Electronic Supporting Information

Probing Halogen Bonds by Scalar Couplings
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General information

The solvent CD$_2$Cl$_2$ was used as delivered (Eurisotop® lot: T1071) or was distilled over CaH$_2$; CH$_2$Cl$_2$ (VWR, AnalAR NORMAPUR Reag. Ph.Eur., ACS, water < 0.01 %, Lot 20G034019) was used as delivered. Dry solvents were stored over 3 Å molecular sieves in a glovebox. All other chemicals were purchased from commercial suppliers and used without further purification. For all synthesis and analytical studies, the glassware had been dried in vacuo, at least overnight. NMR spectra were recorded on an Agilent MR4000-DD2 equipped with a OneNMR probe. Chemical shifts are reported on the δ scale (ppm), with respect to the solvent deuterium lock signal. To assign the $^{19}$F NMR resonances, chemical shifts (δ), multiplicity, coupling constants (J Hz) and integrals were considered. Multiplicities are denoted as s (singlet), d (doublet), t (triplet), q (quartet), hep (heptet), and m (multiplet). MestReNova 12.0.3. was used to process the NMR spectra.

The iodine basicity scale

The iodine basicity (e.g. pK$_{b}$I$_2$ and $\Delta$ν(I-I) scale) gives Lewis base-type dependent correlations to observables that describe the non-covalent binding of Lewis bases to diiodine. NMR-spectroscopy detects a time-averaged signal of the species involved into the binding equilibrium. The pK$_{b}$I$_2$ scale describes the same equilibrium process. The iodine basicity observed for a halogen bond acceptor is interconvertible via a linear correlation justifying the pK$_{b}$I$_2$ dependency of the correlations described in this work. There are a variety of basicity scales available, with the book “Lewis Basicity and Affinity Scales” by C. Laurence and J-F. Gal providing a helpful overview of the scope of each.

1 Experimental Setup and Details

1.1 The Spectrometer settings relevant for the measurement accuracy of $^{19}$F,C$_{s}$

$^{19}$F NMR spectra have been recorded for CD$_2$Cl$_2$ solutions at 25.0 °C, acquiring 128 scans with 1 sec relaxation delay at 376.25 MHz using specifications given in Table S1.

Table S2. Experimental parameters for $^{19}$F measurements of 1-Iodoperfluorobenzene samples.

| Spectral Width                | 30487.8 Hz  |
|------------------------------|-------------|
| Acquired / Processed Size    | 131072 / 262144 points |
| Detected / Processed Digital Resolution | 0.232 Hz / 0.116 Hz |

Table S2. Experimental parameters for $^{19}$F measurements of 1-Iodoperfluoroctane samples.

| Spectral Width                | 39062.5 Hz  |
|------------------------------|-------------|
| Acquired / Processed Size    | 131072 / 262144 points |
| Detected / Processed Digital Resolution | 0.298 Hz / 0.149 Hz |

1.2 Sample preparation

1.2.1 Experiment repetition

Upon repetition of an experiment ($^{19}$F NMR measurement) a fresh sample was used. Each individual sample was measured fresh and prepared on a different day.

1.2.2 1-Iodoperfluorobenzene samples

Each sample was prepared individually by mixing 1-Iodopentafluorobenzene (58.8±1.7% mg, 1.00 eq.) and 2.50 eq. equivalent of a base filled up to 1.00±0.01 mL (CD$_2$Cl$_2$:CH$_2$Cl$_2$ 1:1 v/v) resulting in a set of consistent concentrations for a given halogen bond donor.
The filename format of the NMR rawdata, which is provided at the open access repository Zenodo with DOI: 10.5281/zenodo.4698893: [YYYYMMDD]_[Operatorlabel]_[Systematiclabel]_[nonessentialdescriptions]

Table 3: Weigh-ins of experiments of 1-iodopentafluorobenzene and base with deviations.

| Halogen bond donor...Base | Systematic labels: | Calcd. weigh-in base [mg] | Exp. weigh-in base [mg] | Dev. | Calcd. weigh-in C₆F₅I [mg] | Exp. weigh-in C₆F₅I [mg] | Dev. |
|---------------------------|------------------|--------------------------|------------------------|------|-----------------------------|-----------------------------|------|
| Pentfluoriodobenzene...   | Arl-3            | 0.0611                   | 0.0614                 | 0.5% | 0.0588                      | 0.0586                      | 0.3% |
| 4-Dimethylaminopyridine   | Arl-9            | 0.0611                   | 0.0609                 | 0.3% | 0.0588                      | 0.0594                      | 1.0% |
| Pentfluoriodobenzene...   | Arl-15           | 0.0611                   | 0.0611                 | 0.0% | 0.0588                      | 0.0593                      | 0.9% |
| Pentfluoriodobenzene...   | Arl-4            | 0.0396                   | 0.0391                 | 1.1% | 0.0588                      | 0.0593                      | 0.9% |
| 4-Dimethylaminopyridine   | Arl-10           | 0.0396                   | 0.0398                 | 0.6% | 0.0588                      | 0.0588                      | 0.0% |
| 4-Dimethylaminopyridine   | Arl-29           | 0.0396                   | 0.0394                 | 0.4% | 0.0588                      | 0.0592                      | 0.7% |
| 4-Dimethylaminopyridine   | Arl-5            | 0.0476                   | 0.0474                 | 0.3% | 0.0588                      | 0.0591                      | 0.5% |
| 4-Dimethylaminopyridine   | Arl-11           | 0.0476                   | 0.0476                 | 0.1% | 0.0588                      | 0.059                        | 0.3% |
| 4-Dimethylaminopyridine   | Arl-17           | 0.0476                   | 0.0476                 | 0.1% | 0.0588                      | 0.0596                      | 1.4% |
| 4-Methoxypyridine         | Arl-6            | 0.0546                   | 0.0544                 | 0.3% | 0.0588                      | 0.0591                      | 0.5% |
| Pentfluoriodobenzene...   | Arl-12           | 0.0546                   | 0.0546                 | 0.1% | 0.0588                      | 0.0586                      | 0.3% |
| Pentfluoriodobenzene...   | Arl-18           | 0.0546                   | 0.0546                 | 0.1% | 0.0588                      | 0.0586                      | 0.3% |
| Pentfluoriodobenzene...   | Arl-7            | 0.0376                   | 0.0372                 | 0.9% | 0.0588                      | 0.0589                      | 0.2% |
| Pentfluoriodobenzene...   | Arl-13           | 0.0376                   | 0.0378                 | 0.7% | 0.0588                      | 0.0584                      | 0.7% |
| Pentfluoriodobenzene...   | Arl-19           | 0.0376                   | 0.0375                 | 0.1% | 0.0588                      | 0.0596                      | 1.4% |
| N,N-Dimethyl-2-imidazolidinone | Arl-8        | 0.0571                   | 0.0572                 | 0.2% | 0.0588                      | 0.0592                      | 0.7% |
| Pentfluoriodobenzene...   | Arl-14           | 0.0571                   | 0.0576                 | 0.9% | 0.0588                      | 0.0586                      | 0.3% |
| N,N-Dimethyl-2-imidazolidinone | Arl-20        | 0.0571                   | 0.0576                 | 0.9% | 0.0588                      | 0.0598                      | 1.7% |
| Pentfluoriodobenzene...   | Arl-22           | 0.0366                   | 0.0363                 | 0.7% | 0.0588                      | 0.0591                      | 0.5% |
| Pentfluoriodobenzene...   | Arl-30           | 0.0366                   | 0.0363                 | 0.7% | 0.0588                      | 0.0582                      | 1.0% |
| Pentfluoriodobenzene...   | Arl-41           | 0.0366                   | 0.037                 | 1.2% | 0.0588                      | 0.0592                      | 0.7% |
| Pentfluoriodobenzene...   | Arl-23           | 0.0366                   | 0.0364                 | 0.5% | 0.0588                      | 0.0591                      | 0.5% |
| Butylamine                | Arl-31           | 0.0366                   | 0.0369                 | 0.9% | 0.0588                      | 0.0583                      | 0.9% |
| Pentfluoriodobenzene...   | Arl-42           | 0.0366                   | 0.0363                 | 0.7% | 0.0588                      | 0.0585                      | 0.5% |
| Pentfluoriodobenzene...   | Arl-24           | 0.1227                   | 0.1222                 | 0.4% | 0.0588                      | 0.0583                      | 0.9% |
| Pentfluoriodobenzene...   | Arl-32           | 0.1227                   | 0.1226                 | 0.0% | 0.0588                      | 0.0596                      | 1.4% |
| Halogen bond donor → Base | Systematic labels: | Calcd. weigh-in base [mg] | Exp. weigh-in base [mg] | Dev. | Calcd. weigh-in C$_6$F$_5$I [mg] | Exp. weigh-in C$_6$F$_5$I [mg] | Dev. |
|---------------------------|---------------------|---------------------------|------------------------|------|-------------------------------|-------------------------------|------|
| Pentafluoriodobenzene     | ArI-43              | 0.1227                    | 0.1229                 | 0.2% | 0.0588                        | 0.059                         | 0.3% |
| Triphenylamine            | ArI-25              | 0.1437                    | 0.1395                 | 2.9% | 0.0588                        | 0.0588                        | 0.0% |
| Triphenylphosphine oxide  | ArI-37              | 0.1437                    | 0.1389                 | 3.4% | 0.0588                        | 0.0586                        | 0.3% |
| Triphenylphosphine oxide  | ArI-48              | 0.1437                    | 0.1391                 | 3.2% | 0.0588                        | 0.0594                        | 1.0% |
| Triphenylbenzenes         | ArI-26              | 0.0426                    | 0.0424                 | 0.4% | 0.0588                        | 0.0583                        | 0.9% |
| Triphenylbenzenes         | ArI-33              | 0.0426                    | 0.0425                 | 0.2% | 0.0588                        | 0.0583                        | 0.9% |
| Triphenylbenzenes         | ArI-44              | 0.0426                    | 0.043                  | 1.0% | 0.0588                        | 0.0594                        | 1.0% |
| ArI-27                    | 0.0568              | 0.0565                    | 0.5%                   | 0.0588 | 0.0594                        | 1.0% |
| ArI-34                    | 0.0568              | 0.0566                    | 0.3%                   | 0.0588 | 0.0589                        | 0.2% |
| ArI-45                    | 0.0568              | 0.0565                    | 0.5%                   | 0.0588 | 0.0586                        | 0.3% |
| ArI-28                    | 0.0646              | 0.0642                    | 0.7%                   | 0.0588 | 0.0587                        | 0.2% |
| ArI-35                    | 0.0646              | 0.0645                    | 0.2%                   | 0.0588 | 0.0585                        | 0.5% |
| ArI-46                    | 0.0646              | 0.0646                    | 0.0%                   | 0.0588 | 0.0589                        | 0.2% |
| ArI-74                    | 0.0506              | 0.0503                    | 0.6%                   | 0.0588 | 0.0592                        | 0.7% |
| ArI-47                    | 0.0506              | 0.0506                    | 0.0%                   | 0.0588 | 0.0589                        | 0.2% |
| ArI-50                    | 0.0506              | 0.0507                    | 0.2%                   | 0.0588 | 0.0588                        | 0.0% |
| ArI-39                    | 0.0426              | 0.0427                    | 0.3%                   | 0.0588 | 0.0584                        | 0.7% |
| ArI-49                    | 0.0426              | 0.0423                    | 0.6%                   | 0.0588 | 0.0591                        | 0.5% |
| ArI-51                    | 0.0426              | 0.0426                    | 0.1%                   | 0.0588 | 0.059                            | 0.3% |
| ArI-52                    | 0.0790              | 0.0791                    | 0.1%                   | 0.0588 | 0.0587                        | 0.2% |
| ArI-62                    | 0.0790              | 0.0787                    | 0.4%                   | 0.0588 | 0.0588                        | 0.0% |
| ArI-75                    | 0.0790              | 0.0788                    | 0.3%                   | 0.0588 | 0.0589                        | 0.2% |
| ArI-55                    | 0.0536              | 0.0532                    | 0.7%                   | 0.0588 | 0.0583                        | 0.9% |
| ArI-63                    | 0.0536              | 0.0534                    | 0.3%                   | 0.0588 | 0.0589                        | 0.2% |
| ArI-76                    | 0.0536              | 0.0534                    | 0.3%                   | 0.0588 | 0.0589                        | 0.2% |
| ArI-56                    | 0.0536              | 0.0537                    | 0.2%                   | 0.0588 | 0.0594                        | 1.0% |
| ArI-64                    | 0.0536              | 0.0532                    | 0.7%                   | 0.0588 | 0.0592                        | 0.7% |
| ArI-77                    | 0.0536              | 0.0534                    | 0.3%                   | 0.0588 | 0.0589                        | 0.2% |
| ArI-57                    | 0.0740              | 0.0741                    | 0.1%                   | 0.0588 | 0.0594                        | 1.0% |
| ArI-65                    | 0.0740              | 0.0744                    | 0.5%                   | 0.0588 | 0.0593                        | 0.9% |
| Halogen bond donor...-Base | Systematic labels: | Calcd. weigh-in base [mg] | Exp. weigh-in base [mg] | Dev. | Calcd. weigh-in $C_6F_5I$ [mg] | Exp. weigh-in $C_6F_5I$ [mg] | Dev. |
|--------------------------|-------------------|--------------------------|------------------------|------|------------------------------|--------------------------|------|
| Pentafluoroiodobenzene... | ArI-78            | 0.0740                   | 0.074                  | 0.0% | 0.0588                       | 0.0594                   | 1.0% |
| Pentafluoroiodobenzene... | ArI-58            | 0.0366                   | 0.0369                 | 0.9% | 0.0588                       | 0.0585                   | 0.5% |
| Pentafluoroiodobenzene... | ArI-66            | 0.0366                   | 0.0364                 | 0.5% | 0.0588                       | 0.0589                   | 0.2% |
| Pentafluoroiodobenzene... | ArI-79            | 0.0366                   | 0.0366                 | 0.1% | 0.0588                       | 0.0591                   | 0.5% |
| Pyrrolidinone             | ArI-59            | 0.0356                   | 0.0354                 | 0.5% | 0.0588                       | 0.0594                   | 1.0% |
| Pentfluoroiodobenzene...  | ArI-91            | 0.0356                   | 0.0356                 | 0.1% | 0.0588                       | 0.0588                   | 0.0% |
| Pyrrolidine               | ArI-80            | 0.0356                   | 0.0354                 | 0.5% | 0.0588                       | 0.0594                   | 1.0% |
| Pentafluoroiodobenzene... | ArI-60            | 0.0506                   | 0.0503                 | 0.6% | 0.0588                       | 0.0596                   | 1.4% |
| Diisopropylamine          | ArI-68            | 0.0506                   | 0.0506                 | 0.0% | 0.0588                       | 0.0587                   | 0.2% |
| Pentafluoroiodobenzene... | ArI-81            | 0.0506                   | 0.0504                 | 0.4% | 0.0588                       | 0.0585                   | 0.5% |
| Pentfluoroiodobenzene...  | ArI-61            | 0.0436                   | 0.0439                 | 0.7% | 0.0588                       | 0.0584                   | 0.7% |
| Ethylisopropylamine       | ArI-69            | 0.0436                   | 0.0432                 | 0.9% | 0.0588                       | 0.0591                   | 0.5% |
| Pentfluoroiodobenzene...  | ArI-82            | 0.0436                   | 0.0435                 | 0.2% | 0.0588                       | 0.0588                   | 0.0% |
| tert-Butylamine           | ArI-70            | 0.0366                   | 0.0366                 | 0.1% | 0.0588                       | 0.0593                   | 0.9% |
| Pentafluoroiodobenzene... | ArI-83            | 0.0366                   | 0.0362                 | 1.0% | 0.0588                       | 0.0589                   | 0.2% |
| tert-Butylamine           | ArI-86            | 0.0366                   | 0.0362                 | 1.0% | 0.0588                       | 0.0589                   | 0.2% |
| Pentfluoroiodobenzene...  | ArI-71            | 0.0646                   | 0.0643                 | 0.5% | 0.0588                       | 0.0591                   | 0.5% |
| Pentfluoroiodobenzene...  | ArI-84            | 0.0646                   | 0.0644                 | 0.3% | 0.0588                       | 0.0591                   | 0.5% |
| Pentfluoroiodobenzene...  | ArI-87            | 0.0646                   | 0.0648                 | 0.3% | 0.0588                       | 0.0584                   | 0.7% |
| Tributylamine             | ArI-73            | 0.0927                   | 0.0924                 | 0.3% | 0.0588                       | 0.0593                   | 0.3% |
| Pentfluoroiodobenzene...  | ArI-85            | 0.0927                   | 0.0925                 | 0.2% | 0.0588                       | 0.0588                   | 0.0% |
| Tributylamine             | ArI-88            | 0.0927                   | 0.0928                 | 0.1% | 0.0588                       | 0.0593                   | 0.9% |
| Pentfluoroiodobenzene...  | ArI-89            | 0.0506                   | 0.0505                 | 0.2% | 0.0588                       | 0.0596                   | 1.4% |
| Disopropylamine           | ArI-92            | 0.0506                   | 0.0502                 | 0.8% | 0.0588                       | 0.0585                   | 0.5% |
| Disopropylamine           | ArI-103           | 0.0506                   | 0.051                  | 0.8% | 0.0588                       | 0.0585                   | 0.5% |
| 2-Methylpyridine          | ArI-90            | 0.0466                   | 0.0466                 | 0.1% | 0.0588                       | 0.0583                   | 0.9% |
| Pentfluoroiodobenzene...  | ArI-93            | 0.0466                   | 0.0467                 | 0.3% | 0.0588                       | 0.0583                   | 0.9% |
| Dimethylsulfoxide         | ArI-94            | 0.0391                   | 0.0394                 | 0.8% | 0.0588                       | 0.059                    | 0.3% |
| Pentfluoroiodobenzene...  | ArI-106           | 0.0391                   | 0.0386                 | 1.2% | 0.0588                       | 0.0588                   | 0.0% |
| Dimethylsulfoxide         | ArI-110           | 0.0391                   | 0.0388                 | 0.7% | 0.0588                       | 0.0582                   | 1.0% |
| Halogen bond donor—Base                  | Systematic labels: | Calcd. weigh-in base [mg] | Exp. weigh-in base [mg] | Dev. | Calcd. weigh-in $C_{6}F_{5}I$ [mg] | Exp. weigh-in $C_{6}F_{5}I$ [mg] | Dev. |
|-----------------------------------------|--------------------|---------------------------|------------------------|------|----------------------------------|-------------------------------|------|
| Pentafluoriodobenzene—Dimethylformamide | Arl-95             | 0.0365                    | 0.0361                 | 1.2% | 0.0588                           | 0.0592                        | 0.7% |
| Pentafluoriodobenzene—Dimethylformamide | Arl-105            | 0.0365                    | 0.0361                 | 1.2% | 0.0588                           | 0.0595                        | 1.2% |
| Pentafluoriodobenzene—Dimethylformamide | Arl-111            | 0.0365                    | 0.0365                 | 0.1% | 0.0588                           | 0.0588                        | 0.0% |
| Acetophenone                            | Arl-96             | 0.0601                    | 0.06                   | 0.1% | 0.0588                           | 0.0587                        | 0.2% |
| Acetophenone                            | Arl-101            | 0.0601                    | 0.0602                 | 0.2% | 0.0588                           | 0.059                        | 0.3% |
| Acetophenone                            | Arl-107            | 0.0601                    | 0.06                   | 0.1% | 0.0588                           | 0.0585                        | 0.5% |
| Benzophenone                            | Arl-97             | 0.0911                    | 0.0906                 | 0.6% | 0.0588                           | 0.0583                        | 0.9% |
| Benzophenone                            | Arl-108            | 0.0911                    | 0.0898                 | 1.4% | 0.0588                           | 0.0593                        | 0.9% |
| Benzophenone                            | Arl-112            | 0.0911                    | 0.0911                 | 0.0% | 0.0588                           | 0.0584                        | 0.7% |
| 4-Methylpyridine-N-oxide                | Arl-98             | 0.0546                    | 0.0548                 | 0.4% | 0.0588                           | 0.0585                        | 0.5% |
| 4-Methylpyridine-N-oxide                | Arl-109            | 0.0546                    | 0.0543                 | 0.5% | 0.0588                           | 0.0583                        | 0.9% |
| 4-Methylpyridine-N-oxide                | Arl-113            | 0.0546                    | 0.0548                 | 0.4% | 0.0588                           | 0.0595                        | 1.2% |

Max deviation: **3.4%**
Average weigh-in deviation: **0.5%**

**Control experiments**

| Halogen bond donor—n-pentane              | Systematic labels: | Calcd. weigh-in base [mg] | Exp. weigh-in base [mg] | Dev. | Calcd. weigh-in $C_{6}F_{5}I$ [mg] | Exp. weigh-in $C_{6}F_{5}I$ [mg] | Dev. |
|-----------------------------------------|--------------------|---------------------------|------------------------|------|----------------------------------|-------------------------------|------|
| Pentafluoriodobenzene—n-pentane         | DAN-Arl-9          | 0.0361                    | 57.8 $\mu$L            | 1.0% | 0.0588                           | 0.0593                        | 0.9% |
| Pentafluoriodobenzene—n-pentane         | DAN-Arl-10         | 0.0361                    | 57.8 $\mu$L            | 1.0% | 0.0588                           | 0.0595                        | 1.2% |
| Pentafluoriodobenzene—n-pentane         | DAN-Arl-11         | 0.0361                    | 57.8 $\mu$L            | 1.0% | 0.0588                           | 0.0587                        | 0.2% |
### 1.2.3. 1-Iodoperfluorooctane samples

Each sample was prepared individually by mixing 1-iodoheptadecafluorooctane (109.2mg±0.9%, 1.00 eq.) and 2.50eq.±0.9% of a base filled up to 1.00±0.01 mL (CD$_2$Cl$_2$:CH$_2$Cl$_2$ 1:1 v/v) resulting in a set of consistent concentrations for a given halogen bond donor.

**Table 4:** Weigh-ins of experiments of 1-iodoperfluorooctane and base with deviations.

| Halogen bond donor—Base | Rawdata filename format: [date]_[Operator]_[Label]_[add.descri.].[Labels:| XBA | XBD |
|------------------------|---------------------------------|--------|--------|
|                        | Calcd. weigh-in [mg] | Exp. weigh-in [mg] | Dev. | Calcd. weigh-in [mg] | Exp. weigh-in [mg] | Dev. |
| Heptadecafluoriodooctane—4-Dimethylaminopyridine | AllI-30 | 0.0611 | 0.0609 | 0.3% | 0.1092 | 0.1099 | 0.6% |
| Heptadecafluoriodooctane—4-Dimethylaminopyridine | AllI-36 | 0.0611 | 0.0614 | 0.5% | 0.1092 | 0.1102 | 0.9% |
| Heptadecafluoriodooctane—Pyridine | AllI-31 | 0.0396 | 0.0392 | 0.9% | 0.1092 | 0.1097 | 0.5% |
| Heptadecafluoriodooctane—Pyridine | AllI-37 | 0.0396 | 0.0395 | 0.1% | 0.1092 | 0.1097 | 0.5% |
| Heptadecafluoriodooctane—Pyridine—N-oxide | AllI-32 | 0.0476 | 0.0472 | 0.7% | 0.1092 | 0.1092 | 0.0% |
| Heptadecafluoriodooctane—Pyridine—N-oxide | AllI-38 | 0.0476 | 0.0475 | 0.1% | 0.1092 | 0.1091 | 0.1% |
| Heptadecafluoriodooctane—4-Methoxypyridine | AllI-33 | 0.0546 | 0.0547 | 0.2% | 0.1092 | 0.1093 | 0.1% |
| Heptadecafluoriodooctane—4-Methoxypyridine | AllI-39 | 0.0546 | 0.0545 | 0.1% | 0.1092 | 0.1091 | 0.1% |
| Heptadecafluoriodooctane—4-Methoxypyridine | AllI-49 | 0.0546 | 0.0549 | 0.6% | 0.1092 | 0.1091 | 0.1% |
| Heptadecafluoriodooctane—4-Methoxypyridine | AllI-45 | 0.0546 | 0.0545 | 0.1% | 0.1092 | 0.1092 | 0.0% |
| Heptadecafluoriodooctane—3,5-Dimethylpyridine | AllI-42 | 0.0536 | 0.0536 | 0.0% | 0.1092 | 0.1096 | 0.4% |
| Heptadecafluoriodooctane—3,5-Dimethylpyridine | AllI-46 | 0.0536 | 0.0538 | 0.4% | 0.1092 | 0.1098 | 0.5% |
| Heptadecafluoriodooctane—2,6-Dimethylpyridine | AllI-43 | 0.0536 | 0.0534 | 0.3% | 0.1092 | 0.1099 | 0.6% |
| Heptadecafluoriodooctane—2,6-Dimethylpyridine | AllI-47 | 0.0536 | 0.0535 | 0.1% | 0.1092 | 0.1095 | 0.3% |
| Heptadecafluoriodooctane—3-Bromopyridine | AllI-44 | 0.0790 | 0.0788 | 0.3% | 0.1092 | 0.1089 | 0.3% |
| Heptadecafluoriodooctane—3-Bromopyridine | AllI-48 | 0.0790 | 0.0793 | 0.4% | 0.1092 | 0.110 | 0.7% |
| Heptadecafluoriodooctane—3-Bromopyridine | AllI-50 | 0.0790 | 0.0791 | 0.1% | 0.1092 | 0.1091 | 0.1% |
| Heptadecafluoriodooctane—3-Chloropyridine | AllI-51 | 0.0568 | 0.0565 | 0.5% | 0.1092 | 0.110 | 0.7% |
| Heptadecafluoriodooctane—3-Chloropyridine | AllI-55 | 0.0568 | 0.0567 | 0.1% | 0.1092 | 0.1092 | 0.0% |
| Heptadecafluoriodooctane—3,5-Dichloropyridine | AllI-54 | 0.0740 | 0.0735 | 0.7% | 0.1092 | 0.1093 | 0.1% |
| Heptadecafluoriodooctane—3,5-Dichloropyridine | AllI-56 | 0.0740 | 0.0741 | 0.1% | 0.1092 | 0.1097 | 0.5% |
| Heptadecafluoriodooctane—2-Methylpyridine | AllI-53 | 0.0466 | 0.0464 | 0.4% | 0.1092 | 0.1094 | 0.2% |
| Heptadecafluoriodooctane—2-Methylpyridine | AllI-57 | 0.0466 | 0.0464 | 0.4% | 0.1092 | 0.1096 | 0.4% |

Max deviation: 0.9% 0.9%
Average deviation: 0.3% 0.3%
1.3. Error estimation

We carefully investigated the errors possibly caused by traces of water, solvent and differences between samples (repetition). The acquired digital resolution is 0.232-0.298 Hz, whereas the processed is 0.116-0.149 Hz (see Section 1.1). The reproducibility of the read-out coupling constants has been 0.01-0.10 Hz, with 17 out of 114 $J_{F,C}$ that exceed these limits (see section 2.2). The concentrations of the samples have errors < 1.1%, based on the weigh-ins (see section 1.2.2 and 1.2.3).

1.3.1. The method used for error estimation in this study

The reported error of the $J_{F,C}$ (see 1.2.1) is the averaged ($\bar{x}$) value, based on $\bar{x} = \left(\sum_{i=1}^{n} x_n\right)/n$ “AVERAGE”, and its standard deviation $\sigma$ as $\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n-1}}$ (STDEV)

This method consistently gives the largest $\sigma$ within the dataset/sample size, compared to alternatives tested. Alternative methods for describing variations of a very small datasets do treat $\sigma$ differently, e.g. giving the ± range of the averaged value ($\frac{Max(A)-Min(A)}{2}$) instead of accessing variance.

1.3.2. Curve fitting algorithms

To fit functions to the dataset, a given function has been minimized by reducing its overall $R^2$ value without applying weighing methods, using the software Origin 2018.

1.3.3. Comparison of the observed errors for the $\Delta J_{F,C}$ estimations for 1-iodopentafluorobenzene and 1-iodoheptadecafluorooctane

The pyridine data sets with 1-iodopentafluorobenzene and 1-iodoheptadecafluorooctane have been compared to estimate which of the two halogen bond donors gives more reliable $\Delta J$ values. Despite the closer proximity of the observed $\Delta J_{F,C}$ measured for 1-iodoheptadecafluorooctane higher relative errors have been observed. We therefore decided to conduct the further study with 1-iodopentafluorobenzene.

Table S5. Average of three measurements of the $J_{ortho-F,C}$ of 1-iodopentafluorobenzene. Standard deviation and error in percentage was taken from Table S11.

| Pyrrolidine               | 2.57 | 0.22 | 0.09 |
|---------------------------|------|------|------|
| 4-Dimethylaminopyridine   | 2.14 | 0.03 | 0.01 |
| 3,5-Dimethylpyridine      | 1.03 | 0.02 | 0.02 |
| 4-Methoxypyridine         | 1.02 | 0.01 | 0.01 |
| 2-Methylpyridine          | 0.78 | 0.00 | 0.00 |
| Compound                  | Value 1 | Value 2 | Value 3 |
|--------------------------|---------|---------|---------|
| Pyridine                 | 0.70    | 0.03    | 0.04    |
| 2,6-Dimethylpyridine     | 0.34    | 0.02    | 0.06    |
| 3-Bromopyridine          | 0.28    | 0.01    | 0.04    |
| 3-Chloropyridine         | 0.30    | 0.02    | 0.07    |
| 3,5-Dichloropyridine     | 0.05    | 0.00    | 0.09    |
| **Average**              | **0.043**| **0.00**| **0.03**|
| Compound                  | $\Delta^1J_{a,F,C}$ (Hz) | STDEV | Error in percentage [0.%%] |
|--------------------------|--------------------------|-------|---------------------------|
| 4-Dimethylaminopyridine   | 3.32                     | 0.19  | 0.06                      |
| 3,5-Dimethylpyridine     | 2.33                     | 0.01  | 0.00                      |
| 4-Methoxypyridine        | 2.08                     | 0.15  | 0.07                      |
| 2-Methylpyridine         | 2.00                     | 0.12  | 0.06                      |
| Pyridine                 | 1.65                     | 0.09  | 0.06                      |
| 2,6-Dimethylpyridine     | 1.03                     | 0.02  | 0.02                      |
| 3-Bromopyridine          | 1.35                     | 0.31  | 0.23                      |
| 3-Chloropyridine         | 1.82                     | 0.09  | 0.05                      |
| 3,5-Dichloropyridine     | 0.58                     | 0.09  | 0.16                      |
| **Average**              | **0.079**                |       |                           |
1.4. The influence of moisture

To estimate the influence of moisture on the detected $^{1}J_{\alpha,F,C}$, we recorded the $^{19}$F NMR spectrum of 1-iodoheptadecafluoroctane in dry CD$_2$Cl$_2$ (Eurisotop® lot: T1071) and in mixtures of non-dried CD$_2$Cl$_2$ (Eurisotop® lot: T1071) and CH$_2$Cl$_2$ (VWR, Lot 20G034019).

The influence of water residues was insignificant (Table S1), with the variations between the samples being within the error limits. Averaging the coupling constants read on several individual peaks of a multiplet for a single coupling constant gives a lower error than the digital resolution of the spectra would permit.

Table S7. Comparison of the $^{1}J_{\alpha,F,C}$ determined for 1-iodoheptadecafluoroctane using different solvent sources. Note that the calculated average value and the standard deviation are both below the digital resolution of the NMR data.

| $\alpha$-F, CD$_2$Cl$_2$ distilled from CaH$_2$ and stored over Molecular sieves | Peak | Hz  | Peak | Hz  | $|^{1}J_{\alpha,F,C}|$ (Hz) |
|-------------------------------|-----|-----|------|-----|-----------------|
| 1                             | -22460.30 4 | -22780.79  | 320.49  |
| 2                             | -22475.35 5 | -22795.88  | 320.53  |
| 3                             | -22490.28 6 | -22810.97  | 320.69  |
| Average                       | 320.57  |
| stdev                         | 0.11   |
| digital resolution            | 0.14   |

| $\alpha$-F, 50% technical grade CH$_2$Cl$_2$ + 50% non-dried CD$_2$Cl$_2$ | Peak | Hz  | Peak | Hz  | $|^{1}J_{\alpha,F,C}|$ (Hz) |
|-------------------------------|-----|-----|------|-----|-----------------|
| 1                             | -22457.78 4 | -22778.2 | 320.42 |
| 2                             | -22472.91 5 | -22793.39 | 320.48 |
| 3                             | -22487.78 6 | -22808.35 | 320.57 |
| Average                       | 320.49  |
| stdev                         | 0.08   |
| digital resolution            | 0.15   |
2 Experimental Data

Table S8. Halogen bond donors used in this study and the iodine basicity of the Lewis bases applied.

| Pyridines                  | pK<sub>B</sub> | Amines                  | pK<sub>B</sub> | N-Oxides and Carbonyls    | pK<sub>B</sub> |
|----------------------------|--------------|-------------------------|--------------|---------------------------|--------------|
| Pyrrolidine                | 3.85         | Butylamine              | 3.00         | DMSO                      | 1.56         |
| 4-Dimethylaminopyridine    | 3.78         | sec-butylamine          | 2.78         | 1,3-dimethyl-2-imidazolidinone | 1.22         |
| 3,5-Dimethylpyridine       | 2.78         | tert-butylamine         | 2.86         | 2-Pyridolidone            | 1.20         |
| 4-Methoxypridione          | 2.63         | Diethylamine            | 3.73         | DMF                       | 0.81         |
| 2-Methylypyridine          | 2.35         | Dipropylamine           | 3.58         | Acetophenone              | 0.06         |
| Pyridine                   | 2.22         | Dibutylamine            | 3.58         | Benzophenone              | -0.07        |
| 2,6-Dimethylpyridine       | 1.83         | Ethylisopropylamine     | 2.85         | Pyridine-N-Oxide          | 2.40         |
| 3-Bromopyridine            | 1.40         | Diisopropylamine        | 3.85         | 4-Methylpyridine-N-Oxide  | 2.31         |
| 3-Chloropyridine           | 1.38         | Piperidine              | 3.85         | Triphenylphosphine oxide  | 2.08         |
| 3,5-Dichloropyridine       | 0.81         | Triethylamine           | 3.67         |                           |              |
|                            |              | Tributylamine           | 3.05         |                           |              |
|                            |              | Diisopropylethylamine   |              | Not available             |              |
|                            |              | Triphenylamine          |              | Not available             |              |
|                            |              | 3-°                     |              |                           |              |

Figure S1. Summary of the Lewis bases evaluated for halogen bonding.
2.1 1-Iodoperfluorobenzene: a typical example

Enlarged multiplets of the $^{19}$F NMR spectrum of 1-iodopentafluorobenzene without and in the presence of 4-methoxypyridine. The multiplet patterns don’t change in the presence of the base. The $^{19}$F NMR spectra corresponds to the data given in Figure S2 and Figure S3.

![Figure S2. Enlarged multiplets of the $^{19}$F NMR spectrum of 1-iodopentafluorobenzene without the presence of a Lewis base.](image)

![Figure S3. Enlarged multiplets of the $^{19}$F NMR spectrum of 1-iodopentafluorobenzene in the presence of 4-methoxypyridine.](image)
### Table S9. Extracted peaks and calculated $^{1}J_{F,C}$ coupling constants in 1-Iodopentafluorobenzene without the presence of a base.

| Multiplet information | Rawdata filename format: [date]_[Operator]_[Label]_[add.descri.] | Labels: Peak Hz Peak Hz | $|^{1}J_{F,C}|$ (Hz) |
|-----------------------|---------------------------------------------------------------|-------------------------|---------------------|
| 1 $^{1}J_{ortho-F,C}$ | Arl-Ref1                                                       | 1 -44969.9 15 -45214.2  | 244.3               |
|                       |                                                               | 2 -44971.8 16 -45216.2  | 244.4               |
|                       |                                                               | 3 -44974.5 17 -45218.9  | 244.4               |
|                       |                                                               | 4 -44976.7 18 -45221.1  | 244.4               |
|                       |                                                               | 5 -44978.8 19 -45223.3  | 244.5               |
|                       |                                                               | 6 -44981.5 20 -45226.1  | 244.6               |
|                       |                                                               | 7 -44983.7 21 -45228.1  | 244.4               |
|                       |                                                               | 8 -44993 22 -45237.4    | 244.4               |
|                       |                                                               | 9 -44995.2 23 -45239.5  | 244.3               |
|                       |                                                               | 10 -44997.9 24 -45242.3 | 244.4               |
|                       |                                                               | 11 -44999.9 25 -45244.5 | 244.6               |
|                       |                                                               | 12 -45002.1 26 -45246.5 | 244.4               |
|                       |                                                               | 13 -45004.8 27 -45249.5 | 244.7               |
|                       |                                                               | 14 -45007 28 -45251.5   | 244.5               |
| 2 $^{1}J_{para-F,C}$  | Arl-Ref1                                                       | 1 -57430.2 4 -57684.6  | 254.4               |
|                       |                                                               | 2 -57450.2 5 -57704.6  | 254.4               |
|                       |                                                               | 3 -57470.2 6 -57724.6  | 254.4               |
| 3 $^{1}J_{meta-F,C}$  | Arl-Ref1                                                       | 1 -60128 3 -60382       | 254.0               |
|                       |                                                               | 2 -60164.4 4 -60418.4   | 254.0               |
| 1 $^{1}J_{ortho-F,C}$ | Arl-Ref2                                                       | 1 -44970.1 15 -45214.7  | 244.6               |
|                       |                                                               | 2 -44972.2 16 -45216.6  | 244.4               |
|                       |                                                               | 3 -44974.9 17 -45219.2  | 244.3               |
|                       |                                                               | 4 -44977.1 18 -45221.5  | 244.4               |
|                       |                                                               | 5 -44979.1 19 -45223.7  | 244.6               |
|                       |                                                               | 6 -44982.1 20 -45226.4  | 244.3               |
|                       |                                                               | 7 -44984 21 -45228.4    | 244.4               |
|                       |                                                               | 8 -44993.4 22 -45237.9  | 244.5               |
|                       |                                                               | 9 -44995.5 23 -45239.9  | 244.4               |
|                       |                                                               | 10 -44998.3 24 -45242.7 | 244.4               |
|                       |                                                               | 11 -45000.3 25 -45244.8 | 244.5               |
|                       |                                                               | 12 -45002.5 26 -45246.8 | 244.3               |
|                       |                                                               | 13 -45005.3 27 -45249.9 | 244.6               |
|                       |                                                               | 14 -45007.4 28 -45251.9 | 244.5               |
| 2 $^{1}J_{para-F,C}$  | Arl-Ref2                                                       | 1 -57430.2 4 -57684.6  | 254.4               |
|                       |                                                               | 2 -57450.2 5 -57704.6  | 254.4               |
|                       |                                                               | 3 -57470.2 6 -57724.6  | 254.4               |
Table S10. Extracted peaks and calculated $^{1}J_{F,C}$ coupling constants in 1-iodopentafluorobenzene in the presence of 4-methoxypyridine.

| Multiplet information | Rawdata filename format: [date]_[Operator]_[Label]_[add.descri.] | Labels: | Peak Hz | Peak Hz | $|^{1}J_{F,C}|$ (Hz) |
|-----------------------|--------------------------------------------------|---------|---------|---------|-----------------|
| $^{1}J_{ortho-F,C}$   | Arl-Ref5                                         |         | -44970.1 | 15     | -45214.7       | 244.6           |
|                       |                                                  |         | -44972.2 | 16     | -45216.6       | 244.4           |
|                       |                                                  |         | -44974.9 | 17     | -45219.2       | 244.3           |
|                       |                                                  |         | -44977.1 | 18     | -45221.5       | 244.4           |
|                       |                                                  |         | -44979.1 | 19     | -45223.7       | 244.6           |
|                       |                                                  |         | -44981.1 | 20     | -45226.4       | 244.3           |
|                       |                                                  |         | -44984   | 21     | -45228.4       | 244.4           |
|                       |                                                  |         | -44993.4 | 22     | -45237.9       | 244.5           |
|                       |                                                  |         | -44995.5 | 23     | -45239.9       | 244.4           |
|                       |                                                  |         | -44998.3 | 24     | -45242.7       | 244.4           |
|                       |                                                  |         | -45000.3 | 25     | -45244.8       | 244.5           |
|                       |                                                  |         | -45002.5 | 26     | -45246.8       | 244.3           |
|                       |                                                  |         | -45005.3 | 27     | -45249.9       | 244.6           |
|                       |                                                  |         | -45007.4 | 28     | -45251.9       | 244.5           |
| $^{1}J_{para-F,C}$    | Arl-Ref5                                         |         | -57430.2 | 4      | -57684.6       | 254.4           |
|                       |                                                  |         | -57450.2 | 5      | -57704.6       | 254.4           |
|                       |                                                  |         | -57470.2 | 6      | -57724.6       | 254.4           |
| $^{1}J_{meta-F,C}$    | Arl-Ref5                                         |         | -60128.8 | 3      | -60382.9       | 254.1           |
|                       |                                                  |         | -60165.1 | 4      | -60419.2       | 254.1           |
2.2 1-Iodoperfluorobenzene: Base induced changes in the $^{19}$F NMR

Table S11. The average changes in the $^{19}$F-$^{13}$C-J coupling constants ($\text{AVARAGE}(\Delta J)_{\text{obs}}$), chemical shift ($\text{AVARAGE}(\Delta \delta)$) as well as their standard deviations (STDEV) of 1-iodoperfluorobenzene (c = 0.200 mol/L) by the presence of selected halogen bond acceptors (c = 0.500 mol/L). All samples have been prepared trice.

| Compound                  | $\text{AVARAGE}(\Delta J)_{\text{obs}}$ | STDEV | $\text{AVARAGE}(\Delta \delta)_{\text{ortho}}$ | STDEV | $\text{AVARAGE}(\Delta \delta)_{\text{para}}$ | STDEV | $\text{AVARAGE}(\Delta \delta)_{\text{meta}}$ | STDEV |
|---------------------------|----------------------------------------|-------|-----------------------------------------------|-------|-----------------------------------------------|-------|-----------------------------------------------|-------|
| **Pyridines**             |                                        |       |                                               |       |                                               |       |                                               |       |
| 4-Dimethylaminopyridine   | 2.14                                   | 0.03  | 1.48                                          | 0.02  | 0.52                                          | 0.03  | 0.686                                         | 0.007 |
| 3,5-Dimethylpyridine      | 1.03                                   | 0.02  | 0.28                                          | 0.85  | 0.27                                          | 0.03  | 0.367                                         | 0.005 |
| Methoxypyridine           | 1.02                                   | 0.02  | 0.71                                          | 0.05  | 0.27                                          | 0.03  | 0.355                                         | 0.008 |
| 2-Methylpyridine          | 0.78                                   | 0.00  | 0.53                                          | 0.05  | 0.25                                          | 0.00  | 0.266                                         | 0.004 |
| Pyridine                  | 0.70                                   | 0.03  | 0.47                                          | 0.04  | 0.29                                          | 0.12  | 0.235                                         | 0.005 |
| 2,6-Dimethylpyridine      | 0.34                                   | 0.03  | 0.08                                          | 0.27  | 0.08                                          | 0.03  | 0.097                                         | 0.003 |
| 3-Bromopyridine           | 0.28                                   | 0.03  | 0.19                                          | 0.05  | 0.07                                          | 0.00  | 0.104                                         | 0.001 |
| 3-Chloropyridine          | 0.30                                   | 0.03  | 0.20                                          | 0.13  | 0.10                                          | 0.10  | 0.254                                         | 0.035 |
| 3,5-Dichloropyridine      | 0.05                                   | 0.02  | 0.00                                          | 0.05  | 0.07                                          | 0.02  | 0.061                                         | 0.001 |
| **Primary Amines**        |                                        |       |                                               |       |                                               |       |                                               |       |
| Butylamine                | 1.34                                   | 0.07  | 0.87                                          | 0.03  | 0.32                                          | 0.08  | 0.674                                         | 0.006 |
| Secbutylamine             | 1.06                                   | 0.02  | 0.24                                          | 0.82  | 0.23                                          | 0.08  | 0.533                                         | 0.003 |
| Tertbutylamine            | 1.18                                   | 0.01  | 0.27                                          | 0.95  | 0.27                                          | 0.03  | 0.612                                         | 0.006 |
| **Secondary Amines**      |                                        |       |                                               |       |                                               |       |                                               |       |
| Diethylamine              | 1.99                                   | 0.04  | 1.24                                          | 0.04  | 0.35                                          | 0.05  | 0.920                                         | 0.024 |
| Diisopropylamine          | 1.69                                   | 0.09  | 0.98                                          | 0.15  | 0.22                                          | 0.03  | 0.776                                         | 0.010 |
| N-ethylisopropylamine     | 0.73                                   | 0.03  | 0.18                                          | 0.47  | 0.02                                          | 0.02  | 0.368                                         | 0.003 |
| Piperidine                | 1.23                                   | 0.03  | 0.29                                          | 0.00  | 0.22                                          | 0.00  | 0.566                                         | 0.002 |
| Pyrrolidine               | 2.69                                   | 0.04  | 1.61                                          | 0.04  | 0.25                                          | 0.26  | 1.171                                         | 0.010 |
| **Tertiary Amines**       |                                        |       |                                               |       |                                               |       |                                               |       |
| Triethylamine             | 1.30                                   | 0.06  | 0.92                                          | 0.04  | 0.12                                          | 0.03  | 0.634                                         | 0.011 |
| Tributylamine             | 0.50                                   | 0.00  | 0.11                                          | 0.33  | 0.08                                          | 0.12  | 0.228                                         | 0.007 |
| **Carbonyls**             |                                        |       |                                               |       |                                               |       |                                               |       |
| DMSO                      | 0.61                                   | 0.01  | 0.46                                          | 0.05  | 0.35                                          | 0.13  | 0.183                                         | 0.002 |
| 1,3-dimethyl-2-imidazolidine | 0.49                             | 0.02  | 0.40                                          | 0.00  | 0.32                                          | 0.06  | 0.186                                         | 0.008 |
| 2-Pyrrolidone             | 0.38                                   | 0.01  | 0.24                                          | 0.02  | 0.15                                          | 0.00  | 0.150                                         | 0.004 |
| Dimethylformamide         | 0.39                                   | 0.03  | 0.32                                          | 0.02  | 0.23                                          | 0.06  | 0.181                                         | 0.001 |
| Acetophenone              | 0.07                                   | 0.03  | 0.07                                          | 0.03  | 0.07                                          | 0.08  | 0.046                                         | 0.000 |
| Benzophenone              | 0.03                                   | 0.02  | 0.04                                          | 0.02  | 0.00                                          | 0.05  | 0.181                                         | 0.008 |
| **N-Oxides**              |                                        |       |                                               |       |                                               |       |                                               |       |
| Trimethylamin-N-Oxide     | 4.04                                   | 0.02  | 2.82                                          | 0.07  | 1.10                                          | 0.02  | 1.437                                         | 0.016 |
2.2.1. The $\Delta^{1}J_{F,C}$ and $\Delta\delta$ values for 1-iodopentafluorobenzene induced by Lewis bases

![Graphs showing $\Delta^{1}J_{F,C}$ and $\Delta\delta$ values for 1-iodopentafluorobenzene induced by Lewis bases.](image)

*Figure S4: The $\Delta^{1}J_{F,C}$ and $\Delta\delta$ values for 1-iodopentafluorobenzene induced by the presence of a base, based on Table S11.*

![Graphs showing $\Delta\delta_{ortho}$, $\Delta\delta_{meta}$, and $\Delta\delta_{para}$ values vs $pK_{B}$ for 1-iodopentafluorobenzene induced by Lewis bases.](image)

*Figure S5: The $\Delta\delta_{ortho}$ (blue, $R^2 = 0.79$, slope 0.066), $\Delta\delta_{meta}$ (red, $R^2 = 0.68$, slope 0.052), $\Delta\delta_{para}$ (green, $R^2 = 0.76$, slope 0.10) values vs $pK_{B}$ for 1-iodopentafluorobenzene induced by the presence of a base, based on Table S11.*
2.2.2. Subset analysis of $\Delta^1 J_{\text{ortho-F,C}}$ values for 1-iodopentafluorobenzene induced by Lewis bases

Figure S6: The $\Delta^1 J$ and $\Delta \delta$ values for 1-iodopentafluorobenzene induced by Lewis bases, based on Table S11. Top-left: $\Delta^1 J_{\text{ortho-F,13C}}$ vs $pK_{\text{B}}$ grouped according to the type of base employed. The data points have been fitted to $ax^2 + b$. Top-right: The change of $^1 J_{\text{F,C}}$ in the ortho-position of iodopentafluorobenzene, $\Delta^1 J_{\text{ortho-F,C}}$, as a function of the Lewis basicity, $pK_{\text{B}}^2$, upon binding to various Lewis bases. Errors are given as standard deviations; $pK_{\text{B}} = 0$ refers to a K = 1. The data corresponding to the pyridines is shown in red ($R^2 = 0.98$), to amines in blue ($R^2 = 0.60$), to N-oxides in green ($R^2 = 0.94$), whereas to all data in black ($R^2 = 0.71$).

Bottom-left: $\Delta^1 J_{\text{ortho-F,13C}}$ vs $pK_{\text{B}}^2$ of the amine subset grouped into 1°, 2° and 3° with their linear correlation.
2.3. 1-idoheptadecafluorooctane: A typical example

Expansions of the $^{19}$F NMR spectrum of 1-idoheptadecafluorooctane without and in the presence of 4-methoxypyridine. The multiplet patterns don’t change upon addition of a Lewis base. The $^{19}$F NMR spectra correspond to the data given in Figure S7 and Figure S8.

Figure S7. Cut-outs of the $^{19}$F NMR spectrum of 1-idoheptadecafluorooctane without the presence of a base (AliI_Ref7) showing satellites with peaks picked.

Figure S8. Cut-outs of the $^{19}$F NMR spectrum of 1-iodoheptadecafluorooctane in the presence of 4-methoxypyridine showing satellites with peaks picked.
Table S12. Extracted peaks and calculated $^{1}J_{F,C}$ coupling constants in 1-iodopentafluorobenzene without the presence of a base.

| Multiplet information | Rawdata filename format: [date]_[Operator]_[Label]_[add.descri.] | Peak 1 Hz | Peak 4 Hz | $^{1}J_{F,C}$ (Hz) |
|-----------------------|---------------------------------------------------------------|-----------|-----------|-------------------|
| $^{1}J_{\alpha F,C}$  | Arl-Ref7                                                      | -22459.9  | -22780.5  | 320.6             |
|                       |                                                               | -22475.2  | -22795.6  | 320.4             |
|                       |                                                               | -22490.2  | -22810.8  | 320.6             |
| $^{1}J_{\beta F,C}$   | Arl-Ref7                                                      | -42633    | -42900.6  | 267.6             |
| $^{1}J_{\theta F,C}$  | Arl-Ref7                                                      | -30594.2  | -30882.4  | 288.2             |
|                       |                                                               | -30604.3  | -30892.5  | 288.2             |
|                       |                                                               | -30614.5  | -30902.6  | 288.1             |

Table S13. Extracted peaks and calculated $^{1}J_{F,C}$ coupling constants in 1-iodopentafluorobenzene in the presence of 4-methoxypyridine.

| Multiplet information | Rawdata filename format: [date]_[Operator]_[Label]_[add.descri.] | Peak 1 Hz | Peak 4 Hz | $^{1}J_{F,C}$ (Hz) |
|-----------------------|---------------------------------------------------------------|-----------|-----------|-------------------|
| $^{1}J_{\alpha F,C}$  | Arl-Ref8                                                      | -22459.8  | -22780.4  | 320.6             |
|                       |                                                               | -22475.2  | -22795.6  | 320.4             |
|                       |                                                               | -22490.2  | -22810.7  | 320.7             |
| $^{1}J_{\beta F,C}$   | Arl-Ref8                                                      | -42632    | -42900.3  | 268.3             |
| $^{1}J_{\theta F,C}$  | Arl-Ref8                                                      | -30592.4  | -30880.5  | 288.1             |
|                       |                                                               | -30602.5  | -30890.6  | 288.1             |
|                       |                                                               | -30612.6  | -30900.8  | 288.2             |
2.4 1-Iodoperfluorooctane: Base induced changes in the $^{19}$F NMR

Changes in selected chemical shifts and coupling constants of 1-iodoperfluorooctane are given in Table S14. The changes in coupling constant observed for the terminal CF$_3$ group are within the error of the experiment. Significant chemical shift changes of the terminal CF$_3$ group has been rationalized by Ciancaleoni et. al. as secondary interaction with the aromatic π-system leading to an orientation of the chain above the aromatic cycle and therefore remote Fluorine resonances experience a shielding effect. $^3$

Table S14. The average changes in the $^{19}$F-$^{13}$C-$^{1}$J coupling constants ($\text{AVARAGE} (\Delta J_{^{19}F-^{13}C-^{1}J})$), chemical shift ($\text{AVARAGE} (\Delta \delta_{^{19}F})$) as well as their standard deviations (STDEV) of 1-iodoperfluorooctane ($c = 0.200 \text{ mol/L}$) by the presence of selected halogen bond acceptors ($c = 0.500 \text{ mol/L}$). Samples have been prepared at least twice.

| Compound                        | $\text{AVARAGE} (\Delta J_{^{19}F-^{13}C-^{1}J})$ [Hz] | STDEV | $\text{AVARAGE} (\Delta \delta_{^{19}F})$ [ppm] | STDEV | $\text{AVARAGE} (\Delta \delta_{^{13}C})$ [ppm] | STDEV | $\text{AVARAGE} (\Delta \delta_{^{1}J})$ [ppm] | STDEV |
|--------------------------------|------------------------------------------------------|-------|-----------------------------------------------|-------|-----------------------------------------------|-------|-----------------------------------------------|-------|
| Pyridines                      |                                                      |       |                                               |       |                                               |       |                                               |       |
| 4-Dimethylaminopyridine        | 3.32                                                 | 0.19  | 2.75                                          | 0.28  | 0.07                                         | 0.05  | 8.47                                          | 0.11  | 0.71                                         | 0.01  | 0.13                                         | 0.01  | 3.78                                         | 0.19  | 14.29                                       |
| 3,5-Dimethylpyridine           | 2.33                                                 | 0.01  | 1.70                                          | 0.07  | 0.05                                         | 0.05  | 4.71                                          | 0.03  | 0.39                                         | 0.00  | 0.07                                         | 0.00  | 2.78                                         | 0.07  | 7.73                                        |
| Methoxypyridine$^a$            | 2.08                                                 | 0.15  | 1.98                                          | 0.30  | 0.05                                         | 0.05  | 4.40                                          | 0.11  | 0.38                                         | 0.01  | 0.04                                         | 0.01  | 2.63                                         | 0.04  | 6.92                                        |
| Pyridine-N-oxide               | 1.65                                                 | 0.09  | 1.25                                          | 0.57  | 0.05                                         | 0.02  | 3.24                                          | 0.09  | 0.26                                         | 0.01  | 0.05                                         | 0.02  | 2.40                                         | 0.01  | 5.76                                        |
| Pyridine                       | 1.03                                                 | 0.02  | 1.05                                          | 0.14  | 0.02                                         | 0.04  | 1.84                                          | 0.04  | 0.12                                         | 0.12  | 0.08                                         | 0.04  | 2.22                                         | 0.04  | 4.93                                        |
| 2,6-Dimethylpyridine           | 1.35                                                 | 0.31  | 0.62                                          | 0.21  | 0.02                                         | 0.05  | 1.55                                          | 0.01  | 0.10                                         | 0.10  | 0.05                                         | 0.01  | 1.83                                         | 0.02  | 3.36                                        |
| 3-Bromopyridine$^b$            | 1.82                                                 | 0.09  | 0.60                                          | 0.07  | 0.05                                         | 0.00  | 1.52                                          | 0.02  | 0.10                                         | 0.00  | 0.04                                         | 0.00  | 1.40                                         | 0.02  | 1.96                                        |
| 3-Chloropyridine               | 2.28                                                 | 0.00  | 1.45                                          | 0.14  | 0.00                                         | 0.05  | 3.98                                          | 0.04  | 0.37                                         | 0.01  | 0.00                                         | 0.02  | 1.38                                         | 0.02  | 1.90                                        |
| Control without basic additives (not part of the graphs) | | | | | | | | | | | | | | | |
| n-Pentane                      | 0.42                                                 | 0.11  | 0.10                                          | 0.04  | 2.15                                         | 0.30  | 0.036                                         | 0.002 | 0.173                                        | 0.002 | 0.070                                        | 0.001 | -                                            | -                                            |

$^a$Sample has been prepared four-times, $^b$Sample has been prepared three times.
2.4.1. The $\Delta^1 J_{F,C}$ and $\Delta \delta$ values for 1-iodoheptadecafluorooctane induced by Lewis bases

![Graphs showing $\Delta^1 J_{F,C}$ and $\Delta \delta$ values for 1-iodoheptadecafluorooctane induced by Lewis bases.]

Figure S9. Left: $\Delta^1 J_{F,C}$ in iodoperfluorooctane ($c = 0.200 \text{ mol} \cdot \text{L}^{-1}$) vs the iodine basicity ($pK_{B}I_2$) of a present base ($c = 0.500 \text{ mol} \cdot \text{L}^{-1}$). $\alpha$-F (black), $\beta$-F (red) and $\theta$-F (blue). Right: $\Delta \delta$ in iodoperfluorooctane ($c = 0.200 \text{ mol} \cdot \text{L}^{-1}$) vs the iodine basicity ($pK_{B}I_2$) of a present base ($c = 0.500 \text{ mol} \cdot \text{L}^{-1}$). $\alpha$-F (black), $\beta$-F (red) and $\theta$-F (blue).

2.5. Evaluating the impact of Non-Directional Effects

Addition of Lewis bases does not affect the $^1 J_{F,C}$ of the terminal $\theta$-CF$_3$ group of IC$_8$F$_{17}$ whereas it influences in $^1 J_{F,C}$ $^1 J_{oF,C}$ and $^1 J_{pF,C}$ in a Lewis basicity dependent manner (Figure 4, main text). Significant change, 2.15 Hz, was observed for the $^1 J_{F,C}$ of the $\theta$-CF$_3$ group upon addition of 2.5 eq. pentane to the solution of the halogen bond donor, whereas the $^1 J_{F,C}$ of the $\alpha$- and $\beta$-CF$_2$ groups were not affected by $n$-pentane significantly. This observation indicates that the remote $\theta$-CF$_3$ group serves as an internal reference to detect non-directional solvent effects introduced by changes in the bulk properties of the solution e.g. polarity. Thus, halogen bonding is observable close to the halogen bond donor site at the $\alpha$- and $\beta$-CF$_2$ groups but not at the remote $\theta$-CF$_3$ group whereas bulk solvent effects are detectable on the $\theta$-CF$_3$ but not on the $\alpha$- and $\beta$-CF$_2$ groups.

Iodopentafluorobenzene lacks a comparable reference position. However, upon addition of 2.5 eq. $n$-pentane only minor, $\Delta^1 J_{F,C} < 0.07 \text{ Hz}$, were observed at the ortho and para- $^1 J_{F,C}$ whereas that at the the meta position has been slightly more sensitive ($\Delta^1 J_{F,C} = 0.13 \text{ Hz}$). Halogen bonding shows the opposite effect (larger change at the ortho and para- $^1 J_{F,C}$) whereas no significant Lewis basicity dependent change at the meta position.

Overall, no significant influence of solvent polarity has been observed upon $n$-pentane addition, suggesting that the Lewis bases used in this study did not induce changes in $^1 J_{F,C}$ by changing the solvents bulk properties.

3 Computational Details

All geometry optimization calculations for all halogen bonded complexes investigated in this work were carried out utilizing the B3LYP$^{4,5}$ functional augmented with Grimme’s D3$^6$ dispersion correction in combination with the large correlation consistent Dunning’s aug-cc-pVTZ$^{7,8}$ basis set. Scalar relativistic effects for heavy atoms (e.g. I) were assessed by utilizing the Stuttgart-Dresden (SDD)$^{9,10}$ effective core potential. The B3LYP-D3 functional was chosen as it is known to adequately account for electron correlations for
systems exhibiting noncovalent interactions.\textsuperscript{11-12} Dichloromethane solvation effects were included using the polarizable continuum model (PCM) of Tomasi and co-workers.\textsuperscript{13} Vibrational frequency calculations were followed at the same level of theory to confirm the optimized geometry corresponding to geometry minima.

All calculations were performed using the Gaussian 16 Rev. C.01 package.\textsuperscript{14} The geometries were optimized using an ultrafine grid and tight convergence criteria for the forces and displacements.\textsuperscript{15} Natural population analysis and second-order perturbation of the Fock matrix analysis of two interacting orbitals were carried out utilizing the NBO7 program.\textsuperscript{16} Topological analysis of electron density were carried out using the AIMALL version 19.10.12 program.\textsuperscript{17} The nature of halogen bonding interactions were characterized through the energy density ($H_c$) at the N···I and O···I bond critical points, where a negative value of the energy ($H_c < 0$) indicates covalent bond and a positive value of the energy ($H_c > 0$) points to electrostatic interactions.\textsuperscript{18}

The associated binding energies ($\Delta E$) were calculated by taking the energy difference between halogen bonded complexes (A···B) and its isolated components (A and B) at their equilibrium geometries,

$$A + B \rightarrow A\cdots B$$

$$\Delta E = E_{A\cdots B} - (E_A + E_B).$$

Due to the size of the molecules, the coupling constant calculations of 1-iodoperfluorooctane were replaced with 1-iodoperfluoropropane.
### 4 Computational Results

Table S15. Contributions of the Fermi-contact (F,C), the spin dipolar (SD), the paramagnetic (PSO), and the diamagnetic spin-orbit (DSO) components to the change of $\Delta \chi_{F,C}$ of the halogen bond donor upon halogen bonding. The slope of the computed contribution of the component as a function of $\Delta \chi_{F,C}$ are given, with the variance of the linear fits being shown in brackets. The first three rows show data computed for 1-iodopentafluorobenzene (IC$_6$F$_5$), whereas the next two data for 1-iodoperfluorooctane (IC$_8$F$_{17}$). Visualisation of the data used for extraction of these values can be found in section 4.1.

|                | FC   | SD   | PSO  | DSO  |
|----------------|------|------|------|------|
| $\Delta \chi_{o-F,C}$ | 0.713 | 0.076 | 0.209 | 0.000 |
| IC$_6$F$_5$    | (0.99) | (0.81) | (0.93) | (0.00) |
| $\Delta \chi_{m-F,C}$ | 0.435 | 0.150 | 0.416 | 0.002 |
| IC$_6$F$_5$    | (0.43) | (0.55) | (0.57) | (0.31) |
| $\Delta \chi_{p-F,C}$ | 0.459 | 0.126 | 0.414 | 0.000 |
| IC$_6$F$_5$    | (0.96) | (0.97) | (0.97) | (0.00) |
| $\Delta \chi_{o-F,C}$ | 0.076 | 0.207 | 0.720 | -0.003 |
| IC$_8$F$_{17}$ | (0.18) | (0.97) | (0.97) | (0.89) |
| $\Delta \chi_{o-F,C}$ | 0.615 | 0.098 | 0.281 | -0.020 |
| IC$_8$F$_{17}$ | (0.98) | (0.95) | (0.97) | (0.63) |

*The weak correlation is caused by a single outlier.*
Table S16. Bond distances (R), $^{19}$F-$^{1}$I-coupling constants ($J_{F,C}$), binding energies ($\Delta E$), electron densities ($\rho$) and energy densities ($H$) at the C-F and N-1 bond critical point, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| CsF$_5$-I--Base | $R_{C-F}$ (Å) | $R_{C-I}$ (Å) | $R_{N-I}$ (Å) | $J_{C,F}$ (Hz) | $\Delta E$ (kcal/mol) | $\rho_{C-F}$ (e/Å$^3$) | $H_{C-F}$ (h/Å$^3$) | $\rho_{N-I}$ (e/Å$^3$) | $H_{N-I}$ (h/Å$^3$) |
|-----------------|--------------|--------------|--------------|---------------|--------------------|----------------|----------------|----------------|----------------|
| -               | 1.337        | 2.099        | -            | -132.60       | -                  | 1.8382        | -2.7164        | -              | -              |
| 4-Dimethylaminopyridine | 1.343       | 2.148       | 2.723        | -299.43       | -31.86             | 1.8066        | -2.6495        | 0.22552        | -0.0114        |
| 2-Methylpyridine | 1.342       | 2.135       | 2.819        | -301.99       | 29.02              | 1.8130        | -2.6631        | 0.18682        | -0.0013        |
| 2,6-Dimethylpyridine | 1.341       | 2.131       | 2.904        | -302.69       | -28.86             | 1.8152        | -2.6677        | 0.15958        | +0.0035        |
| 4-Methoxypyridine | 1.342       | 2.139       | 2.773        | -300.79       | 28.53              | 1.8109        | -2.6586        | 0.20322        | -0.0049        |
| 3,5-Dimethylpyridine | 1.342       | 2.139       | 2.775        | -301.02       | -28.44             | 1.8111        | -2.6589        | 0.20344        | -0.0052        |
| Pyridine        | 1.342       | 2.136       | 2.796        | -301.55       | 26.99              | 1.8129        | -2.6628        | 0.19420        | -0.0026        |
| 3-Bromopyridine | 1.341       | 2.129       | 2.840        | -302.49       | -24.51             | 1.8165        | -2.6704        | 0.17639        | +0.0014        |
| 3-Chloropyridine | 1.341       | 2.129       | 2.840        | -302.42       | -24.39             | 1.8164        | -2.6701        | 0.17636        | +0.0014        |
| 3,5-Dichloropyridine | 1.340      | 2.124       | 2.880        | -303.18       | -22.40             | 1.8193        | -2.6764        | 0.16166        | +0.0042        |

Table S17. Hybridization characters and natural population charge analysis (X) of C, F, N, and I atoms, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| CsF$_5$-I--Base | sp$^n$ | sp$^n$ | sp$^n$ | sp$^n$ | $X_{C_{IPSO}}$ (in e) | $X_{I}$ (in e) | $X_{F(ortho)}$ (in e) | $X_{I}$ (in e) |
|-----------------|---------|--------|--------|--------|----------------------|--------------|----------------------|---------------|
| -               | sp$^{19}$ | sp$^{24}$ | sp$^{24}$ | sp$^{24}$ | -0.2931              | +0.2517      | -0.3075              | -              |
| 4-Dimethylaminopyridine | sp$^{26}$ | sp$^{24}$ | sp$^{24}$ | sp$^{24}$ | -0.3197              | +0.2591      | -0.3183              | -0.5211       |
| 2-Methylpyridine | sp$^{15}$ | sp$^{24}$ | sp$^{24}$ | sp$^{24}$ | -0.3158              | +0.2585      | -0.3159              | -0.4768       |
| 2,6-Dimethylpyridine | sp$^{14}$ | sp$^{15}$ | sp$^{20}$ | sp$^{14}$ | -0.3143              | +0.2586      | -0.3149              | -0.4898       |
| 4-Methoxypyridine | sp$^{15}$ | sp$^{24}$ | sp$^{24}$ | sp$^{16}$ | -0.3172              | +0.2601      | -0.3168              | -0.4953       |
| 3,5-Dimethylpyridine | sp$^{15}$ | sp$^{24}$ | sp$^{24}$ | sp$^{16}$ | -0.3171              | +0.2593      | -0.3167              | -0.4577       |
| Pyridine        | sp$^{15}$ | sp$^{24}$ | sp$^{24}$ | sp$^{15}$ | -0.3159              | +0.2599      | -0.3161              | -0.4662       |
| 3-Bromopyridine | sp$^{14}$ | sp$^{24}$ | sp$^{24}$ | sp$^{14}$ | -0.3139              | +0.2605      | -0.3148              | -0.4454       |
| 3-Chloropyridine | sp$^{14}$ | sp$^{24}$ | sp$^{24}$ | sp$^{14}$ | -0.3139              | +0.2606      | -0.3149              | -0.4458       |
| 3,5-Dichloropyridine | sp$^{13}$ | sp$^{24}$ | sp$^{24}$ | sp$^{13}$ | -0.3120              | +0.2606      | -0.3139              | -0.4262       |

*Due to the use of effective core potential for describing relativistic effects of I atom

Table S18. Decomposition terms of calculated $J_{C,F}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $J_{C,F}$ coupling constants at the ortho position as well as the second-order perturbation of the Fock Matrix between C-I and $\sigma^*$ orbital of C-F, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| CsF$_5$-I--Base | Fermi Contact (Hz) | Spin-Dipolar (Hz) | Paramagnetic Spin-orbit (Hz) | Diamagnetic Spin-orbit (Hz) | $J_{C,F}$(Hz) | C-I $\rightarrow$ C-F (kcal/mol) |
|-----------------|--------------------|------------------|-----------------------------|----------------------------|--------------|-------------------------------|
| -               | -310.78            | 3.96             | -6.94                       | 1.17                       | -312.60      | 1.33                           |
| 4-Dimethylaminopyridine | -300.76        | 4.82             | -4.67                       | 1.18                       | -299.43      | 1.68                           |
| 2-Methylpyridine | -302.67            | 4.65             | -5.15                       | 1.18                       | -301.99      | 1.57                           |
| 2,6-Dimethylpyridine | -303.11          | 4.58             | -5.34                       | 1.18                       | -302.69      | 1.52                           |
| 4-Methoxypyridine | -301.69            | 4.17             | -4.98                       | 1.18                       | -300.79      | 1.61                           |
| 3,5-Dimethylpyridine | -301.90          | 4.70             | -5.00                       | 1.18                       | -301.02      | 1.61                           |
| Pyridine        | -302.26            | 4.65             | -5.13                       | 1.18                       | -301.55      | 1.58                           |
| 3-Bromopyridine | -302.83            | 4.56             | -5.39                       | 1.18                       | -302.49      | 1.54                           |
| 3-Chloropyridine | -302.78            | 4.56             | -5.38                       | 1.18                       | -302.42      | 1.53                           |
| 3,5-Dichloropyridine | -303.24          | 4.48             | -5.59                       | 1.18                       | -303.18      | 1.50                           |
Table S19. Decomposition terms of calculated $^1J_{F,C}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $^1J_{F,C}$ coupling constants at the meta position (in Hz), calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C$_6$F$_5$I···Base     | Fermi Contact | Spin-Dipolar | Paramagnetic Spin-orbit | Diamagnetic Spin-orbit | $^1J_{F,C}$(Hz) |
|------------------------|---------------|--------------|-------------------------|------------------------|-----------------|
| –                      | -320.78       | 4.86         | -2.50                   | 1.15                   | -317.26         |
| 4-Dimethylaminopyridine| -319.13       | 5.57         | -0.54                   | 1.16                   | -312.94         |
| 2-Methylpyridine       | -319.32       | 5.42         | -0.96                   | 1.16                   | -313.69         |
| 2,6-Dimethylpyridine   | -319.50       | 5.38         | -1.07                   | 1.16                   | -314.02         |
| 4-Methoxypyridine      | -318.96       | 5.47         | -0.82                   | 1.16                   | -313.15         |
| 3,5-Dimethylpyridine   | -319.07       | 5.47         | -0.83                   | 1.16                   | -313.27         |
| Pyridine               | -318.97       | 5.43         | -0.95                   | 1.16                   | -313.33         |
| 3-Bromopyridine        | -318.96       | 5.34         | -1.17                   | 1.16                   | -313.63         |
| 3-Chloropyridine       | -318.94       | 5.35         | -1.16                   | 1.16                   | -313.60         |
| 3,5-Dichloropyridine   | -318.94       | 5.28         | -1.36                   | 1.16                   | -313.86         |

Table S20. Decomposition terms of calculated $^1J_{F,C}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $^1J_{F,C}$ coupling constants at the para position (in Hz), calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C$_6$F$_5$I···Base     | Fermi Contact | Spin-Dipolar | Paramagnetic Spin-orbit | Diamagnetic Spin-orbit | $^1J_{F,C}$(Hz) |
|------------------------|---------------|--------------|-------------------------|------------------------|-----------------|
| –                      | -320.92       | 4.12         | -5.45                   | 1.15                   | -321.11         |
| 4-Dimethylaminopyridine| -317.03       | 4.97         | -2.58                   | 1.15                   | -313.49         |
| 2-Methylpyridine       | -317.71       | 4.78         | -3.23                   | 1.15                   | -315.01         |
| 2,6-Dimethylpyridine   | -318.12       | 4.73         | -3.39                   | 1.15                   | -315.63         |
| 4-Methoxypyridine      | -317.38       | 4.84         | -3.02                   | 1.15                   | -314.41         |
| 3,5-Dimethylpyridine   | -317.37       | 4.84         | -3.02                   | 1.15                   | -314.41         |
| Pyridine               | -317.55       | 4.78         | -3.21                   | 1.15                   | -314.83         |
| 3-Bromopyridine        | -317.79       | 4.68         | -3.55                   | 1.15                   | -315.51         |
| 3-Chloropyridine       | -317.80       | 4.68         | -3.54                   | 1.15                   | -315.51         |
| 3,5-Dichloropyridine   | -318.05       | 4.60         | -3.82                   | 1.15                   | -316.13         |

Table S21. Calculated $^{19}$F coordination shifts ($\Delta \delta = \delta_{\text{complex}} - \delta_{\text{free}}$) in ppm

| C$_6$F$_5$I···Base     | $\Delta \delta_{\text{ortho}}$ | $\Delta \delta_{\text{meta}}$ | $\Delta \delta_{\text{para}}$ |
|------------------------|-------------------------------|-------------------------------|-------------------------------|
| –                      | 43.55                         | 2.48                          | 10.50                         |
| 4-Dimethylaminopyridine| 40.39                         | 0.47                          | 6.14                          |
| 2-Methylpyridine       | 40.96                         | 0.96                          | 7.20                          |
| 2,6-Dimethylpyridine   | 41.36                         | 1.05                          | 7.50                          |
| 4-Methoxypyridine      | 40.74                         | 0.76                          | 6.83                          |
| 3,5-Dimethylpyridine   | 40.83                         | 0.84                          | 6.86                          |
| Pyridine               | 40.92                         | 0.92                          | 7.14                          |
| 3-Bromopyridine        | 41.20                         | 1.15                          | 7.68                          |
| 3-Chloropyridine       | 41.21                         | 1.19                          | 7.67                          |
| 3,5-Dichloropyridine   | 41.45                         | 1.40                          | 8.13                          |
Table S22. Natural occupation numbers of 2s and 2p orbitals of C atoms in the ortho-position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp.

| Compound | 2s (2s\(_\sigma\)) | 2px (2p\(_\sigma\)) | 2py (2p\(_\sigma\)) | 2pz (2p\(_\pi\)) | \(^1\text{J}_\text{F,C}\) (Hz) | \(\Delta\text{SUM}(2\sigma)^a\) (reference) | \(\Delta(2\pi)^a\) (reference) |
|----------|------------------|------------------|------------------|-----------------|-----------------|-----------------|-----------------|
| -        | 0.8545           | 0.9671           | 0.7921           | 1.0322          | -312.6          | 0.000           | 0.000           |
| 4-Dimethylaminopyridine | 0.8582          | 0.9668           | 0.7919           | 1.0366          | -299.43         | 0.00331         | 0.004           |
| 2-Methylpyridine          | 0.8574           | 0.9673           | 0.7911           | 1.0358          | -301.99         | 0.00212         | 0.004           |
| 2,6-Dimethylpyridine      | 0.8572           | 0.9669           | 0.7919           | 1.0353          | -302.69         | 0.00230         | 0.003           |
| 4-Methoxypyridine         | 0.8577           | 0.9786           | 0.7797           | 1.0362          | -300.79         | 0.00229         | 0.004           |
| 3,5-Dimethylpyridine      | 0.8577           | 0.9668           | 0.7922           | 1.0354          | -301.02         | 0.00305         | 0.003           |
| Pyridine                  | 0.8574           | 0.9669           | 0.7914           | 1.0359          | -301.55         | 0.00205         | 0.004           |
| 3-Bromopyridine           | 0.8570           | 1.0253           | 0.7329           | 1.0355          | -302.49         | 0.00148         | 0.003           |
| 3-Chloropyridine          | 0.8570           | 1.0045           | 0.7537           | 1.0355          | -302.42         | 0.00146         | 0.003           |
| 3,5-Dichloropyridine      | 0.8566           | 0.9669           | 0.7913           | 1.0350          | -303.18         | 0.00111         | 0.003           |

\(a\) The aromatic rings were placed in the XY plane (in-plane), whereas the \(\pi\) orbitals are located in the out-of-plane (Z-axis). The \(\sigma\) orbitals are assumed to have sp\(_2\)-hybridization with equal contribution from 2s, 2px, and 2py.

Figure S10: Trends between calculated \(^1\text{J}_\text{F,C}\) coupling constants and natural occupation of 2s and 2p orbitals of the ortho-C-atom in iodopentafluorobenzene on halogen bond formation with different pyridine bases.
Table S23. Natural occupation numbers of 2s and 2p orbitals of C atoms in the meta-position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C₆F₅I···Base        | 2s  | 2px  | 2py  | 2pz  | ¹J_F,C(Hz) | Δ(SUM(2σ))<sup>a</sup> | Δ(2π)<sup>a</sup> |
|---------------------|-----|------|------|------|------------|-------------------------|------------------|
|                     | 0.871 | 0.966 | 0.773 | 1.068 | -312.6     | 0.000 (reference)       | 0.000 (reference) |
| 4-Dimethylaminopyridine | 0.874 | 0.969 | 0.770 | 1.072 | -299.43    | 0.004                   | 0.00219          |
| 2-Methylpyridine    | 0.873 | 0.968 | 0.771 | 1.072 | -301.99    | 0.004                   | 0.00138          |
| 2,6-Dimethylpyridine | 0.873 | 0.968 | 0.771 | 1.071 | -302.69    | 0.003                   | 0.00143          |
| 4-Methoxy pyridine  | 0.873 | 0.958 | 0.781 | 1.072 | -300.79    | 0.004                   | 0.00152          |
| 3,5-Dimethyl pyridine | 0.873 | 0.969 | 0.771 | 1.071 | -301.02    | 0.003                   | 0.00241          |
| Pyridine            | 0.873 | 0.968 | 0.770 | 1.072 | -301.55    | 0.004                   | 0.00143          |
| 3-Bromopyridine     | 0.873 | 0.904 | 0.835 | 1.071 | -302.49    | 0.003                   | 0.00115          |
| 3-Chloropyridine    | 0.873 | 0.930 | 0.809 | 1.071 | -302.42    | 0.003                   | 0.00114          |

<sup>a</sup> The aromatic rings were placed in the XY plane (in-plane), whereas the π orbitals are located in the out-of-plane (Z-axis). The σ orbitals are assumed to have sp<sub>2</sub>-hybridization with equal contribution from 2s, 2px, and 2py.

Figure S11: Trends between calculated ¹J<sub>F,C</sub> coupling constants and natural occupation of 2s and 2p orbitals of the meta-C-atom in pentafluoriodobenzene on halogen bond formation with different pyridine bases.
Table S24. Natural occupation numbers of 2s and 2p orbitals of C atoms in the para-position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| Base                        | 2s   | 2px  | 2py  | 2pz  | $^1J_{F,C}$ (Hz) | $\Delta$(SUM(2\(\sigma\)))$^a$ | $\Delta$(2\(\pi\))$^a$ |
|-----------------------------|------|------|------|------|-----------------|-------------------------------|-----------------|
| --                          | 0.875| 0.683| 1.055| 1.050| -312.6          | 0.000 (reference)             | 0.000 (reference) |
| 4-Dimethylaminopyridine     | 0.875| 0.680| 1.056| 1.060| -313.49         | 0.010                         | -0.00093 |
| 2-Methylpyridine            | 0.875| 0.680| 1.056| 1.058| -315.01         | 0.008                         | -0.00075 |
| 2,6-Dimethylpyridine        | 0.875| 0.680| 1.056| 1.057| -315.63         | 0.007                         | -0.00074 |
| 4-Methoxypyridine           | 0.875| 0.681| 1.055| 1.058| -314.41         | 0.009                         | -0.00081 |
| 3,5-Dimethylenpyridine      | 0.875| 0.680| 1.056| 1.058| -314.41         | 0.009                         | -0.00079 |
| Pyridine                    | 0.875| 0.680| 1.056| 1.058| -314.83         | 0.008                         | -0.00074 |
| 3-Bromopyridine             | 0.875| 0.693| 1.043| 1.057| -315.51         | 0.007                         | -0.00063 |
| 3-Chloropyridine            | 0.875| 0.685| 1.051| 1.057| -315.51         | 0.007                         | -0.00067 |
| 3,5-Dichloropyridine        | 0.875| 0.681| 1.055| 1.056| -316.13         | 0.006                         | -0.00056 |

$^a$ The aromatic rings were placed in the XY plane (in-plane), whereas the $\pi$ orbitals are located in the out-of-plane (Z-axis). The $\sigma$ orbitals are assumed to have sp$^2$-hybridization with equal contribution from 2s, 2px, and 2py.

Figure S12: Trends between calculated $^1J_{F,C}$ coupling constants and natural occupation of 2s and 2p orbitals of the para-C-atom in iodopentafluorobenzene on halogen bond formation with different pyridine bases.
### Table S25. Bond distances (R), $^{19}$F-13C-J-coupling constants ($J_{F,C}$), binding energies ($\Delta E$), electron densities ($\rho$) and energy densities ($\rho$) at the C-F and N--I bond critical point, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| Base                        | $R_{C-F}$ (Å) | $R_{C-I}$ (Å) | $R_{N-I}$ (Å) | $J_{F,C}$ (Hz) | $\Delta E$ (kJ/mol) | $\rho_{C-F}$ (e/Å$^3$) | $H_{C-F}$ (h/Å$^3$) | $\rho_{N-I}$ (e/Å$^3$) | $H_{N-I}$ (h/Å$^3$) |
|-----------------------------|---------------|---------------|---------------|----------------|-------------------|------------------------|------------------|------------------------|-------------------|
| 3,5-Dichloropyridine        | 1.354         | 2.219         | 2.685         | -388.16        | -34.86            | 1.812                  | -2.682           | 0.246                  | -0.018            |
| 3-Chloropyridine            | 1.356         | 2.209         | 2.785         | -388.35        | -31.38            | 1.828                  | -2.717           | 0.203                  | -0.005            |
| 4-Methoxypyridine           | 1.352         | 2.205         | 2.872         | -386.69        | -30.65            | 1.833                  | -2.729           | 0.173                  | +0.001            |
| 3,5-Dimethoxypyridine       | 1.357         | 2.211         | 2.736         | -388.50        | -31.06            | 1.823                  | -2.705           | 0.222                  | -0.010            |
| Pyridine                    | 1.356         | 2.209         | 2.761         | -389.55        | -29.26            | 1.828                  | -2.717           | 0.211                  | -0.007            |
| 3-Bromopyridine             | 1.354         | 2.204         | 2.805         | -390.12        | -26.34            | 1.837                  | -2.736           | 0.192                  | -0.002            |
| 3-Chloropyridine            | 1.354         | 2.204         | 2.806         | -390.23        | -26.23            | 1.837                  | -2.736           | 0.191                  | -0.002            |
| 3,5-Dichloropyridine        | 1.353         | 2.199         | 2.848         | -390.97        | -23.79            | 1.844                  | -2.735           | 0.175                  | 0.001             |

### Table S26. Hybridization characters and natural population charge analysis (X) of C, F, N, and I atoms, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| Base                        | C$_{ortho}$ | F$_{ortho}$ | C | F | I | X$_C$ | X$_I$ | X$_{F(ortho)}$ | X$_N$ |
|-----------------------------|-------------|-------------|---|---|---|-------|-------|----------------|-------|
| 4-Dimethylaminopyridine     | sp$^3$      | sp$^2$      | sp$^3$ | sp$^3$* | sp$^3$ | +0.5622 | +0.1509 | -0.3370 | -     |
| 2-Methylpyridine            | sp$^3$      | sp$^2$      | sp$^3$ | sp$^3$ | sp$^3$ | +0.4959 | +0.1785 | -0.3577 | -0.5205 |
| 2,6-Dimethylpyridine        | sp$^3$      | sp$^3$ | sp$^3$ | sp$^3$ | sp$^3$ | +0.5074 | +0.1738 | -0.3530 | -0.4758 |
| 4-Methoxypyridine           | sp$^3$      | sp$^3$ | sp$^3$ | sp$^3$ | sp$^3$ | +0.5118 | +0.1718 | -0.3516 | -0.4884 |
| 3,5-Dimethoxypyridine       | sp$^3$      | sp$^3$ | sp$^3$ | sp$^3$ | sp$^3$ | +0.5031 | +0.1775 | -0.3546 | -0.4948 |
| Pyridine                    | sp$^3$      | sp$^3$ | sp$^3$ | sp$^3$ | sp$^3$ | +0.5035 | +0.1761 | -0.3544 | -0.4568 |
| 3-Bromopyridine             | sp$^3$      | sp$^3$ | sp$^3$ | sp$^3$ | sp$^3$ | +0.5067 | +0.1759 | -0.3531 | -0.4656 |
| 3-Chloropyridine            | sp$^3$      | sp$^3$ | sp$^3$ | sp$^3$ | sp$^3$ | +0.5125 | +0.1747 | -0.3505 | -0.4453 |
| 3,5-Dichloropyridine        | sp$^3$      | sp$^3$ | sp$^3$ | sp$^3$ | sp$^3$ | +0.5125 | +0.1748 | -0.3505 | -0.4456 |
*Due to the use of effective core potential for describing relativistic effects of I atom

### Table S27. Decomposition terms of calculated $J_{F,C}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $J_{F,C}$ coupling constants at the carbon $\alpha$ position as well as the second-order perturbation of the Fock Matrix between $\sigma$ orbital of C-I and $\sigma^*$ orbital of C-F and lone pair of I with $\sigma^*$ of C-F orbital, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| Base                        | Fermi Contact | Spin-Dipolar | Paramagnetic Spin-orbit | Diamagnetic Spin-orbit | $J_{F,C}(Hz)$ | C-I $\rightarrow$ C-F (kcal/mol) | Lp(I)$\rightarrow$ C-F |
|-----------------------------|---------------|--------------|-------------------------|------------------------|----------------|---------------------------------|---------------------|
| 4-Dimethylaminopyridine     | -372.42       | 4.36         | -34.92                  | 1.55                   | -401.43        | 1.59                            | 4.76                |
| 2-Methylpyridine            | -372.44       | 7.34         | -24.56                  | 1.50                   | -388.16        | 1.40                            | 4.36                |
| 2,6-Dimethylpyridine        | -370.40       | 6.84         | -26.30                  | 1.51                   | -388.35        | 1.38                            | 4.44                |
| 4-Methoxypyridine           | -370.93       | 6.65         | -26.92                  | 1.52                   | -389.69        | 1.36                            | 4.58                |
| 3,5-Dimethoxypyridine       | -371.34       | 7.03         | -25.70                  | 1.51                   | -388.50        | 1.39                            | 3.77                |
| Pyridine                    | -371.87       | 6.99         | -25.75                  | 1.51                   | -389.12        | 1.40                            | 4.26                |
| 3-Bromopyridine             | -371.67       | 6.86         | -26.25                  | 1.51                   | -389.55        | 1.39                            | 4.35                |
| 3-Chloropyridine            | -371.11       | 6.60         | -27.22                  | 1.51                   | -390.12        | 1.39                            | 4.46                |
| 3,5-Dichloropyridine        | -370.75       | 6.36         | -28.10                  | 1.51                   | -390.97        | 1.38                            | 4.53                |
Table S28. Decomposition terms of calculated $^1J_{F,C}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $^1J_{F,C}$ coupling constants at the carbon β position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C$_8$F$_7$I--Base | Fermi Contact | Spin-Dipolar | Paramagnetic Spin-orbit | Diamagnetic Spin-orbit | $^1J_{F,C}$(Hz) |
|-------------------|---------------|--------------|-------------------------|------------------------|-----------------|
| –                 | -315.14       | 10.27        | -22.61                  | 1.74                   | -325.74         |
| 4-Dimethylaminopyridine | -311.45     | 10.87        | -20.91                  | 1.61                   | -319.88         |
| 2-Methylpyridine   | -312.53       | 10.74        | -21.30                  | 1.61                   | -321.47         |
| 2,6-Dimethylpyridine | -312.70      | 10.70        | -21.44                  | 1.61                   | -321.83         |
| 4-Methoxypyridine  | -312.16       | 10.77        | -21.20                  | 1.61                   | -320.98         |
| 3,5-Dimethylpyridine | -312.23      | 10.78        | -21.17                  | 1.61                   | -321.02         |
| Pyridine           | -312.69       | 10.75        | -21.28                  | 1.61                   | -321.62         |
| 3-Bromopyridine    | -313.33       | 10.67        | -21.52                  | 1.61                   | -322.58         |
| 3-Chloropyridine   | -313.39       | 10.68        | -21.51                  | 1.61                   | -322.62         |
| 3,5-Dichloropyridine | -313.38     | 10.61        | -21.70                  | 1.61                   | -323.35         |

Table S29. Calculated $^{19}$F coordination shifts ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free}}$) in ppm

| C$_8$F$_7$I--Base | $\Delta\delta_{\text{alpha}}$ | $\Delta\delta_{\text{beta}}$ |
|-------------------|-------------------------------|-------------------------------|
| –                 | 114.72                        | 49.42                         |
| 4-Dimethylaminopyridine | 88.71                        | 44.73                         |
| 2-Methylpyridine   | 93.33                         | 45.05                         |
| 2,6-Dimethylpyridine | 95.09                        | 45.17                         |
| 4-Methoxypyridine  | 91.69                         | 44.96                         |
| 3,5-Dimethylpyridine | 91.69                        | 44.92                         |
| Pyridine           | 92.93                         | 45.03                         |
| 3-Bromopyridine    | 95.42                         | 45.23                         |
| 3-Chloropyridine   | 95.40                         | 45.22                         |
| 3,5-Dichloropyridine | 97.54                        | 45.41                         |

Table S30. Natural occupation numbers of 2s and 2p orbitals of C atoms in the α-position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C$_8$F$_7$I--Base | 2s  | 2px | 2py | 2pz | $^1J_{F,C}$(Hz) | $\Delta$(2s) | $\Delta$(2p$_\sigma$)$^a$ |
|-------------------|-----|-----|-----|-----|----------------|--------------|-----------------|
| –                 | 1.031 | 1.077 | 0.780 | 0.638 | 401.43         | 0             | 0               |
| 4-Dimethylaminopyridine | 1.061 | 1.136 | 0.797 | 0.594 | -              | 388.16       | 0.03            | 0.032          |
| 4-Methoxypyridine  | 1.057 | 1.130 | 0.797 | 0.599 | -388.5         | 0.026        | 0.031           |
| Pyridine           | 1.054 | 1.125 | 0.802 | 0.597 | -              | 389.55       | 0.023           | 0.029          |
| 3-Bromopyridine    | 1.051 | 1.118 | 0.770 | 0.634 | -              | 390.12       | 0.02            | 0.027          |
| 3-Chloropyridine   | 1.051 | 1.120 | 0.792 | 0.609 | -              | 390.23       | 0.02            | 0.026          |

$^a$ We separated the contributions of the 2s and sum of 2p$_x$ + 2p$_y$ + 2p$_z$ = 3 x 2p$_\sigma$ as independent contributors.
Figure S13: Trends between calculated $^{1}J_{F,C}$ coupling constants and natural occupation of 2s and 2p$_{\sigma}$ orbitals of the $\alpha$-C-atom in iodoperfluorooctane on halogen bond formation with different pyridine bases.

Table S31. Natural occupation numbers of 2s and 2p orbitals of C atoms in the $\beta$-position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| CsF$_{17}$-I---Base | 2s   | 2px  | 2py  | 2pz  | $^{1}J_{F,C}$(Hz) | $\Delta$(2s) | $\Delta$(2p$_{\sigma}$)$_{a}$ |
|---------------------|------|------|------|------|------------------|-------------|--------------------------|
| -                   | 0.936| 1.061| 0.781| 0.621| -                | 325.74      | -                        |
| 4-Dimethylaminopyridine | 0.940| 1.046| 0.818| 0.602| -                | 319.88      | 0.004 0.003 |
| 4-Methoxypyridine    | 0.939| 1.047| 0.813| 0.604| -                | 321.47      | 0.003 0.001 |
| Pyridine             | 0.939| 1.054| 0.806| 0.604| -                | 321.62      | 0.003 0.001 |
| 3-Bromopyridine      | 0.938| 1.030| 0.783| 0.651| -                | 322.58      | 0.002 0.001 |
| 3-Chloropyridine     | 0.938| 1.042| 0.800| 0.622| -                | 322.62      | 0.002 0.001 |

$^a$ We separated the contributions of the 2s and sum of 2p$_{x}$ + 2p$_{y}$ + 2p$_{z}$ = 3 x 2p$_{\sigma}$ as independent contributors.
Figure S14: Trends between calculated $^{1}J_{F,C}$ coupling constants and natural occupation of 2s and 2p$_{\sigma}$ orbitals of the $\beta$-C-atom in iodoperfluorooctane on halogen bond formation with different pyridine bases.

Table S32: Bond distances ($R$), $^{1}J_{F,C}$-coupling constants ($J_{F,C}$), binding energies ($\Delta E$), electron densities ($\rho$) and energy densities ($H$) at the C-F and N--I bond critical point, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C$_2$F$_5$-I⋯Base | $R_{C-F}$ (Å) | $R_{C-I}$ (Å) | $R_{N-I}$ (Å) | ortho $^{1}J_{F,C}$ (Hz) | $\Delta E$ (kJ/mol) | $\rho_{C-F}$ (e/Å$^3$) | $H_{C-F}$ (h/Å$^3$) | $\rho_{N-I}$ (e/Å$^3$) | $H_{N-I}$ (h/Å$^3$) |
|-------------------|---------------|---------------|---------------|--------------------------|-------------------|---------------------|-------------------|---------------------|-------------------|
| –                 | 1.337         | 2.099         | -             | -312.60                  | -                 | 1.838               | -2.716            | -                   | -                 |
| NEt$_2$H          | 1.343         | 2.154         | 2.751         | -299.31                  | -35.72            | 1.806               | -2.649            | 0.227               | -0.014            |
| NBu$_2$H          | 1.343         | 2.150         | 2.758         | -298.99                  | -29.86            | 1.807               | -2.650            | 0.217               | -0.010            |
| Piperidine        | 1.344         | 2.158         | 2.720         | -298.51                  | -37.14            | 1.804               | -2.644            | 0.239               | -0.017            |
| N(sec-Bu)H$_2$    | 1.343         | 2.148         | 2.795         | -298.93                  | -31.46            | 1.808               | -2.652            | 0.203               | -0.006            |
| Pyrrolidine       | 1.343         | 2.155         | 2.741         | -299.03                  | -37.37            | 1.805               | -2.646            | 0.230               | -0.015            |
| N(iso-Pr)H$_2$    | 1.342         | 2.144         | 2.864         | -299.62                  | -34.05            | 1.810               | -2.656            | 0.181               | -0.003            |
| NEt(iso-Pr)H      | 1.343         | 2.149         | 2.816         | -299.64                  | -36.17            | 1.808               | -2.652            | 0.200               | -0.007            |
| N(tert-Bu)H$_2$   | 1.343         | 2.148         | 2.789         | -298.98                  | -31.65            | 1.808               | -2.652            | 0.205               | -0.007            |
| NBu$_3$H          | 1.343         | 2.151         | 2.782         | -300.08                  | -38.52            | 1.807               | -2.651            | 0.214               | -0.010            |
| NPr$_2$H          | 1.343         | 2.150         | 2.787         | -300.13                  | -37.40            | 1.808               | -2.652            | 0.211               | -0.009            |
| N(iso-Pr)$_3$H     | 1.340         | 2.121         | 3.163         | -303.98                  | -21.65            | 1.822               | -2.682            | 0.108               | 0.005             |
| NEt$_3$           | 1.342         | 2.137         | 2.941         | -301.67                  | -32.26            | 1.814               | -2.665            | 0.160               | 0.001             |
| NBu$_3$           | 1.343         | 2.152         | 2.794         | -299.67                  | -42.67            | 1.807               | -2.650            | 0.214               | -0.012            |
| NPr$_3$           | 1.337         | 2.102         | 3.413         | -307.48                  | -14.87            | 1.836               | -2.711            | 0.059               | 0.007             |
| C_xF_yI_z Base | sp^n_C | sp^n_F | sp^n_I | X_C | X_I | X_F | X_N |
|----------------|--------|--------|--------|-----|-----|-----|-----|
| –              | sp^{1.19} | sp^{2.49} | sp^{10.24} | -0.2931 | +0.2517 | -0.3075 | - |
| NEt_2H        | sp^{1.26} | sp^{2.50} | sp^{17.51} | -0.3156 | +0.2427 | -0.3183 | -0.6475 |
| NBu_2H        | sp^{1.26} | sp^{2.49} | sp^{17.61} | -0.3173 | +0.2451 | -0.3181 | -0.8159 |
| Piperidine     | sp^{1.27} | sp^{2.50} | sp^{18.43} | -0.3174 | +0.2424 | -0.3192 | -0.6411 |
| N(sec-Bu)H_2  | sp^{1.26} | sp^{2.50} | sp^{17.16} | -0.3163 | +0.2440 | -0.3177 | -0.8258 |
| Pyrrolidine    | sp^{1.27} | sp^{2.50} | sp^{17.79} | -0.3168 | +0.2412 | -0.3187 | -0.6529 |
| N(iso-Pr)H_2   | sp^{1.25} | sp^{2.50} | sp^{16.00} | -0.3138 | +0.2413 | -0.3169 | -0.6545 |
| NEt(iso-Pr)H   | sp^{1.26} | sp^{2.50} | sp^{16.64} | -0.3149 | +0.2418 | -0.3175 | -0.6498 |
| N(tert-Bu)H_2 | sp^{1.26} | sp^{2.50} | sp^{17.30} | -0.3163 | +0.2450 | -0.3177 | -0.8290 |
| NBu_3H        | sp^{1.26} | sp^{2.50} | sp^{16.91} | -0.3174 | +0.2437 | -0.3185 | -0.6420 |
| NPr_3H        | sp^{1.26} | sp^{2.50} | sp^{16.78} | -0.3157 | +0.2441 | -0.3177 | -0.6425 |
| N(iso-Pr)_3H   | sp^{1.22} | sp^{2.50} | sp^{14.89} | -0.3125 | +0.2438 | -0.3160 | -0.5289 |
| NBu_3         | sp^{1.26} | sp^{2.50} | sp^{16.57} | -0.3154 | +0.2421 | -0.3183 | -0.5087 |
| NPr_3         | sp^{1.19} | sp^{2.50} | sp^{10.53} | -0.2964 | +0.2496 | -0.3081 | +0.0637 |

*Due to the use of effective core potential for describing relativistic effects of I atom

Table S34. Decomposition terms of calculated $^1J_{C,I}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $^1J_{C,I}$ coupling constants at the ortho position as well as the second-order perturbation of the Fock Matrix between σ orbital of C-I and σ* orbital of C-F, calculated at the B3LYP-D3/aug-cc-pVTZ-pp.

| C_xF_yI_z Base | Fermi Contact | Spin-Dipolar | Paramagnetic Spin-orbit | Diamagnetic Spin-orbit | $^1J_{C,I}$(Hz) | C-I → C-F (kcal/mol) |
|----------------|---------------|--------------|-------------------------|------------------------|---------------|----------------------|
| –              | -310.78       | 3.96         | -6.94                   | 1.17                   | -312.60       | 1.33                 |
| NEt_2H        | -300.69       | 4.83         | -4.63                   | 1.18                   | -299.31       | 1.69                 |
| NBu_2H        | -300.28       | 4.82         | -4.69                   | 1.17                   | -298.99       | 1.68                 |
| Piperidine     | -300.13       | 4.90         | -4.46                   | 1.18                   | -298.51       | 1.73                 |
| N(sec-Bu)H_2  | -300.10       | 4.78         | -4.79                   | 1.18                   | -298.93       | 1.65                 |
| Pyrrolidine    | -300.53       | 4.87         | -4.54                   | 1.18                   | -299.03       | 1.70                 |
| N(iso-Pr)H_2   | -300.69       | 4.75         | -4.86                   | 1.18                   | -299.62       | 1.61                 |
| NEt(iso-Pr)H   | -300.87       | 4.79         | -4.75                   | 1.18                   | -299.64       | 1.63                 |
| N(tert-Bu)H_2 | -300.16       | 4.79         | -4.79                   | 1.18                   | -298.98       | 1.65                 |
| NBu_3H        | -301.36       | 4.81         | -4.71                   | 1.19                   | -300.08       | 1.60                 |
| NPr_3H        | -301.37       | 4.80         | -4.74                   | 1.18                   | -300.13       | 1.64                 |
| N(iso-Pr)_3H   | -303.80       | 4.41         | -5.77                   | 1.19                   | -303.98       | 1.42                 |
| NEt_3         | -302.31       | 4.63         | -5.17                   | 1.19                   | -301.67       | 1.51                 |
| NBu_3         | -300.99       | 4.81         | -4.68                   | 1.19                   | -299.67       | 1.66                 |
| NPr_3         | -305.94       | 4.04         | -6.77                   | 1.19                   | -307.48       | 1.31                 |
Table S35. Decomposition terms of calculated $^{1}J_{F,C}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $^{1}J_{F,C}$ coupling constants at the meta position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| CsF$_{5}$I...Base | Fermi Contact (Hz) | Spin-Dipolar (Hz) | Paramagnetic Spin-orbit (Hz) | Diamagnetic Spin-orbit (Hz) | $^{1}J_{F,C}$ (Hz) |
|------------------|--------------------|------------------|-----------------------------|-----------------------------|-------------------|
| –                | -320.78            | 4.86             | -2.50                       | 1.15                        | -317.26           |
| NEt$_{2}$H      | -319.81            | 5.55             | -0.64                       | 1.16                        | -313.75           |
| NBu$_{2}$H      | -319.18            | 5.53             | -0.67                       | 1.16                        | -313.16           |
| Piperidine      | -319.76            | 5.59             | -0.52                       | 1.16                        | -313.54           |
| N(sec-Bu)H$_{2}$| -319.06            | 5.52             | -0.71                       | 1.16                        | -313.10           |
| Pyrrolidine     | -319.76            | 5.56             | -0.61                       | 1.16                        | -313.65           |
| N(iso-Pr)H$_{2}$| -319.92            | 5.48             | -0.83                       | 1.16                        | -314.11           |
| NEt(iso-Pr)H     | -319.96            | 5.51             | -0.74                       | 1.16                        | -314.04           |
| N(tert-Bu)H$_{2}$| -319.20            | 5.52             | -0.72                       | 1.16                        | -313.25           |
| NBu$_{2}$H       | -319.99            | 5.53             | -0.70                       | 1.16                        | -314.00           |
| NPR$_{2}$H       | -319.92            | 5.52             | -0.72                       | 1.16                        | -313.96           |
| N(iso-Pr)$_{3}$H | -320.10            | 5.24             | -1.48                       | 1.16                        | -315.18           |
| NEt$_{3}$        | -320.20            | 5.40             | -1.05                       | 1.16                        | -314.69           |
| NBu$_{3}$        | -320.50            | 5.53             | -0.71                       | 1.16                        | -314.52           |
| NPR$_{3}$        | -319.62            | 4.89             | -2.43                       | 1.16                        | -316.00           |

Table S36. Decomposition terms of calculated $^{1}J_{F,C}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $^{1}J_{F,C}$ coupling constants at the para position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| CsF$_{5}$I...Base | Fermi Contact (Hz) | Spin-Dipolar (Hz) | Paramagnetic Spin-orbit (Hz) | Diamagnetic Spin-orbit (Hz) | $^{1}J_{F,C}$ (Hz) |
|------------------|--------------------|------------------|-----------------------------|-----------------------------|-------------------|
| –                | -320.92            | 4.12             | -5.45                       | 1.15                        | -321.11           |
| NEt$_{2}$H      | -317.09            | 4.92             | -2.76                       | 1.15                        | -313.76           |
| NBu$_{2}$H      | -317.03            | 4.92             | -2.81                       | 1.15                        | -313.77           |
| Piperidine      | -316.91            | 4.99             | -2.59                       | 1.15                        | -313.36           |
| N(sec-Bu)H$_{2}$| -316.92            | 4.90             | -2.86                       | 1.15                        | -313.73           |
| Pyrrolidine     | -317.03            | 4.96             | -2.70                       | 1.15                        | -313.62           |
| N(iso-Pr)H$_{2}$| -317.22            | 4.86             | -2.97                       | 1.15                        | -314.18           |
| NEt(iso-Pr)H     | -317.40            | 4.90             | -2.88                       | 1.15                        | -314.23           |
| N(tert-Bu)H$_{2}$| -316.94            | 4.90             | -2.87                       | 1.15                        | -313.75           |
| NBu$_{2}$H       | -317.63            | 4.92             | -2.82                       | 1.15                        | -314.39           |
| NPR$_{2}$H       | -317.63            | 4.90             | -2.86                       | 1.15                        | -314.44           |
| N(iso-Pr)$_{3}$H | -318.34            | 4.57             | -3.93                       | 1.15                        | -316.56           |
| NEt$_{3}$        | -317.66            | 4.77             | -3.28                       | 1.15                        | -315.02           |
| NBu$_{3}$        | -317.84            | 4.92             | -2.80                       | 1.15                        | -314.56           |
| NPR$_{3}$        | -319.29            | 4.15             | -5.40                       | 1.15                        | -319.39           |
### Table S37. Calculated $^{19}$F coordination shifts ($\Delta \delta = \delta_{\text{complex}} - \delta_{\text{free}}$) in ppm

| C$_6$F$_5$I---Base | $\Delta \delta_{\text{ortho}}$ | $\Delta \delta_{\text{meta}}$ | $\Delta \delta_{\text{para}}$ |
|-------------------|-----------------|-----------------|-----------------|
| –                 | 43.55           | 2.48            | 10.50           |
| NEt$_2$H         | 40.29           | 0.70            | 6.51            |
| NBuH$_2$         | 40.00           | 0.57            | 6.53            |
| Piperidine       | 40.09           | 0.53            | 6.34            |
| N(sec-Bu)H$_2$   | 39.94           | 0.62            | 6.44            |
| Pyrroldidine     | 40.05           | 0.59            | 6.57            |
| N(iso-Pr)H$_2$   | 40.12           | 0.88            | 6.72            |
| NEt(iso-Pr)H$_2$ | 40.16           | 0.82            | 6.62            |
| N(tert-Bu)H$_2$  | 40.04           | 0.66            | 6.51            |
| NBu$_2$H         | 40.53           | 0.75            | 6.76            |
| NPr$_2$H         | 40.35           | 0.76            | 6.78            |
| N(iso-Pr)$_3$H   | 42.62           | 1.65            | 8.56            |
| NEt$_3$          | 41.25           | 1.20            | 7.43            |
| NBu$_3$          | 41.00           | 0.88            | 6.99            |
| NPr$_3$          | 43.37           | 2.86            | 10.87           |

### Table S38. Bond distances (R), $^{19}$F-$^{13}$C-$^1$J-coupling constants ($J_{CF}$), binding energies ($\Delta E$), electron densities ($\rho$) and energy densities ($H$) at the C-F and N---I bond critical point, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C$_6$F$_5$I---Base | $R_{CF}$ (Å) | $R_{CI}$ (Å) | $R_{O-I}$ (Å) | $J_{CF}$ (Hz) | $\Delta E$ (kJ/mol) | $\rho_{CF}$ (e/Å$^3$) | $H_{CF}$ (h/Å$^3$) | $\rho_{N-I}$ (e/Å$^3$) | $H_{N-I}$ (h/Å$^3$) |
|-------------------|--------------|--------------|--------------|--------------|------------------|----------------|----------------|----------------|----------------|
Table S39. Decomposition terms of calculated perturbation of the Fock Matrix between C,F,N, and I atoms, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C,F,N-I-Base          | spⁿ C | spⁿ F | spⁿ C | spⁿ I | X_C  | X_F  | X_I  | X_O  |
|------------------------|-------|-------|-------|-------|------|------|------|------|
|                        | sp¹.¹⁹| sp².⁴⁹| sp².⁹⁶| sp¹.²⁴| -0.2931| +0.2517| -0.3075| -     |
| Pyridine-N-oxide       | sp³.¹⁴| sp².⁴⁹| sp².⁸²| sp¹.¹⁷| -0.3141| +0.2656| -0.3144| -0.6127|
| Trimethylamin-N-oxide  | sp³.²⁷| sp².⁵⁰| sp².⁷⁷| sp¹.³³| -0.3215| +0.2686| -0.3188| -0.7428|
| N,N-Dimethylpyrrolidine-2-one | sp³.²³| sp².⁴⁹| sp².⁸²| sp¹.⁵⁸| -0.3121| +0.2710| -0.3135| -0.7391|
| Triphenylphosphineoxide| sp³.³³| sp².⁷⁹| sp¹.⁷⁵| -0.3133| +0.2842| -0.3136| -1.1300|
| Pyridoline-N-oxide     | sp³.²³| sp².⁴⁹| sp².⁸²| sp¹.⁶⁴| -0.3131| +0.2662| -0.3135| -0.6797|
| Dimethylsulfoxide      | sp³.²³| sp².⁴⁹| sp².⁸¹| sp¹.⁵⁸| -0.3127| +0.2749| -0.3135| -1.0262|
| Dimethylformamide      | sp³.²²| sp².⁸³| sp¹.²⁶| -0.3092| +0.2725| -0.3121| -0.6932|
| Acetophenone           | sp³.²¹| sp².⁸⁵| sp¹.⁹ⁱ| -0.3060| +0.2716| -0.3108| -0.6032|
| Beroaphenone           | sp³.²¹| sp².⁸⁴| sp¹.³¹| -0.3081| +0.2726| -0.3115| -0.5942|
| 4-Methylpyrindine-N-oxide| sp³.²³| sp².⁴⁹| sp².⁸¹| sp¹.⁶⁹| -0.3154| +0.2659| -0.3151| -0.6256|

*Due to the use of effective core potential for describing relativistic effects of I atom*

Table S40. Decomposition terms of calculated ¹J_{C,F} coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total ¹J_{C,F} coupling constants at the ortho position as well as the second-order perturbation of the Fock Matrix between σ-orbital of C-I and σ* orbital of C-F, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C,F,N-I-Base          | Fermi Contact | Spin-Dipolar | Paramagnetic Spin-orbit | Diamagnetic Spin-orbit | ¹J_{C,F}(Hz) | C-I → C-F (kcal/mol) |
|------------------------|---------------|--------------|--------------------------|------------------------|--------------|----------------------|
|                        | -310.78       | 3.96         | -6.94                    | 1.17                   | -312.60      | 1.33                 |
| Pyridine-N-oxide       | -302.78       | 4.51         | -5.52                    | 1.18                   | -302.60      | 1.51                 |
| Trimethylamin-N-oxide  | -300.44       | 4.88         | -4.49                    | 1.18                   | -298.88      | 1.67                 |
| N,N-Dimethylpyrrolidine-2-one | -303.44 | 4.45      | -5.67                    | 1.18                   | -303.47      | 1.47                 |
| Triphenylphosphineoxide| -302.14       | 4.47         | -5.62                    | 1.20                   | -302.10      | 1.46                 |
| Pyridoline-N-oxide     | -303.47       | 4.46         | -5.64                    | 1.18                   | -303.46      | 1.47                 |
| Dimethylsulfoxide      | -302.64       | 4.43         | -5.73                    | 1.18                   | -302.76      | 1.48                 |
| Dimethylformamide      | -304.39       | 4.33         | -6.01                    | 1.18                   | -304.89      | 1.42                 |
| Acetophenone           | -304.99       | 4.22         | -6.30                    | 1.19                   | -305.88      | 1.39                 |
| Beroaphenone           | -304.19       | 4.28         | -6.15                    | 1.19                   | -304.86      | 1.41                 |
| 4-Methylpyrindine-N-oxide| -302.89      | 4.59         | -5.28                    | 1.18                   | -302.40      | 1.53                 |

Table S41. Decomposition terms of calculated ¹J_{C,F} coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total ¹J_{C,F} coupling constants at the meta position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C,F,N-I-Base          | Fermi Contact | Spin-Dipolar | Paramagnetic Spin-orbit | Diamagnetic Spin-orbit | ¹J_{C,F}(Hz) |
|------------------------|---------------|--------------|--------------------------|------------------------|--------------|
|                        | -320.78       | 4.86         | -2.50                    | 1.15                   | -317.26      |
| Pyridine-N-oxide       | -318.79       | 5.35         | -1.15                    | 1.16                   | -313.43      |
| Trimethylamin-N-oxide  | -319.13       | 5.62         | -0.43                    | 1.16                   | -312.78      |
| N,N-Dimethylpyrrolidine-2-one | -318.76 | 5.31      | -1.27                    | 1.16                   | -313.57      |
| Triphenylphosphineoxide| -318.61       | 5.35         | -1.15                    | 1.17                   | -313.26      |
| Pyridoline-N-oxide     | -318.89       | 5.27         | -1.37                    | 1.16                   | -313.83      |
| Dimethylsulfoxide      | -318.53       | 5.32         | -1.23                    | 1.16                   | -313.29      |
| Dimethylformamide      | -318.79       | 5.21         | -1.54                    | 1.16                   | -313.97      |
| Acetophenone           | -318.86       | 5.14         | -1.73                    | 1.16                   | -314.29      |
| Beroaphenone           | -318.67       | 5.20         | -1.56                    | 1.16                   | -313.87      |
| 4-Methylpyrindine-N-oxide| -318.88      | 5.40         | -1.01                    | 1.16                   | -313.31      |
Table S42. Decomposition terms of calculated $^{1}J_{F,C}$ coupling constants into Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbit (DSO), and the total $^{1}J_{F,C}$ coupling constants at the para position, calculated at the B3LYP-D3/aug-cc-pVTZ-pp

| C$_{6}$F$_{5}$-I...Base         | Fermi Contact | Spin-Dipolar | Paramagnetic Spin-orbit | Diamagnetic Spin-orbit | $^{1}J_{F,C}$(Hz) |
|--------------------------------|---------------|--------------|--------------------------|------------------------|------------------|
| -                              | -320.92       | 4.12         | -5.45                    | 1.15                   | -321.11          |
| Pyridine-N-oxide               | -318.05       | 4.69         | -3.49                    | 1.15                   | -315.70          |
| Trimethylamin-N-oxide          | -317.20       | 5.03         | -2.32                    | 1.15                   | -313.34          |
| N,N-Dimethylpyrroldine-2-one   | -318.17       | 4.64         | -3.64                    | 1.15                   | -316.02          |
| Triphenylphosphineoxide        | -317.95       | 4.68         | -3.44                    | 1.15                   | -315.55          |
| Pyrrolidine-N-oxide            | -318.07       | 4.59         | -3.81                    | 1.15                   | -316.14          |
| Dimethylsulfoxide              | -318.16       | 4.64         | -3.62                    | 1.15                   | -315.98          |
| Dimethylformamide              | -318.67       | 4.51         | -4.05                    | 1.15                   | -317.07          |
| Acetophenone                   | -318.70       | 4.43         | -4.35                    | 1.15                   | -317.47          |
| Benzophenone                   | -318.58       | 4.50         | -4.10                    | 1.15                   | -317.02          |
| 4-Methylpyridine-N-oxide       | -317.88       | 4.76         | -3.22                    | 1.15                   | -315.19          |

Table S43. Calculated $^{19}$F coordination shifts ($\Delta \delta = \delta_{(complex)} - \delta_{(free)}$) in ppm

| C$_{6}$F$_{5}$-I...Base         | $\Delta \delta_{ortho}$ | $\Delta \delta_{meta}$ | $\Delta \delta_{para}$ |
|--------------------------------|--------------------------|------------------------|------------------------|
| -                              | 43.55                    | 2.48                   | 10.50                  |
| Pyridine-N-oxide               | 41.48                    | 0.77                   | 7.44                   |
| Trimethylamin-N-oxide          | 39.98                    | 0.21                   | 5.52                   |
| N,N-Dimethylpyrroldine-2-one   | 41.70                    | 1.05                   | 7.72                   |
| Triphenylphosphineoxide        | 41.58                    | 0.87                   | 7.39                   |
| Pyrrolidine-N-oxide            | 41.42                    | 1.26                   | 8.01                   |
| Dimethylsulfoxide              | 41.58                    | 0.83                   | 7.59                   |
| Dimethylformamide              | 42.10                    | 1.33                   | 8.35                   |
| Acetophenone                   | 42.60                    | 1.65                   | 8.89                   |
| Benzophenone                   | 42.33                    | 1.42                   | 8.49                   |
| 4-Methylpyridine-N-oxide       | 41.16                    | 0.74                   | 6.98                   |
4.1. Decomposition of the computed scalar couplings into FC, SD, PSO and DSO terms

**Figure S15: Calculated $^1J_{\text{ortho-F,C}}$ couplings vs it’s FC, SD, PSO, DSO contributions for Lewis base-IC$_6$F$_5$ adducts.**
Figure S16: Calculated $^1J_{\text{meta-FC}}$ couplings vs it’s FC, SD, PSO, DSO contributions for Lewis base-IC$_6$F$_5$ adducts.
Figure S17: Calculated $^1J_{p-F,C}$ couplings vs its FC, SD, PSO, DSO contributions for Lewist base-$IC_6F_5$ adducts.
Figure S18: Calculated $J_{\alpha,F,C}$ couplings vs its FC, SD, PSO, DSO contributions for Lewis base-IC$_8$F$_{17}$ adducts.
Figure S19: Calculated $^1J_{\beta-F,C}$ couplings vs its FC, SD, PSO, DSO contributions for Lewis base-IC$_6$F$_{17}$ adducts.

Figure S20: Calculated $^1J_{\text{ortho-F,C}}$ couplings vs calculated $E_{\text{XB}}$ and $\rho_{N..I}$ for Lewis base-IC$_6$F$_5$ adducts.
Figure S21: Calculated $^1J_{\alpha\beta-\gamma\delta}$ couplings vs calculated $E_{XB}$ and $\rho_{N..I}$ for different pyridine-IC$_{CF}_2$ adducts (left with ortho-substituted pyridines (2,6-dimethylpyridine and 2-picoline), right without those.)
Figure S22: Calculated $^1J_{o-F,C}$ couplings vs calculated $E_{XB}$ and $\rho_{N..I}$ for pyridine-IC$_6$F$_5$ adducts (left with ortho-substituted pyridines (2,6-dimethylpyridine and 2-picoline), right without those.

Figure S23: Calculated $^1J_{o,F,C}$ couplings vs calculated $\rho_{N..I}$ for Lewis base-IC$_6$F$_5$ adducts for ortho, meta and para-F.
Figure S24: The calculated $^{1}J_{F,C}$ couplings vs calculated $\rho_{N,I}$ for Lewis base-IC$_{6}$F$_{5}$ adducts for alpha and beta-F.

The calculated $^{1}J_{F,C}$ vs $\rho_{N,I}$ agree with the experimentally observed trends in $\Delta^{1}J_{F,C}$ vs $pK_{B12}^{2}$ for IC$_{6}$F$_{5}$, thus $^{1}J_{F,C}$ ortho $>$ para $>$ meta (Figure 2 and Figure S23). For IC$_{8}$F$_{17}$, the $\Delta^{1}J_{F,C}$ follows the trend alpha$>$beta (Figure 4 and Figure S24). We observed good correlations for $^{1}J_{F,C}$ for the $\alpha$-F and $\beta$-F of IC$_{6}$F$_{5}$, and for the ortho-F and para-F of IC$_{6}$F$_{5}$, while weak correlation for the meta-F of IC$_{6}$F$_{5}$ in both the experimental ($R^{2}$=0.13 with $pK_{B12}^{2}$) and calculated ($R^{2}$=0.40 with $\rho_{N,I}$) datasets.

5 Optimized Structures Obtained at the B3LYP-D3/aug-cc-pVTZ-pp Level of Theory

Pentafluoriodobenzene (C$_{6}$F$_{5}$I)

|  |  |  |
|---|---|---|
| I  | -2.30648000 | 0.00000000 | 0.00000000 |
| C  | -0.20705400 | 0.00000200 | -0.00000200 |
| C  | 0.50642600 | 1.19249200 | -0.00000200 |
| C  | 0.50642800 | -1.19249600 | -0.00000400 |
| C  | 1.89344600 | 1.19960400 | -0.00000200 |
| C  | 1.89344000 | -1.19960500 | -0.00000100 |
| C  | 2.58917700 | 0.00000200 | 0.00000000 |
| F  | -0.12543800 | -2.37041800 | 0.00000000 |
| F  | 2.56206300 | -2.35549100 | 0.00000100 |
| F  | 3.92144000 | 0.00000060 | 0.00000200 |
| F  | 2.56205700 | 2.35549600 | 0.00000100 |
| F  | -0.12543000 | 2.37042100 | 0.00000000 |

C$_{6}$F$_{5}$I$\cdots$4-Dimethylaminopyridine

|  |  |  |
|---|---|---|
| I  | -0.20435100 | 0.00000400 | -0.00004300 |
| C  | 3.22238500 | 1.13401200 | -0.11049700 |
| C  | 4.60000000 | 1.19274500 | -0.11634000 |
| C  | 5.35277500 | -0.00000300 | 0.00000220 |
| C  | 4.59998700 | -1.19274700 | 0.11633600 |
| C  | 3.22237300 | -1.13400700 | 0.11041000 |
| N  | 2.51876700 | 0.00000400 | -0.00006400 |
| H  | 2.64543800 | 2.04672000 | -0.19929800 |
| H  | 5.07712700 | 2.15461500 | -0.21020900 |
| H  | 5.07710300 | -2.15462000 | 0.21023000 |
2-Methylpyridine

\[
\begin{array}{cccc}
H & 2.64541600 & -2.04671200 & 0.19917400 \\
C & -2.35213200 & 0.00000200 & -0.00001300 \\
C & -3.07498200 & -1.18388400 & -0.04014500 \\
C & -3.07498600 & 1.18388500 & 0.04014200 \\
C & -4.46200000 & -1.19751900 & -0.04060100 \\
C & -4.46200300 & 1.19751400 & 0.04064800 \\
F & -2.44617700 & 2.36983500 & 0.08052400 \\
F & -5.13304700 & -2.35517900 & -0.08006200 \\
F & -2.44617000 & 2.36983200 & -0.08055100 \\
N & 6.70984600 & -0.00000400 & 0.00006500 \\
C & 7.44345100 & -1.25170100 & 0.12306100 \\
H & 8.50807600 & -1.04426900 & 0.09975800 \\
H & 7.21580800 & 1.75752200 & -1.06431900 \\
H & 7.21163300 & 1.93316600 & 0.69909500 \\
H & 8.50808300 & 1.04425900 & -0.09951700 \\
\end{array}
\]

\( \text{C}_6\text{F}_3\text{I} \cdots \text{2-Methylpyridine} \)

\[
\begin{array}{cccc}
i & -0.61360800 & -0.02975600 & -0.00084000 \\
c & -4.25743700 & 0.88353100 & 0.01252300 \\
c & -5.64150100 & 0.70873200 & 0.01098000 \\
c & -6.17001000 & -0.57419600 & -0.00692700 \\
c & -5.30361400 & -1.65948200 & -0.02296800 \\
c & -3.94016200 & -1.40432600 & -0.02021300 \\
n & -3.42916200 & -0.17163400 & -0.00300500 \\
h & -7.24103100 & -0.72389900 & -0.00833500 \\
h & -6.29101700 & 1.57243000 & 0.02372900 \\
h & -5.66867200 & -2.67599100 & -0.03720400 \\
h & -3.22351000 & -2.21660500 & -0.03222200 \\
c & 1.52168200 & -0.02872300 & -0.00051100 \\
c & 2.24429500 & -1.21395800 & 0.00687000 \\
c & 2.24141000 & 1.15828200 & -0.00765700 \\
c & 3.63131400 & -1.22455900 & 0.00718700 \\
c & 3.62836700 & 1.17239800 & -0.00751500 \\
c & 4.32688600 & -0.02522700 & -0.00005000 \\
f & 1.61038400 & 2.34227700 & -0.01501600 \\
f & 4.29737100 & 2.33104200 & -0.01453100 \\
f & 5.66161500 & -0.02358400 & 0.00017300 \\
f & 4.30321900 & -2.38152200 & 0.01443100 \\
f & 1.61634600 & 2.39954100 & 0.01403000 \\
c & -3.62883700 & 2.24619000 & 0.03145600 \\
h & -2.99242100 & 2.35785400 & 0.91024500 \\
h & -2.99231500 & 2.38217900 & -0.84381000 \\
h & -4.38044500 & 3.03251300 & 0.04232400 \\
\end{array}
\]
| Compound | Coordinates |
|----------|-------------|
| C₆F₅I–2,6-Dimethylpyridine | I: -0.46438900, -0.00000400, -0.00010800; C: -4.03998200, 1.16035700, 0.05540300; C: -5.43343300, 1.19383900, 0.05540300; C: -6.13626100, -0.00000200, 0.00028800; C: -5.43344000, -1.19383800, -0.05668600; C: -4.03998900, -1.16034600, -0.05545400; N: -3.36887400, 0.00000800, -0.00012200; H: -7.21794100, -0.00000700, 0.00044800; H: -5.95043000, 2.14159200, 0.10211300; H: -5.95044400, -2.14159400, -0.10160500; C: 1.66646500, -0.00000400, -0.00002200; C: 2.38699200, -1.18612600, 0.03754100; C: 2.38699100, 1.18612100, -0.03751900; C: 3.77396600, -1.19802100, 0.03804800; C: 3.77396600, 1.19802200, -0.03789600; C: 4.47086500, 0.00000000, 0.00010900; F: 1.75727000, 2.36973600, -0.07504300; F: 4.44413000, 2.35505400, -0.07468800; F: 5.80542800, 0.00000000, 0.00017100; F: 4.44415000, -2.35505000, 0.07490500; F: 1.75727100, -2.36974200, 0.07500700; C: -3.22965600, 2.42335600, 0.11580500; H: -2.58131300, 2.41918200, 0.99274400; H: -2.58297800, 2.50412800, -0.75866200; H: -3.86897000, 3.30253800, 0.15907700; C: -3.22967600, -2.42334200, -0.11608500; H: -2.58136300, -2.41903800, -0.99304300; H: -2.58296900, -2.50425600, 0.75834900; H: -3.86892700, -3.30251100, -0.15946200 | |
| C₆F₅I–4-Methoxypyridine | I: -0.09648900, -0.06588200, 0.00002100; C: -3.58779900, 0.97939000, 0.00009200; C: -4.97524700, 1.00888900, 0.00006800; C: -5.66062500, -0.20792500, -0.00002900; C: -4.91265300, -1.39032300, -0.00009500; C: -3.53572100, -1.30536600, -0.00006400; N: -2.86850600, -0.14280900, 0.00002800; H: -3.02995800, 1.90771800, 0.00016600; H: -5.48619500, 1.95806800, 0.00012400; H: -5.41413000, -2.34685200, -0.00017100; H: -2.93270100, -2.20452900, -0.00011500; C: 2.04134100, 0.00373300, 0.00000500; C: 2.80235200, -1.15710200, 0.00001800; C: 2.72314200, 1.21278600, -0.00001800; C: 4.18902900, -1.12337800, 0.00000600; C: 4.10890900, 1.27205700, -0.00002900 |
C     4.84577500    0.09765300   -0.00001700
F     2.05460400    2.37650800   -0.00003000
F     4.74019600    2.45198000   -0.00005200
F     6.17998800    0.14222800   -0.00002800
F     4.89808000   -2.25825300    0.00001800
F     2.21303700   -2.36283500    0.00004000
C    -7.81052100    0.84041800   -0.00000100
H    -7.62641000    1.43905200    0.89316400
H    -7.62637700    1.43916800   -0.89308200
H    -8.83783300    0.49080500   -0.00004300
O    -6.99924200   -0.34045900   -0.00006400
C
6
F
5
I
\ldots
3,5-Dimethylpyridine
I    -0.24539600   -0.00002400   -0.00004700
C    -3.69762900    1.14471700    0.08989300
C    -5.08949300    1.20780500    0.09444200
C    -5.77615000    0.00003200    0.00006300
C    -5.08954600   -1.20776700   -0.09438000
C    -3.69768000   -1.14473200   -0.08995600
N    -3.02018900   -0.00002000   -0.00006200
H    -6.86005300    0.00005200    0.00011400
H    -3.10518400    2.04934200    0.16122200
H    -3.10527500   -2.04937900   -0.16133800
C     1.89374700   -0.00000800   -0.00001600
C     2.61546900    1.18393100   -0.06370200
C     2.61545200   -1.18393100    0.06370200
C     4.00246800   -1.19665600    0.06441200
C     4.00245100    1.19667400   -0.06436600
C     4.69960700    0.00001400    0.00003600
F     1.98619200    2.36758100   -0.12761500
F     4.67309500    2.35296100   -0.12680400
F     6.03456600    0.00002600    0.00006200
F     4.67312800   -2.35293200    0.12687800
F     1.98622500   -2.36759600    0.12758800
C    -5.81450700    2.52072900    0.19269600
H    -6.41264200    2.70146800   -0.70204400
H    -6.49606900    2.52603900    1.04453400
H    -5.12031800    3.35163400    0.30812700
C    -5.81462000   -2.52066400   -0.19256800
H    -5.12047400   -3.35159500   -0.30861000
H    -6.41268200   -2.70137800    0.70222600
H    -6.49625900   -2.52594800   -1.04434500

\textbf{C}_6\textbf{F}_3\textbf{I}\ldots\text{3,5-Dimethylpyridine}
I    -0.24539600   -0.00002400   -0.00004700
C    -3.69762900    1.14471700    0.08989300
C    -5.08949300    1.20780500    0.09444200
C    -5.77615000    0.00003200    0.00006300
C    -5.08954600   -1.20776700   -0.09438000
C    -3.69768000   -1.14473200   -0.08995600
N    -3.02018900   -0.00002000   -0.00006200
H    -6.86005300    0.00005200    0.00011400
H    -3.10518400    2.04934200    0.16122200
H    -3.10527500   -2.04937900   -0.16133800
C     1.89374700   -0.00000800   -0.00001600
C     2.61546900    1.18393100   -0.06370200
C     2.61545200   -1.18393100    0.06370200
C     4.00246800   -1.19665600    0.06441200
C     4.00245100    1.19667400   -0.06436600
C     4.69960700    0.00001400    0.00003600
F     1.98619200    2.36758100   -0.12761500
F     4.67309500    2.35296100   -0.12680400
F     6.03456600    0.00002600    0.00006200
F     4.67312800   -2.35293200    0.12687800
F     1.98622500   -2.36759600    0.12758800
C    -5.81450700    2.52072900    0.19269600
H    -6.41264200    2.70146800   -0.70204400
H    -6.49606900    2.52603900    1.04453400
H    -5.12031800    3.35163400    0.30812700
C    -5.81462000   -2.52066400   -0.19256800
H    -5.12047400   -3.35159500   -0.30861000
H    -6.41268200   -2.70137800    0.70222600
H    -6.49625900   -2.52594800   -1.04434500

\textbf{C}_6\textbf{F}_3\textbf{I}\ldots\text{Pyridine}
I     0.77469200    0.00000200    0.00000200
C     4.25396600    1.14692800   -0.03376600
C     5.64181200    1.19550300   -0.03523700
C     6.34877300   -0.00003000   -0.00005000
C     5.64180900   -1.19550700    0.03523000

S49
C  4.25396300  -1.14692800  0.03376800
N  3.57077900  0.00000100  0.00000200
H  7.42996500  2.05546000  -0.06050600
H  6.15021900  2.14839300  -0.06334900
H  6.15021300 -2.14839900  0.06334000
H  3.66545400  2.05546000  -0.06050600
H  6.15021300  2.14839300  -0.06334900
H  3.66544900 -2.05545800  0.06051000
C  -1.36095800  0.00000000  0.00000100
C  -2.08226800 -1.18604700  -0.00750300
C  -2.08227000  1.18604700  0.00750300
C  -3.46926200 -1.19843700  -0.00759400
C  -3.46926400  1.19843500  0.00759200
C  -4.16635200  0.00000200  -0.00000200
F  -1.45286800  2.37090800  0.01501100
F  -4.13965200  2.35628100  0.01496000
F  -5.50109300  0.00000300  -0.00000300
F  -4.13964800 -2.35628500  -0.01496300
F  -1.45286500 -2.37090700  -0.01501000

3-Bromopyridine

C  3.28030000  0.07896200  0.00001000
C  4.65131600  0.14604000  0.00000300
C  5.13832200 -1.44470400  -0.00003600
C  4.21790000 -2.48437300  -0.00005500
C  2.86307200 -2.18162000  -0.00004100
N  2.40723100  0.09736600  0.00000800
H  6.20056800 -1.63901800  -0.00004600
H  2.87823100  1.08313300  0.00003600
H  4.54812700  3.51287500  0.00008100
H  2.11652100 -2.96498700  -0.00005500
C  -2.47637100 -0.08562000  0.00000000
C  -3.40187600 -1.04353100  0.00001900
C  -2.96706400  1.29027400  -0.00001800
C  -4.76753000 -0.80192000  0.00002000
C  -4.32849100  1.55570500  -0.00001700
C  -5.23306700  0.50491700  0.00002000
F  -2.13098000  2.33860100  -0.00003700
F  -4.77542800  2.81634800  -0.00003400
F  -6.54488000  0.74924400  0.00000300
F  -5.63837300 -1.81634000  0.00003900
F  -2.99935700 -2.32270200  0.00003600
Br  5.84793100  1.33993600  0.00002500

3-Chloropyridine

I  -0.38357600  -0.39959300  -0.00000100
C  3.28030000  0.07896200  0.00001000
C  4.65131600 -1.14604000  -0.00003600
C  5.13832200 -1.44470400  -0.00003600
C  4.21790000 -2.48437300  -0.00005500
C  2.86307200 -2.18162000  -0.00004100
N  2.40723100  0.09736600  0.00000800
H  6.20056800 -1.63901800  -0.00004600
H  2.87823100  1.08313300  0.00003600
H  4.54812700 -3.51287500  -0.00008100
H  2.11652100 -2.96498700  -0.00005500
C  -2.47637100 -0.08562000  0.00000000
C  -3.40187600 -1.04353100  0.00001900
C  -2.96706400  1.29027400  -0.00001800
C  -4.76753000 -0.80192000  0.00002000
C  -4.32849100  1.55570500  -0.00001700
C  -5.23306700  0.50491700  0.00002000
F  -2.13098000  2.33860100  -0.00003700
F  -4.77542800  2.81634800  -0.00003400
F  -6.54488000  0.74924400  0.00000300
F  -5.63837300 -1.81634000  0.00003900
F  -2.99935700 -2.32270200  0.00003600
Br  5.84793100  1.33993600  0.00002500

C,F,I---3-Chloropyridine

I  -0.19175600  -0.25117100  0.00003000
C  -3.81263300  0.49472300  -0.00009100
C  -5.19629600  0.36904100  -0.00006500
C  -5.77574500  -0.89082500  0.00013600
C  -4.93253300  -1.99341400  0.00030400
C  -3.55915700  -1.78929300  0.00026600
N  -3.01408400  -0.57102000  0.00007200
H  -6.84984600  -1.00302800  0.00015800
H  -3.34424800  1.46986500  -0.00024500
H  -5.33558800  -2.99553200  0.00046300
H  -2.87110400  -2.62441600  0.00039300
C   1.92384300  -0.01271700  0.00000600
C   2.77274400  -1.11139500  -0.00010700
C   2.50649600   1.24753900  0.00010100
C   4.15229200  -0.96751900  -0.00012600
C   3.88341200   1.41466200  0.00008400
C   4.71035000   0.30173300  -0.00003000
F   1.74777800   2.35317400  0.00021300
F   4.41958200   2.64004800  0.00017600
F   6.03631700   0.45149500  -0.00004700
F   4.94798700  -2.04269100  -0.00023600
F   2.27948900  -2.35414000  -0.00020200
Cl  -5.51232900   2.71645200  -0.00082500

C₆F₅I−3,5-Dichloropyridine
I   0.25535000  0.00007600  0.00000500
C  -3.29253100  1.15122800  -0.00035200
C  -4.68196400  1.18338900  -0.00036200
C  -5.40405000  -0.00006600  -0.00000300
C  -4.68186100  -1.18345800  0.00035800
C  -3.29243100  -1.15117600  0.00035200
N  -2.62481500  0.00005500  0.00000100
H  -6.48301200  -0.00011300  -0.00000400
H  -2.71477100  2.06506700  -0.00063100
H  -2.71459200  -2.06496500  0.00063200
C   2.37934800  0.00002500  0.00000400
C   3.09892800  -1.18764500  -0.00044500
C   3.09898800   1.18766100  0.00044800
C   4.48589800  -1.19876700  -0.00045300
C   4.48595800   1.19871100  0.00044800
C   5.18269300  -0.00004600  -0.00000500
F   2.46893500  2.37074000  0.00089500
F   5.15580200  2.35605900  0.00088200
F   6.51675200  -0.00007800  -0.00000800
F   5.15568200  -2.35615000  -0.00089100
F   2.46881600  -2.37069400  -0.00088800
Cl  -5.51232900   2.71645200  -0.00082500
Cl  -5.51209400  -2.71659400  0.00081900

1-Iodoheptadecafluorooctane (C₈F₁₇I)
C   5.70116600  -0.27311400  0.21789800
C   4.37915700   0.17505500  -0.48909500
C   3.07591900  -0.32417500  0.22418500
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 1.78848100 | 0.44684300 | -0.23909700|
| C       | 0.45936500 | -0.31327100| 0.11216400 |
| C       | -0.80790100| 0.61601700 | 0.06242200 |
| C       | -2.15420200| -0.19082300| -0.04473700|
| C       | -3.42098800| 0.65203400 | 0.31423300 |
| F       | 5.68644500 | -1.58981500| 0.44309500 |
| F       | 5.86305400 | 0.36684100 | 1.37592300 |
| F       | 6.73297700 | 0.01766700 | -0.57826800|
| F       | 4.40099200 | -0.31070900| -1.74402700|
| F       | 4.37807400 | 1.52284600 | -0.53870700|
| F       | 2.92528400 | -1.63707400| -0.04259200|
| F       | 3.21683000 | -0.16420800| 1.55488700 |
| F       | 1.84140900 | 0.62135300 | -1.57422500|
| F       | 1.77675300 | 1.65359700 | 0.36053100 |
| F       | 0.30268400 | -1.32331800| -0.76539300|
| F       | 0.56418400 | -0.82526700| 1.35461800 |
| F       | -0.71410300| 1.42810300 | -1.00995600|
| F       | -0.82189800| 1.37073900 | 1.17759000 |
| F       | -2.26686000| -0.63502500| -1.31075000|
| F       | -2.09903300| -1.24809500| 0.79115600 |
| F       | -3.38809600| 1.80434000 | -0.37864500|
| F       | -3.40317700| 0.94728000 | 1.62320600 |
| I       | -5.26576700| -0.42876800| -0.14327900|

**C₈F₁₇I···4-Methylaminopyridine**

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | -7.70933300| 1.00414500 | -0.34152100|
| C       | -6.44816200| 0.60603500 | 0.49493900 |
| C       | -5.12273500| 0.55430800 | -0.33963800|
| C       | -3.96645400| -0.22010800| 0.38842500 |
| C       | -2.54770200| 0.09143500 | -0.20982000|
| C       | -1.46365100| -0.97369900| 0.19018600 |
| C       | 0.00953100 | -0.46449000| -0.00896300|
| C       | 1.09303100 | -1.58053500| -0.02460500|
| F       | -8.05385300| 0.02684300 | -1.18007400|
| F       | -7.47354800| 2.11812300 | -1.04030600|
| F       | -8.72639700| 1.22608900 | 0.49510300 |
| F       | -6.68521600| -0.60437500| 1.04076300 |
| F       | -6.30786300| 1.51222600 | 1.48020700 |
| F       | -5.37315900| -0.05345500| -1.51644200|
| F       | -4.72622500| 1.82039700 | -0.57977300|
| F       | -4.21023800| -1.54140100| 0.28311300 |
| F       | -3.96793200| 0.12225500 | 1.69225600 |
| F       | -2.64225100| 0.12306400 | -1.55496500|
| F       | -2.16196700| 1.30589700 | 0.22916000 |
| F       | -1.66746600| -2.07692000| -0.55653100|
| F       | -1.63337700| -1.29535500| 1.49054600 |
| F       | 0.07734900 | 0.21008400 | -1.18032100|
| F       | 0.27928500 | 0.39222900 | 1.00071400 |
| F       | 0.91186200 | -2.34082200| -1.13410700|
F  0.88261100  -2.38415000   1.05274400  
I  3.16526600   -0.78717900   -0.00363800  
C  6.72971700   -0.75656700   -0.27961300  
C  8.05182700   -0.36751500   -0.30110200  
C  8.39241800    0.97591500   -0.01295700  
C  7.30739600    1.83531000    0.28372200  
C  6.02151200    1.33917200    0.27707400  
N  5.71108800    0.06574200    0.00239800  
H  6.46697600   -1.78399500   -0.50052500  
H  8.80348300   -1.10200200   -0.53999900  
H  7.45908600    2.87650200    0.51702800  
H  5.18982500    1.99520700    0.50373400  
N  9.67668600    1.41218500   -0.02081300  
C  9.98013100    2.80595900    0.27273500  
H 11.05274800    2.95697500    0.21293500  
H  9.50135700    3.47823500   -0.44322200  
H  9.65304600    3.08272200    1.27774400  
C 10.76239500    0.49307000   -0.33276100  
H 11.70589300    1.02600100   -0.28091600  
H 10.80046400   -0.33534600    0.37842200  
H 10.65953600   -0.07949700   -1.33889400  

C₈F₁₇I...2-Methylpyridine

C  -7.11419000   -0.62495100    0.47738300  
C  -5.82986900   -0.50341100   -0.40849700  
C  -4.50530900   -0.34458900    0.41444300  
C  -3.30527800    0.18698500   -0.44784500  
C  -1.90758500   -0.06664100    0.22323200  
C  -0.76505600    0.82809700   -0.38040600  
C   0.67651700    0.28965000   -0.06088700  
C   1.81914500    1.32678600   -0.26959900  
F  -7.40438700    0.53962300    1.05747300  
F  -6.94336600   -1.55429200    1.42198500  
F  -8.14009700   -0.98209500   -0.29922600  
F  -5.99054300    0.56368500   -1.21743300  
F  -5.74378400   -1.61561000   -1.16151500  
F  -4.72232200    0.51784600    1.42740700  
F  -4.18261800   -1.54788700    0.92990100  
F  -3.47213600    1.51121700   -0.63457700  
F  -3.32430200   -0.42973000    1.64632800  
F  -2.00514300    0.19577500    1.54254600  
F  -1.58947300   -1.36588200    0.05920400  
F  -0.90412600    2.07354400    0.11479600  
F  -0.91530400    0.87699700   -1.72106000  
F   0.70828700   -0.12369800    1.22660000  
F   0.89815900   -0.77297300   -0.86413900  
F   1.68542900    2.30947400    0.65272000  
F   1.65691300    1.89255200   -1.49288900  
I   3.83255600    0.43442500   -0.10197300
C                  7.29783500   -0.44109800    0.94452700  
C                  8.55758000   -1.03780800    0.89110400  
C                  8.88160800   -1.86103700   -0.17778800  
C                  7.93891600   -2.07309200   -1.17536100  
C                  6.70844700   -1.44539400   -1.05255600  
N                  6.39529400   -0.65330100   -0.02510500  
H                  9.85478500   -2.32955500   -0.23091500  
H                  9.27090700   -0.85438500    1.68193900  
H                  8.14598900   -2.70567500   -2.02599500  
H                  5.93920200   -1.57845100   -1.80341100  
C                  6.89186200    0.45785000    2.07527700  
H                  6.62821700    1.44669000    1.69791800  
H                  6.00917400    0.06033500    2.57782300  
H                  7.69078400    0.56461500    2.80561500  

C₈F₂₃I ...2,6-Dimethylpyridine
C                 -7.27374400    0.59810900   -0.51402100  
C                 -5.98862000    0.50980400    0.37464200  
C                 -4.66623600    0.30511200   -0.44137600  
C                 -3.46625600   -0.18625800    0.44456900  
C                 -2.06914500    0.02903400   -0.24096900  
C                  0.51412000   -0.31889100    0.05812400  
C                  1.65336900   -1.34931200    0.31765100  
F                 -7.56988800   -0.58905500   -1.04299300  
F                 -7.10044000    1.48525300   -1.49790800  
F                 -8.29691700    0.99277500    0.24795300  
F                 -6.15382700   -0.51786100    1.23225600  
F                 -5.89523100    1.65521800    1.07523400  
F                 -4.88805600   -0.60700600   -1.40873800  
F                 -4.34039800    1.47953000   -1.01781600  
F                 -3.63669600   -1.49886000    0.69806100  
F                 -3.48070200    0.49000900    1.61055800  
F                 -2.16929900   -0.29948900   -1.54513800  
F                 -1.74707400    1.33392500   -0.14317800  
F                 -1.07064300   -2.10566600   -0.02728500  
F                 -1.07679900   -0.81945500    1.74686500  
F                  0.54620500    0.02912800   -1.24825200  
F                  0.73922400    0.78159700    0.80707000  
F                 1.51853800   -2.37320600   -0.55714300  
F                 1.48960500   -1.85550600    1.56557700  
I                 3.66409400   -0.46815400    0.11217500  
C                 7.30319300   -0.17571200   -0.65213600  
C                 8.60210500    0.31060300   -0.78881800  
C                 8.88338500    1.60621200   -0.38337900  
C                 7.86467400    2.38270400    0.14701300  
C                 6.58588900    1.83985700    0.25815900  
N                 6.32458000    0.58449300   -0.13734900  
H                 9.88392800    2.00571700   -0.47945800
H                  9.37307700   -0.32086300   -1.20624600
H                  8.04995700    3.39616000    0.47256300
C                  6.94515400   -1.57118600   -1.07563400
H                  6.55164900   -2.13759500   -0.23083600
H                  6.16595000   -1.55073800   -1.83839700
H                  7.80942200   -2.09728200   -1.47507600
C                  5.44778100    2.63859400    0.82542500
H                  5.77084400    3.63639300    1.11410000
H                  4.64339000    2.73013200    0.09469900
H                  5.02999900    2.14012500    1.70081200

C₈F₁₇I ---4-Methoxypyridine
C                  7.48287400   -0.89883900   -0.17780000
C                  6.19537500   -0.47892400    0.60628600
C                  4.88462600   -0.53291700   -0.25166700
C                  3.69541900    0.26622200    0.39104600
C                  2.29596100   -0.13266100   -0.20149600
C                  1.17965000    0.93469800    0.08824400
C                 -0.27720100    0.37292700   -0.09100100
C                 -1.38180900    1.46160200   -0.22609000
F                  7.81627800    0.02665700   -1.07739500
F                  7.29038500    2.06529700   -0.80010500
F                  8.48950300   -1.03281200    0.68944300
F                  6.38584400    0.77569300    1.06320300
F                  6.06394400   -1.31243400    1.65485500
F                  5.14020100   -0.01744900   -1.47071400
F                  4.52628300   -1.82492700   -0.39255700
F                  3.90650900    1.58062000    0.18053800
F                  3.68193400    0.03228500    1.71858200
F                  2.41487800   -0.27707900   -1.53719100
F                  1.93148700   -1.31423800    0.33441000
F                  1.37022900    1.97550800   -0.74612000
F                  1.31635600    1.36926000    1.35917100
F                 -0.30868400   -0.40322600   -1.19854400
F                 -0.54846300   -0.39609700    0.98563800
F                 -1.20034100    2.11617400   -1.39884800
F                 -1.20707200    2.36478100    0.77364900
I                 -3.43100300    0.63349200   -0.15686600
C                 -6.55178900   -0.90841500   -1.14168200
C                 -7.85380700   -1.36256700   -1.16291300
C                 -8.66092900   -1.14864300   -0.04000500
C                 -8.10762900   -0.48338700    1.05650900
C                 -6.78652300   -0.06836700    0.97290700
N                 -6.01334500   -0.26824500   -0.09432600
H                 -5.90505000   -1.05918600   -1.99659500
H                 -8.25334300   -1.87458600   -2.02576600
H                 -8.67022200   -0.28531400    1.95439100
H                 -6.33051900    0.45067000    1.80678800
O                 -9.92278000   -1.60741400   -0.10833500
| Atomic Symbol | X-Coordinate  | Y-Coordinate  | Z-Coordinate  |
|---------------|---------------|---------------|---------------|
| C             | -10.79264700  | -1.40990000   | 1.01318300    |
| H             | -10.93069600  | -0.34695800   | 1.21576700    |
| H             | -11.74132400  | -1.85432700   | 0.73031400    |
| H             | -10.40289000  | -1.91013800   | 1.90069900    |

**C₆F₁₇-I ...3,5-Dimethylpyridine**

| Atomic Symbol | X-Coordinate  | Y-Coordinate  | Z-Coordinate  |
|---------------|---------------|---------------|---------------|
| C             | 7.39422300    | 0.68413500    | 0.54609600    |
| C             | 6.11618000    | 0.57625000    | -0.35057100   |
| C             | 4.79264700    | 0.34449700    | 0.45627500    |
| C             | 3.60632800    | -0.16186300   | -0.43972200   |
| C             | 2.20176400    | 0.02436100    | 0.23892500    |
| C             | 1.07872200    | -0.85446500   | -0.42179400   |
| C             | -0.37422100   | -0.36550700   | -0.07615300   |
| C             | -1.49590700   | -1.40892000   | -0.35284100   |
| F             | 7.70751100    | -0.49906000   | 1.07408800    |
| F             | 7.20006000    | 1.56584900    | 1.53096100    |
| F             | 8.41504700    | 1.09800800    | -0.20889600   |
| F             | 6.30508800    | -0.44474800   | -1.21128900   |
| F             | 6.00667700    | 1.72278700    | -1.04702500   |
| F             | 5.02438900    | -0.56928500   | 1.41976800    |
| F             | 4.44378100    | 1.50993900    | 1.03746400    |
| F             | 3.80126500    | -1.46958800   | -0.70070200   |
| F             | 3.61602500    | 0.52227000    | -1.60122900   |
| F             | 2.30029800    | -0.31412900   | 1.54076000    |
| F             | 1.85920800    | 1.32478400    | 0.15092200    |
| F             | 1.24142200    | -2.12463300   | -0.00210700   |
| F             | 1.23398000    | -0.81933500   | -1.76236100   |
| F             | -0.41749800   | -0.03269700   | 1.23434300    |
| F             | -0.61415300   | 0.74066300    | -0.81320500   |
| F             | -1.34650200   | -2.44278500   | 0.51047100    |
| F             | -1.31520500   | -1.89890500   | -1.60688700   |
| I             | -3.53119000   | -0.56794200   | -0.14538900   |
| C             | -7.04312000   | -0.40451000   | 0.63718400    |
| C             | -8.36497900   | 0.01099100    | 0.78103700    |
| C             | -8.67815400   | 1.28871500    | 0.32426200    |
| C             | -7.70440600   | 2.10347900    | -0.24785500   |
| C             | -6.41647000   | 1.58020800    | -0.33799300   |
| N             | -6.09633700   | 0.35991600    | 0.09280900    |
| H             | -9.69443200   | 1.65439300    | 0.41523900    |
| H             | -6.73406400   | -1.38768400   | 0.97173000    |
| H             | -5.61286800   | 2.16306100    | -0.77227800   |
| C             | -9.40296900   | -0.88043900   | 1.40296300    |
| H             | -9.81999800   | -0.42212000   | 2.30114900    |
| H             | -10.23044600  | -1.05344000   | 0.71325200    |
| H             | -8.98438400   | -1.84677800   | 1.67953700    |
| C             | -8.02604900   | 3.48381000    | -0.74786000   |
| H             | -7.14157100   | 3.98069300    | -1.14312300   |
| H             | -8.77520100   | 3.44459800    | -1.54025900   |
| H             | -8.43361700   | 4.10214100    | 0.05330100    |
| Atom  | X     | Y     | Z     |
|-------|-------|-------|-------|
| C     | -6.94168900 | 0.66546200 | -0.37476600 |
| C     | -5.65568900 | 0.40851400 | 0.47912100  |
| C     | -4.33019700 | 0.39633200 | -0.35734700 |
| C     | -3.12575200 | -0.25984300 | 0.40739700  |
| C     | -1.73070500 | 0.10840300 | -0.21449100 |
| C     | -0.58171600 | -0.86553900 | 0.23405900  |
| C     | 0.85622300  | -0.27580900 | 0.00027900  |
| C     | 2.00425900  | -1.32723900 | 0.03683400  |
| F     | -7.22170400 | -0.38738400 | -1.14299200 |
| F     | -6.78085500 | 1.74236100  | -1.14883700 |
| F     | -7.97006200 | 0.87635400  | 0.45067300  |
| F     | -5.80884700 | -0.77850800 | 1.10090400  |
| F     | -5.57687300 | 1.38209300  | 1.40505200  |
| F     | -4.54092700 | -0.29056600 | -1.49778300 |
| F     | -4.01649900 | 1.67013600  | -0.66854300 |
| F     | -3.28377900 | -1.59787500 | 0.37763300  |
| F     | -3.14720600 | 0.15464900  | 1.68988300  |
| F     | -1.82913800 | 0.06396600  | -1.55879200 |
| F     | -1.42005700 | 1.36545600  | 0.15898400  |
| F     | -0.71692900 | -2.01607700 | -0.45412700 |
| F     | -0.72666900 | -1.12956900 | 1.54994800  |
| F     | 0.88114000  | 0.33790700  | -1.20476900 |
| F     | 1.07652200  | 0.64607400  | 0.96221400  |
| F     | 1.87094900  | -2.15044000 | -1.03018100 |
| F     | 1.84948200  | -2.08214700 | 1.15450700  |
| I     | 4.01360500  | -0.41010900 | 0.00617000  |
| C     | 7.51573500  | 0.07434900  | -0.81036100 |
| C     | 8.81433300  | 0.56229600  | -0.86784700 |
| C     | 9.14377400  | 1.66852900  | -0.09456600 |
| C     | 8.16401400  | 2.24349100  | 0.70526000  |
| C     | 6.89150100  | 1.68812400  | 0.69991900  |
| N     | 6.57229400  | 0.62505300  | -0.04244000 |
| H     | 10.14540400 | 2.07497200  | -0.11485800 |
| H     | 7.21662800  | -0.78534000 | -1.39661000 |
| H     | 9.54455100  | 0.08372500  | -1.50414200 |
| H     | 8.37606300  | 3.10447000  | 1.32243700  |
| H     | 6.09875800  | 2.10480400  | 1.30831800  |

| Atom  | X     | Y     | Z     |
|-------|-------|-------|-------|
| C     | -7.78156300 | 1.03135800 | -0.53113100 |
| C     | -6.47733800 | 0.97048300 | 0.33157200  |
| C     | -5.21901300 | 0.46694700 | -0.45595300 |
| C     | -4.04569800 | 0.01422300 | 0.48418100  |
| C     | -2.66251700 | -0.06762600 | -0.25673800 |
| C     | -1.60017100 | -0.92702300 | 0.51966200  |
| C     | -0.12460100 | -0.65968300 | 0.04800600  |
| C     | 0.89866100  | -1.75503100 | 0.47314300  |
|   |       |       |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|-------|-------|
| F | -8.22362600 | -0.19421900 | -0.81327100 |
| F | -7.55626000 | 1.68926700 | -1.67185500 |
| F | -8.72460800 | 1.67510400 | 0.13753200 |
| F | -6.71552600 | 0.15042500 | 1.37553200 |
| F | -6.23347700 | 2.21045400 | 0.79467100 |
| F | -5.57749800 | -0.57720700 | -1.22933100 |
| F | -4.78968200 | 1.46871900 | -1.24950800 |
| F | -4.35004400 | -1.19836100 | 0.98740300 |
| F | -3.93763100 | 0.89472300 | 1.49903400 |
| F | -2.85262600 | -0.61832000 | -1.47292600 |
| F | -2.19190500 | 1.18525900 | -0.41385100 |
| F | -1.90381600 | -2.22777300 | 0.34246000 |
| F | -1.68641900 | -0.63818400 | 1.83528100 |
| F | -0.11048500 | -0.56689500 | -1.30078500 |
| F | 0.25936400 | 0.52457300 | 0.56982100 |
| F | 0.60902000 | -2.89931000 | -0.18801600 |
| F | 0.73482500 | -1.99586300 | 1.79750100 |
| I | 2.98588100 | -1.18339300 | 0.05719100 |
| C | 6.46843200 | -1.43544700 | -1.07238200 |
| C | 7.80651900 | -1.17179800 | -1.33059000 |
| C | 8.34604700 | 0.03708900 | -0.91168000 |
| C | 7.51251300 | 0.92729700 | -0.25075200 |
| C | 6.18240900 | 0.59406700 | -0.02791200 |
| N | 5.67780300 | -0.56963300 | -0.43528900 |
| H | 9.38269100 | 0.27867300 | -1.09362900 |
| H | 6.01194900 | -2.36603700 | -1.38286900 |
| H | 8.41595000 | -1.89742000 | -1.84906700 |
| H | 5.51316700 | 1.27146600 | 0.48499100 |
| Br | 8.17461100 | 2.60917200 | 0.35819100 |

**C₆F₅I → 3-Chloropyridine**

|   |       |       |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|-------|-------|
| C | -7.33519100 | 0.90662600 | -0.44743400 |
| C | -6.04907300 | 0.71782500 | 0.42396400 |
| C | -4.75172900 | 0.44156700 | -0.41087000 |
| C | -3.57535600 | -0.13821900 | 0.45350500 |
| C | -2.17538000 | 0.00199300 | -0.24628500 |
| C | -1.08306200 | -0.94561600 | 0.37563000 |
| C | 0.38436800 | -0.51569700 | 0.01172000 |
| C | 1.45885100 | -1.61947100 | 0.24593100 |
| F | -7.71229700 | -0.24799200 | -0.99659900 |
| F | -7.11614300 | 1.80134500 | -1.41512000 |
| F | -8.32281300 | 1.34951300 | 0.33472500 |
| F | -6.27248100 | -0.31254300 | 1.26505600 |
| F | -5.87298700 | 1.84161700 | 1.14337700 |
| F | -5.04224400 | 1.60143400 | -0.97422800 |
| F | -4.35802700 | -0.43995400 | -1.38823600 |
| F | -3.82552100 | -1.44109100 | 0.69032900 |
| F | -3.53787500 | 0.51996300 | 1.62907400 |
| F | -2.31139500 | -0.30772500 | 1.55268700 |
F  -1.77054700  1.27869700  -0.13738000
F  -1.31082000  -2.19786500  -0.06641300
F  -1.21103200  -0.93136500  1.71915500
F   0.42065300  -0.15848800  -1.29180700
F   0.69040200  0.56059700  0.76676900
F   1.24807500  -2.62388400  -0.63559900
F   1.28165600  -2.12565700  1.49139900
I   3.51782100  -0.86852200   0.01664500
C   7.10108600  -0.84152500  -0.77681100
C   8.42807600  -0.46420500  -0.93193800
C   8.81492700   0.80970700  -0.53945500
C   7.84638400  1.64777400  -0.00756500
C   6.53712500  1.20051500  0.11756500
N   6.17945700  -0.02447400  -0.26302800
H   9.83645000   1.14468300  -0.64204700
H   6.76198300  -1.82588500  -1.07120100
H   9.14565400  -1.15368100  -1.35184100
H   5.76845600  1.83999800  0.53020800
Cl  8.25613700  3.26557300  0.50879000

C₆F₁₇...3,5-Dichloropyridine
C    7.81768200   0.66277000   0.72272700
C    6.54497400   0.70690500  -0.18664300
C    5.22632100   0.27805900   0.54352800
C    4.05646500  -0.06024400  -0.44840300
C    2.64508700  -0.04953700   0.24160500
C    1.54763600  -0.80313500  -0.59409900
C    0.08175500  -0.42206600  -0.17283400
C   -1.01003700  -1.42052800  -0.66384900
F    8.15950100  -0.59467400  1.00360900
F    7.59962700  1.32281400   1.86351100
F    8.82908200  1.24489900  -0.07340900
F    6.76457600  -0.10973800  -1.23738800
F    6.40443200  1.96881300  -0.63307300
F    5.47889600  -0.81060700   1.29702500
F    4.84459500  1.28731900   1.35177800
F    4.28412700  -1.28144400  -0.97081800
F    4.05303800   0.84792300  -1.44359000
F    2.74567400  -0.64232100   1.44858000
F    2.26925200  1.23297200   0.41484400
F    1.73544400  -2.12762500  -0.43452800
F    1.70879600  -0.49766500  -1.89868600
F    0.02021500  -0.35620000   1.17577100
F   -0.18151300   0.79969900  -0.68127700
F  -0.84579900  -2.59671700  -0.01876900
F  -0.81512200  -1.64676400  -1.98522700
I   -3.05224100  -0.68080600  -0.31714900
C   -6.64289500  -0.64387400   0.59639500
C   -7.95916100  -0.24365600   0.79312100
C  -8.35274700  1.04117600   0.45187400
C       -7.38672000   1.88046700   -0.08154200
C       -6.08599400   1.42297700   -0.25487700
N       -5.73675100   0.18383800    0.08197000
H       -9.36890700    1.37434300    0.59542000
H       -6.31919900  -1.64192000    0.85689000
H       -5.32053200   2.06396100   -0.66958100
Cl      -7.79755700    3.51174500   -0.53746900
Cl      -9.11143600  -1.36262300    1.46986700
C
6
F
5
I
…
NEt2
H
I      0.88934200   -0.05671600   -0.12273500
C      -1.26238500   -0.01375800   -0.03992100
C      -1.95489400   1.18073100    0.09439200
C      -2.01183300  -1.17853200   -0.11751000
C      -3.34021600   1.22297400    0.15076900
C      -3.39786900  -1.16362300   -0.06391800
C      -4.06544000   0.04402400    0.07115200
F      -1.41155100   2.37283500   -0.24856400
F      -4.09649700  -2.30289900   -0.14109900
F      -5.39942900   0.07155000    0.12416500
F      -3.98301500   2.38988800    0.28150800
F      -1.29759800   2.34912300    0.17556800
N      3.63927400  -0.07821100   -0.20323000
H      3.81955500   -0.23925600   -1.18764200
C      4.09512100  -1.23405700    0.58254200
H      4.16710400  -1.24130100    0.19293900
H      4.41052900   1.19725000   -1.25540000
C      5.37390800   1.71308000   -0.61521900
H      6.22491100   1.04280700   -0.50614800
H      5.12252200   1.77226100   -1.67617600
H      5.67862500  -2.70948700   -0.29141400
C      5.59857200  -1.50758500    0.57524500
H      5.96761800  -1.63720600   -0.44346300
H      6.15753000  -0.69634000    1.04111800
H      5.81202100  -2.42122100    1.13238000

C6F5I—NEt2H

C       -7.38672000   1.88046700   -0.08154200
C       -6.08599400   1.42297700   -0.25487700
N       -5.73675100   0.18383800    0.08197000
H       -9.36890700    1.37434300    0.59542000
H       -6.31919900  -1.64192000    0.85689000
H       -5.32053200   2.06396100   -0.66958100
Cl      -7.79755700    3.51174500   -0.53746900
Cl      -9.11143600  -1.36262300    1.46986700
C
6
F
5
I
…
NBu2H

I      0.88934200   -0.05671600   -0.12273500
C      -1.26238500   -0.01375800   -0.03992100
C      -1.95489400   1.18073100    0.09439200
C      -2.01183300  -1.17853200   -0.11751000
C      -3.34021600   1.22297400    0.15076900
C      -3.39786900  -1.16362300   -0.06391800
C      -4.06544000   0.04402400    0.07115200
F      -1.41155100   2.37283500   -0.24856400
F      -4.09649700  -2.30289900   -0.14109900
F      -5.39942900   0.07155000    0.12416500
F      -3.98301500   2.38988800    0.28150800
F      -1.29759800   2.34912300    0.17556800
N      3.63927400  -0.07821100   -0.20323000
H      3.81955500   -0.23925600   -1.18764200
C      4.09512100  -1.23405700    0.58254200
H      4.16710400  -1.24130100    0.19293900
H      4.41052900   1.19725000   -1.25540000
C      5.37390800   1.71308000   -0.61521900
H      6.22491100   1.04280700   -0.50614800
H      5.12252200   1.77226100   -1.67617600
H      5.67862500  -2.70948700   -0.29141400
C      5.59857200  -1.50758500    0.57524500
H      5.96761800  -1.63720600   -0.44346300
H      6.15753000  -0.69634000    1.04111800
H      5.81202100  -2.42122100    1.13238000

C5F5I—NBu2H

I      0.57766200   -0.03366700   -0.57417500
C      -1.52496500   -0.00550100   -0.12460900
C      -2.24238600   -1.18063700    0.04674800
C      -2.21900300   1.18850400    0.00837200
C      -3.59828200  -1.17617200    0.33926200
C      -3.57463500   1.22042300    0.30049600
C      -4.26785200   0.03113600    0.46703500
F      -1.59202800   2.36637800   -0.14311600
F      -4.21910600   2.38695200    0.42349300
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| F       | -5.57295000 | 0.04850600 | 0.74864100 |
| F       | -4.26564600 | -2.32536200 | 0.49948400 |
| F       | -1.63884300 | -2.37492300 | -0.06642900 |
| N       | 3.28720000  | -0.06603100 | 0.68575700  |
| H       | 3.77141100  | 0.90897000  | 0.68575700  |
| H       | 3.77263700  | -0.83936200 | 0.78216400  |
| C       | 5.58765600  | -0.00644200 | -0.03923800 |
| H       | 5.87289700  | -0.91444000 | 0.78216400  |
| H       | 5.87289700  | -0.91444000 | -0.58030600 |
| C       | 6.35606900  | 0.06581200  | 1.28031100  |
| H       | 6.06122900  | 0.97111400  | 1.81896300  |
| H       | 6.06276700  | -0.77650600 | 1.91366400  |
| C       | 7.87129100  | 0.05651000  | 1.08611800  |
| H       | 8.19328400  | 0.90680400  | 0.48136700  |
| H       | 8.39583400  | 0.10834900  | 2.04112100  |
| H       | 8.19454800  | -0.85339300 | 0.57622400  |

**C₆F₅-I-Piperidine**

| I       | -0.65111500 | -0.17935300 | -0.20353400 |
| C       | 1.49702300  | -0.03365900 | -0.05224800 |
| C       | 2.30279500  | -1.16166300 | -0.09839000 |
| C       | 2.12861600  | 1.19236700  | 0.09534600  |
| C       | 3.68431700  | -1.08164900 | -0.00257000 |
| C       | 3.50803400  | 1.30063700  | 0.19346400  |
| C       | 4.29004700  | 0.15683100  | 0.14424200  |
| F       | 1.41486500  | 2.32936600  | 0.14883000  |
| F       | 4.09126400  | 2.49743400  | 0.33519400  |
| F       | 5.61920000  | 0.24753500  | 0.23763100  |
| F       | 4.43789000  | -2.18729300 | -0.05029300 |
| F       | 1.76354700  | -2.38416000 | -0.23933100 |
| C       | -3.91260600 | -0.87022800 | 0.90213200  |
| C       | -5.44195400 | -0.91506400 | 0.91636400  |
| C       | -6.03011000 | 0.46207900  | 0.59467300  |
| C       | -5.45583600 | 1.00199600  | -0.71856700 |
| C       | -3.92611600 | 0.99368000  | -0.68692500 |
| H       | -7.11872100 | 0.40923200  | 0.54204900  |
| H       | -5.78389100 | -1.64232200 | 0.17343000  |
| H       | -5.78733600 | -1.26729000 | 1.89056200  |
| H       | -3.55264700 | -0.23266200 | 1.71413500  |
| H       | -3.48663800 | -1.86134800 | 1.05749600  |
| H       | -5.79871400 | 0.38038800  | -1.55160100 |
| H       | -5.81100700 | 2.01668400  | -0.91003400 |
| H       | -3.50910700 | 1.30747300  | -1.64374700 |
| H       | -3.56680100 | 1.69757200  | 0.06858200  |
| H       | -5.78581900 | 1.15561900  | 1.40576900  |
| N       | -3.36338800 | -0.32597300 | -0.35182700 |
\[ \begin{align*}
&\text{C}_6\text{F}_5\text{I} \cdots \text{N(sec-Bu)H}_2 \\
&\text{I} & 0.88136100 & -0.14482100 & -0.57688100 \\
&C & -1.22308500 & -0.02527200 & -0.16279500 \\
&C & -1.97124700 & -1.16214600 & 0.10734300 \\
&C & -1.88850400 & 1.19224000 & -0.15252400 \\
&C & -3.33016600 & -1.09793900 & 0.37808200 \\
&C & -3.24644400 & 1.28309100 & 0.11540800 \\
&C & -3.97098100 & 0.13154100 & 0.38233200 \\
&\text{F} & -1.23051400 & 2.33517100 & -0.40464200 \\
&\text{F} & -3.86321400 & 2.47096100 & 0.11888000 \\
&\text{F} & -5.27857300 & 0.20616700 & 0.64183400 \\
&\text{F} & -4.02797100 & -2.21083500 & 0.63502700 \\
&\text{F} & -1.39614700 & -2.37541300 & 0.11516100 \\
&\text{N} & 3.60220800 & -0.30352000 & -1.19550300 \\
&\text{H} & 3.69739000 & -1.15915800 & -1.73097800 \\
&\text{H} & 3.77041500 & 0.46425600 & -1.83612400 \\
&C & 4.57232200 & -0.27526200 & -0.07954800 \\
&C & 4.32800700 & -1.48668000 & 0.81423500 \\
&\text{H} & 4.39048300 & -2.41215400 & 0.23904800 \\
&\text{H} & 5.07022000 & -1.54197100 & 1.60884800 \\
&\text{H} & 3.33711200 & -1.43406900 & 1.26778700 \\
&C & 4.43295200 & 1.05715400 & 0.66134800 \\
&\text{H} & 4.49588400 & 1.86667000 & -0.07190700 \\
&\text{H} & 3.43241100 & 1.11902000 & 1.09745300 \\
&C & 5.49044600 & 1.28005600 & 1.74078200 \\
&\text{H} & 5.38938300 & 2.27304900 & 2.17932000 \\
&\text{H} & 5.40278500 & 0.55398800 & 2.54924400 \\
&\text{H} & 6.49792900 & 1.19957200 & 1.32723000 \\
&\text{H} & 5.59638200 & -0.33704800 & -0.47101500 \\
\end{align*} \]

\[ \begin{align*}
&\text{C}_6\text{F}_5\text{I} \cdots \text{Pyrrolidine} \\
&\text{I} & 1.03536400 & -0.42232200 & -0.08493300 \\
&C & -1.09516600 & -0.10120600 & -0.02717000 \\
&C & -1.63177900 & 1.17788700 & -0.02374700 \\
&C & -1.98526300 & -1.16440800 & 0.00833000 \\
&C & -3.00068500 & 1.39902100 & 0.01336700 \\
&C & -3.35829000 & -0.97090800 & 0.04594900 \\
&C & -3.86853300 & 0.31826000 & 0.04836100 \\
&\text{F} & -1.53990400 & -2.43169700 & 0.00741300 \\
&\text{F} & -4.19458400 & 2.01572400 & 0.07991900 \\
&\text{F} & -5.18844200 & 0.51786100 & 0.08436100 \\
&\text{F} & -3.49163900 & 2.64446500 & 0.01568700 \\
&\text{F} & -0.83225900 & 2.25687400 & 0.05672600 \\
&C & 4.38260500 & 0.03437600 & -1.16763200 \\
&C & 4.43692400 & 1.07722300 & 1.04699800 \\
&\text{H} & 5.39239500 & -0.32003000 & -1.40523800 \\
&C & 4.37195300 & -0.45633900 & 1.12109800 \\
\end{align*} \]
H  3.56376900  1.51612100  1.52670000
H  3.77797100 -0.82333200  1.95676500
C  4.44036900  1.40284400 -0.73357400
H  3.56630800  1.99657900 -0.77526300
H  5.32245600  1.96296200 -0.77526300
N  3.74526600 -0.82894300 -0.15875100
H  3.79804000  0.04169400 -2.08636100
H  5.31936100  1.45916600  1.55637400
H  5.37922400 -0.88103500  1.20256300
H  3.85798300 -1.81300800 -0.36915600

C\text{6}F_{5}I\cdots N\text{(iso-Pr)H}_{2}

\begin{align*}
I & -0.65540500 0.06908000 -0.12550100 \\
C & 1.48697400 0.02420400 -0.03090820 \\
C & 2.17163900 -1.14965000 0.24127900 \\
C & 2.24228300 1.16983000 -0.25983100 \\
C & 3.55673200 -1.19207300 0.30207000 \\
C & 3.62816900 1.14983200 -0.20476800 \\
C & 4.28869400 -0.03609900 0.07760900 \\
F & 1.64830900 2.33854800 -0.53667000 \\
F & 4.33299800 2.26637000 -0.42166400 \\
F & 5.62229500 -0.06480100 0.13311300 \\
F & 4.19243800 -2.33769100 0.57486800 \\
F & 1.50690300 -2.29413800 0.46524900 \\
N & -3.50742000 0.17894100 -0.36001100 \\
H & -3.48984600 0.17894100 -1.23691800 \\
C & -4.20132000 1.03164500 0.63950100 \\
C & -4.13847500 -1.13199900 -0.63435300 \\
H & -5.23972200 0.68708700 0.72138900 \\
H & -5.21367600 -0.97477300 -0.80481000 \\
C & -4.21631100 2.47643700 0.14538900 \\
H & -4.70098500 3.12602100 0.87387900 \\
H & -3.19592800 2.83738300 -0.00097300 \\
H & -4.75369700 2.56720400 -0.80021700 \\
C & -3.55886800 0.94826200 2.02500600 \\
H & -3.44703500 -0.07919000 2.36263000 \\
H & -2.57023400 1.40760900 2.01613300 \\
H & -4.17468000 1.48070800 2.75138700 \\
C & -3.54197700 -1.72299500 -1.90886700 \\
H & -4.06232300 -2.64349500 -2.17293700 \\
H & -3.63580200 -1.03191400 -2.74893600 \\
H & -2.48537600 -1.95499900 -1.77430200 \\
C & -3.98723500 -2.09294600 0.54138800 \\
H & -2.93421300 -2.22496400 0.79425700 \\
H & -4.51271800 -1.73716500 1.42590200 \\
H & -4.40418400 -3.06562700 0.27903500 \\
\end{align*}

C\text{6}F_{5}I\cdots NEt\text{(iso-Pr)H}

\begin{align*}
I & 0.85352300 0.02817700 -0.17472500 \\
\end{align*}
| At. | X       | Y       | Z       |
|-----|---------|---------|---------|
| C   | -1.29218400 | 0.00276100 | -0.05572700 |
| C   | -2.01468800 | 1.16124700 | 0.19043500 |
| C   | -3.39931500 | 1.15715300 | 0.27328000 |
| C   | -3.39395500 | -1.20393000 | -0.14099900 |
| F   | -1.37781600 | -2.33382600 | -0.45932300 |
| F   | -4.06144500 | -2.35282200 | -0.30224000 |
| F   | -4.07195900 | 2.28942000 | 0.51208900 |
| F   | -1.38852100 | 2.33707900 | 0.35860100 |
| N   | 3.66307100 | 0.12771300 | -0.33138100 |
| H   | 3.81452400 | -0.03867300 | -1.32073800 |
| C   | 4.34597600 | -0.94551000 | 0.42210200 |
| C   | 4.11974400 | 1.49009200 | 0.40150100 |
| H   | 5.43293800 | -0.80724400 | 0.32443900 |
| H   | 5.21109500 | 1.51001700 | 0.10651200 |
| C   | 3.98024300 | -2.29699800 | -0.18304900 |
| C   | 3.70605200 | 2.47930900 | -1.09450500 |
| C   | 3.36007600 | -1.16781700 | 0.15255700 |
| C   | 4.02630800 | 0.04556200 | 0.23092100 |
| F   | 1.38493800 | -2.38410900 | -0.09432300 |
| F   | 4.04615400 | -2.31090800 | 0.24909400 |
| F   | 4.14575400 | 2.21353100 | -2.05819400 |
| H   | 2.62286700 | 2.50589300 | -1.20987800 |
| H   | 3.68706000 | 1.78557200 | 0.94125100 |

$\text{C}_6\text{F}_{5}\text{I}---\text{N(tert-Bu)}$

| At. | X       | Y       | Z       |
|-----|---------|---------|---------|
| I   | -0.88631800 | -0.06217300 | -0.39939800 |
| C   | 1.24415800 | -0.01569300 | -0.12800400 |
| C   | 1.93512200 | 1.18480400 | -0.04672900 |
| C   | 1.98445400 | -1.18468100 | -0.02487200 |
| C   | 3.31017200 | 1.22850200 | 0.13048500 |
| C   | 3.36007600 | -1.16781700 | 0.15255700 |
| C   | 4.02630800 | 0.04556200 | 0.23092100 |
| F   | 1.38493800 | -2.38410900 | -0.09432300 |
| F   | 4.04615400 | -2.31090800 | 0.24909400 |
| F   | 4.14575400 | 2.21353100 | -2.05819400 |
| H   | 2.62286700 | 2.50589300 | -1.20987800 |
| H   | 3.68706000 | 1.78557200 | 0.94125100 |
C₆F₅I ---NBu₃H

I   0.24035800  -0.01390600  -0.24378400
C   -1.90262300  0.00204300  -0.06454600
C   -2.59755000  1.17822700   0.17673800
C   -2.64511800  -1.16369200  -0.18432100
C   -3.97932900  1.20158400   0.29586900
C   -4.02747300  -1.16703700  -0.06962400
C   -4.69792800  0.02232400   0.17195600
F   -2.04122300  -2.34019700  -0.4177500
F   -4.71965700  -2.30643500  -0.18958700
F   -6.02839600  0.03207600   0.28453100
F   -6.25057000  2.35065900   0.52915300
F   -1.94615300  2.34557800   0.3053300
N   3.02155100  -0.02627100  -0.30732700
H   3.32630800  -0.08327700  -0.12736100
C   3.48744400  -1.21532000   0.41818700
H   2.97677000  -1.23748200   1.38504100
H   4.56133200  -1.13722900   0.62701900
C   3.49597200  1.23552600   0.27664100
H   2.98728400  1.37086300   1.23521500
H   4.56980600  1.17479600   0.49159900
C   3.19294400  -2.49827000  -0.35143800
H   2.12987800  -2.52310400  -0.59756500
H   3.73509800  -2.47637800  -1.30310000
C   3.20782700  2.42364000  -0.63400000
H   3.74987300  2.29110600  -1.57674100
H   2.14489000  2.42576000  -0.88176800
C   3.58342300  3.77588700  -0.01996500
H   3.22519400  4.56547100  -0.68439000
H   3.04264400  3.90275300   0.92249200
C   5.08226400  3.96780600   0.21839600
H   5.29372100  4.97397500   0.58274400
H   5.47061600  3.26455900   0.95586000
H   5.64463500  3.82297000  -0.70683600
C   3.56209000  -3.77386500   0.41229000
H   3.02234900  -3.78949300  1.36372700
H   3.19827400  -4.63193500  -0.15741800
C  5.06026300 -3.94605000  0.66922700
H  5.45406800 -3.16556700  1.32113100
H  5.26668700 -4.90531300  1.14572300
H  5.62163500 -3.91104400 -0.26719700
C  0.56087200 -0.14203400 -1.15557800
H  0.81412200 -1.18132500  0.59643000
H  1.49919930 -1.13720300  1.56395600
C  1.22382300  0.53899700
H  1.41936320  0.43010000  1.27831300
C  3.61526800 -2.50982800 -0.08651700
H  1.96486100 -2.58384500 -0.27977200
H  2.61653200 -1.80412000  0.02352500
C  3.89453900  4.55707000 -0.77863100
H  3.00728100  3.98106900  0.86119000
C  4.07630900 -3.70189100  0.74960500
H  3.57140100 -3.71905500  1.71737400
H  3.85971600 -4.64312500  0.24412600
H  5.15132700 -3.66198700  0.93568300
H  5.17929500  3.74215000  0.11265300

C₆F₅I⋅NPr₂H
I  0.67318300 -0.02231700 -0.19047700
C  -1.47240400 -0.00095900 -0.05943700
C  -2.16808300  1.17268000  0.19211000
C  -2.21631900 -1.16073600 -0.22121900
C  -3.55206500  1.19915900  0.28129200
C  -3.60087600 -1.16067000 -0.13722700
C  -4.27210500  0.02593300  0.11550200
F  -1.61176600 -2.33430400 -0.46696800
F  -4.29441700 -2.29421300 -0.29752000
F  -5.60465900  0.03877400  0.19876000
F  -4.19843000  2.34554100  0.52549200
F  -1.51532800  2.33412400  0.35973200
N  3.46018300 -0.03392500 -0.19883000
H  3.78087200 -0.14203400 -1.15557800
C  3.91412200 -1.18132500  0.59643000
H  4.99199300 -1.11027800  0.79979900
C  3.92396800  1.25670100  0.32483400
H  3.41778200  1.43010000  1.27831300
H  5.00159300  1.22382300  0.53899700
C  3.61526800 -2.50982800 -0.08651700
H  2.54376600 -2.58384500 -0.27977200
H  4.11192700 -2.52915800 -1.06136100
C  3.63400200  2.40509800 -0.63315100
H  4.12963800  2.20665300 -1.58830800
H  2.56279700  2.44276700 -0.83825400
C  4.10446900  3.74817600 -0.07864800
H  3.89453900  4.55707000 -0.77863100
H  3.60028100  3.98106900  0.86119000
C  4.07630900 -3.70189100  0.74960500
H  3.57140100 -3.71905500  1.71737400
H  3.85971600 -4.64312500  0.24412600
H  5.15132700 -3.66198700  0.93568300
H  5.17929500  3.74215000  0.11265300

C₆F₅I⋅N(iso-Pr)₂H
I  0.15419100  0.15659100 -0.04317400
C  -1.96485500  0.04518700 -0.01045300
C  -2.61653200 -1.18041200  0.02352500
C  -2.74642100  1.19272500 -0.02214900
C  -4.00066500 -1.26639700  0.04552900
C  -4.13179100  1.12763500 -0.00059700
C  -4.76155800 -0.10725400  0.03349800
| Atom | X    | Y    | Z    |
|------|------|------|------|
| F    | -2.18128700 | 2.40720700 | -0.05481700 |
| F    | -4.86424700 | 2.24625700 | -0.01249600 |
| F    | -6.09340600 | -0.17986000 | 0.05446500 |
| F    | -4.60643300 | -2.45799700 | 0.07823300 |
| F    | -1.92205000 | -3.26336300 | 0.03636300 |
| N    | 3.31421400 | 0.02647100 | -0.00398700 |
| C    | 3.85679300 | 1.30430000 | -0.52780500 |
| H    | 3.85846800 | 1.18696800 | -1.61299600 |
| C    | 3.50585900 | -1.12934800 | -0.91469900 |
| H    | 2.94988500 | -0.86313700 | -1.81933700 |
| C    | 2.94262500 | 2.49208200 | -0.20927000 |
| H    | 1.97165500 | 2.38777700 | -0.68672500 |
| H    | 2.78546000 | 2.59884800 | 0.86484300 |
| C    | 2.87919900 | -2.41628400 | -0.37284000 |
| H    | 3.44320400 | -2.82595000 | 0.46417700 |
| H    | 1.85110100 | -2.26983500 | -0.05188900 |
| H    | 3.39608100 | 3.41727400 | -0.56757200 |
| H    | 2.87751400 | -3.16694700 | -1.16303600 |
| C    | 5.29267100 | 1.65759600 | -0.09752800 |
| H    | 5.32636400 | 1.93158800 | 0.95766800 |
| H    | 5.99197000 | 0.84244900 | -0.26073500 |
| H    | 5.63881900 | 2.51959900 | -0.66961700 |
| C    | 4.95389900 | -1.41021900 | -1.36002700 |
| H    | 5.39109500 | -0.56108000 | -1.88170400 |
| H    | 5.59654600 | -1.66296600 | -0.51819700 |
| H    | 4.95802900 | -2.25406300 | -2.05214600 |
| C    | 3.44981900 | -0.19897400 | 1.44068100 |
| H    | 2.63237000 | -0.84926100 | 1.75604400 |
| C    | 4.75384200 | -0.78658200 | 2.00630700 |
| H    | 5.62706400 | -0.18380800 | 1.77323600 |
| H    | 4.66551600 | -0.84215800 | 3.09348500 |
| H    | 4.93551500 | -1.79606000 | 1.64348400 |
| H    | 3.26119400 | 0.75838500 | 1.92636600 |

**C₆F₅I ---NET₃**

| Atom | X    | Y    | Z    |
|------|------|------|------|
| I    | -0.69299000 | -0.04226900 | 0.00464400 |
| C    | 1.44373000 | -0.01198600 | 0.00482300 |
| C    | 2.14549000 | 1.18481000 | -0.03127400 |
| C    | 2.18120000 | -1.18706400 | 0.04149900 |
| C    | 3.53212800 | 1.21795400 | -0.03125300 |
| C    | 3.56824600 | -1.17814700 | 0.04237300 |
| C    | 4.24688200 | 0.03042200 | 0.00581700 |
| F    | 1.56882100 | -2.38018500 | 0.07756100 |
| F    | 4.25655900 | -2.32485800 | 0.07824500 |
| F    | 5.58143700 | 0.05053000 | 0.00635400 |
| F    | 4.18529300 | 2.38505800 | -0.06669400 |
| F    | 1.49743200 | 2.35889300 | -0.06792900 |
| N    | -3.61952400 | -0.05102200 | -0.28163500 |
| C    | -3.87996200 | -1.26611400 | -1.07914900 |
| Atoms | X         | Y         | Z         |
|-------|-----------|-----------|-----------|
| H     | -3.30795  | -1.16852  | 0.00000   |
| C     | -3.81526  | 1.13621   | -1.13782  |
| H     | -3.15609  | 1.02086   | 0.94221   |
| C     | -4.45521  | 0.00331   | 0.94221   |
| H     | -5.28296  | 0.70348   | 0.78839   |
| H     | -4.91724  | -0.96975  | 1.09615   |
| H     | -4.94139  | -1.30345  | -1.36874  |
| H     | -4.84603  | 1.14623   | -1.52486  |
| C     | -3.52236  | 2.47148   | -0.46585  |
| H     | -3.63681  | 3.27051   | -1.19890  |
| H     | -4.20794  | 2.67974   | 0.35441   |
| H     | -2.50463  | 2.50923   | -0.08031  |
| C     | -3.48815  | -2.57080  | -0.39652  |
| H     | -4.05092  | -2.74778  | 0.51933   |
| H     | -3.67721  | 0.37680   | 2.19801   |
| H     | -3.17991  | 1.33934   | 2.09243   |
| C     | -3.45165  | 0.00000   | 0.32235   |
| C     | -2.43423  | 0.00000   | 0.11334   |
| C     | -3.15445  | -1.18514  | 0.18479   |
| C     | -3.15442  | 1.18514   | 0.18480   |
| C     | -4.53165  | -1.19867  | 0.32235   |
| C     | -4.53164  | 1.19867   | 0.32235   |
| C     | -5.22511  | 0.00000   | 0.39167   |
| C     | -5.22511  | 0.00000   | 0.39167   |
| F     | -2.52436  | 2.37105   | 0.12191   |
| F     | -5.19992  | 2.35660   | 0.38887   |
| F     | -6.55378  | 0.00000   | 0.52459   |
| F     | -5.19993  | -2.35660  | 0.38886   |
| F     | -2.52437  | -2.37105  | 0.12190   |
| N     | 2.47786   | 0.00000   | 0.45890   |
| C     | 2.77352   | 1.20185   | 1.26363   |
| H     | 2.13649   | 1.14504   | 2.14929   |
| C     | 2.77353   | -1.20186  | 1.26363   |
| H     | 2.13651   | -1.14505  | 2.14929   |
| C     | 3.09902   | 0.00000   | 0.87744   |
| H     | 2.72017   | 0.86821   | 1.41568   |
| H     | 2.72018   | -0.86821  | 1.41569   |
| H     | 3.81063   | 1.17248   | 1.62657   |
| H     | 3.81064   | -1.17249  | 1.62655   |
| C     | 2.52987   | -2.53353  | -0.56269  |
| H     | 3.26139   | -2.68147  | 0.23492   |
| H     | 1.54521   | -2.52827  | -0.09043  |
| C     | 2.52986   | 2.53352   | -0.56271  |
| H     | 3.26139   | 2.68147   | 0.23490   |

**C₆F₅I ... NBu₃**

| Atoms | X         | Y         | Z         |
|-------|-----------|-----------|-----------|
| I     | -0.29320  | 0.00000   | -0.10243  |
| C     | -2.43423  | 0.00000   | 0.11334   |
| C     | -3.15445  | -1.18514  | 0.18479   |
| C     | -3.15442  | 1.18514   | 0.18480   |
| C     | -4.53165  | -1.19867  | 0.32235   |
| C     | -4.53164  | 1.19867   | 0.32235   |
| C     | -5.22511  | 0.00000   | 0.39167   |
| C     | -5.22511  | 0.00000   | 0.39167   |
| F     | -2.52436  | 2.37105   | 0.12191   |
| F     | -5.19992  | 2.35660   | 0.38887   |
| F     | -6.55378  | 0.00000   | 0.52459   |
| F     | -5.19993  | -2.35660  | 0.38886   |
| F     | -2.52437  | -2.37105  | 0.12190   |
| N     | 2.47786   | 0.00000   | 0.45890   |
| C     | 2.77352   | 1.20185   | 1.26363   |
| H     | 2.13649   | 1.14504   | 2.14929   |
| C     | 2.77353   | -1.20186  | 1.26363   |
| H     | 2.13651   | -1.14505  | 2.14929   |
| C     | 3.09902   | 0.00000   | 0.87744   |
| H     | 2.72017   | 0.86821   | 1.41568   |
| H     | 2.72018   | -0.86821  | 1.41569   |
| H     | 3.81063   | 1.17248   | 1.62657   |
| H     | 3.81064   | -1.17249  | 1.62655   |
| C     | 2.52987   | -2.53353  | -0.56269  |
| H     | 3.26139   | -2.68147  | 0.23492   |
| H     | 1.54521   | -2.52827  | -0.09043  |
| C     | 2.52986   | 2.53352   | -0.56271  |
| H     | 3.26139   | 2.68147   | 0.23490   |
| Atom | X   | Y   | Z    |
|------|-----|-----|------|
| H    | 1.54521200 | 2.52826800 | -0.09043200 |
| C    | 4.62887100 | 0.00000800 | 0.91947500 |
| H    | 5.01747500 | 0.87581000 | 0.39356100 |
| H    | 4.76391200 | 0.87505600 | 2.88121600 |
| C    | 5.15566700 | 0.00001900 | 2.35421500 |
| H    | 4.76391400 | -0.87501000 | 2.88123000 |
| H    | 5.15567000 | 0.00001900 | 2.35421500 |
| C    | 6.68140500 | 0.00002200 | 2.42640300 |
| H    | 7.09593500 | 0.88137700 | 1.93259900 |
| H    | 7.03207900 | 0.00003100 | 3.45936700 |
| H    | 7.09593600 | -0.88134100 | 1.93261400 |
| C    | 2.61886100 | -3.70851700 | -1.53727300 |
| H    | 1.86713400 | -3.58308300 | -2.32163200 |
| C    | 2.61883900 | 3.70850700 | -1.53728900 |
| H    | 1.86710400 | 3.58306900 | -2.32163800 |
| H    | 3.59139300 | 3.69157800 | -2.03806000 |
| C    | 2.42061300 | 5.05788400 | -0.84972200 |
| H    | 3.18089600 | 5.22219100 | -0.08327200 |
| H    | 2.48169500 | 5.88111700 | -1.56268800 |
| H    | 1.44421200 | 5.10821200 | -0.36349500 |
| H    | 3.59142100 | -3.69158700 | -2.03803300 |
| C    | 2.42063000 | -5.05789000 | -0.84970200 |
| H    | 1.44422400 | -5.10821900 | -0.36348600 |
| H    | 3.18090400 | -5.22219300 | -0.08324200 |
| H    | 2.48172200 | -5.88112800 | -1.56266300 |

C₆F₃I ... NPr₃

| Atom | X   | Y   | Z    |
|------|-----|-----|------|
| I    | 0.67153400 | -0.18672700 | -0.09819800 |
| C    | 2.76770600 | -0.07138200 | -0.04717400 |
| C    | 3.54851800 | -1.22048600 | -0.02366100 |
| C    | 3.41291000 | 1.15922800 | -0.03425200 |
| C    | 4.93327200 | -1.14898600 | 0.01113600 |
| C    | 4.79665700 | 1.24614700 | 0.00054000 |
| C    | 5.55948800 | 0.08826600 | 0.02332500 |
| F    | 2.71495000 | 2.29976300 | -0.05470400 |
| F    | 5.39845100 | 2.43857800 | 0.01238400 |
| F    | 6.88960700 | 0.16438900 | 0.05698100 |
| F    | 5.66687100 | -2.26503000 | 0.03324700 |
| F    | 2.98492000 | -2.43316200 | -0.03371700 |
| N    | -2.87912700 | 0.04752900 | 0.03800800 |
| C    | -2.93334000 | 1.42335200 | -0.31834600 |
| C    | -2.12390800 | 2.34936600 | 0.34630600 |
| C    | -3.78744000 | 1.87279200 | -1.32816500 |
| C    | -2.16888200 | 3.69345200 | 0.00544000 |
| H    | -1.46391800 | 2.01172800 | 1.13186800 |
| C    | -3.81705600 | 3.21813100 | -1.67428400 |
| H    | -4.42340100 | 1.16800600 | -1.84371900 |
| C    | -3.01105300 | 4.13717300 | -1.01063500 |
| H    | -1.53283200 | 4.39460900 | 0.52875300 |
H   -4.48327300  3.54827300  -2.46001600
H   -3.03845000  5.18383800  -1.28007100
C   -2.95846300  -0.32180500   1.40777700
C   -2.27799200  -1.45344500   1.86883600
C   -3.70830700   0.43084500   2.31532300
C   -2.34602800  -1.81930700   3.20526000
H   -1.70188600  -2.04881100   1.17551100
C   -3.76052100   0.06659800   3.65515200
H   -4.24577700   1.30256900   1.97199700
C   -3.08271500  -1.05957000   4.10995000
C   -2.37015600  -0.83416700  -2.18054700
C   -3.91882600  -2.02395600  -0.77225400
C   -2.53554400  -1.79302700  -3.16951300
H   -1.71126300   0.00574800  -2.34704700
C   -4.06911900  -2.98760900  -1.76177200
H   -4.46488100  -2.11325500   0.15537600
C   -3.38144100  -2.87983600  -2.96046000
H   -1.99121900  -1.69477200  -4.09908300
H   -4.73761900  -3.82065500  -1.59139000
H   -3.50312400  -3.62995700  -3.73497700
C\textsubscript{6}F\textsubscript{5}I \cdots \text{Pyridine-N-oxide}
I   -0.55552400  -0.45954900  -0.67914600
C   -4.14777800   1.07799400  -0.38554800
C   -4.90627200   1.72600200   0.56650200
C   -5.47878400   1.00658800   1.60822500
C   -5.26312000  -0.36521500   1.65885900
C   -4.49790300  -0.98050800   0.69067600
N   -3.95071200  -0.26326800  -0.32284600
H   -6.07512600  -1.50103300  -2.36002900
H   -3.67121300   1.56371600  -1.22063900
H   -5.03972000   2.79395200   0.48050000
H   -5.68238800  -0.97164300   2.44766600
H   -4.28199900  -2.03551900   0.66177200
C   1.47943700  -0.10124200  -0.17995200
C   2.32217300  -1.13811100   0.19838200
C   2.01487600   1.17953300  -0.21669800
C   3.65053800  -0.91423300   0.52898700
C   3.34027700   1.42550700   0.10982200
C   4.16220700   0.37360200   0.48437400
F   1.25923300   2.22865300  -0.57193800
F   3.83146500   2.66892200   0.06619200
F   5.43888400   0.59949400   0.80019600
F   4.44132400  -1.93052300   0.89068700
F   1.87305800  -2.39978400   0.25723100
Trimethylamine-N-Oxide

I   0.91644300  0.34013200  -0.11091300
C   -1.21594800  0.08745100  -0.03586700
C   -1.79459500 -1.17368500  -0.02382600
C   -2.07309300  1.17819100   0.00228000
C   -3.16938200 -1.35121600   0.02337400
C   -3.45127300  1.02824000   0.04964600
C   -4.00261000 -0.24376100   0.06015700
F   -1.58858500  2.43066200  -0.00535200
F   -4.25369400  2.09934700   0.08564700
F   -5.32818500 -0.40143000   0.10582700
F   -3.69911400 -2.58094200   0.03340400
F   -1.03074800 -2.27863300  -0.05820700
O   3.49644100  0.80415200  -0.25799700
C   5.79790500  0.42707200  -0.14504700
H   6.56535700 -0.30147300   0.10786800
H   5.86245100  0.70890400  -1.19040700
H   5.87943200  1.30778000   0.48269100
C   4.28306900 -0.53733200   1.51873700
H   3.28509300 -0.94215300   1.64717600
H   5.03427200 -1.27402900   1.79489600
H   4.39450100  0.36762000   2.10598800
C   4.26273400 -1.36748900  -0.78811200
H   5.01541700 -2.11498000  -0.54452000
H   3.26644800 -1.75817500  -0.61214500
H   4.35738100 -1.04452900  -1.81915900
N   4.43982000 -0.15940100   0.07858100

N.N-Dimethylimidazolidinone

I   0.27281600 -0.16136600  -0.58928200
C   -1.79415400 -0.06814000  -0.15108900
C   -2.53501600 -1.22099300   0.07679800
C   -2.45952800  1.14926000  -0.08032900
C   -3.89078900 -1.16894000   0.36484900
C   -3.81460900  1.22196300   0.20620600
C   -4.53361200  0.05779200   0.43001300
F   -1.80626900  2.30048100  -0.28807900
F   -4.43216100  2.40628900   0.26875500
F   -5.83721900  0.11769400   0.70683200
F   -4.58206700 -2.29300200   0.58032100
F   -1.95728900 -2.42847400   0.02493000
O   3.06928500 -0.33557500  -1.17050800
C   5.57179100 -0.22357100   1.28905700
C   4.97659300  1.18735200   1.35489300
H   6.54614100 -0.22448700   0.78763600
H   5.73502000  1.96778100   1.35677500
C   3.31569700  2.36114700  -0.14299400
H 2.78545100 2.17737900 -1.07320900
H 2.58312500 2.51914900 0.65523400
H 3.91863100 -2.29086400 0.05406800
C 4.80913500 -2.60871200 -0.56166500
H 3.97228400 -2.94358600 -0.27126400
H 5.73302700 -2.37954400 -0.52758300
H 4.88058900 -2.94358600 0.92338800
C 3.86371600 -0.03929700 -0.27126400
N 4.17149000 1.23058200 0.14052900
N 4.58356600 -0.92852800 0.48219100
H 4.34189800 1.31347000 2.23913000
H 5.68459400 -0.68242900 2.26931300

\[
\text{C}_6\text{F}_5\text{I} \cdots \text{Triphenylphosphineoxide}
\]
I 1.26151000 -0.21377600 -0.77286800
C 3.34395300 -0.09110800 -0.40751800
C 3.94975300 1.12075100 -0.10108200
C 4.15448700 -1.21777000 -0.46255500
C 5.31212900 1.21385800 0.14128400
C 5.51883900 -1.14627400 -0.22337000
C 6.10069600 0.07513700 0.07974600
F 3.63755300 -2.42016200 -0.75132200
F 6.27723900 -2.24632100 -0.28299200
F 7.41248800 0.15435300 0.31130600
F 5.87079400 2.39335400 0.43392900
F 3.22869600 2.24850000 -0.02956300
O -1.50178800 -0.31447500 -1.30032700
C -4.17177800 -0.81508800 -0.78835000
C -5.09099300 -1.31651300 0.13434900
C -4.46634800 -0.85538300 -2.15319400
C -6.29838700 -1.84751400 -0.30536700
H -4.86635700 -1.30133700 1.19185400
C -5.67265700 -1.38907900 -2.58829700
H -3.74850400 -0.47836700 -2.86864800
C -6.58996300 -1.88296800 -1.66493300
H -7.00690200 -2.23714200 0.41259000
H -5.89595200 -1.42190400 -3.64582900
H -7.52824600 -2.29936700 -2.00538700
C -2.17680400 -0.78288700 1.34027900
C -1.48781700 -1.99855600 1.35410100
C -2.52125000 -0.16955440 2.54499500
C -1.15049600 -2.59377700 2.56213400
H -1.20649300 -2.46760200 0.42151300
C -2.18296600 -0.76959500 3.75316700
H -3.04437400 0.77646600 2.54575200
C -1.49910900 -1.98044200 3.76246200
H -0.61283600 -3.53192600 2.56773600
H -2.44907500 -0.28871000 4.68440300
H -1.23361700 -2.44387400 4.70290000
C       -2.90392900  1.69928200 -0.01639400
C       -4.16668200  2.20007800  0.30448700
C       -1.81924100  2.57339900 -0.12315100
H       -5.01552600  1.53455000  0.37781700
C       -1.99755900  3.93354400  0.09472100
H       -0.84221900  2.19031200 -0.38276500
C       -3.25720500  4.42841200  0.42018800
H       -5.32121900  3.94540000  0.76927500
H       -1.15535100  4.60625900  0.00838400
H       -3.39480100  5.48792100  0.58802900
P       -2.59216000 -0.07280000 -0.28147300

C6F5I...Pyrrolidine-N-oxide
I       0.59286300 -0.61440300  0.08484600
C       -1.47043400 -0.12826400  0.02429300
C       -2.44109700 -1.11759900 -0.06459400
C       -1.89975700  1.19159100  0.07154800
C       -3.79281400 -0.80927000 -0.10577500
C       -3.24638100  1.52109200  0.03202200
C       -4.19738800  0.51605600 -0.05726900
F       -1.01692300  2.19687700  0.15704100
F       -3.63407400  2.80008000  0.07887500
F       -5.49511500  0.82275000 -0.09648300
F       -4.70825400 -1.78004200 -0.19176700
F       -2.09739700 -2.41168000 -0.11383700
O       3.34638200 -1.23270800  0.17728500
C       5.71999500 -0.60317100  0.16627000
C       6.33731900  0.69254400 -0.37831300
H       5.95143700 -0.75998900  1.22237900
H       5.23627300  1.74803800 -0.16043100
H       7.26704500  0.96660600  0.11336500
H       5.20503800  2.49604400 -0.95005700
C       4.22267000 -0.37364000  0.05986100
N       4.02126300  0.93774600 -0.16390700
H       6.00980000 -1.50220700  0.37204600
H       6.53591800  0.58859000 -1.44449500
H       5.34969200  2.26206200  0.79699300

C6F5I...Dimethylsulfoxide
I       0.78400200 -0.17432500 -0.25819900
C       -1.32237000 -0.04012200 -0.07214900
C       -1.96114200  1.19067300  0.00902100
C       -2.11563400 -1.17955400 -0.02747500
C       -3.33928200  1.28949100  0.13008500
C       -3.49525100 -1.10226500  0.09318900
C       -4.11014600  0.13786600  0.17240600
F       -1.56682600 -2.39989100 -0.10000700

S73
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| F       | -4.23649800 | -2.21463000 | 0.13419200 |
| F       | -5.43660100 | 0.22268700  | 0.28879400 |
| F       | -3.92995500 | 2.48697600  | 0.20588800 |
| F       | -1.25856300 | 2.33138900  | -0.02796900|
| O       | 3.59017400  | -0.37241400 | -0.56064600|
| S       | 4.52252000  | 0.15541800  | 0.52964900 |
| C       | 5.87110600  | -1.05484600 | 0.64881300 |
| H       | 6.63371600  | -0.66415600 | 1.32010300 |
| H       | 5.44254000  | -1.96661600 | 1.05664400 |
| H       | 6.27389900  | -1.23035300 | -0.34679000|
| C       | 5.46724100  | 1.50355700  | -0.23773200|
| H       | 6.23971100  | 1.83143000  | 0.45744300 |
| H       | 5.90144400  | 1.14266400  | -1.16811000|
| H       | 4.76548100  | 2.31130400  | -0.42898700|

**C₆F₃I --- Dimethylformamide**

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| I       | -0.85283200 | -0.63663300 | -0.15436600|
| C       | 1.19584200  | -0.13785800 | -0.03479200|
| C       | 2.17243700  | -1.12205400 | 0.05362300 |
| C       | 1.61351000  | 1.18710700  | -0.04183600|
| C       | 3.51985700  | -0.80266800 | 0.13292200 |
| C       | 2.95614700  | 1.52771100  | 0.03646400 |
| C       | 3.91360400  | 0.52675800  | 0.12447500 |
| F       | 0.72439300  | 2.18572900  | -0.12458100|
| F       | 3.33318000  | 2.80837200  | 0.02824600 |
| F       | 5.20704800  | 0.84312800  | 0.20089800 |
| F       | 4.44125600  | -1.76747700 | 0.21746100 |
| F       | 1.83925600  | -2.41890500 | 0.06506500 |
| O       | -3.66658700 | -1.35180300 | -0.26085700|
| C       | -4.55213900 | -0.73400800 | 0.33483100 |
| C       | -5.90516600 | 1.20059500  | 0.94567300 |
| H       | -5.48263300 | 2.02692400  | 1.51957700 |
| H       | -6.68744100 | 1.59320400  | 0.29443600 |
| H       | -6.34673700 | 0.48496300  | 1.63512900 |
| C       | -4.17751300 | 1.38219300  | -0.82264700|
| H       | -3.53308900 | 0.75808500  | -1.43219400|
| H       | -4.90851100 | 1.88151200  | -1.45933700|
| H       | -3.57385800 | 2.14023400  | -0.32096700|
| N       | -4.86915300 | 0.55505600  | 0.15487200 |
| H       | -5.17780100 | -1.22694100 | 1.09144900 |

**C₆F₃I --- Acetophenone**

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| I       | 0.13642600  | -0.83807600 | 0.36634400 |
| C       | -1.84511600 | -0.17863000 | 0.08449300 |
| C       | -2.87850900 | -1.07964300 | -0.14063500|
| C       | -2.16047500 | 1.17414100  | 0.11837200 |
| C       | -4.18479000 | -0.65177300 | -0.32597600|
| C       | -3.46105800 | 1.61951500  | -0.06513000|
| C       | -4.47743800 | 0.70303900  | -0.28807300|
| Atoms | AO Coords | X | Y | Z |
|-------|-----------|---|---|---|
| C     | -1.21141200 | 2.09414500 | 0.33083900 |
| F     | -3.74098100 | 2.92593600 | -0.02840600 |
| F     | -5.16300800 | -1.53669900 | -0.54098100 |
| F     | -2.64232100 | -2.39636700 | -0.18574200 |
| O     | 2.93525800 | -1.83165900 | 0.63515400 |
| C     | 3.89829300 | -1.42102200 | -0.00017200 |
| C     | 4.19348100 | 0.03650800 | -0.08155900 |
| C     | 5.10642300 | 0.55548600 | -1.00585500 |
| C     | 3.53471100 | 0.91220000 | 0.78920600 |
| H     | 5.62858100 | -0.09950700 | -1.68763600 |
| C     | 3.77835300 | 2.27521300 | 0.73398200 |
| H     | 2.83987500 | 0.50956800 | 1.51087600 |
| C     | 4.67951700 | 2.78386200 | -0.19877500 |
| H     | 6.04098200 | 2.31603100 | -1.79280300 |
| H     | 3.26847100 | 2.94248200 | 1.41503500 |
| H     | 4.86692000 | 3.84803500 | -0.24510600 |
| C     | 4.80256500 | -2.39249400 | -0.71523400 |
| H     | 5.84715000 | -2.22345900 | -0.45366600 |
| H     | 4.51355200 | -3.40757900 | -0.45945300 |
| H     | 4.71271300 | -2.25833700 | -1.79501600 |

**C₆F₃I --- Benzophenone**

| Atoms | AO Coords | X | Y | Z |
|-------|-----------|---|---|---|
| I     | 0.55657300 | -0.46928000 | 0.55889400 |
| C     | 2.61745800 | -0.32829100 | 0.12711900 |
| C     | 3.37473600 | -1.45868800 | -0.15355500 |
| C     | 3.26251700 | 0.90217200 | 0.11166600 |
| C     | 4.72902200 | -1.37169000 | -0.44021300 |
| C     | 4.61576100 | 1.00845700 | -0.17288600 |
| C     | 5.35225400 | -0.13315400 | -0.45009000 |
| F     | 2.59134200 | 2.03119600 | 0.37288300 |
| F     | 5.21461500 | 2.20363300 | -0.18181900 |
| F     | 6.65408200 | -0.04029000 | -0.72482400 |
| F     | 5.43731600 | -2.47360000 | -0.70693300 |
| F     | 2.81543600 | -2.67525900 | -0.15591400 |
| O     | -2.32353000 | -0.78539700 | 1.03873700 |
| C     | -3.17586600 | -0.14058400 | 0.43232600 |
| C     | -2.92392600 | 1.28644400 | 0.09021800 |
| C     | -3.35682600 | 1.84432000 | -1.11610400 |
| C     | -2.17007000 | 2.06409200 | 0.97476100 |
| C     | -3.03204900 | 3.15695700 | -1.43432400 |
| H     | -3.92447600 | 1.24637600 | -1.81433100 |
| C     | -1.86966800 | 3.38191400 | 0.66704300 |
| H     | -1.83033100 | 1.62505700 | 1.90168300 |
| C     | -2.29614600 | 3.92876500 | -0.54105100 |
| H     | -3.35355000 | 3.57662900 | -2.37745300 |
| H     | -1.29876100 | 3.98155100 | 1.36234000 |
| H     | -2.05315400 | 4.95383800 | -0.78567800 |
| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| C    | -4.45562700 | -0.78987200 | 0.03914700 |
| C    | -4.46970000 | -2.17345200 | 0.00127400 |
| H    | -3.54081000 | -2.72394200 | 0.00127400 |

C₆F₅I ---4-Methylpyridine

| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| I    | -0.19220300 | -1.00289600 | 0.00001600 |
| C    | 1.75797400  | -0.14852200 | 0.00000600 |
| F    | 0.88772700  | 2.05918900  | 0.00003900 |
| F    | 3.35334400  | 3.12647300  | 0.00002500 |
| C    | 5.54767900  | 1.51695900  | -0.00001600 |

O    | -2.73537300 | -1.98600800 | 0.00002700 |
| N    | -3.57283200 | -0.97604000 | 0.00009000 |
| C    | 4.00362500  | -0.44638100 | 1.17013600 |
| C    | 4.00358800  | -0.44639100 | -1.17013600 |
| C    | 4.87536100  | 0.62012200  | 1.18663300 |
| H    | 3.61281500  | -0.92479800 | 2.05285700 |
| H    | 3.61274900  | -0.92481500 | -2.05284000 |
| C    | 5.33711500  | 1.19016400  | -0.00002800 |
| H    | 5.19319000  | 1.00519300  | 2.14500000 |
| H    | 5.19312000  | 1.00517600  | -2.14505000 |
| C    | 6.25737300  | 2.37457000  | -0.00004600 |
| H    | 6.89157800  | 2.38332800  | 0.88506300 |
| H    | 5.67919700  | 3.30167600  | -0.00001700 |
| H    | 6.89151900  | 2.38334700  | -0.88519700 |
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