

Efficient and recyclable rare earth-based catalysts for Friedel-Crafts acylations under microwave heating: dendrimers show the way

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1. Materials

NMR spectra were recorded with Bruker DPX 300, AV 300, AV 400 spectrometers. All spectra were measured at 25 °C in the indicated deuterated solvents. References for NMR chemical shifts are H₃PO₄ (85%) for ³¹P NMR, and SiMe₄ for ¹H and ¹³C NMR spectroscopy. ¹H, ¹³C and ³¹P chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz (Hz). The signals in the spectra are described as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad resonances). Attribution was carried out thanks to two-dimensional experiments when necessary (COSY, HMBC, HMQC).

Chemicals were purchased from Aldrich, Acros, Fluka, Alfa Aesar and Strem, and were used without further purification, except for P₃N₃Cl₆ which was recrystallized from hexane, 4-hydroxybenzaldehyde which was recrystallized from diethyl ether. Organic solvents were dried and distilled according to usual procedures.¹ Dendrimers **Gc_n** were synthesized according to published procedures.²

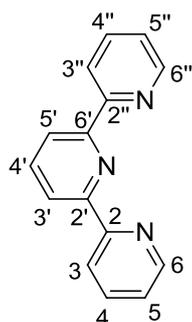
Reactions under microwave irradiation were performed on a CEM, Discover SP apparatus.

Mass spectrometry was carried out with a Thermo Fisher DS QII (DCI/NH₃), GTC Premier Waters (DCI/CH₄) or with Maldi Micro MX Waters (Maldi/DCTB).

Gas chromatographies (GC) were recorded on a Shimadzu instrument with a Shimadzu GC-2010 Plus AF and a HP5-MS 30 m x 0.25 mm capillary apolar column.

Purifications by column chromatography were performed on silica gel (60 Å, 53-250 μm). TLCs were performed on silica gel 60 F254 plates and detection was carried out under UV light or using appropriate dyeing reagent.

General formula of 2,2':6,2''-terpyridine as well as atom numbering recommended³ and used for NMR assignments are given in the following scheme.



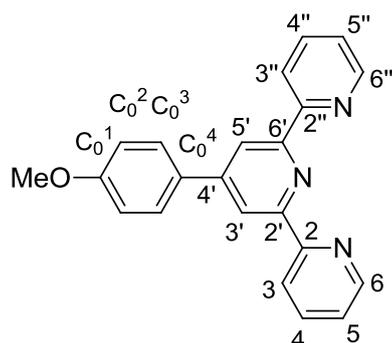
¹ D. D. Perrin et W. L. F. Almerigo, *Purification of Laboratory Chemicals 3rd Ed.*, Pergamon Press. Oxford, **1998**.

² N. Launay, A.-M. Caminade, J.-P. Majoral, *J. Organomet. Chem.* **1997**, 529, 51.

³ a) L. Pazderski, T. Pawlak, J. Sitkowski, L. Kozerski, E. Szlyk, *Magn. Reson. Chem.* **2011**, 49, 237; b) G. R. Newkome, K. S. Yoo, S.-Ho Hwang, C. N. Moorefield, *Tetrahedron Lett.* **2003**, 59, 3955.

2. Complete characterisation of the ligands with attribution of NMR signals

Compound M:



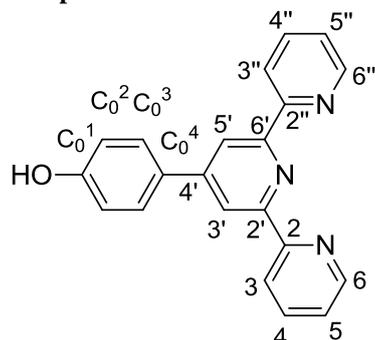
2-Acetylpyridine (2 g, 1.85 mL, 16.5 mmol) was added to a stirred suspension of crushed NaOH (660 mg, 16.5 mmol) in PEG₃₀₀ (20 mL) at 0 °C. After 10 min, 4-methoxybenzaldehyde (1.11 g, 1 mL, 8.2 mmol) was added and stirring was continued at 0 °C for 2 h. Then concentrated aqueous NH₃ solution (20 mL) was added and the suspension stirred at room temperature overnight. The precipitate was isolated by vacuum filtration and washed with water (50 mL) and cold ethanol (10 mL). **M** was obtained as a white powder in 24 % yield (652 mg, 1.92 mmol).

¹H NMR (300.13 MHz, CD₂Cl₂, 25 °C) δ (ppm): 3.92 (s, 3H, OMe), 7.08-7.13 (m, 2H, C₀²-H), 7.40 (ddd, ³J_{H-H} = 7.8 Hz, 4.8 Hz, ⁴J_{H-H} = 1.0 Hz, 2H, C⁵-H, C^{5''}-H), 7.89-7.96 (m, 4H, C₀³-H, C⁴-H, C^{4''}-H), 8.71 (td, ³J_{H-H} = 7.8 Hz, ⁴J_{H-H} = 1.0 Hz, 2H, C³-H, C^{3''}-H), 8.74-8.76 (m, 2H, C⁶-H, C^{6''}-H), 8.77 (s, 2H, C^{3'}-H, C^{5'}-H);

¹³C{¹H} NMR (75.47 MHz, CD₂Cl₂, 25 °C) δ (ppm): 55.36 (OMe), 114.35 (s, C₀²), 117.99 (s, C^{3'}, C^{5'}), 121.04 (s, C³, C^{3''}), 123.79 (s, C⁵, C^{5''}), 128.36 (s, C₀³), 130.66 (s, C₀⁴), 136.77 (s, C⁴, C^{4''}), 149.10 (s, C⁶, C^{6''}), 149.54 (s, C^{4'}), 155.88 (s, C², C^{6'}), 156.19 (s, C², C^{2''}), 160.66 (s, C₀¹).

DCI-MS (NH₃): m/z: 340.1 [M+H]⁺.

Compound 3:



2-Acetylpyridine (931 mg, 7.68 mmol) was added to a stirred suspension of crushed NaOH (231 mg, 7.68 mmol) in PEG₃₀₀ (10 mL) at 0 °C. After 10 min, 4-hydroxybenzaldehyde (3.38 mmol) was added and stirring was continued at 0 °C for 2 h. Then concentrated aqueous NH₃ solution (10 mL) was added and the suspension stirred at room temperature overnight. The precipitate was isolated by vacuum filtration and washed with water (50 mL) and cold ethanol (10 mL). **3** was obtained as a white powder in 20 % yield (220 mg, 0.68 mmol).

¹H NMR (400.13 MHz, CDCl₃, 25 °C) δ (ppm): 6.97-6.99 (m, 2H, C₀²-H), 7.52 (ddd, ³J_{H-H} = 7.5 Hz, 4.2 Hz, ⁴J_{H-H} = 1.4 Hz, 2H, C⁵-H, C^{5''}-H), 7.79-7.81 (m, 2H, C₀³-H), 8.03 (td, ³J_{H-H} = 7.5 Hz, ⁴J_{H-H} = 1.4 Hz, 2H, C⁴-H, C^{4''}-H), 8.66 (d, ³J_{H-H} = 7.5 Hz, 2H, C³-H, C^{3''}-H), 8.66 (s, 2H, C^{3'}-H, C^{5'}-H), 8.76 (d, ³J_{H-H} = 4.2 Hz, 2H, C⁶-H, C^{6''}-H), 9.91 (s, 1H, OH);

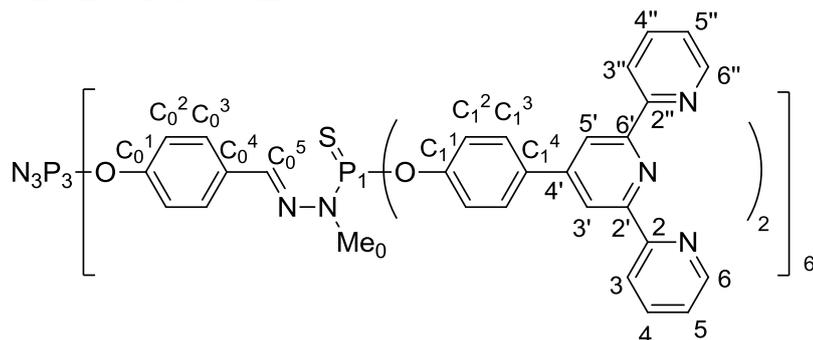
¹³C{¹H} NMR (100.61 MHz, CDCl₃, 25 °C) δ (ppm): 116.69 (s, C₀²), 117.51 (s, C^{3'}, C^{5'}), 121.35 (s, C³, C^{3''}), 124.90 (s, C⁵, C^{5''}), 128.37 (s, C₀⁴), 128.68 (s, C₀³), 138.89 (s, C⁴, C^{4''}), 149.79 (s, C⁶, C^{6''}), 155.61 (s, C², C^{6'}), 155.99 (s, C², C^{2''}, C^{4'}), 159.44 (s, C₀¹).

DCI-MS (NH₃) m/z: 326.1 [M+H]⁺.

General procedure for the synthesis of dendrimers 2-G_n (n = 1-4):

A dendrimer **1-G_n** (130 mg, 0.071 mmol for generation n = 1; 101 mg, 0.021 mmol for n = 2; 203 mg, 0.019 mmol for n = 3; 198 mg, 0.0088 mmol for n = 4) was dissolved in THF (3 mL for 0.01 mmol of **1-G_n**), and then appropriate quantities of compound **3** (1.08 eq. per chlorine; 299 mg, 0.92 mmol for generation n = 1; 176 mg, 0.54 mmol for n = 2; 318 mg, 0.98 mmol for n = 3; 299 mg, 0.92 mmol for n = 4) and of the cesium carbonate (1.67 eq. per chlorine; 466 mg, 1.43 mmol for generation n = 1; 273 mg, 0.84 mmol for n = 2; 495 mg, 1.52 mmol for n = 3; 459 mg, 1.41 mmol for n = 4) were added. The progress of the reaction was monitored by ³¹P NMR. After completion of the reaction, the mixture was centrifuged, filtered and the solvent

was removed under vacuum. The crude product was purified by precipitation in acetone (20 mL for 200 mg). The resulting powder was filtered and dried under vacuum.



Compound 2-G₁:

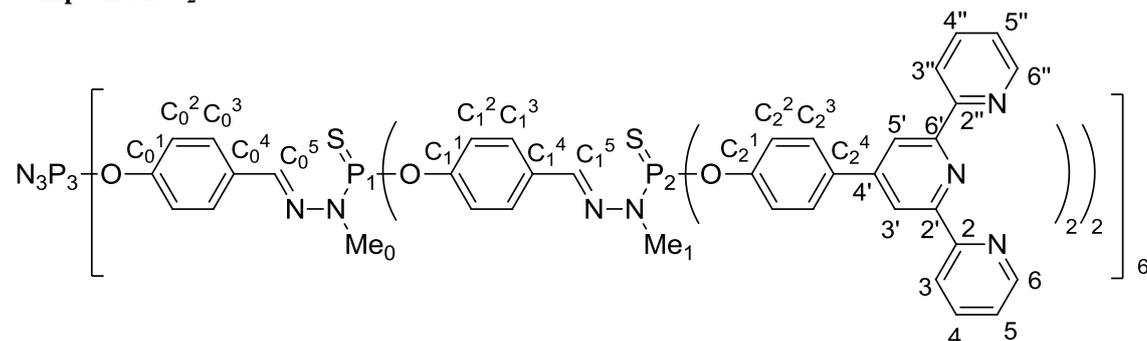
2-G₁ was obtained as a white powder in 88% yield (331 mg, 0.063 mmol).

³¹P{¹H} NMR (121.50 MHz, CD₂Cl₂, 25°C) δ (ppm): 8.82 (s, N₃P₃), 62.44 (s, P₁=S);

¹H NMR (300.13 MHz, CD₂Cl₂, 25°C) δ (ppm): 3.20 (d, ³J_{H-P} = 10.3 Hz, 18H, Me₀), 7.01-7.04 (m, 12H, C₀²-H), 7.23-7.25 (m, 48H, C₁²-H, C⁵-H, C^{5''}-H), 7.64-7.77 (m, 66H, C₀³-H, C₀⁵H=N, C₁³-H, C⁴-H, C^{4''}-H), 8.52-8.55 (m, 48H, C^{3'}-H, C^{5'}-H, C^{3''}-H, C^{6''}-H), 8.61 (d, ²J_{H-H} = 4.2 Hz, 24H, C⁶-H, C^{6''}-H);

¹³C{¹H} NMR (75.47 MHz, CD₂Cl₂, 25°C) δ (ppm): 33.29 (d, ²J_{C-P} = 12.3 Hz, Me₀), 118.80 (s, C^{3'}, C^{5'}), 121.41 (s, C³, C^{3''}), 122.05 (br s, C₀²), 122.29 (d, ³J_{C-P} = 4.3 Hz, C₁²), 124.20 (s, C⁵, C^{5''}), 128.77 (s, C₀³), 128.83 (s, C₁³), 132.74 (s, C₀⁴), 136.07 (s, C₁⁴), 137.11 (s, C⁴, C^{4''}), 139.57 (d, ³J_{C-P} = 14.0 Hz, C₀⁵), 149.06 (s, C^{4'}), 149.38 (s, C⁶, C^{6''}), 151.57-151.78 (m, C₀¹, C₁¹), 156.13 (s, C², C⁶), 156.18 (s, C², C^{2''}).

Compound 2-G₂:



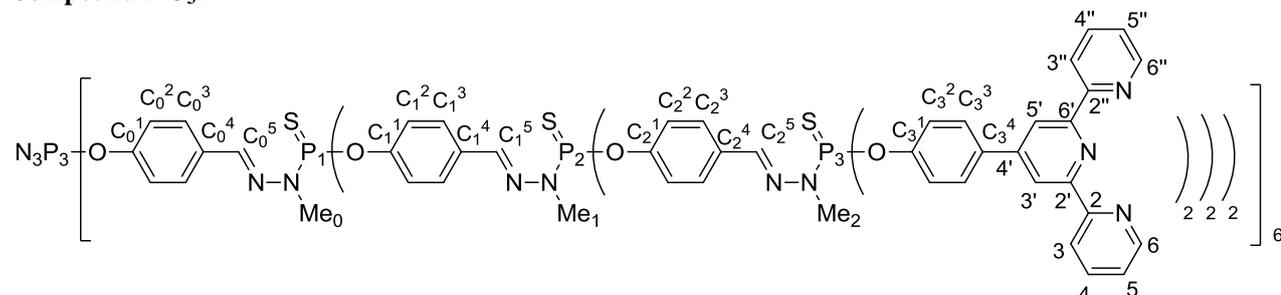
2-G₂ was obtained as a white powder in 83% yield (203 mg, 0.017 mmol).

³¹P{¹H} NMR (161.97 MHz, CD₂Cl₂, 25°C) δ (ppm): 8.22 (s, N₃P₃), 62.19 (s, P₂=S), 62.31 (s, P₁=S);

¹H NMR (400.13 MHz, CD₂Cl₂, 25°C) δ (ppm): 3.03 (d, ³J_{H-P} = 10.4 Hz, 18H, Me₀), 3.20 (d, ³J_{H-P} = 10.4 Hz, 36H, Me₁), 6.77-6.79 (m, 12H, C₀²-H), 7.13-7.24 (m, 120H, C₁²-H, C₂²-H, C⁵-H, C^{5''}-H), 7.40-7.42 (m, 18H, C₀³-H, C₀⁵H=N), 7.51 (s, 12H, C₁⁵H=N), 7.56-7.58 (m, 24H, C₁³-H), 7.62-7.65 (m, 48H, C₂³-H), 7.69-7.74 (m, 48H, C⁴-H, C^{4''}-H), 8.47-8.56 (m, 144H, C^{3'}-H, C^{5'}-H, C³-H, C^{3''}-H, C⁶-H, C^{6''}-H);

¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂, 25°C) δ (ppm): 33.11-33.38 (m, Me₀, Me₁), 118.78 (s, C^{3'}, C^{5'}), 121.38 (s, C³, C^{3''}), 121.55 (s, C₀²), 122.17 (s, C₁²), 122.29 (d, ³J_{C-P} = 3.8 Hz, C₂²), 124.18 (s, C⁵, C^{5''}), 128.59 (s, C₀³), 128.67 (s, C₁³), 128.83 (s, C₂³), 132.37 (s, C₀⁴), 132.68 (s, C₁⁴), 136.06 (s, C₂⁴), 137.05 (s, C⁴, C^{4''}), 139.53-139.67 (m, C₀⁵, C₁⁵), 149.09 (s, C^{4'}), 149.43 (s, C⁶, C^{6''}), 151.63-151.80 (m, C₀¹, C₁¹, C₂¹), 156.19 (s, C², C⁶), 156.22 (s, C², C^{2''}).

Compound 2-G₃:



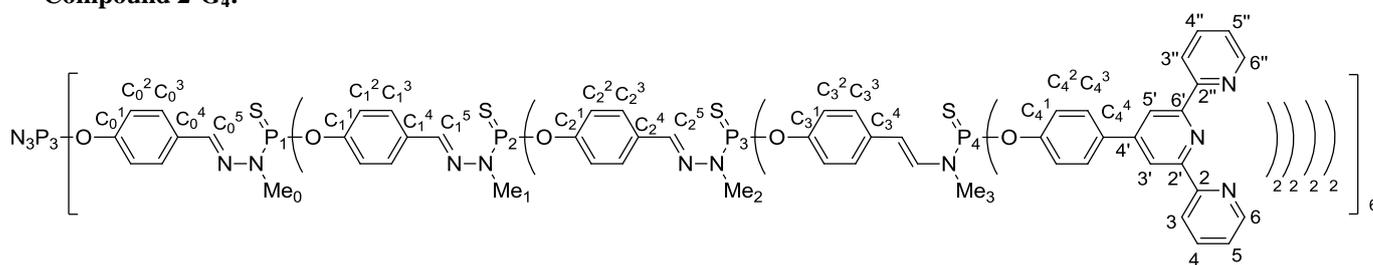
2-G₃ was obtained as a white powder in 91% yield (420 mg, 0.017 mmol).

³¹P{¹H} NMR (121.50 MHz, CD₂Cl₂, 25°C) δ (ppm): 7.96 (s, N₃P₃), 62.24 (br s, P₁=S, P₂=S, P₃=S);

¹H NMR (300.13 MHz, CD₂Cl₂, 25°C) δ (ppm): 2.92-3.34 (m, 126H, Me₀, Me₁, Me₂), 6.81-6.82 (m, 12H, C₀²-H), 7.03-7.43 (m, 306H, C₁²-H, C₂²-H, C₃²-H, C⁵-H, C^{5''}-H), 7.48-7.71 (m, 276H, C₀³-H, C₁³-H, C₂³-H, C₃³-H, C₀⁵-H, C₁⁵-H, C₂⁵-H, C⁴-H, C^{4''}-H), 8.48-8.54 (m, 288H, C^{3'}-H, C^{5'}-H, C³-H, C^{3''}-H, C⁶-H, C^{6''}-H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CD_2Cl_2 , 25°C) δ (ppm): 33.07-33.41 (m, Me_0 , Me_1 , Me_2), 118.73 (s, $\text{C}^{3'}$, $\text{C}^{5'}$), 121.35 (s, C^3 , $\text{C}^{3''}$), 122.24 (br s, C_0^2 , C_1^2 , C_2^2 , C_3^2), 124.17 (s, C^5 , $\text{C}^{5''}$), 128.66 (br s, C_0^3 , C_1^3 , C_2^3), 128.81 (s, C_3^3), 132.64 (br s, C_0^4 , C_1^4 , C_2^4), 135.99 (s, C_3^4), 137.03 (s, C^4 , $\text{C}^{4''}$), 139.52-139.73 (m, C_0^5 , C_1^5 , C_2^5), 149.01 (s, C^4), 148.38 (s, C^6 , $\text{C}^{6''}$), 151.53-151.78 (m, C_0^1 , C_1^1 , C_2^1 , C_3^1), 156.14 (s, C^2 , $\text{C}^{2'}$, $\text{C}^{2''}$, $\text{C}^{6'}$).

Compound 2-G₄:



2-G₄ was obtained as a white powder in 90% yield (400 mg, 0.0080 mmol).

$^{31}\text{P}\{^1\text{H}\}$ NMR (161.97 MHz, CD_2Cl_2 , 25°C) δ (ppm): 62.121 (br s, $\text{P}_1=\text{S}$, $\text{P}_2=\text{S}$, $\text{P}_3=\text{S}$, $\text{P}_4=\text{S}$);

^1H NMR (400.13 MHz, CD_2Cl_2 , 25°C) δ (ppm): 2.84-3.37 (m, 270H, Me_0 , Me_1 , Me_2 , Me_3), 6.91-7.32 (m, 544H, $\text{C}_0^2\text{-H}$, $\text{C}_1^2\text{-H}$, $\text{C}_2^2\text{-H}$, $\text{C}_3^2\text{-H}$, $\text{C}_4^2\text{-H}$, $\text{C}^5\text{-H}$, $\text{C}^{5''}\text{-H}$), 7.34-7.90 (m, 634H, $\text{C}_0^3\text{-H}$, $\text{C}_1^3\text{-H}$, $\text{C}_2^3\text{-H}$, $\text{C}_3^3\text{-H}$, $\text{C}_4^3\text{-H}$, $\text{C}_0^5\text{-H}$, $\text{C}_1^5\text{-H}$, $\text{C}_2^5\text{-H}$, $\text{C}_3^5\text{-H}$, $\text{C}^4\text{-H}$, $\text{C}^{4''}$), 8.16-8.79 (m, 552H, $\text{C}^{3'}\text{-H}$, $\text{C}^{5'}\text{-H}$, $\text{C}^3\text{-H}$, $\text{C}^{3''}\text{-H}$, $\text{C}^6\text{-H}$, $\text{C}^{6''}\text{-H}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CD_2Cl_2 , 25°C) δ (ppm): 33.09-33.38 (m, Me_0 , Me_1 , Me_2 , Me_3), 118.70 (s, $\text{C}^{3'}$, $\text{C}^{5'}$), 121.34 (s, C^3 , $\text{C}^{3''}$), 122.26 (br s, C_0^2 , C_1^2 , C_2^2 , C_3^2 , C_4^2), 124.16 (s, C^5 , $\text{C}^{5''}$), 128.65 (br s, C_0^3 , C_1^3 , C_2^3 , C_3^3), 128.79 (s, C_4^3), 132.62 (br s, C_0^4 , C_1^4 , C_2^4 , C_3^4), 135.95 (s, C_4^4), 137.01 (s, C^4 , $\text{C}^{4''}$), 139.41-139.79 (m, C_0^5 , C_1^5 , C_2^5 , C_3^5), 148.96 (s, C^4), 149.36 (s, C^6 , $\text{C}^{6''}$), 151.53-151.84 (m, C_0^1 , C_1^1 , C_2^1 , C_3^1 , C_4^1), 156.10 (s, C^2 , $\text{C}^{2'}$, $\text{C}^{2''}$, $\text{C}^{6'}$).

3. General procedures for catalytic reactions

Catalytic reactions were carried out under argon atmosphere in Radley Carousel “reaction station RR98030” when using classical heating or in 10 mL-reactors when using microwaves irradiation.

GC yields are calculated using 1,3,5-trimethoxybenzene (or anisole) as the standard. GC method: Initial temperature: 50 °C; Initial time: 2 min; Ramp: 10 °C/min; Final temperature: 230 °C; Final time: 10 min.

Products were purified by removing acetonitrile after precipitation of the catalyst when quantitative yields are obtained and purified by column chromatography if necessary.

General procedure for standard catalytic tests:

A Radley tube Carousel equipped with a magnetic stirring bar was charged with Sc(OTf)₃ (0.035 mmol or 0.053 mmol) and ligand (0.035 mmol or 0.053 mmol for **M**, 0.0029 mmol for **2-G₁**, 0.00145 mmol for **2-G₂**, 0.00073 mmol for **2-G₃**, 0.00036 mmol for **2-G₄**). After another standard cycle of evacuation and back-filling with argon, acetonitrile (2 mL) was added. After 15 minutes stirring at room temperature, aryl derivative (0.35 mmol) and acetic anhydride (0.70 mmol) were introduced. The tube was closed under a positive pressure of argon, stirred, and refluxed or heating by microwaves for the required time period. After cooling to room temperature, standard (0.5 mmol) was added and conversion of crude product was measured by GC.

General procedure for recycling experiments:

A 10-mL reactor equipped with a magnetic stirring bar was charged with Sc(OTf)₃ (0.035 mmol, 15.0 mg), **2-G₄** (0.00036 mmol, 18.1 mg) and acetonitrile (2 mL). After 15 minutes stirring at room temperature, aryl derivative (0.35 mmol) and electrophile (0.70 mmol) were introduced. The tube was closed, stirred, and heated by microwaves (30 W) for the required time period. After cooling to room temperature, standard (0.5 mmol) and Et₂O (25 mL) were added. The resulting precipitate was filtered and washed twice with Et₂O (15 mL). The filtrate was then analyzed by GC and the expected product was isolated by column chromatography if necessary. The precipitate was directly used for a new catalytic run: acetonitrile (2 mL), arene (0.35 mmol) and electrophile (0.70 mmol) were introduced. The flask was closed, stirred and heated by microwaves for the required time period.

All acylated arenes **6a-k** have been described in the literature^{4,5,6,7,8,9,10,11,12}. Some selected spectra of isolated compounds are given in paragraph 4.

It has been checked that acylated compounds could be obtained on 2 mmol scale also.

⁴ For **6a**, see: L.-Q. Cui, K. Liu, C. Zhang, *Org. Biomol. Chem.* **2011**, *9*, 2258.

⁵ For **6b**, see: J. Lindh, P. J. R. Sjöberg, M. Larhed, *Angew. Chem. Int. Ed.* **2010**, *49*, 7733.

⁶ For **6c** and **6d**, see: S. Son, F. D. Toste, *Angew. Chem. Int. Ed.* **2010**, *49*, 3791.

⁷ For **6e**, see: J. Ruan, X. Li, O. Saidi, J. Xiao, *J. Am. Chem. Soc.* **2008**, *130*, 2424.

⁸ For **6f**, see: H. Chen, X. Zhong, J. Wei, *Molecules*, **2007**, *12*, 1170.

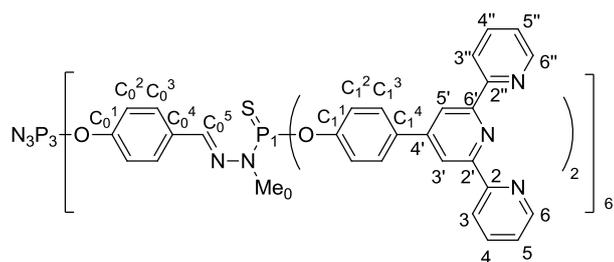
⁹ For **6h**, see: X.-J. Mu, J.-P. Zou, Q.-F. Qian, W. Zhang, *Org. Lett.* **2006**, *8*, 5291.

¹⁰ For **6i**, see: Z. Hyder, J. Ruan, J. Xiao, *Chem. Eur. J.* **2008**, *14*, 5555.

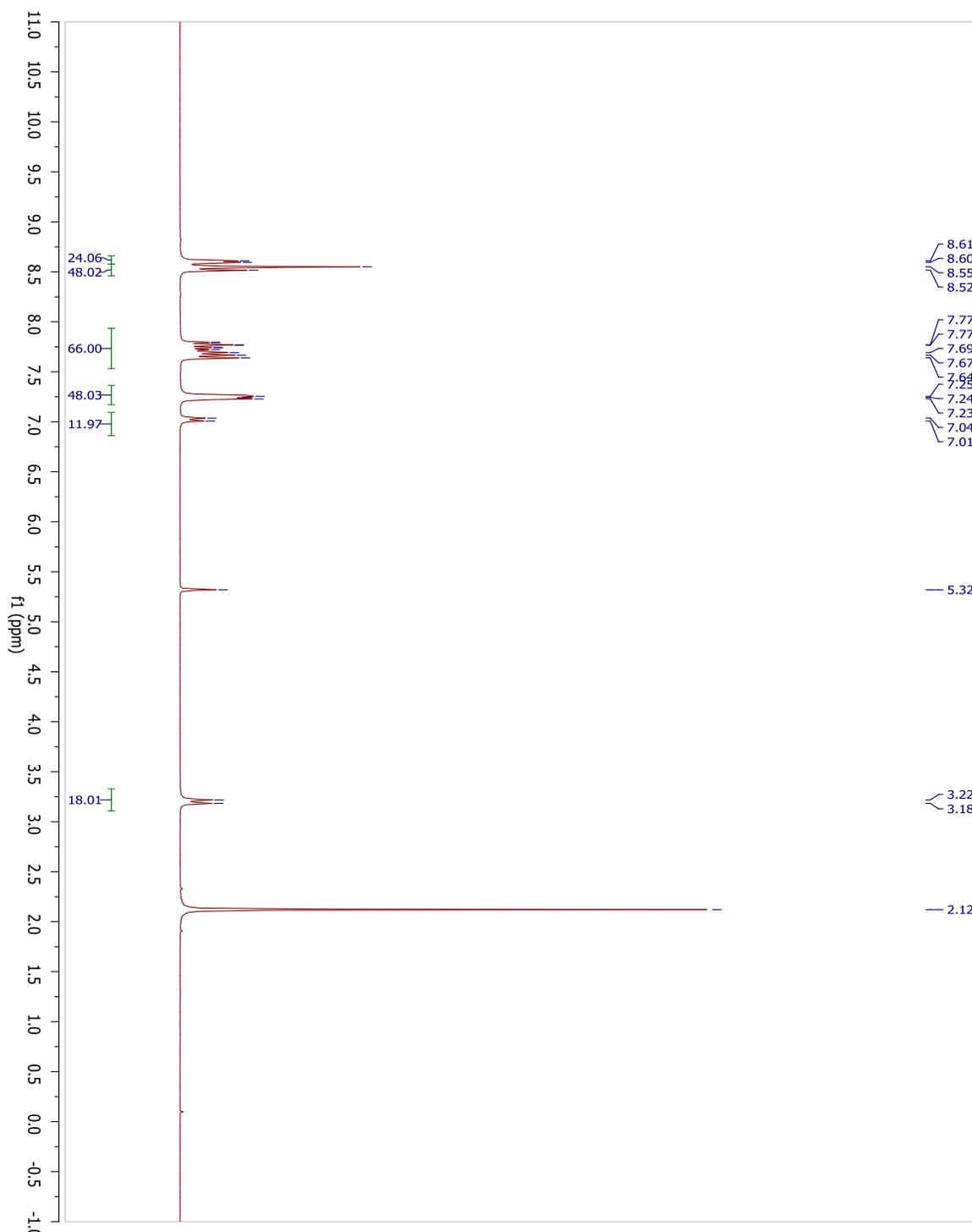
¹¹ For **6j**, see: I. A. Ushakov, A. V. Afonin, V. K. Voronov, Z. V. Stepanova, L. N. SObenina, A. I. Mikhaleva, *Russian J. Org. Chem.* **2003**, *39*, 1318.

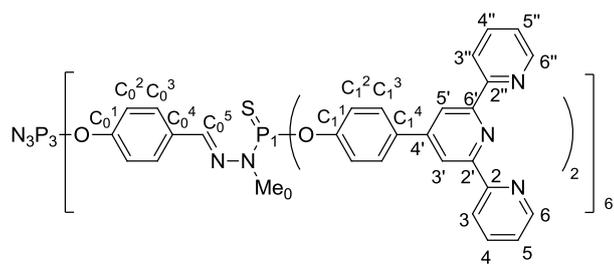
¹² For **6k**, see: T. Yamada, E. Mashima, K. Ueki, S. Yamago, *Chem. Lett.* **2008**, *37*, 650.

4. ^1H , ^{13}C and ^{31}P NMR spectra of dendrimers and of some isolated acylated aromatics

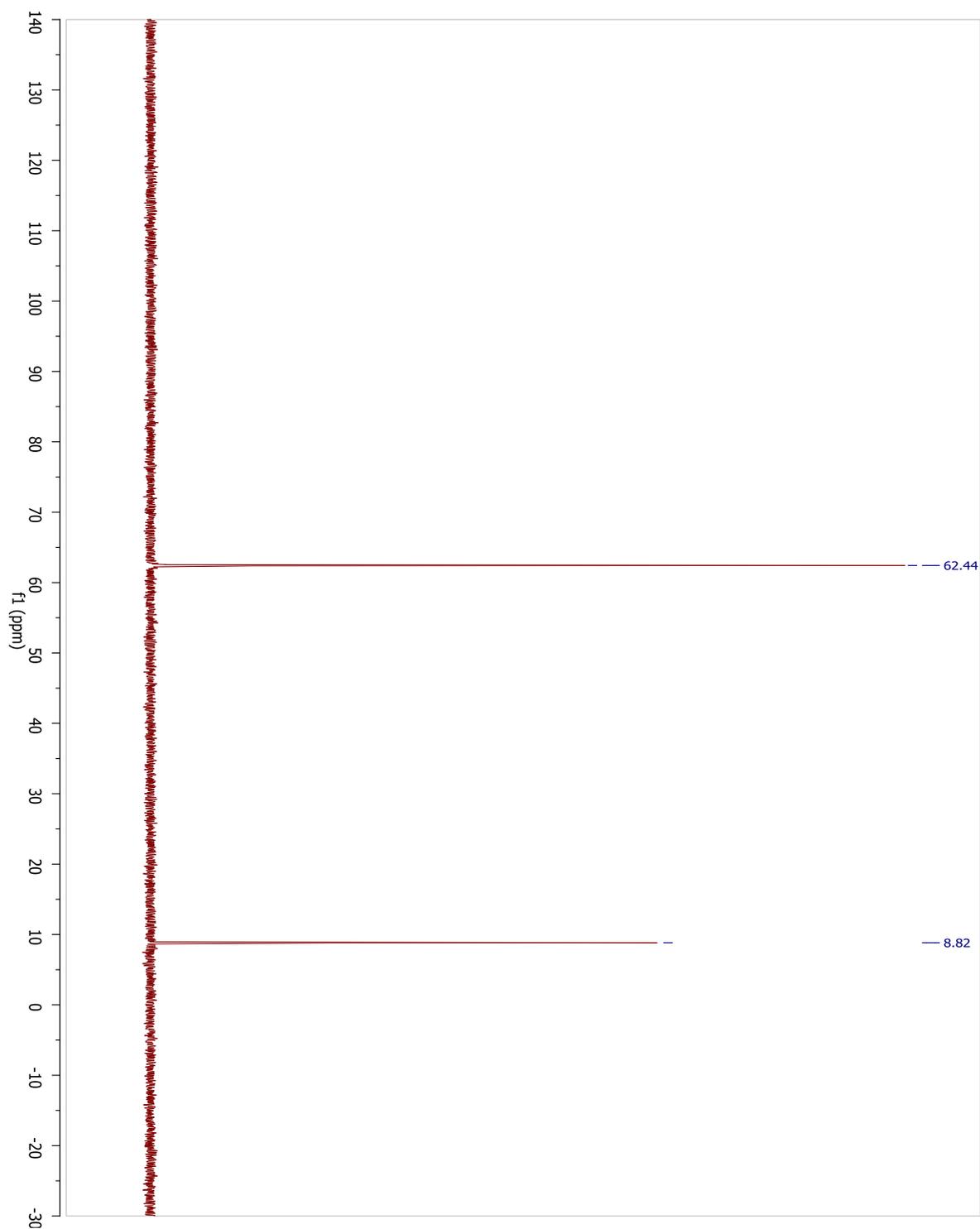


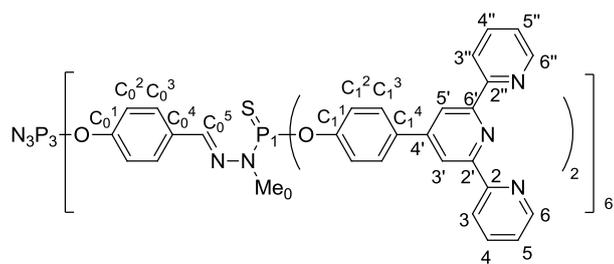
^1H NMR



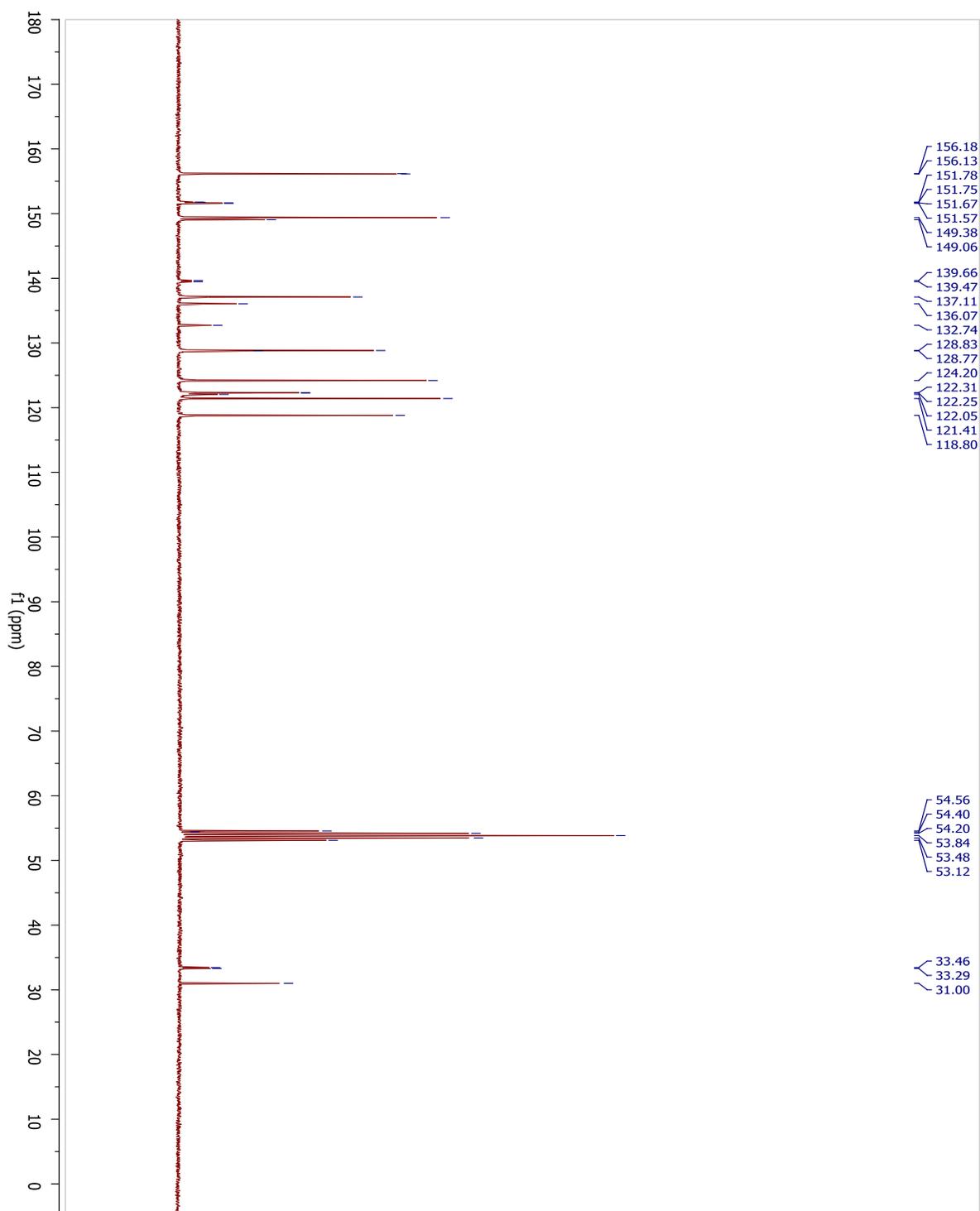


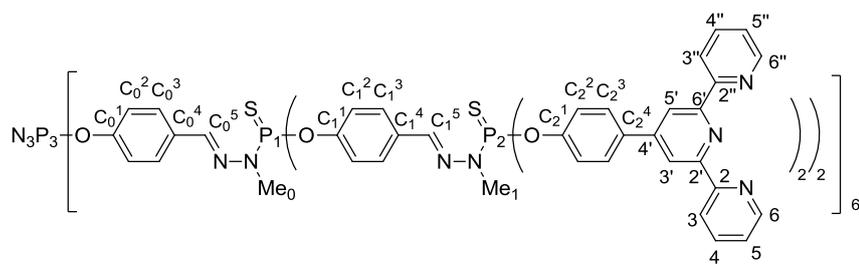
$^{31}\text{P}\{^1\text{H}\}$ NMR



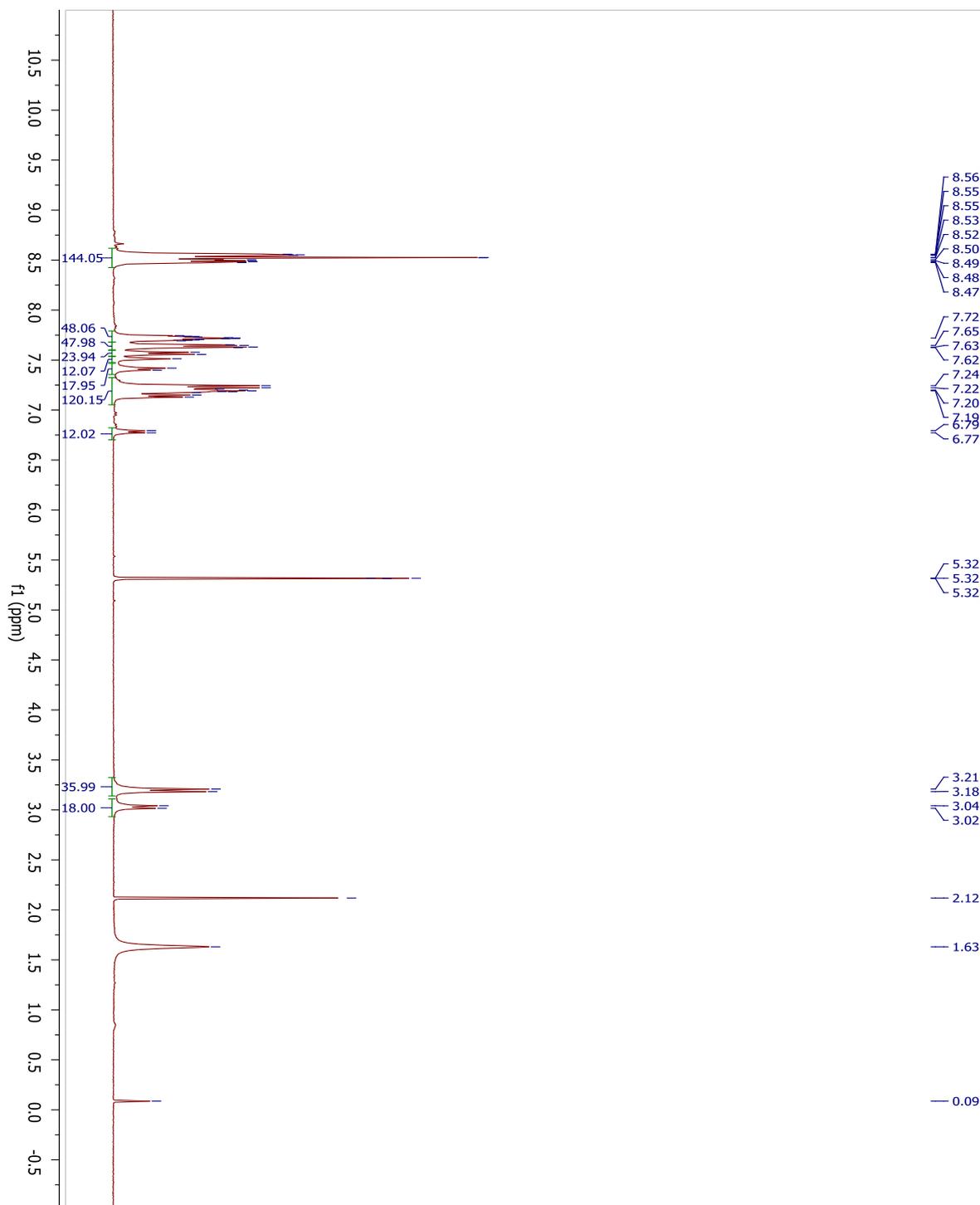


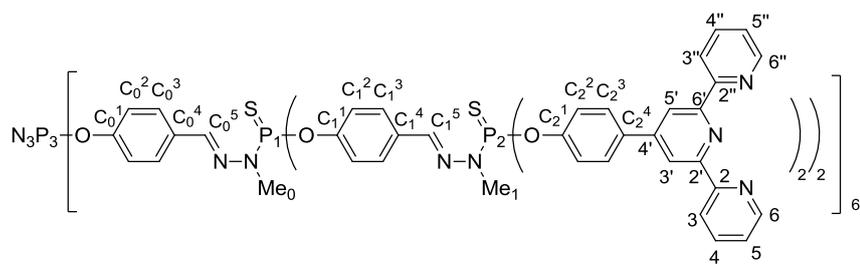
$^{13}\text{C}\{^1\text{H}\}$ NMR



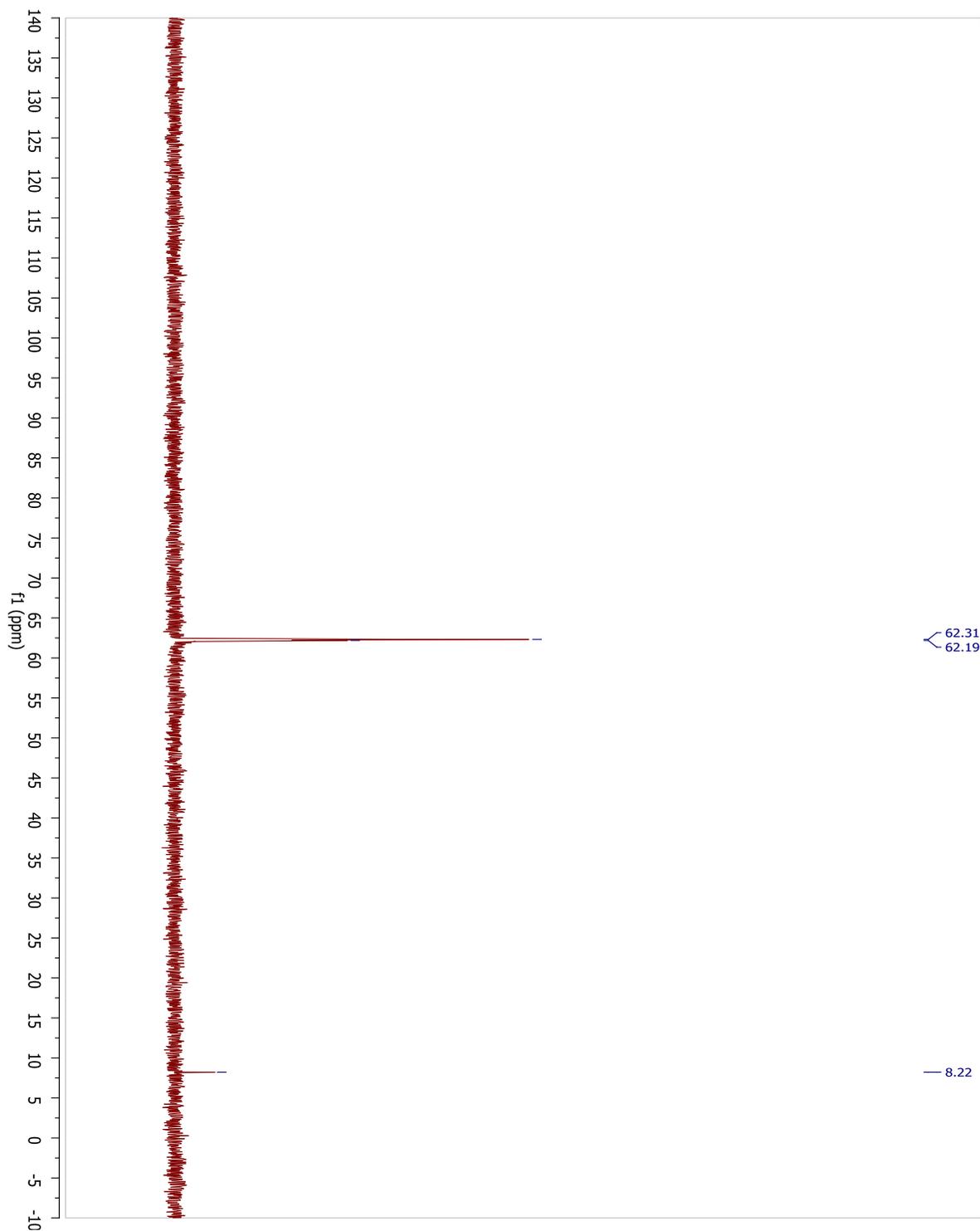


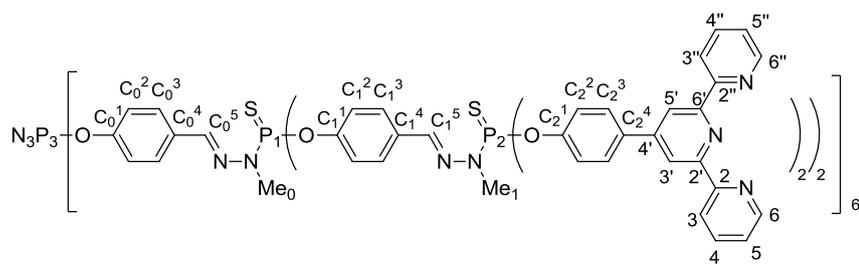
$^1\text{H NMR}$



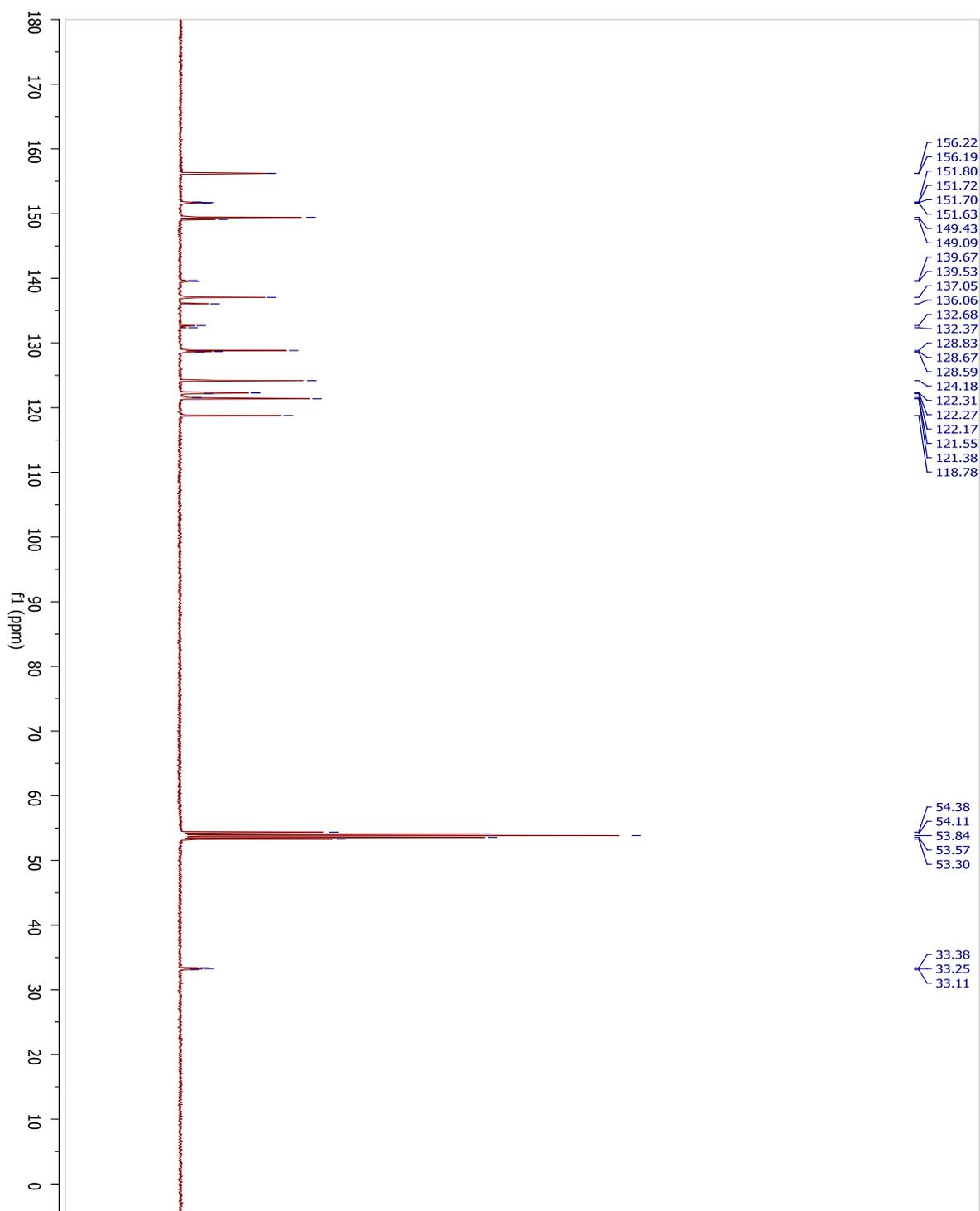


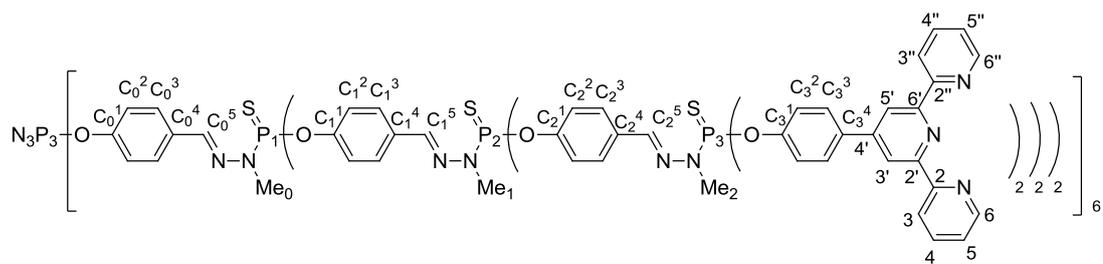
$^{31}\text{P}\{^1\text{H}\}$ NMR



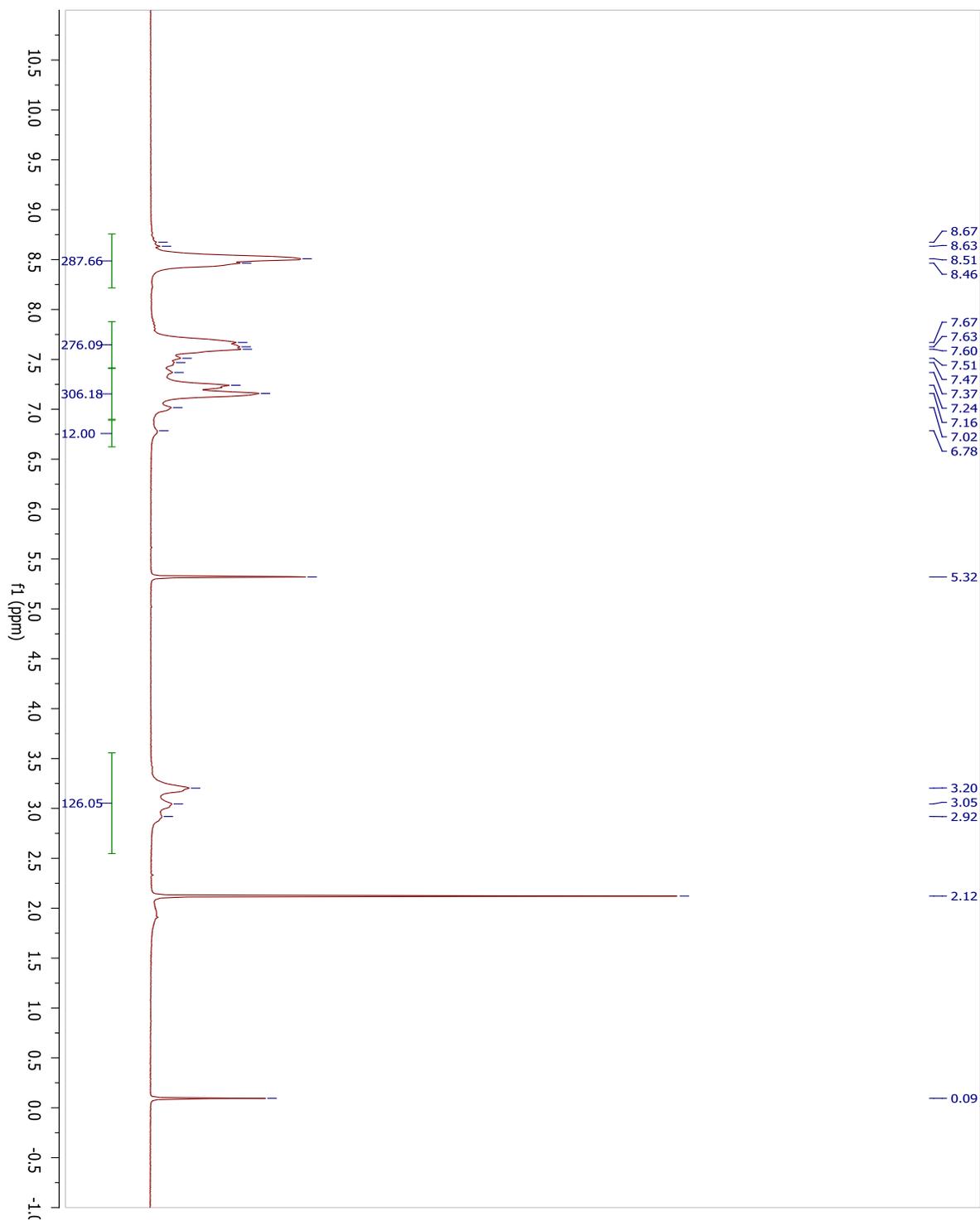


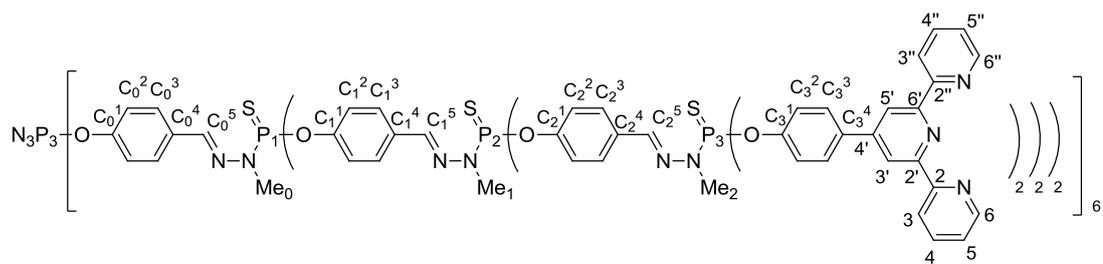
$^{13}\text{C}\{^1\text{H}\}$ NMR



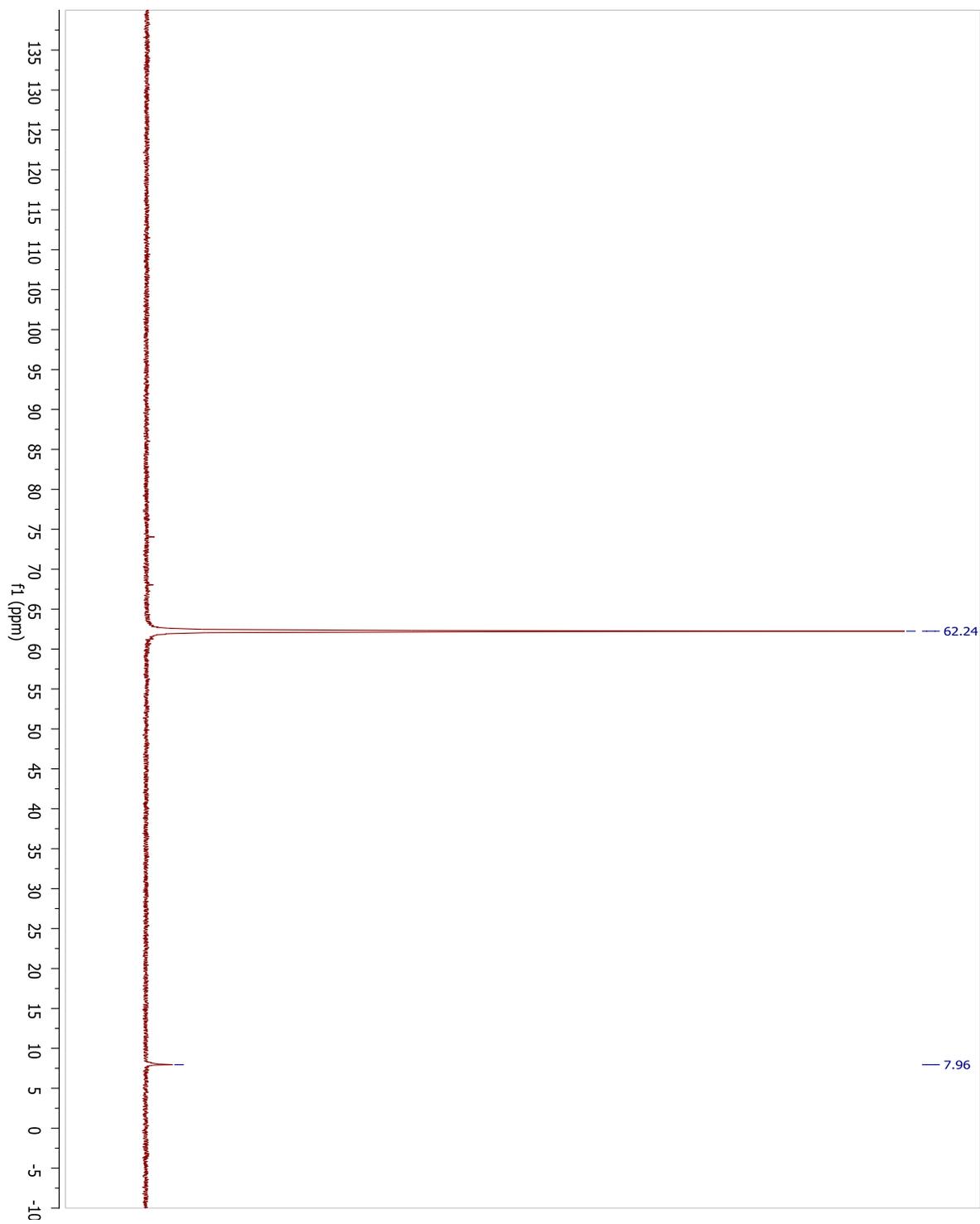


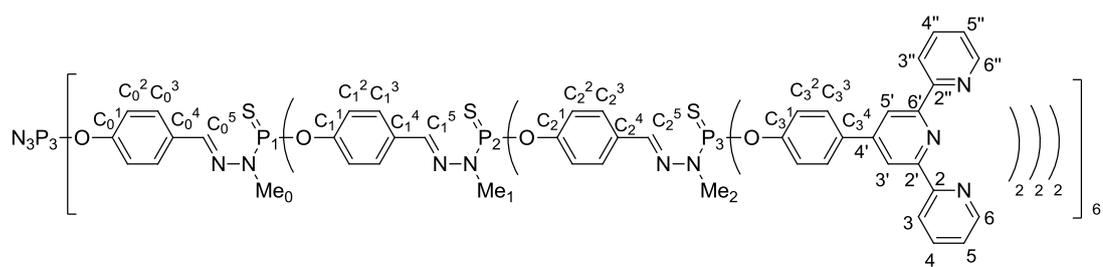
$^1\text{H NMR}$



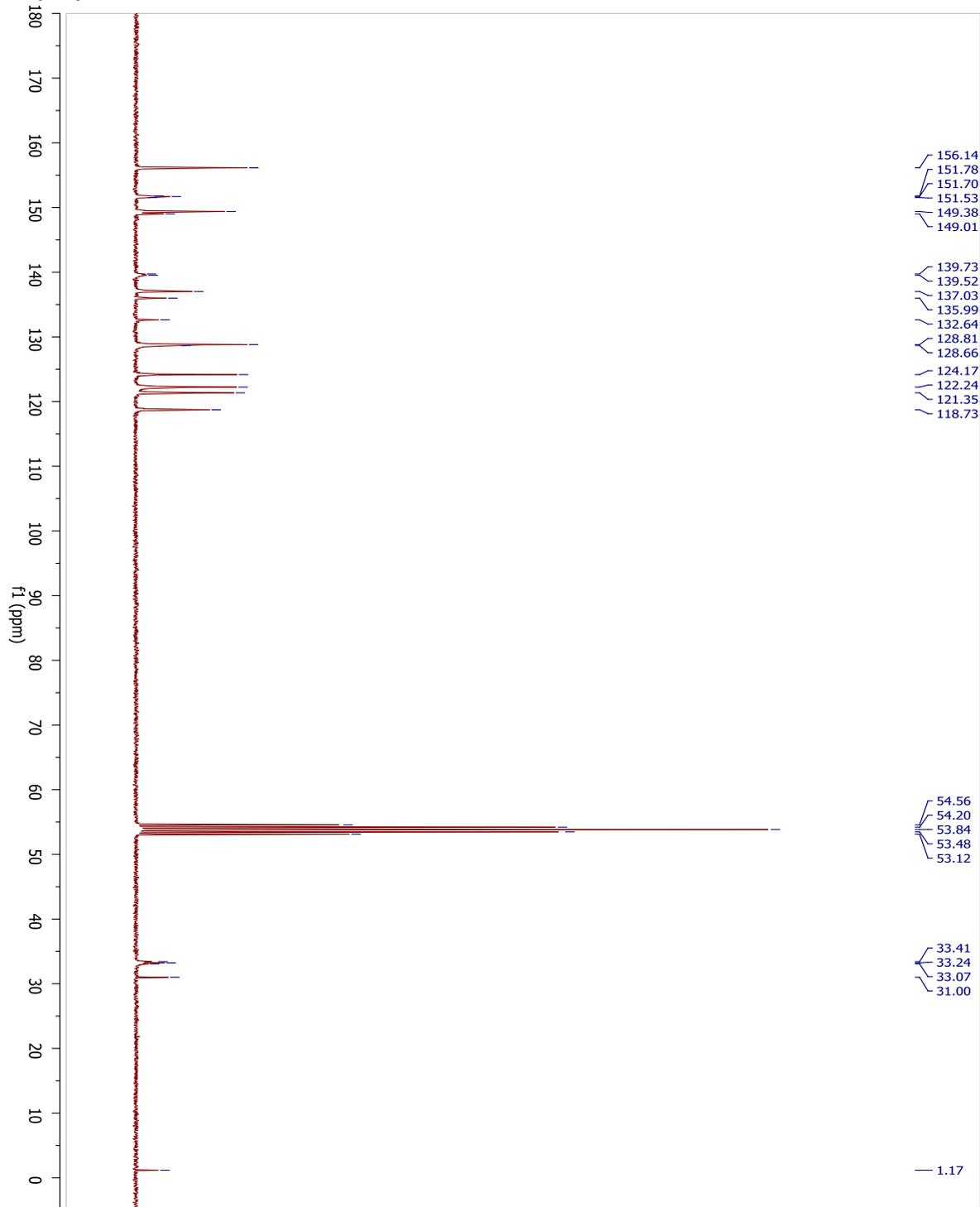


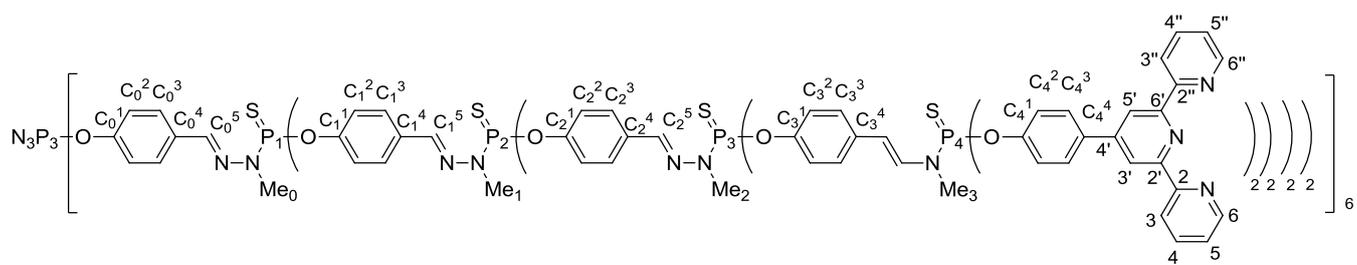
$^{31}\text{P}\{^1\text{H}\}$ NMR



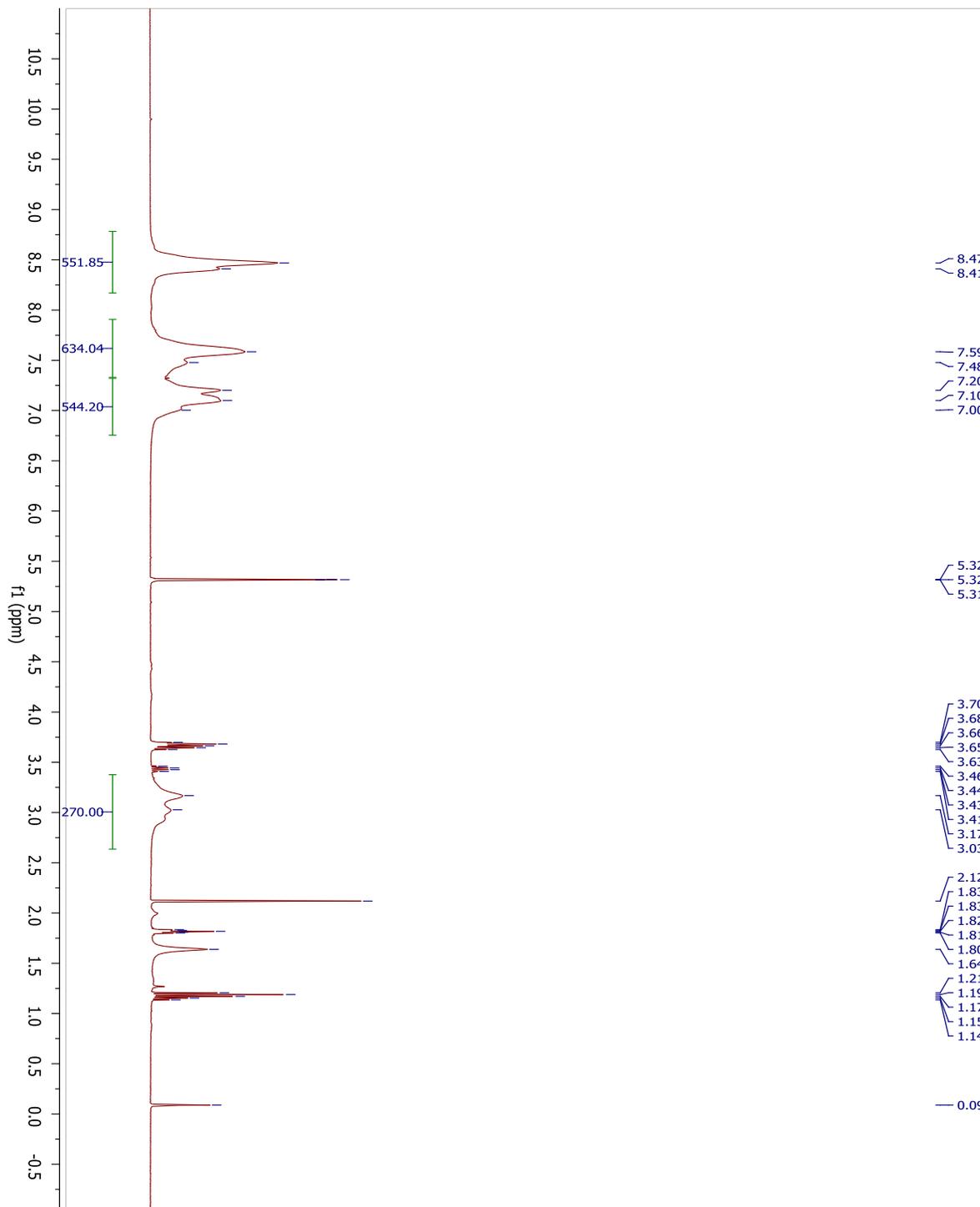


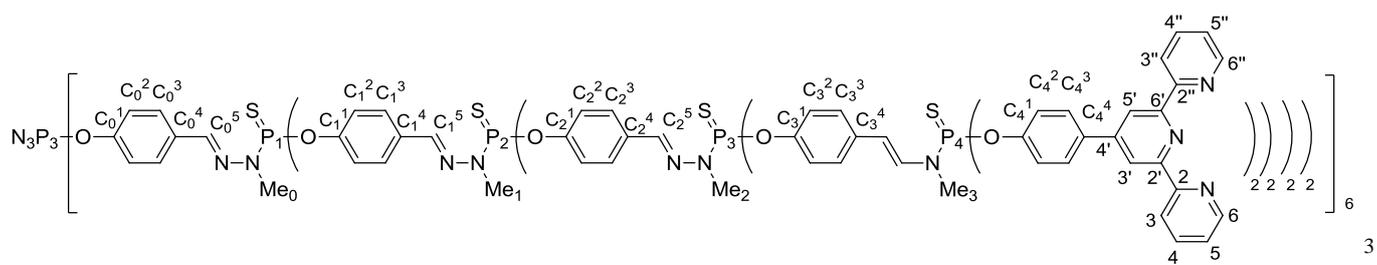
¹³C{¹H} NMR



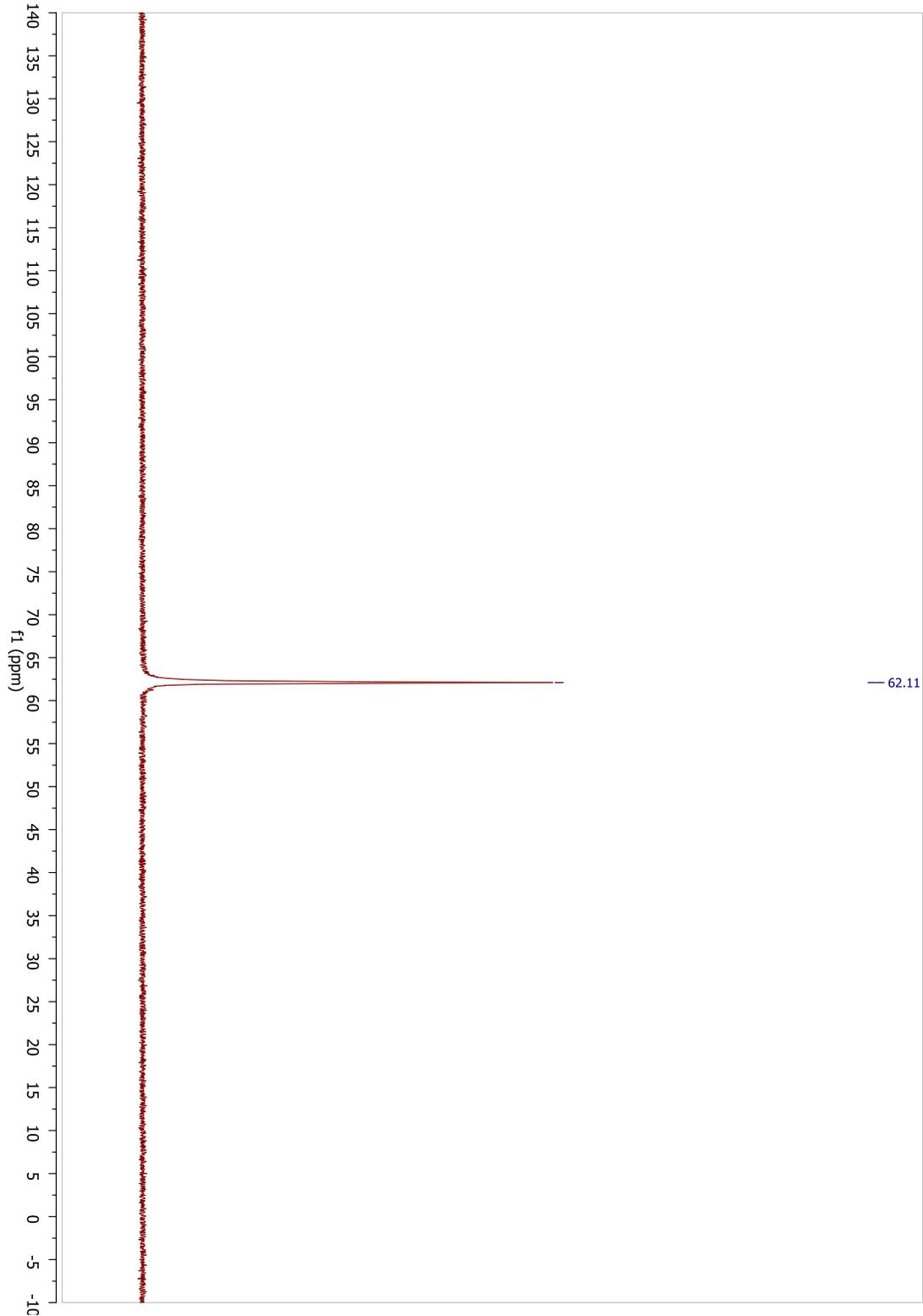


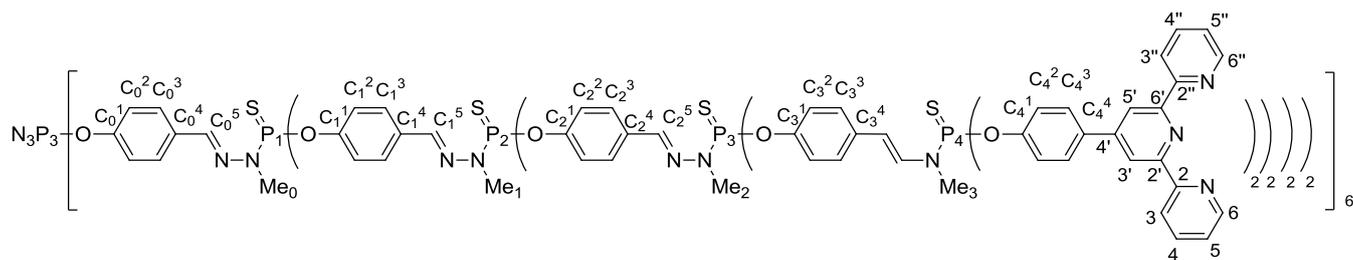
H NMR



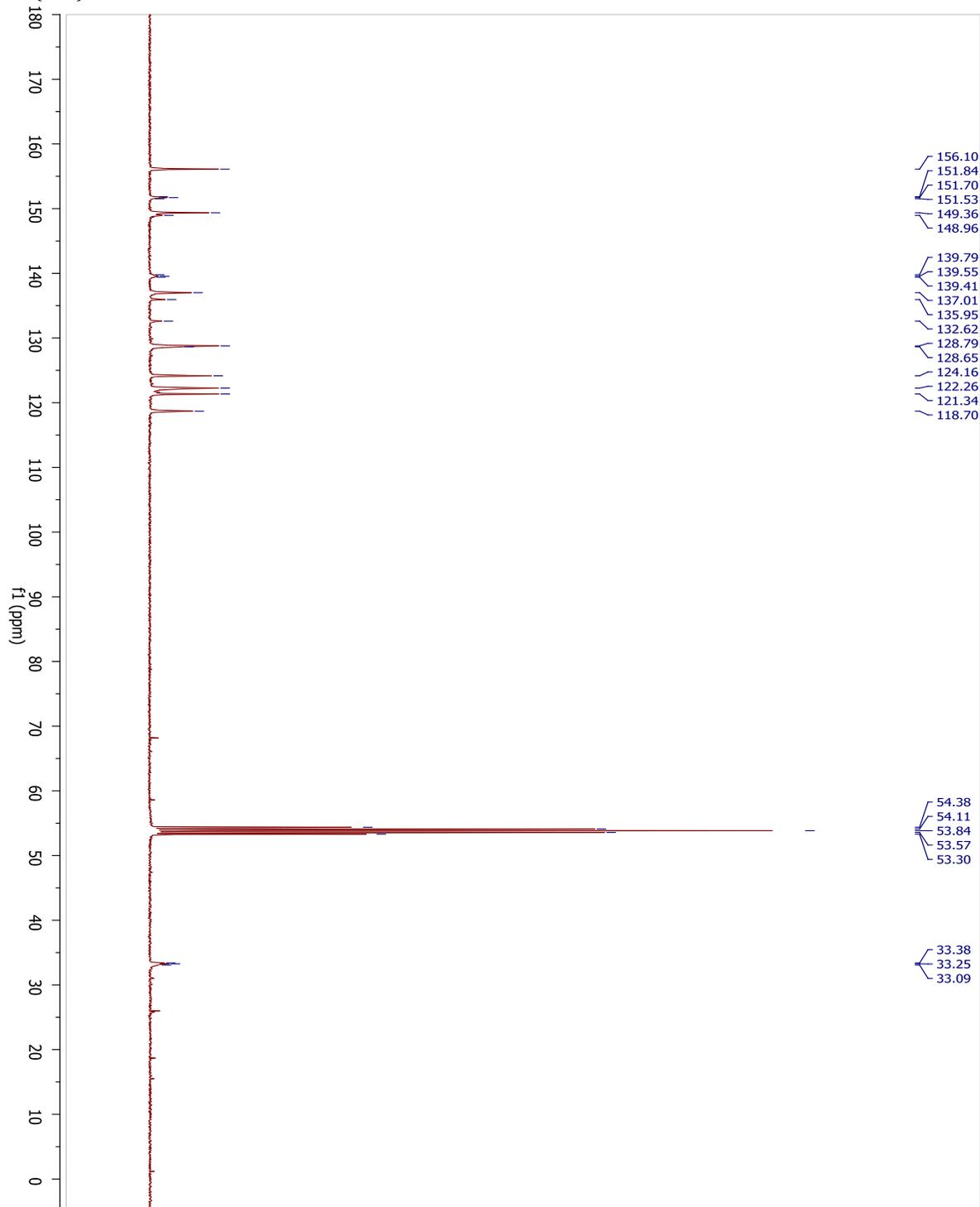


$^1\text{P}\{^1\text{H}\}$ NMR



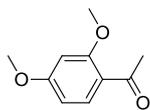


$^{13}\text{C}\{^1\text{H}\}$ NMR



Selected spectra and characterization of some acylated arenes

Compound 6b



The standard procedure described above was applied by using 1,3-dimethoxybenzene (46 μ L, 0.35 mmol) and acetic anhydride (66 μ L, 0.70 mmol). The filtrate obtained after precipitation of the catalyst with diethyl ether was purified by silica column chromatography and product **6b** obtained as a white powder in 99 % yield (62.4 mg). For purity: see spectra below.

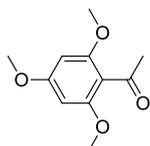
$^1\text{H NMR}$ (300.13 MHz, CDCl_3 , 25°C) δ (ppm): 2.51(s, 3H); 3.78 (s, 3H); 3.83 (s, 3H); 6.40 (d, 1H, $J= 2.3\text{Hz}$); 6.45 (dd, 1H, $J= 8.7\text{ Hz, } 2.3\text{Hz}$); 7.77 (d, 1H, $^3J= 8.7\text{ Hz}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3 , 25°C) δ (ppm): 31.77; 55.36; 55.42; 98.14; 105.10; 120.96; 132.51; 161.05; 164.51; 197.48.

GC: rt = 18.1 min

DCI-MS (NH_3): m/z: 181.0 [M + H] $^+$

Compound 6d



The standard procedure described above was applied by using 1,3,5-trimethoxybenzene (58.9 mg, 0.35 mmol) and acetic anhydride (66 μ L, 0.70 mmol). The filtrate obtained after precipitation of the catalyst with diethyl ether was purified by silica column chromatography and product **6d** obtained as a white powder in 99 % yield (72.8 mg). For purity: see spectra below.

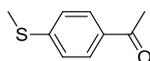
$^1\text{H NMR}$ (300.13 MHz, CDCl_3 , 25°C) δ (ppm): 2.39(s, 3H); 3.72 (s, 6H); 3.75 (s, 3H); 6.05 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3 , 25°C) δ (ppm): 32.44; 55.34; 55.72; 90.51; 113.52; 158.24; 162.32; 201.57.

GC: rt = 19.9 min

DCI-MS (NH_3): m/z: 211.0 [M + H] $^+$

Compound 6e



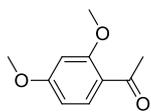
The standard procedure described above was applied by using thioanisole (41 μ L, 0.35 mmol) and acetic anhydride (66 μ L, 0.70 mmol). The filtrate obtained after precipitation of the catalyst with diethyl ether was purified by silica column chromatography and product **6e** obtained as a white powder in 80 % yield (46.5 mg). For purity: see spectra below.

$^1\text{H NMR}$ (300.13 MHz, CDCl_3 , 25°C) δ (ppm): 2.52 (s, 3H); 2.57 (s, 3H); 7.26 (m, 2H); 7.87 (m, 2H).

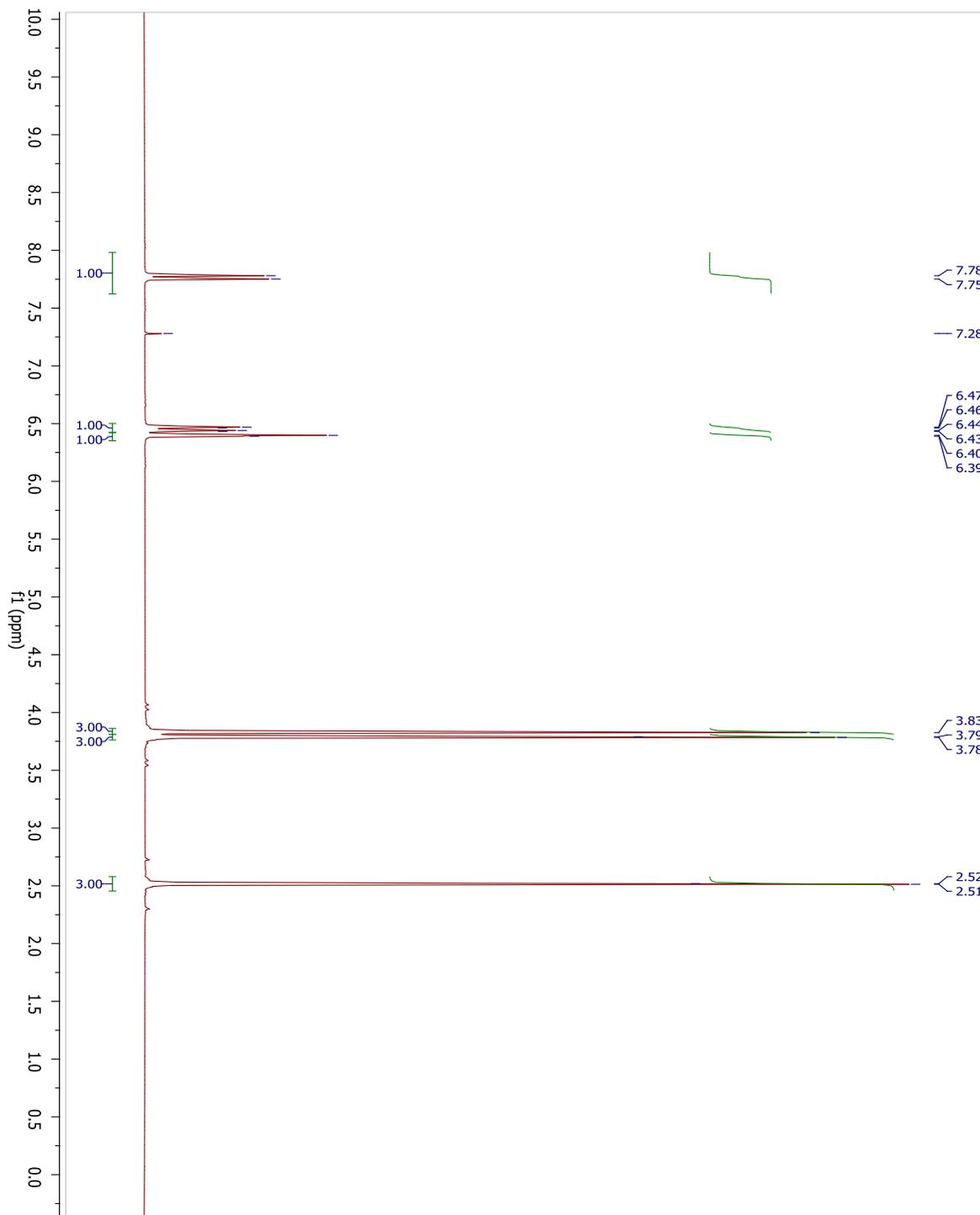
$^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3 , 25°C) δ (ppm): 14.76; 26.41; 124.95; 128.71; 133.48; 145.86; 197.11.

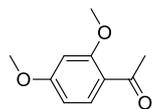
GC: rt = 17.7 min

DCI-MS (NH_3): m/z: 167.0 [M + H] $^+$

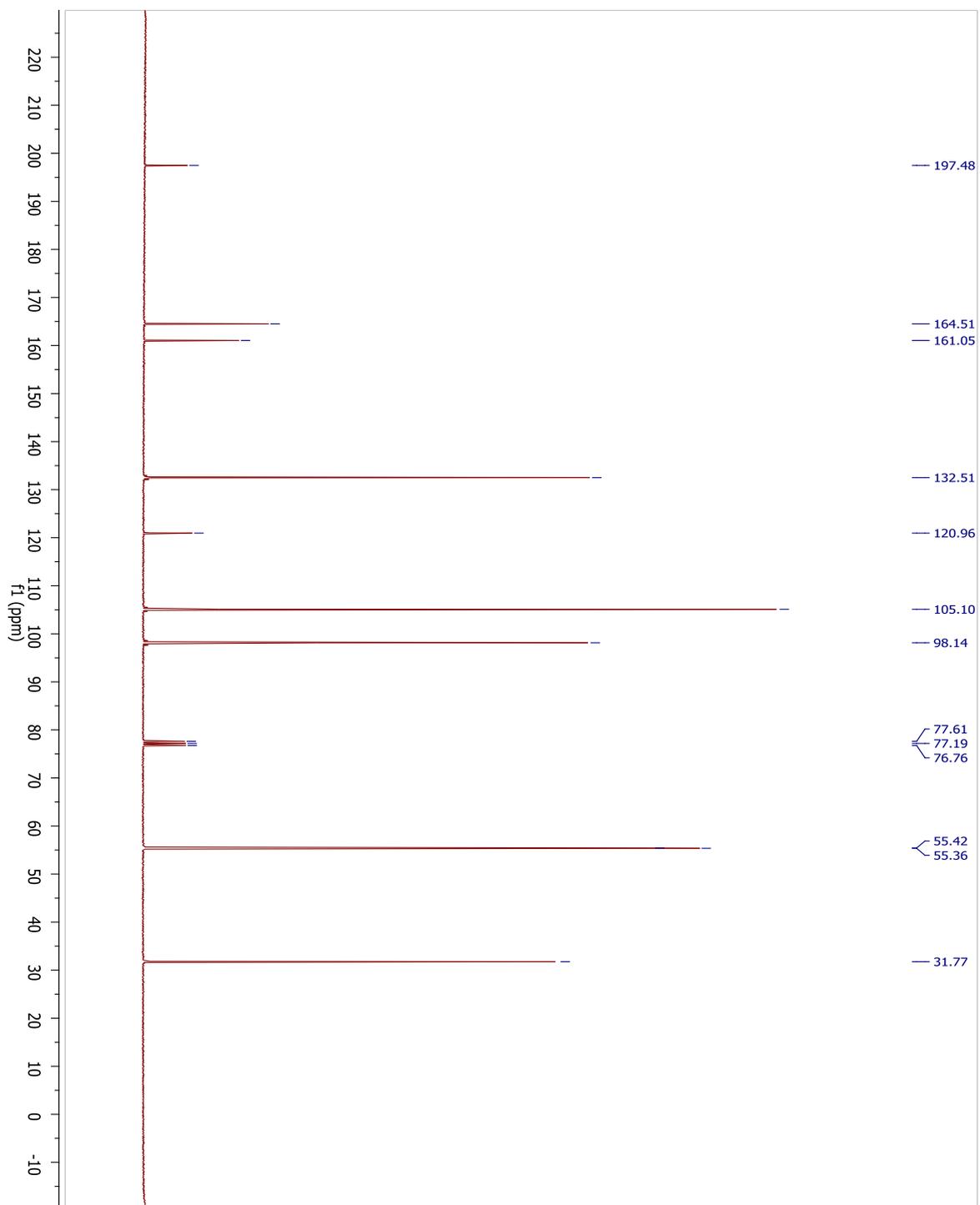


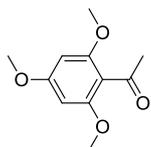
^1H NMR



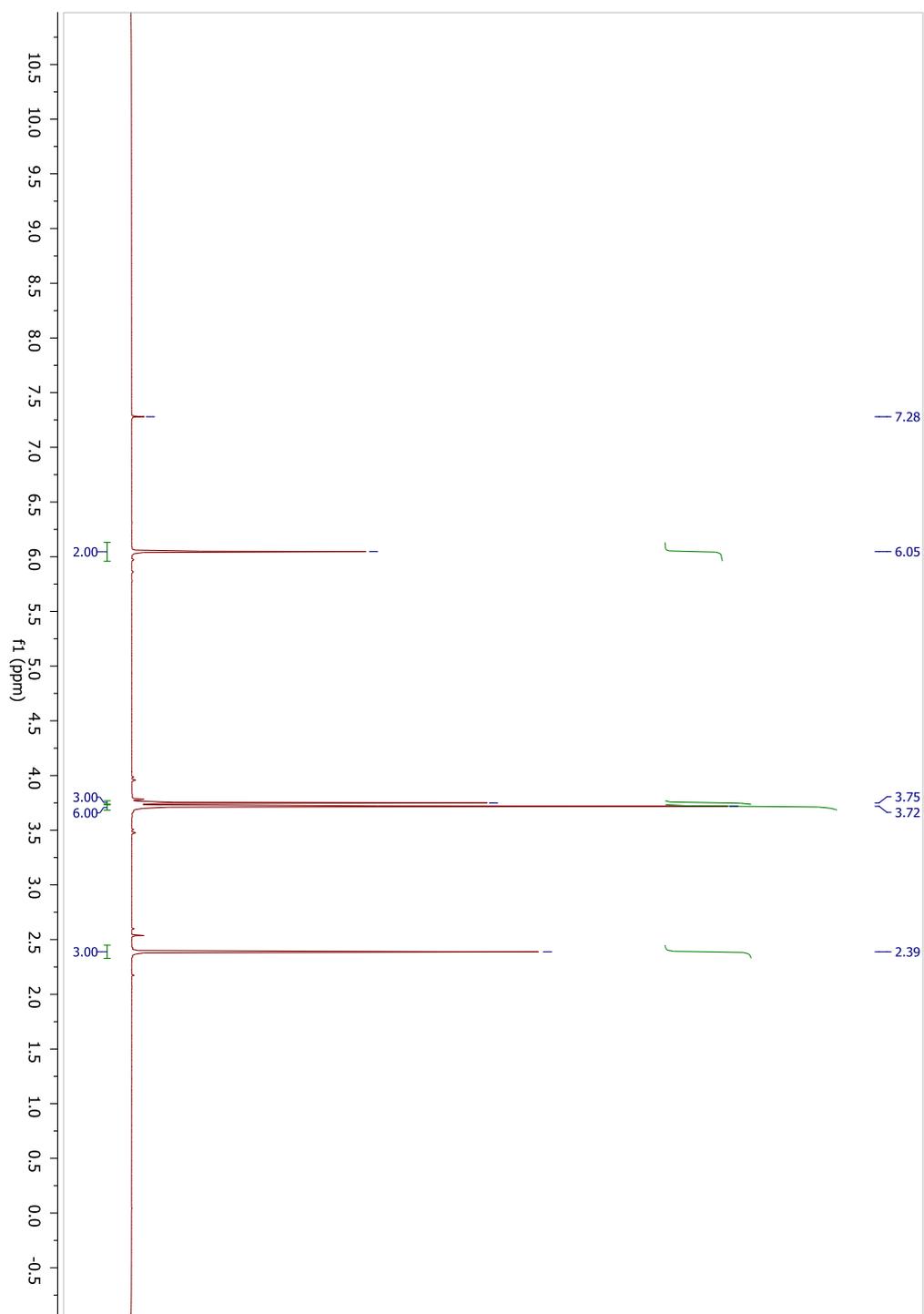


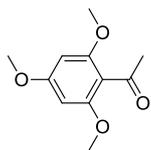
$^{13}\text{C}\{^1\text{H}\}$ NMR



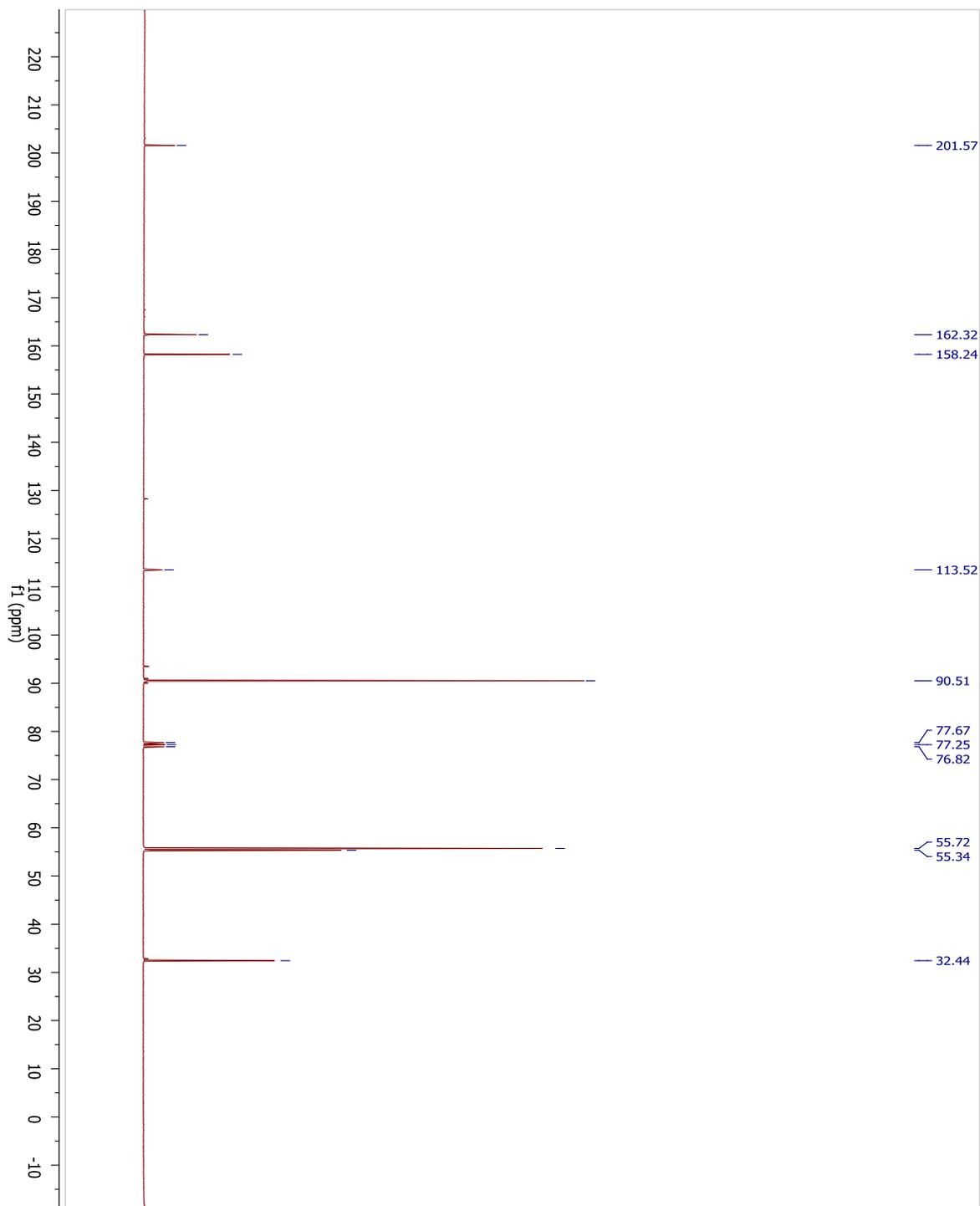


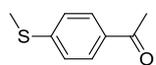
$^1\text{H NMR}$



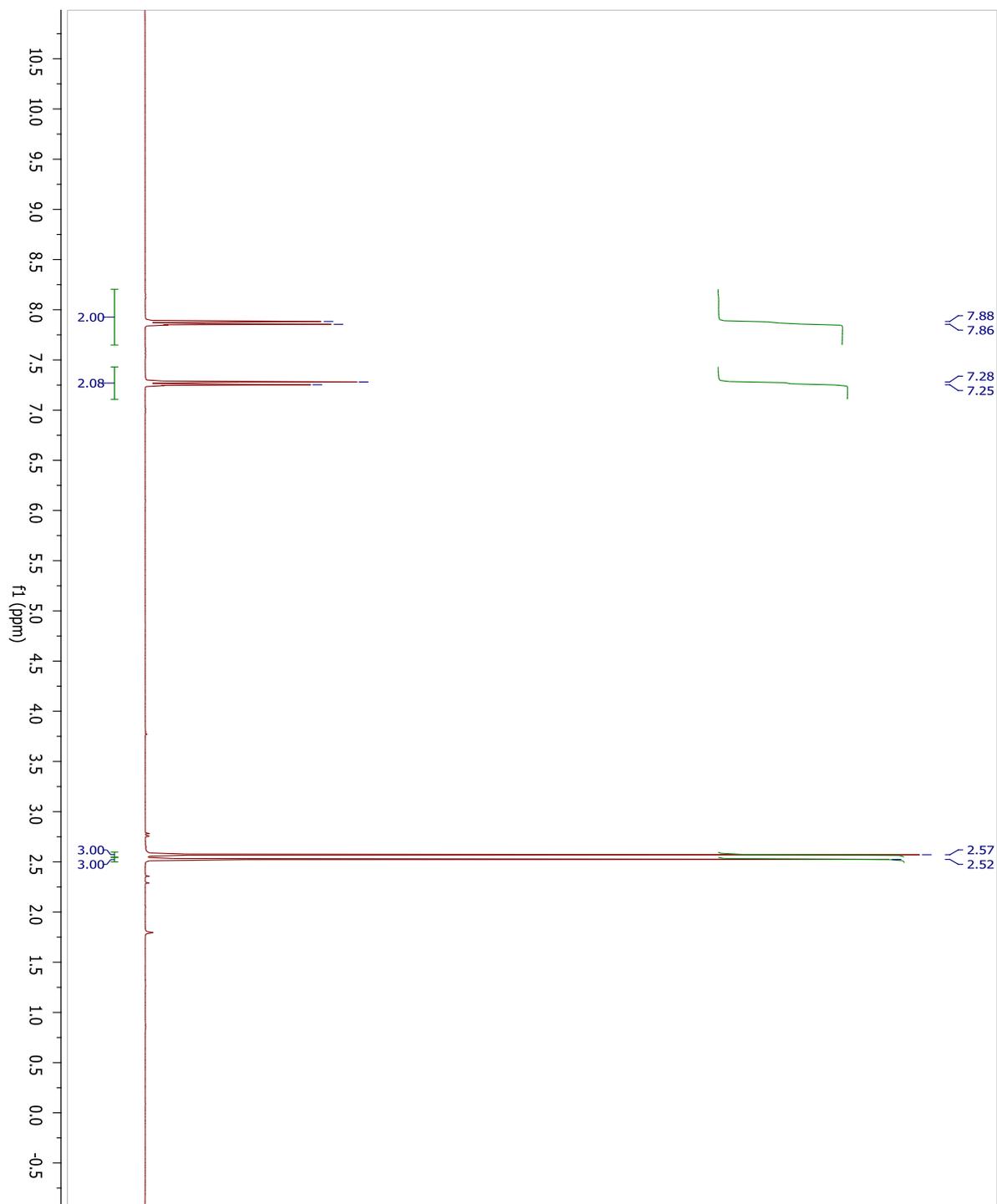


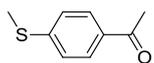
$^{13}\text{C}\{^1\text{H}\}$ NMR





^1H NMR





$^{13}\text{C}\{^1\text{H}\}$ NMR

