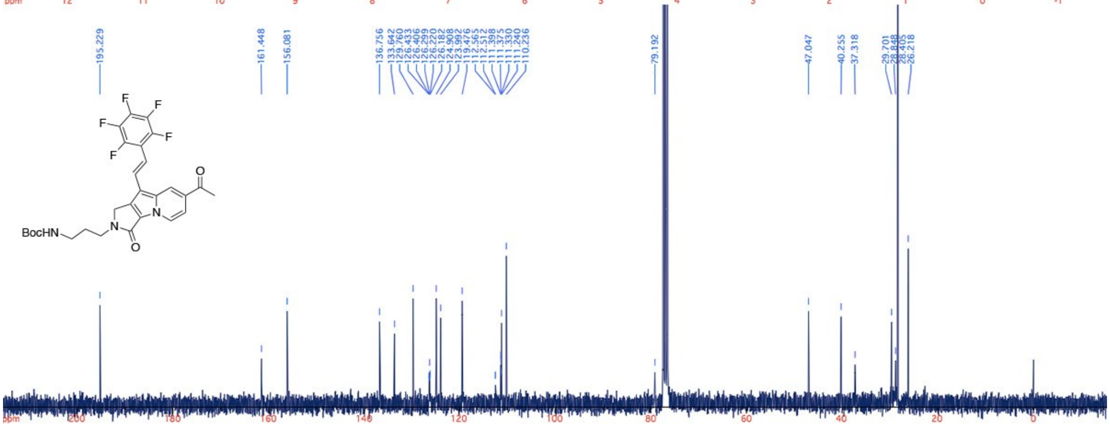
1.01
1.05
0.997
0.819
1.91
2.02
2.02
2.17
9.19
ppm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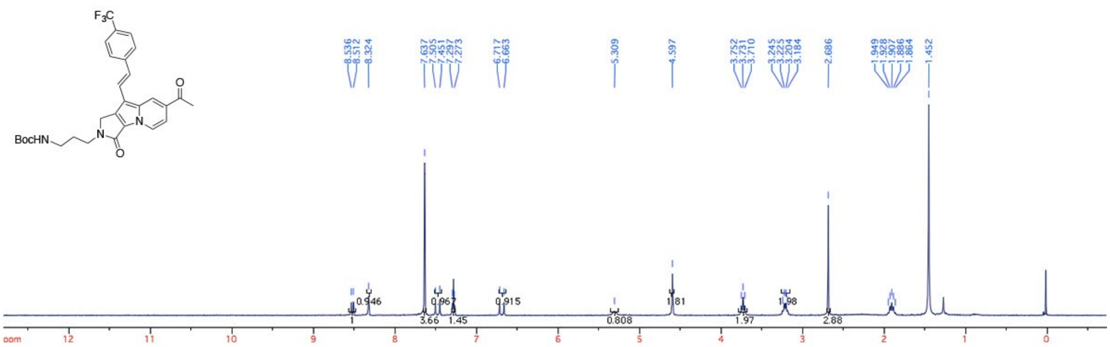
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4.597
3.752
3.731
3.710
3.245
3.225
3.204
3.184
2.686
1.949
1.928
1.907
1.886
1.864
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2.88
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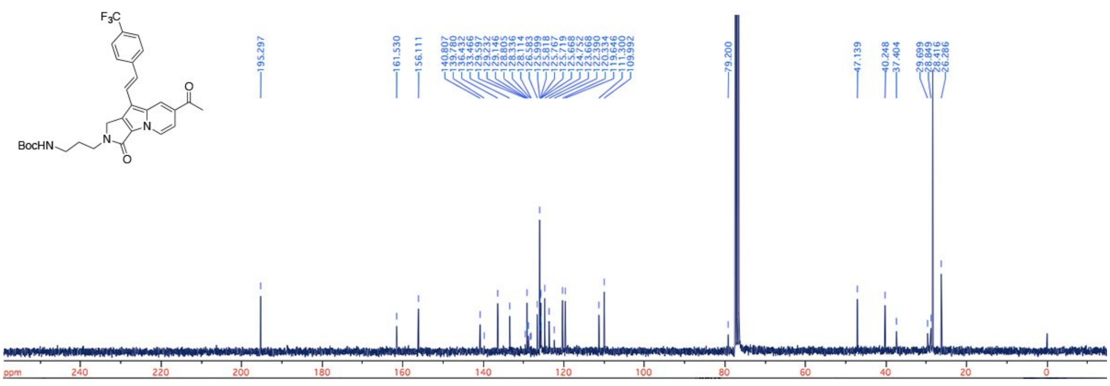
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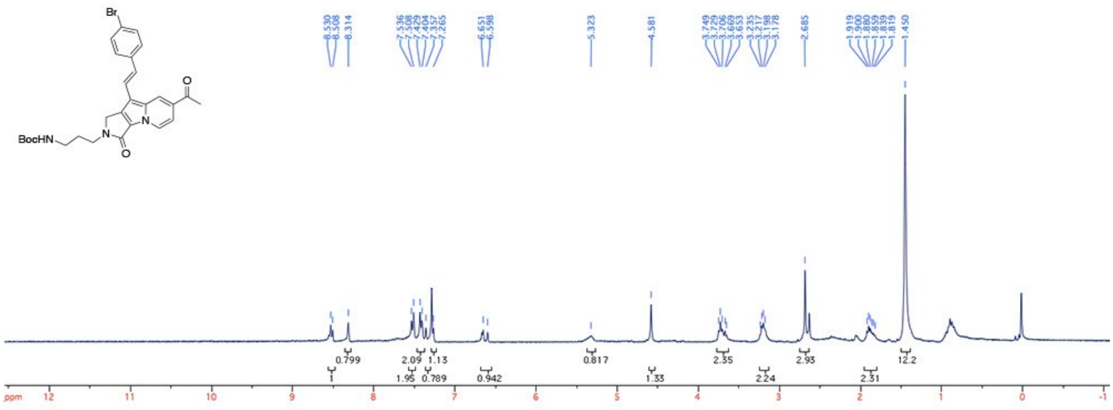
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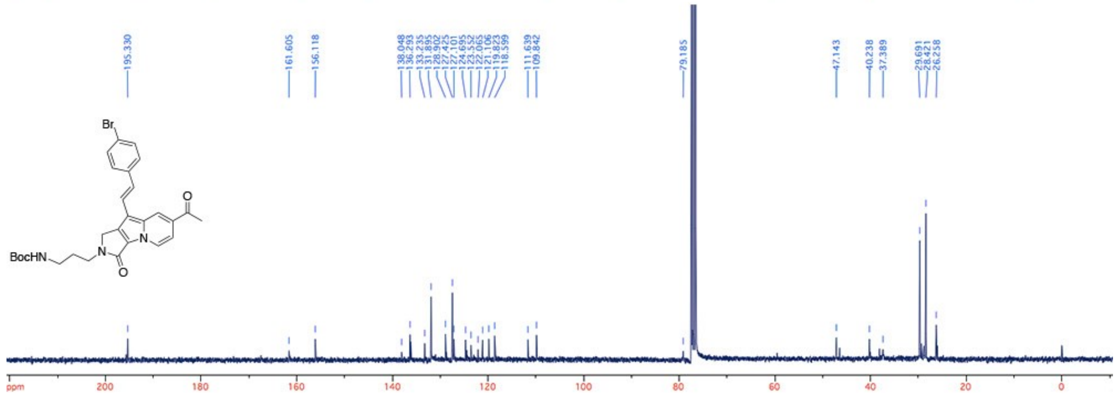
BocHN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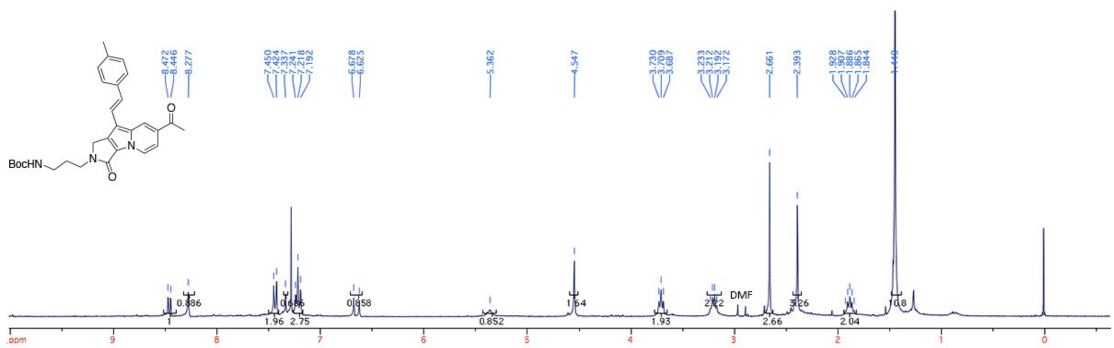
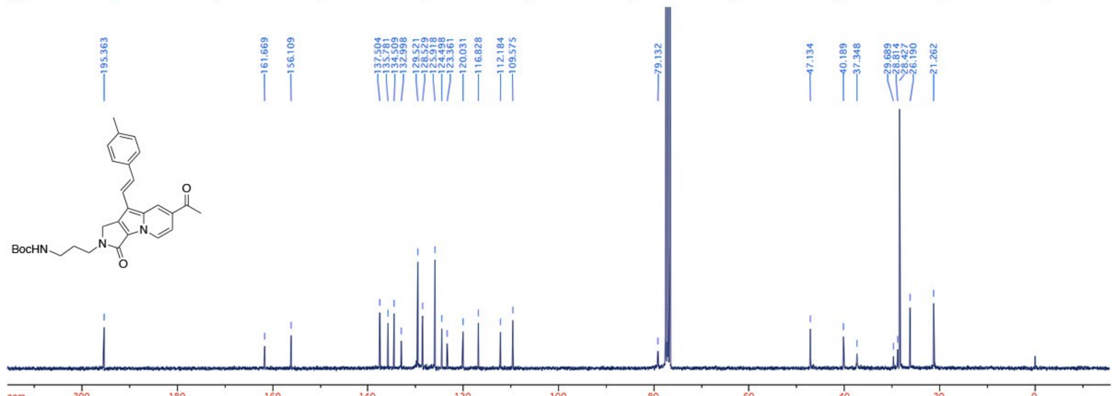
BocHN


BocHN
DMF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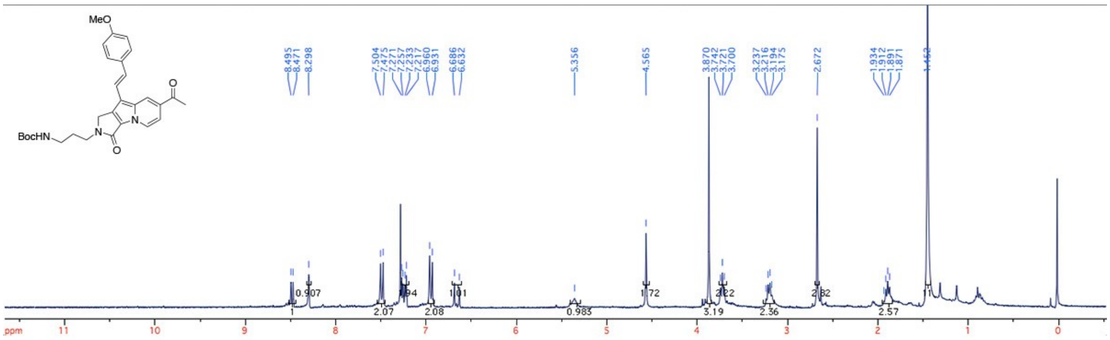
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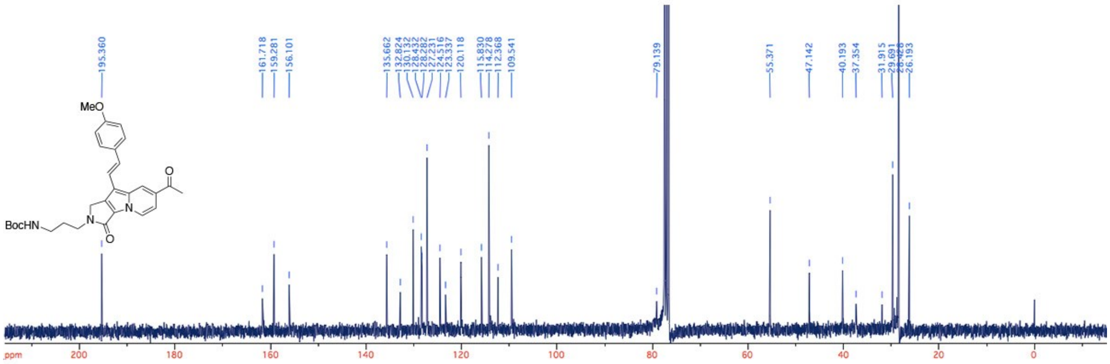
O
N
ppm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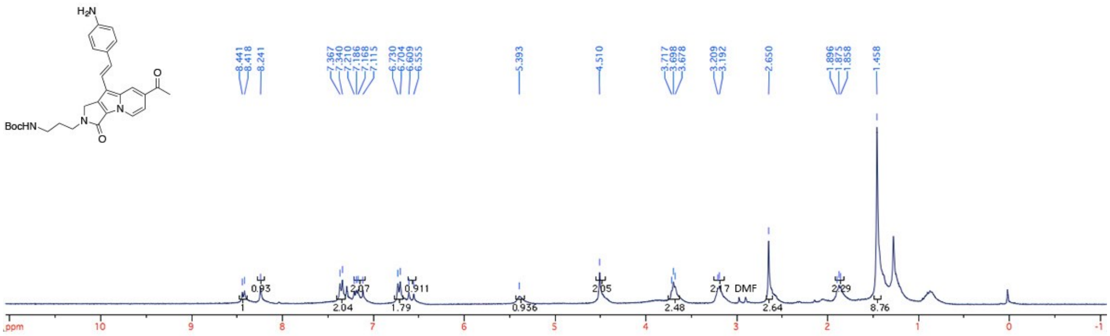
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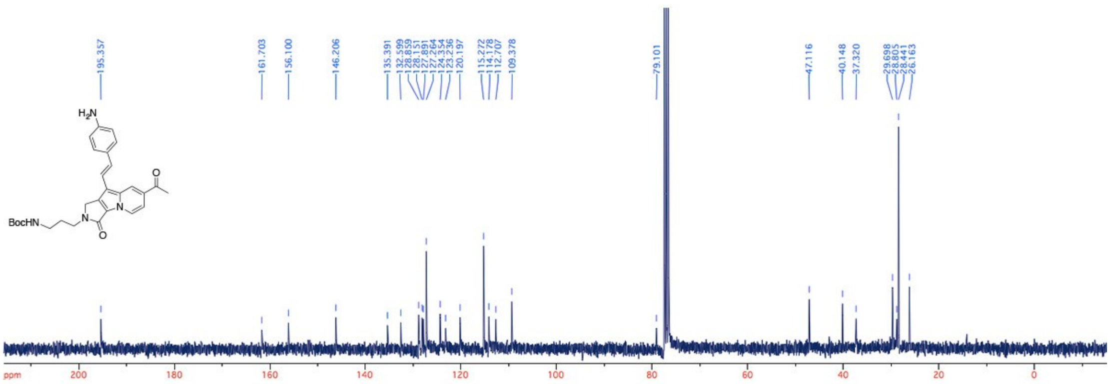
ppm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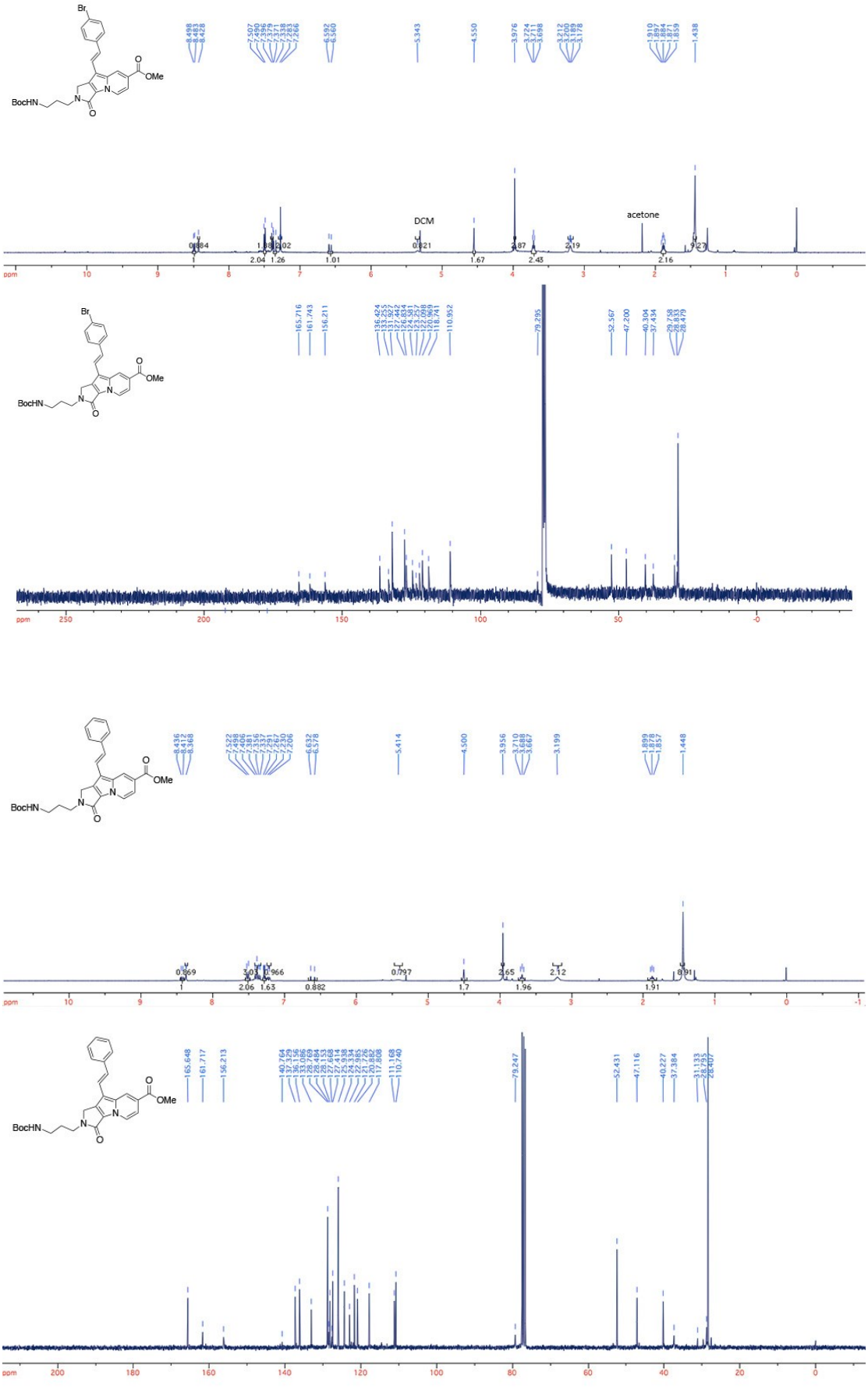
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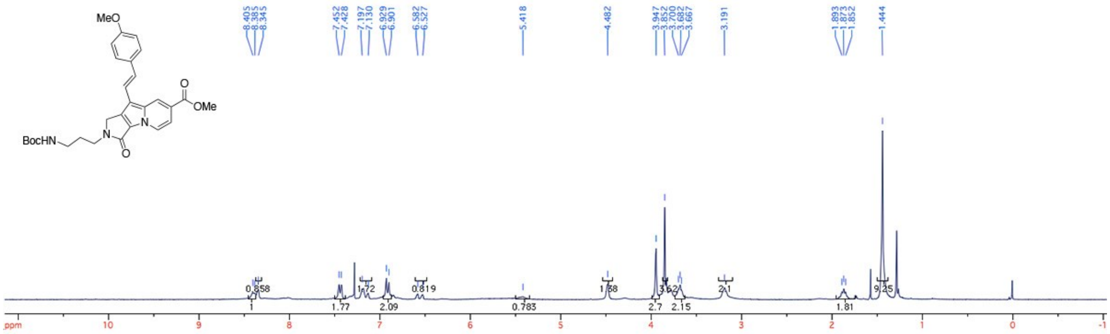
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OMe
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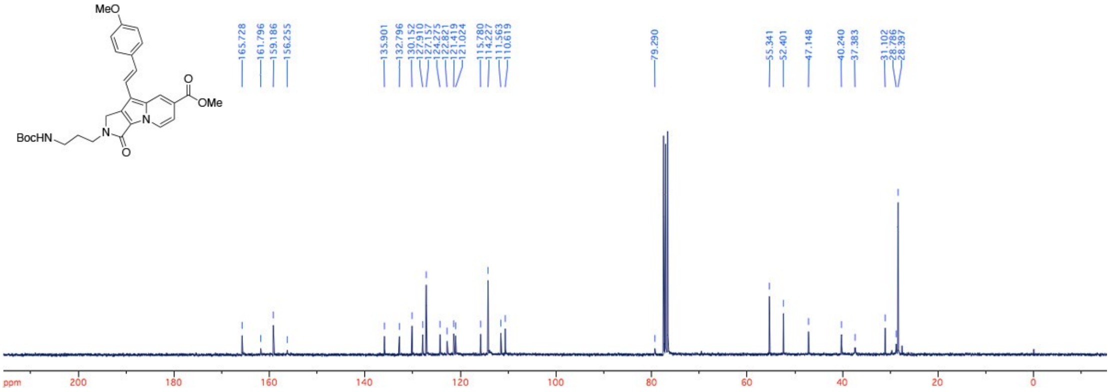
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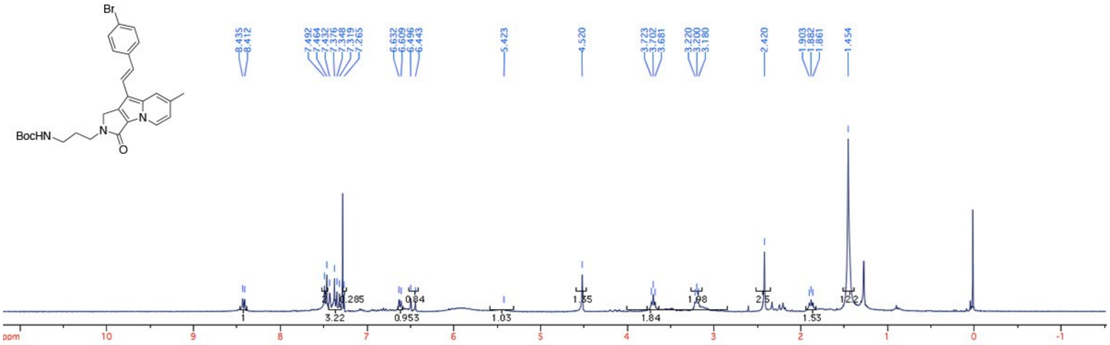
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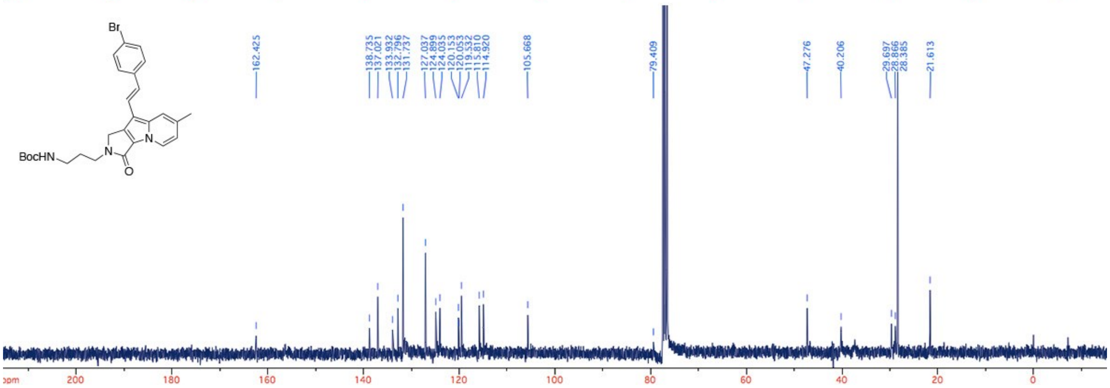
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O
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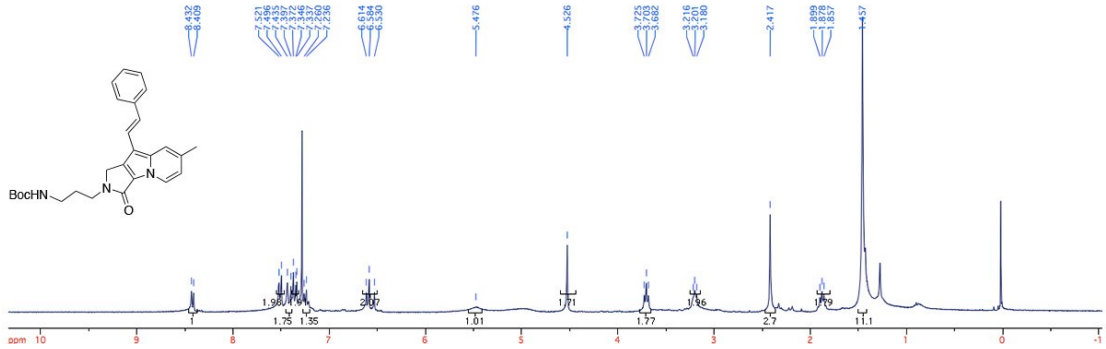

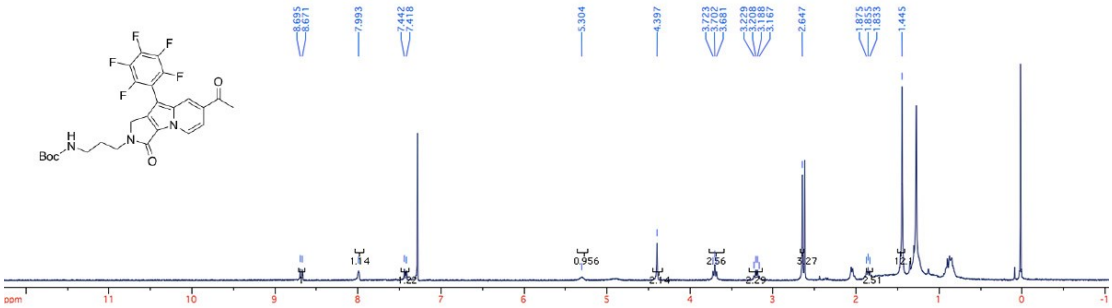

VI References

1. E. Kim, M. Koh, B. J. Lim and S. B. Park, *J. Am. Chem. Soc.,* 2011, **133**, 6642.