Supporting Information for:

Beyond FLP additions: FLP deprotonation and C-O bond cleavage of aliphatic, aryl and ester derived olefins

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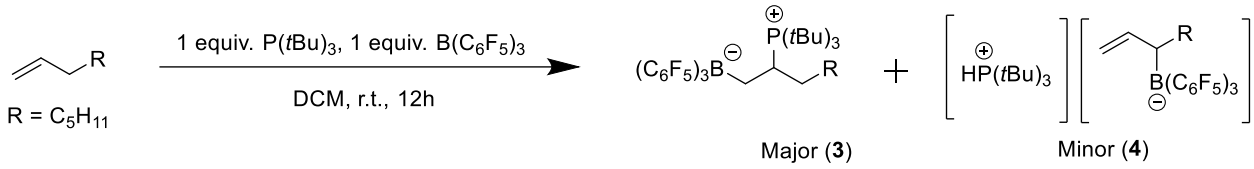
General Considerations

All manipulations were performed in a Glove box MB LABmaster produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N2 unless otherwise mentioned. All glassware and Teflon-coated stir bars were oven-dried and cooled under vacuum before use. Dry, oxygen-free pentane, toluene and dichloromethane were prepared using an Innovative Technologies solvent purification system and stored over activated 4 Å molecular sieves before use. Deuterated chloroform ($CDCl_3$) was purchased from Sigma-Aldrich, distilled from calcium hydride and stored over molecular sieves (4 Å) for at least two days prior to use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise.

All NMR spectra were collected at 298K on a Bruker AvanceIII 400, an Agilent DD2 400, or an Agilent DD2 500 MHz spectrometer equipped with a ^{13}C-sensitive cryogenically cooled probe using 3- or 5-mm diameter NMR tubes or in a J-Young tube. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra are referenced externally to $SiMe_4$ and presented as follows: chemical shift (δ/ppm), coupling constant (Hz), normalized integrals. $^{31}P\{^{1}H\}$, ^{19}F, and ^{11}B NMR chemical shifts (δ/ppm) are reported relative to H_3PO_4, $CFCl_3$, and $(Et_2O)\cdot BF_3$ external standards. X-ray data were collected on a Bruker Apex II diffractometer at 150(±2) K for all crystals.

Reaction of 1-octene, $B(C_6F_5)_3$, and $PtBu_3$



A 5 mL DCM solution of $B(C_6F_5)_3$ (0.100 g, 1.9 mmol, 1 equiv.) was added to a 5 mL DCM solution of $PtBu_3$ (0.039 g, 1.9 mmol, 1 equiv.) and stirred for 5 mins at room temperature. A DCM solution of 1-octene (0.033, 2.8 mmol, 1.5 equiv.) was added and allowed to stir for 12 hours at room temperature. After which, the solvent was removed *in vacuo*, resulting in a yellow residue. This residue was washed twice with 10 mL of pentane. It was then dissolved in a minimum amount of toluene, layered with pentane and stored at -35°C overnight. An off-white oil precipitated from the solution. Decanting the solvent and triturating the oil with 10 mL of pentane 8 times and diethylether twice generated a mixture of **3** and **4** as a white powder (0.120 g, 74% yield).

Spectral data of **3** (same as previously reported).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ -13.4 (br s, 1B)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -130.9 (br s, 6F, *o*-C_6F_5), -162.5 (br s, 3F, *p*-C_6F_5), -166.1 (br s, 6F, *m*-C_6F_5).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298K): δ 56.89 (s, 1P)

^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 56.89 (s, 1P).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 2.83 (br m, 1H, PC*H*), 2.34 (br m, 1H, CHCH_2), 2.01 (br m, 2H, BCH_2), 1.61 (d, 27H, $^{3}J_{HP}$ = 13 Hz, *t*Bu), 1.54 – 0.9 (m, 8H, alkyl chain), 0.81 (t, $^{3}J_{HH}$ = 8 Hz, CH_2CH_3)

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K): δ 41.4 (d, $^{1}J_{CP}$ = 24 Hz, *t*Bu), 39.9 (d, $^{1}J_{CP}$ = 28 Hz, P*C*H), 34.3 (s, PCH*C*H_2), 33.2 (d, $^{3}J_{CP}$ = 3.1 Hz, PCHCH_2), 31.4 (s, *t*Bu), 30.0 (s, PCHCH_2CH_2*C*H_2), 29.7 (s, *C*H_2CH_2CH_3), 22.8 (s, *C*H_2CH_3), 14.0 (s, CH_2*C*H_3)

Spectral data of **4**

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ –13.4 (br s, 1B)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -129.4 (br s, 6F, *o*-C_6F_5), -161.9 (br s, 3F, *p*-C_6F_5), -166.1 (br s, 6F, *m*-C_6F_5).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298K): δ 56.16 (s, 1P)

^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 56.16 (d, $^{1}J_{PH}$ = 446 Hz, 1P).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.53 (d, $^{1}J_{HP}$ = 446 Hz, 1H), 5.49 (ddd, $^{3}J_{HH}$ = 15, 8, 8 Hz, 1H, CH_2CH), 4.75 – 5.67 (m, 2H, CH_2CH) 2.01 (br m, 1H, BC*H*) 1.61 (d, 27H, $^{3}J_{HP}$ = 13 Hz, *t*Bu), 1.54 – 0.9 (m, 10 H, alkyl chain), 0.88 (t, $^{3}J_{HH}$ = 7 Hz, CH_2CH_3)

$^{13}C\{^{1}H\}$ NMR Partial (126 MHz, $CDCl_3$, 298 K): δ 135.8 (s, CH_2*C*H), 128.1 (s, *C*H_2CH), 31.5 (s, *t*Bu), 30.2 (s, *C*$H_2CH_2CH_2CH_3$), 30.1 (s, *C*$H_2CH_2CH_3$), 22.5 (s, *C*H_2CH_3), 14.2 (s, CH_2*C*H_3)

HRMS: $C_{26}H_{15}BF_{15}$ (Negative mode) Calc: 622.1069, Obs: 622.1023; (Positive mode): $C_{12}H_{28}P$ Calc: 203.1923, Obs: 203.1921.

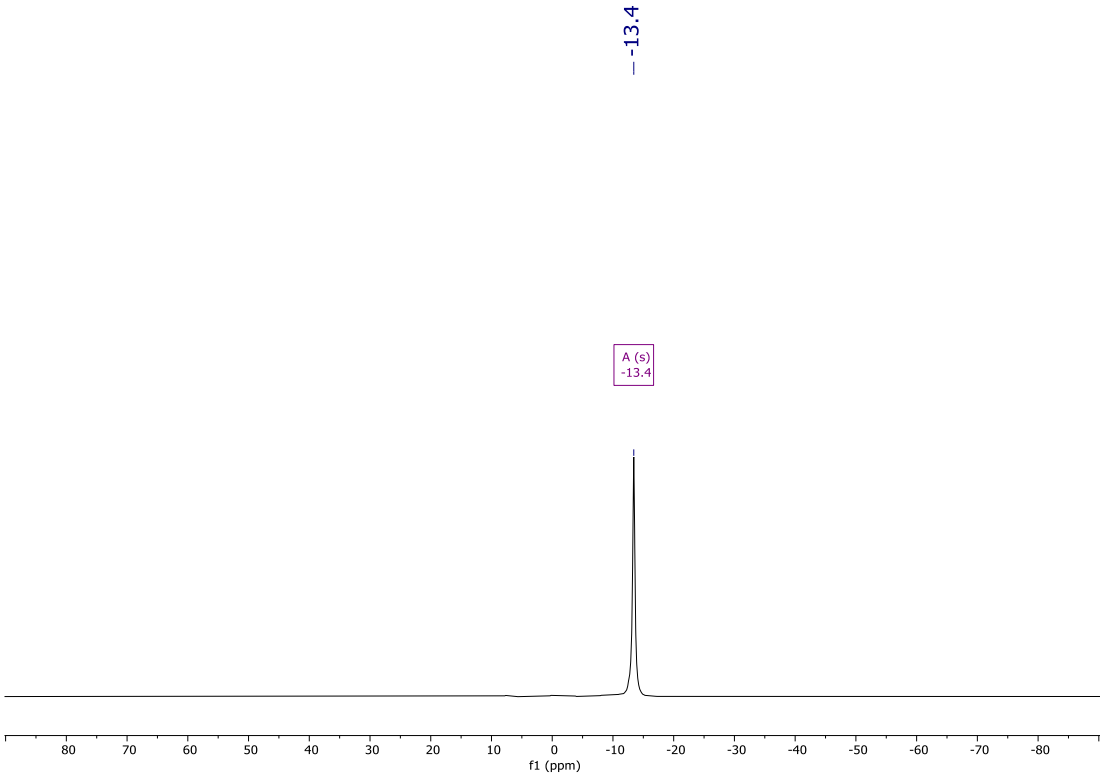


Figure S 1. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **3** and **4**

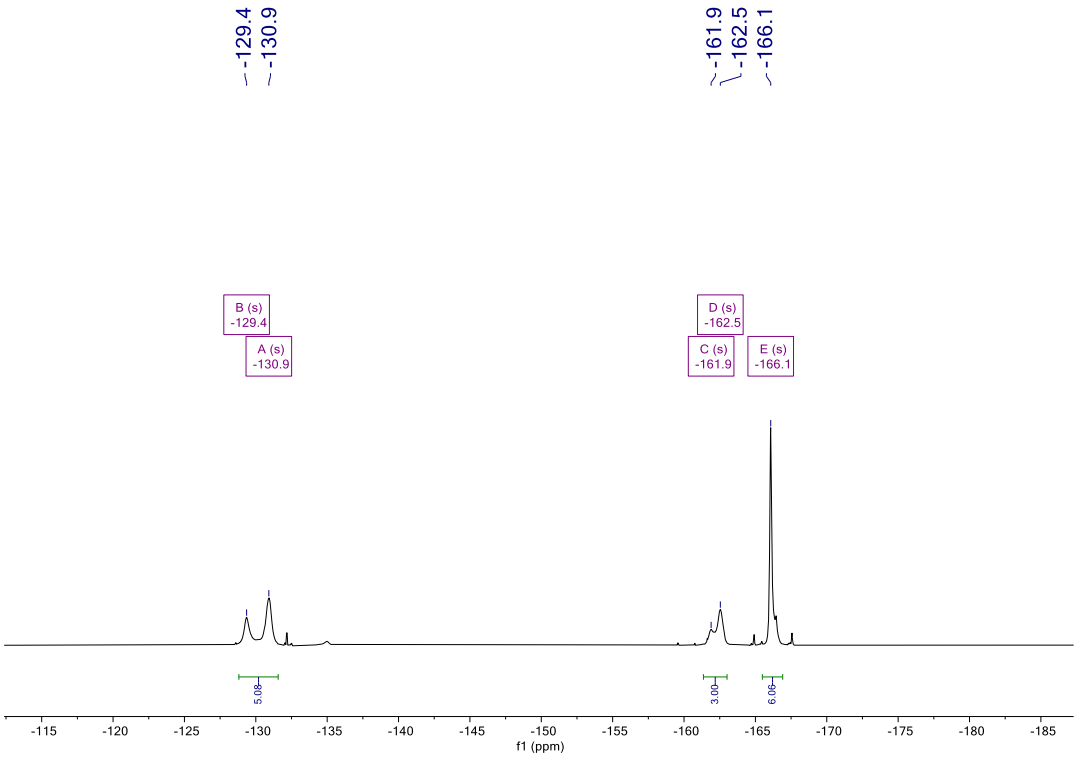


Figure S 2. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **3** and **4**

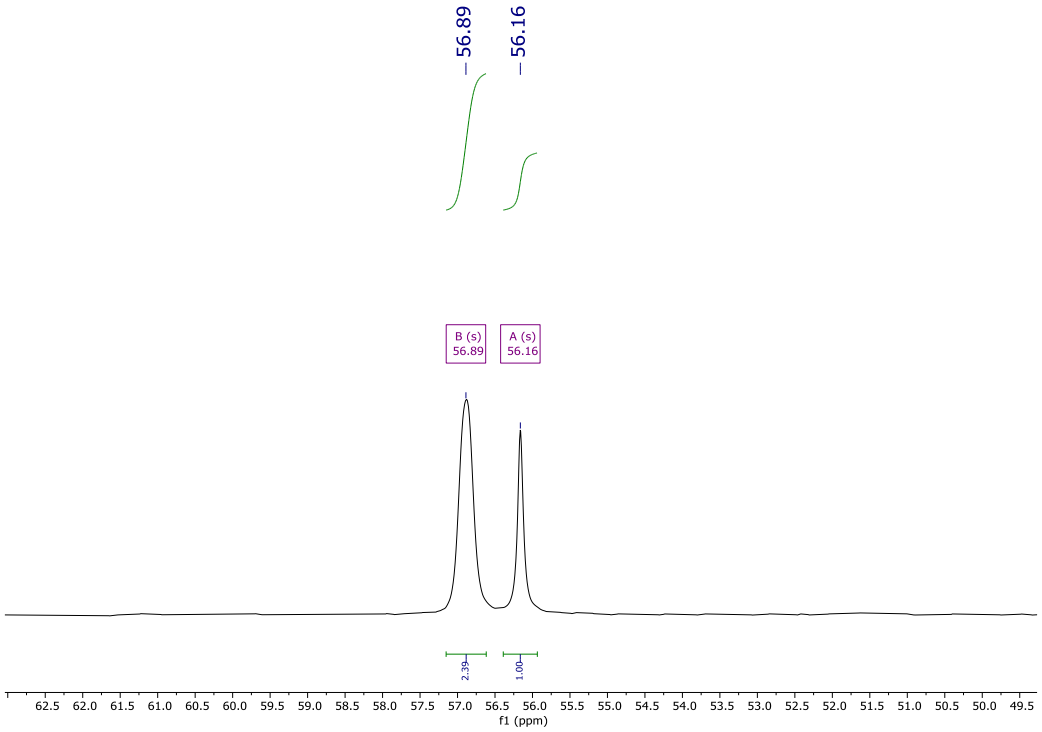


Figure S 3. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **3** and **4**

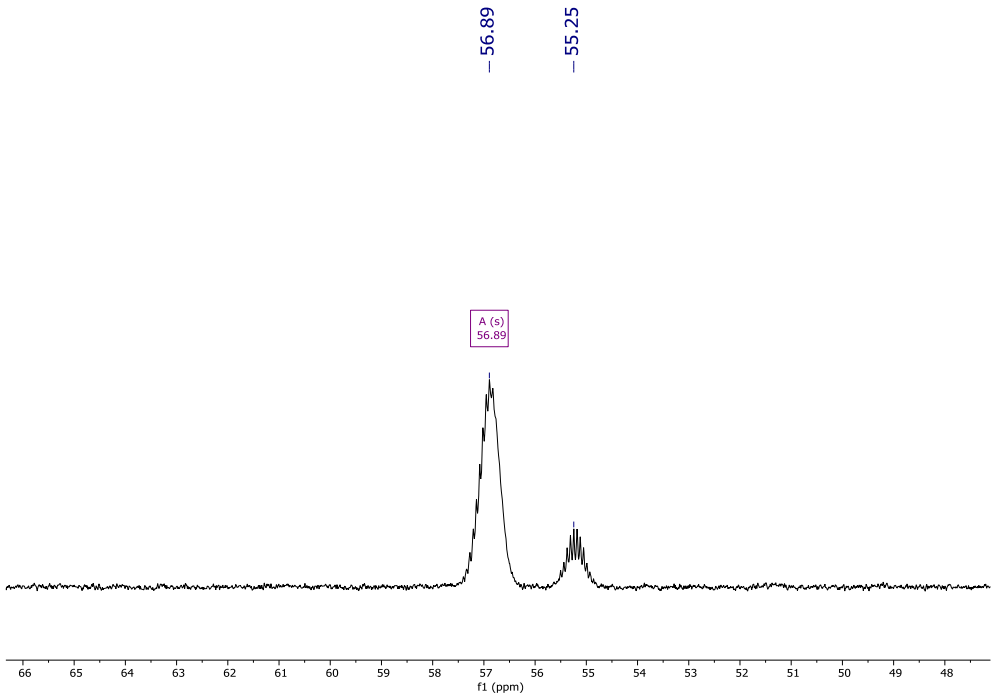


Figure S 4. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **3** and **4**.

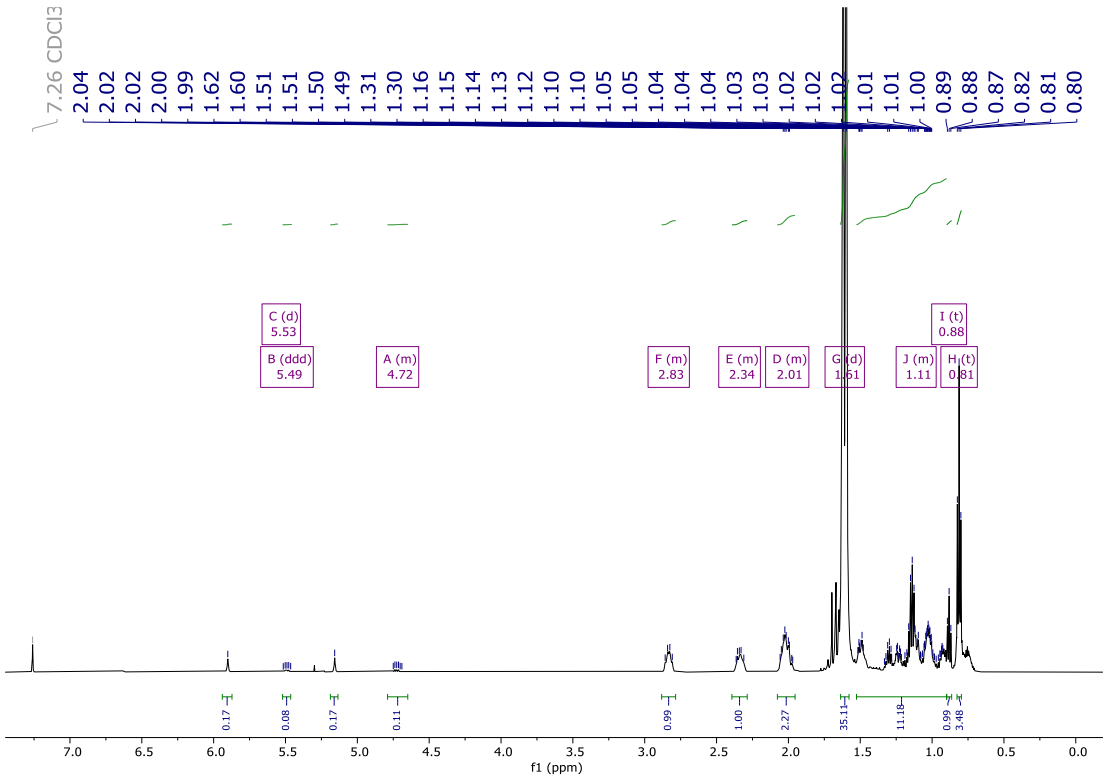


Figure S 5. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3** and **4**.

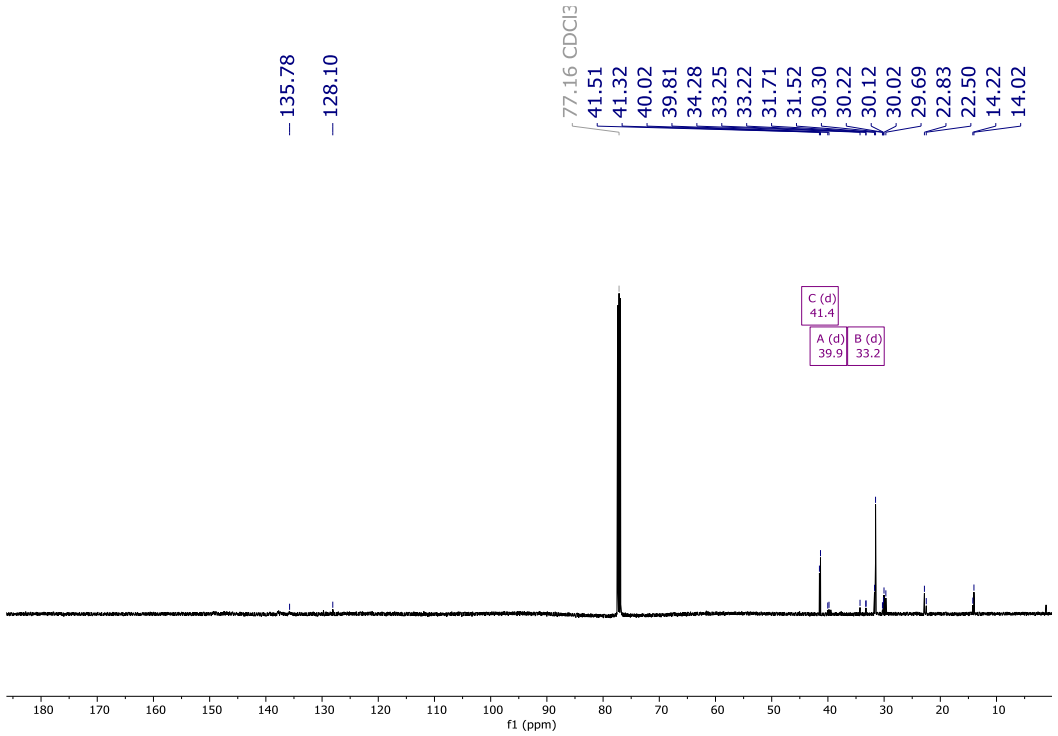
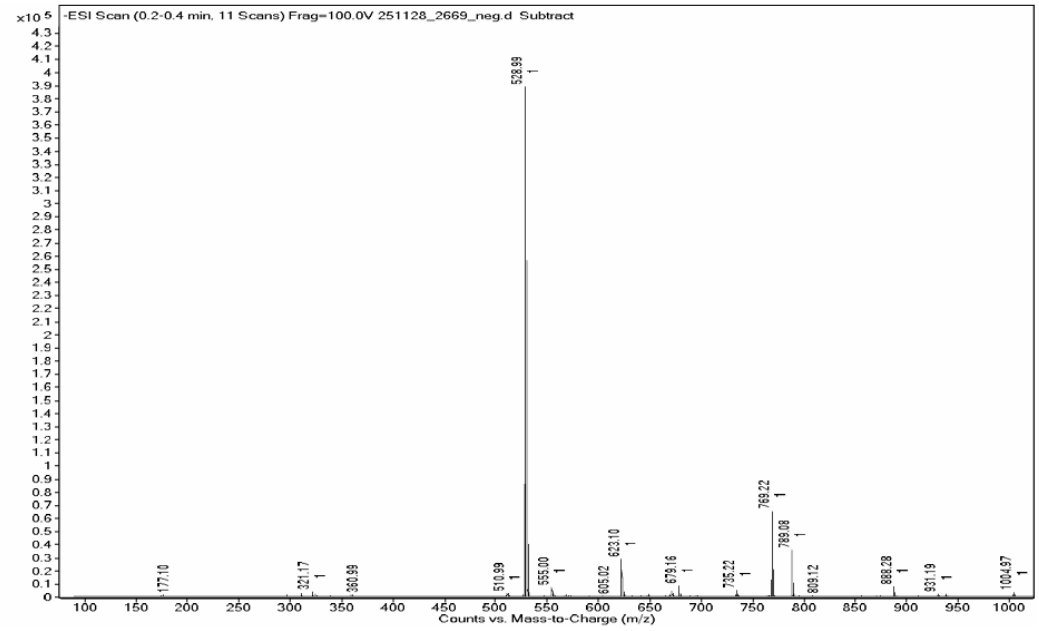


Figure S 6. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **3** and **4**.

Figure S 7. Mass spectra spectrum of **4**

Sample Name	Octene B/P Deprotonation	**Data File**	251128_2669_neg.d	**Acq Method**	HRMS_NEG_AS_80%ACN.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	28/11/2025 11:43:14 AM
Comment	ESI-				

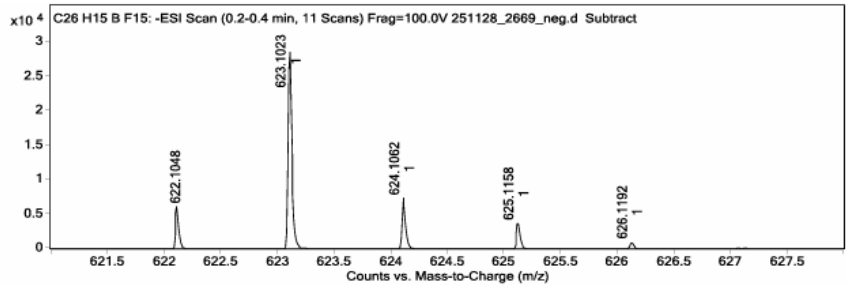


Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	622.1048	C26 H15 B F15

MFG Calculator Results

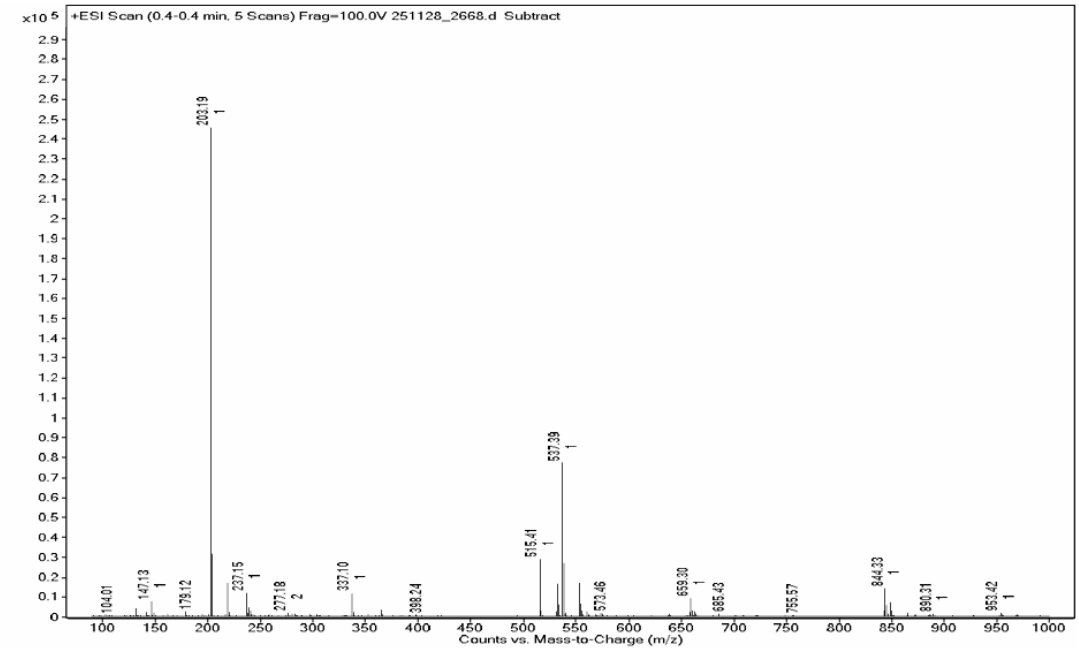
Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
622.1048	C26 H15 B F15	622.1069	-2.1	-3.4	12.5	82.94
622.1048	C10 H15 B F15 N8 O5	622.1061	-1.3	-2.1	0.5	72.92
622.1048	C14 H19 B F15 N2 O7	622.1088	-4.0	-6.4	-0.5	70.60
622.1048	C21 H15 B F15 N2 O2	622.1029	1.9	3.1	8.5	66.64
622.1048	C15 H15 B F15 N6 O3	622.1101	-5.3	-8.5	4.5	62.73



Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	622.1048	622.1069	-2.1	21.3	23.2	1.9
2	623.1023	623.1037	-1.4	100.0	100.0	0.0
3	624.1062	624.1069	-0.7	25.9	27.3	1.4
4	625.1158	625.1102	5.6	13.3	3.7	-9.6
5	626.1192	626.1135	5.7	3.4	0.3	-3.1

Sample Name	Octene B/P Deprotonation	**Data File**	251128_2668.d	**Acq Method**	HRMS_AS_80%ACN_100V.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	28/11/2025 9:46:37 AM
Comment	ESI+				



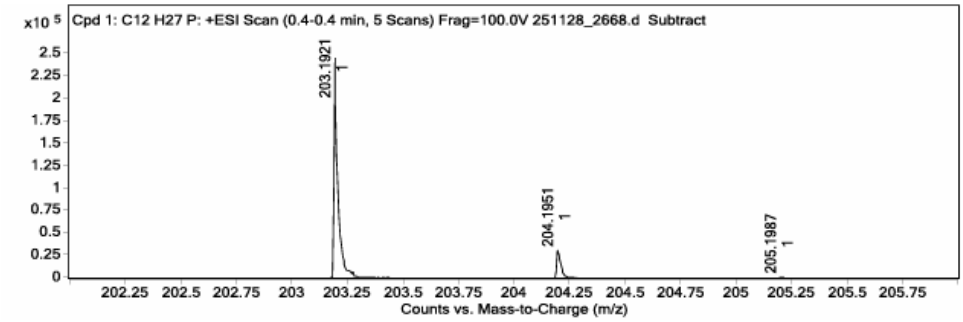
Sample Name	Octene B/P Deprotonation	**Data File**	251128_2668.d
Acq Method	HRMS_AS_80%ACN_100V.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	28/11/2025 9:46:37 AM
Comment	ESI+		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
(M+H)+	203.1921	C12 H28 P

MFG Calculator Results

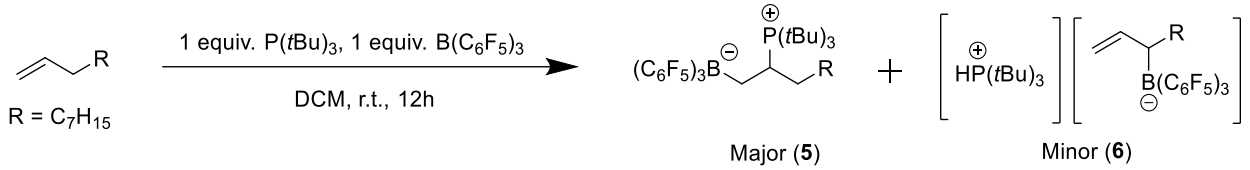
Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
203.1921	C12 H28 P	203.1923	-0.2	-1.0	0.0	87.12



Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	203.1921	203.1923	-0.2	100.0	100.0	0.0
2	204.1951	204.1957	-0.6	13.1	13.3	0.2

Reaction of 1-decene, $B(C_6F_5)_3$, and P*t*Bu$_3$



A 5 mL DCM solution of $B(C_6F_5)_3$ (0.100 g, 1.9 mmol, 1 equiv.) was added to a 5 mL DCM solution of P*t*Bu$_3$ (0.039 g, 1.9 mmol, 1 equiv.) and stirred for 5 mins at room temperature. A DCM solution of 1-decene (0.041, 2.9 mmol, 1.5 equiv.) was added and allowed to stir for 12 hours at room temperature. After which, the solvent was removed *in vacuo*, resulting in a yellow residue. This residue was washed with 10 mL of pentane twice. The residue was then dissolved in a minimum amount of toluene, layered with pentane, and stored at -35°C overnight. An off-white oil precipitated from the solution. Decanting the solvent and triturating the oil with 10 mL of pentane 12 times and diethyl ether twice generated a mixture of **5** and **6** as a white powder (1.05 g, 64% yield).

Spectral data of **5**

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ –13.0 (br s, 1B)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -135.3 (d, $^3J_{FF}$ = 17 Hz, 6F, *o*-C_6F_5), -161.5 (dd, $^3J_{FF}$ = 20 Hz, 20.3, 3F, *p*-C_6F_5), -166.2 (m, 6F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K): δ 56.89 (s, 1P)

^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 56.89 (s, 1P).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 2.83 (br m, PCH), 2.02 (br m, 1H, BCH_2), 1.63 (d, $^3J_{HP}$ = 18 Hz, 27H, *t*Bu), 1.30 - 0.98 (m, 14H, alkyl chain), 0.90 – 0.84 (m, 3H, CH_2CH_3)

Spectral data of **6**

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ –13.0 (br s, 1B)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -132.0 (d, $^3J_{FF}$ = 17 Hz, 6F, *o*-C_6F_5), -161.2 (dd, $^3J_{FF}$ = 20 Hz, 20, 3F, *p*-C_6F_5), -166.2 (m, 6F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K): δ 56.16 (s, 1P)

^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 46.9 (s, $^1J_{PH}$ = 446 Hz, 1P).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.58 (d, $^1J_{HP}$ = 446 Hz, 1H), 5.49 (ddd, $^3J_{HH}$ = 15, 8, 8 Hz, 1H, C*H*CH_2), 4.80 – 4.41 (m, 2H, CH_2CH), 2.02 (br m, 1H, BCH), 1.61 (d, $^3J_{HP}$ = 12.9 Hz, 27H, *t*Bu), 1.30 - 0.98 (m, 10H, alkyl chain), 0.90 – 0.84 (m, 3H, CH_2CH_3)

HRMS: $C_{28}H_{19}F_{15}$ (Negative mode) Calc: 651.1350, Obs: 651.1333; (Positive mode): $C_{12}H_{28}P$ Calc: 203.1923, Obs: 203.1925.

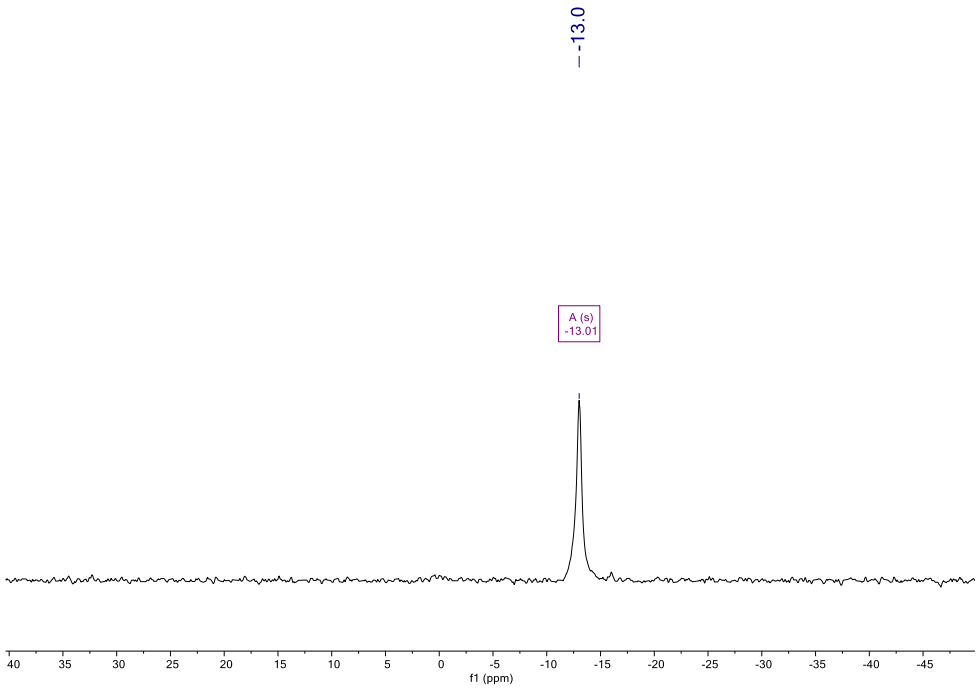


Figure S 8. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **5** and **6**

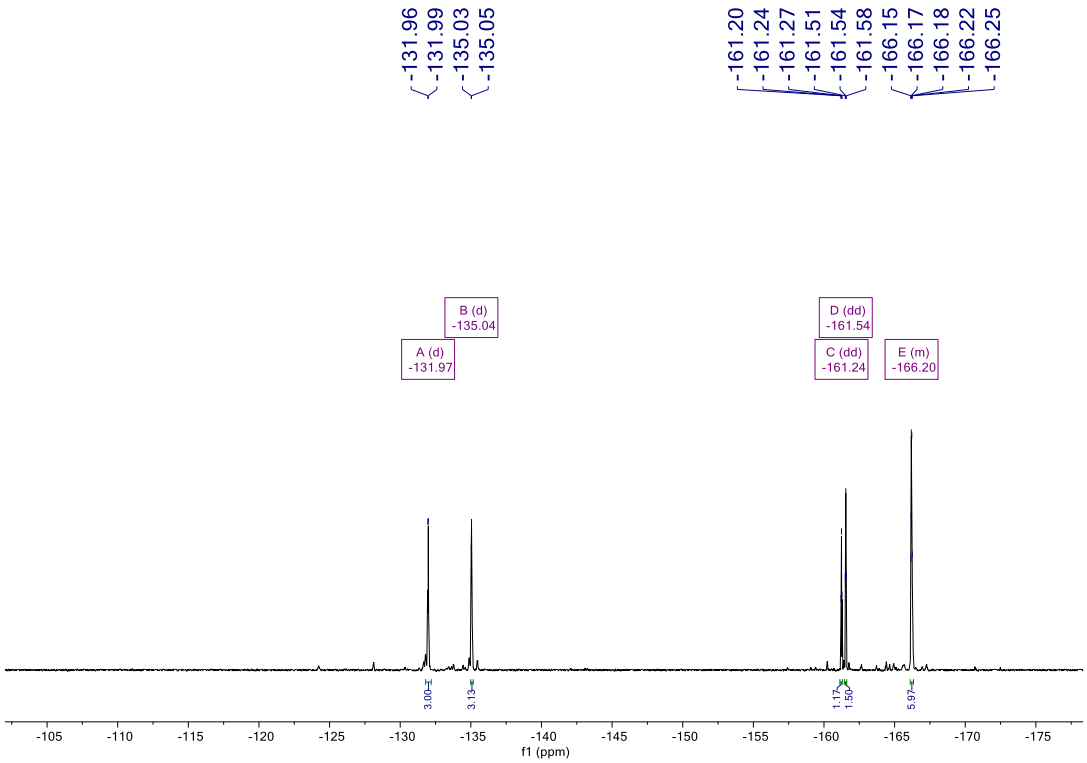


Figure S 9. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **5** and **6**

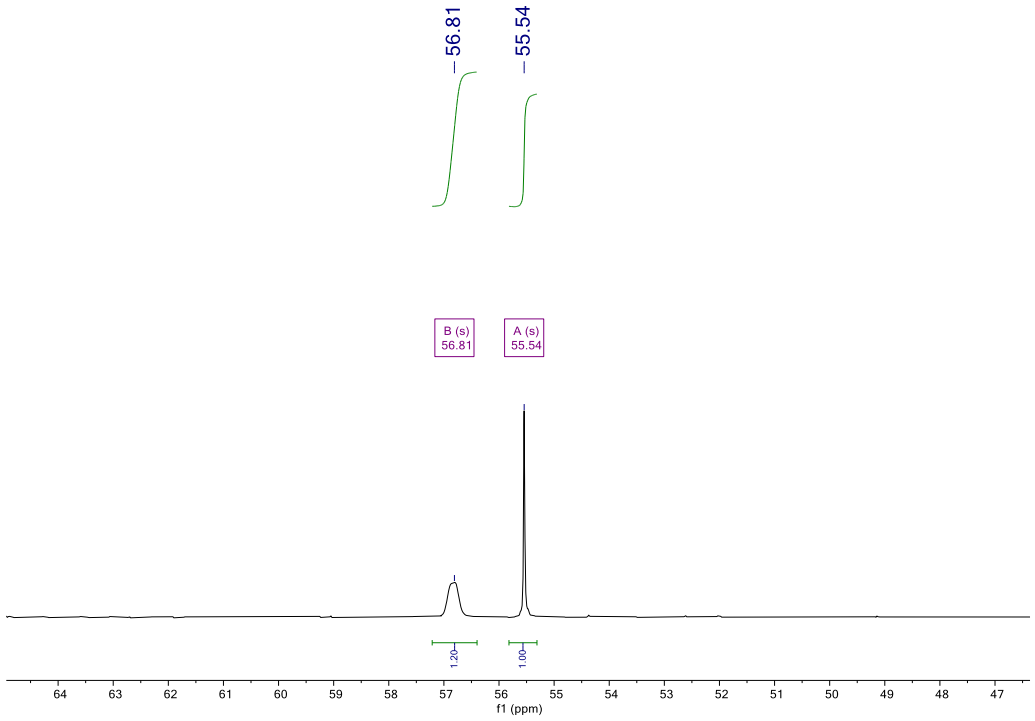


Figure S 10. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **5** and **6**

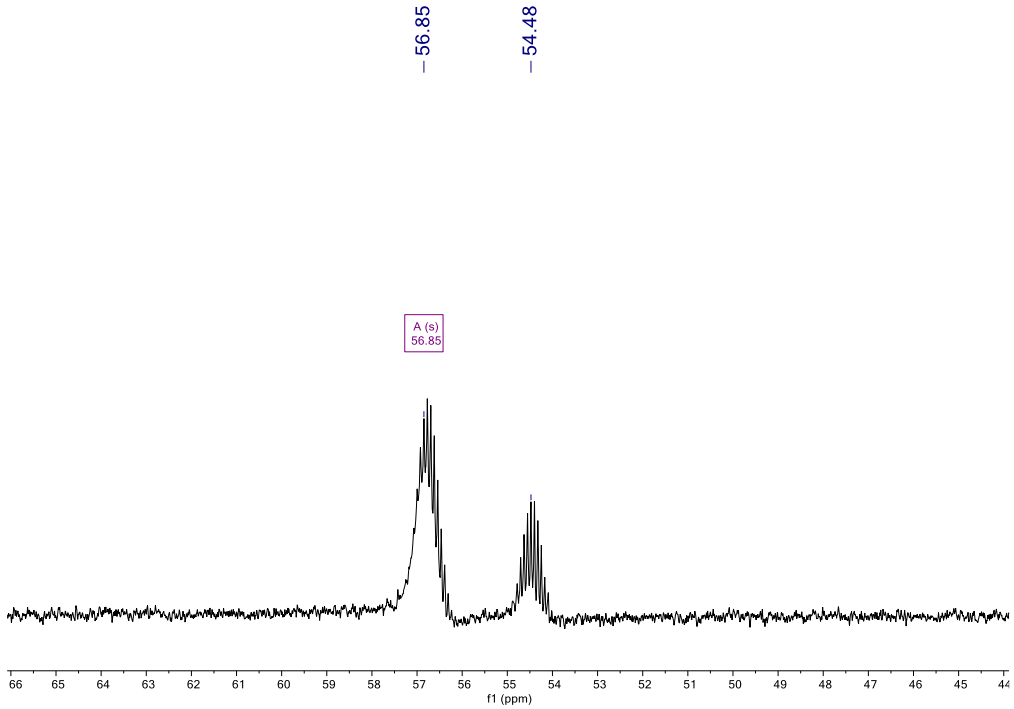


Figure S 11. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **5** and **6**

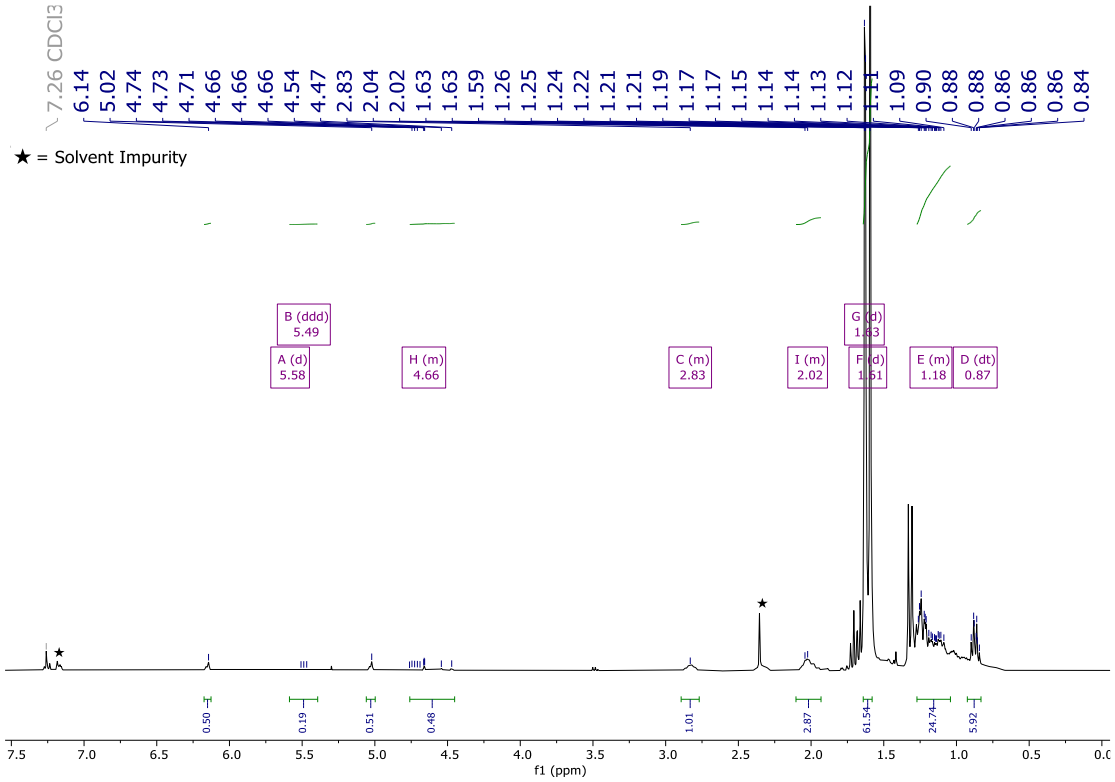
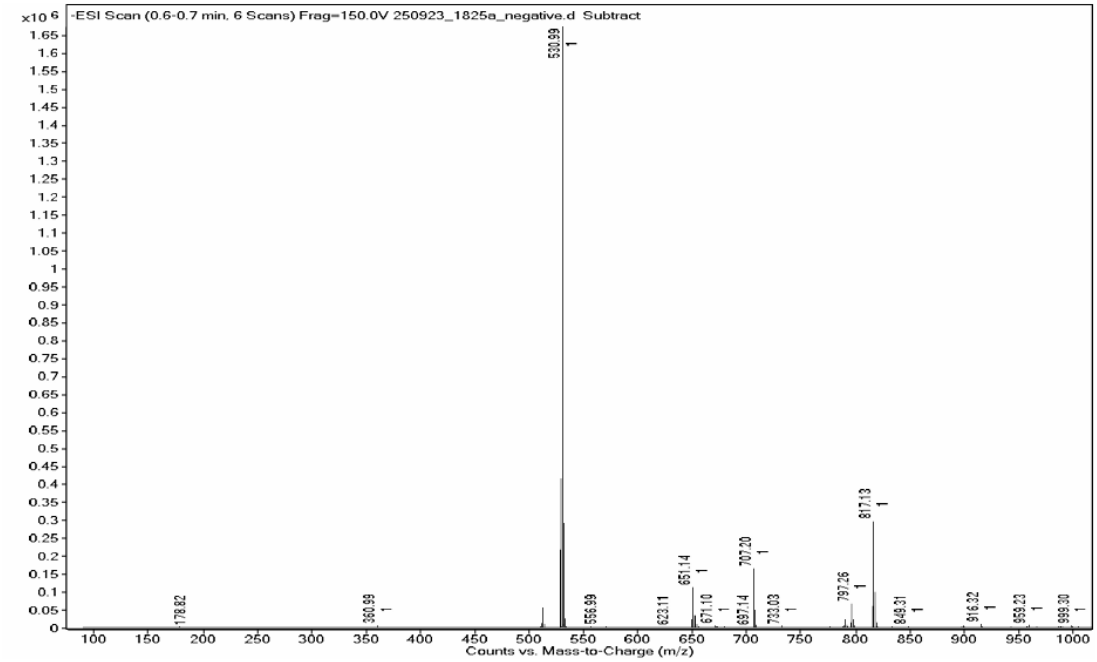


Figure S 12. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **5** and **6**

Figure S 13. Mass spectra spectrum of **6**

Sample Name	Tol Decene	**Data File**	250923_1825a_negative.d	**Acq Method**	HRMS_Negative.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	23/09/2025 3:15:22 PM
Comment	ESI-				



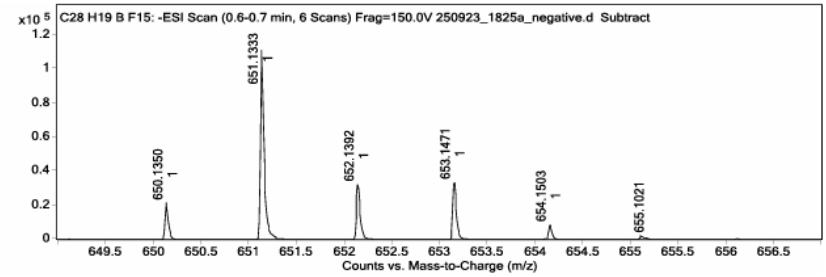
Sample Name	Tol Decene	**Data File**	250923_1825a_negative.d
Acq Method	HRMS_Negative.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	23/09/2025 3:15:22 PM
Comment	ESI-		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	650.135	C28 H19 B F15

MFG Calculator Results

Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
650.1350	C28 H19 B F15	650.1382	-3.2	-4.9	12.5	92.59
650.1350	C16 H23 B F15 N2 O7	650.1401	-5.1	-7.8	-0.5	88.91
650.1350	C12 H19 B F15 N8 O5	650.1374	-2.4	-3.7	0.5	85.69
650.1350	B F15 H23 N10 O12	650.1392	-4.2	-6.5		84.69
650.1350	C23 H19 B F15 N2 O2	650.1342	0.8	1.2	8.5	71.43



Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	650.1350	650.1382	-3.2	19.7	23.1	3.4
2	651.1333	651.1351	-1.8	100.0	100.0	0.0
3	652.1392	652.1382	1.0	29.2	29.4	0.2
4	653.1471	653.1415	5.6	30.6	4.3	-26.3
5	654.1503	654.1448	5.5	8.2	0.4	-7.8
6	655.1490	655.1482	0.8	1.3	0.0	-1.3

Sample Name	Tol Decene	**Data File**	250923_1825.d	**Acq Method**	HRMS.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	23/09/2025 2:57:20 PM
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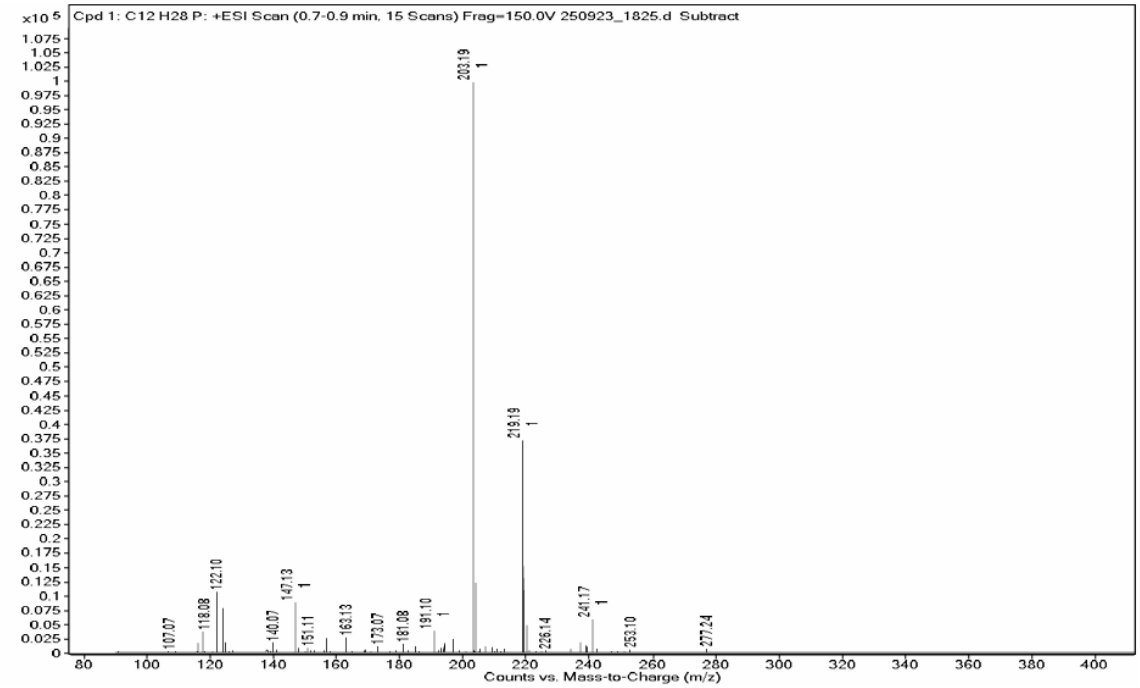


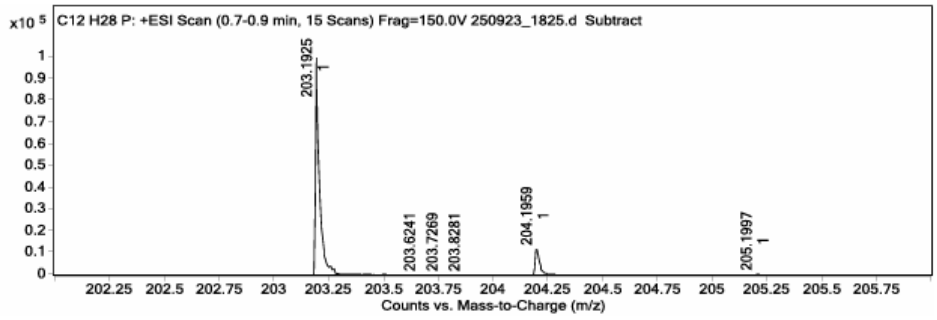
Sample Name	Tol Decene	**Data File**	250923_1825.d
Acq Method	HRMS.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	23/09/2025 2:57:20 PM
Comment	ESI+		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M+	203.1925	C12 H28 P

MFG Calculator Results

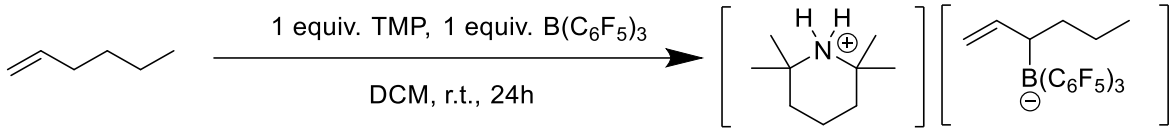
Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
203.1925	C12 H28 P	203.1923	0.2	1.0	-0.5	87.56



Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	203.1925	203.1923	0.2	100.0	100.0	0.0
2	204.1959	204.1957	0.2	12.6	13.3	0.7

Preparation of [TMPH][$(CH_3CH_2CH_2)(CHCH_2)CHB(C_6F_5)_3$]



7

A 5 mL DCM solution of $B(C_6F_5)_3$ (0.100 g, 1.953 mmol, 1 equiv.) was added to a 5 mL DCM solution of 1-hexene (0.049 g, 5.860 mmol, 3 equiv.) and stirred for 5 mins at room temperature. A 5 mL DCM solution of TMP (0.028 g, 1.953 mmol, 1 equiv.) was then added dropwise to the solution over 30 minutes and stirred for 24 hours at room temperature. After which, the solvent was removed *in vacuo,* resulting in a pink oil. It was then dissolved in diethyl ether and filtered with a 0.22 μm syringe membrane filter. The solvent was then removed in vacuo and washed twice with 10 mL of pentane. Upon dissolving in minimum amounts of DCM, layered with pentane and stored at -35 °C overnight, a pink oil precipitated from the solution. Decanting the solvent and triturating the oil with 10 mL of pentane 5 times generated **7** as a light pink oil (0.092 g, 64% yield).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ -13.3 (br s, 1B)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -132.2 (d, $^3J_{FF}$ = 24 Hz, 6F, *o*-C_6F_5), -163.2 (dd, $^3J_{FF}$ = 20, 20 Hz, 3F, *p*-C_6F_5), -166.3 (dd, $^3J_{FF}$ = 23, 23 Hz, 6F, *m*-C_6F_5).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.52 (ddd, $^3J_{HH}$ = 16, 8, 8 Hz, 1H, CH_2CH), 4.80 (m, 2H, NH_2), 2.05 (br m, 2H, BCH), 1.84 (m, 2H, $NCCH_2CH_2$), 1.75 (m, 4H, $NCCH_2$), 1.47 (s, 12H, $NCCH_3$), 1.00 (m, $BCHCH_2CH_2$), 0.68 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_2CH_3). The terminal alkene signals could not be seen due to overlap with NH_2.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K)**:** δ 135.6 (s, $CHCH_2$), 127.2 (s, $CHCH_2$), 60.2 (s, NC), 35.5 (s, NCH_2), 28.0 (s, $NCCH_3$), 23.6 (s, $BCHCH_2CH_2$), 15.9 (s, $NCCH_2CH_2$), 14.2 (s, $BCHCH_2CH_2CH_3$)

HRMS: $C_{24}H_{11}BF_{15}$ (Negative mode) Calc: 595.0724, Obs: 595.0718; (Positive mode): $C_9H_{20}N$ Calc: 142.15908, Obs: 142.15903.

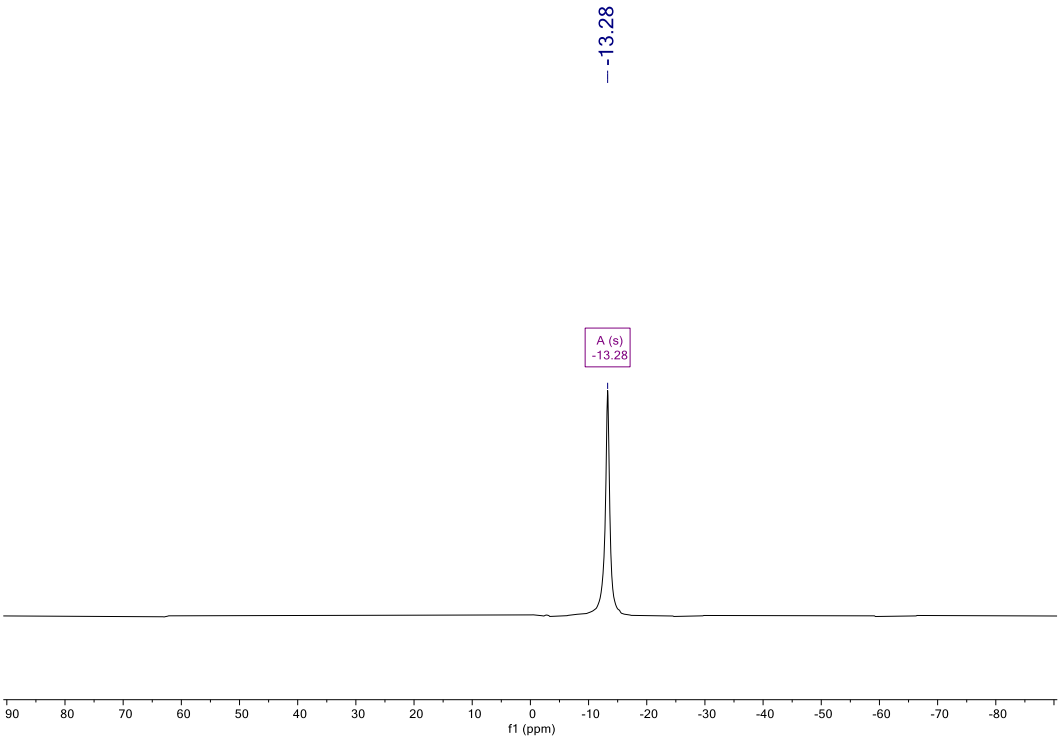


Figure S 14. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **7**

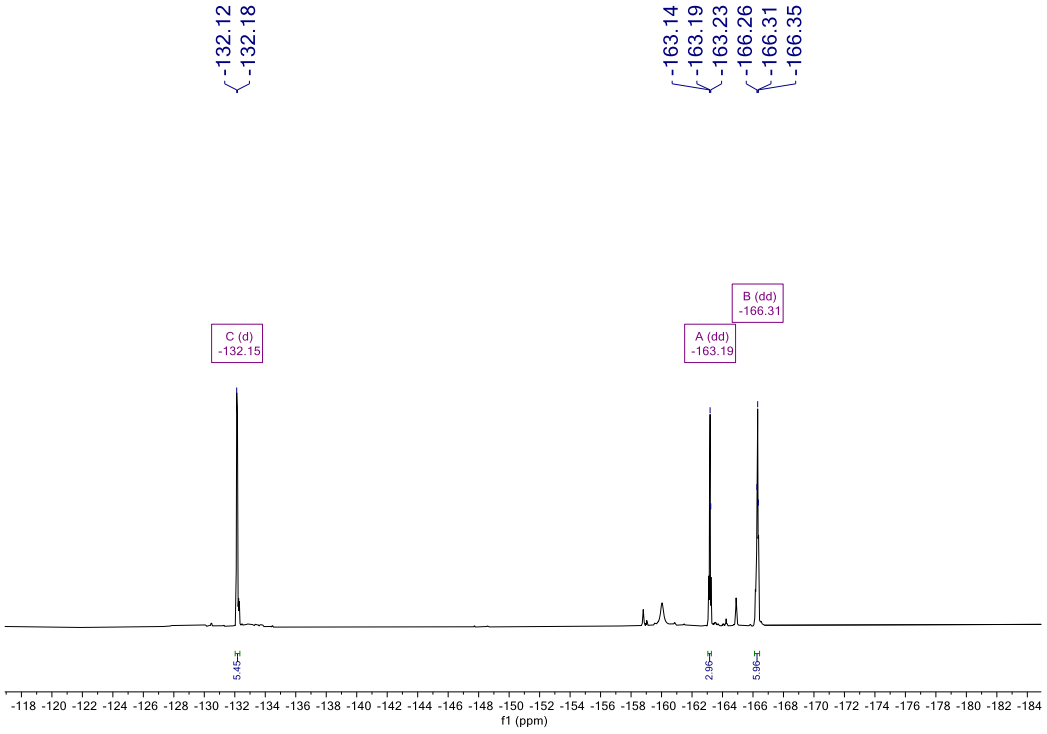


Figure S 15. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **7**

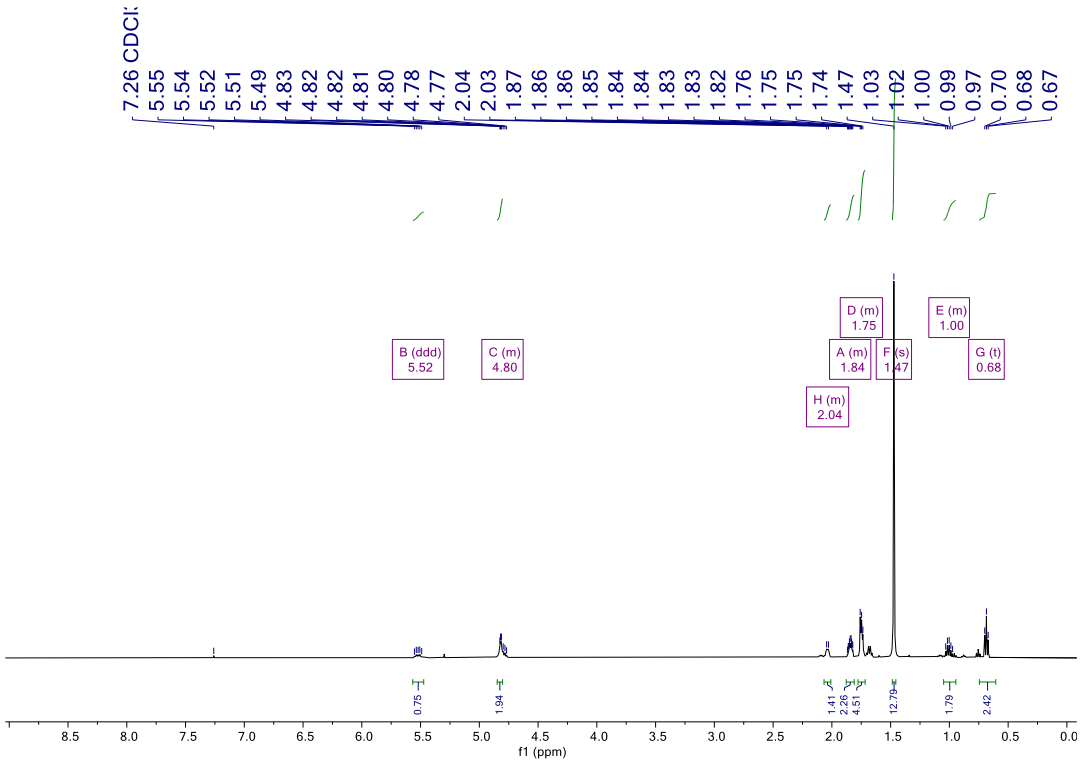


Figure S 16. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **7**

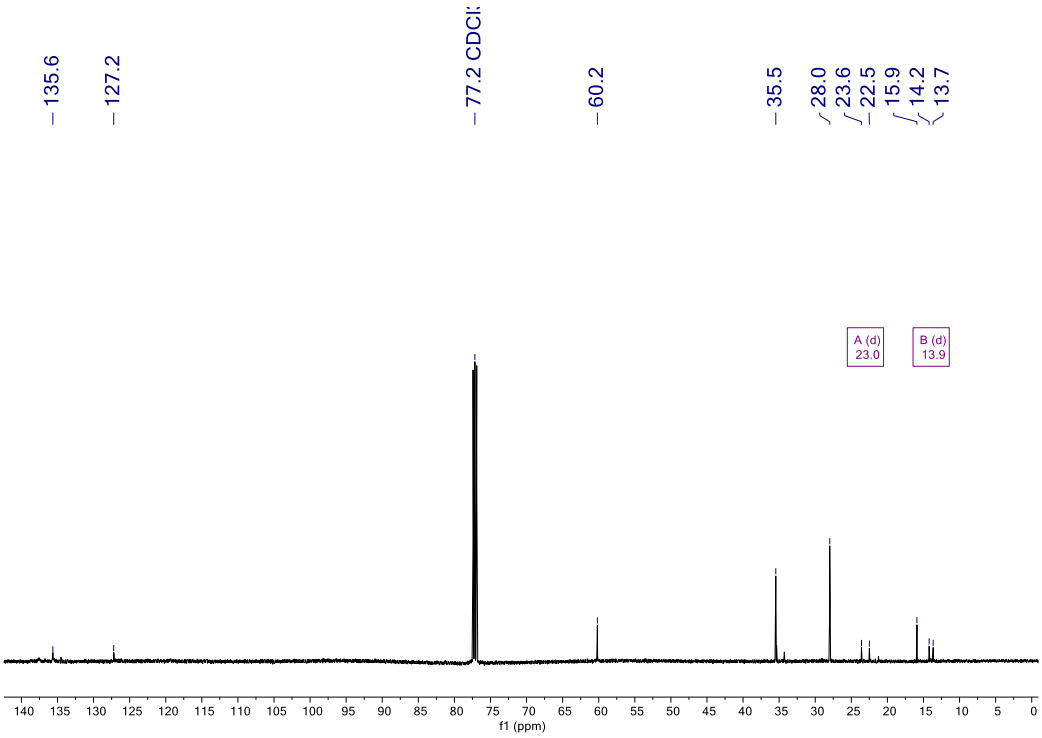
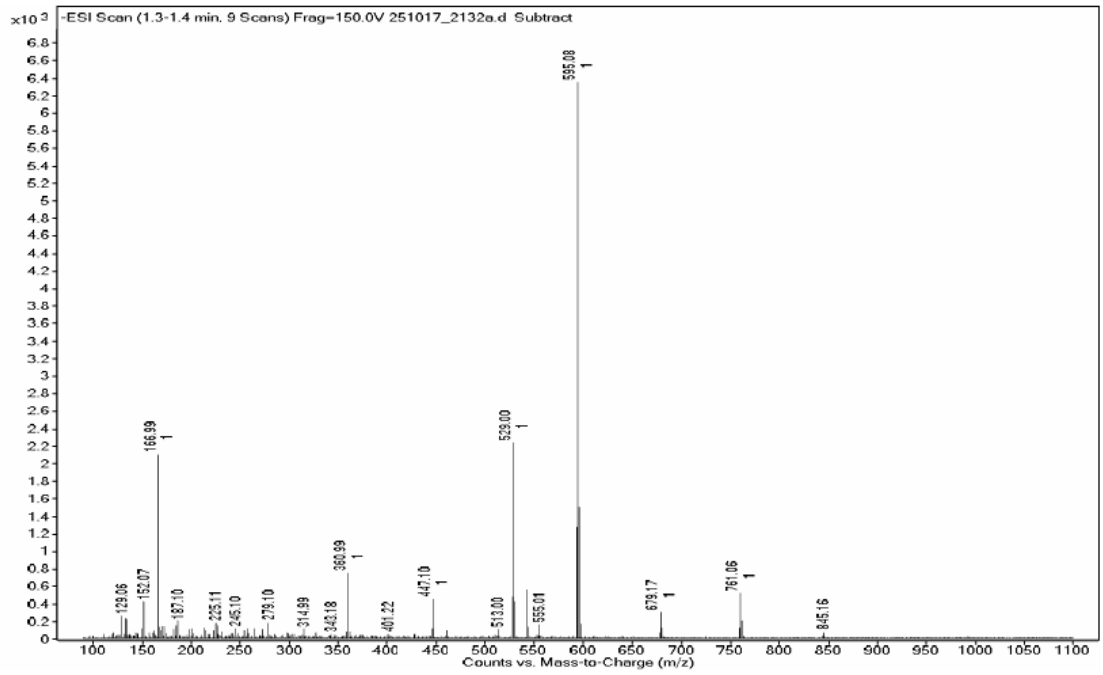


Figure S 17. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **7**

Figure S18. Mass spectra spectrum of **7**

Sample Name	TMP hexene	**Data File**	251017_2132a.d	**Acq Method**	HRMS_Negative.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	17/10/2025 2:39:55 PM
Comment	ESI-				

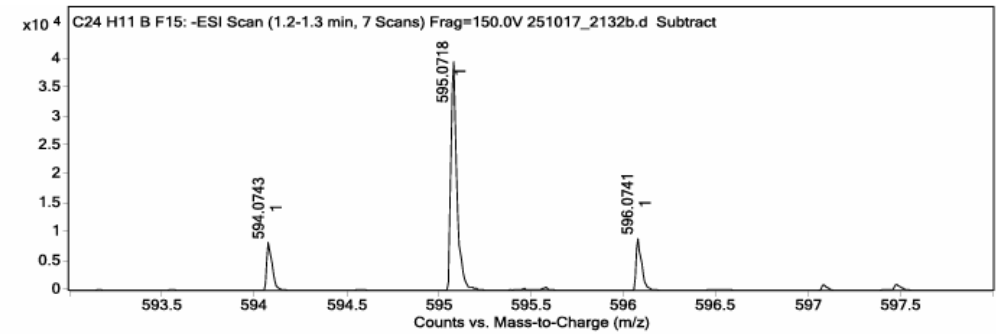


Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	594.0743	C24 H11 B F15

MFG Calculator Results

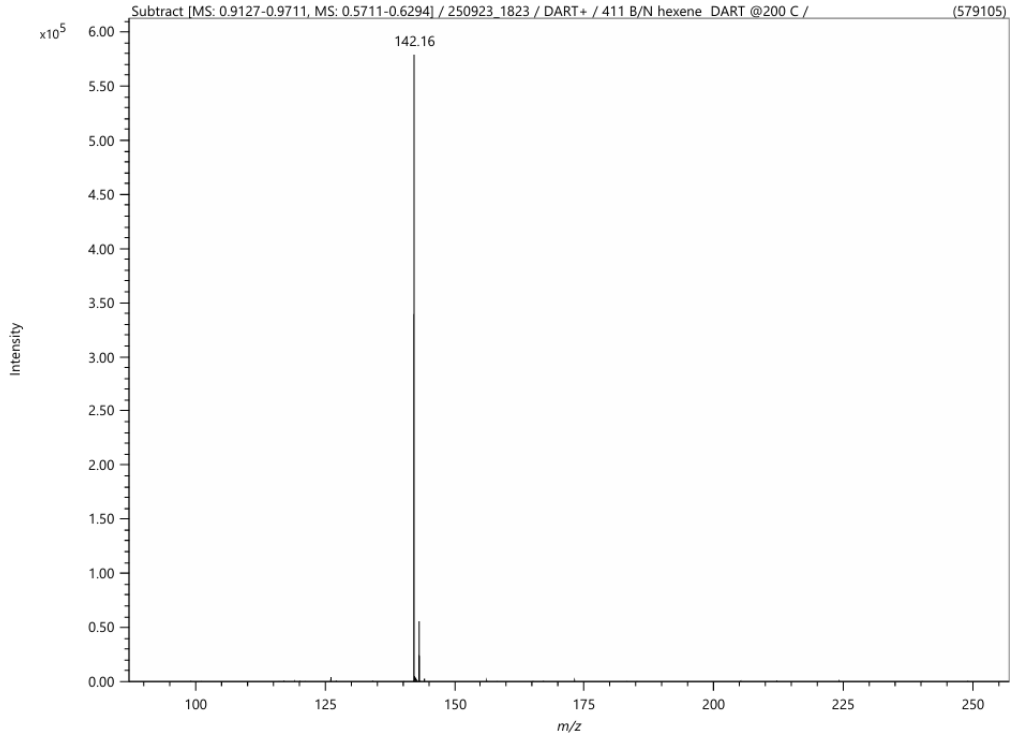
Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
594.0743	C24 H11 B F15	594.0756	-1.3	-2.2	12.5	97.22
594.0743	C19 H11 B F15 N2 O2	594.0716	2.7	4.5	8.5	82.43
594.0743	C8 H11 B F15 N8 O5	594.0748	-0.5	-0.8	0.5	80.26
594.0743	C12 H15 B F15 N2 O7	594.0775	-3.2	-5.4	-0.5	76.40
594.0743	C13 H11 B F15 N6 O3	594.0788	-4.5	-7.6	4.5	71.24



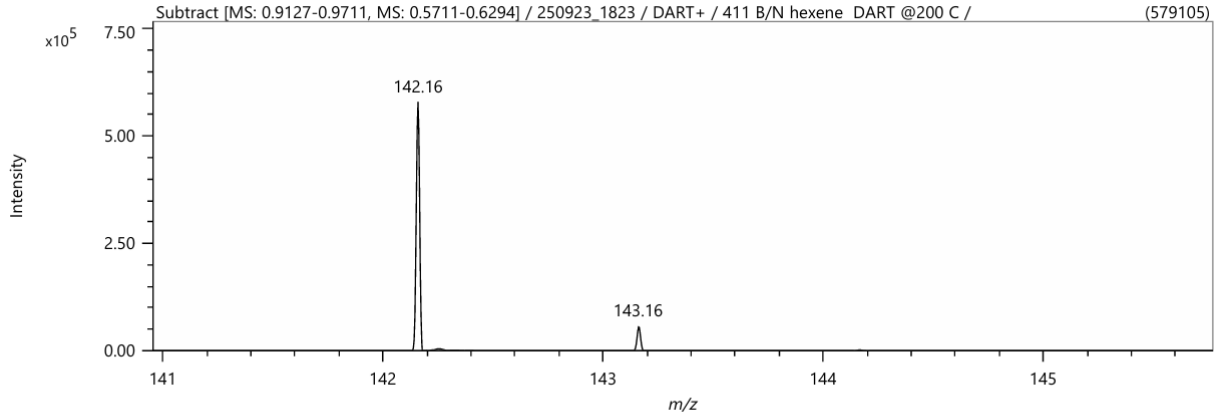
Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	594.0743	594.0756	-1.3	20.9	23.3	2.4
2	595.0718	595.0724	-0.6	100.0	100.0	0.0
3	596.0741	596.0756	-1.5	22.7	25.3	2.6
4	597.0776	597.0789	-1.3	2.7	3.1	0.4

DART IONIZATION **AccuTOF 4G**



Spectrum



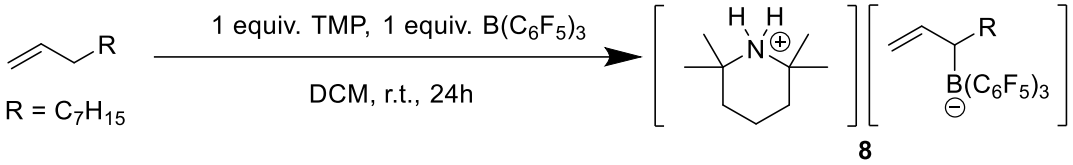
Elemental Composition

Parameters		Elements Set 1:				
Tolerance:	±5.00 mDa	Symbol	C	H	O	N
Electron:	Even	Min	0	0	0	0
Charge:	+1	Max	100	200	20	10
DBE:	-1.5 - 100.0					

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
142.15908	579105.50	C9 H20 N	142.15903	0.05	0.35	0.5

Preparation of [TMPH][$(CH_3(CH_2)_6)(CHCH_2)CHB(C_6F_5)_3$]



8

A 5 mL DCM solution of $B(C_6F_5)_3$ (0.100 g, 1.953 mmol, 1 equiv.) was added to a 5 mL DCM solution of 1-decene (0.055 g, 3.906 mmol, 2 equiv.) and stirred for 5 mins at room temperature. A 5 mL DCM solution of TMP (0.028 g, 1.953 mmol, 1 equiv.) was then added dropwise to the solution over 30 minutes and stirred for 24 hours at room temperature. After which, the solvent was removed *in vacuo,* resulting in a brown oil. It was then dissolved in diethyl ether and filtered with a 0.22 μm syringe membrane filter. The solvent was then removed in vacuo and washed twice with 10 mL of pentane. Upon dissolving in minimum amounts of DCM, layered with pentane and stored at -35 °C overnight, a brown oil precipitated from the solution. Decanting the solvent and triturating the oil with 10 mL of pentane 5 times generated **8** as a light brown oil (0.096 g, 62% yield).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ -13.3 (br s, 1B)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -132.2 (d, $^3J_{FF}$ = 25 Hz, 6F, *o*-C_6F_5), -163.1 (dd, $^3J_{FF}$ = 20, 20 Hz, 3F, *p*-C_6F_5), -166.3 (dd, $^3J_{FF}$ = 23, 23 Hz, 6F, *m*-C_6F_5).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.53 (ddd, $^3J_{HH}$ = 15, 8, 8 Hz, 1H, BCHC*H*CH_2), 4.80 (br s, 2H, NH_2), 2.04 (br m, 1H, BCH), 1.84 (m, 2H, $NCCH_2CH_2$), 1.75 (m, 4H, NCC*H*$_2$), 1.69 (dt, $^3J_{HH}$ = 7, 7 Hz, 2H, BCHC*H*$_2$), 1.47 (s, 12H, NCC*H*$_3$), 1.35 – 0.92 (m, 12H, alkyl chain), 0.86 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_2CH_3). The terminal alkene signals could not be seen due to overlap with N*H*$_2$.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 148.3 (br d, $^1J_{CF}$ = 254.9 Hz, *o*-C_6F_5), 136.6 (br d, $^1J_{CF}$ = 254.9 Hz, *m*-C_6F_5), 133.1 (s, *C*HCH_2), 127.6 (s, CH*C*H_2), 60.5 (s, NC), 35.3 (s, NCH_2), 33.3 (s, BCH_2CH_2), 31.8 (s, $BCH_2CH_2CH_2$), 30.7 (s, $BCH_2CH_2CH_2CH_2$), 29.6 (s, $CH_2CH_2CH_2CH_2CH_3$), 29.3 ($CH_2CH_2CH_2CH_3$), 28.0 (s, NC*C*H$_3$), 22.8 (s, *C*H_2CH_3), 15.8 (s, $NCCH_2CH_2$), 14.1 (s, CH_2CH_3).

HRMS: $C_{28}H_{19}BF_{15}$ (Negative mode) Calc: 651.1351, Obs: 651.1362; (Positive mode): $C_9H_{20}N$ Calc: 142.15935, Obs: 142.1593.

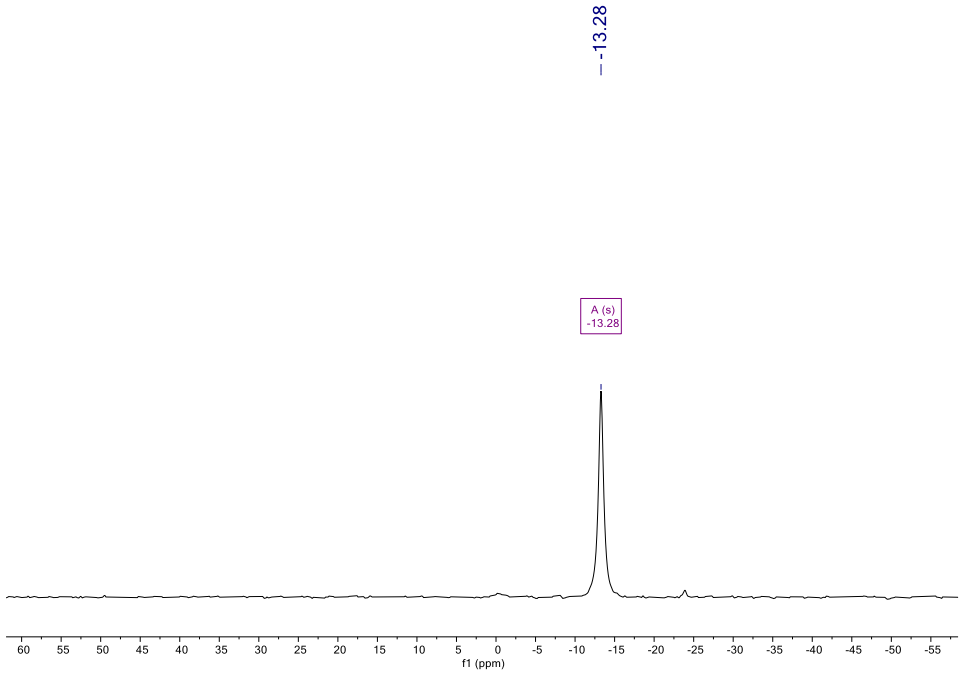


Figure S 19. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **8**

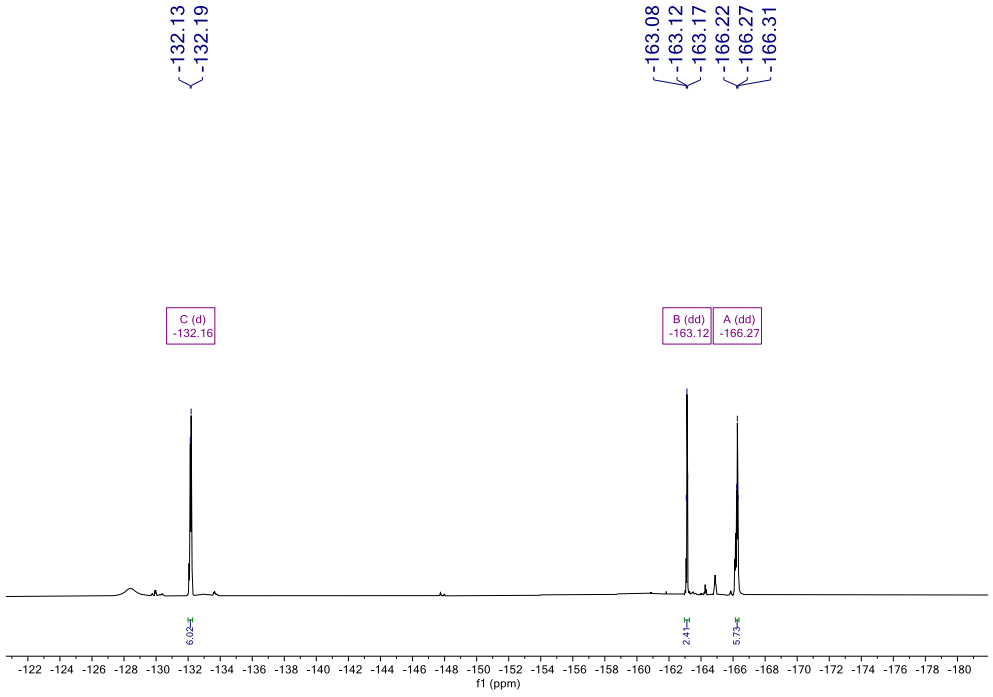


Figure S 20. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **8**

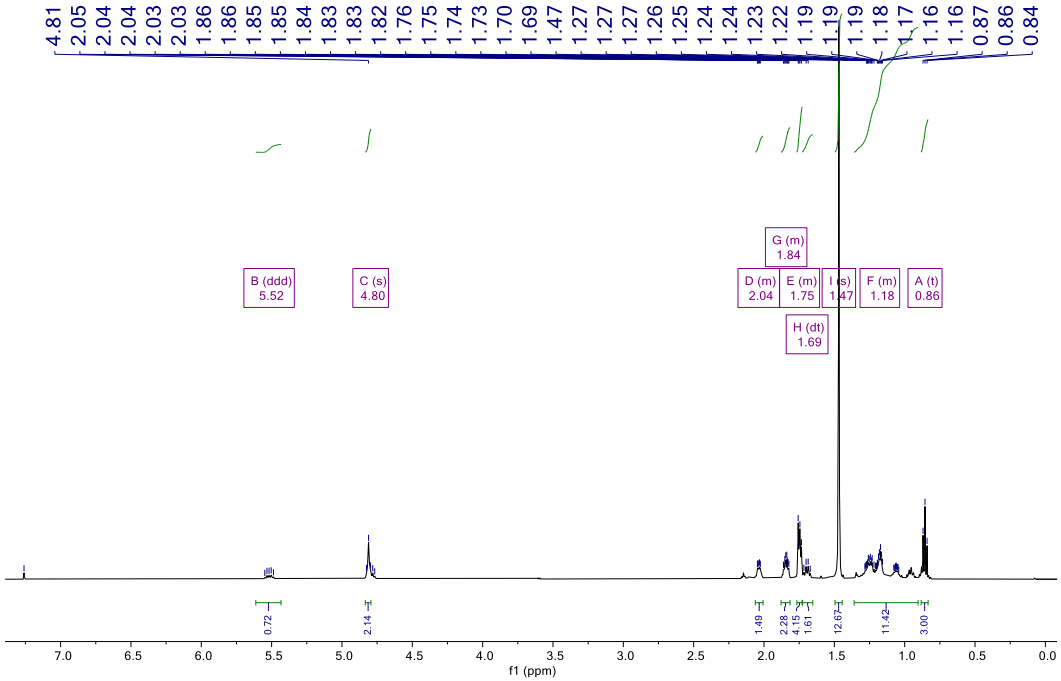


Figure S 21. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **8**

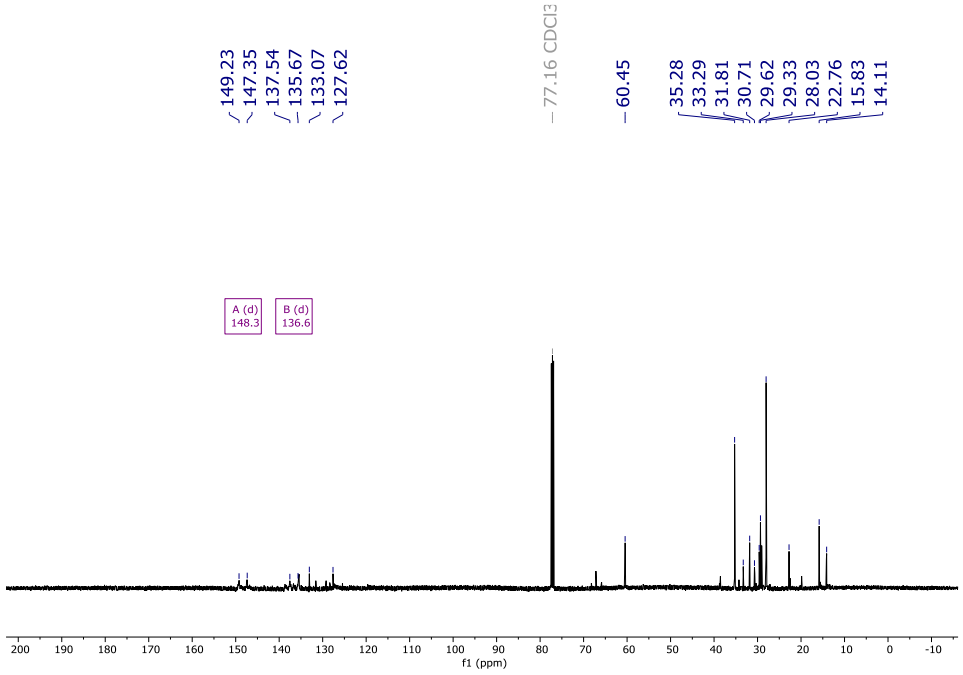
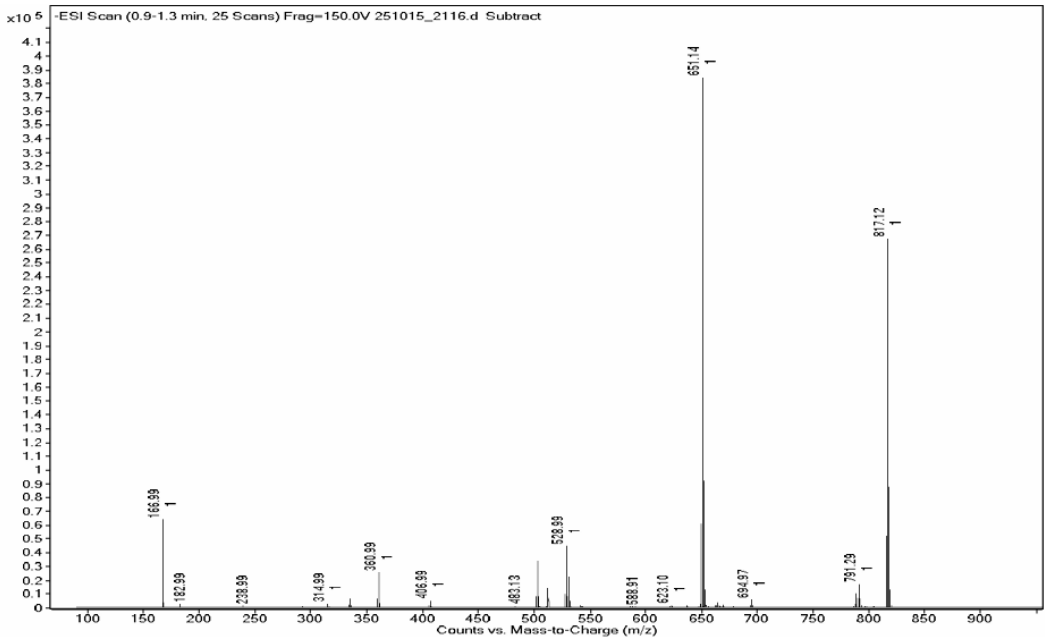


Figure S 22. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **8**

Figure S 23. Mass spectra spectrum of **8**

Sample Name	TMP Decone	**Data File**	251016_2116.d	**Acq Method**	HRMS_Negative.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	16/10/2025 3:13:20 PM
Comment	ESI-				

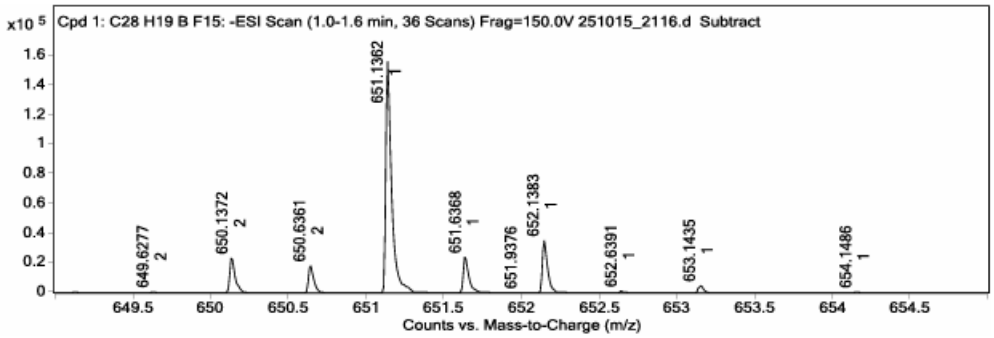


Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	650.1372	C28 H19 B F15

MFG Calculator Results

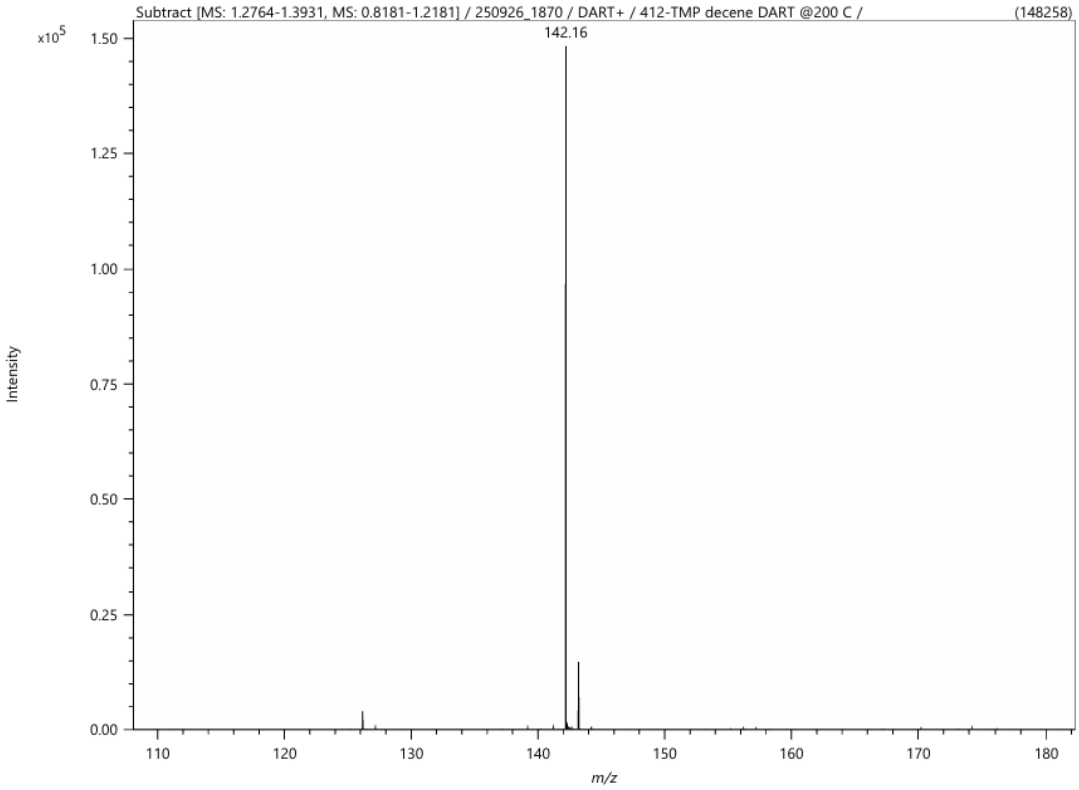
Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
650.1372	C28 H19 B F15	650.1382	-1.0	-1.5	12.5	88.06
650.1372	C16 H23 B F15 N2 O7	650.1401	-2.9	-4.5	-0.5	81.66
650.1372	C17 H19 B F15 N6 O3	650.1414	-4.2	-6.5	4.5	78.63
650.1372	C12 H19 B F15 N8 O5	650.1374	-0.2	-0.3	0.5	72.65
650.1372	C23 H19 B F15 N2 O2	650.1342	3.0	4.6	8.5	64.37



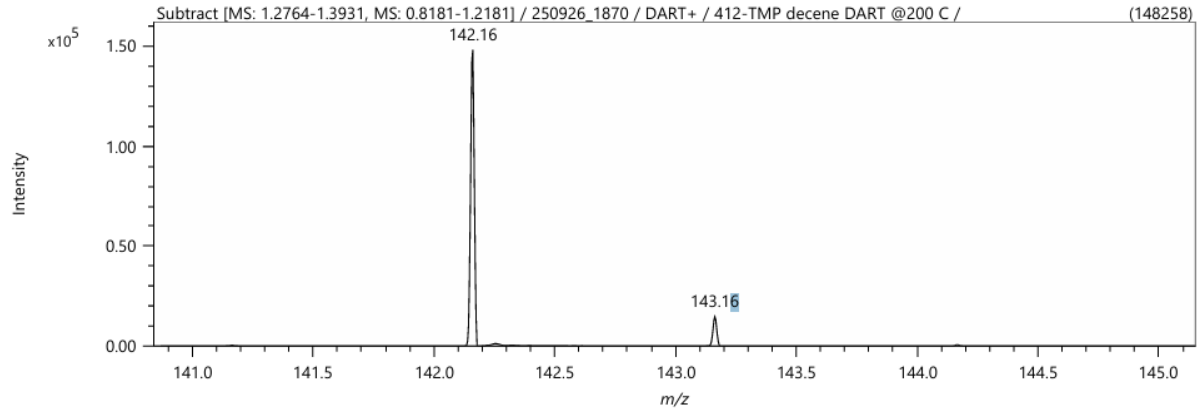
Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	650.1372	650.1382	-1.0	15.9	23.1	7.2
2	651.1362	651.1351	1.1	100.0	100.0	0.0
3	652.1383	652.1382	0.1	22.8	29.4	6.6
4	653.1435	653.1415	2.0	3.2	4.3	1.1

DART IONIZATION **AccuTOF 4G**



Spectrum



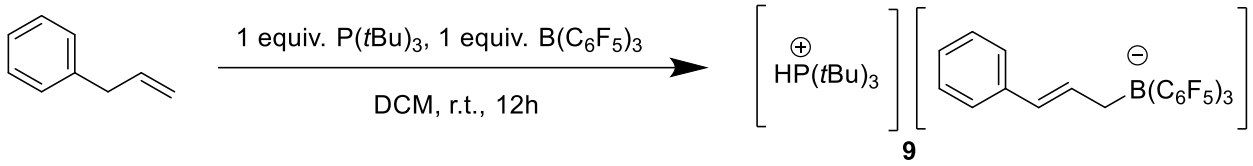
Elemental Composition

Parameters		Elements Set 1:				
Tolerance:	±5.00 mDa	Symbol	C	H	O	N
Electron:	Even	Min	0	0	0	0
Charge:	+1	Max	100	200	20	10
DBE:	-1.5 - 100.0					

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
142.15935	148258.21	C9 H20 N	142.15903	0.33	2.30	0.5

Preparation of [tBu$_3$PH][PhCHCHCH$_2$B(C$_6$F$_5$)$_3$]



9

A 5 mL DCM solution of B(C$_6$F$_5$)$_3$ (0.100 g, 1.953 mmol, 1 equiv.) was added to a 5 mL DCM solution of PtBu$_3$ (0.039 g, 1.953 mmol, 1 equiv.) and stirred for 5 mins at room temperature. Allylbenzene (0.023 g, 1.953 mmol, 1 equiv.) was added and allowed to stir for 12 hours at room temperature. After which, the solvent was removed *in vacuo*, resulting in an off-white residue. This residue was washed with 10 mL of pentane twice. The residue was then dissolved in a minimum amount of toluene, layered with pentane and stored at -35°C overnight. A white oil precipitated from the solution. Decanting the solvent and triturating the oil with 10 mL of pentane 8 times and diethyl ether twice generated a mixture of **9** as a white powder (0.141 g, 87% yield).

^{11}B NMR (128 MHz, CDCl$_3$, 298 K): δ -13.3 (br s, 1B).

^{19}F NMR (376 MHz, CDCl$_3$, 298 K): δ -131.8 (br d, $^3J_{FF}$ = 24 Hz, 6F, *o*- C$_6$F$_5$), -162.8 (dd, $^3J_{FF}$ = 21, 21 Hz, 3F, *p*- C$_6$F$_5$), -166.8 (dd, $^3J_{FF}$ = 20, 20 Hz, 6F, *m*- C$_6$F$_5$).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298K): δ 58.45 (s, 1P).

^{31}P NMR (162 MHz, CDCl$_3$, 298K): δ 58.45 (d, $^1J_{PH}$ = 436 Hz, 1P).

^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 7.16 – 7.1 (t, ^{3}J$_{HH}$ = 8, 2H, Ar*H*), 7.05 – 6.97 (m, 3H, Ar*H*), 6.33 (dt, $^3J_{HH}$ = 8, 16 Hz, 1H), 5.78 (d, $^3J_{HH}$ = 16, 1H), 5.51 - 4.64 (d, $^1J_{PH}$ = 436 Hz, 1H, PH) 2.31 (m, 1H, BCH$_2$), 1.56 (d, 27H, $^3J_{HP}$ = 13 Hz, *t*Bu)

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K): δ 140.21 (s, *i*-Ph), 138.645 (s, Ph-*C*H), 128.31 (s, *o*-Ph), 125.86 (s, BCH$_2$*C*H), 125.40 (s, *m*-Ph), 125.26 (s, *p*-Ph), 37.57 (d, ^{1}J$_{CP}$ = 27 Hz, *t*Bu), 30.03 (s, *t*Bu)

HRMS: C$_{27}$H$_9$BF$_{15}$ (Negative mode) Calc: 629.0552, Obs: 629.9564; (Positive mode): C$_{12}$H$_{28}$P Calc: 203.1923, Obs: 203.1921.

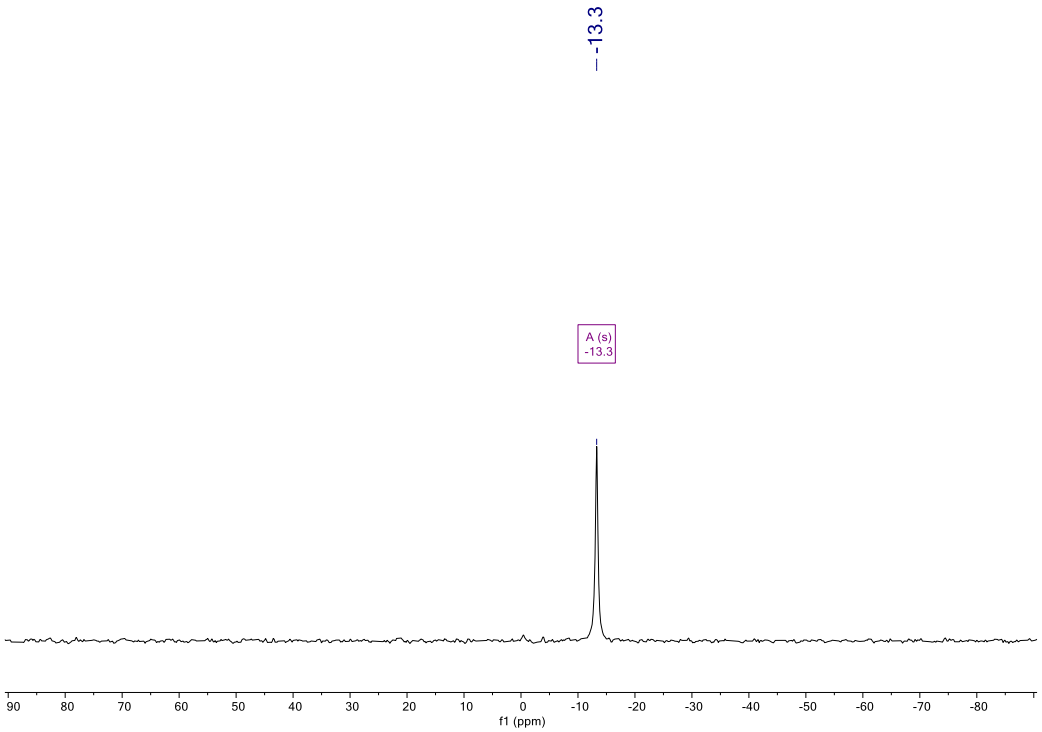


Figure S 24. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **9**

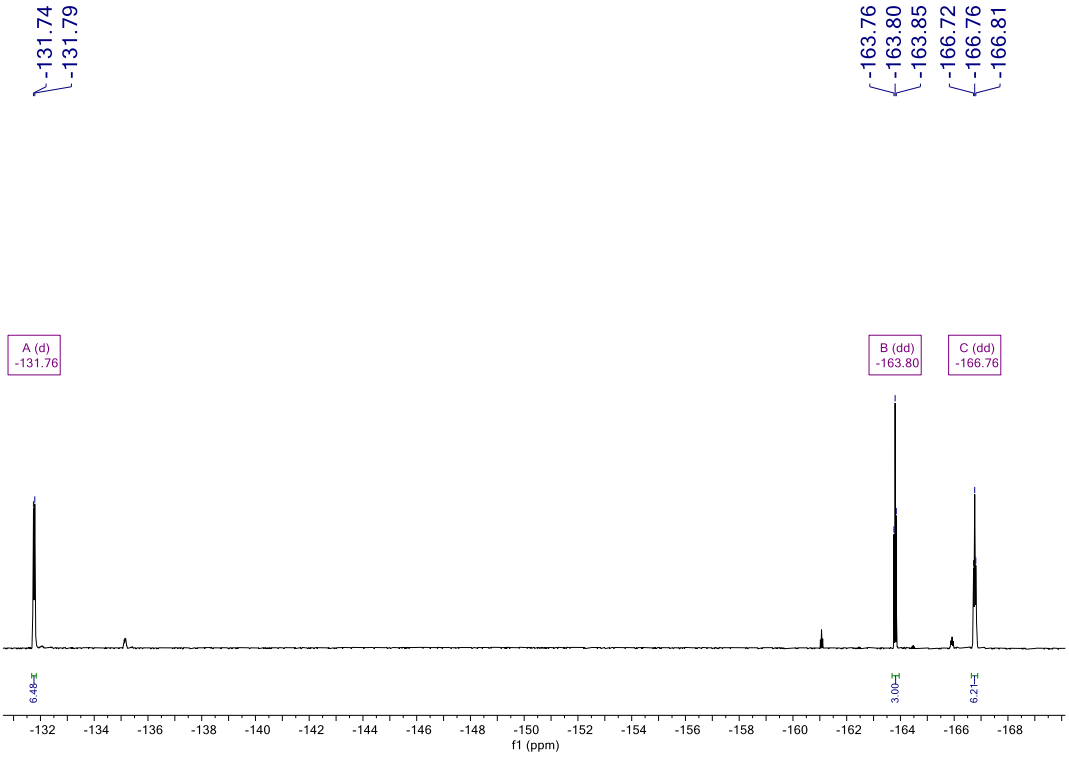


Figure S 25. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **9**

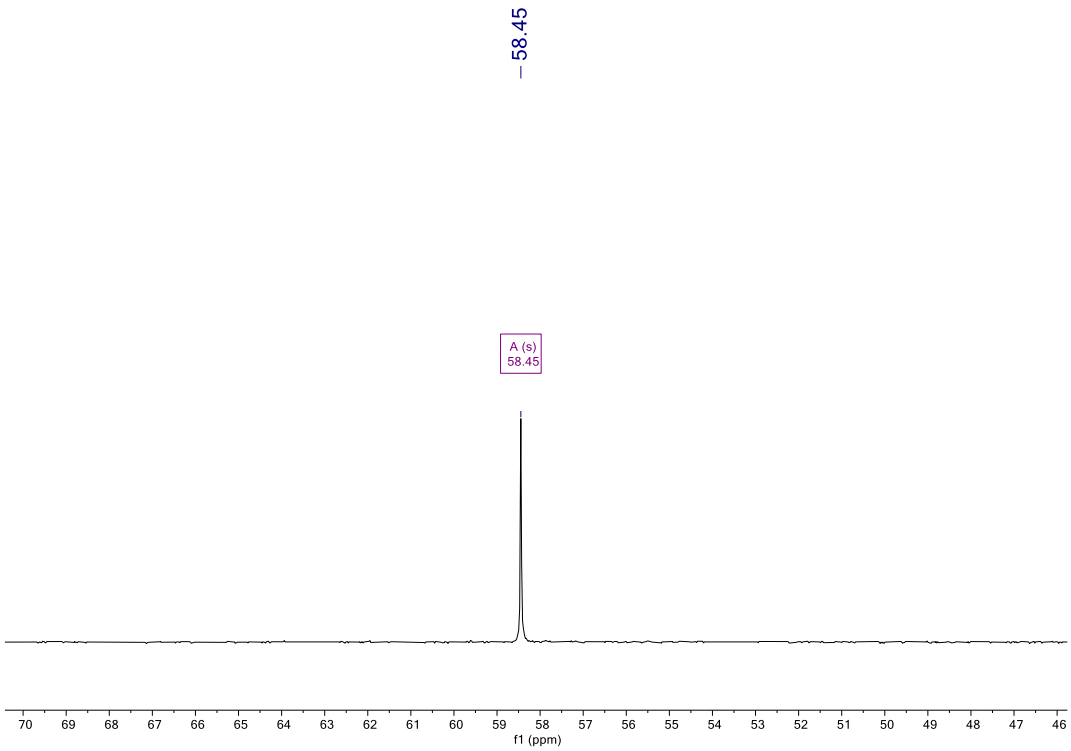


Figure S 26. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **9**

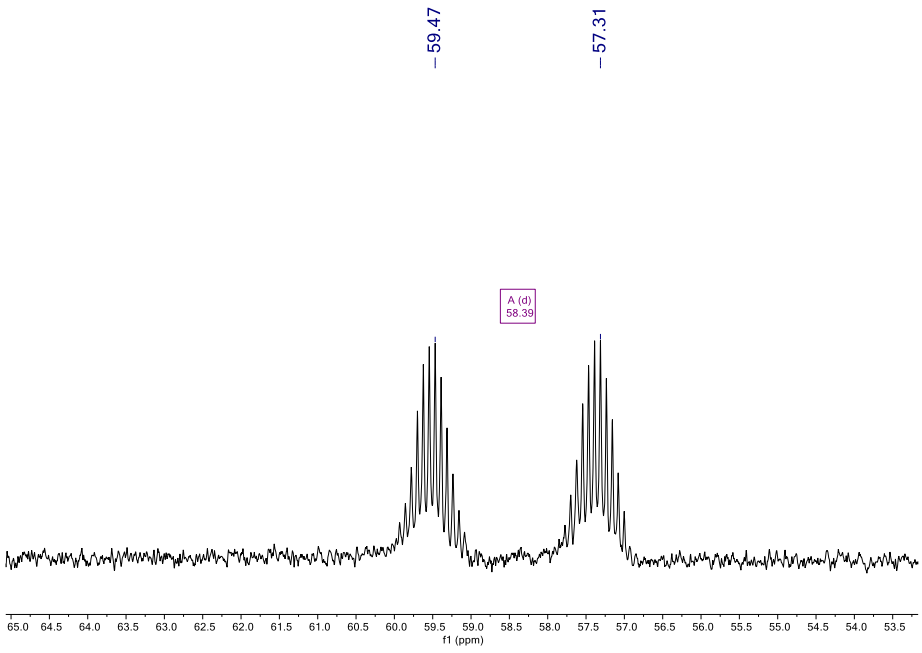


Figure S 27. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **9**

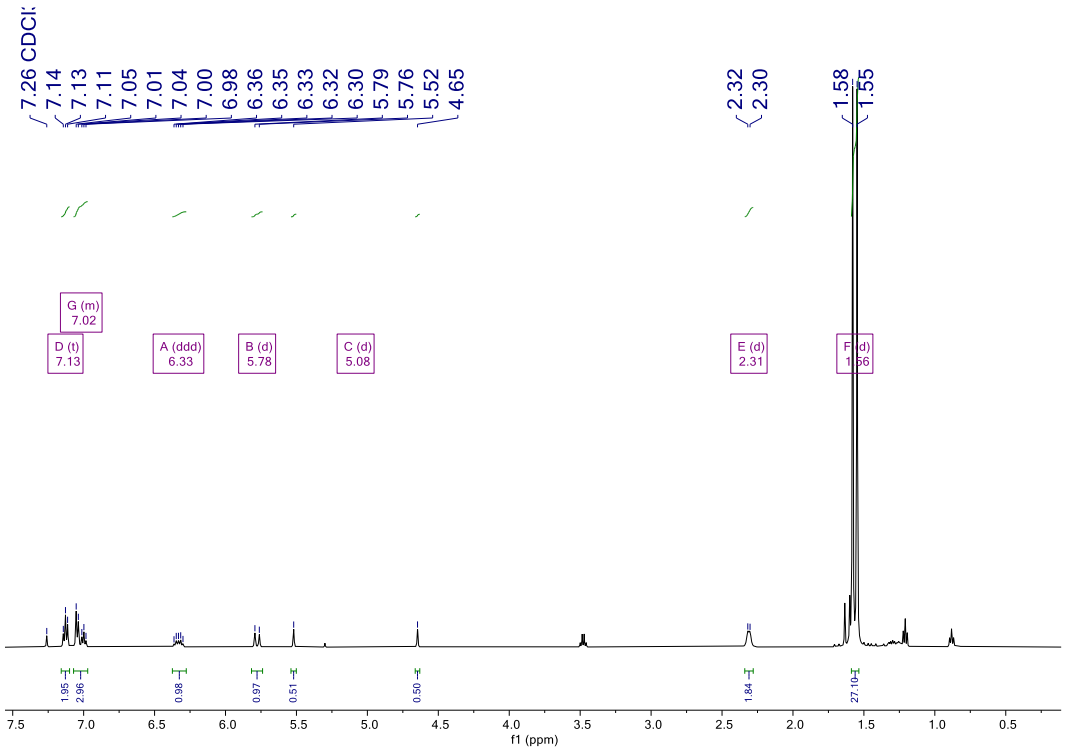


Figure S 28. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **9**

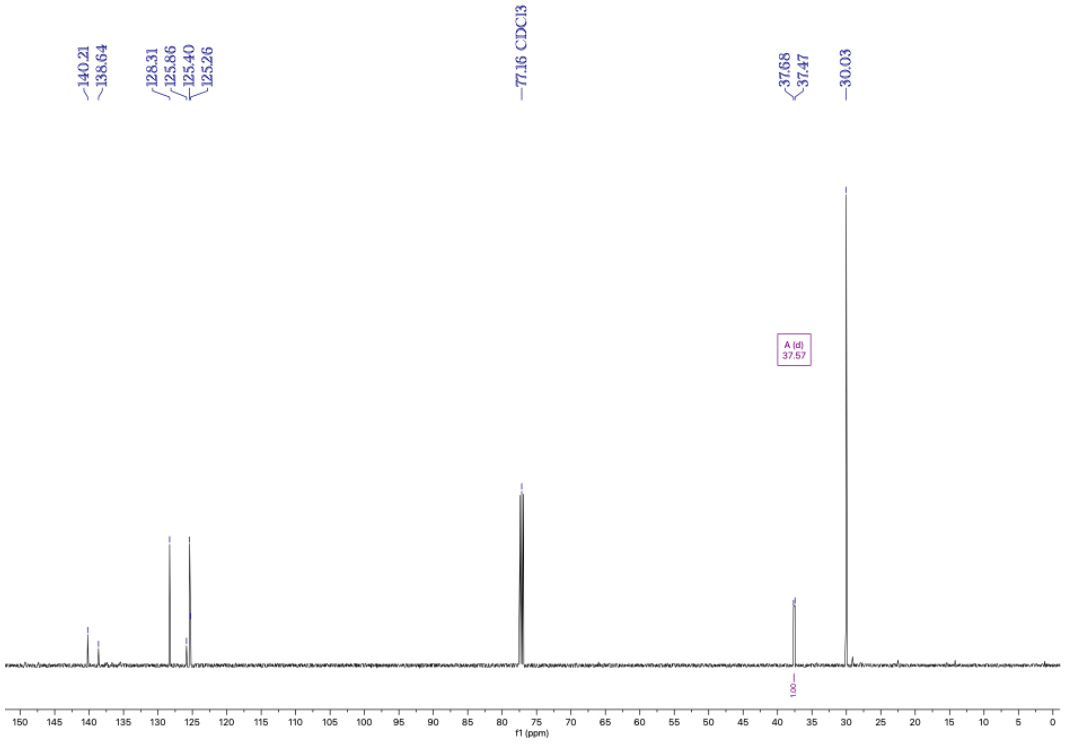
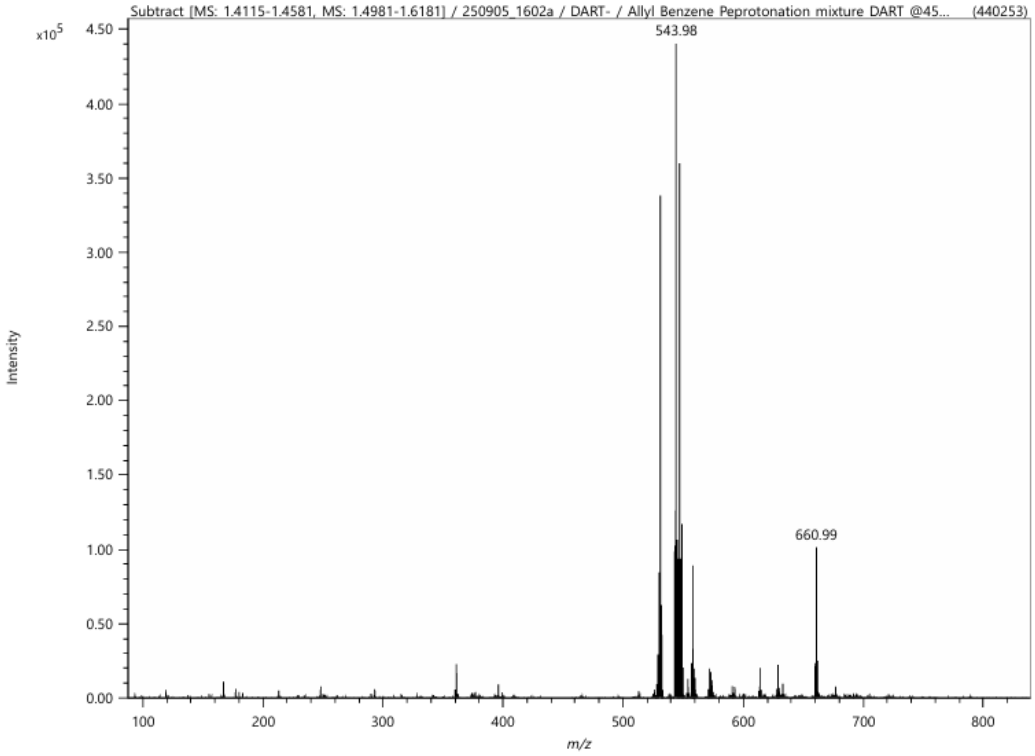


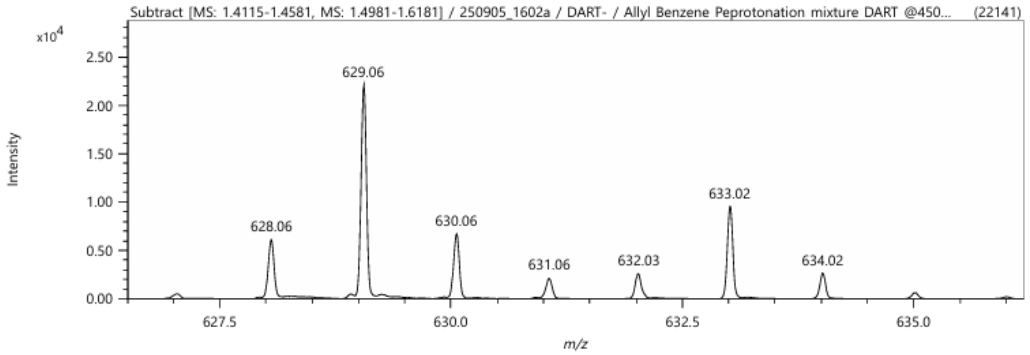
Figure S 29. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **9**

Figure S 30. Mass spectra spectrum of **9**

DART IONIZATION **AccuTOF 4G**



Spectrum



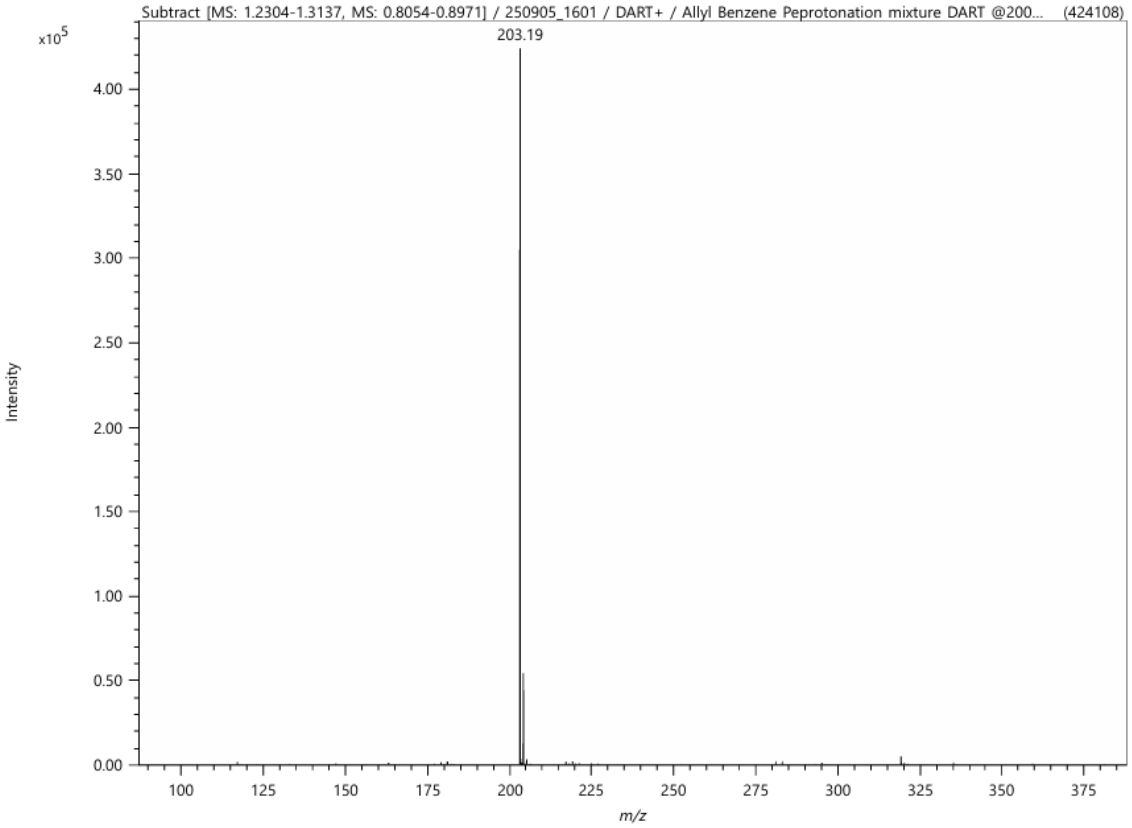
Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±5.00 mDa	Symbol	C	H	O	N	B	F
Electron:	Even	Min	0	0	0	0	1	15
Charge:	+1	Max	100	200	20	10	1	15
DBE:	-1.5 - 100.0							

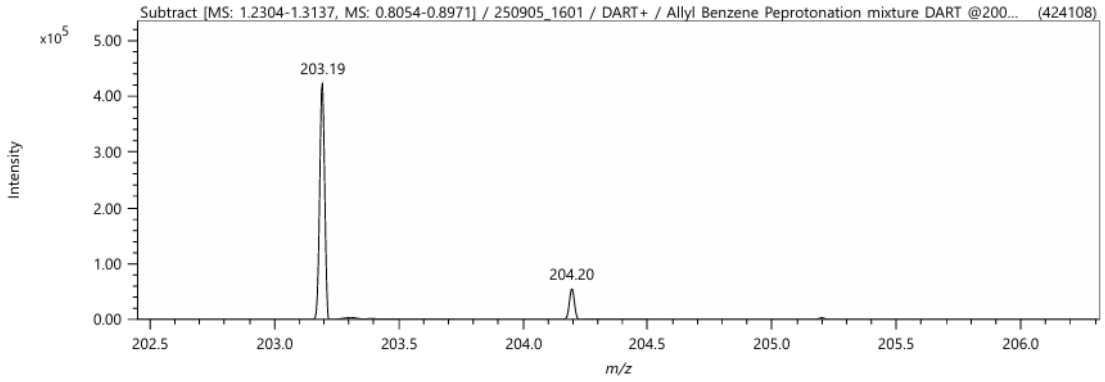
Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
629.05643	22140.80	C15 H13 B N2 O7 F15	629.05708	-0.65	-1.04	3.5
		C27 H9 B F15	629.05523	1.20	1.90	16.5
		C16 H9 B N6 O3 F15	629.05842	-1.99	-3.16	8.5
		C11 H9 B N8 O5 F15	629.05440	2.03	3.23	4.5
		C10 H13 B N4 O9 F15	629.05306	3.37	5.36	-0.5
		C20 H13 B O5 F15	629.06110	-4.68	-7.43	7.5

DART IONIZATION **AccuTOF 4G**



Spectrum



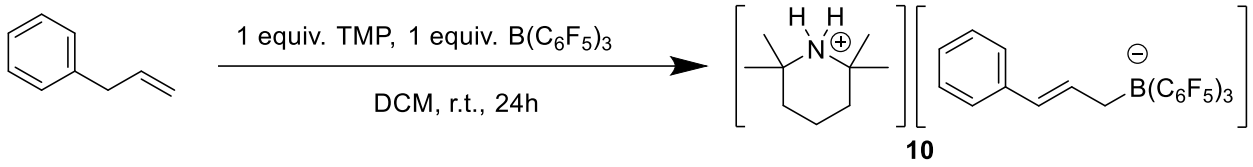
Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±5.00 mDa	Symbol	C	H	O	N	P
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
203.19221	424108.06	C12 H28 P	203.19231	-0.10	-0.50	-0.5

Preparation of [TMPH][PhCHCHCH$_2$B(C$_6$F$_5$)$_3$]



10

A 5 mL DCM solution of B(C$_6$F$_5$)$_3$ (0.100 g, 1.953 mmol, 1 equiv.) was added to a 5 mL DCM solution of allyl benzene (0.0461 g, 3.906 mmol, 2 equiv.) and stirred for 5 mins at room temperature. A 5 mL DCM solution of TMP (0.028 g, 1.953 mmol, 1 equiv.) was then added dropwise to the solution over 30 minutes and stirred for 24 hours at room temperature. After which, the solvent was removed *in vacuo,* resulting in a bright red oil. It was then dissolved in diethyl ether and filtered with a 0.22 µm syringe membrane filter. The solvent was then removed in vacuo and washed twice with 10 mL of pentane. Upon dissolving in minimum amounts of DCM, layered with pentane and stored at -35 °C overnight, a brown oil precipitated from the solution. Decanting the solvent and triturating the oil with 10 mL of pentane 5 times generated **10** as a light red oil (0.108 g, 72% yield).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ -13.3 (br s, 1B)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -132.0 (d, $^3J_{FF}$ = 24 Hz, 6F, *o*- C_6F_5), -162.7 (dd, $^3J_{FF}$ = 21, 21 Hz, 3F, *p*- C_6F_5), -166.1 (dd, $^3J_{FF}$ = 20, 20 Hz, 6F, *m*- C_6F_5).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.19 (d, $^3J_{HH}$ = 7, 8, 2H, Ar*H*), 7.09 – 7.04 (m, 3H, Ar*H*), 6.33 (dt, $^3J_{HH}$ = 8, 16 Hz, 1H, BCH_2CHCH), 5.84 (d, $^3J_{HH}$ = 16, 1H, BCH_2CHCH) 4.80 – 4.39 (br m, 2H, NH_2), 2.33 (br d, $^3J_{HH}$ = 8 Hz, 1H, BCH_2), 1.77 (m, 2H, $NCCH_2CH_2$), 1.65 (m, 4H, $NCCH_2$), 1.34 (s, 12H, $NCCH_3$)

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 148.34 (d, $^3J_{FF}$ = 239 Hz, *o*-C_6F_5), 137.78 (d, $^3J_{FF}$ = 245 Hz, *p*-C_6F_5), 136.65 (d, $^3J_{FF}$ = 235 Hz, *m*-C_6F_5), 139.51 (s, *i*-Ph), 139.14 (s, Ph-*C*H), 128.86 (s, *o*-Ph), 126.32 (s, BCH_2CH), 126.04 (s, *m*-Ph), 125.45 (s, *p*-Ph), 61.17 (s, NC), 35.08 (s, NCH_2), 27.96 (s, $NCCH_3$), 15.6 (s, $NCCH_2CH_2$)

HRMS: $C_{27}H_9BF_{15}$ (Negative mode) Calc: 629.0568, Obs: 629.0577; (Positive mode): $C_9H_{20}N$ Calc: 142.1590, Obs: 142.1602.

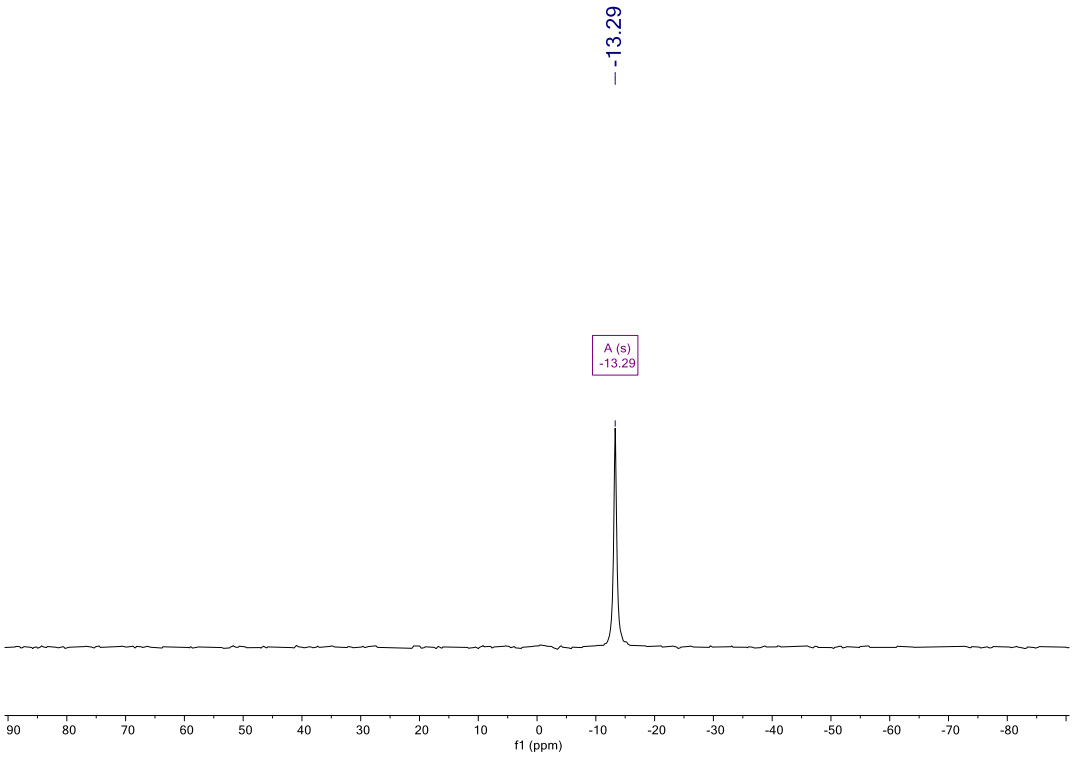


Figure S 31. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **10**

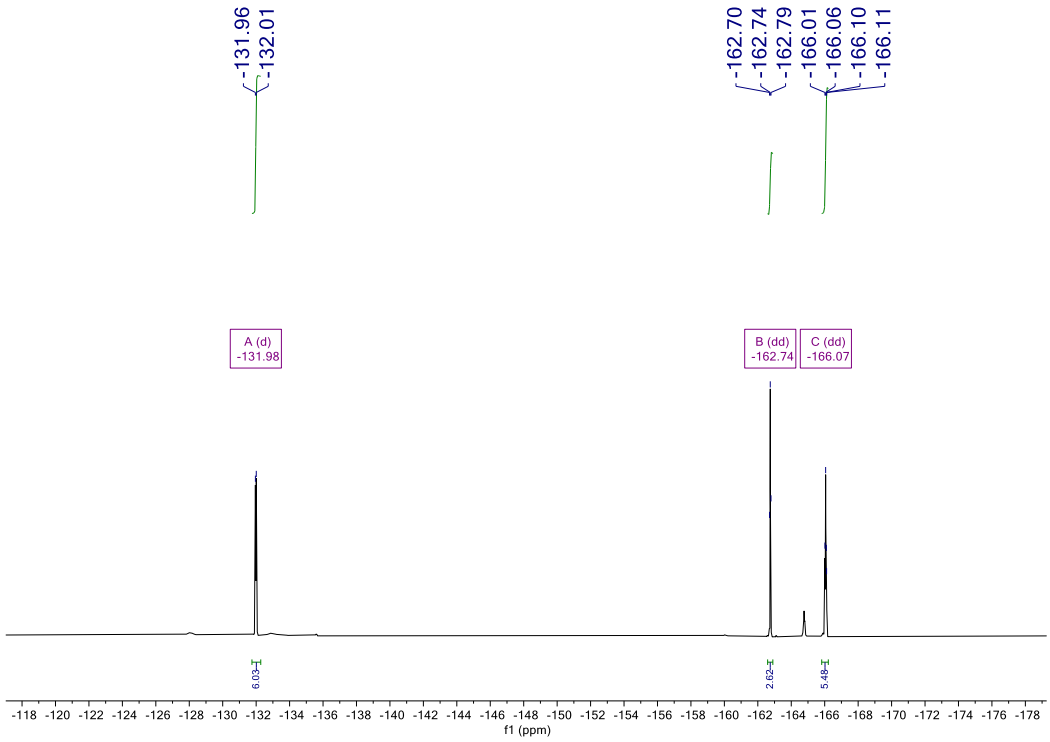


Figure S 32. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **10**

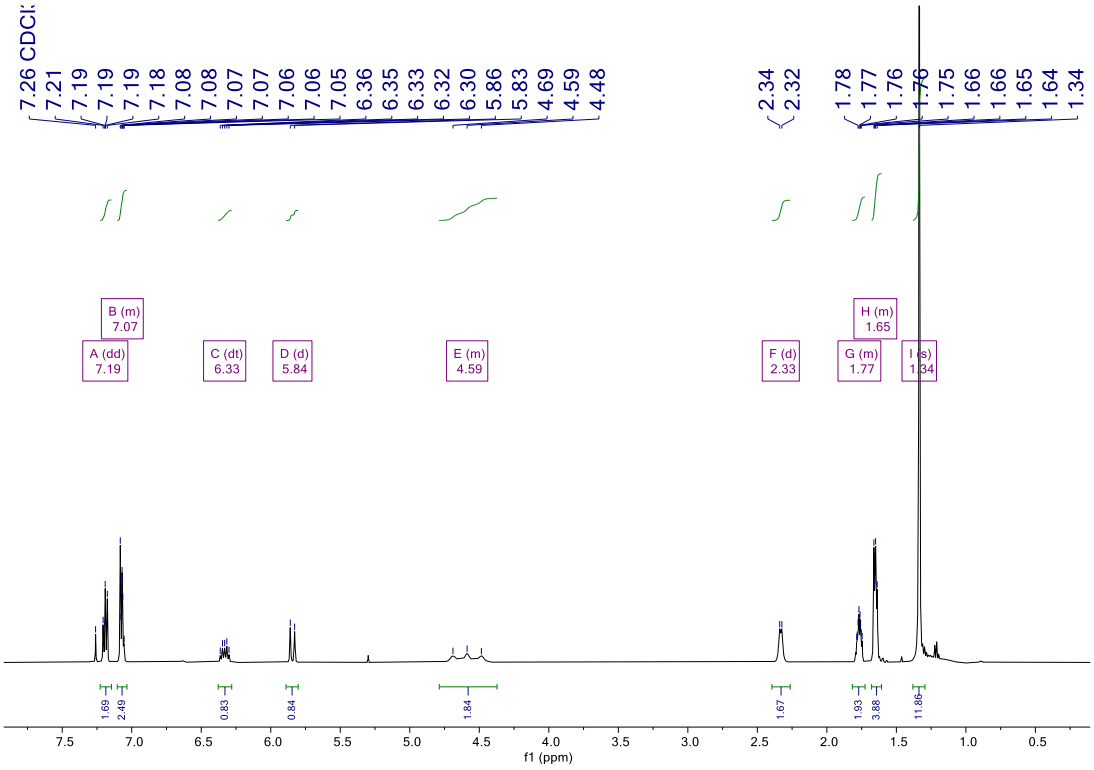


Figure S 33. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **10**

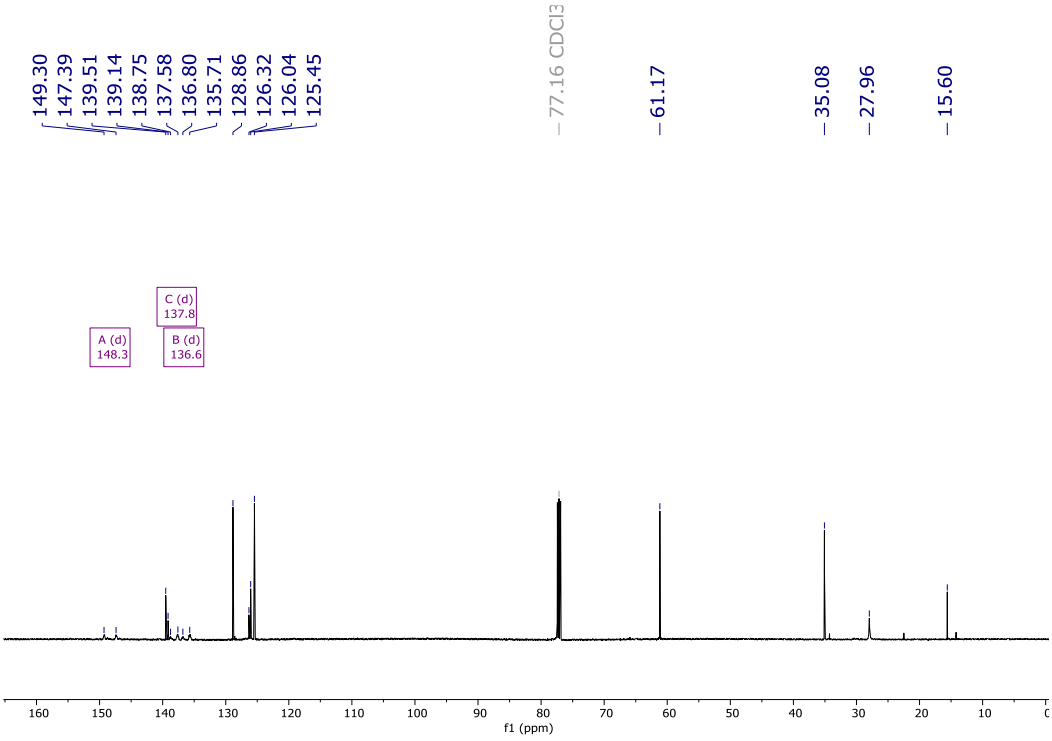
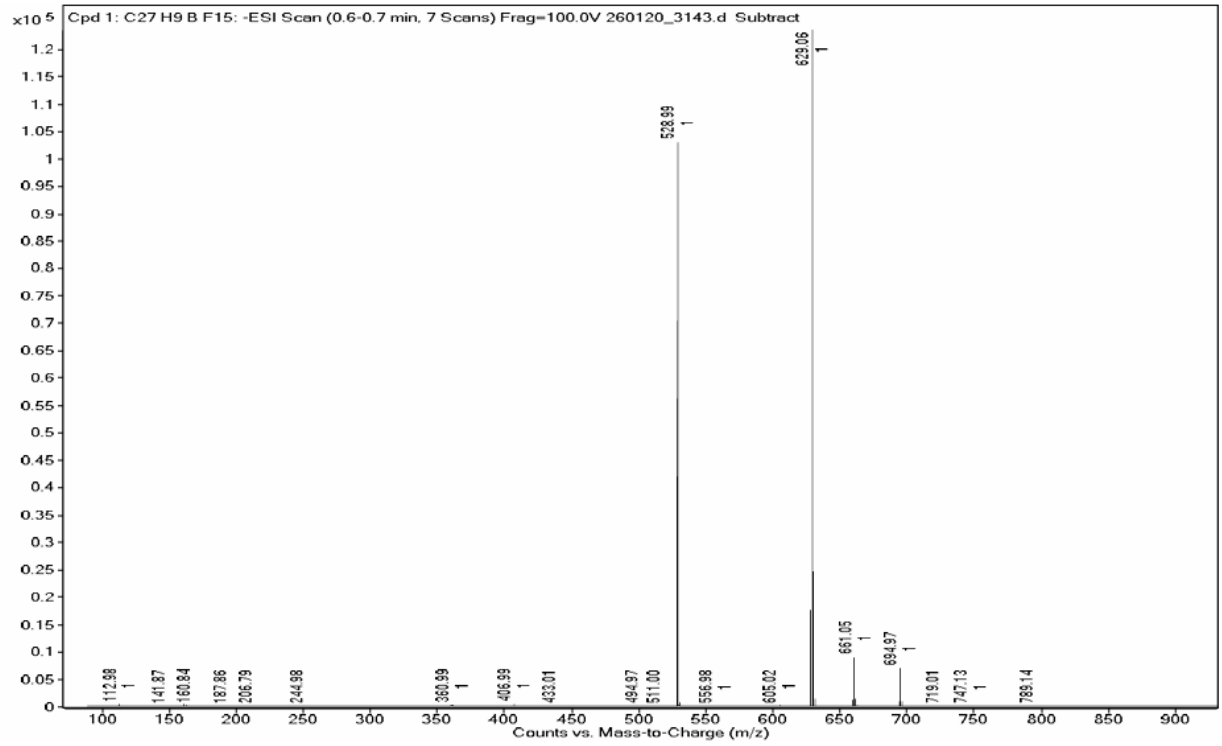
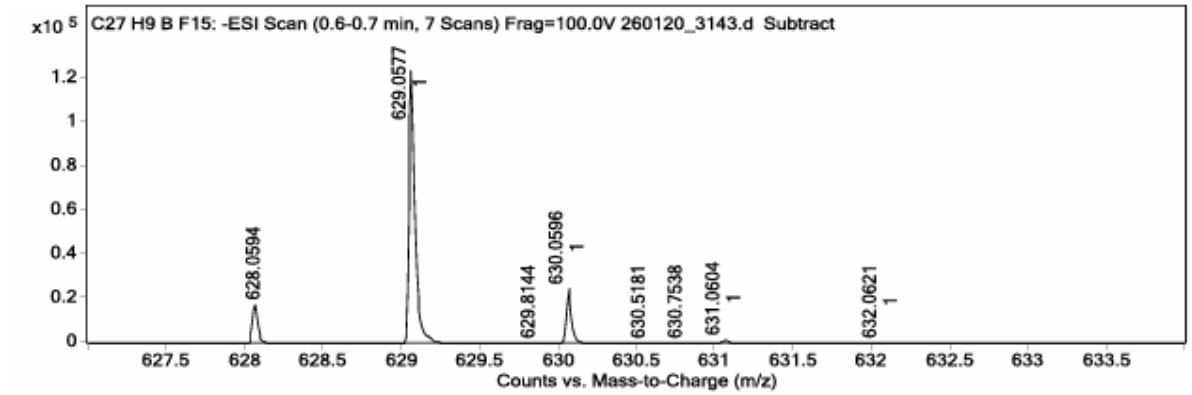


Figure S 34. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **10**

Figure S 35. Mass spectra spectrum of **10**

Sample Name	B/N Allyl Benz	**Data File**	260120_3143.d	**Acq Method**	HRMS_Negative.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	20/01/2026 3:10:35 PM
Comment	ESI-				

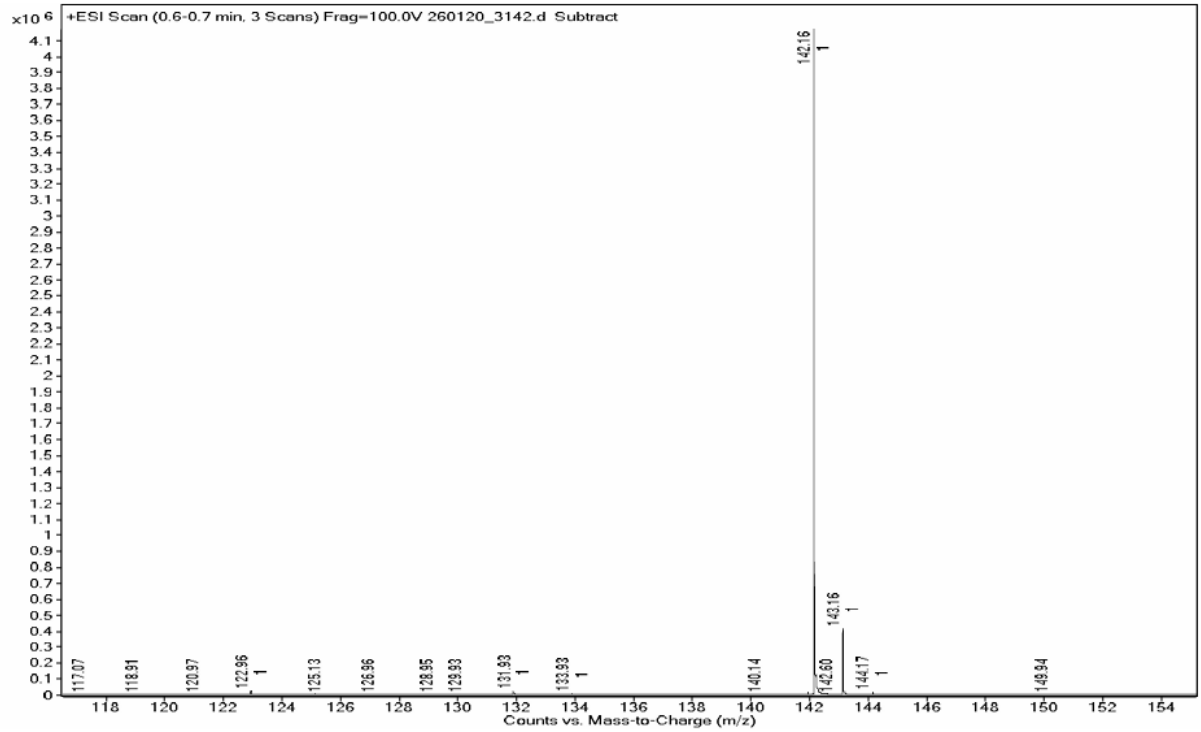


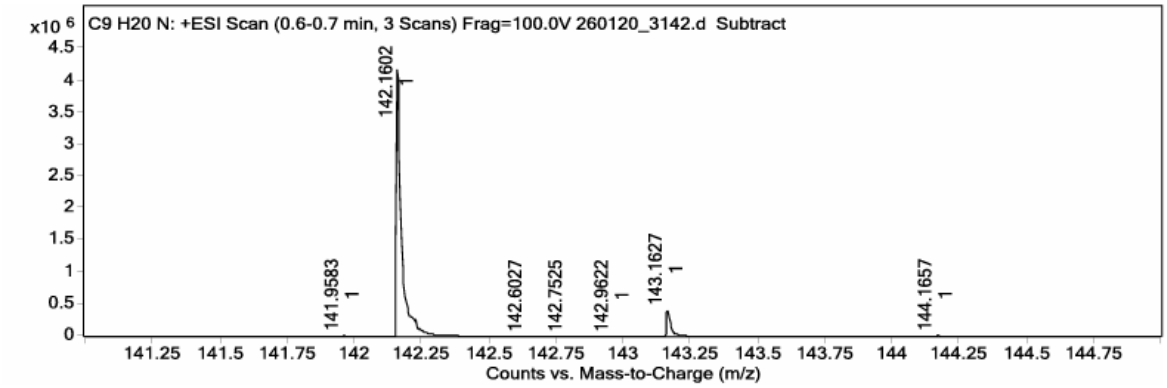


Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	628.0594	628.0600	-0.6	14.4	23.2	8.8
2	629.0577	629.0568	0.9	100.0	100.0	0.0
3	630.0596	630.0599	-0.3	19.9	28.3	8.4
4	631.0604	631.0632	-2.8	1.2	3.9	2.7

Sample Name	B/N Allyl Benz	**Data File**	260120_3142.d	**Acq Method**	HRMS.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	20/01/2026 3:03:12 PM
Comment	ESI+				

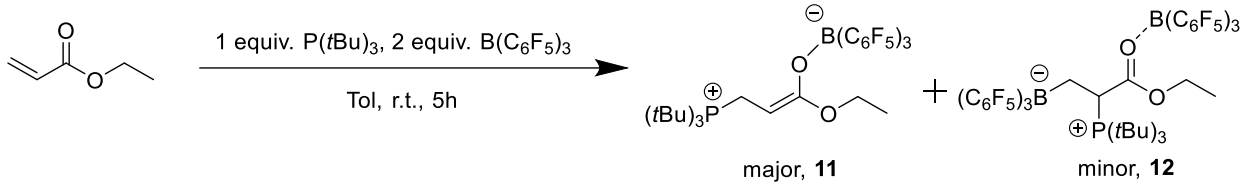




Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	142.1602	142.1590	1.2	100.0	100.0	0.0
2	143.1627	143.1622	0.5	9.5	10.3	0.8

Reaction of ethyl acrylate, $B(C_6F_5)_3$, and tBu_3P



A 5 mL toluene solution of $B(C_6F_5)_3$ (0.100 g, 0.98 mmol, 1 equiv.) was added to a 5 mL toluene solution of P*t*Bu$_3$ (0.039 g, 0.98 mmol, 1 equiv.) A 5 mL toluene solution of ethyl acrylate (0.020 g, 0.98 mmol, 1 equiv.) was then added to the solution and stirred for 5 hours. After which, the solvent was removed *in vacuo,* resulting in an off-white residue. The residue was washed and triturated with 10 mL of pentane 9 times and washed with 10 mL of diethyl ether once. The product was then dried in *vacuo,* generating **11** and **12** as a white powder. (0.128 g, 86.4% yield). Products were found to form in a 3.5:1.0 ratio by signal integrations in $^{31}P\{^1H\}$ NMR spectrum.

Spectral data of **11**,

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ -4.0 (br s, 1B),

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): -134.1 (d, $^3J_{FF}$ = 23 Hz, 6F, *o*-C_6F_5), δ -162.16 (dd, $^3J_{FF}$ = 20, 20 Hz, 3F, *p*-C_6F_5), -166.72 (dd, $^3J_{FF}$ = 19, 19 Hz, 6F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K): δ 44.65 (s, 1P).

^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 44.65 (s, 1P).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 3.39 (q, $^3J_{HH}$ = 7 Hz, 2H, O-C*H*$_2$), 3.27 (dd, $^2J_{HP}$ = 10, $^3J_{HH}$ = 7 Hz, 2H, P-CH$_2$), 3.00 (t, $^3J_{HH}$ = 7 Hz, 1H), O-CC*H*, 1.58 (d, $^3J_{HP}$ = 14 Hz, 27H, *t*Bu), 0.93 (d, $^3J_{HH}$ = 7 Hz, 3H, CH$_2$C*H*$_3$).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 163.6 (s, C-O), 148.0 (br d, $^1J_{CF}$ = 390 Hz, *o*-C_6F_5), 136.5 (br d, $^1J_{CF}$ = 271 Hz, *m*-C_6F_5), 62.7 (s, O-*C*H$_2$), 58.2 (d, $^2J_{CP}$ = 6 Hz, PCH$_2$*C*), 39.1 (d, $^1J_{CP}$ = 28 Hz, *t*Bu), 29.8 (s, *t*Bu), 17.4 (d, $^1J_{CP}$ = 38 Hz, P-*C*H$_2$), 13.8 (s, CH$_2$*C*H$_3$). The resonance signal corresponding to *para* C_6F_5 could not be explicitly identified due to broadening.

Spectral data of **12**

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ -4.0 (br s, 1B), -11.9 (br s, 1B).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): -133.4 (d, $^3J_{FF}$ = 23 Hz, 6F, *o*-C_6F_5), δ -161.3 (dd, $^3J_{FF}$ = 20, 20 Hz, 3F, *p*-C_6F_5), -166.0 (dd, $^3J_{FF}$ = 19, 19 Hz, 6F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K): δ 44.11 (s, 1P).

^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 44.11 (s, 1P).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 4.08 (q, $^3J_{HH}$ = 7 Hz, 2H, O-CH_2), 1.48 (d, $^3J_{HP}$ = 13 Hz, 27H, *t*Bu), 0.88 (d, $^3J_{HH}$ = 7 Hz, 3H, CH_2CH_3)

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 160.2 (s, C=O), 61.0 (s, O-CH_2), 38.9 (d, $^1J_{CP}$ = 28 Hz, *t*Bu), 29.6 (s, *t*Bu), 17.3 (d, $^1J_{CP}$ = 37 Hz, P-CH_2), 15.4 (s, CH_2CH_3). The resonance signals corresponding to *ortho*, *para*, and *meta* C_6F_5 could not be explicitly identified due to broadening.

HRMS: $C_{26}H_{15}BF_{15}$ (Negative mode) Calc: 622.1069, Obs: 622.1023; (Positive mode): $C_{12}H_{28}P$ Calc: 203.1923, Obs: 203.1913.

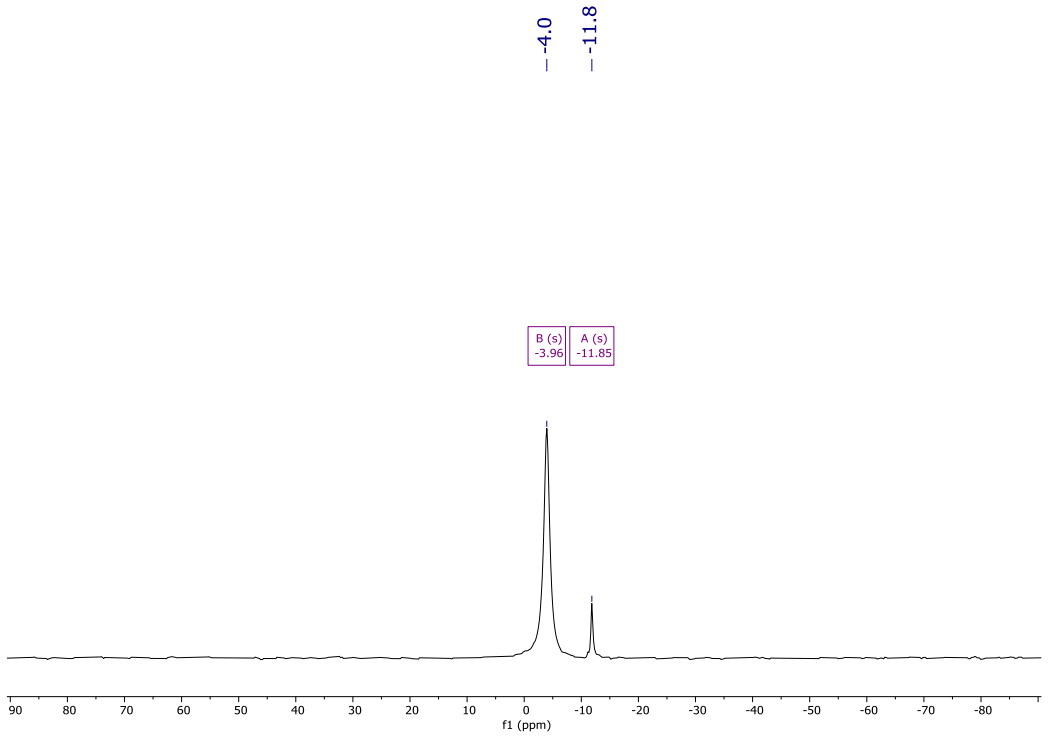


Figure S 36. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **11** and **12**

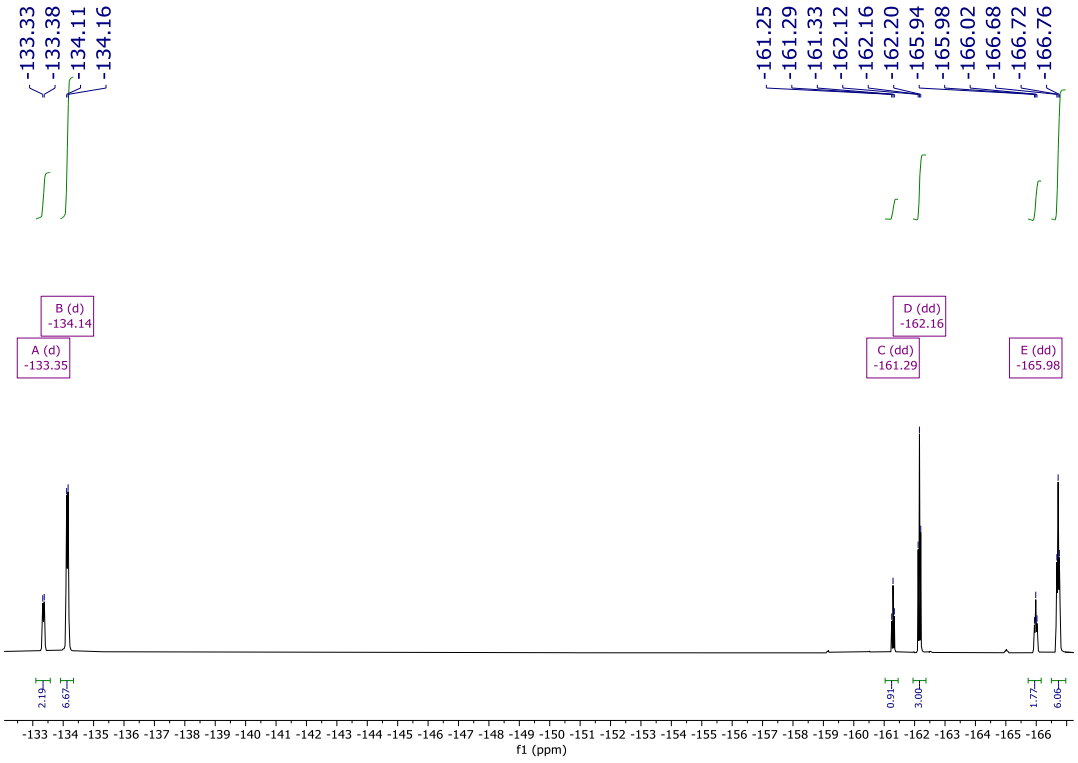


Figure S 37. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **11** and **12**

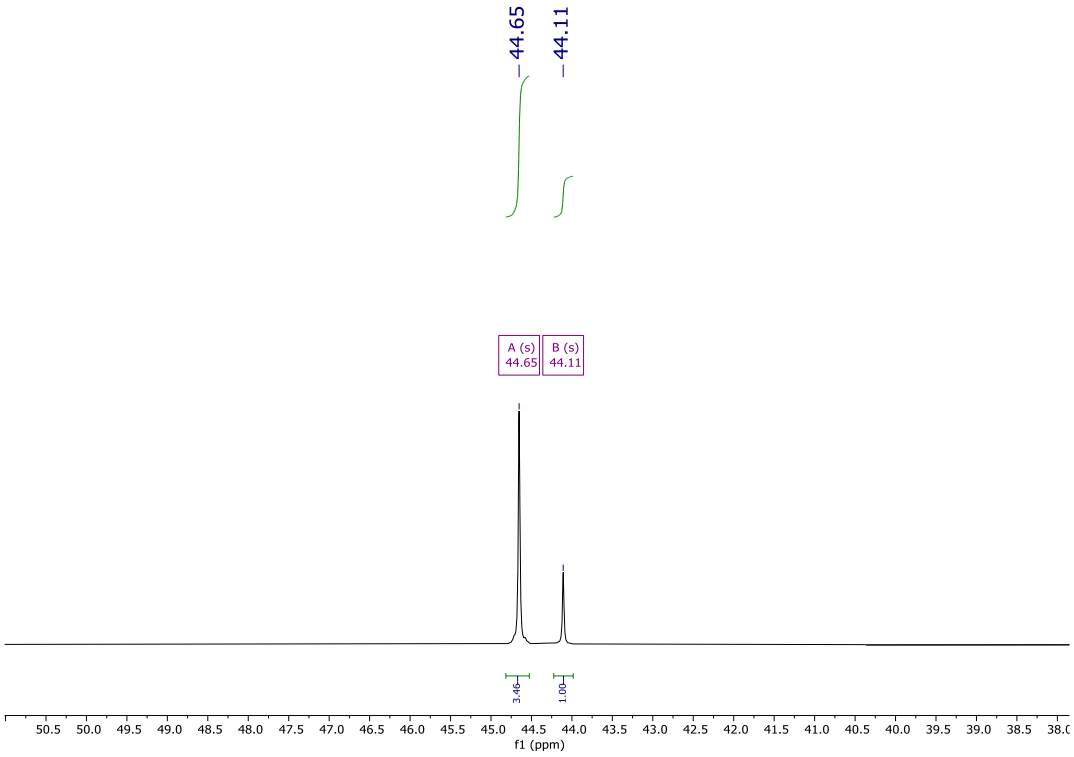


Figure S 38. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **11** and **12**

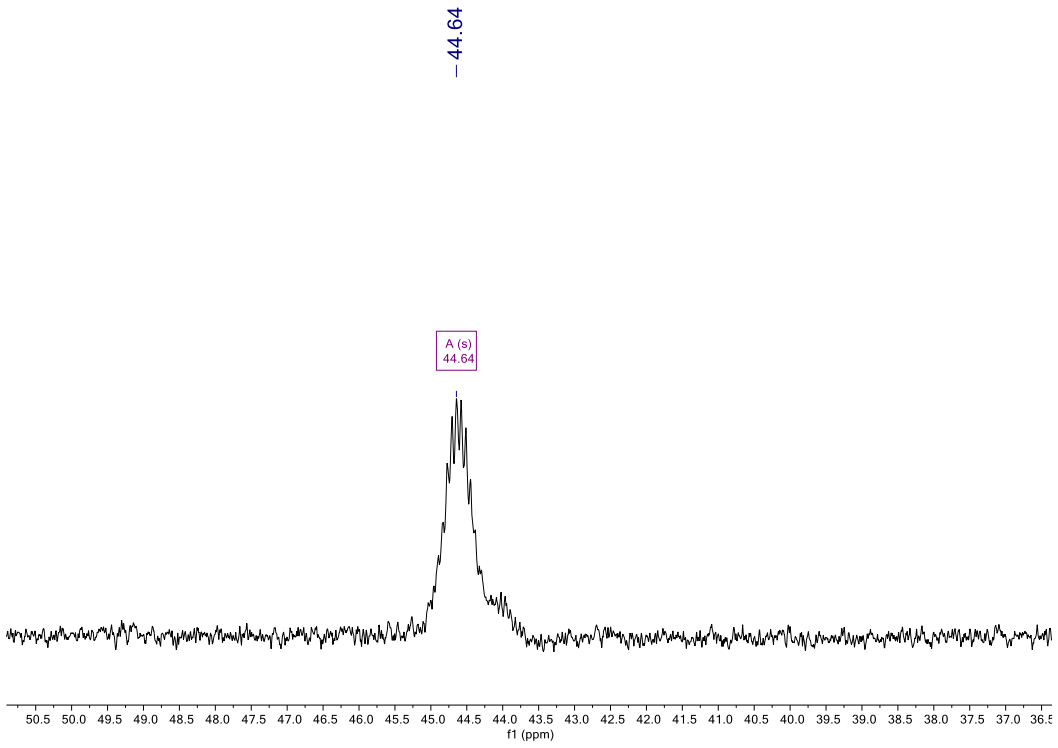


Figure S 39. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **11** and **12**

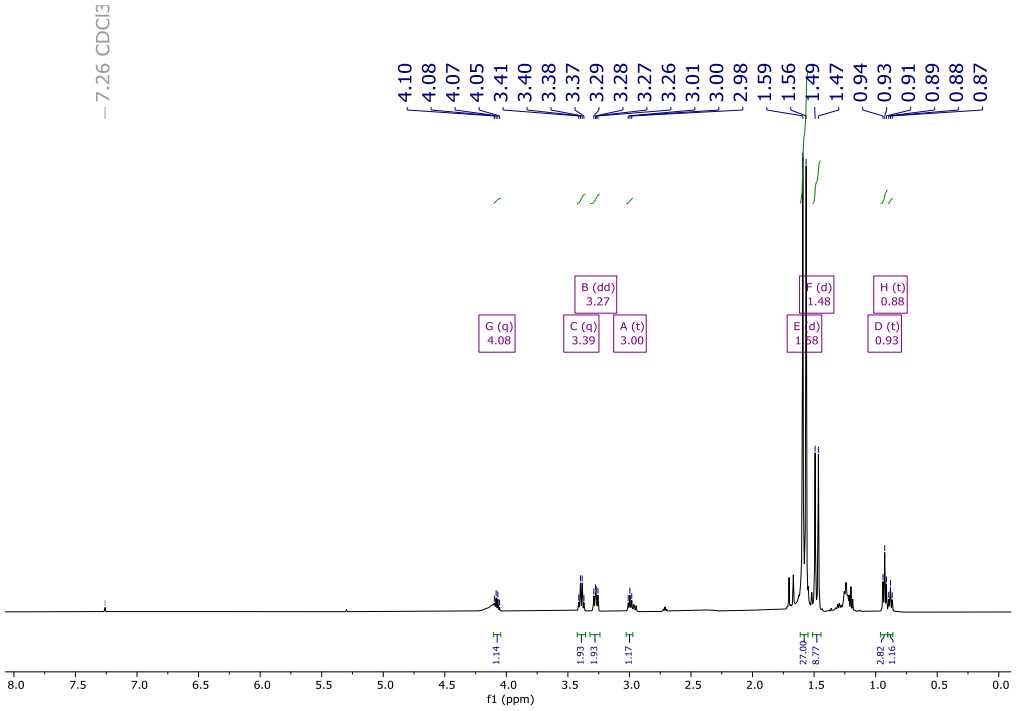


Figure S 40. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **11** and **12**

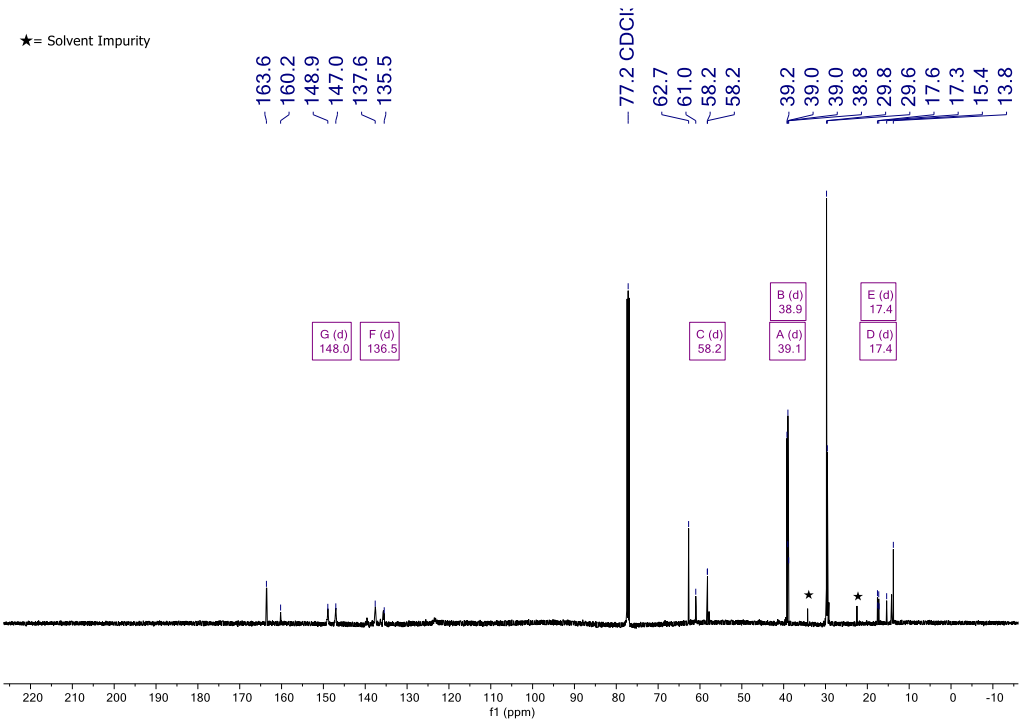
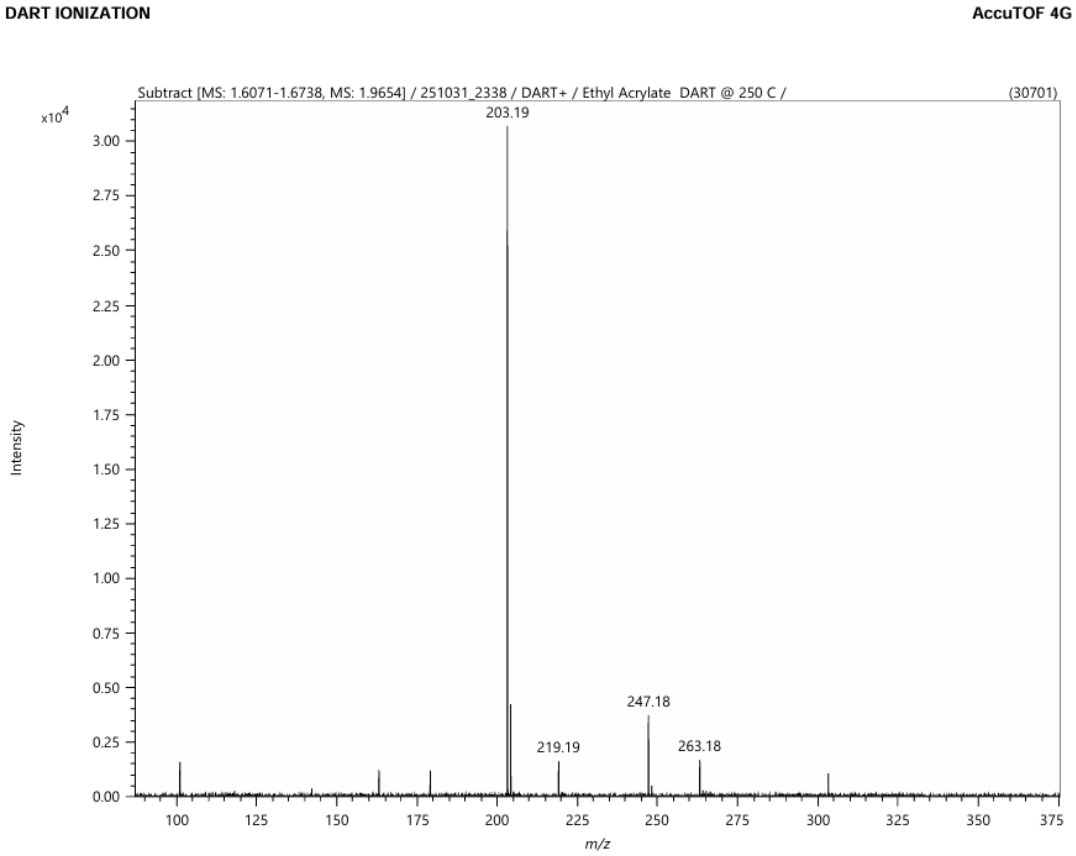
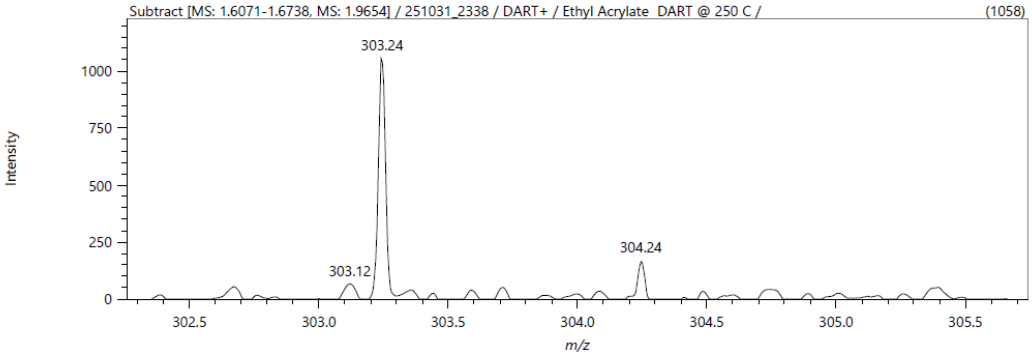


Figure S 41. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **11** and **12**

Figure S 42. Mass spectra spectrum of **11** and **12**



Spectrum



Elemental Composition

Parameters	
Tolerance:	±5.00 mDa
Electron:	Even
Charge:	+1
DBE:	-1.5 - 100.0

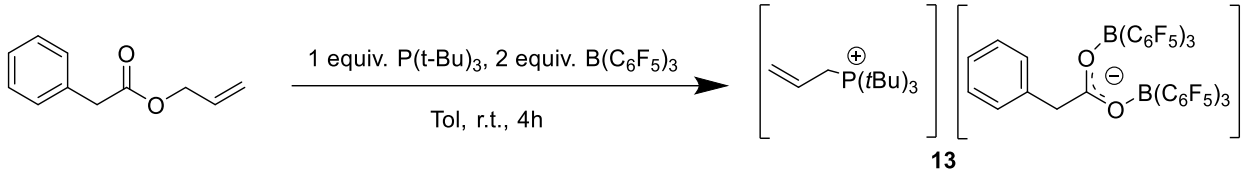
Elements Set 1:

Symbol	C	H	O	N	P
Min	0	0	0	0	0
Max	100	200	20	10	1

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
303.24467	1057.56	C17 H36 O2 P	303.24474	-0.08	-0.26	0.5
		C19 H31 N2 O	303.24309	1.58	5.19	5.5
		C13 H32 N6 P	303.24206	2.61	8.60	1.5

Preparation of [tBu$_3$PCH$_2$CHCH$_2$] [PhCH$_2$CO$_2$(B(C$_6$F$_5$)$_3$)$_2$]



13

A 5 mL toluene solution of B(C$_6$F$_5$)$_3$ (0.10 g, 1.953 mmol, 2 equiv.) was added to a 5 mL toluene solution of PtBu$_3$ (0.019 g, 0.977 mmol, 1 equiv.) and stirred for 5 mins at room temperature. Allyl phenyl acetate (0.019 g, 0.977 mmol, 1 equiv.) was then added to the solution and stirred for 4 hours at room temperature. After which, the solvent was removed *in vacuo,* resulting in a white residue. The residue was washed and triturated with 10 mL of pentane 4 times and dried in *vacuo* once more, generating **13** as a white powder. (0.112 g, 82% yield).

^{11}B NMR (128 MHz, CDCl$_3$, 298 K): δ -0.9 (br s, 1B), -2.8 (br s, 1B)

^{19}F NMR (376 MHz, CDCl$_3$, 298 K): δ -133.6 (br s, 12F, *o*- C$_6$F$_5$), -159.3 (br s, 6F, *p*- C$_6$F$_5$), -165.4 (br s, 12F, *m*- C$_6$F$_5$).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298K): δ 46.8 (s, 1P).

^{31}P NMR (162 MHz, CDCl$_3$, 298K): δ 46.8 (s, 1P).

^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 7.20 – 7.15 (m, 3H, Ar*H*), 7.04 (dd, $^3J_{HH}$ = 7, 2 Hz, 2H, Ar*H*), 6.0 (dddt, $^3J_{HH}$ = 17, 10, 7 Hz, $^3J_{HP}$ = 2.8 Hz, 1H, C*H*=CH$_2$), 5.58 - 5.49 (m, 2H, CH=C*H*$_2$), 3.62 (s, 2H, O$_2$C-C*H*$_2$), 3.00 (ddd, $^3J_{HH}$ = 7 Hz, $^2J_{HP}$ = 13 Hz, 2H, P-C*H*$_2$), (d, 27H, $^3J_{HP}$ = 14 Hz, *t*Bu)

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K): δ 183.1 (s, C-O), 148.0 (br d, $^1J_{CF}$ = 243 Hz, *o*-C$_6$F$_5$), 140 (br d, $^1J_{CF}$ = 247 Hz, *p*-C$_6$F$_5$), 137 (d, $^1J_{CF}$ = 249 Hz, *m*-C$_6$F$_5$), 132.1 (s, *i*-Ph), 129.7 (s, *o*-Ph), 128.1 (s, *m*-Ph), 127.1 (s, *p*-Ph), 126.2 (d, $^2J_{CP}$ = 11 Hz, PCH$_2$CH*C*H$_2$), 125.5 (d, $^3J_{CP}$ = 9 Hz, PCH$_2$*C*H), 42.4 (s, Ph-*C*H$_2$), 39.9 (d, $^1J_{CP}$ = 28 Hz, *t*Bu), 24.2 (d, $^1J_{CP}$ = 38 Hz, PCH$_2$)

HRMS: C$_{44}$H$_7$B$_2$F$_{30}$O$_2$ (Negative mode) Calc: 1159.0173, Obs:1159.0192; (Positive mode): C$_{12}$H$_{28}$P Calc: 243.2247, Obs: 243.2241.

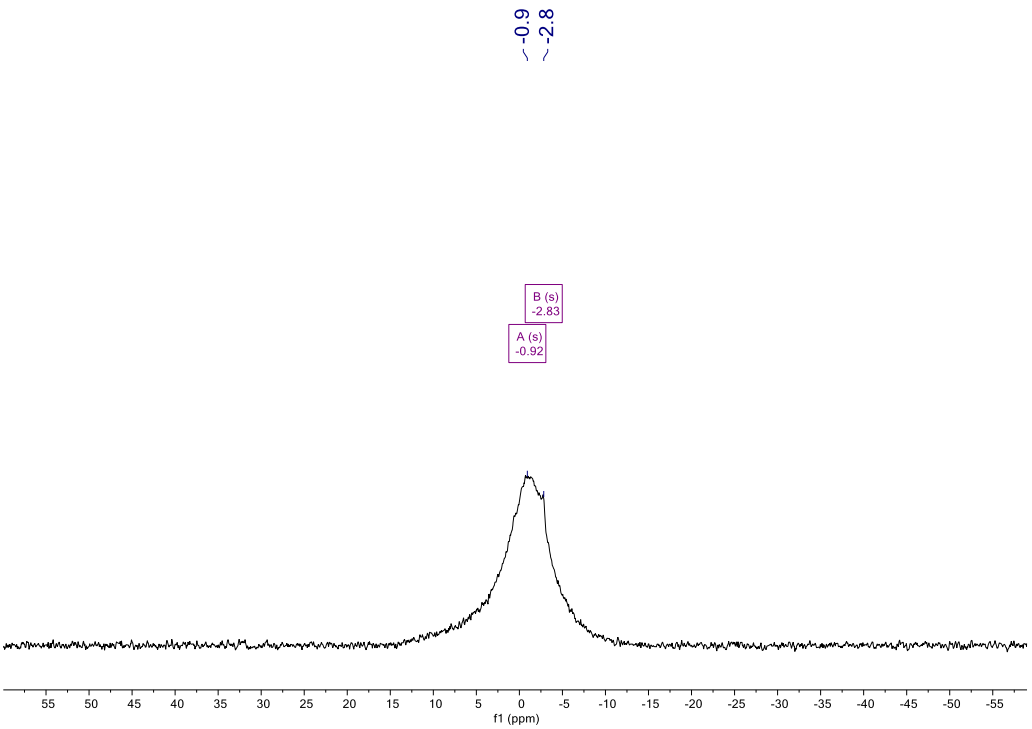


Figure S 43. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **13**

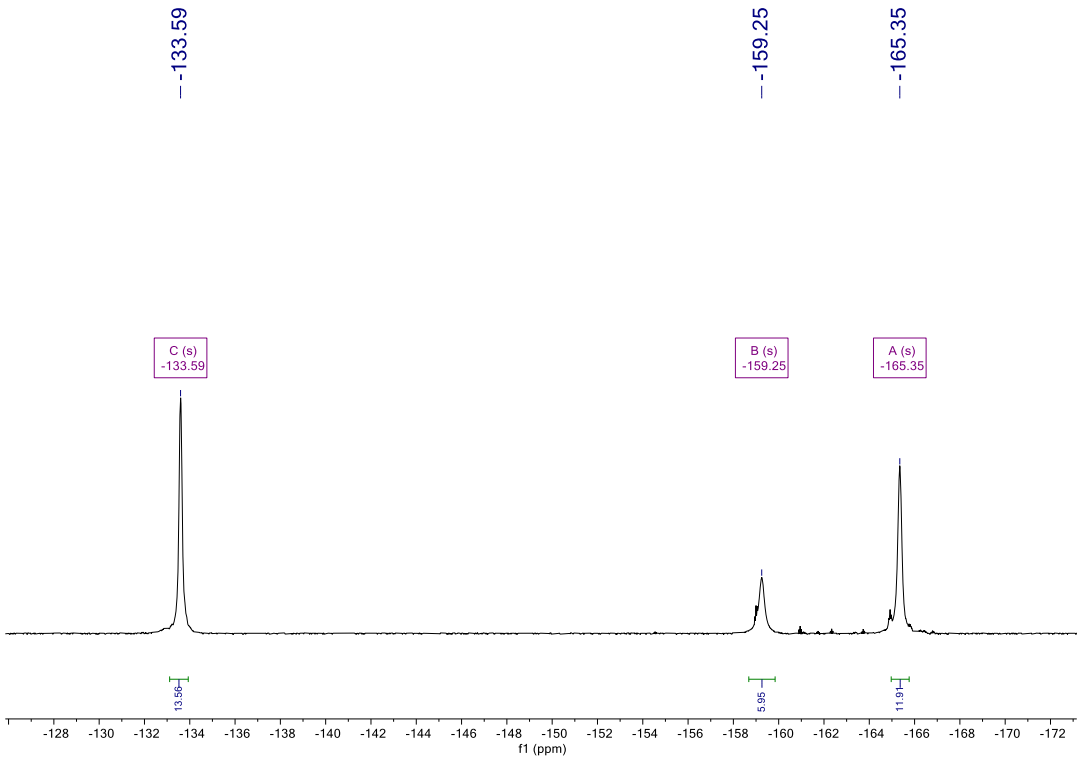


Figure S 44. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **13**

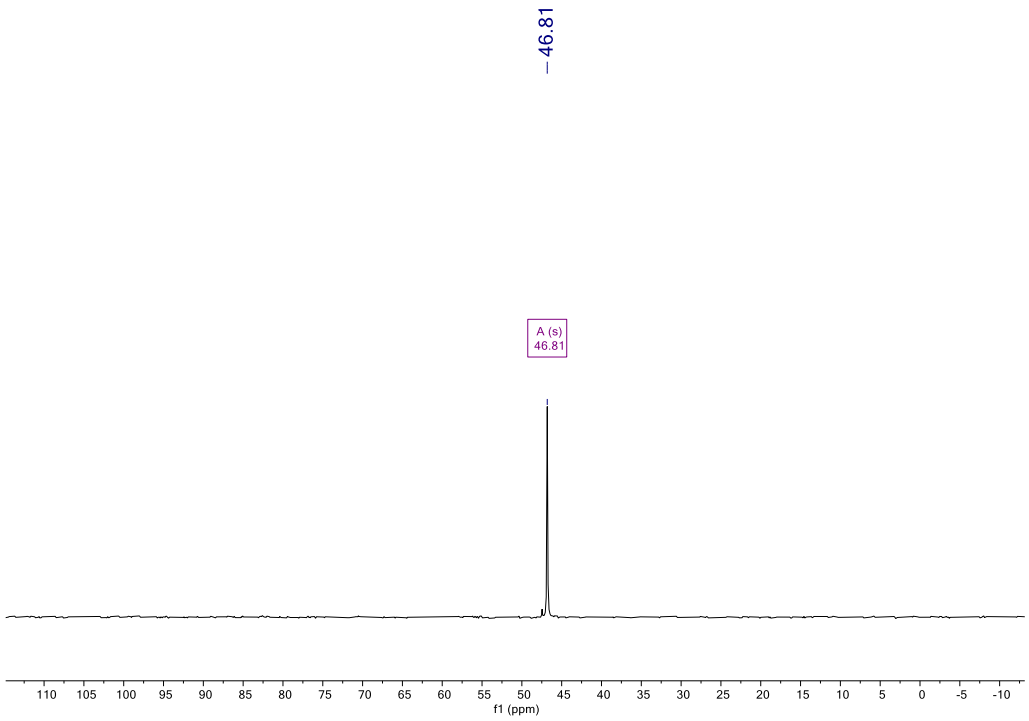


Figure S 45. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **13**

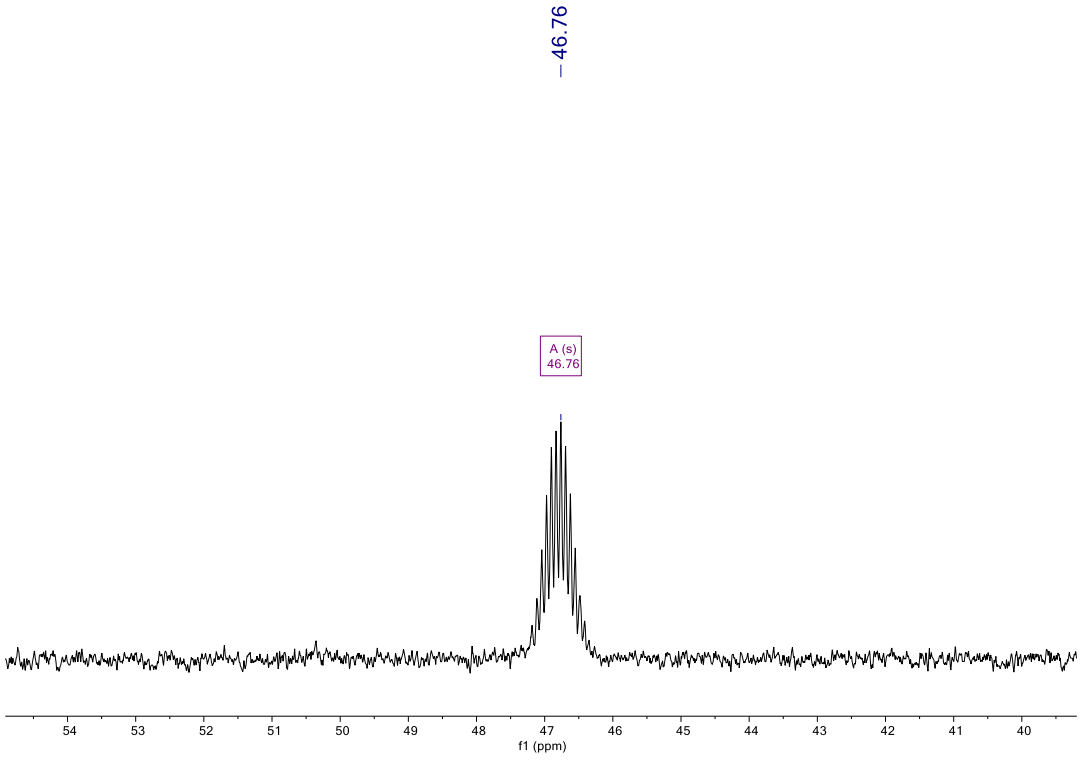


Figure S 46. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **13**

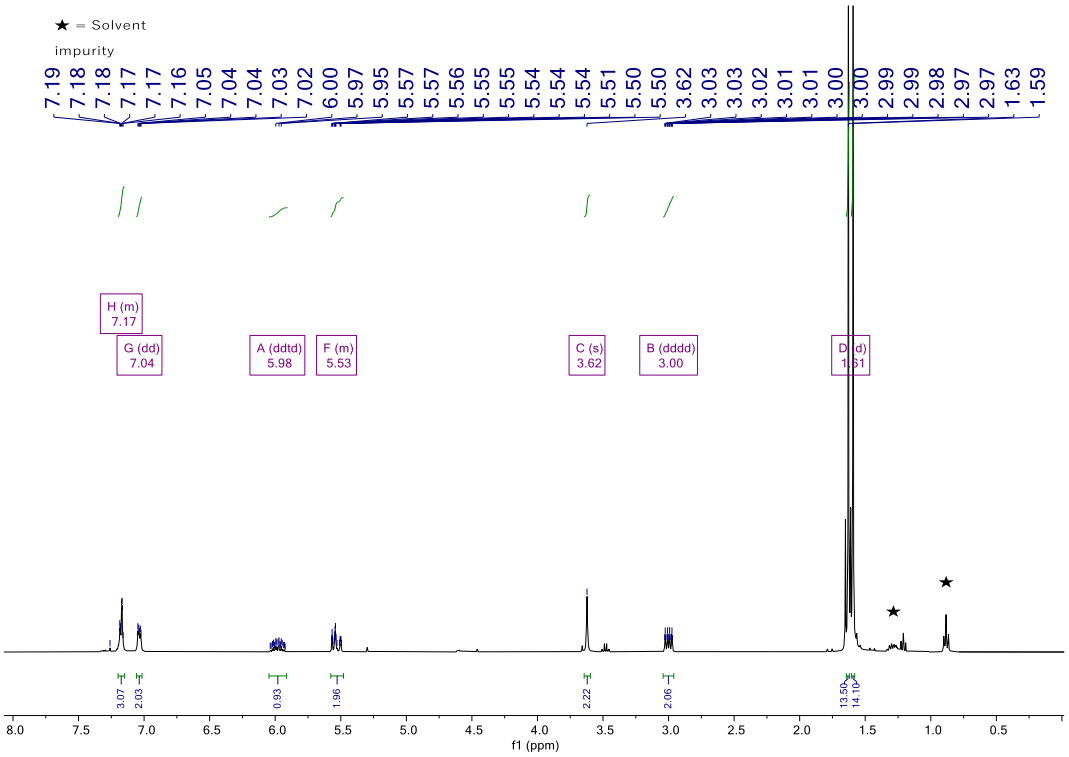


Figure S 47. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **13**

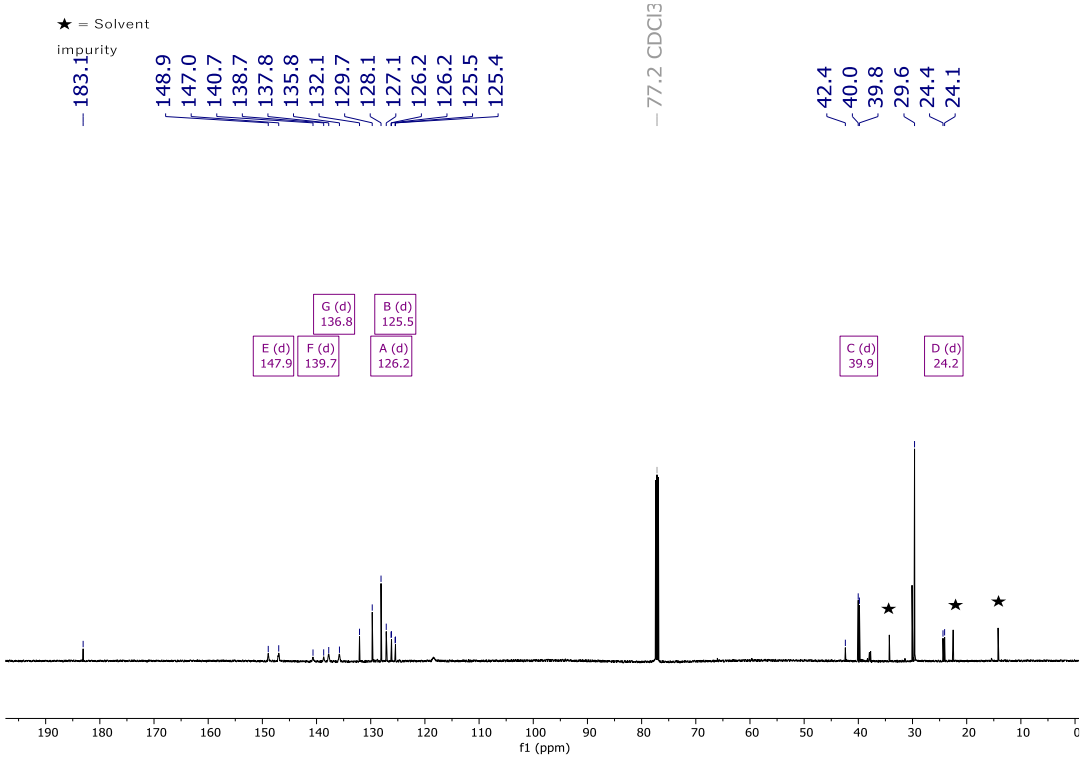
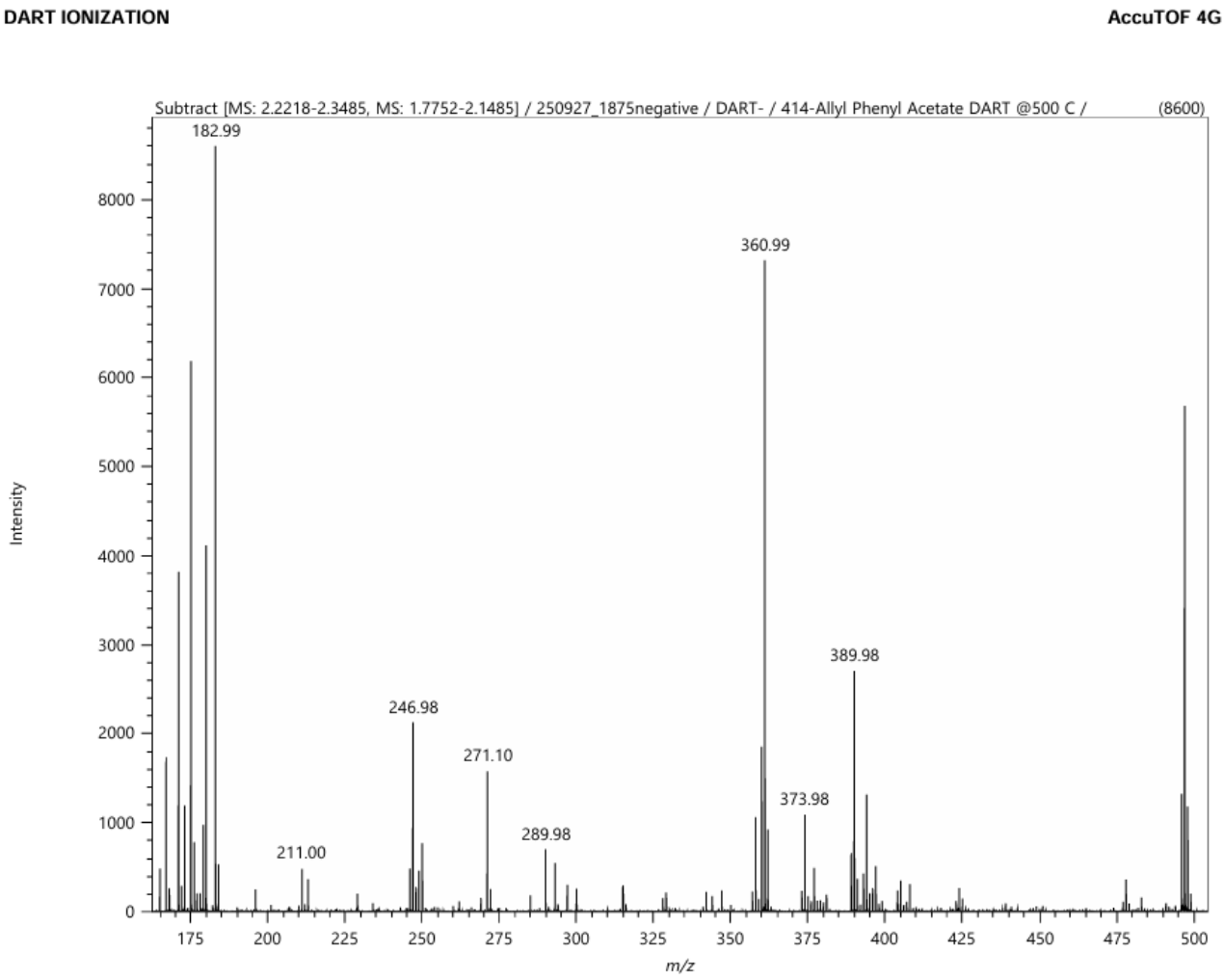
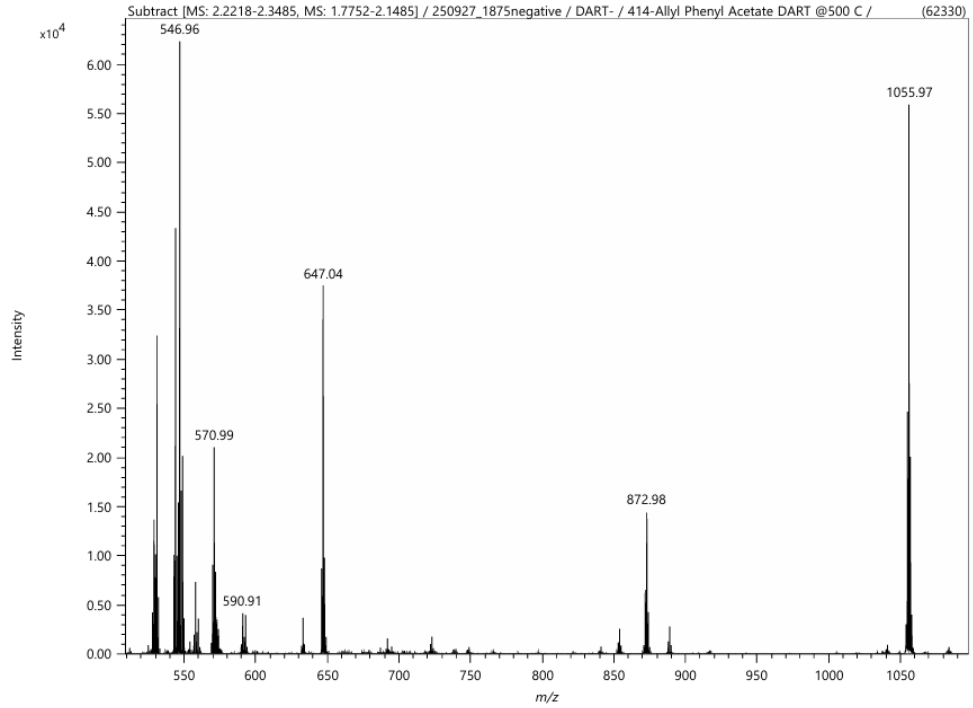


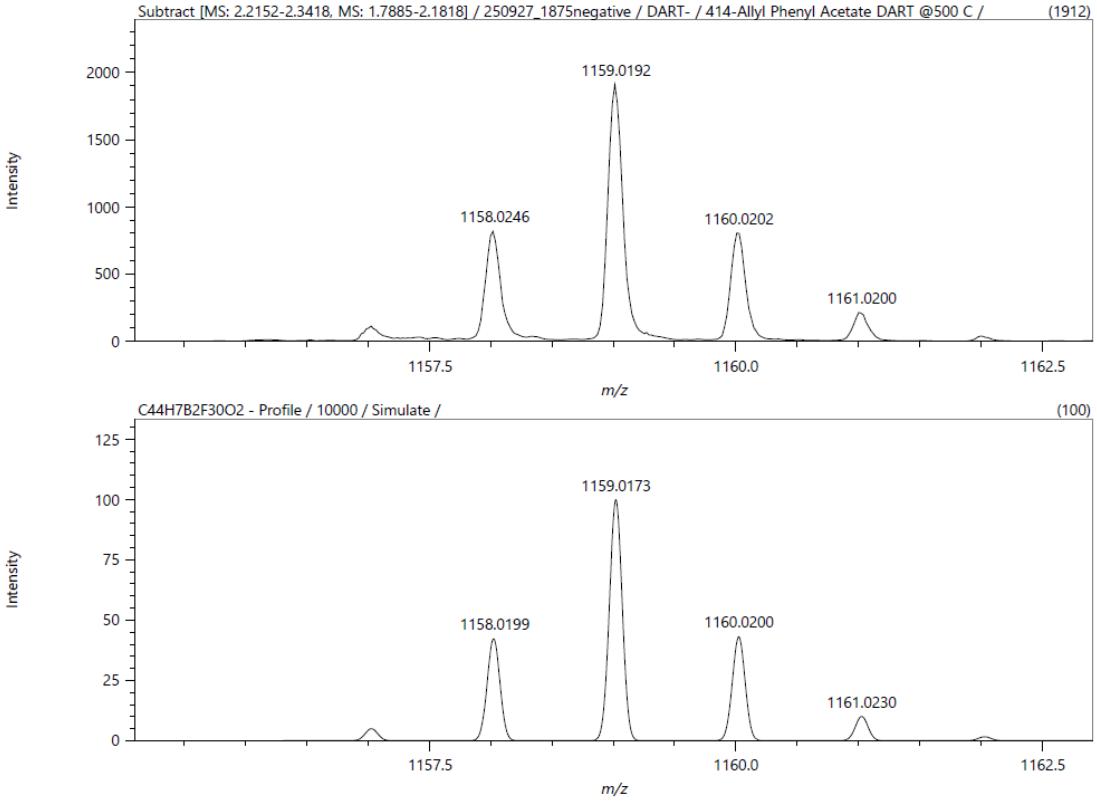
Figure S 48. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **13**

Figure S 49. Mass spectra spectrum of **13**

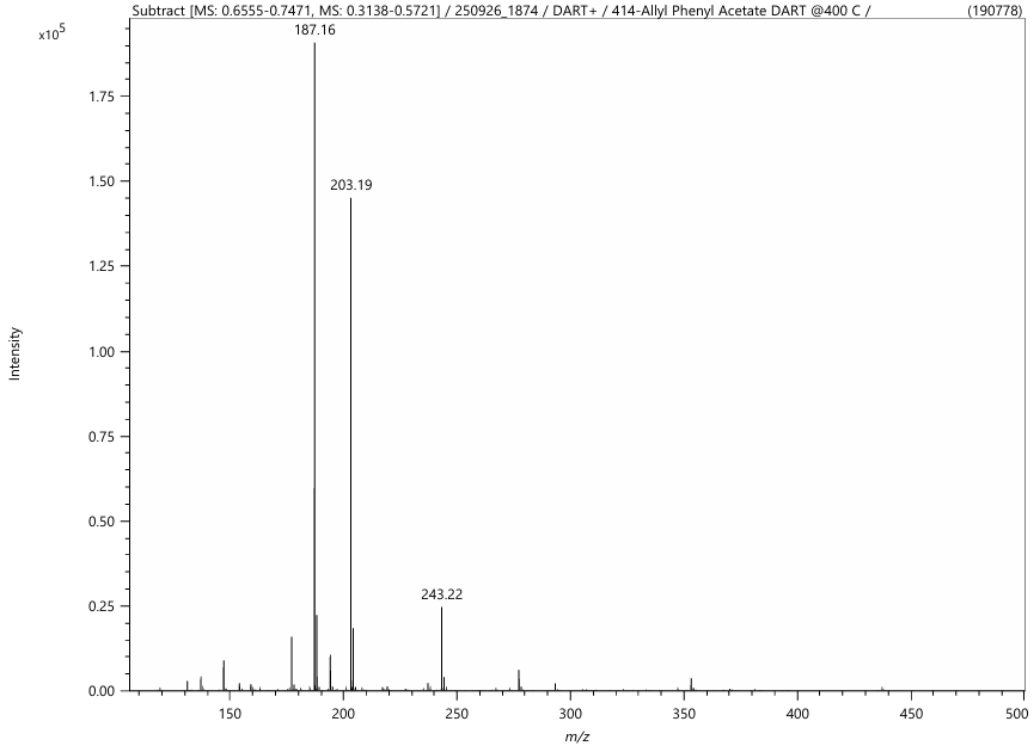


DART IONIZATION **AccuTOF 4G**

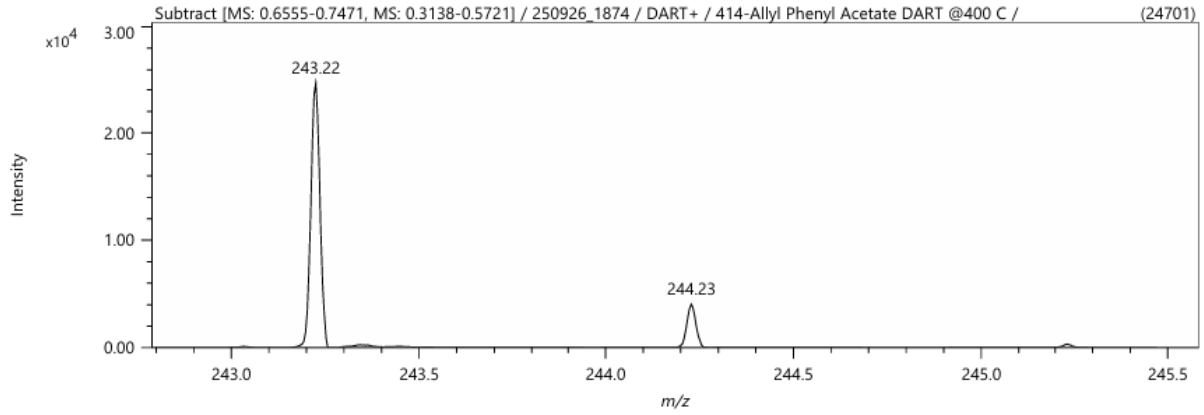




DART IONIZATION **AccuTOF 4G**



Spectrum



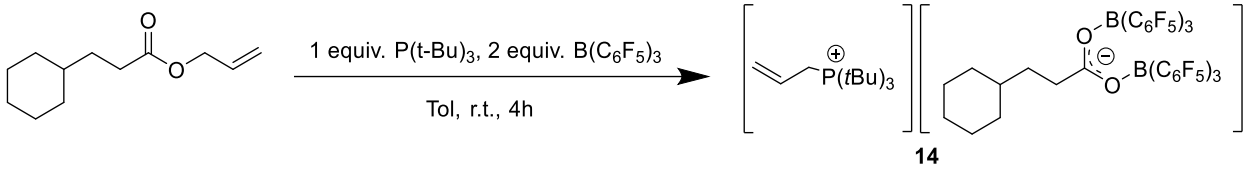
Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±5.00 mDa	Symbol	C	H	O	N	P
Electron:	Even	Min	0	0	0	0	0
Charge:	-1	Max	100	100	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
243.22406	24700.75	C15 H32 P	243.22471	-0.65	-2.66	0.5

Preparation of [tBu$_3$PCH$_2$CHCH$_2$][CyCH$_2$CH$_2$CO$_2$(B(C$_6$F$_5$)$_3$)$_2$]



14

A 5 mL toluene solution of B(C$_6$F$_5$)$_3$ (0.100 g, 1.95 mmol, 2 equiv.) was added to a 5 mL toluene solution of PtBu$_3$ (0.019 g, 0.977 mmol, 1 equiv.) and stirred for 5 mins at room temperature. Cyclohexyl Propionate (0.019 g, 0.977 mmol, 1 equiv.) was then added to the solution and stirred for 4 hours at room temperature. After which, the solvent was removed *in vacuo,* resulting in an off-white residue. The residue was washed and triturated with 10 mL of pentane 4 times and dried in *vacuo* once more, generating **14** as a white powder (0.110 g, 79% yield).

^{11}B NMR (128 MHz, CDCl$_3$, 298 K): δ -2.1 (br s, 1B), -5.1 (br s, 1B)

^{19}F NMR (376 MHz, CDCl$_3$, 298 K): δ -133.9 (br s, 12F, *o*-C$_6$F$_5$), -159.5 (br s, 6F, *p*-C$_6$F$_5$), -165.4 (br s, 12F, *m*-C$_6$F$_5$).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298K): δ 46.9 (s, 1P).

^{31}P NMR (162 MHz, CDCl$_3$, 298K): δ 46.9 (s, 1P).

^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 5.99 (ddtd, $^3J_{HH}$ = 17, 10, 7 Hz, $^3J_{HP}$ = 3 Hz, 1H, C*H*=CH$_2$), 5.58 - 5.50 (m, 2H, CH=C*H*$_2$), 3.00 (ddd, $^3J_{HH}$ = 7 Hz, $^2J_{HP}$ = 13 Hz, 2H, P-C*H*$_2$), 2.37 – 2.30 (m, 2H, O$_2$C-C*H*$_2$), 1.62 (d, 27H, $^3J_{HP}$ = 14 Hz, *t*Bu), 1.52 – 1.02 (m, 11H, Cy)

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K): δ 186.4 (s, C-O), 148.0 (br d, $^1J_{CF}$ = 255 Hz, *o*-C$_6$F$_5$), 137.0 (d, $^1J_{CF}$ = 242 Hz, *m*-C$_6$F$_5$), 126.2 (d, $^2J_{CP}$ = 11 Hz, PCH$_2$CH*C*H$_2$), 125.5 (d, $^3J_{CP}$ = 9 Hz, PCH$_2$*C*H), 39.9 (d, $^1J_{CP}$ = 28 Hz, *t*Bu), 37.2 (s, OOC*C*H$_2$), 33.8 (s, CyCH$_2$), 32.8 (*o*-Cy), 31.6 (s, *i*-Cy), 29.8 (s, *t*Bu), 26.6 (s, *p*-Cy), 26.3 (s, *m*-Cy), 24.2 (d, $^1J_{CP}$ = 38 Hz, PCH$_2$).

HRMS: C$_{45}$H$_{15}$B$_2$F$_{30}$O$_2$ (Negative mode) Calc: 1179.07990, Obs: 1179.07783; (Positive mode): C$_{15}$H$_{32}$P Calc: 243.2247, Obs: 243.2290.

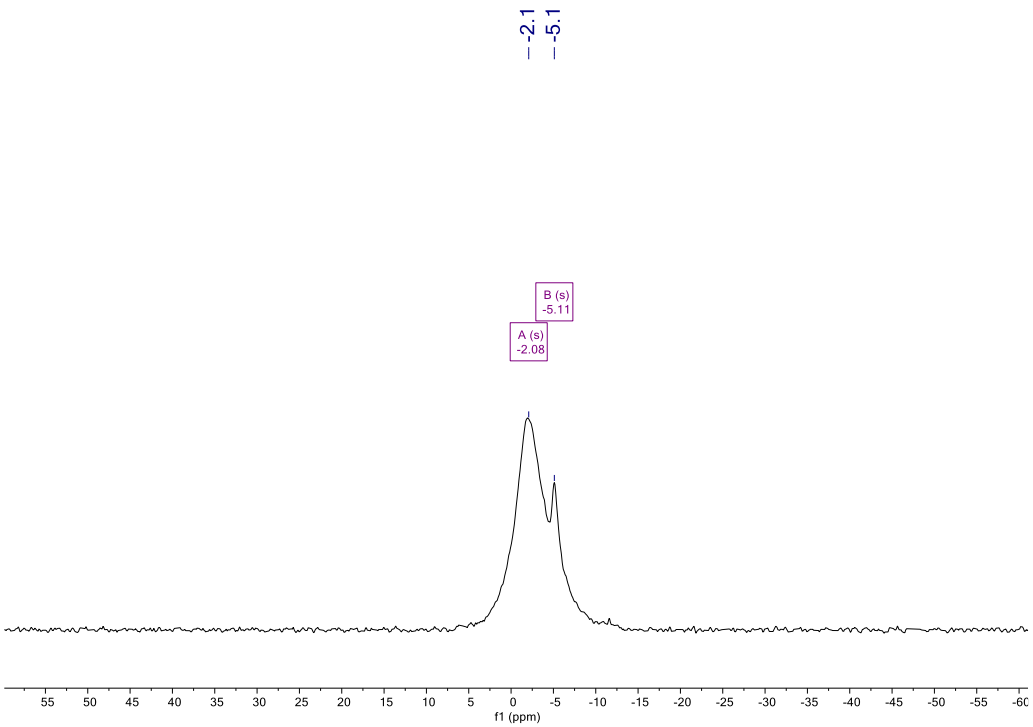


Figure S 50. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **14**

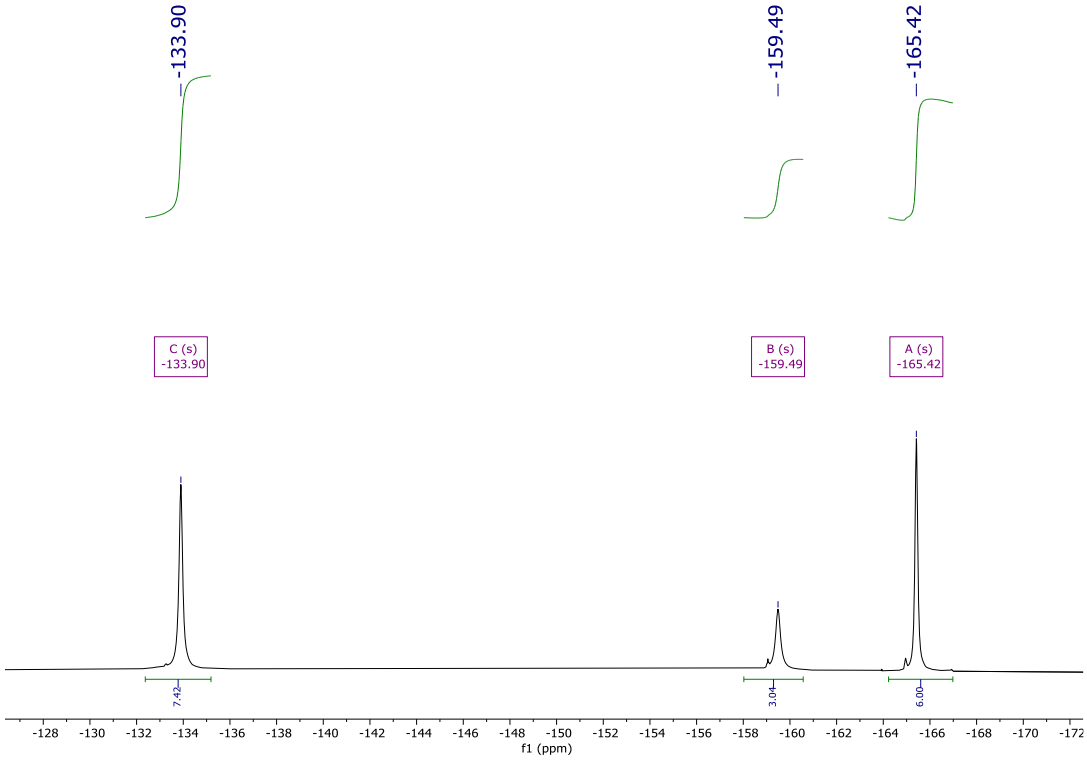


Figure S 51. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **14**

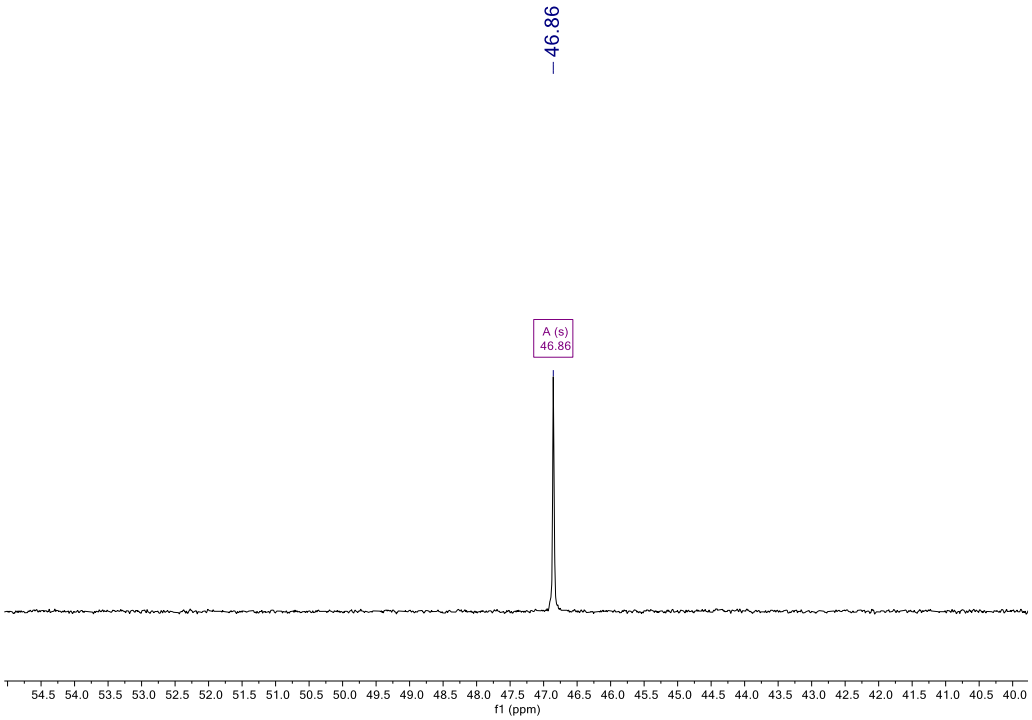


Figure S 52. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **14**

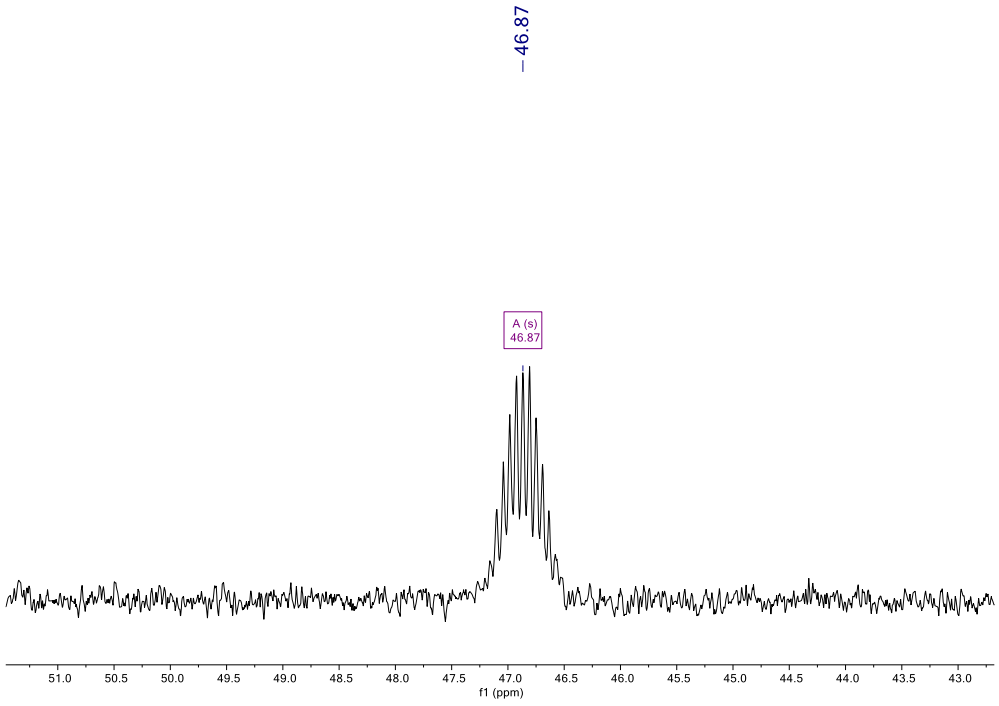


Figure S 53. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **14**

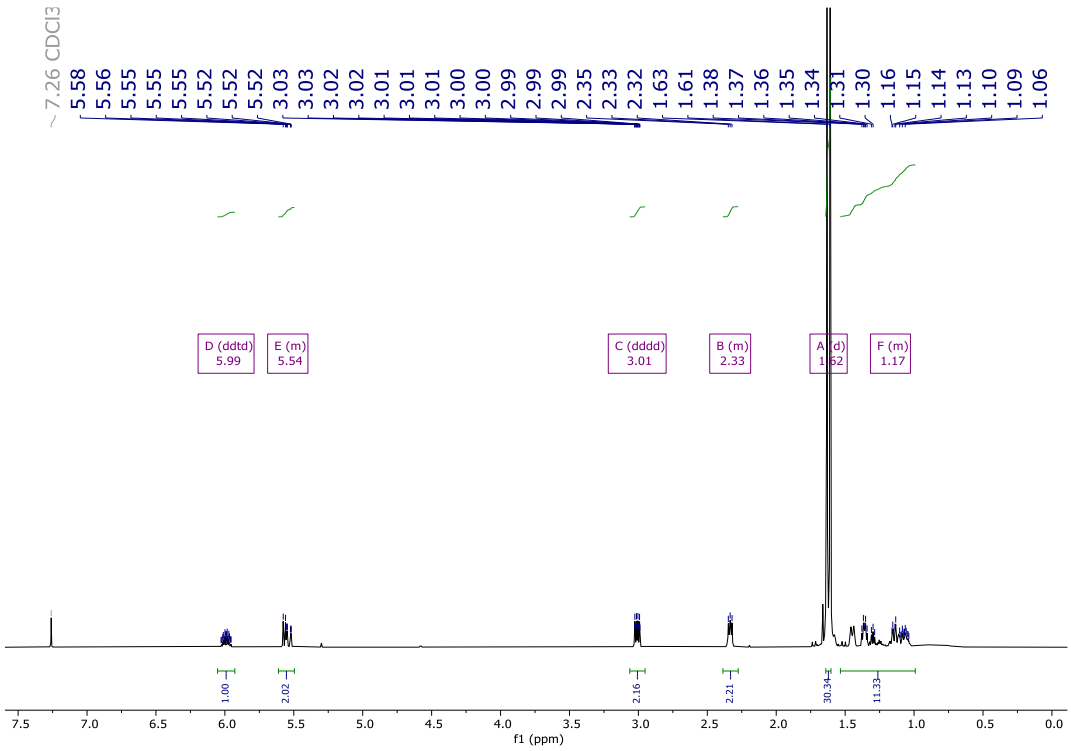


Figure S 54. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **14**

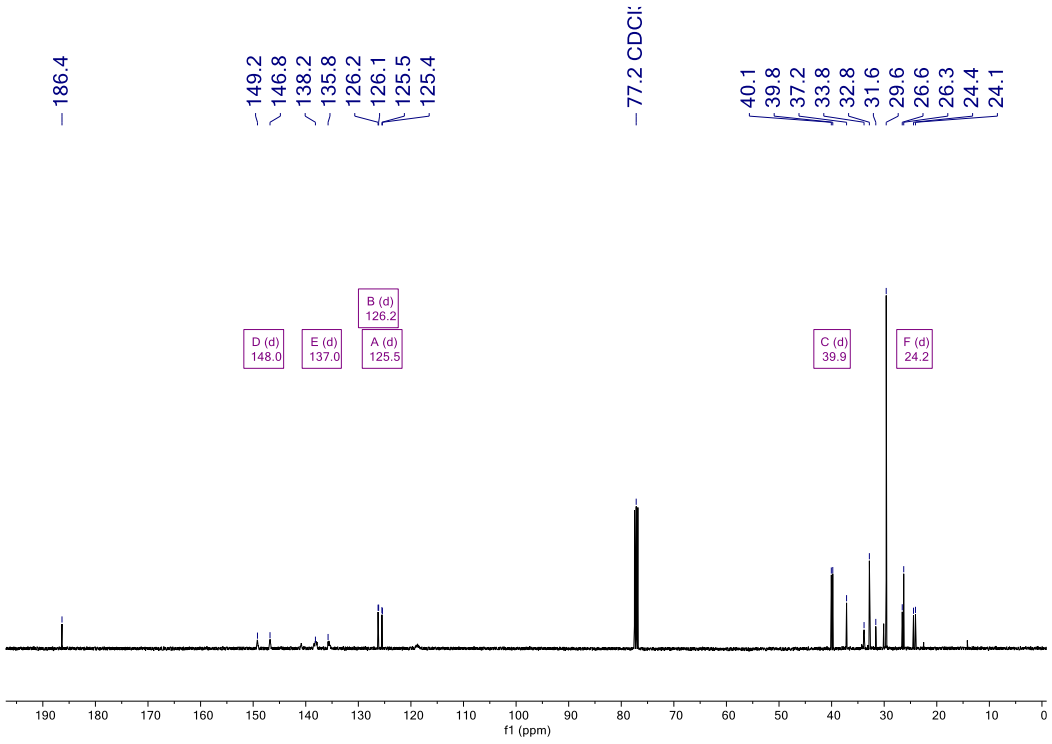
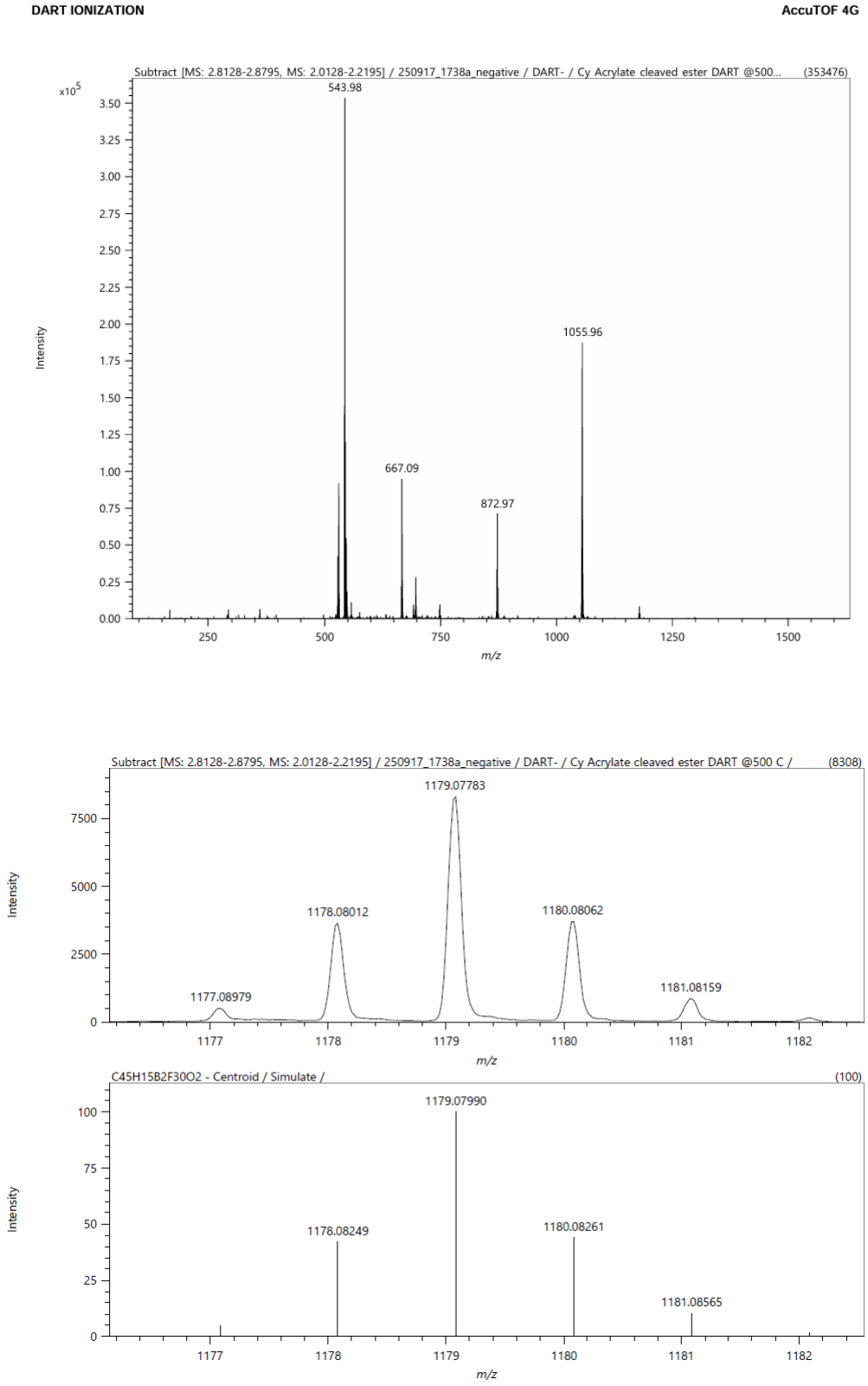
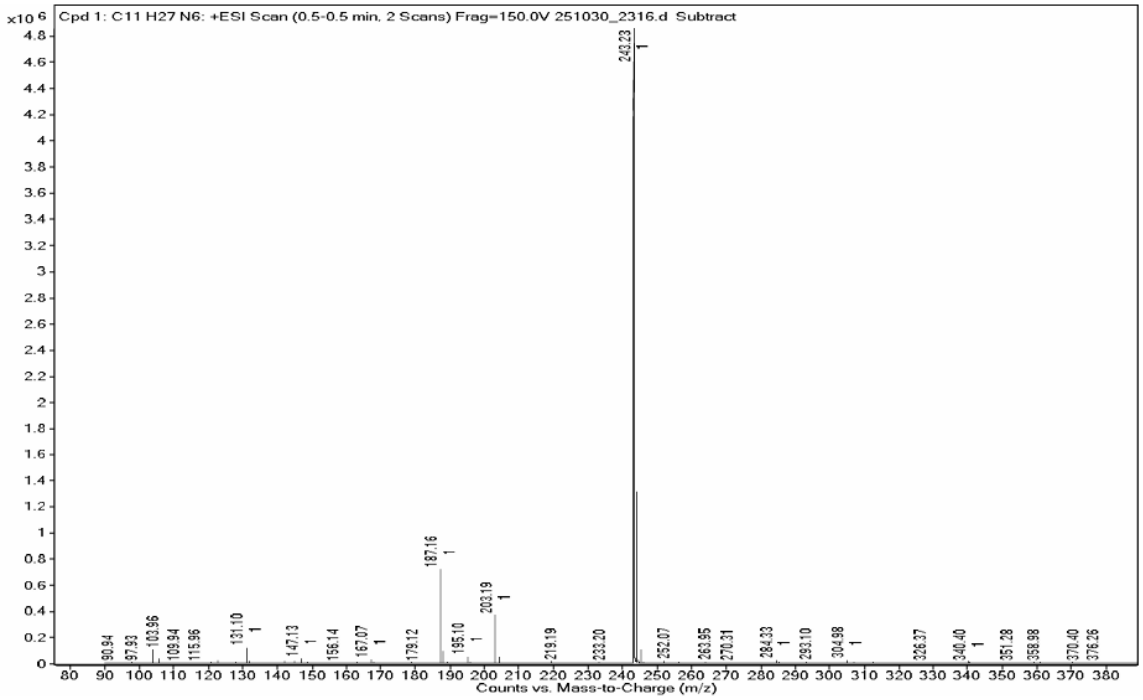


Figure S 55. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **14**

Figure S 56. Mass spectra spectrum of **14**.



Sample Name	Cypropio Cleavage	**Data File**	251030_2316.d	**Acq Method**	HRMS.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	30/10/2025 12:20:58 PM
Comment	ESI+				



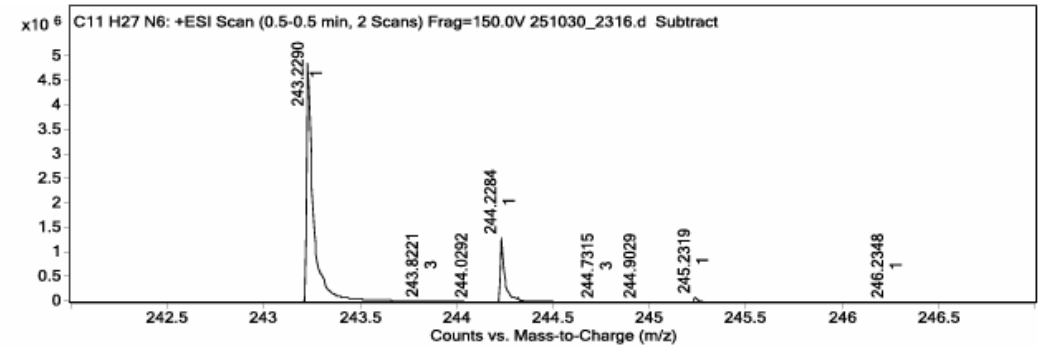
Sample Name	Cypropio Cleavage	**Data File**	251030_2316.d
Acq Method	HRMS.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	30/10/2025 12:20:58 PM
Comment	ESI+		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M+	243.229	C11 H27 N6

MFG Calculator Results

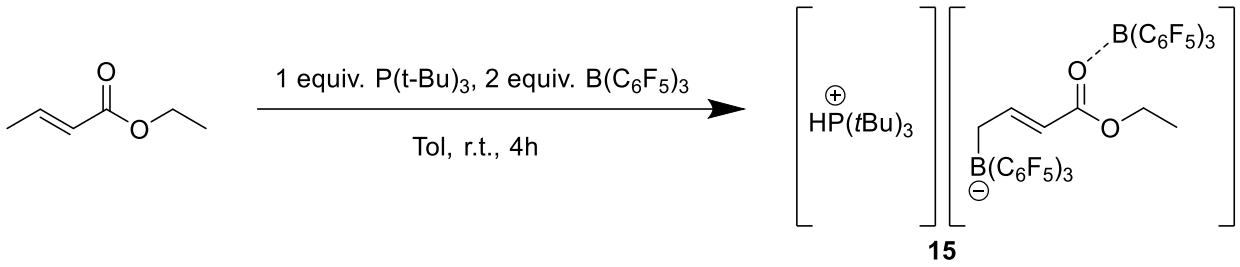
Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
243.2290	C11 H27 N6	243.2292	-0.2	-0.8	1.5	67.11



Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	243.2290	243.2292	-0.2	100.0	100.0	0.0
2	244.2284	244.2316	-3.2	27.8	14.4	-13.4
3	245.2319	245.2340	-2.1	2.1	1.0	-1.1

Preparation of [tBu$_3$PH][(C$_6$F$_5$)$_3$BCH$_2$CHCHC(OB(C$_6$F$_5$)$_3$)OCH$_2$CH$_3$]



15

A 5 mL toluene solution of B(C$_6$F$_5$)$_3$ (0.100 g, 1.95 mmol, 2 equiv.) was added to a 5 mL toluene solution of PtBu$_3$ (0.019 g, 0.98 mmol, 1 equiv.) and stirred for 5 mins at room temperature. A 5 mL toluene solution of trans-ethyl crotonate (0.022 g, 0.98 mmol, 1 equiv.) was then added to the solution and stirred for 4 hours at room temperature. After which, the solvent was removed *in vacuo,* resulting in a white residue. The residue was washed and triturated with 10 mL of pentane 4 times and washed with 10 mL of diethyl ether once. The product was then dried in *vacuo,* generating **15** as a white powder. (0.112 g, 86% yield).

^{11}B NMR (128 MHz, CDCl$_3$, 298 K): δ -1.1 (br s, 1B), -13.4 (br s, 1B)

^{19}F NMR (376 MHz, CDCl$_3$, 298 K): δ -132.3 (d, $^3J_{FF}$ = 23 Hz, 6F, (*o*-C$_6$F$_5$)$_3$B-C), -134.6 (d, $^3J_{FF}$ = 22 Hz, 6F, (*o*-C$_6$F$_5$)$_3$B-O), -158.1 (dd, $^3J_{FF}$ = 20 Hz, 20.4, 3F, (*p*-C$_6$F$_5$)$_3$B-O), -162.5 (dd, $^3J_{FF}$ = 20, 20 Hz, 3F, (*p*-C$_6$F$_5$)$_3$B-C), -164.4 (dd, $^3J_{FF}$ = 21, 21 Hz, 6F, (*m*-C$_6$F$_5$)$_3$B-O), 166.2 (dd, $^3J_{FF}$ = 21, 21 Hz, 3F, (*m*-C$_6$F$_5$)$_3$B-C).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298K): δ 60.73 (s, 1P).

^{31}P NMR (162 MHz, CDCl$_3$, 298K): δ 60.73 (d, $^1J_{PH}$ = 429 Hz, 1P).

^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 7.71 (dt, $^3J_{HH}$ = 15, 9 Hz, 1H), 5.44 (d, $^3J_{HH}$ = 15 Hz, 1H), 5.03 (d, $^1J_{HP}$ = 429 Hz, 1H), 4.35 (q, $^3J_{HH}$ = 7 Hz, 3H, O-C*H*$_2$), 2.67 – 2.42 (br m, 2H, B-C*H*$_2$), 1.63 (d, $^3J_{HP}$ = 16 Hz, 27H, tBu), 1.27 (t, $^3J_{HH}$ = 7 Hz, 3H, CH$_2$C*H*$_3$).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K): 174.5 (s, BCH$_2$*C*H), 147.8 (br d, $^1J_{CF}$ = 239 Hz, o-C$_6$F$_5$), 136.7 (br d, $^1J_{CF}$ = 249 Hz, m-C$_6$F$_5$), 109.7 (s, BCH$_2$CH*C*H), 67.4 (s, O-*C*H$_2$), 37.9 (d, $^1J_{CP}$ = 27 Hz, *t*Bu), 30.1 (s, *t*Bu), 13.6 (s, CH$_2$*C*H$_3$)

HRMS: $C_{24}H_9BF_{15}O_2$ (Negative mode) Calc: 625.0466, Obs: 625.0479.

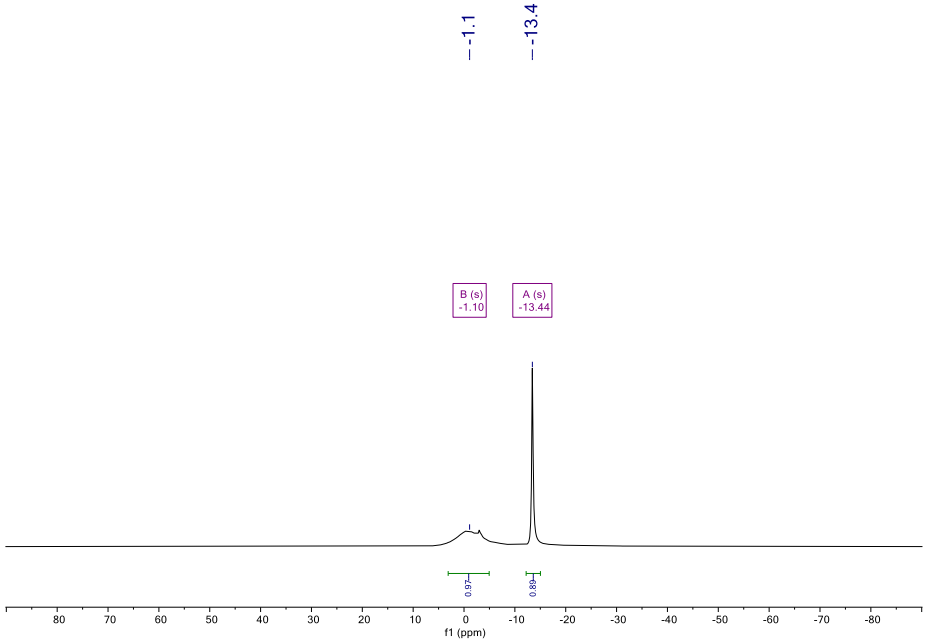


Figure S 57. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **15**

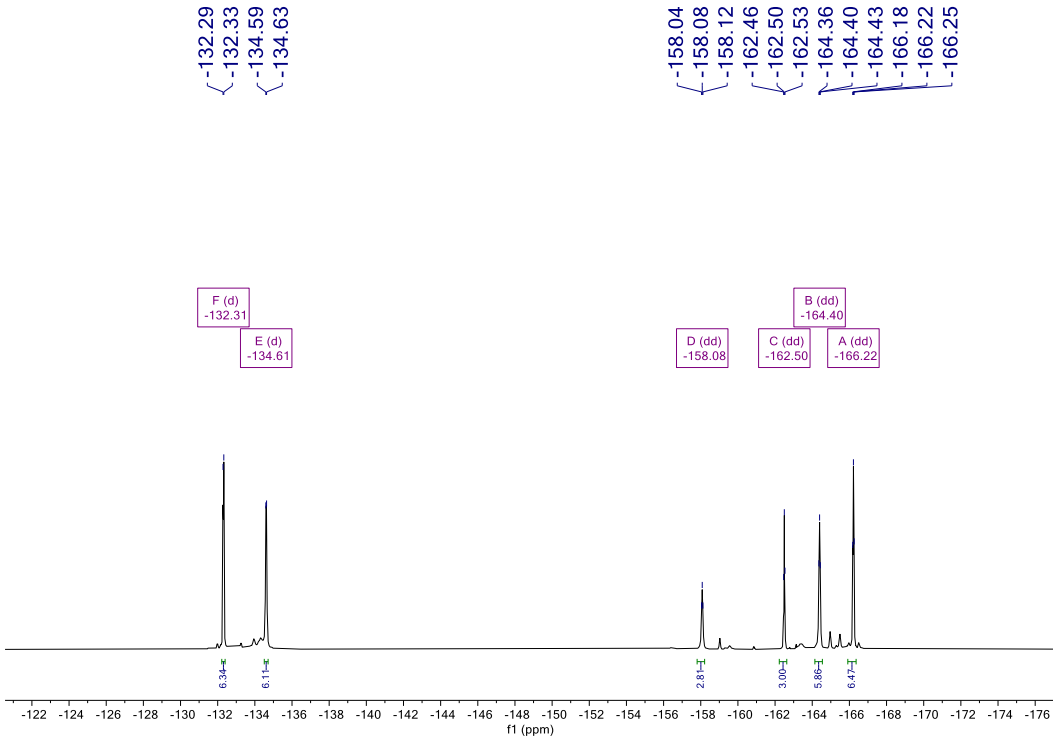


Figure S 58. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of **15**

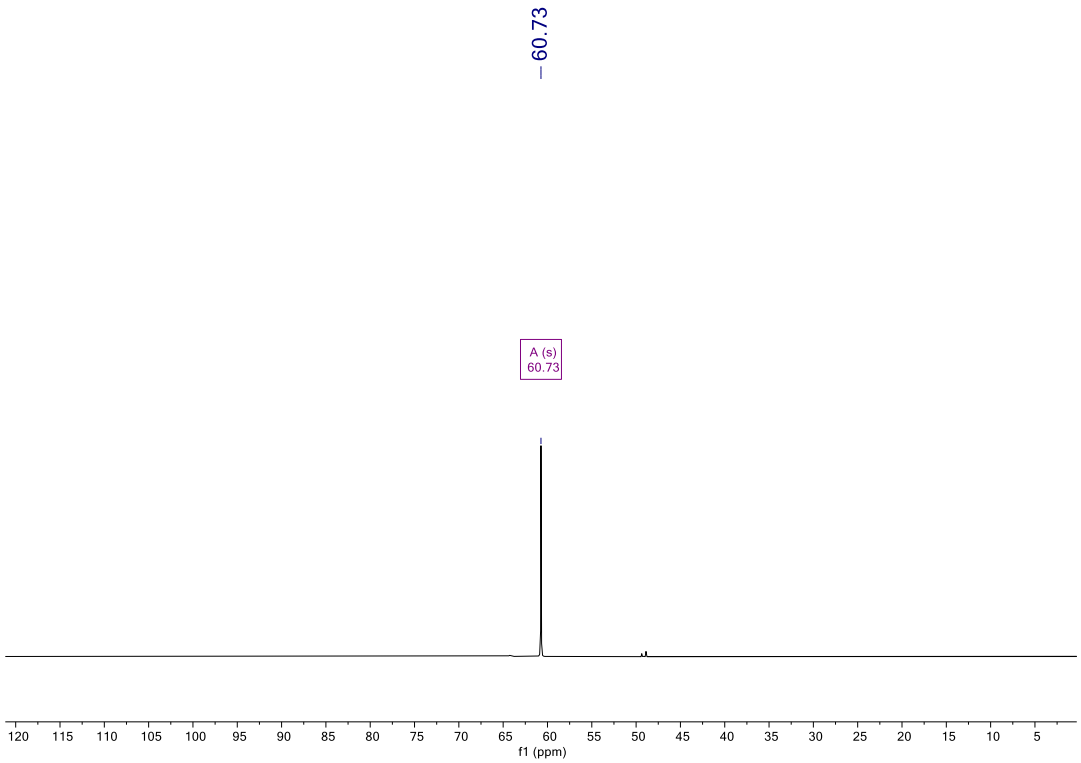


Figure S 59. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **15**

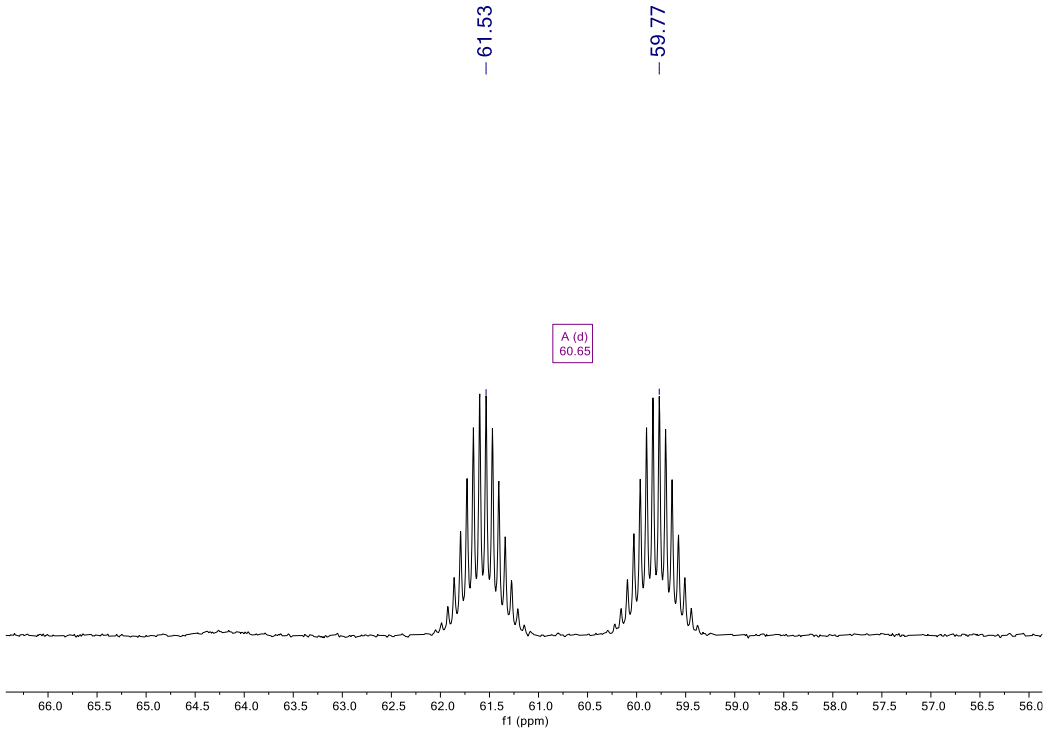


Figure S 60. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **15**

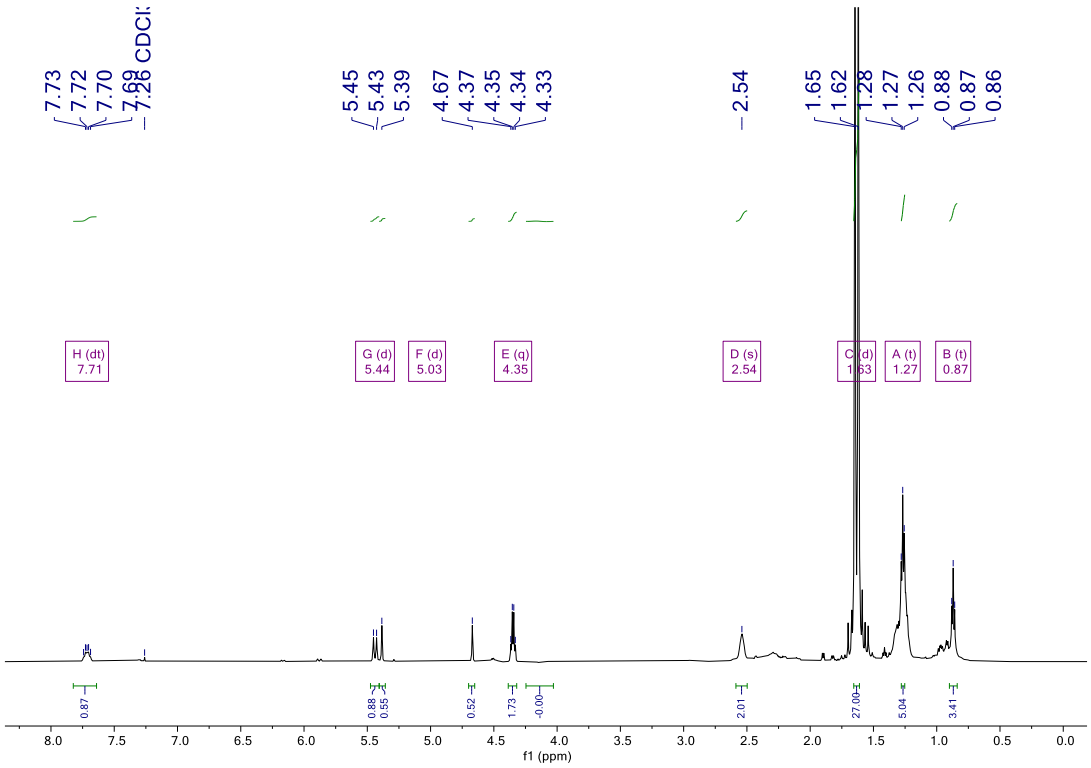


Figure S 61. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **15**

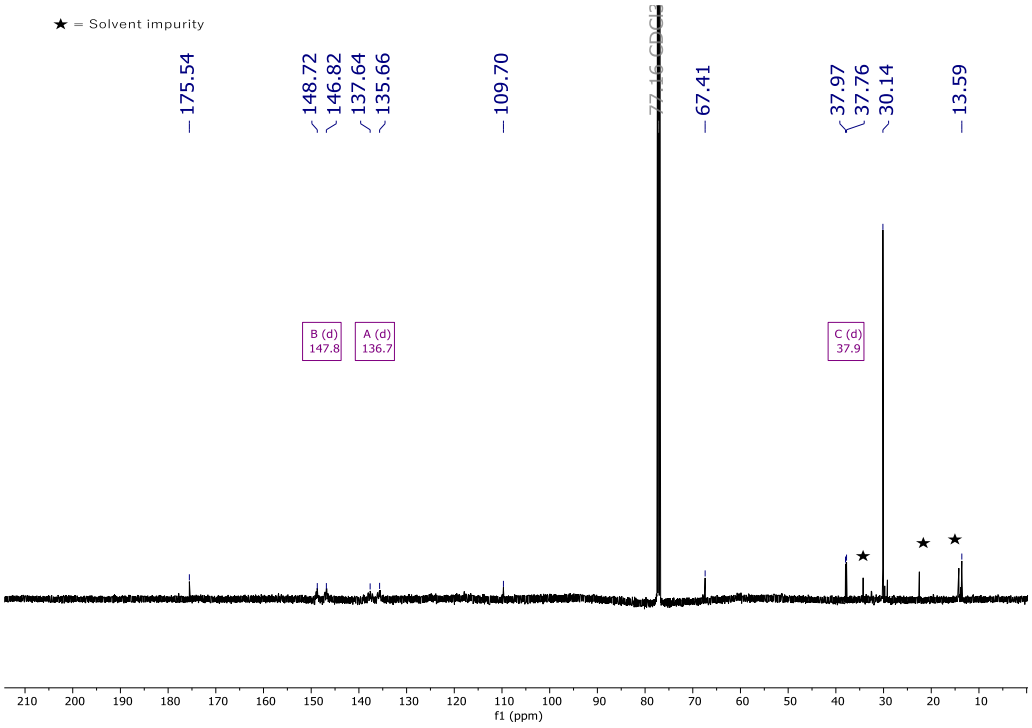
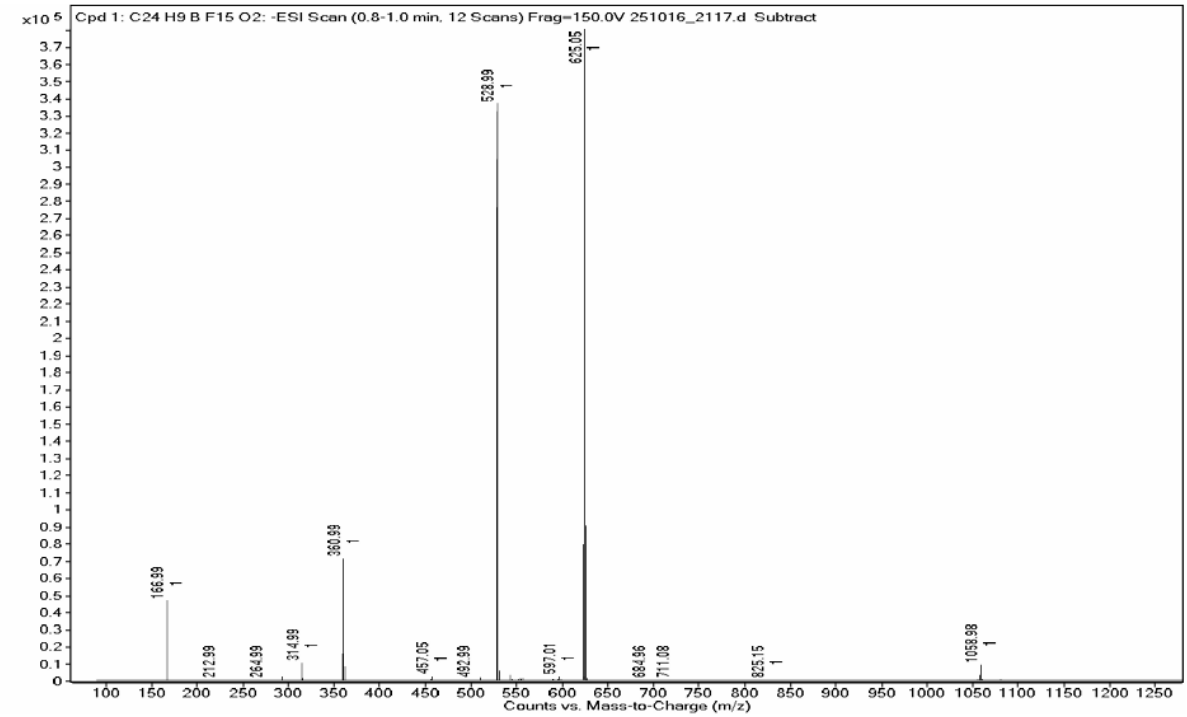


Figure S 62. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **15**

Figure S 64. Mass spectra spectrum of **15**

Sample Name	Trans Crotonate	**Data File**	251016_2117.d	**Acq Method**	HRMS_Negative.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	16/10/2025 3:54:53 PM
Comment	ESI-				



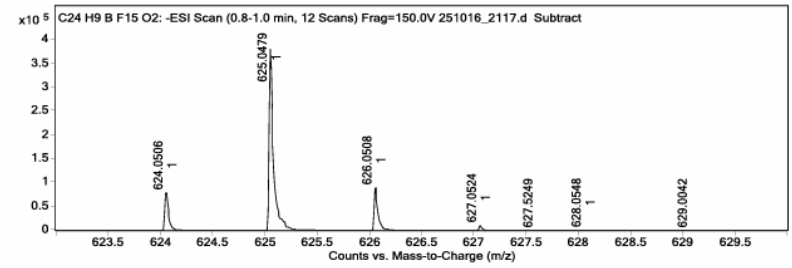
Sample Name	Trans Crotonate	**Data File**	251016_2117.d
Acq Method	HRMS_Negative.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	16/10/2025 3:54:53 PM
Comment	ESI-		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	624.0506	C24 H9 B F15 O2

MFG Calculator Results

Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
624.0506	C24 H9 B F15 O2	624.0498	0.8	1.3	13.5	96.81
624.0506	C12 H13 B F15 N2 O9	624.0516	-1.0	-1.6	0.5	84.03
624.0506	C13 H9 B F15 N6 O5	624.0530	-2.4	-3.8	5.5	83.92
624.0506	C14 H5 B F15 N10 O	624.0543	-3.7	-5.9	10.5	79.77
624.0506	C20 H5 B F15 N6	624.0471	3.5	5.6	14.5	78.46
624.0506	C8 H9 B F15 N8 O7	624.0490	1.6	2.6	1.5	70.45
624.0506	C17 H13 B F15 O7	624.0557	-5.1	-8.2	4.5	68.96



Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	624.0506	624.0498	0.8	21.0	23.3	2.3
2	625.0479	625.0466	1.3	100.0	100.0	0.0
3	626.0508	626.0498	1.0	23.7	25.4	1.7
4	627.0524	627.0528	-0.4	2.8	3.5	0.7