Supporting Information for

Perfluoroalkylative Pyridylation of Alkenes via 4-Cyanopyridine-Boryl Radicals

Jia Cao, Guoqiang Wang, Liuzhou Gao, Hui Chen, Xueting Liu, Xu Cheng, Shuhua Li*

[*] J. Cao, G. Wang, L. Gao, H. Chen, X. Liu, Prof. Dr. X. Cheng, Prof. Dr. S. Li*

Key Laboratory of Mesoscopic Chemistry of Ministry of Education, Institute of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China

Prof. Dr. X. Cheng

Institute of Chemistry and Biomedical Sciences, Jiangsu Key Laboratory of Advanced Organic Material, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China

J. Cao

Shaanxi Key Laboratory of Chemical Reaction Engineering, School of Chemistry and Chemical Engineering, Yan’ an University, Yan’ an 716000, P. R. China

E-mail: shuhua@nju.edu.cn

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1. Computational Investigations

1.1 Computational Details

All calculations were performed with the Gaussian 16 package.[1] A “broken-symmetry” guess was used for calculations on open-shell systems. Geometry structures of all the stationary points were optimized by using the M06-2X[2] method. The LANL2DZ basis set is employed for the iodine atom, and the 6-31G(d,p) basis set is used for all the other atoms. At the same level of theory, vibrational frequencies of all the stationary points were further calculated to check the nature of the minima and the transition states. To confirm that each transition state connects the desired reactants and products along the reaction path, we performed intrinsic reaction coordinate (IRC)[3] calculations at the same level. In order to obtain reliable energies, single point energies (Esol) were computed using M06-2X method with a larger basis set. The cc-PVTZ basis set is used for all the other atoms (the LANL2DZ basis set for the iodine atom). The solvent effect was treated with the polarizable continuum model (PCM) with benzene as the solvent.[4] The 3D structures were generated with CLY view.[5]
Figure S1. Optimized structures of all minimum species and some transition states in the alkene difunctionalization. Interatomic distances are in Å.

1.2 Theoretical studies on the C-I bond homolysis of CF₃I mediated by 4-cyanopyridine-boryl radical at the C4 position

The C-I bond homolysis by the 4-cyanopyridine-boryl radicals at the C4 position is also investigated (shown in Figure S2). This process is endergonic by 31.0 kcal/mol, with a barrier of 37.7 kcal/mol (relative to Int1 and 1b), suggesting that the pathway is less favorable.
Figure S2. Calculated Gibbs free energy (in kcal/mol) profile for the C-I bond homolysis by the 4-cyanopyridine-boryl radicals at the C4 position. Interatomic distances are in Å.

1.3 Theoretical studies on the isomerization of the intermediate Int3a

![Diagram showing the isomerization of Int3a](image)

Figure S3. Computed Gibbs free energy (in kcal/mol) profile for the isomerization of Int3; Interatomic distances are in Å.

We calculate the isomerization reaction of Int3a (see Figure S3). Starting from Int3a, the intramolecular migration of the iodine atom from C2 atom to B atom via TS4, could yield another isomer Int3b, which further proceeds through the breaking of the B-N bond (via TS5) to regenerate 4-cyanopyridine. Overall, the rate-determining barrier height of this process is 10.1 kcal/mol and endergonic by 2.9 kcal/mol (relative to Int3a), indicating that the C-I bond homolysis is a catalytic process by 4-
cyanopyridine. In addition, the generated trifluoromethyl radical can react with Int1 to produce the compound 7, which is exothermic by 25.8 kcal/mol.

1.4 The calculated results for a single electron transfer (SET) process

![Figure S4. SET process between CF₃I (1b) and Int1](image)

Moreover, our calculations suggest that the direct single electron transfer (SET) process from the 4-cyanopyridine-boryl radical to CF₃I is highly endergonic by 60.0 kcal/mol (see Figure S4). Thus, the SET mechanism is unlikely responsible for the generation of the perfluoroalkyl radicals in the reaction.

1.5 Theoretical Investigations on the reactivity of various alkenes

Our calculations suggest that the barrier heights of the addition of trifluoromethyl radical to internal alkene or terminal monosubstituted styrene is higher than that of terminal disubstituted styrene by 1.1~3.4 kcal/mol (see Table S1). Thus, internal alkenes or terminal monodisubstituted styrenes are not suitable for the present transformation.
Table S1 The calculated activation barrier (ΔG°) and reaction energies (ΔG) for the reaction of the trifluoromethyl radical with various alkenes

| Alkenes | CF₃ radical addition | cross-coupling |
|---------|----------------------|---------------|
|         | ΔG°                  | ΔG            | ΔG°       | ΔG        |
| 3a      | 9.0                  | -31.2         | -24.7     | -50.3     |
| 3af     | 9.3                  | -32.7         | -24.8     | -50.5     |
| 3m      | 10.4                 | -31.9         | -23.4     | -56.3     |
| 3r      | 10.2                 | -29.6         | -20.0     | -48.2     |
| 3s      | 12.4                 | -22.6         | -10.1     | -46.6     |

2. Experiment studies on the Substrate Scope

2.1 General information

All reactions were carried out under argon atmosphere. All commercially available reagents were used without further purification. Dry CH₃CN, CH₂Cl₂, methyl tert-butyl ether (MTBE) and THF were purchased from Acros and used as received. All NMR spectra were recorded on a Bruker AVANCE III–400 spectrometer at room temperature with CDCl₃ as the solvent and TMS as the internal standard. Chemical shifts (δ) were reported in ppm with respect to the residue solvent peak. Coupling constant (J) were reported in Hert (Hz), abbreviations for signal couplings are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using neat thin film technique. The electron paramagnetic resonance (EPR) spectra were obtained using a Bruker EMX-10/2 EPR spectrometer at 298.15 K. High-resolution mass spectra (HRMS) were recorded on
Thermo Quest Finnigan LCQDECA system equipped with electrospray ionization (ESI).

2.2 Synthesis of alkenes

Scheme S1 Synthesis of substrates (3n-3q)

Alkenes 3n-3q were synthesized according to the reported procedure (see Scheme S1).[6-8] At first, a sealed reaction bottle charged with a magnetic stir bar, carboxylic acid (10.0 mmol, 1.0 equiv), DCC (dicyclohexylcarbodiimide) (12.0 mmol, 1.2 equiv), DMAP (4-dimethylaminopyridine) (1.5 mmol, 0.15 equiv) and 4-hydroxyacetophenone (12.0 mmol, 1.2 equiv) in CH₂Cl₂ (20 mL). The reaction mixtures were stirred at room temperature for 24 h. Then it was filtered through a plug of silica gel (washed with EA, ethyl acetate). The filtrate was concentrated in *vacuo* and the residue was purified by chromatography on silica gel, eluting with PE/EA=10:1 (v/v) to afford the corresponding product.[6-7] Second, under argon atmosphere, a stirred solution of methyltriphenylphosphonium bromide (5 mmol, 1.8 g) in THF (10 mmol), *n*-butyl lithium (5.0 mmol) in hexane was added dropwise at 0 °C for 30 min. After the addition, the reaction mixture was further stirred 30 min. Subsequently, a THF solution of ketone was added dropwise for 30 min. The reaction mixture was stirred for 12 h at room temperature. Then reaction mixture was quenched with saturated ammonium chloride solution and was extracted with EtOAc. The combined organic layer was dried over Na₂SO₄ and then concentrated in *vacuo*. The crude reaction mixture was purified by flash column chromatography on silica gel to give the corresponding product.[8]
3n, Colorless oil, 40% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 8.7$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 5.83 (s, 1H), 5.44 (s, 1H), 5.35 (s, 1H), 5.09 (t, $J = 1.6$ Hz, 1H), 2.30 – 2.24 (m, 2H), 2.15 (d, $J = 1.3$ Hz, 3H), 2.13 – 2.10 (m, 2H), 2.06 – 1.94 (m, 4H), 1.88 – 1.80 (m, 2H), 1.60 (s, 3H), 1.41 (s, 3H), 1.29 – 1.24 (m, 2H), 1.07 – 1.03 (m, 6H), 0.91 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.0, 150.5, 145.3, 142.4, 138.6, 135.6, 126.4, 122.4, 121.2, 120.4, 112.5, 46.9, 45.1, 38.3, 37.1, 34.9, 34.6, 27.5, 25.8, 22.5, 21.9, 21.4, 20.9, 18.2, 17.1, 14.1. IR (film): 2924, 2870, 1750, 1728, 1584, 1508, 1472, 1264, 1205, 1123, 1047, 803. HRMS (ESI-TOF) exact mass calculated for C$_{27}$H$_{39}$O$_2$ [M+H]$^+$ 419.2945, found 419.2943.

3o, Colorless oil, 30% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 – 7.44 (m, 2H), 7.07 – 7.01 (m, 2H), 5.33 – 5.32 (m, 1H), 5.07 – 5.05 (m, 1H), 2.30 (s, 2H), 2.13 (s, 3H), 2.04 – 1.99 (m, 2H), 1.77 – 1.70 (m, 13H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.2, 150.0, 142.4, 138.8, 126.5, 121.3, 112.5, 63.8, 48.7, 42.4, 36.7, 28.6, 21.9; IR (film): 2902, 2848, 1755, 1629, 1601, 1507, 1452, 1372, 1329, 1008, 1123, 1097, 812. HRMS (ESI-TOF) exact mass calculated for C$_{21}$H$_{26}$O$_2$Na [M+Na]$^+$ 333.1825, found 333.1820.

3p, Colorless oil, 50% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.47 (m, 2H), 7.07 – 7.02 (m, 3H), 6.72 – 6.66 (m, 2H), 5.40 – 5.37 (m, 1H), 5.13 – 5.10 (m, 1H), 4.06 – 4.00 (m, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H), 1.95 – 1.91 (m, 4H), 1.42 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.2, 155.9, 149.3, 141.4, 137.7, 135.4, 129.3, 125.4, 122.6, 120.1, 119.6, 111.1, 110.8, 66.7, 41.3, 36.1, 28.6, 24.2, 24.1, 20.8, 20.3,
14.7; IR (film): 2930, 2872, 1747, 1722, 1601, 1507, 1457, 1385, 1307, 1206, 1168, 1129, 1099, 888, 734. HRMS (ESI-TOF) exact mass calculated for C_{24}H_{31}O_3Na [M+Na]^+ 367.2273, found 367.2268.

3q. White solid, mp 162–163, 50% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 – 7.97 (m, 2H), 7.52 – 7.49 (m, 2H), 5.46 (s, 1H), 5.44 – 5.40 (m, 1H), 5.20 – 5.17 (m, 1H), 4.91 – 4.81 (m, 1H), 2.49 – 2.44 (m, 2H), 2.17 – 2.16 (m, 3H), 2.07 – 1.89 (m, 4H), 1.87 – 1.70 (m, 2H), 1.63 – 1.46 (m, 6H), 1.41 – 1.27 (m, 4H), 1.20 – 0.96 (m, 13H), 0.93 (d, $J$ = 6.5 Hz, 3H), 0.87 (dd, $J$ = 6.6, 1.8 Hz, 6H), 0.69 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.9, 145.6, 142.6, 139.8, 129.7, 129.6, 125.4, 122.8, 114.5, 74.6, 56.8, 56.2, 50.1, 42.4, 29.8, 29.6, 28.3, 37.1, 36.7, 36.3, 35.9, 32.1, 32.0, 28.3, 28.1, 28.0, 24.4, 23.9, 22.9, 22.7, 21.8, 21.2, 19.5, 18.8, 12.0. IR (film): 2939, 2853, 1712, 1602, 1457, 1269, 1124, 1104, 1006, 851. HRMS (ESI-TOF) exact mass calculated for C$_{37}$H$_{54}$O$_2$Na [M+Na]^+ 553.4018, found 553.4016.

2.3 Optimization studies of the reaction conditions

We optimized the reaction conditions using perfluorobutyl iodide 1a and 4-methylisopropenylbenzene 3a as model substrates. As shown in Table S2, a mixture of perfluorobutyl iodide, 4-methylisopropenylbenzene, 4-canopyridine, and B$_2$pin$_2$ in ethyl acetate (EA) was stirred at 80 °C, forming the desired product 4a in 39% yield (entry 1). Notably, the addition of organic base, such as DABCO, NMM, DMEDA, and DIPEA, increased the yield (entry 2-5, 47%~70%). Decreasing the amount of base led to a lower yield (entry 6). When the reaction performed at 60 °C, the yield of 4a was decreased (entry 7). Solvent screening found that tert-butyl methyl ether (MTBE) and trifluoromethyl benzene (PhCF$_3$) were also suitable for the present reaction in good yield (entry 8-9). When the reaction occurred under irradiation with 10 W blue LED for 24 h, the corresponding product 4a was obtained in only about 40% yield (entry 13-14).
Table S2. Optimization of the reaction conditions.\textsuperscript{[a]}

\begin{tabular}{|c|c|c|c|}
\hline
Entry & solvent & base & yield\textsuperscript{[b]} \\
\hline
1 & EA & -- & 39\% \\
2 & EA & DABCO & 47\% \\
3 & EA & NMM & 56\% \\
4 & EA & DMEDA & 68\% \\
5 & EA & DIPEA & 70\% \\
6 & EA & DIPEA & 38\%\textsuperscript{[c]} \\
7 & EA & DIPEA & 39\%\textsuperscript{[d]} \\
8 & EA & DIPEA & 68\%\textsuperscript{[e]} \\
9 & PhCF\textsubscript{3} & DIPEA & 72\% \\
10 & MTBE & DIPEA & 74\% \\
11 & CH\textsubscript{3}CN & DIPEA & 53\% \\
13 & EA & DIPEA & 41\%\textsuperscript{[f]} \\
14 & EA & -- & 43\%\textsuperscript{[f]} \\
\hline
\end{tabular}

[a] Reaction conditions: 1 (0.2 mmol), B\textsubscript{2}pin\textsubscript{2} (0.3 mmol), 4-cyanopyridine (0.3 mmol), 4-methylisopropenylbenzene (0.4 mmol), solvent (1.0 mL), base (0.2 mmol), 80 °C. [b] Isolated yield. [c] with 0.3 equiv. of DIPEA. [d] at 60 °C. [e] with 2.0 equiv. of DIPEA. [f] 24 h irradiated by 10 W blue LED at room temperature. MTBE = tert-butyl methyl ether; EA = ethyl acetate; THF = Tetrahydrofuran; DMEDA = N,N,N',N'-Tetraethylethylenediamine; NMM = 4-Methylmorpholine; DIPEA = Ethyldiisopropylamine; DABCO = 1,4-Diaza[2.2.2]bicyclooctane.

2.4 General procedure for the difunctionalization of alkenes

Under argon atmosphere, a sealed reaction tube was charged with a magnetic stir bar, perfluoroalkyl iodides or bromides (0.2 mmol), 4-cyanopyridine (0.3 mmol, 1.5 equiv), B\textsubscript{2}pin\textsubscript{2} (0.3 mmol, 1.5 equiv), alkene (4 mmol, 2.0 equiv). N, N-diisopropylethylamine (DIPEA, 0.4 mmol, 0.2 equiv) and MTBE (1 mL). The reaction mixture was stirred at 80 °C. After 24 h, the reaction mixture was cooled and quenched with 2 M Na\textsubscript{2}CO\textsubscript{3} aqueous solution (3 mL). Then, the reaction tube was stirred under air for another 15 minutes. The reaction mixture was extracted with EtOAc (3×10 mL).
The combined organic layer was dried over Na₂SO₄ and then concentrated in vacuo to afford the crude product. This crude material was purified by preparative TLC on silica gel to afford the desired product.

3. Experiment studies on the Reaction mechanism

3.1 ¹⁹F NMR spectra analysis

As shown above, samples with varied combination of reagents was measured with ¹⁹F NMR technique. The ¹⁹F NMR chemical shift at ~60 ppm did not show any significantly changes for the mixture of C₄F₉I and B₂pin₂ or DIPEA (see Figure S5a-
S5e), whereas it disapeared in a 1:1.5:1.5 mixtures of C₄F₉I, B₂pin₂ and 4-cyanopyridine, suggesting that the cleavage of C-I bond is induced by 4-cyanopyridine-boryl radicals (see Figure S5d).

**Experimental procedure:** according to the general procedure for the difunctionalization of alkenes. A sealed reaction tube charged with a magnetic stir bar, the corresponding components in each reaction mixture using MTBE as solvent were placed in a heated oil bath at 80 °C. After 24 hours, the reaction tube was cooled to the room temperature, and then subjected to the ¹⁹F NMR analysis.

### 3.2 Trapping the perfluoroalkyl radical by 1.1-diphenylethylene

The involvement of the perfluoroalkyl radical was further confirmed by radical trapping experiment with 1,1-diphenylethylene (shown in Table S2). When 1,1-diphenylethylene and hydrogen source (1,3,5-trimethyl-1,4-cyclohexadiene) was added in the reaction mixture of C₈F₁₇I, B₂pin₂, 4-cyanopyridine (20%), C₈F₁₇ radical reacted with 1,1-diphenylethylene, the product 6 could be obtained in 50% yield. This result indicates the 4-cyanopyridine-boryl radical could activate the C₈F₁₇I to form the C₈F₁₇ radical, then which could be trapped by 1,1-diphenylethylene.

**Table S2.** Radical trapping experiment.

|                   | 1g (0.2 mmol) | 2 (0.4 mmol) | H-source (0.3 mmol) | (1) B₂pin₂, MTBE 80 °C | (2) 2M Na₂CO₃, air | C₈F₁₇radical react with 1,1-diphenylethylene | 6, isolated yield |
|-------------------|---------------|--------------|---------------------|------------------------|-------------------|---------------------------------------------|-----------------|
| C₈F₁₇I            |               |              |                     |                        |                   |                                             |                 |
| R                 |               |              |                     |                        |                   |                                             |                 |
| H-source          |               |              |                     |                        |                   |                                             |                 |
| amount of 4-cyanopyridine | 0.3 mmol (1.5 equiv.) | 0.04 mmol (20%) |                     |                        |                   |                                             | 63% 50%         |

**Experimental procedure:** A sealed reaction tube charged with a magnetic stir bar, 1g (0.20 mmol), B₂pin₂ (0.30 mmol, 1.5 equiv), 4-cyanopyridine, 1,3,5-trimethyl-1,4-cyclohexadiene (0.3 mmol, 1.5 equiv), MTBE (1 mL), 1,1-diphenylethylene (0.4 mmol,
2.0 equiv) were placed in a heated oil bath (80 °C). After 24 hours, the reaction was cooled and quenched with 2M Na₂CO₃ aqueous solution (3 mL). The reaction mixture was stirred under air for another 15 minutes. The reaction mixture was extracted with EtOAc (3×10 mL). The combined organic layer was dried over Na₂SO₄ and then concentrated in vacuo to afford the crude product. This crude material was purified by preparative TLC on silica gel (PE/EA=20:1) to afford the product 6.

3.3 Trapping the intermediates by HRMS

![Figure S5](image1)

![Figure S6](image2)

**Experimental procedure:** A sealed reaction tube charged with a magnetic stir bar, 1a (0.20 mmol), B₂pin₂ (0.30 mmol, 1.5 equiv), 4-cyanopyridine (0.3 mmol, 1.5 equiv),
and MTBE (1 mL) were placed in a heated oil bath (80 °C). After 24 hours, the reaction mixture was cooled to room temperature. The crude reaction mixture was subject to the HRMS analysis.

**Figure S7**

**Figure S8**

**Experimental procedure:** A sealed reaction tube charged with a magnetic stir bar, 1a (0.20 mmol), B$_2$pin$_2$ (0.30 mmol, 1.5 equiv), 4-cyanopyridine (0.3 mmol, 1.5 equiv), MTBE (1 mL), 4-methylisopropenylbenzene 3a (0.4 mmol, 2.0 equiv), DIPEA (0.2
mmol, 1.0 equiv) were placed in a heated oil bath (40 °C). After 24 hours, the reaction mixture was cooled to room temperature. The crude reaction mixture was subject to the HRMS analysis.

3.4 Radical clock experiment

We performed a radical-clock experiment using substrate 3r. After the generation of C₄F₉ radical, which add to the alkene at the terminal position, and simultaneously the resulting alkyl radical coupled to the 4-cyanopyridine-boryl radicals at the C4 position to form the ring-opening product 5r.

**Figure S9**

**Experimental procedure:** A sealed reaction tube charged with a magnetic stir bar, 1a (0.20 mmol), B₂pin₂ (0.30 mmol, 1.5 equiv), 4-cyanopyridine (0.3 mmol, 1.5 equiv), MTBE (1 mL), 3v (0.4 mmol, 2.0 equiv), DIPEA (0.2 mmol, 1.0 equiv) were placed in a heated oil bath (80 °C). After 24 hours, the reaction was cooled and quenched with 2M Na₂CO₃ aqueous solution (3 mL). The reaction tube was stirred under air for another 15 minutes. The reaction mixture was extracted with EtOAc (3×10 mL). The combined organic layer was dried over Na₂SO₄ and then concentrated in vacuo to afford the crude product. This crude material was purified by preparative TLC on silica gel (PE/EA=20:1) to afford the product 5r in 30% yield (E/Z = 5.2: 1).

5r: Pale-yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.61 – 8.50 (m, 1.60H), 8.49 – 8.43 (m, 0.32H), 7.36 – 7.18 (m, 11H), 7.11 – 7.05 (m, 0.50H), 7.04 – 7.01 (m, 0.50H), 5.91 (t, J = 7.1 Hz, 0.84H), 5.66 (t, J = 7.2 Hz, 0.16H), 4.11 – 4.04 (m, 0.85H), 4.01 – 3.94 (m, 0.14H), 3.25 – 3.13 (m, 1.73H), 3.08 – 3.01 (m, 0.36H), 3.00 – 2.94 (m, 1.79H), 2.80 – 2.75 (m, 0.38H). ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 149.7, 133.6, 133.2,
130.7, 129.0, 128.8, 128.5, 128.0, 127.6, 127.3, 127.1, 126.4, 123.5, 50.8, 50.5, 31.3 (t, \( J = 22.2 \) Hz), \(^{13}\)C-NMR for \( \text{C}_4\text{F}_9 \) could not be assigned. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -80.7 – 81.2 (m, 3F), -111.16 – -111.5 (m, 1.83F), -112.3 – -112.6 (m, 0.31F), -123.9 – -124.5 (m, 2F), -125.7 – -125.9 (m, 2F). IR (film): 3061, 3028, 2930, 1596, 1494, 1494, 1453, 1430, 1348, 1235, 1132, 878, 755; HRMS (ESI-TOF) exact mass calculated for \( \text{C}_{26}\text{H}_{20}\text{F}_9\text{N} \) [M+H]\(^+\) 518.1525, found 518.1525.

4. Spectroscopic Characterization of the Products

**4a:** Prepared following *general procedure* using 1a (34.5 \( \mu \)L, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), \( \text{B}_2\text{pin}_2 \) (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 \( \mu \)L, 0.4 mmol, 2.0 equiv), DIPEA (33.1 \( \mu \)L, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4a (63.5 mg, 74% yield).

4a: Pale-yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.55 – 8.51 (m, 2H), 7.14 – 7.10 (m, 4H), 7.05 – 7.02 (m, 2H), 3.02 – 2.91 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 121.4-107.6 (m, 4C, -C\(_4\)F\(_9\)), 122.0, 43.9, 39.8 (t, \( J_{C-F} = 19.6 \) Hz), 27.1, 20.9, \(^{13}\)C-NMR for \( \text{C}_4\text{F}_9 \) could not be assigned. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -80.1 – -81.8 (m, 3F), -108.1 – -110.5 (m, 2F), -124.5 (m, 2F), -125.7 (m, 2F). IR (film): 3026, 2986, 2926, 1682, 1594, 1552, 1439, 1387, 1314, 1236, 1018, 995, 848 cm\(^{-1}\). HRMS (ESI-TOF) exact mass calculated for \( \text{C}_{19}\text{H}_{17}\text{F}_9\text{N} \) [M+H]\(^+\) 430.1212, found 430.1212.

**4b:** Prepared following *general procedure* using prepared trifluoriodomethane solution in MTBE (1b, 0.65 M), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), \( \text{B}_2\text{pin}_2 \) (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 \( \mu \)L, 0.4 mmol, 2.0 equiv), DIPEA (33.1
µL, 0.4 mmol, 0.2 equiv) and MTBE (0.5 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4b (30.2 mg, 54% yield).

4b: Pale-yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.53 (m, 2H), 7.12 (m, 4H), 7.02 (d, J = 8.3 Hz, 2H), 3.01 (s, 2H), 2.32 (s, 3H), 1.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 149.5, 143.0, 136.7, 129.3, 126.6, 126.3 (q, J C-F = 278.9 Hz), 122.3, 44.1 (q, J C-F = 26.5 Hz). 19F NMR (376 MHz, CDCl₃) δ -58.3. IR (film): 3026, 2985, 2925, 1594, 1514, 1411, 1366, 1260, 1121, 1036, 817 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₁₆H₁₇F₃N [M+H]⁺ 280.1308, found 280.1308.

4c: Prepared following general procedure using 1c (28.9 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 µL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4c (54.6 mg, 72% yield).

4c: Pale-yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 4.9 Hz, 2H), 7.20 – 7.07 (m, 4H), 7.06 – 7.01 (m, 2H), 3.02 – 2.89 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.1, 149.7, 143.2, 136.7, 129.3, 126.5, 122.1, 120.2-108.5 (m, 3C, -C₃F₇), 43.9, 39.6 (t, J C-F = 19.5 Hz), 27.1, 20.9. ¹³C-NMR for C₃F₇ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.0 (t, J = 9.9 Hz, 3F), -109.9 – -110.3 (m, 2F), -127.8 (m, 2F). IR (film): 2985, 2985, 2926, 1682, 1595, 1514, 1457, 1351, 1147, 1112, 884 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₁₈H₁₇F₇N [M+H]⁺ 380.1244, found 380.1247.

4d: Prepared following general procedure using 1d (38.3 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv),

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3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4d (67.1 mg, 70% yield).

4d: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.55 – 8.50 (m, 2H), 7.14 – 7.10 (m, 4H), 7.04 (d, J = 8.3 Hz, 2H), 3.02 – 2.90 (m, 2H), 2.32 (s, 3H), 1.89 (m, 3H). 13C NMR (100 MHz, CDCl3) δ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 122.0, 119.2 –107.7 (m, 5C, -C5F11), 43.9, 39.9 (t, J_{C-F} = 19.5 Hz), 27.1, 20.9, 13C-NMR for C5F11 could not be assigned. 19F NMR (376 MHz, CDCl3) δ -80.5 – -80.2 (m, 3F), -107.7 – -110.7 (m, 2F), -121.0 – -122.7 (m, 2F), -123.2 – -124.8 (m, 2F), -125.6 – -127.6 (m, 2F). IR (film): 3026, 2986, 2927, 1594, 1514, 1411, 1306, 1239, 1140, 1040, 741 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C20H17F11N [M+H]+ 480.1180 found 480.1183.

4e: Prepared following general procedure using 1e (43.2 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4e (80.4 mg, 76% yield).

4e: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.55 – 8.49 (m, 2H), 7.14 – 7.10 (m, 4H), 7.04 (d, J = 8.3 Hz, 2H), 3.03 – 2.91 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 156.8, 149.8, 143.2, 136.6, 129.2, 126.4, 121.9, 119.4 – 107.5 (m, 6C, -C5F13), 44.0, 39.9 (t, J_{C-F} = 19.5 Hz), 27.1, 20.9. 13C-NMR for C5F13 could not be assigned. 19F NMR (376 MHz, CDCl3) δ -80.4 – -81.3 (m, 3F), -108.1 – -110.1 (m, 2F), -121.1 – -121.8 (m, 2F), -122.1 – -123.2 (m, 2F), -123.4 – -124.0 (m, 2F), -125.8 – -126.6 (m, 2F). IR (film): 3025, 2986, 2927, 1595, 1514, 1410, 1387, 1239, 1144, 1119, 1050, 813 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C21H17F13N [M+H]+ 530.1148 found 530.1149.
4f: Prepared following general procedure using 1f (47.4 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4f (60.2 mg, 52% yield).

4f: Pale-yellow oil; ¹H NMR (400 MHz, CDCl$_3$) δ 8.55 – 8.50 (m, 2H), 7.14 – 7.10 (m, 4H), 7.05 – 7.02 (m, 2H), 3.03 – 2.90 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ¹³C NMR (100 MHz, CDCl$_3$) δ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 122.1, 121.3 – 108.2 (m, 7C, -C$_7$F$_{15}$), 44.0, 39.9 (t, $J_{C-F} = 19.6$ Hz), 27.1, 20.9. ¹³C-NMR for C$_7$F$_{15}$ could not be assigned. ¹⁹F NMR (376 MHz, CDCl$_3$) δ -80.6 – -81.0 (m, 3F), -108.5 – -109.4 (m, 2F), -121.2 – -121.6 (m, 2F), -121.7 – -122.4 (m, 2F), -122.6 – -123.2 (m, 2F), -123.5 – -123.8 (m, 2F), -126.0 – -126.4 (m, 2F). IR (film): 3026, 2896, 2927, 1595, 1514, 1363, 1211, 1148, 1043, 1005, 815 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{22}$H$_{17}$F$_{15}$N [M+H]$^+$ 580.1116 found 580.1116.

4g: Prepared following general procedure using 1g (52.8 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4g (89.3 mg, 71% yield).

4g: gum; ¹H NMR (400 MHz, CDCl$_3$) δ 8.56 – 8.50 (m, 2H), 7.14 – 7.10 (m, 4H), 7.04 (d, $J = 8.3$ Hz, 2H), 3.02 – 2.90 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ¹³C NMR (100 MHz, CDCl$_3$) δ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 122.1, 121.4 – 107.0 (m, 8C, -C$_8$F$_{17}$), 44.0, 39.9 (t, $J_{C-F} = 19.6$ Hz), 27.1, 20.9. ¹³C-NMR for C$_8$F$_{17}$ could not be assigned. ¹⁹F NMR (376 MHz, CDCl$_3$) δ -80.88 – -80.9 (m, 3F), -108.1 – -109.9 (m,
2F), -121.3 – -121.5 (m, 2F), -121.8 – -122.0 (m, 4F), -122.6 – -122.9 (m, 2F), -123.5 – -123.7 (m, 2F), -125.8 – -126.5 (m, 2F). IR (film): 3026, 2986, 2926, 1594, 1514, 1410, 1363, 1240, 1207, 1150, 1115, 1073, 1036, 816 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₂₃H₁₇F₁₇N [M+H]⁺ 630.1084 found 630.1082.

4h: Prepared following general procedure using 1h (109.8 mg, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4h (70.6 mg, 52% yield).

4h: gum; ¹H NMR (400 MHz, CDCl₃) δ 8.57 – 8.48 (m, 2H), 7.15 – 7.10 (m, 4H), 7.05 – 7.02 (m, 2H), 3.03 – 2.89 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.8, 149.8, 143.2, 136.6, 129.2, 126.4, 121.9, 119.9 – 107.2 (m, 9C, -C₉F₁₉), 43.8, 39.8 (t, J₃₈ = 19.6 Hz), 27.0, 20.8, ¹⁹F NMR for C₉F₁₉ could not be assigned.

19F NMR (376 MHz, CDCl₃) δ -80.8 – -80.7 (m, 3F), -108.4 – -109.3 (m, 2F), -121.1 – -121.5 (m, 2F), -121.7 – -122.2 (m, 6F), -122.6 – -123.2 (m, 2F), -123.4 – -123.8 (m, 2F), -126.0 – -126.4 (m, 2F). IR (film): 3027, 2986, 2927, 1595, 1515, 1456, 1387, 1211, 1149, 1122, 1044, 912, 816 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₂₄H₁₇F₁₉N [M+H]⁺ 680.1052 found 680.1053.

4i: Prepared following general procedure using 1i (129.2 mg, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4i (90.4 mg, 62% yield).
4i: gum; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.55 – 8.51 (m, 2H), 7.14 – 7.10 (m, 4H), 7.04 (d, $J = 8.2$ Hz, 2H), 3.03 – 2.89 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.9, 149.9, 143.3, 136.7, 129.3, 126.5, 122.0, 119.3 – 107.2 (m, 10C, -C$_{10}$F$_{21}$), 44.0, 39.9 (t, $J_{C-F} = 19.6$ Hz). 13C-NMR for C$_{10}$F$_{21}$ could not be assigned. 19F NMR (376 MHz, CDCl$_3$) $\delta$ -80.4 – -81.6 (m, 3F), -108.4 – -109.5 (m, 2F), -121.1 – -121.5 (m, 2F), -121.54 – -122.6 (m, 8F), -122.7 – -123.4 (m, 2F), -123.6 – -124.0 (m, 2F), -125.9 – -126.7 (m, 2F). IR (film): 3025, 2983, 2926, 1593, 1514, 1410, 1305, 1159, 1118, 1074, 1083, 817 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{25}$H$_{17}$F$_{21}$N $[M+H]^+$ 730.1020 found 730.1021.

4j: Prepared following general procedure using 1j (28.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 µL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 ºC. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4j (34.2 mg, 45% yield).

4j: Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.53 – 8.49 (m, 2H), 7.15 – 7.07 (m, 4H), 7.04 – 7.00 (m, 2H), 3.01 (d, $J = 13.3$ Hz, 2H), 2.32 (s, 3H), 1.84 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.0, 149.7, 143.5, 136.6, 129.1, 126.8, 122.4, 119.6 (d, $J_{C-F} = 28.2$ Hz), 93.6 – 89.8 (m, 2C, -2CF$_3$), 45.0, 36.9 (d, $J_{C-F} = 17.8$ Hz). 27.4, 20.9, 13C-NMR for -2CF$_3$ could not be assigned. 19F NMR (376 MHz, CDCl$_3$) $\delta$ -77.1 – -77.7 (m, 6F), -188.7 – -188.1 (m, 1F). IR (film): 3025, 2983, 2926, 1593, 1514, 1410, 1359, 1305, 1269, 1159, 1118, 1038, 995, 817 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{18}$H$_{17}$F$_7$N $[M+H]^+$ 380.1244 found 380.1249.

4k: Prepared following general procedure using 1k (37.8 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv),
3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4k (41.4 mg, 60% yield).

4k: Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.54 – 8.49 (m, 2H), 7.14 – 7.10 (m, 4H), 7.06 – 7.02 (m, 2H), 3.03 – 2.91 (m, 2H), 2.32 (s, 3H), 1.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.8, 149.8, 143.2, 136.5, 129.1, 126.4, 122.0, 121.0 – 114.0 (m, 2C, CF₂CF₂), 43.9, 39.7 (t, J_C=F = 19.7 Hz), 26.9, 20.8, ¹³C-NMR for CF₂CF₂ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -71.6 – –72.4 (m, 2F), -108.2 – -110.1 (m, 2F). IR (film): 3025, 2984, 2925, 1595, 1514, 1410, 1259, 1211, 1151, 1087, 1038, 948, 817, 593 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₁₇H₁₇ClF₄N [M+H]^+ 346.0980 found 346.0981.

4l: Prepared following general procedure using 1l (25.7 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3a (58.4 μL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 4l (30.0 mg, 45% yield).

4l: Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.53 – 8.46 (m, 2H), 7.12 – 7.07 (m, 4H), 7.04 – 7.01 (m, 2H), 3.86 – 3.79 (m, 2H), 3.08 – 2.98 (m, 2H), 2.31 (s, 3H), 1.80 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.7 (t, J_C=F = 32.3 Hz), 157.5, 149.6, 142.7, 136.6, 129.0, 127.2, 122.4, 115.9 (t, J_C=F = 251.9 Hz), 62.9, 44.2 (t, J_C=F = 22.4 Hz), 43.7, 27.3, 20.9, 13.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -95.2 – -100.6 (m). IR (film): 2983, 2927, 1770, 1712, 1594, 1551, 1514, 1455, 1259, 1211, 1087, 835, 593 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₁₉H₂₂F₂NO₂ 334.1613 [M+H]^+ found 334.1614.
**4m**: Prepared following general procedure using **1m** (34.1 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), **3a** (58.4 µL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **4m** (36.2 mg, 49% yield).

**4m**: Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.59 – 8.40 (m, 2H), 7.14 – 7.04 (m, 6H), 4.09 – 3.96 (m, 4H), 3.17 – 3.13 (m, 1H), 2.90 – 2.80 (m, 2H), 2.30 (s, 3H), 1.58 (s, 3H), 1.21 – 1.14 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.8, 169.6, 157.8, 149.6, 142.8, 136.3, 129.1, 127.4, 122.7, 61.7, 61.7, 48.8, 45.8, 39.0, 26.9, 20.9, 14.0, 13.9. IR (film): 2980, 2936, 1732, 1594, 1513, 1463, 1277, 1149, 1019, 819, 586 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{22}$H$_{28}$N$_4$ [M+H]$^+$ 370.2013 found 370.2013.

**5aa**: Prepared following general procedure using **1a** (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 2-Phenyl-1-propene (52.0 µL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5aa** (49.8 mg, 60% yield).

**5aa**: Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 – 8.52 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.17 – 7.12 (m, 4H), 3.04 – 2.93 (m, 2H), 1.91 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.7, 150.0, 146.2, 128.6, 127.0, 126.6, 122.1, 121.4-109.6 (m, 4C, -C$_4$F$_9$), 44.3, 39.8 (t, $J_{C-F} = 19.6$ Hz), 27.1, $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 – -81.1 (m, 3F), -109.1 – -109.4 (m, 2F), -124.5 – -124.5 (m, 2F), -125.6 – -125.7 (m, 2F). IR (film): 3061, 3028, 2928, 1594, 1496, 1446, 1352, 1221, 1133, 1049, 1016, 874, 734 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{18}$H$_{15}$F$_9$N [M+H]$^+$ 416.1055 found 416.1059.
5ab: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B2pin2 (76.2 mg, 0.3 mmol, 1.5 equiv), 3ab (58.0 µL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ab (65.0 mg, 75% yield).

5ab: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.54 (d, J = 5.2 Hz, 2H), 7.15 – 7.10 (m, 4H), 7.05 – 6.94 (m, 2H), 3.00 – 2.89 (m, 2H), 1.89 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 161.5 (d, J_C-F = 247.0 Hz), 156.7, 149.8, 141.6 (d, J_C-F = 3.6 Hz), 128.3 (d, J_C-F = 7.9 Hz), 122.0, 120.2-110.6 (m, 4C, -C4F9), 115.3 (d, J_C-F = 21.4 Hz), 43.9, 39.9 (t, J_C-F = 19.6 Hz), 27.5, 13C-NMR for C4F9 could not be assigned. 19F NMR (376 MHz, CDCl3) δ -80.9 – -81.2 (m, 3F), -109.1 – -109.7 (m, 2F), -114.9 – -116.3 (m, 1F), -124.3 – -124.6 (m, 2F), -125.5 – -125.9 (m, 2F). IR (film): 2986, 2951, 1595, 1511, 1471, 1353, 1232, 1167, 1133, 1015, 875, 735 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C18H14F10N [M+H]⁺ 434.0961 found 434.0962.

5ac: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B2pin2 (76.2 mg, 0.3 mmol, 1.5 equiv), 3ac (57.4 µL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ac (65.6 mg, 73% yield).

5ac: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.58 – 8.52 (m, 2H), 7.34 – 7.22 (m, 2H), 7.12 – 7.07 (m, 4H), 3.00 – 2.88 (m, 2H), 1.88 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 156.7, 149.8, 144.4, 133.1, 128.8, 128.2, 122.0, 121.2-112.3 (m, 4C, -
C₄F₉), 44.1, 39.7 (t, J_{C-F} = 19.6 Hz), 27.3, ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 – 81.1 (m, 3F), -109.2 – 109.4 (m, 2F), -124.4 – 124.5 (m, 2F), -125.6 – 125.7 (m, 2F). IR (film): 3029, 2985, 2930, 1595, 1494, 1411, 1352, 1232, 1133, 1013, 875, 723 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₁₈H₁₄ClF₉N [M+H]$^+$ 450.0666 found 450.0666.

5ad: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3ad (58.4 µL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ad (69.0 mg, 70% yield).

5ad: Pale-yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.57 – 8.50 (m, 2H), 7.47 – 7.39 (m, 2H), 7.11 – 7.08 (m, 2H), 7.05 – 7.02 (m, 2H), 3.00 – 2.87 (m, 2H), 1.87 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.4, 150.0, 145.0, 131.8, 128.6, 121.9, 121.2, 121.3-108.3 (m, 4C, -C₄F₉), 44.1, 39.6 (t, J_{C-F} = 19.5 Hz), 27.2, ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.2 – -82.2 (m, 3F), -108.3 – -110.2 (m, 2F), -123.7 – -124.8 (m, 2F), -125.2 – -126.7 (m, 2F). IR (film): 3027, 2985, 1596, 1491, 1411, 1352, 1221, 1133, 1074, 1008, 875, 738, 585 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₁₈H₁₄F₉NBr [M+H]$^+$ 494.0160 found 494.0162.

5ae: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3ae (80.8 µL, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with
preparative TLC on silica (PE/EA = 20:1) to afford the product 5ae (67.9 mg, 72% yield).

5ae: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.53 (d, $J = 5.8$ Hz, 2H), 7.33 – 7.29 (m, 2H), 7.17 – 7.14 (m, 2H), 7.06 – 7.03 (m, 2H), 3.06 – 2.88 (m, 2H), 1.90 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.6, 149.9, 149.8, 143.4, 126.1, 125.5, 122.2, 121.8-108.2 (m, 4C, -C$_4$F$_9$), 43.9, 39.9 (t, $J_{C:F} = 19.6$ Hz), 34.4, 31.3, 27.0, $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -80.9 – -81.2 (m, 3F), -108.1 – -110.3 (m, 2F), -124.5 – -124.6 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 3030, 2965, 2907, 1594, 1513, 1463, 1352, 1236, 1163, 1048, 1016, 875, 736 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{22}$H$_{23}$F$_9$N [M+H]$^+$ 472.1681 found 472.1681.

5af: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3af (59.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5af (59.7 mg, 67% yield).

5af: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.54 – 8.50 (m, 2H), 7.14 – 7.10 (m, 2H), 7.08 – 7.04 (m, 2H), 6.86 – 6.80 (m, 2H), 3.78 (s, 3H), 3.01 – 2.87 (m, 2H), 1.88 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.2, 157.1, 149.7, 138.0, 127.6, 121.9, 113.8, 121.7-109.6 (m, 4C, -C$_4$F$_9$), 55.3, 43.7, 39.9 (t, $J_{C:F} = 19.5$ Hz), 27.3, $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -80.1 – -81.9 (m, 3F), -108.2 – -110.6 (m, 2F), -124.2 – -124.9 (m, 2F), -125.4 – -126.8 (m, 2F). IR (film): 2998, 2955, 2839, 1595, 1514, 1466, 1411, 1352, 1294, 1232, 1132, 1035, 848 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{17}$F$_9$NO [M+H]$^+$ 446.1161 found 446.1164.
5ag: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3ag (65.7 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ag (66.4 mg, 72% yield).

5ag: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.54 – 8.50 (m, 2H), 7.20 – 7.15 (m, 2H), 7.12 – 7.09 (m, 2H), 7.08 – 7.04 (m, 2H), 3.00 – 2.87 (m, 2H), 2.45 (s, 3H), 1.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.7, 149.9, 142.8, 137.4, 127.2, 126.4, 122.0, 121.8-109.8 (m, 4C, -C$_4$F$_9$), 43.9, 39.7 (t, $J_{C-F} = 19.5$ Hz), 27.1, 15.6. $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.6 – -81.5 (m, 3F), -108.4 – -109.9 (m, 2F), -124.2 – -124.7 (m, 2F), -125.5 – -126.0 (m, 2F). IR (film): 3080, 3025, 2986, 2924, 1594, 1495, 1439, 1352, 1232, 1132, 1073, 1015, 875, 737 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{17}$F$_9$NS [M+H]$^+$ 462.0933 found 462.0932.

5ah: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3ah (64.5 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ah (57.7 mg, 63% yield).

5ah: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.57 – 8.48 (m, 2H), 7.18 – 7.14 (m, 2H), 7.01 – 6.97 (m, 2H), 6.67 – 6.63 (m, 2H), 3.03 – 2.83 (m, 8H), 1.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.5, 149.6, 149.1, 133.8, 127.3, 122.2, 121.3-
112.7 (m, 4C, -C₄F₉), 112.2, 43.4, 40.4, 39.8 (t, JₐC = 19.7 Hz), 27.1, ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 – -81.2 (m, 3F), -108.8 – -109.9 (m, 2F), -124.4 – -124.6 (m, 2F), -125.5 – -125.9 (m, 2F). IR (film): 2984, 2947, 2889, 1614, 1520, 1445, 1352, 1232, 1167, 1132, 874 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₂₀H₂₀F₉N₂ [M+H]^⁺ 459.1477 found 459.1477.

5ai: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3ai (77.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ai (72.7 mg, 74% yield).

5ai: Pale-yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.61 – 8.53 (m, 2H), 7.60 – 7.53 (m, 4H), 7.46 – 7.41 (m, 2H), 7.36 (d, J = 7.3 Hz, 1H), 7.24 – 7.17 (m, 4H), 3.09 – 2.96 (m, 2H), 1.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.7, 149.9, 145.2, 140.2, 139.8, 128.9, 127.6, 127.3, 127.1, 127.1, 122.1, 121.3-108.3 (m, 4C, -C₄F₉), 44.1, 39.8 (t, JₐC = 19.6 Hz), 27.1, ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.6 – -81.5 (m, 3F), -107.4 – -111.2 (m, 2F), -124.0 – -124.7 (m, 2F), -125.2 – -126.2 (m, 2F). IR (film): 3030, 2987, 1594, 1488, 1411, 1352, 1232, 1133, 1072, 1016, 875 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₂₄H₁₉F₉N [M+H]^⁺ 492.1368 found 492.1367.

5aj: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3aj (80.9 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with
preparative TLC on silica (PE/EA = 20:1) to afford the product **5aj** (44.9 mg, 45% yield).

**5aj**: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J$ = 5.2 Hz, 2H), 7.21 – 7.15 (m, 4H), 7.12 – 7.09 (m, 2H), 3.02 – 2.89 (m, 2H), 1.90 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.2, 150.1, 148.1, 144.6, 128.3, 121.9, 120.9, 119.2-108.5 (m, 5C, -C$_4$F$_9$ and –OCF$_3$), 44.1, 39.8 (t, $J_{C,F}$ = 19.6 Hz), 27.4, $^{13}$C-NMR for C$_4$F$_9$ and OCF$_3$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.9 (s, 3F), -80.7 – -81.5 (m, 3F), -107.7 – -110.6 (m, 2F), -124.3 – -124.6 (m, 2F), -125.2 – -126.7 (m, 2F). IR (film): 3029, 2987, 2930, 1595, 1510, 1471, 1353, 1217, 1133, 1072, 1018, 876 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{14}$F$_{12}$NO [M+H]$^+$ 500.0878 found 500.0881.

![](image)

**5ak**: Prepared following general procedure using **1a** (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), **3ak** (78.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product **5ak** (59.2 mg, 60% yield).

**5ak**: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J$ = 5.1 Hz, 2H), 7.91 – 7.87 (m, 2H), 7.40 – 7.37 (m, 2H), 7.09 – 7.06 (m, 2H), 3.06 – 2.95 (m, 5H), 1.94 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.5, 152.0, 150.1, 139.3, 127.8, 127.6, 121.7, 121.2-108.8 (m, 4C, -C$_4$F$_9$), 44.5, 44.4, 39.5 (t, $J_{C,F}$ = 19.7 Hz), 27.1, $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -80.8 – -81.2 (m, 3F), -108.9 – -109.2 (m, 2F), -124.3 – -124.5 (m, 2F), -125.5 – -125.9 (m, 2F). IR (film): 2992, 2954, 1727, 1611, 1594, 1437, 1411, 1352, 1283, 1232, 1132, 1018, 736 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{17}$F$_9$NO$_2$S [M+H]$^+$ 494.0831 found 494.0831.
**5al**: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3al (57.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5al (37.8 mg, 43% yield).

**5al**: Pale-yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, J = 5.2 Hz, 2H), 7.64 – 7.60 (m, 2H), 7.31 – 7.29 (m, 2H), 7.08 – 7.06 (m, 2H), 3.03 – 2.93 (m, 2H), 1.91 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 155.6, 150.9, 150.1, 132.3, 127.6, 121.7, 118.2, 111.2, 121.1-108.8 (m, 4C, -C₄F₉), 44.7, 39.5 (t, J_C-F = 19.7 Hz), 27.1. ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.3 – -81.8 (m, 3F), -108.9 – -109.3 (m, 2F), -124.1 – -124.7 (m, 2F), -125.4 – -126.0 (m, 2F). IR (film): 2987, 2229, 1594, 1506, 1411, 1353, 1232, 1133, 1071, 1018, 876 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₁₉H₁₄F₉N₂ [M+H]⁺ 441.1008 found 441.1010.

**5am**: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3am (57.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5am (71.5 mg, 74% yield).

**5am**: Pale-yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.60 – 8.54 (m, 2H), 7.61 – 7.53 (m, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.11 – 7.07 (m, 2H), 3.04 – 2.93 (m, 2H), 1.92 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 150.2, 149.9, 129.5 (q, J_C-F = 33.1, 32.7 Hz, -CF₃), 127.3, 125.6, 125.6, 121.9, 121.4-108.9 (m, 4C, -C₄F₉), 44.4, 39.73 (t, J_C-F = 19.6 Hz), 27.2. ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.7 (3F), -81.0 – -81.2 (m, 3F), -109.1 – -109.3 (m, 2F), -124.5 – -124.5 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 3026, 2987, 2951, 1620, 1595, 1555, 1412, 1352,
1328, 1224, 1132, 1073, 1016, 853 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{14}$F$_{12}$N 484.0929 [M+H]$^+$ found 484.0932.

5an: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3an (70.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5an (60.5 mg, 64% yield).

5an: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.58 – 8.51 (m, 2H), 7.62 – 7.23 (m, 2H), 7.10 – 7.07 (m, 2H), 3.88 (s, 3H), 3.04 – 2.93 (m, 2H), 1.91 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.6, 156.2, 150.9, 150.0, 129.9, 129.0, 126.9, 121.9, 121.0-108.6 (m, 4C, -$C_4F_9$), 52.2, 44.5, 39.6 (t, $J_{C-F} = 19.6$ Hz), 27.1, $^{13}$C-NMR for $C_4F_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.29 – -81.93 (m, 3F), -108.7 – -109.7 (m, 2F), -124.0 – -124.8 (m, 2F), -125.3 – -126.1 (m, 2F); IR (film): 2992, 2954, 1940, 1747, 1611, 1437, 1411, 1352, 1283, 1232, 1048, 1017, 877 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{20}$H$_{17}$F$_9$NO$_2$ [M+H]$^+$ 474.1110 found 474.1111.

5ao: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3ao (81.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ao (55.0 mg, 55% yield).
5ao: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J = 5.2$ Hz, 2H), 7.15 – 7.12 (m, 2H), 7.05 – 7.02 (m, 2H), 6.84 – 6.81 (m, 2H), 3.85 – 3.82 (m, 4H), 3.16 – 3.13 (m, 4H), 3.00 – 2.87 (m, 2H), 1.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.2, 149.8, 149.7, 137.2, 127.4, 122.1, 115.2, 121.4-108.3 (m, 4C, -C$_4$F$_9$), 66.9, 48.9, 43.6, 39.8 (t, $J_{C-F} = 19.5$ Hz), 27.1, $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -81.0 – -81.1 (m, 3F), -109.2 – -110.2 (m, 2F), -124.6 – -124.7 (m, 2F), -125.6 – -125.7 (m, 2F). IR (film): 2963, 2856, 1612, 1594, 1517, 1451, 1351, 1303, 1232, 1132, 1070, 1017, 932, 732 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{22}$H$_{22}$F$_9$NO$_2$ [M+H]$^+$ 501.1583 found 501.1583.

![Reaction Scheme](image)

5ap: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3ap (52.9 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ap (44.6 mg, 52% yield).

5ap: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 – 8.51 (m, 2H), 7.23 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 7.05 (d, $J = 7.5$ Hz, 1H), 6.96 – 6.92 (m, 2H), 3.05 – 2.90 (m, 2H), 2.31 (s, 3H), 1.90 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.8, 149.9, 146.3, 138.3, 128.5, 127.8, 127.3, 123.7, 122.1, 121.6-109.9 (m, 4C, -C$_4$F$_9$), 44.1, 39.8 (t, $J_{C-F} = 19.5$ Hz), 27.0, 21.7, $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -80.7 – -81.6 (m, 3F), -108.3 – -110.1 (m, 2F), -124.2 – -124.8 (m, 2F), -125.5 – -126.3 (m, 2F). IR (film): 3026, 2885, 2927, 1594, 1553, 1492, 1352, 1236, 1133, 1017, 880 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{17}$F$_9$N [M+H]$^+$ 430.1212 found 430.1216.
**5aq**: Prepared following *general procedure* using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B2pin2 (76.2 mg, 0.3 mmol, 1.5 equiv), 3aq (57.2 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5aq (54.6 mg, 62% yield).

**5aq**: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.66 – 8.55 (m, 2H), 7.57 (d, J = 7.3 Hz, 1H), 7.50 (s, 1H), 7.46 – 7.39 (m, 2H), 7.13 – 7.08 (m, 2H), 3.03 – 2.91 (m, 2H), 1.92 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 156.1, 149.9, 147.3, 131.5, 131.0, 130.4, 129.6, 122.0, 118.5, 113.0, 120.9-108.7 (m, 4C, -C4F9), 44.4, 39.6 (t, J_C-F = 19.6 Hz), 27.2. 13C-NMR for C4F9 could not be assigned. 19F NMR (376 MHz, CDCl3) δ -80.9 – -81.1 (m, 3F), -109.1 – -109.2 (m, 2F), -124.3 – -124.5 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 2986, 2929, 2856, 2231, 1595, 1485, 1421, 1393, 1224, 1133, 1018, 877 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C19H14F9N2 [M+H]+ 441.1008 found 441.1007.

**5ar**: Prepared following *general procedure* using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B2pin2 (76.2 mg, 0.3 mmol, 1.5 equiv), 3ar (64.8 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ar (66.1 mg, 72% yield).

**5ar**: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.55 – 8.50 (m, 2H), 7.13 – 7.10 (m, 2H), 6.73 (d, J = 8.2 Hz, 1H), 6.64 (dd, J = 8.2, 2.0 Hz, 1H), 6.57 (d, J = 2.0 Hz, 1H), 5.92 (s, 2H), 2.99 – 2.83 (m, 2H), 1.85 (s, 3H). 13C NMR (100 MHz, CDCl3)
δ 156.9, 149.9, 148.0, 146.5, 140.1, 121.9, 119.7, 108.0, 107.7, 121.4-108.2 (m, 4C, -C₄F₉), 101.3, 44.1, 39.8 (t, J_C-F = 19.5 Hz), 27.3, ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 - -81.2 (m, 3F), -109.1 - -109.8 (m, 2F), -124.3 - -124.6 (m, 2F), -125.5 - -125.9 (m, 2F). IR (film): 3021, 2986, 2895, 2779, 1730, 1594, 1551, 1505, 1488, 1435, 1352, 1240, 1166, 1132, 1041, 736 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₁₉H₁₅F₅NO₂ [M+H]⁺ 460.0954 found 460.0954.

5as: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3as (70.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5as (66.2 mg, 70% yield).

5as: Pale-yellow oil; 'H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 5.2 Hz, 2H), 7.14 – 7.11 (m, 2H), 6.77 (d, J = 8.5 Hz, 1H), 6.64 (d, J = 2.4 Hz, 1H), 6.58 (dd, J = 8.5, 2.5 Hz, 1H), 4.22 – 4.21 (m, 4H), 2.99 – 2.82 (m, 2H), 1.85 (d, J = 1.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.8, 149.8, 143.3, 142.4, 139.6, 122.0, 119.6, 117.2, 115.8, 121.6-108.3 (m, 4C, -C₄F₉), 64.4, 64.4, 43.7, 39.8 (t, J_C-F = 19.5 Hz), 27.0, ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.0 - -81.1 (m, 3F), -109.0 - -109.8 (m, 2F), -124.5 - -124.6 (m, 2F), -125.6 - -125.8 (m, 2F). IR (film): 2983, 2936, 2882, 1593, 1507, 1459, 1411, 1352, 1288, 1232, 1132, 1068, 1049, 734 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₂₀H₁₇F₉NO₂ [M+H]⁺ 474.1110 found 474.1110.

5ba: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol,
1.5 equiv), 3ba (67.2 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ba (67.9 mg, 73% yield).

5ba: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.55 (d, J = 5.0 Hz, 2H), 7.84 – 7.73 (m, 4H), 7.54 – 7.47 (m, 2H), 7.18 – 7.15 (m, 2H), 7.11 (dd, J = 8.7, 2.1 Hz, 1H), 3.16 – 3.05 (m, 2H), 2.01 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 156.8, 149.9, 143.3, 133.1, 132.2, 128.5, 128.2, 127.6, 126.6, 126.5, 125.5, 124.7, 122.2, 120.7-108.4 (m, 4C, -C4F9), 44.4, 39.63 (t, J_C-F = 19.6 Hz), 27.1, 13C-NMR for C4F9 could not be assigned. 19F NMR (376 MHz, CDCl3) δ -80.1 – -82.1 (m, 3F), -105.9 – -112.3 (m, 2F), -123.6 – -124.9 (m, 2F), -125.1 – -126.8 (m, 2F). IR (film): 3058, 3024, 2985, 1594, 1551, 1494, 1457, 1410, 1351, 1220, 1133, 1017, 733 cm−1. HRMS (ESI-TOF) exact mass calculated for C22H17F9N466.1212 [M+H]+ found 466.1211.

5bb: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), 3bb (79.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5bb (69.3 mg, 70% yield).

5bb: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.54 (d, J = 4.9 Hz, 2H), 7.71 (d, J = 9.0 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.19 – 7.15 (m, 3H), 7.11 – 7.06 (m, 2H), 3.91 (s, 3H), 3.13 – 3.02 (m, 2H), 1.99 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 158.2, 156.9, 149.9, 141.1, 133.3, 129.7, 128.5, 127.4, 126.0, 124.5, 122.2, 119.4, 121.4-107.5 (m, 4C, -C4F9), 105.6, 55.4, 44.2, 39.6 (t, J_C-F = 19.5 Hz), 27.1, 13C NMR for C4F9 could not be assigned. 19F NMR (376 MHz, CDCl3) δ -80.2 – -81.9 (m, 3F), -107.7 – -111.0 (m, 2F), -124.0 – -124.7 (m, 2F), -125.2 – -126.7 (m, 2F). IR (film): 3060, 3000, 2940,
2844, 1633, 1606, 1552, 1504, 1440, 1351, 1221, 1165, 1032, 819 \text{ cm}^{-1}. \) HRMS (ESI-TOF) exact mass calculated for C_{23}H_{19}F_{9}NO [M+H]^+ 496.1317 found 496.1316.

5c: Prepared following general procedure using 1a (34.5 \mu L, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_{2}pin\(_{2}\) (76.2 mg, 0.3 mmol, 1.5 equiv), 3c (63.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 \mu L, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5c (34.6 mg, 38% yield).

5c: Pale-yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.55 (d, \(J = 5.1\) Hz, 2H), 7.54 – 7.38 (m, 1H), 7.27 – 7.19 (m, 4H), 6.55 (s, 1H), 3.21 – 3.07 (m, 1H), 2.98 – 2.86 (m, 1H), 1.97 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.0, 154.8, 153.6, 150.8, 150.1, 128.0, 125.3, 124.5, 123.2, 121.3, 121.1, 111.3, 120.9-108.6 (m, 4C, -C\(_{4}\)F\(_{9}\)), 103.6, 41.8, 38.2 (t, \(J_{C-F} = 19.8\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -81.0 – -81.1 (m, 3F), -109.1 – -112.6 (m, 2F), -124.5 – -124.5 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 3033, 298, 1595, 1454, 1411, 1371, 1223, 1185, 1133, 1050, 1018, 751 \text{ cm}^{-1}. HRMS (ESI-TOF) exact mass calculated for C\(_{20}\)H\(_{15}\)F\(_{9}\)NO [M+H]^+ 456.1004 found 456.1005.

5d: Prepared following general procedure using 1a (34.5 \mu L, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B_{2}pin\(_{2}\) (76.2 mg, 0.3 mmol, 1.5 equiv), 3d (87.2 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 \mu L, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5d (72.1 mg, 70% yield).

5d: Pale-yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.65 – 8.51 (m, 4H), 7.90 (dd, \(J = 7.8, 1.5\) Hz, 1H), 7.80 – 7.59 (m, 5H), 7.33 (dd, \(J = 8.7, 2.1\) Hz, 1H), 7.27 – 7.22 (m, 2H), 3.20 – 3.08 (m, 2H), 2.06 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.1,
149.8, 144.2, 132.2, 129.9, 128.7, 127.8, 126.9, 126.9, 125.8, 125.8, 123.4, 122.7, 122.3, 120.2 – 110.1 (m, 4C, -C₄F₉), 44.4, 39.8 (t, JᵥC-F = 19.6 Hz), 27.3, ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.6 – -81.4 (m, 3F), -108.1 – -110.4 (m, 2F), -124.0 – -124.5 (m, 2F), -125.3 – -125.9 (m, 2F). IR (film): 3028, 2928, 2855, 1594, 1411, 1352, 1232, 1132, 1017, 746 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₂₆H₁₉F₉N [M+H]⁺ 516.1368 found 516.1368.

5e: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3e (82.5 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5e (52.3 mg, 52% yield).

5e: Pale-yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, J = 5.6 Hz, 2H), 7.64 (dd, J = 18.9, 7.8 Hz, 2H), 7.44 (d, J = 7.4 Hz, 1H), 7.29 – 7.17 (m, 3H), 7.10 – 7.06 (m, 3H), 3.77 (s, 2H), 3.02 – 2.90 (m, 2H), 1.88 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 149.9, 144.8, 143.7, 143.5, 141.0, 140.7, 127.0, 126.9, 125.4, 125.1, 123.3, 122.1, 120.1, 119.9, 121.6-108.2 (m, 4C, -C₄F₉), 44.4, 37.1, 39.9 (t, JᵥC-F = 19.5 Hz), 27.4, ¹³C-NMR for C₄F₉ could not be assigned. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.9 – -81.1 (m, 3F), -109.0 – -109.3 (m, 2F), -124.3 – -124.5 (m, 2F), -125.6 – -125.7 (m, 2F); IR (film): 3021, 2987, 2926, 2855, 1687, 1594, 1552, 1466, 1410, 1352, 1224, 1132, 1017, 880, 735 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C₂₅H₁₉F₉N [M+H]⁺ 504.1368 found 504.1368.
5f: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B<sub>2</sub>pin<sub>2</sub> (76.2 mg, 0.3 mmol, 1.5 equiv), 3f (94.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5f (53.2 mg, 50% yield).

5f: Pale-yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.58 – 8.50 (m, 2H), 8.07 (d, J = 7.8 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.32 (d, J = 8.7 Hz, 1H), 7.25 – 7.15 (m, 4H), 4.34 (t, J = 7.2 Hz, 2H), 3.18 – 3.07 (m, 2H), 2.05 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H). 

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.0, 149.7, 140.5, 138.7, 136.7, 126.0, 124.9, 122.8, 122.7, 122.3, 120.4, 119.1, 117.9, 108.7, 121.1-108.6 (m, 4C, C<sub>4</sub>F<sub>9</sub>), 108.6, 44.3, 40.2 (t, J<sub>C-F</sub> = 19.5 Hz), 37.7, 27.7, 14.0, 

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -80.8 – -81.2 (m, 3F), -108.2 – -110.4 (m, 2F), -124.2 – -124.5 (m, 2F), -125.5 – -125.8 (m, 2F). IR (film): 2979, 2933, 2893, 1595, 1493, 1427, 1440, 1350, 1234, 1132, 1016, 878, 747 cm<sup>-1</sup>. HRMS (ESI-TOF) exact mass calculated for C<sub>26</sub>H<sub>22</sub>F<sub>9</sub>N<sub>2</sub>[M+H]<sup>+</sup> 533.1634 found 533.1634.

5ga: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B<sub>2</sub>pin<sub>2</sub> (76.2 mg, 0.3 mmol, 1.5 equiv), 3ga (60.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5ga (49.2 mg, 55% yield).

5ga: Pale-yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.53 (d, J = 5.0 Hz, 2H), 7.96 (d, J = 1.9 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.32 (d, J = 8.7 Hz, 1H), 7.25 – 7.15 (m, 4H), 4.34 (t, J = 7.2 Hz, 2H), 3.18 – 3.07 (m, 2H), 2.05 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H).
not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -81.0 – -81.1 (m, 3F), -110.9 – -111.0 (m, 2F), -115.5 – -115.6 (m, 1F), -124.4 – -124.6 (m, 2F), -125.6 – -125.7 (m, 2F); IR (film): 2980, 2945, 2889, 1595, 1456, 1353, 1234, 1167, 1133, 1025, 879, 735 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{16}$F$_{10}$N [M+H]$^+$ 448.1118 found 448.1120.

5gb: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3gb (66.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5gb (44.5 mg, 48% yield).

5gb: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.58 – 8.50 (m, 2H), 7.32 – 7.23 (m, 2H), 7.11 – 7.03 (m, 4H), 3.00 – 2.88 (m, 2H), 2.43 – 2.34 (m, 2H), 0.72 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.0, 149.7, 143.8, 133.0, 128.8, 128.7, 122.7, 121.3-108.3 (m, 4C, -C$_4$F$_9$), 47.6, 35.2 (t, $J_{C-F}$ = 19.1 Hz), 30.7, 8.49. $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -80.8 – -81.4 (m, 3F), -110.6 – -111.2 (m, 2F), -124.3 – -124.7 (m, 2F), -125.4 – -126.0 (m, 2F). IR (film): 2979, 2944, 2888, 1594, 1494, 1353, 1233, 1133, 1100, 1013, 871, 721 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{16}$F$_{10}$NCl [M+H]$^+$ 464.0822 found 464.0822.

5gc: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3ge (94.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with
preparative TLC on silica (PE/EA = 20:1) to afford the product 5ge (58.2 mg, 60% yield).

5ge: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.50 (d, $J = 4.9$ Hz, 2H), 7.27 (d, $J = 6.6$ Hz, 2H), 7.13 – 7.10 (m, 2H), 7.01 – 6.97 (m, 2H), 3.01 – 2.88 (m, 2H), 2.46 – 2.29 (m, 2H), 1.28 (s, 9H), 0.70 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.6, 149.7, 149.6, 142.0, 126.9, 125.3, 122.9, 122.1-110.3 (m, 4C, -C$_4$F$_9$), 47.5, 35.3 (t, $J_{C:F} = 19.1$ Hz), 34.4, 31.3, 30.6, 8.5. $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 – -81.1 (m, 3F), -110.9 – -111.0 (m, 2F), -124.5 – -124.7 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 3030, 2967, 2907, 1594, 1514, 1410, 1385, 1352, 1235, 1133, 1024, 879, 737 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{23}$H$_{25}$F$_9$N [M+H]$^+$ 486.1838 found 486.1838.

5h: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3h (76.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5h (43.9 mg, 45% yield).

5h: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.51 (d, $J = 5.1$ Hz, 2H), 7.11 – 7.09 (m, 2H), 6.73 (d, $J = 8.2$ Hz, 1H), 6.63 (dd, $J = 8.2$, 2.0 Hz, 1H), 6.50 (d, $J = 1.9$ Hz, 1H), 5.93 (s, 2H), 2.96 – 2.86 (m, 2H), 2.27 – 2.22 (m, 2H), 1.06 – 0.99 (m, 2H), 0.89 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.8, 149.6, 148.0, 146.4, 139.5, 122.5, 120.1, 108.1, 107.8, 121.3-108.3 (m, 4C, -C$_4$F$_9$), 101.3, 47.3, 40.3, 35.9 (t, $J_{C:F} = 19.0$ Hz), 17.4, 14.4. $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.0 – -81.9 (m, 3F), -110.6 – -111.6 (m, 2F), -123.7 – -125.0 (m, 2F), -125.4 – -126.0 (m, 2F). IR (film): 2965, 2936, 2879, 1595, 1505, 1489, 1435, 1352, 1236, 1133, 1041, 1017, 883, 737 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{21}$H$_{19}$F$_9$NO$_2$ 488.1267 [M+H]$^+$ found 488.1267.
5i: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3i (52.8 mg, 0.4 mmol, 2.0 equiv), DIPEA, (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5i (46.4 mg, 54% yield).

5i: Colorless oil; ¹H NMR (400 MHz, CDCl$_3$) δ 8.54 (d, $J = 5.2$ Hz, 2H), 7.21 – 7.13 (m, 5H), 6.75 – 6.71 (m, 2H), 2.97 (d, $J = 13.3$ Hz, 1H), 2.92 – 2.84 (m, 1H), 2.85 – 2.73 (m, 1H), 2.45 – 2.31 (m, 1H), 1.54 (s, 3H). ¹³C NMR (100 MHz, CDCl$_3$) δ 154.5, 149.4, 135.3, 130.5, 127.9, 126.9, 121.5, 121.3-108.3 (m, 4C, -C$_4$F$_9$), 51.0, 40.4, 39.6 (t, $J_{C-F} = 19.9$ Hz), 22.6. ¹⁹F NMR (376 MHz, CDCl$_3$) δ -80.2 – -82.0 (m, 3F), -105.6 – -112.0 (m, 2F), -124.3 – -124.9 (m, 2F), -124.9 – -128.1 (m, 2F). IR (film): 3030, 2984, 2930, 1704, 1596, 1516, 1412, 1353, 1232, 1133, 1075, 1021, 879 cm⁻¹. HRMS (ESI-TOF) exact mass calculated for C$_{19}$H$_{17}$F$_9$N [M+H]$^+$ 430.1212 found 430.1215.

5j: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3j (39.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5j (35.6 mg, 44% yield).

5j: Colorless oil; ¹H NMR (400 MHz, CDCl$_3$) δ 8.58 – 8.52 (m, 2H), 7.23 – 7.19 (m, 2H), 2.68 – 2.52 (m, 1H), 2.38 – 2.24 (m, 1H), 1.77 – 1.64 (m, 2H), 1.53 (d, $J = 1.9$ Hz, 3H), 1.30 – 1.04 (m, 4H), 0.82 (d, $J = 7.1$ Hz, 3H). ¹³C NMR (100 MHz, CDCl$_3$) δ 155.3, 149.9, 121.3, 121.3-108.3 (m, 4C, -C$_4$F$_9$), 43.6, 41.0 (t, $J_{C-F} = 20.5$ Hz), 39.5,
25.8, 23.1, 23.0, 13.9. $^{13}$C NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.6 – -81.6 (m, 3F), -107.9 – -111.7 (m, 2F), -124.3 – -125.0 (m, 2F), -125.4 – -126.2 (m, 2F). IR (film): 2961, 2936, 2865, 1596, 1551, 1412, 1352, 1236, 1132, 1019, 878, 736 cm$^{-1}$; HRMS (ESI-TOF) exact mass calculated for C$_{16}$H$_{19}$F$_9$N [M+H]$^+$ 396.1368 found 396.1372.

5k: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3k (38.4 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 ℃. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5k (26.7 mg, 34% yield).

5k: Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, J = 5.5 Hz, 2H), 7.31 – 7.27 (m, 2H), 2.43 – 2.32 (m, 2H), 2.23 – 2.16 (m, 2H), 1.86-1.78 (m, 2H), 1.61 – 1.54 (m, 2H), 1.49-1.36 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.5, 149.9, 122.2, 121.5-110.3 (m, 4C, -C$_4$F$_9$), 41.8 – 41.6 (m), 39.8, 36.4, 25.8, 22.0, $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.5 – -81.9 (m, 3F), -109.6 – -110.6 (m, 2F), -124.2 – -124.9 (m, 2F), -125.5 – -126.1 (m, 2F). IR (film): 3027, 2939, 2864, 1596, 1551, 1456, 1411, 1351, 1236, 1132, 1012, 735 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{16}$H$_{17}$F$_9$N [M+H]$^+$ 394.1212 found 394.1216.

5l: Prepared following general procedure using 1a (34.5 µL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3l (56.8 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 µL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 ℃. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5l (22.0 mg, 25% yield).
5i: Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.54 (d, $J = 5.2$ Hz, 2H), 7.22 – 7.19 (m, 2H), 4.05 (t, $J = 6.6$ Hz, 2H), 3.14 – 3.00 (m, 1H), 2.60 – 2.46 (m, 1H), 1.72 (s, 3H), 1.52 – 1.45 (m, 2H). 13C NMR (100 MHz, CDCl$_3$) δ 172.9, 151.0, 150.3, 120.8, 118.7-110.1 (m, 4C, -C$_4$F$_9$), 66.1, 47.3, 38.2 (t, $J_{C-F} = 19.7$ Hz), 30.3, 21.7, 19.0, 13.6, 13C-NMR for C$_4$F$_9$ could not be assigned.

19F NMR (376 MHz, CDCl$_3$) δ -81.0 – -81.1 (m, 3F), -106.6 – -113.3 (m, 2F), -124.6 – -124.8 (2F), -125.7 – -125.8 (m, 2F). IR (film): 2985, 2928, 1747, 1710, 1512, 1226, 1130, 913, 743 cm$^{-1}$; HRMS (ESI-TOF) exact mass calculated for C$_{17}$H$_{19}$F$_9$NO$_2$ [M+H]$^+$ 440.1267 found 440.1271.

5m: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3m (53.6 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5m (30.2 mg, 35% yield).

5m: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.59 – 8.49 (m, 2H), 7.21 – 7.18 (m, 2H), 7.16 – 7.12 (m, 2H), 6.88 – 6.85 (m, 2H), 4.38 (t, $J = 7.1$ Hz, 1H), 3.78 (s, 3H), 2.91 – 2.80 (m, 2H). 13C NMR (100 MHz, CDCl$_3$) δ 158.9, 152.3, 150.0, 133.4, 128.5, 122.9, 114.2, 120.4-109.1 (m, 4C, -C$_4$F$_9$), 55.4, 42.9, 35.7 (t, $J_{C-F} = 21.0$ Hz), 13C-NMR for C$_4$F$_9$ could not be assigned. 19F NMR (376 MHz, CDCl$_3$) δ -80.6 – -81.4 (m, 3F), -111.8 – -113.7 (m, 2F), -124.0 – -124.7 (m,2F), -125.6 – -126.3 (m, 2F). IR (film): 2935, 2840, 1611, 1596, 1513, 1464, 1416, 1354, 1235, 1181, 1133, 1036, 880, 740 cm$^{-1}$; HRMS (ESI-TOF) exact mass calculated for C$_{18}$H$_{15}$F$_9$NO [M+H]$^+$ 432.1004 found 432.1004.
5n: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3n (167.3 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5n (57.2 mg, 40% yield).

5n: Pale-yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.54 (d, $J = 5.1$ Hz, 2H), 7.16 – 7.11 (m, 4H), 6.99 – 6.95 (m, 2H), 5.78 (s, 1H), 5.41 – 5.37 (m, 1H), 3.04 – 2.83 (m, 2H), 2.27 – 2.01 (m, 6H), 1.89 (s, 4H), 1.84 – 1.77 (m, 2H), 1.67 – 1.61 (m, 2H), 1.39 – 1.35 (m, 3H), 1.31 – 1.15 (m, 4H), 1.01 (dd, $J = 6.8$, 3.6 Hz, 6H), 0.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.1, 156.8, 150.0, 149.8, 145.7, 143.2, 135.7, 127.7, 122.4, 122.1, 121.7, 120.4, 121.1-110.2 (m, 4C, -C$_4$F$_9$), 51.0, 47.0, 45.2, 44.1, 39.9 (t, $J_{C:F} = 19.7$ Hz), 38.4, 37.1, 35.0, 34.7, 27.5, 27.3, 25.9, 22.6, 21.5, 20.9, 18.2, 17.2, 14.1, $^{13}$C-NMR for C$_4$F$_9$ could not be assigned. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.9 – 81.0 (m, 3F), -109.1 – -109.4 (m, 2F), -124.4- – 125.5 (m, 2F), -125.6- – 125.7 (m, 2F). IR (film): 2931, 2871, 1745, 1594, 1462, 1411, 1352, 1232, 1173, 1132, 1101, 1016, 908, 734 cm$^{-1}$. HRMS (ESI-TOF) exact mass calculated for C$_{38}$H$_{43}$F$_9$NO$_2$ [M+H]$^+$ 716.3145 found 716.3145.

5o: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 1.5 equiv), 3o (124.1 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE
(1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5o (72.9 mg, 60% yield).

5o: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.53 (d, J = 5.6 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.06 – 7.02 (m, 2H), 3.03 – 2.86 (m, 2H), 2.28 (s, 2H), 1.99 (s, 3H), 1.89 (s, 3H), 1.74 – 1.62 (m, 12H). 13C NMR (100 MHz, CDCl3) δ 170.1, 156.4, 149.9, 149.5, 143.5, 127.7, 122.0, 121.8, 121.2-108.5 (m, 4C, -C₄F₉), 48.8, 44.0, 42.5, 39.8 (t, J_C-F = 19.6 Hz), 36.7, 33.3, 28.7, 27.2, 13C-NMR for C₄F₉ could not be assigned. 19F NMR (376 MHz, CDCl3) δ -81.0 – -81.1 (m, 3F), -108.3 – -110.3 (m, 2F), -124.4 – -124.6 (m, 2F), -125.6 – -125.8 (m, 2F). IR (film): 2982, 2905, 2849, 1754, 1594, 1507, 1471, 1411, 1351, 1224, 1132, 1016, 851, 735 cm⁻¹; HRMS (ESI-TOF) exact mass calculated for C₃₀H₃₁F₉NO₂ [M+H]⁺ 608.2206 found 608.2206.

5p: Prepared following general procedure using 1a (34.5 μL, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B₂pin₂ (76.2 mg, 0.3 mmol, 1.5 equiv), 3p (146.5 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 μL, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5p (79.6 mg, 60% yield).

5p: Pale-yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.58 – 8.53 (s, 2H), 7.17 – 7.13 (m, 4H), 7.03 – 6.98 (m, 3H), 6.66 (d, J = 7.4 Hz, 1H), 6.62 (s, 1H), 3.98 (s, 2H), 3.06 – 2.89 (m, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.89 (d, J = 13.8 Hz, 7H), 1.37 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 176.3, 156.9, 156.7, 149.9, 149.8, 143.3, 136.5, 130.4, 127.9, 123.7, 122.1, 121.6, 120.8, 112.0, 120.1-107.3 (m, 4C, -C₄F₉), 67.8, 44.0, 42.5, 39.8 (t, J_C-F = 19.5 Hz), 37.2, 27.3, 25.3, 25.2, 21.4, 15.8, 13C NMR for C₄F₉ could not be assigned. 19F NMR (376 MHz, CDCl3) δ -80.4 – -81.6 (m, 3F), -107.9 – -110.7 (m, 2F), -124.1 – -124.7 (m, 2F), -125.2 – -126.3 (m, 2F). IR (film): 3025, 2976, 2927, 1754, 1184, 1084, 1033 cm⁻¹; HRMS (ESI-TOF) exact mass calculated for C₃₀H₃₁F₉NO₂ [M+H]⁺ 608.2206 found 608.2206.
1594, 1506, 1473, 1412, 1285, 1173, 1110, 875, 735 cm\(^{-1}\); HRMS (ESI-TOF) exact mass calculated for C\(_{33}\)H\(_{35}\)F\(_9\)NO\(_3\) [M+H]\(^+\) 664.2468 found 664.2467.

\[\text{5q: Prepared following general procedure using 1a (34.5 } \mu\text{L, 0.2 mmol, 1.0 equiv), 4-cyanopyridine (31.3 mg, 0.3 mmol, 1.5 equiv), B}_2\text{pin}_2 (76.2 mg, 0.3 mmol, 1.5 equiv), 3q (116.7 mg, 0.4 mmol, 2.0 equiv), DIPEA (33.1 } \mu\text{L, 0.4 mmol, 0.2 equiv) and MTBE (1 mL) at 80 °C. After 24 h, the reaction mixture was isolated with preparative TLC on silica (PE/EA = 20:1) to afford the product 5q (91.0 mg, 55\% yield).}

\[\text{5q: Pale-yellow oil; } ^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 8.46 (d, } J = 5.3 \text{ Hz, 2H), 7.92 (d, } J = 8.6 \text{ Hz, 2H), 7.17 (d, } J = 8.6 \text{ Hz, 2H), 7.03 – 7.00 (m, 2H), 5.34 (dd, } J = 4.9, 1.8 \text{ Hz, 1H), 4.82 – 4.73 (m, 1H), 2.98 – 2.87 (m, 2H), 2.37 (d, } J = 8.1 \text{ Hz, 2H), 1.96 – 1.77 (m, 8H), 1.74 – 1.53 (m, 2H), 1.50 – 1.32 (m, 6H), 1.31 – 1.18 (m, 4H), 1.17 – 1.10 (m, 2H), 1.04 – 0.87 (m, 10H), 0.85 (d, } J = 6.5 \text{ Hz, 3H), 0.79 (dd, } J = 6.6, 1.8 \text{ Hz, 6H), 0.61 (s, 3H).} \]

\[\text{13C NMR (100 MHz, CDCl}_3\text{) } \delta \text{ 165.5, 156.3, 150.7, 150.0, 139.6, 129.9, 129.7, 126.8, 122.9, 121.9, 121.3-108.3 (m, 4C, -C}_4\text{F}_9\text{), 74.8, 56.8, 56.2, 50.1, 44.5, 42.4, 39.8, 39.7 (d, } J_{\text{C-F}} = 21.9 \text{ Hz), 39.4, 38.3, 37.1, 36.7, 36.3, 35.9, 32.1, 32.0, 28.3, 28.1, 27.9, 27.1, 24.4, 23.9, 22.9, 22.6, 21.1, 19.4, 18.8, 11.9, } ^{13}\text{C-NMR for C}_4\text{F}_9 \text{ could not be assigned.} \]

\[\text{19F NMR (376 MHz, CDCl}_3\text{) } \delta \text{ -80.3 – -81.4 (m, 3F), -108.7 – -109.8 (m, 2F), -123.7 – -124.9 (m, 2F), -125.1 – -126.5 (m, 2F). IR (film): 2947, 2868, 2225, 1721, 1611, 1594, 1469, 1410, 1369, 1318, 1275, 1133, 1017, 909, 736 cm}^{-1}. \]

HRMS (ESI-TOF) exact mass calculated for C\(_{46}\)H\(_{59}\)F\(_9\)NO\(_2\) [M+H]\(^+\) 828.4397 found 828.4381.
5. NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)):

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
^{13}\text{C NMR (100 MHz, CDCl}_3\text{):}

\[ \text{Diagram of } 13C \text{ NMR spectrum} \]

$^{19}\text{F NMR (376 MHz, CDCl}_3\text{):}$

\[ \text{Diagram of } 19F \text{ NMR spectrum} \]
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
\[ ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) : \]

\[ ^{19}\text{F NMR} \ (376 \text{ MHz, CDCl}_3) : \]
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

\[ \text{Diagram showing NMR spectra} \]

$^{13}$C NMR (100 MHz, CDCl$_3$):

\[ \text{Diagram showing NMR spectra} \]
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

![NMR spectrum](image)

$^{13}$C NMR (100 MHz, CDCl$_3$):

![NMR spectrum](image)
\[^{19}\text{F} \text{NMR (376 MHz, CDCl}_3\):\]

\[^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\):\]
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

19F NMR (376 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

\[ \text{Chemical shifts and assignments for } \text{H, NMR} \]

$^{13}$C NMR (100 MHz, CDCl$_3$):

\[ \text{Chemical shifts and assignments for } \text{C, NMR} \]
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

![Chemical Structure and NMR Spectrum]

$^{19}$F NMR (376 MHz, CDCl$_3$):

![Chemical Structure and NMR Spectrum]
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^1$H NMR (376 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

![NMR spectrum for $^1$H](image)

$^{13}$C NMR (100 MHz, CDCl$_3$):

![NMR spectrum for $^{13}$C](image)
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

19F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

![F NMR Spectrum](image)

$^1$H NMR (400 MHz, CDCl$_3$):

![H NMR Spectrum](image)
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

![1H NMR spectrum]

$^{13}$C NMR (100 MHz, CDCl$_3$):

![13C NMR spectrum]
$\text{^{19}F NMR (376 MHz, CDCl}_3):$

$\text{^{1}H NMR (400 MHz, CDCl}_3):$
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$): 

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):

$^{19}$F NMR (376 MHz, CDCl$_3$):
$^1$H NMR (400 MHz, CDCl$_3$):

$^{13}$C NMR (100 MHz, CDCl$_3$):
$^{19}$F NMR (376 MHz, CDCl$_3$):

$^1$H NMR (400 MHz, CDCl$_3$):
$^{13}$C NMR (100 MHz, CDCl$_3$):
6. Cartesian Coordinates of the Optimized Structures

**CF$_3$I**
Zero-point correction= 0.014644 (Hartree/Particle)
Thermal correction to Energy= 0.019359
Thermal correction to Enthalpy= 0.020303
Thermal correction to Gibbs Free Energy= -0.015577
Sum of electronic and zero-point Energies= -348.816993
Sum of electronic and thermal Energies= -348.812278
Sum of electronic and thermal Enthalpies= -348.811333
Sum of electronic and thermal Free Energies= -348.847214

Esol = -348.9903869

| Center | Atomic Number | Atomic Number | Type | X       | Y       | Z       |
|--------|---------------|---------------|------|---------|---------|---------|
| 1      | 9             | 0             |      | -1.650388 | 1.239559 | 0.081260 |
| 2      | 9             | 0             |      | -1.650236 | -0.690139 | 1.032892 |
| 3      | 9             | 0             |      | -1.650420 | -0.549094 | -1.113869 |
| 4      | 6             | 0             |      | -1.196314 | 0.000127 | 0.000118 |
| 5      | 53            | 0             |      | 0.988652  | -0.000274 | -0.000230 |

**CF$_3$I anion**
Zero-point correction= 0.012252 (Hartree/Particle)
Thermal correction to Energy= 0.018032
Thermal correction to Enthalpy= 0.018976
Thermal correction to Gibbs Free Energy= -0.021531
Sum of electronic and zero-point Energies= -348.858162
Sum of electronic and thermal Energies= -348.852382
Sum of electronic and thermal Enthalpies= -348.851438
Sum of electronic and thermal Free Energies= -348.891945

Esol = -349.0769734

| Center | Atomic Number | Atomic Number | Type | X       | Y       | Z       |
|--------|---------------|---------------|------|---------|---------|---------|

S126
### 4-cyanopyridine-boryl (Int1)

Zero-point correction= 0.272426 (Hartree/Particle)
Thermal correction to Energy= 0.288834
Thermal correction to Enthalpy= 0.289778
Thermal correction to Gibbs Free Energy= 0.227912

Sum of electronic and zero-point Energies= -751.250341
Sum of electronic and thermal Energies= -751.233933
Sum of electronic and thermal Enthalpies= -751.232989
Sum of electronic and thermal Free Energies= -751.294855

\[ E_{\text{sol}} = -751.791345 \]
Int2a

Zero-point correction= 0.288623 (Hartree/Particle)
Thermal correction to Energy= 0.311740
Thermal correction to Enthalpy= 0.312684
Thermal correction to Gibbs Free Energy= 0.231236
Sum of electronic and zero-point Energies= -1100.065643
Sum of electronic and thermal Energies= -1100.042526
Sum of electronic and thermal Enthalpies= -1100.041581
Sum of electronic and thermal Free Energies= -1100.123029

Esol = -1100.7890144

| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|---------------|-------------|-------------------------|
|        |               |             | X           | Y           | Z           |
| 1      | 6             | 0           | 1.502341    | 0.954554    | -1.249748   |
| 2      | 6             | 0           | 2.857875    | 0.977417    | -1.238711   |
| 3      | 6             | 0           | 3.602109    | -0.202176   | -0.932074   |
| 4      | 6             | 0           | 2.860150    | -1.385438   | -0.646604   |
| 5      | 6             | 0           | 1.501777    | -1.373238   | -0.674785   |
|   |   |   |          |          |          |
|---|---|---|---------|---------|---------|
| 6 | 7 | 0 | 0.787144 | -0.210649 | -0.971231 |
| 7 | 1 | 0 | 0.894308 | 1.823993  | -1.463528 |
| 8 | 1 | 0 | 3.375170 | 1.902709  | -1.461234 |
| 9 | 1 | 0 | 3.377290 | -2.309132 | -0.415098 |
|10 | 1 | 0 | 0.894153 | -2.248330 | -0.480876 |
|11 | 6 | 0 | 5.017037 | -0.198206 | -0.910962 |
|12 | 7 | 0 | 6.179958 | -0.195110 | -0.893610 |
|13 | 5 | 0 |          |          |          |
|14 | 8 | 0 | -1.360834 | -1.277739 | -0.435797 |
|15 | 8 | 0 | -1.398474 | 0.926204  | -1.102411 |
|16 | 6 | 0 | -2.757678 | -0.920335 | -0.571361 |
|17 | 6 | 0 | -2.708918 | 0.647344  | -0.547946 |
|18 | 6 | 0 | -3.526457 | -1.545526 | 0.580706  |
|19 | 1 | 0 |          |          |          |
|20 | 1 | 0 | -3.514262 | -2.633449 | 0.479477  |
|21 | 1 | 0 | -3.077878 | -1.285487 | 1.541027  |
|22 | 6 | 0 | -3.230755 | -1.479426 | -1.909797 |
|23 | 1 | 0 | -3.046622 | -2.559300 | -1.926327 |
|24 | 1 | 0 | -4.299575 | -1.305504 | -2.059000 |
|25 | 1 | 0 | -2.682313 | -1.023930 | -2.739345 |
|26 | 6 | 0 | -3.759800 | 1.328859  | -1.407012 |
|27 | 1 | 0 | -4.763658 | 1.062914  | -1.061814 |
|28 | 1 | 0 | -3.647520 | 2.412801  | -1.329505 |
|29 | 1 | 0 | -3.660645 | 1.047676  | -2.456246 |
|30 | 6 | 0 | -2.715841 | 1.217847  | 0.867509  |
|31 | 1 | 0 | -2.474982 | 2.282188  | 0.818568  |
|32 | 1 | 0 | -3.694071 | 1.100965  | 1.341262  |
|33 | 1 | 0 | -1.966735 | 0.723511  | 1.492404  |
|34 | 53| 0 | 0.771726 | -0.783198 | 2.576765  |
|35 | 6 | 0 | -0.587154 | -0.371659 | 4.230575  |
|36 | 9 | 0 | -0.298213 | 0.789562  | 4.794702  |
|37 | 9 | 0 | -0.508430 | -1.322911 | 5.146339  |
|38 | 9 | 0 | -1.840756 | -0.320359 | 3.784992  |

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**TS1**

Zero-point correction= 0.288206 (Hartree/Particle)
Thermal correction to Energy= 0.311163
Thermal correction to Enthalpy= 0.312107
Thermal correction to Gibbs Free Energy= 0.231338
Sum of electronic and zero-point Energies= -1100.029343
Sum of electronic and thermal Energies = -1100.006387
Sum of electronic and thermal Enthalpies = -1100.005443
Sum of electronic and thermal Free Energies = -1100.086212

Esol = -1100.7486466

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 1.507788 0.931813 -1.367221 |
| 2             | 6             | 0           | 2.864310 0.978608 -1.352614 |
| 3             | 6             | 0           | 3.586362 -0.199540 -0.983917 |
| 4             | 6             | 0           | 2.906172 -1.313349 -0.553069 |
| 5             | 6             | 0           | 1.497359 -1.280012 -0.486072 |
| 6             | 7             | 0           | 0.830691 -0.218072 -1.041383 |
| 7             | 1             | 0           | 0.883214 1.770534 -1.649234 |
| 8             | 1             | 0           | 3.388670 1.882569 -1.631294 |
| 9             | 1             | 0           | 3.427295 -2.202750 -0.221500 |
| 10            | 1             | 0           | 0.909782 -2.175080 -0.339630 |
| 11            | 6             | 0           | 5.020007 -0.206287 -1.053428 |
| 12            | 7             | 0           | 6.174800 -0.203035 -1.126133 |
| 13            | 5             | 0           | -0.639325 -0.199333 -0.930356 |
| 14            | 8             | 0           | -1.322866 -1.299118 -0.553334 |
| 15            | 8             | 0           | -1.364395 0.921883 -1.156141 |
| 16            | 6             | 0           | -2.729297 -0.924237 -0.588884 |
| 17            | 6             | 0           | -2.664054 0.645065 -0.546034 |
| 18            | 6             | 0           | -3.418150 -1.556335 0.607938 |
| 19            | 1             | 0           | -4.457743 -1.219208 0.667170 |
| 20            | 1             | 0           | -3.416576 -2.642983 0.495544 |
| 21            | 1             | 0           | -2.906110 -1.304904 1.538069 |
| 22            | 6             | 0           | -3.289015 -1.466205 -1.899322 |
| 23            | 1             | 0           | -3.123389 -2.545184 -1.934058 |
| 24            | 1             | 0           | -4.362301 -1.275894 -1.978470 |
| 25            | 1             | 0           | -2.788473 -1.012315 -2.759601 |
| 26            | 6             | 0           | -3.739139 1.347644 -1.354409 |
| 27            | 1             | 0           | -4.729050 1.090863 -0.965396 |
| 28            | 1             | 0           | -3.609744 2.428979 -1.270091 |
| 29            | 1             | 0           | -3.692838 1.075002 -2.409652 |
| 30            | 6             | 0           | -2.592965 1.196826 0.873460 |
| 31            | 1             | 0           | -2.361763 2.263395 0.824454 |
| 32            | 1             | 0           | -3.544683 1.069383 1.395578 |
| 33            | 1             | 0           | -1.810638 0.698987 1.454159 |
| Center | Atomic Number | Atomic Number | Atomic Type | X     | Y     | Z     |
|--------|---------------|---------------|-------------|-------|-------|-------|
| 1      | 6             | 0             | 0           | 1.344328 | 0.900812 | -0.624581 |
| 2      | 6             | 0             | 0           | 2.768452 | 0.887494 | -0.840266 |
| 3      | 6             | 0             | 0           | 3.438852 | -0.295425 | -0.799722 |
| 4      | 6             | 0             | 0           | 2.725862 | -1.528797 | -0.582004 |
| 5      | 6             | 0             | 0           | 1.374954 | -1.496322 | -0.595586 |
| 6      | 7             | 0             | 0           | 0.686618 | -0.313535 | -0.772425 |
| 7      | 1             | 0             | 0           | 0.771265 | 1.749837 | -0.973221 |
| 8      | 1             | 0             | 0           | 3.283927 | 1.831435 | -0.967566 |
| 9      | 1             | 0             | 0           | 3.260141 | -2.461085 | -0.462885 |
| 10     | 1             | 0             | 0           | 0.755301 | -2.380568 | -0.508010 |
| 11     | 6             | 0             | 0           | 4.864833 | -0.326806 | -0.980324 |
| 12     | 7             | 0             | 0           | 6.010614 | -0.369670 | -1.133639 |
| 13     | 5             | 0             | 0           | -0.771919 | -0.308714 | -0.805906 |
| 14     | 8             | 0             | 0           | -1.510686 | -1.436680 | -0.638157 |
| 15     | 8             | 0             | 0           | -1.475343 | 0.835623 | -0.997125 |
| 16     | 6             | 0             | 0           | -2.884924 | -1.042071 | -0.910443 |
| 17     | 6             | 0             | 0           | -2.846001 | 0.501848 | -0.642879 |

**Int3a**

Zero-point correction= 0.275542 (Hartree/Particle)
Thermal correction to Energy= 0.293682
Thermal correction to Enthalpy= 0.294626
Thermal correction to Gibbs Free Energy= 0.228064

Sum of electronic and zero-point Energies= -762.600992
Sum of electronic and thermal Energies= -762.582852
Sum of electronic and thermal Enthalpies= -762.581908
Sum of electronic and thermal Free Energies= -762.648470

Esol = -763.1532994
| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|----------------|-------------|-------------------------|
|        |                |             | X           | Y           | Z           |
| 18     | 6              | 0           | -3.805971   | -1.821435  | 0.010789    |
| 19     | 1              | 0           | -4.837437   | -1.474815  | -0.104766   |
| 20     | 1              | 0           | -3.770467   | -2.882566  | -0.246760   |
| 21     | 1              | 0           | -3.510340   | -1.709378  | 1.054481    |
| 22     | 6              | 0           | -3.158183   | -1.385199  | -2.371449   |
| 23     | 1              | 0           | -2.963352   | -2.448570  | -2.527386   |
| 24     | 1              | 0           | -4.197586   | -1.178127  | -2.638436   |
| 25     | 1              | 0           | -2.505935   | -0.812892  | -3.037443   |
| 26     | 6              | 0           | -3.787421   | 1.320346   | -1.507838   |
| 27     | 1              | 0           | -4.824103   | 1.019832   | -1.327682   |
| 28     | 1              | 0           | -3.688798   | 2.377702   | -1.252304   |
| 29     | 1              | 0           | -3.563453   | 1.199826   | -2.568647   |
| 30     | 6              | 0           | -3.012102   | 0.855396   | 0.831681    |
| 31     | 1              | 0           | -2.750373   | 1.906190   | 0.973092    |
| 32     | 1              | 0           | -4.042448   | 0.698257   | 1.161570    |
| 33     | 1              | 0           | -2.341722   | 0.260842   | 1.459218    |
| 34     | 53             | 0           | 1.101959    | 1.595933   | 1.788026    |

**Int2b**

Zero-point correction= 0.288474 (Hartree/Particle)
Thermal correction to Energy= 0.311779
Thermal correction to Enthalpy= 0.312723
Thermal correction to Gibbs Free Energy= 0.228448
Sum of electronic and zero-point Energies= 1100.063363
Sum of electronic and thermal Energies= 1100.040059
Sum of electronic and thermal Enthalpies= 1100.039114
Sum of electronic and thermal Free Energies= 1100.123389

Esol = -1100.7873177

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|----------------|-------------|-------------------------|
|               |                |             | X           | Y           | Z           |
| 1             | 6              | 0           | 1.659096    | 1.185973   | -0.180389   |
| 2             | 6              | 0           | 3.014411    | 1.204109   | -0.183755   |
| 3             | 6              | 0           | 3.757894    | -0.000017  | -0.000053   |
| 4             | 6              | 0           | 3.014407    | -1.204136  | 0.183668    |
| 5             | 6              | 0           | 1.659092    | -1.185990  | 0.180337    |
| E   | C   | T   | TSEOL  |
|-----|-----|-----|--------|
| 6   | 7   | 0   | 0.942727 | -0.00006  | -0.000016 |
| 7   | 1   | 0   | 1.051679 | 2.071756  | -0.314909 |
| 8   | 1   | 0   | 3.531257 | 2.145335  | -0.327519 |
| 9   | 1   | 0   | 3.531249 | -2.145366 | 0.327418  |
| 10  | 1   | 0   | 1.051672 | -2.071769 | 0.314874  |
| 11  | 6   | 0   | 5.172422 | 0.000022  | -0.000072 |
| 12  | 7   | 0   | 6.335976 | -0.000025 | -0.000087 |
| 13  | 5   | 0   | -0.497292 | 0.000000  | 0.000005  |
| 14  | 8   | 0   | -1.235849 | -1.129146 | 0.227042  |
| 15  | 8   | 0   | -1.235845 | 1.129154  | -0.227011 |
| 16  | 6   | 0   | -2.601367 | -0.776254 | -0.104684 |
| 17  | 6   | 0   | -2.601356 | 0.776276  | 0.104543  |
| 18  | 6   | 0   | -3.542222 | -1.540887 | 0.809991  |
| 19  | 1   | 0   | -4.576183 | -1.223153 | 0.642282  |
| 20  | 1   | 0   | -3.473353 | -2.609868 | 0.594657  |
| 21  | 1   | 0   | -3.290618 | -1.385312 | 1.859912  |
| 22  | 6   | 0   | -2.822209 | -1.174404 | -1.561111 |
| 23  | 1   | 0   | -2.597029 | -2.237333 | -1.673512 |
| 24  | 1   | 0   | -3.857039 | -1.002112 | -1.868613 |
| 25  | 1   | 0   | -2.161107 | -0.609992 | -2.225328 |
| 26  | 6   | 0   | -3.542231 | 1.540919  | -0.809886 |
| 27  | 1   | 0   | -4.576192 | 1.223209  | -0.642133 |
| 28  | 1   | 0   | -3.473330 | 2.609901  | -0.594564 |
| 29  | 1   | 0   | -3.290672 | 1.385330  | -1.859815 |
| 30  | 6   | 0   | -2.822149 | 1.174428  | 1.561193  |
| 31  | 1   | 0   | -2.596958 | 2.237355  | 1.673587  |
| 32  | 1   | 0   | -3.856970 | 1.002143  | 1.868728  |
| 33  | 1   | 0   | -2.161030 | 0.610012  | 2.225389  |

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**TSI’**

Zero-point correction= 0.288218 (Hartree/Particle)
Thermal correction to Energy= 0.311310
Thermal correction to Enthalpy= 0.312254
Thermal correction to Gibbs Free Energy= 0.229019
Sum of electronic and zero-point Energies= -1100.018179
Sum of electronic and thermal Energies= -1099.995088
Sum of electronic and thermal Enthalpies= -1099.994144
Sum of electronic and thermal Free Energies= -1100.077379

Esol = -1100.7382104
| Center Number | Atomic Number | Atomic Type | X       | Y       | Z       |
|---------------|---------------|-------------|---------|---------|---------|
| 1             | 6             | 0           | 1.298074| 1.054842| -1.314851|
| 2             | 6             | 0           | 2.637879| 1.153919| -1.420122|
| 3             | 6             | 0           | 3.489706| 0.021438| -1.087111|
| 4             | 6             | 0           | 2.786836| -1.246121| -0.953204|
| 5             | 6             | 0           | 1.442524| -1.275382| -0.863620|
| 6             | 7             | 0           | 0.671238| -0.133406| -0.984613|
| 7             | 1             | 0           | 0.632200| 1.889459| -1.497484|
| 8             | 1             | 0           | 3.095624| 2.094849| -1.696568|
| 9             | 1             | 0           | 3.359540| -2.160636| -0.869842|
| 10            | 1             | 0           | 0.884867| -2.190966| -0.708578|
| 11            | 6             | 0           | 4.757433| -0.036959| -1.790862|
| 12            | 7             | 0           | 5.730717| -0.097790| -2.412908|
| 13            | 5             | 0           | -0.771986| -0.195010| -0.839385|
| 14            | 8             | 0           | -1.420745| -1.342636| -0.499941|
| 15            | 8             | 0           | -1.570844| 0.889427| -1.036907|
| 16            | 6             | 0           | -2.833232| -1.063891| -0.695733|
| 17            | 6             | 0           | -2.884652| 0.495771| -0.556528|
| 18            | 6             | 0           | -3.630357| -1.822310| 0.350558|
| 19            | 1             | 0           | -4.689663| -1.555360| 0.286930|
| 20            | 1             | 0           | -3.537158| -2.896301| 0.173922|
| 21            | 1             | 0           | -3.271236| -1.607710| 1.357741|
| 22            | 6             | 0           | -3.186547| -1.544774| -2.100112|
| 23            | 1             | 0           | -2.928577| -2.602540| -2.186216|
| 24            | 1             | 0           | -4.254378| -1.428434| -2.301842|
| 25            | 1             | 0           | -2.625778| -0.990208| -2.858181|
| 26            | 6             | 0           | -3.940947| 1.175947| -1.409063|
| 27            | 1             | 0           | -4.938238| 0.822156| -1.130391|
| 28            | 1             | 0           | -3.903233| 2.255347| -1.245457|
| 29            | 1             | 0           | -3.781413| 0.983645| -2.470755|
| 30            | 6             | 0           | -2.979215| 0.957752| 0.894584|
| 31            | 1             | 0           | -2.798022| 2.033971| 0.934614|
| 32            | 1             | 0           | -3.968962| 0.754406| 1.311170|
| 33            | 1             | 0           | -2.229399| 0.459657| 1.516044|
| 34            | 53            | 0           | 4.398413| 0.526253| 1.204558|
| 35            | 6             | 0           | 5.347502| 1.149689| 4.101568|
| 36            | 9             | 0           | 5.881949| 2.353157| 4.118095|
| 37            | 9             | 0           | 6.224246| 0.240165| 4.472868|
| 38            | 9             | 0           | 4.273000| 1.103588| 4.863981|
Zero-point correction= 0.275222 (Hartree/Particle)
Thermal correction to Energy= 0.293334
Thermal correction to Enthalpy= 0.294279
Thermal correction to Gibbs Free Energy= 0.227704
Sum of electronic and zero-point Energies= -762.591352
Sum of electronic and thermal Energies= -762.573240
Sum of electronic and thermal Enthalpies= -762.572295
Sum of electronic and thermal Free Energies= -762.638870

Esol = -763.143816

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 1.393481 0.880304 -0.834736 |
| 2             | 6             | 0           | 2.736459 0.910364 -0.779910 |
| 3             | 6             | 0           | 3.501953 -0.297174 -0.455921 |
| 4             | 6             | 0           | 2.710971 -1.529588 -0.522654 |
| 5             | 6             | 0           | 1.368830 -1.483842 -0.586758 |
| 6             | 7             | 0           | 0.669545 -0.291787 -0.686305 |
| 7             | 1             | 0           | 0.797294 1.766030 -1.018311 |
| 8             | 1             | 0           | 3.267545 1.842848 -0.920602 |
| 9             | 1             | 0           | 3.222410 -2.481710 -0.465462 |
| 10            | 1             | 0           | 0.753967 -2.375797 -0.584381 |
| 11            | 6             | 0           | 4.795409 -0.380716 -1.119394 |
| 12            | 7             | 0           | 5.788266 -0.453261 -1.707753 |
| 13            | 5             | 0           | -0.777761 -0.279710 -0.715787 |
| 14            | 8             | 0           | -1.521439 -1.410561 -0.554886 |
| 15            | 8             | 0           | -1.495644 0.862439 -0.910646 |
| 16            | 6             | 0           | -2.882239 -1.034213 -0.892848 |
| 17            | 6             | 0           | -2.874568 0.509084 -0.624821 |
| 18            | 6             | 0           | -3.839663 -1.826426 -0.020225 |
| 19            | 1             | 0           | -4.868651 -1.493000 -0.186080 |
| 20            | 1             | 0           | -3.777804 -2.886201 -0.278066 |
| 21            | 1             | 0           | -3.598071 -1.716031 1.037595 |
| 22            | 6             | 0           | -3.082162 -1.377715 -2.366229 |
| 23            | 1             | 0           | -2.865565 -2.438049 -2.513426 |
| 24            | 1             | 0           | -4.110129 -1.184227 -2.683090 |
| 25            | 1             | 0           | -2.406103 -0.796566 -3.000165 |
| Center | Atomic Number | Atomic Type | X       | Y       | Z       |
|--------|---------------|--------------|---------|---------|---------|
| 1      | 6             | 0            | -0.477950 | -0.276754 | 0.025720 |
| 2      | 9             | 0            | 0.935391  | 0.369695  | 1.078557 |
| 3      | 9             | 0            | 0.935457  | -1.511919 | -0.007741|
| 4      | 9             | 0            | -0.838805 | -0.257324 | -0.007879|

**CF₃ radical**

Zero-point correction= 0.012690 (Hartree/Particle)
Thermal correction to Energy= 0.016102
Thermal correction to Enthalpy= 0.017046
Thermal correction to Gibbs Free Energy= -0.013995
Sum of electronic and zero-point Energies= -337.425185
Sum of electronic and thermal Energies= -337.421773
Sum of electronic and thermal Enthalpies= -337.420829
Sum of electronic and thermal Free Energies= -337.451870

Esol = -337.5898162

| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|---------------|--------------|-------------------------|
| 1      | 6             | 0            | 0.477950 -0.276754 0.025720 |
| 2      | 9             | 0            | 0.935391 0.369695 1.078557 |
| 3      | 9             | 0            | 0.935457 -1.511919 -0.007741 |
| 4      | 9             | 0            | -0.838805 -0.257324 -0.007879 |

**3a**

Zero-point correction= 0.190866 (Hartree/Particle)
Thermal correction to Energy= 0.200724
Thermal correction to Enthalpy= 0.201668
Thermal correction to Gibbs Free Energy= 0.155120
Sum of electronic and zero-point Energies= -387.916954
Sum of electronic and thermal Energies = -387.907096
Sum of electronic and thermal Enthalpies = -387.906152
Sum of electronic and thermal Free Energies = -387.952700

Esol = -388.2364733

| Center Number | Atomic Number | Atomic Type | X            | Y            | Z            |
|---------------|---------------|-------------|--------------|--------------|--------------|
| 1             | 6             | 0           | -2.192137    | -0.607695    | -0.538838    |
| 2             | 6             | 0           | -0.806015    | -0.640159    | -0.515333    |
| 3             | 6             | 0           | -0.065449    | 0.411851     | 0.042856     |
| 4             | 6             | 0           | -0.776189    | 1.478533     | 0.601383     |
| 5             | 6             | 0           | -2.167770    | 1.508663     | 0.574137     |
| 6             | 6             | 0           | -2.900382    | 0.471272     | 0.000733     |
| 7             | 1             | 0           | -2.740352    | -1.441348    | -0.970796    |
| 8             | 1             | 0           | -0.284891    | -1.507066    | -0.909297    |
| 9             | 1             | 0           | -0.241495    | 2.305760     | 1.057185     |
| 10            | 1             | 0           | -2.692781    | 2.354784     | 1.009594     |
| 11            | 6             | 0           | 1.421064     | 0.387475     | 0.056289     |
| 12            | 6             | 0           | 2.12236     | -0.274903    | -0.868562    |
| 13            | 1             | 0           | 3.206530     | -0.301171    | -0.834808    |
| 14            | 1             | 0           | 1.643621     | -0.789566    | -1.694787    |
| 15            | 6             | 0           | 2.116915     | 1.159923     | 1.148632     |
| 16            | 1             | 0           | 1.707570     | 0.909042     | 2.132008     |
| 17            | 1             | 0           | 3.187907     | 0.949965     | 1.148888     |
| 18            | 1             | 0           | 1.990185     | 2.239172     | 1.011029     |
| 19            | 6             | 0           | -4.406113    | 0.501271     | -0.042925    |
| 20            | 1             | 0           | -4.804648    | 1.306663     | 0.577847     |
| 21            | 1             | 0           | -4.765286    | 0.657340     | -1.065229    |
| 22            | 1             | 0           | -4.830191    | -0.442712    | 0.310830     |

TS2

Zero-point correction= 0.203710 (Hartree/Particle)
Thermal correction to Energy= 0.218171
Thermal correction to Enthalpy= 0.219115
Thermal correction to Gibbs Free Energy = 0.158546
Sum of electronic and zero-point Energies = -725.347459
Sum of electronic and thermal Energies = -725.332998
Sum of electronic and thermal Enthalpies = -725.332054
Sum of electronic and thermal Free Energies = -725.392623

\[ E_{\text{sol}} = -725.8294859 \]

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
| 1             | 6             | 0           | -0.361868 -1.562230 1.374790 |
| 2             | 6             | 0           | 0.726134 -0.978167 0.743905 |
| 3             | 6             | 0           | 0.673829 0.351250 0.296105 |
| 4             | 6             | 0           | -0.523332 1.052684 0.480602 |
| 5             | 6             | 0           | -1.609689 0.463022 1.118282 |
| 6             | 6             | 0           | -1.548242 -0.850851 1.581357 |
| 7             | 1             | 0           | -0.298039 -2.597007 1.701644 |
| 8             | 1             | 0           | 1.617047 -1.571703 0.563467 |
| 9             | 1             | 0           | -0.609391 2.077175 0.132904 |
| 10            | 1             | 0           | -2.523926 1.034290 1.255514 |
| 11            | 6             | 0           | 1.832940 0.980147 -0.373589 |
| 12            | 6             | 0           | 3.093414 0.547871 -0.156445 |
| 13            | 1             | 0           | 3.935971 1.031141 -0.641333 |
| 14            | 1             | 0           | 3.324567 -0.172634 0.621461 |
| 15            | 6             | 0           | 1.562119 2.083923 -1.360027 |
| 16            | 1             | 0           | 1.172016 2.977683 -0.861111 |
| 17            | 1             | 0           | 2.475791 2.369526 -1.884477 |
| 18            | 1             | 0           | 0.815744 1.770942 -2.097186 |
| 19            | 6             | 0           | -2.715693 -1.490125 2.286717 |
| 20            | 1             | 0           | -2.530156 -1.561309 3.363415 |
| 21            | 1             | 0           | -3.630785 -0.911338 2.143738 |
| 22            | 1             | 0           | -2.892105 -2.504350 1.918318 |
| 23            | 6             | 0           | 3.190396 -1.297887 -1.781204 |
| 24            | 9             | 0           | 3.311369 -2.438763 -1.112357 |
| 25            | 9             | 0           | 2.021251 -1.255511 -2.395484 |
| 26            | 9             | 0           | 4.174206 -1.181283 -2.658966 |
Zero-point correction=                           0.206938 (Hartree/Particle)
Thermal correction to Energy=                    0.219764
Thermal correction to Enthalpy=                  0.220708
Thermal correction to Gibbs Free Energy=         0.165924
Sum of electronic and zero-point Energies=       -725.419174
Sum of electronic and thermal Energies=          -725.406348
Sum of electronic and thermal Enthalpies=        -725.405403
Sum of electronic and thermal Free Energies=     -725.460187

E_{\text{Sol}} = -725.901591

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z            |
| 1             | 6             | 0           | -0.342146   | -1.793973   | 1.254712     |
| 2             | 6             | 0           | 0.730181    | -1.265287   | 0.561420     |
| 3             | 6             | 0           | 0.664067    | 0.024360    | -0.025144    |
| 4             | 6             | 0           | -0.555401   | 0.728087    | 0.124861     |
| 5             | 6             | 0           | -1.620716   | 0.185291    | 0.824717     |
| 6             | 6             | 0           | -1.540661   | -1.083198   | 1.405813     |
| 7             | 1             | 0           | -0.257956   | -2.788261   | 1.686379     |
| 8             | 1             | 0           | 1.621893    | -1.869459   | 0.438294     |
| 9             | 1             | 0           | -0.656513   | 1.721125    | -0.299932    |
| 10            | 1             | 0           | -2.538216   | 0.758912    | 0.927239     |
| 11            | 6             | 0           | 1.761437    | 0.604145    | -0.734246    |
| 12            | 6             | 0           | 3.121622    | -0.029297   | -0.732426    |
| 13            | 1             | 0           | 3.900992    | 0.738503    | -0.779554    |
| 14            | 1             | 0           | 3.306370    | -0.628497   | 0.162790     |
| 15            | 6             | 0           | 1.601214    | 1.887151    | -1.492695    |
| 16            | 1             | 0           | 1.491966    | 2.748439    | -0.818695    |
| 17            | 1             | 0           | 2.465740    | 2.072203    | -2.132519    |
| 18            | 1             | 0           | 0.712829    | 1.867652    | -2.132645    |
| 19            | 6             | 0           | -2.702302   | -1.684014   | 2.150758     |
| 20            | 1             | 0           | -3.487190   | -0.944620   | 2.324156     |
| 21            | 1             | 0           | -3.142662   | -2.513982   | 1.588211     |
| 22            | 1             | 0           | -2.387627   | -2.080251   | 3.120621     |
| 23            | 6             | 0           | 3.347812    | -0.932792   | -1.925498    |
| 24            | 9             | 0           | 2.500744    | -1.972422   | -1.930478    |
TS3

Zero-point correction= 0.482086 (Hartree/Particle)
Thermal correction to Energy= 0.512671
Thermal correction to Enthalpy= 0.513615
Thermal correction to Gibbs Free Energy= 0.417978
Sum of electronic and zero-point Energies= -1476.684014
Sum of electronic and thermal Energies= -1476.653429
Sum of electronic and thermal Enthalpies= -1476.652485
Sum of electronic and thermal Free Energies= -1476.748122

Esol = -1477.7062327

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 6             | 0           | -4.106907   | 2.439404    | 0.432584    |
| 2             | 6             | 0           | -3.772324   | 1.098874    | 0.393780    |
| 3             | 6             | 0           | -2.643834   | 0.644528    | -0.333729   |
| 4             | 6             | 0           | -1.899083   | 1.625633    | -1.028875   |
| 5             | 6             | 0           | -2.254288   | 2.967468    | -0.988743   |
| 6             | 6             | 0           | -3.358529   | 3.404706    | -0.256296   |
| 7             | 1             | 0           | -4.973558   | 2.752598    | 1.009220    |
| 8             | 1             | 0           | -4.383489   | 0.394116    | 0.944880    |
| 9             | 1             | 0           | -1.036274   | 1.329958    | -1.615326   |
| 10            | 1             | 0           | -1.661741   | 3.692420    | -1.541285   |
| 11            | 6             | 0           | -2.214612   | -0.726955   | -0.312771   |
| 12            | 6             | 0           | -3.113400   | -1.816208   | 0.196070    |
| 13            | 1             | 0           | -2.523432   | -2.698810   | 0.466610    |
| 14            | 1             | 0           | -3.683521   | -1.524385   | 1.082090    |
| 15            | 6             | 0           | -1.044178   | -1.155479   | -1.141333   |
| 16            | 1             | 0           | -0.165200   | -0.528286   | -0.947315   |
| 17            | 1             | 0           | -0.770972   | -2.191612   | -0.928865   |
| 18            | 1             | 0           | -1.267629   | -1.086108   | -2.214278   |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 19 | 6  | 0 | -3.757625 | 4.855762 | -0.219358 |
| 20 | 1  | 0 | -4.697591 | 5.018372 | -0.756989 |
| 21 | 1  | 0 | -3.909460 | 5.197873 | 0.808681  |
| 22 | 1  | 0 | -2.995694 | 5.488847 | -0.679697 |
| 23 | 6  | 0 | -4.106941 | -2.247944 | -0.848198 |
| 24 | 9  | 0 | -4.950448 | -1.295775 | -1.202726 |
| 25 | 9  | 0 | -3.490750 | -2.692925 | -1.968862 |
| 26 | 6  | 0 | -3.909460 | 5.197873 | 1.801739  |
| 27 | 6  | 0 | -2.995694 | 5.488847 | -0.679697 |
| 28 | 6  | 0 | -0.687419 | -0.408901 | 1.893470  |
| 29 | 6  | 0 | -0.135478 | 0.853565  | 1.493579  |
| 30 | 6  | 0 | 1.110951  | 0.921903  | 0.971569  |
| 31 | 7  | 0 | 1.927172  | -0.205097 | 0.856615  |
| 32 | 1  | 0 | 2.102644  | -2.268141 | 1.182706  |
| 33 | 1  | 0 | -0.168341 | -2.520913 | 2.140794  |
| 34 | 1  | 0 | -0.731854 | 1.754455  | 1.575274  |
| 35 | 1  | 0 | 1.559206  | 1.847381  | 0.632558  |
| 36 | 6  | 0 | -1.892143 | -0.464384 | 2.637811  |
| 37 | 7  | 0 | -2.898837 | -0.517925 | 3.219626  |
| 38 | 5  | 0 | 3.257154  | -0.103022 | 0.313068  |
| 39 | 8  | 0 | 3.809746  | 1.088648  | -0.06943  |
| 40 | 8  | 0 | 4.064858  | -1.191454 | 0.131735  |
| 41 | 6  | 0 | 5.021234  | 0.746486  | -0.785706 |
| 42 | 6  | 0 | 5.373882  | -0.658118 | -0.189775 |
| 43 | 6  | 0 | 6.061277  | 1.842030  | -0.533729 |
| 44 | 5  | 0 | 7.017225  | 1.543911  | -0.986805 |
| 45 | 1  | 0 | 5.731332  | 2.763033  | -0.984623 |
| 46 | 1  | 0 | 6.210825  | 1.990391  | 0.538350  |
| 47 | 6  | 0 | 4.655664  | 0.684066  | -2.266418 |
| 48 | 1  | 0 | 4.219536  | 1.640849  | -2.561927 |
| 49 | 1  | 0 | 5.535895  | 0.495019  | -2.886290 |
| 50 | 1  | 0 | 3.919749  | -0.103071 | -2.455063 |
| 51 | 6  | 0 | 6.064296  | -1.604293 | -1.156575 |
| 52 | 1  | 0 | 7.015057  | -1.178573 | -1.491950 |
| 53 | 1  | 0 | 6.272088  | -2.552217 | -0.654753 |
| 54 | 1  | 0 | 5.440467  | -1.807162 | -2.028016 |
| 55 | 6  | 0 | 6.149425  | -0.564993 | 1.121629  |
| 56 | 1  | 0 | 6.173375  | -1.552829 | 1.587024  |
| 57 | 1  | 0 | 7.177215  | -0.232985 | 0.953628  |
| 58 | 1  | 0 | 5.666032  | 0.130367  | 1.814051  |
Int5

Zero-point correction=                           0.486587 (Hartree/Particle)
Thermal correction to Energy=                    0.516472
Thermal correction to Enthalpy=                  0.517416
Thermal correction to Gibbs Free Energy=         0.424399

Sum of electronic and zero-point Energies=        -1476.730969
Sum of electronic and thermal Energies=           -1476.701084
Sum of electronic and thermal Enthalpies=          -1476.700140
Sum of electronic and thermal Free Energies=       -1476.793157

Esol= -1477.753334

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X    | Y    | Z    |
|---------------|---------------|-------------|------------------------------|------|------|
| 1             | 6             | 0           | 7.704005                     | 0.964369 | -3.971408 |
| 2             | 6             | 0           | 6.621777                     | 1.368646 | -3.199504 |
| 3             | 6             | 0           | 6.004633                     | 0.491535 | -2.297857 |
| 4             | 6             | 0           | 6.527230                     | -0.801478 | -2.204424 |
| 5             | 6             | 0           | 7.610679                     | -1.203421 | -2.980523 |
| 6             | 6             | 0           | 8.217557                     | -0.330552 | -3.881290 |
| 7             | 1             | 0           | 8.158586                     | 1.672856 | -4.658917 |
| 8             | 1             | 0           | 6.275577                     | 2.390821 | -3.303295 |
| 9             | 1             | 0           | 6.093928                     | -1.516343 | -1.514457 |
| 10            | 1             | 0           | 7.989334                     | -2.217390 | -2.880933 |
| 11            | 6             | 0           | 4.852849                     | 0.947454 | -1.393719 |
| 12            | 6             | 0           | 3.854619                     | 1.844111 | -2.154951 |
| 13            | 1             | 0           | 3.131682                     | 2.277054 | -1.456783 |
| 14            | 1             | 0           | 4.359446                     | 2.677421 | -2.647203 |
| 15            | 6             | 0           | 4.106774                     | -0.243131 | -0.776920 |
| 16            | 1             | 0           | 4.724481                     | -0.741033 | -0.024920 |
| 17            | 1             | 0           | 3.190101                     | 0.092694 | -0.289007 |
| 18            | 1             | 0           | 3.837993                     | -0.967137 | -1.548687 |
| 19            | 6             | 0           | 9.369716                     | -0.770198 | -4.746613 |
| 20            | 1             | 0           | 9.873500                     | -1.641878 | -4.322597 |
| 21            | 1             | 0           | 9.022956                     | -1.041797 | -5.748976 |
| 22            | 1             | 0           | 10.106167                    | 0.029430 | -4.860182 |
| 23            | 6             | 0           | 3.026346                     | 1.149669 | -3.211527 |
Zero-point correction=                           0.275165 (Hartree/Particle)
Thermal correction to Energy= 0.292695
Thermal correction to Enthalpy= 0.293639
Thermal correction to Gibbs Free Energy= 0.228582
Sum of electronic and zero-point Energies= -762.593986
Sum of electronic and thermal Energies= -762.576456
Sum of electronic and thermal Enthalpies= -762.575512
Sum of electronic and thermal Free Energies= -762.640570

Esol = -763.1522273

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 1.392252 0.846388 -0.583086 |
| 2             | 6             | 0           | 2.777818 0.844172 -0.649114 |
| 3             | 6             | 0           | 3.432775 -0.365252 -0.857800 |
| 4             | 6             | 0           | 2.696237 -1.552984 -1.004338 |
| 5             | 6             | 0           | 1.323157 -1.477589 -0.969710 |
| 6             | 7             | 0           | 0.699924 -0.293971 -0.797635 |
| 7             | 1             | 0           | 0.802295 1.736944 -0.413070 |
| 8             | 1             | 0           | 3.328588 1.764248 -0.504454 |
| 9             | 1             | 0           | 3.191961 -2.504633 -1.141927 |
| 10            | 1             | 0           | 0.672768 -2.339163 -1.059329 |
| 11            | 6             | 0           | 4.869430 -0.404340 -0.923474 |
| 12            | 7             | 0           | 6.022982 -0.439557 -0.991819 |
| 13            | 5             | 0           | -0.797659 -0.260719 -0.603700 |
| 14            | 8             | 0           | -1.499071 -1.411802 -0.523868 |
| 15            | 8             | 0           | -1.490819 0.867923 -0.858930 |
| 16            | 6             | 0           | -2.875098 -1.047222 -0.843741 |
| 17            | 6             | 0           | -2.887638 0.511793 -0.621410 |
| 18            | 6             | 0           | -3.801642 -1.820544 0.076625 |
| 19            | 1             | 0           | -4.838452 -1.508493 -0.081458 |
| 20            | 1             | 0           | -3.727147 -2.888261 -0.142624 |
| 21            | 1             | 0           | -3.536723 -1.662202 1.122354 |
| 22            | 6             | 0           | -3.090571 -1.448560 -2.299517 |
| 23            | 1             | 0           | -2.887470 -2.516716 -2.405599 |
| 24            | 1             | 0           | -4.119314 -1.257757 -2.615035 |
| 25            | 1             | 0           | -2.415362 -0.900214 -2.963022 |
| 26            | 6             | 0           | -3.744799 1.279900 -1.613012 |
| 27            | 1             | 0           | -4.790479 0.969758 -1.525218 |
| 28            | 1             | 0           | -3.686434 2.347109 -1.388334 |
| 29            | 1             | 0           | -3.414852 1.124810 -2.641277 |
Int3b

Zero-point correction= 0.274903 (Hartree/Particle)
Thermal correction to Energy= 0.292892
Thermal correction to Enthalpy= 0.293836
Thermal correction to Gibbs Free Energy= 0.227883
Sum of electronic and zero-point Energies= -762.608633
Sum of electronic and thermal Energies= -762.590644
Sum of electronic and thermal Enthalpies= -762.589700
Sum of electronic and thermal Free Energies= -762.655653

Esol = -763.1611282

| Center | Atomic Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|---------------|---------------|-------------|-------------------------|
| 1      | 6             | 0             |            | 1.255771 0.856533 -0.685721 |
| 2      | 6             | 0             |            | 2.518009 0.790752 -1.248180 |
| 3      | 6             | 0             |            | 3.121903 -0.462545 -1.380663 |
| 4      | 6             | 0             |            | 2.446331 -1.608537 -0.954041 |
| 5      | 6             | 0             |            | 1.186016 -1.461913 -0.401576 |
| 6      | 7             | 0             |            | 0.627104 -0.251953 -0.272468 |
| 7      | 1             | 0             |            | 0.706952 1.780796 -0.543243 |
| 8      | 1             | 0             |            | 3.021893 1.690748 -1.576976 |
| 9      | 1             | 0             |            | 2.893777 -2.589398 -1.052328 |
| 10     | 1             | 0             |            | 0.581970 -2.288496 -0.043733 |
| 11     | 6             | 0             |            | 4.434679 -0.573000 -1.961858 |
| 12     | 7             | 0             |            | 5.486759 -0.662156 -2.432337 |
| 13     | 5             | 0             |            | -0.835155 -0.128050 0.409534 |
| 14     | 8             | 0             |            | -1.573074 -1.309789 0.235426 |
| 15     | 8             | 0             |            | -1.494234 0.974467 -0.155148 |
| 16     | 6             | 0             |            | -2.654917 -0.982813 -0.656598 |
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       T
ype             X           Y           Z

17          6           0        -2.846416    0.545750    -0.395772
18          6           0        -3.855818    -1.844292    -0.303208
19           1           0         -4.730604    -1.544526    -0.889331
20           1           0        -3.636866    -2.891798     -0.526146
21           1           0         -4.092978    -1.763052     0.758178
22           6           0        -2.187382    -1.273154    -2.083747
23           1           0         -1.848317    -2.311218    -2.139159
24           1           0         -2.992272    -1.133114    -2.810674
25           1           0        -3.545830    -0.618540    -2.360725
26           6           0        -3.399225     1.326448    -1.577603
27           1           0         -4.385335     0.945425    -1.861746
28           1           0        -3.506867     2.378425    -1.301840
29           1           0         -2.734628     1.264908    -2.441254
30           6           0        -3.669558     0.824049     0.860898
31           1           0        -3.561945     1.879802     1.120742
32           1           0        -4.729175     0.607940     0.696235
33           1           0        -3.308963     0.230612     2.170590
34          53           0        -0.206104     0.163192     2.674290

Zero-point correction=                           0.275165(Hartree/Particle)
Thermal correction to Energy=                    0.292695
Thermal correction to Enthalpy=                  0.293639
Thermal correction to Gibbs Free Energy=         0.228582
Sum of electronic and zero-point Energies=        -762.593986
Sum of electronic and thermal Energies=           -762.576456
Sum of electronic and thermal Enthalpies=         -762.575512
Sum of electronic and thermal Free Energies=      -762.640570

Esol = -763.152273

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TS5

Zero-point correction=                           0.275165(Hartree/Particle)
Thermal correction to Energy=                    0.292695
Thermal correction to Enthalpy=                  0.293639
Thermal correction to Gibbs Free Energy=         0.228582
Sum of electronic and zero-point Energies=        -762.593986
Sum of electronic and thermal Energies=           -762.576456
Sum of electronic and thermal Enthalpies=         -762.575512
Sum of electronic and thermal Free Energies=      -762.640570

Esol = -763.152273

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X       | Y       | Z       |
| 1             | 6             | 0           | 1.392252 | 0.846388 | -0.583086 |
| 2             | 6             | 0           | 2.777818 | 0.844172 | -0.649114 |
| 3             | 6             | 0           | 3.432775 | -0.365252 | -0.857800 |
| IBpin                  | Zero-point correction= | 0.183964 (Hartree/Particle) |
|-----------------------|------------------------|-----------------------------|
|                       | Thermal correction to Energy= | 0.194929                   |
|                       | Thermal correction to Enthalpy= | 0.195873                   |
|                       | Thermal correction to Gibbs Free Energy= | 0.146765                   |
|                       | Sum of electronic and zero-point Energies= | -422.284105                |
|                       | Sum of electronic and thermal Energies= | -422.273140                |
|                       | Sum of electronic and thermal Enthalpies= | -422.272196                |
|                       | Sum of electronic and thermal Free Energies= | -422.321304                |
Esol = -422.6251154

| Center Number | Atomic Number | Atomic Type |
|---------------|---------------|-------------|
|               |               |             |
|               |               |             |

4-cyanopyridine

Zero-point correction= 0.088413 (Hartree/Particle)
Thermal correction to Energy= 0.094380
Thermal correction to Enthalpy= 0.095324
Thermal correction to Gibbs Free Energy= 0.058181
Sum of electronic and zero-point Energies= -340.300304
Sum of electronic and thermal Energies= -340.294337
Sum of electronic and thermal Enthalpies= -340.293393
Sum of electronic and thermal Free Energies= -340.330537

Esol = -340.5096342
| Center Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|-------------|---------------|---------------|---------------|
| 1             | 6             | 0           | 1.501787      | 1.140544      | -0.000004     |
| 2             | 6             | 0           | 0.111946      | 1.203226      | 0.000009      |
| 3             | 6             | 0           | -0.594341     | 0.000000      | 0.000000      |
| 4             | 6             | 0           | 0.111946      | -1.203225     | -0.000009     |
| 5             | 6             | 0           | 1.501788      | -1.140543     | 0.000005      |
| 6             | 7             | 0           | 2.193304      | 0.000000      | 0.000000      |
| 7             | 1             | 0           | 2.087034      | 2.056307      | 0.000016      |
| 8             | 1             | 0           | -0.408026     | 2.153948      | 0.000025      |
| 9             | 1             | 0           | -0.408026     | -2.153948     | -0.000024     |
| 10            | 1             | 0           | 2.087034      | -2.056307     | -0.000016     |
| 11            | 6             | 0           | -2.035592     | 0.000000      | 0.000000      |
| 12            | 7             | 0           | -3.192093     | 0.000000      | 0.000000      |

Zero-point correction= 0.291215 (Hartree/Particle)
Thermal correction to Energy= 0.311002
Thermal correction to Enthalpy= 0.311946
Thermal correction to Gibbs Free Energy= 0.243296
Sum of electronic and zero-point Energies= -1088.780983
Sum of electronic and thermal Energies= -1088.761196
Sum of electronic and thermal Enthalpies= -1088.760252
Sum of electronic and thermal Free Energies= -1088.828902

Esol = -1089.484127

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 1.663492 1.220623 0.300410 |
| 2             | 6             | 0           | 3.083370 1.122599 -0.191455 |
| 3             | 6             | 0           | 3.713341 -0.064227 -0.141742 |
| 4             | 6             | 0           | 3.014414 -1.283824 0.252027 |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 5 | 6 | 0 | 1.676328 | -1.232801 | 0.354783 |
| 6 | 7 | 0 | 0.961812 | -0.053527 | 0.193742 |
| 7 | 1 | 0 | 1.103687 | 1.975326 | -0.260317 |
| 8 | 1 | 0 | 3.579824 | 2.019053 | -0.541719 |
| 9 | 1 | 0 | 3.554134 | -2.212893 | 0.364484 |
| 10 | 1 | 0 | 1.063820 | -2.112827 | 0.520984 |
| 11 | 6 | 0 | 5.088311 | -0.162802 | -0.562759 |
| 12 | 7 | 0 | 6.192345 | -0.589467 | -0.894378 |
| 13 | 5 | 0 | -0.467660 | -0.052148 | 0.085770 |
| 14 | 8 | 0 | -1.234116 | -1.173619 | 0.254984 |
| 15 | 8 | 0 | -1.17406 | 1.084413 | -0.195107 |
| 16 | 6 | 0 | -2.576497 | -0.795524 | -0.138445 |
| 17 | 6 | 0 | -2.598383 | 0.754803 | 0.080203 |
| 18 | 6 | 0 | -3.570712 | -1.548436 | 0.728491 |
| 19 | 1 | 0 | -4.590213 | -1.208549 | 0.521338 |
| 20 | 1 | 0 | -3.514479 | -2.616854 | 0.506899 |
| 21 | 1 | 0 | -3.359077 | -1.406105 | 1.789005 |
| 22 | 6 | 0 | -2.737212 | -1.181675 | -1.606274 |
| 23 | 1 | 0 | -2.524841 | -2.247569 | -1.715275 |
| 24 | 1 | 0 | -3.753743 | -0.989907 | -1.959688 |
| 25 | 1 | 0 | -2.036859 | -0.624406 | -2.235123 |
| 26 | 6 | 0 | -3.451547 | 1.540525 | -0.865139 |
| 27 | 1 | 0 | -4.495958 | 1.236534 | -0.744401 |
| 28 | 1 | 0 | -3.376990 | 2.606262 | -0.636433 |
| 29 | 1 | 0 | -3.157597 | 1.391065 | -1.904961 |
| 30 | 6 | 0 | -2.826059 | 1.149348 | 1.531055 |
| 31 | 1 | 0 | -2.574850 | 2.204675 | 1.658429 |
| 32 | 1 | 0 | -3.875560 | 1.001395 | 1.798825 |
| 33 | 1 | 0 | -2.201345 | 0.567754 | 2.214992 |
| 34 | 6 | 0 | 1.636616 | 1.695192 | 1.756015 |
| 35 | 9 | 0 | 2.171450 | 2.917661 | 1.854818 |
| 36 | 9 | 0 | 2.316378 | 0.876395 | 2.562497 |
| 37 | 9 | 0 | 0.376459 | 1.757869 | 2.213953 |

$$\text{(pin)B-N}^+\text{CN}^-$$

Zero-point correction= 0.275528 (Hartree/Particle)
Thermal correction to Energy= 0.291487
Thermal correction to Enthalpy= 0.292431
Thermal correction to Gibbs Free Energy= 0.232592
Sum of electronic and zero-point Energies= -751.038204
Sum of electronic and thermal Energies= -751.022246
Sum of electronic and thermal Enthalpies = -751.021302
Sum of electronic and thermal Free Energies = -751.081140

Esol = -751.609417

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 6             | 0           | 1.645404    | 1.169582   | -0.157746  |
| 2             | 6             | 0           | 3.024294    | 1.202433   | -0.163653  |
| 3             | 6             | 0           | 3.723220    | -0.000017  | -0.000054  |
| 4             | 6             | 0           | 3.024288    | -1.202461  | 0.163564   |
| 5             | 6             | 0           | 1.645399    | -1.169598  | 0.157697   |
| 6             | 7             | 0           | 0.985695    | -0.000005  | -0.000015  |
| 7             | 1             | 0           | 1.023470    | 2.050137   | -0.275684  |
| 8             | 1             | 0           | 3.548928    | 2.141337   | -0.291191  |
| 9             | 1             | 0           | 3.548917    | -2.141370  | 0.291088   |
| 10            | 1             | 0           | 1.023460    | -2.050148  | 0.275654   |
| 11            | 6             | 0           | 5.160311    | -0.000023  | -0.000075  |
| 12            | 7             | 0           | 6.316228    | -0.000028  | -0.000092  |
| 13            | 5             | 0           | -0.529990   | 0.000002   | 0.000007   |
| 14            | 8             | 0           | -1.206442   | -1.136048  | 0.198568   |
| 15            | 8             | 0           | -1.206438   | 1.136058   | -0.198533  |
| 16            | 6             | 0           | -2.609807   | -0.778523  | -0.108497  |
| 17            | 6             | 0           | -2.609797   | 0.778546   | 0.108574   |
| 18            | 6             | 0           | -3.516829   | -1.548994  | 0.830185   |
| 19            | 1             | 0           | -4.554494   | -1.236154  | 0.682931   |
| 20            | 1             | 0           | -3.450308   | -2.616440  | 0.610668   |
| 21            | 1             | 0           | -3.246810   | -1.391249  | 1.874729   |
| 22            | 6             | 0           | -2.838444   | -1.185104  | -1.557882  |
| 23            | 1             | 0           | -2.629097   | -2.251072  | -1.666959  |
| 24            | 1             | 0           | -3.875405   | -1.006323  | -1.850595  |
| 25            | 1             | 0           | -2.186850   | -0.630159  | -2.239416  |
| 26            | 6             | 0           | -3.516839   | 1.549026   | -0.830081  |
| 27            | 1             | 0           | -4.554503   | 1.236196   | -0.682796  |
| 28            | 1             | 0           | -3.450301   | 2.616471   | -0.610567  |
| 29            | 1             | 0           | -3.246853   | 1.391278   | -1.874634  |
| 30            | 6             | 0           | -2.838386   | 1.185129   | 1.557965   |
| 31            | 1             | 0           | -2.629026   | 2.251095   | 1.667036   |
| 32            | 1             | 0           | -3.875340   | 1.006358   | 1.850710   |
| 33            | 1             | 0           | -2.186777   | 0.630178   | 2.239480   |
I anion

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016848

Sum of electronic and zero-point Energies= -11.419267
Sum of electronic and thermal Energies= -11.417851
Sum of electronic and thermal Enthalpies= -11.416907
Sum of electronic and thermal Free Energies= -11.436116

Esol = -11.476239

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