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Aluminium oxide-mediated cross-coupling of pyrroles with 1-bromo-2-(trifluoroacetyl)acetylene: a quantum-chemical insight

Denis N. Tomilin, Dmitri Yu. Soshnikov, Alexander B. Trofimov, Maxim D. Gotsko, Lyubov N. Sobenina, Igor A. Ushakov, Andrey V. Afonin, Andrey B. Koldobsky, Nadezhda M. Vitkovskaya and Boris A. Trofimov

Details of quantum-chemical calculations.

The ground-state equilibrium molecular structures of **4a** were obtained by means of the full geometry optimization carried out using second-order Møller-Plesset perturbation theory (MP2) and cc-pVTZ basis set.[1-3] The located structures are the minima of potential energy surfaces, which was confirmed by the positive eigenvalues of the corresponding Hessians. The vertical ionization potentials (IPs) and the probabilities of the corresponding ionization events, the pole strengths (P), were calculated using the outer-valence Green's function (OVGF) method[4] and cc-pVTZ basis set. The above calculations were performed using the Gaussian 09 suite of programs.[5] The natural bond orbital (NBO) analysis[6, 7] and the Wiberg bond indices (WBI)[8] evaluation were performed using the NBO 6.0 program[9, 10] linked to the GAMESS suite of quantum-chemical programs[11, 12] The Hartree–Fock (HF) electronic wavefunctions obtained using cc-pVDZ basis set[1-3] were used in these calculations. The analysis of the electron density $\rho(\boldsymbol{r})$ distribution within the framework of the "atoms-in-molecules" (AIM) approach[13] was carried out using the AIMall program[14] 20 for $\rho(\boldsymbol{r})$ obtained at the MP2(full)/cc-pVTZ level of theory using Gaussian 09 program. The results of the quantum-chemical calculations are presented at length as Supporting Information, where the results obtained for CH_3-substituted analogue of **4a** (**5a**) are also shown for comparison.

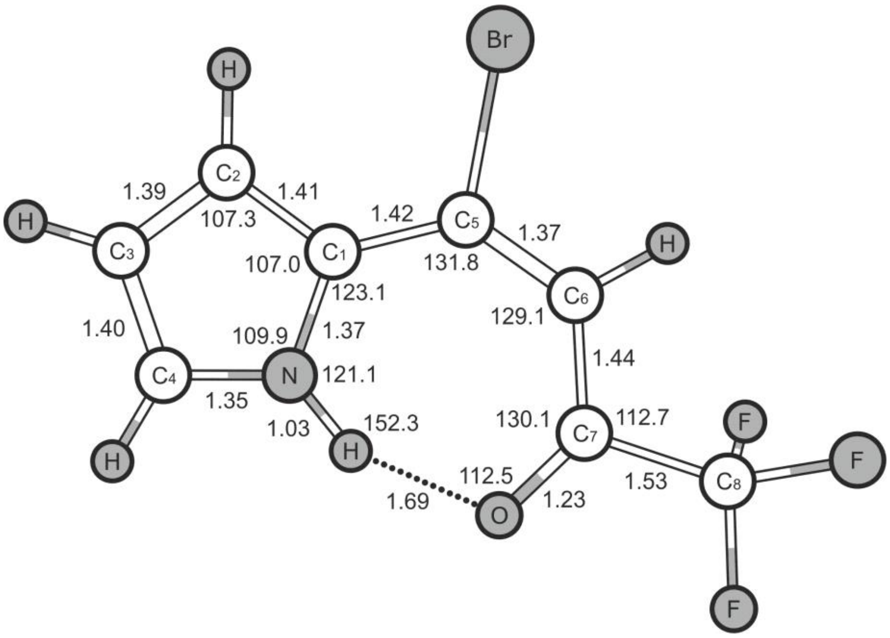

Figure S1 Schematic representation of pyrrole **4a** showing geometrical parameters calculated at the MP2/cc-pVTZ level of theory.

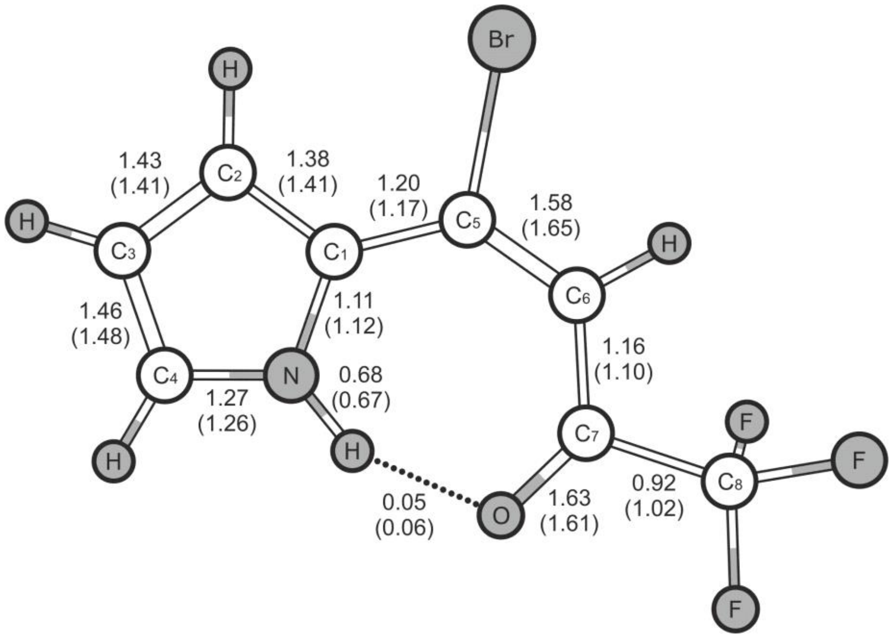

Figure S2 Schematic representation of pyrrole **4a** showing the Wiberg bond indexes (WBI) calculated using NBO approach at the HF/cc-pVTZ level of theory. The results for CH_3 substituted analogue **5a** are shown in parentheses. (The WBI values for the bond in pyrrole are NH: 0.80, NC_α: 1.16, $C_\alpha C_\beta$: 1.60, $C_\beta C_{\beta'}$: 1.30; for the C=C bond in ethylene: 2.04).

Equilibrium structure of pyrrole **4a** ($R_{H\text{-}O} = 1.69$ Å)

E (MP2/cc-pVTZ) = -3308.848690 hartree

Probable alcohol structure with fixed HO-distance ($R_{H\text{-}O} = 1.05$ Å)

E (MP2/cc-pVTZ) = -3308.832861 hartree

Figure S3 Schematic representation of the equilibrium pyrrole **4a** structure obtained by the full geometry optimization at the MP2/cc-pVTZ level of theory in comparison with the most probable (hypothetical) structure of the corresponding alcohol obtained by the restricted geometry optimization with the fixed HO-bond length ($R_{H\text{-}O} = 1.05$ Å). The total electronic MP2/cc-pVTZ energies are also shown.

Table S1 Geometrical parameters (bond lengths in Å and angles in degrees) calculated at the MP2/cc-pVTZ level of theory for pyrrole **4a** and its CH_3 substituted analogue **5a** in comparison with the geometrical parameters of pyrrole and ethylene.

Parameter	**4a**	**5a**	Pyrrole	Ethylene
Bond lengths				
N-H	1.03	1.03	1.00	
O-H	1.69	1.66		
N-C_1	1.37	1.37	1.37	
C_1-C_2	1.41	1.41	1.38	
C_2-C_3	1.39	1.40		
C_3-C_4	1.40	1.39	1.38	
C_4-N	1.35	1.35	1.37	
C_1-C_5	1.42	1.42		
C_5-C_6	1.37	1.37		1.33
C_6-C_7	1.44	1.46		
C7-C_8	1.55	1.51		
C_7-O	1.23	1.24		
Angles				
C_4-N-C_1	109.9	109.9	110.2	
H-N-C_1	121.1	120.4	124.9	
N-C_1-C_2	107.0	107.1	107.5	
C_1-C_2-C_3	107.3	107.2	107.4	
N-C_1-C_5	123.1	122.6	121.3	
C_1-C_5-C_6	131.8	132.1		121.3
C_5-C_6-C_7	129.1	130.3		121.3
C6-C7-O	130.1	126.6		
C_7-O-H	112.5	114.6		
O-H-N	152.3	153.5		
C_6-C_7-C_8	112.7	114.1		

Table S2 Atomic charges (in electron units) calculated using NBO approach at the HF/cc-pVDZ level of theory for pyrrole **4a** and its CH_3 substituted analogue **5a** in comparison with the charges in pyrrole and ethylene.

Atom [a]	**4a**	**5a**	Pyrrole	Ethylene
H	0.49	0.49	0.41	
N	–0.61	–0.61	–0.63	
C_1	0.02	0.02	–0.01	
C_2	–0.18	–0.20	–0.32	
C_3	–0.34	–0.34	–0.32	
C_4	0.09	0.07	–0.01	
C_5	0.07	0.05		–0.39
C_6	–0.48	–0.46		–0.39
C_7	0.57	0.68		
C_8	1.23	–0.66		
O	–0.68	–0.72		

[a] Atoms are numbered as shown in Figure S1.

Table S3 Mulliken atomic population in the outer-valence molecular orbitals of pyrrole **4a** and its CH_3 substituted analogue **5a** (units are electrons; sum over all atoms is 2) calculated at the HF/cc-pVTZ level of theory; vertical ionization energies (IP, eV) and pole strengths (P, a.u.), calculated using OVGF/cc-pVTZ approach.

Atom [a]	Molecular orbitals (symmetry and assignment)								
	π C=O	σ Skel.	σ C-Br	π C=C, Br	σ O_{LP}	σ Br_{LP}	π C=C, Br	π Pyrrole	π Pyrrole
4a									
C_1	0.05	0.30	0.15	0.04	0.02	0.01	0.11	0.04	0.54
C_2	0.03	0.36	0.11	0.0	0.0	0.01	0.01	0.65	0.15
C_3	0.04	0.36	0.04	0.03	0.01	0.01	0.04	0.67	0.21
C_4	0.08	0.02	0.06	0.10	0.01	0.00	0.08	0.04	0.45
C_5	0.01	0.19	0.38	0.41	0.04	0.03	0.25	0.0	0.04
C_6	0.10	0.23	0.06	0.20	0.14	0.04	0.39	0.0	0.43
C_7	0.53	0.04	0.05	0.02	0.17	0.03	0.02	0.0	0.04
C_8	0.0	0.02	0.0	0.0	0.17	0.02	0.0	0.0	0.0
N	0.14	0.01	0.18	0.12	0.05	0.01	0.02	0.56	0.0
Br	0.0	0.05	0.73	0.93	0.25	1.73	0.98	0.01	0.0
O	0.95	0.04	0.13	0.15	0.99	0.09	0.11	0.0	0.09
H(N)	0.0	0.0	0.02	0.0	0.02	0.00	0.0	0.01	0.0
IP	13.93	13.51	13.44	12.44	10.96	10.98	10.03	9.58	8.28
P	0.80	0.88	0.89	0.85	0.86	0.90	0.88	0.87	0.89
5a									
C_1	0.01	0.29	0.13	0.03	0.02	0.0	0.11	0.04	0.53
C_2	0.01	0.34	0.09	0.0	0.01	0.01	0.0	0.65	0.17
C_3	0.02	0.33	0.03	0.03	0.01	0.01	0.05	0.66	0.21
C_4	0.04	0.02	0.05	0.09	0.01	0.01	0.09	0.04	0.47
C_5	0.05	0.21	0.35	0.37	0.03	0.02	0.27	0.0	0.05
C_6	0.10	0.24	0.07	0.17	0.10	0.10	0.39	0.0	0.43
C_7	0.30	0.04	0.07	0.04	0.12	0.09	0.01	0.0	0.03
C_8	0.27	0.07	0.08	0.0	0.14	0.08	0.0	0.0	0.0
N	0.05	0.01	0.16	0.11	0.04	0.02	0.02	0.57	0.02
Br	0.03	0.06	0.68	0.92	0.71	1.25	0.95	0.01	0.0
O	0.79	0.04	0.13	0.22	0.74	0.37	0.10	0.0	0.06
H(N)	0.0	0.0	0.02	0.0	0.01	0.01	0.0	0.01	0.0
IP	12.91	13.06	12.92	12.07	10.60	10.32	9.68	9.12	7.84
P	0.89	0.88	0.84	0.85	0.87	0.89	0.88	0.88	0.89

[a] Atoms are numbered as shown in Figure S1.

The observed systematic increase of the vertical IPs in **4a** with respect to **5a** is likely a basis set superposition effect. Since the basis set for fluorine is more extended than that for hydrogen, the ground-state electronic structure in the former case is better described. This leads to the lower ground-state energy and increases the ionization energies.

Table S4 AIM characteristics of H···O bond: electron density [$\rho(\mathbf{r})$, e Å^{-3}], its Laplacian [$\nabla^2\rho(\mathbf{r})$, e Å^{-5}], electron energy density [$E_e(\mathbf{r})$, hartree Å^{-3}] at BCP(3,−1), and RCP(3,+1), electron potential energy [V_e, kcal/mol], and bond energy [E_{HO}, kcal/mol], estimated using the equation $E_{HO} = -V_e/2$.[a]

Molecule	$\rho(\mathbf{r})$ [b]	$\nabla^2\rho(\mathbf{r})$	$E_e(\mathbf{r})$	V_e	E_{HO}
BCP(3,−1)					
4a	0.338	2.938	-0.078	-33.66	16.83
5a	0.361	2.931	-0.093	-36.46	18.23
RCP(3,+1)					
4a	0.062	1.340	0.018		
5a	0.063	1.352	0.018		

[a] Ref. [15]

[b] The electron density computed at the MP2(full)/cc-pVTZ level of theory.

Note that the present $\rho(\mathbf{r})$ and $E_e(\mathbf{r})$ values for **4a** and **5a** at BCP(3,−1) meet the criterion ($\rho(\mathbf{r}) \geq 0.2$ e Å^{-3}, $E_e(\mathbf{r}) \leq -0.04$ hartree Å^{-3}) suggested in refs [16-18] for hydrogen bonds with covalent contribution. The presently obtained $\nabla^2\rho(\mathbf{r}) > 0$ and $E_e(\mathbf{r}) < 0$ also suggest that the H···O bond is of an intermediate ionic (electrostatic) / covalent type.

Table S5 Coordinates (Å) of atoms of 4-bromo-1,1,1-trifluoro-4-(pyrrol-2-yl)but-3-en-2-one (**4a**).

Atomic Symbol	Coordinates (Å)		
	X	Y	Z
C	0.000378	0.059683	0.006007
N	-0.000620	-0.119747	1.368860
C	1.268787	-0.179969	1.826307
C	2.134991	-0.037813	0.740324
C	1.349714	0.112468	-0.402243
C	-1.188589	0.161614	-0.762270
C	-2.515899	0.116896	-0.406782
C	-3.101083	-0.051834	0.894158
C	-4.646322	-0.043972	0.859421
F	-5.101322	-1.032553	0.075113
Br	-0.888305	0.402668	-2.612086
O	-2.563456	-0.196531	1.994160
F	-5.160137	-0.200065	2.069032
F	-5.096945	1.113785	0.353962
H	1.685092	0.245102	-1.415071
H	3.209909	-0.045110	0.791455
H	1.474380	-0.317770	2.873971
H	-3.226845	0.222832	-1.211922
H	-0.878951	-0.186870	1.894513

Table S6 Coordinates (Å) of atoms of 4-bromo-4-(pyrrol-2-yl)but-3-en-2-one (**5a**).

Atomic Symbol	Coordinates (Å)		
	X	Y	Z
C	0.000223	-0.024586	-0.005980
C	-0.001677	0.062880	1.388616
C	1.341885	0.034923	1.810530
N	2.118001	-0.067304	0.682619
C	1.331099	-0.104051	-0.416422
C	1.897042	0.094323	3.120513
C	3.190541	0.069668	3.572426
C	4.443872	-0.027524	2.836275
C	5.674369	-0.021862	3.710813
Br	0.591954	0.233133	4.488449
O	4.573940	-0.110373	1.608425
H	-0.854514	0.138306	2.038935
H	-0.857782	-0.030491	-0.655701
H	1.757584	-0.182807	-1.401638
H	3.310205	0.131931	4.644500
H	3.143933	-0.104713	0.758624
H	6.561487	-0.097823	3.090852
H	5.638897	-0.855920	4.411245
H	5.710488	0.894962	4.298770

Experimental

General Information. IR spectra were obtained with a Bruker Vertex 70 spectrometer (400–4000 cm^{-1}, KBr pellets or films). ^{1}H (400.1 MHz), ^{13}C (100.6 MHz), ^{19}F (376.5 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer at ambient temperature in $CDCl_3$ solutions and referenced to $CDCl_3$ (residual protons of $CDCl_3$ in ^{1}H NMR $\delta = 7.26$ ppm; ^{13}C NMR $\delta = 77.1$ ppm). The C, H, N microanalyses were performed on a Flash EA 1112 CHNS-O/MAS analyzer. Melting point (uncorrected) was determined on a Kofler micro hot stage apparatus. Pyrroles were obtained from ketoximes and acetylene by the Trofimov reaction.[19] Bromotrifluoroacetylacetylene was obtained by procedure described.[20]

General procedure for synthesis of 3a-c. Pyrrole **1a-c** (1.5 mmol) and 4-bromobut-3-yn-2-one (**2a**) (1.5 mmol, 0.220 g) were carefully grinded in china mortar with alumina (10-fold excess relative to the total substrate weight) at room temperature for 5 min. The reaction mixture was allowed to stay for 2 h and then placed on the column with silica gel and eluted with hexane and a mixture of hexane and diethyl ether (10:1) to afford pure product.

General procedure for synthesis of 3d-f. Pyrrole **1d-f** (1.5 mmol) and 4-bromo-1,1,1-trifluorobut-3-yn-2-one (**2b**) (1.5 mmol, 0.302 g) were carefully grinded in china mortar with alumina (10-fold excess relative to the total substrate weight) at room temperature for 5 min. The reaction mixture was allowed to stay for 1 h and then placed on the column with silica gel and eluted with hexane and a mixture of hexane and diethyl ether (10:1) to afford pure product.

General procedure for synthesis of 4a-c. Pyrrole **1a-c** (1.5 mmol) and 4-bromo-1,1,1-trifluorobut-3-yn-2-one (**2b**) (1.5 mmol, 0.302 g) were carefully grinded in china mortar with alumina (10-fold excess relative to the total substrate weight) at room temperature for 5 min. The reaction mixture was allowed to stay for 1 h and then placed on the column with silica gel and eluted with hexane and a mixture of hexane and diethyl ether (10:1) to afford pure product.

4-(1H-Pyrrol-2-yl)but-3-yn-2-one **(3a)** was prepared from pyrrole **1a** and acetylene **2a** and isolated in 30% yield, yellow crystals, mp 79-81 ^{o}C. ^{1}H NMR, δ: 2.41 (s, 3H, Me), 6.28 (m, 1H, H-4), 6.79 (m, 1H, H-3), 6.95 (m, 1H, H-5), 8.73 (br s, 1H, NH). ^{13}C NMR, δ: 32.1 (Me), 83.4 (C≡), 93.2 (≡C), 109.8 (C-4), 110.7 (C-3), 120.9 (C-5), 123.8 (C-2), 184.6 (C=O). IR (cm^{-1}), ν: 1661 (C=O), 2178 (C≡C). Anal. Calcd for C_8H_7NO: C, 72.16; H, 5.30; N, 10.52%. Found: C, 71.80; H, 5.26; N, 10.31%.

4-(5-Phenyl-1H-pyrrol-2-yl)but-3-yn-2-one **(3b)** was prepared from pyrrole **1b** and acetylene **2a** and isolated in 38% yield, yellow crystals, mp 128-130 °C. ^{1}H NMR, *δ*: 2.43 (s, 3H, Me), 6.55 (m, 1H, H-3), 6.84 (m, 1H, H-4), 7.31 (m, 1H, H-4 Ph), 7.42 (m, 2H, H-3,5 Ph), 7.52 (m, 2H, H-2,6 Ph), 8.90 (br s, 1H, NH). ^{13}C NMR, *δ*: 32.2 (Me), 86.3 (C≡), 94.4 (≡C), 108.3 (C-4), 110.6 (C-2), 122.6 (C-3), 124.7 (C-3,5 Ph), 128.0 (C-4 Ph), 129.2 (C-2,6 Ph), 131.1 (C-1 Ph), 137.5 (C-5), 184.2 (C=O). IR (cm^{-1}), *ν*: 1648 (C=O), 2166 (C≡C). Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69%. Found: C, 80.09; H, 5.32; N, 6.51%.

4-[5-(3-Fluorophenyl)-1H-pyrrol-2-yl]but-3-yn-2-one **(3c)** was prepared from pyrrole **1c** and acetylene **2a** and isolated in 55% yield, yellow crystals, mp 155-157 °C. ^{1}H NMR, *δ*: 2.44 (s, 3H, Me), 6.56 (m, 1H, H-4), 6.83 (m, 1H, H-3), 7.00 (m, 1H, H-4 Ph), 7.22 (m, 1H, H-2 Ph), 7.29 (m, 1H, H-5 Ph), 7.38 (m, 1H, H-6 Ph), 8.99 (br s, 1H, NH). ^{13}C NMR, *δ*: 32.2 (Me), 85.8 (C≡), 94.2 (≡C), 109.0 (C-4), 111.2 (C-2), 111.7 (d, *J* 23.2 Hz, C-4 Ph), 114.8 (d, *J* 21.3 Hz, C-2 Ph), 120.3 (d, *J* = 2.7 Hz, C-6 Ph), 122.5 (C-3), 130.9 (d, *J* 8.6 Hz, C-5 Ph), 133.2 (d, *J* 8.3 Hz, C-1 Ph), 136.1 (d, *J* 2.4 Hz, C-5), 163.4 (d, *J* 246.3 Hz, C-3 Ph), 184.3 (C=O). ^{19}F NMR, *δ*: -111.76 (m, 3-F Ph). IR (cm^{-1}), *ν*: 1615 (C=O), 2185 (C≡C). Anal. Calcd for $C_{14}H_{10}FNO$: C, 74.00; H, 4.44; F, 8.36; N, 6.16%. Found: C, 73.80; H, 4.43; F, 8.56; N, 5.95%.

1,1,1-Trifluoro-4-(5-phenyl-1-vinyl-1H-pyrrol-2-yl)but-3-yn-2-one **(3d)** was prepared from pyrrole **1d** and acetylene **2b** and isolated in 58% yield, yellow crystals, mp 40 °C. ^{1}H NMR, *δ*: 5.27 (dd, *J* = 8.8, 1.3 Hz, 1*H*, H_A), 5.66 (dd, *J* 15.8, 1.3 Hz, 1*H*, H_B), 6.41 (d, *J* 4.0 Hz, 1*H*, H-4), 6.79 (dd, *J* 15.8, 8.8 Hz, 1*H*, H_X), 7.13 (d, *J* 4.0 Hz, 1*H*, H-3), 7.41-7.47 (m, 5*H*, H Ph). ^{13}C NMR, *δ*: 94.3 (C≡), 97.4 (≡C), 110.4 (=CH_2), 111.7 (C-2), 112.4 (C-4), 115.4 (q, *J* = 288.8 Hz, CF_3), 127.1 (C-3), 128.9 (C-3,5 Ph), 129.0 (C-4 Ph), 129.2 (C-2,6 Ph), 130.4 (HC=), 130.9 (C-1 Ph), 141.9 (C-5), 166.1 (q, *J* 41.2 Hz, C=O). ^{19}F NMR, *δ*: -77.5 (s, CF_3). IR (cm^{-1}), *ν*: 1644 (NCH=CH_2), 1681 (C=O), 2154 (C≡C). Anal. Calcd for $C_{16}H_{10}F_3NO$: C, 66.44; H, 3.48; F, 19.70; N, 4.84%. Found: C, 66.21; H, 3.30; F, 19.86; N, 4.65%.

1,1,1-Trifluoro-4-[5-(3-fluorophenyl)-1-vinyl-1H-pyrrol-2-yl]but-3-yn-2-one **(3e)** was prepared from pyrrole **1e** and acetylene **2b** and isolated in 42% yield, yellow crystals, mp 37-39 °C. ^{1}H NMR, *δ*: 5.32 (dd, *J* 8.7, 1.4 Hz, 1*H*, H_A), 5.64 (dd, *J* 15.8, 1.4 Hz, 1H, H_B), 6.42 (d, *J* 4.0 Hz, 1*H*, H-4), 6.78 (dd, *J* 15.8, 8.7 Hz, 1*H*, H_X), 7.12 (d, *J* 4.0 Hz, 1*H*, H-3), 7.09-7.14 (m, 1*H*, H-4 Ph), 7.16-7.20 (m, 1*H*, H-2 Ph), 7.25-7.27 (m, 1*H*, H-5 Ph), 7.39-7.45 (m, 1*H*, H-6 Ph). ^{13}C

NMR, δ: 93.9 (C≡), 96.5 (≡C), 111.3 (=CH_2), 112.3 (C-2), 112.7 (C-4), 115.4 (q, *J* 288.6 Hz, CF_3), 115.9 (d, *J* 21.1 Hz, C-4 Ph), 116.0 (d, *J* 22.6 Hz, C-2 Ph), 124.9 (d, *J* 2.9 Hz, C-6 Ph), 126.8 (C-3), 130.1 (HC=), 130.6 (d, *J* 8.5 Hz, C-5 Ph), 132.9 (d, *J* 8.3 Hz, C-1 Ph), 140.1 (d, *J* 1.9 Hz, C-5), 162.8 (d, *J* 247.5 Hz, C-3 Ph), 166.2 (q, *J* 41.5 Hz, C=O). ^{19}F NMR, δ: -77.2 (s, CF_3), -112.9 (m, 3-F Ph). IR (cm^{-1}), *v*: 1644 (NCH=CH_2), 1681 (C=O), 2155 (C≡C). Anal. Calcd for $C_{16}H_9F_4NO$: C, 62.55; H, 2.95; F, 24.73; N, 4.56%. Found: C, 62.46; H, 2.98; F, 24.48; N, 4.64%.

1,1,1-Trifluoro-4-(1-vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)but-3-yn-2-one **(3f)** was prepared from pyrrole **1f** and acetylene **2b** and isolated in 48% yield, yellow crystals, mp 42-44 °C. ^{1}H NMR, δ: 1.75-1.76 (m, 2*H*, CH_2-5), 1.83-1.85 (m, 2*H*, CH_2-6), 2.50-2.53 (m, 2*H*, CH_2-4), 2.66-2.69 (m, 2*H*, CH_2-7), 5.10 (dd, *J* 9.1, 1.4 Hz, 1*H*, H_A), 5.47 (dd, *J* 15.9, 1.4 Hz, 1*H*, H_B), 6.83 (s, 1*H*, H-3), 6.88 (dd, *J* 15.9, 9.1 Hz, 1*H*, H_X). ^{13}C NMR, δ: 22.7, 22.8, 22.9, 24.2 (CH_2-4,5,6,7), 95.5 (C≡), 98.7 (≡C), 106.6 (=CH_2), 109.0 (C-2), 115.5 (q, *J* 288.5 Hz, CF_3), 122.7 (C-4), 125.7 (C-3), 129.1 (HC=), 138.7 (C-5), 165.8 (q, *J* 41.2 Hz, C=O). ^{19}F NMR, δ: -77.4 (s, CF_3). IR (cm^{-1}), *v*: 1645 (NCH=CH_2), 1674 (C=O), 2157 (C≡C). Anal. Calcd for $C_{14}H_{12}F_3NO$: C, 62.92; H, 4.53; F, 21.33; N, 5.24%. Found: C, 62.71; H, 4.62; F, 21.17; N, 5.32%.

(E)-4-Bromo-1,1,1-trifluoro-4-(1H-pyrrol-2-yl)but-3-en-2-one **(4a)** was prepared from pyrrole **1a** and acetylene **2b** and isolated in 21% yield, yellow oil. ^{1}H NMR, δ: 6.50 (m, 1*H*, H-4), 6.72 (s, 1*H*, HC=), 7.26 (m, 1*H*, H-3), 7.34 (m, 1*H*, H-5), 13.30 (br s, 1*H*, NH). ^{13}C NMR, δ: 110.4 (=CH), 114.5 (C-4), 117.2 (q, *J* 290.6 Hz, CF_3), 127.1 (C-3), 129.0 (C-5), 131.1 (C-2), 141.6 (=C-Br), 176.2 (q, *J* 34.1 Hz, C=O). ^{19}F NMR, δ: -75.3 (s, CF_3). IR (cm^{-1}), *v*: 1516 (C=C), 1666 (C=O). Anal. Calcd for $C_8H_5BrF_3NO$: C, 35.85; H, 1.88; Br, 29.81; F, 21.26; N, 5.23%. Found: C, 35.98; H, 2.02; Br, 29.69; F, 21.28; N, 5.32%.

(E)-4-Bromo-1,1,1-trifluoro-4-(5-phenyl-1H-pyrrol-2-yl)but-3-en-2-one **(4b)** was prepared from pyrrole **1b** and acetylene **2b** and isolated in 17% yield, orange crystals, mp 87-89 °C. ^{1}H NMR, δ: 6.67 (s, 1*H*, =CH), 6.88 (m, 1*H*, H-4), 7.31 (m, 1*H*, H-3), 7.40-7.44 (m, 1*H*, H-4 Ph), 7.47-7.51 (m, 2*H*, H-3,5 Ph), 7.76-7.78 (m, 2*H*, H-2,6 Ph), 14.07 (br s, 1*H*, NH). ^{13}C NMR, δ: 109.2 (=CH), 113.2 (C-4), 117.6 (q, *J* 289.5 Hz, CF_3), 125.6 (C-2,6 Ph), 128.9 (C-3), 129.5 (C-2), 129.5 (C-3,5 Ph), 129.9 (C-4 Ph), 132.3 (C-1 Ph), 140.2 (=C-Br), 142.8 (C-5), 175.3 (q, *J* 33.7 Hz, C=O). ^{19}F NMR, δ: -75.8 (s, CF_3). IR (cm^{-1}), *v*: 1502 (C=C), 1652 (C=O). Anal. Calcd for $C_{14}H_9BrF_3NO$: C, 48.86; H, 2.64; Br, 23.22; F, 16.56; N, 4.07%. Found: C, 48.79; H, 2.72; Br, 23.29; F, 16.43; N, 4.10%.

(E)-4-Bromo-1,1,1-trifluoro-4-[5-(3-fluorophenyl)-1H-pyrrol-2-yl]but-3-en-2-one **(4c)** was prepared from pyrrole **1c** and acetylene **2b** and isolated in 12% yield, orange crystals, mp 84-86 °C. ^{1}H NMR, δ: 6.73 (s, 1*H*, =CH), 6.86 (dd, *J* 4.2, 2.5 Hz, 1*H*, H-4), 7.09-7.14 (m, 1*H*, H-4 Ph), 7.32 (dd, *J* 4.2, 2.5 Hz, 1*H*, H-3), 7.44 (m, 1*H*, H-2 Ph), 7.47-7.49 (m, 1*H*, H-5 Ph), 7.56-7.58 (m, 1*H*, H-6 Ph), 14.02 (br s, 1*H*, NH). ^{13}C NMR, δ: 110.0 (=CH), 112.4 (d, *J* 23.0 Hz, C-2 Ph), 113.8 (C-4), 116.6 (d, *J* 21.5 Hz, C-4 Ph), 117.4 (q, *J* 290.1 Hz, CF_3), 121.0 (d, *J* 3.1 Hz, C-6 Ph), 128.6 (C-3), 131.2 (d, *J* 8.5 Hz, C-5 Ph), 132.0 (d, *J* 8.1 Hz, C-1 Ph), 132.3 (C-2), 140.5 (=C-Br), 140.9 (d, *J* 2.9 Hz, C-5), 163.4 (d, *J* 247.5 Hz, C-3 Ph), 175.6 (q, *J* 34.2 Hz, C=O). ^{19}F NMR, δ: -75.9 (s, CF_3), -111.6 (m, 3-F Ph). IR (cm^{-1}), ν: 1504 (C=C), 1655 (C=O). Anal. Calcd for $C_{14}H_8BrF_4NO$: C, 46.44; H, 2.23; Br, 22.07; F, 20.99; N, 3.87%. Found: C, 46.56; H, 2.16; Br, 22.01; F, 21.14; N, 3.70%.

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