

Supporting information for
Crystal Engineering of Alkylethynyl Fluoroanthradithiophenes

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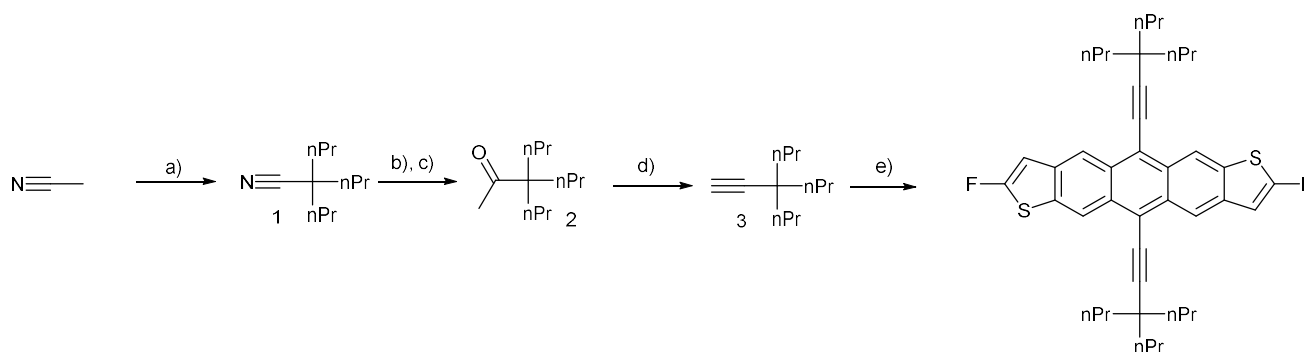
Synthetic Details

General synthetic details

Anhydrous tetrahydrofuran, lithium diisopropylamide, *n*-butyllithium, methyllithium, cyclohexanecarbonitrile, diethylchlorophosphate, cyclohexanone, trimethylsilylacetylene and diethyl sulfate were purchased from Sigma Aldrich. Acetonitrile and diethyl ether were purchased from VWR. Bromopropane and butyronitrile were purchased from Oakwood. All purchased chemicals were used without further purification. FADT quinone was synthesised as reported.¹

Proton and carbon NMR spectra were collected using a Bruker Avance NEO 400 MHz spectrometer. Chemical shifts of each spectrum are reported in ppm and referenced to deuterated chloroform solvent. High resolution mass spectra were acquired using a ThermoScientific Q-Exactive Orbitrap mass spectrometer equipped with a heated electrospray ionization source (HESI) set to 50 C. Analytes were injected by a syringe pump flowing at 5.0 μ L/min. Solutions were prepared for direct injection at analyte concentration of 10.0 μ g/mL in a 1:1 MeOH/water (v/v) solution for positive mode analysis. GC-MS analysis was performed using a Scion-SQ instrument with a Bruker BR-5HT column (15 m, 0.25 mm ID, 0.1 μ m df). A carrier gas (high purity Helium) flow rate of 1.0 mL/min was used. Column temperature was held at 45 $^{\circ}$ C for 3 minutes, then increased to 275 $^{\circ}$ C at 20 $^{\circ}$ C/min.

Synthetic Procedures



Scheme S 1. a) 3.3 eq. LiNiPr_2 , 3.3 eq $n\text{Pr-Br}$, THF, 0 $^{\circ}$ C; b) 1.6 eq. MeLi, Et_2O , 0 $^{\circ}$ C; c) sat. $\text{NH}_4\text{Cl}_{(\text{aq})}$, THF; d) 1 eq. LiNiPr_2 , THF, -78 $^{\circ}$ C, then $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$, then 2 eq. LiNiPr_2 , -78 $^{\circ}$ C; e) $n\text{BuLi}$, hexanes, 0 $^{\circ}$ C, then FADT quinone, then $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, acetone, MeOH, HCl.

2,2-di-*n*-Propyl-valeronitrile (TnPC-CN): Acetonitrile (2.0 mL, 38.2 mmol) and bromopropane (12.2 mL, 133.7 mmol) were dissolved in dry THF (120 mL) in a round bottom flask, and cooled to 0 $^{\circ}$ C. Lithium diisopropylamide (1M, 126.0 mL, 126.0 mmol) was added slowly. The reaction was stirred for 1 hour at room temperature, and then quenched with H_2O (100 mL). The product was extracted with Et_2O (100 mL) and the solvent removed in vacuo. The crude product was passed through a short silica plug with CH_2Cl_2 and distilled under reduced pressure by Kugelrohr to yield the clean product as a clear oil (6.19 g, 97 %)

^1H NMR (CDCl_3 , 400 MHz) δ 1.48-1.53 (2H, m), 1.38-1.45 (2H, m), 0.94 (3H, t, $J = 7.2$ Hz)

^{13}C NMR (CDCl_3 , 101 MHz) δ 124.3, 40.6, 38.4, 17.6, 14.2

m/z (GC-MS, ESI +ve mode) $\text{C}_{11}\text{H}_{21}\text{N}$ requires 167.17; observed 138.1 (Product minus CH_2CH_3)

3,3-di-n-Propylhexan-2-one (TnPC-COMe): TnPC Nitrile (5.0 g, 29.89 mmol) was dissolved in Et_2O (120 mL) and cooled to 0 °C. Methyllithium-lithium bromide complex solution (1.5 M in Et_2O , 29.89 mL, 44.8 mmol) was added slowly, and the mixture stirred for 5 hours at room temperature. The reaction was quenched with H_2O (100 mL), the organic layer was separated and the aqueous layer washed with Et_2O (100 mL). The crude material was redissolved in THF (100 mL) and saturated NH_4Cl (aq) solution (100 mL) was added. The reaction was stirred overnight at 50 °C. The product was then extracted with Et_2O (100 mL) and the solvent removed. The mixture was passed through a silica plug with CH_2Cl_2 to yield the crude product, and then with EtOAc to recover intermediate imine whose hydrolysis could be repeated by stirring with saturated NH_4Cl . Combined fractions of ketone product were distilled at reduced pressure by Kugelrohr to yield clean product as a clear oil (3.22 g, 58 %).

^1H NMR (CDCl_3 , 400 MHz) δ 2.07 (3H, s), 1.45-1.50 (6H, m), 1.04-1.14 (6H, m), 0.88 (9H, t, J = 7.5 Hz)

^{13}C NMR (CDCl_3 , 101 MHz) δ 214.2, 54.6, 36.2, 25.4, 17.1, 14.8

m/z (GC-MS, ESI +ve mode) $\text{C}_{12}\text{H}_{24}\text{O}$ requires 184.18; observed 142.1 (Product minus $\text{CH}_2\text{CH}_2\text{CH}_3$)

3,3-di-n-Propylhexyne (TnPC-CCH):

TnPC methyl ketone (4.0 g, 21.7 mmol) was dissolved in dry THF (40 mL) and cooled to -78 °C. Lithium diisopropylamide solution (1M, 23.9 mL, 23.9 mmol) was added and the reaction stirred at -78 °C for 1 hour. Diethyl chlorophosphate (3.52 mL, 24.3 mmol) was then added, and the reaction was allowed to warm to room temperature and stirred for 5 hours. The mixture was cooled to -78 °C, and lithium diisopropylamide solution (1M, 43.4 mL, 43.4 mmol). The mixture was allowed to slowly warm to room temperature and then stirred for 16 hours. The reaction was then quenched with H_2O (100 mL) and extracted with Et_2O (100 mL). Solvent was very carefully removed under reduced pressure due to the low boiling point of the product. The crude mixture was passed through a silica plug with hexanes to yield the alkyne product as a clear oil (2.62 g, 73 %).

^1H NMR (CDCl_3 , 400 MHz) δ 2.07 (1H, s), 1.36-1.39 (12H, m), 0.86-0.97 (15H - overlapping with hexanes, m)

^{13}C NMR (CDCl_3 , 101 MHz) δ 91.1, 69.0, 40.6, 38.3, 17.5, 14.6

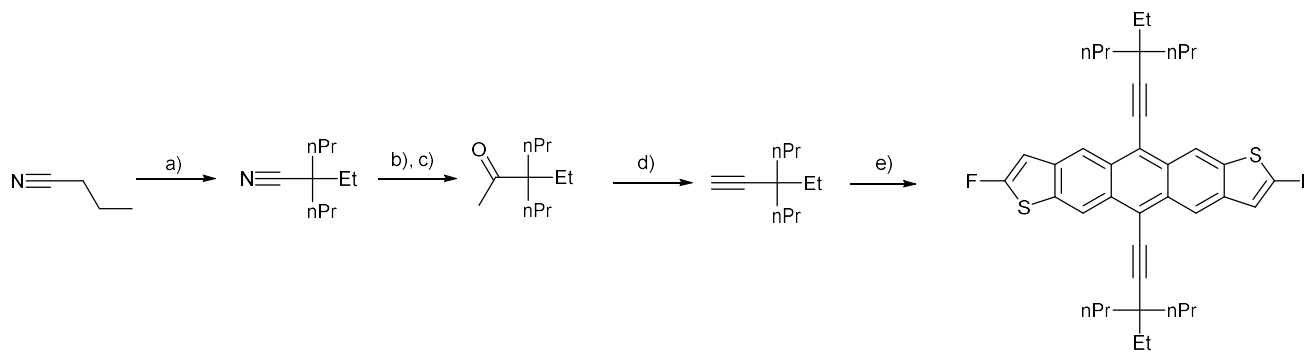
m/z (GC-MS, ESI +ve mode) $\text{C}_{12}\text{H}_{22}$ requires 166.17; observed 122.9 (Product minus $\text{CH}_2\text{CH}_2\text{CH}_3$)

5,11-bis(3,3-di-n-Propylhexynyl) fluoroanthradithiophene (TnPC-FADT): TNPC-CCH (0.35 g, 2.1 mmol) was dissolved in hexanes (25 mL) and cooled to 0 °C. n-Butyllithium (2.5M, 0.67 mL, 1.68 mmol) was added slowly, and the mixture stirred for 1 hour. FADT quinone (0.150 g, 0.42 mmol) was added in one portion and the mixture stirred at room temperature for 16 hours. The reaction was quenched by addition of saturated NH₄Cl solution (5 mL) and the mixture poured directly onto a silica plug. Excess alkyne was eluted with hexanes, and then the intermediate FADT diol was eluted with 1:1 CH₂Cl₂/acetone. After removal of the solvents, the diol was redissolved in 1:1 acetone/MeOH (100 mL). Tin(II) chloride (0.48 g, 2.1 mmol) and 10 % HCl (aq) solution (10 mL) was added, and the mixture stirred for 1 hour. The product was extracted using CH₂Cl₂ (100 mL) and then purified on silica eluting with 10:1 hexanes/CH₂Cl₂. The product was recrystallised from hexanes to yield red crystals (0.160 g, 58 %) which was a mixture of syn and anti isomers.

¹H NMR (CDCl₃, 400 MHz) δ 8.85 (2H, d, J = 1.9 Hz), 8.77 (2H, d, J = 1.9 Hz), 6.77 (2H, d, J = 2.5 Hz), 1.72-1.77 (12H, m), 1.62-1.70 (12H, m), 1.06 (18H, t, J = 6.7 Hz)

¹³C NMR (CDCl₃, 101 MHz) δ 136.1, 136.0, 133.2, 130.0, 129.8, 120.8, 120.7, 120.7, 120.4, 120.3, 117.1, 110.9, 102.7, 102.6, 79.0, 41.1, 41.1, 41.0, 40.4, 18.1, 14.8

HRMS (ESI, +ve) calculated for C₄₂H₄₈F₂S₂: 654.3166. Found: 654.3170



Scheme S 2. a) 2.2 eq. LiNiPr₂, 2.2 eq nPr-Br, THF, 0 °C; b) 1.6 eq. MeLi, Et₂O, 0 °C; c) sat. NH₄Cl(aq), THF; d) 1 eq. LiNiPr₂, THF, -78 °C, then (EtO)₂P(O)Cl, then 2 eq. LiNiPr₂, -78 °C; e) nBuLi, hexanes, 0 °C, then FADT quinone, then SnCl₂·2H₂O, acetone, MeOH, HCl.

2-Ethyl-2-n-propylvaleronitrile (EDnPC-CN): Butyronitrile (2.6 mL, 30.0 mmol) and bromopropane (6.6 mL, 72.0 mmol) were dissolved in dry THF (100 mL) in a round bottom flask, and cooled to 0 °C. Lithium diisopropylamide (1M, 66.0 mL, 66.0 mmol) was added slowly. The reaction was stirred for 1 hour at room temperature, and then quenched with H₂O (100 mL). The product was extracted with Et₂O (100 mL) and the solvent removed in vacuo. The crude product was passed through a short silica plug with CH₂Cl₂ and distilled under reduced pressure by Kugelrohr to yield the clean product as a clear oil (4.31 g, 94 %)

^1H NMR (CDCl_3 , 400 MHz) δ 1.60 (2H, q, $J = 7.4$ Hz), 1.38-1.56 (8H, m), 0.94-1.01 (9H, m)

^{13}C NMR (CDCl_3 , 101 MHz) δ 124.3, 41.1, 37.9, 29.0, 17.6, 14.2, 8.7

m/z (GC-MS, ESI +ve mode) $\text{C}_{10}\text{H}_{19}\text{N}$ requires 153.15; observed 124.1 (Product minus CH_2CH_3)

3-Ethyl-3-n-propylhexan-2-one (EDnPC-COMe): EDnPC Nitrile (6.0 g, 39.1 mmol) was dissolved in Et_2O (150 mL) and cooled to 0°C . Methyl lithium-lithium bromide complex solution (1.5 M in Et_2O , 39.1 mL, 58.65 mmol) was added slowly, and the mixture stirred for 5 hours at room temperature. The reaction was quenched with H_2O (100 mL), the organic layer was separated and the aqueous layer washed with Et_2O (100 mL). The crude material was redissolved in THF (100 mL) and saturated NH_4Cl (aq) solution (100 mL) was added. The reaction was stirred overnight at room temperature. The product was then extracted with Et_2O and the solvent removed. The mixture was passed through a silica plug with CH_2Cl_2 to yield the crude product, and then with EtOAc to recover intermediate imine whose hydrolysis could be repeated by stirring with saturated NH_4Cl . Combined fractions of ketone product were distilled at reduced pressure by Kugelrohr to yield clean product as a clear oil (3.01 g, 45 %).

^1H NMR (CDCl_3 , 400 MHz) δ 2.07 (3H, s), 1.53-1.59 (2H, m), 1.46-1.50 (4H, m), 1.04-1.14 (4H, m), 0.89 (6H, t, $J = 7.5$ Hz), 0.72 (3H, t, $J = 7.5$ Hz)

^{13}C NMR (CDCl_3 , 101 MHz) δ 214.2, 54.7, 35.8, 26.1, 25.4, 17.1, 14.8, 8.1

m/z (GC-MS, ESI +ve mode) $\text{C}_{11}\text{H}_{22}\text{O}$ requires 170.17; observed 127.1 (Product minus $\text{CH}_2\text{CH}_2\text{CH}_3$)

3-Ethyl-3-n-propylhexyne (EDnPC-CCH):

EDnPC methyl ketone (1.72 g, 10.1 mmol) was dissolved in dry THF (25 mL) and cooled to -78°C . Lithium diisopropylamide solution (1M, 11.1 mL, 11.1 mmol) was added and the reaction stirred at -78°C for 1 hour. Diethyl chlorophosphate (1.64 mL, 11.3 mmol) was then added, and the reaction was allowed to warm to room temperature and stirred for 5 hours. The mixture was cooled to -78°C , and lithium diisopropylamide solution (1M, 20.2 mL, 20.2 mmol). The mixture was allowed to slowly warm to room temperature and then stirred for 16 hours. The reaction was then quenched with H_2O (50 mL) and extracted with Et_2O (50 mL). Solvent was very carefully removed under reduced pressure due to the low boiling point of the product. The crude mixture was passed through a silica plug with hexanes to yield the alkyne product as a clear oil (0.87 g, 57 %).

^1H NMR (CDCl_3 , 400 MHz) δ 2.07 (1H, s), 1.46 (2H, q, $J = 7.4$ Hz), 1.36-1.39 (8H, m), 0.88-0.97 (18H - overlapping with hexanes, m)

^{13}C NMR (CDCl_3 , 101 MHz) δ 90.8, 69.1, 40.1, 38.6, 30.7, 17.4, 14.6, 8.6 (sample contains hexanes)

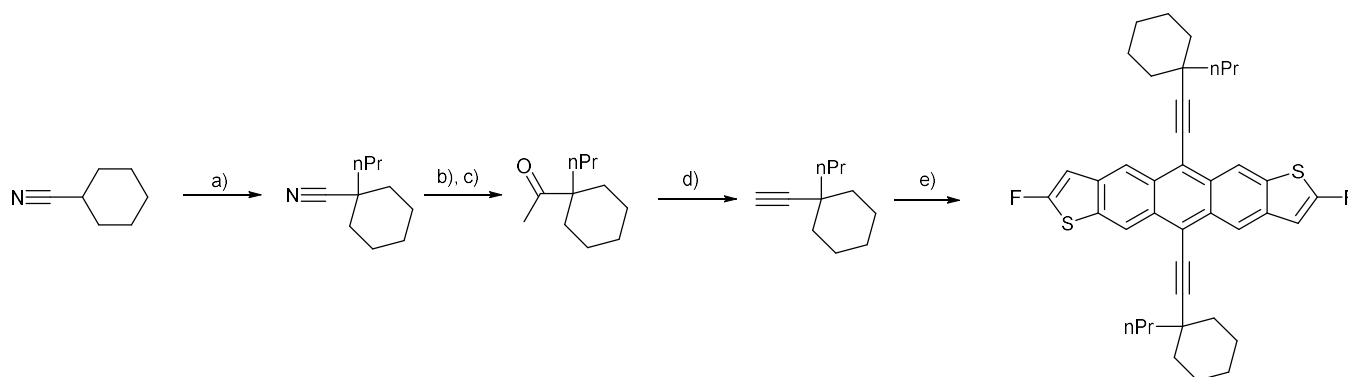
m/z (GC-MS, ESI +ve mode) $\text{C}_{12}\text{H}_{20}$ requires 152.16; observed 123.1 (Product minus CH_2CH_3)

5,11-bis(3-Ethyl-3-n-propylhexynyl) fluoroanthradithiophene (EDnPC-FADT): EDNPC alkyne (0.32 g, 2.1 mmol) was dissolved in hexanes (25 mL) and cooled to 0 °C. n-Butyllithium (2.5M, 0.67 mL, 1.68 mmol) was added slowly, and the mixture stirred for 1 hour. FADT quinone (0.15 g, 0.42 mmol) was added in one portion and the mixture stirred at room temperature for 16 hours. The reaction was quenched by addition of saturated NH₄Cl solution (5 mL) and the mixture poured directly onto a silica plug. Excess alkyne was eluted with hexanes, and then the intermediate FADT diol was eluted with 1:1 CH₂Cl₂/acetone. After removal of the solvents, the diol was redissolved in 1:1 acetone/MeOH (100 mL). Tin(II) chloride (0.47 g, 2.1 mmol) and 10 % HCl (aq) solution (10 mL) was added, and the mixture stirred for 1 hour. The product was extracted using CH₂Cl₂ (100 mL) and then purified on silica eluting with 10:1 hexanes/CH₂Cl₂. The product was recrystallised from hexanes to yield orange crystals (0.15 g, 57 %) which was a mixture of syn and anti isomers.

¹H NMR (CDCl₃, 400 MHz) δ 8.86 (2H, s), 8.78 (2H, d, J = 1.8 Hz), 6.78 (2H, d, J = 2.2 Hz), 1.81 (4H, q, J = 7.4 Hz), 1.63-1.77 (16H, m), 1.17 (6H, m), 1.06 (12H, t, J = 6.9 Hz)

¹³C NMR (CDCl₃, 101 MHz) δ 167.0, 164.0, 136.1, 133.3, 130.0, 129.8, 120.8, 120.8, 120.7, 120.4, 120.3, 117.1, 110.6, 102.7, 102.6, 79.1, 40.7, 40.6, 40.6, 40.5, 31.1, 18.1, 14.8, 9.2

HRMS (ESI, +ve) calculated for C₄₀H₄₄F₂S₂: 626.2853. Found: 626.2845.



Scheme S3. a) 1.1 eq. LiNiPr₂, 1.1 eq nPr-Br, THF, 0 °C; b) 1.6 eq. MeLi, Et₂O, 0 °C; c) sat. NH₄Cl(aq), THF; d) 1 eq. LiNiPr₂, THF, -78 °C, then (EtO)₂P(O)Cl, then 2 eq. LiNiPr₂, -78 °C; e) nBuLi, hexanes, 0 °C, then FADT quinone, then SnCl₂·2H₂O, acetone, MeOH, HCl.

1-n-Propyl-cyclohexane carbonitrile (cXPr-CN): Cyclohexane nitrile (5.94 mL, 50.0 mmol) and bromopropane (5.24 mL, 57.5 mmol) were dissolved in dry THF (120 mL) in a round bottom flask, and cooled to 0 °C. Lithium diisopropylamide (1M, 55.0 mL, 55.0 mmol) was added slowly. The reaction was stirred for 1 hour at room temperature, and then quenched with H₂O (100 mL). The product was extracted with Et₂O (100 mL) and the solvent removed in vacuo. The crude product was passed through a short silica plug with CH₂Cl₂ and distilled under reduced pressure by Kugelrohr to yield the clean product as a clear oil (7.32 g, 97 %)

¹H NMR (CDCl₃, 400 MHz) δ 1.95 (2H, d, J = 13.0 Hz), 1.44-1.75 (9H, m), 1.11-1.25 (3H, m), 0.95 (3H, t, J = 6.6 Hz)

^{13}C NMR (CDCl_3 , 101 MHz) δ 123.9, 42.8, 39.0, 35.7, 25.5, 23.1, 17.7, 14.2

m/z (GC-MS, ESI +ve mode) $\text{C}_{10}\text{H}_{17}\text{N}$ requires 151.14; observed 150.1

1-(1-n-Propylcyclohexyl)ethanone (cXPr-COMe): n-Propyl cyclohexane nitrile (7.0 g, 46.28 mmol) was dissolved in Et_2O (200 mL) and cooled to 0 °C. Methyl lithium solution (1.6 M in Et_2O , 43.4 mL, 69.4 mmol) was added slowly, and the mixture stirred for 5 hours at room temperature. The reaction was quenched with H_2O (200 mL), the organic layer was separated and the aqueous layer washed with Et_2O (200 mL). The crude material was redissolved in THF (100 mL) and saturated NH_4Cl (aq) solution (100 mL) was added. The reaction was stirred overnight at room temperature. The product was then extracted with Et_2O and the solvent removed. The mixture was passed through a silica plug with CH_2Cl_2 to yield the crude product, and then with EtOAc to recover intermediate imine whose hydrolysis could be repeated by stirring with saturated NH_4Cl . Combined fractions of ketone product were combined and distilled at reduced pressure by Kugelrohr to yield clean product as a clear oil (3.78 g, 49 %).

^1H NMR (CDCl_3 , 400 MHz) δ 2.08 (3H, s), 1.92-1.99 (2H, m), 1.41-1.57 (5H, m), 1.21-1.33 (5H, m), 1.04-1.45 (2H, m), 0.84 (3H, t, $J = 7.0$ Hz)

^{13}C NMR (CDCl_3 , 101 MHz) δ 213.8, 52.2, 41.5, 33.4, 26.1, 25.2, 23.0, 17.1, 14.7

m/z (GC-MS, ESI +ve mode) $\text{C}_{11}\text{H}_{20}\text{O}$ requires 168.15; observed 125.1 (minus $\text{CH}_2\text{CH}_2\text{CH}_3$)

1-Ethynyl-1-n-propylcyclohexane (cXPr-CCH): cXPr methyl ketone (3.5 g, 20.79 mmol) was dissolved in dry THF (60 mL) and cooled to -78 °C. Lithium diisopropylamide solution (1M, 22.9 mL, 22.9 mmol) was added and the reaction stirred at -78 °C for 1 hour. Diethyl chlorophosphate (3.37 mL, 23.3 mmol) was then added, and the reaction was allowed to warm to room temperature and stirred for 5 hours. The mixture was cooled to -78 °C, and lithium diisopropylamide solution (1M, 41.6 mL, 41.6 mmol). The mixture was allowed to slowly warm to room temperature and then stirred for 16 hours. The reaction was then quenched with H_2O (100 mL) and extracted with Et_2O (100 mL). Solvent was very carefully removed under reduced pressure due to the low boiling point of the product. The crude mixture was passed through a silica plug with hexanes to yield the alkyne product as a clear oil (1.02 g, 33 %).

^1H NMR (CDCl_3 , 400 MHz) δ 2.12 (1H, s), 1.75 (2H, d, 3.0 Hz), 1.64 (2H, d, 3.0 Hz), 1.50-1.61 (6H, m), 1.38-1.45 (2H, m), 1.24-1.29 (3H, m), 1.10-1.17 (4H, m), 0.84-0.98 (6H, m). Spectrum contains hexanes.

^{13}C NMR (CDCl_3 , 101 MHz) δ 90.2, 70.0, 45.5, 37.7, 36.5, 26.2, 23.0, 17.4, 14.6. Spectrum contains hexanes.

m/z (GC-MS, ESI +ve mode) $\text{C}_{11}\text{H}_{18}$ requires 150.14; observed 135.1 (Product minus CH_3)

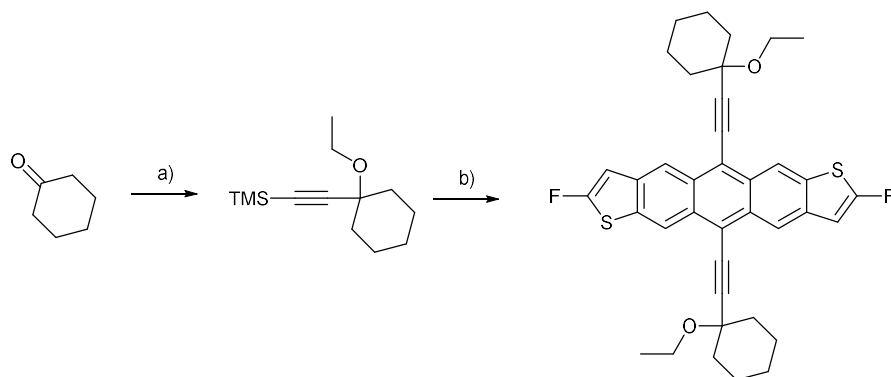
5,11-bis(n-propylcyclohexyl ethynyl) fluoroanthradithiophene (cXPr-FADT): Alkyne (0.25 g, 1.68 mmol) was dissolved in hexanes (20 mL) and cooled to 0 °C. n-Butyllithium (2.5M, 0.54 mL, 1.36 mmol) was added

slowly, and the mixture stirred for 1 hour. FADT quinone (0.12 g, 0.34 mmol) was added in one portion and the mixture stirred at room temperature for 16 hours. The reaction was quenched by addition of saturated NH₄Cl solution (5 mL) and the mixture poured directly onto a silica plug. Excess alkyne was eluted with hexanes, and then the intermediate FADT diol was eluted with 1:1 CH₂Cl₂/acetone. After removal of the solvents, the diol was redissolved in 1:1 acetone/MeOH (50 mL). Tin(II) chloride (0.38 g, 1.68 mmol) and 10 % HCl (aq) solution (5 mL) was added, and the mixture stirred for 1 hour. The product was extracted using CH₂Cl₂ (100 mL) and then purified on silica eluting with 10:1 hexanes/CH₂Cl₂. The product was recrystallised from acetone to yield orange crystals (0.075 g, 35 %) which was a mixture of syn and anti isomers.

¹H NMR (CDCl₃, 400 MHz) δ 8.89 (2H, d, J = 1.7 Hz), 8.83 (2H, d, J = 1.9 Hz), 6.78 (2H, d, J = 2.7 Hz), 2.13 (4H, d, J = 12.0 Hz), 1.89-2.00 (4H, m), 1.69-1.76 (15H, m), 1.41-1.48 (4H, m), 1.29-1.38 (2H, m), 1.08 (6H, t, J = 7.5 Hz)

¹³C NMR (CDCl₃, 101 MHz) δ 136.1, 133.3, 130.1, 129.9, 120.8, 120.5, 120.4, 117.1, 110.0, 102.7, 102.6, 79.9, 45.9, 38.6, 38.1, 38.1, 38.1, 26.4, 13.7, 18.2, 14.9

HRMS (ESI, +ve) calculated for C₄₀H₄₀F₂S₂: 622.2540 Found: 622.2534.



Scheme S4. a) Trimethylsilyl acetylene / nBuLi, THF, 0 °C, b) diethyl sulfide, c) K₂CO₃, MeOH, d) nBuLi, THF, 0 °C, then FADT quinone, then SnCl₂·2H₂O, acetone, MeOH, HCl.

1-ethoxy-1-trimethylsilylethynyl-cyclohexane: To a 100 mL round-bottom flask with stir bar that had been flame-dried and then cooled under dry nitrogen was added 24 mL anhydrous tetrahydrofuran followed by 3.6 mL (2.48 g, 25.3 mmol) of trimethylsilyl acetylene. 10 mL of a 2.5 M solution of n-butyllithium (2.5 M, 10 mL, 25.0 mmol) was then added slowly, and the mixture was allowed to stir at room temperature for 25 minutes. Cyclohexanone (2.6 mL, 25 mmol) was then added, and the mixture stirred a further 5 hours. After this time, diethyl sulfide (3.5 mL, 27 mmol) was added, and the mixture was heated at 64 °C with stirring for 4 days. At this time, GC/MS analysis showed the presence of the intermediate alcohol, so a further 1 mL of diethyl sulfide was added and the mixture stirred for an additional 3 days. The reaction mixture was cooled to room temperature, poured into water and hexanes, and the organic fraction was extracted with water three times. The organic phase was dried over magnesium sulfate, filtered, and the solvent removed. Chromatography on silica (hexanes → 8 : 1 hexanes : dichloromethane) yielded the silyl-protected acetylene (4.4 g, 80 %) as a pale yellow oil.

^1H NMR (CDCl_3 , 400 MHz) δ 3.61 (2H, q, $J = 6.8$ Hz), 1.88 (2H, broad m), 1.66 (2H, broad m), 1.53 (6H, broad m), 1.21 (3H, t, $J = 6.8$ Hz), 0.17 (9H, s).

^{13}C NMR (CDCl_3 , 101 MHz) δ 107.6, 89.7, 73.7, 58.3, 37.3, 25.5, 22.9, 15.7, 0.06.

HRMS (ESI, +ve) calculated for $\text{C}_{13}\text{H}_{24}\text{OSi}$: 224.1596. Found: 224.1599.

5,11-bis(ethoxy cyclohexyl ethynyl) 2,8-difluoro anthradithiophene: 1-ethoxy-1-trimethylsilylethynyl-cyclohexane (1.0 g, 4.45 mmol) was dissolved in 60 mL of methanol, and an excess of K_2CO_3 (3 g) was added. The stirred reaction mixture was monitored by TLC (4:1 hexanes:dichloromethane) until all starting material was consumed. The reaction mixture was poured into water, hexanes was added, and the organic layer was extracted four times with water. The organic layer was dried (MgSO_4), and filtered by passing through a thin pad of silica gel using 1:1 hexanes:dichloromethane (to remove any baseline materials). The filtrate was evaporated at low temperature (rotary evaporator bath never above 0°C) to yield a colorless oil. 0.5 grams of this oil was added to a flame-dried 100 mL round bottom flask, followed by anhydrous tetrahydrofuran (20 mL) and then a solution of LiHMDS (1 M, 3.3 mL, 3.3 mmol). After 2 hours, 2,8-difluoro-5,11-anthradithiophene quinone (0.2 g, 0.56 mmol) was added. This mixture was allowed to stir overnight, by which time all of the quinone had dissolved. Stannous chloride dihydrate (1.0 g, 4.4 mmol) was then added to the mixture, along with 10 mL of 10% aq HCl, and then 20 mL of acetone. The mixture was stirred at room temperature for 30 minutes, and was then poured into dichloromethane. The organic fraction was extracted 4x with water, dried over MgSO_4 , diluted 1:1 with hexanes, and filtered through a thin pad of silica gel. The solvent was evaporated, and the resulting deep red solid was recrystallized twice from hexanes to yield 0.15 grams (43%) of the functionalized anthradithiophene as a mixture of syn/anti isomers.

^1H NMR (CDCl_3 , 400 MHz) δ 8.87 (2H, s), 8.79 (2H, two overlapping singlets due to presence of syn/anti isomers), 6.83 (2H, two overlapping singlets due to presence of syn/anti isomers), 3.93 (4H, two overlapping quartets due to presence of syn/anti isomers), 2.37 (4H, br m), 2.26 (4H, br m), 1.83 (12H, br m), 1.37 (6H, t, $J = 7.0$ Hz).

HRMS (ESI, +ve) calculated for $\text{C}_{38}\text{H}_{36}\text{F}_2\text{O}_2\text{S}_2$: 626.2125. Found: 626.2121.

Copies of NMR spectra

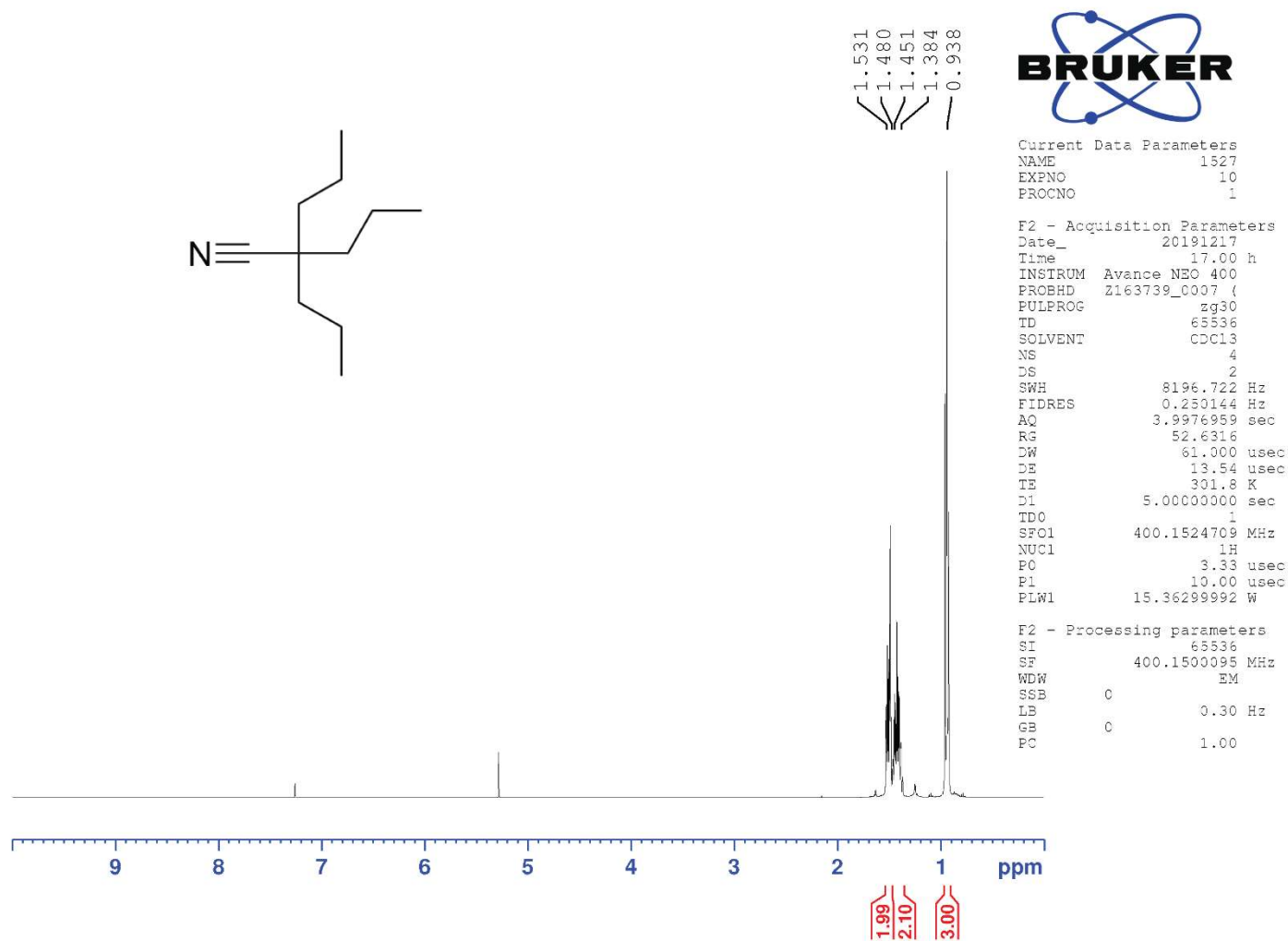


Figure S 1. 400 MHz ¹H NMR spectrum of TnPC-CN measured in CDCl₃ at 298 K.

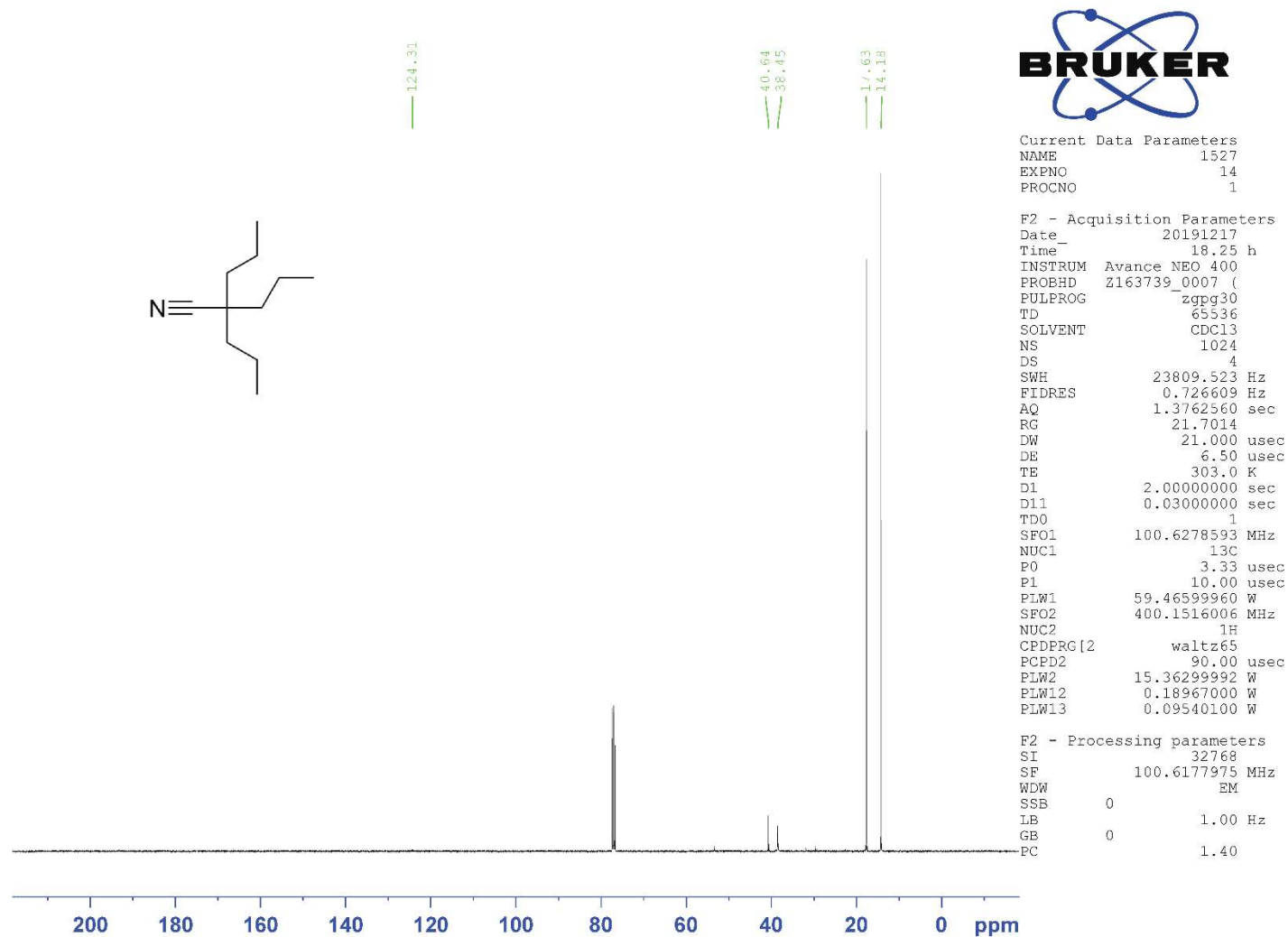


Figure S 2. 101 MHz ¹³C NMR spectrum of TnPC-CN measured in CDCl₃ at 298 K

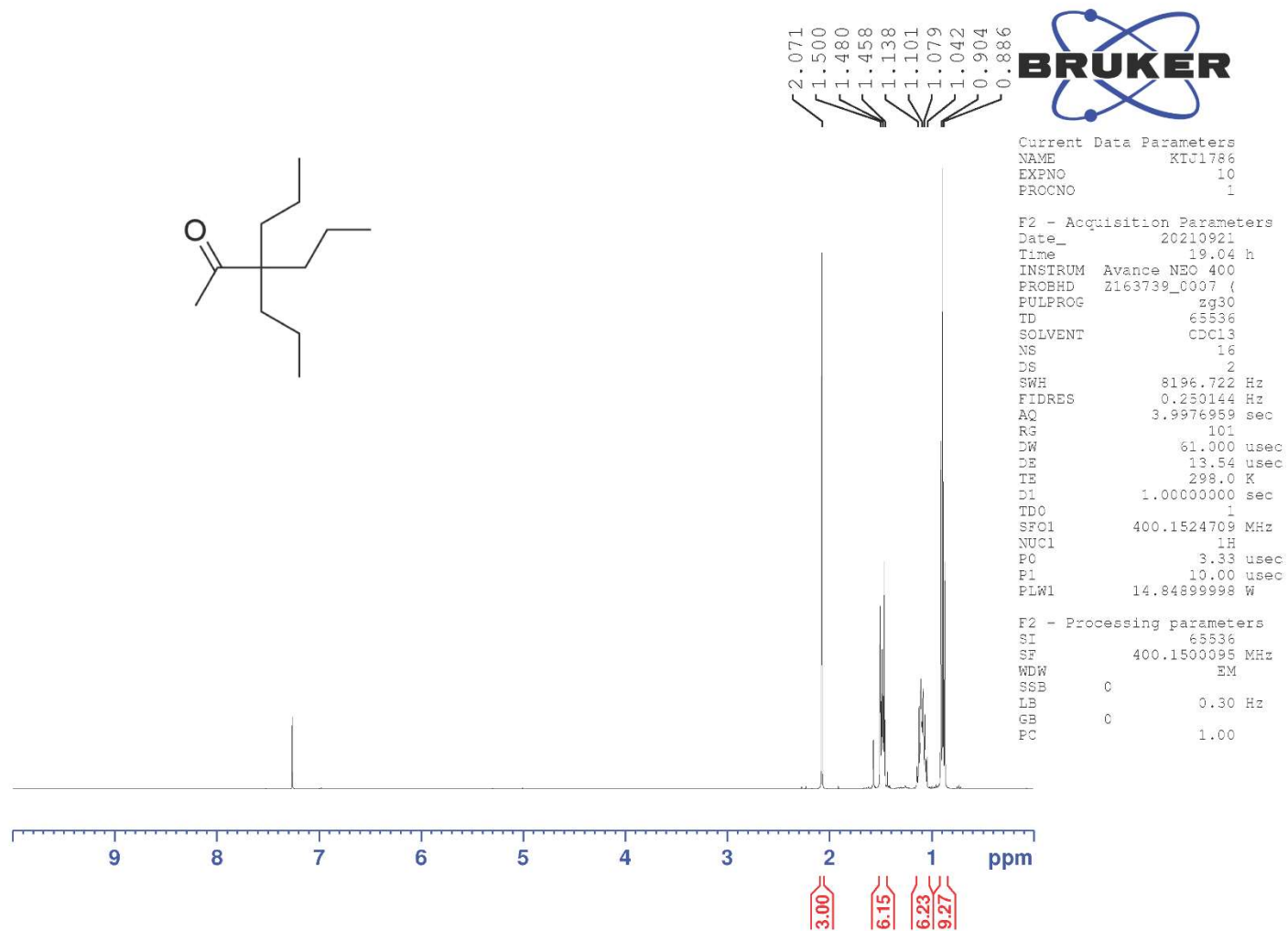
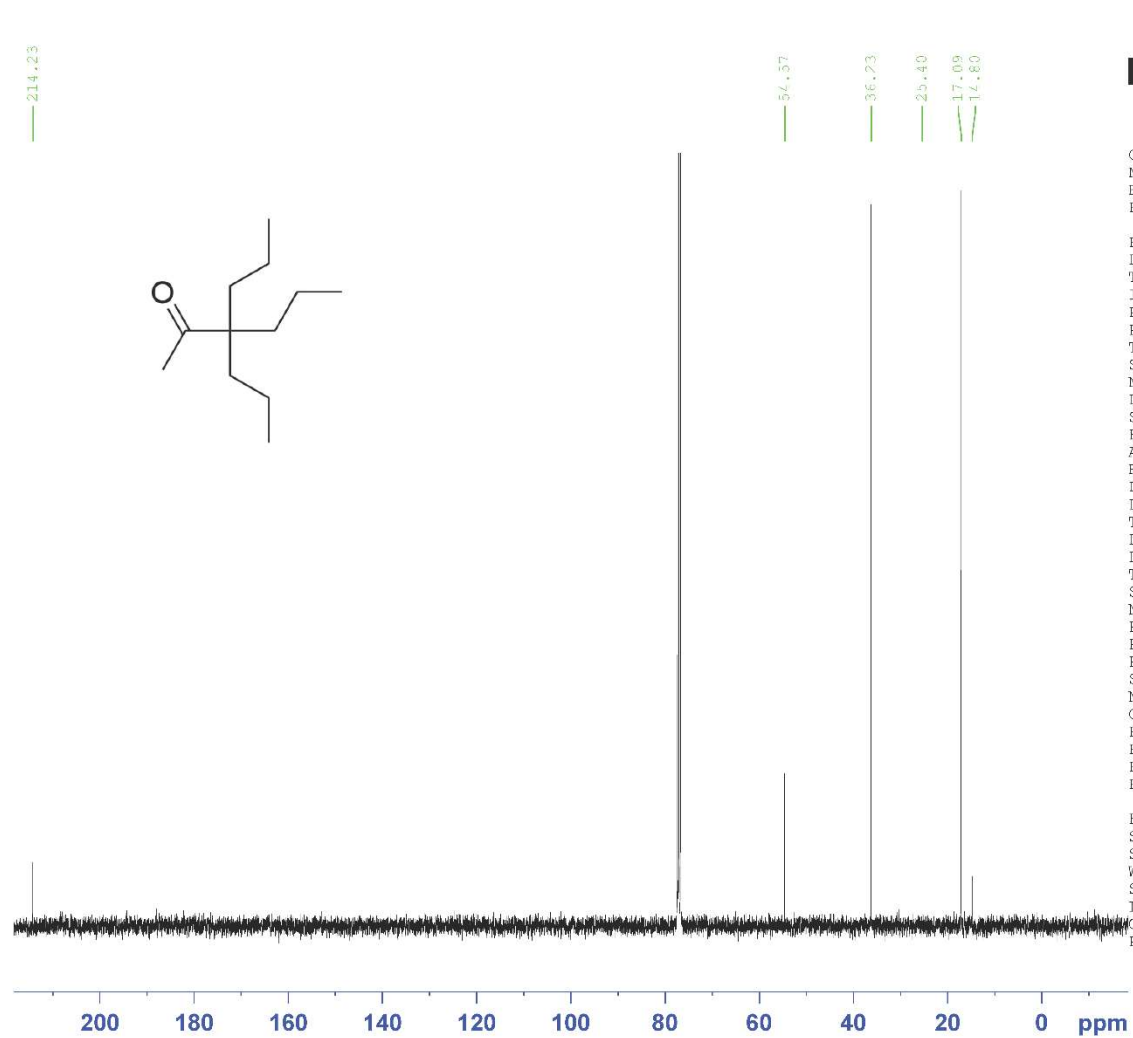


Figure S 3. 400 MHz ^1H NMR spectrum of TnPC-COMe measured in CDCl_3 at 298 K



Current Data Parameters
 NAME KTJ1786
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20210921
 Time_ 19.35 h
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 PROBHD Z163739 0007 {
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 512
 DS 4
 SWH 23809.523 Hz
 FIDRES 0.726609 Hz
 AQ 1.3762560 sec
 RG 19.9298
 DW 21.000 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1
 SFO1 100.6278593 MHz
 NUC1 13C
 P0 3.33 usec
 P1 10.00 usec
 PLW1 63.61999893 W
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG[2] waltz65
 PCPD2 90.00 usec
 PLW2 14.84899998 W
 PLW12 0.18332000 W
 PLW13 0.09221000 W

F2 - Processing parameters

SI 32768
 SF 100.6177975 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S 4. 101 MHz ¹³C NMR spectrum of TnPC-COMe measured in CDCl₃ at 298 K

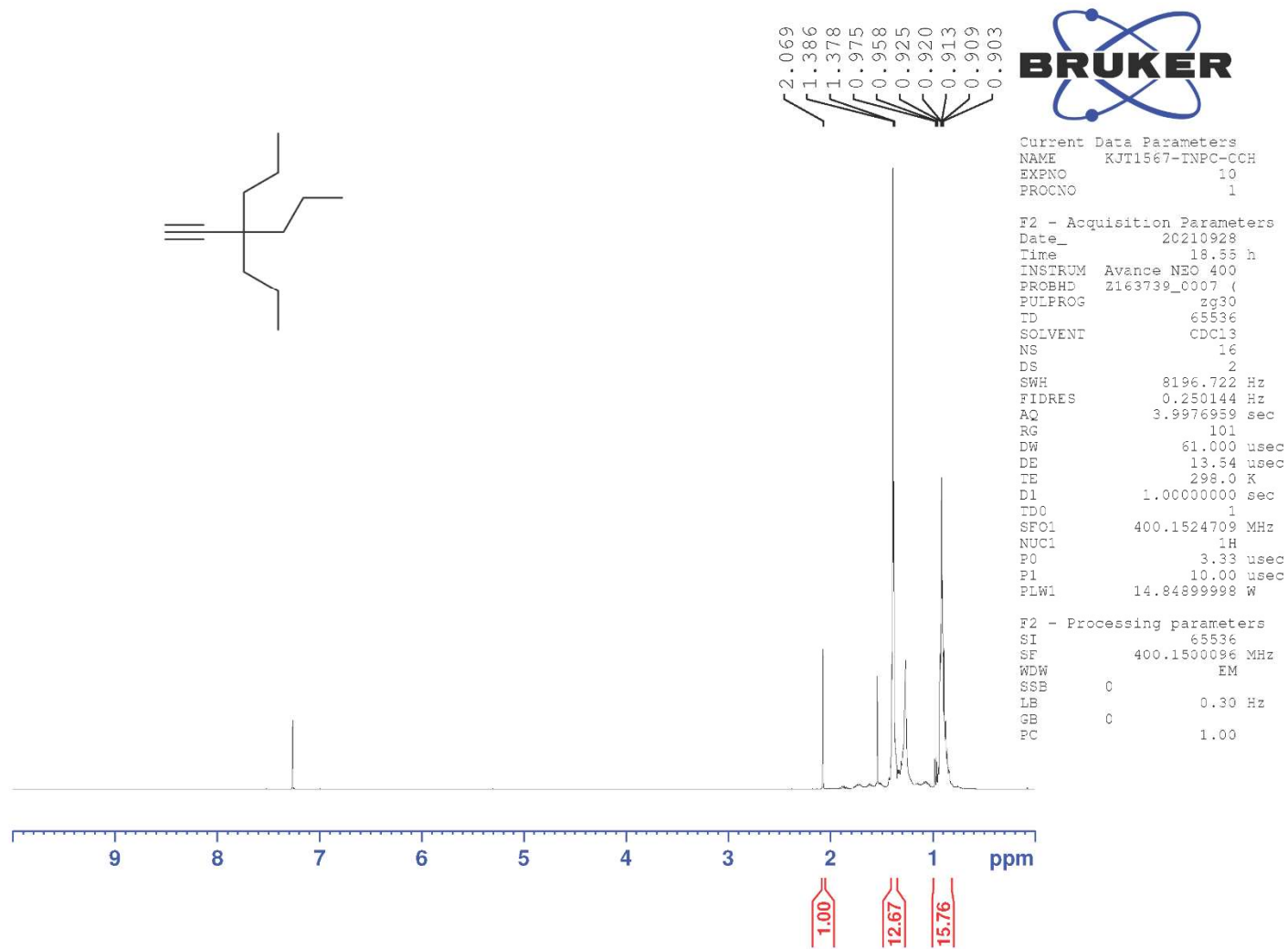


Figure S 5. 400 MHz ^1H NMR spectrum of TnPC-CCH measured in CDCl_3 at 298 K.

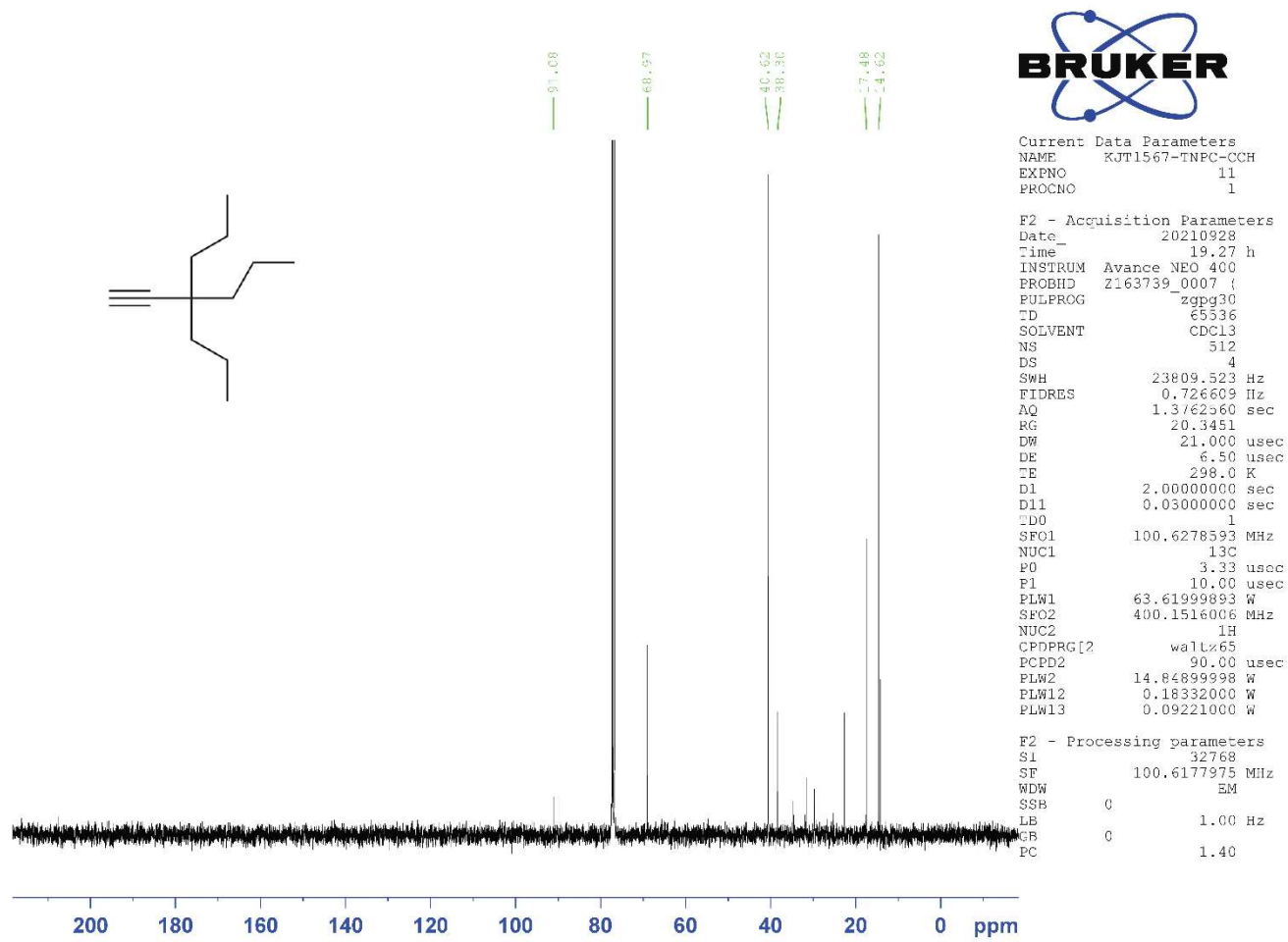


Figure S 6. 101 MHz ^{13}C NMR spectrum of TnPC-CCH measured in CDCl_3 at 298 K

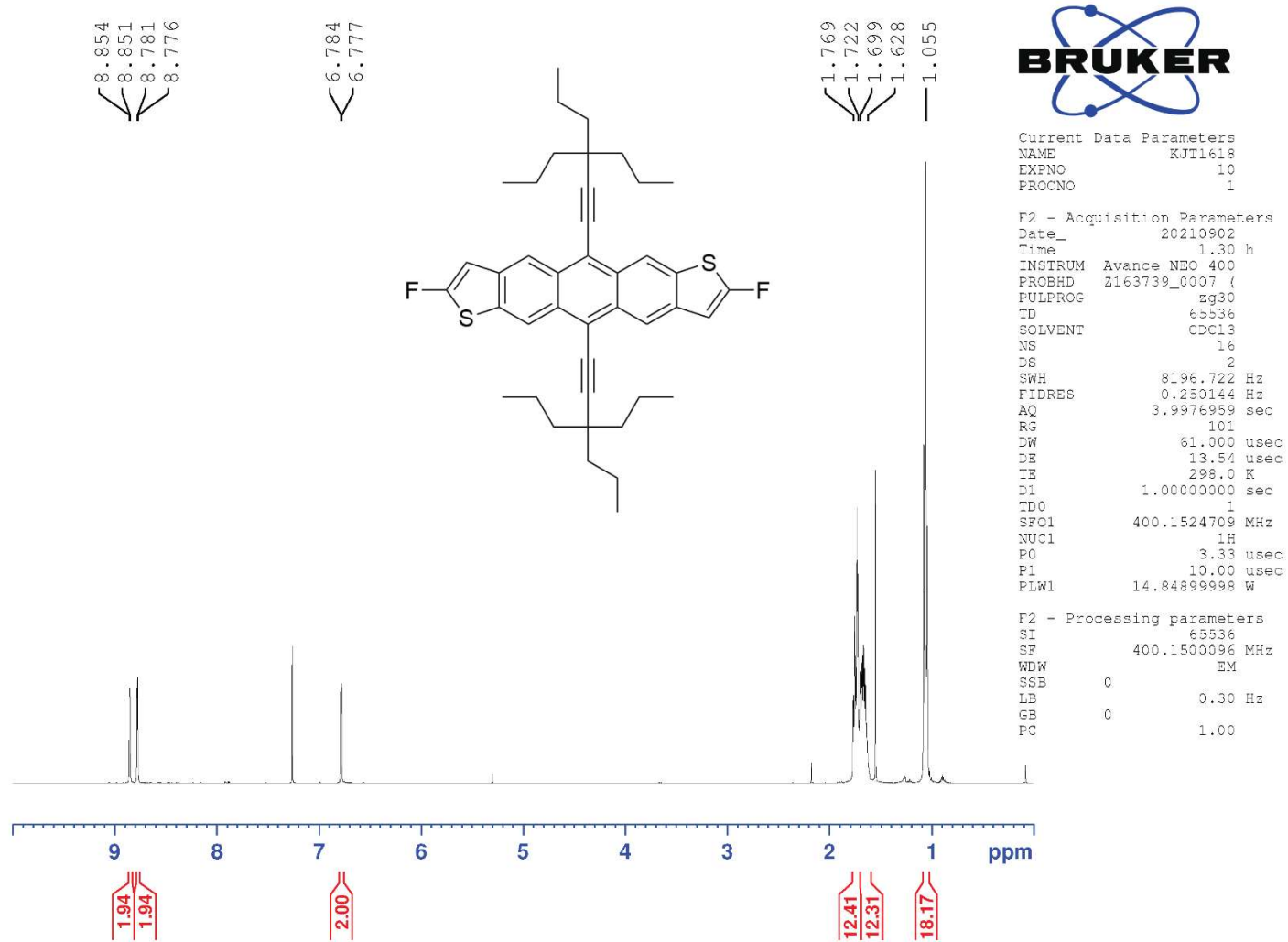


Figure S 7. 400 MHz ¹H NMR spectrum of TnPC-FADT measured in CDCl₃ at 298 K

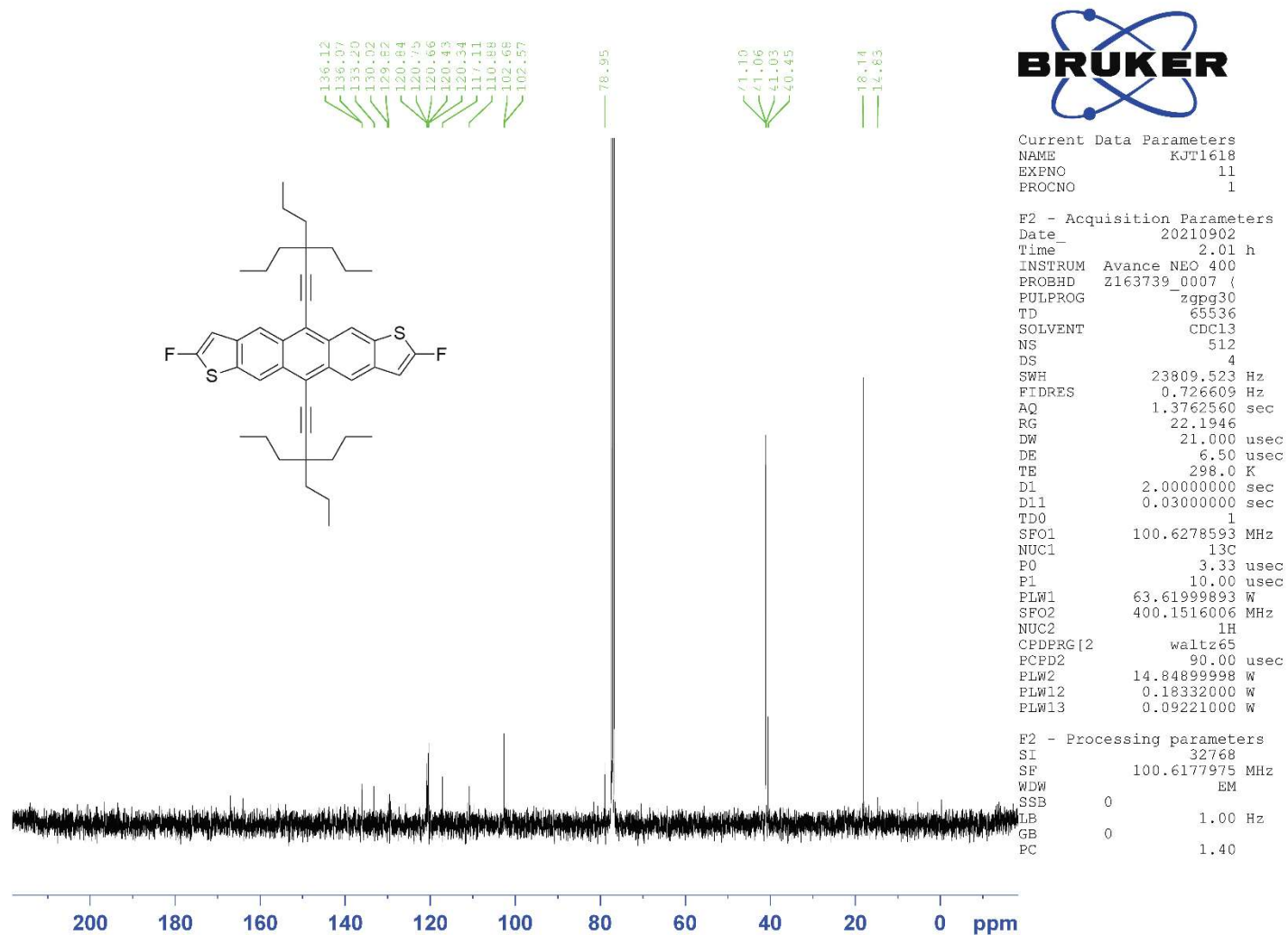


Figure S 8. 101 MHz ^{13}C NMR spectrum of TnPC-FADT measured in CDCl_3 at 298 K

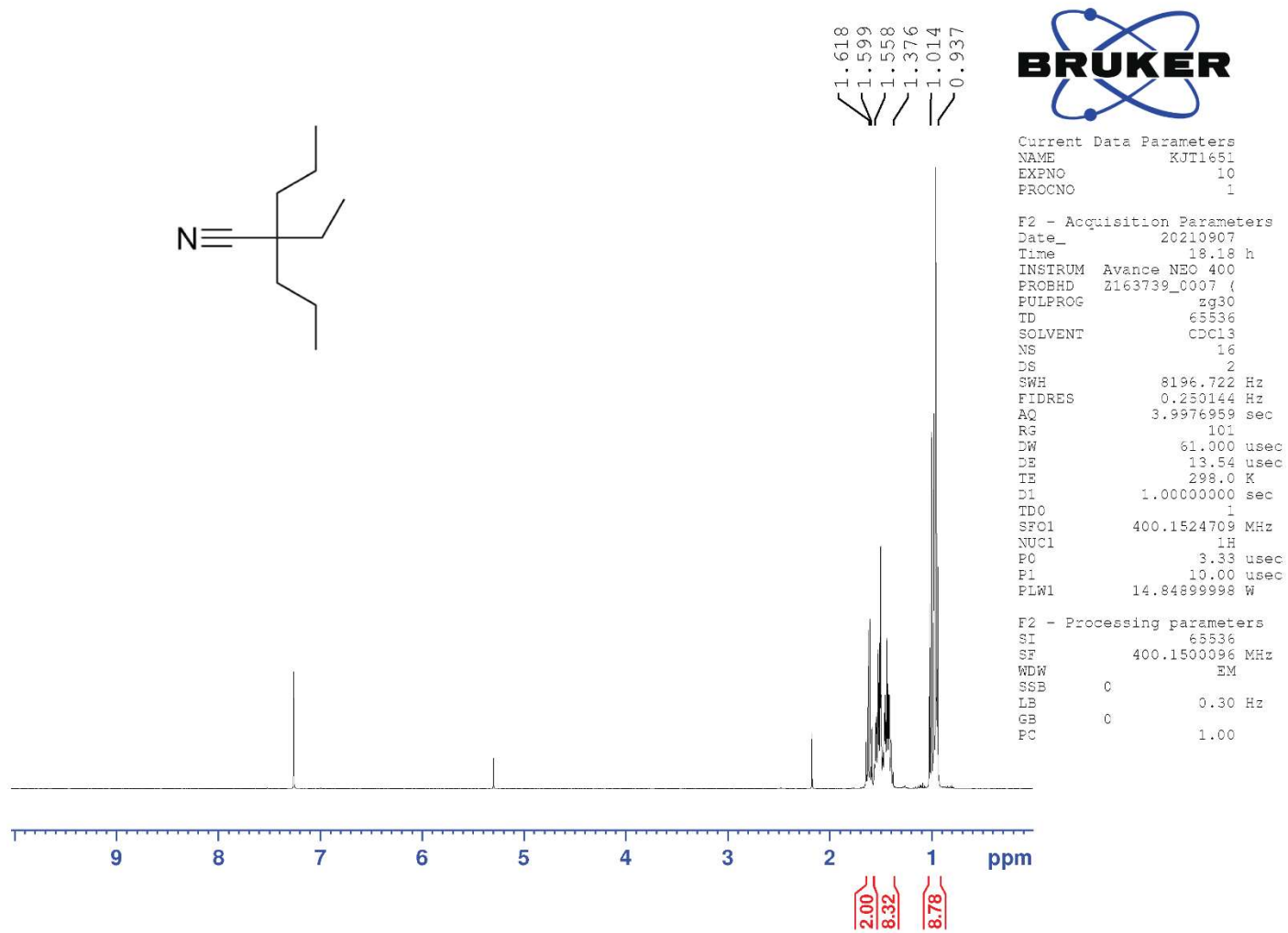


Figure S 9. 400 MHz ^1H NMR spectrum of EDnPC-CN measured in CDCl_3 at 298 K

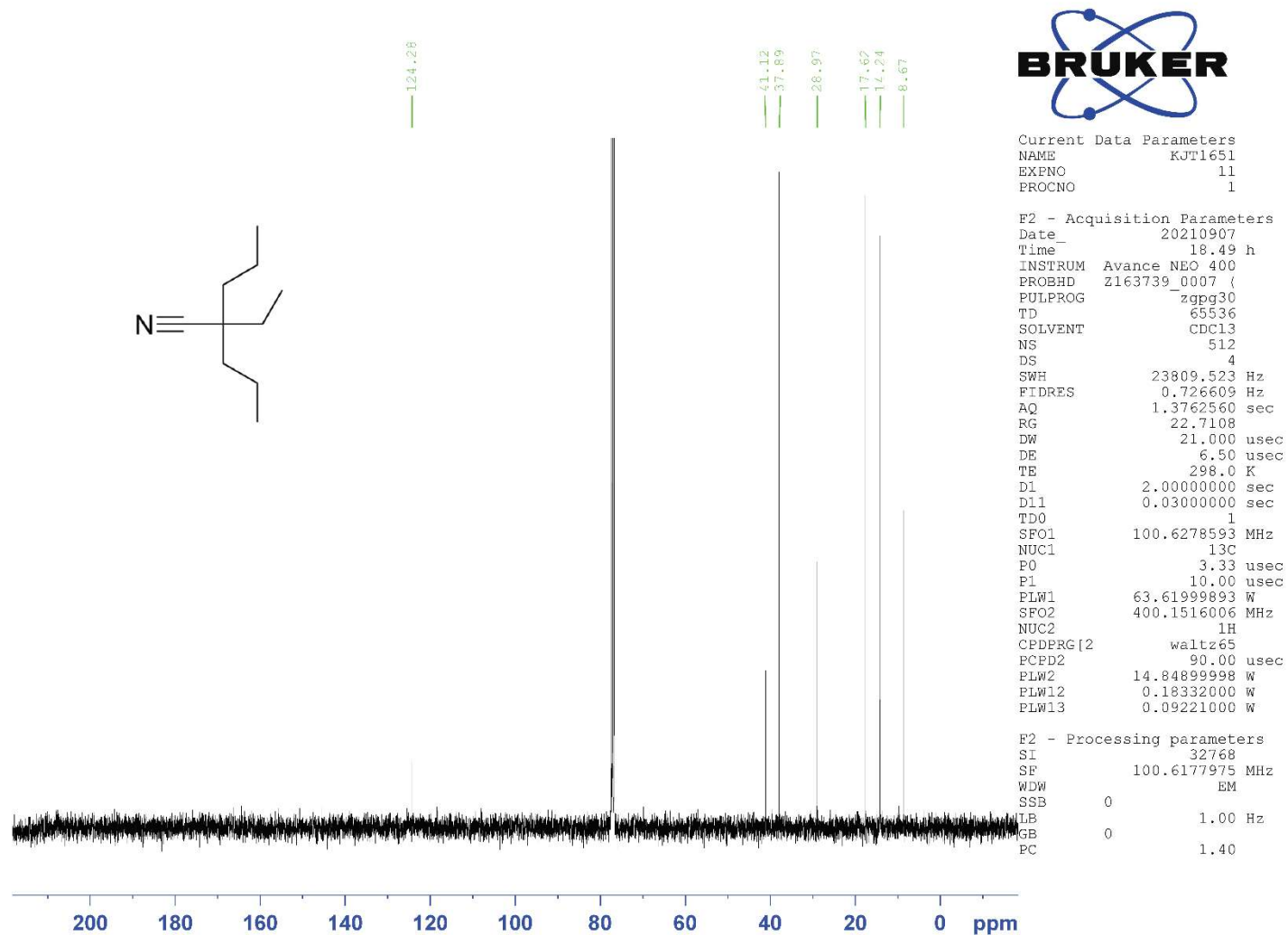


Figure S 10. 101 MHz ^{13}C NMR spectrum of EDnPC-CN measured in CDCl_3 at 298 K

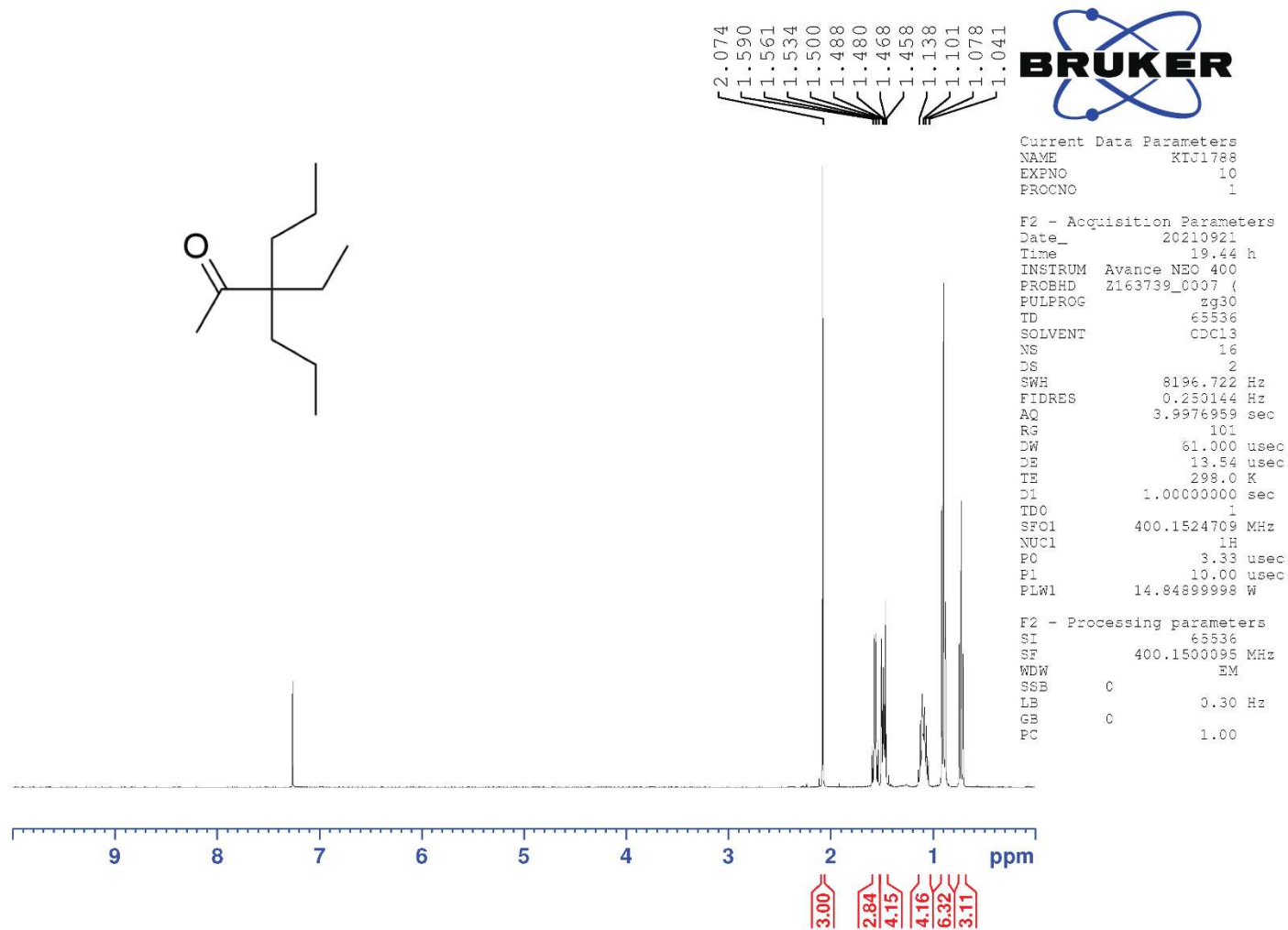
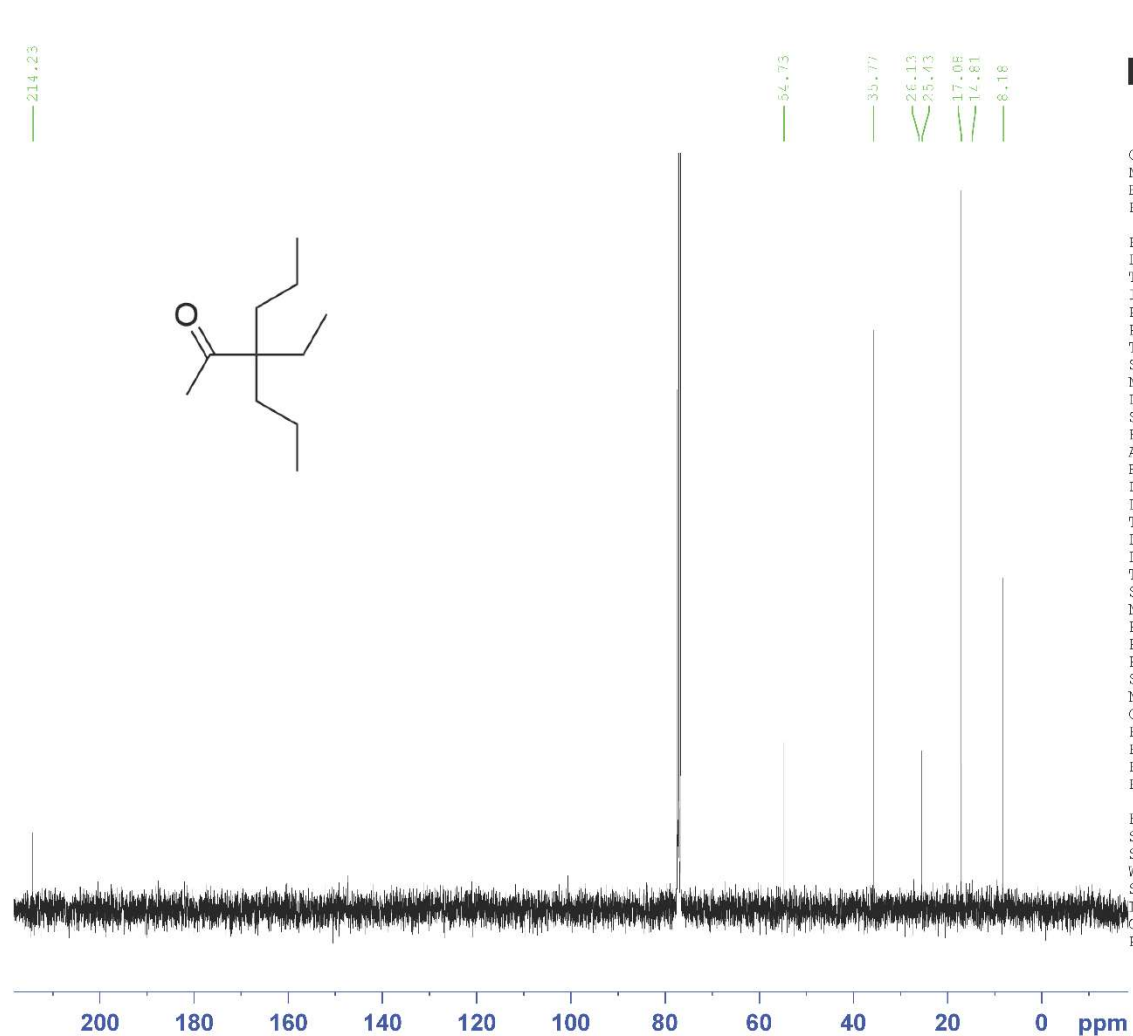


Figure S 11. 400 MHz ^1H NMR spectrum of EDnPC-COMe measured in CDCl_3 at 298 K



Current Data Parameters
 NAME KTJ1788
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20210921
 Time_ 20.15 h
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 PROBHD Z163739 0007 {
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 512
 DS 4
 SWH 23809.523 Hz
 FIDRES 0.726609 Hz
 AQ 1.3762560 sec
 RG 20.3451
 DW 21.000 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1
 SFO1 100.6278593 MHz
 NUC1 13C
 P0 3.33 usec
 P1 10.00 usec
 PLW1 63.61999893 W
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG[2] waltz65
 PCPD2 90.00 usec
 PLW2 14.84899998 W
 PLW12 0.18332000 W
 PLW13 0.09221000 W

F2 - Processing parameters
 SI 32768
 SF 100.6177975 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S 12. 101 MHz ¹³C NMR spectrum of EDnPC-COMe measured in CDCl₃ at 298 K

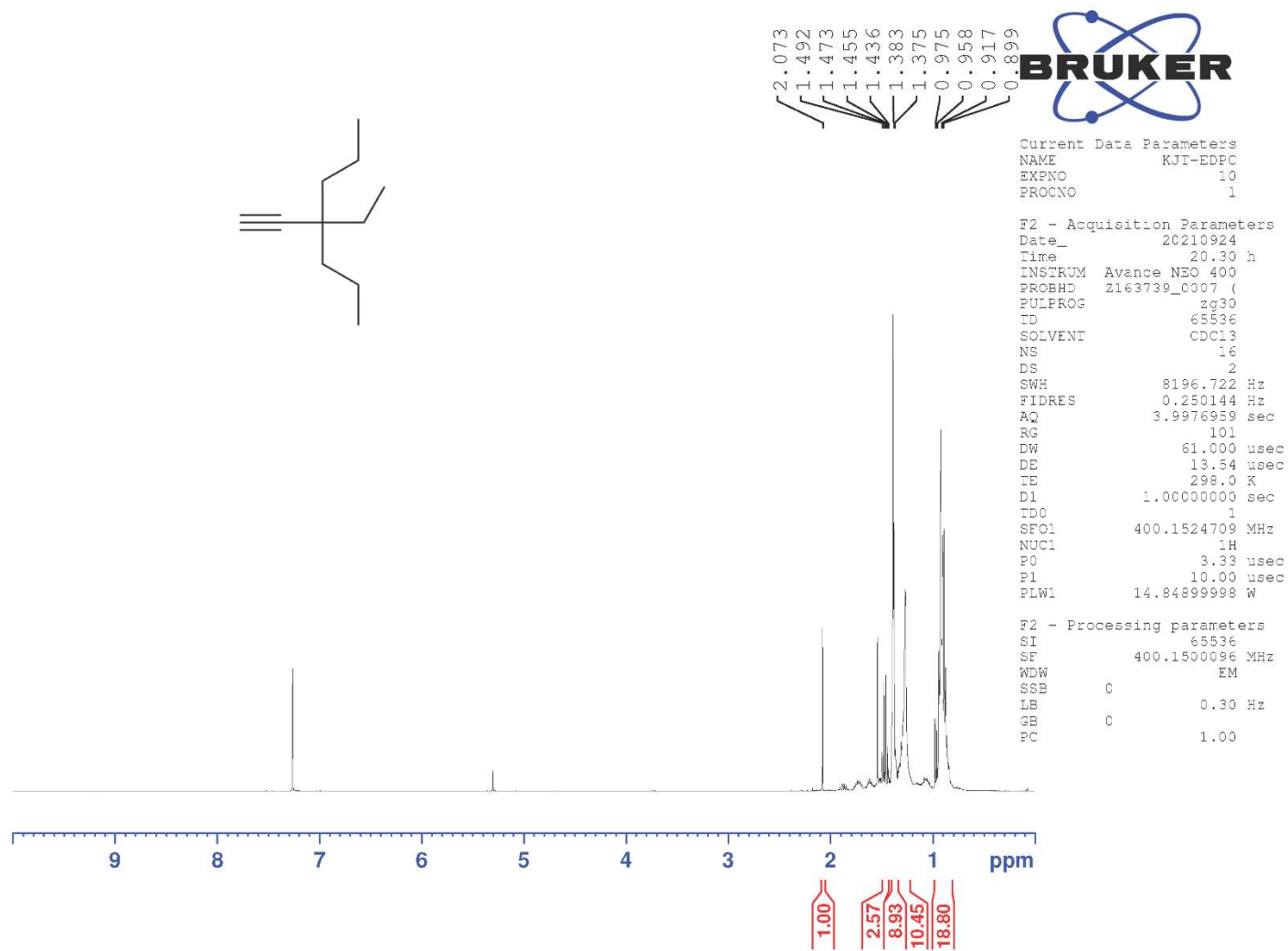


Figure S 13. 400 MHz ^1H NMR spectrum of EDnPC-CCH measured in CDCl_3 at 298 K

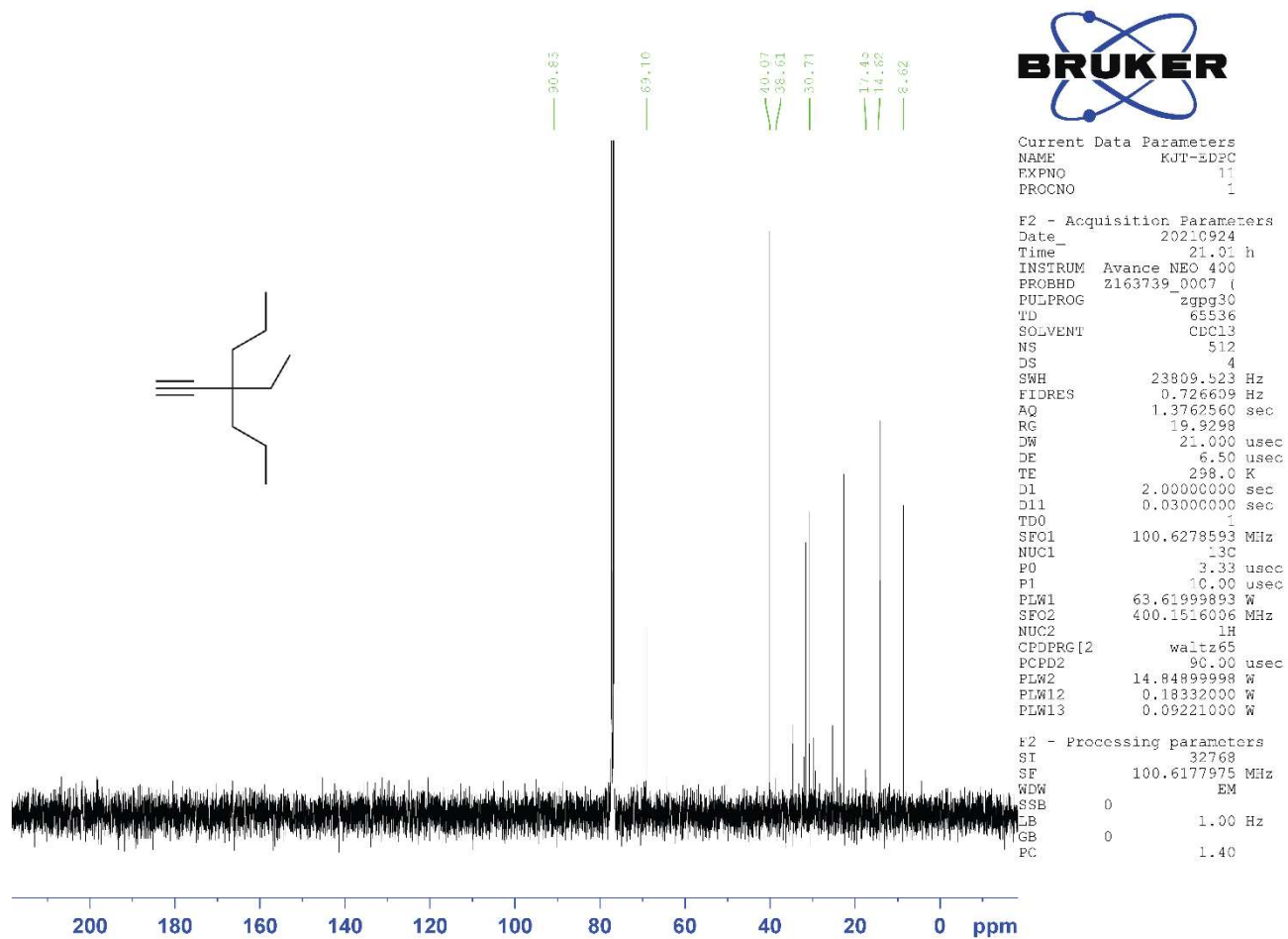


Figure S 14. 101 MHz ^{13}C NMR spectrum of EDnPC-CCH measured in CDCl_3 at 298 K

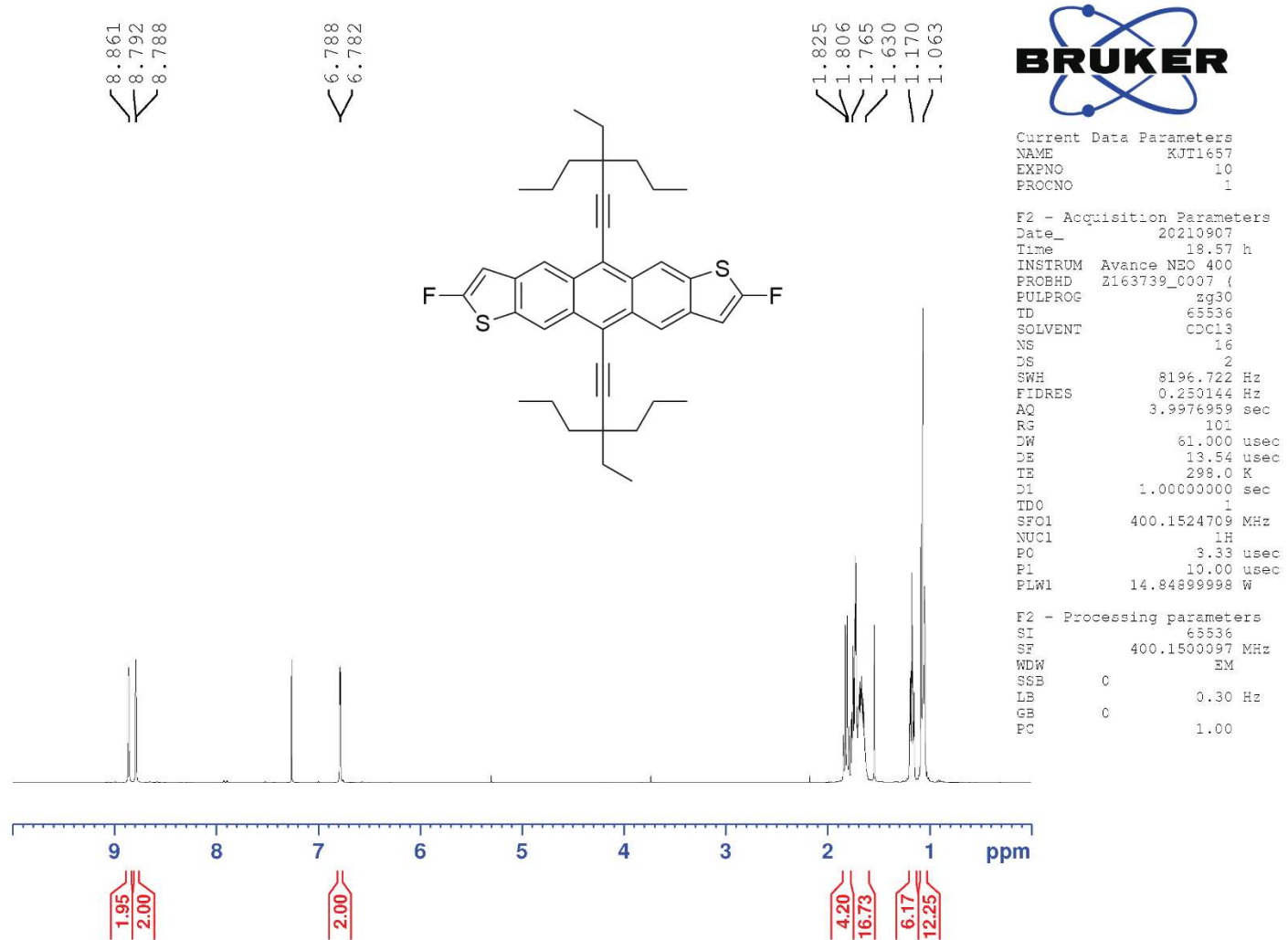


Figure S 15. 400 MHz ^1H NMR spectrum of EDnPC-FADT measured in CDCl_3 at 298 K

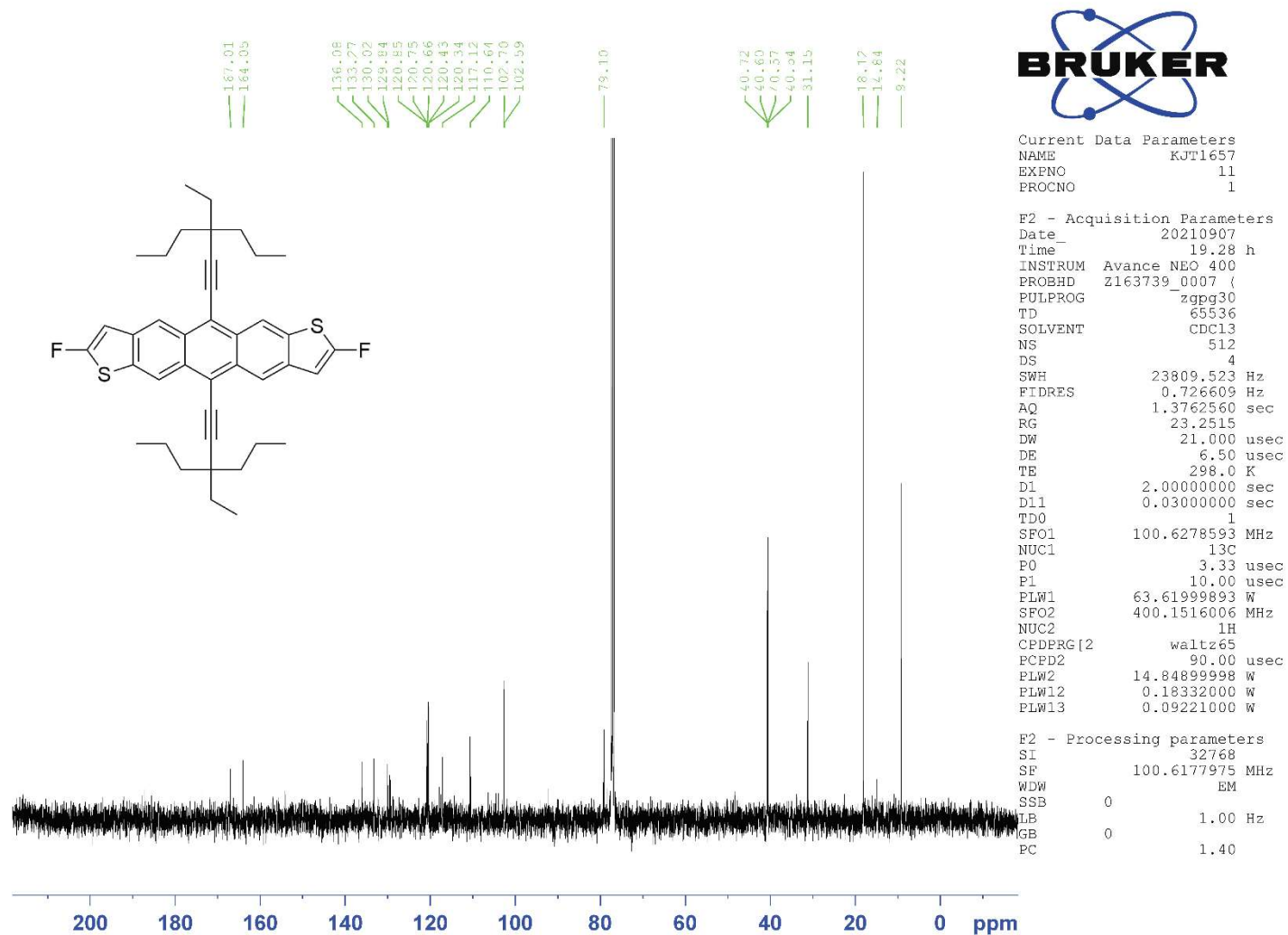


Figure S 16. 101 MHz ^{13}C NMR spectrum of EDnPC-FADT measured in CDCl_3 at 298 K

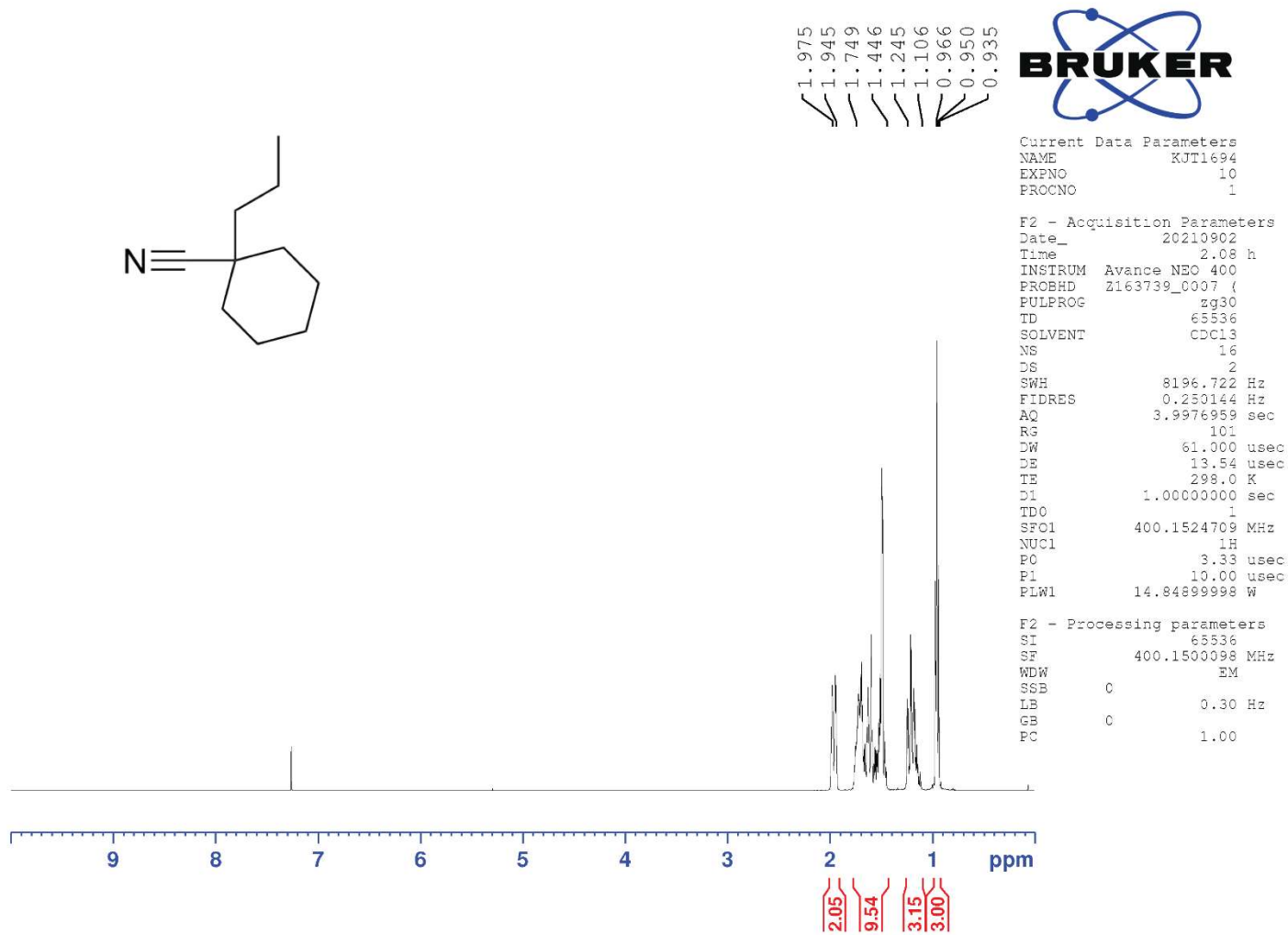
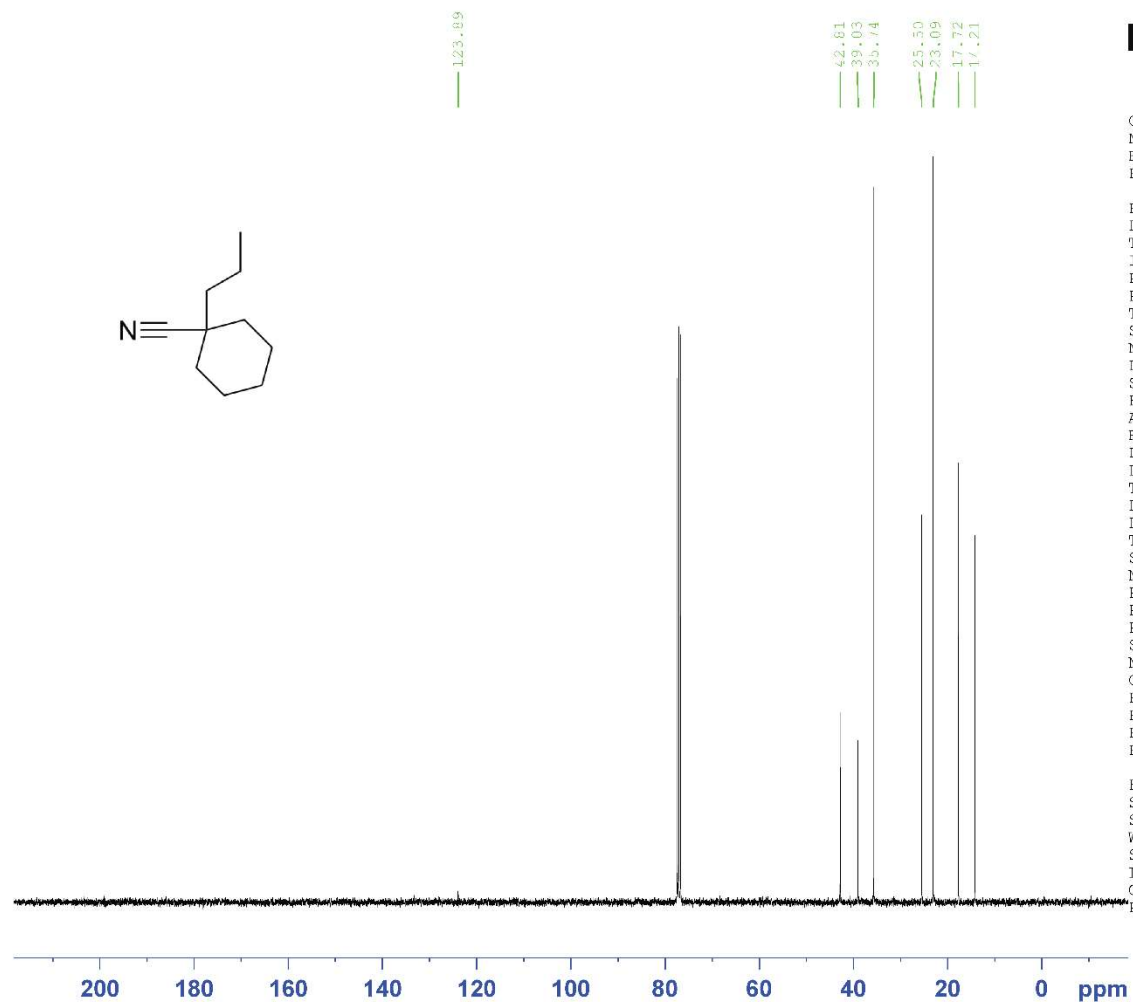


Figure S 17. 400 MHz ^1H NMR spectrum of cXPr-CN measured in CDCl_3 at 298 K



Current Data Parameters
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 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters

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 Time_ 2.40 h
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 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 512
 DS 4
 SWH 23809.523 Hz
 FIDRES 0.726609 Hz
 AQ 1.3762560 sec
 RG 22.1946
 DW 21.000 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SFO1 100.6278593 MHz
 NUC1 13C
 P0 3.33 usec
 P1 10.00 usec
 PLW1 63.61999893 W
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG[2] waltz65
 PCPD2 90.00 usec
 PLW2 14.84899998 W
 PLW12 0.18332000 W
 PLW13 0.09221000 W

F2 - Processing parameters

SI 32768
 SF 100.6177975 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S 18. 101 MHz ^{13}C NMR spectrum of cXPr-CN measured in CDCl_3 at 298 K

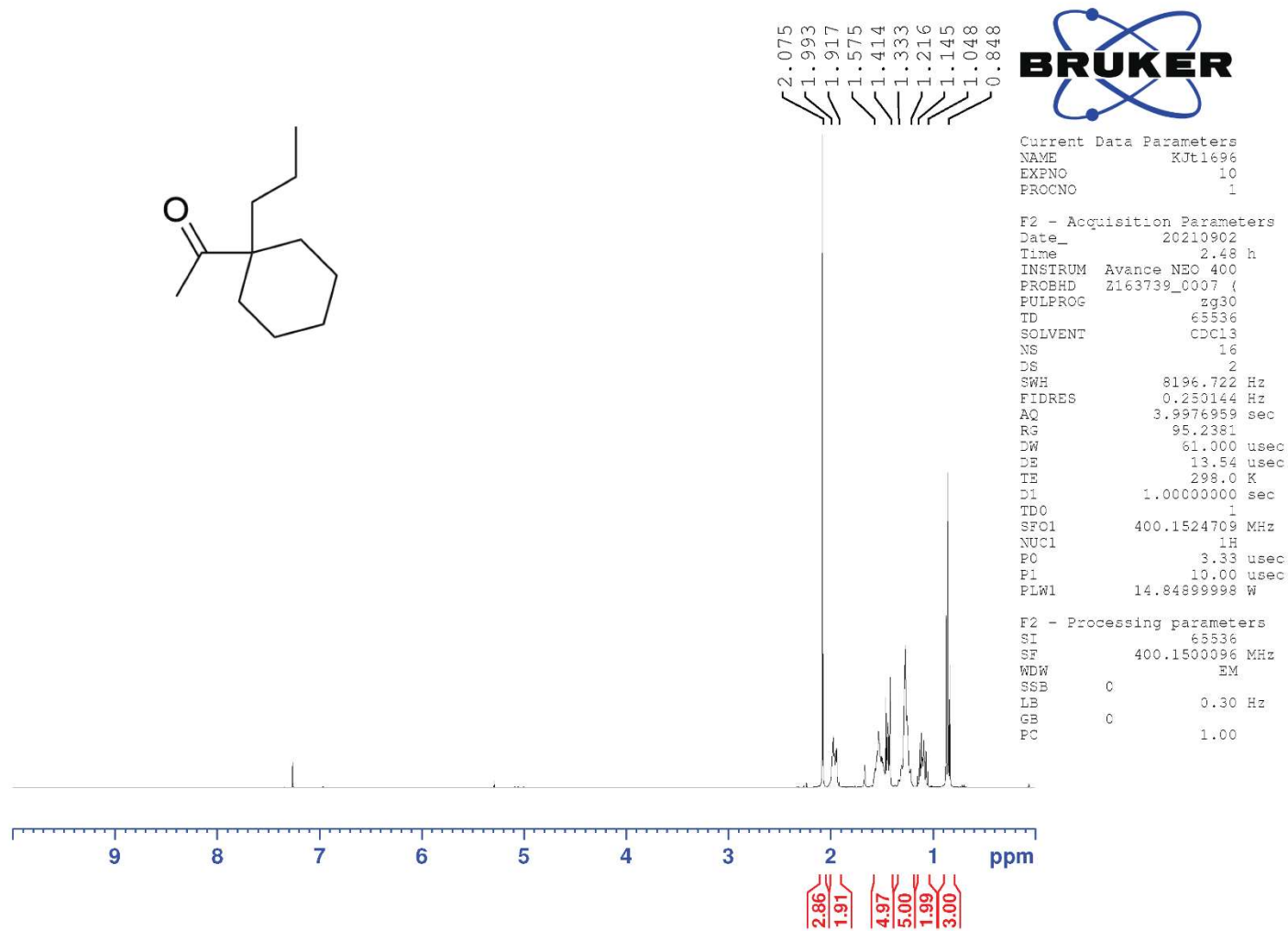
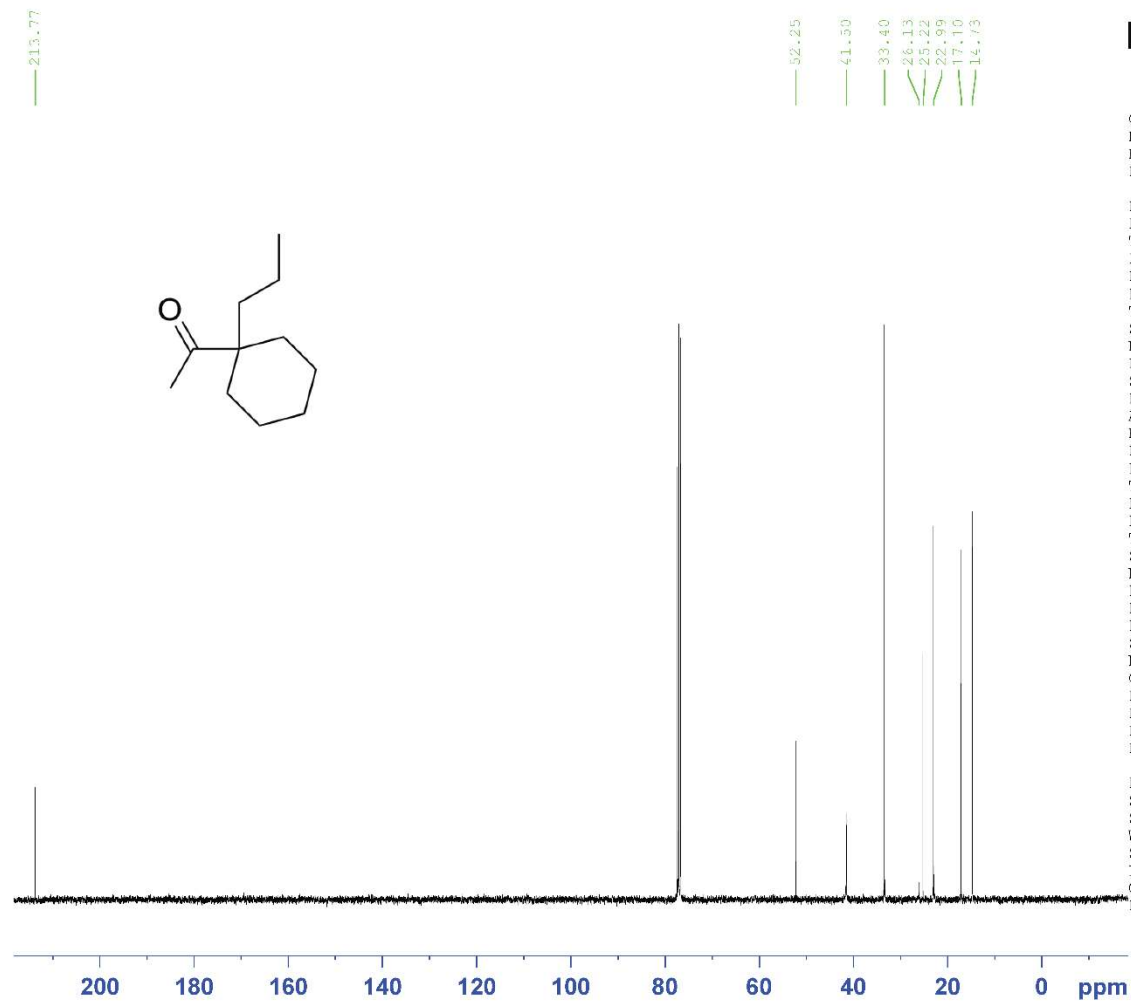


Figure S 19. 400 MHz ¹H NMR spectrum of cXPr-COMe measured in CDCl₃ at 298 K



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Current Data Parameters
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EXPNO        11
PROCNO       1

F2 - Acquisition Parameters
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Time_        3.19 h
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PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
NS           512
DS           4
SWH          23809.523 Hz
FIDRES       0.726609 Hz
AQ           1.3762560 sec
RG           22.1946
DW           21.000 usec
DE           6.50 usec
TE           298.0 K
D1           2.0000000 sec
D11          0.0300000 sec
TD0          1
SFO1         100.6278593 MHz
NUC1         13C
P0           3.33 usec
P1           10.00 usec
PLW1         63.61999893 W
SFO2         400.1516006 MHz
NUC2         1H
CPDPRG[2]    waltz65
PCPD2        90.00 usec
PLW2         14.84899998 W
PLW12        0.18332000 W
PLW13        0.09221000 W

F2 - Processing parameters
SI           32768
SF           100.6177975 MHz
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.40
  
```

Figure S 20. 101 MHz ¹³C NMR spectrum of cXPr-COMe measured in CDCl₃ at 298 K

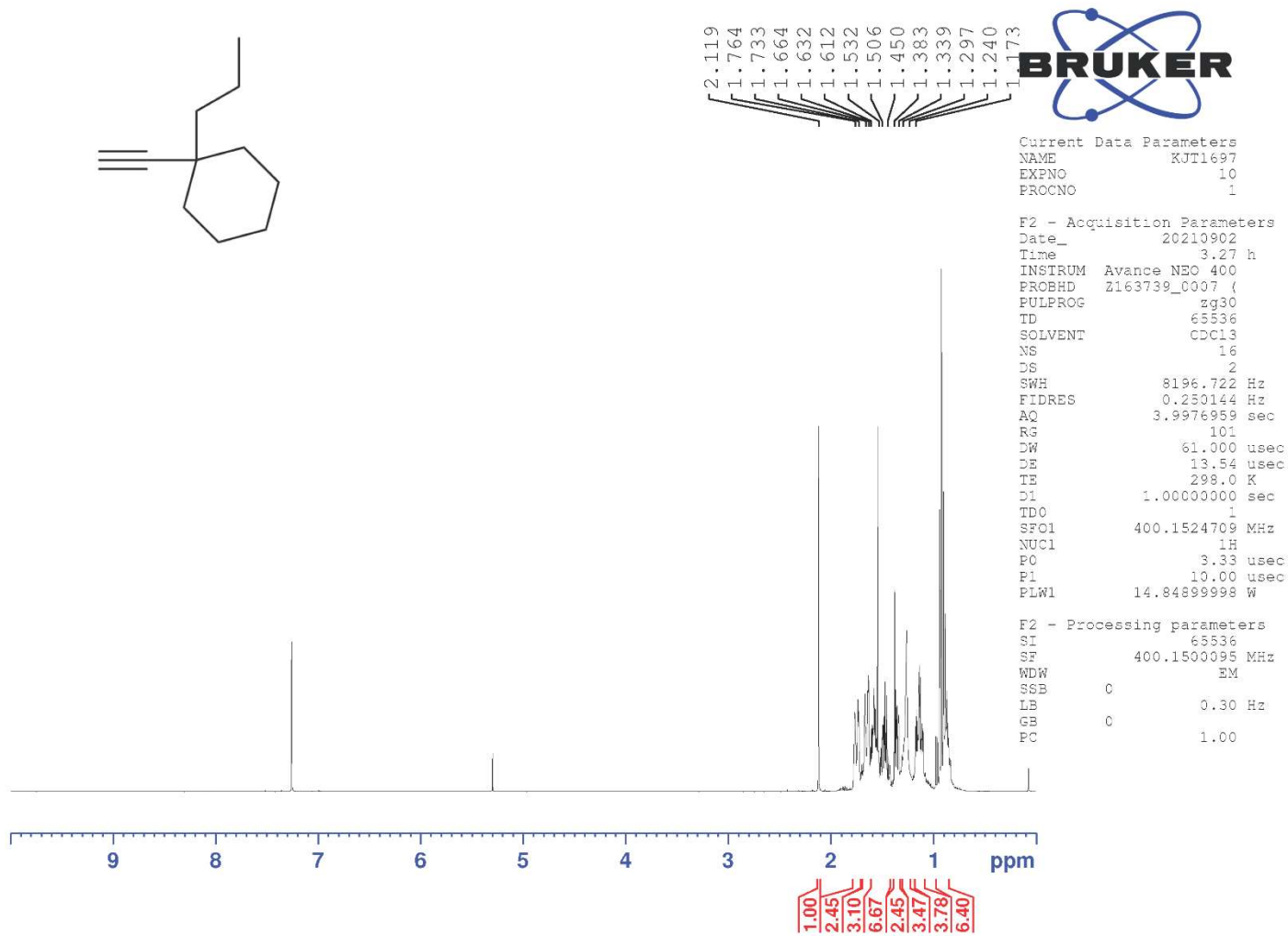


Figure S 21. 400 MHz ¹H NMR spectrum of cXPr-CCH measured in CDCl₃ at 298 K

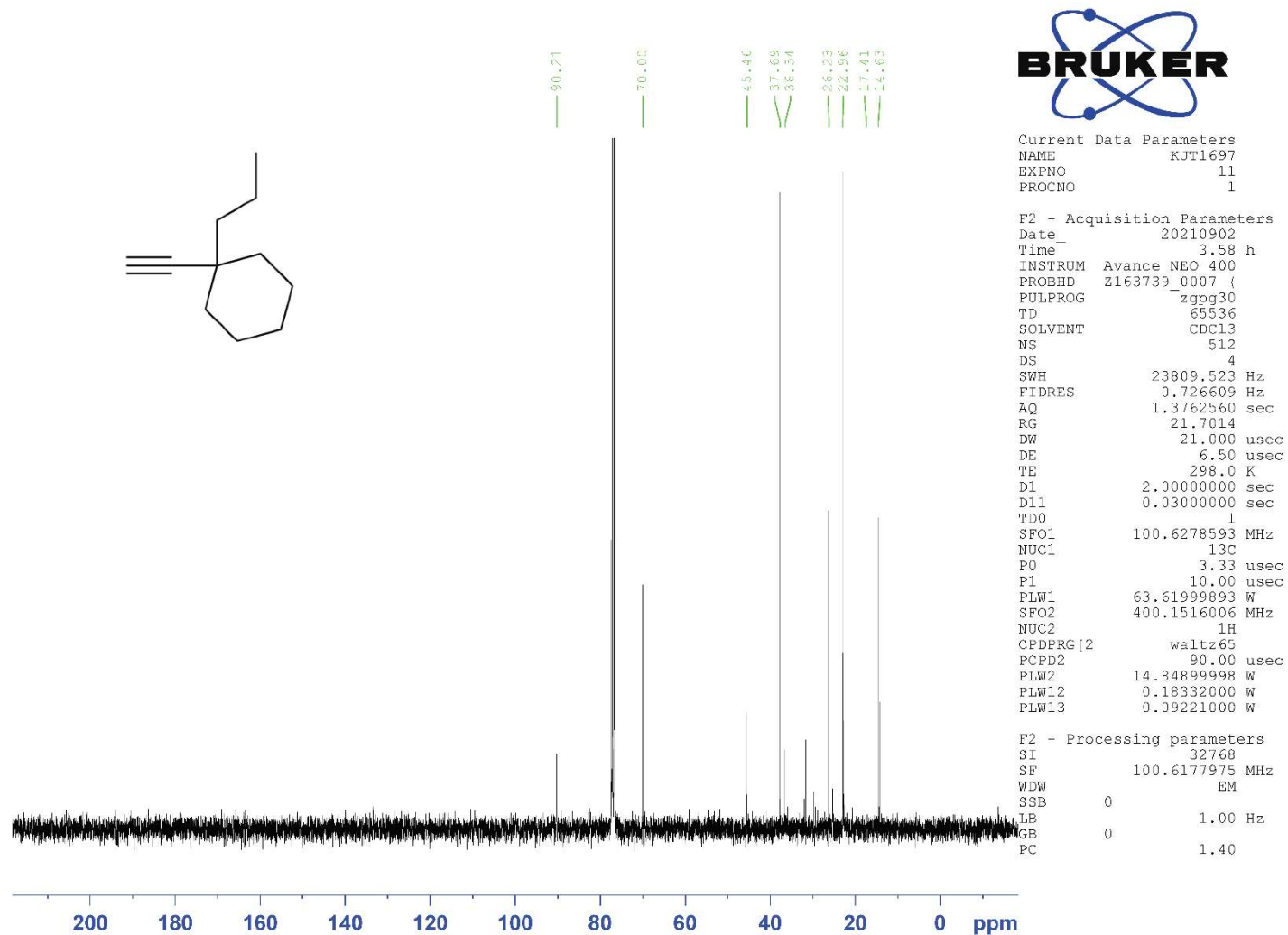


Figure S 22. 101 MHz ^{13}C NMR spectrum of cXPr-CCH measured in CDCl_3 at 298 K

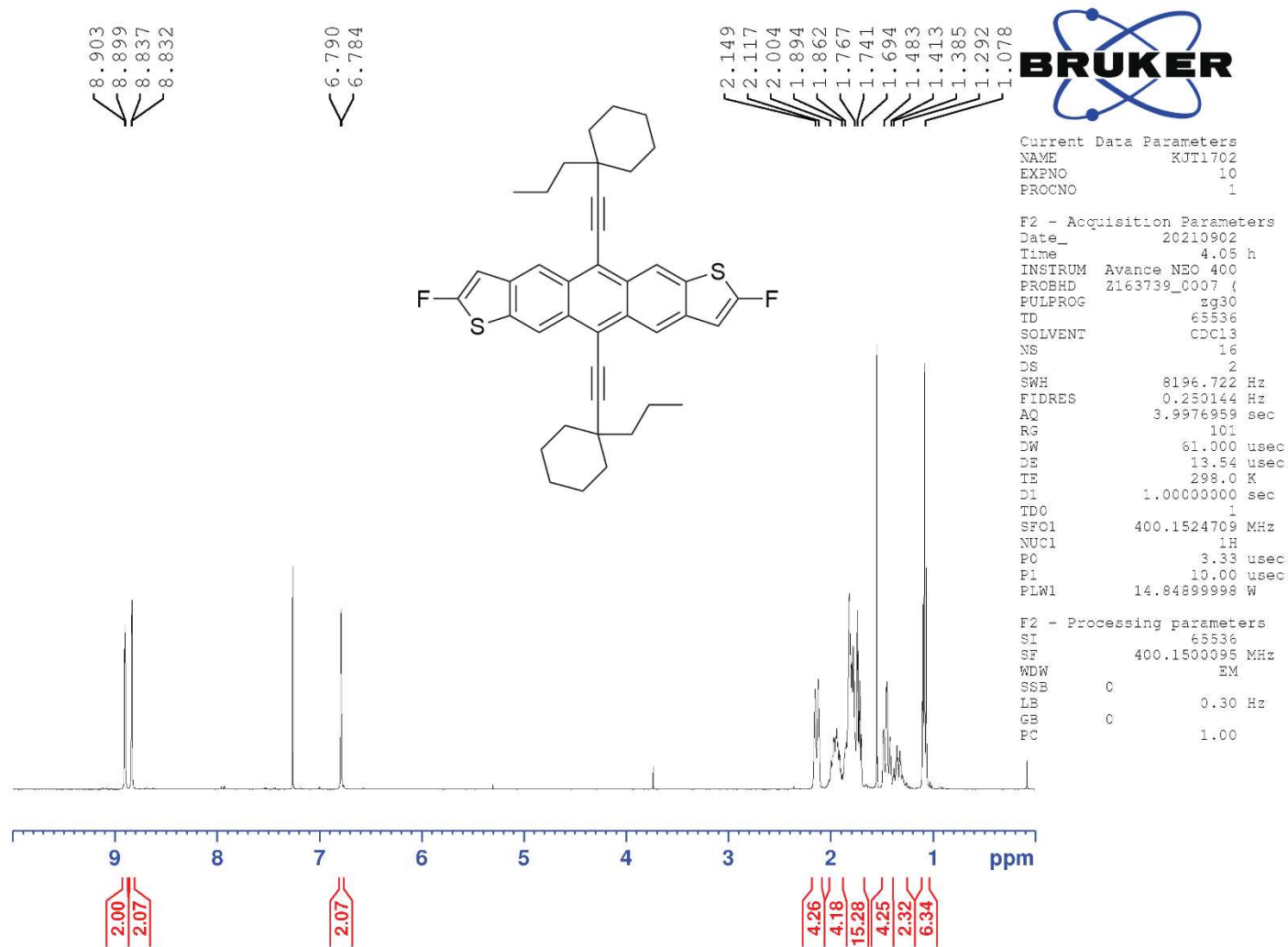


Figure S 23. 400 MHz ¹H NMR spectrum of cXPr-FADT measured in CDCl₃ at 298 K

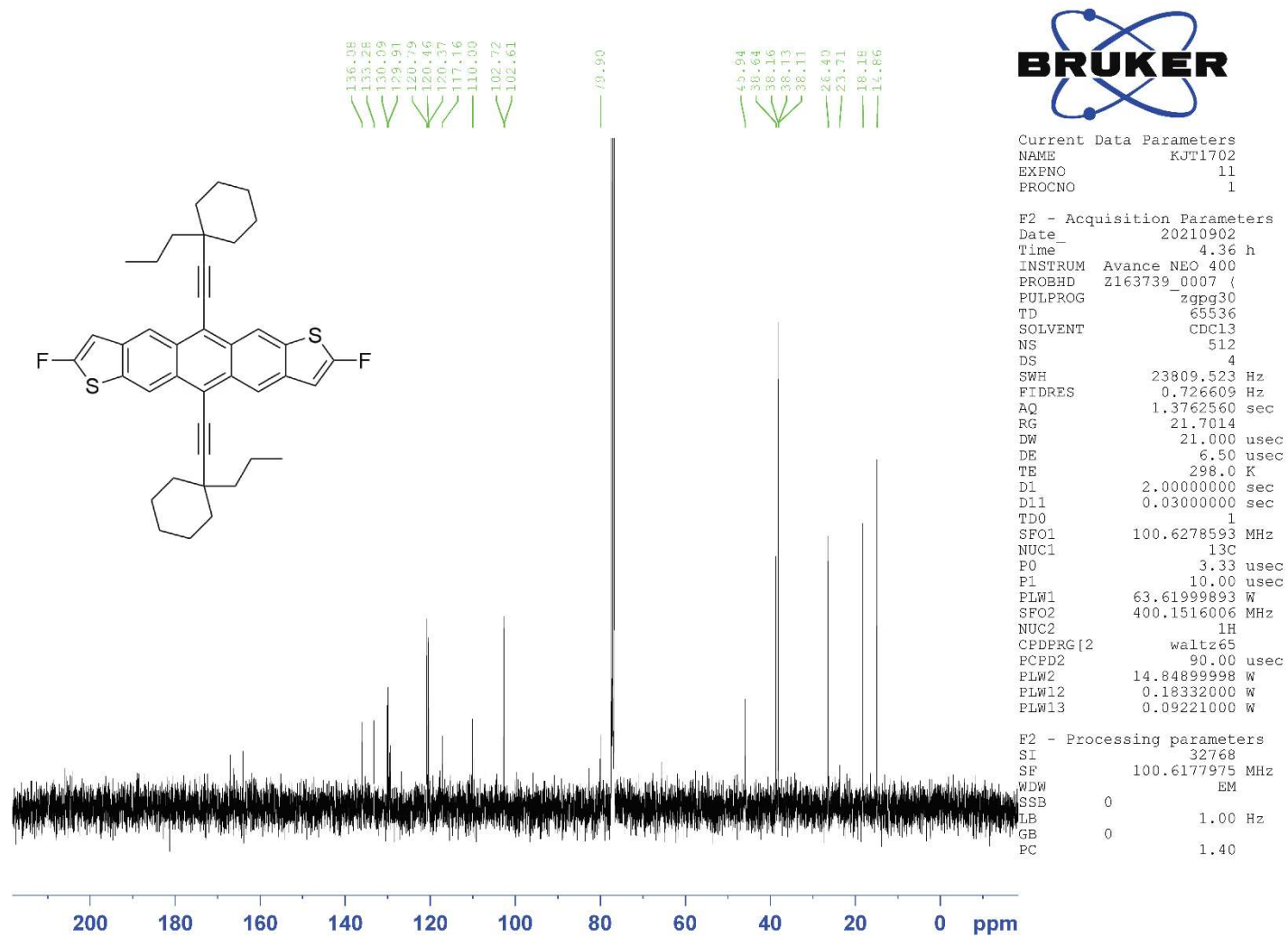


Figure S 24. 101 MHz ^{13}C NMR spectrum of cXPr-FADT measured in CDCl_3 at 298 K

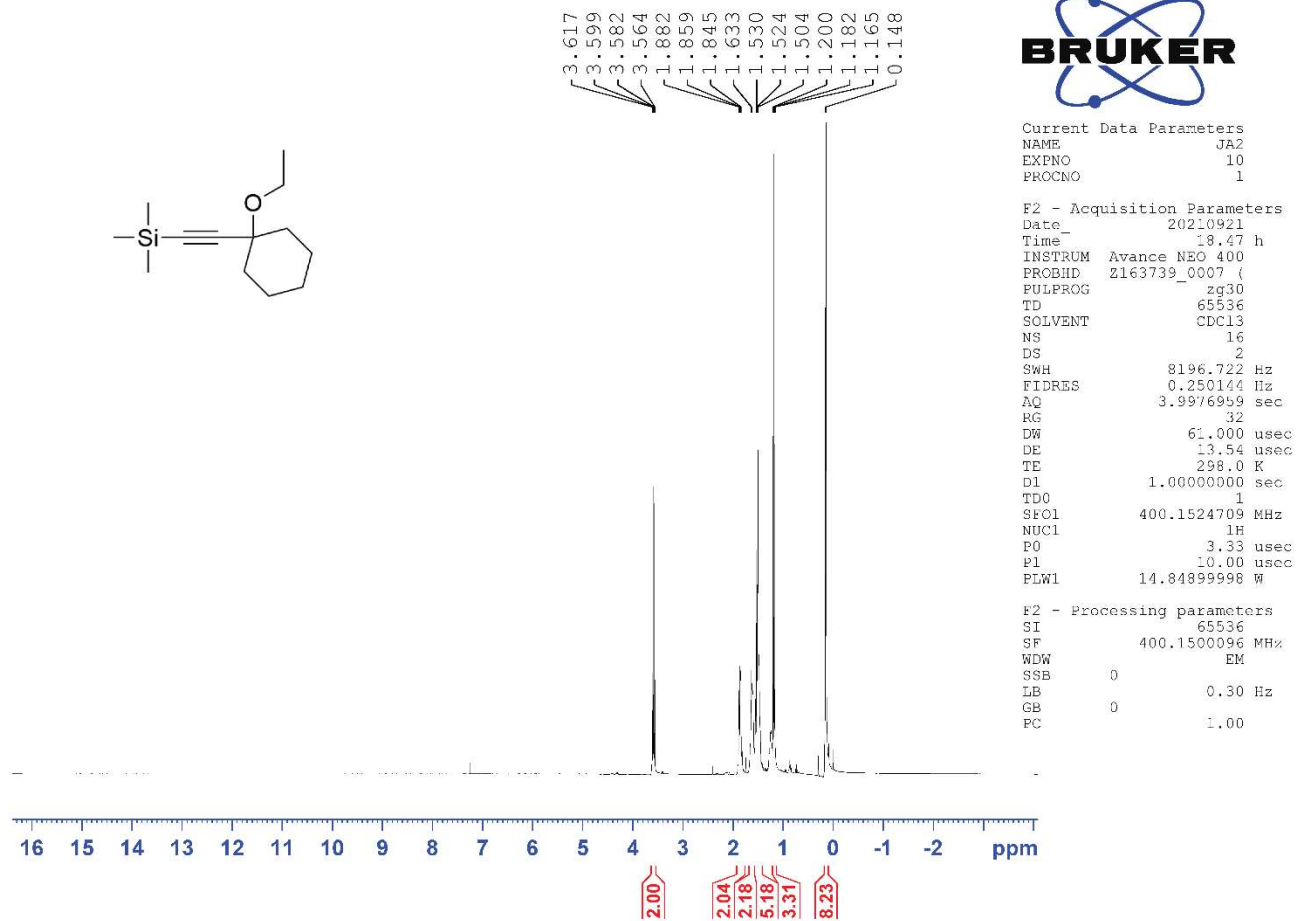


Figure S 25. 400 MHz ^1H NMR spectrum of cXOEt-CC-TMS measured in CDCl_3 at 298 K

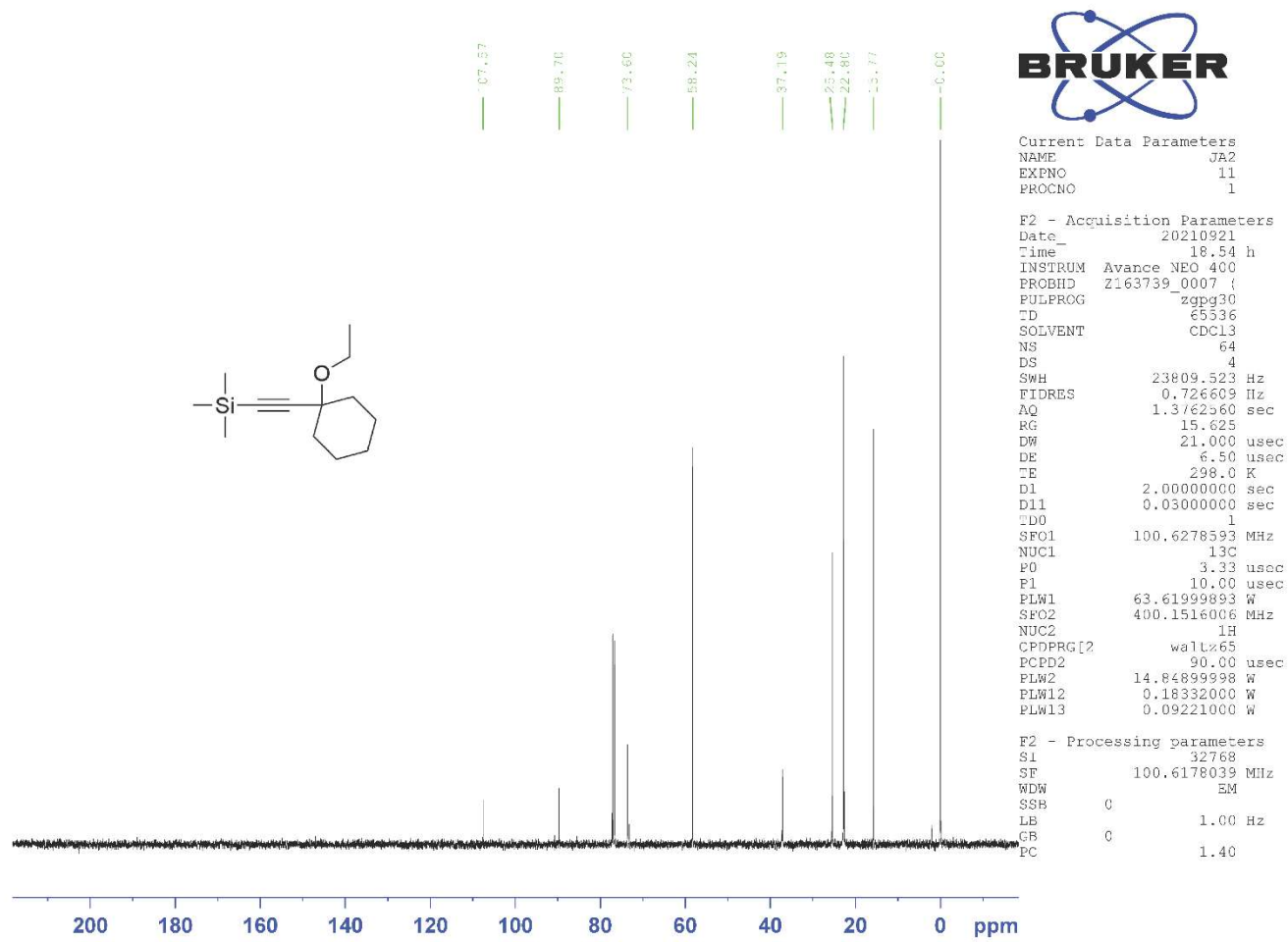


Figure S 26. 101 MHz ^{13}C NMR spectrum of cXOEt-CC-TMS measured in CDCl_3 at 298 K

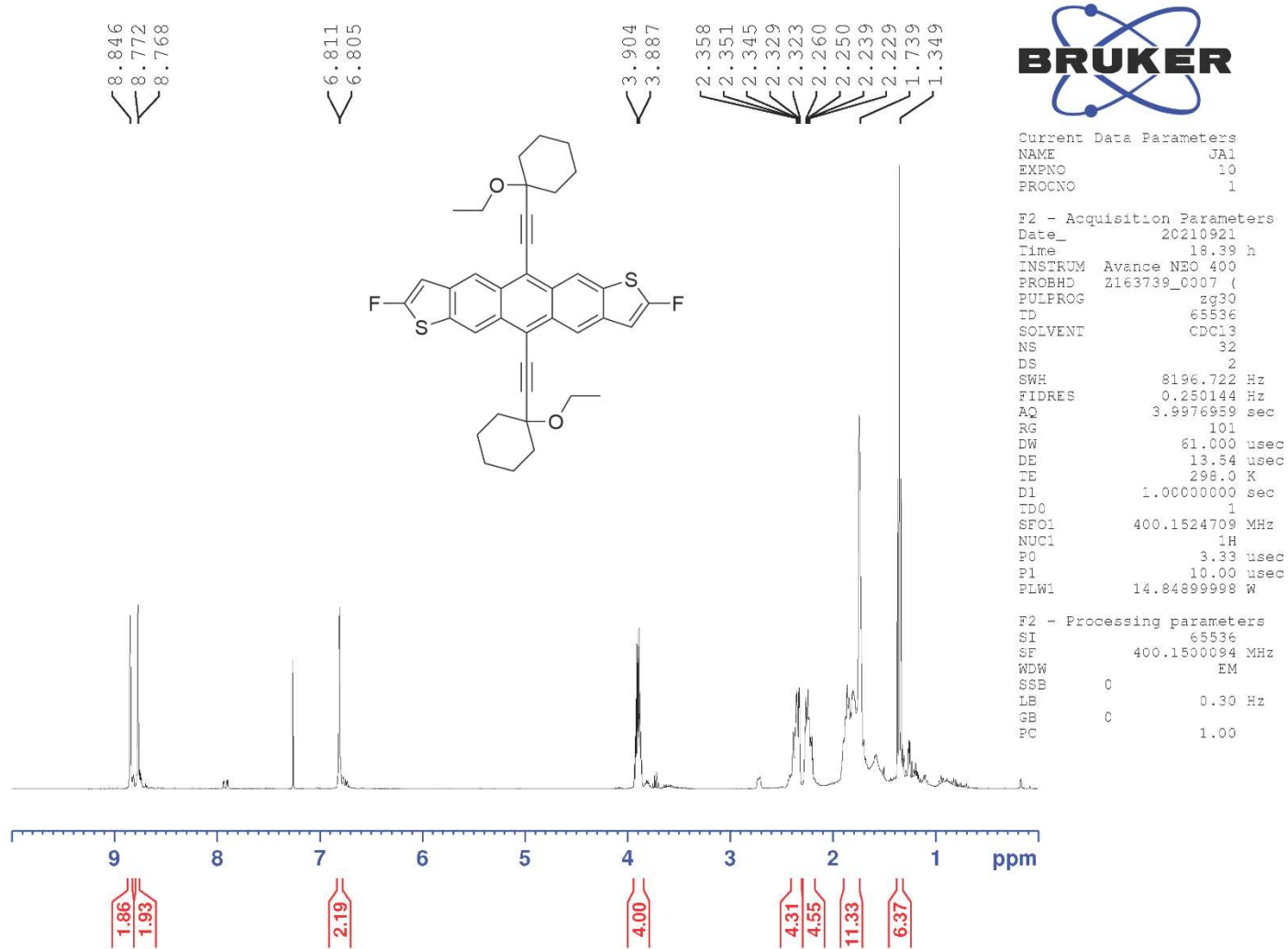


Figure S 27. 400 MHz ^1H NMR spectrum of cXOEt-FADT measured in CDCl_3 at 298 K

Copies of GC-MS spectra

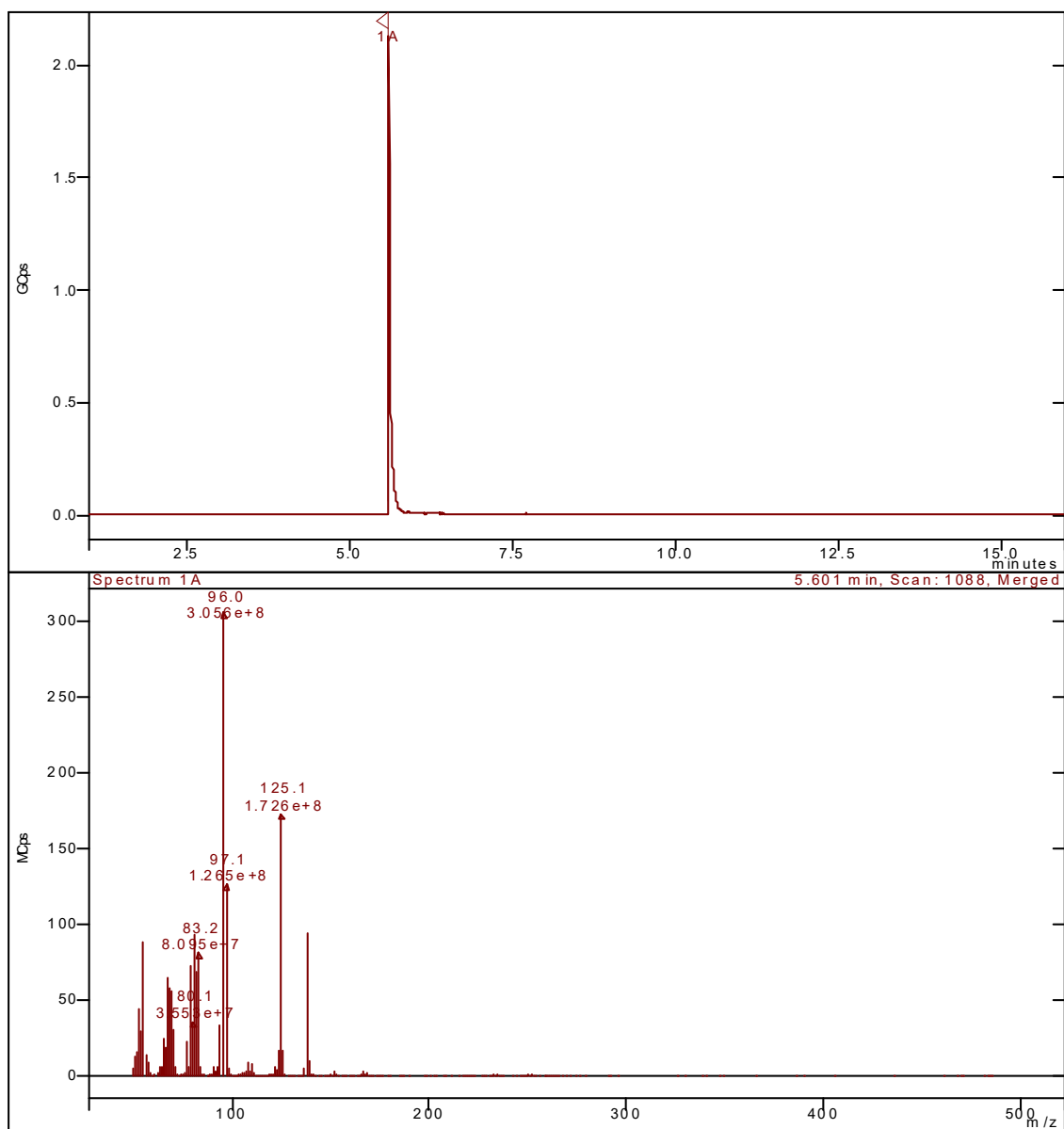


Figure S 28. GCMS chromatograph (top) and mass spectrum (bottom) of TnPC-CN.

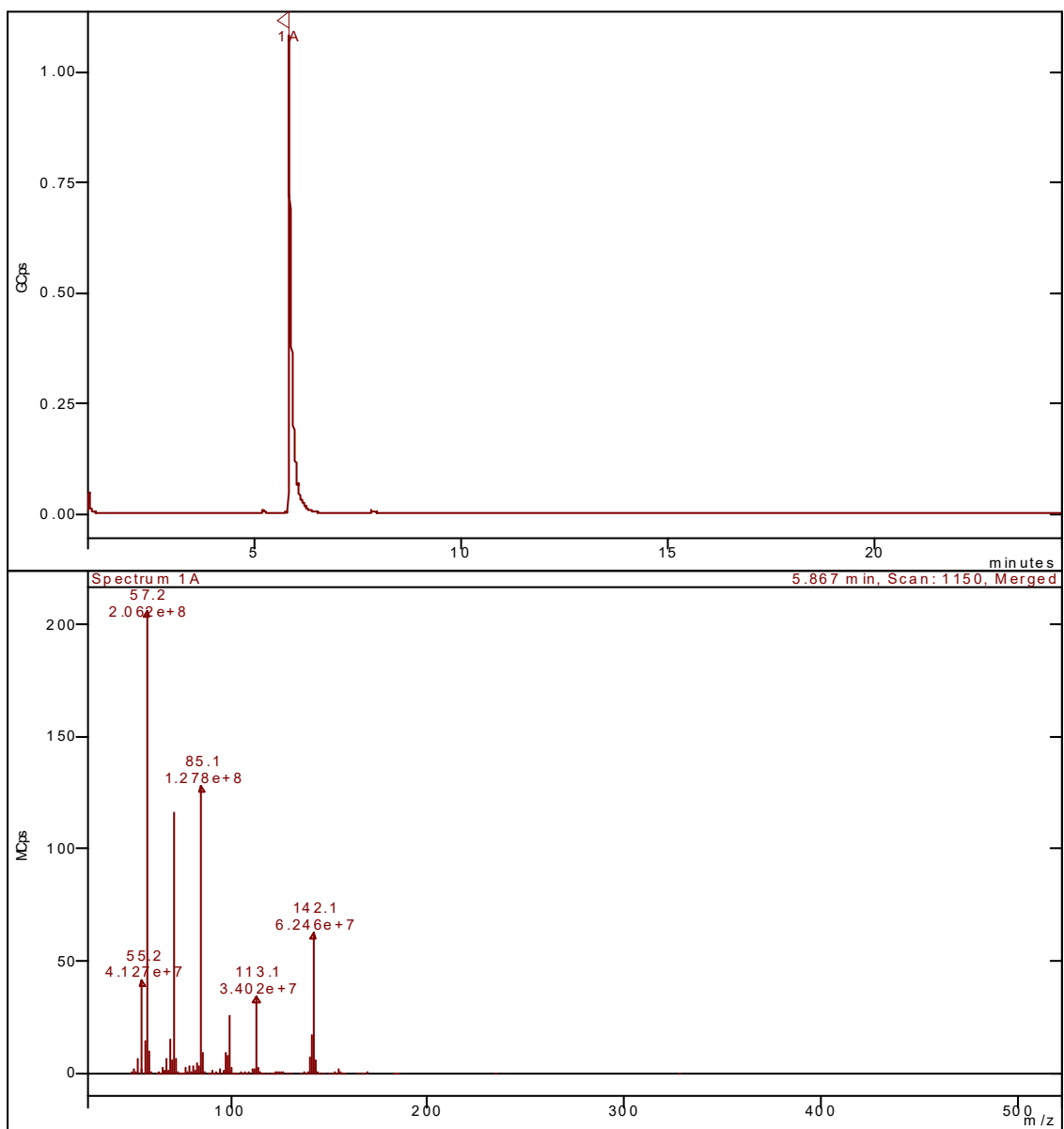


Figure S 29 GCMS chromatograph (top) and mass spectrum (bottom) of TnPC-COMe.

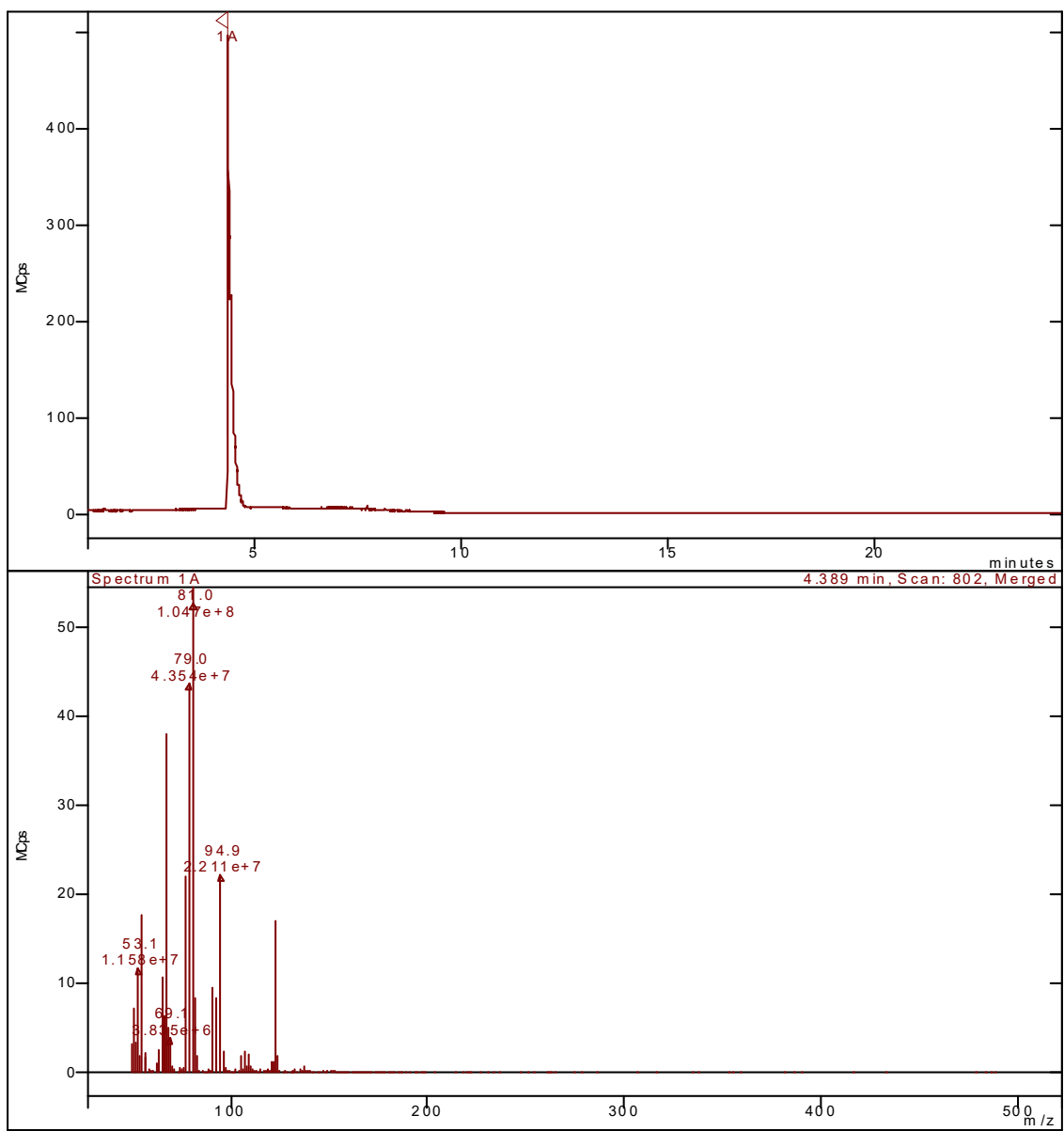


Figure S 30 GCMS chromatograph (top) and mass spectrum (bottom) of TnPC-CCH.

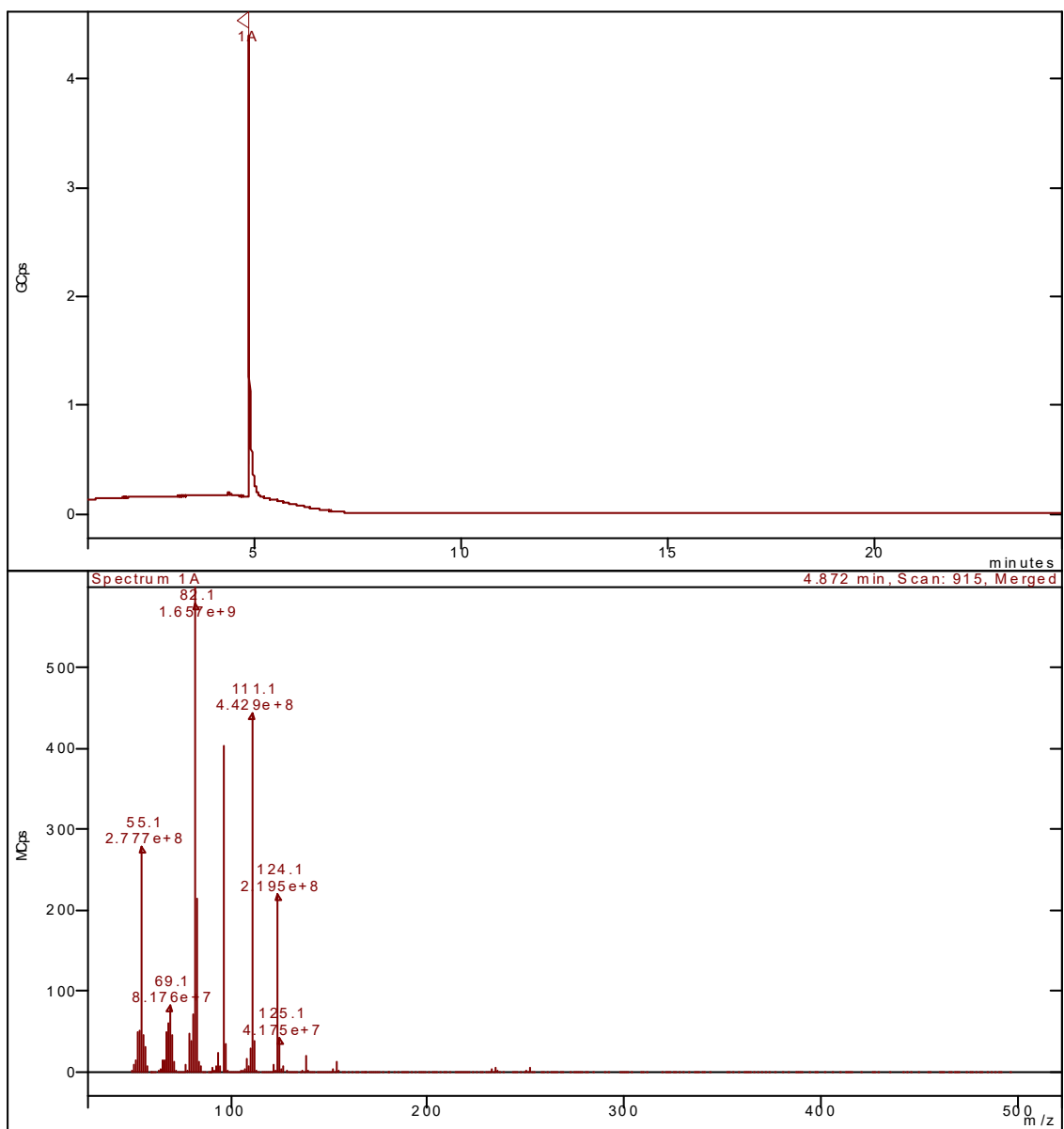


Figure S 31 GCMS chromatograph (top) and mass spectrum (bottom) of EDnPC-CN.

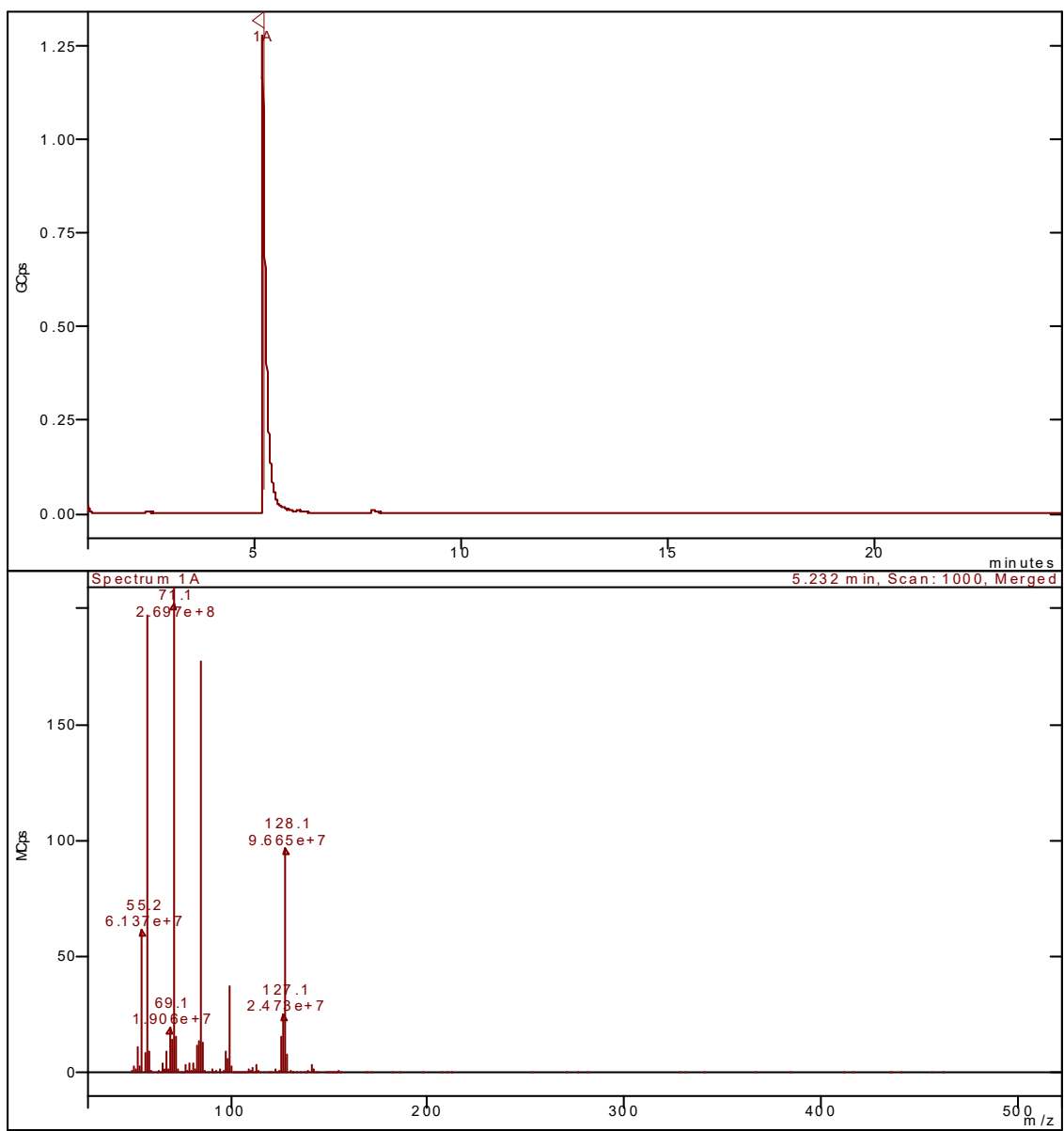


Figure S 32 GCMS chromatograph (top) and mass spectrum (bottom) of EDnPC-COMe.

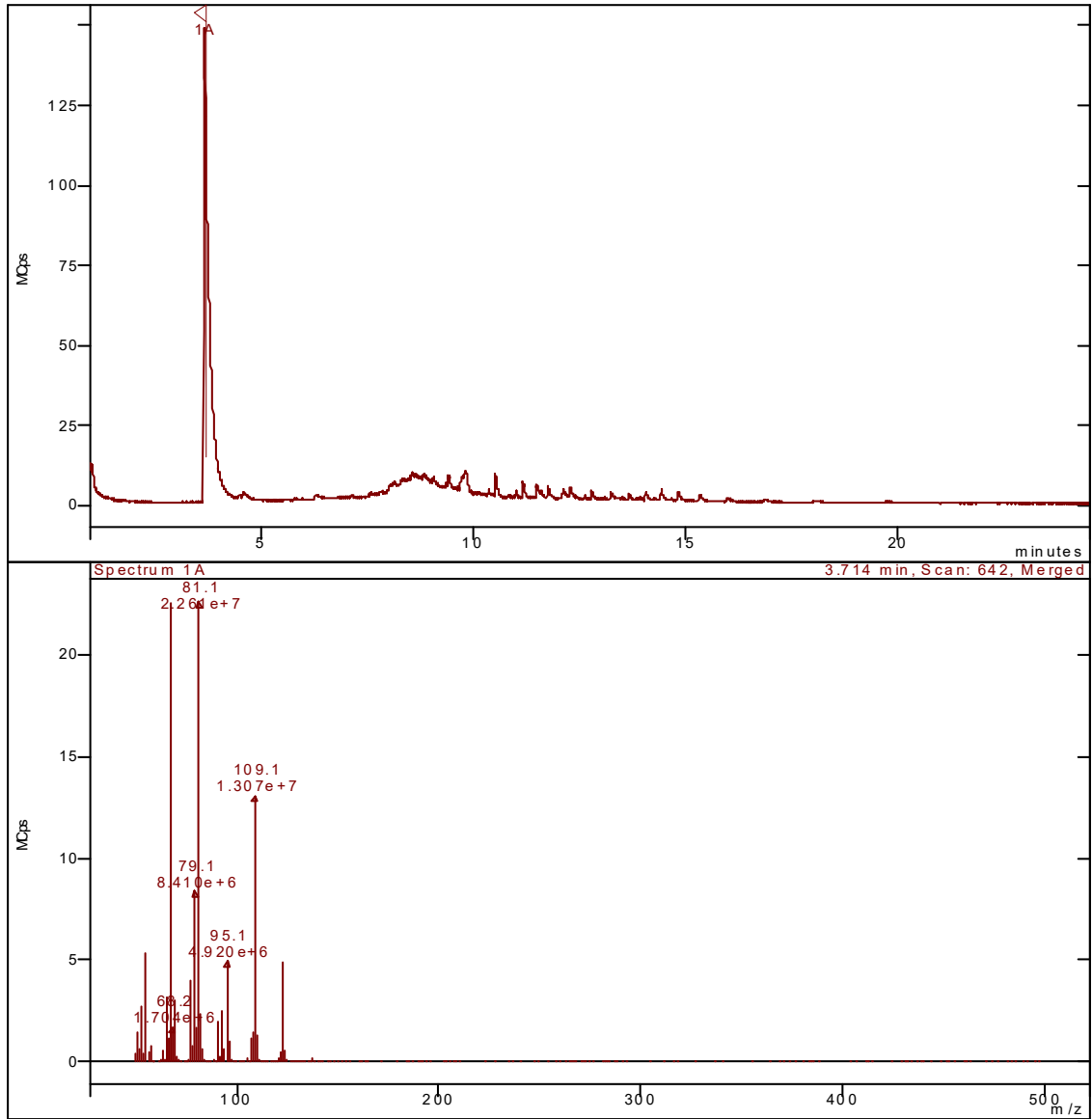


Figure S 33. GCMS chromatograph (top) and mass spectrum (bottom) of EDnPC-CCH

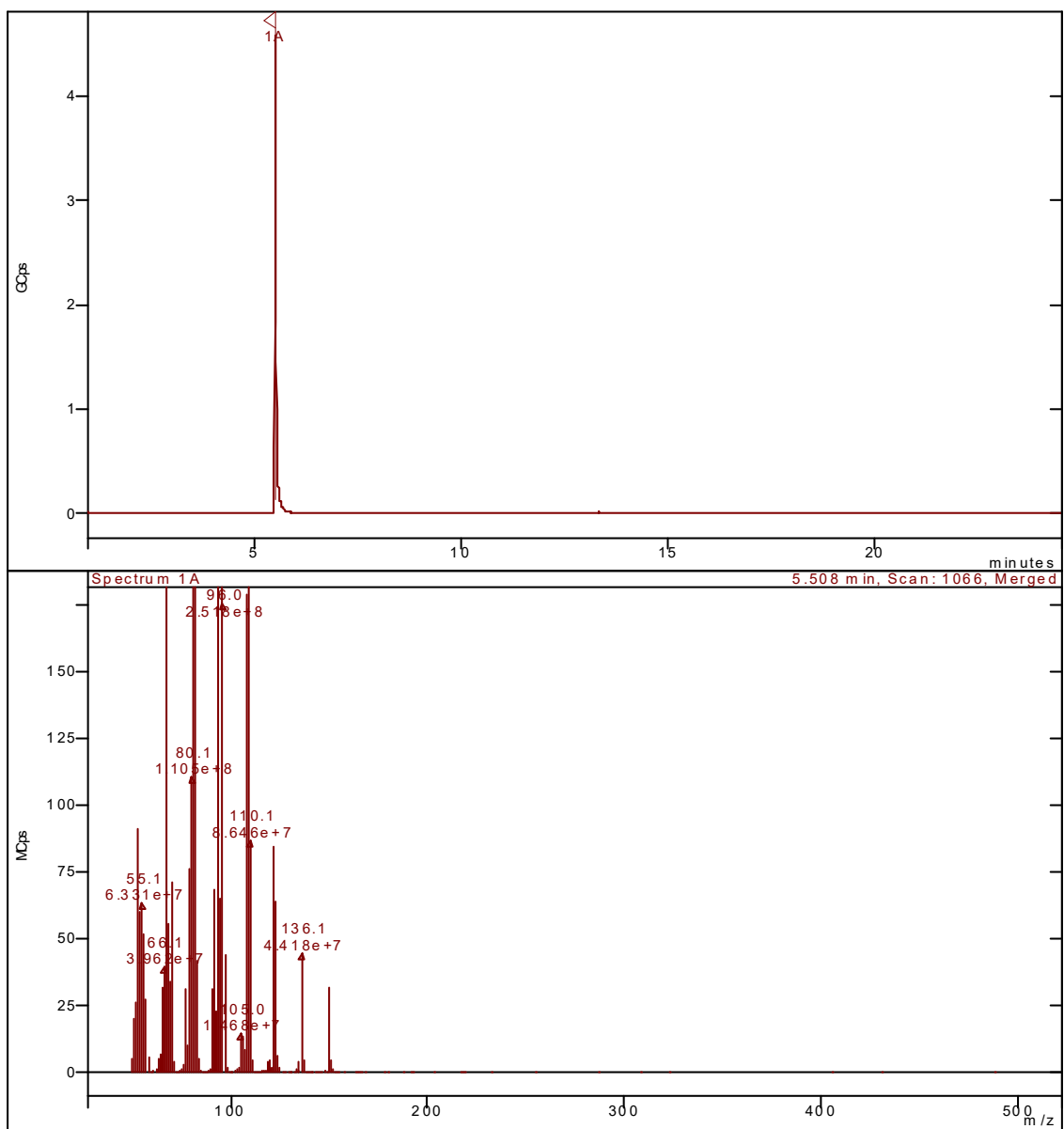


Figure S 34 GCMS chromatograph (top) and mass spectrum (bottom) of cXPr-CN.

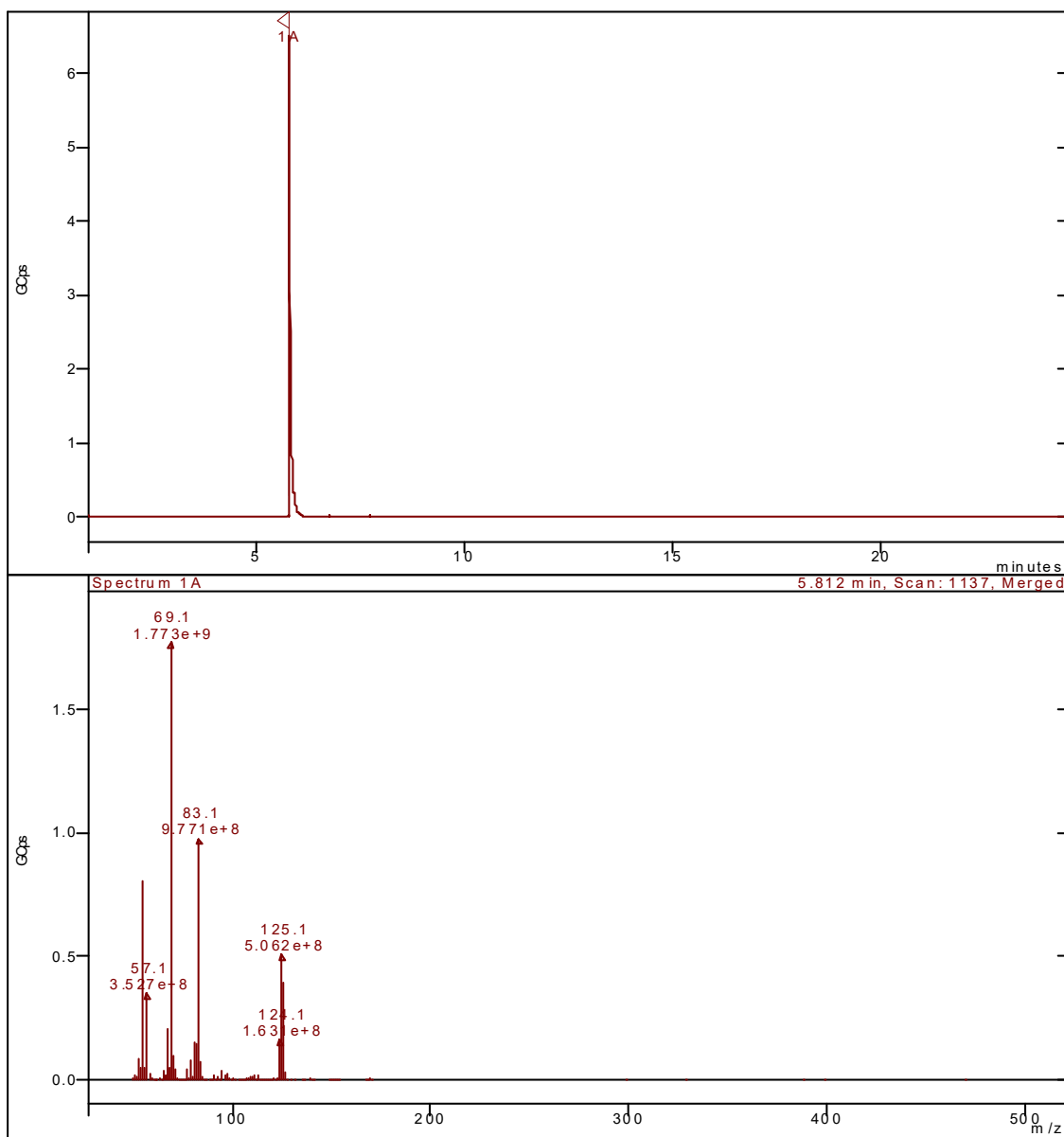


Figure S 35 GCMS chromatograph (top) and mass spectrum (bottom) of cXPr-COMe

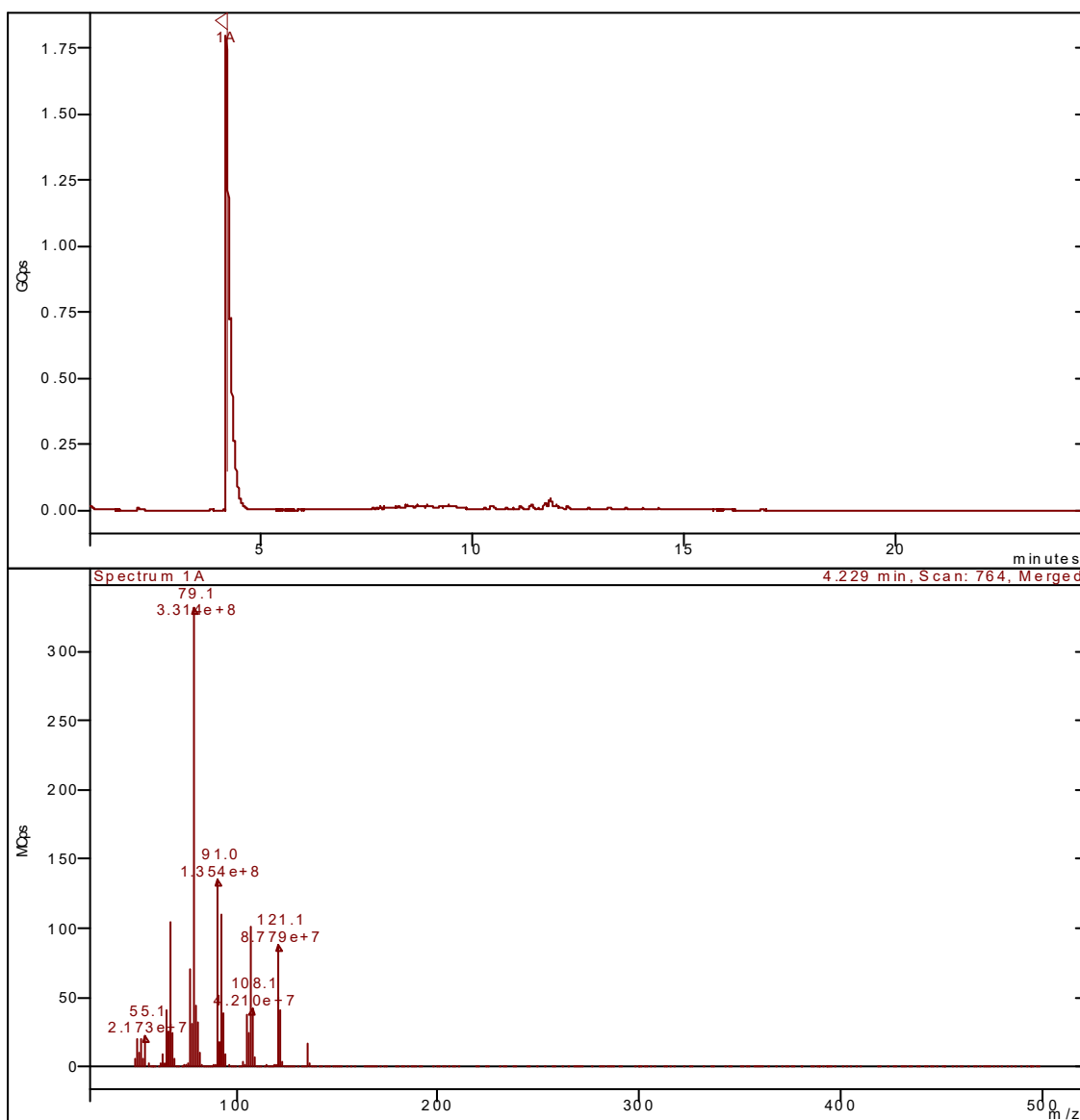


Figure S 36 GCMS chromatograph (top) and mass spectrum (bottom) of *cXPr-CCH*

X-ray crystallography data

X-ray diffraction data were collected at 90.0(2) K on a Bruker D8 Venture dual-source diffractometer with graded-multilayer focused MoK(α) X-rays. Raw data were integrated, scaled, merged and corrected for Lorentz-polarization effects using the APEX3 package.² Corrections for absorption were applied using SADABS.³ The structures were solved by dual-space methods (SHELXT⁴) and refined against F^2 by weighted full-matrix least-squares (SHELXL-2018).⁵ Hydrogen atoms were found in difference maps but subsequently placed at calculated positions and refined using riding models. Non-hydrogen atoms were refined with anisotropic displacement parameters. The F-ADT core and the alkyl groups were disordered over two sets of positions. The final structure model was checked using established methods.⁶ Atomic scattering factors were taken from the International Tables for Crystallography.⁷

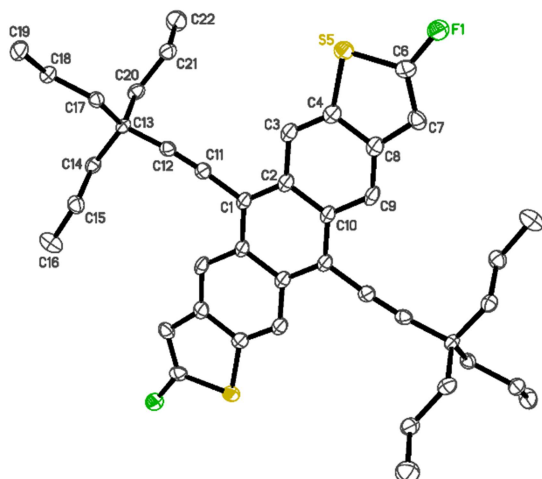


Figure S 37. Ellipsoid plot (50%) for TnPC-FADT

Table S1. Crystal data and structure refinement for m20136 (TnPC-FADT).	
Identification code	m20136
Empirical formula	C ₄₂ H ₄₈ F ₂ S ₂
Formula weight	654.92
Temperature	90.0(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 5.6444(8) Å alpha = 90 deg. b = 17.785(2) Å beta = 94.919(5) deg. c = 17.849(2) Å gamma = 90 deg.
Volume	1785.2(4) Å ³
Z, Calculated density	2, 1.218 Mg/m ³
Absorption coefficient	0.188 mm ⁻¹
F(000)	700
Crystal size	0.300 x 0.030 x 0.020 mm
Theta range for data collection	2.290 to 25.249 deg.
Limiting indices	-6 ≤ h ≤ 6, -21 ≤ k ≤ 21, -21 ≤ l ≤ 21
Reflections collected / unique	20189 / 3237 [R(int) = 0.1063]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.971 and 0.736
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3237 / 83 / 225
Goodness-of-fit on F ²	1.032
Final R indices [I > 2σ(I)]	R ₁ = 0.0526, wR ₂ = 0.1002
R indices (all data)	R ₁ = 0.0996, wR ₂ = 0.1212
Extinction coefficient	0.0122(13)
Largest diff. peak and hole	0.258 and -0.233 e.Å ⁻³

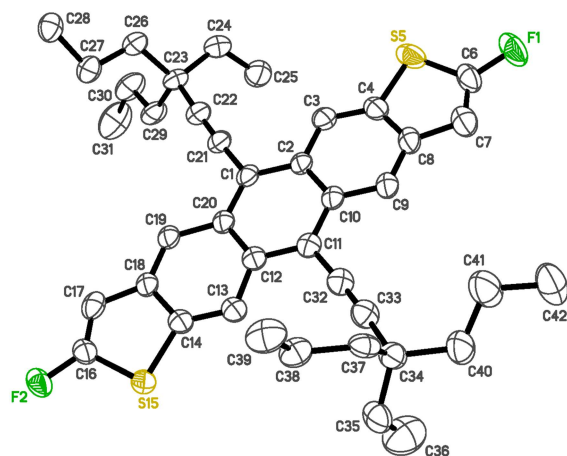


Figure S 38. Ellipsoid plot (50%) for EDnPC-FADT

Table S2. Crystal data and structure refinement for m20233 (EDnPC-FADT).	
Identification code	m20233
Empirical formula	C ₄₀ H ₄₄ F ₂ S ₂
Formula weight	626.87
Temperature	90.0(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.6939(2) Å alpha = 90 deg. b = 22.8849(6) Å beta = 103.168(1) deg. c = 17.5749(5) Å gamma = 90 deg.
Volume	3404.74(15) Å ³
Z, Calculated density	4, 1.223 Mg/m ³
Absorption coefficient	0.194 mm ⁻¹
F(000)	1336
Crystal size	0.260 x 0.170 x 0.130 mm
Theta range for data collection	2.141 to 27.509 deg.
Limiting indices	-11<=h<=10, -29<=k<=29, -22<=l<=22
Reflections collected / unique	63297 / 7826 [R(int) = 0.0391]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.971 and 0.922
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7826 / 1052 / 594
Goodness-of-fit on F ²	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0589, wR2 = 0.1711
R indices (all data)	R1 = 0.0721, wR2 = 0.1846
Extinction coefficient	0.0026(8)
Largest diff. peak and hole	0.566 and -0.541 e.Å ⁻³

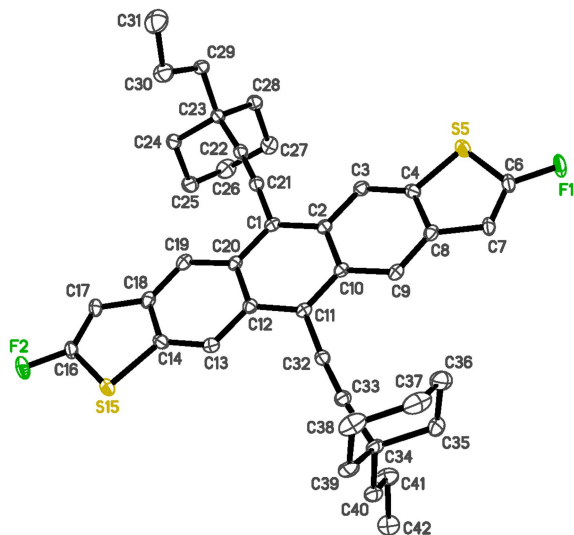


Figure S 39 Ellipsoid plot (50%) for *cXPr-FADT*

Table S3. Crystal data and structure refinement for m21072 (<i>cXPr-FADT</i>).	
Identification code	m21072
Empirical formula	C ₄₀ H ₄₀ F ₂ S ₂
Formula weight	622.84
Temperature	90.0(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.2512(9) Å alpha = 76.585(3) deg. b = 10.3808(9) Å beta = 83.153(2) deg. c = 15.5348(16) Å gamma = 80.974(4) deg.
Volume	1582.2(3) Å ³
Z, Calculated density	2, 1.307 Mg/m ³
Absorption coefficient	0.209 mm ⁻¹
F(000)	660
Crystal size	0.340 x 0.130 x 0.040 mm
Theta range for data collection	2.019 to 27.519 deg.
Limiting indices	-13<=h<=13, -13<=k<=13, -20<=l<=20
Reflections collected / unique	38615 / 7272 [R(int) = 0.0386]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.914 and 0.880
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7272 / 190 / 425
Goodness-of-fit on F ²	1.114
Final R indices [I>2sigma(I)]	R1 = 0.0425, wR2 = 0.0973
R indices (all data)	R1 = 0.0513, wR2 = 0.1016
Extinction coefficient	n/a
Largest diff. peak and hole	0.351 and -0.269 e.Å ⁻³

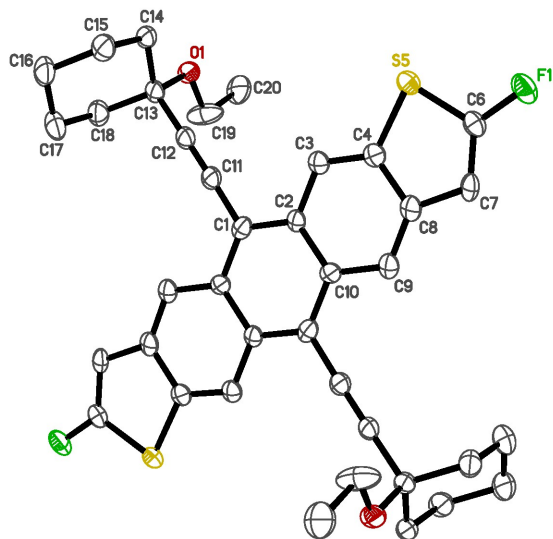


Figure S 40 Ellipsoid plot (50%) for *cXOEt-FADT*

Table S4. Crystal data and structure refinement for m20188.(cXOEt-FADT)	
Identification code	m20188
Empirical formula	C ₃₈ H ₃₆ F ₂ O ₂ S ₂
Formula weight	626.79
Temperature	90.0(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.658(3) Å alpha = 76.164(14) deg. b = 7.709(3) Å beta = 89.602(13) deg. c = 15.689(8) Å gamma = 89.59(2) deg.
Volume	782.0(6) Å ³
Z, Calculated density	1, 1.331 Mg/m ³
Absorption coefficient	0.216 mm ⁻¹
F(000)	330
Crystal size	0.160 x 0.080 x 0.040 mm
Theta range for data collection	2.674 to 26.361 deg.
Limiting indices	-8<=h<=8, -9<=k<=9, -19<=l<=19
Reflections collected / unique	12045 / 3177 [R(int) = 0.0810]
Completeness to theta = 25.242	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.971 and 0.774
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3177 / 193 / 239
Goodness-of-fit on F ²	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0676, wR2 = 0.1589
R indices (all data)	R1 = 0.1027, wR2 = 0.1809
Extinction coefficient	0.031(5)
Largest diff. peak and hole	0.301 and -0.348 e.Å ⁻³

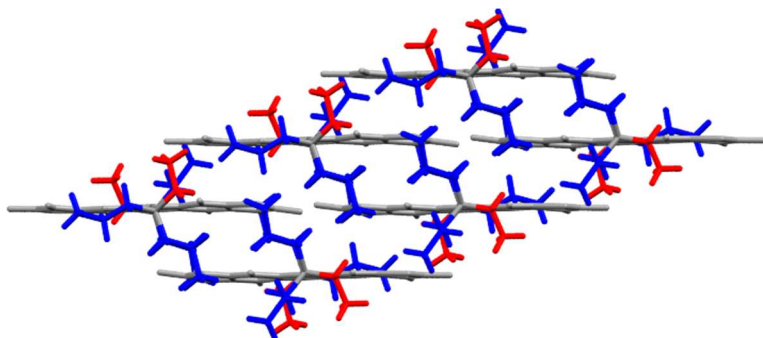


Figure S 41. Side chain alignment in the crystal packing of EDnPC-FADT, where *n*-propyl chains are shown in blue and ethyl chains shown in red.

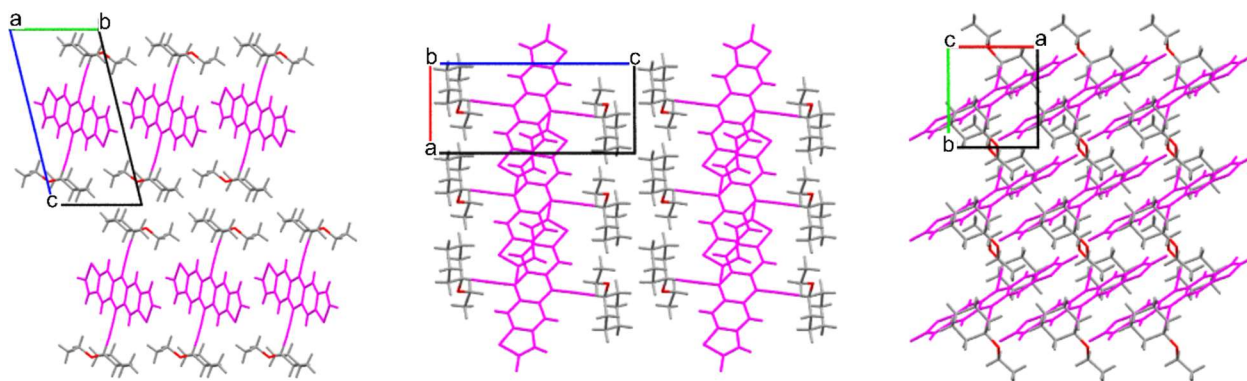


Figure S 42. 2D brickwork packing in single crystals of cXOEt-FADT, viewed along the *a*, *b*, and *c* crystallographic axes, respectively.

Thermal Analysis

Thermal analysis was performed by differential scanning calorimetry using a TA instruments Q100 instrument. Samples of around 5mg were prepared from crystalline materials from the same batches as the single crystals obtained for X-ray diffraction. Samples were sealed in standard aluminium pans, and subjected to a heat/cool/heat cycle between 35 and 250 °C degrees at heating and cooling rates of 10 °C per minute. Melting points were taken from the peak minima and enthalpies extracted by linear integration in the TA instruments software.

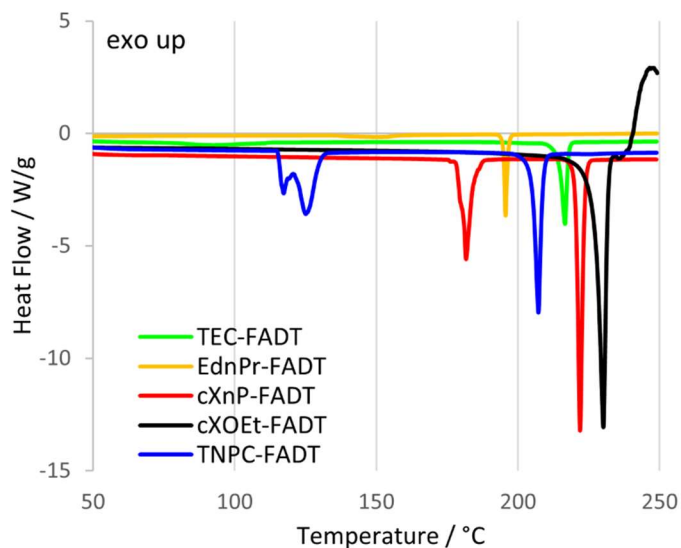


Figure S 43. Differential scanning calorimetry traces for FADT materials discussed in this manuscript.

Computational Details

Unit cell optimisation was performed using Quantum Espresso^{8,9} software. Calculations used the PBE0 functional with Grimme’s DFT-D3 dispersion correction and the projector-augmented wave (PAW) method.¹⁰ Pseudopotentials from pslibrary¹¹ were used, along with a kinetic energy cutoff of 80 Ry. Unit cell optimisations used a Monkhorst-Pack grid of 2×2×2, while gas phase approximations were performed only at the Γ point.

Lattice binding energies E_{binding} were calculated by comparing the unit cell energy E_{uc} , number of molecules in the unit cell, N_{uc} , and the energy of a “gas phase” molecule E_{mol} which was optimised at the same theory level, extending unit cell parameters until energy convergence. These values were used in the equation:

$$E_{\text{binding}} = \frac{E_{\text{uc}}}{N_{\text{uc}}} - E_{\text{mol}}$$

Table S 1. DFT derived lattice binding energies for hypothetical 2D brickwork packings of TnPC- and EDnPC-FADT. Energies for the structures optimised from the experimental crystal structures are given for reference.

Sidechain	Packing	$E_{\text{binding}} / \text{kcalmol}^{-1}$
TnPC	exp	-59.3
	2D-A	-45.6
	2D-B	-47.5
	2D-C	-46.2
EDnPC	exp	-54.9
	2D-A	-47.9
	2D-B	-49.3
	2D-C	-39.4

Symmetry adapted perturbation theory calculations were performed using Psi4 software¹² at the SAPTO level with the recommended truncated diffuse jun-cc-pvdz basis set.¹³ SAPTO calculations were performed on pairs of molecules from the solid-state DFT optimisations, such that we could compare experimentally derived structures with hypothetical ones.

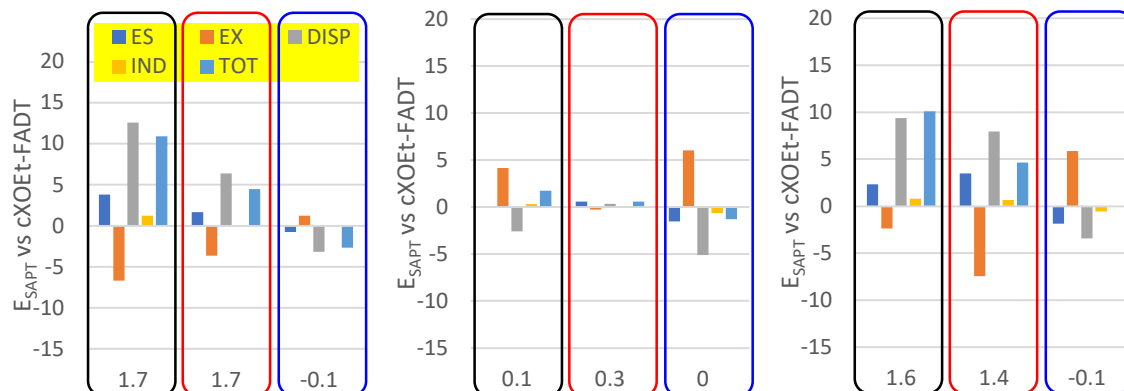


Figure S 44. Decomposition analysis by SAPTO on molecular pairs from hypothetical DFT optimised 2D brickwork structures of EDnPC-FADT. Bars within each coloured box belong to the same molecular pair, and the colour correlates to the data points in Figure XYZ. Values are reported versus equivalent interactions in cXOEt-FADT, where a positive value means the interaction is less stabilising (ES,DISP,IND and TOT) or less repulsive (EX). ES = electrostatic, EX = exchange, DISP = dispersion, IND = induction, TOT= total SAPTO energy. Values underneath each data set represent the change in centre-to-centre displacement.

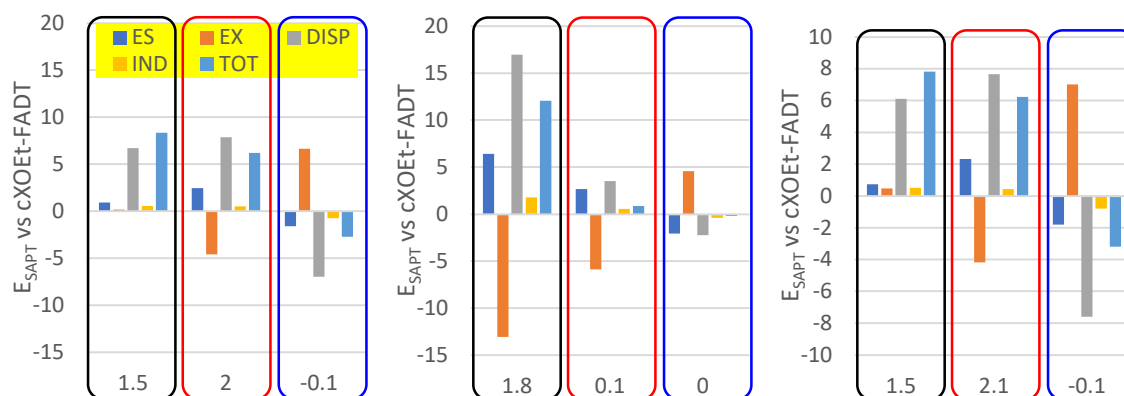


Figure S 45. Decomposition analysis by SAPTO on molecular pairs from hypothetical DFT optimised 2D brickwork structures of TnPC-FADT. Bars within each coloured box belong to the same molecular pair, and the colour correlates to the data points in Figure XYZ. Values are reported versus equivalent interactions in cXOEt-FADT, where a positive value means the interaction is less stabilising (ES,DISP,IND and TOT) or less repulsive (EX). ES = electrostatic, EX = exchange, DISP = dispersion, IND = induction, TOT= total SAPTO energy. Values underneath each data set represent the change in centre-to-centre displacement.

Transfer integrals were calculated using Gaussian 16 Rev A.03¹⁴ at the B3LYP/6-31G* level using the approach of Valeev et al.¹⁵ These were performed on geometries extracted from the crystal structures without further refinement.

Device Fabrication

To fabricate the OFETs we started with 1.5 cm x 1.5 cm pre-cut wafers consisting of a 200 nm layer of thermally grown SiO₂ at the surface of heavily doped Si wafer, which served as bottom gate dielectric and bottom gate electrode, respectively. These substrates were cleaned by consecutive baths in hot acetone and hot isopropyl alcohol (IPA) (85 °C), followed by UV-Ozon exposure and a thorough rinse with DI water. A shadow mask was placed over the SiO₂ side for each sample and the ensembles were then loaded into the evaporator for contact deposition. A 3 nm Ti layer and a 40 nm Au layer were evaporated as source and the drain electrodes with channel lengths, L, varying between 30 and 100 μm and channel widths, W, between 200 and 1000 μm. Next, the testbeds were cleaned again following the same procedure outlined above, immersed for 30 min in a pentafluorobenzenethiol (PFBT) solution consisting of 20 μL of PFBT in 5 mL of high purity Ethanol, and then sonicated in Ethanol. 1 wt% solutions of cXOEt-FADT and cXPr-FADT were prepared in Chlorobenzene (CB), 1,2 Dichlorobenzene (DCB) and n-Butylbenzene (NBB), respectively, and casted over the substrates by spin-coating (1000 rpm) or drop-casting. CB solution was deposited at room-temperature, DCB solution was heated at 60° C for 5 minutes before deposition, and the NBB solution was heated at 160° C for 15 minutes. All samples were annealed 100° C for 10 minutes before the electrical characterization. The devices were measured immediately after fabrication and the OFET characterization was performed in a probe-station placed in ambient atmosphere using an Agilent 4155 C parameter analyzer.

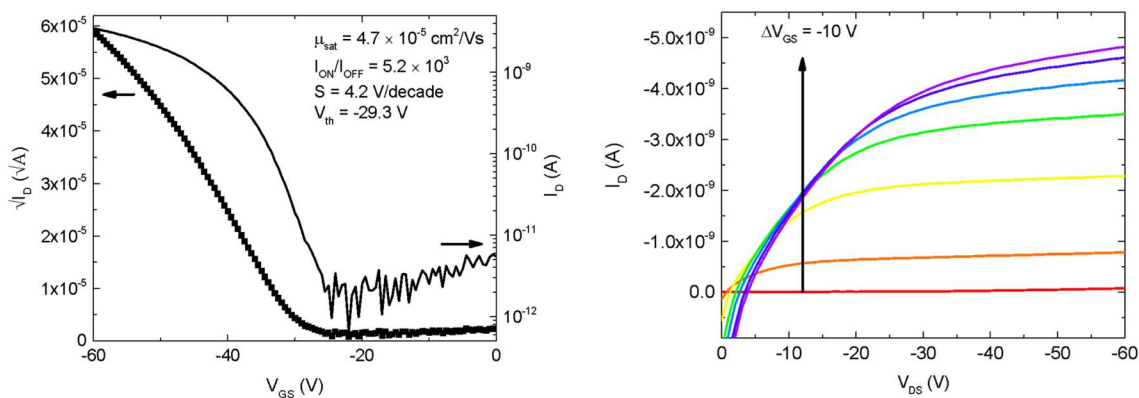


Figure S 46. Transfer (left) and transport curves for OFETs fabricated on cXPr-FADT thin films spun from a Chlorobenzene solution.

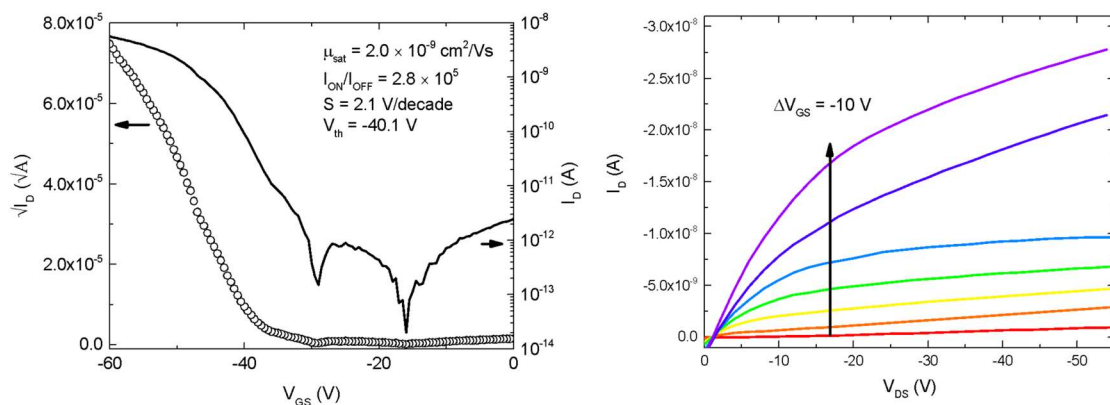


Figure S 47. Transfer (left) and transport curves for OFETs fabricated on cXOEt-FADT thin films spun from a Chlorobenzene solution.

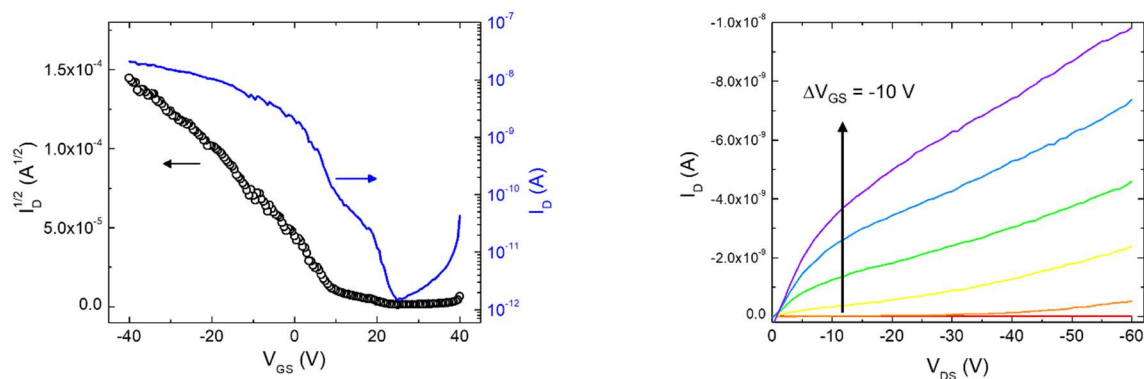


Figure S 48. Transfer (left) and transport curves for OFETs fabricated on cXOEt-FADT thin films drop casted from a n-Butylbenzene solution.

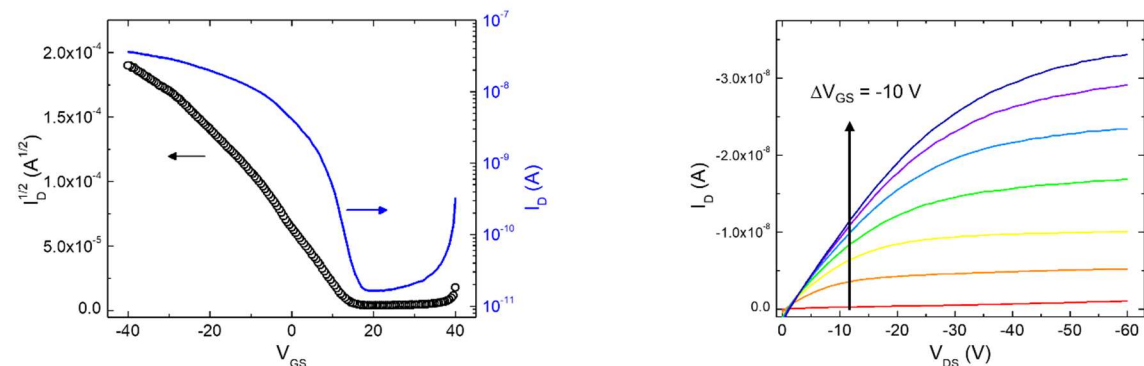


Figure S 49. Transfer (left) and transport curves for OFETs fabricated on cXPr-FADT thin films drop casted from a n-Butylbenzene solution.

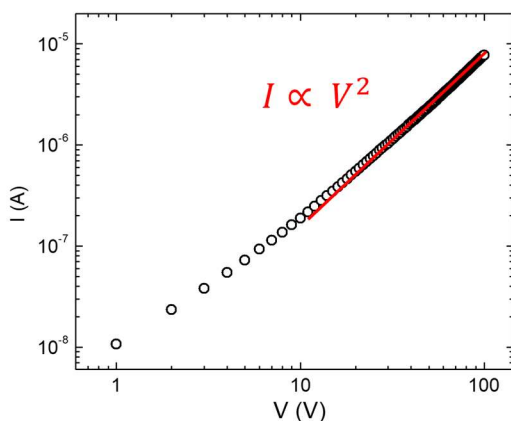


Figure S 50. Typical SCLC current-voltage curve used for bulk mobility calculation. The SCLC regime occurs at high voltage and it is marked in red.

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