Supporting Information for

Selectfluor™-Catalyzed Oxidative Cyclization of Ynamides Enables Facile Synthesis of Oxazolidine-2,4-diones

Guangke He,*[a] Yuan Li,[a] Zilun Yu,[a] Zhaoqiang Chen,[a] Yongming Tang,[a] Guangliang Song,[a] and Teck-Peng Loh*[a,b]

*E-mail: hegk@njtech.edu.cn;*E-mail: teckpeng@ntu.edu.sg

Table of Contents

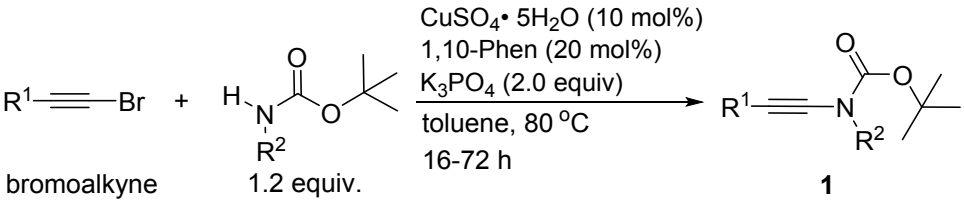
1. General Information.

All NMR spectra were recorded on a Bruker ASCEND™ 400 or a JEOL ECZS 400 MHz spectrometer. ^{1}H and ^{13}C NMR spectral data are reported as chemical shifts (δ) in parts per million (ppm) relative to tetramethylsilane. ^{19}F NMR spectra are referenced relative to $CFCl_3$ (as the external standard) in $CDCl_3$. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (J) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities s=singlet, d=doublet, t=triplet, q=quartet, pent=pentet, br=broad, m=multiplet. NMR spectra were processed in Bruker's TopSpin™ or MestReNova software package. High resolution mass spectra (HRMS, m/z) were recorded on a Bruker MicroTOF spectrometer using positive electrospray ionization (ESI) or on a Micromass GCT spectrometer using field ionization (EI/FI) or chemical ionization (CI). IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. Absorptions are measured in wavenumbers and only peaks of interest are reported. Melting points of solids were measured on a Griffin apparatus and are uncorrected. IUPAC names were obtained using the ACD/ILab service. Weighing was perfomed with a 4 decimal place balance. Reactions were monitored by thin-layer chromatography, carried out on 0.25 mm silica gel plates. Visualization was performed with a 254 nm UV lamp or iodine. Flash column chromatography was performed using silica gel. Characterization data for those compounds not described in the literature are provided.

Phenylacetylene, *p*-methylphenylacetylene, *p*-methoxylphenylacetylene, *p*-bromophenylacetylene, *p*-fluorophenylacetylene, 1-hexyne, 1-heptyne, and 2-(phenylethynyl)thiophene were purchased from commercial sources and used as received.

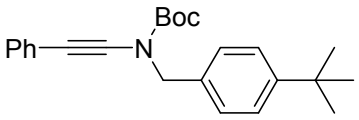
2. Synthesis of Starting Materials

The ynamide substrates **1a-z** were synthesized following a procedure previously reported by Hsung and coworkers.[1]



To a mixture of *tert*-butyloxycarbamates (24 mmol), K_3PO_4 (40 mmol), $CuSO_4$•$5H_2O$ (2 mmol), and 1,10-phenanthroline (2 mmol) in a reaction vial was added a solution of bromoalkyne (20 mmol) in dry toluene (40 mL). The reaction mixture was capped and heated in an oil bath at 80 °C for 16-72 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. Then, the reaction was quenched by the addition of H_2O and extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified on silica gel by flash column chromatography to give the desired products **1**.

(4-*tert*-Butylbenzyl)-phenylethynyl-carbamic acid *tert*-butyl ester (1b)



Aspect: brown oil;

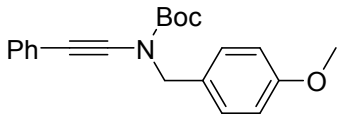
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.20 (m, 9H), 4.63 (s, 2H), 1.53 (m, 9H), 1.32 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 150.9, 133.4, 130.6, 129.7, 128.2, 127.0, 126.0, 125.5, 123.8, 34.6, 31.4, 31.1, 28.1.

IR (KBr, cm^{-1}) ν 3057, 2905, 2869, 2243, 1716, 1600, 1516, 1456, 1393, 1368, 1300, 1242, 1155, 1107, 1069, 1025.

HRMS (ESI/[M+H]$^+$) Calc. for: $C_{24}H_{30}NO_2$ 364.2277, found 364.2276.

(4-Methoxybenzyl)-phenylethynyl-carbamic acid *tert*-butyl ester (1c)



Aspect: yellow oil;

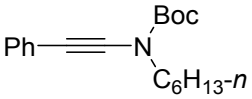
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 7H), 6.89-6.87 (m, 2H), 4.59 (s, 2H), 3.79 (s, 3H), 1.52 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.9, 130.6, 129.9, 128.6, 127.1, 123.8, 113.9, 82.6, 55.3, 28.1.

IR (KBr, cm^{-1}) ν 3036, 2978, 2934, 2836, 2243, 1716, 1612, 1514, 1393, 1369, 1298, 1250, 1155, 1034, 949 cm^{-1}.

HRMS (ESI/[M+H]$^+$) Calc. for: $C_{21}H_{24}NO_3$ 338.1756, found 338.1759.

***n*-Hexyl-phenylethynyl-carbamic acid *tert*-butyl ester (1d)**



Aspect: yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5H), 3.50 (t, J = 7.29 Hz, 2H), 1.75-1.65 (m, 2H), 1.53 (s, 9H), 1.39-1.29 (m, 6H), 0.91-0.88 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 130.6, 128.2, 127.0, 123.9, 84.2, 83.3, 49.2, 31.5, 28.1, 27.9, 26.1, 22.6, 14.0.

IR (KBr, cm^{-1}) ν 2932, 2860, 2245, 1722, 1601, 1456, 1394, 1369, 1306, 1255, 1233, 1147, 1087, 1026 cm^{-1}.

HRMS (ESI/[M+H]$^+$) Calc. for: $C_{19}H_{28}NO_2$ 302.2120, found 302.2123.

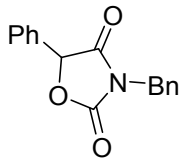
3. Oxidative Cyclization of Ynamides

3.1 *In situ*-generated HBF_4-catalyzed oxidative cyclization of ynamides

General Procedure I: To a 25 mL reaction tubes were added **1** (0.2 mmol), selectfluor^{TM} (0.02 mmol) and un-pretreated commercial DMSO (2.0 mL). The reaction mixture was stirred at 100 ^{o}C, while being monitored by TLC analysis. Then,

upon the completion, the reaction was quenched by the addition of H_2O (10 mL) and extracted with ethyl acetate (20 mL × 3) The combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified on silica gel by flash column chromatography (eluent: PE/EA=10/1) to give the desired product **2**.

3-Benzyl-5-phenyloxazolidine-2,4-dione (2a)[2]



Aspect: white solid (50.6 mg, 92% yield).

Mp: 114.1-114.9 °C.

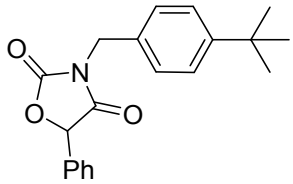
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 10H), 5.71 (s, 1H), 4.75-4.67 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 155.1, 134.6, 131.6, 129.8, 129.1, 128.9, 128.8, 128.6, 126.1, 80.2, 44.0.

IR (KBr, cm^{-1}) ν 3036, 2930, 1822, 1728, 1605, 1499, 1442, 1340, 1159, 1007.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{14}NO_3$ 268.0974, found 268.0971.

3-(4-*tert*-Butylbenzyl)-5-phenyloxazolidine-2, 4-dione (2b)[2]



Aspect: white solid (48.3 mg, 75 % yield).

Mp: 77.0-77.4 °C.

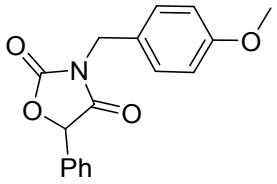
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.24 (m, 9H), 5.69 (s, 1H), 4.72-4.64 (m, 2H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 155.1, 151.6, 131.6, 131.6, 129.8, 129.1, 128.6, 126.1, 125.8, 80.2, 43.7, 34.6, 31.3.

IR (KBr, cm^{-1}) ν 2961, 1800, 1730, 1435, 1407, 1347, 1162, 1041, 1027.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{26}H_{22}NO_3$ 324.1600, found 334.1600.

3-(4-Methoxybenzyl)-5-phenyloxazolidine-2,4-dione (2c)[2]



Aspect: white solid (44.8 mg, 75 % yield).

Mp: 87.6-88.0 °C.

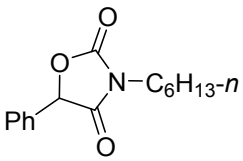
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.33 (m, 7H), 6.87-6.83 (m, 2H), 5.68 (s, 1H), 4.68-4.60 (m, 2H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 171.0, 159.7, 155.1, 131.5, 130.4, 129.8, 129.1, 126.8, 126.1, 80.2, 55.3, 43.6.

IR (KBr, cm^{-1}) ν 2938, 1808, 1732, 1615, 1518, 1436, 1419, 1329, 1254, 1159.

HRMS (ESI/$[M+Na]^+$) Calc. for: $C_{17}H_{15}NO_4Na$ 320.0899, found 320.0898.

3-*n*-Hexyl-5-phenyloxazolidine-2,4-dione (2d)[2]



Aspect: white solid (36.4 mg, 69 % yield).

Mp: 73.3-75.4 °C.

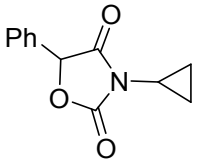
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 5H), 5.71 (s, 1H), 3.60-3.54 (m, 2H), 1.69-1.63 (m, 2H), 1.33-1.26 (m, 6H), 0.89-0.85 (m, 3H),

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 155.4, 131.7, 129.8, 126.0, 80.1, 40.5, 31.2, 27.5, 26.2, 22.4, 13.9.

IR (KBr, cm^{-1}) ν 2955, 2936, 2916, 2856, 1802, 1732, 1457, 1340, 1128, 1106, 923.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{20}NO_3$ 262.1443, found 262.1441.

3-Cyclopropyl-5-phenyloxazolidine-2,4-dione (2e)[2]



Aspect: white solid (39.6 mg, 90 % yield).

Mp: 66.4-67.7 °C.

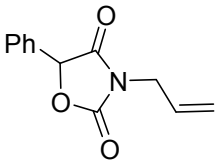
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 -7.40 (m, 5H), 5.65 (s, 1H), 2.76-2.73 (m, 1H), 1.03-1.01 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 154.1, 130.6, 128.7, 128.1, 124.8, 78.2, 21.9, 4.0, 3.9.

IR (KBr, cm^{-1}) ν 3074, 2911, 1820, 1732, 1607, 1595, 1492, 145, 1412, 1243, 1179, 1140, 1062, 1038, 1025.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{12}H_{12}NO_3$ 218.0817, found 218.0819.

3-Allyl-5-phenyloxazolidine-2,4-dione (2f)



Aspect: white solid (38.9 mg, 89 % yield).

Mp: 60.1-61.5 °C.

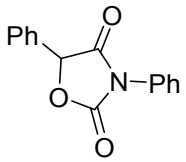
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 5H), 5.88-5.80 (m, 1H), 5.75 (s, 1H), 5.29 (t, J = 10.2 Hz, 2H), 4.20-4.18 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.9, 131.5, 129.8, 129.6, 129.2, 126.0, 119.6, 80.2, 42.4.

IR (KBr, cm^{-1}) ν 3048, 1805, 1732, 1440, 1416, 1347, 1325, 1192, 1128, 1104, 1008, 932.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{11}H_{12}NO_3$ 218.0817, found 218.0816.

3-Phenyl-5-phenyloxazolidine-2,4-dione (2g)[3, 5]



Aspect: white solid (45.7 mg, 90% yield).

Mp: 118.7-120.4 °C.

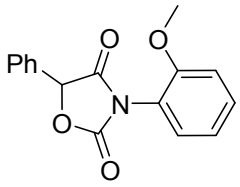
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.51(m, 10H), 5.92 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 154.0, 131.5, 130.7, 130.0, 129.4, 129.2, 129.1, 126.1, 125.6, 79.9.

IR (KBr, cm^{-1}) ν 3063, 2918, 1811, 1739, 1596, 1503, 1456, 1288, 1176, 1013.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{12}NO_3$ 254.0817, found 254.0818.

3-(2-Methoxyphenyl)-5-phenyloxazolidine-2,4-dione (2h)



Aspect: white solid (48.3 mg, 85% yield).

Mp: 112.5-114.3 °C.

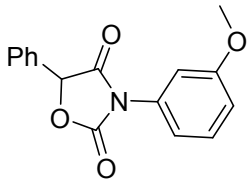
^{1}H NMR (400 MHz, $CDCl_3$) (*denotes minor rotamer peaks) δ 7.44-7.54 (m, 6H), 7.30-7.31* (m, 1H), 7.02-7.11* (m, 1H), 7.02-7.18 (m, 2H), 5.97* (s, 1H), 5.87* (s, 1H), 1.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 154.9, 154.8, 154.2, 154.0, 132.0, 131.7, 131.6, 131.6, 130.8, 129.8, 129.3, 129.2, 129.2, 129.1, 127.1, 126.1, 121.1, 121.0, 119.2, 119.0, 112.4, 112.2, 81.2, 80.5, 56.0, 55.9.

IR (KBr, cm^{-1}) ν 3062, 2927, 1813, 1743, 1601, 1509, 1468, 1459, 1411, 1301, 1190, 1113, 1019, 966.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{14}NO_4$ 284.0923, found 284.0923.

3-(3-Methoxybenzyl)-5-phenyloxazolidine-2,4-dione (2i)



Aspect: white solid (50.9 mg, 90 % yield).

Mp: 100.8-101.2 °C.

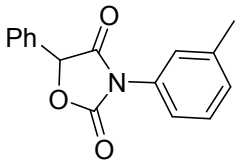
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.38 (m, 6H), 7.04-6.96 (m, 3H), 5.90 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 160.2, 153.9, 131.7, 131.5, 130.1, 130.0, 129.2, 126.1, 117.8, 115.0, 111.4, 79.9, 55.5.

IR (KBr, cm^{-1}) ν 3074, 2922, 1820, 1732, 1607, 1595, 1492, 1456, 1412, 1179, 1038, 1026.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{14}NO_4$ 284.0923, found 284.0925.

3-(3-Methylphenyl)-5-phenyloxazolidine-2,4-dione (2j)[2].



Aspect: white solid (48.1 mg, 90 % yield).

Mp: 116.0-117.8 °C.

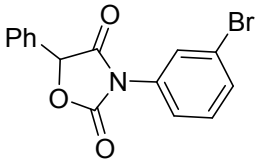
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.36 (m, 6H), 7.25-7.23 (m, 3H), 5.89 (s, 1H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 154.1, 139.6, 131.6, 130.6, 130.0, 129.9, 129.2, 126.3, 126.1, 122.8, 79.9, 21.4.

IR (KBr, cm^{-1}) ν 3069, 2922, 1813, 1746, 1603, 1516, 1456, 1425, 1346, 1287, 1198, 1173, 1064, 1021.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{14}NO_3$ 268.0974, found 268.0973.

3-(3-Bromophenyl)-5-phenyloxazolidine-2,4-dione (2k)



Aspect: white solid (52.6 mg, 79 % yield).

Mp: 141.0-141.6 °C.

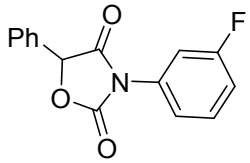
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.57-7.37 (m, 8H), 5.91 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 153.4, 132.2, 131.2, 130.6, 130.1, 129.3, 128.6, 126.0, 124.1, 122.7, 80.0.

IR (KBr, cm^{-1}) ν 2922, 1813, 1732, 1603, 1516, 1425, 1173.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{11}NO_3Br$ 331.9922, found 331.9922.

3-(3-Fluorophenyl)-5-phenyloxazolidine-2,4-dione (2l)[4]



Aspect: white solid (40.7 mg, 75 % yield).

Mp: 133.1-132.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 6H), 7.32-7.26 (m, 2H), 7.16-7.13 (m, 1H), 5.91 (s, 1H).

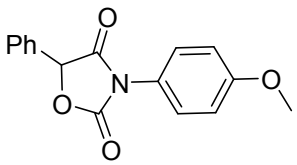
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 162.6 (J = 246.5 Hz), 153.4, 131.9 (J = 10.2 Hz), 131.1, 130.5 (J = 8.8 Hz), 130.0, 129.2, 126.0, 121.0 (J = 2.7 Hz), 116.0 (J = 20.2 Hz), 113.0 (J = 24.3 Hz), 79.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -110.14 ppm.

IR (KBr, cm^{-1}) ν 3074, 2922, 1820, 1732, 1647, 1595, 1456, 1179.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{11}NO_3F$ 272.0723, found 272.0710.

3-(4-Methoxyphenyl)-5-phenyloxazolidine-2,4-dione (2m)[3]



Aspect: white solid (53.4 mg, 94 % yield).

Mp: 114.1-114.9 °C.

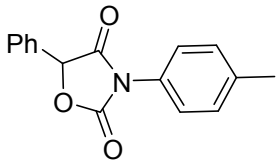
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 5H), 7.33 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 5.88 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.9, 154.3, 131.6, 129.9, 129.2, 127.1, 126.1, 123.2, 114.7, 80.0, 55.6.

IR (KBr, cm^{-1}) v 3046, 2935, 2838, 1813, 1740, 1519, 1419, 1303, 1255, 1182, 1170, 1064, 1030, 1014.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{14}NO_4$ 384.0923, found 384.0925.

3-(4-Methylphenyl)-5-phenyloxazolidine-2,4-dione (2n)[2,6]



Aspect: white solid (49 mg, 91 % yield).

Mp: 106.3-107.2 °C.

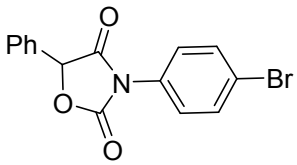
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 5H), 7.32-7.25 (m, 4H), 5.88 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 154.2, 139.3, 131.6, 130.0, 130.0, 129.2, 128.1, 126.1, 125.5, 80.0, 21.3.

IR (KBr, cm^{-1}) v 3040, 2921, 1811, 1740, 1518, 1414, 1172, 1062, 1012, 963, 808, 785, 707, 643.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{14}NO_3$ 268.0974, found 268.0975.

3-(4-Bromophenyl)-5-phenyloxazolidine-2,4-dione (2o)[2]



Aspect: white solid (56.3 mg, 85% yield).

Mp: 163.8-165.2 °C.

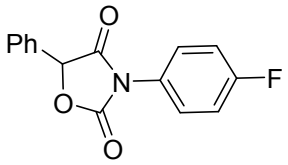
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.7 Hz, 2H), 7.49-7.47 (m, 5H), 7.37 (d, J = 8.7 Hz, 2H), 5.91 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 153.5, 132.6, 131.2, 130.1, 129.8, 129.3, 127.0, 126.03, 122.9, 80.0.

IR (KBr, cm^{-1}) v 3072, 2922, 1820, 1732, 1607, 1595, 1492, 1456, 1414, 1243, 1206, 1179, 1038.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{11}NO_3Br$ 331.9922, found 331.9922.

3-(4-Fluorophenyl)-5-phenyloxazolidine-2,4-dione (2p)[2,3]



Aspect: white solid (42.1 mg, 78 % yield).

Mp: 133.5-135.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.43 (m, 7H), 7.21-7.17 (m, 2H), 5.91 (s, 1H).

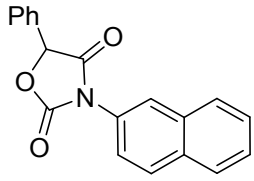
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 162.3 (J = 247.3 Hz), 153.8, 131.3, 130.0, 129.2, 127.5 (J = 8.9 Hz), 126.6 (J = 2.6 Hz), 126.0, 116.5 (J = 23.7 Hz), 79.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -111.21 ppm.

IR (neat, cm^{-1}) v 3069, 2922, 1813, 1732, 1603, 1516, 1425, 1287, 1231, 1173, 1021.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{11}NO_3F$ 272.0723, found 272.0728.

3-(2-Naphthyl)-5-phenyloxazolidine-2,4-dione (2q)[5]



Aspect: white solid (55.4 mg, 91% yield).

Mp: 138.2-140.1 °C.

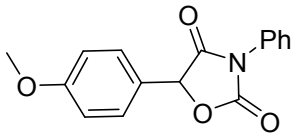
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.89-7.87 (m, 2H), 7.56-7.49 (m, 8H), 5.96 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 154.1, 133.1, 132.9, 131.5, 131.5, 130.8, 130.0, 129.5, 129.4, 129.3, 129.2, 129.1, 128.3, 128.1, 127.8, 127.3, 127.0, 126.1, 126.1, 125.6, 125.0, 122.8, 80.1.

IR (KBr, cm^{-1}) v 3060, 2926, 1808, 1742, 1598, 1454, 1183, 1068.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{19}H_{14}NO_3$ 304.0974, found 304.0974.

5-(4-Methoxylphenyl)-3-phenyloxazolidin-2,4-dione (2r)[3]



Aspect: white solid (50 mg, 88 % yield).

Mp: 109.9-110.0 °C.

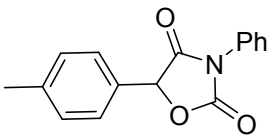
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.40 (m, 7H), 6.99 (d, J = 7.8 Hz, 2H), 5.86 (s, 1H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 160.9, 154.0, 130.8, 129.4, 129.0, 128.0, 125.6, 123.4, 114.7, 80.1, 5.4.

IR (KBr, cm^{-1}) v 3014, 2962, 2930, 2838, 1808, 1743, 1610, 1519, 1503, 1442, 1259, 1197, 1181, 1166, 1002.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{14}NO_4$ 284.0923, found 284.0921.

5-(4-Methylphenyl)-3-phenyloxazolidin-2,4-dione (2s)



Aspect: white solid (48.9 mg, 91 % yield).

Mp: 114.0-115.3 °C.

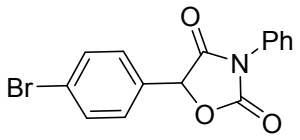
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.37 (m, 7H), 7.28-7.26 (m, 2H), 5.86 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 154.1, 140.2, 130.8, 129.9, 129.4, 129.0, 128.5, 126.2, 125.6, 80.1, 21.3.

IR (KBr, cm^{-1}) v 3544, 2924, 1816, 1740, 1517, 1502, 1410, 1303, 1289, 1198, 1176, 1063, 1004, 963.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{14}NO_3$ 268.0974, found 268.0973.

5-(4-Bromophenyl)-3-phenyloxazolidin-2,4-dione (2t)



Aspect: white solid (51.5 mg, 77% yield).

Mp: 146.2-148.7 °C.

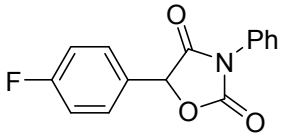
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.51-7.49 (m, 2H), 7.46-7.41 (m, 5H), 5.87 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 153.7, 132.4, 130.6, 130.4, 129.5, 129.2, 127.6, 125.6, 124.3, 79.1.

IR (KBr, cm^{-1}) v 3058, 1812, 1752, 1732, 1593, 1506, 1425, 1410, 1302, 1195, 1179, 1073, 1006.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{12}NO_3Br$ 331.9922, found 331.9927.

5-(4-Fluorophenyl)-3-phenyloxazolidin-2,4-dione (2u)[3]



Aspect: white solid (46.1 mg, 84 % yield).

Mp: 126.6-128.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 4H), 7.46-7.44 (m, 3H), 7.18 (t, J = 8.5 Hz, 2H), 5.89 (s, 1H).

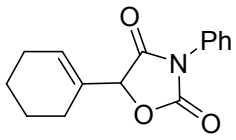
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 163.5 (J = 248.2 Hz), 130.6, 129.4, 129.1, 128.1 (J = 8.7 Hz), 127.2 (J = 2.7 Hz), 125.5, 116.3 (J = 21.7 Hz), 79.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -110.70 ppm.

IR (KBr, cm^{-1}) ν 3062, 1823, 1748, 1732, 1607, 1515, 1503, 1416, 1287, 1236, 1199, 1171, 1062, 1029.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{12}NO_3F$ 272.0723, found 272.0720.

5-Cyclohexenyl-3-phenyloxazolidine-2,4-dione (2v)



Aspect: white solid (58.2 mg, 75 % yield).

Mp: 111.7-112.0 °C.

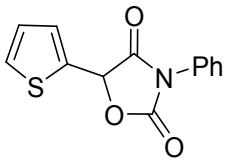
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.44-7.41 (m, 3H), 6.10 (s, 1H), 5.23 (s, 1H), 2.16-2.15 (m, 3H), 1.95-1.90 (m, 1H), 1.76-1.60 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 154.1, 132.5, 130.9, 129.4, 129.1, 129.0, 125.6, 83.5, 25.2, 23.1, 21.8, 21.6.

IR (KBr, cm^{-1}) ν 2936, 1810, 1743, 1500, 1437, 1414, 1297, 1209, 1183, 1154, 1065.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{15}H_{16}NO_3$ 258.1130, found 258.1129.

3-Phenyl-5-(2-thienyl)oxazolidin-2,4-dione (2w)[3]



Aspect: white solid (46.4 mg, 89 % yield).

Mp: 123.1-124.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.45 (m, 6H), 7.31 (d, J = 3.5 Hz, 1H), 7.11-7.08 (t, J = 4.3 Hz, 1H), 6.13 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 153.4, 132.8, 130.7, 129.5, 129.2, 128.1, 128.1, 127.5, 125.6.

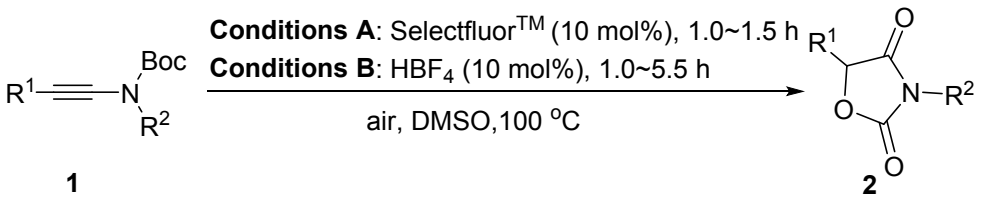
IR (KBr, cm^{-1}) ν 3102, 2925, 1819, 1747, 1595, 1501, 1410, 1368, 1280, 1194, 1170, 1055, 995, 956.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{13}H_{10}NO_3S$ 260.0381, found 260.0379.

3.2 A comparison of catalytic activity for selectfluor^{TM} and HBF_4-catalyzed oxidative cyclization of ynamides

General Procedure II: To a 25 mL reaction tubes were added **1** (0.2 mmol), un-pretreated commercial DMSO (2.0 mL) and HBF_4 (50% aqueous solution, 0.02 mmol). The reaction mixture was stirred at 100 ^oC, while being monitored by TLC analysis. Then, upon the completion, the reaction was quenched by the addition of H_2O (10 mL) and extracted with ethyl acetate (20 mL × 3) The combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The NMR yields of **2** was determined by ^1H NMR of the crude reaction mixture using 1,3,5-trimethylbenzene as an internal standard.

Table S1 A comparison of catalytic activity for selectfluor^{TM} and HBF_4-catalyzed oxidative cyclization of ynamides



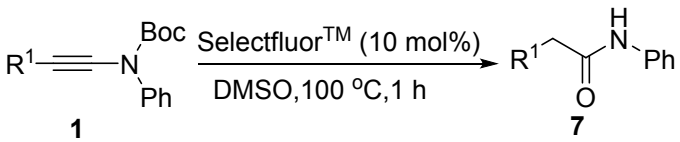
Entry	R^1	R^2	Comp.	NMR yield of **2** (%)	
				Conditions A	**Conditions B**
1		Bn	**2a**	＞99	89
2		4-*t*-BuBn	**2b**	80	62
3		4-MeOBn	**2c**	85	60
4		*n*-C_6H_{13}	**2d**	73	52
5		*cyclo*-Pr	**2e**	94	75
6		2-allyl	**2f**	95	76
7		Ph	**2g**	98	73
8		2-$MeOC_6H_4$	**2h**	91	77
9	Ph	3-$MeOC_6H_4$	**2i**	99	80
10		3-MeC_6H_4	**2j**	94	77
11		3-BrC_6H_4	**2k**	88	38
12		3-FC_6H_4	**2l**	87	56
13		4-$MeOC_6H_4$	**2m**	＞99	80
14		4-MeC_6H_4	**2n**	96	78
15		4-BrC_6H_4	**2o**	88	46
16		4-FC_6H_4	**2p**	85	64
17		2-naphthyl	**2q**	＞99	64
18	4-$MeOC_6H_4$	Ph	**2r**	95	87

19	4-MeC_6H_4	**2s**	＞99	92
20	4-BrC_6H_4	**2t**	81	33
21	4-FC_6H_4	**2u**	91	71
22	cyclohexenyl	**2v**	91	77
23	2-thienyl	**2w**	91	79

3.3 Selectfluor™ catalyzed oxidative reaction of *N*-alkylethynyl *tert*-butyloxycarbamates

The experimental procedure is same to General Procedure I: To a 25 mL reaction tubes were added **1** (0.2 mmol), selectfluor™ (0.02 mmol) and un-pretreated commercial DMSO (2.0 mL). The reaction mixture was stirred at 100 °C, while being monitored by TLC analysis. Then, upon the completion, the reaction was quenched by the addition of H_2O (10 mL) and extracted with ethyl acetate (20 mL × 3) The combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified on silica gel by flash column chromatography (eluent: PE/EA=10/1) to give the desired products **7**.

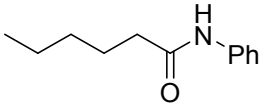
Table S2 Selectfluor™ catalyzed oxidative reaction of *N*-alkylethynyl *tert*-butyloxycarbamates



1 **7**

Entry	R^1	Isolated yield of **7** (%)
1	*n*-C_4H_9 (**1x**)	91 (**7x**)
2	*n*-C_8H_{17} (**1y**)	85 (**7y**)
3	*tert*-Bu (**1z**)	87 (**7z**)

***N*-Phenylhexanamide (7x)**[7]



Aspect: white solid (52.1 mg, 91 % yield).

Mp: 90.6-91.9 °C.

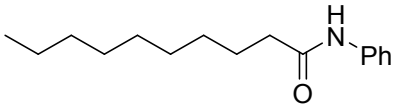
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.33-7.29 (m, 3H), 7.11-7.08 (t, J = 7.39 Hz, 1H), 2.35 (t, J = 7.61 Hz, 2H), 1.75-1.69 (m, 2H), 1.38-1.34 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 138.1, 128.9, 124.2, 120.0, 37.8, 31.5, 25.4, 22.5, 14.0.

IR (KBr, cm^{-1}) v 3305, 3266, 3202, 3144, 3093, 2955, 2931, 2862, 1667, 1605, 1556, 1499, 1443, 1325, 1304, 1259, 1188, 965.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{12}H_{18}NO$ 192.1388, found 192.1387.

_N_-phenyldecanamide (7y)



Aspect: white solid (41.9 mg, 85 % yield).

Mp: 53.6-54.3 °C.

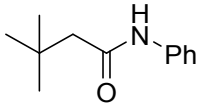
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (d, J = 7.89 Hz, 2H), 7.34-7.30 (t, J = 7.82 Hz, 2H), 7.17 (s, 1H), 7.10 (t, J = 7.38 Hz, 1H), 2.35 (t, J = 7.63 Hz, 2H), 1.73 (m, 2H), 1.35-1.27 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 138.0, 124.2, 119.8, 37.9, 31.9, 29.5, 29.4, 29.3, 25.7, 22.7, 14.1.

IR (KBr, cm^{-1}) v 3315, 2954, 2919, 2849, 1749, 1656, 1601, 1543, 1501, 1444, 1381, 1311, 1260.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{26}NO$ 248.2014, found 248.2014.

3,3-Dimethyl-_N_-phenylbutanamide (7z)



Aspect: white solid (49.8 mg, 87 % yield).

Mp: 117.5-118.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 7.33-7.29 (m, 2H), 7.16 (s, 1H), 7.10 (t, J = 7.26 Hz, 1H), 2.22 (s, 2H), 1.10 (s, 9H).

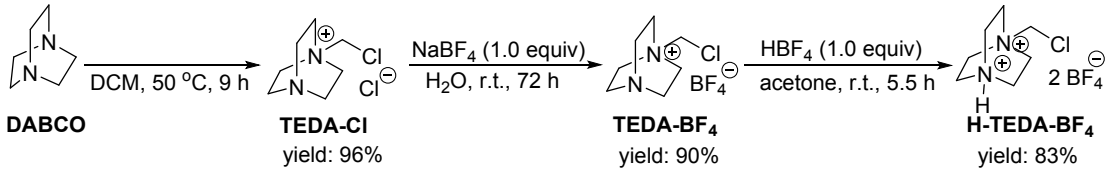
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 137.9, 129.0, 124.2, 120.0, 51.6, 31.3, 29.8.

IR (KBr, cm^{-1}) v 3278, 3249, 2962, 1654, 1597, 1545, 1503, 1491, 1441, 1344, 1259, 1136.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{12}H_{18}NO$ 192.1388, found 192.1388.

4. Verification of Reaction Mechanism

4.1 Synthesis of H-TEDA-BF_4[8~9]

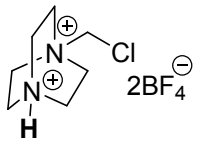


The reaction mixture of 1,4-Diazabicyclo[2.2.2]octane (DABCO) (11.12 g, 100 mmol) and DCM (30 mL) was stirred under reflux overnight. The resulting white solid was filtered, washed with DCM and dried under vacuum to give **TEDA-Cl** (18.92 g, yield: 96%).

Thereafter, to a $NaBF_4$ (2.32 g, 20 mmol) aqueous solution (20 mL of water) was added **TEDA-Cl** (3.92 g, 20 mmol), and the resulting mixture was stirred for 3 days at room temperature. Removal of solvent gave a white solid, which was recrystallized from ether/acetonitrile mixture to afford the pure BF_4 salt **TEDA-BF_4** (3.6 g, 90%).

Finally, **TEDA-BF_4** (1.24 g, 5 mmol) was dissolved in minimum amount of acetone (9 mL). To this solution was added HBF_4 (0.88 g, 50 wt. % in H_2O, 5 mmol) and stirred for 6.5 h at room temperature. The precipitated white solid was filtered, washed with acetone and dried under vacuum to give **H-TEDA-BF_4** (1.39 g, yield 83%).

1-(Chloromethyl)-4-aza-1-azoniabicyclo[2.2.2]octane tetrafluoroborate, tetrafluoroboric acid (1:1), *abbr.* **H-TEDA-BF_4**



H-TEDA-BF_4

Aspect: white solid (1.39 g, 83% yield).

Mp: 242.3-244.1 °C.

^{1}H NMR (400 MHz, CD_3CN) δ 5.22 (s, 2H), 3.91-3.87 (m, 6H), 3.79-3.75 (m, 6H).

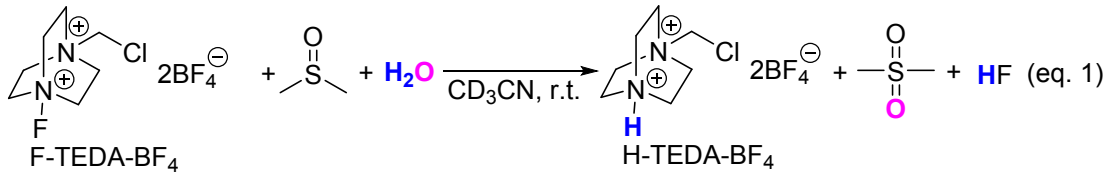
^{13}C NMR (100 MHz, CD_3CN) δ 69.9, 5.8, 44.9.

^{19}F NMR (376 MHz, CD_3CN): δ -151.09 and -151.15 ppm.

IR (KBr, cm^{-1}) ν 3015, 3000, 2991, 2455, 1497, 1493, 1471, 1444, 1410, 1389, 1364, 1305, 1083, 1035.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_7H_{16}N_2Cl$ 161.0846, found 161.0848.

4.2 The redox reaction of selectfluor^{TM} with DMSO in CD_3CN at r.t.



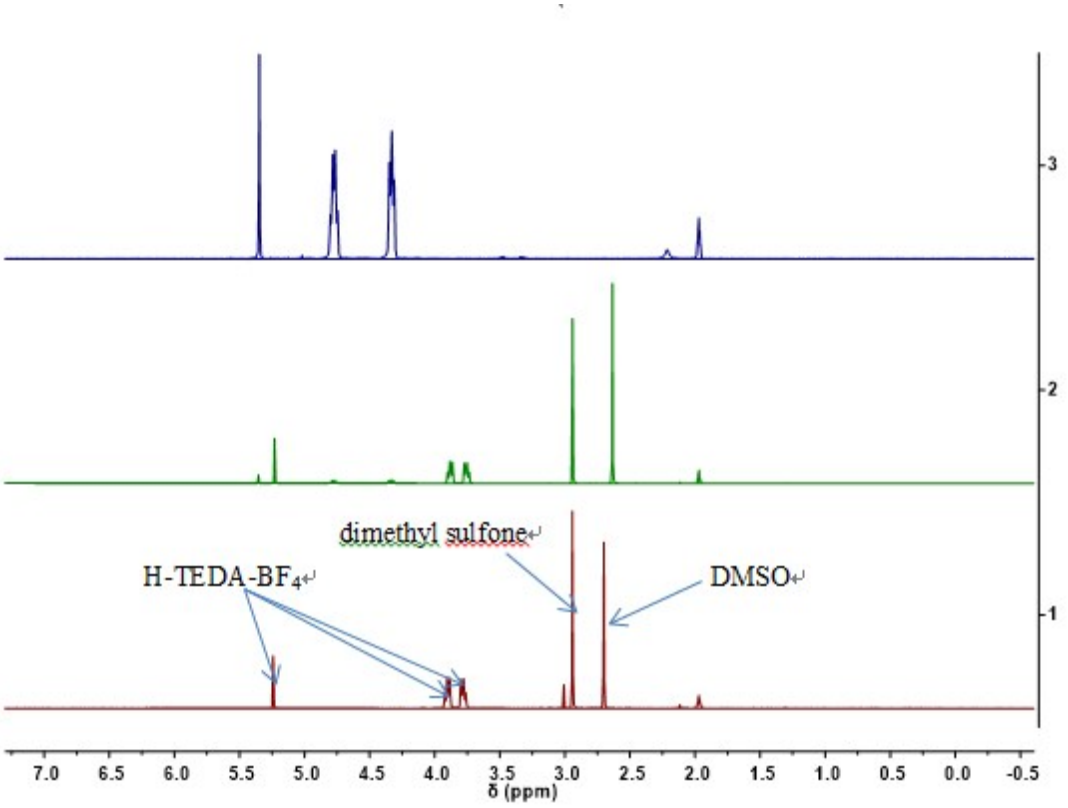


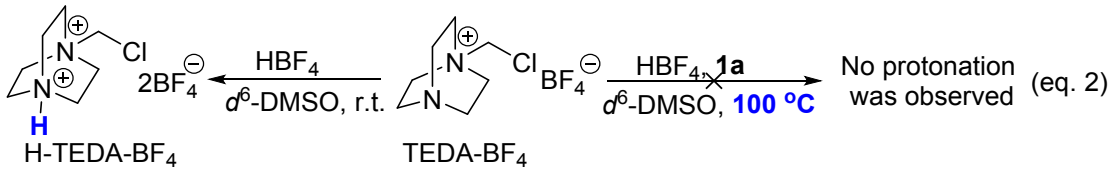
Fig. S1 Monitoring the redox reaction of DMSO by Selectfluor™ in d^3-CH_3CN by ^1H NMR spectroscopy. All reactions were performed in a borosilicate NMR tube with d^3-CH_3CN as solvent (400 MHz, 298 K).

(**Top**, **blue**): Reference spectrum of Selectfluor™ (0.083 M);

(**Middle**, **green**): Reaction mixture of Selectfluor™ (0.083 M) and DMSO (0.166 M) after 30 minutes of being mixed;

(**Bottom**, **pink**): Reaction mixture after 24 h.

4.3 The protonation of TEDA-BF_4 with HBF_4 (50 wt.% aq.) in d^6-DMSO at 100 °C



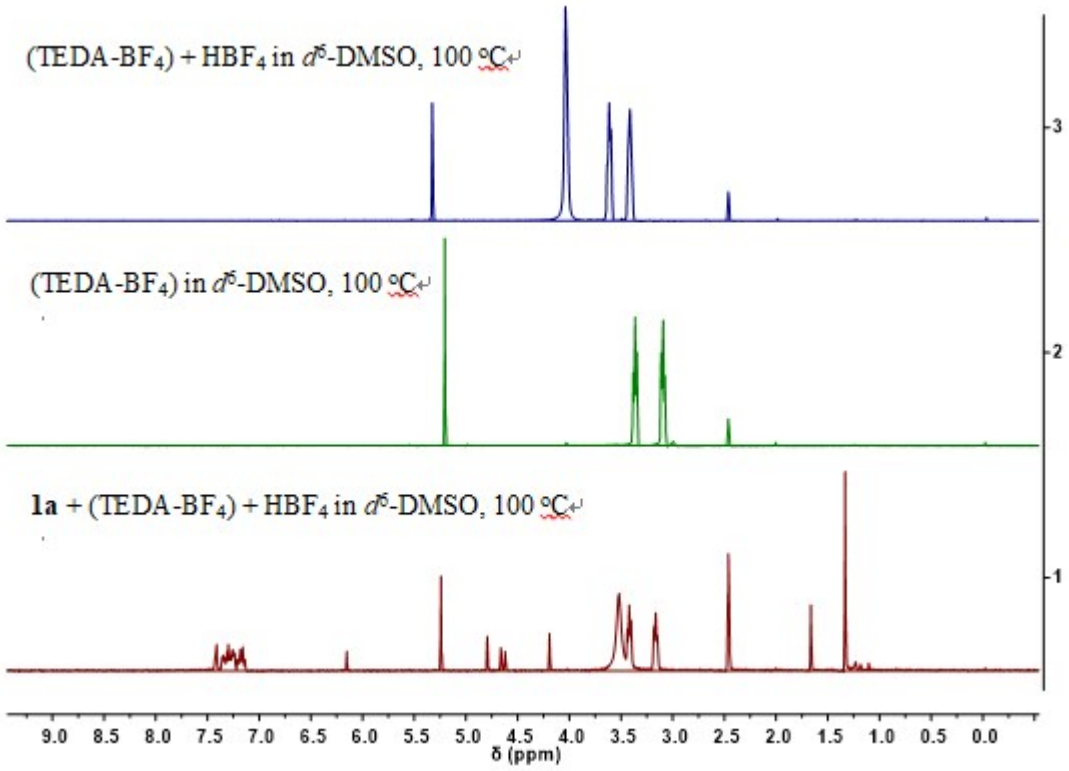


Fig. S2 Detecting the protonation reaction of TEDA-BF_4 by HBF_4 in d^6-DMSO by variable temperature ^1H NMR spectroscopy. All reactions were performed in a borosilicate NMR tube with d^6-DMSO as solvent (400 MHz, 373 K).

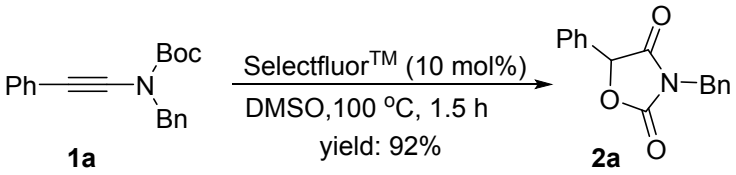
(**Top**, **blue**): Reaction mixture of TEDA-BF_4 (0.167 M) and HBF_4 (0.167 M) after 5 minutes of being mixed;

(**Middle**, **green**): Reference spectrum of TEDA-BF_4 (0.167 M);

(**Bottom**, **pink**): Reaction mixture of **1a** (0.033 M), TEDA-BF_4 (0.033 M) and HBF_4 (0.166 M) after 5 minutes of being mixed.

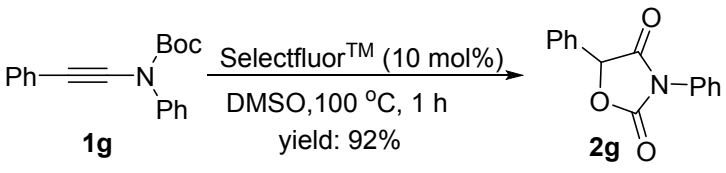
5. Large Scale Reactions

5.1 Synthesis of 3-benzyl-5-phenyloxazolidine-2,4-dione (2a)



To a 100 mL glassware were added **1a** (6 mmol, 1.8425 g), selectfluor™ (0.6 mmol, 0.2129 g) and un-pretreated commercial DMSO (60 mL). The reaction mixture was stirred at 100 °C, while being monitored by TLC analysis. Then, upon the completion, the reaction was quenched by the addition of H_2O (50 mL) and extracted with ethyl acetate (60 mL × 3). The combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified on silica gel by flash column chromatography (eluent: PE/EA=10/1) to give the desired product **2a** (1.4821 g, yield: 92%).

5.2 Synthesis of 3-phenyl-5-phenyloxazolidine-2,4-dione (2g)

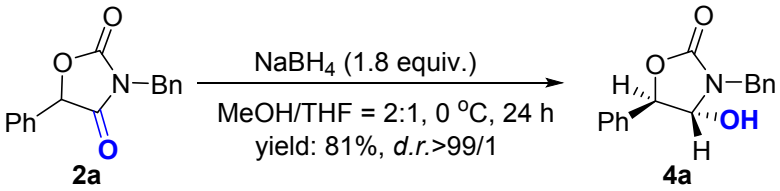


To a 100 mL glassware were added **1g** (6 mmol, 1.7581 g), selectfluor™ (0.6 mmol, 0.2123 g) and un-pretreated commercial DMSO (60 mL). The reaction mixture was stirred at 100 °C, while being monitored by TLC analysis. Then, upon the completion, the reaction was quenched by the addition of H_2O (50 mL) and extracted

with ethyl acetate (60 mL × 3). The combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified on silica gel by flash column chromatography (eluent: PE/EA=10/1) to give the desired product **2g** (1.3983 g, yield: 92%).

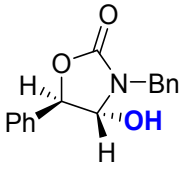
6. Synthetic Applications of Product 2a

6.1 *trans*-4-hydroxy-5-phenyloxazolidin-2-one (4a)



In a 25 mL reaction tubes were placed **2a** (0.3 mmol), $NaBH_4$ (1.8 equiv) and MeOH (2 mL) and THF (1 mL). The reaction mixture was stirred at 0 °C, while being monitored with TLC analysis. Then, the reaction was quenched by the addition of H_2O (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4. and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (Eluent: PE/EA = 2/1) to give the desired product **4a**.

(*trans*)-3-benzyl-4-hydroxy-5-phenyloxazolidin-2-one (4a).



Aspect: white solid (65.8 mg, 81 % yield).

Mp: 130.1-131.3 °C.

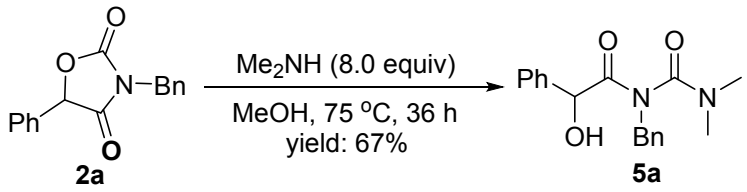
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 10H), 5.51 (d, J = 5.88 Hz, 1H), 5.18 (dd, J_1 = 8.08 Hz, J_2 = 6.00 Hz, 1H), 4.85 (d, J = 8.32 Hz, 1H), 1.92 (d, J = 8.31 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 135.9, 132.4, 128.9, 128.9, 128.7, 128.5, 128.1, 126.8, 80.3, 80.2, 45.6.

IR (KBr, cm^{-1}) *v* 3298, 1717, 1497, 1455, 1441, 1356, 1341, 1237, 1121, 1096, 1020, 951.

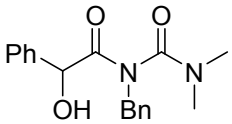
HRMS (ESI/$[M+H]^+$) Calc. for: $C_{16}H_{16}NO_3$ 270.1130, found270.1131.

6.2 *N*-mandelylurea (5a)



In a 25 mL reaction tubes were placed **2a** (0.3 mmol), Me_2NH (8.0 equiv) and MeOH (3 mL). The reaction mixture was stirred at 75 °C, while being monitored with TLC analysis. Then, the reaction was quenched by the addition of H_2O (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4. and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE : EA=1:1) to give the desired product **5a**.

***N*-mandelylurea (5a).**



Aspect: white solid (63.3 mg, 67 % yield).

Mp: 94.7-95.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.18 (m, 10H), 6.62 (s, 1H), 6.07 (s, 1H), 4.45-4.43 (m, 2H), 2.97 (s, 3H), 2.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 155.0, 138.0, 136.1, 128.8, 128.7, 127.5, 127.5, 127.3, 76.5, 43.3, 36.7, 36.1.

IR (KBr, cm^{-1}) *v* 3272, 1712, 1661, 1559, 1497, 1454, 1340, 1371, 1271, 1186, 1071, 982.

HRMS (ESI/$[M+H]^+$) Calc. for: $C_{18}H_{21}N_2O_3$ 313.1552, found 312.1553.

7. X-ray structure of 2a

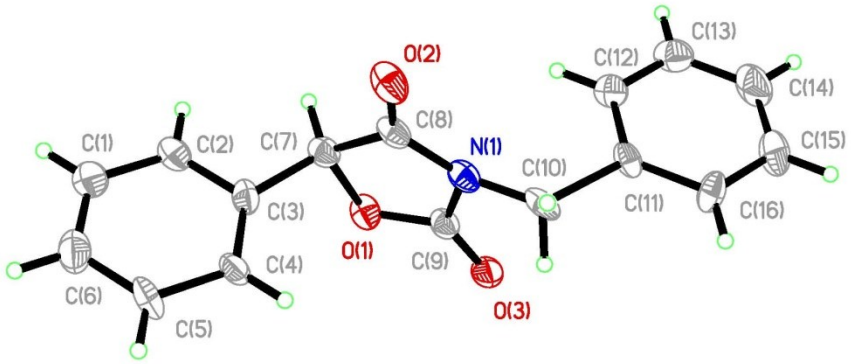


Fig. S1 ORTEP drawing of the X-ray structure of 2a with 30% thermal ellipsoids.

Crystal data for **2a**: $C_{16}H_{13}NO_3$, $M = 267.27$, monoclinic, space group $P1c1$, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0410$, w$R_2 = 0.1183$, R indices (all data): $R_1 = 0.0506$, $wR_2 = 0.1268$, $a = 14.099(2)$, $b = 5.2916(9)$, $c = 9.1495(16)$ Å, $\beta = 101.496(7)$ °, $V = 668.9(2)$ Å^3, $T = 273(2)$ K, $Z = 2$, reflections collected/unique: 12828/3765 ($R_{int} = 0.0247$), number of observations [$I > 2\sigma(I)$]: 3062, parameters: 315. CCDC 1881795 data for this paper contains the supplementary crystallographic.

8. References

[1] (a) X. Zhang, Y. Zhang, J. Huang, R. P. Hsung, K. C. M. Kurtz, J. Oppenheimer, M. E. Petersen, I. K. Sagamanove, L. Shen and M. R. Tracey, *J. Org. Chem.* 2006, **71**, 4170-4177; (b) Y. Zhang, J. Huang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz and E. L. Vera, *Org. Lett.* 2004, **6**, 1151-1154.

[2] W.-Z. Zhang, T. Xia, X.-T. Yang and X.-B. Lu, *Chem. Commun.*, 2015, **51**, 6175-6178.

[3] T. Ooi, K. Fukumoto and K. Maruoka, *Angew. Chem. Int. Ed.*, 2006, **45**, 3839-3842.

[4] T. Kurz and K. Widyan, *Tetrahedron*, 2005, **61**, 7247-7251.

[5] R. A. Aitken and A. W. Thomas, *Archivoc*, 2002, **2002**, 71-79.

[6] H. Aoyama, M. Sakamoto and Y. Omote, *Tetrahedron Lett.*, 1983, **24**, 1169-1170.

[7] H. Huang, L. Tang, Y. Xi, G. He and H. Zhu, *Tetrahedron Lett.*, 2016, **57**, 1873-1876.

[8] K. Laali, A. Jamalian and C. Zhao, *Tetrahedron Lett.* 2014, **55**, 6643-6646.

[9] A. Dixit, G. Yadav, M. Chauhan and S. Singh, *Current Catalysis*, 2016, **5**, 203-211.