

A New Pyrrole Synthesis via Silver(I)-Catalyzed Cycloaddition of Vinylogous Diazoester and Nitrile.

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Supporting Information

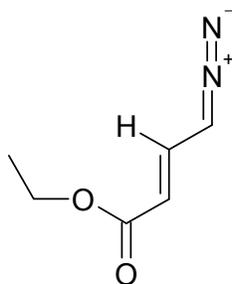
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Materials: ¹H and ¹³C NMR spectra were recorded on Bruker 300, 400 or 500 MHz spectrometers. Chemical shifts are reported in ppm and are referenced to the residual solvent signal (CDCl₃: 7.26 ppm for ¹H NMR and 77.16 ppm for ¹³C NMR or DMSO-d₆: 2.50 ppm for ¹H NMR and 39.5 ppm for ¹³C NMR). Multiplicities are reported as broad (br), singlet (s), doublet (d), double doublet (dd), four doublets (dddd), triplet (t), three triplets (tt), quartet (qt), septet (sep) and multiplet (m). Coupling constants (J) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin-Elmer Custom GX FT-IR. Absorption maxima of selected peaks are quoted in wave numbers (cm⁻¹). Accurate mass spectrum was performed using a Thermo-Finnigan LTQ Orbitrap spectrometer operating in positive ion electrospray mode. Melting points are reported uncorrected.

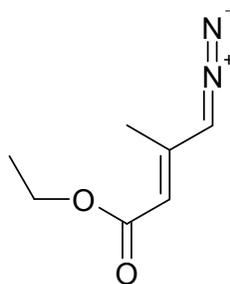
Thin layer chromatography was performed on 250 μm glass or aluminum backed silica gel plates. Preparative thin layer chromatography was performed using 1000 micron silica gel GF plates. The plates were visualized using UV light (254 nm). Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on 60 Å (40 – 60 μm) mesh silica gel (SiO₂). All reagents were obtained from commercial sources and unless specified, used without further purification. All the silver(I)-catalyzed reactions were performed using oven dried glassware and under argon or nitrogen charged atmosphere. All catalysts were weighed in air.

(E)-4-Diazo-but-2-enoic acid ethyl ester (1)



To a solution of (E)-4-oxo-but-2-enoic acid ethyl ester (2 g, 15.61 mmol) in anhydrous dichloromethane (10 ml) was added p-toluenesulfonyl hydrazide (2.907 g, 15.61 mmol). The mixture was then cooled in an ice bath under nitrogen atmosphere. Triethylamine (4.4 ml, 31.22 mmol) was added followed by the addition of DBU (4.66 ml, 31.22 mmol) and the material was stirred for 10 minutes. The crude reaction mixture was immediately loaded onto a silica gel column (60 g) and purified by flash column chromatography, eluting with a gradient of 10%-50% diethyl ether/hexanes. Product fractions were collected in Erlenmeyer flasks (each cooled in ice and wrapped in aluminum foil). The pooled product fractions were condensed (rotary evaporator, distillation flask cooled in ice) to provide the desired product 1 as a red colored oil (1.57 g, 72.7% yield). The diazo product was stored as a dichloromethane solution (use 2.5 mL of CH_2Cl_2 for every 100 mg of 1) in a sub-zero freezer, under argon atmosphere). HRMS m/z calculated for $\text{C}_6\text{H}_8\text{N}_2\text{O}_2$ $[\text{M}+1]^+$: 141.0659, found: 141.0659; ^1H NMR (400 MHz, CDCl_3) δ 7.22 (1H, dd, $J=15.16, 9.09$ Hz), 5.55 (1H, d, $J=15.16$ Hz), 4.84 (1H, d, $J=9.09$ Hz), 4.18 (2H, q, $J=7.07$ Hz), 1.28 (3H, t, $J=7.10$ Hz).

(E)-4-Diazo-3-methyl-but-2-enoic acid ethyl ester (4)



Step 1: To a solution of (E)-3-methyl-4-oxo-but-2-enoic acid ethyl ester (2 g, 14.06 mmol) in dichloromethane (10 mL) under nitrogen atmosphere was added p-toluenesulfonyl hydrazide (2.62 g, 14.06 mmol). A slight exotherm was observed and a precipitate of intermediate tosyl hydrazone formed almost immediately. The material was cooled to 0 °C (ice bath) and triethylamine (3.92 ml, 28.14 ml) was added via drop-wise addition, providing a bright yellow solution. Next DBU (4.21 ml, 28.14 ml) was added to the cooled mixture, providing an orange colored solution. After 10 minutes stirring the crude material was loaded onto a silica gel column (60 g) and purified by flash column chromatography, eluting with a gradient of 10% to 50% diethyl ether / hexane. Product fractions were

S3

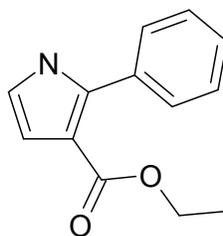
collected in Erlenmeyer flasks which were cooled in ice and wrapped in aluminum foil. The product fractions were pooled and stripped on a rotary evaporator, with the distillation flask cooled in ice. This provided diazo product **4** as a red oil (1.5 g, 68.7% yield). Note: product initially contains a low percentage of 4-methyl-1H-pyrazole-3-carboxylic acid ethyl ester (electrocyclic side product). It is recommended to use this material immediately as it is much less stable than diazo isomer **1** (**4** rapidly converts to pyrazole side product). HRMS m/z calculated for $C_7H_{10}N_2O_2$ $[M+1]^+$: 155.0815, found: 155.0812; 1H NMR (300 MHz, $CDCl_3$) δ 5.41 (1H, s), 4.78 (1H, s), 4.13 (2H, q, $J=7.2$ Hz), 2.27 - 2.22 (3H, m), 1.30 - 1.22 (3H, m).

General experimental procedure for the synthesis of pyrroles:



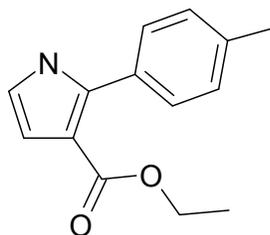
An oven dried flask was charged with alkyl or aryl nitrile (3.56 mmol, 10 equivalents) and silverhexafluoroantimonate (12.2 mg, 0.036 mmol, 10 molpercent). The flask was covered in aluminum foil to protect from light and placed under a nitrogen atmosphere. Anhydrous methylene chloride (5 ml) was added. Next a solution of vinylogous diazo ester (**1** or **4**, 0.356 mmol, 1 equivalent) in dry methylene chloride (1.25 ml) was added via slow drop-wise addition (syringe pump), over 1 hour. The syringe barrel was covered with aluminum foil for the course of the injection. After complete addition the mixture was stirred for at least 1 hour and then the solvent was evaporated on the rotary evaporator to provide the crude pyrroles.

2-Phenyl-1H-pyrrole-3-carboxylic acid ethyl ester (3a**)¹**



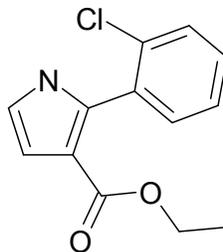
Using the general procedure for the synthesis of pyrroles, **1** was reacted with benzonitrile and converted to crude **3a**. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes) gave pure **3a** as a viscous light yellow oil (54 mg, 0.25 mmol, 62%).

2-p-Tolyl-1H-pyrrole-3-carboxylic acid ethyl ester (3b)



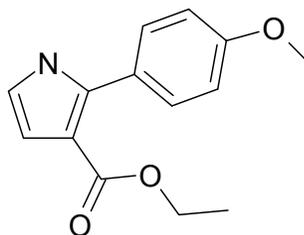
Using the general procedure for the synthesis of pyrroles, **1** was reacted with p-tolunitrile and converted to crude **3b**. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes) gave pure **3b** as a white solid (44 mg, 0.19 mmol, 53.7%). M.p. 93-94 °C; HRMS m/z calculated for $C_{14}H_{15}NO_2$ $[M+1]^+$: 230.11756, found: 230.11717; 1H NMR (300 MHz, $CDCl_3$) δ 7.79 (1 H, br s), 7.48 (2 H, d, $J = 8$ Hz), 7.22 (2 H, d, $J = 8$ Hz), 6.75 (2 H, m), 4.21 (2 H, q, $J = 7$ Hz), 2.39 (3 H, s), and 1.27 ppm (3 H, t, $J = 7$ Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.9, 138.2, 137.3, 132.8, 128.89, 128.86, 117.4, 112.2, 112.1, 59.6, 21.3, and 14.4 ppm; FTIR (KBr): 3421, 3278, 3133, 2988, 1670, 1512, 1448, 1384, 1365, 1319, 1306, 1291, 1192, 1182, 1162, 1025, 822, 791, 758, and 580 cm^{-1} .

2-(2-Chloro-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester (3c)



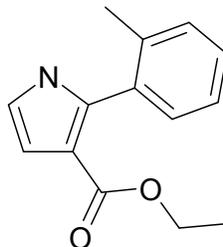
Using the general procedure for the synthesis of pyrroles, **1** was reacted with 2-chlorobenzonitrile and converted to crude **3c**. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes) gave pure **3c** as a light yellow oil (51 mg, 0.21 mmol, 57%). HRMS m/z calculated for $C_{13}H_{12}ClNO_2$ $[M+1]^+$: 250.06293, found: 250.06259; 1H NMR (300 MHz, $CDCl_3$) δ 8.47 (1 H, br s), 7.46 (2 H, m), 7.31 (2 H, m), 6.82 (1 H, t, $J = 3$ Hz), 6.76 (1 H, t, $J = 3$ Hz), 4.14 (2 H, q, $J = 6.9$ Hz), and 1.15 ppm (3 H, t, $J = 6.9$ Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.6, 133.9, 133.3, 132.7, 131.2, 129.8, 129.6, 126.3, 117.8, 114.4, 111.2, 59.7, and 14.1 ppm; FTIR (KBr): 3421, 2981, 1684, 1571, 1479, 1447, 1385, 1367, 1323, 1293, 1257, 1146, 1072, 1054, 1024, 984, 758, 457, and 406 cm^{-1} .

2-(4-Methoxy-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester (3d)¹



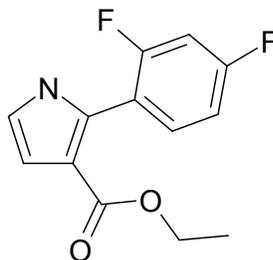
Using the general procedure for the synthesis of pyrroles, **1** was reacted with 4-methoxy-benzonitrile and converted to crude **3d**. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes and re-developing with 20% ethyl acetate in hexanes) gave semi-pure **3d** as a light yellow oil (37 mg, 0.15 mmol, 42%).

2-o-Tolyl-1H-pyrrole-3-carboxylic acid ethyl ester (3e)



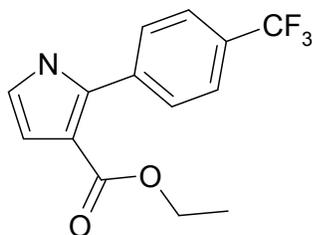
Using the general procedure for the synthesis of pyrroles, **1** was reacted with o-tolunitrile and converted to crude **3e**. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes) gave pure **3e** as a white solid (34 mg, 0.15 mmol, 42%): M.p. 96-97 °C; HRMS m/z calculated for $C_{14}H_{15}NO_2$ $[M+1]^+$: 230.11756, found: 230.11708; 1H NMR (500 MHz, $CDCl_3$) δ 8.21 (1 H, br s), 7.25 (4 H, m), 7.67 (2 H, d, $J = 8$ Hz), 6.77 (1 H, t, $J = 3$ Hz), 6.74 (1 H, t, $J = 3$ Hz), 4.12 (2 H, q, $J = 6.91$ Hz), 2.20 (3 H, s), and 1.28 ppm (3 H, t, $J = 6.91$ Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165, 138, 136, 132, 130.2, 129.8, 128.6, 125, 117, 113, 111, 59, 20, and 14 ppm; FTIR (KBr): 3299, 2985, 1677, 1569, 1444, 1400, 1366, 1313, 1292, 1276, 1199, 1142, 1028, 979, 899, 794, 762, and 725 cm^{-1} .

2-(2,4-Difluoro-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester (3f)



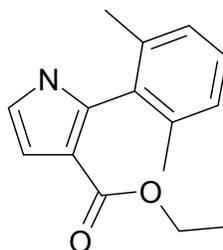
Using the general procedure for the synthesis of pyrroles, 1 was reacted with 2,4-difluorobenzonitrile and converted to crude 3f. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes) gave pure 3f as a white solid (32 mg, 0.13 mmol, 36%): M.p. 114-115 °C; HRMS m/z calculated for $C_{13}H_{11}F_2NO_2$ $[M+1]^+$: 252.08306, found: 252.08264 ; 1H NMR (300 MHz, $CDCl_3$) δ ppm 8.6 (1 H, br s), 7.65 (1 H, m), 6.94 (1 H, m), 6.86 (1 H, t, $J = 3$ Hz), 6.81 (1 H, t, $J = 3$ Hz), 4.23 (2 H, q, $J = 7$ Hz), and 1.28 ppm (3 H, t, $J = 7$ Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.6, 161.54 (dd, $J=251.40, 17.30$ Hz), 132.63-133.53 (m), 129.2, 118.2, 116.2, 114.3, 111.9 111.2 (m), 104.1 (t, $J = 26.9$ Hz), 59.8, and 14.3 ppm; FTIR (KBr): 3295, 2987, 1675, 1509, 1487, 1448, 1384, 1325, 1299, 1267, 1148, 1116, 1093, 1063, 1034, 989, 960, 849, 749, and 609 cm^{-1} .

2-(4-Trifluoromethyl-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester (3g)



Using the general procedure for the synthesis of pyrroles, 1 was reacted with 4-trifluoromethylbenzonitrile and converted to crude 3g. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes) gave pure 3g as a white solid (55 mg, 0.19 mmol, 54%): M.p. 97-98°C; HRMS m/z calculated for $C_{14}H_{12}F_3NO_2$ $[M+1]^+$: 284.08929, found: 284.08951 ; 1H NMR (500 MHz, $CDCl_3$) δ 8.45 (1 H, br s), 7.72 (2 H, d, $J = 8$ Hz), 7.67 (2 H, d, $J = 8$ Hz), 6.84 (1 H, t, $J = 3$ Hz), 6.79 (1 H, t, $J = 3$ Hz), 4.24 (2 H, q, $J = 7$ Hz), and 1.28 ppm (3 H, t, $J = 7$ Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 164.67, 135.53, 135.12, 130.02 (q, $J=32.40$ Hz), 129.22, 125.07 (q, $J=3.70$ Hz), 124.02 (q, $J=271.80$ Hz), 118.43, 112.63, 59.89, 14.25; FTIR (KBr): 3298, 2996, 1678, 1618, 1449, 1405, 1370, 1327, 1293, 1276, 1213, 1164, 1124, 1068, 1018, 985, 902, 846, 792, 743, 606, and 522 cm^{-1} .

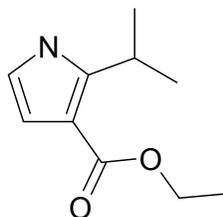
2-(2,6-Dimethyl-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester (3h)



Using the general procedure for the synthesis of pyrroles, 1 was reacted with 2,6-dimethylbenzonitrile and converted to crude 3h. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes and re-developing twice more with 20% ethyl acetate in hexanes) gave pure 3h as a

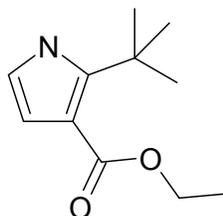
white solid (33.7 mg, 0.14 mmol, 39%): m.p. 151-152 °C; HRMS m/z calculated for $C_{15}H_{17}NO_2$ $[M+1]^+$: 244.13321, found: 244.13284 ; 1H NMR (500 MHz, $CDCl_3$) δ 8.1 (1 H, br s), 7.21 (1 H, d of d, $J_1 = 7$ Hz; $J_2 = 8$ Hz), 7.08 (2 H, d, $J = 8$ Hz), 6.80 (1 H, t, $J = 3$ Hz), 6.76 (1 H, t, $J = 3$ Hz), 4.07 (2 H, q, $J = 7$ Hz), 2.24 (6 H, s), and 1.06 ppm (3 H, t, $J = 7$ Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.7, 138.3, 135.8, 132.5, 128.5, 126.9, 117.3, 113.7, 110.7, 59.3, 20.1, and 14.0 ppm; FTIR (KBr): 3298, 2985, 1677, 1444, 1400, 1385, 1366, 1313, 1292, 1276, 1211, 1199, 1142, 1093, 1061, 1048, 1028, 979, 762, 738, and 725 cm^{-1} .

2-Isopropyl-1H-pyrrole-3-carboxylic acid ethyl ester (3i)



Using the general procedure for the synthesis of pyrroles, 1 was reacted with isobutyronitrile and converted to crude 3i. Chromatography on silica gel (preparative TLC, eluting with 20% ethyl acetate in hexanes) gave pure 3i as a light yellow oil (30 mg, 0.17 mmol, 46%). HRMS m/z calculated for $C_{10}H_{15}NO_2$ $[M+1]^+$: 182.11756, found: 182.11701 ; 1H NMR (300 MHz, $CDCl_3$) δ 8.27 (1 H, br s), 6.57 (2 H, m), 4.29 (2 H, q, $J = 7$ Hz), 3.80 (1 H, heptet, $J = 7$ Hz), 1.34 (3 H, t, $J = 7$ Hz) and 1.28 ppm (6 H, d, $J = 7$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.7, 145.4, 115.9, 111.1, 110.8, 59.7, 26.4, 22.4, and 14.9 ppm; FTIR (KBr): 3336, 2971, 1674, 1570, 1497, 1470, 1384, 1369, 1335, 1311, 1265, 1192, 1157, 1129, 1077, 1044, 903, 791, and 736 cm^{-1} .

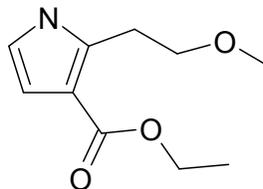
2-tert-Butyl-1H-pyrrole-3-carboxylic acid ethyl ester (3j)



Using the general procedure for the synthesis of pyrroles, 1 was reacted with 2,2-dimethylpropionitrile and converted to crude 3j. Chromatography on silica gel (preparative TLC, eluting with 20% ethyl acetate in hexanes) gave pure 3j as a light yellow oil (31.6 mg, 0.16 mmol, 45%). HRMS m/z calculated for $C_{10}H_{15}NO_2$ $[M+1]^+$: 196.1338, found: 196.1331 ; 1H NMR (300 MHz, $CDCl_3$) δ 8.35 (1 H, br s), 6.68 (1 H, t, $J = 3$ Hz), 6.52 (1 H, t, $J = 3$ Hz), 4.25 (2 H, q, $J = 7$ Hz), 1.47 (9 H, s), and 1.34 ppm (3 H, t, $J = 7$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.4, 146.6, 114.2, 113.6, 111.2,

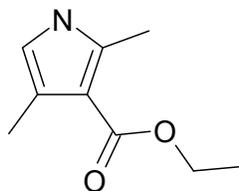
59.9, 33.4, 29.1, and 14.9 ppm; FTIR (KBr): 3386, 2959, 1684, 1556, 1480, 1446, 1397, 1383, 1365, 1297, 1274, 1173, 1114, 1085, 1048, 1023, 1003, 898, 791, and 734 cm^{-1} .

2-(2-Methoxy-ethyl)-1H-pyrrole-3-carboxylic acid ethyl ester (3k)



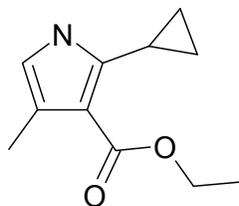
Using the general procedure for the synthesis of pyrroles, 1 was reacted with 3-methoxypropionitrile and converted to crude 3k. Chromatography on silica gel (preparative TLC, eluting with 20% ethyl acetate in hexanes) gave pure 3k as a light yellow oil (36 mg, 0.18 mmol, 51%). HRMS m/z calculated for $\text{C}_{10}\text{H}_{15}\text{NO}_3$ $[\text{M}+1]^+$: 198.11247, found: 198.11214; ^1H NMR (500 MHz, CDCl_3) δ 9.11 (1 H, br s), 6.59 (1 H, t, $J = 7$ Hz), 6.55 (1 H, t, $J = 7$ Hz), 4.26 (2 H, q, $J = 7$ Hz), 3.67 (2 H, t, $J = 6$ Hz), 3.40, (3 H, s), 3.29 (2 H, t, $J = 6$ Hz), and 1.34 ppm (3 H, t, $J = 7$ Hz); ^{13}C NMR (75.4 MHz, CDCl_3) $\delta = 166.1, 138.2, 116.6, 111.8, 110.3, 72.3, 59.7, 59.1, 27,$ and 14.9 ppm; FTIR (KBr): 3318, 2981, 2931, 2900, 1676, 1574, 1495, 1463, 1370, 1327, 1300, 1261, 1197, 1176, 1126, 1057, 902, 789, 733, and 612 cm^{-1} .

2,4-Dimethyl-1H-pyrrole-3-carboxylic acid ethyl ester (6a)²



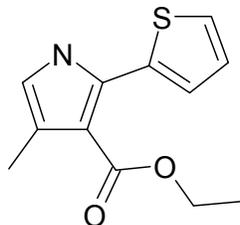
Using the general procedure for the synthesis of pyrroles, 4 was reacted with acetonitrile and converted to crude 6a. Chromatography on silica gel (preparative TLC, eluting with 16% ethyl acetate in hexanes and re-developing again with 16% ethyl acetate in hexanes) gave pure 6a as a yellow oil which solidified on standing (6.5 mg, 0.04 mmol, 15%).

2-Cyclopropyl-4-methyl-1H-pyrrole-3-carboxylic acid ethyl ester (6b)³



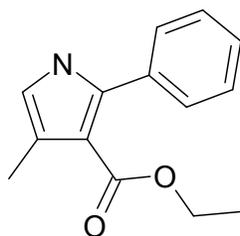
Using the general procedure for the synthesis of pyrroles, **4** was reacted with cyclopropanecarbonitrile and converted to crude **6b**. Chromatography on silica gel (preparative TLC, eluting with 20% ethyl acetate in hexanes) gave pure **6b** as a light pink oil (4 mg, 0.02 mmol, 12%).

4-Methyl-2-thiophen-2-yl-1H-pyrrole-3-carboxylic acid ethyl ester (**6c**)⁴



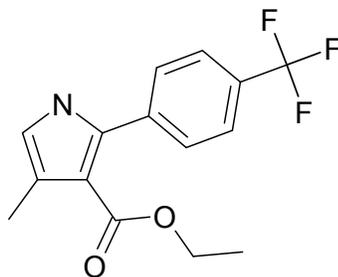
Using the general procedure for the synthesis of pyrroles, **4** was reacted with thiophene-2-carbonitrile and converted to crude **6c**. Chromatography on silica gel (preparative TLC, eluting with 15% ethyl acetate in hexanes and re-developing again with 18% ethyl acetate in hexanes) gave pure **6c** as a light yellow semi-solid product (22 mg, 0.06 mmol, 19%). HRMS m/z calculated for $C_{12}H_{13}NO_2S$ $[M+1]^+$: 236.0739, found: 236.0736; 1H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 8.36 (br. s., 1 H) 7.38 (dd, $J=3.54, 1.13$ Hz, 1 H) 7.35 (dd, $J=5.27, 1.13$ Hz, 1 H) 7.08 (dd, $J=5.27, 3.54$ Hz, 1 H) 6.58 (br. d, $J=1.30$ Hz, 1 H) 4.28 (q, $J=7.19$ Hz, 2 H) 2.32 (s, 3 H) 1.31 (t, $J=7.19$ Hz, 3 H); ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 165.52, 133.89, 130.33, 127.18, 126.98, 125.85, 122.87, 116.98, 112.19, 59.64, 14.32, 12.73.

4-Methyl-2-phenyl-1H-pyrrole-3-carboxylic acid ethyl ester (**6d**)³



Using the general procedure for the synthesis of pyrroles, **4** was reacted with benzonitrile and converted to crude **6d**. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes) gave pure **6d** as a light yellow oil (18 mg, 0.08 mmol, 24%).

4-Methyl-2-(4-trifluoromethyl-phenyl)-1H-pyrrole-3-carboxylic acid ethyl ester (**6e**)



Using the general procedure for the synthesis of pyrroles, **4** was reacted with 4-trifluoromethylbenzotrile and converted to crude **6e**. Chromatography on silica gel (preparative TLC, eluting with 30% ethyl acetate in hexanes and re-developing again with 30% ethyl acetate in hexanes) gave pure **6e** as a white solid (9 mg, 0.03 mmol, 9%). M.p. 138-139 °C; HRMS m/z calculated for $C_{15}H_{14}F_3NO_2$ $[M+1]^+$: 298.1049, found: 298.1045 ; 1H NMR (400 MHz, $CDCl_3$) δ 8.19 (1H, br. s.), 7.66 - 7.60 (4H, m), 6.63 (1H, s), 4.20 (2H, q, $J = 7.07$ Hz), 2.31 (3H, s), 1.22 (3H, t, $J = 7.07$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) 164.8, 136.7, 134.7, 129.6, 127.5 (q, $J = 31.7$ Hz), 124.5 (q, $J = 3.8$ Hz), 124.4 (q, $J = 272.8$ Hz), 121.3, 118.5, 111.3, 58.9, 13.9 and 12.4 ppm; FTIR (KBr): 3307, 2989, 2938, 1669, 1620, 1540, 1448, 1389, 1330, 1291, 1165, 1127, 1085, 1066, 1020, 848, 790, 619, 606 cm^{-1} .

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NMR Spectra

