Synthesis and Reactivity of Bis(2,2,2-trifluoroethyl)cyclopropane-1,1-dicarboxylates via Indole Addition

Supporting Information

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General Information. All solvents for routine isolation of products and chromatography were reagent grade. Flash chromatography was performed using silica gel (230–400 mesh) with indicated solvents. All reactions were monitored by thin-layer chromatography on 0.25 mm silica plates (60F-254) visualizing with UV light and developed using acidic anisaldehyde. $^1$H, $^{19}$F, and $^{13}$C NMR spectra were recorded either on a 400 MHz, 479 MHz, or on a 600 MHz NMR spectrometer. Chemical shifts, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant in hertz (Hz), and number of protons. HRMS were measured with electron impact (EI) ionization and quadrupolar mass analyzer.

General Experimental Procedure for the Synthesis of of Bis(2,2,2-trifluoroethyl)cyclopropane-1,1-dicarboxylates 10a-j.

To a solution of styrene (1.0 equiv.) and Rh$_2$(esp)$_4$ (0.1 mol %) in anhydrous DCM was added diazomalonate (1.3 equiv) drop wise over 20 minutes at 0°C. The solution was stirred under argon until complete (as determined by TLC analysis). The reaction was quenched with sodium bicarbonate and extracted with EtOAc (3 times). The organic layers were then combined and dried with magnesium sulfate. Following filtration, the solvent was removed under reduced pressure and the crude mixture purified by flash chromatography (EtOAc/hexanes, 5:95) to yield the desired products 13a-f.
bis(2,2,2-trifluoroethyl) 2-phenylcyclopropane-1,1-dicarboxylate (10a) Reagents employed: styrene (0.100 g, 0.960 mmol), bis(2,2,2-trifluoroethyl) 2-diazomalonate (0.367 g, 1.248 mmol), Rh$_2$(esp)$_2$ (0.001 g, 0.0001 mmol), 2 mL anhydrous DCM at 0 °C to room temperature for 5 hours: yield 94 % (334 mg), as a clear oil; Rf= 0.55, 20% EtOAc in hexanes; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.34- 7.26 (m, 3H), 7.25- 7.21 (m, 2H), 4.69- 4.59 (m, 1H), 4.57- 4.48 (m, 1H), 4.21- 4.12 (m, 1H), 4.10- 4.00 (m, 1H), 3.42 ( dd, J= 9.0, 9.0 Hz, 1H), 2.37 ( dd, J= 8.2, 5.4 Hz, 1H), 1.89 (dd, J= 9.4, 5.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 167.6, 164.4, 133.0, 128.6, 128.4, 127.9, 122.6 (q, J$_{C,F}$= 277 Hz, 1C), 122.4 (q, J$_{C,F}$= 277 Hz, 1C), 61.3 (q, J$_{C,F}$= 77 Hz, 1C), 61.0 (q, J$_{C,F}$= 37 Hz, 1C), 36.3, 34.1, 19.8; $^{19}$F NMR (479 MHz, CDCl$_3$) $\delta$= -73.95 (t, J= 9.3 Hz, 3F), -74.01 (t, J= 10.6 Hz, 3F); IR (thin film) 3034, 2976, 1748, 1500, 1414, 1278, 1211, 1168, 1122, 977, 842, 747, 697, 650, 563; HRMS (El) calculated for C$_{15}$H$_{12}$F$_6$O$_4$ 370.0640 found 370.0631.

bis(2,2,2-trifluoroethyl) 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (10b) Reagents employed: 1-methoxy-4-vinylbenzene (0.750 g, 5.000 mmol), bis(2,2,2-trifluoroethyl) 2-diazomalonate (1.909 g, 6.492 mmol), Rh$_2$(esp)$_2$ (0.004 g, 0.0050 mmol), 5 mL anhydrous DCM at 0 °C for 5 hours: yield 87 % (1.74 g), as a clear oil; Rf= 0.65, 20% EtOAc in hexanes; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.14 (d, J= 8.6 Hz, 2H), 6.81 (d, J= 8.6 Hz, 2H), 4.67- 4.58 (m, 1H), 4.55- 4.46 (m, 1H), 4.24- 4.14 (m, 1H), 4.11- 4.02 (m, 1H), 3.78 (s, 3H), 3.36 (dd, J= 8.8, 9.0 Hz, 1H), 2.32 (dd, J= 8.3, 5.4 Hz, 1H), 1.86 (dd, J= 9.2, 5.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 167.7, 164.5, 129.8, 124.8, 122.6 (q, J$_{C,F}$= 277 Hz, 1C), 122.4 (q, J$_{C,F}$= 277 Hz, 1C), 113.7, 61.3 (q, J$_{C,F}$= 37 Hz, 1C), 61.1 (q, J$_{C,F}$= 37 Hz, 1C), 55.2, 36.2, 34.9, 33.9, 20.08; $^{19}$F NMR (479 MHz, CDCl$_3$) $\delta$= -73.94 (t, J= 6.6 Hz, 3F), -73.96 (t, J= 6.6 Hz, 3F); IR (thin film) 2934, 2855, 2118, 1747, 1613, 1518, 1442, 1414, 1279, 1257, 1167, 1119, 1033, 977, 836, 810, 650, 559.; HRMS (El) calculated for C$_{16}$H$_{14}$F$_6$O$_5$ 400.0745 found 400.0736.

bis(2,2,2-trifluoroethyl) 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (10c) Reagents employed: 1-bromo-4-vinylbenzene (0.993 g, 5.425 mmol), bis(2,2,2-trifluoroethyl) 2-diazomalonate (2.074 g, 7.052 mmol), Rh$_2$(esp)$_2$ (0.004 g, 0.0054 mmol), 5 mL anhydrous DCM at 0 °C to room temperature overnight: yield 78 % (1.90 g), as a clear oil; Rf= 0.63, 20% EtOAc in hexanes; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.42 (d, J= 8.6 Hz, 2H), 7.09 (d, J= 8.6 Hz, 2H), 4.68- 4.59 (m, 1H), 4.57- 4.46 (m, 1H), 4.28- 4.18 (m, 1H), 4.17- 4.08 (m, 1H), 3.34 (dd, J= 8.8, 8.8 Hz, 1H), 2.31 (dd, J= 8.2, 5.4 Hz, 1H), 1.88 (dd, J= 8.4, 5.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 167.4, 164.2, 132.0, 131.5, 130.4, 122.5 (q, J$_{C,F}$= 277 Hz, 1C), 122.3 (q, J$_{C,F}$= 277 Hz, 1C), 122.1, 61.4 (q, J$_{C,F}$= 37 Hz, 1C), 61.1 (q, J$_{C,F}$= 37 Hz, 1C), 36.2, 33.1, 19.8; $^{19}$F NMR (479 MHz, CDCl$_3$) $\delta$= -73.93 (t, J= 10.6 Hz, 3F), -73.99 (t, J= 8.0 Hz, 3F); IR (thin film) 3063, 3031, 2972, 1754, 1602, 1495, 1449, 1411, 1286, 1234, 1170, 1104, 1053, 1015, 980, 894, 837, 797, 743, 699, 650, 536, 509, 469.; HRMS (El) calculated for C$_{15}$H$_{11}$BrF$_6$O$_4$ 447.9745 found 447.9745.
Reagents employed: 1-chloro-4-vinylbenzene (0.100g, 0.722 mmol), bis[2,2,2-trifluoroethyl] 2-diazomalonate (0.276g, 0.938 mmol), Rh$_2$(esp)$_2$ (0.0005g, 0.0007 mmol), 2 mL anhydrous DCM at 0 ºC then allow to warm to room temperature and stir overnight: yield 72% (210 mg), as a clear oil; Rf = 0.49, 30% EtOAc in hexanes; $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.27 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 4.69- 4.61 (m, 1H), 4.56- 4.47 (m, 1H), 4.27- 4.18 (m, 1H), 4.17- 4.08 (m, 1H), 3.36 (dd, J = 8.6, 8.6 Hz, 1H), 2.32 (dd, J = 8.2, 5.4 Hz, 1H), 1.88 (dd, J = 9.4, 5.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 167.4, 164.3, 134.0, 131.5, 130.0, 128.6, 122.5 (q, J$_{C,F}$ = 277 Hz, 1C), 122.3 (q, J$_{C,F}$ = 277 Hz, 1C), 61.4 (q, J$_{C,F}$ = 37 Hz, 1C), 61.1 (q, J$_{C,F}$ = 37 Hz, 1C), 36.3, 33.2, 19.8; $^{19}$F NMR (479 MHz, CDCl$_3$) δ = -73.94 (t, J = 6.6 Hz, 3F), -74.03 (t, J = 6.6 Hz, 3F); IR (thin film) 2976, 2360, 1748, 1497, 122.5 (q, J = 6.6 Hz, 1C), 122.3 (q, J = 6.6 Hz, 1C), 122.3 (q, J = 277 Hz, 1C), 116.7, 112, 1094, 1050, 1016, 977, 835, 787, 714, 666, 535; HRMS (EI) calculated for C$_{15}$H$_{11}$Cl F$_{3}$O$_{4}$ 404.0250 found 404.0258.

Reagents employed: 4-vinylbenzonitrile (0.100g, 0.774 mmol), bis[2,2,2-trifluoroethyl] 2-diazomalonate (0.296g, 1.007 mmol), Rh$_2$(esp)$_2$ (0.001g, 0.0006 mmol), 2 mL anhydrous DCM at 0 ºC to room temperature overnight: yield 66% (202 mg), as a clear oil; Rf = 0.45, 20% EtOAc in hexanes; $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.58 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 4.71- 4.59 (m, 1H), 4.57- 4.46 (m, 1H), 4.23- 4.09 (m, 2H), 3.40 (dd, J = 8.6, 8.6 Hz, 1H), 2.34 (dd, J = 8.2, 5.4 Hz, 1H), 1.92 (dd, J = 9.4, 5.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 167.0, 163.9, 138.4, 132.1, 129.4, 122.4 (q, J$_{C,F}$ = 277 Hz, 1C), 122.1 (q, J$_{C,F}$ = 277 Hz, 1C), 118.2, 111.9, 61.5 (q, J$_{C,F}$ = 37 Hz, 1C), 61.1 (q, J$_{C,F}$ = 37 Hz, 1C), 36.5, 33.1, 19.7; $^{19}$F NMR (479 MHz, CDCl$_3$) δ = -73.94 (t, J = 8.0 Hz, 3F), -74.08 (t, J = 9.3 Hz, 3F); IR (thin film) 3025, 2936, 2858, 2230, 1749, 1672, 1611, 1509, 1414, 1278, 1261, 1167, 1121, 976, 845, 770, 650, 558; HRMS (EI) calculated for C$_{16}$H$_{11}$F$_{6}$NO$_{4}$ 395.0592 found 395.0588.

Reagents employed: methyl 4-vinylbenzoate (0.200g, 1.233 mmol), bis(2,2,2-trifluoroethyl) 2-diazomalonate (0.472g, 1.603 mmol), Rh$_2$(esp)$_2$ (0.001g, 0.0009 mmol), 2 mL anhydrous DCM at 0 ºC then allow to warm to room temperature and stir for 4 hours: yield 74% (391 mg), as a clear oil; Rf = 0.32, 20% EtOAc in hexanes; $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.97 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 4.69-4.59 (m, 1H), 4.57- 4.48 (m, 1H), 4.24- 4.13 (m, 1H), 4.11- 4.02 (m, 1H), 3.90 (s, 3H), 3.42 (dd, J = 9.0, 9.0 Hz, 1H), 2.38 (dd, J = 8.2, 5.4 Hz, 1H), 1.92 (dd, J = 9.4, 5.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 167.3, 166.5, 164.2, 138.2, 129.8, 129.6, 128.7, 125 (q, J$_{C,F}$ = 277 Hz, 1C), 122.3 (q, J$_{C,F}$ = 277 Hz, 1C), 61.6 (q, J$_{C,F}$ = 37 Hz, 1C), 60.6 (q, J$_{C,F}$ = 37 Hz, 1C), 52.2, 36.5, 33.6, 19.9; $^{19}$F NMR (479 MHz, CDCl$_3$) δ = -73.88 (t, J = 7.9 Hz, 3F), -73.96 (t, J = 7.8 Hz, 3F); IR (thin film) 2958, 1749, 1724, 1613, 1574, 1438, 1415, 1281, 1168, 1117, 1050, 977, 862, 788, 756, 703, 659, 537; HRMS (EI) calculated for C$_{17}$H$_{14}$F$_{6}$O$_{5}$ 428.0695 found 428.0693.
bis(2,2,2-trifluoroethyl) 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate

(10g) 1-fluoro-4-vinylbenzene (0.500 g, 4.094 mmol), bis(2,2,2-trifluoroethyl) 2-diazomalonate (1.565 g, 5.328 mmol), Rh₂(esp)₂ (0.003 g, 0.0041 mmol), 5 mL anhydrous DCM at 0 °C then allow to warm to room temperature and stir overnight: yield 76 % (1.589 g), as a clear oil; Rf= 0.57, 30% EtOAc in hexanes; \(^1\)H NMR (400 MHz, CDCl₃) δ = 7.97 (m, 2H), 7.29 (m, 2H), 4.69- 4.58 (m, 1H), 4.57- 4.46 (m, 1H), 4.24- 4.15 (m, 1H), 4.14- 4.07 (m, 1H), 3.37 (dd, J= 9.0, 9.0 Hz, 1H), 2.31 (dd, J= 8.6, 5.9 Hz, 1H), 1.88 (dd, J= 9.4, 5.4 Hz, 1H); \(^13\)C NMR (100 MHz, CDCl₃) δ = 167.5, 164.4, 162.5 (d, J= 246 Hz), 130.4 (d, J= 8.4 Hz), 122.6 (q, J_C-F= 277 Hz, 1C), 122.4 (q, J_C-F= 277 Hz, 1C), 115.5, 115.3, 61.4 (q, J_C-F= 37 Hz, 1C), 61.1 (q, J_C-F= 37 Hz, 1C), 36.2, 33.3, 20.0; \(^19\)F NMR (479 MHz, CDCl₃) δ = -73.88 (t, J= 6.6 Hz, 3F), -73.96 (t, J= 6.6 Hz, 3F); IR (thin film) 2978, 1749, 1608, 1515, 1444, 1279, 1669, 1122, 977, 842, 823, 761, 721, 664, 550, 525, 428; HRMS (EI) calculated for C₁₅H₁₁F₇O₄ 388.0546 found 388.0542.

bis((2,2,2-trifluoroethyl)dithiophen-2-yl)cyclopropane-1,1-dicarboxylate (10h) 1- 2-vinylthiophene (0.200 g, 1.816 mmol), bis(2,2,2-trifluoroethyl) 2-diazomalonate (0.694 g, 2.360 mmol), Rh₂(esp)₂ (0.001 g, 0.0002 mmol), 2 mL anhydrous DCM at 0 °C then allow to warm to room temperature and stir overnight: yield 60 % (410 mg), as a clear oil; Rf= 0.52, 20% EtOAc in hexanes; \(^1\)H NMR (400 MHz, CDCl₃) δ = 7.97 (dd, J= 4.2, 1.2 Hz, 1H), 7.29 (dd, J= 5.1, 5.5 Hz, 1H), 6.89- 6.86 (m, 1H), 4.67- 4.57 (m, 1H), 4.56- 4.46 (m, 1H), 4.35- 4.25 (m, 1H), 4.19- 4.10 (m, 1H), 3.46 (dd, J= 9.0, 9.0 Hz, 1H), 2.50- 2.42 (m, 1H), 1.72 (dd, J= 8.2, 5.4 Hz, 1H), 1.62 (dd, J= 9.4, 5.4 Hz, 1H), 1.44 (s, 9H); \(^13\)C NMR (100 MHz, CDCl₃) δ = 167.2, 164.1, 126.9, 126.8, 125.8, 122.5 (q, J_C-F= 277 Hz, 1C), 122.4 (q, J_C-F= 277 Hz, 1C), 61.3 (q, J_C-F= 37 Hz, 1C), 61.2 (q, J_C-F= 37 Hz, 1C), 37.0, 28.7, 21.5; \(^19\)F NMR (479 MHz, CDCl₃) δ = -74.02 (t, J= 10.6 Hz, 3F), -74.06 (t, J= 6.6 Hz, 3F); IR (thin film); 3111, 2976, 1747, 1414, 1375, 1330, 1279, 1170, 1121, 1036, 978, 851, 706, 564, 560, 522, 470 HRMS (EI) calculated for C₁₃H₁₀F₆O₄S 376.0204 found 376.0208.

bis(2,2,2-trifluoroethyl) 2-((tert-butoxycarbonyloxy)methyl)cyclopropane-1,1-dicarboxylate (10i) Reagents employed: allyl tert-butyl carbonate (0.200 g, 1.264 mmol), bis(2,2,2-trifluoroethyl) 2-diazomalonate (0.483 g, 1.644 mmol), Rh₂(esp)₂ (0.001 g, 0.00001 mmol), 2 mL anhydrous DCM at 0 °C then allow to warm to room temperature and stir overnight: yield 75 % (402 mg), as a clear oil; Rf= 0.66, 20% EtOAc in hexanes; \(^1\)H NMR (400 MHz, CDCl₃) δ = 4.60- 4.41 (m, 4H), 4.22 (dd, J= 12.1, 5.8 Hz, 1H), 3.94 (dd, J= 12.1, 8.6 Hz, 1H), 2.50-2.42 (m, 1H), 1.72 (dd, J= 8.2, 5.4 Hz, 1H), 1.62 (dd, J= 9.4, 5.4 Hz, 1H), 1.44 (s, 9H); \(^13\)C NMR (100 MHz, CDCl₃) δ = 167.2, 165.4, 152.9, 122.6 (q, J_C-F= 277 Hz, 1C), 122.3 (q, J_C-F= 277 Hz, 1C), 82.6, 63.9, 61.4 (q, J_C-F= 37 Hz, 1C), 61.3 (q, J_C-F= 37 Hz, 1C), 32.3, 27.6, 27.5,
19.9; \(^{19}\text{F NMR}\) (479 MHz, CDCl\(_3\)) \(\delta= -73.84\) (t, J= 6.6 Hz, 3F), -74.03 (t, J= 6.7 Hz, 3F); IR (thin film) 2983, 1747, 1454, 1416, 1371, 1281, 1167, 1123, 1047, 977, 860, 793, 766, 661, 562, 462; HRMS (EI) calculated for C\(_{18}\)H\(_{18}\)F\(_6\)O; 424.0957 found 424.0960.

**TBSO**

\[\text{CF}_3\]

\[\text{CF}_3\]

**Experimental Procedure for the Synthesis of bis(2,2,2-trifluoroethyl) 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate 10k.**

To a solution of H\(_2\)O/MeOH (20 mL:15 mL) was added KOH (7.0 equiv) at room temperature and stirred until dissolved. The solution was then cooled to 0°C and dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (12c) (1.0 equiv) was added drop wise over 15 min. The solution was stirred at room temperature until complete (as determined by TLC analysis). The reaction mixture was acidified and washed with Et\(_2\)O (3 times). The organic layers were then combined and dried with magnesium sulfate. Following filtration, the solvent was removed under reduced pressure and the crude mixture was collected as a white crystalline solid. The crude material (1 equiv) was then solvated in 40 mL anhydrous DCM, 2,2,2-trifluoroethanol (5.0 equiv), 4-dimethylaminopyridine (0.4 equiv) and placed in an ice bath at 0°C. \(N,N'\)-dicyclohexylcarbodiimide (1.95 equiv) was added in 500 mg portions over 5 min at 0°C. The solution was stirred under argon until complete (as determined by TLC analysis). The solution was filtered through celite and washed with DCM (3 times). The organic layers were then combined and dried with magnesium sulfate. Following filtration, the solvent was removed under reduced pressure and the crude mixture purified by flash chromatography (EtOAc/hexanes, 1:100) to yield the desired product 10k.

\[\text{O}_2\text{N}\]

\[\text{CF}_3\]

**bis(2,2,2-trifluoroethyl) 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (10k)** dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (12c) (3.000 g, 10.743 mmol), KOH (4.219 g, 75.743 mmol), 20 mL H\(_2\)O, 15 mL MeOH at 0°C then allow to warm to room temperature and stir overnight: yield 77% (2.078...
g), as a white crystalline compound. The crude diacid (2.451 g, 9.757 mmol), 2,2,2-trifluoroethanol (4.881 g, 48.787 mmol), 4-dimethylaminopyridine (0.477 g, 3.903 mmol) in 125 mL anhydrous DCM was stirred at 0°C for 15 min. N,N'-dicyclohexylcarbodiimide (3.926 g, 19.027 mmol) was added portion wise at 0°C and stirred for 22 hours at room temperature: yield 31% (1.256 g); Rf = 0.31, 30% EtOAc in hexanes; 1H NMR (400 MHz, CDCl3) δ = 8.15 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 4.69-4.63 (m, 1H), 4.56-4.50 (m, 1H), 4.25-4.15 (m, 2H), 3.45 (dd, J = 8.8, 8.8 Hz, 1H), 2.38 (dd, J = 8.2, 5.4 Hz, 1H), 1.97 (dd, J = 9.4, 5.4 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ = 167.0, 163.9, 147.6, 140.5, 129.6, 123.5, 122.5 (q, J_{CF} = 277 Hz, 1C), 122.4 (q, J_{CF} = 37 Hz, 1C), 61.5 (q, J_{CF} = 36 Hz, 2 overlapping C); 19F NMR (479 MHz, CDCl3) δ = -73.92 (t, J = 8.0 Hz, 3F), -74.07 (t, J = 9.3 Hz, 3F); IR (thin film) 3089, 1743, 1603, 1523, 1448, 1416, 1349, 1286, 1164, 1120, 1032, 971, 859, 773, 695, 664, 531; HRMS (EI) calculated for C15H11F6NO6 415.0491 found 415.0502.

(12c) as prepared through Corey-Chaykovsky cyclopropanation conditions in accordance to the previously reported synthesis: Goldberg, A. F. G.; O’Connor, N. R.; Craig, R. A.; Stoltz, B. M. Org. Lett. 2012, 14, 5314.


To a solution of N-methyl indole (3) (2.0 equiv) in anhydrous MeCN was added cyclopropane (1.0 equiv). The solution was stirred under argon for 20 minutes. Ytterbium triflate (10 mol %) was added and the reaction mixture was stirred until complete (as determined by TLC analysis). The reaction was quenched with sodium bicarbonate and extracted with EtOAc (3 times). The organic layers were then combined and dried with magnesium sulfate. Following filtration, the solvent was removed under reduced pressure and the crude mixture purified by flash chromatography (EtOAc/hexanes, 7:93) to yield the desired products 13a-f.

![Diagram of molecule 13a](image-url)
bis(2,2,2-trifluoroethyl) 2-(2-(4-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)malonate (13b) Reagents employed: N-methyl indole (0.112 g, 0.854 mmol), bis(2,2,2-trifluoroethyl) 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (0.171 g, 0.427 mmol), ytterbium triflate (0.027 g, 0.0427 mmol), 8 mL anhydrous MeCN at room temperature, for 50 minutes: yield 74 % (171 mg) as a yellow oil; Rf= 0.38, 30% EtOAc in hexanes; 1H NMR (400 MHz, CDCl₃) δ = 7.48 (d, J= 8.2 Hz, 1H), 7.32-7.20 (m, 4H), 7.06 (t, J= 7.0, 1H), 6.89-6.85 (m, 3H), 4.62-4.43 (m, 4H), 4.21 (dd, J= 8.2, 8.2 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.61 (dd, J= 8.0, 8.0 Hz, 1H), 2.94-2.85 (m, 1H), 2.71-2.62 (m, 1H); 13C NMR (100 MHz, CDCl₃) δ = 167.2, 167.1, 158.3, 137.3, 134.8, 128.7, 126.9, 126.1, 122.6 (q J_C-F = 277 Hz, 1C), 122.5 (q, J_C-F = 277 Hz, 1C) 121.8, 119.4, 119.0, 116.7, 114.0, 109.2, 60.9 (q, J_C-F = 37 Hz, 1C), 61.1 (q, J_C-F = 37 Hz, 1C), 55.1, 49.4, 39.7, 34.7, 32.6; 19F NMR (479 MHz, CDCl₃) δ= -73.73 (t, J= 8.2 Hz, 3F), -73.81 (t, J= 8.2 Hz, 3F); IR (thin film) 3008, 2936, 2838, 2348, 1755, 1611, 1467, 1412, 1374, 1282, 1249, 1170, 977, 840, 743, 665, 568; HRMS (EI) calculated for C₂₅H₂₀F₆N₂O₅ 531.1480, found 531.1481.

bis(2,2,2-trifluoroethyl) 2- (2-(1-methyl-1H-indol-3-yl)-2-(4-nitrophenyl)ethyl)malonate (13c) Reagents employed: N-methyl indole (0.112 g, 0.854 mmol), bis(2,2,2-trifluoroethyl) 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (0.177 g, 0.427 mmol), ytterbium triflate (0.027 g, 0.0427 mmol), 8 mL anhydrous MeCN at reflux, for 1.5 hours: yield 72 % (168 mg) as a yellow oil; Rf= 0.38, 30% EtOAc in hexanes; 1H NMR (400 MHz, CDCl₃) δ = 8.15 (d, J= 8.7 Hz, 2H), 7.49, (d, J= 9.0 Hz, 2H), 7.38-7.31 (m, 2H), 7.24 (t, J= 6.8 Hz, 1H), 7.06 (t, J= 7.1 Hz, 1H), 6.98 (s, 1H), 4.60-4.42 (m, 4H), 4.38 (dd, J= 7.1, 1 Hz, 1H), 3.81 (s, 3H), 3.61 (dd, J= 8.0, 8.0 Hz, 1H), 2.94-2.85 (m, 1H), 2.79-2.69 (m, 1H); 13C NMR (100 MHz, CDCl₃) δ = 166.9, 166.8, 151.0, 146.8, 137.5, 128.5, 126.5, 126.4, 123.9, 122.5, 122.3 (q, J_C-F = 277 Hz, 2 overlapping C), 119.5, 118.9, 114.2, 109.6, 61.1 (q, J_C-F = 37 Hz, 1C), 61.0 (q, J_C-F = 37 Hz, 1C), 49.3, 40.3, 36.2, 32.8; 19F NMR (479 MHz, CDCl₃) δ= -73.73 (t, J= 8.2 Hz, 3F), -73.81 (t, J= 8.2 Hz, 3F); IR (thin film) 2939, 2838, 2348, 1755, 1611, 1511, 1467, 1412, 1374, 1282, 1249, 977, 856, 743, 706, 555; HRMS (EI) calculated for C₂₆H₂₂F₁₀N₂O₆ 566.1226 found 566.1222.

dimethyl 2-(2-(1-methyl-1H-indol-3-yl)-2-phenylethyl)malonate (13d); N-methyl indole (0.112 g, 0.854 mmol), dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (0.100 g, 0.427 mmol), ytterbium triflate (0.027 g, 0.0427 mmol), 8 mL anhydrous MeCN at room temperature, for 48 hours: yield 94 %, BRSM 96 % (146 mg) as a yellow oil; Rf= 0.45, 30% EtOAc in hexanes; 1H NMR (400 MHz, CDCl₃) δ = 7.48 (d, J= 8.2 Hz, 1H), 7.36-7.27 (m, 5H), 7.23-7.19 (m, 2H), 7.05 (t, J= 7.4 Hz, 1H), 6.91 (s, 1H), 4.23 (dd, J= 8.2, 8.2 Hz, 1H), 3.76 (s, 6H) 3.69 (s, 3H), 3.43 (dd, J= 7.0, 7.0 Hz, 1H), 2.89-2.81 (m, 1H) 2.69-2.58 (m, 1H); 13C NMR
(100 MHz, CDCl₃) δ = 169.9, 169.8, 143.5, 137.2, 128.5, 127.9, 127.1, 126.4, 126.0, 121.6, 119.4, 118.8, 117.2, 109.1, 52.5, 52.4, 50.1, 40.6, 34.9, 32.7; IR (thin film) 3026, 2951, 1750, 1733, 1659, 1558, 1472, 1279, 1153, 1042, 1014, 741, 703, 570; HRMS (EI) calculated for C₂₂H₂₃NO₄ 365.1627 found 365.1626.

**dimethyl 2-(2-(4-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)malonate (13e)**

Reagents employed: N-methyl indole (0.112 g, 0.854 mmol), dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (0.113 g, 0.427 mmol), ytterbium triflate (0.027 g, 0.0427 mmol), 8 mL anhydrous MeCN at room temperature, for 3 hours: yield 70 % (123 mg) as a yellow oil; Rf= 0.29, 30% EtOAc in hexanes; ¹H NMR (400 MHz, CDCl₃) δ= 7.47 (d, J= 8.2 Hz, 1H), 7.30-7.18 (m, 4H), 7.04 (t, J= 7.0 Hz, 1H), 6.89-6.83 (m, 3H), 4.17 (dd, J= 7.0, 7.0 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.42 (dd, J= 6.6, 6.6 Hz, 1H), 2.88- 2.78 (m, 1H), 2.63-2.54 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ= 169.9, 169.8, 158.1, 137.2, 135.4, 128.8, 127.0, 125.9, 121.6, 119.5, 118.8, 117.5, 113.8, 109.1, 55.1, 52.4, 52.4, 50.0, 39.7, 35.1, 32.6; IR (thin film) 3000, 2952, 2836, 2360, 1733, 1610, 1510, 1465, 1405, 1176, 1153, 1034, 883, 742, 667, 566; HRMS (EI) calculated for C₂₂H₂₃NO₄ 395.1733, found 395.1732.

**dimethyl 2-(2-(1-methyl-1H-indol-3-yl)-2-(4-nitrophenyl)ethyl)malonate (13f)**

Reagents employed: N-methyl indole (0.112 g, 0.854 mmol), dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (0.119 g, 0.427 mmol), ytterbium triflate (0.027 g, 0.0427 mmol), 8 mL anhydrous MeCN at room temperature, for 4 hours: yield 71 %, (124 mg) as a yellow oil; Rf= 0.29, 30% EtOAc in hexanes; ¹H NMR (400 MHz, CDCl₃) δ= 8.14 (d, J= 8.6 Hz, 2H), 7.48 (d, J= 8.6 Hz, 2H) 7.37-7.29 (m, 2H), 7.22 (t, J= 8.2 Hz, 1H), 7.04 (t, J= 7.0 Hz, 1H), 6.99 (s, 1H), 4.36 (dd, J= 8.2, 8.1 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.42 (dd, J= 7.4, 1H), 2.88-2.78 (m, 1H), 2.71-2.63 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ = 169.5, 169.4, 151.6, 146.5, 137.3, 128.7, 126.7, 126.2, 123.7, 122.0, 119.2, 118.9, 115.1, 109.4, 52.6, 52.5, 49.8, 40.4, 34.5, 32.7; IR (thin film) 2952, 2360, 1749, 1733, 1595, 1518, 1473, 1435, 1345, 1153, 855, 753, 706, 667; HRMS (EI) calculated for C₂₂H₂₂N₂O₆ 410.1478 found 410.1484.