Supplementary Information

Metallamacrocycle-Modified Gold Nanoparticles: A New Pathway for Surface Functionalization

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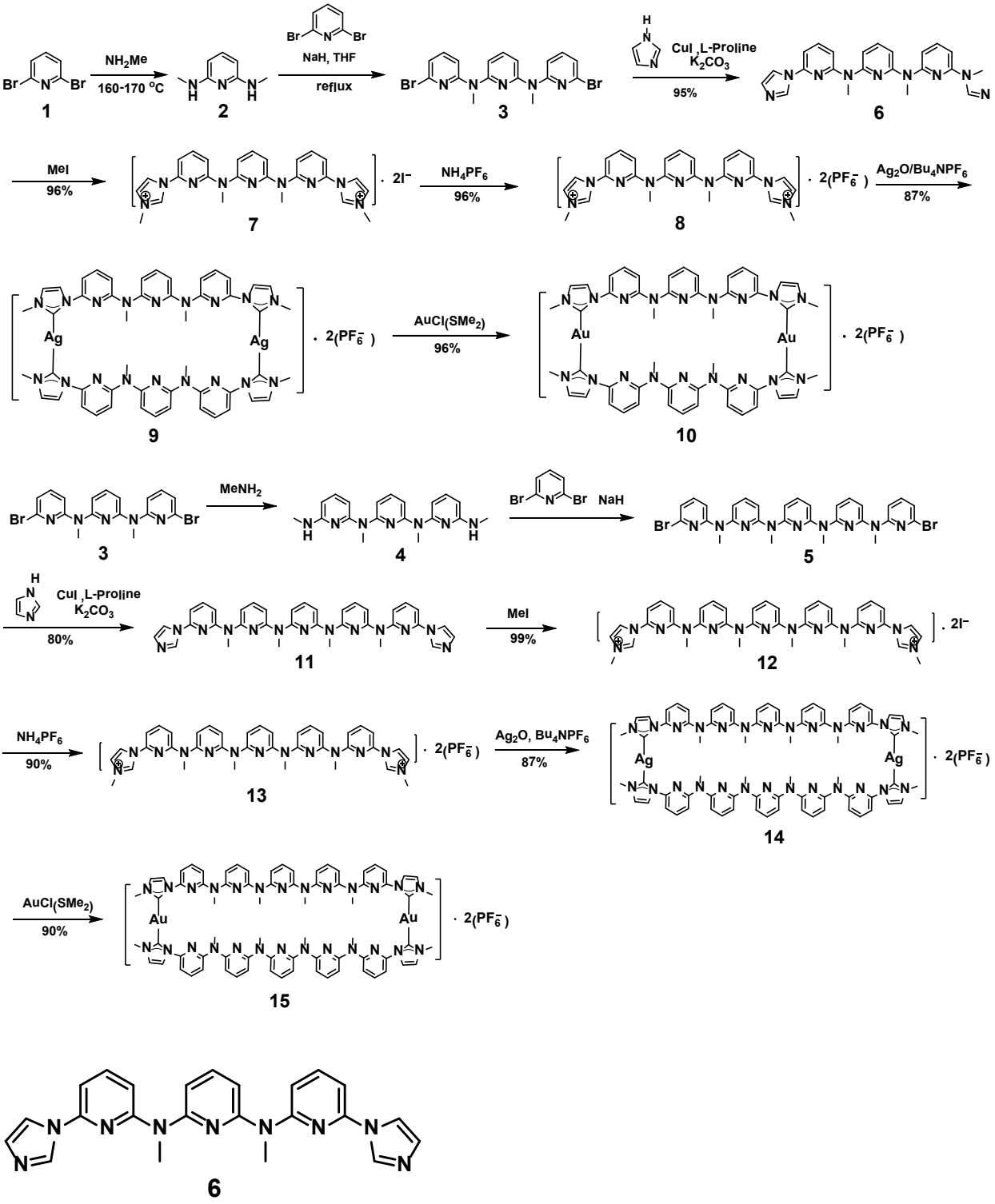
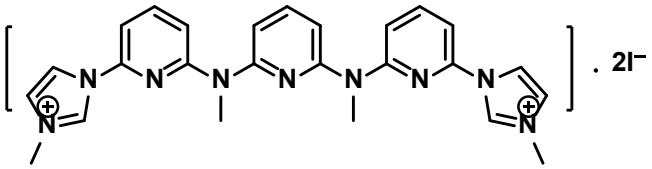
Synthesis of MMC-1-4:

All commercially available chemicals were used without further purification. Compounds **2**-**5** were synthesized according to the literature method.[1] The ^{1}H- and ^{13}C-NMR spectra were included below.



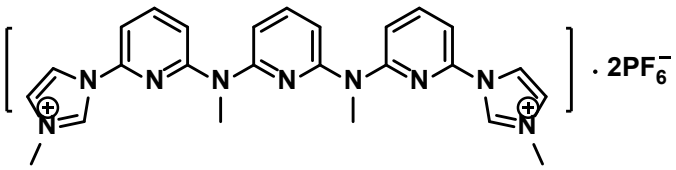
A 50 mL three-neck flask was charged with purified CuI (175 mg, 0.92 mmol), L-proline (212 mg, 1.84 mmol), K_2CO_3 (2.376 g, 17.22 mmol), imidazole (859 mg, 12.63 mmol) and compound **3** (2.577 g, 5.74 mmol), evacuated and backfilled with argon. To this mixture 9 mL

DMSO was added by syringe under argon and the mixture was heated to 90 °C for 22 h. After complete reaction, water was added in one portion to form a clear solution (20-40 mL). The reaction mixture was extracted with EtOAc (3 × 30 mL) and the organic layers were combined, washed with brine (20 mL), dried over $MgSO_4$, and concentrated in vacuo. The residual oil was then purified via column chromatography with ethyl acetate as eluent to give pure **6** (2.31g, 95%) as a pale yellow solid: m.p. 155-156 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.35 (s, 2H), 7.62-7.57 (m, 5H), 7.18 (s, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 7.6 Hz, 2H), 6.84 (d, J = 7.6 Hz, 2H), 3.65 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 156.8, 156.0, 147.5, 139.6, 138.9, 135.1, 130.4, 116.2, 110.9, 109.6, 103.2, 36.0; IR (KBr, cm^{-1}): 3126 (m), 1574 (s), 1446 (s), 1302 (m), 1172 (s), 1507 (s), 973 (m), 769 (m), 743 (m), 714 (m); MALDI-TOF MS: *m/z* = 424.0 ([M+H]$^+$).



7

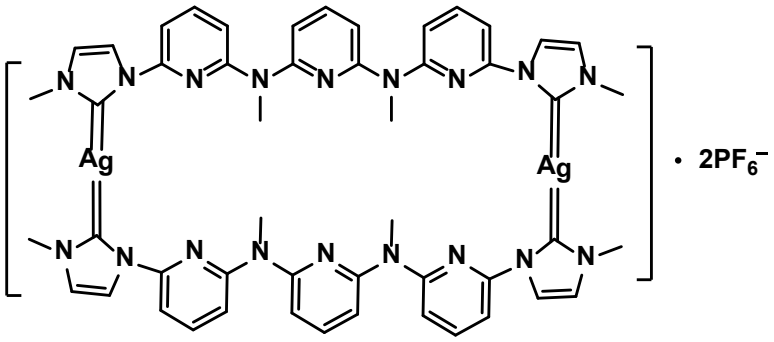
Compound **6** (0.85 g, 2 mmol) was dissolved in 25 mL toluene in a sealed tube and MeI (2.5 mL, 40 mmol) was added by syringe. The mixture was heated to 90 °C for 6 h. The reaction mixture was cooled to room temperature and a yellow solid appeared. Recrystallize the solid by methanol /diethyl ether to produce pure **7** (1.36 g, 96%) as a yellow solid: m.p.: 180-181 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 9.96 (s, 2H), 8.47 (t, J = 2 Hz, 2H), 7.97-7.92 (m, 4H), 7.86 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 3.99 (s, 6H), 3.61 (s, 6H); ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): δ 156.0, 155.1, 144.5, 140.7, 140.5, 135.2, 124.7, 118.9, 113.8, 110.4, 104.5, 36.4, 36.1; IR (KBr, cm^{-1}): 3082 (m), 1618 (s), 1432 (s), 1319 (m), 1220 (m), 1175 (m), 1088 (m), 950 (m), 793 (s); MALDI-TOF MS: *m/z* = 580.0 ([M-I]$^+$).



8

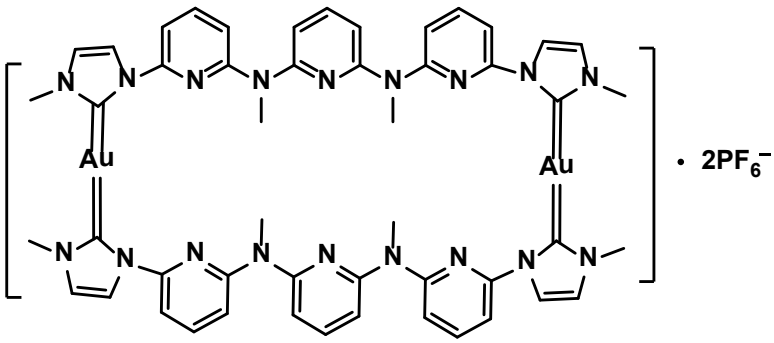
In a 100 mL round-bottom flask were charged with 3 mL methanol solution of NH_4PF_6 (489 mg, 3mmol) and 20 mL methanol solution of compound **7** (707 mg, 1 mmol). A yellow solid appeared immediately, which was filtered, washed by cool methanol and diethyl ether to yield pure **8** (713 mg, 96%) as a yellow solid: m.p.: 177-178 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 9.94 (s, 2H), 8.46 (s, 2H), 7.95-7.91 (m, 4H), 7.85 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 3.98 (s, 6H), 3.61 (s, 6H); ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): δ 156.1, 155.1, 144.5, 140.7, 140.5, 135.2, 124.7, 118.9, 113.8, 110.4, 104.5, 36.4, 36.0; IR (KBr, cm^{-1}): ν 3169 (m), 1622 (s), 1487 (s), 1326 (m), 1220 (s),

1178 (m), 1093 (s), 955 (m), 843 (s), 784 (m), 736 (m), 558 (s); MALDI-TOF MS: *m/z* = 598.1 ($[M\text{-}PF_6]^+$).



9 (MMC-1)

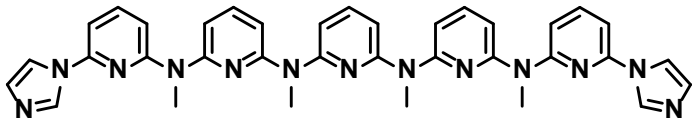
To a mixed solution of CH_2Cl_2 (30 mL) and CH_3CN (10 mL) were added compound **8** (500 mg, 0.67 mmol), Ag_2O (232 mg, 1 mmol) and catalytic amounts of Bu_4NPF_6. After the reaction mixture was refluxed for 3 h in dark, NaOH solution (1 N, 5 mL) was added. The reaction mixture was refluxed for further 8 h. The resulting suspension was then filtered through celite and the resulting filtrate was concentrated in vacuo. Recrystallize by CH_3CN/Et_2O repeatedly to give pure **9** (411 mg, 87%) as an off-white powder: m.p.: 186-187 °C; ^{1}H-NMR (400 MHz, CD_3CN, ppm): δ 7.78 (s, 4H), 7.55 (t, *J* = 7.6 Hz, 4H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.33 (s, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 7.09 (d, *J* = 8.4 Hz, 4H), 6.67 (d, J = 8.4 Hz, 4H), 3.88 (s, 12H), 3.28 (s, 12H); ^{13}C-NMR (100 MHz, CD_3CN, ppm): δ 157.1, 155.6, 149.6, 140.6, 139.9, 124.4, 120.4, 115.3, 107.3, 107.1, 40.3, 36.6; IR (KBr, cm^{-1}): 3151 (w), 2951 (w), 1566 (m), 1429 (s), 1327 (m), 1237 (m), 1174 (m), 1117 (m), 954 (w), 842 (s), 788 (m), 740 (m), 559 (s); MALDI-TOF MS: *m/z* = 559.9 ($[M\text{-}2PF_6]^{2+}$).



10 (MMC-3)

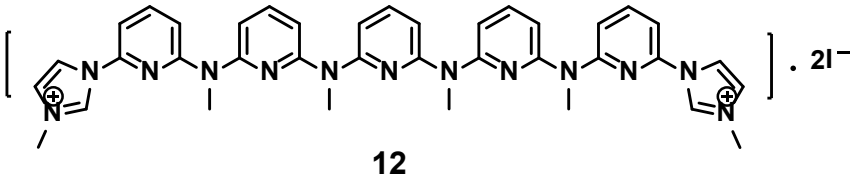
To a 30 mL CH_2Cl_2 solution of **9** (300 mg, 0.21 mmol) was added $AuCl(SMe_2)$ (126 mg, 0.43 mmol). The mixture was stirred for 36 h at room temperature. The resulting suspension was then filtered through celite and the filtrate was concentrated in vacuo. Recrystallize by CH_3CN/Et_2O repeatedly to produce pure **10** (320 mg, 96%) as an off-white powder: m.p.: 192-193 °C; ^{1}H-NMR (400 MHz, CD_3CN, ppm): δ 7.70 (d, *J* = 2.0 Hz, 4H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 4H), 7.35 (d, *J* = 1.6 Hz, 4H), 7.28 (d, *J* = 7.6 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 6.84 (d, *J* = 8.4 Hz, 4H), 3.99 (s, 12H), 3.35 (s, 12H); ^{13}C-NMR (100 MHz, CD_3CN, ppm): δ 183.3, 157.2, 156.0, 149.4, 140.3, 124.5, 121.5, 114.4, 110.0, 108.9, 39.6, 36.5; IR

(KBr): 3152 (w), 2951 (w), 1566 (m), 1429 (s), 1330 (m), 1239 (m), 1174 (m), 1121 (m), 955 (w), 842 (s), 789 (m), 741 (m), 559 (s); MALDI-TOF MS: *m/z* = 1441.0 ($[M-PF_6]^+$).



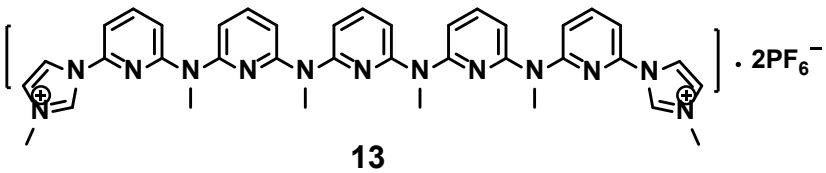
11

Compound **11** was prepared from **5** by a similar procedure to the synthesis of **6**. Quantities: 5 (4.63 g, 7 mmol), imidazole (1.19g, 17.5 mmol), K_2CO_3 (2.90 g, 21 mol), CuI (335 mg, 1.75 mmol), L-proline (403 mg, 3.5 mmol), DMSO (25 mL). The product **11** is a yellow solid (3.56 g, 80%): m.p.: 136-137 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.35 (s, 2H), 7.62 (s, 2H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.18 (s, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.84-6.79 (m, 6H), 3.65 (s, 6H), 3.60 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 157.0, 156.6, 156.4, 155.8, 147.5, 139.3, 138.4, 138.3, 135.1, 130.4, 116.2, 110.7, 108.4, 107.9, 107.4, 102.6, 36.0, 35.9; IR (KBr, cm^{-1}): 3126 (w), 1573 (s), 1434 (s),1336 (m), 1312 (m), 1286 (m), 1175 (s), 1055 (m), 995 (m), 786 (m); MALDI-TOF MS: *m/z* = 636.1 ($[M+H]^+$).



12

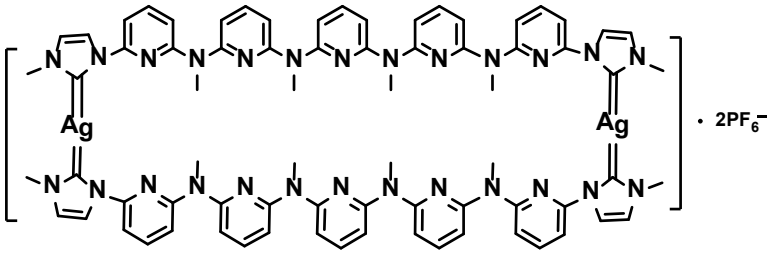
Compound **12** was prepared from **11** by a similar procedure to the synthesis of **7**. Quantities: **11** (1.91 g, 3 mmol), MeI (3.8 mL, 60 mmol), toluene (45 mL). The product is a yellow solid (2.73 g, 99%): mp 136-138 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, 50 °C, ppm): δ 9.93 (s, 2H), 8.44 (s, 2H), 7.94 (s, 2H), 7.89 (t, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H),7.39-7.36 (m, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 6H), 3.61 (s, 6H), 3.48 (s, 6H); ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): δ 156.2, 155.8, 155.5, 154.8, 144.5, 140.4, 139.5, 139.0, 135.2, 124.7, 118.9, 113.5, 108.9, 108.0, 107.5, 103.9, 36.4, 36.0, 35.7; IR (KBr, cm^{-1}): 3058 (m), 1563 (s), 1418 (s), 1321 (w), 1220 (s), 1169 (s), 1088 (m), 980 (m), 785 (m), 733 (m); 616 (m); MALDI-TOF MS: *m/z* = 792.0 ($[M-I]^+$).



13

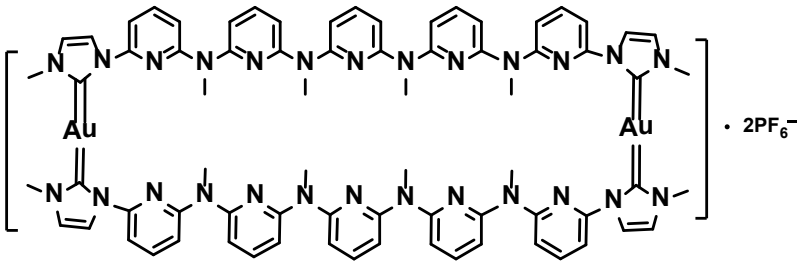
Compound **13** was prepared from **12** by a similar procedure to the synthesis of **8**. Quantities: **12** (1.84 g, 2 mmol), NH_4PF_6 (978 mg, 6 mmol), methonal (18 mL). The product was a yellow solid (1.72 g, 90%): m.p.: 202-204 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, 50 °C, ppm): δ 9.86 (s, 2H), 8.40 (s, 2H), 7.92 (s, 2H), 7.80 (t, *J* = 8.0 Hz, 2H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 4.01 (s, 6H), 3.60 (s, 6H), 3.46 (s, 6H); ^{13}C-NMR (100

MHz, DMSO-d_6, ppm): δ156.2, 154.6, 154.5, 153.2, 144.8, 140.7, 140.4, 135.5, 125.2, 119.3, 114.4, 108.5, 108.2, 107.8, 104.5, 36.9, 36.8, 36.7; IR (KBr, cm^{-1}): 3169 (m), 1589 (m), 1429 (s), 1345 (w), 1221 (m), 1173 (m), 1093 (m), 985 (m), 839 (s), 783 (m), 557 (s); MALDI-TOF MS: m/z = 810.1 ($[M\text{-}PF_6]^+$).



14 (MMC-2)

Compound **14** was prepared from **13** by a similar procedure to the synthesis of **9**. Quantities: **13** (1.15 g, 1.2 mmol), Ag_2O (696 mg, 3 mmol), Catalytic amounts of Bu_4NPF_6, NaOH solution (1 N, 10 mL), CH_2Cl_2 (60 mL) and CH_3CN (15 mL). The product is a yellow solid (955 mg, 87%): mp 168-170 °C; ^{1}H-NMR (400 MHz, CD_3CN, 70 °C, ppm): δ 7.69 (d, J = 1.2 Hz, 4H), 7.50-7.43 (m, 8H), 7.37 (t, J = 8.0 Hz, 2H), 7.26 (d, J = 1.2 Hz, 4H), 7.13-7.10 (m, 8H), 6.71 (d, J = 8.4 Hz, 4H), 6.70 (d, J = 8.0 Hz, 4H), 6.67 (d, J = 7.6 Hz, 4H), 3.87 (s, 12H), 3.36 (s, 12H), 3.34 (s, 12H); ^{13}C-NMR (100 MHz, CD_3CN, ppm): δ 157.2, 156.8, 155.8, 149.7, 140.6, 139.8, 139.0, 124.2, 120.5, 113.8, 109.3, 107.7, 106.7, 40.1, 36.6; IR (KBr, cm^{-1}): ν 3146 (w), 2948 (w), 1563 (s), 1419 (s), 1323 (w), 1237 (w), 1169 (m), 1114 (m), 983 (m), 841 (s), 786 (m), 732 (m), 558 (s); MALDI-TOF MS: m/z = 772.1 ($[M\text{-}2PF_6]^{2+}$).



15 (MMC-4)

Compound **15** was prepared from **14** by a similar procedure to the synthesis of **10**. Quantities: **14** (385 mg, 0.21 mmol), $AuCl(SMe_2)$ (126 mg, 0.43 mmol), CH_2Cl_2 (30 mL). The product was a yellow solid (380 mg, 90%): m.p.: 185-187 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, 150 °C, ppm): δ 7.91 (s, 4H), 7.75 (t, J = 8.0 Hz, 4H), 7.61 (s, 4H), 7.40-7.34 (m, 10H), 7.30 (d, J = 7.2 Hz, 4H), 6.82-6.80 (m, 8H), 6.68 (d, J = 8.4 Hz, 4H), 4.06 (s, 12H), 3.49 (s, 12H), 3.39(s, 12H); ^{13}C-NMR (100 MHz, DMSO-d_6, 100 °C, ppm): δ 180.7, 156.3, 155.7, 155.4, 154.7, 147.4, 139.9, 138.4, 137.4, 123.5, 120.6, 113.6, 108.3, 107.5, 107.3, 106.9, 37.9, 36.0, 35.5; IR (KBr, cm^{-1}): ν 3150 (w), 2951 (w), 1565 (s), 1422 (s), 1337 (w), 1240 (m), 1168 (m), 1120 (m), 985 (m), 843 (s), 789 (m), 740 (m), 557 (s); MALDI-TOF MS: m/z = 860.5 ($[M\text{-}2PF_6]^{2+}$).

Preparation of MMC-Au NPs

The Au NPs was prepared by the literature method.[2] The concentration of the Au NPs solution was described as 2.95×10^{-4} M based on $HAuCl_3$. MMC (9.87×10^{-7} mol) in 0.5 mL DMF was added into Au NPs (2.95×10^{-6} mol, 10 mL aqueous solution) and stirred at room temperature for 2 hours.

X-ray Crystallographic Analysis

Data for **MMC-1**·$CH_3OCH_2CH_2OCH_3$ was collected at 173 K with Mo-*K*α radiation (λ = 0.71073 Å) with frames of oscillation range 0.5º. Data for $[H_2Au_2(\mathbf{2})_2(H_2O)_2]$ $(CF_3SO_3)_4 \cdot H_2O$ (a protonated **MMC-4**) was collected at 143 K with Cu-*K*α radiation (λ = 1.54178 Å) with frames of oscillation range 1º. All structures were solved by direct methods, and non-hydrogen atoms were located from difference Fourier maps. All non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 by using the SHELXTL program unless otherwise noticed. All figures are drawn by using X-seed program.[3]

Crystal data for compound **MMC-1**·$CH_3OCH_2CH_2OCH_3$: $C_{54}H_{60}Ag_2F_{12}N_{18}O_2P_2$, M = 1498.88, triclinic, space group $P\bar{1}$ (No. 1), a = 8.3519(17) Å, b = 12.047(2) Å, c = 15.107(3) Å, α = 98.79(3) °, β = 98.78(3) °, γ = 99.16(3) °, V = 1458.4(5) Å^3, Z = 1, T = 173 K, D_c = 1.707 g cm^{-3}, Flack parameter = 0.55(6). The structure, refined on F^2, converged for 7642 unique reflections (R_{int} = 0.0715) and 6894 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0681 and wR_2 = 0.1667 and a goodness-of-fit = 1.062. Two oxygen atoms O1 and O2 is disordered at two positions with a refined site-occupancy ratio of 0.50:0.50. The whole $CH_3OCH_2CH_2OCH_3$ molecule is highly disordered. Therefore, total six non-hydrogen atoms (O1, O2, C51, C52, C53, C54) were refined isotropically. There are four A level alerts in the checkcif report, which are all due to the severe disorder of the solent molecule $CH_3OCH_2CH_2OCH_3$.

Crystal data for compound $[H_2Au_2(\mathbf{2})_2(H_2O)_2](CF_3SO_3)_4 \cdot H_2O$ (a protonated **MMC-4**): $C_{78}H_{79}Au_2F_{12}N_{26}O_{15}S_4$, M = 2370.86, monoclinic, space group $P2_1/n$ (No. 14), a = 21.3858(9) Å, b = 13.9075(7) Å, c = 30.0241(13) Å, α = 90.00 °, β = 102.410(3) °, γ = 90.00 °, V = 8721.2(7) Å^3, Z = 4, T = 143(2) K, D_c = 1.801 g cm^{-3}. The structure, refined on F^2, converged for 16317 unique reflections (R_{int} = 0.0872) and 14640 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0740 and wR_2 = 0.2043 and a goodness-of-fit = 1.047. Gold atoms Au1 and Au2 are disordered over two closely separated positions because of twin crystal. Several disordered atoms including Au1', Au2' and C78 were refined isotropically. There are three A level alerts in the checkcif report. The first A alert arising from the large Hirshfeld difference between F5 and C76 can be explained by the existence of disordered positions for this uncoordinated ligand. Due to twin crystal and low quality data, it is hard to split the CF_3 moiety into two sets of positions. The second A alert because of high Ueq of O2W compared with its neighboring gold atom can be explained by the large atomic difference between the oxygen and the gold. The third A alert because of the short intramolecular distance between H8A and H10A can be ascribed to the theoretical hydrogen addition.

References

[1] Zhang, E.-X.; Wang, D.-X.; Zheng, Q.-Y.; Wang, M.-X. *Org. Lett.* **2008**, *10*, 2565.
[2] Frens, G. *Nat. Phys. Sci.* **1973**, *241*, 20.
[3] (a) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189. (b) Atwood, J. L.; Barbour, L. J. *Cryst. Growth Des.* **2003**, *3*, 3.

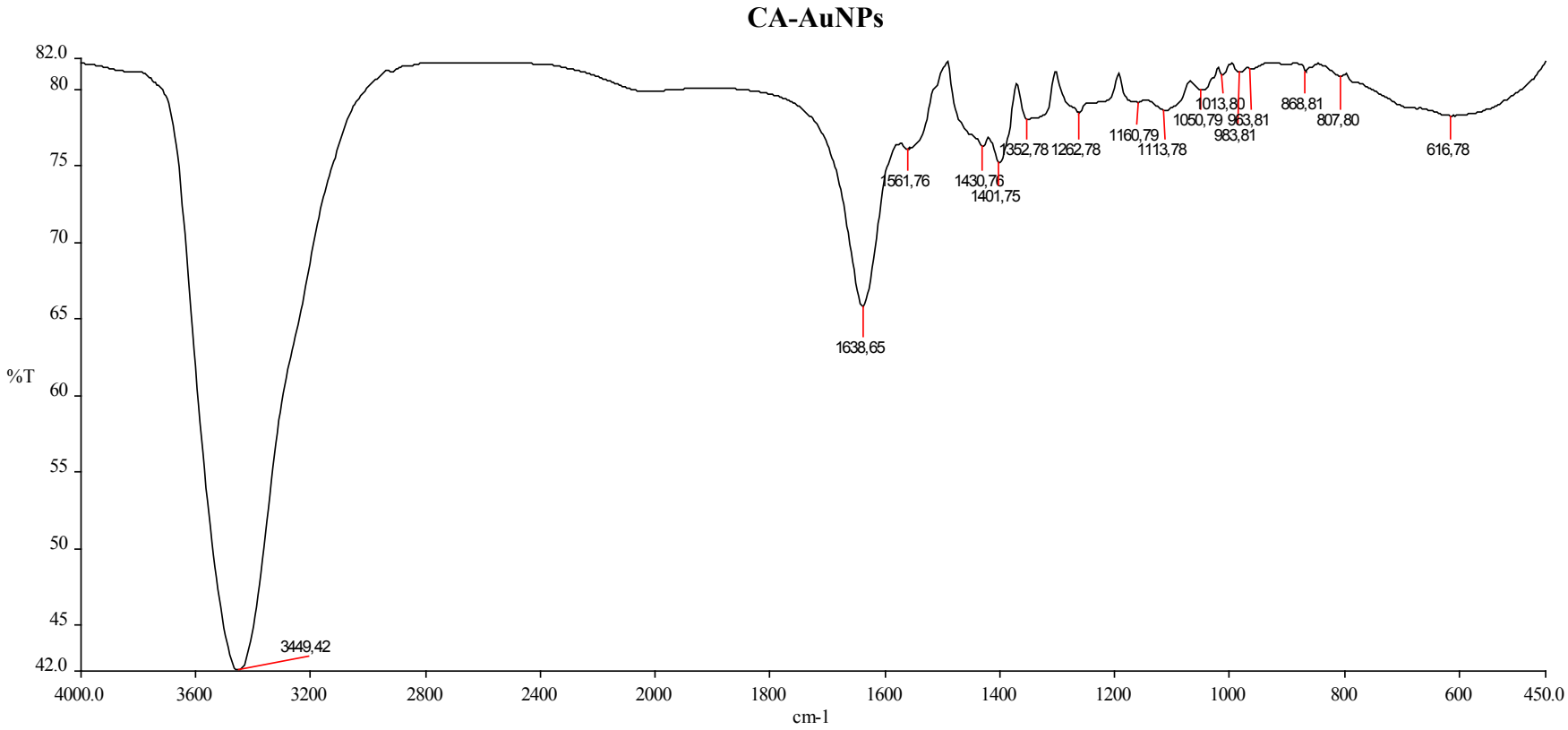


Figure S1. IR spectra of **CA-AuNPs**.

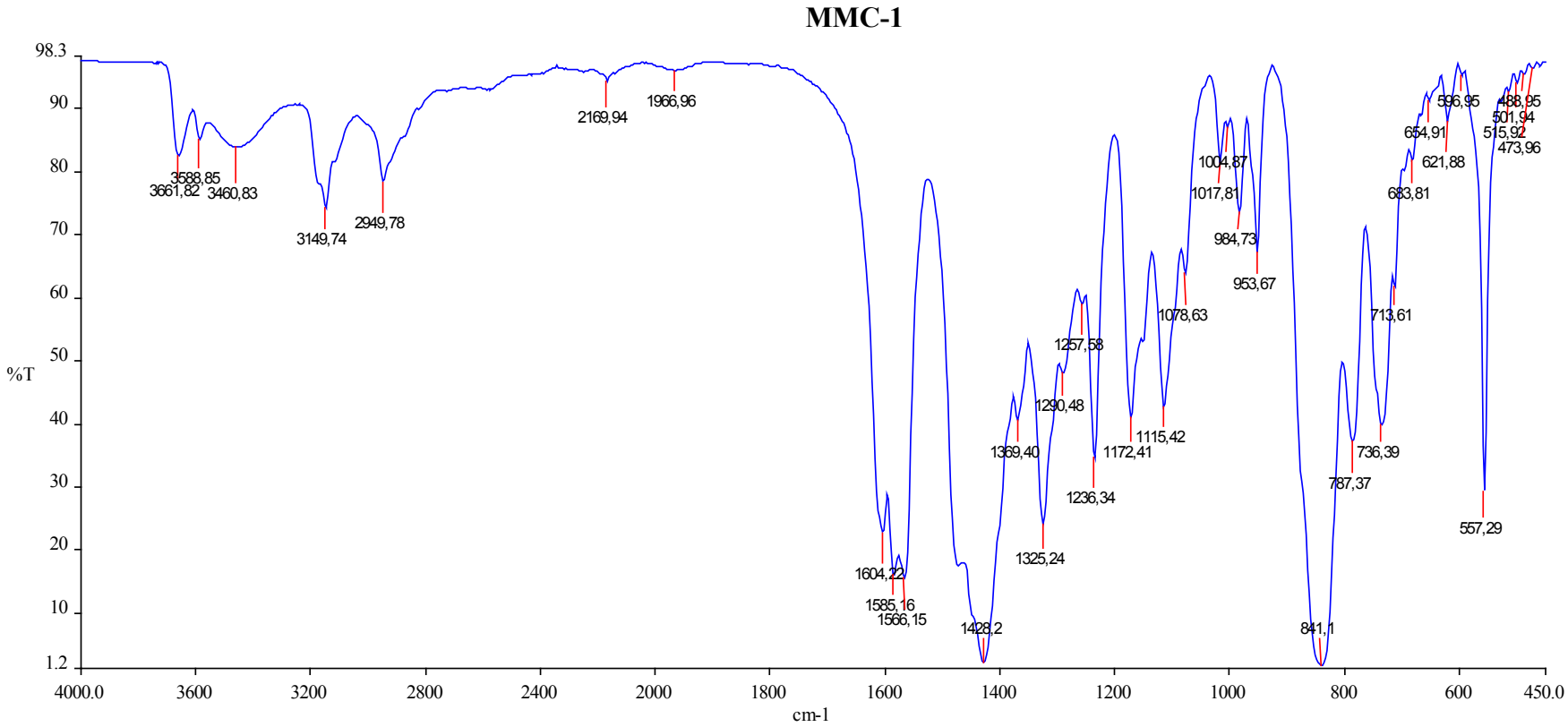


Figure S2. IR spectra of **MMC-1**.

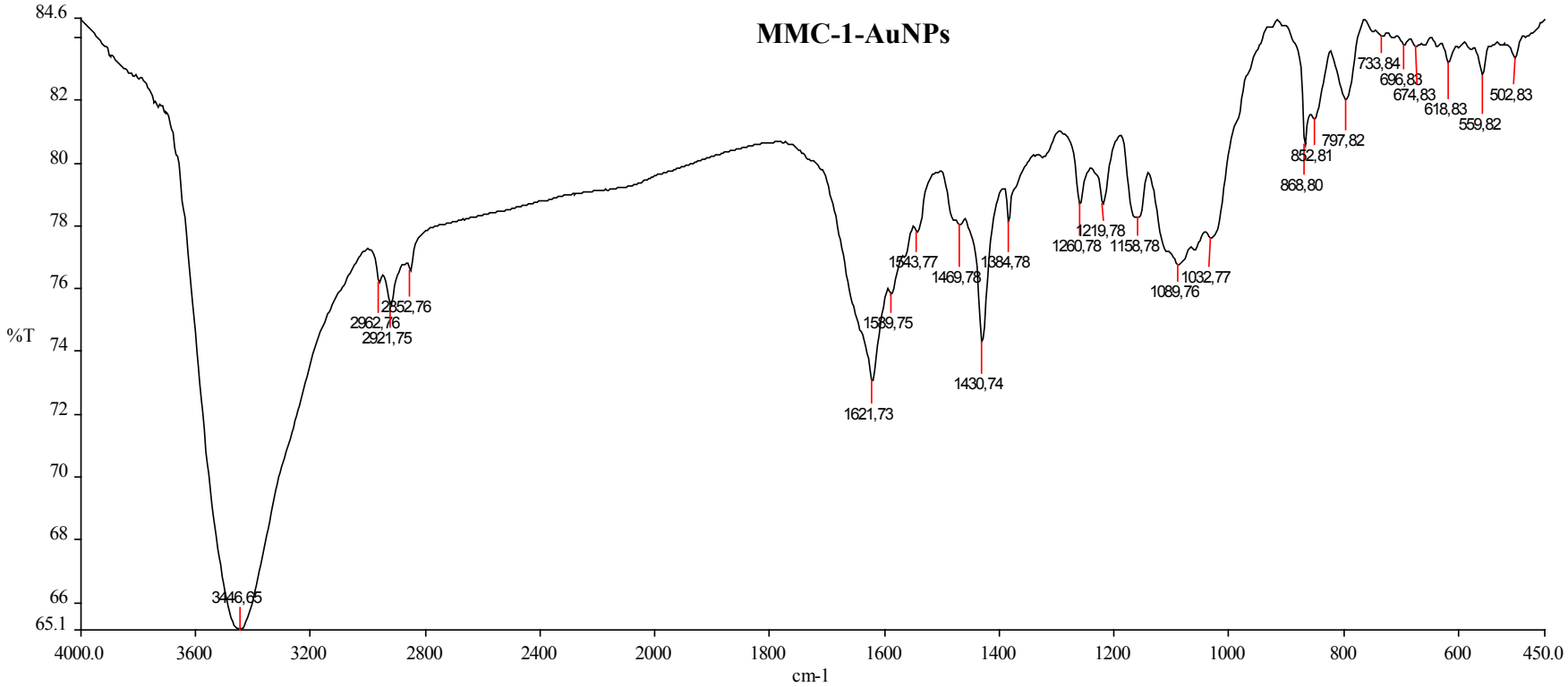


Figure S3. IR spectra of **MMC-1-AuNPs**.

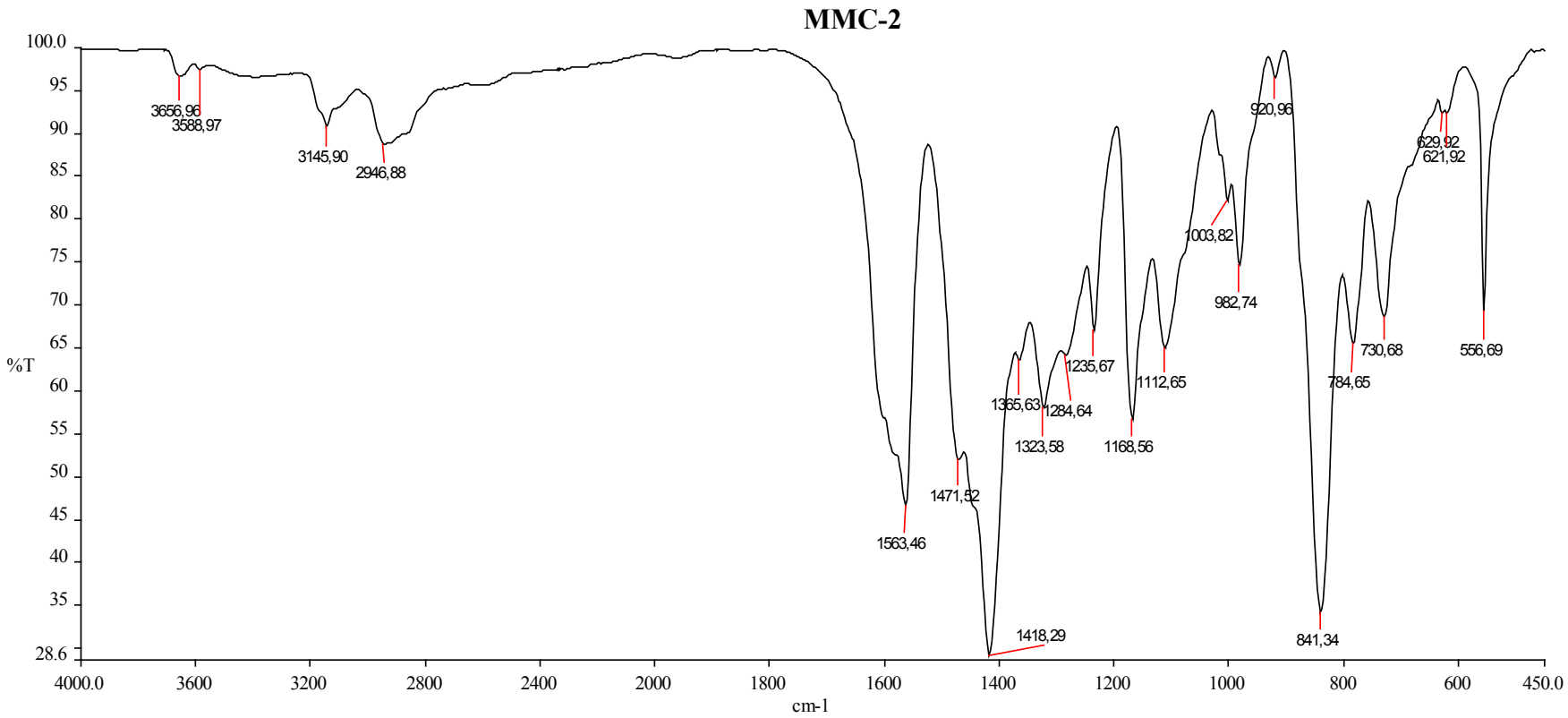


Figure S4. IR spectra of **MMC-2**.

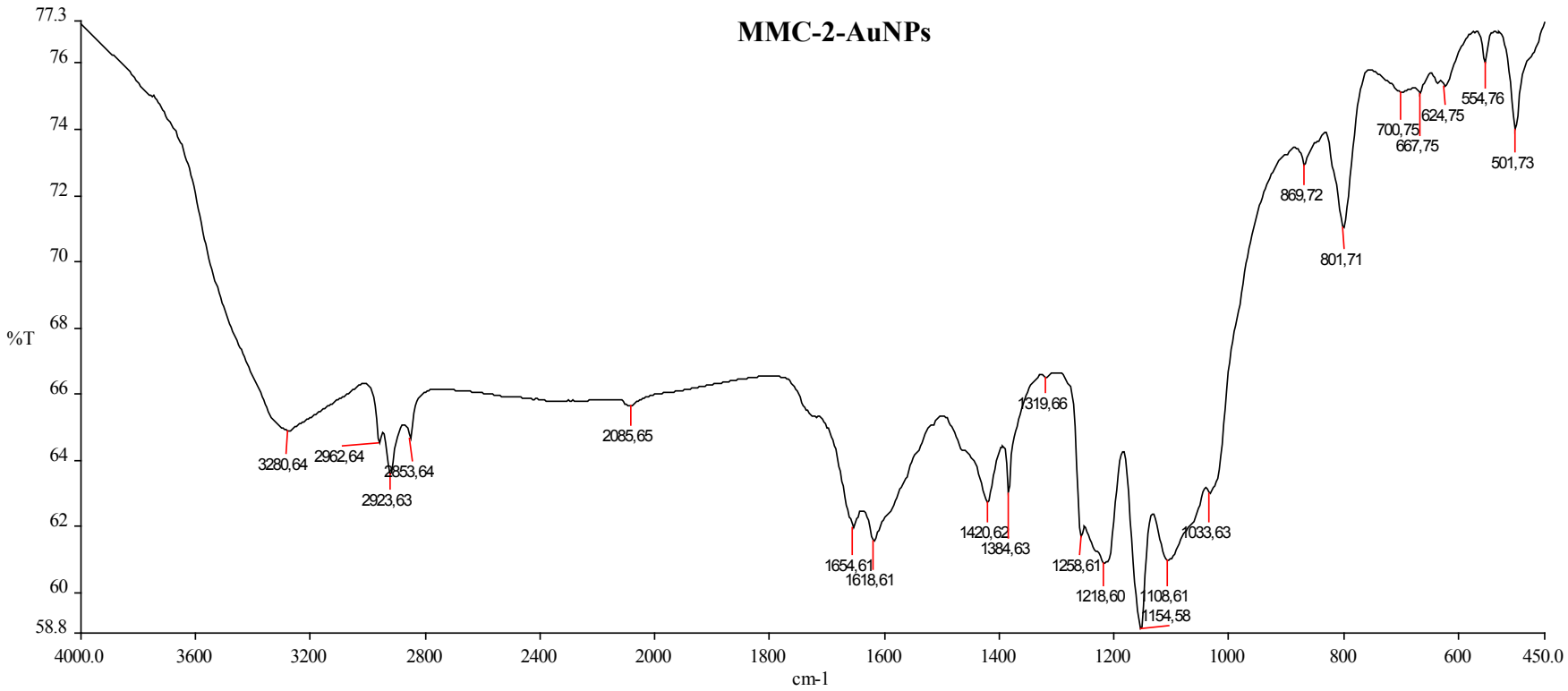


Figure S5. IR spectra of **MMC-2-AuNPs**.

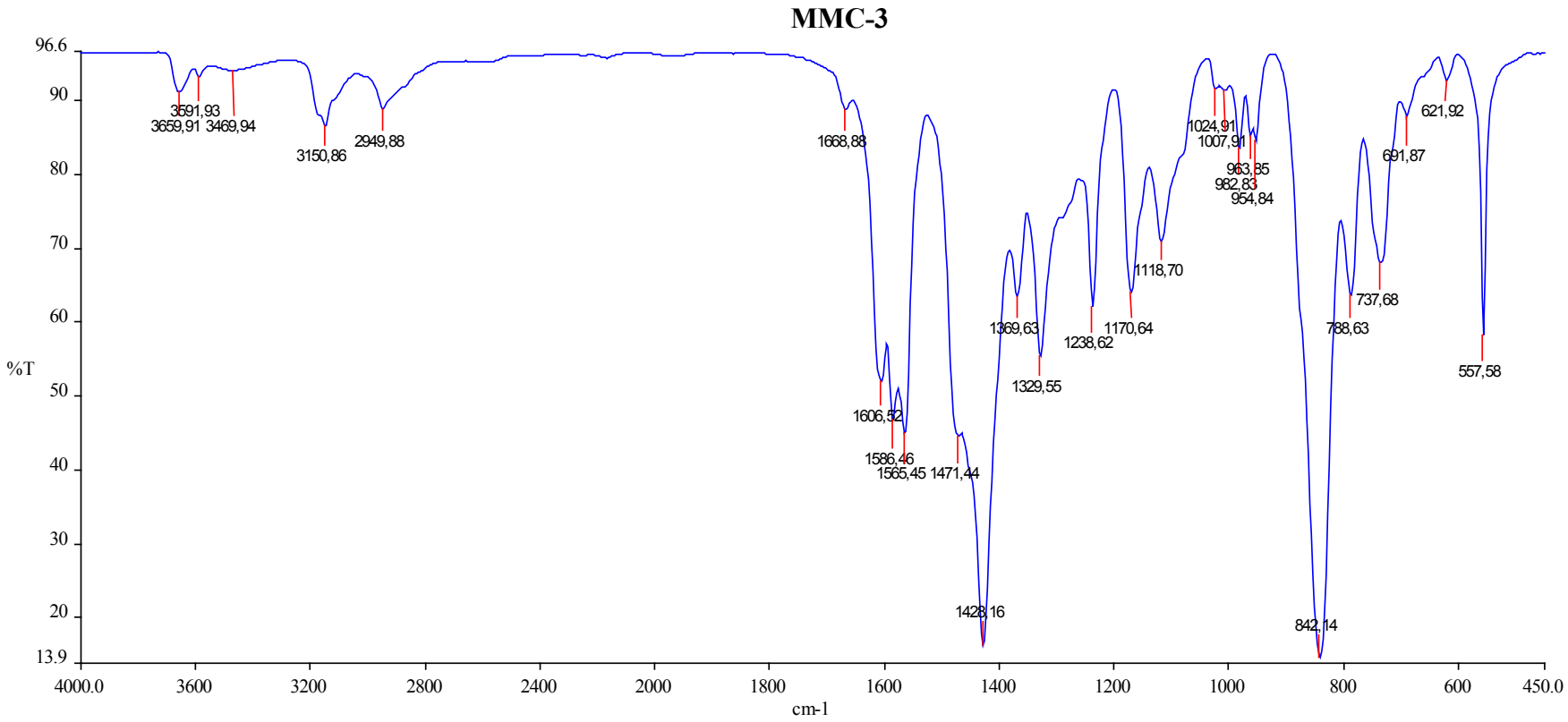


Figure S6. IR spectra of **MMC-3**.

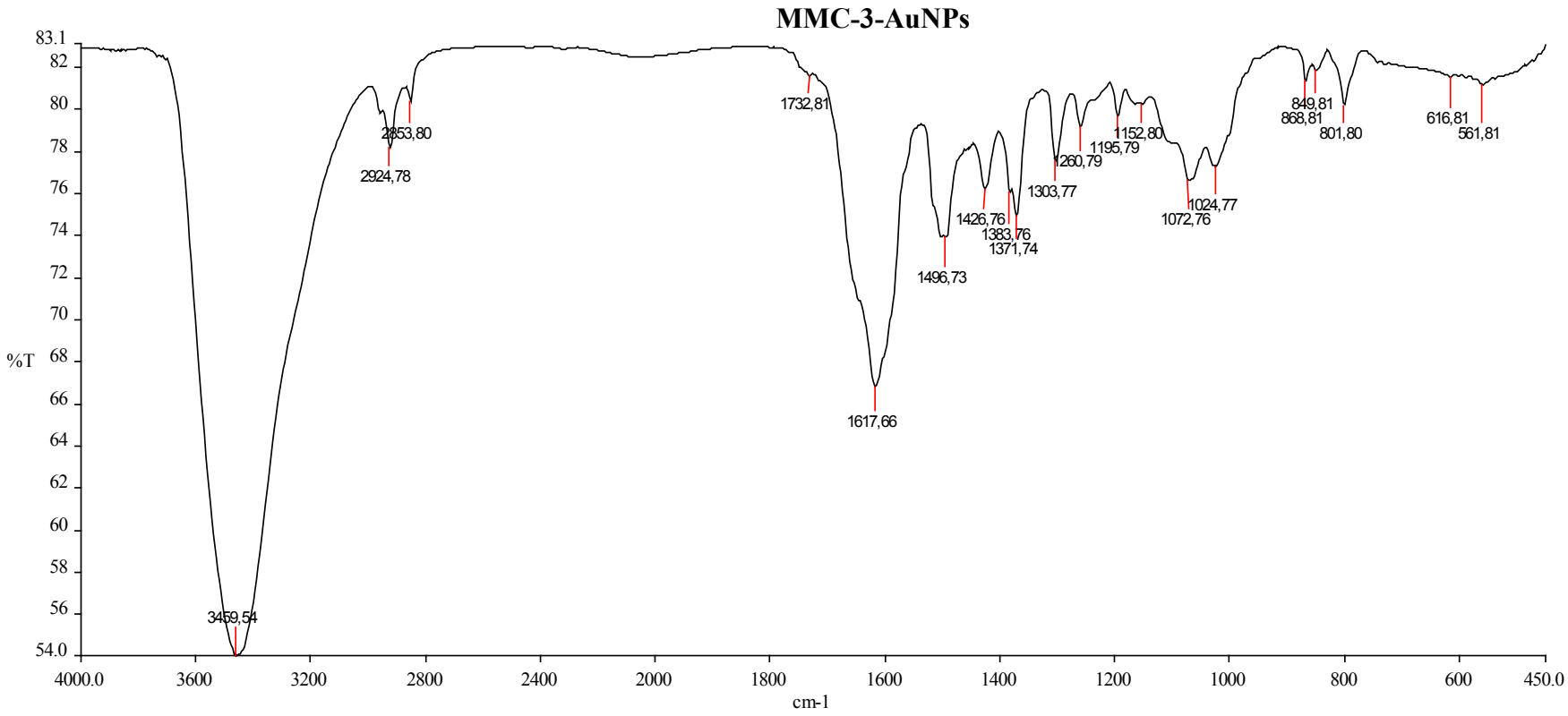


Figure S7. IR spectra of **MMC-3-AuNPs**.

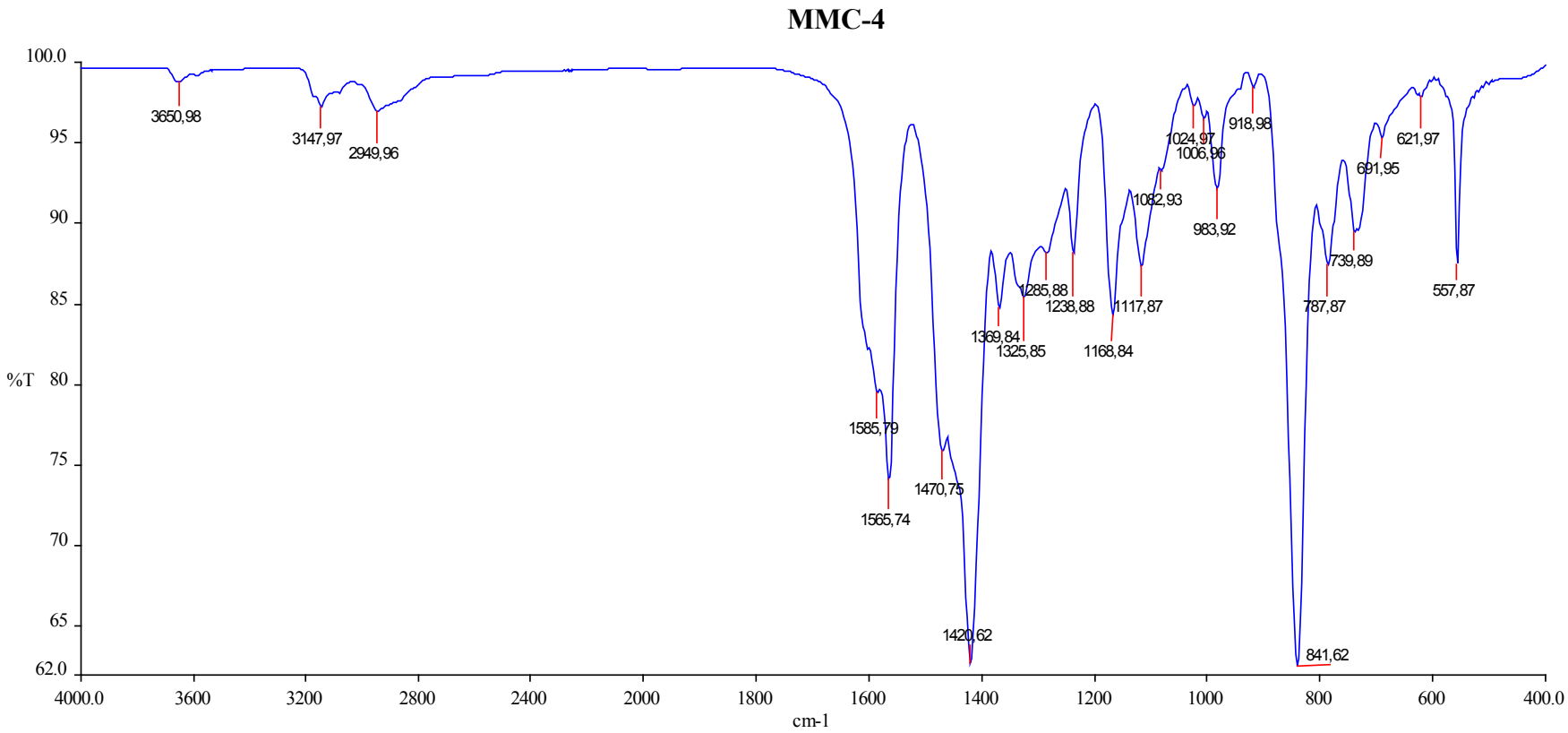


Figure S8. IR spectra of **MMC-4**.

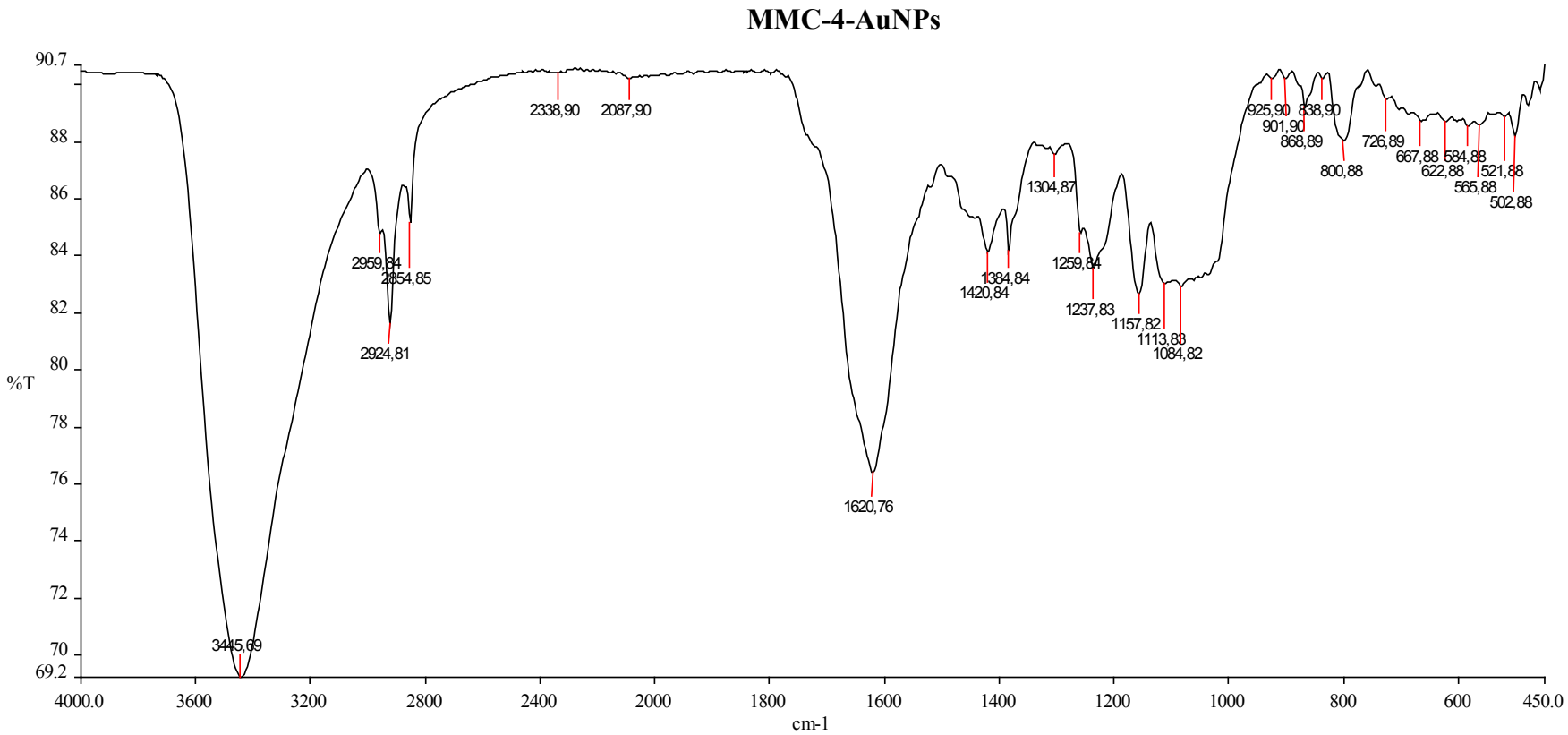
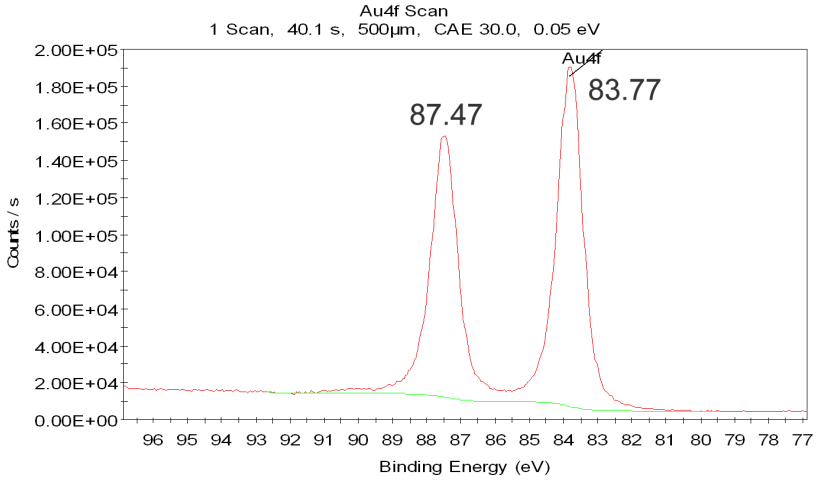
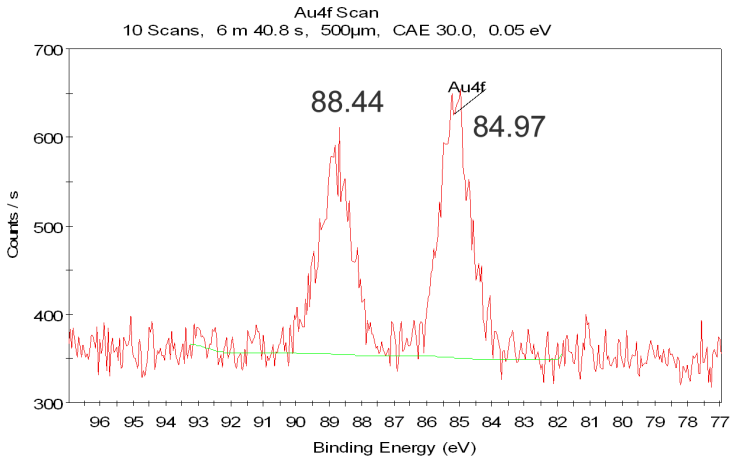


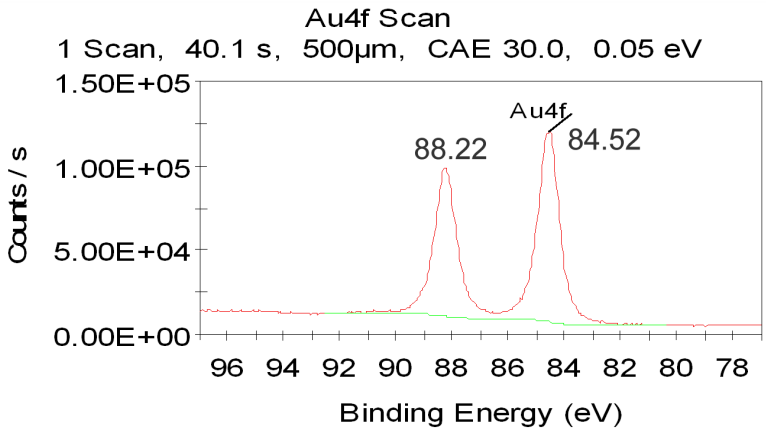
Figure S9. IR spectra of **MMC-4-AuNPs**.



CA-AuNPs



MMC-4



MMC-4-AuNPs

Figure S10. XPS spectra of **CA-AuNPs**, **MMC-4** and the centrifuged **MMC-4-AuNPs**.

General procedures for UV-Vis titration experiments

UV-Vis spectroscopic titrations experiments were carried out using a UV-Vis spectrometer at 298 K. All spectra were collected using a quartz cuvette with 10 mm path length. For each spectrum acquired, the range of 290-800 nm was surveyed at a resolution of 1.0 nm and an integration time of 0.1s. The pH values for each titration were measured by a pH meter.

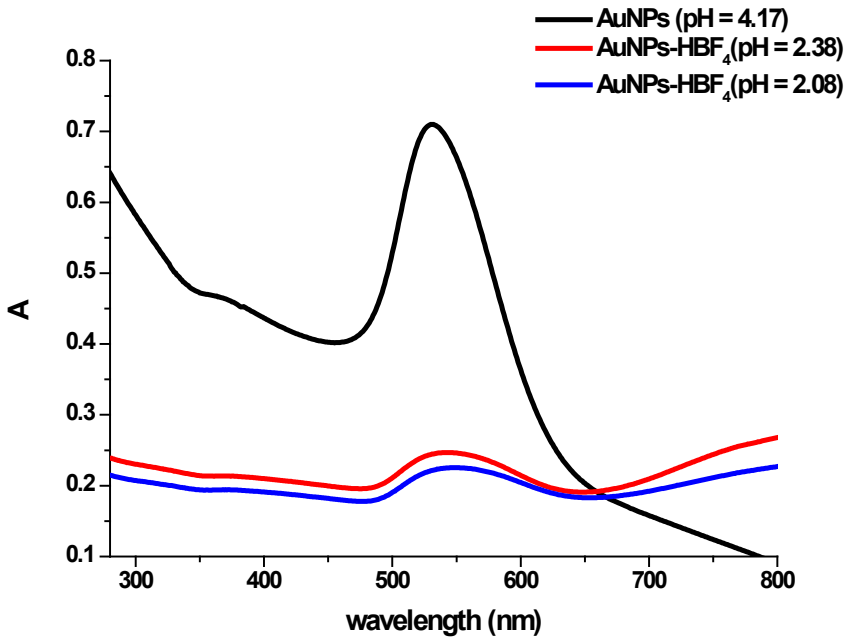


Figure S11. UV-Vis titration curves of **CA-AuNPs** and HBF_4. The DMF/H_2O (v/v = 1:20) solution of HBF_4 (c = 3.17 × 10^{-2} M) was added into 3 mL DMF/H_2O (v/v = 1:20) solution of **CA-AuNPs** (c = 2.95 × 10^{-4} M based on $HAuCl_3$) at 25 °C. The volume of HBF_4 was 0, 60 μL, 120 μL from top to down.

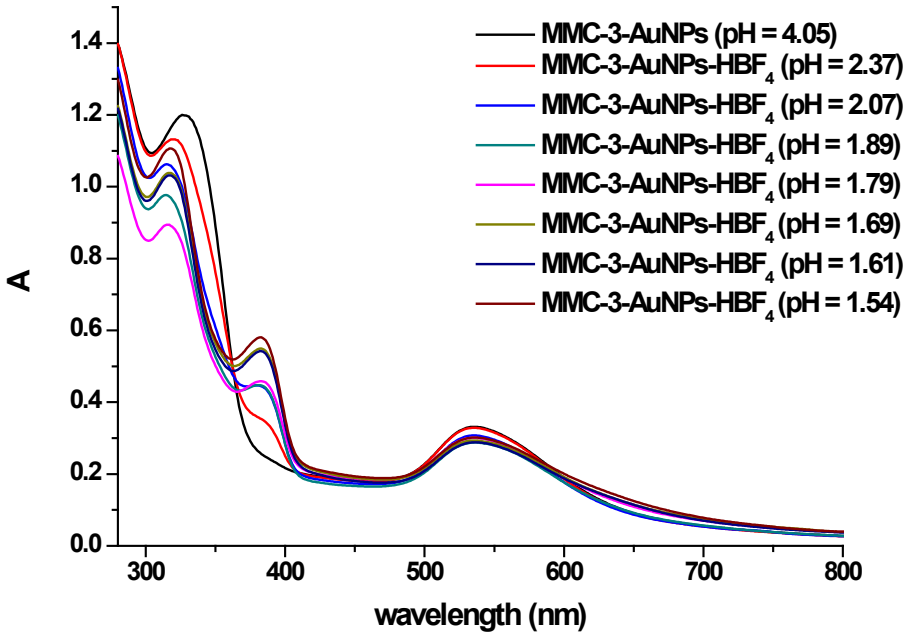


Figure S12. UV-Vis titration curves of **MMC-3-AuNPs** and HBF_4. The DMF/H_2O (v/v = 1:20) solution of HBF_4 (c = 3.17 × 10^{-2} M) was added into 3 mL DMF/H_2O (v/v = 1:20) solution of

MMC-3-AuNPs at 25 °C. The volume of HBF_4 was 0, 60 μL, 120 μL, 180 μL, 240 μL, 300 μL, 360 μL, 420 μL from top to down.

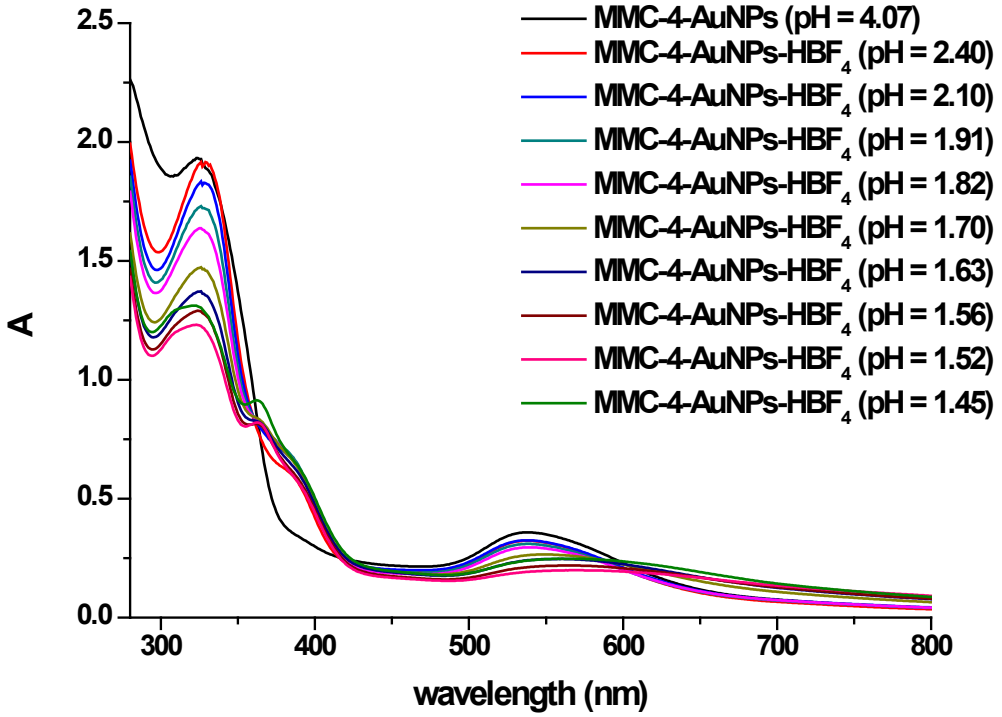


Figure S13. UV-Vis titration curves of **MMC-4-AuNPs** and HBF_4. The DMF/H_2O (v/v = 1:20) solution of HBF_4 (c = 3.17 × 10^{-2} M) was added into 3 mL DMF/H_2O (v/v = 1:20) solution of **MMC-4-AuNPs** at 25 °C. The volume of HBF_4 was 0, 60 μL, 120μL, 180 μL, 240 μL, 300 μL, 360 μL, 420 μL, 480 μL, 540 μL from top to down.

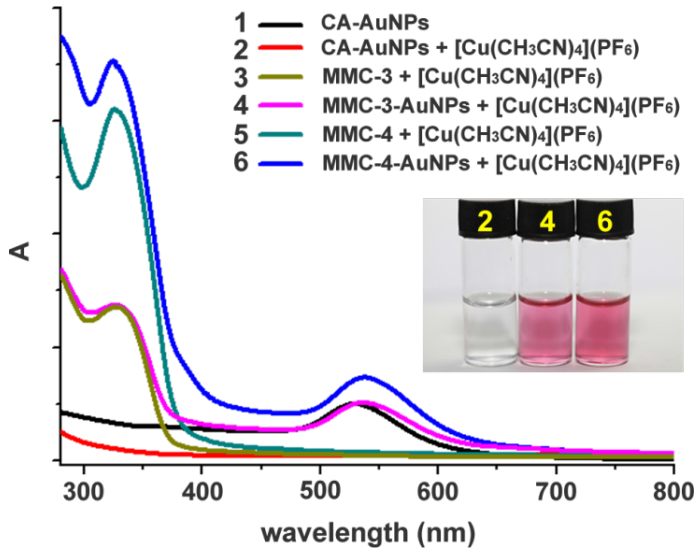
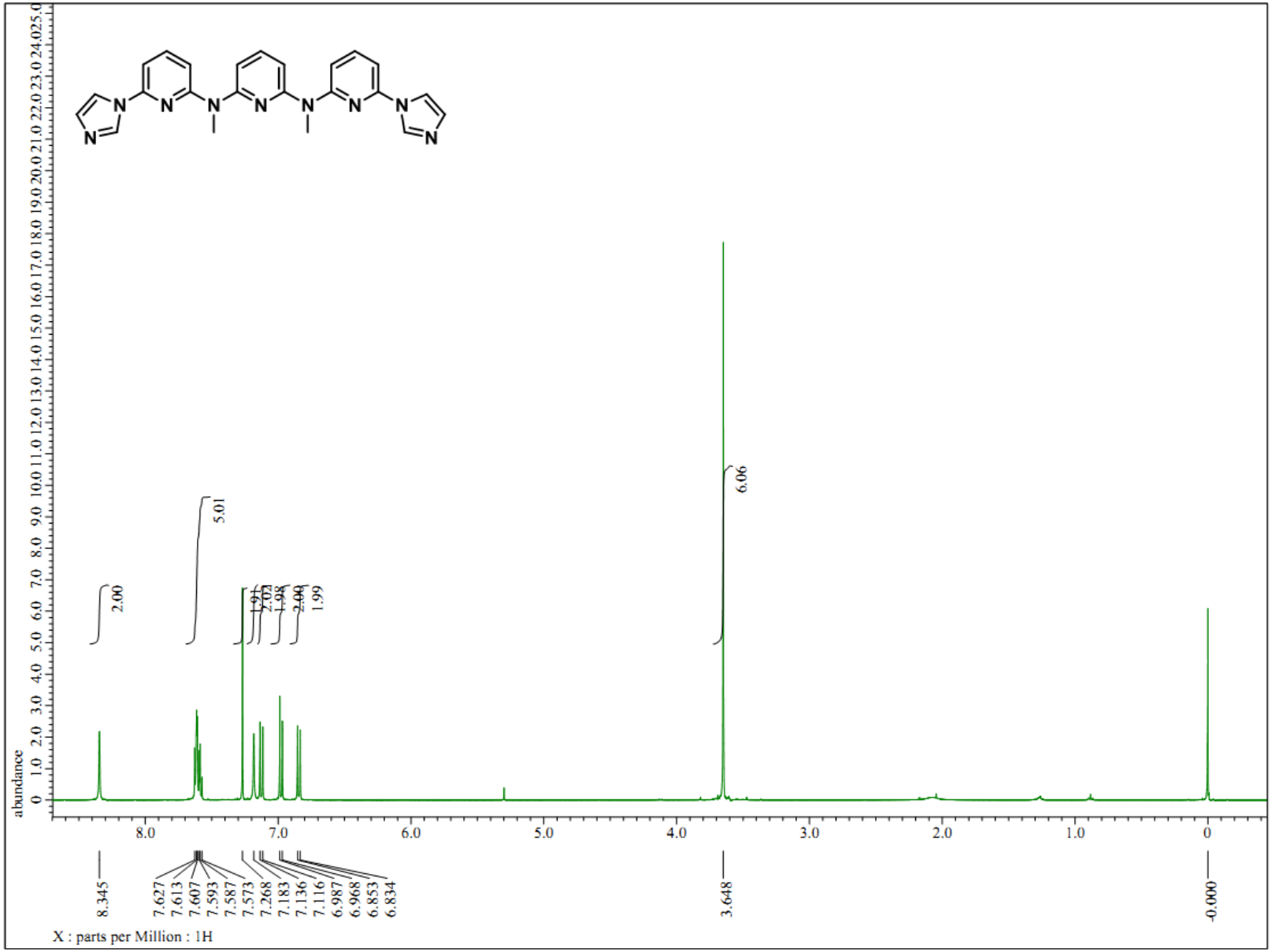


Figure S14. UV-Vis spectra of **CA-AuNPs** and the mixed solution samples of **MMC-3**, **MMC-4**, **MMC-3-AuNPs**, **MMC-4-AuNPs** with $Cu(MeCN)_4PF_6$ (1 μM) in 1:3 ratio.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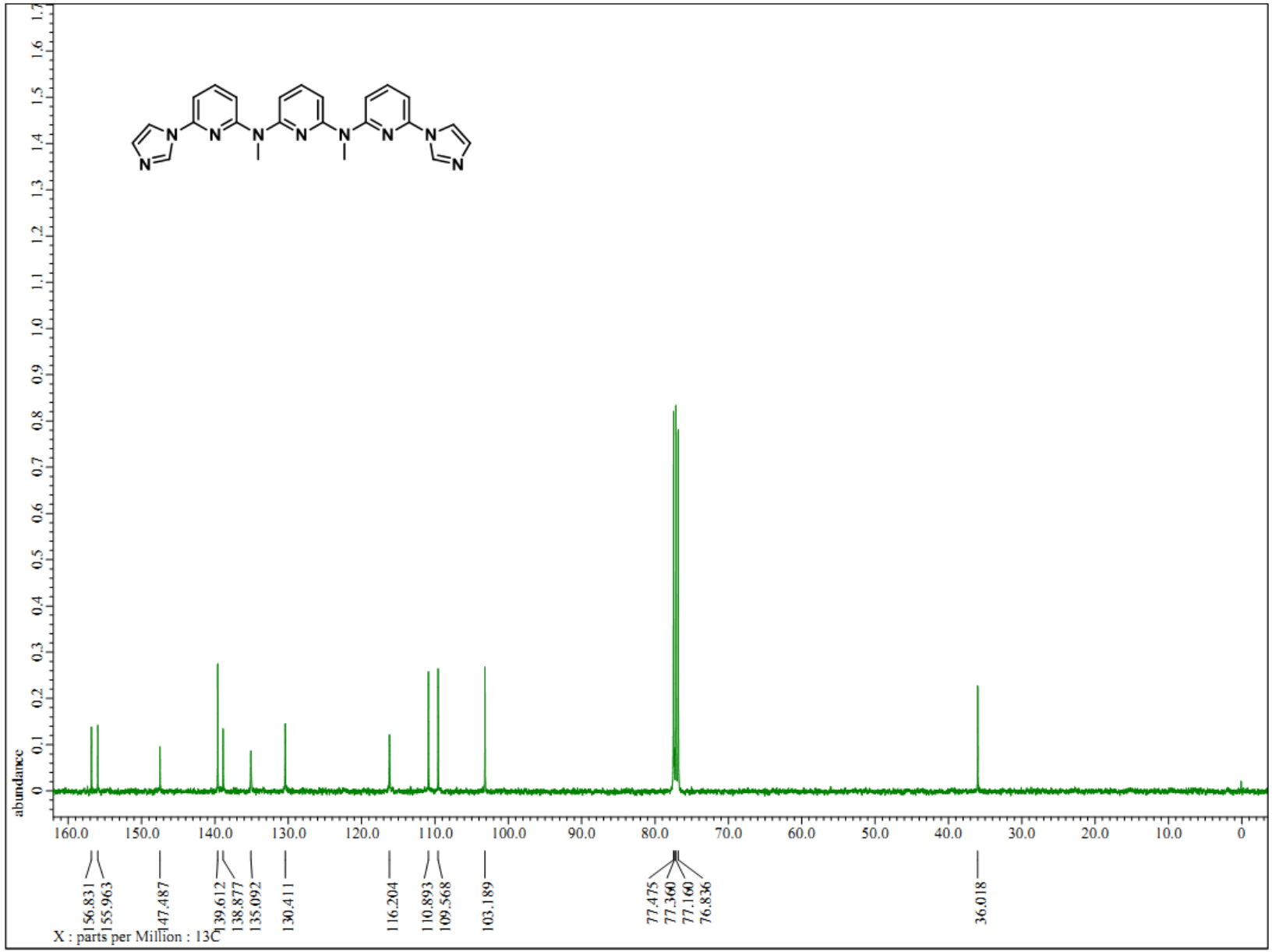
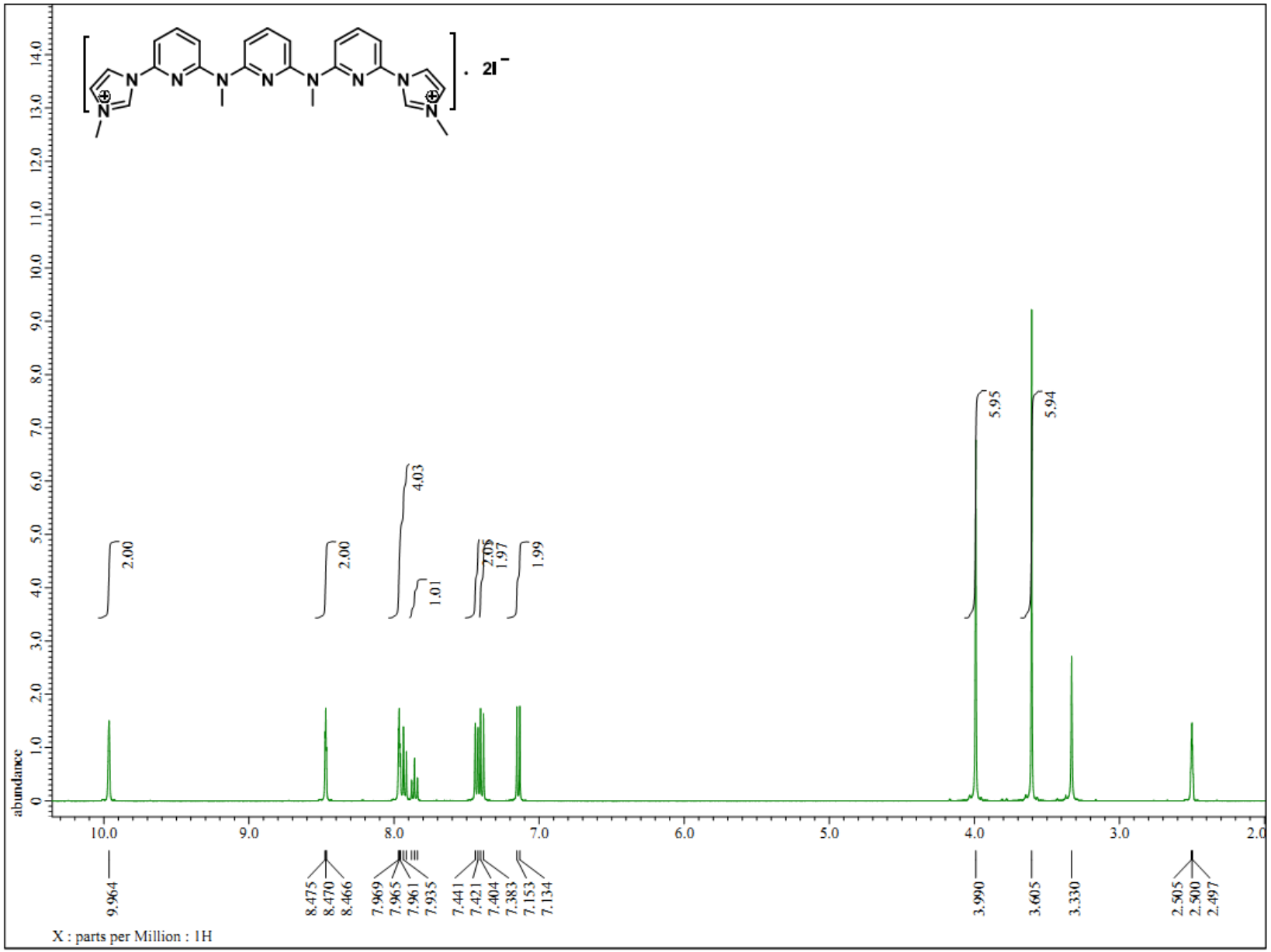
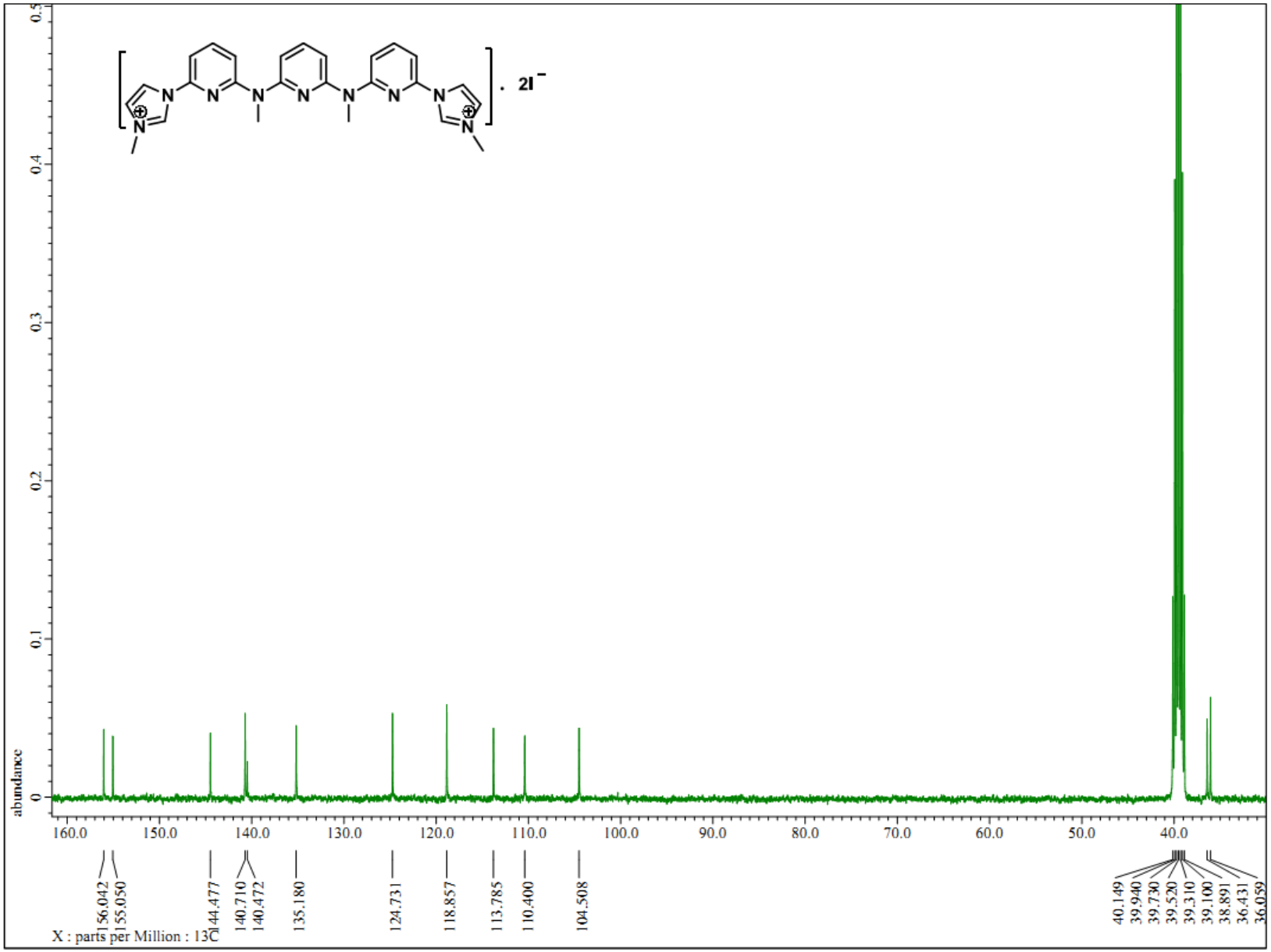
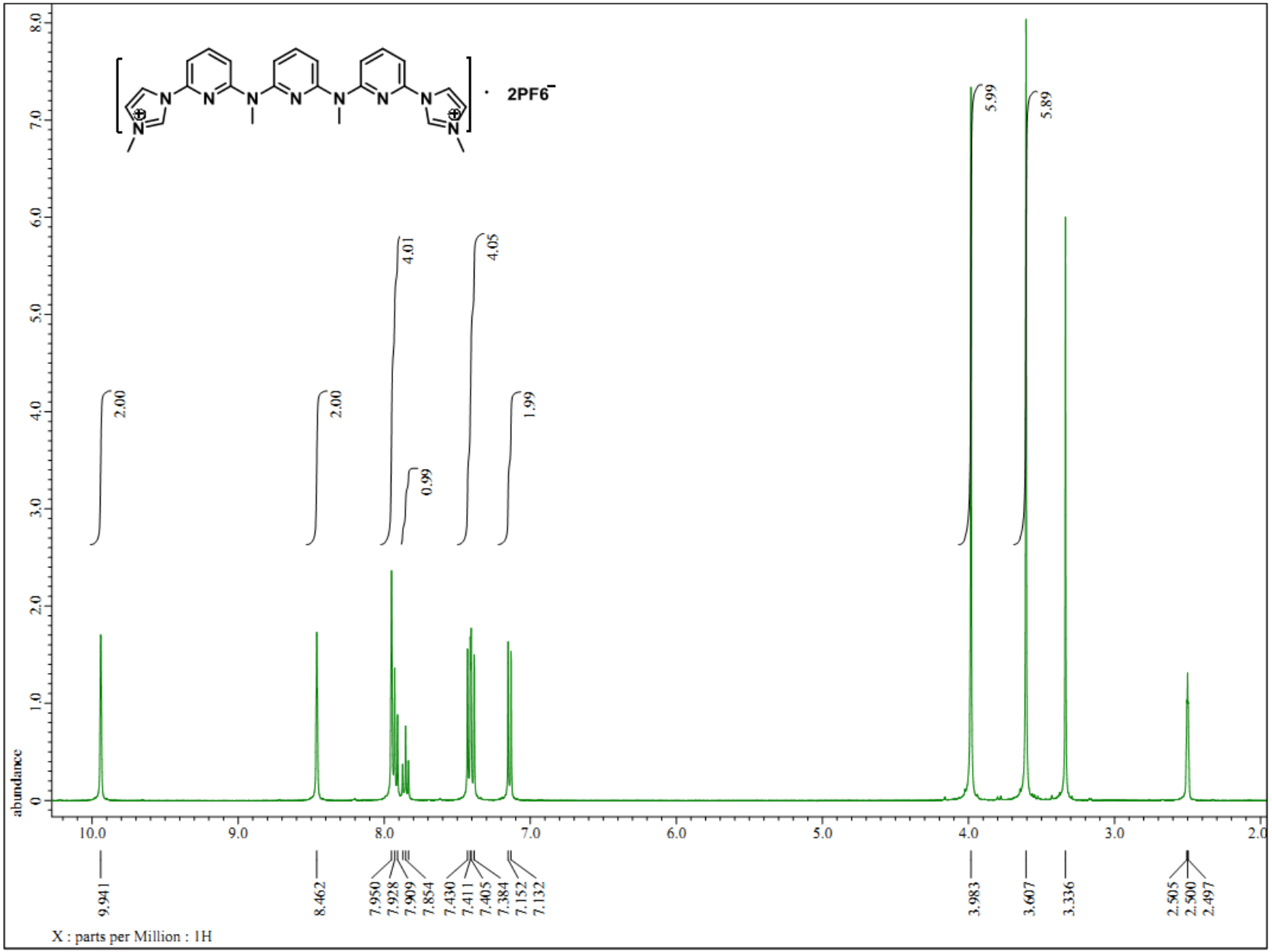
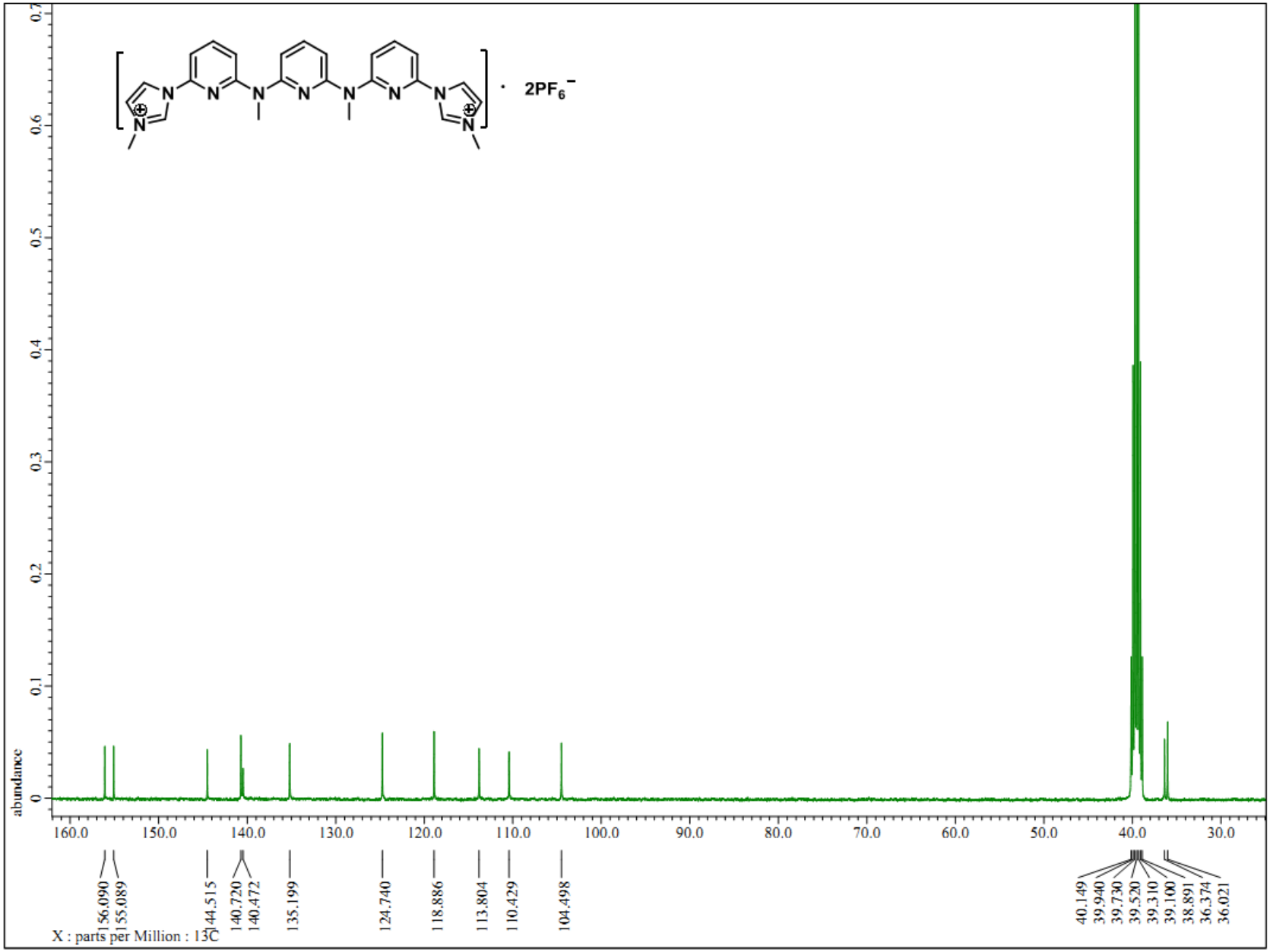
1.91
2.02
1.98
2.00
1.99
6.06
8.345
7.627
7.613
7.607
7.593
7.587
7.573
7.268
7.183
7.136
7.116
6.987
6.968
6.853
6.834
3.648
-0.000
X : parts per Million : 1H

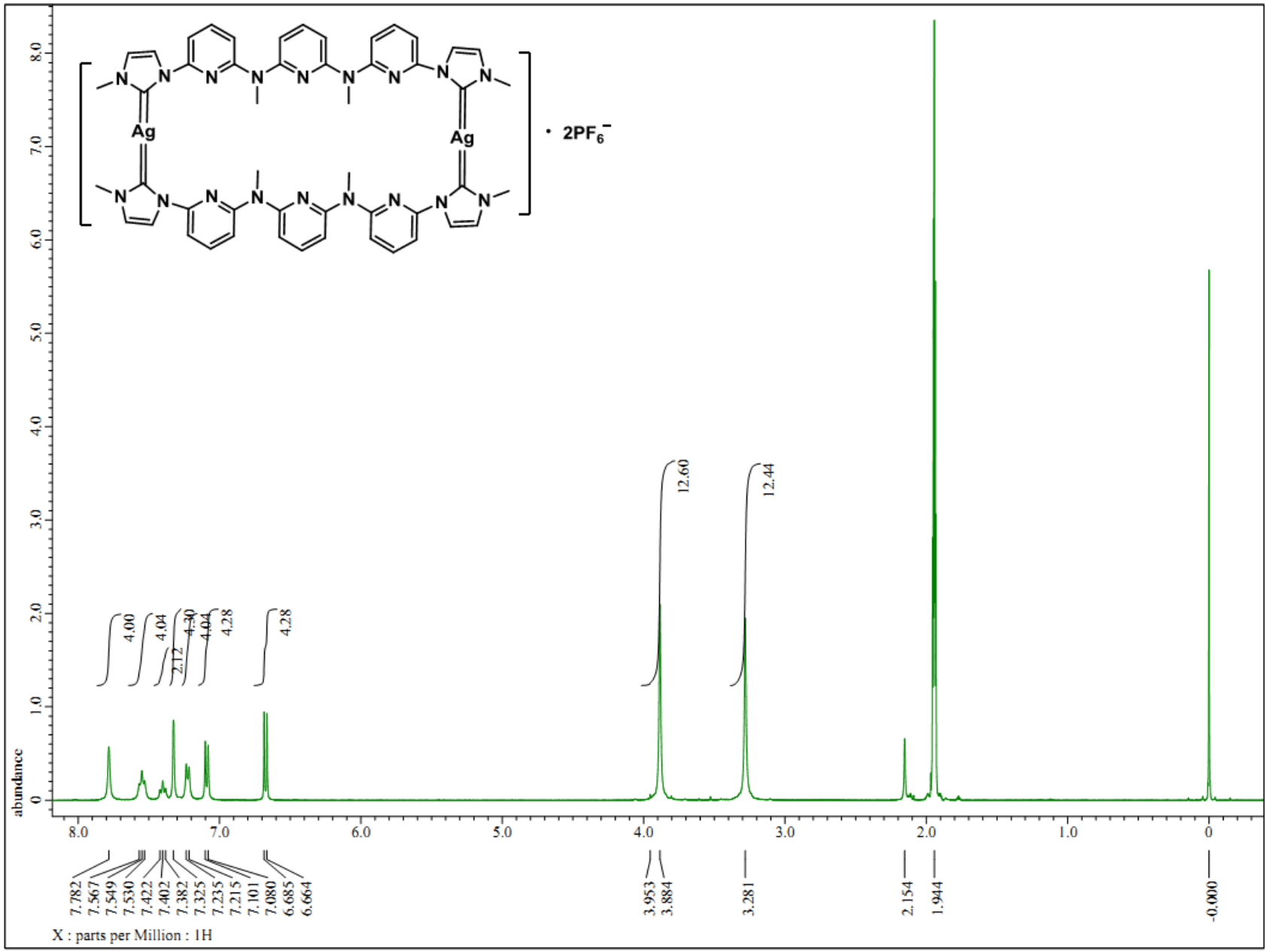


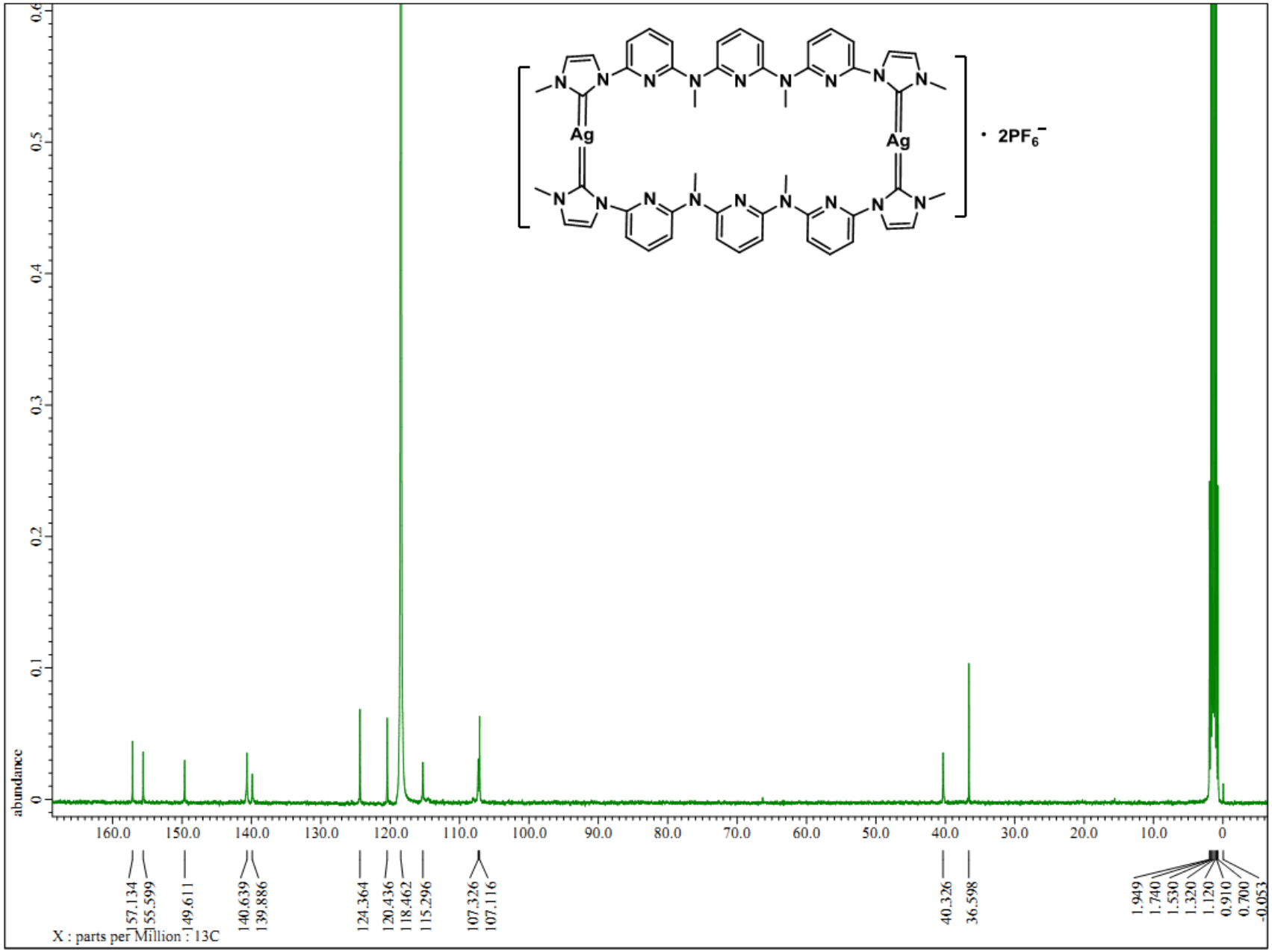


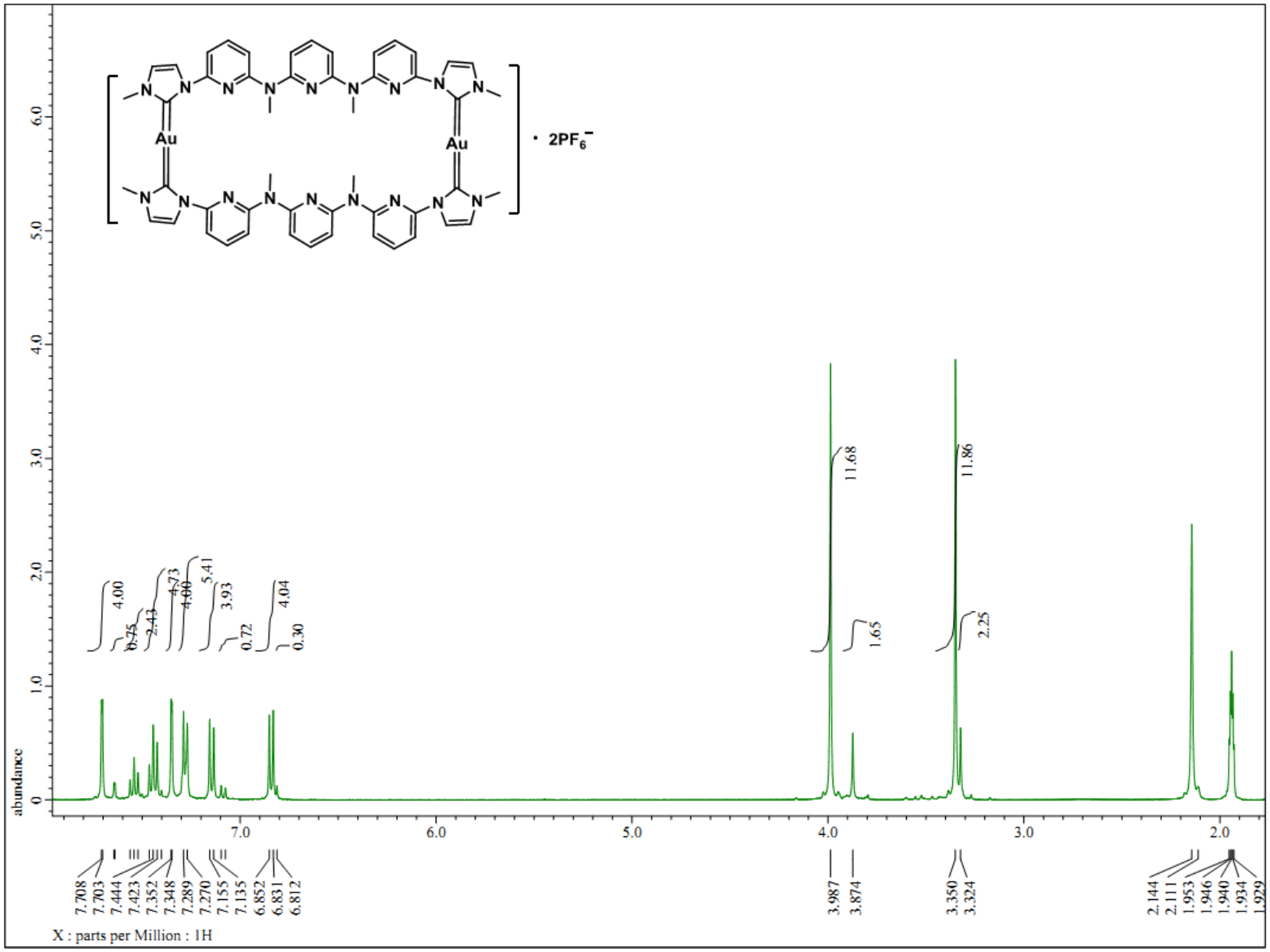


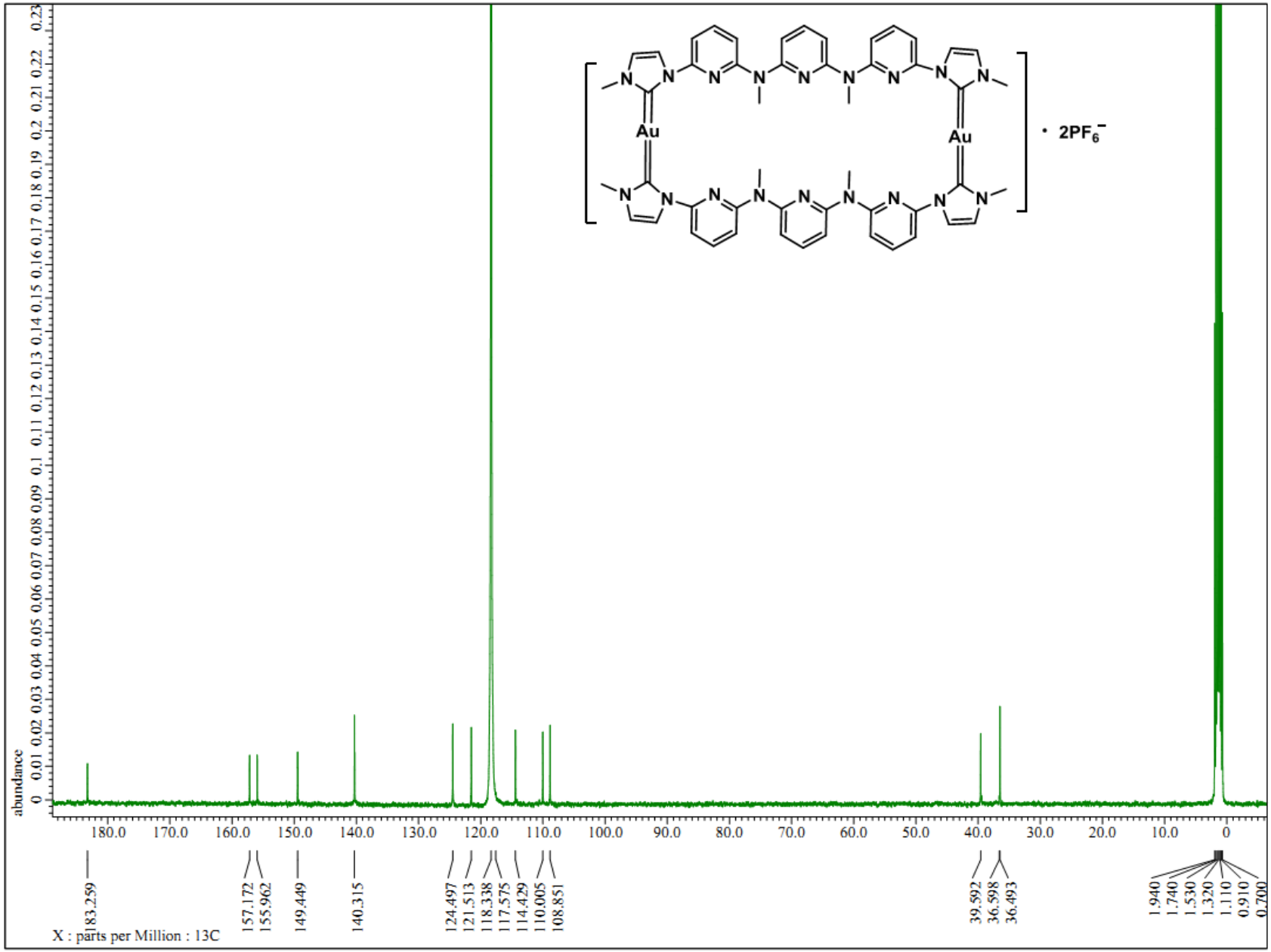








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180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
183.259
157.172
155.962
149.449
140.315
124.497
121.513
118.338
117.575
114.429
110.005
108.851
39.592
36.598
36.493
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1.320
1.110
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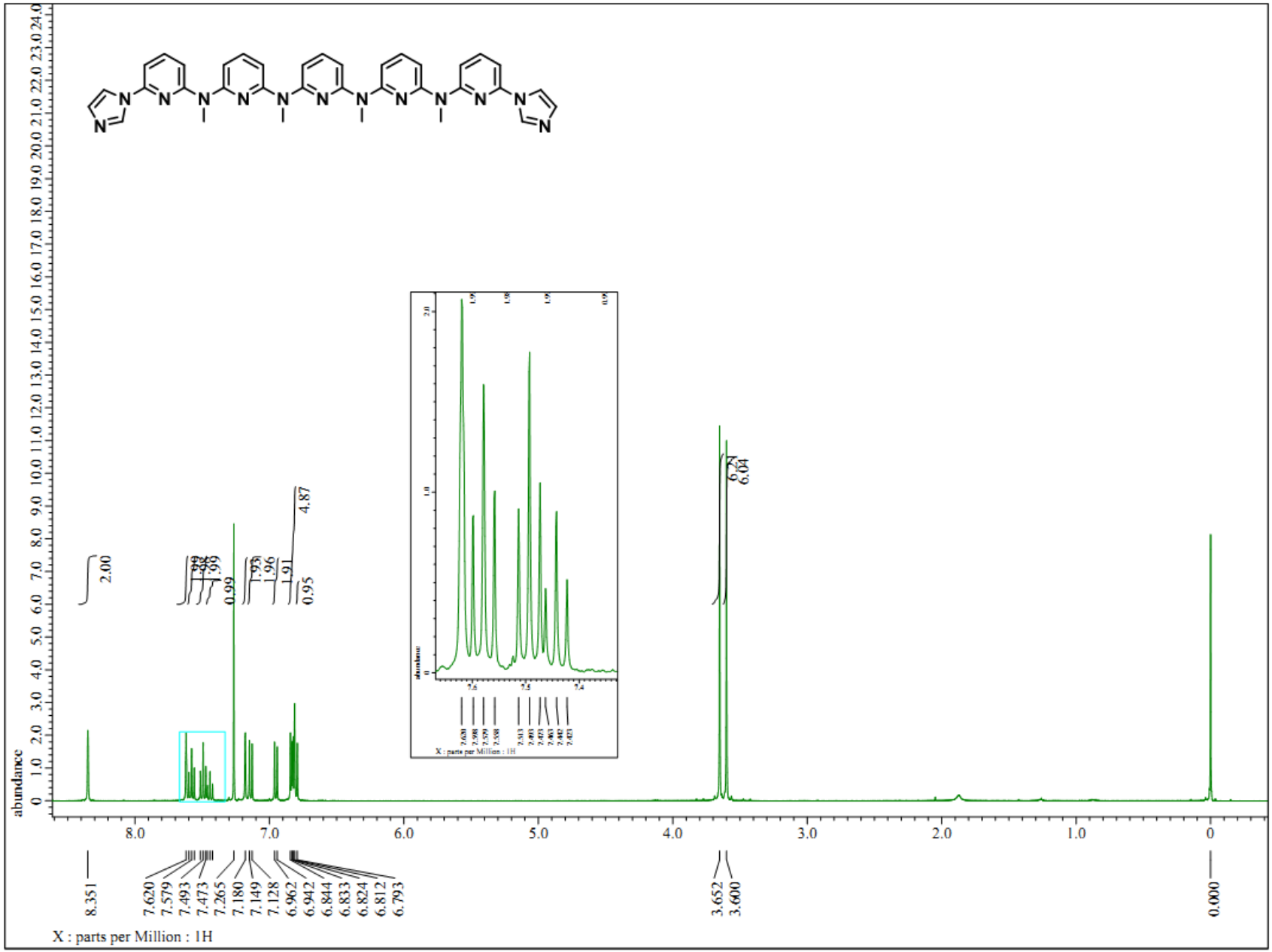
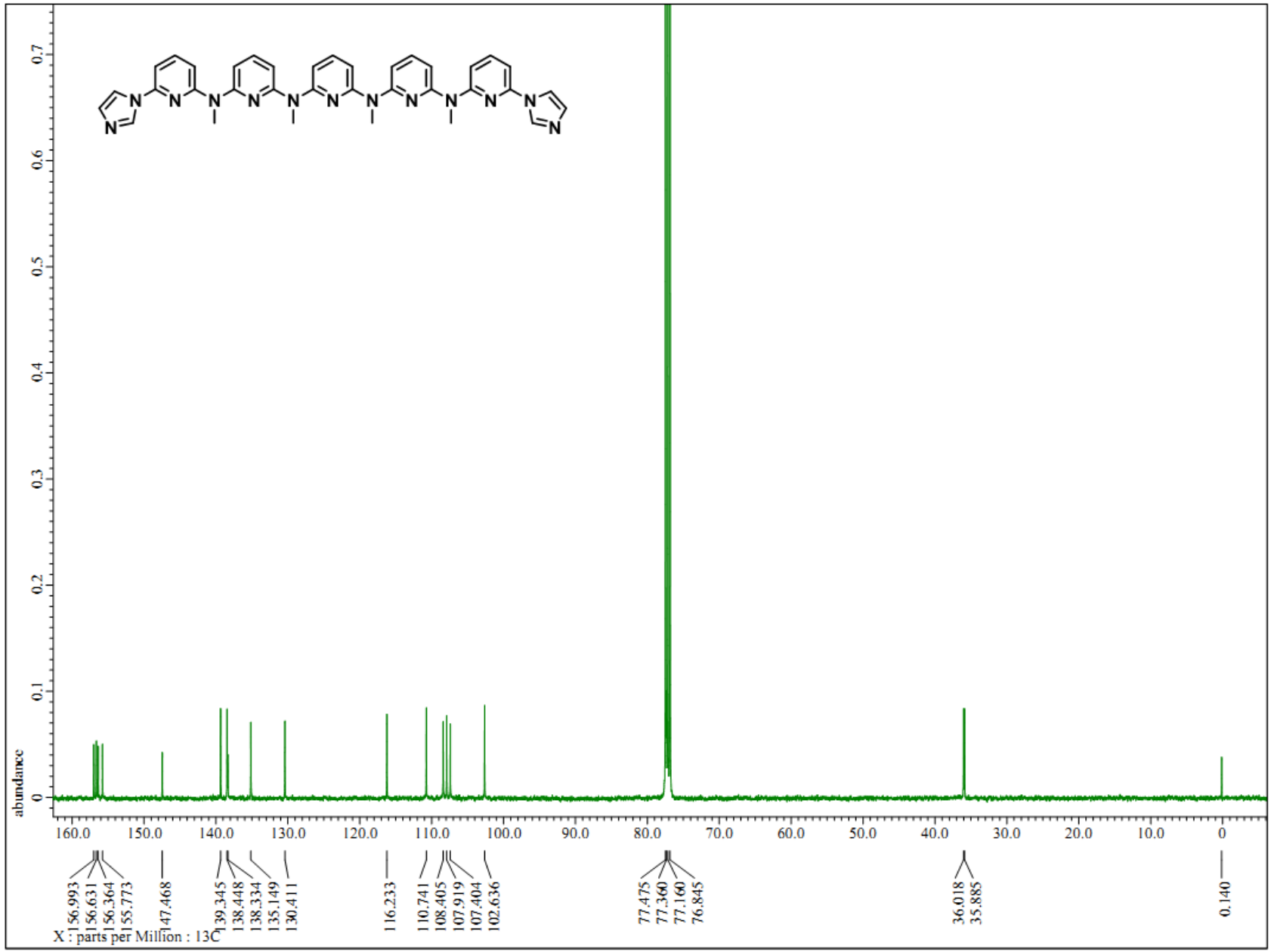
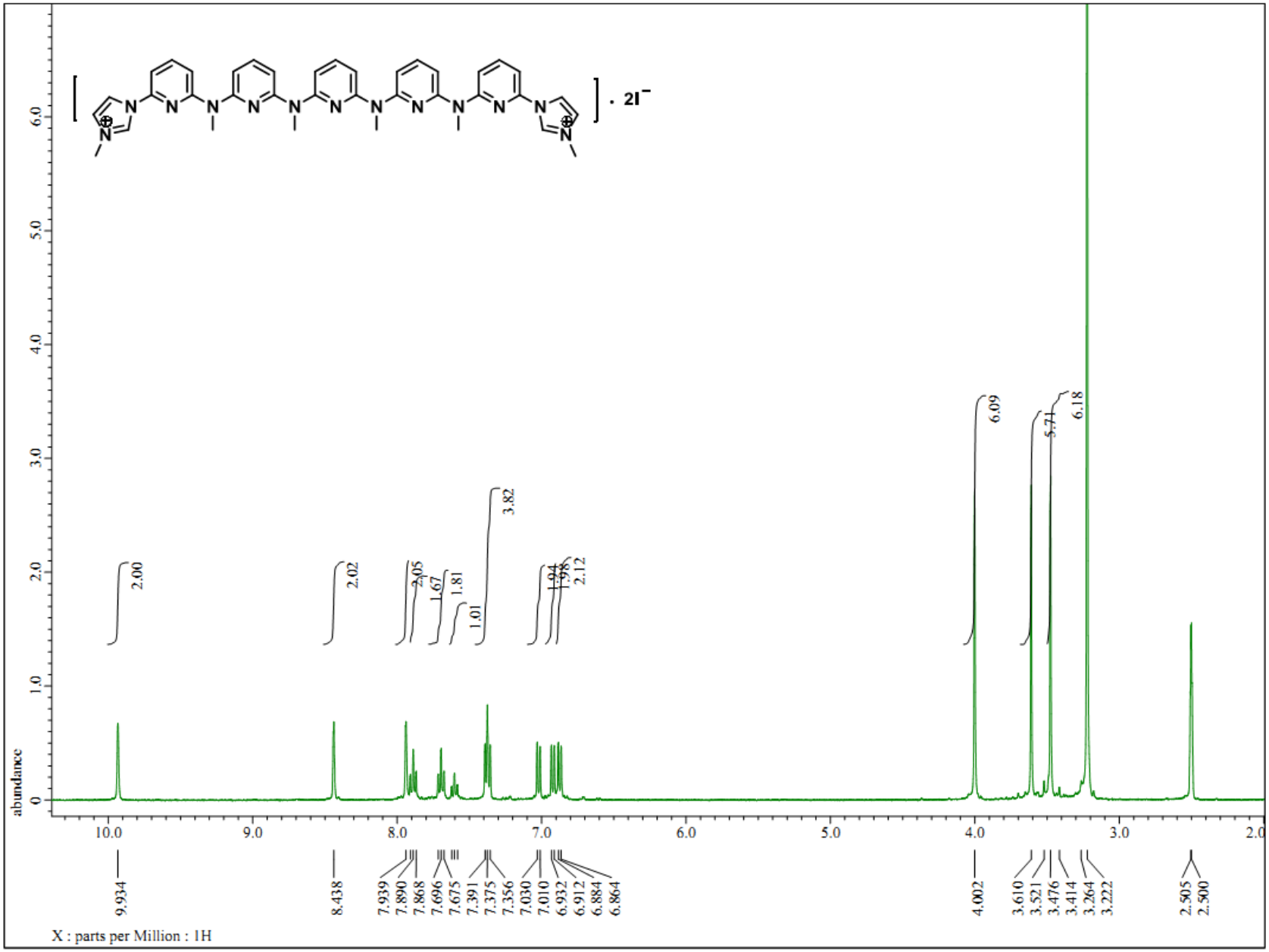
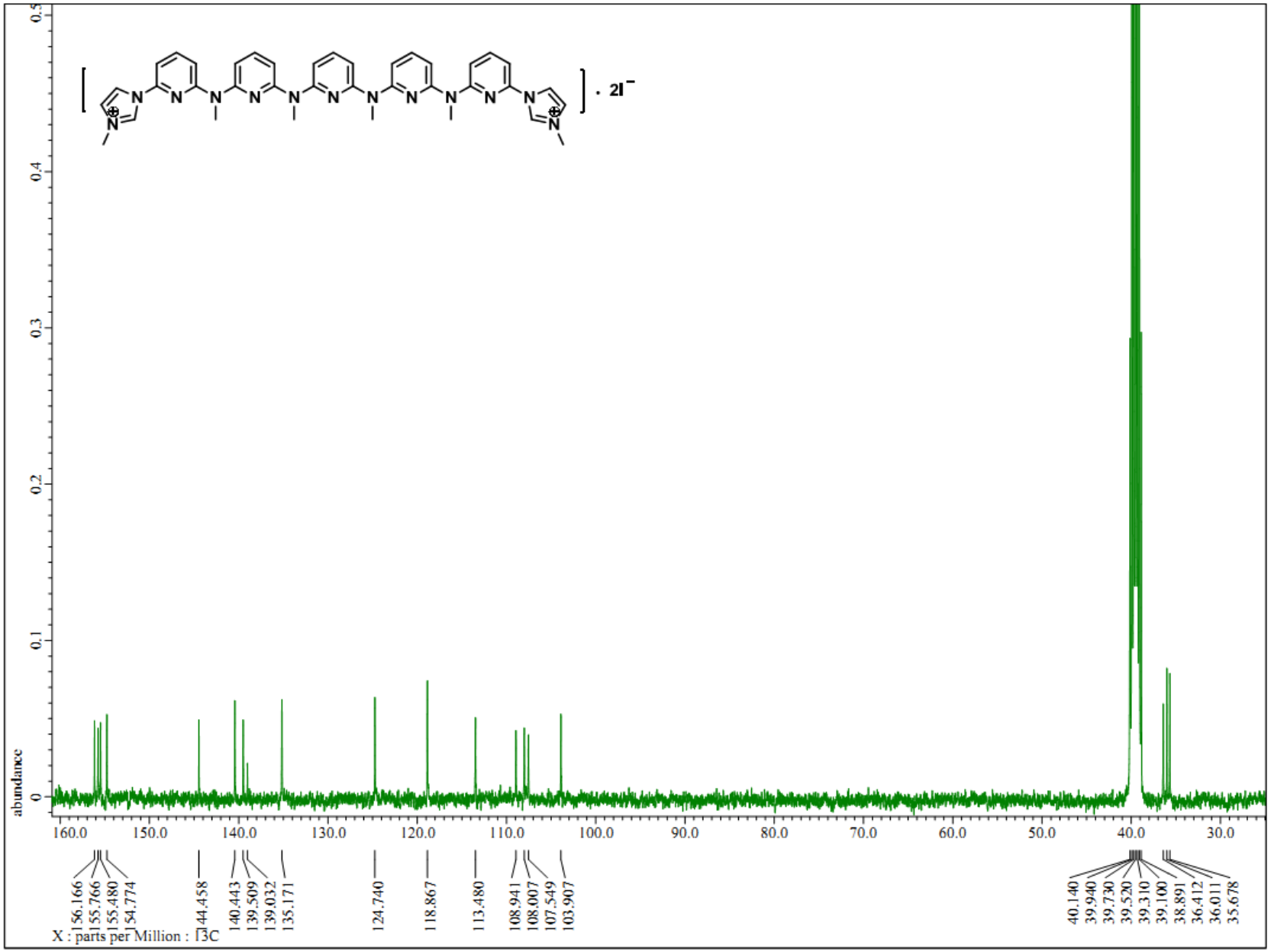
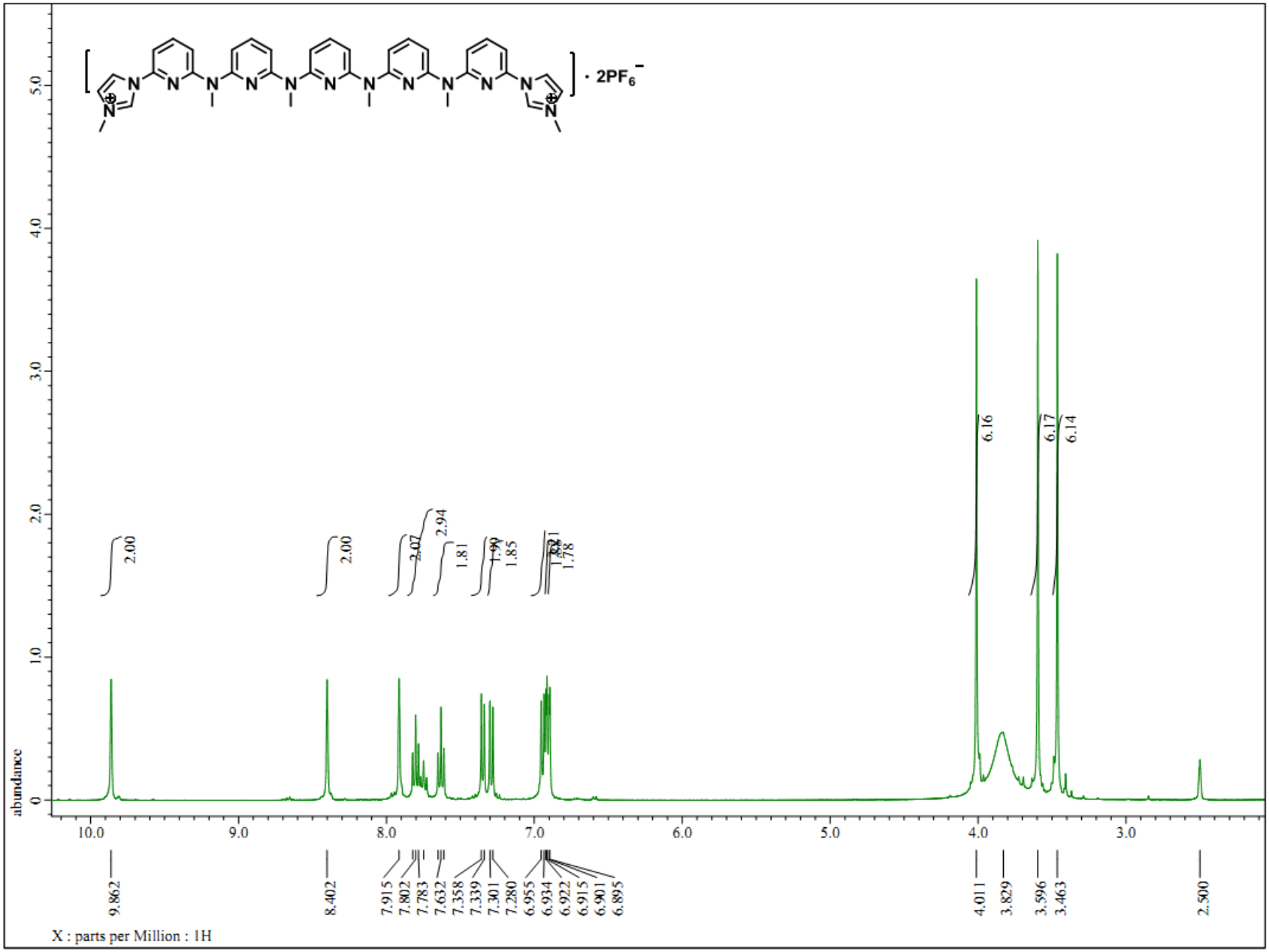
0.700
X : parts per Million : 13C
Au
Au
· 2PF6−

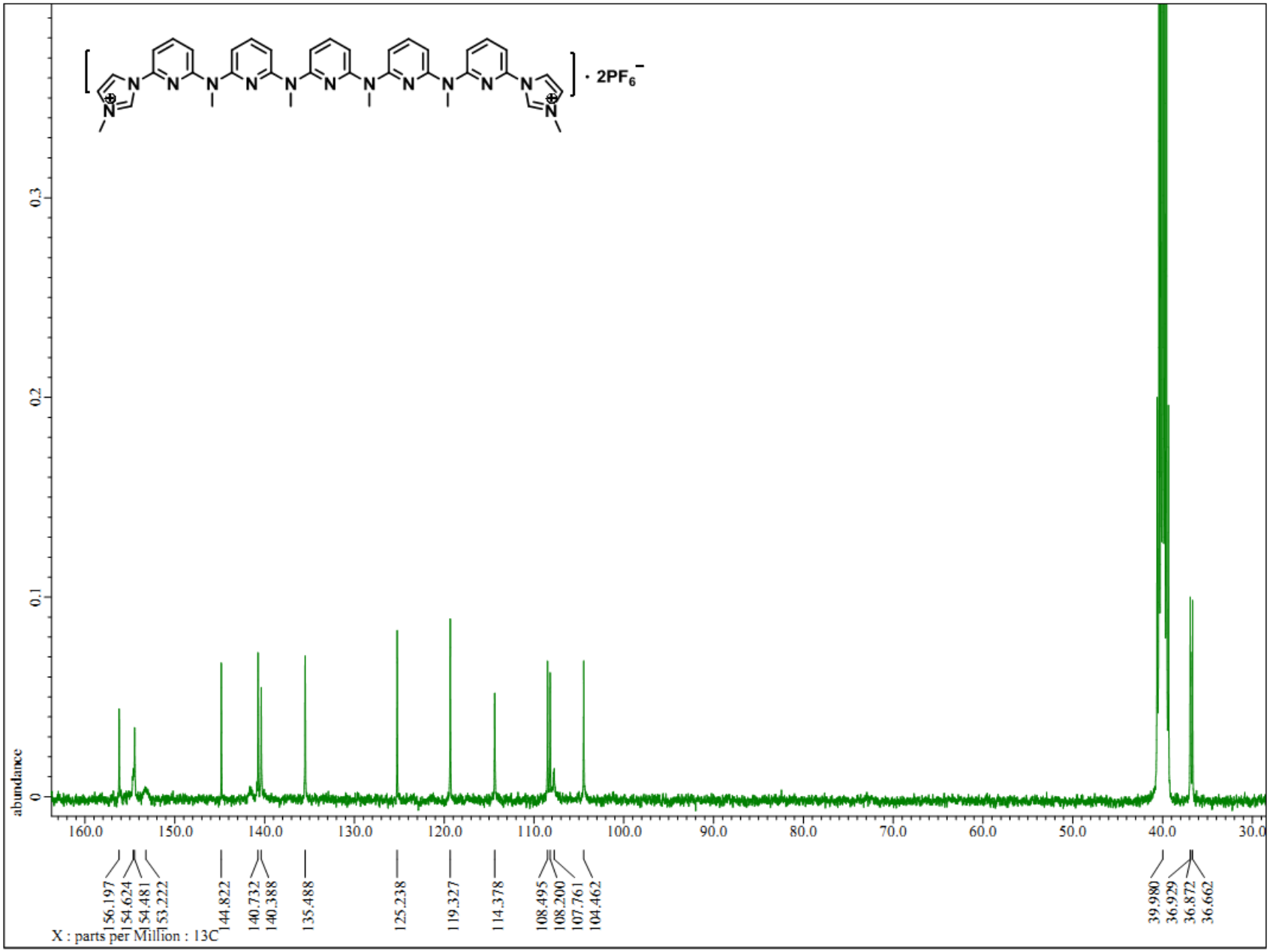


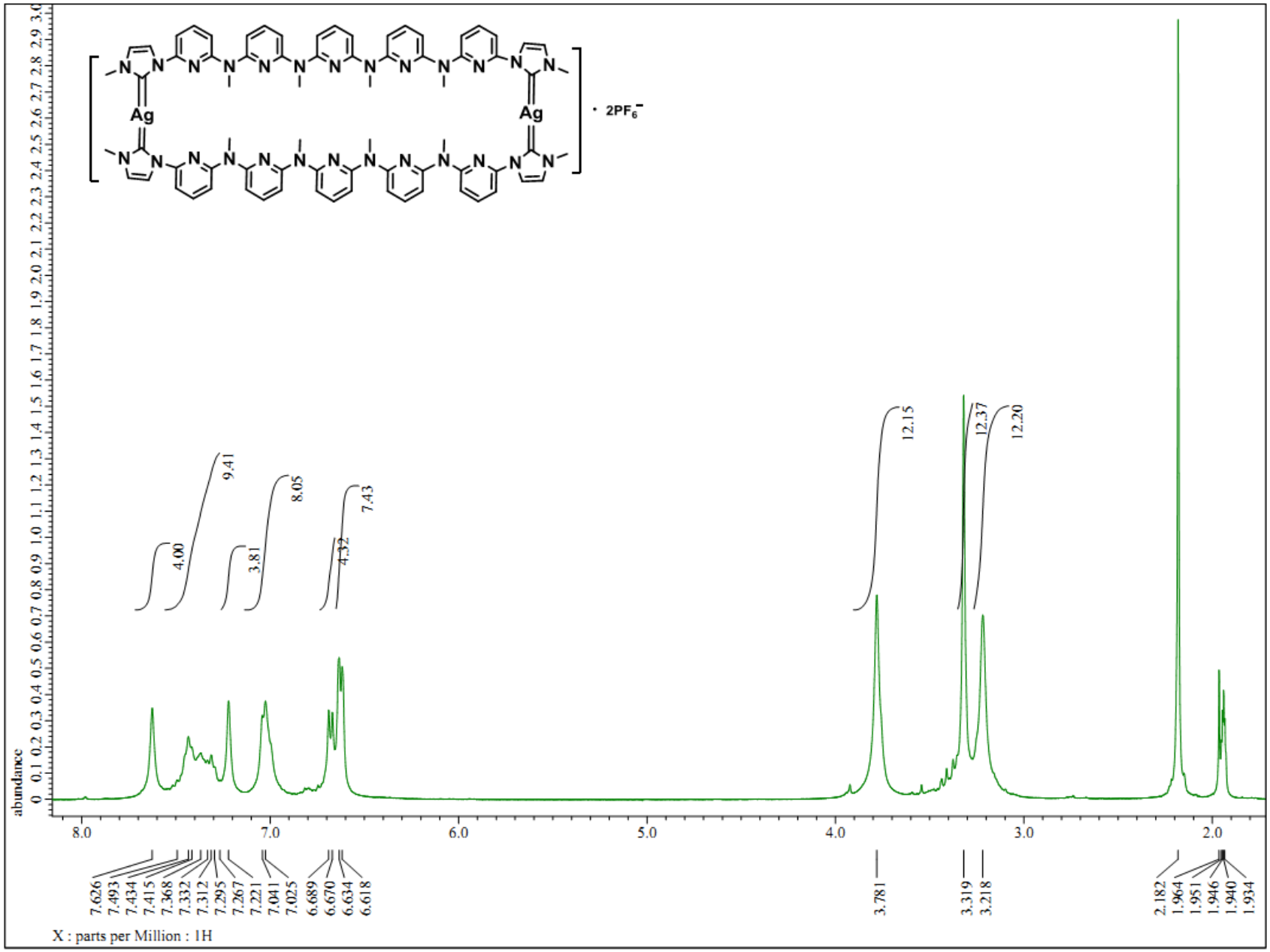


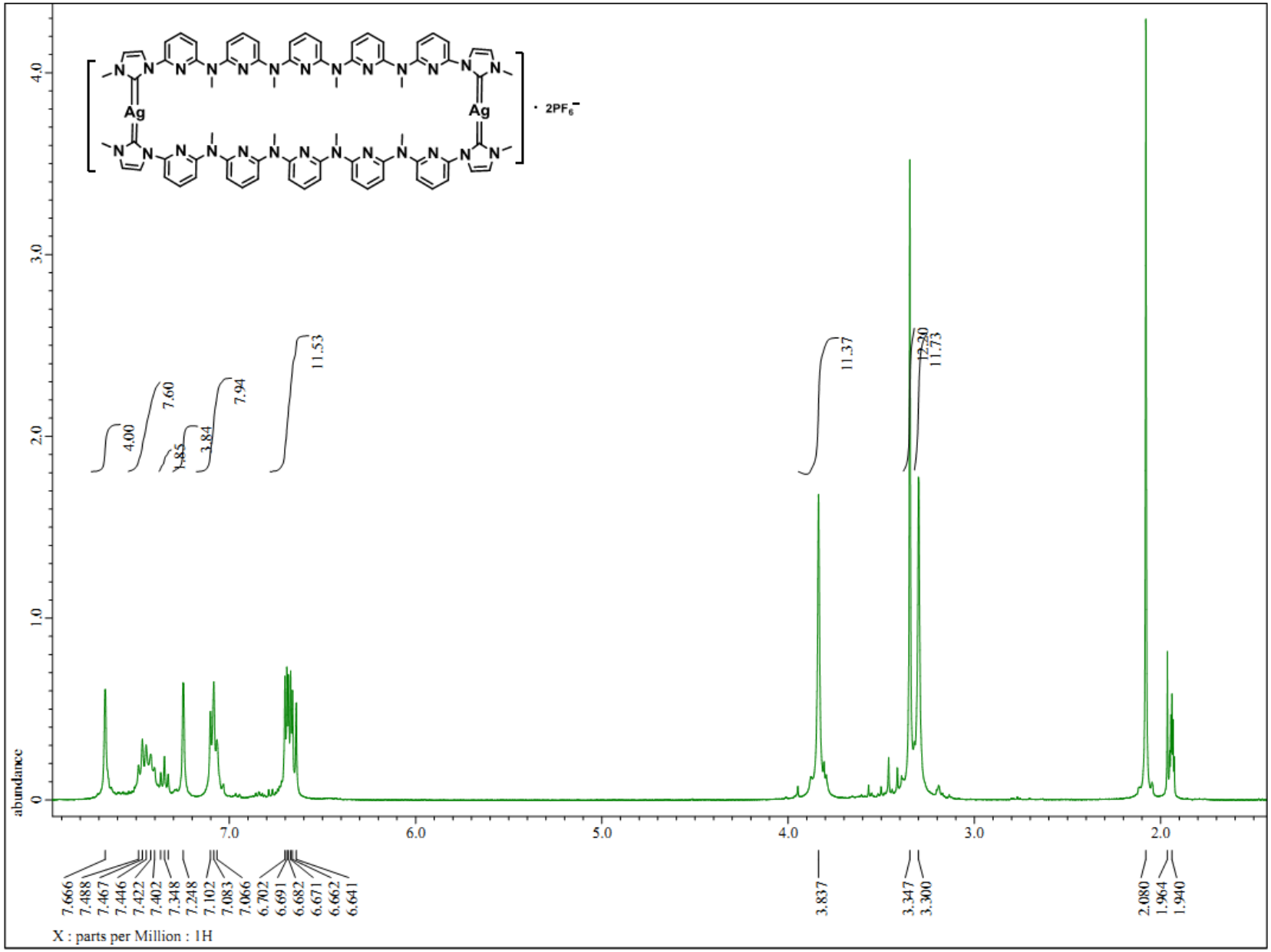


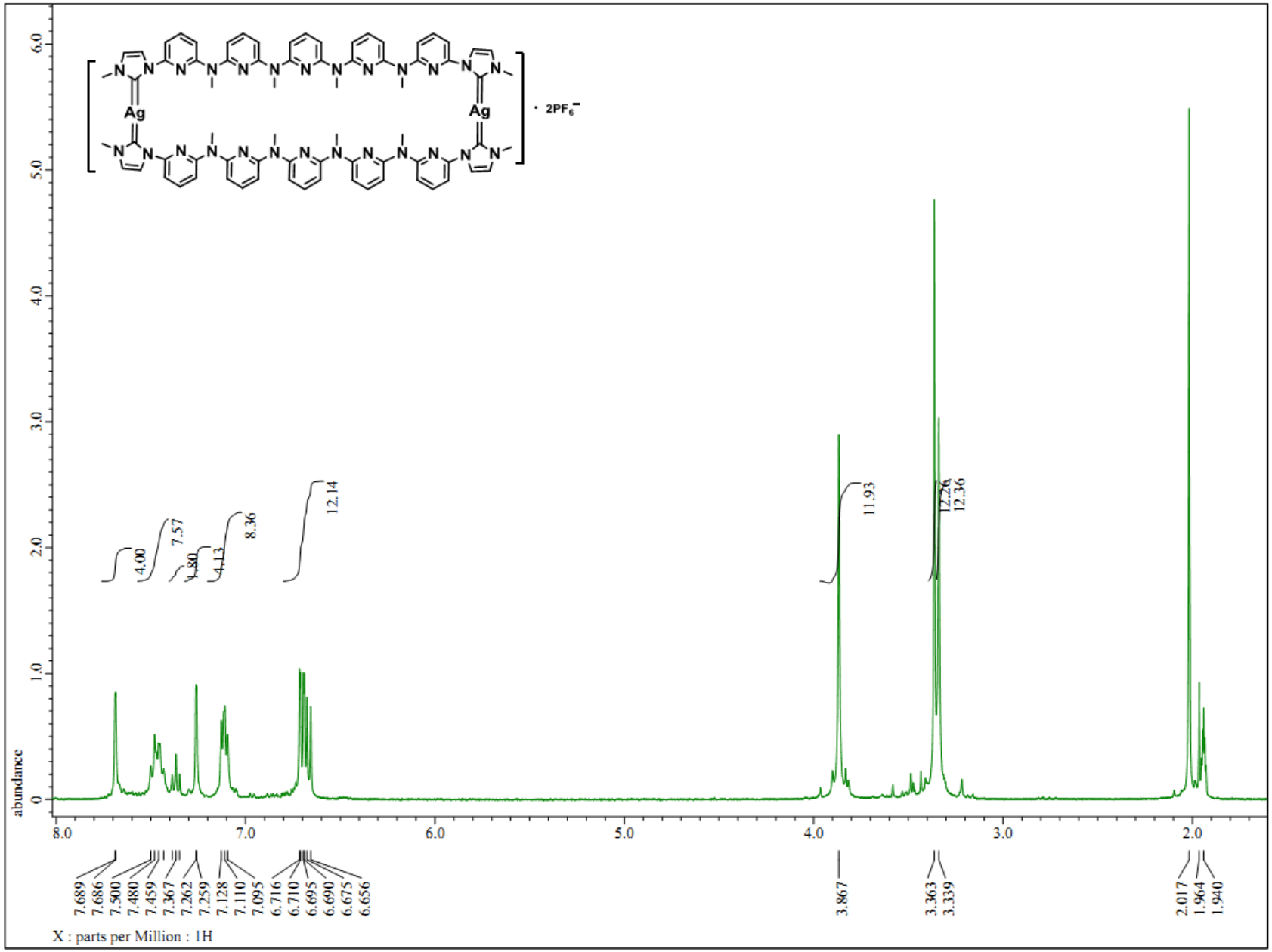


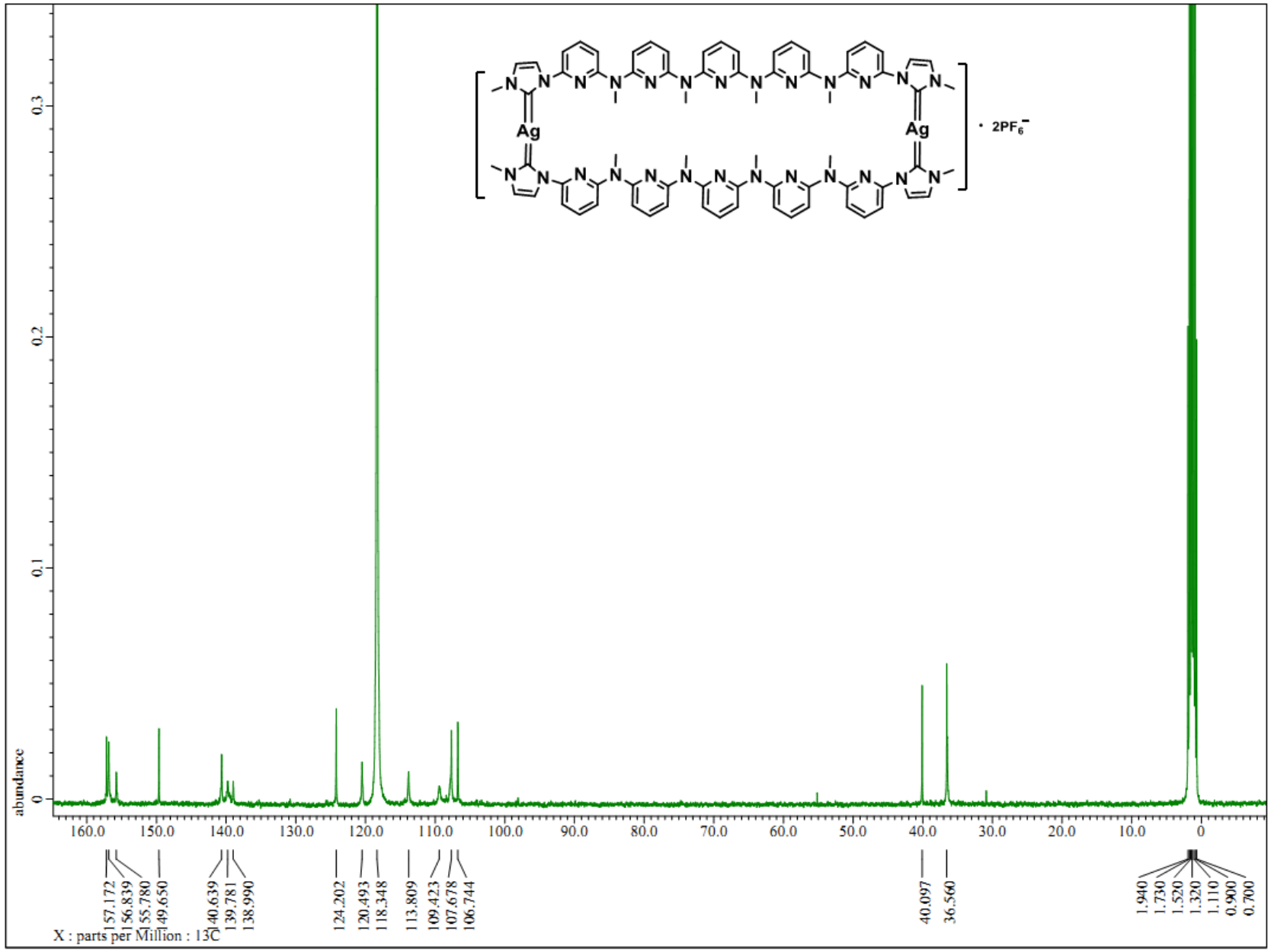











Ag
Ag
· 2PF6−
abundance
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0.2
0.3
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.172
156.839
155.780
149.650
140.639
139.781
138.990
124.202
120.493
118.348
113.809
109.423
107.678
106.744
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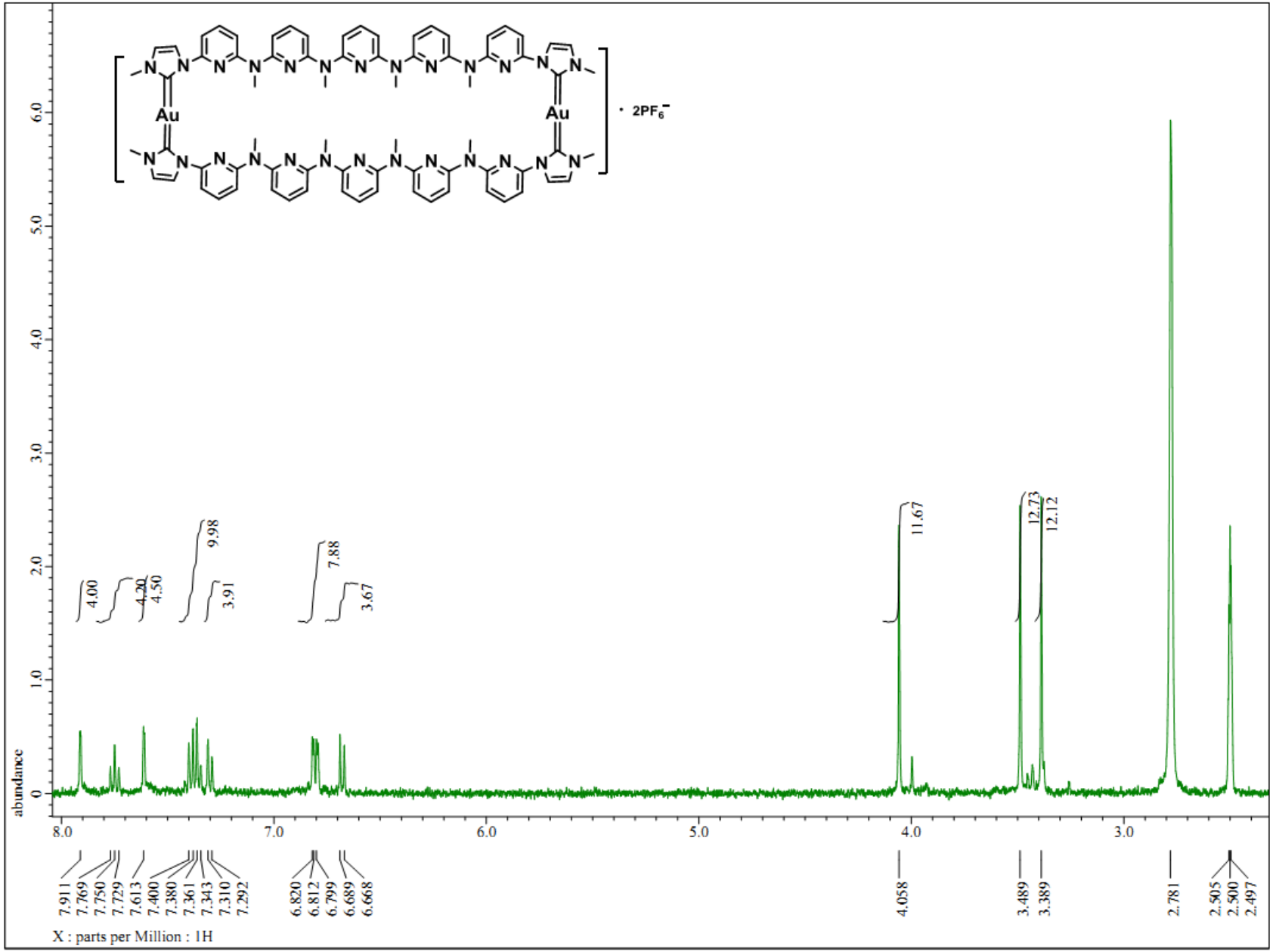
1.940
1.730
1.520
1.320
1.110
0.900
0.700
X : parts per Million : 13C


Au
Au
· 2PF6−
abundance
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2.0
3.0
4.0
5.0
6.0
8.0
7.0
6.0
5.0
4.0
3.0
4.00
4.20
4.50
9.98
3.91
7.88
3.67
11.67
12.73
12.12
7.911
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6.799
6.689
6.668
4.058
3.489
3.389
2.781
2.505
2.500
2.497
X : parts per Million : 1H