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Combinations of IL-oxidizer/IL-fuel as greener hypergols

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General methods: ^1H , ^{13}C , and ^{11}B NMR spectra were collected on a Bruker AVANCE 600 spectrometer operating at 600 MHz, 151 MHz and 193 MHz, respectively. All ^1H and ^{13}C chemical shifts were measured relative to internal residual protons or carbons in the lock solvents and are referenced to Me_4Si (0.0 ppm). The ^{11}B chemical shifts were referenced to external $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. The glass transition and decomposition points were recorded using a Mettler-Toledo DSC1 calorimeter at a scan rate of $10\text{ }^\circ\text{C min}^{-1}$ in closed aluminum containers. Infrared (IR) spectra were recorded by using KBr pellets on a Thermo Nicolet 380 FTIR spectrometer. Densities were measured at $25\text{ }^\circ\text{C}$ using a Micromeritics Accupyc 1340 gas pycnometer. High-resolution mass spectra were performed on a Bruker QTOF mass spectrometer. Viscosity was measured with a TA Rheometer DHR-2 at $25\text{ }^\circ\text{C}$. Elemental analyses were obtained by using a Vario EL cube elemental analyzer. Specific impulse data were calculated by Explo5 (version 6.02) software. The ignition process was recorded at 1000 frames per second with a high-speed camera.

Reactants: All the organic solvents used in the study were of analytical grade without further purification unless otherwise noted. N-methylimidazole (99%, Energy Chemical), 1-methyl-1,2,4-triazole (99%, Energy Chemical), 1, 3-propane sulfonate (98%, Aladdin), chlorosulfonic acid (99%, Energy Chemical), dichloromethane (Xilong Scientific, 99.5%), N-ethylimidazole (99%, Energy Chemical), N-butylimidazole (98%, Aladdin), 1-allylimidazole (98%, Aladdin), iodoethane (99%, Energy Chemical), 1-iodobutane (99%, Energy Chemical), 3-bromopropene (99%, Energy Chemical), 1,3-propane sulfone (99%, Aladdin), sodium borohydride (98%, FUCHEN), diglyme (SCRC, 99.5%), boron trifluoride ether complex $\text{BF}_3 \cdot \text{OEt}_2$ (98%, SCRC).

Synthesis of the IL Oxidizers

Procedure for preparation of IL oxidizer 1-methyl-3-sulfoimidazolium nitrate (O1): The synthesis used is a slight modification of the literature procedure.¹ A dichloromethane solution (50 mL) of 1-methylimidazole (8.20 g, 10 mmol) was placed in a round-bottomed flask (250 mL), and a dichloromethane solution of chlorosulfonic acid (1.20 g, 10.3 mmol) was added dropwise over a period of 30 min at room temperature. The reaction mixture was then stirred for another 30 min, and the dichloromethane was decanted after the reaction mixture was allowed to settle for 5 min. The residue was washed with dry dichloromethane ($3 \times 30\text{ mL}$) to remove excess of chlorosulfonic acid and dried under vacuum to give 1-methyl-3-sulfoimidazolium chloride, $[\text{Msim}]\text{Cl}$. Then, $[\text{Msim}]\text{Cl}$ (0.993 g, 5 mmol) was placed into a round-bottomed flask with a magnetic stirrer, and 100 % nitric acid (0.315 g, 5 mmol) was added dropwise to the flask at room temperature under a continuous flow of nitrogen to remove the HCl gas that is produced. The resulting

mixture was constantly stirred until clarification occurred. The flask and the viscous product were transferred to a vacuum line and kept under vacuum for 5 min at $\sim 0\text{ }^{\circ}\text{C}$ to give 1-methyl-3-sulfoimidazolium nitrate as a viscous light yellow oil. Yield 96% (1.10 g). ^1H NMR (600 MHz, d^6 -DMSO) $\delta = 14.30$ (s, 1H, OH), 9.09 (s, 1H, CH), 7.72 (t, $J = 1.6$ Hz, 1H, CH), 7.68 (t, $J = 1.6$ Hz, 1H, CH), 3.90 ppm (s, 3H, CH₃). ^{13}C NMR (151 MHz, d^6 -DMSO) $\delta = 135.81, 123.13, 119.69, 35.34$ ppm. HRMS (ESI) m/z : calcd for C₃H₆N₃SO₃ [M]⁺: 163.0177, found: 163.0180; C₄H₇N₂ [M-SO₃]⁺: 84.0609, found: 83.0590; calcd for [NO₃]⁻: 61.9883, found: 61.9850.

The procedure for preparation of IL oxidizers (O2 and O3): 1-Methylimidazole (4.15 g, 50 mmol) was combined with toluene (100 mL). First, 1, 3-propane sulfonate (6.1 g, 50 mmol) was added to the solution. The reaction mixture was added to a flask which was equipped with a reflux condenser and stirred at 80 $^{\circ}\text{C}$ for 12 h. After the reaction was completed, the reaction was allowed to cool, and then filtered. The solids were washed with ethyl acetate (3 \times 50 mL). After vacuum drying, the white zwitterionic precursor (9.50 g) was obtained in a yield of 93%. The zwitterionic precursor (2.04 g, 10 mmol) was ground in an agate mortar, and 100% HNO₃ (1.90 g, 30 mmol) was added dropwise into the mortar while grinding. After grinding to clarification, the resulting liquid was transferred into a round-bottom flask and stirred for 3 hours. The liquid was washed with dichloromethane (3 \times 50 mL), and then dissolved in 20 mL acetonitrile. Activated carbon (1 g) was added to the solution. Before filtration to obtain the product solution, the mixture was stirred for 30 min. The filtrate was reduced via rotary evaporation. The resulting liquid was dried under high vacuum at 50 $^{\circ}\text{C}$ for 12 hours to collect a clear light yellow liquid (**O2**).² The other IL oxidizers (**O3**) was synthesized in the same way, except 1-methylimidazole was replaced with 1-methyl-1,2,4-triazole.

1-methyl-3-(3-sulfopropyl)-imidazolium nitrate (O2): Yield 60.0% (1.60 g). ^1H NMR (600 MHz, CD₃CN) $\delta = 14.79$ (s, 1H, OH), 8.54 (s, 1H, CH), 7.45 (t, $J = 1.6$ Hz, 1H, CH), 7.36 (t, $J = 1.6$ Hz, 1H, CH), 4.36 (t, $J = 7.0$ Hz, 2H, CH₂), 3.84 (s, 3H, CH₃), 2.91 (t, $J = 7.2$ Hz, 2H, CH₂), 2.31 ppm (p, $J = 7.1$ Hz, 2H, CH₂). ^{13}C NMR (151 MHz, CD₃CN) $\delta = 137.11, 124.47, 123.07, 48.52, 47.90, 36.60, 26.11$ ppm; HRMS (ESI) m/z : calcd for cation C₇H₁₃N₂O₃S [M]⁺: 205.0641, found: 205.0649; calcd for anion NO₃⁻ [M]⁻: 61.9884, found: 61.9963.

1-methyl-4-(3-sulfopropyl)-1,2,4-triazolium nitrate (O3): Yield 66.8% (1.79 g). ^1H NMR (600 MHz, CD₃CN) $\delta = 14.92$ (s, 1H, OH), 9.44 (s, 1H, CH), 8.67 (s, 1H, CH), 4.47 (t, $J = 7.1$ Hz, 2H, CH₂), 4.07 (s, 3H, CH₃), 2.96 (t, $J = 7.1$ Hz, 2H, CH₂), 2.36 ppm (p, $J = 7.1$ Hz, 2H, CH₂); ^{13}C NMR (151 MHz, CD₃CN) $\delta = 144.88, 143.03, 47.68, 47.06, 39.43, 25.64$ ppm; HRMS (ESI) m/z : calcd for cation C₇H₁₃N₂O₃S [M]⁺: 206.0594, found: 206.0606; calcd for anion NO₃⁻ [M]⁻: 61.9884, found: 61.9728

Synthesis of the IL Fuels

Preparation of ionic liquid precursors. According to the reported methods in the literature, 3-butyl-1-methylimidazolium iodide,³ 1-butyl-3-ethylimidazolium iodide,⁴

and 1,3-diallylimidazolium bromide⁵ were prepared by quaternization of 1-methylimidazole, 1-butylimidazole and 1-allylimidazole with 1-iodobutane, iodoethane and 3-bromopropene, respectively.

General procedure for preparation of [B₆H₇]-based ionic liquids (F1-F3). The synthesis used is referenced by our previous work.⁶ In a 500 mL, three-necked flask, 15 g (0.4 mol) of powdered sodium borohydride was added to 250 cm³ of anhydrous diglyme. The flask was equipped with a magnetic stirrer, a 150 cm³ pressure equalizing funnel, a condenser connected to an oil bubbler and a nitrogen inlet. The flask was placed in a silicone oil bath, flushed with nitrogen and the bath heated to 55-60 °C. The effluent gas was bubbled through acetone solution to destroy any diborane which may have formed. The dropping funnel was filled with diglyme (80 mL) and 25 cm³ (0.19 mol) of distilled BF₃ O(C₂H₅)₂. With the flow of nitrogen stopped and the nitrogen inlet closed, addition of BF₃ O(C₂H₅)₂ was started and continued over a period of 90 min. The temperature of the oil bath was raised to 100 °C and kept at this temperature for 1 h. Then the temperature was raised to 165-180 °C and the solution was refluxed for 36 h. A gentle stream of nitrogen was allowed to flow, heating was stopped and the flask which contained a white precipitate was cooled to 50 °C. The diglyme solution was filtered, and the white precipitate was collected and added to the solid remaining in the round-bottomed flask. The reaction flask was placed in an ice bath and 50 cm³ of cold water was added to the solid; a vigorous reaction occurred and the mixture was stirred until effervescence subsided. The aqueous solution was filtered and the solid borates were washed with 10 cm³ of cold water. The hydrochloric acid solution (1 M) was added dropwise into the solution, adjusting pH to ~ 7.0. The ionic liquid precursor (30 mmol) was dissolved in water (20 mL) and added to the aqueous filtrate. The mixture was stirred until the system was emulsified. The mixture was poured into a separating funnel, allowed to stand for several hours until stratification occurred (in this process, heating accelerated the two-phase separation). After the aqueous layer was removed (another small portion of hydrochloric acid solution was dropped into the aqueous solution to test the completion of precipitation), the upper layer was dissolved in 15 mL acetonitrile, and poured into a round-bottom flask after drying over anhydrous sodium sulfate. The solvent was removed by evaporation leaving behind the required ionic liquid. After further drying under a dynamic vacuum at ambient temperature, a pure ionic liquid was obtained.

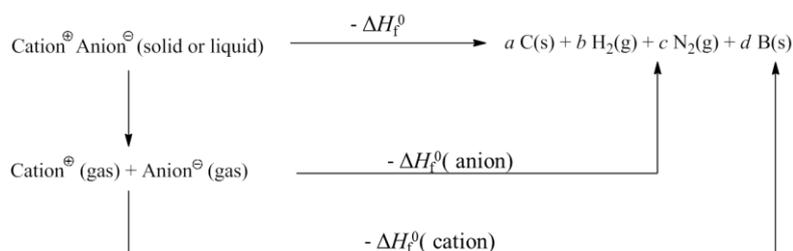
[3-butyl-1-methylimidazolium][B₆H₇] (F1): ¹¹B NMR (193 MHz, CD₃CN) δ -13.13 ppm; ¹H NMR (600 MHz, CD₃CN) δ = 8.52 (s, 1H, CH), 7.42 (t, *J* = 1.7 Hz, 1H, CH), 7.38 (t, *J* = 1.6 Hz, 1H, CH), 4.17 (t, *J* = 7.3 Hz, 2H, CH₂), 3.86 (s, 3H, CH₃), 1.84 (ddd, *J* = 15.0, 11.2, 7.5 Hz, 2H, CH₂), 1.41 – 1.28 (m, 2H, CH₂), 1.04 – 0.90 (t, *J* = 7.4 Hz, 3H, CH₃), 0.62 – 1.39 (m, 11H, B-H^{exo} overlapped by CH₂ and CH₃), -5.55 ppm (s, 1H, B-H^{fac}); ¹³C NMR (151 MHz, CD₃CN) δ = 136.66, 124.46, 123.09, 50.18, 36.87, 32.39, 19.80, 13.55 ppm. IR (KBr): σ = 3147, 3113, 2960, 2934, 2874, 2529, 1571, 1463, 1167, 1056, 833, 748, 619 cm⁻¹. Elemental analysis: calcd (%) for C₈H₂₂B₆N₂: C 45.51, H 10.50, N 13.27; found: C 45.41, H 9.96, N 13.43.

[1-butyl-3-ethylimidazolium][B₆H₇]⁺ (F2): ¹H NMR (600 MHz, CD₃CN) δ = 8.55 (s, 1H, CH), 7.44 (t, *J* = 1.6 Hz, 1H, CH), 7.42 (t, *J* = 1.7 Hz, 1H, CH), 4.21 (q, *J* = 7.3 Hz, 2H, CH₂), 4.16 (t, *J* = 7.3 Hz, 2H, CH₂), 1.85 (ddd, *J* = 15.0, 11.2, 7.5 Hz, 2H, CH₂), 1.50 (t, *J* = 7.3 Hz, 3H, CH₃), 1.36 (dq, *J* = 14.8, 7.4 Hz, 2H, CH₂), 0.97 (t, *J* = 7.4 Hz, 3H, CH₃), 0.49 – 1.69 (m, 14H, B-H^{exo} overlapped by CH₂ and 2CH₃), -5.55 ppm (s, 1H, B-H^{fac}); ¹³C NMR (151 MHz, CD₃CN) δ = 136.77, 124.57, 123.20, 118.24, 50.26, 36.90, 32.49, 19.89, 13.61 ppm; ¹¹B NMR (193 MHz, CD₃CN) δ = -13.14 ppm; IR (KBr): σ = 3140, 3108, 2961, 2935, 2875, 2531, 1595, 1563, 1465, 1385, 1163, 1108, 1029, 833, 748, 638, 612 cm⁻¹. Elemental analysis: calcd (%) for C₉H₂₄B₆N₂: C 48.01, H 10.74, N 12.44; found: C 48.50, H 10.46, N 13.06.

[1,3-diallylimidazolium][B₆H₇]⁺ (F3): ¹H NMR (600 MHz, CD₃CN) δ = 8.57 (s, 1H), 7.43 (d, *J* = 1.6 Hz, 2H), 6.06 (ddt, *J* = 16.6, 10.3, 6.2 Hz, 2H, 2CH), 5.43 (ddd, *J* = 18.1, 13.7, 1.0 Hz, 4H, 2CH₂), 4.81 (d, *J* = 6.2 Hz, 4H, 2CH₂), 1.65 – 0.47 (m, 6H, B-H^{exo}), -5.55 ppm (s, 1H, B-H^{fac}); ¹³C NMR (151 MHz, CD₃CN) δ = 136.42, 131.51, 123.53, 121.97, 118.25, 52.58 ppm; ¹¹B NMR (193 MHz, CD₃CN) δ = -13.13 ppm; IR (KBr): σ = 3137, 3108, 3079, 2983, 2530, 1562, 1423, 1161, 991, 943, 841, 745, 635 cm⁻¹. Elemental analysis: calcd (%) for C₉H₂₀B₆N₂: C 48.88, H 9.13, N 12.67; found: C 49.21, H 8.86, N 12.74.

Theoretical Studies

In this study, structure optimization, the single-point energies, and the heats of formation of the ionic liquids were calculated and studied. All of the theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.⁷ For all of the new ionic liquids, geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G(d, p) basis set. Single energy points were calculated at the MP2/6-311++G(d, p) level of theory. For all of the compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Heats of formation (HOFs, Δ*H*_f) of all of the ionic liquids were calculated based on a Born–Haber energy cycle (Scheme 2).⁸



Scheme S1. Born-Haber cycle for the formation of ionic liquids; The number of moles of the respective products are given by a-d.

$$\Delta H_f (\text{ionic salts, 298K}) = \Sigma \Delta H_f (\text{cation, 298K}) + \Sigma \Delta H_f (\text{anion, 298K}) - \Delta H_L \quad (1)$$

in which ΔH_L is the lattice energy of the ionic salts, which could be predicted by equation (2) proposed by et al.⁹

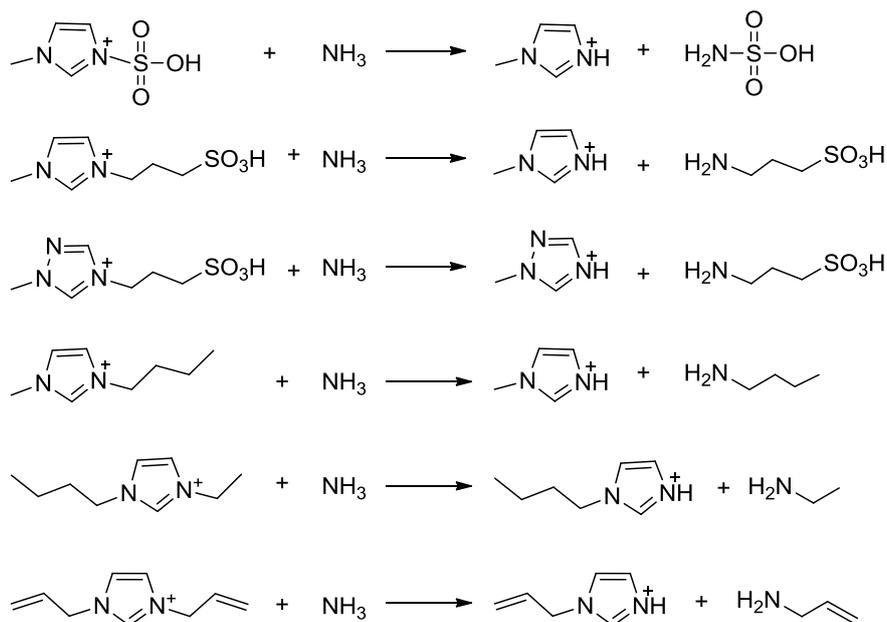
$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

for M_pX_q salts, $n_M = n_X = 6$ for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form shown in equation (3).

$$U_{\text{POT}}(\text{kJ mol}^{-1}) = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

For MX (1:1) salts, where $\gamma = 1981.2 \text{ kJ mol}^{-1} \text{ cm}$ and $\delta = 103.8 \text{ kJ mol}^{-1}$. ρ_m is density (g cm^{-3}) and M_m is the chemical formula mass of the ionic material.

The heats of formation (ΔH_f) of the cations were computed by using the method of isodesmic reactions.¹⁰ The isodesmic reactions for cations are shown in Scheme S2. The enthalpy of isodesmic reactions ($\Delta_r H_{298}$) is obtained by combining the MP2/6-311+G(d, p) energy difference for the reaction, the scaled zero-point energy, and other thermal factors.



Scheme S2. Isodesmic reactions for the ΔH_f calculation.

Table S2. Enthalpies of gas-phase species in isodesmic reactions (based on G2 method)

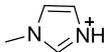
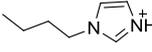
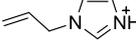
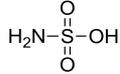
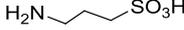
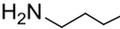
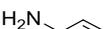
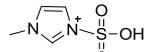
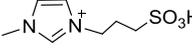
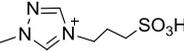
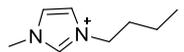
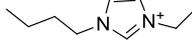
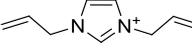
ions or compounds	ΔH_f (kJ mol ⁻¹)
	693.68
	805.98
	610.47
	770.21
	-506.52
	-548.74
	-88.80
	-50.49
	59.68
	-45.10

Table S3. Enthalpies of the gas-phase species of cations based on isodesmic reactions

Cations	ZPE	H _{corr}	E(MP2)	ΔH_{corr} (kJ/mol)	ΔH_f (kJ/mol)
	0.125938	0.136892	-888.0245743	-887.89	283.19
	0.212191	0.227314	-1005.645463	-1005.42	150.88
	0.200260	0.215221	-1021.652296	-1021.44	247.93
	0.225992	0.238125	-421.9972302	-421.77	588.31
	0.254666	0.26797	-461.1971790	-460.94	555.62
	0.207397	0.219484	-458.7547526	-458.54	818.59

^[a] Zero-point correction (Hartree); ^[b] Thermal correction to enthalpy (Hartree); ^[c] Total energy calculated by B3LYP/6-31+G**//MP2/6-311++G** method (Hartree); ^[d] Heat of formation (kJ/mol).

Table S4. Calculated enthalpies of ten new ionic liquids

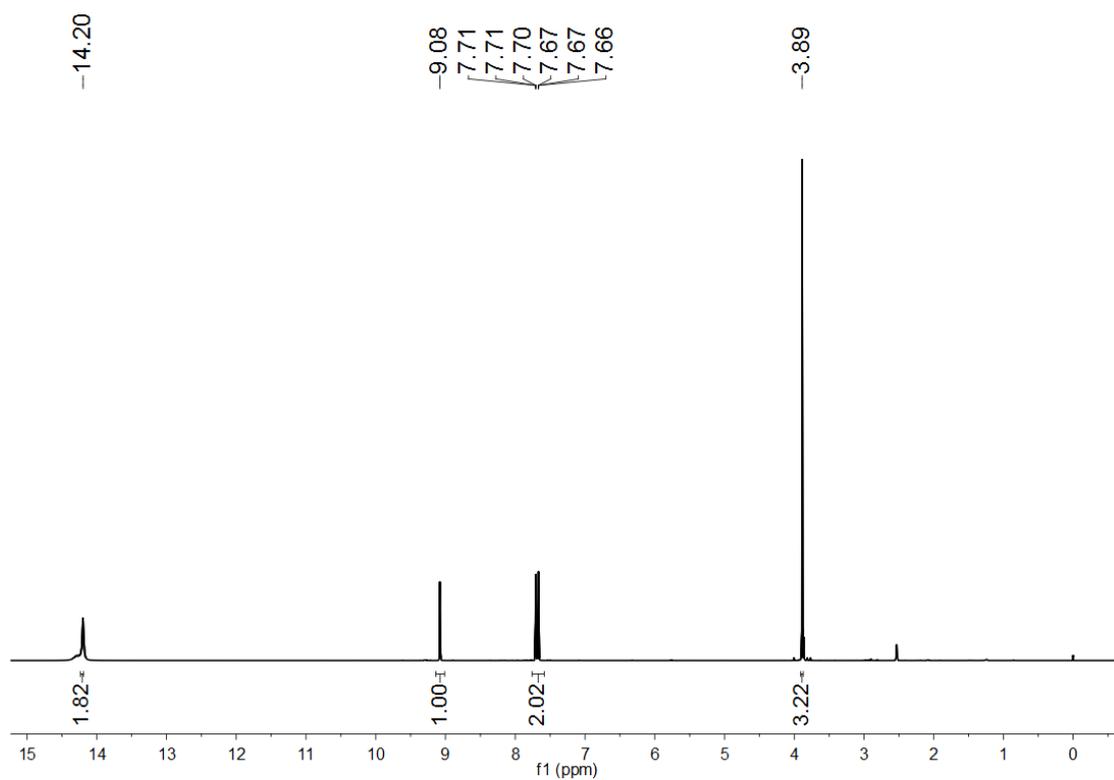
ILs	ΔH_f cations (kJ/mol)	ΔH_f anions(kJ/mol)	ΔH_L (kJ/mol)	ΔH_f salts(kJ/mol)
O1	283.19	-320.26	481.49	-518.56
O2	150.88	-320.26	456.07	-625.45
O3	247.93	-320.26	458.90	-531.23
F1	588.31	-8.12	432.72	147.49
F2	610.47	-8.12	424.59	177.76
F3	818.59	-8.12	430.69	379.78

Table S5. Data of the I_{sp} and ΔH_c

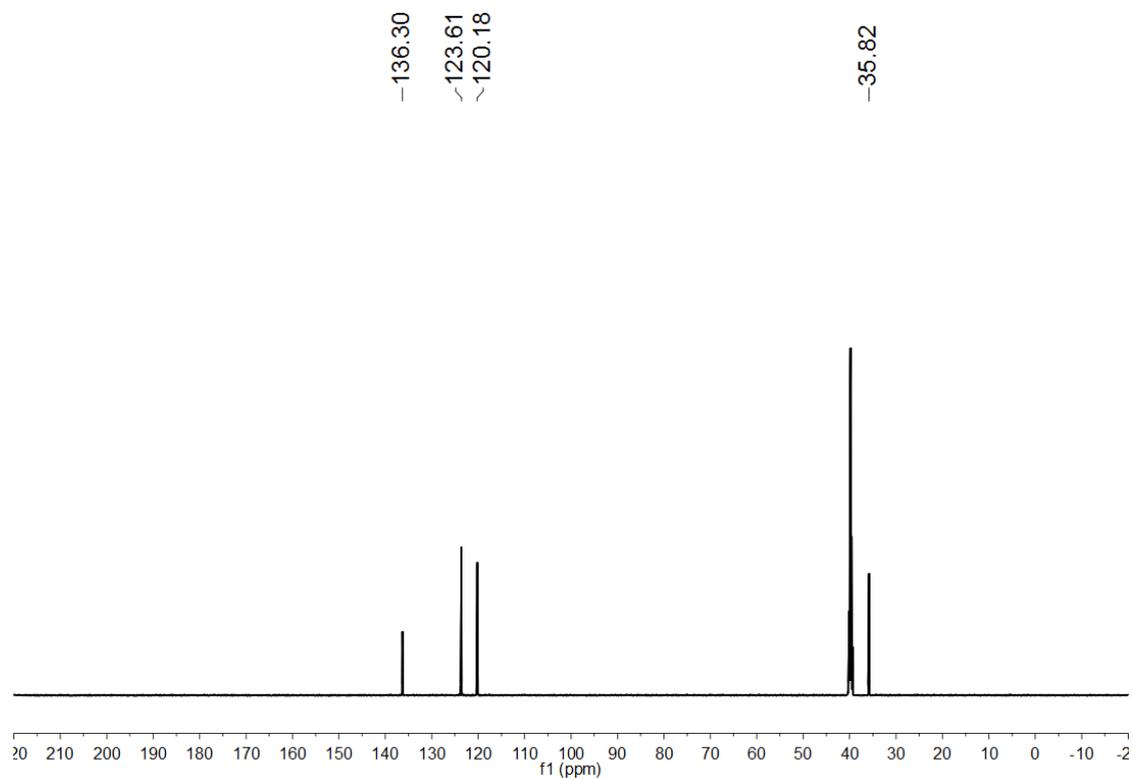
ILs	F1		F2		F3	
	$I_{sp}^{[a]}$ (s)	$\Delta H_c^{[b]}$ (J g ⁻¹)	$I_{sp}^{[a]}$ (s)	$\Delta H_c^{[b]}$ (J g ⁻¹)	$I_{sp}^{[a]}$ (s)	$\Delta H_c^{[b]}$ (J g ⁻¹)
O1	204.0	-3011.0	202.4	-2921.2	203.3	-2984.1
O2	182.5	-2738.0	181.6	-2670.5	180.9	-2695.8
O3	193.1	-2939.0	192.6	-2874.6	191.9	-2903.9

^[a]Specific impulse; ^[b] Heat of isobaric combustion. (Explo5 v6.02. O/F = 80/20, w/w; isobaric conditions (p=const.), equilibrium expansion, 7.0 MPa chamber pressure)

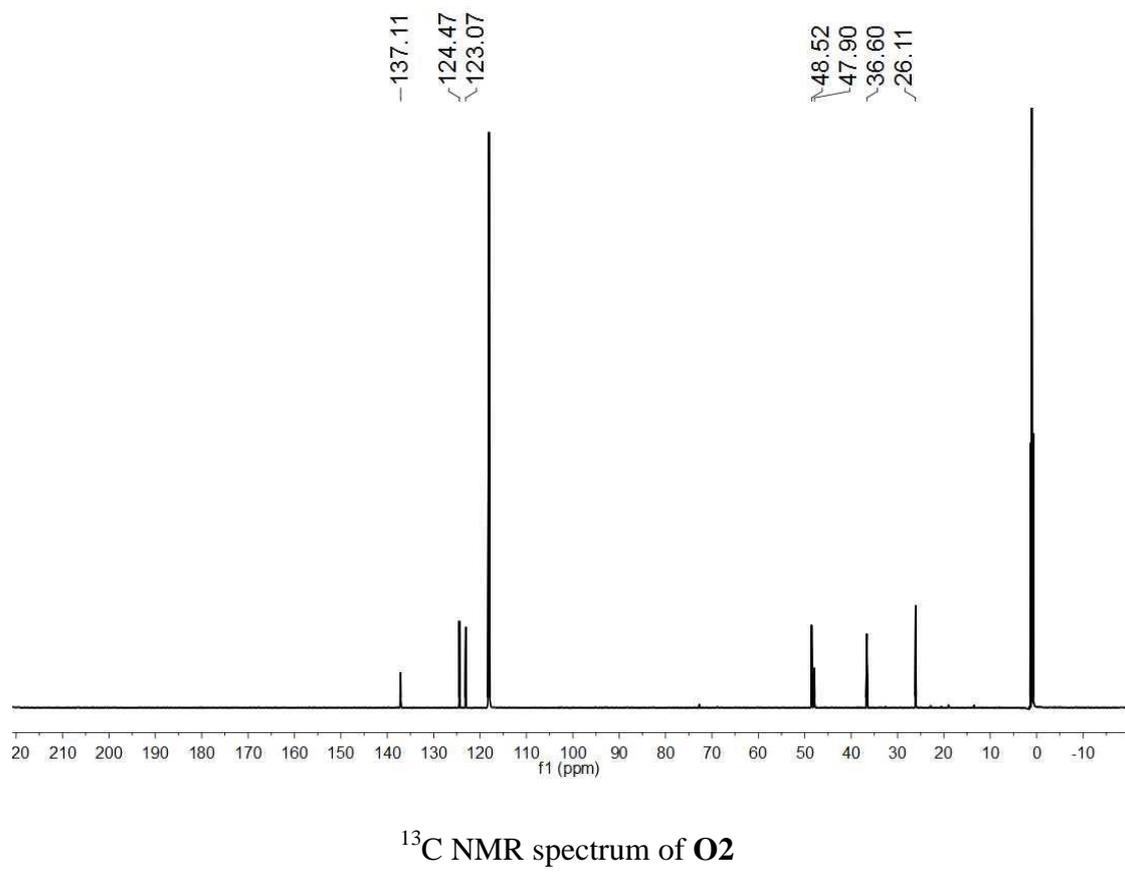
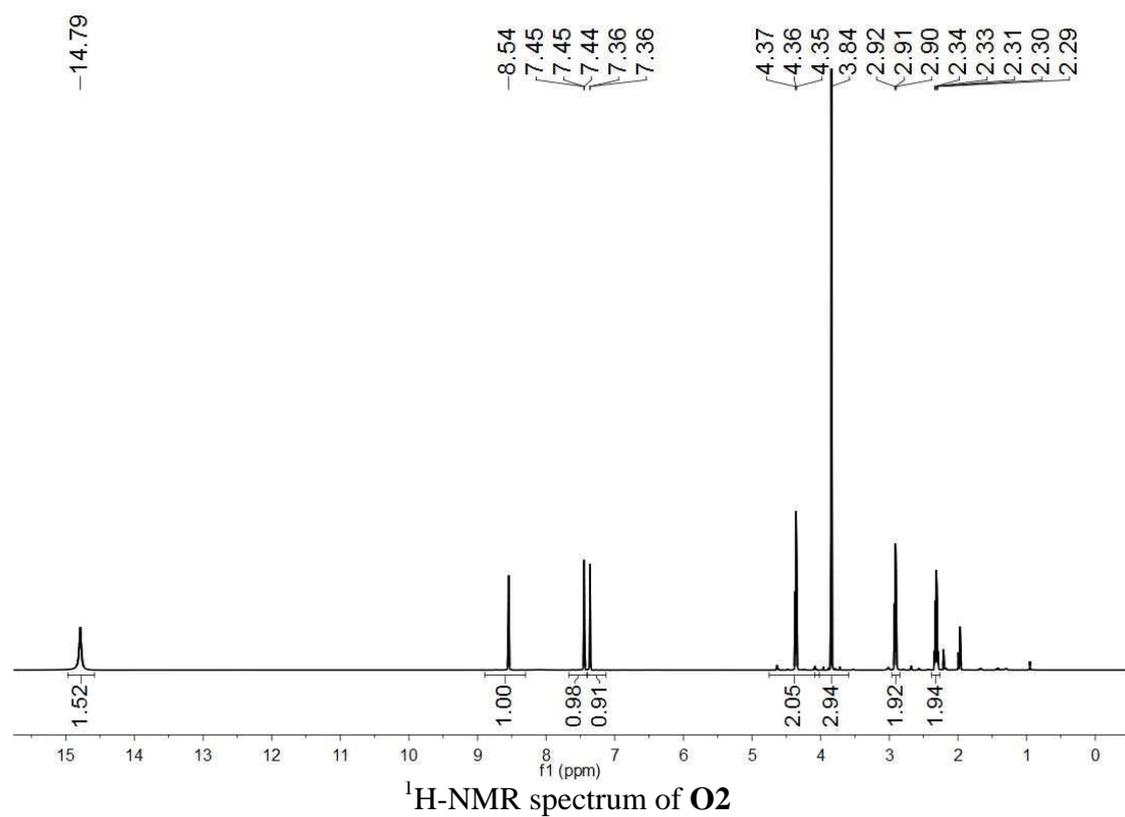
NMR spectra

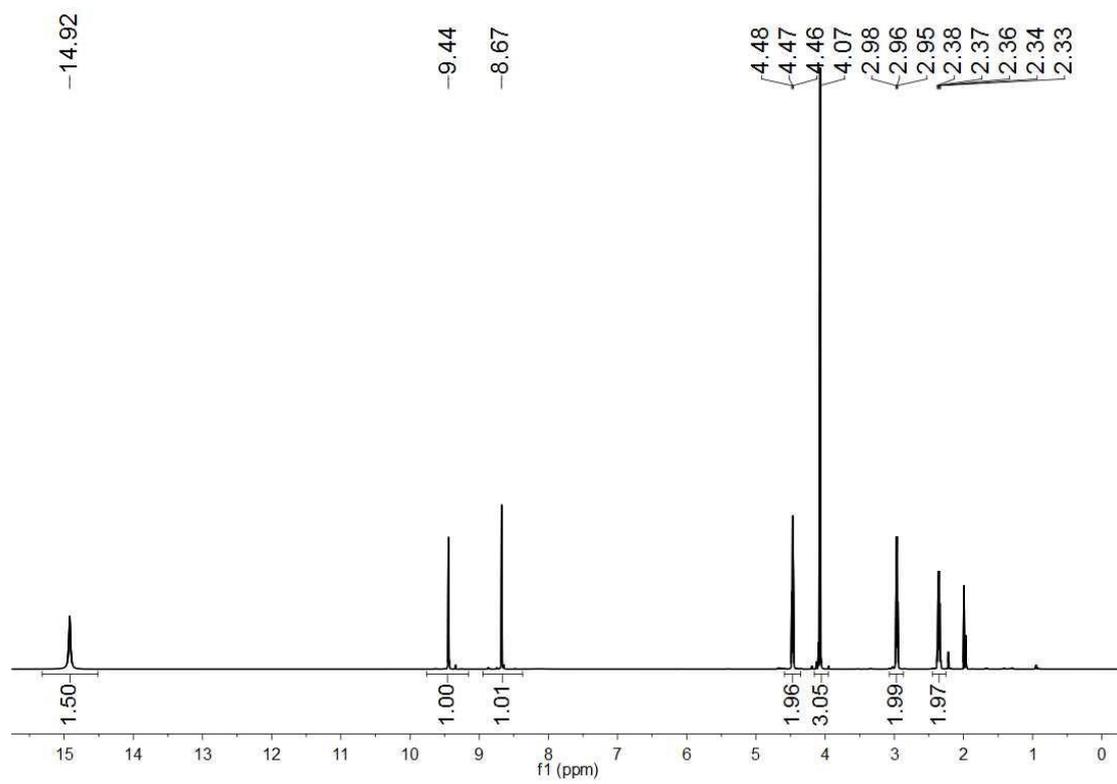


$^1\text{H-NMR}$ spectrum of **O1**

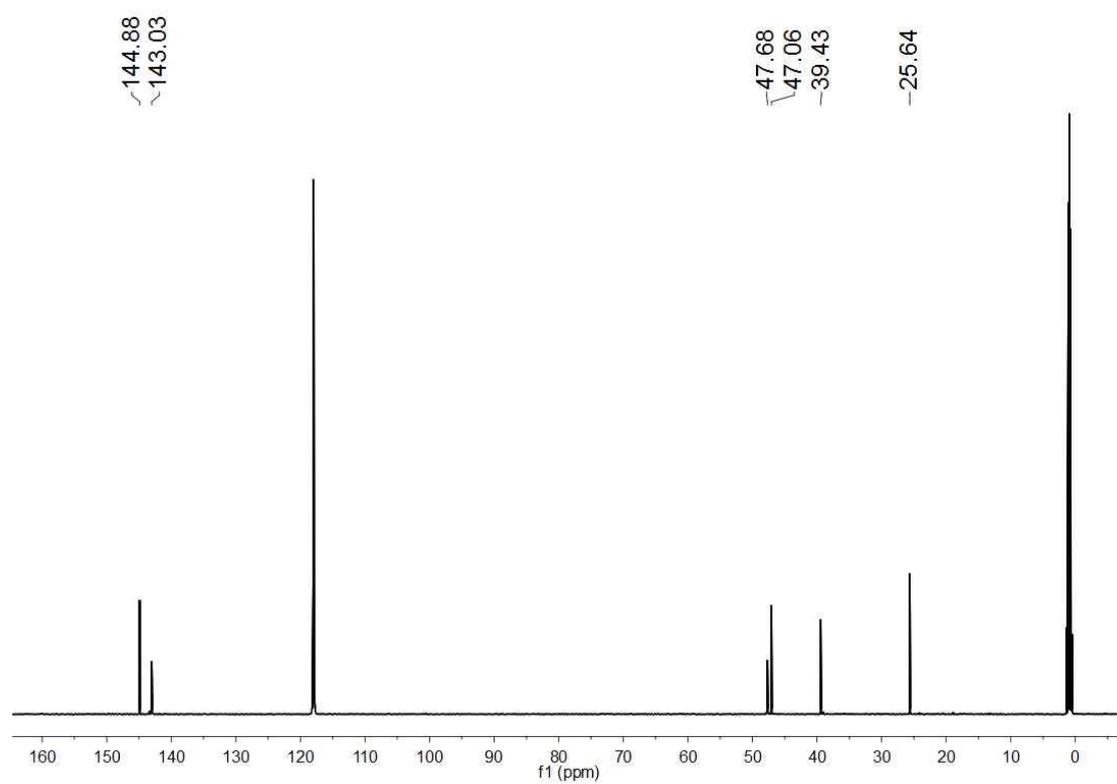


$^{13}\text{C-NMR}$ spectrum of **O1**

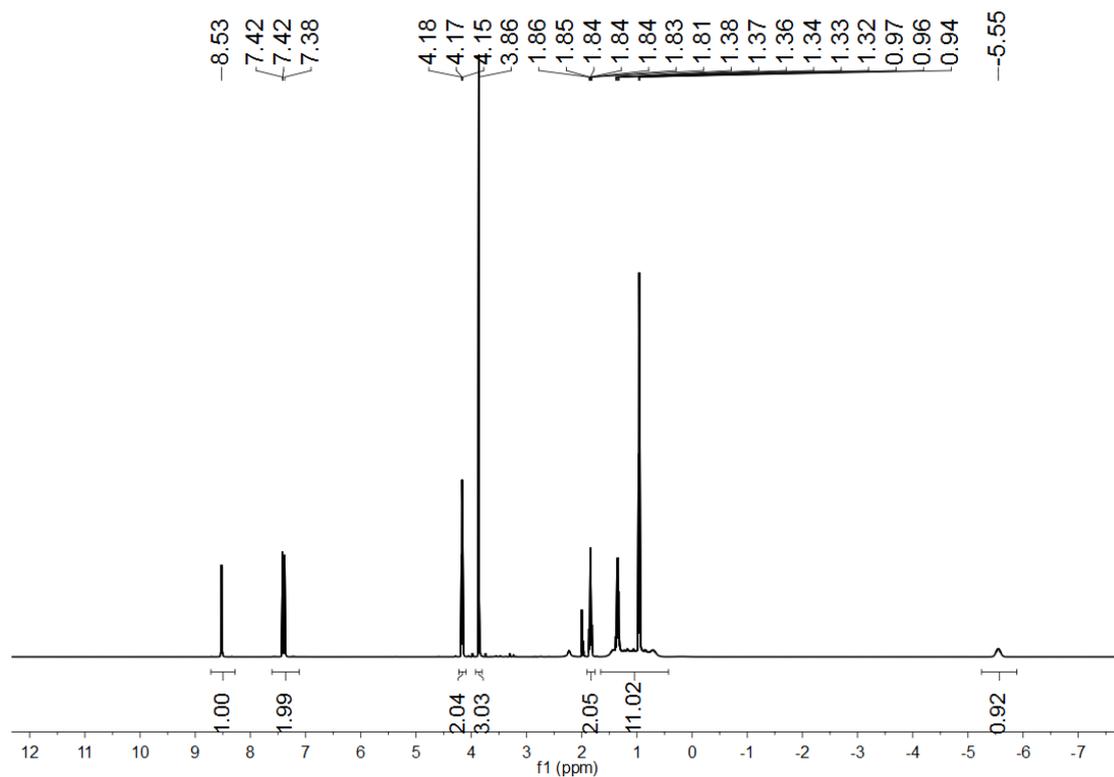




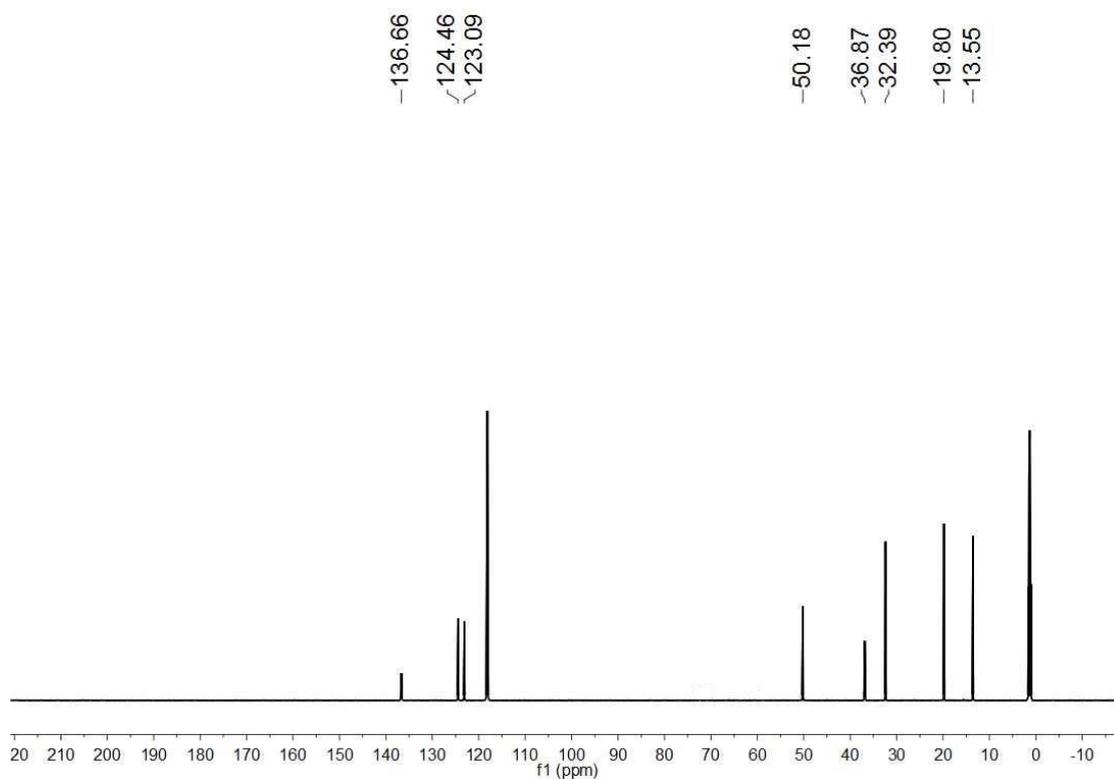
¹H-NMR spectrum of O3



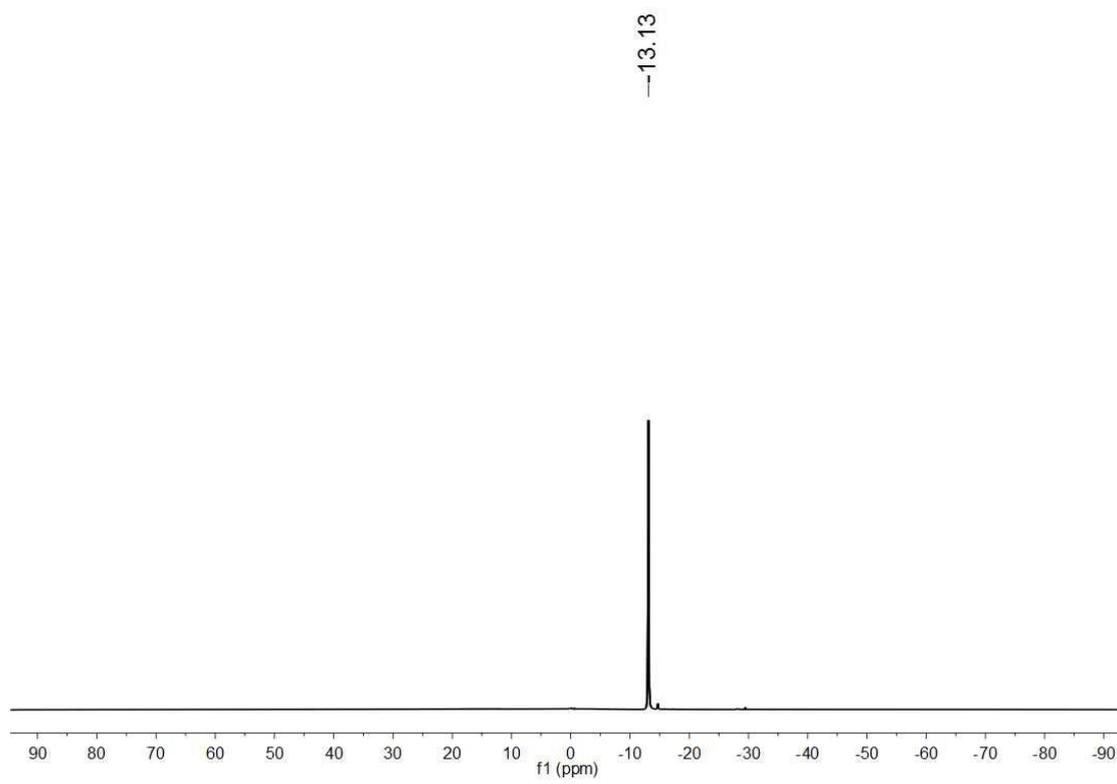
¹³C NMR spectrum of O3



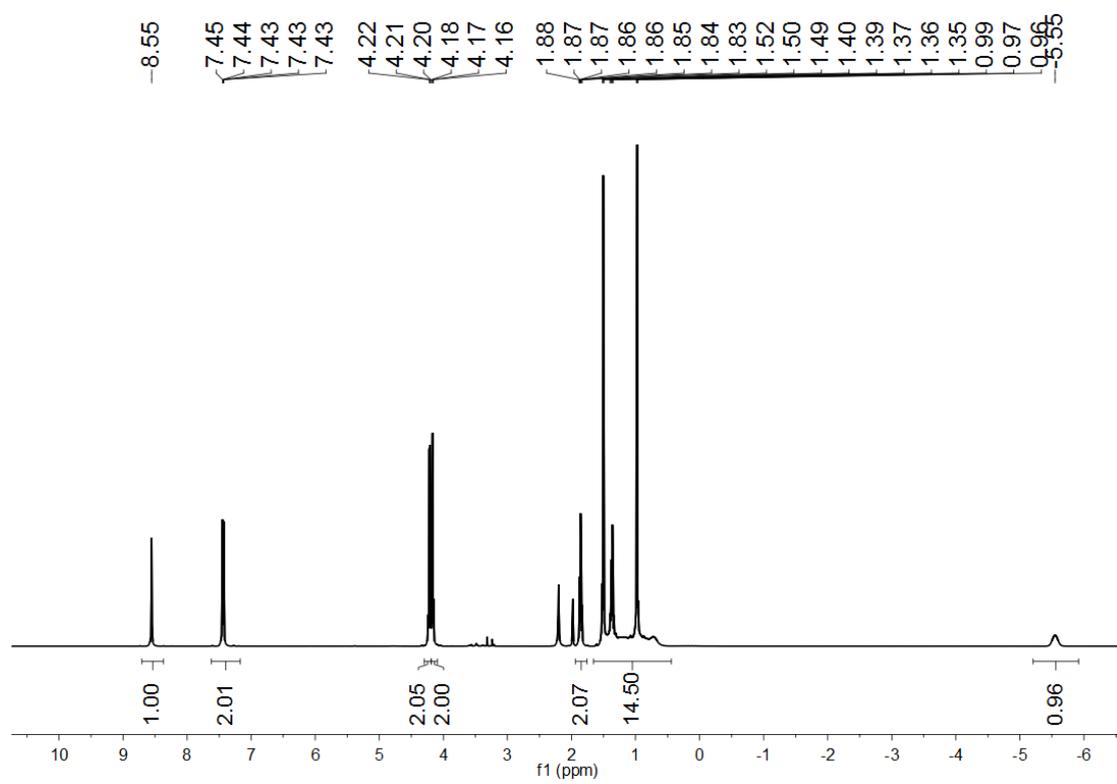
¹H NMR spectrum of **F1**



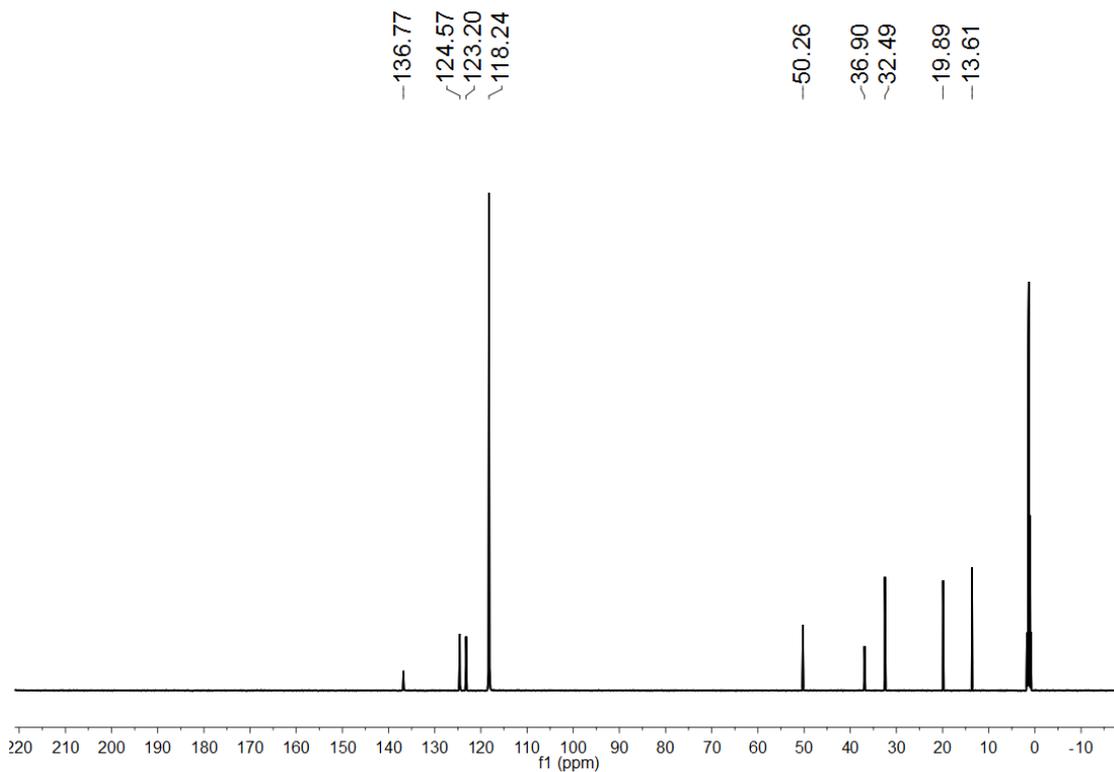
¹³C NMR spectrum of **F1**



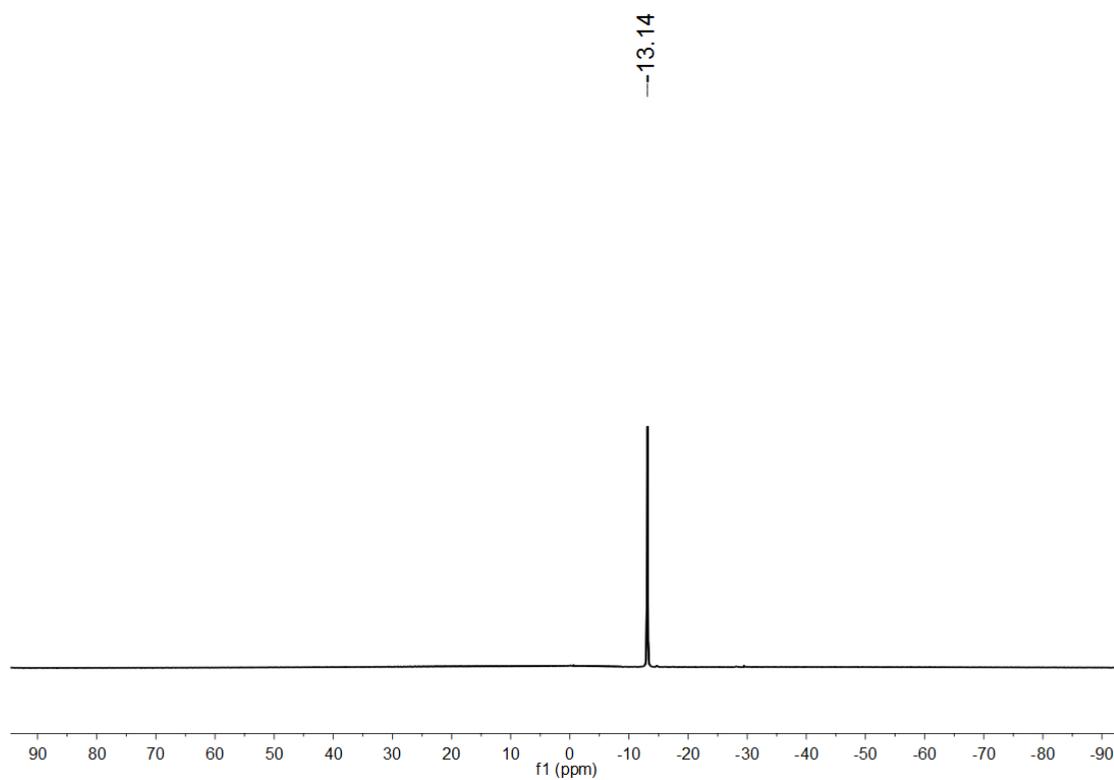
^{11}B NMR spectrum of F1



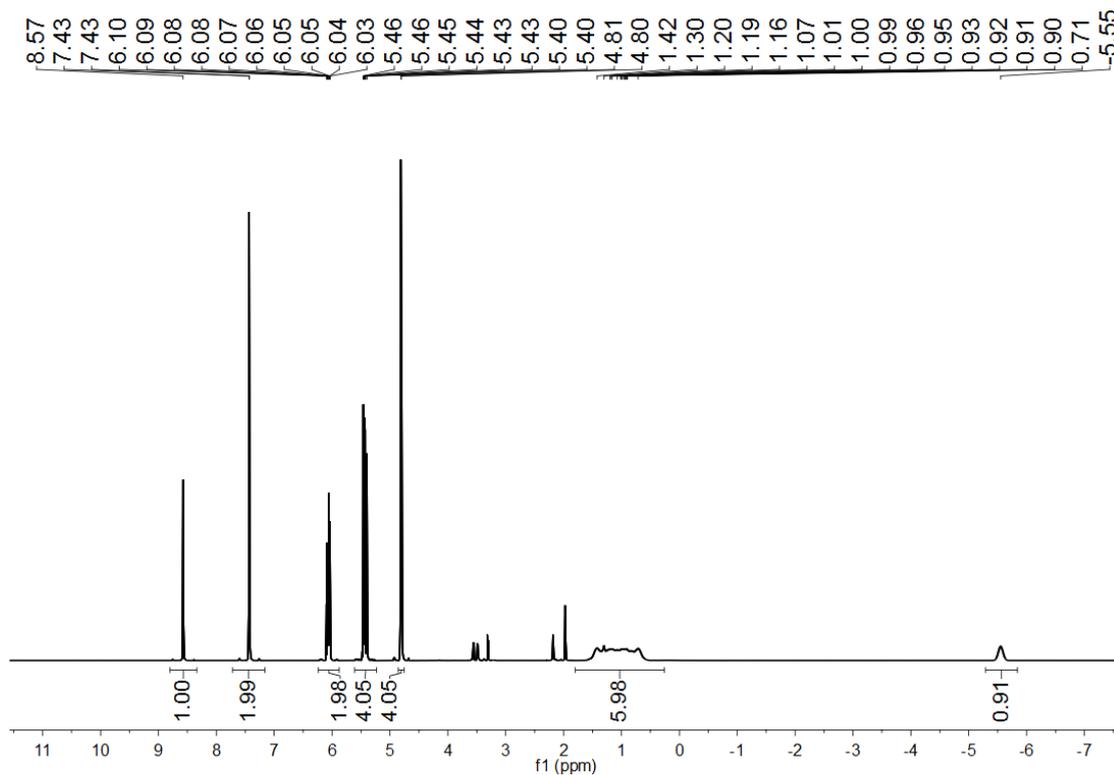
^1H NMR spectrum of F2



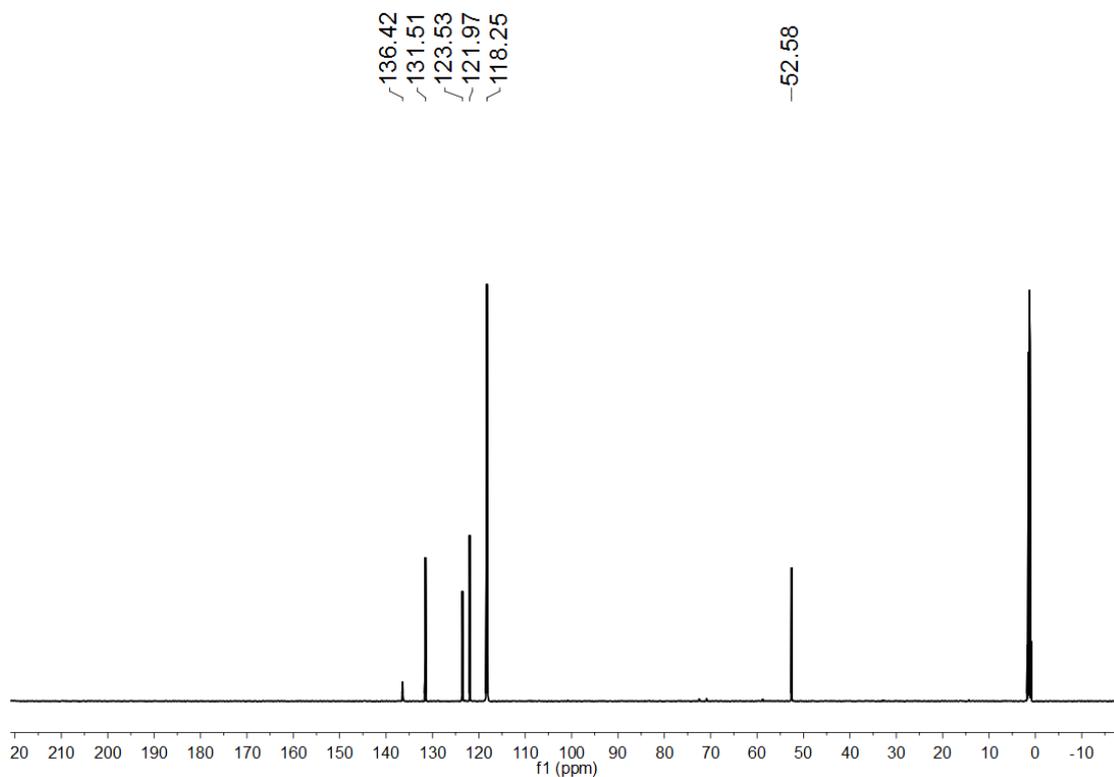
^{13}C NMR spectrum of **F2**



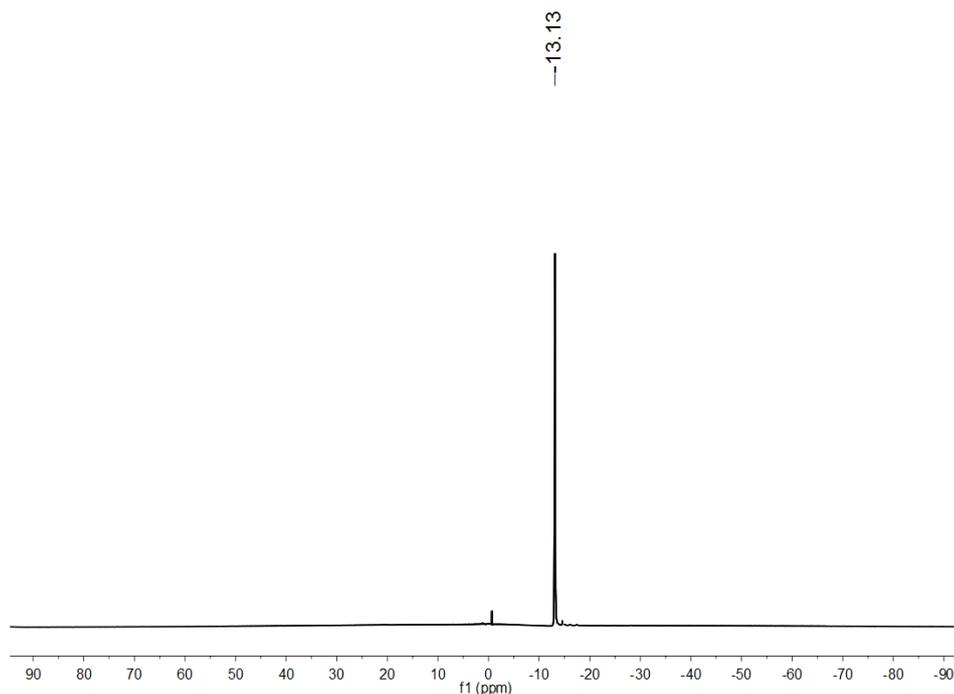
^{11}B NMR spectrum of **F2**



¹H NMR spectrum of F3



¹³C NMR spectrum of F3



^{11}B NMR spectrum of **F3**

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