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Supporting Information

N-Heterocyclic Carbene-Catalyzed Formal [6+2] Annulation Reaction via Cross-Conjugated Aza-Trienolate Intermediates

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1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Dry CHCl_3 was purchased from commercial sources and stored under argon over 4 Å molecular sieves. 1*H*-Pyrrole-2-carbaldehyde and 2,2,2-trifluoro-1-phenylethan-1-one were purchased from commercial sources. The trifluoroacetophenone derivatives **2b-2t** were synthesized from the following literature procedure.^{1a,1b} The heteroaryl trifluoromethyl ketones **2t-2w** were synthesized from the following the literature procedure.^{1c} The 4-bromo/iodo-1*H*-pyrrole-2-carbaldehyde was synthesized from the following the literature procedure.² The 1*H*-indole-2-carbaldehyde **1d**, **1e-1f** were synthesized following the literature procedure.³ The triazolium salt **4** was synthesized following the literature procedure.⁴ The Kharasch oxidant **5** was synthesized following the literature procedure.⁵ The Cs_2CO_3 was dried by heating at 120 °C under vacuum and cooling under argon. 30 °C Corresponds to the room temperature of the lab when the experiments were performed.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F₂₅₄. Visualization was accomplished with short wave UV light or KMnO_4 staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 400 and Bruker Ultrashield spectrometer in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl_3 : $\delta\text{H} = 7.26$ ppm, $\delta\text{C} = 77.16$ ppm). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, ν -max in cm^{-1} . HRMS (ESI) data were recorded on a Micromass Q-TOF Micro instrument. HPLC analysis was performed on an Agilent Technologies 1260 Infinity II with UV detector.

¹ a) S. Crotti, N. D. Iorio, A. Mazzanti, P. Righi, G. Bencivenni, *J. Org. Chem.* **2018**, 83, 12440; b) H. Cheng, Y. Pei, F. Leng, J. Li, A. Liang, D. Zou, Y. Wu, Y. Wu, *Tetrahedron Lett.* **2013**, 54, 4483; c) E. Martinelli, A. C. Vicini, M. Mancinelli, A. Mazzanti, P. Zani, L. Bernardi, M. Fochi, *Chem. Commun.* **2015**, 51, 658.

² V. K. Outlaw, F. B.-Andrea, C. A. Townsend, *Org. Lett.* **2015**, 17, 1822.

³ H. Mora-Radó, L. Sotorrios, M. P. Ball-Jones, L. Bialy, W. Czechitzky, M. Méndez, E. Gómez-Bengoa, J. P. A. Harrity, *Chem.-Eur. J.* **2018**, 24, 9530.

⁴ M. S. Kerr, J. Read de Alaniz, T. Rovis, *J. Org. Chem.* **2005**, 70, 5725.

⁵ M. S. Kharasch, B. S. Joshi, *J. Org. Chem.* **1957**, 22, 1439.

2. General Procedure for the Optimization of Reaction Conditions

To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the 1*H*-pyrrole-2-carbaldehyde **1a** (0.25 mmol), followed by Kharasch oxidant **5** (0.25 mmol), triazolium salt **4** (18.2 mg, 0.05 mmol), and Cs₂CO₃ (41 mg, 0.125 mmol). The mixture was kept under argon atmosphere and dry CHCl₃ (2.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon and stirred the reaction mixture. To this mixture, 2,2,2-trifluoro-1-phenylethan-1-one **2a** (65.3 mg, 53 μL, 0.375 mmol) was added and stirred the reaction mixture at 30 °C for 12 h under argon atmosphere. The solvent was evaporated, and the crude residue was purified by flash column chromatography on silica gel to afford the corresponding 3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3a**.

Optimization Table

entry	variation of the standard conditions ^a	yield of 3a (%) ^b
1	None	83
2	6 instead of 4	31

3	7 instead of 4	<5
4	8 instead of 4	18
5	9 instead of 4	16
6	K ₂ CO ₃ instead of Cs ₂ CO ₃	41
7	KOt-Bu instead of Cs ₂ CO ₃	<5
8	DBU instead of Cs ₂ CO ₃	<5
9	DABCO instead of Cs ₂ CO ₃	30
10	THF instead of CHCl ₃	16
11	DCE instead of CHCl ₃	22
12	DCM instead of CHCl ₃	32
13	toluene instead of CHCl ₃	19
14	1.0 equiv. of 2a instead of 1.5 equiv.	52
15	5 mol % of 4 instead of 20 mol %	<5
16	10 mol % of 4 instead of 20 mol %	55
17	15 mol % of 4 instead of 20 mol %	58
18	without 4	<5
19	without 5	<5

^a Standard Conditions: **1a** (0.25 mmol), **2a** (0.375 mmol), cat (20 mol %), base (0.5 equiv), **5** (1.0 equiv), solvent (2.0 mL), 30 °C, and 12 h. ^b Yield of chromatographically purified product is given.

3. General Procedure for the Synthesis of Pyrrolooxazolones

To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the 1*H*-pyrrole-2-carbaldehyde **1a** (0.5 mmol), oxidant **5** (0.5 mmol), triazolium salt **4** (36.3 mg, 0.1 mmol), and Cs₂CO₃ (81.5 mg, 0.25 mmol) was successively added. The mixture was kept under argon atmosphere and dry CHCl₃ (4.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon and stirred the reaction mixture. To this mixture 2,2,2-trifluoro-1-phenylethan-1-one **2a** (130.6 mg, 105 μL, 0.75 mmol) was added and stirred the reaction mixture at 30 °C for 12 h under argon atmosphere, the solvent was evaporated, and the crude residue was purified by flash column chromatography on silica gel to afford the corresponding pyrrolooxazolones.

Procedure for the Enantioselective Synthesis of 3-Phenyl-3-(trifluoromethyl)-1*H*, 3*H*-oxazolo[3,4-*a*]indol-1-one (3*aa*)

To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the nitrogen containing heterocyclic aldehyde **1d** (0.25 mmol), and oxidant **5** (0.25 mmol), chiral triazolium salt (11.7 mg, 0.025 mmol), and Cs₂CO₃ (40.7 mg, 0.125 mmol) were successively added. The mixture was kept under argon atmosphere and dry CHCl₃ (2.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon and stirred the reaction mixture. To this mixture trifluoroacetophenone **2a** (0.375 mmol) was added and stirred the reaction mixture at -5 °C for 12 h under argon atmosphere, then the solvent was evaporated, and the crude residue was purified by flash column chromatography on silica gel to afford the corresponding 3-phenyl-3-(trifluoromethyl)-1*H*, 3*H*-oxazolo[3,4-*a*]indol-1-one (**3aa**) (72% yield, 89:11 er). **HPLC** (Chiralpak IC, 99:1 Hexane / i-PrOH, 1.0 mL/min, 254 nm) Minor: 6.0 min, Major: 6.4 min.

4. X-Ray Data of 3q

Single crystal of **3q** (recrystallized from Methanol at 25 °C) was mounted and the diffraction data was collected at 298 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-K α radiation (71.073 pm). The structure was solved by direct methods using the SHELX-97⁶ and refined by full-matrix least-squares on F². Empirical absorption corrections were applied with SADABS.⁷ All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3.

⁶ G. M. SHELXL-2013 Sheldrick, University of Göttingen: Göttingen, Germany, **2014**.

⁷ G. M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany, **1999**.

Figure S1. ORTEP diagram of (**3q**) with an atomic crystallographic numbering. Thermal ellipsoids are scaled to the 50% probability level.

Table S1. Crystal data and structure refinement for **3q**.

Identification code	3q
CCDC	1920209
Empirical formula	C ₂₆ H ₁₂ Cl ₄ F ₆ N ₂ O ₄
Formula weight	672.18
Temperature/K	298K
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	15.0273(7)
b/Å	12.9985(5)
c/Å	15.5043(8)
α /°	90
β /°	115.722(6)
γ /°	90
Volume/Å ³	2728.4
Z	4
ρ_{calc} /mm ³	1.64
μ /mm ⁻¹	0.513
F(000)	1344.0
Crystal size/mm ³	0.1 × 0.2 × 0.3
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection	3.3 to 27.5
Index ranges	-19 ≤ h ≤ 19, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	47,069

Independent reflections	6244[R _{int} = 8.33, R _{sigma} = 5.12]
Data/restraints/parameters	6244/0/379
Goodness-of-fit on F ²	1.041
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.067, wR ₂ = 0.119
Final R indexes [all data]	R ₁ = 0.123, wR ₂ = 0.143
Largest diff. peak/hole / e Å ⁻³	0.225/-0.298

5. DFT Studies

All calculations were performed at the SMD_{Chloroform}/B3LYP/6-31G(d,p) level of theory using Gaussian 09, Rev. C.01 suite of quantum chemical program.^{8,9} For Cs, LANDL2DZ basis set was used.¹⁰ The solvent effects were taken into account by continuum solvation model (SMD) developed by Cramer and Truhlar.¹¹ The stationary points were characterized as minima or maxima (first order saddle point) by frequency calculation. For a transition state, only one unique imaginary frequency was obtained. The transition state was further verified by carrying out IRC (intrinsic reaction coordinate) calculations which enables the identification of the reactant and product connected to the transition state.¹²

The optimized geometries of intermediates discussed in the main text are provided in Figure S2.

⁸ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. 80 P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. Vincent Ortiz, J. Cioslowski, D. J. Fox. D. J. Gaussian09, Revision C.01; Gaussian, Inc.: Wallingford CT, 2009.

⁹ a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, 37, 785, b) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648.

¹⁰ P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, 82, 299.

¹¹ A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B.* **2009**, 113, 6378.

¹² C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, 94, 5523.

Figure S2. Optimized geometries and relative free energies (kcal/mol) of key intermediates. The energies of the protonated and deprotonated forms were evaluated by taking Cs_2CO_3 and $(\text{Cs}_2\text{HCO}_3)^+$.

Coordinates

E-E Sum of electronic and thermal Free Energies = -1408.278299				Z-E Sum of electronic and thermal Free Energies= -1408.270601			
6	-3.406814	-0.855300	0.273206	7	0.409512	3.732308	0.203870
6	-2.775695	-1.147046	-0.934496	6	-0.296676	4.235759	-0.804638
6	-1.389117	-1.119276	-1.012201	6	-0.525333	3.291862	-1.854292
6	-0.626982	-0.811661	0.114933	6	0.084930	2.121919	-1.442374
6	-1.267269	-0.529800	1.320538	6	0.660251	2.416171	-0.158659
6	-2.655378	-0.540457	1.401992	6	1.444495	1.566755	0.653795
7	0.788796	-0.830662	0.041405	8	2.070552	1.801321	1.702107
6	1.653752	0.191096	0.204194	6	1.627212	0.125423	0.189404
7	2.859956	-0.380800	0.104250	7	2.818450	-0.477050	0.101783
6	2.695901	-1.719229	-0.132923	6	2.623791	-1.808094	-0.155110
7	1.431848	-2.042187	-0.172905	7	1.353069	-2.097719	-0.227496
6	4.268939	0.032236	0.221689	7	0.737288	-0.870471	-0.009012
6	4.993182	-1.199238	-0.380613	6	4.233749	-0.103562	0.265875
6	4.020662	-2.405939	-0.223272	6	4.942393	-1.347399	-0.329632
6	1.460385	1.649156	0.602949	6	3.931941	-2.528591	-0.222151
6	0.548004	2.392566	-0.172714	6	-0.678588	-0.817220	0.075047
6	0.179636	3.763370	-0.025878	6	-1.458429	-1.125882	-1.040609
6	-0.708466	4.018229	-1.056002	6	-2.845101	-1.122989	-0.954372
6	-0.831831	2.791186	-1.782489	6	-3.459050	-0.813459	0.257616
7	-0.089140	1.815228	-1.266902	6	-2.691795	-0.503276	1.378022
9	-0.790314	-1.380324	-2.172805	6	-1.304619	-0.520702	1.287098

9	-0.546266	-0.234110	2.406056	9	-0.870656	-1.396648	-2.208416
9	-3.506118	-1.438782	-2.015512	9	-0.570229	-0.238185	2.364223
9	-3.265770	-0.267462	2.559087	9	-3.588008	-1.408730	-2.026692
9	-4.738326	-0.876471	0.347155	9	-3.287631	-0.212259	2.536280
8	2.188631	2.010948	1.545203	9	-4.788541	-0.806331	0.342703
1	4.073047	-3.111219	-1.054465	1	3.988815	-3.220762	-1.063936
1	4.204989	-2.962454	0.702453	1	4.074167	-3.106083	0.697870
1	5.949316	-1.376512	0.113070	1	5.875574	-1.558769	0.193558
1	4.491439	0.196400	1.278008	1	4.426495	0.042762	1.330797
1	4.440591	0.956689	-0.328955	1	4.446112	0.822202	-0.268548
1	0.531826	4.442154	0.740139	1	-0.640563	5.266892	-0.782311
1	-1.213092	4.951743	-1.276178	1	-1.062335	3.465210	-2.779317
1	-1.444371	2.621816	-2.663989	1	5.175382	-1.161941	-1.381157
1	5.184682	-1.022278	-1.441946	1	0.134281	1.189513	-1.990823
C Sum of electronic and thermal Free Energies = -1408.733565				D Sum of electronic and thermal Free Energies = -1408.703232			
6	-3.918494	-2.494961	0.608495	6	-3.972325	-2.479612	0.116306
6	-4.944777	-1.327156	0.512673	6	-4.977040	-1.307490	0.317388
6	-4.253902	-0.190481	-0.282878	6	-4.288564	-0.033805	-0.235062
6	-2.621023	-1.784532	0.408219	6	-2.667964	-1.755666	0.054217
6	-1.637796	0.067351	-0.239041	6	-1.660908	0.177782	-0.189246
1	-3.957915	-3.024024	1.562065	1	-4.002430	-3.214695	0.922343
1	-4.053864	-3.231685	-0.190565	1	-4.139327	-3.008931	-0.828185
1	-5.869785	-1.636764	0.025997	1	-5.925117	-1.490412	-0.188844
1	-4.446091	-0.232824	-1.357051	1	-4.519011	0.162593	-1.284324
7	-2.826940	-0.512774	-0.062529	7	-2.861781	-0.414728	-0.140091
7	-0.736930	-0.872672	0.114015	7	-0.770843	-0.828441	-0.053161
7	-1.345616	-2.045366	0.524715	7	-1.394263	-2.046564	0.106242
1	-4.479182	0.809034	0.087706	1	-4.478958	0.862357	0.354701
6	-1.443793	1.433209	-0.881875	6	-1.441071	1.614848	-0.402917
8	-2.006195	1.565264	-1.967914	8	-2.274748	2.078563	-1.347778
6	-0.330814	3.706773	-0.706914	6	-0.203779	3.747711	0.239540
6	0.387260	4.371767	0.293143	6	0.705076	3.960282	1.227483
1	-0.573252	4.066329	-1.696797	1	-0.579368	4.464600	-0.479099
6	0.453995	3.515648	1.393441	6	0.882473	2.677265	1.904252
1	0.815840	5.362205	0.240480	1	1.209706	4.885103	1.475193
1	0.906668	3.658238	2.364368	1	1.533666	2.495083	2.753588
6	-0.687947	2.444115	-0.208336	6	-0.551435	2.335579	0.335962
7	-0.182967	2.362849	1.085811	7	0.156171	1.720101	1.389141
6	0.683359	-0.825259	0.024702	6	0.646457	-0.796312	-0.142655
6	1.454327	-0.772917	1.188041	6	1.418736	-1.233025	0.934572
6	1.316133	-0.927900	-1.216976	6	1.273486	-0.384629	-1.318912
6	2.841197	-0.794377	1.116441	6	2.804462	-1.259838	0.836232
6	2.704637	-0.943158	-1.296533	6	2.660023	-0.394976	-1.417963
6	3.463175	-0.883715	-0.128788	6	3.423087	-0.839337	-0.340279
9	0.591360	-1.009082	-2.331715	9	0.540012	0.043673	-2.351700
9	3.308583	-1.028555	-2.481096	9	3.256576	0.008218	-2.541312
9	4.789918	-0.899944	-0.202060	9	4.750547	-0.855532	-0.431499
9	3.574387	-0.724245	2.227509	9	3.542888	-1.674671	1.867011
9	0.853830	-0.672695	2.378285	9	0.830245	-1.615003	2.065229
1	-0.312259	1.598702	1.735662	1	-5.177393	-1.176768	1.383341
1	-5.189339	-0.971340	1.516178	1	-2.215472	3.047179	-1.424482
E--2a (pre-reacting complex between E and 2a) Sum of electronic and thermal Free Energies = -2090.807931				TS(E-F) Sum of electronic and thermal Free Energies = -2090.783680			

6	2.290786	-0.663747	-1.367932	6	-3.947679	-1.946289	-0.924742
6	2.406195	0.213510	-0.288617	6	-3.450248	-0.839208	-0.222464
6	3.401386	-0.004123	0.664413	6	-4.224757	-0.289019	0.807861
6	4.260889	-1.091384	0.555624	6	-5.459290	-0.840114	1.143985
6	4.142411	-1.954801	-0.529496	6	-5.948765	-1.944053	0.441208
6	3.159430	-1.741226	-1.493065	6	-5.191235	-2.489901	-0.595714
7	1.550427	1.339275	-0.190958	6	-2.126194	-0.142364	-0.526230
6	0.687482	1.657452	0.796263	6	-1.501569	-0.460859	-1.910069
7	0.195581	2.845963	0.432423	9	-2.341191	-0.048251	-2.891185
6	0.751110	3.205559	-0.765343	8	-2.003455	1.065266	-0.187026
7	1.599943	2.306938	-1.184200	9	-0.342406	0.202114	-2.077400
6	-0.762843	3.829695	0.961774	9	-1.242054	-1.771376	-2.149105
6	-1.024968	4.694063	-0.298107	7	-0.911296	-1.144123	0.531387
6	0.223435	4.529653	-1.215302	6	-0.488538	-0.549061	1.709040
6	0.399960	1.012199	2.146433	6	-0.246841	-1.546581	2.675145
8	0.465715	1.803111	3.104377	6	-0.511538	-2.775260	2.057800
9	3.526720	0.827686	1.703042	6	-0.943124	-2.477435	0.758073
9	5.208321	-1.297140	1.475693	6	-0.203694	0.846097	1.892245
9	4.973321	-2.991873	-0.646734	8	-0.245260	1.456086	2.963400
9	3.047978	-2.578902	-2.529183	6	0.355304	1.680476	0.749540
9	1.346633	-0.478045	-2.288426	7	1.454523	1.472238	-0.009837
6	0.059624	-0.356203	2.123722	7	1.786729	2.588983	-0.766617
7	-0.087530	-1.027456	0.914370	6	0.872371	3.458416	-0.431356
6	-0.440483	-2.266008	1.251954	7	0.014571	2.947131	0.500821
6	-0.530874	-2.443587	2.668225	6	0.495484	4.861743	-0.780229
6	-0.216842	-1.216309	3.227337	6	-0.955994	4.947318	-0.218523
9	-1.426833	-1.198910	-1.903404	6	-1.072256	3.860532	0.883110
6	-2.028663	0.003051	-1.874504	6	2.305634	0.337883	-0.069436
9	-2.875726	0.059127	-2.932127	6	2.862261	-0.201247	1.094570
6	-2.822302	0.256752	-0.561959	6	3.717180	-1.295369	1.039323
8	-2.620964	1.313692	0.010906	6	4.066789	-1.834477	-0.194961
6	-3.818177	-0.744806	-0.124104	6	3.550983	-1.286510	-1.365582
6	-4.132235	-1.896520	-0.868496	6	2.680585	-0.203341	-1.304707
6	-5.096978	-2.784559	-0.399006	9	2.577017	0.332639	2.286269
6	-5.749875	-2.538366	0.810717	9	2.227879	0.312071	-2.445377
6	-5.440720	-1.396255	1.556774	9	3.896977	-1.797705	-2.550182
6	-4.482719	-0.503647	1.092166	9	4.898391	-2.874065	-0.256786
9	-1.093007	0.944774	-2.055479	9	4.226137	-1.806399	2.163234
1	-0.021582	4.542605	-2.278593	1	0.552126	5.052609	-1.853106
1	0.975073	5.305369	-1.031528	1	1.173448	5.559807	-0.276729
1	-1.210865	5.736406	-0.036293	1	-1.184917	5.938450	0.174805
1	-0.281897	4.377168	1.774999	1	-0.873339	4.237915	1.888558
1	-1.649998	3.320999	1.334590	1	-2.015618	3.317093	0.868619
1	-0.175914	-0.947039	4.274978	1	0.151010	-1.370776	3.665934
1	-0.793544	-3.357384	3.188431	1	-0.413834	-3.762544	2.490381
1	-0.634765	-3.017473	0.491836	1	-1.314362	-3.157420	0.003720
1	-1.904713	4.304660	-0.816136	1	-1.666519	4.723679	-1.017929
1	-4.228480	0.385193	1.659006	1	-3.842827	0.579375	1.332810
1	-3.635223	-2.105749	-1.807605	1	-3.379734	-2.388657	-1.733938
1	-5.946380	-1.207065	2.498674	1	-6.043116	-0.404493	1.950167
1	-5.337144	-3.671367	-0.977290	1	-5.566362	-3.342901	-1.154291
1	-6.498357	-3.236589	1.173950	1	-6.913902	-2.372049	0.697189
F Sum of electronic and thermal Free Energies = -2090.789306				TS(F-3a) Sum of electronic and thermal Free Energies = -2090.775555			
6	-2.732068	-0.155116	1.286122	6	4.265902	-0.232444	-1.564005
6	-2.344612	0.387528	0.056869	6	3.844358	-0.647175	-0.294379
6	-2.903921	-0.128966	-1.113971	6	4.713100	-1.408265	0.499995

6	-3.789068	-1.198433	-1.071865	6	5.983109	-1.743607	0.027893
6	-4.160517	-1.734664	0.157961	6	6.398518	-1.328506	-1.237529
6	-3.633231	-1.213495	1.336320	6	5.534636	-0.573045	-2.032009
7	-1.472691	1.503364	0.007398	6	2.413056	-0.293249	0.138856
6	-0.328693	1.668144	-0.693859	6	2.303731	0.059905	1.647107
7	0.018056	2.939783	-0.463440	9	1.081288	0.521063	1.958310
6	-0.883319	3.492931	0.402173	8	1.933245	0.812960	-0.586466
7	-1.828211	2.650475	0.715587	9	2.525844	-1.019467	2.435568
6	1.138582	3.827123	-0.810460	9	3.197314	1.009310	1.982260
6	0.982047	4.940780	0.258233	7	1.453250	-1.356959	-0.181172
6	-0.503551	4.901782	0.726476	6	0.518822	-0.951165	-1.094281
6	0.379285	0.778461	-1.699955	6	-0.229984	-2.047885	-1.468120
8	0.683312	1.335268	-2.751948	6	0.291041	-3.155322	-0.734448
9	-2.573342	0.397018	-2.298659	6	1.342490	-2.704939	0.046660
9	-4.295198	-1.697699	-2.202788	6	0.703506	0.490251	-1.386234
9	-5.018887	-2.753180	0.207339	8	0.577316	1.065285	-2.461290
9	-3.995123	-1.728906	2.514380	6	-0.598474	1.475969	-0.227514
9	-2.251837	0.335305	2.427319	7	-1.923752	1.388625	0.039622
6	0.380861	-0.688939	-1.519334	7	-2.530825	2.609453	0.385450
7	1.084989	-1.278543	-0.494583	6	-1.529934	3.437168	0.310397
6	0.955819	-2.639848	-0.586256	7	-0.369148	2.790756	-0.040335
6	0.142787	-2.926480	-1.669181	6	-1.295752	4.904763	0.475042
6	-0.208212	-1.691533	-2.274941	6	0.259412	4.972957	0.534877
6	2.029840	-0.402896	0.304651	6	0.781712	3.695876	-0.172332
8	1.860176	0.858326	-0.117172	6	-2.719558	0.219524	0.066165
6	3.478424	-0.918739	0.109059	6	-2.411008	-0.844011	0.917818
6	4.083610	-1.913790	0.888257	6	-3.211713	-1.980573	0.958383
6	5.391026	-2.326475	0.617108	6	-4.349398	-2.053310	0.160407
6	6.106480	-1.758474	-0.437004	6	-4.676941	-0.998188	-0.686823
6	5.507831	-0.766303	-1.217121	6	-3.862023	0.127557	-0.734101
6	4.207675	-0.346669	-0.940572	9	-1.329935	-0.788951	1.699335
6	1.567507	-0.498243	1.789874	9	-4.183294	1.123329	-1.563750
9	1.448931	-1.772492	2.256750	9	-5.765965	-1.075357	-1.459726
9	2.426222	0.144215	2.605799	9	-5.125576	-3.138782	0.203344
9	0.354841	0.073514	1.952313	9	-2.900108	-2.995267	1.771722
1	-0.627376	5.133174	1.785670	1	-1.776266	5.312740	1.366494
1	-1.133164	5.592096	0.153962	1	-1.694329	5.440349	-0.393851
1	1.261377	5.917221	-0.139518	1	0.649957	5.878210	0.067498
1	0.999107	4.184818	-1.832975	1	0.990090	3.846864	-1.234704
1	2.071171	3.270470	-0.737865	1	1.660332	3.259335	0.300417
1	-0.846170	-1.536523	-3.133818	1	-1.046993	-2.056980	-2.175699
1	-0.154011	-3.915687	-1.991588	1	-0.062385	-4.177142	-0.774064
1	1.467516	-3.298740	0.097817	1	2.002162	-3.229084	0.720440
1	1.633967	4.717994	1.106681	1	0.582420	4.965089	1.579305
1	3.739030	0.435042	-1.527592	1	3.596624	0.359047	-2.177482
1	3.551592	-2.369904	1.714310	1	4.416806	-1.739700	1.487294
1	6.056225	-0.313669	-2.038826	1	5.847405	-0.243500	-3.018568
1	5.847817	-3.094413	1.235354	1	6.647300	-2.329863	0.656194
1	7.122071	-2.082256	-0.646974	1	7.387957	-1.591061	-1.600693
2a Sum of electronic and thermal Free Energies = -682.541401				3a Sum of electronic and thermal Free Energies= -1004.799106			
6	2.344135	-1.434488	0.018417	6	1.893293	-1.008709	-1.101839
6	1.004048	-1.054470	0.028941	6	1.350977	-0.175422	-0.117263
6	0.662457	0.310027	0.014188	6	2.134460	0.190277	0.986942
6	1.682636	1.278954	-0.011955	6	3.442893	-0.278363	1.100223
6	3.017202	0.892705	-0.024121	6	3.981388	-1.110950	0.117785
6	3.349864	-0.466007	-0.009084	6	3.203801	-1.472806	-0.982176
1	2.603128	-2.488578	0.031212	6	-0.099080	0.282951	-0.240159

1	0.239277	-1.820932	0.051643	6	-0.279900	1.823101	-0.115420
1	1.406327	2.327759	-0.023127	9	-1.544267	2.171908	-0.403252
1	3.799024	1.645731	-0.045293	8	-0.644796	-0.061602	-1.510121
1	4.392921	-0.768543	-0.018286	9	-0.020851	2.243968	1.141611
6	-0.734388	0.799651	0.023770	9	0.538942	2.471020	-0.954616
8	-1.045746	1.976156	0.045050	7	-1.012217	-0.379242	0.695268
6	-1.891760	-0.237831	-0.008749	6	-2.044287	-0.997990	0.029351
9	-3.080128	0.372843	0.004343	6	-2.877421	-1.588016	0.966677
9	-1.824658	-0.999255	-1.123137	6	-2.310155	-1.298734	2.231808
9	-1.837422	-1.066469	1.058240	6	-1.153944	-0.546383	2.038699
				6	-1.843151	-0.797316	-1.387007
				8	-2.461068	-1.130733	-2.364531
				1	-3.773450	-2.155829	0.761230
				1	-2.694970	-1.606573	3.194354
				1	-0.451349	-0.137567	2.748180
				1	1.295402	-1.288082	-1.960766
				1	1.742100	0.845836	1.755051
				1	3.614407	-2.116788	-1.753994
				1	4.041057	0.012404	1.958537
				1	5.001568	-1.471943	0.208338
Free NHC				Cs₂CO₃			
Sum of electronic and thermal Free Energies= -1086.020880				Sum of electronic and thermal Free Energies= -303.695934			
6	-1.702926	0.760741	-0.995270	6	0.000000	0.000000	-1.273051
7	-0.940886	0.026670	-0.131318	8	0.000000	-1.125891	-1.913658
7	-1.638549	-0.760160	0.810850	8	0.000000	1.125891	-1.913658
6	-2.870377	-0.491907	0.499055	8	0.000000	0.000000	0.045682
7	-2.936075	0.398726	-0.549222	55	0.000000	3.020423	0.344467
6	-4.238961	-0.890590	0.953187	55	0.000000	-3.020423	0.344467
6	-5.123876	0.195570	0.272974				
6	-4.314027	0.705030	-0.947319				
6	0.469598	0.021932	-0.081954				
6	1.189555	1.209487	0.078596				
6	2.579994	1.204059	0.129481				
6	3.272664	0.000416	0.045285				
6	2.572858	-1.193392	-0.101047				
6	1.184035	-1.176803	-0.171812				
9	0.551965	2.378099	0.197662				
9	0.537578	-2.334745	-0.342498				
9	3.238057	-2.351586	-0.193713				
9	4.607916	-0.009291	0.102719				
9	3.252315	2.351733	0.282504				
1	-4.338998	-0.902851	2.040515				
1	-4.477087	-1.895428	0.585921				
1	-6.101289	-0.190214	-0.021892				
1	-4.558309	0.161194	-1.865277				
1	-4.433698	1.773814	-1.130231				
1	-5.283747	1.021679	0.971673				
Cs₂HCO₃⁺							
Sum of electronic and thermal Free Energies= -304.225952							
6	0.778773	-1.044203	0.000000				
8	0.122454	-2.293698	0.000000				
8	2.028413	-1.083725	0.000000				
8	0.000000	-0.060855	0.000000				
55	2.479311	1.984510	0.000000				
55	-2.892291	-1.316817	0.000000				
1	0.834358	-2.951679	0.000000				

6. Mechanistic Experiments

Control experiment

To an oven-dried Schlenk reaction vessel with a Teflon screw cap was taken the 1*H*-pyrrole-2-carbaldehyde **1a** (23.7 mg, 0.25 mmol), and oxidant **5** (102. mg, 0.25 mmol), and Cs_2CO_3 (40.7 mg, 0.125 mmol) was successively added. The mixture was kept under argon atmosphere and dry CHCl_3 (2.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon and stirred the reaction mixture. To this mixture, 2,2,2-trifluoro-1-phenylethan-1-one **2a** (5.36 mg, 53 μL , 0.375 mmol) was added and stirred the reaction mixture at 30 °C for 12 h under argon atmosphere. The solvent was evaporated, and the crude residue was analyzed by using ^1H NMR using CH_2Br_2 (18.0 μL , 0.25 mmol) as an internal standard. Based on the ^1H NMR studies, there is no background reaction or formation of hemiacetal intermediate in absence of carbene catalyst and both the starting materials were unreacted.

^1H -NMR of 1*H*-pyrrole-2-carbaldehyde in CDCl_3

^1H -NMR of 2,2,2-Trifluoro-1-phenylethan-1-one **2a** in CDCl_3

¹H-NMR of Kharasch Oxidant **5** in CDCl₃

¹H-NMR of Crude Reaction Mixture after 12 h in the absence of catalyst (CDCl₃)

¹H NMR analysis shows that the desired product **3a** was not formed indicating the role of NHC in this [6+2] annulation (Scheme 3, eq 6). Moreover, the acetal **10a** (likely formed by the addition N-H of **1a** to **2a** followed by intramolecular cyclization) was not observed under these conditions showing that the direct N-H addition of initially formed acylazolium and cyclization in a [3+2] pathway is not operating in this case.

Reaction using N-Boc aldehyde

To an oven-dried Schlenk reaction vessel with a Teflon screw cap was taken **4** (18.1 mg, 0.05 mmol), oxidant **5** (102.1 mg, 0.25 mmol), and Cs₂CO₃ (40.7 mg, 0.125 mmol) was successively added. The mixture was kept under argon atmosphere and dry CHCl₃ (2.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon and stirred

the reaction mixture. To this mixture, *tert*-butyl 2-formyl-1*H*-pyrrole-1-carboxylate **11a** (49. mg, 0.25 mmol) and 2,2,2-trifluoro-1-phenylethan-1-one **2a** (65.3 mg, 53 μ L, 0.375 mmol) was added and stirred the reaction mixture at 30 $^{\circ}$ C for 12 h under argon atmosphere, the solvent was evaporated, and the crude residue was subjected under 1 H NMR analysis using CH₂Br₂ (18.0 μ L, 0.25 mmol) as the internal standard.

1 H-NMR of Crude Reaction Mixture

Under these conditions, the desired product **3a** was not formed signifying the role of *N*-*H* moiety in forming the NHC-bound cross-conjugated aza-trienolates.

Studies towards the detection of NHC-aldehyde adduct using NMR

The reaction was set up as follows. 1*H*-pyrrole-2-carbaldehyde **1a** (5.9 mg, 0.0625 mmol), catalyst **4** (22.7 mg, 0.0625 mmol), Cs₂CO₃ (20.3 mg, 0.0625 mmol), oxidant **5** (25.5 mg, 0.0625 mmol), (ratio 1:1:1:1) were mixed in CDCl₃ (0.5 mL) in the presence of CH₂Br₂ as the internal standard in an NMR tube and the mixture was monitored at different time intervals

by ^1H NMR. Broad singlet was observed after 10 min at 9.86 ppm indicating that acylazolium (**B**) or azolium aza-trienol (**C**) intermediates may be present in the reaction mixture.

^1H -NMR of 1*H*-pyrrole-2-carbaldehyde **1** in CDCl_3

^1H -NMR of Kharasch Oxidant **5** in CDCl_3

^1H -NMR of Reaction Mixture after 10 min in CDCl_3

^1H NMR experiments were carried out at different time intervals. After 30 min, broad singlet was converted into two peaks at 9.78 ppm and 9.62 ppm, which is likely an indication of the formation of **B** and **C**.

¹H-NMR of Reaction Mixture after 30 min in CDCl₃

After time intervals at 60 min and 90 min, there was no change in the spectral pattern and both peaks were present in that region.

¹H-NMR of Reaction Mixture after 60 min in CDCl₃

¹H-NMR of Reaction Mixture after 90 min in CDCl₃

The HRMS data of the crude reaction mixture showed an intense peak at 369.0774 (M^+ of the acyl azolium **B** or the aza-trienol **C**). Notably, we cannot rule out the possibility of $(M+H)^+$ of the aza-trienolate formed from B/C (which is also having the same mass).

7. Synthesis and Characterization of Pyrrolooxazolones

3-Phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3a**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-phenylethan-1-one **2a** (130.6 mg, 105 μ L, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.3 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3a** as a light brown liquid (111 mg, 83% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 7.4 Hz, 2H), 7.54-7.46 (m, 3H), 7.34 (s, 1H), 6.91 (d, *J* = 3.8 Hz, 1H), 6.66 - 6.64 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.7, 131.4, 130.5, 129.2, 126.2, 121.7 (q, *J* = 287 Hz), 121.1, 120.5, 118.6, 111.0, 90.9 (q, *J* = 34.6 Hz). HRMS (ESI) calculated [M+H] for C₁₃H₉F₃NO₂: 268.0580, found: 268.0585. FTIR (cm⁻¹) 3137, 1818, 1548, 1451, 1191, 1083, 914.

3-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3b**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(*p*-tolyl)ethan-1-one **2b** (141.1 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3b** as a light yellow oil (88 mg, 62% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.6; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.30-7.28 (m, 3H), 6.91 (d, *J* = 3.7 Hz, 1H), 6.65 - 6.63 (m, 1H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.9, 141.7, 129.9, 127.6, 126.1, 121.7 (q, *J* = 287 Hz), 121.0, 120.6, 118.5, 110.9, 91.0 (q, *J* = 35 Hz), 21.3. HRMS (ESI) calculated [M+H] for C₁₄H₁₁F₃NO₂: 282.0742, found: 282.0742. FTIR (cm⁻¹) 3137, 2961, 2925, 2858, 1815, 1513, 1318, 1285, 1188, 1087, 1004.

3-([1,1'-Biphenyl]-4-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3c**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one **2c** (187.7 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 36 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-([1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3c** as a white solid (125 mg, 72% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.51; ¹H NMR (400 MHz, CDCl₃) δ 7.77-7.70 (m, 4H), 7.60-7.58 (m, 2H), 7.49-7.36 (m, 4H), 6.95 (d, *J* = 3.2 Hz, 1H), 6.68 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.8, 144.4, 139.6, 129.2, 129.1, 128.4, 127.9, 127.3, 126.8, 126.7, 121.7 (q, *J* = 286 Hz), 121.1, 120.6, 118.7, 111.1, 90.9 (q, *J* = 35 Hz). HRMS (ESI) calculated [M+H] for C₁₉H₁₃F₃NO₂: 344.0898, found: 344.0896, FTIR (cm⁻¹) 3583, 3136, 3032, 2922, 2852, 1812, 1610, 1547, 1316, 1190, 1086.

3-(4-Bromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3d**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-(4-bromophenyl)-2,2,2-trifluoroethan-1-one **2d** (189.8 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(4-bromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3d** as a light yellow oil (107 mg, 68% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.72; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.29 (s, 1H), 6.94 (d, *J* = 3.8 Hz, 1H), 6.67 - 6.66 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 156.3, 132.5, 129.5, 127.9, 126.2, 121.4 (q, *J* = 286 Hz), 120.9, 120.4, 118.9, 111.4, 90.4 (q, *J* = 34 Hz). HRMS (ESI) calculated [M+H] for C₁₃H₈BrF₃NO₂: 345.9690, found: 345.9683. FTIR (cm⁻¹) 3417, 2959, 2364, 1814, 1639, 1547, 1452, 1283, 1190, 1002, 909.

3-(4-Chlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3e**):

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-(4-chlorophenyl)-2,2,2-trifluoroethan-1-one **2e** (156.4 mg, 149 μ L, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(4-chlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3e** as a pale yellow liquid (109 mg, 72% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.66; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.30 (s, 1H), 6.94 (d, *J* = 3.8 Hz, 1H), 6.68 - 6.66 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.4, 137.9, 129.6, 129.1, 127.8, 121.5 (q, *J* = 287 Hz), 120.9, 120.5, 118.9, 111.3, 90.4 (q, *J* = 35 Hz). HRMS (ESI) calculated [M+H] for C₁₃H₈F₃NO₂Cl: 302.0196, found: 302.0198. FTIR (cm⁻¹) 3137, 2923, 1815, 1548, 1451, 1194, 1089, 953.

3-(4-Fluorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3f**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(4-fluorophenyl)ethan-1-one **2f** (144.1 mg, 105.2 μ L, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(4-fluorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3f** as a light yellow oil (99 mg, 74% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.63; ¹H NMR (400 MHz, CDCl₃) δ 7.70-7.67 (m, 2H), 7.31 (s, 1H), 7.21-7.16 (m, 2H), 6.94 (d, *J* = 3.8 Hz, 1H), 6.68-6.66 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 164.3 (d, *J* = 253.2 Hz), 156.5, 128.6 (dd, *J* = 8.8, 1.5 Hz), 126.5 (d, *J* = 3.3 Hz), 121.6 (q, *J* = 287 Hz), 121.0, 120.5, 118.9, 116.5 (d, *J* = 22.29), 111.3, 90.5 (q, *J* = 35 Hz). HRMS (ESI) calculated [M+H] for C₁₃H₈F₄NO₂: 286.0491, found: 286.0493. FTIR (cm⁻¹) 3590, 3137, 2332, 1819, 1548, 1606, 1513, 1285, 1193, 1084, 956.

3-(4-Nitrophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3g**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(4-nitrophenyl)ethan-1-one **2g** (164.3 mg, 0.75 mmol) with

triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 36 h followed by

flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(4-nitrophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3g** as a pale yellow liquid (54 mg, 35% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.42; ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.37 (s, 1H), 6.98 (d, *J* = 3.6 Hz, 1H), 6.73 - 6.71 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 155.8, 149.7, 136.8, 127.8, 124.4, 121.3 (q, *J* = 287 Hz), 121.1, 120.2, 119.5, 112.0, 89.9 (q, *J* = 35.1 Hz). HRMS (ESI) calculated [M+H] for C₁₃H₈F₃N₂O₄: 313.0436, found: 313.0429. FTIR (cm⁻¹) 3135, 2923, 2363, 2330, 1817, 1530, 1194, 1006, 951, 850.

4-(1-Oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)benzonitrile (**3h**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 4-(2,2,2-trifluoroacetyl)benzonitrile **2h** (130.5 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction

mixture at 30 °C for 36 h followed by flash column chromatography (hexane-EtOAc: 98:3 to 90:15) to afford 4-(1-oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)benzonitrile **3h** as a pale yellow liquid (48 mg, 32% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.32; ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.80 (m, 4H), 7.34 (s, 1H), 6.97 (d, *J* = 3.8 Hz, 1H), 6.71 - 6.69 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 155.7, 135.1, 133.0, 127.3, 122.0 (q, *J* = 287 Hz), 121.0, 120.2, 119.4, 117.5, 115.7, 111.9, 89.9 (q, *J* = 35.5 Hz). FTIR (cm⁻¹) 3136, 2923, 2235, 1819, 1549, 1451, 1188, 1085, 952, 910.

3-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3i**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(4-(trifluoromethyl)phenyl)ethan-1-one **2i** (182 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 36 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford

3-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3i** as a yellow liquid (104 mg, 62% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.61; ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.84 (m, 2H), 7.79-7.77 (m, 2H), 7.34 (d, *J* = 1.6 Hz, 1H), 6.96 (d, *J* = 3.9 Hz, 1H), 6.70 - 6.68 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.1, 134.4, 133.7 (q, *J* = 33 Hz), 127.1, 127.0, 126.4 (q, *J* = 3.8 Hz), 123.5 (q, *J* = 273 Hz), 122.9, 121.5 (q, *J* = 285 Hz), 121.0, 120.4, 119.2, 111.6, 90.2 (q, *J* = 34.6 Hz). HRMS (ESI) calculated [M+H] for C₁₄H₈F₆NO₂: 336.0459, found: 336.0468. FTIR (cm⁻¹) 3450, 2922, 1817, 1631, 1548, 1377, 1325, 1202, 1085, 910.

Methyl-4-(1-oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)benzoate (**3j**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and methyl 4-(2,2,2-trifluoroacetyl)benzoate **2j** (174.02 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.3 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 36 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford methyl-4-(1-oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)benzoate **3j** as a pale yellow liquid (65 mg, 40% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.45; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 9.6 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.38 (s, 1H), 6.97 (d, *J* = 3.8 Hz, 1H), 6.71 - 6.69 (m, 1H), 3.97 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 156.3, 134.7, 133.0, 130.3, 126.4, 121.5 (q, *J* = 286 Hz), 121.0, 120.4, 119.0, 111.4, 90.4 (q, *J* = 35 Hz), 52.6. HRMS (ESI) calculated [M+Na] for C₁₅H₁₀F₃NO₄Na: 348.0460, found: 348.0462. FTIR (cm⁻¹) 3135, 2957, 2329, 1816, 1728, 1548, 1447, 1283, 1193, 1084, 1006, 910.

3-(3-Methoxyphenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3k**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(3-methoxyphenyl)ethan-1-one **2k** (153.07 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(3-methoxyphenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3k** as a pale yellow liquid (82 mg, 55% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.53; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (t, J = 7.9 Hz, 2H), 7.32 (s, 1H), 7.27-7.25 (m, 1H), 7.21 (s, 1H), 7.04 (dd, J = 8.3 Hz, J = 2.3 Hz, 1H), 6.92 (d, J = 3.8 Hz, 1H), 6.65 - 6.63 (m, 1H), 3.83 (s, 3H) ^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 156.7, 131.9, 130.4, 121.6 (q, J = 287 Hz), 121.1, 120.5, 118.6, 118.1, 116.5, 112.5, 111.1, 90.7 (q, J = 34.6 Hz), 55.6. **HRMS (ESI)** calculated $[\text{M}+\text{Na}]$ for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{NO}_3\text{Na}$: 320.0510, found: 320.0510. **FTIR** (cm^{-1}) 3136, 2963, 2840, 2328, 1813, 1606, 1548, 1453, 1188, 1086, 973, 914.

3-(*m*-Tolyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3l**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-phenylethan-1-one **2l** (141.1 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs_2CO_3 (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl_3 (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(*m*-tolyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3l** as a light yellow oil (108 mg, 76% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.57; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (bs, 2H), 7.39-7.34 (m, 3H), 6.91 (d, J = 3.8 Hz, 1H), 6.65 - 6.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.9, 139.3, 132.1, 130.4, 129.1, 126.8, 123.2, 121.7 (q, J = 286.5 Hz), 121.1, 120.5, 118.6, 111.0, 90.9 (q, J = 34.4 Hz), 21.6. **HRMS (ESI)** calculated $[\text{M}+\text{H}]$ for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NO}_2$: 282.0742, found: 282.0745 **FTIR** (cm^{-1}) 3137, 2923, 2856, 2384, 1789, 1548, 1452, 1288, 1180, 1086, 879.

3-(3-Bromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3m**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-(3-bromophenyl)-2,2,2-trifluoroethan-1-one **2m** (190 mg, 116.0 μL , 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs_2CO_3 (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl_3 (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(3-bromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3m** as a pale yellow liquid (109 mg, 69% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.70; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (s, 1H), 7.68-7.64 (m, 2H), 7.40-7.34 (m, 2H), 6.94 (d, J = 3.8 Hz, 1H), 6.68 - 6.67 (m, 1H). ^{13}C NMR (100 MHz,

CDCl₃) δ 156.2, 134.6, 132.6, 130.8, 129.4 (q, J = 1.6 Hz), 124.9, 124.9, 123.4, 121.5 (q, J = 287 Hz), 121.1, 120.3, 119.0, 90.0 (q, J = 34.8 Hz). **HRMS (ESI)** calculated [M+H] for C₁₃H₈BrF₃NO₂: 345.9691, found: 345.9691. **FTIR (cm⁻¹)** 3584, 3137, 2925, 1820, 1547, 1452, 1279, 1197, 1083, 1006, 913.

3-(3-Chlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3n**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-(3-chlorophenyl)-2,2,2-trifluoroethan-1-one **2n** (156.4 mg, 112.0 μ L, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(3-chlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3n** as a pale yellow liquid (101 mg, 67% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.50; **¹H NMR (400 MHz, CDCl₃)** δ 7.67 (s, 1H), 7.61-7.59 (m, 1H), 7.53-7.51 (m, 1H), 7.47-7.43 (m, 1H), 7.33 (s, 1H), 6.95-6.94 (m, 1H), 6.68 - 6.67 (m, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ 156.3, 135.5, 132.5, 131.7, 130.6, 126.7, 124.5, 121.5 (q, J = 287 Hz), 121.0, 120.4, 119.0, 111.5, 90.2 (q, J = 35.3 Hz). **HRMS (ESI)** calculated [M+H] for C₁₃H₈ClF₃NO₂: 302.0196, found: 302.0197. **FTIR (cm⁻¹)** 3583, 3420, 2924, 2690, 1817, 1547, 1422, 1194, 1082, 913.

3-(3-Nitrophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3o**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(3-nitrophenyl)ethan-1-one **2o** (164.2 mg, 105 μ L, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), **5** oxidant (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 36 h followed by flash column chromatography (hexane-EtOAc: 97:3 to 85:15) to afford 3-(3-nitrophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3o** as a pale yellow liquid (49 mg, 31% yield).

R_f (Pet. ether / EtOAc = 10/90): 0.43; **¹H NMR (400 MHz, CDCl₃)** δ 8.57 (s, 1H), 8.42 (d, 8.44 Hz, 1H), 8.08, d, 7.59 Hz, 1H), (7.75, t, 8.17 Hz, 1H), 7.41 (bs, 1H), 6.98, d, 4.25 Hz, 1H), 6.74-6.72 (m, 1H). **¹³C NMR (125 MHz, CDCl₃)** δ 155.8, 148.6, 132.7, 132.4, 130.7, 126.3, 121.6, 121.3 (q, J = 35 Hz), 121.0, 120.3, 119.5, 112.0, 89.8 (q, J = 35 Hz). **HRMS (ESI)**

calculated [M+H] for C₁₃H₈F₃N₂O₄: 313.0436, found: 313.0432. **FTIR** (cm⁻¹) 2958, 2921, 2849, 1818, 1537, 1457, 1352, 1195, 1088, 1015, 911.

3-(Naphthalen-2-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3p**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-one **2p** (168.1 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:5) to afford 3-(naphthalen-2-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3p**) as a pale yellow solid (91 mg, 57% yield).

R_f(Pet. ether / EtOAc = 95/5): 0.45; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.93-7.88 (m, 2H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.63-7.56 (m, 2H), 7.41 (s, 1H), 6.97 (d, *J* = 4.0 Hz, 1H), 6.69-6.68 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.8, 134.2, 132.5, 129.4, 128.9, 128.2, 127.8, 127.5, 127.4, 126.8, 122.3, 121.8 (q, *J* = 286 Hz), 121.2, 118.7, 111.2, 91.1 (q, *J* = 34 Hz). **HRMS (ESI)** calculated [M+H] for C₁₇H₁₁F₃NO₂: 318.0742, found: 318.0742. **FTIR** (cm⁻¹) 3137, 3063, 2924, 2328, 1812, 1547, 1450, 1315, 1184, 1092, 911.

3-(3,4-Dichlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3q**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-(3,4-dichlorophenyl)-2,2,2-trifluoroethan-1-one **2q** (182.2 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(3,4-dichlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3q** as a white solid (124 mg, 75% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (s, 1H), 7.59-7.53 (m, 2H), 7.32 (s, 1H), 6.95 (d, *J* = 3.5 Hz, 1H), 6.69 - 6.68 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 136.3, 134.0, 131.4, 130.5, 128.5, 125.5, 121.3 (q, *J* = 287.3 Hz), 121.0, 120.2, 119.2, 111.7, 89.7 (q, *J* = 35.2 Hz). **HRMS (ESI)** calculated [M+H] for C₁₃H₇Cl₂F₃NO₂: 335.9806, found: 335.9804. **FTIR** (cm⁻¹) 3146, 3078, 2920, 1811, 1546, 1317, 1184, 1092, 972, 892.

3-(3,5-Dibromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3r**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde (47.6 mg, 0.5 mmol) and 1-(3,5-dibromophenyl)-2,2,2-trifluoroethan-1-one **2r** (248 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃

(4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(3,5-dibromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3r** as a white solid (77 mg, 37% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.65; ¹H NMR (400 MHz, CDCl₃) δ 7.84-7.83 (m, 1H), 7.77-7.76 (m, 2H), 7.33-7.32 (m, 1H), 6.97-6.96 (m, 1H), 6.70-6.69 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 155.8, 137.3, 134.2, 128.3, 124.0, 121.3 (q, *J* = 286 Hz), 121.0, 120.2, 119.4, 111.9, 89.3 (q, *J* = 34.6 Hz). HRMS (ESI) calculated [M+H] for C₁₃H₇Br₂F₃NO₂: 423.8795, found: 423.8799. FTIR (cm⁻¹) 3139, 3087, 1810, 1647, 1557, 1375, 1195, 1087, 1031, 870.

3-(Pyren-1-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3s**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(pyren-1-yl)ethan-1-one **2s** (224 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 24 h followed by flash column chromatography (hexane-

EtOAc: 98:2 to 90:10) to afford 3-(pyren-1-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3s** as a pale yellow solid (53 mg, 27% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.52; ¹H NMR (400 MHz, CDCl₃) δ 8.68-8.66 (m, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 8.30-8.18 (m, 5H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.07 (d, *J* = 3.8 Hz, 1H), 6.79 - 6.78 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.9, 133.9, 131.3, 130.6, 130.3, 130.0, 129.2, 127.0, 126.9, 126.6, 126.5, 125.9, 124.7, 124.3, 124.1, 124.0, 123.4, 122.4 (q, *J* = 288 Hz), 121.5, 121.1, 118.7, 111.5, 94.2 (q, *J* = 35.2 Hz). HRMS (ESI) calculated [M+H] for C₂₃H₁₃F₃NO₂: 392.0898, found: 392.0897. FTIR (cm⁻¹) 3138, 3047, 2922, 2851, 1797, 1551, 1376, 1305, 1184, 1083, 1005, 948.

3-(1*H*-Indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3t**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-(1*H*-indol-3-yl)ethan-1-one **2t** (160 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by

3t

flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(1*H*-indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3t** as a white solid (99 mg, 65% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 9.81 (s, 1H), 8.63 (d, *J* = 1.4 Hz, 1H), 8.43-8.39 (m, 1H), 8.28-8.25 (m, 1H), 7.51-7.46 (m, 2H), 7.28 (s, 1H), 6.94 (s, 1H), 6.50 - 6.48 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 176.2 (q, *J* = 36 Hz), 159.5, 136.3, 136.2, 127.2, 127.1, 126.7, 125.9, 123.6, 122.5, 119.2, 116.7 (q, *J* = 290.7 Hz) 115.4, 113.4, 112.3. HRMS (ESI) calculated [M+H] for C₁₅H₁₀F₃N₂O₂: 307.0694, found: 307.0693. FTIR (cm⁻¹) 3317, 3157, 1659, 1530, 1430, 1354, 1273, 1177, 1050, 955, 877, 830.

3-(6-Bromo-1*H*-indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3u**)

3u

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-(6-bromo-1*H*-indol-3-yl)-2,2,2-trifluoroethan-1-one **2u** (219.0 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(6-bromo-1*H*-indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3u** as a white solid (98mg, 51% yield).

R_f(Pet. ether / EtOAc = 90/10): 0.72; ¹H NMR (400 MHz, CDCl₃) δ 9.80 (s, 1H), 8.60-8.59 (m, 1H), 8.47-8.46 (m, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J_l* = 8.5 Hz, *J_f* = 1.8 Hz, 1H), 7.32-7.30 (m, 1H), 6.95-6.93 (m, 1H), 6.52 - 6.50 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 176.1 (q, *J* = 36 Hz), 158.9, 136.8, 129.2, 127.2, 126.0, 123.6, 123.3, 120.5, 119.2, 119.1, 118.7, 116.6 (q, *J* = 291 Hz), 113.2, 112.6. HRMS (ESI) calculated [M+H] for C₁₅H₉BrF₃N₂O₂: 384.9800, found: 384.9807. FTIR (cm⁻¹) 3784, 3581, 3432, 3334, 3106, 2920, 1917, 1697, 1391, 1360, 1131, 1052.

3-(6-Chloro-1*H*-indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3v**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-(6-Chloro-1*H*-indol-3-yl)-2,2,2-trifluoroethan-1-one **2v** (186.0 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), **5** oxidant (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(6-chloro-1*H*-indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3v** as a white solid (104 mg, 60 % yield).

R_f (Pet. ether / EtOAc = 90/10): 0.52; ¹H NMR (400 MHz, CDCl₃) δ 9.78 (s, 1H), 8.60 (d, *J* = 1.2 Hz, 1H), 8.32-8.30 (m, 2H), 7.44 (d, *J*₁ = 8.4 Hz, *J*₁ = 1.6 Hz, 1H), 7.30 (s, 1H), 6.93 (s, 1H), 6.51 - 6.49 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 176.1 (q, *J* = 36.8 Hz), 159.0, 136.6, 136.3, 132.8, 127.2, 126.6, 125.6, 123.3, 123.2, 119.1, 116.6 (q, *J* = 290 Hz), 115.8, 113.2, 112.5. HRMS (ESI) calculated [M+H] for C₁₅H₉ClF₃N₂O₂: 341.0305, found: 341.0308 FTIR (cm⁻¹) 3450, 2920, 2847, 1647, 1535, 1418, 1272, 1101, 855.

Methyl-3-(1-oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)-1*H*-indole-6-carboxylate (**3w**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and methyl 3-(2,2,2-trifluoroacetyl)-1*H*-indole-6-carboxylate **2w** (203.4 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford methyl-3-(1-oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)-1*H*-indole-6-carboxylate **3w** as a white solid (102 mg, 56% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.48; ¹H NMR (400 MHz, CDCl₃) δ 9.84 (s, 1H), 8.93 (s, 1H), 8.72 (d, *J* = 1.6 Hz, 1H), 8.45 (d, *J* = 8.5 Hz, 1H), 7.17-7.14 (m, 1H), 7.34-7.32 (m, 1H), 6.95 - 6.94 (m, 1H), 6.52 - 6.50 (m, 1H), 3.97 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.0 (q, *J* = 35.7 Hz), 167.0, 158.8, 138.0 (q, *J* = 5.0 Hz), 135.8, 130.7, 128.5, 127.4, 126.9, 123.4, 122.3, 119.3, 117.3, 116.6 (q, *J* = 289.1 Hz), 113.0, 112.6, 52.6. HRMS (ESI) calculated [M+H] for C₁₇H₁₂F₃N₂O₄: 365.0749, found: 365.0752. FTIR (cm⁻¹) 3794, 3731, 3583, 3320, 2920, 2850, 2558, 2328, 1934, 1698, 1533, 1252, 1138, 848.

3-(Benzofuran-2-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3x**)

Following the general procedure, treatment of 1*H*-pyrrole-2-carbaldehyde **1a** (47.6 mg, 0.5 mmol) and 1-(benzofuran-2-yl)-2,2,2-trifluoroethan-1-one **2x** (160.6 mg, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-(benzofuran-2-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3x** as a light yellow oil (106 mg, 68% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.61; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.34-7.30 (m, 2H), 7.19 (s, 1H), 6.98 (d, *J* = 3.5 Hz, 1H), 6.67 - 6.65 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 155.7, 144.6, 126.9, 126.5, 124.2, 122.4, 121.4, 121.0 (q, *J* = 286.6 Hz), 119.6, 118.8, 112.1, 111.7, 109.6, 86.9 (q, *J* = 36.3 Hz). HRMS (ESI) calculated [M+H] for C₁₅H₉F₃NO₃: 308.0535, found: 308.0534. FTIR (cm⁻¹) 3133, 1813, 1615, 1546, 1451, 1378, 1308, 1274, 1199, 1082, 985, 910.

6-Bromo-3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3y**)

Following the general procedure, treatment of 4-bromo-1*H*-pyrrole-2-carbaldehyde **1b** (86.9 mg, 0.5 mmol) and 2,2,2-trifluoro-1-phenylethan-1-one **2a** (130.6 mg, 105 μL, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 14 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 6-Bromo-3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3y** as a pale yellow liquid (67 mg, 39% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.66; ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.45 Hz, 2H), 7.58-7.49 (m, 3H), 7.35 (s, 1H), 6.95 (d, *J* = 1.2 Hz, 1H), ¹³C NMR (100 MHz, CDCl₃) δ 156.6, 131.8, 129.8, 129.4, 126.1, 121.4 (q, *J* = 285 Hz), 120.7, 120.3, 113.0, 105.4, 91.4 (q, *J* = 34.5 Hz). HRMS (ESI) calculated [M+H] for C₁₃H₈BrF₃NO₂: 345.9691, found: 345.9691. FTIR (cm⁻¹) 3137, 2959, 2920, 2859, 1805, 1599, 1544, 1322, 1202, 1107, 1019, 953, 876.

6-Iodo-3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (**3z**)

Following the general procedure, treatment of 4-Iodo-1*H*-pyrrole-2-carbaldehyde **1c** (110.0 mg, 0.5 mmol) and 2,2,2-trifluoro-1-phenylethan-1-one **2a** (130.6 mg, 105 μL, 0.75 mmol)

with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), **5** oxidant (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 36 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 6-Iodo-3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one **3z** as a pale yellow liquid (36 mg, 18% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.72; ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.57-7.49 (m, 3H), 7.39 (s, 1H), 7.03 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.9, 131.6, 129.9, 129.4, 126.1, 124.9, 121.8, 121.5 (q, *J* = 287 Hz), 117.6, 91.1 (q, *J* = 35 Hz), 70.0. HRMS (ESI) calculated [M+H] for C₁₃H₈F₃NO₂I: 393.9552, found: 393.9547. FTIR (cm⁻¹) 3137, 2924, 1794, 1548, 1452, 1147, 1083, 914.

3-Phenyl-3-(trifluoromethyl)-1*H*,3*H*-oxazolo[3,4-*a*]indol-1-one (**3aa**)

Following the general procedure, treatment of 1*H*-indole-2-carbaldehyde **1d** (72.6 mg, 0.5 mmol) and 2,2,2-trifluoro-1-phenylethan-1-one **2a** (130.6 mg, 105 μL, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column

chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-oxazolo[3,4-*a*]indol-1-one **3aa** as a white solid (114mg, 72% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.83; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.55-7.41 (m, 4H), 7.34-7.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.0, 134.0, 133.2, 131.6, 130.2, 129.4, 127.1, 124.8, 124.6, 122.9, 122.4 (q, *J* = 288.2 Hz), 112.7, 112.6, 104.7, 92.4 (q, *J* = 34.4 Hz). HRMS (ESI) calculated [M+H] for C₁₇H₁₁F₃NO₂: 318.0742, found: 318.0745. FTIR (cm⁻¹) 3449, 3066, 2925, 2854, 1812, 1648, 1615, 1349, 1197, 1011, 950.

3-Phenyl-9-(phenylethynyl)-3-(trifluoromethyl)-1*H*,3*H*-oxazolo[3,4-*a*]indol-1-one (**3ab**)

Following the general procedure, treatment of 3-(phenylethynyl)-1*H*-indole-2-carbaldehyde **1e** (122.64 mg, 0.5 mmol) and 2,2,2-trifluoro-1-phenylethan-1-one **2a** (130.6 mg, 105 μL, 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs₂CO₃ (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl₃ (4.0 mL) and stirring the reaction mixture at 30 °C for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 3-phenyl-9-(phenylethynyl)-3-(trifluoromethyl)-1*H*,3*H*-oxazolo[3,4-*a*]indol-1-one **3ab** as a light yellow oil (89 mg, 43% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.68; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 7.86 Hz, 1H), 7.69-7.66 (m, 2H), 7.64-7.62 (m, 2H), 7.57-7.53 (m, 1H), 7.51-7.46 (m, 3H), 7.42-7.40

(m, 4H), 7.33-7.31 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.5, 134.1, 133.2, 132.0, 131.7, 129.8, 129.4, 129.1, 128.6, 127.9, 127.0, 124.9, 123.5, 123.4, 122.8, 122.2 (q, J = 287.4 Hz), 112.7, 101.6, 98.8, 92.3 (q, J = 35.35 Hz), 78.7. HRMS (ESI) calculated $[M+H]$ for $\text{C}_{25}\text{H}_{14}\text{F}_3\text{NO}_2\text{Na}$: 440.0874, found: 440.0878. FTIR (cm^{-1}) 3584, 3065, 2960, 2923, 2852, 2212, 1808, 1577, 1491, 1444, 1392, 1360, 1194, 1106, 998, 950, 873.

9-Iodo-3-phenyl-3-(trifluoromethyl)-1H,3H-oxazolo[3,4-a]indol-1-one (3ac)

Following the general procedure, treatment of 3-Iodo-1H-indole-2-carbaldehyde **1f** (135 mg, 0.5 mmol) and 2,2,2-trifluoro-1-phenylethan-1-one **2a** (130.6 mg, 105 μL , 0.75 mmol) with triazolium salt **4** (36.3 mg, 0.1 mmol), Cs_2CO_3 (81.5 mg, 0.25 mmol), oxidant **5** (204.31 mg, 0.5 mmol) in CHCl_3 (4.0 mL) and stirring the reaction mixture at 30 $^\circ\text{C}$ for 12 h followed by flash column chromatography (hexane-EtOAc: 98:2 to 90:10) to afford 9-iodo-3-phenyl-3-(trifluoromethyl)-1H,3H-oxazolo[3,4-a]indol-1-one **3ac** as a white solid (112 mg, 51% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.59; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 8.3 Hz, 1H), 7.61-7.52 (m, 3H), 7.49-7.45 (m, 3H), 7.39 (t, J = 7.3 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 157.2, 136.0, 134.2, 131.7, 129.6, 129.4, 128.2, 127, 125.7, 124.7, 123.6, 122.0 (q, J = 288 Hz), 112.8, 92.1 (q, J = 34 Hz), 61.2; HRMS (ESI) calculated $[M+H]$ for $\text{C}_{17}\text{H}_9\text{F}_3\text{NO}_2\text{INa}$: 465.9528, found: 465.9524. FTIR (cm^{-1}) 3585, 3064, 2924, 1811, 1610, 1561, 1363, 1191, 1102, 955.

8. ^1H and ^{13}C NMR Spectra of Pyrrolooxazolones.

3-Phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3a)

3-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3b)

3-([1,1'-Biphenyl]-4-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3c)

3-(4-Bromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3d)

3-(4-Chlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3e):

3-(4-Fluorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3f)

3-(4-Nitrophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3g)

4-(1-Oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)benzonitrile (3h)

3-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one
(3i)

Methyl-4-(1-oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)benzoate (3j)

3-(3-Methoxyphenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3k)

3-(m-Tolyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3I)

3-(3-Bromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3m)

3-(3-Chlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3n)

3-(3-Nitrophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3o)

3-(Naphthalen-2-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3p)

3-(3,4-Dichlorophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3q)

3-(3,5-Dibromophenyl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3r)

3-(Pyren-1-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3s)

3-(1*H*-Indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3t)

3-(6-Bromo-1*H*-indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3u)

3-(6-Chloro-1*H*-indol-3-yl)-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3v)

Methyl-3-(1-oxo-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-yl)-1*H*-indole-6-carboxylate (3w)

Chemical structure of **3x** is shown. The ¹H NMR spectrum (CDCl₃) displays peaks in the aromatic region (6.5–7.7 ppm) and a trifluoromethyl singlet (~7.3 ppm). The inset provides a detailed view of the aromatic signals with their corresponding chemical shifts and integrations.

Chemical Shift (ppm)	Integration
7.66	1.01
7.64	1.00
7.54	1.05
7.52	2.02
7.44	0.98
7.42	0.97
7.40	1.00
7.34	1.00
7.32	1.00
7.30	1.00
7.26	1.00
7.19	1.00
6.98	1.00
6.97	1.00
6.67	1.00
6.66	1.00
6.65	1.00

6-Bromo-3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3y)

6-Iodo-3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-1-one (3z)

3-Phenyl-3-(trifluoromethyl)-1*H*,3*H*-oxazolo[3,4-*a*]indol-1-one (3aa)

3-phenyl-9-(phenylethynyl)-3-(trifluoromethyl)-1*H*,3*H*-oxazolo[3,4-*a*]indol-1-one (3ab)

9-Iodo-3-phenyl-3-(trifluoromethyl)-1*H*,3*H*-oxazolo[3,4-*a*]indol-1-one (3ac)

9. HPLC Data of 3aa

3-Phenyl-3-(trifluoromethyl)-1*H*, 3*H*-oxazolo[3,4-*a*]indol-1-one (3aa)

Sample Info : CHIRALPAK IC, 1 %IPA-HEXANE, 1 mL -min, 254nm