SUPPLEMENTARY MATERIALS FOR

Direct Observation of Bis(dicarbollyl)nickel Conformers in Solution by Fluorescence Spectroscopy: An Approach to Redox-Controlled Metallacarborane Molecular Motors

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I. Experimental part

Physical Measurements. The ^{1}H, ^{11}B, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$, [^{1}H-^{1}H] COSY and [^{1}H-$^{13}C\{^{1}H\}$] HMQC NMR spectra were measured on Bruker Avance-400 and Avance-500 NMR spectrometers. Boron NMR spectra were referenced to 15% $BF_3{\cdot}Et_2O$ in $CDCl_3$. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the residual solvent peak. Chemical shifts are reported in ppm and coupling constants in hertz. Mass spectra were obtained on an ABI QSTAR and Mariner Biospectrometry Workstation by PerSeptive Biosystems.

Materials. All reactions were carried out in an argon atmosphere using standard Schlenk-line techniques. Thallium dicarbollide was ($Tl_2C_2B_9H_{11}$) prepared according to the published procedure[1] and dried in an Abderhalden apparatus using methanol as a jacket heater prior to use. 1-Pyrenebutanol, 1-bromopyrene, tetrabromomethane (CBr_4), triphenylphosphine (PPh_3), *n*-buthyl lithium (BuLi, 2.5 M solution in hexane), lithium chloride (LiCl), copper(II) chloride ($CuCl_2$), dibromoborane-dimethylsulfide complex ($HBBr_2{\cdot}Me_2S$,1 M solution in DCM), boron trichloride (BCl_3, 1 M solution in heptane), allylmagnesium bromide (1 M solution in diethyl ether) and nickel acetylacetonate [$Ni(acac)_2$] were purchased from Aldrich. Potassium *tert*-butoxide (*t*BuOK) was purchased from Fluka. Tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] was purchased from Strem Chemicals. Triphenylmethylphosphonium bromide was purchased from Alfa Aesar. Tetrabutylammonium fluoride (TBAF) was purchased from TCI America as a 1 M solution in THF and used as received. THF was distilled in an argon atmosphere from sodium benzophenone ketyl before use. Dichloromethane (DCM) and chloroform ($CHCl_3$) were freshly distilled in an argon atmosphere over calcium hydride prior to use. Ethyl acetate (EtOAc) was purchased from VWR and used for chromatography separations without purification. Column chromatography was performed in air using Merck silica gel (63-200 mesh). Thin-layer chromatography was run on Merck precoated glass plates (silica 60 F_{254}) using a palladium stain solution for spot developing. Signals marked with an asterisk (*) in the $^{13}C\{^{1}H\}$ NMR of compounds **2b** and **14** are partially overlapped with the residual solvent signal.

Synthesis of substituted pyrenes

1-Allylpyrene (4). To a mixture of 1-bromopyrene (**3**, 1.00 g, 3.55 mmol) and $Pd(PPh_3)_4$ (0.205 g, 0.177 mmol) in 20 mL of THF was added 5.33 mL (5.33 mmol) of 1 M solution of allylmagnesium bromide in diethyl ether and the reaction mixture was heated at reflux temperature for 20 h (TLC control of the starting material **3**). After cooling, the reaction mixture was quenched by water (2 mL) and extracted with EtOAc (3×15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The compound was purified by column chromatography on silica gel in hexane. After evaporation and drying in vacuum the compound **4** was obtained as a pale yellow oil (0.700 g, 80%). ^1H and ^{13}C NMR spectra correspond to the published in literature.[2]

4-(Pyren-1-yl)butanal (6). Solid of 1-pyrenebutanol (**5**, 1.00 g, 3.64 mmol) was rapidly added to a suspension of pyridinium chlorochromate (1.17 g, 5.40 mmol) in 25 mL of DCM at room temperature during 3 h (TLC control). The reaction mixture was decanted, and the residue was washed with DCM, and the combined DCM extracts were evaporated. The compound was purified by column chromatography on silica gel using EtOAc gradient (0→10%) in hexane. After drying in vacuum, the compound **6** was isolated as a pale yellow crystalline solid (0.740 g, 73%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.80 (t, 1H, CHO), 8.29 (d, 1H, CH_{pyr}), 8.18–8.16 (m, 2H, CH_{pyr}), 8.13–8.10 (m, 2H, CH_{pyr}), 8.03 (m, 2H, CH_{pyr}), 7.99 (t, 1H, CH_{pyr}), 7.85 (d, 1H, CH_{pyr}), 3.39 (m, 2H, CH_2), 2.57 (td, 2H, CH_2), 2.20 (m, 2H, CH_2). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$): δ 202.44 (C=O), 135.84, 131.78, 131.24, 130.41, 129.10, 127.84, 127.82, 127.65, 127.14, 126.24, 125.49, 125.33, 125.17, 123.55 (C_{pyr}), 43.81 (CH_2–C=O), 32.97 (CH_2–C_{pyr}), 24.36 (CH_2). HRMS (APCI): *m/z* = 273.1043 $[M+H]^-$ (calcd for $C_{20}H_{16}O$ 272.1201).

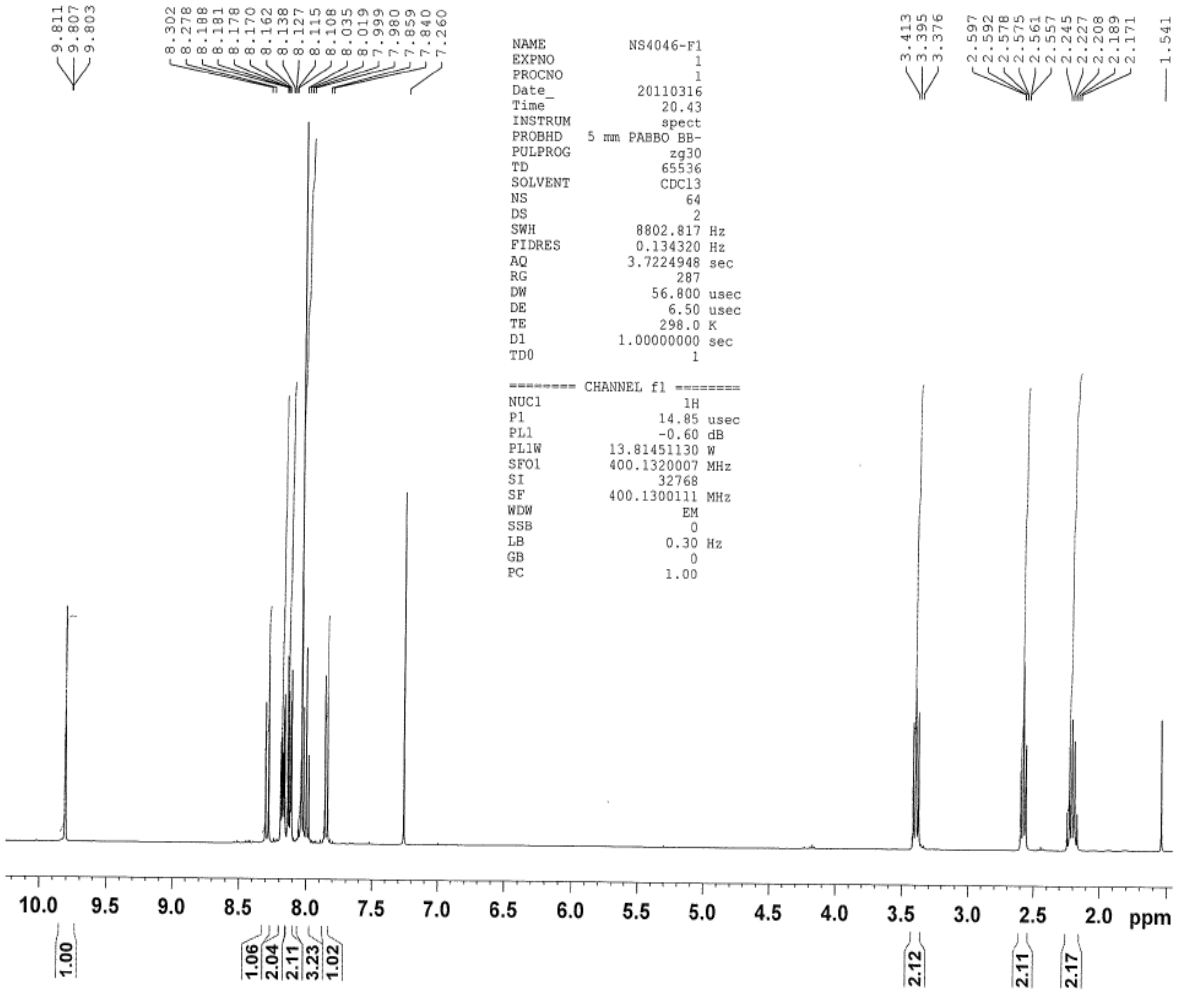
1-(Pent-4-en-1-yl)pyrene (7). To a cooled (–70 °C) suspension of triphenylmethylphosphonium bromide (1.28 g, 3.58 mmol) in 15 mL of anhydrous THF was added 1.43 mL (3.58 mmol) of BuLi solution. The reaction mixture was stirred at –70 °C for 15 min and then 1h at room temperature. A solution of **6** (0.890 g, 3.26 mmol) in 7 mL of anhydrous THF was added via syringe to the formed methylenetriphenylphosphorane at –70 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The reaction mixture was quenched with water and extracted with EtOAc (3×15 mL). The combined organic extracts were dried over Na_2SO_4, evaporated and purified by column chromatography in hexane. The compound **7** was obtained after evaporation and drying in vacuum as a pale yellow

oil (0.730 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, 1H, CH_{pyr}), 8.18-8.16 (m, 2H, CH_{pyr}), 8.13-8.10 (m, 2H, CH_{pyr}), 8.03 (m, 2H, CH_{pyr}), 8.00 (t, 1H, CH_{pyr}), 7.89 (d, 1H, CH_{pyr}), 5.95 (m, 1H, –CH=), 5.12 (m, 2H, CH_2=), 3.37 (m, 2H, CH_2), 2.27 (m, 2H, CH_2), 1.99 (m, 2H, CH_2). ^{13}C{^{1}H} (100 MHz, $CDCl_3$): δ 138.8, 137.1, 131.8, 131.2, 130.1, 128.9, 127.8, 127.6, 127.4, 126.8, 126.1, 125.46, 125.41, 125.15, 125.11, 124.9, 123.7, 115.3, 34.1, 33.2, 31.3. HRMS (APCI): *m/z* = 271.1166 $[M+H]^-$ (calcd for $C_{21}H_{18}$ 270.1408).

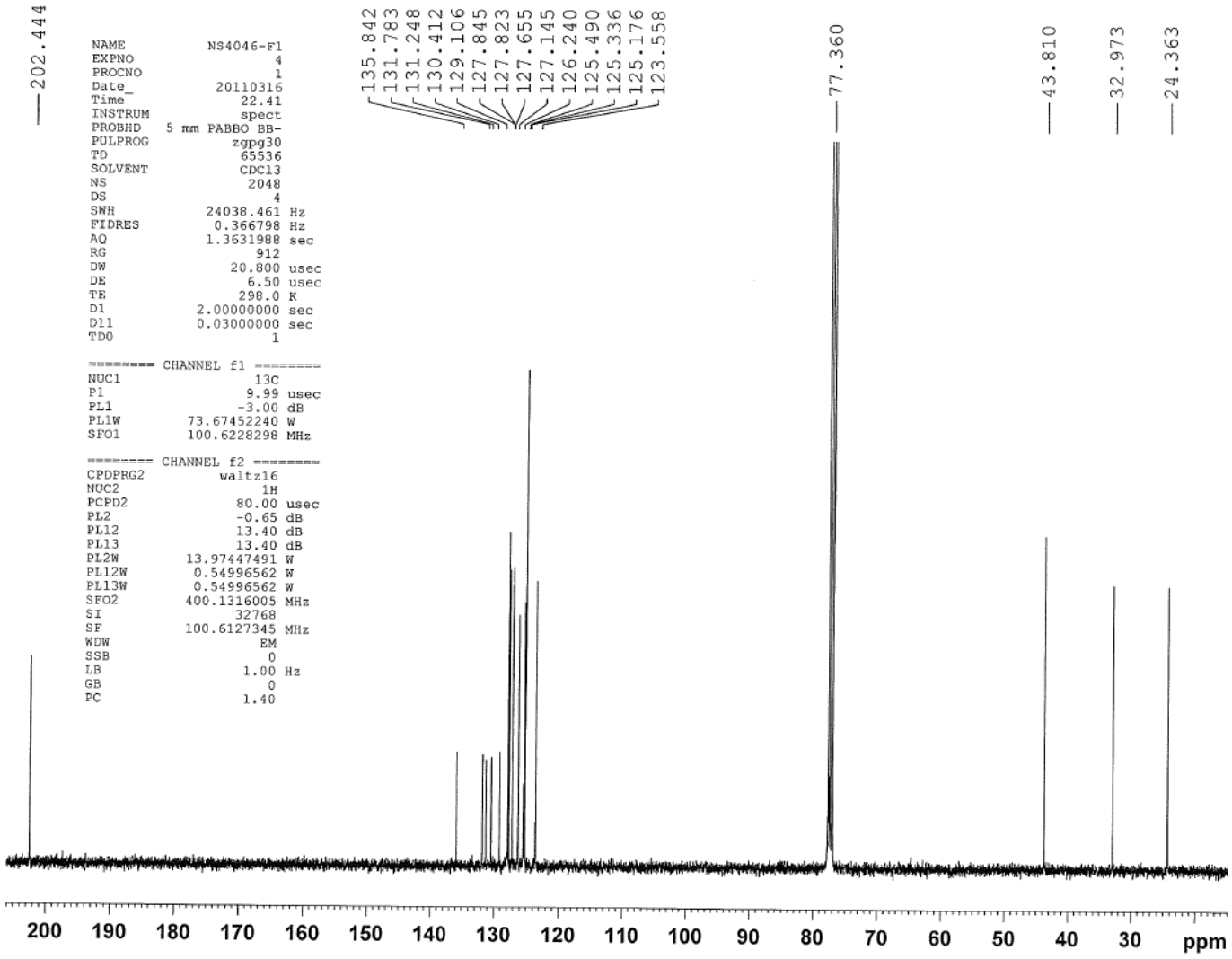
1-(4-Bromobutyl)pyrene (8). A solution of PPh_3 (1.43 g, 5.47 mmol) in 5 mL of DCM was slowly added dropwise to a solution of 1-pyrenebutanol (**5**, 0.500 g, 1.82 mmol) and CBr_4 (1.21 g, 3.64 mmol) in 8 mL of anhydrous DCM on an ice bath. The reaction mixture was stirred at room temperature for 3 h; then it was filtered on a glass frit and evaporated. The product was isolated by column chromatography on silica gel using $CHCl_3$ gradient (0→10%) in hexane. The compound **8** was obtained after evaporation and drying in vacuum as a greenish-brown crystalline solid (0.500 g, 80%). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **6** correspond to the published data.[3]

1-(Hept-6-en-1-yl)pyrene (9). A mixture of anhydrous LiCl (0.0180 g, 0.420 mmol) and anhydrous $CuCl_2$ (0.0290 g, 0.210 mmol) was dissolved in 2 mL of anhydrous THF and stirred at room temperature for 1 h. The formed solution of Li_2CuCl_4 was cooled to 0 °C and a solution of **8** (0.490 g, 1.44 mmol) in 10 mL of anhydrous THF was added dropwise. The formed reaction mixture was cooled to –20 °C, and 4.32 mL (4.32 mmol) of 1M solution of allylmagnesium bromide in diethyl ether was added. The reaction mixture was stirred for 2 h at –20 °C and then 18 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc (3×5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated. Flash chromatography in hexane and further recrystallization of the material from hexane gave **9** as a pale yellow crystalline solid (260 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, 1H, CH_{pyr}), 8.17-8.14 (m, 2H, CH_{pyr}), 8.12-8.09 (m, 2H, CH_{pyr}), 8.03 (m, 2H, CH_{pyr}), 7.98 (t, 1H, CH_{pyr}), 7.87 (d, 1H, CH_{pyr}), 5.83 (m, 1H, –CH=), 4.99 (m, 2H, CH_2=), 3.34 (m, 2H, CH_2), 2.08 (m, 2H, CH_2), 1.87 (m, 2H, CH_2), 1.50 (m, 4H, CH_2). ^{13}C{^{1}H} (100 MHz, $CDCl_3$): δ 139.3, 137.5, 131.8, 131.3, 130.1, 128.9, 127.8, 127.5, 127.4, 126.8, 126.1, 125.47, 125.45, 125.1, 124.9, 123.8, 114.6, 34.1, 33.9, 32.1, 29.6, 29.2. HRMS (APCI): *m/z* = 299.0931 $[M+H]^-$ (calcd for $C_{23}H_{22}$ 298.1721).

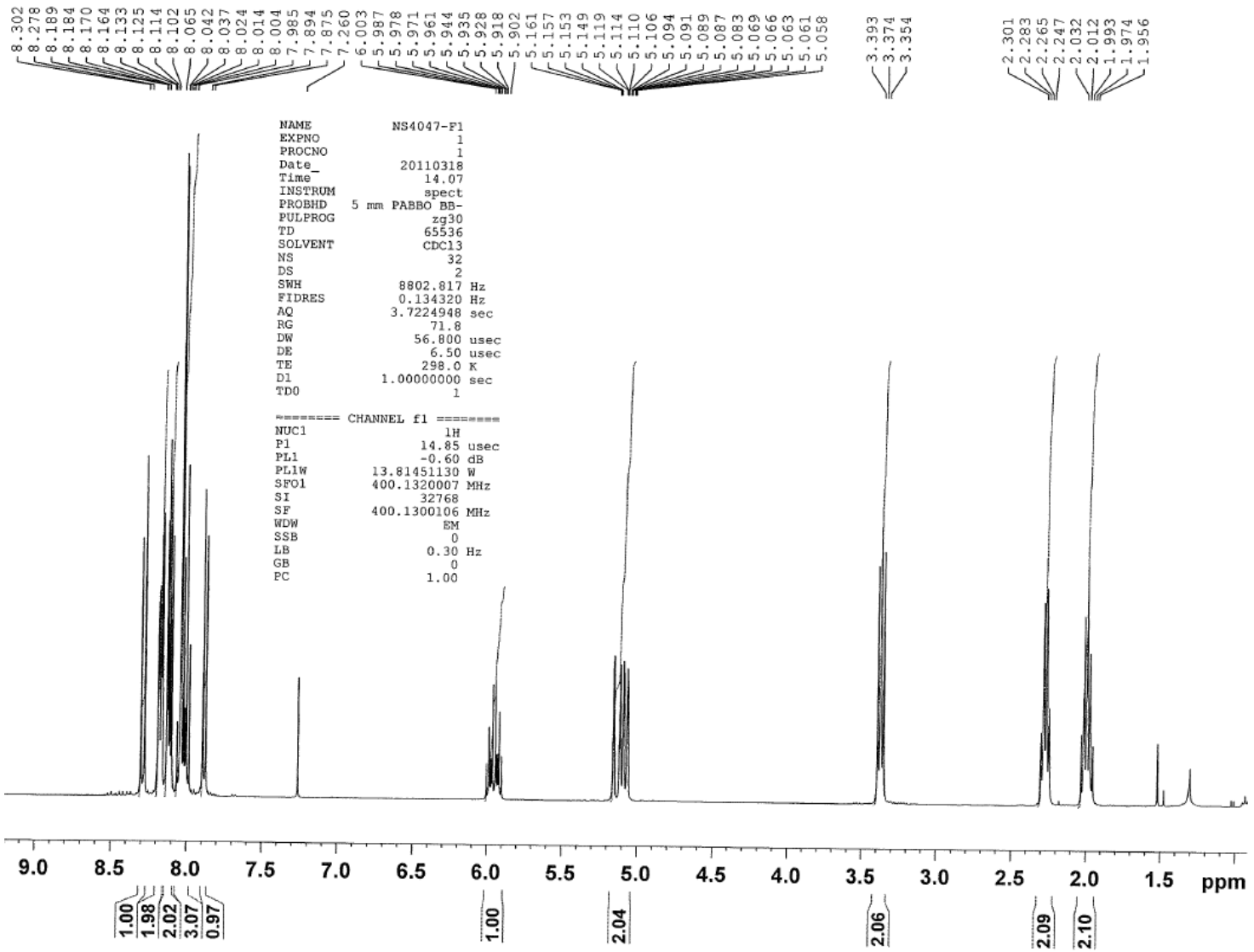
4-(Pyren-1-yl)butanal, **6**, ^{1}H NMR



4-(Pyren-1-yl)butanal, **6**, $^{13}C\{^{1}H\}$ NMR



1-(Pent-4-en-1-yl)pyrene, **7**, ^{1}H NMR



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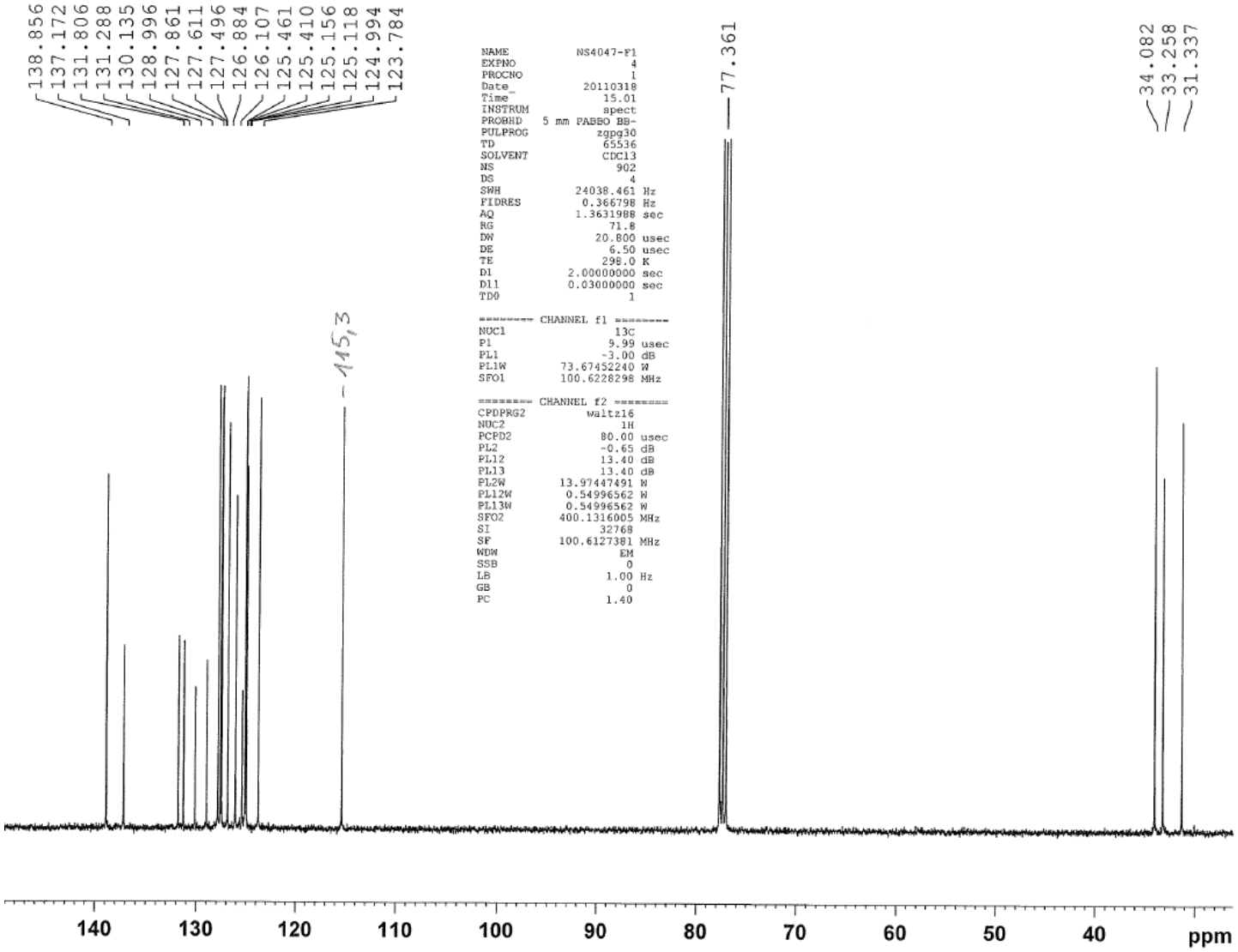
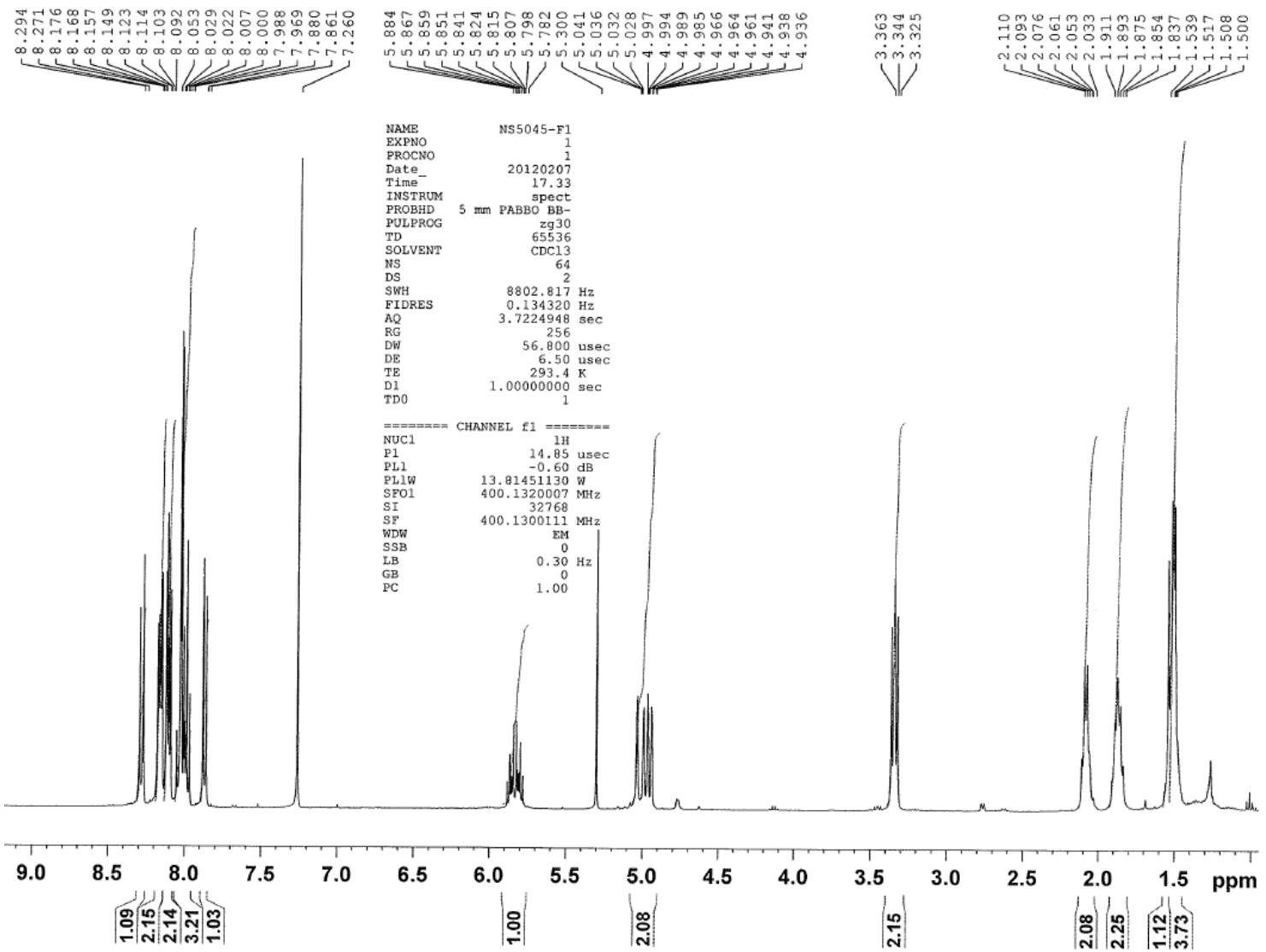
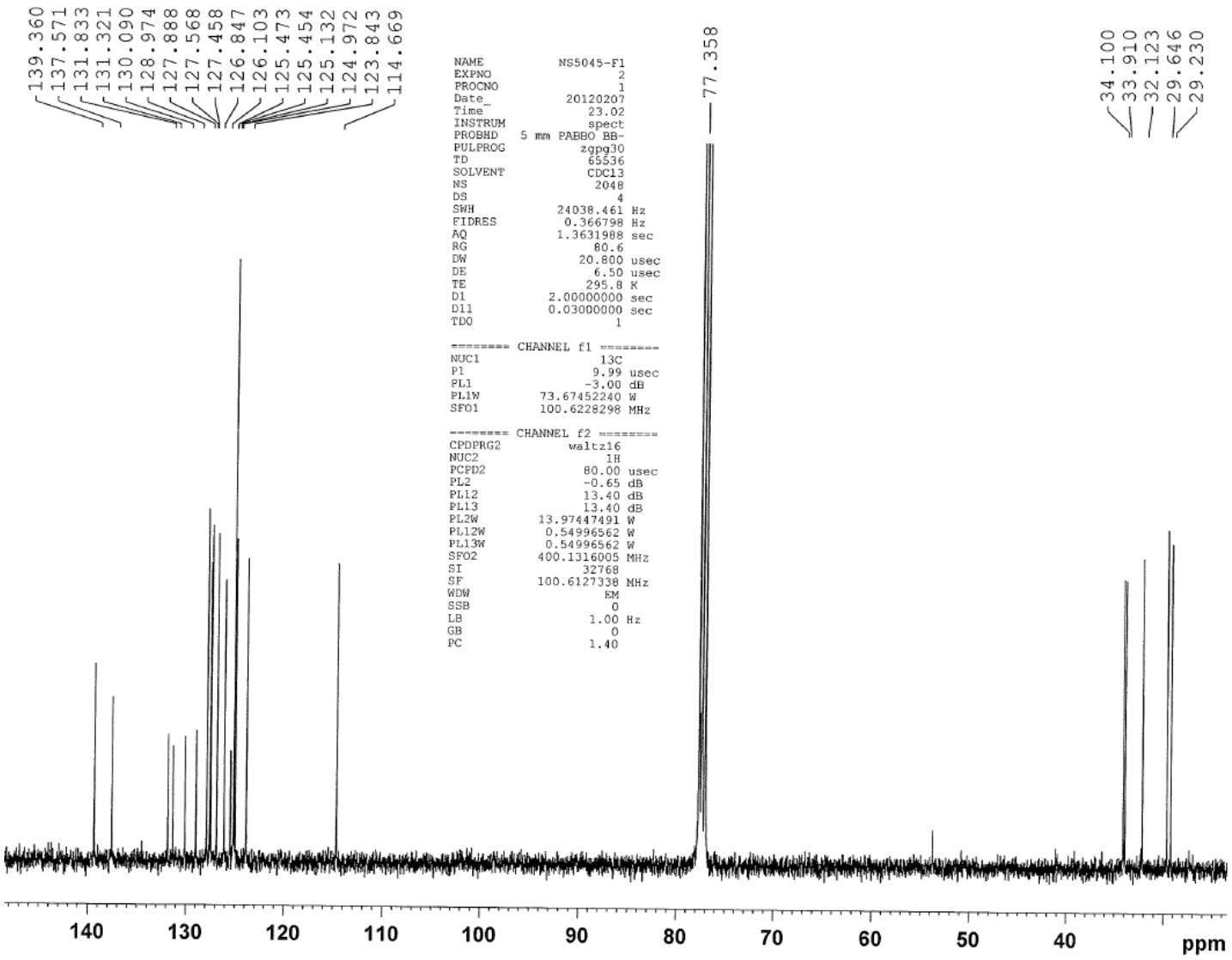


1-(Hept-6-en-1-yl)pyrene, **9**, ^{1}H NMR



1-(Hept-6-en-1-yl)pyrene, **9**, $^{13}C\{^{1}H\}$ NMR



Synthesis of substituted *closo*- and *nido*-carboranes

3-(3′-(Pyren-1″-yl)propyl)-1,2-dicarba-*closo*-dodecaborane (10a). To a solution of **4** (0.574 g, 2.37 mmol) in 20 mL of anhydrous DCM was slowly added 2.37 mL (2.37 mmol) of BCl_3 (1M in heptane). After 10 min $HBBr_2{\cdot}Me_2S$ (1M in DCM, 2.37 mL, 2.37 mmol) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. A solution of the formed alkyldichloroborane was added to a suspension of thallium dicarbollide (2.56 g, 4.74 mmol) in 20 ml of anhydrous DCM, and the reaction mixture was vigorously stirred at room temperature for 18 h. The reaction mixture was filtered through a paper filter, and the white precipitate of thallium(I) chloride was washed on a filter with 15 mL of DCM. The product was isolated by column chromatography on silica gel using EtOAc gradient (0→5%) in hexane. After evaporation and drying in vacuum **10a** was isolated as a white crystalline solid (1.07 g, 44%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, 1H, CH_{pyr}), 8.18–8.16 (m, 2H, CH_{pyr}), 8.13–8.11 (m, 2H, CH_{pyr}), 8.03 (m, 2H, CH_{pyr}), 8.00 (m, 1H, CH_{pyr}), 7.86 (d, 1H, CH_{pyr}), 3.42 (t, ^3J = 7.5, 2H, CH_2–pyr), 3.28 (br s, 2H, C_{cb}–H), 2.69–1.61 (m, 9H, B-*H*), 2.02 (m, 2H, CH_2), 1.18 (m, 2H, CH_2–B). ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ 136.4, 131.7, 131.2, 130.2, 129.0, 127.8, 127.77, 127.74, 127.0, 126.2, 125.4, 125.35, 125.33, 125.13, 125.11, 123.6, 56.8 (C_{cb}–H), 36.1, 30.6, 15.6 (br m, C–B). ^{11}B NMR (160 MHz, $CDCl_3$): δ –2.6 (d, 2B, J = 152), –3.9 [s, 1B, B(3)], –9.0 (d, 1B, J =150), –12.9 (d, 3B, J = 155), –13.8 (d, 3B). HRMS (APCI): m/z = 422.2654 $[M+H+Cl]^-$ (calcd for $C_{21}H_{26}B_{10}Cl$ 421.2762).

3-(5′-(Pyren-1″-yl)pentyl)-1,2-dicarba-*closo*-dodecaborane (10b). The compound **10b** was prepared from **7** (0.625 g, 2.31 mmol) according to the procedure discribed for **10a**. After evaporation and drying in vacuum, the product **10b** was isolated as a white crystalline solid (0.640 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, 1H, CH_{pyr}), 8.17-8.15 (m, 2H, CH_{pyr}), 8.12-8.09 (m, 2H, CH_{pyr}), 8.02 (m, 2H, CH_{pyr}), 7.99 (t, 1H, CH_{pyr}), 7.86 (d, 1H, CH_{pyr}), 3.35 (t, ^3J = 7.8, 2H, CH_2–pyr), 3.23 (br s, 2H, C_{cb}–H), 2.70-1.68 (m, 9H, B–*H*), 1.88 (m, 2H, CH_2), 1.50 (m, 4H, CH_2), 0.99 (m, 2H, CH_2–B). ^{13}C{^{1}H} (100 MHz, $CDCl_3$): δ 137.3, 131.8, 131.2, 130.1, 128.9, 127.8, 127.6, 127.5, 126.9, 126.1, 125.4, 125.3, 125.2, 125.1, 125.0, 123.7, 56.7 (C_{cb}–H), 33.7, 32.4, 31.7, 28.3, 15.8 (br m, C–B). ^{11}B NMR (160 MHz, $CDCl_3$): δ –2.9 (d, 2B, J = 156), –4.0 [s, 1B, B(3)], –9.1 (d, 1B, J =152), –13.1 (d, 3B, J = 151), –13.9 (d, 3B). MS (TIS): m/z = 451.4158 $[M+H+Cl]^-$ (calcd for $C_{23}H_{32}B_{10}Cl$ 451.3195).

3-(7′-(Pyren-1″-yl)heptyl)-1,2-dicarba-*closo*-dodecaborane (10c). The compound **10c** was prepared from **9** (0.251 g, 0.840 mmol) according to the procedure discribed for **10a**. After evaporation and drying in vacuum, the product **10c** was isolated as a white crystalline solid (0.150 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, 1H, CH_{pyr}), 8.17-8.14 (m, 2H, CH_{pyr}), 8.12-8.09 (m, 2H, CH_{pyr}), 8.02 (m, 2H, CH_{pyr}), 7.98 (t, 1H, CH_{pyr}), 7.87 (d, 1H, CH_{pyr}), 3.34 (t, ^{3}J = 7.6, 2H, CH_2-pyr), 3.31 (br s, 2H, C_{cb}–H), 2.79–1.63 (m, 9H, B-*H*), 1.86 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.37 (m, 6H, CH_2), 0.98 (m, 2H, CH_2–B). ^{13}C{^{1}H} (100 MHz, $CDCl_3$): δ 137.5, 131.8, 131.3, 130.1, 129.0, 127.8, 127.6, 127.4, 126.8, 126.1, 125.4, 125.19, 125.13, 124.9, 123.8, 56.7 (C_{cb}–H), 33.8, 32.4, 32.1, 29.8, 29.5, 28.4, 15.6 (br m, C–B). ^{11}B NMR (160 MHz, $CDCl_3$): δ –2.9 (d, 2B, J = 150), –4.0 [s, 1B, B(3)], –9.1 (d, 1B, J =145), –13.1 (d, 3B, J = 157), –14.0 (d, 3B). HRMS (APCI): m/z = 441.3063 [M–H]$^-$ (calcd for $C_{25}H_{34}B_{10}$ 442.3663).

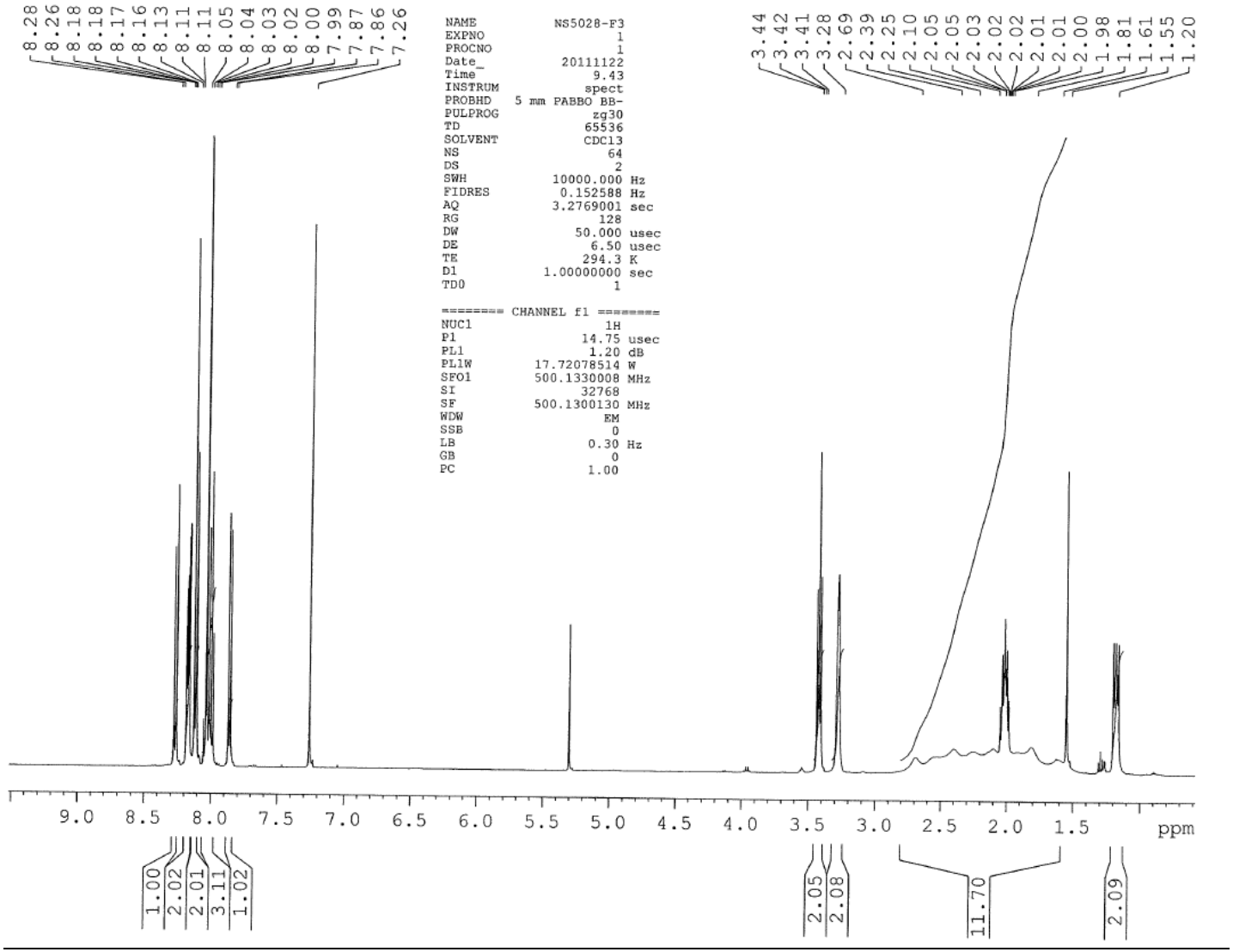
Tetrabutylammonium 3-(3′-(pyren-1″-yl)propyl)-7,8-dicarba-*nido*-undecaborate (11a). To a solution of **10a** (0.385 g, 1.00 mmol) in 4 mL of THF was added 5 mL of a 1M TBAF in THF (5.00 mmol), and the reaction mixture was refluxed for 3 h (TLC control). The solvent was removed under reduced pressure, and 5 mL of water was added to the residue. The precipitate formed was filtered on a fine-porosity glass filter and washed with water (3×5 mL) to give after drying under vacuum over P_2O_5 product **11a** as a white solid (0.600 g, 97%). ^{1}H NMR (500 MHz, acetone-d_6): δ 8.47 (d, 1H, CH_{pyr}), 8.28–8.21 (m, 4H, CH_{pyr}), 8.15–8.09 (m, 2H, CH_{pyr}), 8.07–8.01 (m, 2H, CH_{pyr}), 3.46 (m, 10H, TBA+CH_2-pyr), 2.42–1.10 (m, 8H, B-*H*), 1.97 (m, 2H, CH_2), 1.85 (m, 10H, TBA), 1.66 (br s, 2H, C_{cb}–H), 1.45 (m, 8H, TBA), 1.01 (t, 14H, ^{3}J = 10.0, TBA+CH_2–B), -2.66 (br m, 1H, B-*H*-B). ^{13}C{^{1}H} (125 MHz, acetone-d_6): δ 140.2, 133.1, 132.7, 131.2, 130.2, 129.28, 129.23, 128.5, 127.8, 127.4, 126.60, 126.58, 126.52, 126.27, 126.21, 125.6, 60.1, 48.2 (C_{cb}–H), 38.1, 33.2, 25.1, 21.1, 14.1. ^{11}B NMR (160 MHz, acetone-d_6): δ –9.0 [s, 1B, B(3)], –10.9 (d, 2B, J = 142), –16.6 (d, 2B, J = 142), –21.5 (d, 2B, J = 142), –35.9 (d,1B, J = 144), –36.8 (d, 1B). HRMS (TIS): m/z = 376.3251 [M]$^-$ (calcd for $C_{21}H_{26}B_9$ 376.2908).

Tetrabutylammonium 3-(5′-(pyren-1″-yl)pentyl)-7,8-dicarba-*nido*-undecaborate (11b). The compound **11b** was prepared from **10b** (0.200 g, 0.480 mmol) according to the procedure discribed for **11a**. The product was isolated as a white solid (0.300 g, 96%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.44 (d, 1H, CH_{pyr}), 8.29–8.22 (m, 4H, CH_{pyr}), 8.16 –8.10 (m, 2H, CH_{pyr}), 8.06 (t, 1H, CH_{pyr}), 8.00 (d, 1H, CH_{pyr}), 3.46 (m, 8H, TBA), 3.40 (m, 2H, CH_2–pyr), 2.54–(–0.11) (m, 8H, B-*H*), 1.84 (m, 10H, TBA+CH_2), 1.65 (br s, 2H, C_{cb}–H), 1.57 (m, 4H, CH_2), 1.47 (m, 8H, TBA), 1.01 (t, 12H, ^{3}J = 7.6, TBA), 0.80 (m, 2H, CH_2–B), –2.65 (br m, 1H, B-*H*-B). ^{13}C{^{1}H}

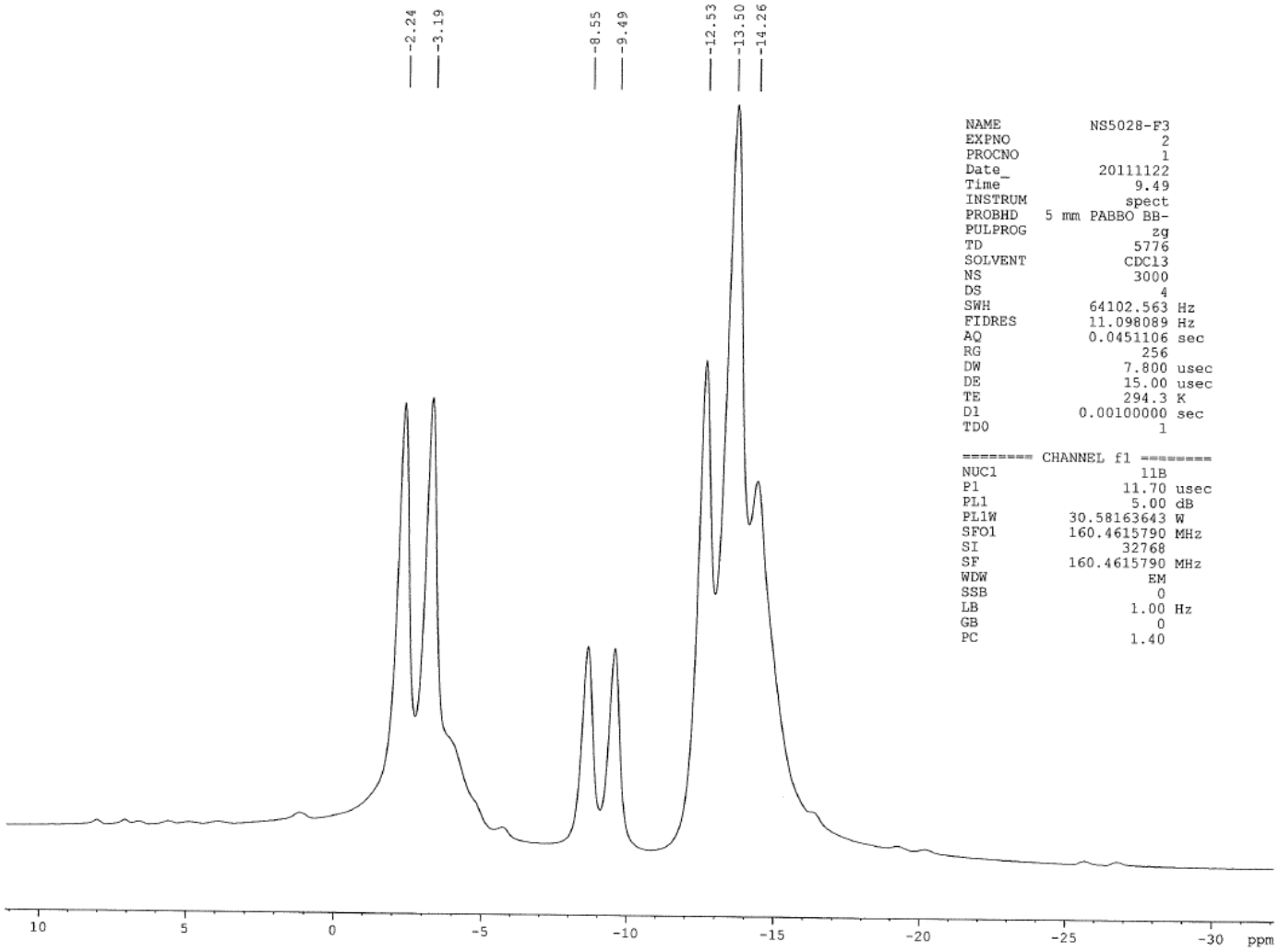
(100 MHz, acetone-d_6): δ 139.5, 133.2, 132.7, 131.4, 130.2, 129.2, 129.1, 128.7, 128.0, 127.5, 126.6, 126.5, 126.4, 126.3, 125.3, 60.25, 48.16 (C_{cb}–H), 34.9, 34.6, 33.7, 25.2, 21.1, 14.6. ^{11}B NMR (128 MHz, acetone-d_6): δ –9.0 [s, 1B, B(3)], –11.1 (d, 2B, J = 133), –16.6 (d, 2B, J = 133), –21.6 (d, 2B, J = 145), –36.1 (d,1B), –36.8 (d, 1B, J = 133). HRMS (TIS): m/z = 404.3206 $[M]^-$ (calcd for $C_{23}H_{30}B_9$ 404.3221).

Tetrabutylammonium 3-(7′-(pyren-1″-yl)heptyl)-7,8-dicarba-*nido*-undecaborate (11c). The compound **11c** was prepared from **10c** (0.239 g, 0.53 mmol) according to the procedure discribed for **11a**. The product was extracted from water by DCM (3×10 mL) and purified by column chromatography using $CHCl_3$ gradient (0→100%) in hexane. The product **11c** was isolated as a pale yellow oil (0.325 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, 1H, CH_{pyr}), 8.16–8.08 (m, 4H, CH_{pyr}), 8.03–7.95 (m, 3H, CH_{pyr}), 7.86 (d, 1H, CH_{pyr}), 3.31 (m, 2H, CH_2-pyr), 3.06 (m, 8H, TBA), 2.42–(–0.42) (m, 8H, B–*H*), 1.81 (m, 4H, CH_2), 1.53 (m, 12H, TBA+CH_2+C_{cb}–H), 1.36 (m, 12H, TBA+CH_2), 1.25 (m, 14H, CH_2+TBA-CH_2), 0.97 (t, 12H, ^3J = 7.2, TBA), 0.76 (m, 2H, CH_2–B), –2.62 (br m, 1H, B-*H*-B). ^{13}C{^{1}H} (100 MHz, $CDCl_3$): δ 138.0, 131.8, 131.3, 129.9, 128.9, 127.9, 127.6, 127.4, 126.7, 126.0, 125.5, 125.4, 125.1, 125.0, 124.9, 124.0, 59.3, 47.9 (C_{cb}–H), 34.0, 33.2, 32.4, 30.2, 29.9, 29.1, 24.3, 20.0, 13.9. ^{11}B NMR (128 MHz, $CDCl_3$): δ –7.9 [s, 1B, B(3)], –11.5 (d, 2B, J = 128), –17.0 (d, 2B, J = 120), –21.2 (d, 2B, J = 147), –36.2 (d,1B), –36.9 (d, 1B). HRMS (TIS): m/z = 432.3248 $[M]^-$ (calcd for $C_{25}H_{34}B_9$ 432.3534).

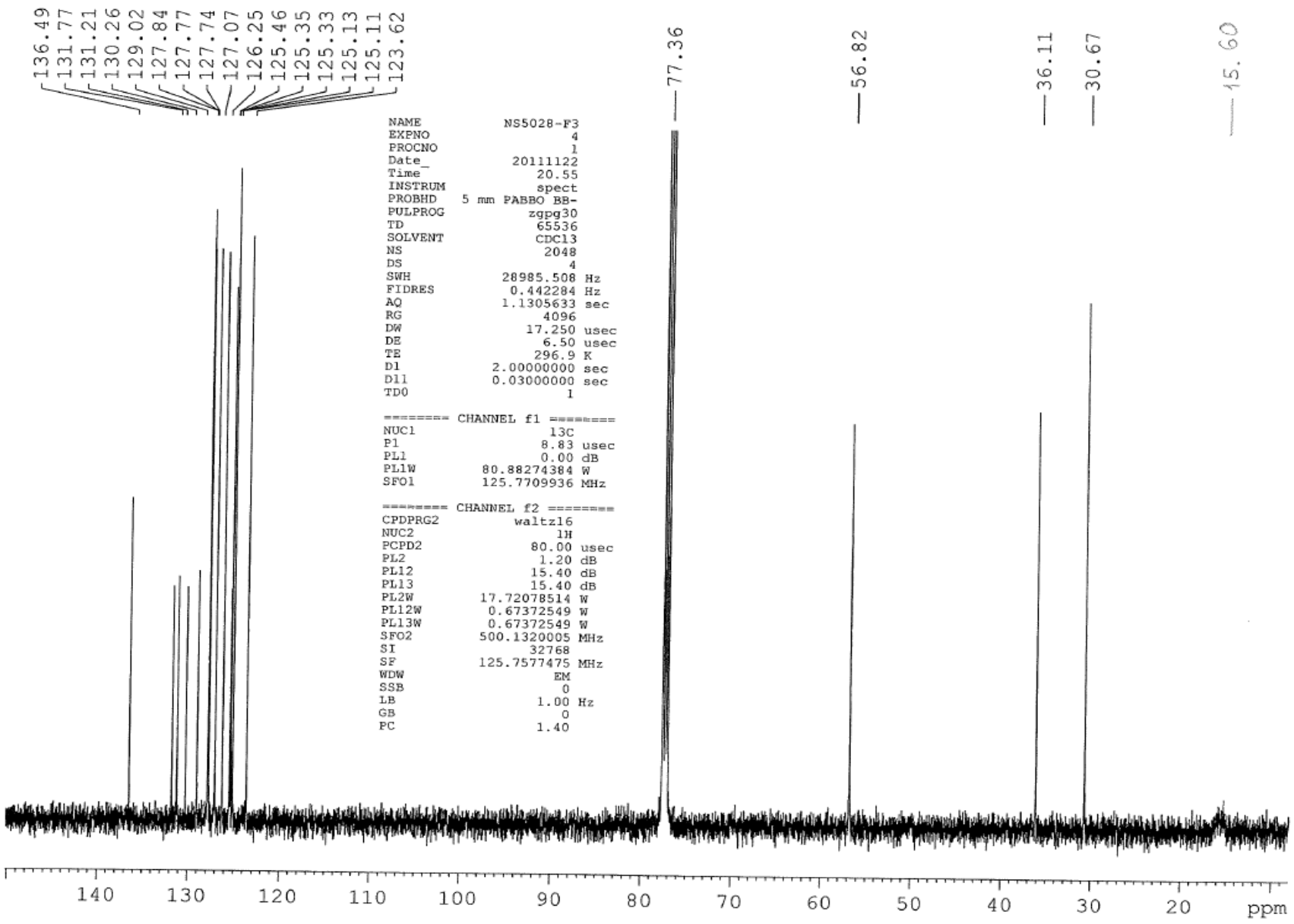
3-(3′-(Pyren-1″-yl)propyl)-1,2-dicarba-*closo*-dodecaborane, **10a**, ^{1}H NMR



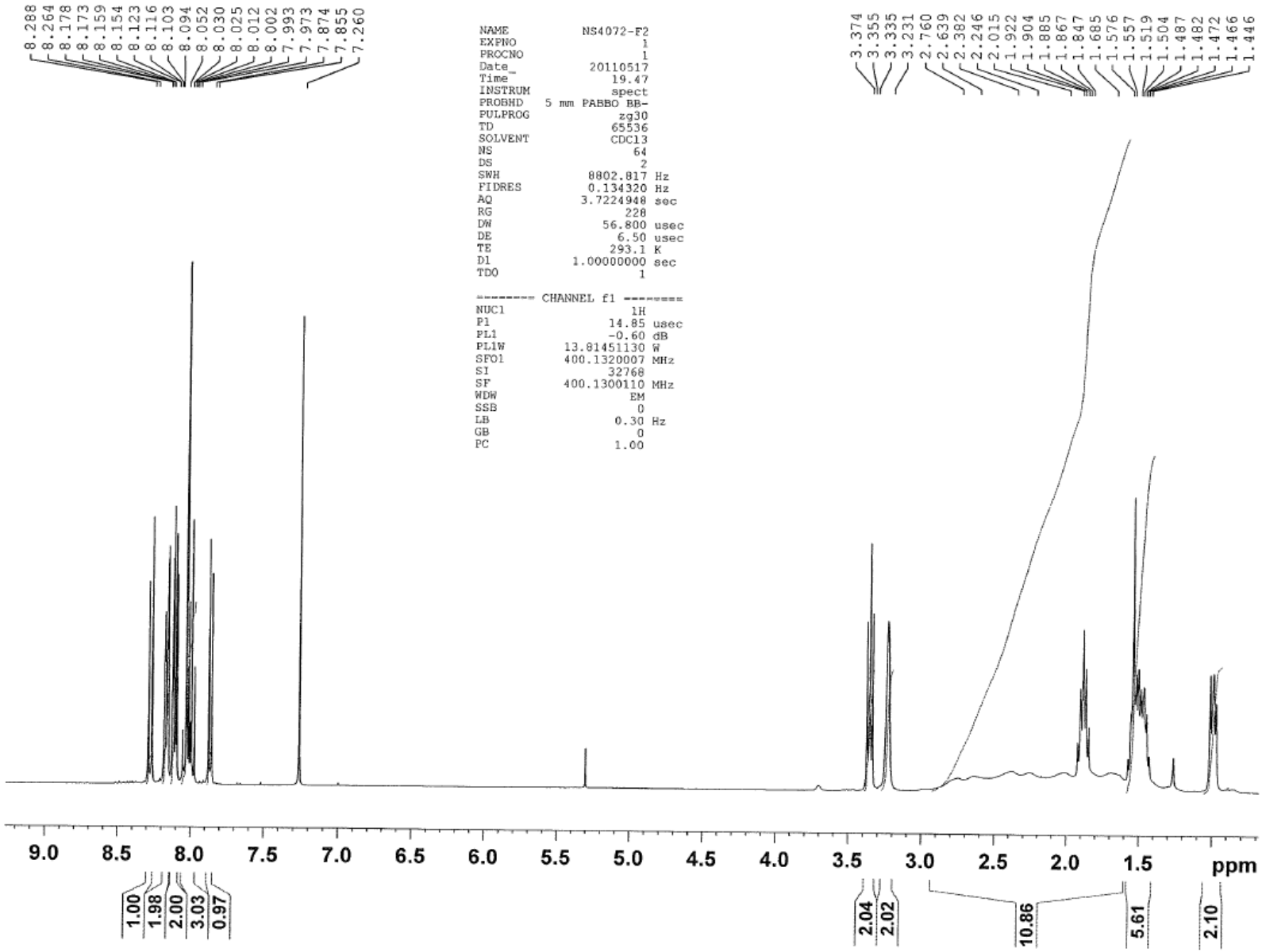
3-(3′-(Pyren-1″-yl)propyl)-1,2-dicarba-*closo*-dodecaborane, **10a**, ^{11}B NMR



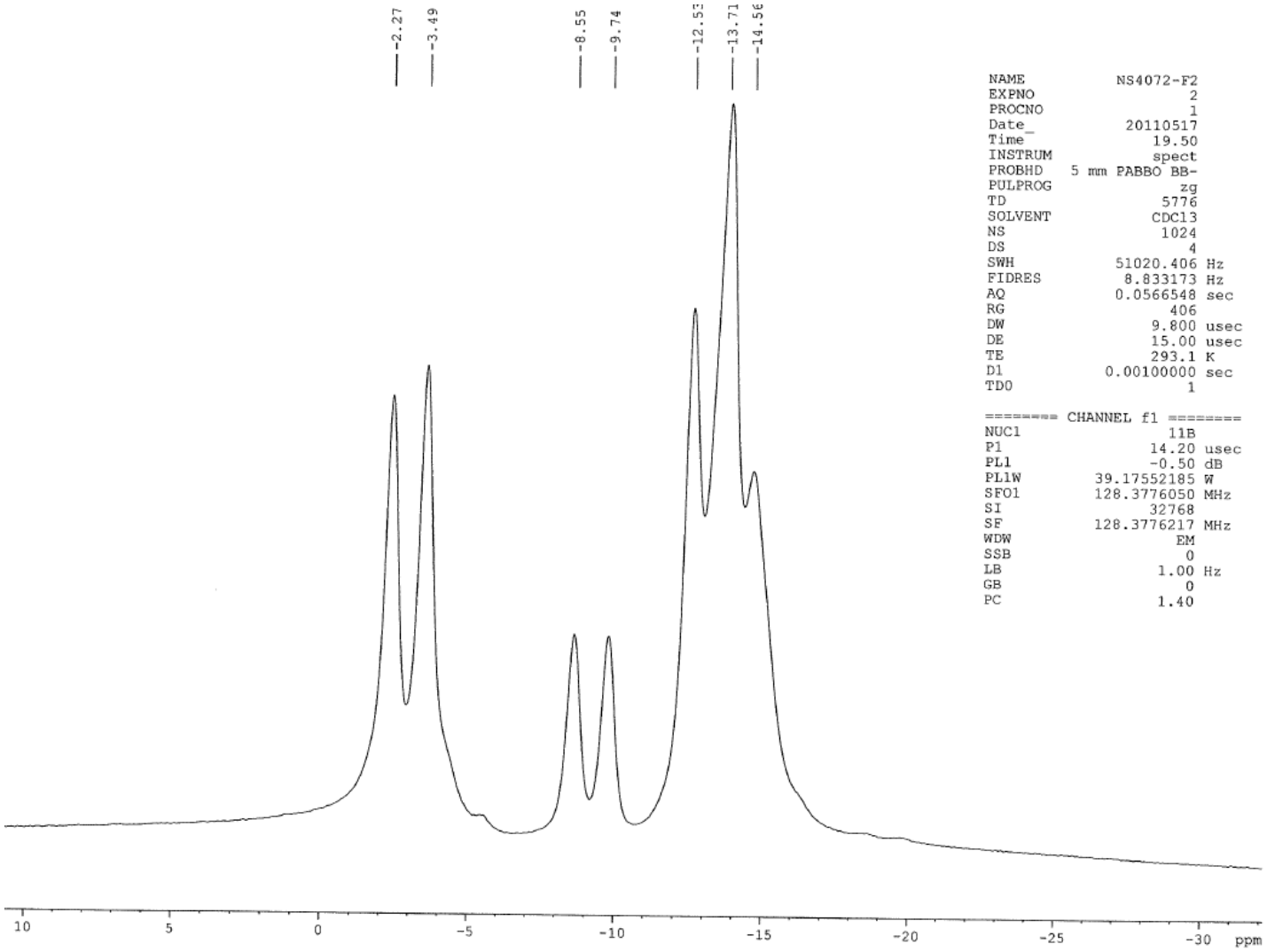
3-(3′-(Pyren-1″-yl)propyl)-1,2-dicarba-*closo*-dodecaborane, **10a**, $^{13}C\{^{1}H\}$ NMR



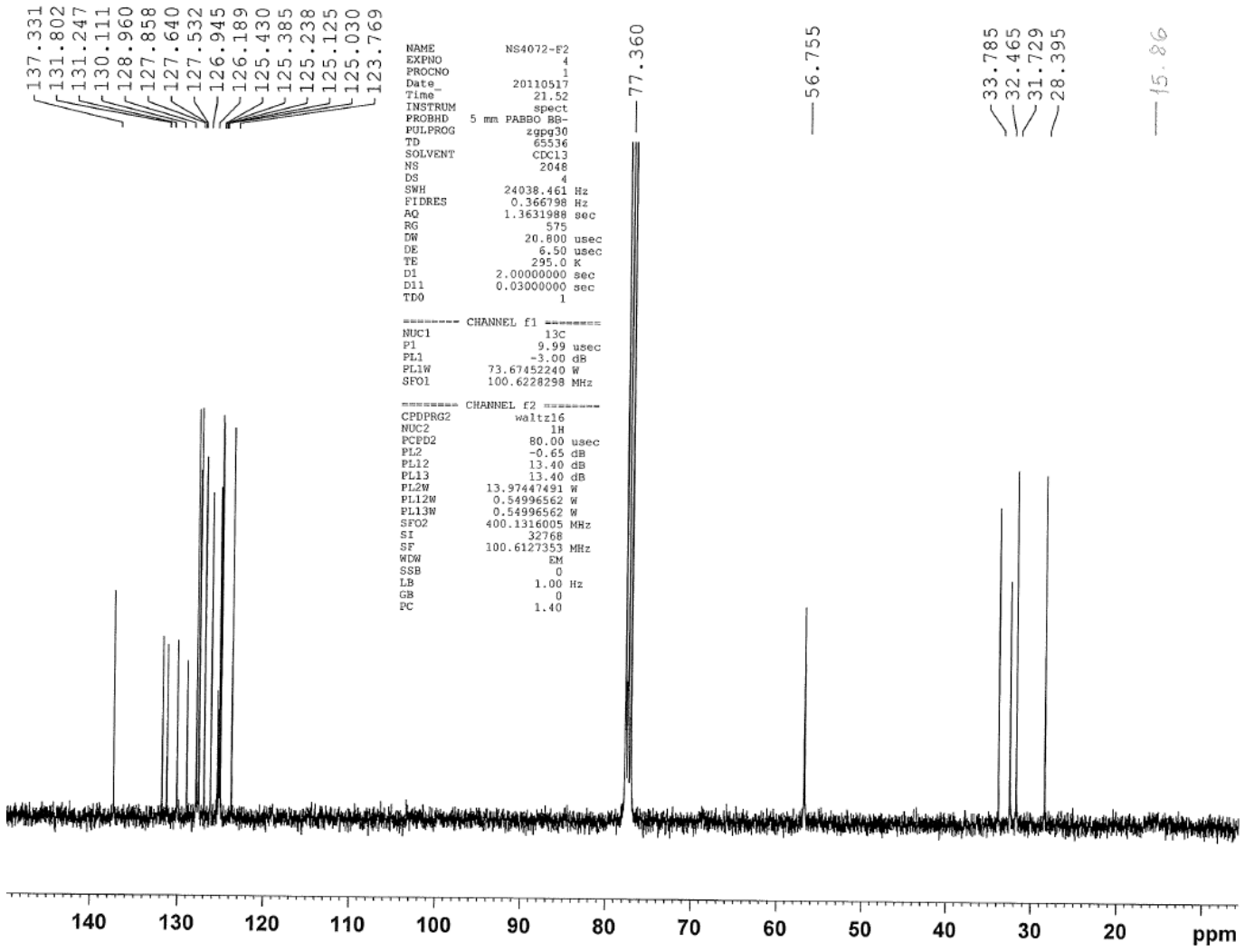
3-(5′-(Pyren-1″-yl)pentyl)-1,2-dicarba-*closo*-dodecaborane, **10b**, ^{1}H NMR



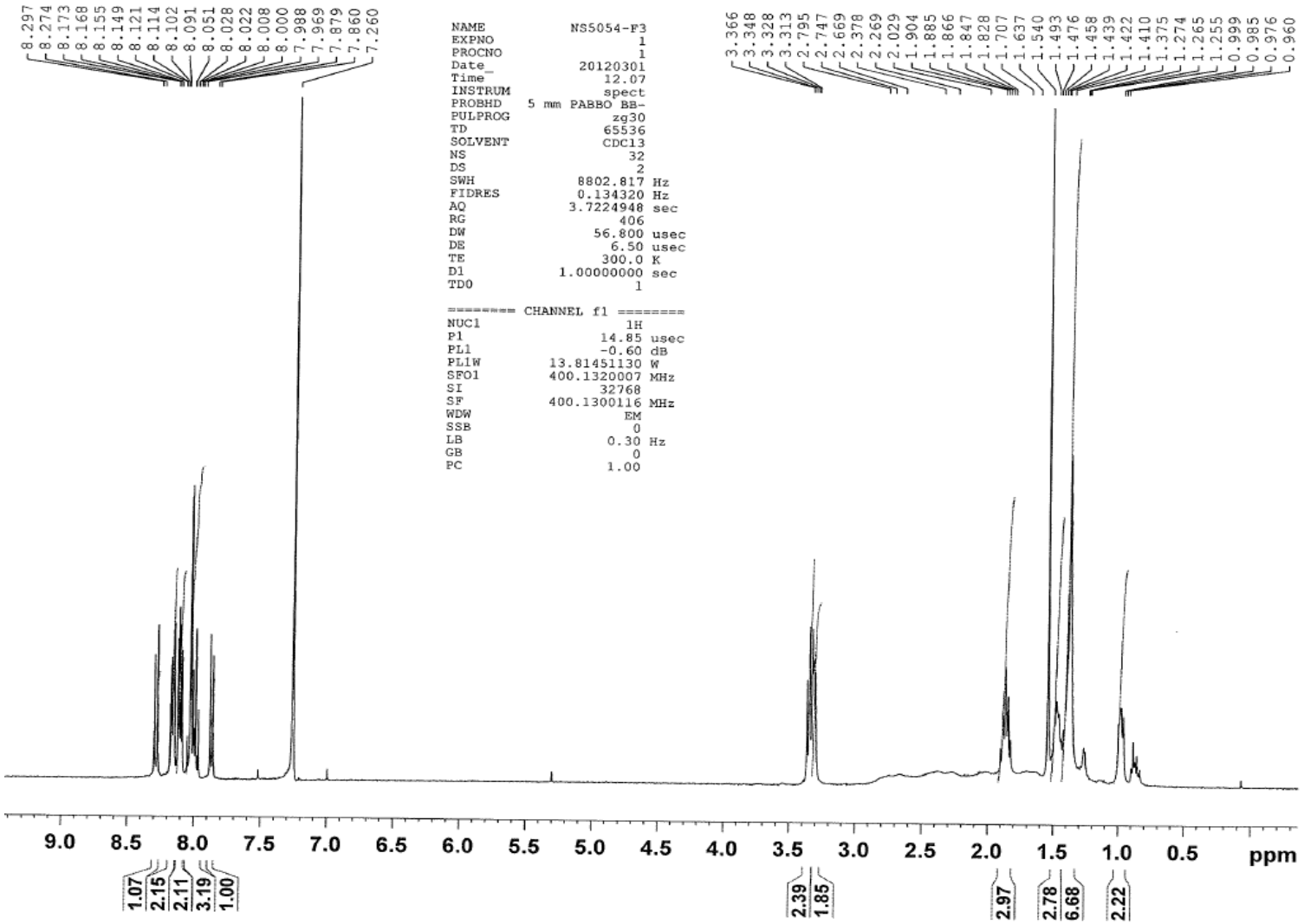
3-(5′-(Pyren-1″-yl)pentyl)-1,2-dicarba-*closo*-dodecaborane, **10b**, ^{11}B NMR



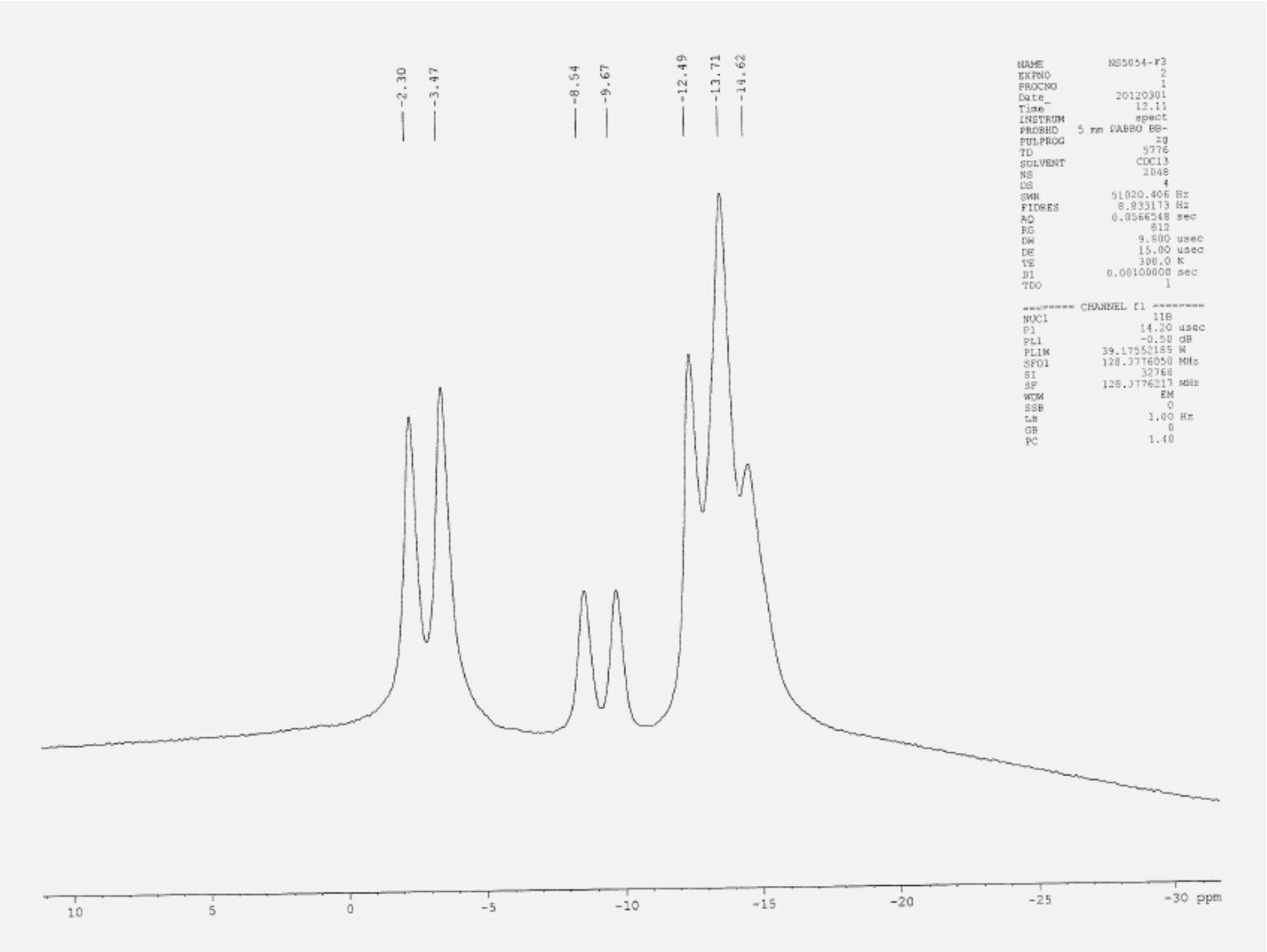
3-(5′-(Pyren-1″-yl)pentyl)-1,2-dicarba-*closo*-dodecaborane, **10b**, $^{13}C\{^{1}H\}$ NMR



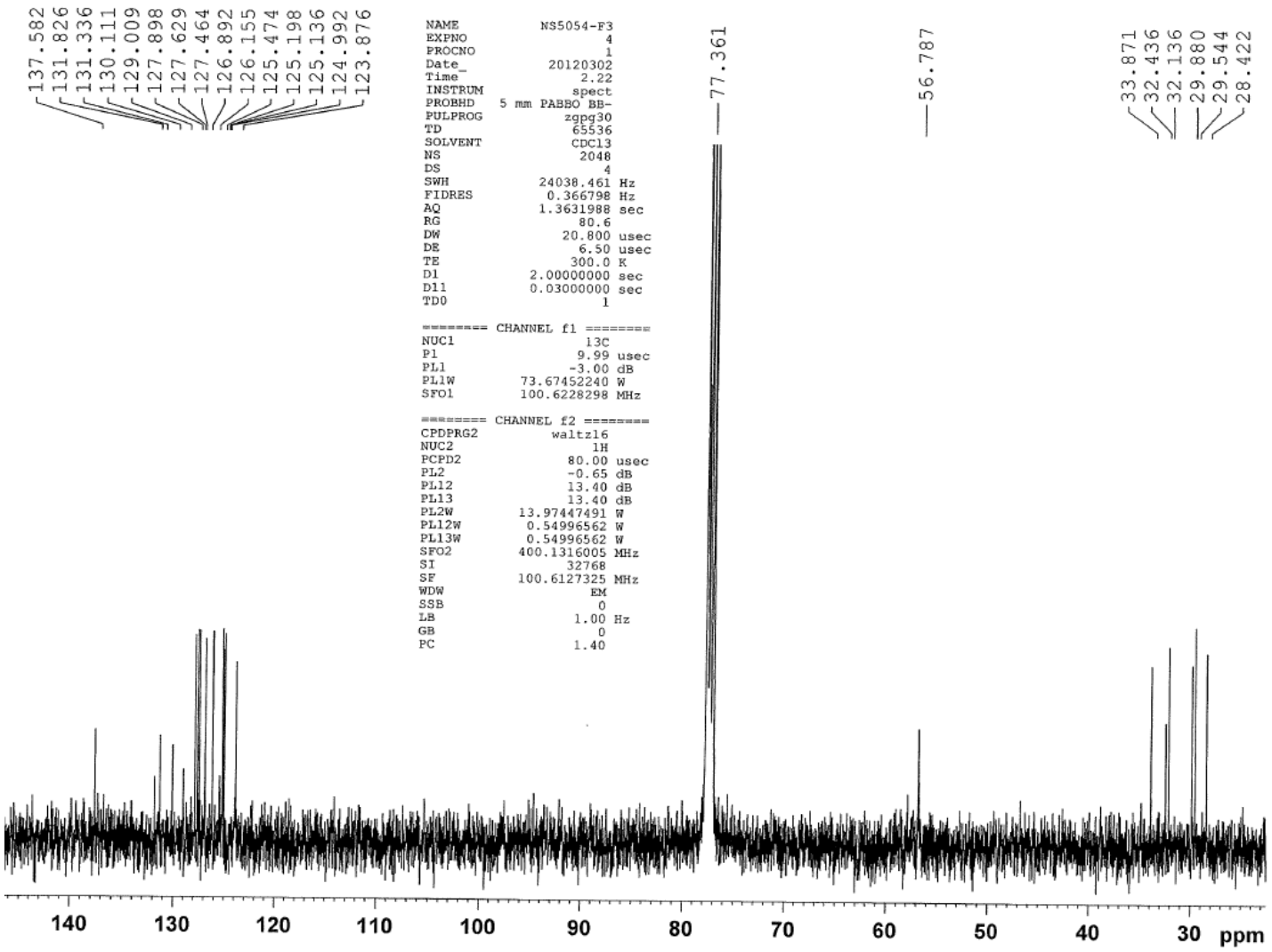
3-(7′-(Pyren-1″-yl)heptyl)-1,2-dicarba-*closo*-dodecaborane, **10c**, ^{1}H NMR



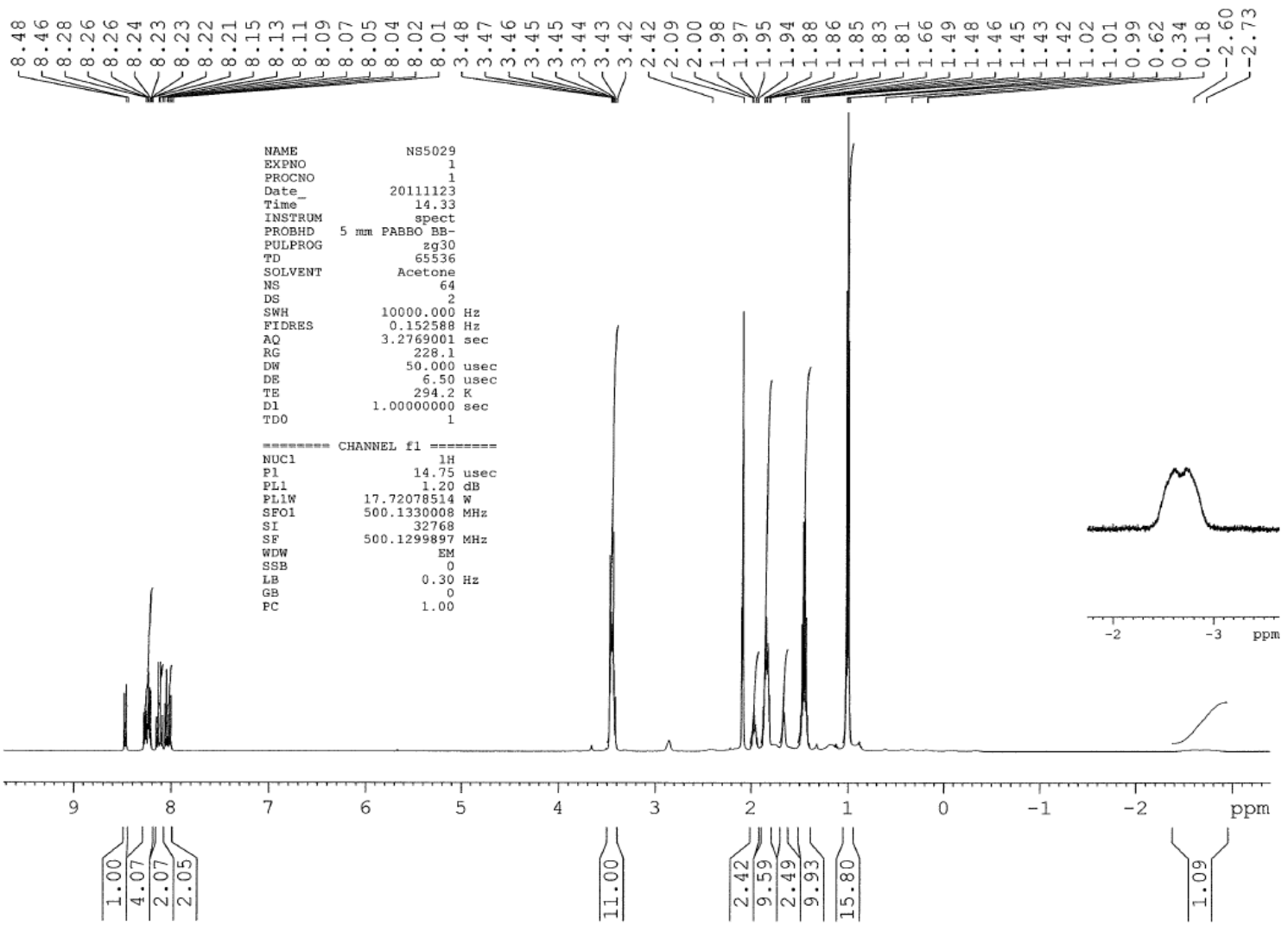
3-(7′-(Pyren-1″-yl)heptyl)-1,2-dicarba-*closo*-dodecaborane, **10c**, ^{11}B NMR



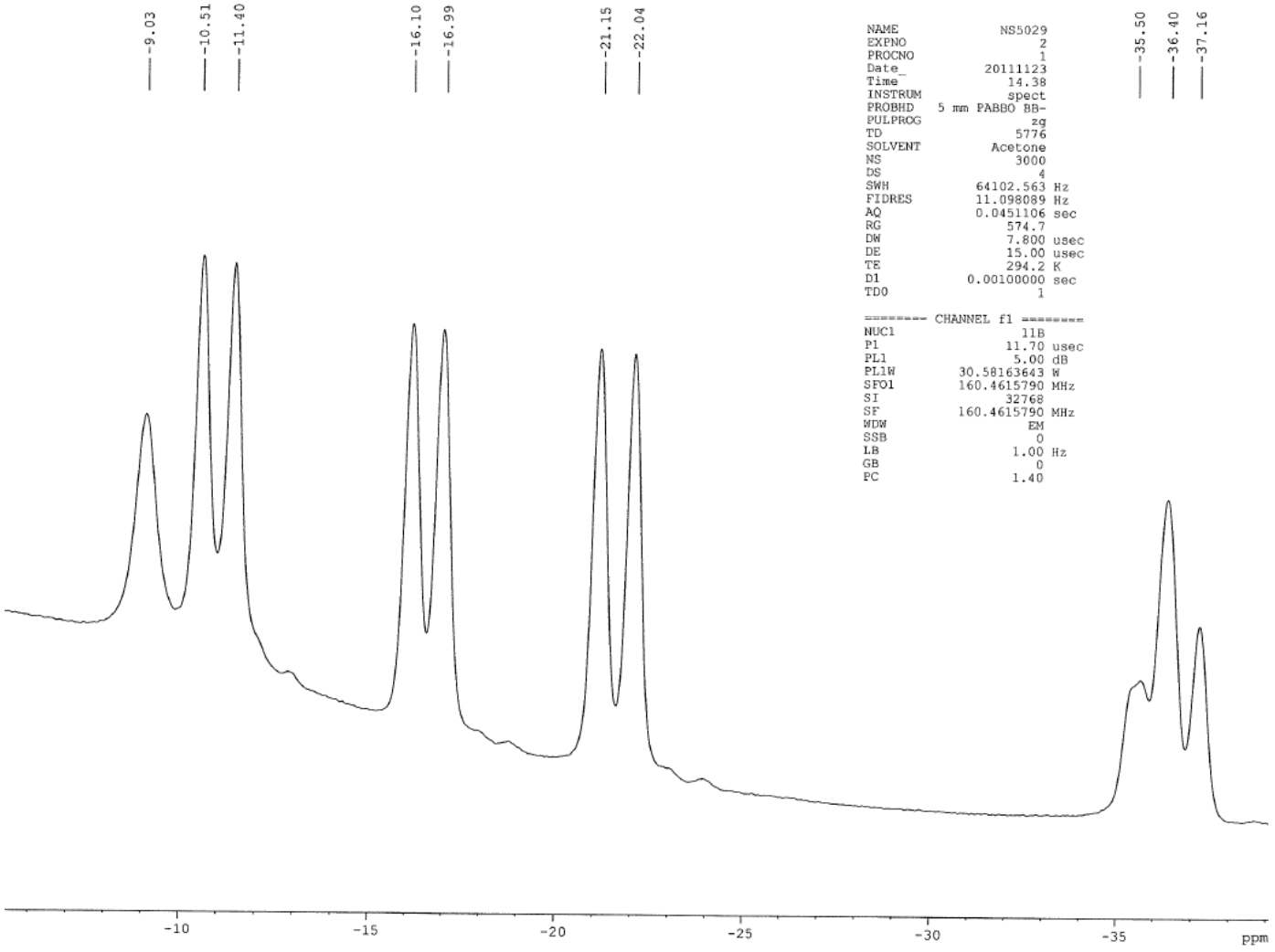
3-(7′-(Pyren-1″-yl)heptyl)-1,2-dicarba-*closo*-dodecaborane, **10c**, $^{13}C\{^{1}H\}$ NMR



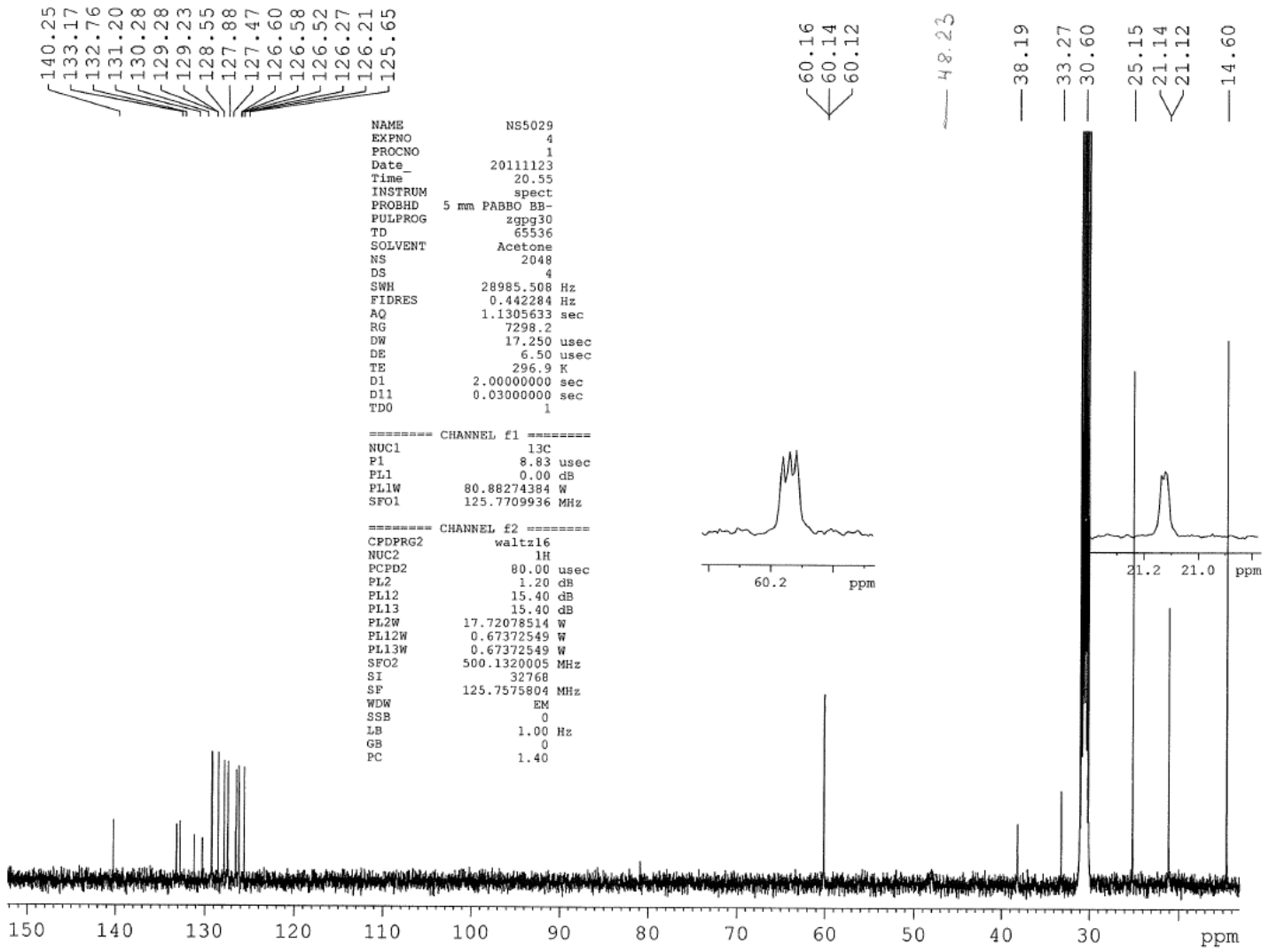
Tetrabutylammonium 3-(3′-(pyren-1″-yl)propyl)-7,8-dicarba-*nido*-undecaborate, **11a**, ^{1}H NMR



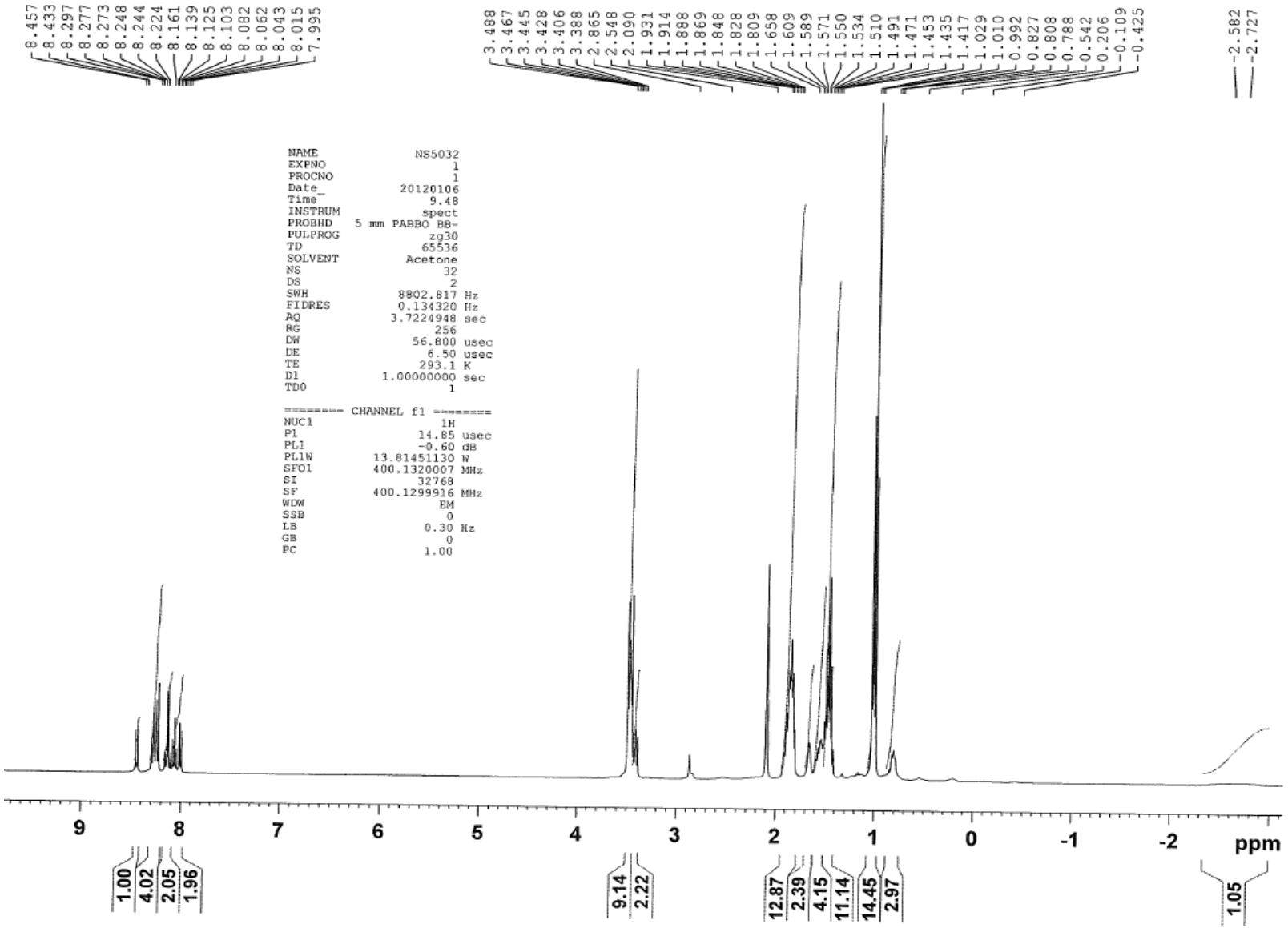
Tetrabutylammonium 3-(3′-(pyren-1″-yl)propyl)-7,8-dicarba-*nido*-undecaborate, **11a**, ^{11}B NMR



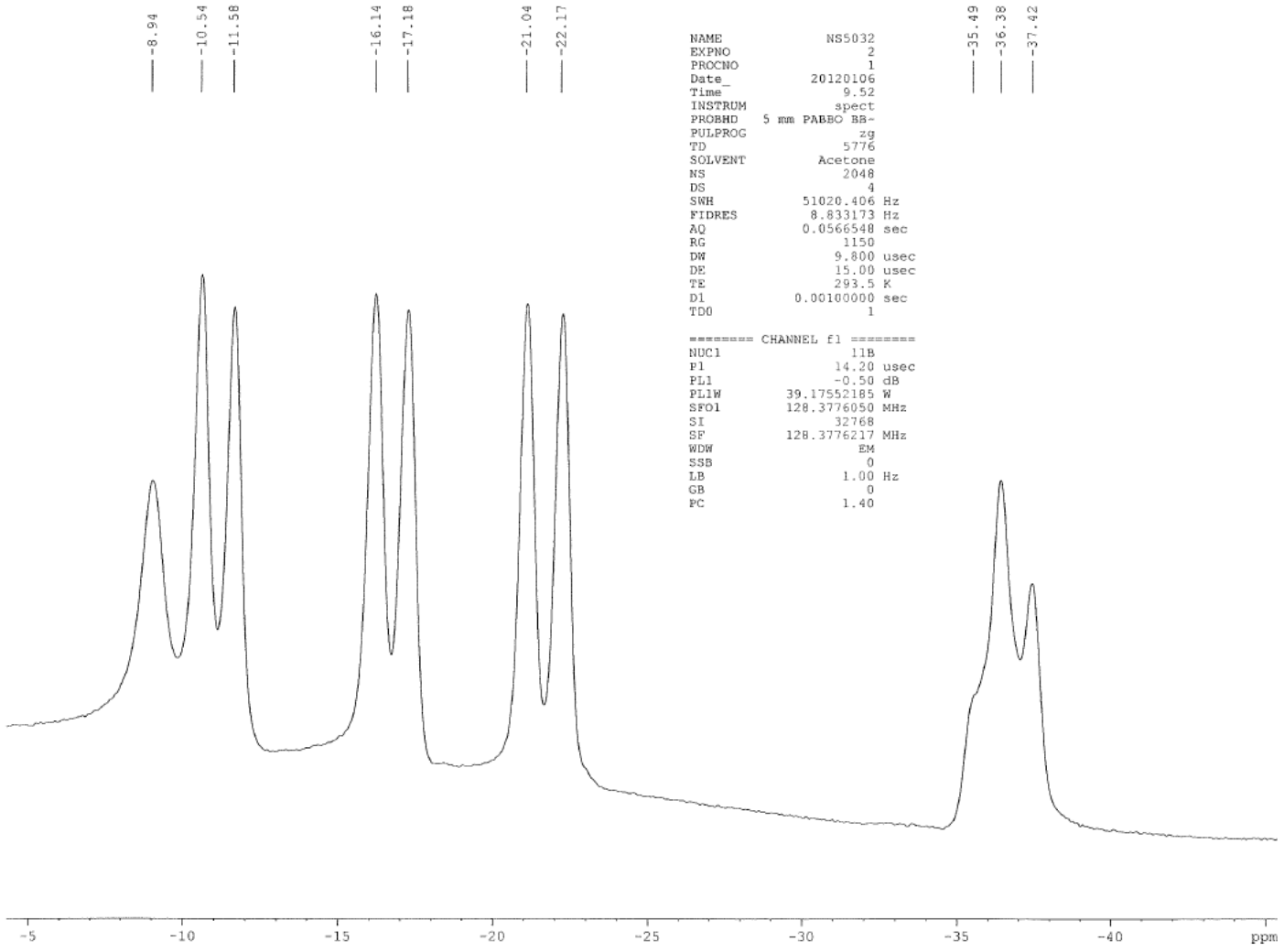
Tetrabutylammonium 3-(3′-(pyren-1″-yl)propyl)-7,8-dicarba-*nido*-undecaborate, **11a**, $^{13}C\{^{1}H\}$ NMR



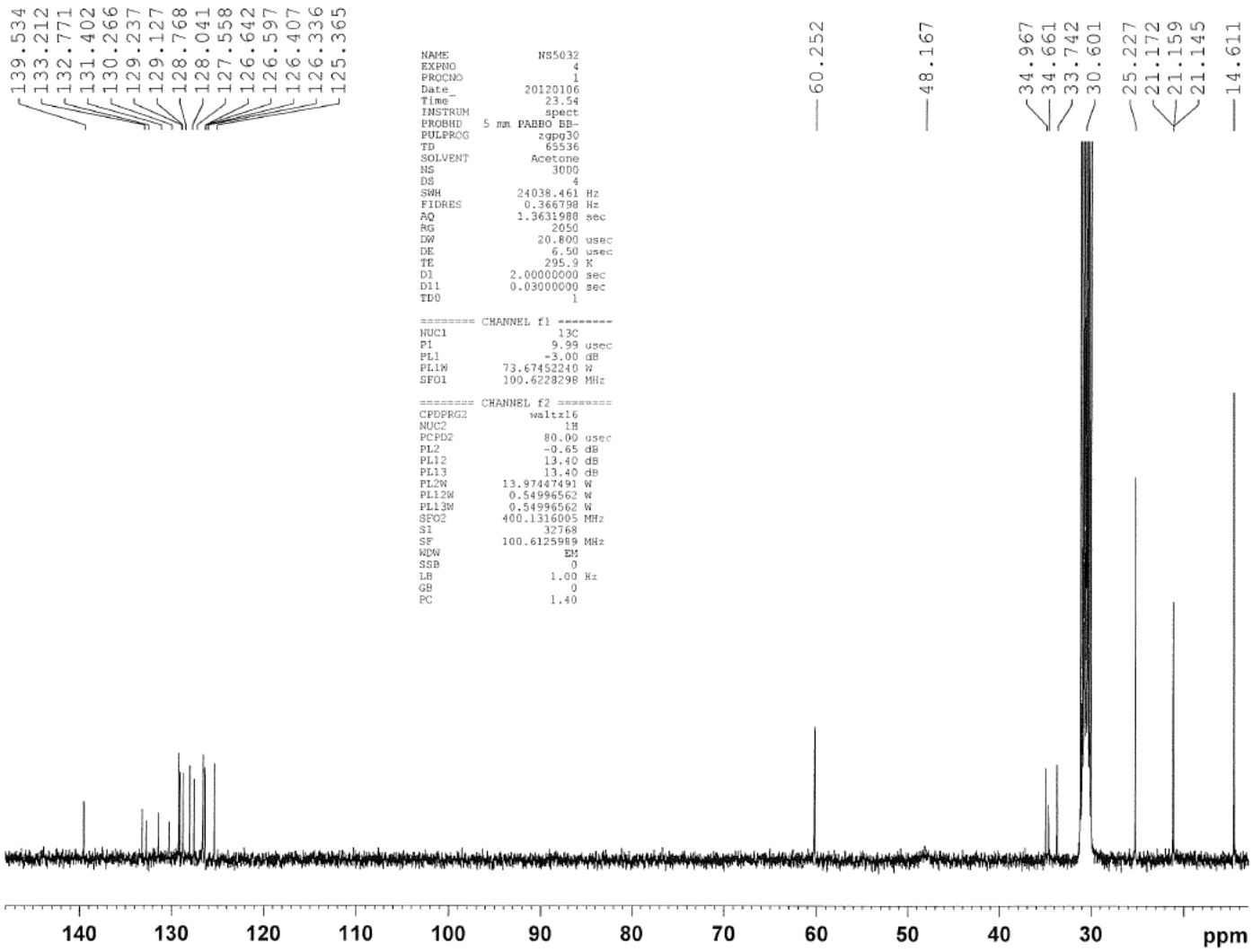
Tetrabutylammonium 3-(5′-(pyren-1″-yl)pentyl)-7,8-dicarba-*nido*-undecaborate, **11b**, ^{1}H NMR



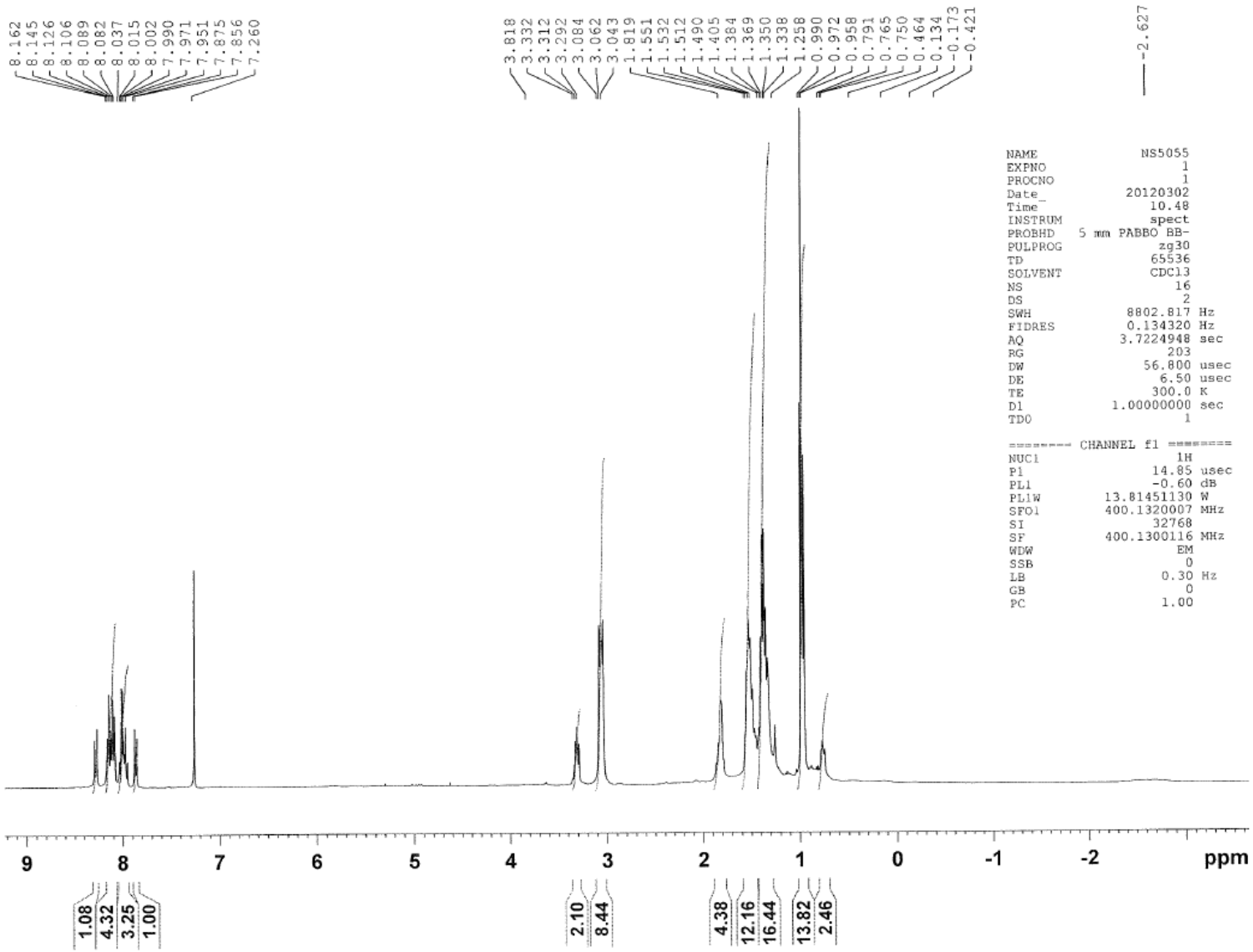
Tetrabutylammonium 3-(5′-(pyren-1″-yl)pentyl)-7,8-dicarba-*nido*-undecaborate, **11b**, ^{11}B NMR



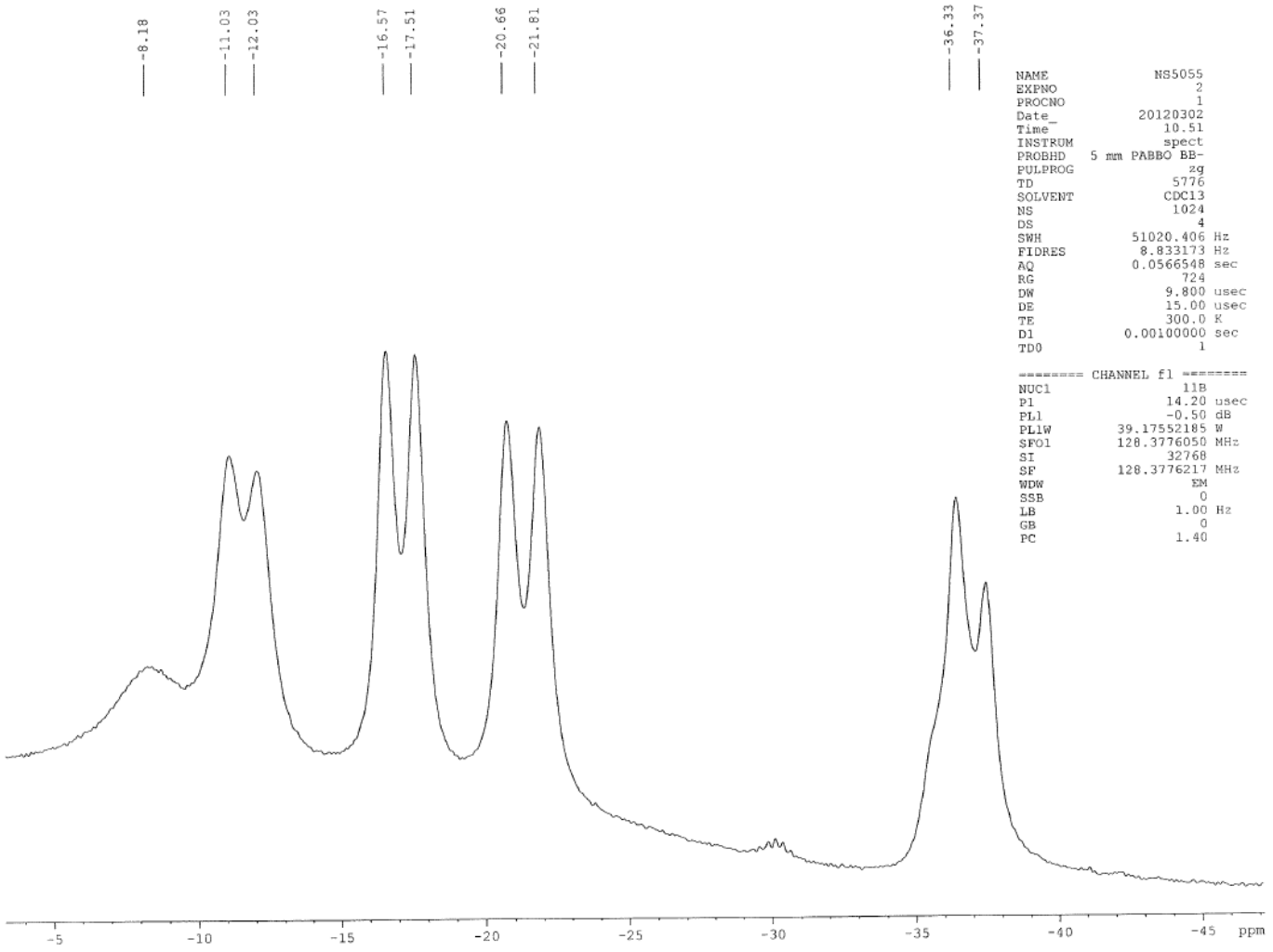
Tetrabutylammonium 3-(5′-(pyren-1″-yl)pentyl)-7,8-dicarba-*nido*-undecaborate, **11b**, $^{13}C\{^{1}H\}$ NMR



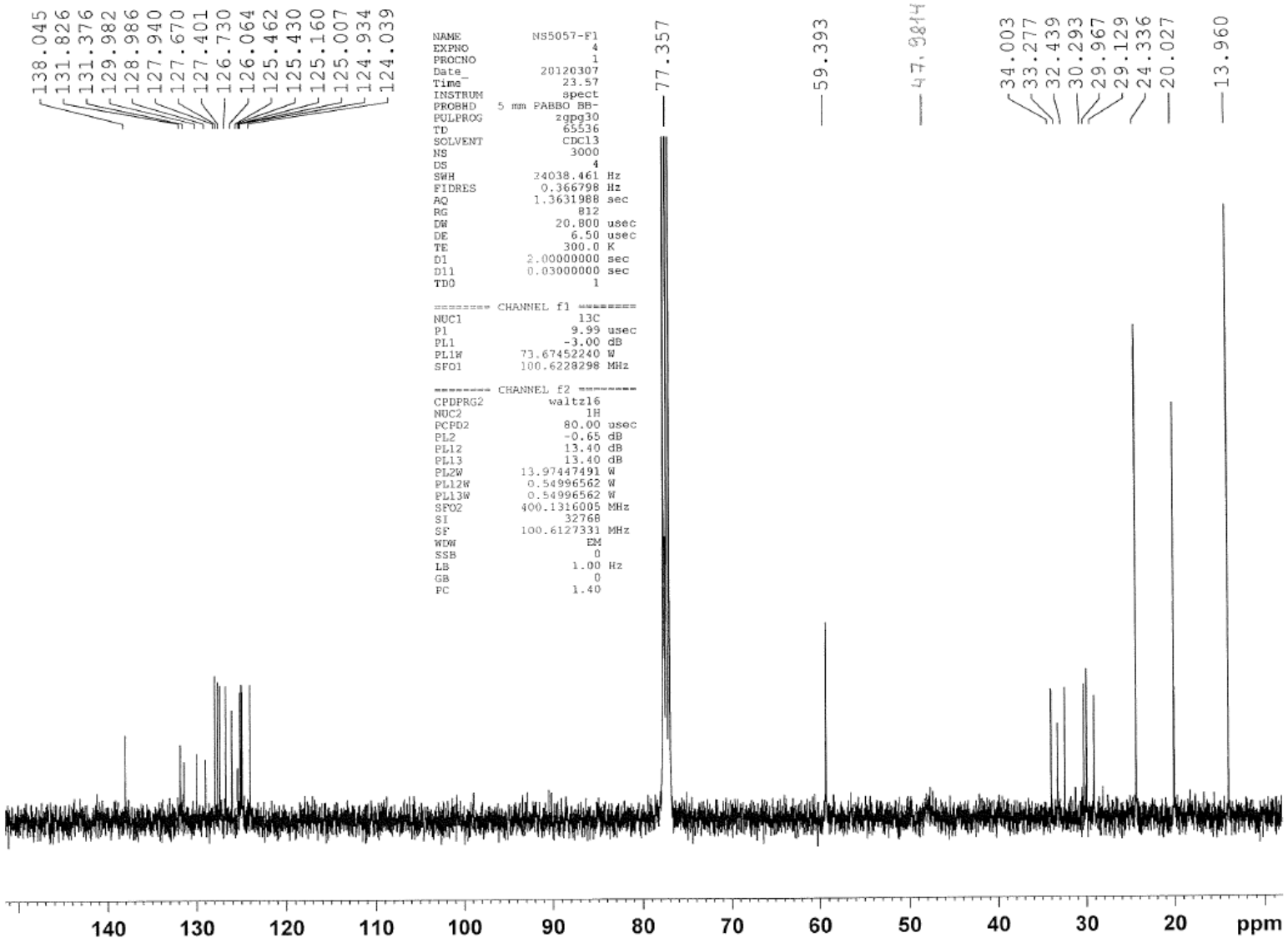
Tetrabutylammonium 3-(7′-(pyren-1″-yl)heptyl)-7,8-dicarba-*nido*-undecaborate, **11c**, ^{1}H NMR



Tetrabutylammonium 3-(7′-(pyren-1″-yl)heptyl)-7,8-dicarba-*nido*-undecaborate, **11c**, ^{11}B NMR



Tetrabutylammonium 3-(7′-(pyren-1″-yl)heptyl)-7,8-dicarba-*nido*-undecaborate, **11c**, $^{13}C\{^{1}H\}$ NMR



Synthesis of nickelacarboranes

Tetrabutylammonium 3,3′-*commo*-bis[(6-(pyren-1″-yl)propyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane] (1a). To a solution of **11a** (0.500 g, 0.810 mmol) in 5 mL of anhydrous THF was added dropwise a solution of *t*BuOK (0.100 g, 0.890 mmol) in 1 mL of anhydrous THF at 0 ^{o}C, and the reaction mixture was stirred at room temperature for 2 h. A solution of $Ni(acac)_2$ (0.103 g, 0.410 mmol) in 1 mL of anhydrous THF was added and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was then quenched with methanol (3 mL), co-evaporated with 5 mL of silica, and placed on top of a chromatography column filled with 20 mL of silica gel in hexane. The product was eluted with $CHCl_3$ gradient (0→70%) in hexane, evaporated, and dried in vacuum to give compound **1a** as a brown solid (0.340 g, 40%). HRMS (TIS): m/z = 807.3506 $[M]^-$ (calcd for $C_{42}H_{50}B_{18}Ni$ 807.5049).

Tetrabutylammonium 3,3-*commo*-bis[(6-(pyren-1′-yl)pentyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane] (1b). The compound **1b** was prepared from **11b** (0.150 g, 0.230 mmol) according to the procedure discribed for **1a**. The complex **1b** was isolated as a brown solid (0.107 g, 42%). HRMS (TIS): *m/z* = 864.5954 $[M–H]^-$ (calcd for $C_{46}H_{58}B_{18}Ni$ 863.5675).

Tetrabutylammonium 3,3-*commo*-bis[(6-(pyren-1′-yl)heptyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane) (1c). The compound **1c** was prepared from **11c** (0.170 g, 0.250 mmol) according to the procedure discribed for **1a**. The complex **1c** was isolated as a brown solid (0.120 g, 41%). HRMS (TIS): *m/z* = 920.5974 $[M+H]^-$ (calcd for $C_{50}H_{66}B_{18}Ni$ 919.6301).

3,3-*commo*-bis[(6-(pyren-1′-yl)propyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane] (2a). To a solution of **1a** (0.154 g, 0.146 mmol) in 3 mL of ACN was added 0.146 mL (0.146 mmol) of a 1 M $FeCl_3$ water solution in one portion. The reaction mixture was stirred at room temperature for 1 h (TLC control). ACN was evaporated and the product was isolated by column chromatography on silica gel using $CHCl_3$ gradient (0→50%) in hexane. After evaporation and drying in vacuum the product **2a** was isolated as a greenish-brown solid (0.0820 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, 2H, CH_{pyr}), 8.20–8.17 (m, 4H, CH_{pyr}), 8.09–8.00 (m, 10H, CH_{pyr}), 7.80 (d, 2H, CH_{pyr}), 3.95 (br s, 4H, C_{cb}–H), 4.50–1.75 (m, 16H, B–*H*), 3.38 (m, 4H, CH_2), 1.96 (m, 4H, CH_2), 1.06 (m, 4H, CH_2–B). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ 136.3, 131.7, 131.1, 130.2, 129.0, 127.9, 127.8, 127.7, 127.1, 126.3, 125.45, 125.42, 125.3, 125.18, 125.10, 123.6, 67.8, 35.9, 30.3, 17.2 (C-B). ^{11}B NMR (160 MHz, $CDCl_3$): δ 18.4, 4.4, 2.5, -6.7. HRMS (ESI): *m/z* = 807.4627 $[M]^-$ (calcd for $C_{42}H_{50}B_{18}Ni$ 807.5049).

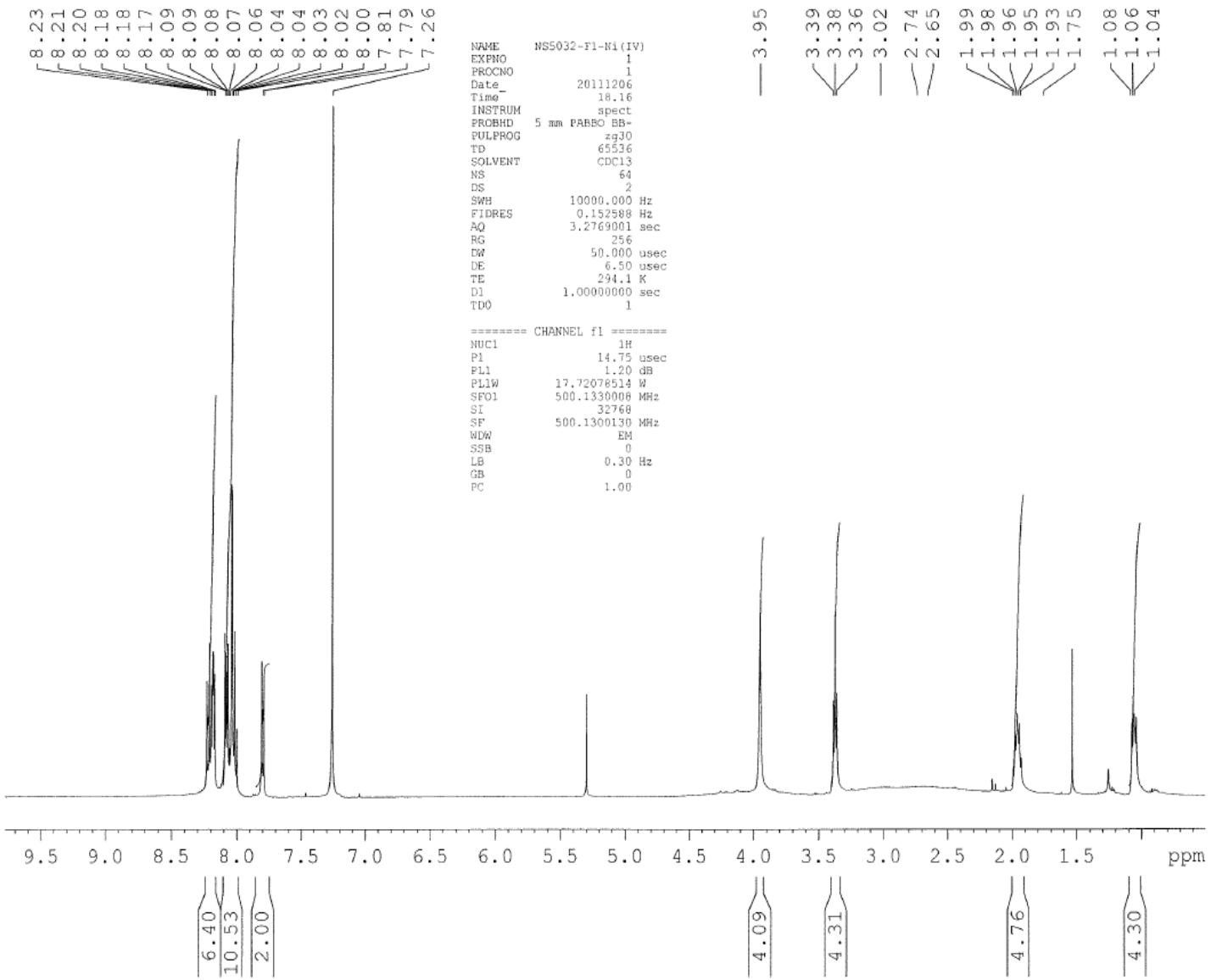
3,3-*commo*-bis[(6-(pyren-1′-yl)pentyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane) (2b). The compound **2b** was prepared from **1b** (0.0820 g, 0.0742 mmol) according to the procedure discribed for **2a**. The complex **2b** was isolated as a greenish brown solid (0.0470 g, 73%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.38 (d, 2H, CH_{pyr}), 8.27 (d, 4H, CH_{pyr}), 8.23–8.19 (m, 4H, CH_{pyr}), 8.13 (m, 4H, CH_{pyr}), 8.06 (t, 2H, CH_{pyr}), 7.95 (d, 2H, CH_{pyr}), 5.27 (br s, 4H, C_{cb}–H), 4.50–1.75 (m, 16H, B–*H*), 3.39 (m, 4H, CH_2), 1.87 (m, 4H, CH_2), 1.56 (m, 8H, CH_2), 1.10 (br m, 4H, CH_2–B). ^{13}C{^{1}H} (125 MHz, acetone-d_6): δ 138.9, 133.1, 132.6, 131.4, 130.1, 129.16, 129.10, 128.8, 128.1, 127.6, 126.58, 126.54, 126.50, 126.3, 125.1, 34.7, 33.4, 31.1*, 31.0*, 30.8*, 30.7*. ^{11}B NMR (160 MHz, acetone-d_6): δ 17.5, 2.3, –7.2. HRMS (TIS): *m/z* = 864.4905 $[M–H]^-$ (calcd for $C_{46}H_{58}B_{18}Ni$ 863.5675).

3,3-*commo*-bis[(6-(pyren-1′-yl)heptyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane) (2c). The compound **2c** was prepared from **1c** (0.138 g, 0.12 mmol) according to the procedure discribed for **2a**. The complex **2c** was isolated as a greenish brown solid (0.0610 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, 2H, CH_{pyr}), 8.14 (d, 4H, CH_{pyr}), 8.10–8.07 (m, 4H, CH_{pyr}), 8.03-7.96 (m, 6H, CH_{pyr}), 7.85 (d, 2H, CH_{pyr}), 4.12 (br s, 4H, C_{cb}-H), 4.50–1.50 (m, 16H, B-*H*), 3.33 (m, 4H, CH_2), 1.85 (m, 4H, CH_2), 1.45 (m, 4H, CH_2), 1.36 (m, 12H, CH_2), 0.97 (m, 4H, CH_2). ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ 137.4, 131.7, 131.2, 130.0, 128.9, 127.8, 127.6, 127.4, 126.8, 126.1, 125.4, 125.3, 125.1, 125.1, 124.9, 123.8, 68.1, 33.8, 32.4, 32.1, 30.0, 29.9, 29.5, 28.3, 17.51 (C-B). ^{11}B NMR (160 MHz, $CDCl_3$): δ 18.4, 4.3, –6.6. HRMS (TIS): *m/z* = 920.6734 $[M+H]^-$ (calcd for $C_{50}H_{66}B_{18}Ni$ 919.6301).

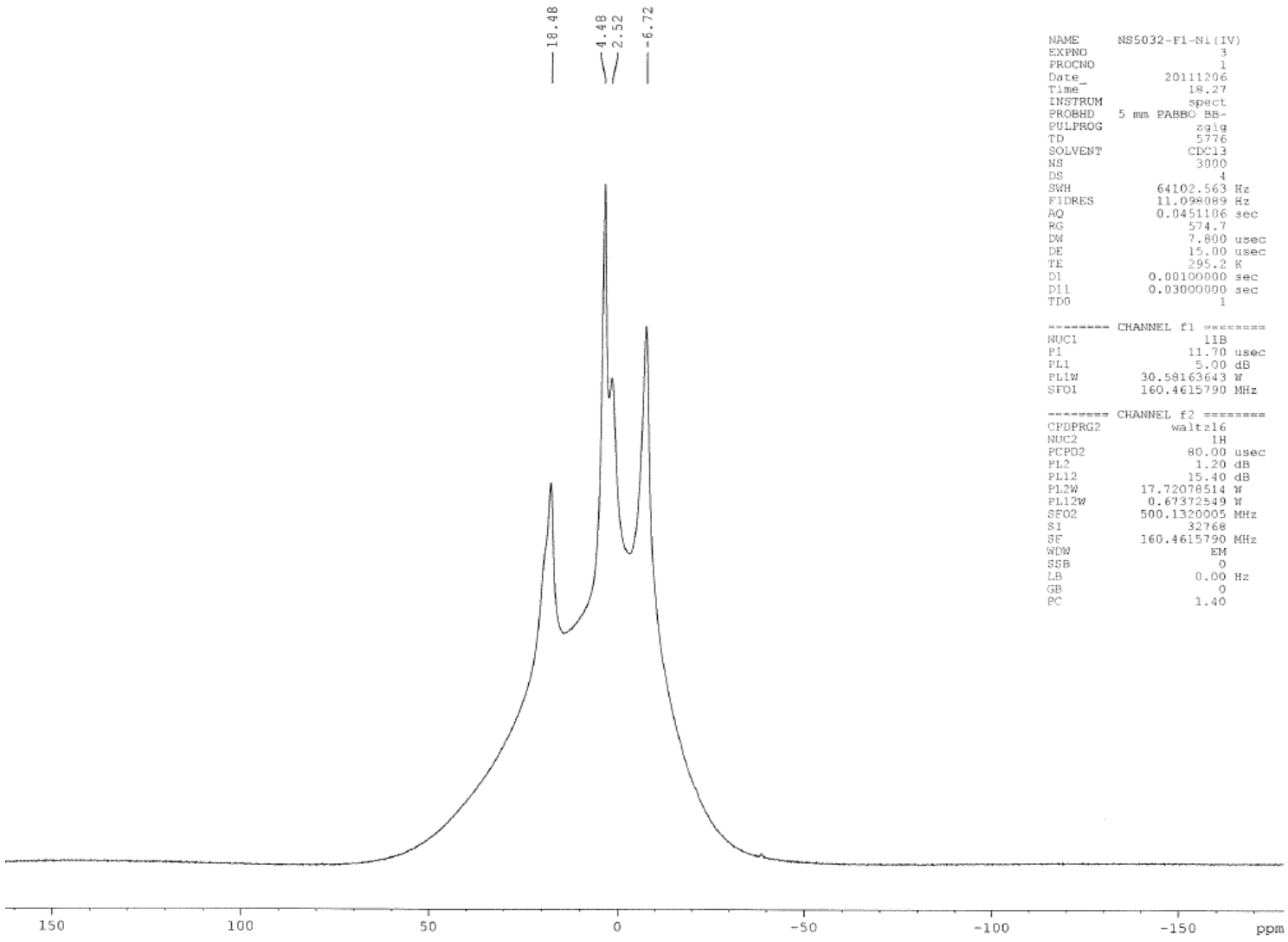
Tetrabutylammonium 3,3'-*commo*-(1,2-dicarba-3-nickela-*closo*-dodecaborane)-[(6′-(pyren-1″-yl)pentyl)-1′,2′-dicarba-3′-nickela-*closo*-dodecaborane] (13). To a solution of **11b** (0.265 g, 0.410 mmol) and **12** (0.154 g, 0.410 mmol) in 5 mL of anhydrous THF was added dropwise a solution of *t*BuOK (0.114 g, 1.02 mmol) in 2 mL of anhydrous THF at 0 ^{o}C, and the reaction mixture was stirred at room temperature for 2 h. A solution of $Ni(acac)_2$ (0.116 g, 0.451 mmol) in 1 mL of anhydrous THF was added and the reaction mixture was stirred at room temperature for 16 h. Reaction mixture was then quenched with methanol (3 mL), co-evaporated with 5 mL of silica and placed on top of a chromatography column filled with 20 mL of silica gel in hexane. Mixture was eluted with $CHCl_3$ gradient (0→100%) in hexane, evaporated, and dried in vacuum to give compound **13** as a brown solid (0.085 g, 35%). HRMS (TIS): *m/z* = 593.3882 $[M]^-$ (calcd for $C_{25}H_{40}B_{18}Ni$ 593.4267).

3,3′-*commo*-(1,2-dicarba-3-nickela-*closo*-dodecaborane)-[(6′-(pyren-1″-yl)pentyl)-1′,2′-dicarba-3′-nickela-*closo*-dodecaborane] (14). The compound **14** was prepared from **13** (0.100 g, 0.120 mmol) according to the procedure discribed for **2a**. The complex **14** was isolated as a greenish-brown solid (0.0490 g, 70%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.40 (d, 1H, CH_{pyr}), 8.30–8.27 (m, 2H, CH_{pyr}), 8.24–8.21 (m, 2H, CH_{pyr}), 8.15 (m, 2H, CH_{pyr}), 8.08 (t, 1H, CH_{pyr}), 7.97 (d, 1H, CH_{pyr}), 5.01 (br s, 4H, C_{cb}–H), 4.50–1.35 (m, 16H, B–*H*), 3.42 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 1.60 (m, 4H, CH_2), 1.32 (br s, 2H, CH_2). ^{13}C{^{1}H} (100 MHz, acetone-d_6): δ 138.9, 133.1, 132.6, 131.5, 130.2, 129.17, 129.10, 128.8, 128.1, 127.6, 126.6, 126.55, 126.3, 125.1, 34.6, 33.9, 33.2, 31.5*. ^{11}B NMR (128 MHz, acetone-d_6): δ 18.1, 16.0, 2.9, 2.0, –6.7, –7.4, –16.6. HRMS (TIS): *m/z* = 593.4103 $[M]^-$ (calcd for $C_{25}H_{40}B_{18}Ni$ 593.4267).

3,3-*commo*-bis[(6-(pyren-1′-yl)propyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane], **2a**, ^{1}H NMR



3,3-*commo*-bis[(6-(pyren-1′-yl)propyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane], **2a**, $^{11}B\{^{1}H\}$ NMR



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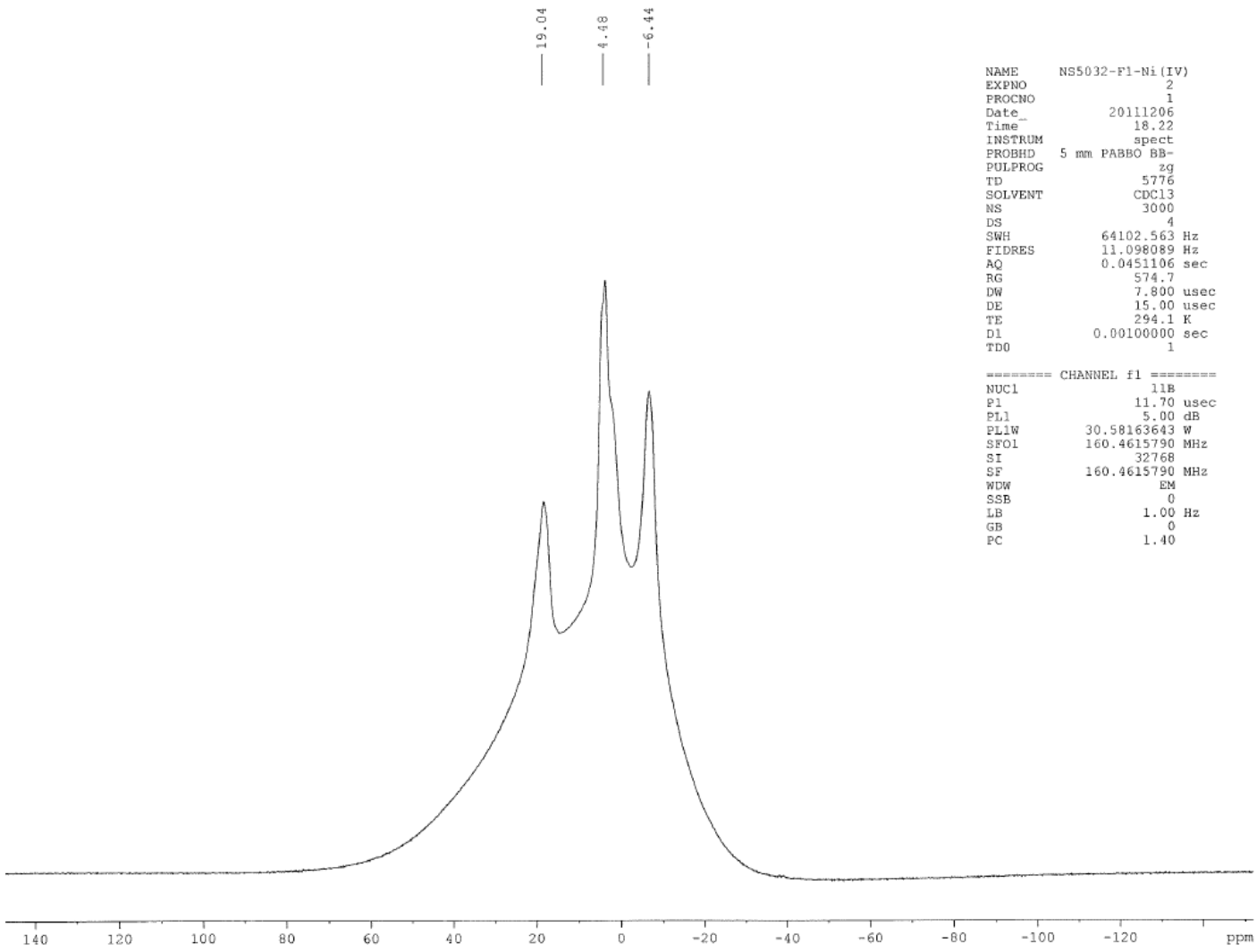
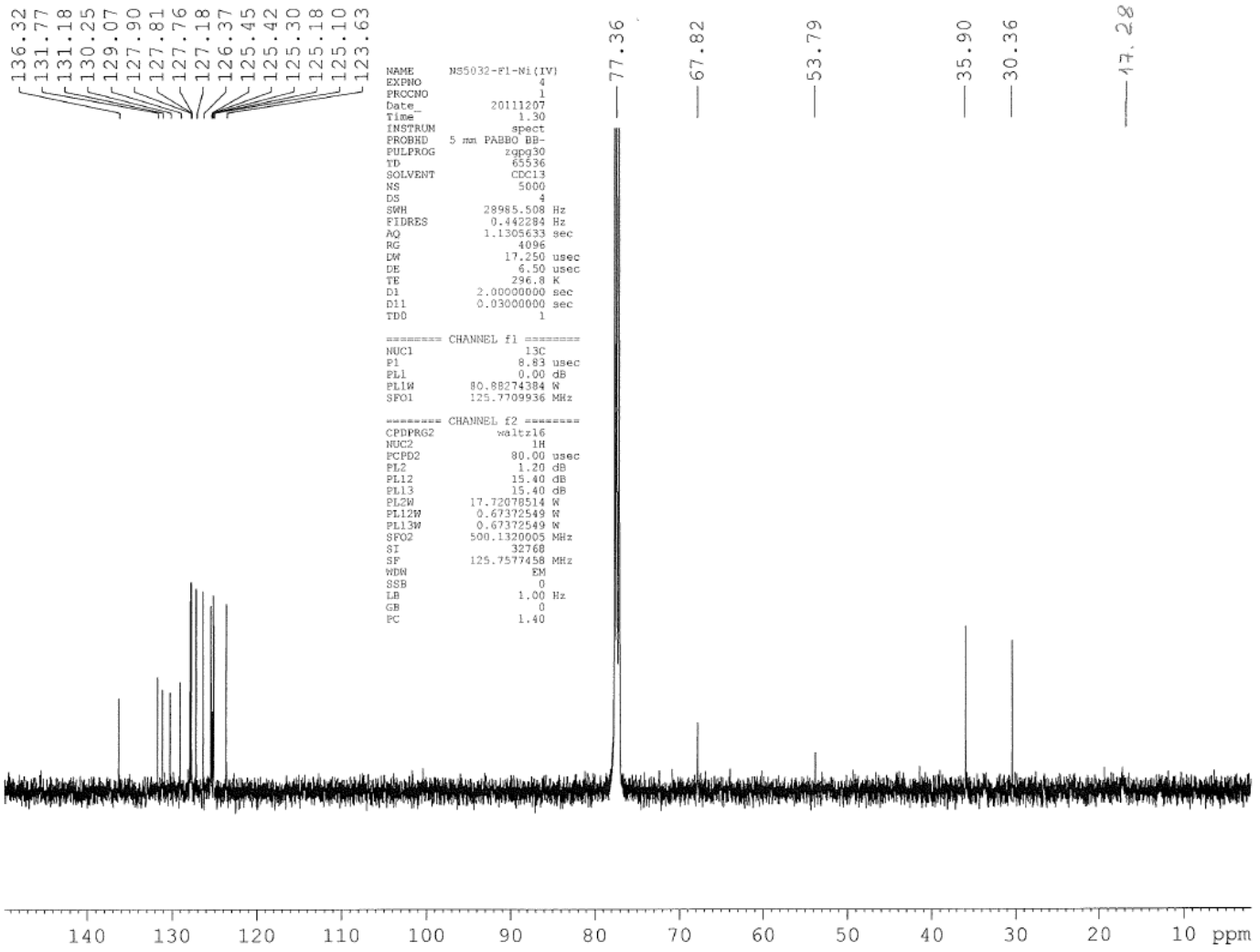
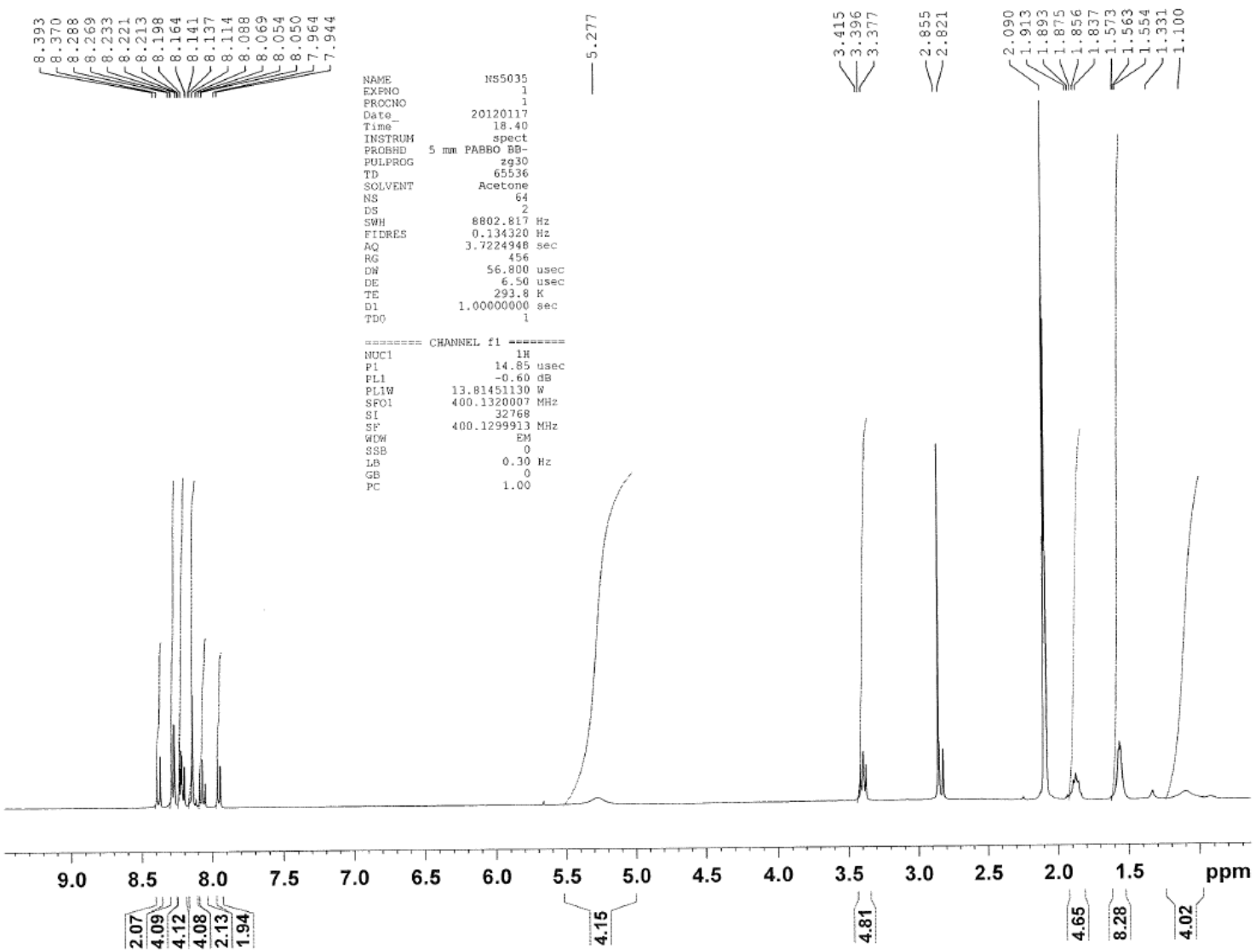
3,3-*commo*-bis[(6-(pyren-1′-yl)propyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane], **2a**, ^{11}B NMR



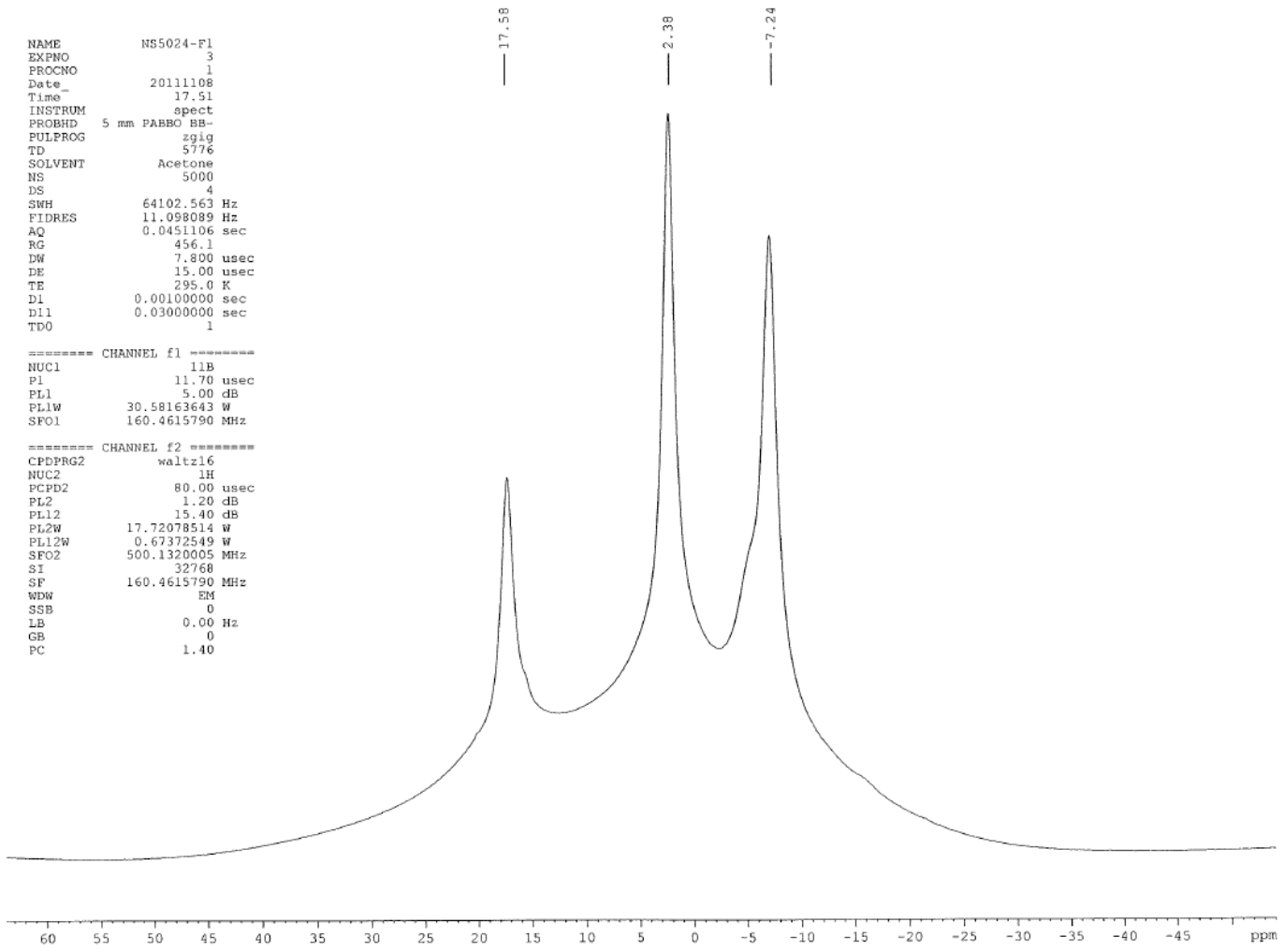
3,3-*commo*-bis[(6-(pyren-1′-yl)propyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane], **2a**, $^{13}C\{^{1}H\}$ NMR



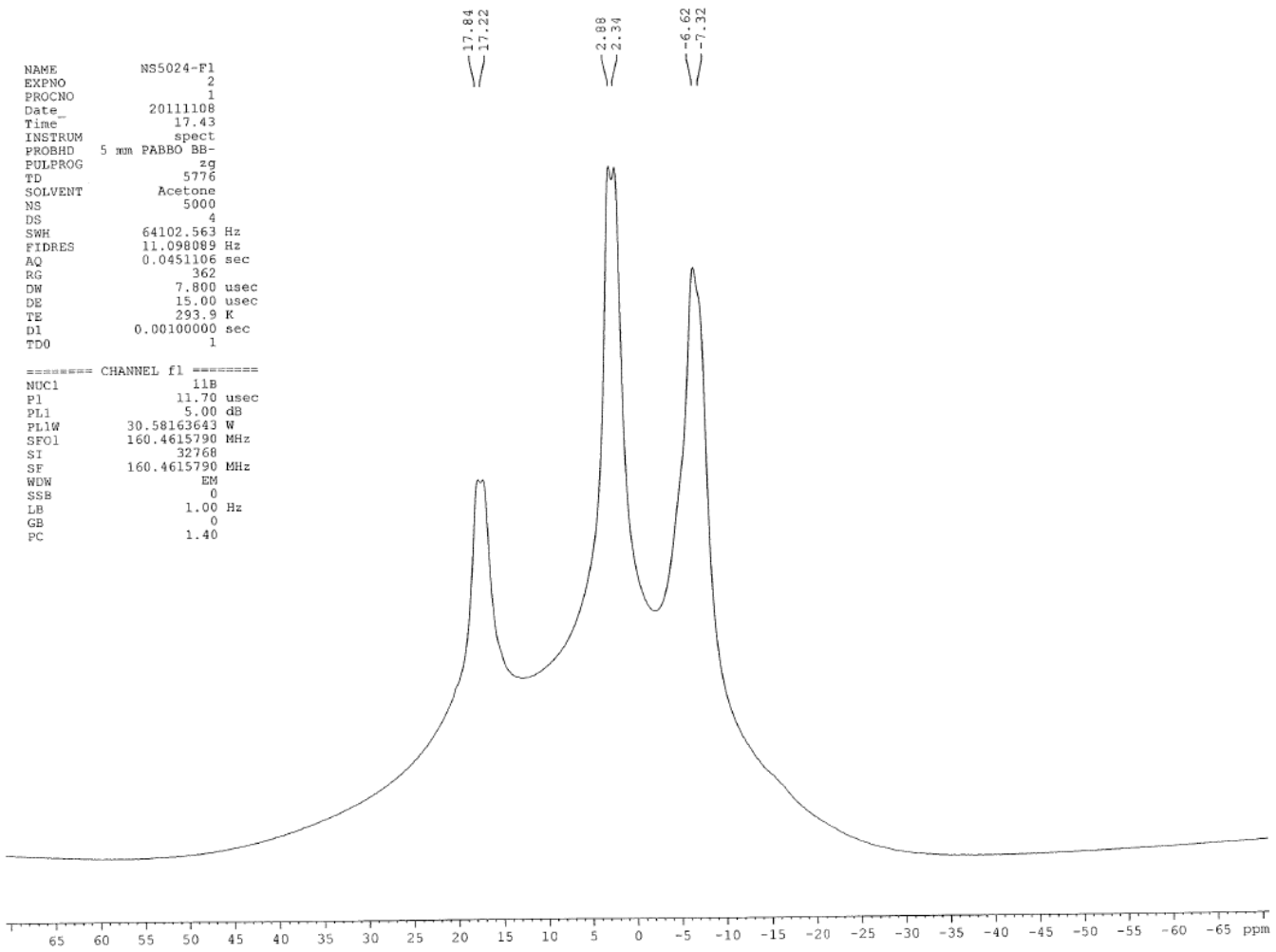
3,3-*commo*-bis[(6-(pyren-1′-yl)pentyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane), **2b**, ^{1}H NMR



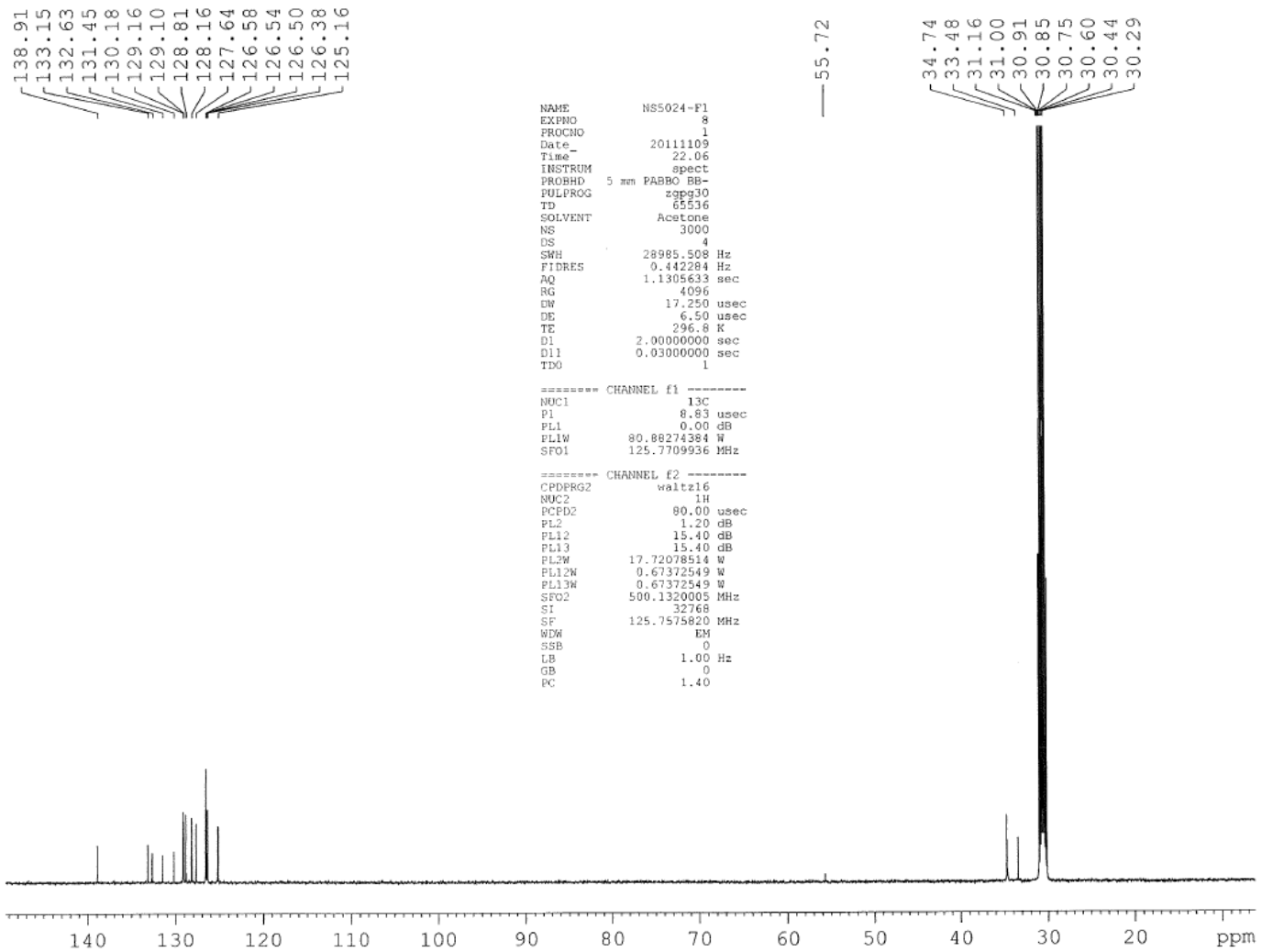
3,3-*commo*-bis[(6-(pyren-1′-yl)pentyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane), **2b**, $^{11}B\{^{1}H\}$ NMR



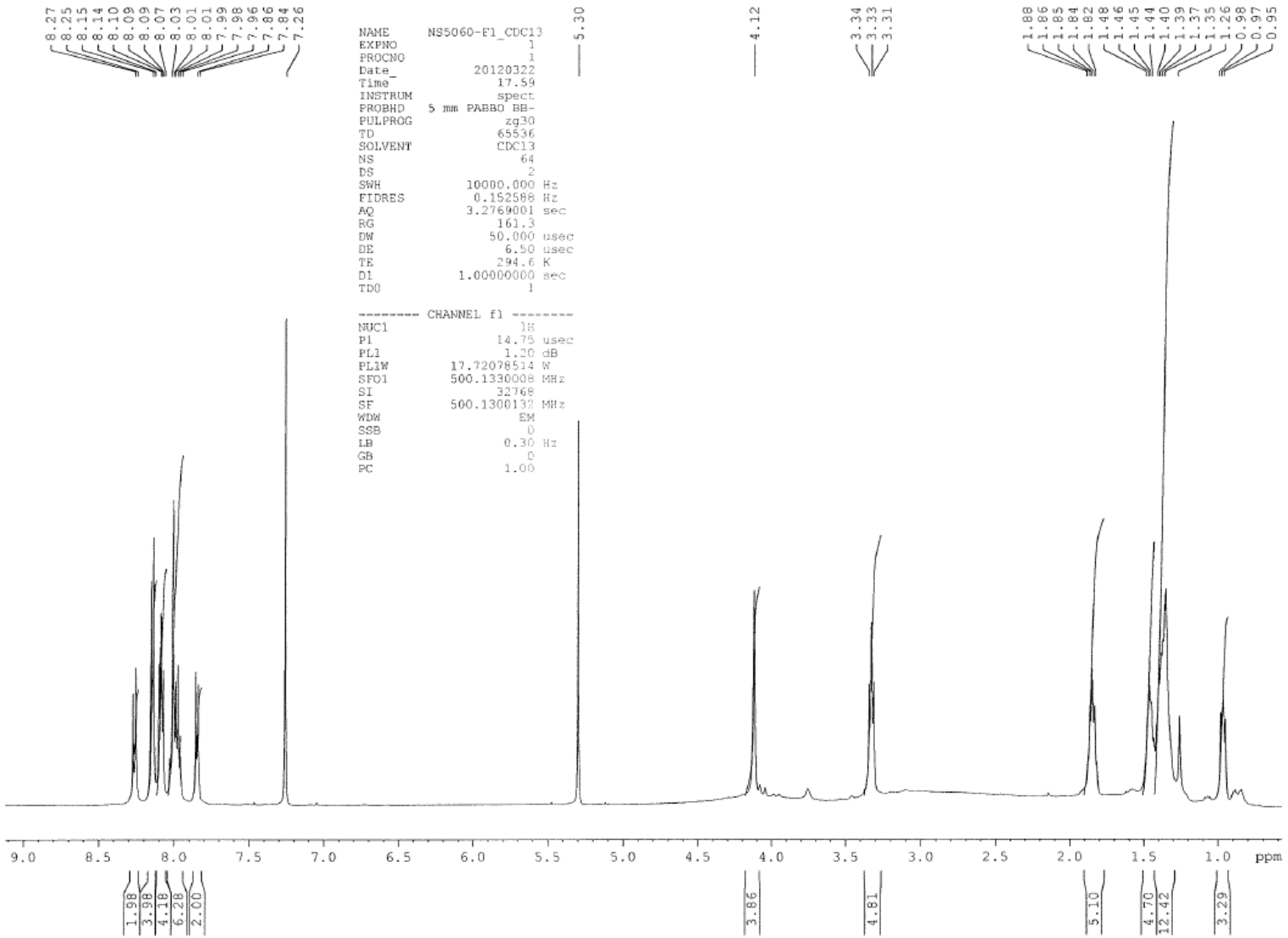
3,3-*commo*-bis[(6-(pyren-1′-yl)pentyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane), **2b**, ^{11}B NMR



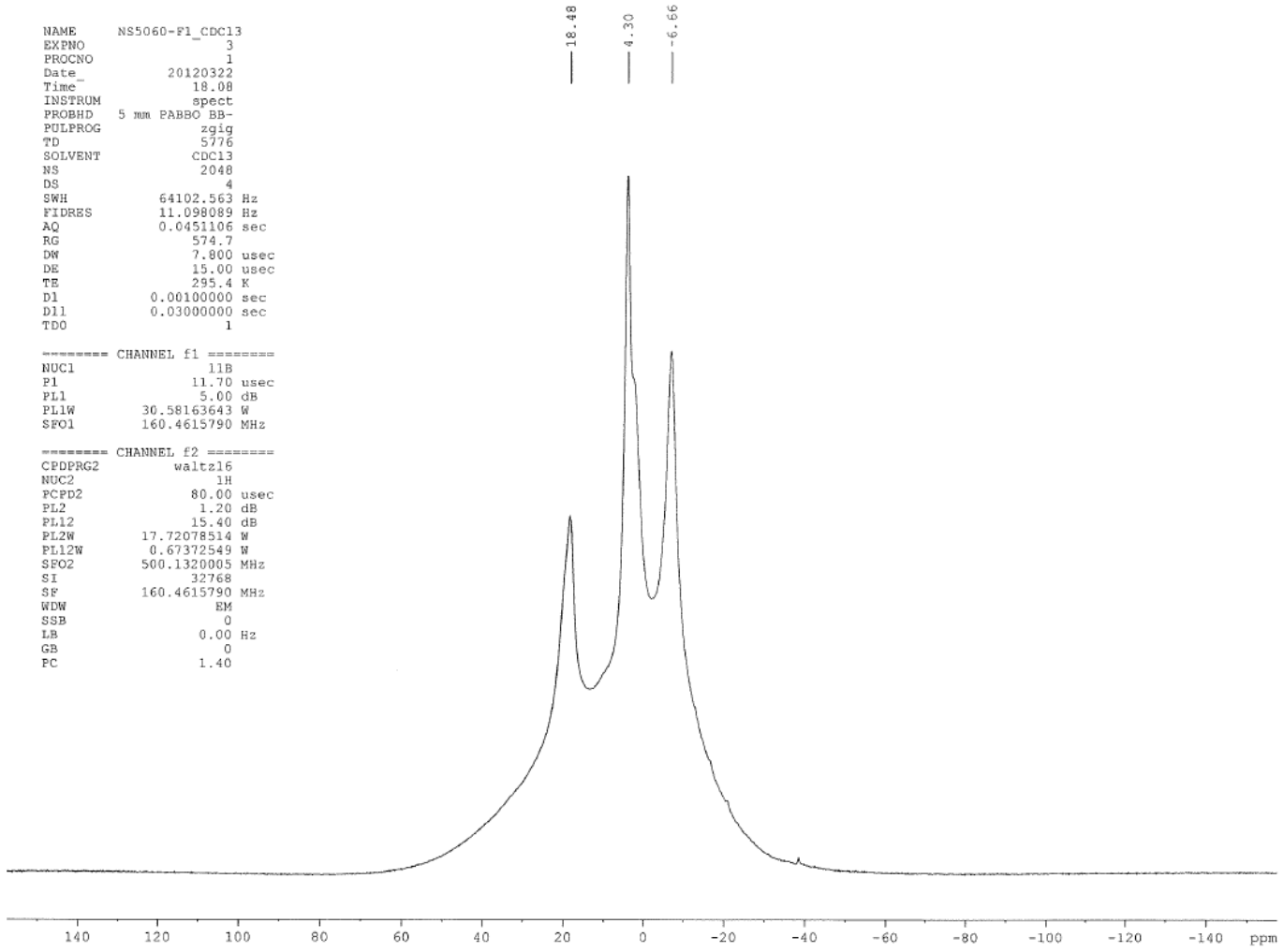
3,3-*commo*-bis[(6-(pyren-1′-yl)pentyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane), **2b**, $^{13}C\{^{1}H\}$ NMR



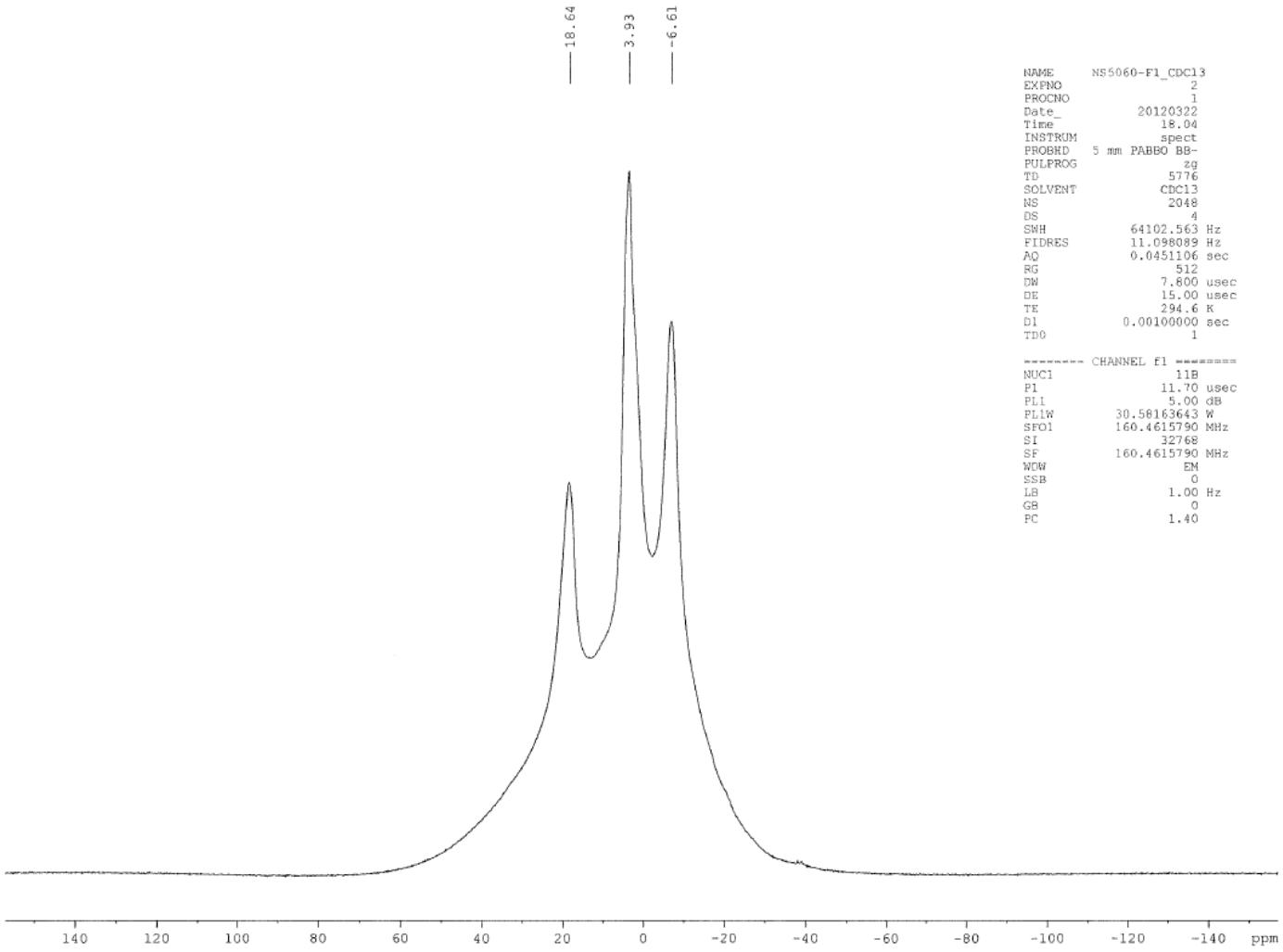
3,3-*commo*-bis[(6-(pyren-1′-yl)heptyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane), **2c**, ^{1}H NMR



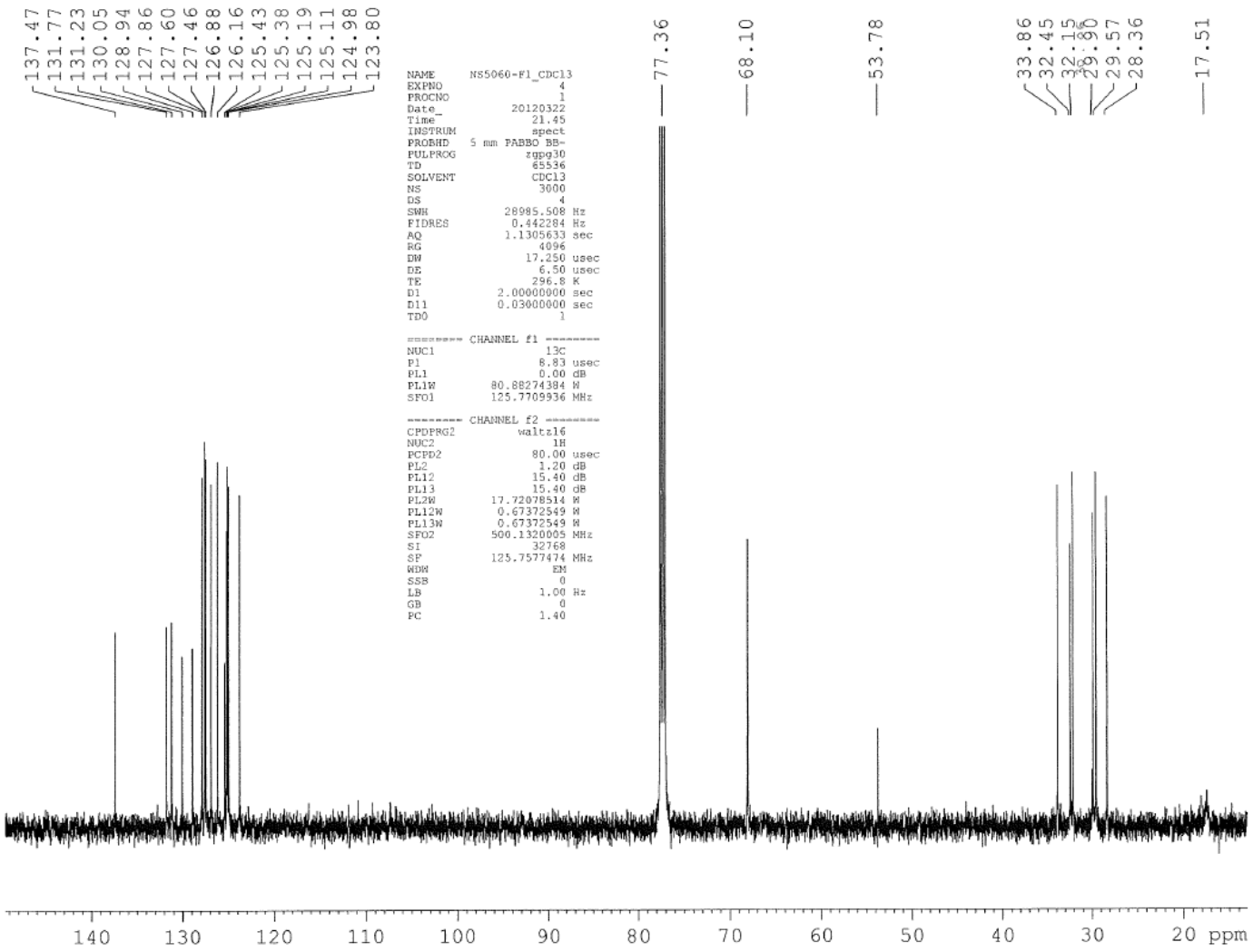
3,3-*commo*-bis[(6-(pyren-1′-yl)heptyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane), **2c**, $^{11}B\{^{1}H\}$ NMR



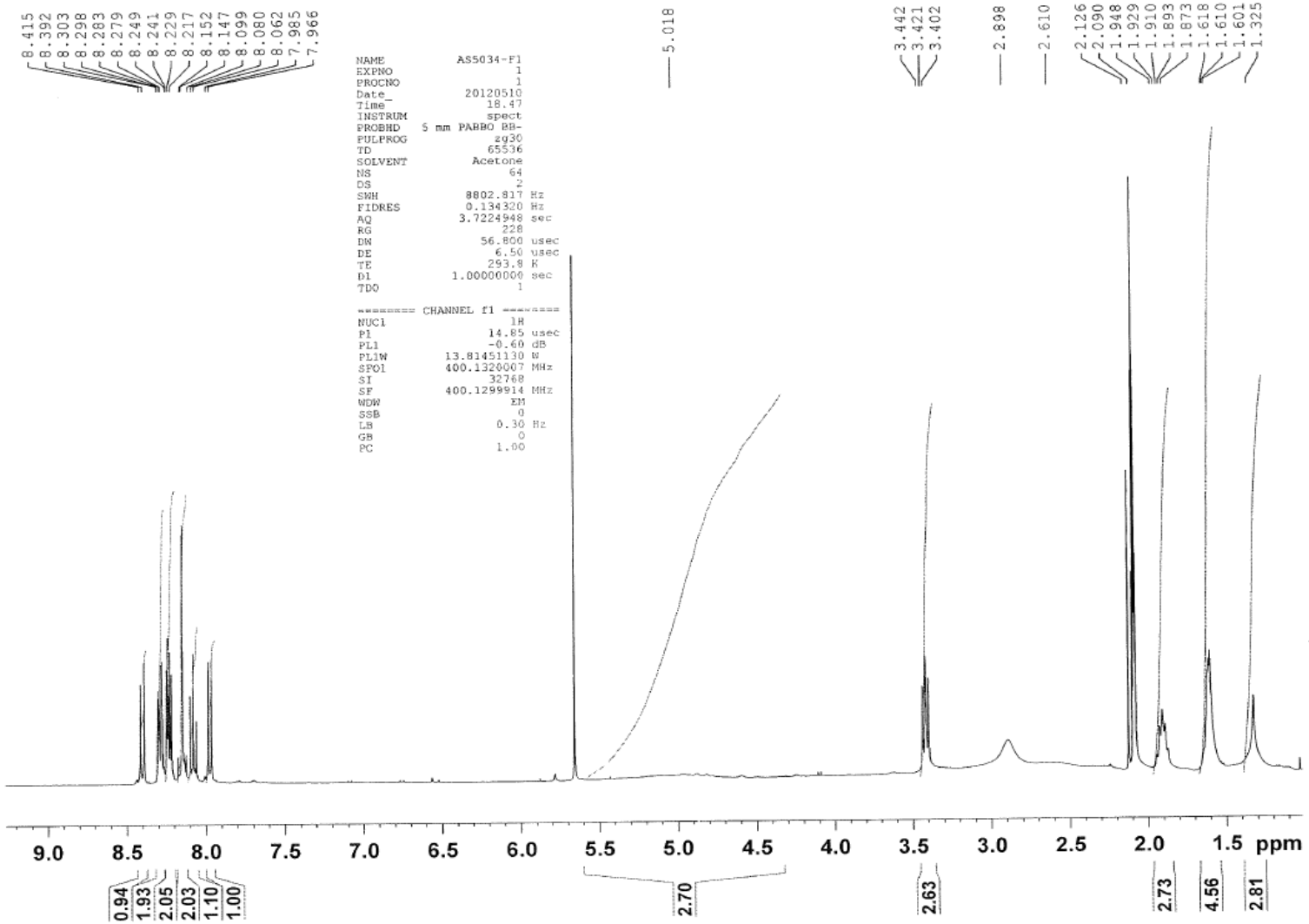
3,3-*commo*-bis[(6-(pyren-1′-yl)heptyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane), **2c**, ^{11}B NMR



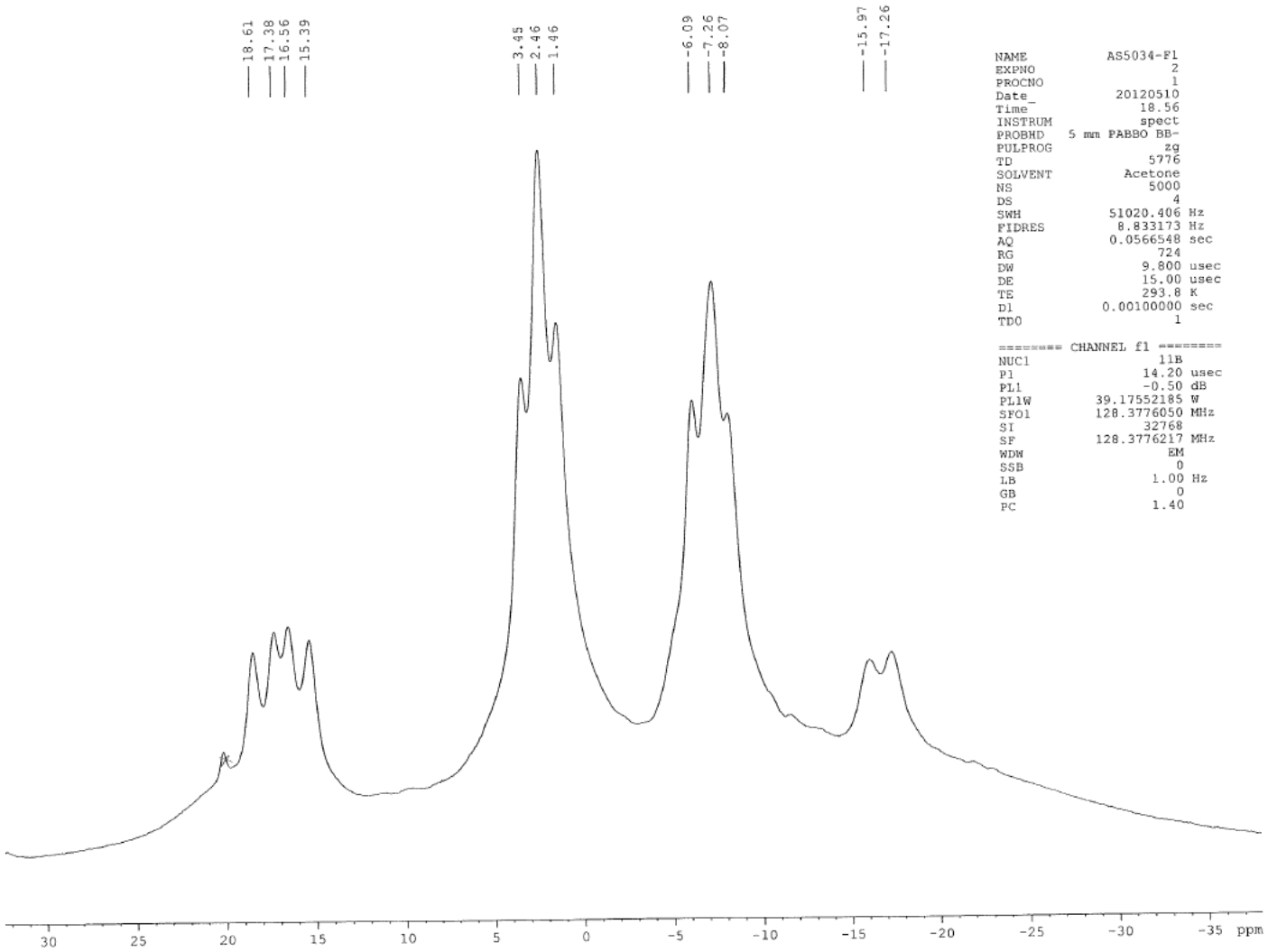
3,3-*commo*-bis[(6-(pyren-1′-yl)heptyl)-1,2-dicarba-3-nickela-*closo*-dodecaborane), **2c**, $^{13}C\{^{1}H\}$ NMR



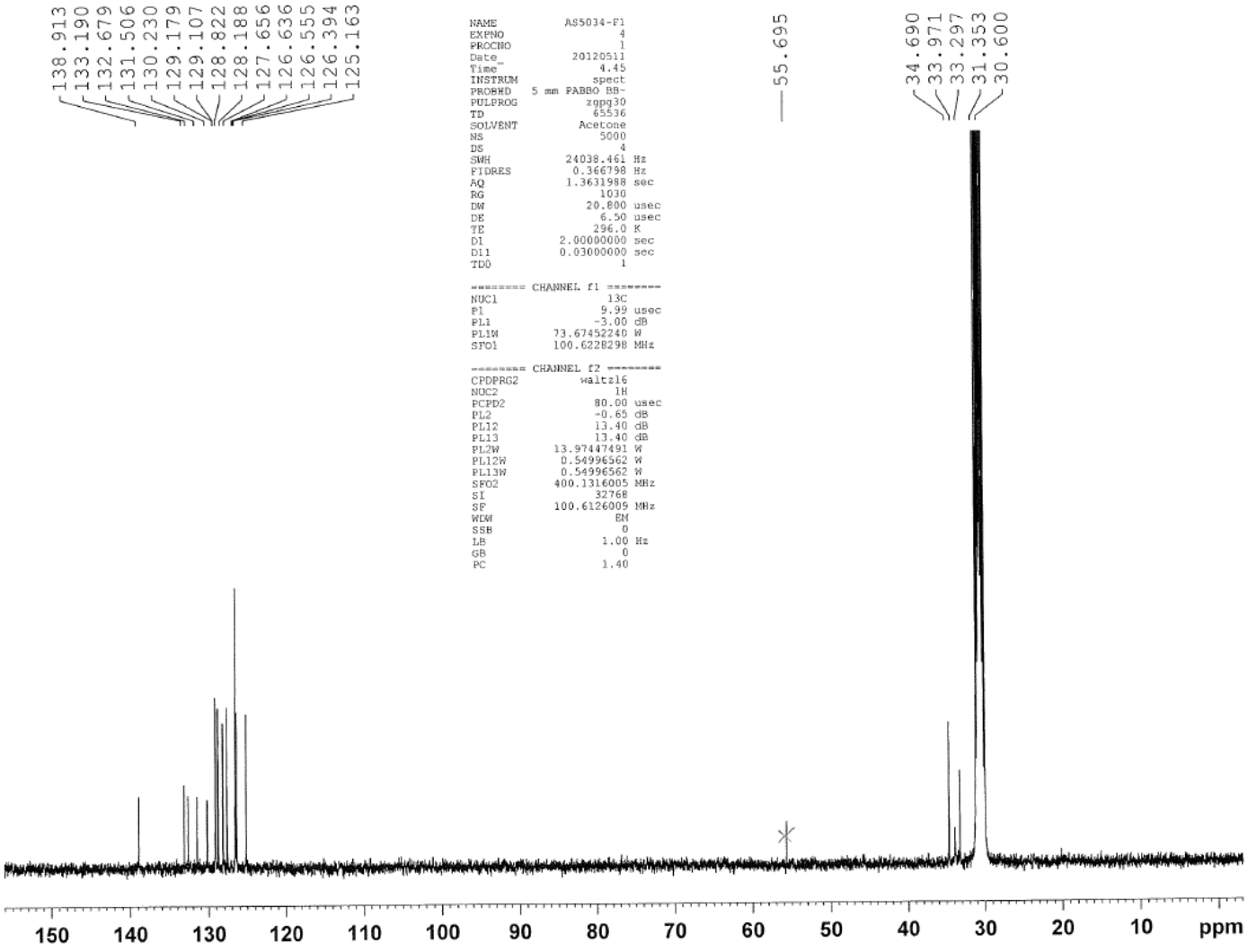
3,3′-*commo*-(1,2-dicarba-3-nickela-*closo*-dodecaborane)-[(6′-(pyren-1″-yl)pentyl)-1′,2′-dicarba-3′-nickela-*closo*-dodecaborane], **14**, ^{1}H NMR



3,3′-*commo*-(1,2-dicarba-3-nickela-*closo*-dodecaborane)-[(6′-(pyren-1″-yl)pentyl)-1′,2′-dicarba-3′-nickela-*closo*-dodecaborane], **14**, ^{11}B NMR



3,3′-*commo*-(1,2-dicarba-3-nickela-*closo*-dodecaborane)-[(6′-(pyren-1″-yl)pentyl)-1′,2′-dicarba-3′-nickela-*closo*-dodecaborane], **14**, $^{13}C\{^{1}H\}$ NMR



II. X-ray Diffraction Studies

X-ray quality crystals of the compound **2b** were obtained by the slow vapor diffusion of hexane into chloroform. Yellow plate of **2b** was coated with paratone oil and mounted onto a MiTeGen MicroMount fiber. Complete and redundant data were collected on a single flash-cooled crystal (T = 100 K with an Oxford Cryostream LT device) using a Bruker X8 Prospector Ultra X-ray diffractometer system with a three-circle goniometer and an APEX II CCD area detector mounted on D8-platform and equipped with a Cu-IμS (λ = 1.54178 Å) microfocus X-ray source operated at 30 W. The frames were collected with a scan width of 0.5° in ω and an exposure time of 20 s/frame. The intensity datasets consisted of φ and ω scans at a crystal to detector distance of 4.00 cm. The APEX II[4] and SAINT[5] software packages were used for data collection and data integration. The data were corrected for absorption effects using the SADABS empirical method.[6] The structures were solved and refined using the Bruker SHELXTL[7] software package. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms, except for those on carbon atoms of dicabollide cages, were included at geometrically idealized positions. The H-atoms of dicarbollide cage carbons were located in difference Fourier maps and were refined individually, with C–H bond distances restrained to 1.0 Å using DFIX; thus, the refinement was mixed. In a single crystallographically unique molecule, one of the methylpyrenyl groups is severely disordered over two orientations with an occupancy ratio of 0.69:0.31. In the same plane, both conformations are rotated orthogonally with respect to each other (angle formed by the top carbon vertices of pyrenyl and the common internal carbon vertex, C(32), is 87.59°). The structure refined with the extreme anisotropic ellipsoid for one of the boron vertex, B(22). Since there was no chemical reason for this atom to have any partial non-boron character, its U^{ij} components were restrained using ISOR. The crystallographic data and the details of data collection and structure refinement are provided in Table 1S. Figures were prepared using molecular graphics in X-SEED.[89]

Table 1S. Crystallographic details for **2b**.

compound	**2b**
empirical formula	$C_{46}H_{58}B_{18}Ni$
Fw	864.21
crystal size (mm^3)	$0.15 \times 0.09 \times 0.01$
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	21.6452(7)
b (Å)	11.2557(4)
c (Å)	19.6863(6)
β (deg)	107.216(2)
V ($Å^3$)	4581.3(3)
Z	4
T (K)	100(2)
λ (Å)	1.54178
d_{calc} ($g \cdot cm^{-3}$)	1.253
μ (mm^{-1})	0.845
θ_{max} (deg)	66.50
unique data	60569
observed data [$I > 2\sigma(I)$]	4562
Parameters	747
GOF[a] on F^2	1.038
$R1$[b], $wR2$[c] [$I > 2\sigma(I)$]	0.0906, 0.2386
$R1$[b], $wR2$[c] (all data)	0.1501, 0.2856
$\Delta\rho_{max,min}$ ($e \cdot A^{-3}$)	0.799, −0.582
T_{min}/T_{max}	0.66 /0.75

[a] GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$.

[b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

The solid state structure of **2b** (Figure 1S) showed that Ni(IV) center is sandwiched between two η^5-coordinated dicarbollide ligands, $\{[C_2B_9H_{10}](CH_2)_5C_{16}H_9\}^{2-}$, in a *cis* conformation, typical for bis(dicarbollide)nickel(IV) complexes. The distances from the Ni atom to the pentagonal bonding faces of the dicarbollide ligands are 1.47 and 1.51 Å, which is within the reported range. The averaged Ni–C and Ni–B distances are 2.076(9) and 2.11(1) Å, respectively. The η^5-coordinated-C_2B_3 faces are nearly parallel (the dihedral angle is 8.0(4)°). In the crystallographically unique molecule two pentamethylene–pyrenyl arms are widely opened with the distance between internal carbon vertices of two different pyrenyl groups, C(47) and C(32), being equal to 22.56 Å. Pyrenyl groups are tilted with respect to each other at the 75° angle. In the structure, pyrenyl groups participate in a complex network of $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions.

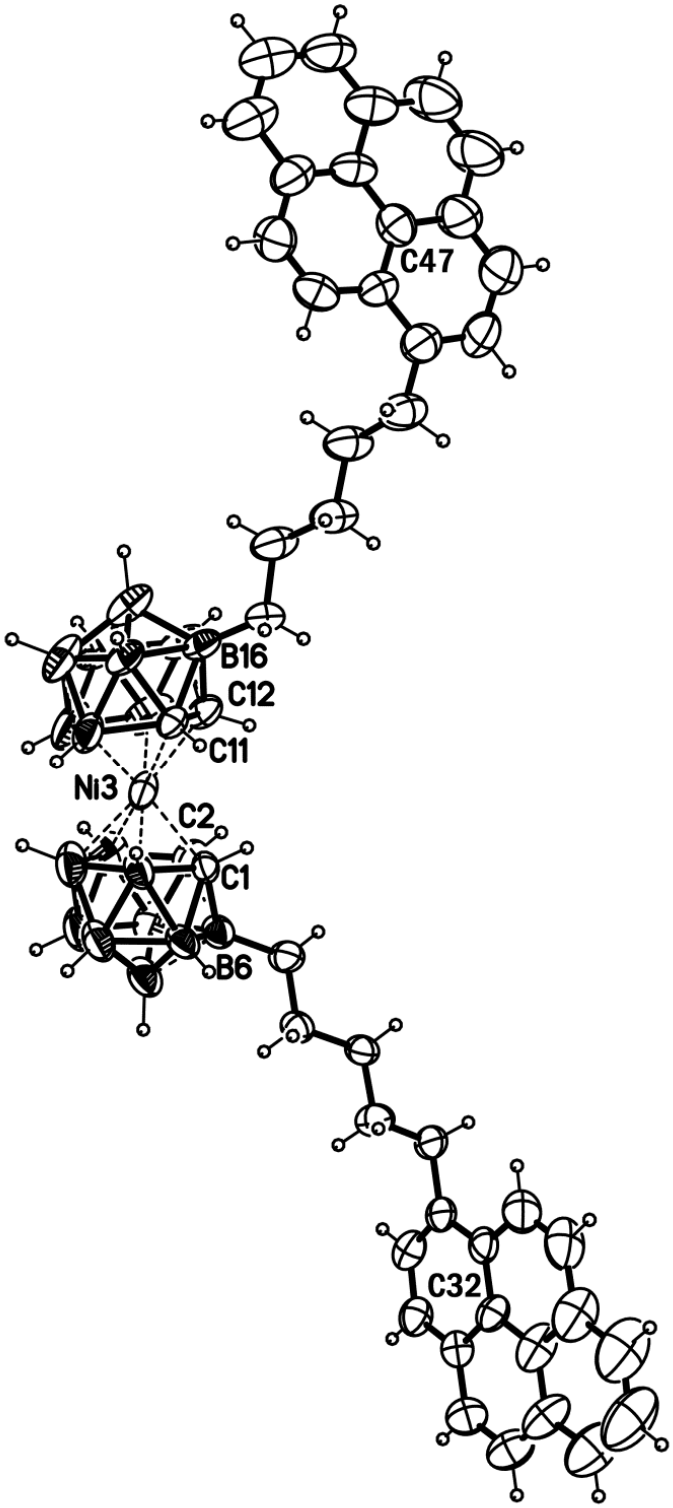
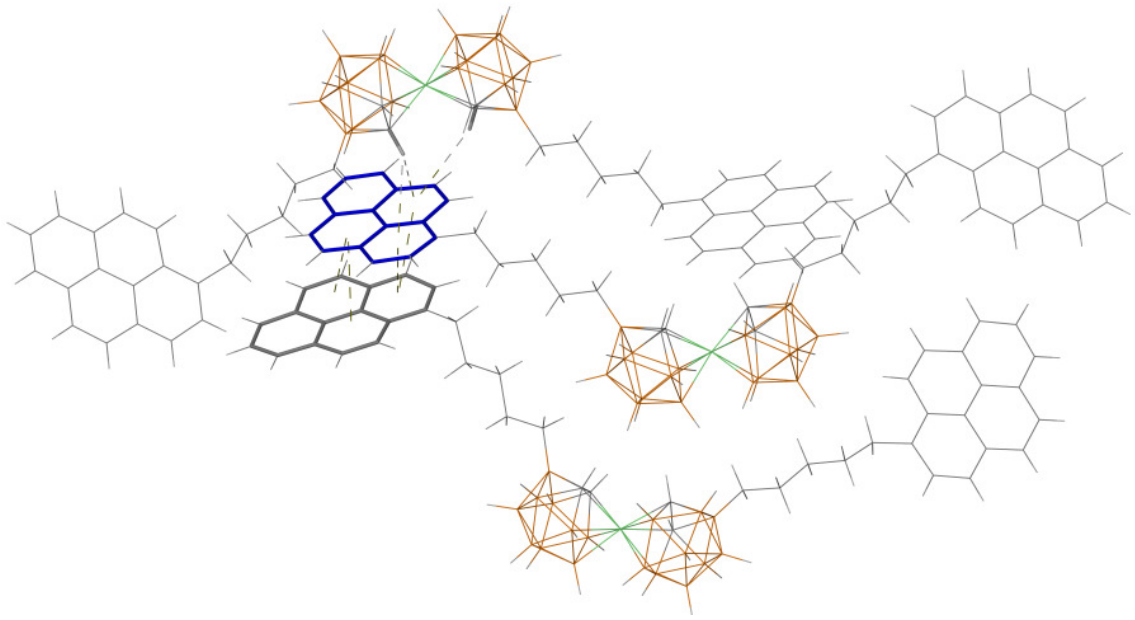


Figure 1S. The ORTEP representation of **2b** drawn at the 40% probability level. For the disordered methylpyrenyl group only the major orientation is displayed for clarity.

Pyrenyl group of one of the pentamethylene–pyrenyl arms is severely disordered over two orientations. In the solid state this disordered pyrenyl group is sandwiched between the dicarbollide cage and the ordered pyrenyl group of another molecule at the C(47)···C(32) distance of 3.94(1) Å (the dihedral angle between the planes is 4.4(2)°). Two different orientations of the disordered pyrenyl group in their nearest neighborhood are displayed in Figure 2S. Depending on the orientation, pyrenyl groups form distinct intermolecular bonding patterns given in detail in Table 2S. Intermolecular contacts are dominated by the C–H···π interactions, where H-donor is the acidic C–H of the dicarbollide cage, as well as by π···π interactions formed between the two slipped-parallel pyrenyl groups. The intermolecular $C_{carborane}$–H···π contacts have been described elsewhere as weak non-classical C–H···π hydrogen bonds[10] and are common in supramolecular assemblies of carboranes.[11]

The ordered pyrenyl group is sandwiched between the face-to-face (the dihedral angle between the planes is 4.4(2)°) and point-to-face aligned pyrenyl groups (the dihedral angle between the planes is 76.3(2)° and 71.6(2)°). In face-to-face alignment with the disordered pyrenyl group, multiple π···π contacts are observed and those were described above. In point-to-face alignment, the ordered pyrenyl group interacts with two pyrenyl groups, one of which is disordered, through numerous C–H···π contacts summarized in Table 2 and displayed in Figure 3S.

Orientation 1



Orientation 2

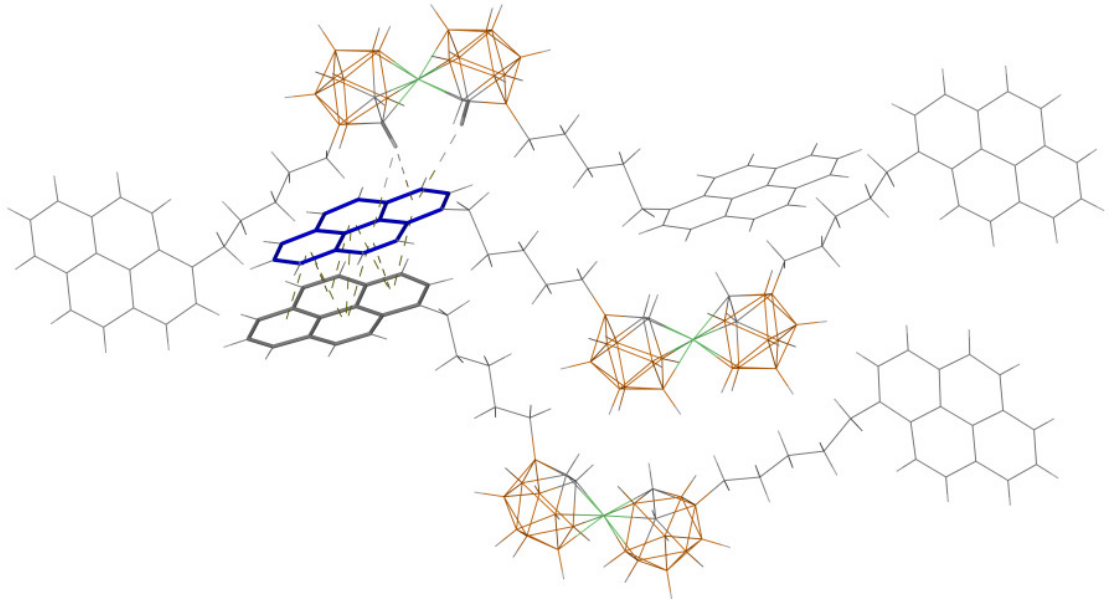
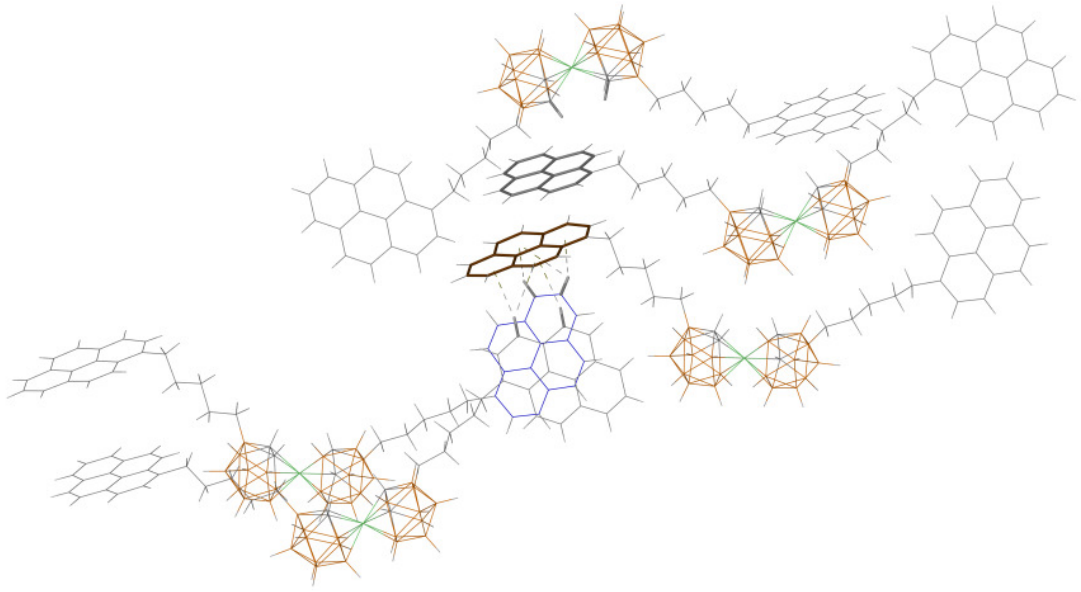


Figure 2S. A fragment of the packing alignment displaying interactions of the disordered pyrenyl group. The selected intermolecular $\pi\cdots\pi$ and $C_{carborane}$–H$\cdots\pi$ bonding interactions are displayed with dashed lines.

Table 2S. Summary of intermolecular interactions (Å) in the structure of **2b**.

Pyrenyl groups:		Disordered		Ordered
Ordered		Orientation 1	Orientation 2	
	$C_{carborane}$–H$\cdots\pi$	3.250	3.053	
		3.353	3.490	
		3.775	3.643	
Face-to-face	$\pi\cdots\pi$	4.229	3.956	
		3.873	3.736	
		3.842	4.064	
		3.770	3.869	
			3.506	
			4.061	
			3.511	
			4.020	
			4.187	
Point-to-face	C–H$\cdots\pi$	2.986	3.975	3.004
		3.408		2.998
		2.873		3.576

Orientation 1



Orientation 2

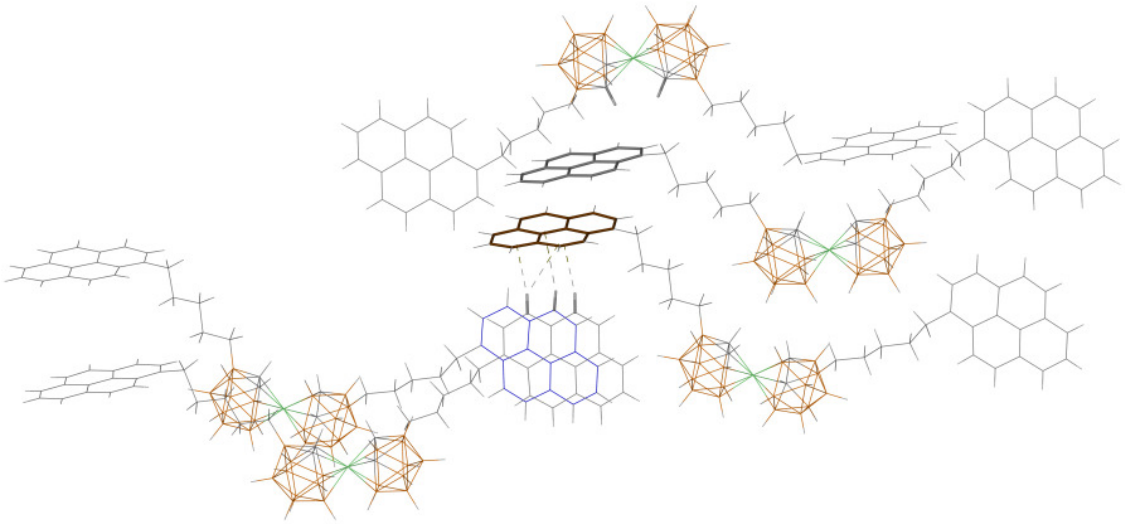


Figure 3S. A fragment of the packing alignment displaying interactions of the ordered pyrenyl group. The selected intermolecular C–H$\cdots\pi$ bonding interactions are displayed with dashed lines.

III. Electrochemistry of the disubstituted nickel compexes 1 and 2

Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 potentiostat using a traditional three electrode cell where the electrodes were; a 1.6 mm diameter platinum working electrode, platinum wire counter electrode, and a platinum quasi-reference electrode. CV's were recorded using a scan rate of 100 mV/s in an argon atmosphere. All half-wave potentials are referenced against the ferrocene/ferrocenium redox couple. Electrochemical experiments were all carried out in a solution of 0.1 M tetrabutylammonium hexafluorophosphate in degassed acetonitrile. For electrochemical experiments the final compound concentration was 1-3 mg mL^{-1}. Half-wave potentials for compounds **1a-c** versus the Fc^{+}/Fc couple were -225, -231, and -232 mV, respectively.

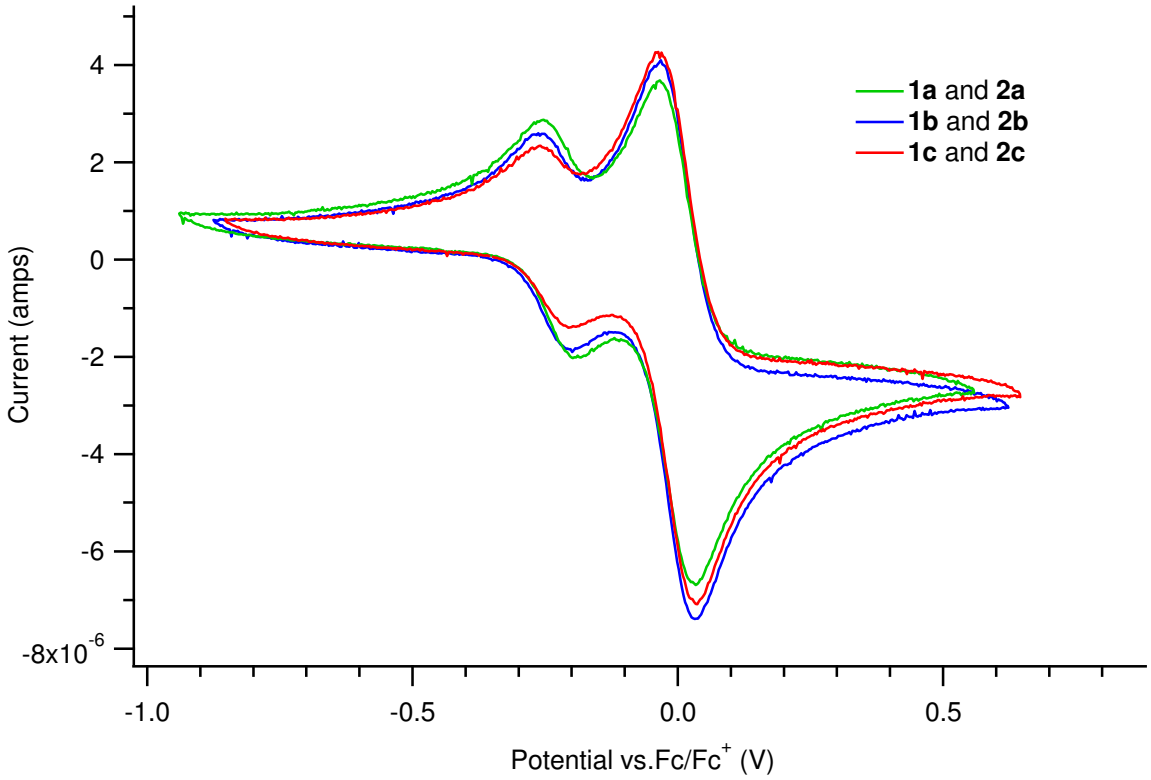


Figure 4S. Cyclic voltammetries of complexes **1/2**

IV. UV spectra of the nickel complexes 1, 2 and 14

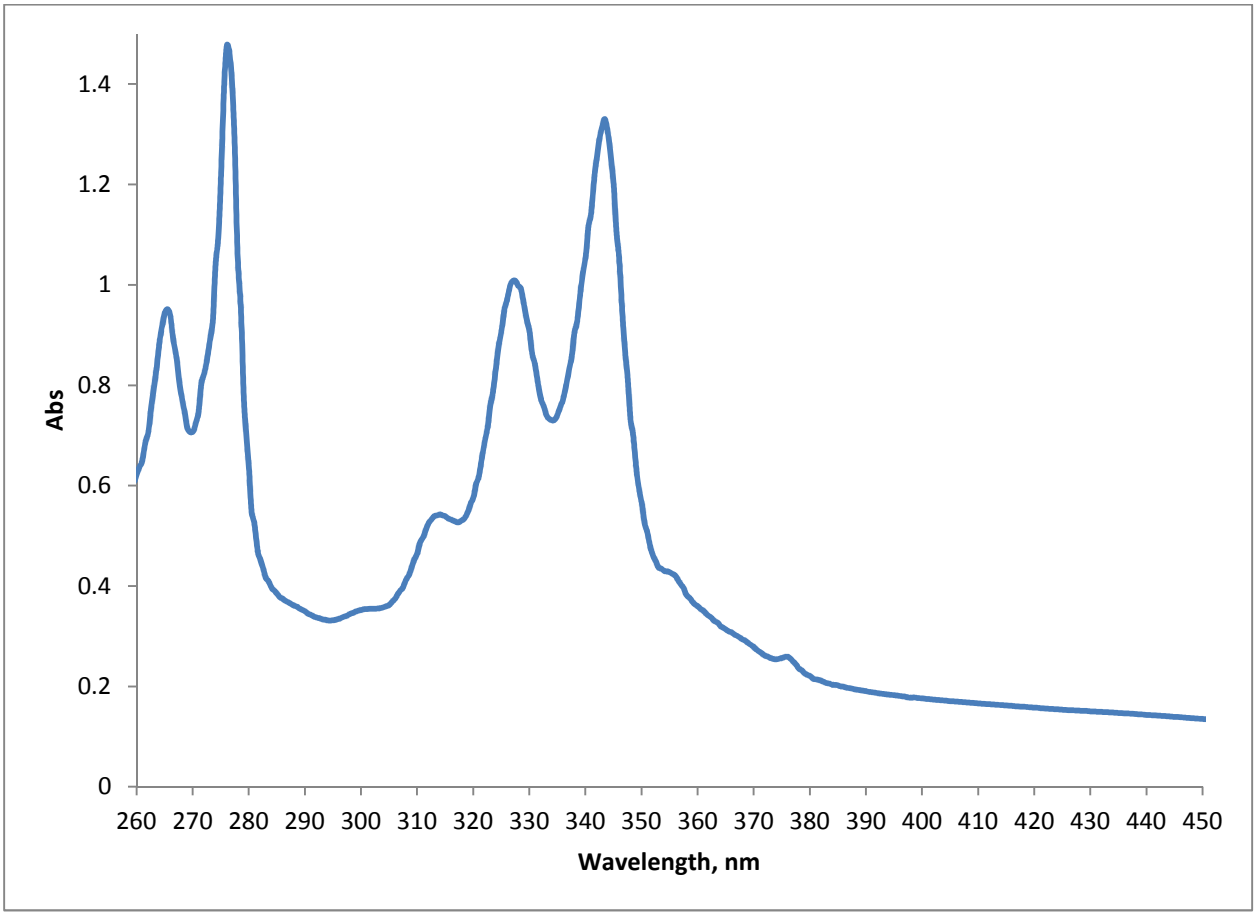


Figure 5S. Absorption spectrum of the compound **1a** in (ACN, 10^{-5} M)

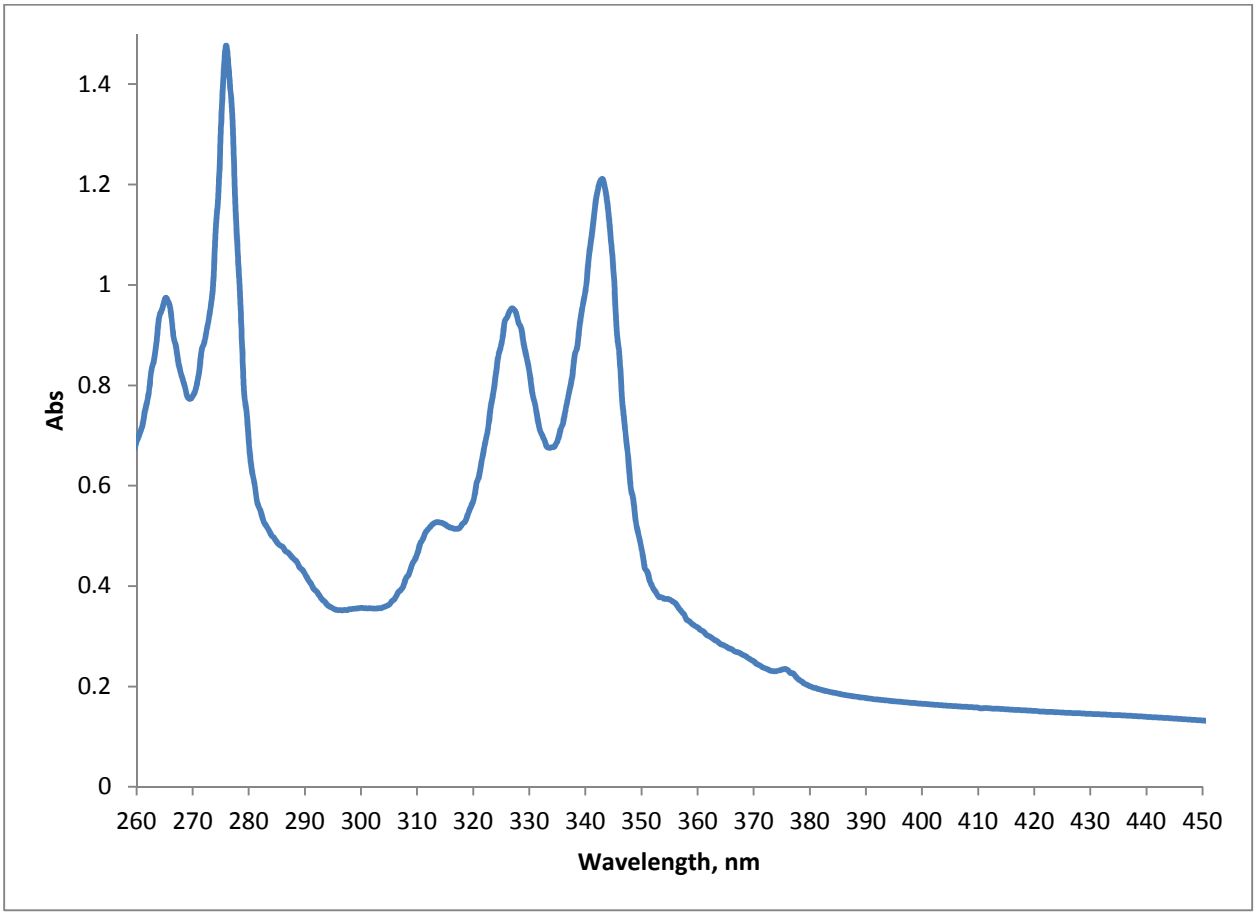


Figure 6S. Absorption spectrum of the compound **1b** in (ACN, 10^{-5} M)

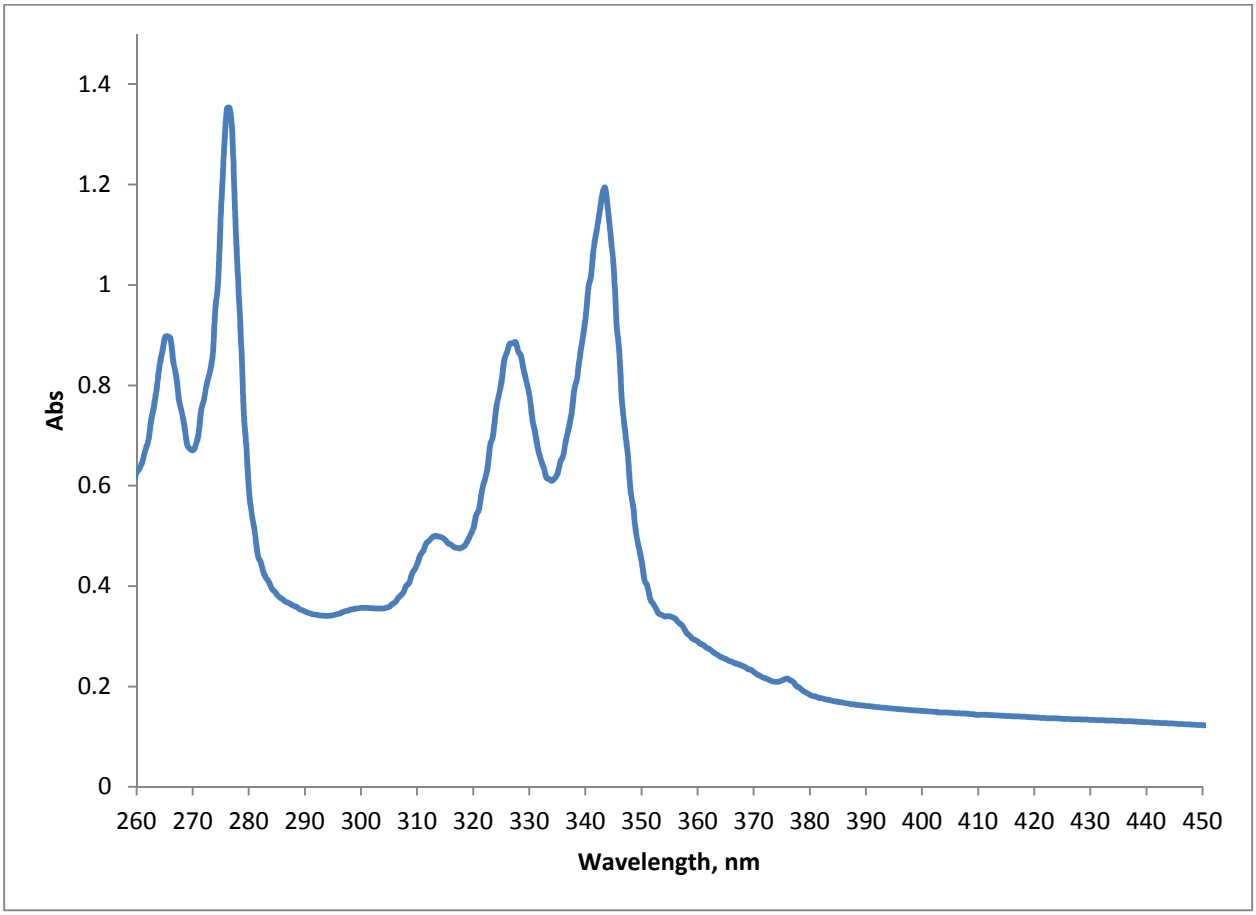


Figure 7S. Absorption spectrum of the compound **1c** in (ACN, 10^{-5} M)

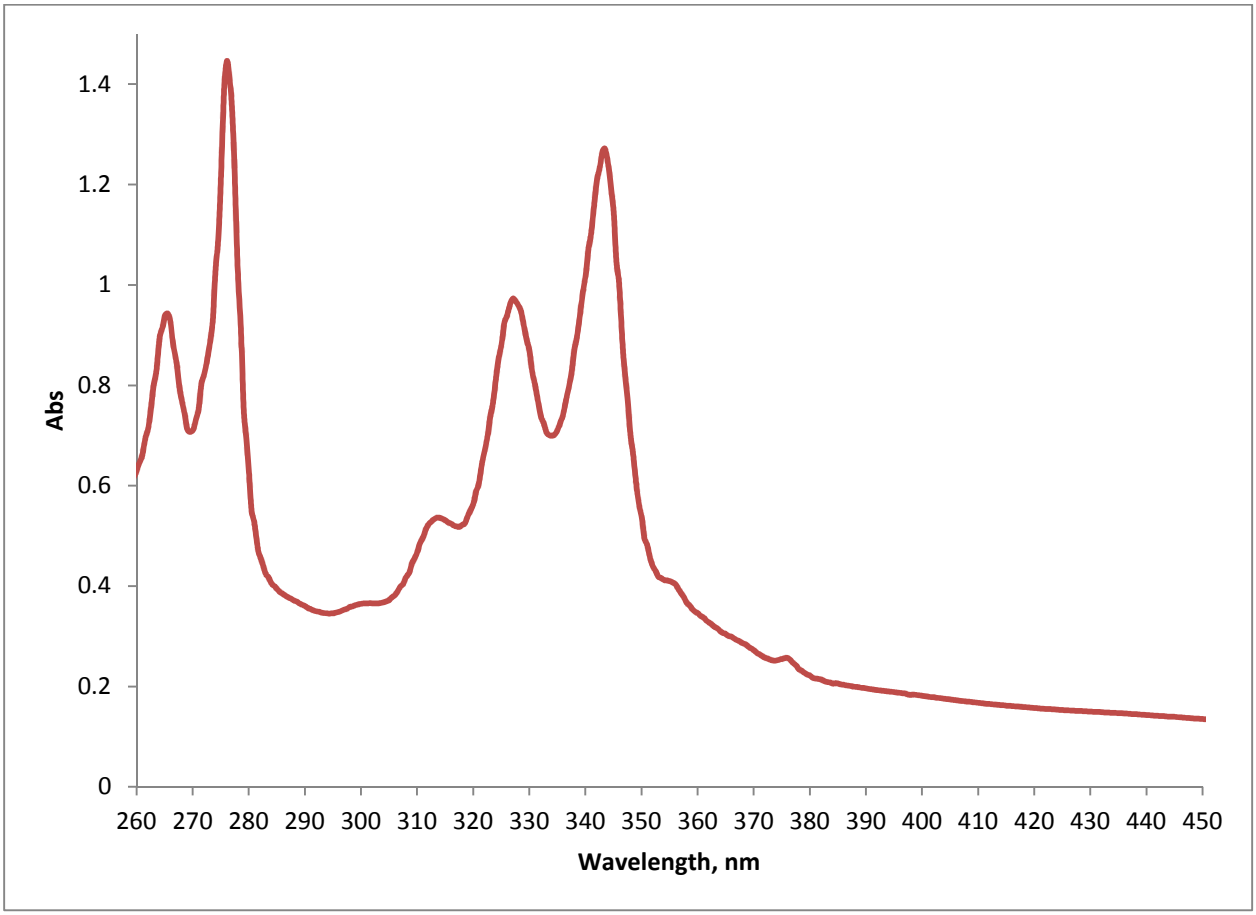


Figure 8S. Absorption spectrum of the compound **2a** in (ACN, 10^{-5} M)

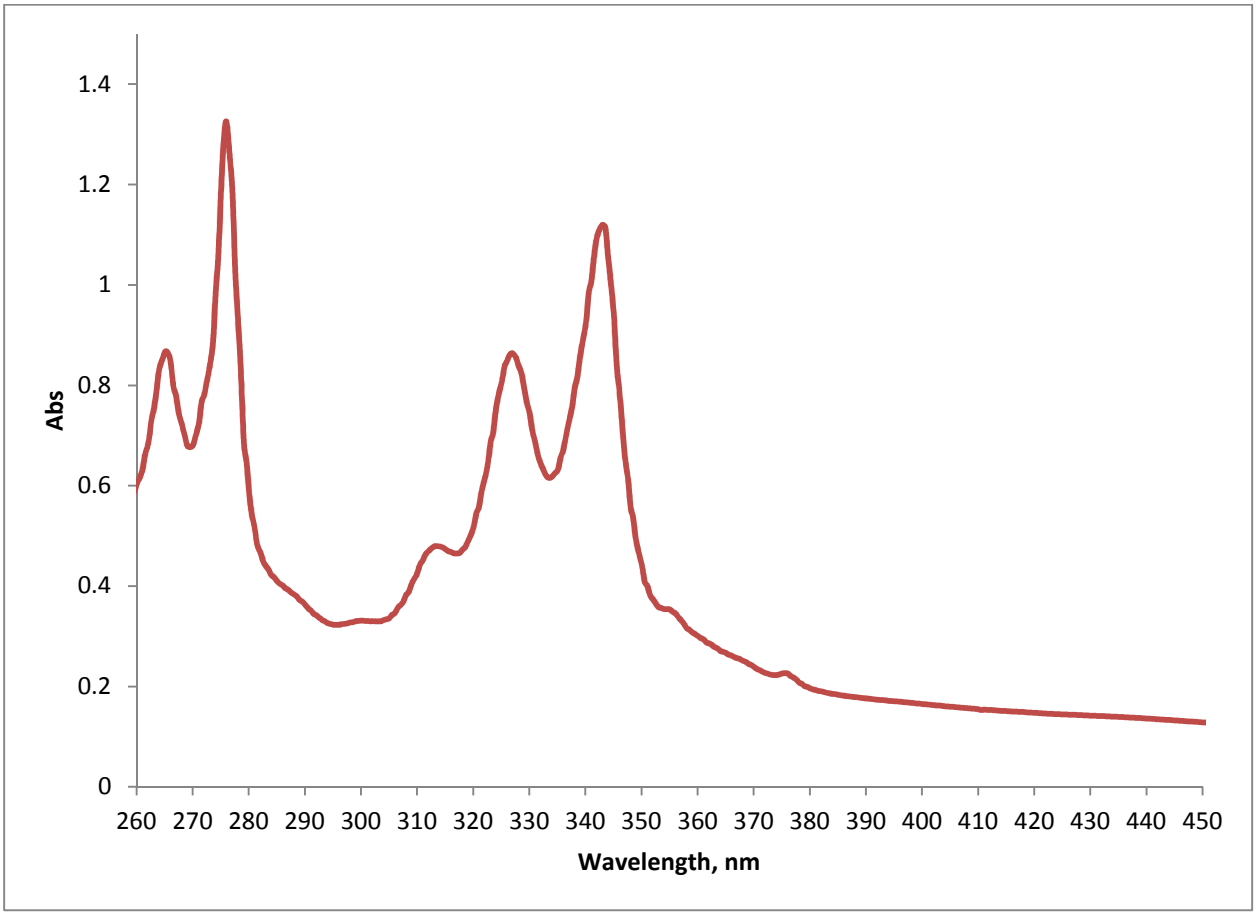


Figure 9S. Absorption spectrum of the compound **2b** in (ACN, 10^{-5} M)

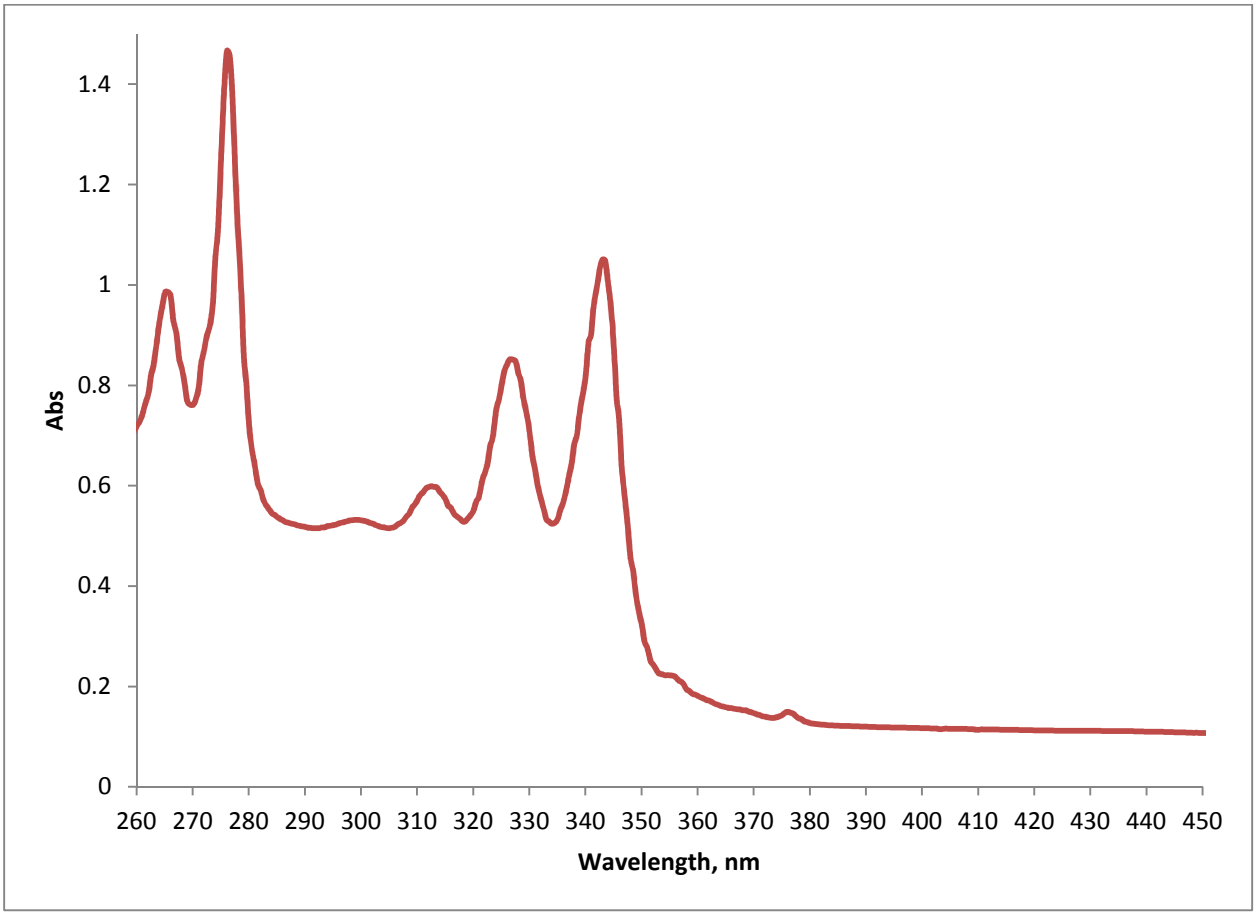


Figure 10S. Absorption spectrum of the compound **2c** in (ACN, 10^{-5} M)

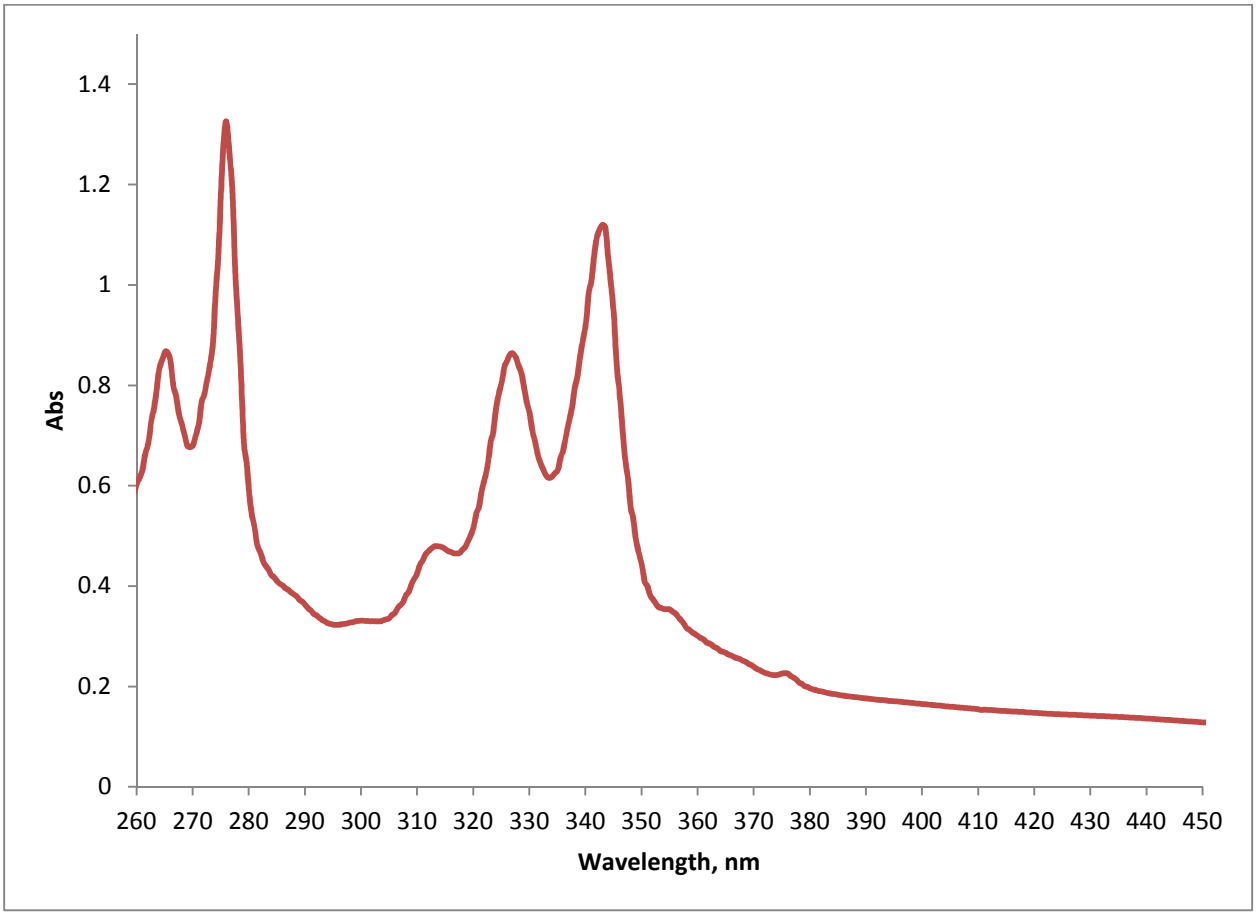
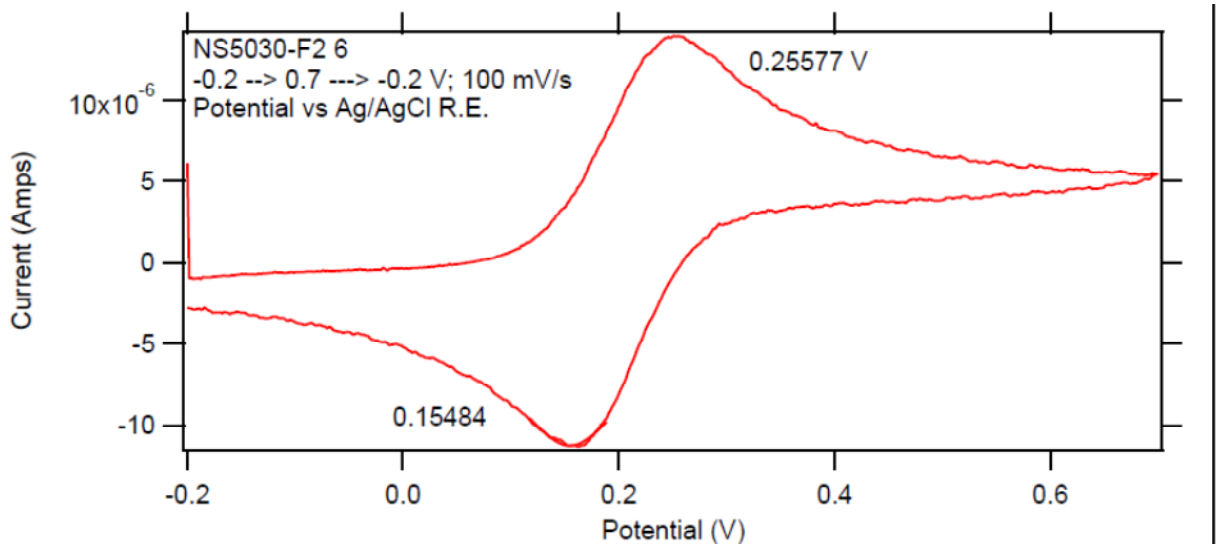


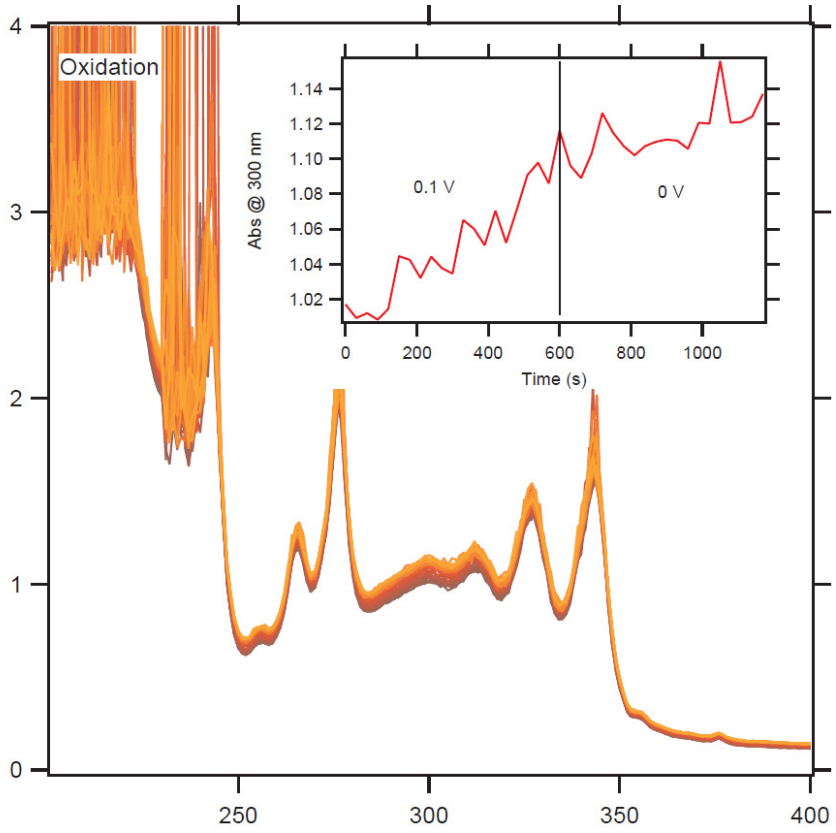
Figure 11S. Absorption spectrum of the compound **14** in (ACN, 10^{-5} M)

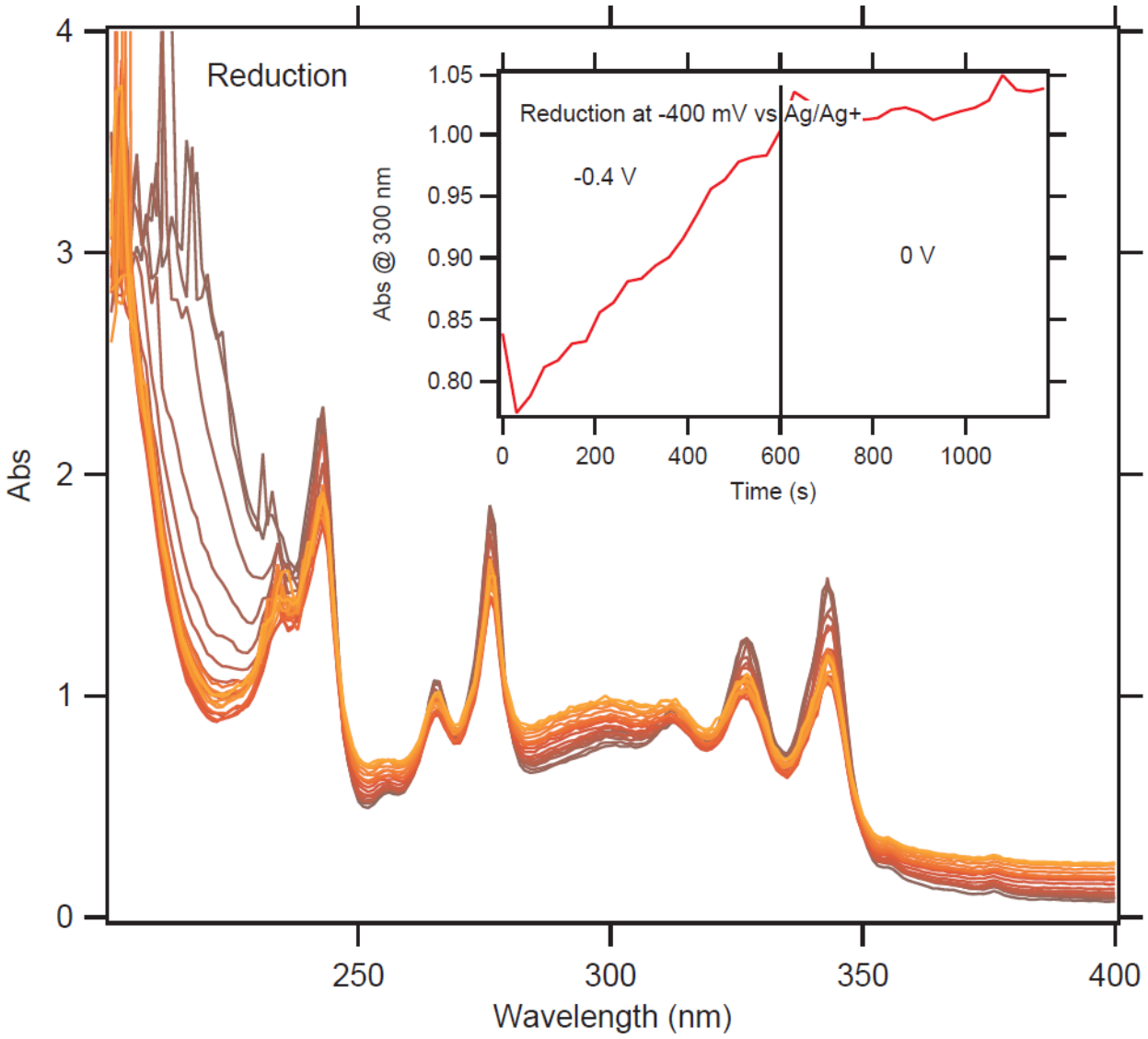
V. Spectroelectrochemical data for the nickel complexes 1, 2, and 14

 Color/time scale: earliest scans are in blue, latest scans are in yellow.

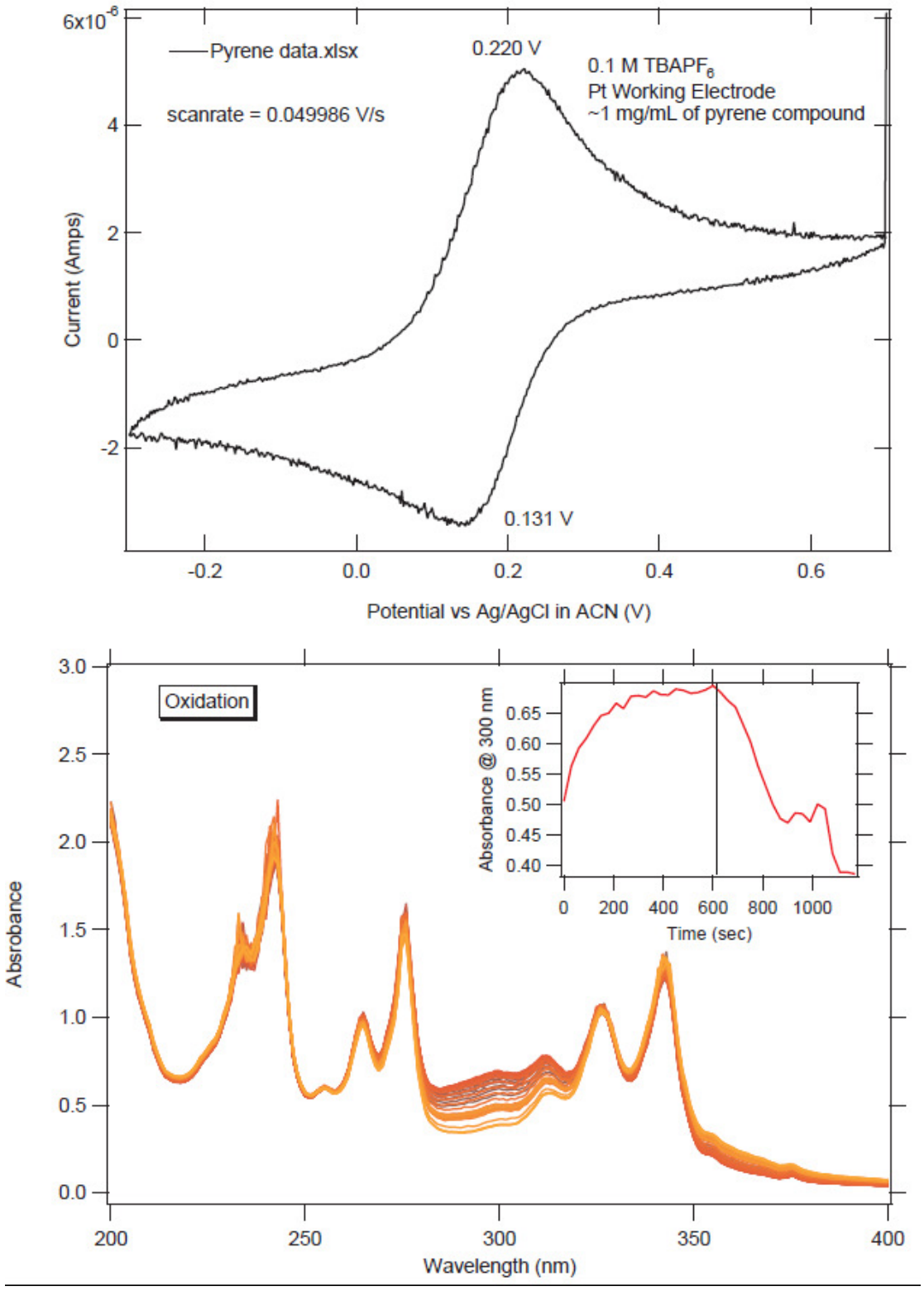
Complex 1a/2a

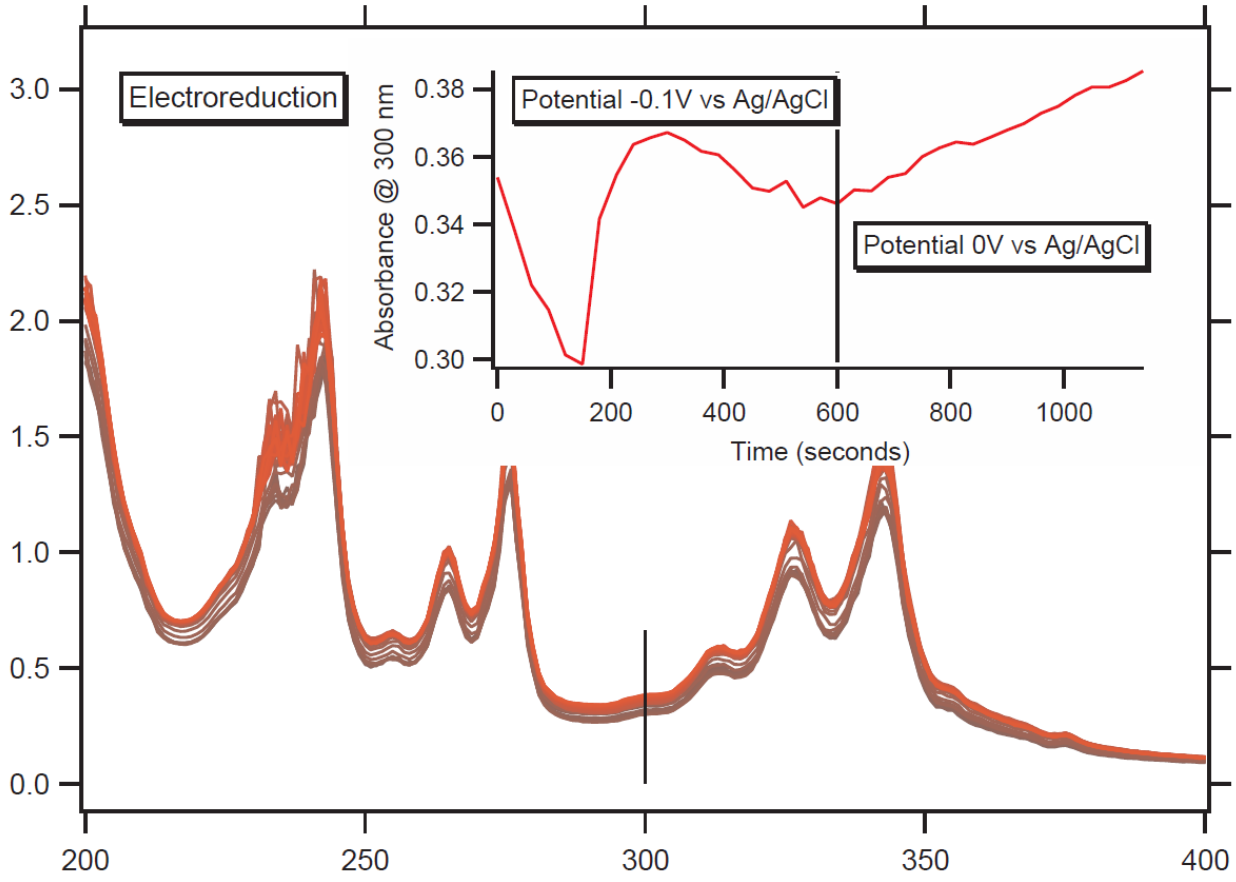




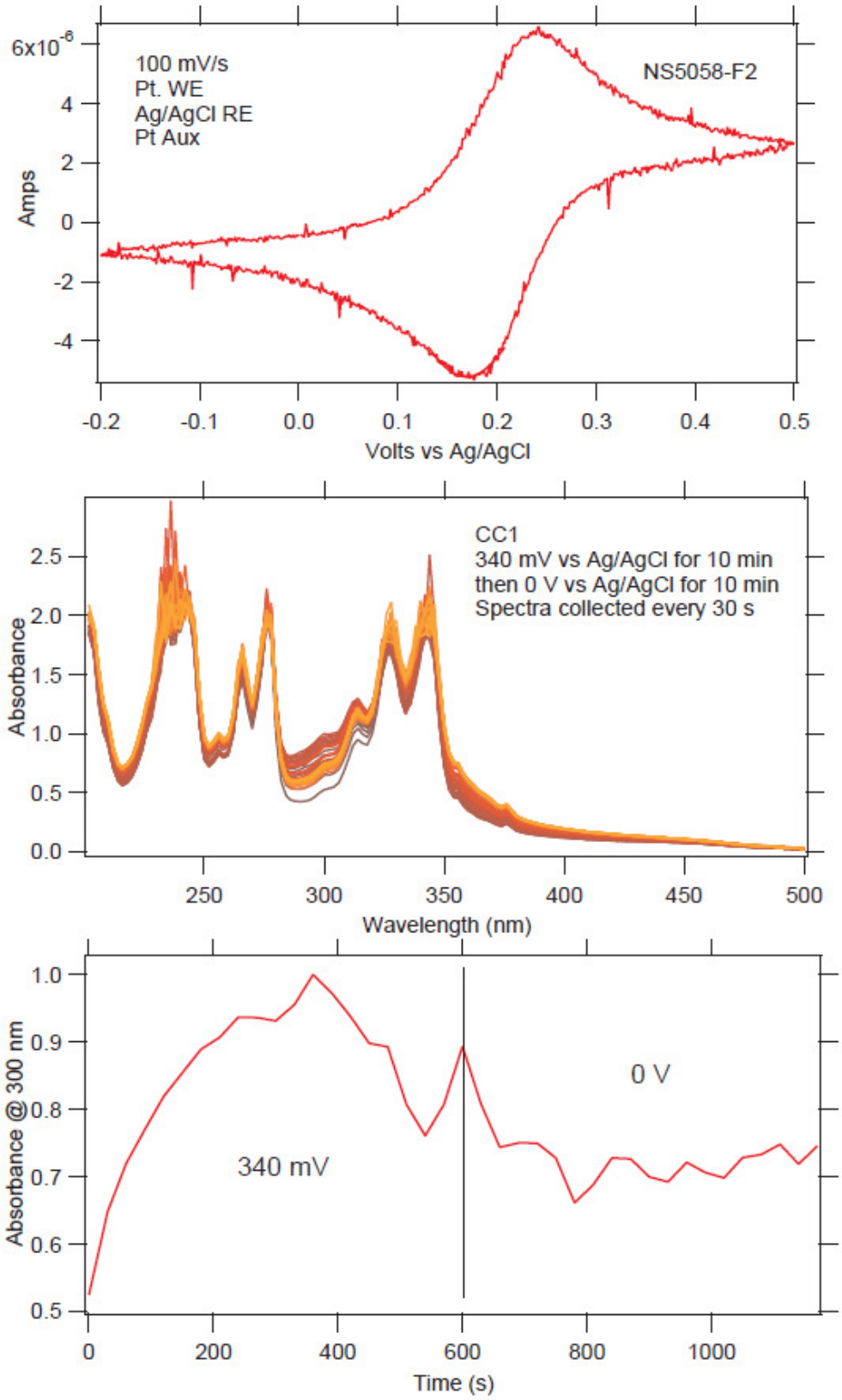

Reduction
Reduction at -400 mV vs Ag/Ag+
-0.4 V
0 V
Abs @ 300 nm
Time (s)
Abs
Wavelength (nm)

Complex 1b/2b

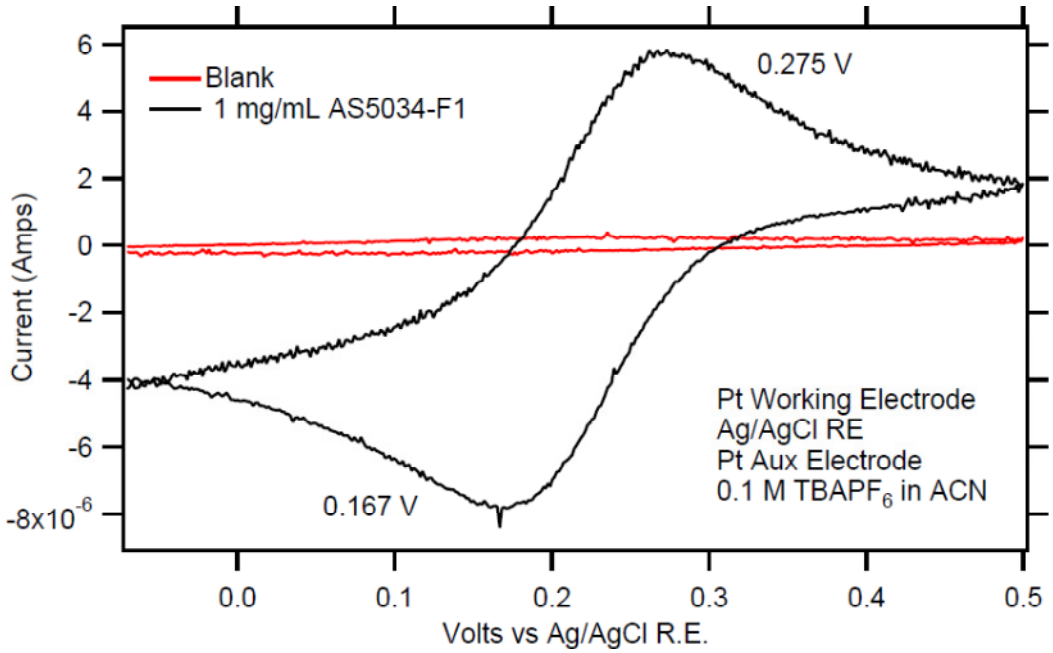


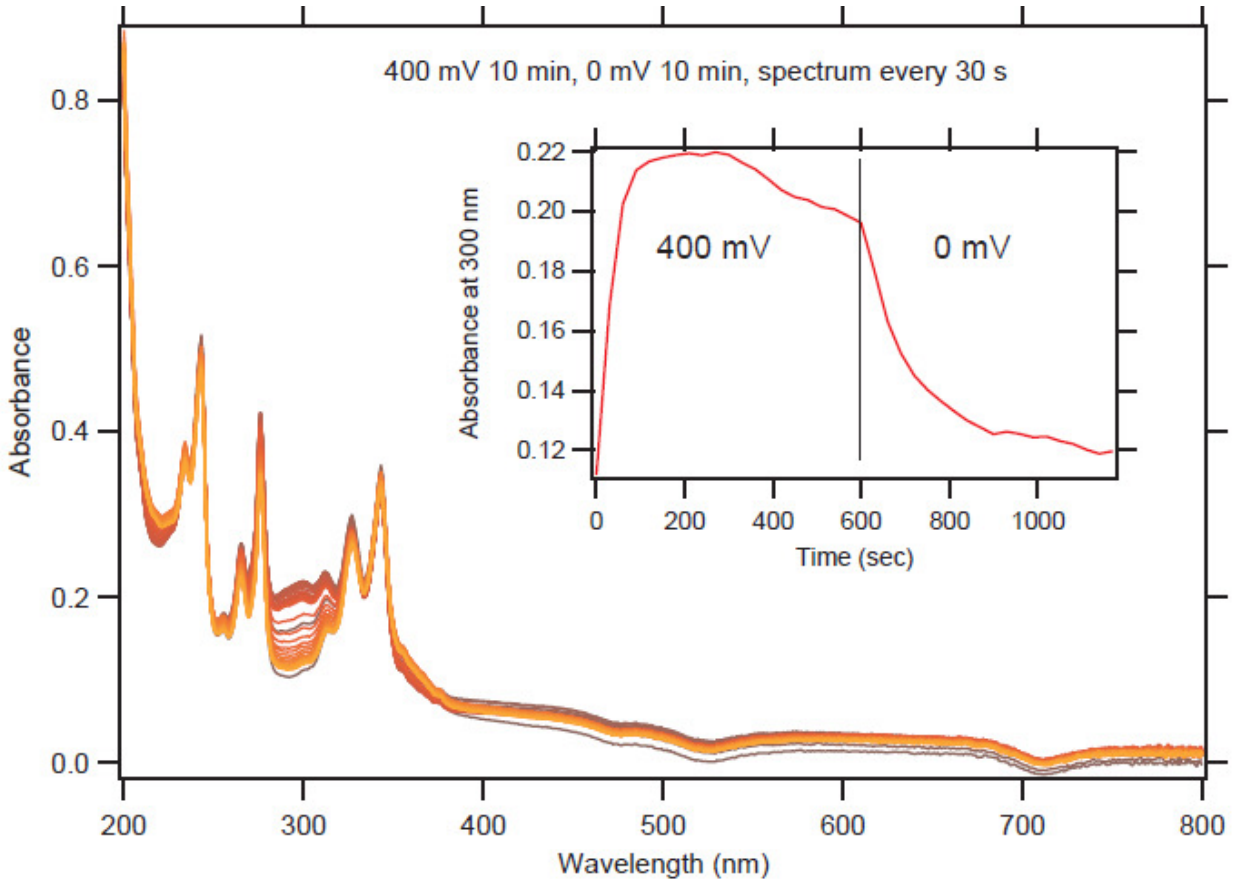

Electroreduction
Potential -0.1V vs Ag/AgCl
Potential 0V vs Ag/AgCl
Absorbance @ 300 nm
Time (seconds)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
200
250
300
350
400
0.38
0.36
0.34
0.32
0.30
0
200
400
600
800
1000

Complex 1c/2c



Complex 14


Blank
1 mg/mL AS5034-F1
0.275 V
0.167 V
Pt Working Electrode
Ag/AgCl RE
Pt Aux Electrode
0.1 M TBAPF6 in ACN
Current (Amps)
Volts vs Ag/AgCl R.E.


400 mV 10 min, 0 mV 10 min, spectrum every 30 s
400 mV
0 mV
Absorbance at 300 nm
Time (sec)
Absorbance
Wavelength (nm)

VI. Fluorescence spectra of the nickel complexes 1, 2, and 14

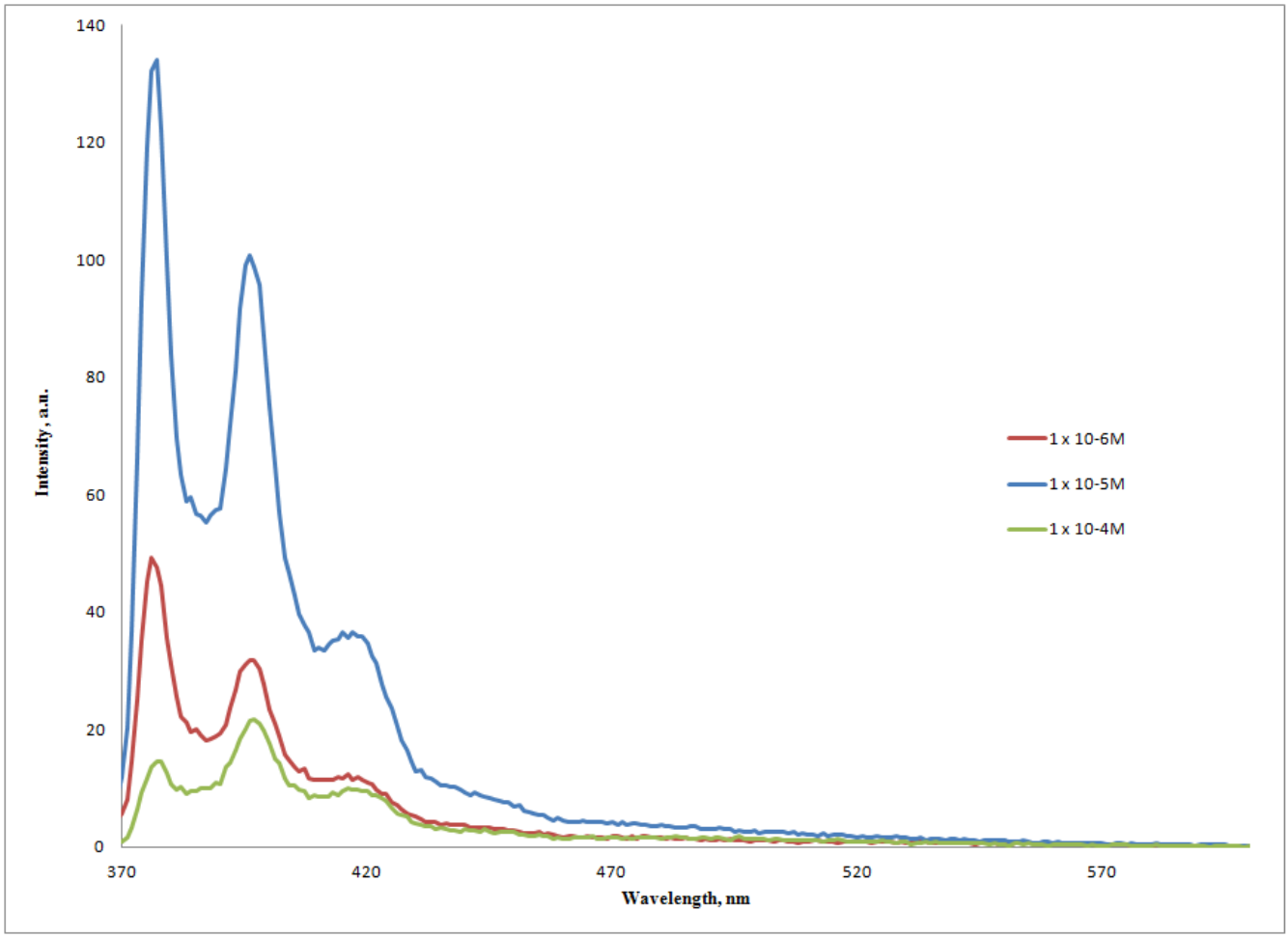


Figure 12S. Concentration dependence of the fluorescence spectra of the Ni(III) complex **1b** (acetonitrile, 20 °C, λ_{ex} 360 nm).

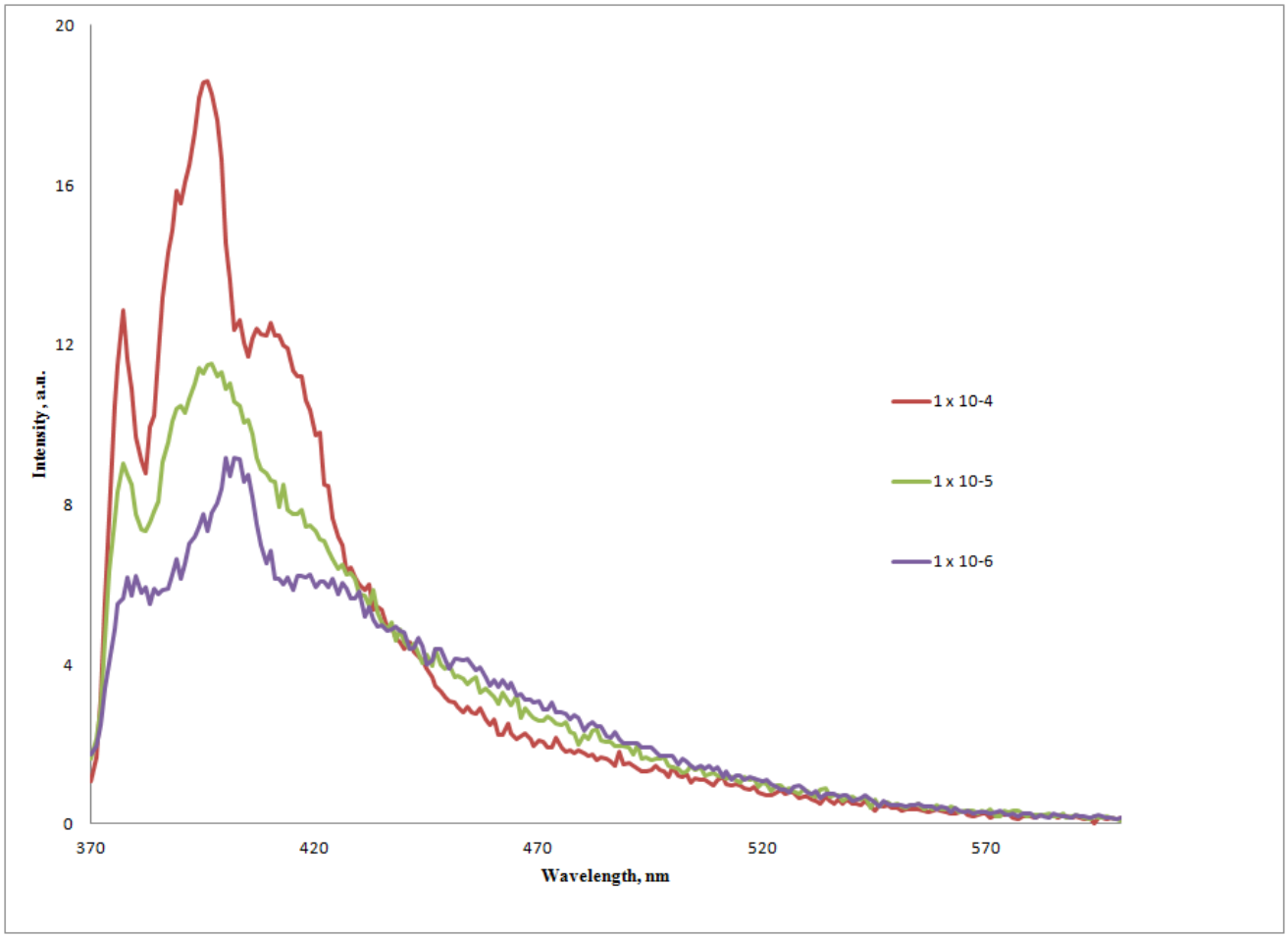


Figure 13S. Concentration dependence of the fluorescence spectra of the Ni(IV) complex **2a** (acetonitrile, 20 °C, λ_{ex} 360 nm).

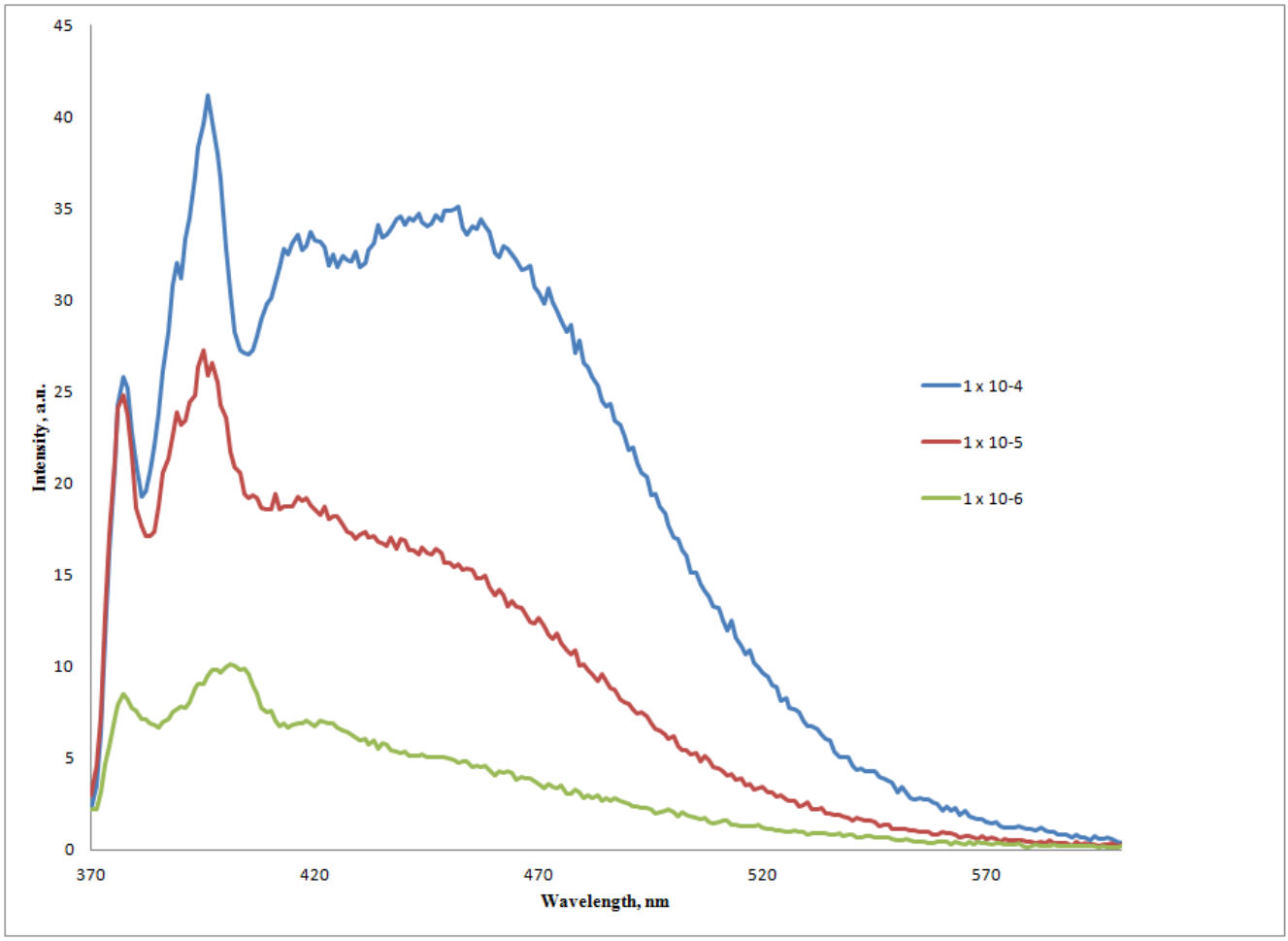


Figure 14S. Concentration dependence of the fluorescence spectra of the Ni(IV) complex **2b** in acetonitrile (20 °C, λ_{ex} 360 nm).

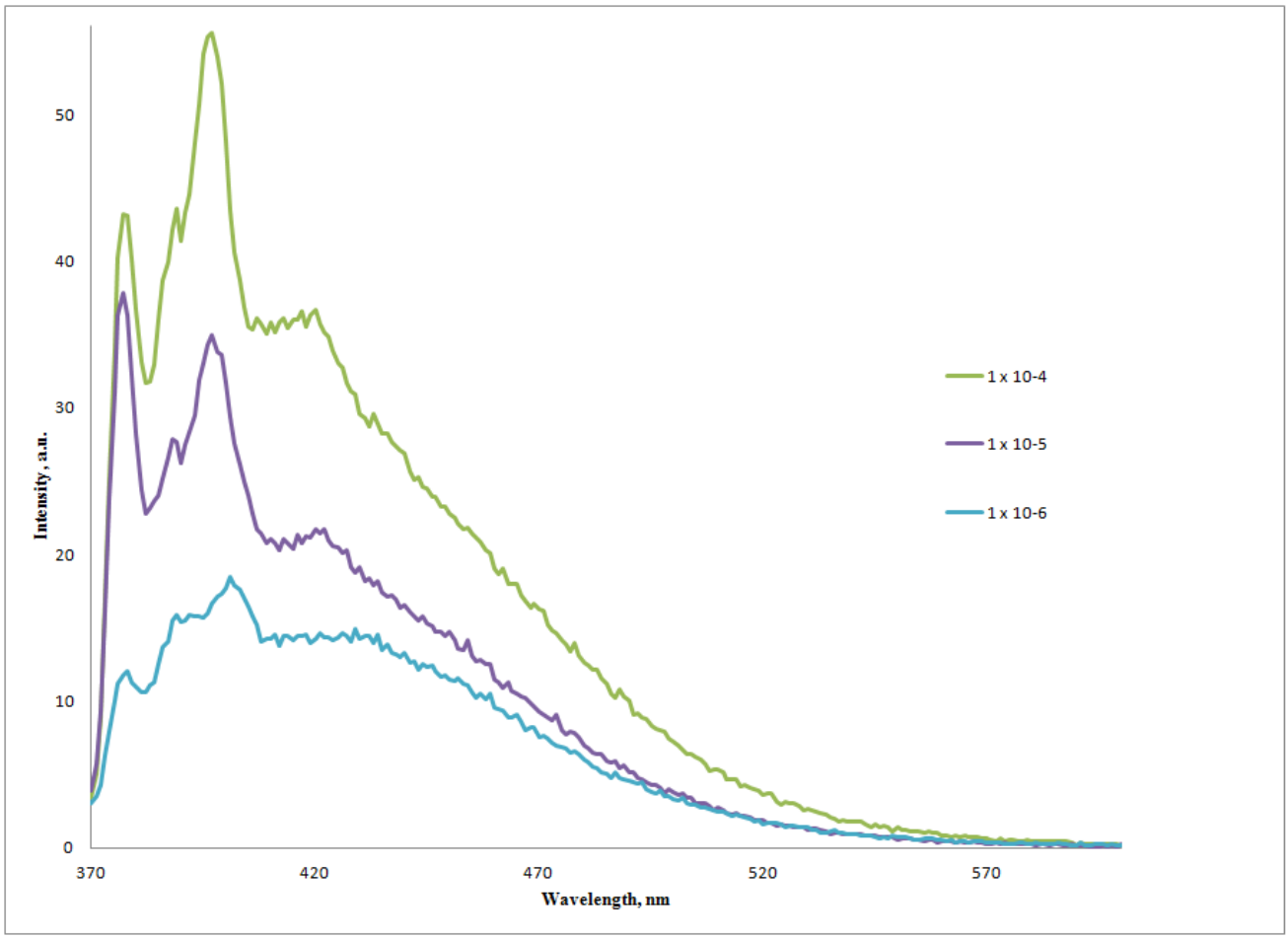


Figure 15S. Concentration dependence of the fluorescence spectra of the Ni(IV) complex **2b** in THF (20 °C, λ_{ex} 360 nm).

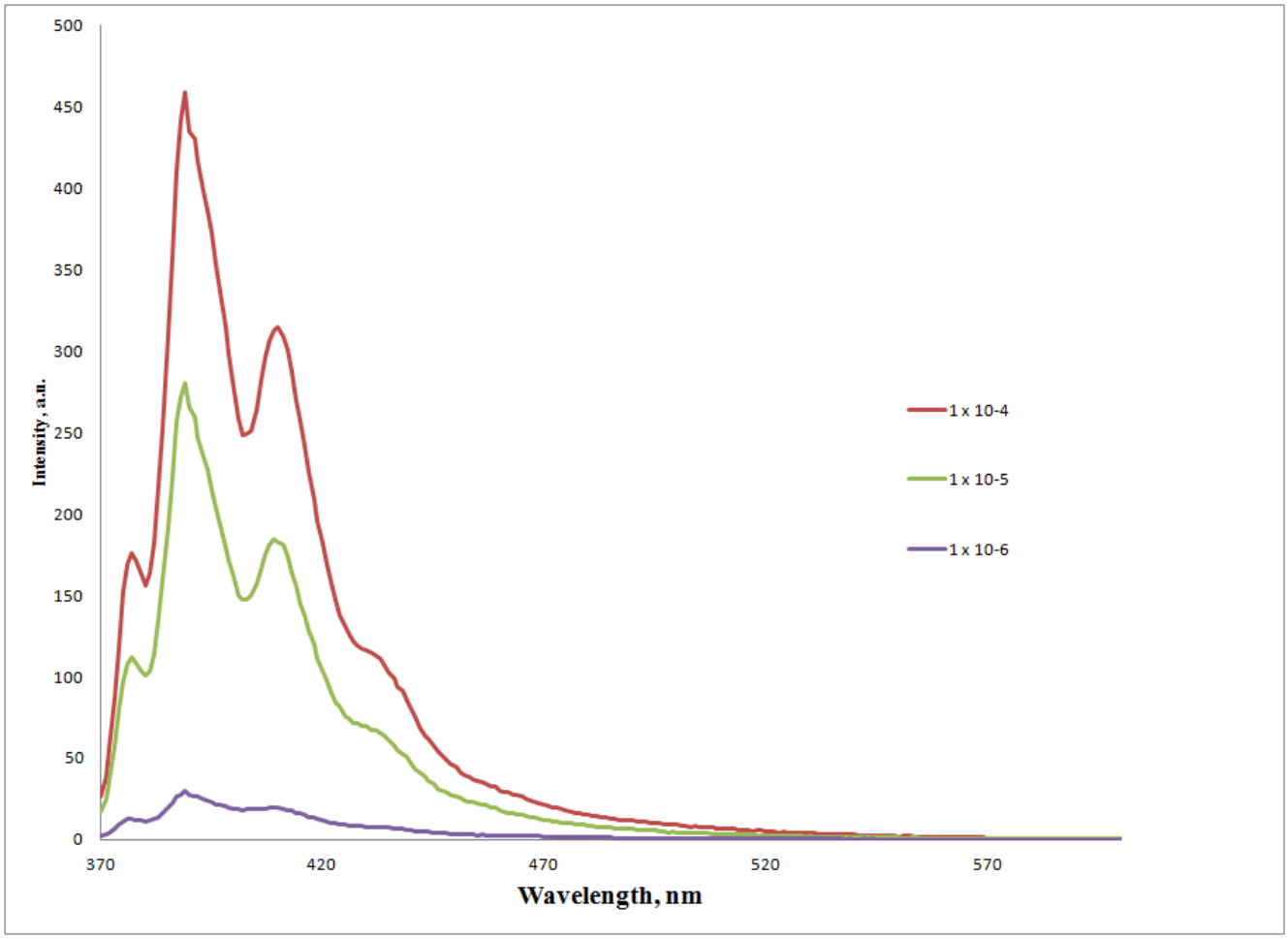


Figure 16S. Concentration dependence of the fluorescence spectra of the Ni(IV) complex **2c** (acetonitrile, 20 °C, λ_{ex} 360 nm).

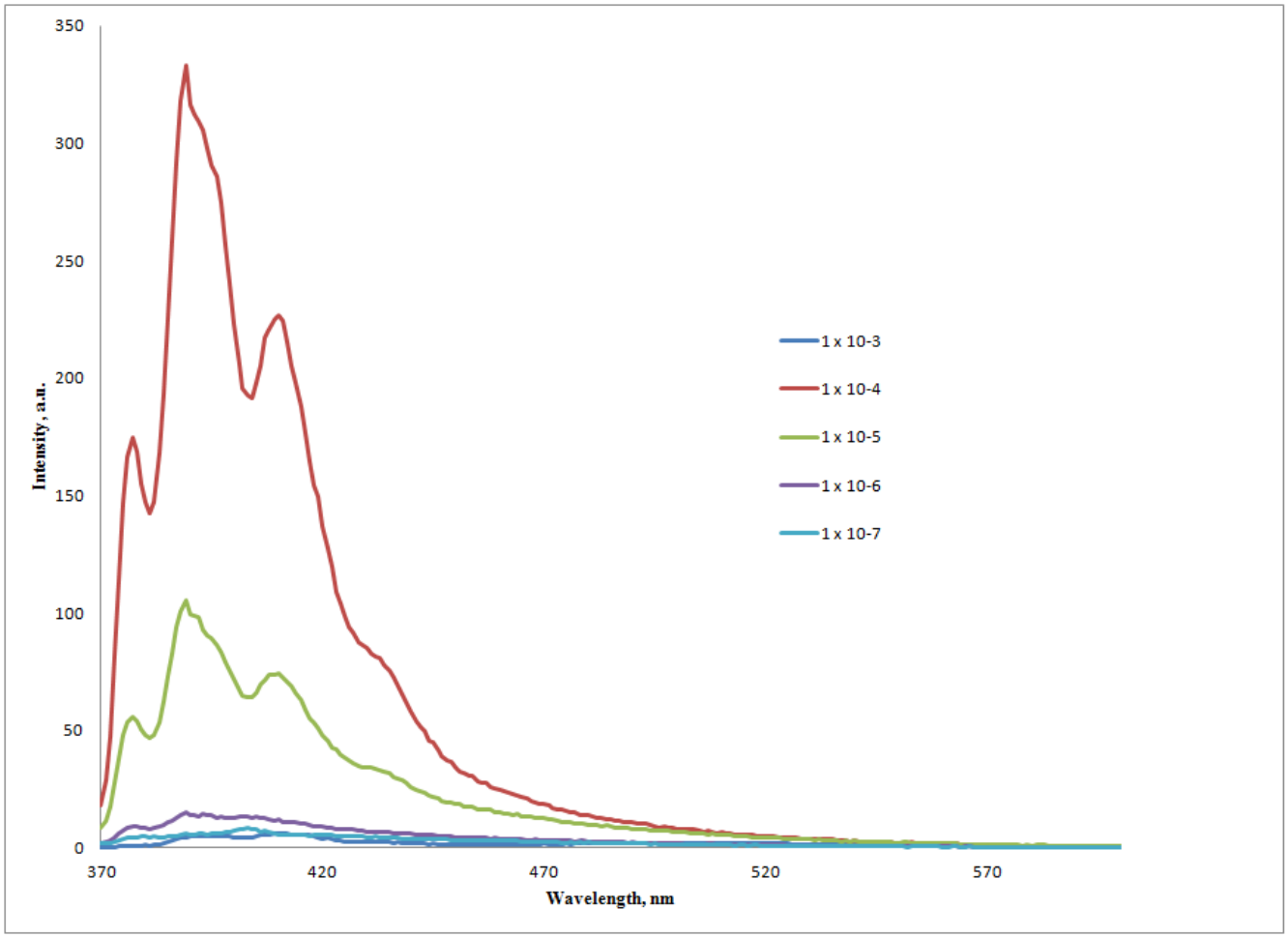


Figure 17S. Concentration dependence of the fluorescence spectra of the Ni(IV) complex **14** (acetonitrile, 20 °C, λ_{ex} 360 nm).

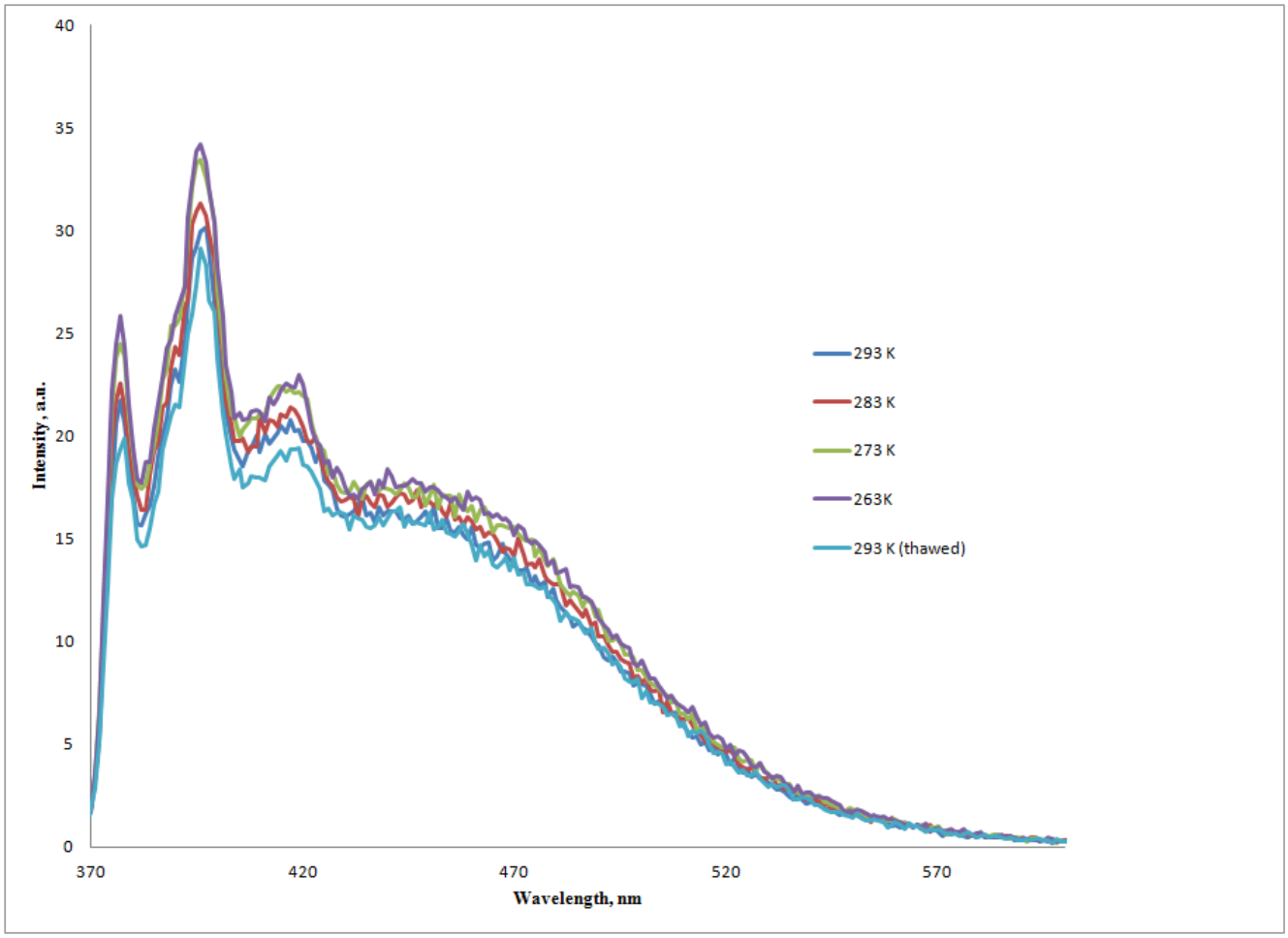


Figure 18S. Temperature dependence of the fluorescence spectra of the 10-4 M solution of the Ni(IV) complex **2b** (acetonitrile, λ_{ex} 360 nm).

VII. Computational studies in acetonitrile

Bis(dicarbollyl)nickels may adopt three conformations: *cis, gauche* and *trans*, defined by the respective position of the cage carbon atoms in the opposite cages (Figure 19S). The most stable conformation of the cage carbon atoms depends on the oxidation state of the metal atom: *trans* conformation corresponds to the Ni(III) and *cis* to the Ni(IV) complex.

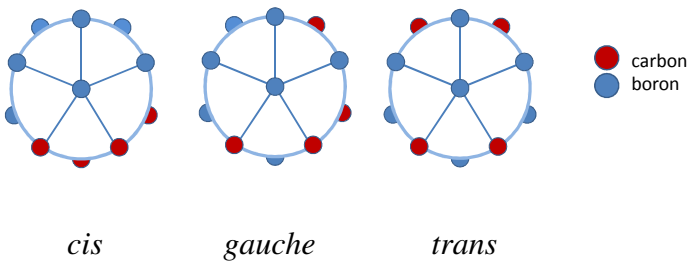


Figure 19S. Schematic representation of the *cis, gauche* and *trans* conformers of bis(dicarbollyl)nickel.

The geometry optimization of the *trans* and *gauche* Ni(III), *cis* and *gauche* Ni(IV) as well as single point energy calculations of *cis* Ni(III) and *trans* Ni(IV) bis(dicarbollyl)nickel structures at the B3LYP/6-31G(d) level of theory was carried out in acetonitrile (conductor-like polarizable continuum model, CPCM) using the Gaussian09 suite of programs. The total energies and relative total energies of the optimized, substituted bis(dicarbollide) complexes **1b** and **2b** are shown in Table 3S. The most negative total energies correspond to the bis(dicarbollyl)nickel(III) in the *trans* and bis(dicarbollyl)nickel(IV) in the *cis* conformations.

Table 3S. Total energies and relative total energies of bis(dicarbollide) structures optimized in acetonitrile.

	Ni(III), 1b		Ni(IV), 2b	
	Total energy [Hartree]	Relative energy [kcal/mol]	Total energy [Hartree]	Relative energy [kcal/mol]
cis	-3743.87912	10.60	-3743.72679	0.00
gauche	-3743.89588	0.09	-3743.72490	1.18
trans	-3743.89602	0.00	-3743.70438	14.06

It was calculated[12] that in vacuum the oxidation of the Ni(III) compound to its Ni(IV) counterpart required 64 kcal/mol, which was followed by recovery of 2.8 kcal/mol on rotation to Ni(IV) ground state. In acetonitrile, the predicted energy required for oxidation of Ni(III) to Ni(IV) was 120.2 kcal/mol and the energy recovery from the rotation was estimated to be approximately 14.1 kcal/mol.

Boltzmann factors of conformers were calculated according to the equation:

$$\frac{F1}{F2} = e^{\frac{E2-E1}{kT}} = e^{\Delta E/kT}$$

where F_i – population of the i state, E_i – energy of the i state, k – Boltzmann constant ($1.38 \cdot 10^{-23}$ J/K), T – observation temperature (293 K). Results of the calculations are presented in the Table 4S.

Table 4S. Calculated conformer ratios based on Boltzmann equation.

	Energy, Ha	**Energy, J**	**Population, %**
1b *dl-cis*	-3743.87912	$-1.632235581017760 \cdot 10^{-14}$	$9.09 \cdot 10^{-7}$
1b *dl-gauche*	-3743.89588	$-1.632242886615190 \cdot 10^{-14}$	46.36
1b *meso-trans*	-3743.89602	$-1.632242946618350 \cdot 10^{-14}$	53.64
2b *dl-cis*	-3743.72679	$-1.632169169555360 \cdot 10^{-14}$	88.07
2b *dl-gauche*	-3743.72490	$-1.632168346623100 \cdot 10^{-14}$	11.93
2b *meso-trans*	-3743.70438	$-1.632159398718690 \cdot 10^{-14}$	$4.33 \cdot 10^{-9}$

VIII. References

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