Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C
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High-Performance Two-Photon Absorption Luminophores: Large Action Cross Sections, Free from Fluorescence Quenching, and Tunable Emission of Efficient Non-Doped Organic Light-Emitting Diodes

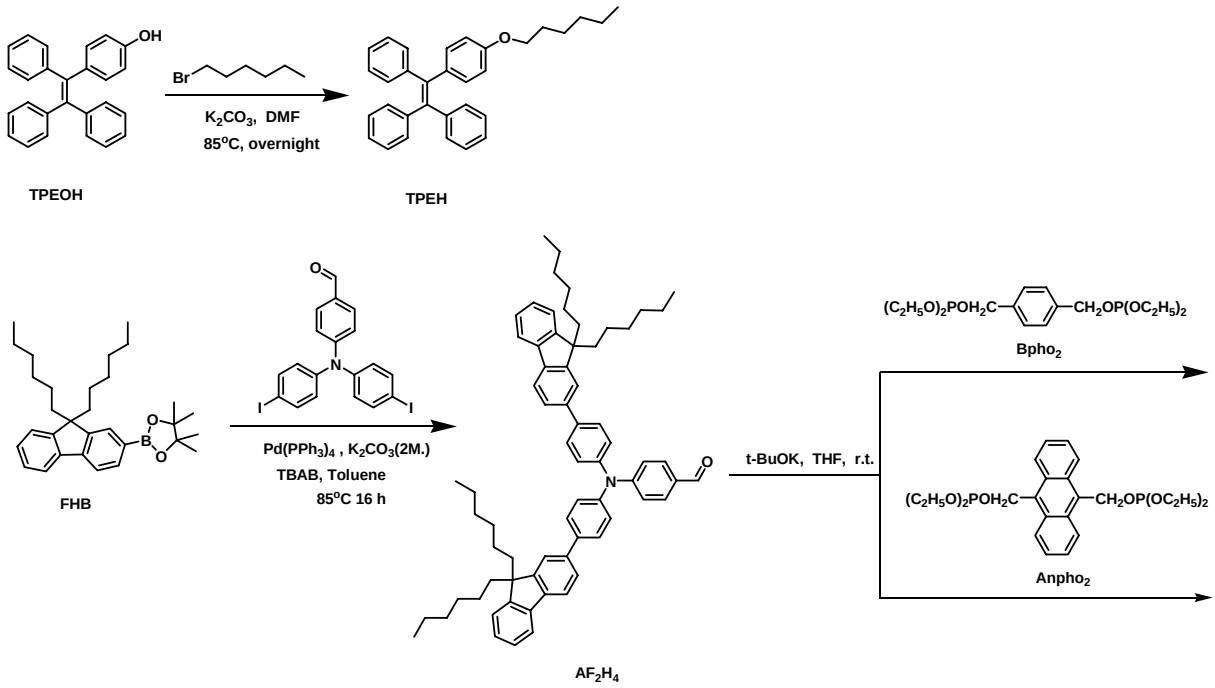
Bingjia Xu, [‡a] Jiajun He, [‡a] Yang Liu,[b] Bin Xu,[b] Qiangzhong Zhu,[c] Mingyuan Xie,[c] Zebo Zheng,[c] Zhenguo Chi,*[a] Wenjing Tian,[b] Chongjun Jin,[c] Fuli Zhao,[c] and Jiarui Xu*[a].

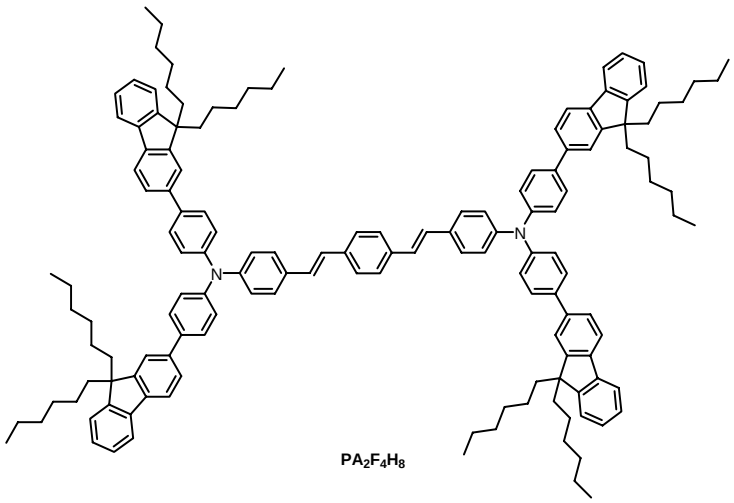
[a] PCFM Lab, DSAPM Lab, KLGHEI of Environment and Energy Chemistry, State Key Laboratory of Optoelectronic Material and Technologies, School of Chemistry and Chemical Engineering, Sun Yet-sen University, Guangzhou 510275, P. R. China.

[b] State Key Laboratory of Supermolecular Structure and Material, Jilin University, Changchun 130012, P. R. China

[c] School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, P.R. China.

Supporting Information





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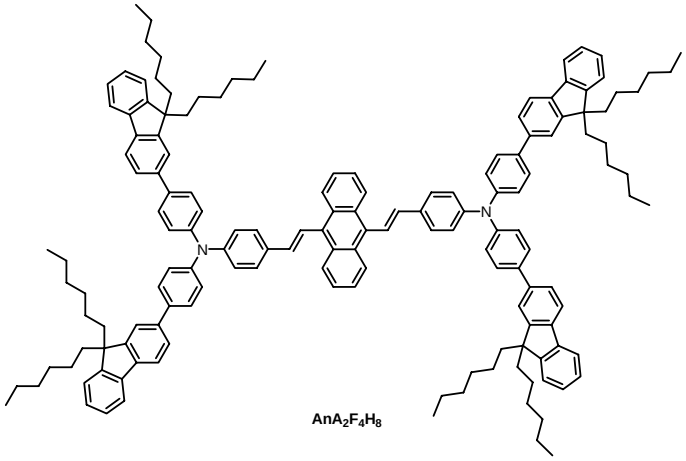


Scheme S1. Synthetic routes of $PA_2F_4H_8$ and $AnA_2F_4H_8$

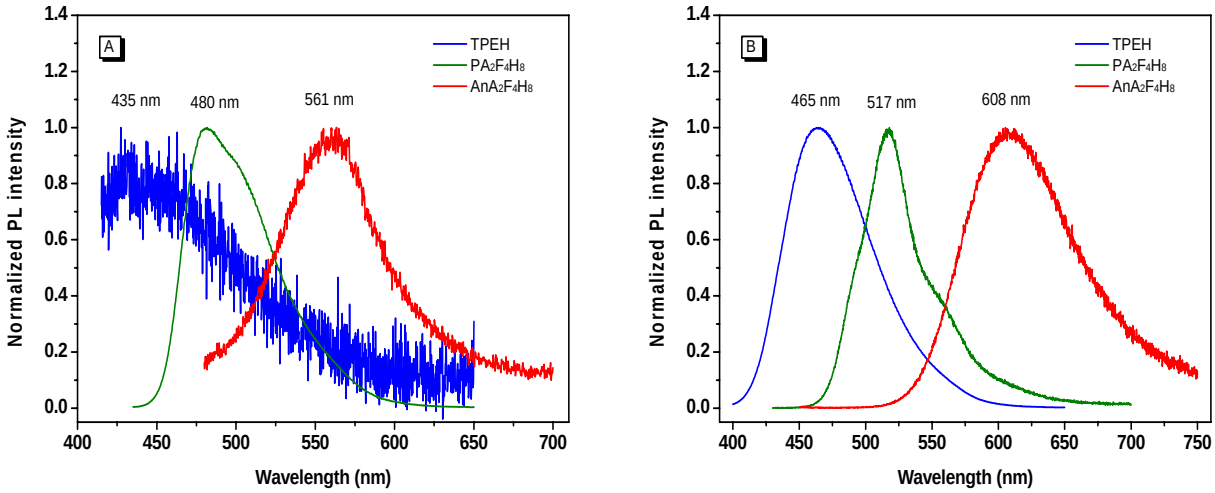


Fig. S1 PL spectra of TPEH, $PA_2F_4H_8$, and $AnA_2F_4H_8$: (A) 10μM in THF solution; (B) at solid state.

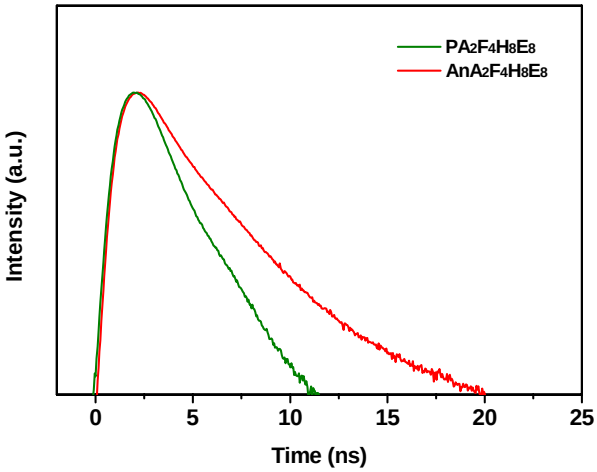


Fig. S2 Time-resolved emission decay curves of the compounds

Table S1. Fluorescence decay parameters of the compounds

Compound	$PA_2F_4H_8E_8$	$AnA_2F_4H_8E_8$
τ_1 (ns) [a]	0.74	0.65
A_1 [b]	0.60	0.22
τ_2 (ns)	1.27	1.72
A_2	0.39	0.70
τ_3 (ns)	12.22	5.30
A_2	0.01	0.06
τ_4 (ns)	N/A	27.33
A_4	N/A	0.01
$<\tau>$(ns) [c]	1.04	2.05

[a] Fluorescence lifetime, [b] Fractional contribution, [c] mean lifetime.

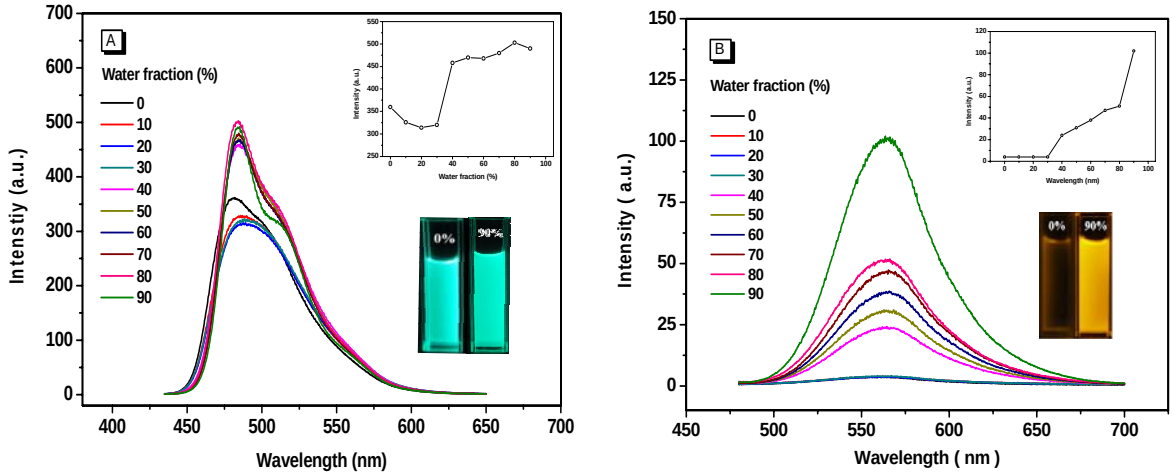
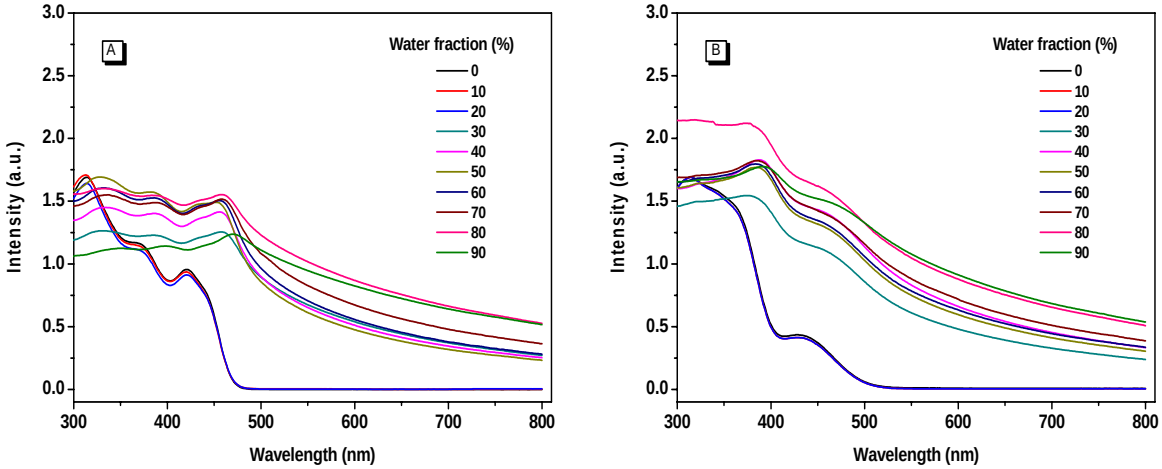


Fig. S3 PL spectra of the dilute solutions of $PA_2F_4H_8$ (A) and $AnA_2F_4H_8$ (B) in water/THF mixtures with different volume fractions of water (concentration: 10 μM). The insets depict changes in PL peak intensity (up) and emission images of the compounds in pure THF and 90% water fraction mixture under 365 nm UV illumination (10 μM) (down).



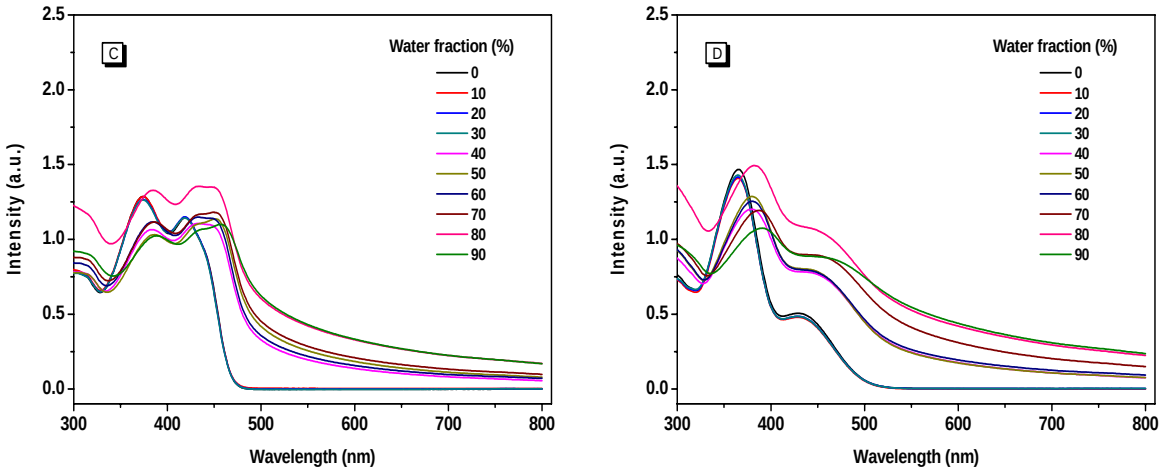


Fig. S4 UV absorption spectra of $PA_2F_4H_8E_8$ (A), $AnA_2F_4H_8E_8$ (B), $PA_2F_4H_8$ (C), and $AnA_2F_4H_8$ (D) in water/THF mixtures with different volume fractions of water (concentration: 10 μM)

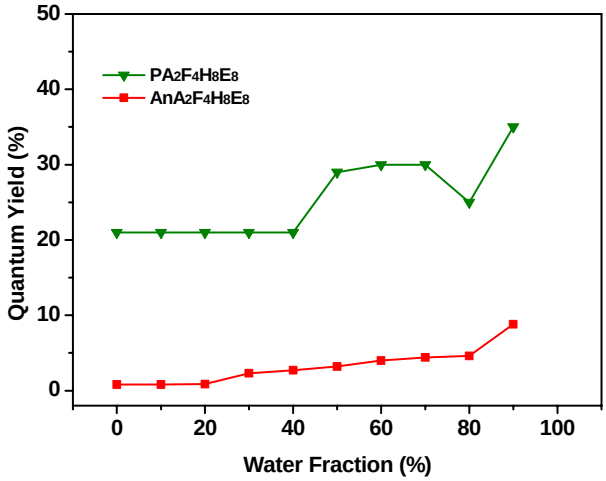


Fig. S5 The quantum yields of the compounds in water/THF mixtures (Standard: fluorescein in 0.1 N sodium hydroxide)

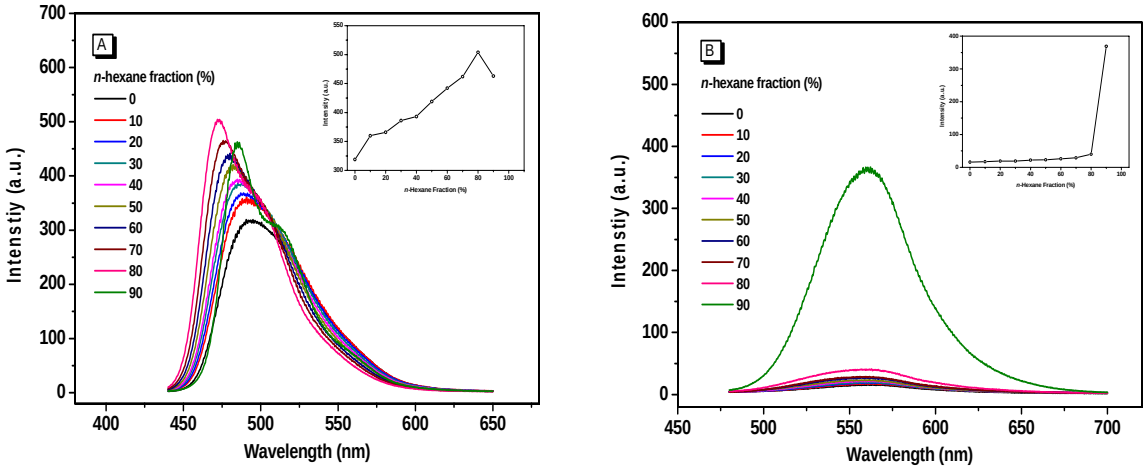


Fig. S6 PL spectra of the dilute solutions of $PA_2F_4H_8E_8$ (A) and $AnA_2F_4H_8E_8$ (B) in *n*-hexane/CH_2Cl_2 mixtures with different volume fractions of *n*-hexane (concentration: 10 μM).

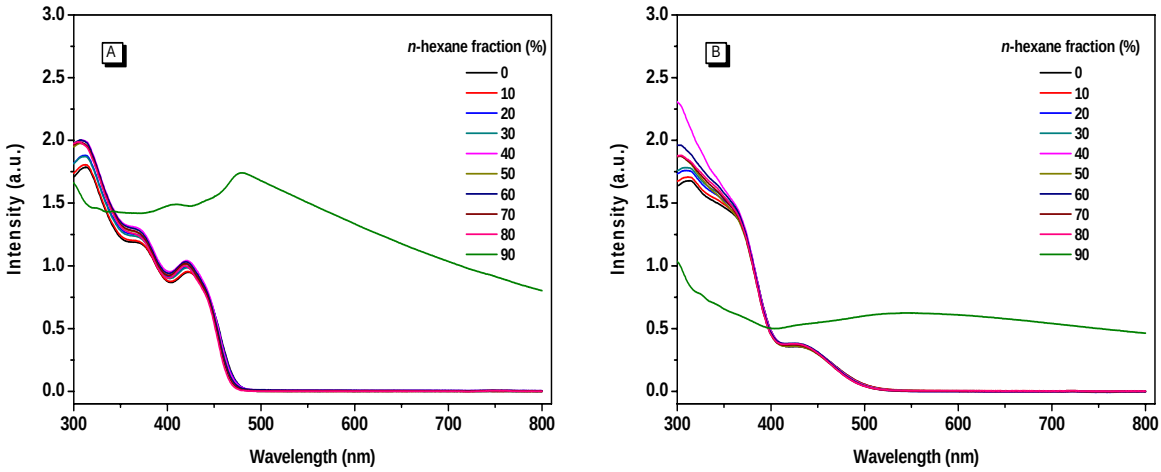


Fig. S7 UV absorption spectra of $PA_2F_4H_8E_8$ (A), $AnA_2F_4H_8E_8$ (B), $PA_2F_4H_8$ (C), and $AnA_2F_4H_8$ (D) in *n*-hexane/CH_2Cl_2 mixtures with different volume fractions of *n*-hexane (concentration: 10 μM)

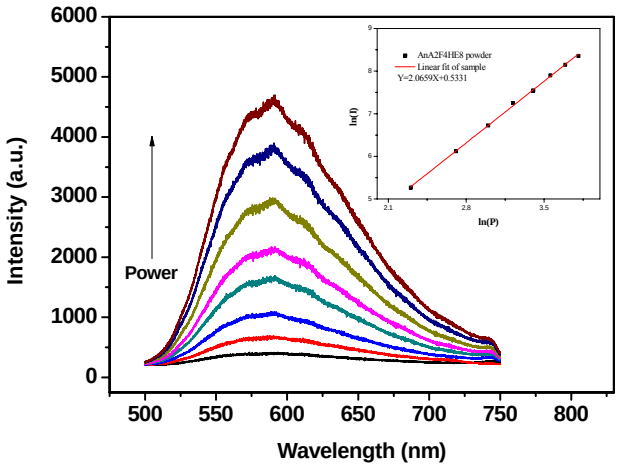


Fig. S8 Two Photon Fluorescence (TPF) emission spectra of $AnA_2F_4H_8E_8$ at solid state with different input power; the inset depicts the plot of the emission intensity versus input laser power for $AnA_2F_4H_8E_8$ on a log/log scale. The fit of the experimental data is shown in black, and the corresponding equation is reported in the inset. (The excitation was 800 nm femtosecond laser).

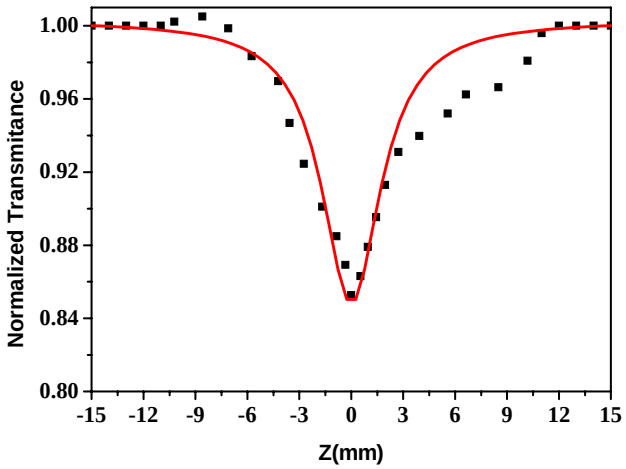


Fig. S9 Normalized Z-scan transmittance of $PA_2F_4H_8E_8$ (Using femtosecond pulse at λ=800 nm, concentration of $PA_2F_4H_8E_8$: 5 mM in THF). The solid line is the theoretical result.

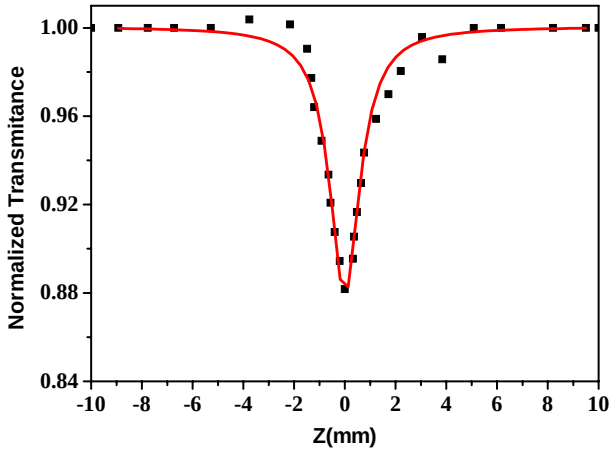


Fig. S10 Normalized Z-scan transmittance of $AnA_2F_4H_8E_8$ (Using femtosecond pulse at λ=800 nm, concentration of $AnA_2F_4H_8E_8$: 5 mM in THF). The solid line is the theoretical result.

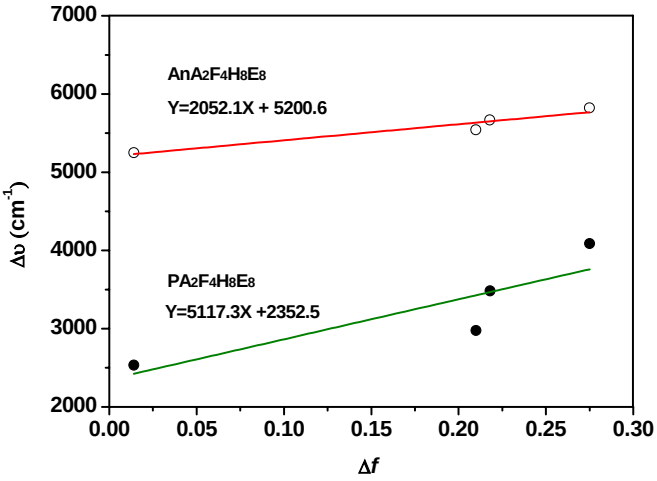


Fig. S11 Plots of Stokes shift ($\Delta\nu$) of $PA_2F_4H_8E_8$ and $AnA_2F_4H_8E_8$ *vs.* solvent polarity

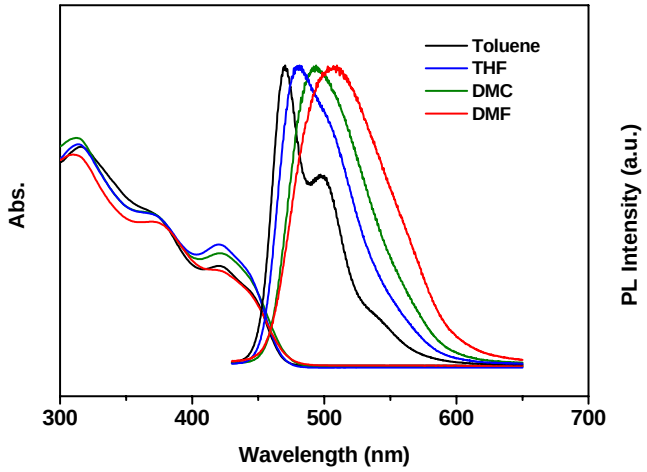


Fig. S12 UV-Visible absorption and PL spectra of $PA_2F_4H_8E_8$ in different solvents

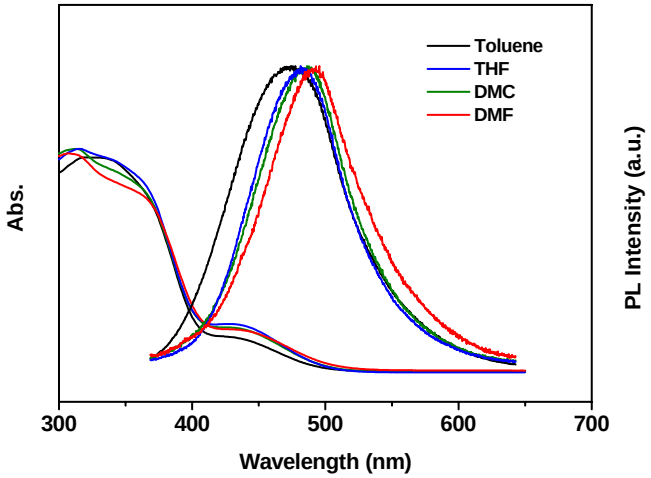


Fig. S13 UV-Visible absorption and PL spectra of $AnA_2F_4H_8E_8$ in different solvents

Table S2. Photophysical properties of the compounds in different solvents

Solvent	λ_{abs} (nm)	λ^{em}_{max} (nm)	Δf	$\Delta\nu$ (cm^{-1})
		$PA_2F_4H_8E_8$		
Toluene	317; 370; 420	470	0.014	2532.9
THF	314; 370; 420	480	0.210	2976.2
DCM	312; 370; 420	492	0.218	3484.3
DMF	311; 374; 420	507	0.275	4085.7
		$AnA_2F_4H_8E_8$		
Toluene	317; 360; 428	552	0.014	5248.5
THF	314; 360; 428	561	0.210	5539.2
DCM	312; 360; 428	565	0.218	5665.4
DMF	308; 365 428	570	0.275	5820.6

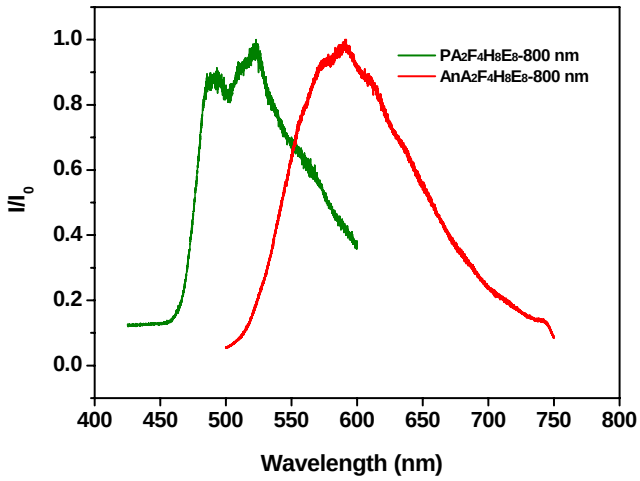


Fig. S14 Two Photon Fluorescence (TPF) emission spectra of the compounds at solid state

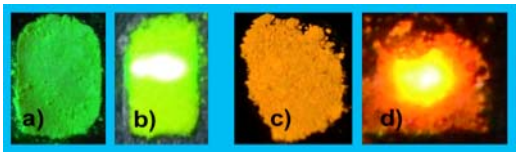


Fig. S15 Photos of one- and two-photonfluorescence emission of the compounds at solid state: a) one-photon fluorescence of $PA_2F_4H_8E_8$; b) two-photon fluorescence of $PA_2F_4H_8E_8$; c) one-photon fluorescence of $AnA_2F_4H_8E_8$; d) two-photon fluorescence of $AnA_2F_4H_8E_8$.

Table S3. Thermal and electrochemical properties of the compounds

Compounds	$T_{d,5\%}$ (°C)	T_g (°C) [a]	T_m (°C) [b]	$E^{ox.}_{onset}$ (V)	$E^{ox.}_{p1}$ (V)	$E^{ox.}_{p2}$ (V)	HOMO (eV)	LUMO (eV)	ΔE_g (eV)
$PA_2F_4H_8E_8$	423	118	N/A	1.17	1.35	1.54	-5.44	-2.79	2.65
$AnA_2F_4H_8E_8$	438	118	N/A	1.17	1.35	1.51	-5.44	-2.95	2.49

[a b] Obtained from second run

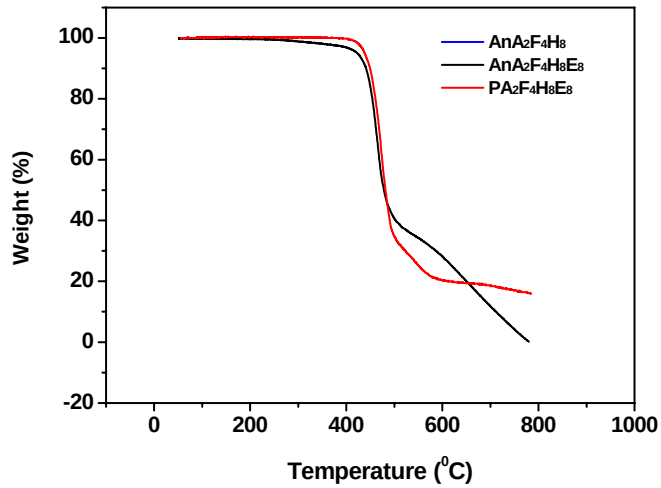


Fig. S16 TGA curves of the compounds.

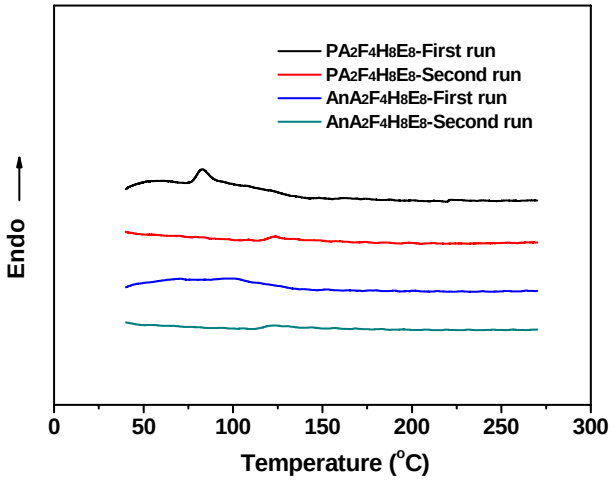


Fig. S17 DSC analysis of the compounds

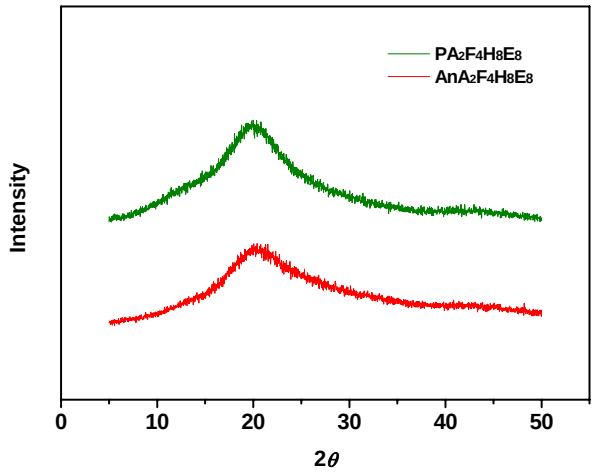


Fig. S18 The powder XRD diffraction patterns of the compounds

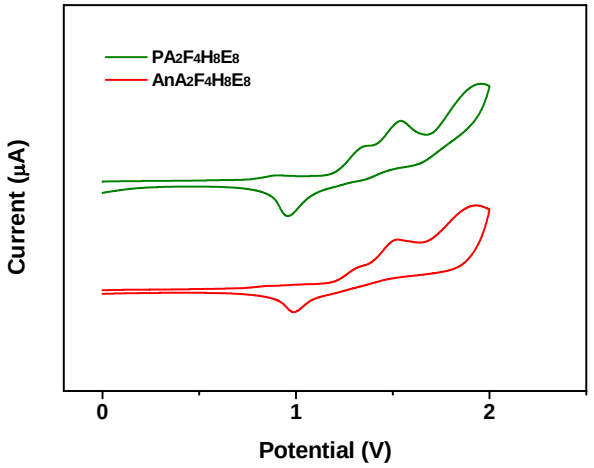


Fig. S19 Cyclic voltammetry curves of the compounds

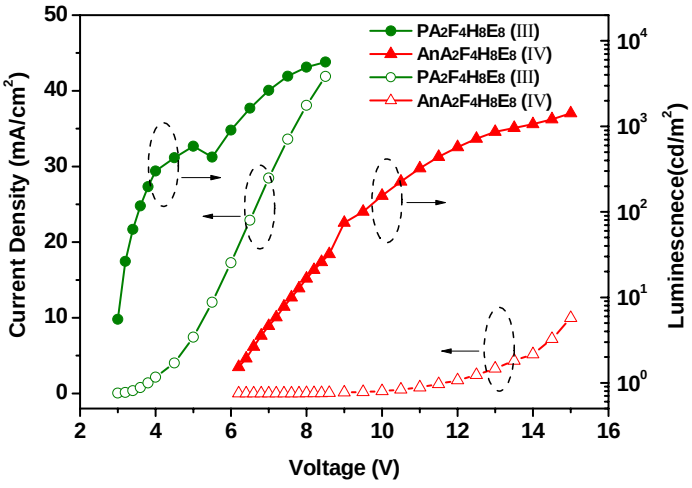


Fig. S20 Current density–voltage–luminance characteristics for the EL devices of (III) and (IV)

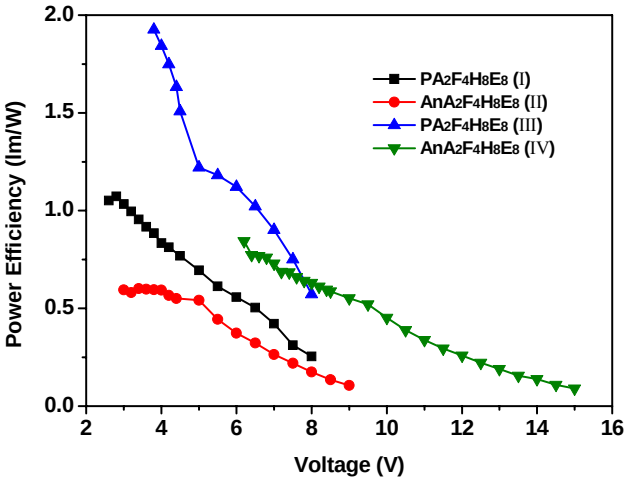


Fig. S21 Power efficiency–voltage characteristics of the EL devices

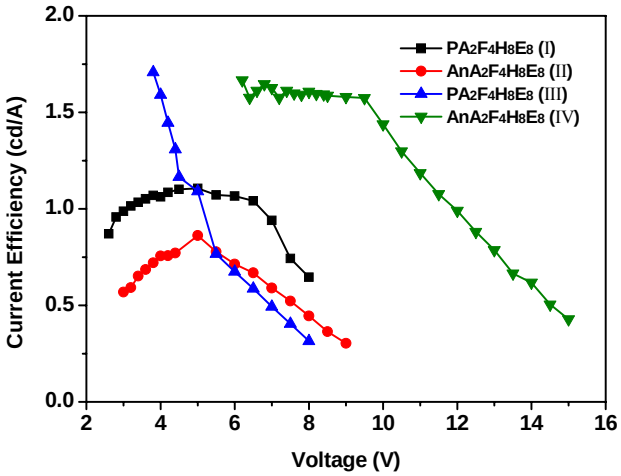


Fig. S22 Current efficiency–voltage characteristics of the EL devices

Structure Information of the Intermediate and Final products

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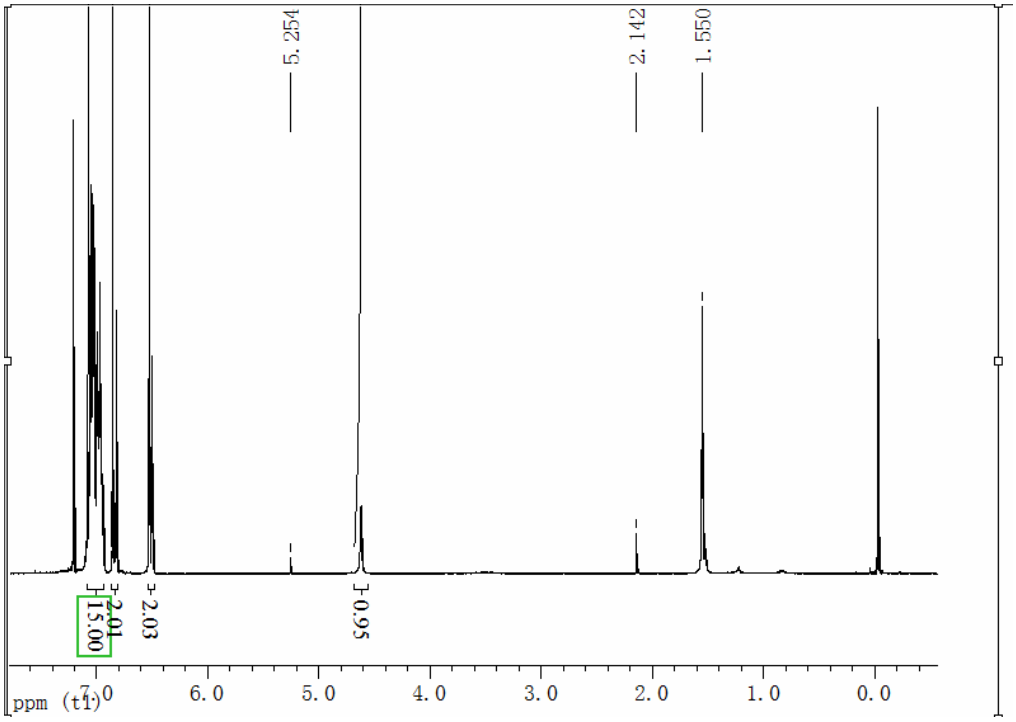
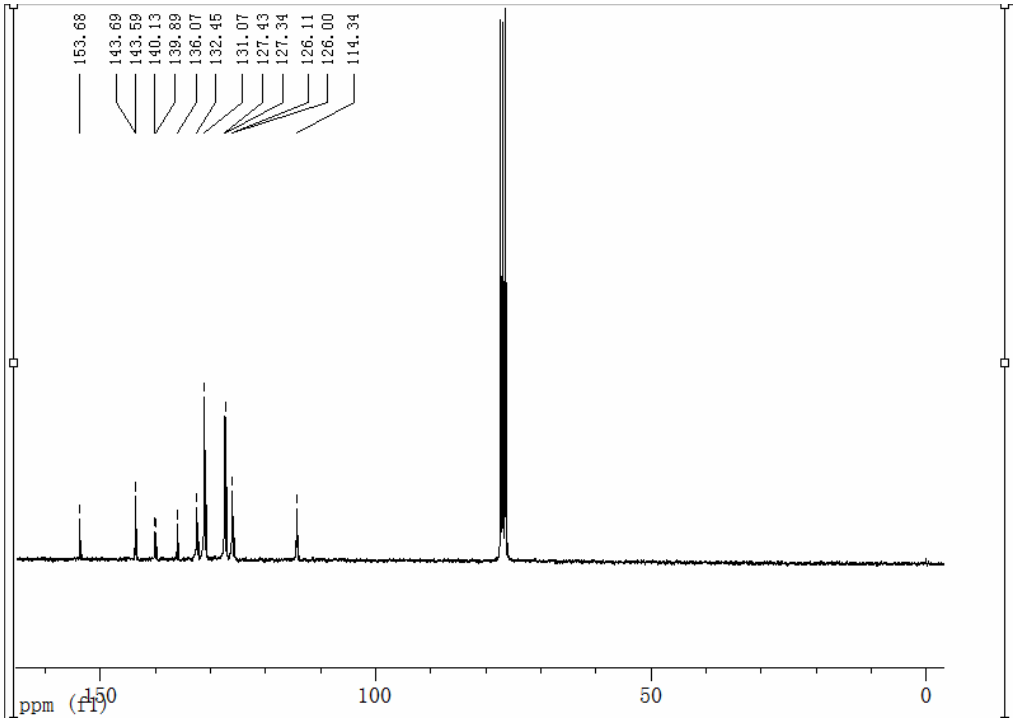
^{1}H NMR



^{13}C NMR



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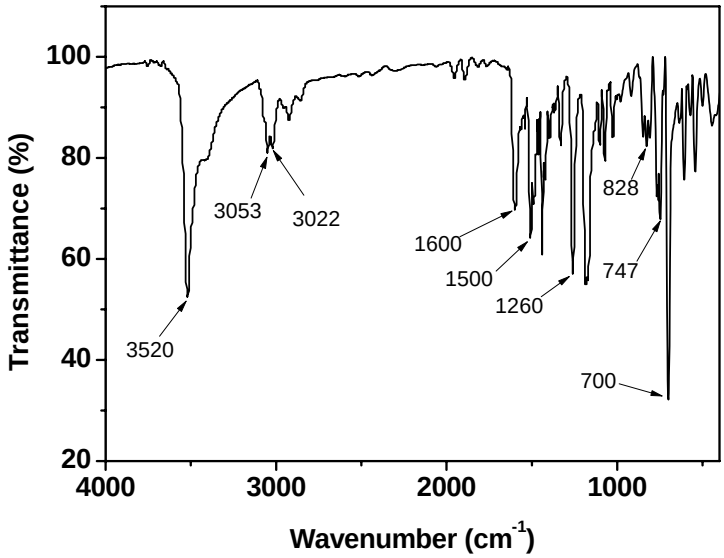
FT-IR



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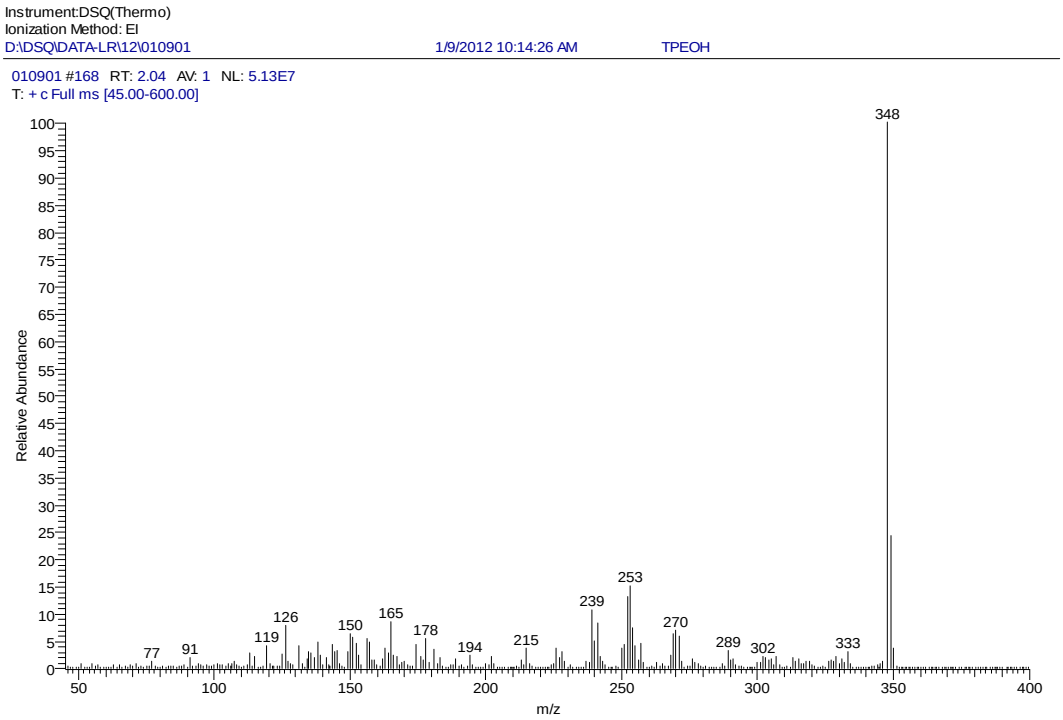

2. TPEH

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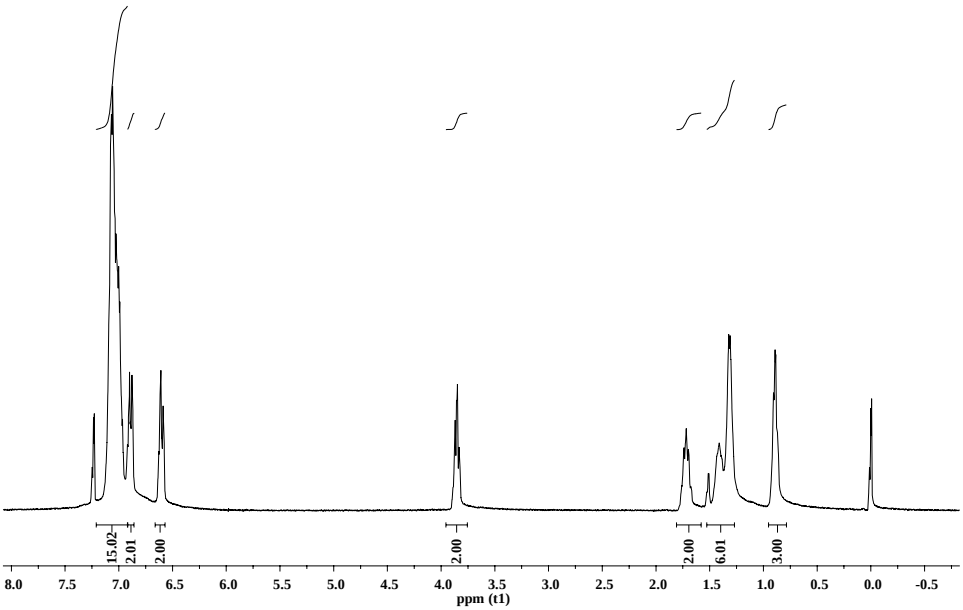

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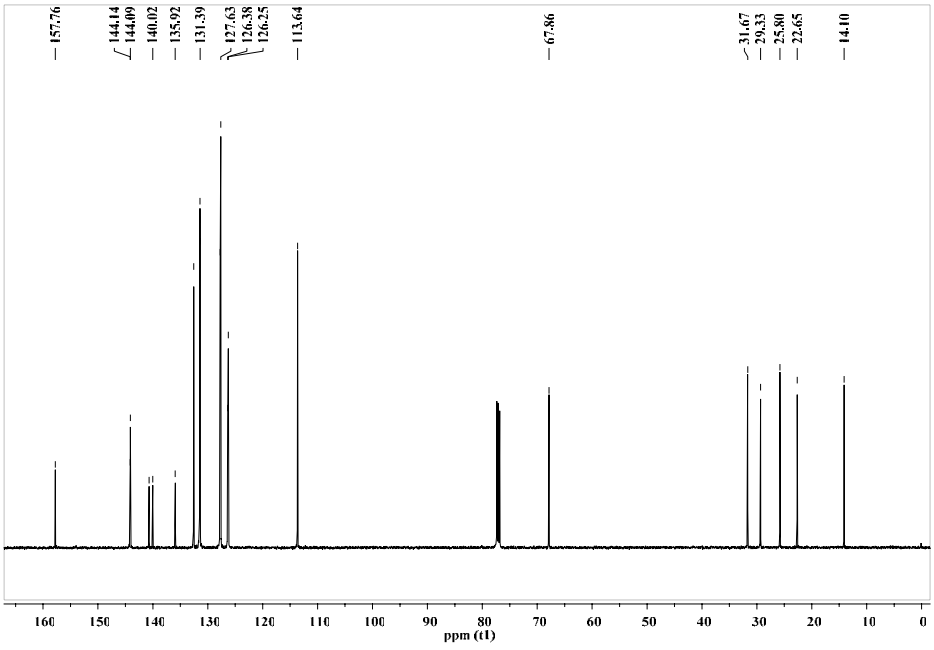

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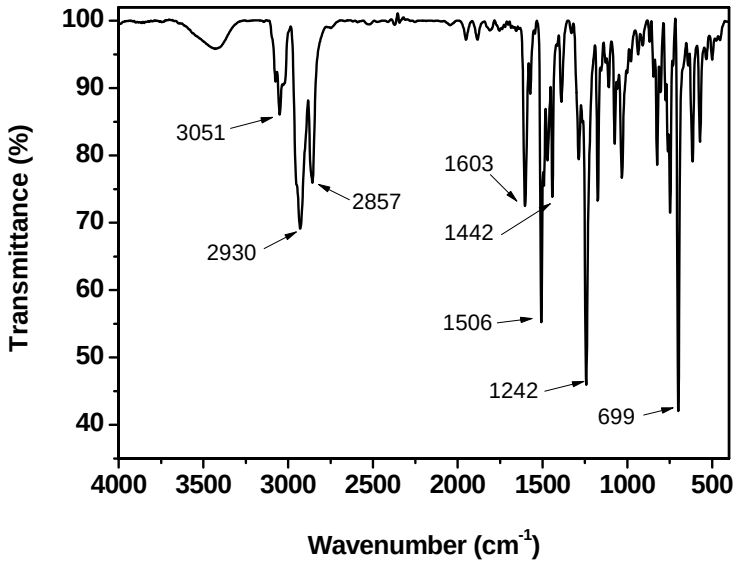

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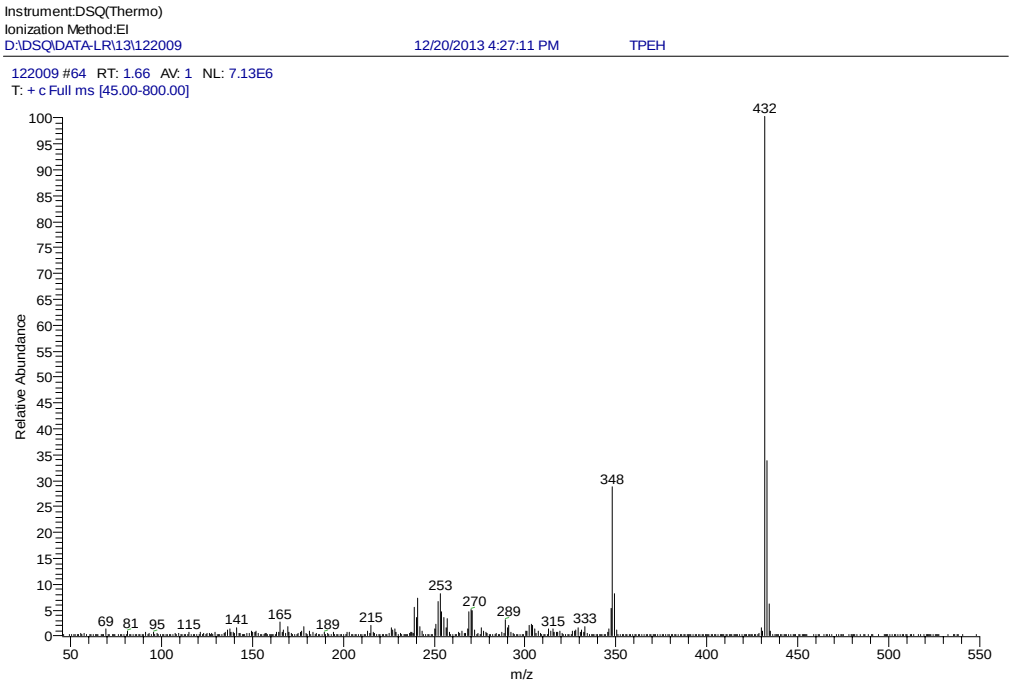

3. EHBr

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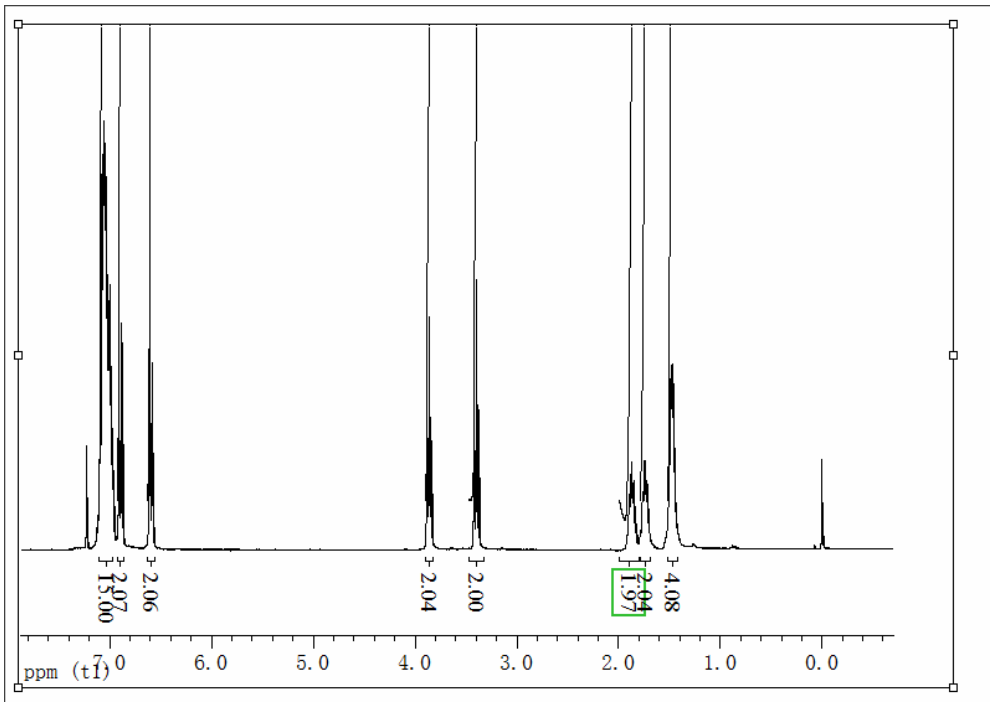

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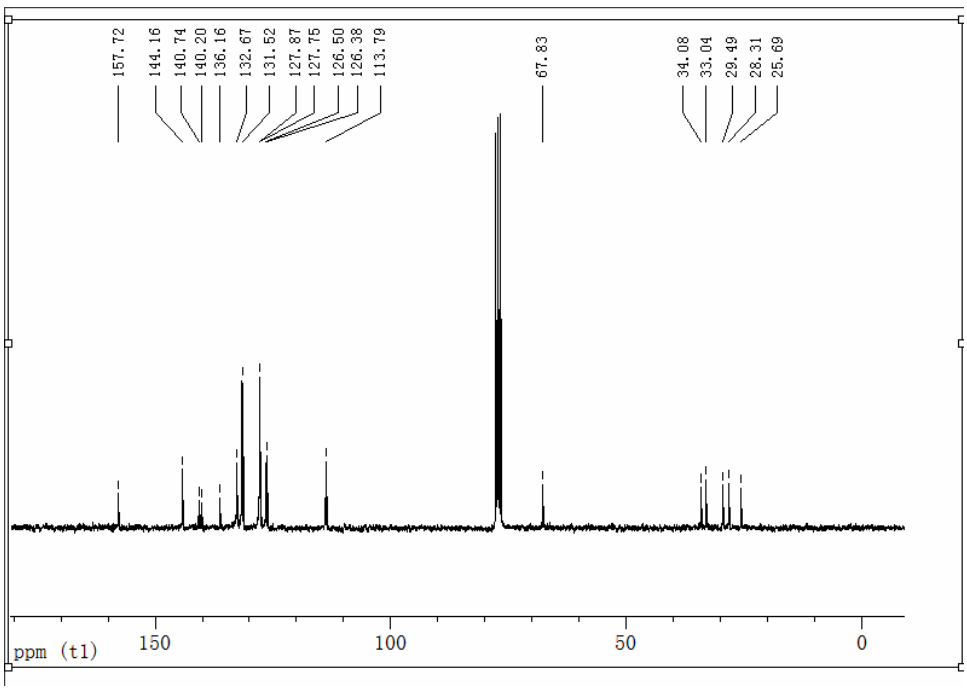

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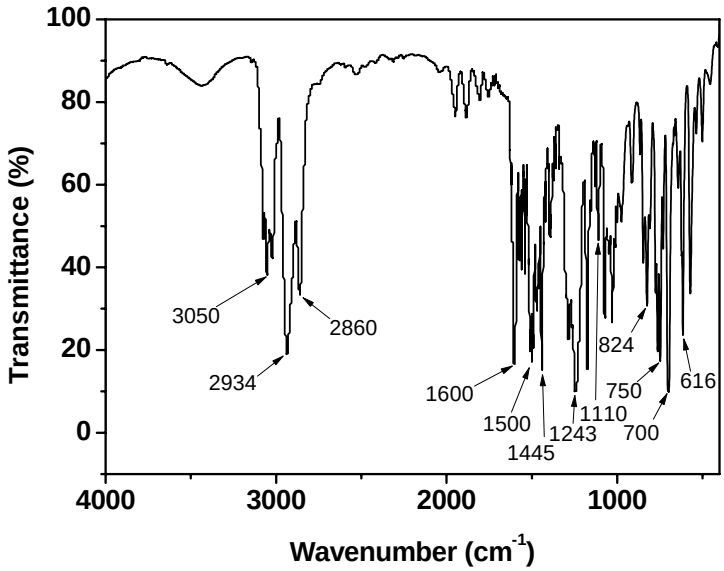
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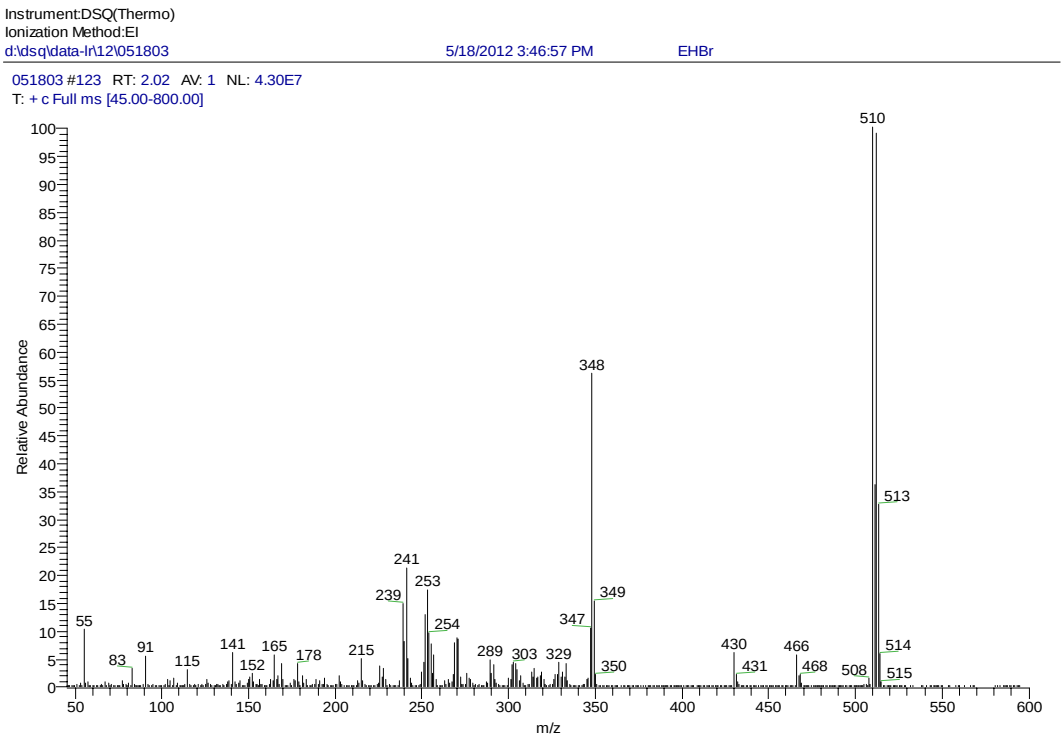
EI-MS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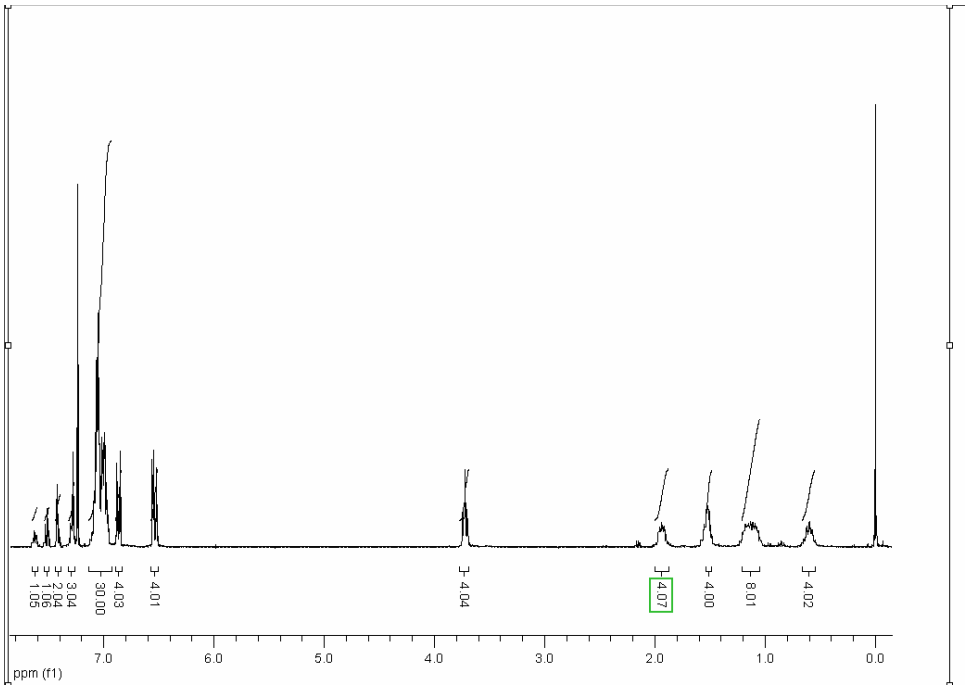
Relative Abundance
m/z

4. FHE_2Br

^1H NMR



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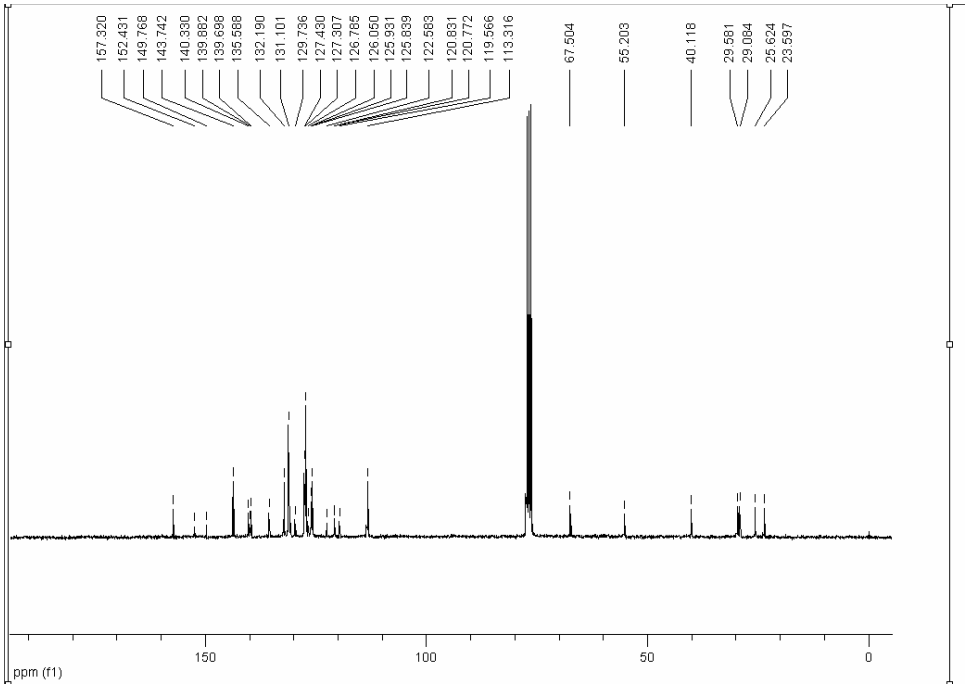

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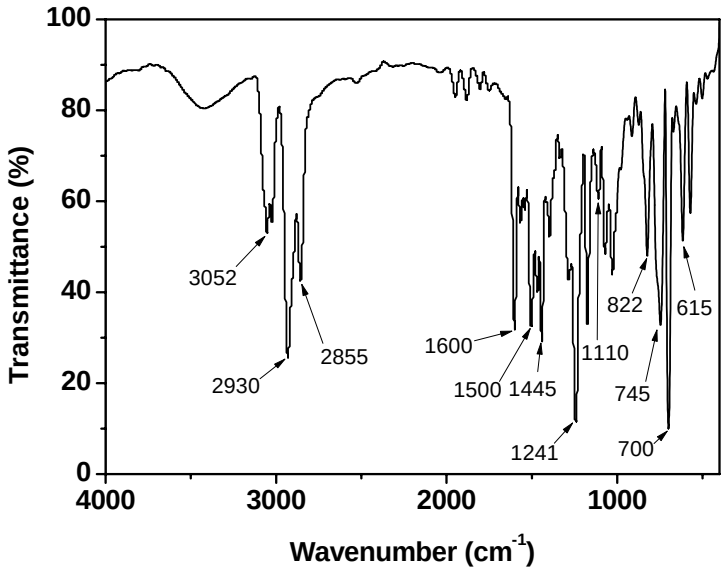
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1500
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1241
1110
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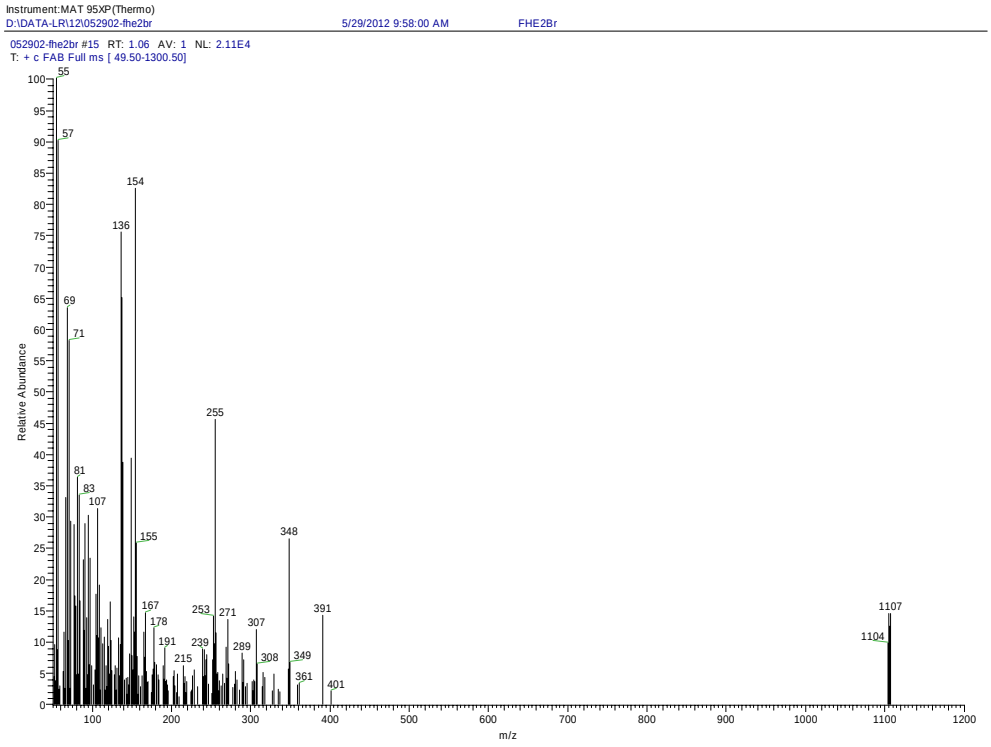
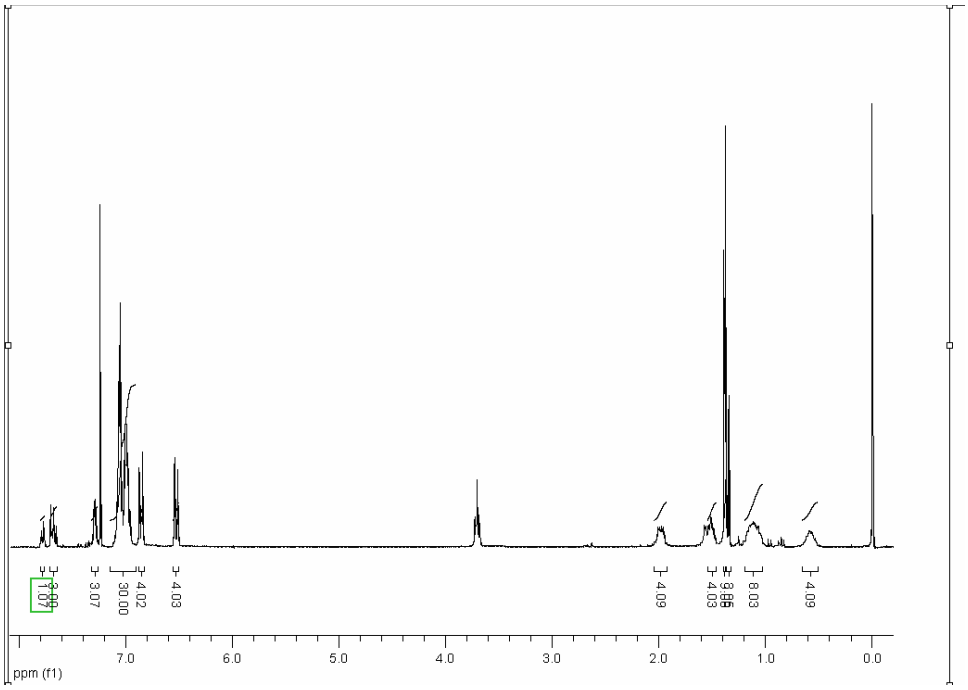
745
700
615

EI-MS

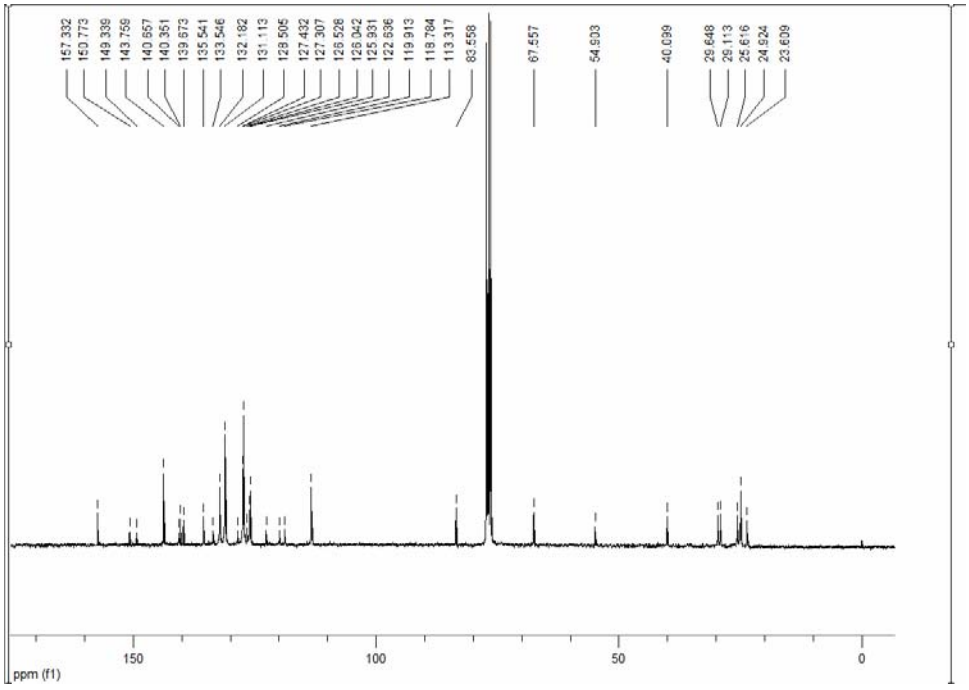

Instrument:MAT 95XP(Thermo)
D:\DATA-LR\12\052902-fhe2br
5/29/2012 9:58:00 AM
FHE2Br
052902-fhe2br #15 RT: 1.06 AV: 1 NL: 2.11E4
T: + c FAB Full ms [49.50-1300.50]
Relative Abundance
m/z

5. FHE_2B

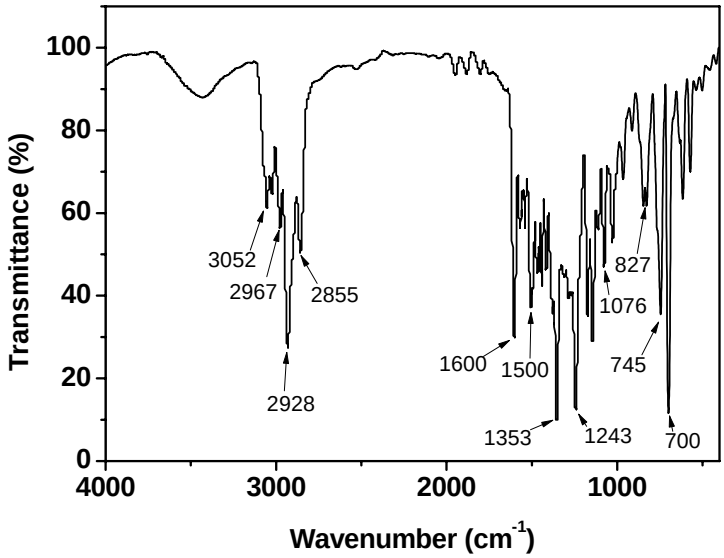
^1H NMR



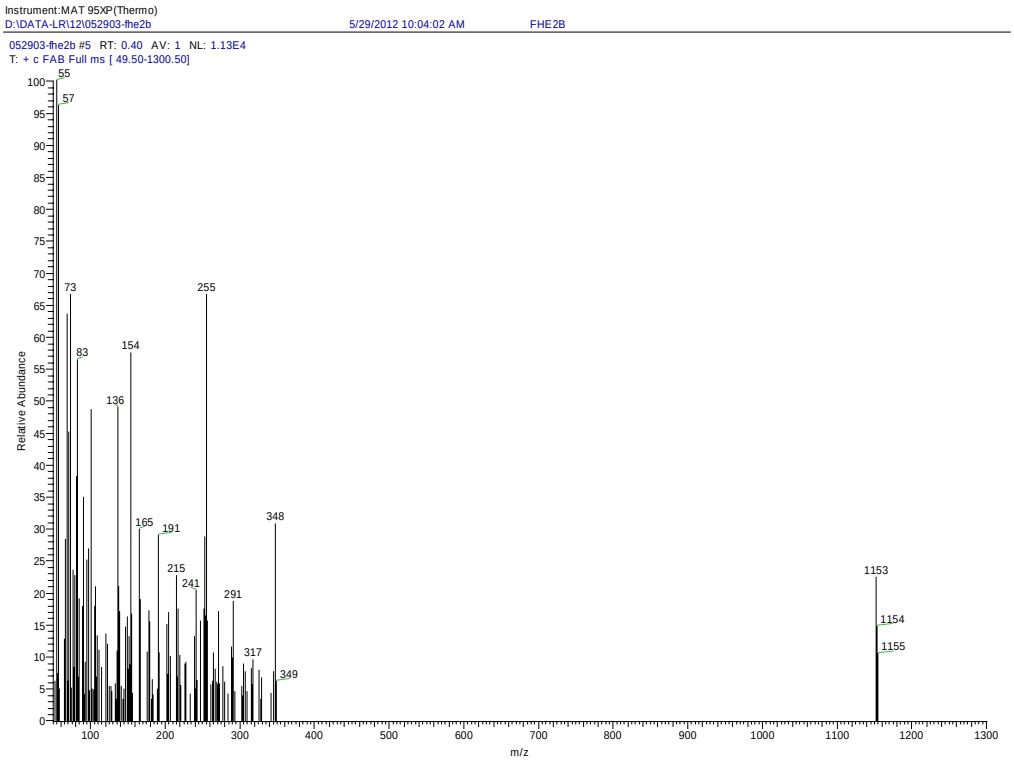
^{13}C NMR



FT-IR

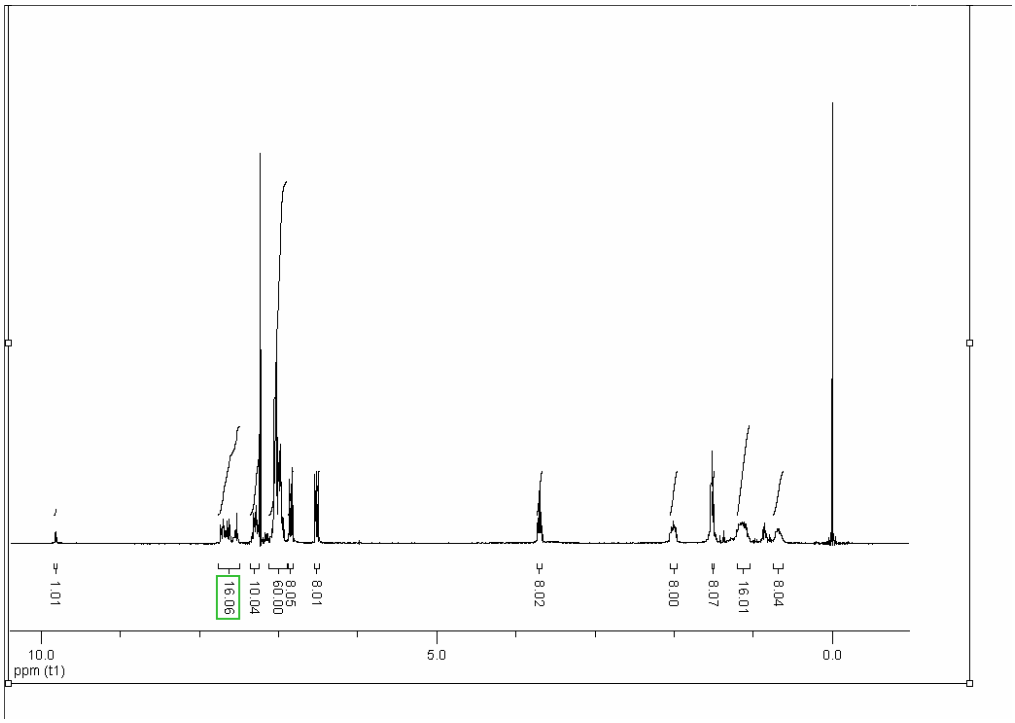

Transmittance (%)
Wavenumber (cm-1)
3052
2967
2855
2928
1600
1500
1353
1243
827
1076
745
700

EI-MS

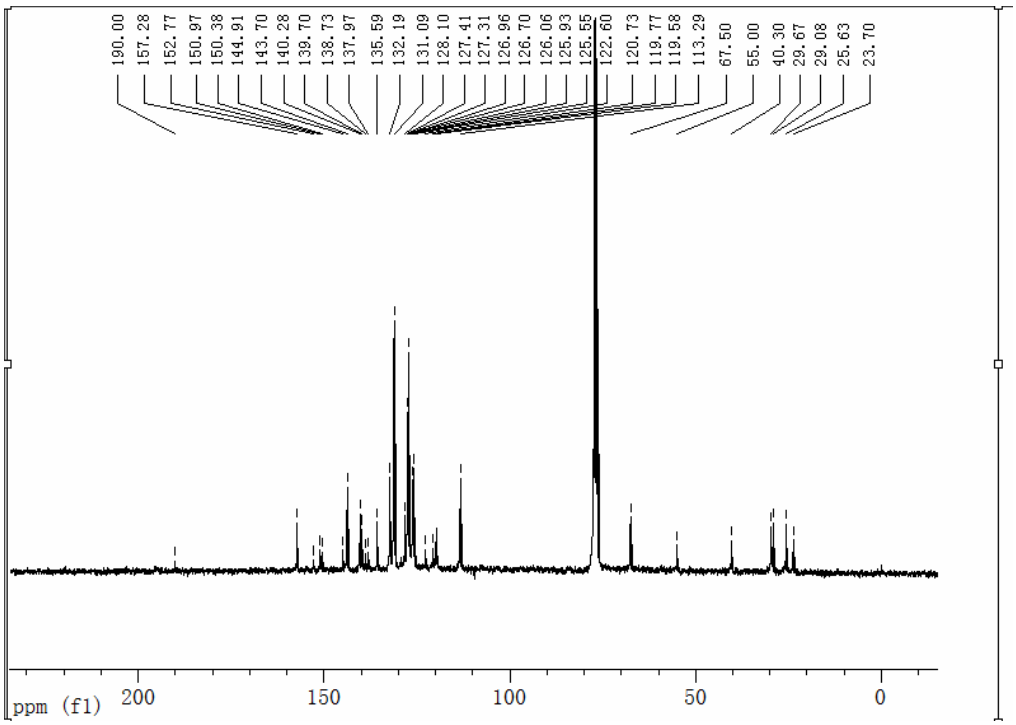

Instrument:MAT 95XP(Thermo)
D:\DATA-LR\12\052903-fhe2b
5/29/2012 10:04:02 AM
FHE2B
052903-fhe2b #5 RT: 0.40 AV: 1 NL: 1.13E4
T: + c FAB Full ms [49.50-1300.50]
Relative Abundance
m/z

6. $AF_2H_4E_4$

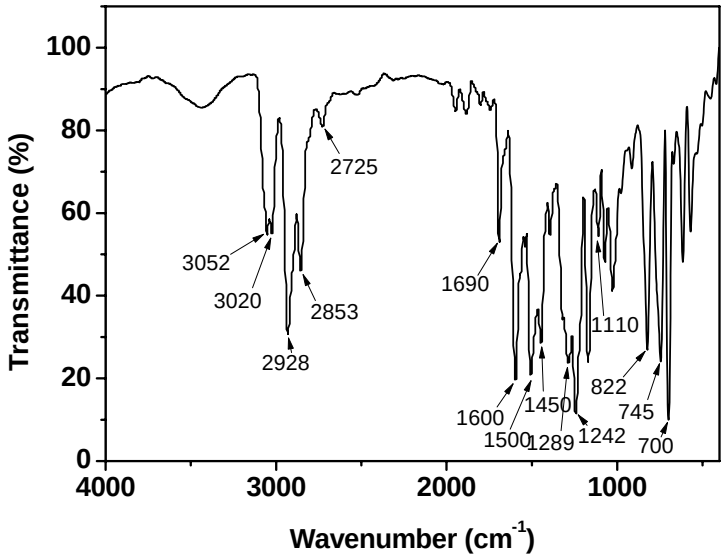
^{1}H NMR



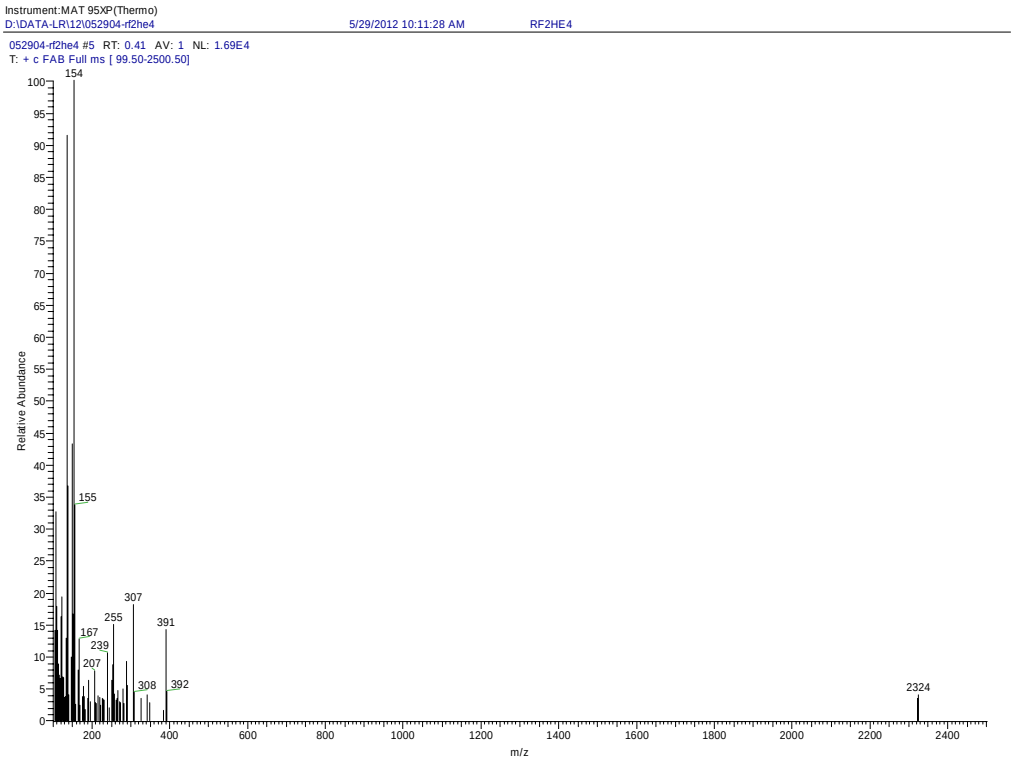
^{13}C NMR



FT-IR

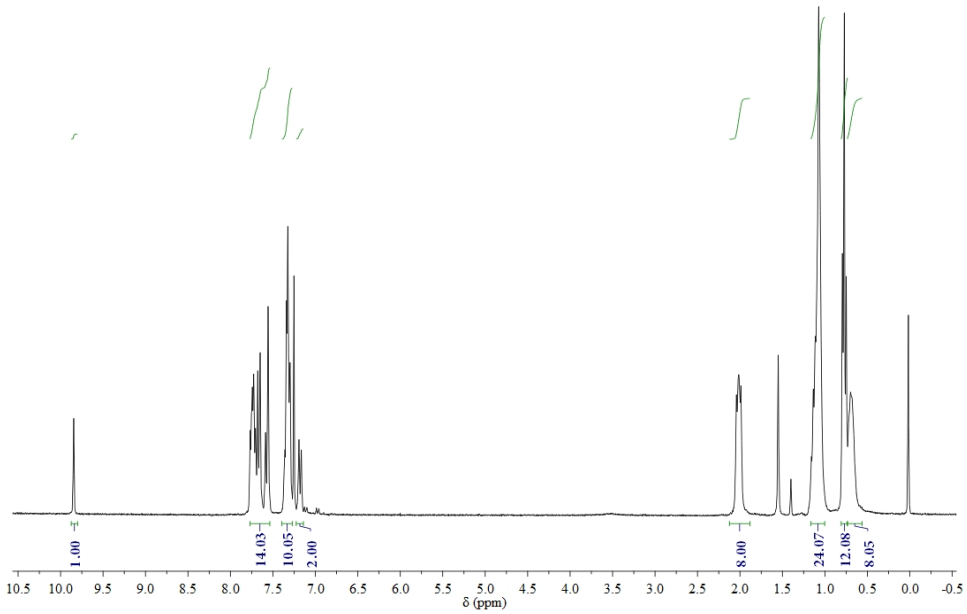

Transmittance (%)
Wavenumber (cm-1)
3052
3020
2928
2853
2725
1690
1600
1500
1450
1289
1242
1110
822
745
700

EI-MS

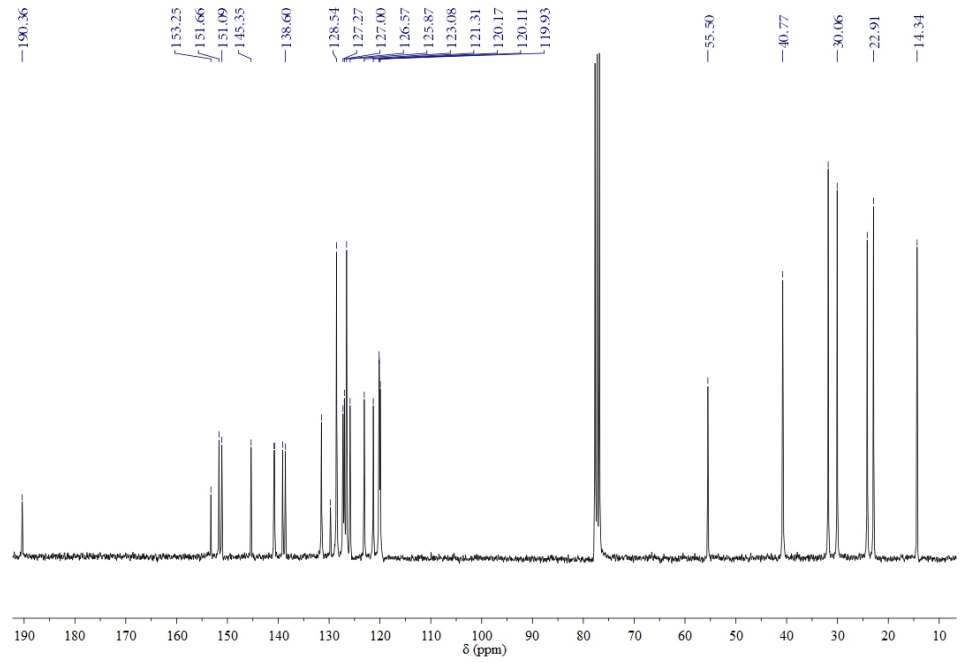

Instrument:MAT 95XP(Thermo)
D:\DATA-LR\12\052904-rf2he4
5/29/2012 10:11:28 AM
RF2HE4
052904-rf2he4 #5 RT: 0.41 AV: 1 NL: 1.69E4
T: + c FAB Full ms [99.50-2500.50]
Relative Abundance
m/z
154
155
307
255
391
167
239
207
308
392
2324

7. AF_2H_4

^{1}H NMR



^{13}C NMR



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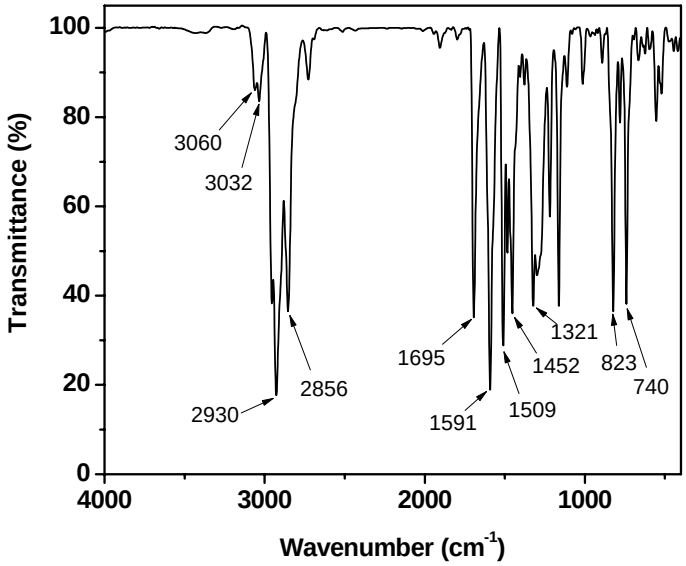
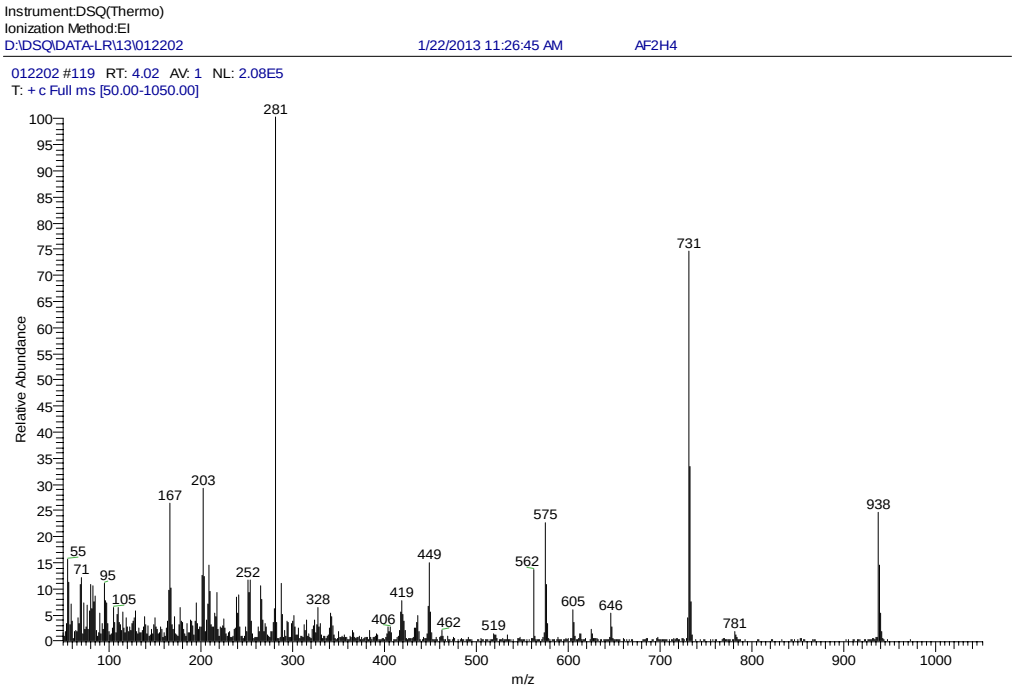
FT-IR

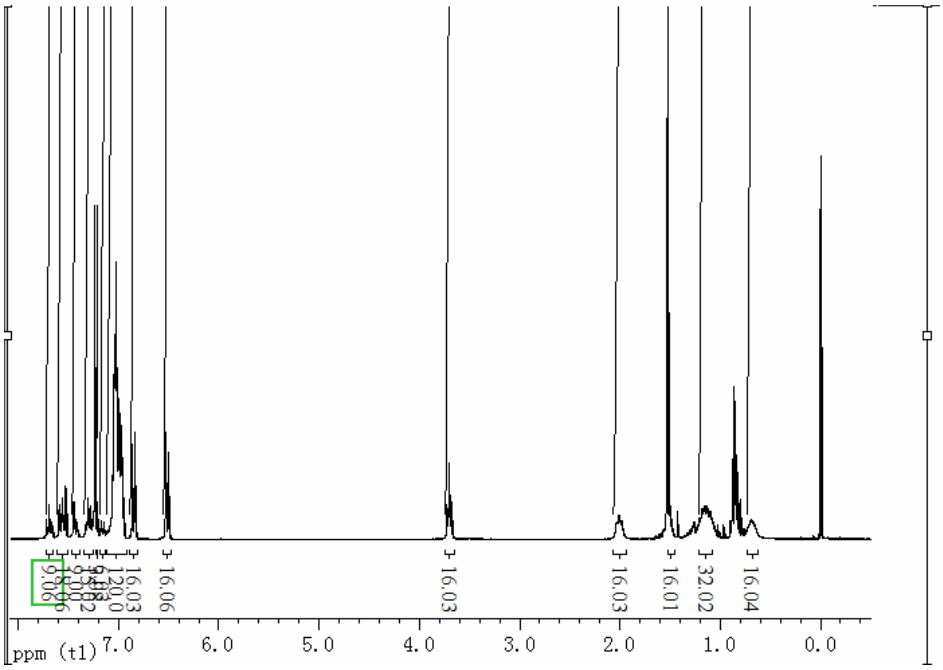


EI-MS

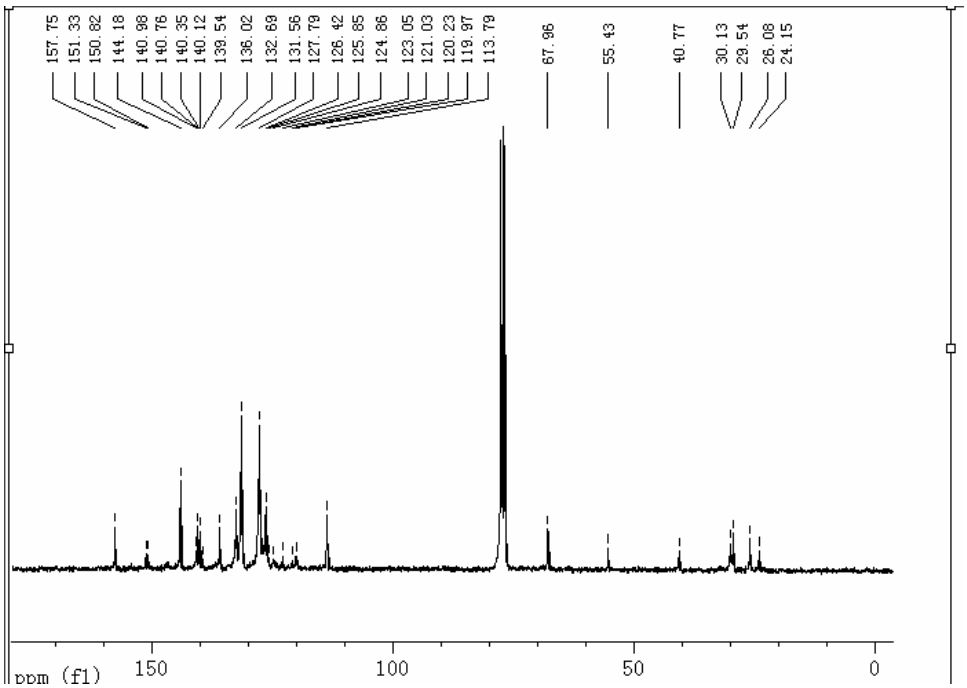


8. $PA_2F_4H_8E_8$

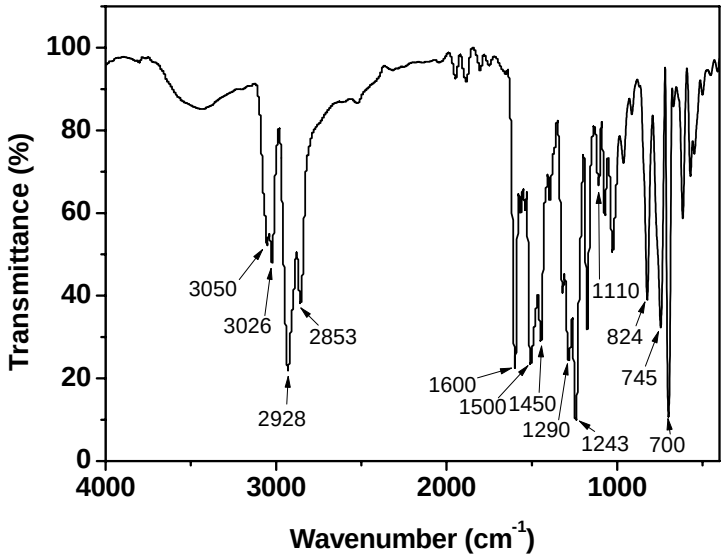
^{1}H NMR



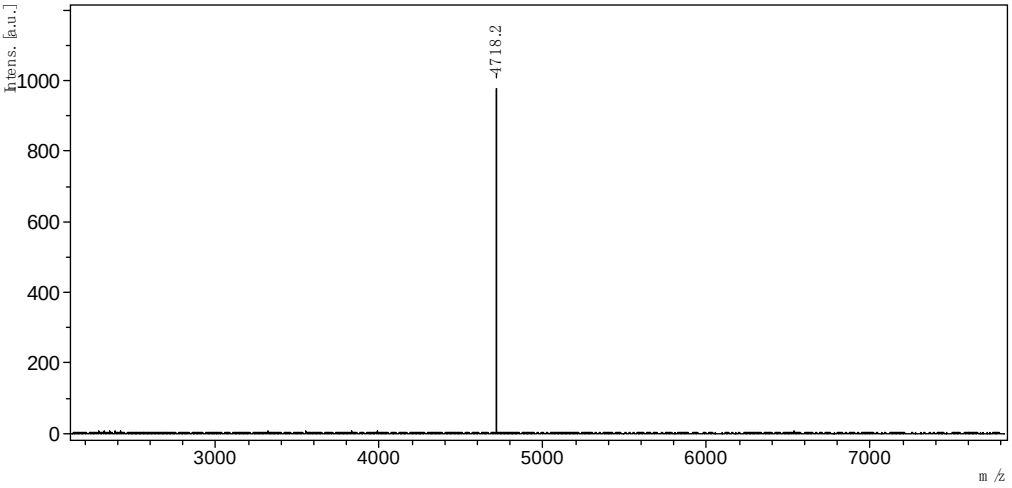
^{13}C NMR



FT-IR

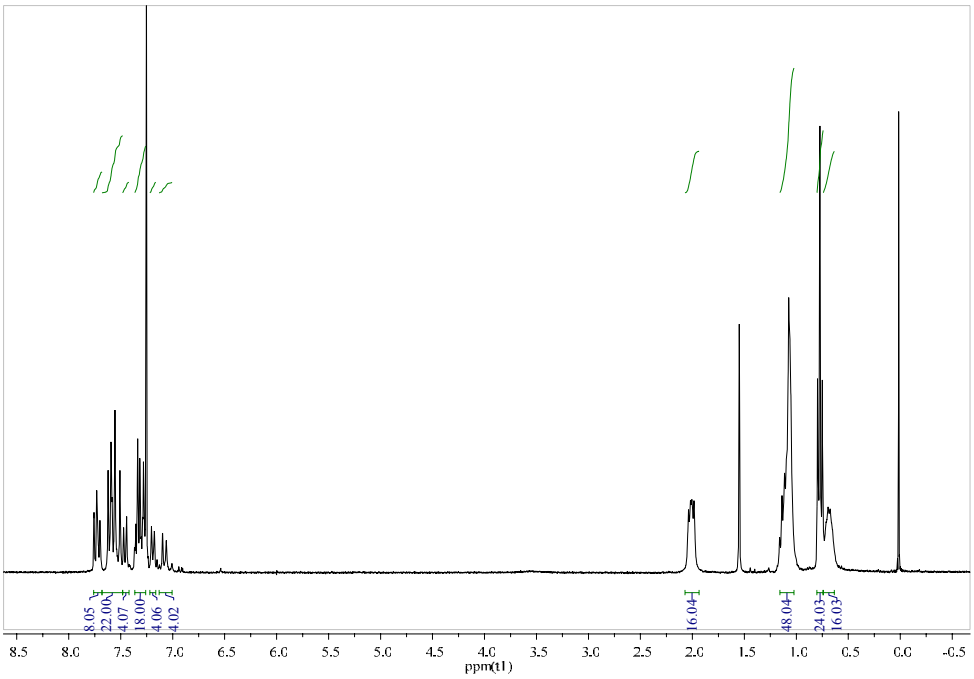


MALDI-TOF-MS

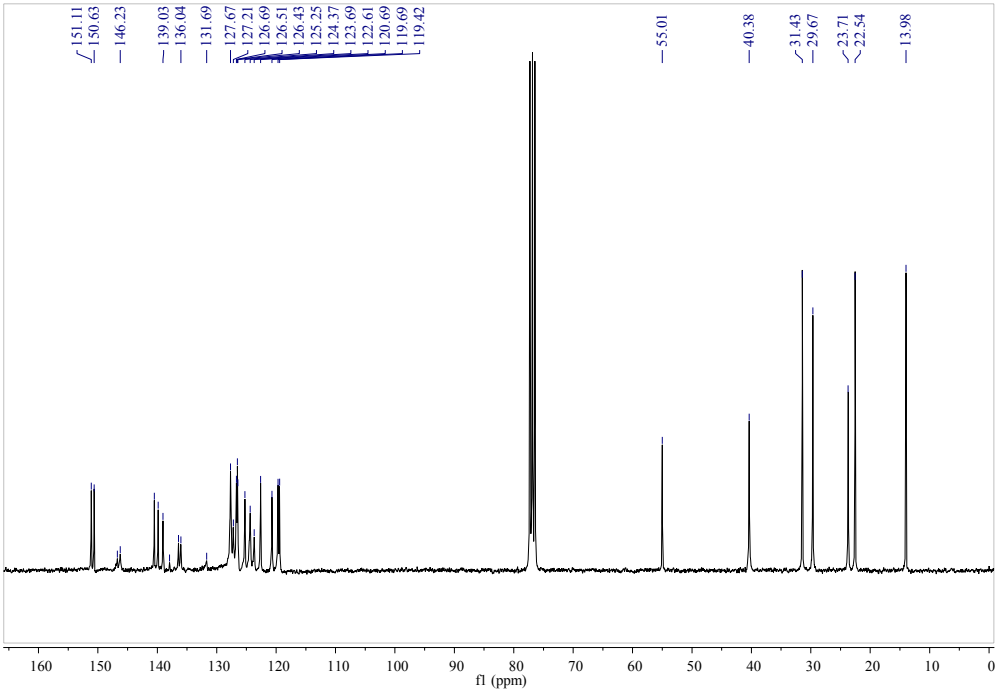


9. $PA_2F_4H_8$

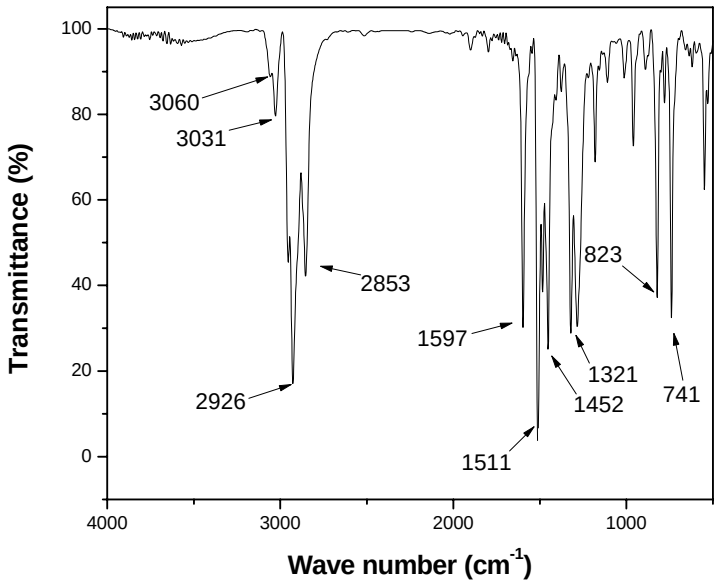
^1H NMR



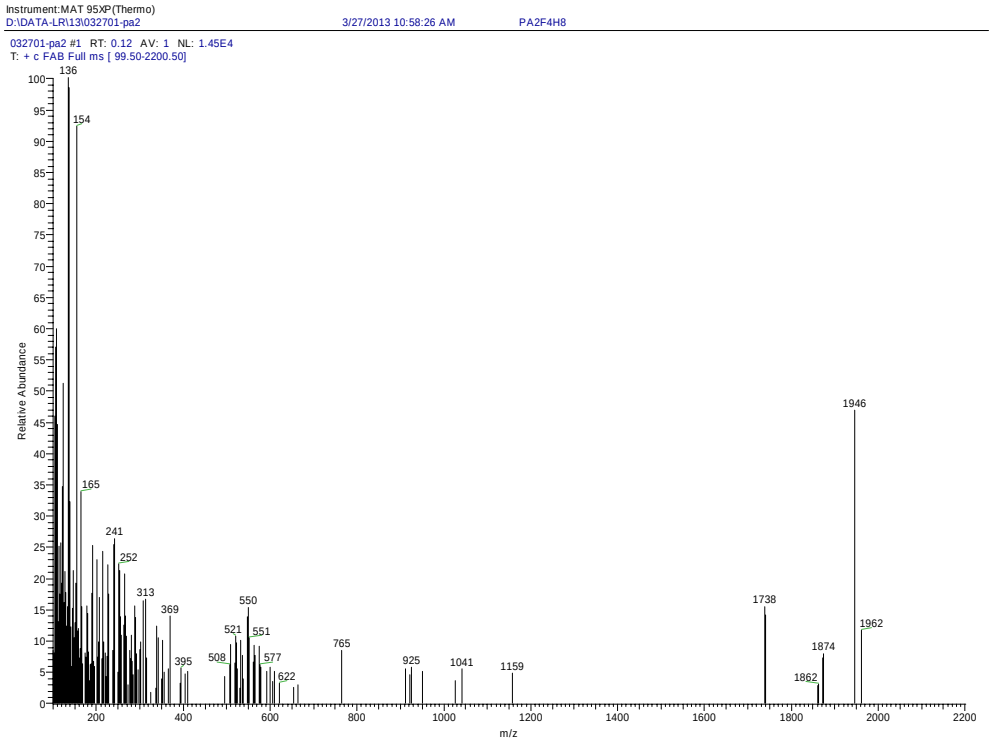
^{13}C NMR



FT-IR

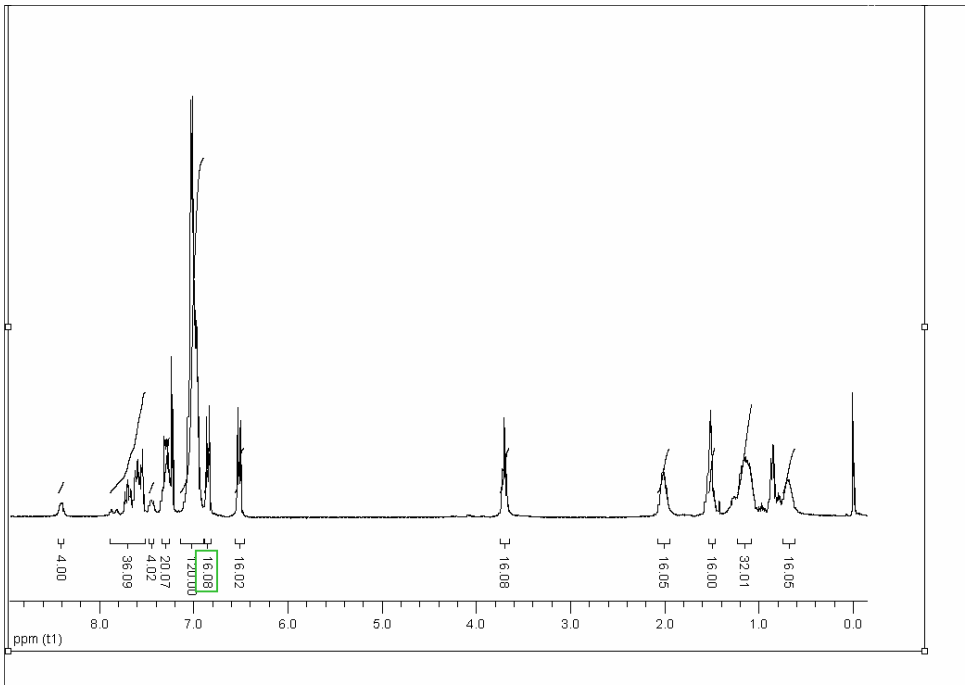

Transmittance (%)
Wave number (cm-1)
3060
3031
2926
2853
1597
1511
1452
1321
823
741

FAB-MS

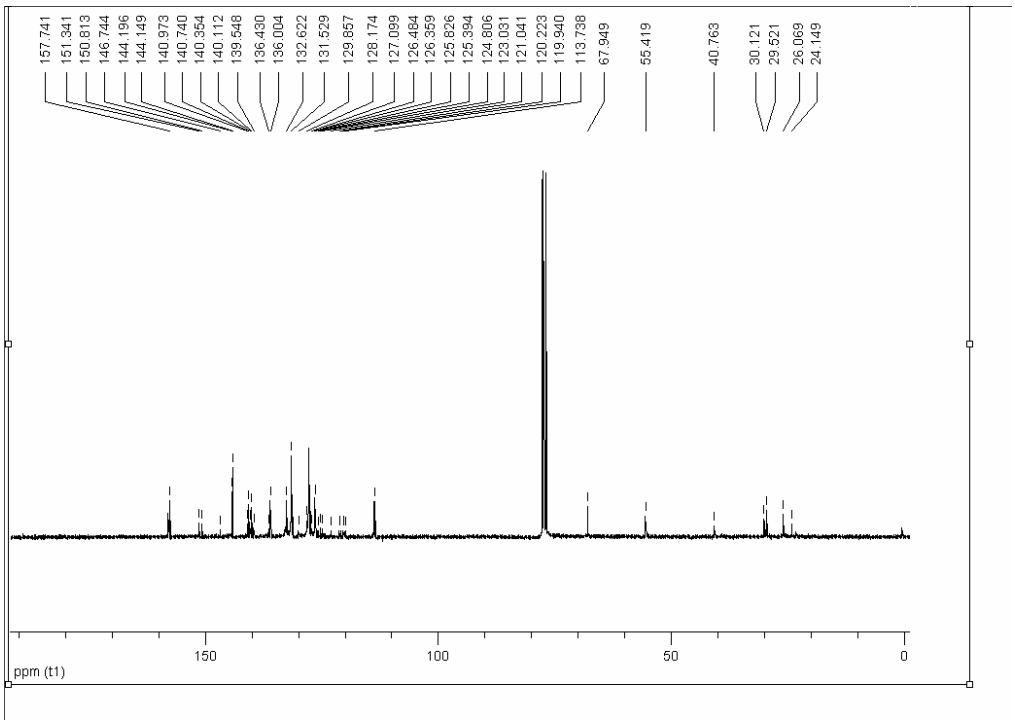

Instrument:MAT 95XP(Thermo)
D:\DATA-LR\13\032701-pa2
3/27/2013 10:58:26 AM
PA2F4H8
032701-pa2 #1 RT: 0.12 AV: 1 NL: 1.45E4
T: + c FAB Full ms [99.50-2200.50]
Relative Abundance
m/z

10. $AnA_2F_4H_8E_8$

^1H NMR



^{13}C NMR



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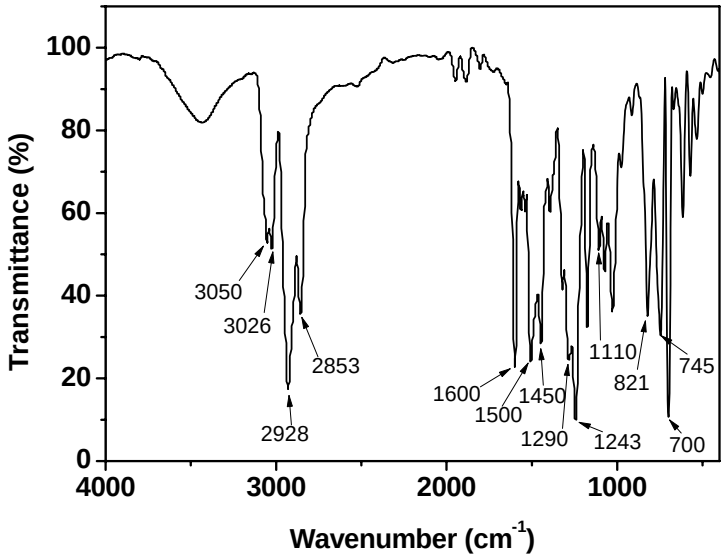
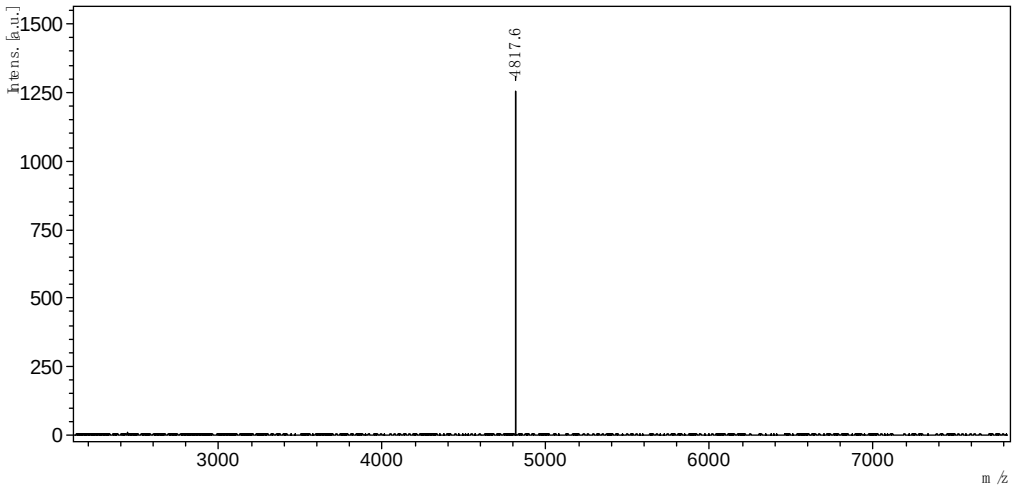
FT-IR

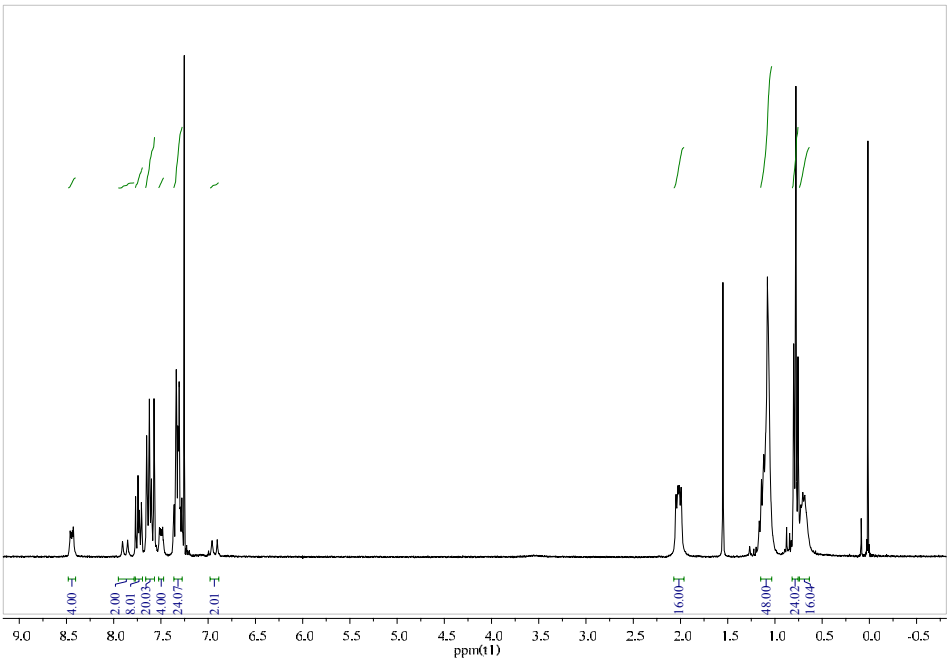


MALDI-TOF-MS

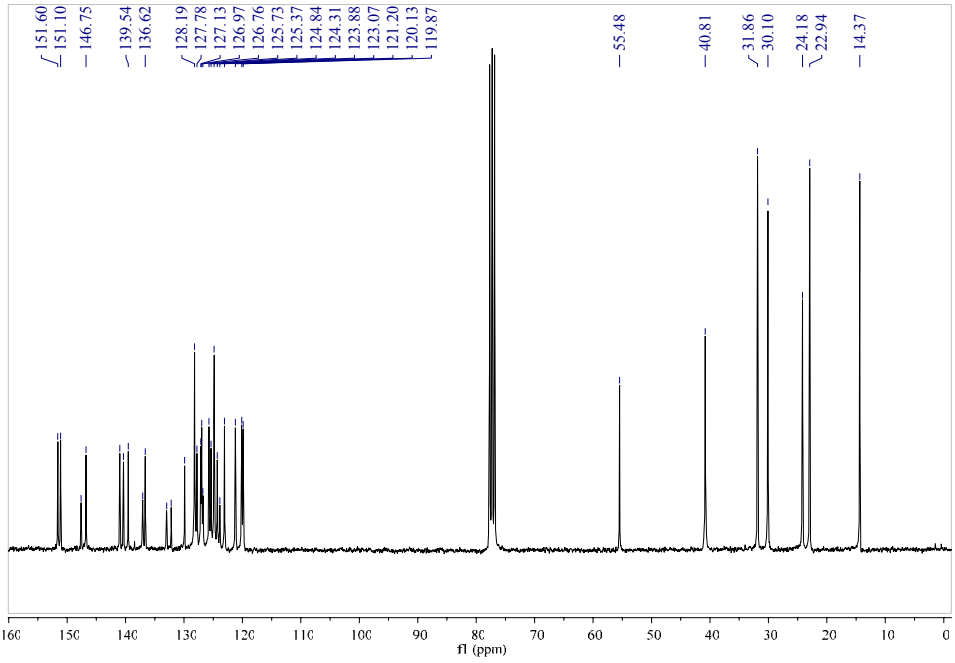


11. $AnA_2F_4H_8$

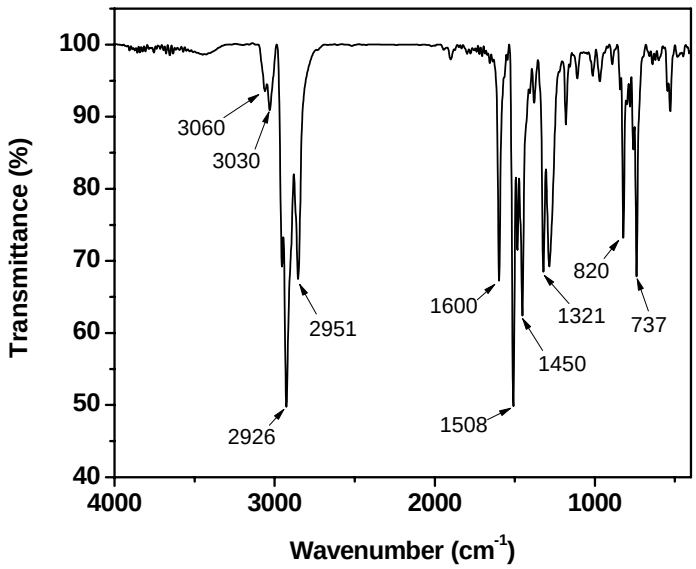
^1H NMR



^{13}C NMR



FT-RI



MALDI-TOF-MS