Electronic Supplementary Information

POSS-based organic-inorganic hybrid nanomaterials: aggregation-enhanced emission, highly sensitive and selective detection of nitroaromatic explosive in aqueous media

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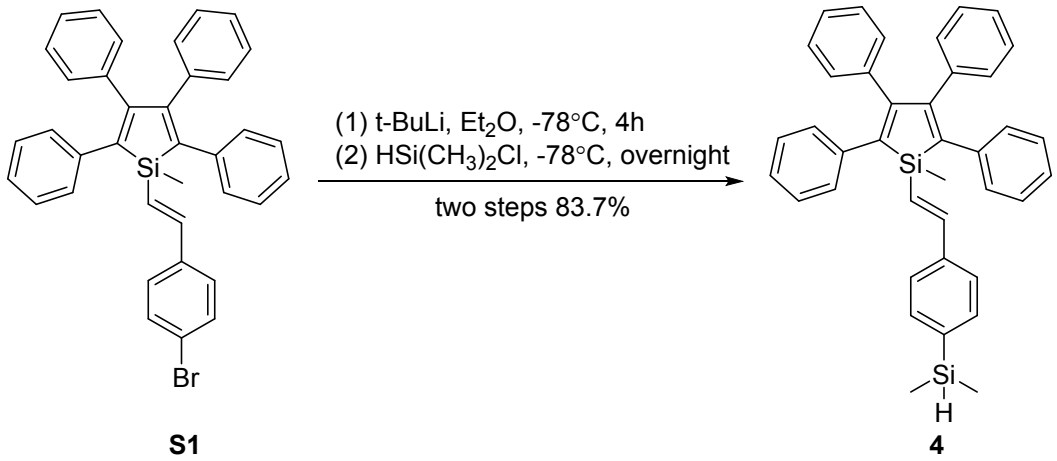


S1 **4**

Scheme S1. Synthetic routes to **4**. **S1** was synthesized according to previous published procedures.[1]

To an Et_2O (250 mL) solution **S1** (3.22g, 5.54 mmol) was added t-BuLi (1.3 M in pentane, 14.9 mL, 19.4 mmol) at −78 °C. After being stirred for 4 h at −78 °C, chlorodimethylsilane (2.4 mL, 22.2 mmol) was then injected slowly to the solution at -78°C. The obtained solution was stirred overnight at -78°C. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (50 mL). The organic layer was separated and aqueous layer was extracted with Et_2O (200 mL x 2). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$ and concentrated under vacuum to get residue. The residue was purified by silica gel column chromatography using hexane as eluent to give 2.61 g (83.7%) of compound **S2** as a yellow solid. **m. p.** 143-144 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.56 (d, 2H, Ar-H), 7.48 (d, 2H, Ar-H), 7.20-7.09 (m, 5H, Ar-H), 7.09-7.03 (m, 8H, Ar-H), 7.03-6.98 (m, 4H, Ar-H), 6.93-6.86 (m, 4H, Ar-H), 6.74 (d, 2H, J=20Hz, Z-SiCH=), 4.51-4.41 (m, 1H, SiH), 0.71 (s, 3H, Si-CH_3), 0.38 (d, 6H, Si$(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) , δ (ppm): 155.1, 147.9, 140.2, 139.5, 138.8, 138.7, 138.1, 134.2, 129.9, 129.00, 127.9, 127.5, 126.3, 126.1, 125.6, 123.0, -3.78, -6.11. **FT-IR** (KBr), υ (cm^{-1}): 3062, 3022, 2961, 2120 (Si-H stretching), 1600, 1485, 1436, 1396, 1298, 1253 (Si-CH_3 bending), 1106 (Si-Ph stretching), 1079, 1031, 991, 885 (Si-CH_3 stretching), 799, 758, 703. **MS** (MALDI-TOF): m/z ($[M]^+$) = 560.3, (calcd for $C_{39}H_{36}Si_2$ = 560.2).

1. Y. Zhang, S. Li, R. Wang, L. Chen and C. Xu, *Synthetic Communications*, 2012, **42**, 2171-2180.

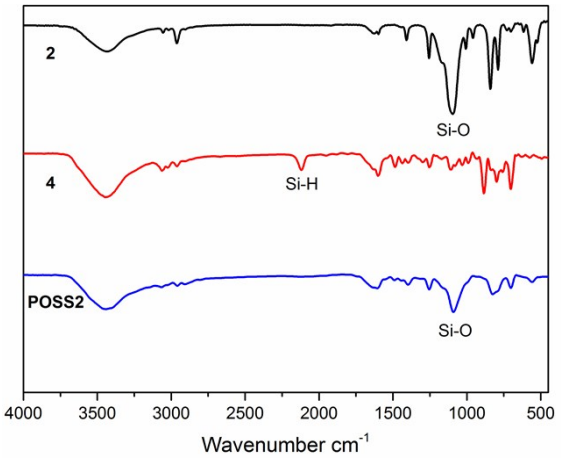


Figure S1. FT-IR spectra of **2**, **4** and **POSS2**.

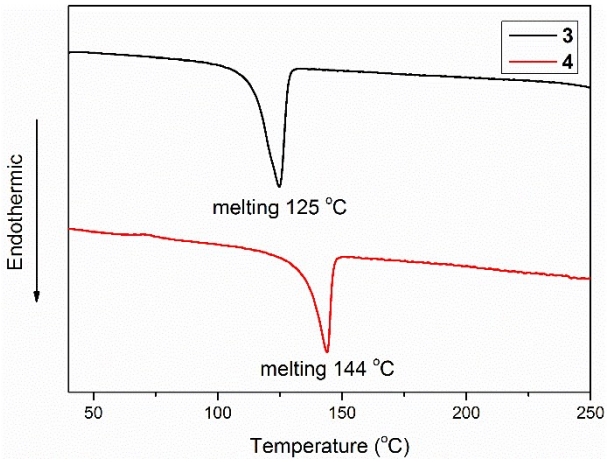


Figure S2. DSC curves of **3** and **4** under N_2 at a heating rate of 10 °C/min.

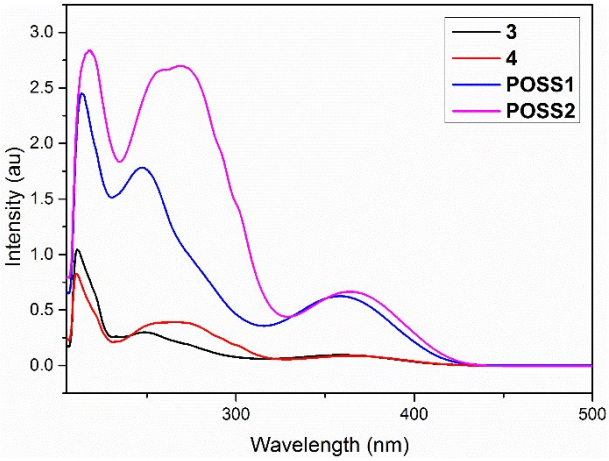


Figure S3. Absorption spectra of THF solutions of **3**, **4**, **POSS1**, **POSS2**. Solution concentration: 10 μM.

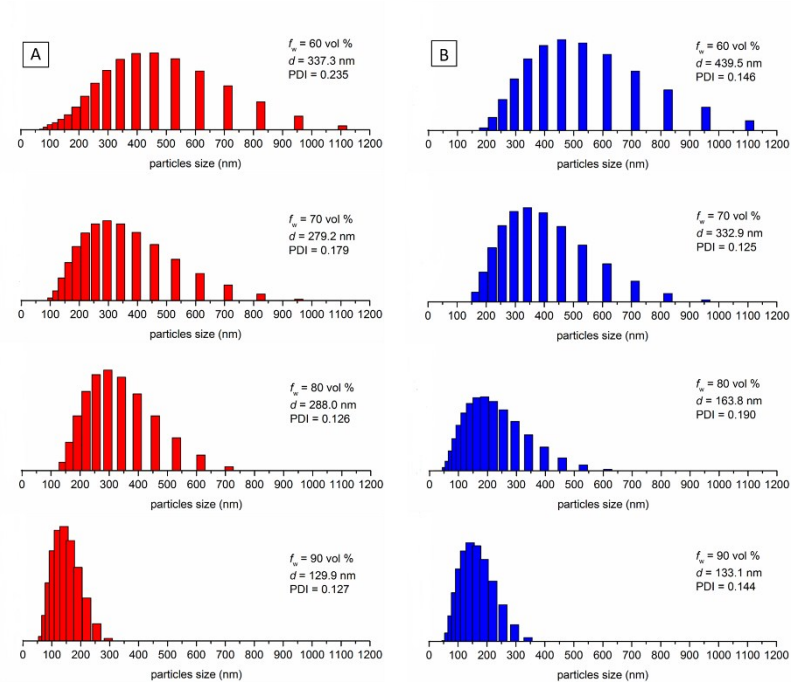


Figure S4. Particle size distributions of aggregates of **POSS1** (A) and **POSS2** (B) suspended in THF/water mixtures with water fractions (f_w) of 60, 70, 80 and 90 vol %. Abbreviation: d = Z-average diameter, PDI = polydispersity.

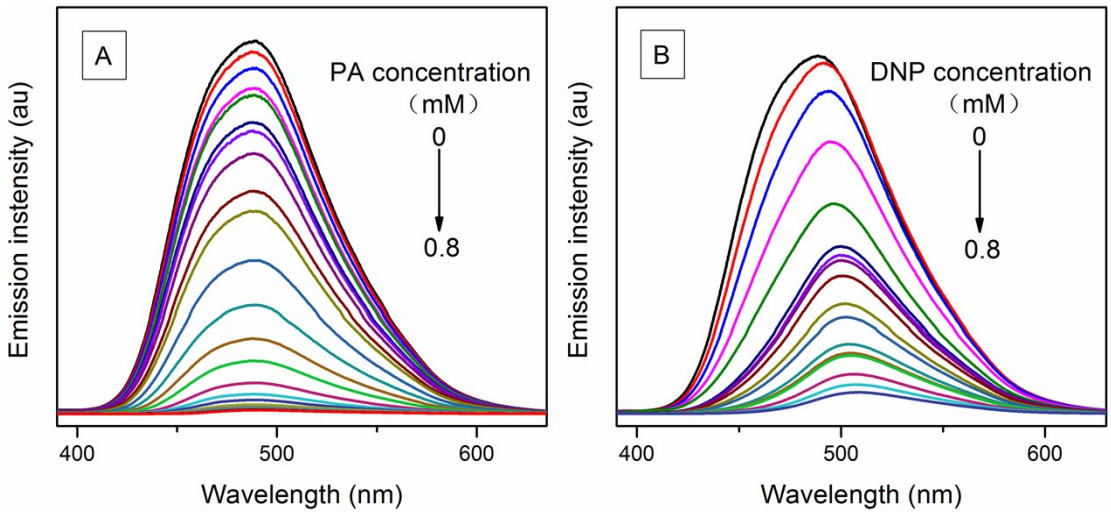


Figure S5. Emission spectra of **POSS2** in THF/water mixtures with 90% water contents containing different amounts of PA (A) and DNP (B). Solution concentration: 10 μM; excitation wavelength: 365 nm to **POSS2.**

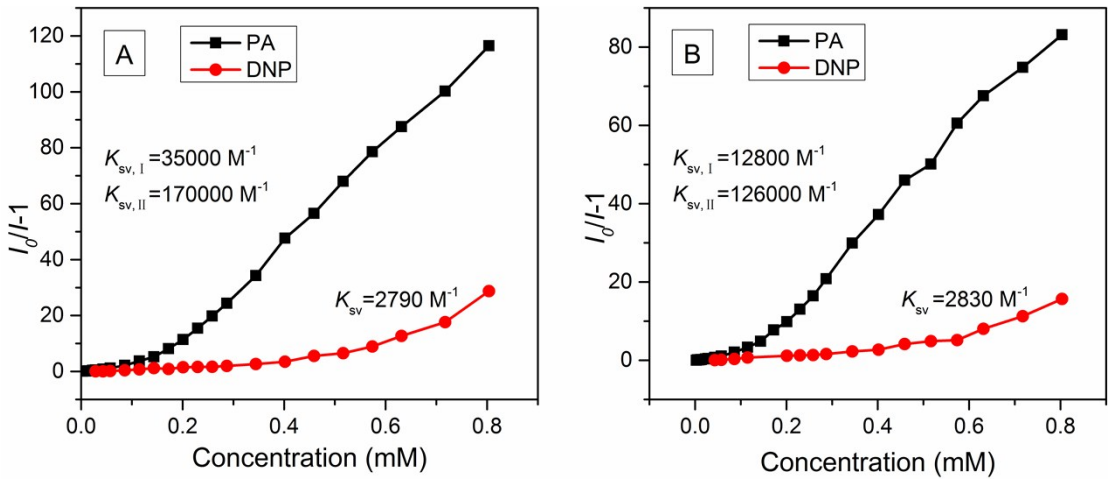


Figure S6. Stern-Volmer plot of I_0/I-1 *vs*. concentrations of PA and DNP in 1:9 THF/water mixtures (*v*/*v*) for **POSS1** (A) and **POSS2** (B) with K_{sv} values indicated in different concentration regions. I_0 = PL intensity without added analyte.

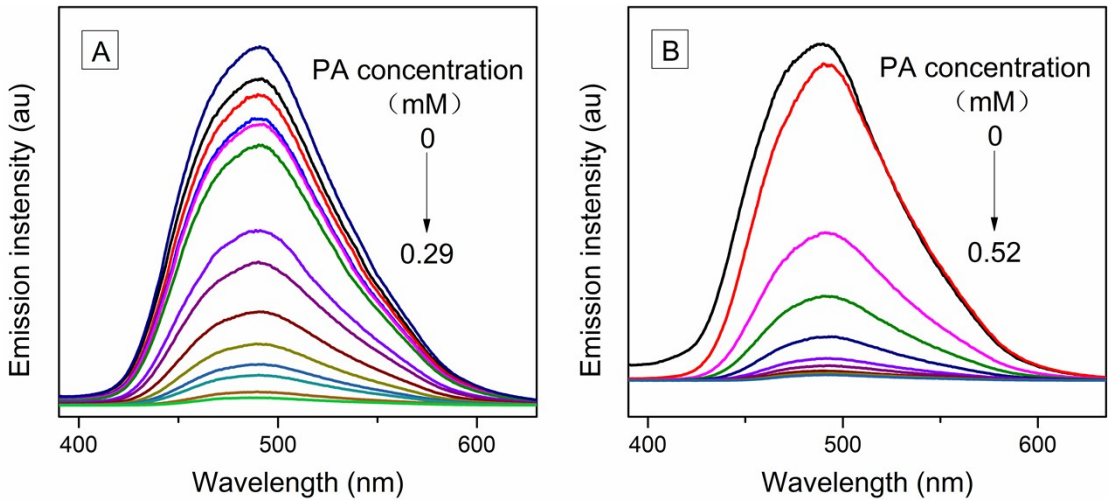


Figure S7. Emission spectra of monomer **3** (A) and **4** (B) in 1:9 THF/water mixtures (*v*/*v*) containing different amounts of PA. Solution concentration: 10 μM; excitation wavelength: 360 nm for **3**, 365 nm for **4**,

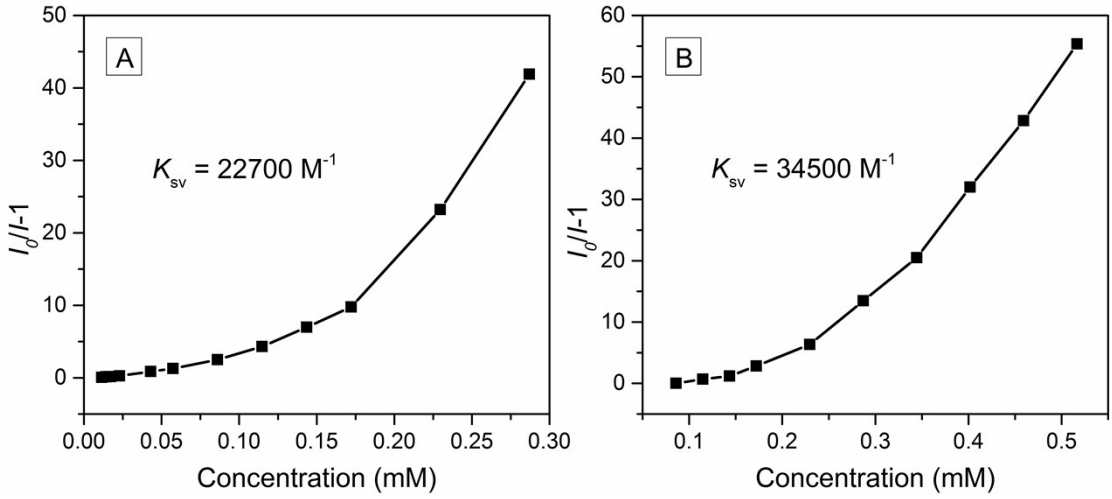
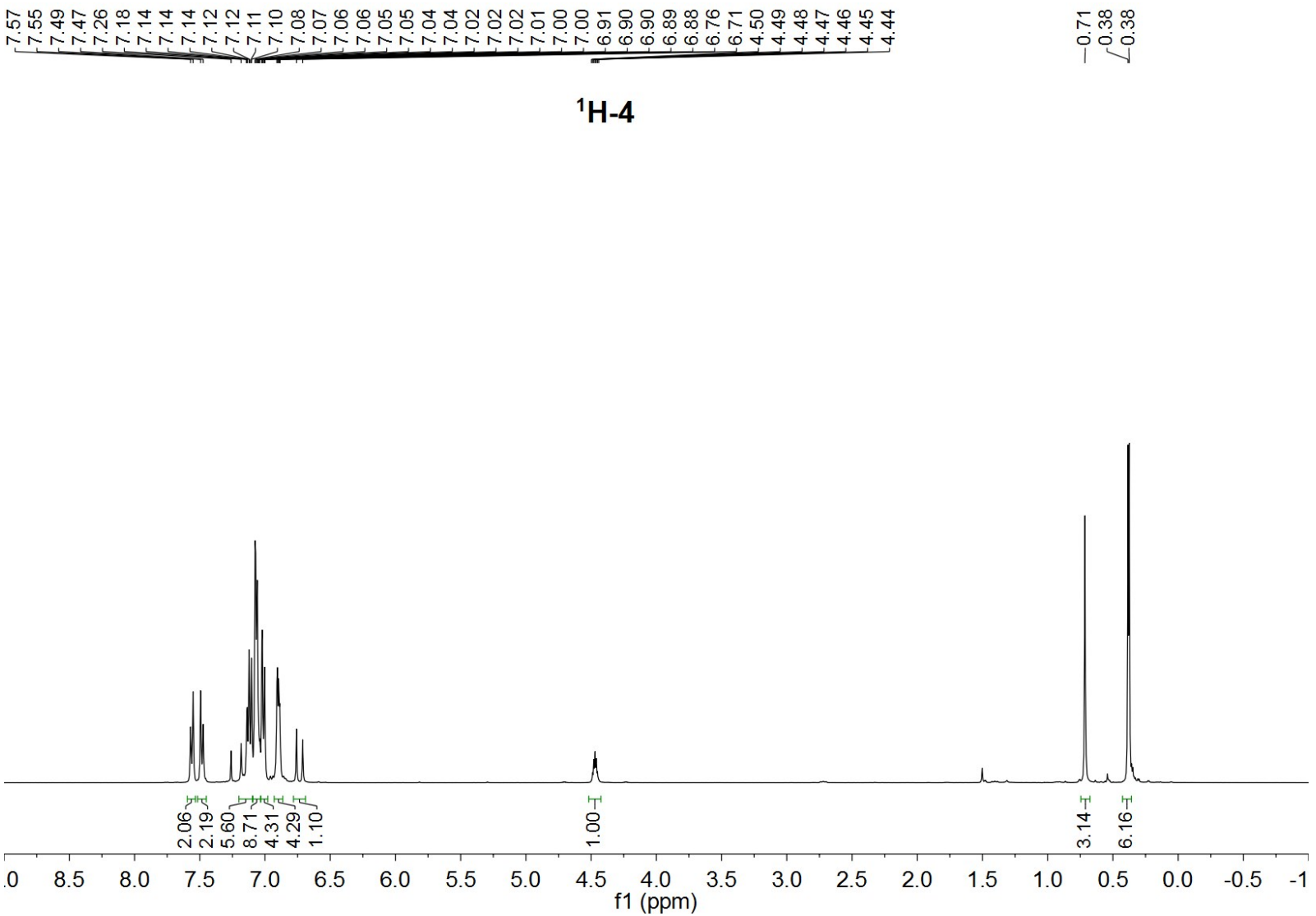
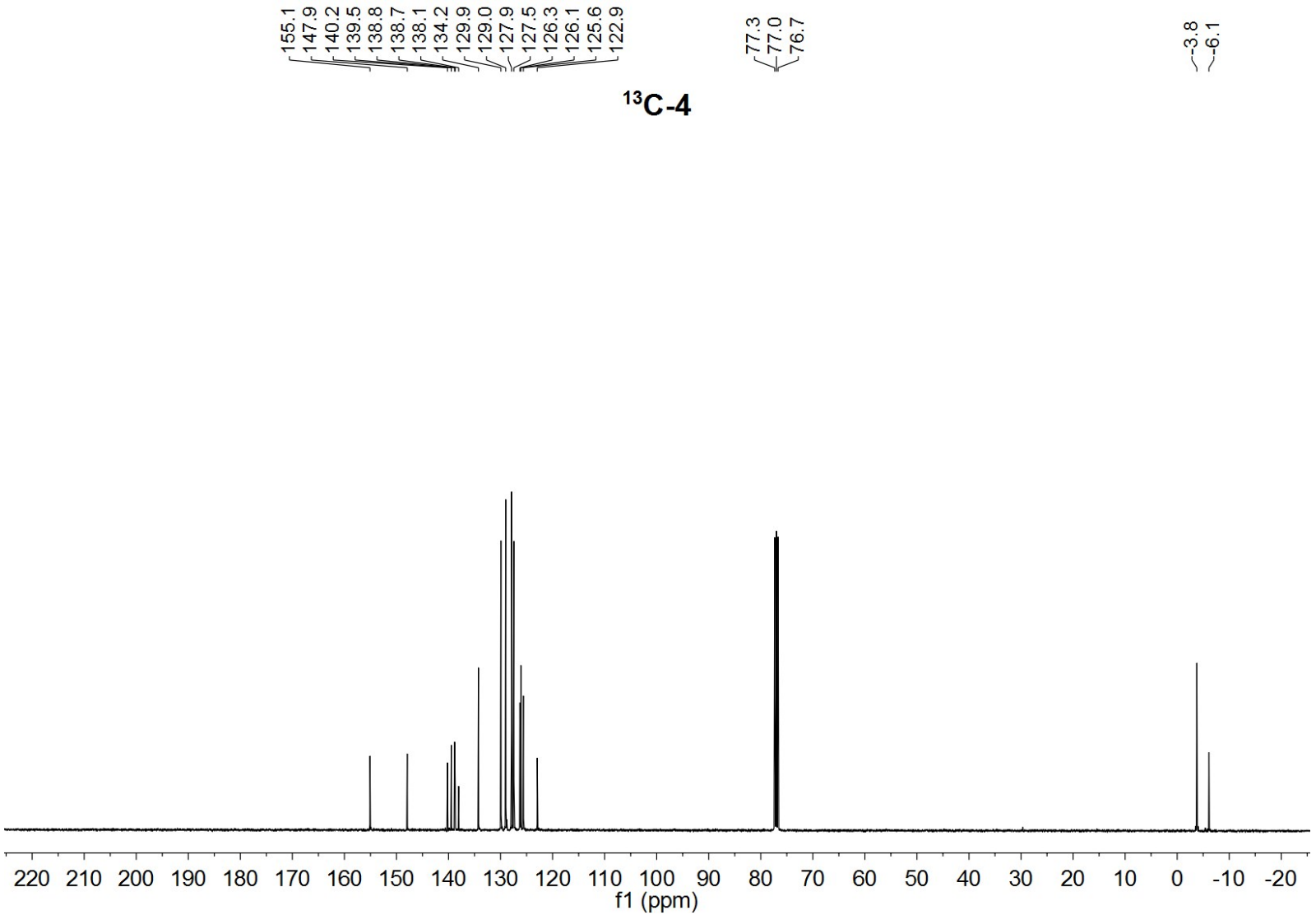


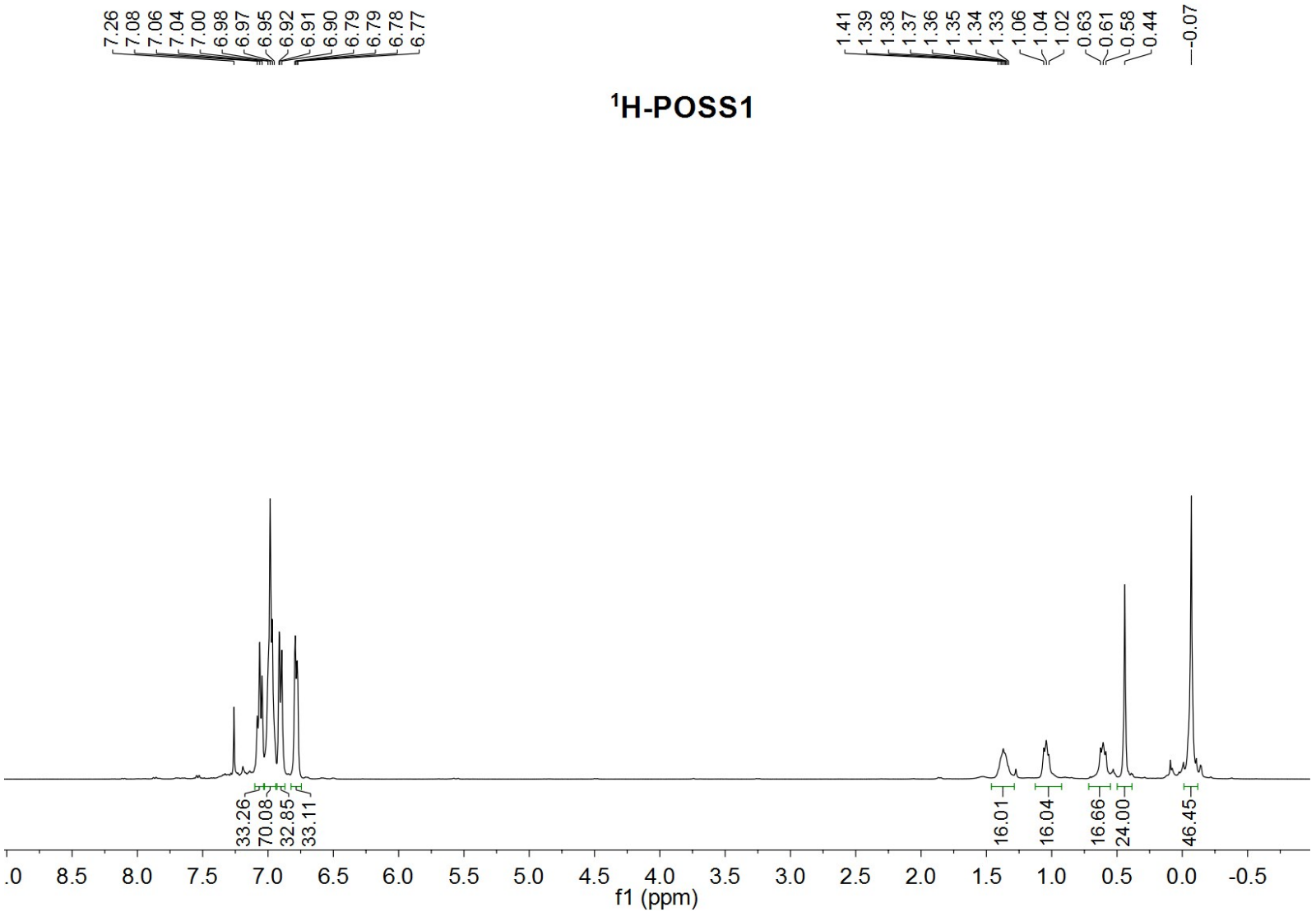
Figure S8. Stern-Volmer plot of I_0/I-1 *vs*. concentrations of PA in 1:9 THF/water mixtures (*v*/*v*) for **3** (A) and **4** (B) with K_{sv} values indicated in different concentration regions. I_0 = PL intensity without added analyte.


7.57
7.55
7.49
7.47
7.26
7.18
7.14
7.14
7.14
7.12
7.12
7.11
7.10
7.08
7.07
7.06
7.06
7.05
7.05
7.04
7.04
7.02
7.02
7.02
7.01
7.00
7.00
6.91
6.90
6.90
6.89
6.88
6.76
6.71
4.50
4.49
4.48
4.47
4.46
4.45
4.44
0.71
0.38
0.38
2.06
2.19
5.60
8.71
4.31
4.29
1.10
1.00
3.14
6.16
f1 (ppm)

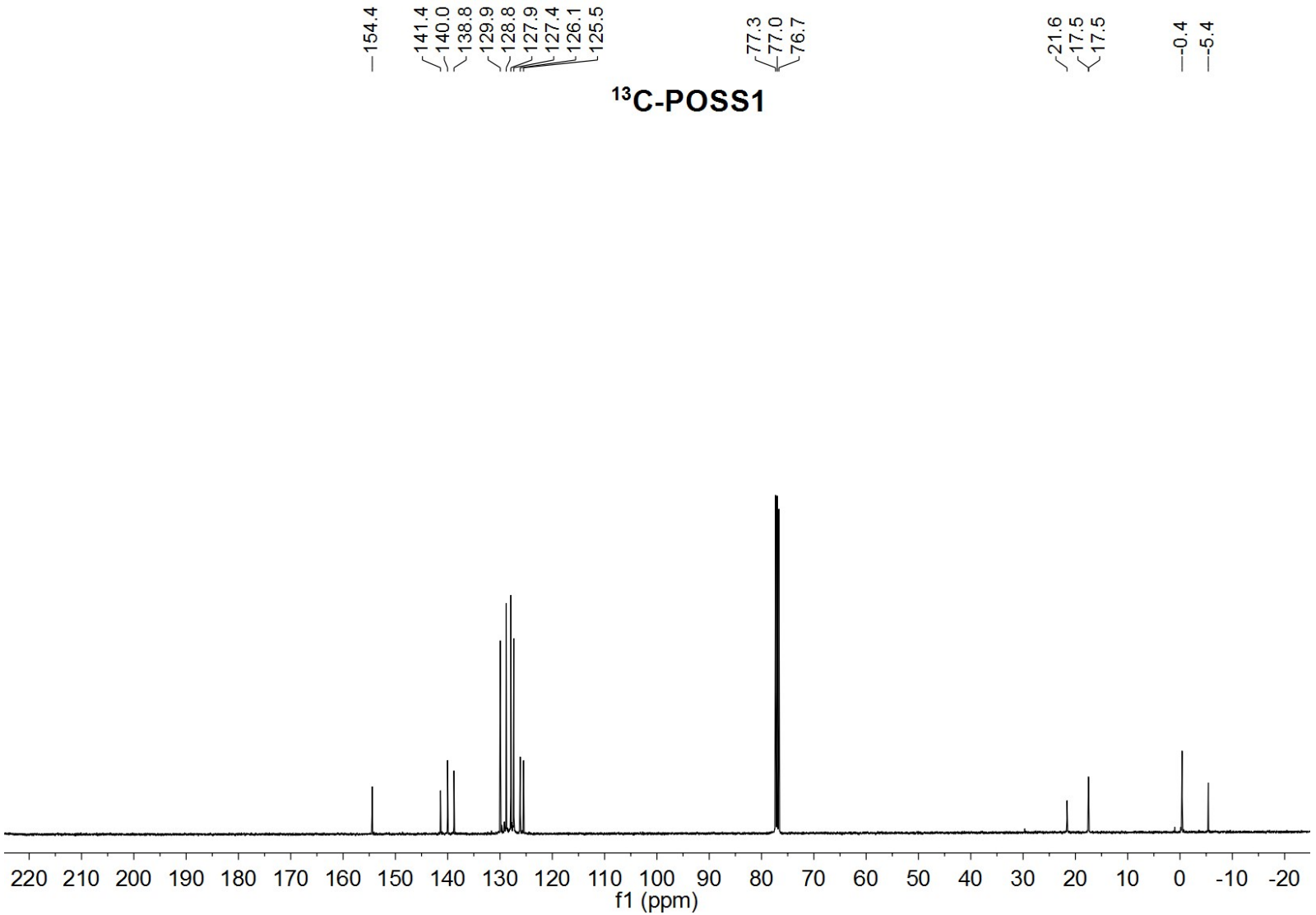
^{1}H-4


155.1
147.9
140.2
139.5
138.8
138.7
138.1
134.2
129.9
129.0
127.9
127.5
126.3
126.1
125.6
122.9
77.3
77.0
76.7
-3.8
-6.1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

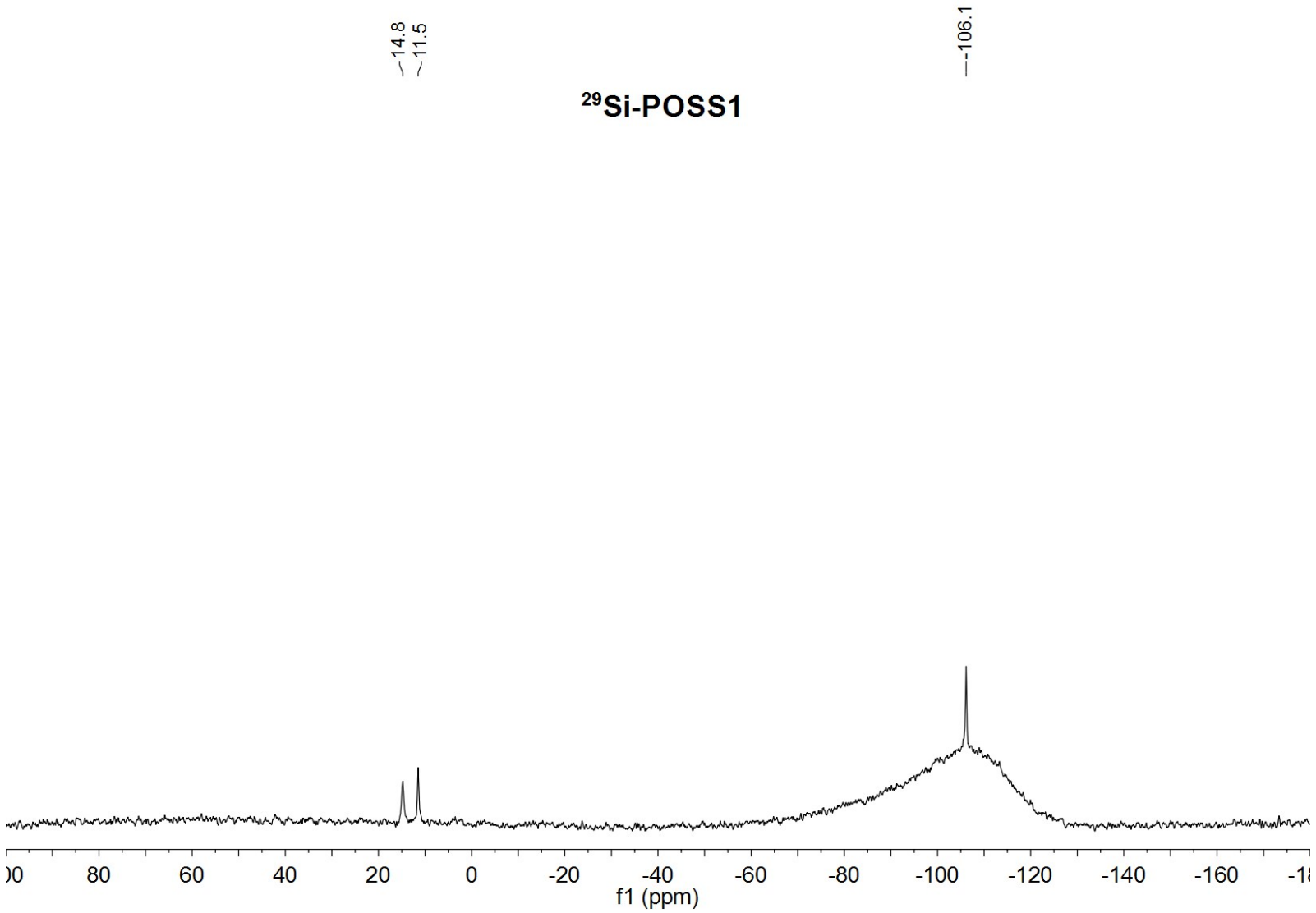
^{13}C-4

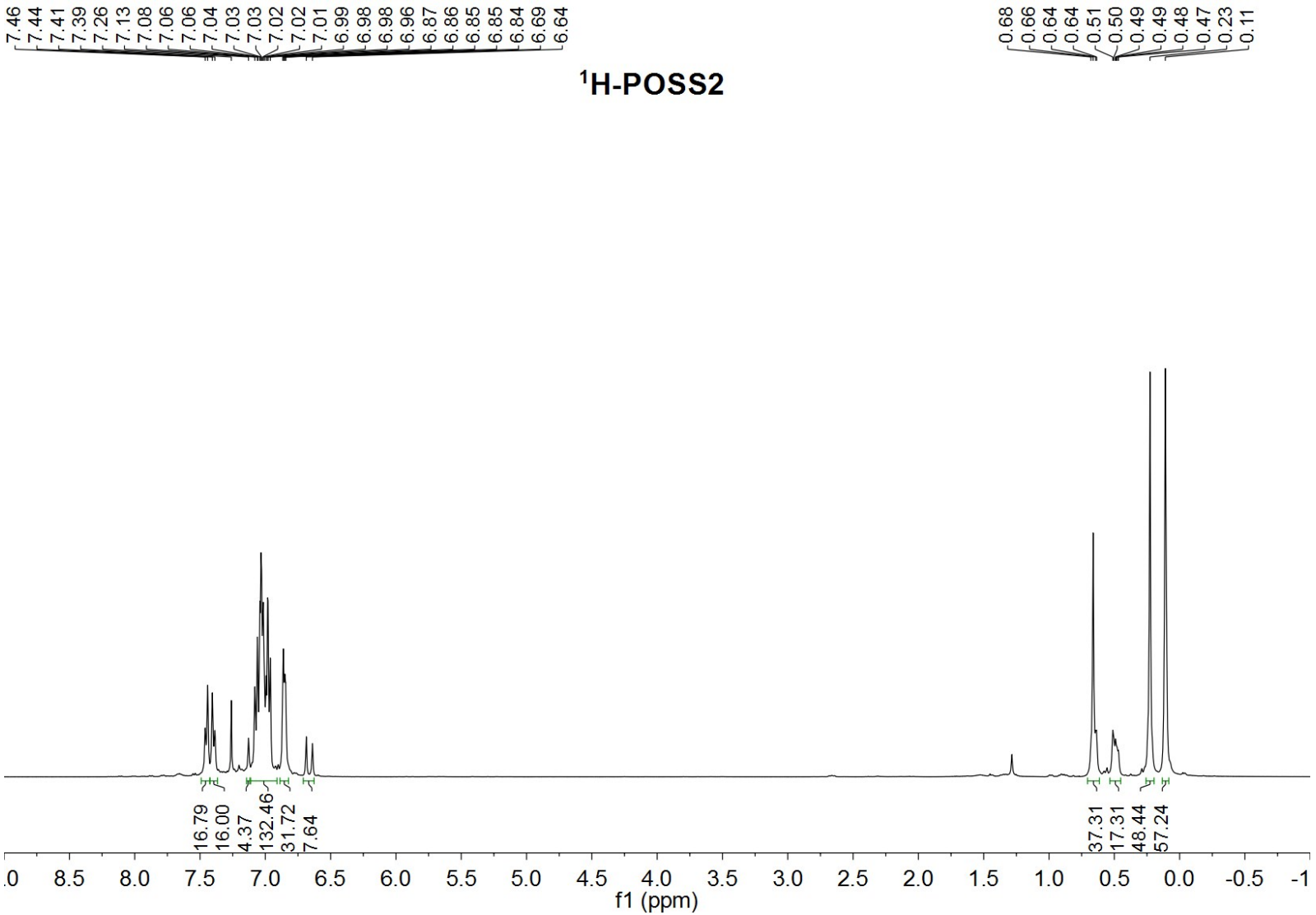

7.26
7.08
7.06
7.04
7.00
6.98
6.97
6.95
6.92
6.91
6.90
6.79
6.79
6.78
6.77
1.41
1.39
1.38
1.37
1.36
1.35
1.34
1.33
1.06
1.04
1.02
0.63
0.61
0.58
0.44
-0.07
33.26
70.08
32.85
33.11
16.01
16.04
16.66
24.00
46.45
f1 (ppm)

^{1}H-POSS1

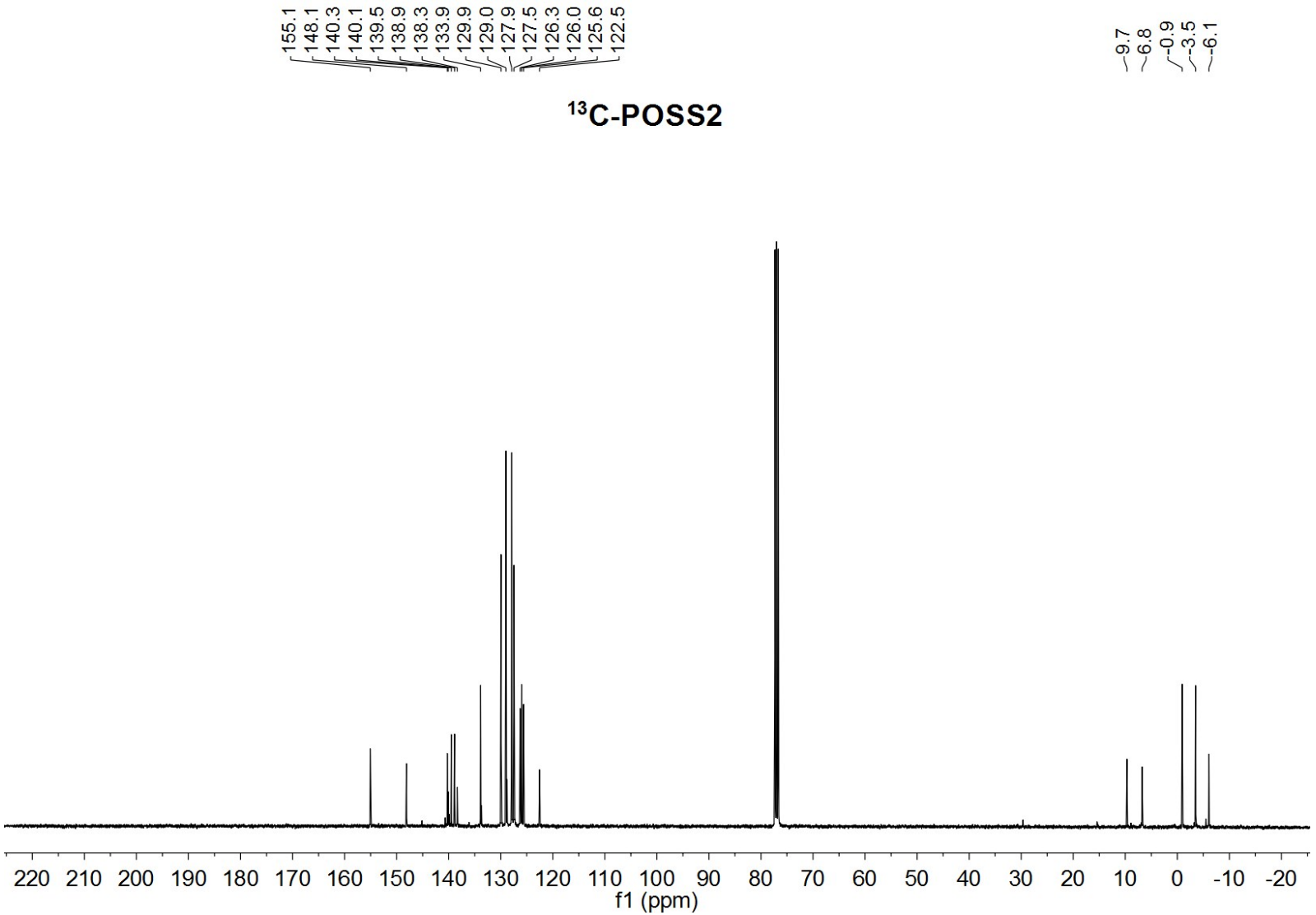

154.4
141.4
140.0
138.8
129.9
128.8
127.9
127.4
126.1
125.5
77.3
77.0
76.7
21.6
17.5
17.5
0.4
-5.4
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

^{13}C-POSS1

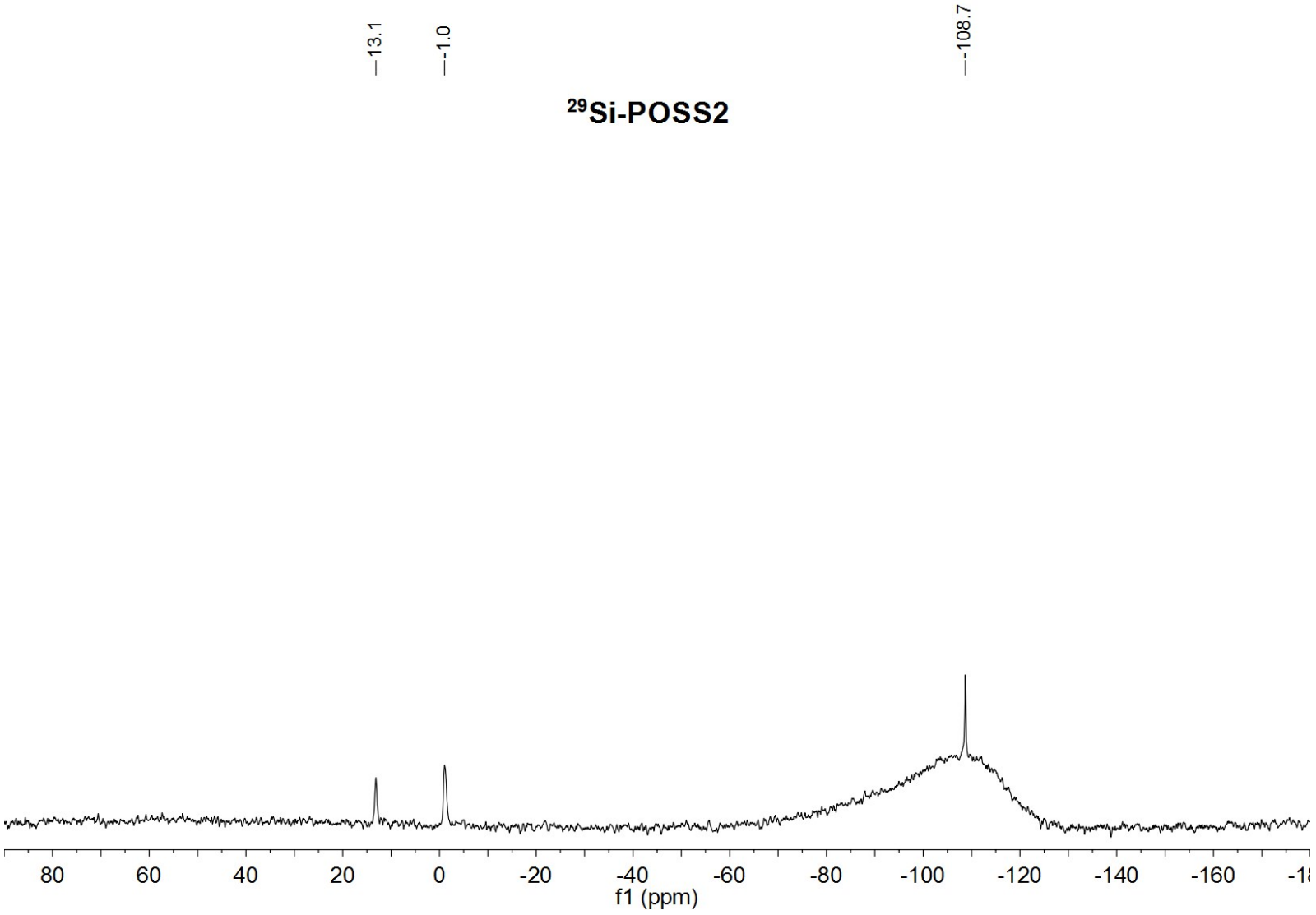

14.8
11.5
-106.1
29Si-POSS1
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
f1 (ppm)


7.46
7.44
7.41
7.39
7.26
7.13
7.08
7.06
7.06
7.04
7.03
7.03
7.02
7.02
7.01
6.99
6.98
6.98
6.96
6.87
6.86
6.85
6.85
6.84
6.69
6.64
0.68
0.66
0.64
0.64
0.51
0.50
0.49
0.49
0.48
0.47
0.23
0.11
16.79
16.00
4.37
132.46
31.72
7.64
37.31
17.31
48.44
57.24
f1 (ppm)

^{1}H-POSS2


155.1
148.1
140.3
140.1
139.5
138.9
138.3
133.9
129.9
129.0
127.9
127.5
126.3
126.0
125.6
122.5
9.7
6.8
0.9
3.5
6.1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

^{13}C-POSS2


13.1
-1.0
-108.7
29Si-POSS2
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
f1 (ppm)