Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Liquid crystalline dihydroazulene photoswitches

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Synthesis – Experimentals

4-((5-Bromopentyl)oxy)benzonitrile (**7a**); A mixture consisting of 4-cyanophenol **6** (9.35 g, 78.5 mmol), 1,5-dibromopentane **5a** (27 mL, 198 mmol) and K_2CO_3 (16.70 g, 121 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution of petroleum spirit to toluene) to afford **7a** (14.92 g, 71%) as a white solid. R_f=0.50 (toluene). M.p. = 54.0-55.9 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 1.97-1.91 (m, 2H), 1.87–1.81 (m, 2H), 1.67–1.60 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 134.1, 119.4, 115.3, 104.0, 68.1, 33.6, 32.5, 28.3, 24.8 ppm. MS (ESP +ve): *m/z* = 290 [$(M+Na)^+$]. Analysis calcd (%) for $C_{12}H_{14}BrNO$ (268.15): C 53.75, H 5.26, N 5.22; found: C 53.75, H 4.90, N 5.13.

4-((6-Bromohexyl)oxy)benzonitrile (**7b**); A mixture consisting of 4-cyanophenol **6** (3.50 g, 29.4 mmol), 1,6-dibromohexane **5b** (10 mL, 65.0 mmol) and K_2CO_3 (8.51 g, 61.6 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution of petroleum spirit to toluene) to afford **7b** (5.75 g, 69%) as a white solid. R_f=0.50 (toluene). M.p. = 44.0-46.5 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 1.90 (p, *J* = 6.6 Hz, 2H), 1.82 (p, *J* = 6.6 Hz, 2H), 1.53-1.50 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5, 134.1, 119.4, 115.3, 103.9, 68.3, 33.8, 32.7, 29.0, 28.0, 25.3 ppm. MS (ESP +ve): *m/z* = 282 [$(M+H)^+$]. Analysis calcd (%) for $C_{13}H_{16}BrNO$ (282.18): C 55.33, H 5.72, N 4.96; found: C 55.66, H 5.72, N 4.98.

4-((8-Bromooctyl)oxy)benzonitrile (**7c**); A mixture consisting of 4-cyanophenol **6** (5.49 g, 46.1 mmol), 1,8-dibromooctane **5c** (25.95 g, 95.4 mmol) and K_2CO_3 (9.40 g, 68.0 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution; petroleum spirit to toluene) to afford **7c** (9.92 g, 69%) as a white solid. R_f=0.50 (toluene). M.p. = 68.5-69.8 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.89-1.84 (m, 2H), 1.82-1.77 (m, 2H), 1.49–1.42 (m, 4H), 1.39-1.33 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5, 134.1, 119.4, 115.3, 103.8, 68.5, 34.1, 32.9, 29.2, 29.1, 28.8, 28.2, 26.0 ppm. MS (ESP +ve): *m/z* = 310 [$(M+H)^+$]. Analysis calcd (%) for $C_{15}H_{20}BrNO$ (310.24): C 58.07, H 6.50, N 4.51; found: C 58.26, H 6.53, N 4.51.

4-((9-Bromononyl)oxy)benzonitrile (**7d**); A mixture consisting of 4-cyanophenol **6** (5.17 g, 43.4 mmol), 1,9-dibromononane **5d** (24.71 g, 86.4 mmol) and K_2CO_3 (8.97 g, 64.9 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution; petroleum spirit to toluene) to afford **7d** (9.98 g, 71%) as a white solid. R_f=0.50 (toluene). M.p. = 64.1-65.7 ^oC.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.39 (t, *J* = 6.5 Hz, 2H), 1.86-1.75 (m, 4H), 1.46-1.39 (m, 4H), 1.36-1.29 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5, 134.0, 119.4, 115.2, 103.7, 68.4, 34.1, 32.8, 29.3, 29.2, 29.0, 28.7, 28.2, 25.9 ppm. MS (ESP +ve): *m/z* = 324 [$(M+H)^+$]. Analysis calcd (%) for $C_{16}H_{22}BrNO$ (324.26): C 59.27, H 6.84, N 4.32; found: C 59.52, H 6.93, N 4.32.

4-((10-Bromodecyl)oxy)benzonitrile (**7e**); A mixture consisting of 4-cyanophenol **6** (4.97 g, 41.7 mmol), 1,10-dibromodecane **5e** (30.68 g, 102 mmol) and K_2CO_3 (9.20 g, 66.6 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution; petroleum spirit to toluene) to afford **7e** (11.00 g, 78%) as a white solid. R_f=0.50 (toluene). M.p. = 73.2-74.7 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.88-1.77 (m, 4H), 1.48-1.40 (m, 4H), 1.36-1.28 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.6, 134.1, 119.5, 115.3, 103.8, 68.5, 34.2, 32.9, 29.5, 29.5, 29.4, 29.1, 28.9, 28.3, 26.1 ppm. MS (ESP +ve): *m/z* = 360 [$(M+Na)^+$]. Analysis calcd (%) for $C_{17}H_{24}BrNO$ (338.29): C 60.36, H 7.15, N 4.14; found: C 60.53, H 7.19, N 4.15.

4-((5-(4-Acetylphenoxy)pentyl)oxy)benzonitrile (**9a**); A mixture consisting of 4-hydroxyacetophenone **8** (2.69 g, 19.8 mmol), **7a** (4.48 g, 16.7 mmol) and K_2CO_3 (2.98 g, 21.6 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH_2Cl_2 (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO_2 column (CH_2Cl_2) to afford **9a** (4.42 g, 82%) as a white solid. R_f=0.39. M.p. = 100.8-102.8 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.06 (t, *J* = 6.2 Hz, 2H), 4.04 (t, *J* = 6.3 Hz, 2H), 2.55 (s, 3H), 1.92-1.87 (m, 4H), 1.70-1.64 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.0, 162.4, 134.1, 130.7, 130.4, 119.4, 115.3, 114.2, 104.0, 68.2, 68.0, 29.0, 28.9, 26.5, 22.8 ppm. HRMS (MALDI +ve) calcd for $C_{20}H_{22}NO_3$ ([M+H]$^+$): *m/z* = 324.1594; exp 324.1595. Analysis calcd (%) for $C_{20}H_{21}NO_3$ (323.39): C 74.28, H 6.55, N 4.33; found: C 74.09, H 6.28, N 4.27.

4-((6-(4-Acetylphenoxy)hexyl)oxy)benzonitrile (**9b**); A mixture consisting of 4-hydroxyacetophenone **8** (2.26 g, 16.6 mmol), **7b** (4.00 g, 14.2 mmol) and K_2CO_3 (4.27 g, 30.9 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH_2Cl_2 (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO_2 column (CH_2Cl_2) to afford **9b** (4.26 g, 89%) as a white solid. R_f=0.33. M.p. = 99.5-101.3 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.55 (s, 3H), 1.87-1.82 (m, 4H), 1.57-1.55 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.1, 162.5, 134.1, 130.7, 130.4, 119.4, 115.3, 114.2, 103.9, 68.3, 68.1, 29.2, 29.1, 26.5, 25.9, 25.9 ppm. HRMS (MALDI +ve) calcd for $C_{21}H_{24}NO_3$ ([M+H]$^+$): *m/z* = 338.1751; exp 338.1751. Analysis calcd (%) for $C_{21}H_{23}NO_3$ (337.42): C 74.75, H 6.87, N 4.15; found: C 74.60, H 6.73, N 3.99.

4-((8-(4-Acetylphenoxy)octyl)oxy)benzonitrile (**9c**); A mixture consisting of 4-hydroxyacetophenone **8** (2.61 g, 19.2 mmol), **7c** (4.94 g, 15.9 mmol) and K_2CO_3 (4.75 g, 34.4 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH_2Cl_2 (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO_2 column (CH_2Cl_2) to afford **9c** (3.64 g, 63%) as a white solid. R_f=0.35. M.p. = 91.1-92.3 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.99 (d, *J* = 6.5 Hz, 2H), 2.55 (s, 3H), 1.84-1.78 (m, 4H), 1.50-1.45 (m, 4H), 1.41-1.38 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.2, 162.5, 134.1, 130.7, 130.3, 119.4, 115.3, 114.2, 103.8, 68.5, 68.3, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.0 ppm. HRMS (MALDI +ve) calcd for $C_{23}H_{28}NO_3Na$ ($[M+Na]^+$): *m/z* = 388.1883; exp 388.1884. Analysis calcd (%) for $C_{23}H_{27}NO_3$ (365.47): C 75.59, H 7.45, N 3.83; found: C 75.51, H 7.28, N 3.78.

4-((9-(4-Acetylphenoxy)nonyl)oxy)benzonitrile (**9d**); A mixture consisting of 4-hydroxyacetophenone **8** (2.47 g, 18.1 mmol), **7d** (4.96 g, 15.3 mmol) and K_2CO_3 (5.20 g, 37.6 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH_2Cl_2 (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO_2 column (CH_2Cl_2) to afford **9d** (5.54 g, 95%) as a white solid. R_f=0.35. M.p. = 86.4-87.2 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 2.55 (s, 3H), 1.83-1.77 (m, 4H), 1.49-1.43 (m, 4H), 1.39-1.35 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.2, 162.6, 134.1, 130.7, 130.3, 119.5, 115.3, 114.3, 103.8, 68.5, 68.3, 29.6, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.1 ppm. HRMS (MALDI +ve) calcd for $C_{24}H_{30}N_3O_2$ ($[M+H]^+$): *m/z* = 380.2220; exp 380.2221. Analysis calcd (%) for $C_{24}H_{29}NO_3$ (379.50): C 75.96, H 7.70, N 3.69; found: C 75.82, H 7.68, N 3.55.

4-((10-(4-Acetylphenoxy)decyl)oxy)benzonitrile (**9e**); A mixture consisting of 4-hydroxyacetophenone **8** (2.51 g, 18.4 mmol), **7e** (5.16 g, 15.3 mmol) and K_2CO_3 (5.10 g, 36.9 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH_2Cl_2 (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO_2 column (CH_2Cl_2) to afford **9e** (5.12 g, 85%) as a white solid. R_f=0.40. M.p. = 71.5-73.5 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.99 (d, *J* = 6.5 Hz, 2H), 2.55 (s, 3H), 1.83-1.76 (m, 4H), 1.48-1.42 (m, 4H), 1.37-1.32 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 163.2, 162.6, 134.1, 130.7, 130.3, 119.4, 115.3, 114.2, 103.8, 68.5, 68.4, 29.6, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.1 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{25}H_{32}NO_3$ ($[M+H]^+$): *m/z* = 394.2377; exp 394.2377. Analysis calcd (%) for $C_{25}H_{31}NO_3$ (393.53): C 76.30, H 7.94, N 3.56; found: C 76.29, H 7.90, N 3.52.

2-(1-(4-((5-(4-Cyanophenoxy)pentyl)oxy)phenyl)ethylidene)malononitrile (**13a**); A biphasic mixture of **9a** (2.27 g, 7.02 mmol), malononitrile (1.66 g, 25.1 mmol), NH_4OAc (2.20 g, 28.5 mmol) in toluene (100 mL) and AcOH (4 mL) was heated using a Dean-Stark

apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was recrystallized from CH_2Cl_2/MeOH to give **13a** (2.02 g, 77%), as a yellowish solid. R_f=0.65 (CH_2Cl_2). M.p. = 83.2-84.9, 95.6-100.3 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H) 6.97 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.06 (t, J = 6.2 Hz, 2H), 4.04 (t, J = 6.2 Hz, 2H), 2.61 (s, 3H), 1.92-1.87 (m, 4H), 1.70-1.64 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.1, 162.7, 162.4, 134.1, 130.0, 127.9, 119.4, 115.3, 115.0, 113.8, 113.5, 104.0, 82.0, 68.2, 28.9, 28.8, 23.9, 22.8 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{23}H_{22}N_3O_2$ ($[M+H]^+$): m/z = 372.1707; exp 372.1707. Analysis calcd (%) for $C_{23}H_{21}N_3O_2$ (371.44): C 74.37, H 5.70, N 11.31; found: C 73.41, H 5.76, N 10.80.

2-(1-(4-((6-(4-Cyanophenoxy)hexyl)oxy)phenyl)ethylidene)malononitrile (**13b**); A biphasic mixture of **9b** (2.57 g, 7.62 mmol), malononitrile (1.85 g, 28.0 mmol), NH_4OAc (3.40 g, 44.1 mmol) in toluene (100 mL) and AcOH (4 mL) was heated using a Dean-Stark apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2) to give **13b** (2.42 g, 82%), as a white solid. R_f=0.61 (CH_2Cl_2). M.p. = 62.5-64.5 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H) 6.97 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 4.02 (t, J = 6.3 Hz, 2H), 2.61 (s, 3H), 1.86-1.83 (m, 4H), 1.57-1.54 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.1, 162.8, 162.5, 134.1, 130.0, 127.9, 119.4, 115.3, 115.0, 113.8, 113.5, 103.9, 82.0, 68.3, 29.1, 29.1, 25.9, 25.9, 23.9 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{24}H_{24}N_3O_2$ ($[M+H]^+$): m/z = 386.1858; exp 386.1864. Analysis calcd (%) for $C_{24}H_{23}N_3O_2$ (385.47): C 74.78, H 6.01, N 10.90; found: C 74.75, H 5.73, N 10.81.

2-(1-(4-((8-(4-Cyanophenoxy)octyl)oxy)phenyl)ethylidene)malononitrile (**13c**); A biphasic mixture of **9c** (2.53 g, 6.92 mmol), malononitrile (1.56 g, 23.6 mmol), NH_4OAc (2.88 g, 37.4 mmol) in toluene (100 mL) and AcOH (4 mL) was heated using a Dean-Stark apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2) to give **13c** (2.02 g, 71%), as a white solid. R_f=0.62 (CH_2Cl_2). M.p. = 67.0-67.7 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.9 Hz, 2H) 7.00 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.64 (s, 3H), 1.87-1.81 (m, 4H), 1.54-1.48 (m, 4H), 1.46-1.41 ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 119.5, 115.2, 114.9, 113.9, 113.6, 103.7, 81.8, 68.4, 29.4, 29.1, 29.1, 26.0, 26.0, 24.0 ppm. HRMS (MALDI +ve) calcd for $C_{26}H_{28}N_3O_2$ ($[M+H]^+$): m/z = 414.2176; exp 414.2177. Analysis calcd (%) for $C_{26}H_{27}N_3O_2$ (413.52): C 75.52, H 6.58, N 10.16; found: C 75.13, H 6.29, N 10.19.

2-(1-(4-((9-(4-Cyanophenoxy)nonyl)oxy)phenyl)ethylidene)malononitrile (**13d**); A biphasic mixture of **9d** (3.11 g, 8.19 mmol), malononitrile (2.47 g, 37.4 mmol), NH_4OAc (6.15 g, 79.8 mmol) in toluene (100 mL) and AcOH (7 mL) was heated using a Dean-Stark apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2) to give **13d** (3.08 g, 88%), as a white solid. R_f=0.68 (CH_2Cl_2). M.p. = 87.1-88.1 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 2.61 (s, 3H), 1.83-1.77 (m, 4H), 1.49-1.43 (m, 4H), 1.39-1.35 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 119.5, 115.3, 115.0, 113.9, 113.6, 103.7, 81.8, 68.5, 68.5, 29.6, 29.4, 29.1, 29.1, 26.1, 26.0, 23.9 ppm, 1C masked. HRMS (MALDI +ve) calcd for $C_{27}H_{29}N_3O_2Na$ ($[M+Na]^+$): *m/z* = 450.2157; exp 450.2153. Analysis calcd (%) for $C_{27}H_{29}N_3O_2$ (427.55): C 75.85, H 6.84, N 9.83; found: C 75.50, H 6.81, N 9.80.

2-(1-(4-((10-(4-Cyanophenoxy)decyl)oxy)phenyl)ethylidene)malononitrile (**13e**); A biphasic mixture of **9e** (3.01 g, 7.65 mmol), malononitrile (2.39 g, 36.2 mmol), NH_4OAc (4.95 g, 64.2 mmol) in toluene (100 mL) and AcOH (6 mL) was heated using a Dean-Stark apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2) to give **13e** (2.80 g, 83%), as a white solid. R_f=0.65 (CH_2Cl_2). M.p. = 62.6-63.8 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 2.61 (s, 3H), 1.83-1.77 (m, 4H), 1.47-1.43 (m, 4H), 1.37-1.31 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 199.5, 115.3, 115.0, 113.9, 113.6, 103.7, 81.8, 68.5, 68.5, 29.6, 29.4, 29.1, 29.1, 26.1, 26.0, 23.9 ppm, 2Cs masked. HRMS (MALDI +ve) calcd for $C_{28}H_{32}N_3O_2$ ($[M+H]^+$): *m/z* = 442.2489; exp 442.2491. Analysis calcd (%) for $C_{28}H_{31}N_3O_2$ (441.58): C, 76.16; H, 7.08; N, 9.52; found: C 76.30, H 7.07, N 9.50.

2-(1-(4'-(Octyloxy)-[1,1'-biphenyl]-4-yl)ethylidene)malononitrile (**13f**); A mixture of **9f** (5.57 g, 17.2 mmol), malononitrile (3.55 g, 53.7 mmol) and NH_4OAc (4.69 g, 60.8 mmol) in toluene (300 mL) and AcOH (6.5 mL, 113 mmol) was equipped with a Dean-Stark trap and heated to reflux point for 5 h. Additional malononitrile (2.13 g, 32.2 mmol), NH_4OAc (2.26 g, 29.3 mmol) and glacial AcOH (3.2 mL, 56 mmol) were added and the mixture heated an additional 2 h. A third portion of malononitrile (2.18 g, 33.0 mmol), NH_4OAc (2.39 g, 31.0 mmol) and glacial AcOH (3.2 mL, 56 mmol) was added and the mixture heated an additional 3 h. The contents of the vessel were allowed to cool to rt, washed with water (4 x 250 mL) and brine (1 x 250 mL), dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude residue was crystallized from CH_2Cl_2/heptane to give pure **13f** (4.60 g, 70%) as a white solid. R_f=0.56 (toluene). M.p. = 58.6–59.4 ^oC. ^1H NMR

(500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 2.67 (s, 3H), 1.84–1.78 (m, 2H), 1.51–1.45 (m, 2H), 1.40–1.26 (m, 8H), 0.90 (t, *J* = 6.9 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.7, 159.9, 145.2, 133.8, 131.5, 128.4, 128.3, 127.1, 115.2, 113.2, 83.8, 68.3, 32.0, 29.5, 29.4, 29.4, 26.2, 24.1, 22.8, 14.3 ppm. HRMS (MALDI +ve) calcd for $C_{25}H_{28}N_2ONa$ [$(M+Na)^+$]: *m/z* = 395.2094; exp 395.2102. Analysis calcd (%) for $C_{25}H_{28}N_2O$ (372.51): C 80.61, H 7.58, N 7.52; found: C 80.67, H 7.67, N 7.38.

2-(1-(2',3'-Difluoro-4'-(octyloxy)-[1,1'-biphenyl]-4-yl)ethylidene)malononitrile (**13g**); A mixture of **9g** (4.62 g, 12.8 mmol), malononitrile (2.38 g, 36.0 mmol) and NH_4OAc (3.39 g, 44.0 mmol) in toluene (300 mL) and AcOH (4.8 mL, 84 mmol) was equipped with a Dean-Stark trap and heated to reflux point for 3 h. Additional malononitrile (2.76 g, 41.8 mmol), NH_4OAc (3.53 g, 45.8 mmol) and AcOH (4.8 mL, 84 mmol) were added and the mixture was refluxed for a further 2 h. TLC analysis indicated the presence of **9g** and therefore additional malononitrile (1.89 g, 28.6 mmol), NH_4OAc (1.98 g, 25.7 mmol) and AcOH (2.52 g, 2.4 mL, 41.9 mmol) were added and the reaction mixture was refluxed for 2 h. The reaction mixture was allowed to cool to rt, washed with water (4 x 250 mL), dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and the residue crystallized from CH_2Cl_2/heptane to give **13g** (3.75 g, 72%) as a white solid. R_f=0.61 (toluene). M.p. = 59.5–60.4 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (apparent s, 4H), 7.16–7.10 (ddd, *J* = 8.7, 8.2, 2.4, 1H), 6.83 (ddd, *J* = 9.1, 7.5, 1.8 Hz, 1H), 4.09 (t, *J* = 6.6 Hz, 2H), 2.68 (s, 3H), 1.92–1.81 (m, 2H), 1.54–1.44 (m, 2H), 1.42–1.22 (m, 8H), 0.89 (t, *J* = 6.8, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.7, 149.1 (dd, *J* = 250, 11.4 Hz), 149.0 (dd, *J* = 8.1, 3.1 Hz), 141.9 (dd, *J* = 248.2, 14.8 Hz), 139.3, 134.9, 129.4, 129.4, 127.9, 123.8, 123.7, 123.7, 121.2, 121.1, 113.1, 112.9, 109.9, 84.7, 70.1, 31.9, 29.4, 29.4, 29.3, 26.0, 24.3, 22.8, 14.2 ppm. HRMS (MALDI +ve) calcd for $C_{25}H_{27}F_2N_2O$ [$(M+H)^+$]: *m/z* = 409.2086; exp 409.2095. Analysis calcd (%) for $C_{25}H_{26}F_2N_2O$ (408.49): C 73.51, H 6.42, N 6.86; found: C 73.33, H 6.30, N 6.78.

2-(1-(2,3-Difluoro-4-(octyloxy)phenyl)ethylidene)malononitrile (**13h**); A mixture consisting of **9h** (5.84 g, 20.6 mmol), malononitrile (3.83 g, 57.9 mmol) and NH_4OAc (5.44 g, 70.6 mmol) in toluene (250 mL) and AcOH (7.75 mL, 135 mmol) was heated using a Dean-Stark apparatus for 1 h. The reaction was not determined to be complete by TLC and malononitrile (3.98 g 60.3 mmol), NH_4OAc (5.32 g, 69.0 mmol) and AcOH (7.75 mL, 135 mmol) were added to the vessel and the mixture was refluxed for a further 2 h. Extra malononitrile (3.71 g, 56.2 mmol), NH_4OAc (5.45 g, 70.7 mmol) and AcOH (7.75 mL, 135 mmol) were again added and the reaction mixture was heated for 2 h and allowed to cool to rt. The reaction mixture was washed with water (4 x 240 mL) and brine (1 x 250 mL), dried with $MgSO_4$, filtered and concentrated under reduced pressure to the give pure **13h** (6.79 g, 99%) as an off-white solid. R_f=0.62 (toluene); M.p. = 59.1–60.5 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13 (ddd, *J* = 9.9, 7.6, 2.2 Hz, 1H), 6.82 (ddd, *J* = 9.9, 7.2, 1.8 Hz, 1H), 4.09 (t, *J* = 6.5 Hz, 2H), 2.61 (d, *J* = 1.6 Hz, 3H), 1.92–1.74 (m, 2H), 1.50–1.39 (m, 2H), 1.41–1.19 (m, 8H), 0.94–0.76 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3 (dd, *J* = 2.5, 1.5 Hz), 151.9 (dd, *J* = 8.1, 3.7 Hz), 148.5 (dd, *J* = 254.3, 12.1 Hz), 141.6, (dd, *J* = 251.7, 13.8 Hz), 123.2 (dd, *J* = 4.5, 3.2 Hz), 117.4 (d, *J* = 10.6 Hz), 112.2, 112.1, 109.3 (dd, *J* = 3.1, 1.3 Hz),

87.3, 70.1, 31.8, 29.2, 29.2, 28.9, 25.8, 24.1 (d, *J* = 4.6 Hz), 22.7, 14.1 ppm; HRMS (MALDI +ve) calcd for $C_{19}H_{22}F_2N_2ONa$ [(M+Na)$^+$]:*m/z*: 355.1592, found *m/z* = 355.1600.

2-(1-(4-Octylphenyl)ethylidene)malononitrile (**13i**); A biphasic mixture consisting of **9i** (20.02 g, 86.16 mmol), malononitrile (15.39 g, 233.0 mmol) and NH_4OAc (22.03 g, 285.8 mmol) in toluene (250 mL) and AcOH (32.0 mL, 559 mmol) was heated using a Dean-Stark apparatus for 3 h. The vessel was allowed to cool to rt and the reaction mixture washed with water (5 x 200 mL), dried over $MgSO_4$, filtered and concentrated under vacuum to give **13i** (24.16 g; 100%) as a white solid. R_f=0.65 (toluene). M.p. = 51.5–52.0 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.63 (s, 3H), 1.66-1.1.60 (m, 2H), 1.35-1.27 (m, 10H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.3, 148.5, 133.3, 129.3, 127.7, 113.3, 113.2, 83.7, 36.1, 32.0, 31.2, 29.5, 29.4, 29.3, 24.2, 22.8, 14.2 ppm. HRMS (MALDI +ve) calcd for $C_{19}H_{24}N_2Na$ ([M+Na]$^+$): *m/z* = 303.1831; exp 303.1838. Analysis calcd (%) for $C_{19}H_{24}N_2$ (280.42): C 81.38, H 8.63, N 9.99; found: C 81.60, H 8.62, N 10.05.

4-((5-Azidopentyl)oxy)benzonitrile (**14a**); To a solution of **7a** (2.04 g, 7.61 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN_3 (876 mg, 13.5 mmol) and the contents of the reaction vessel were heated to 50 ^oC for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et_2O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over $MgSO_4$, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave **14a** (1.66 g, 95%) as a white solid. R_f=0.41. M.p. = 29.1-30.5 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 3.32 (t, *J* = 6.7 Hz, 2H), 1.84 (p, *J* = 6.3 Hz, 2H), 1.68 (p, *J* = 6.7 Hz, 2H), 1.65–1.51 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 134.1, 119.4, 115.3, 104.0, 68.1, 51.4, 28.7, 28.7, 23.5 ppm. HRMS (ESP +ve) calcd for $C_{12}H_{14}N_4ONa$ ([M+Na]$^+$): *m/z* = 231.1060; exp 253.1060.

4-((6-Azidohexyl)oxy)benzonitrile (**14b**); To a solution of **7b** (1.14 g, 4.04 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN_3 (550 mg, 8.46 mmol) and the contents of the vessel allowed to stir at 50 ^oC for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et_2O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over $MgSO_4$, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave **14b** (870 mg, 88%) as a white solid. R_f=0.42. M.p. = 37.4-40.5 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 3.29 (t, *J* = 6.8 Hz, 2H), 1.82 (p, *J* = 6.4 Hz, 2H), 1.64 (p, *J* = 6.8 Hz, 2H), 1.57–1.42 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5, 134.1, 119.4, 115.3, 103.9, 68.3, 51.5, 29.0, 28.9, 26.6, 25.7 ppm. HRMS (ESP +ve) calcd for $C_{13}H_{16}N_4ONa$ ([M+Na]$^+$): *m/z* = 267.1217; exp 267.1216.

4-((8-Azidooctyl)oxy)benzonitrile (**14c**); To a solution of **7c** (1.56 g, 5.03 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN_3 (512 mg, 7.88 mmol) and the contents of the vessel were allowed to stir at 50 ^oC for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et_2O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over $MgSO_4$, filtered and the volatiles

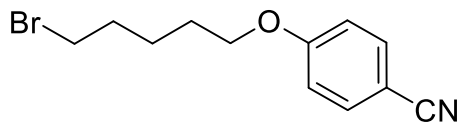
removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) afforded **14c** (966 mg, 71%) as a white solid. R_f=0.44. M.p. = 33.9-36.5 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.26 (t, *J* = 6.6 Hz, 2H), 1.80 (p, *J* = 6.5 Hz, 2H), 1.63–1.56 (m, 2H), 1.53–1.16 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5, 134.1, 119.4, 115.3, 103.8, 68.5, 51.6, 29.3, 29.2, 29.1, 28.9, 26.8, 26.0 ppm. HRMS (ESP +ve) calcd for $C_{15}H_{20}N_4ONa$ ($[M+Na]^+$): *m/z* = 295.1529; exp 295.1530.

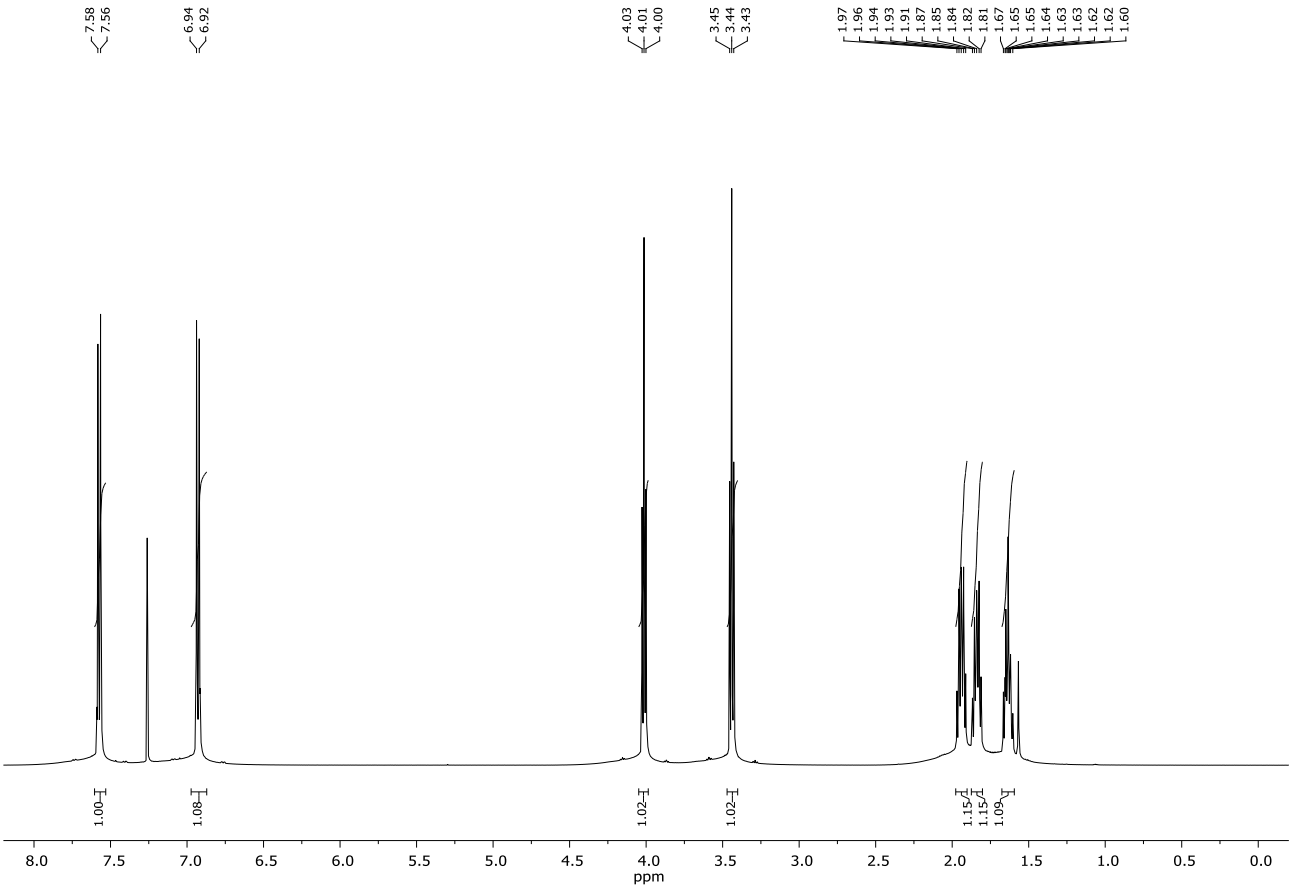
4-((9-Azidononyl)oxy)benzonitrile (**14d**); To a solution of **7d** (3.35 g, 10.3 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN_3 (1.01 g, 15.5 mmol) and the contents of the vessel allowed to stir at 50 ^{o}C for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et_2O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over $MgSO_4$, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave **14d** (2.52 g, 85%) as a white solid. R_f=0.49. M.p. = 42.5-43.2 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.99 (t, *J* = 6.56 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 1.79 (t, *J* = 6.56 Hz, 2H), 1.60 (t, *J* = 6.8 Hz, 2H), 1.51–1.25 (m, 10H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.6, 134.1, 119.5, 115.3, 103.8, 68.5, 51.6, 29.5, 29.3, 29.2, 29.1, 29.0, 26.8, 26.0 ppm. HRMS (ESP +ve) calcd for $C_{16}H_{22}N_4ONa$ ($[M+Na]^+$): *m/z* = 309.1687; exp 309.1686.

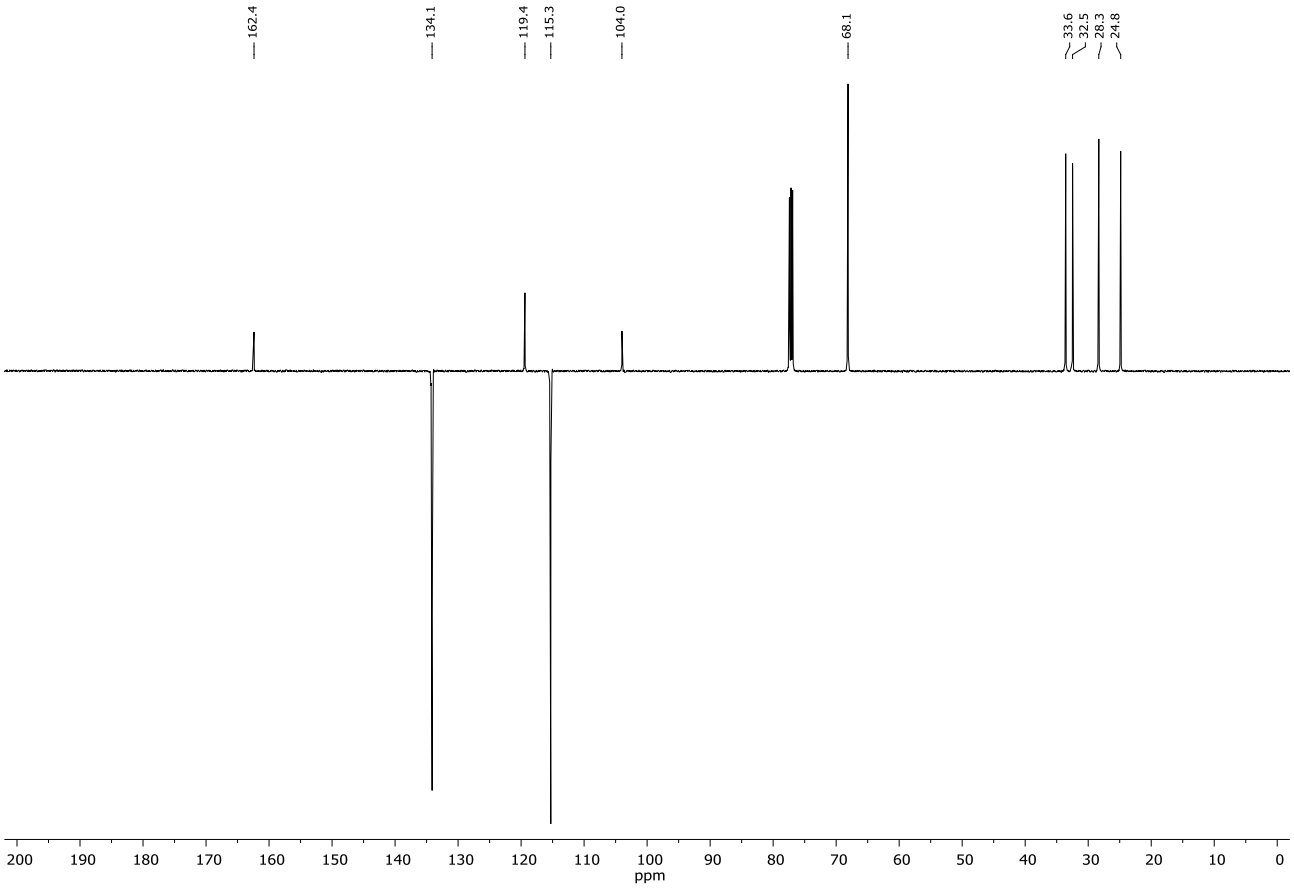
4-((10-Azidodecyl)oxy)benzonitrile (**14e**); To a solution of **7f** (3.40 g, 10.1 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN_3 (982 mg, 15.1 mmol) and the contents of the vessel allowed to stir at 50 ^{o}C for 2 h. The cooled reaction mixture was poured into ice- water (ca. 50 g) and extracted with Et_2O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over $MgSO_4$, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave **14f** (2.68 g, 89%) as a white solid. R_f=0.49. M.p. = 46.7-47.7 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.26 (t, *J* = 6.9 Hz, 2H), 1.80 (p, *J* = 6.6 Hz, 2H), 1.60 (p, *J* = 6.9 Hz, 2H), 1.48–1.31 (m, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4, 134.0, 119.3, 115.2, 103.7, 68.4, 51.5, 29.4, 29.4, 29.3, 29.1, 29.0, 28.8, 26.7, 25.9 ppm. HRMS (ESP +ve) calcd for $C_{17}H_{24}N_4ONa$ ($[M+Na]^+$): *m/z* = 323.1842; exp 323.1842.

NMR Spectra

Compound 7a



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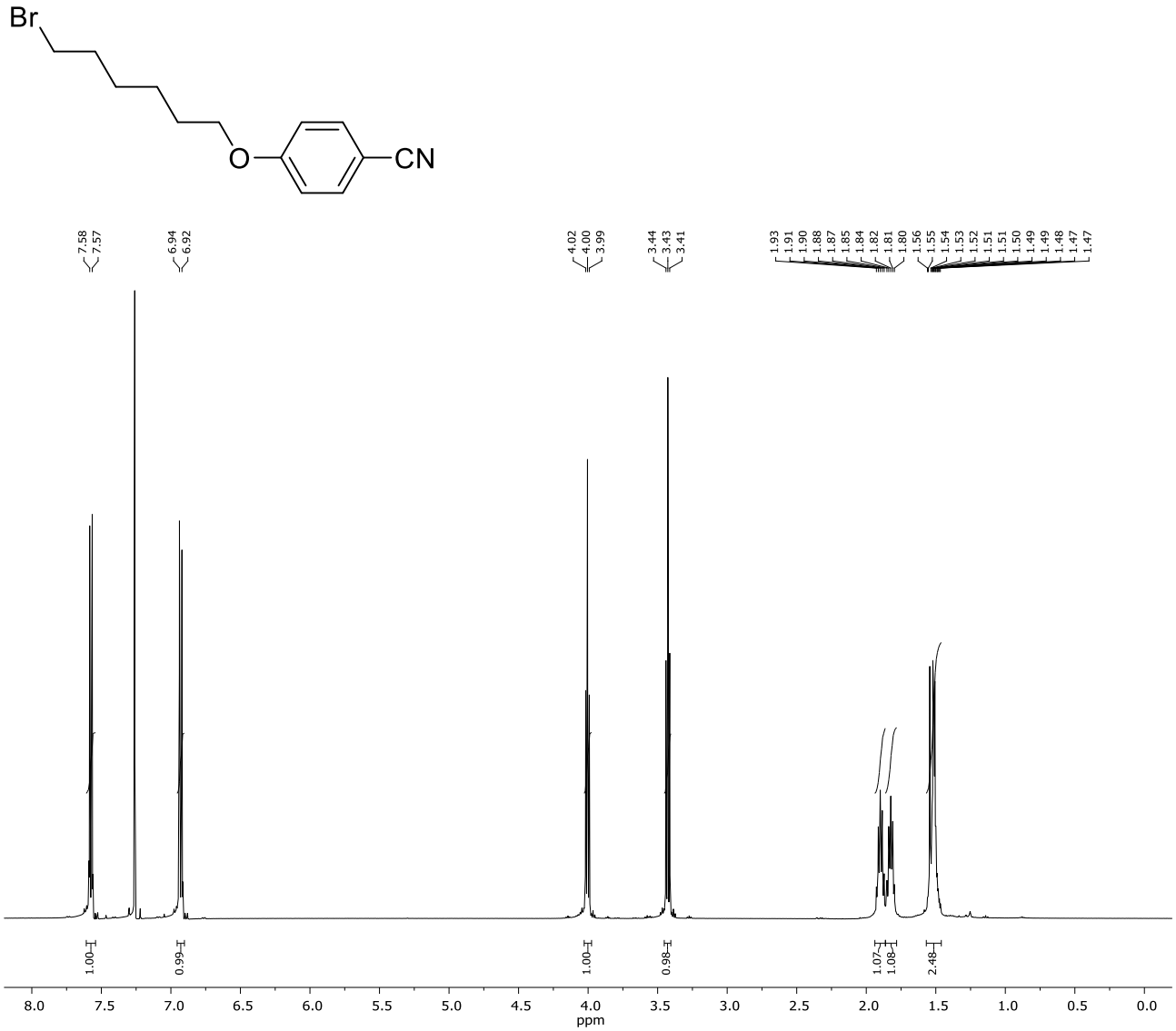
Compound 7b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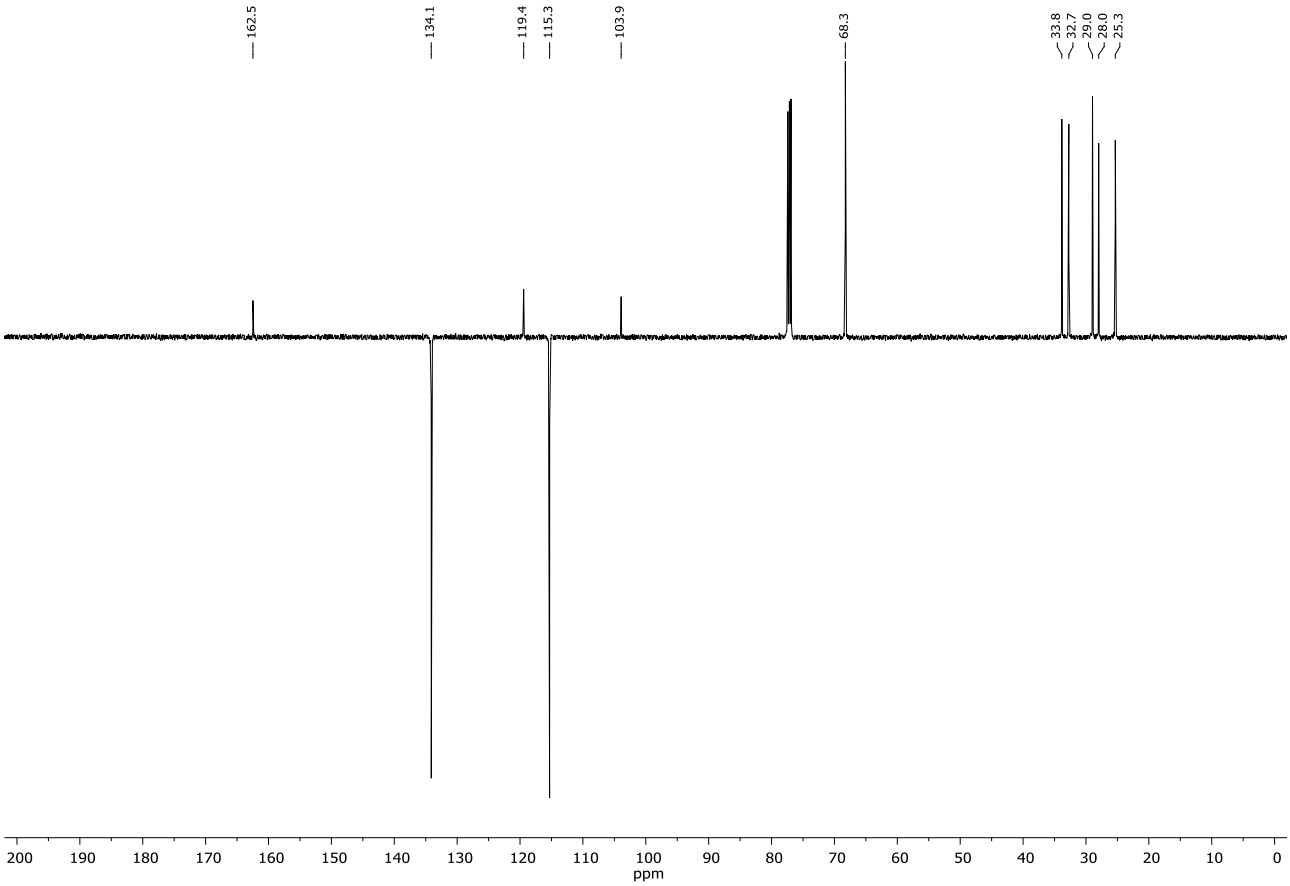
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134.1
119.4
115.3
103.9
68.3
33.8
32.7
29.0
28.0
25.3
200
190
180
170
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120
110
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80
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60
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40
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0
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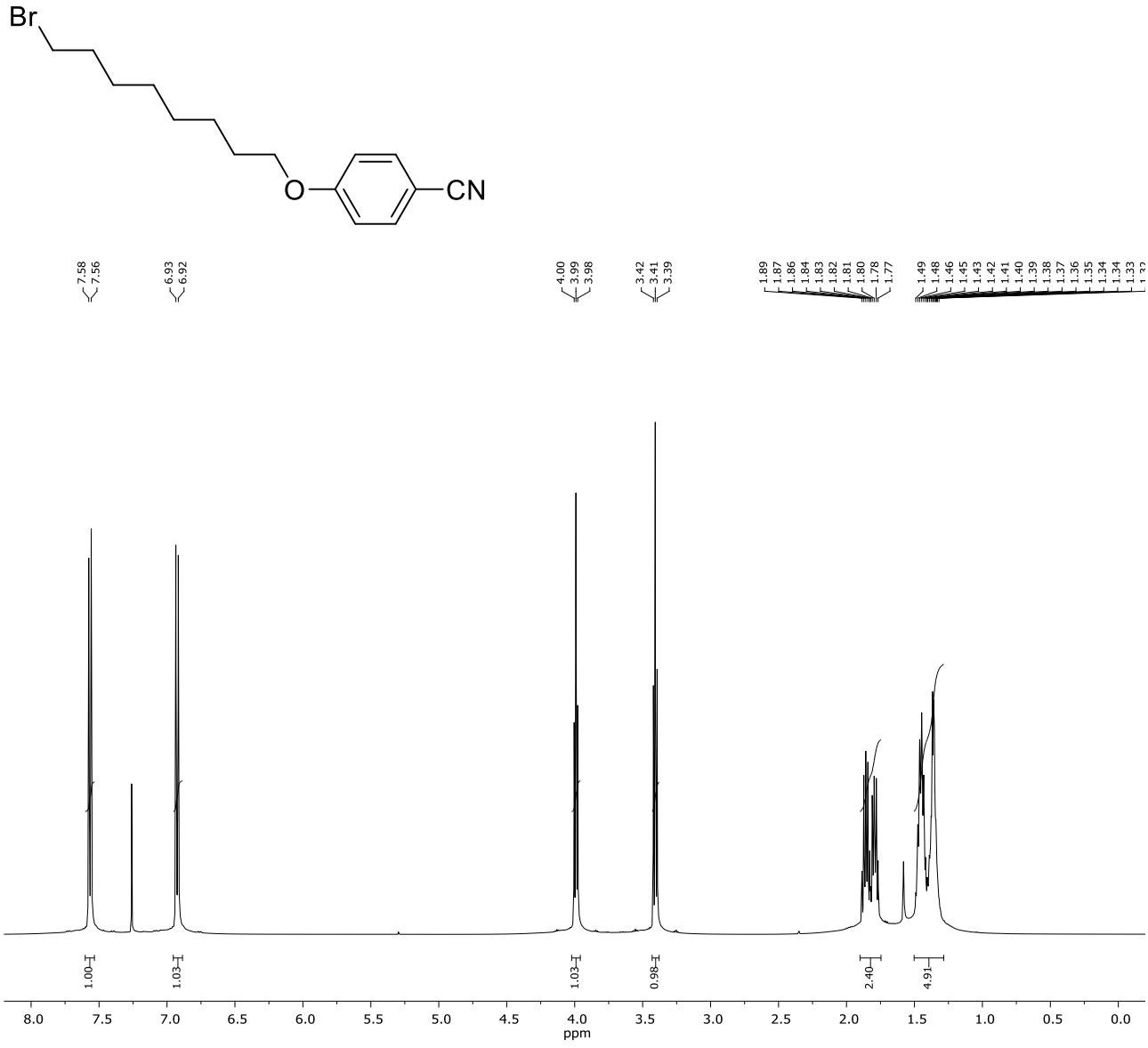
Compound 7c


Br
O
CN
7.58
7.56
6.93
6.92
4.00
3.99
3.98
3.42
3.41
3.39
1.89
1.87
1.86
1.84
1.83
1.82
1.81
1.80
1.78
1.77
1.49
1.48
1.46
1.45
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.36
1.35
1.34
1.34
1.33
1.00
1.03
1.03
0.98
2.40
4.91
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
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1.5
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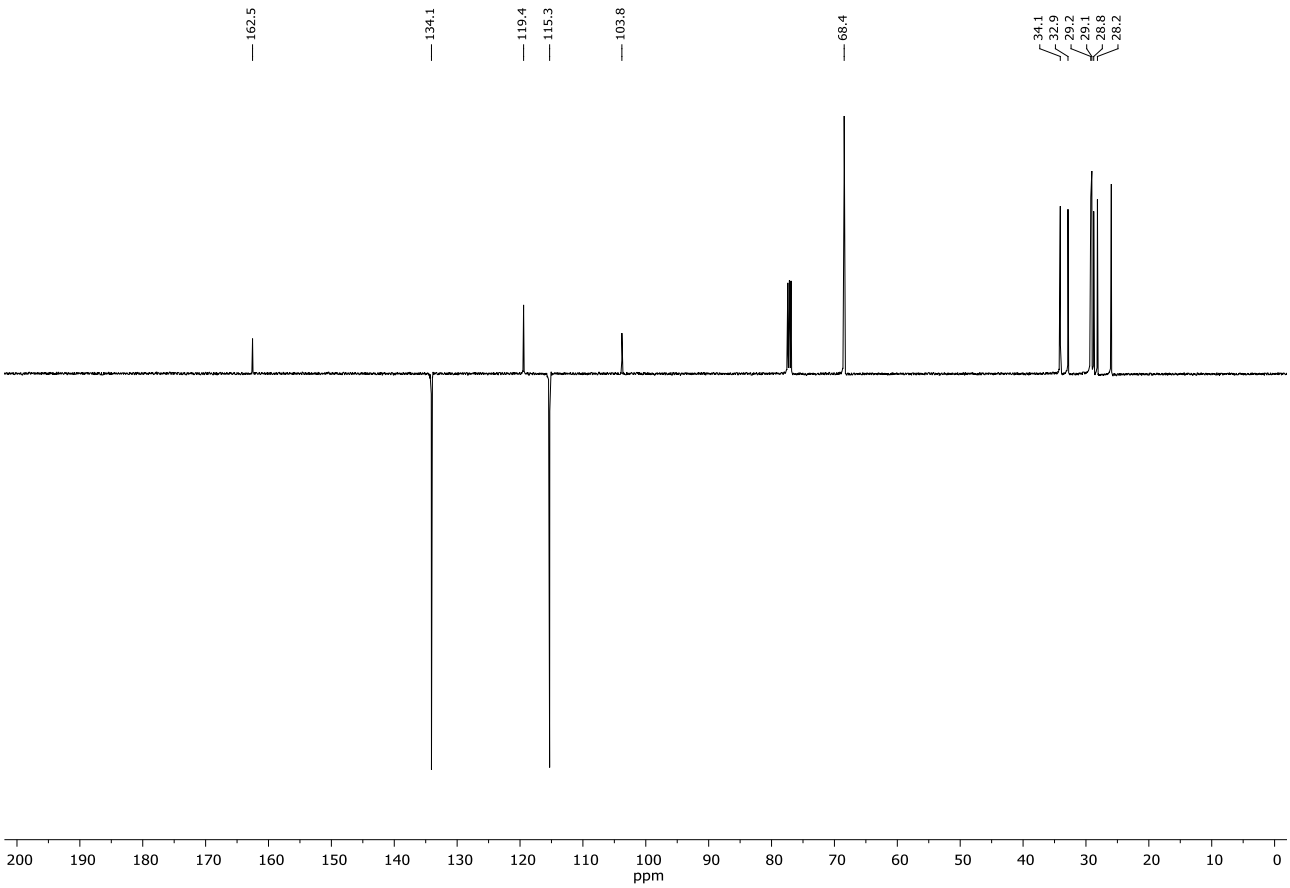
ppm


162.5
134.1
119.4
115.3
103.8
68.4
34.1
32.9
29.2
29.1
28.8
28.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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40
30
20
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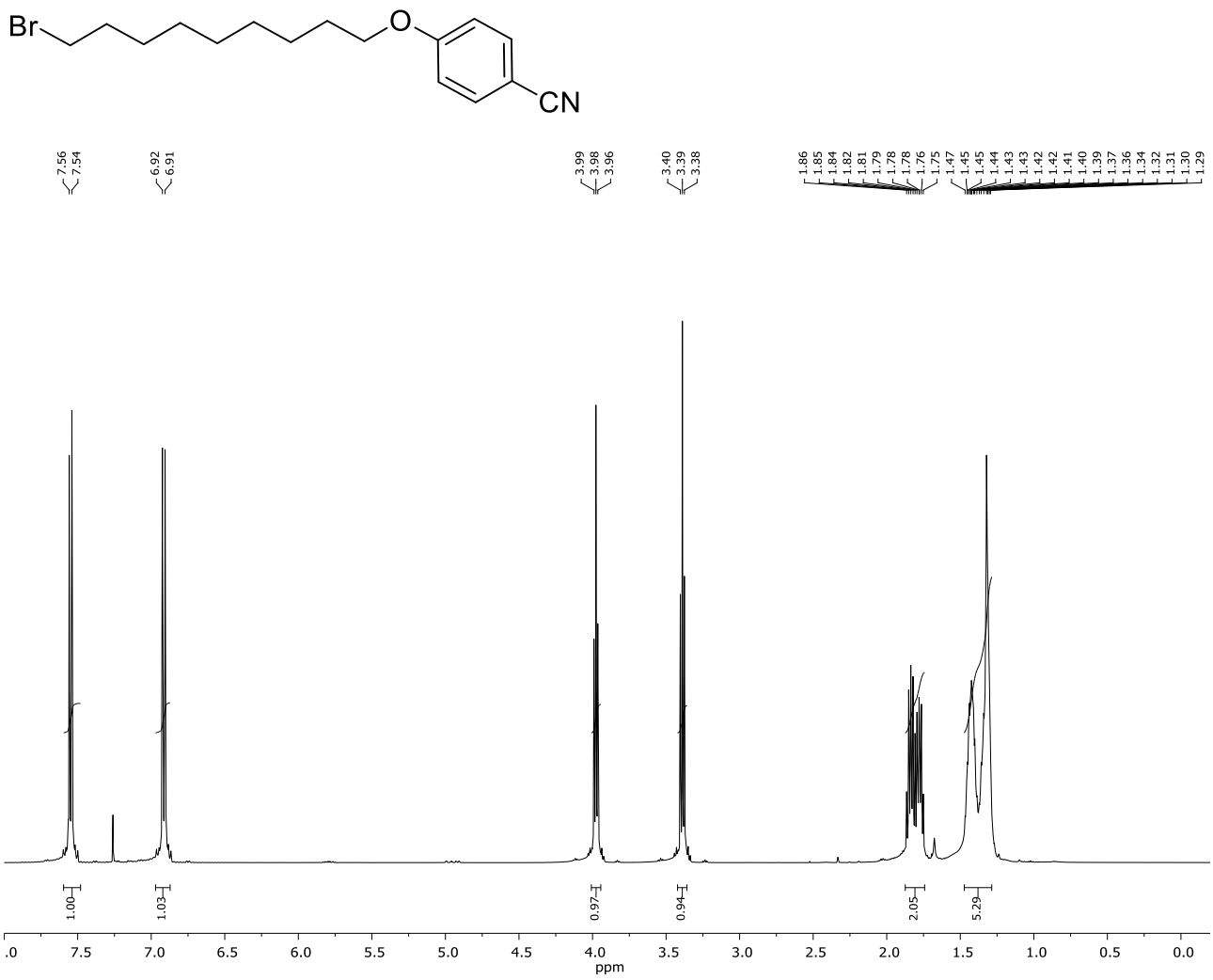
0
ppm

Compound 7d


Br
O
CN
7.56
7.54
6.92
6.91
3.99
3.98
3.96
3.40
3.39
3.38
1.86
1.85
1.84
1.82
1.81
1.79
1.78
1.78
1.76
1.75
1.47
1.45
1.45
1.44
1.43
1.43
1.42
1.42
1.41
1.40
1.39
1.37
1.36
1.34
1.32
1.31
1.30
1.29
1.00
1.03
0.97
0.94
2.05
5.29
.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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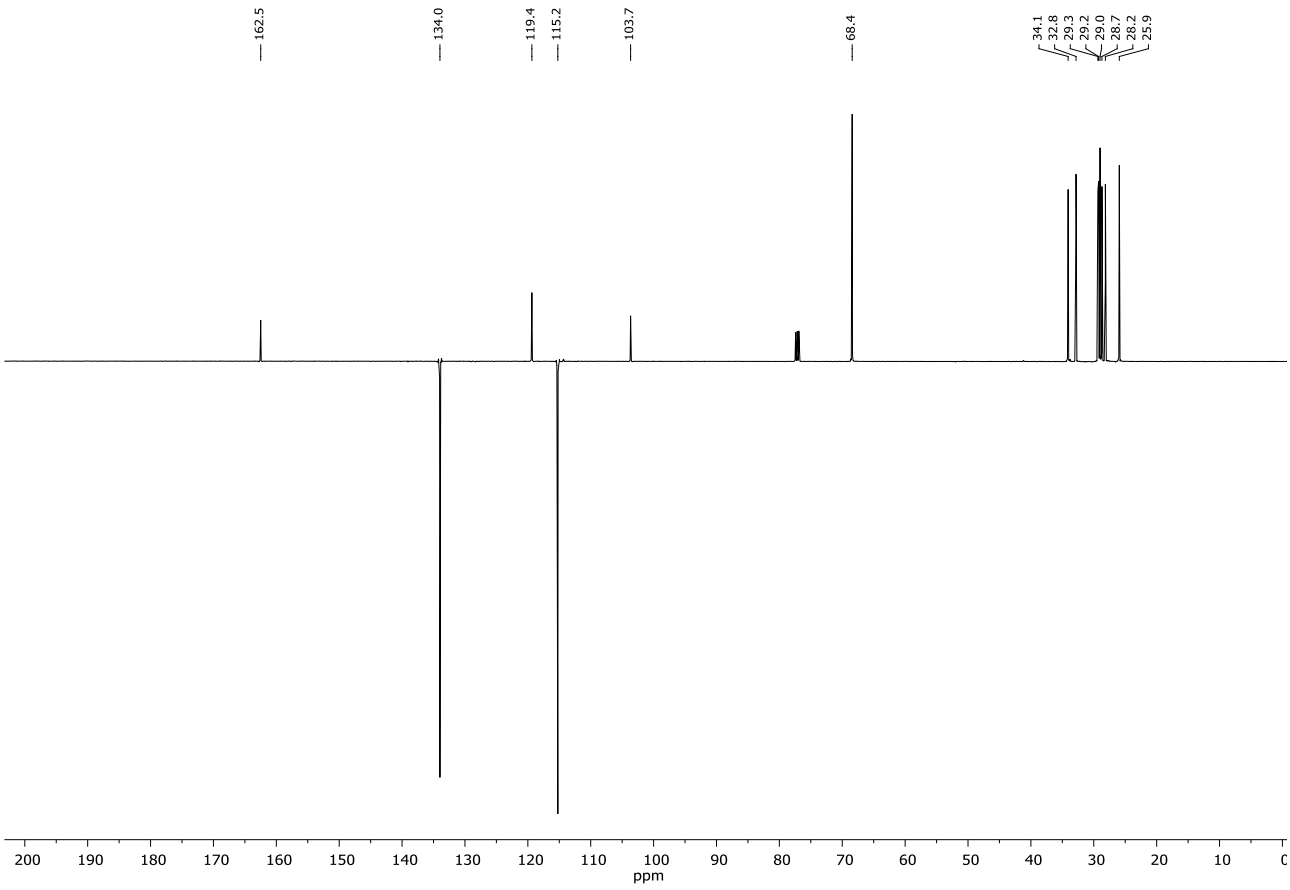
ppm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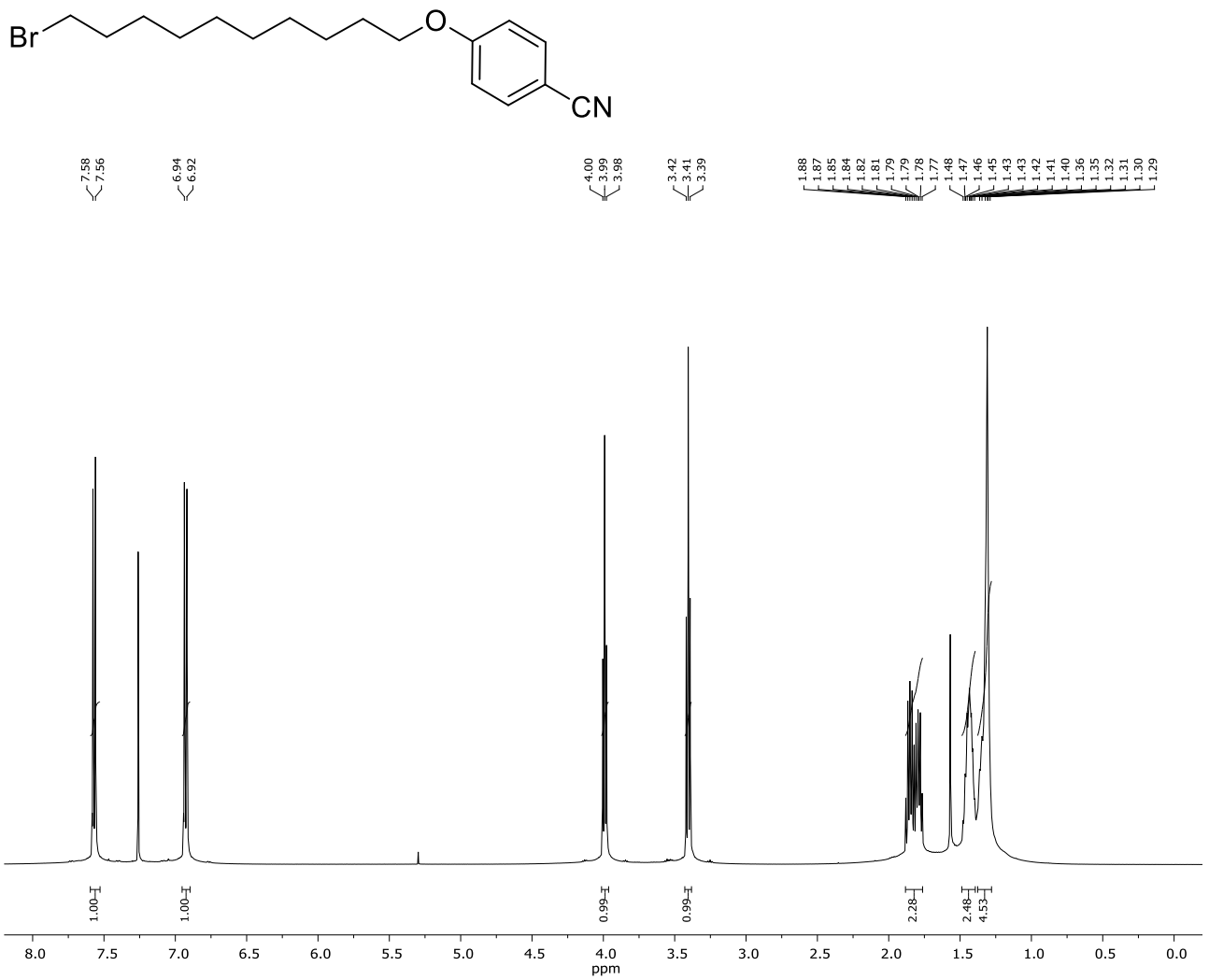
134.0
119.4
115.2
103.7
68.4
34.1
32.8
29.3
29.2
29.0
28.7
28.2
25.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 7e


Br
O
CN
7.58
7.56
6.94
6.92
4.00
3.99
3.98
3.42
3.41
3.39
1.88
1.87
1.85
1.84
1.82
1.81
1.79
1.79
1.78
1.77
1.48
1.47
1.46
1.45
1.43
1.43
1.42
1.41
1.40
1.36
1.35
1.32
1.31
1.30
1.29
1.00
1.00
0.99
0.99
2.28
2.48
4.53
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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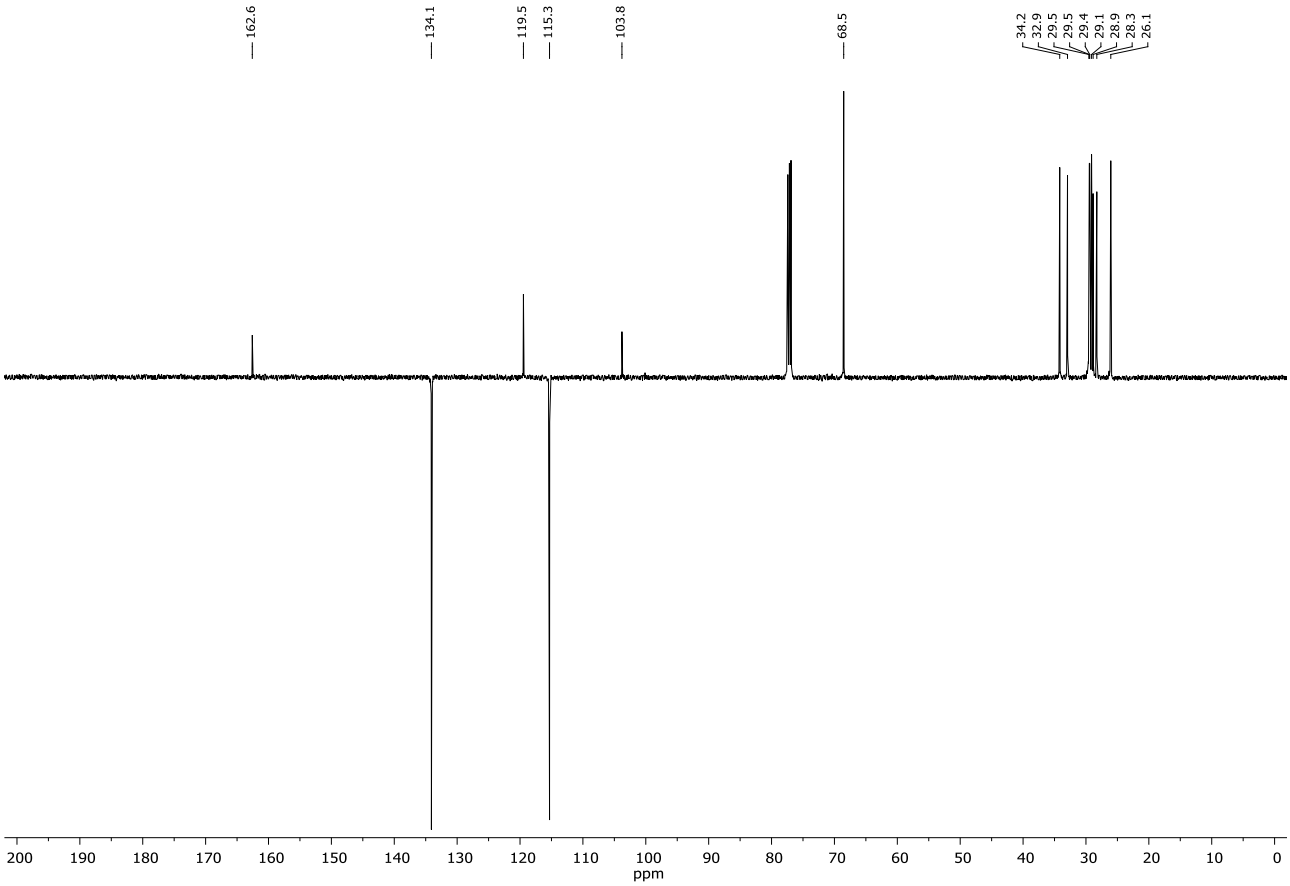
1.5
1.0
0.5
0.0
ppm


162.6
134.1
119.5
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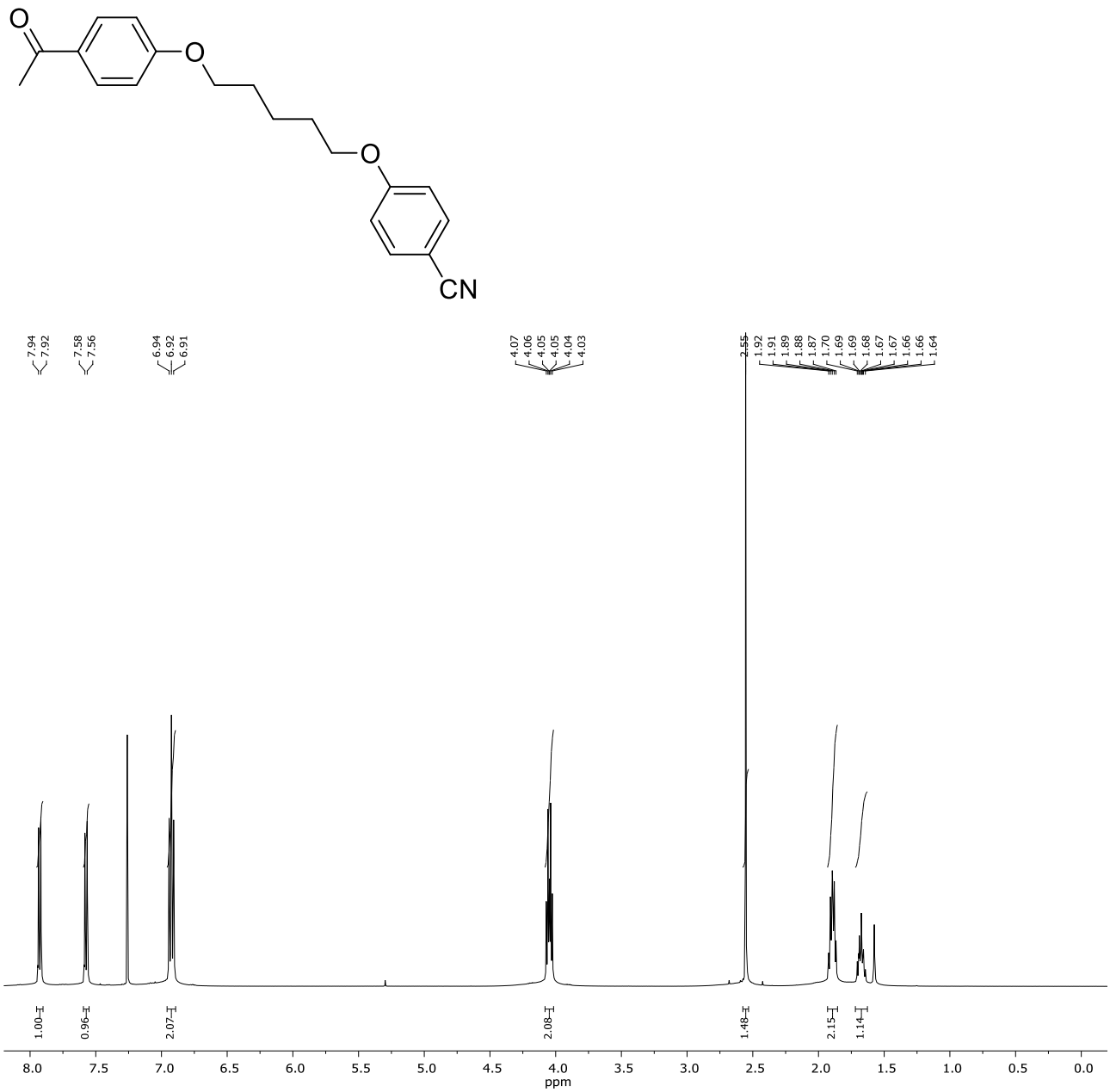
103.8
68.5
34.2
32.9
29.5
29.5
29.4
29.1
28.9
28.3
26.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 9a


O
O
O
CN
7.94
7.92
7.58
7.56
6.94
6.92
6.91
4.07
4.06
4.05
4.05
4.04
4.03
2.55
1.92
1.91
1.89
1.88
1.87
1.70
1.69
1.69
1.68
1.67
1.67
1.66
1.66
1.64
1.00
0.96
2.07
2.08
1.48
2.15
1.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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1.5
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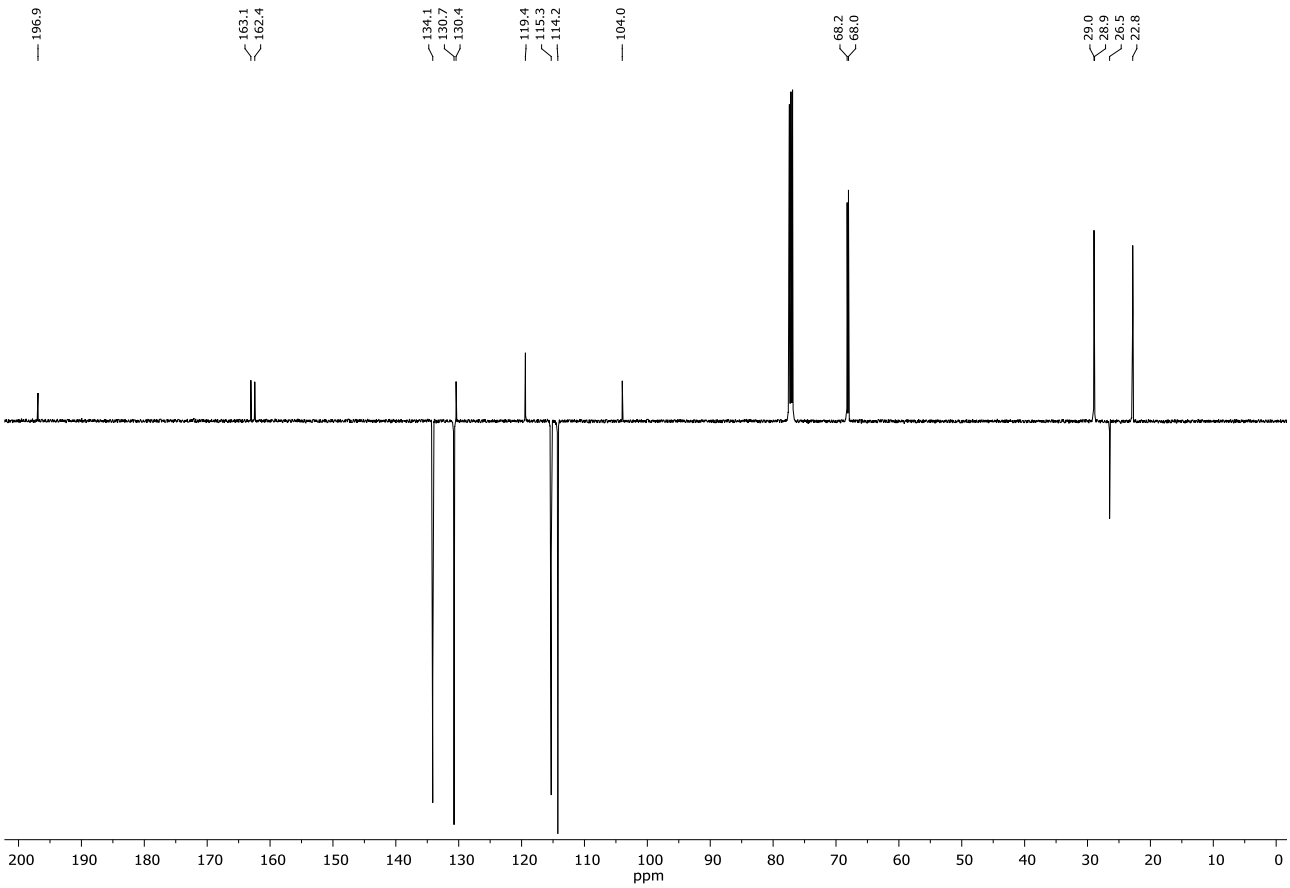
0.5
0.0
ppm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163.1
162.4
134.1
130.7
130.4
119.4
115.3
114.2
104.0
68.2
68.0
29.0
28.9
26.5
22.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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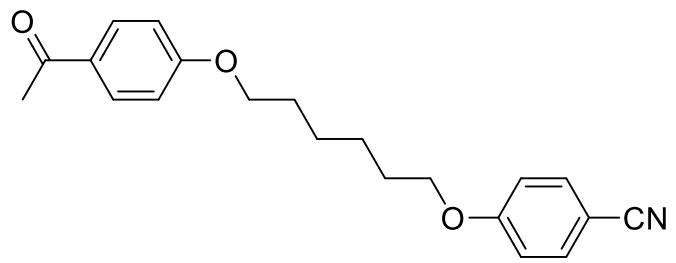
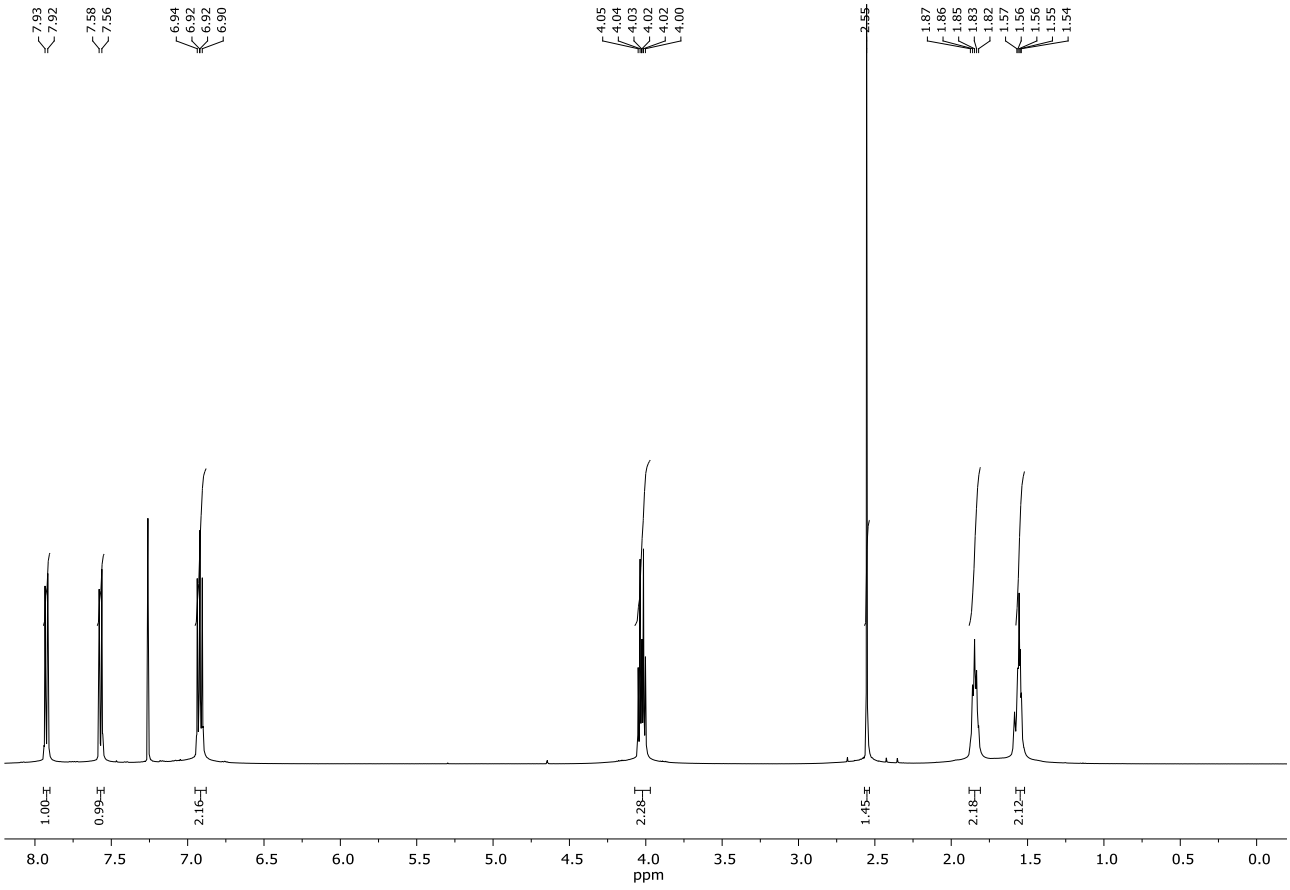
0
ppm

Compound 9b


O
O
O
CN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7.92
7.58
7.56
6.94
6.92
6.92
6.90
4.05
4.04
4.03
4.02
4.02
4.00
2.55
1.87
1.86
1.85
1.83
1.82
1.57
1.56
1.56
1.55
1.54
1.00
0.99
2.16
2.28
1.45
2.18
2.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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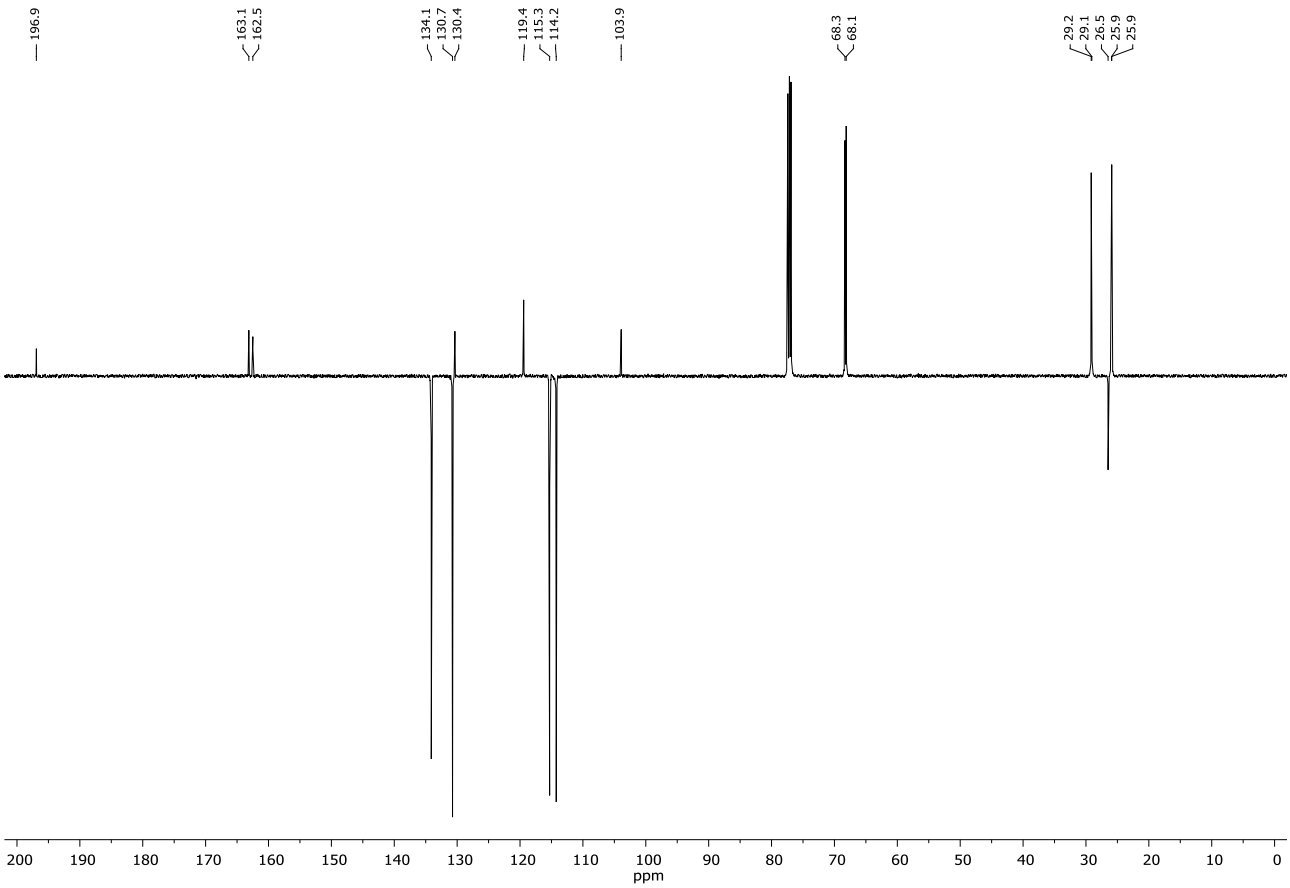
0.5
0.0
ppm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119.4
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114.2
103.9
68.3
68.1
29.2
29.1
26.5
25.9
25.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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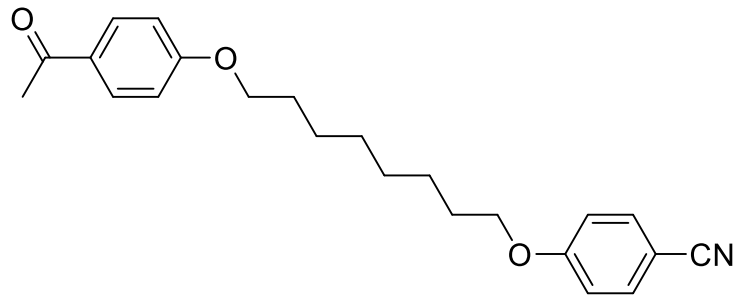
0
ppm

Compound 9c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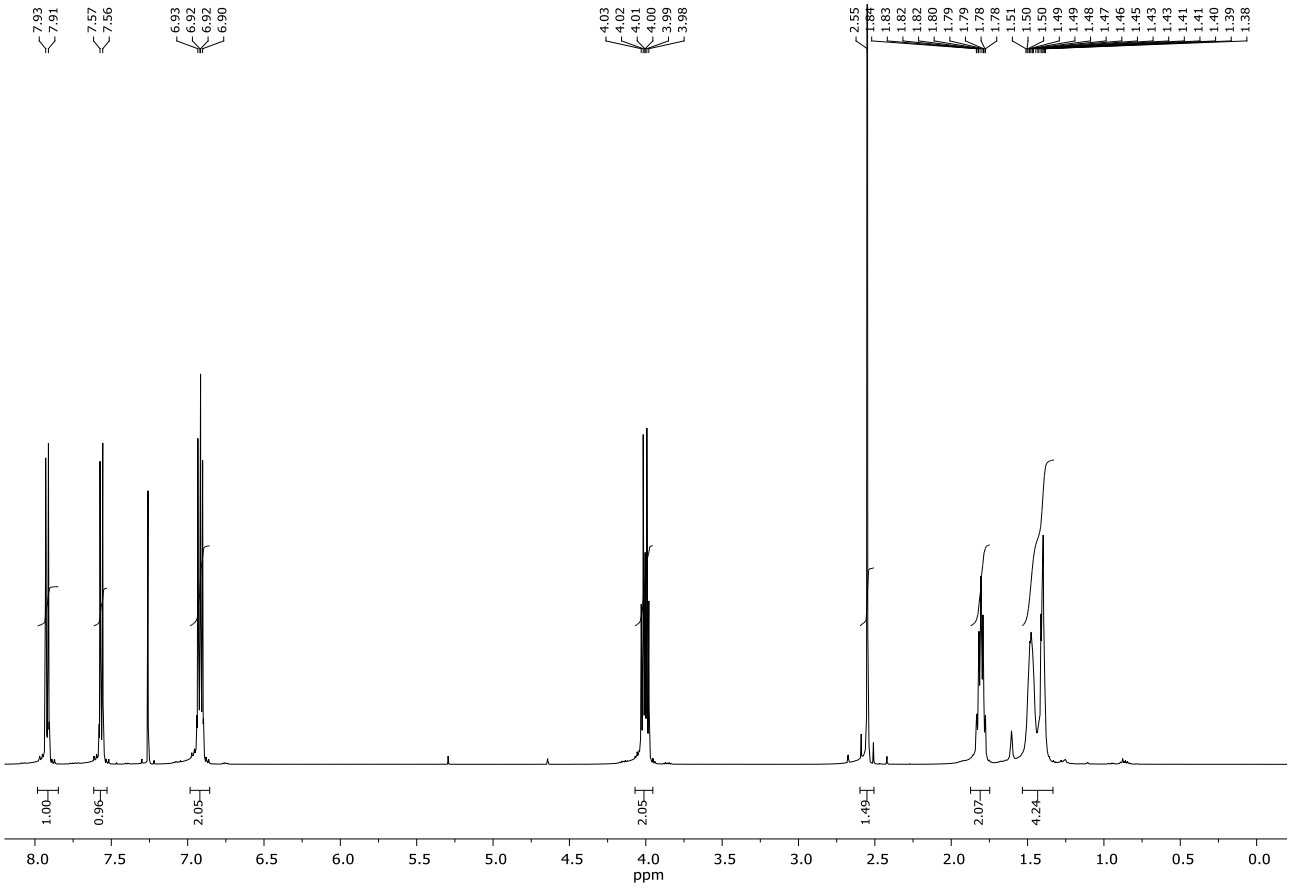
O
CN


7.93
7.91
7.57
7.56
6.93
6.92
6.92
6.90
4.03
4.02
4.01
4.00
3.99
3.98
2.55
1.84
1.83
1.82
1.82
1.80
1.79
1.79
1.78
1.78
1.51
1.50
1.50
1.49
1.49
1.48
1.47
1.46
1.45
1.43
1.41
1.41
1.40
1.39
1.38
1.00
0.96
2.05
2.05
1.49
2.07
4.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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1.5
1.0
0.5
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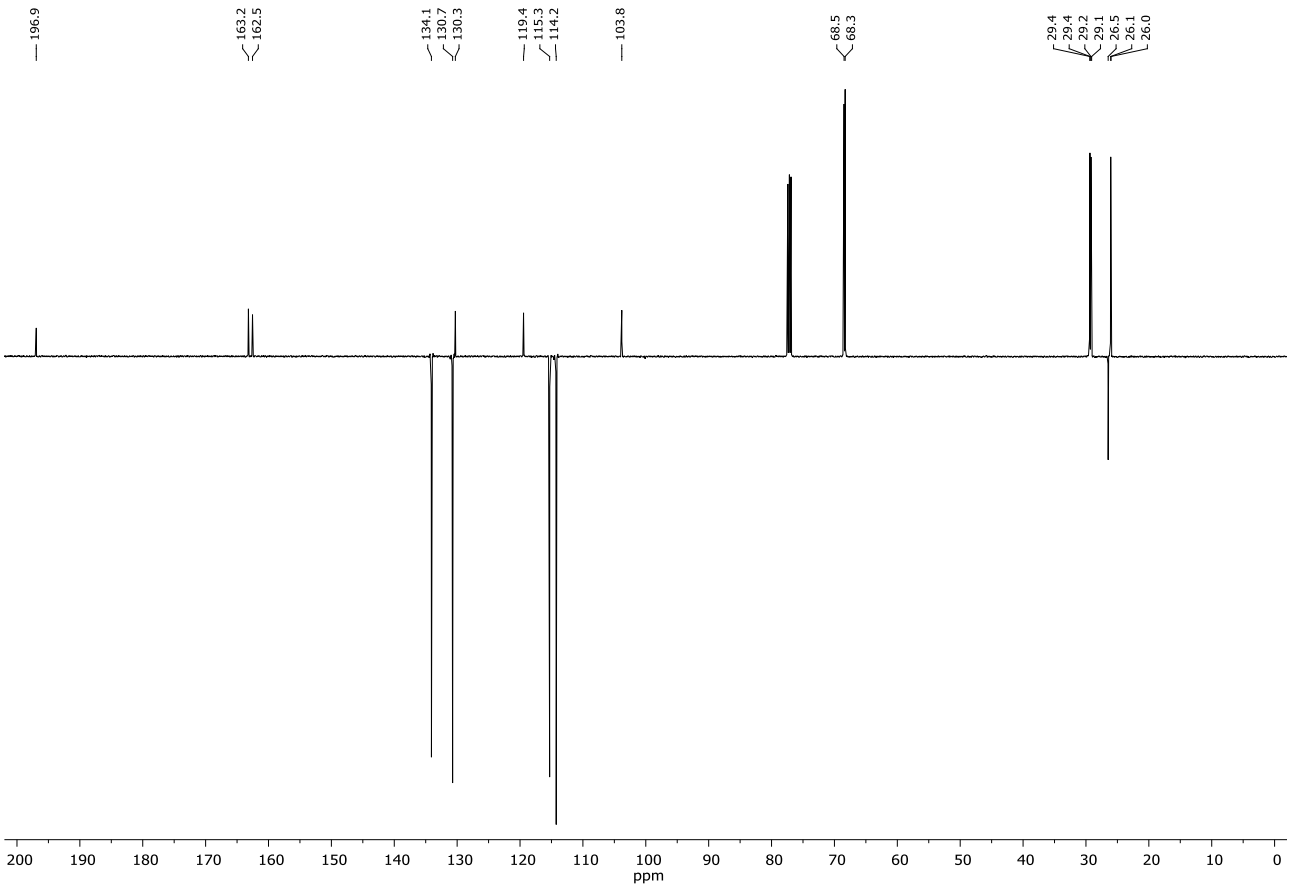
ppm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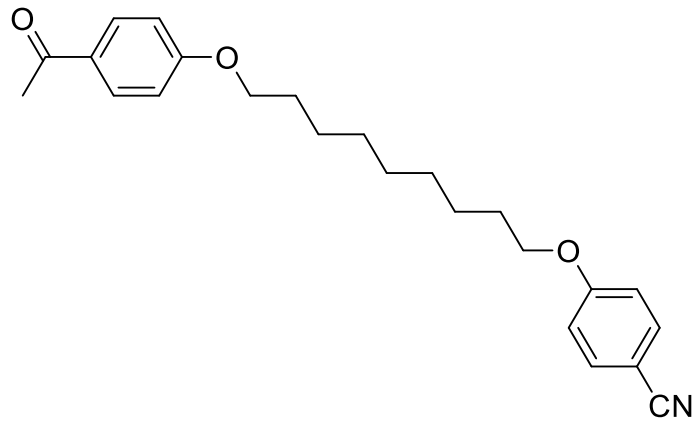
119.4
115.3
114.2
103.8
68.5
68.3
29.4
29.4
29.2
29.1
26.5
26.1
26.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 9d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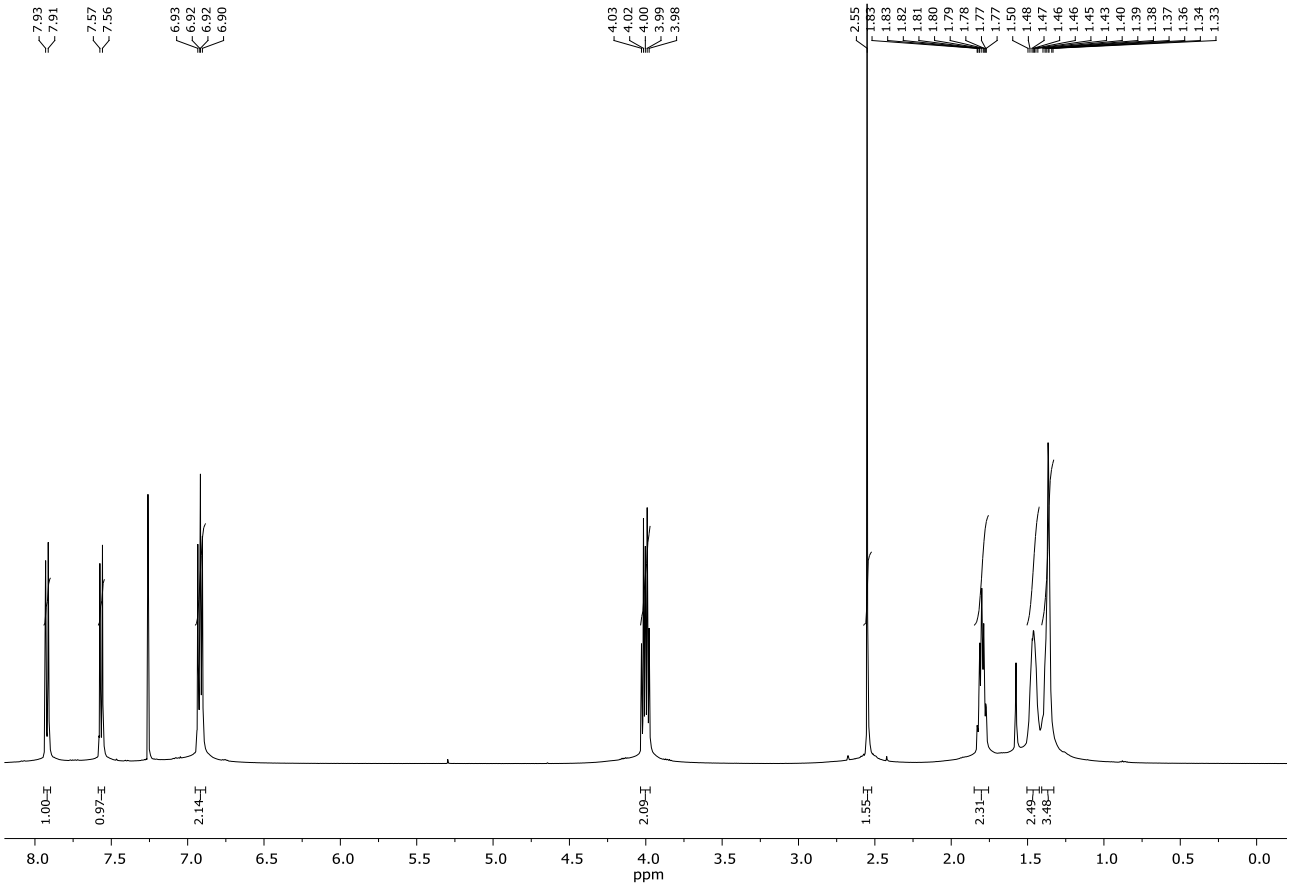
O
CN


7.93
7.91
7.57
7.56
6.93
6.92
6.92
6.90
4.03
4.02
4.00
3.99
3.98
2.55
1.83
1.83
1.82
1.81
1.80
1.79
1.78
1.77
1.77
1.50
1.48
1.47
1.46
1.46
1.45
1.43
1.40
1.39
1.38
1.37
1.36
1.34
1.33
1.00
0.97
2.14
2.09
1.55
2.31
2.49
3.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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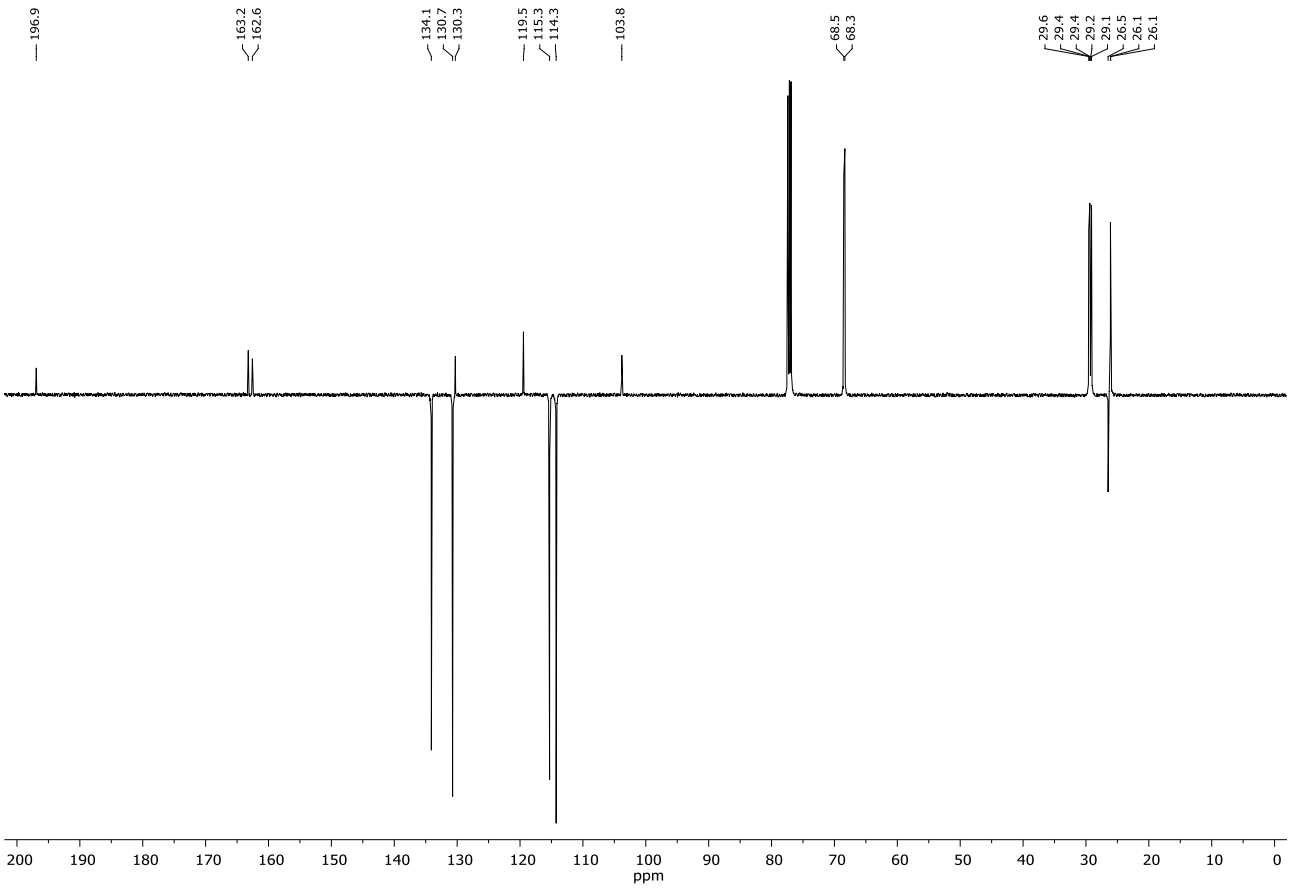
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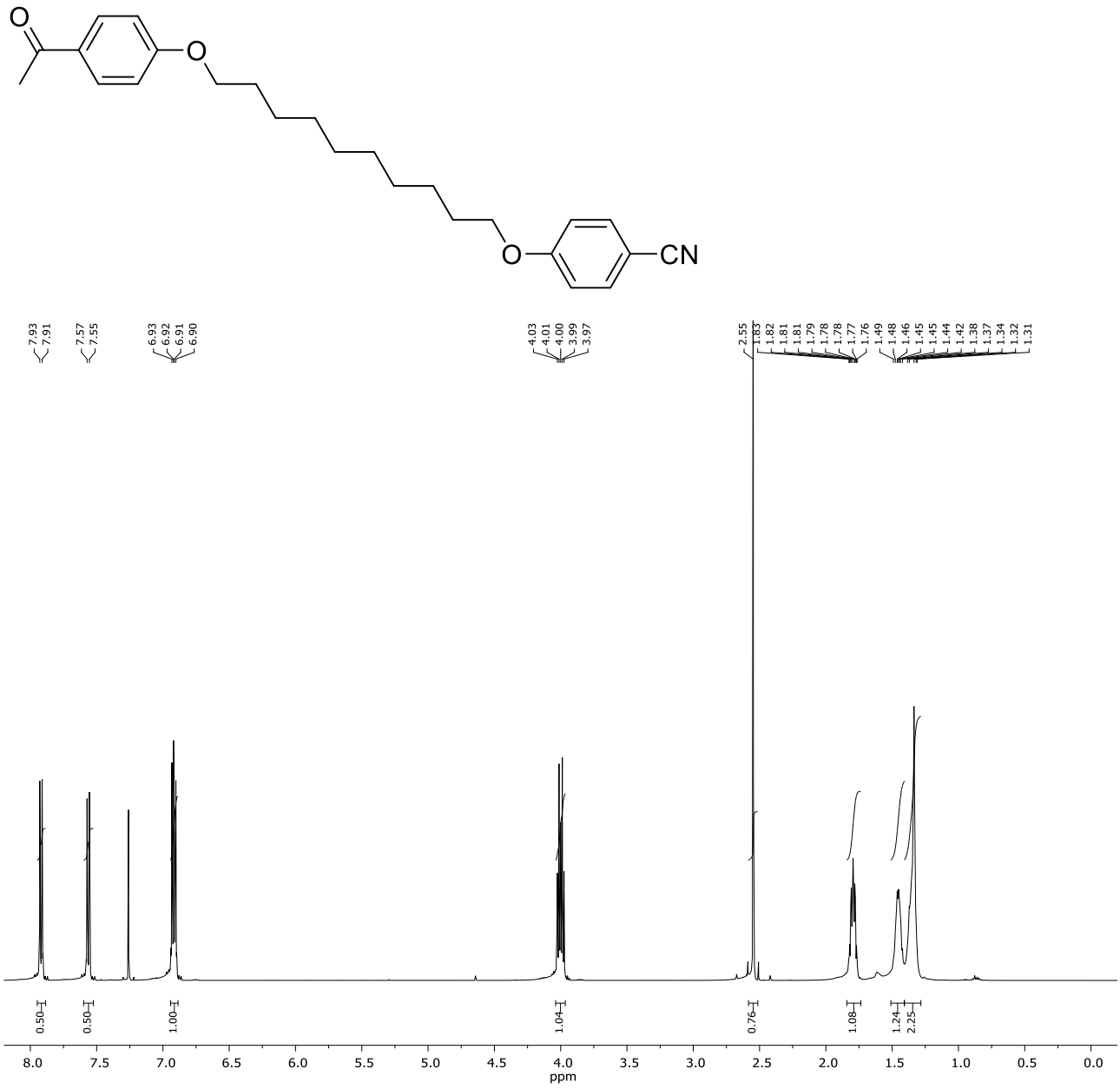
115.3
114.3
103.8
68.5
68.3
29.6
29.4
29.4
29.2
29.1
26.5
26.1
26.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 9e


O
O
O
CN
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7.91
7.57
7.55
6.93
6.92
6.91
6.90
4.03
4.01
4.00
3.99
3.97
2.55
1.83
1.82
1.81
1.81
1.79
1.78
1.78
1.77
1.76
1.49
1.48
1.46
1.45
1.45
1.44
1.42
1.38
1.37
1.34
1.32
1.31
0.50
0.50
1.00
1.04
0.76
1.08
1.24
2.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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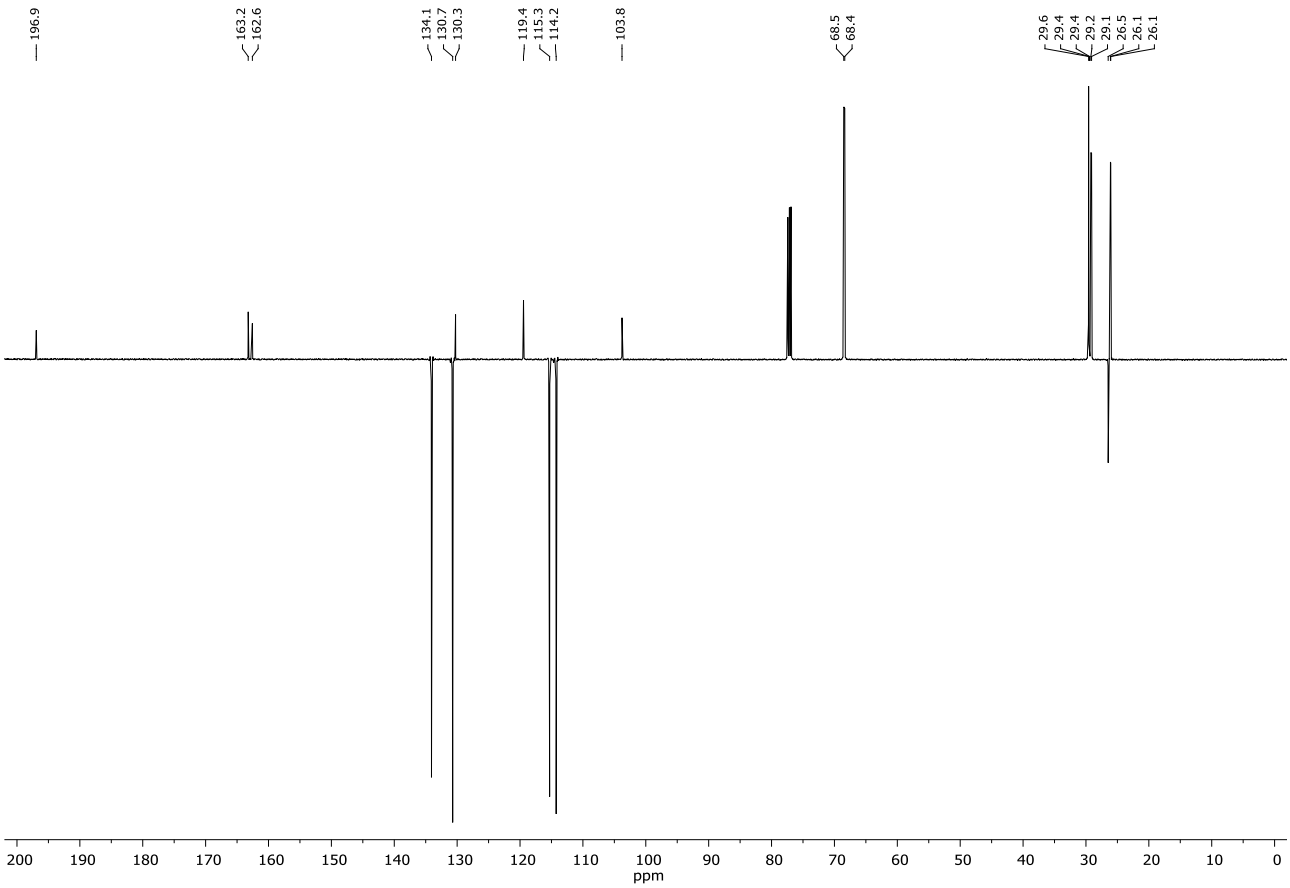
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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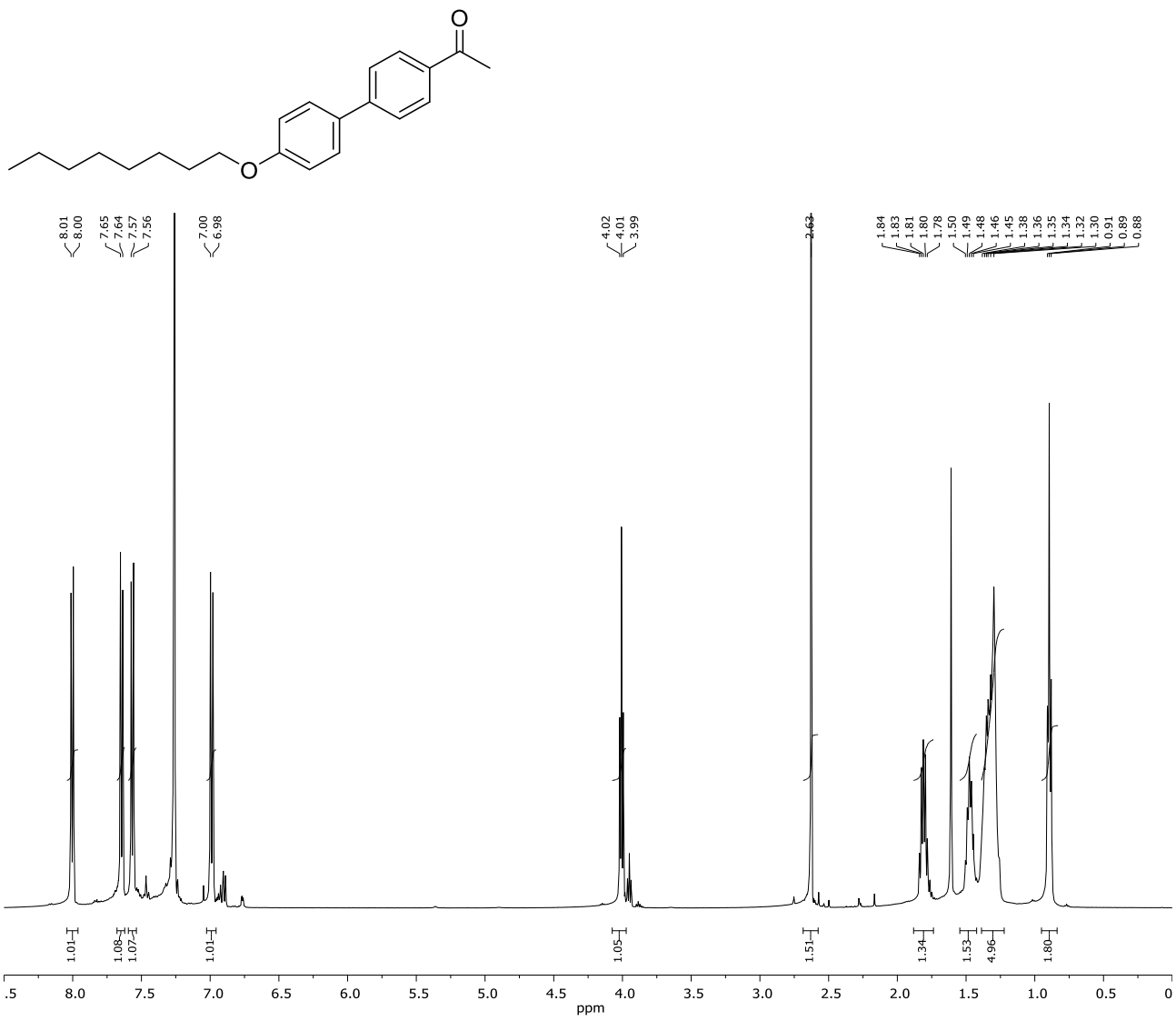
162.6
134.1
130.7
130.3
119.4
115.3
114.2
103.8
68.5
68.4
29.6
29.4
29.4
29.2
29.1
26.5
26.1
26.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 9f


O
O
8.01
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7.57
7.56
7.00
6.98
4.02
4.01
3.99
2.63
1.84
1.83
1.81
1.80
1.78
1.50
1.49
1.48
1.46
1.45
1.38
1.36
1.35
1.34
1.32
1.30
0.91
0.89
0.88
1.01
1.08
1.07
1.01
1.05
1.51
1.34
1.53
4.96
1.80
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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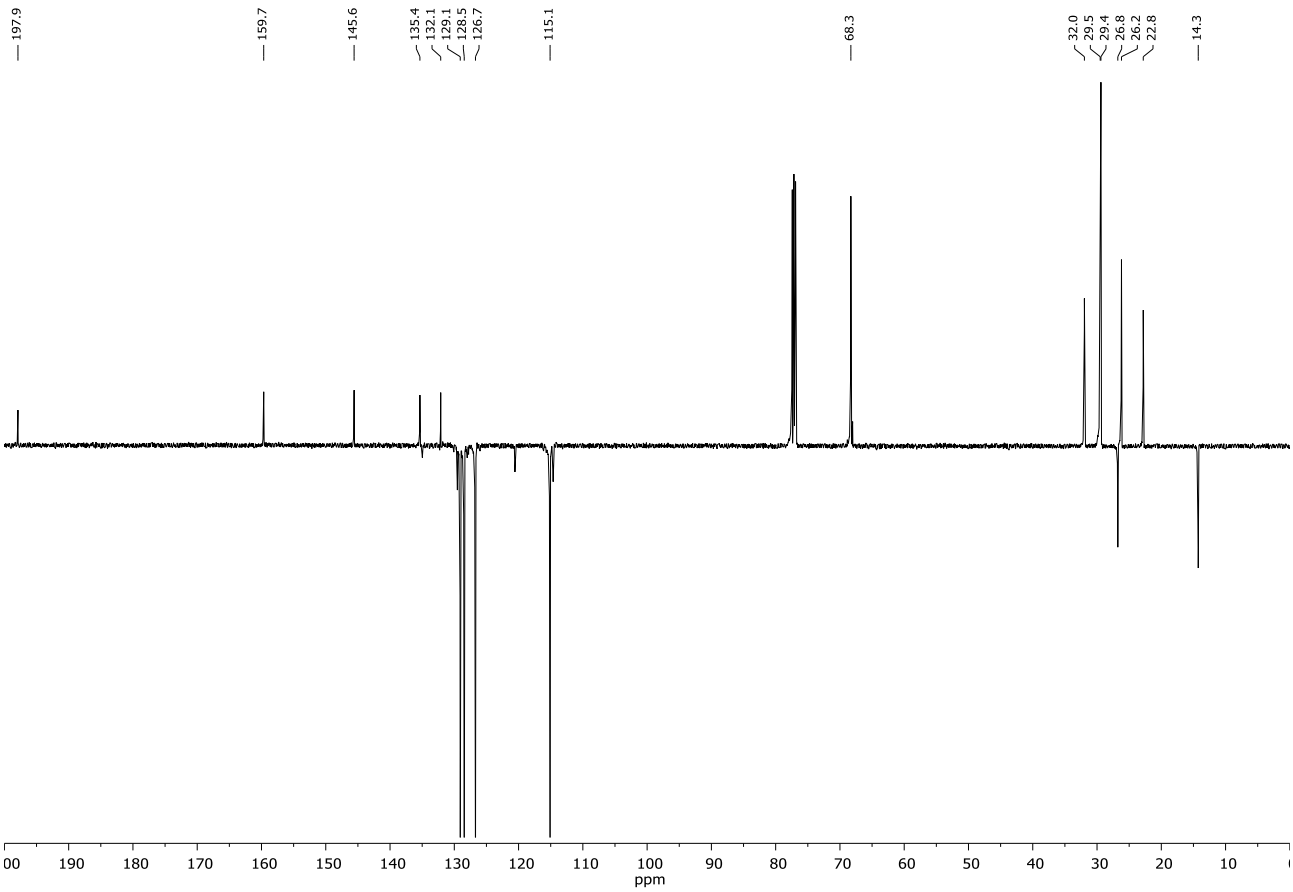
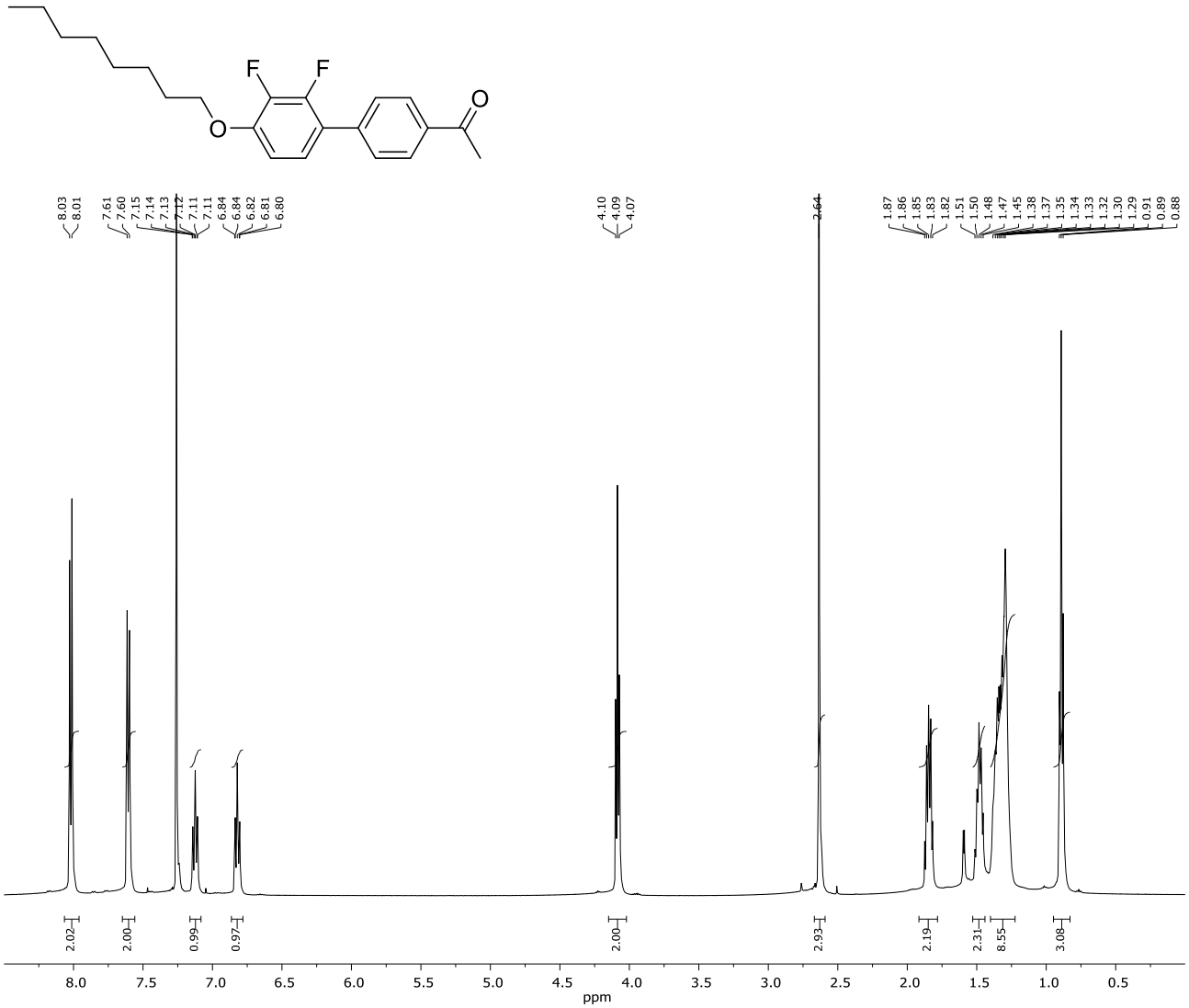
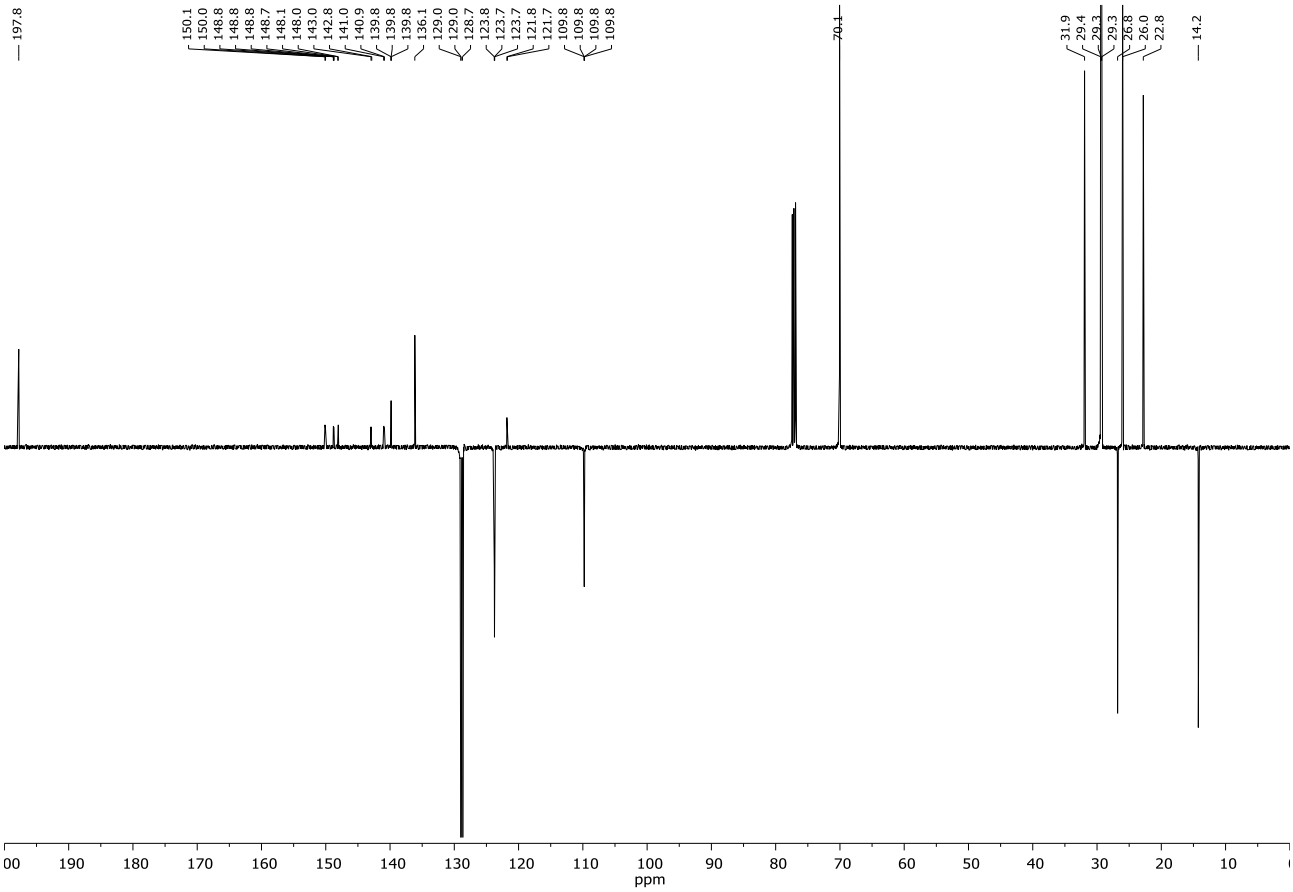
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
ppm


197.9
159.7
145.6
135.4
132.1
129.1
128.5
126.7
115.1
68.3
32.0
29.5
29.4
26.8
26.2
22.8
14.3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 9g


F
F
O
O
8.03
8.01
7.61
7.60
7.15
7.14
7.13
7.12
7.11
7.11
6.84
6.84
6.82
6.81
6.80
4.10
4.09
4.07
2.64
1.87
1.86
1.85
1.83
1.82
1.51
1.50
1.48
1.47
1.45
1.38
1.37
1.35
1.34
1.33
1.32
1.30
1.29
0.91
0.89
0.88
2.02
2.00
0.99
0.97
2.00
2.93
2.19
2.31
8.55
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


197.8
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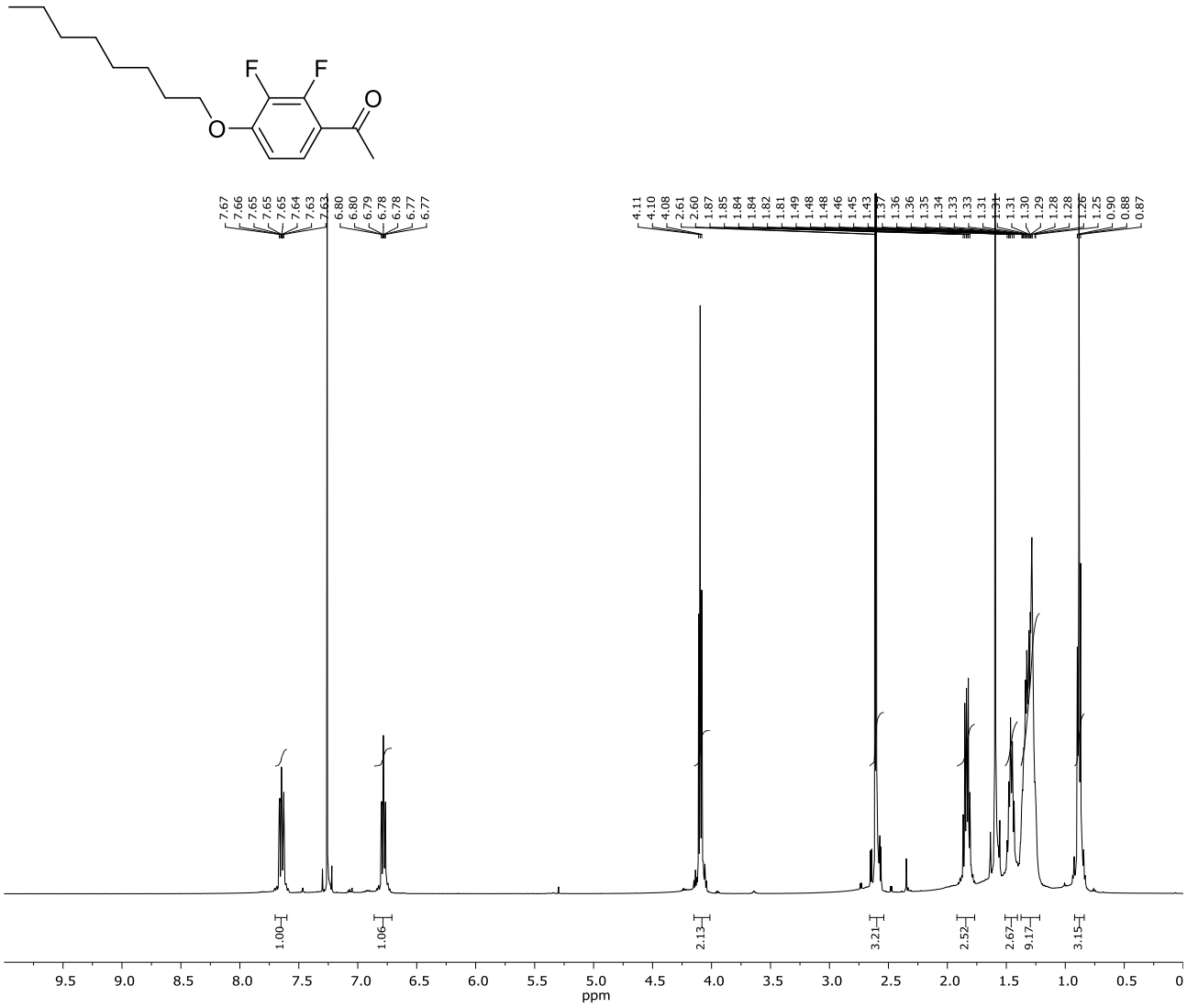
148.8
148.8
148.7
148.1
148.0
143.0
142.8
141.0
140.9
139.8
139.8
139.8
136.1
129.0
129.0
128.7
123.8
123.7
123.7
121.8
121.7
109.8
109.8
109.8
109.8
70.1
31.9
29.4
29.3
29.3
26.8
26.0
22.8
14.2
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 9h


F
F
O
O
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7.65
7.65
7.65
7.64
7.63
7.63
6.80
6.80
6.79
6.78
6.78
6.77
6.77
4.11
4.10
4.08
2.61
2.60
1.87
1.85
1.84
1.84
1.82
1.81
1.49
1.48
1.48
1.46
1.45
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1.36
1.36
1.35
1.34
1.33
1.33
1.31
1.31
1.31
1.30
1.29
1.28
1.28
1.26
1.25
0.90
0.88
0.87
1.00
1.06
2.13
3.21
2.52
2.67
9.17
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
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1.0
0.5
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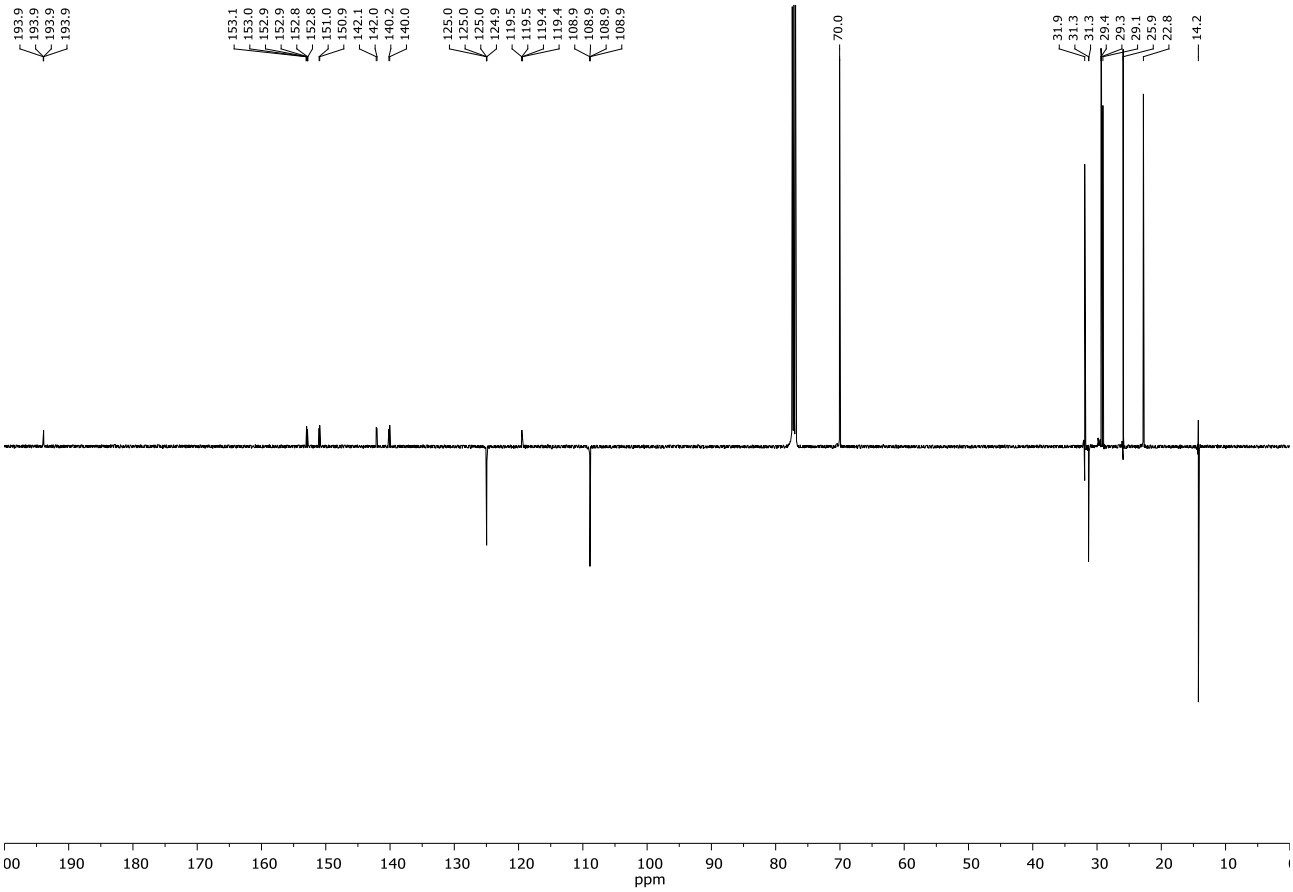
193.9
193.9
193.9
193.9
153.1
153.0
152.9
152.9
152.8
152.8
151.0
150.9
142.1
142.0
140.2
140.0
125.0
125.0
125.0
124.9
119.5
119.5
119.4
119.4
108.9
108.9
108.9
108.9
70.0
31.9
31.3
31.3
29.4
29.3
29.1
25.9
22.8
14.2
00
190
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50
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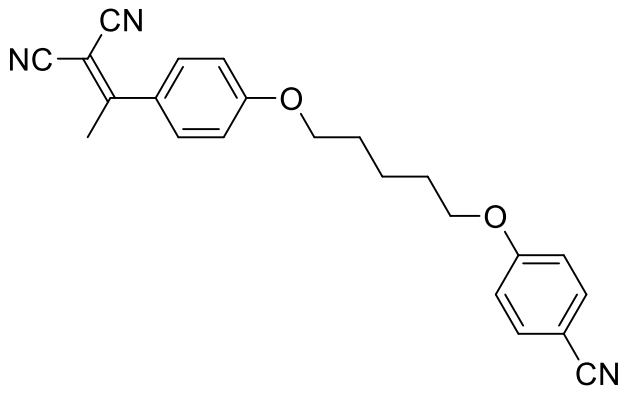
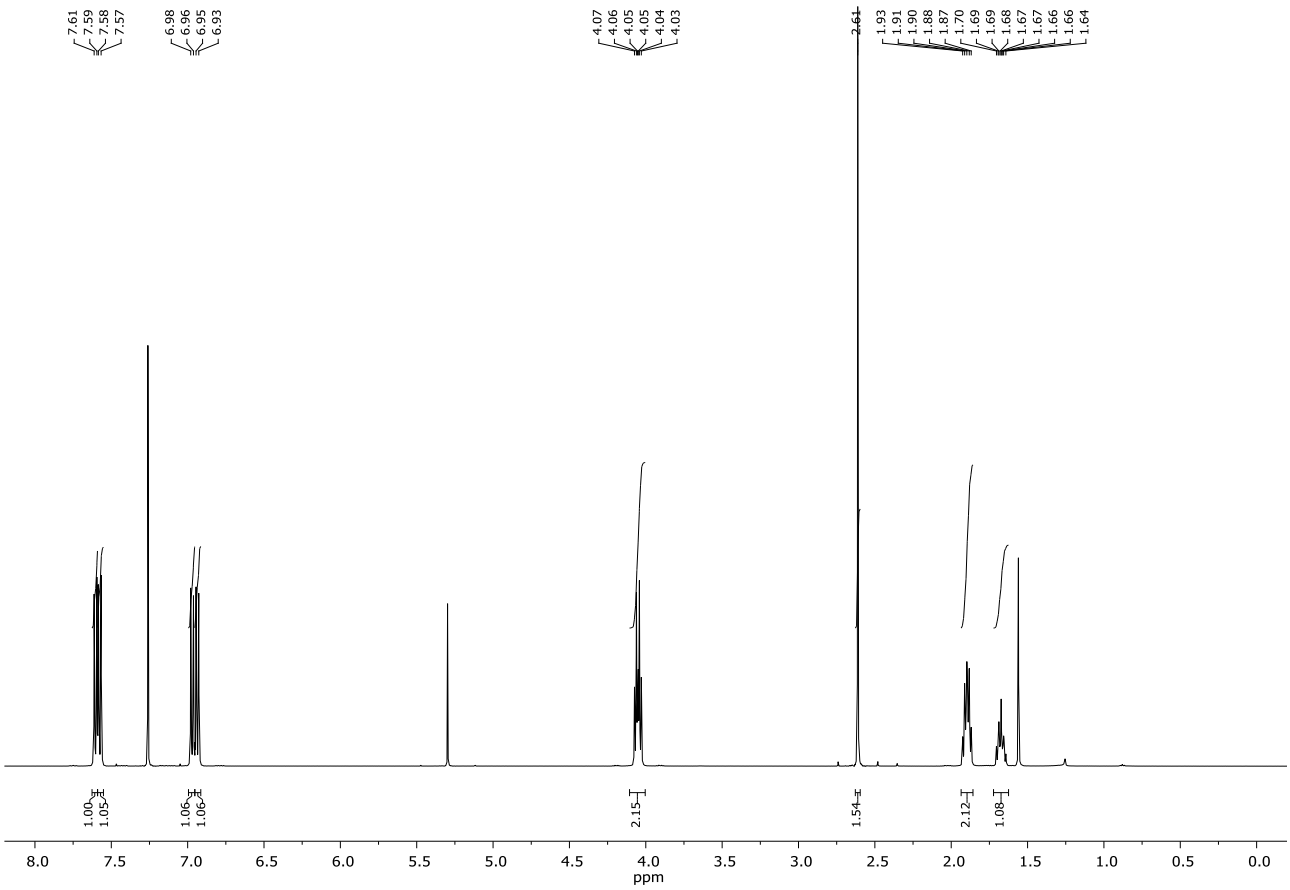
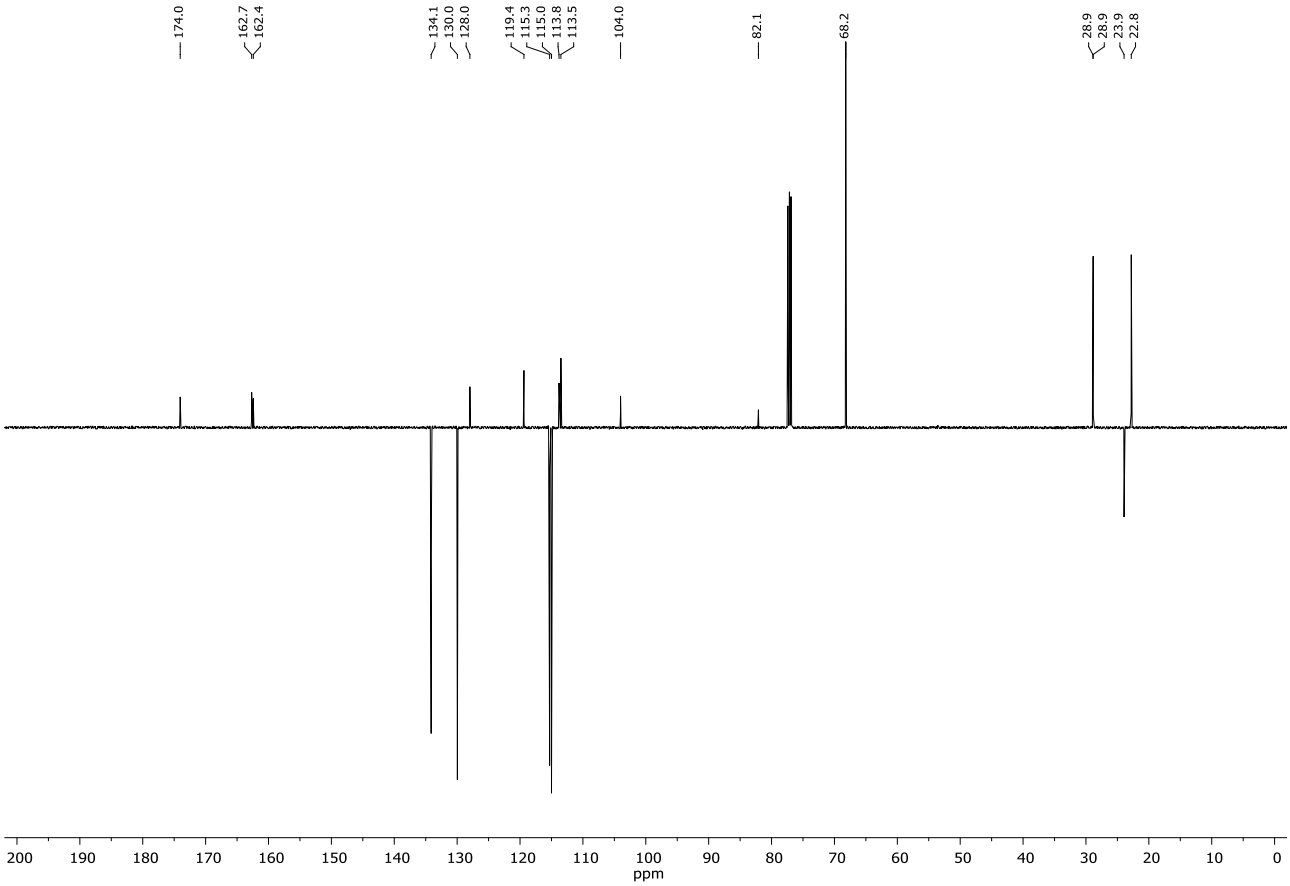
30
20
10
ppm

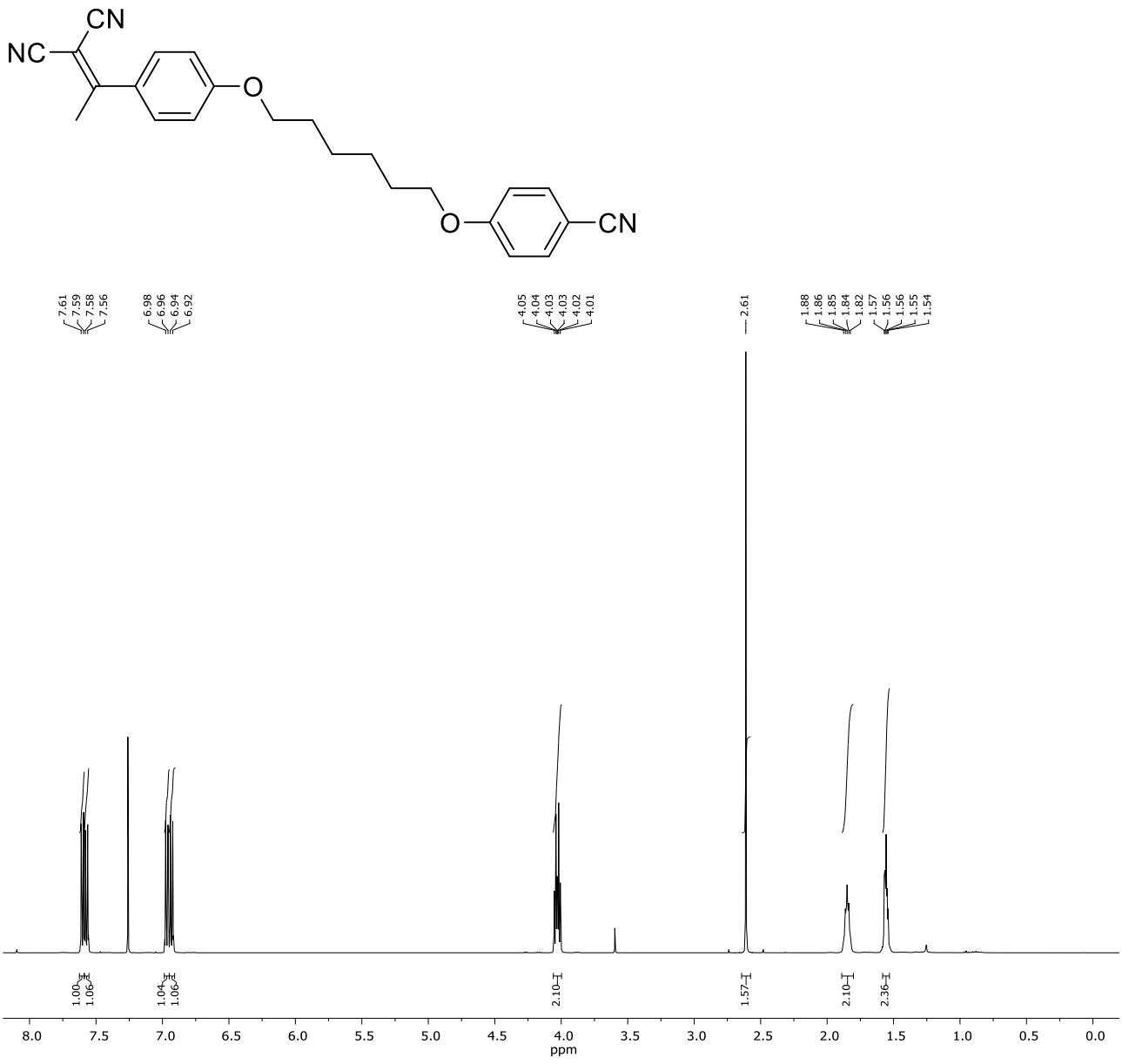
Compound 13a

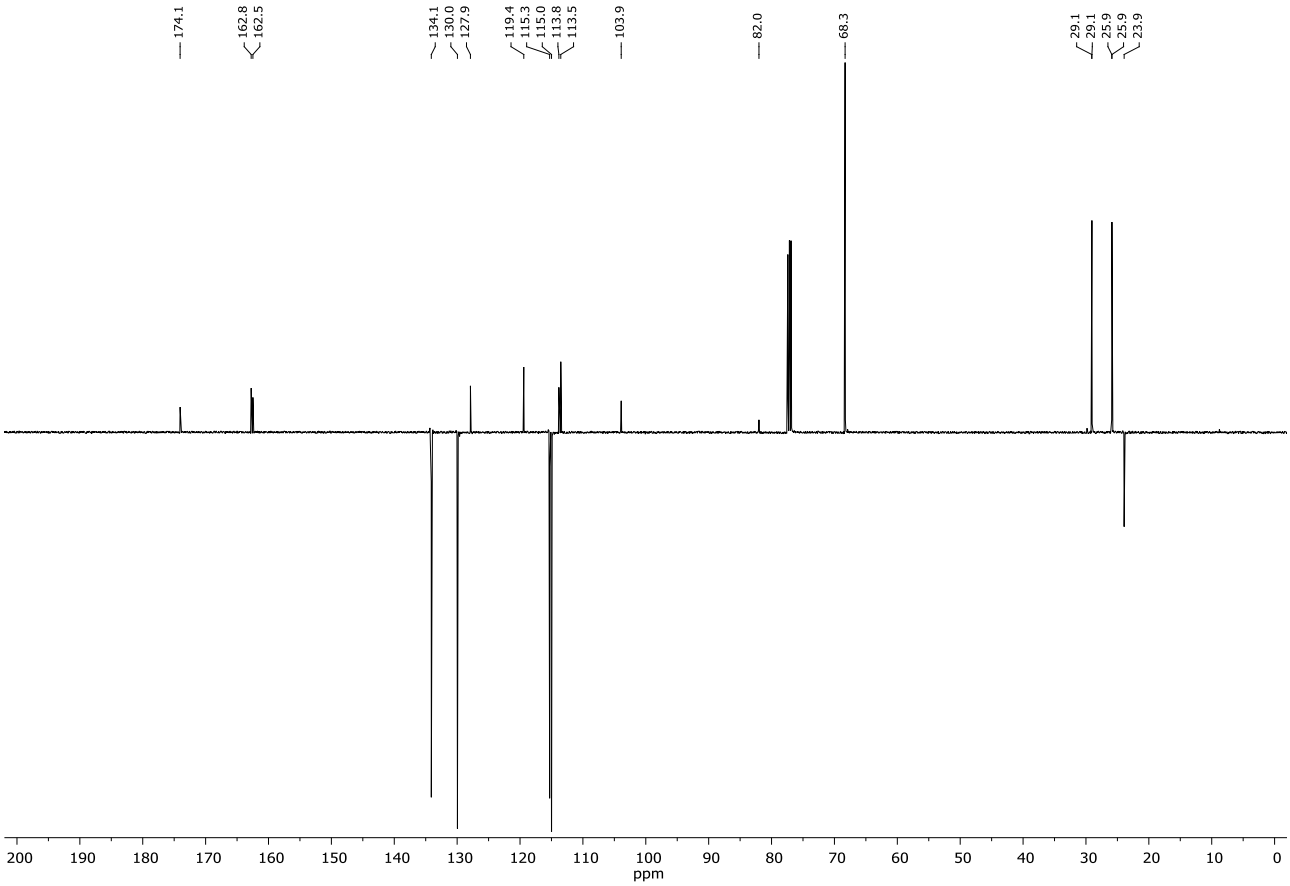




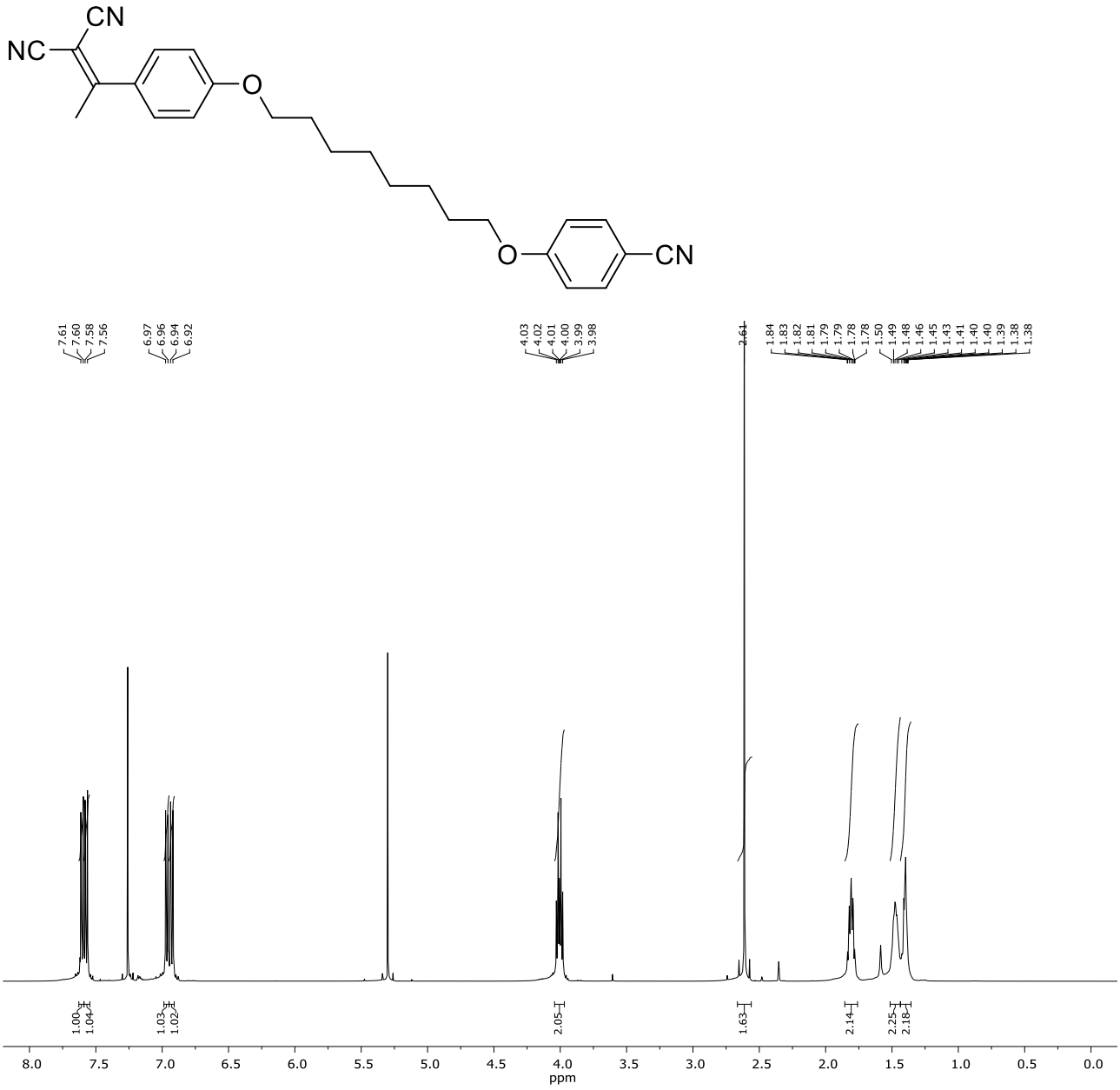

174.0
162.7
162.4
134.1
130.0
128.0
119.4
115.3
115.0
113.8
113.5
104.0
82.1
68.2
28.9
28.9
23.9
22.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

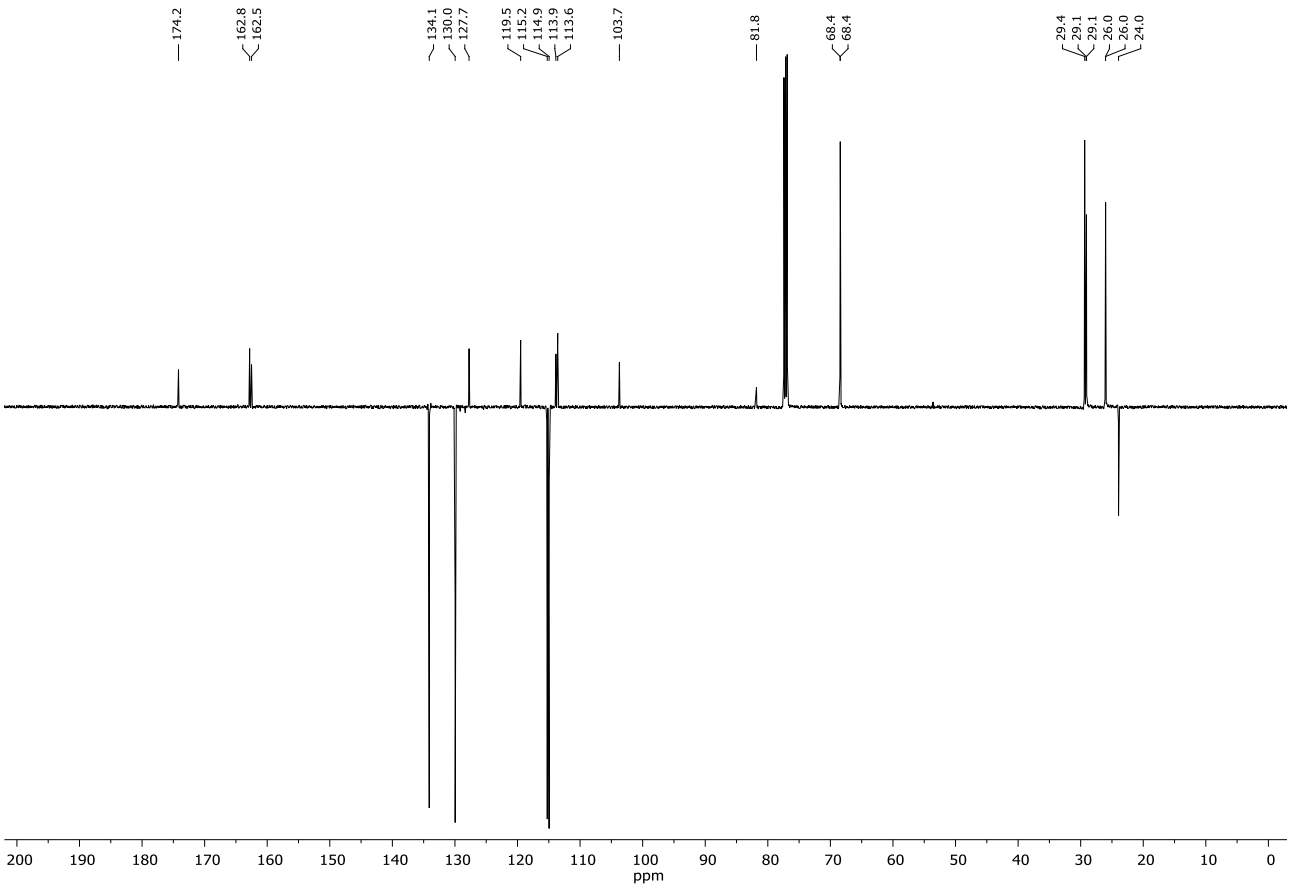
Compound 13b



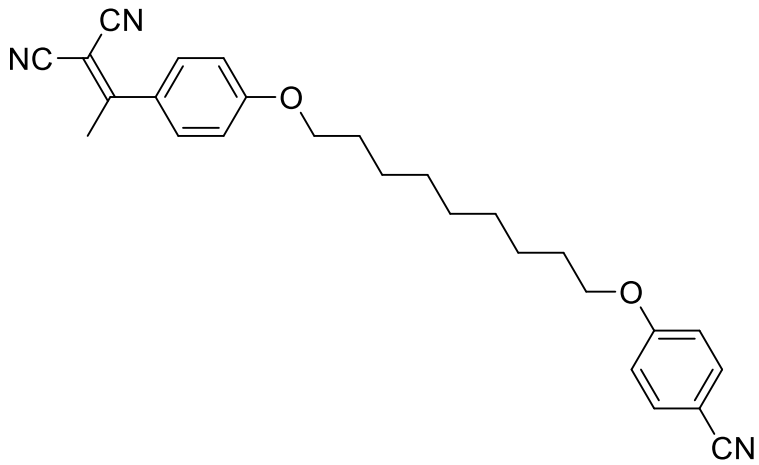

174.1
162.8
162.5
134.1
130.0
127.9
119.4
115.3
115.0
113.8
113.5
103.9
82.0
68.3
29.1
29.1
25.9
25.9
23.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

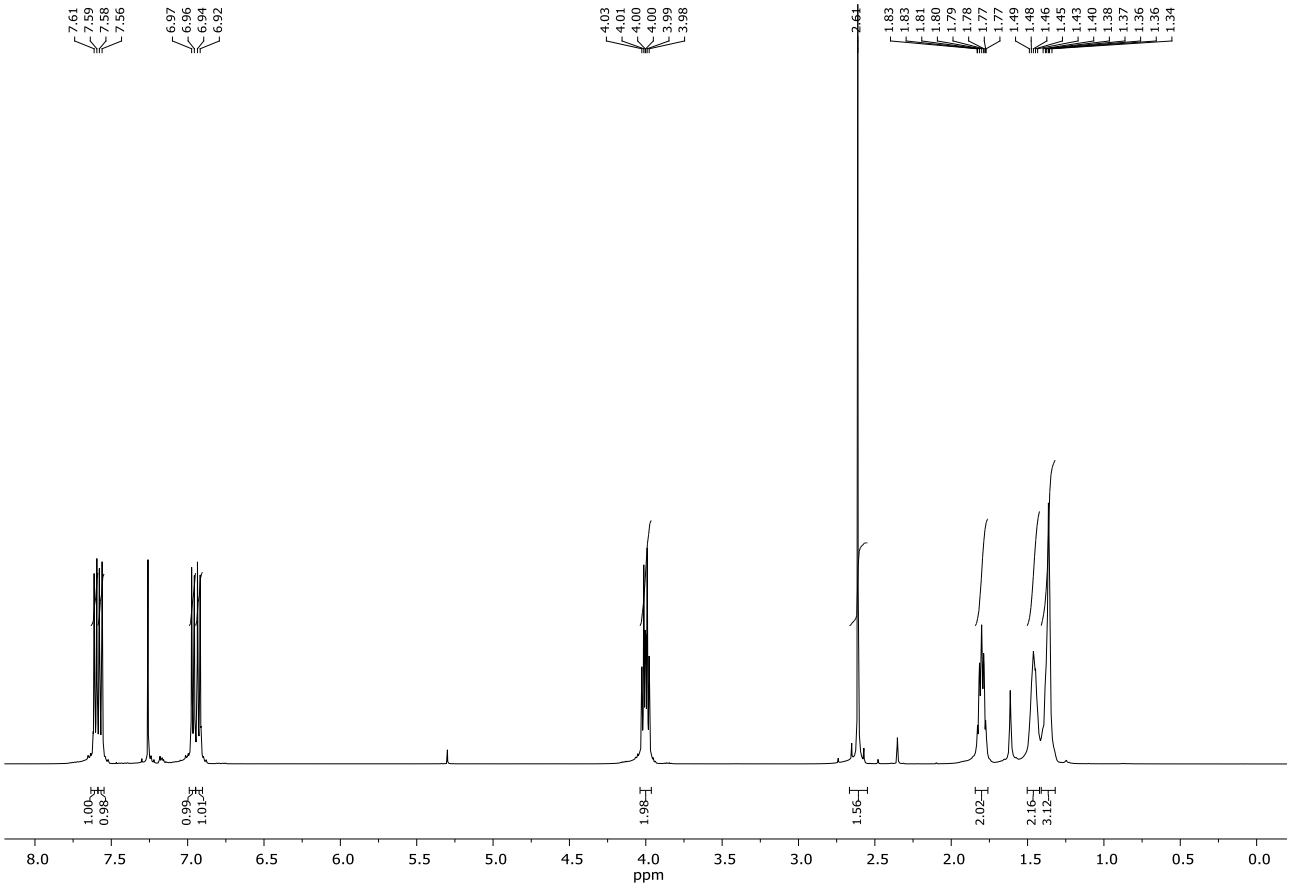
Compound 13c

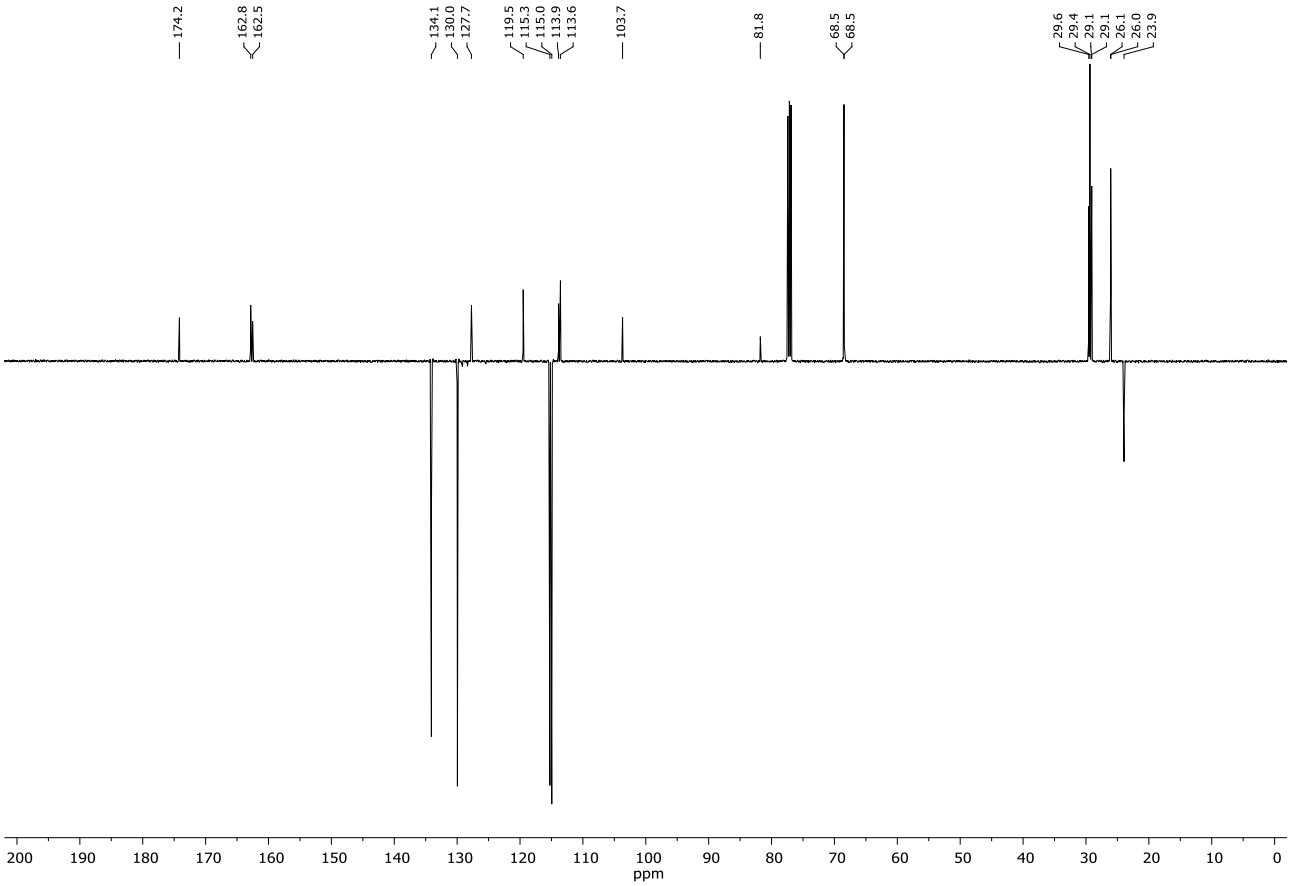



174.2
162.8
162.5
134.1
130.0
127.7
119.5
115.2
114.9
113.9
113.6
103.7
81.8
68.4
68.4
29.4
29.1
29.1
26.0
26.0
24.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 13d






174.2
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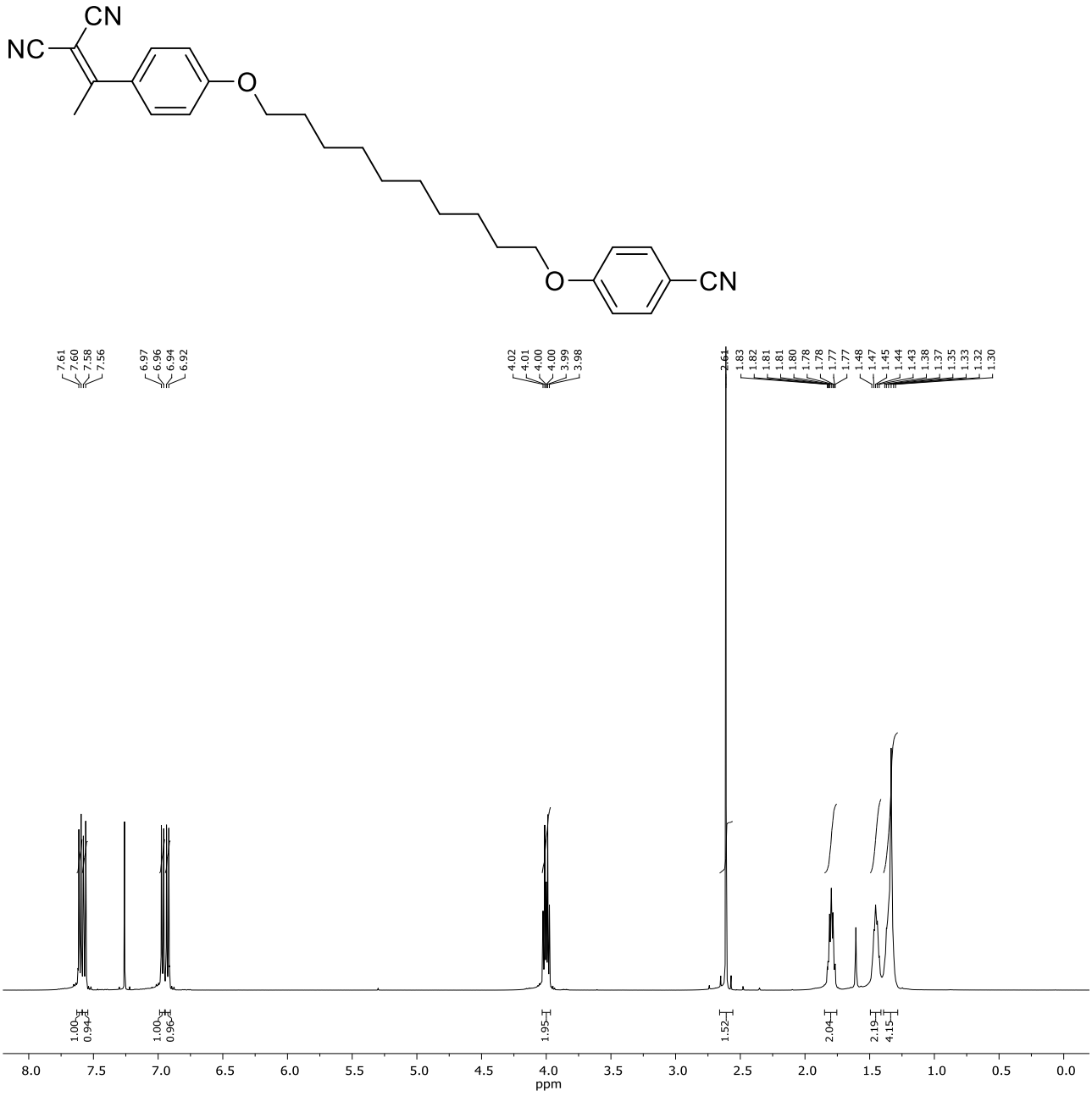
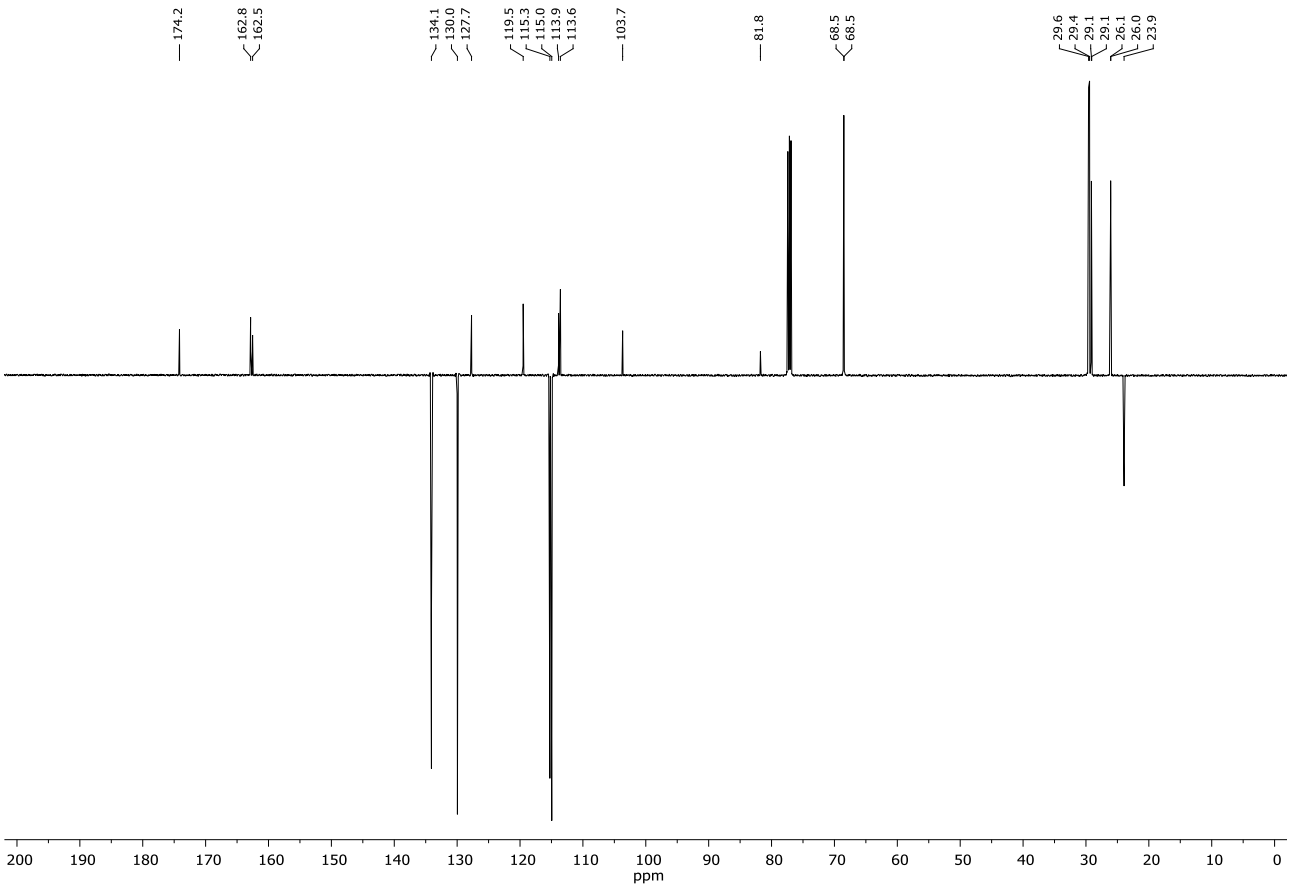
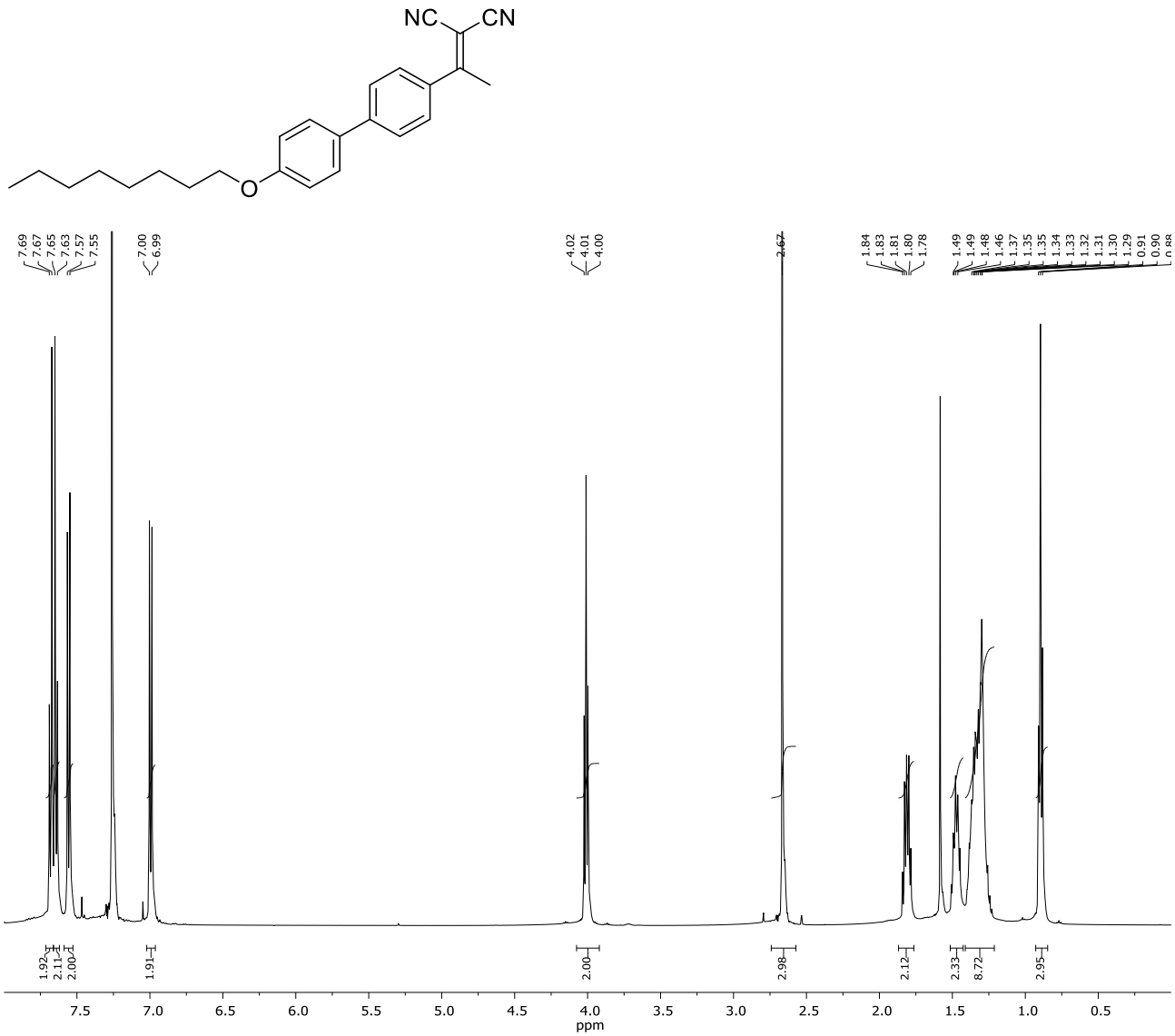
162.5
134.1
130.0
127.7
119.5
115.3
115.0
113.9
113.6
103.7
81.8
68.5
68.5
29.6
29.4
29.1
29.1
26.1
26.0
23.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

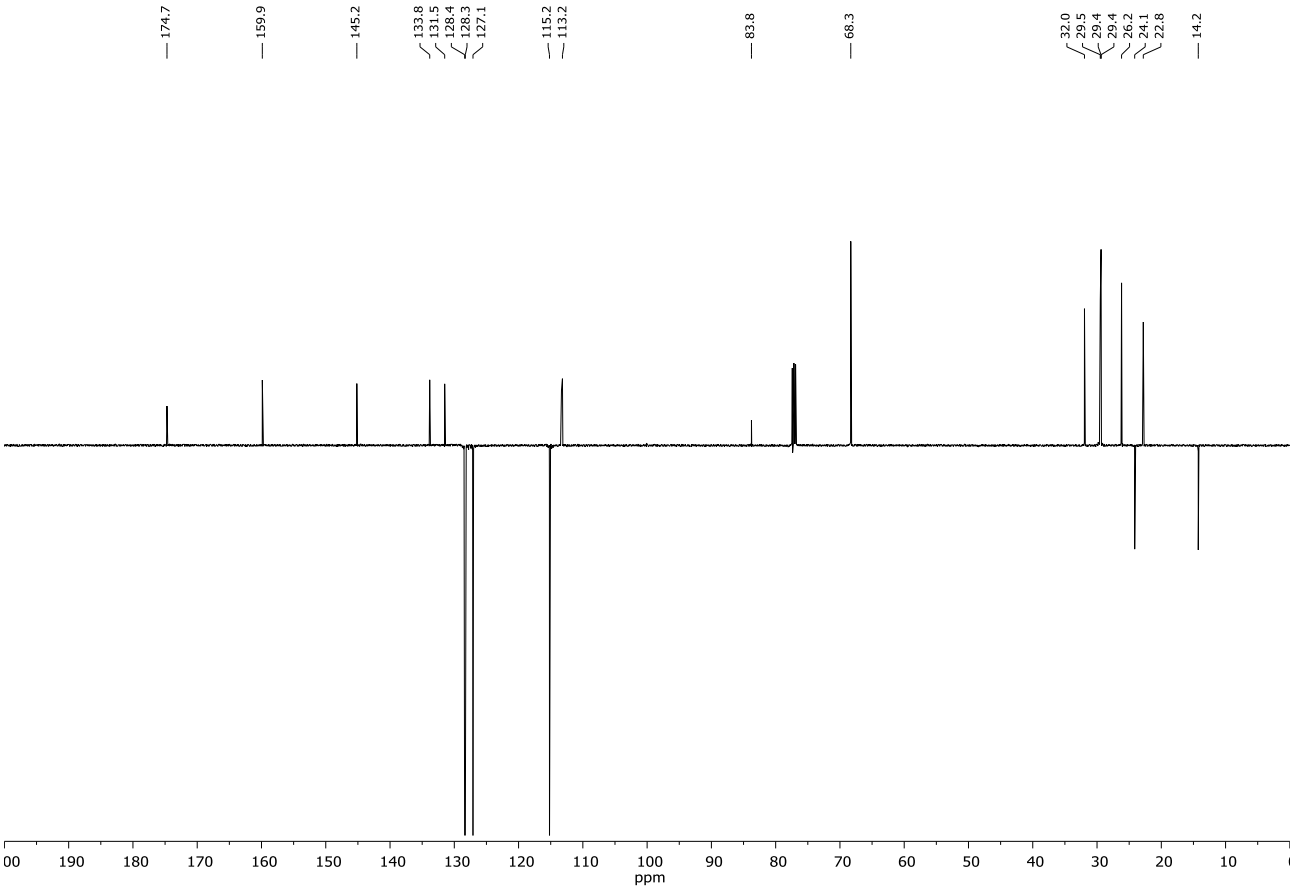
Compound 13e



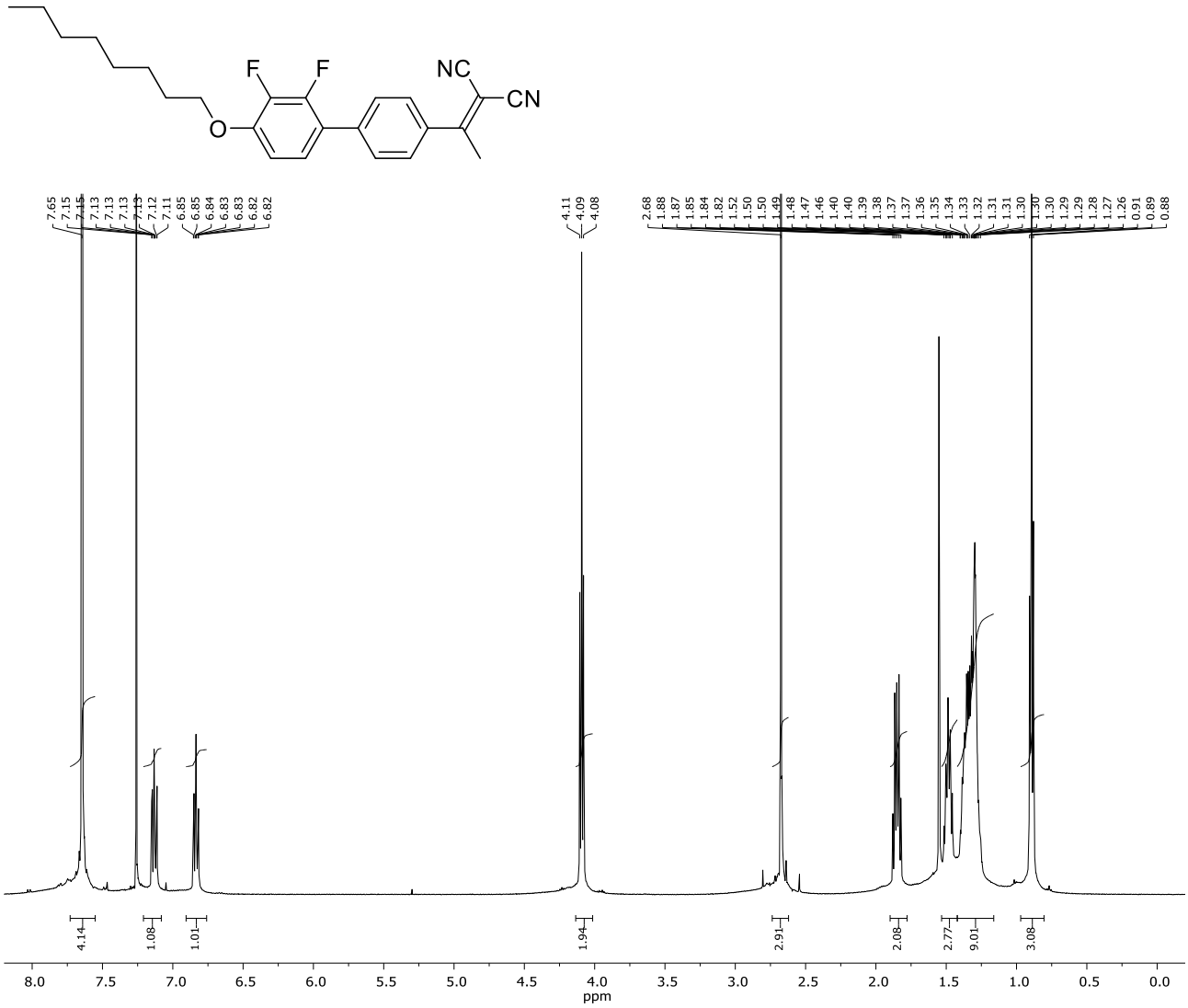

174.2
162.8
162.5
134.1
130.0
127.7
119.5
115.3
115.0
113.9
113.6
103.7
81.8
68.5
68.5
29.6
29.4
29.1
29.1
26.1
26.0
23.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

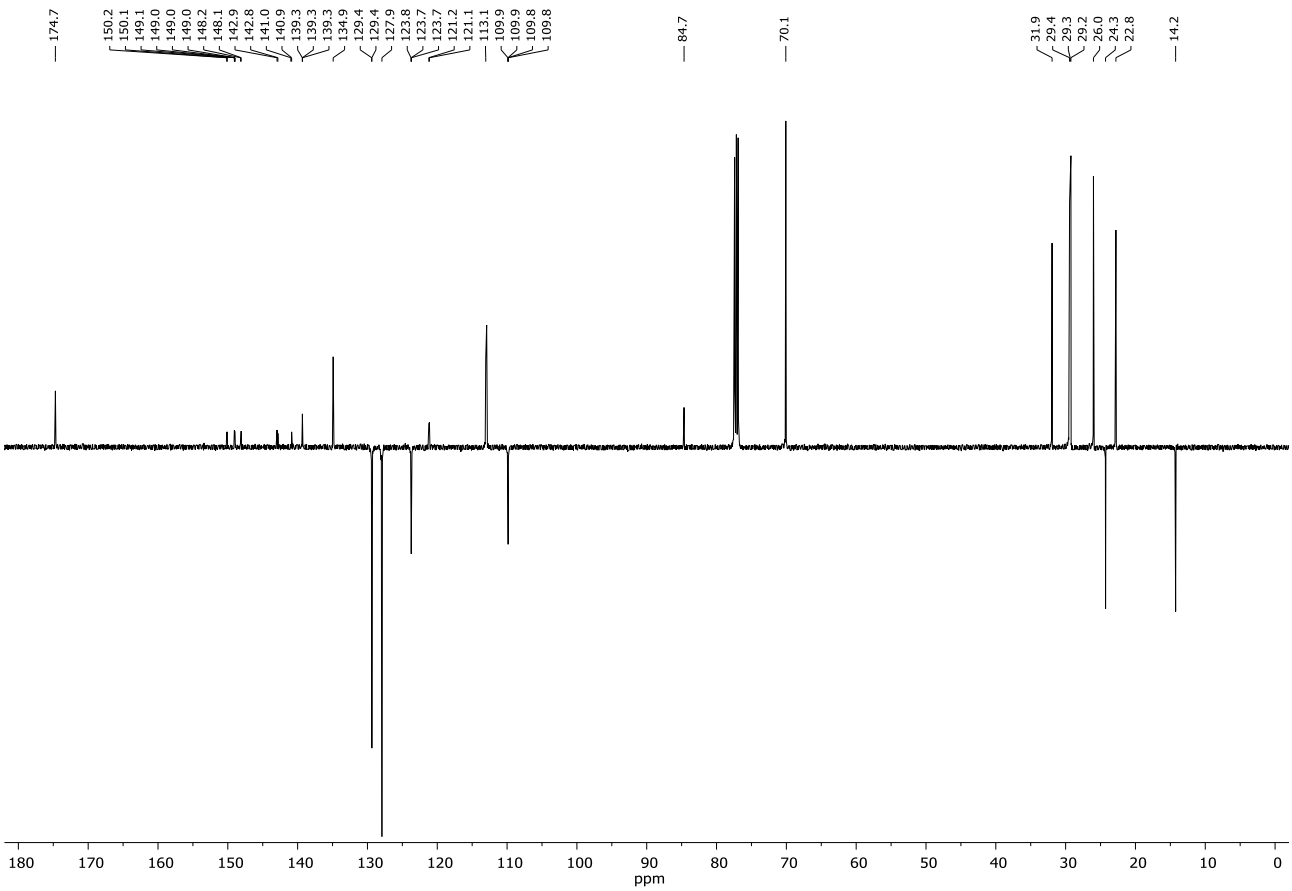
Compound 13f



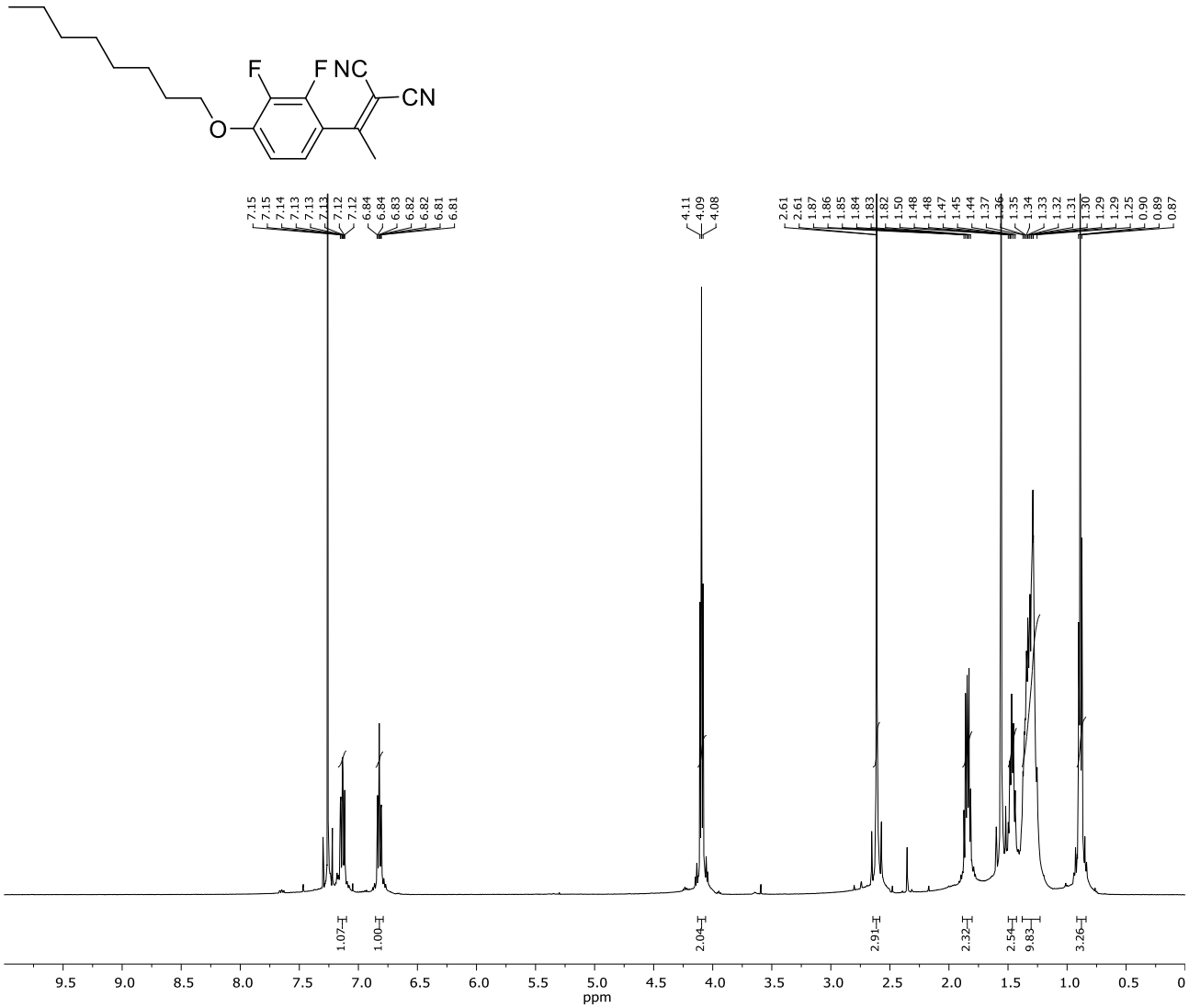

174.7
159.9
145.2
133.8
131.5
128.4
128.3
127.1
115.2
113.2
83.8
68.3
32.0
29.5
29.4
29.4
26.2
24.1
22.8
14.2
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

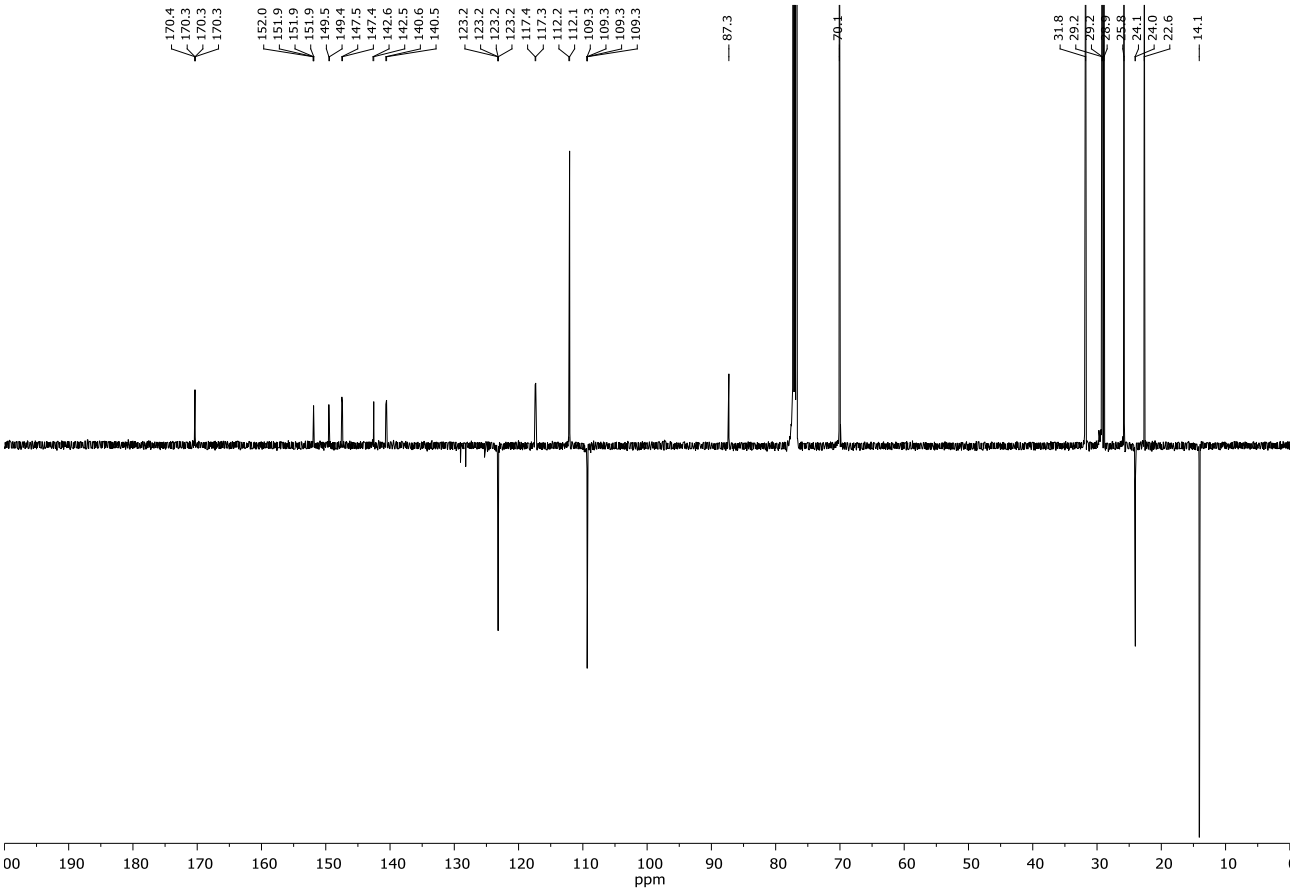
Compound 13g



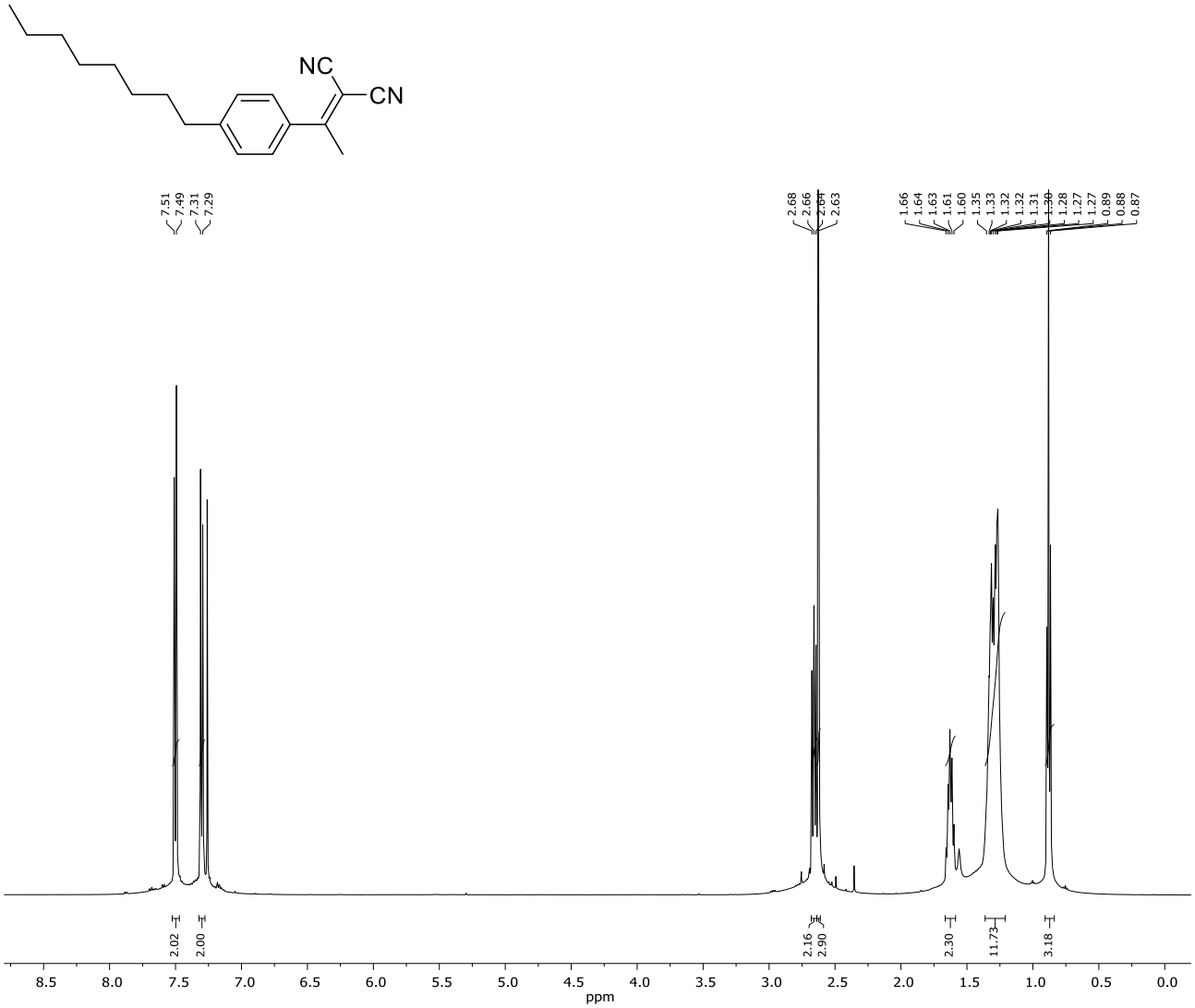

174.7
150.2
150.1
149.1
149.0
149.0
149.0
148.2
148.1
142.9
142.8
141.0
140.9
139.3
139.3
139.3
134.9
129.4
129.4
127.9
123.8
123.7
123.7
121.2
121.1
113.1
109.9
109.9
109.8
109.8
84.7
70.1
31.9
29.4
29.3
29.2
26.0
24.3
22.8
14.2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

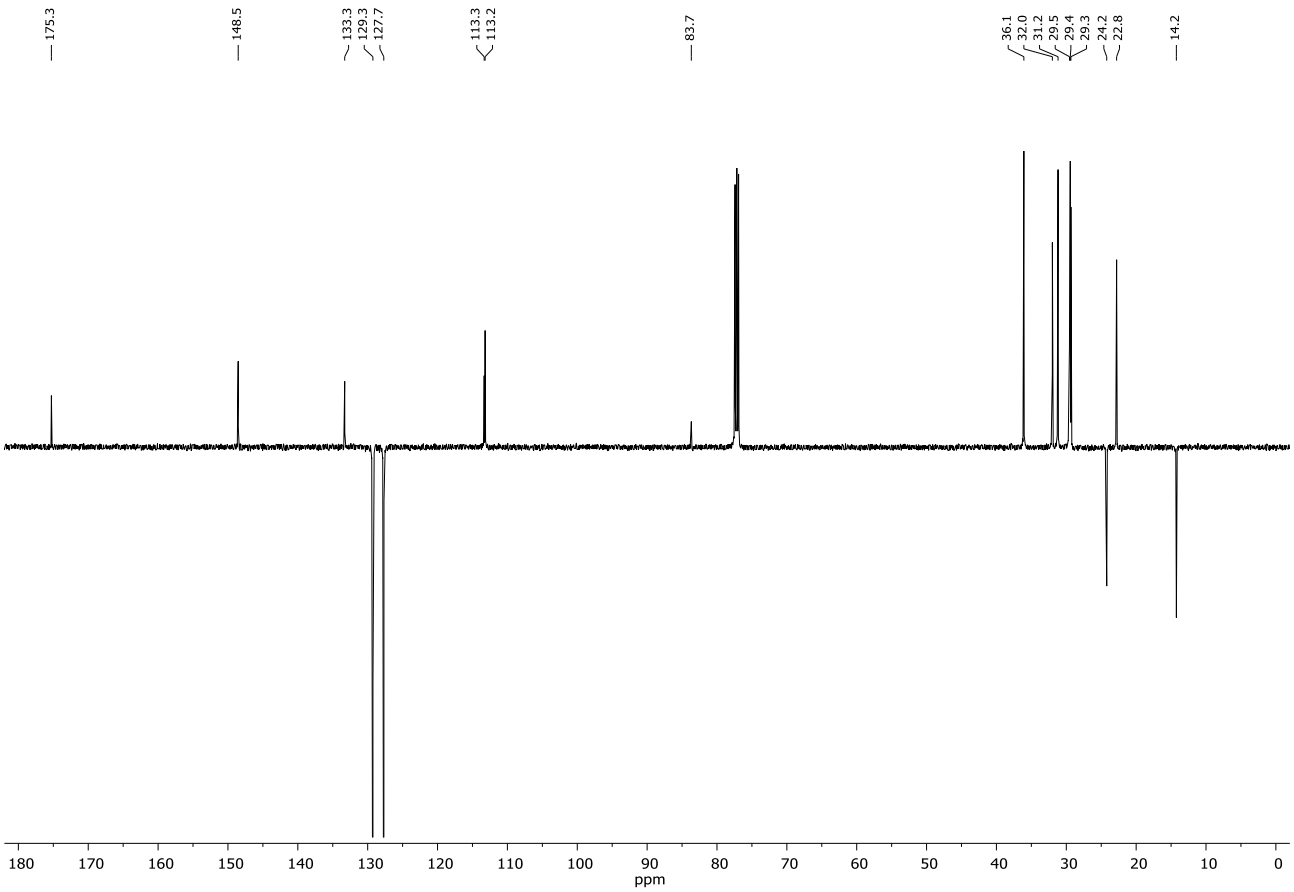
Compound 13h




170.4
170.3
170.3
170.3
152.0
151.9
151.9
151.9
149.5
149.4
147.5
147.4
142.6
142.5
140.6
140.5
123.2
123.2
123.2
123.2
117.4
117.3
112.2
112.1
109.3
109.3
109.3
109.3
87.3
70.1
31.8
29.2
29.2
28.9
25.8
24.1
24.0
22.6
14.1
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 13i

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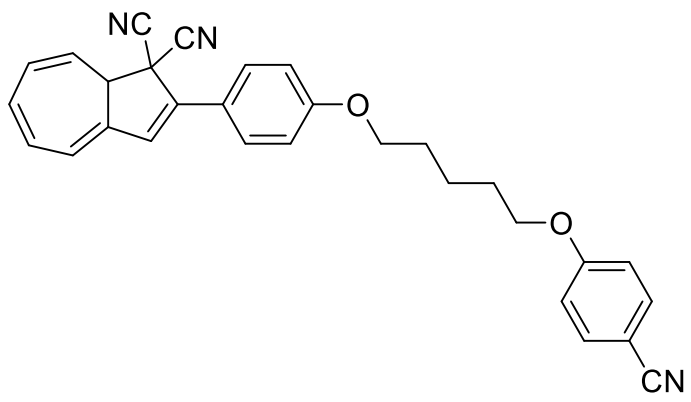
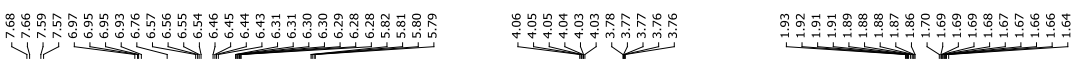
148.5
133.3
129.3
127.7
113.3
113.2
83.7
36.1
32.0
31.2
29.5
29.4
29.3
24.2
22.8
14.2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 3a


NC
CN
O
O
CN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7.66
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6.95
6.95
6.93
6.76
6.57
6.56
6.55
6.54
6.46
6.45
6.44
6.43
6.31
6.31
6.30
6.30
6.29
6.28
6.28
5.82
5.81
5.80
5.79
4.06
4.05
4.05
4.04
4.03
4.03
3.78
3.77
3.77
3.76
3.76
1.93
1.92
1.91
1.91
1.89
1.88
1.88
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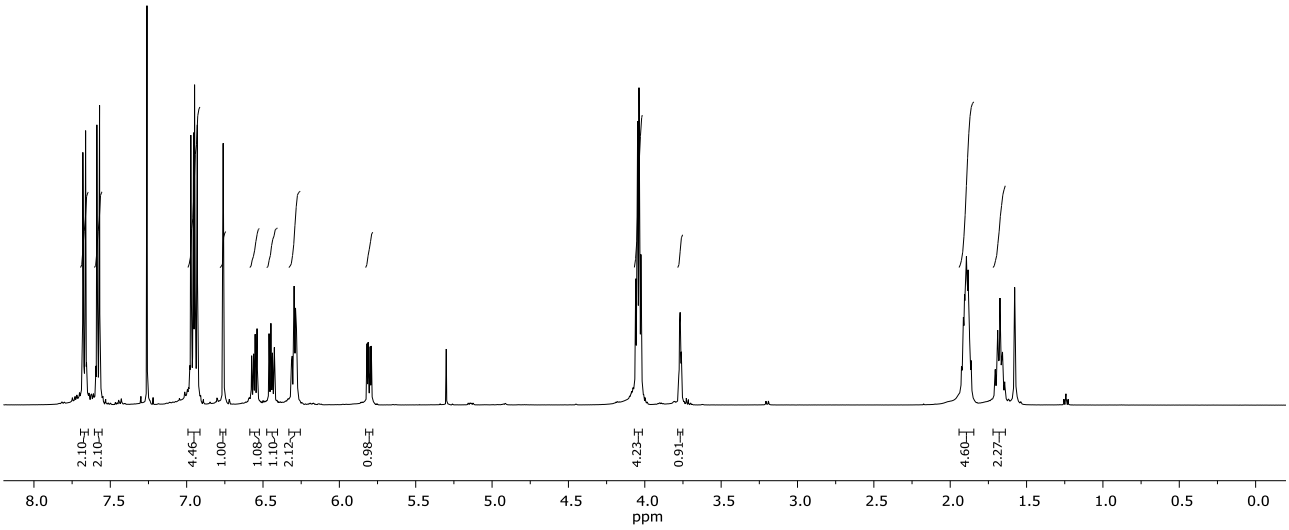
1.68
1.67
1.67
1.66
1.66
1.64


2.10
2.10
4.46
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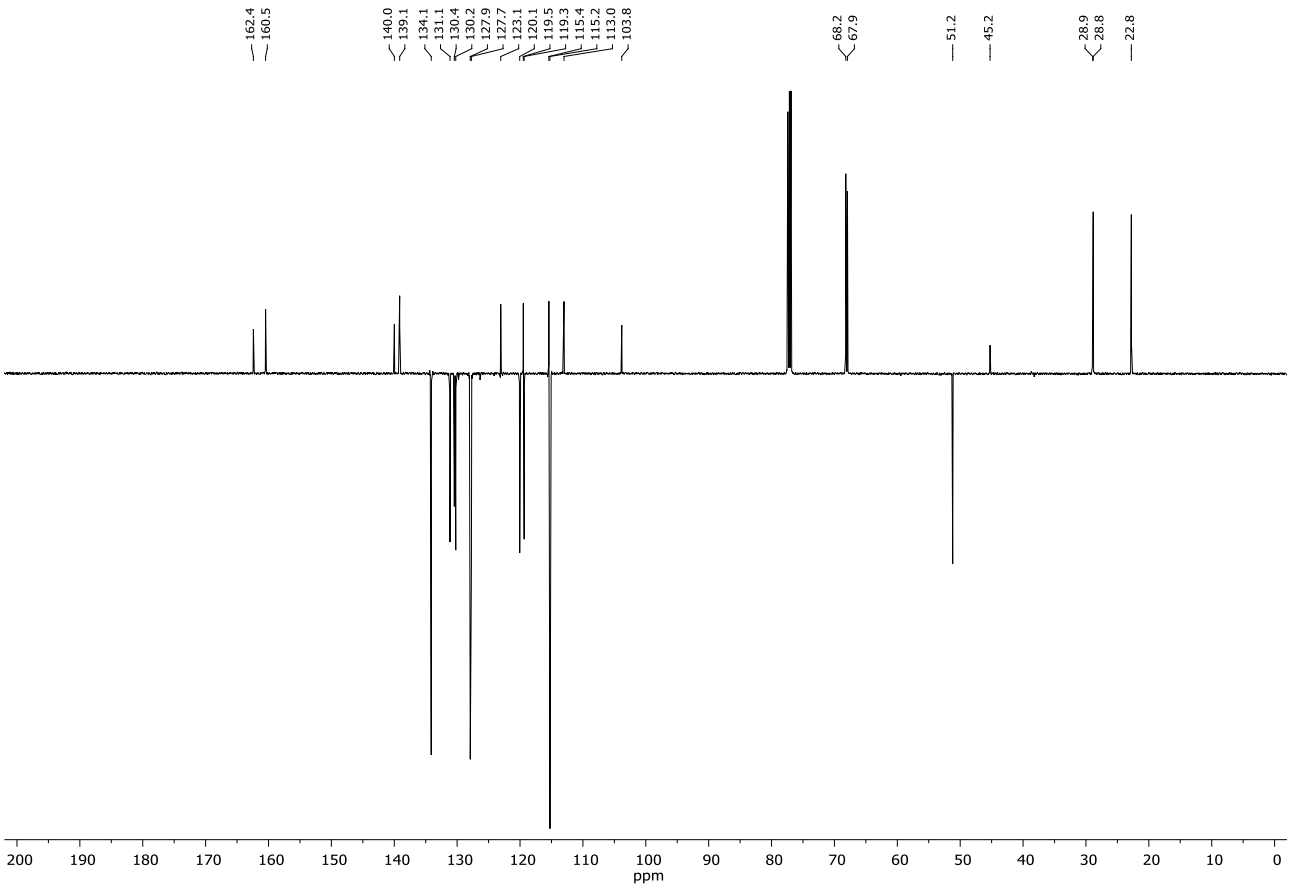
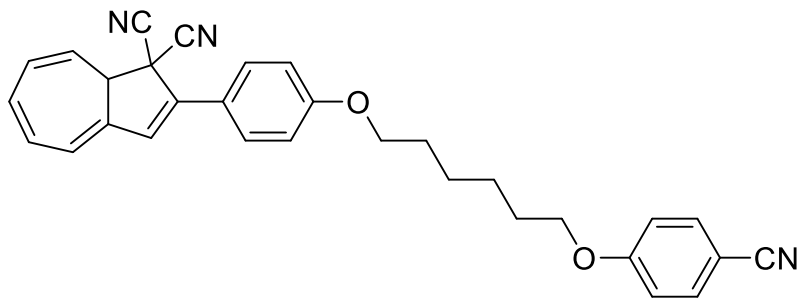
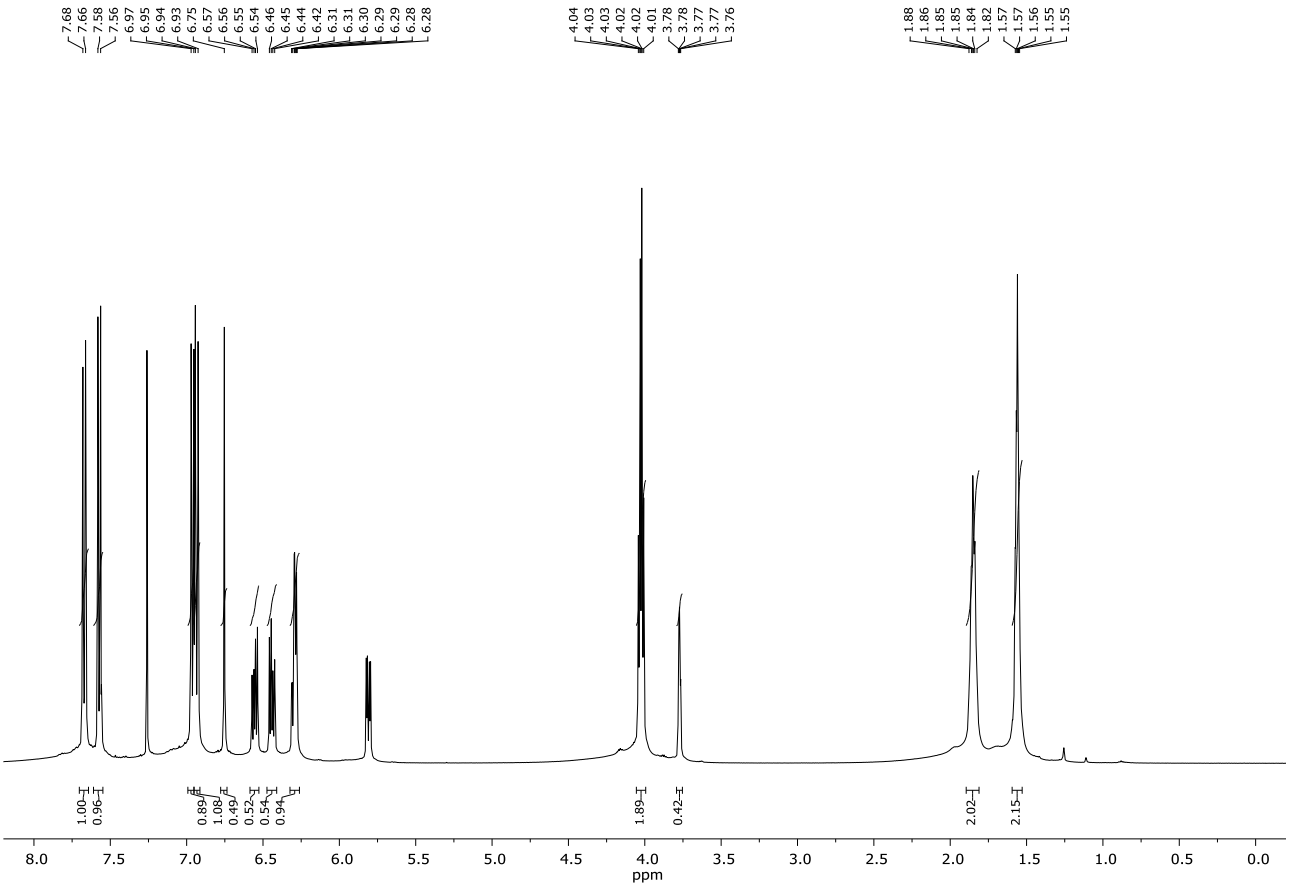
1.08
1.10
2.12
0.98
4.23
0.91
4.60
2.27
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


162.4
160.5
140.0
139.1
134.1
131.1
130.4
130.2
127.9
127.7
123.1
120.1
119.5
119.3
115.4
115.2
113.0
103.8
68.2
67.9
51.2
45.2
28.9
28.8
22.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 3b


NC
CN
O
O
CN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7.58
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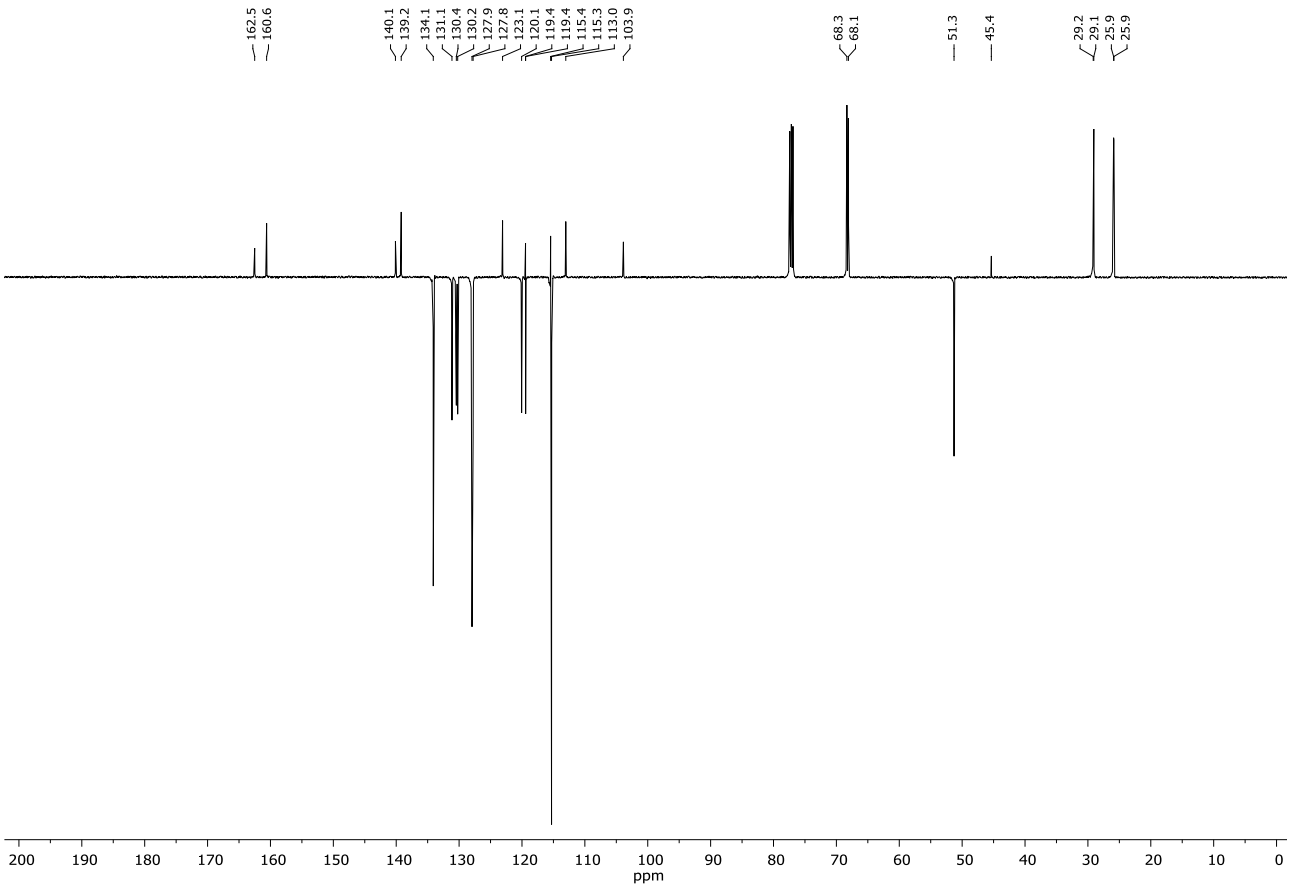
6.95
6.94
6.93
6.75
6.57
6.56
6.55
6.54
6.46
6.45
6.44
6.42
6.31
6.30
6.29
6.29
6.28
6.28
4.04
4.03
4.03
4.02
4.02
4.01
3.78
3.78
3.77
3.77
3.76
1.88
1.86
1.85
1.85
1.84
1.82
1.57
1.57
1.56
1.55
1.55
1.00
0.96
0.89
1.08
0.49
0.52
0.54
0.94
1.89
0.42
2.02
2.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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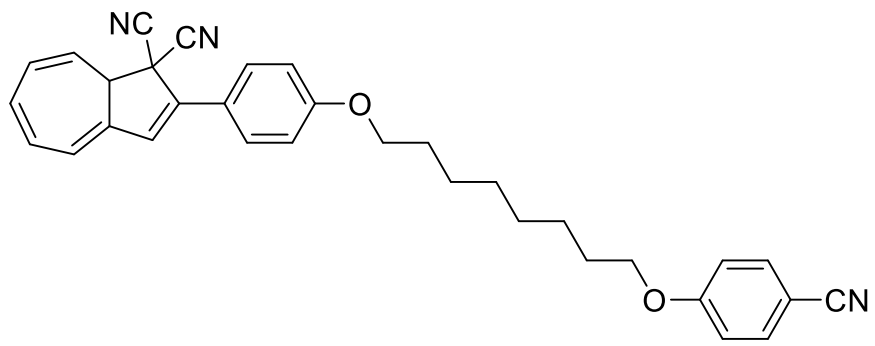
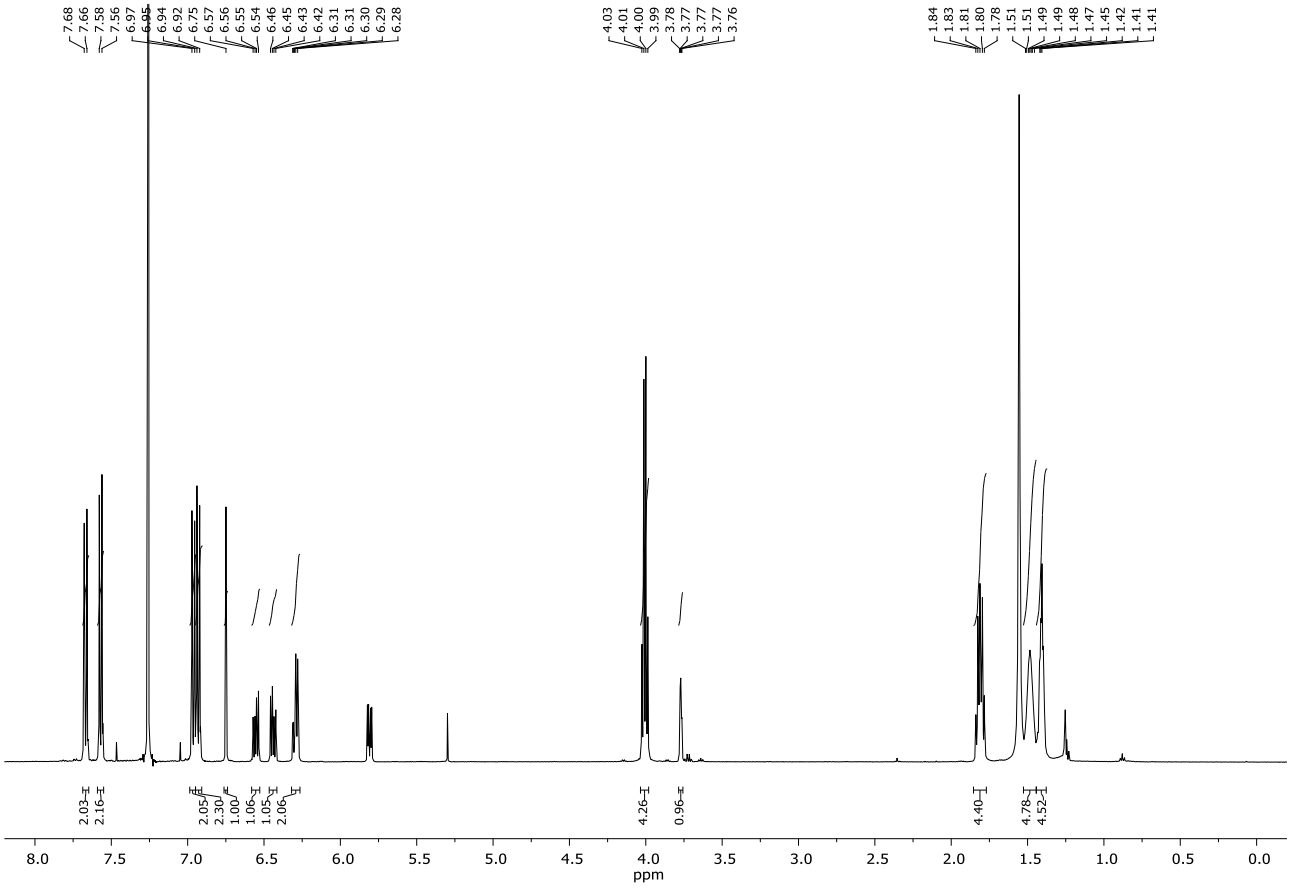
160.6
140.1
139.2
134.1
131.1
130.4
130.2
127.9
127.8
123.1
120.1
119.4
119.4
115.4
115.3
113.0
103.9
68.3
68.1
51.3
45.4
29.2
29.1
25.9
25.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 3c


NC
CN
O
O
CN


7.68
7.66
7.58
7.56
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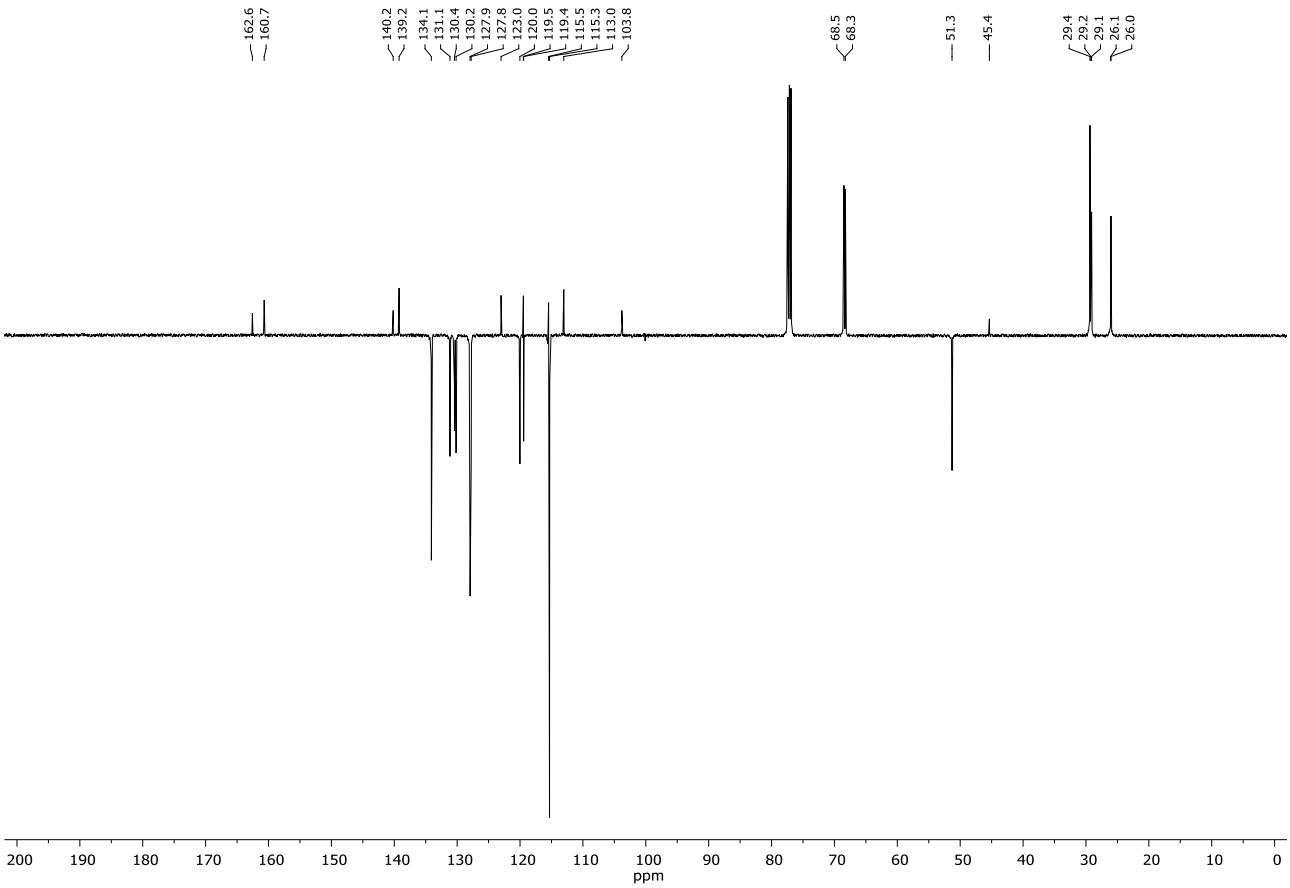
6.94
6.92
6.75
6.57
6.56
6.55
6.54
6.46
6.45
6.43
6.42
6.31
6.30
6.29
6.28
4.03
4.01
4.00
3.99
3.78
3.77
3.77
3.77
3.76
1.84
1.83
1.81
1.80
1.78
1.51
1.51
1.49
1.49
1.48
1.47
1.45
1.42
1.41
1.41
2.03
2.16
2.05
2.30
1.00
1.06
1.05
2.06
4.26
0.96
4.40
4.78
4.52
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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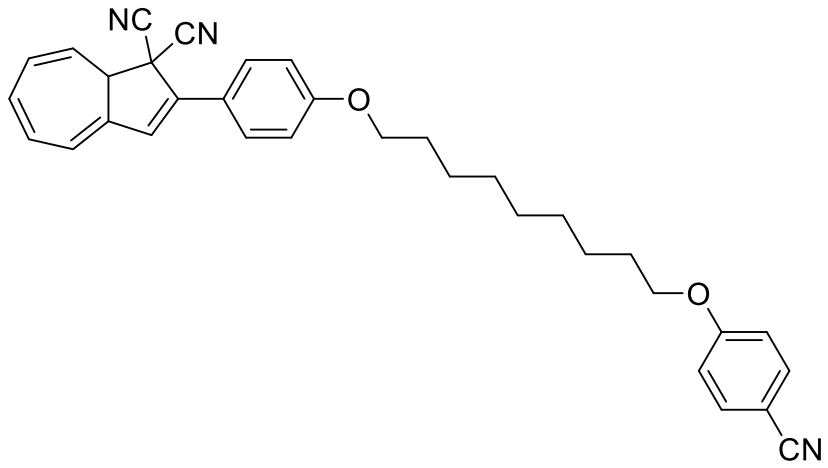
140.2
139.2
134.1
131.1
130.4
130.2
127.9
127.8
123.0
120.0
119.5
119.4
115.5
115.3
113.0
103.8
68.5
68.3
51.3
45.4
29.4
29.2
29.1
26.1
26.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 3d


NC
CN
O
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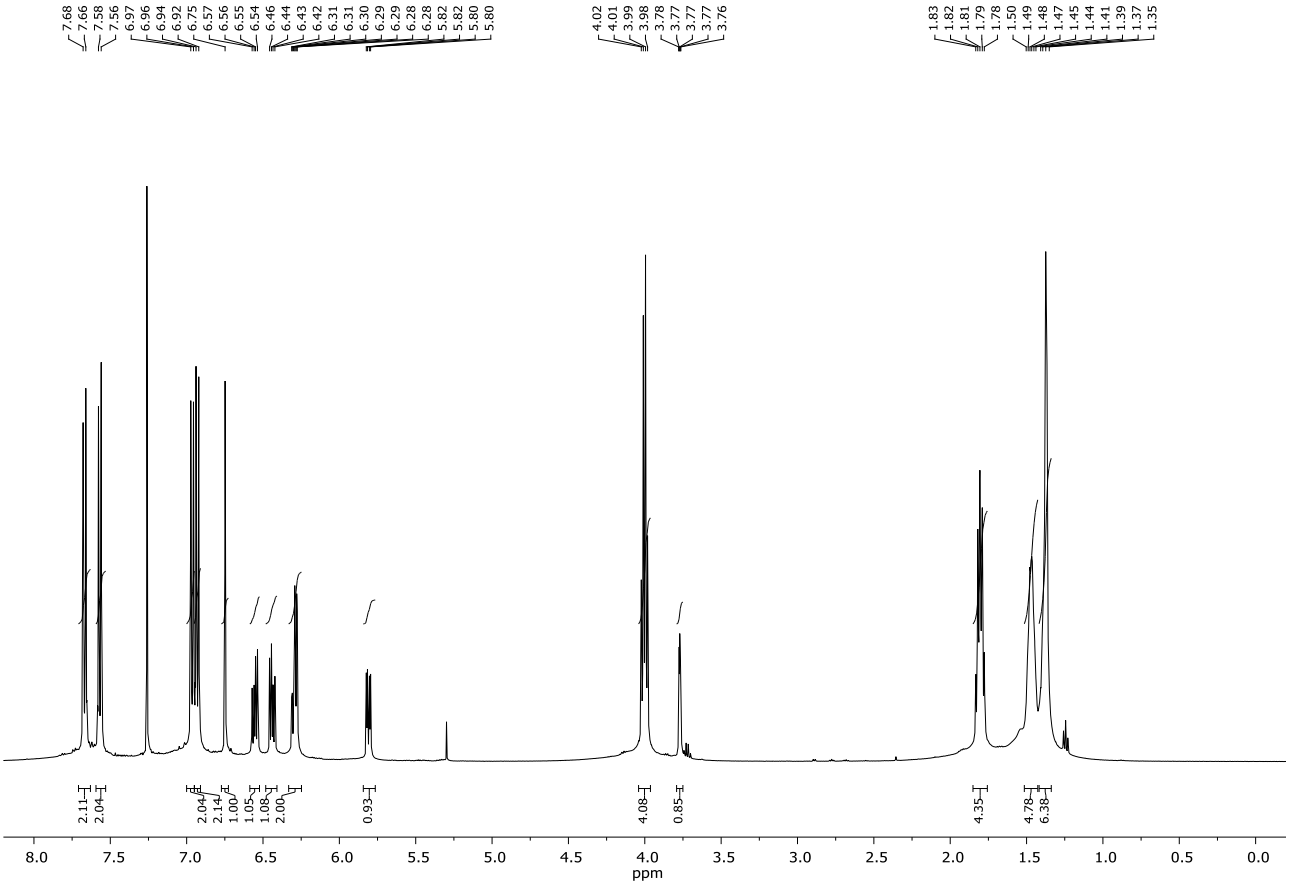
CN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6.54
6.46
6.44
6.43
6.42
6.31
6.30
6.29
6.29
6.28
6.28
5.82
5.82
5.80
5.80
4.02
4.01
3.99
3.98
3.78
3.77
3.77
3.77
3.76
1.83
1.82
1.81
1.79
1.78
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1.49
1.48
1.47
1.45
1.44
1.41
1.39
1.37
1.35
2.11
2.04
2.04
2.14
1.00
1.05
1.08
2.00
0.93
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0.85
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4.78
6.38
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7.0
6.5
6.0
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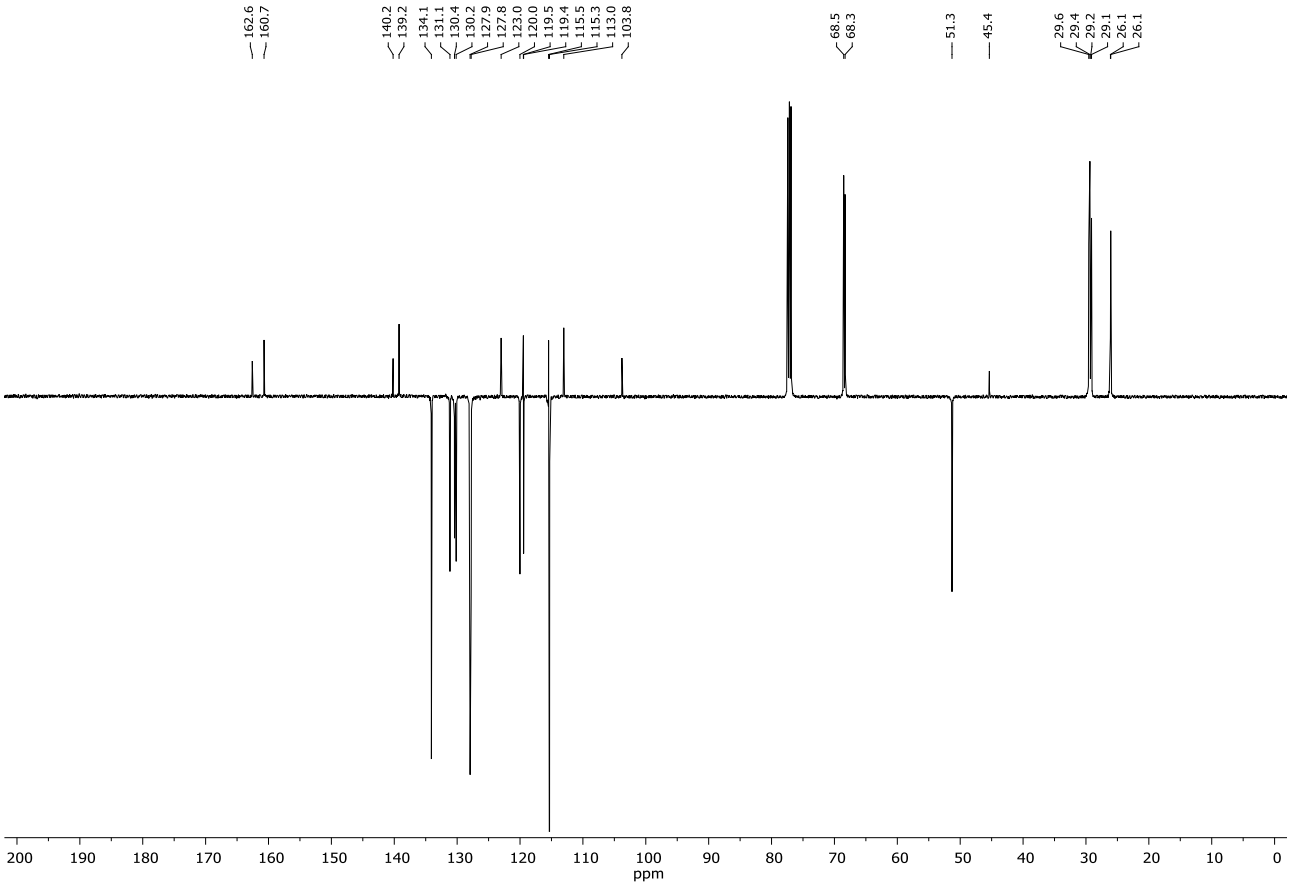
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130.2
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127.8
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120.0
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119.4
115.5
115.3
113.0
103.8
68.5
68.3
51.3
45.4
29.6
29.4
29.2
29.1
26.1
26.1
200
190
180
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120
110
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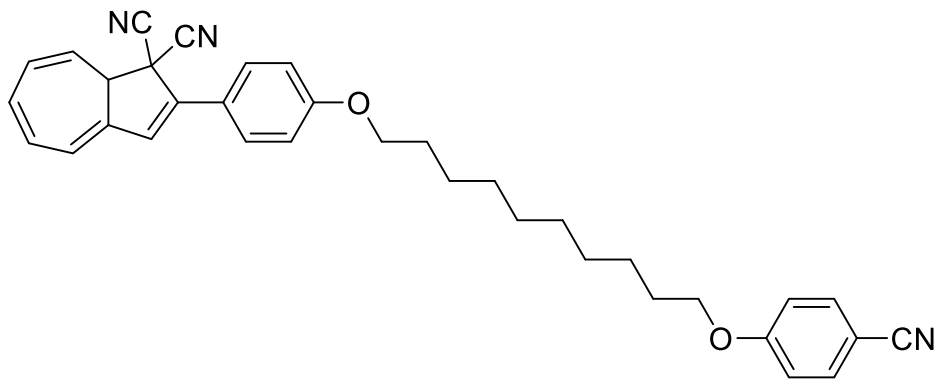
Compound 3e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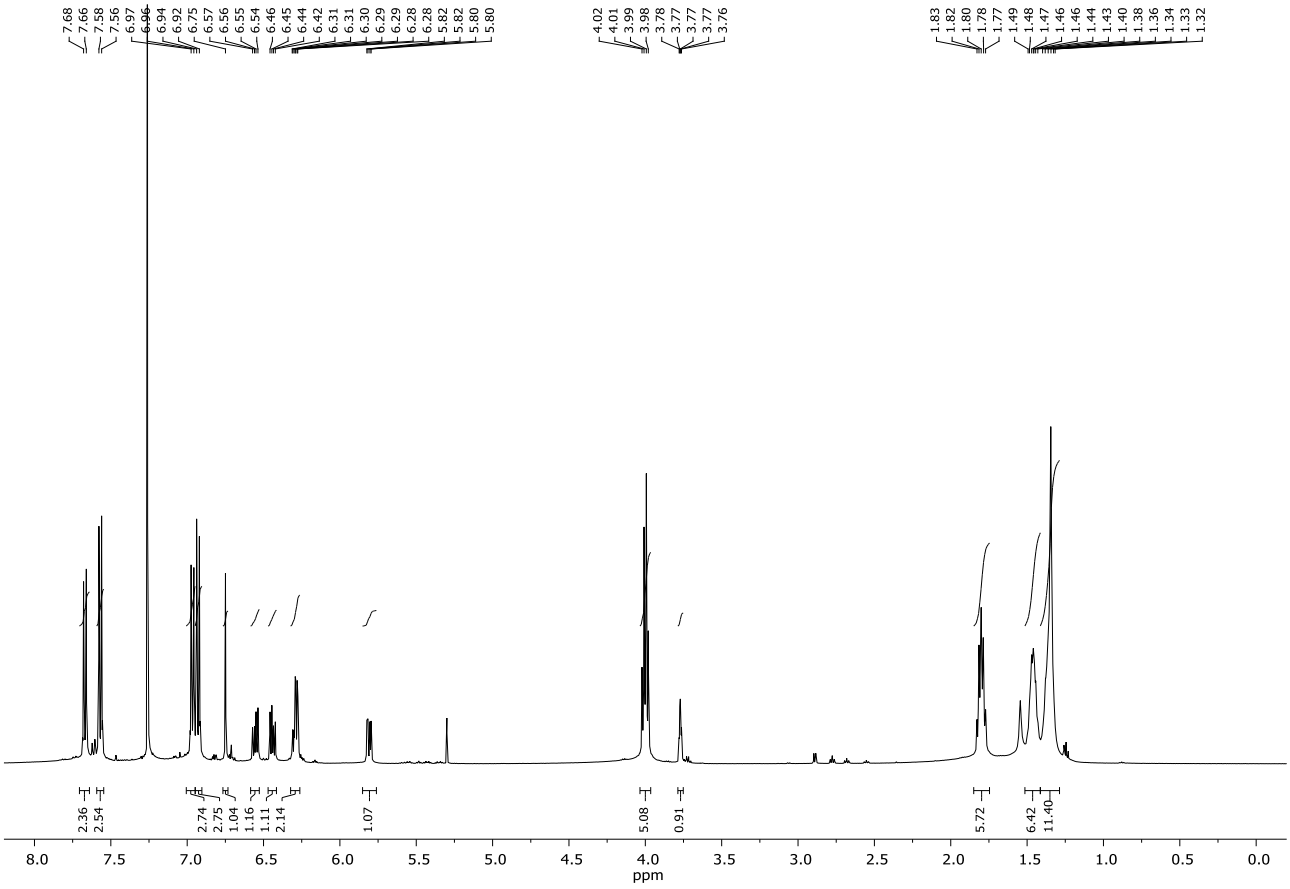
CN
O
O
CN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6.57
6.56
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6.54
6.46
6.45
6.44
6.42
6.31
6.30
6.29
6.28
5.82
5.80
4.02
4.01
3.99
3.98
3.78
3.77
3.77
3.77
3.76
1.83
1.82
1.80
1.78
1.77
1.49
1.48
1.47
1.46
1.46
1.44
1.43
1.40
1.38
1.36
1.34
1.33
1.32
2.36
2.54
2.74
2.75
1.04
1.16
1.11
2.14
1.07
5.08
0.91
5.72
6.42
11.40
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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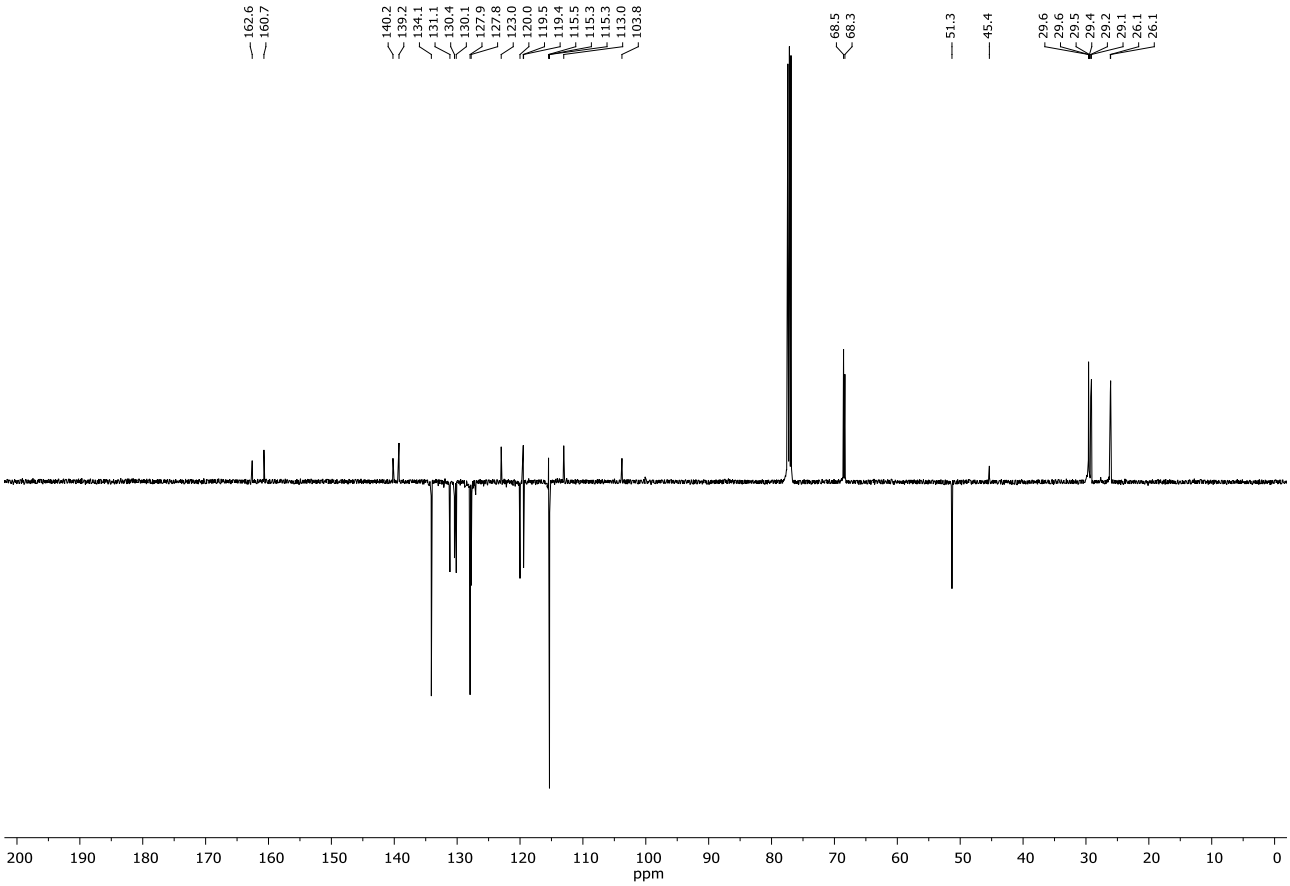
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130.1
127.9
127.8
123.0
120.0
119.5
119.4
115.5
115.3
115.3
113.0
103.8
68.5
68.3
51.3
45.4
29.6
29.6
29.5
29.4
29.2
29.1
26.1
26.1
200
190
180
170
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140
130
120
110
100
90
80
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40
30
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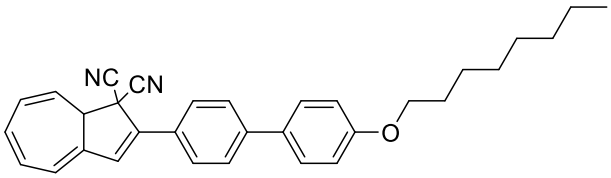
0
ppm

Compound 3f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CN
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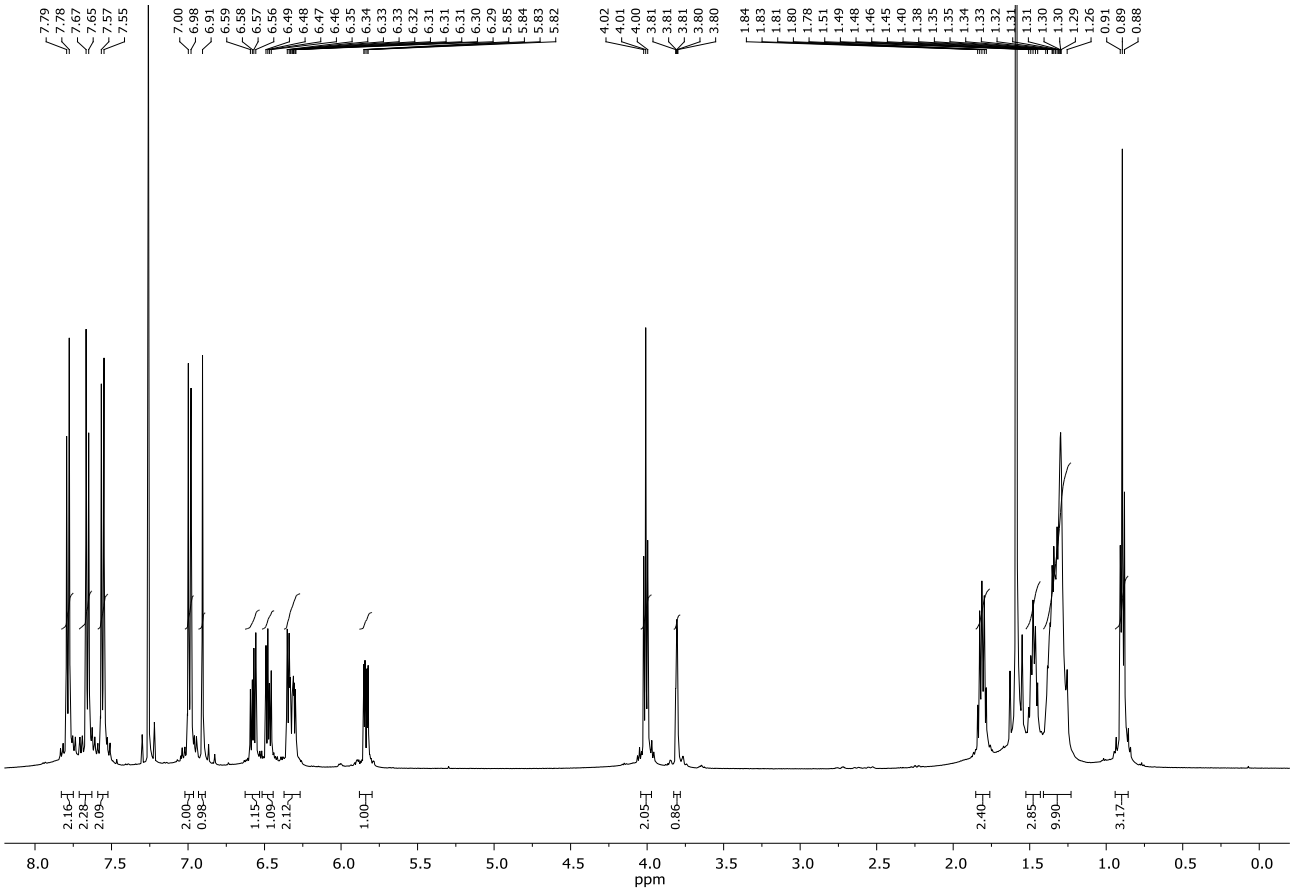
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6.98
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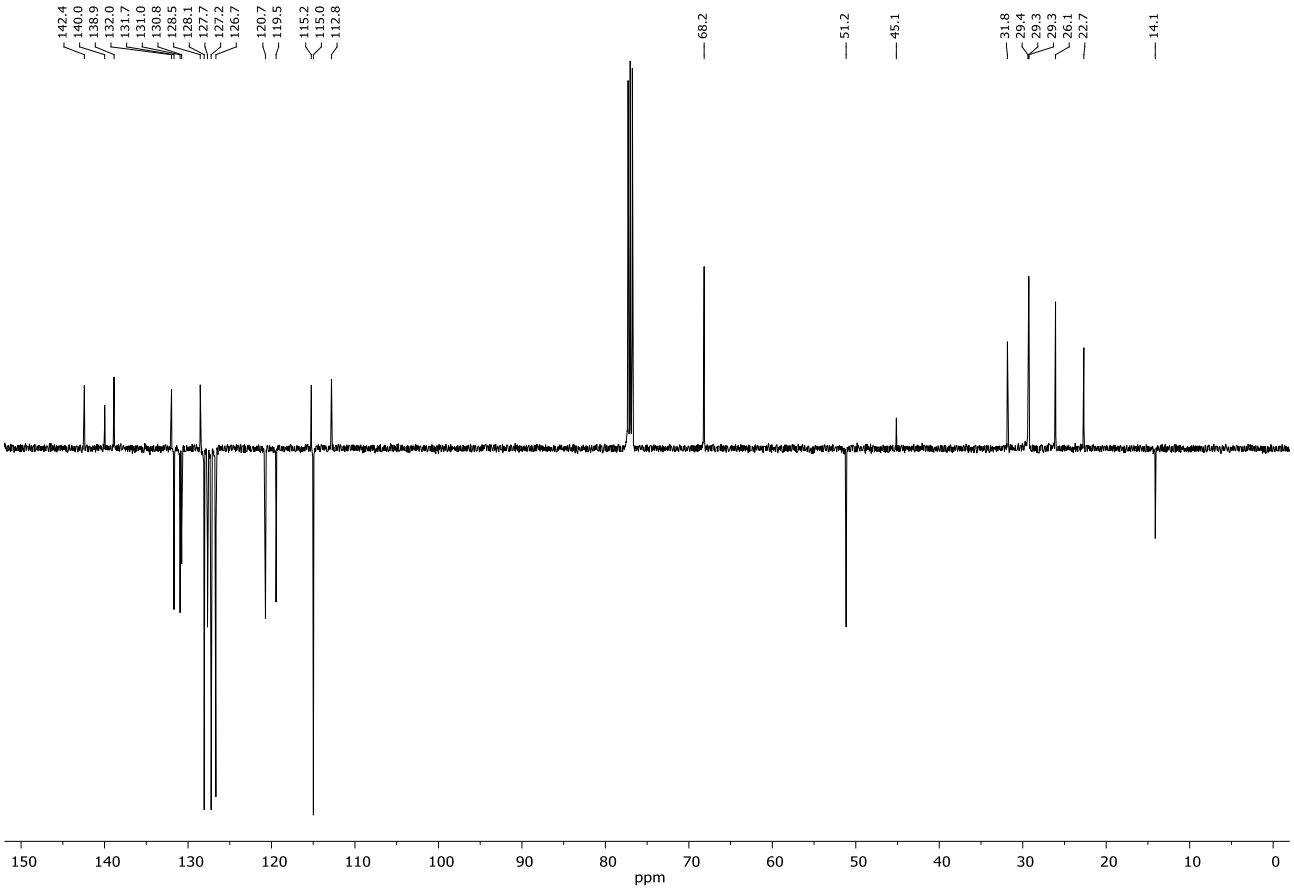
6.59
6.58
6.57
6.56
6.49
6.48
6.47
6.46
6.35
6.34
6.33
6.33
6.32
6.31
6.31
6.31
6.30
6.29
5.85
5.84
5.83
5.82
4.02
4.01
4.00
3.81
3.81
3.81
3.80
3.80
1.84
1.83
1.81
1.80
1.78
1.51
1.49
1.48
1.46
1.45
1.40
1.38
1.35
1.35
1.34
1.33
1.32
1.31
1.31
1.30
1.30
1.29
1.26
0.91
0.89
0.88
2.16
2.28
2.09
2.00
0.98
1.15
1.09
2.12
1.00
2.05
0.86
2.40
2.85
9.90
3.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


142.4
140.0
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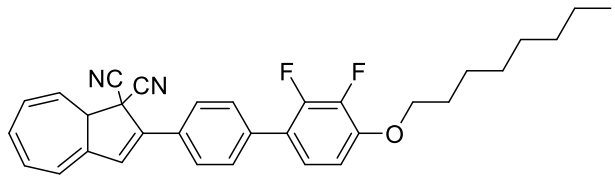
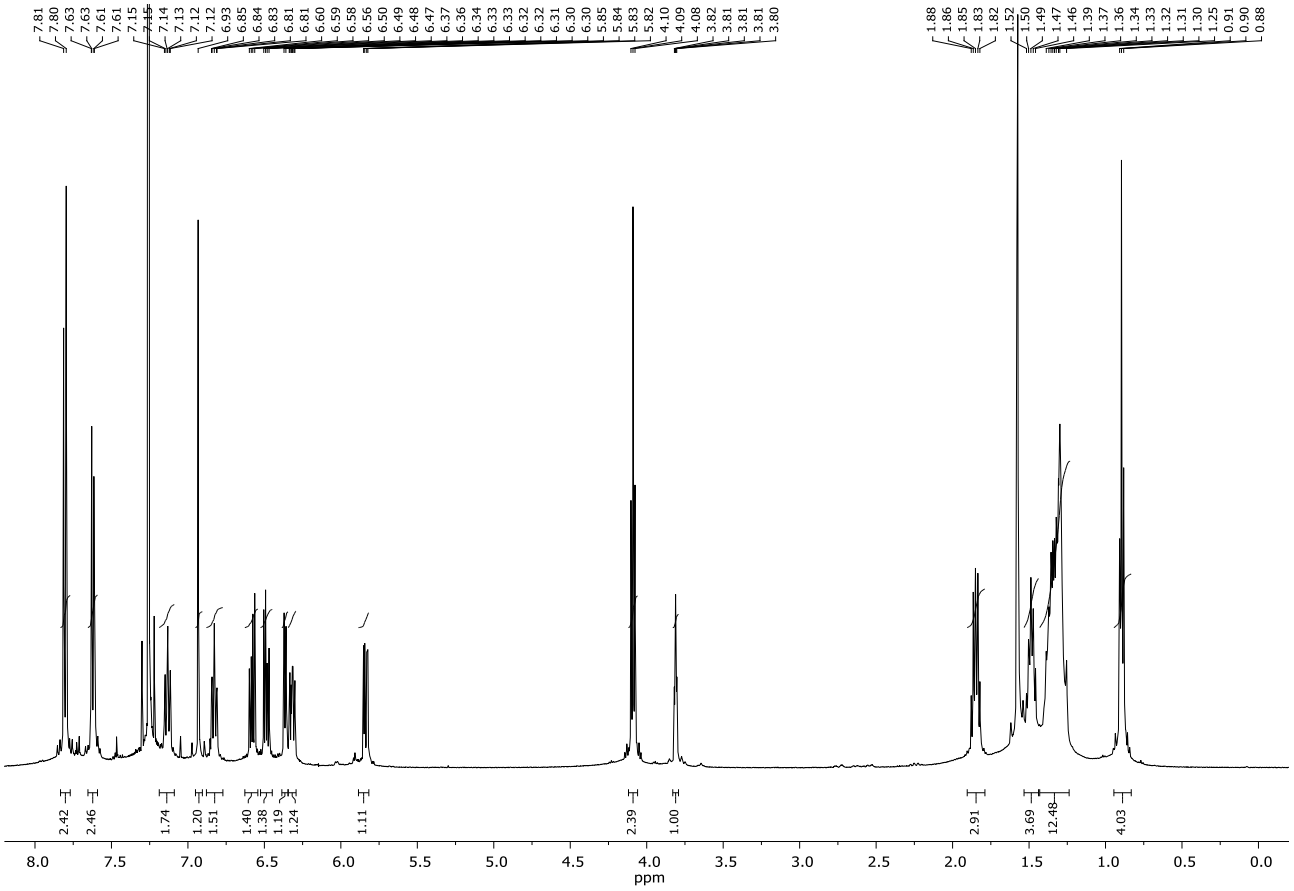
132.0
131.7
131.0
130.8
128.5
128.1
127.7
127.2
126.7
120.7
119.5
115.2
115.0
112.8
68.2
51.2
45.1
31.8
29.4
29.3
29.3
26.1
22.7
14.1
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 3g


NC
CN
F
F
O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7.14
7.13
7.12
7.12
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6.84
6.83
6.81
6.81
6.60
6.59
6.58
6.56
6.50
6.49
6.48
6.47
6.37
6.36
6.34
6.33
6.33
6.32
6.32
6.31
6.30
6.30
5.85
5.84
5.83
5.82
4.10
4.09
4.08
3.82
3.81
3.81
3.81
3.80
1.88
1.86
1.85
1.83
1.82
1.52
1.50
1.49
1.47
1.46
1.39
1.37
1.36
1.34
1.33
1.32
1.31
1.30
1.25
0.91
0.90
0.88
2.42
2.46
1.74
1.20
1.51
1.40
1.38
1.19
1.24
1.11
2.39
1.00
2.91
3.69
12.48
4.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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2.0
1.5
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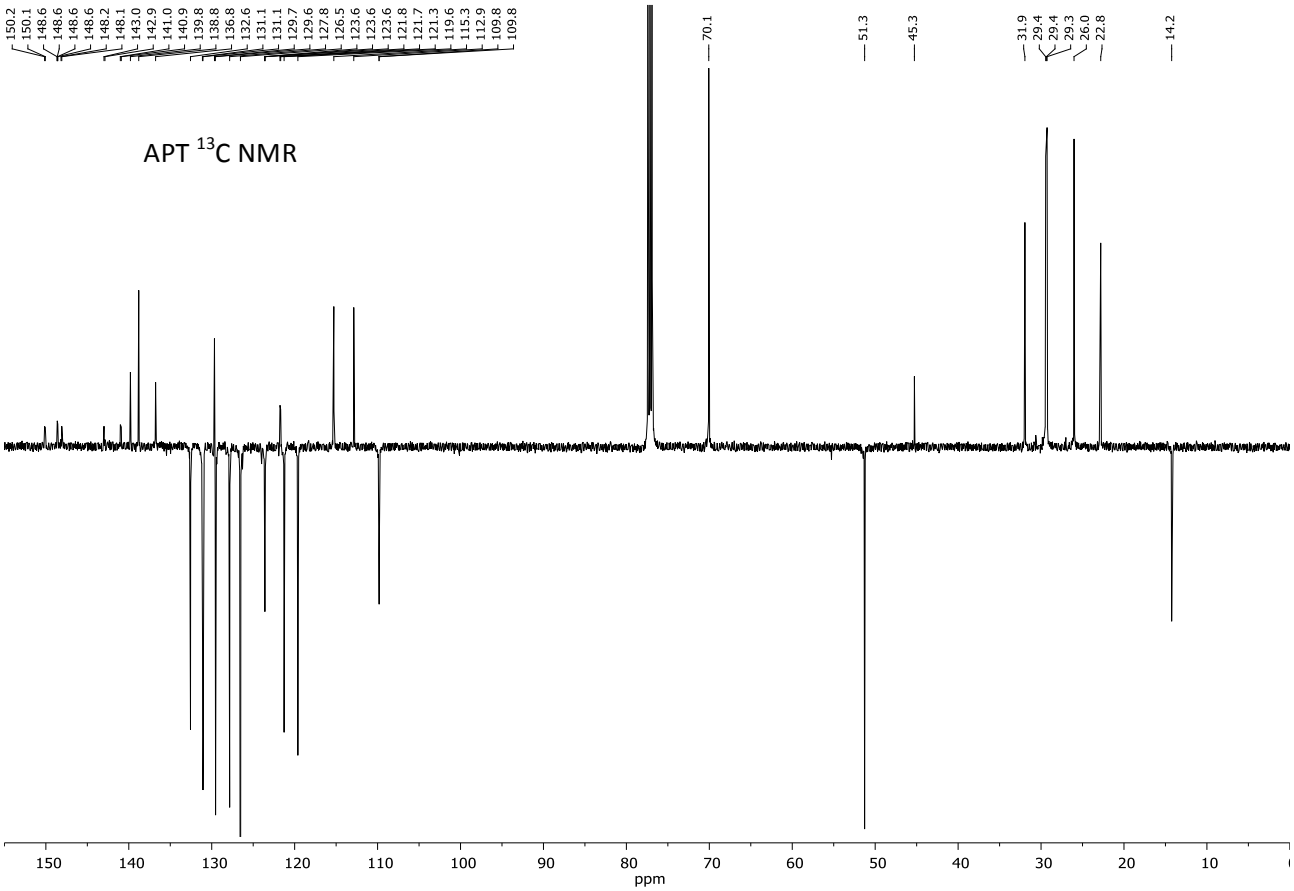
0.0
ppm


APT ^{13}C NMR
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148.6
148.6
148.6
148.6
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148.1
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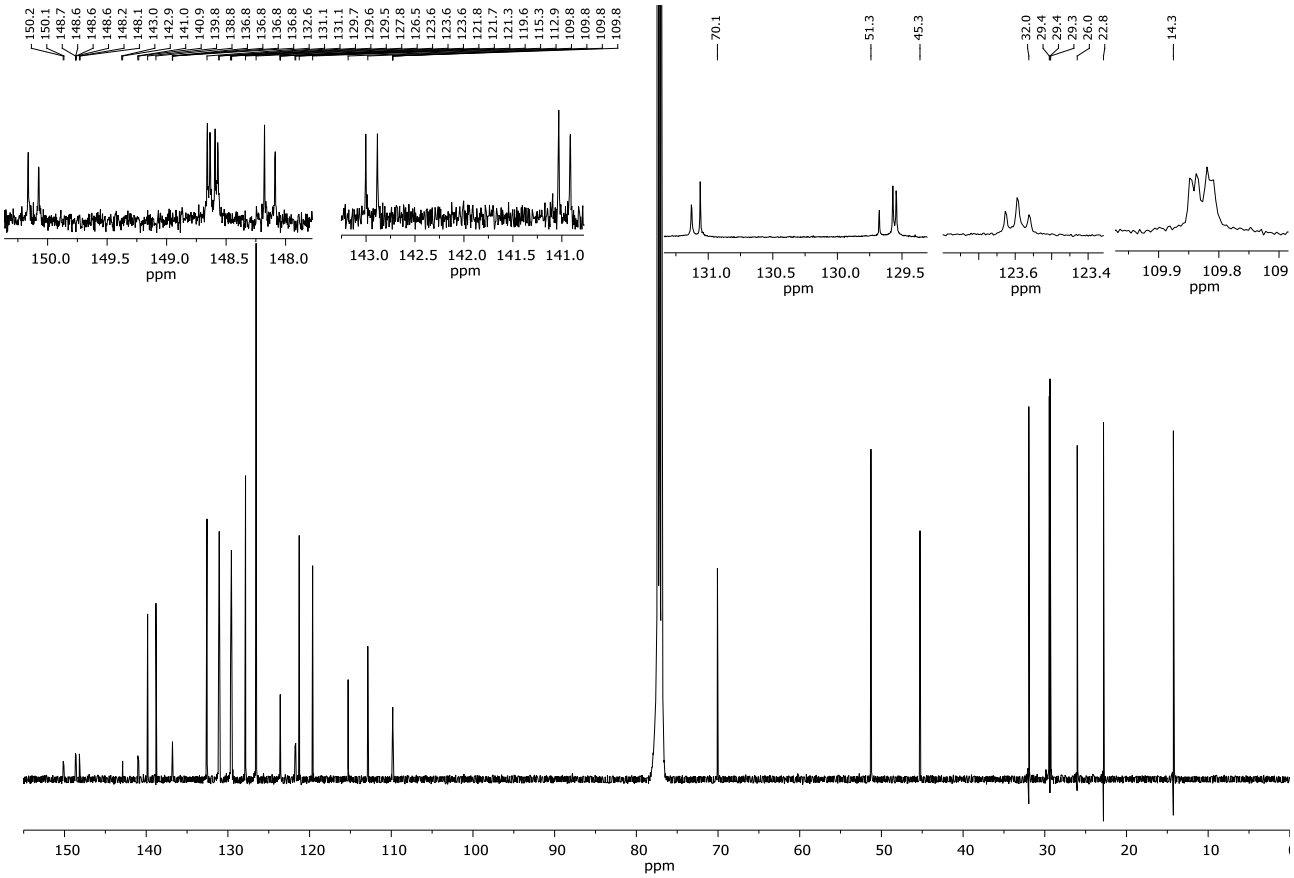
141.0
140.9
139.8
138.8
136.8
132.6
131.1
131.1
129.7
129.6
127.8
126.5
123.6
123.6
123.6
121.8
121.7
121.3
119.6
115.3
112.9
109.8
109.8
70.1
51.3
45.3
31.9
29.4
29.4
29.3
26.0
22.8
14.2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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148.6
148.6
148.2
148.1
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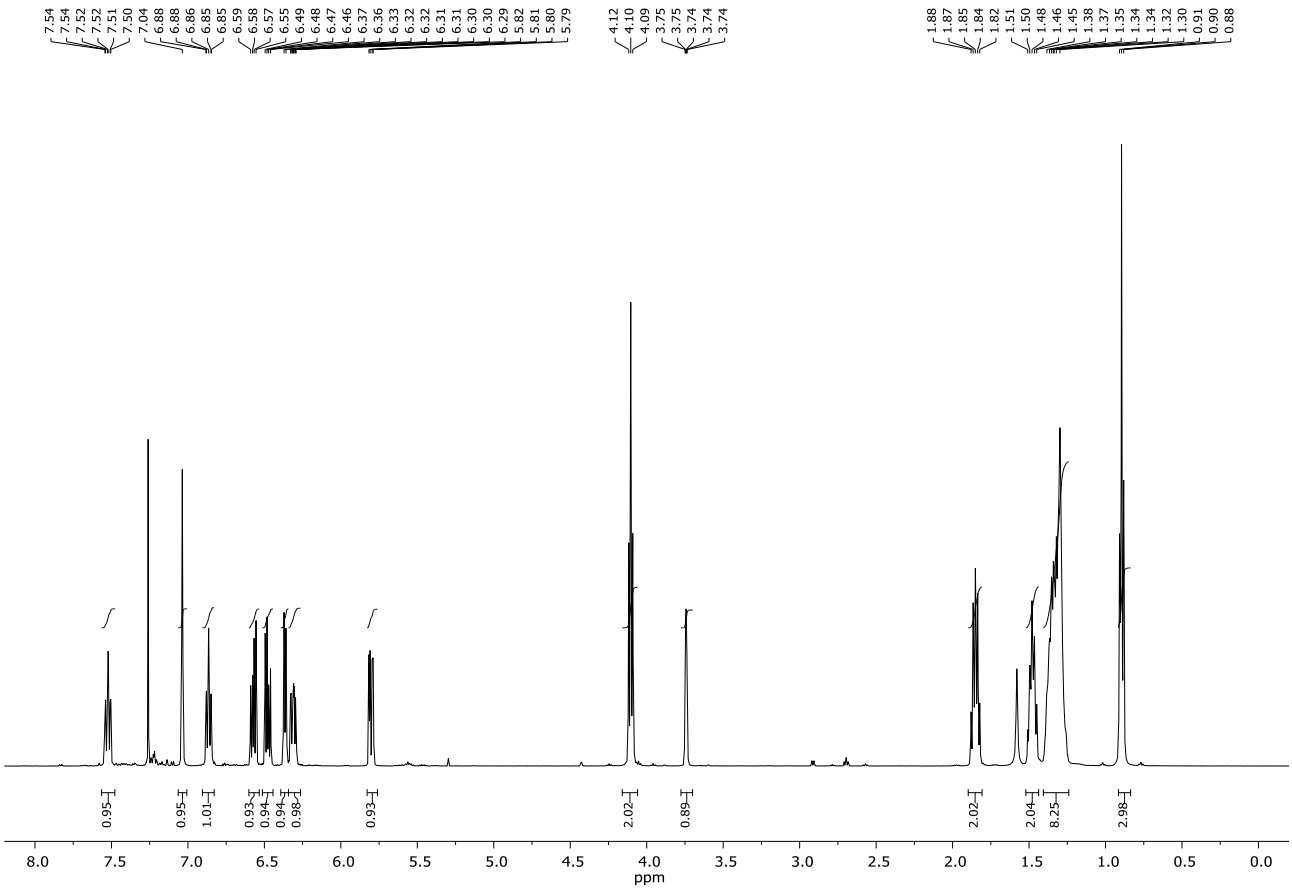
142.9
141.0
140.9
139.8
138.8
136.8
136.8
136.8
136.8
132.6
131.1
131.1
129.7
129.6
129.5
127.8
126.5
123.6
123.6
123.6
121.8
121.7
121.3
119.6
115.3
112.9
109.8
109.8
109.8
70.1
51.3
45.3
32.0
29.4
29.4
29.3
26.0
22.8
14.3
150.0
149.5
149.0
148.5
148.0
ppm
143.0
142.5
142.0
141.5
141.0
ppm
131.0
130.5
130.0
129.5
ppm
123.6
123.4
ppm
109.9
109.8
109
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 3h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7.04
6.88
6.88
6.86
6.85
6.85
6.59
6.58
6.57
6.55
6.49
6.48
6.47
6.46
6.37
6.36
6.33
6.32
6.32
6.31
6.31
6.30
6.30
6.29
5.82
5.81
5.80
5.79
4.12
4.10
4.09
3.75
3.75
3.74
3.74
3.74
1.88
1.87
1.85
1.84
1.82
1.51
1.50
1.48
1.46
1.45
1.38
1.37
1.35
1.34
1.34
1.32
1.30
0.91
0.90
0.88
0.95
0.95
1.01
0.93
0.94
0.94
0.98
0.93
2.02
0.89
2.02
2.04
8.25
2.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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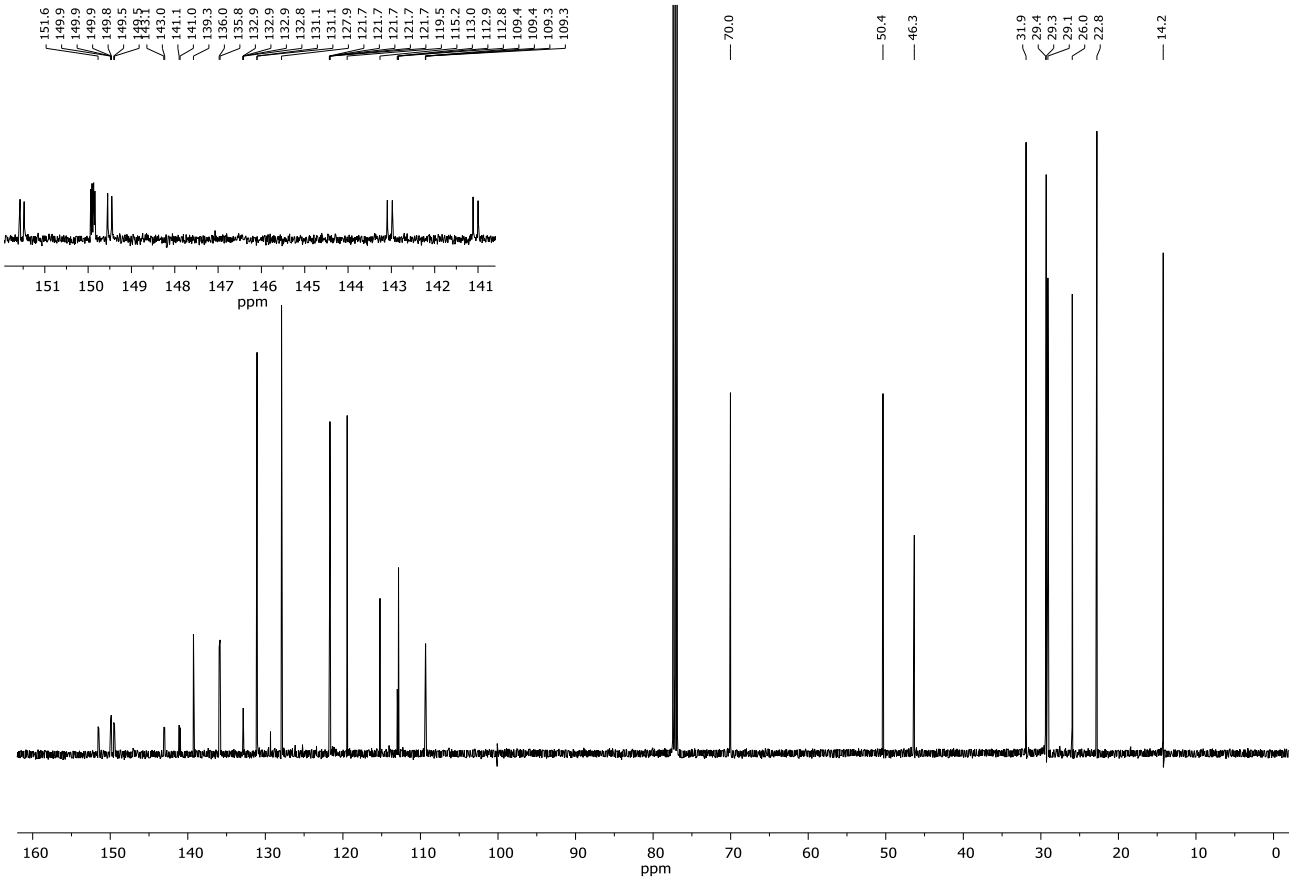
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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141.0
139.3
136.0
135.8
132.9
132.9
132.9
132.8
131.1
131.1
127.9
121.7
121.7
121.7
121.7
121.7
119.5
115.2
113.0
112.9
112.8
109.4
109.4
109.3
109.3
70.0
50.4
46.3
31.9
29.4
29.3
29.1
26.0
22.8
14.2
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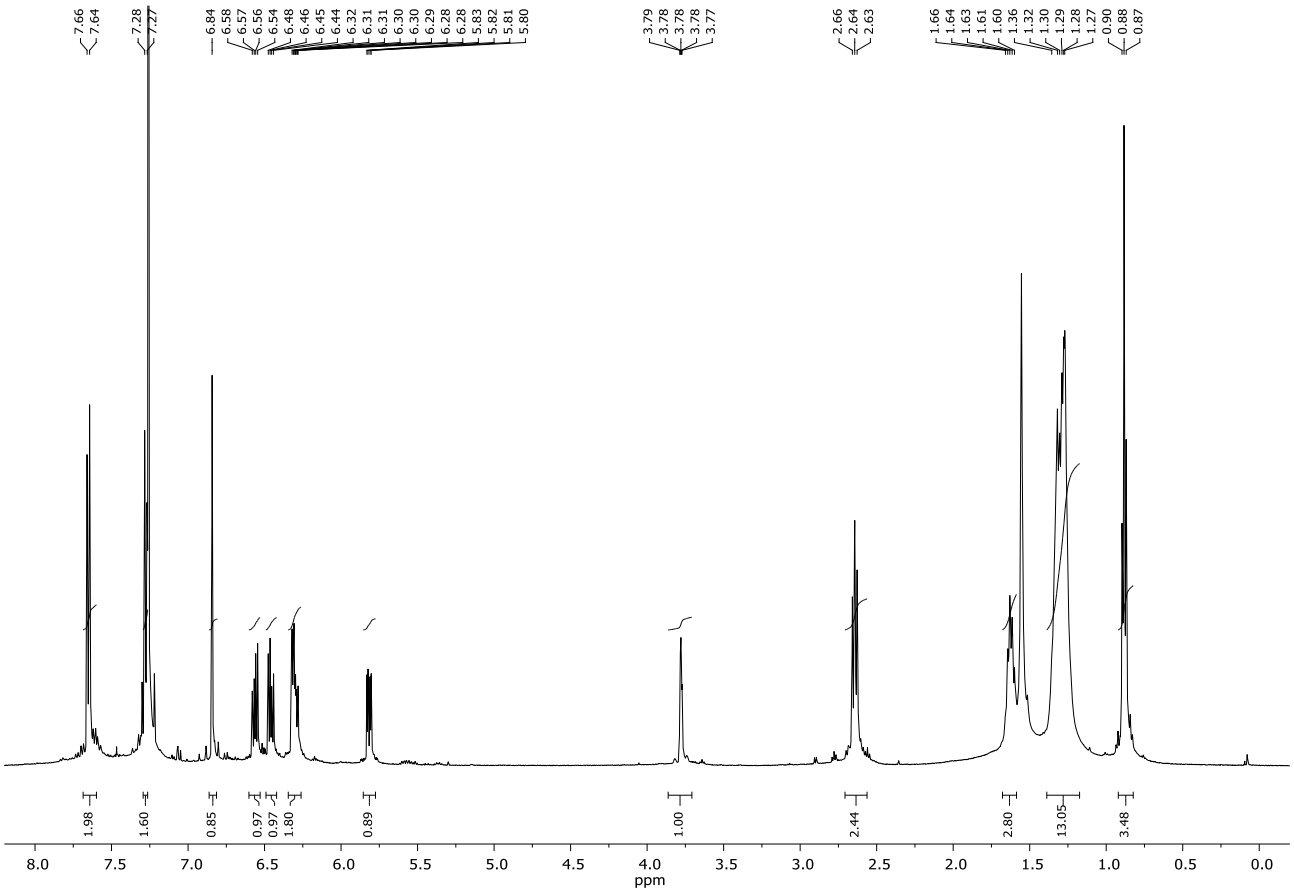
ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Compound 3i


NC
CN


7.66
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6.56
6.54
6.48
6.46
6.45
6.44
6.32
6.31
6.31
6.30
6.30
6.29
6.28
6.28
5.83
5.82
5.81
5.80
3.79
3.78
3.78
3.78
3.77
2.66
2.64
2.63
1.66
1.64
1.63
1.61
1.60
1.36
1.32
1.30
1.29
1.28
1.27
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0.88
0.87
1.98
1.60
0.85
0.97
0.97
1.80
0.89
1.00
2.44
2.80
13.05
3.48
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
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1.5
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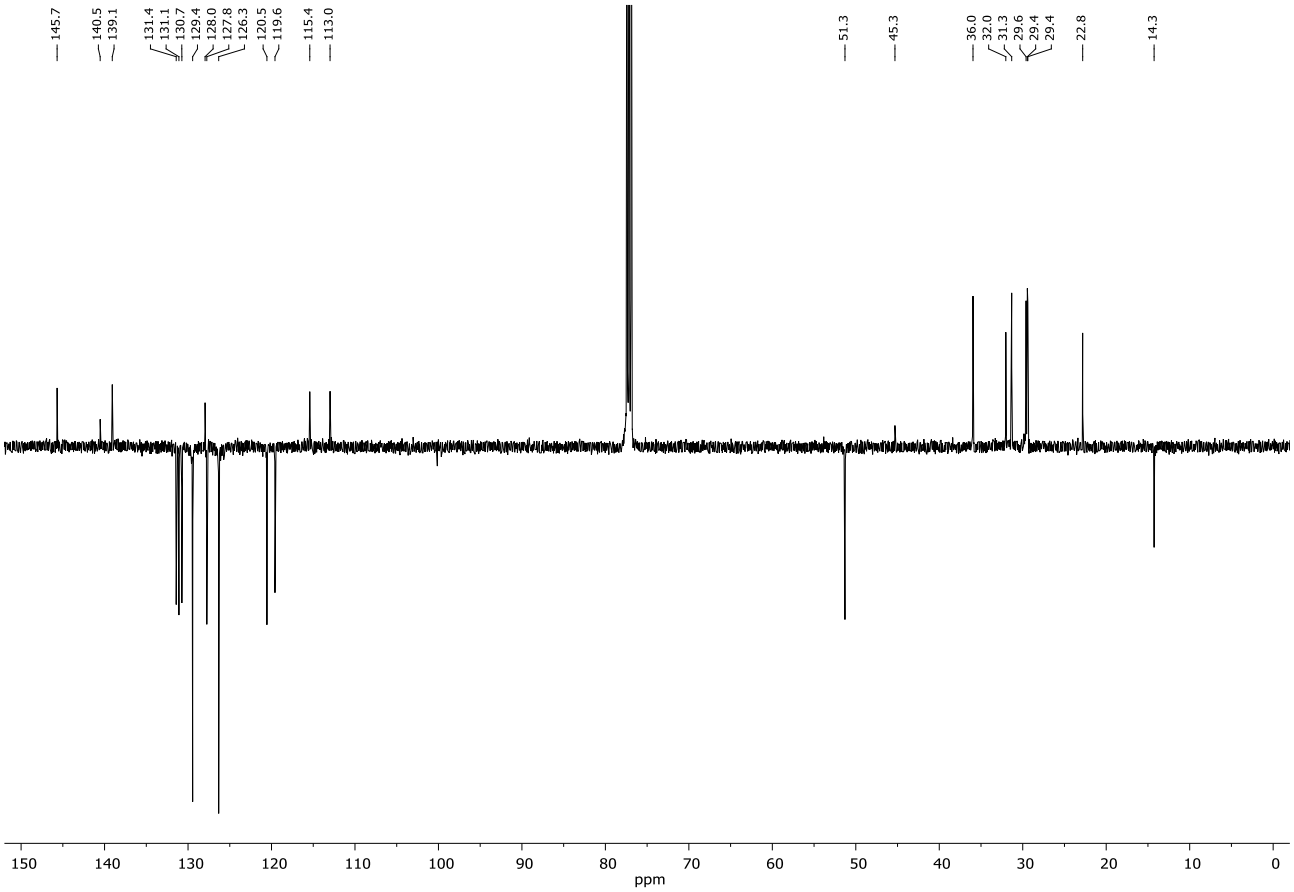
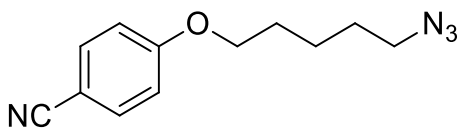
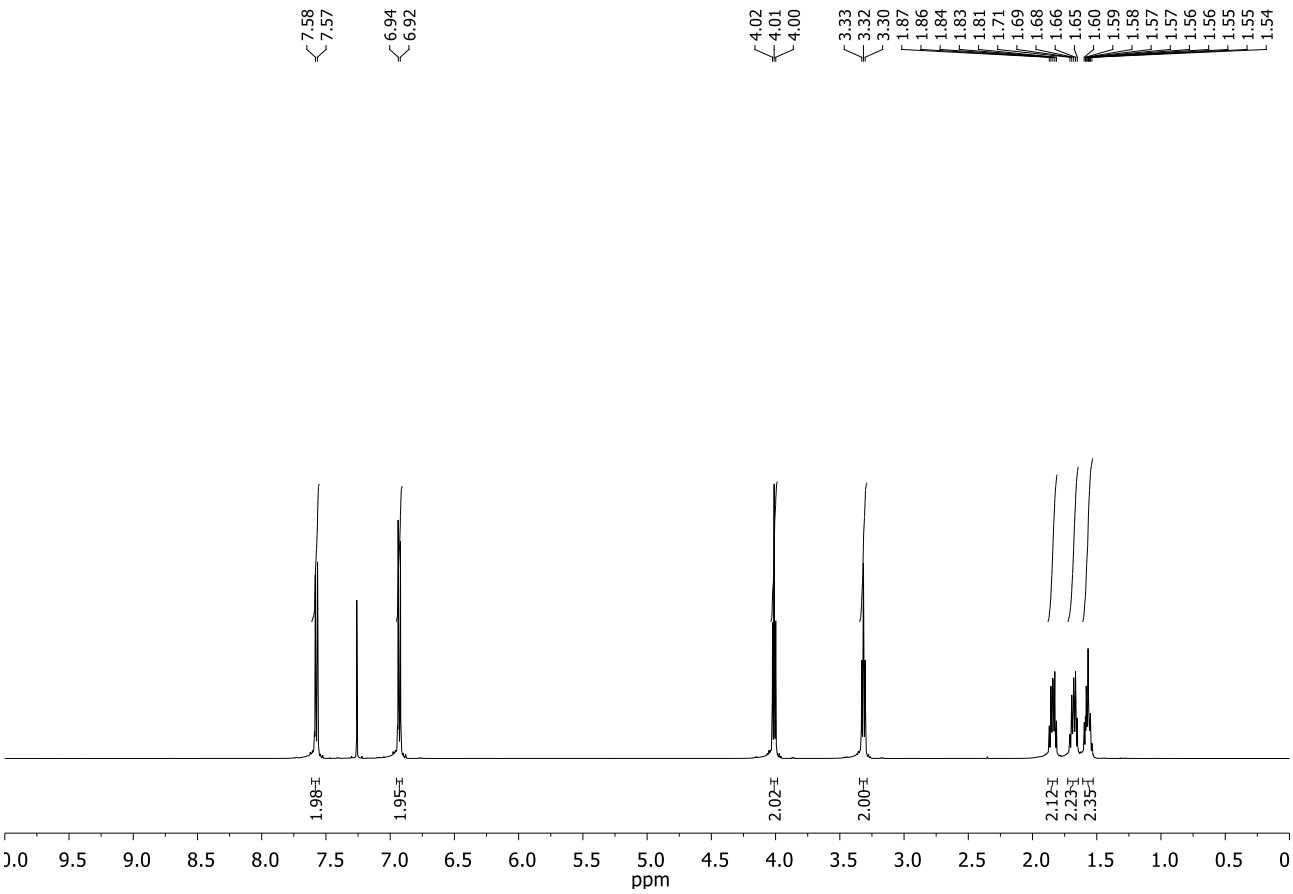
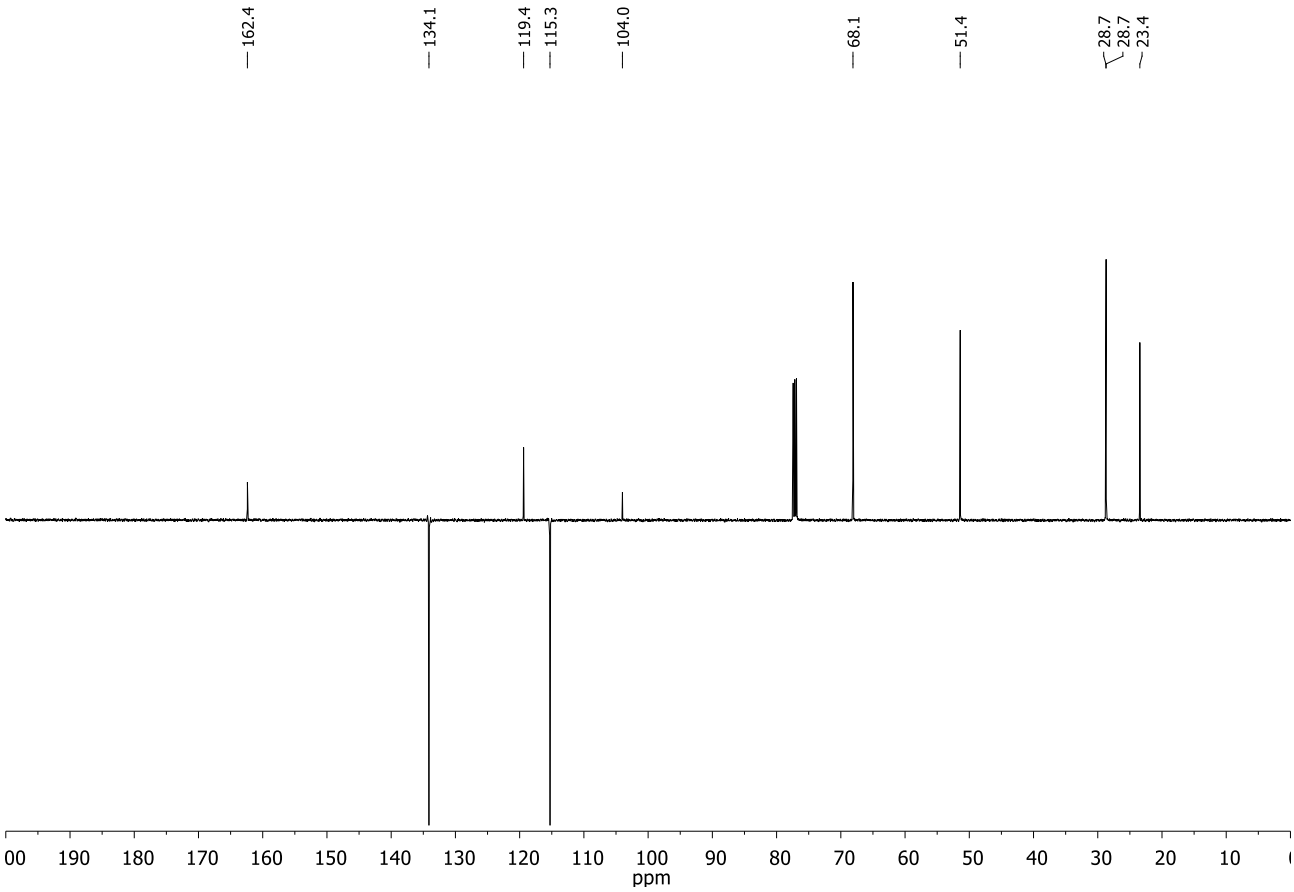
ppm


145.7
140.5
139.1
131.4
131.1
130.7
129.4
128.0
127.8
126.3
120.5
119.6
115.4
113.0
51.3
45.3
36.0
32.0
31.3
29.6
29.4
29.4
22.8
14.3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

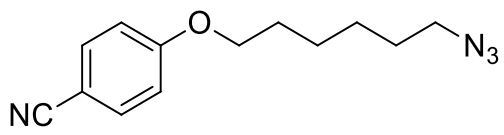
Compound 14a

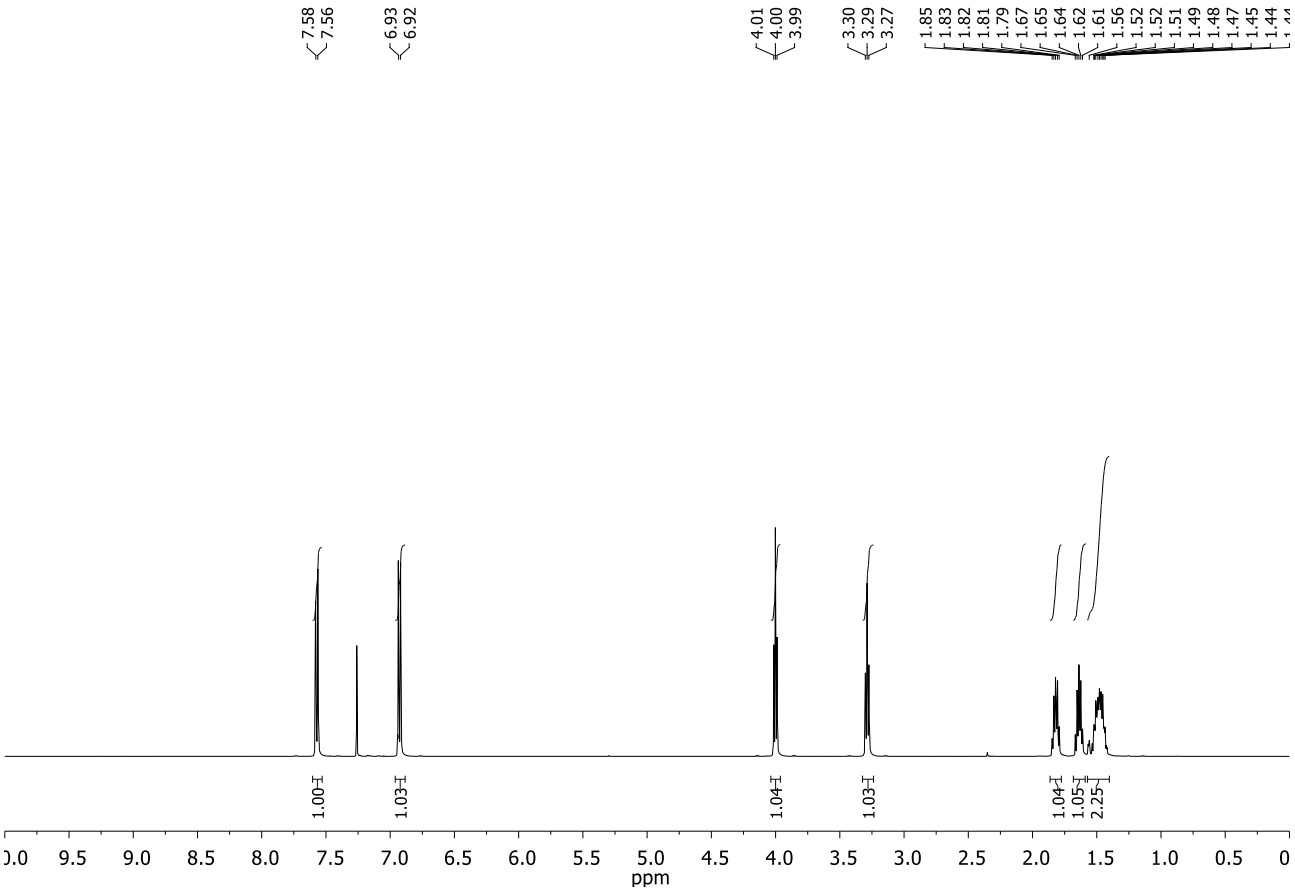


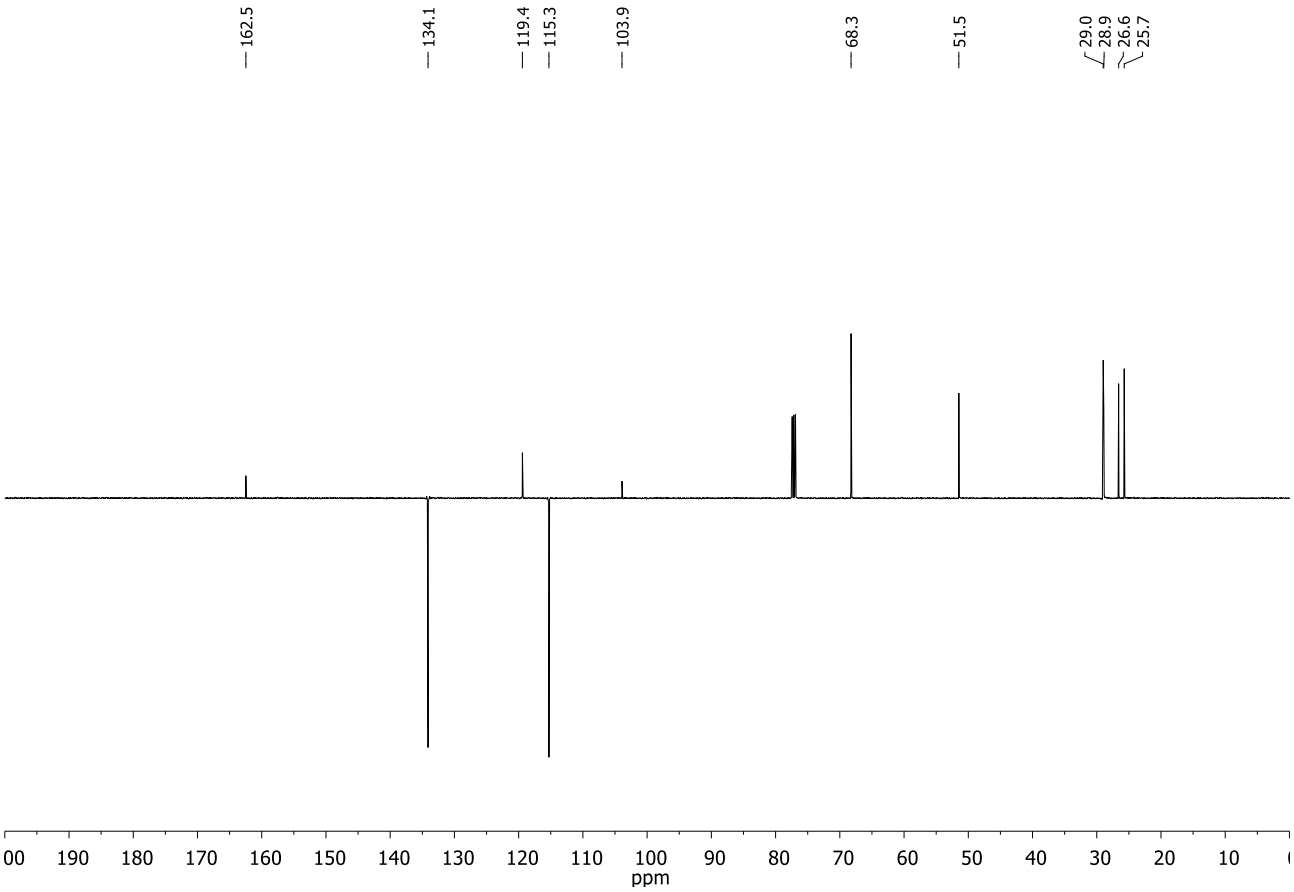



162.4
134.1
119.4
115.3
104.0
68.1
51.4
28.7
28.7
23.4
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

Compound 14b






162.5
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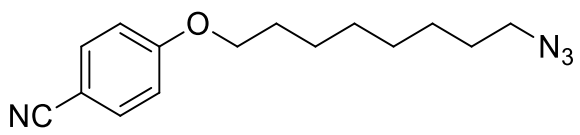
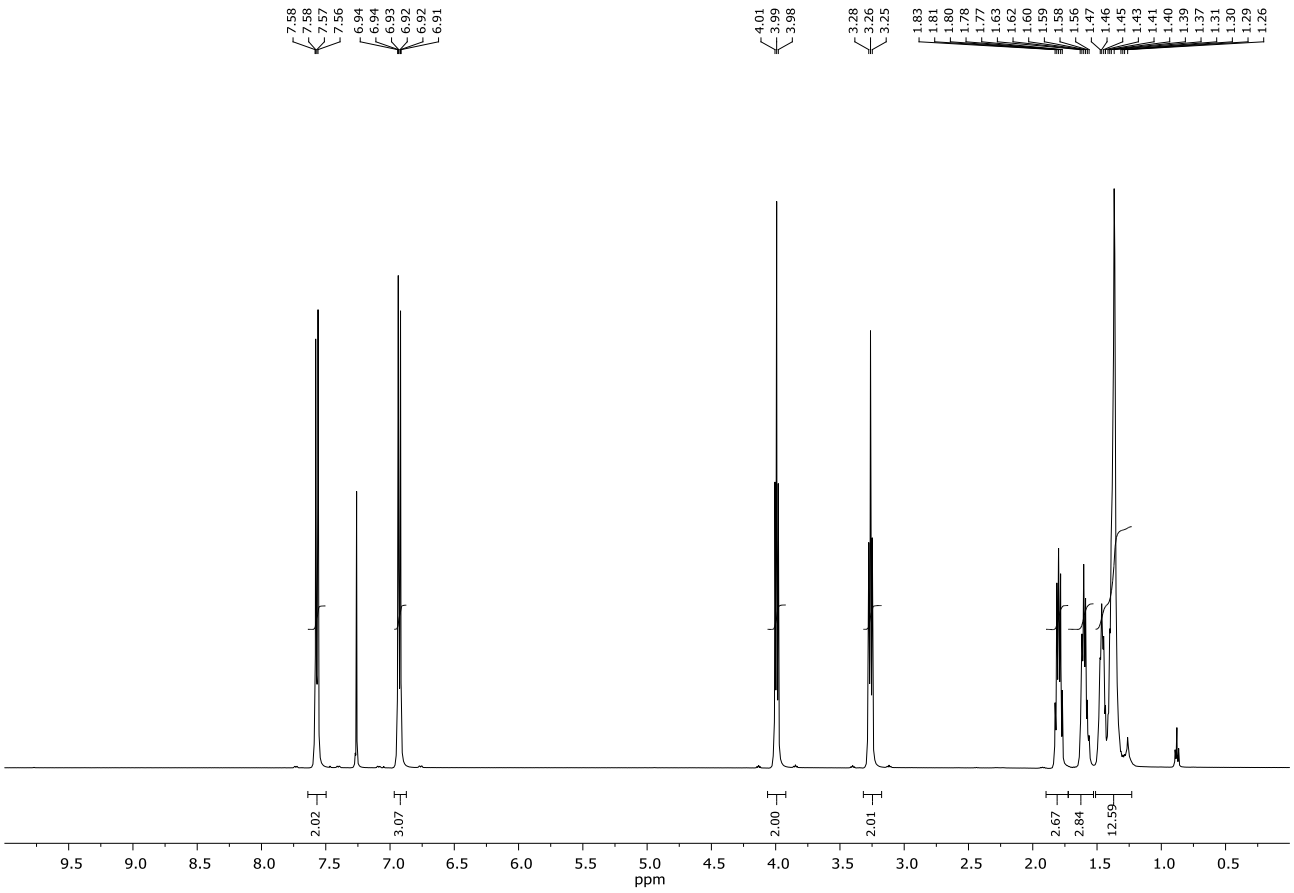
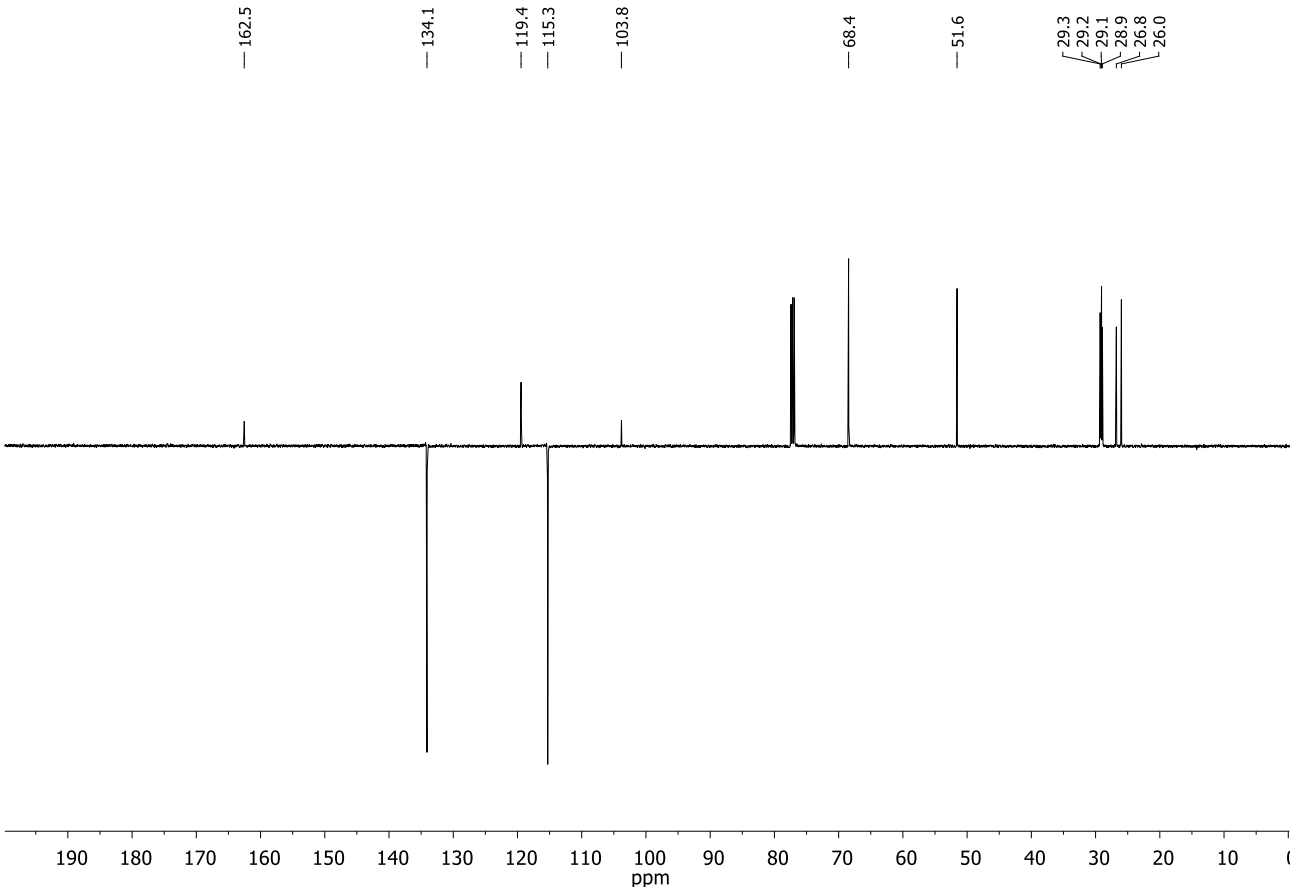
119.4
115.3
103.9
68.3
51.5
29.0
28.9
26.6
25.7
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

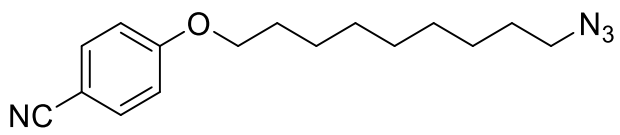
Compound 14c

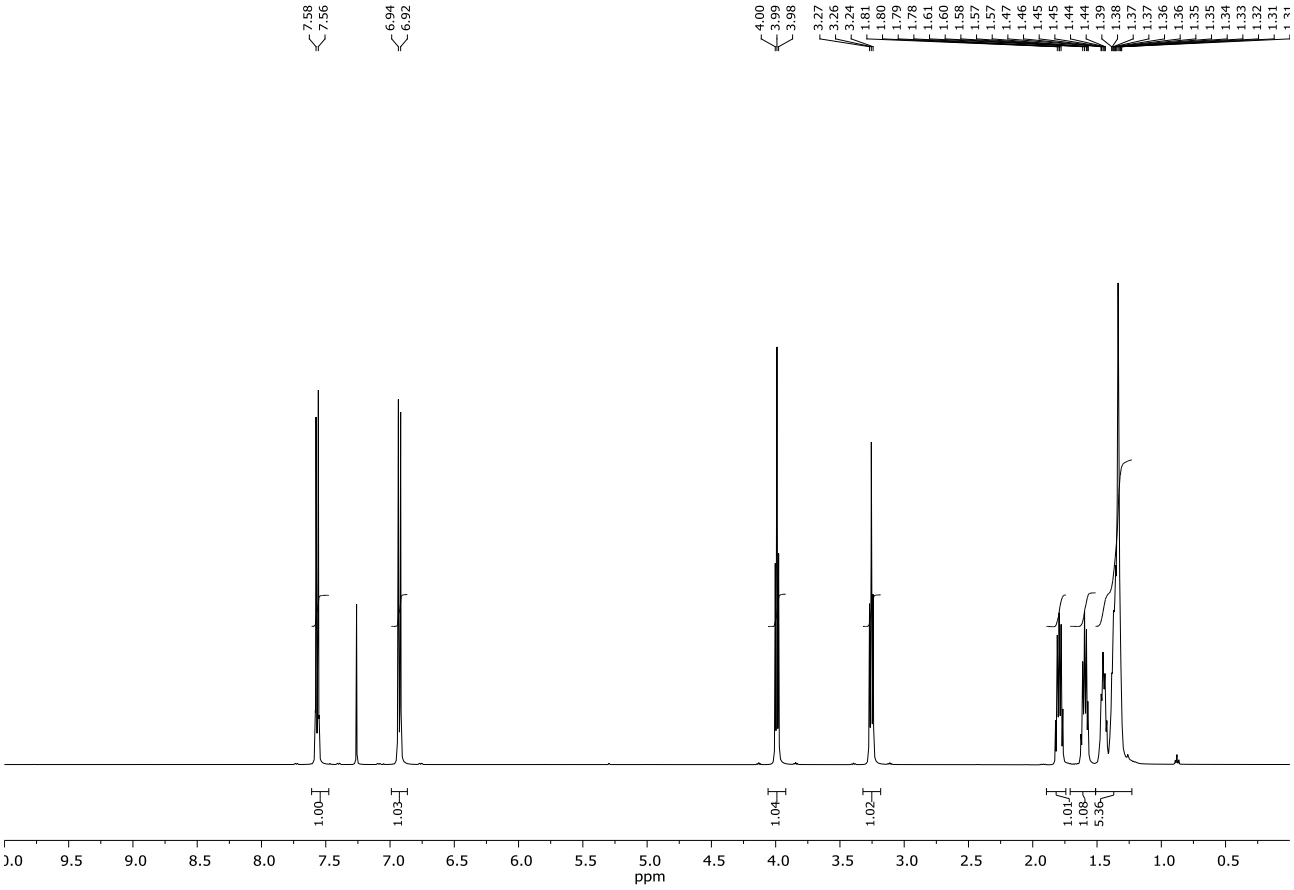


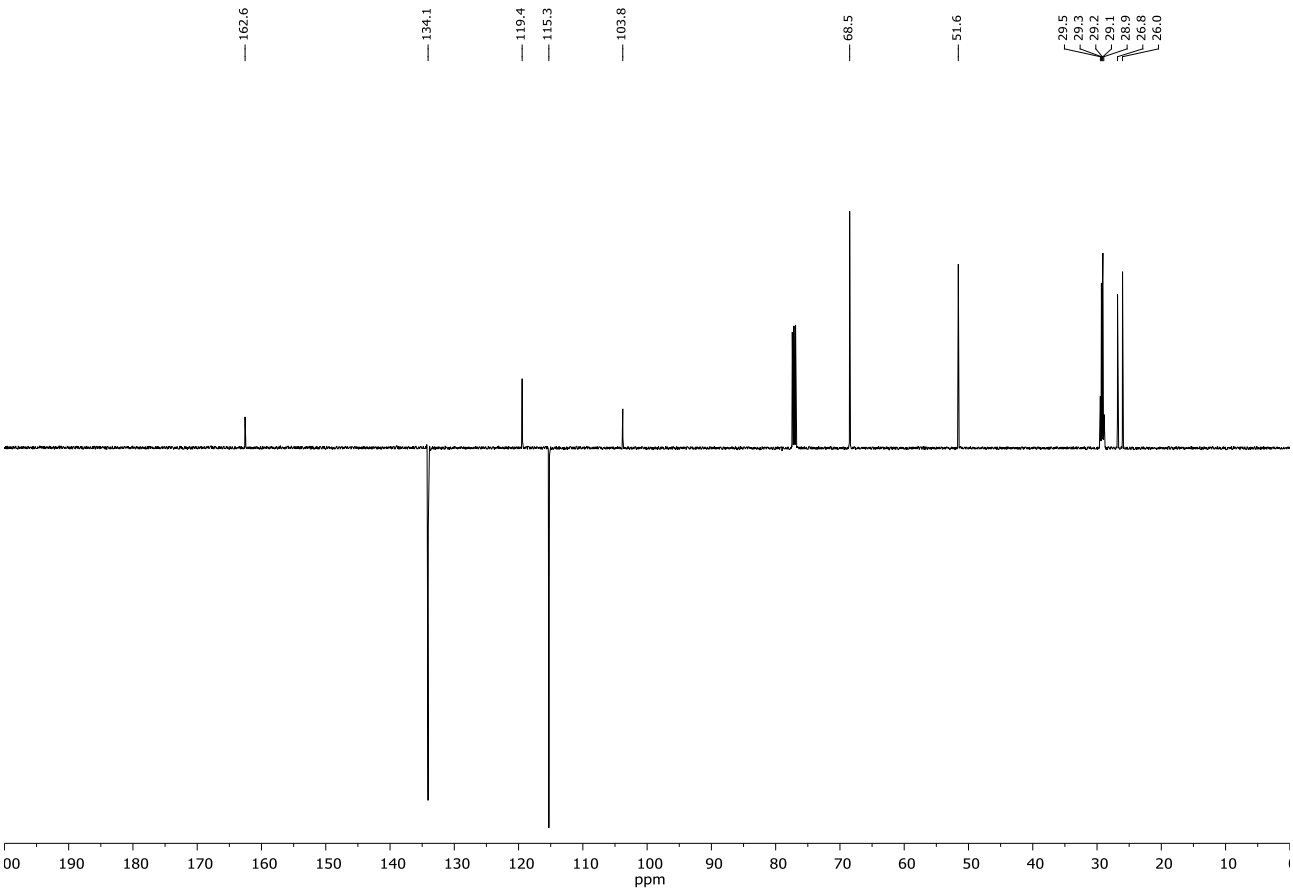



162.5
134.1
119.4
115.3
103.8
68.4
51.6
29.3
29.2
29.1
28.9
26.8
26.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

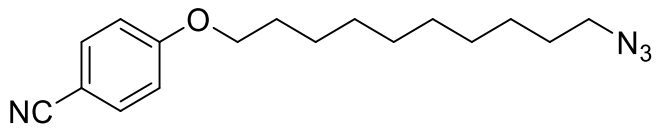
Compound 14d

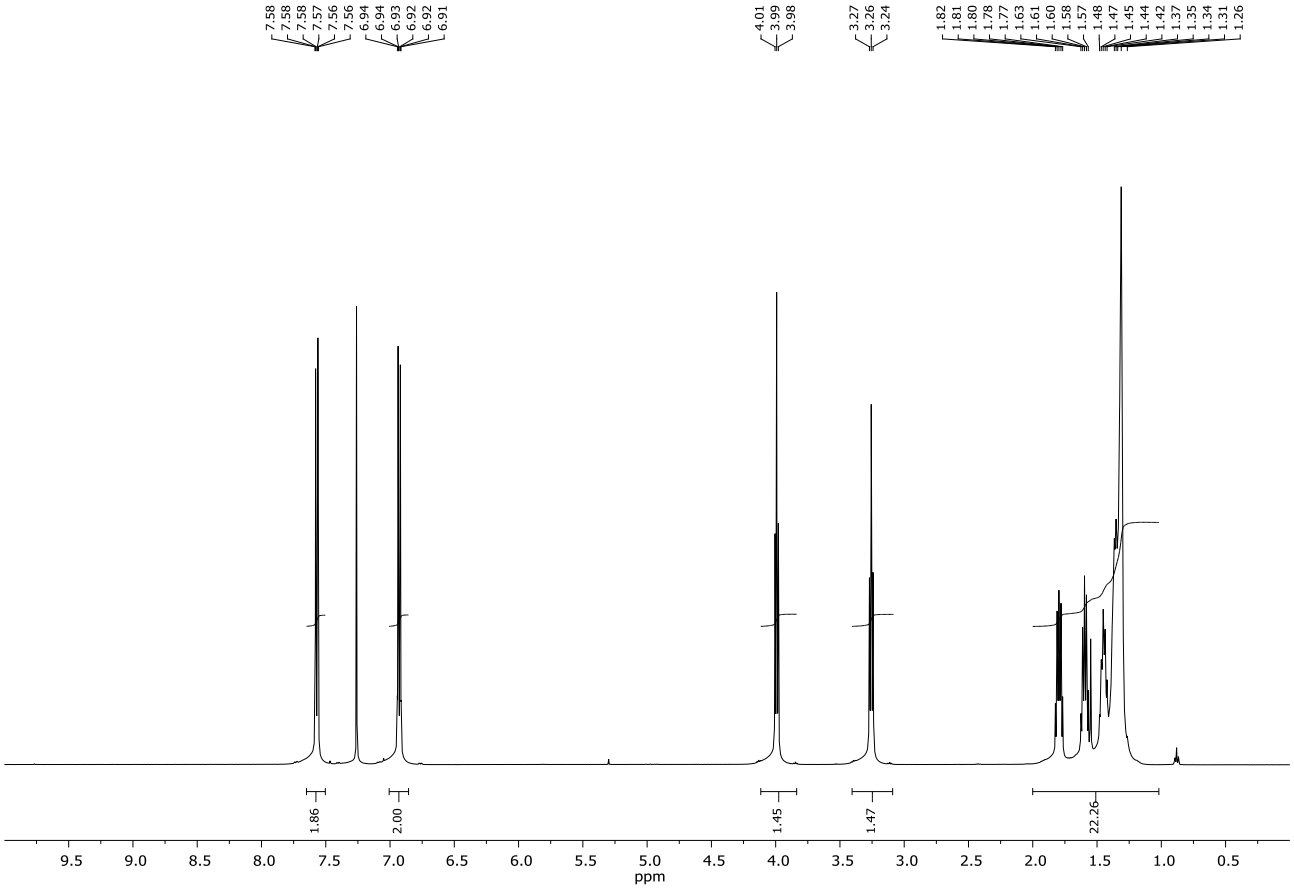


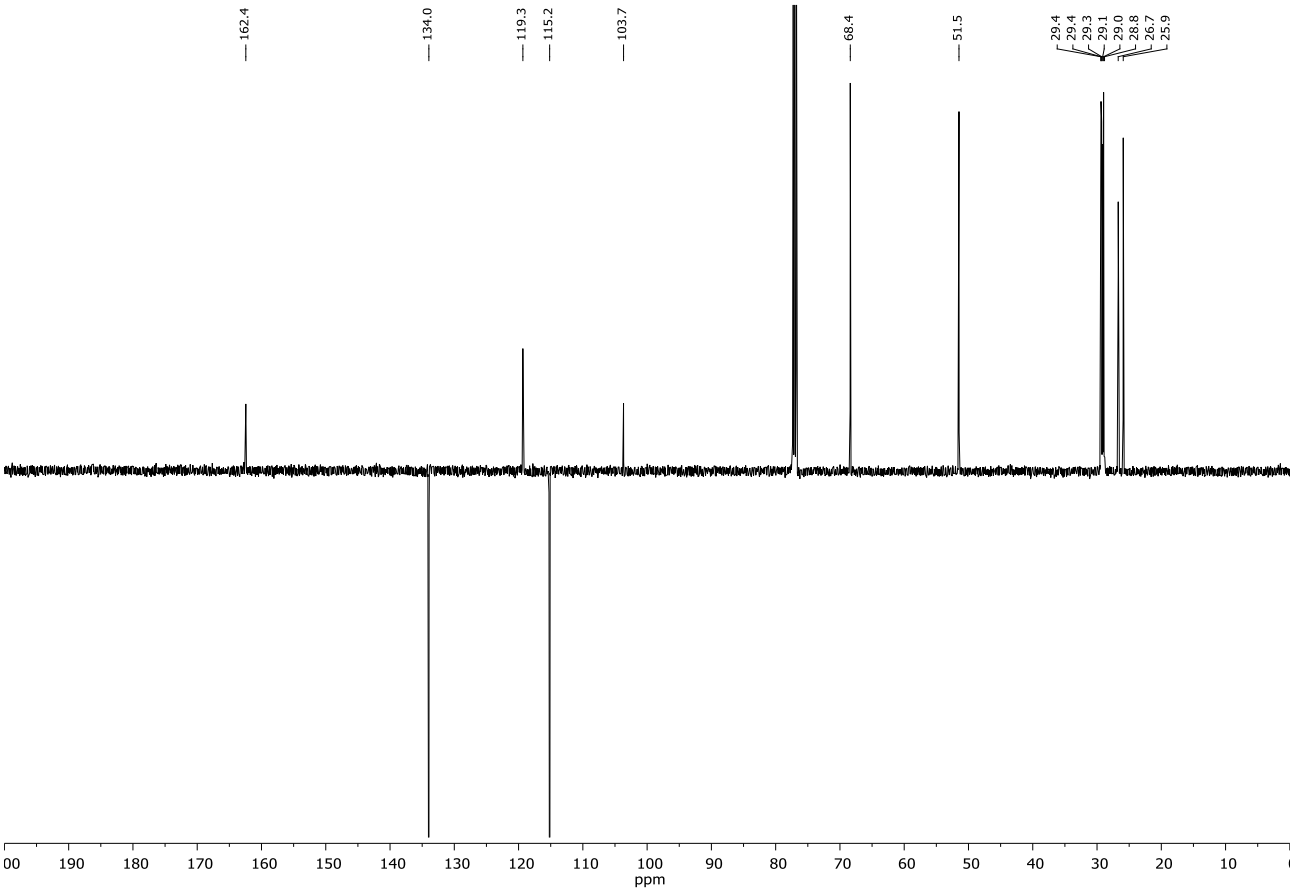



162.6
134.1
119.4
115.3
103.8
68.5
51.6
29.5
29.3
29.2
29.1
28.9
26.8
26.0
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

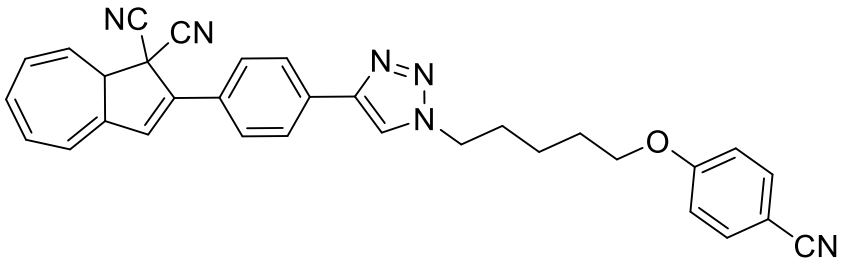
Compound 14e

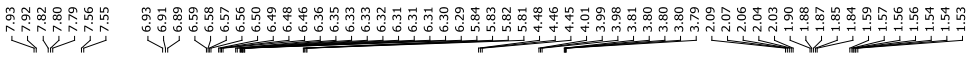


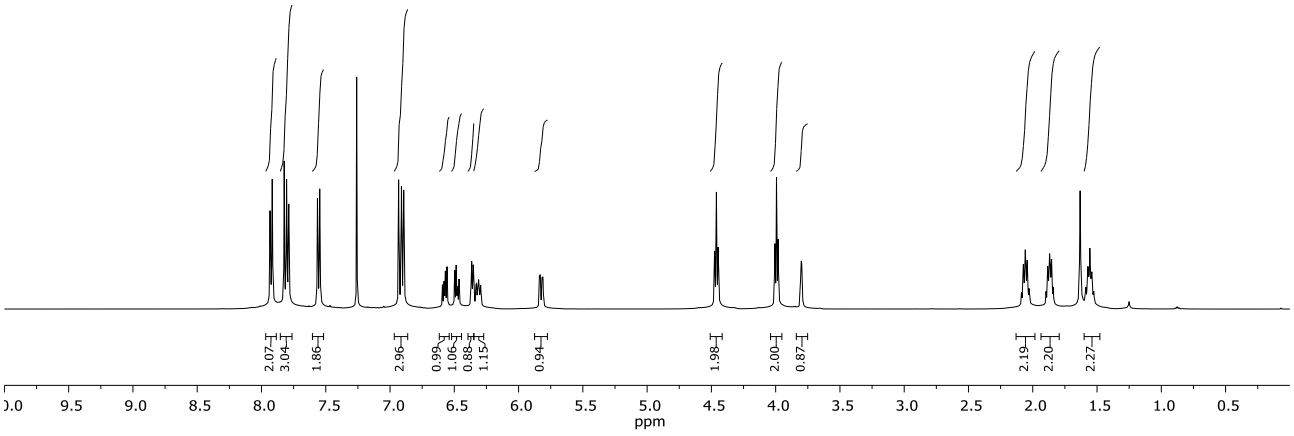


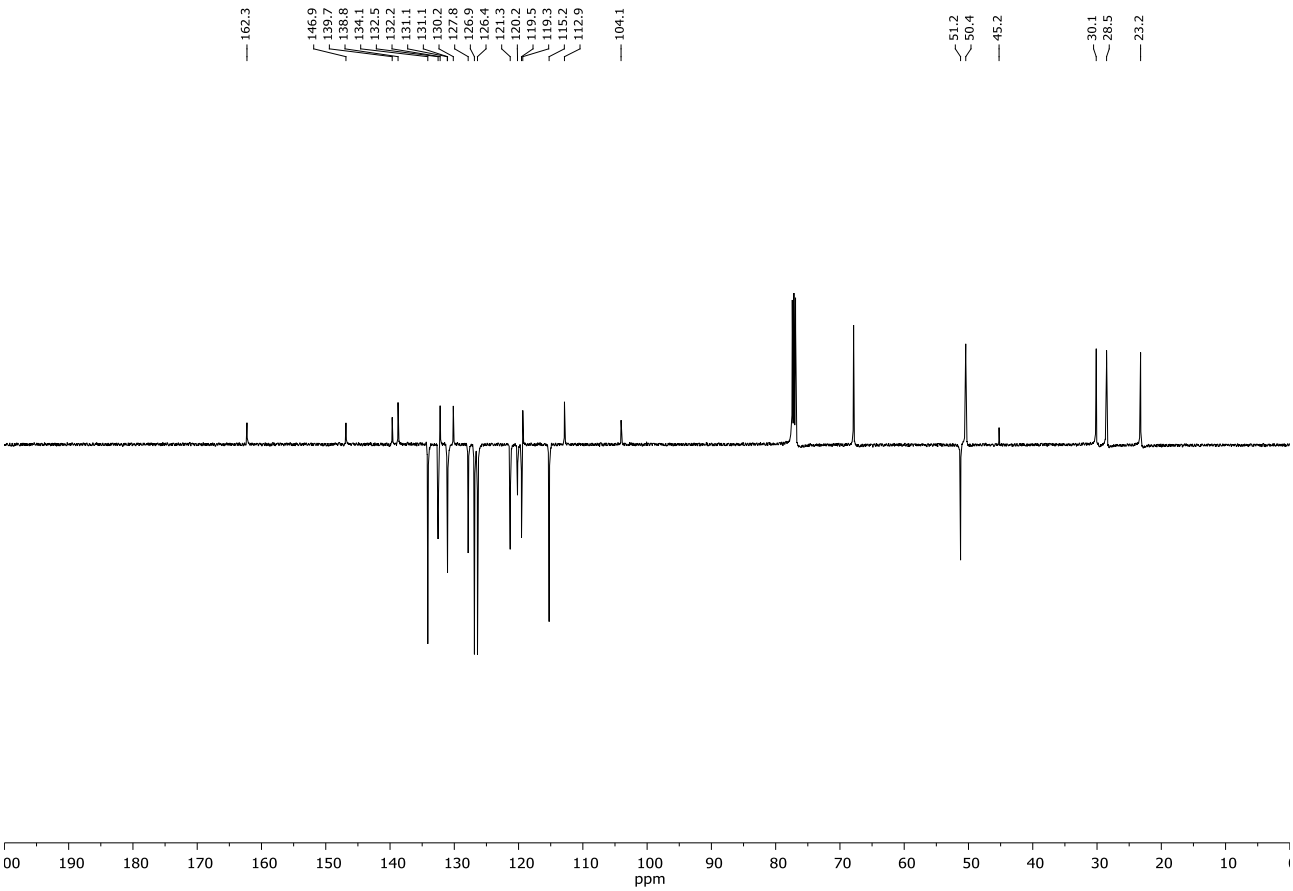

162.4
134.0
119.3
115.2
103.7
68.4
51.5
29.4
29.4
29.3
29.1
29.0
28.8
26.7
25.9
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 4a

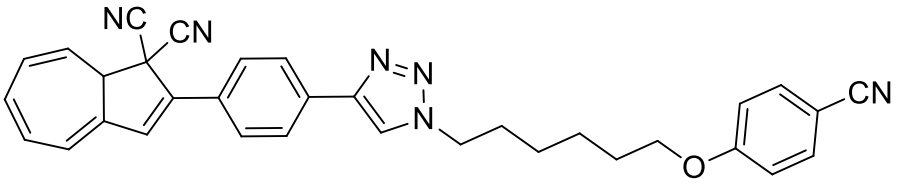

NC
CN
N
N
N
O
CN

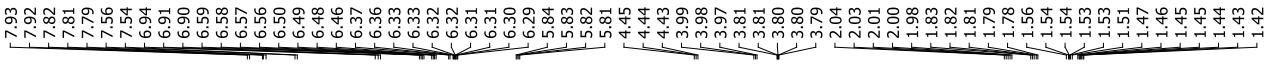

7.93
7.92
7.82
7.80
7.79
7.56
7.55
6.93
6.91
6.89
6.59
6.58
6.57
6.56
6.50
6.49
6.48
6.46
6.36
6.35
6.33
6.33
6.32
6.31
6.31
6.31
6.30
6.29
5.84
5.83
5.82
5.81
4.48
4.46
4.45
4.01
3.99
3.98
3.81
3.80
3.80
3.80
3.79
2.09
2.07
2.06
2.04
2.03
1.90
1.88
1.87
1.85
1.84
1.59
1.57
1.56
1.56
1.54
1.54
1.53

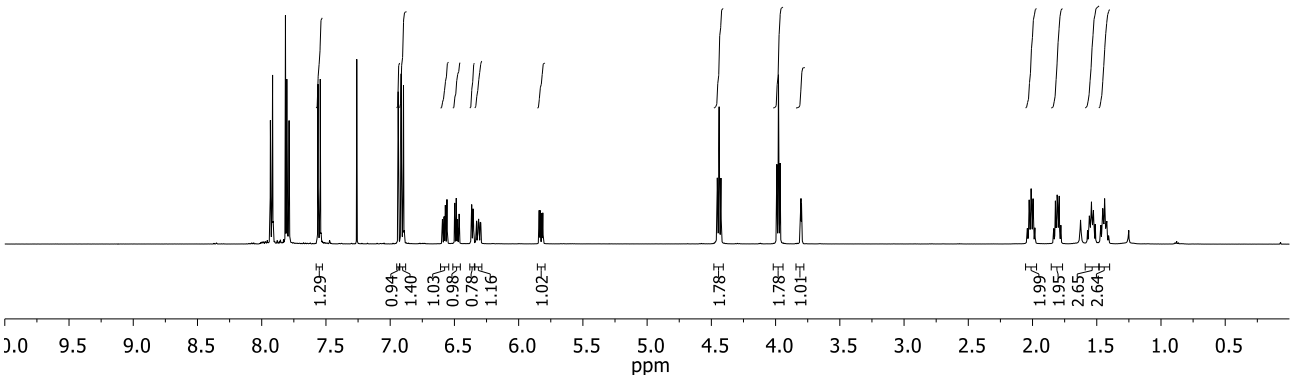

2.07
3.04
1.86
2.96
0.99
1.06
0.88
1.15
0.94
1.98
2.00
0.87
2.19
2.20
2.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

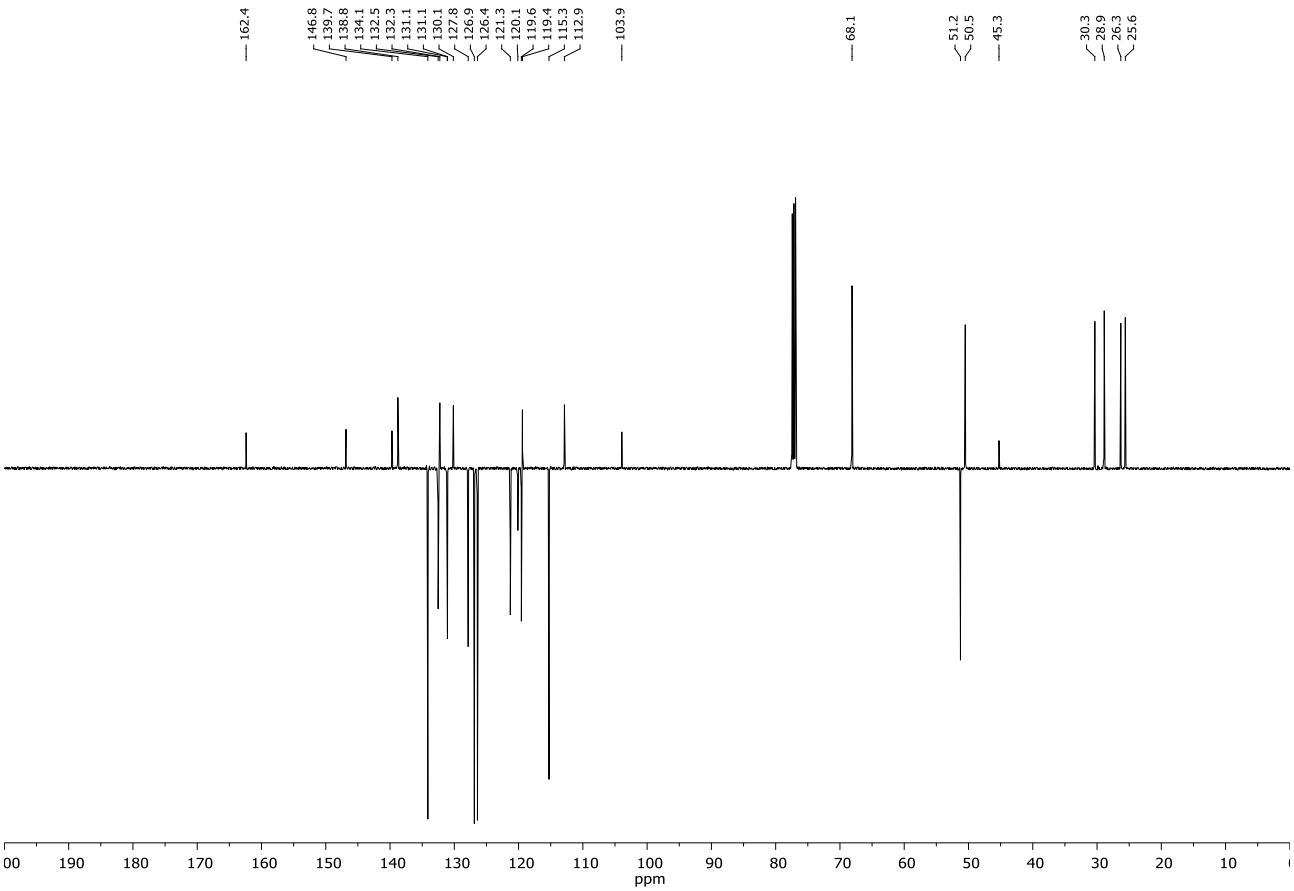

162.3
146.9
139.7
138.8
134.1
132.5
132.2
131.1
131.1
130.2
127.8
126.9
126.4
121.3
120.2
119.5
119.3
115.2
112.9
104.1
51.2
50.4
45.2
30.1
28.5
23.2
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 4b

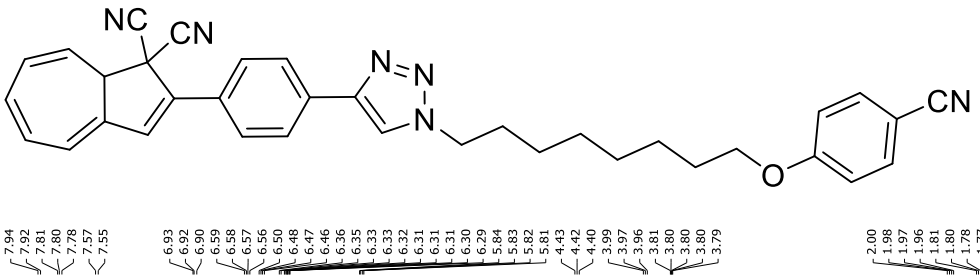

NC
CN
N
N
N
O
CN


7.93 7.92 7.82 7.81 7.79 7.56 7.54 6.94 6.91 6.90 6.59 6.58 6.57 6.56 6.50 6.49 6.48 6.46 6.37 6.36 6.33 6.33 6.32 6.32 6.31 6.31 6.30 6.29 5.84 5.83 5.82 5.81
4.45 4.44 4.43 3.99 3.98 3.97 3.81 3.80 3.80 3.79
2.04 2.03 2.01 2.00 1.98 1.83 1.82 1.81 1.79 1.78 1.56 1.54 1.54 1.53 1.53 1.51 1.47 1.46 1.45 1.45 1.44 1.43 1.42

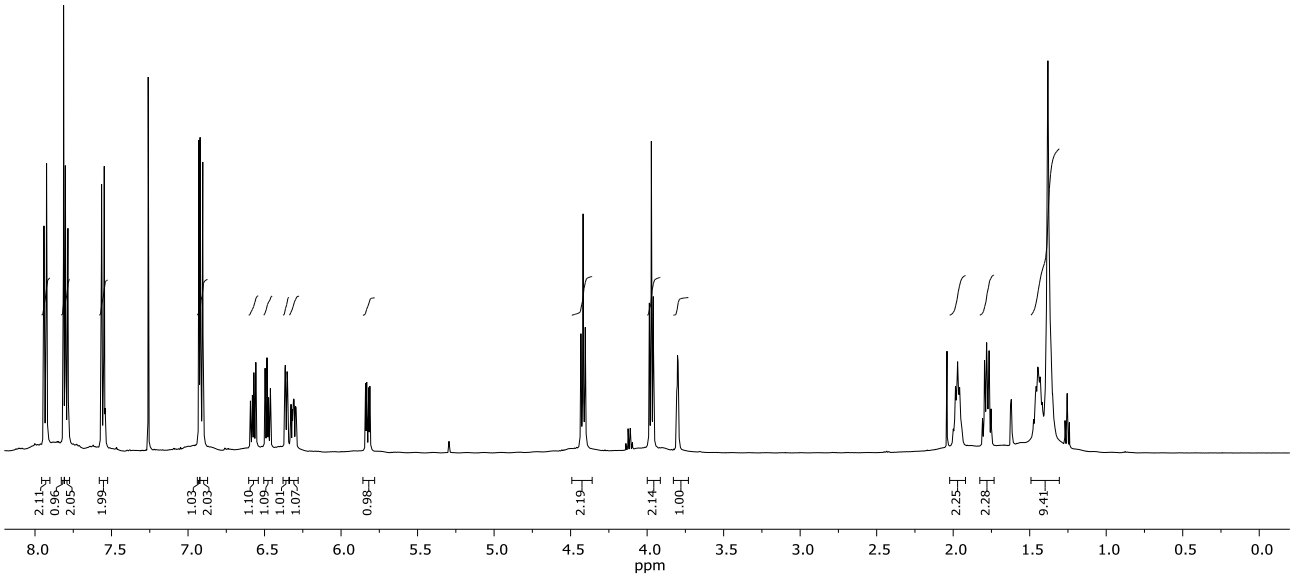

1.29
0.94
1.40
1.03
0.98
0.78
1.16
1.02
1.78
1.78
1.01
1.99
1.95
2.65
2.64
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

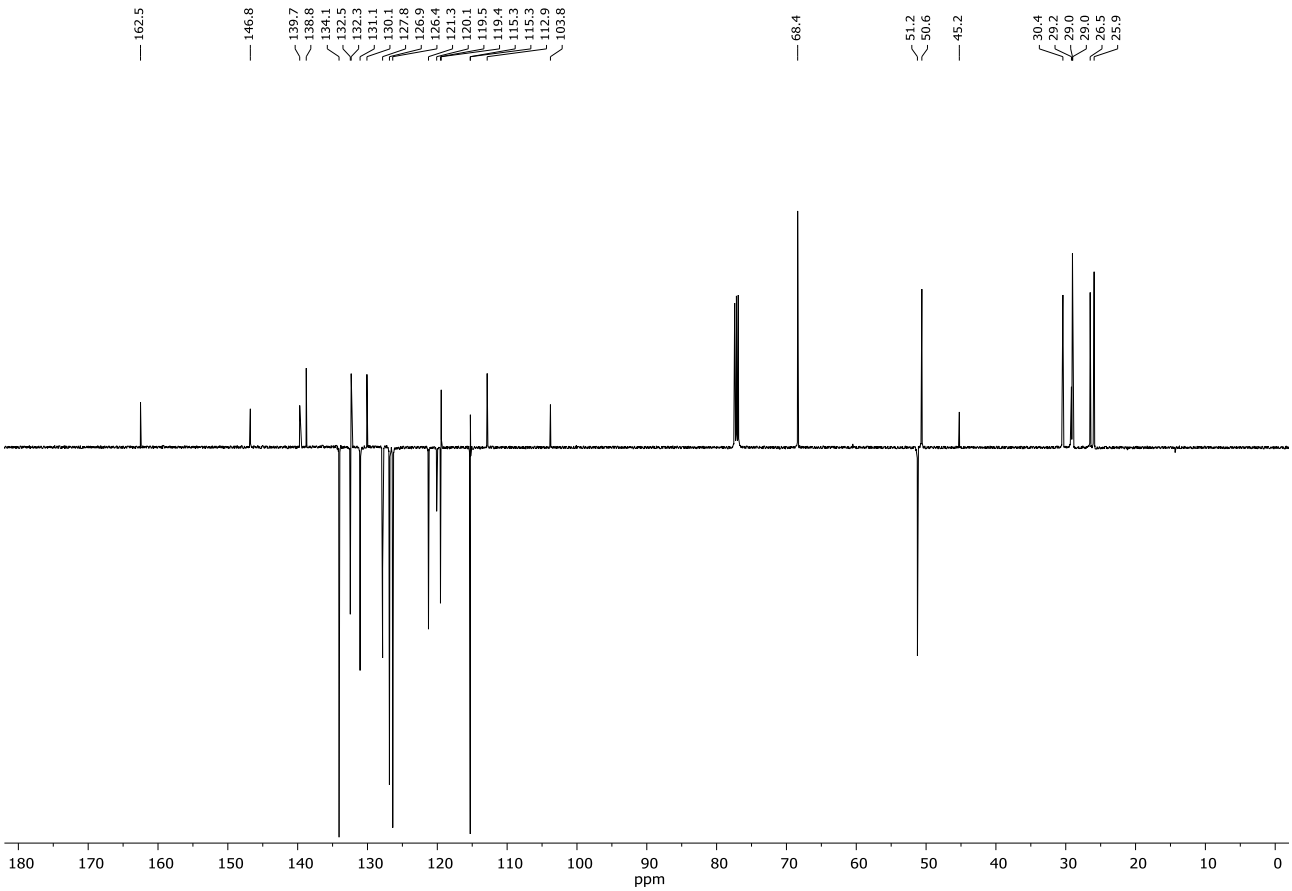

162.4
146.8
139.7
138.8
134.1
132.5
132.3
131.1
131.1
130.1
127.8
126.9
126.4
121.3
120.1
119.6
119.4
115.3
112.9
103.9
68.1
51.2
50.5
45.3
30.3
28.9
26.3
25.6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound 4c

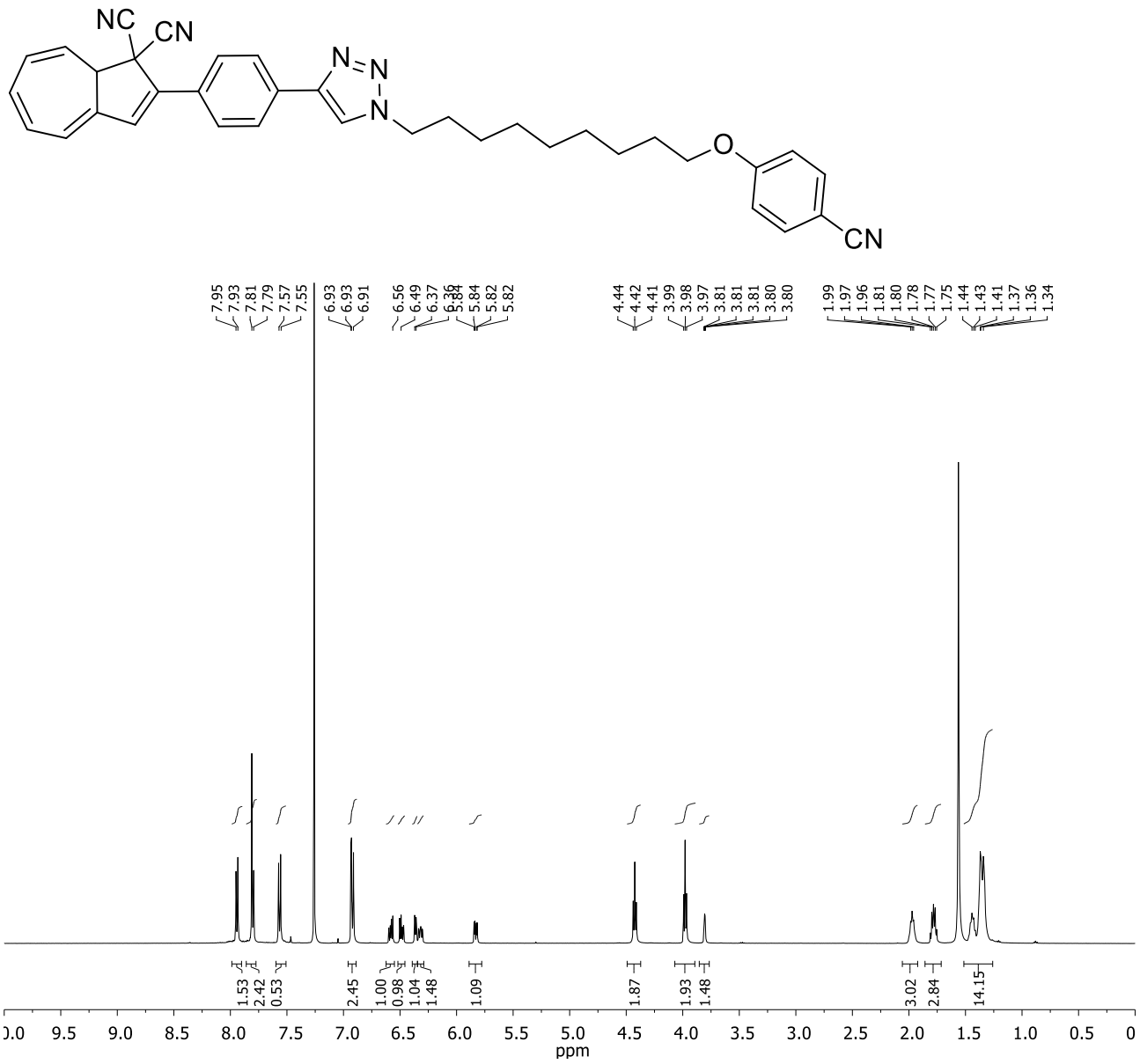

NC
CN
N
N
N
O
CN

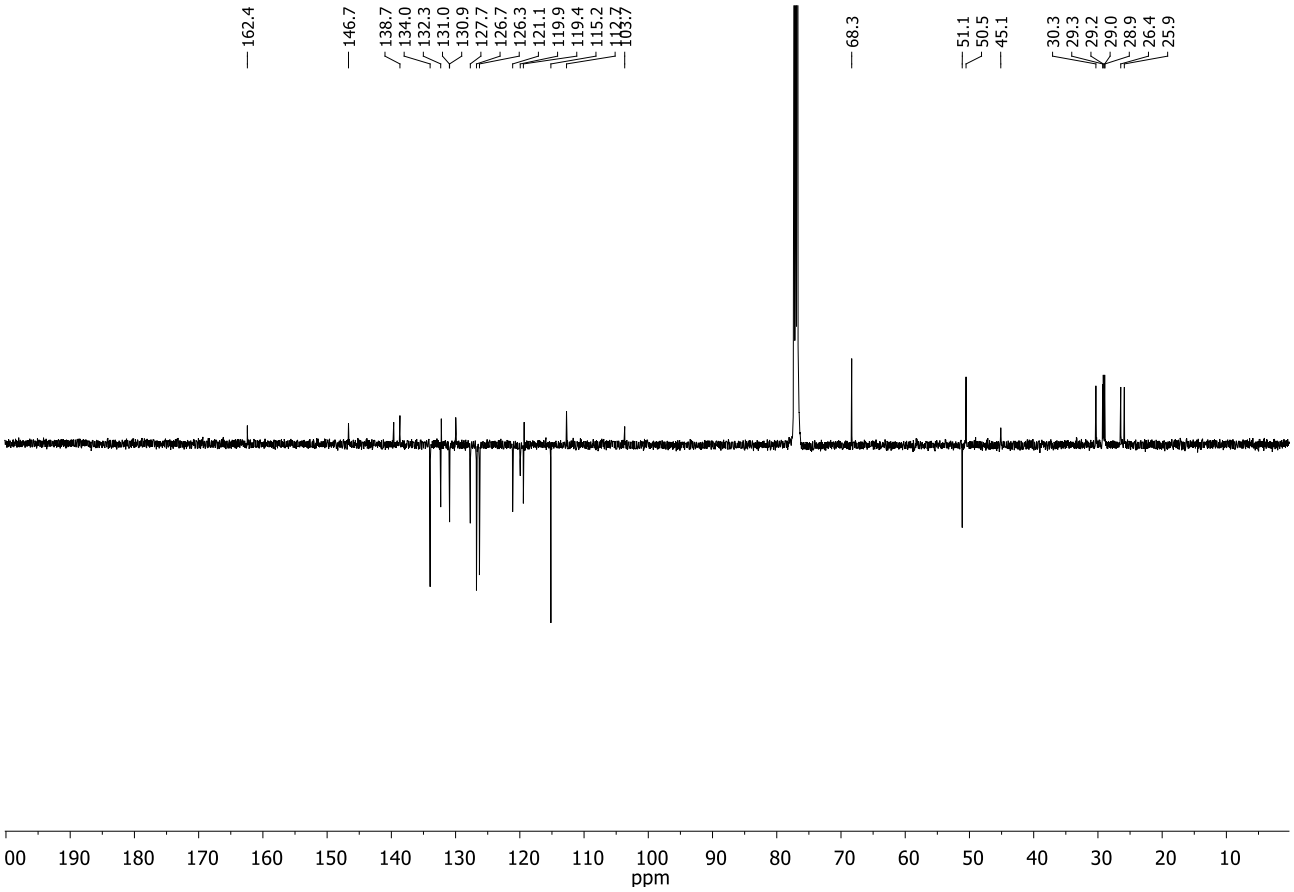
7.94
7.92
7.81
7.80
7.78
7.57
7.55
6.93
6.92
6.90
6.59
6.58
6.57
6.56
6.50
6.48
6.47
6.46
6.36
6.35
6.33
6.33
6.32
6.31
6.31
6.31
6.30
6.29
5.84
5.83
5.82
5.81
4.43
4.42
4.40
3.99
3.97
3.96
3.81
3.80
3.80
3.80
3.79
2.00
1.98
1.97
1.96
1.81
1.80
1.78
1.77
1.75
1.47
1.46
1.45
1.43
1.42
1.38
1.35


2.11
0.96
2.05
1.99
1.03
2.03
1.10
1.09
1.01
1.07
0.98
2.19
2.14
1.00
2.25
2.28
9.41
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

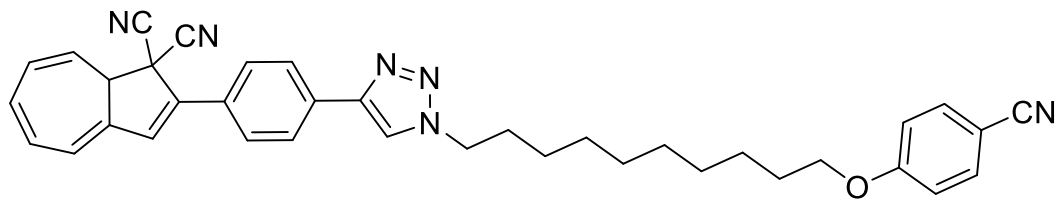

162.5
146.8
139.7
138.8
134.1
132.5
132.3
131.1
130.1
127.8
126.9
126.4
121.3
120.1
119.5
119.4
115.3
115.3
112.9
103.8
68.4
51.2
50.6
45.2
30.4
29.2
29.0
29.0
26.5
25.9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

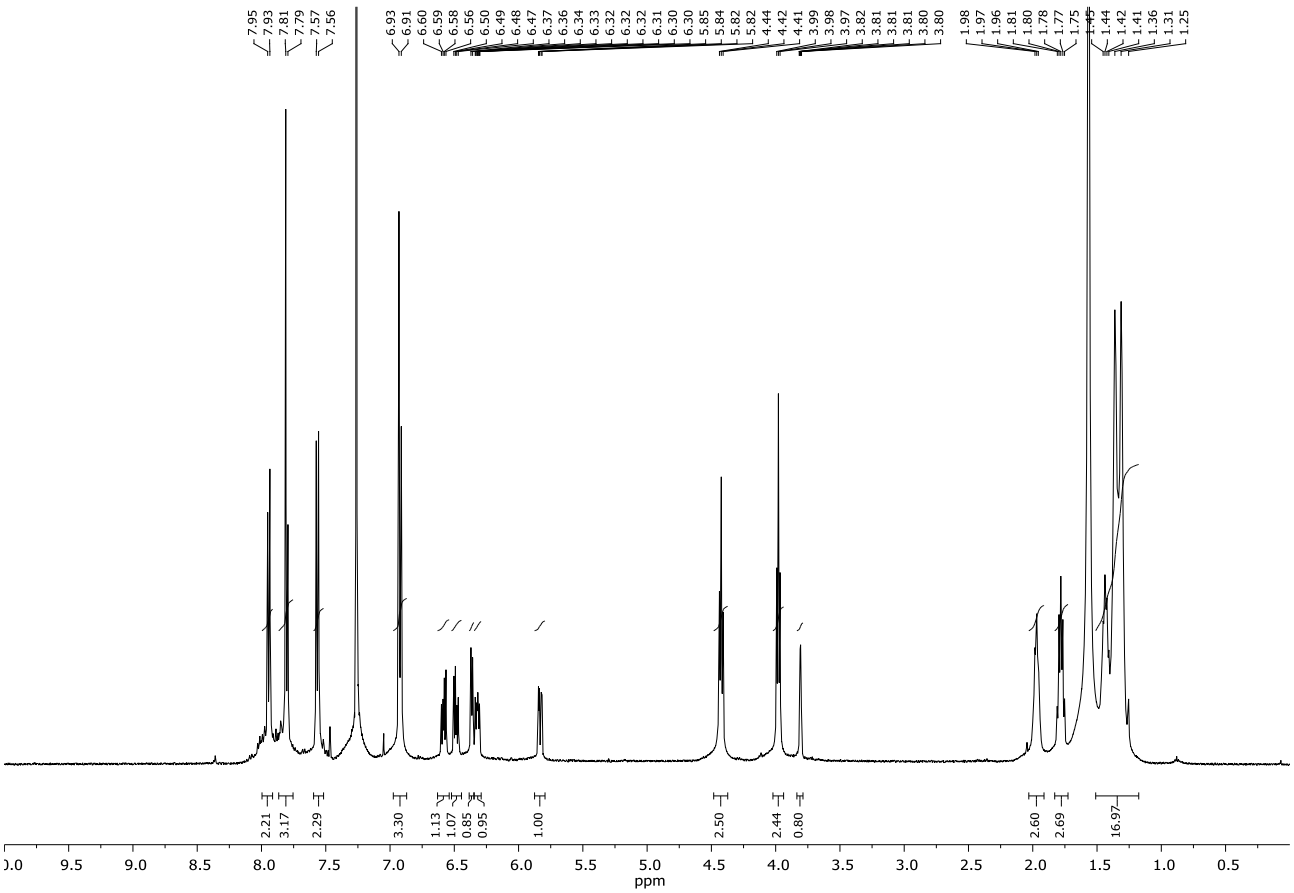
Compound 4d

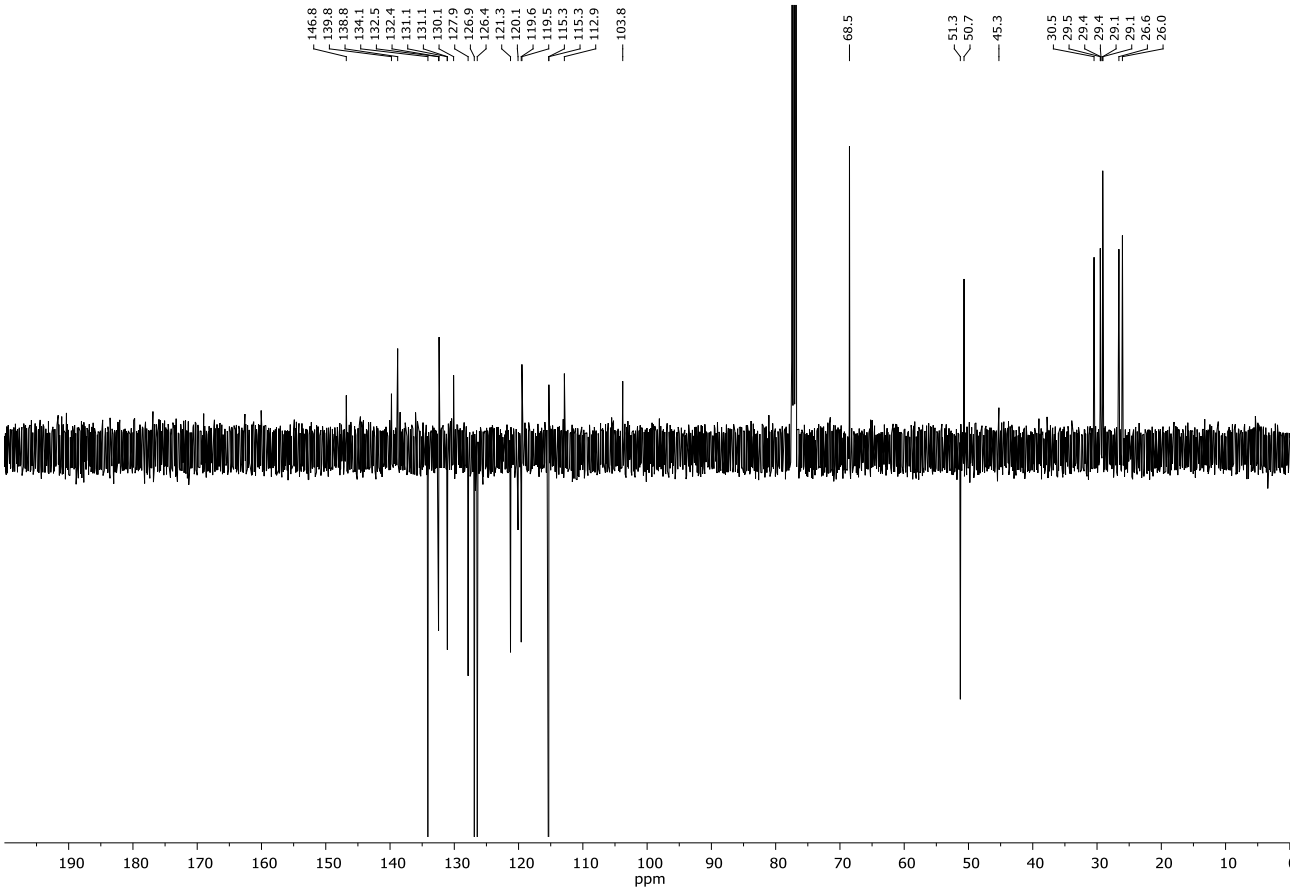

NC
CN
N
N
N
O
CN
7.95
7.93
7.81
7.79
7.57
7.55
6.93
6.93
6.91
6.56
6.49
6.37
5.84
5.84
5.82
5.82
4.44
4.42
4.41
3.99
3.98
3.97
3.81
3.81
3.81
3.80
3.80
1.99
1.97
1.96
1.81
1.80
1.78
1.77
1.75
1.44
1.43
1.41
1.37
1.36
1.34
1.53
2.42
0.53
2.45
1.00
0.98
1.04
1.48
1.09
1.87
1.93
1.48
3.02
2.84
14.15
ppm


162.4
146.7
138.7
134.0
132.3
131.0
130.9
127.7
126.7
126.3
121.1
119.9
119.4
115.2
112.7
103.7
68.3
51.1
50.5
45.1
30.3
29.3
29.2
29.0
28.9
26.4
25.9
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

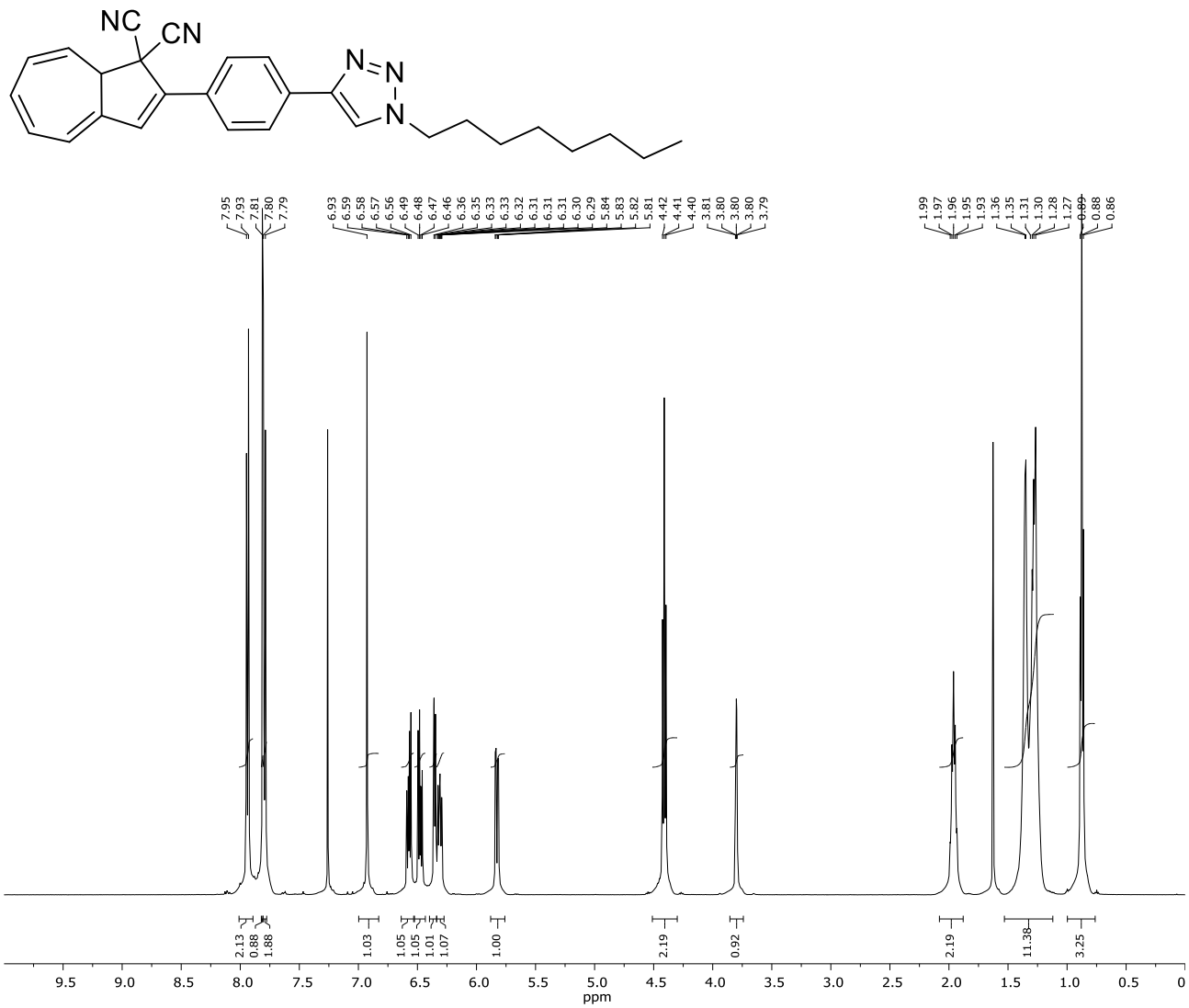
Compound 4e

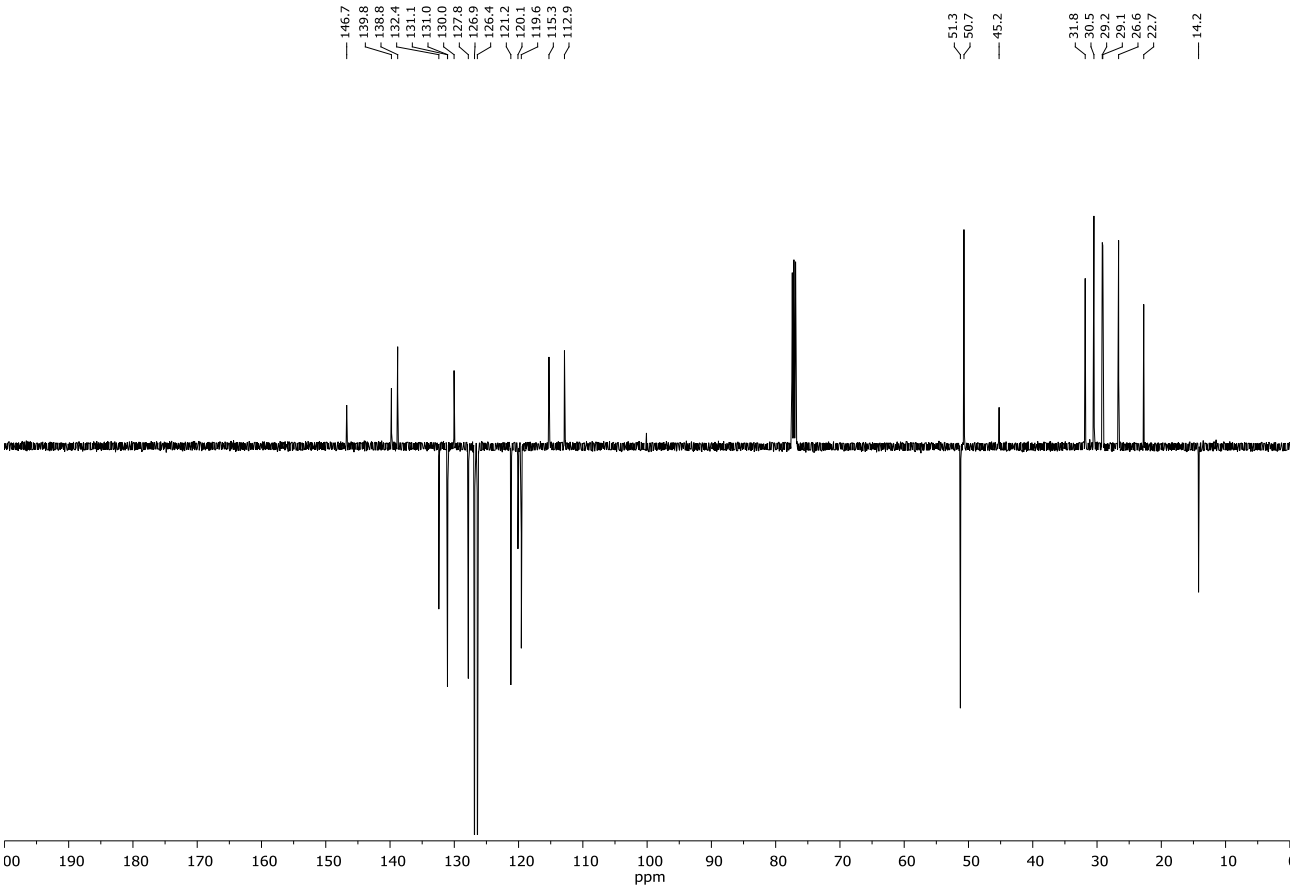

NC
CN
N
N
N
O
CN


7.95 7.93 7.81 7.79 7.57 7.56
6.93 6.91 6.60 6.59 6.58 6.56 6.50 6.49 6.48 6.47 6.37 6.36 6.34 6.33 6.32 6.32 6.32 6.31 6.30 6.30 5.85 5.84 5.82 5.82 4.44 4.42 4.41 3.99 3.98 3.97 3.82 3.81 3.81 3.81 3.80 3.80
1.98 1.97 1.96 1.81 1.80 1.78 1.77 1.75 1.45 1.44 1.42 1.41 1.36 1.31 1.25
2.21 3.17 2.29 3.30 1.13 1.07 0.85 0.95 1.00 2.50 2.44 0.80 2.60 2.69 16.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

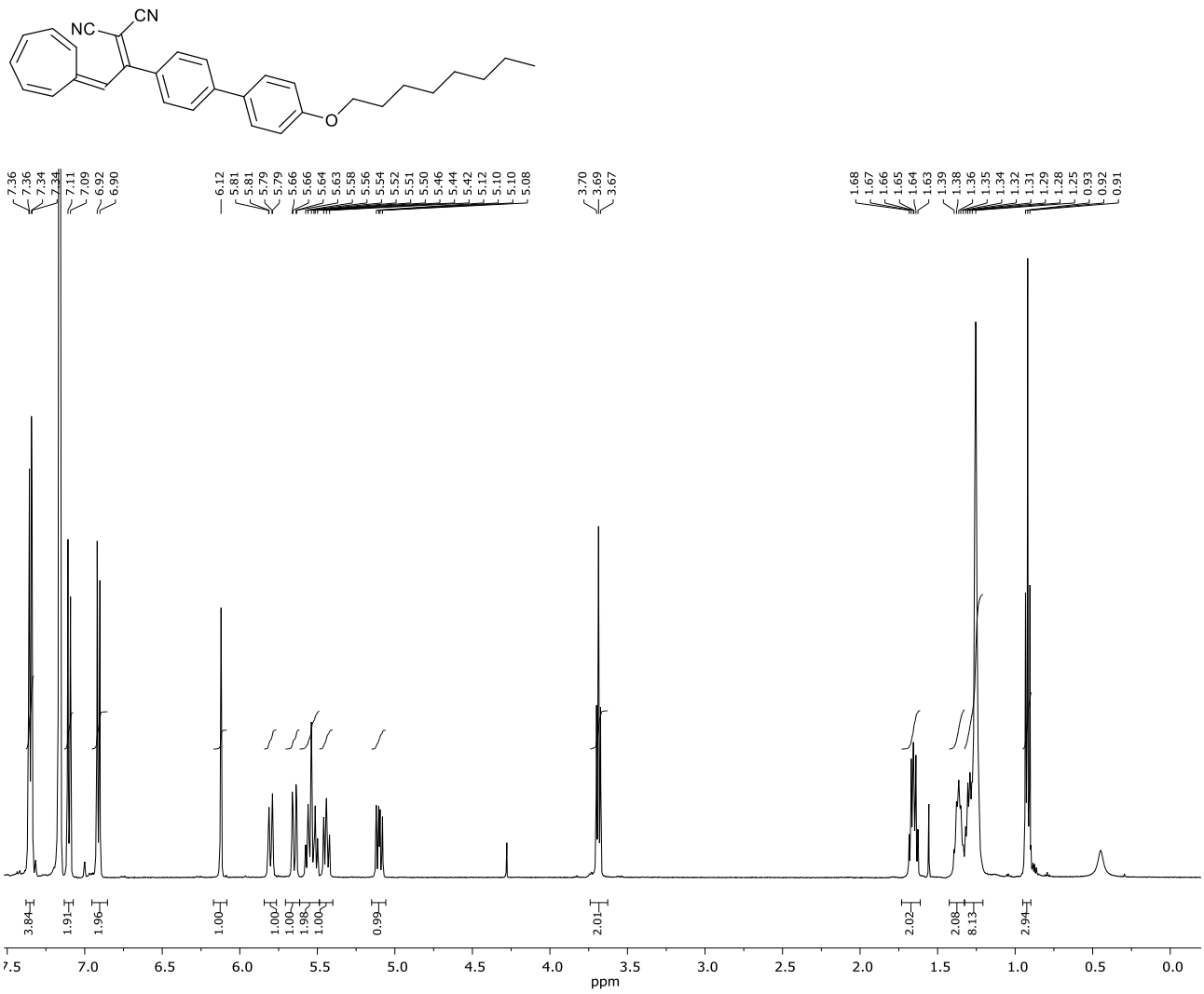

146.8
139.8
138.8
134.1
132.5
132.4
131.1
131.1
130.1
127.9
126.9
126.4
121.3
120.1
119.6
119.5
115.3
115.3
112.9
103.8
68.5
51.3
50.7
45.3
30.5
29.5
29.4
29.4
29.1
29.1
26.6
26.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

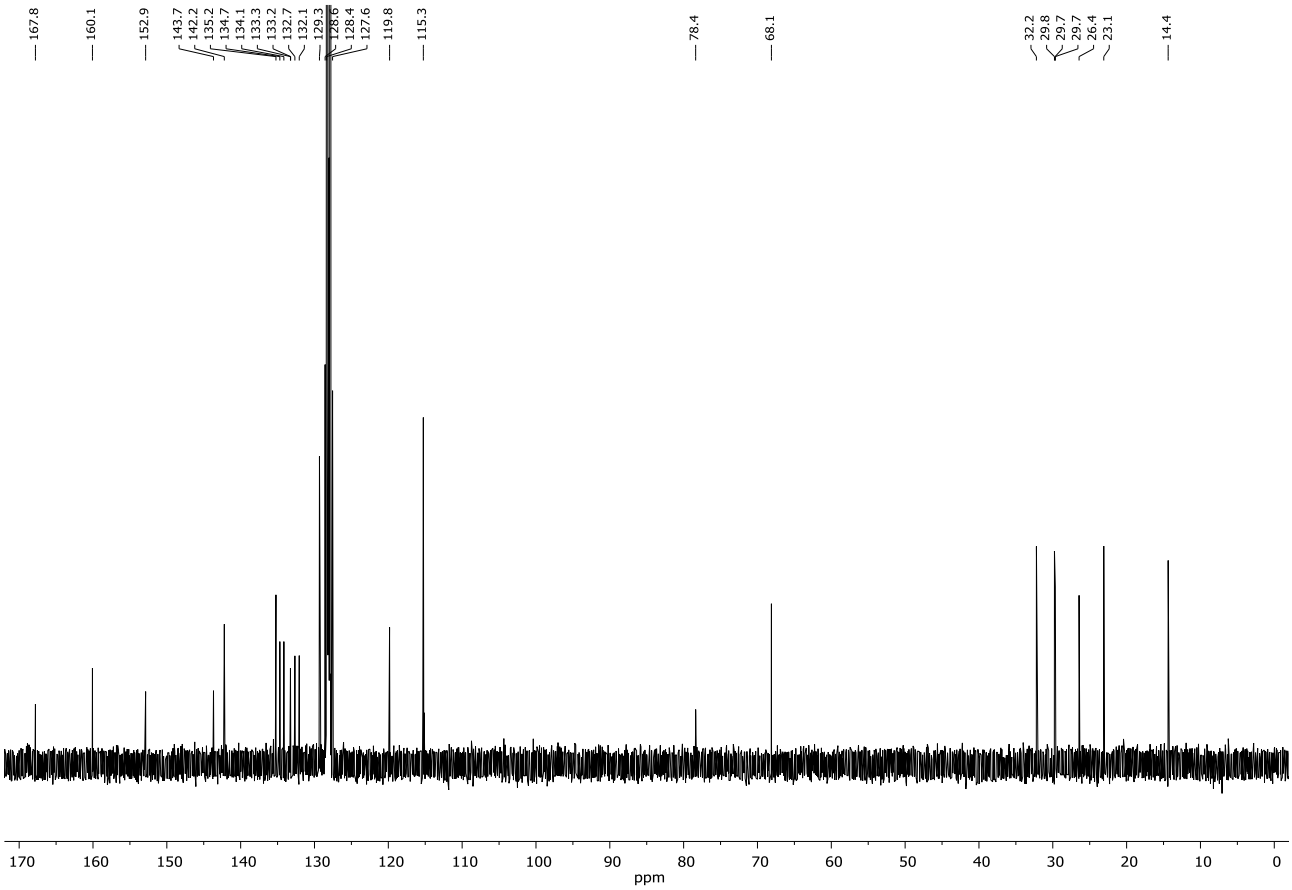
Compound 4J


NC
CN
N
N
N
7.95
7.93
7.81
7.80
7.79
6.93
6.59
6.58
6.57
6.56
6.49
6.48
6.47
6.46
6.36
6.35
6.33
6.33
6.32
6.31
6.31
6.31
6.30
6.29
5.84
5.83
5.82
5.81
4.42
4.41
4.40
3.81
3.80
3.80
3.80
3.79
1.99
1.97
1.96
1.95
1.93
1.36
1.35
1.31
1.30
1.28
1.27
0.89
0.88
0.86
2.13
0.88
1.88
1.03
1.05
1.05
1.01
1.07
1.00
2.19
0.92
2.19
11.38
3.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
ppm

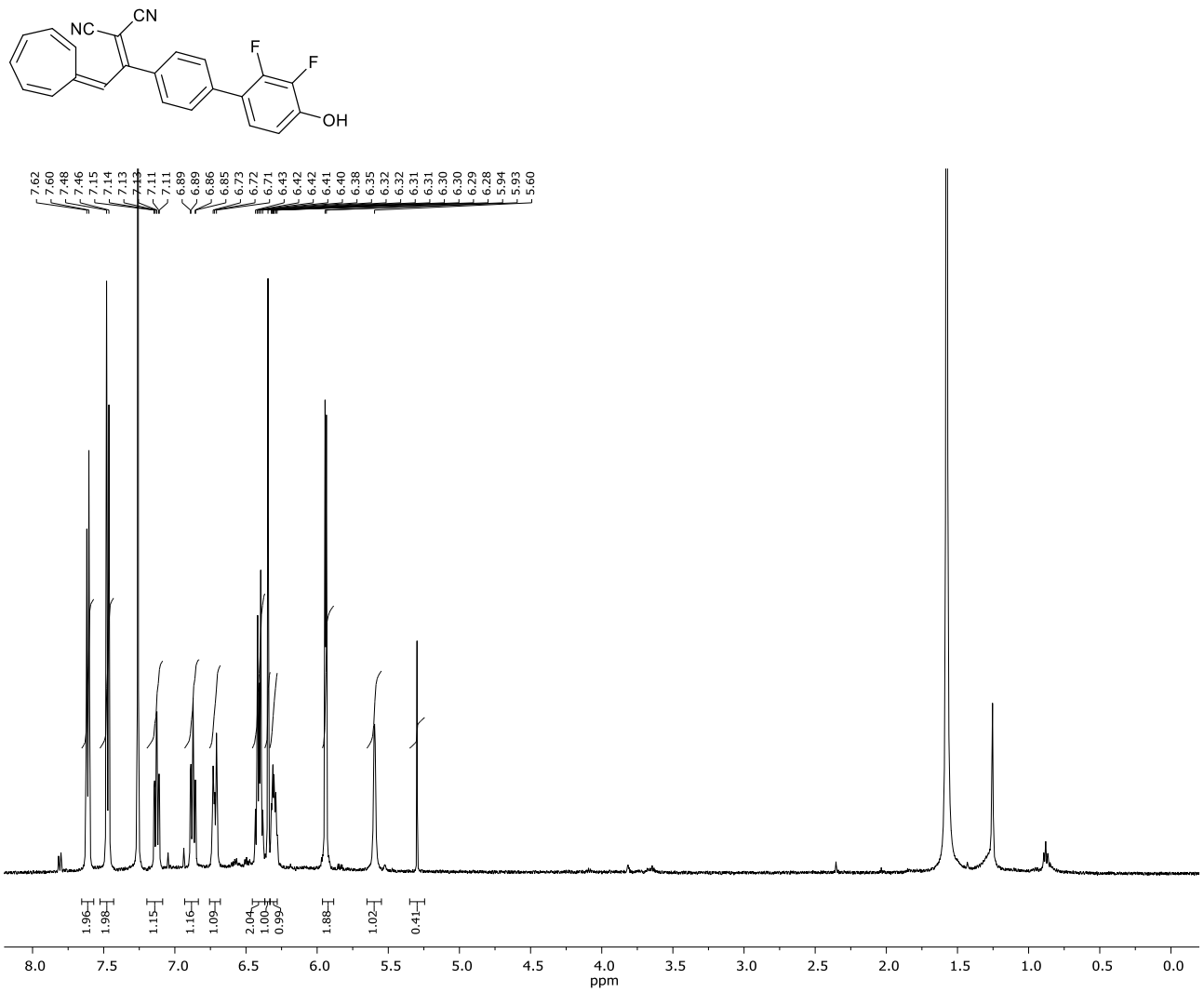

146.7
139.8
138.8
132.4
131.1
131.0
130.0
127.8
126.9
126.4
121.2
120.1
119.6
115.3
112.9
51.3
50.7
45.2
31.8
30.5
29.2
29.1
26.6
22.7
14.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

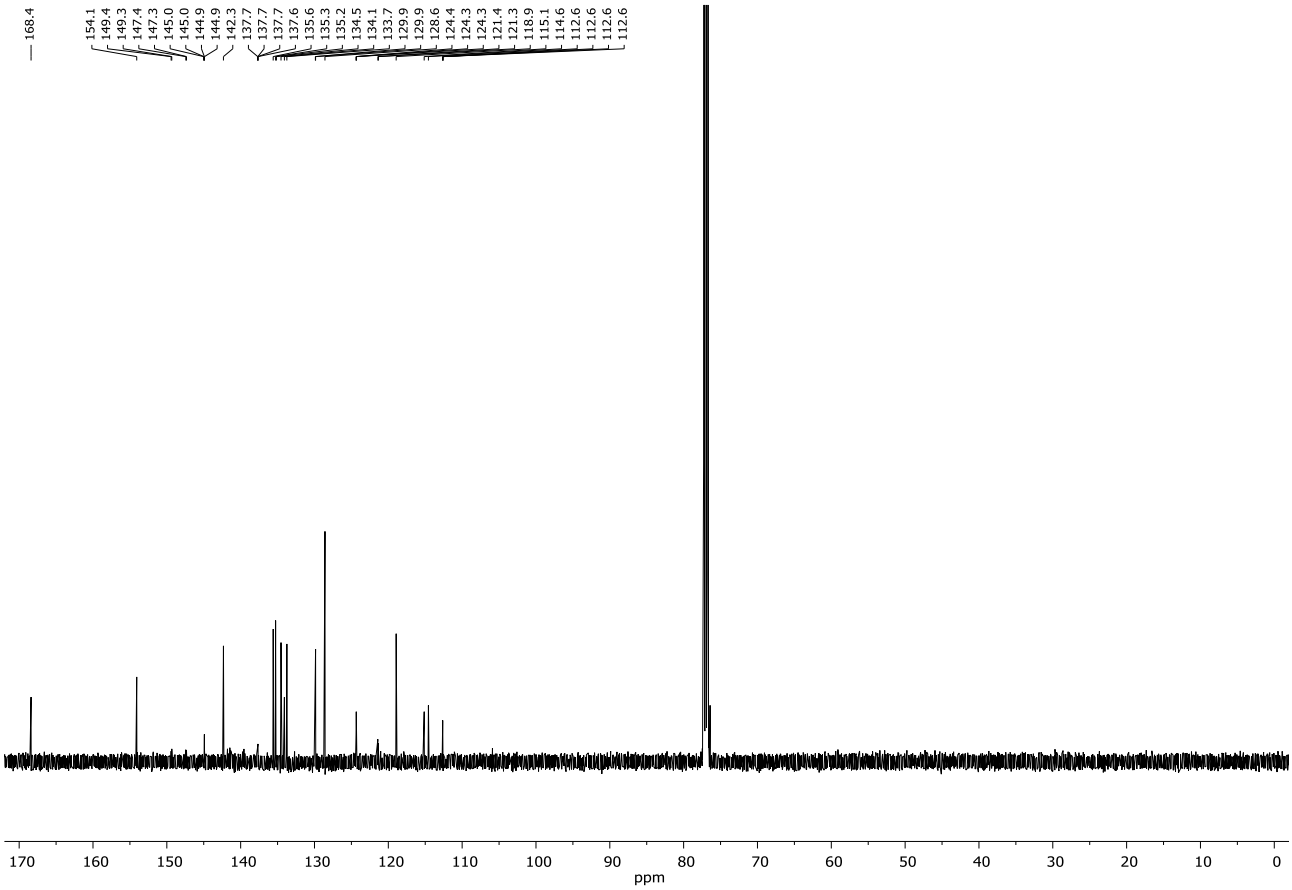
Compound 17


NC
CN
O
7.36
7.36
7.34
7.34
7.11
7.09
6.92
6.90
6.12
5.81
5.81
5.79
5.79
5.66
5.66
5.64
5.63
5.58
5.56
5.54
5.52
5.51
5.50
5.46
5.44
5.42
5.12
5.10
5.10
5.08
3.70
3.69
3.67
1.68
1.67
1.66
1.65
1.64
1.63
1.39
1.38
1.36
1.35
1.34
1.32
1.31
1.29
1.28
1.25
0.93
0.92
0.91
3.84
1.91
1.96
1.00
1.00
1.00
1.98
1.00
0.99
2.01
2.02
2.08
8.13
2.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


167.8
160.1
152.9
143.7
142.2
135.2
134.7
134.1
133.3
133.2
132.7
132.1
129.3
128.6
128.4
127.6
119.8
115.3
78.4
68.1
32.2
29.8
29.7
29.7
26.4
23.1
14.4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

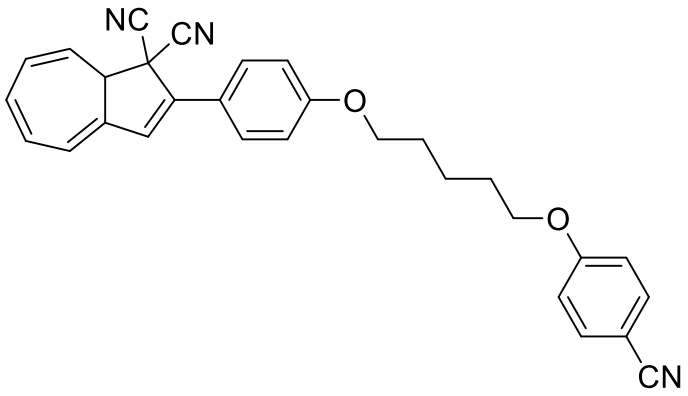
Compound 18

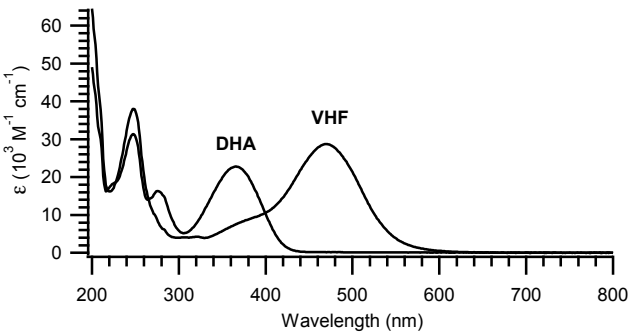

NC
CN
F
F
OH
7.62
7.60
7.48
7.46
7.15
7.14
7.13
7.13
7.11
7.11
6.89
6.89
6.86
6.85
6.73
6.72
6.71
6.43
6.42
6.42
6.41
6.40
6.38
6.35
6.32
6.32
6.31
6.31
6.30
6.30
6.29
6.28
5.94
5.93
5.60
1.96
1.98
1.15
1.16
1.09
2.04
1.00
0.99
1.88
1.02
0.41
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

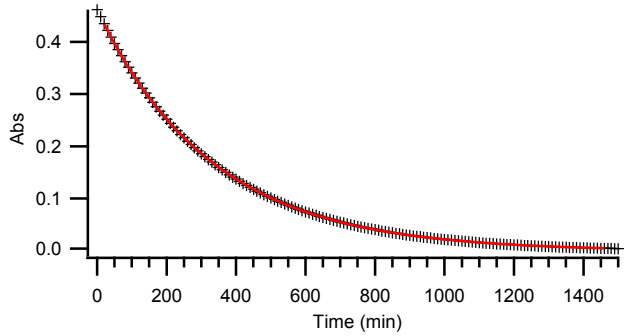

168.4
154.1
149.4
149.3
147.4
147.3
145.0
145.0
144.9
144.9
142.3
137.7
137.7
137.7
137.6
135.6
135.3
135.2
134.5
134.1
133.7
129.9
129.9
128.6
124.4
124.3
124.3
121.4
121.3
118.9
115.1
114.6
112.6
112.6
112.6
112.6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

UV-Vis Absorption Spectra and Decay of VHF Absorbance at $\lambda_{max,VHF}$ in MeCN at 25°C

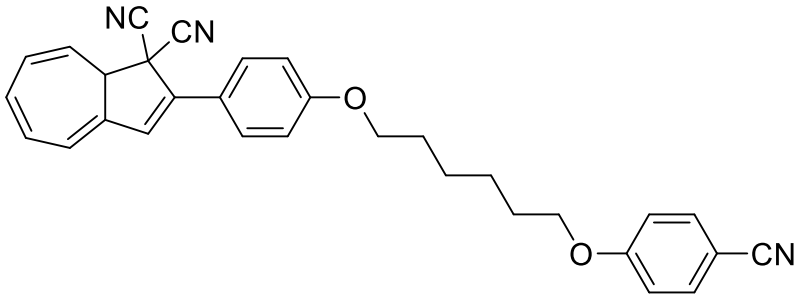
Compound 3a

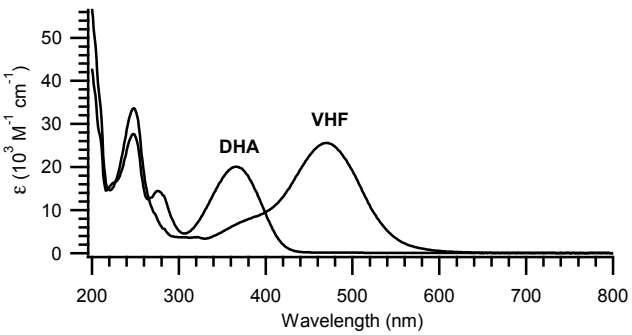


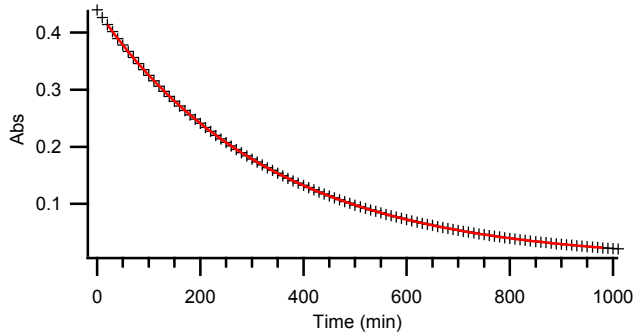




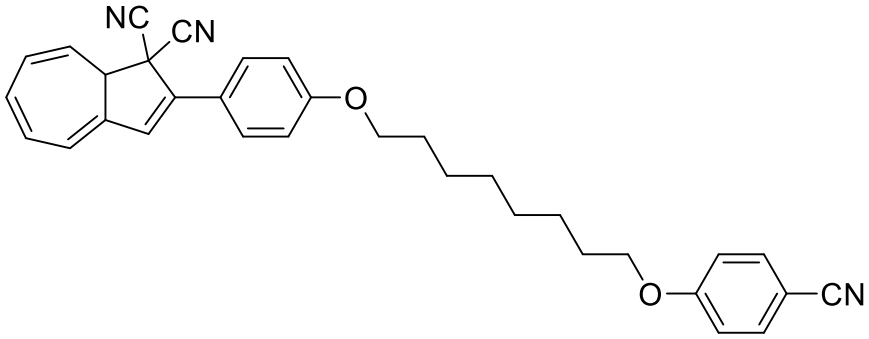
Compound 3b

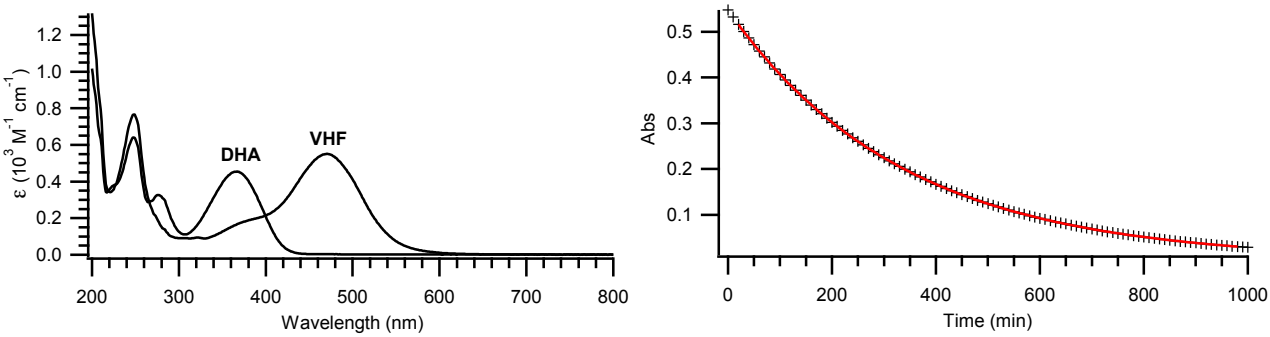




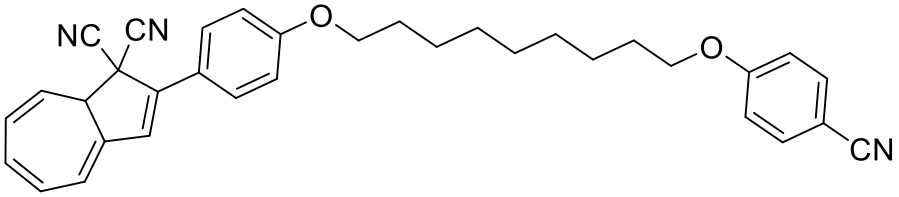


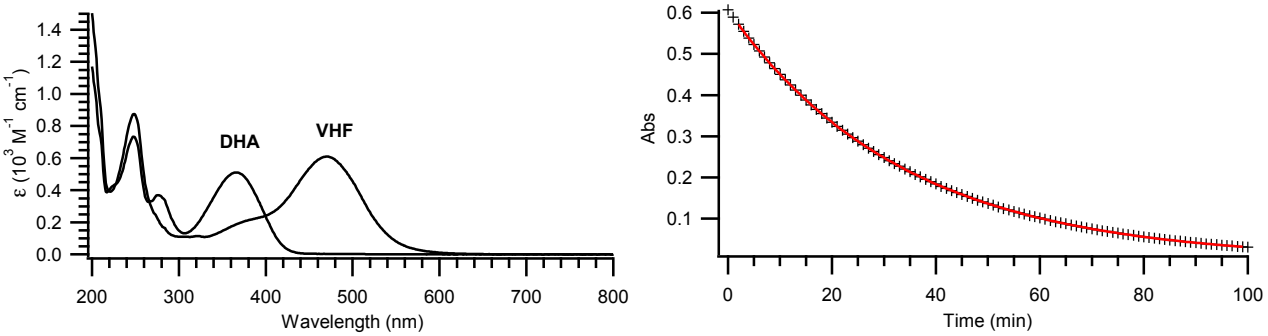
Compound 3C



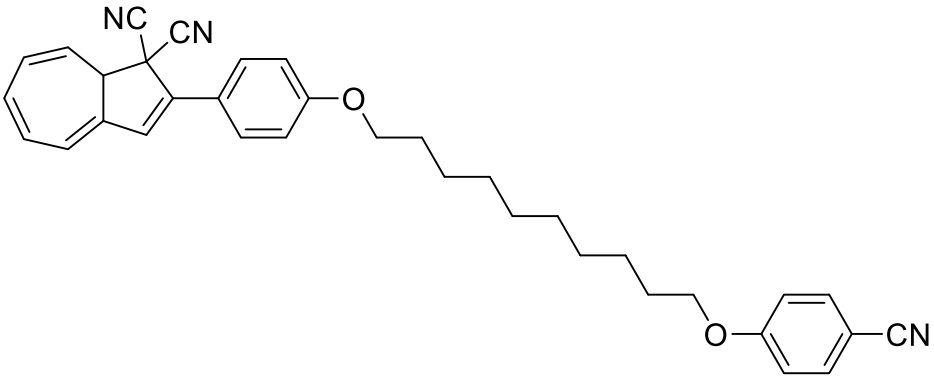


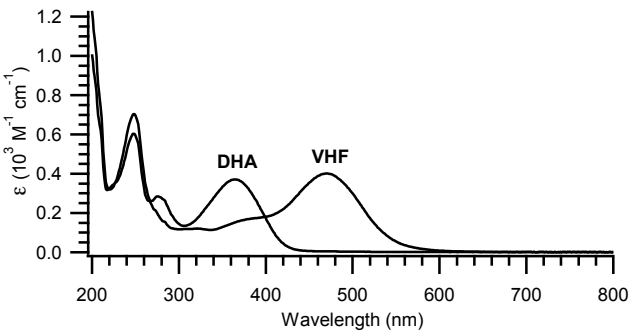
Compound 3d

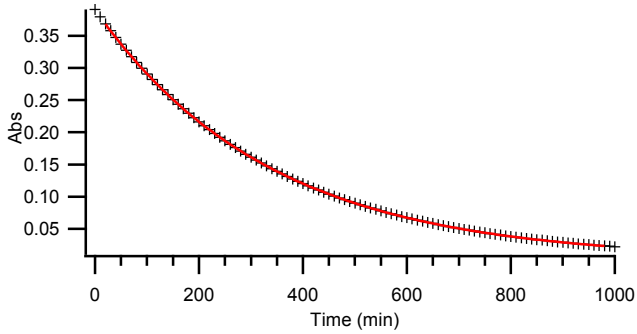




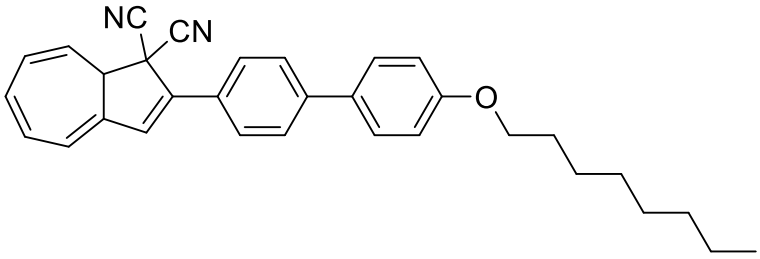
Compound 3e

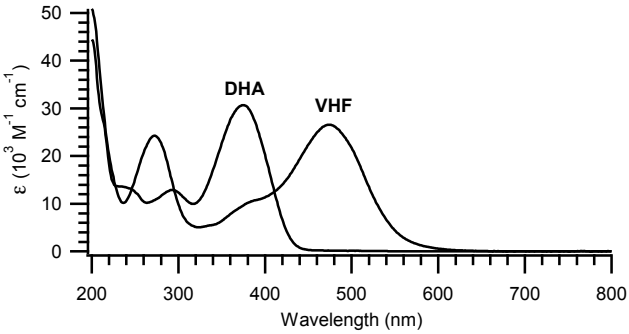


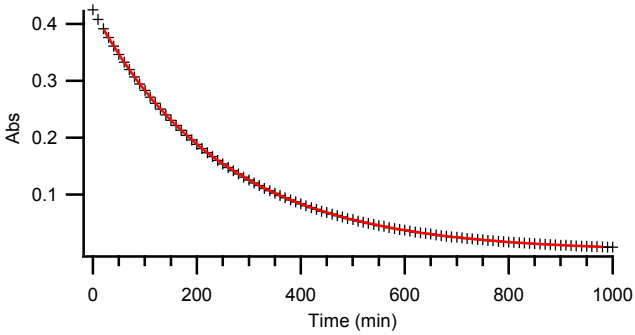




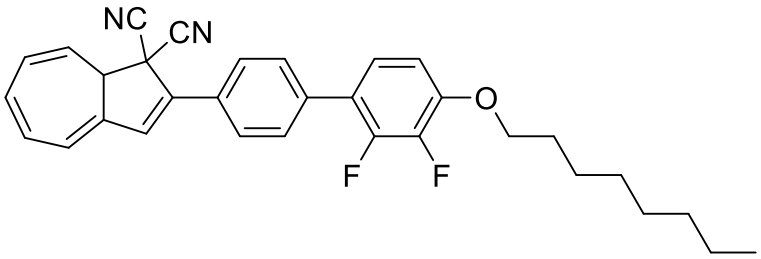
Compound 3f

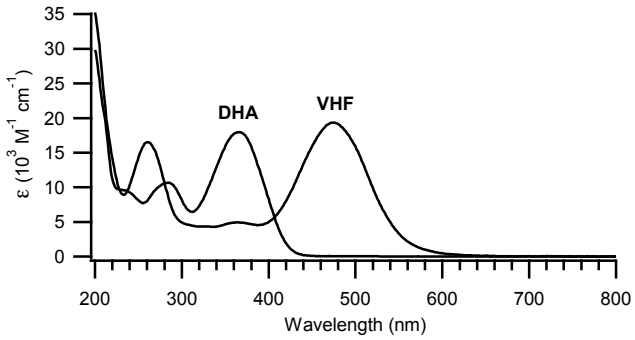


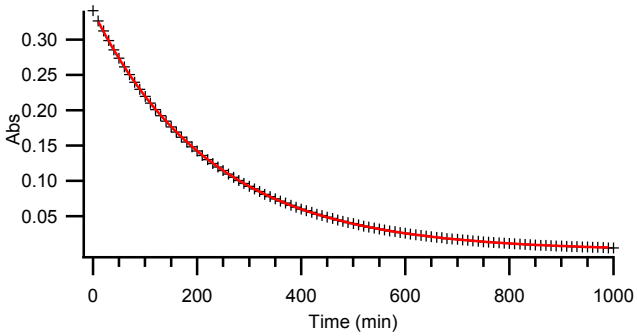




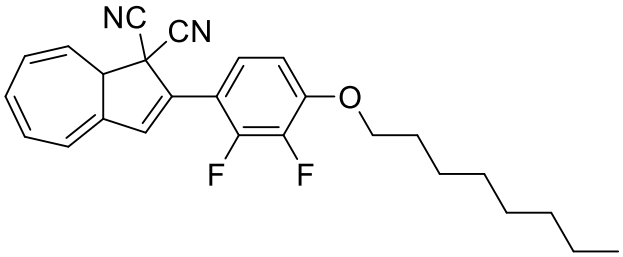
Compound 3g

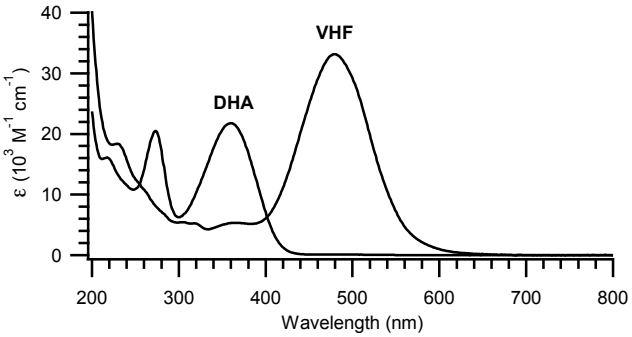


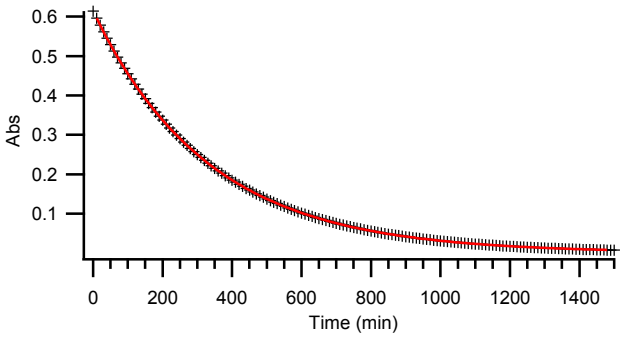




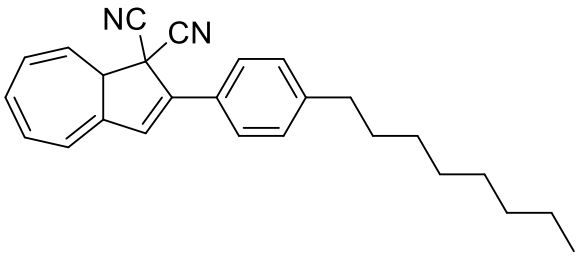
Compound 3h

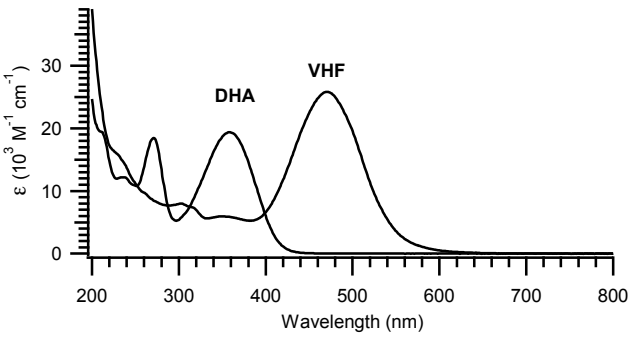


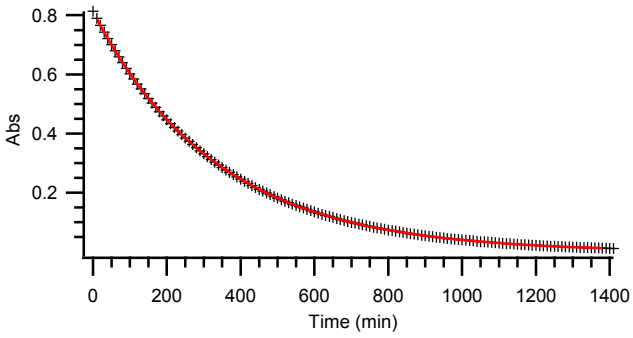




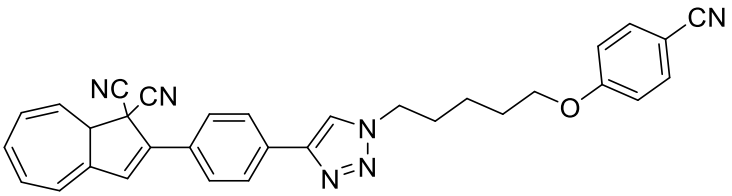
Compound 3i

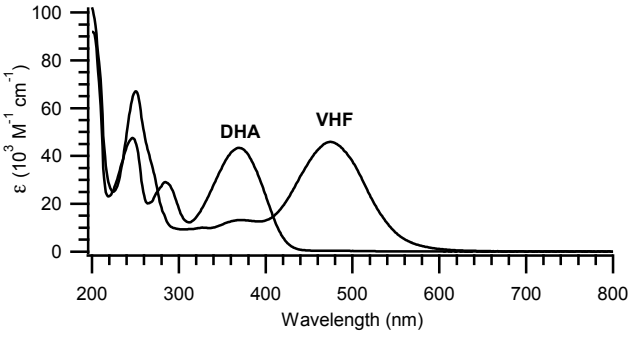


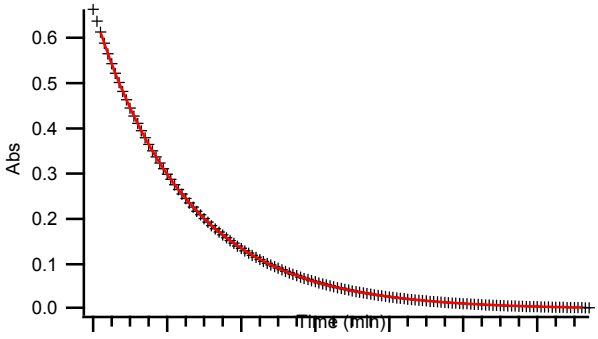




Compound 4a







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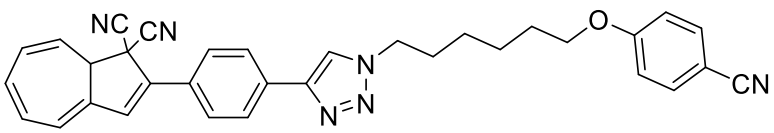
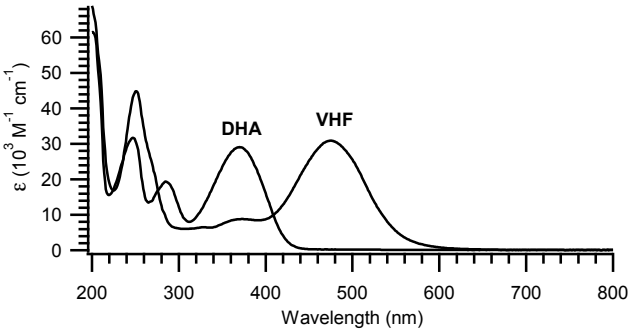
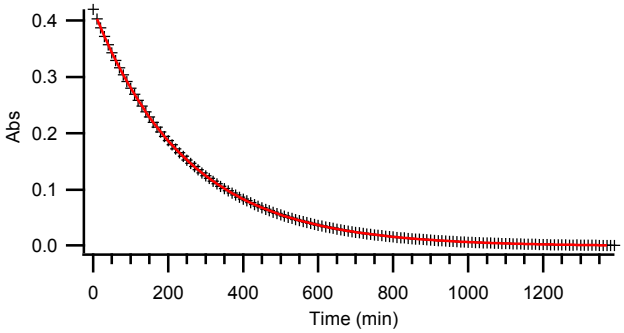
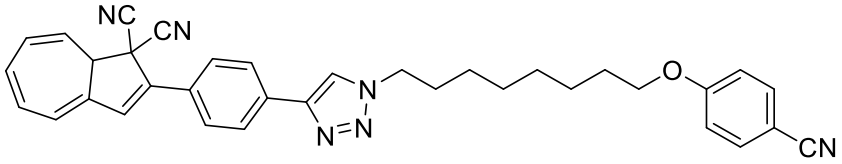
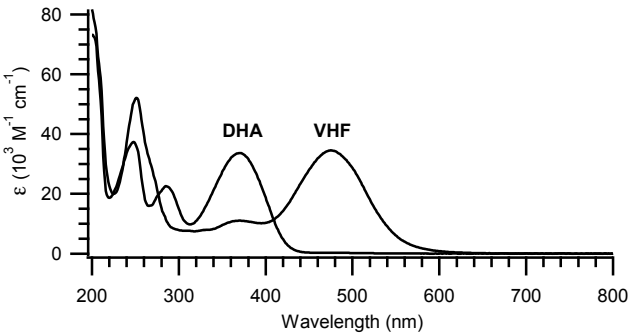


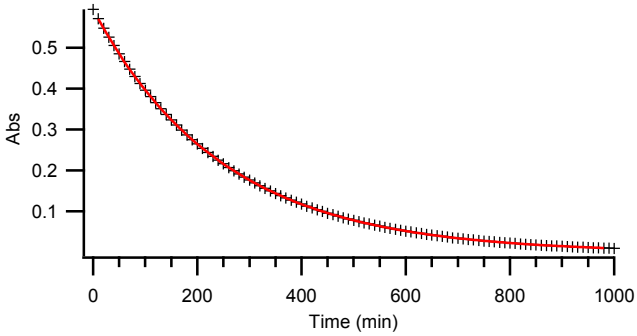




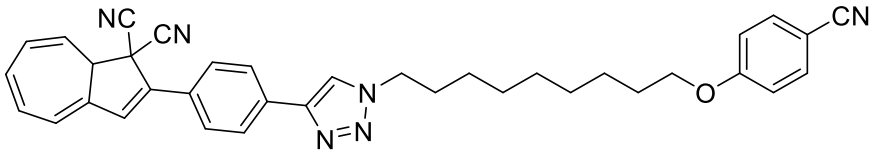
Compound 4c

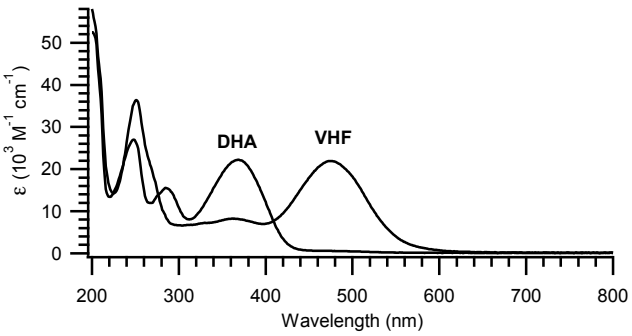


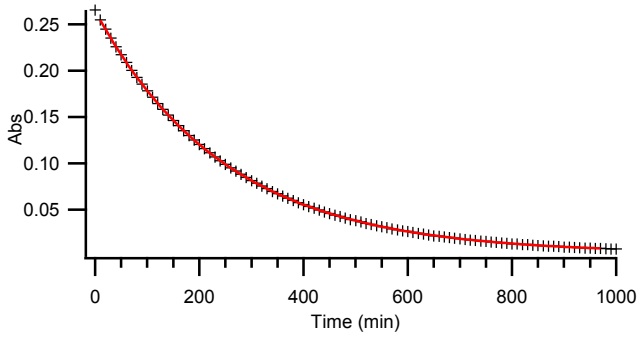




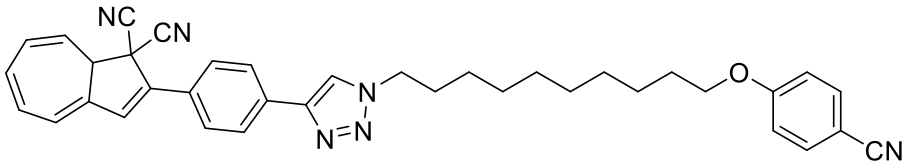
Compound 4d

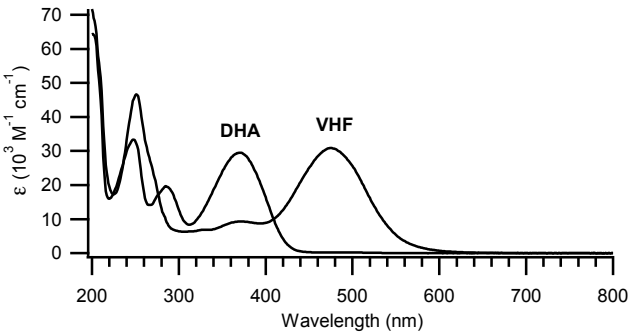


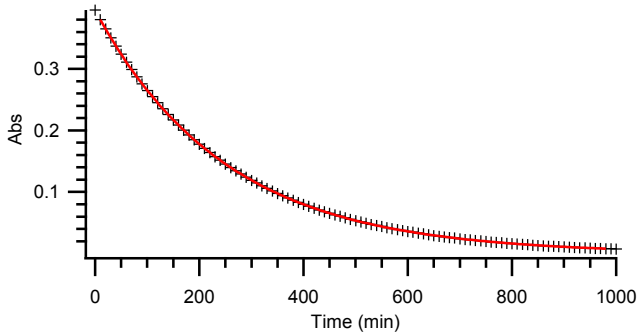




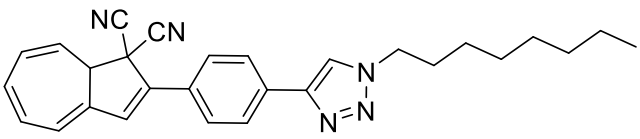
Compound 4e

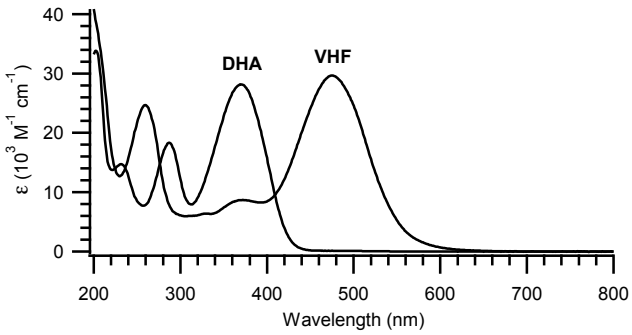


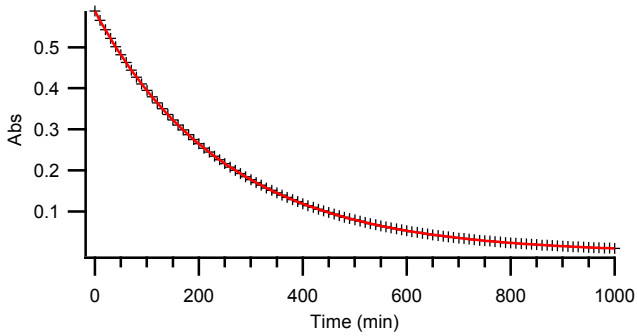




Compound 4j

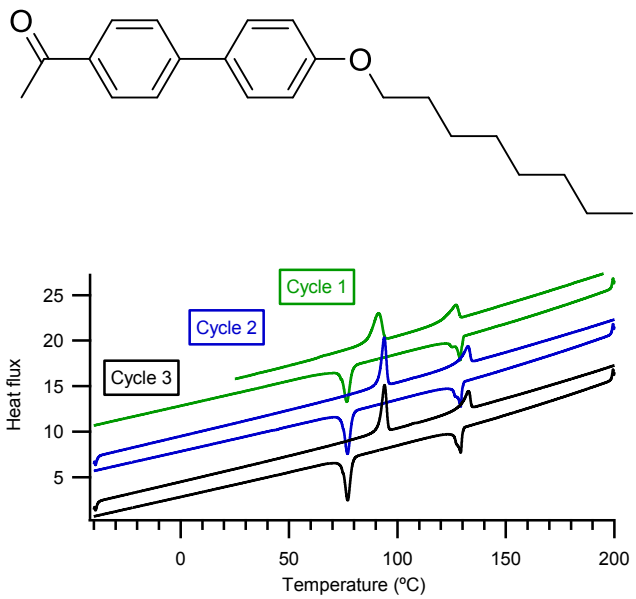

NC
CN
N
N
N


DHA
VHF
ε (10^3 M^-1 cm^-1)
Wavelength (nm)
0
10
20
30
40
200
300
400
500
600
700
800

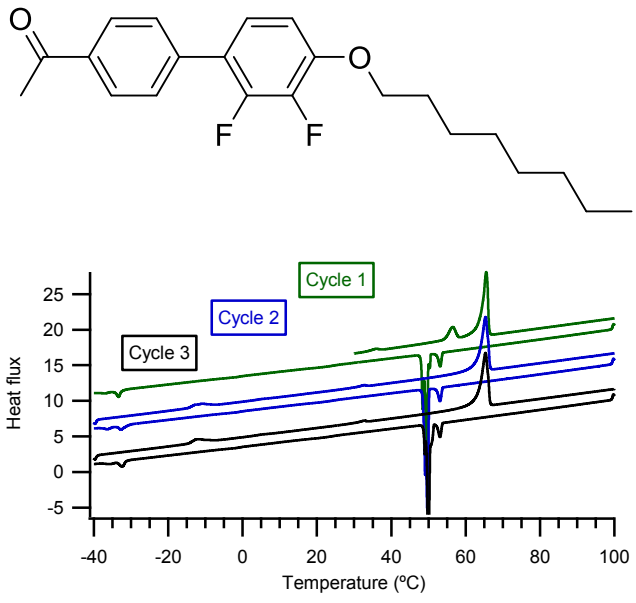

Abs
Time (min)
0.1
0.2
0.3
0.4
0.5
0
200
400
600
800
1000

DSC Thermograms

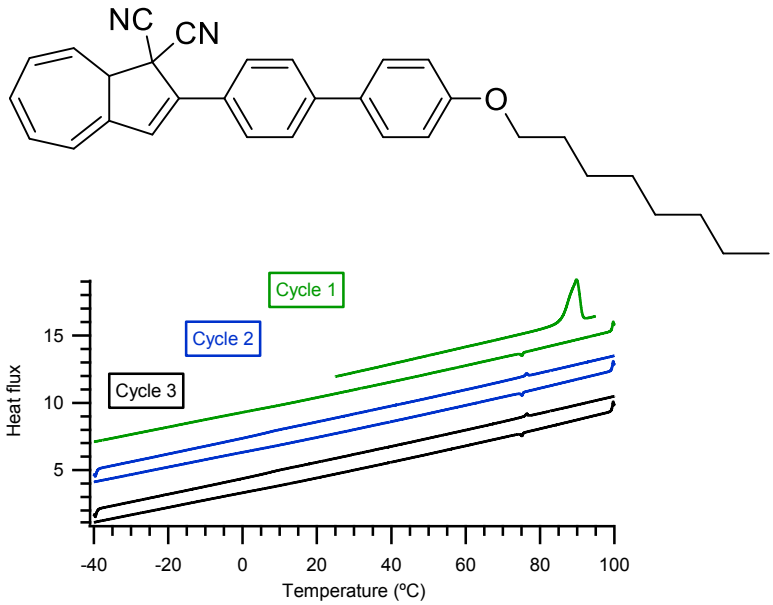
Compound 9f



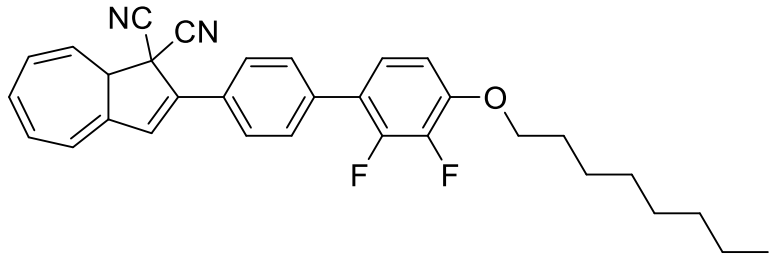
Compound 9g

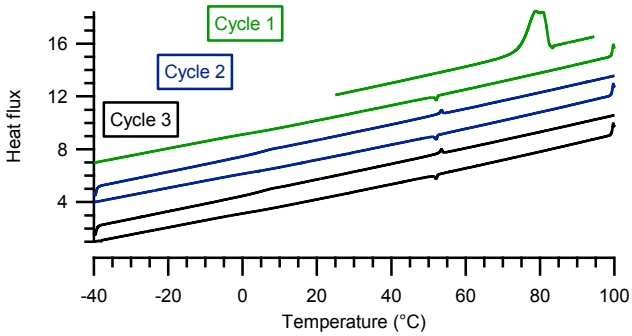


Compound 3f



Compound 3g



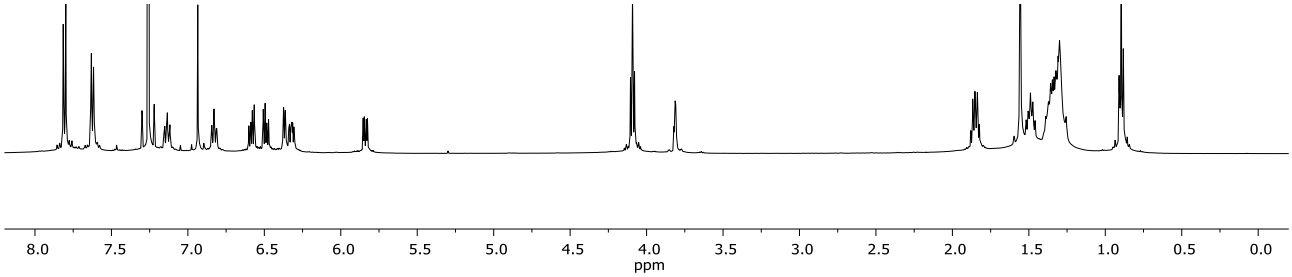


Conversion of 3g to the corresponding VHF in the nematic phase

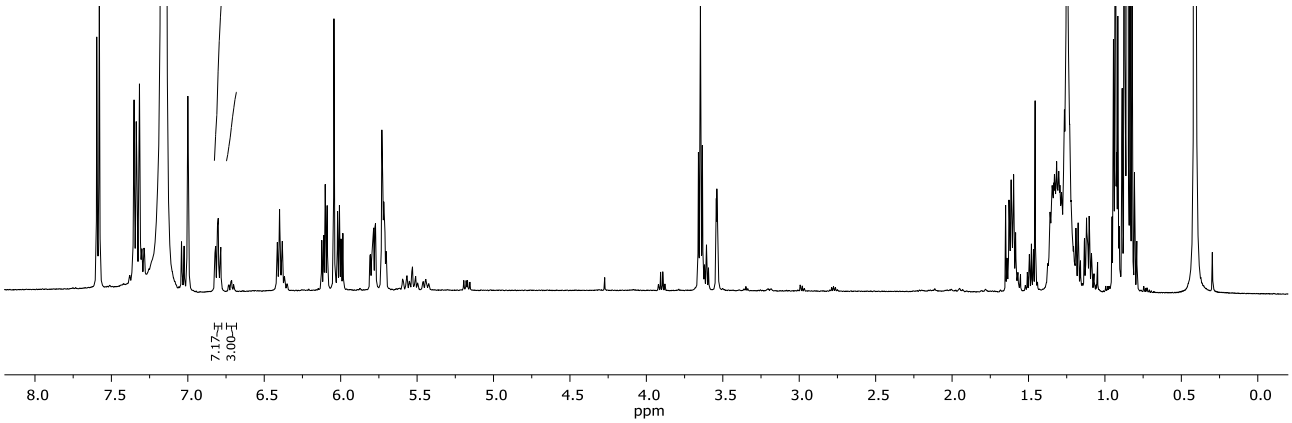
– NMR Characterization

Compound **3g** (spectrum a) was heated to over the melt and allowed to cool back to 40 °C, where **3g** in the nematic phase was exposed to UV irradiation at 365 nm (TLC lamp) for 1 hour, after which time, the sample was dissolved in C_6D_6 (spectrum b) and checked for VHF content. This solvent was chosen in order to retard the back reaction. In addition **3g** was treated in the same manner, but instead exposed to the TLC lamp for 24 hours (spectrum c).

a) Pure 3g in $CDCl_3$



b) **3g** irradiated at 40 °C in the nematic phase for 1h



c) **3g** irradiated at 40 °C in the nematic phase for 24h