Supporting Information

Selective Radical Amination of Aldehydic C(sp^2)–H Bonds with Fluoroaryl Azides via Co(II)-Based Metalloradical Catalysis: Synthesis of *N*-Fluoroaryl Amides from Aldehydes

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I. General information

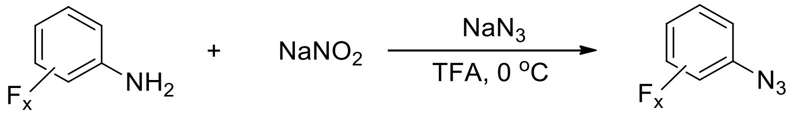
General considerations: Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254), visualizing with UV-light 254 nm or 365 nm fluorescence quenching. Flash column chromatography was performed with silica gel (60 Å, 230-400 mesh, 32-63 μm).

Instrumentation:

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian 400-MHz or 500-MHz instruments. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = 7.24 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = 77.00 ppm). ^{19}F spectra were recorded on a Varian 400 spectrometer (376 MHz), using $CFCl_3$ (δ=0) as internal standard. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory, High-resolution mass spectra were obtained on an Agilent 6220 using electrospray ionization time-of-flight mass spectrometry (ESI-TOF).

II. Preparation of azides and catalyst

a. Preparation of fluoroaryl azides[1]



Fluoroaniline (10 mmol) was dissolved in TFA (25 mL) and cooled to 0 °C. $NaNO_2$ (12

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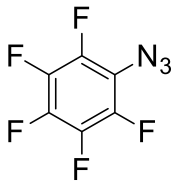
[1] Jin, L. M.; Xu, X. Lu, H.; Cui, X.; Wojtas, L.; Zhang, X. P. *Angew. Chem. Int. Ed.* **2013**, 52, 5309.

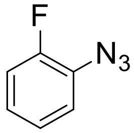
mmol) was added in portions with stirring. After stirred at 0 °C for 1h, NaN_3 (15 mmol) was added and the mixture was stirred at 0 °C for another 1h. The mixture was diluted with Et_2O (50 mL) and washed with water and then saturated $NaHCO_3$ and dried over $MgSO_4$. After removal of solvent, the residue was purified by flash column chromatography (silica gel, pentanes) to give pure azide. These fluoroaryl azides can be stored in a freezer for several months without any obvious decomposition.



Pentafluorophenyl azide (2a)

Yield: 82%.

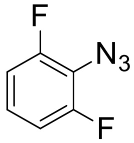
^{13}C NMR (125 MHz, $CDCl_3$): δ 141.04 (dm, J = 250.0 Hz), 138.13 (dm, J = 261.2 Hz), 115.94 (dt, J = 4.6, 12.5 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -152.04 (m, 2 F), -160.28 (m, 1 F), -162.09 (m, 2F). IR (neat, cm^{-1}): 2120, 1505, 1242, 1102, 1014, 994, 940, 802.



2-Fluorophenyl azide (2b)

Yield: 70%.

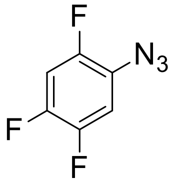
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 – 7.04 (m, 4 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 154.79 (d, J = 247.6 Hz), 127.81 (d, J = 10.8 Hz), 125.67 (d, J = 7.1 Hz), 124.77 (d, J = 3.8 Hz), 120.93, 116.61 (d, J = 18.6 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -126.78 (m, 1 F). IR (neat, cm^{-1}): 2117, 1492, 1315, 1228, 1096, 746, 648.



2, 6-Difluorophenyl azide (2c)

Yield: 63%.

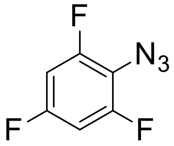
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04 – 6.99 (m, 1 H), 6.92 – 6.86 (m, 2 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 155.81 (dd, J = 3.7, 248.7 Hz), 124.76 (t, J = 9.3 Hz), 117.44 (t, J = 13.8 Hz), 112.10 (dd, J = 5.1, 17.6 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -123.30 (m, 2 F). IR (neat, cm^{-1}): 2115, 1474, 1323, 1010, 773, 704, 612.



2,4,5-Trifluorophenyl azide (2d)

Yield: 79%.

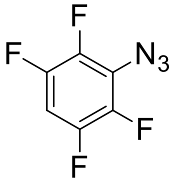
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00 – 6.95 (m, 1 H), 6.90 – 6.85 (m, 1 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 150.22 (ddd, J = 3.1, 9.1, 246.8 Hz), 146.77 (dm, J = 248.3 Hz), 124.22 (m), 109.50 (dm, J = 22.0 Hz), 106.62 (ddd, J = 1.0, 21.8, 24.5 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -128.08 (m, 1 F), -138.00 (m, 1 F), -140.46 (m, 1 F). IR (neat, cm^{-1}): 3070, 2109, 1426, 1255, 1199, 1146, 834, 772, 638.



2,4,6-Trifluorophenyl azide (2e)

Yield: 97%.

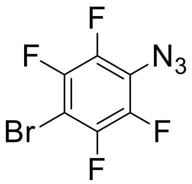
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.70 (m, 2 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 158.66 (dt, J = 247.2, 14.3 Hz), 155.67 (ddd, J = 6.7, 14.3, 250.0 Hz), 114.15 (dt, J = 5.3, 14.3 Hz), 101.1 (m). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -122.5 (m, 1 F), -120.19 (m, 2 F). IR (neat, cm^{-1}): 2129, 1499, 1046, 998, 841, 648, 607.



2,3,5,6-Tetrafluorophenyl azide (2f)

Yield: 72%.

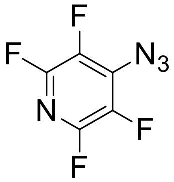
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86 – 6.79 (m, 1 H).^{13}C NMR (125 MHz, $CDCl_3$): δ 146.16 (ddt, J = 4.1, 247.1, 12.0 Hz), 140.53 (dddd, J = 2.5, 4.3, 16.0, 248.1 Hz), 120.66 (tt, J = 3.1, 11.8 Hz), 101.34 (dt, J = 1.4, 22.9 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -139.06 (m, 2 F), -152.11 (m, 2 F). IR (neat, cm^{-1}): 3088, 2118, 1639, 1511, 1477, 1212, 1172, 986, 938, 832, 711, 651.



4-bromo- 2,3,5,6-tetrafluorophenyl azide (2g)

Yield: 91%.

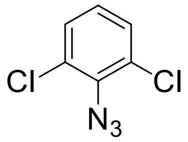
^{13}C NMR (125 MHz, $CDCl_3$): δ 145.12 (ddt, J = 13.6, 242.3, 4.2, Hz), 140.78 (dm, J = 251.0 Hz), 119.59 (tt, J = 2.3, 12.2 Hz), 94.97 (tm, J = 22.7 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -133.31 (m, 2 F), -150.61 (m, 2 F). IR (neat, cm^{-1}): 2119, 1488, 1473, 1303, 1221, 1006, 972, 828, 773.



2,3,5,6-tetrafluoropyridyl azide (2h)

Yield: 59%.

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.59 (ddt, J = 3.0, 14.7, 242.5 Hz), 135.44 (dm, J = 259.0 Hz), 132.22 (m). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -89.84 (s, 2 F), -153.29 (m, 2 F). IR (neat, cm^{-1}): 2125, 1638, 1471, 1209, 995, 959.



2,6-dichlorophenyl azide (2i)

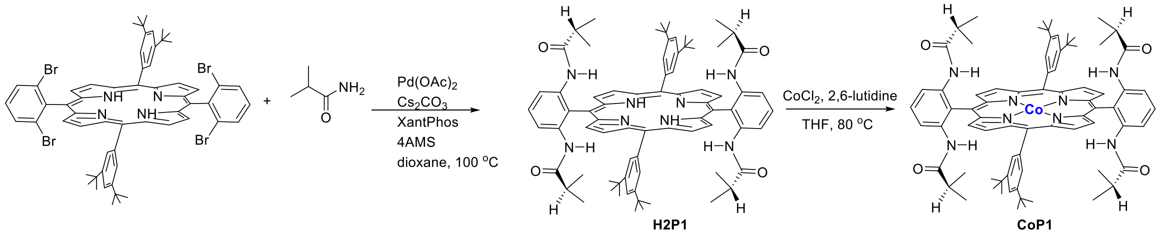
Yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.0 Hz, 2 H), 7.04 (t, J = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 134.10, 129.56, 129.02, 126.39.

IR (neat, cm^{-1}): 2102, 1562, 1436, 1307, 768.

b. Preparation of catalyst[2,3]



H2P1 was synthesized according to our previous reported procedure with 80% yield[2]. The 5,15-bis(2,6-dibromophenyl)-10,20-bis[3,5-di(*tert*-butyl)phenyl]porphyrin[3] (1 g, 0.87 mmol), isobutyramide (1.2 g, 13.8 mmol, 16 eq), $Pd(OAc)_2$ (78 mg, 0.35 mmol), Xantphos (402 mg, 0.7 mmol), and Cs_2CO_3 (4.5 g, 13.8 mmol) were placed in an oven-dried, re-sealable Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. The screw cap was replaced with a rubber septum, and dioxane (45 mL) was added via syringe. The tube was purged with nitrogen for 30 sec, and then the septum was replaced with the Teflon screw cap. The tube was sealed and the mixture was heated with stirring at 100 ^{o}C for 48 h. The resulting mixture was cooled to room temperature, filtered through a short pad of silica gel using ethyl acetate as eluent. The mixture was concentrated under vacuum and the crude product was then purified by flash chromatography (v/v: Ethyl acetate/hexanes = 1/5 to 3/7) to give the product 800 mg as purple solid.

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2. Chen, Y.; Fields, K. B.; Zhang, X. P. *J. Am. Chem. Soc*. **2004**, *126*, 4718.

3. Ruppel, J. V.; Jones, J. E.; Huff, C. A.; Kamble, R. M.; Chen, Y.; Zhang, X. P. *Org. Lett.*, **2008**, *10*, 1995.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (d, J = 4.8 Hz, 4 H), 8.85 (d, J = 4.8 Hz, 4 H), 8.48 (d, J = 7.6 Hz, 4 H), 8.0 (s, 4 H), 7.90-7.85 (m, 4 H), 6.46 (s, 4 H), 1.52 (s, 36 H), 1.20 (m, 4 H), 0.31 (d, J = 7.4 Hz, 24 H), -2.53 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.7, 149.4, 139.7, 138.8, 133.5, 130.5, 130.1, 123.1, 121.8, 117.8, 108.0, 35.8, 35.0, 31.6, 18.5.

[CoP1] was synthesized according to our previous reported procedure with 90% yield[2]. The free base porphyrin **H2P1** (500 mg, 0.42 mmol) and anhydrous $CoCl_2$ (552 mg, 4.2 mmol) were placed in an oven-dried, re-sealable Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. The screw cap was replaced with a rubber septum, 2,6-lutidine (450 mg, 4.2 mmol) and dry THF (20 mL) were added via syringe. The tube was purged with nitrogen for 30 sec, and then the septum was replaced with the Teflon screw cap. The tube was sealed and the mixture was heated with stirring at 100 °C for 24 h. The resulting mixture was cooled to room temperature, diluted with ethyl acetate (100 mL) and was washed with water 2 times and concentrated under vacuum. The residue was purified by flash chromatography (v/v: Ethyl acetate/hexanes = 1/2) to give the product 470 mg as red solid.

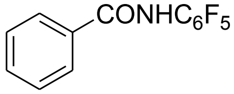
HRMS (ESI): Calcd. for C76H88N8O4Co ($[M]^+$) m/z 1235.6255, Found 1235.6264.

III. General procedure for amidation of aldehydes with perfluorophenyl azide

$$\underset{\mathbf{1}}{\text{R-CHO}} \quad + \quad \underset{\mathbf{2a}}{C_6F_5N_3} \xrightarrow[\text{4Å MS, 80 °C, PhCl, 24 h}]{[\text{Co}(\mathbf{P1})],\ 3\text{ mol }\%} \underset{\mathbf{3}}{\text{R-CONHC}_6\text{F}_5}$$

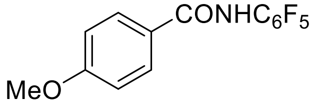
An oven dried Schlenk tube was charged with catalyst (3 mol %), aldehyde (if solid, 0.2 mmol, 1 eq) and 4 Å molecular sieves. The Schlenk tube was then evacuated for 30 min and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and aldehyde (if liquid, 0.2 mmol, 1 eq), azide (0.24 mmol, 1.2 eq) and PhCl (1 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 80 °C for

24h. Following completion of the reaction, the reaction mixture was purified by flash chromatography.



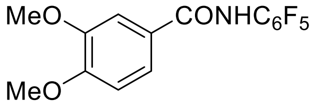
3aa

^{1}H NMR (500 MHz, $CDCl_3$): δ. 7.89 ~ 7.88 (m, 2 H), 7.61 ~ 7.58 (m, 1 H), 7.57 ~ 7.47 (m, 3 H, overlapped with NH peak). ^{13}C NMR (125 MHz, $CDCl_3$): δ. 165.59, 143.03 (md, J = 265.1 Hz), 140.12 (md, J = 252.7 Hz), 137.85 (md, J = 252.4 Hz), 132.88, 132.39, 128.95, 127.64, 112.09 (m). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.2 (m, 2 F), -156.98 (t, J = 21.4 Hz, 1 F), -162.66 (m, 2 F). IR (neat, cm^{-1}): 3231, 1670, 1501, 1489, 1288, 981, 906, 795, 689, 618. HRMS (ESI) ([M+H]$^+$) Calcd. for: C13H6F5NO•H$^+$: 288.0448, Found 288.0446.



3ba

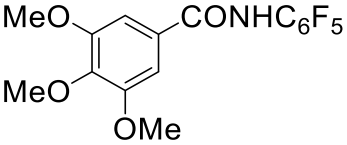
^{1}H NMR (500 MHz, $CDCl_3$): δ. 7.86 (d, J = 8.0 Hz, 2 H), 7.38 (s, 1 H), 6.96 (d, J = 8.0 Hz, 2 H), 3.87 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ. 165.07, 163.26, 142.97 (md, J = 241.0 Hz), 139.92 (md, J = 126.1 Hz), 137.81 (md, J = 125.6 Hz), 129.67, 124.51, 114.10, 112.33 (m), 55.53. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.44 (m, 2 F), -157.49 (t, J = 21.4 Hz, 1 F), -162.89 (m, 2 F). IR (neat, cm^{-1}): 3359, 1668, 1512, 1484, 1254, 1003, 980, 905, 845, 760, 620. HRMS (ESI) ([M+H]$^+$) Calcd. for: C14H8F5NO2•H$^+$: 318.0553, Found: 318.0554.



3ca

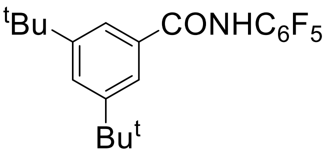
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 ~ 7.44 (m, 3 H), 6.90 (d, J = 8.0 Hz, 1 H), 3.94 (s, 3 H), 3.91 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ.165.13, 152.94, 149.28, 144.18 ~ 136.57 (m), 124.84, 120.56, 112.29 (m), 110.99, 110.39, 56.11, 56.06. ^{19}F NMR (376

MHz, $CFCl_3$, $CDCl_3$): δ -145.46 (m, 2 F), -157.32 (t, J = 21.6 Hz, 1 F), -162.83 (m, 2 F). IR (neat, cm^{-1}): 3259, 2919, 1668, 1512, 1484, 1254, 1003, 980, 905, 845, 760, 620. HRMS (ESI) ($[M+H]^+$) Calcd. for: C15H10F5NO3•H^+: 348.0659, Found: 348.0681.



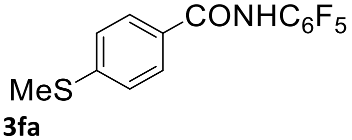
3da

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (s, 1 H), 7.09 (s, 2 H), 3.87 (s, 3 H), 3.85 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.63, 153.33, 143.02 (md, J = 249.5 Hz), 142.03, 140.03 (md, J = 257.2 Hz), 137.77 (md, J = 252.7 Hz), 127.48, 112.14 (mt, J = 14.9 Hz), 105.11, 60.96, 56.29. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.38 (m, 2 F), -156.94 (t, J = 21.6 Hz, 1 F), -162.70 (m, 2 F). IR (neat, cm^{-1}): 3243, 2951, 1672, 1583, 1488, 1338, 1229, 1126, 994, 958, 842, 681, 616. HRMS (ESI) ($[M+H]^+$) Calcd. for: C16H12F5NO4•H^+: 378.0765, Found: 378.0758.



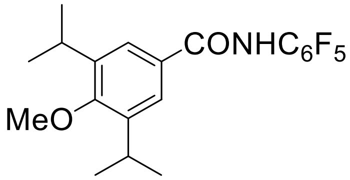
3ea

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.68 (s, 1 H), 7.94 (d, J = 1.5 Hz, 2 H), 7.78 (t, J = 1.5 Hz, 1 H), 1.37 (s, 18 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 166.87, 152.25, 144.43 (md, J = 242.0 Hz), 140.64 (md, J = 249.4 Hz), 138.60 (md, J = 233.5 Hz), 133.23, 127.56, 122.97, 114.52 (m), 35.65, 31.60. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.20 (m, 2 F), -157.36 (t, J = 21.4 Hz, 1 F), -162.89 (m, 2 F). IR (neat, cm^{-1}): 2959, 1650, 1521, 1494, 1248, 991, 944, 703, 640. HRMS (ESI) ($[M+H]^+$) Calcd. for: C21H22F5NO•H^+: 400.1700, Found:400.1685.



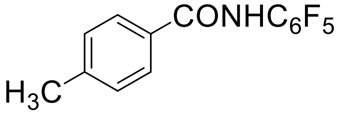
3fa

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ. 9.57 (s, 1 H), 7.99 (d, J = 9.0 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 2.57 (s, 3 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ.165.85, 146.18, 144.53 (md, J = 246.8 Hz), 140.84 (md, J = 235.5 Hz), 138.78 (md, J = 249.8 Hz), 129.71, 129.32, 126.12, 114.50 (m), 14.75. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.30 (m, 2 F), -157.14 (t, J = 21.4 Hz, 1 F), -162.72 (m, 2 F). IR (neat, cm^{-1}): 3257, 1671, 1650, 1594, 1522, 1482, 1456, 1293, 1108, 1004, 982, 898, 834, 750, 625. HRMS (ESI) ([M+H]$^+$) Calcd. for: C14H8F5NOS•H$^+$: 334.0325, Found: 334.0329.



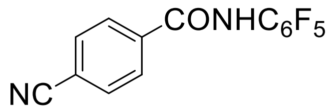
3ga

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.64 (s, 1 H), 7.89 (s, 2 H), 3.80 (s, 3 H), 3.40 (septet, J = 7.0 Hz, 2 H), 1.26 (d, J = 7.0 Hz, 12 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 166.14, 159.35, 144.49 (md, J = 246.0 Hz), 143.20, 140.65 (md, J = 244.8 Hz), 138.65 (md, J = 245.5 Hz), 129.73, 125.15, 114.54 (mt, J = 15.2 Hz), 62.69, 27.43, 24.08. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.30 (m, 2F), -157.39 (t, J = 21.4Hz, 1F), -162.92 (m, 2F). IR (neat, cm^{-1}): 3187, 2964, 1645, 1520, 1497, 1459, 1300, 1202, 990, 956, 611. HRMS (ESI) ([M+Na]$^+$) Calcd. for: C20H20F5NO2•Na$^+$: 424.1312, Found: 424.1306.



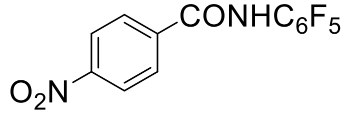
3ha

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.55 (s, 1 H), 7.95 (d, J = 8.5 Hz, 2 H), 7.37 (d, J = 8.5 Hz, 2 H), 2.42 (s, 3 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 166.17, 144.50 (md, J = 246.8 Hz), 143.96, 140.67 (md, J = 249.1 Hz), 138.67 (md, J = 249.6 Hz), 130.97, 130.15, 128.80, 114.46 (m), 21.46. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -144.84 (m, 2F), -156.82 (t, J = 21.4 Hz, 1F), -162.34 (m, 2F). IR (neat, cm^{-1}): 3215, 1667, 1511, 1486, 1459, 1285, 1097, 980, 906, 835, 748, 663, 625. HRMS (ESI) ([M+H]$^+$) Calcd. for: C14H8F5NO•H$^+$: 302.0604, Found: 302.0614.



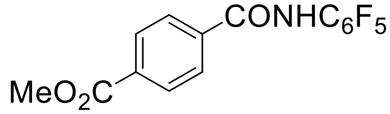
3ia

^{1}H NMR (500 MHz, (DMSO-d_6): δ. 10.84 (s, 1 H), 8.14 (d, J = 7.5 Hz, 2 H), 8.06 (d, J = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.18, 143.85 (md, J = 247.4 Hz), 140.39 (md, J = 249.5 Hz), 138.29 (md, J = 249.3 Hz), 137.16, 133.75 (m), 129.70 (m), 119.05, 115.77, 113.60 (mt, J = 16.4 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, DMSO-d_6): δ -144.63 (m, 2 F), -156.59 (m, 1 F), -162.75 (m, 2 F). IR (neat, cm^{-1}): 2917, 1667, 1508, 1491, 1303, 1102, 982, 906, 865, 761, 653. HRMS (ESI) ([M+Na]$^+$) Calcd. for: C14H5F5N2O•Na$^+$: 335.0220, Found: 335.0217.



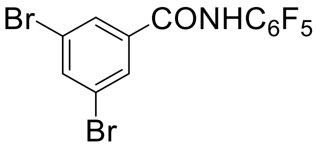
3ja

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.94 (s, 1 H), 8.40 (d, J = 8.4 Hz, 2 H), 8.22 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.10, 149.79, 144.12 ~ 136.11 (m), 137.86, 129.55, 123.90, 112.63 (m). ^{19}F NMR (376 MHz, $CFCl_3$, DMSO-d_6): δ -144.61 (d, J = 18.4 Hz, 2 F), -156.22 (dt, J = 4.5, 22.9 Hz, 1 F), -162.53 (t, J = 21.8 Hz, 2 F). IR (neat, cm^{-1}): 2917, 1677, 1520, 1283, 985. HRMS (ESI) ([M+H]$^+$) Calcd. for: C13H5F5N2O3•H$^+$: 333.0299, Found: 333.0296.



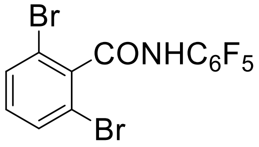
3ka

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.0 Hz, 2 H), 7.95 (d, J = 8.0 Hz, 2 H), 7.50 (s, 1 H), 3.95 (s, 3 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 166.47, 165.61, 144.43 (md, J = 254.1 Hz), 140.9 (md, J = 249.6 Hz), 138.7 (md, J = 251.3 Hz), 137.59, 134.47, 130.49, 129.01, 114.00 (m), 52.74. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.01 (m, 2 F), -156.31 (t, J = 21.4 Hz, 1 F), -162.37 (m, 2 F). IR (neat, cm^{-1}): 3259, 1722, 1671, 1522, 1483, 1457, 1285, 1114, 1007, 983, 903, 735, 625. HRMS (ESI) ([M+H]$^+$) Calcd. for: C15H8F5NO3•H$^+$: 346.0503, Found: 346.0486.



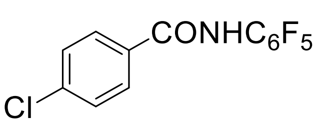
3la

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.88 (s, 1 H), 8.18 (d, J = 2.0 Hz, 2 H), 8.04 (t, J = 1.8 Hz, 1 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 163.63, 144.30 (md, J = 243.6 Hz), 140.97 (md, J = 249.8 Hz), 138.73 (md, J = 247.1 Hz), 138.30, 137.18, 130.84, 123.86, 113.65 (m). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.00 (m, 2 F), -155.80 (t, J = 21.4 Hz, 1 F), -162.09 (m, 2 F). IR (neat, cm^{-1}): 3149, 2953, 1670, 1654, 1544, 1520, 1498, 1464, 1285, 1002, 987, 929, 874, 763, 711, 699, 629. HRMS (ESI) ($[M+H]^+$) Calcd. for: C13H4Br2F5NO•H^+: 443.8658, Found: 443.8641.



3ma

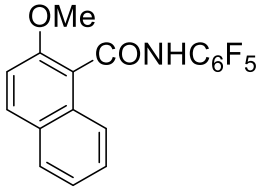
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.77 (s, 1 H), 7.73 (d, J = 8.0 Hz, 2 H), 7.36 (t, J = 8.0 Hz, 1 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 164.99, 144.51 (dm, J = 247.8 Hz), 141.18 (dm, J = 249.9 Hz), 140.31, 138.89 (dm, J = 249.0 Hz), 133.21, 132.95, 120.90, 112.88 (m). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -143.46 (m, 2 F), -155.76 (t, J = 21.4 Hz, 1 F), -162.36 (m, 2 F). IR (neat, cm^{-1}): 3199, 1688, 1543, 1527, 1494, 1424, 1287, 1125, 1003, 980, 904, 769, 619. HRMS (ESI) ($[M+H]^+$) Calcd. for: C13H4Br2F5NO•H^+: 443.8658, Found: 443.8640.



3na

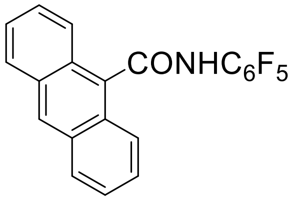
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.73 (s, 1 H), 8.07 (d, J = 8.5 Hz, 2 H), 7.61 (d, J = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 165.34, 144.44 (md, J = 246.5 Hz), 140.81 (md, J = 246.1 Hz), 139.03, 138.71 (md, J = 248.9 Hz), 132.45, 130.59, 129.77, 114.00 (m). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.22 (m, 2 F), -156.55 (t, J = 21.4 Hz, 1 F),

-162.43 (m, 2 F). IR (neat, cm^{-1}): 3223, 2919, 1670, 1652, 1522, 1482, 1459, 1295, 1106, 1015, 982, 905, 847, 755, 623. HRMS (ESI) ([M+H]$^+$) Calcd. for C13H5ClF5NO•H$^+$: 322.0058, Found: 322.0045.



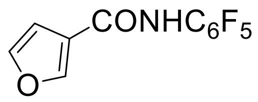
3oa

^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): δ 9.48 (s, 1 H), 8.05 (d, J = 9.0 Hz, 1 H), 7.98 (d, J = 8.5 Hz, 1 H), 7.91 (d, J = 8.5 Hz, 1 H), 7.56 (m, 1 H), 7.52 (d, J = 9.0 Hz, 1 H), 7.42 (m, 1H), 4.03 (s, 3 H). ^{13}C NMR (125 MHz, (CD$_3$)$_2$CO): δ 166.32, 155.16, 144.37 (md, J = 243.9 Hz), 140.73 (md, J = 235.3 Hz), 138.24 (md, J = 243.3 Hz), 132.52, 132.31, 129.64, 128.98, 128.38, 124.95, 124.76, 120.27, 114.33, 114.05 (m), 57.13. ^{19}F NMR (376 MHz, CFCl$_3$, CDCl$_3$): δ -144.80 (d, J = 16.5 Hz, 2 F), -157.68 (d, J = 21.4 Hz, 1 F), -163.00 (m, 2 F). IR (neat, cm^{-1}): 2925, 1664, 1649, 1510, 1493, 1254, 1081, 1002, 977, 922, 813, 749, 620. HRMS (ESI) ([M+H]$^+$) Calcd. for: C18H10F5NO2•H$^+$: 368.0710, Found: 368.0700.



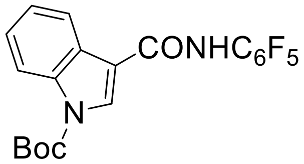
3pa

^{1}H NMR (500 MHz, DMSO-d$_6$): δ 11.17 (s, 1 H), 8.81 (s, 1 H), 8.22 (d, J = 8.5 Hz, 2 H), 8.09 (d, J = 9.0 Hz, 2 H), 7.70 (t, J = 7.5 Hz, 2 H), 7.63 (t, J = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 165.58, 143.02 (md, J = 265.1 Hz), 140.11 (md, J = 252.8 Hz), 137.83 (md, J = 252.4 Hz), 132.87, 132.37, 128.93, 127.63, 112.08 (mt, J = 15.1 Hz). ^{19}F NMR (376 MHz, CFCl$_3$, DMSO-d$_6$): δ -144.26 (m, 2 F), -155.76 (t, J = 21.4 Hz, 1 F), -162.23 (m, 2 F). IR (neat, cm^{-1}): 1640, 1518, 1491, 999, 978, 731, 601. HRMS (ESI) ([M+H]$^+$) Calcd. for: C21H10F5NO•H$^+$: 388.0761, Found: 388.0765.



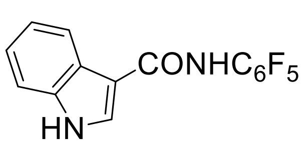
3qa

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.42 (s, 1 H), 8.33 (m, 1 H), 7.72 (t, J = 1.8 Hz, 1 H), 6.96 (m, 1 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 161.26, 147.30, 145.42, 144.53 (md, J = 247.3 Hz), 140.76 (md, J = 249.0 Hz), 138.68 (md, J = 248.5 Hz), 122.40, 113.79, 109.83. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.20 (m, 2 F), -156.67 (t, J = 21.4 Hz, 1 F), -162.60 (m, 2 F). IR (neat, cm^{-1}): 2932, 1676, 1520, 1491, 1459, 1318, 1121, 1006, 989, 965, 875, 824, 749, 647, 625. HRMS (ESI) ([M+H]$^+$) Calcd. for: C11H4F5NO2•H$^+$: 278.0240, Found: 278.0246.



3ra

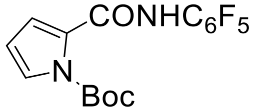
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1 H), 8.14 (d, J = 8.4 Hz, 1 H), 8.06 (d, J = 8.0 Hz, 1 H), 7.53 (s, 1 H), 7.38 (t, J = 8.0 Hz, 1 H), 7.32 (t, J = 7.6 Hz, 1 H), 1.67 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.09, 148.83, 142.93 (md, J = 127.6 Hz), 140.07 (md, J = 108.5 Hz), 137.55 (d, J = 108.8 Hz), 135.36, 129.04, 127.09, 125.58, 124.14, 120.98, 115.30, 113.98, 111.8 (m), 85.50, 28.00. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.29 (m, 2 F), -157.32 (t, J = 21.4 Hz, 1 F), -162.87 (m, 2 F). IR (neat, cm^{-1}): 1746, 1644, 1504, 1448, 1375, 1278, 1219, 1143, 1113, 993, 747, 647. HRMS (ESI) ([M+H]$^+$) Calcd. for: C20H15F5N2O3•H$^+$: 427.1081, Found: 427.1078.



3sa

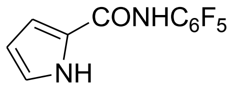
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 10.98 (s, 1 H), 9.17 (s, 1 H), 8.29 (d, J = 3.0 Hz, 1 H), 8.27 (d, J = 8.0 Hz, 1 H), 7.52 (d, J = 8.0 Hz, 1 H), 7.22 (m, 2 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 162.96, 143.67 (md, J = 246.1 Hz), 139.31 (md, J = 248.2 Hz), 137.84 (md, J = 245.2 Hz), 136.71, 129.21, 126.49, 122.77. 121.28, 121.18, 113.96 (mt, J =

13.1 Hz), 111.94, 109.62. ^{19}F NMR (376 MHz, CFCl$_3$, (CD$_3$)$_2$CO): δ -145.59 (m, 2 F), -158.09 (t, J = 21.8 Hz, 1 F), -163.03 (m, 2 F). HRMS (ESI) ([M+H]$^+$) Calcd. for: C15H7F5N2O•H$^+$: 327.0557, Found: 327.0558.



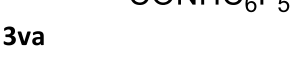
3ta

^{1}H NMR (400 MHz, CDCl$_3$): δ 10.38 (s, 1 H), 7.43 (dd, J = 2.0, 3.2 Hz, 1 H), 7.34 (dd, J = 2.0, 3.6 Hz, 1 H), 6.26 (t, J = 3.4 Hz, 1 H), 1.62 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 157.71, 150.59, 144.26 ~ 136.55 (m), 128.56, 127.63, 125.44, 112.51 (m), 111.09, 86.90, 27.84. ^{19}F NMR (376 MHz, CFCl$_3$, CDCl$_3$): δ -145.04 (m, 2 F), -158.34 (t, J = 21.8 Hz, 1 F), -163.45 (m, 2 F). IR (neat, cm^{-1}): 2918, 1742, 1670, 1522, 1492, 1460, 1316, 1149, 1094, 1004, 978, 843, 741, 654. HRMS (ESI) ([M+H]$^+$) Calcd. for: C16H13F5N2O3•Na$^+$: 399.0744, Found: 399.0728.



3ua

^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): δ 11.04 (s, 1 H), 9.39 (s, 1 H), 7.09 (m, 1 H), 7.07 (m, 1 H), 6.24 (m, 1 H). ^{13}C NMR (125 MHz, (CD$_3$)$_2$CO): δ 159.93, 144.47 (md, J = 246.0 Hz), 140.54 (md, J =228.0 Hz), 138.69 (md, J = 234.0 Hz), 125.53, 124.15, 114.23 (m), 113.00, 110.44. ^{19}F NMR (376 MHz, CFCl$_3$, (CD$_3$)$_2$CO): -145.39 (m, 2 F), -157.34 (t, J = 21.4 Hz, 1 F), -162.77 (m, 2 F). IR (neat, cm^{-1}): 3283, 1625, 1519, 1499, 1124, 989, 751, 650, 605. HRMS (ESI) ([M+H]$^+$) Calcd. for: C11H5F5N2O•Na$^+$: 299.0220, Found: 299.0208.



3va

^{1}H NMR (500 MHz, CDCl$_3$): δ 6.73 (s, 1 H), 2.44 (t, J = 7.5 Hz, 2 H), 1.73 (quint, J = 8 Hz, 2 H), 1.43 (sextet, J = 8 Hz, 2 H), 0.96 (t, J = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 168.3, 144.1 ~ 136.7 (m), 36.0, 27.4, 22.2, 13.7. ^{19}F NMR (376 MHz, CFCl$_3$,

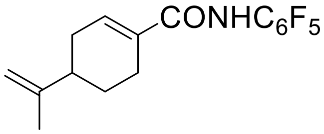
$CDCl_3$): δ -145.43 (m, 2 F), -157.08 (m, 1 F), -162.88 (m, 2 F). IR (neat, cm^{-1}): 3235, 2920, 1715, 1514, 1380, 1005, 990. HRMS (ESI) ($[M+H]^+$) Calcd. For C11H10F5NO•H^+: 268.0761, Found: 268.0756.

3wa

^1H NMR (400 MHz, $CDCl_3$): δ 2.11 (m, 1 H), 1.19 (m, 2 H), 0.98 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.26, 143.22 ~ 109.86 (m), 15.57, 11.26. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -144.72 (m, 2 F), -152.54 (m, 1 F), -161.70 (m, 2 F). IR (neat, cm^{-1}): 2916, 1719, 1513, 1379, 1175, 992. HRMS (ESI) ($[M+H]^+$) Calcd. for C10H6F5NO•H^+: 252.0448, Found: 252.0441.

3xa

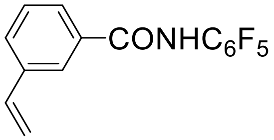
^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 15.6 Hz, 1 H), 7.52 (m, 2 H), 7.39 (m, 3 H), 7.03 (s, 1 H), 6.59 (d, J = 15.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.99, 144.62, 144.19 ~ 136.58 (m), 134.02, 130.58, 128.98, 128.15, 118.00, 111.84. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.05 (m, 2 F), -157.01 (t, J = 19.9 Hz, 1 F), -162.73 (t, J = 20.3 Hz, 2 F). IR (neat, cm^{-1}): 3251, 1680, 1632, 1520, 1488, 1334, 1193, 1137, 1022, 1002, 977, 966, 863, 761, 711. HRMS (ESI) ($[M+H]^+$) Calcd. for: C15H8F5NO·H^+: 314.0604, Found 314.0640.



3ya

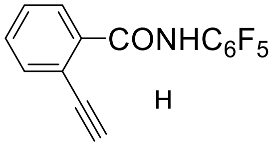
^1H NMR (500 MHz, $CDCl_3$): δ 7.00 (s, 1 H), 6.88 (m, 1 H), 4.79 (s, 1 H), 4.75 (s, 1 H), 2.55 ~ 2.52 (m, 1 H), 2.39 ~ 2.37 (m, 2 H), 2.23 ~ 2.18 (m, 2 H), 1.98 ~ 1.95 (m, 1 H), 1.77 (s, 3 H), 1.57 ~ 1.53 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.00, 148.34, 142.93 (md, J = 238.4 Hz), 139.84 (md, J = 259.4 Hz), 137.81 (md, J = 235.1 Hz), 136.61, 131.91, 112.21 (m), 109.52, 39.93, 30.95, 26.88, 24.77, 20.70. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.55 (m, 2 F), -157.62 (t, J = 21.4 Hz, 1 F), -162.99 (m, 2 F).

IR (neat, cm^{-1}): 3240, 2927, 1671, 1632, 1518, 1479, 1458, 1000, 975, 896, 641. HRMS (ESI) ([M+H]$^+$) Calcd. for: C16H14F5NO•H$^+$: 332.1074, Found: 332.1080.



3za

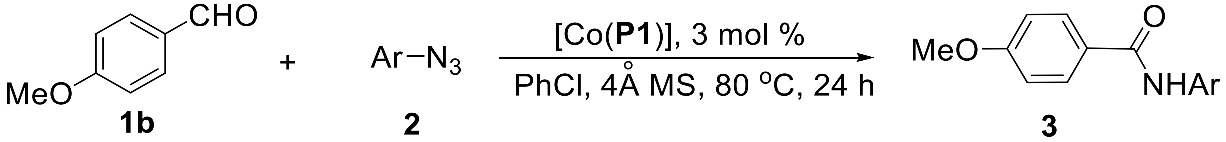
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.94 (t, J = 1.5 Hz, 1 H), 7.78 (d, J = 7.5 Hz, 1 H), 7.65 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 7.8 Hz, 1 H), 7.43 (brs, 1 H), 6.77 (dd, J = 10.5, 17.5 Hz, 1 H), 5.86 (d, J = 17.5 Hz, 1 H), 5.38 (d, J = 11.0 Hz, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 165.44, 144.00 ~ 136.93 (m), 138.52, 136.93, 135.58, 132.77, 130.40, 129.15, 126.61, 125.56, 115.89. ^{19}F NMR (376 MHz, CFCl$_3$, CDCl$_3$): δ -145.18 (m, 2 F), -156.90 (t, J = 21.4 Hz, 1 F), -162.62 (m, 2 F). IR (neat, cm^{-1}): 3215, 2918, 2850, 1704, 1669, 1500, 1298, 987, 813, 619. HRMS (ESI) ([M+H]$^+$) Calcd. for C15H8F5NO•H$^+$: 314.0604, Found: 314.0600.



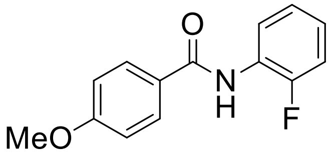
3zaa

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.84 (brs, 1 H), 8.15 (m, 1 H), 7.66 (m, 1 H), 7.54 (m, 2 H), 3.64 (s, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 164.02, 144.26 ~ 136.86 (m), 136.86, 134.39, 134.35, 131.77, 130.77, 129.76, 118.75, 85.08, 81.97. ^{19}F NMR (376 MHz, CFCl$_3$, CDCl$_3$): δ -144.19 (m, 2 F), -157.14 (t, J = 21.4 Hz, 1 F), -162.83 (m, 2 F). IR (neat, cm^{-1}): 3295, 3256, 2921, 2108, 1668, 1519, 1280, 1233, 1003, 979, 756, 560. HRMS (ESI) ([M+H]$^+$) Calcd. for C15H6F5NO•H$^+$: 312.0448, Found: 312.0441.

IV. General procedure for amidation of aldehyde with various aryl azides

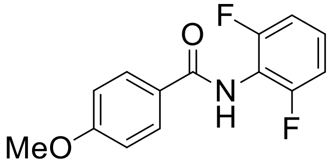


An oven dried Schlenk tube was charged with catalyst (3 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated for 30 min and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and aldehyde (0.2 mmol, 1 eq), azide (0.24 mmol, 1.2 eq) and PhCl (1 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 80 °C for 24h. Following completion of the reaction, the reaction mixture was purified by flash chromatography.



3bb

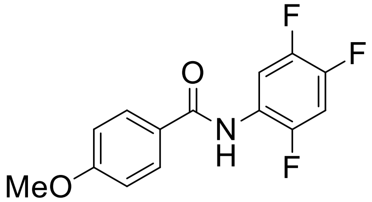
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.43 (dt, J = 1.5, 8.0 Hz, 1 H), 7.98 (s, 1 H), 7.84 (m, 2 H), 7.16 ~ 7.03 (m, 3 H), 6.96 (m, 2 H), 3.85 (s, 3 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 164.92, 162.67, 152.57 (d, J = 241.3 Hz), 128.91, 126.61 (t, J = 4.9 Hz), 124.57 (d, J = 3.6 Hz), 124.112 (d, J = 7.8 Hz), 121.66, 114.67 (d, J = 19.1 Hz), 113.97, 55.39 (d, J = 2.4 Hz). ^{19}F NMR (376 MHz, CFCl$_3$, CDCl$_3$): δ -132.2 (m, 1 F). IR (neat, cm^{-1}): 3307, 1652, 1509, 1453, 1252, 1179. HRMS (ESI) ([M+H]$^+$) Calcd. For C14H12FNO2•H$^+$: 246.0930, Found: 246.0916.



3bc

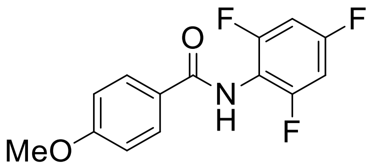
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.87 (d, J = 8.5 Hz, 2 H), 7.40 (s, 1 H), 7.18 (m, 1 H), 6.95 (m, 4 H), 3.85 (s, 3 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 165.16, 162.83, 157.75 (dd, J = 4.9, 249.0 Hz), 129.56, 127.27 (t, J = 9.8 Hz), 125.56, 114.41 (t, J = 16.1 Hz), 113.94, 111.72 (dd, J = 4.4, 19.2 Hz), 55.48 (d, J = 2.5 Hz). ^{19}F NMR (376 MHz, CFCl$_3$, CDCl$_3$):

δ -118.48 (m, 2 F). IR (neat, cm^{-1}): 3214, 2922, 1655, 1605, 1505, 1466, 1256, 1005, 781. HRMS (ESI) ($[M+H]^+$) Calcd. for C14H11F2NO2•H^+: 264.0836, Found: 264.0835.



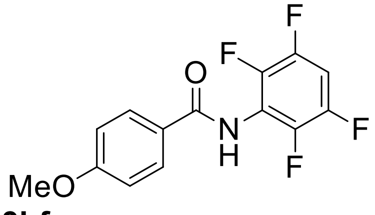
3bd

^1H NMR (500 MHz, $CDCl_3$): δ 8.36 (m, 1 H), 7.92 (s, 1 H), 7.80 (m, 2 H), 6.95 (m, 3 H), 3.84 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.84, 162.96, 148.67 ~ 144.39 (m), 129.02, 125.96, 123.01 (m), 114.13, 110.53 (dd, J = 2.0, 24.8 Hz), 104.73 (dd, J = 22.1, 24.4 Hz), 55.49 (d, J = 1.8 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -133.99 (m, 1 F), -140.18 (m, 1 F), -140.64 (m, 1 F). IR (neat, cm^{-1}): 3295, 1652, 1516, 1428, 1253, 868. HRMS (ESI) ($[M+H]^+$) Calcd. for C14H10F3NO2•H^+: 282.0742, Found 282.0735.



3be

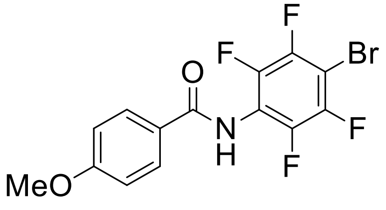
^1H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 8.5 Hz, 2 H), 7.26 (s, 1 H), 6.95 (d, J = 9.0 Hz, 2 H), 6.74 (t, J = 8.5 Hz, 2 H), 3.86 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.29, 162.92, 160.69 (td, J = 14.6, 247.9 Hz), 158.13 (ddd, J = 7.4, 15.1, 250.1 Hz), 129.51, 125.29, 113.98, 110.94 (m), 100.61 (t, J = 28.5 Hz), 55.49 (d, J = 2.4 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -109.93 (m, 1F), -115.11 (m, 2 F). IR (neat, cm^{-1}): 3282, 2963, 2922, 1652, 1604, 1514, 1440, 1256, 1040, 796. HRMS (ESI) ($[M+H]^+$) Calcd. for C14H10F3NO2•H^+: 282.0742, Found:282.0739.



3bf

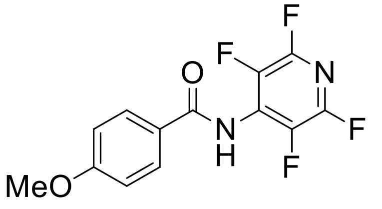
^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 8.5 Hz, 2 H), 7.49 (s, 1 H), 7.00 (m, 1 H), 6.97 (d, J = 9.0 Hz, 2 H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.79, 163.22, 146.01

(md, J = 246.8 Hz), 142.07 (md, J = 247.8 Hz), 129.72, 124.76, 117.44 (m), 114.10, 103.46 (t, J = 22.5 Hz), 55.53 (d, J = 2.4 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -139.65 (m, 2 F), -146.03 (m, 2 F). IR (neat, cm^{-1}): 3266, 2923, 1670, 1495, 1463, 1251, 1174, 1025, 876. HRMS (ESI) ($[M+H]^+$) Calcd. for C14H9F4NO2•H^+: 300.0648, Found: 300.0642.



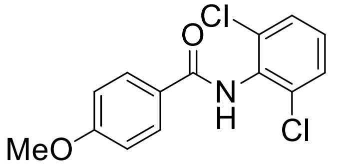
3bg

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.58 (s, 1 H), 8.04 (d, J = 8.5 Hz, 2 H), 7.07 (d, J = 9.0 Hz, 2 H), 3.90 (s, 3 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 165.19, 163.79, 145.97 (md, J = 200.4 Hz), 143.94 (md, J = 221.3 Hz), 130.84, 125.82, 118.72 (m), 114.75, 97.61 (t, J = 22.7 Hz), 55.96 (d, J = 2.0 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -133.43 (m, 2 F), -143.86 (m, 2 F). IR (neat, cm^{-1}): 3249, 1668, 1492, 1458, 1250, 1180, 981, 837. HRMS (ESI) ($[M+H]^+$) Calcd. For C14H8BrF4NO2•H^+: 377.9753, Found: 377.9746.



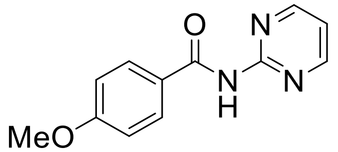
3bh

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.99 (s, 1 H), 8.05 (d, J = 8.5 Hz, 2 H), 7.09 (d, J = 8.5 Hz, 2 H), 3.91 (s, 3 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 164.90, 164.45, 144.42 (md, J = 238.1 Hz), 138.17 (md, J = 257.0 Hz), 131.27, 125.34, 114.81, 56.01 (d, J = 2.1 Hz). ^{19}F NMR (376 MHz, $CFCl_3$, $(CD_3)_2CO$): δ -90.37 (m, 2 F), -146.53 (m, 2 F). IR (neat, cm^{-1}): 3265, 2961, 2932, 1677, 1602, 1451, 1257, 1019, 848. HRMS (ESI) ($[M+H]^+$) Calcd. for C13H8F4N2O2•H^+:301.0600, Found: 301.0590.



3bi

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.28 (s, 1 H), 8.05 (d, J = 9.0 Hz, 2 H), 7.52 (d, J = 8.0 Hz, 2 H), 7.36 (t, J = 8.5 Hz, 1 H), 7.07 (d, J = 9.0 Hz, 2 H), 3.89 (s, 3 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 165.55, 163.63, 130.49, 129.74, 129.24, 127.06, 115.27, 114.59, 114.49, 55.89. IR (neat, cm^{-1}): 1649, 1605, 1491, 1254, 781. HRMS (ESI) ($[M+H]^+$) Calcd. for C14H11Cl2NO2•H$^+$: 296.0245, Found : 296.0226.



3bj[4]

^{1}H NMR (400 MHz, $(CDCl_3)$: δ 9.10 (m, 1 H), 8.61 (d J = 4.5 Hz, 2 H), 8.10 (d, J = 8.8 Hz, 2 H), 7.06 (t, J = 4.8 Hz, 1 H), 6.98 (d, J = 8.8 Hz, 2 H), 3.90 (s, 3 H). HRMS (ESI) ($[M+H]^+$) Calcd. for C12H11N3O2•H$^+$: 230.0930, Found : 230.0920.

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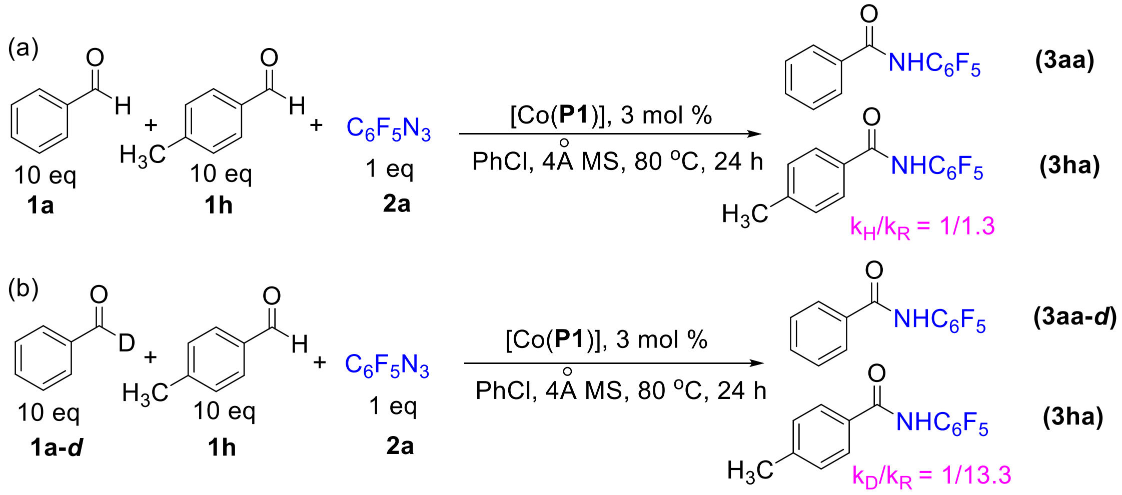
[4] Vimolratana, M.; Simard, J. L.; Brown, S. P. *Tetrahedron Lett*. **2011**, *52*, 1020–1022.

V. General procedure for Kinetic Isotope Effect (KIE)



An oven dried Schlenk tube was charged with catalyst (3 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated for 30 min and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and benzaldehyde (**1a**, 1 mmol, 10 eq), 4-methylbenzaldehyde (**1h**, 1mmol, 10 eq), pentafluorophenyl azide (**2a**, 0.1 mmol, 1 eq) and PhCl (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 80 °C for 24 h. Following completion of the reaction, the distribution of the amides **3aa** and **3ha** was determined as 1/1.3 by ^{19}F NMR.

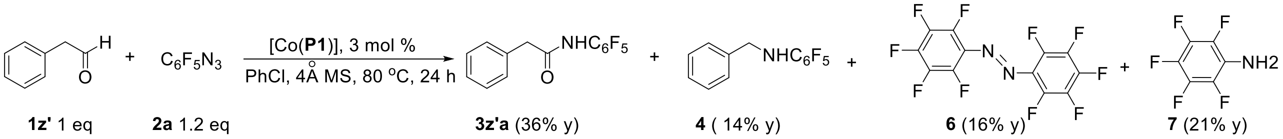
Thus, $k_H/k_R = 1/1.3$ (a)

An oven dried Schlenk tube was charged with catalyst (3 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated for 30 min and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and benz(aldehyde-*d)* (**1a-*d***, 1 mmol, 10 eq), 4-methylbenzaldehyde (**1h**, 1mmol, 10 eq), pentafluorophenyl azide (**2a**, 0.1 mmol, 1 eq) and PhCl (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 80 °C for 24 h. Following completion of the reaction, the distribution of the amides **3aa-*d*** and **3ha** was determined as 1/13.3 by ^{19}F NMR.

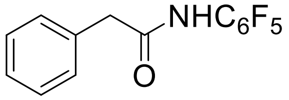
Thus, $k_D/k_R = 1/13.3$ (b)

Based on the equation (a) and (b), $k_H/k_D = 10.2$

VI. Procedure for radical clock reaction

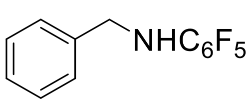


An oven dried Schlenk tube was charged with [Co(**P1**)] (3 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated for 30 min and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and phenylacetaldehyde (**1z'**, 0.2 mmol, 1 eq), pentafluorophenyl azide (**2a**, 0.24 mmol, 1.2 eq), and PhCl (1 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 80 °C for 24 h. Following completion of the reaction, the mixture was monitored by ^{19}F NMR to give amide **3z'a** (36% y), amine **4** (14% y), azo compound **6** (16% y) and aniline **7** (21% y). After purified by column the residue gave amide **3za** (20 mg, yield: 33%), amine **4** (5 mg, yield: 9%) and azo **6** (10 mg, yield: 14%). The aniline **7** was not isolated due to the low boiling point.



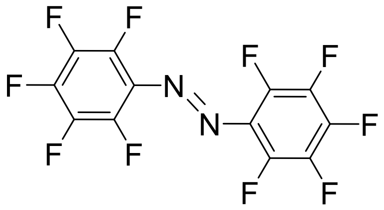
3z'a

^1H NMR (500 MHz, $(CD_3)_2CO$): δ 9.26 (s, 1 H), 7.38 ~ 7.26 (m, 5 H), 3.82 (s, 2 H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 170.19, 144.21 (md, J = 247.1 Hz), 140.60 (md, J = 231.3 Hz), 138.58 (md, J = 247.5 Hz), 136.04, 130.05, 129.32, 127.73, 114.10 (t, J = 14.8 Hz), 43.10. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -145.33 (d, J = 16.2 Hz, 2 F), -156.66 (t, J = 20.3 Hz, 1 F), -162.81 (t, J = 19.2 Hz, 2 F). IR (neat, cm^{-1}): 3168, 2989, 1673, 1652, 1523, 1495, 1149, 998, 955, 704, 654, 462. HRMS (ESI) ($[M+H]^+$) Calcd. for C14H8F5NO•H^+:302.0604, Found: 302.0606.



Compound **4**[5]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 ~ 7.26 (m, 5 H), 4.48 (d, J = 6.5 Hz, 2 H), 3.91 (brs, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.64, 139.06 ~ 132.82 (m), 128.83, 127.83, 127.57, 50.40. ^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -158.63 (d, J = 19.9 Hz, 2 F), -164.12 (t, J = 22.6 Hz, 2 F), -171.04 (m, 1 F). MS (EI): m/z (%) = 273.0 (14), 272 (100), 194 (40), 77 (21).



Compound **6**[6]

^{19}F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -148.47 (d, J = 17.3 Hz, 4 F), -148.80 (t, J = 21.1 Hz, 2 F), -161.49 (m, 4 F). MS (EI): m/z (%) = 363.0 (4), 362 (30), 195 (22), 167 (100), 117 (62).

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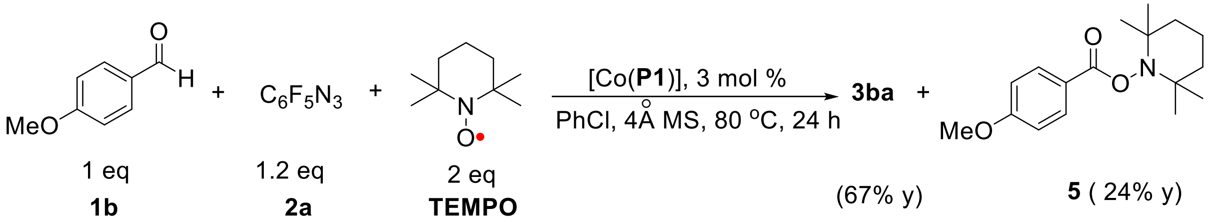
5. Liu, X.; Zhu, S.; Wang S. *Synthesis*, **2004**, 683-691.

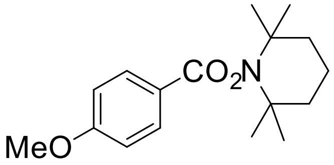
6. Leyva, E.; Medina, C.; Moctezuma, E.; Leyva, S. *Can. J. Chem.* **2004**, *82*, 1712-1715.

VII. Procedure for radical intermediate trapping reaction by TEMPO



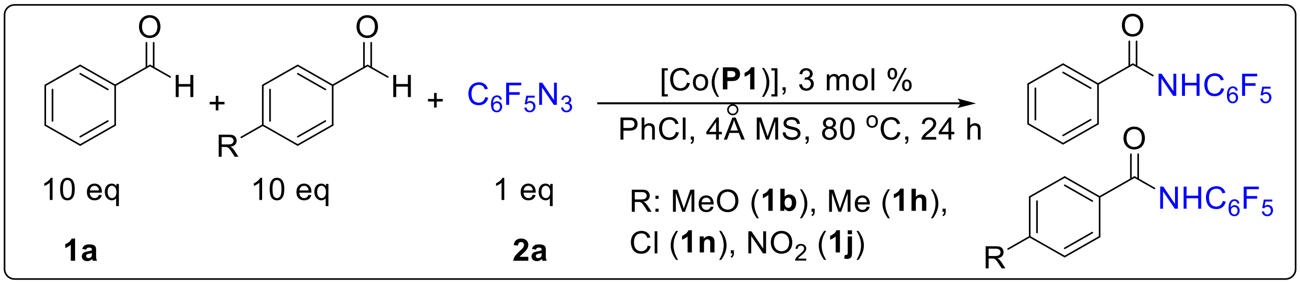
An oven dried Schlenk tube was charged with [Co(**P1**)] (3 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated for 30 min and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and 4-methoxybenzaldehyde (**1b**, 0.1 mmol, 1 eq), pentafluorophenyl azide (**2a**, 0.12 mmol, 1.2 eq), (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (**TEMPO**, 2 eq) and PhCl (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 80 ^{o}C for 24 h. Following completion of the reaction, the mixture was purified by column to give amide **3ba** (yield: 67%) and TEMPO trapped product **5** (yield: 24%).

Compound 5



^{1}H NMR (500 MHz, CDCl$_3$): δ 8.01 (d, J = 9.0 Hz, 2 H), 6.92 (d, J = 8.5 Hz, 2 H), 3.84 (s, 3 H), 1.77 ~ 1.41 (m, 6 H), 1.24 (s, 6 H), 1.08 (s, 6 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 166.11, 163.25, 131.54, 122.00, 113.67, 60.29, 55.41, 39.04, 31.95, 20.83, 17.01. IR (neat, cm^{-1}): 2926, 1747, 1602, 1511, 1247, 1160, 1070. HRMS (ESI) ([M+H]$^{+}$) Calcd. for C17H25NO3•H^{+}: 292.1913**,** Found 292.1921.

VIII. Experimental procedure for linear free-energy correlation



An oven dried Schlenk tube was charged with [Co(**P1**)] (3 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated for 30 min and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and benzaldehyde (**1a**, 1 mmol, 10 eq), 4-methoxybenzaldehyde (**1e**, 1mmol, 10 eq), pentafluorophenyl azide (**2a**, 0.1 mmol, 1 eq) and PhCl (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 80 °C for 24 h. Following completion of the reaction, the distribution of the amides **3aa** and **3ea** was determined as 1/2.4 by ^{19}FNMR.

Thus, $k_H/k_{MeO} = 1/2.4$ (c)

In a similar way, the distribution of the amides **3aa** and **3ia** was determined as 1/1.8 by ^{19}FNMR. Thus, $k_H/k_{Me} = 1/1.8$ (d)

The distribution of the amides **3aa** and **3la** was determined as 1.4/1 by ^{19}FNMR. Thus, $k_H/k_{Cl} = 1.4/1$ (e)

The distribution of the amides **3aa** and **3oa** was determined as 1.4/1 by ^{19}FNMR. Thus, $k_H/k_{NO2} = 3.6/1$ (f)

Based on the eqs (c) – (f), the plot of linear free-energy correlation of log k_X/k_H versus σ_p was obtained as shown in Figure S1.

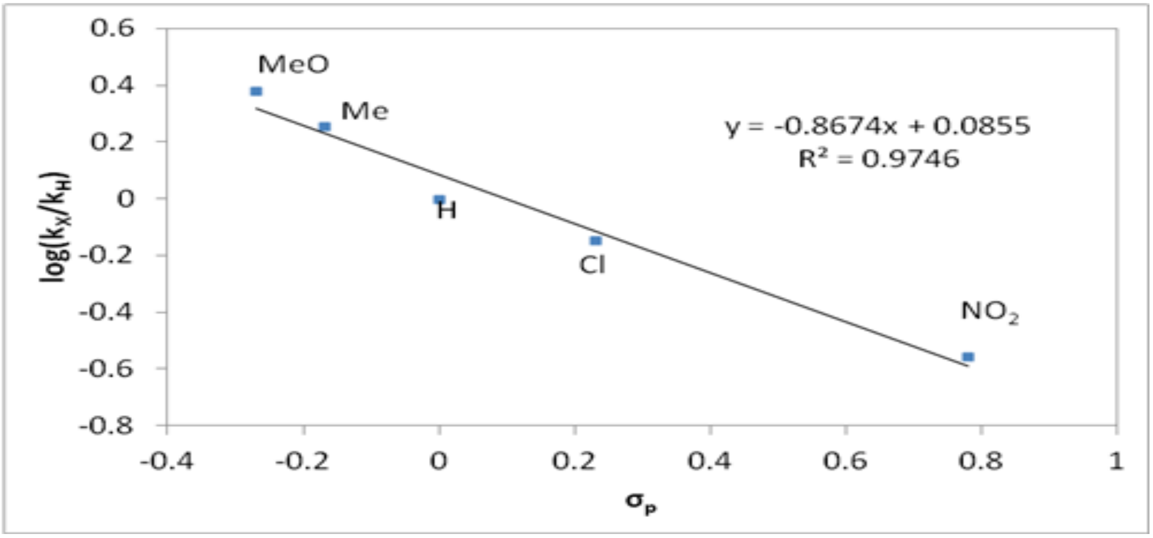


Figure S1. Correlation of log(k_X/k_H) versus σ_p plot for amination of *para*-substituted benzaldehydes with pentafluorophenyl azide by [Co(**P1**)].

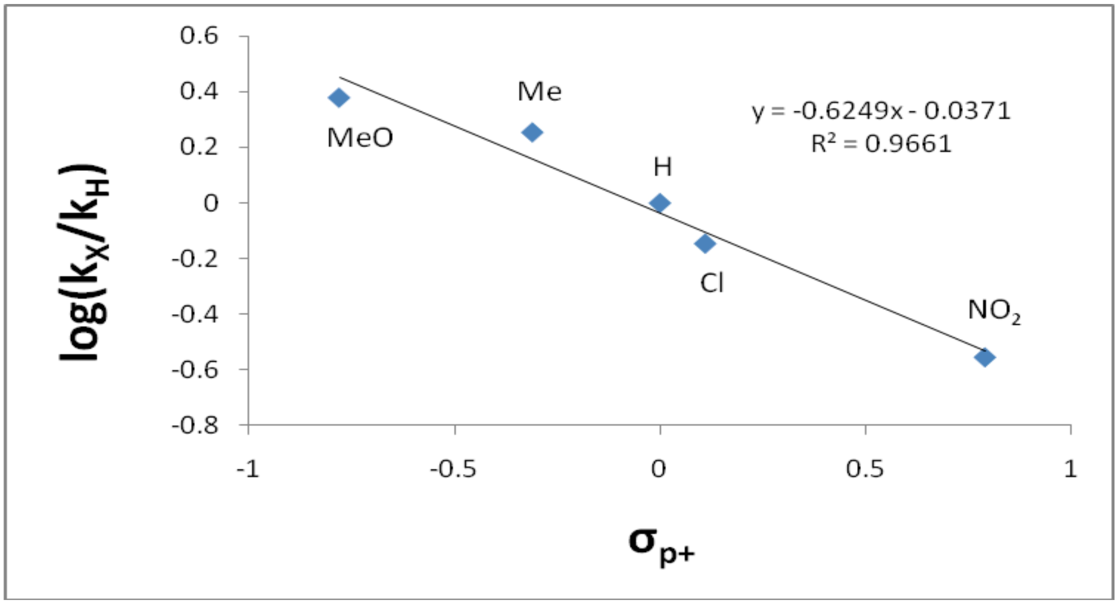


Figure S2. Correlation of log(k_X/k_H) versus σ_{p+} plot for amination of *para*-substituted benzaldehydes with pentafluorophenyl azide by [Co(**P1**)].

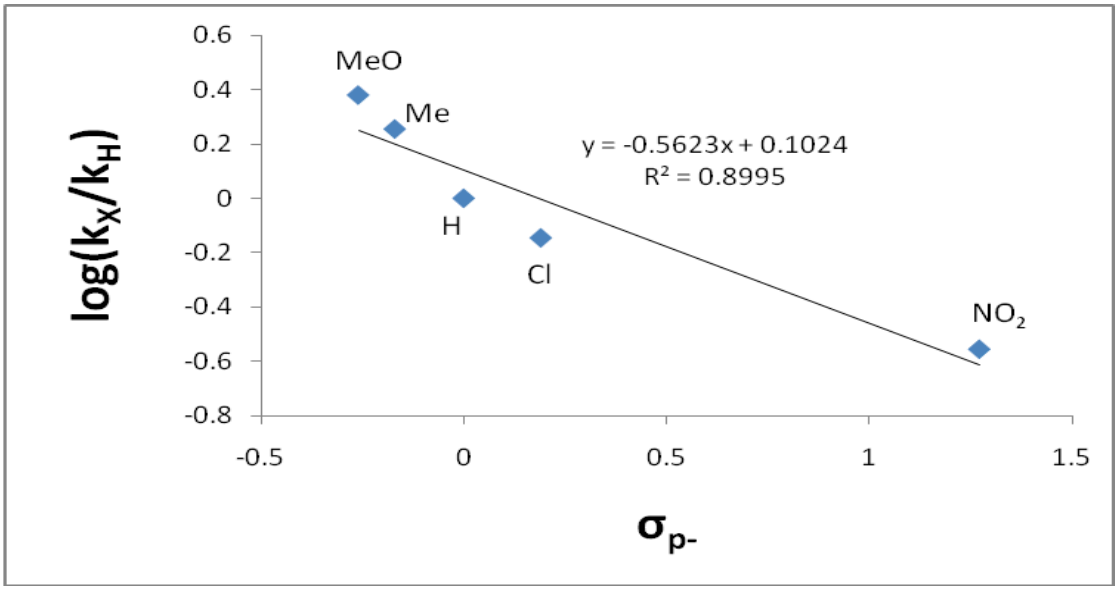


Figure S3. Correlation of log(k_X/k_H) versus σ_{p-} plot for amination of *para*-substituted benzaldehydes with pentafluorophenyl azide by [Co(**P1**)].

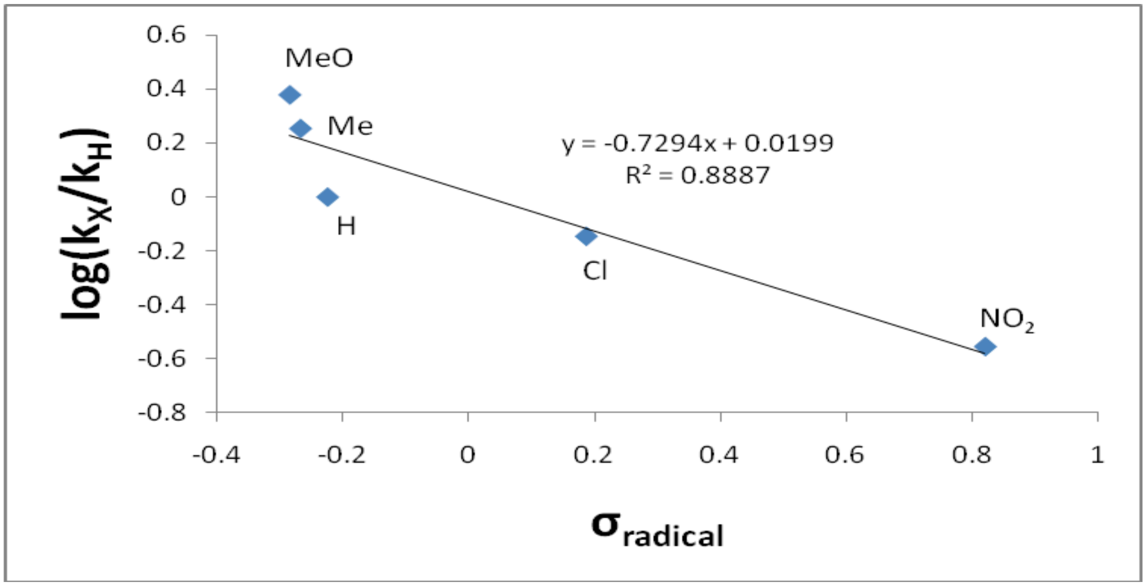


Figure S4. Correlation of log(k_X/k_H) versus $\sigma_{radical}$ plot for amination of *para*-substituted benzaldehydes with pentafluorophenyl azide by [Co(**P1**)].

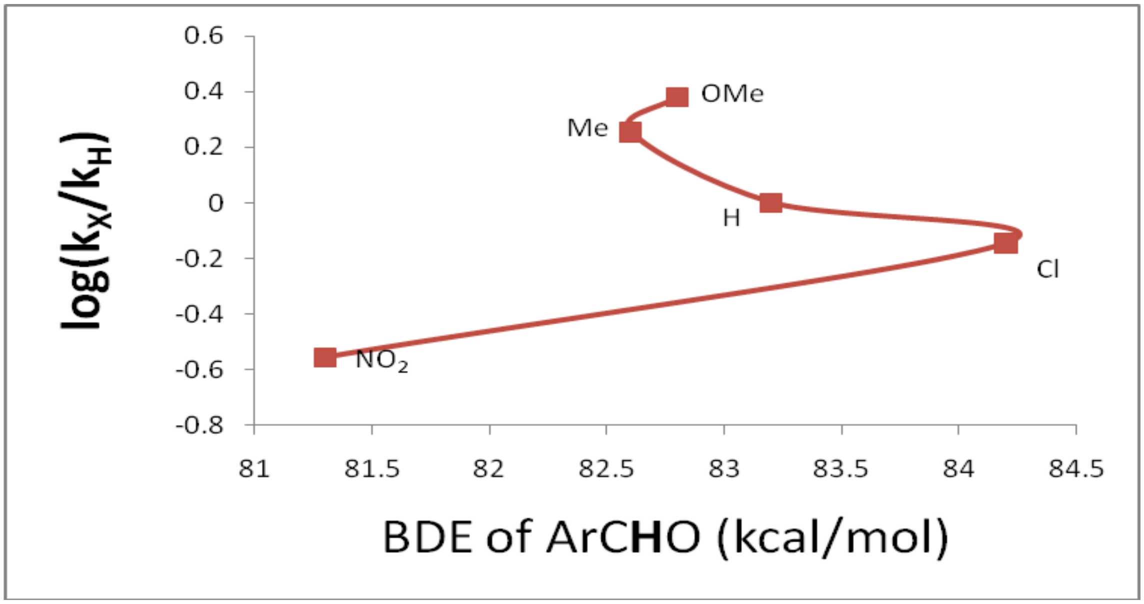


Figure S5. Correlation of log(k_X/k_H) versus bond dissociation energy of aldehydic C–H bonds plot for amination of *para*-substituted benzaldehydes with pentafluorophenyl azide by [Co(**P1**)].

IX. X-ray Crystallography

The X-ray diffraction data for **3ra** (Figure S6) were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2* [7] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [8]. Absorption correction was performed by multi-scan method implemented in SADABS [9]. Space groups were determined using XPREP implemented in APEX2 [7]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in APEX2 [7] and WinGX v1.70.01 [10,11,12,13] programs packages. The X-ray diffraction data for **3bb** (Figure S7) were measured on a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K_{α} INCOATEC Imus micro-focus source (λ = 1.54178 Å).

3ra: All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2[1.5]Ueq(-CH,-NH[-CH3]). Crystal data and refinement conditions are shown in Table S1.

3bb: All non-hydrogen atoms were refined anisotropically. Hydrogen atom of –NH group has been found from Fourier difference map and was freely refined. Remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2[1.5]Ueq(-CH[-CH3]). Crystal data and refinement conditions are shown in Table S2.

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7. Bruker (**2008**). *APEX2* (Version 2008.1-0). Bruker AXS Inc., Madison, Wisconsin, USA.
8. Bruker (**2001b**). SAINT-V6.28A. Data Reduction Software.
9. Sheldrick, G. M. (**1996**). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.
10. Farrugia L.*J. Appl. Cryst.* **1999**, *32*, 837.
11. Sheldrick, G.M. (**1997**) SHELXL-97. Program for the Refinement of Crystal
12. Sheldrick, G.M. *Acta Cryst*. **1990,** *A46*, 467.
13. Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112.

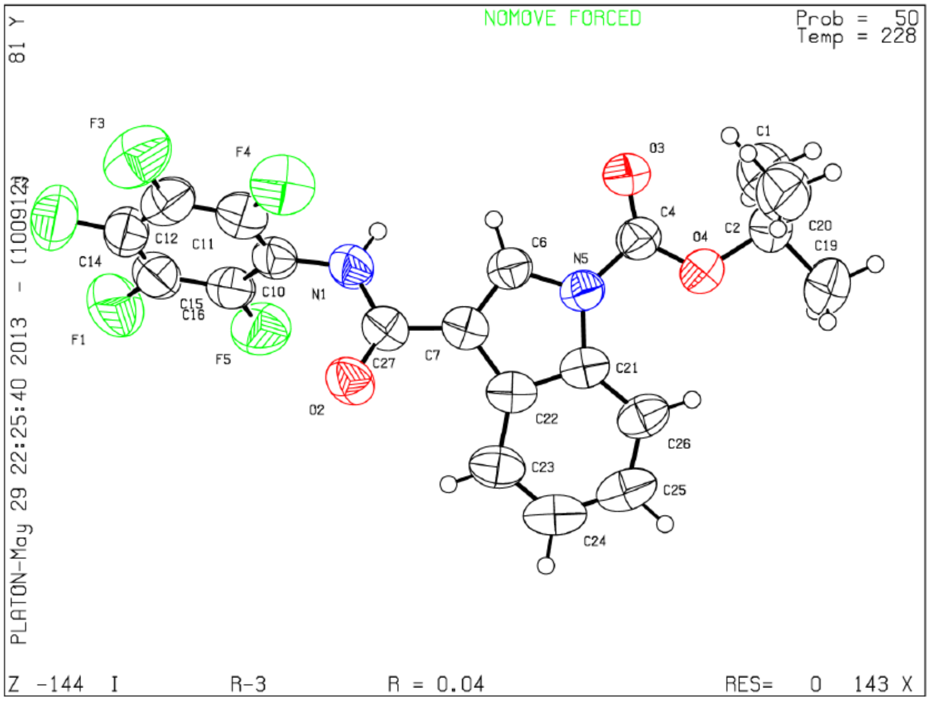

Figure S6. Single-crystal X-ray structure of **3ra**.

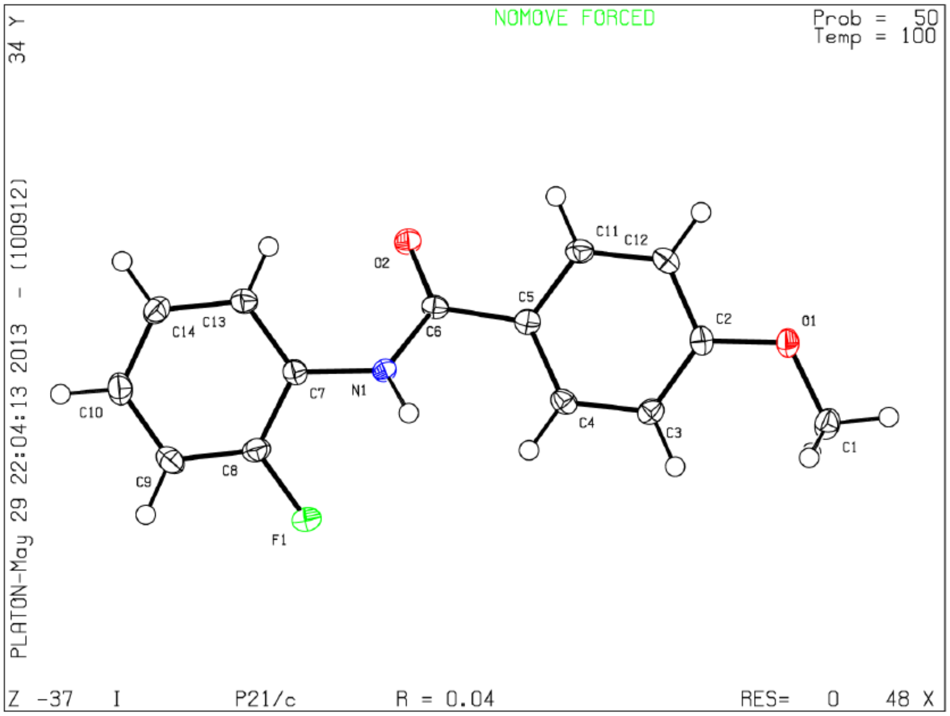

Figure S7. Single-crystal X-ray structure of **3bb**.

Table S1. Crystal data and structure refinement for compound **3ra**

Identification code	**3ra**
Empirical formula	$C_{20}H_{15}F_5N_2O_3$
Formula weight	426.34
Temperature/K	228(2)
Crystal system	Trigonal
Space group	R-3
a/Å	24.8585(5)
b/Å	24.8585(5)
c/Å	16.8633(3)
α/°	90.00
β/°	90.00
γ/°	120.00
Volume/Å^3	9024.5(3)
Z	18
ρ_{calc}mg/mm^3	1.412
m/mm^{-1}	1.108
F(000)	3924.0
Crystal size/mm^3	0.21 × 0.05 × 0.02
2Θ range for data collection	6.66 to 133.54°
Index ranges	$-29 \le h \le 29$, $-27 \le k \le 29$, $-20 \le l \le 19$
Reflections collected	22245

Independent reflections	3555[R(int) = 0.0506]
Data/restraints/parameters	3555/0/275
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1095
Final R indexes [all data]	R_1 = 0.0585, wR_2 = 0.1229
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.16

Table S2. Crystal data and structure refinement for compound **3bb**	
Identification code	**3bb**
Empirical formula	$C_{14}H_{12}FNO_2$
Formula weight	245.25
Temperature/K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	17.7553(6)
b/Å	4.9562(2)
c/Å	13.1145(4)
α/°	90.00
β/°	95.520(2)
γ/°	90.00
Volume/$Å^3$	1148.71(7)
Z	4

ρ_{calc}mg/mm^3	1.418
m/mm^{-1}	0.886
F(000)	512.0
Crystal size/mm^3	0.14 × 0.12 × 0.04
2Θ range for data collection	10 to 133.04°
Index ranges	$-20 \le h \le 21$, $-5 \le k \le 5$, $-15 \le l \le 15$
Reflections collected	13588
Independent reflections	2003[R(int) = 0.0670]
Data/restraints/parameters	2003/0/168
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0358, wR_2 = 0.0844
Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.0907
Largest diff. peak/hole / e Å^{-3}	0.19/-0.20