– Supplementary Information –

Photocontrol of Ion Permeation in Lipid Vesicles with Amphiphilic Dithienylethenes

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Procedures for the synthesis of 1 and 2

1-(4-Bromophenyl)-12-(*N,N*-dimethylamino)dodecan-1-one (4)

The preparation of **4** has been adapted from a previously published procedure.[1] Starting material, 12-(*N,N*-dimethylamino)dodecanoyl chloride, was prepared following reported procedures[2, 3] in two steps (36%) from commercially available 12-aminododecanoic acid. Anhydrous aluminum chloride (2.99 g, 22.4 mmol) was added to a stirred solution of the acid chloride (1.92 g, 7.48 mmol) in bromobenzene (11 mL) at 0 °C. After stirring at 50 °C for 2 h, icy water (15 mL) and aqueous hydrochloric acid (2.0 mL, 6.0 M) was added to the reaction mixture and stirred at room temperature for 12 h. After adjusting the pH of the mixture to above 12 with aqueous sodium hydroxide (2.0 M), the mixture was extracted with dichloromethane (3 × 50 mL), washed with a saturated aqueous solution of sodium chloride (80 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (3:1:0.1 petroleum ether/dichloromethane/ triethylamine) gave pure **4** as an off-white solid (1.60 g, 56%). ^{1}H NMR ($CDCl_3$, δ): 1.20–1.41 (br m, 14H, CH_2), 1.47 (m, 2H, CH_2), 1.68 (m, 2H, CH_2), 2.25 (s, 6H, CH_3), 2.29 (t, J = 7.6 Hz, 2H, CH_2), 2.91 (t, J = 7.4 Hz, 2H, CH_2), 7.56–7.62 (m, 2H, Ar H), 7.78–7.84 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 24.5, 27.7, 29.5, 29.7, 29.8, 38.8, 45.5, 60.0, 128.2, 129.8, 132.1, 136.0, 199.7. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{32}{}^{79}BrNO$, 381.1662; found 381.1656.

1-(4-Bromophenyl)-6-(*N,N*-dimethylamino)hexan-1-one (5)

This method is similar to that used for **4**. Starting material, 6-(*N,N*-dimethylamino)hexanoyl chloride, was prepared following reported procedures[2, 3] (95%

in two steps) from commercially available 6-aminohexanoic acid. Purification of the crude product by flash column chromatography (10:1:0.2 ethyl acetate/methanol/triethylamine) gave pure **5** as a pale yellow solid (57%). ^{1}H NMR ($CDCl_3$, δ): 1.38 (m, 2H, CH_2), 1.50 (m, 2H, CH_2), 1.73 (m, 2H, CH_2), 2.20 (s, 6H, CH_3), 2.26 (t, J = 7.3 Hz, 2H, CH_2), 2.92 (t, J = 7.4 Hz, 2H, CH_2), 7.55–7.61 (m, 2H, Ar H), 7.76–7.83 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 23.8, 26.0, 26.8, 38.3, 44.3, 58.9, 128.4, 129.8, 132.1, 135.8, 199.2. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{14}H_{20}{}^{79}BrNO$, 297.0722; found 297.0724.

12-(4-Bromophenyl)-*N*,*N*-dimethyldodecan-1-amine (6)

This method has been adapted from a previously published procedure.[4] Compound **4** (1.22 g, 3.19 mmoL) and hydrazine monohydrate (0.801 g, 16.0 mmol) were added to a stirred suspension of KOH (0.845 g, 12.8 mmol) in triethylene glycol (7 mL). The reaction mixture was stirred at 135 °C for 3 h and then at 195 °C for 4 h. Water produced during this reaction was removed using a Dean-Stark trap. After allowing the mixture to cool to room temperature, the viscous mixture was diluted with water (15 mL) and extracted with ethyl acetate (3 × 35 mL). The combined organic extracts were washed with a saturated aqueous solution of sodium chloride (40 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (2:1:0.1 petroleum ether/dichloromethane/triethylamine) gave pure **6** as a pale yellow oil (0.808 g, 69%). ^{1}H NMR ($CDCl_3$, δ): 1.19–1.38 (m, 16H, CH_2), 1.45 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 2.22 (s, 6H, CH_3), 2.24 (t, J = 7.3 Hz, 2H, CH_2). 2.45 (t, J = 7.7 Hz, 2H, CH_2), 7.00–7.06 (m,

2H, Ar H), 7.35–7.41 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 27.5, 27.6, 29.4, 29.7, 29.8, 31.5, 35.6, 45.3, 59.9, 119.4, 130.4, 131.5, 142.1. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{34}{}^{79}BrN$, 367.1869; found 367.1888.

6-(4-Bromophenyl)-*N*,*N*-dimethylhexan-1-amine (7)

This method is similar to that used for **6**. Purification of the crude product by flash column chromatography (7:1 chloroform/methanol) gave pure **7** as a pale yellow oil (81%). ^{1}H NMR ($CDCl_3$, δ): 1.32(m, 4H, CH_2), 1.44 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 2.20 (s, 6H, CH_3), 2.26 (t, J = 7.3 Hz, 2H, CH_2), 2.55 (t, J = 7.6 Hz, 2H, CH_2), 7.00–7.08 (m, 2H, Ar H), 7.34–7.42 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 27.2, 27.4, 29.2, 31.4, 35.5, 45.2, 59.7, 119.5, 130.4, 131.5, 141.8. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{14}H_{22}{}^{79}BrN$, 284.1008; found 284.1035.

12-(4-(4-Bromothiophen-2-yl)phenyl)-*N*,*N*-dimethyldodecan-1-amine (8)

The preparation of the boronic acid intermediate has been adapted from a previously published procedure.[5] Briefly, *n*-BuLi (1.96 mL of a 2.5 M solution in hexanes, 4.90 mmol) was added dropwise to a solution of **6** (0.602 g, 1.63 mmol) in THF (11 mL) at –78 °C under an atmosphere of argon. After stirring for 60 min, trimethoxyborane (0.42 mL, 3.75 mmol) was added dropwise to the reaction mixture at –78 °C and then the mixture was allowed to warm to room temperature. After stirring for 12 h, aqueous hydrochloric acid (8.0 mL, 2.0 M) was added and the mixture was stirred for another 20 min. The mixture was basified to a pH of 9 with saturated aqueous solution of sodium bicarbonate and was extracted with ethyl acetate (3 × 30 mL). The combined organic

extracts were washed with a saturated aqueous solution of sodium chloride (50 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The boronic acid was obtained as a pale yellow oil (0.545 g, 100%) and was used to prepare **8** without further purification. The preparation of **8** has been adapted from a previously published procedure.[6] 2,4-Dibromothiophene (0.414g, 1.71mmol) and aqueous sodium carbonate (3.3 mL) were added consecutively in a dropwise manner to a stirred mixture of the boronic acid (0.545 g, 1.63 mmol) and $Pd(PPh_3)_4$ (0.188 g, 0.163 mmol) in 1,4-dioxane (20 mL) under an atmosphere of argon. After stirring at 100 °C for 4.5 h, the reaction mixture was allowed to cool to room temperature, diluted with water (30 mL) and was extracted with ethyl acetate (3 × 40 mL). The combined organic extracts were washed with a saturated aqueous solution of sodium chloride (60 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (3:1:0.1 petroleum ether/dichloromethane/triethylamine) gave pure **8** as an off-white solid (0.569 g, 78%). ^{1}H NMR ($CDCl_3$, δ): 1.19–1.40 (m, 16H, CH_2), 1.53 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 2.31 (s, 6H, CH_3), 2.36 (t, J = 7.3 Hz, 2H, CH_2), 2.61 (t, J = 7.7 Hz, 2H, CH_2), 7.13 (d, J = 1.4 Hz, 1H, H3), 7.16 (d, J = 1.4 Hz, 1H, H5), 7.17–7.22 (m, 2H, Ar H), 7.43–7.49 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 27.8, 28.0, 29.5, 29.7, 29.8, 29.9, 31.6, 35.9, 45.8, 60.2, 110.6, 121.6, 125.4, 125.9, 129.3, 130.9, 143.6, 145.9. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{24}H_{36}{}^{79}BrNS$, 449.1746; found 449.1736.

6-(4-(4-Bromothiophen-2-yl)phenyl)-*N,N*-dimethylhexan-1-amine (9)

This method is similar to that used for **8**. Purification of the crude product by flash column chromatography (10:1:0.1 ethyl acetate/methanol/triethylamine) gave pure **9** as a pale yellow oil (73%). ^{1}H NMR ($CDCl_3$, δ): 1.36 (m, 4H, CH_2), 1.46 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 2.21 (s, 6H, CH_3), 2.24 (t, J = 7.2 Hz, 2H, CH_2), 2.62 (t, J = 7.7 Hz, 2H, CH_2), 7.13 (d, J = 1.4 Hz, 1H, H3), 7.16 (d, J = 1.4 Hz, 1H, H5), 7.16–7.22 (m, 2H, Ar H), 7.43–7.49 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 27.5, 27.8, 29.4, 31.5, 35.8, 45.6, 60.0, 110.6, 121.6, 125.4, 125.9, 129.3, 130.9, 143.4, 145.8. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{24}{}^{79}BrNS$, 365.0807; found 365.0814.

12-(4-(4, 5-Dibromothiophen-2-yl)phenyl)-*N,N*-dimethyldodecan-1-amine (10)

This method has been adapted from a previously published procedure.[7] NBS (0.220g, 99%, 1.23 mmol) was added to a solution containing **8** (0.502 g, 1.11 mmol) in a mixture of acetic anhydride (4.0 mL) and glacial acetic acid (0.65 mL). After stirring at 80 °C for 80 min, the reaction mixture was allowed to cool to room temperature, diluted with water (10 mL), basified to a pH above 11 with a saturated aqueous solution of sodium carbonate and extracted with ethyl acetate (3 × 35 mL). The combined organic extracts were washed with a saturated aqueous solution of sodium chloride (40 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (3:1:0.1 petroleum ether/dichloromethane/triethylamine) gave pure **10** as an off-white solid (0.446 g, 76%). ^{1}H NMR ($CDCl_3$, δ): 1.26 (m, 16H, CH_2), 1.44 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 2.21 (s, 6H, CH_3), 2.23 (t, J = 7.4 Hz, 2H, CH_2), 2.61 (t, J = 7.6 Hz, 2H, CH_2), 7.05 (s, 1H, H3),

7.15–7.22 (m, 2H, Ar H), 7.35–7.42 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 27.3, 27.6, 29.5, 29.7, 29.8, 31.5, 35.9, 45.2, 60.0, 109.6, 114.7, 125.2, 125.6, 129.4, 130.4, 144.0, 145.8. HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{24}H_{35}{}^{79}Br_2NS$, 528.0930; found 528.0929.

6-(4-(4, 5-Dibromothiophen-2-yl)phenyl)-*N*,*N*-dimethylhexan-1-amine (11)

This method is similar to that used for **10**. Purification of the crude product by flash column chromatography (10:1:0.1 ethyl acetate/methanol/triethylamine) gave pure **11** as a pale yellow oil (83%). ^{1}H NMR ($CDCl_3$, δ): 1.36 (m, 4H, CH_2), 1.45 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 2.20 (s, 6H, CH_3), 2.23 (t, J = 7.2 Hz, 2H, CH_2), 2.61 (t, J = 7.6 Hz, 2H, CH_2), 7.05 (s, 1H, H3), 7.15–7.22 (m, 2H, Ar H), 7.35–7.42 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 27.3, 27.4, 29.3, 31.4, 35.8, 45.3, 59.8, 109.7, 114.7, 125.3, 125.6, 129.4, 130.5, 143.7, 145.8. HRMS-EI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{23}{}^{79}Br_2NS$, 444.9897; found 444.9887.

12-(4-(4-Bromo-5-phenylethynyl)thiophen-2-yl)phenyl)-*N*,*N*-dimethyldodecan-1-amine (12)

This method has been adapted from a previously published procedure.[8] Ethynylbenzene (0.052 g, 0.650 mmol) in triethylamine (1 mL) was added dropwise to a stirred mixture of **10** (0.312 g, 0.589 mmol) in triethylamine (2 mL) followed by the addition of $Pd(PPh_3)_2Cl_2$ (1.5 mg, 0.002 mmol) and triphenylphosphine (0.6 mg, 0.002 mmol) under an atmosphere of argon. After stirring at 35 °C for 15 min, copper (I) iodide (0.8 mg, 0.004 mmol) was added and the reaction mixture was stirred at 60 °C for 3.5 h. After allowing the reaction mixture to cool to room temperature, it was diluted with ethyl

acetate (20 mL) and poured into water (20 mL) to give a biphasic mixture. This mixture was extracted with ethyl acetate (3 × 20 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (3:1:0.1 petroleum ether/dichloromethane/triethylamine) and followed by recrystallization from hexanes gave pure **12** as a pale yellow solid (0.250 g, 77%). ^{1}H NMR ($CDCl_3$, δ): 1.26 (m, 16H, CH_2), 1.45 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 2.22 (s, 6H, CH_3), 2.24 (t, J = 7.4 Hz, 2H, CH_2), 2.62 (t, J = 7.6 Hz, 2H, CH_2), 7.16 (s, 1H, H3), 7.17–7.24 (m, 2H, Ar H), 7.32–7.40 (m, 3H, Ar H), 7.42–7.49 (m, 2H, Ar H), 7.52–7.60 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 27.7, 28.0, 29.5, 29.7, 29.8, 29.9, 31.5, 35.9, 45.7, 60.2, 81.7, 97.7, 116.8, 119.4, 122.9, 125.5, 125.8, 128.6, 128.9, 129.4, 130.4, 131.7, 144.2, 145.7. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{32}H_{40}{}^{81}BrNS$, 551.2044; found 551.2053.

6-(4-(4-Bromo-5-phenylethynyl)thiophen-2-yl)phenyl)-*N*,*N*-dimethylhexan-1-amine (13)

This method is similar to that used for **12**. Purification of the crude product by flash column chromatography (7:1 chloroform/methanol) and followed by recrystallization chloroform/diethyl ether gave pure **13** as a waxy pale yellow solid (72%). ^{1}H NMR ($CDCl_3$, δ): 1.36 (m, 4H, CH_2), 1.48 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 2.24 (s, 6H, CH_3), 2.27 (t, J = 7.3 Hz, 2H, CH_2), 2.62 (t, J = 7.6 Hz, 2H, CH_2), 7.16 (s, 1H, H3), 7.17–7.24 (m, 2H, Ar H), 7.32–7.40 (m, 3H, Ar H), 7.42–7.49 (m, 2H, Ar H), 7.53–7.60 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 27.0, 27.4, 29.3, 31.4, 35.8, 45.0, 59.6, 81.7, 97.7, 116.9,

119.4, 122.9, 125.5, 125.8, 128.6, 128.9, 129.4, 130.5, 131.7, 143.9, 145.6. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{26}H_{28}{}^{79}BrNS$, 465.1120; found 465.1112.

3-(Perfluorocyclopent-1-enyl)-5-phenyl-2-(phenylethynyl)thiophene (14)

Starting material, 3-bromo-5-phenyl-2-(phenylethynyl)thiophene, was prepared following a reported procedure (11% in five steps).[9] *n*-BuLi (0.25 mL of a 2.5 M solution in hexanes, 0.630 mmol) was added dropwise to a solution of the substituted thiophene (0.202 g, 0.595 mmol) in THF (4 mL) at –78 °C under an atmosphere of argon. After stirring for 20 min, the reaction mixture was added dropwise via cannula to a solution of OFCP (1.27 g, 6.0 mmol) in THF (3 mL) at –78 °C. The mixture was stirred for another 3.5 h at –78 °C and then allowed to warm to room temperature. After 2 h, aqueous hydrochloric acid (3.0 mL, 1.0 M) was added. Following 10 min of vigorous stirring, THF was removed under reduced pressure. After neutralization of the acid with a saturated aqueous solution of sodium bicarbonate, the mixture was extracted with dichloromethane (3 × 20 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (hexanes) gave pure **14** as a light yellow solid (0.189 g, 70%). ^{1}H NMR (CD_3Cl, δ): 7.30–7.47 (m, 6H, Ar H), 7.47–7.54 (m, 2H, Ar H), 7.56–7.64 (m, 3H, Ar H). ^{19}F NMR ($CDCl_3$, δ): –108.1 (m, 2F), –118.4 (m, 2F), –122.1 (m, 1F), –130.8 (m, 2F). ^{13}C NMR (CD_3Cl, δ): 80.8, 101.0, 122.2, 122.3, 126.3, 127.0, 128.8, 129.2, 129.5, 131.6, 132.7, 146.5. HRMS-ESI (*m*/*z*): $[M]^+$ calcd for $C_{23}H_{11}F_7S$, 452.0464; found 452.0467.

12-(4-(4-(3, 3, 4, 4, 5, 5-Hexafluoro-2-(5-phenyl-2-(phenylethynyl)thiophen-3-yl)cyclopent-1-enyl)-5-(phenylethynyl)thiophen-2-yl)phenyl)-*N*,*N*-dimethyldodecan-1-amine (15)

This method has been adapted from a previously published procedure.[10] *n*-BuLi (0.042 mL of a 2.5 M solution in hexanes, 0.105 mmol) was added dropwise to a solution of **12** (0.055 g, 0.100 mmol) in THF (1.5 mL) at –78 °C under an atmosphere of argon. After stirring for 20 min, a solution of **14** (0.050 g, 0.11 mmol) in THF (1.0 ml) was added dropwise via cannula to the reaction mixture at –78 °C. The mixture was stirred for another 4 h at –78 °C and then allowed to warm to room temperature. After 2 h, aqueous hydrochloric acid (1 mL, 1.0 M) was added. Following 10 min of vigorous stirring, THF was removed under reduced pressure. The reaction mixture was diluted with water (10 mL), basified to a pH above 11 with a saturated aqueous solution of sodium carbonate and extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with a saturated aqueous solution of sodium chloride (25 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (3:1:0.1 petroleum ether/dichloromethane/triethylamine) gave pure **15** as a waxy yellow solid (35 mg, 39%). ^{1}H NMR ($CDCl_3$, δ): 1.28 (m, 16H, CH_2), 1.45 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 2.22 (s, 6H, CH_3), 2.24 (t, J = 1.5 Hz, 2H, CH_2), 2.59 (t, J = 1.5 Hz, 2H, CH_2), 7.02–7.14 (m, 8H, Ar), 7.15–7.21 (m, 6H, Ar H), 7.21–7.28 (m, 7H, Ar H). ^{19}F NMR ($CDCl_3$, δ): –109.7 (m, 4F), –131.6 (m, 2F). ^{13}C NMR ($CDCl_3$, δ): 26.5, 26.8, 28.2, 28.5, 28.6, 30.4, 34.6, 44.5, 59.0, 79.9, 80.1, 98.7, 98.9, 121.2, 121.3, 121.8, 122.3, 122.8, 124.7, 124.8, 127.3,

127.4, 127.5, 127.8, 128.0, 129.2, 130.3, 130.4, 130.5, 131.4, 131.5, 131.7, 142.5, 144.6, 145.0. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{55}H_{51}F_6NS_2$, 904.3440; found 904.3430.

6-(4-(4-(3, 3, 4, 4, 5, 5-Hexafluoro-2-(5-phenyl-2-(phenylethynyl)thiophen-3-yl)cyclopent-1-enyl)-5-(phenylethynyl)thiophen-2-yl)phenyl)-*N*,*N*-dimethylhexan-1-amine (16)

This method is similar to that used for **15**. Purification of the crude product by column chromatography (7:1 chloroform/methanol) gave pure **16** as a yellow oil (42%). ^{1}H NMR ($CDCl_3$, δ): 1.36 (m, 4H, CH_2), 1.48 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 2.24 (s, 6H, CH_3), 2.29 (t, J = 7.3 Hz, 2H, CH_2). 2.60 (t, J = 7.6 Hz, 2H, CH_2), 7.02–7.14 (m, 8H, Ar), 7.14–7.21 (m, 6H, Ar H), 7.21–7.28 (m, 7H, Ar H). ^{19}F NMR ($CDCl_3$, δ): –109.7 (m, 4F), –131.6 (m, 2F). ^{13}C NMR ($CDCl_3$, δ): 27.6 27.8, 29.4, 31.6, 35.8, 45.6, 60.1, 81.2, 81.3, 100.0, 100.1, 122.4, 122.5, 123.0, 125.9, 126.0, 128.5, 128.7, 129.0, 129.2, 130.5, 131.6, 131.6, 132.6, 132.7, 133.0, 143.6, 145.8, 146.2. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{49}H_{39}F_6NS_2$, 820.2501; found 820.2500.

12-(4-(4-(3, 3, 4, 4, 5, 5-Hexafluoro-2-(5-phenyl-2-(phenylethynyl)thiophen-3-yl)cyclopent-1-enyl)-5-(phenylethynyl)thiophen-2-yl)phenyl)-*N*,*N*,*N*-trimethyldodecan-1-ammonium iodide (1)

This method has been adapted from a previously published procedure.[11] Iodomethane (59 mg, 99%, 0.41 mmol) was added to a solution of **15** (25 mg, 0.027 mmol) in dry dichloromethane (1 mL) and then stirred for 24 h at room temperature. The dichloromethane was removed under reduced pressure and the residue was washed with

diethyl ether (2 × 3 mL). Recrystallization of the precipitate from dichloromethane/diethyl ether gave pure **1** as a yellow solid (22 mg, 80%). ^{1}H NMR ($CDCl_3$, δ): 1.18–1.45 (m, 16H, CH_2), 1.58 (m, 2H, CH_2), 1.75 (m, 2H, CH_2), 2.59 (t, J = 7.5 Hz, 2H, CH_2), 3.44 (s, 9H, CH_3), 3.58 (m, 2H, CH_2), 7.02–7.14 (m, 8H, Ar), 7.14–7.20 (m, 6H, Ar H), 7.20–7.28 (m, 7H, Ar H). ^{19}F NMR ($CDCl_3$, δ): –109.6 (m, 4F), –131.6 (m, 2F). ^{13}C NMR ($CDCl_3$, δ): 23.4, 26.3, 29.4, 29.6, 29.7, 29.8, 31.6, 35.9, 54.0, 67.6, 81.2, 81.3, 100.0, 100.1, 122.4, 123.0, 125.9, 126.0, 128.5, 128.7, 129.0, 129.1, 129.3, 130.4, 131.6, 132.6, 132.9,143.7, 145.9, 146.2. HRMS-ESI (*m*/*z*): $[M]^+$ calcd for $C_{56}H_{54}F_6NS_2^+$, 918.3596; found 918.3583.

6-(4-(4-(3, 3, 4, 4, 5, 5-Hexafluoro-2-(5-phenyl-2-(phenylethynyl)thiophen-3-yl)cyclopent-1-enyl)-5-(phenylethynyl)thiophen-2-yl)phenyl)-*N,N,N*-trimethylhexan-1-ammonium iodide (2)

This method is similar to that used for **1**. Compound **2** was obtained as a waxy yellow solid (72%). ^{1}H NMR (CD_3OD, δ): 1.42 (m, 4H, CH_2), 1.68 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.62 (t, J = 7.5 Hz, 2H, CH_2), 3.30 (s, 9H, CH_3), 3.38 (m, 2H, CH_2), 7.06–7.18 (m, 8H, Ar), 7.18–7.32 (m, 13H, Ar H). ^{19}F NMR ($CDCl_3$, δ): –109.7 (m, 4F), –131.6 (m, 2F). ^{13}C NMR (CD_3OD, δ): 22.8, 26.0, 28.5, 31.0, 35.2, 52.4, 66.7, 80.2, 80.3, 100.0, 100.1, 122.0, 122.5, 125.6, 125.8, 128.5, 128.8, 128.9, 129.0, 130.2, 131.1, 131.2, 132.4, 132.5, 143.6, 146.3, 146.5. HRMS-ESI (*m*/*z*): $[M]^+$ calcd for $C_{50}H_{42}F_6NS_2^+$, 834.2657; found 834.2660.

Procedures for the synthesis of 3

6-(4-(4-Bromo-5-methylthiophen-2-yl)phenyl)-*N,N*-dimethylhexan-1-amine (17)

This method is similar to that used for **9**. Starting material, 3,5-dibromo-2-methylthiophene, was prepared following a reported procedure (80%).[12] Purification of the crude product by flash column chromatography (10:1:0.1 ethyl acetate/methanol/triethylamine) and followed by recrystallization from methanol gave pure **17** as a colorless solid (34%). ^{1}H NMR ($CDCl_3$, δ): 1.34 (m, 4H, CH_2), 1.45 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 2.20 (s, 6H, CH_3), 2.23 (t, J = 7.8 Hz, 2H, CH_3), 2.63 (s, 3H, CH_3), 2.60 (t, J = 7.8 Hz, 2H, CH_2), 7.05 (s, 1H, H3), 7.12–7.22 (m, 2H, Ar H), 7.37–7.45 (m, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 15.0, 27.4, 27.9, 29.4, 31.4, 35.7, 45.7, 60.1, 109.8, 125.2, 125.4, 129.1, 131.1, 133.2, 141.4, 142.8. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{26}{}^{81}BrNS$, 381.0949; found 381.0946.

6-(4-(4-(3, 3, 4, 4, 5, 5-Hexafluoro-2-(5-phenyl-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)phenyl)-*N,N*-dimethylhexan-1-amine (18)

This method is similar to that used for **16**. Starting material, 3-(perfluorocyclopent-1-enyl)-5-phenyl-2-methylthiophene, was prepared following reported procedures (27% in three steps).[9, 12, 13] Purification of the crude product by column chromatography (10:1 methanol/chloroform) gave pure **18** as a colorless solid (54%). ^{1}H NMR ($CDCl_3$, δ): 1.35 (m, 4H, CH_2), 1.46 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 1.96 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 2.22 (s, 6H, CH_3), 2.25 (t, J = 7.5 Hz, 2H, CH_2), 2.61 (t, J = 7.5 Hz, 2H, CH_2), 7.14–7.22 (m, 2H, Ar H), 7.23 (s, 1H, Ar H), 7.26–7.33 (m, 2H, Ar H), 7.34–7.42 (m, 2H, Ar H), 7.43–7.48 (m, 2H, Ar H), 7.51–7.57 (m, 2H, Ar H). ^{19}F NMR ($CDCl_3$, δ): –

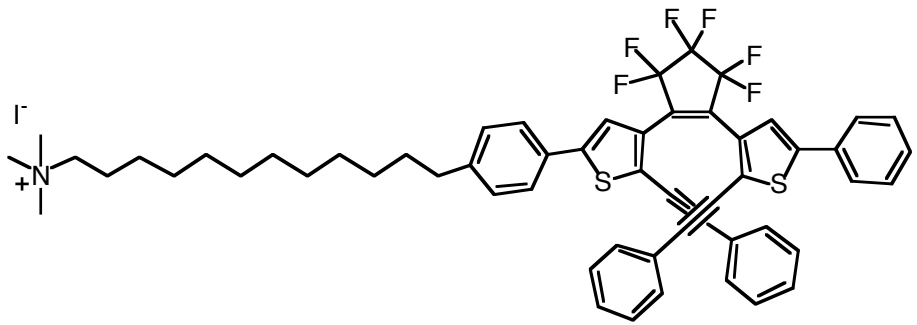
110.4 (m, 4F), –132.2 (m, 2F). ^{13}C NMR ($CDCl_3$, δ): 14.7, 27.5, 27.8, 29.3, 31.5, 35.7, 45.6, 60.0, 122.0, 122.6, 125.6, 125.8, 125.9, 126.0, 128.0, 129.1, 129.2, 131.0, 133.5, 140.9, 141.4, 142.3, 142.5, 143.0. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{35}H_{35}F_6NS_2$, 647.2115; found 647.2106.

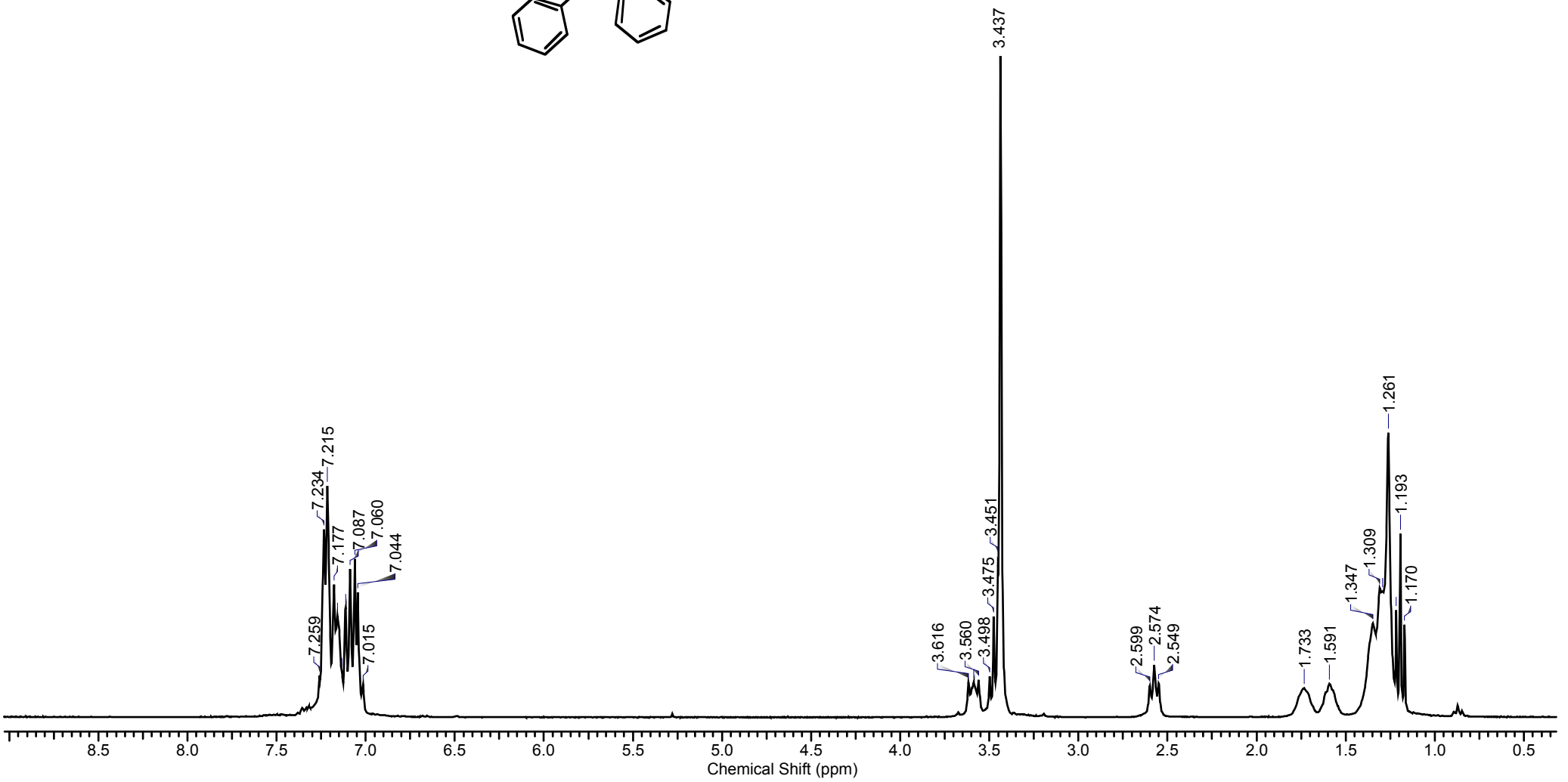
6-(4-(4-(3, 3, 4, 4, 5, 5-Hexafluoro-2-(5-phenyl-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)phenyl)-*N*,*N*,*N*-trimethylhexan-1-ammonium iodide (3)

This method is similar to that used for **2**. Compound **3** was obtained as a light yellow solid (72%). ^{1}H NMR ($CDCl_3$, δ): 1.41 (m, 4H, CH_2), 1.62 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), 1.93 (m, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.61 (t, J = 7.5 Hz, 2H, CH_2), 3.40 (s, 9H, CH_3), 3.60 (m, 2H, CH_2), 7.15–7.20 (m, 2H, Ar H), 7.22 (s, 1H, Ar H), 7.26–7.32 (m, 2H, Ar H), 7.33–7.40 (m, 2H, Ar H), 7.41–7.47 (m, 2H, Ar H), 7.48–7.56 (m, 2H, Ar H). ^{19}F NMR ($CDCl_3$, δ): –110.4 (m, 4F), –132.3 (m, 2F)**.** ^{13}C NMR ($CDCl_3$, δ): 14.6, 23.2, 26.0, 28.8, 31.1, 35.4, 53.9, 67.2, 122.0, 122.4, 125.7, 125.9, 125.9, 128.0, 129.1, 129.2, 131.0, 133.4, 141.0, 141.4,142.4, 142.4. HRMS-ESI (*m*/*z*): $[M]^+$ calcd for $C_{36}H_{38}F_6NS_2^+$, 662.2344; found 662.2333.

Compound 1

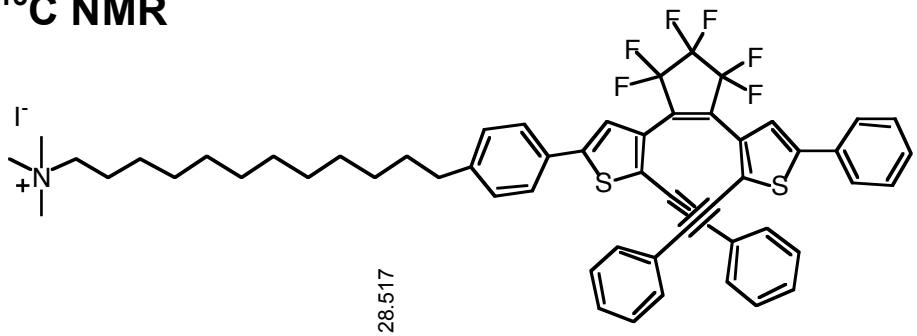
^{1}H NMR

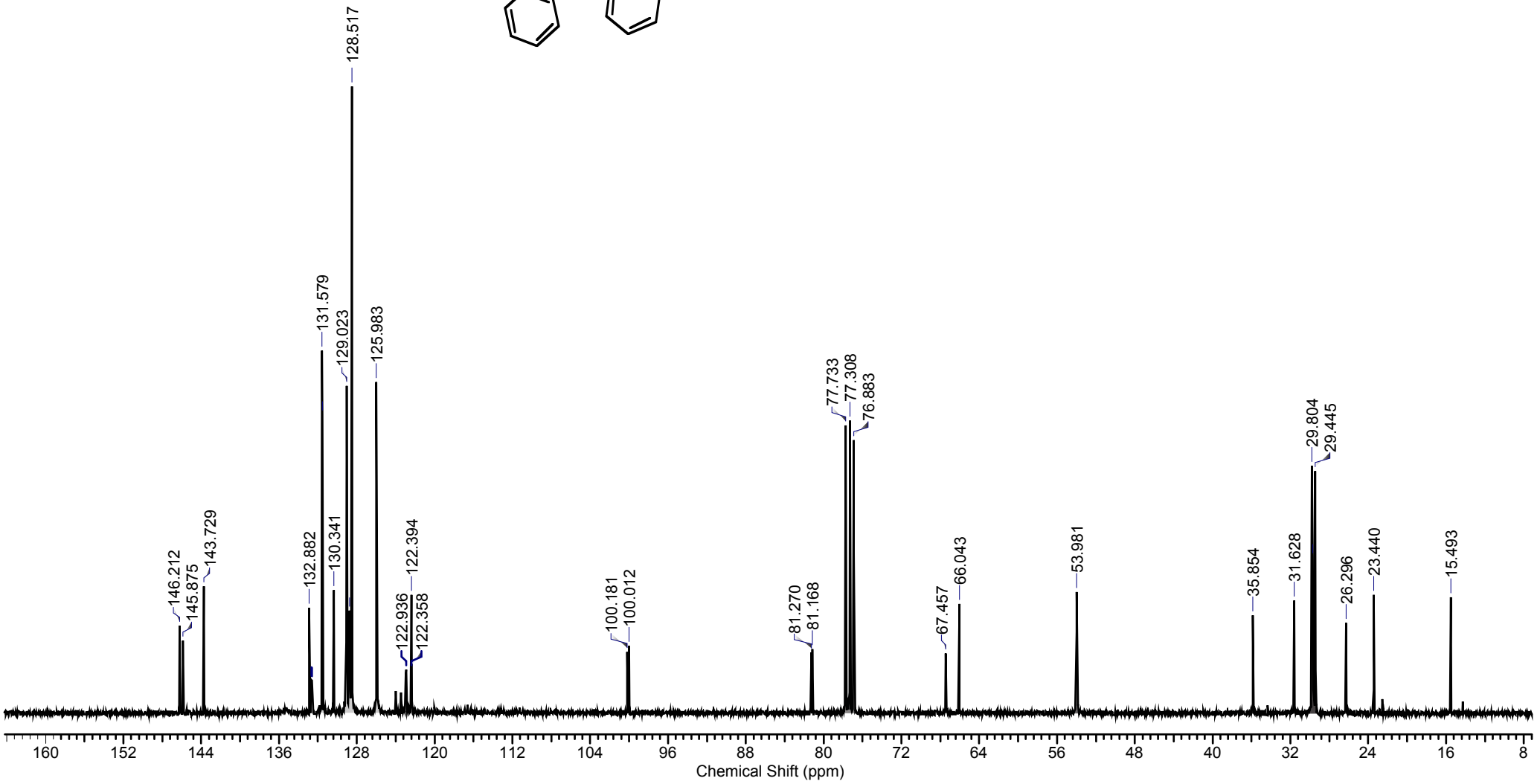




Compound 1

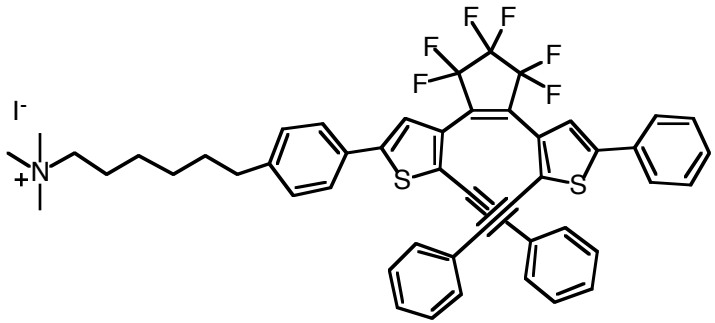
^{13}C NMR

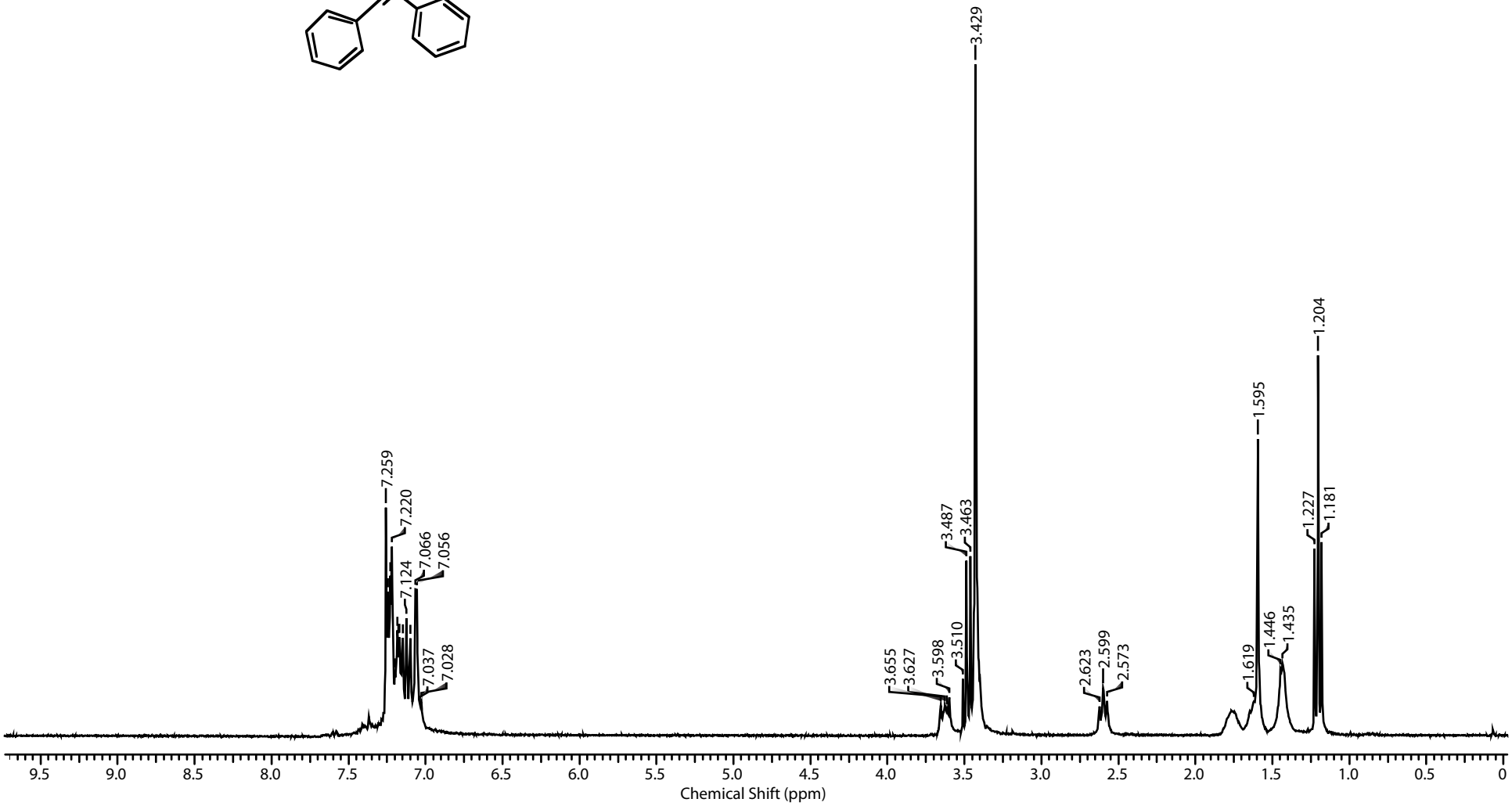




Compound 2

^{1}H NMR





Compound 2

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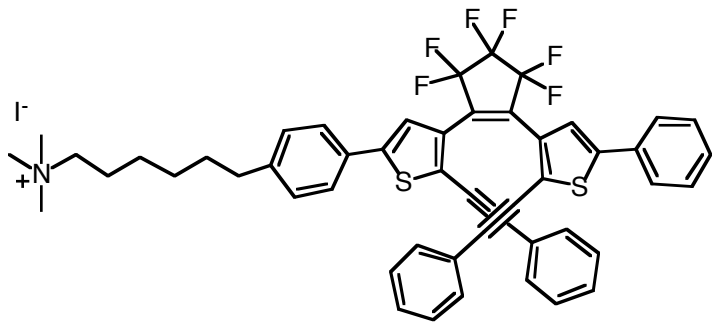
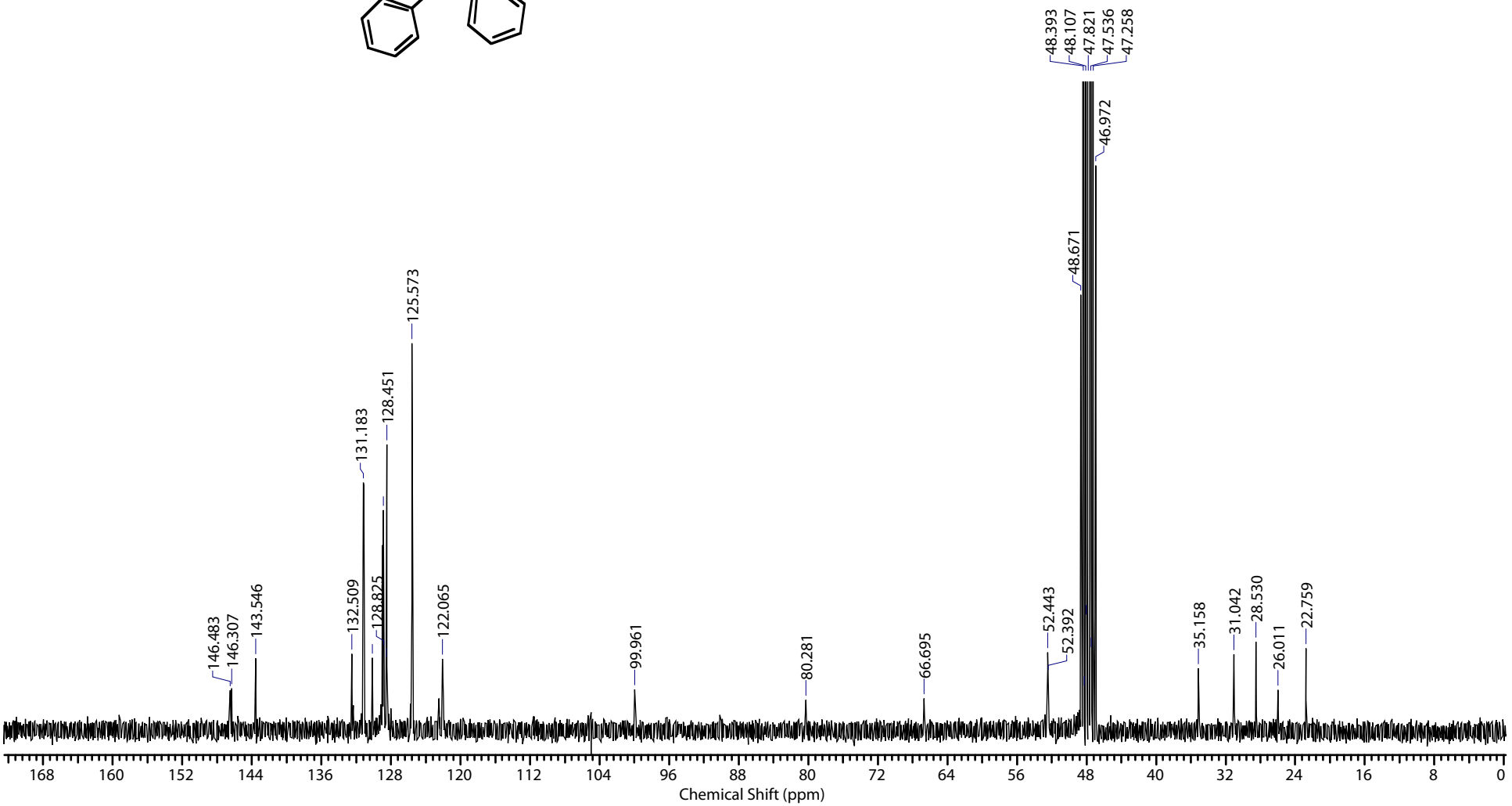
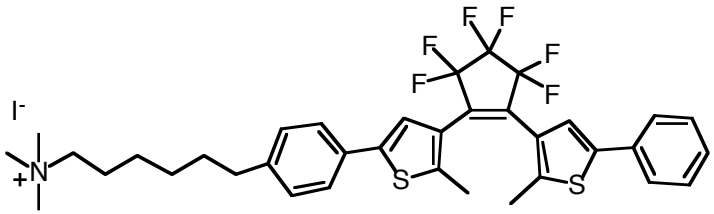
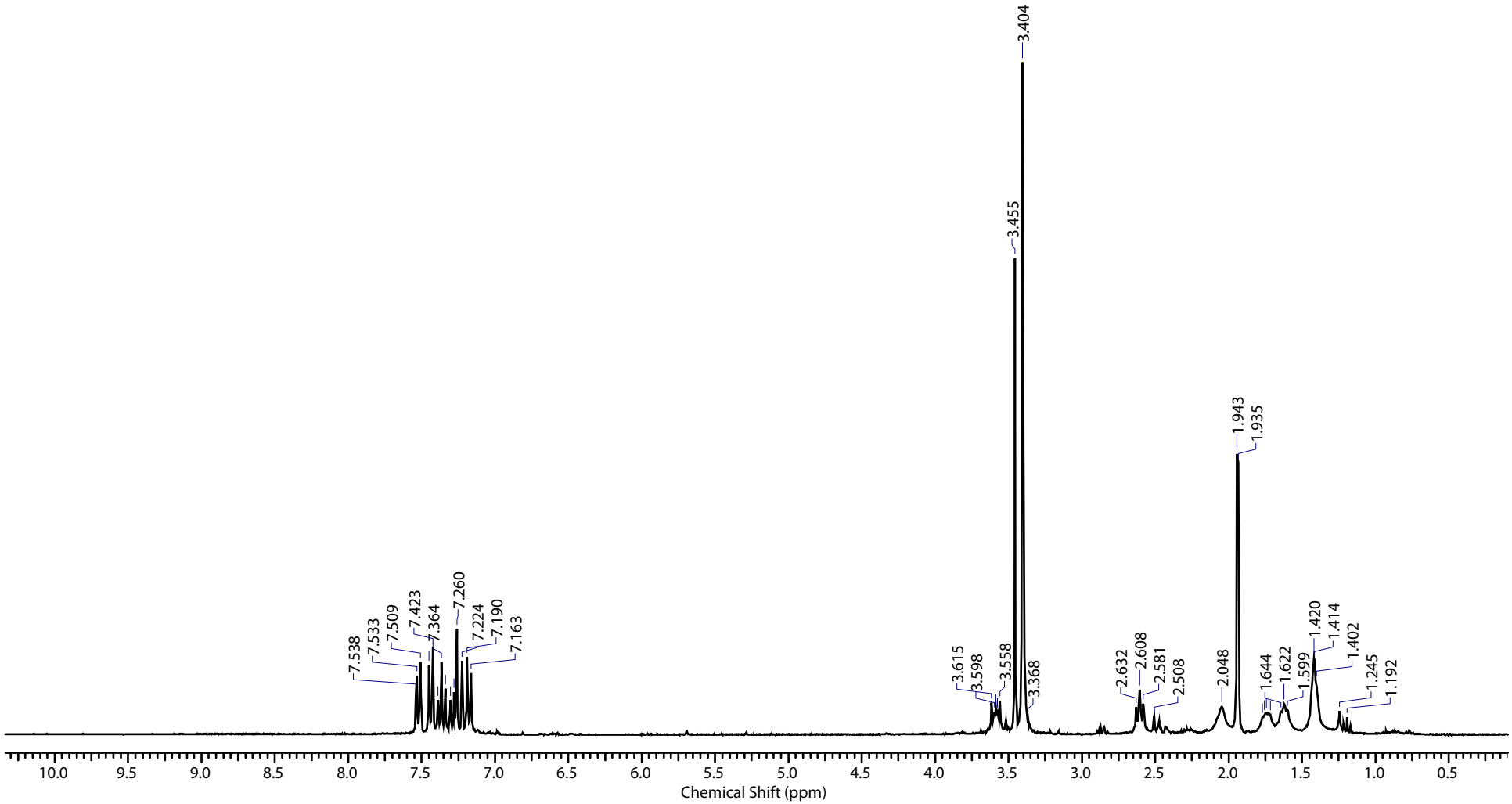




Compound 3

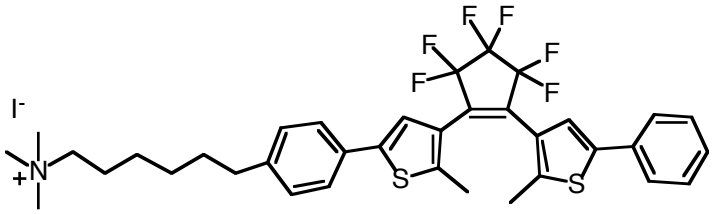
^{1}H NMR

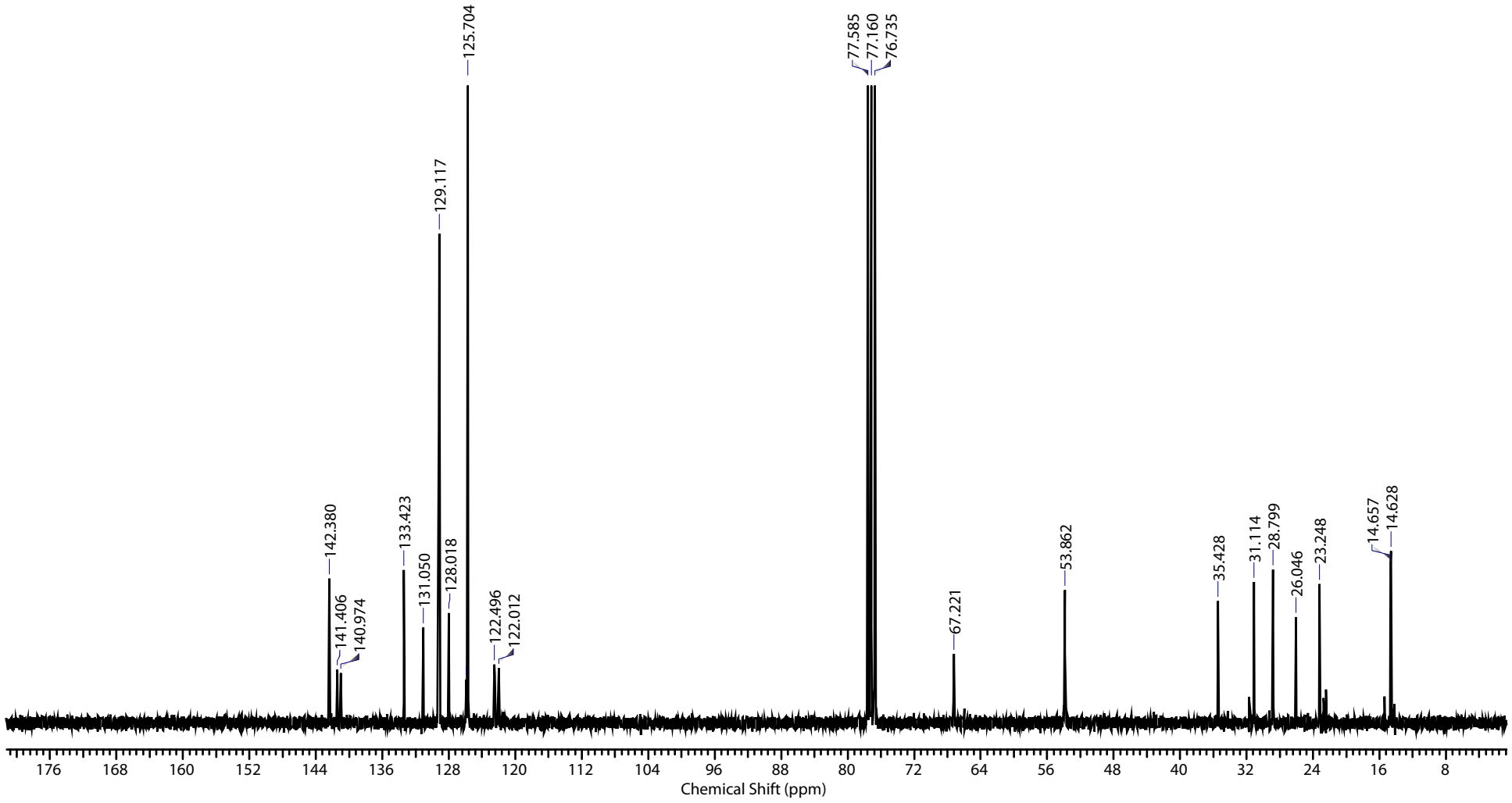




Compound 3

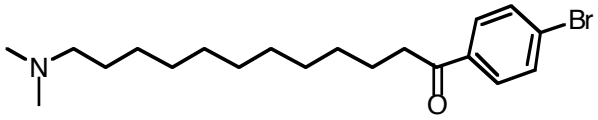
^{13}C NMR

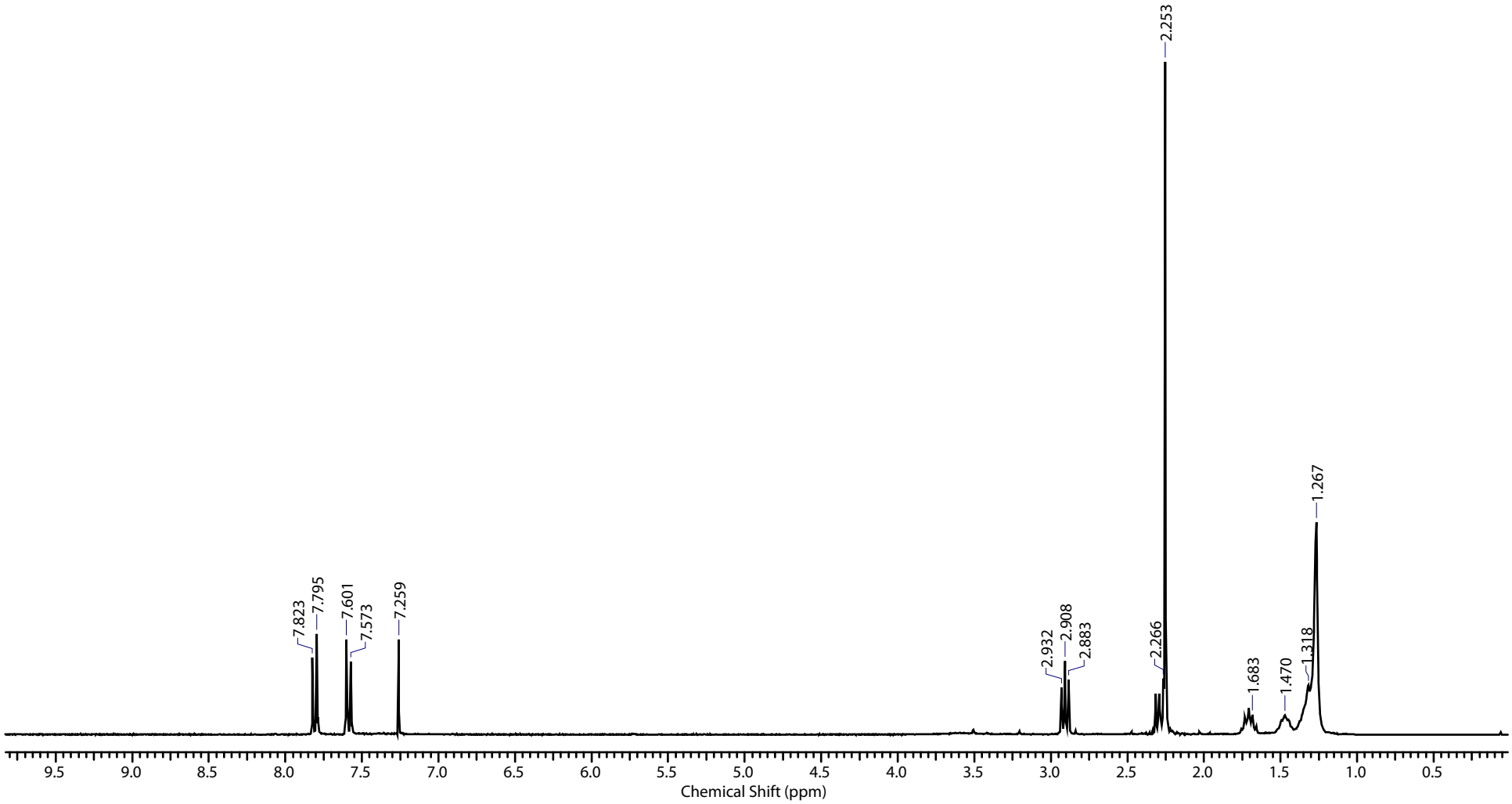




Compound 4

^{1}H NMR





Compound 4

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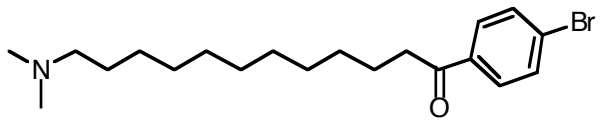
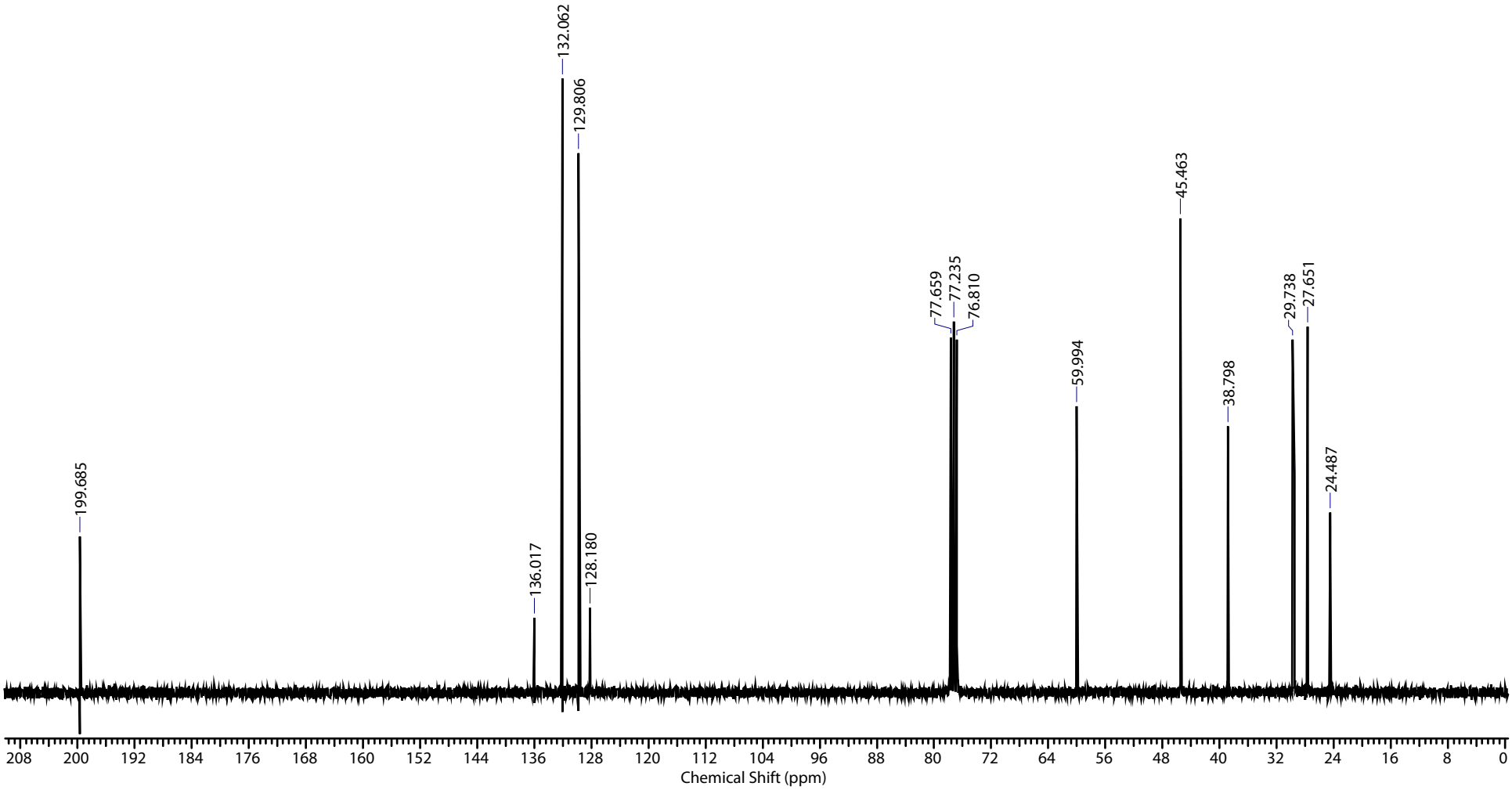
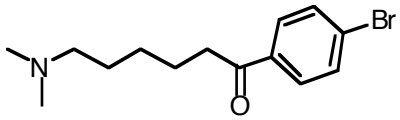
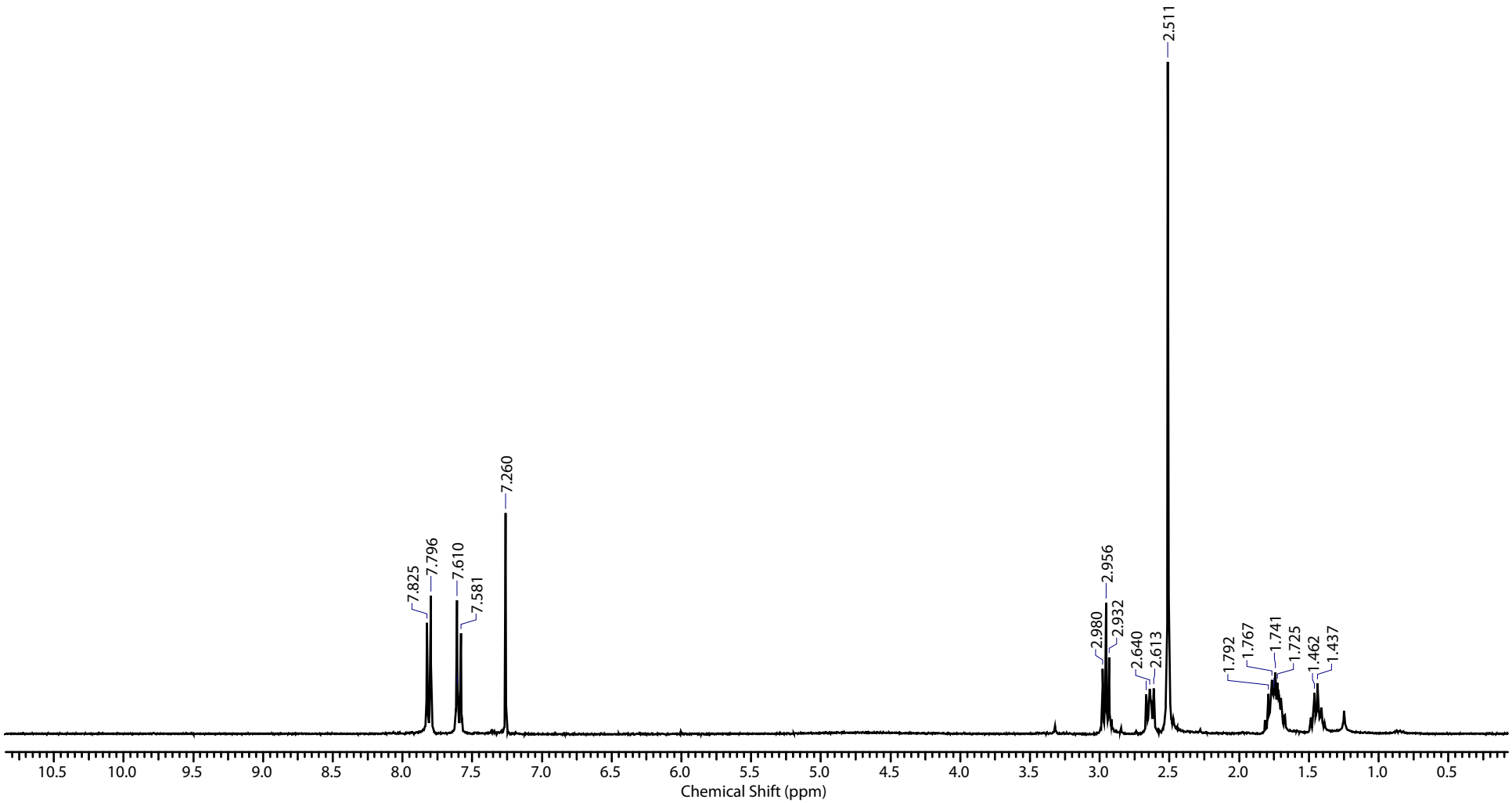




Compound 5

^{1}H NMR





Compound 5

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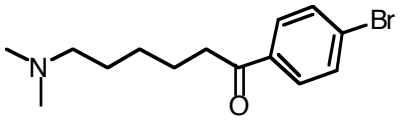
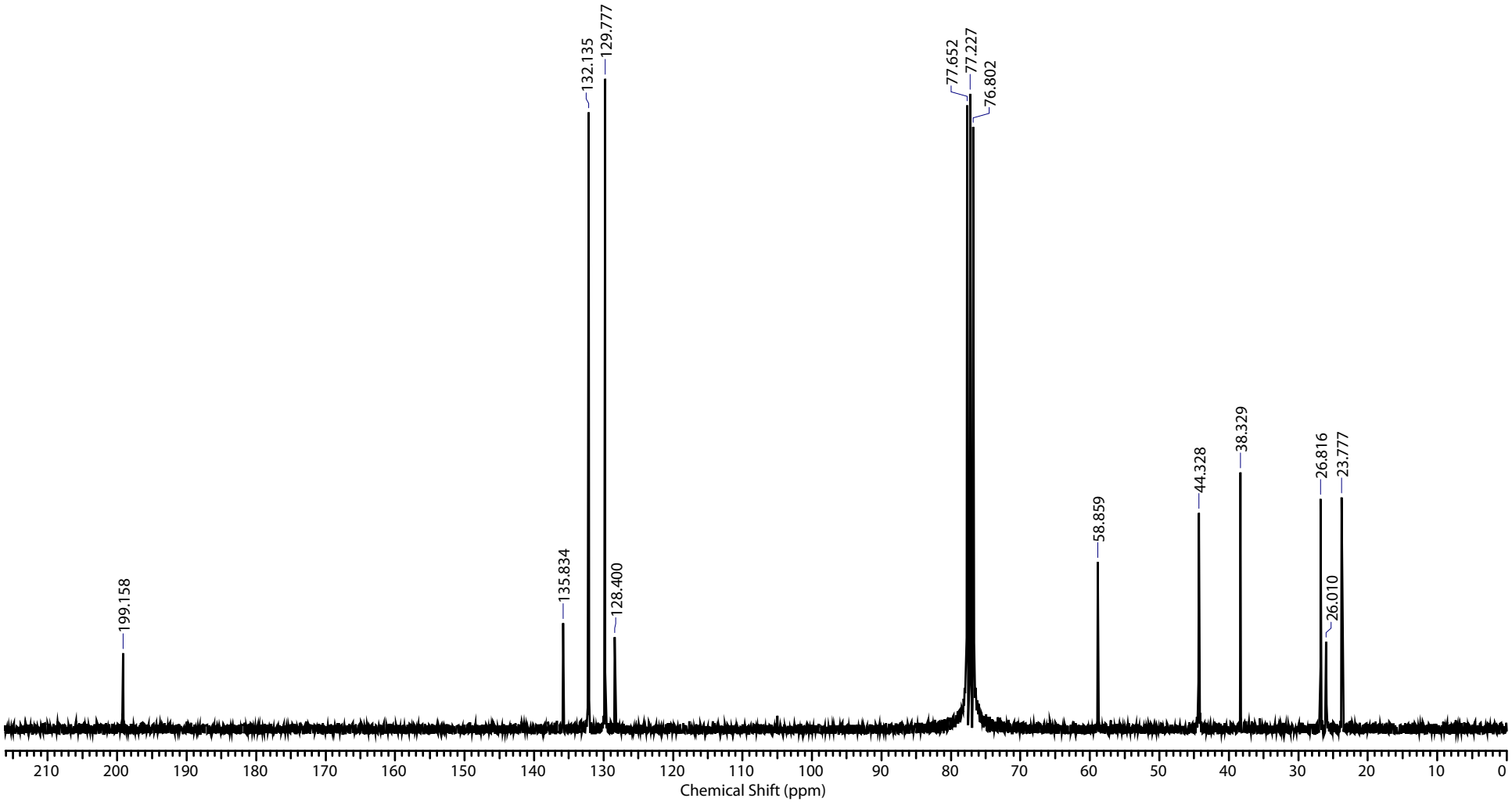
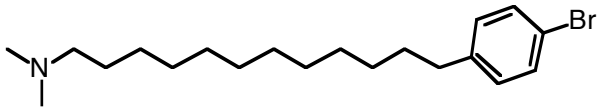
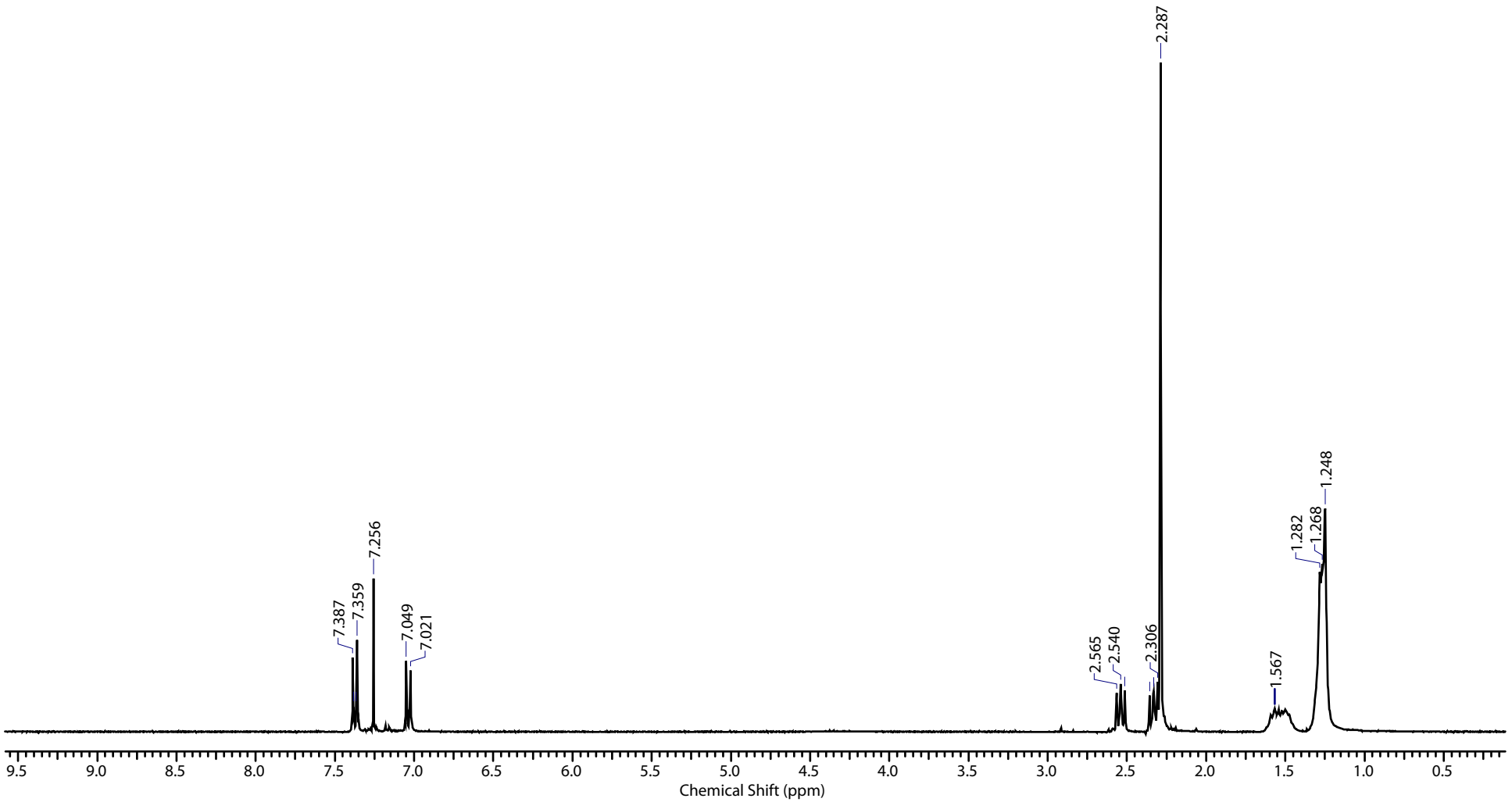




Compound 6

^{1}H NMR





Compound 6

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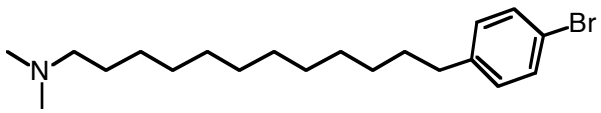
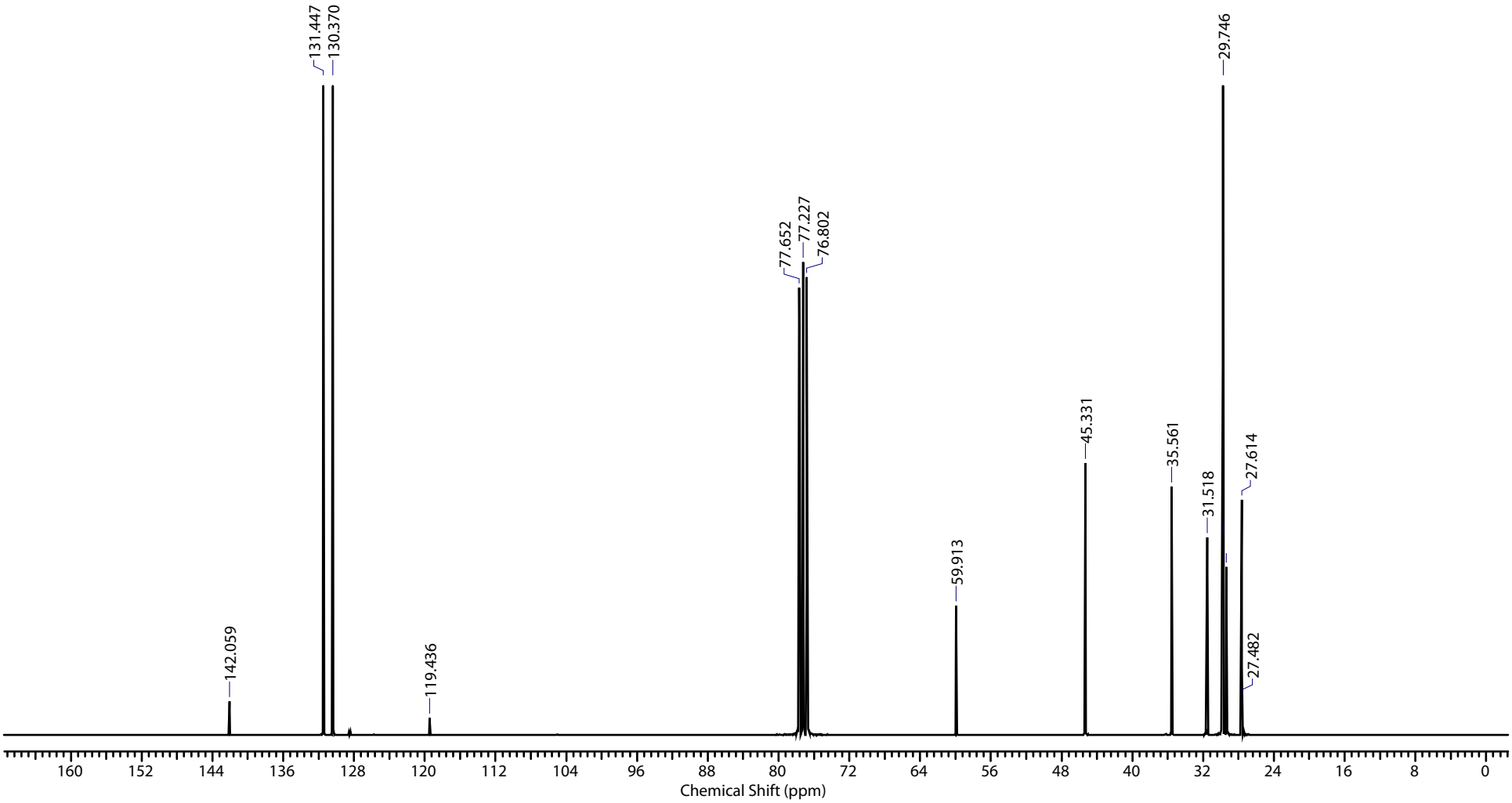
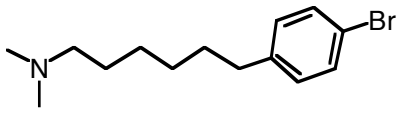
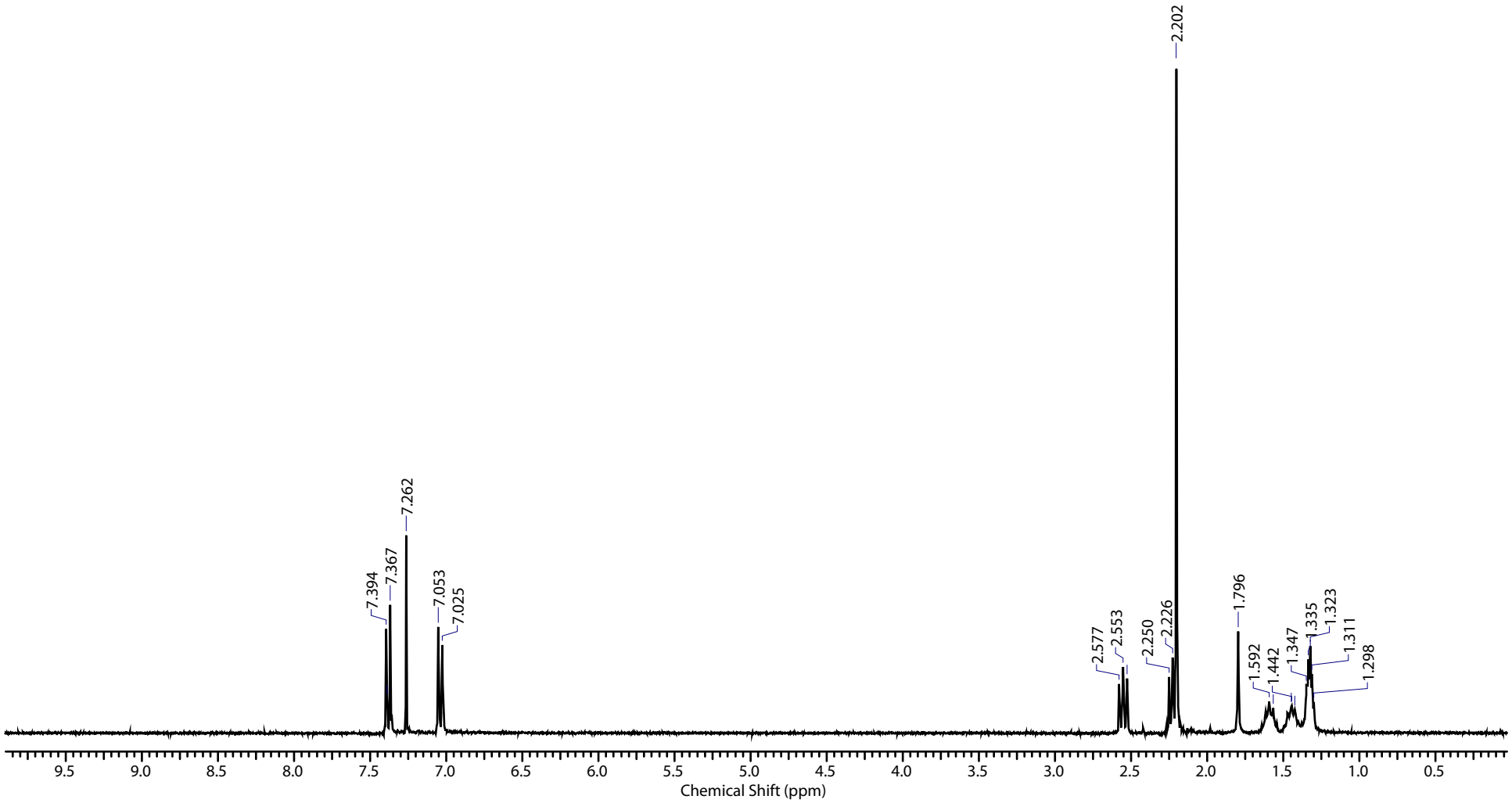




Compound 7

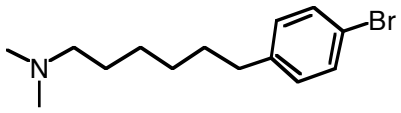
^{1}H NMR

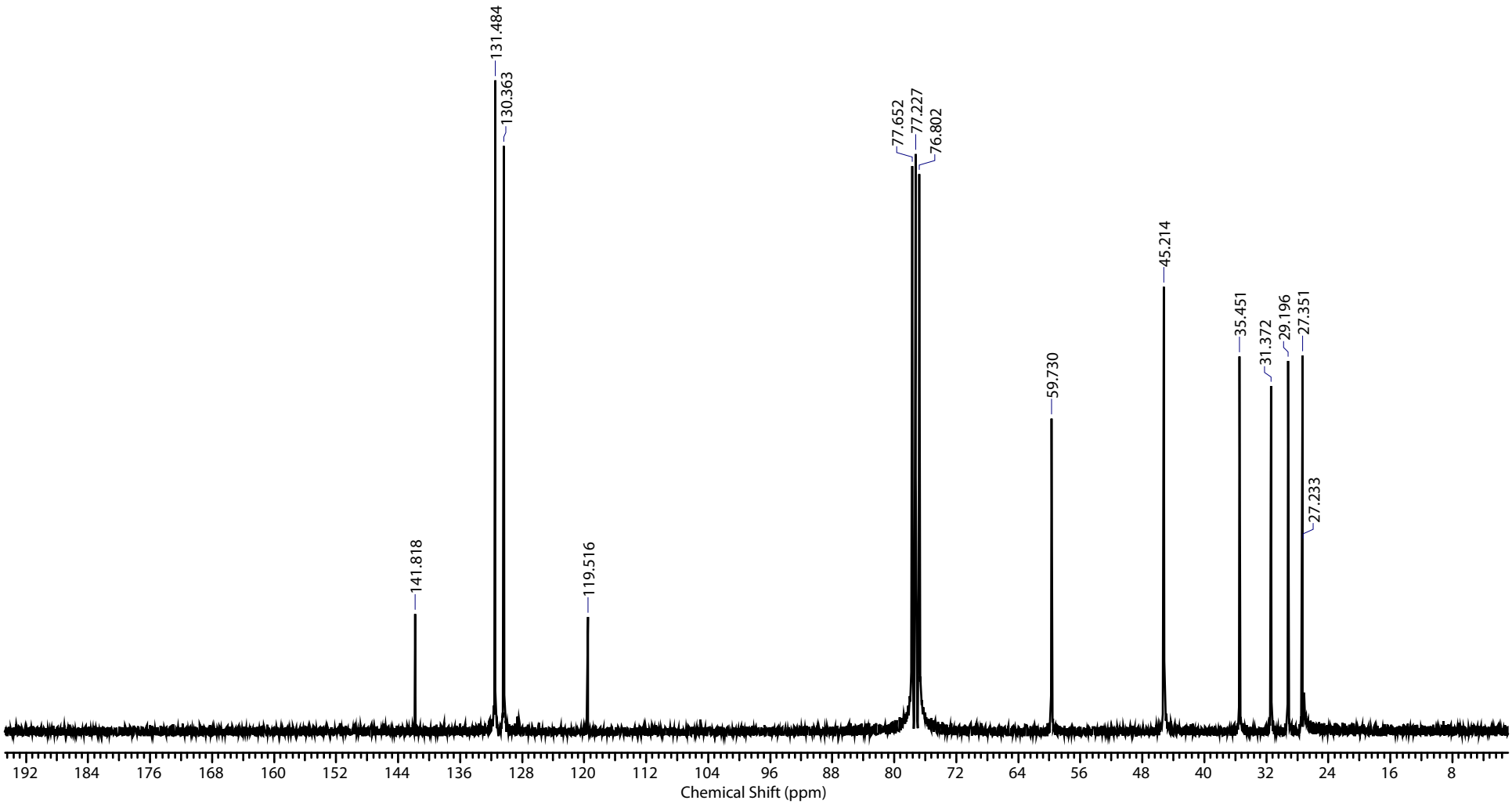




Compound 7

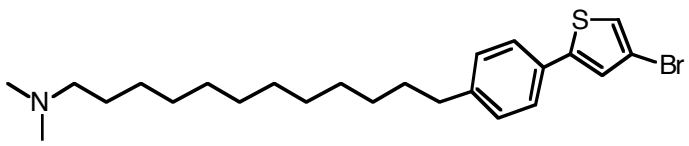
^{13}C NMR

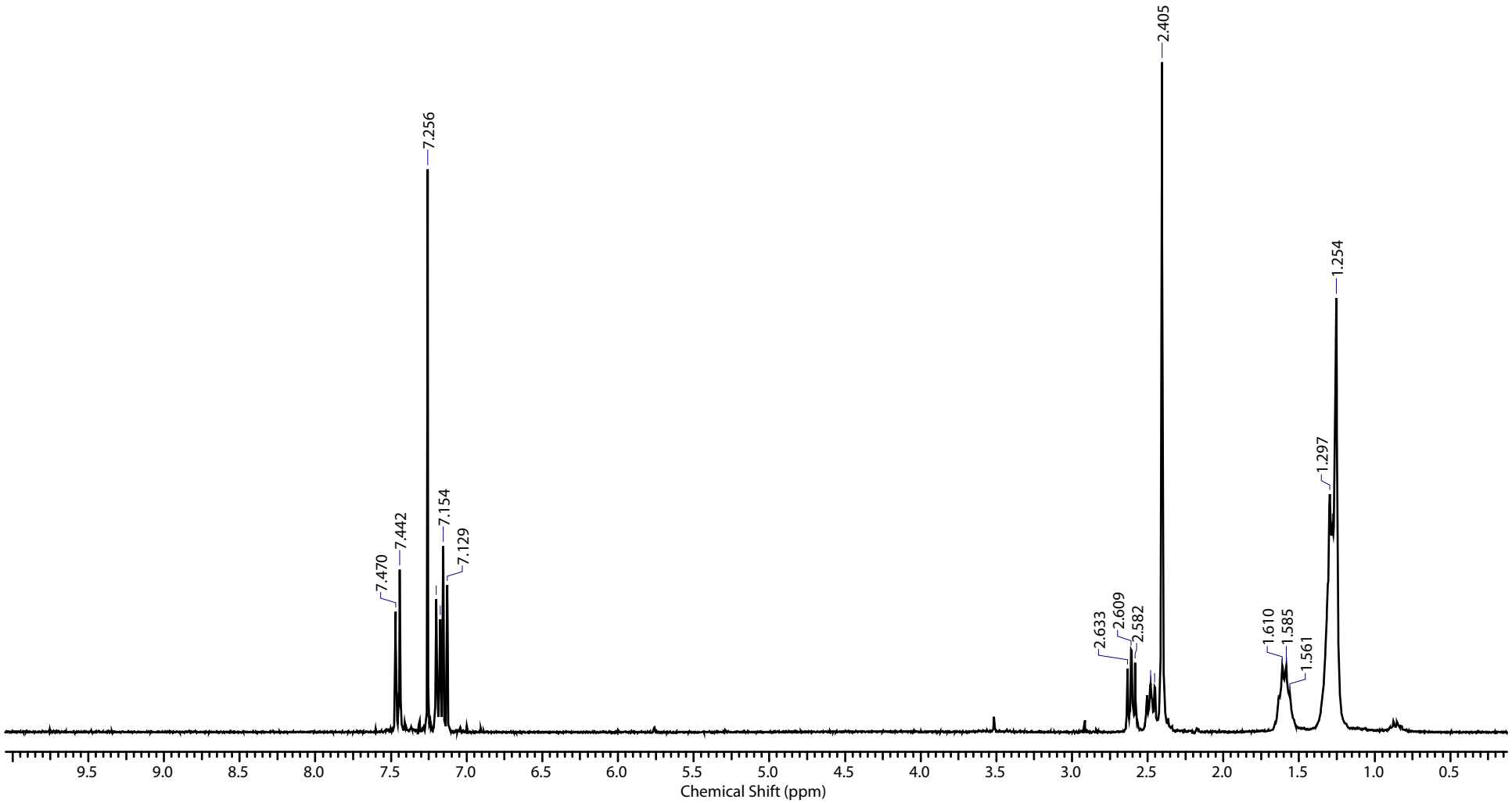




Compound 8

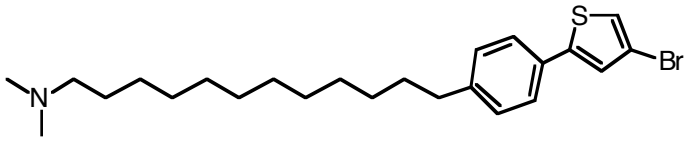
^{1}H NMR

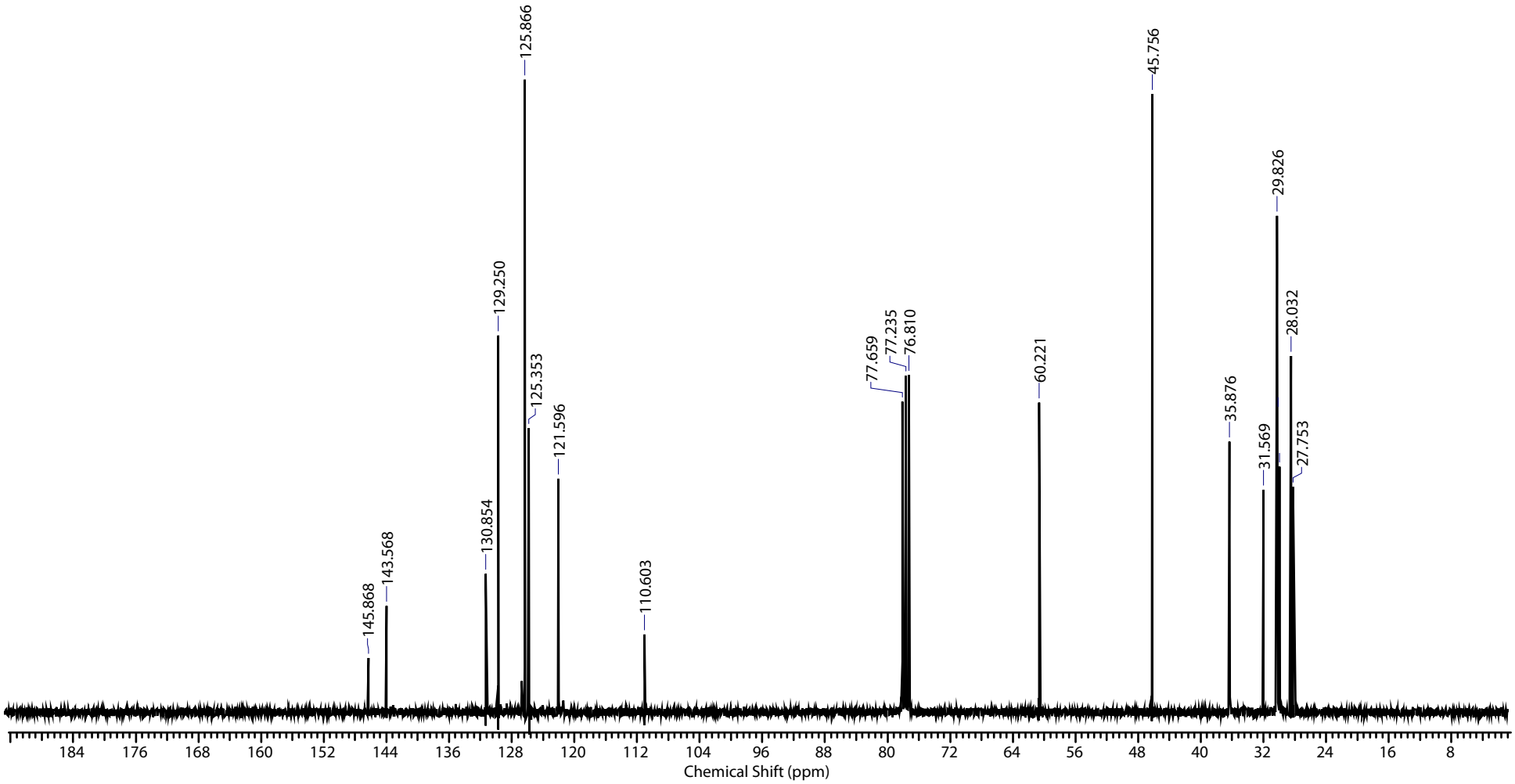




Compound 8

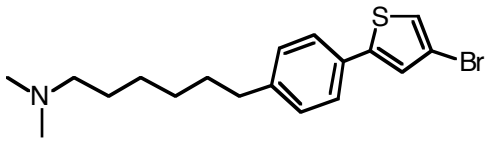
^{13}C NMR

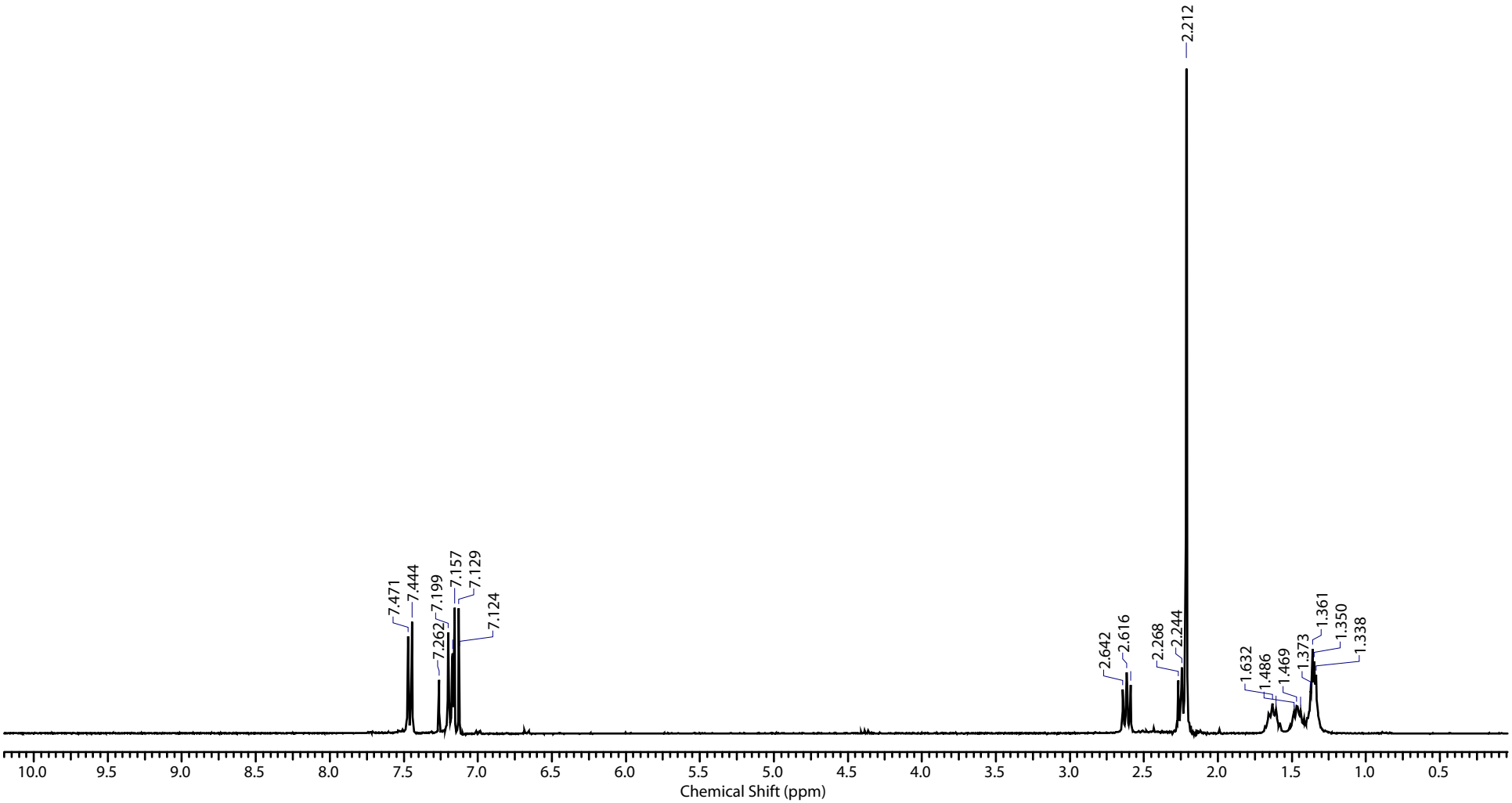




Compound 9

^{1}H NMR





Compound 9

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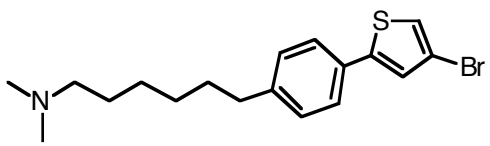
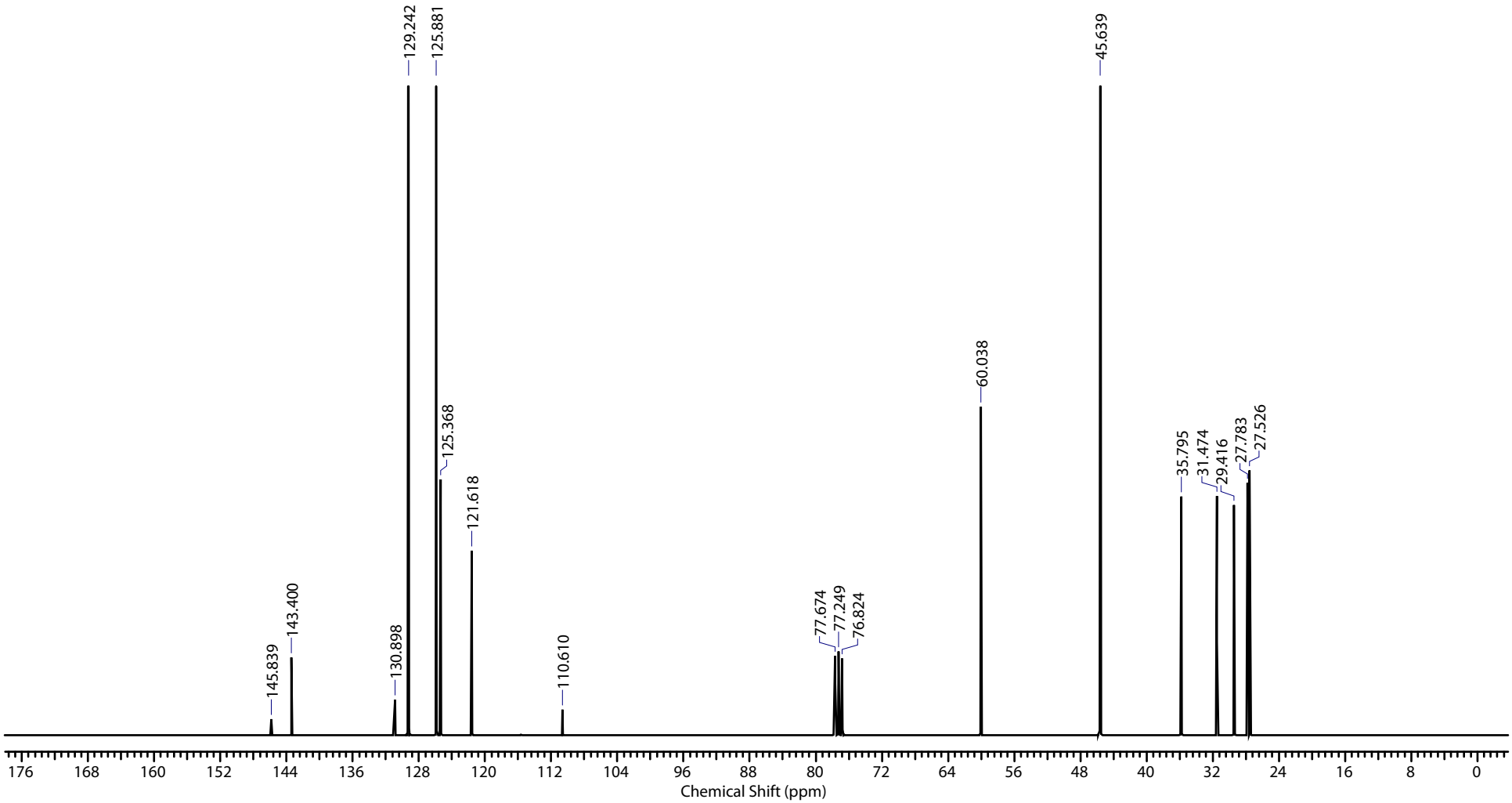
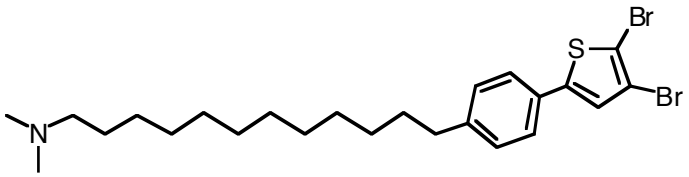
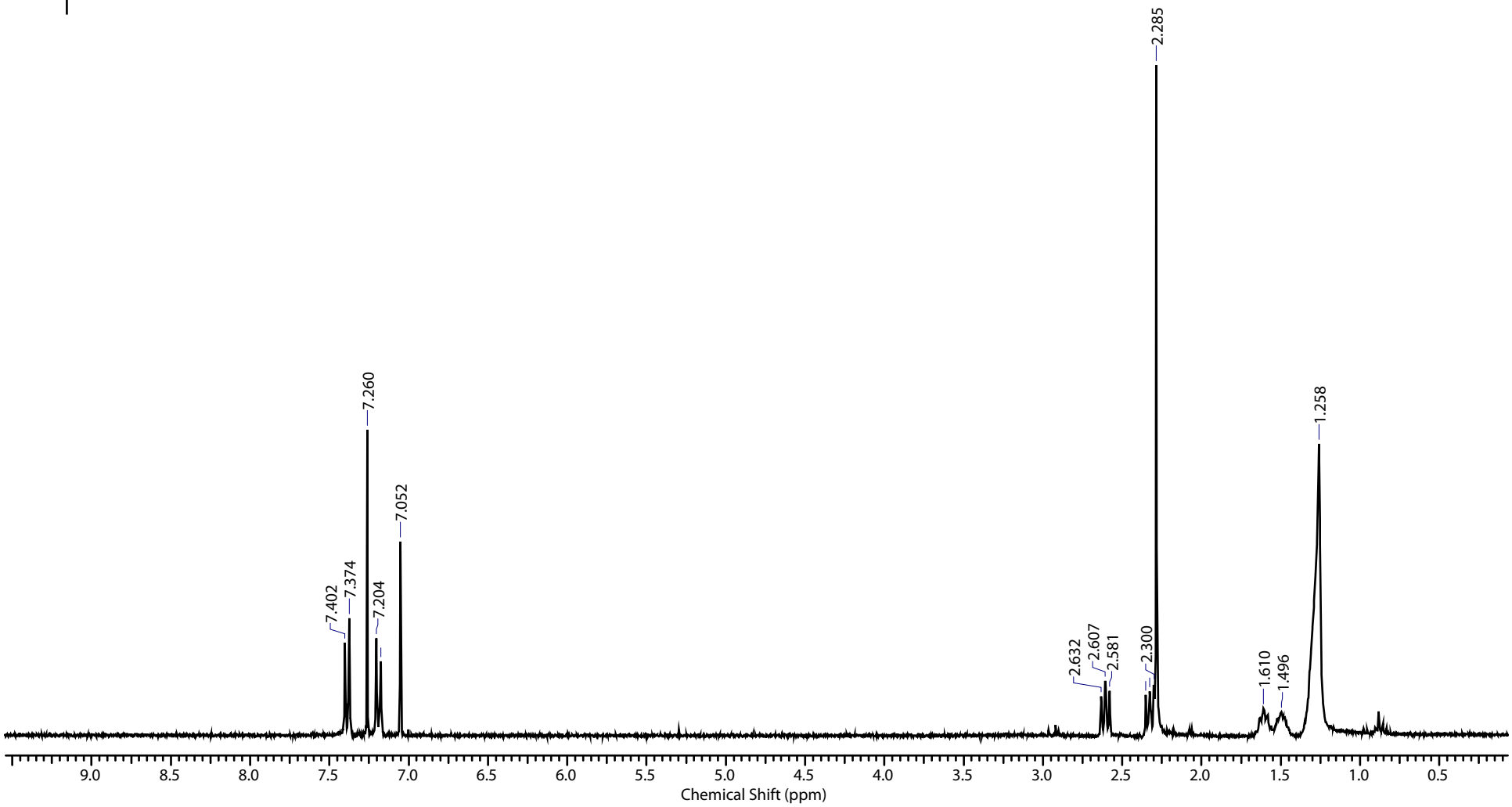




Compound 10

^{1}H NMR





Compound 10

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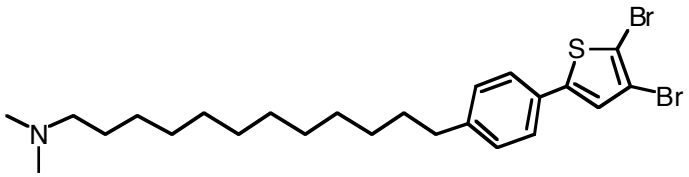
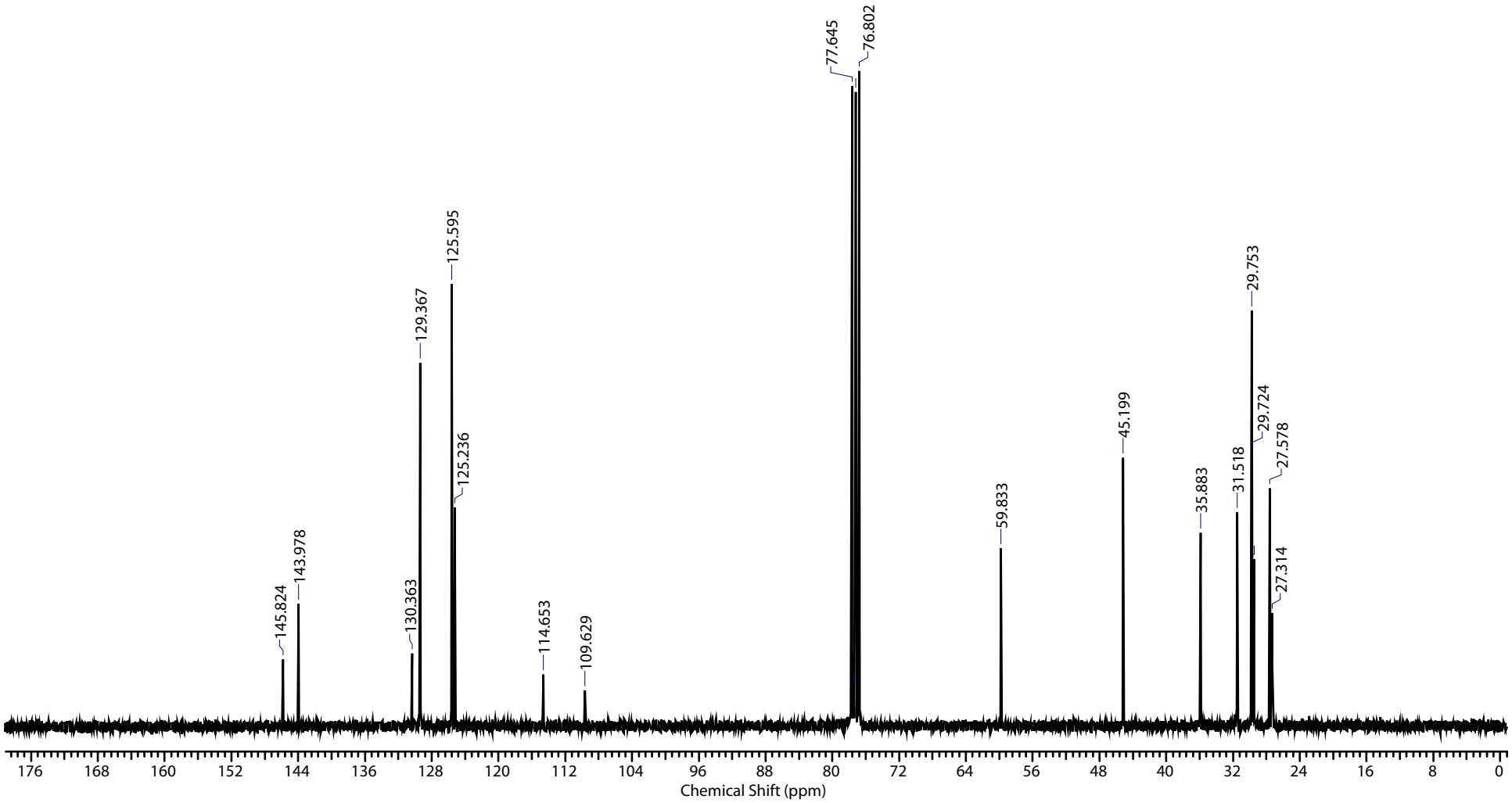
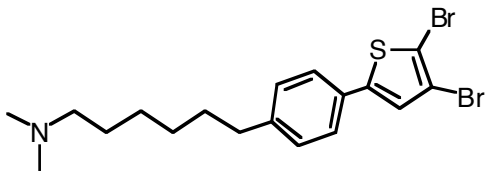
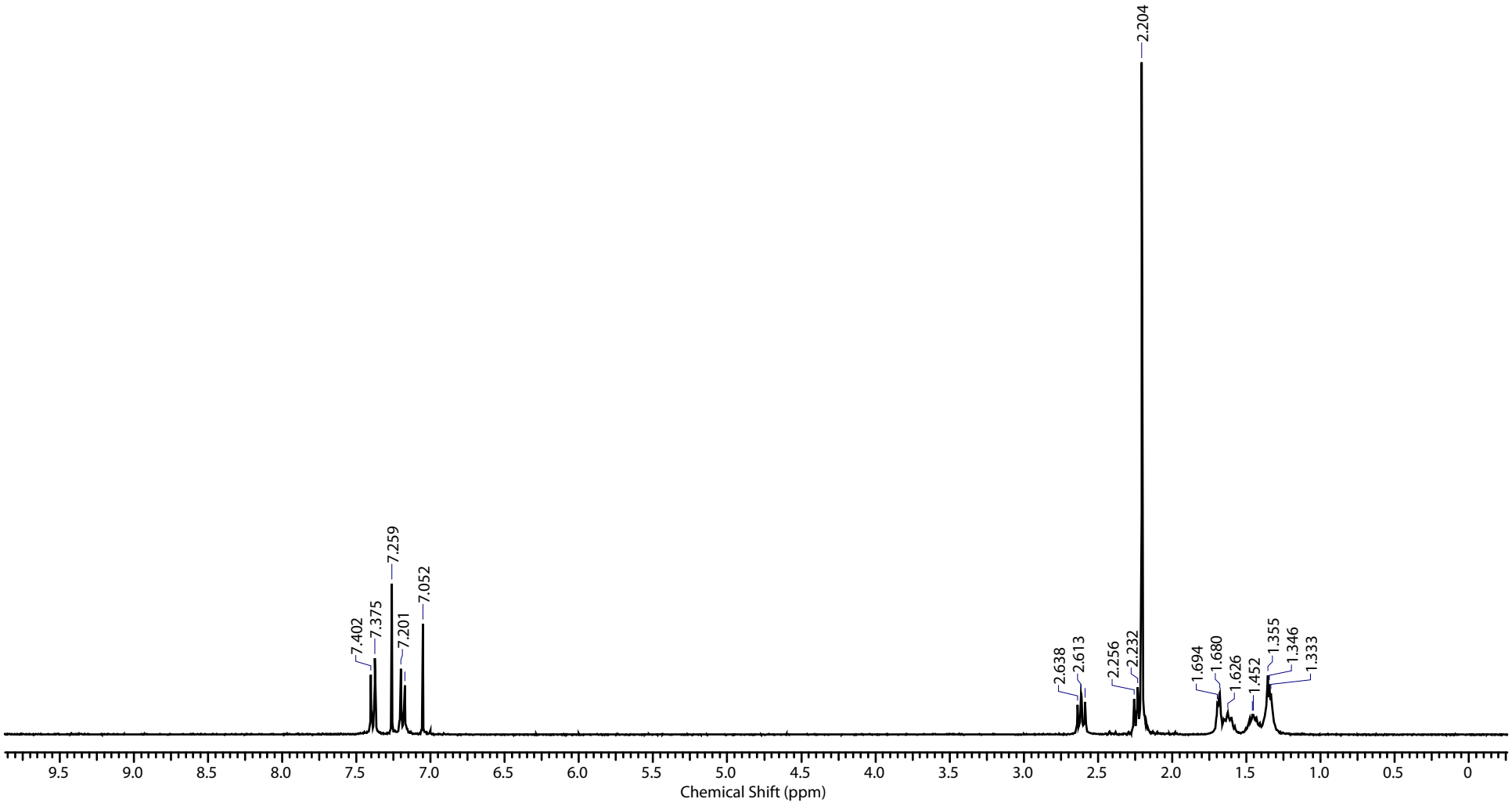




Compound 11

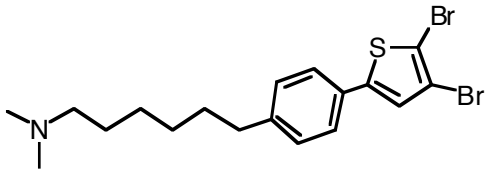
^{1}H NMR

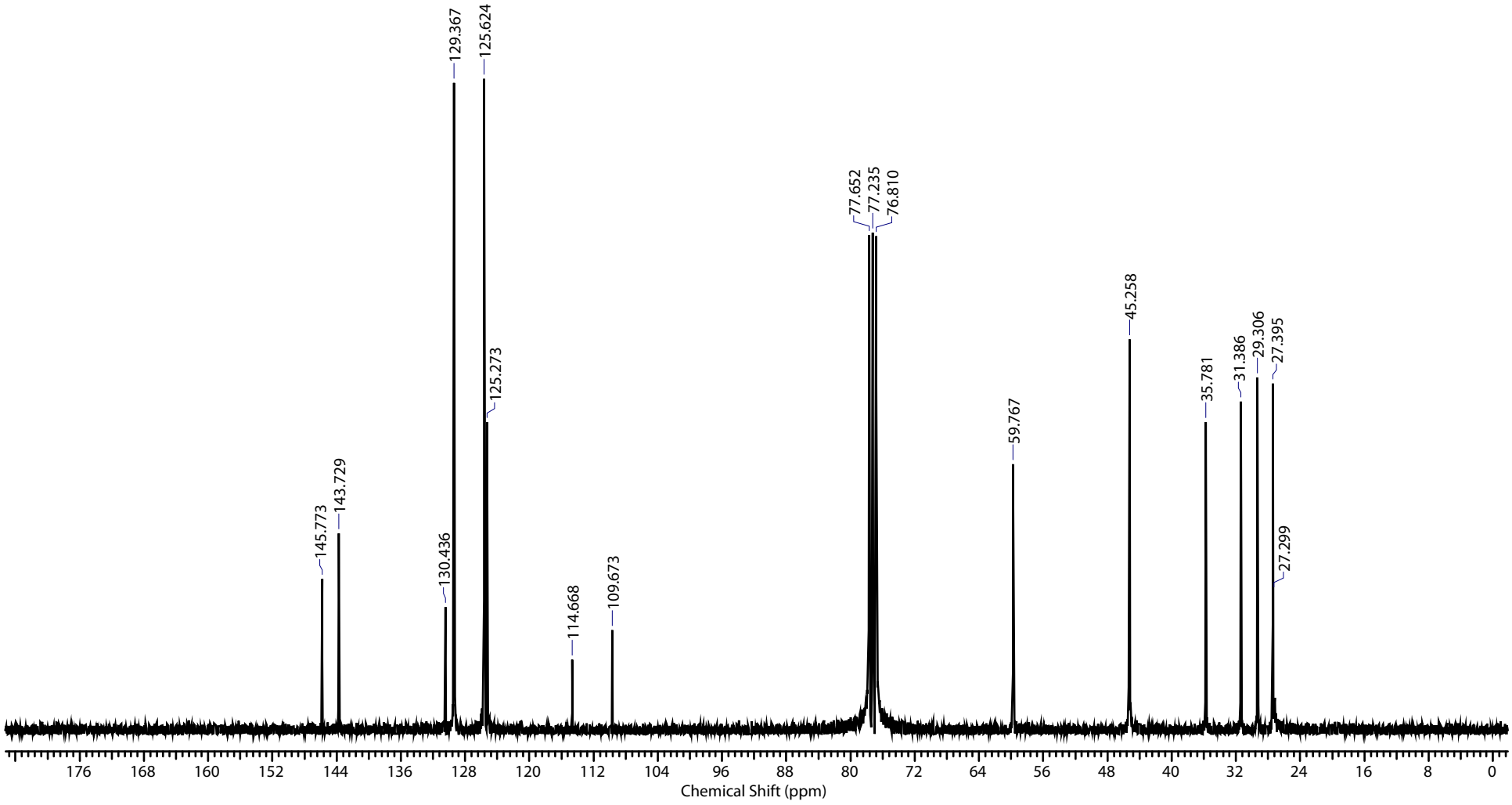




Compound 11

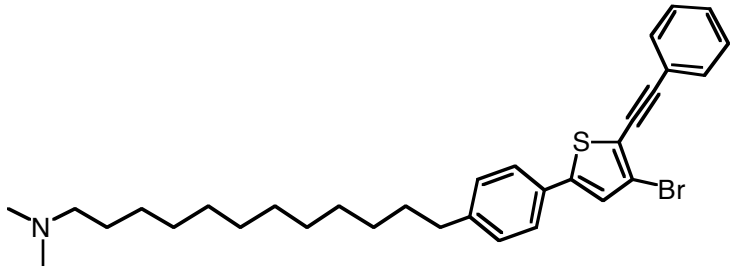
^{13}C NMR

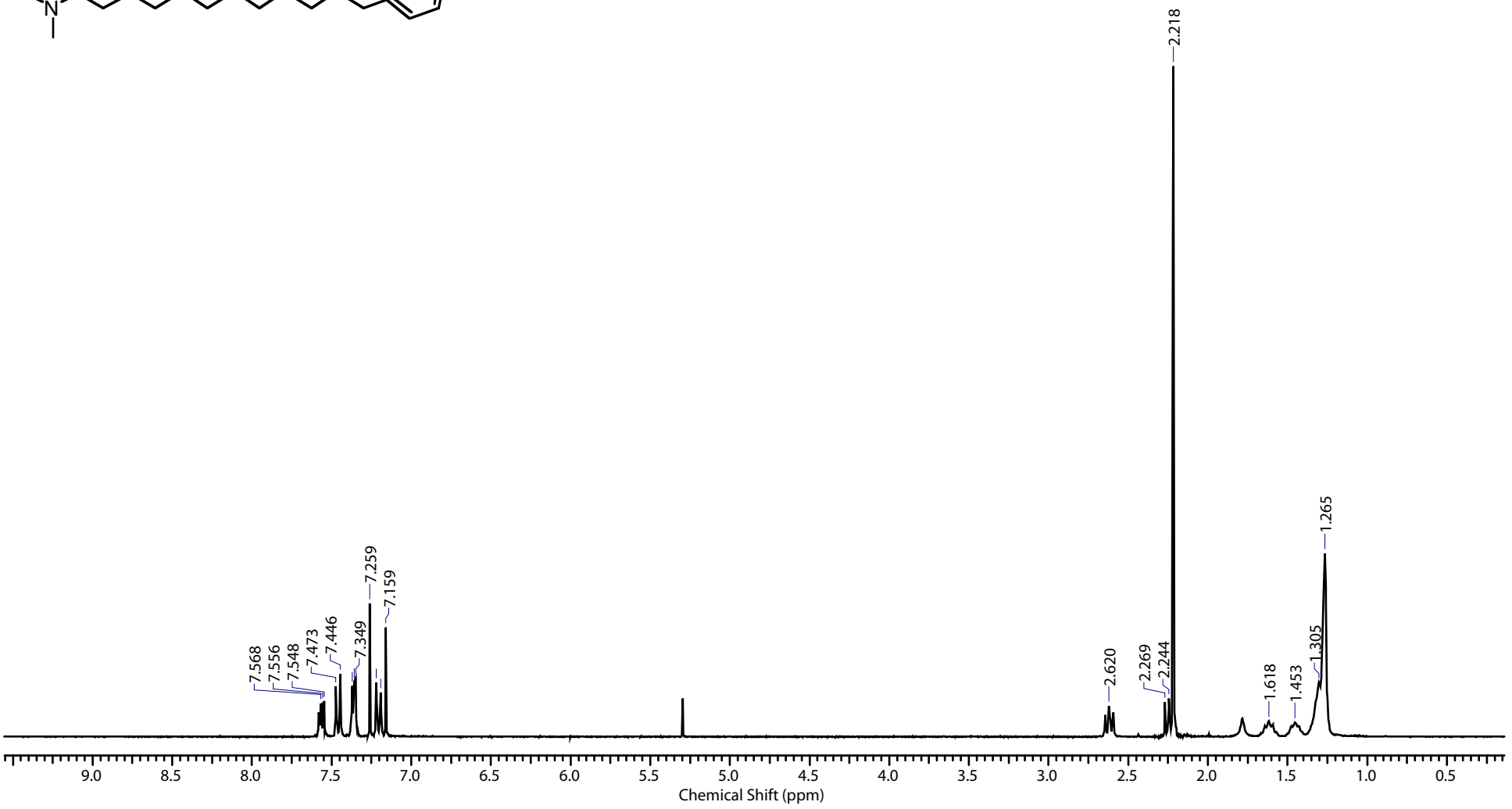




Compound 12

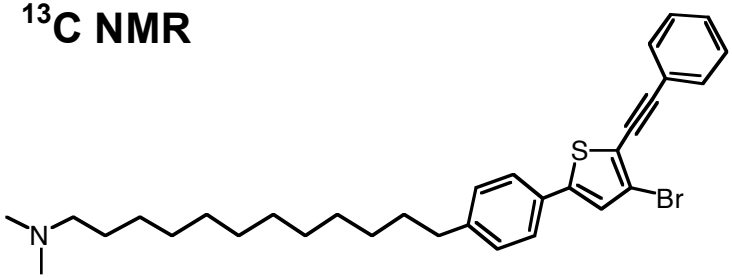
^{1}H NMR

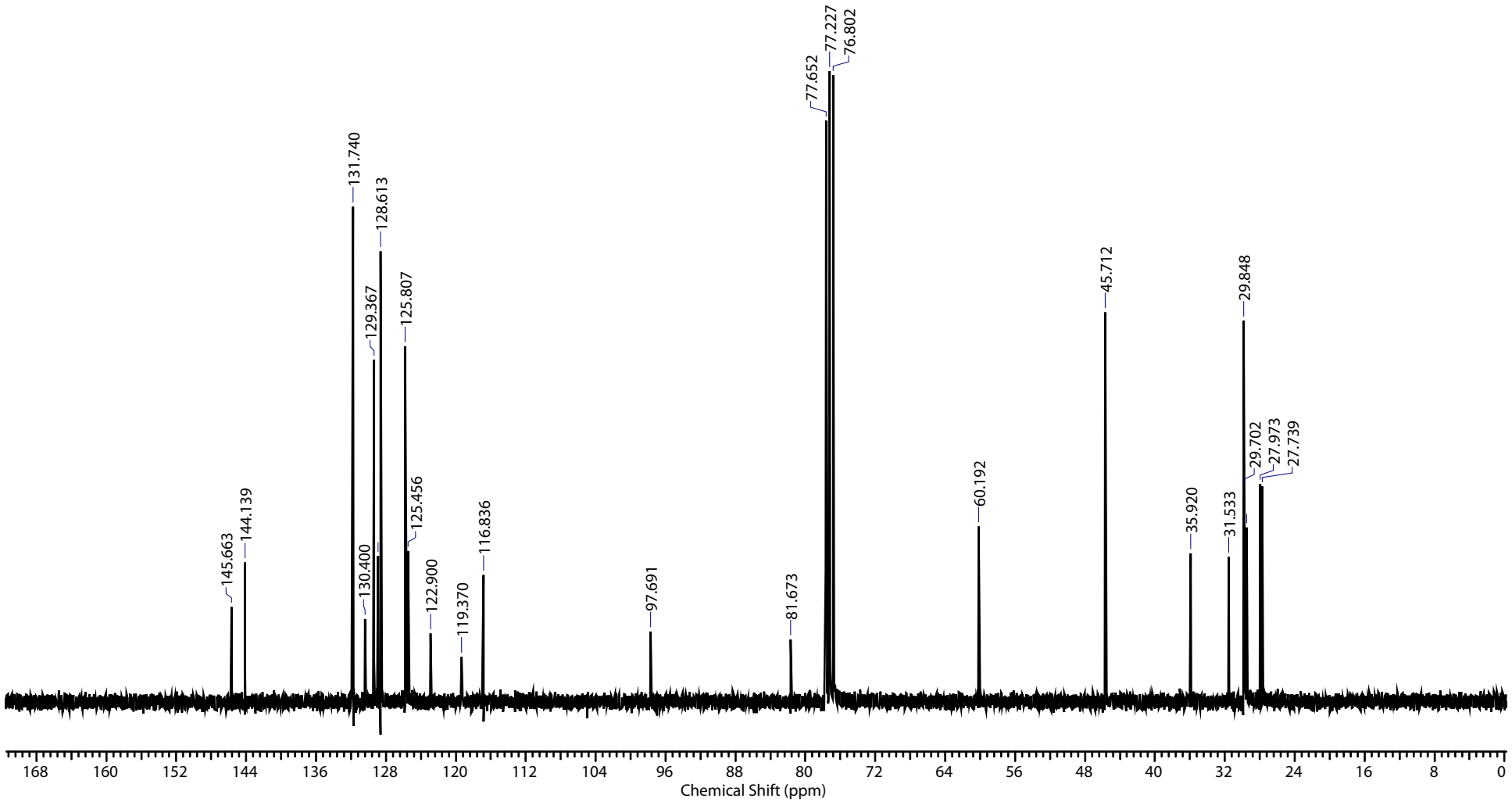




Compound 12

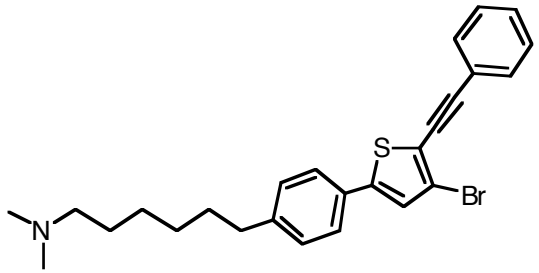
^{13}C NMR

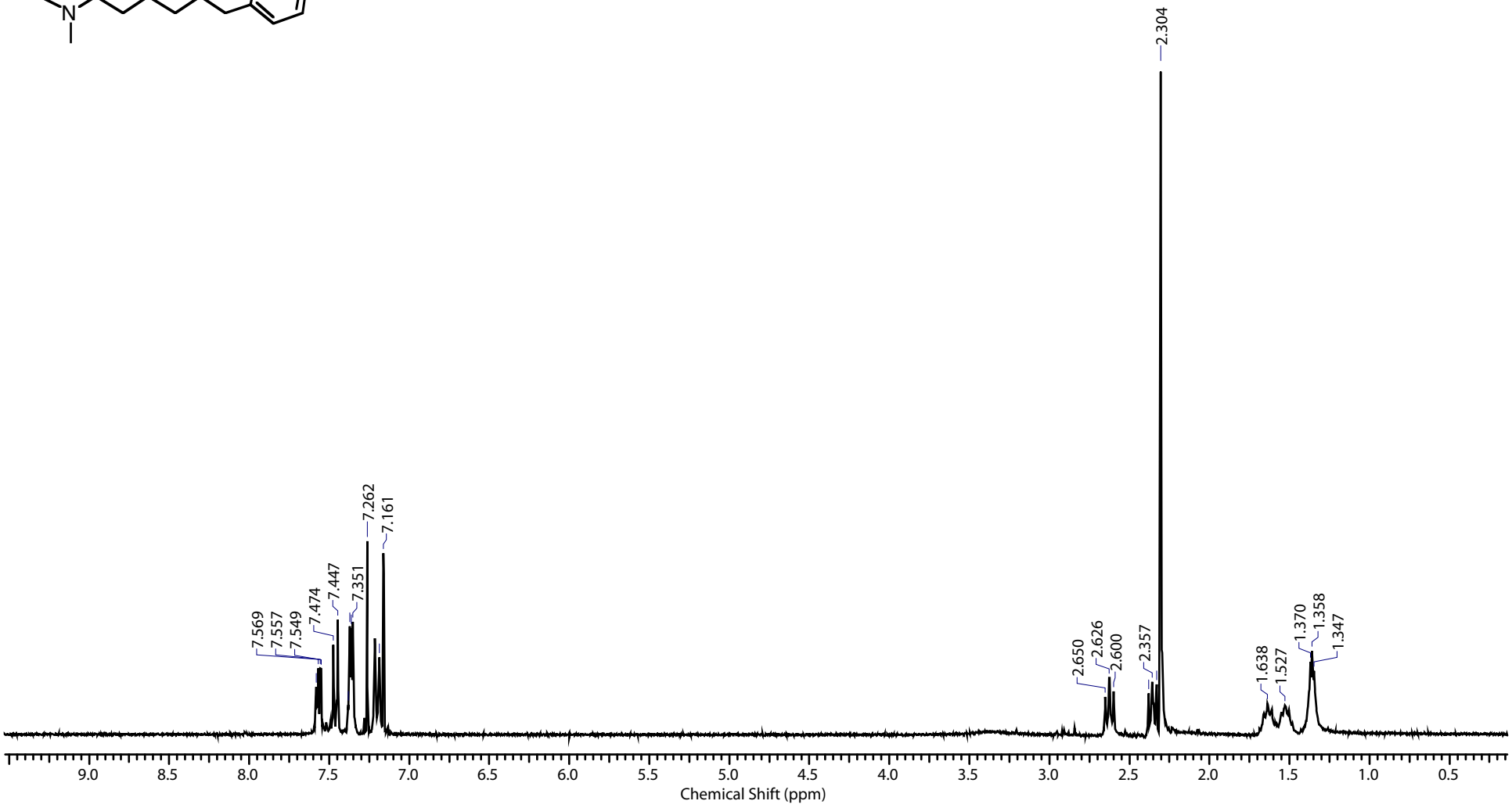




Compound 13

^{1}H NMR





Compound 13

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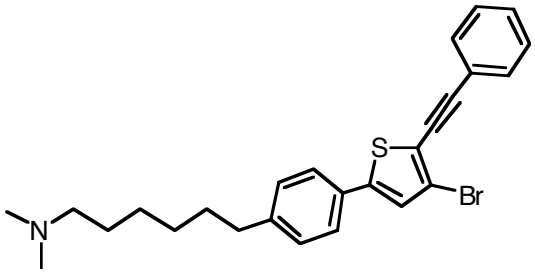
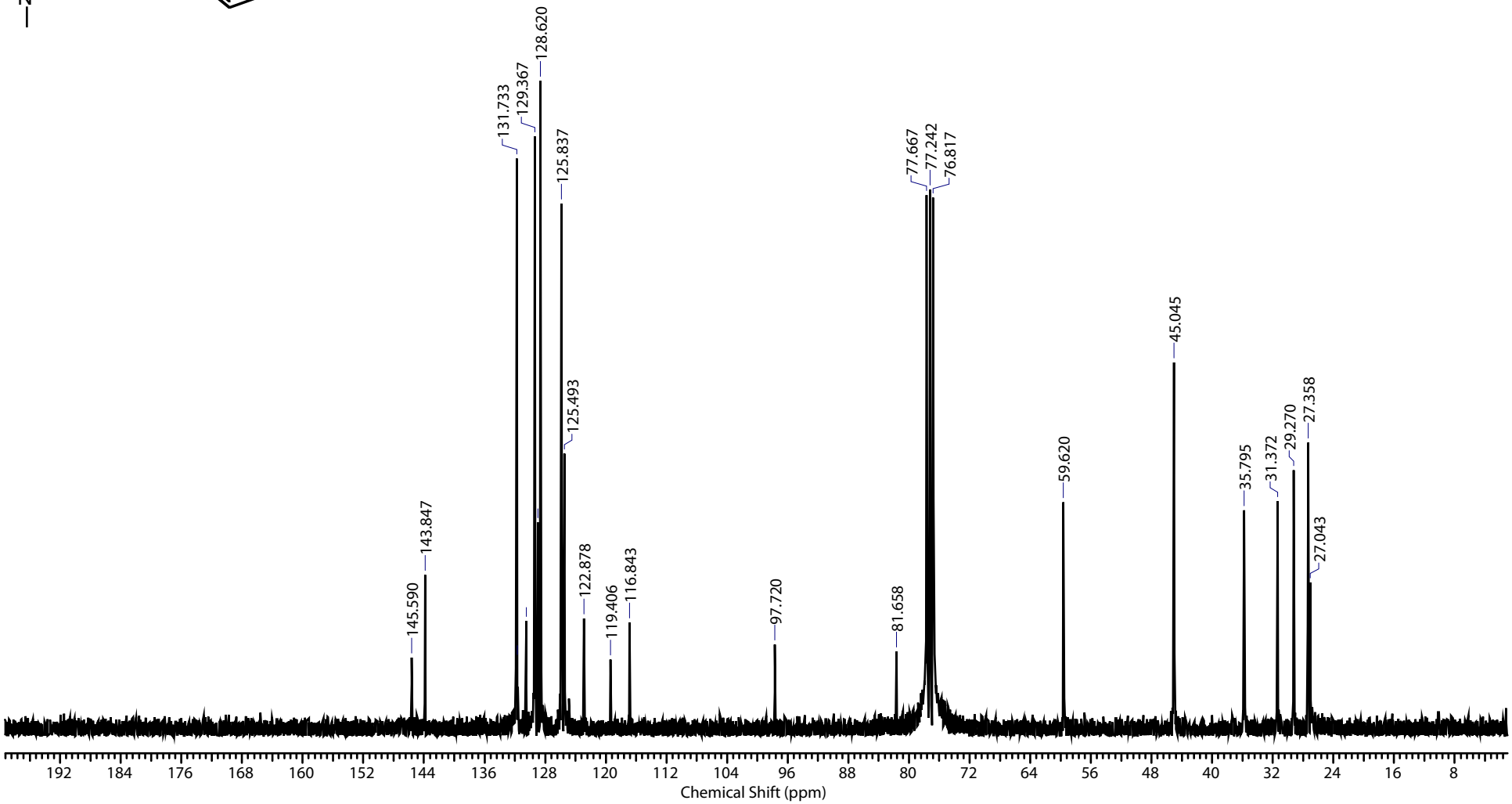
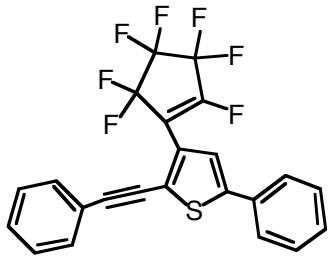
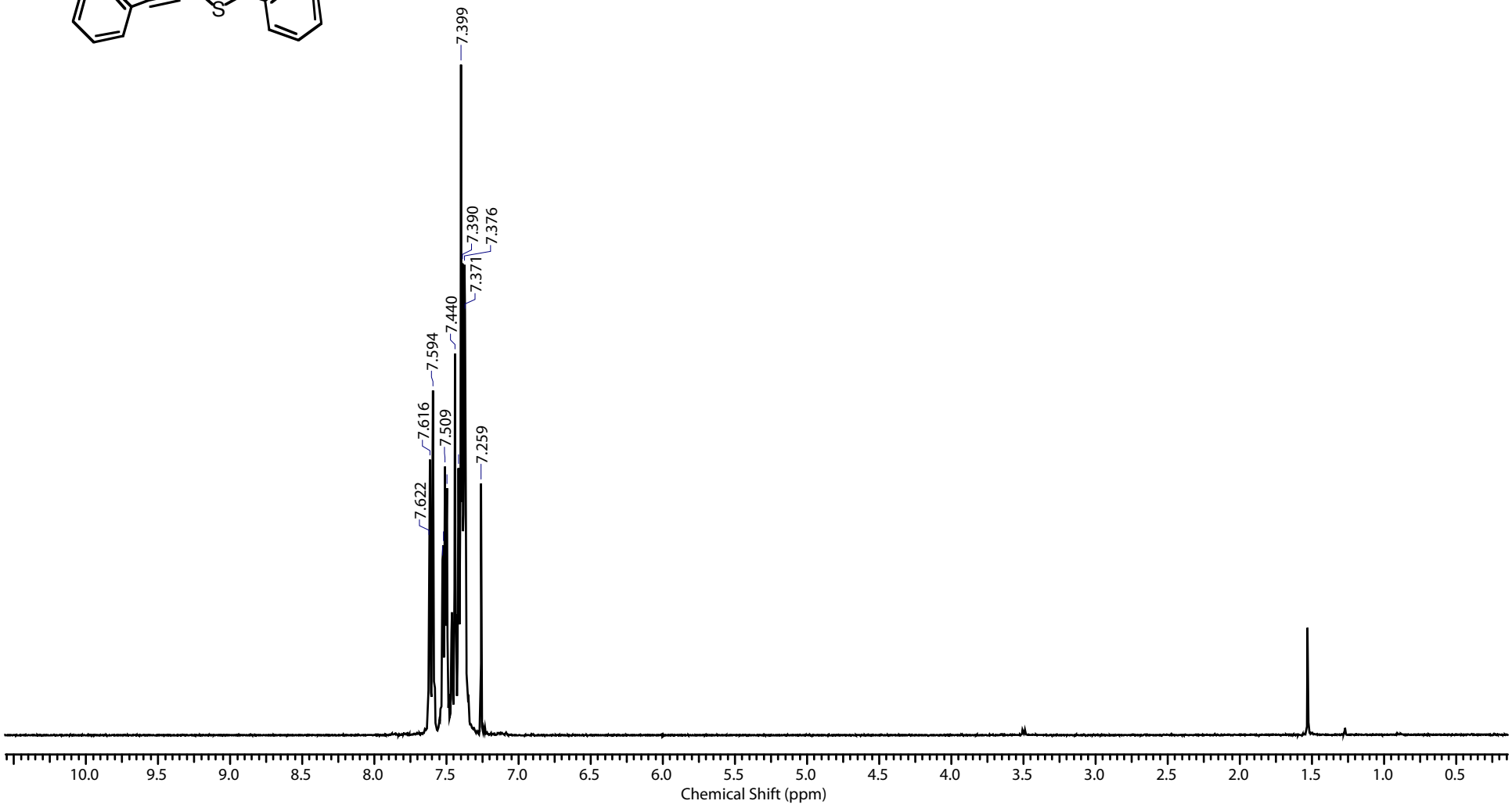




Compound 14

^{1}H NMR





Compound 14

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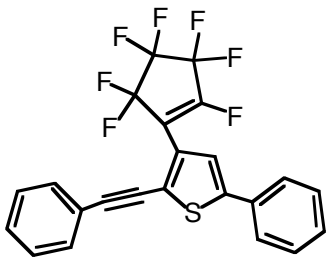
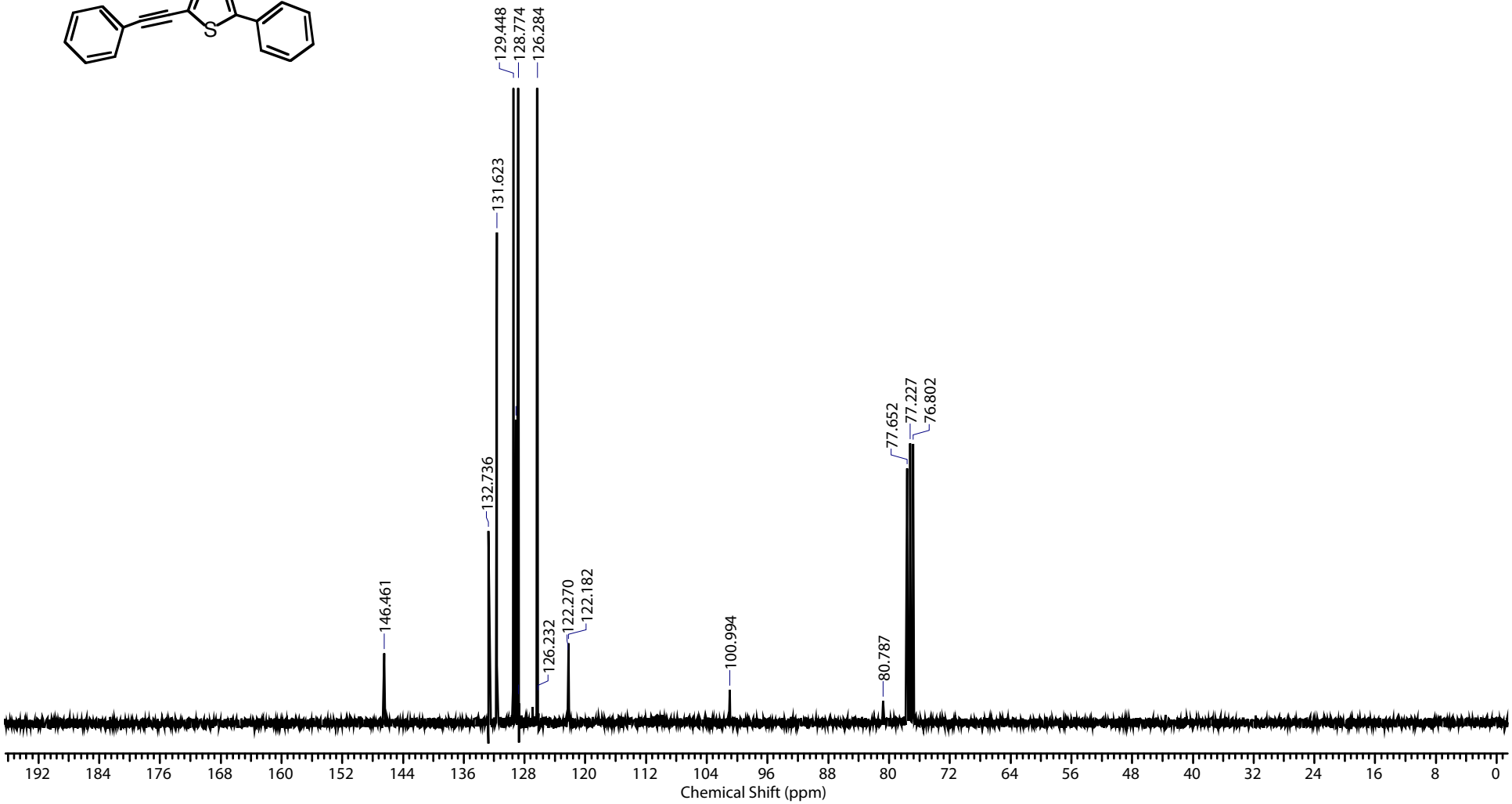
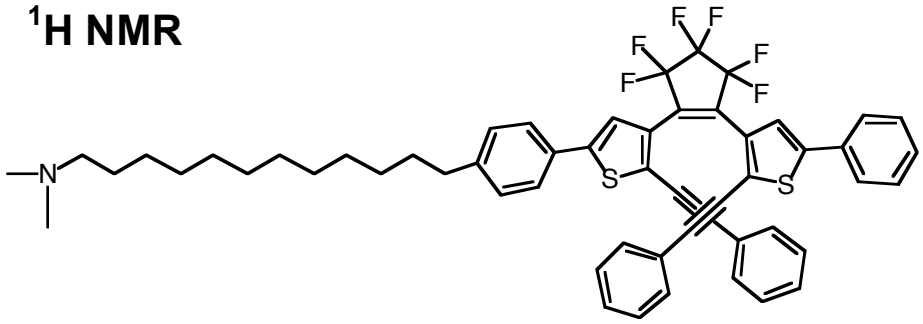
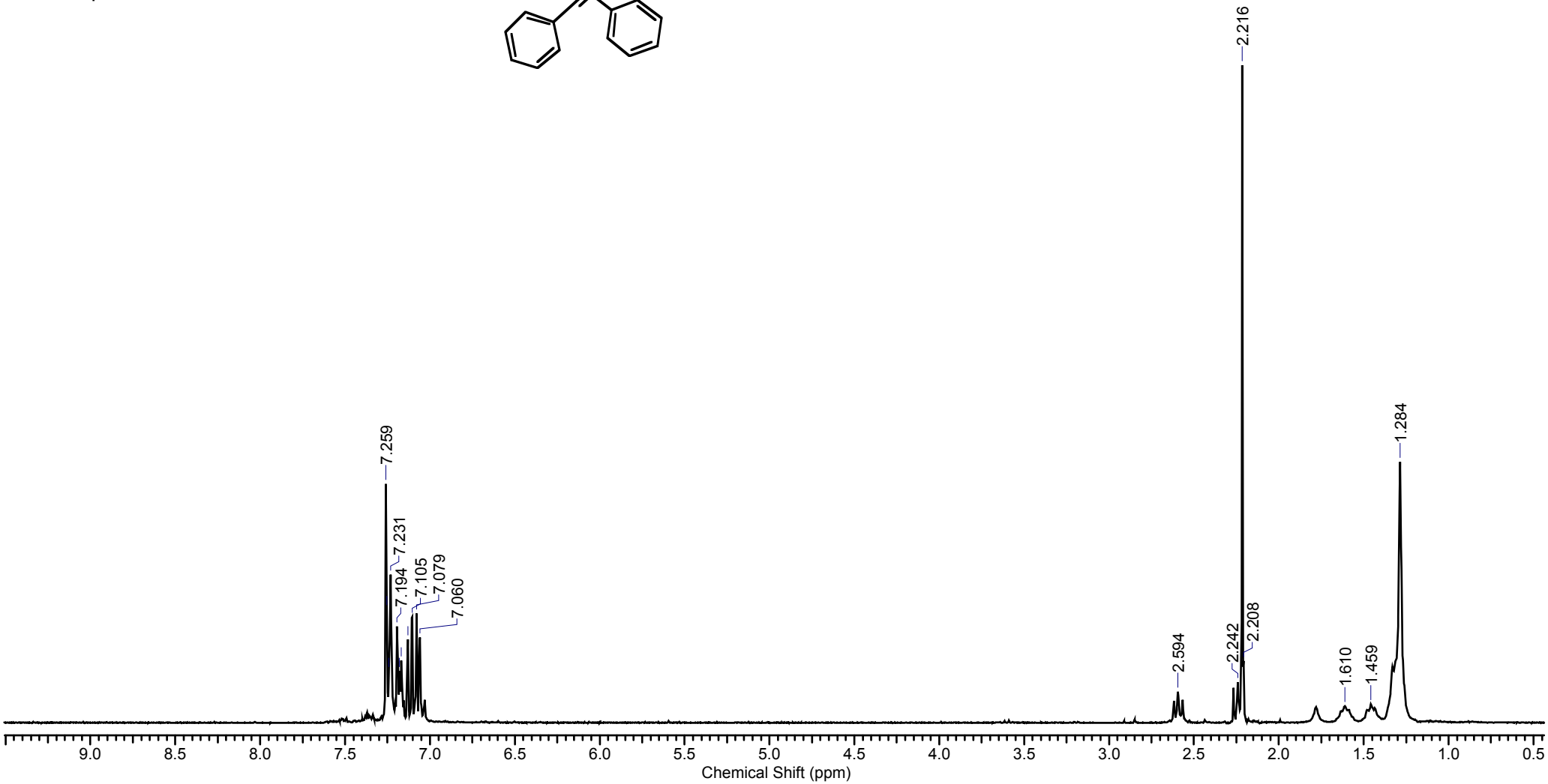




Compound 15

^{1}H NMR





Compound 15

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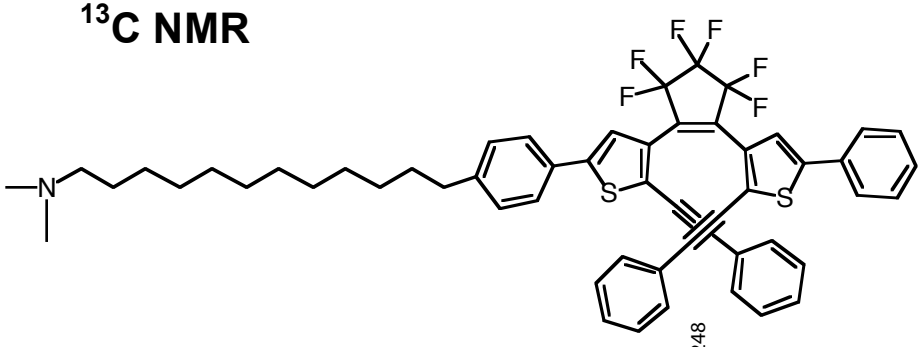
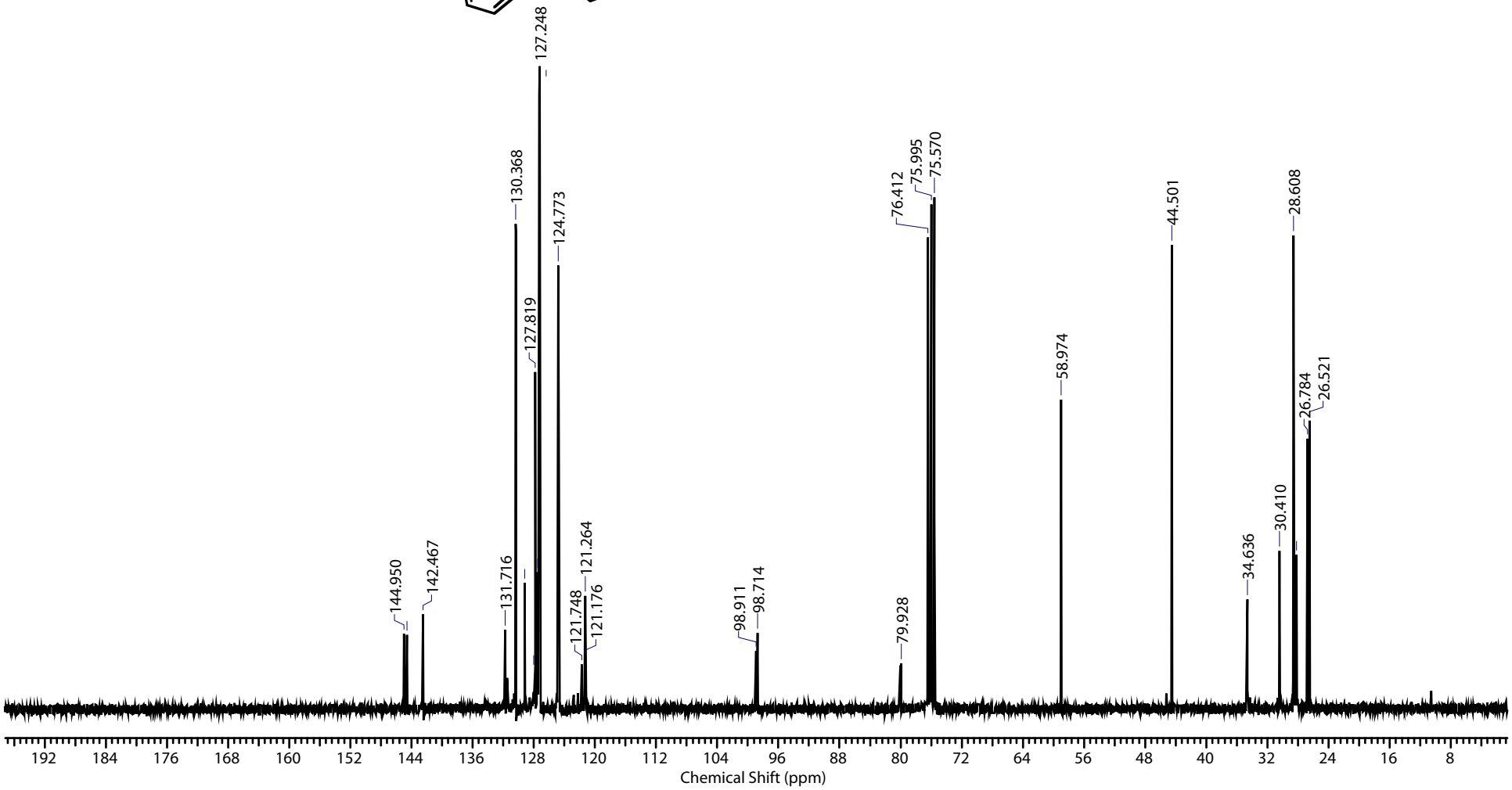
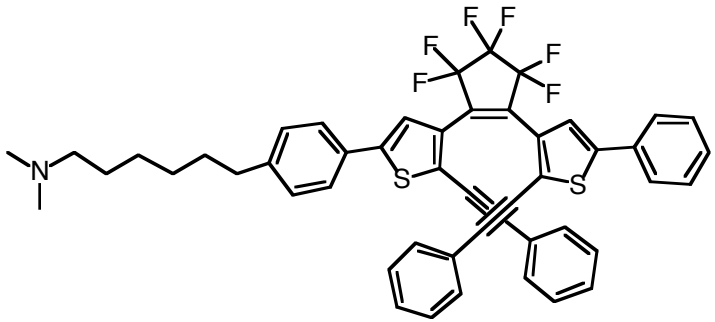
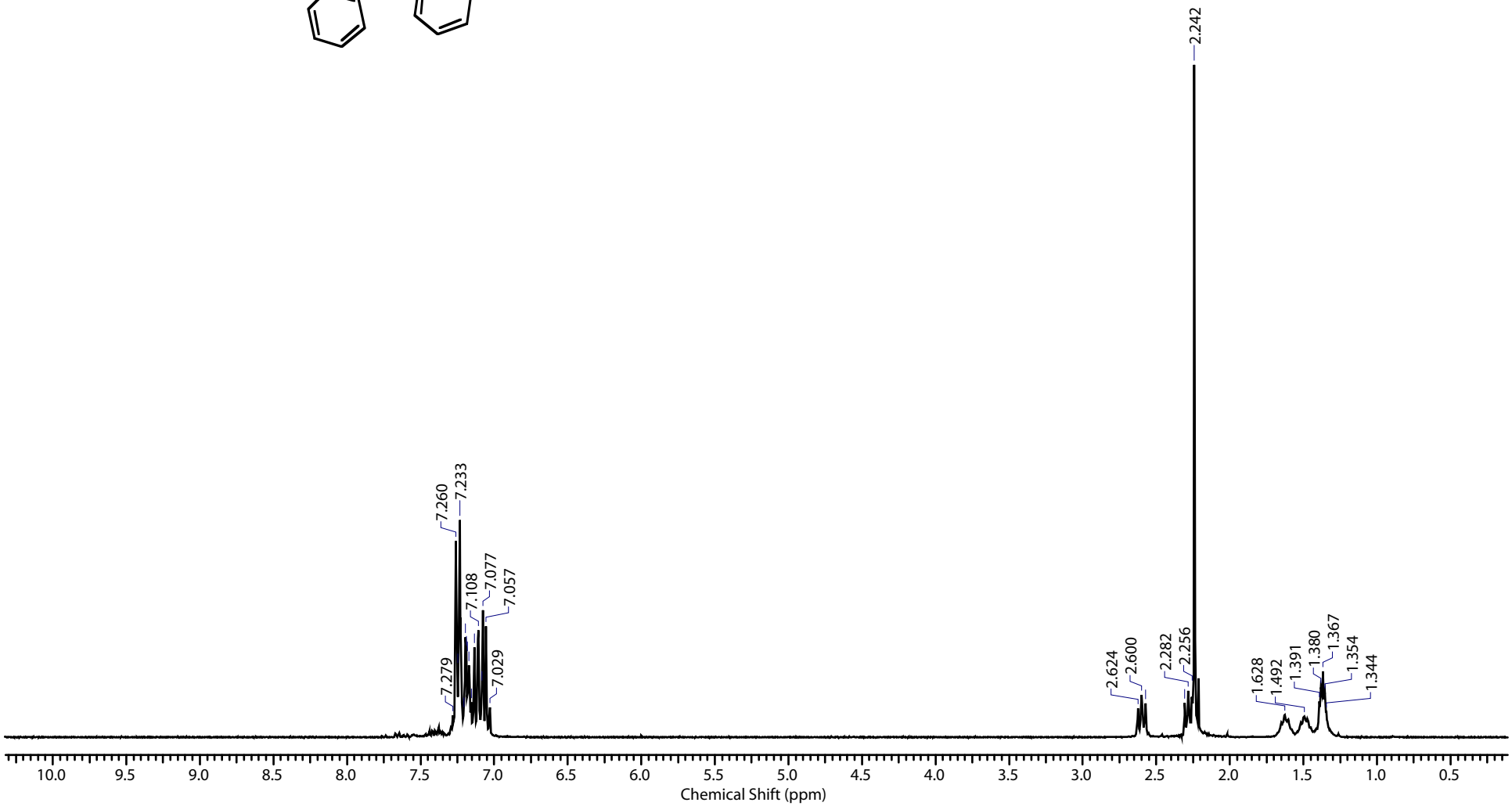




Compound 16

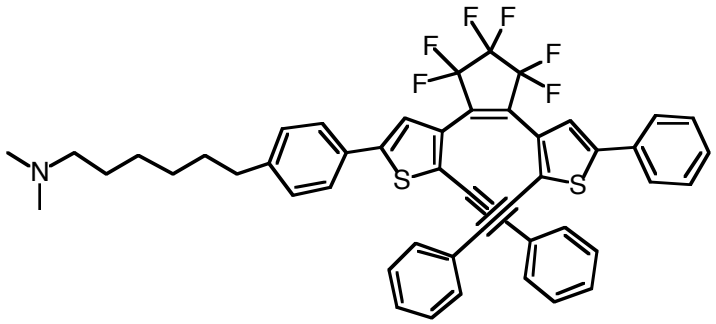
^{1}H NMR

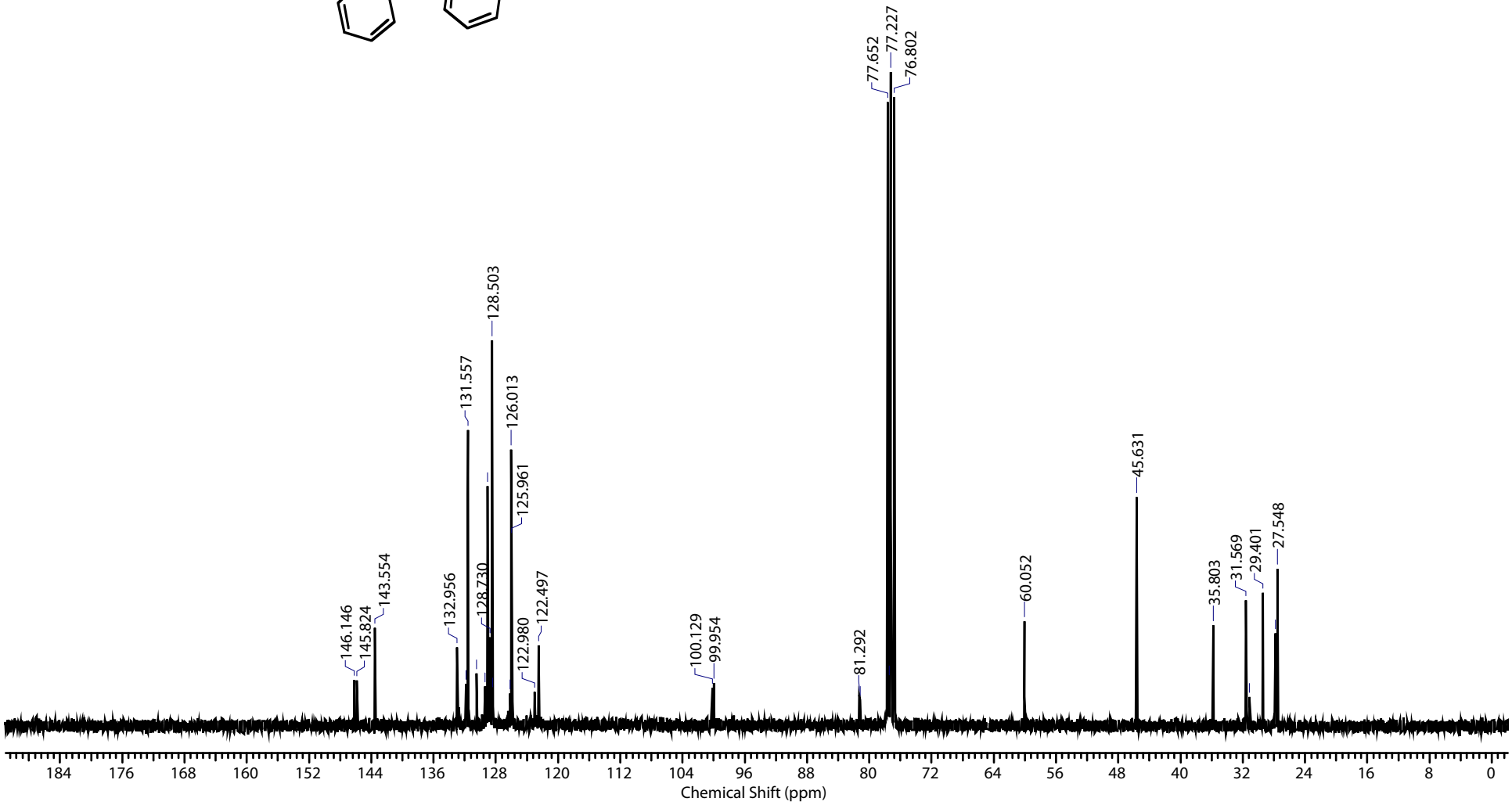




Compound 16

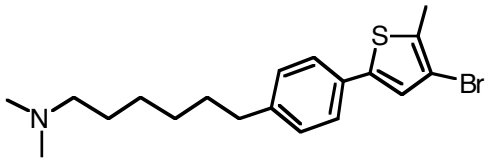
^{13}C NMR

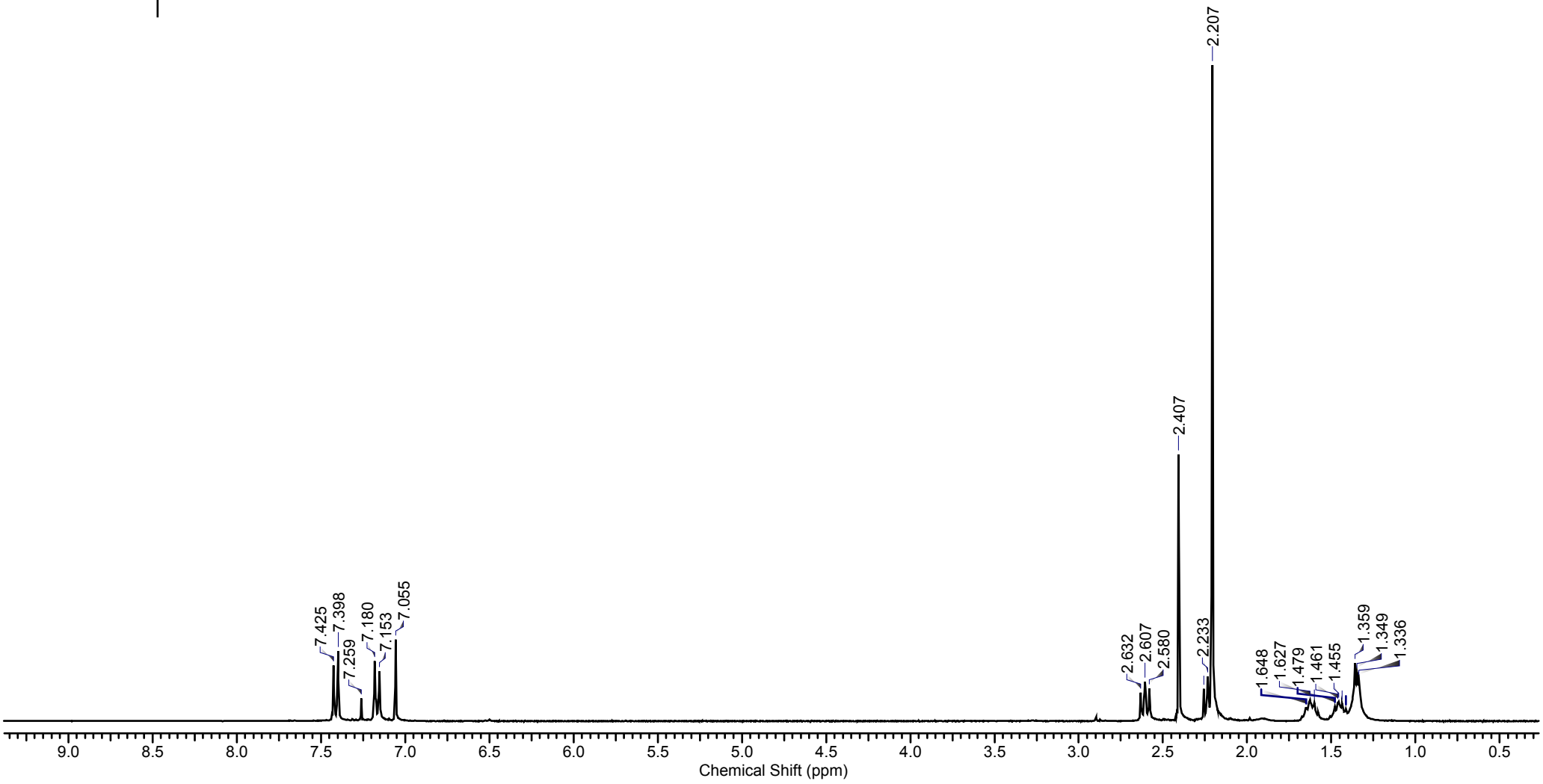




Compound 17

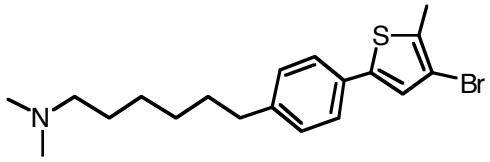
^{1}H NMR

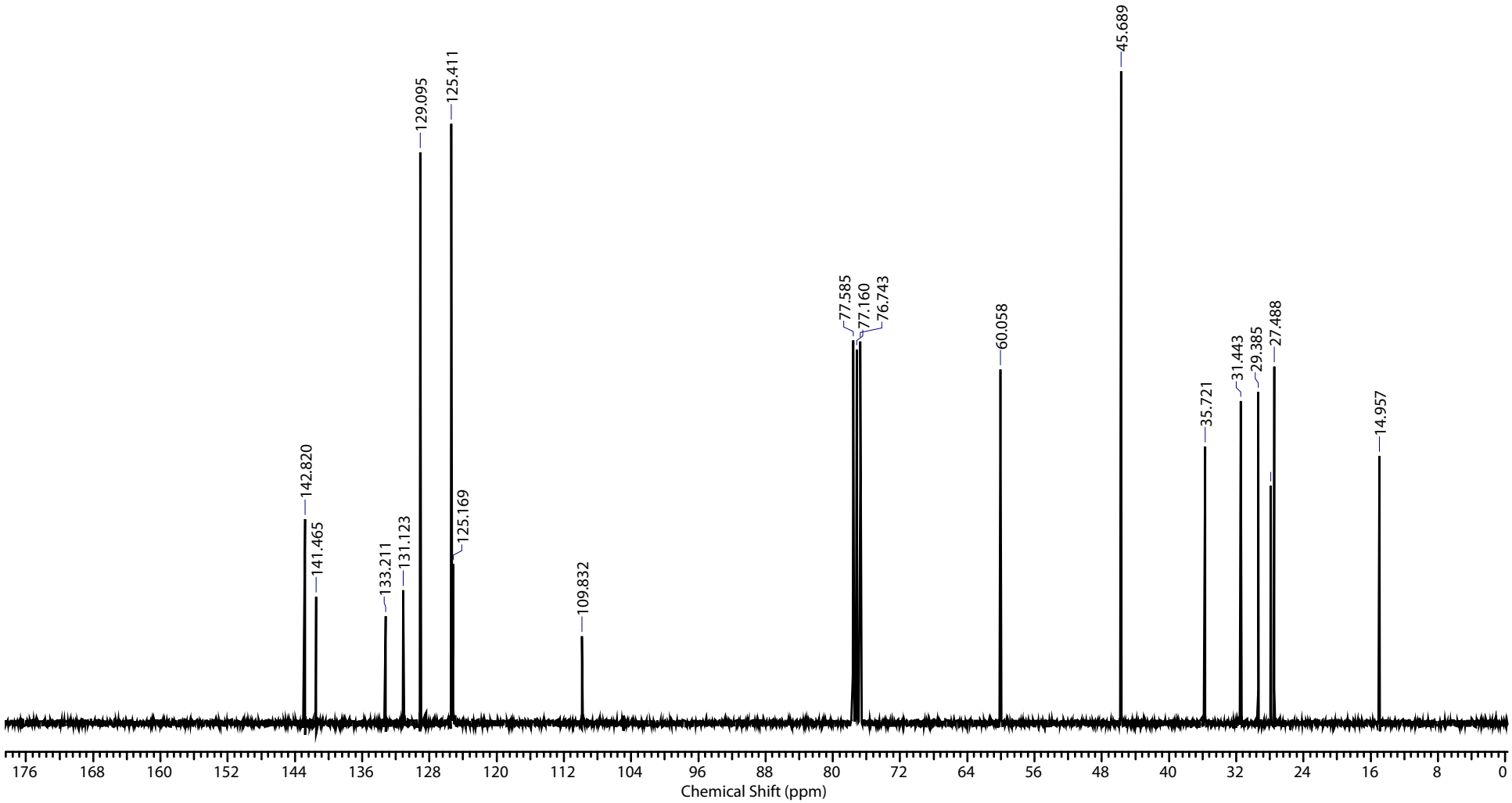




Compound 17

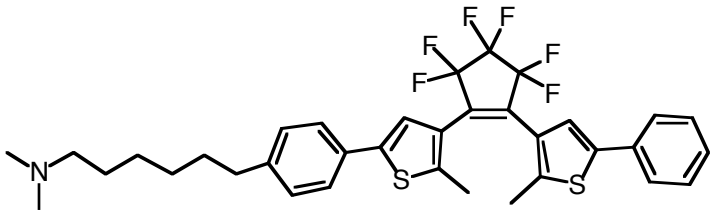
^{13}C NMR

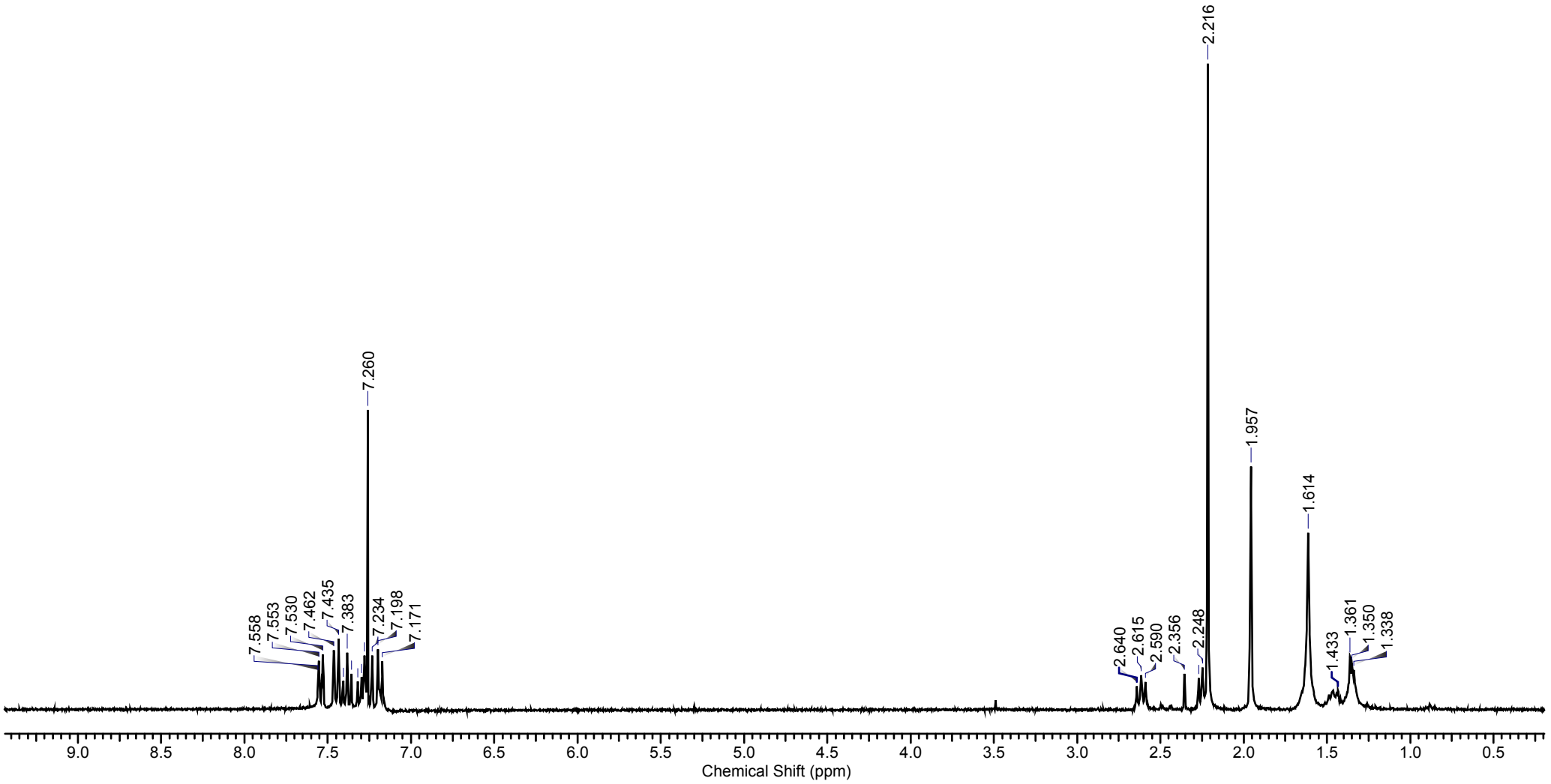




Compound 18

^{1}H NMR





Compound 18

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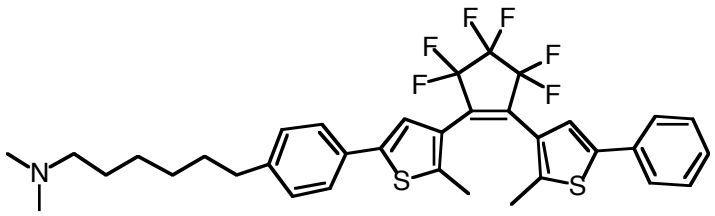
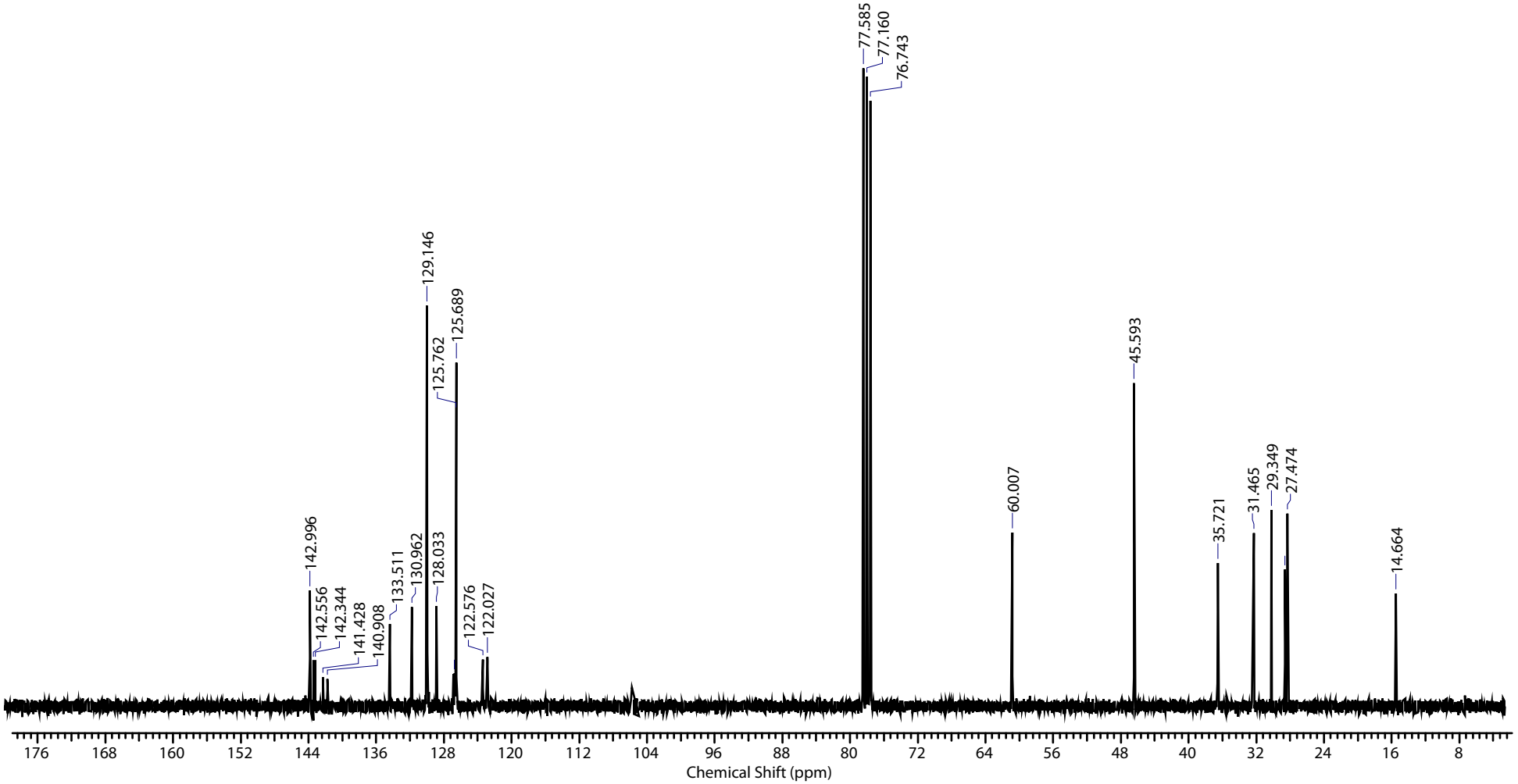
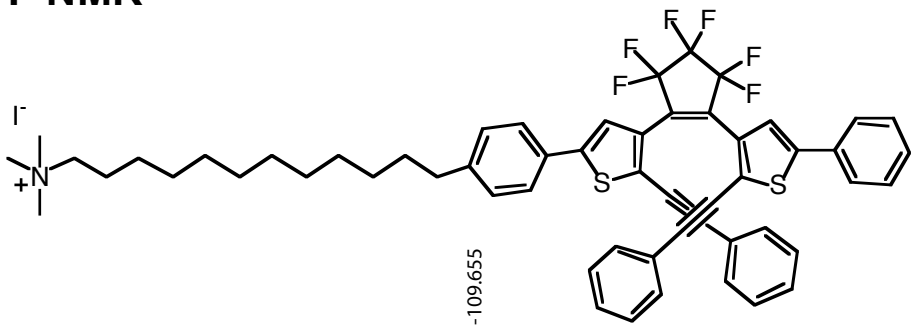
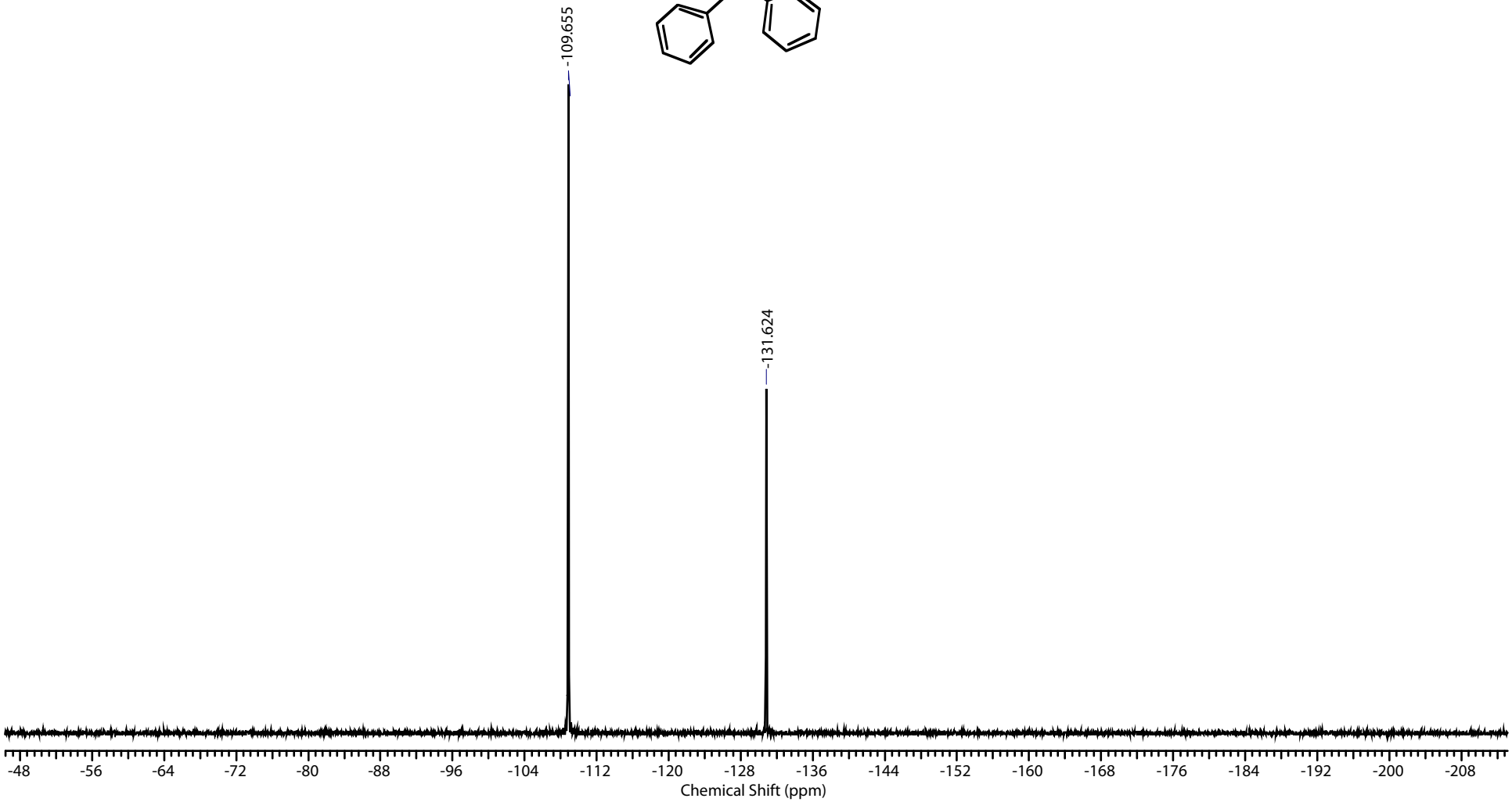




Compound 1

^{19}F NMR





Compound 2

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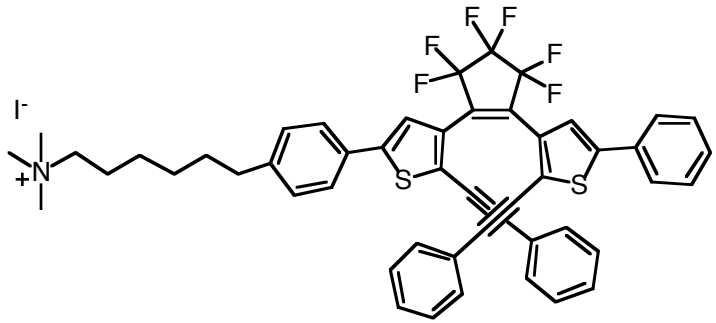

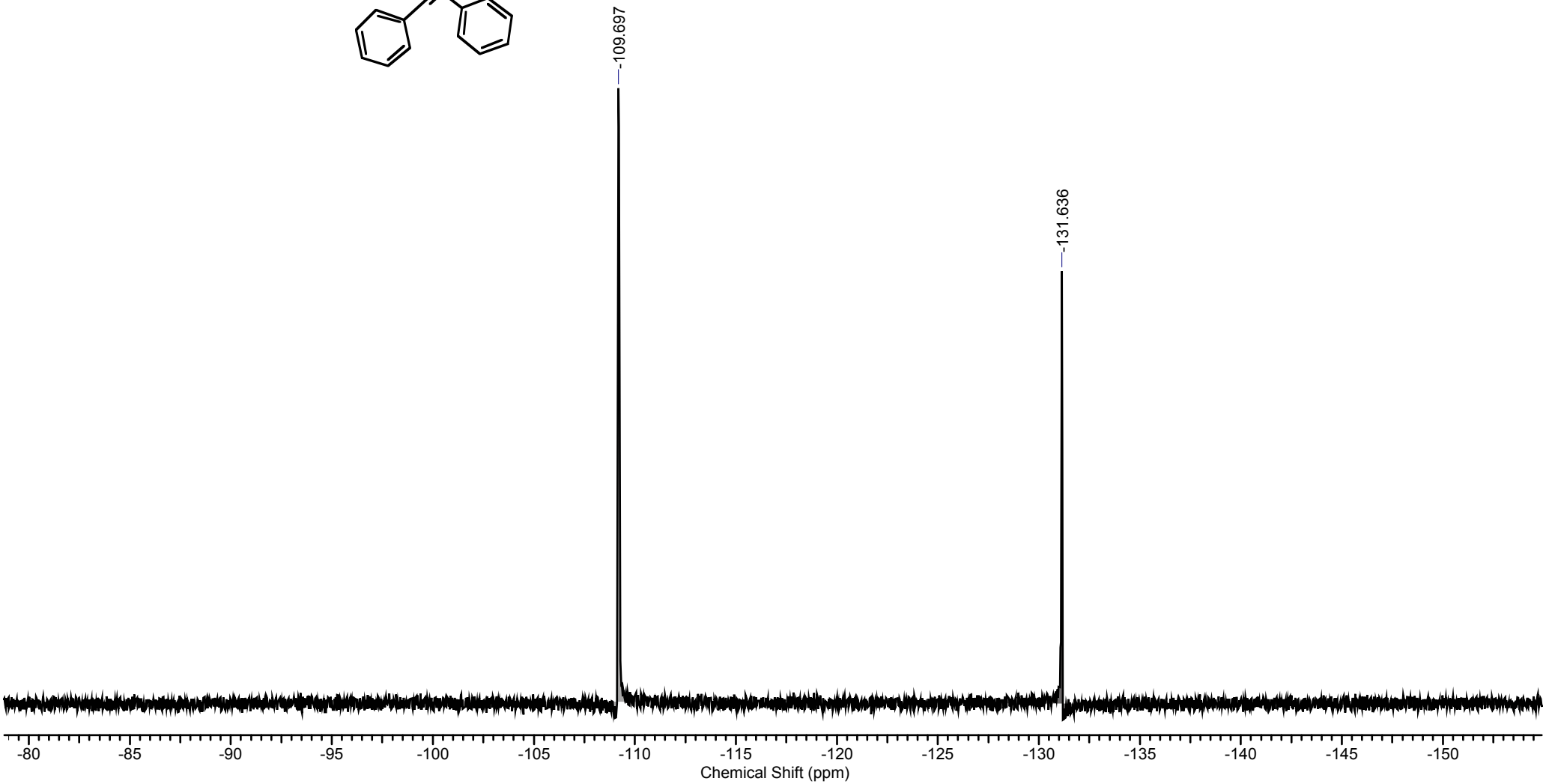

Compound 3

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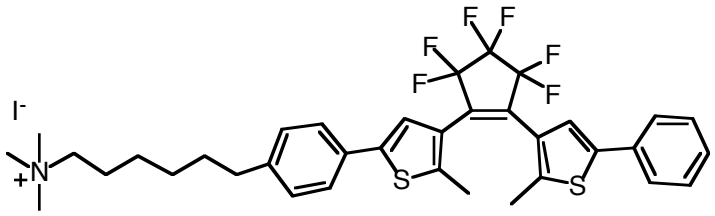

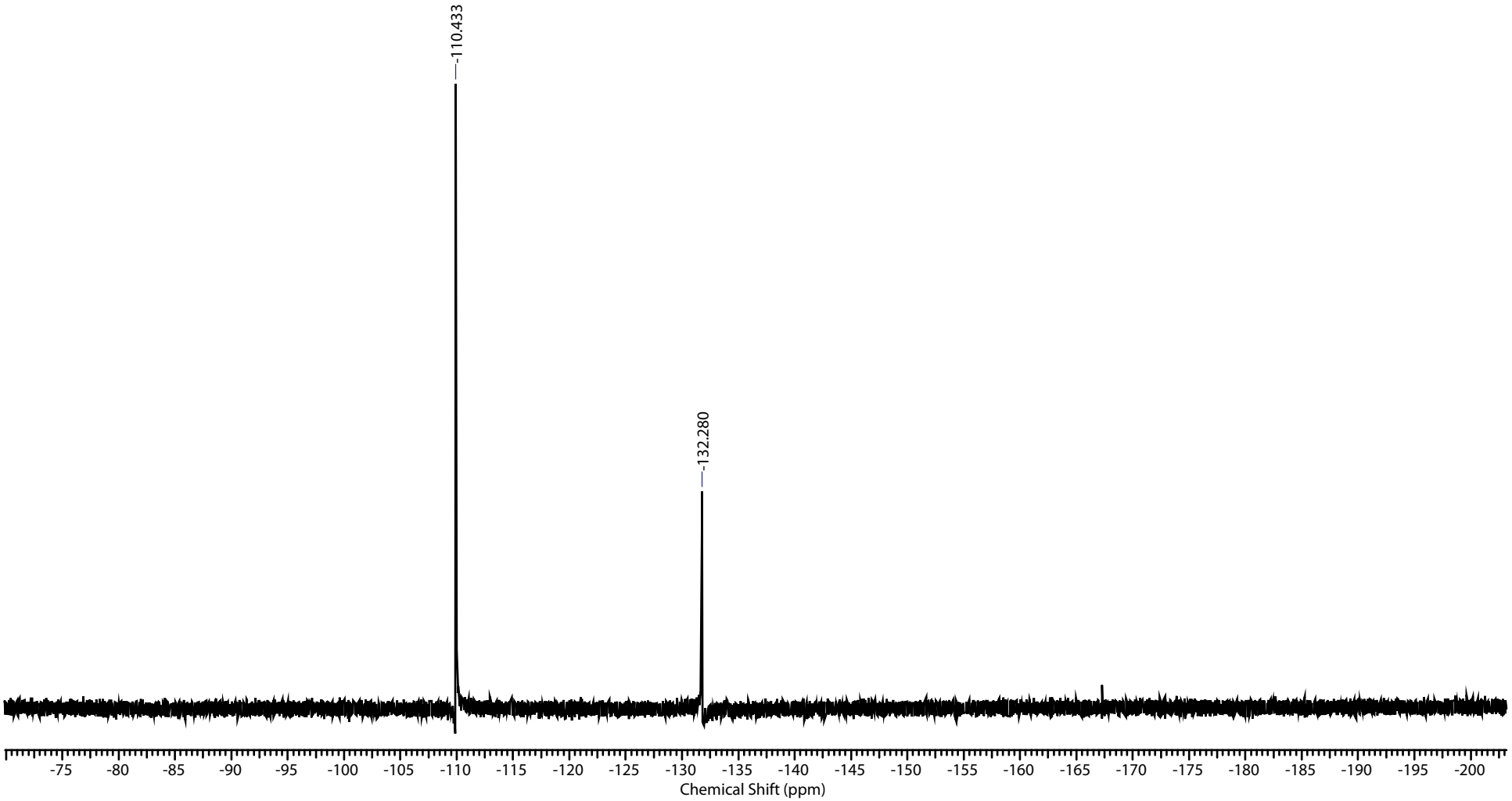

Compound 14

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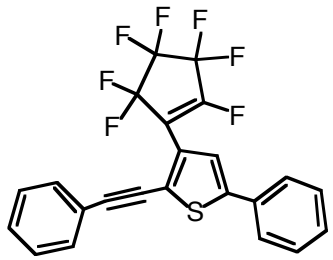

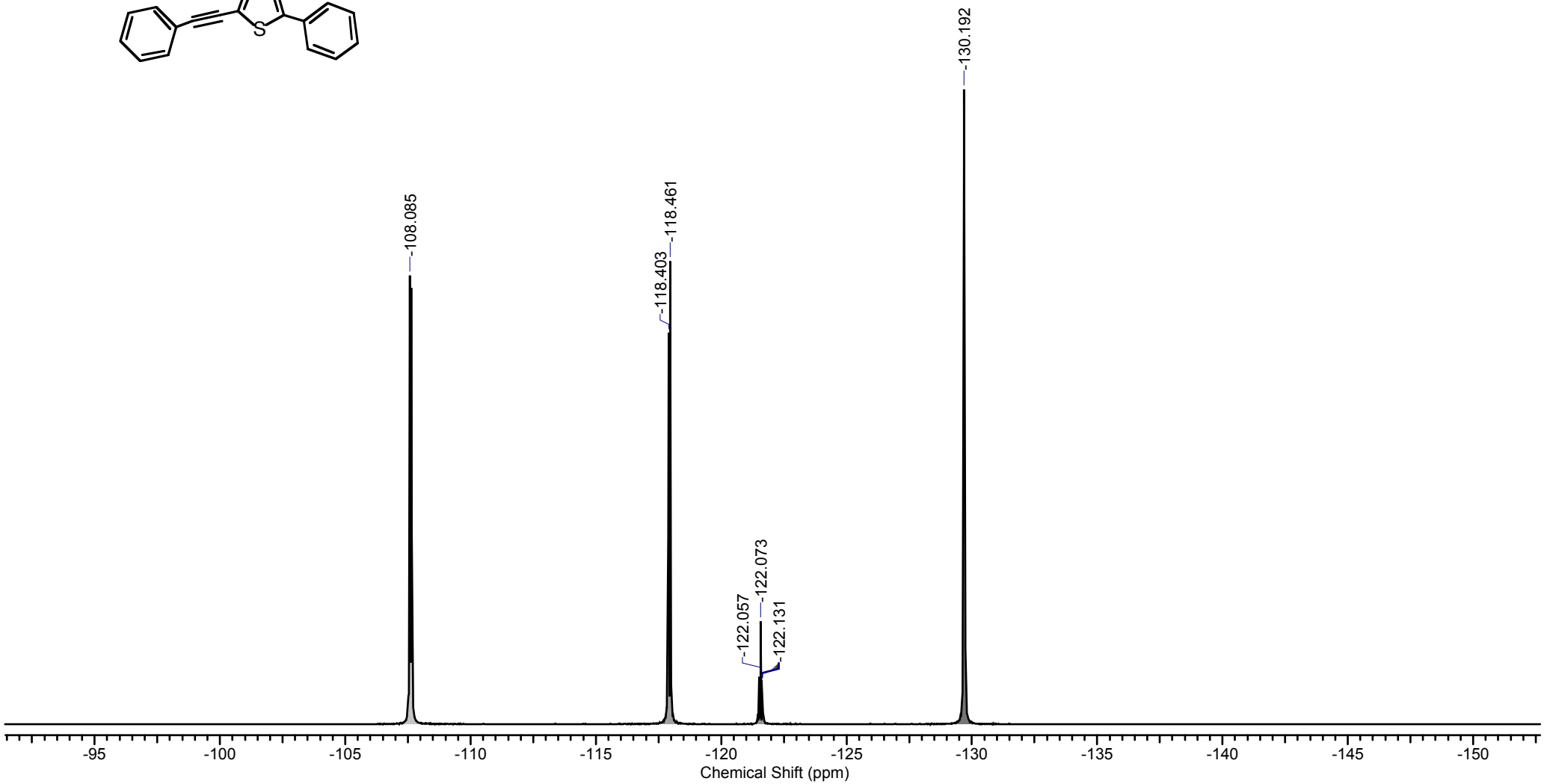

Compound 15

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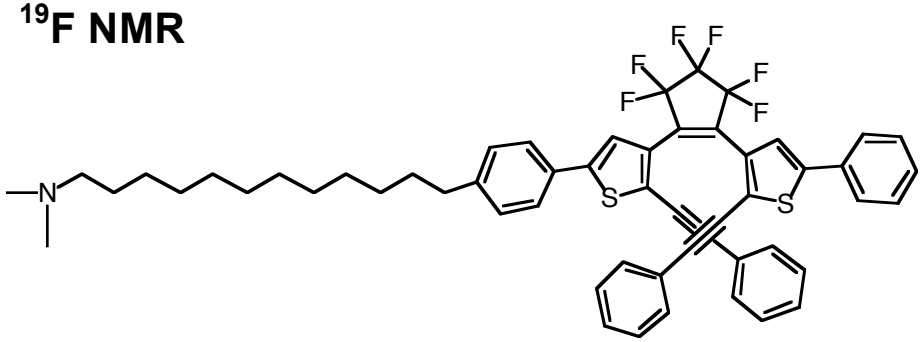

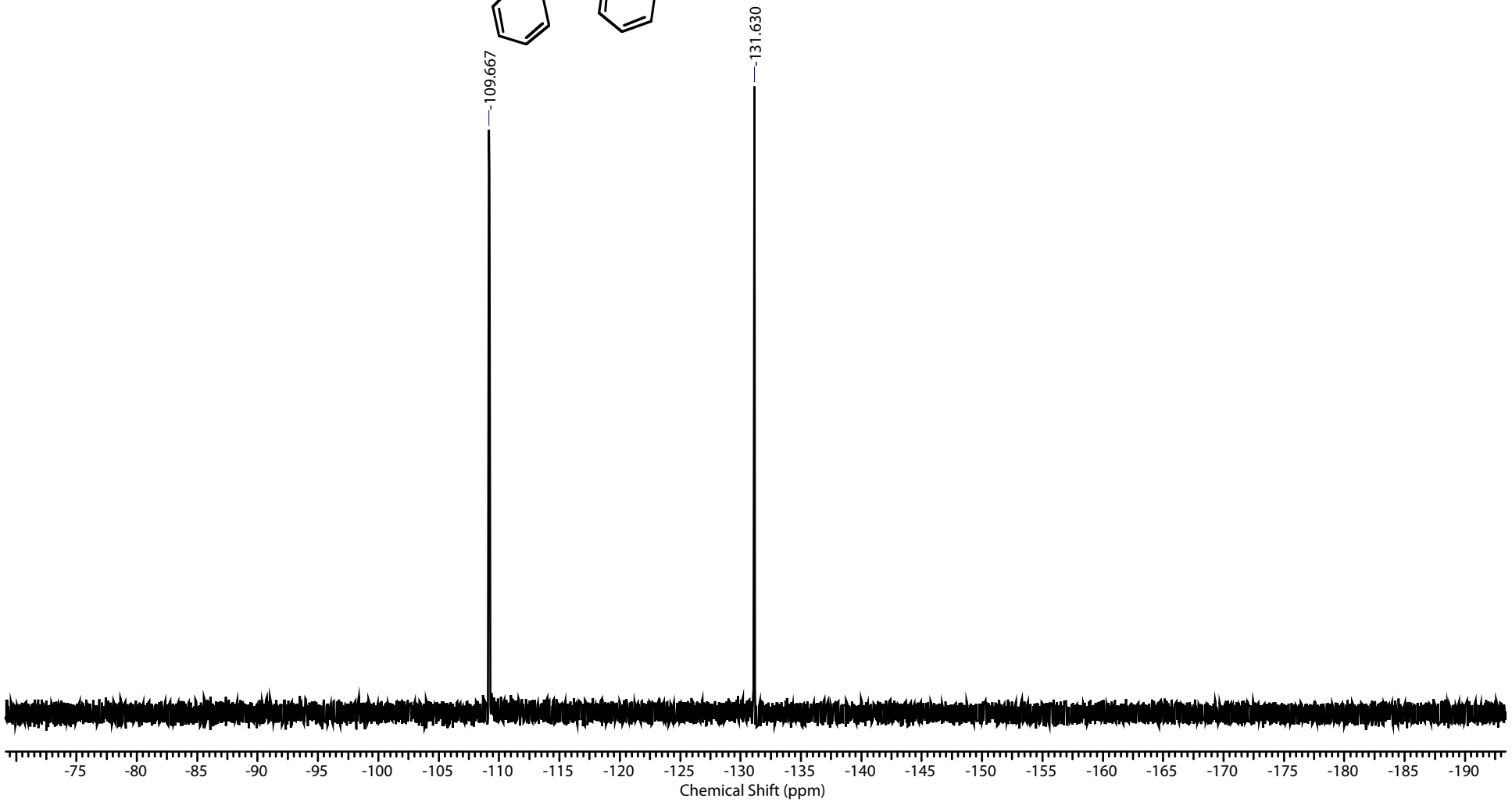

Compound 16

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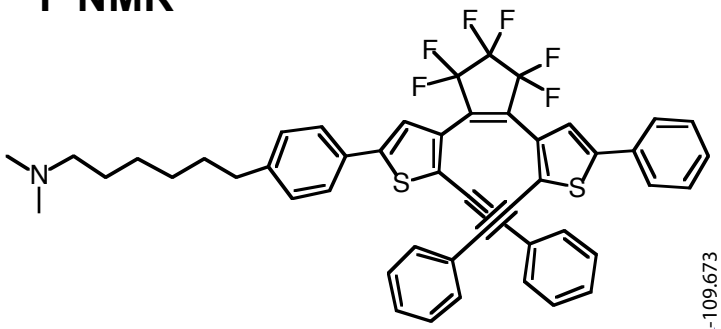
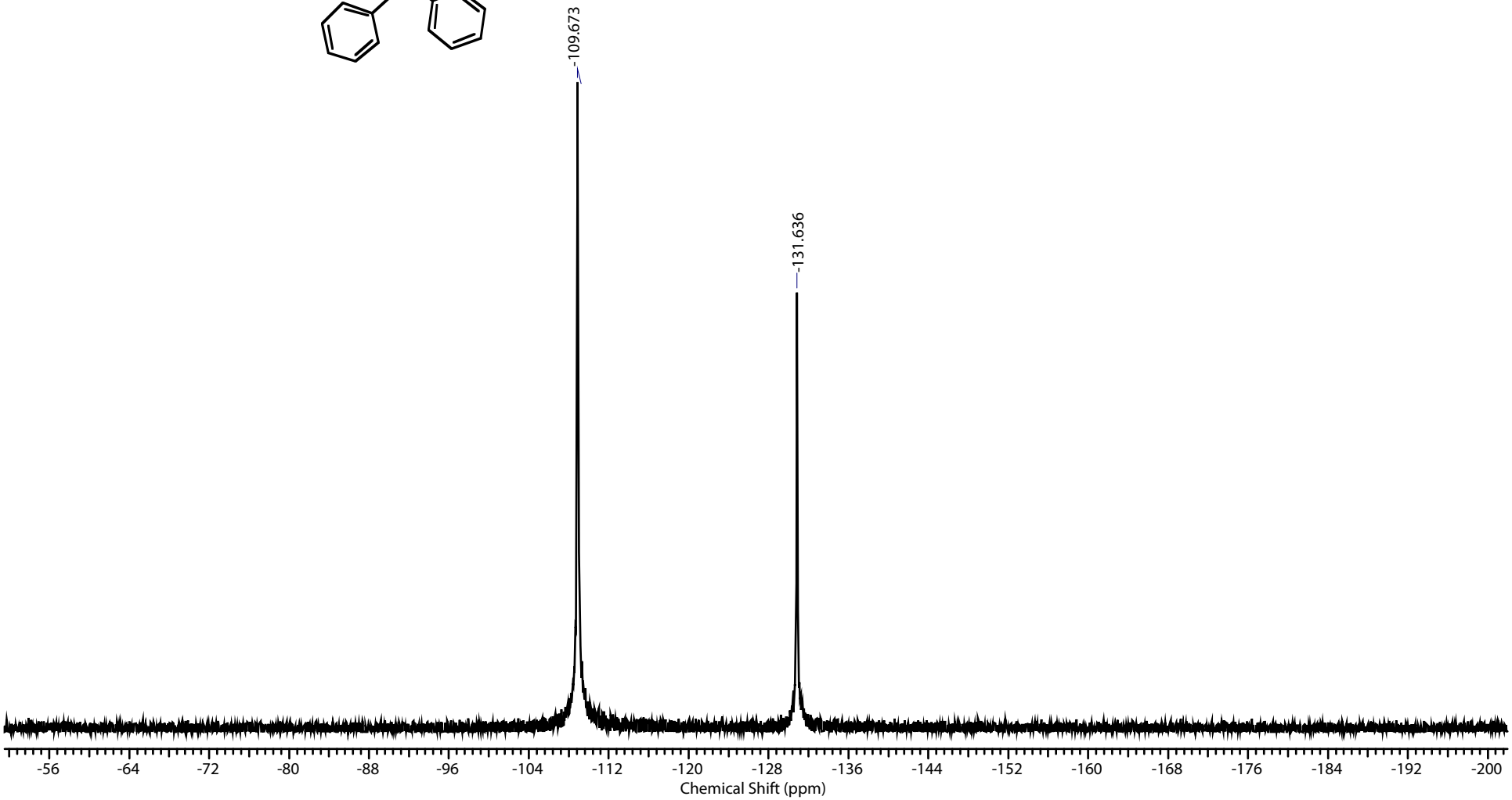
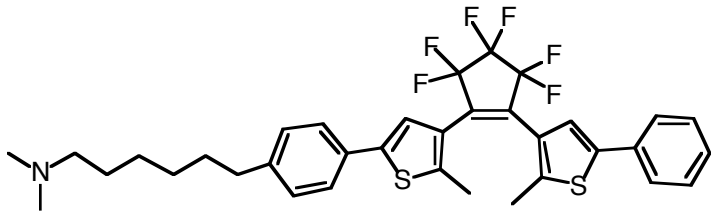
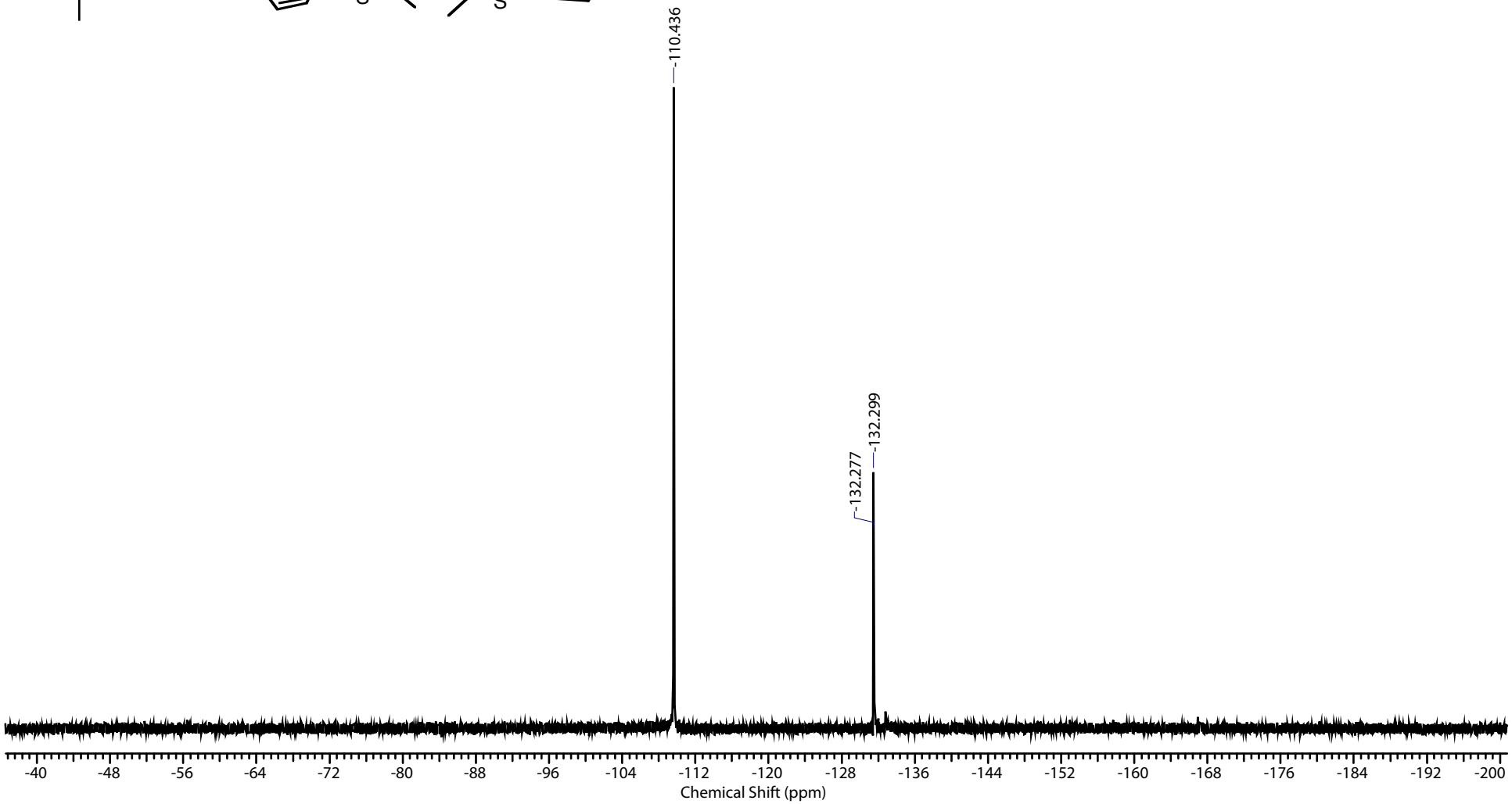




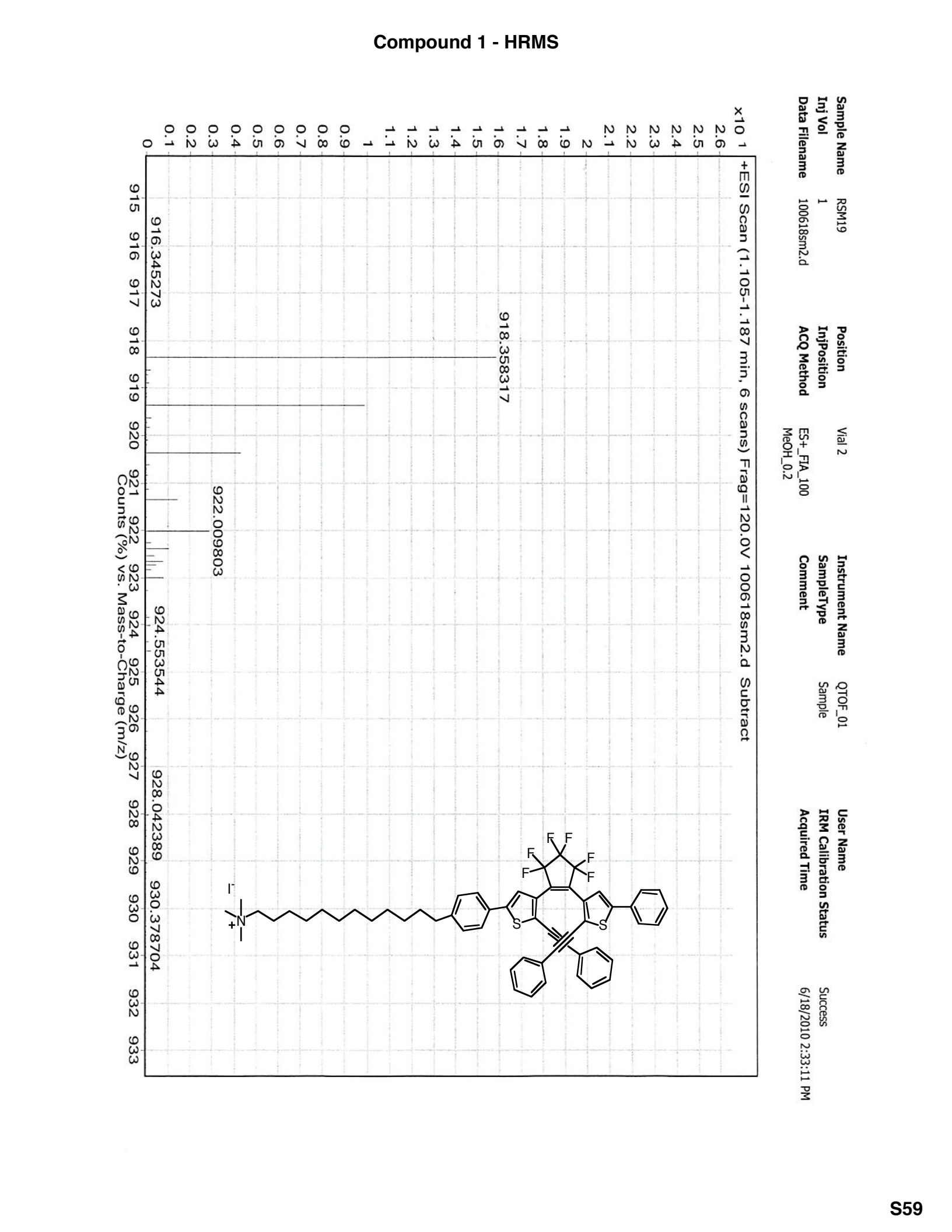
Compound 18

^{19}F NMR



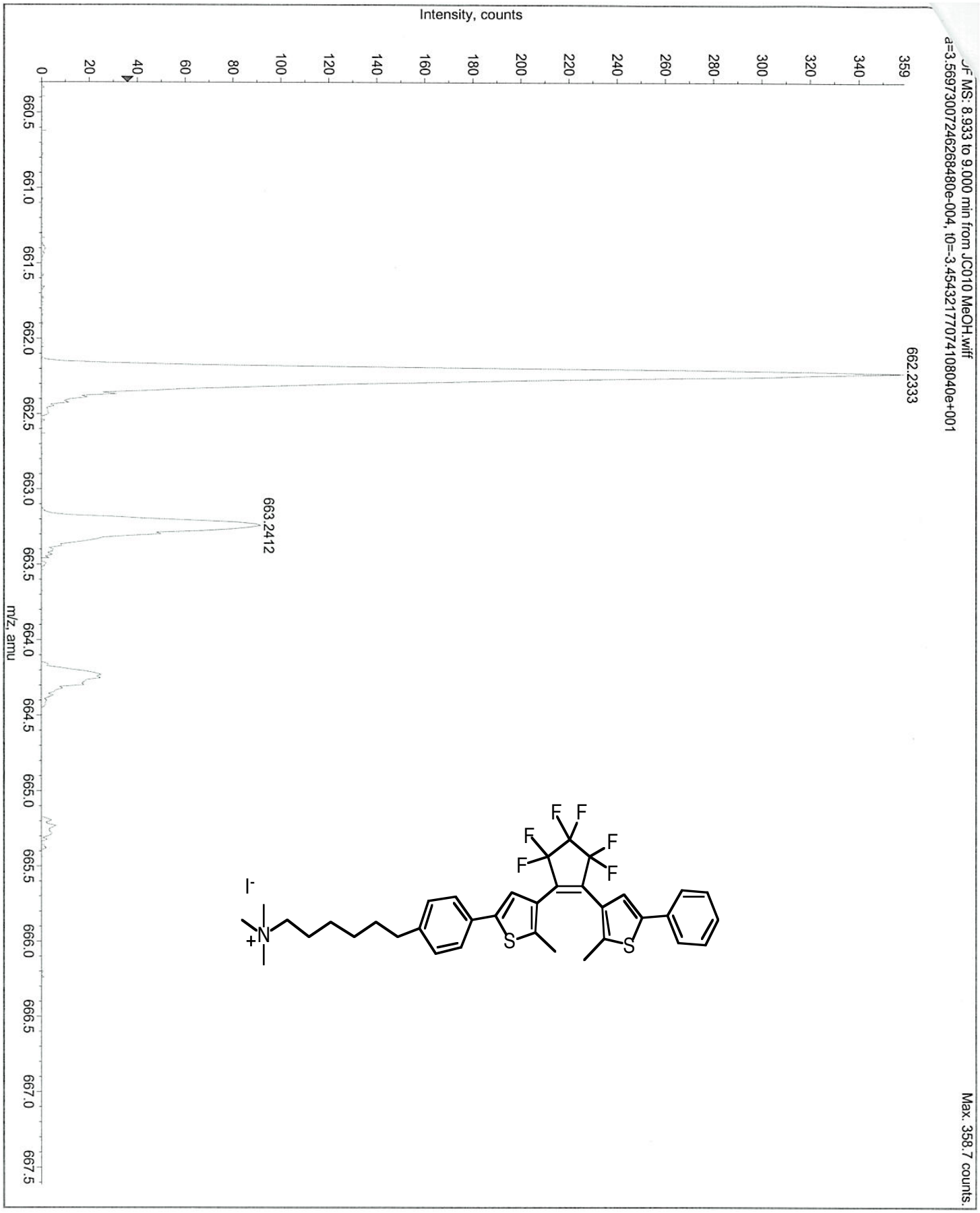


Compound 1 - HRMS



Compound 2 - HRMS

Compound 3 - HRMS



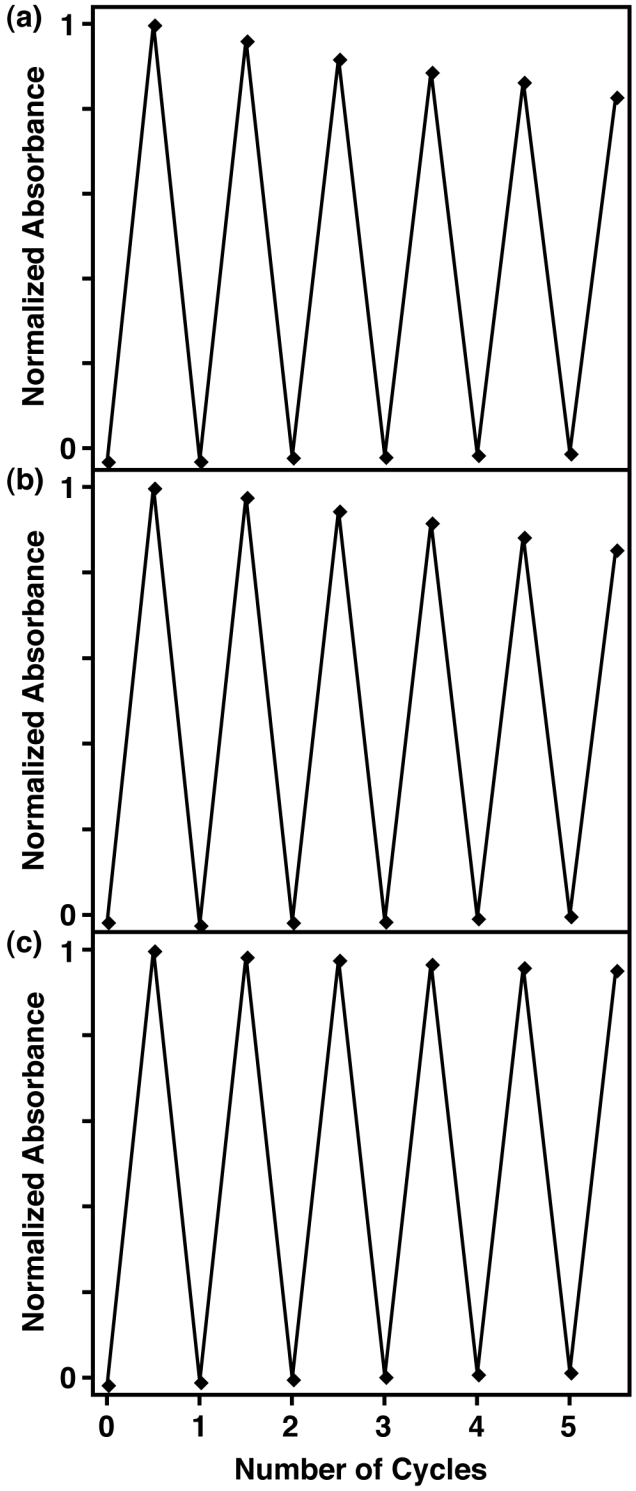


Fig. S1. Changes in the absorbance at the λ_{max} for **1c**–**3c** (a–c, respectively) in ethyl acetate, upon alternating irradiation with UV and visible light.

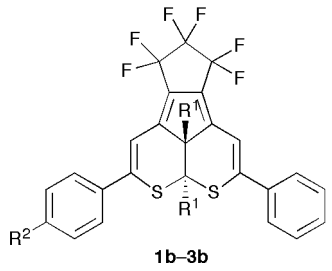


Chart S1. Structure of the dithienylethene photostable byproducts **1b**–**3b**.

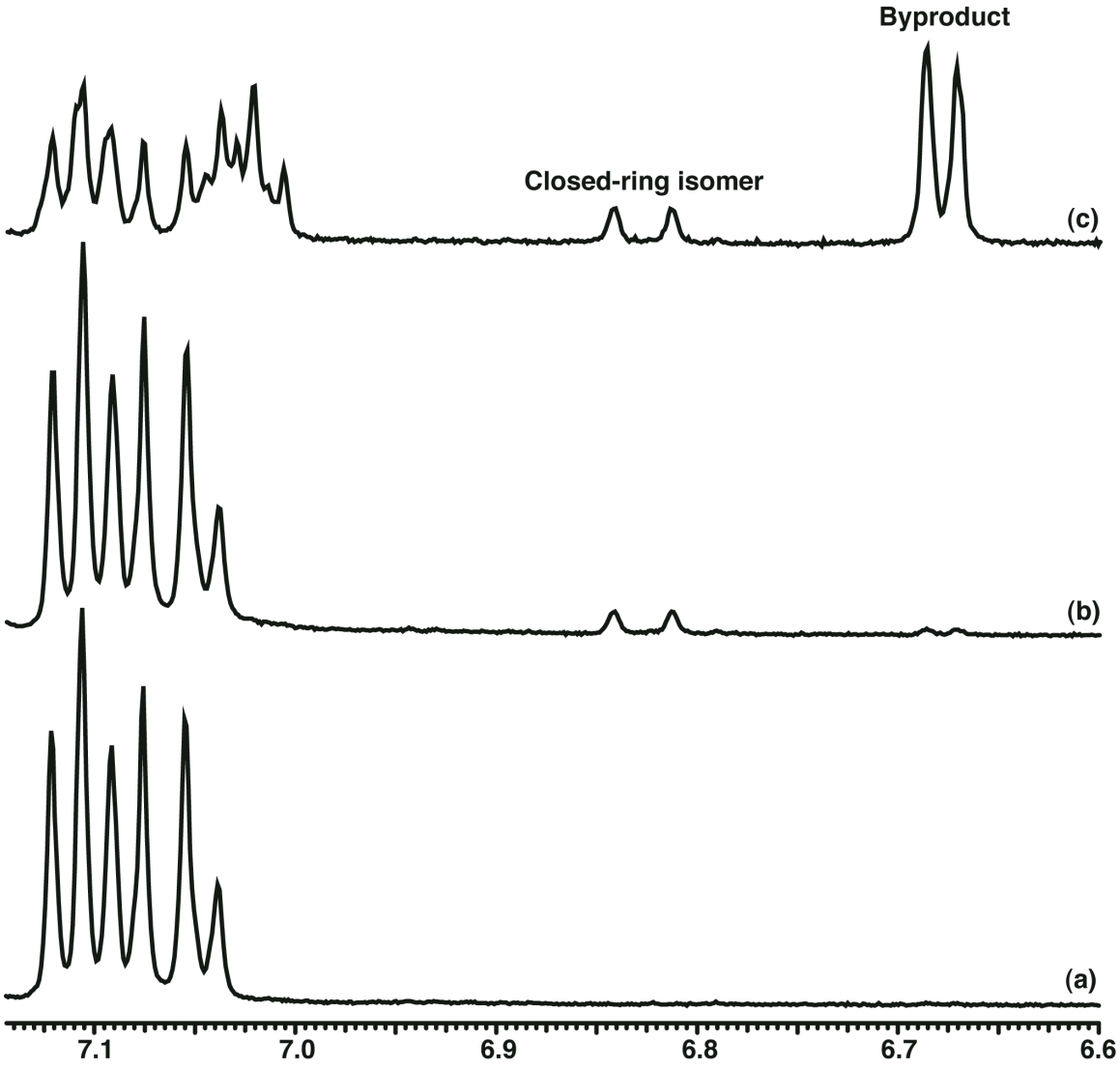


Fig. S2. ^{1}H NMR spectra of **1** from 6.60–7.14 ppm prior to UV irradiation (a) and after prolonged irradiation with UV light for 45 min (b) and 8 h (c).

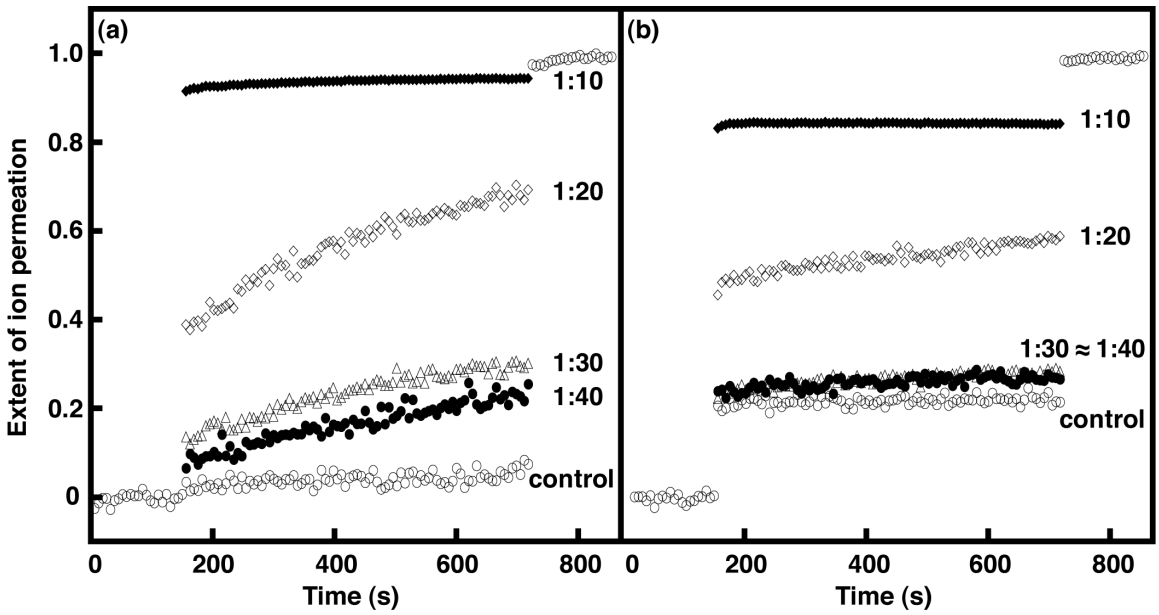


Fig. S3. Extent of ion permeation as a function of time for various mole ratios of **2** in DPPC vesicles (i.e., **2**/DPPC) prior to UV irradiation (a) and after 3 min of UV irradiation (b). For clarity only the control is shown before the base pulse and after the addition of detergent.

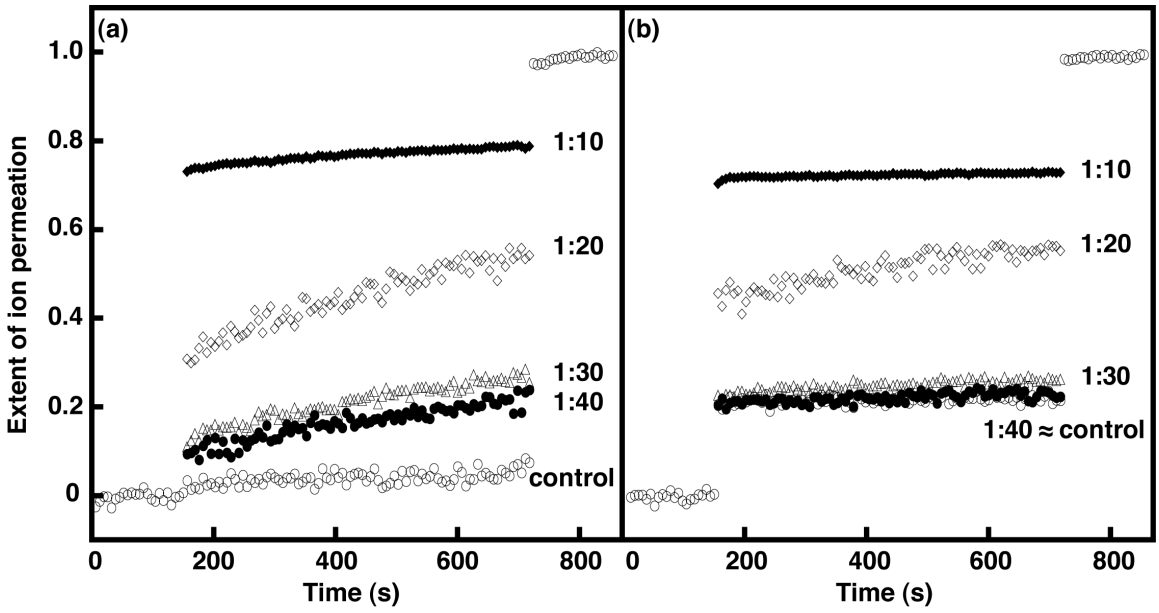


Fig. S4. Extent of ion permeation as a function of time for various mole ratios of **1** in DPPC vesicles (i.e., **1**/DPPC) prior to UV irradiation (a) and after 3 min of UV irradiation (b). For clarity only the control is shown before the base pulse and after the addition of detergent.

Table S1. Hill coefficients *n* for **1–3** in DPPC vesicles.

DTE	*n*
1o	0.9 ± 0.3
2o	1.1 ± 0.4
3o	1.4 ± 0.2
1c	1.2 ± 0.4
2c	0.9 ± 0.4
3c	2.2 ± 0.9

Table S2. Ion permeation rate constants and normalized extent of ion permeation determined for **2** in DPPC vesicles at various mole ratios[a]

2/DPPC	k (10^{-4} s^{-1})		Ratio[b]		*N*		Ratio[c]	
UV	No	Yes	No	Yes	No	Yes	No	Yes
Control	0.46 ± 0.26	0.31 ± 0.28	1	1	0.07 ± 0.06	0.22 ± 0.07	1	1
1:10	0.34± 0.06	0.04 ± 0.04	0.74	0.13	0.95 ± 0.01	0.84 ± 0.03	13.3	3.7
1:20	4.8 ± 1.0	1.6 ± 0.5	10.4	5.2	0.69 ± 0.04	0.59 ± 0.07	9.9	2.7
1:30	2.9 ± 0.5	0.61 ± 0.22	6.3	2.0	0.30 ± 0.06	0.29 ± 0.07	4.9	1.5
1:40	2.6 ± 0.5	0.55 ± 0.18	5.7	1.8	0.24 ± 0.07	0.27 ± 0.15	4.3	1.4

[a] The error is the standard deviation for the mean taken from a minimum of three independent measurements.
[b] Represents the ratio of the rate constants of ion permeation for the sample versus the control.
[c] Represents the ratio of the extents of ion permeation for the sample versus the control.

Table S3. Ion permeation rate constants and normalized extent of ion permeation determined for **1** in DPPC vesicles at various mole ratios[a]

1/DPPC	k (10^{-4} s^{-1})		Ratio[b]		*N*		Ratio[c]	
UV	No	Yes	No	Yes	No	Yes	No	Yes
Control	0.46 ± 0.26	0.31 ± 0.28	1	1	0.07 ± 0.06	0.22 ± 0.07	1	1
1:10	0.85± 0.13	0.20 ± 0.06	1.8	0.65	0.79 ± 0.03	0.73 ± 0.03	11.3	3.3
1:20	4.2 ± 1.4	2.3 ± 1.1	9.1	7.4	0.54 ± 0.08	0.56 ± 0.11	7.7	2.5
1:30	2.4 ± 0.2	0.56 ± 0.10	5.2	1.8	0.28 ± 0.05	0.27 ± 0.04	4.0	1.2
1:40	2.1 ± 0.1	0.54 ± 0.15	4.6	1.7	0.23 ± 0.02	0.23 ± 0.04	3.3	1.0

[a] The error is the standard deviation for the mean taken from a minimum of three independent measurements.
[b] Represents the ratio of the rate constants of ion permeation for the sample versus the control.
[c] Represents the ratio of the extents of ion permeation for the sample versus the control.

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