

Polymerized phosphonium-based ionic liquids as gas chromatography stationary phases

SUPPORTING INFORMATION

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Synthesis of polymerizable phosphonium-based ionic liquids (ILs 1-4).

Some manipulations were performed under an inert atmosphere of dinitrogen using standard Schlenk techniques due to the air sensitivity of n-tributylphosphine. Dichloromethane was distilled over calcium hydride under dinitrogen to remove traces of water. Chemicals were purchased from commercial sources and used without further purification. ^1H , ^{31}P and ^{13}C NMR spectra were recorded on Bruker Avance 400 and DPX 300 spectrometers.

Synthesis of [(^nBu) $_3$ (allyl)P]Br (IL 1).

Manipulations were carried out using Schlenk techniques under a dinitrogen atmosphere due to the air sensitivity of n-tributylphosphine. Allyl bromide (0.83 mL, 9.60 mmol) was added to a solution of n-tributylphosphine (2 mL, 8.00 mmol) in dichloromethane (20 mL), previously cooled to 0° C. The reaction mixture was allowed to reach room temperature and stirred for 1 hour. The resulting solution was evaporated to dryness, and after approx 6 h. under vacuum IL 1 was obtained as a white solid (2.379 gr, 92%).¹

Synthesis of [(^nBu) $_3$ (crotyl)P]NTf $_2$ (IL 2).

Crotyl chloride (0.94 mL, 9.60 mmol) was added to a solution of n-tributylphosphine (2 mL, 8.00 mmol) in CH_2Cl_2 at 0° C. The mixture was allowed to warm to room temperature, stirred for 1 hour and then the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in methanol (20 mL), lithium bis(trifluoromethane)sulfonamide (2.756 g, 9.60 mmol) was added and the reaction mixture was stirred for 48 h. The solvent was then evaporated under vacuum, the residue extracted with CH_2Cl_2 (20 mL) and the organic layer was washed with distilled

water (3 × 20 mL). Dichloromethane was evaporated and IL 2 was obtained as colorless oil (2.709 g, 63 %).

Synthesis of [(ⁿBu)₃(allyl)P][BAr'₄] (IL 3).

Compound IL 3 was obtained through a metathesis reaction between IL 1 and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAr'₄).²

In a Schlenk flask, 100 mg of IL 1 (0.31 mmol) were dissolved in 20 mL of dichloromethane, NaBAr'₄ (330 mg, 0.37 mmol) was added, and the reaction mixture was stirred for 48 hours. Then the mixture was filtered through diatomaceous earth, and the resulting colorless solution was evaporated to dryness and the white residue dried under vacuum for 6 hours. IL3 was obtained as a white solid (343 mg, 70 %. m.p 75°).

Synthesis of [(Ph)₂(allyl)₂P]NTf₂ (IL 4).

IL 4 was prepared as described above for IL2, starting from allyldiphenylphosphine (1.90 mL, 8.00 mmol), allyl bromide (0.83 mL, 9.60 mmol) and LiNTf₂ (2.756 g, 9.60 mmol). IL 4 was obtained as colorless oil (2.891 g, 66 %).

Preparation of polymeric phosphonium-based ILs capillary columns.

All capillary columns were coated using the static method on a 30 m capillary column (0.25 mm i.d.) at 40 °C using 0.30% (w/v) of ILs dissolved in dichloromethane. Prior to adding the solvent to the monomer, 3 mg of AIBN [2,2'-azobis(2-methylpropionitrile)] (~10 wt %) were added as initiator of the radical polymerization. Capillaries were filled with the solution of the initiator and the ionic liquid. The AIBN decomposition constant was lower in comparison with the coating rate at this temperature so polymerization was almost insignificant during the filling of the column³. After coating, the ends of the capillary were sealed and the capillaries placed in a GC oven and heated from 40 to 80 °C at 1 °C/min and kept at 80 °C for 5 h in order to ensure complete polymerization. Equation 2 was used to approximate the stationary phase film thickness (d_f) of capillaries columns.⁴

Equation 2.

$$d_f = d_c c / 400$$

where d_c is the diameter of the capillary tubing (in micrometers), and c is the percentage by weight (%) concentration of the stationary phase dissolved in an appropriate solvent.

In all cases, optimum film thickness was found to be 0.16 microns that corresponds to 0.25% w/v of IL.

Table S1. Probe molecules and values of solute descriptors used in the characterization of phosphonium PILs.

Probe molecules	E	S	A	B	L
1-Hexanol	0.21	0.44	0.344	0.52	3.643
Anisole	0.712	0.768	0	0.311	3.808
Cyclohexanone	0.403	0.895	0	0.53	3.759
1,2-Dichlorobenzene	0.872	0.771	0	0.054	4.516
Butylbenzene	0.595	0.499	0	0.139	4.734
Nonanal	0.121	0.636	0	0.414	4.838
Butyl acetate	0.079	0.57	0	0.438	3.409
Iodobenzene	1.182	0.784	0	0.135	4.548
1-Hexyne	0.167	0.274	0.09	0.117	2.544
1-Nitropropane	0.243	0.925	0.049	0.27	2.878
1-Pentanol	0.219	0.44	0.344	0.52	3.128
Pyridine	0.635	0.843	0	0.532	3.006
Benzonitrile	0.742	1.135	0	0.331	4.04
Phenyl acetate	0.648	1.055	0	0.521	4.378
Nitrobenzene	0.846	1.138	0	0.269	4.539
Naphthalene	1.24	0.906	0	0.193	5.154
Heptanal	0.14	0.642	0	0.441	3.856
2-Heptanone	0.123	0.662	0	0.496	3.781
1-Phenyl ethanol	0.823	0.819	0.351	0.648	4.424
Benzaldehyde	0.813	1.025	0	0.394	4.005
1-Octanol	0.199	0.44	0.344	0.52	4.648
1-Chloronaphthalene	1.419	0.951	0	0.135	6.175
Aniline	0.955	1.003	0.249	0.425	3.956
Fluorene	1.664	1.12	0	0.252	6.921
4-Chloroaniline	1.017	1.128	0.366	0.309	4.972
Benzyl alcohol	0.803	0.882	0.4	0.557	4.244
Butyl benzoate	0.668	0.851	0	0.393	5.974
Cinnamic alcohol	1.119	0.971	0.451	0.606	5.475
Phenol	0.769	0.759	0.716	0.319	3.844
Acetophenone	0.806	1.026	0	0.503	4.533
3-Methyl-1-butanol	0.198	0.423	0.351	0.501	2.963
1-Butanol	0.224	0.44	0.344	0.52	2.578
Ethyl benzoate	0.694	0.886	0	0.444	5.032
2-Phenyl ethanol	0.787	0.797	0.39	0.636	4.741
1-Decanol	0.191	0.44	0.344	0.52	5.589
Triethylamine	0.101	0.14	0	0.78	3.017
Ethylbenzene	0.613	0.499	0	0.139	3.814
1,3-Dinitrobenzene	0.079	0.57	0	0.438	3.409

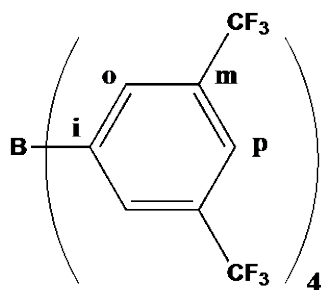
Table S2. Regression parameter coefficients of phosphonium PILS.

IL	T (°C)	c	e	s	a	b	l	R ²	n	SE	F
IL 1	50	-4.68 (0.12)	-0.20 (0.09)	1.83 (0.12)	5.68 (0.19)	0.09 (0.14)	0.72 (0.03)	0.99	28	0.05	338
	80	-4.32 (0.16)	-0.23 (0.14)	1.74 (0.16)	4.83 (0.20)	-0.64 (0.22)	0.59 (0.02)	0.99	32	0.07	212
	110	-4.61 (0.15)	-0.28 (0.12)	1.22 (0.17)	3.60 (0.26)	-0.66 (0.29)	0.48 (0.03)	0.98	24	0.09	188
IL 2	50	-3.52 (0.13)	-0.20 (0.09)	1.28 (0.12)	0.97 (0.17)	1.72 (0.11)	0.49 (0.03)	0.98	32	0.08	137
	80	-3.85 (0.11)	-0.21 (0.07)	1.05 (0.08)	0.91 (0.11)	0.97 (0.10)	0.42 (0.02)	0.98	35	0.07	171
	110	-3.99 (0.12)	-0.24 (0.08)	0.90 (0.10)	0.88 (0.11)	0.55 (0.14)	0.40 (0.03)	0.98	30	0.07	116
IL 3	50	-3.98 (0.11)	-0.14 (0.07)	1.57 (0.08)	4.22 (0.14)	1.27 (0.10)	0.62 (0.03)	0.99	25	0.07	216
	80	-3.38 (0.13)	-0.28 (0.08)	0.96 (0.12)	3.75 (0.18)	0.90 (0.15)	0.55 (0.02)	0.98	26	0.06	120
	110	-5.33 (0.22)	-0.35 (0.16)	0.94 (0.19)	2.93 (0.22)	0.29 (0.23)	0.41 (0.04)	0.98	21	0.11	174
IL 4	50	-3.90 (0.20)	-0.06 (0.15)	1.39 (0.21)	1.42 (0.32)	1.40 (0.26)	0.63 (0.04)	0.97	29	0.12	91
	80	-4.26 (0.13)	-0.10 (0.09)	1.33 (0.13)	1.07 (0.16)	1.09 (0.17)	0.51 (0.03)	0.98	32	0.10	193
	110	-3.74 (0.10)	-0.43 (0.08)	1.27 (0.12)	0.08 (0.14)	0.14 (0.16)	0.39 (0.02)	0.98	30	0.06	221

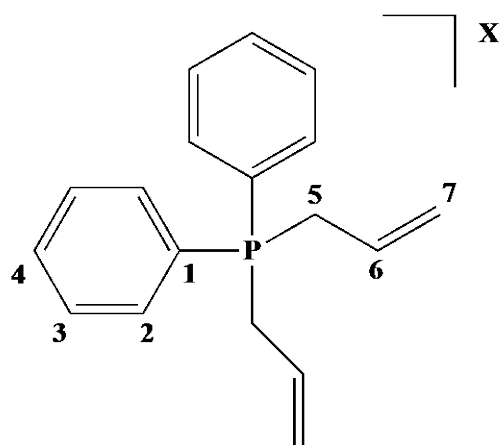
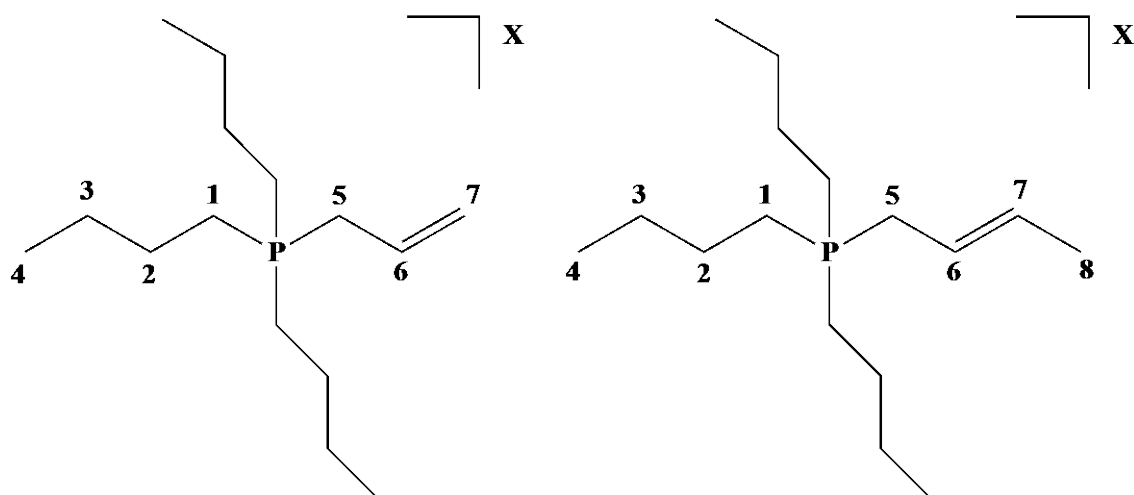
Preparation of polymeric phosphonium based ILs with graphene oxide sheets capillary columns.

The coating of the GC columns was performed using the static method. Before performing the static coating, the capillaries were pre-treated with sodium hydroxide (NaOH 1 M) and hydrochloric acid (HCl 1 M), and then purged with nitrogen for 15 min. Then, a dispersion of graphene oxide sheets in acetone was introduced in the capillary. After coating, the ends of the capillary were sealed and the capillaries were introduced in a GC oven and heated from 50 to 120 °C at 3 °C min⁻¹. Then, the capillaries were filled with the solution of the initiator and the ionic liquid.

Labeling scheme for BAr'_4 and phosphonium salts.

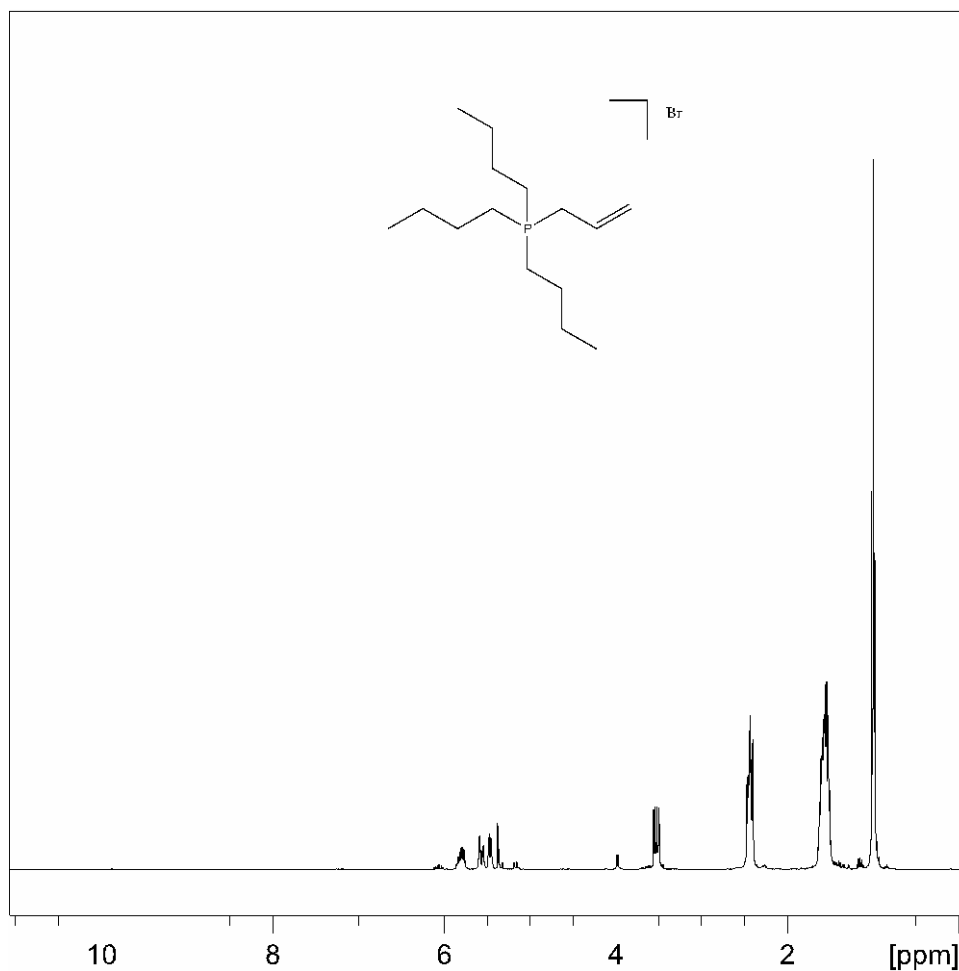


BAr'_4 : tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate

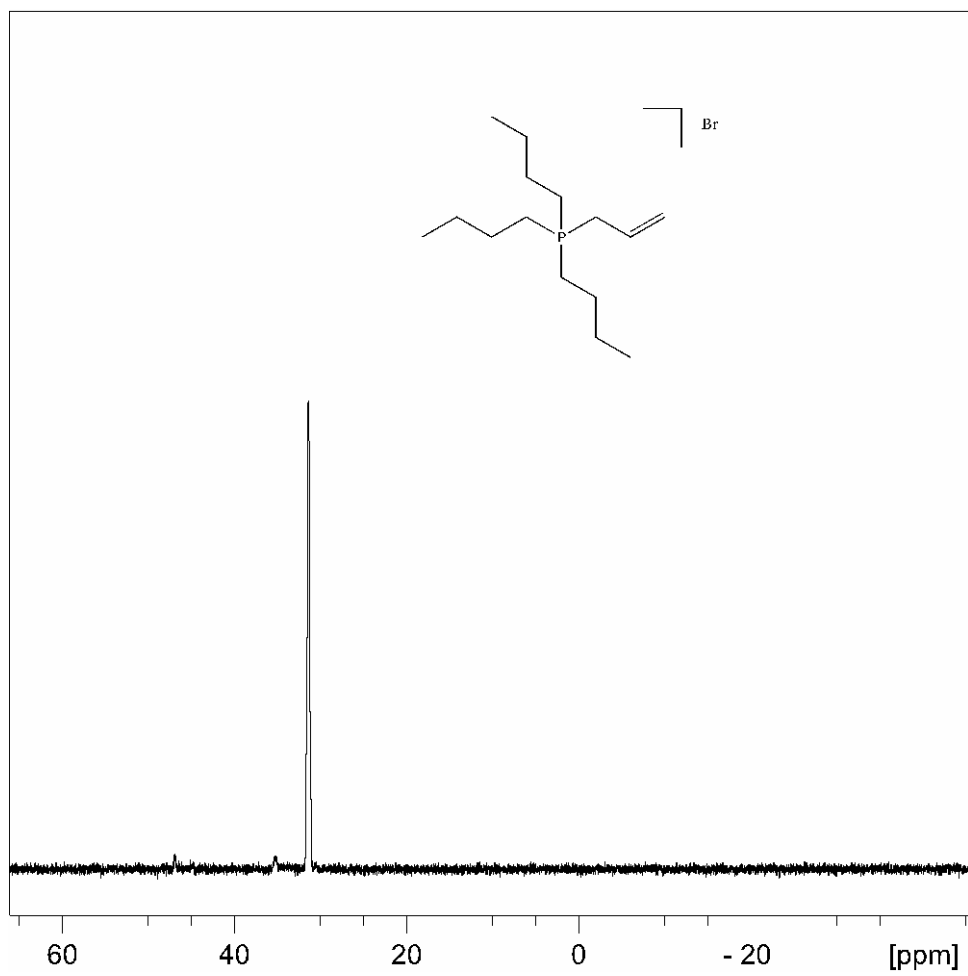


NMR spectra ($^1\text{H-NMR}$, $^{31}\text{P-NMR}$ { ^1H }, $^{13}\text{C-NMR}$ { ^1H }) of phosphonium salts

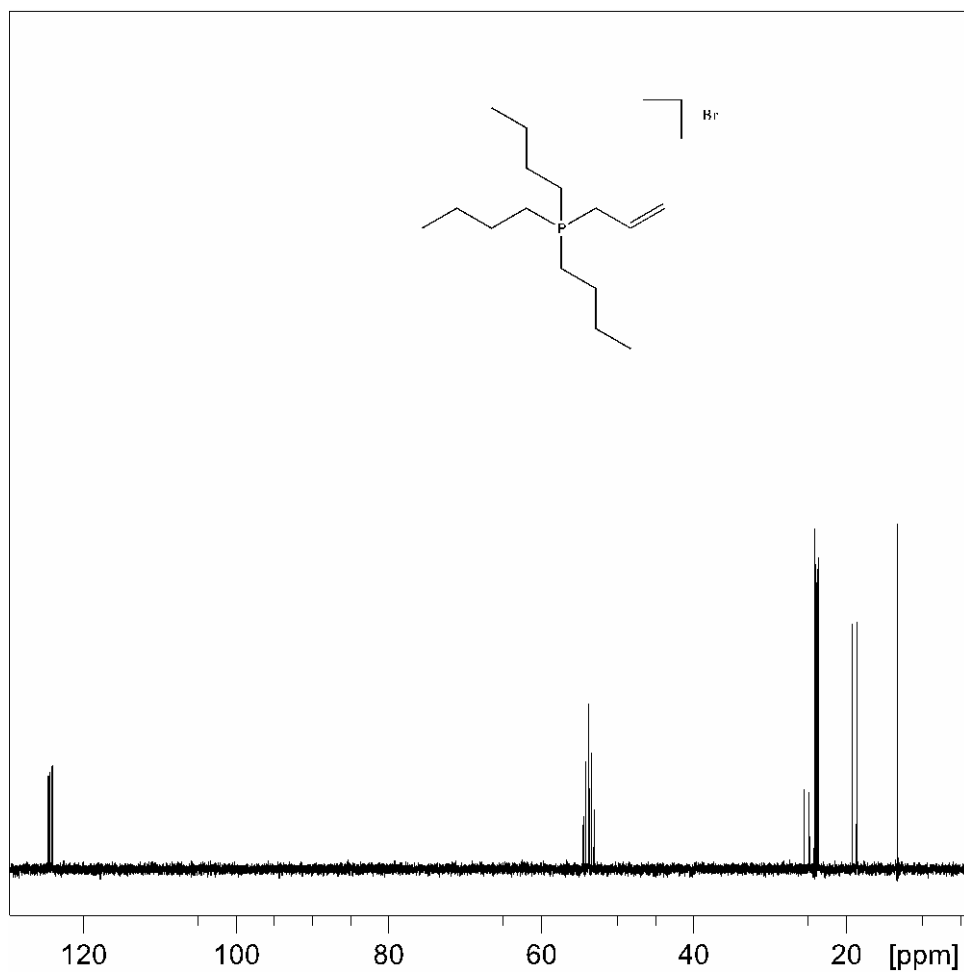
IL 1 : Allyltributylphosphonium bromide.



$^1\text{H-NMR}$ (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).

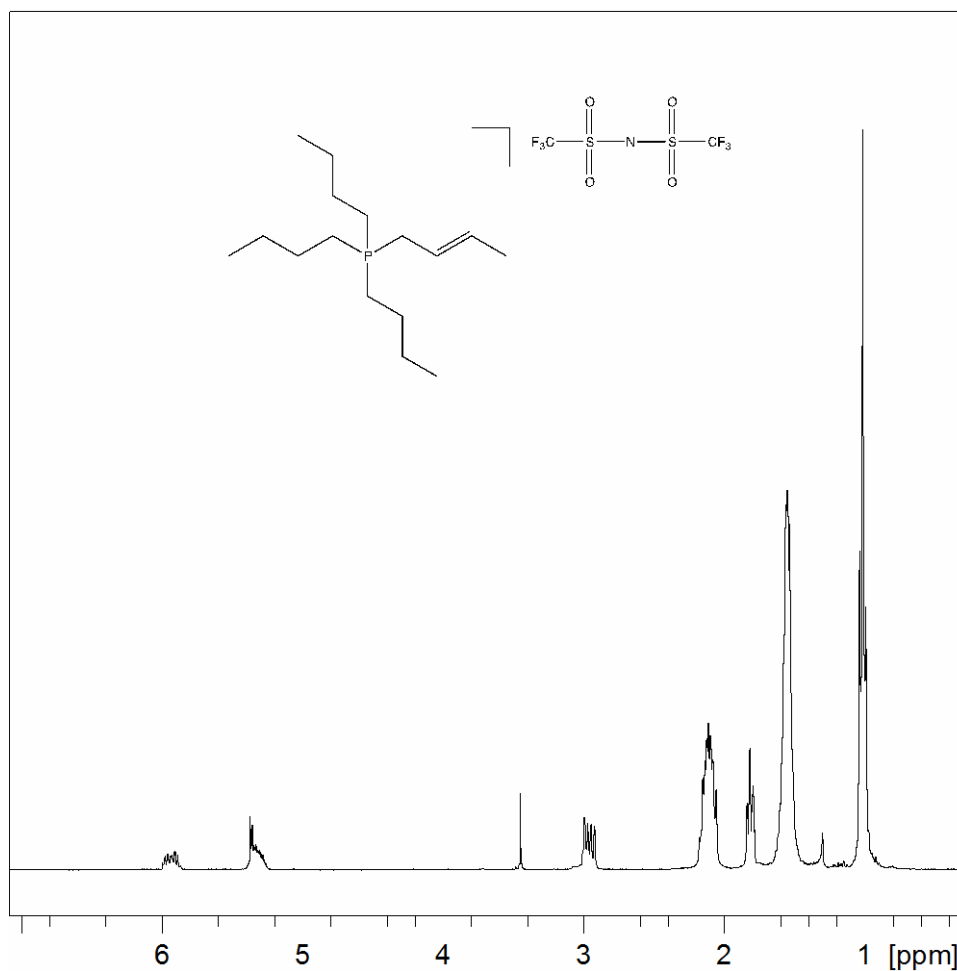


^{31}P -NMR { ^1H } (CD_2Cl_2): δ 31.3 (s).

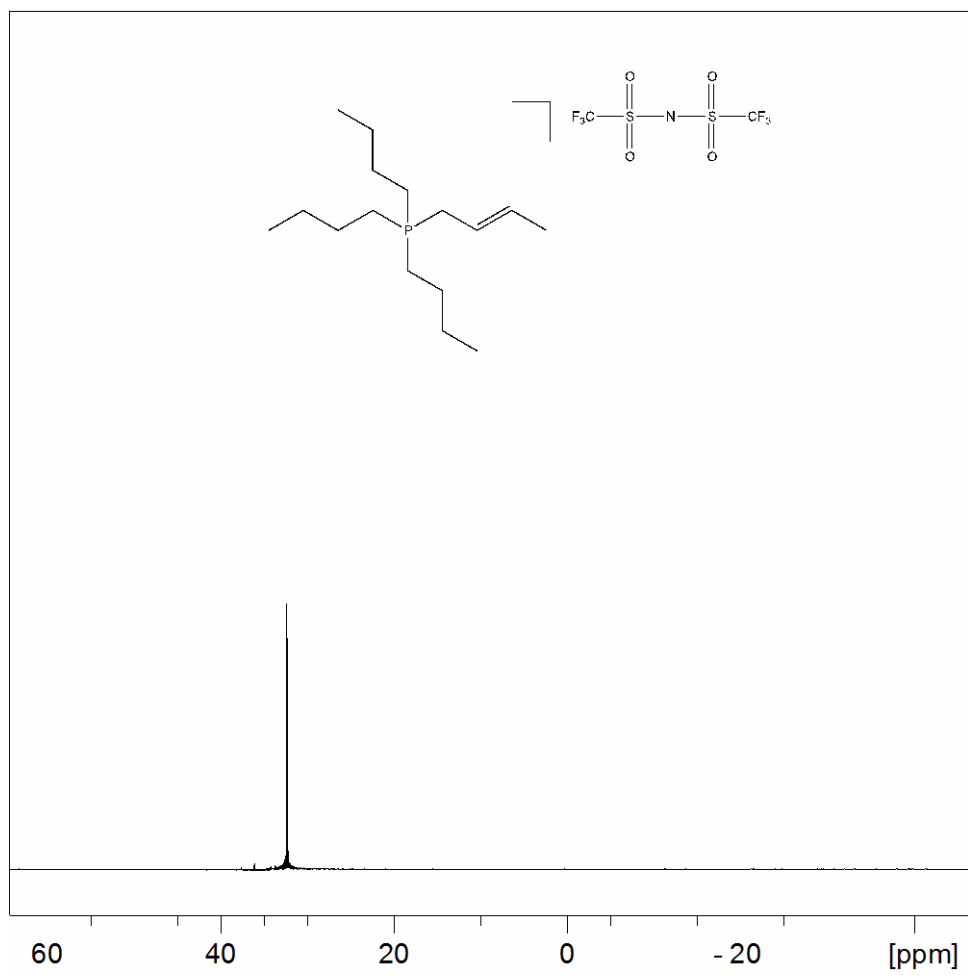


^{13}C -NMR $\{^1\text{H}\}$ (CD_2Cl_2): δ 124.4 (d, ($J_{\text{C,P}} = 9.8$), C_7 of allyl), 124.0 (d, ($J_{\text{C,P}} = 11.7$), C_6 of allyl), 25.0 (d, ($J_{\text{C,P}} = 46.9$), C_5 of allyl), 23.9 (d, ($J_{\text{C,P}} = 15.3$), C_2 of butyl), 23.6 (d, ($J_{\text{C,P}} = 4.7$), C_3 of butyl), 18.8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

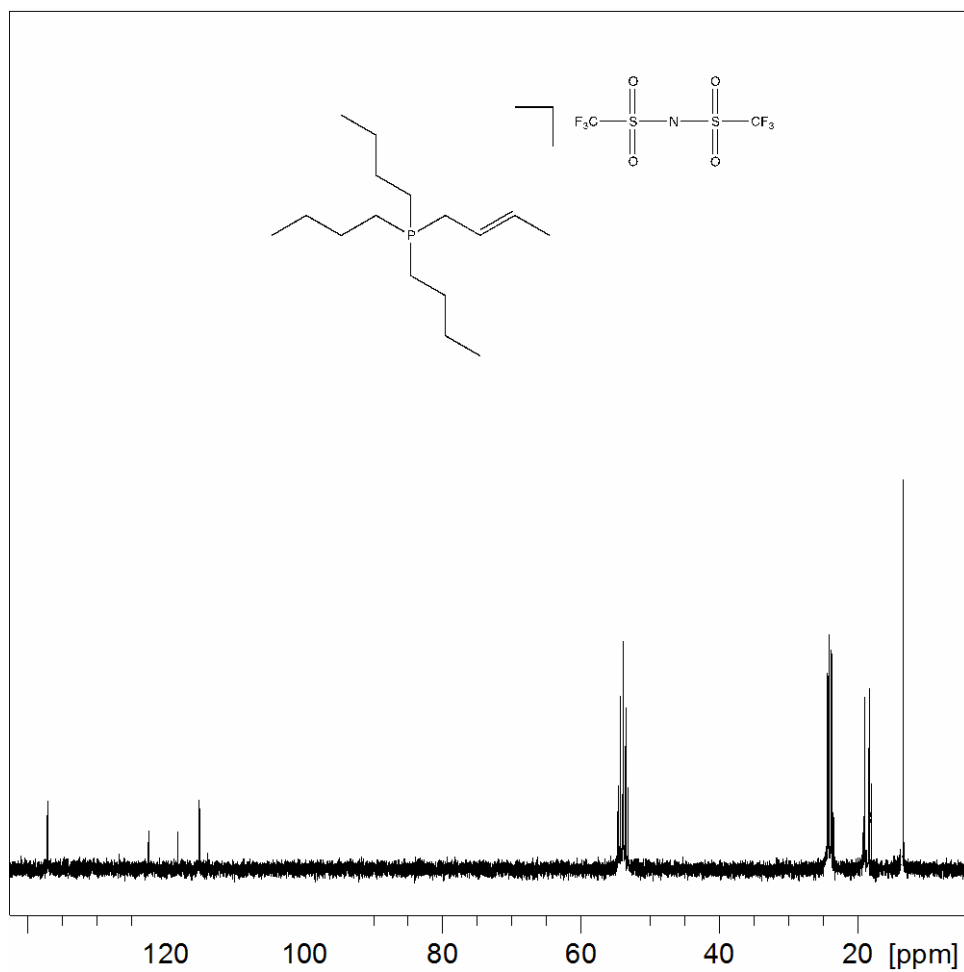
IL 2: Crotyltributylphosphonium bis(trifluoromethane)sulfonimide.



¹H-NMR (CD₂Cl₂): δ 5.90 (m, 1H, H₆ of crotyl), 5.30 (m, 1H, H₇ of crotyl), 2.96 (dd, (J₁ = 14.3, J₂ = 7.5), 2H, H₅ of crotyl), 2.09 (m, 6H, H₁ of butyl), 1.80 (t, (J = 5.7), 3H, H₈ of crotyl), 1.51 (m, 12H, H₂₊₃ of butyl), 1.01 (t, (J = 7.0), 9H, H₄ of butyl).

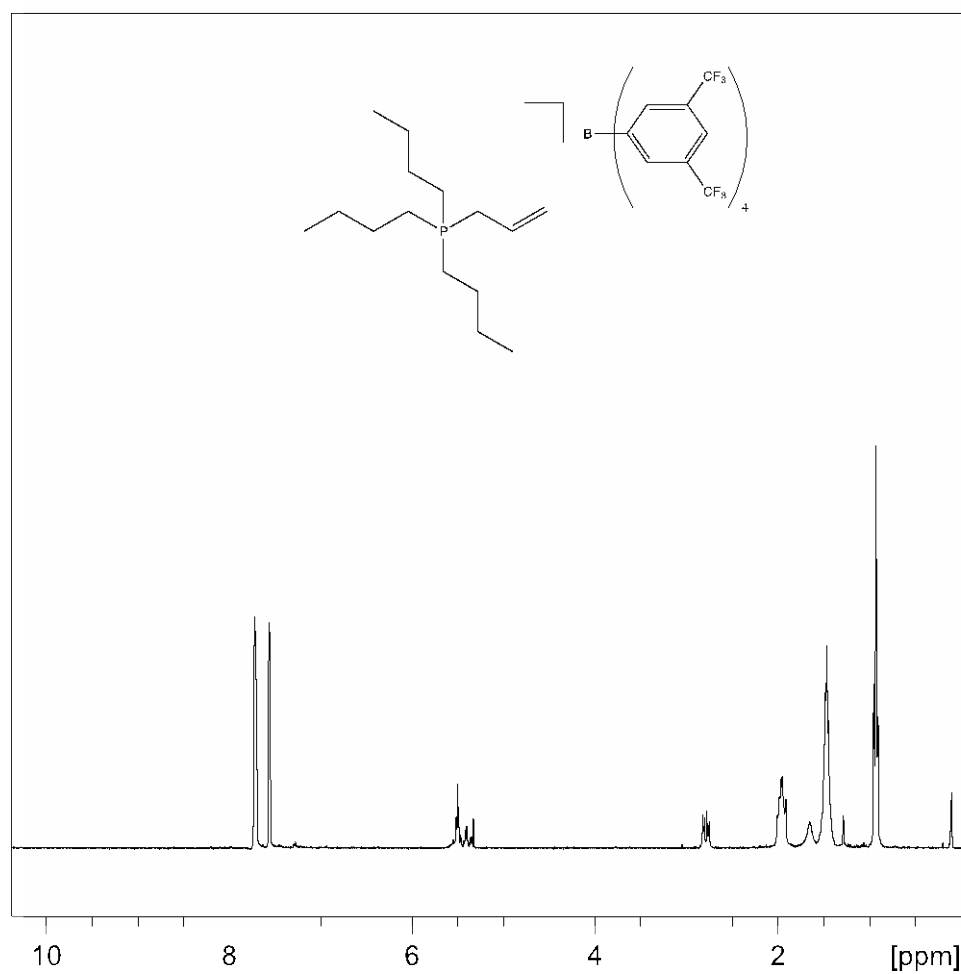


^{31}P -NMR $\{^1\text{H}\}$ (CD_2Cl_2): δ 32.2 (s).

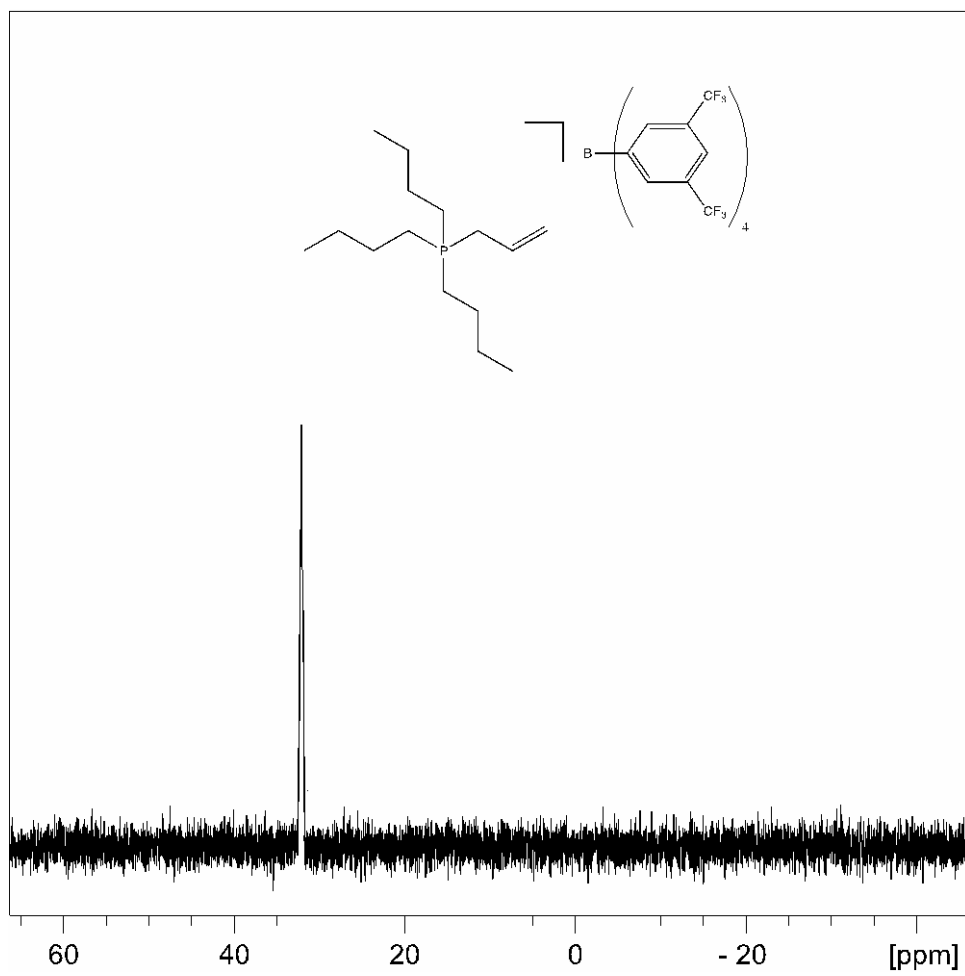


$^{13}\text{C-NMR}$ $\{^1\text{H}\}$ (CD_2Cl_2): δ 137.0 (d, ($J_{\text{C,P}} = 12.1$), C_6 of crotyl), 120.1 (c, ($J_{\text{C,F}} = 322.3$), CF_3 of NTf_2), 115.1 (d, ($J_{\text{C,P}} = 10.7$), C_7 of crotyl), 24.1 (d, ($J_{\text{C,P}} = 15.3$), C_2 of butyl), 23.8 (d, ($J_{\text{C,P}} = 63.6$), C_5 of crotyl), 23.7 (d, ($J_{\text{C,P}} = 4.7$), C_3 of butyl), 18.6 (d, ($J_{\text{C,P}} = 47.1$), C_1 of butyl), 18.2 (s, C_8 of crotyl), 13.3 (s, C_4 of butyl).

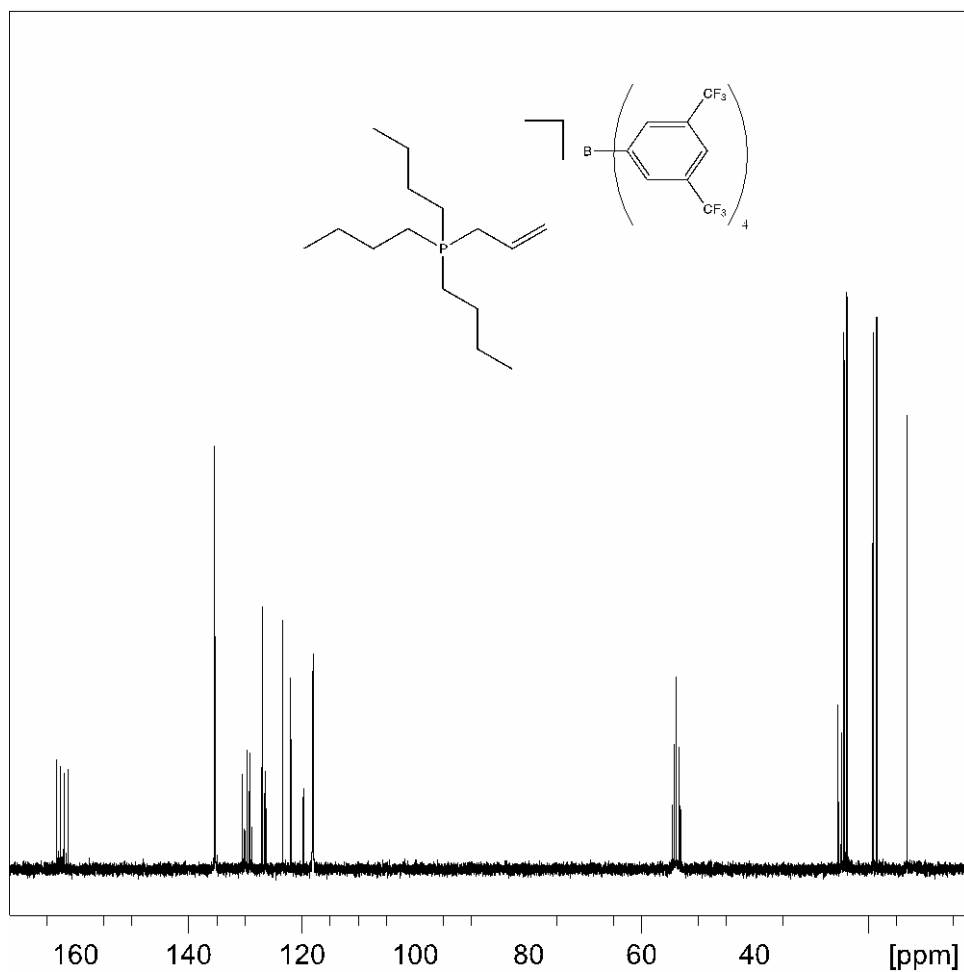
IL 3: Allyltributylphosphonium tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate.



$^1\text{H-NMR}$ (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_I of butyl), 1.46 (m, 12H, H_{2+3} of butyl), 0.92 (t, ($J = 7.0$), 9H, H_4 of butyl).

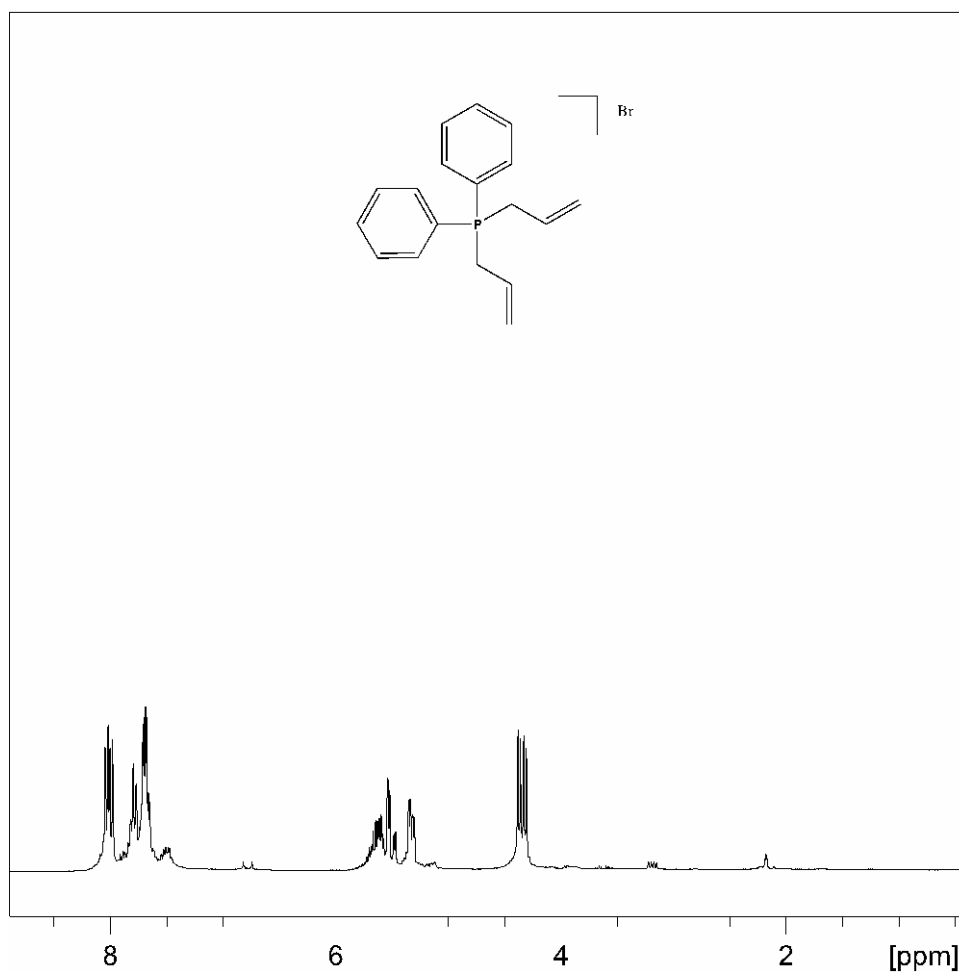


^{31}P -NMR $\{^1\text{H}\}$ (CD_2Cl_2): δ 32.0 (s).

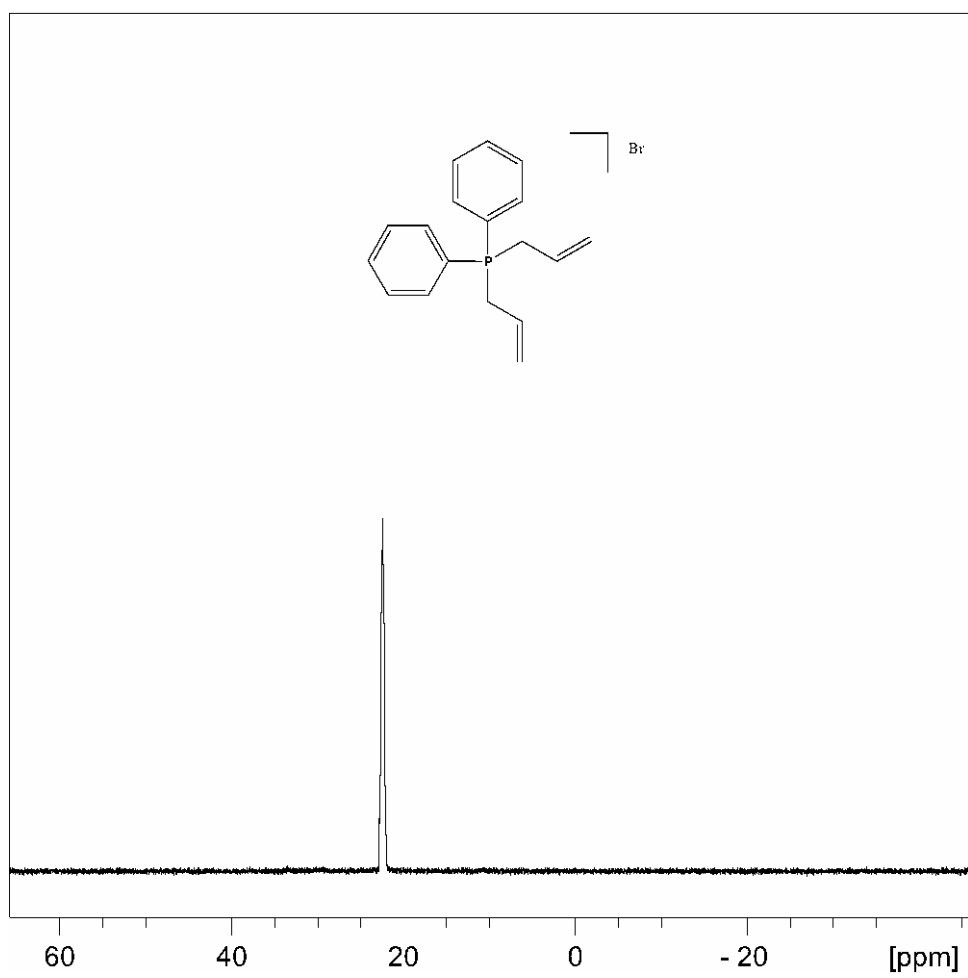


$^{13}\text{C-NMR}$ $\{^1\text{H}\}$ (CD_2Cl_2): δ 162.2 (q, ($J_{\text{C,B}} = 49.9$), C_i of BAr_4'), 135.2 (s, C_o of BAr_4'), 129.3 (q, ($J_{\text{C,F}} = 31.6$), C_m of BAr_4'), 126.3 (d, ($J_{\text{C,P}} = 11.6$), C_6 of allyl), 125.0 (c, ($J_{\text{C,F}} = 272.6$), CF_3 of BAr_4'), 121.9 (d, ($J_{\text{C,P}} = 9.5$), C_7 of allyl), 119.6 (s, C_p of BAr_4'), 24.9 (d, ($J_{\text{C,P}} = 46.9$), C_5 of allyl), 24.1 (d, ($J_{\text{C,P}} = 15.2$), C_2 of butyl), 23.6 (d, ($J_{\text{C,P}} = 4.9$), C_3 of butyl), 18.7 (d, ($J_{\text{C,P}} = 47.5$), C_1 of butyl), 13.0 (s, C_4 of butyl).

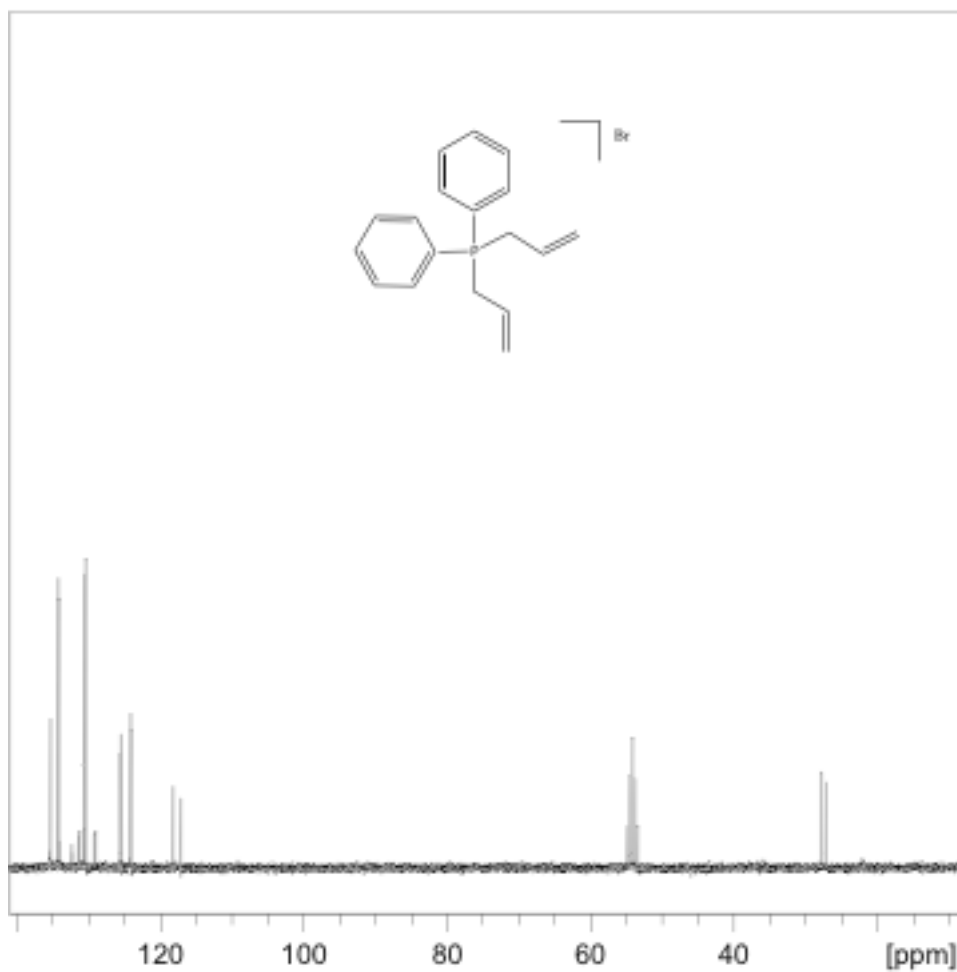
Precursor of IL 4: Diallyldiphenylphosphonium bromide.



¹H-NMR (CD₂Cl₂): 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).

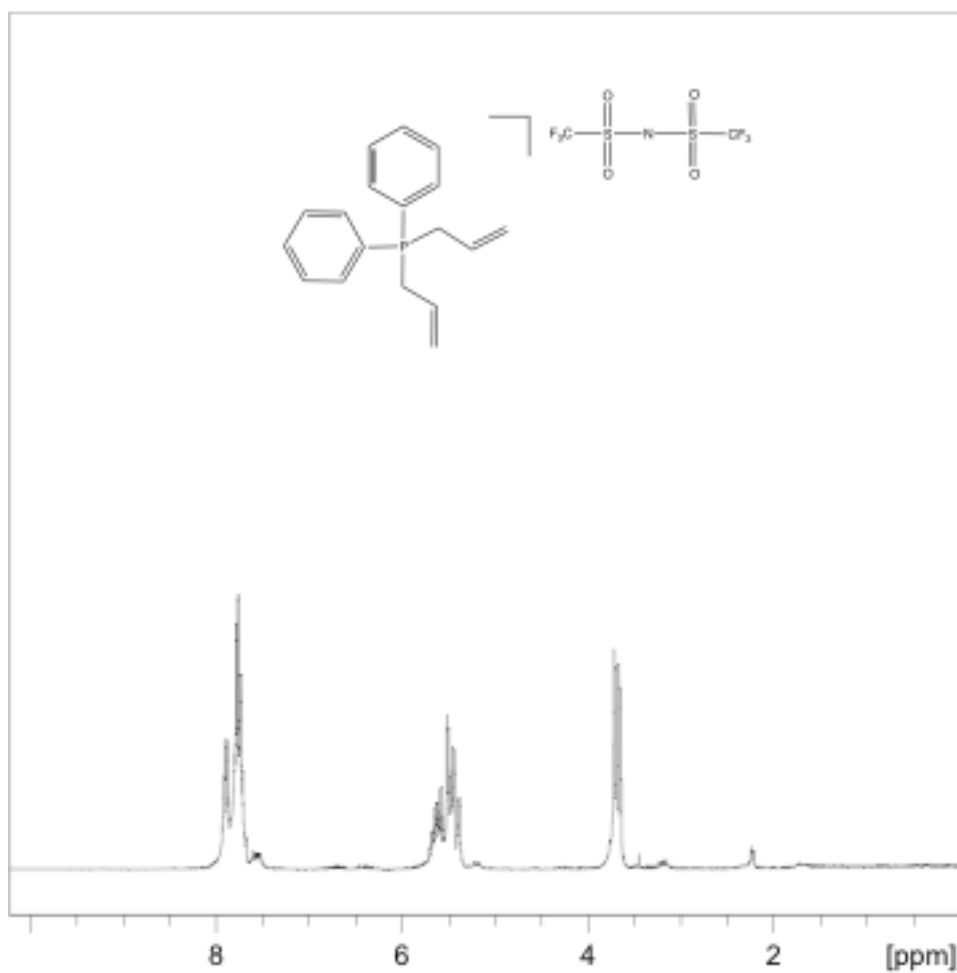


^{31}P -NMR $\{^1\text{H}\}$ (CD_2Cl_2): δ 22.3 (s).

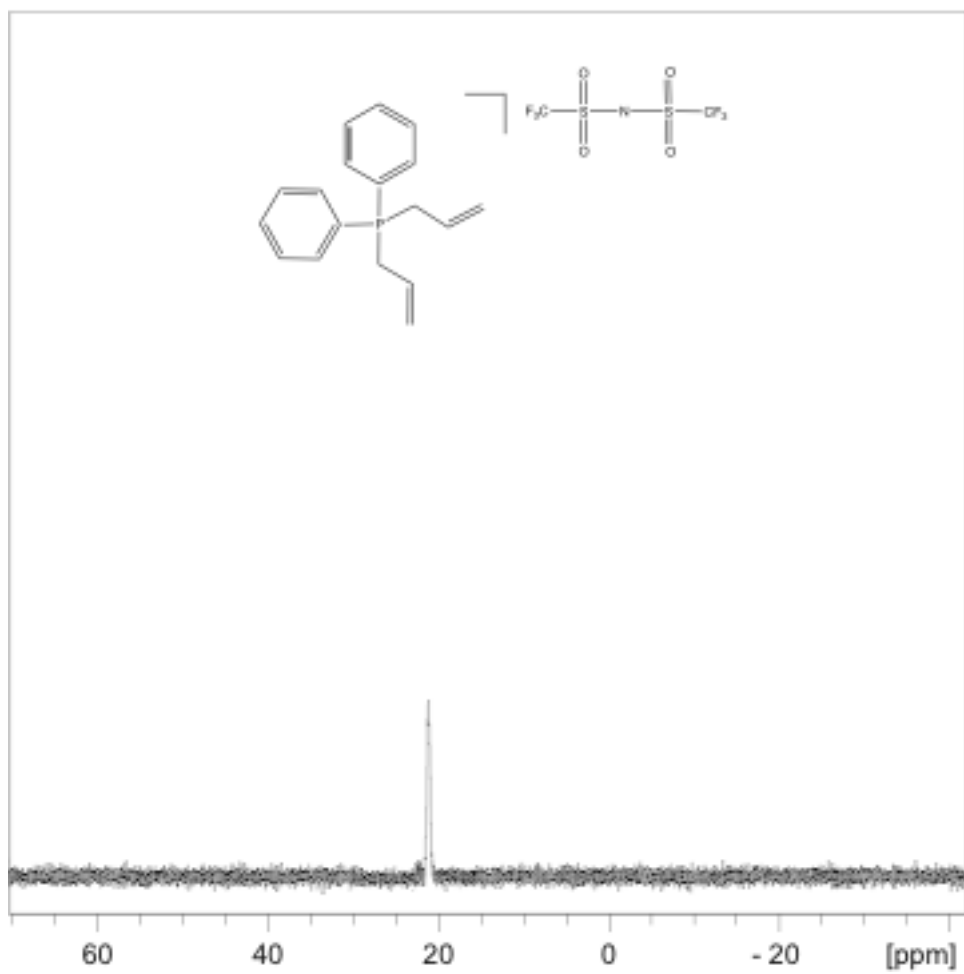


$^{13}\text{C-NMR}$ $\{^1\text{H}\}$ (CD_2Cl_2): δ 135.2 (d, ($J_{\text{C,P}} = 3.0$), C_4 of phenyl), 134.1 (d, ($J_{\text{C,P}} = 9.4$), C_3 of phenyl), 130.4 (d, ($J_{\text{C,P}} = 12.2$), C_2 of phenyl), 125.4 (d, ($J_{\text{C,P}} = 12.9$), C_6 of allyl), 124.0 (d, ($J_{\text{C,P}} = 9.7$), C_7 of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

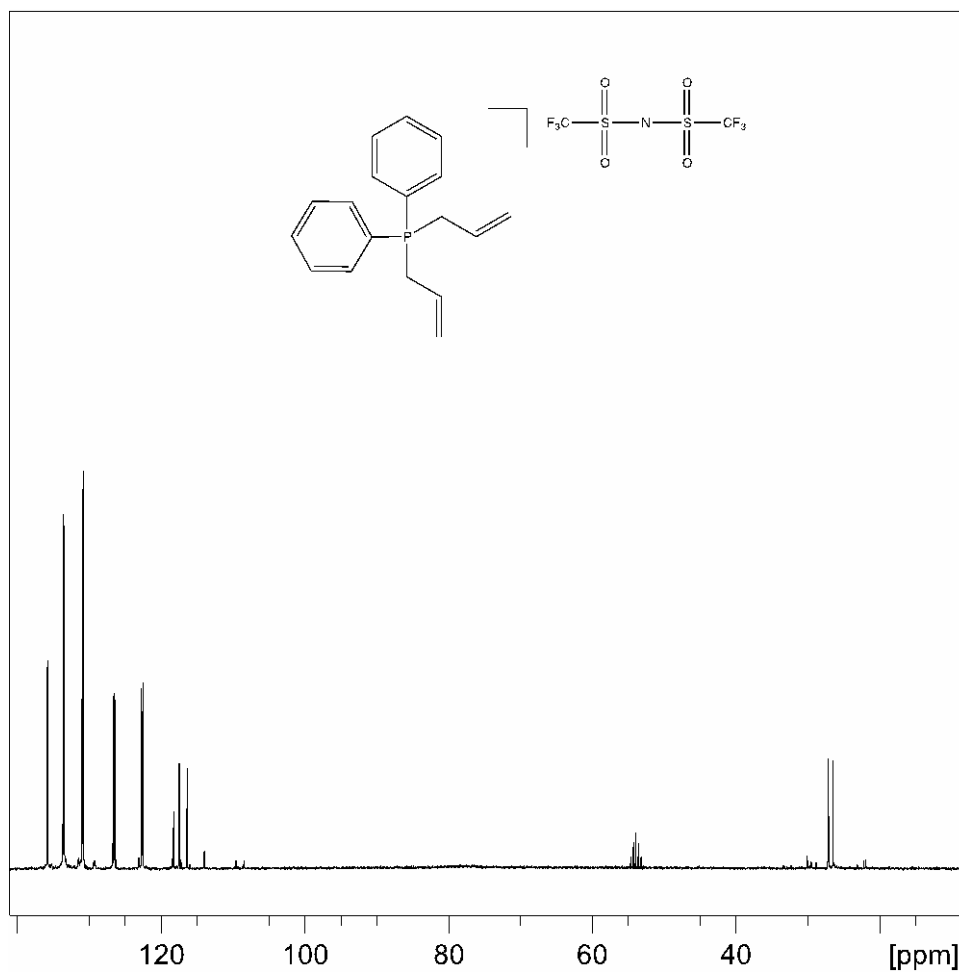
IL 4: Diallyldiphenylphosphonium bis(trifluoromethane)sulfonimide.



$^1\text{H-NMR}$ (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 $\{^1\text{H}\}$ (CD_2Cl_2): δ 21.1 (s).



^{13}C -NMR $\{^1\text{H}\}$ (CD_2Cl_2): δ 135.7 (d, ($J_{\text{C,P}} = 3.0$), C_4 of phenyl), 133.4 (d, ($J_{\text{C,P}} = 9.0$), C_3 of phenyl), 130.8 (d, ($J_{\text{C,P}} = 12.4$), C_2 of phenyl), 126.4 (d, ($J_{\text{C,P}} = 12.8$), C_6 of allyl), 122.5 (d, ($J_{\text{C,P}} = 9.6$), C_7 of allyl), 120.3 (c, ($J_{\text{C,F}} = 321.6$), CF_3 of NTf_2), 116.8 (d, ($J_{\text{C,P}} = 83.0$), C_1 of phenyl), 26.8 (d, ($J_{\text{C,P}} = 50.3$), C_5 of allyl).

HRMS data of phosphonium salts.

IL1: Allyltributylphosphonium bromide.

HRMS (ESI⁺, *m/z*) calcd for (C₁₅H₃₂P)⁺ (M⁺): 243.2237, found: 243.2223; MS (ESI, *m/z*): 79 [⁷⁹Br⁻, 100%], 81 [⁸¹Br⁻, 95%].

IL 2: Crotyltributylphosphonium bis(trifluoromethane)sulfonimide.

HRMS (ESI⁺, *m/z*) calcd for (C₁₆H₃₄P)⁺ (M⁺): 257.2393, found: 257.2374; HRMS (ESI, *m/z*) calcd for (C₂F₆NO₄S₂)⁻ (NTf₂⁻): 279.9178, found 279.9191.

IL3: Allyltributylphosphonium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate.

HRMS (ESI⁺, *m/z*) calcd for (C₁₅H₃₂P)⁺ (M⁺): 243.2237, found: 243.2228; HRMS (ESI, *m/z*) calcd for (C₃₂H₁₂BF₂₄)⁻ (BAr'₄)⁻: 863.0654, found 863.0650.

Precursor of IL 4: Diallyldiphenylphosphonium bromide.

HRMS (ESI⁺, *m/z*) calcd for (C₁₈H₂₀P)⁺ (M⁺): 267.1298, found: 267.1308; MS (ESI, *m/z*): 79 [⁷⁹Br⁻, 100%], 81 [⁸¹Br⁻, 95%].

IL 4: Diallyldiphenylphosphonium bis(trifluoromethane)sulfonimide.

HRMS (ESI⁺, *m/z*) calcd for (C₁₈H₂₀P)⁺ (M⁺): 267.1298, found: 267.1292; HRMS (ESI, *m/z*) calcd for (C₂F₆NO₄S₂)⁻ (NTf₂⁻): 279.9178, found 279.9182.

References.

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2. M. Brookhart, B. Grant, A. F. Volpe Jr., *Organometallics*, 11, (1992) 3920-3922.
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