Tetraaryl Pyrazole Polymers: Versatile Synthesis, Aggregation Induced Emission Enhancement and Detection of Explosives

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Experimental Section:

General

Reagents and starting materials were purchased from Alfa-Aesar, Sigma-Aldrich and Spectrochem chemical companies and used as received unless otherwise noted. Chlorinated solvents were distilled from CaH_2. THF was distilled from Na/benzophenone prior to use. 1,3,5-triphenyl-1*H*-pyrazole was prepared according to literature procedure.[1] All 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at 400 MHz and referenced internally to solvent signals. All NMR spectra were recorded at ambient temperature. ESI mass spectra were recorded on Bruker, micrOTOF-QII mass spectrometer. The absorbance spectra were recorded on a Perkin Elmer Lambda 750 UV–visible spectrometer. The fluorescence spectra were recorded on a Perkin Elmer LS-55 Fluorescence Spectrometer. The fluorescence spectra were corrected for the instrumental response. Thermogravimetric analyses (TGA) were recorded on a PerkinElmer Pyris 6 TGA model in a nitrogen atmosphere at a heating rate of 20 °C min^{-1}. Differential scanning calorimetric (DSC) analyses were recorded on a PerkinElmer Pyris 6 DSC model in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Gel-permeation chromatography (GPC) analyses were performed on a Shimadzu-LC20AD system referenced to poly(styrene) standards. THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1}. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II diffractometer equipped with an Oxford Instruments low-temperature attachment. The data were collected at 296 K using Mo-Kα radiation (0.71073 Å). Crystallographic data for **3c** and details of X-ray diffraction experiments and crystal structure refinements are given in Table S2. SADABS absorption corrections were applied in both cases.[2] The structures were solved and

refined with SHELX suite of programs.[3] All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. Crystallographic data for the structure **3c** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1413712. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Reference:

1. R. Mamidala, V. Mukundam, K. Dhanunjayarao, K. Venkatasubbaiah, *Dalton Trans.* **2015**, *44*, 5805.
2. G. M. Sheldrick, SADABS Program for Correction of Area Detector Data; University of Gottingen: Gottingen, Germany, 1999.
3. SHELXTL, Package v. 6.10, BrukerAXS, Madison and WI.

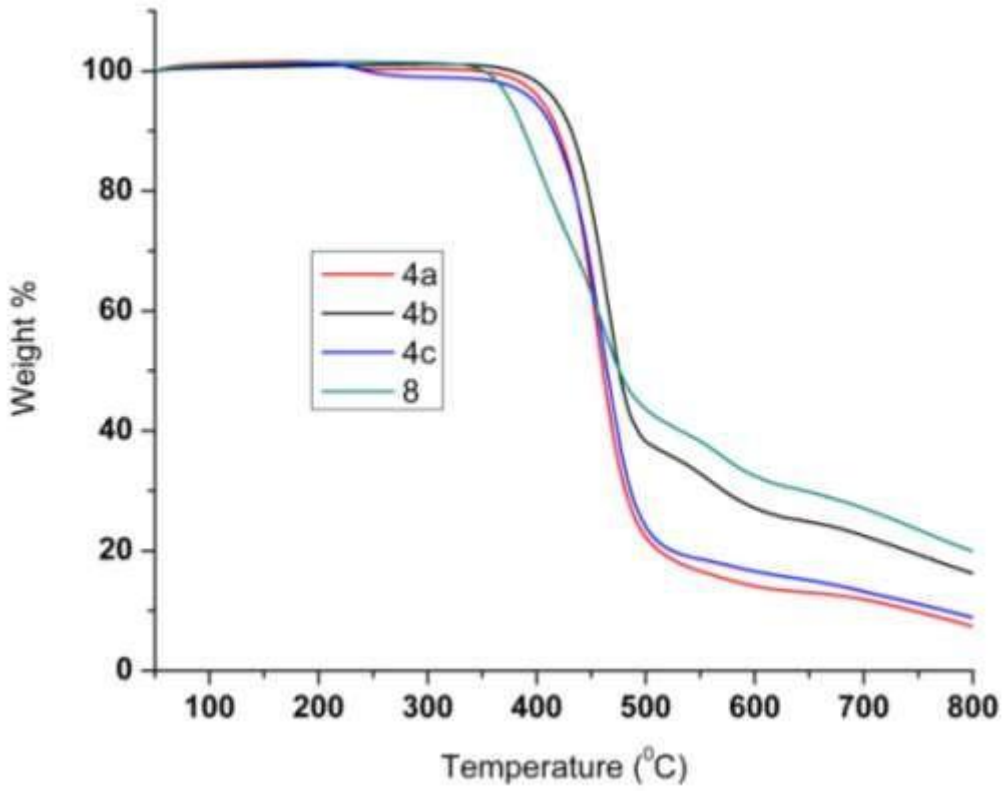


Figure S1. Thermogravimetric analysis traces of polymer **4a-4c** & **8** recorded under nitrogen at a heating rate of 20 °C/min

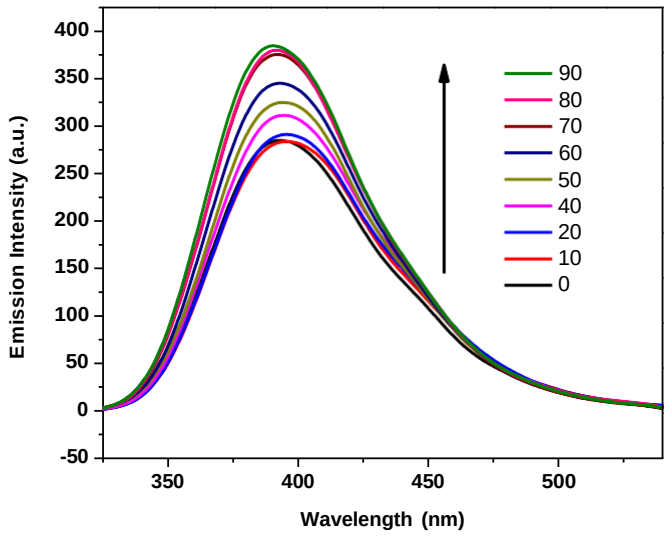


Figure S2. Fluorescence spectra of polymer **4b** (2.2 x 10^{-5} M) in THF/water mixtures with different water fraction (fw).

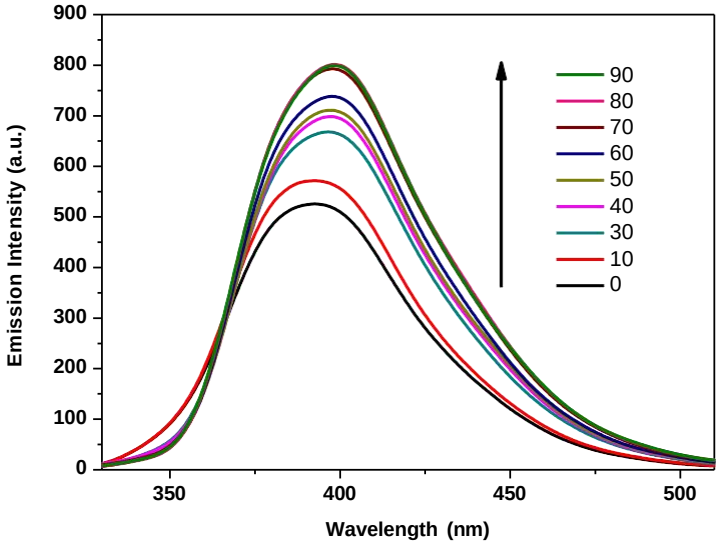


Figure S3. Fluorescence spectra of polymer **4c** (2.2 x 10^{-5} M) in THF/water mixtures with different water fraction (fw).

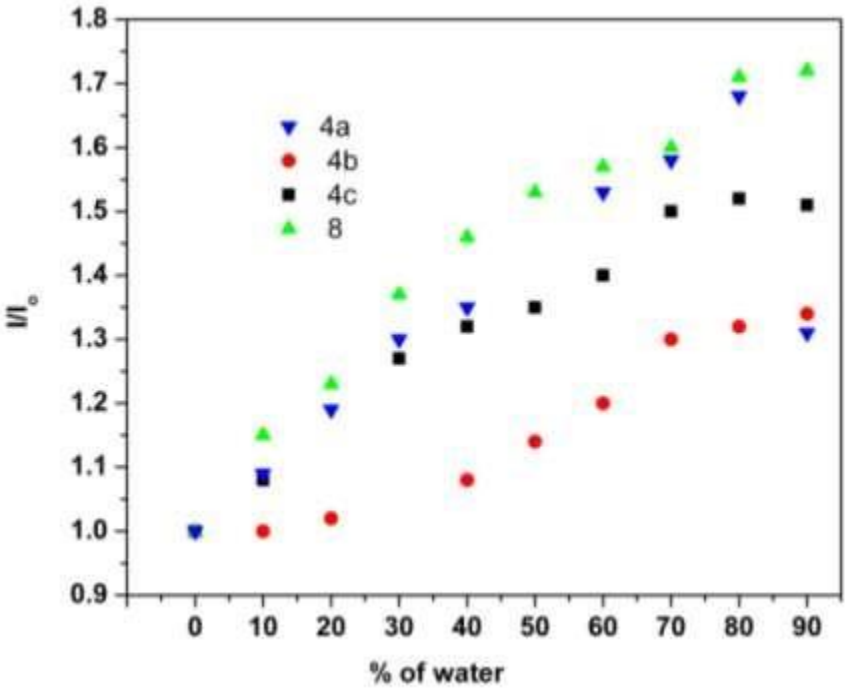


Figure S4. Effects of water addition on Fluorescence Intensity (I) of Polymers

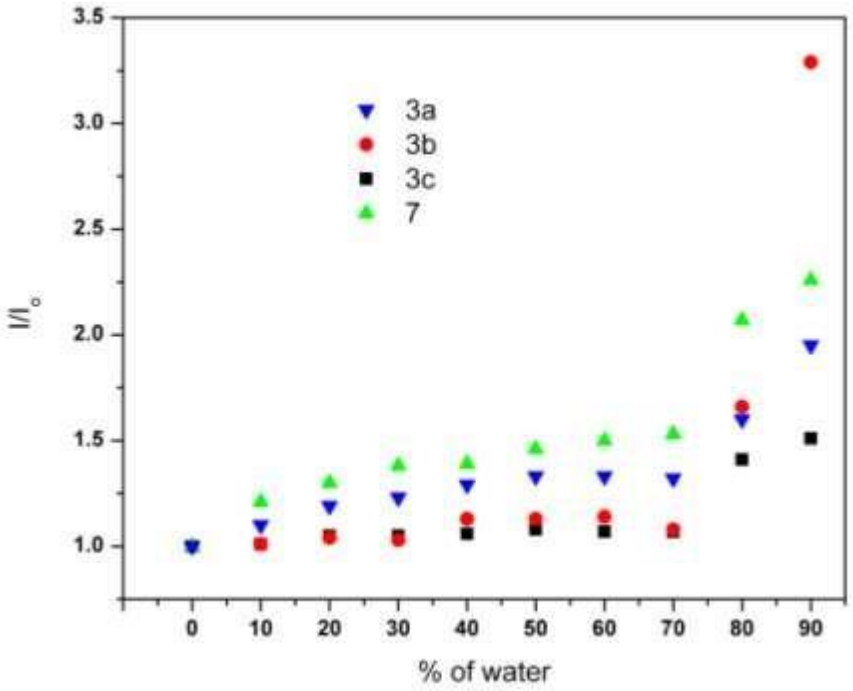


Figure S5. Effects of water addition on Fluorescence Intensity (I) of Monomers

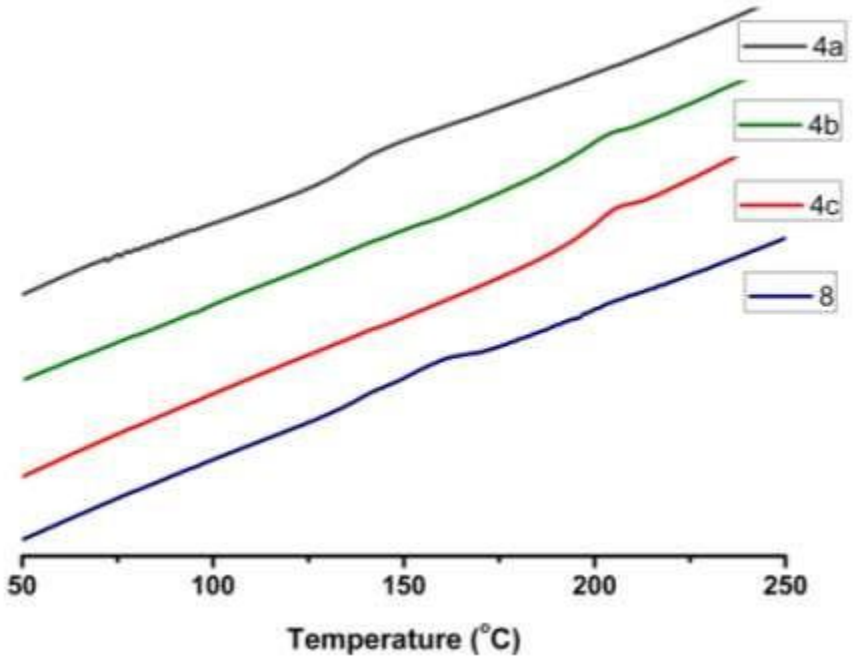


Figure S6. DSC traces of polymer **4a-4c** & **8** recorded under nitrogen at a heating rate of 20 °C/min

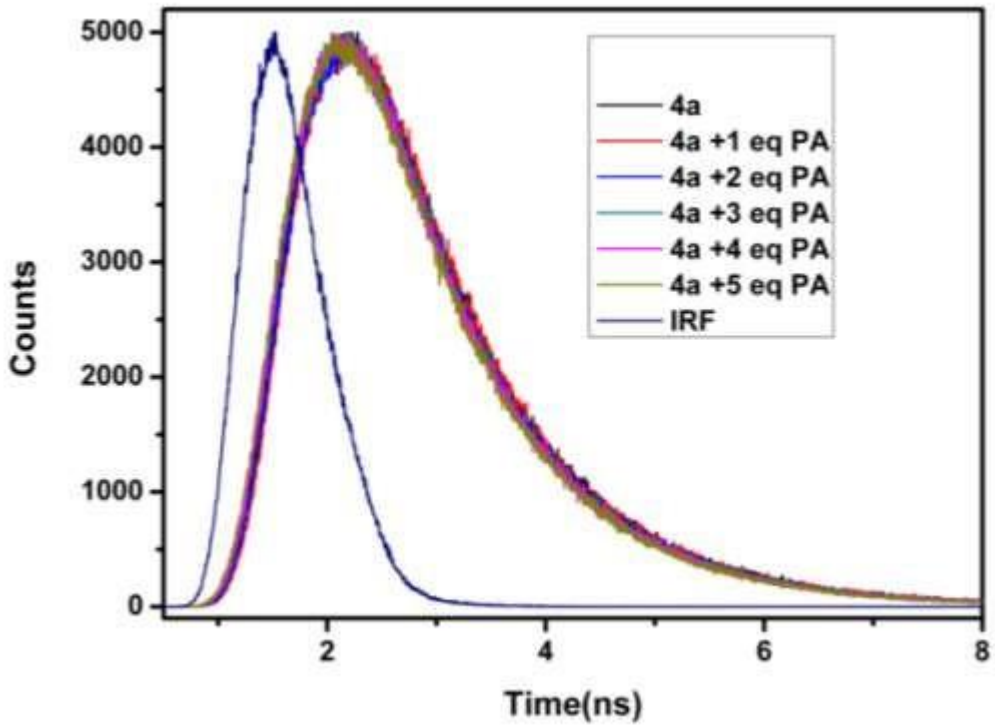


Figure S7. Fluorescence lifetime decay profile of polymer **4a** (2.2 x 10^{-5} M) in THF/H_2O (3:7) mixture for different concentrations of picric acid (PA). IRF= instrument response function. λ_{ex} = 280 nm.

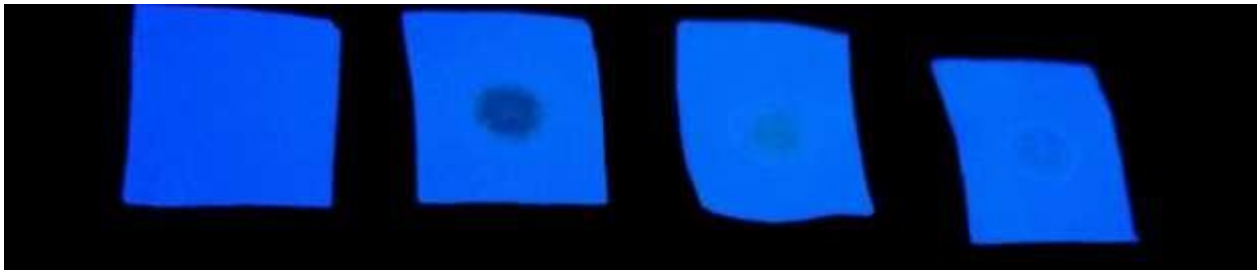


Figure S8. Color of fluorescent strips under UV light before and after addition of different concentration of picric acid (from left to right: blank, 10^{-3}, 10^{-4}, 10^{-5} M (PA).

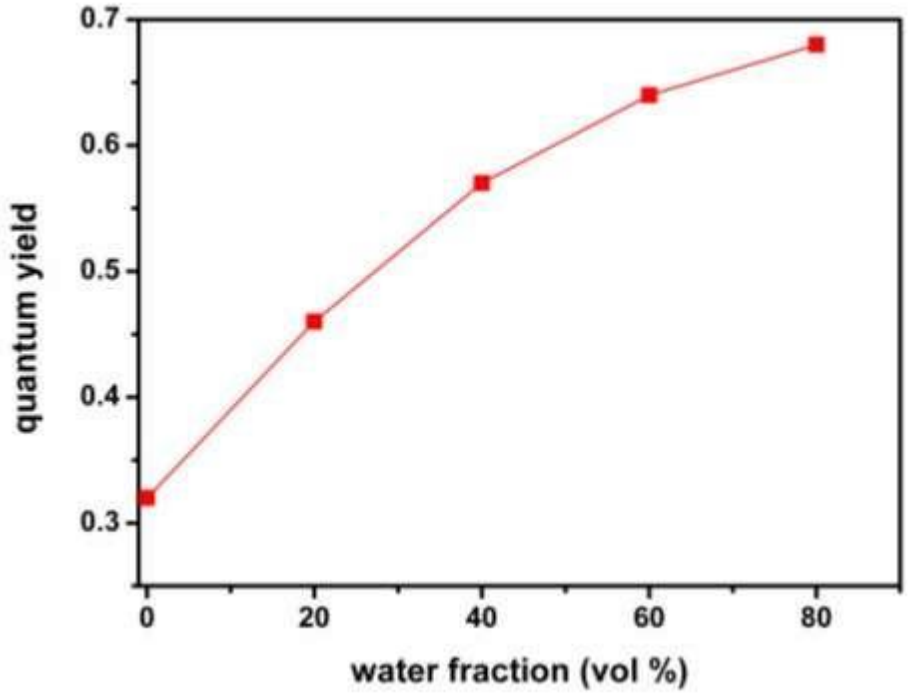


Figure S9. Variation of quantum yields of polymer 4a with water fraction in the THF/H2O mixture

Table S1. Optical properties of the monomers **(3a-3c** & **7**) and polymers (**4a-4c** & **8**) in the solution and aggregated state

Compound	λ_{ab}/nm	λ_{em}/nm	Φ_F(THF) [a]	Φ_F,agg [a,b]
3a	282	379	0.34	0.64
3b	282	392	0.33	0.58
3c	281	394	0.53	0.93
7	295	387	0.38	0.76
4a	281	379	0.32	0.68
4b	282	394	0.35	0.55
4c	281	396	0.52	0.95
8	296	387	0.42	0.80

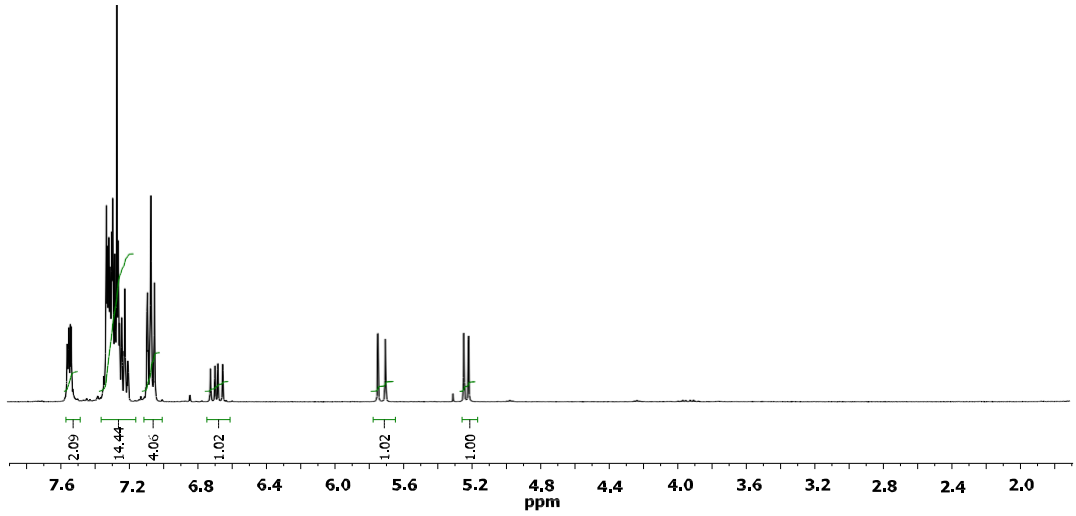
[a] Measured using *p*-terphenyl in cyclohexane (Φ_F = 0.82). [b] Aggregates formed in THF/water mixture (20:80).

Table S2. Details of X-ray crystal structure analyses of compound **3c**.

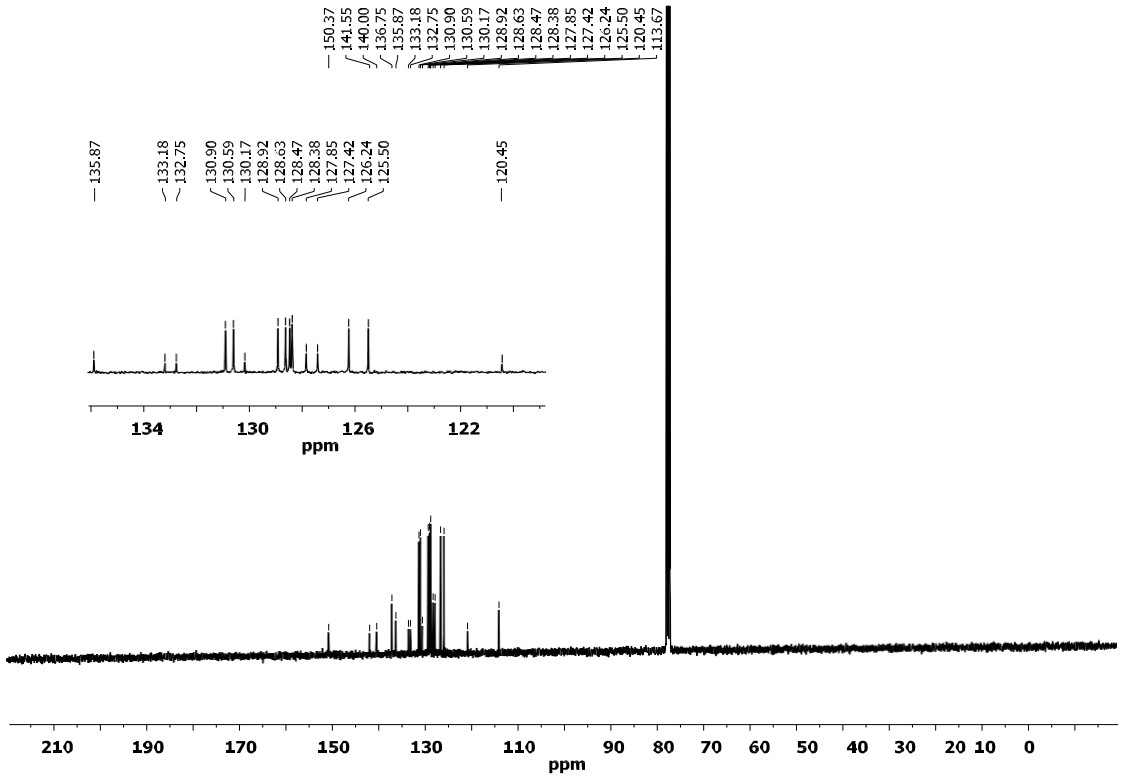
	Compound **3c**
Empirical formula	$C_{30}H_{21}F_3N_2$
M_r	466.49
T [K]	296(2)
wavelength [Å]	0.71073 Å
crystal system	Monoclinic
space group	*C*2/*c*
a [Å]	28.3793(16)
b [Å]	8.2635(4)
c [Å]	21.2253(14)
α [°]	90
β [°]	112.455(7)
γ [°]	90
V [Å^3]	4600.2(5)
Z	8
ρ_{calc} [g cm^{-3}]	1.347
μ (MoKα) [mm^{-1}]	0.096
F (000)	1936
Crystal size [mm]	0.25 x 0.23 x 0.21
θ range [°]	1.55 – 25.80
limiting indices	-34<=h<=34
	-10<=k<=9
	-25<=l<=25
reflns collected	27952
independent reflns	4370
	[*R*(int) = 0.0873]
absorption correction	Semi-empirical from equivalents
refinement method	Full-matrix least square on F^2
data / restraints / parameters	4370 / 0 / 316
Goodness-of-fit on F^2	1.076
final R indices	R_1 = 0.0618
[I >2σ(I)] [a]	wR_2 = 0.1703
R indices (all data) [a]	R_1 = 0.1000
	wR_2 = 0.2030
peak$_{max}$/hole$_{min}$ [e Å^{-3}]	0.700 and -0.487

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

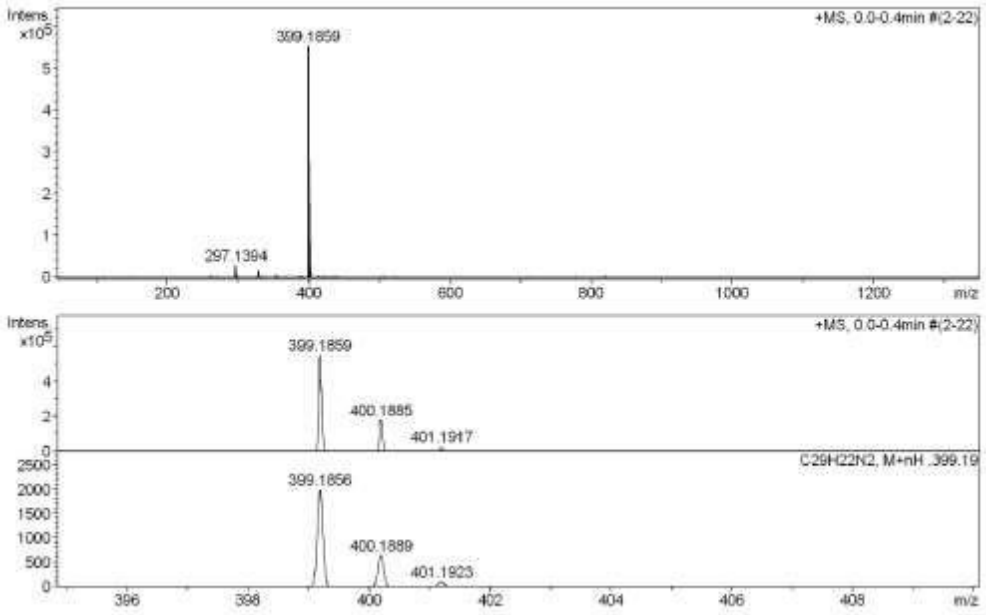
Compound **3a** ^{1}H NMR



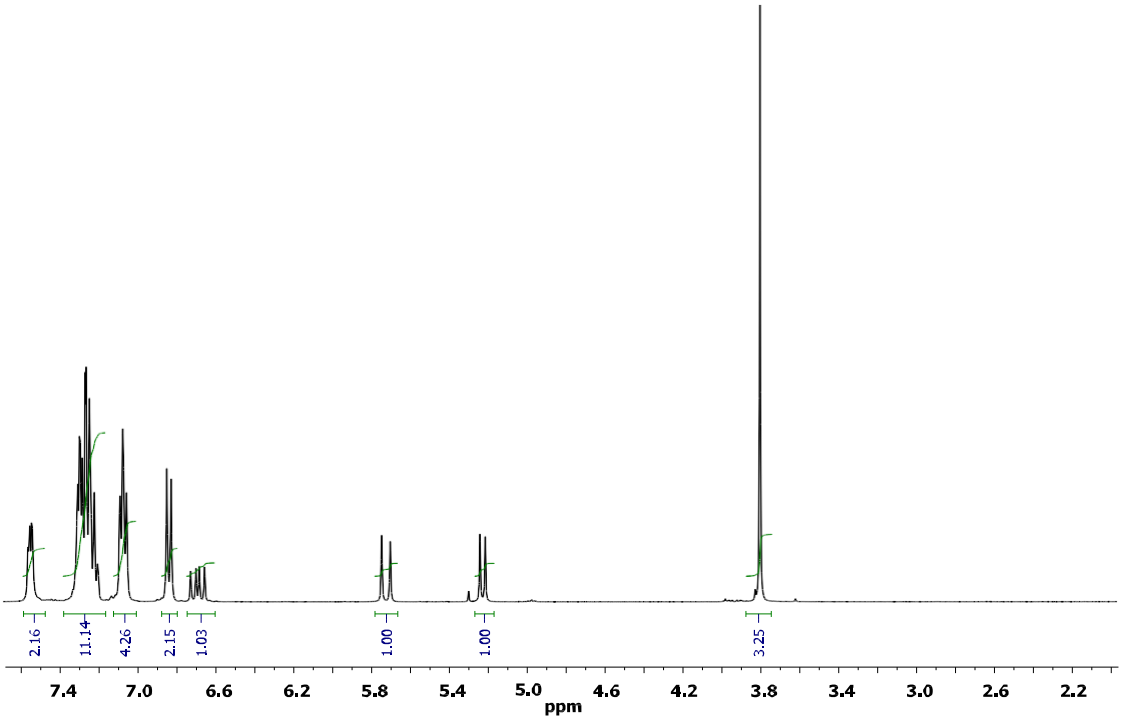
Compound **3a** ^{13}C NMR



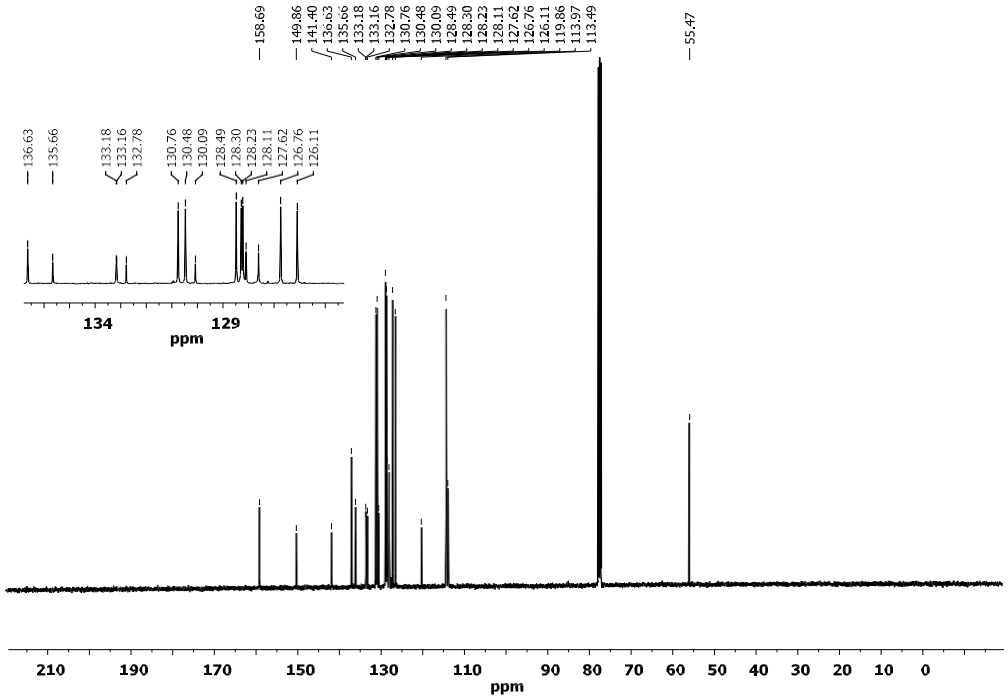
Compound **3a** HRMS



Compound **3b** ^{1}H NMR



Compound **3b** ^{13}C NMR



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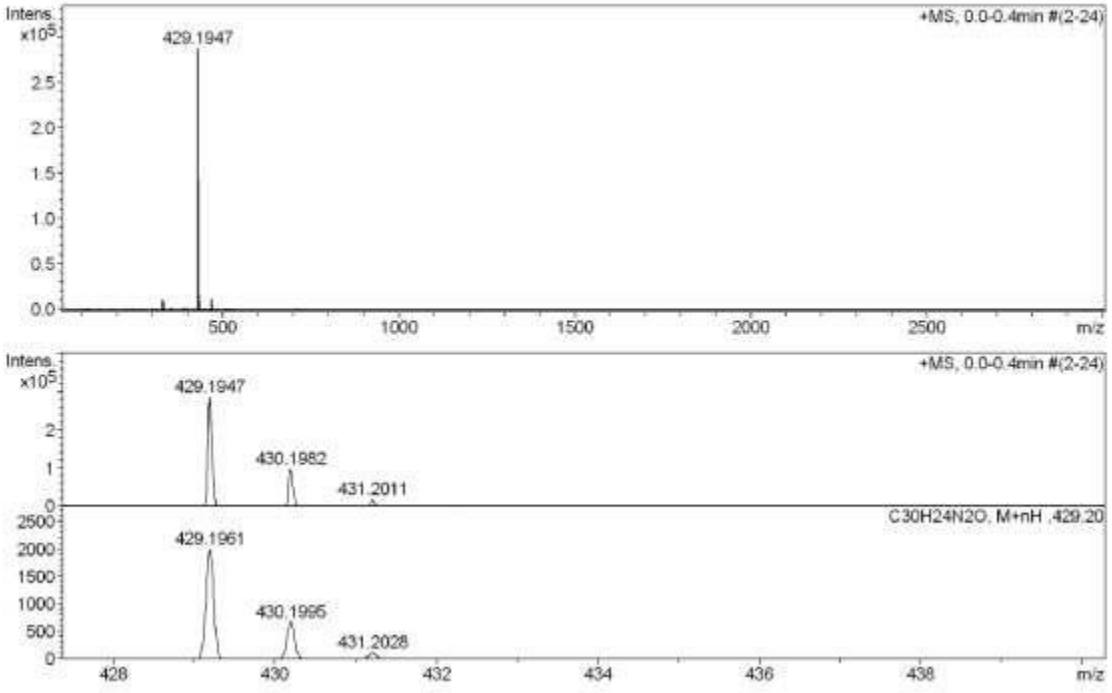
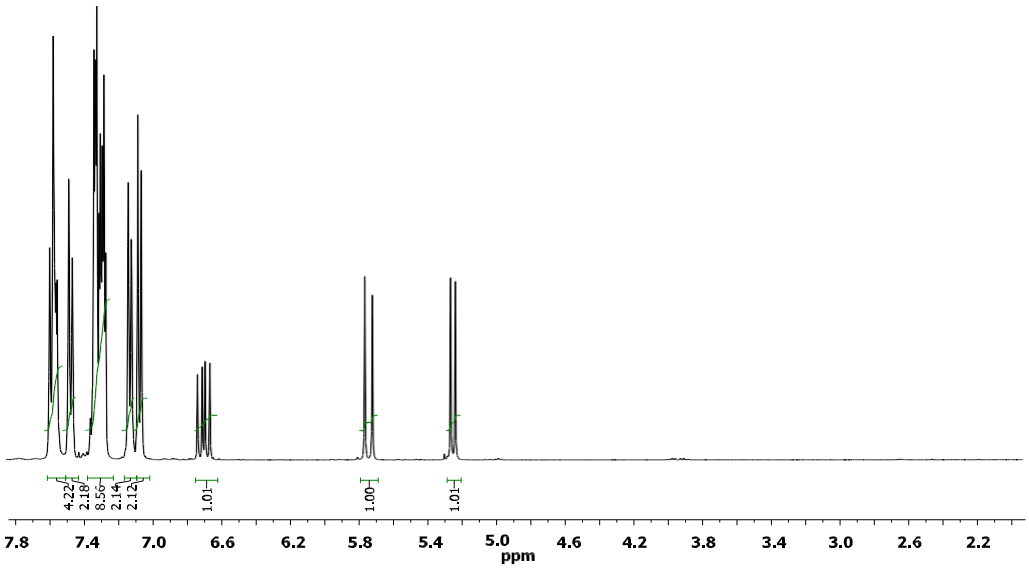
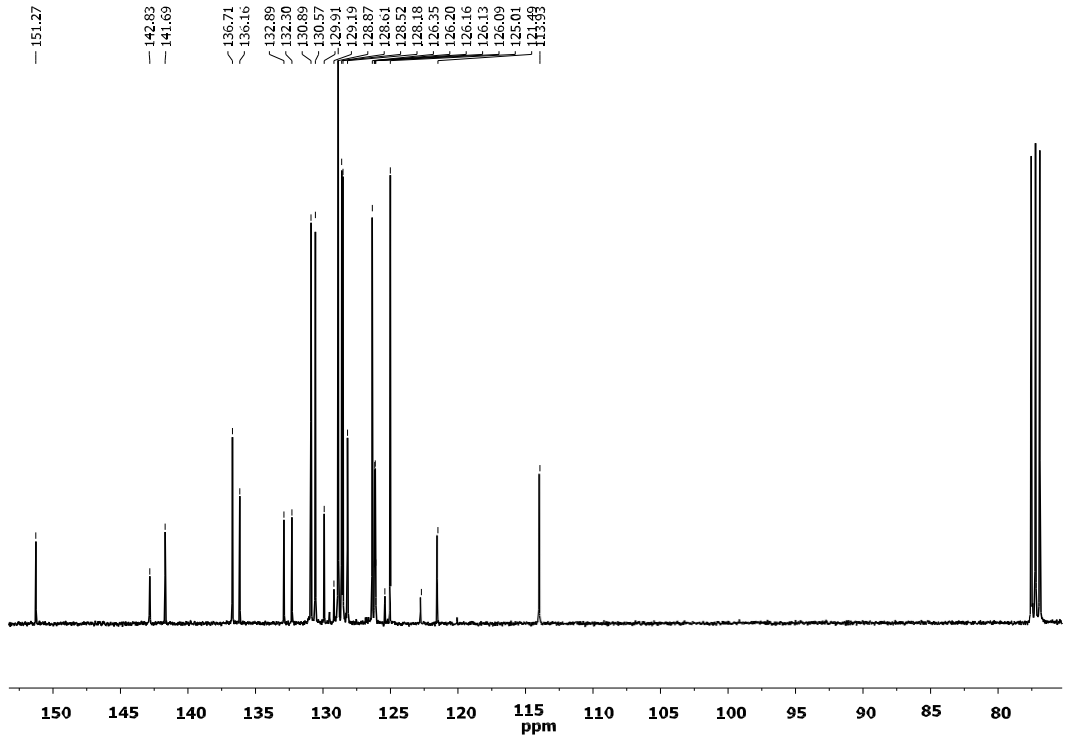


Compound **3c** ^{1}H NMR



Compound **3c** ^{13}C NMR



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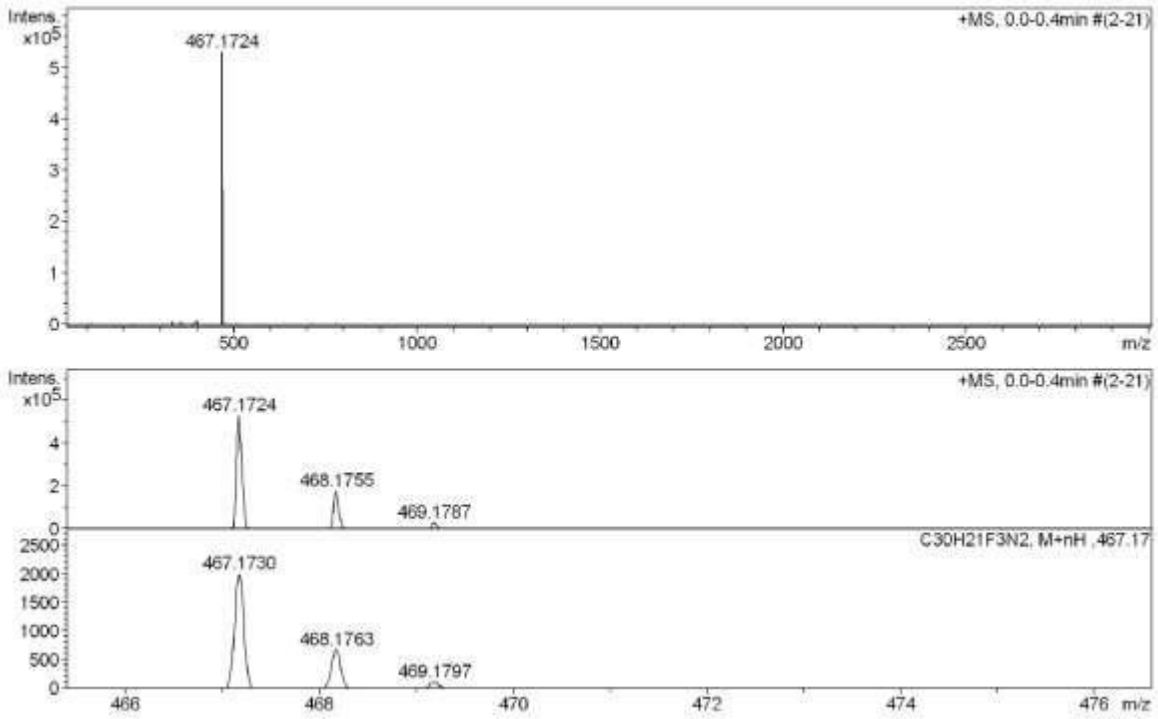
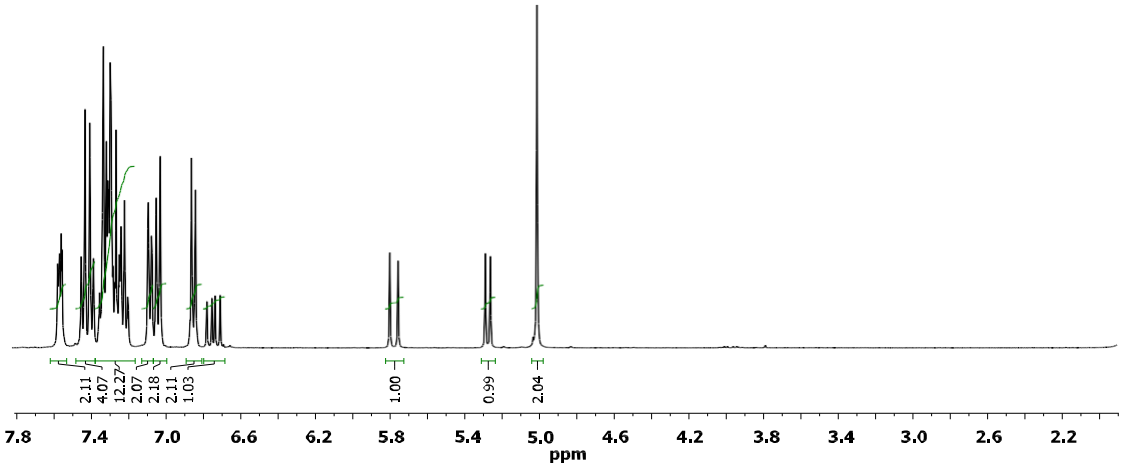
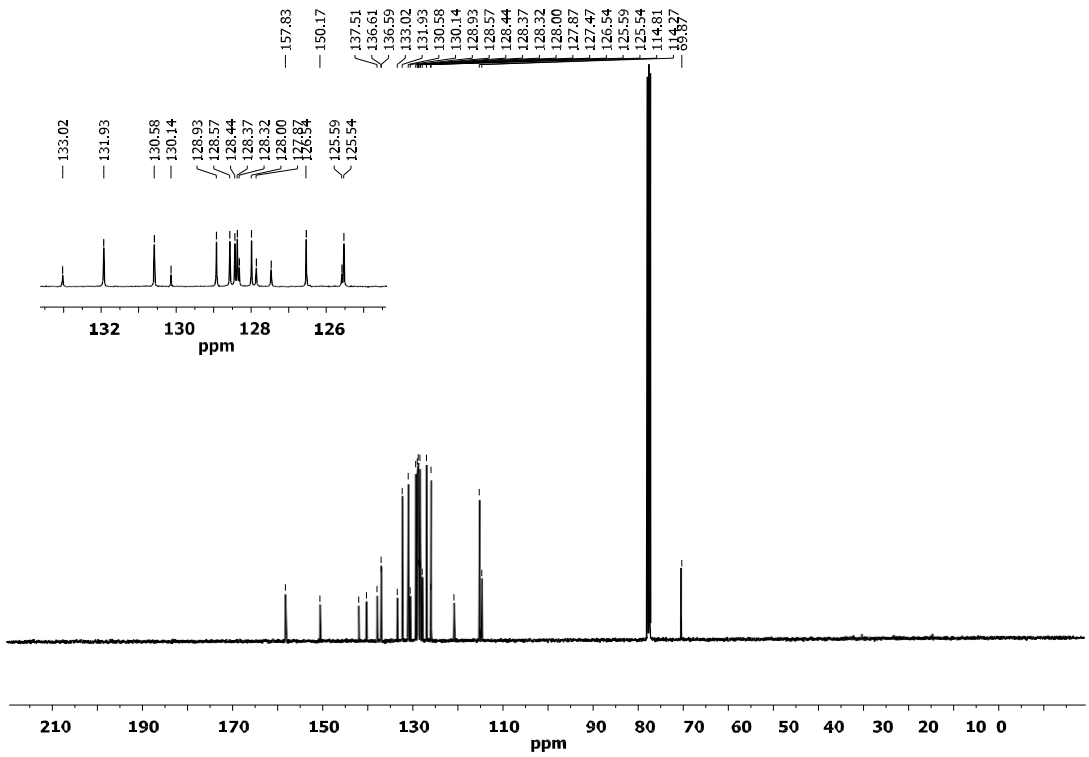


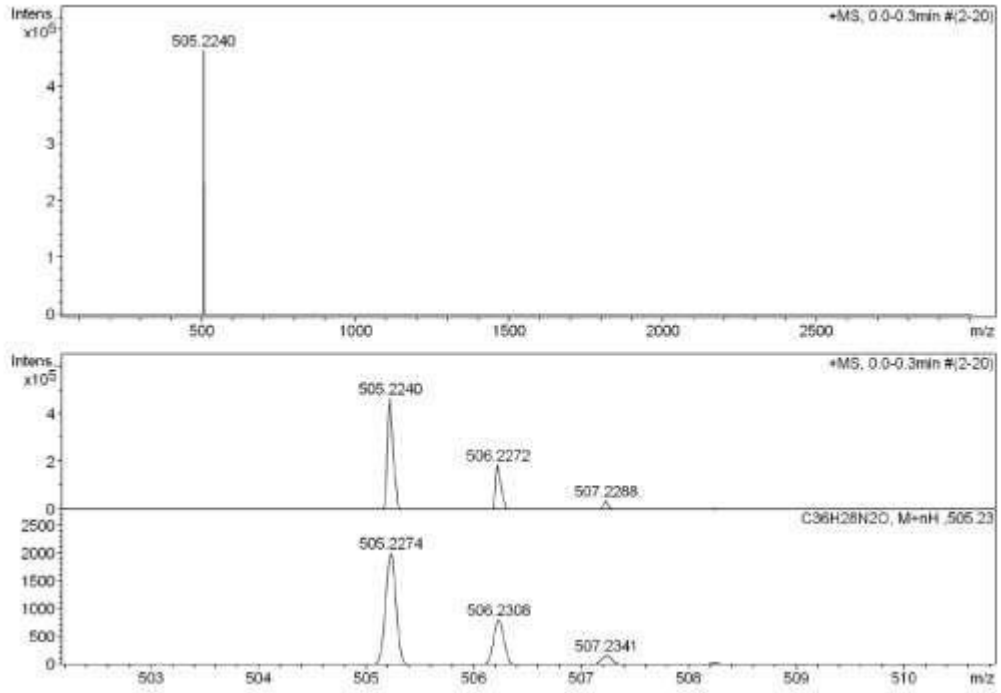
Compound **7** ^{1}H NMR



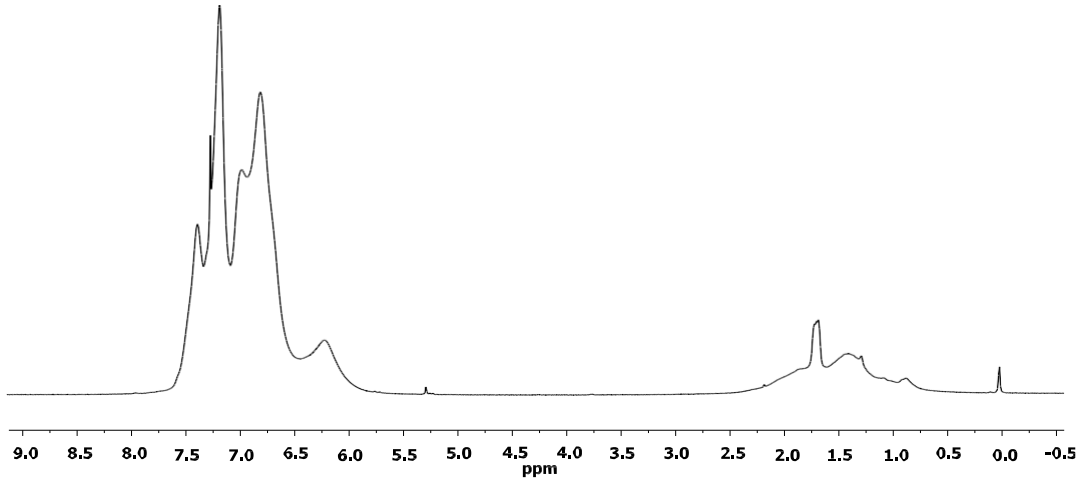
Compound **7** ^{13}C NMR



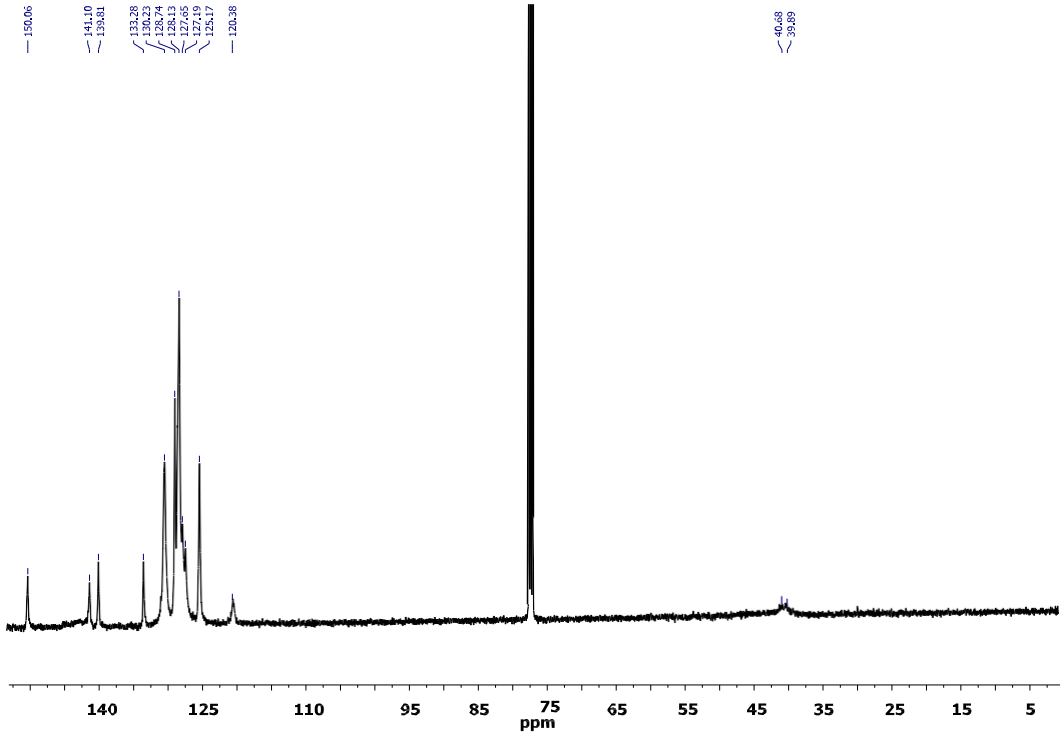
Compound **7** HRMS



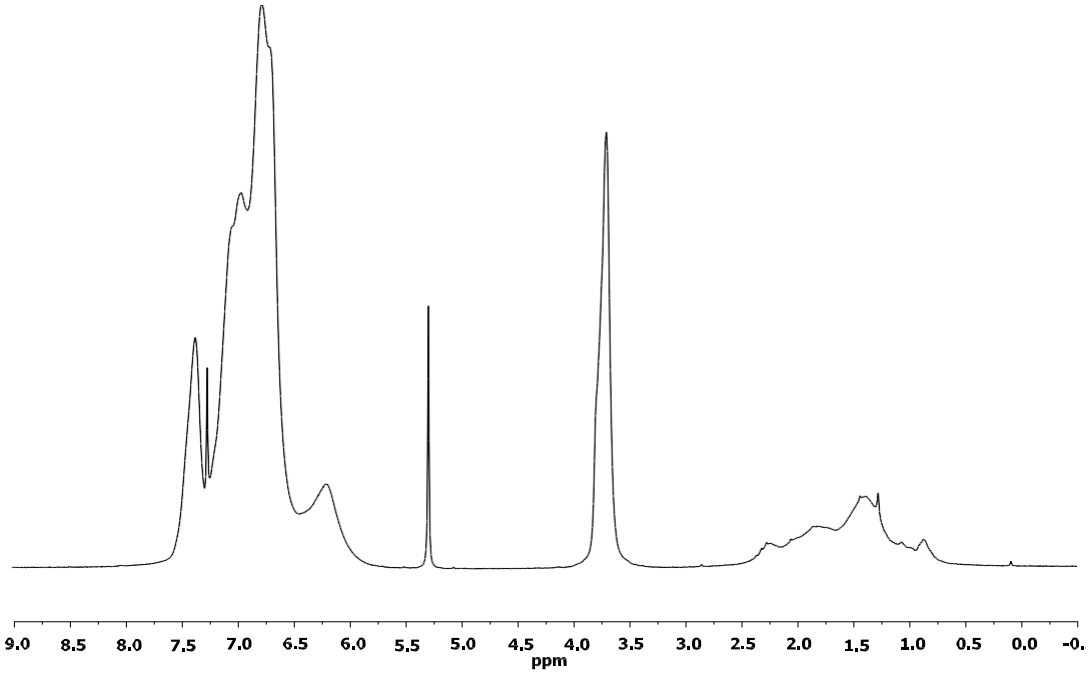
Polymer **4a** ^{1}H NMR



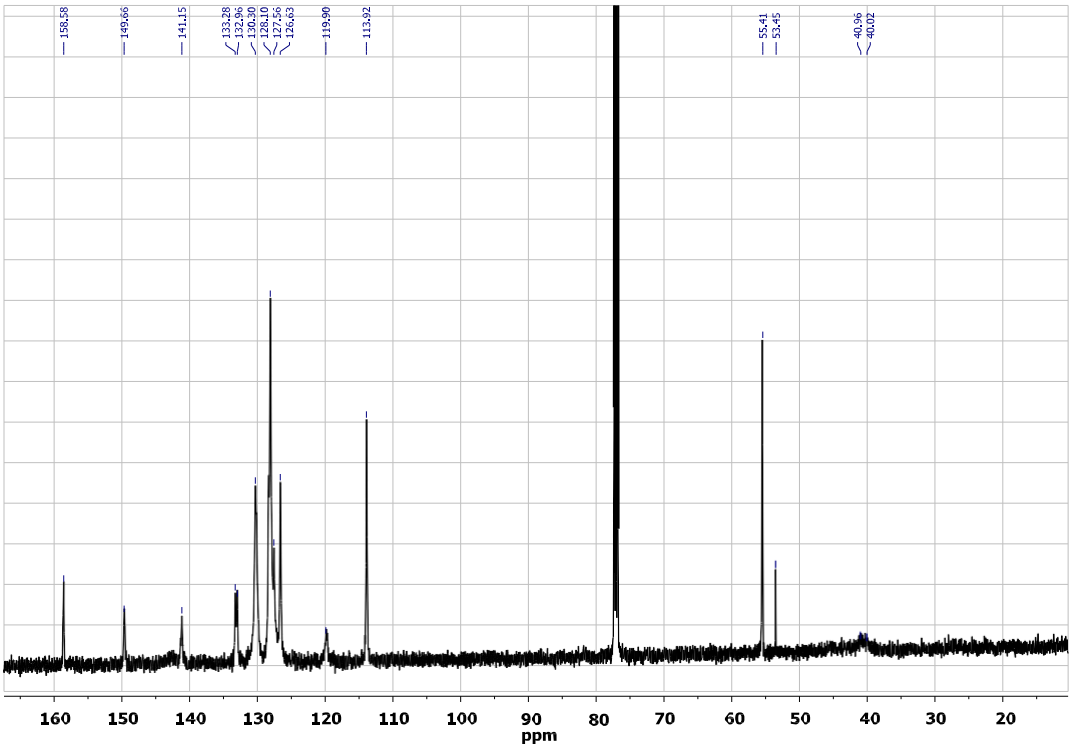
Polymer **4a** ^{13}C NMR



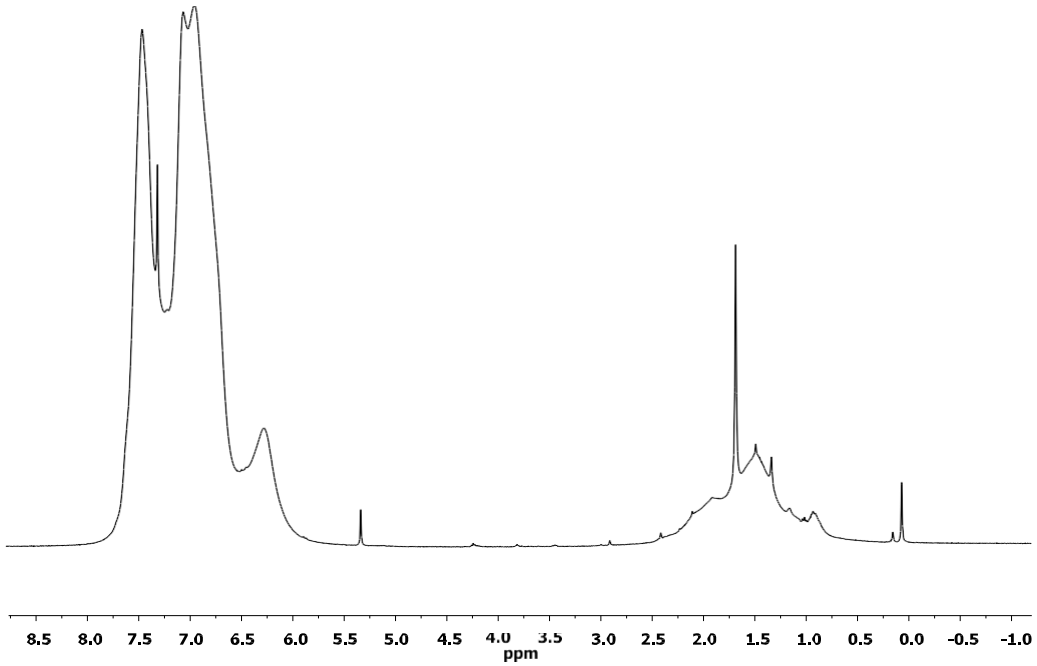
Polymer **4b** ^{1}H NMR



Polymer **4b** ^{13}C NMR



Polymer **4c** ^{1}H NMR



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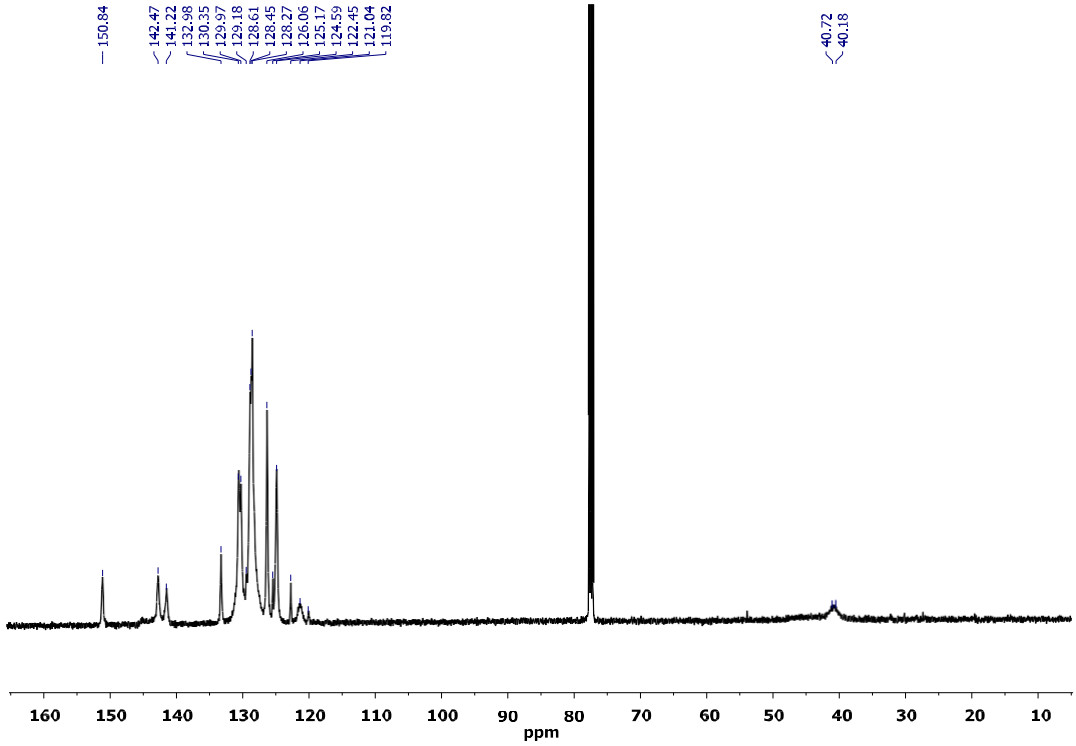
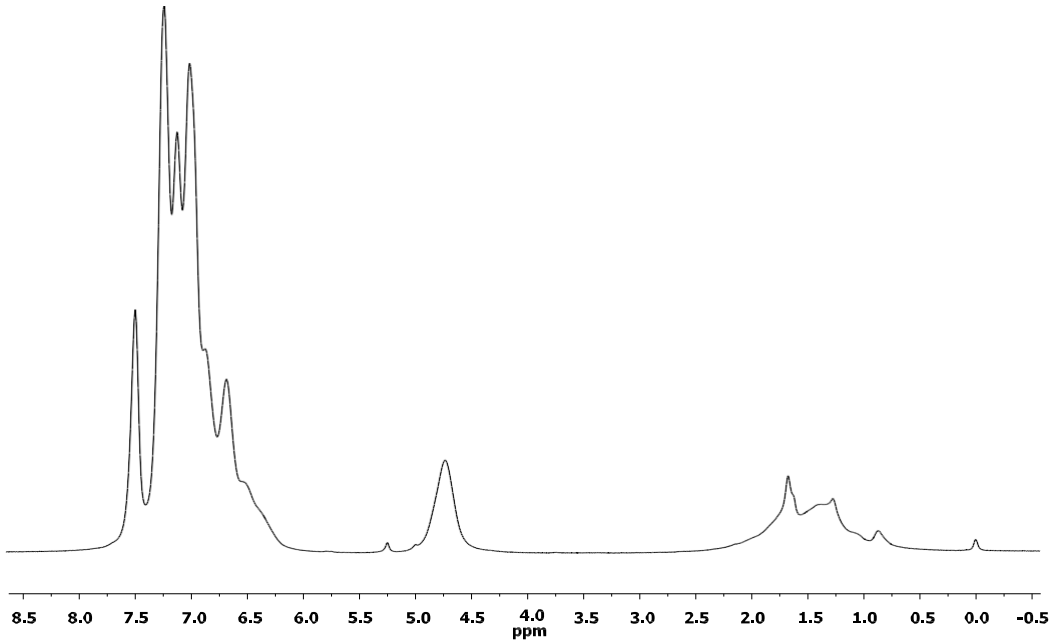


Polymer **8** ^{1}H NMR



Polymer **8** ^{13}C NMR