Supplementary Material (ESI) for Chemical Communications

$BF_3{\cdot}OEt_2$ and TMSOTf: A Synergistic Combination of Lewis Acids

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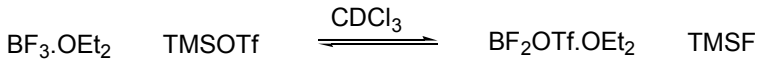
Supplementary Information

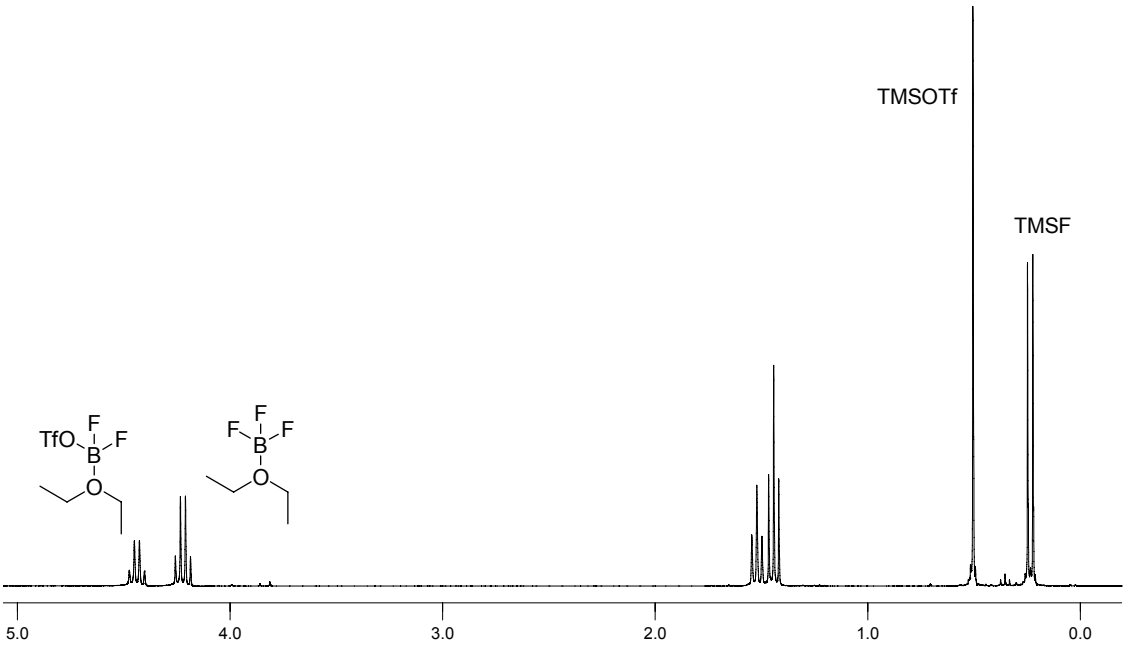
Contents

(a) Analysis of mixtures of TMSOTf and $BF_3{\cdot}OEt_2$ in $CDCl_3$ by NMR spectroscopy

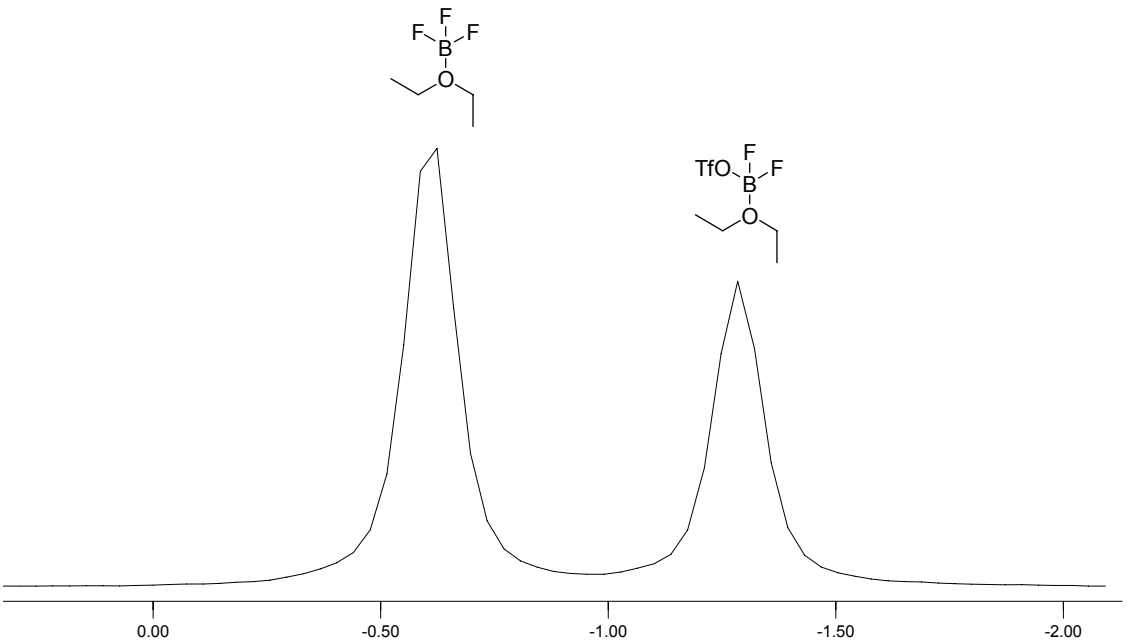


To a dry quartz NMR tube with a Young® valve was added dry $CDCl_3$ (0.8 ml) under a stream of nitrogen. To this was added $BF_3{\cdot}OEt_2$ (18 µl, 0.10 mmol) and TMSOTf (15 µl, 0.10 mmol). The NMR tube was sealed and NMR data was acquired on a multinuclear Eclipse ECP-300 instrument. Five species were observed, namely $BF_3{\cdot}OEt_2$, TMSOTf, $BF_2OTf{\cdot}OEt_2$, TMSF and Me_2SiF_2 in an apparent ratio of 1.18: 0.95: 0.84: 1.00: 0.02 respectively. Data for **$BF_3{\cdot}OEt_2$**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.44 (6H, t, *J* = 7.1 Hz, $OCH_2\mathit{CH_3}$), 4.22 (4H, q, *J* = 7.1 Hz, $O\mathit{CH_2}CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.2, 69.8; ^{11}B NMR (96 MHz, $CDCl_3$) δ = -0.62 (bs); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -152.8 (bs). Data for **TMSOTf**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.50 (9H, s, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -76.9 (bs, OTf). Data for **$BF_2OTf{\cdot}OEt_2$**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.52 (6H, t, *J* = 7.1 Hz, $OCH_2\mathit{CH_3}$), 4.44 (4H, q, *J* = 7.1 Hz, $O\mathit{CH_2}CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.2, 72.5 (t, $^3J_{C\text{-}F}$ = 2.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ = -1.30 (bs); ^{19}F NMR (282 MHz, $CDCl_3$) δ = [-146.4 (1.6F, bs, $^{11}BF_2$) and -146.3 (0.4F, bs, $^{10}BF_2$)], -76.7 (3F, *t*, $^5J_{F\text{-}F}$ = 2.8 Hz, OTf). Data for **TMSF**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.23 (9H, d, $^3J_{H\text{-}F}$ = 7.5 Hz,, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -157.7

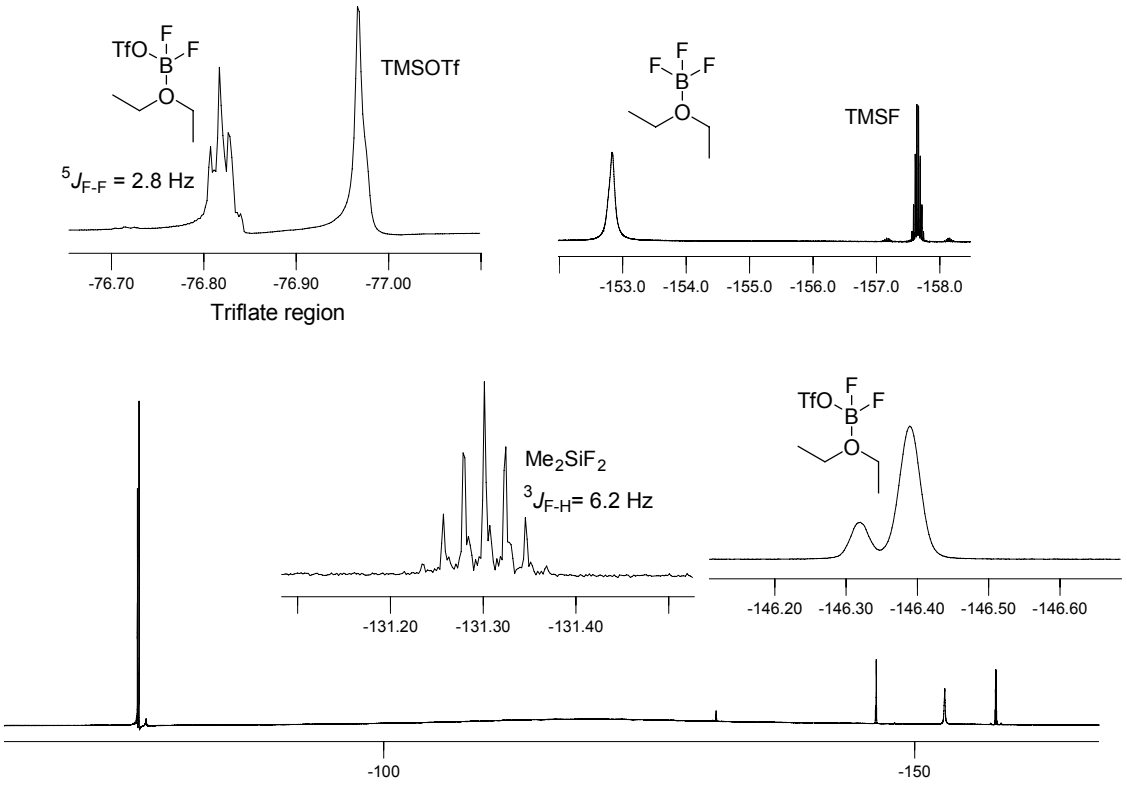
(1F, decet, $^{3}J_{F\text{-}H}$ = 7.5 Hz, Si*F*). Data for **Me_2SiF_2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.35 (6H, t, $^{3}J_{H\text{-}F}$ = 6.2 Hz,, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -131.3 (2F, septet, $^{3}J_{F\text{-}H}$ = 6.2 Hz, Si*F*).



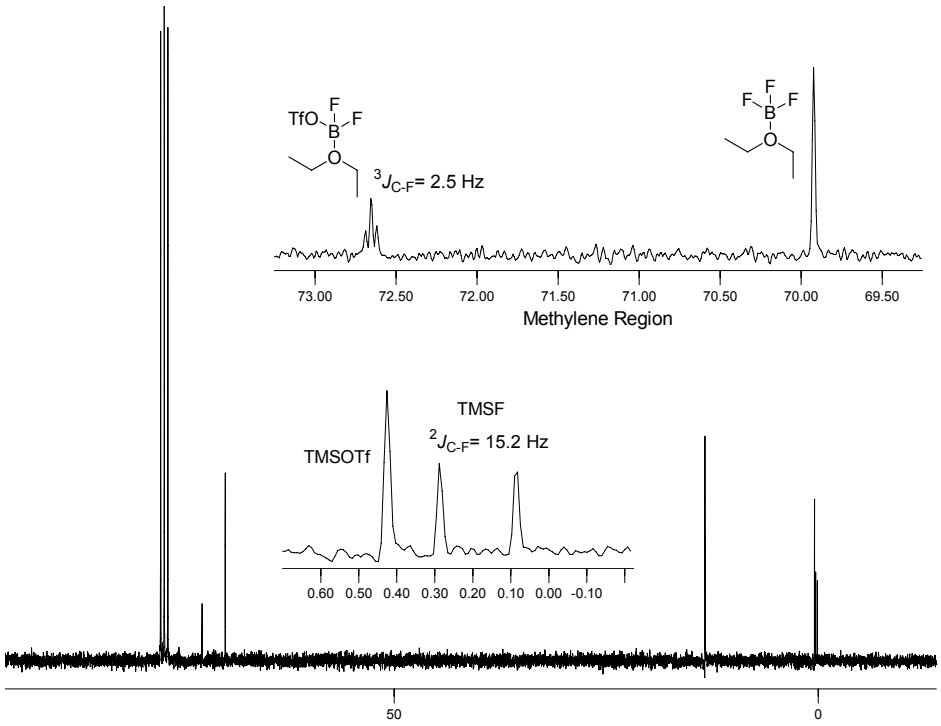
^{1}H NMR spectrum of 1:1 mixture of TMSOTf:BF_3·OEt_2 in $CDCl_3$



^{11}B NMR spectrum of 1:1 mixture of TMSOTf:BF_3·OEt_2 in $CDCl_3$

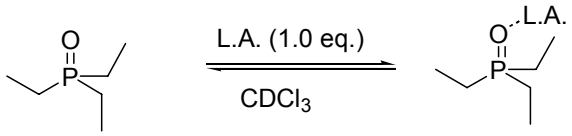


^{19}F NMR spectrum of 1:1 mixture of TMSOTf:BF_3·OEt_2 in $CDCl_3$



^{13}C NMR spectrum of 1:1 mixture of TMSOTf:BF_3·OEt_2 in $CDCl_3$

(B) Preparation of triethylphosphine complexes and discussion



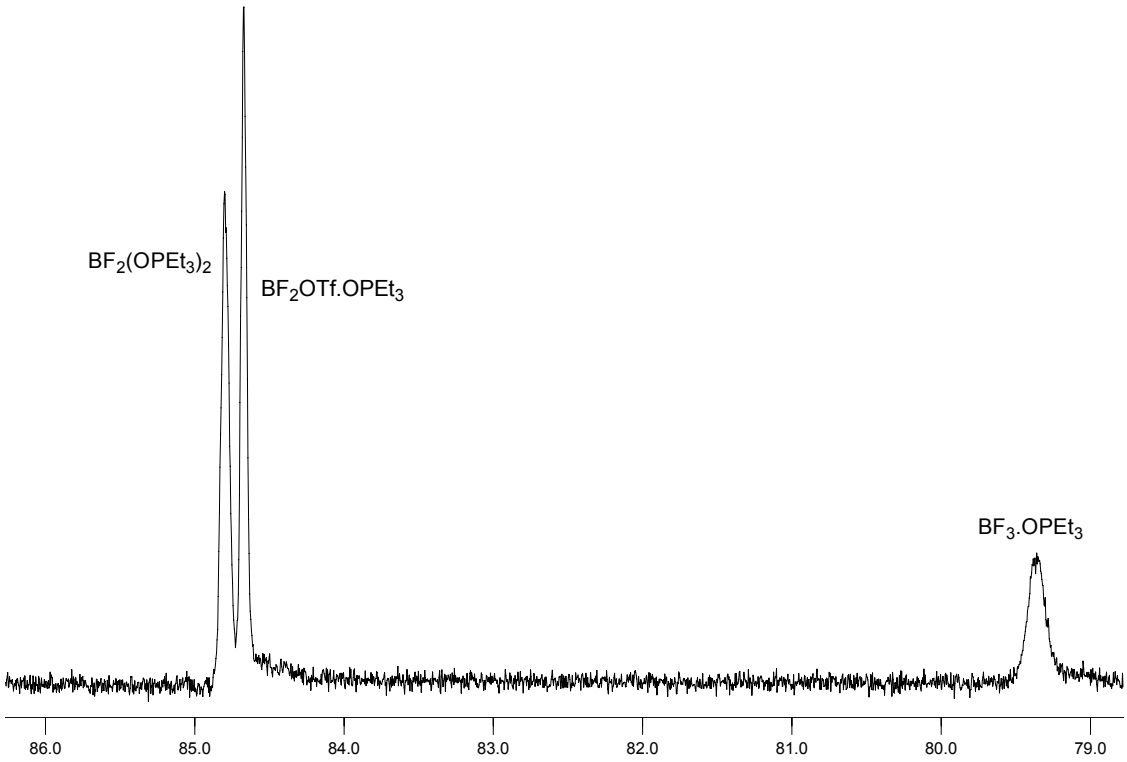
To a dry NMR tube was added dry $CDCl_3$ (0.8 ml) followed by Lewis acid (0.10 mmol) and triethylphosphine oxide (varying amounts). The sample was sealed and analysed by ^{1}H NMR, ^{31}P NMR and/or ^{19}F spectroscopy. The following data was acquired

(i) $OPEt_3$ **without Lewis acid**: ^{31}P NMR (121 MHz, hexane) δ = 47.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ = 56.0; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.17 (9H, dt, $^{3}J_{H\text{-}P}$ = 15.8 Hz and $^{1}J_{H\text{-}H}$ = 7.6 Hz, CH_3), 1.71 (6H, dq, $^{2}J_{H\text{-}P}$ = 11.8 Hz and $^{1}J_{H\text{-}H}$ = 7.6 Hz, CH_2).

(ii) $OPEt_3$ (0.25 eq.) with **BF_3·OEt_2**: ^{31}P NMR (121 MHz, $CDCl_3$) δ = 79.0 (q, $^{3}J_{P\text{-}F}$ = 5.6 Hz, BF_3·$OPEt_3$); ^{1}H NMR (300 MHz, $CDCl_3$) free diethyl ether and BF_3·$OPEt_3$ adduct with the following chemical shifts δ = 1.28 (9H, dt, $^{3}J_{H\text{-}P}$ = 18.0 Hz and $^{1}J_{H\text{-}H}$ = 7.7 Hz, CH_3), 2.09 (6H, dq, $^{2}J_{H\text{-}P}$ = 12.3 Hz and $^{1}J_{H\text{-}H}$ = 7.6 Hz, CH_2).

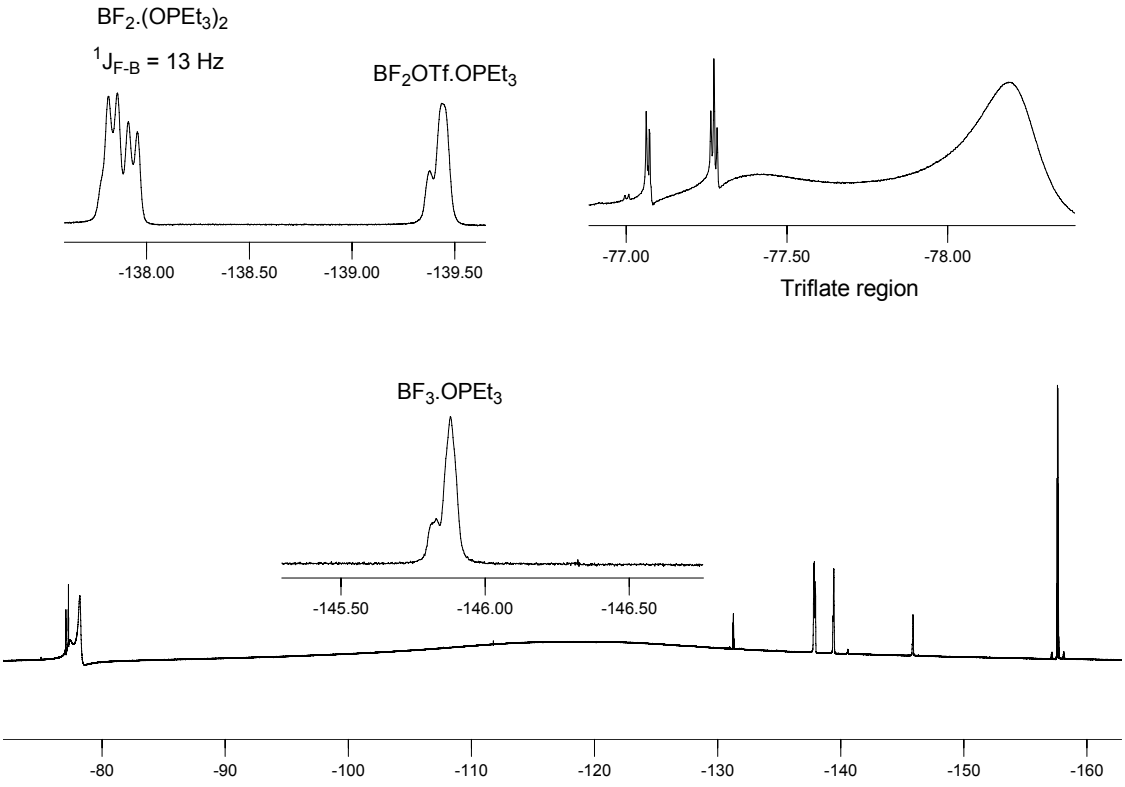
(iii) $OPEt_3$ (0.25 eq.) with **TMSOTf** (1.0 eq.): ^{31}P NMR (121 MHz, $CDCl_3$) δ = 88.1 (s, tentatively assigned as HOTf.$OPEt_3$), 92..8 (s, TMSOTf.$OPEt_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.41 (9H, s, *TMS*OTf.$OPEt_3$), 0.50 (33H, s, TMSOTf), 1.30 (10.8H, m, methyl of HOTf.$OPEt_3$ and TMSOTf.$OPEt_3$), 2.21 (1.2H, m, tentatively assigned to methylene of HOTf.$OPEt_3$), 2.40 (6H, m, methylene of TMSOTf.$OPEt_3$).

(iv) $OPEt_3$ (1.65 eq.) with **TMSOTf** (1.0 eq.) and **BF_3·OEt_2** (2.0 eq.): ^{31}P NMR (121 MHz, $CDCl_3$) δ = 79.0 (q, $^{3}J_{P\text{-}F}$ = 5.6 Hz, BF_3·$OPEt_3$), 84.6 (br. s, BF_2OTf·$OPEt_3$), 84.8 (t, $^{3}J_{P\text{-}F}$ = 2.2 Hz, $BF_2(OPEt_3)_2$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.22 (9H, d, $^{3}J_{H\text{-}F}$ = 7.5 Hz, TMSF), 1.19-1.35 (22.9H, m, methyl moieties of Et_2O, BF_3·$OPEt_3$, BF_2OTf·$OPEt_3$ and $BF_2(OPEt_3)_2$), 2.10-2.21 (9.9H, m, methylene moieties of BF_3·$OPEt_3$, BF_2OTf·$OPEt_3$ and $BF_2(OPEt_3)_2$), 3.70 (12H, br. s, O*CH*$_2$).



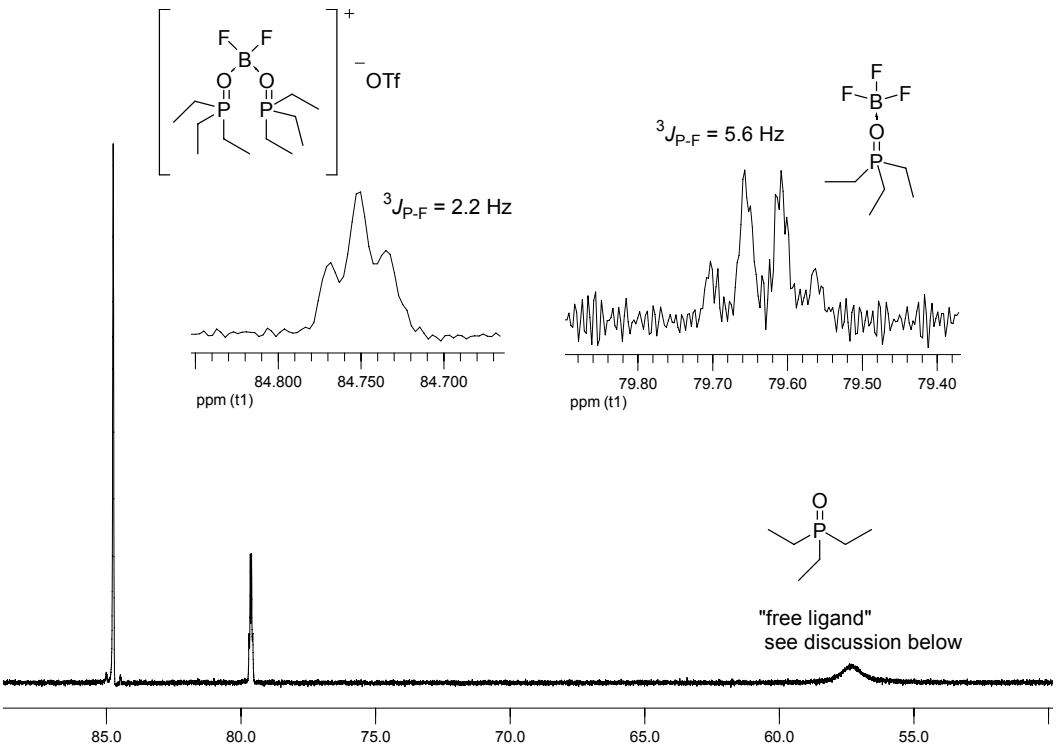
^{31}P spectrum of (iv)

(v) $OPEt_3$ (1.5 eq.) with **TMSOTf** (1.0 eq.) and **BF_3·OEt_2** (1.1 eq.): ^{19}F NMR (282 MHz, $CDCl_3$) δ = -157.6 (decet, $^3J_{F\text{-}H}$ = 7.5 Hz, TMSF), [δ = -145.9 (br. s, $^{11}BF_3$·$OPEt_3$) and -145.8 (br. s, $^{10}BF_3$·$OPEt_3$)], [δ = -139.5 (br. s, $^{11}BF_2$OTf·$OPEt_3$) and -139.4 (br. s, $^{10}BF_2$OTf·$OPEt_3$)], -137.9 (1:1:1:1 q, $^1J_{F\text{-}B}$ = 13.0 Hz, $^{11}BF_2(OPEt_3)_2$), -78.5-77.0 (m, OTf).

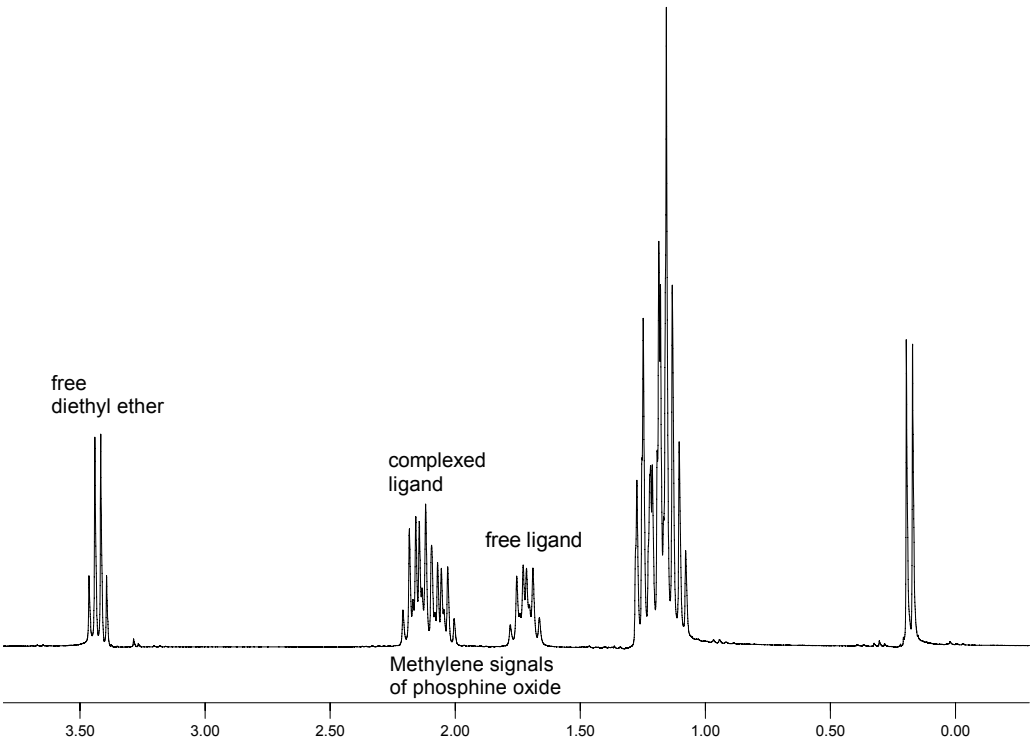


^{19}F spectrum of (v)

(vi) $OPEt_3$ (4.7 eq.) with **TMSOTf** (1.0 eq.) and **BF_3·OEt_2** (2.0 eq.): ^{31}P NMR (121 MHz, $CDCl_3$) δ = 79.0 (q, $^3J_{P\text{-}F}$ = 5.6 Hz, BF_3·$OPEt_3$), 84.8 (t, $^3J_{P\text{-}F}$ = 2.2 Hz, BF_2·$(OPEt_3)_2$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.22 (9H, d, $^3J_{H\text{-}F}$ = 7.5 Hz, TMSF), 1.07-1.30 (76H, m, methyl moieties of Et_2O, BF_3·$OPEt_3$ and $BF_2(OPEt_3)_2$), 1.72 (11H, methylene of free $OPEt_3$), 2.10-2.21 (26H, m, methylene moieties of BF_3·$OPEt_3$ and $BF_2(OPEt_3)_2$), 3.70 (9H, q, O*C*H_2).

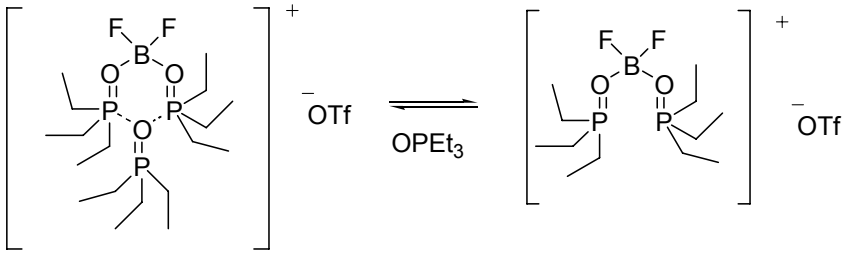


^{31}P spectrum of (vi)



^{1}H spectrum of (vi)

In the ^{31}P spectrum of (vi) the signal for "free ligand" is extremely broad. Since the resonances of the complexed species are still relatively sharp, there remains at least two possibilities for such a phenomenon: (i) trace amounts of protic acid are present and the broad signal represents an average of two species (free and protonated ligand). (ii) in the existing BF_3 and BF_2 complexes there exists a rapidly exchanging second coordination sphere of ligand (see figure below)

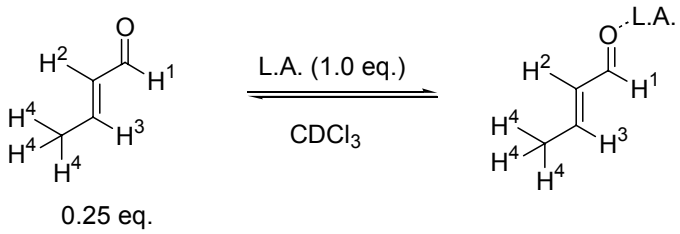


Possible second coordination sphere of ligand

In the 1970s Gutmann introduced a quantitative parameter for describing the electrophilic character of solvents.[1] They found that the ^{31}P chemical shift of triethylphosphine oxide was very sensitive to solvent; donation of electron density from oxygen to the electrophilic solvent, decreased the electron density on phosphorous causing a downfield shift. The δ values were normalised relative to that of the Et_3PO-$SbCl_5$ adduct dissolved in 1,2-dichloroethane, which was given the arbitrary number of 100; the chemical shift for Et_3PO in hexane was given the value 0. These values are termed "acceptor numbers" or *AN*s. This method has been extended by Beckett and co-workers to include Lewis acids.[2] The phosphine oxide complexes described herein, in addition to providing further evidence for $BF_2OTf{\cdot}OEt_2$ also provides us with a relative order of Lewis acidity. The downfield shift of the ^{31}P resonance upon complexation suggests the following order of decreasing Lewis acidity: TMS^+ (92.8 ppm) > H^+ (88.1 ppm) > BF_2OTf (84.6 ppm)> BF_3 (79.0 ppm). As a caveat, although Beckett and co-workers have shown that there is a linear correlation between the Gutmann and Childs methods, others have shown that this trend doesn't strictly apply to all Lewis acids.[3, 4] Britozsek and co-workers suggest that the non-linear behavior can be rationalised in terms of the *hard soft acid base* classification; for example taking a hard Lewis acid such as BF_3, its interaction with a carbonyl group (having a π orbital covalent which is largely

covalent in character) will be weaker than its interaction with phosphine oxide, whose double bond has more ionic character.[3] As we have shown in this communication, the concentration of the Lewis acid-Lewis base complex can be just as important as the reactivity of the Lewis acid-Lewis base complex.

(C) Quantification of Lewis acidity: Method of Childs[5]



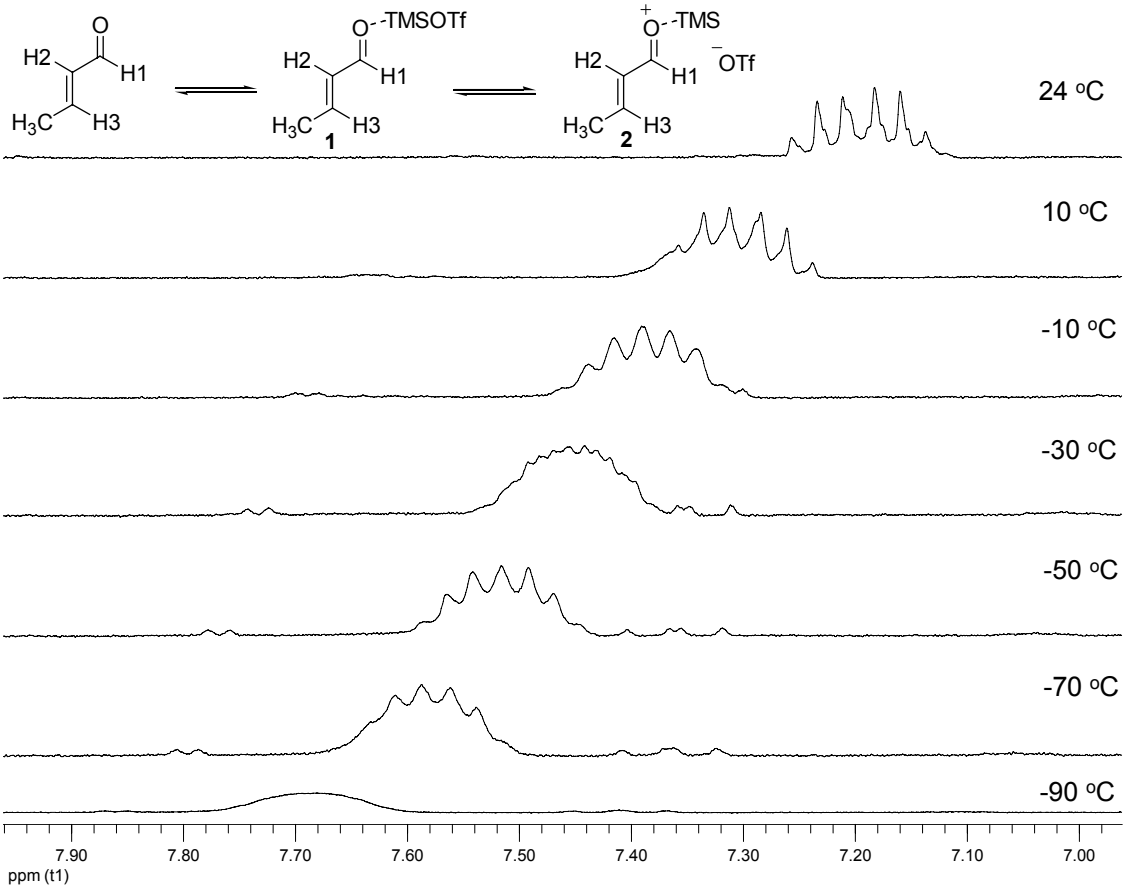
To a dry NMR tube was added dry $CDCl_3$ (0.8 ml) followed by Lewis acid (0.10 mmol) and crotonaldehyde (0.03 mmol). The sample was sealed and analysed by ^{1}H NMR spectroscopy. In most cases data was acquired at low temperatures (as low as -55 ^{o}C) in order to reduce the rate of ligand exchange. The following data was acquired:

(a) *trans*-crotonaldehyde **without Lewis acid**: ^{1}H NMR ($CDCl_3$, r.t.) δ = 2.03 (3H, dd, J = 6.8, 1.7 Hz, H4), 6.15 (1H, ddq, J = 15.5, 8.0, 1.7 Hz, H2), 6.88 (1H, dq, J = 15.5, 6.8 Hz, H3), 9.50 (1H, d, J = 8.0 Hz, H1).

(b) *trans*-crotonaldehyde with **BF_3·OEt_2**: ^{1}H NMR ($CDCl_3$, -55 ^{o}C.) the spectrum showed free crotonaldehyde which was ~0.05 ppm downfield of those chemical shifts given in (a), free diethyl ether, BF_3·OEt_2 and a new species which is assigned as the BF_3 crotonaldehyde complex with the following chemical shifts δ = 2.45 (3H, br. d, J = 7.0 Hz, H4), 6.77 (1H, br. dd, J = 15.2, 9.5 Hz, H2), 8.05 (1H, br. dq, J = 15.2, 7.0 Hz, H3), 9.15 (1H, br. d, J = 9.3 Hz, H1).

(c) *trans*-crotonaldehyde with **TMSOTf**: ^{1}H NMR (CD_2Cl_2, r.t.) the spectrum showed one set of signals for the TMS moiety (δ = 0.50, s) and one for crotonaldehyde with the following chemical shifts δ = 2.13 (3H, dd, J = 6.9, 1.5 Hz, H4), 6.31 (1H, ddq, J = 15.6,

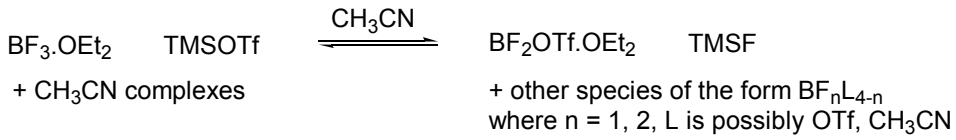
8.3, 1.5 Hz, H2), 7.17 (1H, dq, *J* = 15.6, 6.9 Hz, H3), 9.42 (1H, br. d, *J* = 8.3 Hz, H1).The NMR sample was then cooled from room temperature to -90 ºC in increments of 20 ºC (See figure below). As the temperature was lowered, the H3 resonance broadened slightly and was observed to shift further downfield; at -90 ºC [Δδ(H3)] was measured to be 0.70 ppm. Although chemical shift of free crotonaldehyde is inherently dependent upon temperature [Δδ(H3) is ~0.1 ppm between room temperature and -55 ^{o}C], the large downfield shift observed here indicates an increase in the concentration of complexed species **1** and/or **2** due to the decreasing TΔS term. The large temperature effect on K_{eq} suggests that ΔS is of significant magnitude which suggests that the entropically more demanding hypervalent species **1** rather than **2** predominates. Unfortunately, even at -90 ^{o}C the H3 resonance remained averaged and thus we are unable to compare the reactivity of complex **1** or **2** to that of the BF_3 or BF_2OTf complex.



VT-NMR of a solution of TMSOTf and crotonaldehyde

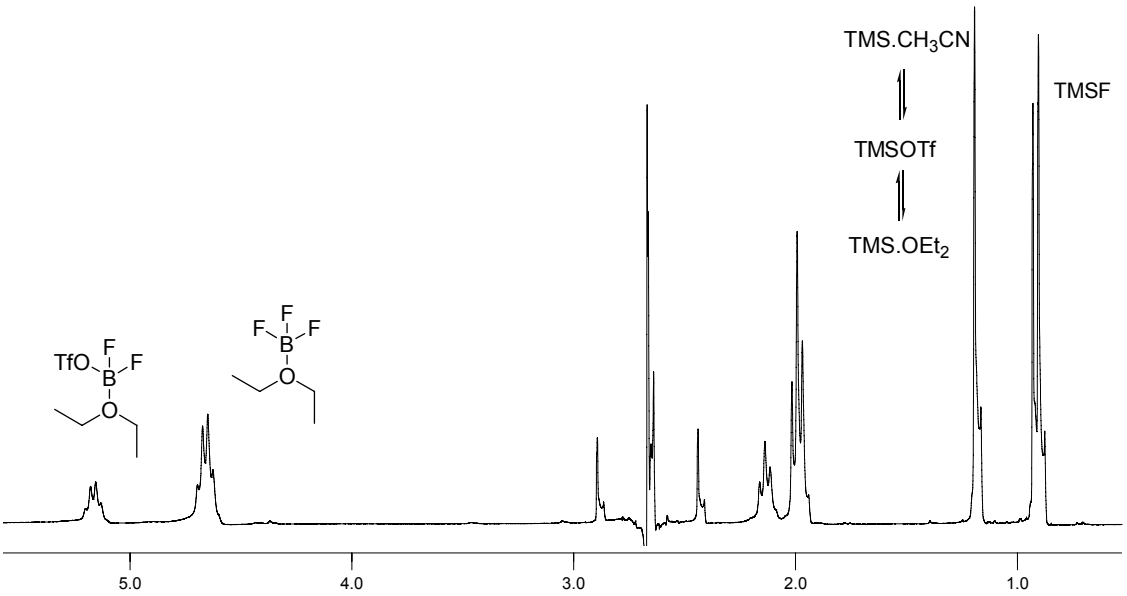
(d) *trans*-crotonaldehyde with **TMSOTf** and **BF_3·OEt_2**: ^{1}H NMR ($CDCl_3$, -55 ^{o}C) the spectrum showed a set of crotonaldehyde signals which are assigned as the BF_3-crotonaldehyde complex as given in (b); signals for TMSF, BF_3·OEt_2, BF_2OTf·OEt_2, the TMS moiety (TMSOTf and other species) and broad signals for free etherate and crotonaldehyde were also apparent; a further set of relatively sharp crotonaldehyde signals are assigned as the BF_2OTf-crotonaldehyde complex with the following chemical shifts δ = 2.13 (3H, br. d, *J* = 7.0 Hz, H4), 6.89 (1H, br. dd, *J* = 14.9, 9.3 Hz, H2), 8.34 (1H, br. dq, *J* = 14.9, 7.0 Hz, H3), 9.14 (1H, br. d, *J* = 9.3 Hz, H1).

(D) Analysis of mixtures of TMSOTf and BF_3·OEt_2 in CH_3CN by NMR spectroscopy

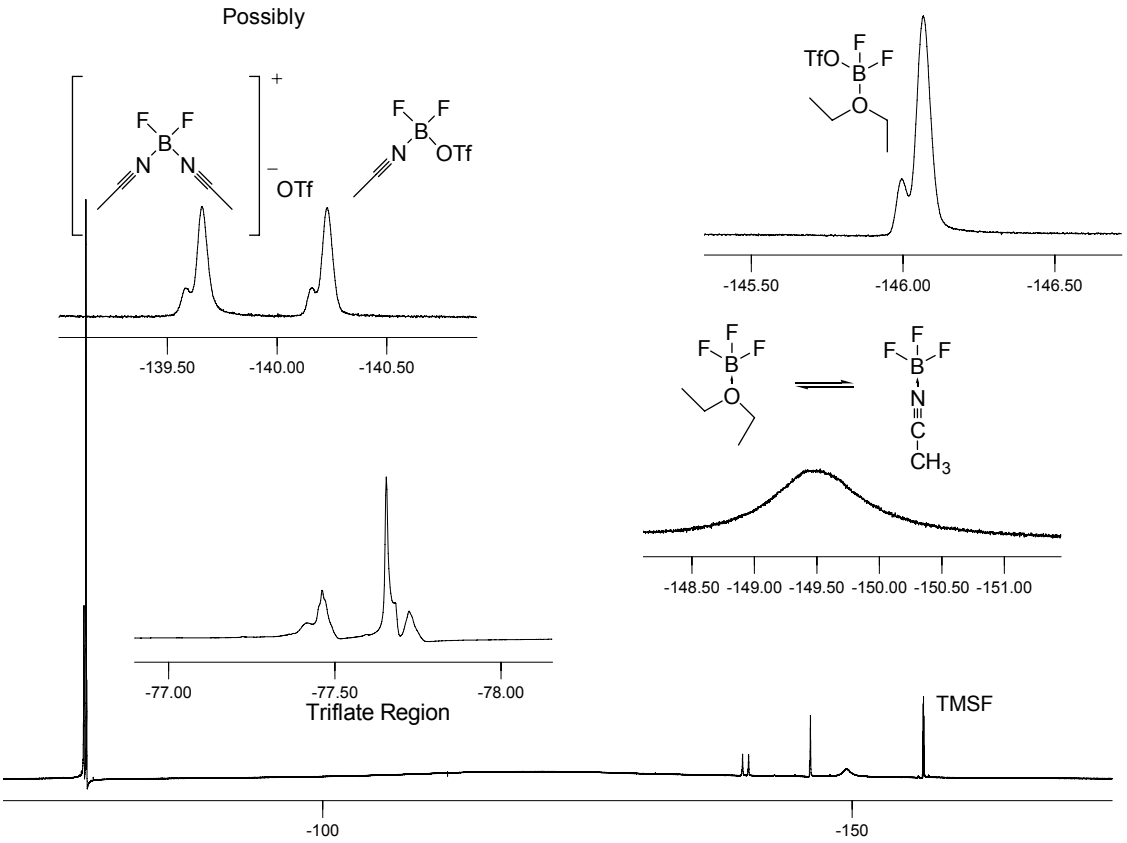


To a dry quartz NMR tube with a Young® valve was added dry CH_3CN (0.8 ml) under a stream of nitrogen. To this was added BF_3·OEt_2 (18 µl, 0.10 mmol) and TMSOTf (15 µl, 0.10 mmol). The NMR tube was sealed and NMR data was acquired on a multinuclear ECP-300 instrument. For ^{1}H the spectrum, the solvent signal was pre-saturated; the signals are broad due to the lack of a deuterium lock. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.23 (21.0H, br. d, $^3J_{H\text{-}F}$ = 7.4 Hz, TMSF), 0.50 (14.1H, br. s, averaged signal of TMSOTf, TMS.CH_3CN and TMS.OEt_2), 1.31 (16.2H, br. t, *J* = 7.1 Hz, methyl of Et_2O, BF_3·OEt_2 and perhaps TMS.O*Et*$_2$). 1.45 (6H, br. q, *J* = 7.1 Hz, methyl of BF_2OTf·OEt_2), 3.93 (10.8H, br. q, *J* = 7.1 Hz, methylene of Et_2O, BF_3·OEt_2 and perhaps TMS.O*Et*$_2$), 4.48 (4H, br. q, *J* = 7.1 Hz, methylene of BF_2OTf·OEt_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -156.7 (~3F, decet, $^3J_{F\text{-}H}$ = 7.4 Hz, TMSF), -149.3 (~6.0F, br. s, BF_3·OEt_2 and BF_3·CH_3CN), [δ = -146.1 (~2.4F, bs, ^{11}B*F*$_2$OTf·OEt_2) and -146.0 (~0.6F, bs, ^{10}B*F*$_2$OTf·OEt_2)], [-140.2 (~0.8F, bs, ^{11}B*F*$_n$L$_{n\text{-}4}$) and -140.1 (~0.2, bs, ^{10}B*F*$_n$L$_{n\text{-}4}$)], [-139.7 (~0.8F, bs, ^{11}B*F*$_n$L$_{n\text{-}4}$) and -139.6 (~0.2F, bs, ^{10}B*F*$_n$L$_{n\text{-}4}$)], -77.8—77.6 (~9.0F, m, OTf), -77.5 (~4.5F, *t*, $^5J_{F\text{-}F}$ = 2.9 Hz, BF_2*OTf*·OEt_2), -77.4 (~1.0F, br. s, OTf); ^{11}B NMR

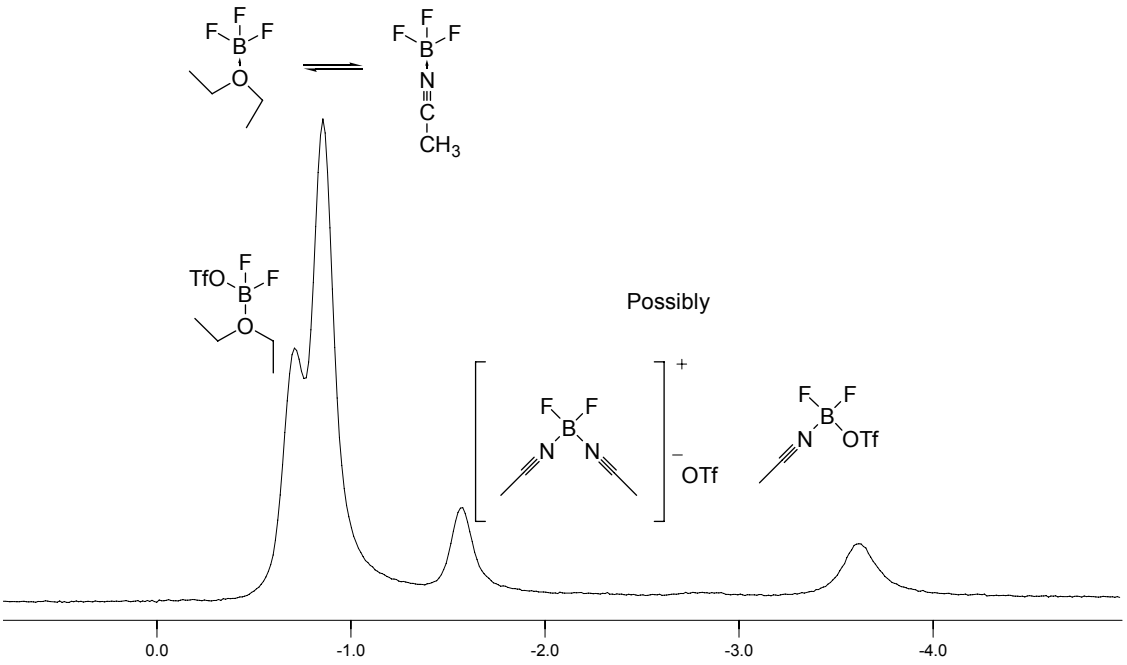
(96 MHz, $CDCl_3$) δ = -3.59 (1B, br. s), -1.56 (1B, bs), [-0.86 (br. s) and -0.70 (br. s), ~10B].



^{1}H NMR spectrum of 1:1 mixture of TMSOTf:BF_3·OEt_2 in CH_3CN



^{19}F NMR spectrum of 1:1 mixture of TMSOTf:BF_3·OEt_2 in CH_3CN



^{11}B NMR spectrum of 1:1 mixture of TMSOTf:BF_3·OEt_2 in CH_3CN

Supplementary Material (ESI) for Chemical Communications

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