Supporting Information

Copper-Promoted Intramolecular Aminotrifluoromethylation of Alkenes with Langlois Reagent as the Trifluoromethyl Source

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Supporting Information

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I. General Methods and Materials

All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AC-P 400 spectrometer (400 MHz for $^1$H and 101 MHz for $^{13}$C) in CDCl$_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for $^1$H, or to chloroform δ = 77.0 for $^{13}$C as internal standard. $^{19}$F NMR spectra were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, $J$, are reported in hertz. Mass spectra were measured using Bruker microTOF-Q II (2a, 2c, 2j-2l, 2u) and Thermo Scientific DSQ II mass spectrometer (2b, 2d-2i, 2m-2p, 2v-2w). The starting materials were purchased from Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from “Purification of Laboratory Chemicals book”. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Substrates were prepared according to literature methods A$^1$ and literature methods B$^{2,3}$.

II. Typical Procedures for the Synthesis of Substrates

Method A

\[ \text{BrCH}_2\text{CH}==\text{CH}_2 + \text{K}_2\text{CO}_3 \rightarrow \text{CH}_2==\text{CH}_2 + \text{H}_2\text{O} \]

Typical procedure:

Allyl bromide (16.24 mmol) was added dropwise to a solution of commercially available aniline (16.24 mmol) and K$_2$CO$_3$ (38.97 mmol) in DMF (37 mL). The solution was heated to 80 °C and stirred at this temperature overnight. The reaction mixture was then filtered, washed with H$_2$O (3 × 20 mL) and extracted with EtOAc (2 × 15 mL). The combined organic extracts were washed with brine (30 mL), dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography to afford N-allyl-aniline.

Next, BF$_3$·OEt$_2$ (7.36 mmol) was added to a solution of N-allyl-aniline (7.36 mmol) in xylene (4 mL) at 0 °C under Ar atmosphere. The mixture was heated to 180 °C in a sealed tube and stirred at this temperature for 12 hours. After cooling, the reaction mixture was poured into 10% NaOH (10 mL), and extracted with EtOAc (3 × 15 mL). The combined organic extracts were washed
with brine (10 mL), dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography to yield 2-allylaniline as a colorless oil.

Subsequently, 2-allylaniline (4.08 mmol) and pyridine (8.58 mmol) in CH₂Cl₂ (10 mL) was treated sequentially with tosyl chloride (4.49 mmol) at 0 °C. The solution was allowed to warm to room temperature, and stirring was continued at this temperature overnight. Next, the reaction mixture was washed with a solution of 1 N HCl (20 mL) and extracted with EtOAc (3×20 mL). The combined organic extracts were washed with sat. aq. NaHCO₃ (20 mL) and then dried over Na₂SO₄. The solvents were removed in vacuo followed by flash chromatography to obtain the 2-allyl-N-tosylaniline as a white solid.

Method B

Typical procedure:

To a solution of diphenylacetonitrile (10 mmol) in DMF (5 mL) was added slowly a suspension of NaH (10.5 mmol) in DMF (10 mL) and the resulting mixture was stirred at room temperature for 1 h. The mixture was cooled to 0 °C, treated with allyl bromide (11 mmol), and warmed to room temperature overnight with stirring. The resulting solution was poured into an ice/water mixture (300 mL) and extracted with benzene (3×20 mL). The combined organic layers were washed with water (2×20 mL), dried over anhydrous Na₂SO₄, and concentrated to afford 2,2-diphenyl-4-pentenenitrile, which was used without further purification.

2,2-Diphenyl-4-pentenenitrile (8.2 mmol) was added to a suspension of LiAlH₄ (32.7 mmol) in ether (13 mL) at 0 °C and then warmed slowly to room temperature and stirred overnight. The resulting suspension was cooled to 0 °C and quenched by slow addition of 6 M NaOH (20 mL). The resulting mixture was extracted with ether (4×15 mL) and the combined organic layers were dried over anhydrous Na₂SO₄, and concentrated to give 2,2-diphenyl-4-pentenylamine as a pale yellow, viscous oil.

The 2,2-diphenyl-4-pentenylamine (9.5 mmol) was dissolved in dry methylene chloride (20 mL), and the solution was treated with p-toluenesulfonyl chloride (10.5 mmol) and pyridine (28.5 mmol) at 0 °C. The mixture was stirred at room temperature for 24 h, diluted with H₂O (20 mL) and extracted with CH₂Cl₂ (3×20 mL). The combined organic layers were washed with brine,
dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting residue was chromatographed (0-20% EtOAc in hexanes gradient) to give N-(2,2-Diphenyl-pent-4-enyl)-4-methyl-benzenesulfonamide.

III. General Procedures for Copper-Promoted Intramolecular Aminotrifluoromethylation of Alkenes

To a Schlenk tube were added 1a (0.2 mmol), CF₃SO₂Na (0.4 mmol), Cu(TFA)₂·xH₂O (0.2 mmol) and charged with argon for three times. Anhydrous CH₃CN (1.5 mL) and TBHP (0.6 mmol) was added via syringe and the mixture was stirred at 60 °C under Ar. When the substrate was consumed (monitored by TLC), the reaction mixture was cooled to room temperature. The solvent was removed by rotary and the resulting residue was purified by column chromatography on silica gel to afford the product 2a in 73 % yield.

IV. Mechanistic Research

In order to gain insight into the catalytic procedure, we carried out a series of control experiments. As illustrated in SI-Scheme 1, this reaction was completely suppressed by 2.0 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), even after longer reaction time. The process was remarkably suppressed in the presence of 2.0 equiv of 1,1-diphenylethylene as a radical scavenger. Only trace amounts of the desired product was detected and a trapped compound 5a was obtained. These results suggested that the formation of the CF₃ radical was the first step in this transformation. However, it was difficult to trap further intermediate radical to explain cyclization process. Hence, on the basis of the above experimental results and the literature reports,4,5,6,7 a tentative mechanism was proposed in SI-Scheme 2. First of all, the CF₃ radical is generated from CF₃SO₂Na promoted by Cu catalyst/K₂S₂O₈.4 An classic catalytic mechanism (Path A) is proposed to explain cyclization process, which proceeds by the formation of a primary carbon radical 1A, and subsequent coupling of this intermediate and the CF₃ radical. However, considering the fact that a small amount of byproduct 3a was formed, we also depicted an alternative mechanism (Path B).6 Firstly, the addition of the CF₃ radical to alkene 1a affords alkyl radical 2A. The byproduct 3a might be generated from 2A. Alternatively, 2A also might undergo single-electron oxidation providing 3A.7 Subsequent trapping of the resultant carbocation with a nitrogen nucleophile leads to the desired product 3a. But the exact mechanism for the aminotrifluoromethylation reaction remains unclear at present and deserves further detailed studies.
V. Characterization of the Products:

2a: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, $J = 8.1$ Hz 1H), 7.55 (d, $J = 8.3$ Hz 2H), 7.25-7.22 (m, 1H), 7.19 (d, $J = 8.0$ Hz 2H), 7.08-7.03 (m, 2H), 4.47-4.40 (m, 1H), 3.01-2.88 (m, 2H), 2.80-2.75 (m, 1H), 2.49-2.40 (m, 1H), 2.36 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.39, 140.74, 134.18, 130.63, 129.77, 128.11, 127.14, 125.66 (q, $J = 278.5$ Hz), 125.26, 125.11, 117.26, 56.82, 40.61 (q, $J = 26.9$ Hz), 34.15, 21.54; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.09 (s, 3F); MS (EI): found [M]$^+$ 355.

2b: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72-7.66 (m, 3H), 7.57-7.53 (m, 1H), 7.43-7.39 (m, 2H), 7.27-7.23 (m, 1H), 7.07 (d, $J = 4.2$ Hz 2H), 4.49-4.42 (m, 1H), 3.00-2.87 (m, 2H), 2.80-2.75 (m, 1H), 2.52-2.38 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.59, 137.18, 133.41, 130.62, 129.15, 128.16, 127.09, 125.61 (q, $J = 278.8$ Hz), 125.30, 125.24, 117.29, 56.88 (d, $J = 3.3$ Hz), 40.57 (q, $J = 26.8$ Hz), 34.09; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.07 (s, 3F); HRMS (ESI) m/z calcd for C$_{16}$H$_{18}$F$_3$N$_2$O$_2$S [M+NH$_4$]$^+$ 359.1041, found 359.1036.

2c: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.27-8.24 (m, 2H), 7.89-7.86 (m, 2H), 7.71 (d, $J = 8.1$ Hz 1H), 7.32-7.27 (m, 1H), 7.14-7.10 (m, 2H), 4.50-4.44 (m, 1H), 2.98-2.81 (m, 3H), 2.56-2.42 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.55, 142.79, 139.68, 130.49, 128.52, 128.33, 125.97, 125.72, 125.41 (q, $J = 278.4$ Hz), 124.38, 117.15, 57.25 (d, $J = 3.3$ Hz), 40.56 (q, $J = 27.1$ Hz), 34.07; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.06 (s, 3F); MS (EI): found [M]$^+$ 386.

2d: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48-7.45 (m, 1H), 7.26-7.22 (m, 2H), 7.13-7.09 (m,
1H), 4.60-4.53 (m, 1H), 3.56-3.50 (m, 1H), 3.07-2.89 (m, 2H), 2.84 (s, 3H), 2.52-2.44 (m, 1H); 13C NMR (101 MHz, CDCl₃) δ 140.60, 129.77, 128.45, 125.55, 125.54 (q, J = 278.7 Hz), 125.02, 115.68, 57.28 (d, J = 3.0 Hz), 40.93 (q, J = 27.3 Hz), 35.57, 34.48; 19F NMR (376 MHz, CDCl₃) δ: -63.00 (s, 3F); HRMS (ESI) m/z calcd for C₁₁H₁₆F₃N₂O₂S [M+NH₄]^+ 297.0885, found 297.0879.

2e: colourless oil; 1H NMR (400 MHz, CDCl₃) δ 7.45-7.42 (m, 1H), 7.25-7.22 (m, 2H), 7.13-7.09 (m, 1H), 4.66-4.59 (m, 1H), 3.67-3.60 (m, 2H), 3.56-3.50 (m, 1H), 3.17-3.13 (m, 2H), 3.09-3.04 (m, 1H), 2.92-2.85 (m, 1H), 2.55-2.41 (m, 1H), 2.30-2.24 (m, 2H); 13C NMR (101 MHz, CDCl₃) δ 140.32, 129.61, 128.48, 125.72, 124.96, 115.40, 125.36 (q, J = 256.1 Hz), 57.33 (d, J = 4.0 Hz), 46.82, 42.64, 40.78 (q, J = 27.3 Hz), 34.34, 26.18; 19F NMR (376 MHz, CDCl₃) δ: -62.90 (s, 3F); HRMS (ESI) m/z calcd for C₁₃H₁₉ClF₃N₂O₂S [M+NH₄]^+ 359.0808, found 359.0802.

2f: colourless oil; 1H NMR (400 MHz, CDCl₃) δ 7.39-7.37 (m, 2H), 7.17-7.06 (m, 4H), 6.89 (d, J = 7.2 Hz 1H), 4.61-4.55 (m, 1H), 2.57 (s, 3H), 2.51-2.44 (m, 1H), 2.39 (s, 3H), 2.24 (d, J = 4.1 Hz 2H), 2.20-2.09 (m, 1H); 13C NMR (101 MHz, CDCl₃) δ 143.92, 139.38, 134.94, 134.02, 132.98, 130.30, 129.14, 127.29, 126.66, 125.12 (q, J = 278.6 Hz), 122.07, 58.12 (d, J = 3.0 Hz), 38.42 (q, J = 27.6 Hz), 33.59, 21.22, 19.36; 19F NMR (376 MHz, CDCl₃) δ: -63.07 (s, 3F); HRMS (ESI) m/z calcd for C₁₈H₁₉F₃NO₂S [M+H]^+ 370.1089, found 370.1083.

2g: colourless oil; 1H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 8.3 Hz 2H), 7.22 (d, J = 8.1 Hz 2H), 7.10 (dd, J = 7.8 Hz 1H), 6.84 (d, J = 8.3 Hz 1H), 6.73 (d, J = 7.4 Hz 1H), 4.88-4.82 (m, 1H), 3.83 (s, 3H), 2.78-2.72 (m, 1H), 2.56-2.46 (m, 2H), 2.40 (s, 3H), 2.32-2.18 (m, 1H); 13C NMR (101 MHz, CDCl₃) δ 152.54, 143.88, 136.23, 136.00, 129.43, 129.31, 127.86, 127.57, 125.56 (q, J = 278.7 Hz), 117.52, 112.53, 58.65 (d, J = 3.0 Hz), 56.04, 39.16 (q, J = 27.3 Hz), 34.67, 21.54; 19F NMR (376 MHz, CDCl₃) δ: -63.03 (s, 3F); HRMS (ESI) m/z calcd for C₁₈H₁₉F₃NO₃S [M+H]^+ 386.1038, found 386.1031.
2h: colourless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (d, \(J = 8.3\) Hz 2H), 7.23 (d, \(J = 8.0\) Hz 2H), 7.13-7.01 (m, 2H), 6.90 (dd, \(J = 7.28, 0.44\) Hz 1H), 4.76-4.70 (m, 1H), 2.73-2.67 (m, 1H), 2.64-2.51 (m, 2H), 2.40 (s, 3H), 2.36-2.22 (m, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 152.01 (d, \(J = 256.7\) Hz), 142.22, 134.77, 132.48, 125.82 (q, \(J = 278.6\) Hz), 125.51 (d, \(J = 6.6\) Hz), 125.21, 118.58 (d, \(J = 3.0\) Hz), 114.09, 113.89, 56.57 (d, \(J = 3.0\) Hz). 19F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -63.07 (s, 3F), -118.36 (s, 1F); HRMS (ESI) m/z calcd for C\(_{17}\)H\(_{15}\)F\(_4\)NNaO\(_2\)S\([\text{M+Na}]^+\) 396.0657, found 396.0674.

\[\text{MeO}\]

2i: colourless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57-7.53 (m, 3H), 7.19 (d, \(J = 8.1\) Hz 2H), 7.04 (d, \(J = 8.0\) Hz 1H), 6.86 (s, 1H), 4.43-4.37 (m, 1H), 2.96-2.83 (m, 2H), 2.73-2.68 (m, 1H), 2.44-2.41 (m, 1H), 2.36 (s, 3H), 2.28 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.21, 138.38, 134.95, 134.29, 130.78, 129.73, 128.73, 127.21, 125.81, 125.68 (q, \(J = 278.7\) Hz), 117.15, 56.96 (d, \(J = 3.0\) Hz), 40.58 (q, \(J = 26.9\) Hz), 34.10, 21.54, 20.95; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -63.08 (s, 3F); MS (EI): found [M]+ 369.

\[\text{Cl}\]

2j: colourless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 8.8\) Hz 1H), 7.51 (d, \(J = 8.3\) Hz 2H), 7.20-7.17 (m, 2H), 6.80-6.77 (m, 1H), 6.60-6.59 (m, 1H), 4.44-4.38 (m, 1H), 3.77 (s, 3H), 2.94-2.76 (m, 2H), 2.70-2.64 (m, 1H), 2.52-2.40 (m, 1H), 2.37 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.74, 144.22, 133.99, 133.97, 132.62, 129.71, 127.22, 125.60 (q, \(J = 278.6\) Hz), 118.62, 113.29, 110.83, 57.14 (d, \(J = 3.3\) Hz), 55.59, 40.42 (q, \(J = 26.9\) Hz), 34.25, 21.54; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -63.07 (s, 3F); MS (EI): found [M]+ 385.

\[\text{F}\]

2k: colourless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63-7.61 (d, \(J = 8.6\) Hz 1H), 7.55 (d, \(J = 8.3\) Hz 2H), 7.23-7.20 (m, 3H), 7.04-7.03 (m, 1H), 4.46-4.40 (m, 1H), 2.98-2.88 (m, 2H), 2.79-2.74 (m, 1H), 2.50-2.43 (m, 1H), 2.38 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.55 (d, \(J = 245.1\) Hz), 154.70, 139.54, 133.87, 132.54, 130.38, 129.93, 128.25, 127.14, 125.52 (q, \(J = 277.8\) Hz), 125.44, 118.16, 57.14 (d, \(J = 3.2\) Hz), 40.56 (q, \(J = 26.9\) Hz), 33.95, 21.58; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -63.09 (s, 3F); MS (EI): found [M]+ 389.

2l: colourless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65-7.62 (m, 1H), 7.53 (d, \(J = 8.3\) Hz 2H), 7.21 (d, \(J = 8.1\) Hz 2H), 6.97-6.92 (m, 1H), 6.78-6.75 (m, 1H), 4.48-4.42 (m, 1H), 2.94-2.83 (m, 2H), 2.75-2.70 (m, 1H), 2.49-2.40 (m, 1H), 2.38 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.55 (d, \(J = 245.1\) Hz),
144.57, 136.79 (d, J = 2.1 Hz), 133.84, 132.95 (d, J = 8.8 Hz), 129.84, 127.17, 125.53 (q, J = 278.8 Hz), 118.57 (d, J = 8.8 Hz), 114.83 (d, J = 23.6 Hz), 112.42 (d, J = 24.3 Hz), 57.29 (q, J = 3.1 Hz), 40.46 (q, J = 27.0 Hz), 34.09, 21.54; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.09 (s, 3F), -117.49 (s, 1F); HRMS (ESI) m/z calcd for C$_{17}$H$_{19}$F$_4$N$_2$O$_2$S [M+NH$_4$]$^+$ 391.1103, found 391.1098.

2m: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, J = 8.3 Hz 2H), 7.36 (s, 1H), 7.20 (d, J = 8.0 Hz 2H), 6.69 (s, 1H), 4.44-4.37 (m, 1H), 3.04-2.91 (m, 1H), 2.83-2.77 (m, 1H), 2.67-2.62 (m, 1H), 2.46-2.42 (m, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 2.07 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.17, 140.60, 138.24, 134.36, 134.30, 129.72, 127.17, 126.83, 126.22, 51.44 (q, J = 280.4 Hz), 114.97, 56.94, 40.90 (q, J = 27.3 Hz), 32.85, 21.54, 21.51, 18.58; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.09 (s, 3F); HRMS (ESI) m/z calcd for C$_{19}$H$_{21}$F$_3$NO$_2$S [M+H]$^+$ 384.1245, found 384.1238.

2n: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.62-7.60 (m, 2H), 7.29-7.25 (m, 4H), 7.23-7.12 (m, 6H), 7.06-7.04 (m, 2H), 4.46 (dd, J = 10.24, 0.64 Hz, 1H), 3.88-3.81 (m, 1H), 3.53-3.50 (d, J = 10.2 Hz, 1H ), 3.07-2.93 (m, 1H), 2.80-2.74 (m, 1H), 2.55-2.50 (m, 1H), 2.40 (s, 3H), 1.85-1.70 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.48, 144.25, 143.81, 133.00, 129.83, 128.71, 128.67, 127.54, 126.83, 126.66, 126.58, 126.28, 125.81 (q, J = 275.4 Hz), 57.86, 53.82 (d, J = 3.0 Hz), 52.34, 42.92, 39.75 (q, J = 26.26 Hz), 21.50; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.87 (s, 3F); HRMS (ESI) m/z calcd for C$_{25}$H$_{25}$F$_3$NO$_2$S [M+H]$^+$ 460.1558, found 460.1554.

2o: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.19 (m, 10H), 4.24 (d, J =11.2 Hz, 1H), 4.16-4.13 (m, 1H), 4.05-3.98 (m, 1H), 3.38-3.33 (m, 1H), 3.15-3.01 (m, 1H), 2.44-2.39 (m, 1H), 2.22 (s, 3H), 2.17-2.04 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.48, 143.81, 129.13, 128.85, 127.38, 126.99, 126.76, 126.40, 125.72 (q, J = 278.4 Hz), 59.29, 54.28, 53.37, 43.25, 40.45 (q, J = 26.26 Hz), 35.06; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.43 (s, 3F); HRMS (ESI) m/z calcd for C$_{10}$H$_{24}$F$_3$N$_2$O$_2$S [M+NH$_4$]$^+$ 401.1511, found 401.1505.

N

OMe

CF$_3$
2p: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, $J = 7.5$ Hz 1H), 7.65-7.61 (m, 1H), 7.55-7.50 (m, 2H), 4.95-4.92 (m, 1H), 4.01 (s, 3H), 3.05-2.91 (m, 1H), 2.61-2.47 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.01, 140.90, 132.88, 129.45, 125.75 (q, $J = 278.1$ Hz), 123.28, 123.26, 121.62, 64.03, 54.26 (d, $J = 3.4$ Hz), 36.24 (q, $J = 29.0$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -62.64 (s, 3F); MS (EI): found [M]+ 245.

2q: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45-7.21 (m, 10H), 4.53-4.46 (m, 1H), 3.86 (s, 3H), 3.07 (dd, $J = 12.7$, 4.6 Hz 1H), 2.90-2.76 (m, 1H), 2.71-2.65 (m, 1H), 2.51-2.37 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.96, 142.20, 141.21, 128.77, 128.13, 128.07, 127.62, 127.59, 127.13, 125.10 (q, $J = 278.0$ Hz), 73.87 (d, $J = 3.0$ Hz), 62.74, 57.41, 45.44, 38.84 (q, $J = 28.3$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.70 (s, 3F); HRMS (ESI) m/z calcd for C$_{19}$H$_{19}$F$_3$NO$_2$ [M+H]+ 350.1368, found 350.1362.

2r: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40-7.24 (m, 10H), 4.63-4.56 (m, 1H), 3.19 (dd, $J = 13.1$, 3.2 Hz 1H), 2.78-2.65 (m, 2H), 2.52-2.39 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 176.01, 141.33, 138.94, 129.15, 128.56, 127.58, 127.52, 127.21, 125.02 (q, $J = 278.3$ Hz), 70.47 (d, $J = 3.0$ Hz), 57.52, 43.44, 39.17 (q, $J = 29.3$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -63.76 (s, 3F); HRMS (ESI) m/z calcd for C$_{18}$H$_{19}$F$_3$NO$_2$ [M+NH$_4$]+ 338.1368, found 338.1362.

4a & 5a: colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40-7.38 (m, 2.53H), 7.36-7.32 (m, 11.44H), 7.25-7.24 (m, 3.02H), 6.12 (q, $J = 8.28$ Hz, 0.70H), 5.46 (s, 2.00H); MS (EI): 4a: found [M]+ 180; 5a: found [M]+ 248.

VI. References and Notes:
2013, 78, 10288;


8. The spectrum (1H, 13C, 19F NMR and HRMS) of compounds 2a, 2c, 2j, 2k and 2l were reported in Lin et al, Chem. Eur. J. 2014, 20, 1332-1340 and the compound 2u was reported in Shen et al, Org. Chem. Front. 2016, 3, 222-226.
VII. NMR Charts

[Chemical Structure Image]

2a-H
2b-F
2g-C
SI-33
2p-H

SI-56
2p-C