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Organocatalytic Radical Relay Trifunctionalization of Unactivated Alkenes by a Combination of Cyano Migration and Alkylacylation

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Supporting Information

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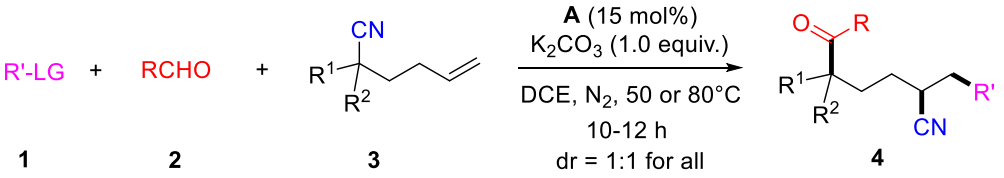
1. General methods

All reactions were carried out in dry glassware and were monitored by analytical thin layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of the products was accomplished by flash chromatography using silica gel (200-300 mesh). All NMR spectra were recorded on Bruker spectrometers, running at 300 MHz or 400 MHz for ^{1}H and 75 MHz or 101 MHz for ^{13}C respectively. Chemical shifts (δ) and coupling constants (J) are reported in ppm and Hz respectively. The solvent signals were used as references (residual $CHCl_3$ in $CDCl_3$: δH = 7.26 ppm, δc = 77.16 ppm). The following abbreviations are used to indicate the multiplicity in NMR spectra: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). High resolution mass spectrometry (HRMS) was recorded on TOF perimer for ESI^{+}.

2. Preparation of substrates

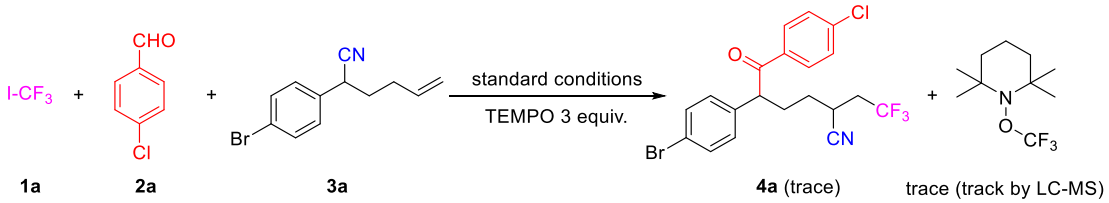
Trifluoroiodomethane, dibromodifluoromethane, perfluoro-1-iodohexane, ethyl 2-bromo-2,2-difluoroacetate, and aldehydes except **2u-2w** are commercially available. Aldehydes **2u-2w**,[1-3] hexenenitrile substrates, [4-5] and iodomethane bearing a tosyl group[6] are known compounds which are prepared according to the literature procedures.

3. General procedure for radical trifunctionalization of hexenenitriles



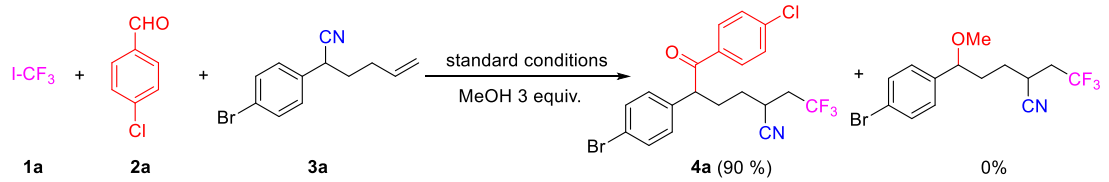
To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added NHC-**A** (12 mg, 0.03 mmol, 15 mol%) and K_2CO_3 (27.64 mg, 0.2 mmol, 1.0 equiv.). Then, the reaction tube was evacuated and back-filled with nitrogen three times. Subsequently, dry 1,2-dichloroethane (DCE) (2 mL), aldehyde **2** (0.2 mmol, 1.0 equiv.), hexenenitrile **3** (0.3 mmol, 1.5 equiv.) and radical precursor **1** (0.8 mmol, 4.0 equiv.) were added under the protection of nitrogen. The reaction was stirred at 50 ℃ or 80 ℃ (oil bath) for 10-12 hours. The reaction mixture was concentrated under reduced pressure, and the resulting crude material was purified by column chromatography on silica gel (petroleum ether / acetone from 20/1 to 15/1) to afford the desired products **4**.

4. Radical trapping experiment



To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added NHC-**A** (12 mg, 0.03 mmol, 15 mol%) and K_2CO_3 (27.64 mg, 0.2 mmol, 1.0 equiv.), after which the tube was evacuated and back-filled with nitrogen three times. Subsequently, dry 1,2-dichloroethane (DCE) (2 mL), 4-chlorobenzaldehyde **2a** (0.2 mmol, 1.0 equiv.), hexenenitrile **3a** (0.3 mmol , 1.2 equiv.) and trifluoromethyl iodide **1a** (156.7 mg, 0.8 mmol, 25% w/w in N,N-dimethylformamide, 4.0 equiv.) were added under the protection of nitrogen. TEMPO (93.8 mg, 0.6 mmol) was then added. The reaction was stirred at 50 ℃ (oil bath) for 10-12 hours. The reaction mixture was monitored by TLC and was further concentrated under reduced pressure. The resulting crude material was tested by LC-MS. No product was observed.

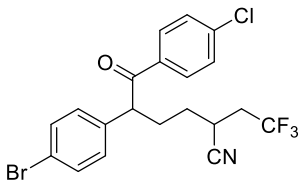
5. Carbocation trapping experiment



To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added NHC-**A** (12 mg, 0.03 mmol, 15 mol%) and K_2CO_3 (27.64 mg, 0.2 mmol, 1.0 equiv.), after which the tube was evacuated and back-filled with nitrogen three times. Subsequently, dry 1,2-dichloroethane (DCE) (2 mL), 4-chlorobenzaldehyde **2a** (0.2 mmol, 1.0 equiv.), hexenenitrile **3a** (0.3 mmol , 1.2 equiv.) and trifluoromethyl iodide **1a** (156.7 mg, 0.8 mmol, 25% w/w in N,N-dimethylformamide, 4.0 equiv.) were added under the protection of nitrogen. The reaction was stirred at 25 ℃ for 5 minutes, and methanol (0.6 mmol, 3.0 equiv.) was added. After stirring at 50 ℃ (oil bath) for another 10 hours, the reaction mixture was concentrated under reduced pressure. The resulting crude material was monitored by crude ^{1}H NMR and was purified by column chromatography on silica gel (petroleum ether / acetone from 20/1) to afford **4a** (82 mg, 90%).

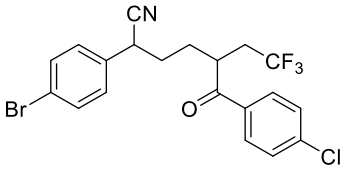
6. Characterization of the products

5-(4-bromophenyl)-6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile



(4a) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (75.9 mg, 83% yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.7, 2.1 Hz, 2H, two isomers), 7.44 (d, *J* = 8.4 Hz, 2H, two isomers), 7.37 (d, *J* = 8.1 Hz, 2H, two isomers), 7.13 (dd, *J* = 8.4, 1.7 Hz, 2H, two isomers), 4.47 (t, *J* = 7.2 Hz, 1H, two isomers), 2.93 – 2.79 (m, 1H, two isomers), 2.60 – 2.42 (m, 1H, two isomers), 2.38 – 2.21 (m, 2H, two isomers), 2.13 – 1.92 (m, 1H, two isomers), 1.78 – 1.66 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.13 & 197.06 (two isomers), 140.09 & 140.07 (two isomers), 137.3 & 137.2 (two isomers), 134.34 & 134.31 (two isomers), 132.7 (overlap, two isomers), 130.2 (overlap, two isomers), 129.8 & 129.7 (two isomers), 129.2 (overlap, two isomers), 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) & 125.10 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 122.0 (overlap, two isomers), 119.47 & 119.46 (two isomers), 52.52 & 52.48 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.9 & 30.6 (two isomers), 30.1 & 29.9 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.7 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{16}BrClF_3NNaO$ $[M+Na]^+$: 479.9947; found: 479.9944. HRMS (ESI) calcd. for $C_{20}H_{17}BrClF_3NO$ $[M+H]^+$: 460.0108; found: 460.0089.

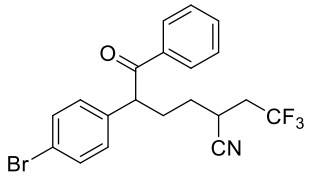
2-(4-bromophenyl)-5-(4-chlorobenzoyl)-7,7,7-trifluoroheptanenitrile (4a') The



title compound was obtained when the reaction was carried out using Cs_2CO_3 as a base in 1,2-DCE in the presence of precatalyst **A** (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.6, 3.4 Hz, 2H, one isomers), 7.48 (dt, *J* = 8.2, 4.6 Hz, 4H, one isomers), 7.11 (dd, *J* = 8.2, 6.0 Hz, 2H, one isomers), 3.75 (dd, *J* = 9.4, 4.1 Hz, 1H, one isomers), 3.69 (dd, *J* = 13.6, 7.1 Hz, 1H, one isomers), 2.87 – 2.72 (m, 1H, one isomers), 2.27 – 2.17 (m, 1H, one isomers), 1.98 – 1.90 (m, 1H, one isomers), 1.86 – 1.77 (m, 2H, one isomers), 1.75 – 1.62 (m, 1H, one isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2 & 199.1 (two isomers), 140.7 (overlap, two isomers), 134.15 & 134.10 (two

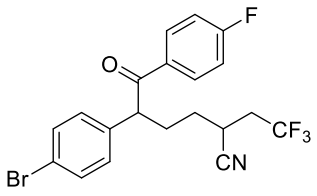
isomers), 133.9 & 133.8 (two isomers), 132.54 & 132.53 (two isomers), 130.4 (overlap, two isomers), 129.55 & 129.53 (two isomers), 128.91 & 128.87 (two isomers), 126.3 (q, $^{1}J_{C\text{-}F}$ = 278.0 Hz) (overlap, two isomers), 122.7 & 122.6 (two isomers), 119.59 & 119.57 (two isomers), 38.9 (q, $^{3}J_{C\text{-}F}$ = 3.2 Hz) (overlap, two isomers), 36.8 & 36.7 (two isomers), 35.5 (q, $^{2}J_{C\text{-}F}$ = 29.0 Hz) & 35.4 (q, $^{2}J_{C\text{-}F}$ = 29.1 Hz) (two isomers), 32.5 & 32.3 (two isomers), 29.9 & 29.8 (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.59 (s, one isomer), -64.64 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{16}BrClF_3NNaO$ $[M+Na]^+$: 479.9947; found: 479.9944. HRMS (ESI) calcd. for $C_{20}H_{17}BrClF_3NO$ $[M+H]^+$: 460.0108; found: 460.0089.

5-(4-bromophenyl)-6-oxo-6-phenyl-2-(2,2,2-trifluoroethyl)hexanenitrile (4b) The



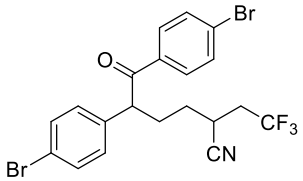
title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (63.5 mg, 84% yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H, two isomers), 7.56 – 7.50 (m, 1H, two isomers), 7.46 – 7.39 (m, 2H, two isomers), 7.33 – 7.28 (m, 2H, two isomers), 7.28 – 7.21 (m, 2H, two isomers), 4.58 (t, *J* = 7.1 Hz, 1H, two isomers), 2.96 – 2.81 (m, 1H, two isomers), 2.58 – 2.47 (m, 1H, two isomers), 2.43 – 2.27 (m, 2H, two isomers), 2.13 – 1.98 (m, 1H, two isomers), 1.81 – 1.72 (m, 1H, two isomers), 1.67 – 1.56 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5 & 198.4 (two isomers), 137.1 & 137.0 (two isomers), 136.2 & 136.1 (two isomers), 133.7 & 133.5 (two isomers), 129.6 (overlap, two isomers), 129.50 & 129.46 (two isomers), 128.84 & 128.78 (two isomers), 125.1 (q, $^{1}J_{C\text{-}F}$ = 275.1 Hz) (overlap, two isomers), 119.50 & 119.48 (two isomers), 52.33 & 52.28 (two isomers), 36.6 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.0 (q, $^{2}J_{C\text{-}F}$ = 29.4 Hz) (two isomers), 31.0 & 30.8 (two isomers), 30.2 & 30.0 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.4 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.89 (s, one isomer), -64.95 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{18}BrF_3NO$ $[M+H]^+$: 424.0518, 426.0498; found: 424.0500, 426.0517.

5-(4-bromophenyl)-6-(4-fluorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile



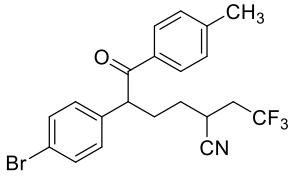
(4c) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (72.3 mg, 82% yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H, two isomers), 7.49 – 7.41 (m, 2H, two isomers), 7.14 (dd, J = 8.4, 1.9 Hz, 2H, two isomers), 7.11 – 7.02 (m, 2H, two isomers), 4.48 (t, J = 7.2 Hz, 1H, two isomers), 2.95 – 2.79 (m, 1H, two isomers), 2.61 – 2.43 (m, 1H, two isomers), 2.43 – 2.19 (m, 2H, two isomers), 2.15 – 1.88 (m, 1H, two isomers), 1.80 – 1.63 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.72 & 196.66 (two isomers), 165.91 (d, $^{1}J_{C\text{-}F}$ = 257.1 Hz) & 165.89 (d, $^{1}J_{C\text{-}F}$ = 256.9 Hz) (two isomers), 137.43 & 137.40 (two isomers), 132.7 (overlap, two isomers), 131.5 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz) (overlap, two isomers), 129.8 & 129.7 (two isomers), 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.6 Hz) & 125.09 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 121.9 (overlap, two isomers), 119.50 & 119.48 (two isomers), 116.0 (q, $^{2}J_{C\text{-}F}$ = 22.0 Hz) (overlap, two isomers), 52.45 & 52.41 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 31.0 & 30.7 (two isomers), 30.2 & 30.0 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.88 (s, one isomer), -64.94 (s, one isomer), -104.06 (s, one isomers), -104.10 (s, one isomers). HRMS (ESI) calcd. for $C_{20}H_{17}BrF_4NO$ $[M+H]^+$: 442.0425, 444.0404; found: 442.0426, 444.0409.

5,6-bis(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4d) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (68.4 mg, 68% yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H, two isomers), 7.54 (d, J = 8.5 Hz, 2H, two isomers), 7.49 – 7.41 (m, 2H, two isomers), 7.16 – 7.09 (m, 2H, two isomers), 4.46 (t, J = 7.2 Hz, 1H, two isomers), 2.93 – 2.80 (m, 1H, two isomers), 2.59 – 2.45 (m, 1H, two isomers), 2.40 – 2.24 (m, 2H, two isomers), 2.11 – 1.94 (m, 1H, two isomers), 1.80 – 1.54 (m, 2H, two isomers). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3 & 197.2 (two isomers), 137.2 & 137.2 (two isomers), 134.7 & 134.7 (two isomers), 132.7 (overlap, two isomers), 132.2 (overlap, two isomers), 130.3 (overlap, two isomers), 129.8 & 129.7 (two isomers), 128.9 & 128.8 (two isomers), 125.11 (q,



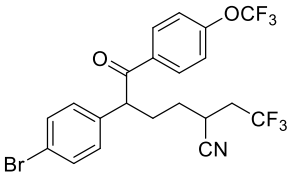
$^{1}J_{C\text{-}F}$ = 275.5 Hz) & 125.09 (q, $^{1}J_{C\text{-}F}$ = 275.8 Hz) (two isomers), 122.0 (overlap, two isomers), 119.47 & 119.46 (two isomers), 52.50 & 52.47 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz) (two isomers), 30.9 & 30.6 (two isomers), 30.1 & 29.9 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.87 (s, one isomer), -64.92 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{17}Br_2F_3NO$ $[M+H]^+$: 503.9604, 501.9624; found: 503.9601, 501.9622.

5-(4-bromophenyl)-6-oxo-6-(p-tolyl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4e) The



title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (63.8 mg, 73%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.2, 1.9 Hz, 2H, two isomers), 7.43 (d, *J* = 8.3 Hz, 2H, two isomers), 7.22 – 7.13 (m, 4H, two isomers), 4.52 (t, J = 7.2 Hz, 1H, two isomers), 2.93 – 2.81 (m, 1H, two isomers), 2.56 – 2.45 (m, 1H, two isomers), 2.36 (s, 3H, two isomers), 2.35 – 2.16 (m, 2H, two isomers), 2.09 – 1.94 (m, 1H, two isomers), 1.82 – 1.69 (m, 1H, two isomers), 1.69 – 1.61 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.94 & 197.87 (two isomers), 144.6 & 144.5 (two isomers), 137.9 & 137.8 (two isomers), 133.59 & 133.56 (two isomers), 132.5 (overlap, two isomers), 129.83 & 129.78 (two isomers), 129.6 (overlap, two isomers), 128.94 & 128.93 (two isomers), 125.16 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) & 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 121.7 (overlap, two isomers), 119.54 & 119.49 (two isomers), 52.3 & 52.2 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 31.0 & 30.7 (two isomers), 30.3 & 30.1 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) (two isomers), 21.8 (overlap, two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{20}BrF_3NO$ $[M+H]^+$: 438.0675, 440.0655; found: 438.0685, 440.0662.

5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)-6-(4-(trifluoromethoxy)phenyl)



hexanenitrile (4f) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow colorless liquid (87.2 mg, 86%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H, two isomers), 7.32 – 7.28 (m, 2H, two isomers), 7.24 – 7.17 (m, 4H, two

isomers), 4.50 (t, J = 7.1 Hz, 1H, two isomers), 2.95 – 2.82 (m, 1H, two isomers), 2.58 – 2.44 (m, 1H, two isomers), 2.39 – 2.24 (m, 2H, two isomers), 2.11 – 1.99 (m, 1H, two isomers), 1.77 – 1.68 (m, 1H, two isomers), 1.63 – 1.56 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 & 196.8 (two isomers), 152.9 (q, $^3J_{C\text{-}F}$ = 2.8 Hz) (overlap, two isomers), 136.7 & 136.6 (two isomers), 134.24 & 134.21 (two isomers), 134.0 (overlap, two isomers), 130.9 (overlap, two isomers), 129.8 (overlap, two isomers), 129.44 & 129.40 (two isomers), 125.14 (q, $^1J_{C\text{-}F}$ = 278.3 Hz) & 125.11 (q, $^1J_{C\text{-}F}$ = 278.6 Hz) (two isomers), 120.5 (overlap, two isomers), 120.3 (q, $^1J_{C\text{-}F}$ = 260.2 Hz) (overlap, two isomers), 119.47 & 119.46 (two isomers), 52.53 & 52.51 (two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.2 Hz) (two isomers), 31.0 & 30.8 (two isomers), 30.1 & 29.9 (two isomers), 25.8 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6 (overlap, two isomers), -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{17}BrF_6NO_2$ $[M+H]^+$: 508.0341; found: 508.0331. HRMS (ESI) calcd. for $C_{21}H_{16}BrF_6NO_2$ $[M+Na]^+$: 532.0141; found: 532.0137.

6-([1,1'-biphenyl]-4-yl)-5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexane nitrile (4g) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (44.9 mg, 60%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H, two isomers), 7.63 (d, J = 8.4 Hz, 2H, two isomers), 7.58 (d, J = 7.1 Hz, 2H, two isomers), 7.49 – 7.42 (m, 4H, two isomers), 7.42 – 7.37 (m, 1H, two isomers), 7.23 – 7.17 (m, 2H, two isomers), 4.58 (t, J = 7.1 Hz, 1H, two isomers), 2.95 – 2.85 (m, 1H, two isomers), 2.57 – 2.47 (m, 1H, two isomers), 2.42 – 2.28 (m, 2H, two isomers), 2.13 – 2.00 (m, 1H, two isomers), 1.80 – 1.72 (m, 1H, two isomers), 1.65 – 1.58 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 & 197.8 (two isomers), 146.27 & 146.25 (two isomers), 139.7 (overlap, two isomers), 137.71 & 137.66 (two isomers), 134.8 & 134.7 (two isomers), 132.6 (overlap, two isomers), 129.9 (overlap, two isomers), 129.8 (overlap, two isomers), 129.4 (overlap, two isomers), 129.1 (overlap, two isomers), 128.5 (overlap, two isomers), 127.5 (overlap, two isomers), 127.3 (overlap, two isomers), 125.2 (q, $^1J_{C\text{-}F}$ = 277.5 Hz) (overlap, two isomers), 121.8 & 121.0 (two isomers), 119.52 & 119.49 (two isomers), 52.5 & 52.4 (two isomers),

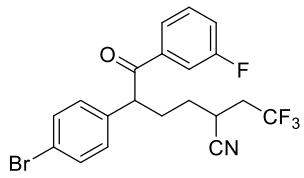
36.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.3 Hz) (two isomers), 31.0 & 30.7 (two isomers), 30.3 & 30.1 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). HRMS (ESI) calcd. for $C_{26}H_{22}BrF_3NO$ $[M+H]^+$: 500.0832, 502.0811; found: 500.0831, 502.0813.

5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)-6-(4-(trifluoromethyl)phenyl) hexanenitrile (4h) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (73.8 mg, 75%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H, two isomers), 7.66 (d, *J* = 8.2 Hz, 2H, two isomers), 7.32 – 7.28 (m, 2H, two isomers), 7.19 (dd, *J* = 8.4, 1.7 Hz, 2H, two isomers), 4.53 (t, *J* = 7.2 Hz, 1H, two isomers), 2.96 – 2.82 (m, 1H, two isomers), 2.60 – 2.46 (m, 1H, two isomers), 2.40 – 2.25 (m, 2H, two isomers), 2.15 – 2.00 (m, 1H, two isomers), 1.79 – 1.68 (m, 1H, two isomers), 1.67 – 1.61 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5 & 197.4 (two isomers), 138.75 & 138.74 (two isomers), 136.33 & 136.28 (two isomers), 134.71 (q, $^{2}J_{C\text{-}F}$ = 33.1 Hz) & 134.70 (q, $^{2}J_{C\text{-}F}$ = 32.9 Hz) (two isomers), 134.1 (overlap, two isomers), 129.9 (overlap, two isomers), 129.5 & 129.4 (two isomers), 129.1 (overlap, two isomers), 125.9 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz) (overlap, two isomers), 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.1 Hz) & 125.09 (q, $^{1}J_{C\text{-}F}$ = 278.0 Hz) (two isomers), 123.5 (q, $^{1}J_{C\text{-}F}$ = 273.8 Hz) (overlap, two isomers), 119.5 & 119.4 (two isomers), 52.8 (overlap, two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 30.8 & 30.6 (two isomers), 30.0 & 29.9 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.4 Hz) (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3 (overlap, two isomers), -64.89 (s, one isomer), -64.94 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{16}BrF_6NO$ $[M+Na]^+$: 514.0212; found: 514.0189. HRMS (ESI) calcd. for $C_{21}H_{17}BrF_6NO$ $[M+H]^+$: 494.0372; found: 494.0381.

5-(4-bromophenyl)-6-(4-nitrophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4i) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (51.5 mg, 55%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 2H, two isomers), 8.03 (dd, *J* = 8.9, 1.9 Hz, 2H, two isomers), 7.31 (d, *J* = 8.4 Hz, 2H, two isomers), 7.18 (dd,

J = 8.4, 1.8 Hz, 2H, two isomers), 4.53 (t, J = 7.1 Hz, 1H, two isomers), 2.97 – 2.83 (m, 1H, two isomers), 2.61 – 2.45 (m, 1H, two isomers), 2.43 – 2.25 (m, 2H, two isomers), 2.15 – 1.99 (m, 1H, two isomers), 1.80 – 1.69 (m, 1H, two isomers), 1.68 – 1.60 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 & 196.9 (two isomers), 150.4 (overlap, two isomers), 140.60 & 140.58 (two isomers), 135.92 & 135.86 (two isomers), 134.3 (overlap, two isomers), 130.0 (overlap, two isomers), 129.8 (overlap, two isomers), 129.50 & 129.46 (two isomers), 125.11 (q, $^1J_{C\text{-}F}$ = 277.4 Hz) & 125.09 (q, $^1J_{C\text{-}F}$ = 277.7 Hz) (two isomers), 124.0 (overlap, two isomers), 119.4 (overlap, two isomers), 53.2 (overlap, two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 29.4 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.7 & 30.6 (two isomers), 29.9 & 29.8 (two isomers), 25.7 (q, $^3J_{C\text{-}F}$ = 2.7 Hz) (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{16}BrF_3N_2O_3$ $[M+Na]^+$: 491.0189; found: 491.0189. HRMS (ESI) calcd. for $C_{20}H_{17}BrF_3N_2O_3$ $[M+H]^+$: 471.0349; found: 471.0352.

5-(4-bromophenyl)-6-(3-fluorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile



(4j) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (65.3 mg, 74%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 1H, two isomers), 7.61 – 7.55 (m, 1H, two isomers), 7.45 (d, J = 8.4 Hz, 2H, two isomers), 7.41 – 7.33 (m, 1H, two isomers), 7.21 (td, J = 8.2, 2.5 Hz, 1H, two isomers), 7.14 (dd, J = 8.4, 1.7 Hz, 2H, two isomers), 4.48 (t, J = 7.2 Hz, 1H, two isomers), 2.93 – 2.82 (m, 1H, two isomers), 2.57 – 2.45 (m, 1H, two isomers), 2.39 – 2.24 (m, 2H, two isomers), 2.11 – 1.96 (m, 1H, two isomers), 1.77 – 1.67 (m, 1H, two isomers), 1.64 – 1.54 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 & 197.1 (two isomers), 162.9 (d, $^1J_{C\text{-}F}$ = 249.5 Hz) (overlap, two isomers), 138.21 & 138.19 (two isomers), 137.1 (d, $^3J_{C\text{-}F}$ = 5.1 Hz) (overlap, two isomers), 132.7 (overlap, two isomers), 130.5 (d, $^3J_{C\text{-}F}$ = 7.6 Hz) (overlap, two isomers), 129.80 & 129.76 (two isomers), 125.13 (q, $^1J_{C\text{-}F}$ = 278.6 Hz) & 125.11 (q, $^1J_{C\text{-}F}$ = 278.6 Hz) (two isomers), 124.5 (d, $^4J_{C\text{-}F}$ = 2.0 Hz) (overlap, two isomers), 122.0 (overlap, two isomers), 120.6 (d, $^2J_{C\text{-}F}$ = 21.6 Hz) (overlap, two isomers), 119.45 & 119.43 (two isomers), 115.5 (d, $^2J_{C\text{-}F}$ = 22.5 Hz) (overlap, two isomers), 52.69 & 52.67 (two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ =

30.0 Hz) (two isomers), 30.9 & 30.7 (two isomers), 30.1 & 29.9 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.87 (s, one isomer), -64.93 (s, one isomer), -111.24 (s, one isomer), -111.23 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{17}BrF_4NO$ $[M+H]^+$: 442.0425, 444.0404; found: 442.0426, 444.0411.

6-(3-bromophenyl)-5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4k) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (71.1 mg, 71%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (q, *J* = 1.6 Hz, 1H, two isomers), 7.82 – 7.77 (m, 1H, two isomers), 7.66 – 7.60 (m, 1H, two isomers), 7.48 – 7.43 (m, 2H, two isomers), 7.29 – 7.24 (m, 1H, two isomers), 7.13 (dt, *J* = 6.6, 1.8 Hz, 2H, two isomers), 4.47 (t, *J* = 7.2 Hz, 1H, two isomers), 2.93 – 2.82 (m, 1H, two isomers), 2.57 – 2.45 (m, 1H, two isomers), 2.38 – 2.25 (m, 2H, two isomers), 2.11 – 1.95 (m, 1H, two isomers), 1.77 – 1.67 (m, 1H, two isomers), 1.62 – 1.55 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.03 & 196.96 (two isomers), 137.84 & 137.81 (two isomers), 137.03 & 136.97 (two isomers), 136.4 (overlap, two isomers), 132.7 (overlap, two isomers), 131.8 (overlap, two isomers), 130.4 (overlap, two isomers), 129.79 & 129.75 (two isomers), 127.3, 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.6 Hz) & 125.09 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 123.2 (overlap, two isomers), 122.0 (overlap, two isomers), 119.4 (overlap, two isomers), 52.60 & 52.57 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz) (two isomers), 30.9 & 30.6 (two isomers), 30.1 & 29.9 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.85 (s, one isomer), -64.91 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{17}Br_2F_3NO$ $[M+H]^+$: 503.9604, 501.9624; found: 503.9601, 501.9622.

5-(4-bromophenyl)-6-oxo-6-(m-tolyl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4l) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (64.7 mg, 74%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 11.4, 8.2 Hz, 4H, two isomers), 7.30 (t, J = 7.9 Hz, 1H, two isomers), 7.16 (dd, J = 8.3, 1.7 Hz, 2H, two isomers), 7.05

(dd, J = 8.2, 2.2 Hz, 1H, two isomers), 4.52 (t, J = 7.2 Hz, 1H, two isomers), 3.81 (s, 3H, two isomers), 2.92 – 2.82 (m, 1H, two isomers), 2.58 – 2.45 (m, 1H, two isomers), 2.40 – 2.25 (m, 2H, two isomers), 2.10 – 1.96 (m, 1H, two isomers), 1.78 – 1.68 (m, 1H, two isomers), 1.63 – 1.56 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2 & 198.1 (two isomers), 160.0 (overlap, two isomers), 137.64 & 137.59 (two isomers), 137.48 & 137.46 (two isomers), 132.6 (overlap, two isomers), 129.81 & 129.78 (two isomers), 125.15 (q, $^1J_{C\text{-}F}$ = 278.2 Hz) & 125.12 (q, $^1J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 121.8 (overlap, two isomers), 121.3 (overlap, two isomers), 119.9 (overlap, two isomers), 119.49 & 119.46 (two isomers), 113.33 & 113.30 (two isomers), 55.5 (overlap, two isomers), 52.52 & 52.47 (two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 31.0 & 30.8 (two isomers), 30.2 & 30.0 (two isomers), 25.8 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.6 (q, $^3J_{C\text{-}F}$ = 2.8 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.89 (s, one isomer), -64.95 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{20}BrF_3NO$ $[M+H]^+$: 438.0675, 440.0655; found: 438.0700, 440.0630.

5-(4-bromophenyl)-6-(3-methoxyphenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexane nitrile (4m) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (52.2 mg, 61%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H, two isomers), 7.43 (d, *J* = 8.4 Hz, 2H, two isomers), 7.31 (dd, *J* = 16.1, 7.5 Hz, 2H, two isomers), 7.16 (dd, *J* = 8.5, 2.0 Hz, 2H, two isomers), 4.54 (t, *J* = 7.2 Hz, 1H, two isomers), 2.93 – 2.82 (m, 1H, two isomers), 2.57 – 2.46 (m, 1H, two isomers), 2.36 (s, 3H, two isomers), 2.34 – 2.21 (m, 2H, two isomers), 2.09 – 1.97 (m, 1H, two isomers), 1.75 – 1.69 (m, 1H, two isomers), 1.65 – 1.58 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6 & 198.5 (two isomers), 138.8 (overlap, two isomers), 137.71 & 137.66 (two isomers), 136.19 & 136.17 (two isomers), 134.4 (overlap, two isomers), 132.5 (overlap, two isomers), 129.84 & 129.80 (two isomers), 129.3 (overlap, two isomers), 128.7 (overlap, two isomers), 126.0 (overlap, two isomers), 125.15 (q, $^1J_{C\text{-}F}$ = 278.5 Hz) & 125.12 (q, $^1J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 121.7 (overlap, two isomers), 119.51 & 119.47 (two isomers), 52.4 & 52.3 (two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 29.9 Hz) (two isomers), 31.0 & 30.7 (two isomers), 30.2 & 30.0 (two

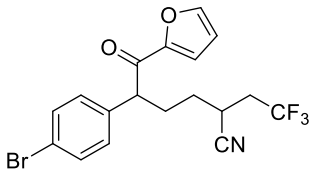
isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 2.6 Hz) (two isomers), 21.5 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.87 (s, one isomer), -64.95 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{20}BrF_3NO_2$ $[M+H]^+$: 454.0625, 456.0604; found: 454.0617, 456.0615.

5-(4-bromophenyl)-6-(2-fluorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4n) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (57.3 mg, 65%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 7.0 Hz, 1H, two isomers), 7.43 (dd, *J* = 19.7, 7.0 Hz, 3H, two isomers), 7.20 – 7.02 (m, 4H, two isomers), 4.47 (t, *J* = 7.0 Hz, 1H, two isomers), 2.93 – 2.81 (m, 1H, two isomers), 2.58 – 2.46 (m, 1H, two isomers), 2.40 – 2.22 (m, 2H, two isomers), 2.07 – 1.92 (m, 1H, two isomers), 1.79 – 1.71 (m, 1H, two isomers), 1.63 – 1.52 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5 & 197.4 (two isomers), 161.1 (d, $^{1}J_{C\text{-}F}$ = 254.6 Hz) (overlap, two isomers), 136.6 (d, $^{3}J_{C\text{-}F}$ = 7.4 Hz) (overlap, two isomers), 135.0 (d, $^{3}J_{C\text{-}F}$ = 9.2 Hz) (overlap, two isomers), 132.3 (overlap, two isomers), 131.26 & 131.24 (two isomers), 131.25 & 131.22 (two isomers), 130.2 (overlap, two isomers), 125.14 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) & 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.1 Hz) (two isomers), 125.38 (d, $^{2}J_{C\text{-}F}$ = 12.7 Hz) & 125.37 (d, $^{2}J_{C\text{-}F}$ = 12.8 Hz) (two isomers), 124.8 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz) (overlap, two isomers), 121.9 (overlap, two isomers), 119.45 & 119.44 (two isomers), 116.8 (d, $^{2}J_{C\text{-}F}$ = 24.1 Hz) (overlap, two isomers), 56.4 (overlap, two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.6 & 30.4 (two isomers), 30.2 & 30.1 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer), -109.6 (d, *J* = 25.2 Hz, two isomers). HRMS (ESI) calcd. for $C_{20}H_{17}BrF_4NO$ $[M+H]^+$: 442.0425, 444.0404; found: 442.0420, 444.0410.

5-(4-bromophenyl)-6-(naphthalen-2-yl)-6-oxo-2-(2,2,2-trifluoroethyl)hexane nitrile (4o) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (72.9 mg, 77%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 3.2 Hz, 1H, two isomers), 7.96 (dt, *J* = 8.5, 1.5 Hz, 1H, two isomers), 7.91 (d, *J* = 8.0 Hz, 1H, two isomers), 7.83

(dd, J = 8.4, 3.2 Hz, 2H, two isomers), 7.56 (dt, J = 21.4, 6.9 Hz, 2H, two isomers), 7.44 (d, J = 8.4 Hz, 2H, two isomers), 7.23 (dd, J = 8.4, 1.7 Hz, 2H, two isomers), 4.71 (t, J = 7.2 Hz, 1H, two isomers), 2.97 – 2.84 (m, 1H, two isomers), 2.61 – 2.47 (m, 1H, two isomers), 2.45 – 2.27 (m, 2H, two isomers), 2.18 – 2.00 (m, 1H, two isomers), 1.84 – 1.73 (m, 1H, two isomers), 1.71 – 1.64 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.35 & 198.27 (two isomers), 137.75 & 137.69 (two isomers), 135.7 (overlap, two isomers), 133.44 & 133.41 (two isomers), 132.6 (overlap, two isomers), 132.5 (overlap, two isomers), 130.68 & 130.67 (two isomers), 129.85 & 129.81 (two isomers), 129.8 (overlap, two isomers), 129.0 (overlap, two isomers), 128.8 (overlap, two isomers), 127.9 (overlap, two isomers), 127.1 (overlap, two isomers), 125.16 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) & 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 124.3 (overlap, two isomers), 121.8 (overlap, two isomers), 119.54 & 119.51 (two isomers), 52.5 & 52.4 (two isomers), 36.5 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz) (two isomers), 31.1 & 30.8 (two isomers), 30.3 & 30.1 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.86 (s, one isomer), -64.92 (s, one isomer). HRMS (ESI) calcd. for $C_{24}H_{20}BrF_3NO$ $[M+H]^+$: 474.0675, 476.0655; found: 474.0680, 476.0664.

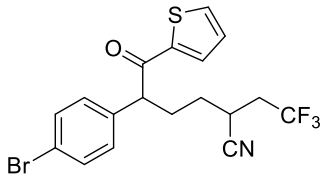
5-(4-bromophenyl)-6-(furan-2-yl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4p)



The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 15/1, v/v) as a yellow liquid (49.6 mg, 60%yield, dr =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 1H, two isomers), 7.48 – 7.40 (m, 2H, two isomers), 7.20 (dd, J = 8.4, 1.8 Hz, 3H, two isomers), 6.50 (dd, J = 3.6, 1.7 Hz, 1H, two isomers), 4.36 (t, J = 7.4 Hz, 1H, two isomers), 2.94 – 2.79 (m, 1H, two isomers), 2.62 – 2.41 (m, 1H, two isomers), 2.38 – 2.20 (m, 2H, two isomers), 2.13 – 1.94 (m, 1H, two isomers), 1.79 – 1.67 (m, 1H, two isomers), 1.64 – 1.52 (dd, J = 13.1, 4.1 Hz, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.32 & 187.30 (two isomers), 152.09 & 152.08 (two isomers), 146.95 & 146.94 (two isomers), 137.02 & 136.95 (two isomers), 132.3 (overlap, two isomers), 129.99 & 129.96 (two isomers), 125.13 (q, $^{1}J_{C\text{-}F}$ = 278.5 Hz) & 125.09 (q, $^{1}J_{C\text{-}F}$ = 278.4 Hz) (two isomers), 121.9 (overlap, two isomers), 119.44 & 119.41 (two isomers), 118.55 & 118.52 (two isomers), 112.8 (overlap, two isomers), 52.41 & 52.37 (two isomers),

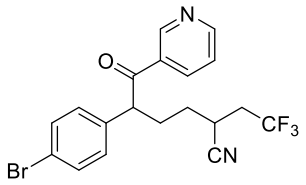
36.4 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 30.1 & 30.0 (two isomers), 29.9 & 29.7 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{18}H_{16}BrF_3NO_2$ $[M+H]^+$: 414.0312, 412.0291; found: 414.0310, 416.0291.

5-(4-bromophenyl)-6-oxo-6-(thiophen-2-yl)-2-(2,2,2-trifluoroethyl)hexanenitrile



(4q) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (47.2 mg, 55%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 1H, two isomers), 7.64 – 7.58 (m, 1H, two isomers), 7.49 – 7.41 (m, 2H, two isomers), 7.24 – 7.16 (m, 2H, two isomers), 7.11 – 7.04 (m, 1H, two isomers), 4.36 (t, *J* = 7.3 Hz, 1H, two isomers), 2.87 (d, *J* = 7.6 Hz, 1H, two isomers), 2.57 – 2.44 (m, 1H, two isomers), 2.40 – 2.24 (m, 2H, two isomers), 2.12 – 1.96 (m, 1H, two isomers), 1.78 – 1.69 (m, 1H, two isomers), 1.65 – 1.59 (m, 1H, two isomers). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2 & 191.1 (two isomers), 143.24 & 143.21 (two isomers), 137.55 & 137.52 (two isomers), 134.68 & 134.65 (two isomers), 132.94 & 132.90 (two isomers), 132.5 (overlap, two isomers), 129.8 & 129.7 (two isomers), 128.5 (overlap, two isomers), 125.11 (q, $^{1}J_{C\text{-}F}$ = 275.6 Hz) & 125.08 (q, $^{1}J_{C\text{-}F}$ = 275.6 Hz) (two isomers), 121.9 (overlap, two isomers), 119.5 & 119.4 (two isomers), 53.85 & 53.79 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz) & 36.2 (q, $^{2}J_{C\text{-}F}$ = 29.7 Hz) (two isomers), 30.8 & 30.5 (two isomers), 30.2 & 29.9 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{18}H_{16}BrF_3NOS$ $[M+H]^+$: 430.0083, 432.0063; found: 430.0082, 432.0065.

5-(4-bromophenyl)-6-oxo-6-(pyridin-3-yl)-2-(2,2,2-trifluoroethyl)hexanenitrile



(4r) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (50.9 mg, 60%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.7 Hz, 1H, two isomers), 8.02 (d, *J* = 7.8 Hz, 1H, two isomers), 7.81 (t, *J* = 7.7 Hz, 1H, two isomers), 7.50 – 7.38 (m, 3H, two isomers), 7.28 (dd, *J* = 8.5, 2.2 Hz, 2H, two isomers), 5.40 (q, *J* = 7.4 Hz,

1H, two isomers), 3.01 – 2.86 (m, 1H, two isomers), 2.61 – 2.45 (m, 1H, two isomers), 2.44 – 2.23 (m, 2H, two isomers), 2.21 – 2.03 (m, 1H, two isomers), 1.84 – 1.71 (m, 1H, two isomers), 1.68 – 1.59 (m, 1H, two isomers). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0 & 199.9 (two isomers), 152.36 & 152.30 (two isomers), 149.0 (overlap, two isomers), 137.19 & 137.17 (two isomers), 137.0 (overlap, two isomers), 132.0 (overlap, two isomers), 130.63 & 130.60 (two isomers), 127.57 & 127.56 (two isomers), 125.15 (q, $^1J_{C\text{-}F}$ = 275.7 Hz) & 125.12 (q, $^1J_{C\text{-}F}$ = 275.6 Hz) (two isomers), 122.97 & 122.95 (two isomers), 121.5 (overlap, two isomers), 119.5 (overlap, two isomers), 49.5 & 49.3 (two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 29.8 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 29.7 Hz) (two isomers), 30.2 & 30.1 (two isomers), 29.74 & 29.69 (two isomers), 25.6 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.5 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{19}H_{17}BrF_3N_2O$ $[M+H]^+$: 425.0471, 427.0451; found: 425.0478, 427.0460.

6-(benzo[b]thiophen-2-yl)-5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl) hexanenitrile (4s) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (71.9 mg, 75%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 5.8 Hz, 1H, two isomers), 7.83 (t, J = 7.7 Hz, 2H, two isomers), 7.47 (dt, J = 6.7, 2.2 Hz, 2H, two isomers), 7.45 – 7.42 (m, 1H, two isomers), 7.38 (t, J = 7.5 Hz, 1H, two isomers), 7.24 (dd, J = 8.4, 1.8 Hz, 2H, two isomers), 4.49 (t, J = 7.3 Hz, 1H, two isomers), 2.95 – 2.86 (m, 1H, two isomers), 2.59 – 2.46 (m, 1H, two isomers), 2.43 – 2.24 (m, 2H, two isomers), 2.15 – 2.00 (m, 1H, two isomers), 1.81 – 1.73 (m, 1H, two isomers), 1.69 – 1.61 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8 & 192.7 (two isomers), 142.7 (overlap, two isomers), 142.6 & 142.5 (two isomers), 139.0 (overlap, two isomers), 137.35 & 137.31 (two isomers), 132.6 (overlap, two isomers), 130.15 & 130.11 (two isomers), 129.8 & 129.7 (two isomers), 128.0 (overlap, two isomers), 126.5 (overlap, two isomers), 125.3 (overlap, two isomers), 125.13 (q, $^1J_{C\text{-}F}$ = 278.4 Hz) & 125.09 (q, $^1J_{C\text{-}F}$ = 278.4 Hz) (two isomers), 123.0 (overlap, two isomers), 122.1 (overlap, two isomers), 119.5 & 119.4 (two isomers), 53.78 & 53.72 (two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 30.9 & 30.5 (two

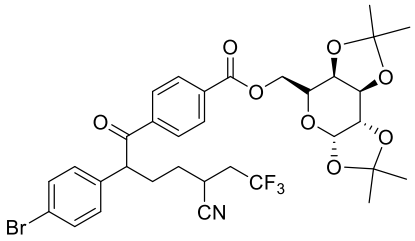
isomers), 30.2 & 29.9 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.86 (s, one isomer), -64.91 (s, one isomer). HRMS (ESI) calcd. for $C_{22}H_{18}BrF_3NOS$ $[M+H]^+$: 480.0240, 482.0219; found: 480.0246, 482.0230.

6-(benzofuran-2-yl)-5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexane nitrile (4t) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (48.2 mg, 52%yield, dr = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 1H, two isomers), 7.54 (d, *J* = 8.4 Hz, 1H, two isomers), 7.50 (dd, *J* = 1.7, 0.8 Hz, 2H, two isomers), 7.48 – 7.43 (m, 3H, two isomers), 7.33 – 7.28 (m, 1H, two isomers), 7.27 (d, *J* = 1.6 Hz, 1H, two isomers), 7.24 (d, *J* = 1.6 Hz, 1H, two isomers), 4.52 (t, *J* = 7.4 Hz, 1H, two isomers), 2.98 – 2.82 (m, 1H, two isomers), 2.65 – 2.45 (m, 1H, two isomers), 2.44 – 2.24 (m, 2H, two isomers), 2.20 – 1.97 (m, 1H, two isomers), 1.83 – 1.60 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.32 & 189.28 (two isomers), 155.8 (overlap, two isomers), 151.87 & 151.85 (two isomers), 136.8 & 136.7 (two isomers), 132.5 (overlap, two isomers), 130.1 & 130.0 (two isomers), 128.8 (overlap, two isomers), 127.0 (overlap, two isomers), 125.13 (q, $^{1}J_{C\text{-}F}$ = 279.3 Hz) & 125.09 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 124.3 (overlap, two isomers), 123.5 (overlap, two isomers), 122.1 (overlap, two isomers), 119.42 & 119.40 (two isomers), 52.9 & 52.8 (two isomers), 36.5 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz) (two isomers), 30.1 & 30.0 (two isomers), 29.9 & 29.7 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.86 (s, one isomer), -64.93 (s, one isomer). HRMS (ESI) calcd. for $C_{22}H_{18}BrF_3NO_2$ $[M+H]^+$: 464.0468, 466.0448; found 464.0473, 466.0452.

(1R,2R,5S)-2-isopropyl-5-methylcyclohexyl-4-(2-(4-bromophenyl)-5-cyano-7,7,7-trifluoroheptanoyl)benzoate (4u) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (62.9 mg, 52%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H, two isomers), 7.94 (d, *J* = 8.0 Hz, 2H, two isomers), 7.44 (dd, *J* = 8.5, 2.6 Hz, 2H, two

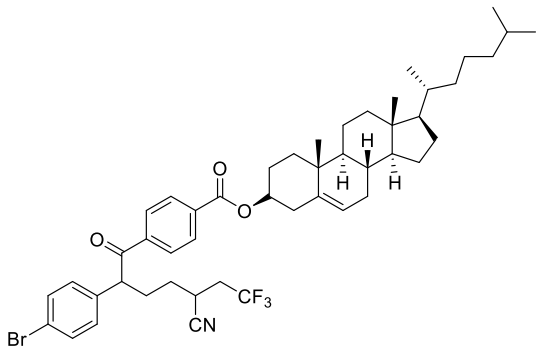
isomers), 7.13 (ddd, J = 8.3, 3.4, 1.5 Hz, 2H, two isomers), 4.92 (tdd, J = 10.8, 4.2, 2.2 Hz, 1H, two isomers), 4.53 (t, J = 7.1 Hz, 1H, two isomers), 2.95 – 2.81 (m, 1H, two isomers), 2.58 – 2.45 (m, 1H, two isomers), 2.43 – 2.26 (m, 2H, two isomers), 2.15 – 2.00 (m, 2H, two isomers), 1.95 – 1.87 (m, 1H, two isomers), 1.77 – 1.69 (m, 3H, two isomers), 1.68 – 1.45 (m, 4H, two isomers), 1.15 – 1.03 (m, 2H, two isomers), 0.90 (t, J = 6.8 Hz, 6H, two isomers), 0.76 (d, J = 6.9 Hz, 3H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 & 197.8 (two isomers), 165.1 (overlap, two isomers), 139.1 & 139.0 (two isomers), 137.1 & 137.0 (two isomers), 134.9 (overlap, two isomers), 132.7 (overlap, two isomers), 130.0 (overlap, two isomers), 129.84 & 129.80 (two isomers), 128.7 & 128.6 (two isomers), 125.12 (q, $^1J_{C\text{-}F}$ = 278.0 Hz) & 125.10 (q, $^1J_{C\text{-}F}$ = 278.1 Hz) (two isomers), 122.0 (overlap, two isomers), 119.5 & 119.4 (two isomers), 75.7 (overlap, two isomers), 52.88 & 52.82 (two isomers), 47.32 & 47.31 (two isomers), 41.0 (overlap, two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 29.9 Hz) (two isomers), 34.3 (overlap, two isomers), 31.5 (overlap, two isomers), 30.8 & 30.6 (two isomers), 30.1 (overlap, two isomers), 29.9 (overlap, two isomers), 26.7 & 26.6 (two isomers), 25.7 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.6 (q, $^3J_{C\text{-}F}$ = 2.8 Hz) (two isomers), 23.7 & 23.6 (two isomers), 22.1 (overlap, two isomers), 20.9 & 20.8 (two isomers), 16.6 & 16.5 (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.87 (s, one isomer), -64.92 (s, one isomer). HRMS (ESI) calcd. for $C_{31}H_{36}BrF_3NO_3$ $[M+H]^+$: 606.1826, 608.1805; found: 606.1823, 608.1818.

((3aS,5R,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl-4-(2-(4-bromophenyl)-5-cyano-7,7,7-trifluoroheptanoyl)benzoate (4v) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 15/1, v/v) as a colorless liquid (90.8 mg, 64%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 2H, two isomers), 7.92 (dd, J = 8.5, 1.8 Hz, 2H, two isomers), 7.43 (d, J = 8.3 Hz, 2H, two isomers), 7.12 (d, J = 8.1 Hz, 2H, two isomers), 5.54 (d, J = 5.0 Hz, 1H, two isomers), 4.64 (dd, J = 7.9, 2.4 Hz, 1H, two isomers), 4.54 – 4.48 (m, 2H, two isomers), 4.42 (dd, J = 11.6, 7.7 Hz, 1H, two isomers), 4.34 (dd, J = 5.0, 2.5 Hz, 1H, two isomers), 4.29 (dd, J = 7.9, 1.5 Hz, 1H, two isomers), 4.17 – 4.12 (m, 1H, two isomers), 2.94 – 2.81



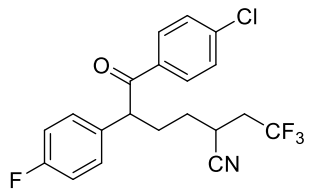
(m, 1H, two isomers), 2.58 – 2.44 (m, 1H, two isomers), 2.42 – 2.24 (m, 2H, two isomers), 2.14 – 1.97 (m, 1H, two isomers), 1.77 – 1.69 (m, 1H, two isomers), 1.65 – 1.56 (m, 1H, two isomers), 1.48 (s, 3H, two isomers), 1.45 (s, 3H, two isomers), 1.34 (s, 3H, two isomers) , 1.32 (s, 3H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 & 197.8 (two isomers), 165.4 (overlap, two isomers), 139.34 & 139.31 (two isomers), 137.01 & 136.96 (two isomers), 134.11 & 134.09 (two isomers), 132.7 (overlap, two isomers), 130.1 (overlap, two isomers), 129.83 & 129.79 (two isomers), 128.7 (overlap, two isomers), 125.11 (q, $^1J_{C\text{-}F}$ = 278.8 Hz) & 125.08 (q, $^1J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 122.0 (overlap, two isomers), 119.43 & 119.42 (two isomers), 109.9 (overlap, two isomers), 108.9 (overlap, two isomers), 96.4 (overlap, two isomers), 71.2 (overlap, two isomers), 70.8 (overlap, two isomers), 70.6 (overlap, two isomers), 66.2 (overlap, two isomers), 64.5 (overlap, two isomers), 52.9 & 52.8 (two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.2 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.8 & 30.5 (two isomers), 30.1 & 29.9 (two isomers), 26.11 (overlap, two isomers), 26.07 (overlap, two isomers), 25.74 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) & 25.65 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) (two isomers), 25.6 (overlap, two isomers), 25.0 (overlap, two isomers), 24.6 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.87 (s, one isomer), -64.92 (s, one isomer). HRMS (ESI) calcd. for $C_{33}H_{36}BrF_3NO_8$ $[M+H]^+$: 710.1571, 712.1551; found: 710.1577, 712.1566.

(3R,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl-4-(2-(4-bromophenyl)-5-cyano-7,7,7-trifluoroheptanoyl)benzoate (4w) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a white solid (81.9 mg, 49%yield, dr = 1:1, MP: 78-79ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H, two isomers), 7.92 (dd, *J* = 8.4, 1.5 Hz, 2H, two isomers), 7.44 (d, *J* = 8.4 Hz, 2H, two isomers), 7.13 (dd, *J* = 8.4, 1.7 Hz, 2H, two isomers), 5.41 (d, *J* = 4.0 Hz, 1H, two isomers), 4.89 – 4.80 (m, 1H, two isomers), 4.53 (t, *J* = 7.1 Hz, 1H, two isomers), 2.94 – 2.82 (m, 1H, two isomers), 2.59 – 2.47 (m, 1H, two isomers), 2.43 (d, *J* = 7.6 Hz, 2H, two isomers), 2.40 – 2.24 (m, 2H,



two isomers), 2.22 – 2.00 (m, 2H, two isomers), 2.00 – 1.88 (m, 3H, two isomers), 1.88 – 1.64 (m, 4H, two isomers), 1.64 – 1.42 (m, 8H, two isomers), 1.40 – 1.32 (m, 3H, two isomers), 1.21 – 1.09 (m, 6H, two isomers), 1.05 (s, 3H, two isomers), 1.03 – 0.96 (m, 3H, two isomers), 0.92 (d, J = 6.5 Hz, 3H, two isomers), 0.86 (dd, J = 6.6, 1.6 Hz, 6H, two isomers), 0.68 (s, 3H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 & 197.9 (two isomers), 165.0 (overlap, two isomers), 139.5 (overlap, two isomers), 139.12 &139.09 (two isomers), 137.10 & 137.05 (two isomers), 134.97 &134.95 (two isomers), 132.7 (overlap, two isomers), 130.0 (overlap, two isomers), 129.85 & 129.81 (two isomers), 128.6 (overlap, two isomers), 125.12 (q, $^1J_{C\text{-}F}$ = 278.5 Hz) & 125.10 (q, $^1J_{C\text{-}F}$ = 278.6 Hz) (two isomers), 123.2 (overlap, two isomers), 122.0 (overlap, two isomers), 119.45 & 119.43 (two isomers), 75.4 (overlap, two isomers), 56.8 (overlap, two isomers), 56.3 (overlap, two isomers), 52.92 & 52.88 (two isomers), 50.2 (overlap, two isomers), 42.5 (overlap, two isomers), 39.9 (overlap, two isomers), 39.7 (overlap, two isomers), 38.3 (overlap, two isomers), 37.1 (overlap, two isomers), 36.8 (overlap, two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) & 36.33 (q, $^2J_{C\text{-}F}$ = 30.2 Hz) (two isomers), 36.32 (overlap, two isomers), 35.9 (overlap, two isomers), 32.06 & 32.00 (two isomers), 30.8 & 30.5 (two isomers), 30.1 & 30.0 (two isomers), 28.4 (overlap, two isomers), 28.2 (overlap, two isomers), 27.9 (overlap, two isomers), 25.8 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^3J_{C\text{-}F}$ = 3.1 Hz) (two isomers), 24.4 (overlap, two isomers), 24.0 (overlap, two isomers), 23.0 (overlap, two isomers), 22.7 (overlap, two isomers), 21.2 (overlap, two isomers), 19.5 (overlap, two isomers), 18.9 (overlap, two isomers), 12.0 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.87 (s, one isomer), -64.92 (s, one isomer). HRMS (ESI) calcd. for $C_{48}H_{62}BrF_3NO_3$ $[M+H]^+$: 836.3860, 838.3840; found: 836.3860, 838.3857.

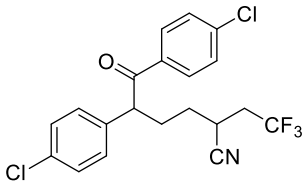
6-(4-chlorophenyl)-5-(4-fluorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile



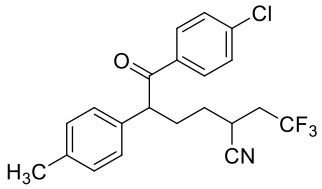
(4aa) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (67.5 mg, 85%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H, two isomers), 7.36 (d, J = 8.2 Hz, 2H, two isomers), 7.25 – 7.19 (m, 2H, two isomers), 7.00 (t, J = 8.5 Hz, 2H, two isomers), 4.50 (t, J = 7.1 Hz, 1H, two isomers), 2.93 – 2.81 (m, 1H, two isomers), 2.59 – 2.46 (m, 1H, two isomers), 2.39 – 2.24 (m, 2H, two isomers), 2.11 –

1.96 (m, 1H, two isomers), 1.79 – 1.68 (m, 1H, two isomers), 1.66 – 1.57 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.44 & 197.37 (two isomers), 162.3 (d, $^1J_{C\text{-}F}$ = 246.8 Hz) (overlap, two isomers), 140.0 (overlap, two isomers), 134.42 (d, $^4J_{C\text{-}F}$ = 1.7 Hz) (overlap, two isomers), 134.04 & 134.01 (two isomers), 130.2 (overlap, two isomers), 129.7 (d, $^3J_{C\text{-}F}$ = 3.9 Hz) & 129.6 (d, $^3J_{C\text{-}F}$ = 3.8 Hz) (two isomers), 129.1 (overlap, two isomers), 125.17 (q, $^1J_{C\text{-}F}$ = 279.0 Hz) & 125.13 (q, $^1J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 119.5 (overlap, two isomers), 116.5 (d, $^2J_{C\text{-}F}$ = 21.6 Hz) (overlap, two isomers), 52.3 (overlap, two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 29.5 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 31.0 & 30.8 (two isomers), 30.1 & 29.9 (two isomers), 25.73 (q, $^3J_{C\text{-}F}$ = 1.6 Hz) & 25.68 (q, $^3J_{C\text{-}F}$ = 1.7 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.89 (s, one isomer), -64.95 (s, one isomer), -114.2 (overlap, two isomers). HRMS (ESI) calcd. for $C_{20}H_{17}ClF_4NO$ $[M+H]^+$: 398.0929; found: 398.0954.

5,6-bis(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4ab) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (62.8 mg, 76%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H, two isomers), 7.36 (d, J = 7.9 Hz, 2H, two isomers), 7.32 – 7.27 (m, 2H, two isomers), 7.23 – 7.14 (m, 2H, two isomers), 4.49 (t, J = 6.9 Hz, 1H, two isomers), 2.94 – 2.81 (m, 1H, two isomers), 2.57 – 2.45 (m, 1H, two isomers), 2.40 – 2.25 (m, 2H, two isomers), 2.11 – 1.96 (m, 1H, two isomers), 1.78 – 1.68 (m, 1H, two isomers), 1.65 – 1.57 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 & 197.1 (two isomers), 140.0 (overlap, two isomers), 136.8 (overlap, two isomers), 134.3 (overlap, two isomers), 133.9 (overlap, two isomers), 129.7 (overlap, two isomers), 129.4 (overlap, two isomers), 129.2 (overlap, two isomers), 125.04 (q, $^1J_{C\text{-}F}$ = 261.0 Hz) & 125.00 (q, $^1J_{C\text{-}F}$ = 259.3 Hz) (two isomers), 119.5 (overlap, two isomers), 52.4 (overlap, two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 29.6 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 29.2 Hz) (two isomers), 30.9 & 30.7 (two isomers), 30.1 & 29.9 (two isomers), 25.7 (q, $^3J_{C\text{-}F}$ = 1.7 Hz) & 25.6 (q, $^3J_{C\text{-}F}$ = 1.9 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.87 (s, one isomer), -64.93 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{16}Cl_2F_3NNaO$ $[M+Na]^+$: 436.0453; found: 436.0448.

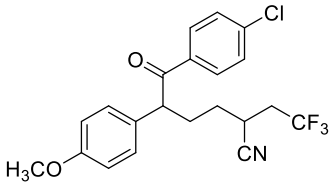


6-(4-chlorophenyl)-6-oxo-5-(p-tolyl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4ac)



The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (66.8 mg, 85%yield, dr = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.7, 1.8 Hz, 2H, two isomers), 7.34 (d, *J* = 8.4 Hz, 2H, two isomers), 7.12 (s, 4H, two isomers), 4.45 (t, *J* = 7.1 Hz, 1H, two isomers), 2.95 – 2.77 (m, 1H, two isomers), 2.59 – 2.36 (m, 2H, two isomers), 2.29 (s, 3H, two isomers), 2.24 – 1.92 (m, 2H, two isomers), 1.76 – 1.59 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.53 & 197.47 (two isomers), 139.54 & 139.52 (two isomers), 137.5 (overlap, two isomers), 135.12 & 135.07 (two isomers), 134.53 & 134.51 (two isomers), 130.2 (overlap, two isomers), 130.1 (overlap, two isomers), 128.9 (overlap, two isomers), 127.9 & 127.8 (two isomers), 125.07 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) & 125.04 (q, $^{1}J_{C\text{-}F}$ = 278.5 Hz) (two isomers), 119.5 (overlap, two isomers), 52.8 (overlap, two isomers), 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.2 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.8 & 30.5 (two isomers), 30.1 & 29.9 (two isomers), 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (overlap, two isomers), 21.0 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{20}ClF_3NO$ [M+H]+: 394.1180; found: 394.1184.

6-(4-chlorophenyl)-5-(4-methoxyphenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexane nitrile (4ad) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (58.9 mg, 72%yield, dr = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.6, 1.8 Hz, 2H, two isomers), 7.34 (d, *J* = 8.3 Hz, 2H, two isomers), 7.19 – 7.12 (m, 2H, two isomers), 6.89 – 6.81 (m, 2H, two isomers), 4.43 (t, *J* = 7.2 Hz, 1H, two isomers), 3.75 (s, 3H, two isomers), 2.95 – 2.77 (m, 1H, two isomers), 2.59 – 2.40 (m, 1H, two isomers), 2.39 – 2.18 (m, 2H, two isomers), 2.11 – 1.92 (m, 1H, two isomers), 1.77 – 1.67 (m, 1H, two isomers), 1.65 – 1.54 (m, 1H, two isomers). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7 & 197.6 (two isomers), 159.2 (overlap, two isomers), 139.6 (overlap, two isomers), 134.6 (overlap, two isomers), 130.3 (overlap, two isomers), 130.13 & 130.09 (two isomers), 129.2 & 129.1 (two isomers), 129.0 (overlap, two isomers), 125.16 (q, $^{1}J_{C\text{-}F}$ = 275.7 Hz) & 125.14 (q, $^{1}J_{C\text{-}F}$ = 275.5 Hz) (two isomers), 119.6



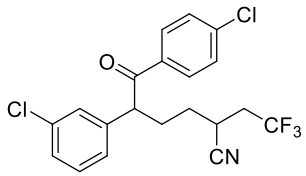
(overlap, two isomers), 114.9 (overlap, two isomers), 55.4 (overlap, two isomers), 52.3 (overlap, two isomers), 36.7 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz) & 36.0 (q, $^{2}J_{C\text{-}F}$ = 29.5 Hz) (two isomers), 30.9 & 30.7 (two isomers), 30.1 & 30.0 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.2 Hz) (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{20}ClF_3NO_2$ $[M+H]^+$: 410.1129; found: 410.1110.

5-(4-(tert-butyl)phenyl)-6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexane nitrile (4ae) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (73.1 mg, 84%yield, dr = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.16 (dd, *J* = 8.3, 1.7 Hz, 2H), 4.47 (t, *J* = 7.1 Hz, 1H), 2.91 – 2.79 (m, 1H), 2.57 – 2.43 (m, 1H), 2.38 – 2.23 (m, 2H), 2.08 – 1.95 (m, 1H), 1.80 – 1.71 (m, 1H), 1.66 – 1.59 (m, 1H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7 & 197.6 (two isomers), 150.8 (overlap, two isomers), 139.7 (overlap, two isomers), 135.1 & 135.0 (two isomers), 134.69 & 134.67 (two isomers), 130.3 (overlap, two isomers), 129.0 (overlap, two isomers), 127.7 & 127.6 (two isomers), 126.4 (overlap, two isomers), 125.18 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) & 125.15 (q, $^{1}J_{C\text{-}F}$ = 278.6 Hz) (two isomers), 119.6 (overlap, two isomers), 52.73 & 52.71 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.8 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 34.6 (overlap, two isomers), 31.4 (overlap, two isomers), 31.0 & 30.7 (two isomers), 30.3 & 30.1 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{24}H_{26}ClF_3NO$ $[M+H]^+$: 436.1650; found: 436.1653.

6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)-5-(3-(trifluoromethyl)phenyl) hexanenitrile (4af) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (48.8 mg, 65%yield, dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.7, 2.5 Hz, 2H, two isomers), 7.55 – 7.44 (m, 4H, two isomers), 7.39 (d, *J* = 8.0 Hz, 2H, two isomers), 4.59 (t, *J* = 7.1 Hz, 1H, two isomers), 2.95 – 2.83 (m, 1H, two isomers), 2.59 – 2.46 (m, 1H, two isomers), 2.44 – 2.24 (m, 2H, two isomers), 2.13 – 1.97 (m,

1H, two isomers), 1.81 – 1.70 (m, 1H, two isomers), 1.67 – 1.62 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 & 196.9 (two isomers), 140.3 & 140.3 (two isomers), 139.31 & 139.28 (two isomers), 134.3 & 134.2 (two isomers), 131.4 (q, $^2J_{C\text{-}F}$ = 32.8 Hz) (overlap, two isomers), 130.20 & 130.19 (two isomers), 130.1 (overlap, two isomers), 129.3 (overlap, two isomers), 125.11 (q, $^1J_{C\text{-}F}$ = 278.4 Hz) & 125.08 (q, $^1J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 124.8 (q, $^3J_{C\text{-}F}$ = 3.6 Hz) (overlap, two isomers), 123.9 (q, $^1J_{C\text{-}F}$ = 273.6 Hz) (overlap, two isomers), 119.44 & 119.39 (two isomers), 52.7 (overlap, two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.2 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 31.2 & 30.9 (two isomers), 30.2 & 30.0 (two isomers), 25.8 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^3J_{C\text{-}F}$ = 3.1 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63 (s, one isomer), -62.64 (s, one isomer), -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{16}ClF_6NNaO$ $[M+Na]^+$: 470.0717; found: 470.0709.

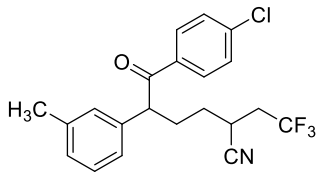
5-(3-chlorophenyl)-6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile



(4ag) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (62.8 mg, 73%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.5, 1.7 Hz, 2H, two isomers), 7.38 (d, *J* = 8.4 Hz, 2H, two isomers), 7.27 – 7.22 (m, 3H, two isomers), 7.14 (d, *J* = 6.9 Hz, 1H, two isomers), 4.48 (t, *J* = 7.2 Hz, 1H, two isomers), 2.95 – 2.82 (m, 1H, two isomers), 2.58 – 2.44 (m, 1H, two isomers), 2.41 – 2.23 (m, 2H, two isomers), 2.11 – 1.97 (m, 1H, two isomers), 1.79 – 1.69 (m, 1H, two isomers), 1.68 – 1.61 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 & 196.9 (two isomers), 140.3 & 140.23 (two isomers), 140.15 & 140.1 (two isomers), 135.4 (overlap, two isomers), 134.34 & 134.31 (two isomers), 130.8 (overlap, two isomers), 130.2 (overlap, two isomers), 129.20 (overlap, two isomers), 128.15 (overlap, two isomers), 128.2 (overlap, two isomers), 126.3 & 126.2 (two isomers), 125.13 (q, $^1J_{C\text{-}F}$ = 278.4 Hz) & 125.10 (q, $^1J_{C\text{-}F}$ = 278.4 Hz) (two isomers), 119.5 & 119.4 (two isomers), 52.72 & 52.70 (two isomers), 36.4 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 31.0 & 30.8 (two isomers), 30.2 & 30.0 (two isomers), 25.8 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -

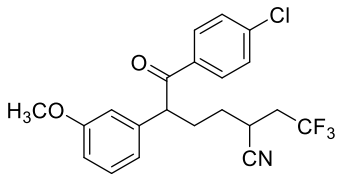
64.89 (s, one isomer), -64.95 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{16}Cl_2F_3NNaO$ $[M+Na]^+$: 436.0453; found: 436.0448.

6-(4-chlorophenyl)-6-oxo-5-(m-tolyl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4ah)



The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (55.8 mg, 71%yield, dr = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.6, 1.7 Hz, 2H, two isomers), 7.35 (d, *J* = 8.4 Hz, 2H, two isomers), 7.20 (t, *J* = 7.8 Hz, 1H, two isomers), 7.05 (d, *J* = 8.0 Hz, 3H, two isomers), 4.44 (t, *J* = 7.0 Hz, 1H, two isomers), 2.93 – 2.78 (m, 1H, two isomers), 2.58 – 2.44 (m, 1H, two isomers), 2.42 – 2.32 (m, 1H, two isomers), 2.31 (s, 3H, two isomers), 2.30 – 2.19 (m, 1H, two isomers), 2.12 – 1.98 (m, 1H, two isomers), 1.81 – 1.69 (m, 1H, two isomers), 1.65 – 1.57 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5 & 197.4 (two isomers), 139.60 & 139.58 (two isomers), 139.2 (overlap, two isomers), 138.12 & 138.06 (two isomers), 134.54 & 134.52 (two isomers), 130.2 (overlap, two isomers), 129.3 (overlap, two isomers), 128.9 (overlap, two isomers), 128.5 (overlap, two isomers), 128.43 & 128.42 (two isomers), 125.15 & 125.09 (two isomers), 125.07 (q, $^1J_{C\text{-}F}$ = 278.2 Hz) & 125.04 (q, $^1J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 119.50 & 119.47 (two isomers), 53.15 & 53.11 (two isomers), 36.3 (q, $^2J_{C\text{-}F}$ = 30.0 Hz) & 36.2 (q, $^2J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.9 & 30.6 (two isomers), 30.1 & 30.0 (two isomers), 25.6 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) & 25.5 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) (two isomers), 21.4 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{20}ClF_3NO$ $[M+H]^+$: 394.1180; found: 394.1184.

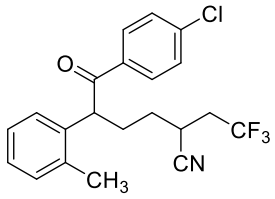
6-(4-chlorophenyl)-5-(3-methoxyphenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexane nitrile (4ai) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (52.8 mg, 65%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.85 – 6.73 (m, 3H), 4.44 (t, *J* = 7.1 Hz, 1H), 3.77 (s, 3H), 2.95 – 2.78 (m, 1H), 2.59 – 2.43 (m, 1H), 2.37 – 2.23 (m, 2H), 2.16 – 1.97 (m, 1H), 1.79 – 1.69 (m, 1H), 1.68 – 1.61 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4 & 197.3 (two isomers), 160.4 (overlap, two isomers), 139.80 &



139.78 (two isomers), 139.7 (overlap, two isomers), 134.61 & 134.59 (two isomers), 130.6 (overlap, two isomers), 130.3 (overlap, two isomers), 129.1 (overlap, two isomers), 125.17 (q, $^{1}J_{C\text{-}F}$ = 278.5 Hz) & 125.15 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 120.50 & 120.46 (two isomers), 119.6 (overlap, two isomers), 113.92 & 113.88 (two isomers), 112.9 (overlap, two isomers), 55.4 (overlap, two isomers), 53.30 & 53.28 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.8 & 30.6 (two isomers), 30.2 & 30.1 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.93 (s, one isomer), -64.98 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{20}ClF_3NO_2$ $[M+H]^+$: 410.1129; found: 410.1110.

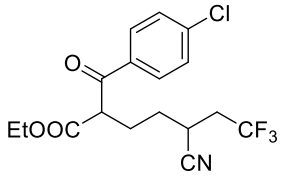
5-(2-chlorophenyl)-6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4aj) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (63.6 mg, 77%yield, dr = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.6, 1.8 Hz, 2H, two isomers), 7.44 (dd, *J* = 7.2, 2.1 Hz, 1H, two isomers), 7.36 (d, *J* = 8.5 Hz, 2H, two isomers), 7.23 – 7.13 (m, 2H, two isomers), 7.13 – 7.05 (m, 1H, two isomers), 5.02 (t, *J* = 6.9 Hz, 1H, two isomers), 2.97 – 2.83 (m, 1H, two isomers), 2.61 – 2.45 (m, 1H, two isomers), 2.41 – 2.21 (m, 2H, two isomers), 2.12 – 1.91 (m, 1H, two isomers), 1.89 – 1.77 (m, 1H, two isomers), 1.71 – 1.62 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4 & 197.3 (two isomers), 140.04 & 140.03 (two isomers), 136.3 & 136.2 (two isomers), 134.2 (overlap, two isomers), 133.4 (overlap, two isomers), 130.42 & 130.41 (two isomers), 130.1 (overlap, two isomers), 129.22 & 129.19 (two isomers), 128.7 & 128.6 (two isomers), 128.09 & 128.07 (two isomers), 125.17 (q, $^{1}J_{C\text{-}F}$ = 278.4 Hz) & 125.14 (q, $^{1}J_{C\text{-}F}$ = 278.1 Hz) (two isomers), 119.5 & 119.4 (two isomers), 48.8 & 48.7 (two isomers), 36.5 (q, $^{2}J_{C\text{-}F}$ = 30.3 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 30.4 & 30.1 (two isomers), 29.9 & 29.8 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). HRMS (ESI) calcd. for $C_{20}H_{16}Cl_2F_3NNaO$ $[M+Na]^+$: 436.0453; found: 436.0448.

6-(4-chlorophenyl)-6-oxo-5-(o-tolyl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4ak)



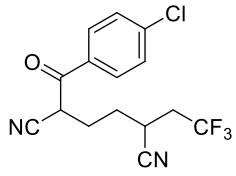
The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (68.4 mg, 87%yield, dr = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 7.9 Hz, 2H, two isomers), 7.35 – 7.30 (m, 2H, two isomers), 7.24 (d, J = 7.2 Hz, 1H, two isomers), 7.17 – 7.05 (m, 2H, two isomers), 6.95 (dd, J = 8.2, 4.3 Hz, 1H, two isomers), 4.65 – 4.59 (m, 1H, two isomers), 2.92 – 2.83 (m, 1H, two isomers), 2.53 (s, 3H, two isomers), 2.51 – 2.40 (m, 1H, two isomers), 2.39 – 2.22 (m, 2H, two isomers), 2.05 – 1.87 (m, 1H, two isomers), 1.86 – 1.78 (m, 1H, two isomers), 1.70 – 1.59 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3 & 198.2 (two isomers), 139.6 & 139.5 (two isomers), 137.14 (overlap, two isomers), 137.07 (overlap, two isomers), 134.83 & 134.78 (two isomers), 131.6 (overlap, two isomers), 129.93 & 129.92 (two isomers), 129.0 (overlap, two isomers), 127.7 (overlap, two isomers), 127.3 (overlap, two isomers), 127.2 & 127.1 (two isomers), 125.20 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) & 125.15 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 119.6 & 119.5 (two isomers), 49.7 & 49.4 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.2 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.5 & 30.4 (two isomers), 30.1 & 29.9 (two isomers), 25.9 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers), 19.87 & 19.85 (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.86 (s, one isomer), -64.95 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{20}ClF_3NO$ $[M+H]^+$: 394.1180; found: 394.1184.

Ethyl-2-(4-chlorobenzoyl)-5-cyano-7,7,7-trifluoroheptanoate (4al) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (48.8 mg, 65%yield, dr =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.6, 1.7 Hz, 2H, two isomers), 7.51 – 7.40 (m, 2H, two isomers), 4.28 (t, J = 7.0 Hz, 1H, two isomers), 4.14 (q, J = 8.0 Hz, 2H, two isomers), 3.02 – 2.85 (m, 1H, two isomers), 2.63 – 2.48 (m, 1H, two isomers), 2.45 – 2.31 (m, 1H, two isomers), 2.29 – 2.10 (m, 2H, two isomers), 1.84 – 1.71 (m, 2H, two isomers), 1.16 (t, J = 7.1 Hz, 3H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.84 & 192.82 (two isomers), 169.02 & 168.96 (two isomers), 140.63 & 140.62 (two isomers), 134.23 & 134.19 (two isomers), 130.1 (overlap, two isomers),

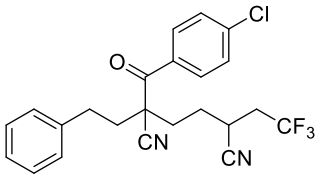


129.3 (overlap, two isomers), 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) & 125.11 (q, $^{1}J_{C\text{-}F}$ = 278.6 Hz) (two isomers), 119.29 & 119.27 (two isomers), 62.1 (overlap, two isomers), 53.4 &, 53.3 (two isomers), 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.2 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 29.8 & 29.7 (two isomers), 25.8 (overlap, two isomers), 25.6 (q, $^{3}J_{C\text{-}F}$ = 1.9 Hz) (overlap, two isomers), 14.0 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.89 (s, one isomer), -64.90 (s, one isomer). HRMS (ESI) calcd. for $C_{17}H_{18}ClF_3NO_3$ $[M+H]^+$: 376.0922; found: 376.0927.

2-(4-chlorobenzoyl)-5-(2,2,2-trifluoroethyl)hexanedinitrile (4am) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (36.1 mg, 55%yield, dr =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H, two isomers), 7.57 – 7.50 (m, 2H, two isomers), 4.37 (t, *J* = 7.7 Hz, 1H, two isomers), 3.05 – 2.94 (m, 1H, two isomers), 2.68 – 2.55 (m, 1H, two isomers), 2.47 – 2.28 (m, 2H, two isomers), 2.25 – 2.15 (m, 1H, two isomers), 2.06 – 1.92 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2 & 188.2 (two isomers), 141.9 (overlap, two isomers), 132.0 (overlap, two isomers), 130.3 (overlap, two isomers), 129.8 (overlap, two isomers), 125.0 (q, $^{1}J_{C\text{-}F}$ = 278.4 Hz) (overlap, two isomers), 118.9 & 118.8 (two isomers), 116.3 & 116.2 (two isomers), 38.7 & 38.5 (two isomers), 36.5 (q, $^{2}J_{C\text{-}F}$ = 30.4 Hz) & 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz) (two isomers), 29.4 & 29.1 (two isomers), 26.3 & 26.1 (two isomers), 25.6 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz) & 25.4 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.78 (s, one isomer), -64.83 (s, one isomer). HRMS (ESI) calcd. for $C_{15}H_{13}ClF_3N_2O$ $[M+H]^+$: 329.0663; found: 329.0662.



2-(4-chlorobenzoyl)-2-phenethyl-5-(2,2,2-trifluoroethyl)hexanedinitrile (4an) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (47.5 mg, 55%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.6, 1.6 Hz, 2H, two isomers), 7.51 (d, *J* = 8.7 Hz, 2H, two isomers), 7.29 (t, *J* = 7.1 Hz, 2H, two isomers), 7.22 (t, *J* = 7.1 Hz, 1H, two isomers), 7.17 – 7.10 (m, 2H, two isomers), 3.00 – 2.89 (m, 1H, two isomers), 2.81 – 2.73 (m, 2H, two isomers), 2.61 – 2.47 (m, 2H, two isomers), 2.45 – 2.25 (m, 2H, two isomers), 2.23 – 2.16 (m, 1H, two isomers), 2.11 – 1.96 (m, 1H, two



isomers), 1.95 – 1.78 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3 & 192.2 (two isomers), 141.18 & 141.16 (two isomers), 139.24 & 139.22 (two isomers), 132.7 (overlap, two isomers), 130.74 & 130.72 (two isomers), 129.4 (overlap, two isomers), 128.9 (overlap, two isomers), 128.5 (overlap, two isomers), 126.9 (overlap, two isomers), 124.96 (q, $^1J_{C\text{-}F}$ = 278.3 Hz) & 124.94 (q, $^1J_{C\text{-}F}$ = 278.1 Hz) (two isomers), 120.4 & 120.3 (two isomers), 118.8 & 118.7 (two isomers), 50.8 & 50.7 (two isomers), 39.51 & 39.49 (two isomers), 36.5 (q, $^2J_{C\text{-}F}$ = 30.3 Hz) & 36.4 (q, $^2J_{C\text{-}F}$ = 30.3 Hz) (two isomers), 33.53 & 33.52 (two isomers), 31.44 & 31.37 (two isomers), 28.1 & 27.9 (two isomers), 25.7 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.6 (q, $^3J_{C\text{-}F}$ = 3.1 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). HRMS (ESI) calcd. for $C_{23}H_{21}ClF_3N_2O$ $[M+H]^+$: 433.1289; found: 433.1295.

Ethyl-7-(4-bromophenyl)-8-(4-chlorophenyl)-4-cyano-2,2-difluoro-8-oxooctanoate (4ao) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (59.3 mg, 58%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.6, 2.1 Hz, 2H, two isomers), 7.44 (d, *J* = 8.3 Hz, 2H, two isomers), 7.36 (d, *J* = 8.3 Hz, 2H, two isomers), 7.13 (dd, *J* = 8.4, 1.6 Hz, 2H, two isomers), 4.47 (t, *J* = 7.2 Hz, 1H, two isomers), 4.38 – 4.30 (m, 2H, two isomers), 2.94 – 2.82 (m, 1H, two isomers), 2.58 – 2.44 (m, 1H, two isomers), 2.40 – 2.20 (m, 2H, two isomers), 2.08 – 1.95 (m, 1H, two isomers), 1.78 – 1.67 (m, 1H, two isomers), 1.67 – 1.61 (m, 1H, two isomers), 1.36 (td, *J* = 7.2, 2.3 Hz, 3H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 & 197.1 (two isomers), 163.1 (t, $^2J_{C\text{-}F}$ = 32.0 Hz) (overlap, two isomers), 140.02 & 140.01 (two isomers), 137.35 & 137.29 (two isomers), 134.40 & 134.38 (two isomers), 132.6 (overlap, two isomers), 130.2 (overlap, two isomers), 129.81 & 129.78 (two isomers), 129.2 (overlap, two isomers), 121.9 (overlap, two isomers), 120.1 (overlap, two isomers), 114.3 (t, $^1J_{C\text{-}F}$ = 254.1 Hz) (overlap, two isomers), 63.7 (overlap, two isomers), 52.5 (overlap, two isomers), 36.8 (t, $^2J_{C\text{-}F}$ = 24.1 Hz) & 36.7 (t, $^2J_{C\text{-}F}$ = 24.4 Hz) (two isomers), 30.9 & 30.7 (two isomers), 30.6 & 30.5 (two isomers), 25.09 (t, $^3J_{C\text{-}F}$ = 8.7 Hz) & 25.05 (t, $^3J_{C\text{-}F}$ = 8.0 Hz) (two isomers), 14.0 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.0 (d, *J* = 36.5 Hz, one

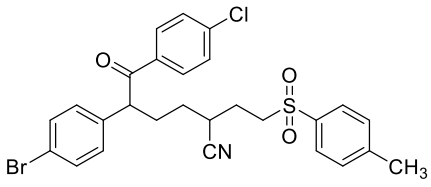
isomer), -104.7 (d, J = 36.4 Hz, one isomer), -105.7 (d, J = 14.8 Hz, one isomer), -106.4 (d, J = 14.7 Hz, one isomer). HRMS (ESI) calcd. for $C_{23}H_{22}BrClF_2NO_3$ $[M+H]^+$: 512.0435, 514.0414; found: 512.0444, 514.0421.

2-(2-bromo-2,2-difluoroethyl)-5-(4-bromophenyl)-6-(4-chlorophenyl)-6-oxohexanenitrile (4ap) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (67.2 mg, 65%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.7, 2.1 Hz, 2H, two isomers), 7.36 (d, J = 8.4 Hz, 2H, two isomers), 7.29 (d, J = 8.4 Hz, 2H, two isomers), 7.19 (dd, J = 8.5, 1.8 Hz, 2H, two isomers), 4.49 (t, J = 7.2 Hz, 1H, two isomers), 3.00 – 2.89 (m, 1H, two isomers), 2.87 – 2.73 (m, 1H, two isomers), 2.63 – 2.49 (m, 1H, two isomers), 2.40 – 2.25 (m, 1H, two isomers), 2.11 – 1.96 (m, 1H, two isomers), 1.77 – 1.68 (m, 1H, two isomers), 1.67 – 1.61 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 & 197.1 (two isomers), 140.03 & 140.02 (two isomers), 136.75 & 136.69 (two isomers), 134.4 & 134.3 (two isomers), 133.9 (overlap, two isomers), 130.2 (overlap, two isomers), 129.7 (overlap, two isomers), 129.43 & 129.40 (two isomers), 129.2 (overlap, two isomers), 119.70 (t, $^1J_{C\text{-}F}$ = 307.0 Hz) & 119.67 (t, $^1J_{C\text{-}F}$ = 307.0 Hz) (two isomers), 119.59 & 119.57 (two isomers), 52.4 & 52.4 (two isomers), 46.2 (t, $^2J_{C\text{-}F}$ = 22.9 Hz) & 46.1 (t, $^2J_{C\text{-}F}$ = 22.9 Hz) (two isomers), 30.8 & 30.6 (two isomers), 30.2 & 30.0 (two isomers), 27.3 (t, $^3J_{C\text{-}F}$ = 2.7 Hz) & 27.2 (t, $^3J_{C\text{-}F}$ = 2.6 Hz) (two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.9 (d, J = 13.2 Hz, one isomer), -44.3 (d, J = 13.1 Hz, one isomer), -44.8 (d, J = 30.3 Hz, one isomer), -45.3 (d, J = 30.3 Hz, one isomer). HRMS (ESI) calcd. for $C_{20}H_{16}Br_2ClF_2NNaO$ $[M+Na]^+$: 541.9127,; found: 541.9141. HRMS (ESI) calcd. for $C_{20}H_{17}Br_2ClF_2NO$ $[M+H]^+$: 517.9328,; found: 517.9341.

2-(3-(4-bromophenyl)-4-(4-chlorophenyl)-4-oxobutyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanenitrile (4aq) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (59.4 mg, 42%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.7, 2.4 Hz, 2H, two isomers), 7.48 (d, J = 8.3 Hz, 2H, two isomers), 7.40 (d, J = 8.5 Hz, 2H, two isomers), 7.16 (dd, J = 8.4, 2.0 Hz, 2H, two isomers), 4.50 (t, J = 7.2 Hz, 1H, two isomers), 3.06 – 2.95 (m, 1H, two

isomers), 2.62 – 2.50 (m, 1H, two isomers), 2.42 – 2.28 (m, 2H, two isomers), 2.14 – 2.04 (m, 1H, two isomers), 1.81 – 1.74 (m, 1H, two isomers), 1.70 – 1.65 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.12 & 197.05 (two isomers), 140.15 & 140.12 (two isomers), 137.3 & 137.2 (two isomers), 134.34 & 134.32 (two isomers), 132.7 (overlap, two isomers), 130.2 (overlap, two isomers), 129.8 & 129.7 (two isomers), 129.2 (overlap, two isomers), 122.0 (overlap, two isomers), 119.67 & 119.66 (two isomers), 52.6 & 52.5 (two isomers), 37.7 (overlap, two isomers), 31.0 & 30.8 (two isomers), 30.7 & 30.6 (two isomers), 29.9 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 (t, *J* = 9.1 Hz, 3F), -113.3 – -113.6 (m, 2F), -121.7 – -121.9 (m, 2F), -122.7 – -123.0 (m, 2F), -123.3 – -123.6 (m, 2F), -126.1 – -126.2 (m, 2F). HRMS (ESI) calcd. for $C_{25}H_{16}BrClF_{13}NO$ $[M+Na]^+$: 729.9789, 731.9768; found: 729.9796, 731.9736.

5-(4-bromophenyl)-6-(4-chlorophenyl)-6-oxo-2-(2-tosylethyl)hexanenitrile (4ar)



The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (78.0 mg, 70%yield, dr =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H, two isomers), 7.76 (dd, *J* = 8.3, 1.7 Hz, 2H, two isomers), 7.42 (d, *J* = 8.3 Hz, 2H, two isomers), 7.36 (dd, *J* = 7.8, 5.4 Hz, 4H, two isomers), 7.11 (d, *J* = 8.4 Hz, 2H, two isomers), 4.45 (t, *J* = 7.2 Hz, 1H, two isomers), 3.27 – 3.12 (m, 2H, two isomers), 2.88 – 2.73 (m, 1H, two isomers), 2.45 (s, 3H, two isomers), 2.37 – 2.17 (m, 1H, two isomers), 2.11 – 1.97 (m, 2H, two isomers), 1.96 – 1.84 (m, 1H, two isomers), 1.65 – 1.45 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.21 & 197.18 (two isomers), 145.4 (overlap, two isomers), 140.0 & 139.9 (two isomers), 137.4 (overlap, two isomers), 135.79 & 135.76 (two isomers), 134.37 & 134.36 (two isomers), 132.6 (overlap, two isomers), 130.3 (overlap, two isomers), 130.2 (overlap, two isomers), 129.81 & 129.77 (two isomers), 129.1 (overlap, two isomers), 128.08 & 128.07 (two isomers), 121.84 & 121.83 (two isomers), 120.47 & 120.46 (two isomers), 53.6 (overlap, two isomers), 52.41 & 52.38 (two isomers), 31.0 & 30.8 (two isomers), 30.6 & 30.5 (two isomers), 30.1 & 29.8 (two isomers), 25.4 & 25.2 (two isomers), 21.8 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ HRMS (ESI) calcd. for $C_{27}H_{26}BrClFNO_3S$ $[M+H]^+$: 558.0500, 560.0480; found: 558.0507, 560.0486.

4-(4-bromophenyl)-5-(4-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentane nitrile (6') The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (62.0 mg, 70%yield, dr = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H, one isomers), 7.79 – 7.71 (m, 2H, one isomers), 7.55 – 7.47 (m, 4H, one isomers), 7.48 – 7.41 (m, 4H, one isomers), 7.21 – 7.17 (m, 2H, one isomers), 7.08 – 7.01 (m, 2H, one isomers), 4.11 – 4.00 (m, 1H, one isomers), 3.80 (t, *J* = 7.6 Hz, 1H, one isomers), 3.77 – 3.69 (m, 1H, one isomers), 3.60 (dd, *J* = 10.8, 5.4 Hz, 1H, one isomers), 2.85 – 2.62 (m, 2H, one isomers), 2.57 – 2.37 (m, 2H, one isomers), 2.36 – 2.20 (m, 2H, one isomers), 2.18 – 2.08 (m, 2H, one isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9 & 197.9 (two isomers), 141.3 & 141.0 (two isomers), 133.8 (overlap, two isomers), 133.4 (overlap, two isomers), 133.0 (overlap, two isomers), 132.68 & 132.65 (two isomers), 130.1 & 129.9 (two isomers), 129.7 & 129.6 (two isomers), 129.2 & 128.9 (two isomers), 125.95 (q, $^1J_{C\text{-}F}$ = 278.4 Hz) & 125.88 (q, $^1J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 123.1 & 122.9 (two isomers), 119.44 & 119.37 (two isomers), 38.5 & 37.2 (two isomers), 37.7 (q, $^3J_{C\text{-}F}$ = 2.0 Hz) & 37.3 (q, $^3J_{C\text{-}F}$ = 2.2 Hz) (two isomers), 36.9 (q, $^2J_{C\text{-}F}$ = 29.5 Hz) & 35.7 (q, $^2J_{C\text{-}F}$ = 29.4 Hz) (two isomers), 35.1 & 34.6 (two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.0 (s, one isomer), -64.3 (s, one isomer). HRMS (ESI) calcd. for $C_{19}H_{15}BrClF_3NO$ $[M+H]^+$: 443.9973, 445.9952; found: 443.9962, 445.9945.

7. DFT calculations

Density functional theory (DFT) calculations have been performed to explore the detailed reaction mechanism and origin of the high regioselectivity for 1,4-cyano migration in the process of trifunctionalization of hexenenitrile **3a** (Figure S1). The combination of NHC **A'** generated from precatalyst **A** under basic conditions with 4-chlorobenzaldehyde **2a** leads to enolate form of Breslow intermediate **Int-1**. The SET process between **Int-1** and CF_3I proceeds smoothly to give transient trifluoromethyl radical and persistent NHC-bound ketyl radical **S1**. Subsequent addition of trifluoromethyl radical to hexenenitrile **3a** generates intermediate **S2** through the transition state **TS1** ($\Delta G^{\ddagger}$ = 9.3 kcal/mol).

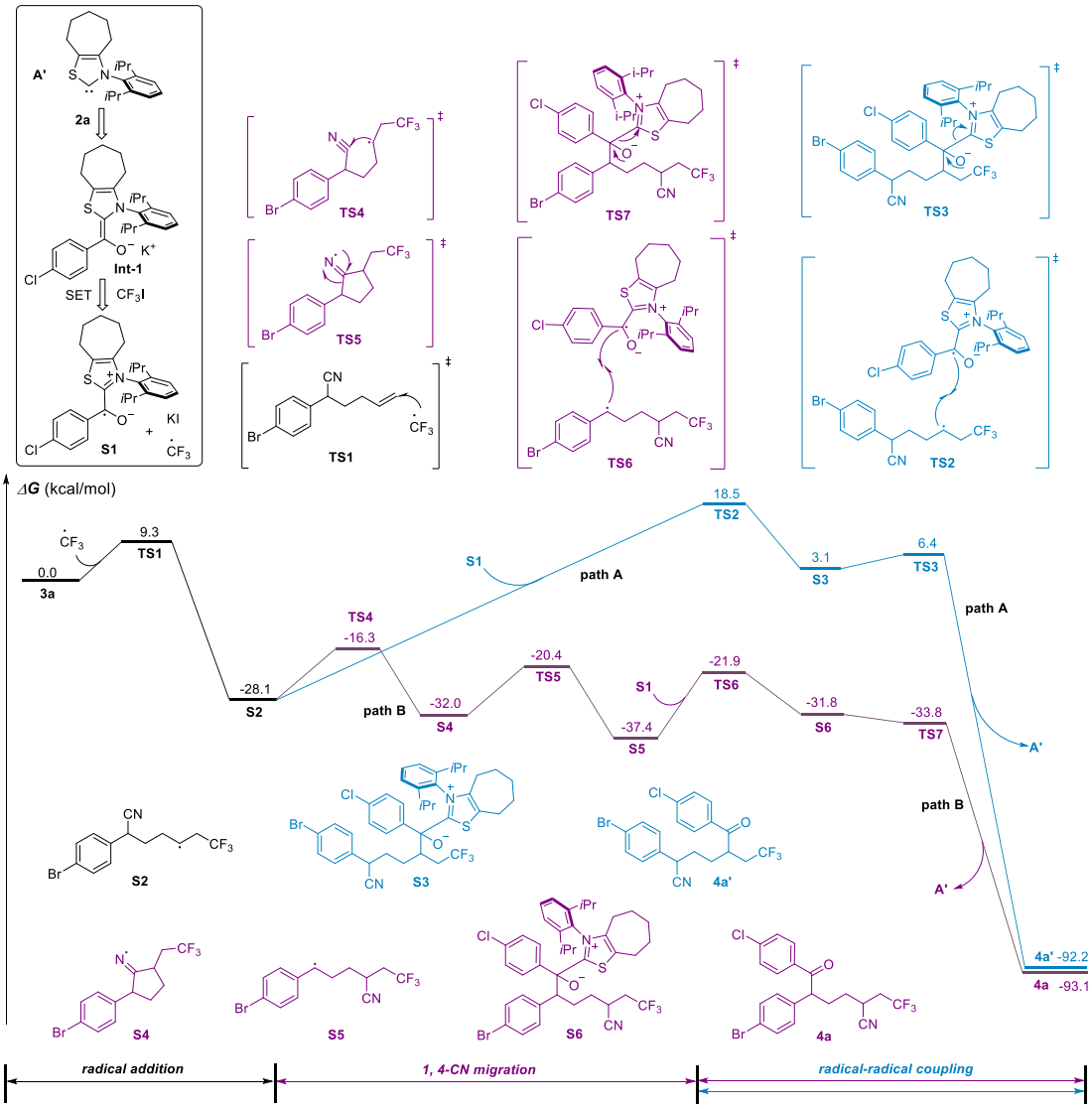


Figure S1. Relative Gibbs free energy profiles of the reaction.

There are two possible pathways (path A & path B) for the radical-radical coupling of ketyl radical **S1** with the generated alkyl radical through addition of CF_3 radical. In path A, the direct radical-radical coupling of **S1** with **S2** gives intermediate **S3** through transition state **TS2** ($\Delta G^{‡}$ = 46.6 kcal/mol). The collapse of **S3** through transition state **TS3** gives birth to product **4a'** and **NHC A'** for the next catalytic cycle. In path B, the intramolecular radical addition of **S2** to the cyano group forms a five-member imine radical intermediate **S4** through transition state **TS4** ($\Delta G^{‡}$ = 11.8 kcal/mol). The following ring-opening of **S4** occurs to generate the cyano migrated benzylic radical intermediate **S5** through transition state **TS5** ($\Delta G^{‡}$ = 12.4 kcal/mol). The subsequent radical-radical coupling of **S5** with **S1** gives intermediate **S6** through transition state **TS6** ($\Delta G^{‡}$

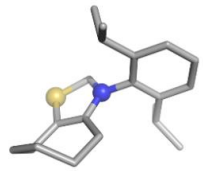
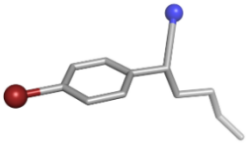
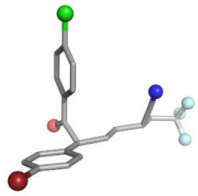
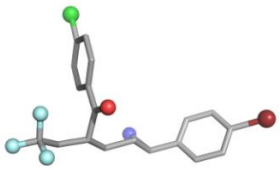
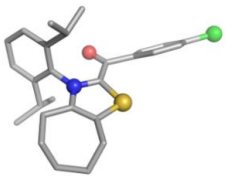
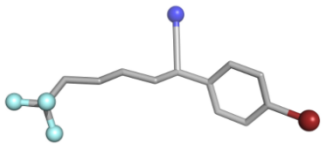
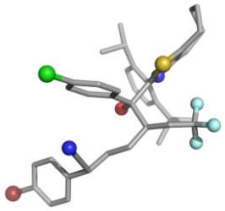
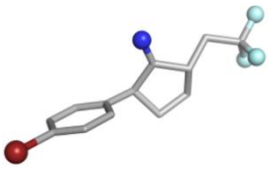
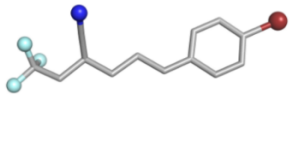
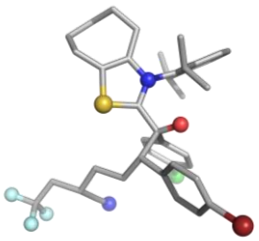
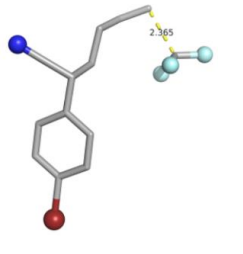
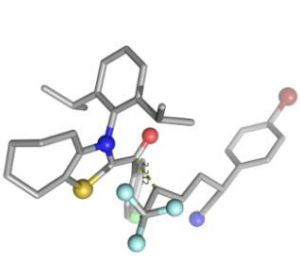
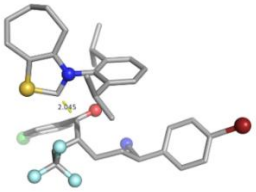
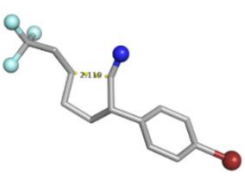
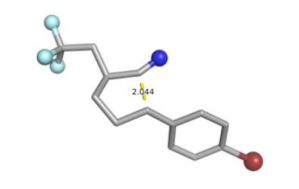
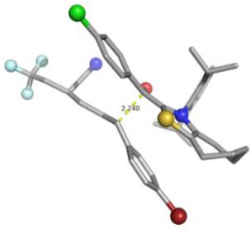
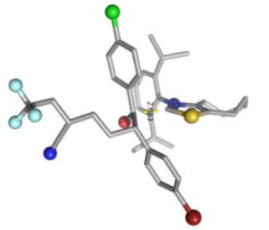
= 15.5 kcal/mol). At the final step, the C-C bond cleavage leads to the dissociation of the final product **4a** along with NHC **A'**. It is obvious that benzylic radical **S5** generated by cyano migration is more stable than radical **S2** without cyano migration. Moreover, radical-radical coupling of **S1** with **S2** in path A requires much higher energy barrier than that in path B, thus disfavoring the direct radical-radical coupling and facilitating the cyano migration process. Therefore, high regioselectivity of this protocol can be rationalized by the above calculation results that path B associated with the 1,4-cyano migration process is much more energetically favorable than path A although the obtained migration product **4a** shows similar stability to product **4a'**.

All density functional theory (DFT) calculations were performed with the Gaussian 16 program package. [7]

Full geometry optimizations were operated to locate all of the stationary points, using (U)M06-2X density functional theory method[8-9] with def2SVP [10]basis for all atoms, and a polarized continuum model based on solute electron density (PCM)[11-12] was employed to simulate the solvent effect of dichloroethane solvent in optimization. The spin-restricted DFT method was used for closed-shell species and the spin-unrestricted DFT method for radical species and open-shell singlet species (TS2, TS6) with the "guess (mix, always)" keyword. In the meantime, the stability of the density function theory (DFT) wave-function of the auxiliary Kohn–Sham determinant was examined.[13] Harmonic vibrational frequency calculations were conducted to characterize all stationary point. Herein, minima have zero imaginary frequencies, and transition states have only one imaginary vibrational frequency. Intrinsic reaction coordinate (IRC) calculations[14-15] were implemented to track minimum energy paths connecting each transition state structure to two corresponding minima. The single point energy calculations of all stationary points were performed at the (U)M06-2X/def2TZVP,SDD level using the PCM-SMD model with dichloroethane as solvent.This theoretical level is denoted as PCM-SMD(dichloroethane)-(U)M06-2X/def2TZVP.

Unless mentioned otherwise, the Gibbs free energy of formation (ΔG) are obtained at the PCM-SMD (dichloroethane)-(U)M06-2X/def2TZVP level.

Figure S2. DFT-optimized geometries of intermediates and transition states (Bond lengths are reported in angstroms (Å)).

		
NHC-A	**3a**	**4a**
		
4a'	**S1**	**S2**
		
S3	**S4**	**S5**
		
S6	**TS1**	**TS2**
		
TS3	**TS4**	**TS5**
		
TS6	**TS7**	

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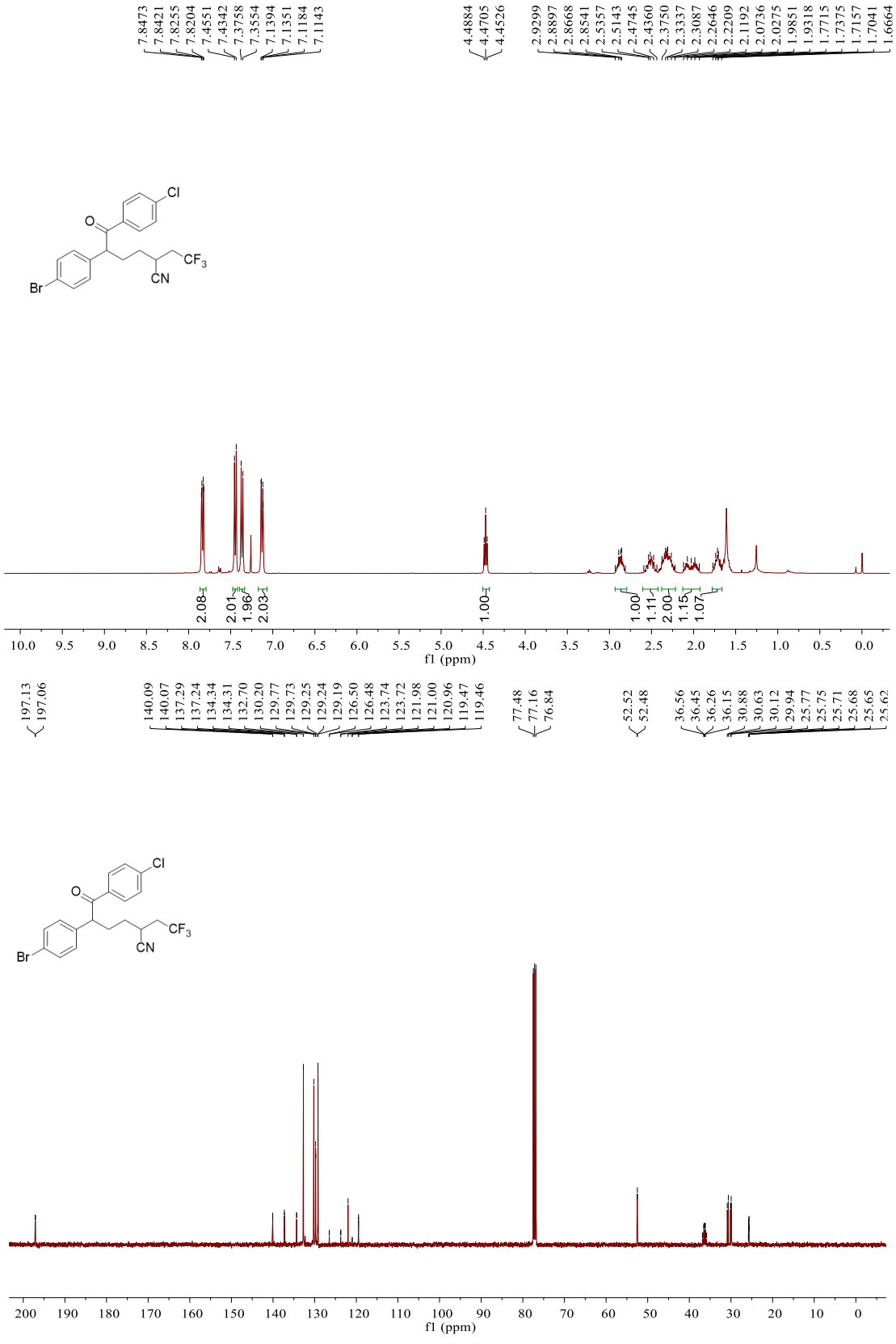
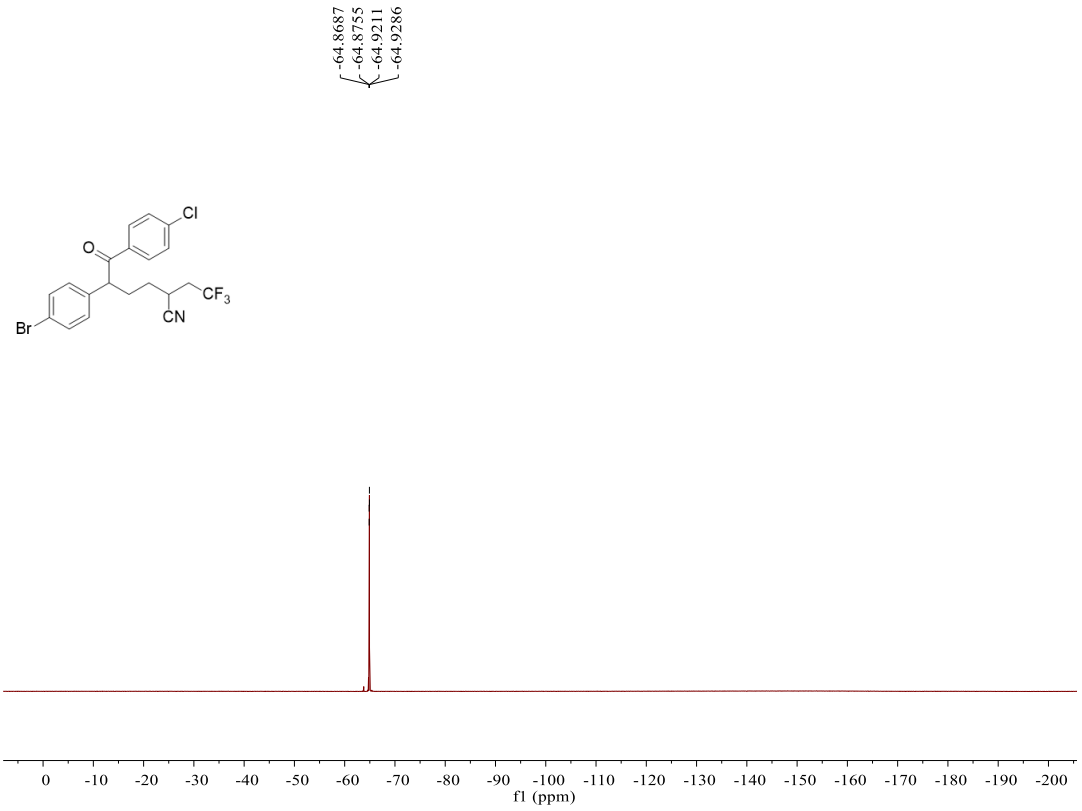
8. Copies of NMR spectra

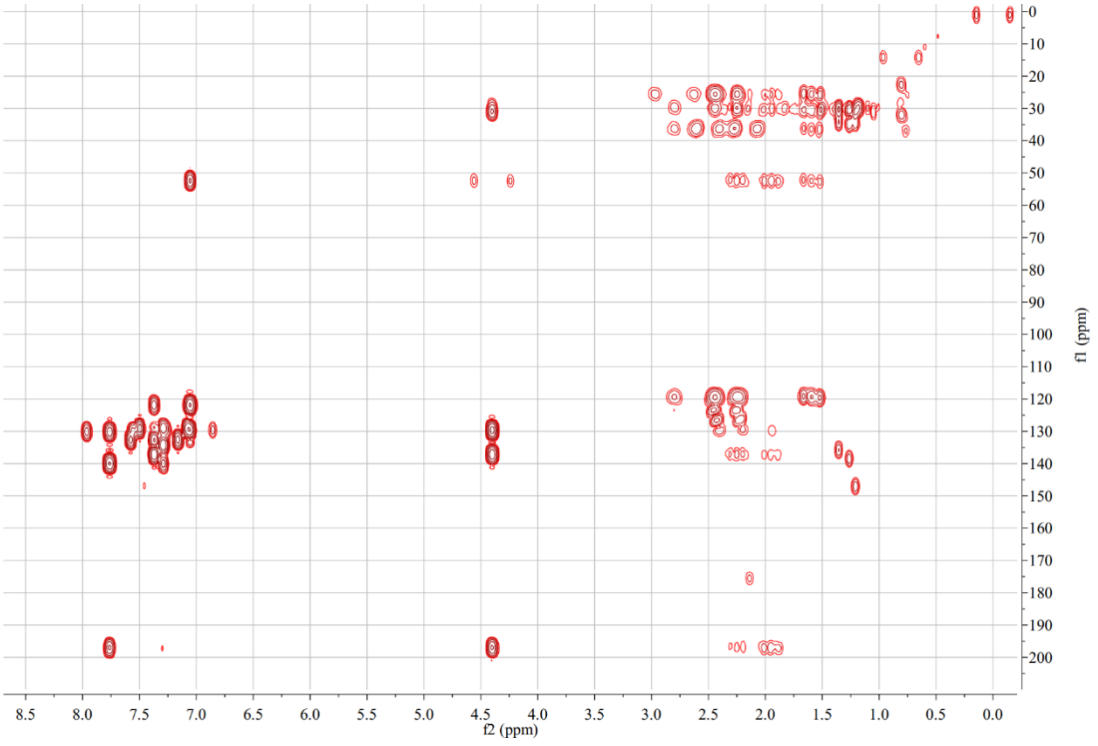
4a ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



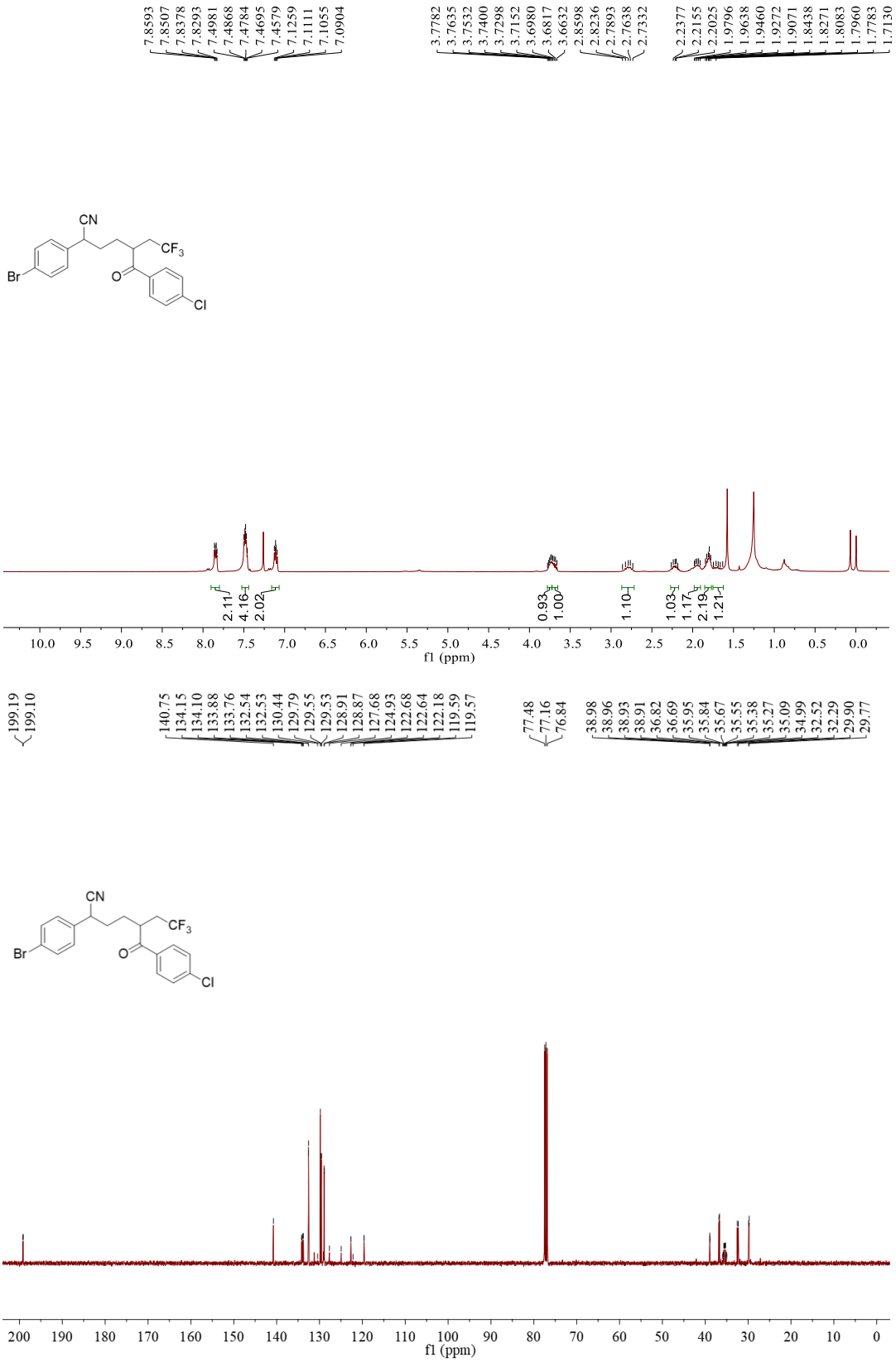
4a ^{19}F NMR (376 MHz, Chloroform-*d*)



C-H HMBC of **4a**



4a'^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (376 MHz, Chloroform-*d*)



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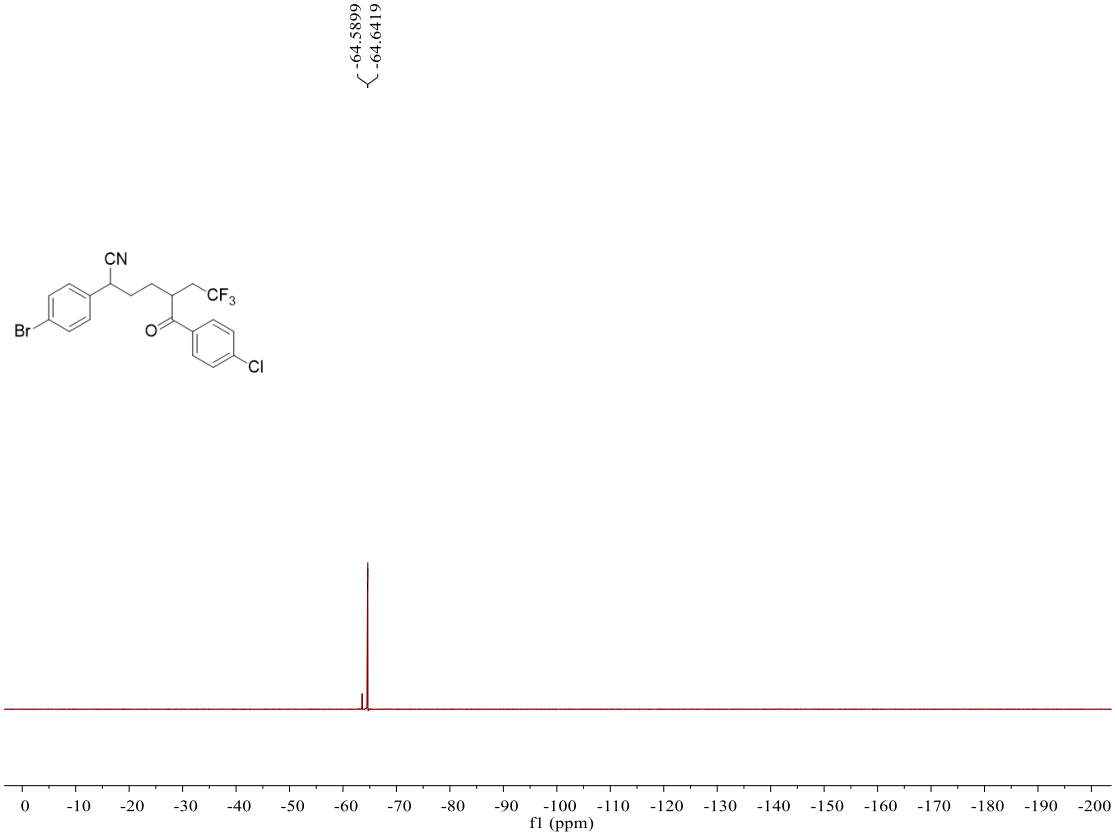

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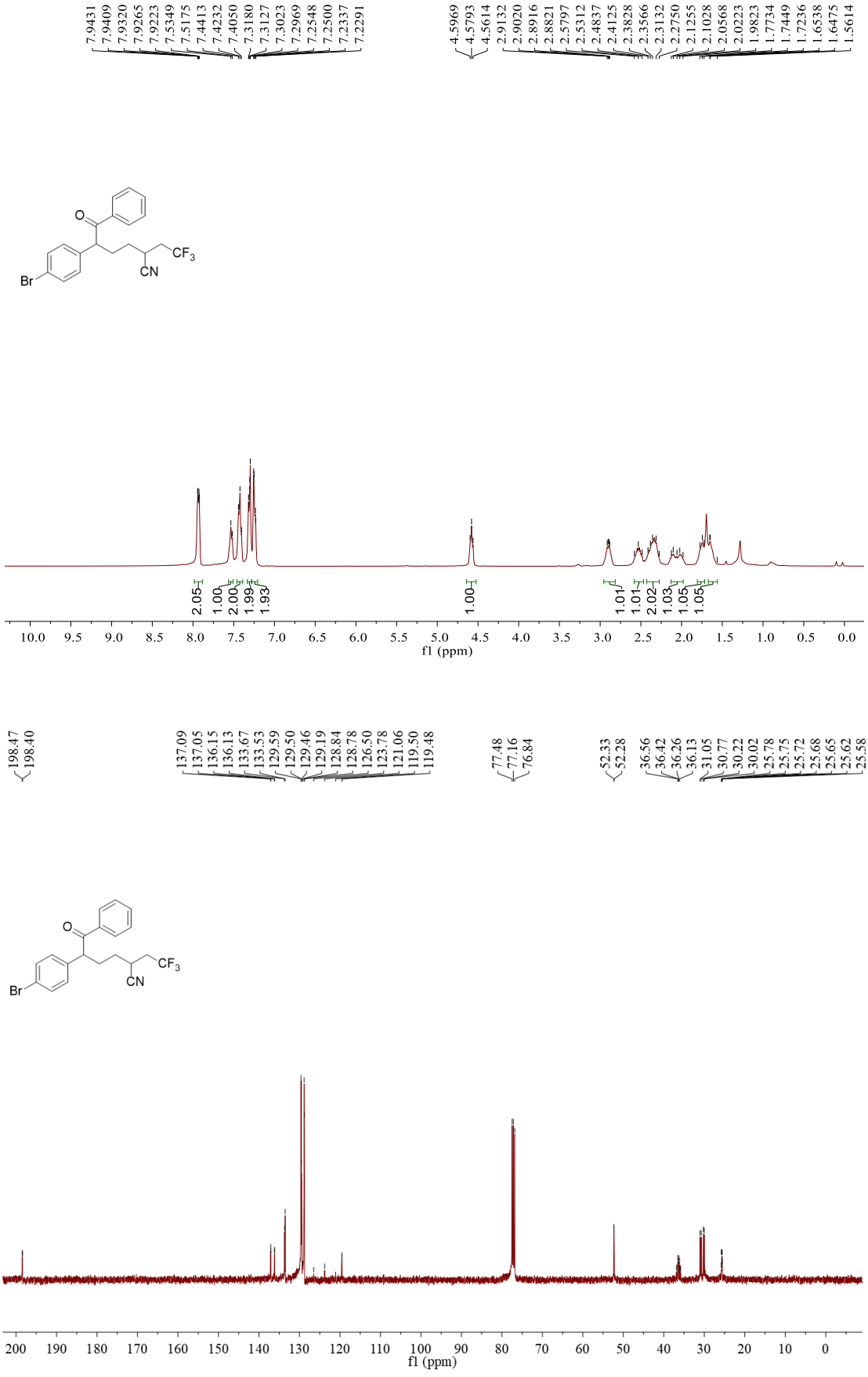
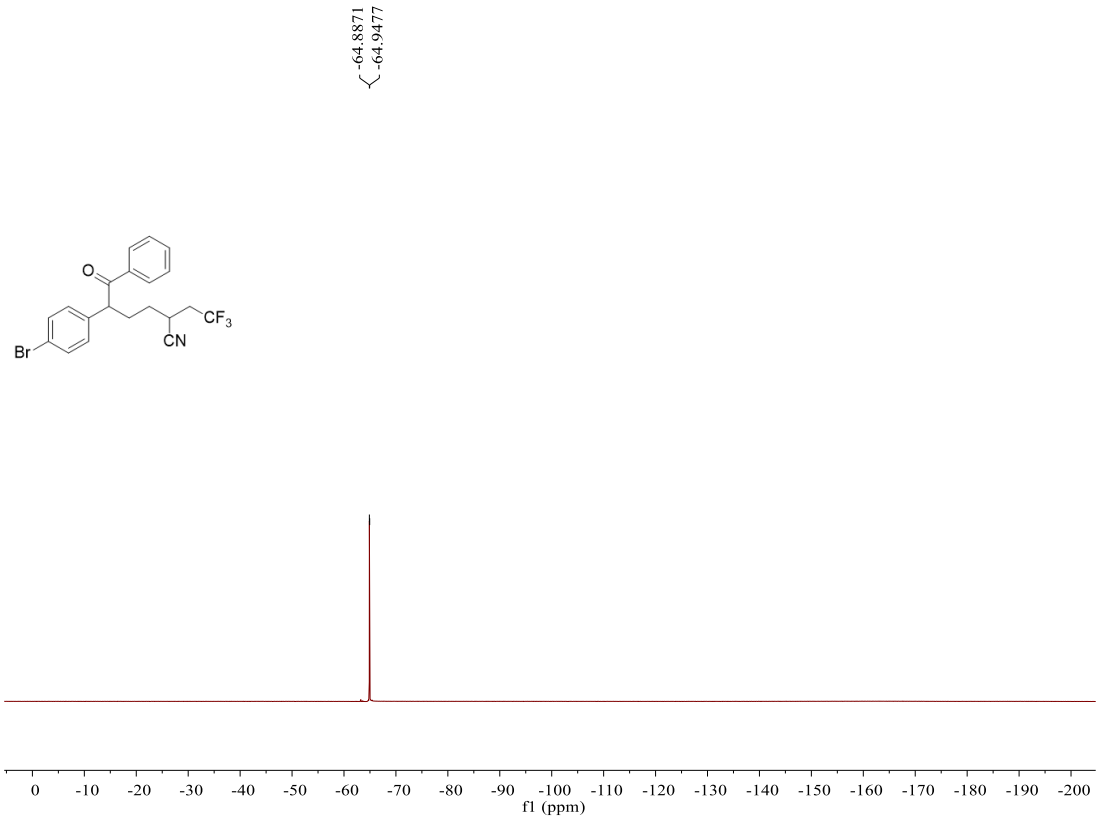


4b ^{19}F NMR (376 MHz, Chloroform-*d*)



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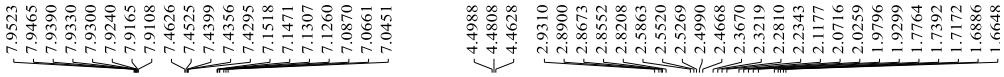
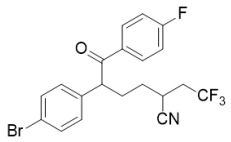
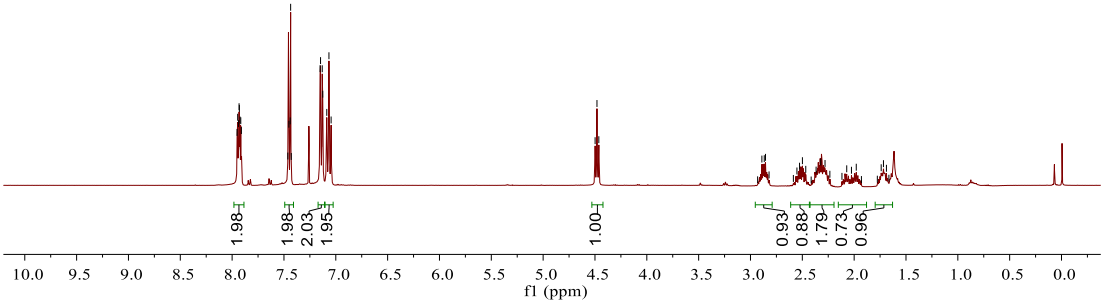
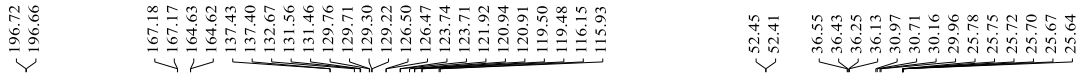
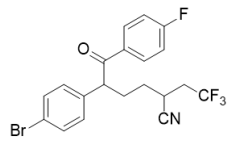
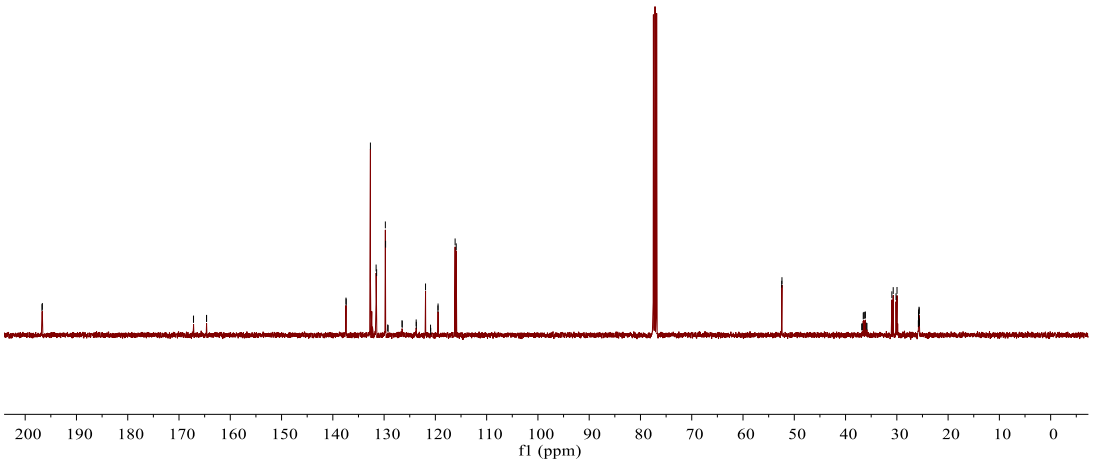




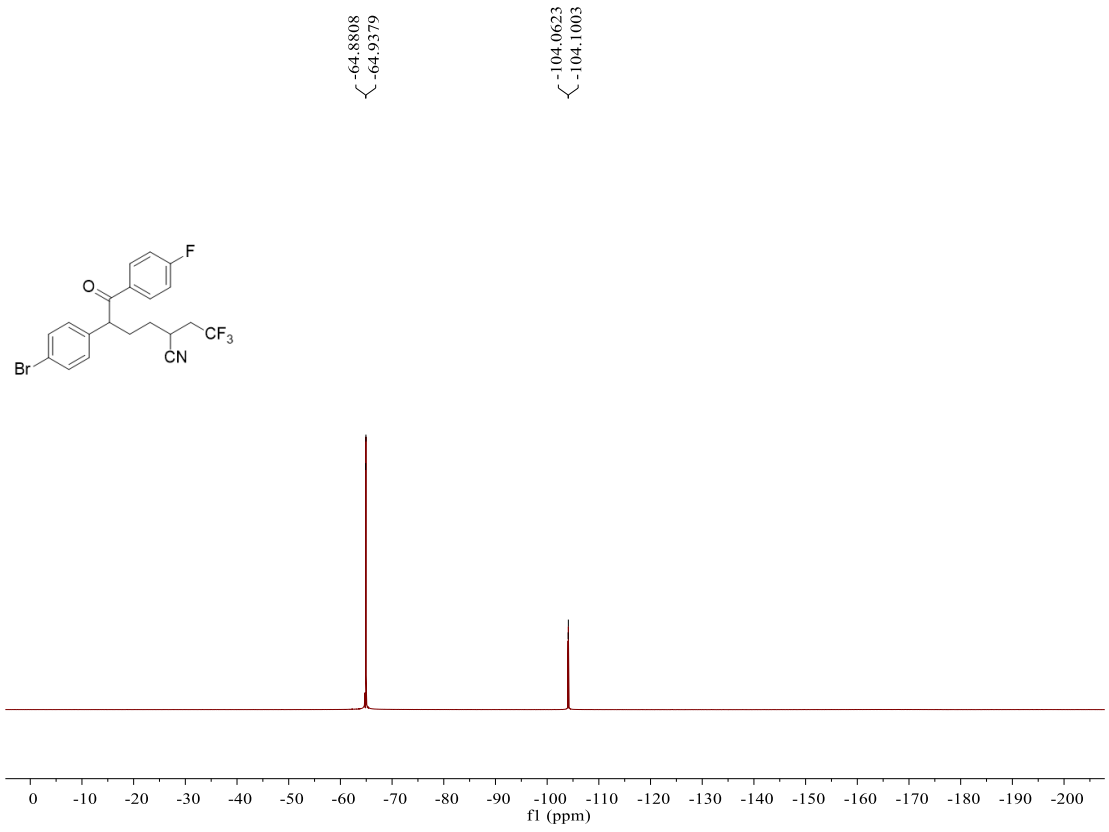




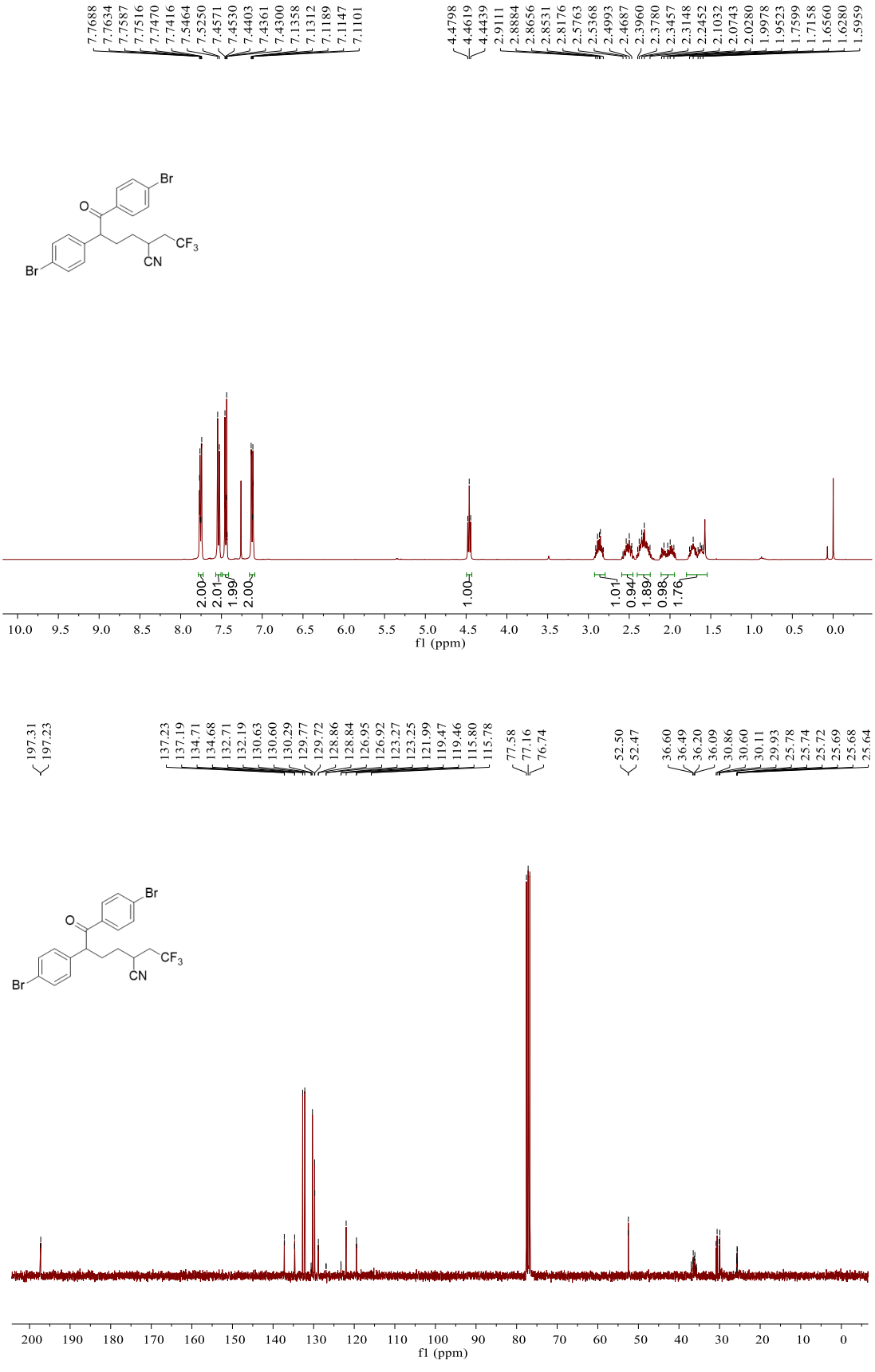




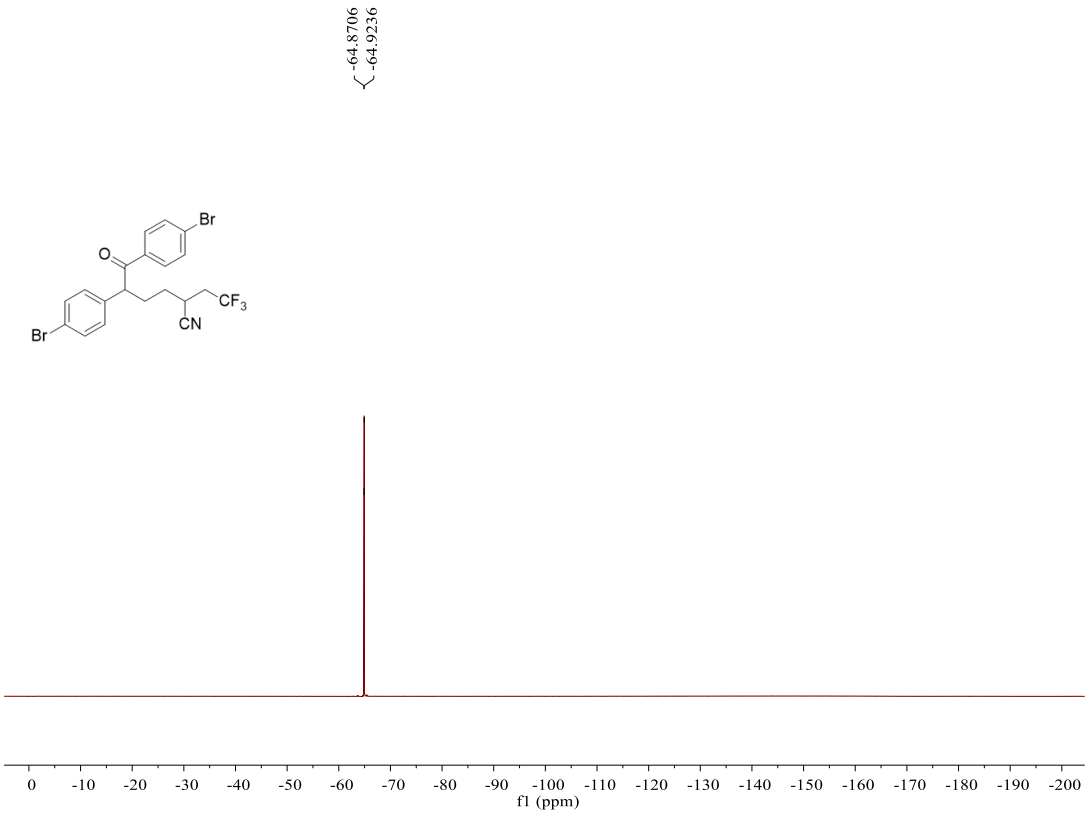
4c ^{19}F NMR (376 MHz, Chloroform-*d*)



4d ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (75 MHz, Chloroform-*d*)



4d ^{19}F NMR (376 MHz, Chloroform-*d*)



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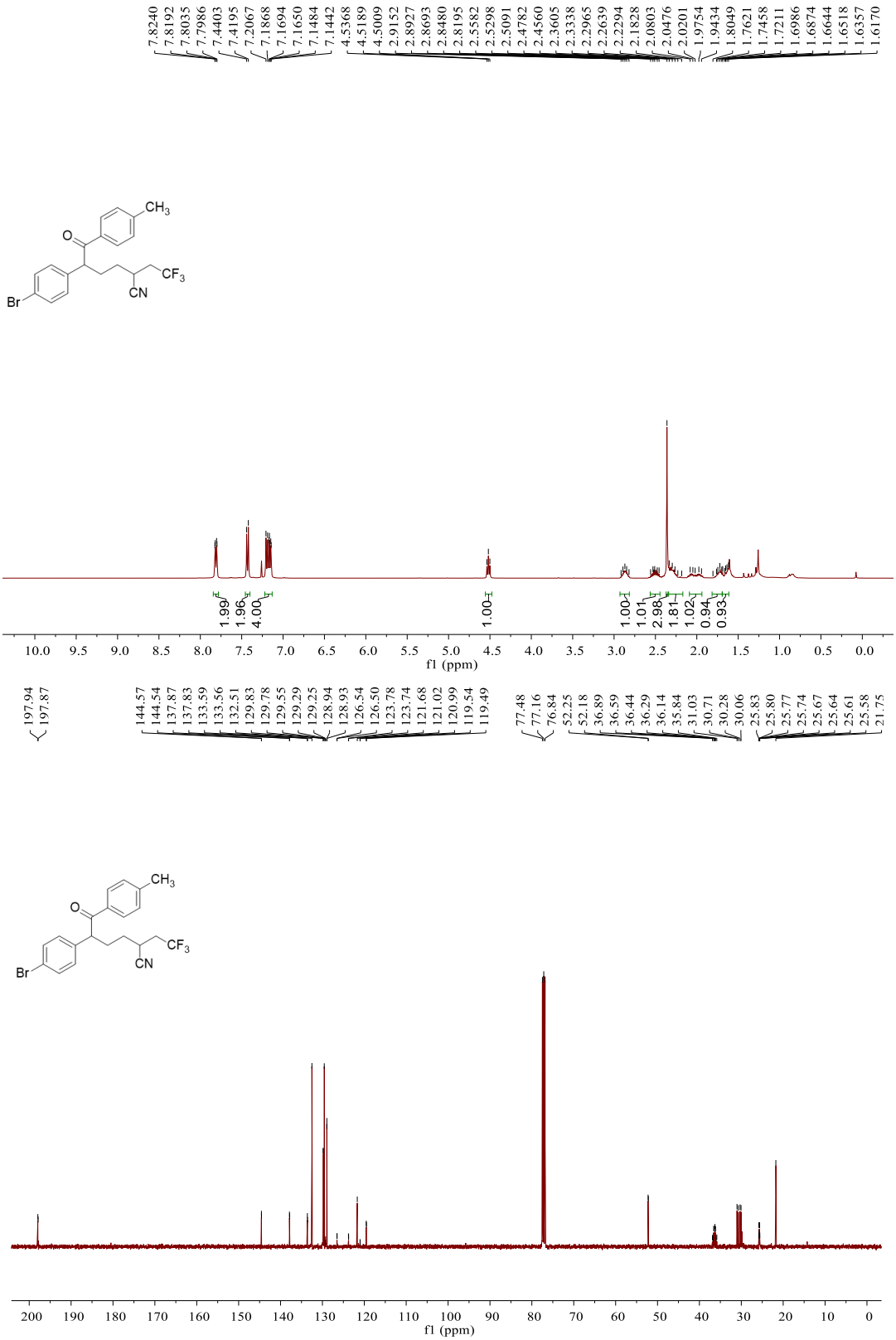
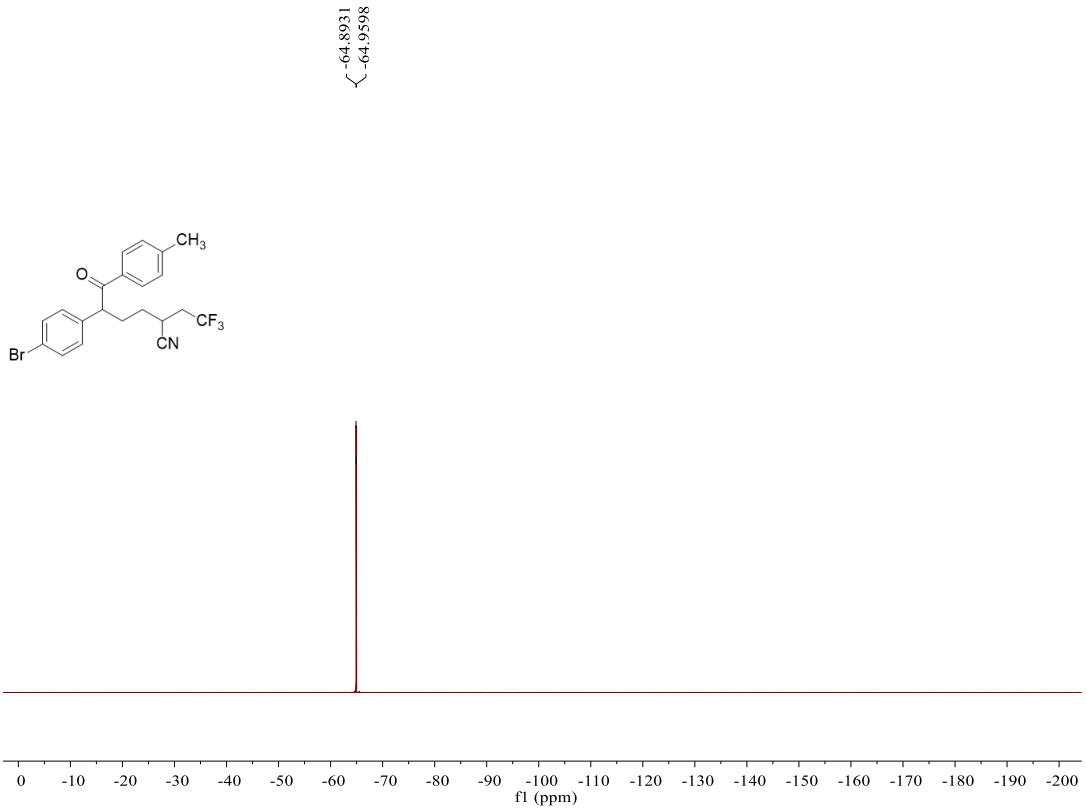


4e ^{19}F NMR (376 MHz, Chloroform-*d*)



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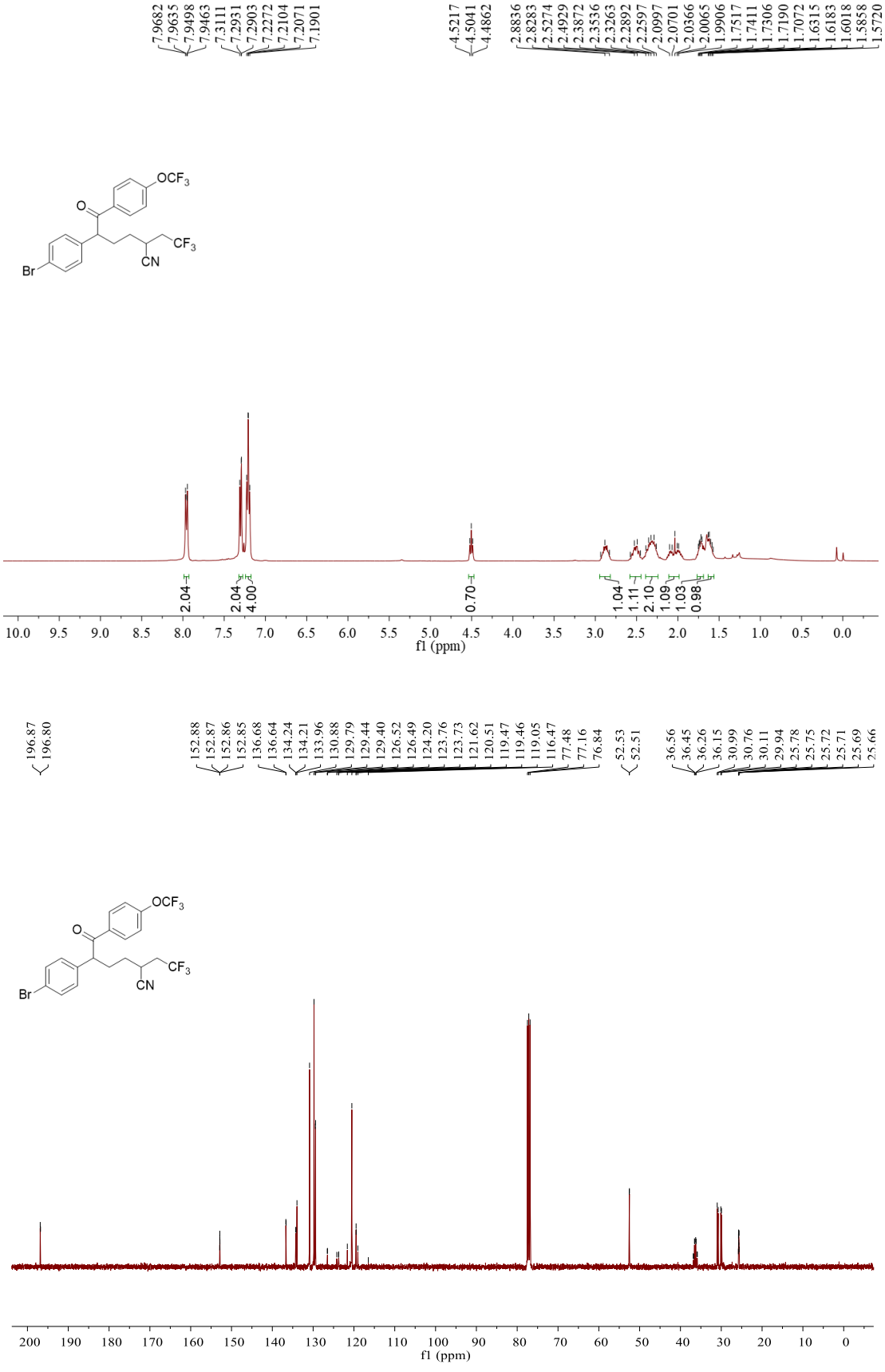
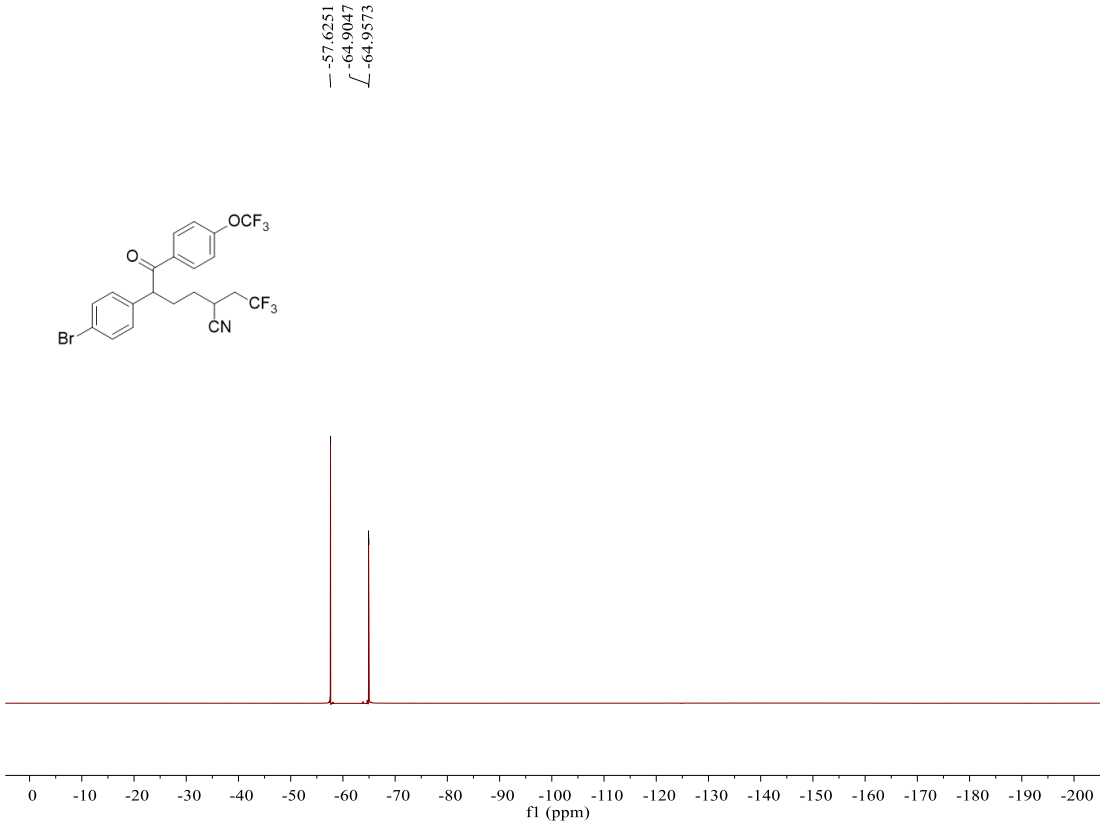


4f ^{19}F NMR (376 MHz, Chloroform-*d*)



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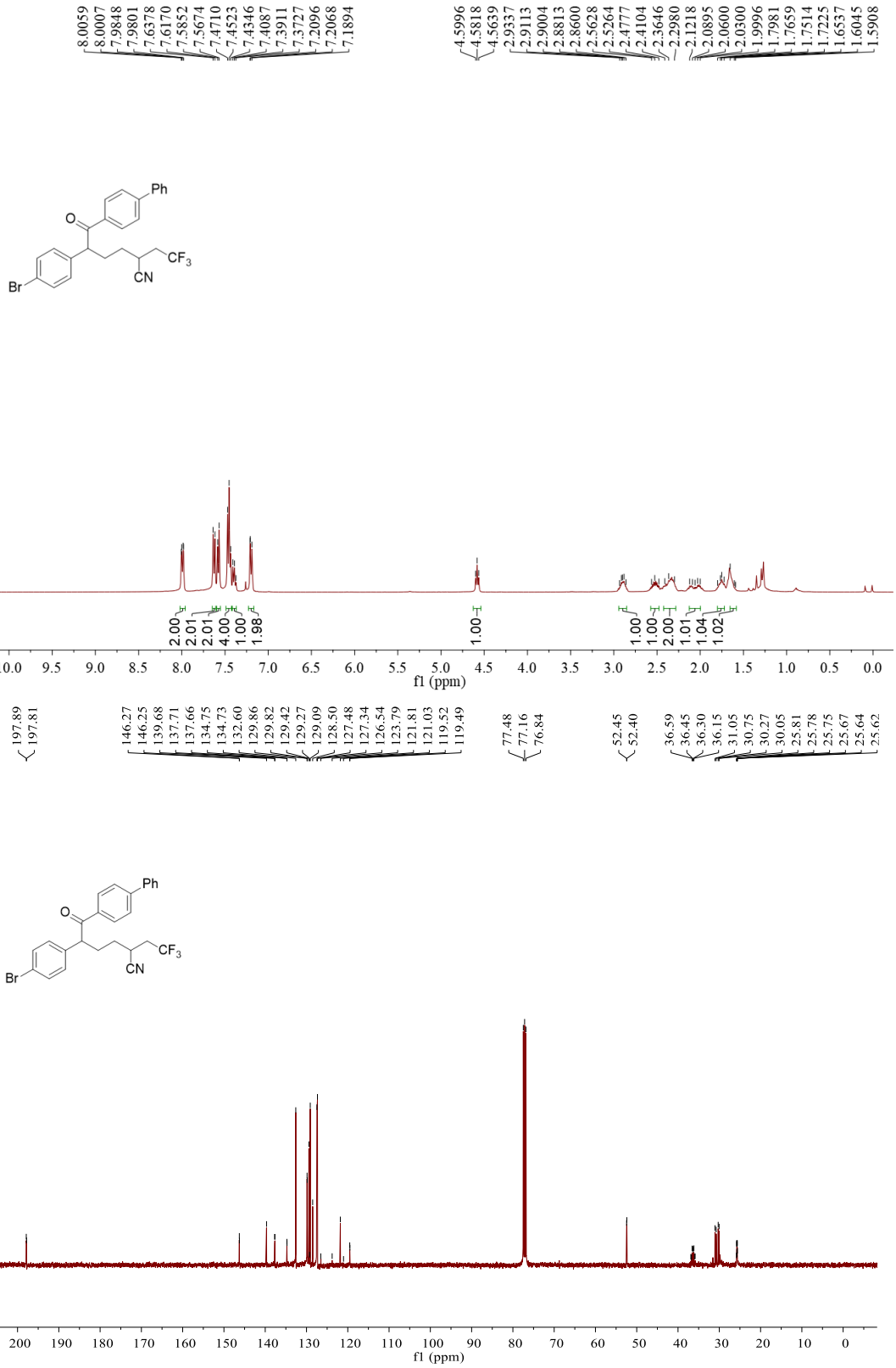

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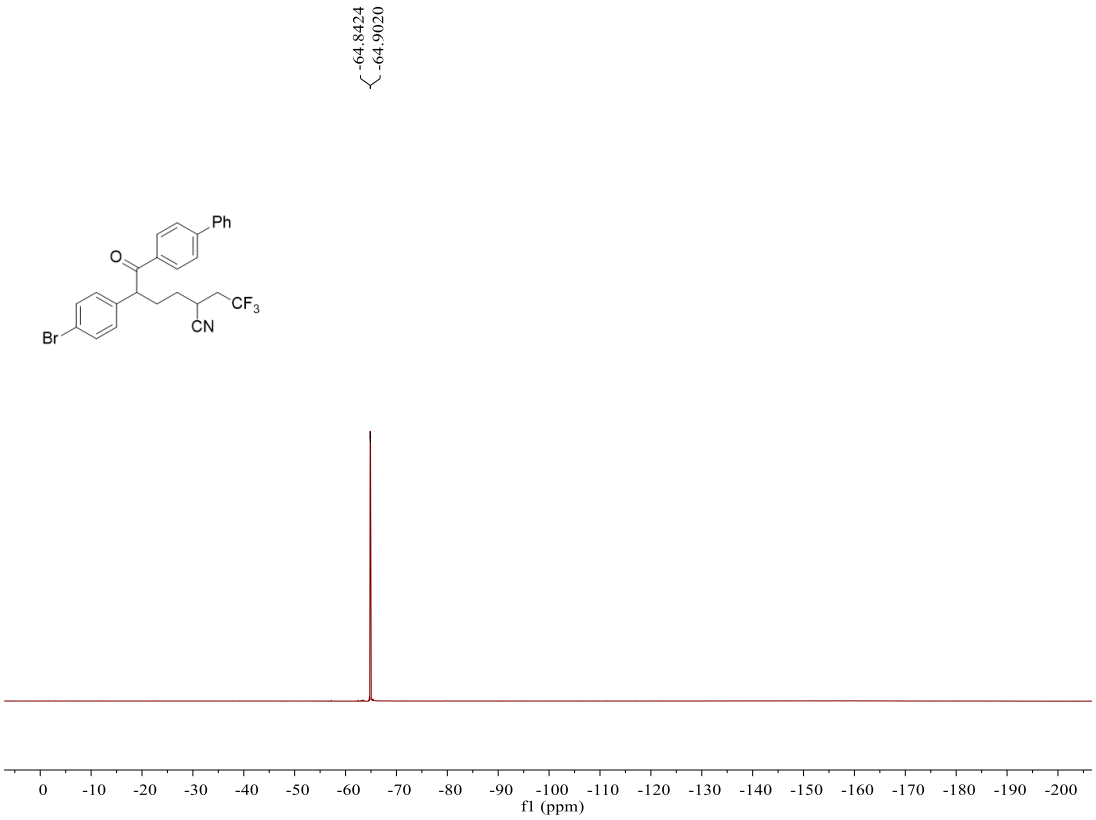

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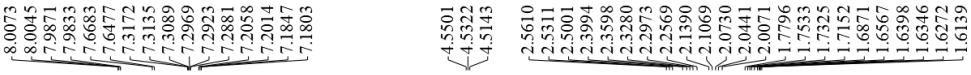

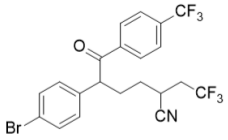

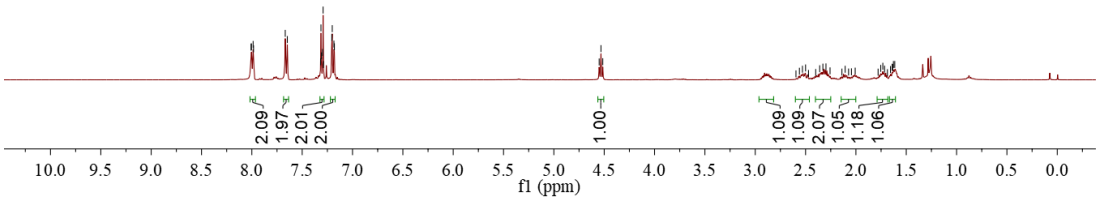

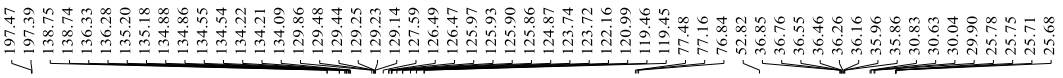

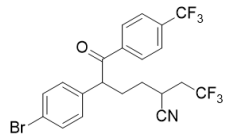

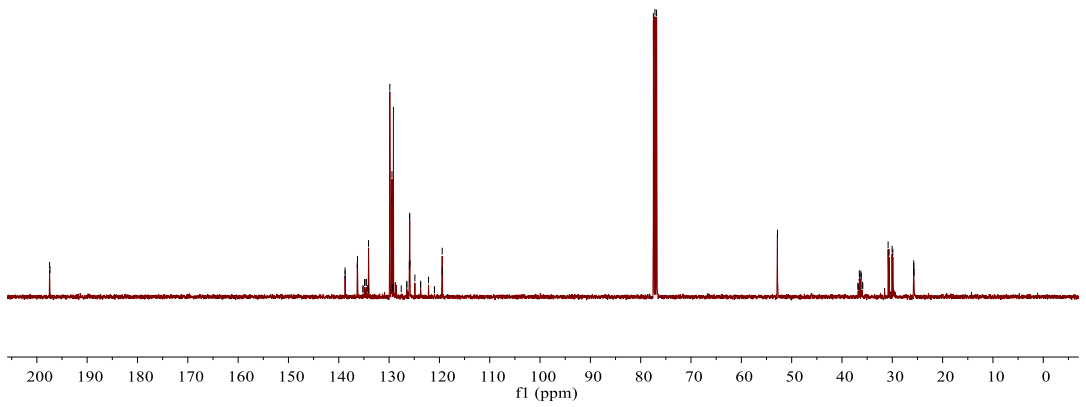

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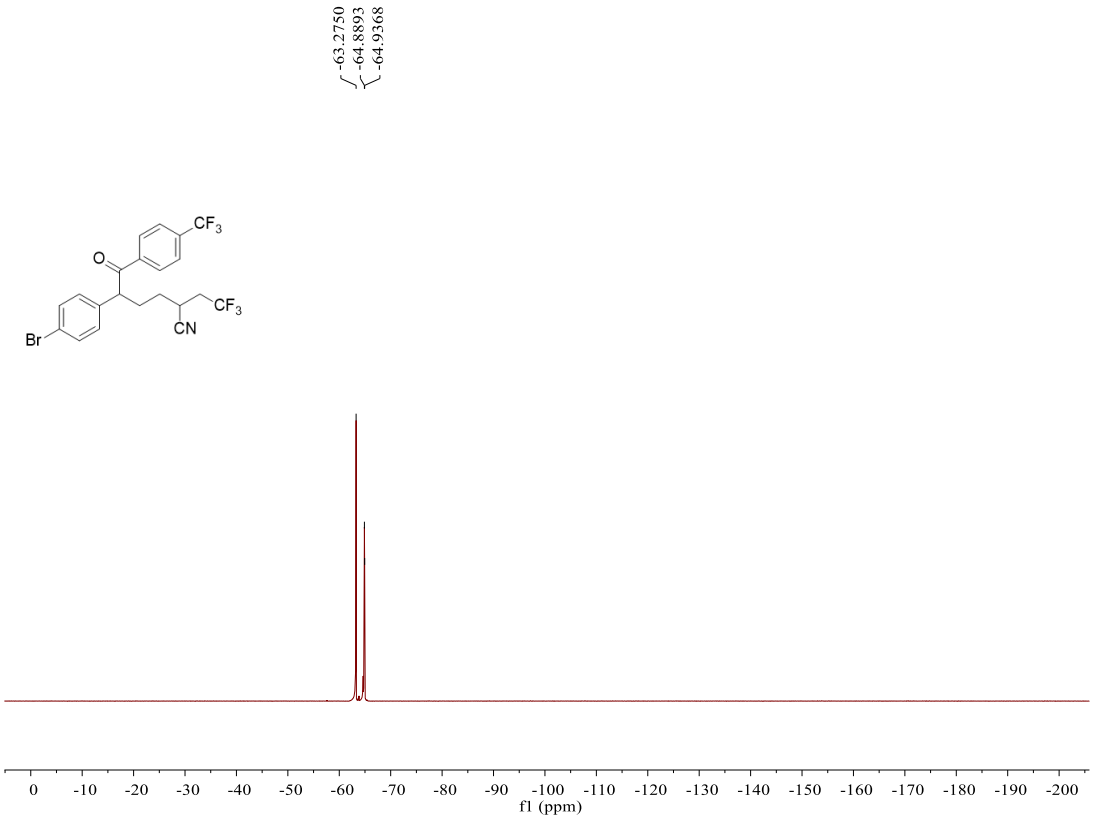
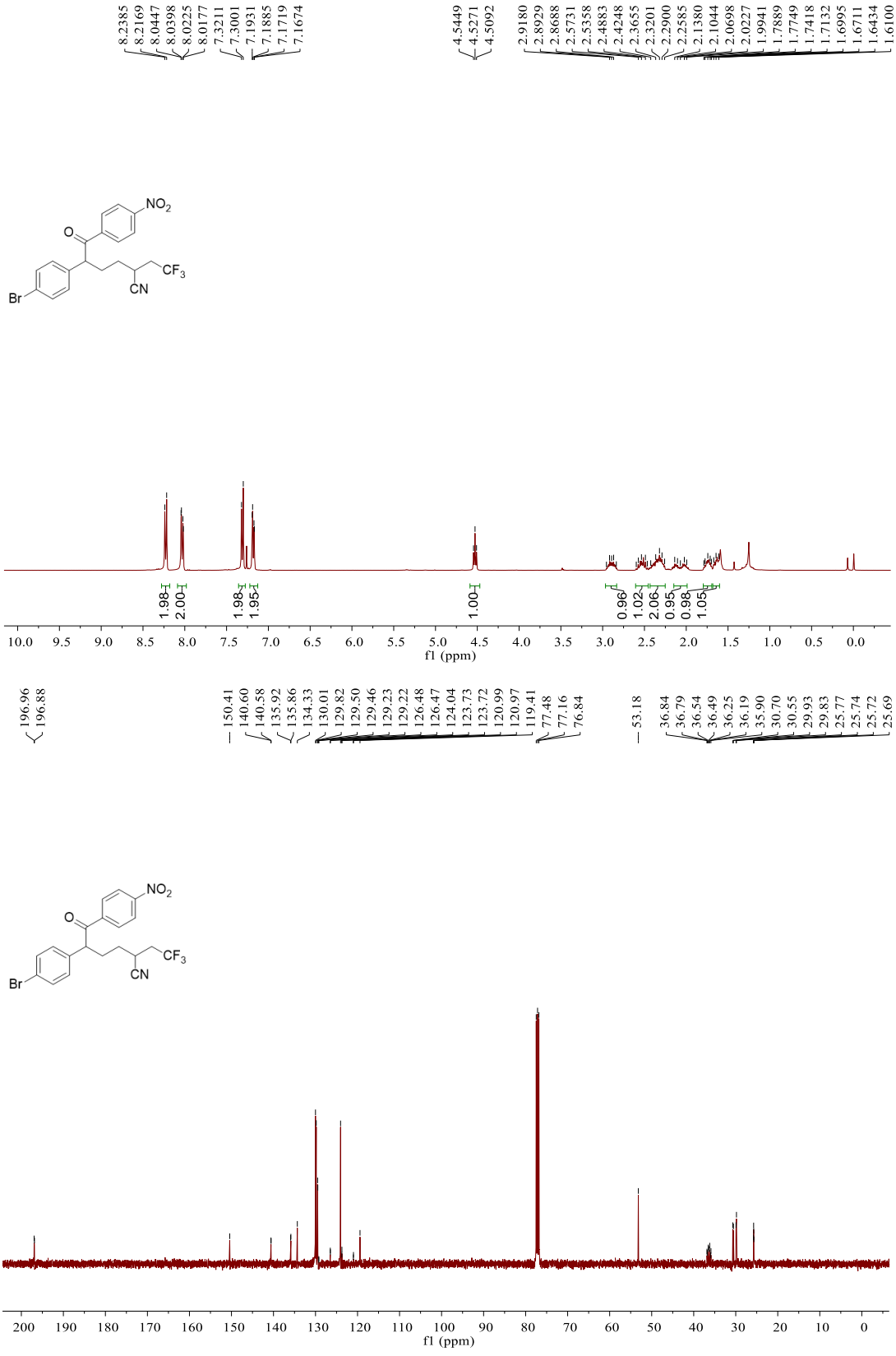


4i ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



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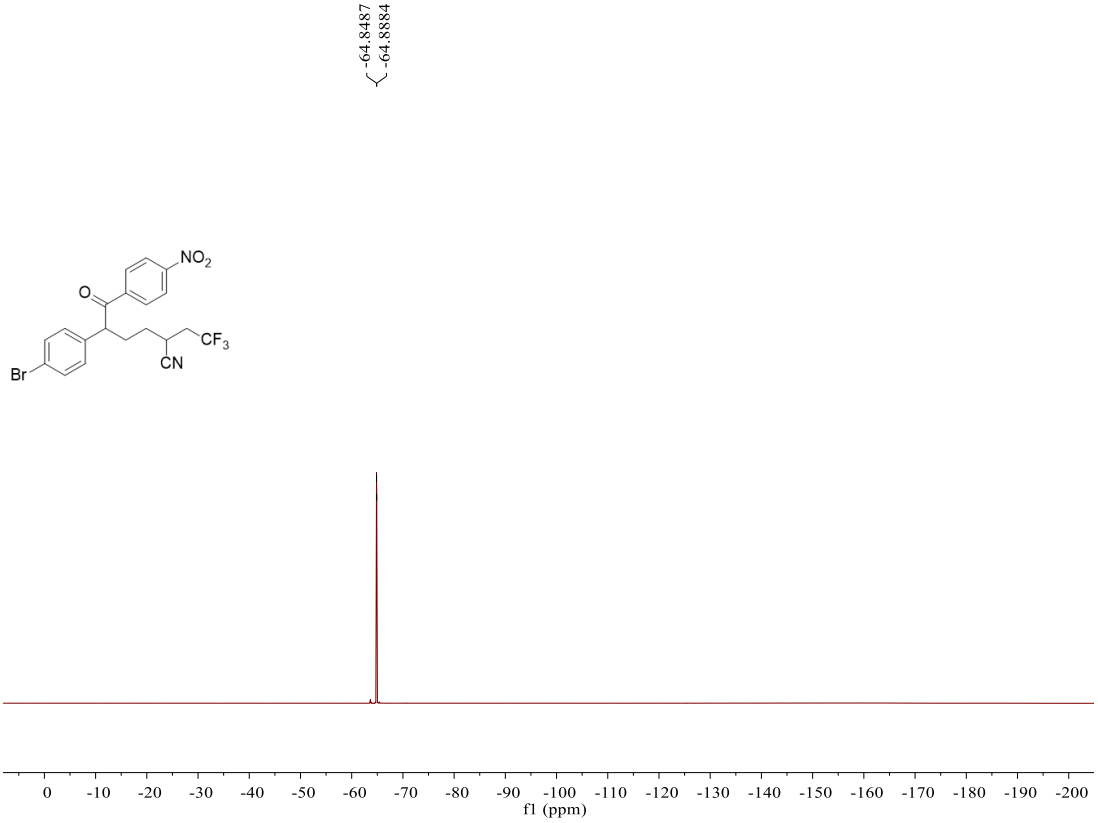

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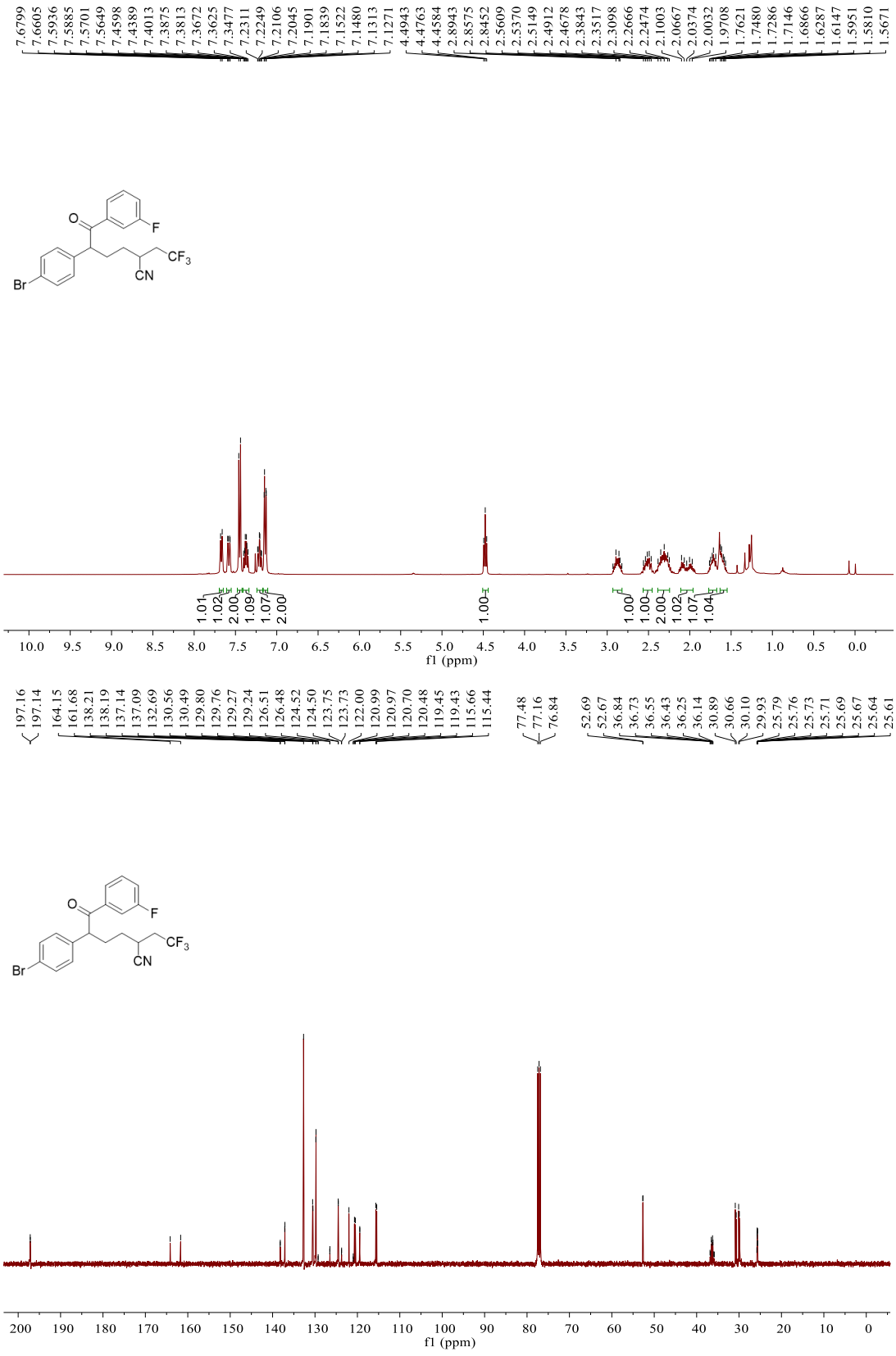

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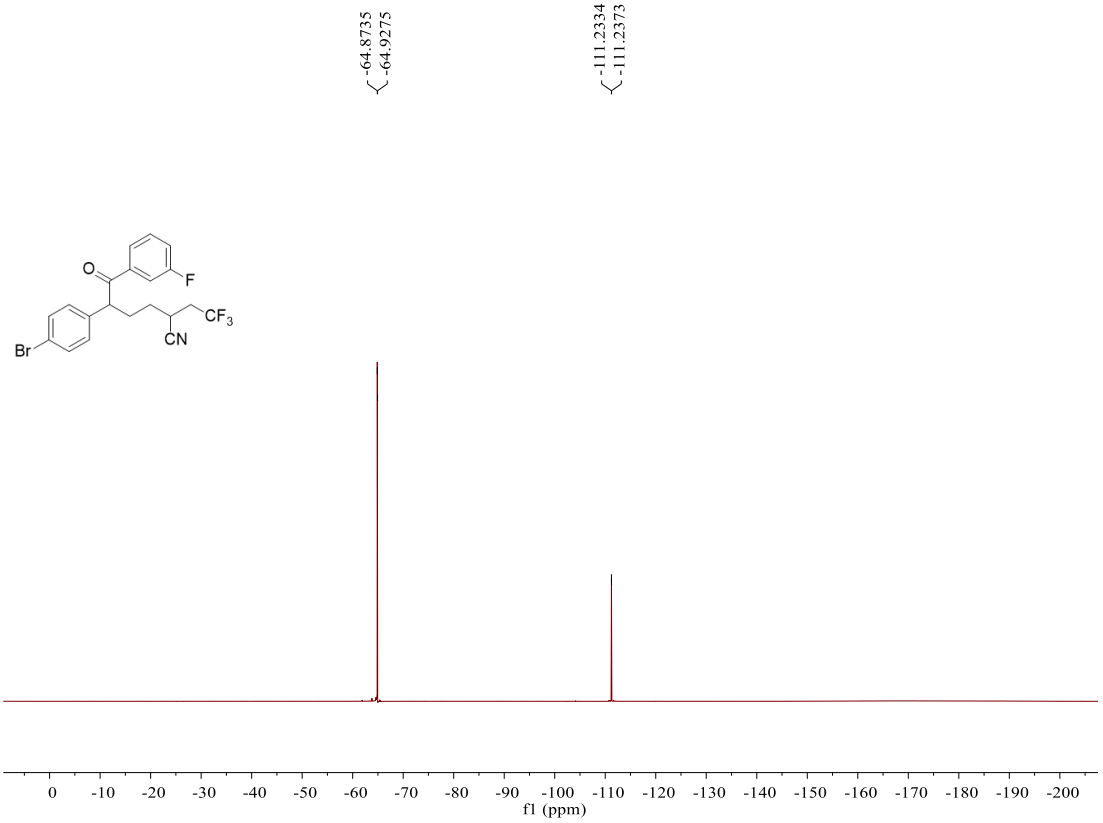

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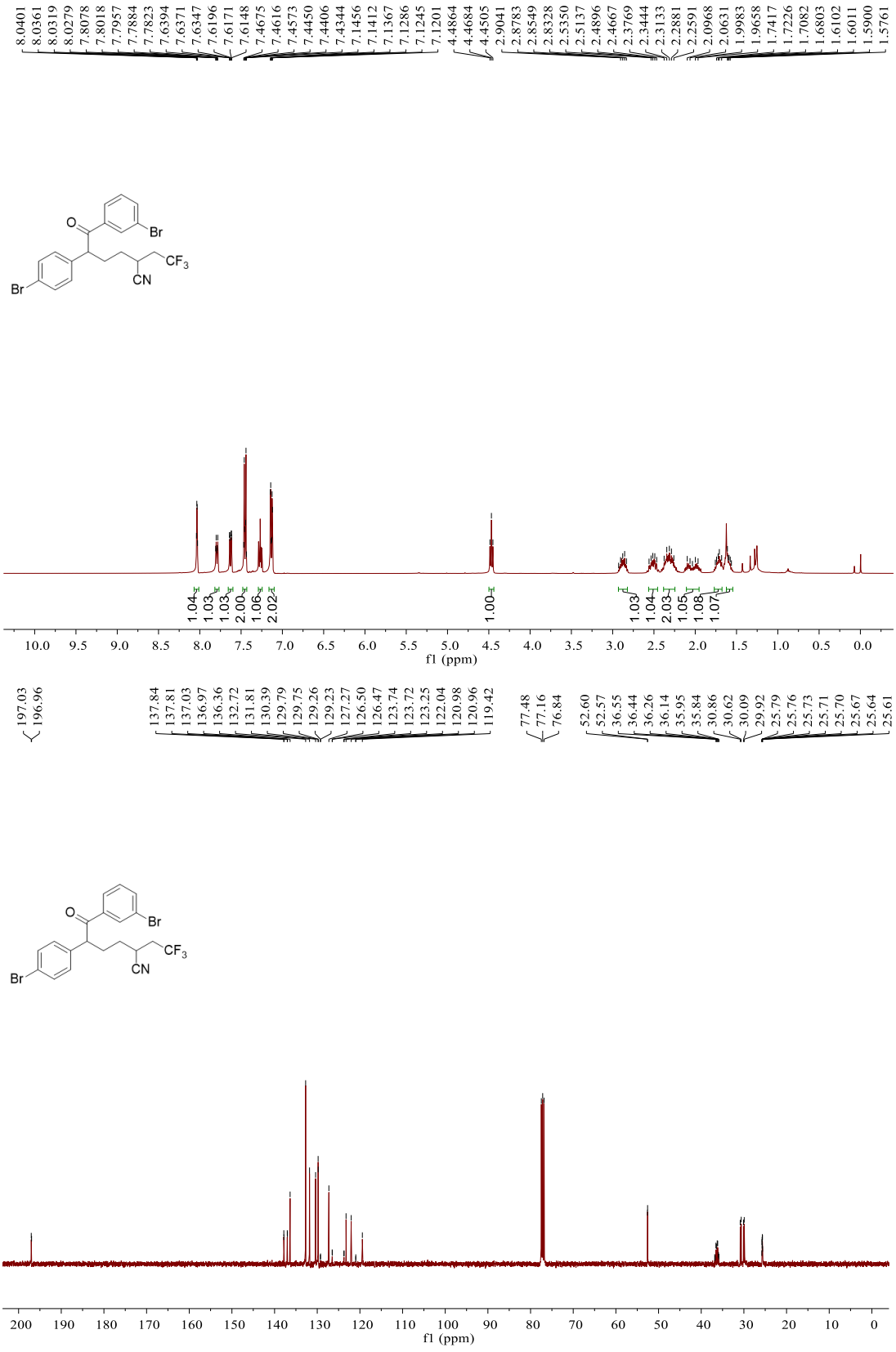

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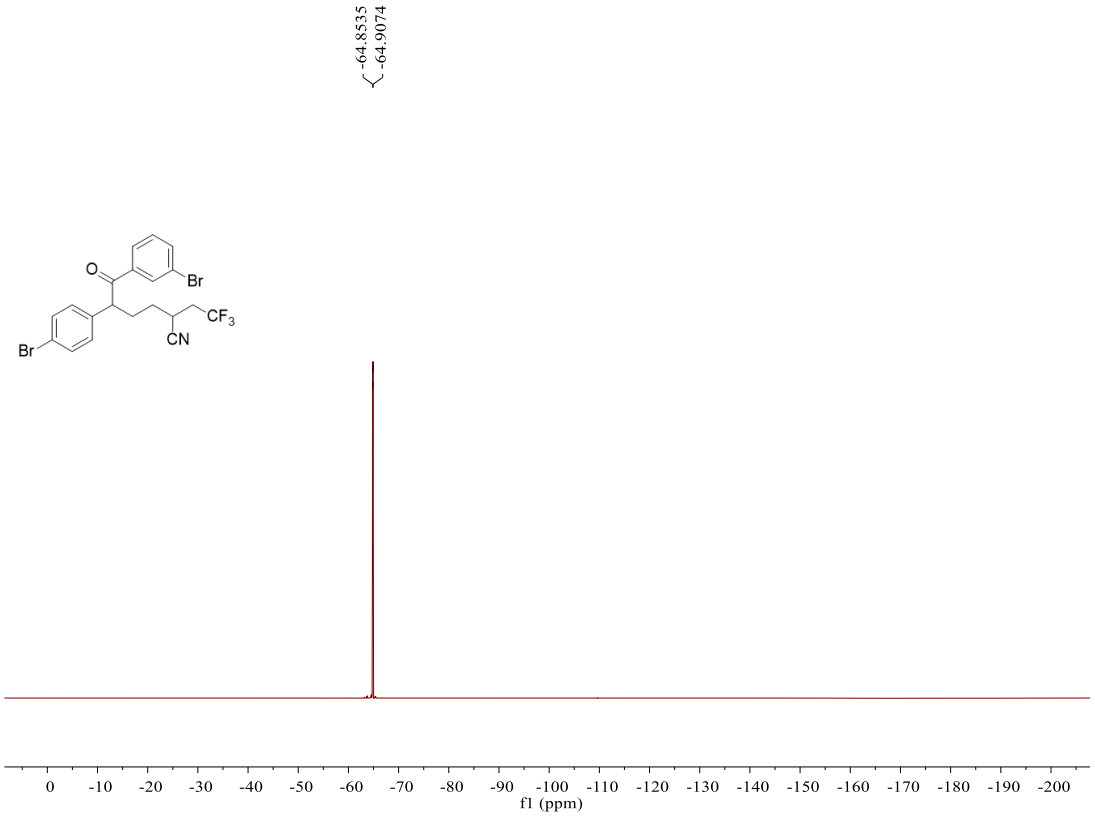

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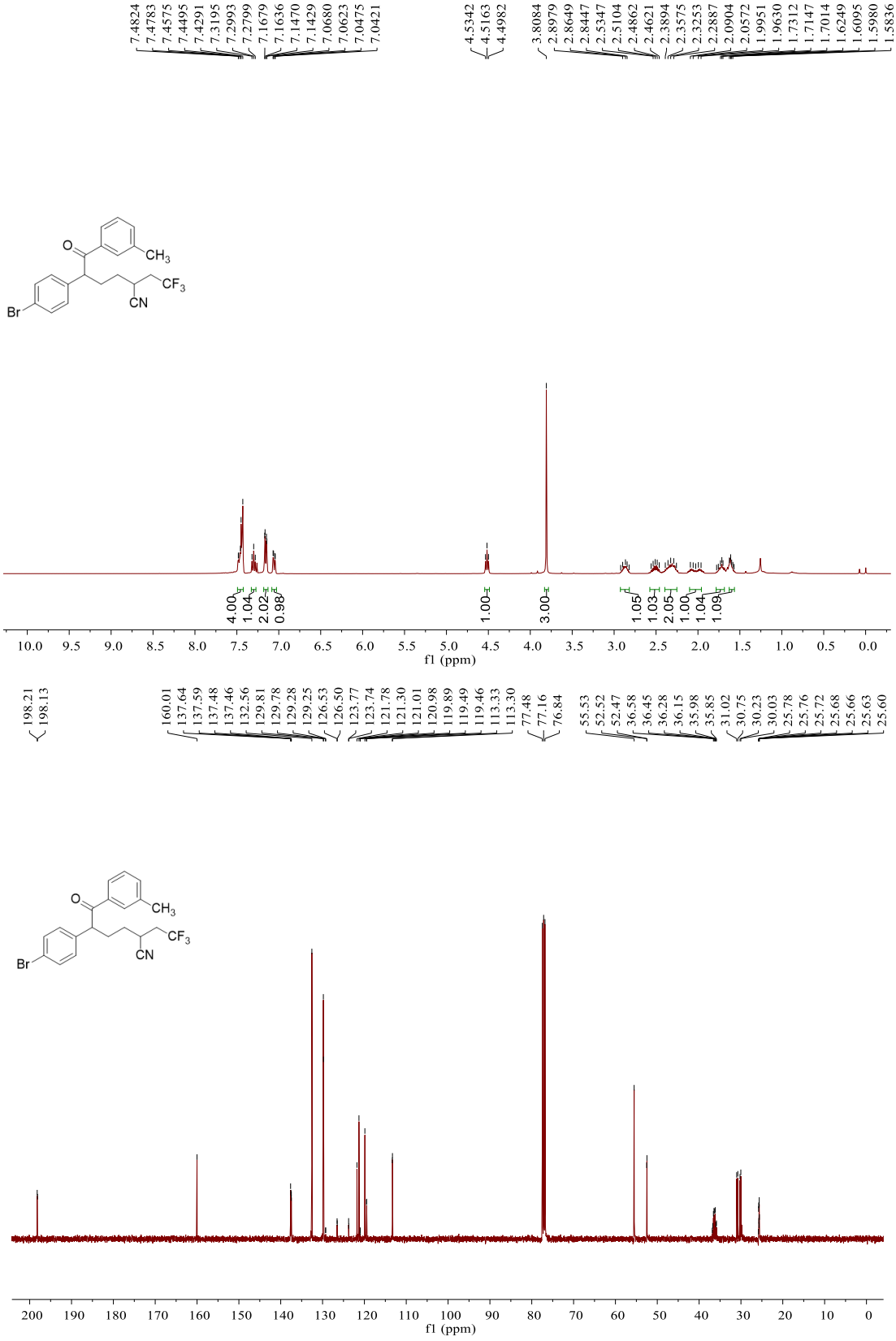

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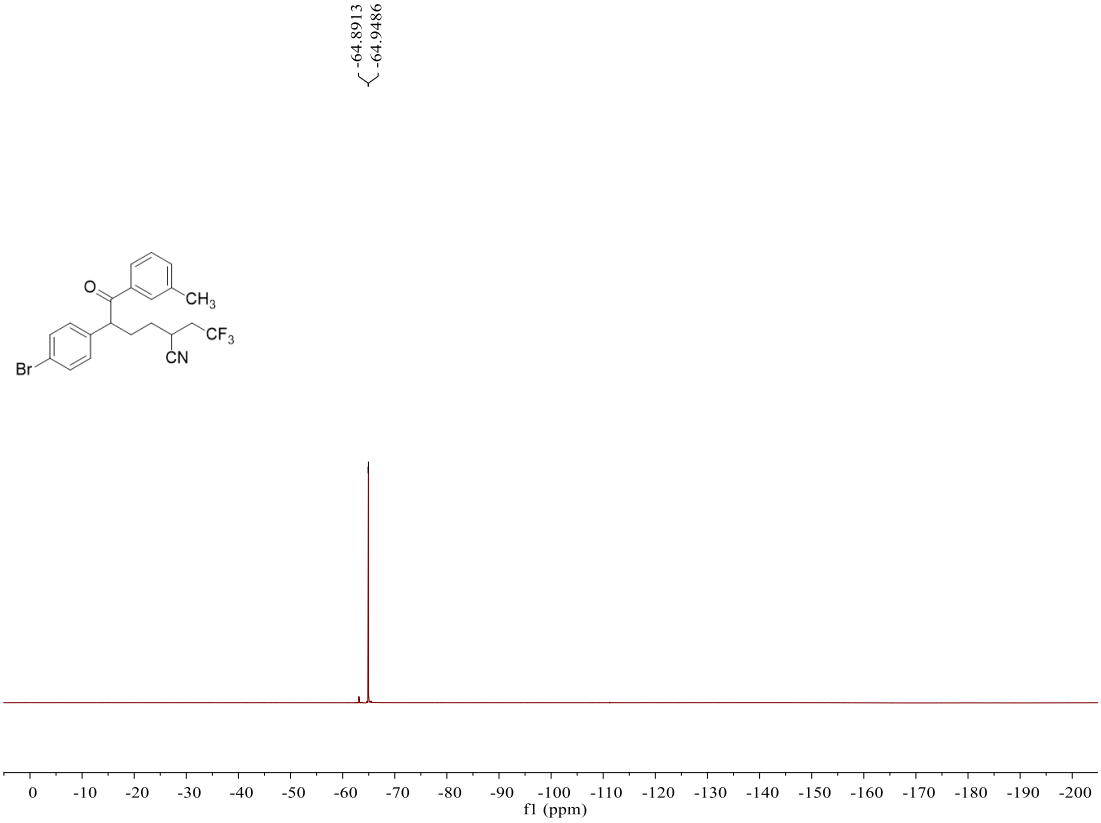

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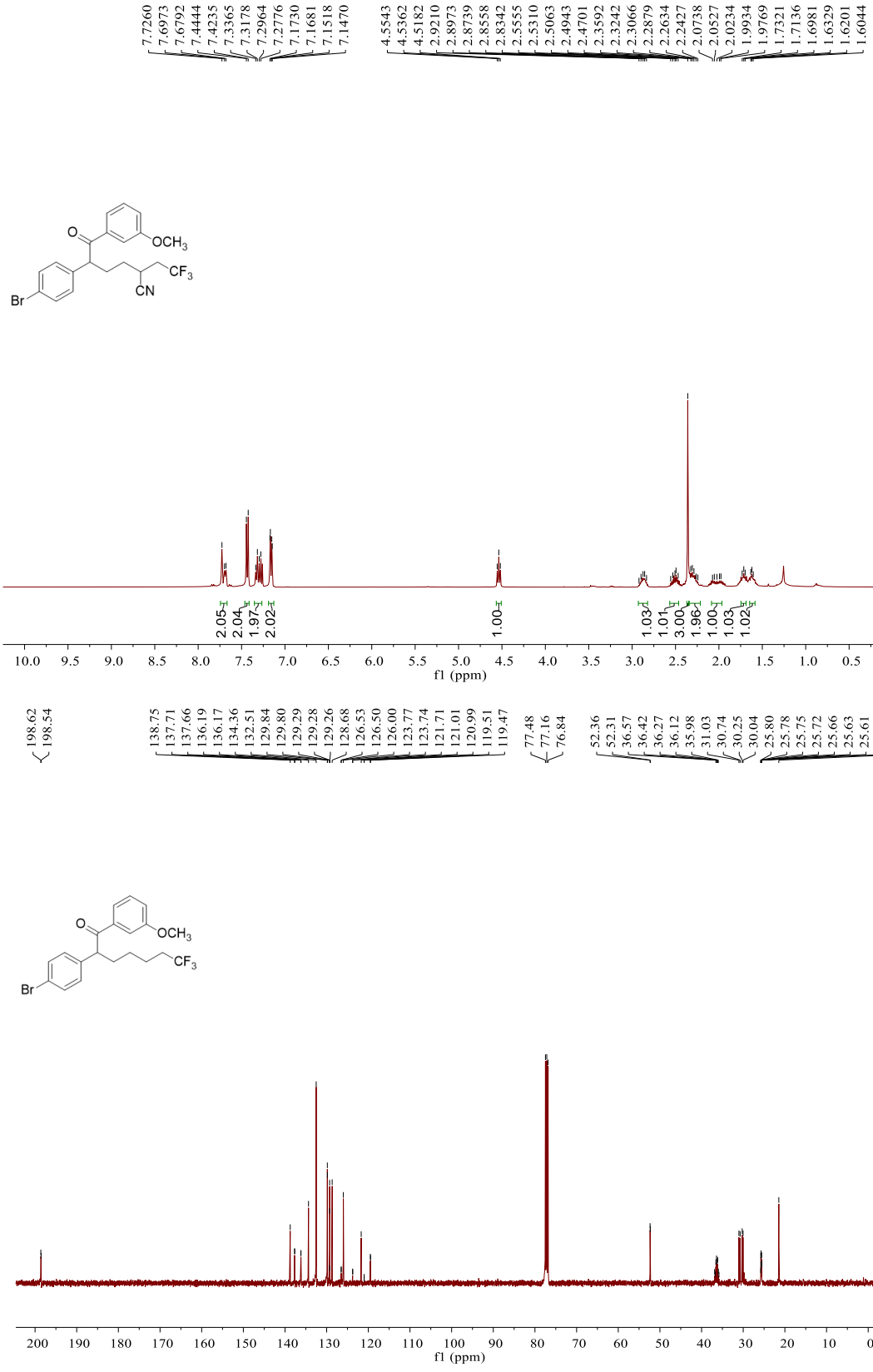

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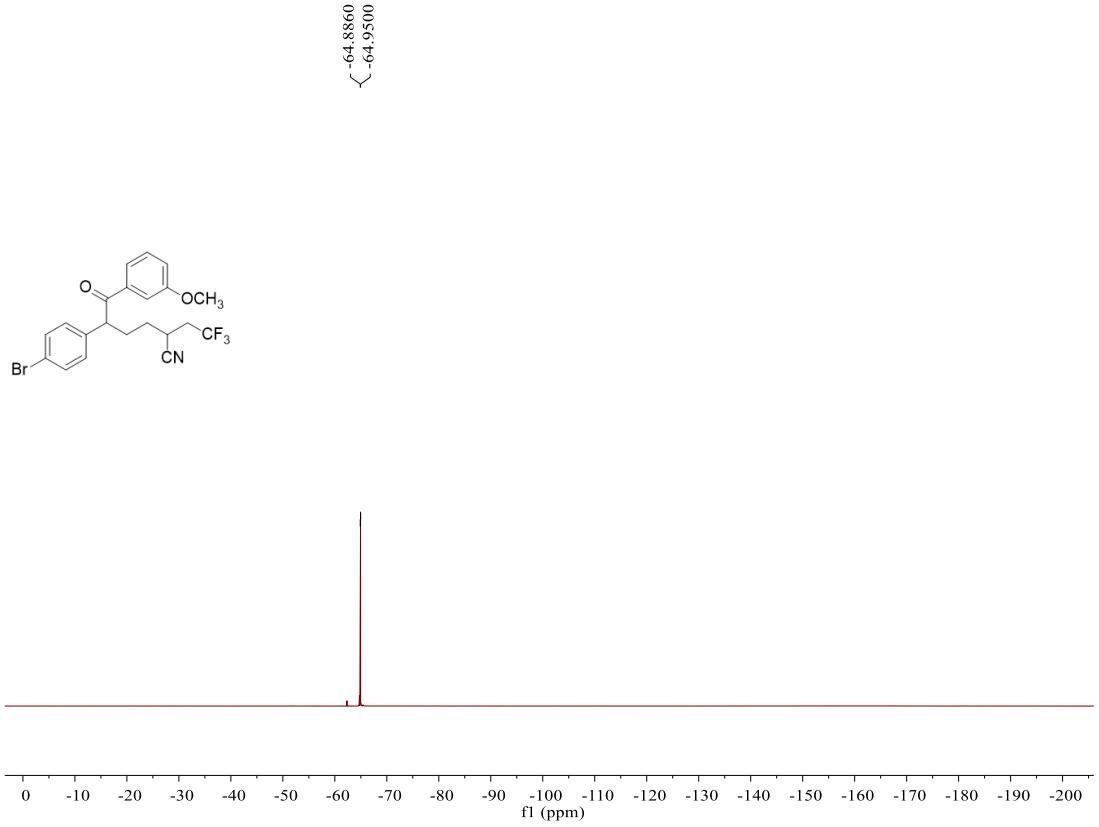

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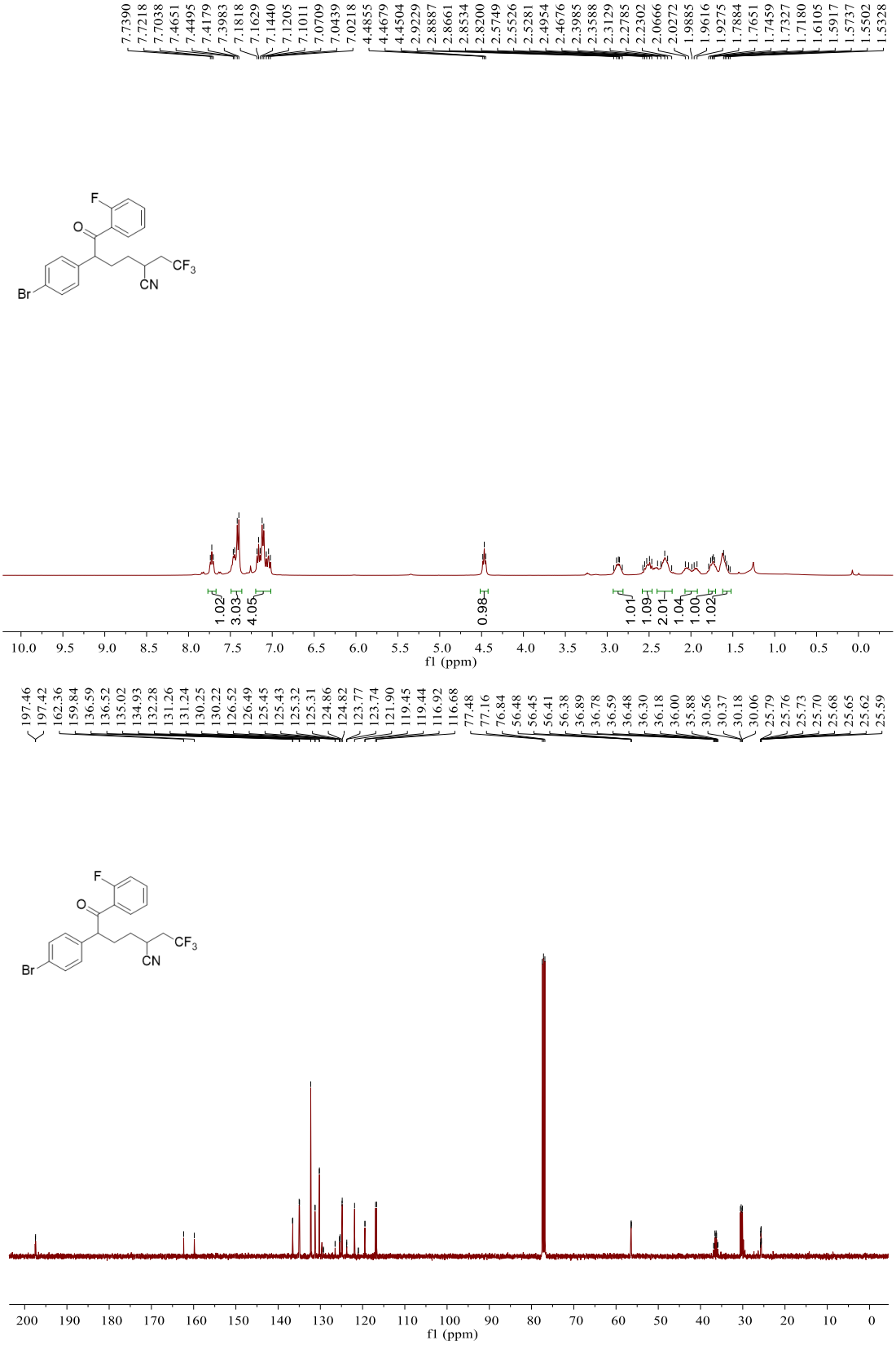

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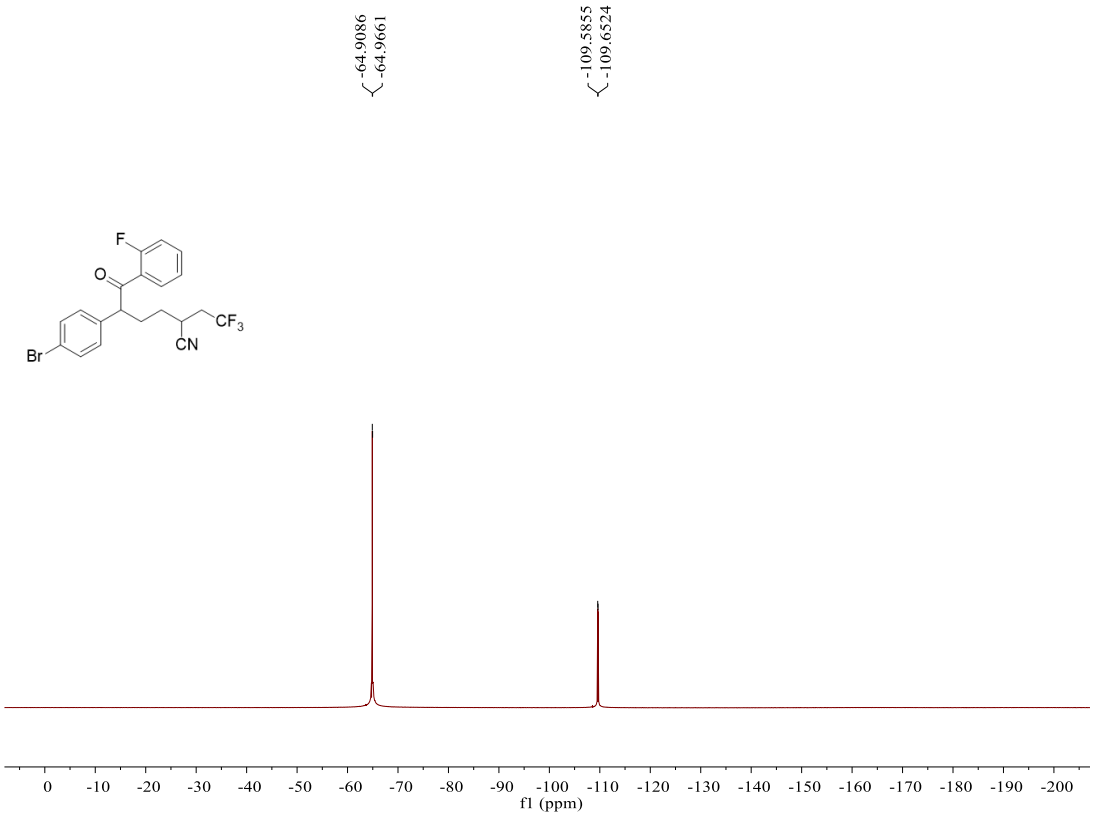

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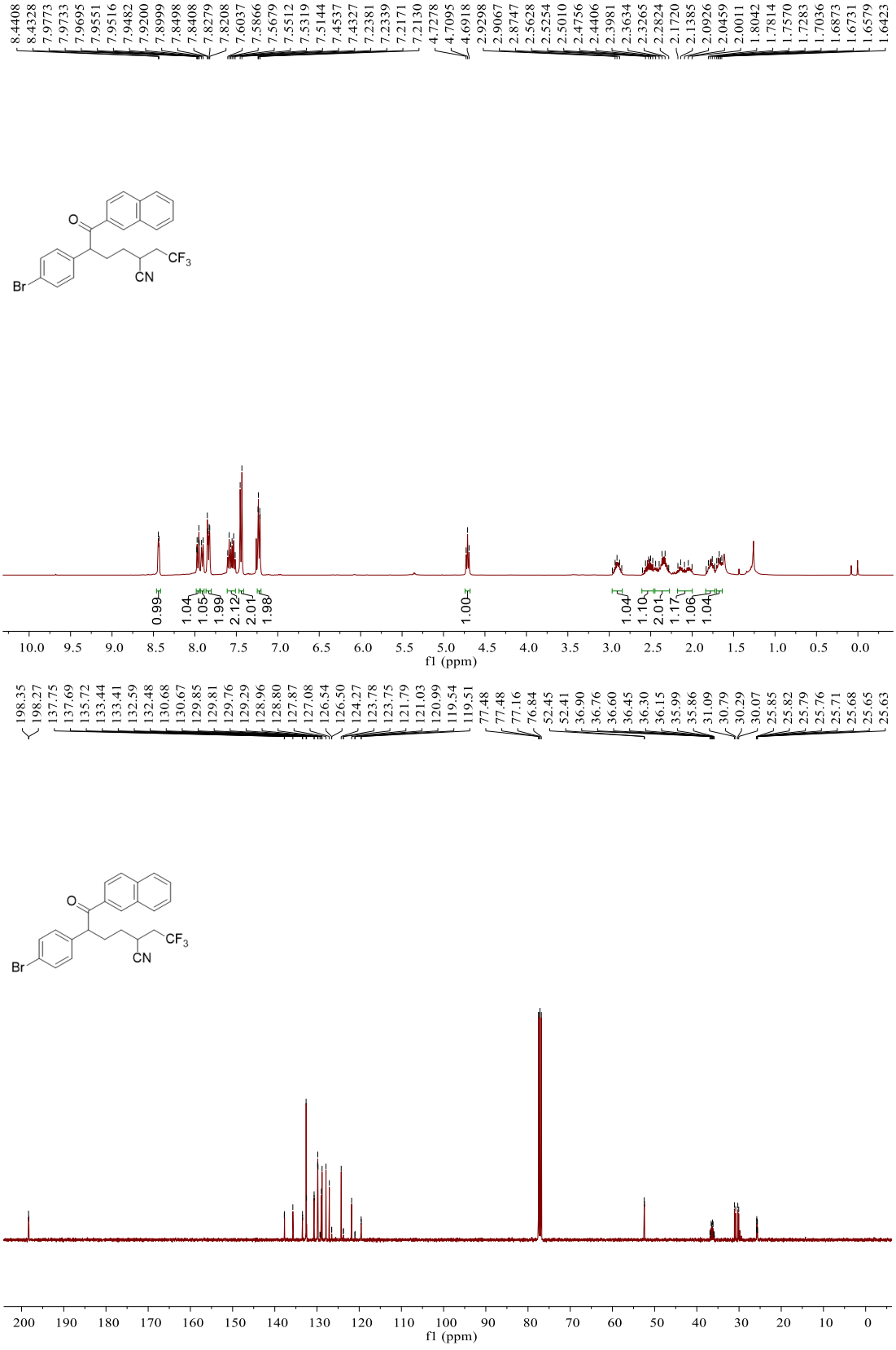
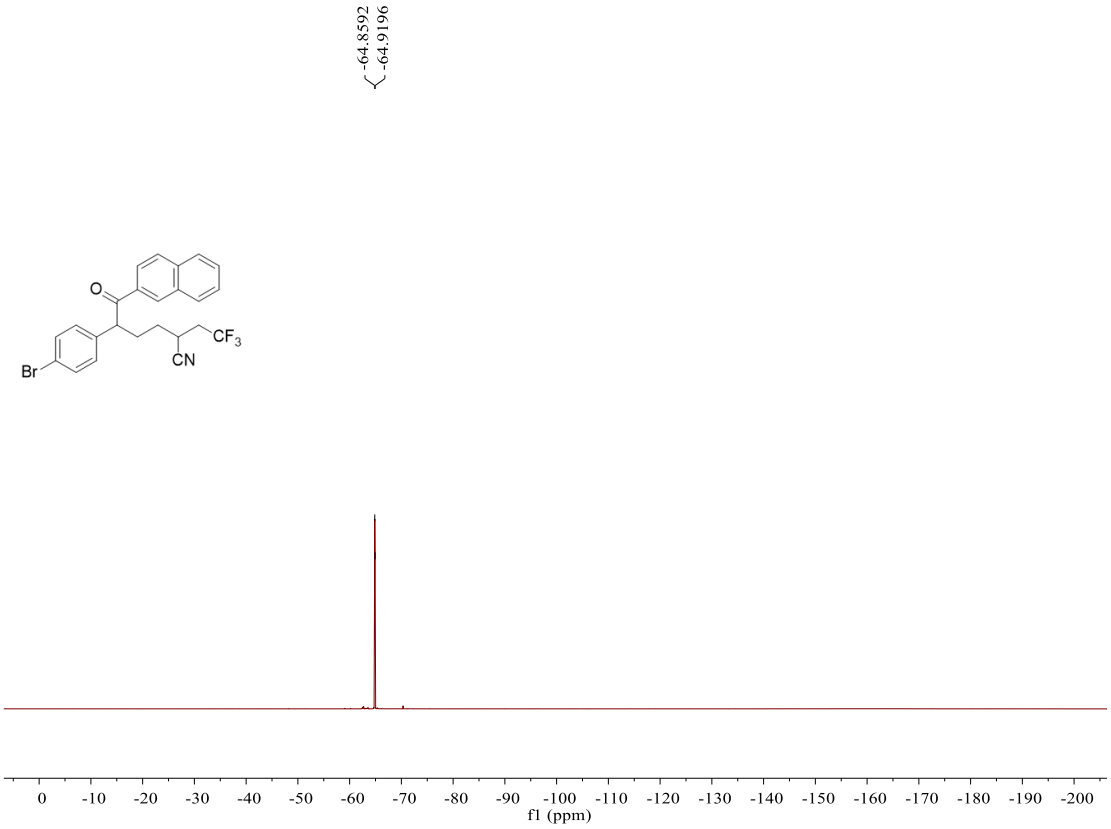


4o ^{19}F NMR (376 MHz, Chloroform-*d*)



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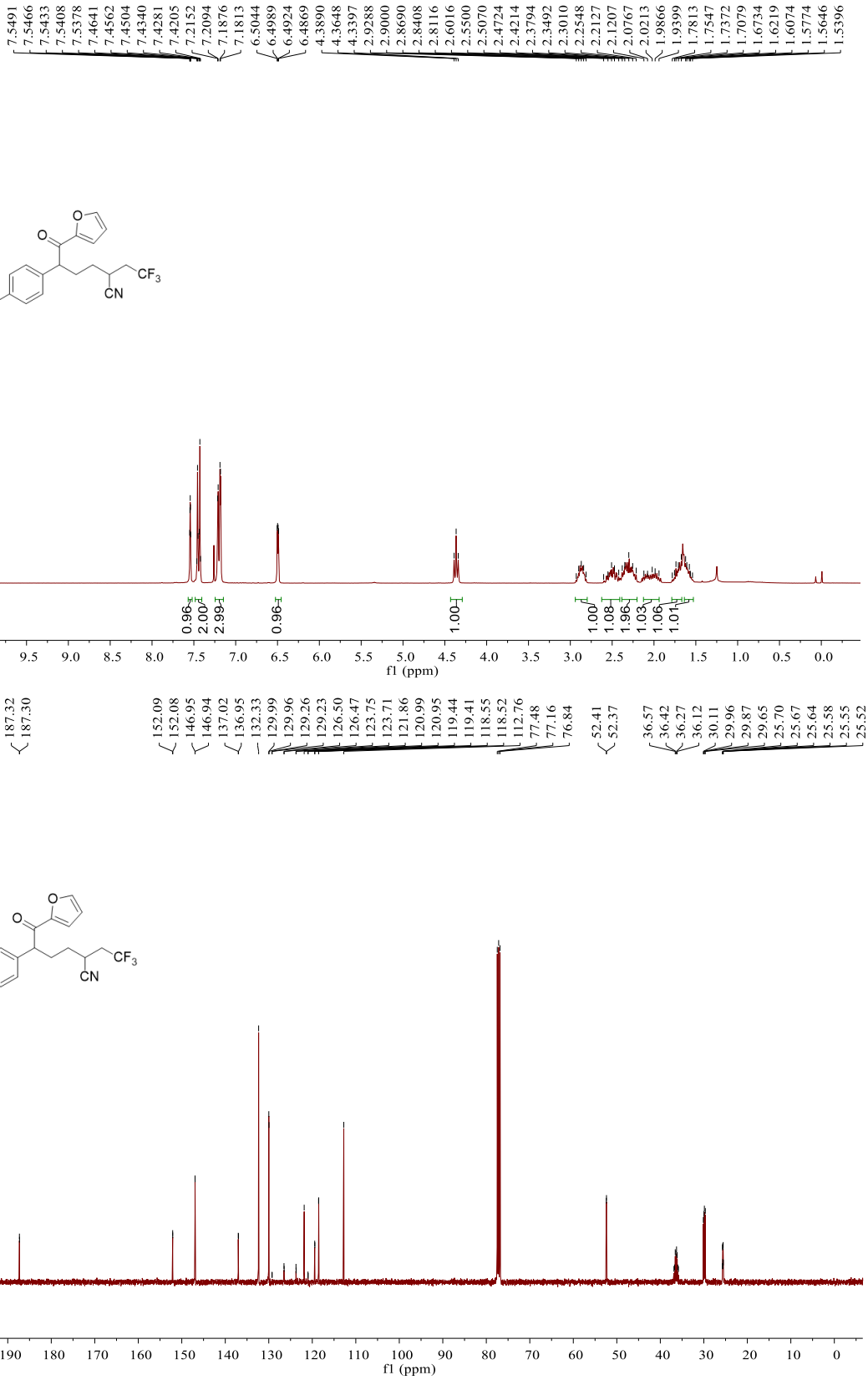

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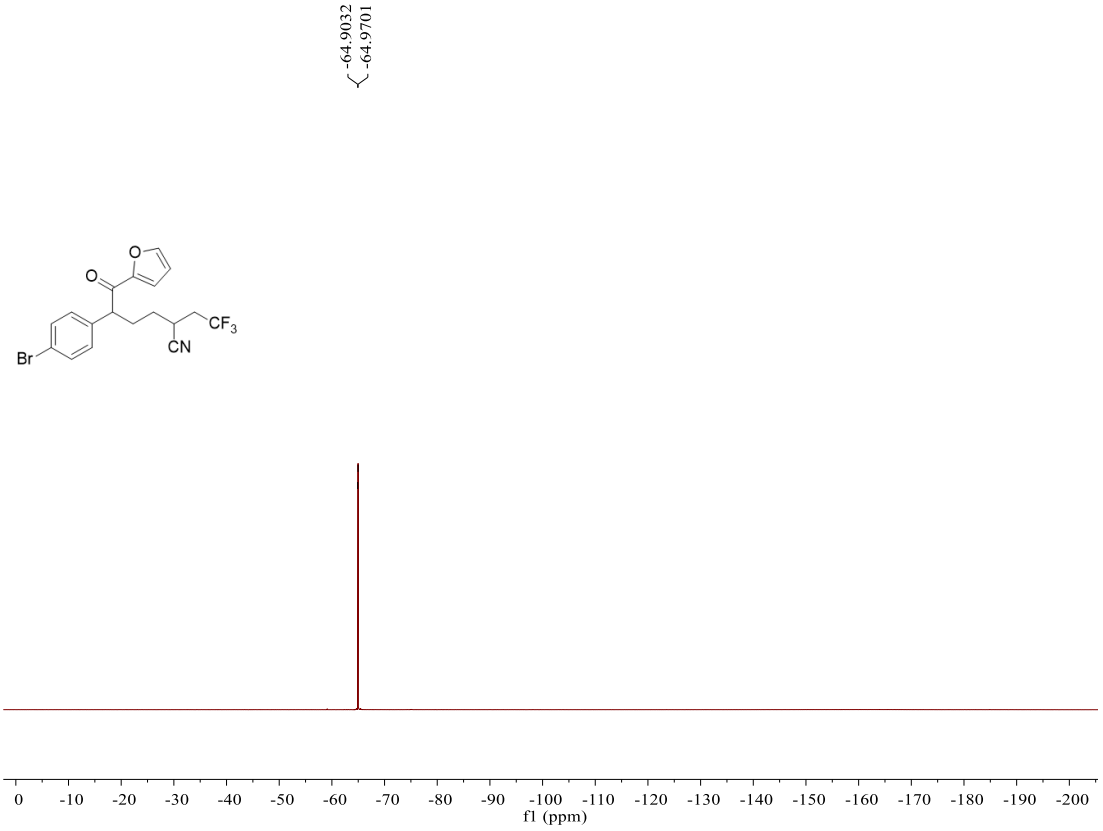

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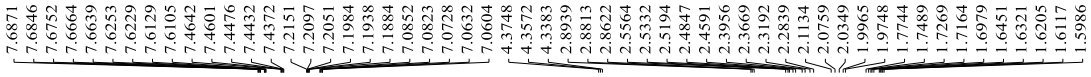
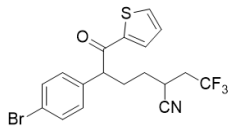
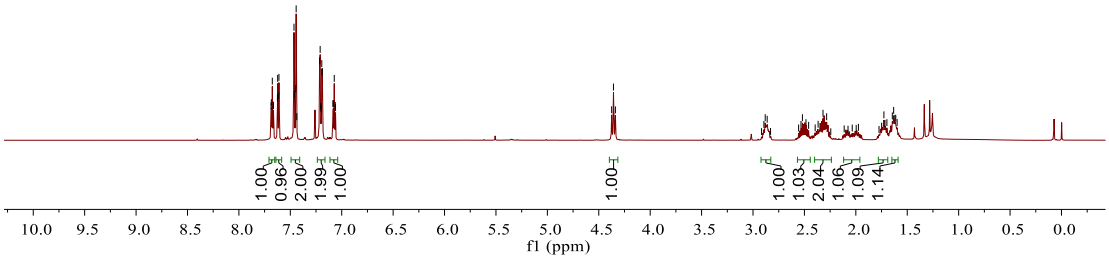
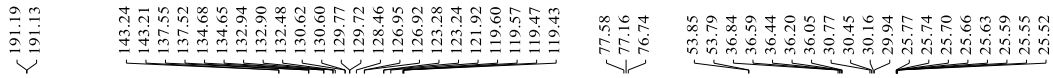
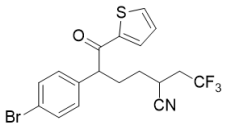
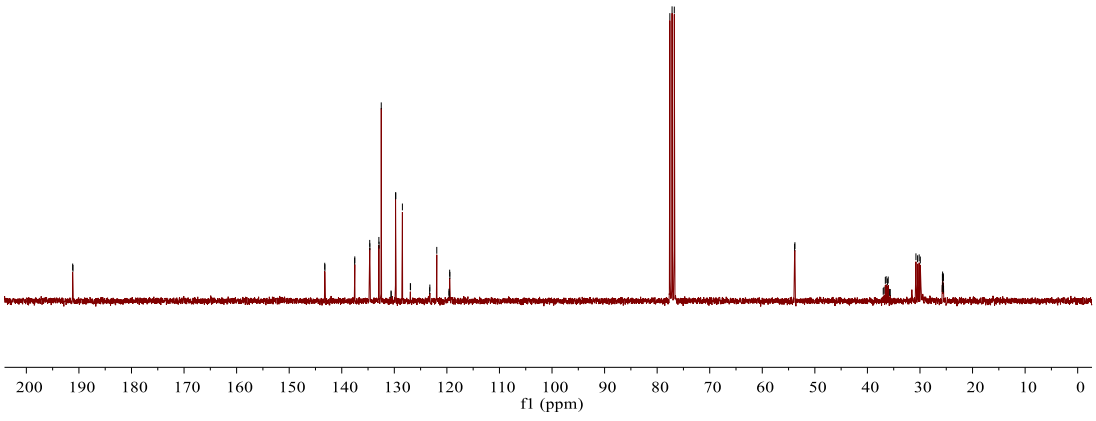




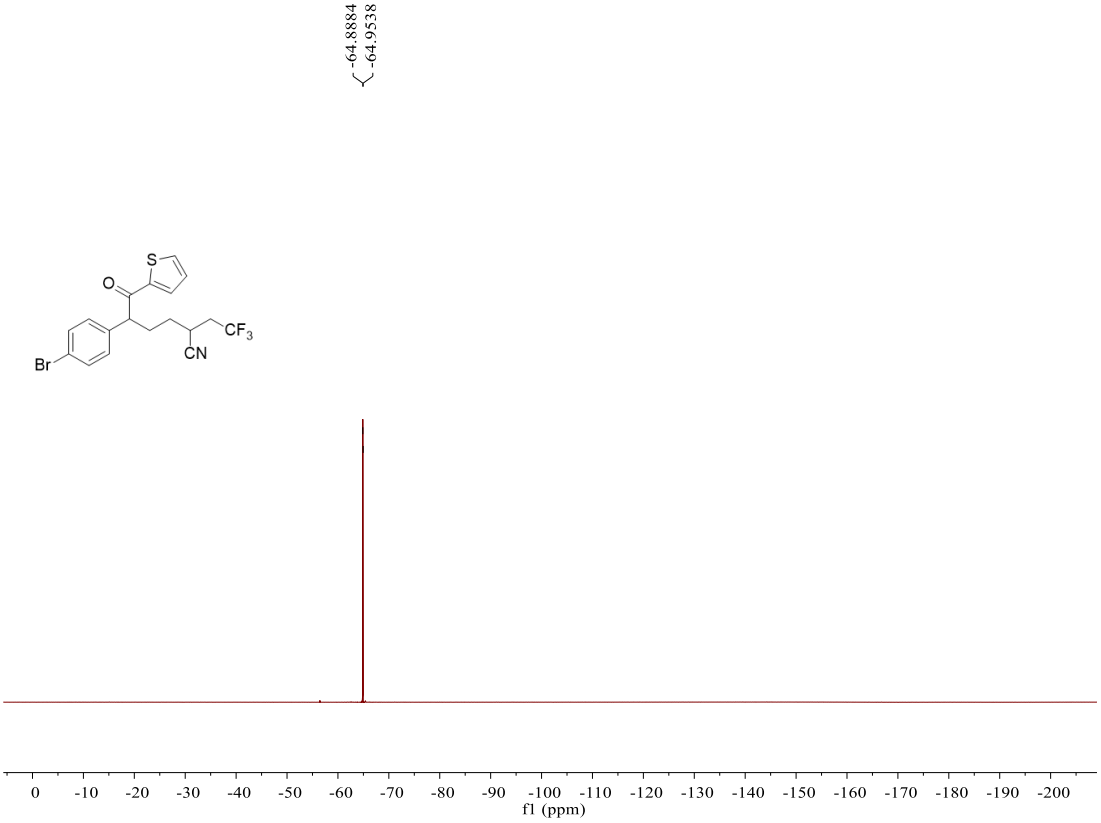




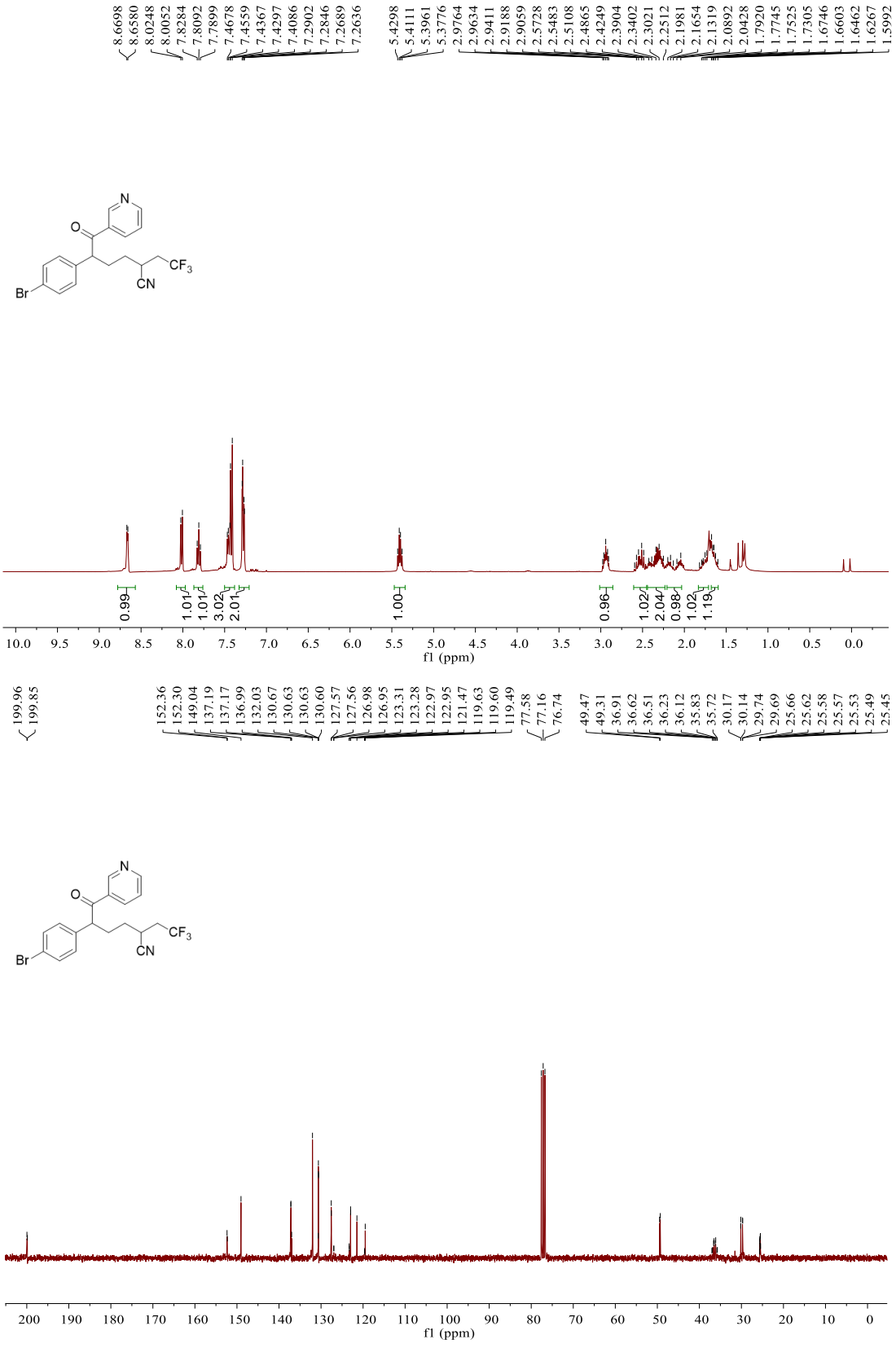




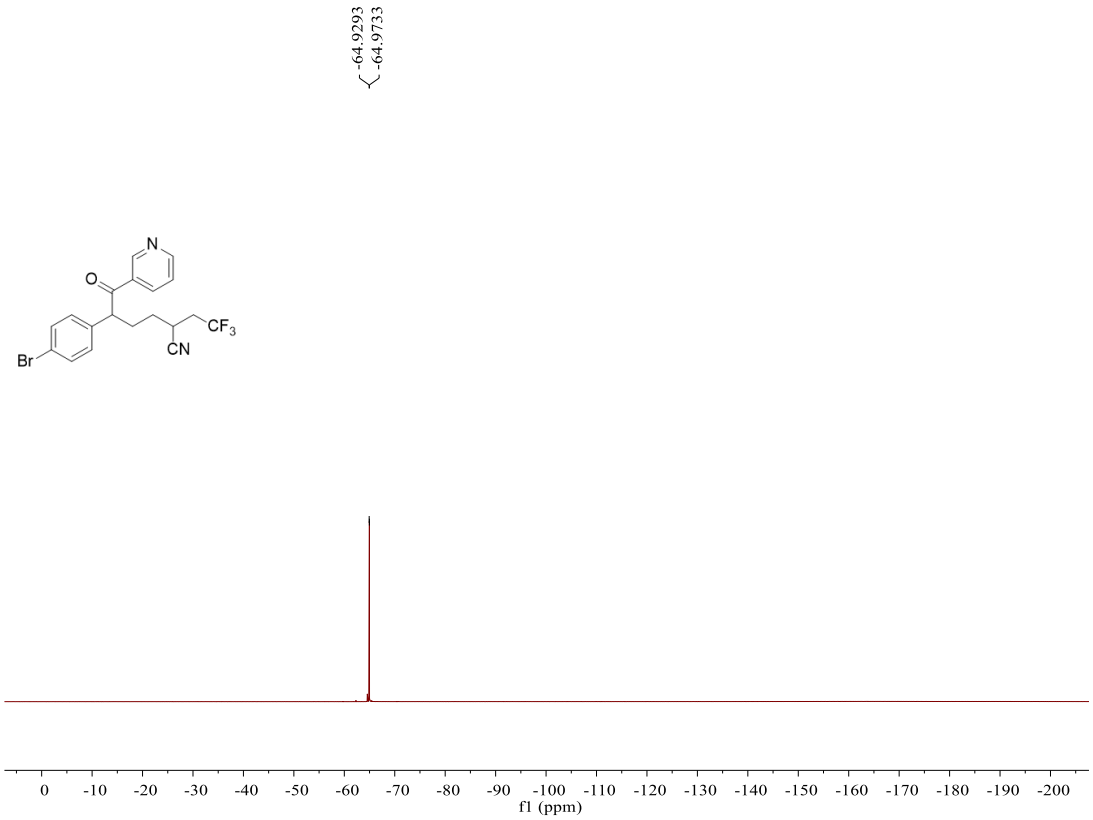
4q ^{19}F NMR (376 MHz, Chloroform-*d*)



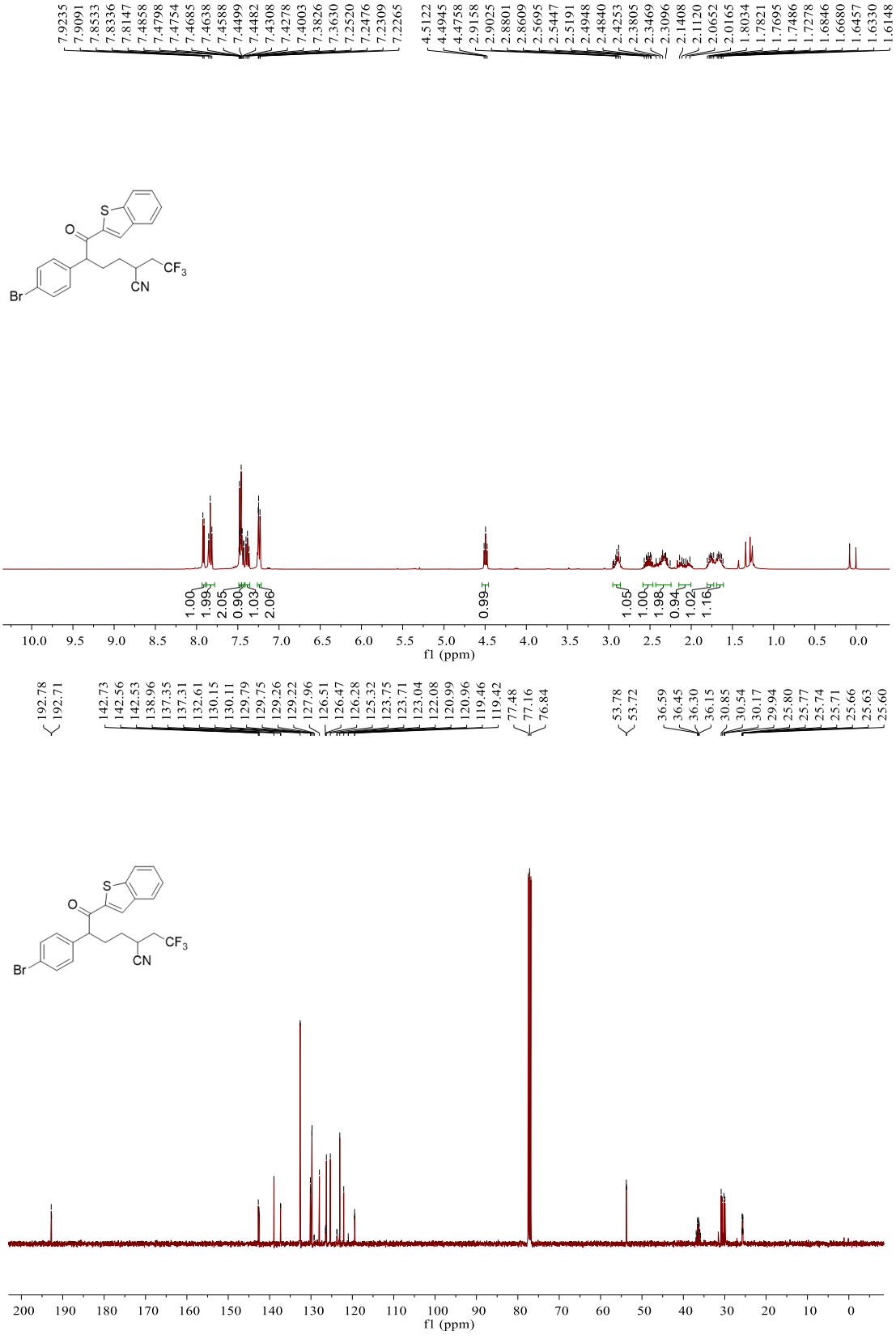
4r ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (75 MHz, Chloroform-*d*)



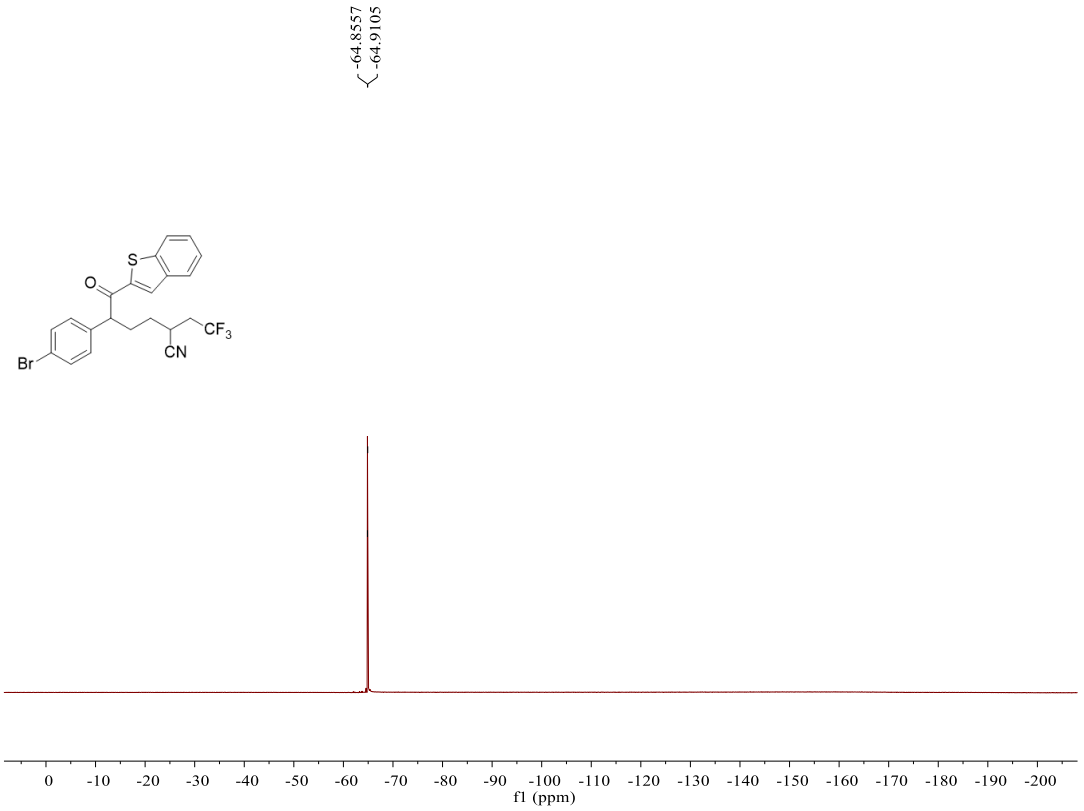
4r ^{19}F NMR (376 MHz, Chloroform-*d*)



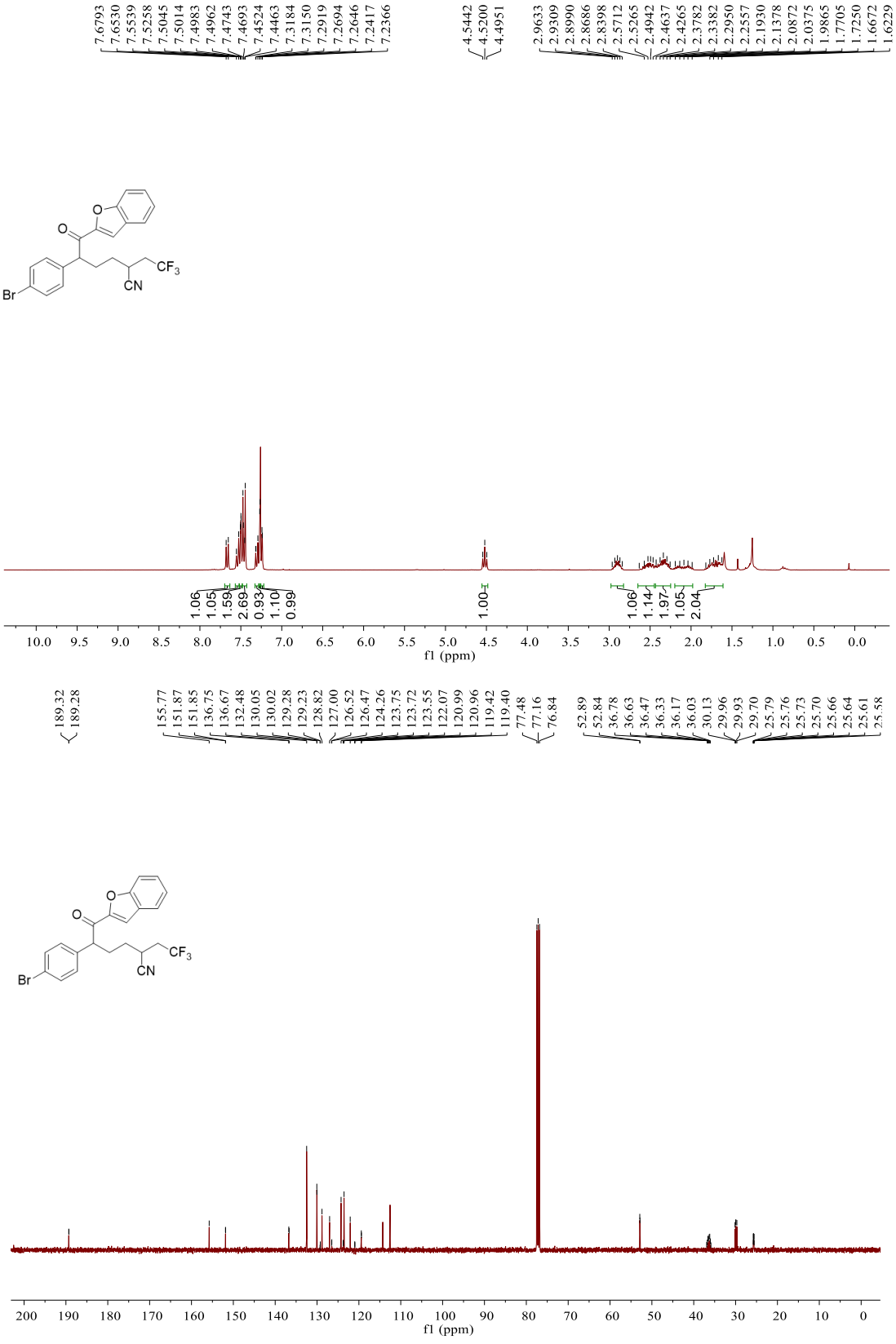
4s ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



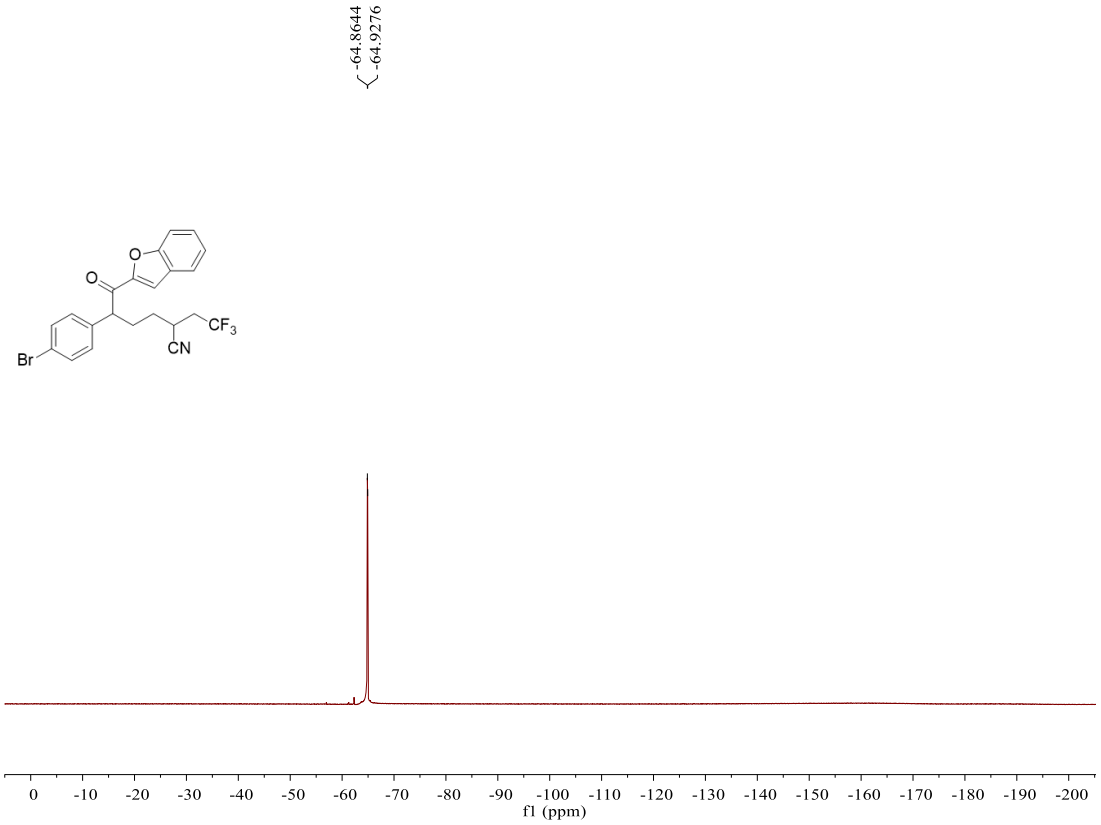
4s ^{19}F NMR (376 MHz, Chloroform-*d*)



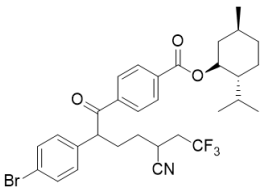
4t ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)

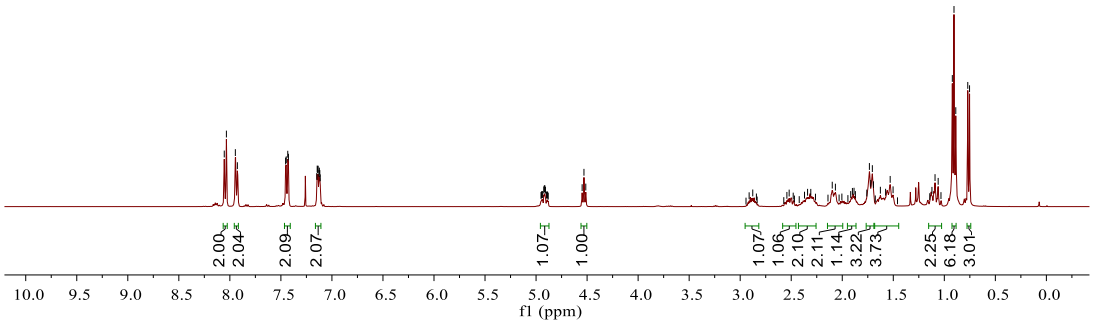


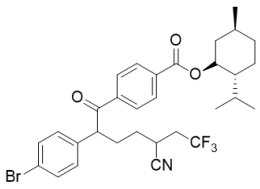
4t ^{19}F NMR (376 MHz, Chloroform-*d*)

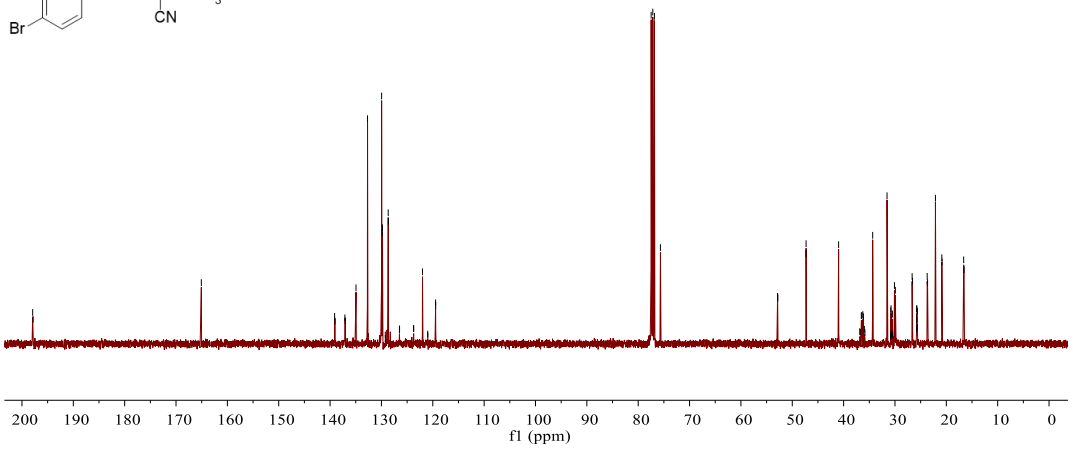


4u ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)

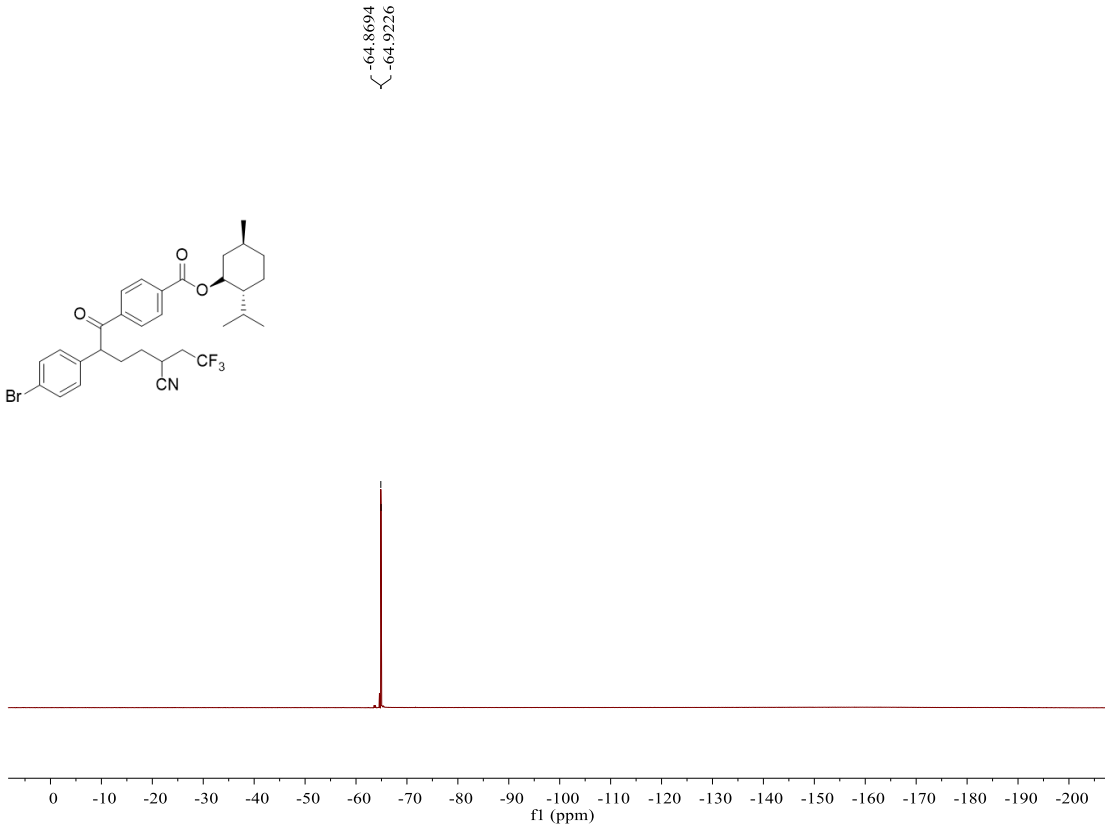




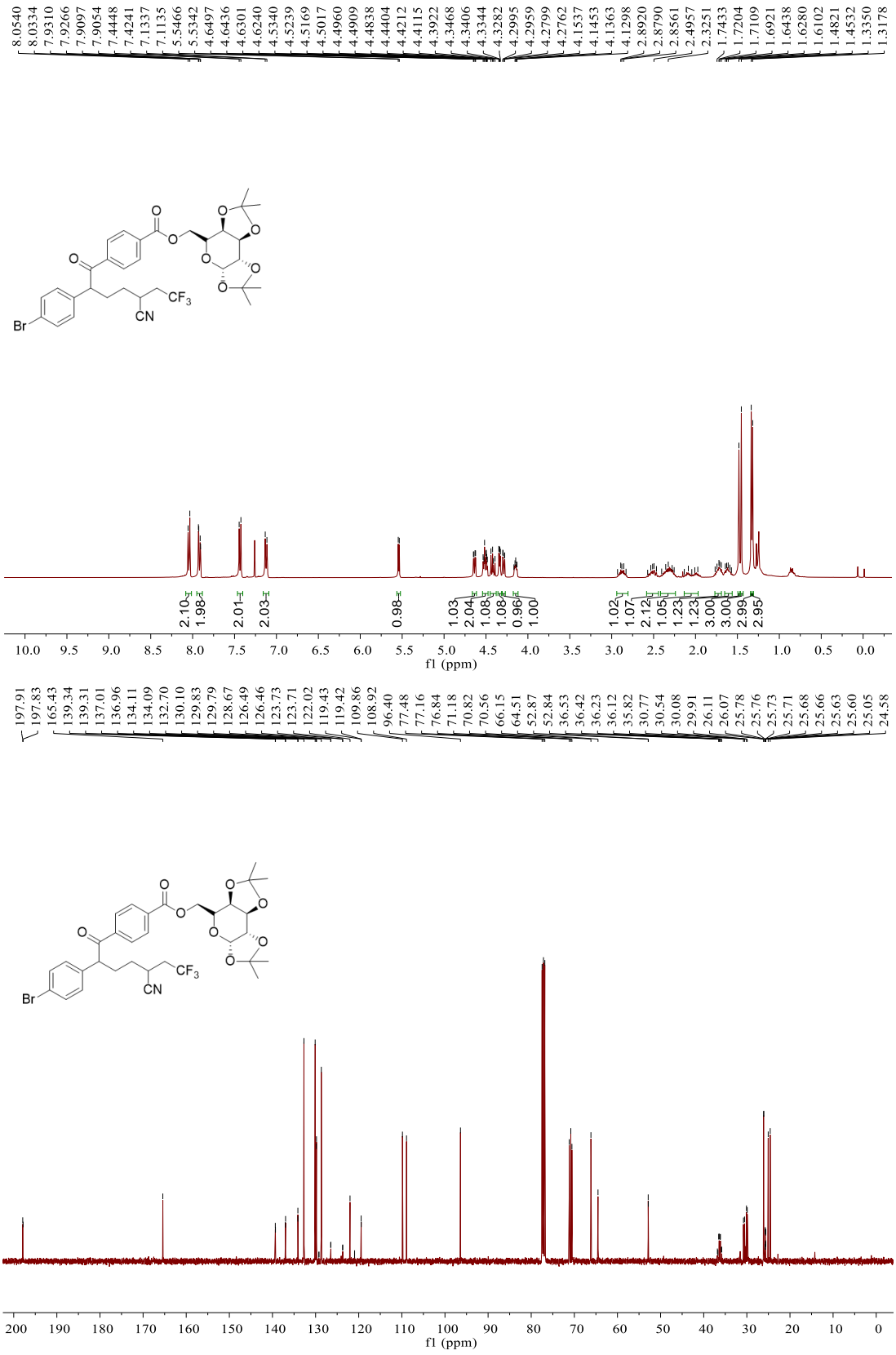




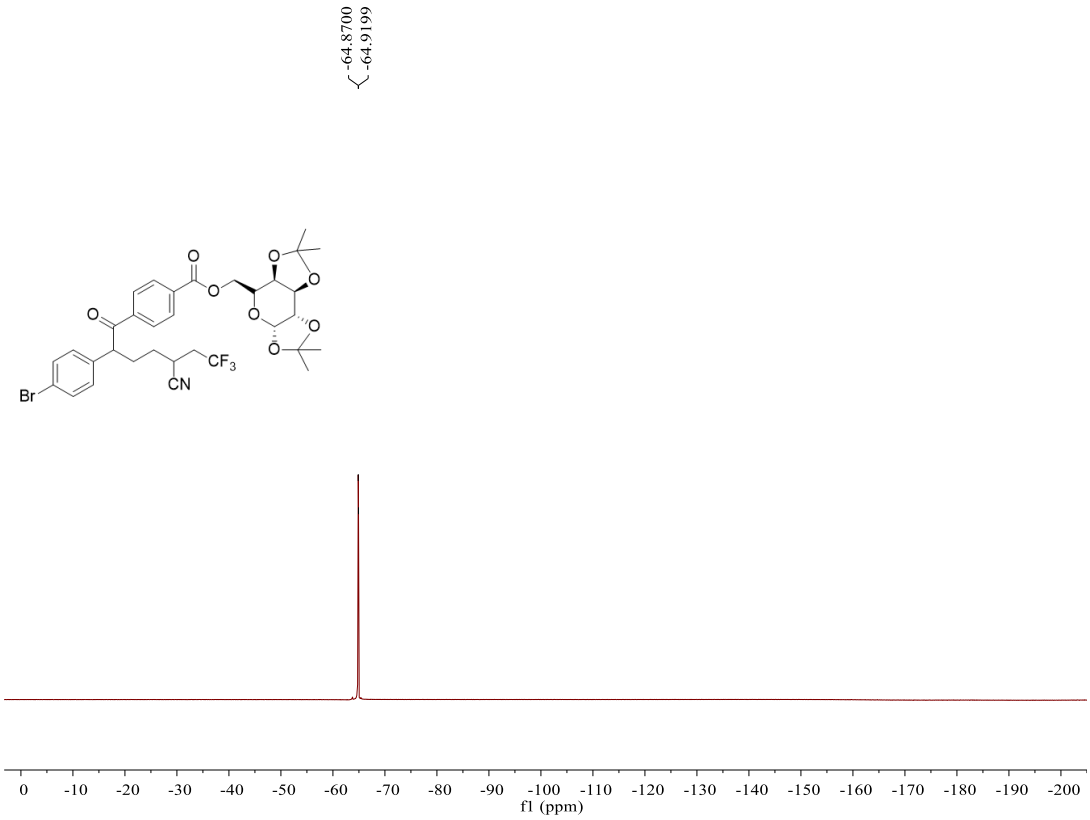
4u ^{19}F NMR (376 MHz, Chloroform-*d*)



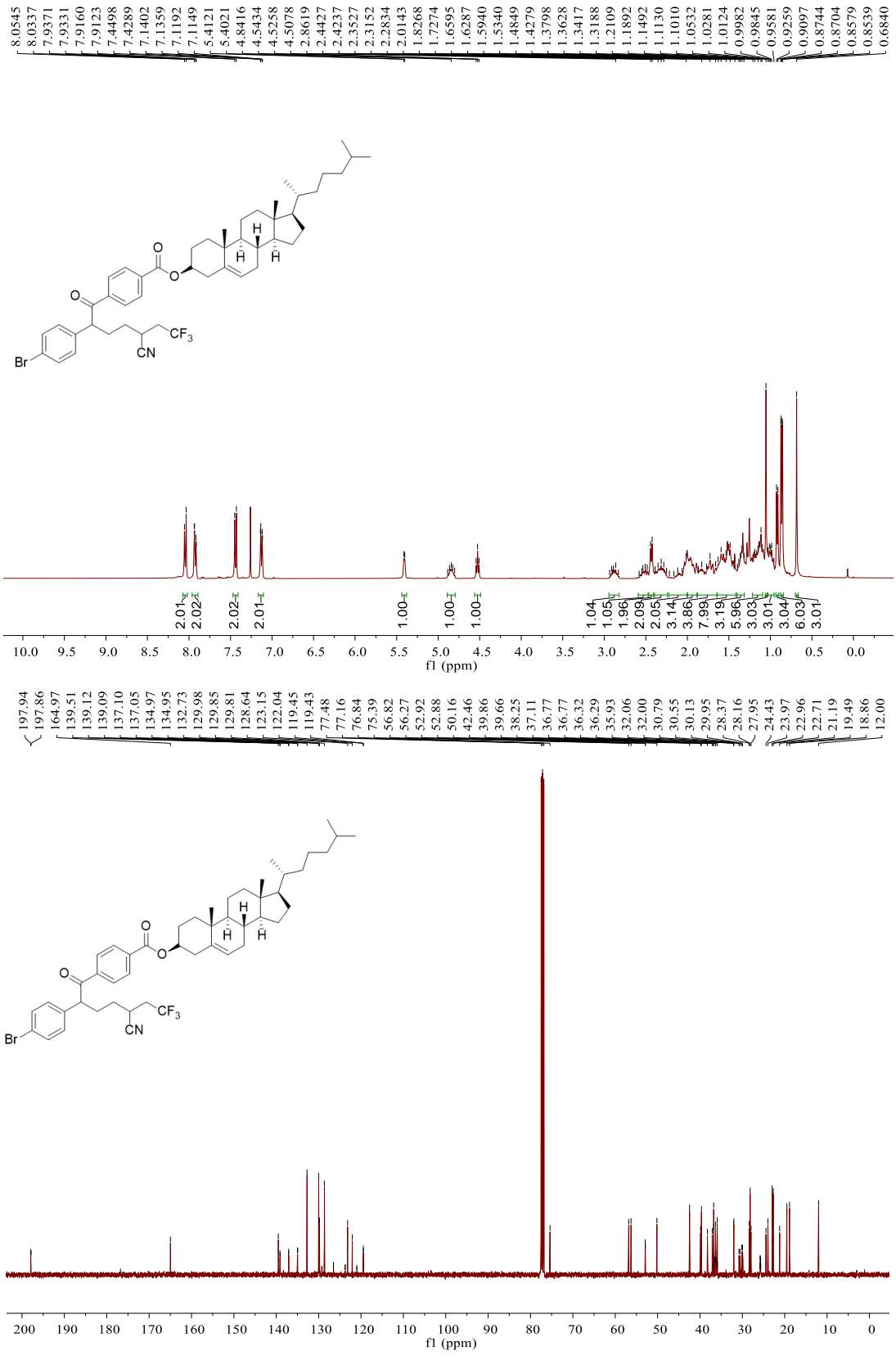
4v ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



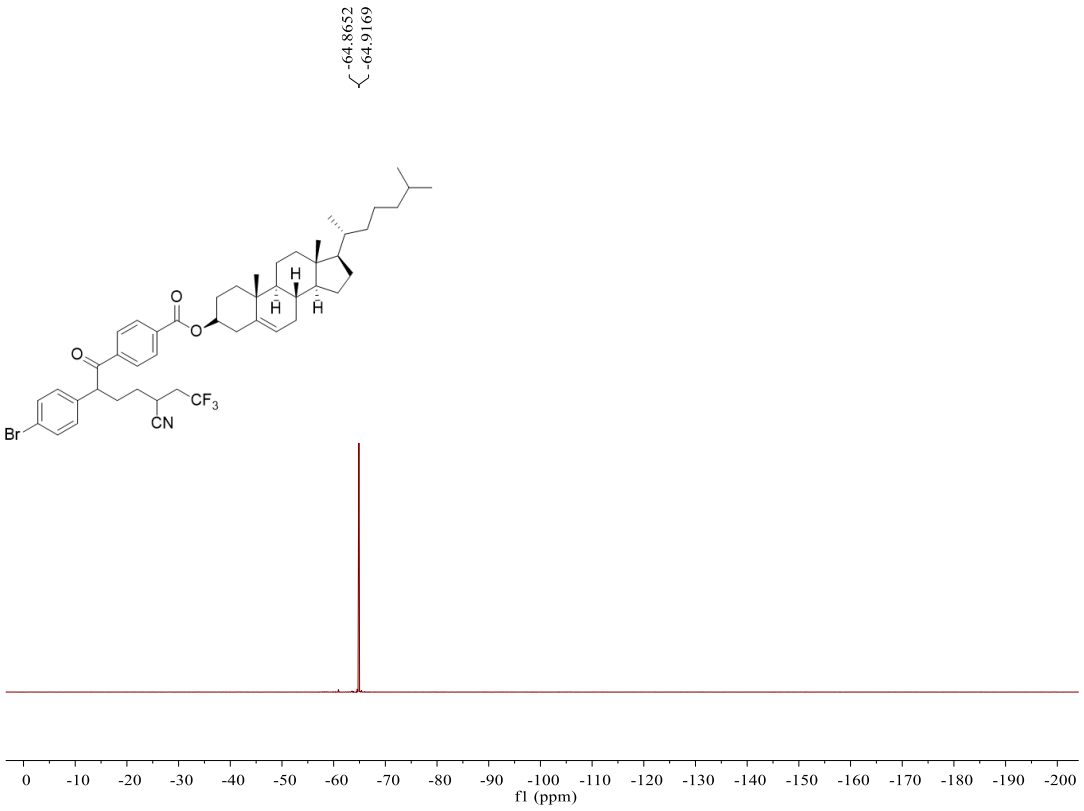
4v ^{19}F NMR (376 MHz, Chloroform-*d*)



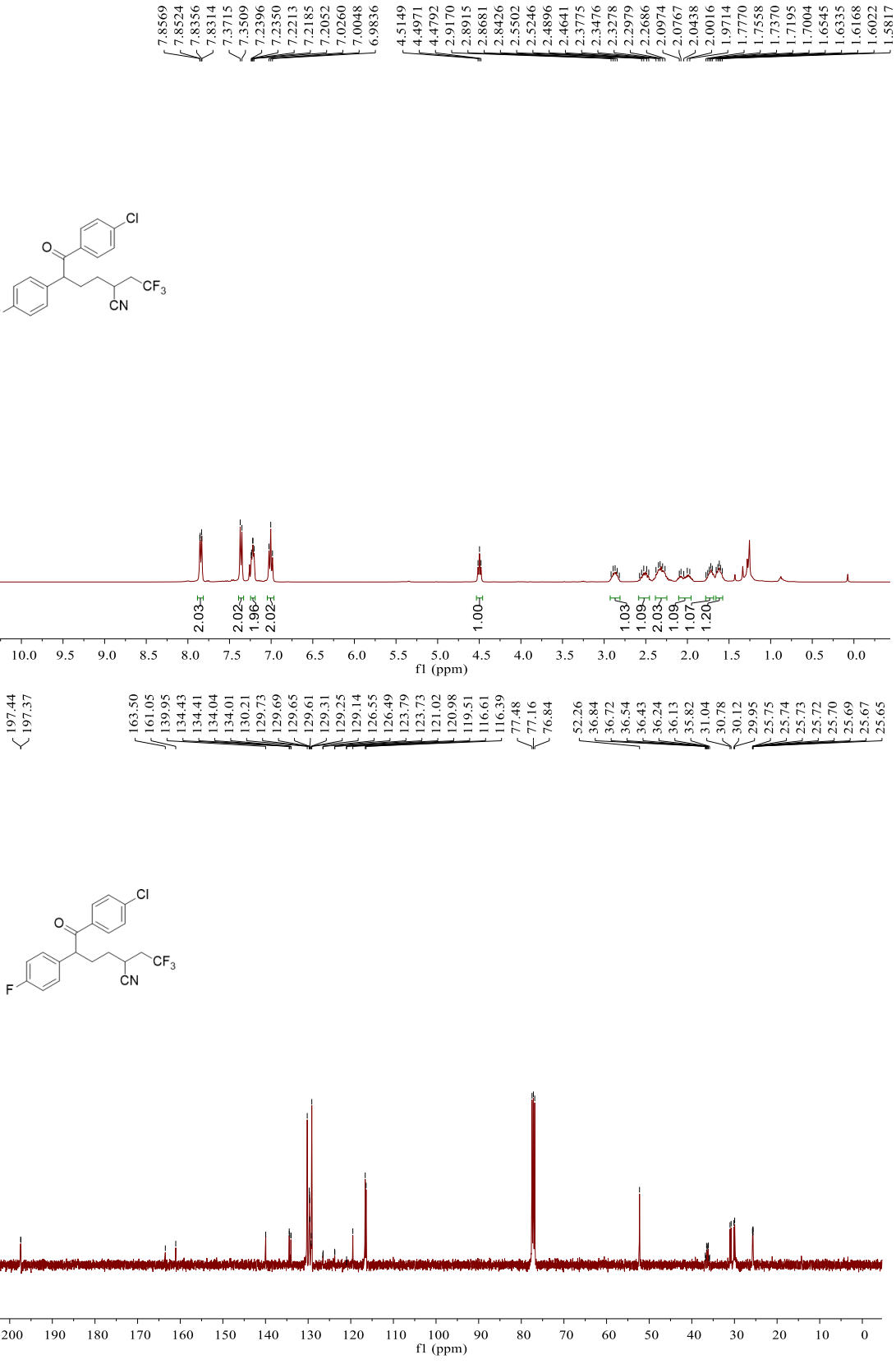
4w ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



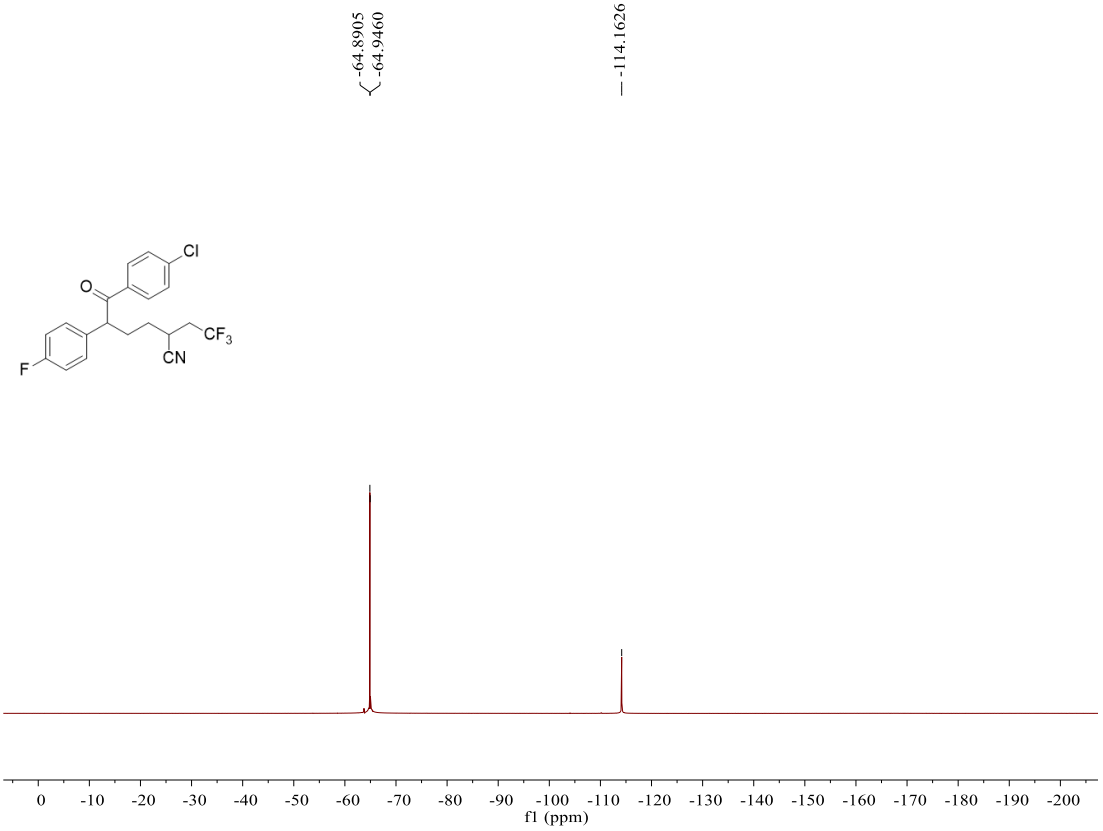
4w ^{19}F NMR (376 MHz, Chloroform-*d*)



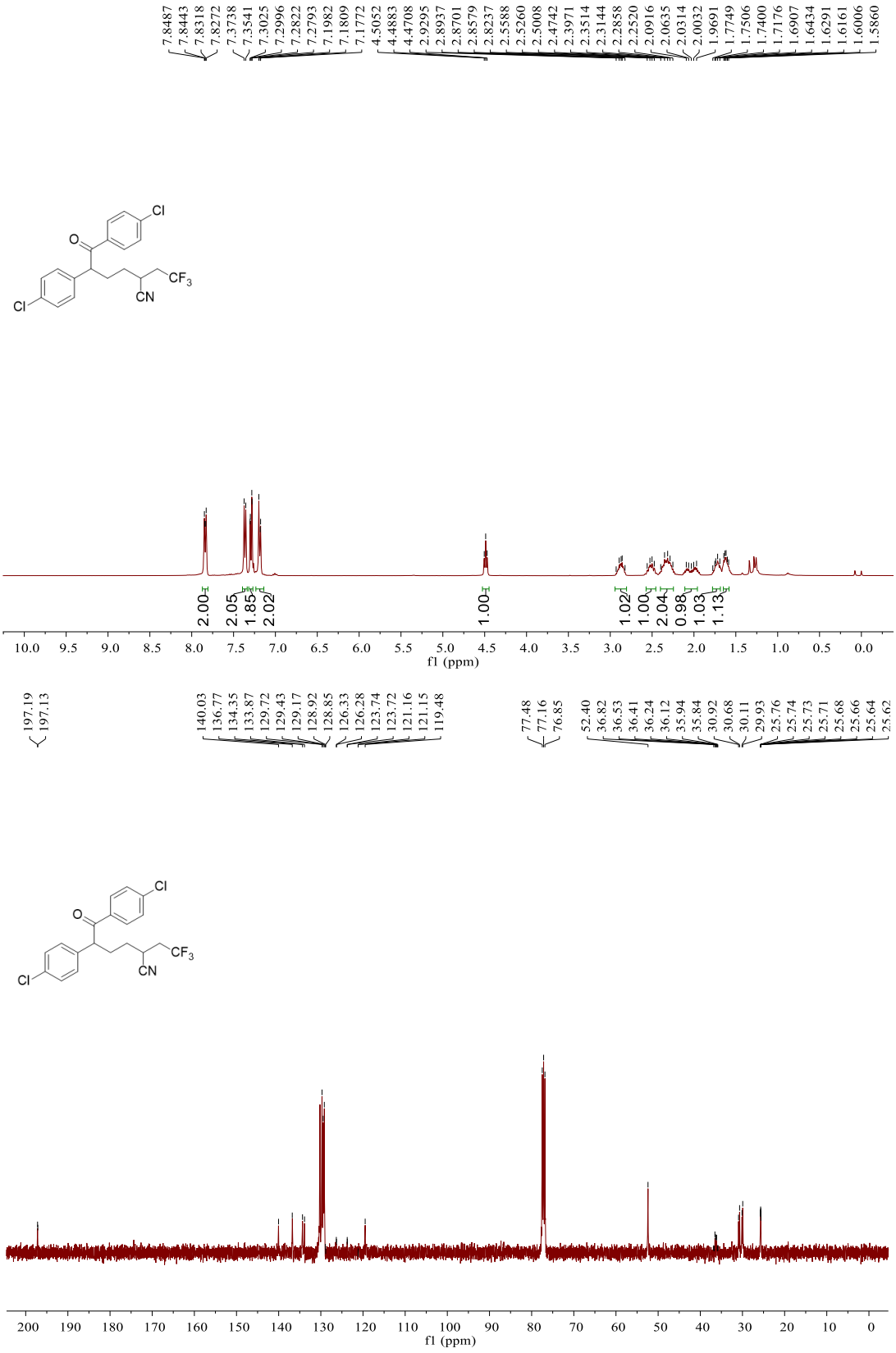
4aa ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



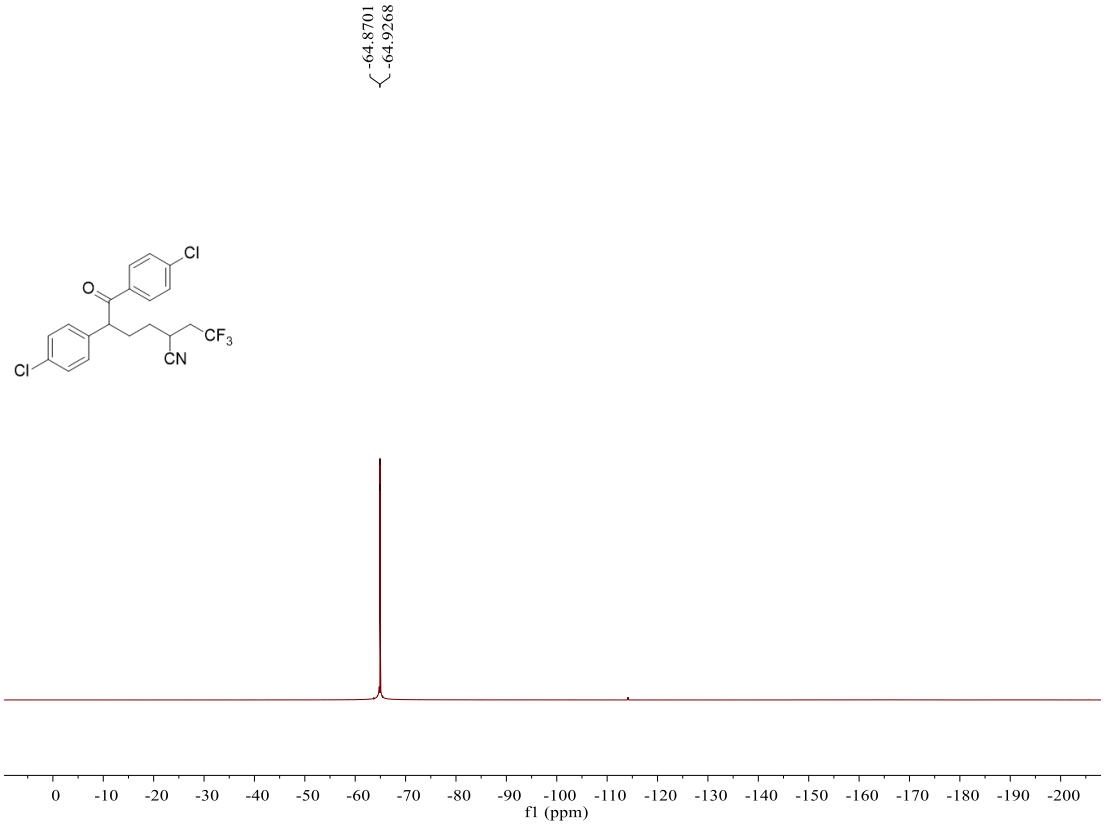
4aa ^{19}F NMR (376 MHz, Chloroform-*d*)



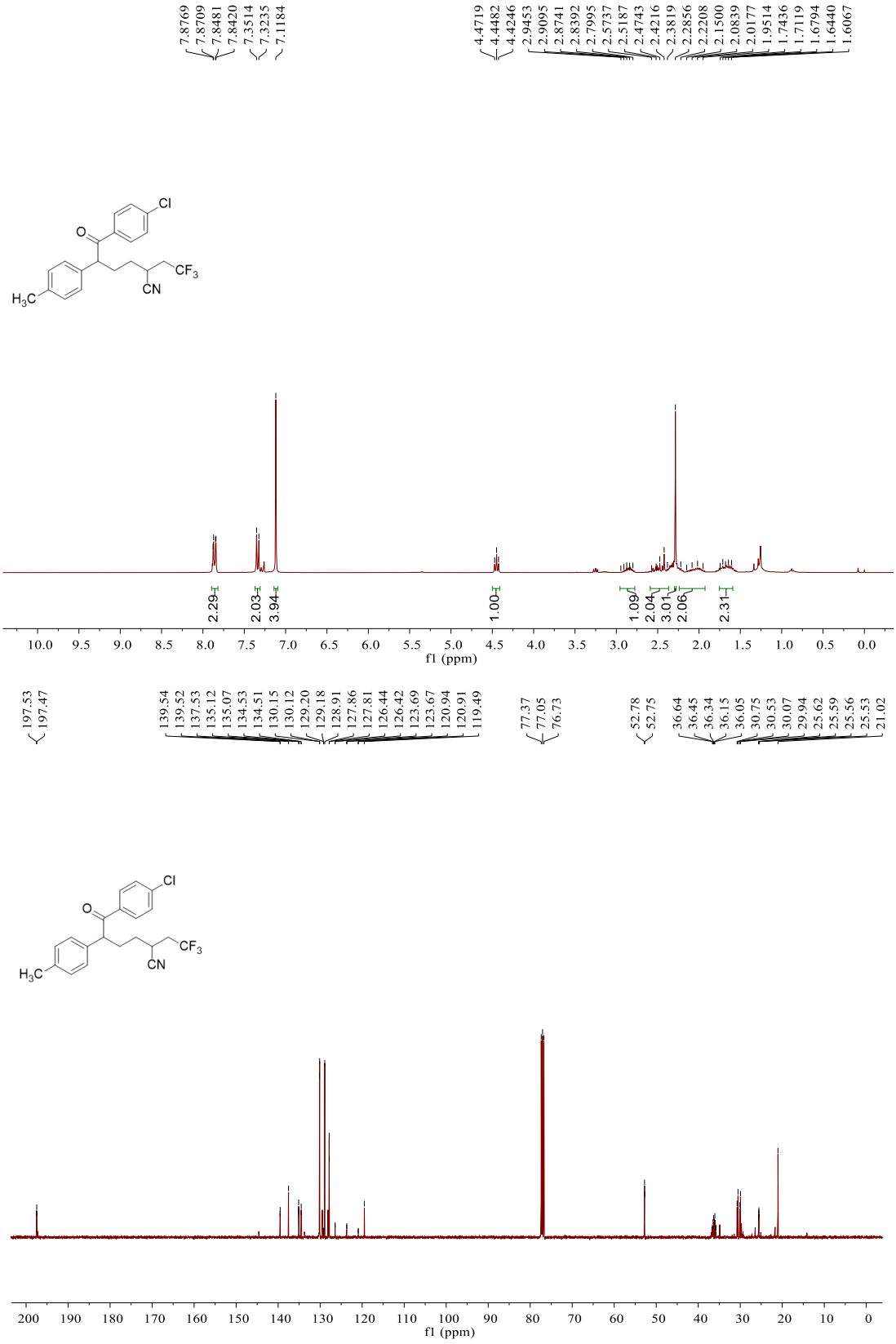
4ab ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



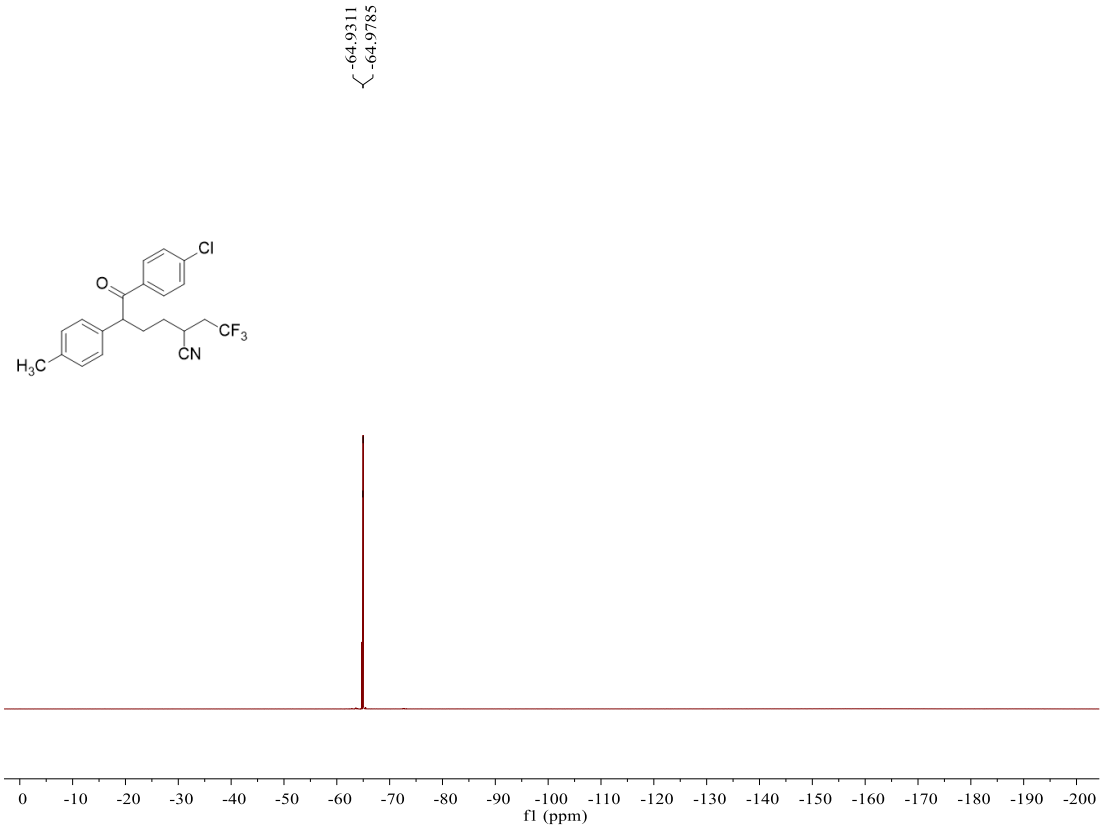
4ab ^{19}F NMR (376 MHz, Chloroform-*d*)



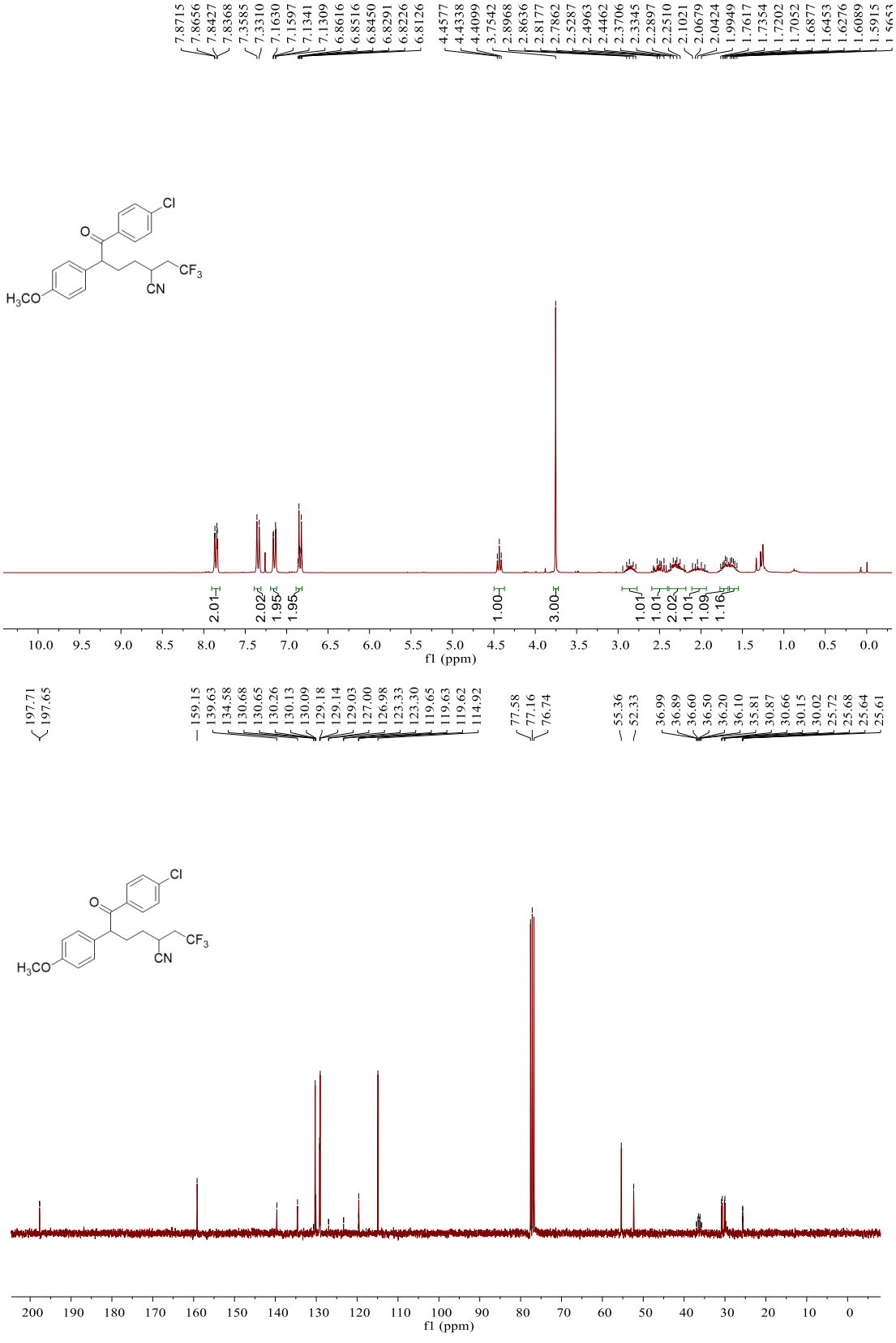
4ac ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



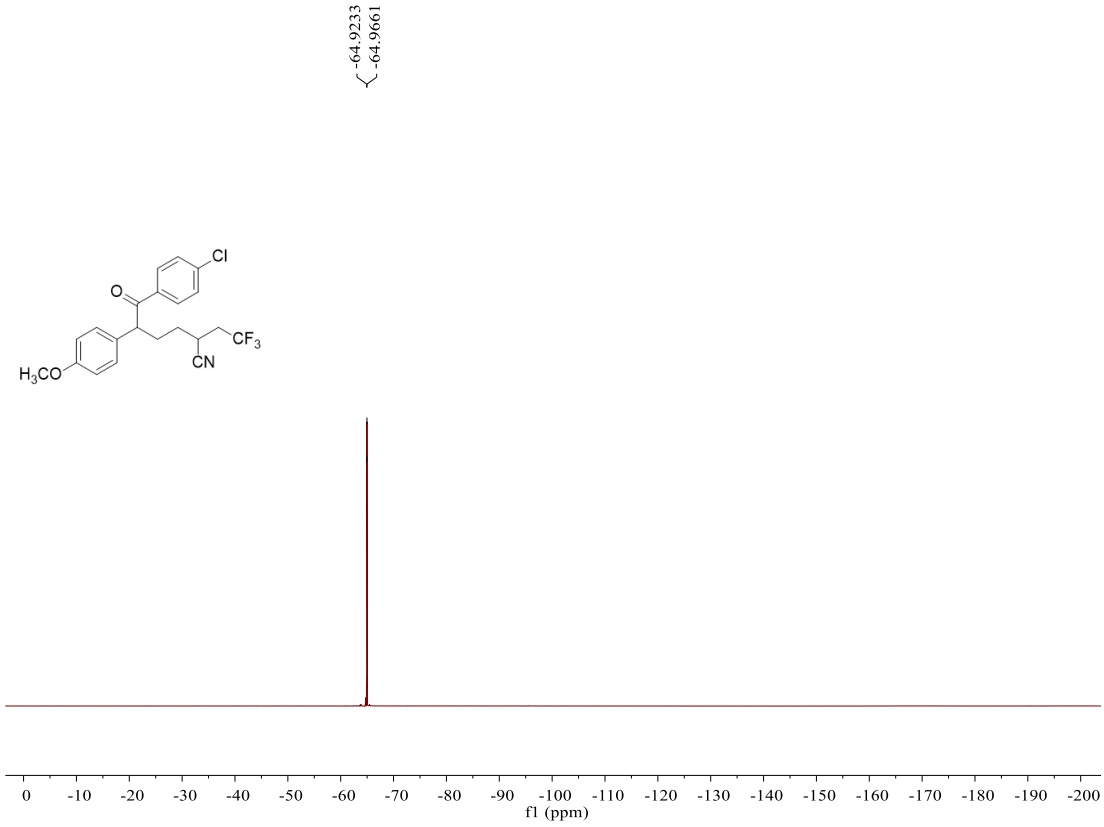
4ac ^{19}F NMR (376 MHz, Chloroform-*d*)



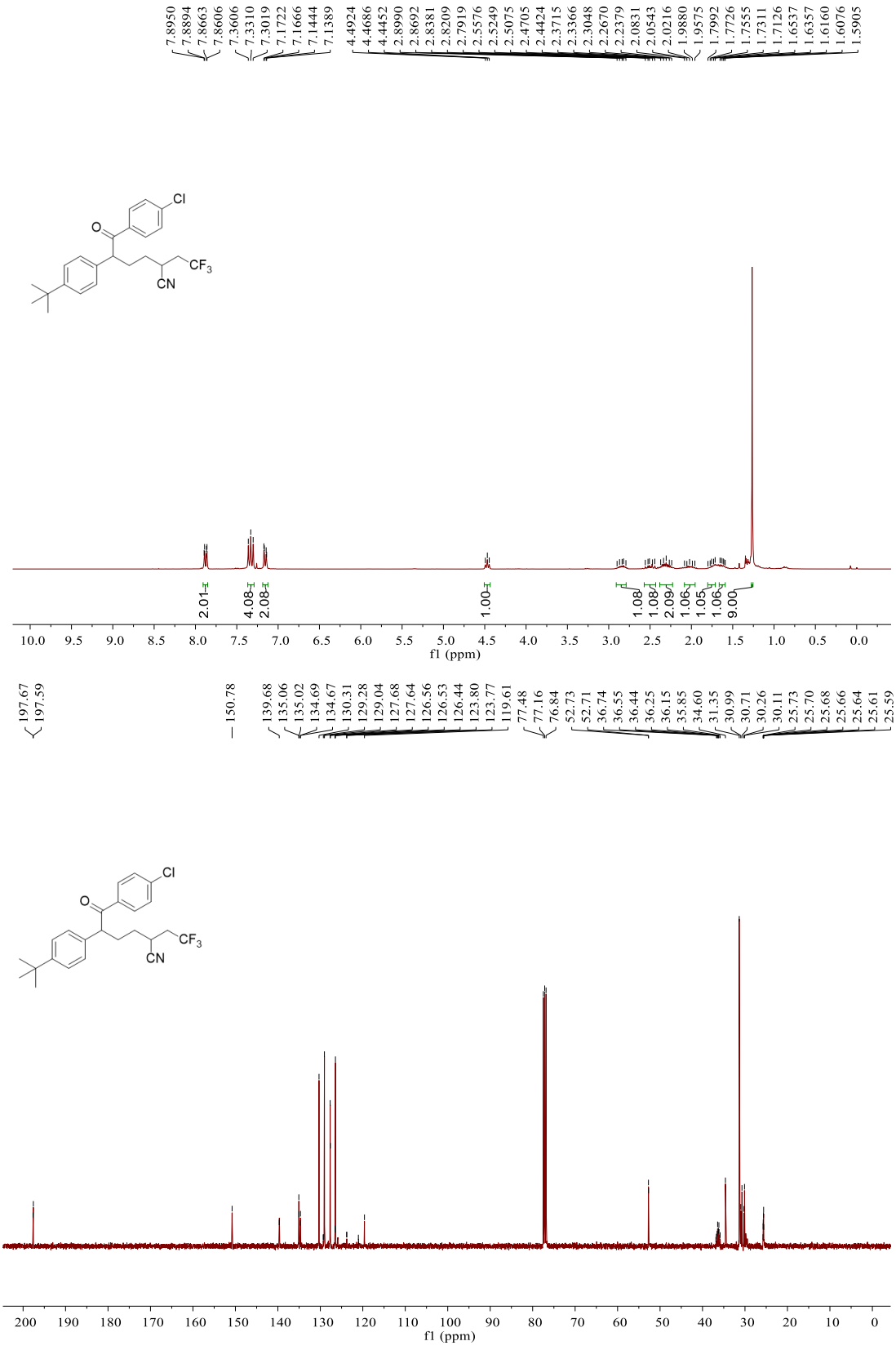
4ad ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (75 MHz, Chloroform-*d*)



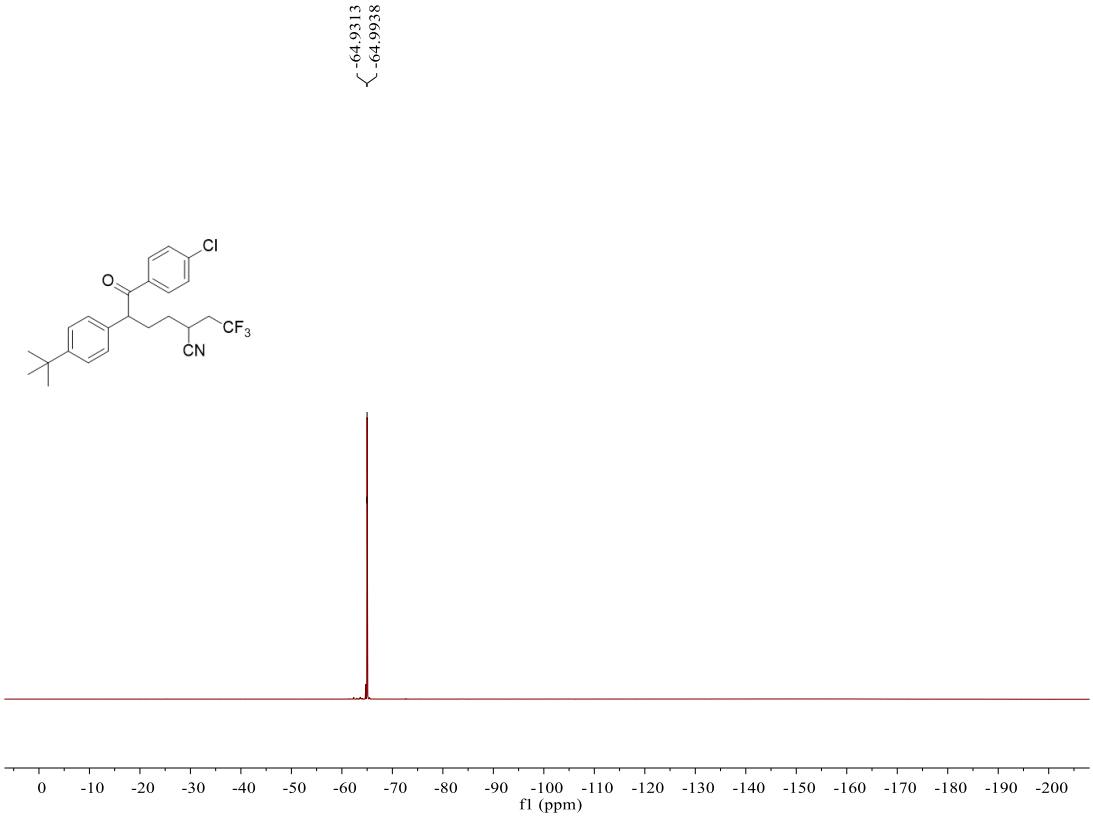
4ad ^{19}F NMR (376 MHz, Chloroform-*d*)



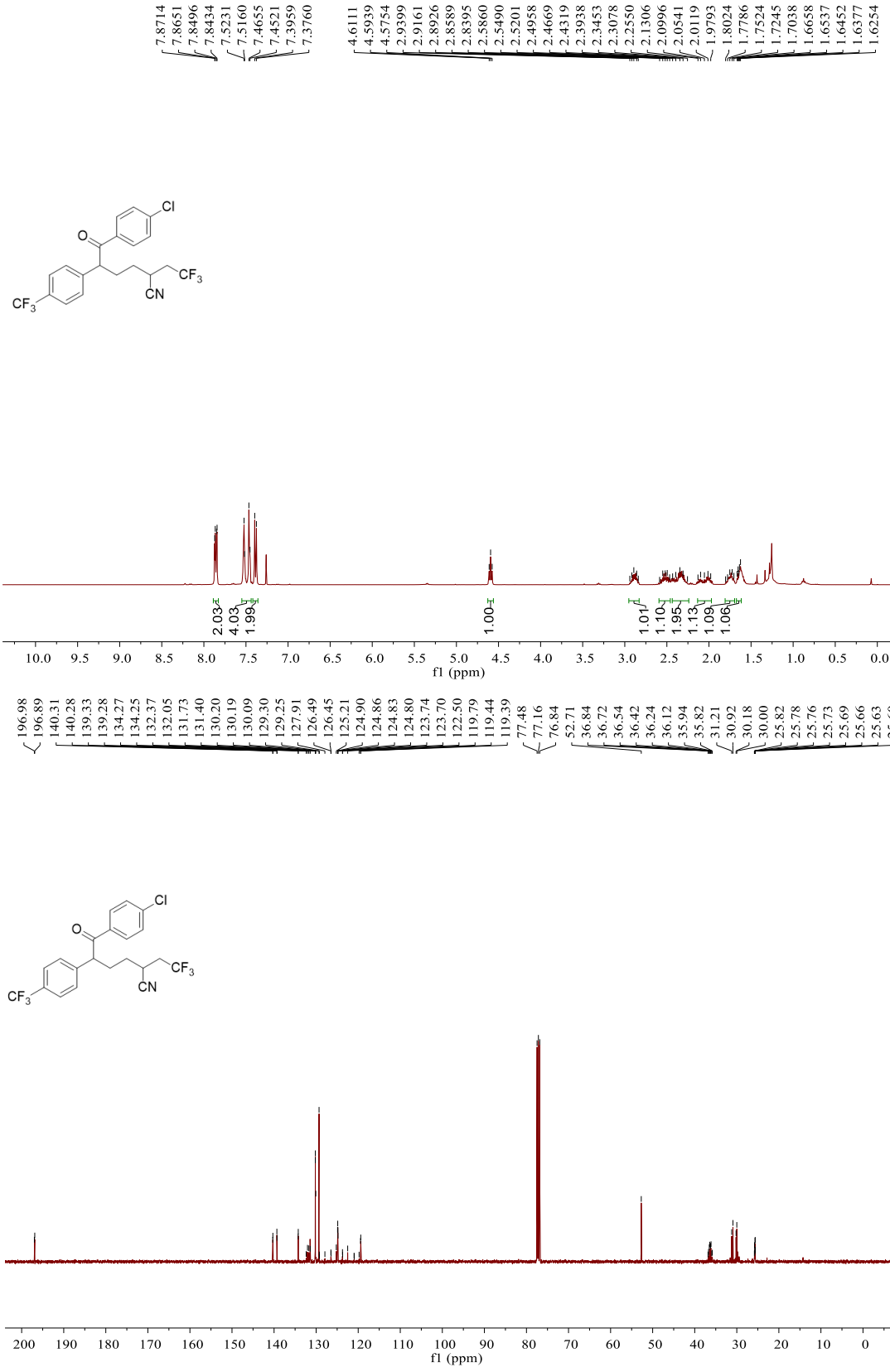
4ae ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



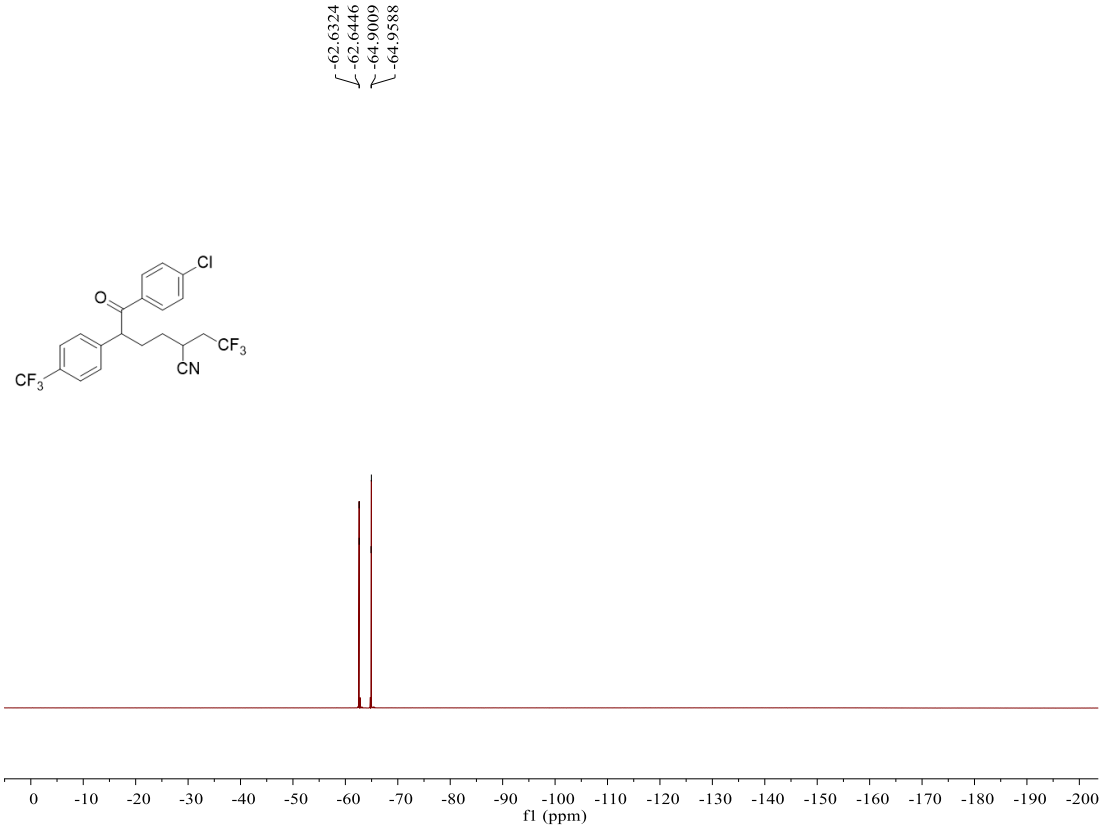
4ae ^{19}F NMR (376 MHz, Chloroform-*d*)



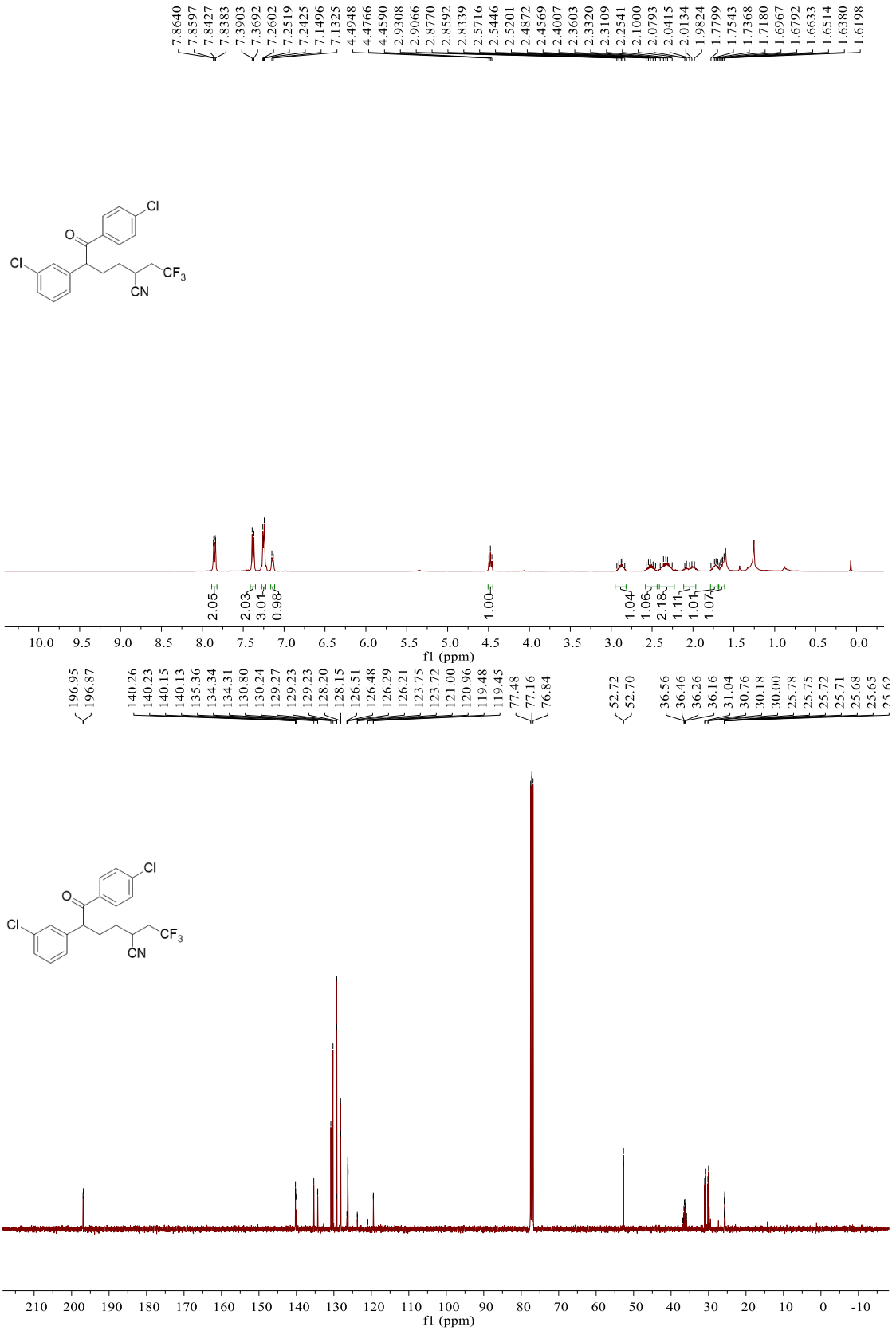
4af ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



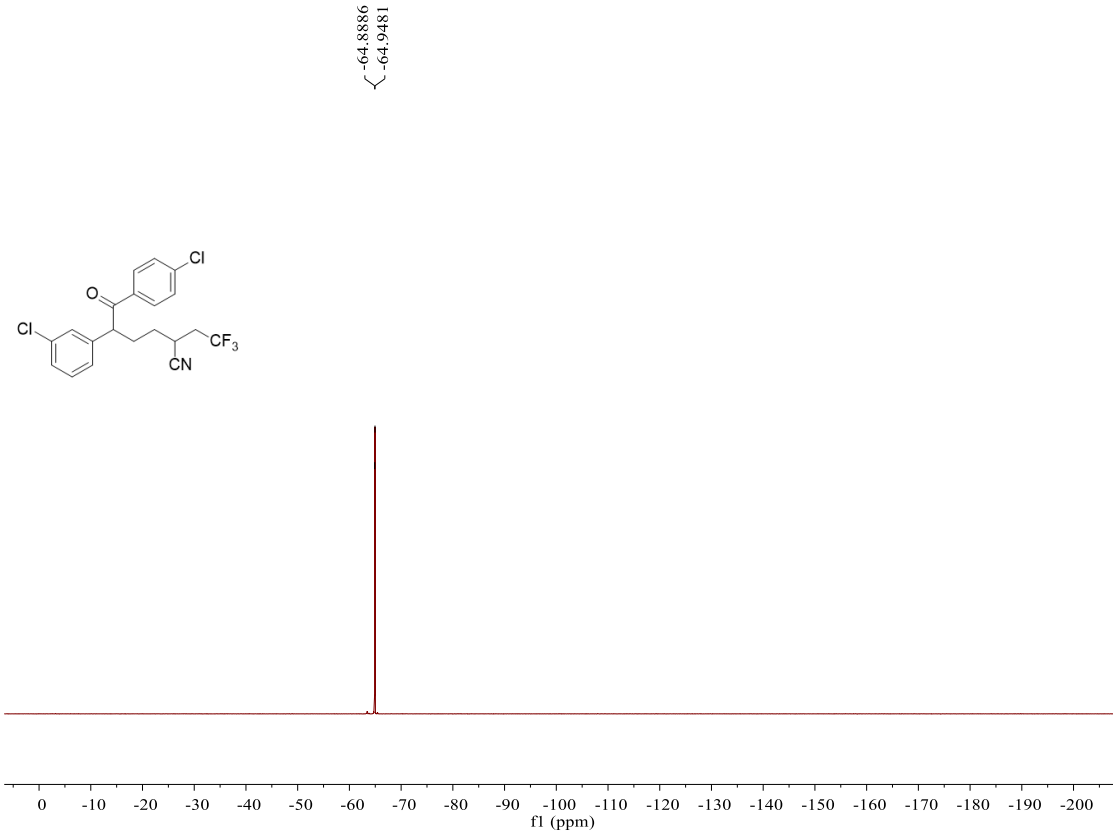
4af ^{19}F NMR (376 MHz, Chloroform-*d*)



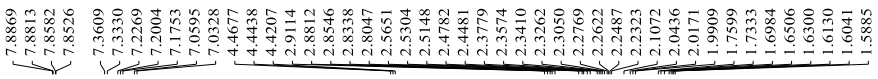
4ag ^{1}H NMR 400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



4ag ^{19}F NMR (376 MHz, Chloroform-*d*)



4ah ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)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7.8813
7.8582
7.8526
7.3609
7.3330
7.2269
7.2004
7.1753
7.0595
7.0328
4.4677
4.4438
4.4207
2.9114
2.8812
2.8546
2.8338
2.8047
2.5651
2.5304
2.5148
2.4782
2.4481
2.3779
2.3574
2.3410
2.3262
2.3050
2.2769
2.2622
2.2487
2.2323
2.1072
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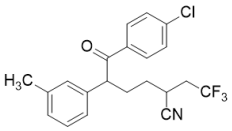
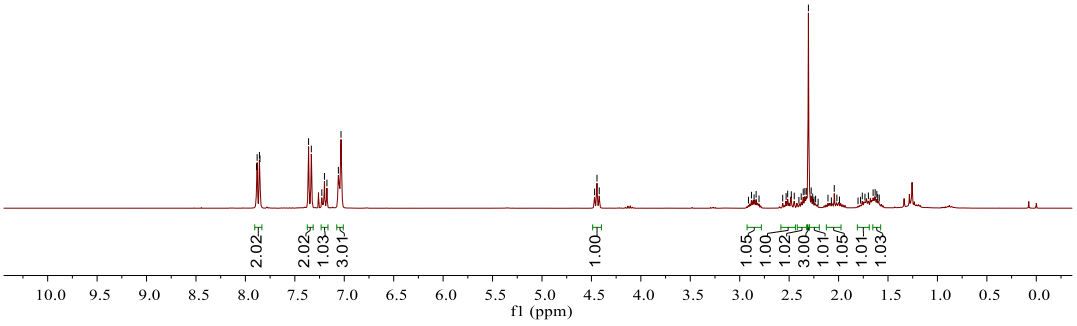
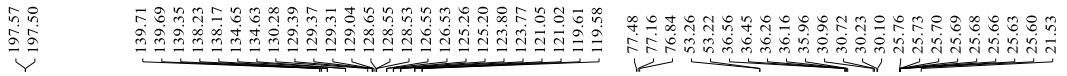
1.6506
1.6300
1.6130
1.6041
1.5885


Cl
O
H3C
CF3
CN


2.02
2.02
1.03
3.01
1.00
1.05
1.00
1.02
3.00
1.01
1.05
1.01
1.03
10.0 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 0.0
f1 (ppm)


197.57
197.50
139.71
139.69
139.35
138.23
138.17
134.65
134.63
130.28
129.39
129.37
129.31
129.04
128.65
128.55
128.53
126.55
126.53
125.26
125.20
123.80
123.77
121.05
121.02
119.61
119.58
77.48
77.16
76.84
53.26
53.22
36.56
36.45
36.26
36.16
35.96
30.96
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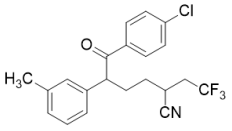
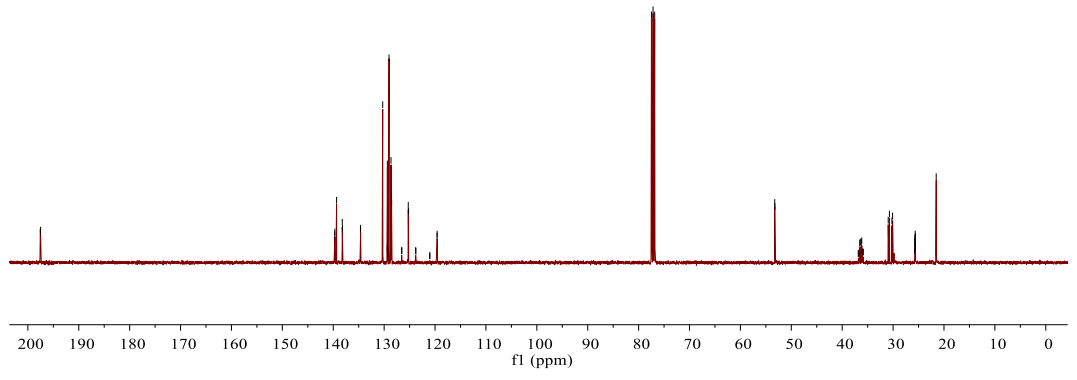
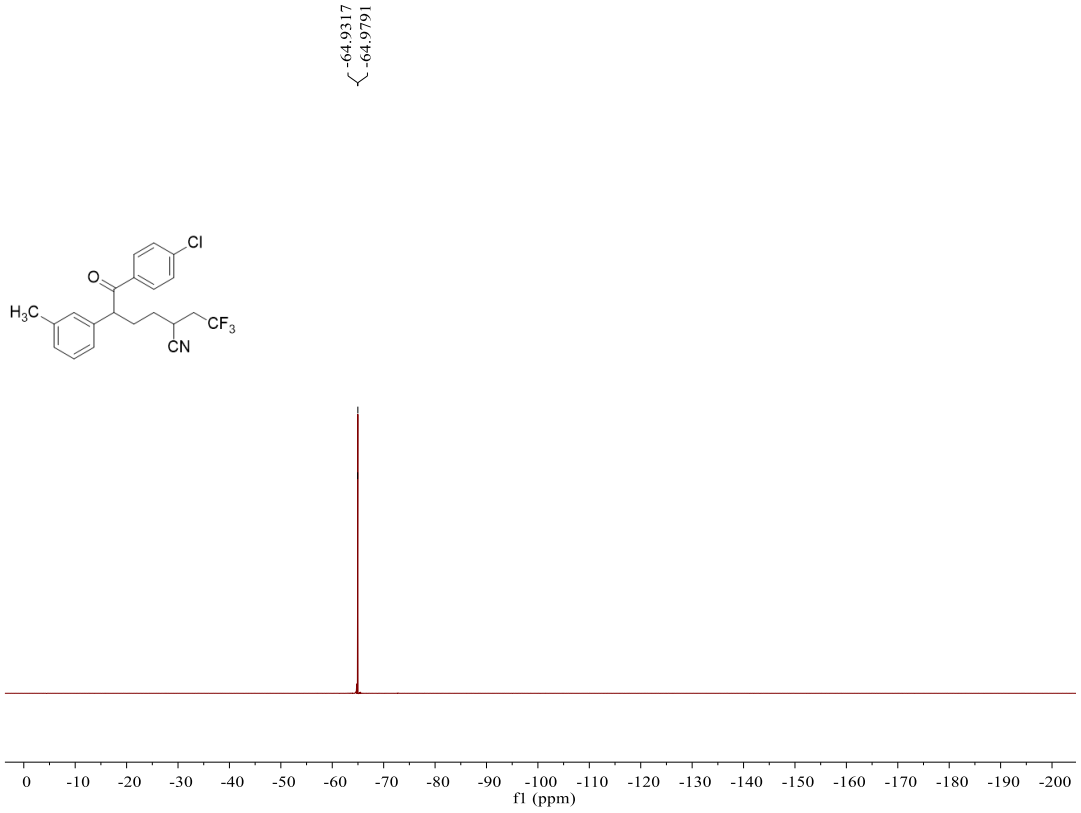
30.23
30.10
25.76
25.73
25.70
25.69
25.68
25.66
25.63
25.60
21.53

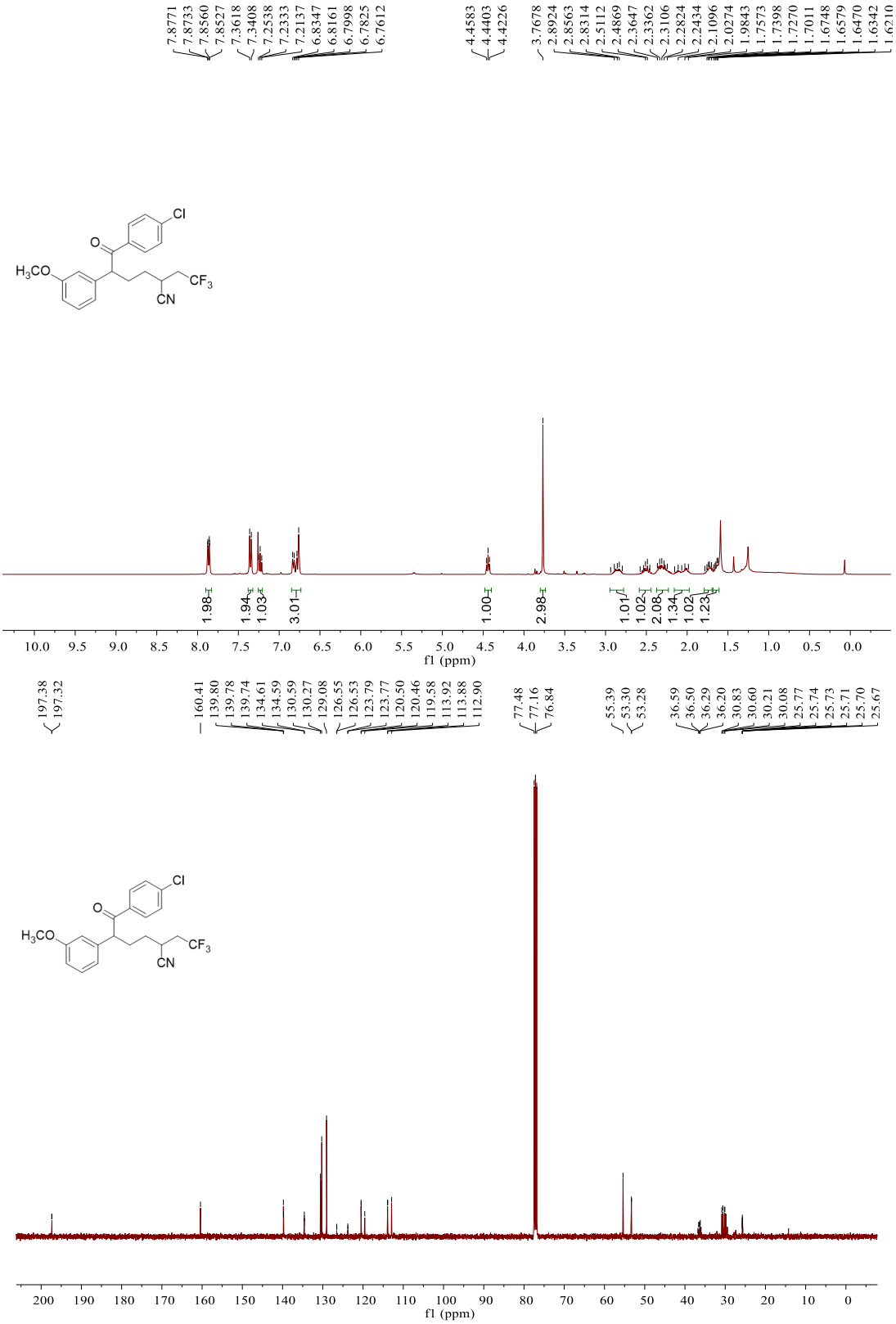

Cl
O
H3C
CF3
CN


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

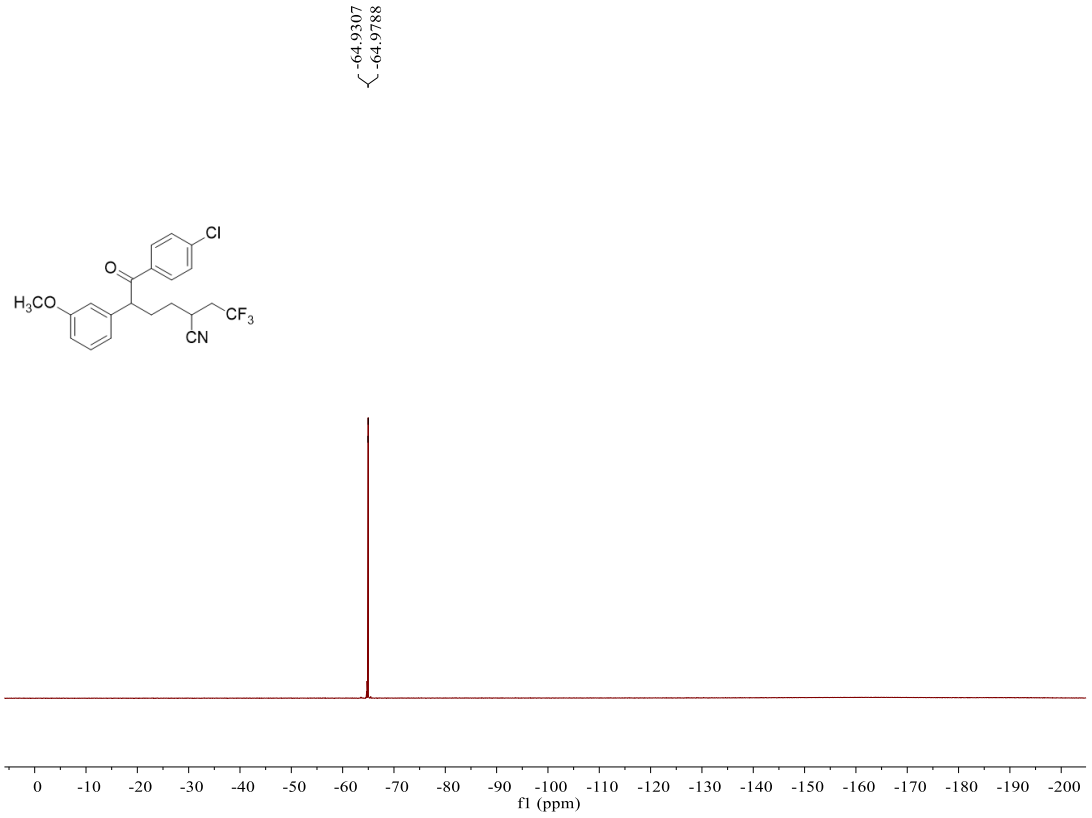
4ah ^{19}F NMR (376 MHz, Chloroform-*d*)



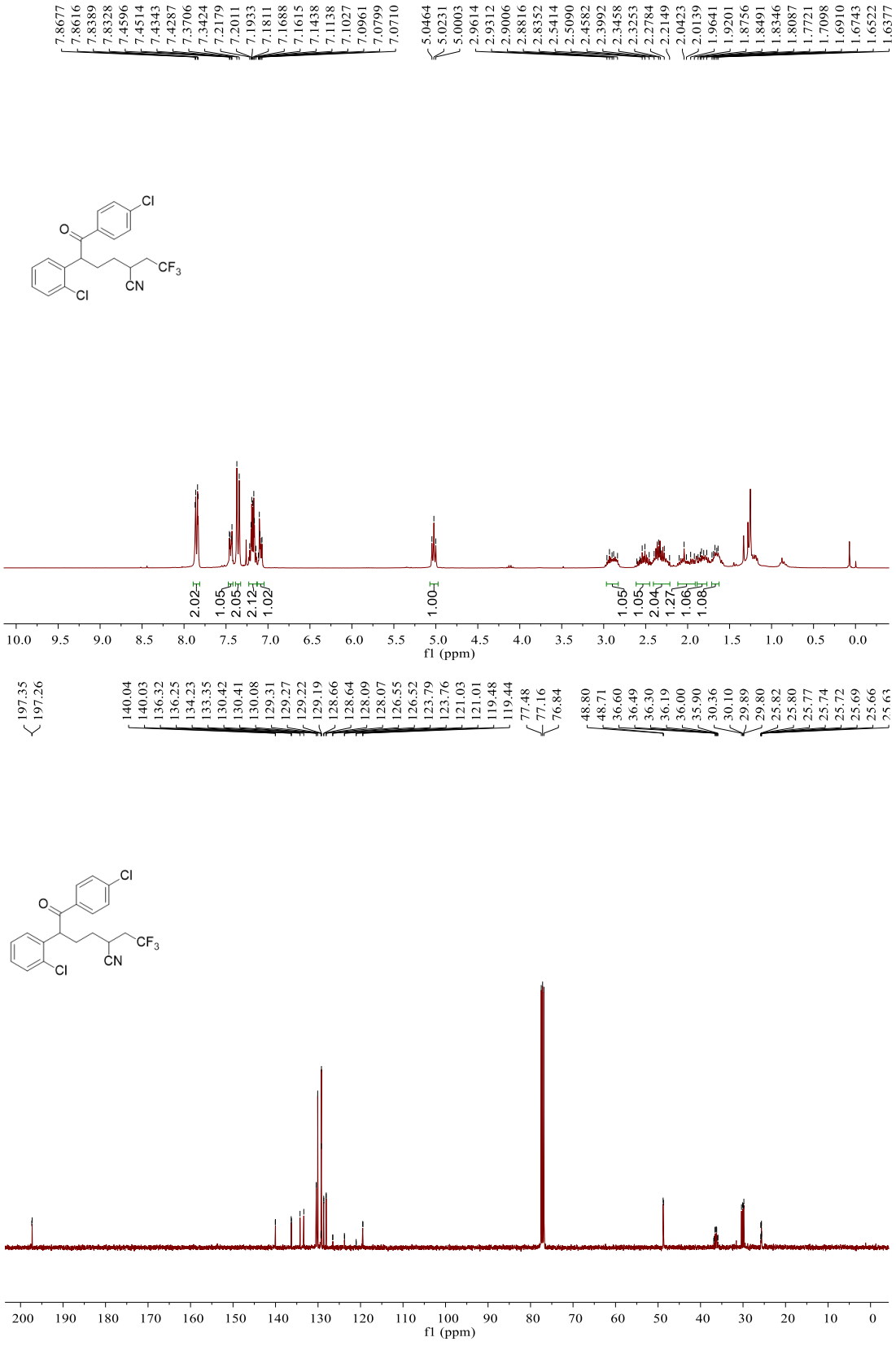
4ai ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



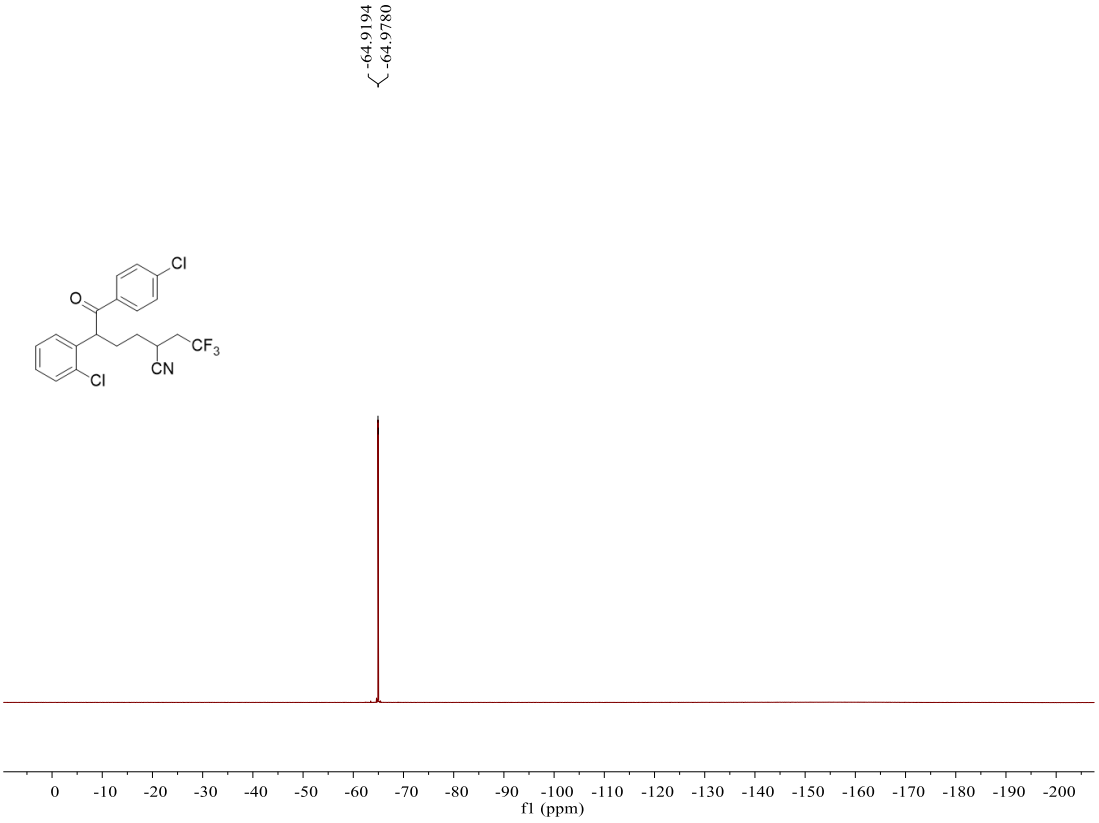
4ai ^{19}F NMR (376 MHz, Chloroform-*d*)



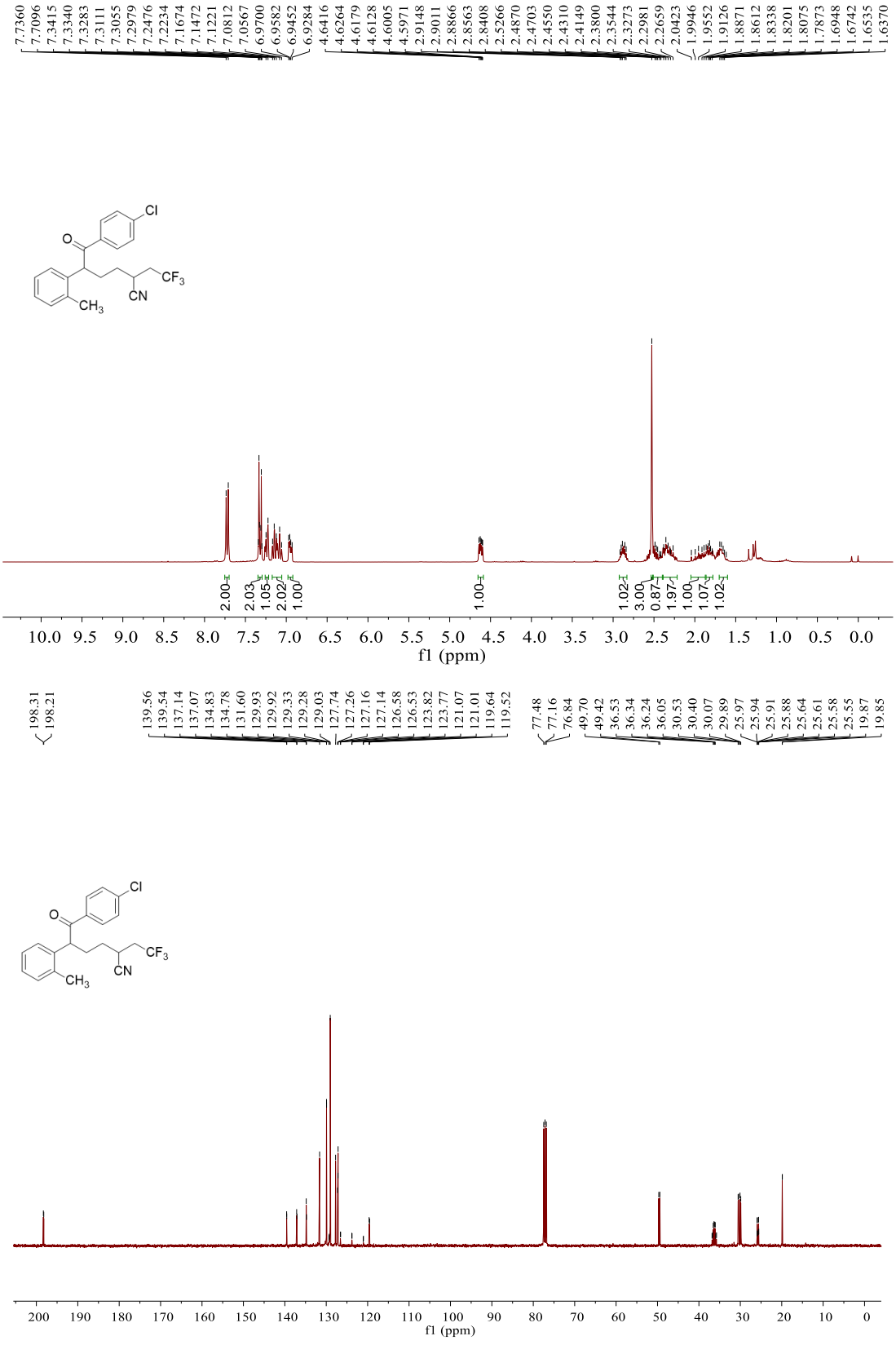
4aj ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



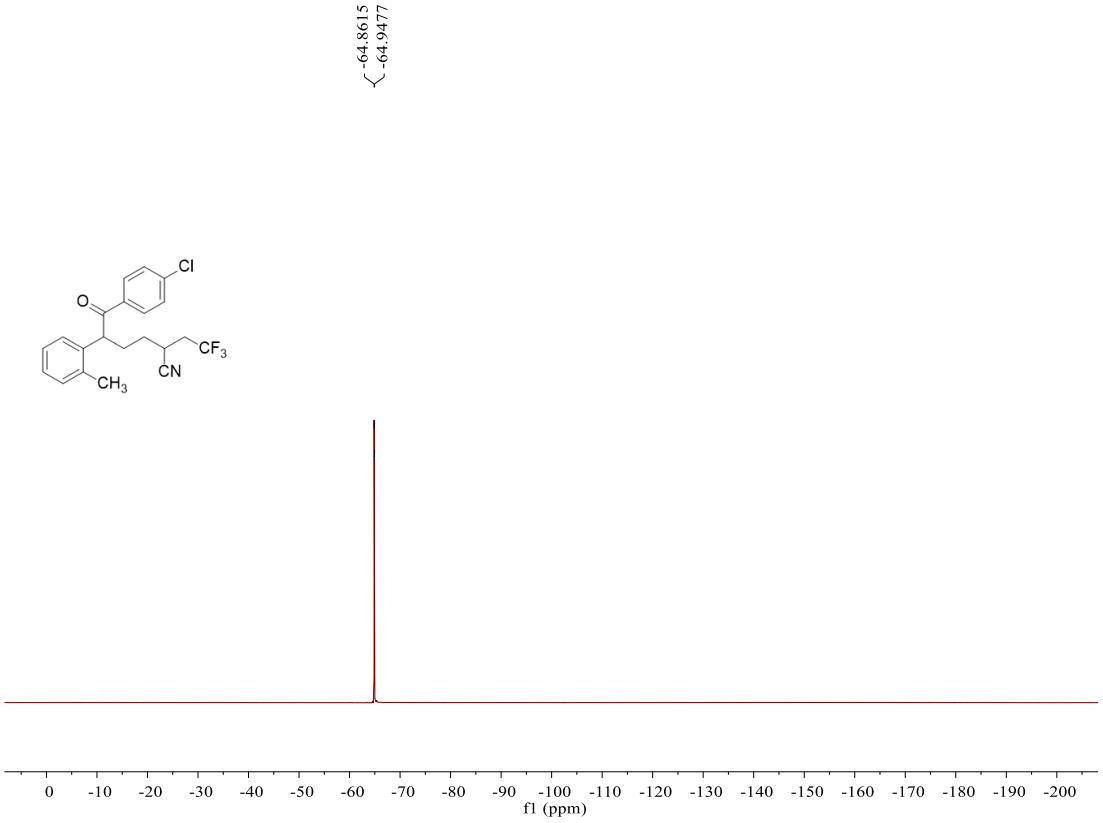
4aj ^{19}F NMR (376 MHz, Chloroform-*d*)



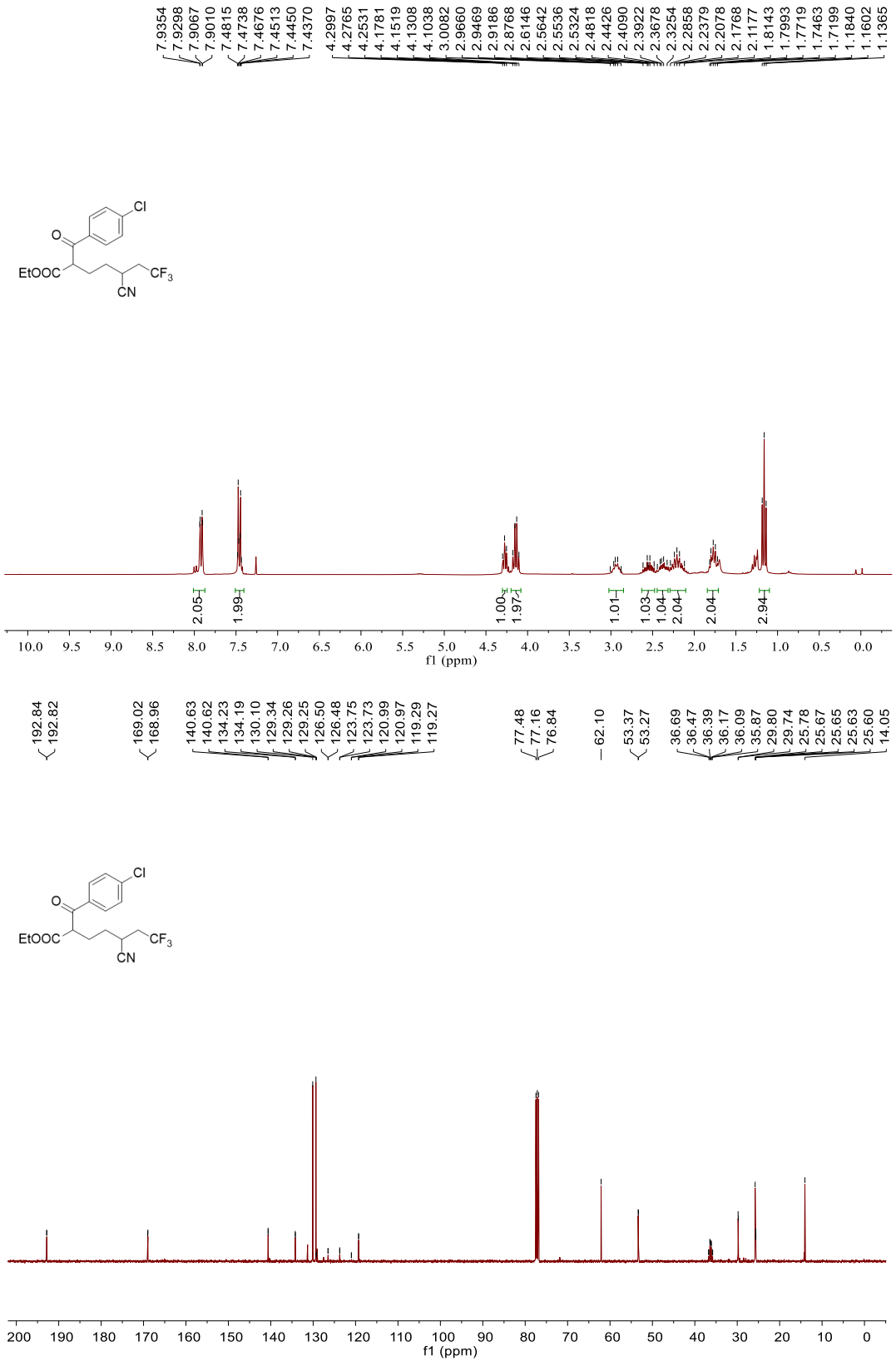
4ak ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



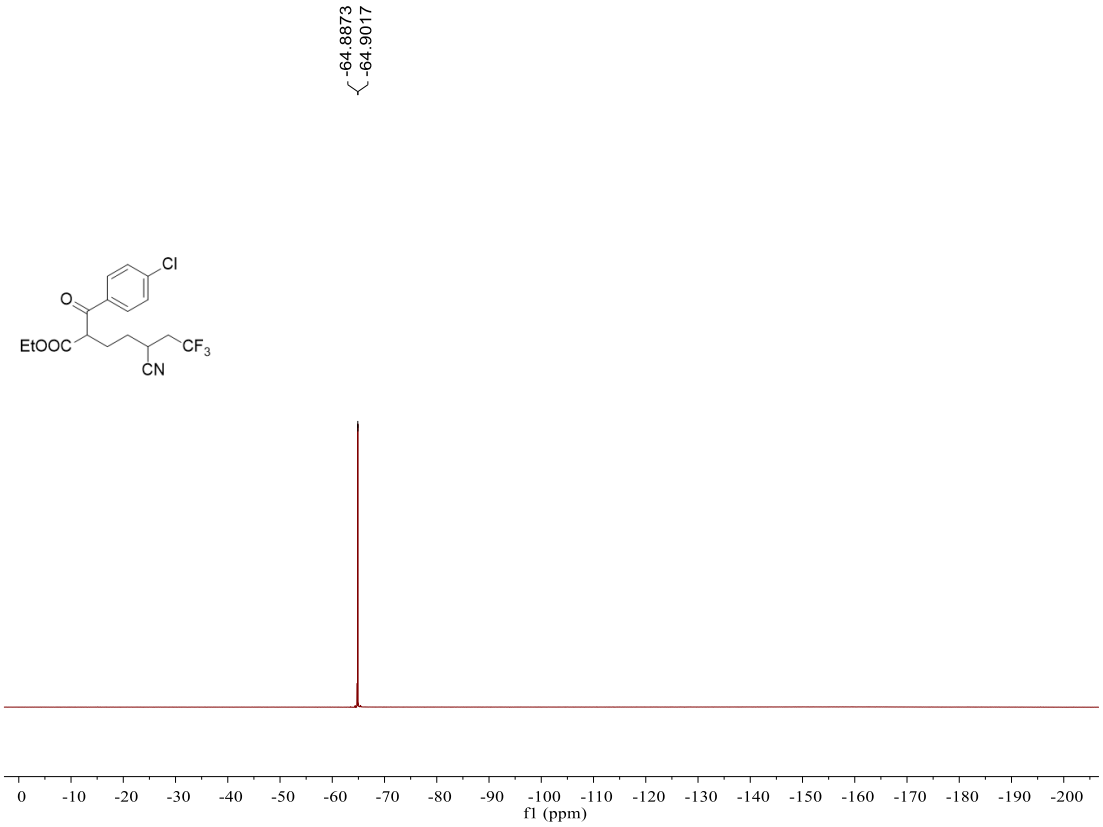
4ak ^{19}F NMR (376 MHz, Chloroform-*d*)



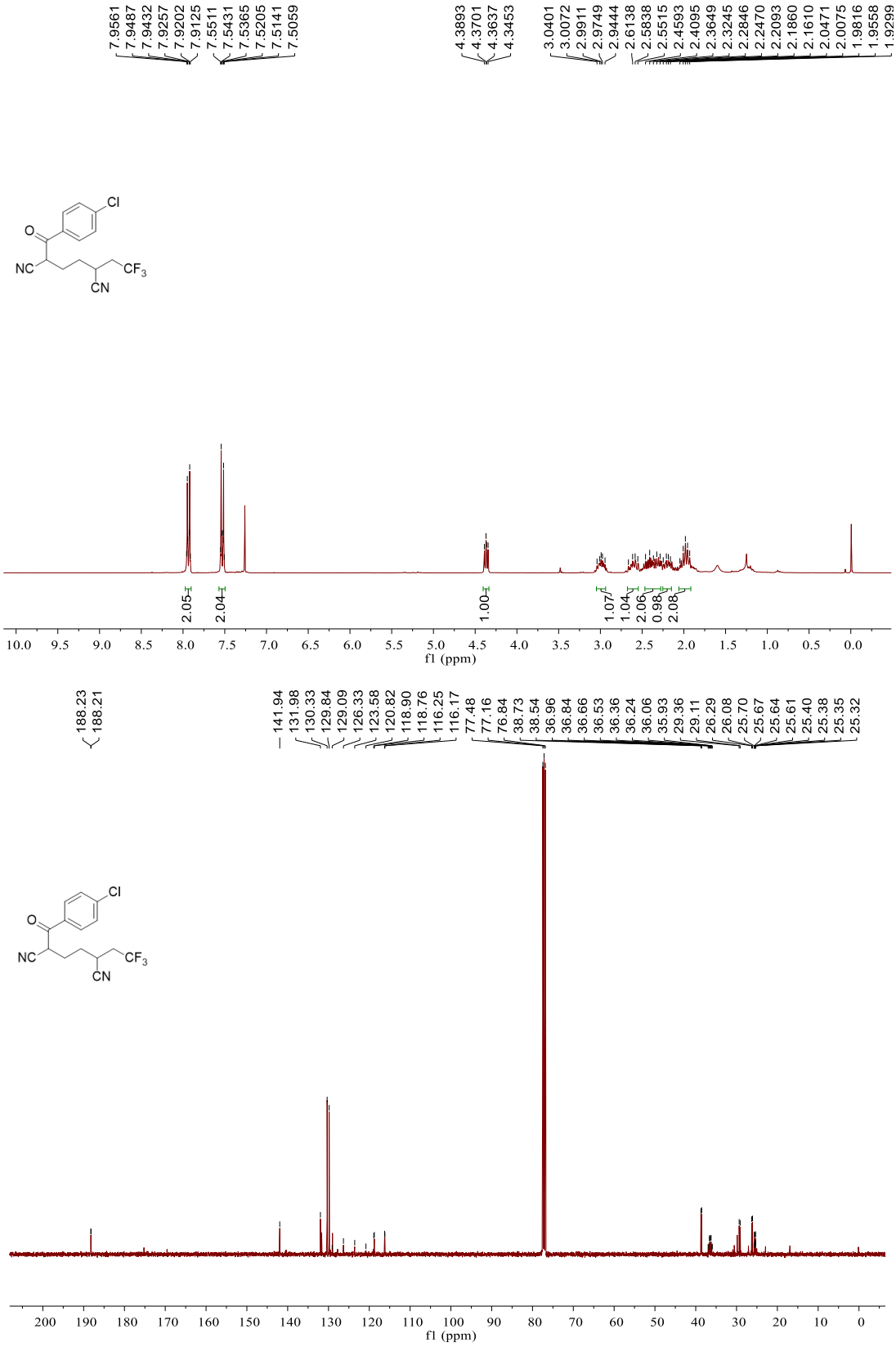
4al ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



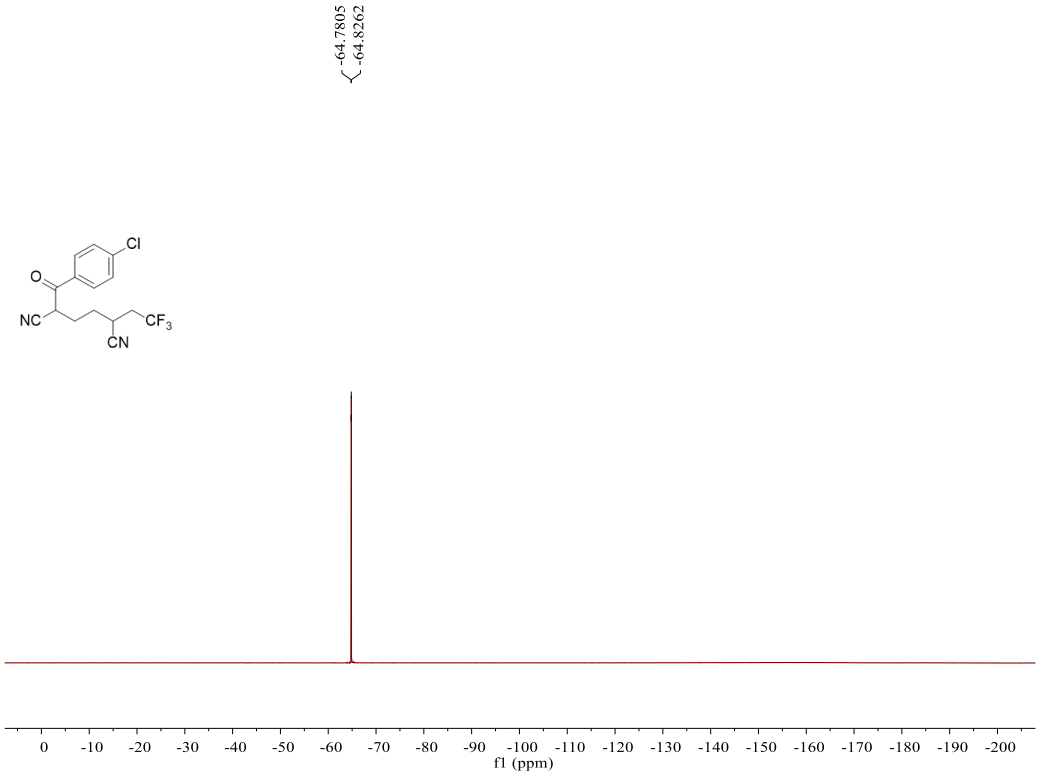
4al ^{19}F NMR (376 MHz, Chloroform-*d*)



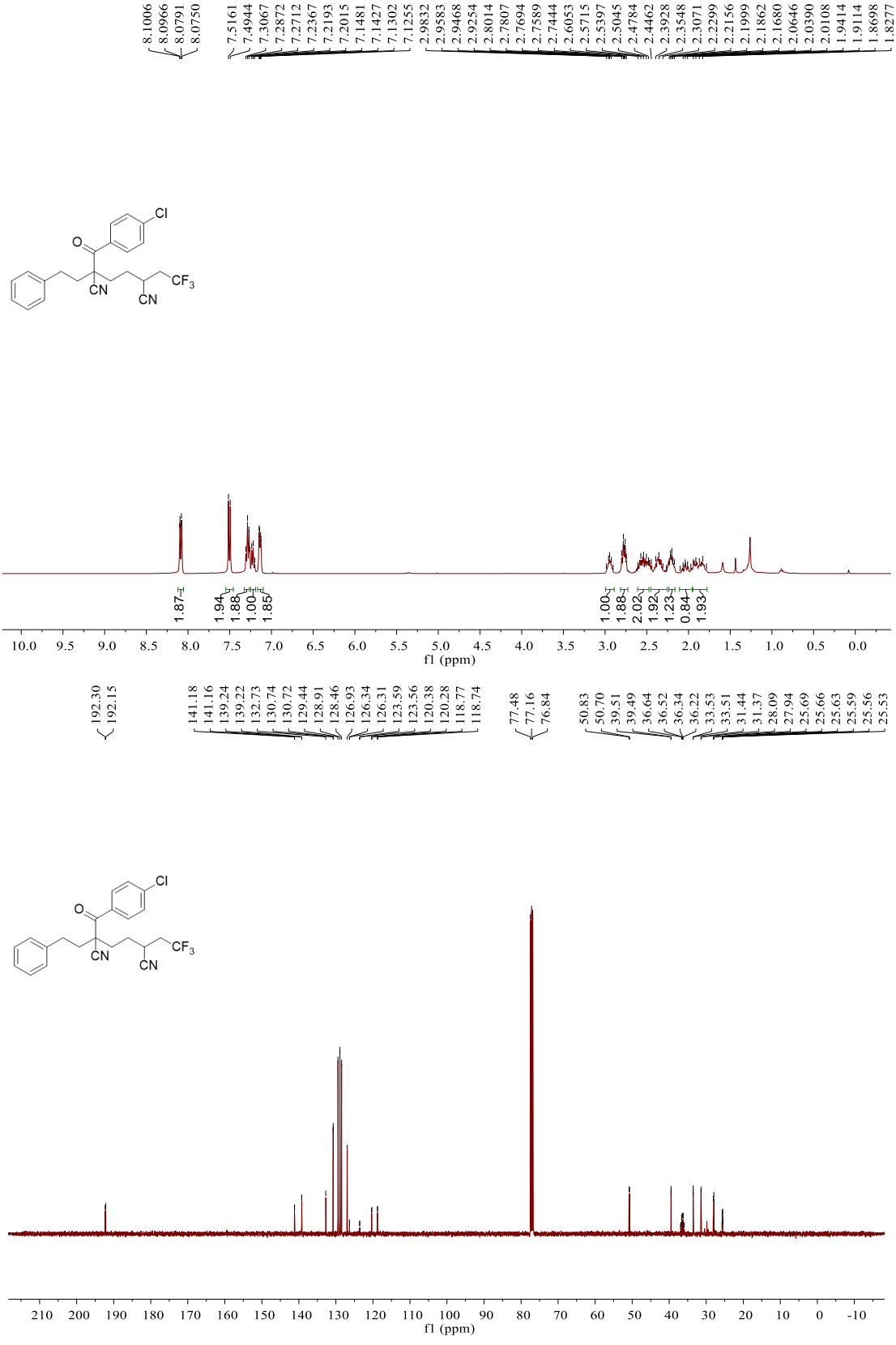
4am[1]H NMR (400 MHz, Chloroform-*d*)/ [13]C {1H}NMR (101 MHz, Chloroform-*d*)



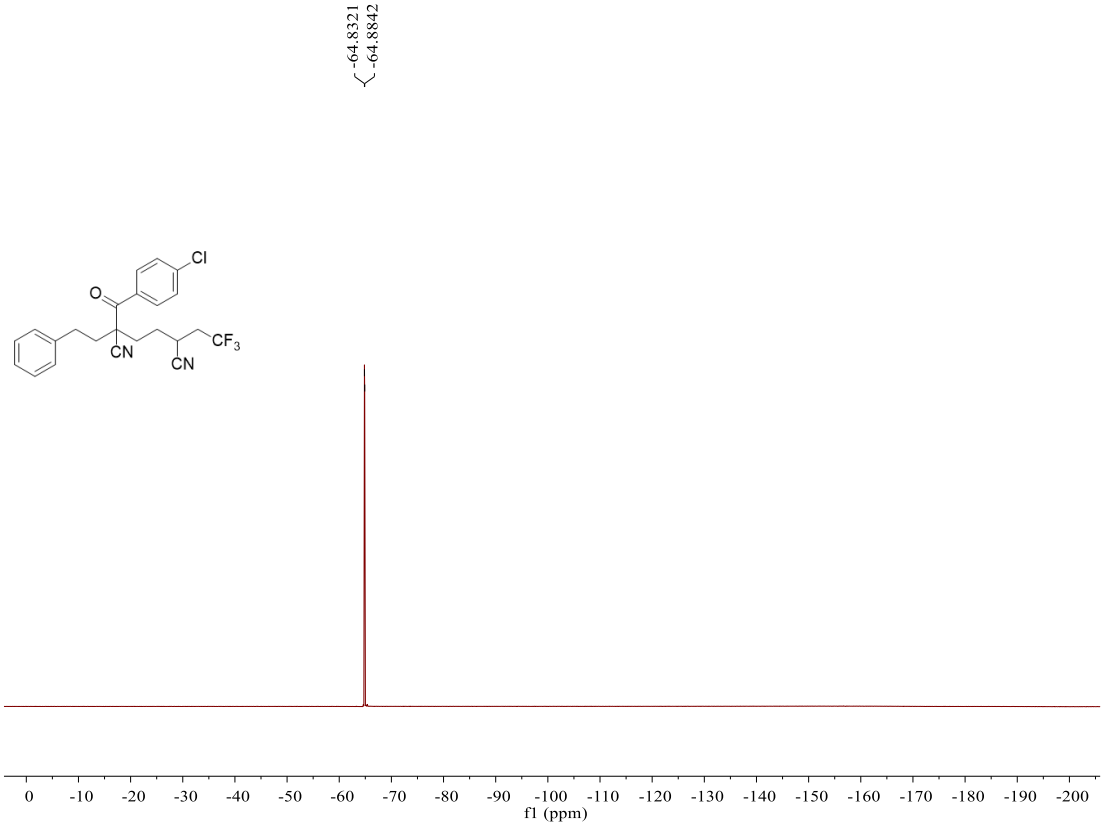
4am^{19}F NMR (376 MHz, Chloroform-*d*)



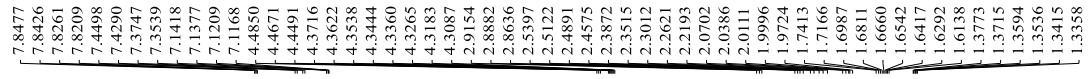
4an[1]H NMR (400 MHz, Chloroform-*d*)/ [13]C {1H}NMR (101 MHz, Chloroform-*d*)

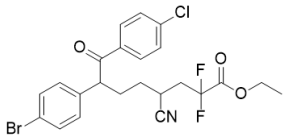


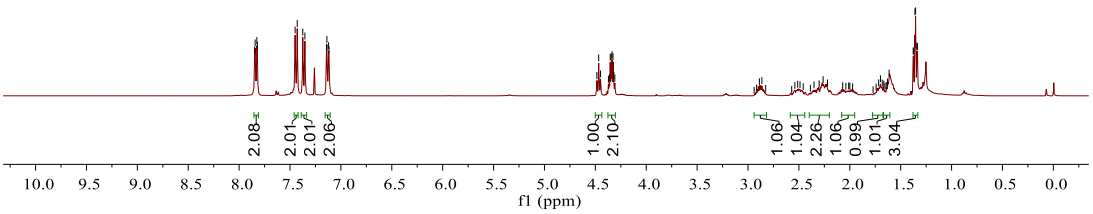
4an ^{19}F NMR (376 MHz, Chloroform-*d*)

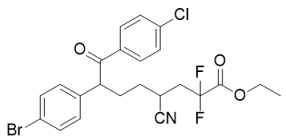


4ao[1]H NMR (400 MHz, Chloroform-*d*)/ [13]C {1H}NMR (101 MHz, Chloroform-*d*)

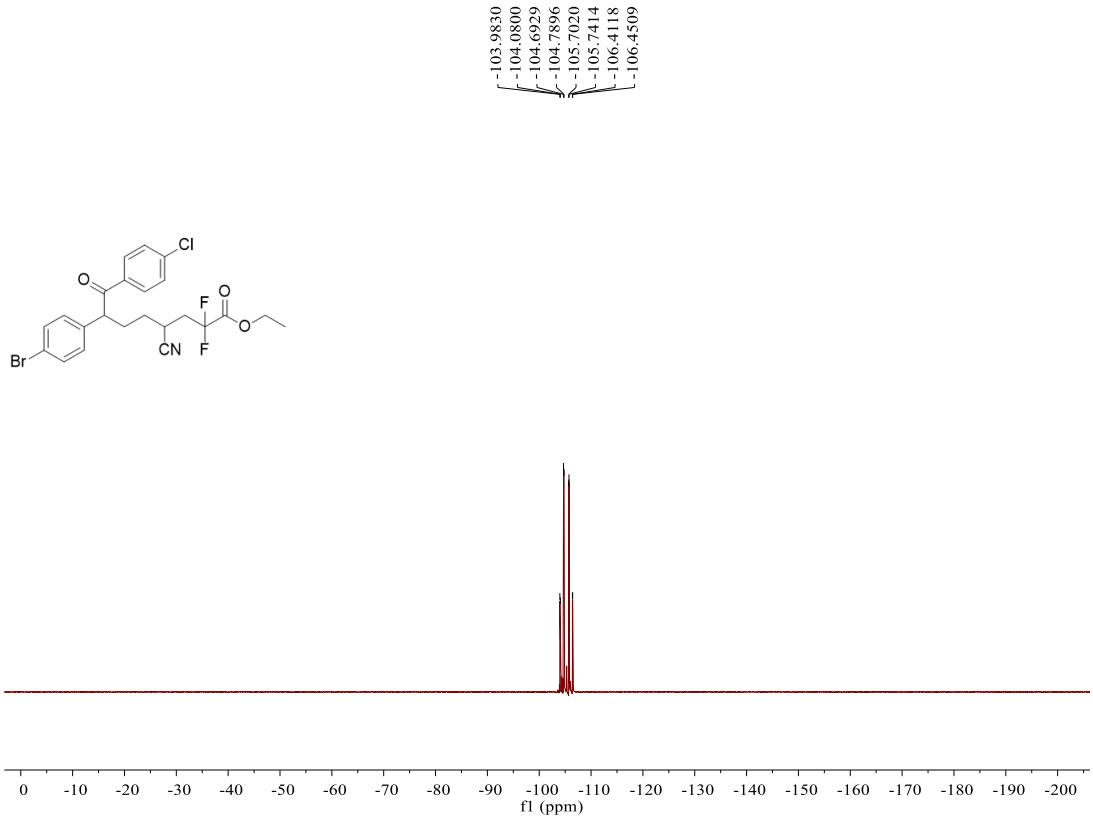




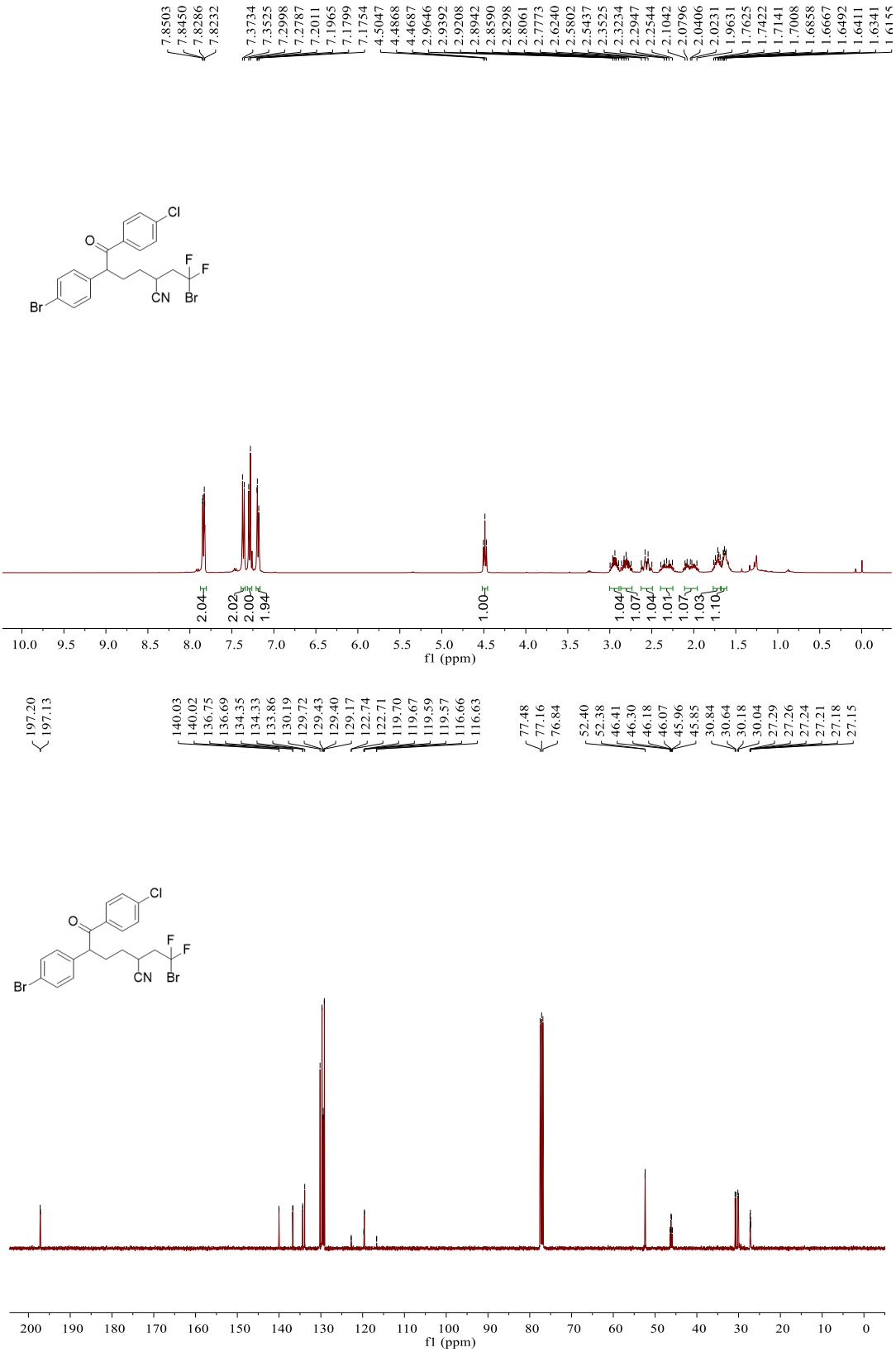




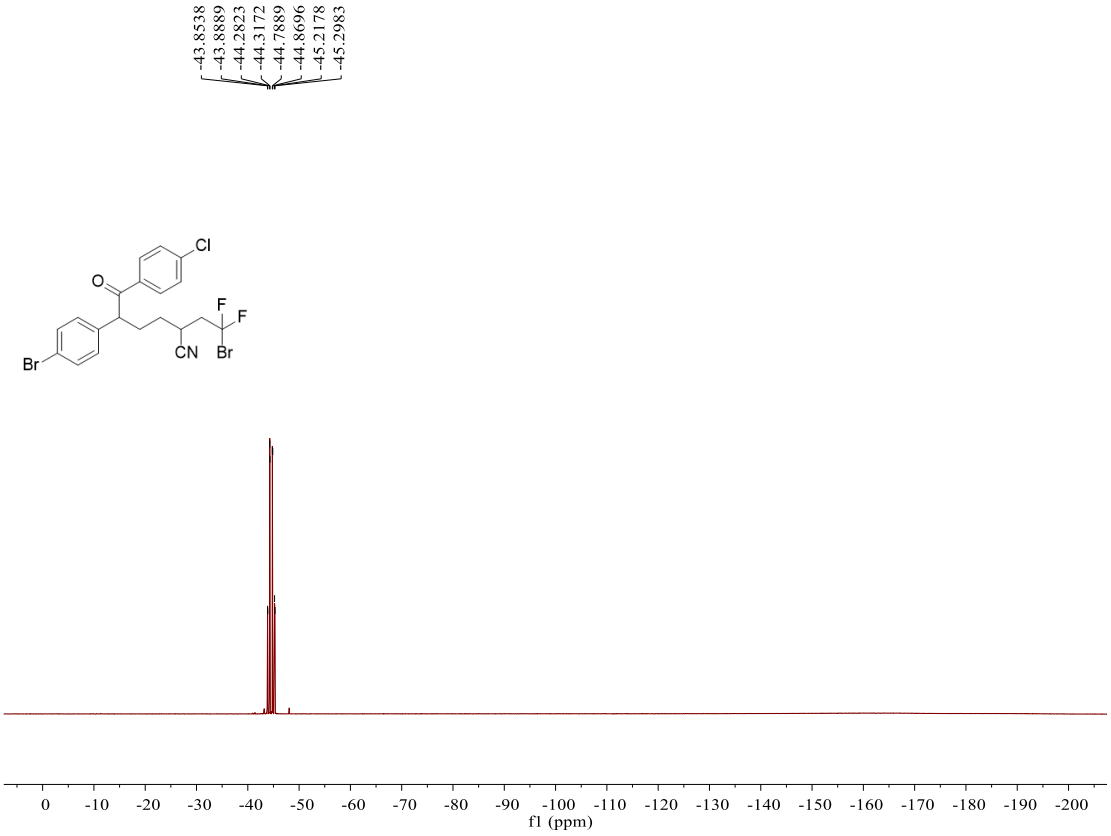
4ao^{19}F NMR (376 MHz, Chloroform-*d*)



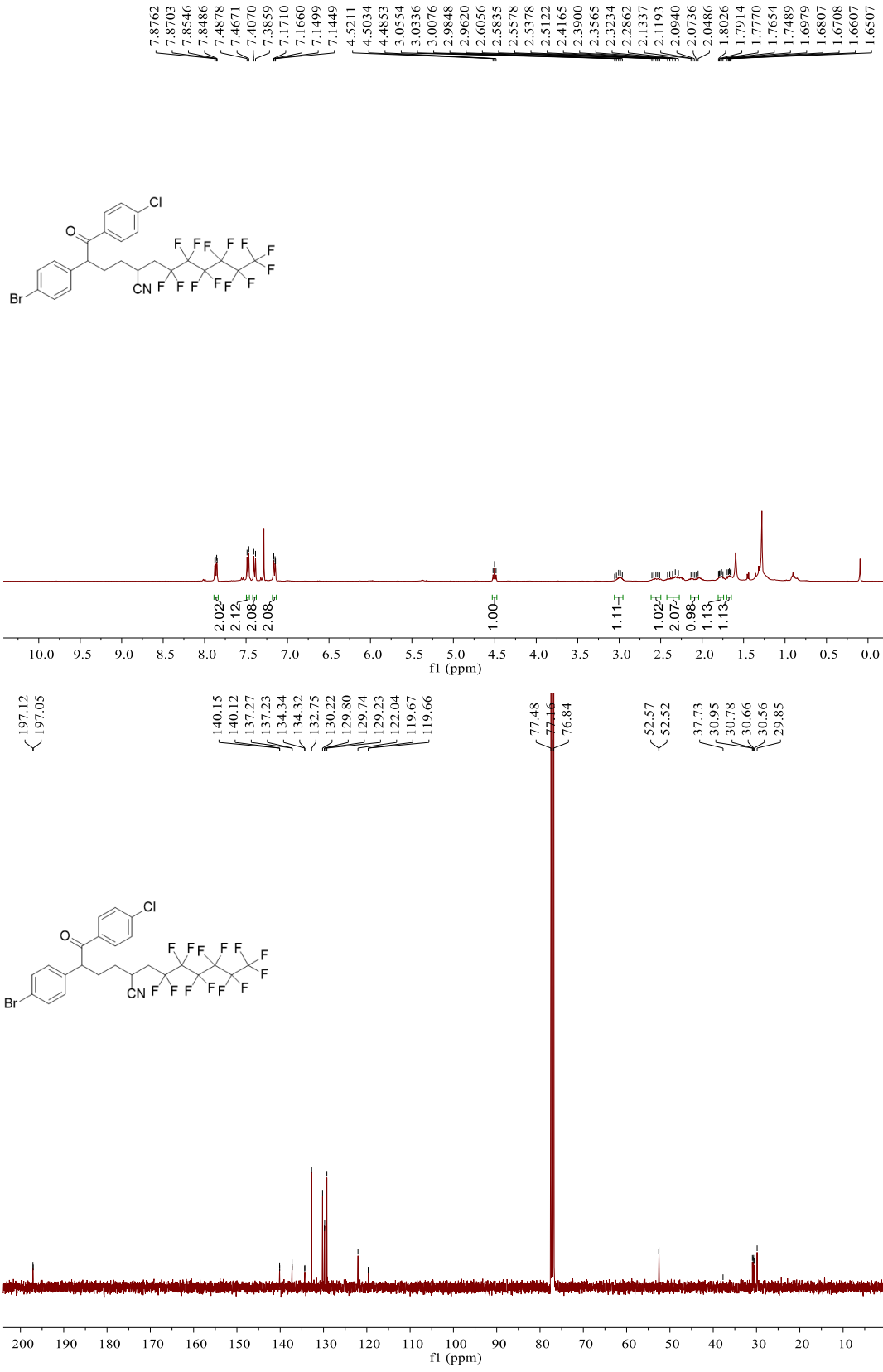
4ap[1]H NMR (400 MHz, Chloroform-*d*)/ [13]C {1H}NMR (101 MHz, Chloroform-*d*)



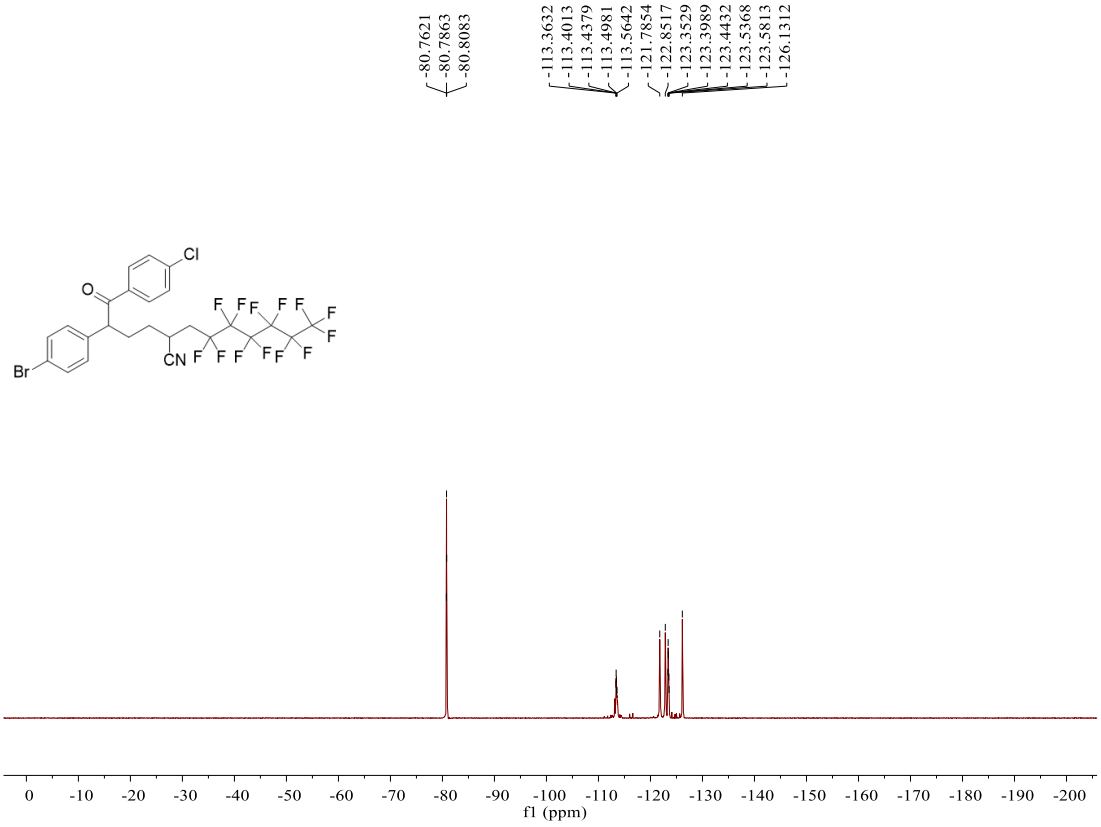
4ap ^{19}F NMR (376 MHz, Chloroform-*d*)



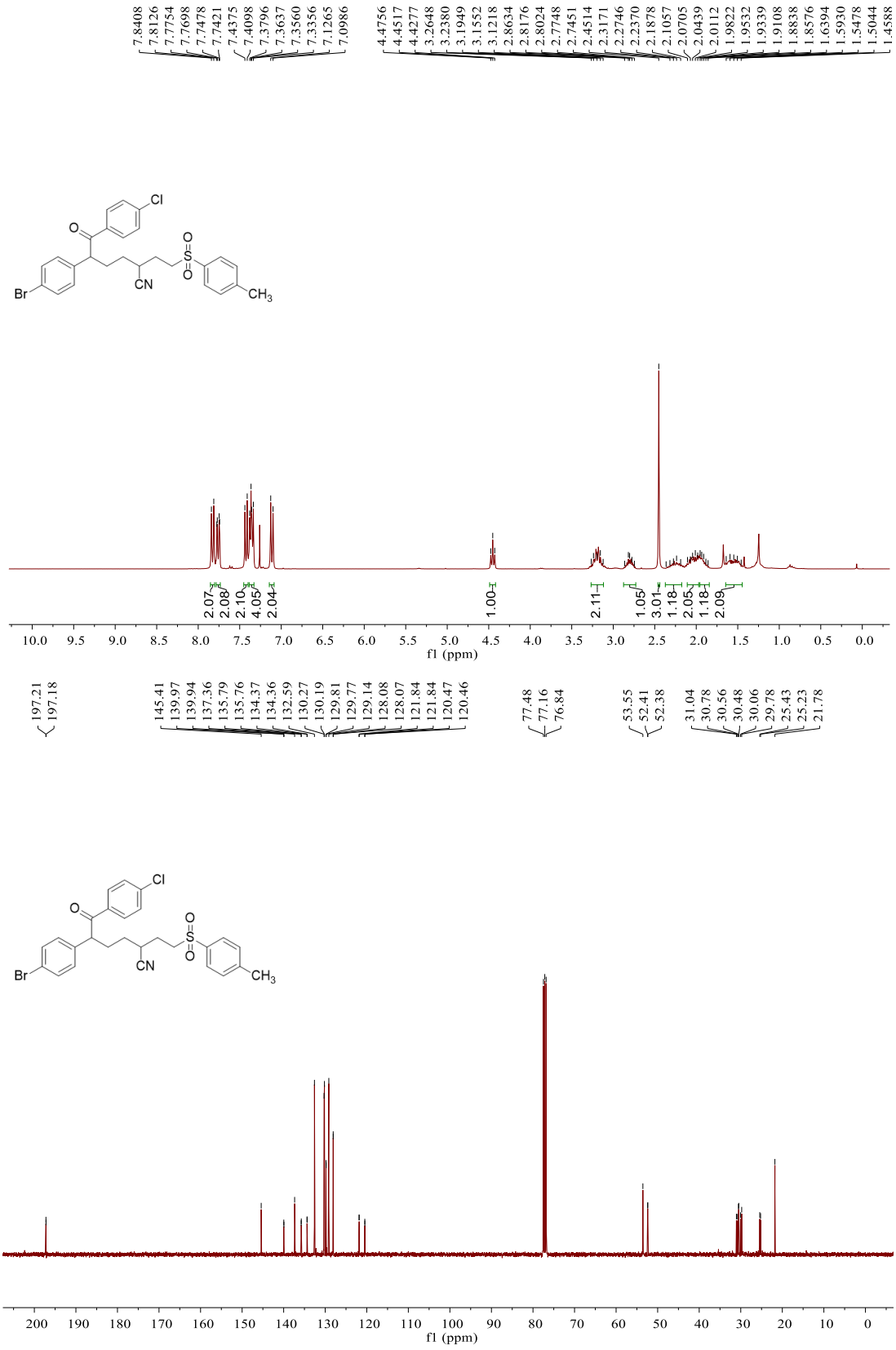
4aq[1]H NMR (400 MHz, Chloroform-*d*)/ [13]C {1H}NMR (101 MHz, Chloroform-*d*)



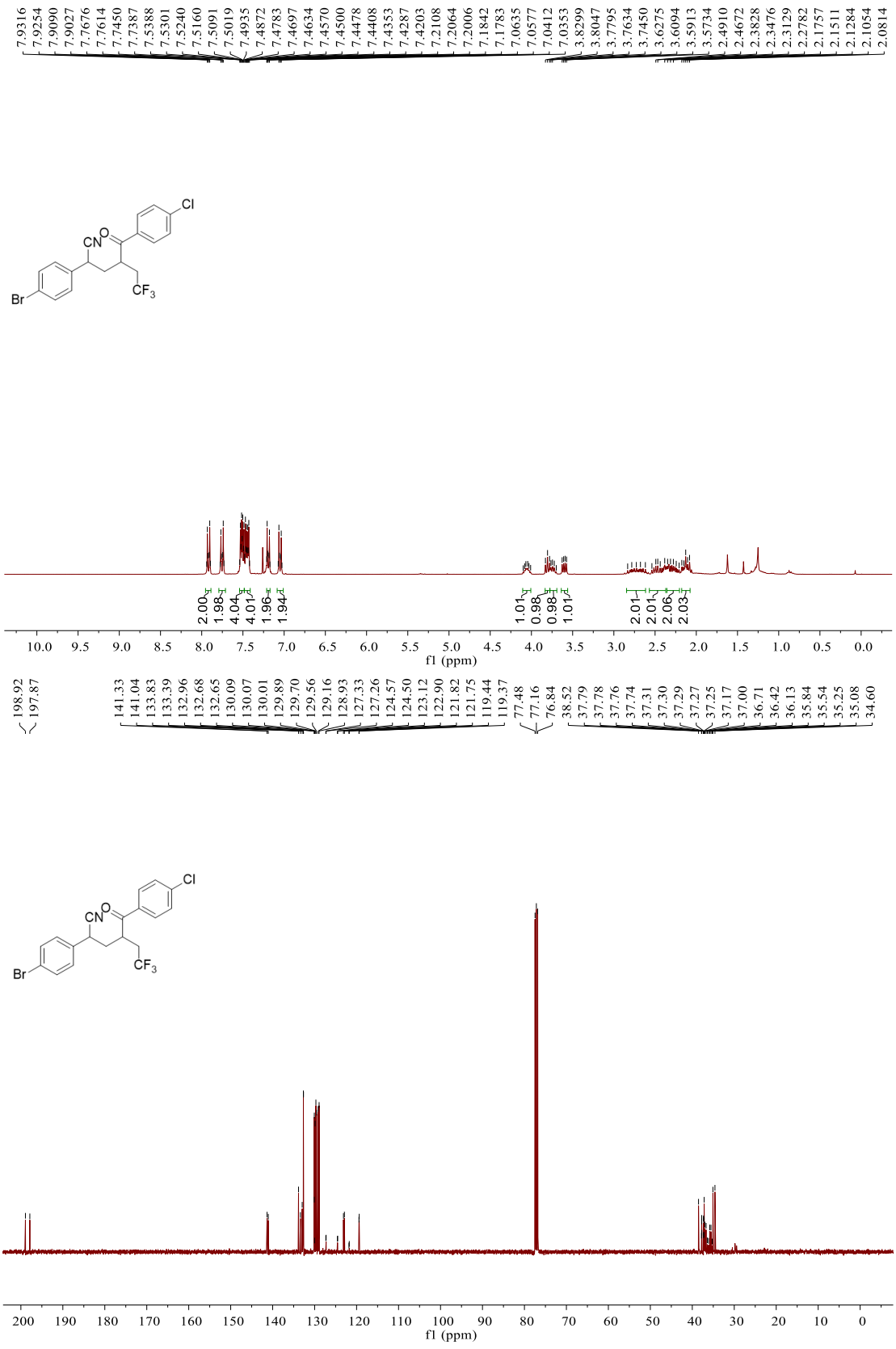
4aq ^{19}F NMR (376 MHz, Chloroform-*d*)



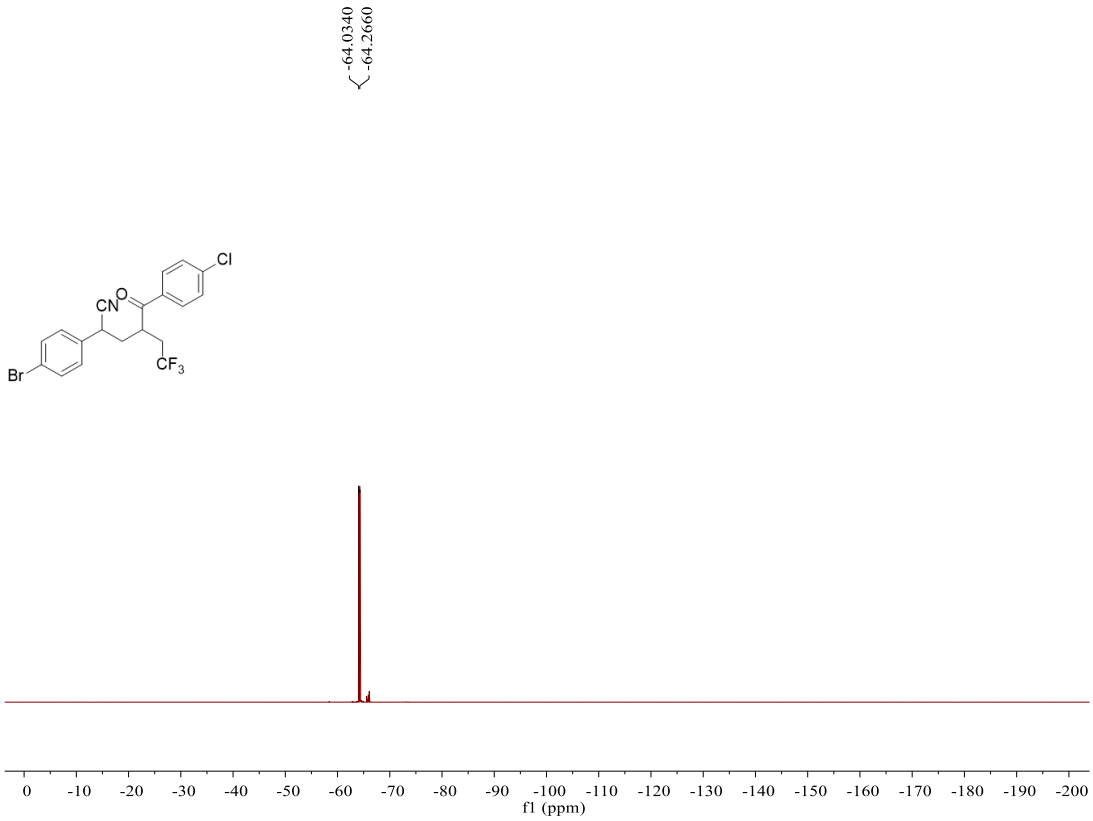
4ar^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



6' ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



6' ^{19}F NMR (376 MHz, Chloroform-*d*)



9. The Cartesian coordinates of all the stationary points

NHC-A

C	2.2373	-0.7877	0.5793
C	1.1482	-0.4196	-0.1426
C	1.0306	-0.1731	-1.6202
C	3.6244	-1.0922	0.0884
C	2.3661	-0.1460	-2.3703
C	4.2940	0.0702	-0.6591
C	3.3993	0.7684	-1.6986
H	2.7679	-1.1646	-2.4828
H	3.5764	-1.9760	-0.5653
H	5.1916	-0.3325	-1.1528
H	0.3460	-0.9176	-2.0617
H	4.2528	-1.3857	0.9408
H	2.1583	0.2083	-3.3894
H	4.6480	0.8157	0.0686
H	4.0458	1.2270	-2.4605
H	2.8595	1.6037	-1.2217
S	1.7702	-0.8928	2.2586
N	0.0212	-0.2485	0.6862
C	0.1341	-0.4527	2.0097
C	-1.2423	0.1528	0.1161
C	-2.1284	-0.8427	-0.3234
C	-1.5163	1.5246	-0.0025
C	-3.3492	-0.4271	-0.8658
C	-2.7489	1.8925	-0.5513
C	-3.6586	0.9262	-0.9740
H	-4.0679	-1.1720	-1.2103
H	-3.0010	2.9491	-0.6524

H	-4.6158	1.2316	-1.3993
C	-0.5259	2.5681	0.4867
C	-0.8483	2.9553	1.9353
C	-0.4663	3.8017	-0.4150
H	0.4748	2.1073	0.4827
H	-0.8341	2.0688	2.5849
H	-0.1145	3.6825	2.3132
H	-1.8484	3.4126	1.9922
H	-0.2882	3.5261	-1.4650
H	-1.3979	4.3848	-0.3670
H	0.3496	4.4625	-0.0893
C	-1.7952	-2.3168	-0.1665
C	-2.2834	-3.1667	-1.3400
C	-2.3536	-2.8375	1.1639
H	-0.6985	-2.4086	-0.1237
H	-1.9318	-2.7663	-2.3022
H	-1.9086	-4.1949	-1.2370
H	-3.3816	-3.2213	-1.3720
H	-1.9543	-2.2550	2.0061
H	-3.4515	-2.7544	1.1728
H	-2.0867	-3.8950	1.3073
H	0.5319	0.8015	-1.7574

S1

C	1.0965	2.3842	0.4684
C	1.8242	1.2422	0.3751
C	3.3055	1.0752	0.5677
C	1.5626	3.7739	0.8007
C	4.1046	2.3795	0.6496
C	2.6188	4.3277	-0.1656

C	3.7649	3.3524	-0.4866
H	3.9629	2.8629	1.6280
H	1.9577	3.7758	1.8277
H	3.0268	5.2440	0.2878
H	3.4808	0.4475	1.4572
H	0.6958	4.4494	0.8157
H	5.1675	2.1056	0.6032
H	2.1309	4.6341	-1.1027
H	4.6548	3.9378	-0.7582
H	3.5102	2.7607	-1.3818
S	-0.6013	2.0672	0.1965
N	1.0503	0.1201	0.0752
C	-0.3000	0.3664	-0.0499
C	1.6264	-1.1996	0.0809
C	1.5282	-1.9675	1.2509
C	2.3044	-1.6462	-1.0654
C	2.1225	-3.2344	1.2466
C	2.8886	-2.9145	-1.0201
C	2.7962	-3.7047	0.1238
H	2.0546	-3.8619	2.1376
H	3.4159	-3.2957	-1.8964
H	3.2540	-4.6950	0.1389
C	2.3436	-0.8184	-2.3389
C	1.2855	-1.3353	-3.3219
C	3.7297	-0.7858	-2.9854
H	2.0734	0.2166	-2.0782
H	0.2998	-1.3780	-2.8387
H	1.2323	-0.6874	-4.2093
H	1.5439	-2.3530	-3.6546
H	4.5009	-0.4417	-2.2800

H	4.0262	-1.7789	-3.3542
H	3.7255	-0.1035	-3.8476
C	0.7711	-1.4834	2.4758
C	1.6248	-1.5558	3.7447
C	-0.5321	-2.2763	2.6384
H	0.5047	-0.4275	2.3190
H	2.5572	-0.9835	3.6336
H	1.0683	-1.1439	4.5991
H	1.8898	-2.5949	3.9907
H	-1.1196	-2.2638	1.7096
H	-0.3124	-3.3272	2.8837
H	-1.1408	-1.8579	3.4536
H	3.6857	0.4868	-0.2828
C	-1.2753	-0.6091	-0.4244
O	-0.9582	-1.7424	-0.8373
C	-2.7317	-0.2502	-0.3491
C	-3.5781	-0.7943	-1.3254
C	-3.2960	0.5086	0.6844
C	-4.9471	-0.5541	-1.3027
H	-3.1411	-1.4181	-2.1060
C	-4.6683	0.7499	0.7263
H	-2.6703	0.8984	1.4890
C	-5.4810	0.2234	-0.2746
H	-5.6037	-0.9656	-2.0693
H	-5.1090	1.3318	1.5357
Cl	-7.1952	0.5251	-0.2329

2a

C	-2.2974	-0.0857	0.0462
C	-1.6172	-0.7226	1.0823

C	-0.2656	-0.4453	1.2752
C	0.4062	0.4575	0.4461
C	-0.2960	1.0828	-0.5876
C	-1.6486	0.8175	-0.7929
H	-2.1372	-1.4242	1.7346
H	0.2706	-0.9412	2.0873
H	0.2117	1.7956	-1.2414
H	-2.1930	1.3114	-1.5976
C	1.8967	0.6769	0.6412
H	2.1389	0.5349	1.7063
C	2.7262	-0.3284	-0.1864
H	2.3892	-1.3370	0.0958
H	2.4808	-0.1942	-1.2522
C	4.2339	-0.2012	0.0355
H	4.4663	-0.3361	1.1037
H	4.5507	0.8194	-0.2400
C	5.0043	-1.1965	-0.7827
H	4.8807	-1.1224	-1.8697
C	5.7935	-2.1457	-0.2807
H	5.9379	-2.2497	0.7986
H	6.3248	-2.8461	-0.9280
C	2.2838	2.0572	0.3091
N	2.5978	3.1297	0.0223
Br	-4.1379	-0.4491	-0.2224

4a'

C	0.0636	0.4167	1.9423
O	-0.1117	0.4836	3.1388
C	0.0300	1.6638	1.1067
C	-0.4691	2.8255	1.7125

C	0.4617	1.7207	-0.2251
C	-0.5544	4.0186	1.0066
H	-0.7949	2.7737	2.7518
C	0.3874	2.9116	-0.9428
H	0.8825	0.8434	-0.7152
C	-0.1250	4.0486	-0.3211
H	-0.9486	4.9220	1.4714
H	0.7257	2.9618	-1.9772
Cl	-0.2294	5.5331	-1.2147
C	0.2674	-0.9516	1.2846
C	1.6850	-1.0958	0.7512
C	-0.8423	-1.2672	0.2747
C	1.9670	-1.6198	-0.5141
C	2.7564	-0.7041	1.5653
H	-0.7163	-0.6661	-0.6389
H	-0.7499	-2.3226	-0.0259
C	-2.2343	-1.0308	0.8516
C	3.2824	-1.7465	-0.9625
H	1.1618	-1.9363	-1.1778
C	4.0740	-0.8210	1.1329
H	2.5595	-0.3009	2.5617
H	-2.3608	0.0258	1.1410
H	-2.3711	-1.6316	1.7636
C	-3.3604	-1.4005	-0.1282
C	4.3259	-1.3432	-0.1350
H	3.4897	-2.1553	-1.9515
H	4.8977	-0.5097	1.7753
H	-3.2597	-2.4636	-0.4009
C	-4.7372	-1.1843	0.5102
C	-3.2080	-0.6253	-1.3723

Br	6.1150	-1.5067	-0.7382
H	-4.9473	-0.1150	0.6500
H	-4.7521	-1.6664	1.4969
C	-5.8663	-1.7834	-0.2868
N	-3.0407	0.0046	-2.3239
F	-5.9793	-1.2306	-1.4981
F	-7.0339	-1.6202	0.3357
F	-5.6926	-3.0969	-0.4723
H	0.1635	-1.6520	2.1284

4a

C	2.0965	-0.7068	-0.9873
O	1.6931	-0.9206	-2.1088
C	2.5289	0.6804	-0.6061
C	2.6602	1.6106	-1.6474
C	2.7733	1.0969	0.7085
C	3.0354	2.9227	-1.3923
H	2.4615	1.2810	-2.6673
C	3.1401	2.4127	0.9815
H	2.6721	0.4122	1.5485
C	3.2709	3.3133	-0.0730
H	3.1442	3.6450	-2.2011
H	3.3227	2.7399	2.0045
Cl	3.7319	4.9531	0.2598
C	2.1279	-1.8695	0.0108
C	1.0576	-1.7457	1.1100
C	3.5087	-2.1549	0.6078
H	1.8523	-2.7322	-0.6136
C	-0.2886	-1.2721	0.5737
H	0.9426	-2.7395	1.5710

H	1.3934	-1.0763	1.9159
H	3.4405	-3.0132	1.2914
H	3.9109	-1.3080	1.1794
C	4.5320	-2.5046	-0.4395
C	-1.4027	-1.2746	1.6410
H	-0.6195	-1.9191	-0.2530
H	-0.2091	-0.2511	0.1654
F	4.1574	-3.5553	-1.1760
F	5.7109	-2.8034	0.1090
F	4.7385	-1.4879	-1.2894
C	-2.7309	-0.8317	1.0512
H	-1.5114	-2.2976	2.0343
C	-1.0096	-0.4285	2.7795
C	-3.5753	-1.7861	0.4775
C	-3.0944	0.5165	1.0028
N	-0.6715	0.2497	3.6494
C	-4.7675	-1.4070	-0.1356
H	-3.3031	-2.8433	0.5081
C	-4.2846	0.9115	0.3949
H	-2.4478	1.2747	1.4506
C	-5.1109	-0.0570	-0.1706
H	-5.4247	-2.1552	-0.5788
H	-4.5667	1.9637	0.3633
Br	-6.7316	0.4714	-0.9979

S2

C	-3.8196	-0.3039	0.0371
C	-3.0828	-0.6256	1.1753
C	-1.8391	-0.0279	1.3673
C	-1.3304	0.8823	0.4366

C	-2.0858	1.1880	-0.6984
C	-3.3325	0.5998	-0.9044
H	-3.4769	-1.3312	1.9065
H	-1.2595	-0.2758	2.2593
H	-1.7063	1.9019	-1.4329
H	-3.9202	0.8450	-1.7890
C	0.0610	1.4561	0.6447
H	0.2576	1.5222	1.7266
C	1.1412	0.5584	0.0064
H	1.0119	-0.4520	0.4223
H	0.9480	0.4874	-1.0758
C	2.5644	1.0463	0.2576
H	2.7425	1.1410	1.3440
H	2.6754	2.0733	-0.1473
C	3.5884	0.1483	-0.3430
H	3.3252	-0.4459	-1.2221
C	5.0343	0.3149	-0.0229
H	5.1790	0.7088	0.9940
C	0.1592	2.8279	0.1211
N	0.2507	3.8930	-0.3129
Br	-5.5164	-1.1042	-0.2307
H	5.5390	1.0150	-0.7147
C	5.7869	-0.9872	-0.1104
F	5.3307	-1.8879	0.7661
F	7.0901	-0.8228	0.1357
F	5.6828	-1.5402	-1.3250

S3

C	4.5729	0.7396	-0.1217
C	4.1548	-0.5380	-0.3334

C	5.0005	-1.7434	-0.6370
C	5.9697	1.2908	-0.0656
C	6.4868	-1.4503	-0.8599
C	6.7924	1.0700	-1.3411
C	6.7172	-0.3568	-1.9108
H	6.9848	-1.1944	0.0873
H	6.4751	0.8315	0.7963
H	7.8355	1.3206	-1.0976
H	4.8577	-2.4888	0.1615
H	5.9204	2.3654	0.1568
H	6.9448	-2.3910	-1.1938
H	6.4715	1.7872	-2.1107
H	7.6437	-0.5593	-2.4659
H	5.9048	-0.4179	-2.6547
S	3.2082	1.7641	0.1371
N	2.7525	-0.6549	-0.2731
C	2.1031	0.4704	0.0377
C	2.1695	-1.9142	-0.7462
C	1.8284	-2.9236	0.1572
C	2.1651	-2.1024	-2.1402
C	1.4593	-4.1655	-0.3714
C	1.7793	-3.3567	-2.6190
C	1.4336	-4.3842	-1.7438
H	1.1807	-4.9710	0.3111
H	1.7557	-3.5367	-3.6940
H	1.1433	-5.3595	-2.1369
C	2.5136	-0.9733	-3.0977
C	1.2603	-0.1298	-3.3554
C	3.1465	-1.4505	-4.4038
H	3.2519	-0.3198	-2.6058

H	0.7814	0.1386	-2.4046
H	1.5065	0.7830	-3.9180
H	0.5298	-0.7127	-3.9385
H	4.0094	-2.1089	-4.2219
H	2.4241	-1.9955	-5.0288
H	3.4918	-0.5840	-4.9854
C	1.7884	-2.6970	1.6526
C	2.8333	-3.5265	2.4019
C	0.3756	-2.9489	2.1880
H	2.0244	-1.6428	1.8251
H	3.8523	-3.3066	2.0512
H	2.7897	-3.3004	3.4775
H	2.6533	-4.6048	2.2714
H	-0.3429	-2.3709	1.5902
H	0.1139	-4.0165	2.1361
H	0.3090	-2.6347	3.2410
H	4.6053	-2.2138	-1.5506
C	0.5617	0.5470	0.3316
O	-0.0272	-0.5249	-0.1467
C	0.0352	1.8806	-0.3067
C	-0.9131	1.7526	-1.3252
C	0.3843	3.1749	0.1017
C	-1.4838	2.8647	-1.9403
H	-1.1973	0.7389	-1.6116
C	-0.1778	4.3023	-0.4962
H	1.0885	3.3449	0.9173
C	-1.1081	4.1358	-1.5177
H	-2.2239	2.7518	-2.7334
H	0.0931	5.3041	-0.1630
Cl	-1.8289	5.5393	-2.2580

C	0.3556	0.6171	1.9370
C	-1.0605	1.1145	2.2778
C	1.3449	1.3728	2.8499
H	0.3987	-0.4454	2.2047
C	-2.2150	0.3948	1.5909
H	-1.1930	1.0202	3.3690
H	-1.1154	2.1937	2.0573
H	0.8010	1.8117	3.6992
H	1.8713	2.2075	2.3710
C	2.4040	0.5140	3.4911
C	-3.5644	1.1122	1.8033
H	-2.3174	-0.6277	1.9865
H	-2.0281	0.2859	0.5173
F	1.8812	-0.5429	4.1267
F	3.1048	1.2069	4.3934
F	3.2993	0.0214	2.6152
C	-4.6937	0.3507	1.1336
H	-3.7737	1.1909	2.8818
C	-3.5016	2.4937	1.2922
C	-4.8304	0.3731	-0.2584
C	-5.5633	-0.4362	1.8902
N	-3.4478	3.5722	0.8843
C	-5.8223	-0.3726	-0.8893
H	-4.1542	0.9864	-0.8603
C	-6.5608	-1.1914	1.2737
H	-5.4660	-0.4639	2.9775
C	-6.6800	-1.1509	-0.1129
H	-5.9283	-0.3495	-1.9739
H	-7.2395	-1.8032	1.8679
Br	-8.0350	-2.1709	-0.9611

S4

C	-2.6991	-0.8502	-0.5811
C	-1.3551	-0.5110	-0.4588
C	-0.9605	0.6442	0.2281
C	-1.9460	1.4573	0.7926
C	-3.2989	1.1347	0.6792
C	-3.6622	-0.0188	-0.0089
H	-2.9977	-1.7530	-1.1139
H	-0.6006	-1.1664	-0.9008
H	-1.6573	2.3604	1.3340
H	-4.0607	1.7746	1.1248
C	0.4957	1.0220	0.3178
C	1.4325	-0.1120	0.7859
C	1.1500	1.4808	-0.9983
H	0.6124	1.8242	1.0642
C	2.7195	-0.0779	-0.0560
C	2.6458	1.2866	-0.7551
H	0.8746	2.5121	-1.2530
H	0.8141	0.8284	-1.8201
H	2.5975	-0.8705	-0.8141
H	3.0291	2.0696	-0.0810
H	3.2406	1.3162	-1.6765
C	3.9582	-0.3787	0.7762
H	3.8481	-1.3484	1.2814
H	4.1103	0.3890	1.5486
C	5.2137	-0.4474	-0.0499
N	1.1989	-0.9154	1.7031
Br	-5.4961	-0.4741	-0.1692
F	5.5303	0.7366	-0.5908

F	5.0974	-1.3160	-1.0616
F	6.2612	-0.8329	0.6830

S5

C	4.3339	0.0489	0.0521
C	3.3370	-0.8878	0.3363
C	2.0035	-0.5322	0.1952
C	1.6292	0.7696	-0.2333
C	2.6736	1.6914	-0.5130
C	4.0060	1.3411	-0.3737
H	3.6080	-1.8910	0.6662
H	1.2352	-1.2733	0.4191
H	2.4158	2.6989	-0.8455
H	4.7943	2.0617	-0.5927
C	0.2715	1.1536	-0.3819
H	0.0648	2.1726	-0.7191
C	-0.8803	0.2452	-0.1063
H	-0.8123	-0.6525	-0.7498
H	-0.8227	-0.1364	0.9307
C	-2.2263	0.9290	-0.3185
H	-2.3097	1.2837	-1.3580
H	-2.2974	1.8147	0.3307
C	-3.4277	0.0250	0.0018
H	-3.3452	-0.3161	1.0468
C	-4.7477	0.7878	-0.1612
H	-4.9471	1.0189	-1.2166
Br	6.1538	-0.4371	0.2449
H	-4.6789	1.7360	0.3886
C	-5.9405	0.0508	0.3895
F	-6.1706	-1.0959	-0.2565

F	-7.0467	0.7897	0.2943
F	-5.7748	-0.2552	1.6814
C	-3.3884	-1.1834	-0.8405
N	-3.3173	-2.1142	-1.5179

S6

C	2.2207	-2.3025	-2.0945
C	3.0615	-1.6787	-1.2244
C	4.5345	-1.9199	-1.0428
C	2.5401	-3.3582	-3.1138
C	5.0688	-3.2015	-1.6961
C	3.0974	-4.6515	-2.5028
C	4.1833	-4.4274	-1.4379
H	5.2150	-3.0552	-2.7769
H	3.2635	-2.9347	-3.8252
H	3.5043	-5.2520	-3.3300
H	5.0942	-1.0408	-1.3956
H	1.6381	-3.5821	-3.6991
H	6.0720	-3.3695	-1.2816
H	2.2743	-5.2362	-2.0664
H	4.8035	-5.3324	-1.3770
H	3.7130	-4.3186	-0.4466
S	0.6217	-1.6794	-1.9047
N	2.3952	-0.7204	-0.4447
C	1.0847	-0.5970	-0.6756
C	3.1929	0.1041	0.4547
C	3.8147	1.2429	-0.0922
C	3.4463	-0.3604	1.7519
C	4.7276	1.9191	0.7168
C	4.3668	0.3652	2.5228

C	5.0069	1.4859	2.0125
H	5.2270	2.8082	0.3269
H	4.5889	0.0328	3.5383
H	5.7259	2.0304	2.6262
C	2.7961	-1.5983	2.3542
C	2.0973	-1.2559	3.6744
C	3.8073	-2.7284	2.5870
H	2.0305	-1.9623	1.6526
H	1.4005	-0.4159	3.5532
H	1.5311	-2.1247	4.0407
H	2.8339	-0.9878	4.4468
H	4.2754	-3.0765	1.6563
H	4.6076	-2.3993	3.2668
H	3.3048	-3.5899	3.0502
C	3.5200	1.7689	-1.4890
C	4.7357	1.6536	-2.4160
C	3.0340	3.2208	-1.4251
H	2.6948	1.1767	-1.9084
H	5.0538	0.6127	-2.5672
H	4.4962	2.0752	-3.4032
H	5.5921	2.2144	-2.0112
H	2.1621	3.2782	-0.7630
H	3.8308	3.8913	-1.0675
H	2.7435	3.5608	-2.4314
H	4.7307	-1.9632	0.0374
C	0.2017	0.5294	-0.0311
O	0.9393	1.6082	0.0179
C	-0.2998	0.0356	1.3471
C	-0.5412	1.0298	2.2997
C	-0.6007	-1.2909	1.6702

C	-1.1170	0.7202	3.5308
H	-0.2601	2.0518	2.0424
C	-1.1678	-1.6219	2.8999
H	-0.3857	-2.0979	0.9649
C	-1.4331	-0.6073	3.8155
H	-1.3153	1.4954	4.2717
H	-1.4057	-2.6559	3.1496
Cl	-2.1456	-1.0115	5.3549
C	-1.1398	0.7593	-0.9647
C	-1.4135	2.2461	-0.9146
C	-2.4285	-0.0241	-0.6527
C	-2.3273	2.8117	-0.0197
C	-0.7050	3.1059	-1.7633
H	-2.6360	0.0133	0.4281
H	-3.2592	0.5125	-1.1399
C	-2.5084	-1.4706	-1.1259
C	-2.5294	4.1928	0.0364
H	-2.8961	2.1776	0.6622
C	-0.8956	4.4833	-1.7303
H	0.0226	2.6847	-2.4588
H	-1.7589	-2.1097	-0.6379
H	-2.3237	-1.5243	-2.2104
C	-3.8932	-2.0918	-0.8693
C	-1.8100	5.0163	-0.8221
H	-3.2426	4.6193	0.7420
H	-0.3366	5.1394	-2.3982
H	-4.6567	-1.4691	-1.3634
C	-3.9724	-3.5127	-1.4400
C	-4.1960	-2.0721	0.5729
Br	-2.0810	6.8967	-0.7647

H	-3.3497	-4.2095	-0.8621
H	-3.6021	-3.5015	-2.4741
C	-5.3728	-4.0654	-1.4856
N	-4.3961	-2.0480	1.7087
F	-5.9134	-4.1793	-0.2692
F	-5.3931	-5.2766	-2.0443
F	-6.1861	-3.2819	-2.2028
H	-0.8358	0.5422	-2.0020

TS1

C	-3.1523	-0.1913	0.0444
C	-2.2033	-0.7647	0.8894
C	-0.9871	-0.1141	1.0797
C	-0.7132	1.0974	0.4367
C	-1.6784	1.6525	-0.4062
C	-2.9018	1.0139	-0.6062
H	-2.4129	-1.7068	1.3959
H	-0.2401	-0.5602	1.7404
H	-1.4840	2.6004	-0.9125
H	-3.6532	1.4531	-1.2624
C	0.6569	1.7275	0.6215
H	0.9772	1.5736	1.6645
C	1.7007	1.0736	-0.3083
H	1.6746	-0.0075	-0.1098
H	1.3830	1.2165	-1.3532
C	3.1197	1.6108	-0.1013
H	3.4054	1.5091	0.9579
H	3.1322	2.6883	-0.3406
C	4.1089	0.8892	-0.9632
H	3.9332	0.9200	-2.0441

C	5.1222	0.1390	-0.4819
H	5.3746	0.1603	0.5823
C	0.6214	3.1824	0.4100
N	0.6080	4.3199	0.2177
Br	-4.8124	-1.0662	-0.2204
H	5.8322	-0.3485	-1.1530
C	3.9735	-1.8673	0.0148
F	3.3115	-1.5542	1.1148
F	4.7043	-2.9432	0.2170
F	3.1235	-2.0706	-0.9708

TS2

C	4.3760	0.8558	0.0649
C	3.9963	-0.4309	-0.0747
C	4.8498	-1.6614	0.0179
C	5.7202	1.4319	0.4125
C	6.3498	-1.4001	0.1715
C	6.8536	1.0343	-0.5419
C	6.8978	-0.4592	-0.9085
H	6.5736	-1.0108	1.1766
H	5.9669	1.1286	1.4418
H	7.7991	1.3280	-0.0614
H	4.4732	-2.2753	0.8535
H	5.6434	2.5280	0.4397
H	6.8533	-2.3745	0.1077
H	6.7765	1.6294	-1.4641
H	7.9365	-0.7276	-1.1480
H	6.3230	-0.6295	-1.8334
S	2.9901	1.9265	-0.0881

N	2.6097	-0.5863	-0.3043
C	1.8926	0.5739	-0.1822
C	2.1872	-1.7240	-1.1088
C	1.7984	-2.9241	-0.4949
C	2.3001	-1.6030	-2.5056
C	1.4822	-4.0090	-1.3186
C	1.9640	-2.7117	-3.2888
C	1.5562	-3.9066	-2.7040
H	1.1653	-4.9493	-0.8632
H	2.0268	-2.6377	-4.3761
H	1.3004	-4.7624	-3.3303
C	2.7463	-0.3162	-3.1829
C	1.5494	0.3952	-3.8247
C	3.8570	-0.5611	-4.2081
H	3.1627	0.3549	-2.4194
H	0.7522	0.5694	-3.0888
H	1.8566	1.3622	-4.2499
H	1.1285	-0.2182	-4.6367
H	4.7042	-1.0990	-3.7578
H	3.4957	-1.1505	-5.0637
H	4.2260	0.3980	-4.5996
C	1.6431	-3.0552	1.0069
C	2.3768	-4.2687	1.5820
C	0.1512	-3.0924	1.3638
H	2.0856	-2.1592	1.4610
H	3.4434	-4.2634	1.3140
H	2.2980	-4.2678	2.6791
H	1.9417	-5.2116	1.2186
H	-0.3829	-2.2825	0.8474
H	-0.2941	-4.0493	1.0501

H	0.0081	-2.9855	2.4505
H	4.6884	-2.2599	-0.8942
C	0.4551	0.6398	-0.4304
O	-0.1587	-0.3769	-0.7942
C	-0.1889	1.9963	-0.6163
C	-1.2206	2.0598	-1.5611
C	0.1480	3.1616	0.0849
C	-1.8835	3.2546	-1.8263
H	-1.4996	1.1441	-2.0845
C	-0.5057	4.3642	-0.1680
H	0.9007	3.1414	0.8748
C	-1.5155	4.4006	-1.1263
H	-2.6841	3.3007	-2.5646
H	-0.2521	5.2645	0.3910
Cl	-2.3502	5.8951	-1.4304
C	0.6508	0.4585	1.7659
C	-0.7558	0.8778	2.1761
C	1.6595	1.0614	2.7240
H	0.7452	-0.6250	1.6518
C	-1.9464	0.2088	1.5004
H	-0.8313	0.6745	3.2627
H	-0.8467	1.9746	2.0856
H	1.1571	1.6727	3.4891
H	2.3964	1.7293	2.2401
C	2.4603	0.0334	3.4754
C	-3.2904	0.8142	1.9562
H	-1.9712	-0.8638	1.7465
H	-1.8928	0.2745	0.4088
F	1.6843	-0.8824	4.0690
F	3.2087	0.5936	4.4301

F	3.3025	-0.6425	2.6761
C	-4.4528	0.1009	1.2893
H	-3.3853	0.7160	3.0491
C	-3.3320	2.2577	1.6626
C	-4.7768	0.3690	-0.0446
C	-5.1598	-0.8875	1.9763
N	-3.3607	3.3866	1.4234
C	-5.7942	-0.3327	-0.6858
H	-4.2299	1.1413	-0.5924
C	-6.1801	-1.6010	1.3481
H	-4.9149	-1.1082	3.0173
C	-6.4872	-1.3150	0.0203
H	-6.0461	-0.1187	-1.7243
H	-6.7316	-2.3705	1.8884
Br	-7.8737	-2.2777	-0.8429

TS3

C	4.2056	-2.0397	0.5142
C	3.0142	-2.5746	0.1353
C	2.7136	-3.9936	-0.2609
C	5.5243	-2.7287	0.7214
C	3.9436	-4.8950	-0.4073
C	6.0674	-3.4278	-0.5328
C	5.0300	-4.2716	-1.2934
H	4.3522	-5.1629	0.5790
H	5.4049	-3.4580	1.5357
H	6.9036	-4.0667	-0.2110
H	1.9848	-4.4324	0.4378
H	6.2607	-1.9966	1.0801

H	3.5942	-5.8371	-0.8516
H	6.4933	-2.6767	-1.2142
H	5.5609	-5.0594	-1.8461
H	4.5351	-3.6508	-2.0594
S	4.0071	-0.3308	0.7485
N	2.0050	-1.5924	0.0752
C	2.3460	-0.3334	0.3671
C	0.6539	-1.9658	-0.3008
C	-0.2961	-2.1553	0.7159
C	0.3683	-2.1286	-1.6652
C	-1.5960	-2.4860	0.3166
C	-0.9437	-2.4659	-2.0086
C	-1.9186	-2.6334	-1.0300
H	-2.3720	-2.6291	1.0686
H	-1.2086	-2.5872	-3.0605
H	-2.9400	-2.8889	-1.3172
C	1.4094	-1.9228	-2.7565
C	1.1766	-0.5996	-3.4947
C	1.4424	-3.0893	-3.7503
H	2.4009	-1.8613	-2.2811
H	1.1511	0.2359	-2.7848
H	1.9683	-0.4374	-4.2412
H	0.2095	-0.6247	-4.0217
H	1.5710	-4.0617	-3.2520
H	0.5148	-3.1346	-4.3399
H	2.2743	-2.9545	-4.4566
C	0.0570	-2.0468	2.1949
C	0.6327	-3.3624	2.7359
C	-1.1299	-1.6078	3.0539
H	0.8436	-1.2863	2.3036

H	1.6012	-3.6041	2.2783
H	0.7911	-3.2833	3.8213
H	-0.0605	-4.1967	2.5486
H	-1.6275	-0.7199	2.6363
H	-1.8803	-2.4075	3.1401
H	-0.7836	-1.3646	4.0669
H	2.1968	-3.9600	-1.2312
C	1.0308	1.1926	0.0131
O	0.1829	0.7345	-0.7760
C	1.9773	2.2572	-0.5751
C	1.5419	2.8601	-1.7623
C	3.1803	2.7054	-0.0142
C	2.2813	3.8640	-2.3845
H	0.5916	2.5333	-2.1863
C	3.9384	3.7020	-0.6257
H	3.5681	2.2814	0.9103
C	3.4812	4.2739	-1.8107
H	1.9305	4.3290	-3.3062
H	4.8793	4.0344	-0.1873
Cl	4.4243	5.5215	-2.5790
C	0.4999	1.4754	1.4481
C	-0.6776	2.4618	1.2699
C	1.5119	1.9419	2.4920
H	0.0827	0.5154	1.7846
C	-1.9764	1.7078	0.9813
H	-0.7978	3.0919	2.1613
H	-0.4377	3.1428	0.4356
H	1.7200	3.0186	2.4130
H	2.4644	1.4027	2.4004
C	1.0629	1.6591	3.9014

C	-3.0212	2.4962	0.1687
H	-2.4595	1.4100	1.9252
H	-1.7390	0.7940	0.4192
F	-0.1580	2.1305	4.1828
F	1.9011	2.1881	4.7980
F	1.0231	0.3382	4.1433
C	-4.2509	1.6393	-0.0756
H	-3.3140	3.4050	0.7173
C	-2.4467	2.9483	-1.1110
C	-4.1773	0.5420	-0.9412
C	-5.4391	1.8856	0.6130
N	-1.9960	3.2941	-2.1156
C	-5.2742	-0.2957	-1.1224
H	-3.2503	0.3367	-1.4839
C	-6.5463	1.0532	0.4451
H	-5.5079	2.7369	1.2931
C	-6.4514	-0.0310	-0.4227
H	-5.2167	-1.1462	-1.8018
H	-7.4730	1.2486	0.9845
Br	-7.9486	-1.1705	-0.6576

TS4

C	-2.8954	-0.9156	-0.5517
C	-1.5262	-0.7305	-0.3771
C	-1.0367	0.3540	0.3579
C	-1.9450	1.2562	0.9181
C	-3.3189	1.0868	0.7519
C	-3.7813	-0.0007	0.0151
H	-3.2710	-1.7654	-1.1216
H	-0.8314	-1.4522	-0.8121

H	-1.5786	2.1071	1.4963
H	-4.0219	1.7924	1.1947
C	0.4498	0.6099	0.4901
C	1.2215	-0.6615	0.7087
C	1.0432	1.3684	-0.7047
H	0.6274	1.2100	1.3978
C	2.9769	-0.0688	-0.3203
C	2.5612	1.3540	-0.5374
H	0.6313	2.3851	-0.7493
H	0.7596	0.8504	-1.6348
H	2.8365	-0.7364	-1.1776
H	2.8554	1.9724	0.3252
H	3.0552	1.7775	-1.4278
C	4.1130	-0.4311	0.5836
H	4.0514	-1.4908	0.8712
H	4.1053	0.1748	1.5017
C	5.4559	-0.2209	-0.0721
N	1.3297	-1.7493	1.1433
Br	-5.6466	-0.2448	-0.2182
F	5.6402	1.0590	-0.4233
F	5.5872	-0.9512	-1.1846
F	6.4610	-0.5538	0.7409

TS5

C	-2.8570	0.8839	-0.8271
C	-1.5411	1.1498	-0.4608
C	-0.9842	0.5930	0.7057
C	-1.7961	-0.2523	1.4882
C	-3.1088	-0.5302	1.1311

C	-3.6321	0.0437	-0.0289
H	-3.2786	1.3272	-1.7293
H	-0.9496	1.8096	-1.0957
H	-1.3780	-0.7054	2.3892
H	-3.7246	-1.1868	1.7457
C	0.3979	0.8124	1.1120
C	1.4873	-0.8191	0.5393
C	1.2968	1.8480	0.4992
H	0.5848	0.6290	2.1760
C	2.6701	-0.0939	-0.0467
C	2.7260	1.3130	0.5490
H	1.2118	2.8011	1.0459
H	1.0212	2.0439	-0.5465
H	2.4555	-0.0069	-1.1251
H	3.0805	1.2583	1.5909
H	3.4224	1.9522	-0.0076
C	3.9171	-0.9588	0.1389
H	3.7658	-1.9409	-0.3285
H	4.1282	-1.1206	1.2053
C	5.1496	-0.3544	-0.4818
N	1.0075	-1.8640	0.8135
Br	-5.4225	-0.3253	-0.5252
F	5.5816	0.7221	0.1873
F	4.9319	0.0349	-1.7435
F	6.1580	-1.2280	-0.5038

TS6

C	-2.9808	0.5857	-1.4779
C	-3.0068	0.6145	-0.1224
C	-4.1924	0.4315	0.7790

C	-4.1010	0.3214	-2.4430
C	-5.5513	0.4255	0.0701
C	-5.2700	1.3095	-2.3369
C	-5.7229	1.6034	-0.8972
H	-5.7080	-0.5319	-0.4510
H	-4.4557	-0.7068	-2.2669
H	-6.1066	0.8845	-2.9118
H	-4.0529	-0.5045	1.3471
H	-3.7042	0.3280	-3.4681
H	-6.3193	0.4683	0.8544
H	-4.9986	2.2536	-2.8321
H	-6.7747	1.9210	-0.9210
H	-5.1578	2.4627	-0.4997
S	-1.3554	0.8164	-2.0548
N	-1.7349	0.8322	0.4392
C	-0.7235	0.8618	-0.4631
C	-1.6469	1.5248	1.7259
C	-1.6749	0.8255	2.9412
C	-1.6365	2.9311	1.6736
C	-1.6188	1.5690	4.1230
C	-1.5688	3.6291	2.8847
C	-1.5504	2.9580	4.1014
H	-1.6218	1.0441	5.0802
H	-1.5368	4.7198	2.8701
H	-1.4955	3.5187	5.0355
C	-1.6821	3.7200	0.3731
C	-0.3014	4.3047	0.0546
C	-2.7522	4.8153	0.4030
H	-1.9581	3.0396	-0.4437
H	0.4733	3.5247	0.0544

H	-0.3048	4.7957	-0.9299
H	-0.0205	5.0544	0.8106
H	-3.7381	4.4031	0.6630
H	-2.5083	5.6024	1.1313
H	-2.8268	5.2918	-0.5852
C	-1.7317	-0.6847	3.0207
C	-2.8723	-1.1748	3.9178
C	-0.3843	-1.2455	3.4877
H	-1.9177	-1.0531	2.0050
H	-3.8383	-0.7372	3.6263
H	-2.9568	-2.2701	3.8560
H	-2.6910	-0.9183	4.9723
H	0.4175	-0.9063	2.8173
H	-0.1552	-0.8965	4.5065
H	-0.4098	-2.3463	3.5095
H	-4.1823	1.2453	1.5227
C	0.6912	0.8179	-0.0277
O	0.8957	0.7793	1.2068
C	1.7827	1.4162	-0.8964
C	2.9024	1.8835	-0.1943
C	1.8007	1.4956	-2.2964
C	4.0118	2.4032	-0.8558
H	2.8901	1.8076	0.8926
C	2.9000	2.0190	-2.9733
H	0.9756	1.1232	-2.9034
C	4.0024	2.4657	-2.2470
H	4.8800	2.7565	-0.2988
H	2.9085	2.0700	-4.0619
Cl	5.3835	3.1068	-3.0925
C	0.9313	-1.2656	-0.8139

C	-0.3133	-2.0046	-0.8786
C	1.9981	-1.6532	0.1702
C	-0.9409	-2.5094	0.2803
C	-0.9993	-2.1669	-2.1052
H	1.9579	-0.9579	1.0364
H	1.8136	-2.6642	0.5716
C	3.3896	-1.6066	-0.4615
C	-2.2342	-3.0169	0.2445
H	-0.4147	-2.4532	1.2338
C	-2.2872	-2.6896	-2.1590
H	-0.5082	-1.8686	-3.0330
H	3.5382	-0.6451	-0.9779
H	3.4826	-2.3967	-1.2224
C	4.5374	-1.8028	0.5423
C	-2.9164	-3.0628	-0.9733
H	-2.7216	-3.3562	1.1602
H	-2.8072	-2.7850	-3.1132
H	4.4094	-2.7749	1.0459
C	5.8908	-1.7909	-0.1790
C	4.4861	-0.7707	1.5928
Br	-4.7251	-3.6397	-1.0156
H	6.1320	-0.7835	-0.5466
H	5.8388	-2.4648	-1.0448
C	7.0369	-2.2674	0.6735
N	4.4341	0.0545	2.3973
F	7.2310	-1.4937	1.7455
F	8.1779	-2.2803	-0.0181
F	6.8300	-3.5110	1.1227
H	1.3017	-0.9769	-1.8040

TS7

C	3.4824	-0.5116	-1.5628
C	3.3475	-1.2660	-0.4398
C	4.4219	-2.0632	0.2513
C	4.6852	-0.3370	-2.4497
C	5.8132	-1.4450	0.0722
C	5.5634	-1.5924	-2.4906
C	6.4764	-1.7548	-1.2722
H	5.7319	-0.3541	0.2059
H	5.2747	0.5357	-2.1210
H	6.1817	-1.5710	-3.3994
H	4.1754	-2.1300	1.3193
H	4.3291	-0.0993	-3.4623
H	6.4664	-1.8041	0.8804
H	4.9036	-2.4701	-2.5887
H	7.3533	-1.0978	-1.3833
H	6.8620	-2.7864	-1.2604
S	1.9585	0.2455	-1.9227
N	2.0232	-1.2265	0.0505
C	1.1522	-0.4461	-0.5930
C	1.6799	-1.9839	1.2388
C	1.8547	-1.3537	2.4817
C	1.2717	-3.3260	1.1002
C	1.6754	-2.1325	3.6293
C	1.1119	-4.0566	2.2842
C	1.3270	-3.4748	3.5310
H	1.8103	-1.6800	4.6126
H	0.8053	-5.1004	2.2359
H	1.2015	-4.0723	4.4352
C	0.9462	-3.9600	-0.2536

C	0.1466	-5.2588	-0.1205
C	2.1687	-4.2441	-1.1386
H	0.3122	-3.2335	-0.7870
H	-0.7040	-5.1595	0.5657
H	-0.2511	-5.5459	-1.1046
H	0.7857	-6.0819	0.2362
H	2.6640	-3.3315	-1.4915
H	2.9027	-4.8648	-0.6017
H	1.8464	-4.8024	-2.0295
C	2.2341	0.1147	2.6010
C	3.7363	0.3011	2.8464
C	1.4263	0.8219	3.6914
H	1.9768	0.5987	1.6484
H	4.3441	-0.0747	2.0126
H	3.9670	1.3696	2.9704
H	4.0492	-0.2239	3.7627
H	0.3530	0.6538	3.5366
H	1.7102	0.4778	4.6974
H	1.6234	1.9043	3.6537
H	4.4175	-3.1021	-0.1180
C	-0.7218	0.0056	0.1950
O	-0.6052	0.1231	1.4257
C	-1.3900	-1.2685	-0.3278
C	-1.9082	-2.1479	0.6246
C	-1.5242	-1.5833	-1.6847
C	-2.5554	-3.3202	0.2411
H	-1.7892	-1.8894	1.6777
C	-2.1557	-2.7581	-2.0864
H	-1.0994	-0.9289	-2.4485
C	-2.6636	-3.6195	-1.1142

H	-2.9606	-4.0088	0.9835
H	-2.2457	-3.0151	-3.1419
Cl	-3.4110	-5.1162	-1.6018
C	-1.0488	1.2882	-0.6190
C	-0.0087	2.3839	-0.5183
C	-2.3927	1.8598	-0.1181
C	0.5940	2.7258	0.6994
C	0.3409	3.1127	-1.6605
H	-2.2607	2.1427	0.9382
H	-2.5892	2.7884	-0.6789
C	-3.5956	0.9322	-0.2551
C	1.5597	3.7299	0.7640
H	0.3139	2.1760	1.5977
C	1.2963	4.1263	-1.6132
H	-0.1250	2.8692	-2.6188
H	-3.5153	0.0850	0.4414
H	-3.6389	0.5082	-1.2707
C	-4.9326	1.6497	-0.0010
C	1.9076	4.4176	-0.3964
H	2.0369	3.9782	1.7131
H	1.5679	4.6773	-2.5137
H	-5.0432	2.4654	-0.7341
C	-6.1088	0.6798	-0.1624
C	-4.9260	2.2792	1.3310
Br	3.2288	5.7793	-0.3179
H	-6.1319	-0.0560	0.6531
H	-5.9909	0.1340	-1.1084
C	-7.4495	1.3631	-0.2167
N	-4.8817	2.7569	2.3798
F	-7.7345	2.0115	0.9165

F	-8.4303	0.4842	-0.4288
F	-7.5018	2.2638	-1.2052
H	-1.1584	1.0307	-1.6837