Polymerized Phosphonium-Based Ionic Liquids as Stationary Phases in Gas Chromatography: Performance Improvements by Addition of Graphene Oxide

SUPPORTING INFORMATION

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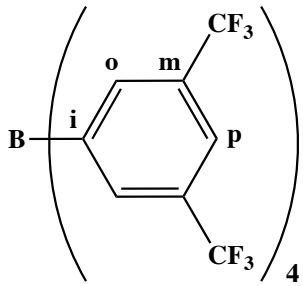
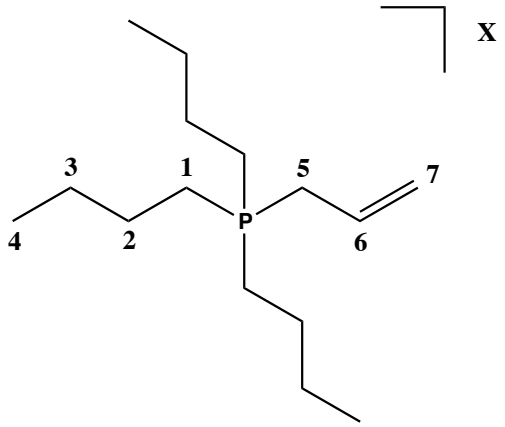
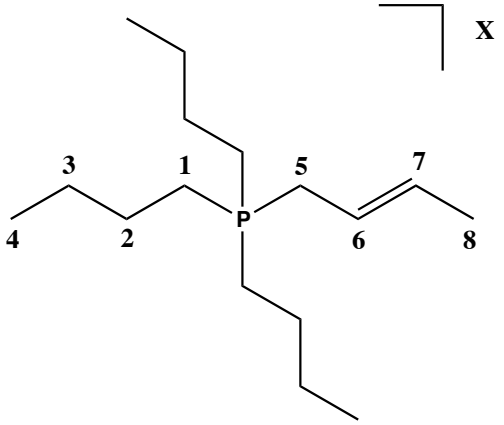
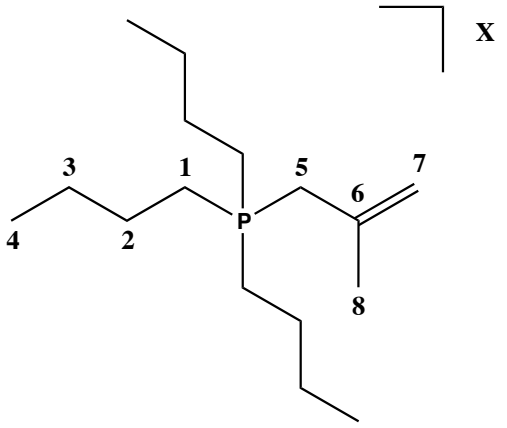
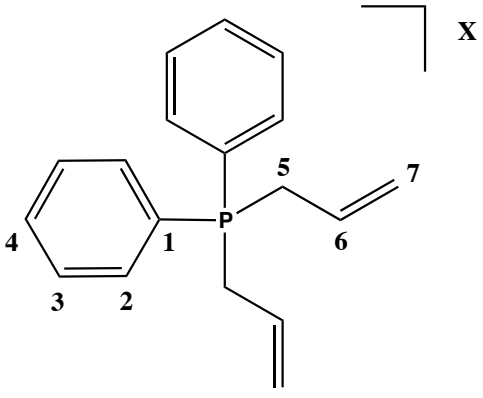


(BAr'$_4$: tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate

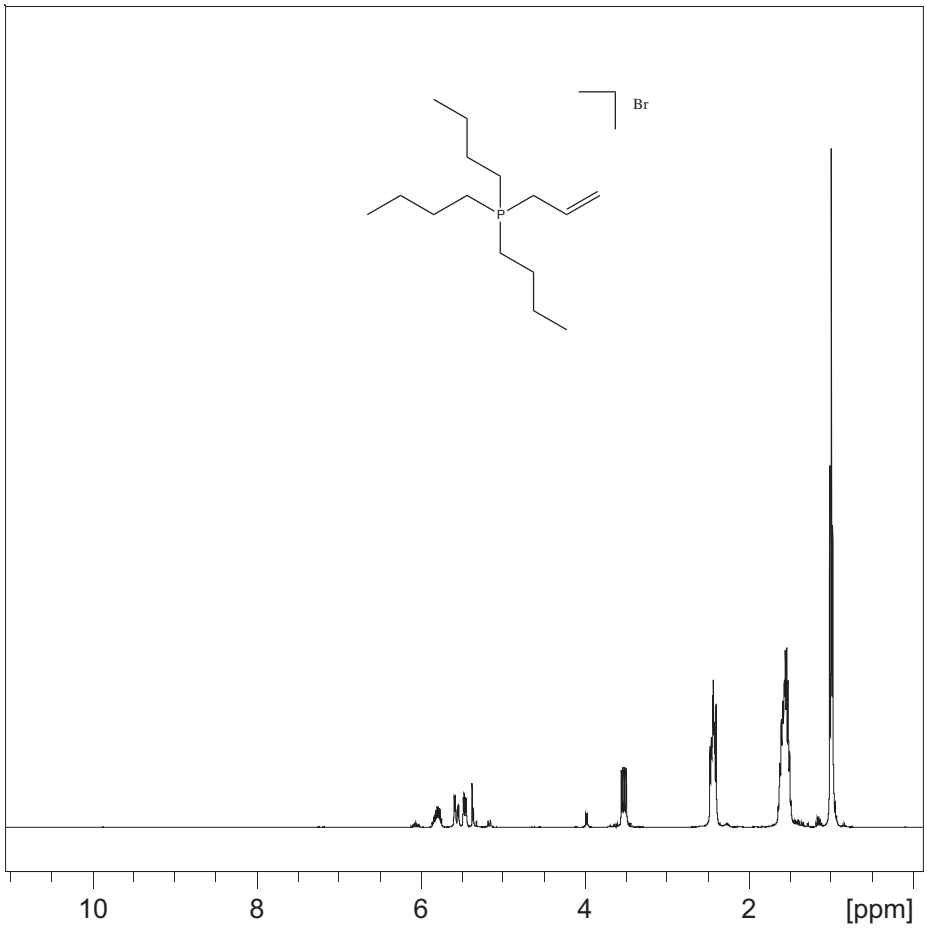




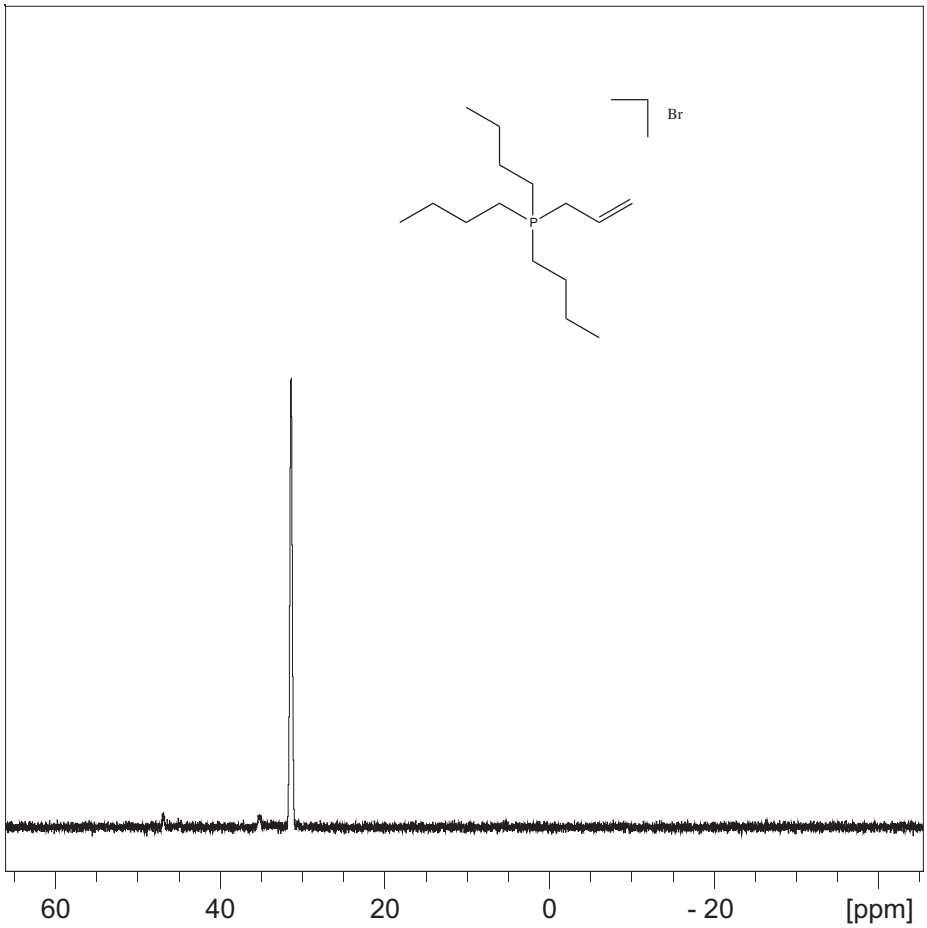




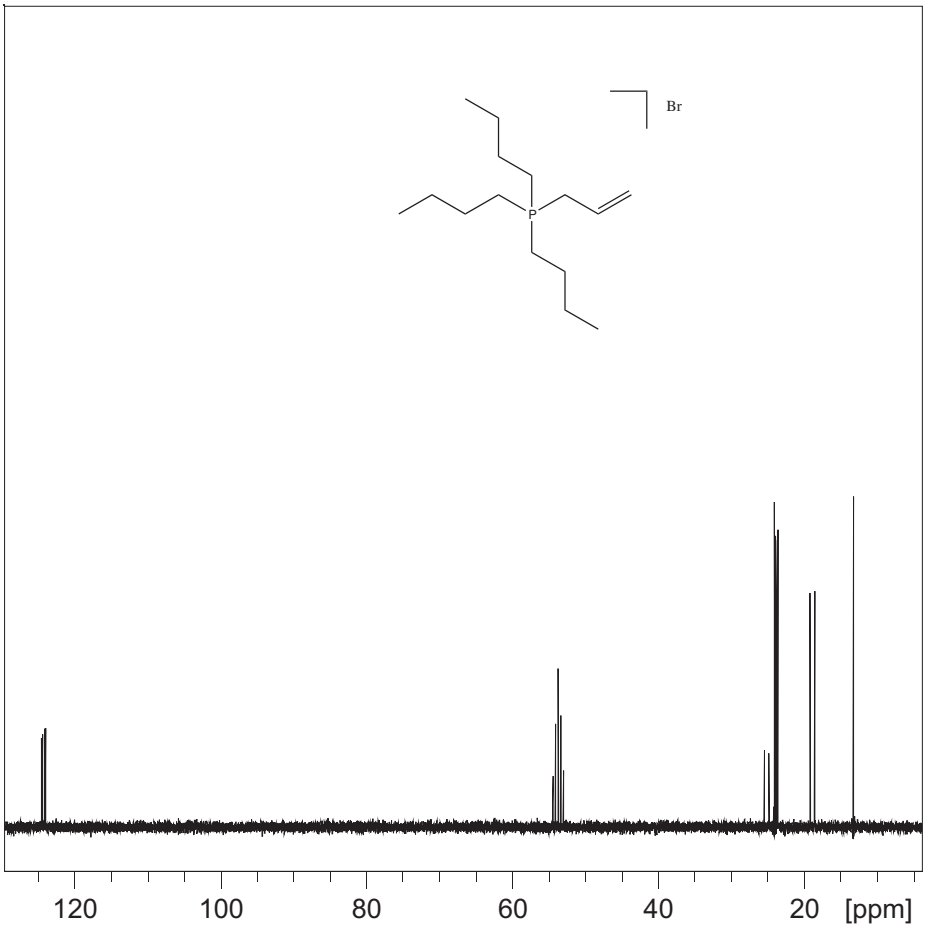
IL 1 : Allyltributylphosphonium bromide.



^{1}H-NMR (CD_2Cl_2): δ 5.79 (m, 1H, H_6 of allyl), 5.51 (m, 2H, H_7 of allyl), 3.52 (dd, (J_1 = 15.7, J_2 = 7.5), 2H, H_5 of allyl), 2.43 (m, 6H, H_1 of butyl), 1.56 (m, 12H, H_{2+3} of butyl), 0.99 (t, (J = 7.1), 9H, H_4 of butyl).

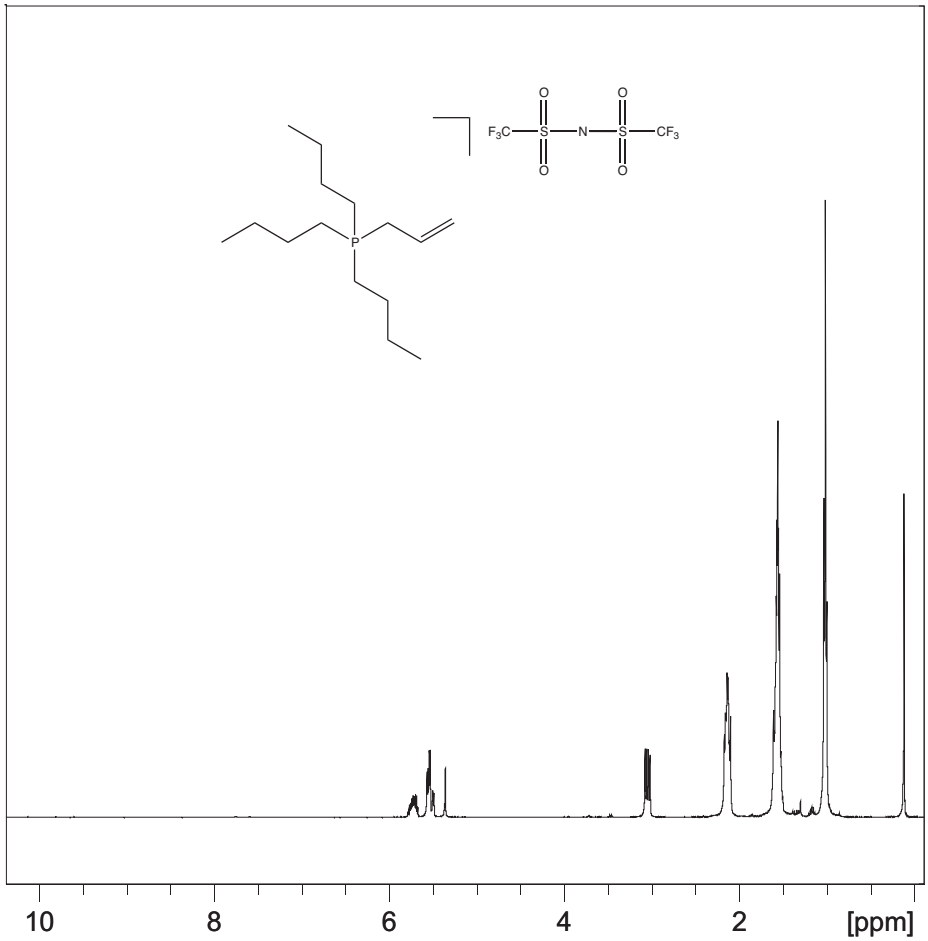


^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 31.3 (s).

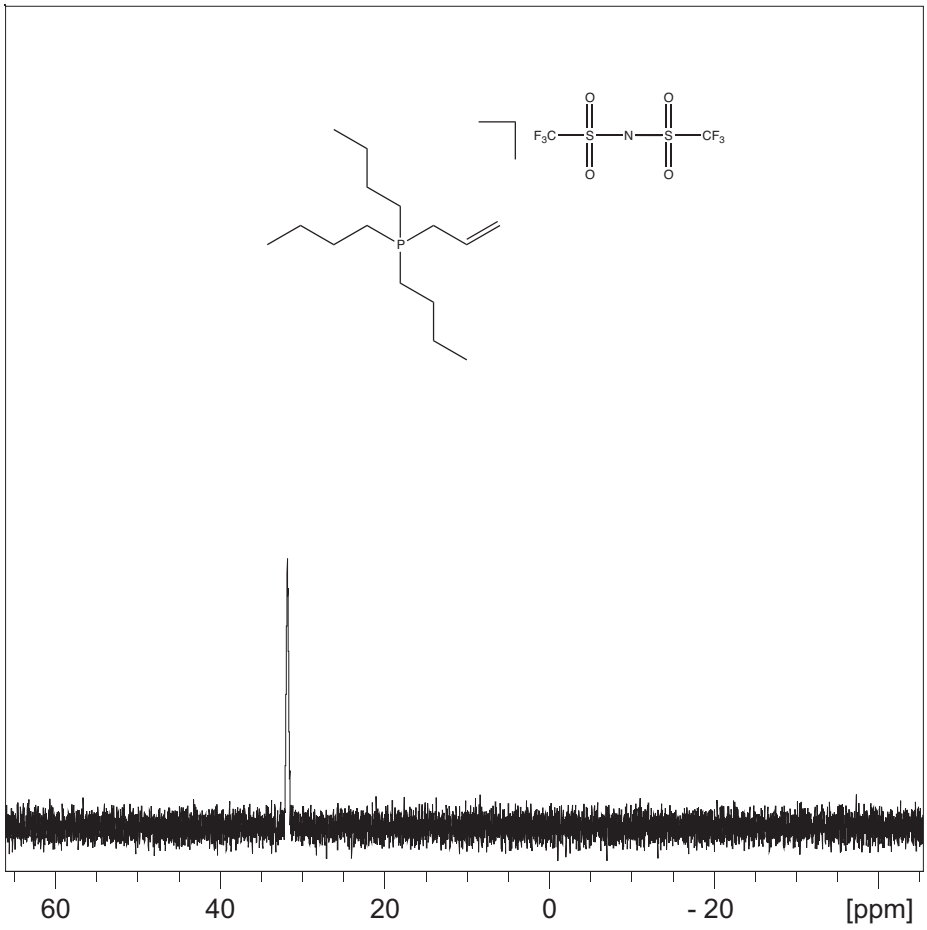


^{13}C-NMR {^{1}H} (CD_2Cl_2): δ 124.4 (d, ($J_{C,P}$ = 9.8), *C_7* of allyl), 124.0 (d, ($J_{C,P}$ = 11.7), *C_6* of allyl), 25.0 (d, ($J_{C,P}$ = 46.9), *C_5* of allyl), 23.9 (d, ($J_{C,P}$ = 15.3), *C_2* of butyl), 23.6 (d, ($J_{C,P}$ = 4.7), *C_3* of butyl), 18.8 (d, ($J_{C,P}$ = 47.1), *C_1* of butyl), 13.2 (s, *C_4* of butyl).

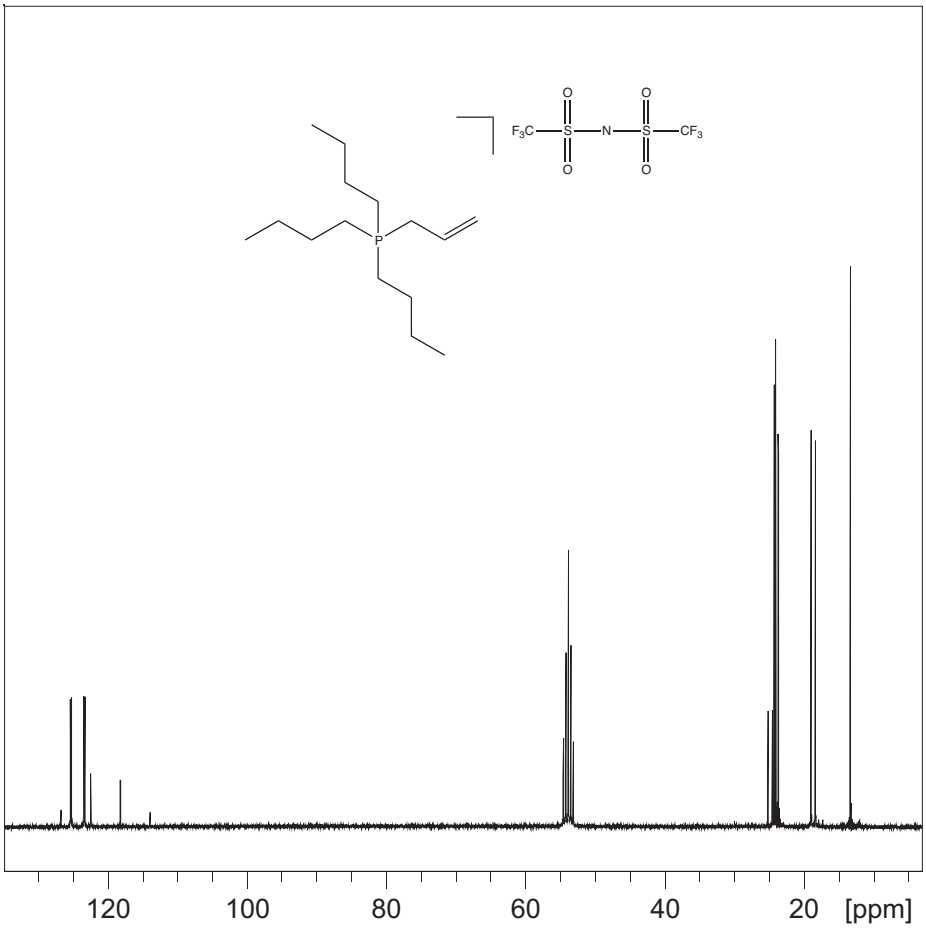
IL 2: Allyltributylphosphonium bis(trifluoromethane)sulfonimide.



^{1}H-NMR (CD_2Cl_2): δ 5.69 (m, 1H, *H_6* of allyl), 5.52 (m, 2H, *H_7* of allyl), 3.04 (dd, (J_1 = 14.9, J_2 = 7.4), 2H, *H_5* of allyl), 2.13 (m, 6H, *H_1* of butyl), 1.57 (m, 12H, *H_{2+3}* of butyl), 1.01 (t, (J = 7.0), 9H, *H_4* of butyl).

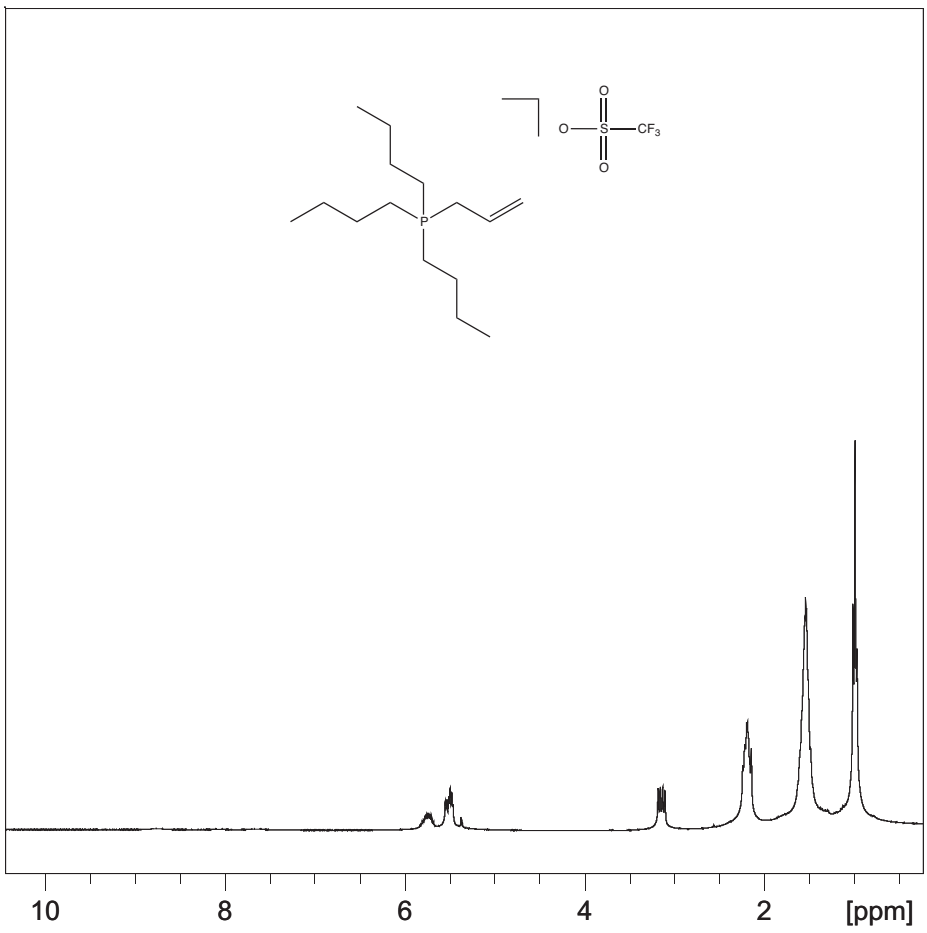


^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 31.8 (s).

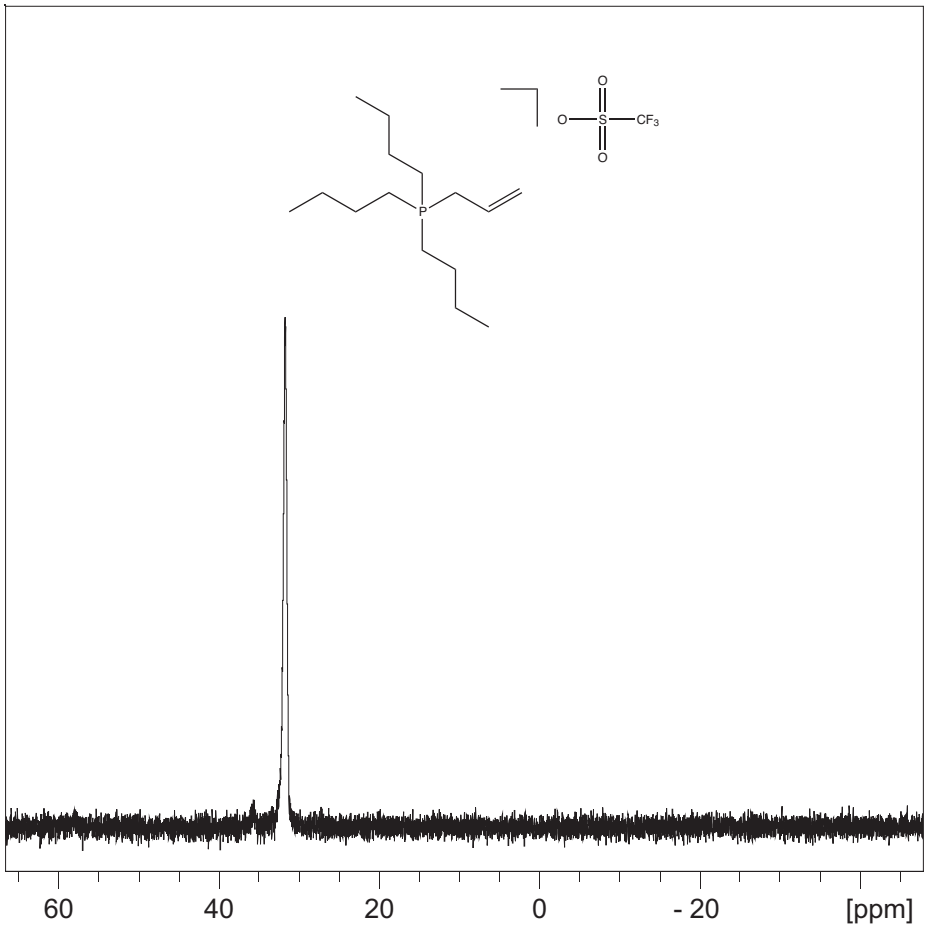


^{13}C-NMR {^{1}H} (CD_2Cl_2): δ 125.3 (d, ($J_{C,P}$ = 11.8), *C₆* of allyl), 123.3 (d, ($J_{C,P}$ = 9.7), *C₇* of allyl), 120.3 (c, ($J_{C,F}$ = 321.5), *C*F_3 of NTf_2), 24.8 (d, ($J_{C,P}$ = 47.5), *C₅* of allyl), 24.1 (d, ($J_{C,P}$ = 15.4), *C₂* of butyl), 23.6 (d, ($J_{C,P}$ = 4.8), *C₃* of butyl), 18.6 (d, ($J_{C,P}$ = 47.4), *C₁* of butyl), 13.3 (s, *C₄* of butyl).

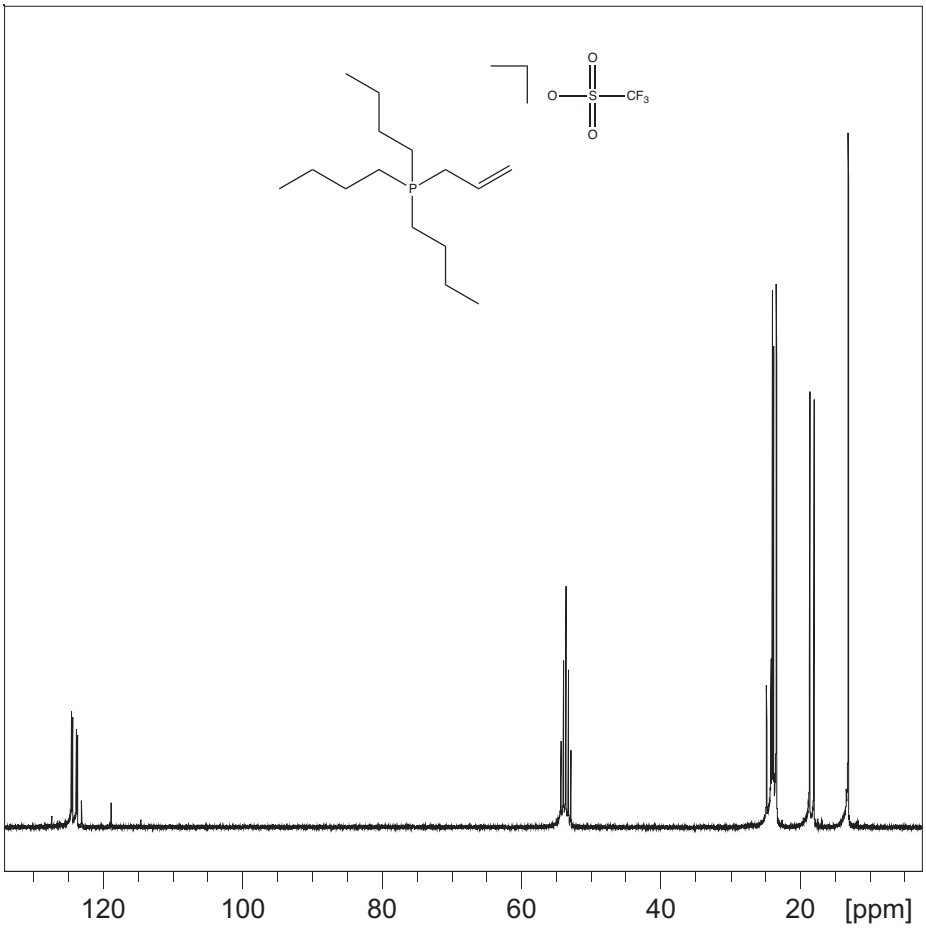
IL 3: Allyltributylphosphonium trifluoromethanesulfonate.



^{1}H-NMR (CD_2Cl_2): δ 5.74 (m, 1H, *H_6* of allyl), 5.52 (m, 2H, *H_7* of allyl), 3.14 (dd, (J_1 = 15.3, J_2 = 7.5), 2H, *H_5* of allyl), 2.19 (m, 6H, *H_1* of butyl), 1.54 (m, 12H, *H_{2+3}* of butyl), 0.99 (t, (J = 7.0), 9H, *H_4* of butyl).

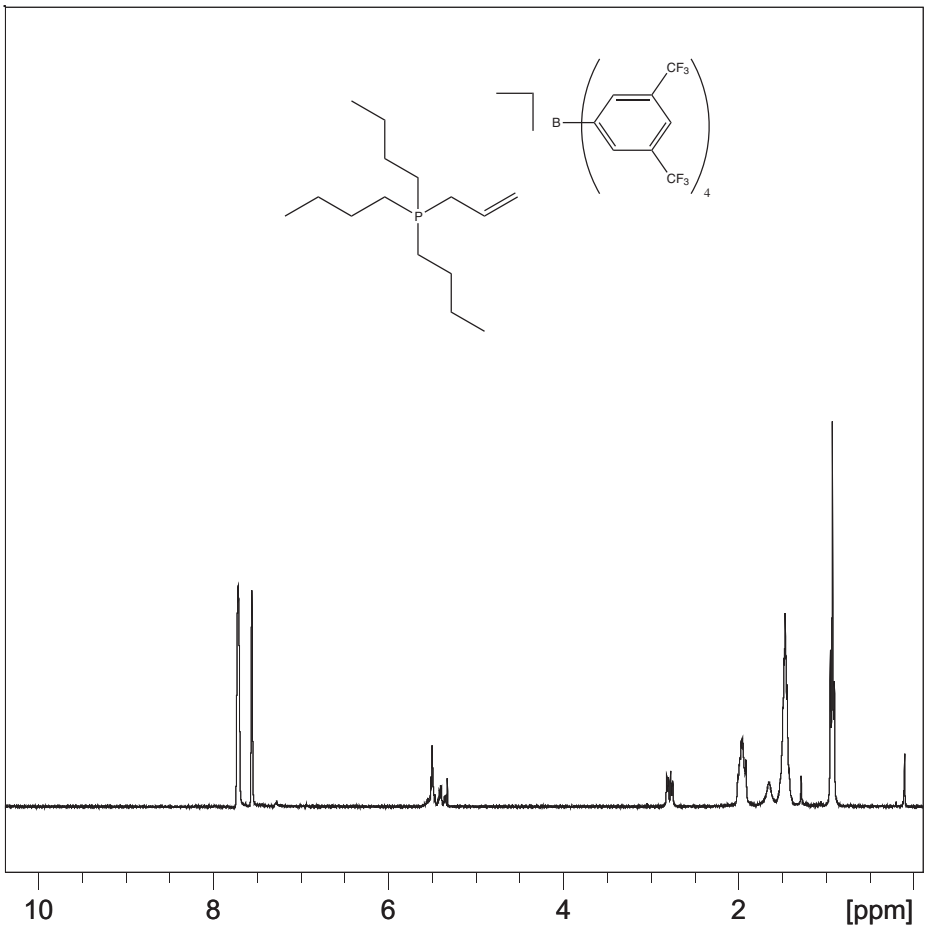


^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 31.6 (s).

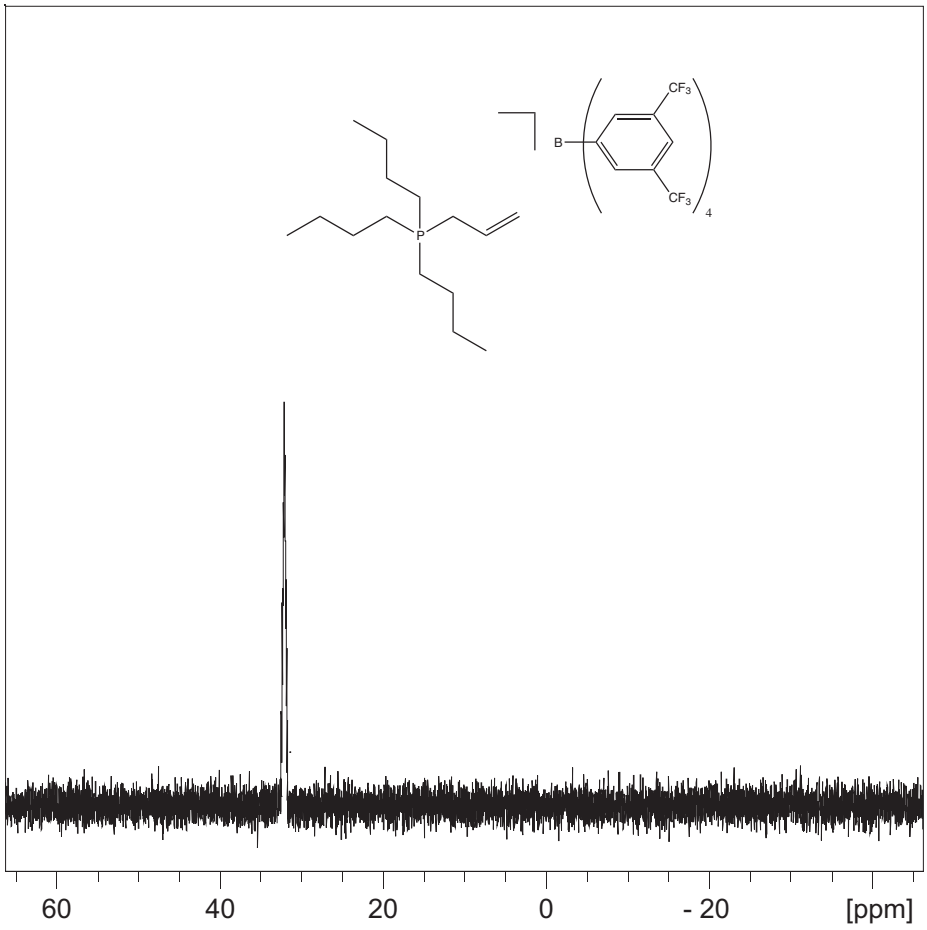


^{13}C-NMR {^{1}H} (CD_2Cl_2): δ 124.4 (d, ($J_{C,P}$ = 11.7), *C6* of allyl), 123.7 (d, ($J_{C,P}$ = 9.7), *C7* of allyl), 120.9 (c, ($J_{C,F}$ = 320.8), *C*F_3 of OTf), 24.4 (d, ($J_{C,P}$ = 47.2), *C5* of allyl), 23.8 (d, ($J_{C,P}$ = 15.4), *C2* of butyl), 23.3 (d, ($J_{C,P}$ = 4.8), *C3* of butyl), 18.2 (d, ($J_{C,P}$ = 47.3), *C1* of butyl), 13.0 (s, *C4* of butyl).

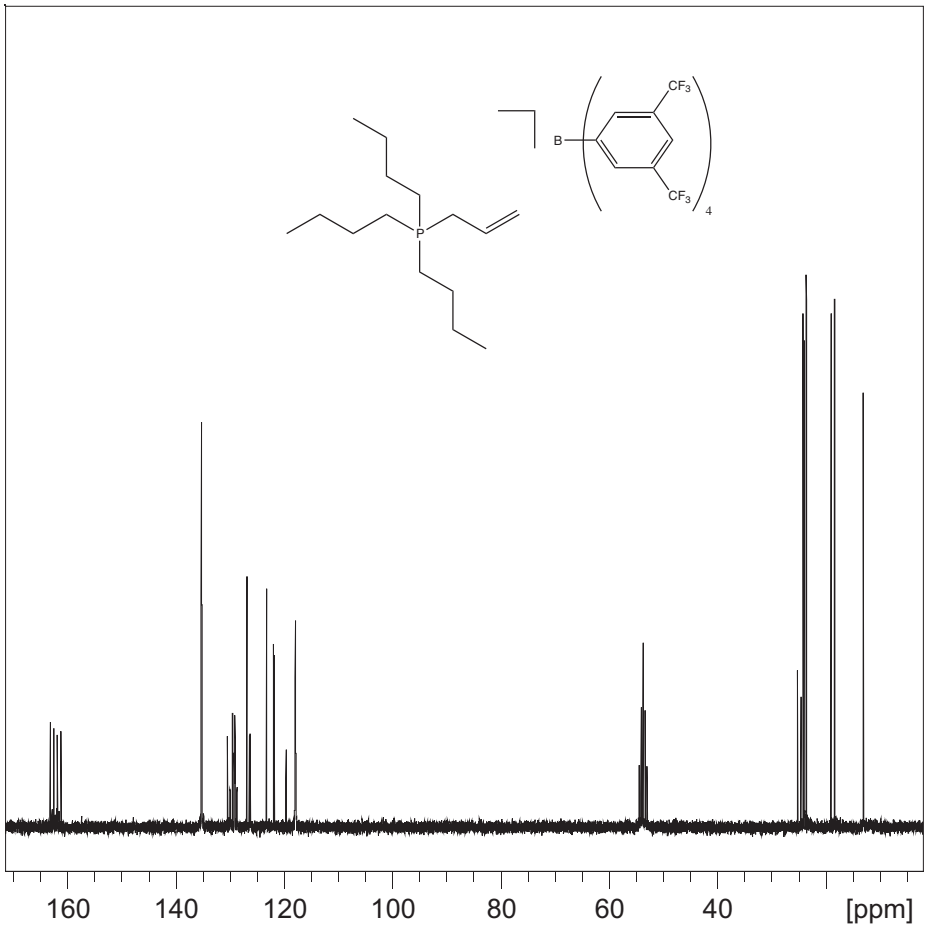
IL 4: Allyltributylphosphonium tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate.



^{1}H-NMR (CD_2Cl_2): δ 7.71 (s, 8H, H_o of BAr_4'), 7.56 (s, 4H, H_p of BAr_4'), 5.43 (m, 3H, H_{6+7} of allyl), 2.78 (dd, (J_1 = 13.9, J_2 = 6.2), 2H, H_5 of allyl), 1.96 (m, 6H, H_1 of butyl), 1.46 (m, 12H, H_{2+3} of butyl), 0.92 (t, (J = 7.0), 9H, H_4 of butyl).

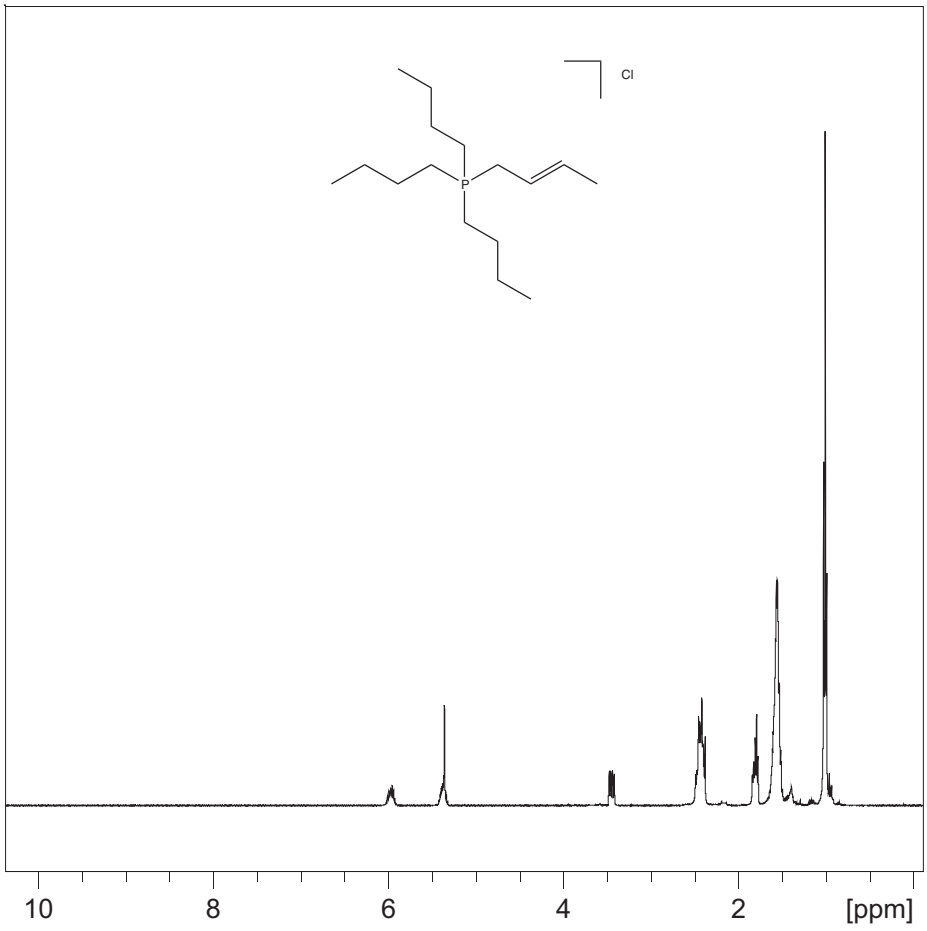


^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 32.0 (s).

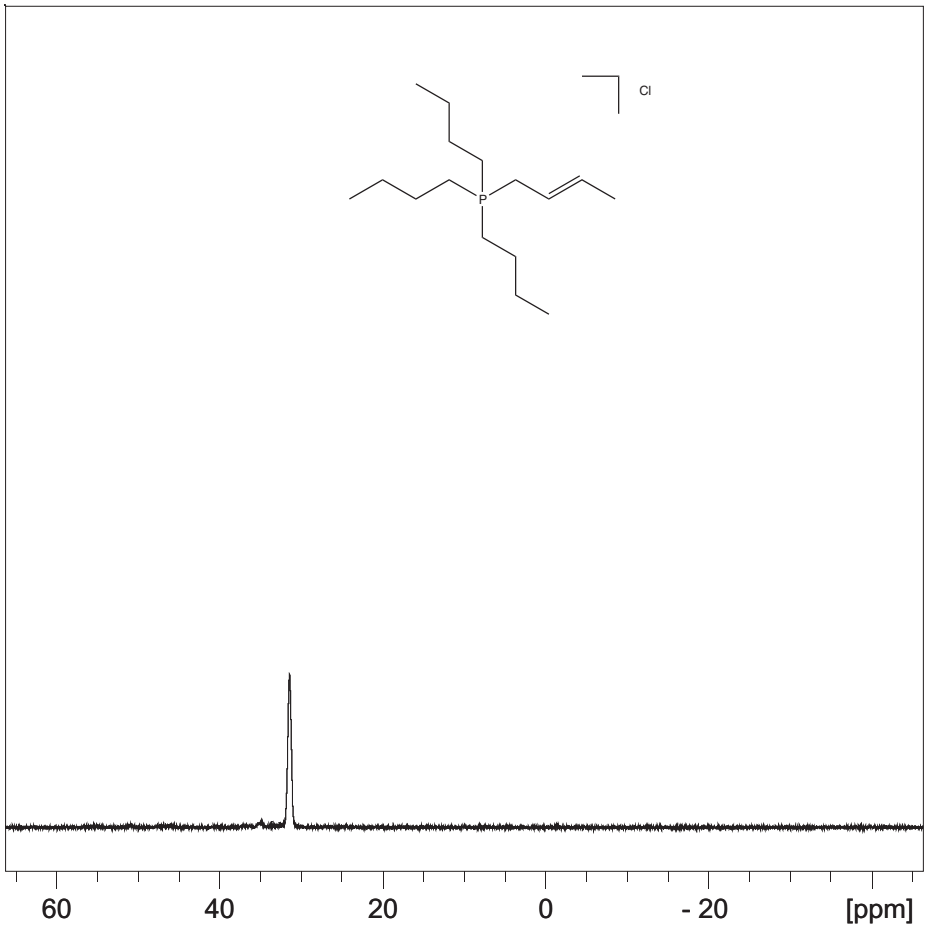


^{13}C-NMR {^{1}H} (CD_2Cl_2): δ 162.2 (q, ($J_{C,B}$ = 49.9), *C$_i$* of BAr_4'), 135.2 (s, *C$_o$* of BAr_4'), 129.3 (q, ($J_{C,F}$ = 31.6), *C$_m$* of BAr_4'), 126.3 (d, ($J_{C,P}$ = 11.6), *C$_6$* of allyl), 125.0 (c, ($J_{C,F}$ = 272.6), *C*F_3 of BAr_4'), 121.9 (d, ($J_{C,P}$ = 9.5), *C$_7$* of allyl), 119.6 (s, *C$_p$* of BAr_4'), 24.9 (d, ($J_{C,P}$ = 46.9), *C$_5$* of allyl), 24.1 (d, ($J_{C,P}$ = 15.2), *C$_2$* of butyl), 23.6 (d, ($J_{C,P}$ = 4.9), *C$_3$* of butyl), 18.7 (d, ($J_{C,P}$ = 47.5), *C$_1$* of butyl), 13.0 (s, *C$_4$* of butyl).

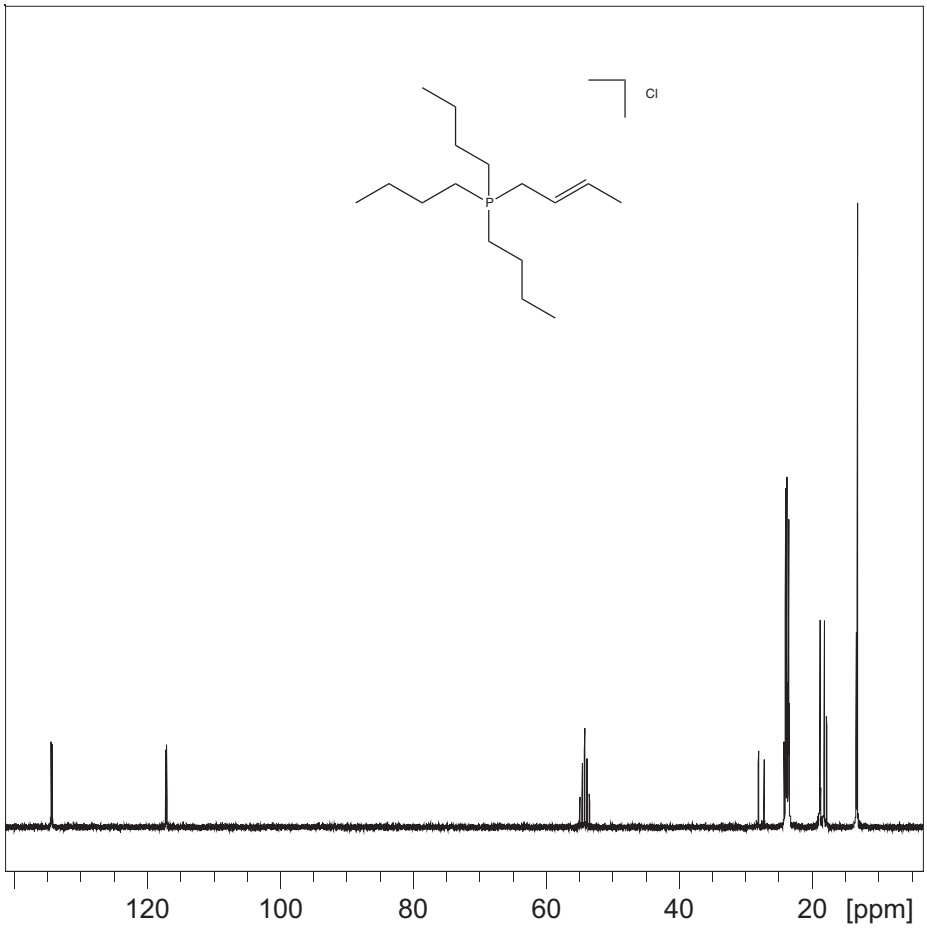
IL 5: Crotyltributylphosphonium chloride.



^{1}H-NMR (CD_2Cl_2): δ 5.96 (m, 1H, H_6 of crotyl), 5.37 (m, 1H, H_7 of crotyl), 3.43 (dd, (J_1 = 15.3, J_2 = 7.6), 2H, H_5 of crotyl), 2.43 (m, 6H, H_1 of butyl), 1.80 (m, 3H, H_8 of crotyl), 1.56 (m, 12H, H_{2+3} of butyl), 1.01 (t, (J = 7.1), 9H, H_4 of butyl).

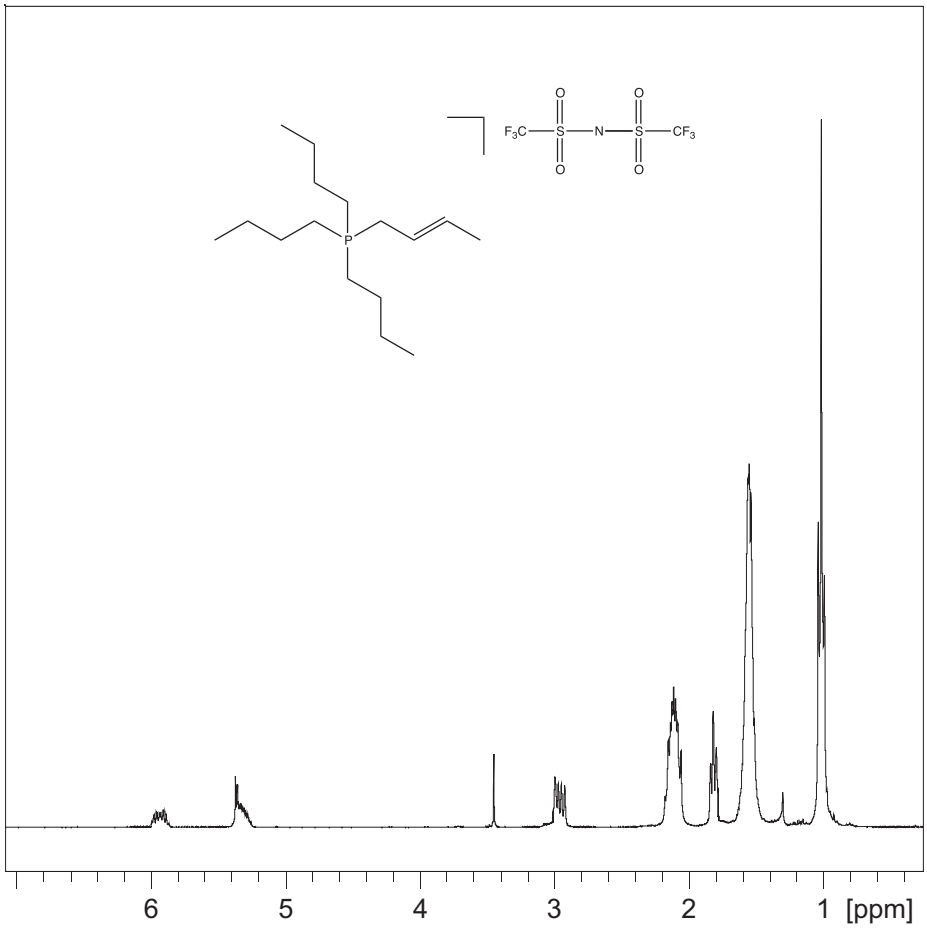


^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 31.4 (s).

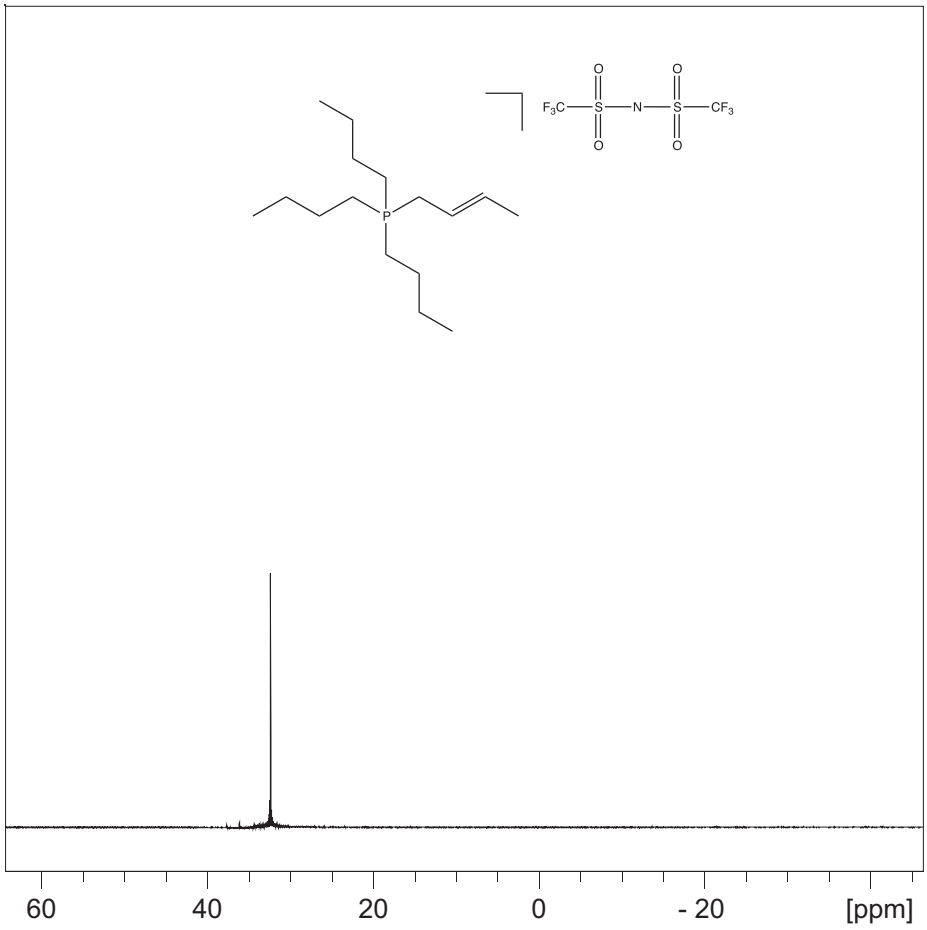


^{13}C-NMR $\{^1H\}$ (CD_2Cl_2): δ 134.3 (d, ($J_{C,P}$ = 12.1), *C₆* of crotyl), 117.5 (d, ($J_{C,P}$ = 9.9), *C₇* of crotyl), 27.5 (d, ($J_{C,P}$ = 64.9), *C₅* of crotyl), 23.8 (d, ($J_{C,P}$ = 16.5), *C₂* of butyl), 23.5 (d, ($J_{C,P}$ = 5.6), *C₃* of butyl), 18.3 (d, ($J_{C,P}$ = 47.2), *C₁* of butyl), 17.7 (d, ($J_{C,P}$ = 2.7), *C₈* of crotyl), 13.5 (s, *C₄* of butyl).

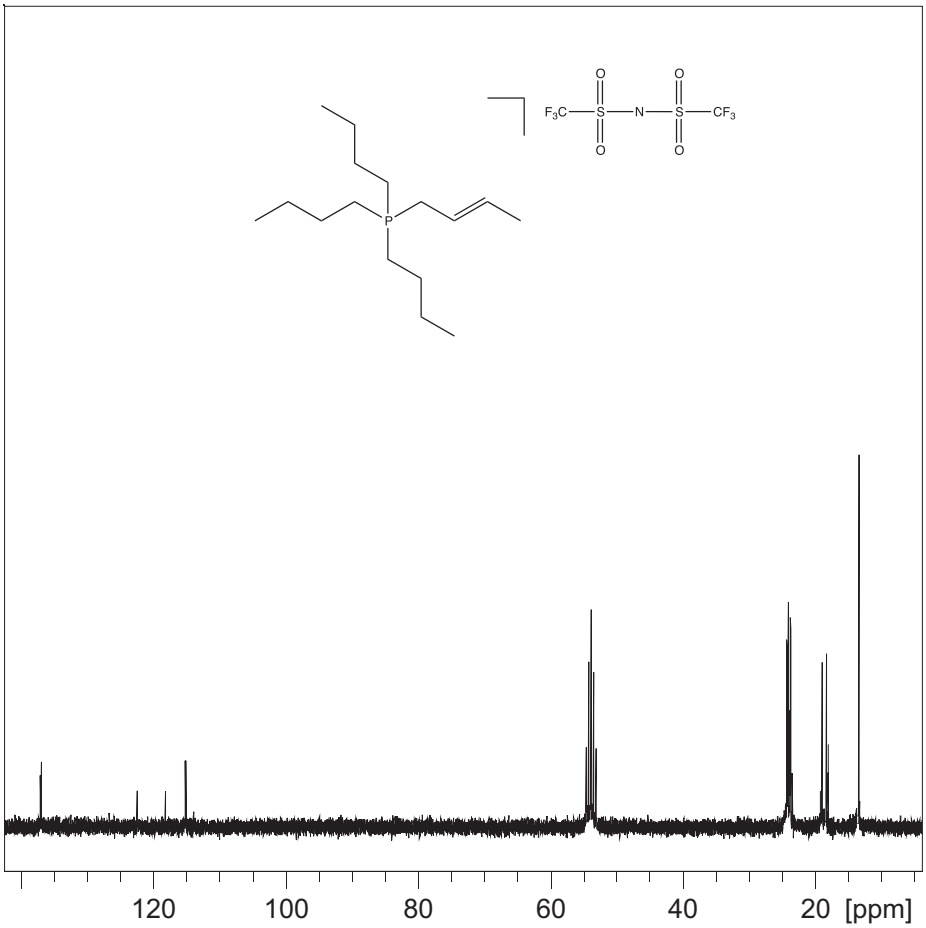
IL 6: Crotyltributylphosphonium bis(trifluoromethane)sulfonimide.



^{1}H-NMR (CD_2Cl_2): δ 5.90 (m, 1H, H_6 of crotyl), 5.30 (m, 1H, H_7 of crotyl), 2.96 (dd, (J_1 = 14.3, J_2 = 7.5), 2H, H_5 of crotyl), 2.09 (m, 6H, H_1 of butyl), 1.80 (t, (J = 5.7), 3H, H_8 of crotyl), 1.51 (m, 12H, H_{2+3} of butyl), 1.01 (t, (J = 7.0), 9H, H_4 of butyl).

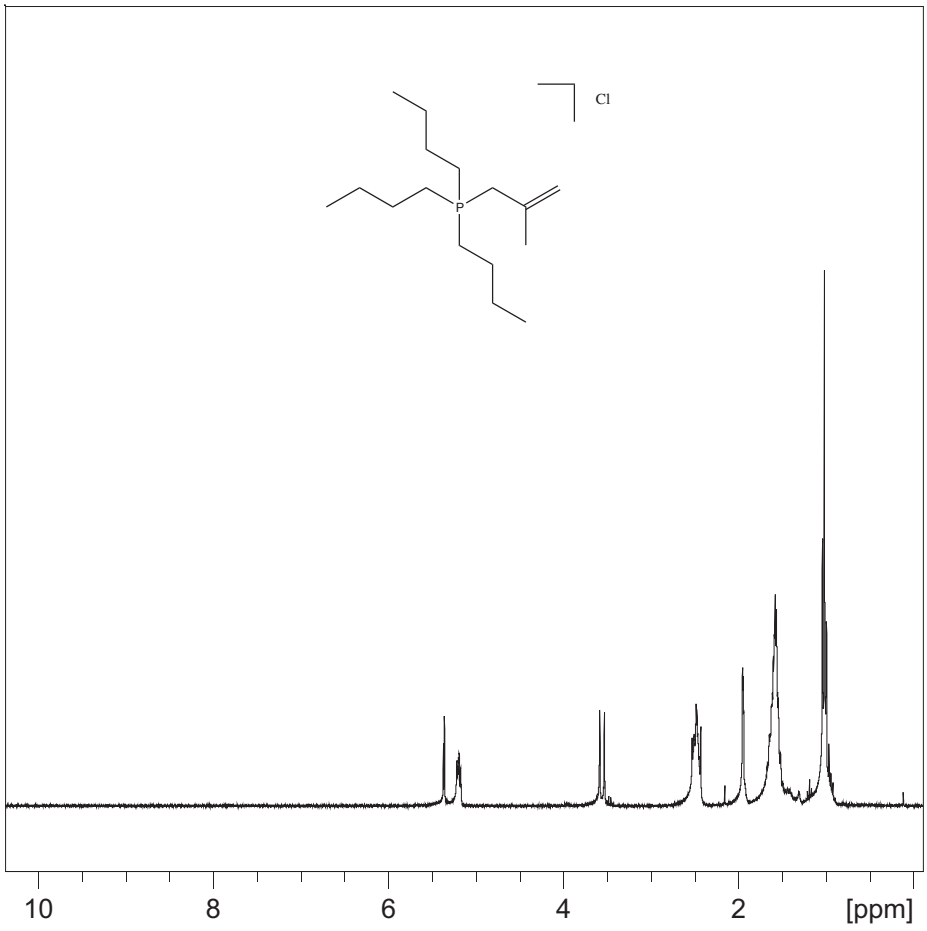


^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 32.2 (s).



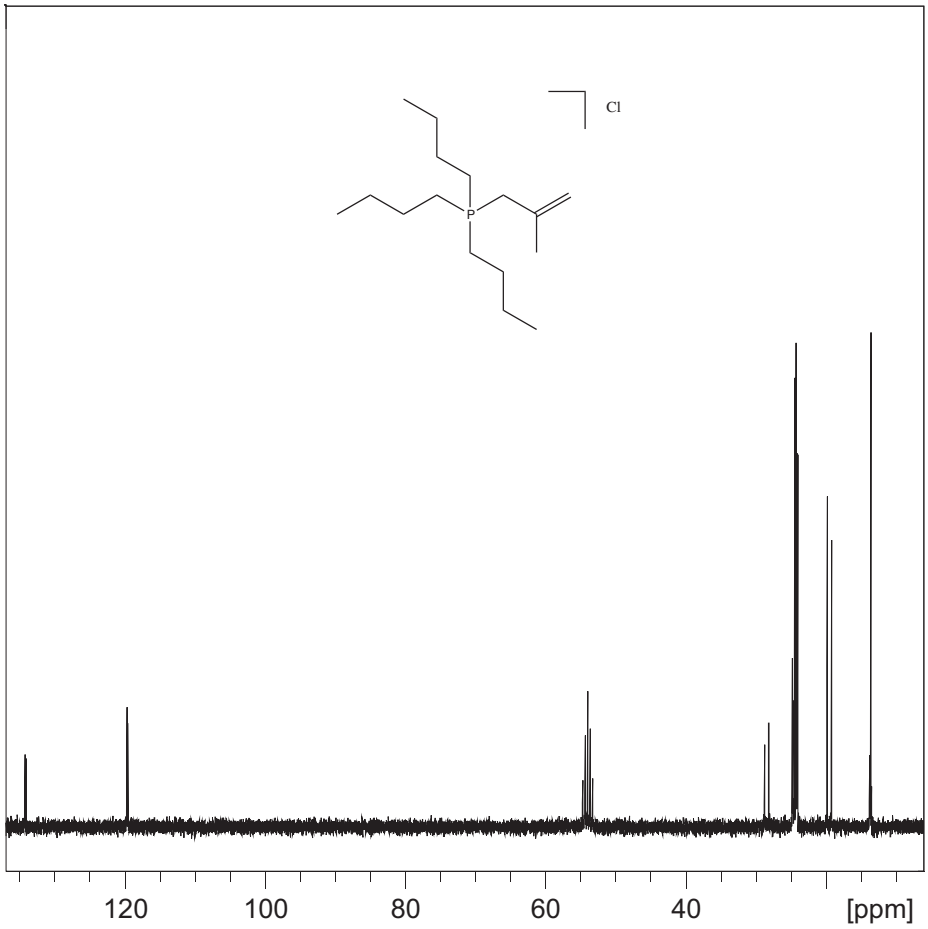
^{13}C-NMR {^{1}H} (CD_2Cl_2): δ 137.0 (d, ($J_{C,P}$ = 12.1), *C6* of crotyl), 120.1 (c, ($J_{C,F}$ = 322.3), *C*F_3 of NTf_2), 115.1 (d, ($J_{C,P}$ = 10.7), *C7* of crotyl), 24.1 (d, ($J_{C,P}$ = 15.3), *C2* of butyl), 23.8 (d, ($J_{C,P}$ = 63.6), *C5* of crotyl), 23.7 (d, ($J_{C,P}$ = 4.7), *C3* of butyl), 18.6 (d, ($J_{C,P}$ = 47.1), *C1* of butyl), 18.2 (s, *C8* of crotyl), 13.3 (s, *C4* of butyl).

Precursor of IL 7: Methallyltributylphosphonium chloride.



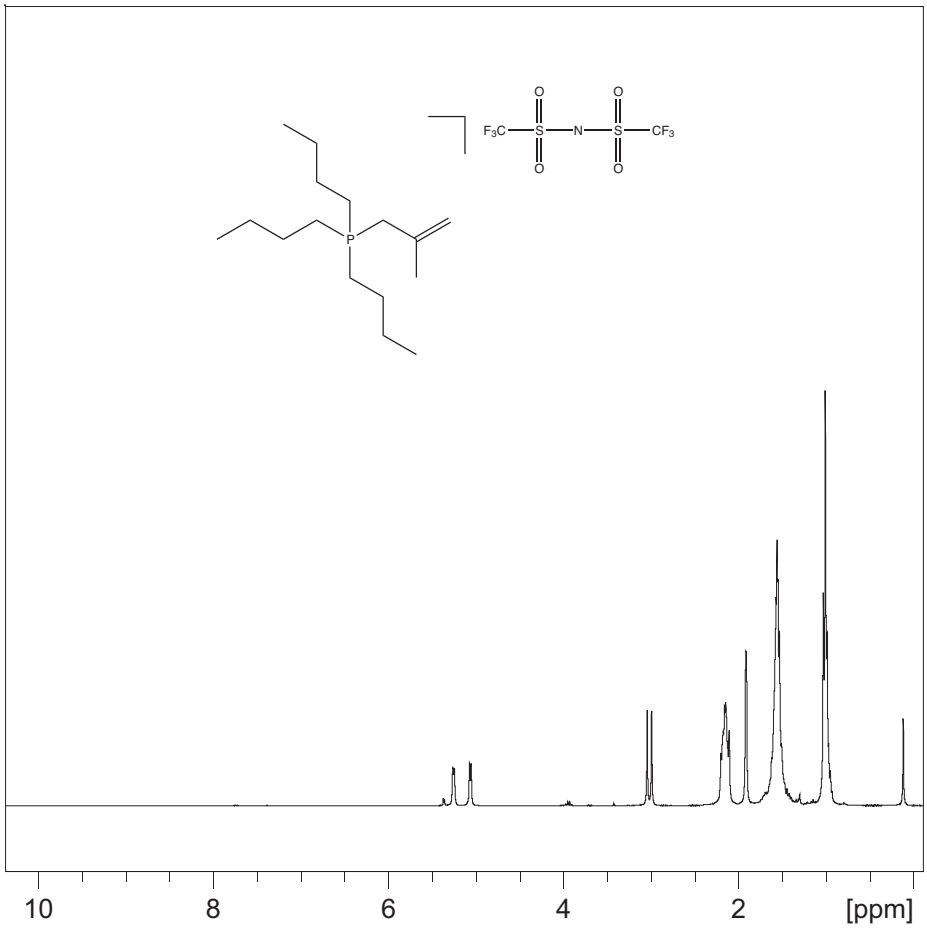
^{1}H-NMR (CD_2Cl_2): δ 5.19 (m, 2H, H_7 of methallyl), 3.56 (d, (J = 16.3), 2H, H_5 of methallyl), 2.48 (m, 6H, H_1 of butyl), 1.94 (s, 3H, H_8 of methallyl), 1.58 (m, 12H, H_{2+3} of butyl), 1.02 (t, (J = 7.1), 9H, H_4 of butyl).

^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 31.3 (s).

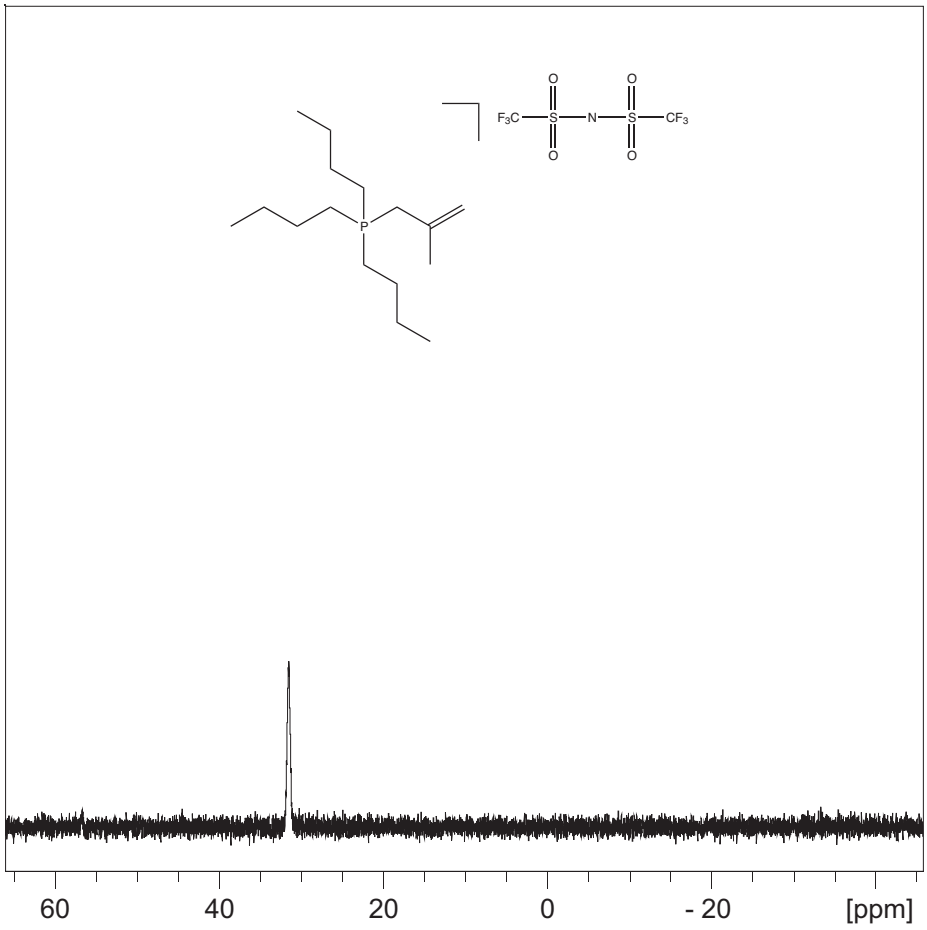


^{13}C-NMR {^{1}H} (CD_2Cl_2): δ 134.2 (d, ($J_{C,P}$ = 10.1), *C6* of methallyl), 119.6 (d, ($J_{C,P}$ = 10.0), *C7* of methallyl), 28.1 (d, ($J_{C,P}$ = 44.8), *C5* of methallyl), 24.8 (d, ($J_{C,P}$ = 2.1), *C8* of methallyl), 24.3 (d, ($J_{C,P}$ = 15.5), *C2* of butyl), 24.0 (d, ($J_{C,P}$ = 4.8), *C3* of butyl), 19.3 (d, ($J_{C,P}$ = 46.6), *C1* of butyl), 13.6 (s, *C4* of butyl).

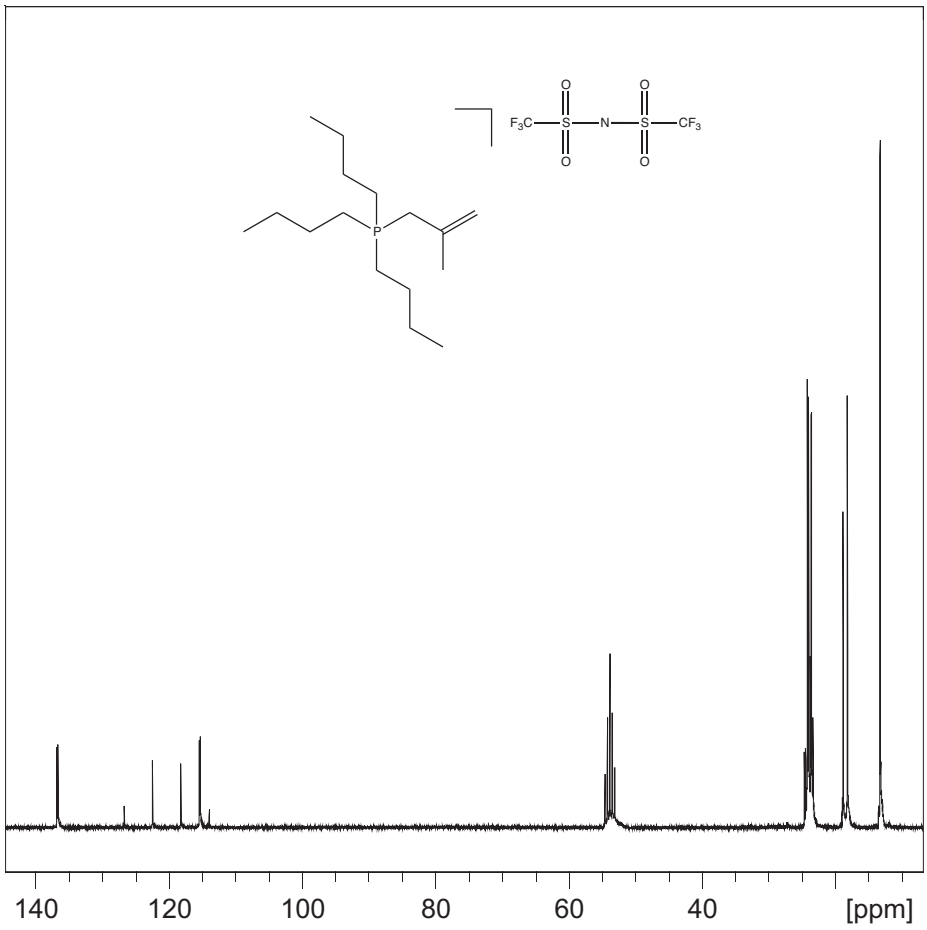
IL 7: Methallyltributylphosphonium bis(trifluoromethane)sulfonimide.



^{1}H-NMR (CD_2Cl_2): δ 5.25 (d, (J = 4.3), 1H, H_{7a} of methallyl), 5.06 (d, (J = 5.0), 1H, H_{7b} of methallyl), 3.02 (d, (J = 15.2), 2H, H_5 of methallyl), 2.15 (m, 6H, H_1 of butyl), 1.91 (s, 3H, H_8 of methallyl), 1.56 (m, 12H, H_{2+3} of butyl), 1.01 (t, (J = 6.9), 9H, H_4 of butyl).

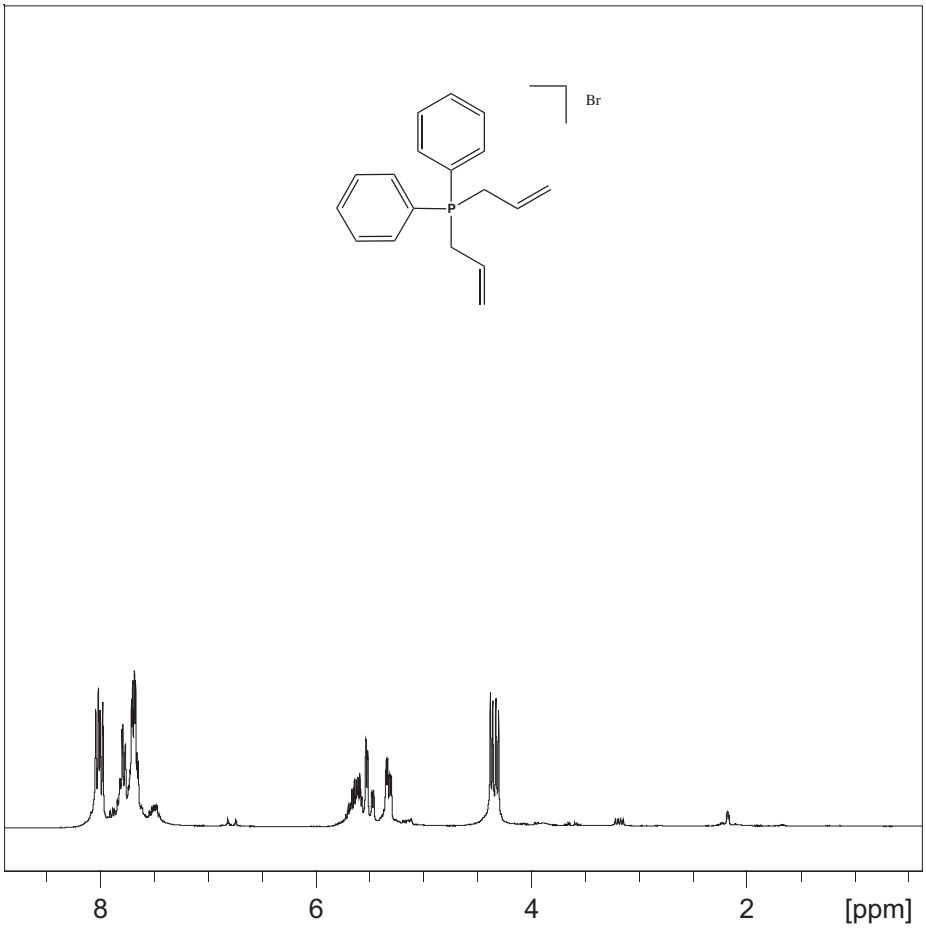


^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 31.4 (s).

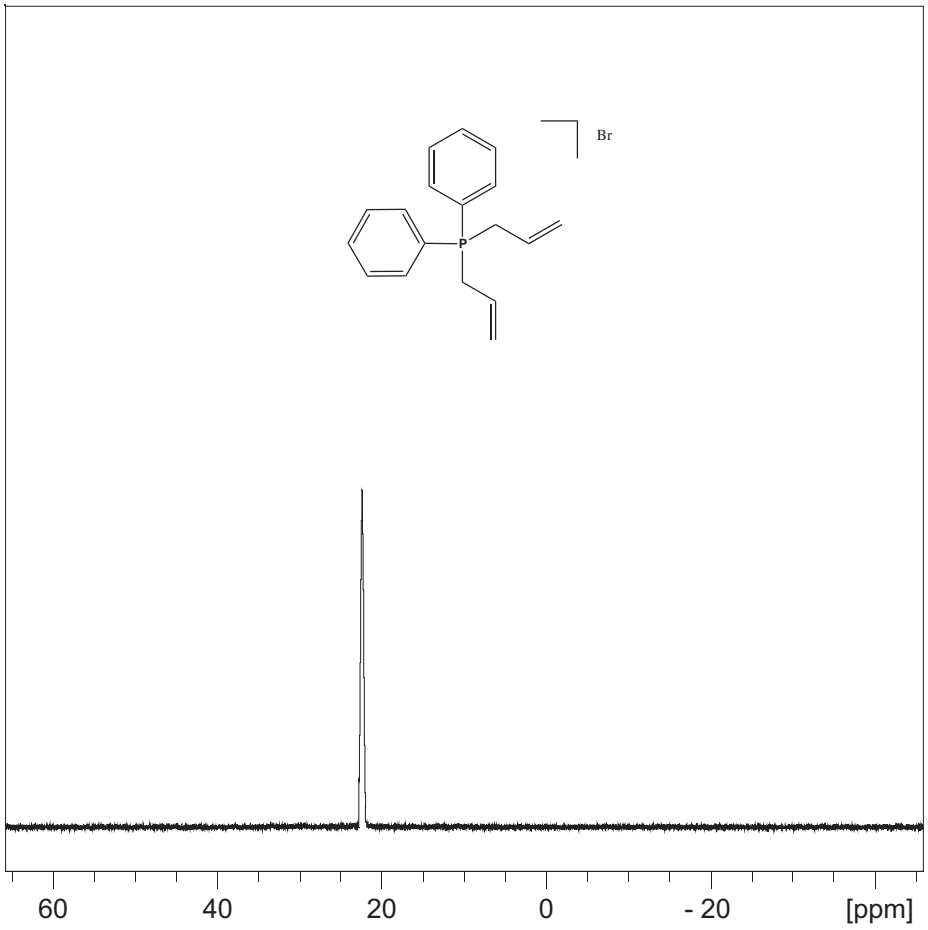


^{13}C-NMR {^{1}H} (CD_2Cl_2): δ 136.7 (d, ($J_{C,P}$ = 12.0), *C_6* of methallyl), 115.3 (d, ($J_{C,P}$ = 9.7), *C_7* of methallyl), 120.3 (c, ($J_{C,F}$ = 321.5), *C*F_3 of NTf_2), 24.4 (d, ($J_{C,P}$ = 2.0), *C_8* of methallyl), 24.3 (d, ($J_{C,P}$ = 44.9), *C_5* of methallyl), 24.1 (d, ($J_{C,P}$ = 15.4), *C_2* of butyl), 23.6 (d, ($J_{C,P}$ = 4.8), *C_3* of butyl), 18.5 (d, ($J_{C,P}$ = 47.5), *C_1* of butyl), 13.3 (s, *C_4* of butyl).

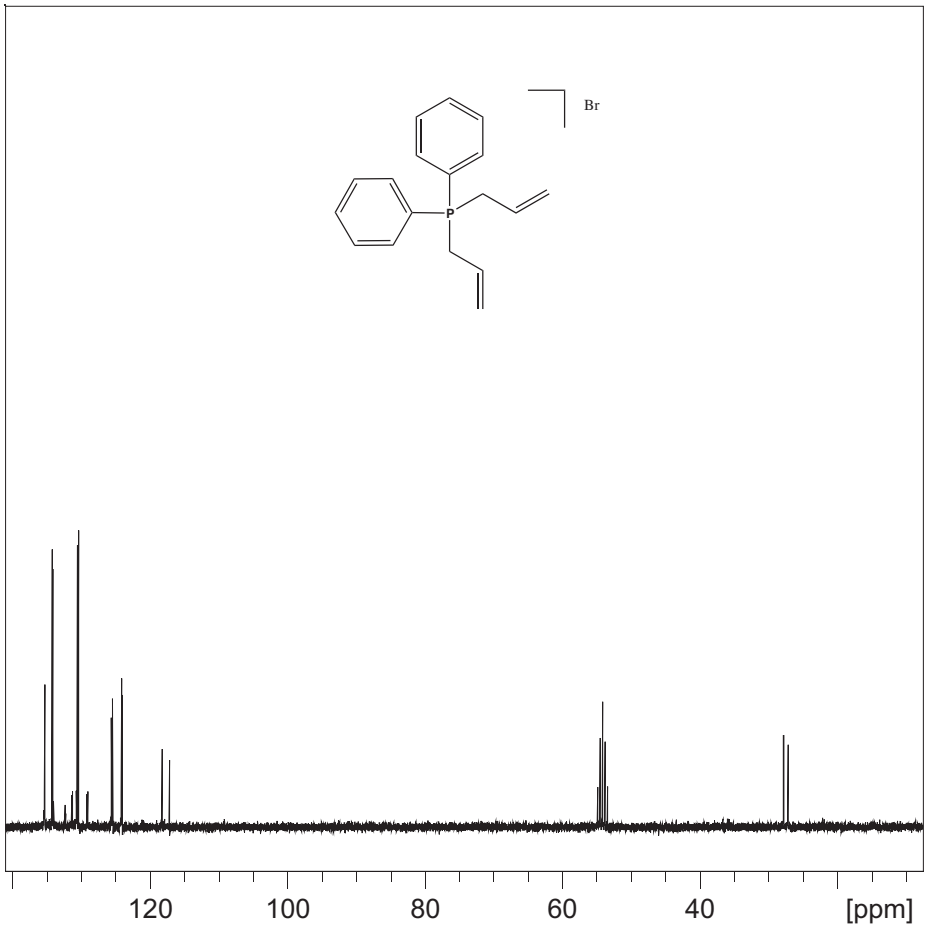
Precursor of IL 8: Diallyldiphenylphosphonium bromide.



^{1}H-NMR (CD_2Cl_2): δ 7.72 (m, 10H, *H* of phenyl), 5.50 (m, 6H, H_{6+7} of allyl), 4.34 (dd, (J_1 = 15.7, J_2 = 6.9), 4H, H_5 of allyl).

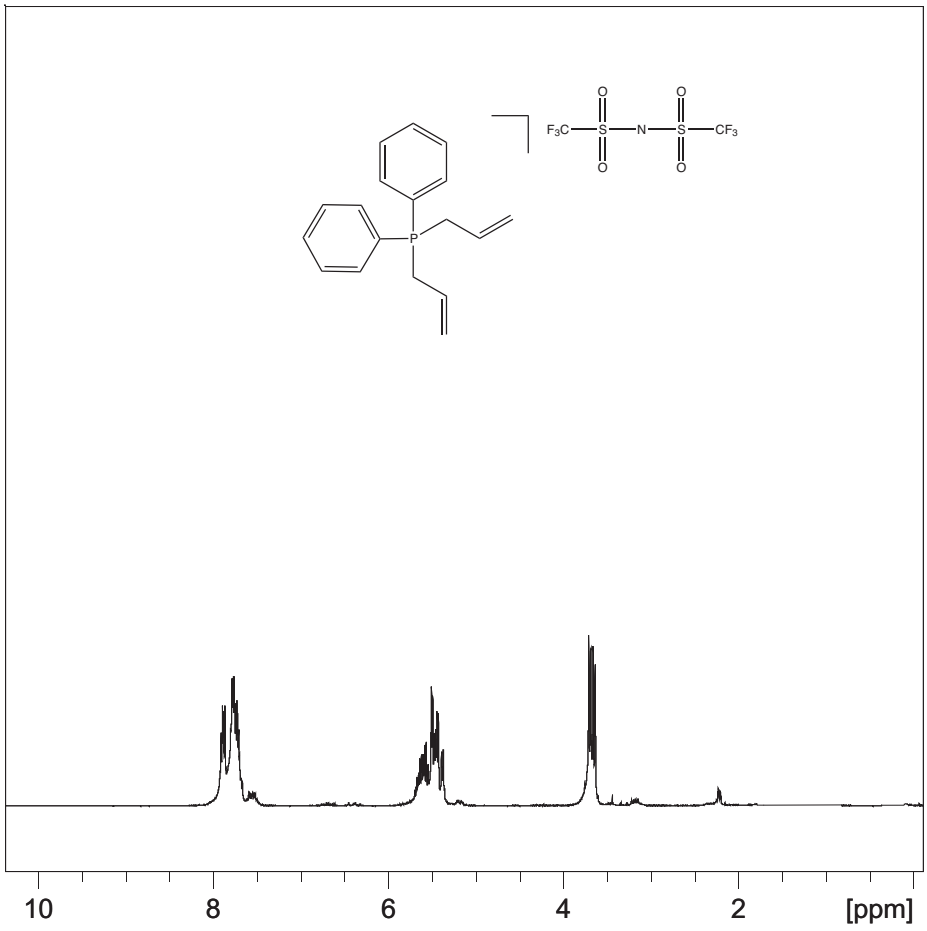


^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 22.3 (s).

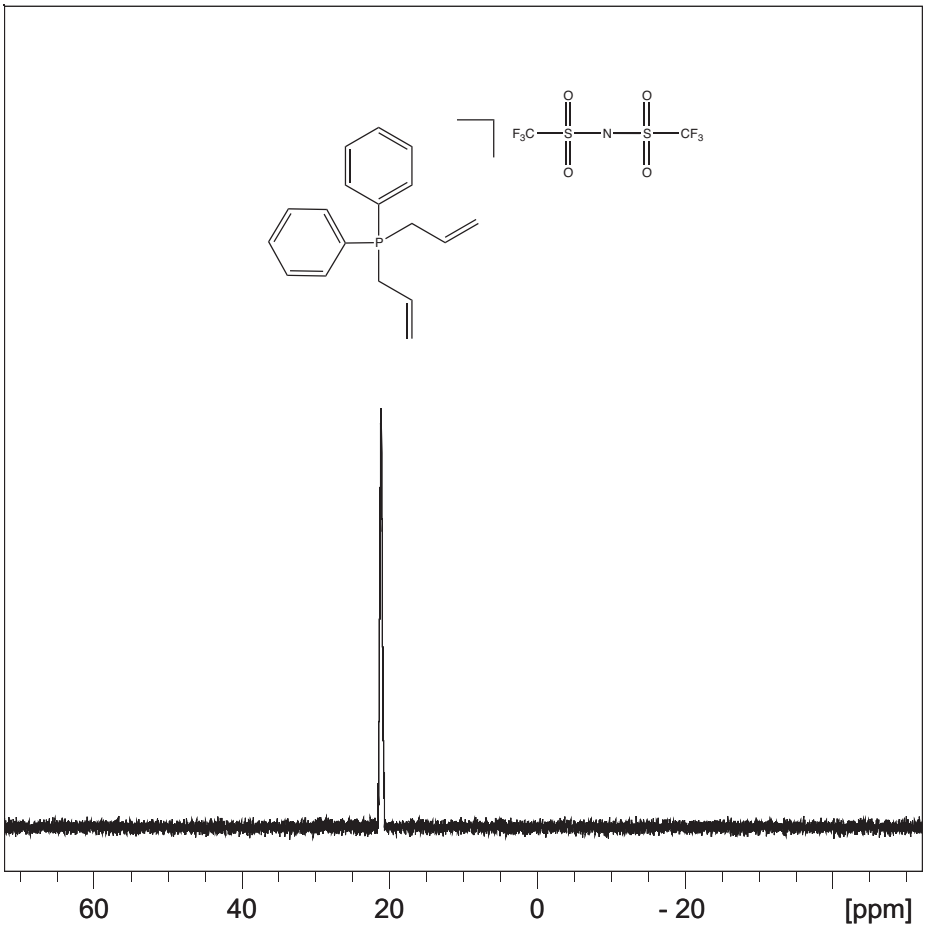


^{13}C-NMR $\{^1H\}$ (CD_2Cl_2): δ 135.2 (d, ($J_{C,P}$ = 3.0), *C_4* of phenyl), 134.1 (d, ($J_{C,P}$ = 9.4), *C_3* of phenyl), 130.4 (d, ($J_{C,P}$ = 12.2), *C_2* of phenyl), 125.4 (d, ($J_{C,P}$ = 12.9), *C_6* of allyl), 124.0 (d, ($J_{C,P}$ = 9.7), *C_7* of allyl), 117.6 (d, ($J_{C,P}$ = 82.4), *C_1* of phenyl), 27.5 (d, ($J_{C,P}$ = 49.1), *C_5* of allyl).

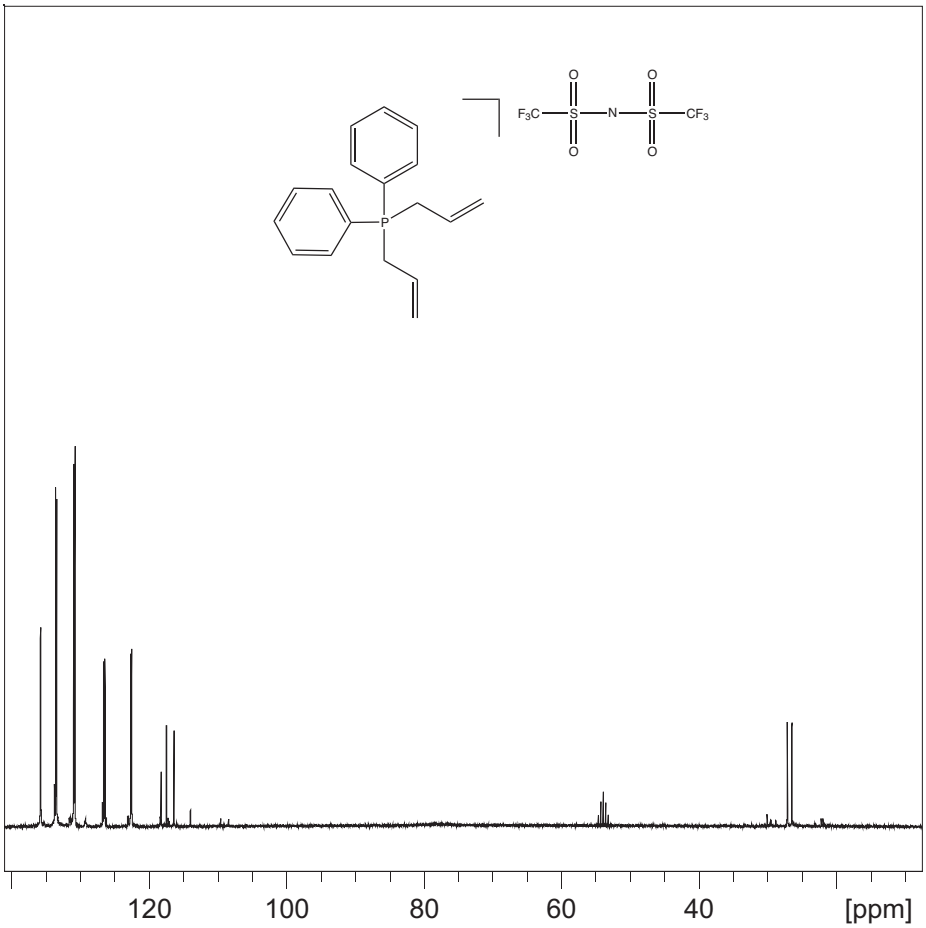
IL 8: Diallyldiphenylphosphonium bis(trifluoromethane)sulfonimide.



^{1}H-NMR (CD_2Cl_2): δ 7.82 (m, 10H, *H* of phenyl), 5.52 (m, 6H, H_{6+7} of allyl), 3.67 (dd, (J_1 = 15.0, J_2 = 7.0), 4H, H_5 of allyl).



^{31}P-NMR {^{1}H} (CD_2Cl_2): δ 21.1 (s).



^{13}C-NMR {^{1}H} (CD_2Cl_2): δ 135.7 (d, ($J_{C,P}$ = 3.0), *C_4* of phenyl), 133.4 (d, ($J_{C,P}$ = 9.0), *C_3* of phenyl), 130.8 (d, ($J_{C,P}$ = 12.4), *C_2* of phenyl), 126.4 (d, ($J_{C,P}$ = 12.8), *C_6* of allyl), 122.5 (d, ($J_{C,P}$ = 9.6), *C_7* of allyl), 120.3 (c, ($J_{C,F}$ = 321.6), *C*F_3 of NTf_2), 116.8 (d, ($J_{C,P}$ = 83.0), *C_1* of phenyl), 26.8 (d, ($J_{C,P}$ = 50.3), *C_5* of allyl).

IL1: Allyltributylphosphonium bromide.

HRMS (ESI^+, $^m/_z$) calcd for $(C_{15}H_{32}P)^+$ (M^+): 243.2237, found: 243.2223; MS (ESI^-, $^m/_z$): 79 [$^{79}Br^-$, 100%], 81 [$^{81}Br^-$, 95%].

IL2: Allyltributylphosphonium bis(trifluoromethane)sulfonimide.

HRMS (ESI^+, $^m/_z$) calcd for $(C_{15}H_{32}P)^+$ (M^+): 243.2237, found: 243.2241; HRMS (ESI^-, $^m/_z$) calcd for $(C_2F_6NO_4S_2)^-$ (NTf_2^-): 279.9178, found 279.9195.

IL3: Allyltributylphosphonium trifluoromethanesulfonate.

HRMS (ESI^+, $^m/_z$) calcd for $(C_{15}H_{32}P)^+$ (M^+): 243.2237, found: 243.2230; HRMS (ESI^-, $^m/_z$) calcd for $(CF_3O_3S)^-$ (OTf^-): 148.9525, found 148.9529.

IL4: Allyltributylphosphonium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate.

HRMS (ESI^+, $^m/_z$) calcd for $(C_{15}H_{32}P)^+$ (M^+): 243.2237, found: 243.2228; HRMS (ESI^-, $^m/_z$) calcd for $(C_{32}H_{12}BF_{24})^-$ (BAr'_4^-): 863.0654, found 863.0650.

IL 5: Crotyltributylphosphonium chloride.

HRMS (ESI^+, $^m/_z$) calcd for $(C_{16}H_{34}P)^+$ (M^+): 257.2393, found: 257.2378.

IL 6: Crotyltributylphosphonium bis(trifluoromethane)sulfonimide.

HRMS (ESI^+, $^m/_z$) calcd for $(C_{16}H_{34}P)^+$ (M^+): 257.2393, found: 257.2374; HRMS (ESI^-, $^m/_z$) calcd for $(C_2F_6NO_4S_2)^-$ (NTf_2^-): 279.9178, found 279.9191.

Precursor of IL 7: Methallyltributylphosphonium chloride.

HRMS (ESI^+, $^m/_z$) calcd for $(C_{16}H_{34}P)^+$ (M^+): 257.2393, found: 257.2388.

IL 7: Methallyltributylphosphonium bis(trifluoromethane)sulfonimide.

HRMS (ESI^+, $^m/_z$) calcd for $(C_{16}H_{34}P)^+$ (M^+): 257.2393, found: 257.2399; HRMS (ESI^-, $^m/_z$) calcd for $(C_2F_6NO_4S_2)^-$ (NTf_2^-): 279.9178, found 279.9185.

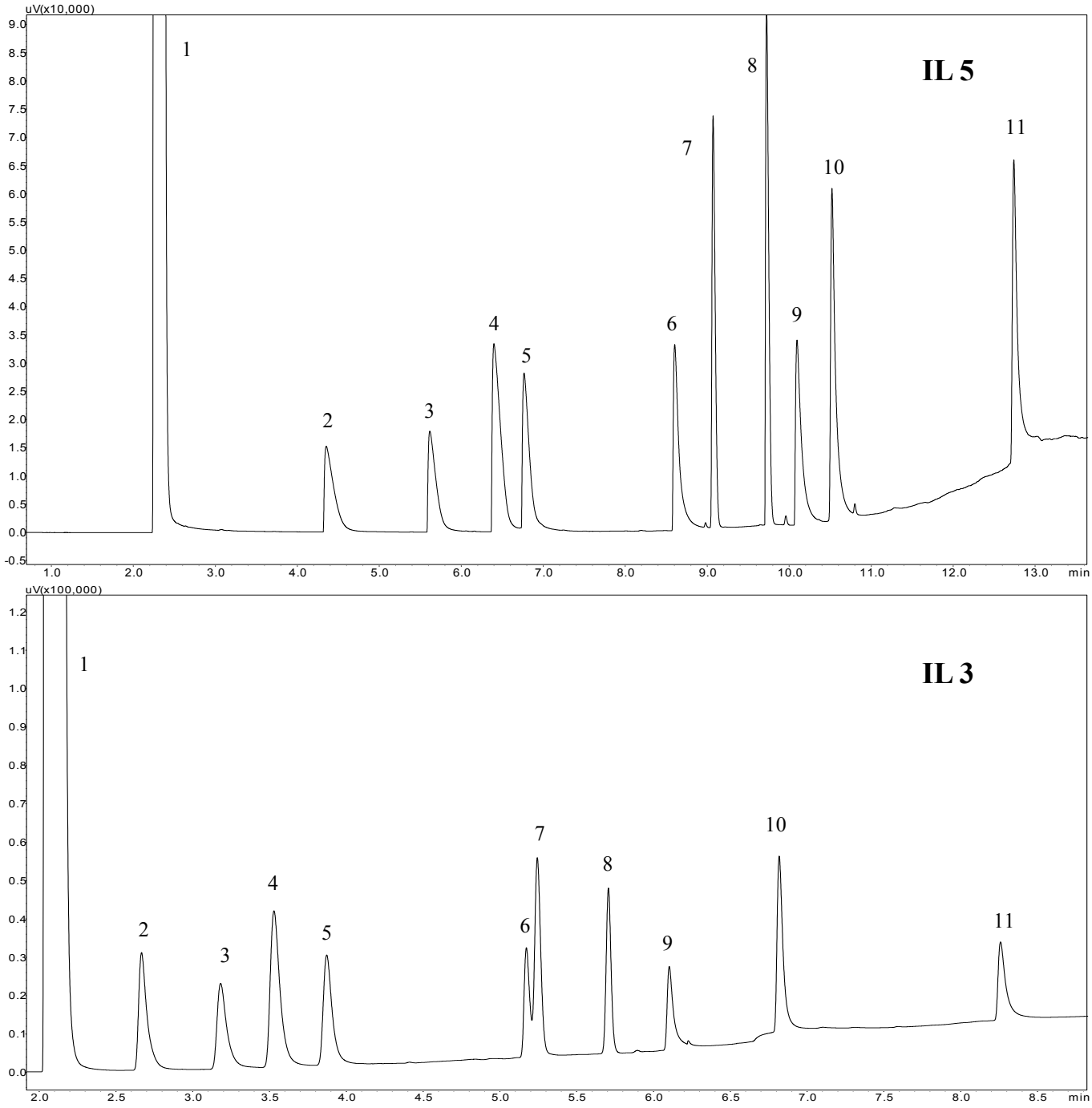
Precursor of IL 8: Diallyldiphenylphosphonium bromide.

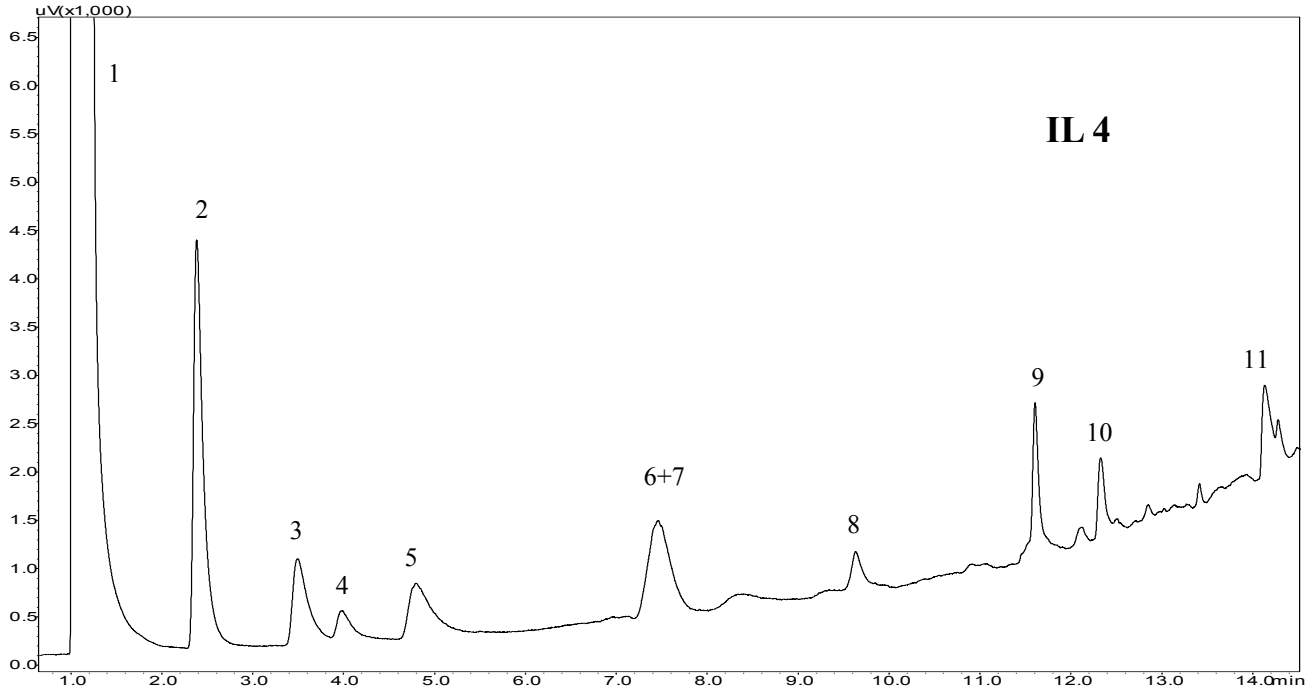
HRMS (ESI^+, $^m/_z$) calcd for $(C_{18}H_{20}P)^+$ (M^+): 267.1298, found: 267.1308; MS (ESI^-, $^m/_z$): 79 [$^{79}Br^-$, 100%], 81 [$^{81}Br^-$, 95%].

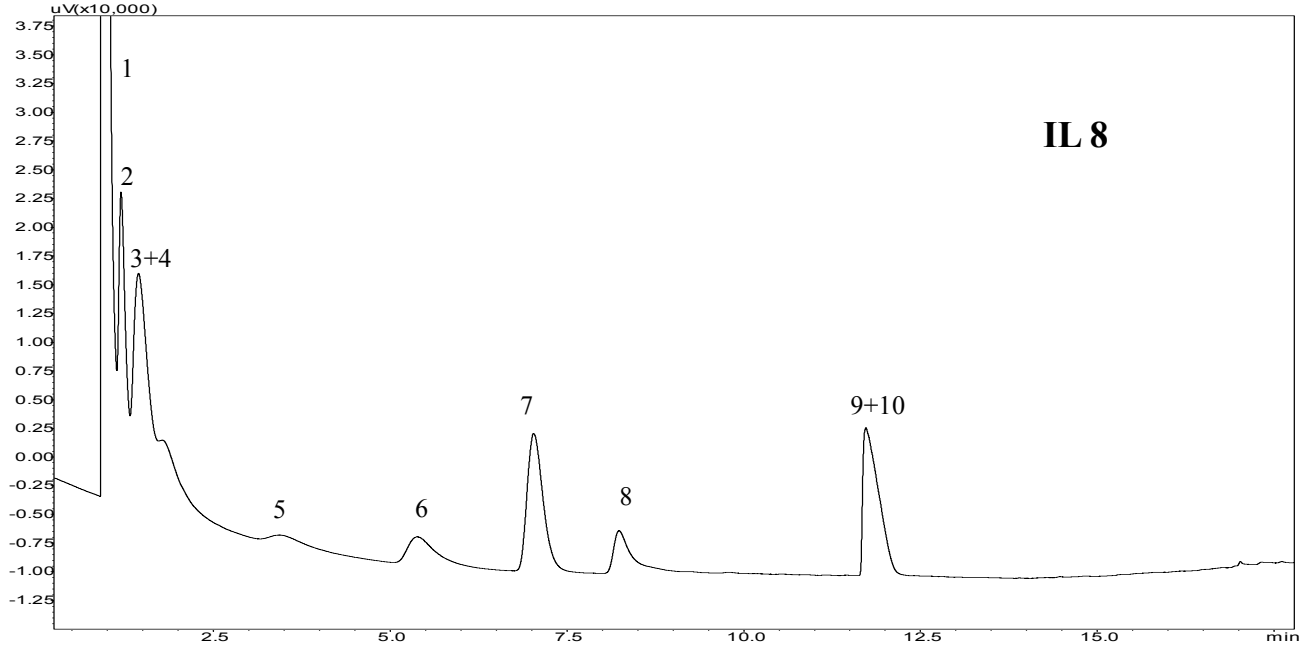
IL 8: Diallyldiphenylphosphonium bis(trifluoromethane)sulfonimide.

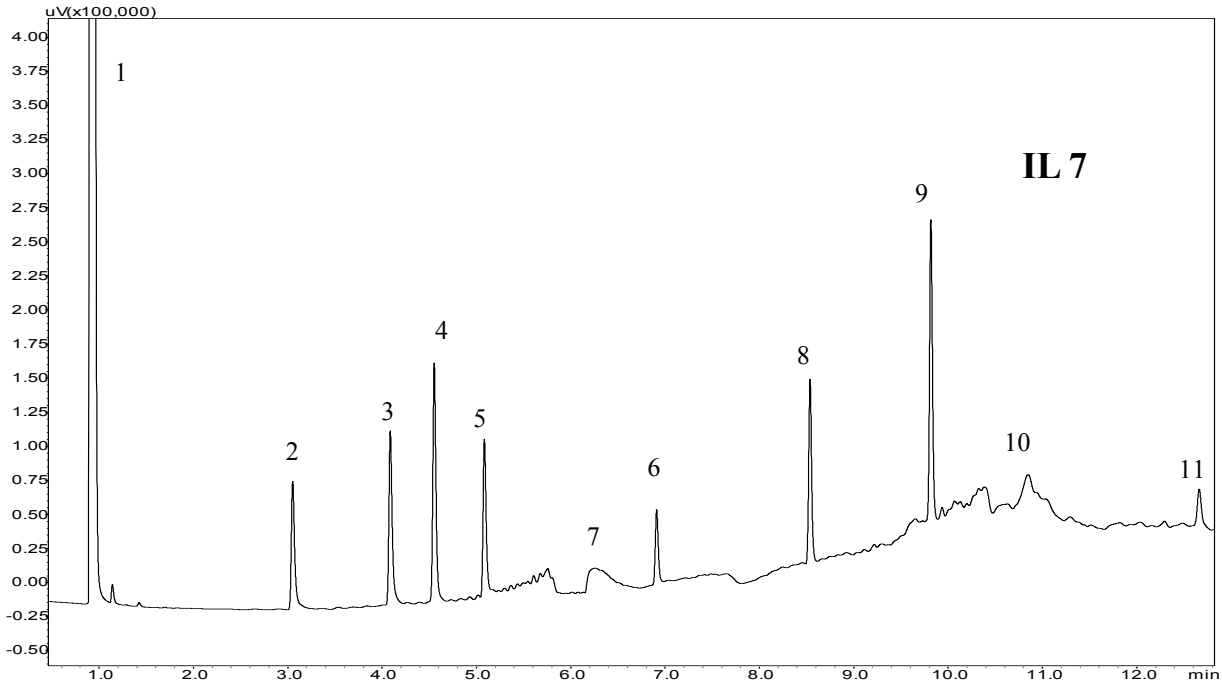
HRMS (ESI^+, $^m/_z$) calcd for $(C_{18}H_{20}P)^+$ (M^+): 267.1298, found: 267.1292; HRMS (ESI^-, $^m/_z$) calcd for $(C_2F_6NO_4S_2)^-$ (NTf_2^-): 279.9178, found 279.9182.

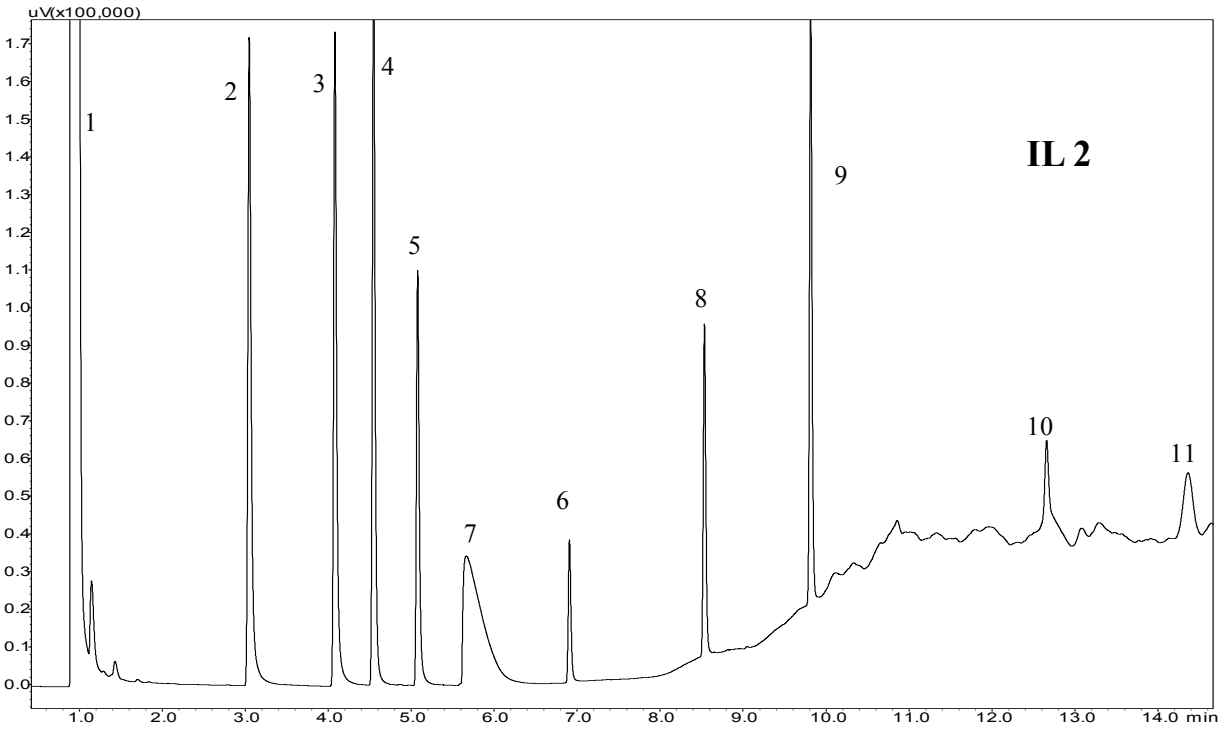
Separation of a mixture containing alcohols and amines using phosphonium PILs columns



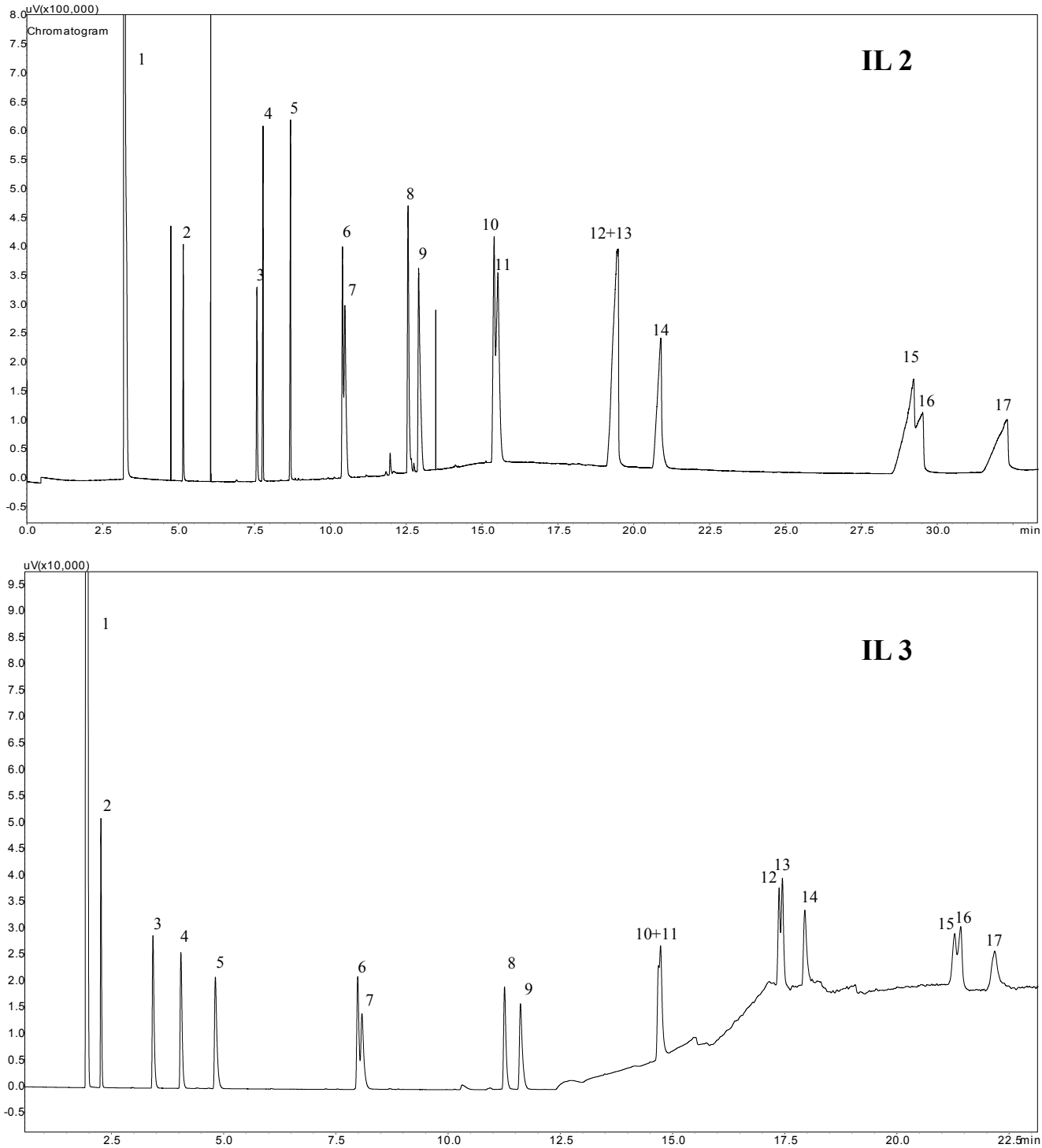

uV(x1,000)
IL 4
1
2
3
4
5
6+7
8
9
10
11
min

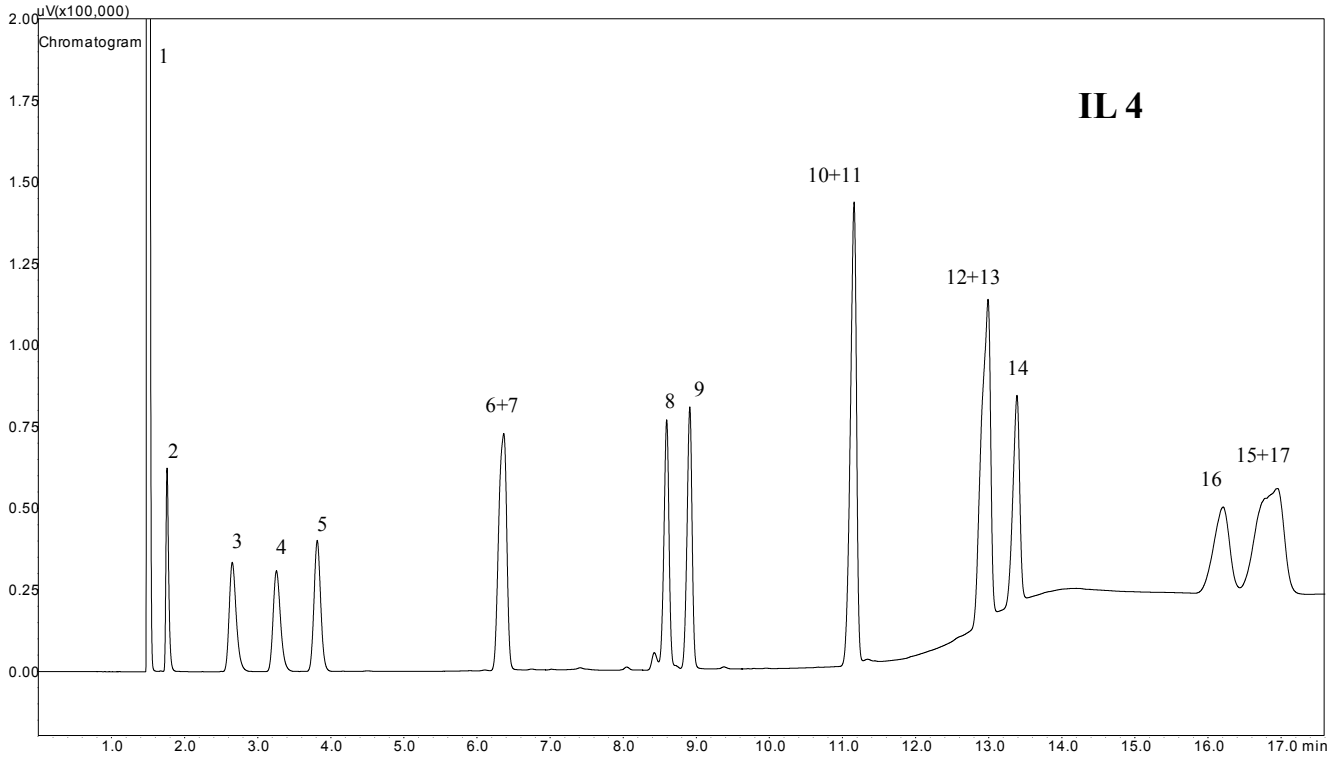

uV(x10,000)
IL 8
1
2
3+4
5
6
7
8
9+10
min

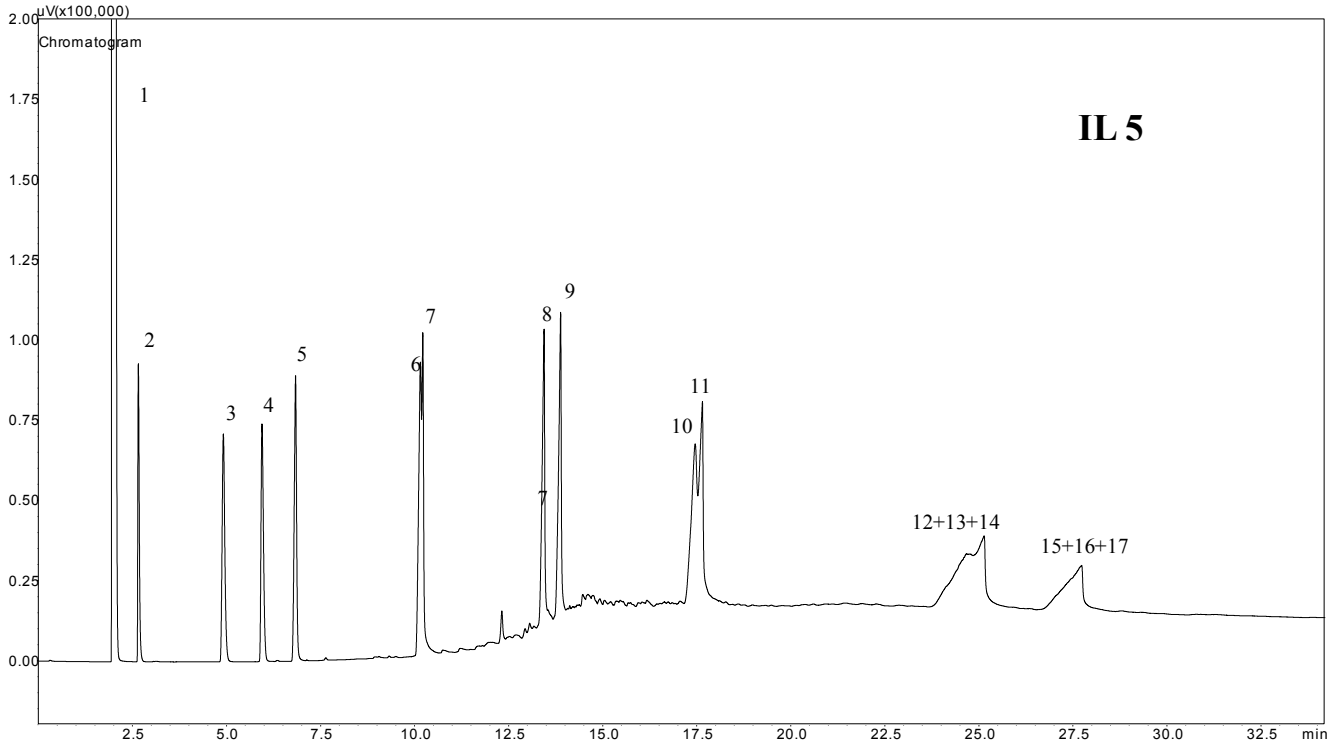

uV(x100,000)
IL 7
1
2
3
4
5
6
7
8
9
10
11
min

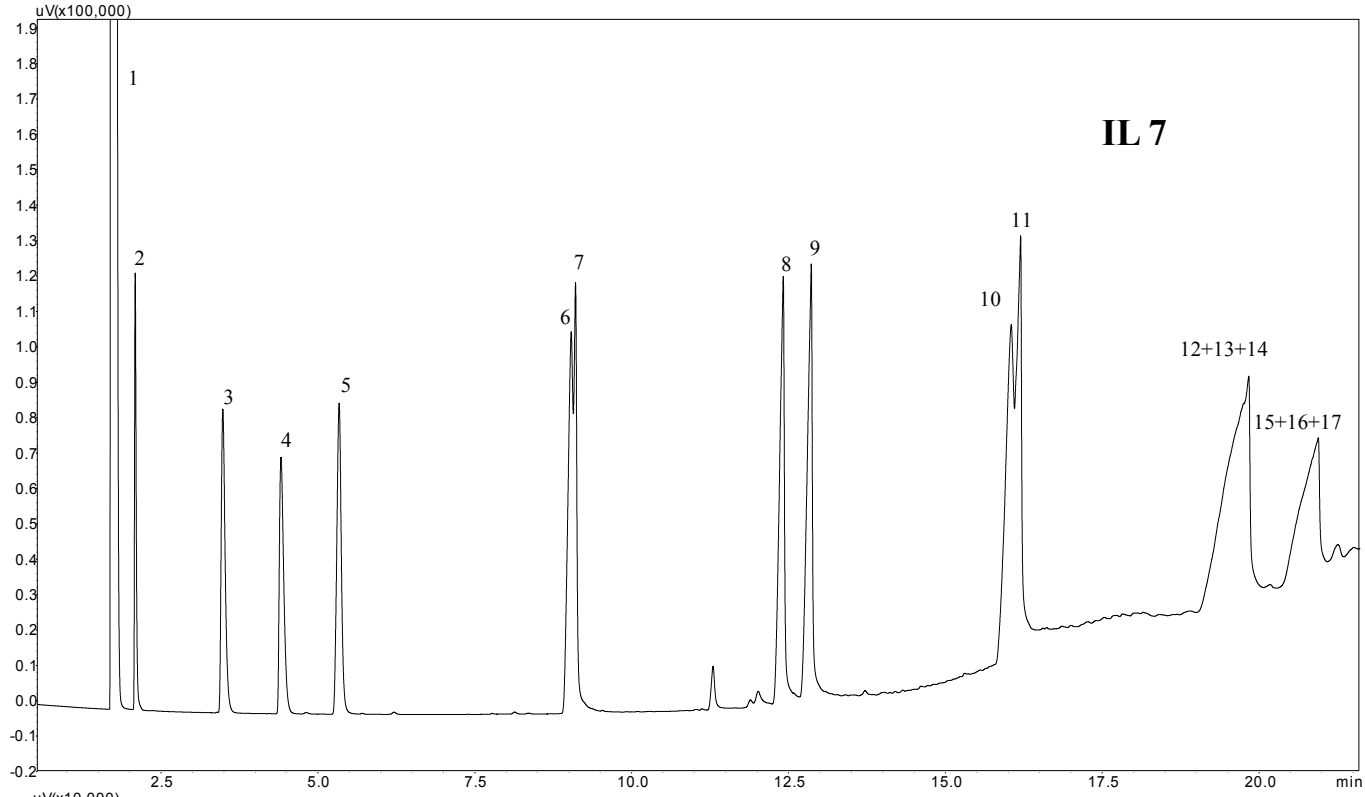

uV(x100,000)
IL 2
1
2
3
4
5
6
7
8
9
10
11
min

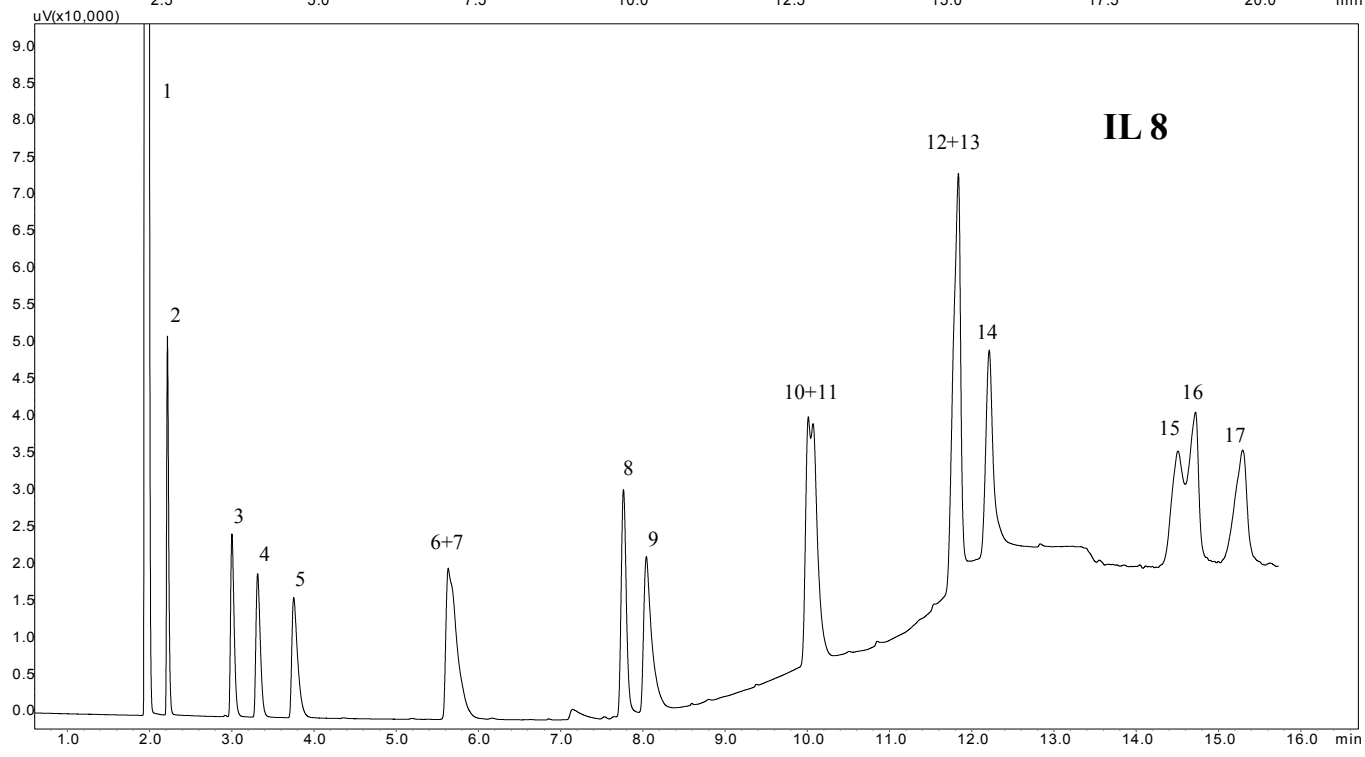
Separation of Polycyclic Aromatic Hydrocarbons mixture with Phopsphonium PILs columns




uV(x100,000)
Chromatogram
IL 4
1
2
3
4
5
6+7
8
9
10+11
12+13
14
16
15+17
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0 min


uV(x100,000)
Chromatogram
IL 5
1
2
3
4
5
6
7
8
9
10
11
12+13+14
15+16+17
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
min


uV(x100,000)
IL 7
1
2
3
4
5
6
7
8
9
10
11
12+13+14
15+16+17
min


uV(x10,000)
IL 8
1
2
3
4
5
6+7
8
9
10+11
12+13
14
15
16
17
min