Regioselective Iodoamination of Terminal Ynamides for the Synthesis of $\alpha$-amino-$\beta,\beta$-diiodo-enamides

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1. General Method

All reactions were performed in reaction tubes under air atmosphere. \(^1\)H NMR and \(^{13}\)C NMR were recorded at respectively 400 MHz and 100 MHz spectrometer using CDCl\(_3\) as solvent. The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets. Coupling constants are reported in Hertz (Hz). Chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (\(\delta = 0\) ppm) for \(^1\)H NMR and deuteriochloroform (\(\delta = 77.00\) ppm) for \(^{13}\)C NMR. High-resolution mass spectra (HRMS) were recorded on an ESI-TOF (time-of-flight) mass spectrometer. Melting points were measured with micro melting point apparatus.

2. Preparation of terminal ynamides

**Procedure A**: 1-bromo-2-triisopropylsilylacetylene was prepared according to Hofmeister’s procedure.\(^3\) A solution of ethynyltriisopropylsilane (50 mmol) in acetone (60 mL) is treated at rt with N-bromosuccinimide (NBS, 55 mmol) and AgNO\(_3\) (2.5 mmol). After 2h, the reaction mixture is concentrated in vacuum. The crude products were purified by silica gel flash chromatography on a silica gel column with petroleum ether (PE) as eluent to afford the 1-bromo-2-triisopropylsilylacetylene.

**Procedure B**: TIPS-substituted ynamides were prepared according to a modified version of Hsung’s procedure.\(^2\) To a stirred solution of the appropriate amide (1.0 equiv, 1.0 M in toluene)
were added K₂CO₃ or K₃PO₄ (2.0 equiv), CuSO₄•5H₂O (10 mol%), 1,10-phenanthroline (20 mol% equiv) and 1-bromo-2-triisopropylsilylacetylene (1.25 equiv). The reaction was capped under a blanket of nitrogen and heated at 85 °C for 48 h while being monitored with TLC analysis. Upon completion, the reaction mixture was cooled to room temperature and diluted with EtOAc and filtered through Celite, and the filtrate was concentrated in vacuum. The crude products were purified by silica gel flash chromatography on a silica gel column with petroleum ether (PE) and ethyl acetate (EA) as eluent to afford directing products.

**Procedure C**: Terminal ynamides 1a-It were prepared by the modified version of Oestreich’s procedure:³ To a stirred solution of the appropriate TIPS-substituted ynamide (1.0 equiv, 0.2 M in THF) cooled to 0 °C was added a solution of TBAF (1.2 equiv, 1.0 M in THF). After 1 h stirring at 0 °C, the reaction was allowed to warm to room temperature and then quenched with sat. aq. NH₄Cl. The aqueous layer was extracted with Et₂O (x 3). The combined organics were washed with brine (x 2), dried (Na₂SO₄), filtered and the solvents were evaporated under reduced pressure to afford the crude product.

### 2.1. Characterization data for new compounds.

**tert-butyl ethynyl(o-tolyl)carbamate (1b)**: Prepared according to the general Procedure C. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1b as a yellow oil. Rf 0.20 (vPE/vEA = 80:1); ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.20 (m, 4 H), 2.79 (s, 1 H), 2.31 (s, 3 H), 1.49 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 137.9, 135.3, 131.0, 128.5, 127.3, 126.9, 83.2, 76.9, 57.3, 27.9, 17.4; IR ν (KBr, cm⁻¹) 2309, 2104, 1716, 1558, 1458, 1349, 1206, 968, 742; HRMS (ESI⁺): m/z calcd. for C₁₄H₁₇NO₂ ([M+Na⁺]⁺) 254.1157, Found: 245.1158.

**tert-butyl ethynyl(m-tolyl)carbamate (1c)**: Prepared according to the general Procedure C. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1c as a yellow oil. Rf 0.20 (vPE/vEA = 80:1); ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.22 (m, 3 H), 7.09-7.04 (m, 1 H), 2.87 (s,
tert-butyl ethynyl(3-fluorophenyl)carbamate (1d): Prepared according to the general Procedure C. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1d as a yellow oil. Rf 0.20 (vPE/vEA = 80:1); 1H NMR (400 MHz, CDCl3) δ 7.37-7.24 (m, 3 H), 6.97-6.92 (m, 1 H), 2.93 (s, 1 H), 1.55 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ 162.5 (d, J = 244.2 Hz), 152.6, 140.5 (d, J = 10.0 Hz), 129.8 (d, J = 9.0 Hz), 119.8 (d, J = 2.9 Hz), 113.5 (d, J = 20.8 Hz), 111.9 (d, J = 25.1 Hz), 84.1, 76.0, 59.1, 27.9; IR ν (KBr, cm⁻¹) 2302, 2118, 1721, 1531, 1446, 1325, 1277, 960, 728; HRMS (ESI⁺): m/z calcd. for C14H17NO2 ([M+Na]+) 254.1157, Found: 254.1157.

tert-butyl (3-chlorophenyl)(ethynyl)carbamate (1e): Prepared according to the general Procedure C. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1e as a yellow oil. Rf 0.20 (vPE/vEA = 80:1); 1H NMR (400 MHz, CDCl3) δ 7.52 (t, J = 2.0 Hz, 1 H), 7.41-7.37 (m, 1 H), 7.30 (t, J = 8.0 Hz, 1 H), 2.92 (s, 1 H), 1.54 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ 152.6, 140.2, 134.3, 129.6, 126.7, 124.7, 122.6, 84.2, 76.0, 59.0, 27.9; IR ν (KBr, cm⁻¹) 2298, 2076, 1736, 1520, 1429, 1311, 1293, 933, 754; HRMS (ESI⁺): m/z calcd. for C13H14ClNO2 ([M+Na]+) 274.0611, Found: 274.0621.

tert-butyl (3-bromophenyl)(ethynyl)carbamate (1f): Prepared according to the general Procedure C. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1f as a yellow oil. Rf 0.20 (vPE/vEA = 80:1); 1H NMR (400 MHz, CDCl3) δ 7.67 (t, J = 2.0 Hz, 1 H), 7.46-7.41 (m, 1 H), 7.39-7.35 (m, 1 H), 7.24 (t, J = 8.0 Hz, 1 H), 2.91 (s, 1 H), 1.54 (s, 9 H); 13C NMR (100 MHz, CDCl3) δ 152.5, 140.3, 129.9, 129.7, 127.6, 123.1, 84.2, 76.0, 59.1, 27.9; IR ν (KBr, cm⁻¹) 2301, 2133, 1703, 1558, 1431, 1321, 1299, 918, 733; HRMS (ESI⁺): m/z calcd. for C13H14BrNO2 ([M+Na]+) 318.0106, Found: 318.0113.
**tert-butyl ethynyl(3-methoxyphenyl)carbamate (1g):** Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1g as a yellow oil. $R_f$ 0.20 ($v_{PE}/v_{EA} = 80:1$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 (t, $J = 8.0$ Hz, 1 H), 7.08-7.04 (m, 1 H), 7.03 (t, $J = 2.4$ Hz, 1 H), 6.82-6.78 (m, 1 H), 3.81 (s, 3 H), 2.88 (s, 1 H), 1.53 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.8, 152.9, 140.2, 129.4, 117.0, 112.5, 110.7, 83.7, 76.8, 58.4, 55.4, 27.9; IR $\nu$ (KBr, cm$^{-1}$) 2287, 2113, 1720, 1536, 1427, 1380, 1220, 886, 731; HRMS (ESI$^+$): m/z calcd. for C$_{14}$H$_{17}$NO$_3$ ([M+Na]$^+$) 270.1106, Found: 270.1109.

**tert-butyl ethynyl(3-(trifluoromethyl)phenyl)carbamate (1h):** Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 50:1) afforded analytically pure 1h as a yellow oil. $R_f$ 0.20 ($v_{PE}/v_{EA} = 60:1$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (s, 1 H), 7.73-7.67 (m, 1 H), 7.50 (d, $J = 4.8$ Hz, 2 H), 2.94 (s, 1 H), 1.55 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.5, 139.8, 131.3 (d), 129.3, 127.5, 125.0, 123.5 (m), 121.3 (m), 84.4, 75.8, 59.3, 27.9; IR $\nu$ (KBr, cm$^{-1}$) 2321, 2103, 1699, 1513, 1421, 1354, 1234, 957, 757; HRMS (ESI$^+$): m/z calcd. for C$_{14}$H$_{14}$F$_3$NO$_2$ ([M+Na]$^+$) 308.0874, Found: 308.0880.

**tert-butyl ethynyl(p-tolyl)carbamate (1i):** Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1i as a yellow oil. $R_f$ 0.20 ($v_{PE}/v_{EA}$ = 80:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.29 (m, 2 H), 7.17 (d, $J = 8.0$ Hz, 1 H), 6.82-6.78 (m, 1 H), 2.85 (s, 1 H), 2.34 (s, 3 H), 1.52 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.2, 136.8, 136.6, 129.4, 124.7, 83.5, 77.1, 57.9, 27.9, 21.0; IR $\nu$ (KBr, cm$^{-1}$) 2310, 2098, 1731, 1502, 1444, 1337, 1211, 932, 734; HRMS (ESI$^+$): m/z calcd. for C$_{14}$H$_{17}$NO$_2$ ([M+Na]$^+$) 254.1157, Found: 245.1157.
**tert-butyl (4-chlorophenyl)(ethynyl)carbamate (1j):** Prepared according to the general Procedure C. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1j as a yellow oil. R_f 0.20 (v_{PE}/v_{EA} = 80:1); ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.39 (m, 2 H), 7.36-7.31 (m, 2 H), 2.89 (s, 1 H), 1.53 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 137.7, 132.2, 128.9, 125.9, 84.1, 76.3, 58.7, 27.9; IR ν(KBr, cm⁻¹) 2290, 2104, 1767, 1503, 1468, 1388, 1222, 912, 727; HRMS (ESI⁺): m/z calcd. for C₁₃H₁₄ClNO₂ ([M+Na]⁺) 274.0611, Found: 274.0623.

**tert-butyl (4-bromophenyl)(ethynyl)carbamate (1k):** Prepared according to the general Procedure C. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure 1k as a yellow oil. R_f 0.20 (v_{PE}/v_{EA} = 80:1); ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.46 (m, 2 H), 7.38-7.34 (m, 2 H), 2.90 (s, 1 H), 1.53 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 152.6, 138.3, 131.8, 126.2, 120.1, 84.1, 76.2, 58.8, 27.9; IR ν(KBr, cm⁻¹) 2306, 2098, 1741, 1487, 1455, 1338, 1204, 883, 756; HRMS (ESI⁺): m/z calcd. for C₁₃H₁₄BrNO₂ ([M+Na]⁺) 318.0106, Found: 318.0094.

**tert-butyl ethynyl(naphthalen-2-yl)carbamate (1l):** Prepared according to the general Procedure C. Purification by flash chromatography on silica gel (PE:AcOEt = 50:1) afforded analytically pure 1l as a yellow oil. R_f 0.20 (v_{PE}/v_{EA} = 60:1); ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 2.0 Hz, 1 H), 7.86-7.80 (m, 3 H), 7.57 (dd, J₁ = 2.0 Hz, J₂ = 8.8 Hz, 1 H), 7.52-7.45 (m, 2 H), 2.93 (s, 1 H), 1.55 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 136.6, 133.2, 131.9, 128.6, 127.9, 127.6, 126.5, 126.2, 123.3, 122.8, 83.8, 76.9, 58.3, 28.0; IR ν(KBr, cm⁻¹) 2305, 2122, 1732, 1498, 1453, 1230, 1210, 954, 727; HRMS (ESI⁺): m/z calcd. for C₁₇H₁₆ClNO₂ ([M+Na]⁺) 290.1157, Found: 290.1161.

**tert-butyl benzo[d][1,3]dioxol-5-yl(ethynyl)carbamate (1m):** Prepared...
according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 50:1) afforded analytically pure **1m** as a yellow oil. \( R_f \) 0.20 (vPE/vEA= 60:1); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.92-6.87 (m, 2 H), 6.78 (d, \( J = 8.0 \) Hz, 1 H), 5.98 (s, 2 H), 2.85 (s, 1 H), 1.52 (s, 9 H); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 153.3, 147.7, 146.5, 133.1, 118.8, 107.9, 106.9, 101.6, 77.1, 57.9, 27.9; \( \text{IR} \) \( \nu \) (KBr, cm\(^{-1}\)) 2298, 2132, 1741, 1501, 1466, 1277, 1248, 886, 731; \( \text{HRMS} \) (ESI\(^+\)): m/z calcd. for C\(_{14}\)H\(_{15}\)NO\(_4\) ([M+Na]\(^+\)) 284.0899, Found: 284.0898.

**tert-butyl ethynyl(4-methoxybenzyl)carbamate (1o):** Prepared according to the general **Procedure C**. Purification by flash chromatography on silica gel (PE:AcOEt = 60:1) afforded analytically pure **1o** as a yellow oil. \( R_f \) 0.20 (vPE/vEA= 80:1); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.28 (d, \( J = 8.8 \) Hz, 2 H), 6.89-6.84 (m, 2 H), 4.50 (s, 2 H), 3.80 (s, 3 H), 2.76 (m, 1 H), 1.49 (s, 9 H); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 159.3, 154.1, 129.6, 128.5, 113.8, 82.8, 58.7, 55.2, 52.5, 28.0; \( \text{IR} \) \( \nu \) (KBr, cm\(^{-1}\)) 2308, 2146, 1738, 1479, 1438, 1289, 1253, 911, 757; \( \text{HRMS} \) (ESI\(^+\)): m/z calcd. for C\(_{15}\)H\(_{19}\)NO\(_3\) ([M+Na]\(^+\)) 284.1263, Found: 284.1265.

**3. General Procedure for diiodo-enamides**

In a 10 mL flame-dried Schlenk tube under air condition, I\(_2\) (0.6 mmol) and amines (0.9 mmol) were dissolved in toluene (2.0 mL) and stirred, then terminal ynamides **1** (0.3 mmol) and TBHP (70% in water, 0.9 mmol) were added successively. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford the corresponding diiodo-enamides.

**3.1. Characterization data for New compounds.**
**tert-butyl (2,2-diiodo-1-morpholinovinyl)(phenyl)carbamate (2a):**
yield 71% (118.7 mg); pale yellow solid; Mp 96-97 °C (n-hexane/ethyl acetate); $R_f$ 0.20 ($v_{PE}/v_{EA}$ = 15:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.31 (m, 2 H), 7.28 (d, $J$ = 8.0 Hz, 2 H), 7.19 (t, $J$ = 7.42 Hz, 1 H), 3.60-3.48 (m, 4 H), 3.11-3.03 (m, 2 H), 2.88-2.80 (m, 2 H), 1.57 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.0, 150.3, 139.1, 128.7, 125.7, 124.0, 82.2, 66.6, 50.4, 28.3; MS (ESI) m/z (%) 579.0 (100) [M+Na]$^+$; IR $\nu$ (KBr, cm$^{-1}$) 1697, 1568, 1530, 1441, 1367, 1331, 1310, 1260, 1244, 1166, 1115, 1018, 887, 746, 701; Anal. calcd for C$_{17}$H$_{22}$I$_2$N$_2$O$_3$: C 36.71, H 3.99, N 5.04. Found: C 36.82, H 3.63, N 5.07.

Crystal data for 2a: C$_{17}$H$_{22}$I$_2$N$_2$O$_3$; M = 556.17; Orthorhombic; space group P2$_1$2$_1$2$_1$; final R indices [$I$$>$$2\sigma(I)$]: $R_1$=0.0202, $wR_2$ =0.0479, R indices(all data): $R_1$=0.0216, $wR_2$=0.0487, $a$ = 9.1833(5) Å, $b$ = 10.6603(6) Å, $c$ = 20.8558(12) Å; $V$ = 2041.7(2) Å$^3$; $T$ = 296K; $Z$ = 4; reflection measured/independent: 15181/3599 ($R_{int}$ = 0.030), number of observations [$I$$>$$2\sigma(I)$]: 3451, parameters: 220. CCDC-1425989 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**tert-butyl phenyl(1,2,2-triiodovinyl)carbamate (3a):** pale yellow solid; Mp 102-103 °C (n-hexane/ethyl acetate); $R_f$ 0.20 ($v_{PE}/v_{EA}$ = 60:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44-7.35 (m, 4 H), 7.31-7.25 (m, 1 H), 1.57 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.0, 138.5, 128.9, 126.6, 124.4, 110.5, 83.2, 32.1, 28.2; MS (ESI) m/z (%) 619.8 (100) [M+Na]$^+$; IR $\nu$ (KBr, cm$^{-1}$) 1651, 1598, 1552, 1466, 1338, 1321, 1299, 1236, 1112, 1003, 948, 767; Anal. calcd for C$_{13}$H$_{14}$I$_3$NO$_2$: C 26.16, H 2.36, N 2.35. Found: C 26.26, H 2.49, N 2.67.

**tert-butyl (2,2-diiodo-1-morpholinovinyl)(o-tolyl)carbamate (2b):**
yield 34% (58.2 mg); pale yellow solid; Mp 84-85 °C (n-hexane/ethyl acetate); $R_f$ 0.20 ($v_{PE}/v_{EA}$ = 15:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44-7.35 (m, 4 H), 7.31-7.25 (m, 1 H), 1.57 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.0, 138.5, 128.9, 126.6, 124.4, 110.5, 83.2, 32.1, 28.2; MS (ESI) m/z (%) 619.8 (100) [M+Na]$^+$; IR $\nu$ (KBr, cm$^{-1}$) 1651, 1598, 1552, 1466, 1338, 1321, 1299, 1236, 1112, 1003, 948, 767; Anal. calcd for C$_{13}$H$_{14}$I$_3$NO$_2$: C 26.16, H 2.36, N 2.35. Found: C 26.26, H 2.49, N 2.67.
acetate); $R_f 0.20$ ($v_{PE}/v_{EA}= 15:1$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24-7.15 (m, 4 H), 3.57-3.40 (m, 4 H), 3.01 (br, 2 H), 2.73 (br, 2 H), 2.21 (s, 3 H), 1.60 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.5, 134.4, 131.7, 131.6, 126.9, 126.3, 124.7, 81.9, 66.7, 50.4, 28.3, 19.2; MS (ESI) m/z (%) 571.3 (100) [M+H]$^+$; IR $\nu$ (KBr, cm$^{-1}$) 1689, 1648, 1602, 1588, 1561, 1466, 1352, 1318, 1288, 1224, 1153, 1101, 951, 757; Anal. calcd for C$_{18}$H$_{24}$I$_2$N$_2$O$_3$: C 37.91, H 4.24, N 4.91. Found: C 38.04, H 4.33, N 4.85.

tert-butyl (2,2-diiodo-1-morpholinovinyl)(m-tolyl)carbamate (2c): yield 65% (111.3 mg); pale yellow solid; Mp 111-112 °C (n-hexane/ethyl acetate); $R_f 0.20$ ($v_{PE}/v_{EA}= 15:1$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (t, $J = 8.0$ Hz, 1 H), 7.11 (s, 1 H), 7.05 (d, $J = 8.0$ Hz, 1 H), 3.60-3.48 (m, 4 H), 3.10-3.02 (m, 2 H), 2.86-2.79 (m, 2 H), 2.36 (s, 3 H), 1.57 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.0, 150.3, 139.0, 138.6, 128.5, 126.5, 124.6, 124.6, 121.0, 82.1, 66.6, 50.4, 28.3, 21.5; MS (ESI) m/z (%) 571.6 (100) [M+H]$^+$; IR $\nu$ (KBr, cm$^{-1}$) 1727, 1692, 1650, 1575, 1558, 1488, 1369, 1323, 1301, 1252, 1153, 1114, 858, 734; Anal. calcd for C$_{18}$H$_{24}$I$_2$N$_2$O$_3$: C 37.91, H 4.24, N 4.91. Found: C 38.04, H 4.33, N 4.85.

tert-butyl (2,2-diiodo-1-morpholinovinyl)(3-fluorophenyl)carbamate (2d): yield 69% (118.6 mg); pale yellow solid; Mp 121-123 °C (n-hexane/ethyl acetate); $R_f 0.20$ ($v_{PE}/v_{EA}= 15:1$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.25 (m, 1 H), 7.12-7.02 (m, 2 H), 6.90 (td, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1 H), 3.63-3.52 (m, 4 H), 3.11-3.08 (m, 2 H), 2.93-2.85 (m, 2 H), 1.58 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.7 (d, $J = 244.2$ Hz), 151.6, 149.8, 140.7 (d, $J = 9.7$ Hz), 129.8 (d, $J = 8.6$ Hz), 119.0, 112.4 (d, $J = 20.9$ Hz), 111.2 (d, $J = 24.2$ Hz), 82.7, 66.6, 50.5, 28.3; MS (ESI) m/z (%) 575.3 (100) [M+H]$^+$; IR $\nu$ (KBr, cm$^{-1}$) 1698, 1615, 1370, 1319, 1265, 1220, 1152, 1117, 867, 771; Anal. calcd for C$_{17}$H$_{21}$F$_2$N$_2$O$_3$: C 35.56, H 3.69, N 4.88. Found: C 35.63, H 3.58, N 4.68.

tert-butyl (3-chlorophenyl)(2,2-diiodo-1-morpholinovinyl)carbamate (2j): yield 70% (124.1 mg); pale yellow
solid; Mp 124-125 °C (n-hexane/ethyl acetate); $R_f$ 0.20 ($v_{PE}/v_{EA} = 15:1$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 (s, 1 H), 7.27 (t, $J = 8.0$ Hz, 1 H), 7.19-7.13 (m, 2 H), 3.62-3.51 (m, 4 H), 3.11-3.03 (m, 2 H), 2.91-2.84 (m, 2 H), 1.57 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.6, 149.7, 140.3, 134.4, 129.6, 125.7, 124.0, 121.7, 82.8, 66.6, 50.5, 28.3; MS (ESI) m/z (%) 591.0 (100) [M+H]$^+$; IR ν (KBr, cm$^{-1}$) 1735, 1694, 1569, 1474, 1368, 1320, 1265, 1212, 1152, 1115, 1005, 891, 777, 668; Anal. calcd for C$_{17}$H$_{21}$ClI$_2$N$_2$O$_3$: C 34.57, H 3.58, N 4.74. Found: C 34.66, H 3.48, N 4.91.

**tert-butyl (3-bromophenyl)(2,2-diiodo-1-morpholinovinyl)carbamate (2f):** yield 72% (136.9 mg); pale yellow solid; Mp 131-133 °C (n-hexane/ethyl acetate); $R_f$ 0.20 ($v_{PE}/v_{EA} = 15:1$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (s, 1 H), 7.32 (dt, $J_1 = 6.8$ Hz, $J_2 = 2.0$ Hz, 1 H), 7.24-7.17 (m, 2 H), 3.62-3.50 (m, 4 H), 3.11-3.03 (m, 2 H), 2.91-2.83 (m, 2 H), 1.57 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.6, 149.7, 140.5, 130.0, 128.6, 126.8, 122.2, 122.1, 82.8, 66.6, 50.5, 28.3; MS (ESI) m/z (%) 635.4 (100) [M+H]$^+$; IR ν (KBr, cm$^{-1}$) 1719, 1577, 1475, 1369, 1309, 1265, 1230, 1154, 1140, 1114, 1001, 891, 759; Anal. calcd for C$_{17}$H$_{21}$BrI$_2$N$_2$O$_3$: C 32.15, H 3.33, N 4.41. Found: C 32.39, H 3.61, N 4.29.

**tert-butyl (2,2-diiodo-1-morpholinovinyl)(3-methoxyphenyl)carbamate:** yield 44% (77.4 mg); pale yellow solid; Mp 107-108 °C (n-hexane/ethyl acetate); $R_f$ 0.20 ($v_{PE}/v_{EA} = 15:1$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26-7.22 (m, 1 H), 6.90-6.85 (m, 2 H), 6.76-6.72 (m, 1 H), 3.81 (s, 3 H), 3.63-3.50 (m, 4 H) 3.11-3.04 (m, 2 H), 2.89-2.82 (m, 2 H), 1.57 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.8, 151.8, 150.2, 140.2, 129.3, 116.3, 110.7, 110.3, 82.3, 66.6, 55.4, 50.5, 28.3; MS (ESI) m/z (%) 587.1 (100) [M+H]$^+$; IR ν (KBr, cm$^{-1}$) 1719, 1577, 1475, 1369, 1309, 1265, 1230, 1154, 1140, 1114, 1001, 891, 759; Anal. calcd for C$_{18}$H$_{24}$I$_2$N$_2$O$_4$: C 36.88, H 4.13, N 4.78. Found: C 36.73, H 4.28, N 4.87.

**tert-butyl (2,2-diiodo-1-morpholinovinyl)(3-(trifluoromethyl)phenyl)carbamate:** yield 76% (142.1 mg); pale
yellow solid; Mp 115-116 °C (n-hexane/ethyl acetate); \( R_f \) 0.20 (\( v_{PE}/v_{EA} \) = 10:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 (s, 1 H), 7.51-7.42 (m, 3 H), 3.61-3.49 (m, 4 H) 3.11-3.03 (m, 2 H), 2.91-2.89 (m, 2 H), 1.58 (s, 9 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 151.6, 149.5, 139.8, 131.3 (d, \( J = 32.8 \) Hz), 129.3, 126.5, 125.0, 122.3, 122.1 (q, \( J = 4.1 \) Hz), 120.6 (p), 83.0, 66.5, 50.4, 28.3; MS (ESI) m/z (%) 625.1 (100) [M+H]\(^+\); IR \( \nu\) (KBr, cm\(^{-1}\)) 1685, 1549, 1528, 1436, 1359, 1327, 1302, 1288, 1255, 1149, 1103, 1001, 976, 748; Anal. calcd for C\(_{18}\)H\(_{21}\)F\(_3\)I\(_2\)N\(_2\)O\(_3\): C 34.64, H 3.39, N 4.49. Found: C 34.72, H 3.48, N 4.51.

\begin{center}
\textbf{tert-butyl (2,2-diiodo-1-morpholinovinyl)(m-tolyl)carbamate: yield 68% (116.5 mg); pale yellow solid; Mp 117-118 °C (n-hexane/ethyl acetate); \( R_f \) 0.20 (\( v_{PE}/v_{EA} \) = 15:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.19-7.11 (m, 4 H), 3.61-3.51 (m, 4 H), 2.33 (s, 3 H), 1.56 (s, 9 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 152.1, 150.4, 136.4, 135.5, 129.3, 123.9, 82.2, 66.6, 50.4, 28.3, 20.9; MS (ESI) m/z (%) 571.3 (100) [M+H]\(^+\); IR \( \nu\) (KBr, cm\(^{-1}\)) 1696, 1562, 1449, 1367, 1317, 1310, 1262, 1218, 1156, 1116, 1107, 887, 839, 771; Anal. calcd for C\(_{18}\)H\(_{24}\)I\(_2\)N\(_2\)O\(_3\): C 37.91, H 4.24, N 4.91. Found: C 37.83, H 4.47, N 4.81.}
\end{center}

\begin{center}
\textbf{tert-butyl (4-chlorophenyl)(2,2-diiodo-1-morpholinovinyl)carbamate (2j): yield 63% (111.3 mg); pale yellow solid; Mp 123-124 °C (n-hexane/ethyl acetate); \( R_f \) 0.20 (\( v_{PE}/v_{EA} \) = 15:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.34-7.29 (m, 2 H), 7.23 (d, \( J = 8.8 \) Hz, 2 H), 3.62-3.51 (m, 4 H), 3.09-3.02 (m, 2 H), 1.57 (s, 9 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 151.8, 149.8, 137.7, 130.9, 128.8, 125.1, 82.7, 66.6, 50.5, 28.3; MS (ESI) m/z (%) 591.1 (100) [M+H]\(^+\); IR \( \nu\) (KBr, cm\(^{-1}\)) 1716, 1563, 1490, 1366, 1313, 1300, 1239, 1213, 1155, 1108, 992, 882, 668; Anal. calcd for C\(_{17}\)H\(_{21}\)ClI\(_2\)N\(_2\)O\(_3\): C 34.57, H 3.58, N 4.74. Found: C 34.65, H 3.53, N 4.90.}
\end{center}

\begin{center}
\textbf{tert-butyl (4-bromophenyl)(2,2-diiodo-1-morpholinovinyl)carbamate (2k): yield 66% (125.1 mg); pale yellow solid; Mp 131-133 °C (n-hexane/ethyl acetate); \( R_f \) 0.20}
\end{center}
(v<sub>PE</sub>/v<sub>EA</sub>= 15:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48-7.43 (m, 2 H), 7.17 (d, J = 8.8 Hz, 2 H), 3.62-3.51 (m, 4 H), 3.09-3.02 (m, 2 H), 2.90-2.83 (m, 2 H), 1.56 (s, 9 H); <sup>1</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.7, 149.8, 138.3, 131.8, 125.4, 118.7, 82.7, 66.6, 50.5, 28.3; MS (ESI) m/z (%) 635.4 (100) [M+H]<sup>+</sup>; IR ν(KBr, cm<sup>-1</sup>) 1716, 1652, 1633, 1558, 1488, 1311, 1154, 1108, 991, 668; Anal. calcd for C<sub>17</sub>H<sub>21</sub>BrI<sub>2</sub>N<sub>2</sub>O<sub>3</sub>: C 32.15, H 3.33, N 4.41. Found: C 32.27, H 3.41, N 4.55.

**tert-butyl (2,2-diiodo-1-morpholinovinyl)(naphthalen-2-yl)carbamate (2l)**: yield 62% (112.6 mg); pale yellow solid; Mp 156-157 °C (n-hexane/ethyl acetate); R<sub>f</sub> 0.20 (v<sub>PE</sub>/v<sub>EA</sub>= 10:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84-7.77 (m, 3 H), 7.68 (b, 1 H), 7.52-7.42 (m, 3 H), 3.58-3.45 (m, 4 H), 3.13-3.05 (m, 2 H), 2.89-2.82 (m, 2 H), 1.60 (s, 9 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.1, 150.4, 136.7, 133.4, 131.4, 128.5, 127.7, 127.6, 126.5, 125.8, 123.2, 121.3, 82.4, 66.6, 50.5, 28.4; MS (ESI) m/z (%) 607.1 (100) [M+H]<sup>+</sup>; IR ν(KBr, cm<sup>-1</sup>) 1695, 1652, 1635, 1575, 1558, 1507, 1370, 1317, 1253, 1153, 1113, 1008, 861, 755, 668; Anal. calcd for C<sub>21</sub>H<sub>24</sub>BrI<sub>2</sub>N<sub>2</sub>O<sub>3</sub>: C 41.61, H 3.99, N 4.62. Found: C 41.59, H 3.88, N 4.79.

**tert-butyl benzo[d][1,3]dioxol-5-yl(2,2-diiodo-1-morpholinovinyl)carbamate (2m)**: yield 54% (96.9 mg); pale yellow solid; Mp 161-163 °C (n-hexane/ethyl acetate); R<sub>f</sub> 0.20 (v<sub>PE</sub>/v<sub>EA</sub>= 10:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.86 (s, 1 H), 7.19-7.10 (m, 2 H), 6.41-6.37 (m, 2 H), 4.07-3.92 (m, 4 H), 3.52-3.40 (m, 2 H), 3.25-3.14 (m, 2 H), 1.56 (s, 9 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.1, 150.4, 147.6, 145.5, 133.0, 117.4, 107.7, 106.2, 101.5, 82.1, 66.7, 50.4, 28.3; MS (ESI) m/z (%) 601.6 (100) [M+H]<sup>+</sup>; IR ν(KBr, cm<sup>-1</sup>) 1697, 1652, 1506, 1488, 1325, 1250, 1214, 1107, 1036; Anal. calcd for C<sub>18</sub>H<sub>22</sub>BrI<sub>2</sub>N<sub>2</sub>O<sub>5</sub>: C 36.02, H 3.69, N 4.67. Found: C 36.17, H 3.57, N 4.39.

**tert-butyl benzyl(2,2-diiodo-1-morpholinovinyl)carbamate (2n)**: yield 52% (89.1 mg); pale yellow solid; Mp 81-82 °C (n-hexane/ethyl acetate); R<sub>f</sub> 0.20 (v<sub>PE</sub>/v<sub>EA</sub>= 15:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36-7.27 (m, 5 H), 4.75 (d, J = 14.0 Hz, 1 H), 4.38 (d, J = 14.4 Hz, 1 H), 3.59-3.41 (m,
13C NMR (100 MHz, CDCl$_3$) δ 153.7, 150.8, 137.1, 129.7, 128.5, 127.9, 81.5, 66.6, 51.9, 50.1, 28.4; MS (ESI) m/z (%) 571.6 (100) [M+H]$^+$; IR ν (KBr, cm$^{-1}$) 1693, 1560, 1387, 1365, 1342, 1263, 1165, 1114, 1014, 946, 862, 761; Anal. calcd for C$_{18}$H$_{24}$I$_2$N$_2$O$_3$: C 37.91, H 4.24, N 4.91. Found: C 37.82, H 4.36, N 5.03.

tert-butyl (2,2-diiodo-1-morpholinovinyl)(3-methoxyphenyl)carbamate: yield 53% (95.4 mg); pale yellow solid; Mp 91-93 °C (n-hexane/ethyl acetate); $R_f$ 0.20 (v$_{PE}$/v$_{EA}$= 15:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, $J$ = 7.2 Hz, 2 H), 6.85 (d, $J$ = 8.4 Hz, 2 H), 4.66 (d, $J$ = 14.4 Hz, 1 H), 4.36 (d, $J$ = 14.8 Hz, 1 H), 3.80 (s, 3 H), 3.60-3.47 (m, 4 H), 2.92-2.78 (m, 4 H), 1.53 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.3, 153.6, 131.0, 129.3, 113.8, 81.4, 66.6, 55.3, 51.3, 50.1, 28.4; MS (ESI) m/z (%) 601.6 (100) [M+H]$^+$; IR ν (KBr, cm$^{-1}$) 1706, 1635, 1568, 1487, 1456, 1367, 1303, 1235, 1217, 1115, 1049, 888, 765; Anal. calcd for C$_{19}$H$_{26}$I$_2$N$_2$O$_4$: C 38.02, H 4.37, N 4.67. Found: C 38.16, H 4.59, N 4.73.

ethyl (2,2-diiodo-1-morpholinovinyl)(phenyl)carbamate (2p): yield 65% (103.2 mg); pale yellow solid; Mp 106-107 °C (n-hexane/ethyl acetate); $R_f$ 0.20 (v$_{PE}$/v$_{EA}$= 15:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.33 (m, 2 H), 7.28 (d, $J$ = 7.6 Hz, 2 H), 7.25-7.20 (m, 1 H), 4.41-4.25 (m, 2 H), 3.60-3.49 (m, 4 H), 3.10-3.03 (m, 2 H), 2.87-2.80 (m, 2 H), 1.38 (t, $J$ = 6.8 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.5, 150.0, 138.9, 128.8, 126.1, 124.1, 66.6, 63.0, 50.4, 14.7; MS (ESI) m/z (%) 529.2 (100) [M+H]$^+$; IR ν (KBr, cm$^{-1}$) 1716, 1635, 1568, 1487, 1456, 1367, 1303, 1235, 1217, 1115, 1049, 888, 765; Anal. calcd for C$_{15}$H$_{18}$I$_2$N$_2$O$_3$: C 34.11, H 3.44, N 5.30. Found: C 34.23, H 3.67, N 5.09.

$N$-benzyl-$N$-(2,2-diiodo-1-morpholinovinyl)benzenesulfonamide (2q): yield 61% (111.7 mg); pale yellow solid; Mp 171-172 °C (n-hexane/ethyl acetate); $R_f$ 0.20 (v$_{PE}$/v$_{EA}$= 20:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99-7.95 (m, 2 H), 7.63 (tt, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1 H), 7.58-7.52 (m, 2 H),
7.35 (m, 5 H), 4.74 (d, J = 14.4 Hz, 1 H), 4.64 (d, J = 14.4 Hz, 1 H), 3.62-3.55 (m, 2 H), 3.45-3.38 (m, 2 H), 3.10-3.03 (m, 2 H), 2.61-2.53 (m, 2 H), 1.57 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 139.9, 135.7, 133.4, 130.3, 129.3, 128.7, 128.3, 66.3, 53.7, 49.8; MS (ESI) m/z (%) 611.3 (100) [M+H$^+$]; IR $\nu$ (KBr, cm$^{-1}$) 1636, 1617, 1558, 1541, 1507, 1345, 1161, 1109, 854, 732; Anal. calcd for C$_{19}$H$_{20}$I$_2$N$_2$O$_3$S: C 37.40, H 3.30, N 4.59. Found: C 37.45, H 3.46, N 4.37.

$N$-benzyl-$N$-(2,2-diiodo-1-morpholinovinyl)-4-methylbenzenesulfonamide (2r): yield 58% (108.5 mg); pale yellow solid; Mp 168-169 °C (n-hexane/ethyl acetate); $R_f$ 0.20 ($v_{PE}/v_{EA}$ = 20:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.4$ Hz, 2 H), 7.38-7.31 (m, 7 H), 4.69 (d, $J = 14.4$ Hz, 1 H), 4.62 (d, $J = 14.4$ Hz, 1 H), 3.61-3.54 (m, 2 H), 3.45-3.38 (m, 2 H), 3.10-3.02 (m, 2 H), 2.61-2.58 (m, 2 H), 2.44 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.5, 144.3, 137.0, 135.8, 130.3, 129.8, 128.4, 66.3, 53.6, 49.9, 21.7; MS (ESI) m/z (%) 625.6 (100) [M+H$^+$]; IR $\nu$ (KBr, cm$^{-1}$) 1630, 1540, 1508, 1457, 1358, 1343, 1206, 1152, 1112, 1025, 827, 720; Anal. calcd for C$_{20}$H$_{22}$I$_2$N$_2$O$_3$S: C 38.48, H 3.55, N 4.49. Found: C 38.31, H 3.49, N 4.54.

$N$-butyl-$N$-(2,2-diiodo-1-morpholinovinyl)-4-methylbenzenesulfonamide (2s): yield 33% (58.1 mg); pale yellow oil; $R_f$ 0.20 ($v_{PE}/v_{EA}$ = 25:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.4$ Hz, 2 H), 7.30 (d, $J = 8.0$ Hz, 2 H), 3.86-3.79 (m, 2 H), 3.77-3.70 (m, 2 H), 3.48-3.32 (m, 4 H), 3.23-3.15 (m, 2 H), 2.43 (s, 3 H), 1.69-1.56 (m, 1 H), 1.54-1.43 (m, 1 H), 1.38-1.27 (m, 2 H), 0.95 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.4, 144.2, 136.3, 129.6, 128.5, 66.6, 50.6, 50.4, 31.2, 21.6, 20.2, 13.8; IR $\nu$ (KBr, cm$^{-1}$) 1641, 1538, 1503, 1486, 1366, 1329, 1213, 1149, 1106, 1008, 979, 737; HRMS (ESI$^+$): m/z calcd. for C$_{17}$H$_{25}$I$_2$N$_2$O$_3$S ([M+Na$^+$]$^+$) 612.9495, Found: 612.9507.

ethyl 1-(2,2-diiodo-1-morpholinovinyl)-1H-indole-2-carboxylate (2t): yield 78% (129.2 mg); pale yellow solid; Mp 141-142 °C (n-hexane/ethyl acetate); $R_f$ 0.20 ($v_{PE}/v_{EA}$ = 20:1); $^1$H NMR (400 MHz,
CDCl$_3$ δ 7.69 (d, $J = 7.6$ Hz, 1 H), 7.47-7.41 (m, 1 H), 7.40 (d, $J = 0.4$ Hz, 1 H), 7.34 (dd, $J_1 = 0.4$ Hz, $J_2 = 8.0$ Hz, 1 H), 7.27-7.21 (m, 1 H), 4.48-4.32 (m, 2 H), 3.67-3.57 (m, 4 H), 3.11-3.04 (m, 2 H), 3.01-2.93 (m, 2 H), 1.44 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.8, 146.3, 138.4, 128.3, 126.5, 126.3, 122.8, 122.2, 113.0, 111.9, 66.9, 61.1, 49.9, 14.4; MS (ESI) m/z (%) 553.5 (100) [M+H]$^+$; IR ν (KBr, cm$^{-1}$) 1711, 1564, 1538, 1443, 1396, 1306, 1260, 1205, 1114, 1004, 880, 747; Anal. calcd for C$_{17}$H$_{18}$I$_2$N$_2$O$_3$: C 36.98, H 3.29, N 5.07. Found: C 37.01, H 3.08, N 5.16.

**tert-butyl (2,2-diiodo-1-thiomorpholinovinyl)(phenyl)carbamate (2ab):**
yield 74% (127.1 mg); pale yellow solid; Mp 125-127 °C (n-hexane/ethyl acetate); $R_f$ 0.20 (vPE/vEA = 15:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.31 (m, 2 H), 7.27-7.23 (m, 2 H), 7.22-7.17 (m, 1 H), 3.28-3.20 (m, 2 H), 3.11-3.03 (m, 2 H), 2.61-2.58 (m, 2 H), 2.49-2.41 (m, 2 H), 1.57 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.1, 151.5, 139.2, 128.7, 125.8, 124.2, 82.2, 52.8, 28.3, 27.4; MS (ESI) m/z (%) 573.2 (100) [M+H]$^+$; IR ν (KBr, cm$^{-1}$) 1695, 1566, 1496, 1371, 1319, 1309, 1283, 1248, 1157, 1122, 956, 873, 765; Anal. calcd for C$_{17}$H$_{22}$I$_2$N$_2$O$_2$S: C 35.68, H 3.88, N 4.90. Found: C 35.71, H 3.79, N 5.04.

**tert-butyl 4-(1-((tert-butoxycarbonyl)(phenyl)amino)-2,2-diiodovinyl)piperazine-1-carboxylate (2ac):**
yield 56% (110.1 mg); brown oil; $R_f$ 0.20 (vPE/vEA = 20:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.31 (m, 2 H), 7.26 (d, $J = 7.6$ Hz, 2 H), 7.21-7.16 (m, 1 H), 3.35-3.20 (m, 4 H), 3.05-2.96 (m, 2 H), 2.82-2.74 (m, 2 H), 1.57 (s, 9 H), 1.40 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.6, 152.0, 150.4, 139.1, 128.7, 125.8, 124.2, 82.2, 79.9, 50.0, 28.3; IR ν (KBr, cm$^{-1}$) 1695, 1597, 1529, 1421, 1367, 1319, 1230, 1283, 1157, 1122, 956, 873, 765; HRMS (ESI$^+$): m/z calcd. for C$_{22}$H$_{31}$I$_2$N$_3$O$_4$ ([M+Na]$^+$) 678.0302, Found: 678.0303.

**methyl 1-(1-((tert-butoxycarbonyl)(phenyl)amino)-2,2-diiodovinyl)piperidine-4-carboxylate (2ae):**
yield 34% (62.5 mg); brown oil; $R_f$ 0.20 (vPE/vEA = 20:1); $^1$H NMR (400 MHz,
CDCl$_3$ δ 7.36-7.30 (m, 2 H), 7.29-7.24 (m, 2 H), 7.20-7.15 (m, 1 H), 7.24-7.17 (m, 2 H), 3.63 (s, 3 H), 3.43-3.36 (m, 1 H), 3.28-3.21 (m, 1 H), 2.69 (td, $J_1 = 11.8$ Hz, $J_2 = 2.8$ Hz, 1 H), 2.50-2.41 (m, 1 H), 2.24-2.15 (m, 1 H), 1.82-1.75 (m, 1 H), 1.74-1.67 (m, 1 H), 1.60-1.48 (m, 11 H), 1.20 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.0, 152.1, 151.0, 139.4, 128.6, 125.6, 124.0, 82.1, 51.7, 50.7, 49.3, 40.7, 28.4, 28.0, 27.9; IR $\nu$ (KBr, cm$^{-1}$) 1725, 1591, 1529, 1492, 1440, 1201, 1035, 747; HRMS (ESI$^+$): m/z calcd. for C$_{20}$H$_{26}$I$_2$N$_2$O$_4$ ([M+Na$^+$]) 634.9880, Found: 634.9891.

ethyl 1-(1-((tert-butoxycarbonyl)(phenyl)amino)-2,2-diiodovinyl)piperidine-4-carboxylate (2af): yield 36% (67.6 mg); brown oil; $R_f$ 0.20 (vPE/vEA = 20:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.30 (m, 2 H), 7.29-7.25 (m, 2 H), 7.20-7.14 (m, 1 H), 4.07 (q, $J = 7.2$ Hz, 2 H), 3.42-3.35 (m, 1 H), 3.28-3.20 (m, 1 H), 2.69 (td, $J_1 = 11.8$ Hz, $J_2 = 2.8$ Hz, 1 H), 2.50-2.41 (m, 1 H), 2.24-2.13 (m, 1 H), 1.82-1.74 (m, 1 H), 1.74-1.67 (m, 1 H), 1.65-1.43 (m, 11 H), 1.20 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.5, 152.1, 150.9, 139.3, 128.6, 125.5, 123.9, 82.0, 60.3, 50.6, 49.4, 40.7, 28.3, 27.9, 27.9; IR $\nu$ (KBr, cm$^{-1}$) 1727, 1548, 1440, 1322, 1206, 1103, 1023, 767; HRMS (ESI$^+$): m/z calcd. for C$_{21}$H$_{28}$I$_2$N$_2$O$_4$ ([M+Na$^+$]) 649.0036, Found: 649.0048.

4 Experiment for Mechanistic Study

The reaction of 3a: In a 10 mL flame-dried Schlenk tube under air condition, I$_2$ (0.6 mmol) and amines (0.9 mmol) were dissolved in toluene (2.0 mL) and stirred, then 3a (0.3 mmol) and TBHP (70% in water, 0.9 mmol) were added successively. And the resulting solution was stirred at room temperature for 12h and monitored by TLC.
**Condition 1:** In a 10 mL flame-dried Schlenk tube were placed terminal ynamide 1a (0.3 mmol) and N-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL). Then the reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford 2a (35.0 mg, 21%) and 3a (78.7 mg, 44%).

**Condition 2:** In a 10 mL flame-dried Schlenk tube were placed terminal ynamide 1a (0.3 mmol) and N-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL) and stirred, then TBHP (70% in water, 0.9 mmol) were added. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford 2a (93.3 mg, 56%) and 3a (33.9 mg, 19%).

**Condition 3:** In a 10 mL flame-dried Schlenk tube were placed terminal ynamide 1a (0.3 mmol), morpholine (0.9 mmol) and N-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL). Then the reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford 2a (56.8 mg, 34%) and 3a (66.4 mg, 37%).

**Condition 4:** In a 10 mL flame-dried Schlenk tube were placed terminal ynamide 1a (0.3 mmol), morpholine (0.9 mmol) and N-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL) and stirred, then TBHP (70% in water, 0.9 mmol) were added. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford 2a (125.2 mg, 75%).

**Condition 5:** In a 10 mL flame-dried Schlenk tube were placed terminal ynamide 1a (0.3 mmol), I₂ (0.6 mmol) and N-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0...
mL) and stirred, then TBHP (70% in water, 0.9 mmol) were added. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford 3a (120.1 mg, 67%).

In a 10 mL flame-dried Schlenk tube under air condition, I₂ (0.6 mmol) and amines (0.9 mmol) were dissolved in toluene (2.0 mL) and stirred, then terminal ynamides 1a (0.3 mmol), Additive (0.9 equiv) and TBHP (70% in water, 0.9 mmol) were added successively. The reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford 2a.

In a 10 mL flame-dried Schlenk tube were placed terminal ynamide 1a (0.3 mmol), thiomorpholine (0.6 mmol) and N-iodomorpholine-hydrogen iodide (0.6 mmol) were dissolved in toluene (2.0 mL). Then the reaction solution kept stirring for 12 h under air. Upon completion, the reaction mixture was filtered and the filtrate was concentrated in vacuum to give a crude product, which was purified by silica gel column chromatography to afford 2a (40.0 mg, 24%) and 2ab (73.8 mg, 43%).

A 10 mL flame-dried Schlenk tube was charged with Pd(PPh₃)₄ (5.0 mol%), tert-butyl (2,2-diiodo-1-morpholinovinyl)(phenyl)carbamate 2a (0.3 mmol), and boronic acids (0.33 mmol). The flask was capped and then backfilled with nitrogen (this was repeated two additional times). Toluene (1.0 mL), ethanol (0.5 mL), Na₂CO₃ (0.6 mmol) in H₂O (0.5 mL) were added via syringe. The reaction solution was heated to 75 °C for 10 h under nitrogen while being stirred. After completion of the reaction, the reaction solution was neutralized by 5% aqueous HCl, then the aqueous phase was separated and further extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. Then, the solution was concentrated to give a crude product, which was purified by silica gel column chromatography (PE/EA =8:1) to afford 4-morpholino-3,5-diphenyloxazol-2(3H)-one (4a): yield 62% (67.6 mg); yellow oil; Rf 0.20 (vPE/vEA = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 7.6 Hz, 2 H), 7.55-7.491 (m, 2 H), 7.48-7.40 (m, 5 H), 7.33 (t, J = 7.6 Hz, 1 H), 3.58 (t, J = 4.4 Hz, 4 H), 2.89 (t, J = 4.8 Hz, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 133.8, 131.2, 130.7, 129.5, 129.0, 128.6, 128.0, 127.9, 127.6, 125.6, 66.9, 49.9; IR ν (KBr, cm⁻¹) 1758, 1677, 1532, 1460, 1400, 1373, 1240, 1102, 1039, 998, 902, 743; HRMS (ESI⁺): m/z calcd. for C₁₉H₁₈N₂O₃ ([M+Na⁺]⁺) 345.1215, Found: 345.1223.


A 10 mL flame-dried Schlenk tube was charged with Pd(OAc)₂ (5.0 mol %), Na₂CO₃ (2.0 equiv),
$n$-Bu$_4$NCl (1.0 equiv) and 2a (0.3 mmol). The flask was capped and then backfilled with nitrogen (this was repeated two additional times). DMF (2.00 mL) was added via syringe, followed by the addition of methyl acrylate (0.375 mmol). The reaction solution was heated to 100 °C for 5 h under nitrogen while being stirred. After completion of the reaction, the reaction solution was neutralized by H$_2$O, then the aqueous phase was separated and further extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. Then, the solution was concentrated to give a crude product, which was purified by silica gel column chromatography (PE/EA = 4:1) to afford (E)-methyl 3-(4-morpholino-2-oxo-3-phenyl-2,3-dihydrooxazol-5-yl)acrylate (4b): yield 46% (45.4 mg); yellow oil; $R_f$ 0.20 ($v_{PE}/v_{EA}$ = 6:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54-7.39 (m, 6 H), 6.08 (d, $J = 14.8$ Hz, 1 H), 3.78 (s, 3 H), 3.56 (t, $J = 4.4$ Hz, 4 H), 3.00 (t, $J = 4.8$ Hz, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.6, 151.4, 137.9, 133.0, 129.5, 128.9, 127.1, 126.4, 124.2, 112.8, 66.2, 51.6, 50.4; IR $\nu$ (KBr, cm$^{-1}$) 1747, 1612, 1488, 1402, 1388, 1302, 1277, 1154, 1103, 1049, 1003, 913, 757; HRMS (ESI$^+$): m/z calcd. for C$_{17}$H$_{18}$N$_2$O$_5$ ([M+Na]$^+$) 353.1113, Found: 353.1126.

Reference

NMR spectra

1b
1i
2m
2n