Synthesis of Six-Membered Metallodendrimers via [3+3] Coordination-Driven Self-Assembly

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General Experimental Methods

Diethylamine was distilled from sodium hydroxide and toluene was distilled from Na(s)/benzophenone. *trans*-$PtI_2(PEt_3)_2$ was prepared according to literature procedures.[1] NMR solvents (CD_2Cl_2) and all other reagents were purchased and used without further purification. The ^1H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P {1H} NMR resonance is referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0).

General procedure for the synthesis of 4a-c. To a solution of dendritic carboxylic acid (for G1, 353 mg, 1.06 mmol; for G2, 213 mg, 0.28 mmol; for G3, 246 mg, 0.153 mmol) in anhydrous dichloromethane (for G1, 5.0 ml; for G2, 3.0 ml; for G3, 2.0 ml) were added a catalytic amount (10 %) of DMAP and 3, 5-diethynyl-phenol **3** (for G1, 150 mg, 1.06 mmol; for G2, 39.8 mg, 0.28 mmol; for G3, 22 mg, 0.154 mmol). DCC (for G1, 221 mg, 1.06 mmol; for G2, 62 mg, 0.30 mmol; for G3, 33 mg, 0.16 mmol) was then added to the reaction mixture at 0 °C, followed by stirring for 5 min at 0 °C and 3 h at room temperature. Precipitated urea was then filtered off, and the filtrate was evaporated under vacuum. The residue was taken up in 25 mL of CH_2Cl_2, washed twice with 0.5N HCl and with saturated $NaHCO_3$ solution, and then dried over $MgSO_4$. The residue was purified by column chromatography on silica gel (acetone/hexane: ~1/2) to give compounds **4a-c**.

4a. Yield: 369 mg (colorless oil), 76%. ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.52 (s, 1H), 7.35-7.46 (m, 14H), 6.89 (s, 1H), 5.12 (s, 4H), 3.21 (s, 2H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 164.8, 160.5, 151.2, 137.0, 133.7, 131.4, 129.1, 128.7, 128.2, 126.5, 124.2, 109.4, 108.5, 81.6, 79.4, 70.9. HR-TOF-MS Calculated for $C_{32}H_{23}O_4$ (M+H$^+$): 459.1596, found: 459.1598.

4b. Yield: 200 mg (colorless oil), 81%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.52 (s, 1H), 7.32-7.43 (m, 24H), 6.86 (s, 1H), 6.93 (d, J = 2.1 Hz, 4H), 6.57 (s, 2H), 5.06 (s, 4H), 5.04 (s, 8H), 3.21 (s, 2H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 164.8, 160.7, 160.4, 151.2, 139.5, 137.4, 133.7, 131.4, 129.1, 128.5, 128.1, 126.5, 124.3, 109.5, 108.4, 106.9, 102.1, 82.0, 79.4, 70.7, 70.6. HR-TOF-MS Calculated for $C_{59}H_{46}O_8K$ (M+K$^+$): 921.2830, found: 921.2849.

4c. Yield: 205 mg (colorless oil), 75%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.51 (s, 1H), 7.30-7.38 (m, 44H), 6.88 (s, 1H), 6.66 (d, J = 2.1 Hz,, 12H), 6.54 (s, 6H), 4.98-5.04 (m, 28H), 3.20 (s, 2H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 164.7, 160.7, 160.4, 151.2, 139.9, 139.7, 139.5, 137.5, 133.7, 131.4, 129.1, 128.7, 128.5, 128.1, 126.5, 124.2, 109.5, 108.3, 106.8, 102.1, 101.9, 82.0, 79.4, 70.7, 70.6, 70.5. HR-TOF-MS Calculated for $C_{115}H_{94}O_{16}K$ (M+K$^+$): 1769.6179, found: 1769.6199.

General procedure for the synthesis of 5a-c. To a 50 mL round-bottom Schlenk flask were added *trans*-diiodobis(triethylphosphine)platinum (for G1, 1.76 g, 2.56 mmol; for G2, 0.54 g, 0.792 mmol; for G3, 323 mg, 0.472 mmol) and **4a-c** (**4a**, 295 mg, 0.64 mmol; **4b**, 175 mg, 0.198 mmol; **4c**, 205 mg, 0.118 mmol). Then the mixture solvent of toluene (for G1, 15 mL; for G2, 10 mL; for G3, 5 mL) and dry diethylamine (for G1, 8 mL; for G2, 6 mL; for G3, 5 mL) were added under nitrogen. The solution was stirred for 10 min at room temperature before cuprous iodide (for **4a**, 37 mg; for **4b**, 12 mg; for **4c**, 10 mg) was added in one portion. After 12 h at room temperature, a small amount of diethylammonium iodide started precipitating out of solution. The solvent was removed under vacuum and the resulting yellow residue was separated by column chromatography on silica gel with a solvent mixture of hexane/DCM (~2/1) to give the product of **5a**-**c**.

5a, Yield: 0.84 g (pale yellow solid), 83%. mp 218-219 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.32-7.46 (m, 12H), 7.09 (s, 1H), 6.88 (br, 3H), 5.12 (s, 4H), 2.18-2.23 (m, 24H), 1.10-1.21 (m, 36H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 165.3, 160.5, 151.3, 137.1, 132.1, 131.1, 130.1, 129.1, 128.7, 128.2, 121.4, 109.3, 108.1, 99.6, 92.1, 70.9, 17.1, 8.6. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 11.26 (s, $^1J_{Pt\text{-}P}$ = 2314.9 Hz). MS (ESI) *m/z*: 1573.2 $[M+H]^+$. Anal. Calcd for $C_{55}H_{80}I_2O_4P_4Pt_2$: C, 41.99; H, 5.13; Found: C, 42.18; H, 5.10.

5b, Yield: 310 mg (pale yellow solid), 79%. mp 171-172 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.32-7.43 (m, 22H), 7.10 (s, 1H), 6.89 (s, 2H), 6,85 (s, 1H), 6.69 (d, J = 2.1 Hz, 4H), 6.57 (t, J = 2.1 Hz, 2H), 5.07 (s, 4H), 5.04 (s, 8H), 2.17-2.23 (m, 24H), 1.10-1.20 (m, 36H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 165.2, 160.7, 160.4, 151.3, 139.5, 137.4, 132.1, 131.1, 130.1, 129.1, 128.5, 128.1, 121.4, 109.4, 108.0, 106.8, 102.0, 99.6, 70.6, 17.1, 8.6. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 11.37 (s, $^1J_{Pt\text{-}P}$ = 2314.9 Hz). MS (ESI) *m/z*: 1997.4 $[M+H]^+$. Anal. Calcd for $C_{83}H_{104}I_2O_8P_4Pt_2$: C, 49.91; H, 5.25; Found: C, 50.31; H, 5.45.

5c Yield: 251 mg (pale yellow glassy solid), 75%. mp 72-73 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.30-7.42 (m, 42H), 7.09 (s, 1H), 6.89 (br, 3H), 6.67 (d, J = 2.1 Hz, 12H), 6.54 (s, 6H), 4.98-5.04 (m, 28H), 2.17-2.23 (m, 24H), 1.10-1.20 (m, 36H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 165.3, 160.7, 160.5, 151.3, 139.9, 139.7, 139.5, 137.5, 132.1, 131.1, 130.1, 129.1, 128.7, 128.5, 128.1, 121.4, 109.4, 107.9, 106.8, 102.1, 101.9, 99.6, 92.2, 70.6, 70.5, 17.1, 8.6. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 11.28 (s, $^1J_{Pt\text{-}P}$= 2314.9 Hz). MS (ESI) *m/z*: 2845.7 [M+H]$^+$. Anal. Calcd for $C_{139}H_{152}I_2O_{16}P_4Pt_2$: C, 58.65; H, 5.38; Found: C, 58.31; H, 5.74.

General procedure for the synthesis of 2a-c. A 50 ml round bottom Schlenk flask was charged with 0.053 mmol diiodie complex **5a-c** (**5a**, 83 mg, 0.0528 mmol; **5b**, 106 mg, 0.0530 mmol; **5c**, 151 mg, 0.0531 mmol) and 15 ml of dichloromethane. To the solution, 30 mg (0.117 mmol) of AgOTf were added at once, resulting in a yellowish precipitate of AgI. After 4 h at room temperature the suspension was filtered through a glass fiber filter and the volume of the solution reduced to 5 ml. Subsequent addition of diethylether resulted in the precipitation of the bistriflate salt **2a**-**c**.

2a Yield: 80 mg (pale yellow solid), 93%. mp 90-91°C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.35-7.46 (m, 12H), 7.09 (br, 1H), 6.85-6,89 (m, 3H), 5.12 (s, 4H), 2.03-2.08 (m, 24H), 1.16-1.27 (m, 36H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 22.18 (s, $^1J_{Pt\text{-}P}$ = 2361.4 Hz). MS (ESI) *m/z*: 1467.4 [M-OTf]$^+$. Anal. Calcd for $C_{57}H_{80}F_6O_{10}P_4Pt_2S_2$: C, 42.33; H, 4.99; Found: C, 42.06; H, 5.08.

2b Yield: 102 mg (pale yellow glassy solid), 94%. mp 87-89°C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.32-7.43 (m, 22H), 6.95 (s, 1H), 6.85 (s, 1H), 6.83 (s, 2H), 6.69 (d, J = 2.1 Hz, 4H), 6.57 (s, 2H), 5.06 (s, 4H), 5.04 (s, 8H), 2.02-2.06 (m, 24H), 1.15-1.26 (m, 36H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 22.65 (s, $^1J_{Pt\text{-}P}$ = 2373.5 Hz). MS (ESI) *m/z*: 1891.6 [M-OTf]$^+$. Anal. Calcd for $C_{85}H_{104}F_6O_{14}P_4Pt_2S_2$: C, 50.00; H, 5.13; Found: C, 49.78; H, 5.41.

2c Yield: 144 mg (pale yellow glassy solid), 94%. mp 69-70°C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.34-7.39 (m, 42H), 6.90-6.93 (m, 4H), 6.68 (s, 12H), 6.56 (s, 6H), 4.98-5.02 (m, 28H), 2.04 (br, 24H), 1.17-1.27 (m, 36H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 22.56

(s, $^{1}J_{\mathrm{Pt\text{-}P}}$ = 2372.4 Hz). MS (ESI) *m/z*: 2739.9 $[\mathrm{M\text{-}OTf}]^{+}$. Anal. Calcd for $C_{141}H_{152}F_6O_{22}P_4Pt_2S_2$: C, 58.58; H, 5.30; Found: C, 58.39; H, 5.47.

REFERENCES.

1. Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

Figure S1. ^{1}H (A) and ^{13}C (B) NMR spectra of **4a** in CD_2Cl_2

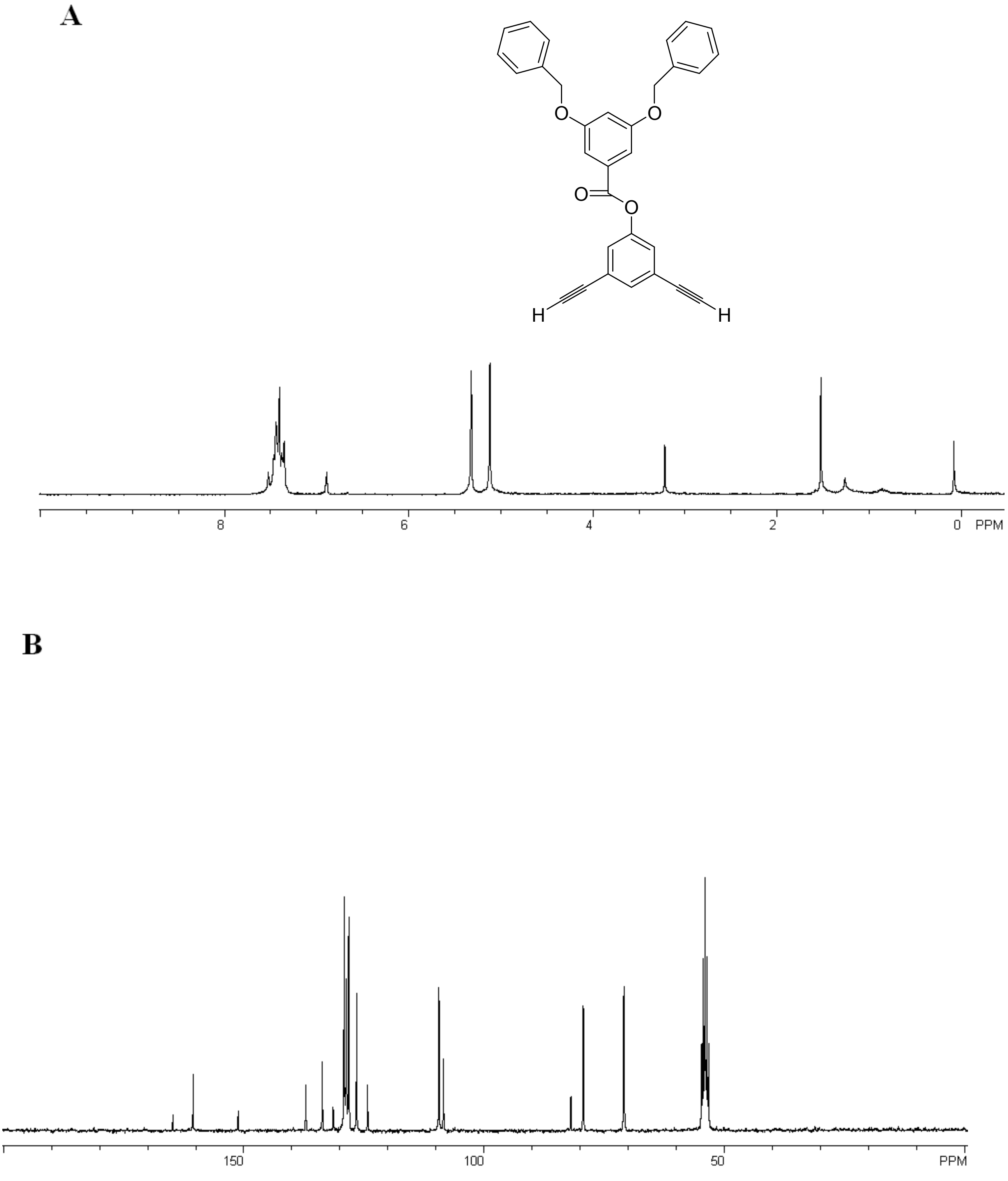
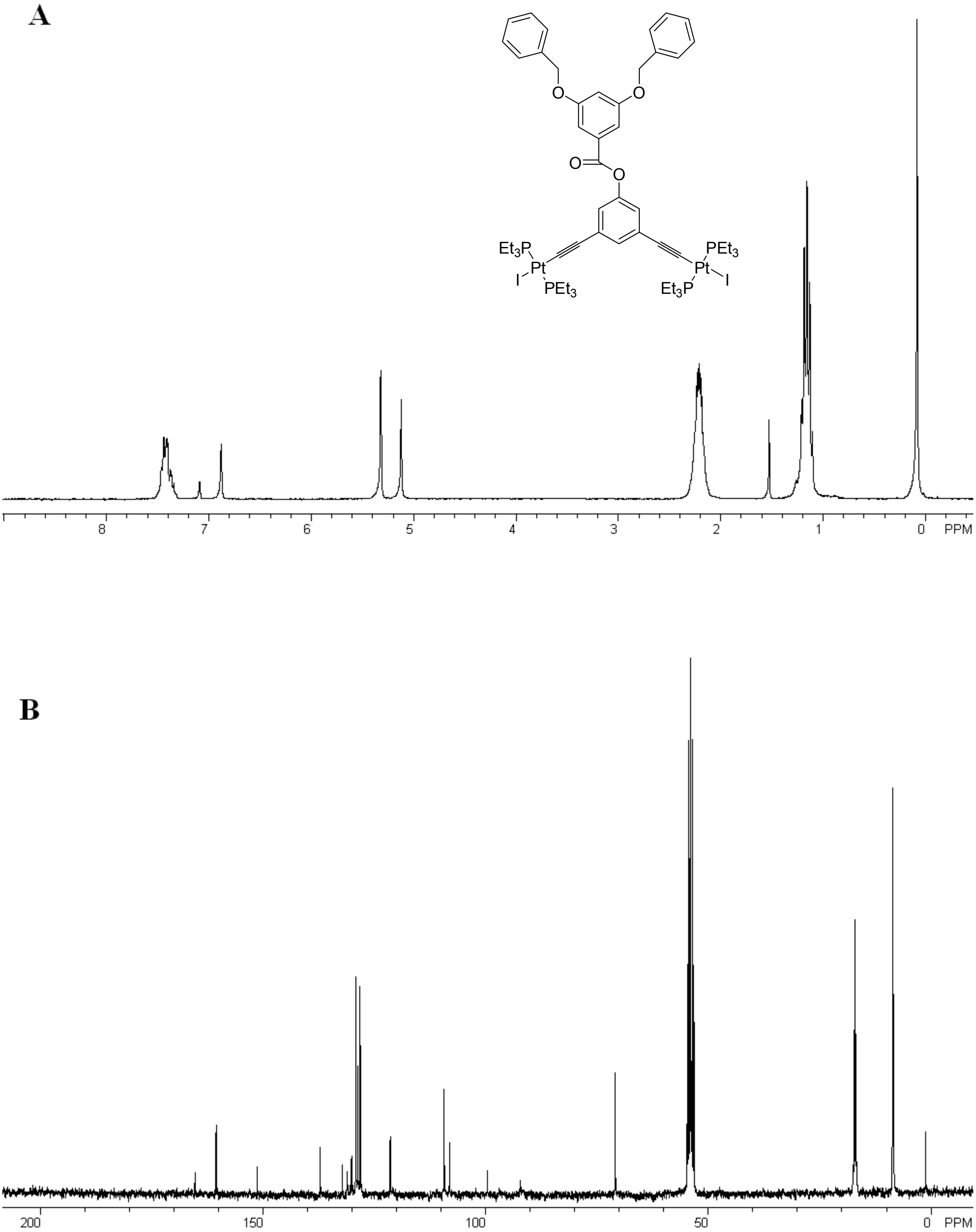


Figure S2. ^{1}H (A), ^{13}C (B), and ^{31}P(C) NMR spectra of **5a** in CD_2Cl_2



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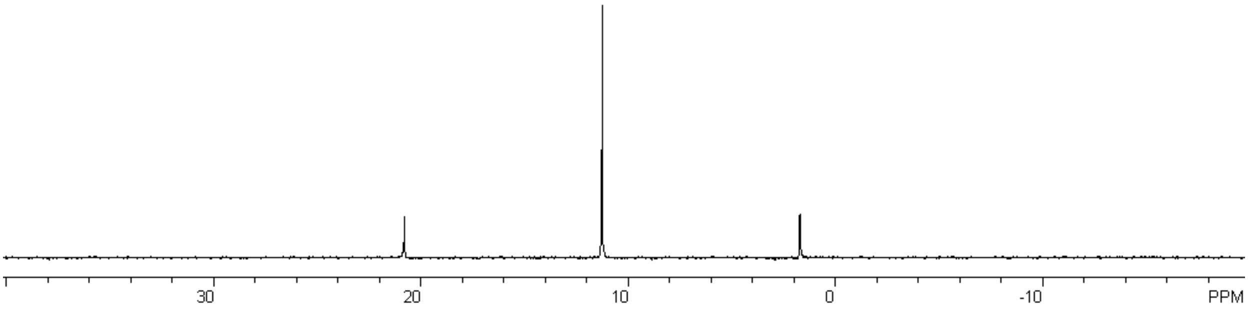


Figure S3. ^{1}H (A) and ^{31}P (B) NMR spectra of **2a** in CD_2Cl_2

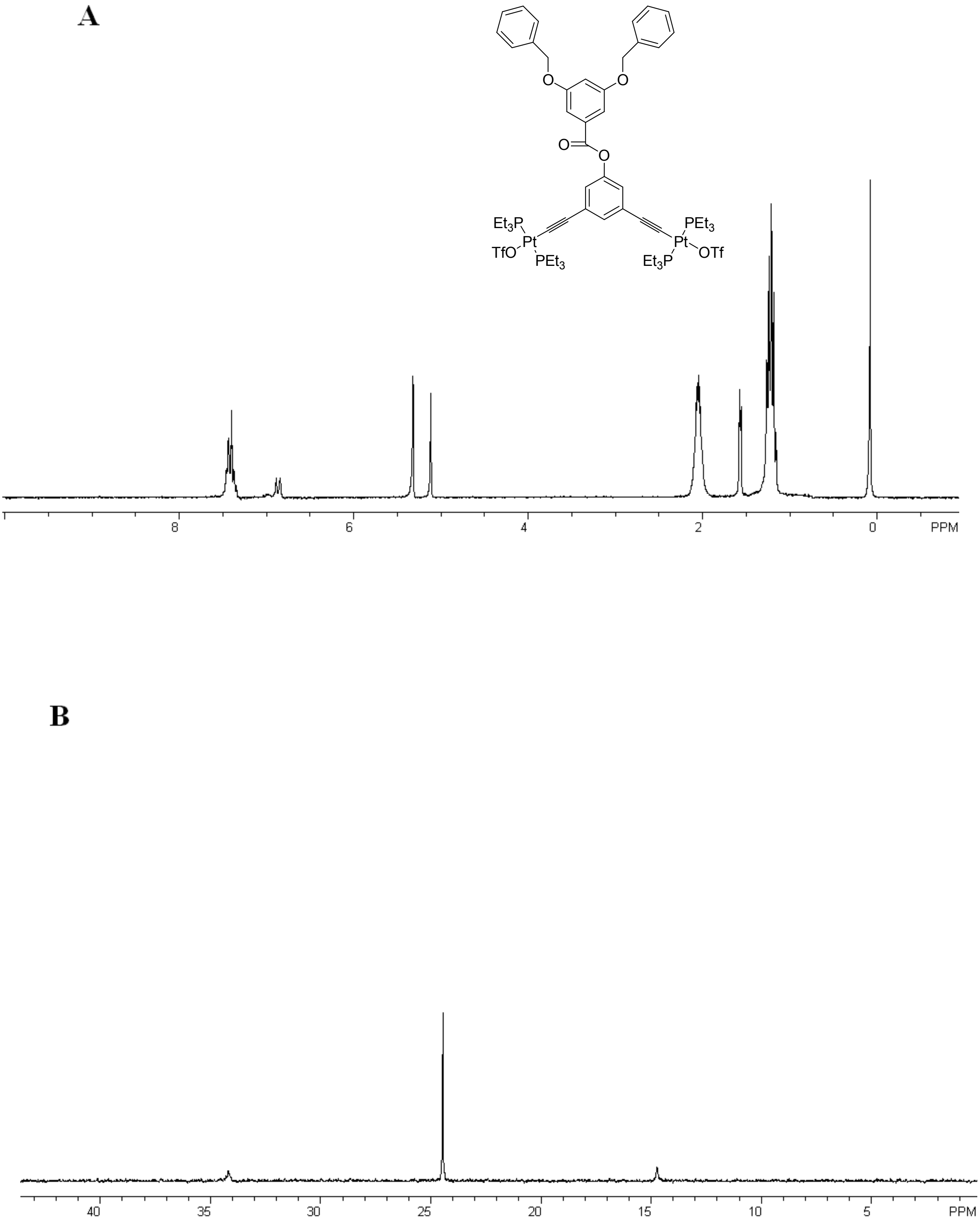


Figure S4. ^{1}H (A) and ^{13}C (B) NMR spectra of **4b** in CD_2Cl_2

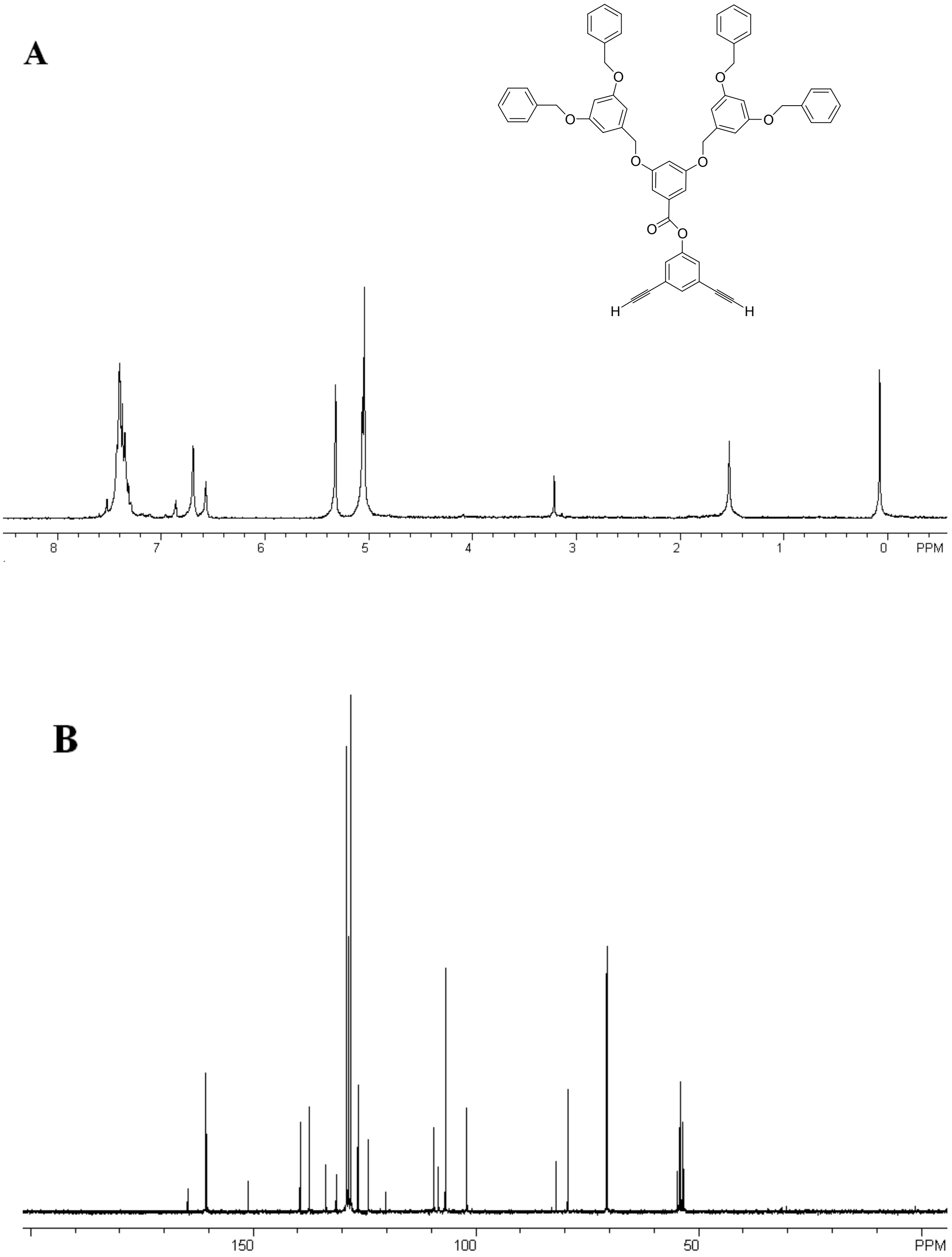
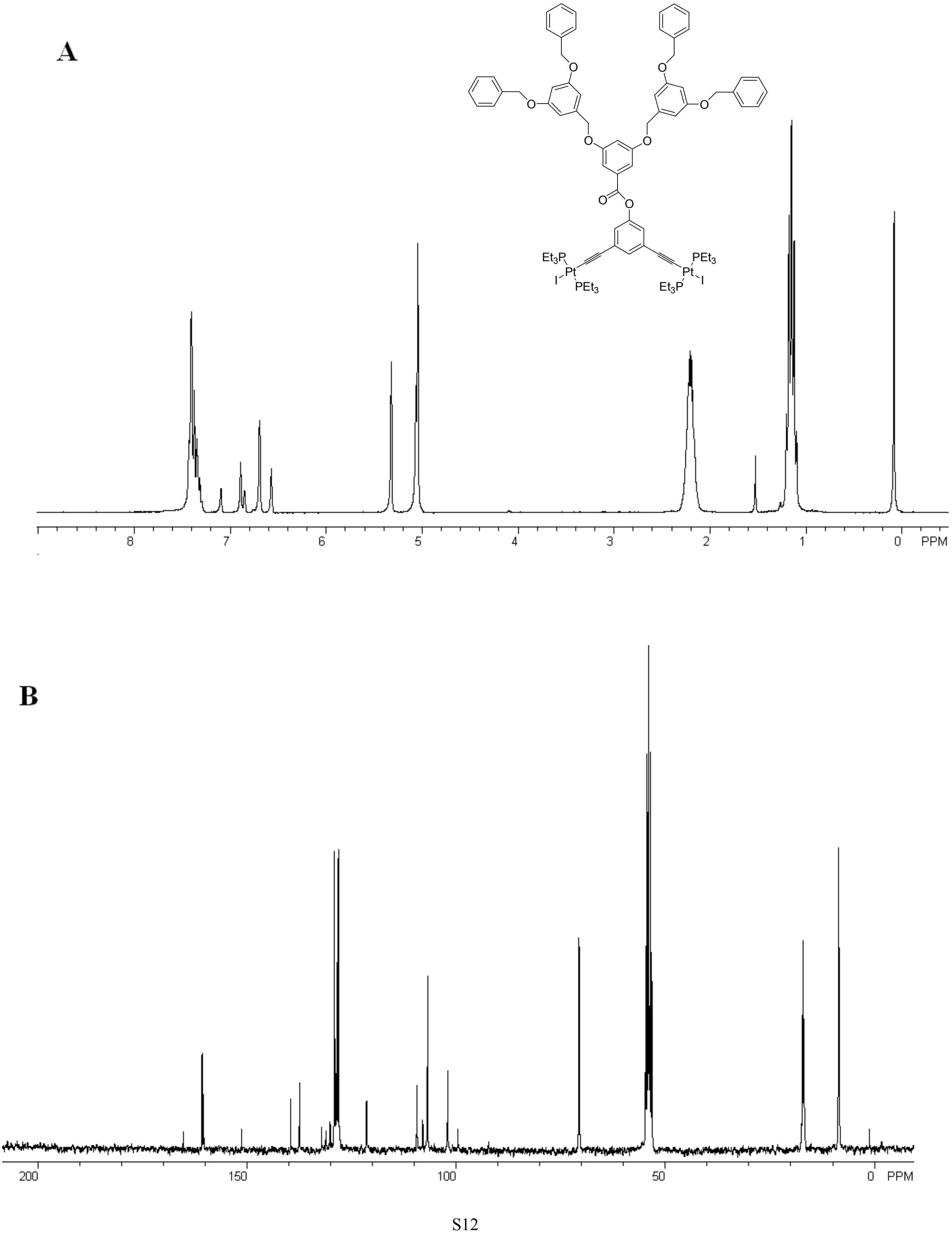


Figure S5. ^{1}H (A), ^{13}C (B), and ^{31}P(C) NMR spectra of **5b** in CD_2Cl_2



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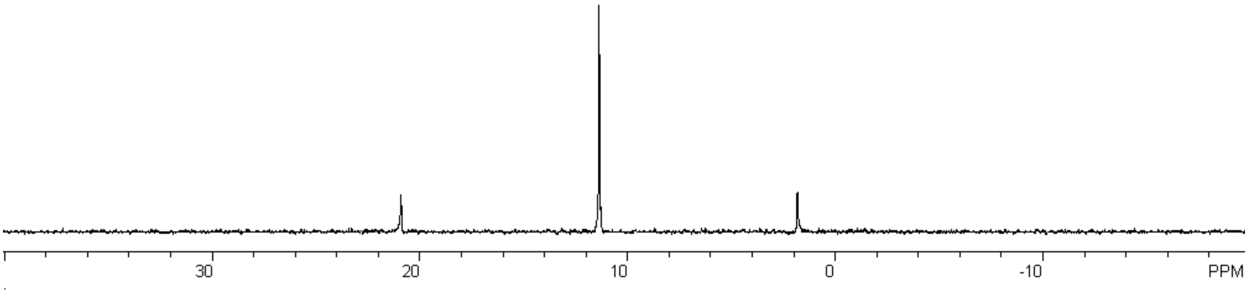


Figure S6. ^{1}H (A) and ^{31}P (B) NMR spectra of **2b** in CD_2Cl_2

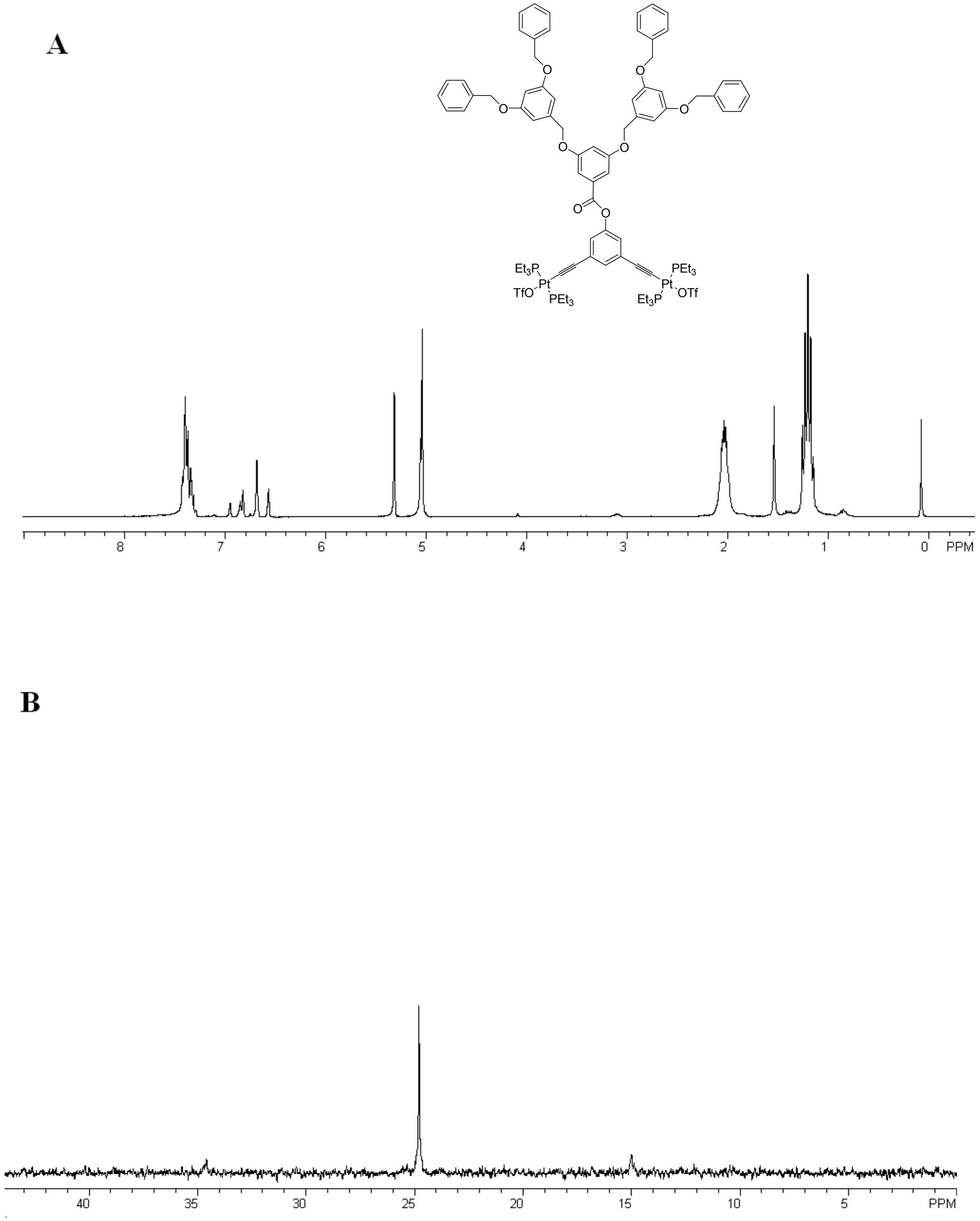


Figure S7. ^1H (A) and ^{13}C (B) NMR spectra of **4c** in CD_2Cl_2

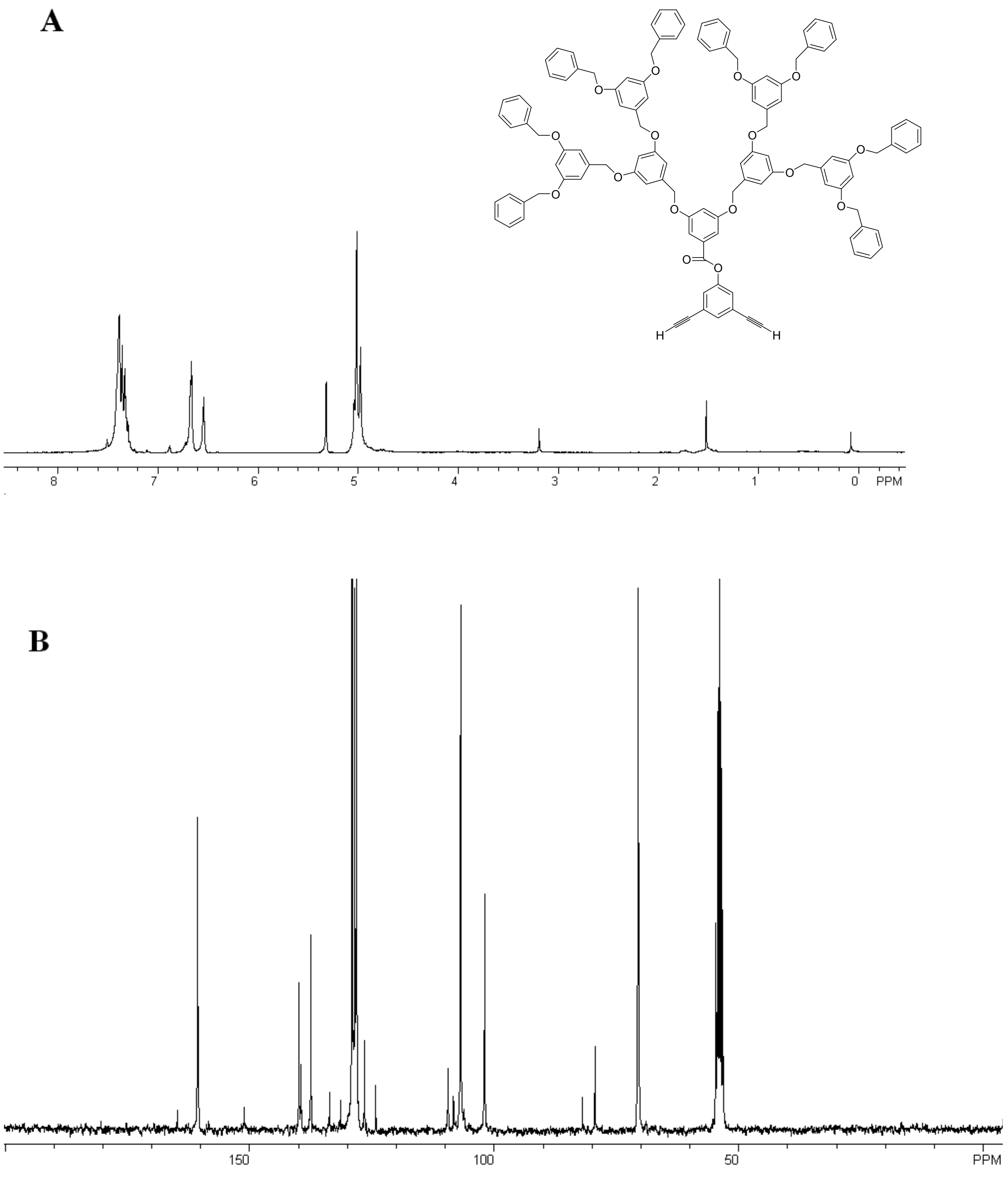
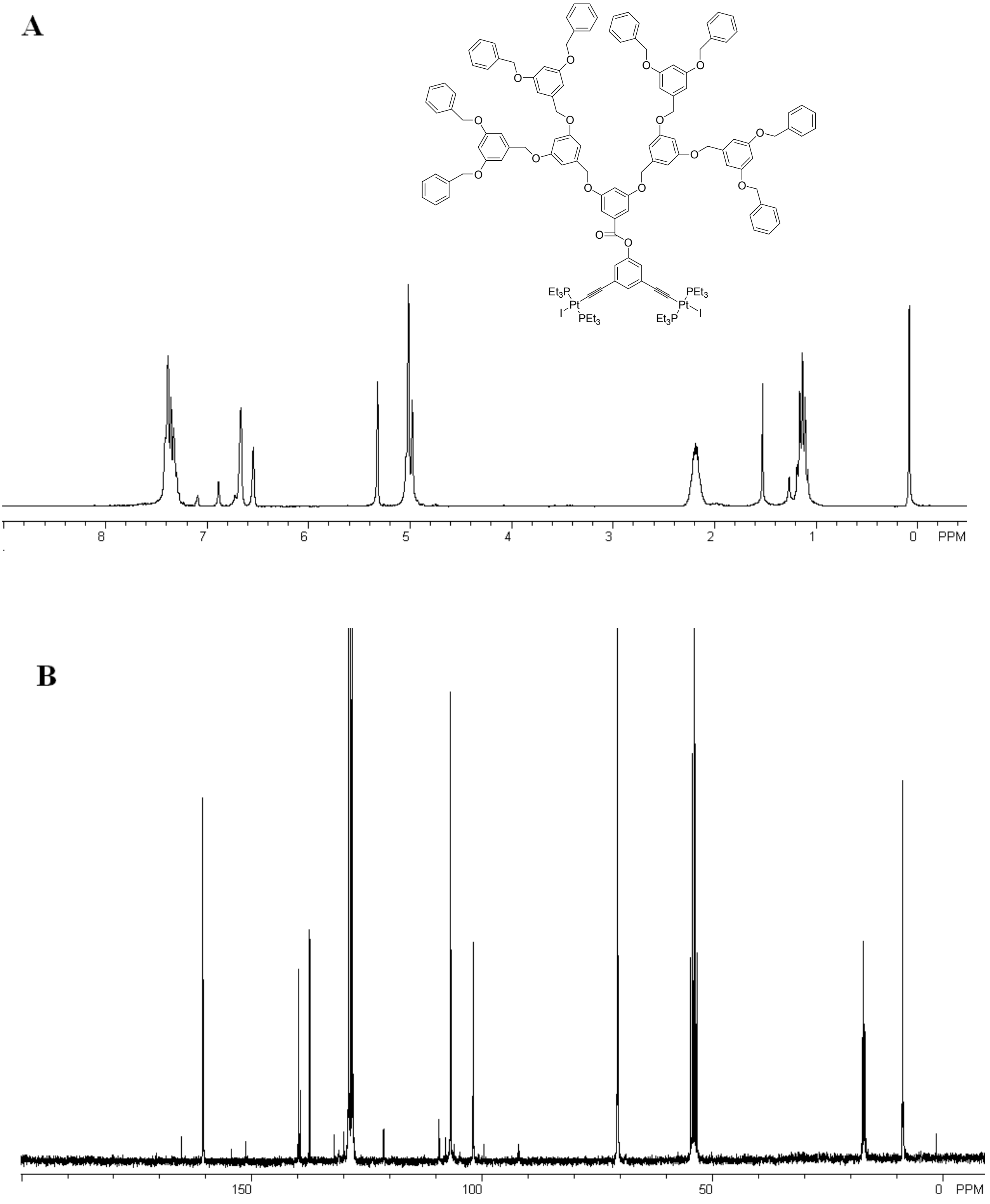


Figure S8. ^{1}H (A), ^{13}C (B), and ^{31}P(C) NMR spectra of **5c** in CD_2Cl_2



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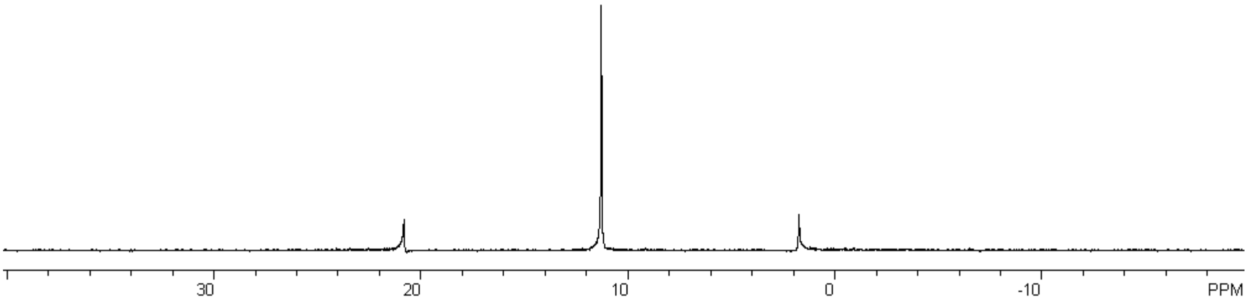
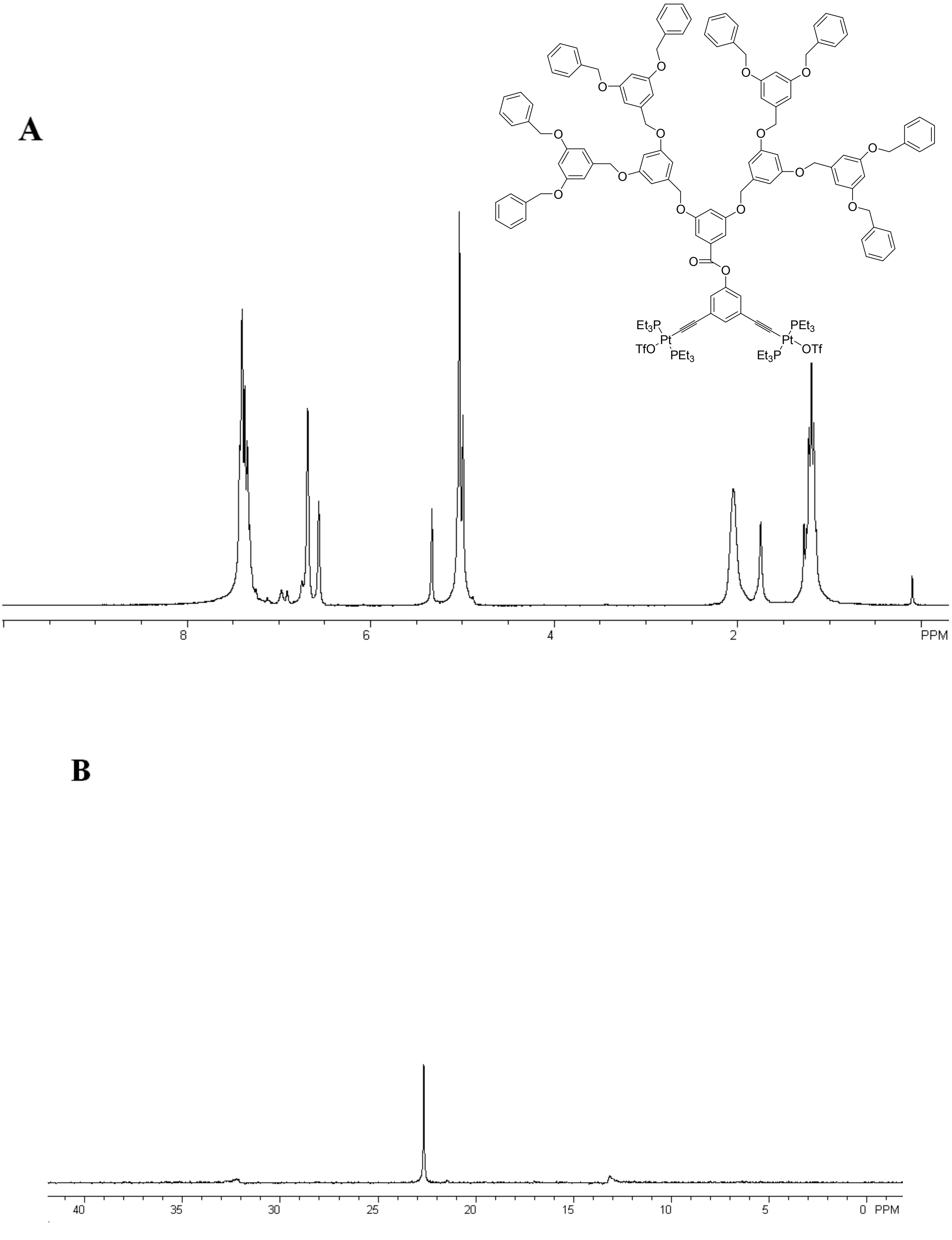
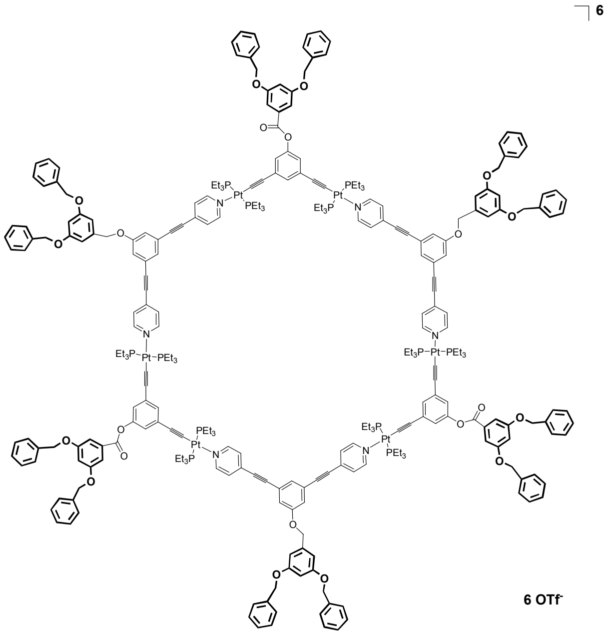


Figure S9. ^{1}H (A) and ^{31}P (B) NMR spectra of **2c** in CD_2Cl_2



(A)



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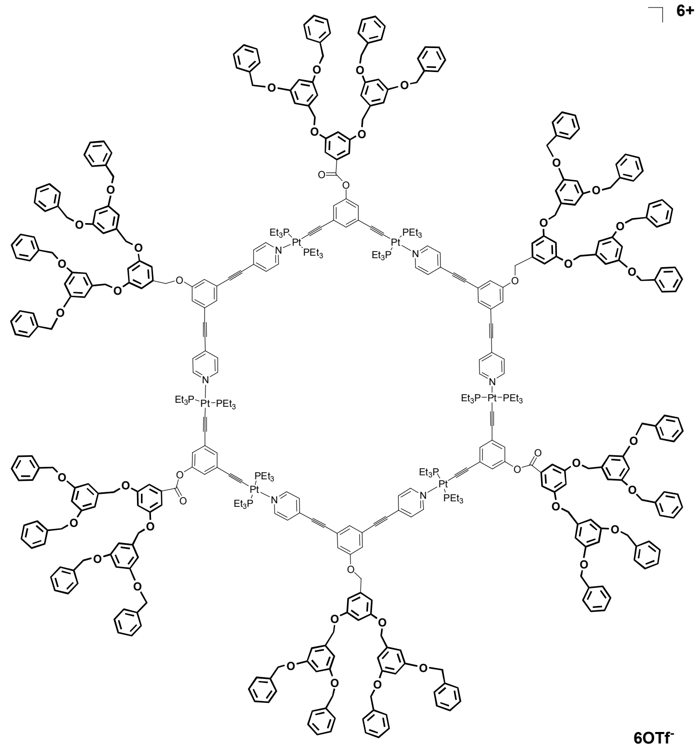


(C)

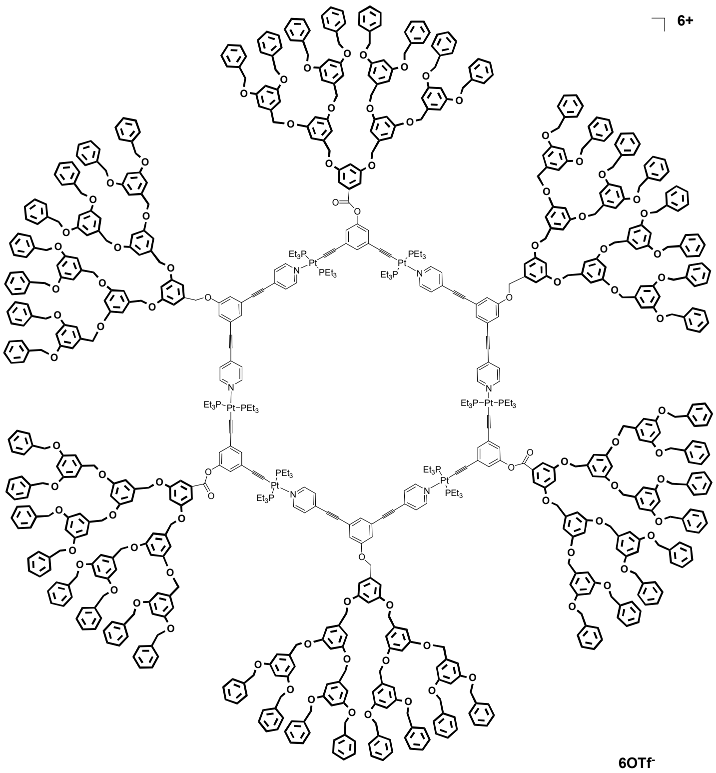
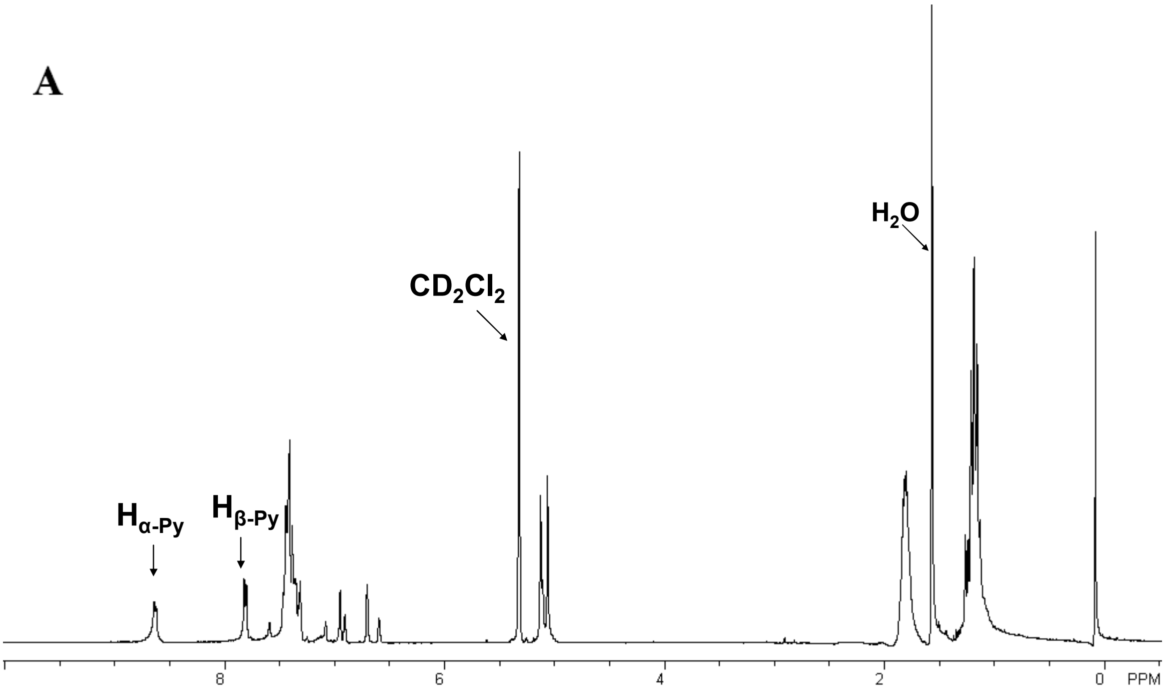


Figure S10. The molecular structure of metallodendrimers **6a**(A), **6b**(B), and **6c**(C).

Figure S11. ^{1}H (A) and ^{31}P (B) NMR spectra of **6a** in CD_2Cl_2



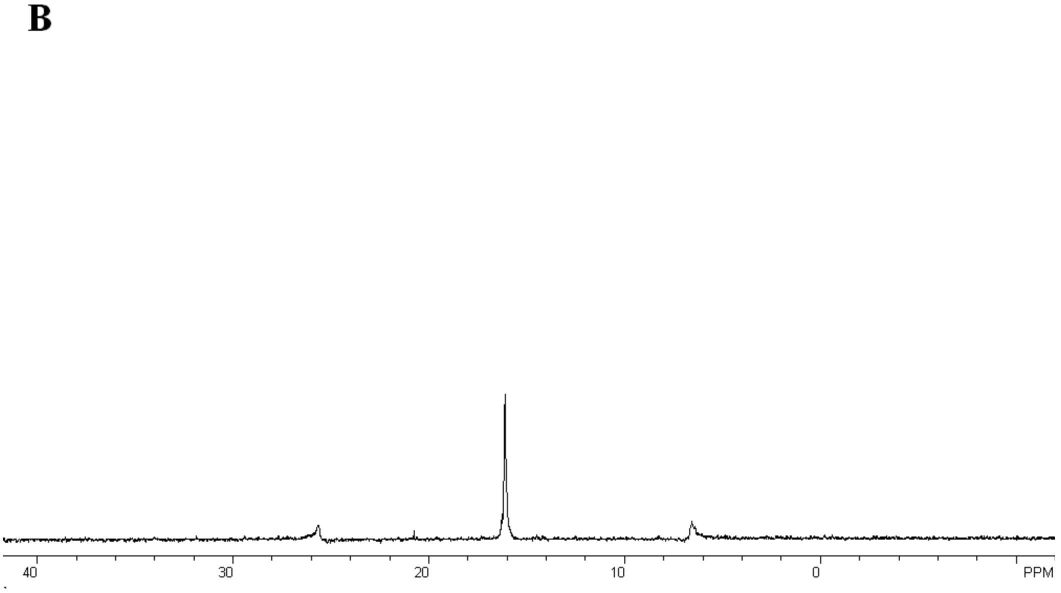


Figure S12. ^{1}H (A) and ^{31}P (B) NMR spectra of **6b** in CD_2Cl_2

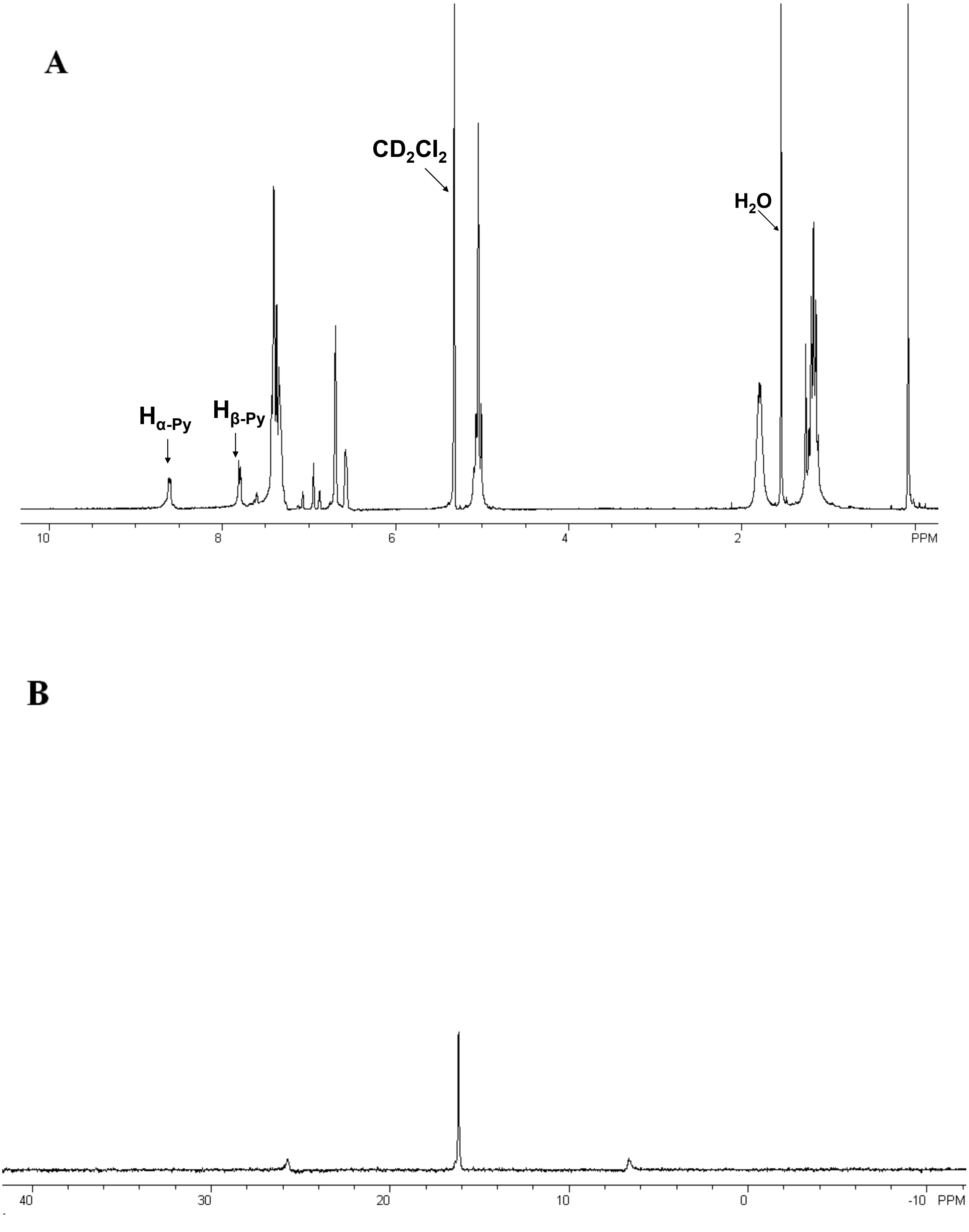
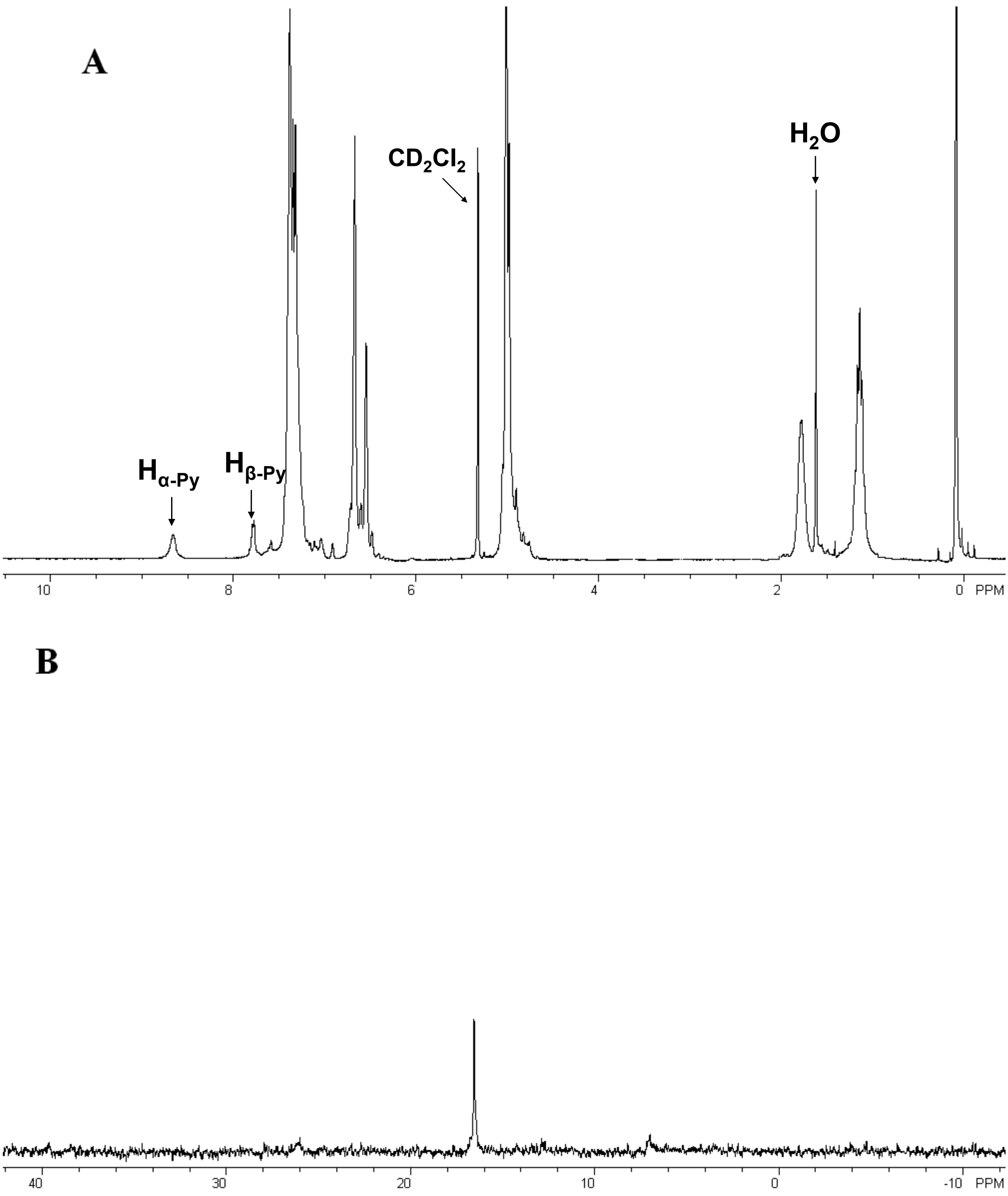


Figure S13. ^{1}H (A) and ^{31}P (B) NMR spectra of **6c** in CD_2Cl_2



General procedure for molecular modeling studies: The structures of metallodemdrimers **6a**-**c** were constructed within the input mode of the program Maestro v8.0.110. Each individual metallodendrimer was then subjected to a 1.0 ns molecular dynamics simulation (1.5 fs time step, GB/SA solvent model for CHCl3) at 300 K using the MMFF force field in order to equilibrate their structures. Upon full equilibration, the metallodendrimers were then minimized to full convergence.

Figure S14. Simulated molecular model of [G1] six-membered hexagonal metallodendrimer **6a** (hydrogen atoms have been removed for clarity). Internal radius = 1.4 nm; average outer radius = 2.6 nm.

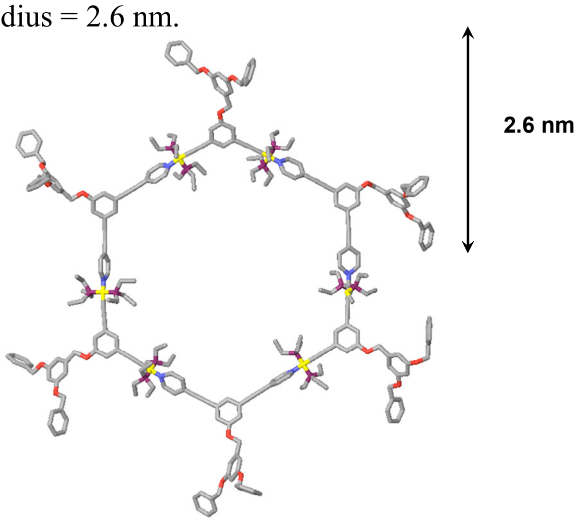


Figure S15. Simulated molecular model of [G2] six-membered hexagonal metallodendrimer **6b** (hydrogen atoms have been removed for clarity). Internal radius = 1.4 nm; average outer radius = 3.1 nm.