Dual Visible-Light and NHC-Catalyzed Relay Trifunctionalization of Unactivated Alkenes

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Supporting Information

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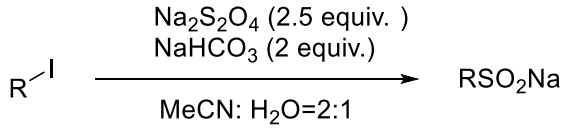
1. General methods

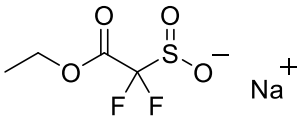
All reactions were carried out in dry glassware and were monitored by analytical thin layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of the products was 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. General procedure for synthesis of sodium sulfinate

Sodium trifluoromethanesulfinate, Sodium difluoromethanesulfinate and Sodium fluoromethanesulfinate were commercially available. Other sodium sulfinates **3aa**, **3ad** and **3ae** were synthesized according to the following procedures.

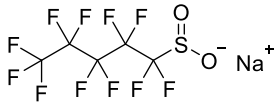


Iodoalkanes (1 mmol 1 equiv.) was dissolved into CH_3CN (5 mL) in a round bottomed flask. The solid $NaHCO_3$ (164 mg, 2 mmol), $Na_2S_2O_4$ (435 mg, 2.5mmol) and H_2O (2 mL) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature overnight. When the reaction was finished (monitored via TLC). The reaction mixture was then extracted with ethyl acetate (3 × 25 mL). The obtaining organic phase was dried over anhydrous $MgSO_4$ and concentrated to afford solids. The solid was dried at 30-40 °C in vacuum to yield the relative sodium sulfinate. The sodium sulfinate was used without any other purification.



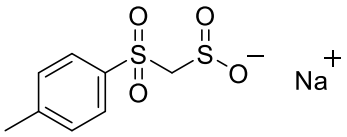
2-ethoxy-1,1-difluoro-2-oxoethane-1-sulfinate sodium (**3aa**)

The title compound was obtained according to the general condition (178.0 mg, 85% yield). ^{1}H NMR (300 MHz, D_2O) δ 3.53 (q, J = 7.1 Hz, 2H), 1.06 (t, J = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, D_2O) δ -103.8, -104.8, -105.6, -106.6.



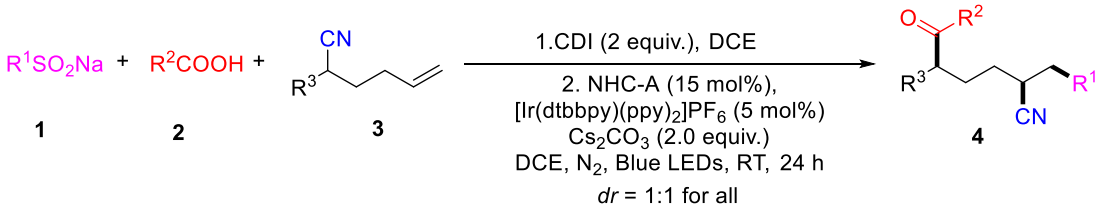
1,1,2,2,3,3,4,4,5,5,5-undecafluoropentane-1-sulfinate sodium （**3ad**）

The title compound was obtained according to the general condition (337.0 mg, 95% yield, ^{19}F NMR (282 MHz, D_2O) δ -82.1, -123.0 -123.5, -127.1, -130.8.



tosylmethanesulfinate sodium(**3ae**). The title compound was obtained according to the general condition (205mg, 85% yield) ^{1}H NMR (400 MHz, D_2O) δ 7.77 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 3.18 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, D_2O) δ 146.2，136.9，130.1，126.9，46.2，18.77

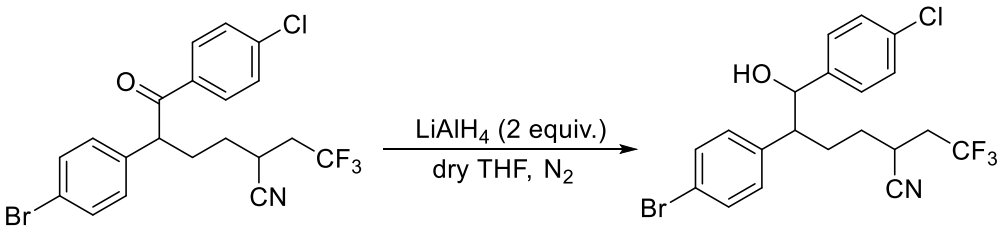
3. General procedure for radical trifunctionalization of hexenenitriles



To a reaction tube (5 mL) quipped with a Teflon® stir bar and fitted with a rubber septum were added acid (0.2 mmol, 1.0 equiv.), CDI (0.2 mmol, 1.0 equiv.), DCE 1 mL. The mixture was stirred at room temperature for 2 hours. To another quartz tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added NHC-A (9.5 mg, 0.03 mmol, 15 mol%), Cs_2CO_3 (130 mg, 0.4 mmol, 2.0 equiv.), sodium sulfite **1** (0.4 mmol, 2.0 equiv.). The mixture wa charged with the in-situ prepared acylazole via springe**.** Then, the reaction tube was evacuated and back-filled with nitrogen three times. Subsequently, dry 1,2-dichloroethane (DCE) (1 mL), hexenenitrile **3** (0.2 mmol, 1.0 equiv.) were added under the protection of nitrogen. The reaction was stirred at Blue LEDs for 24 hours. The reaction mixture was concentrated under reduced

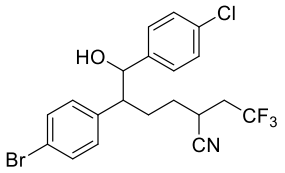
pressure, and the resulting crude material was purified by column chromatography on silica gel (petroleum ether / acetone from 20/1 to 15/1) to afford the desired products **4**.

4. Procedure for reduction of product 4a to produce compound 5



4a **5**

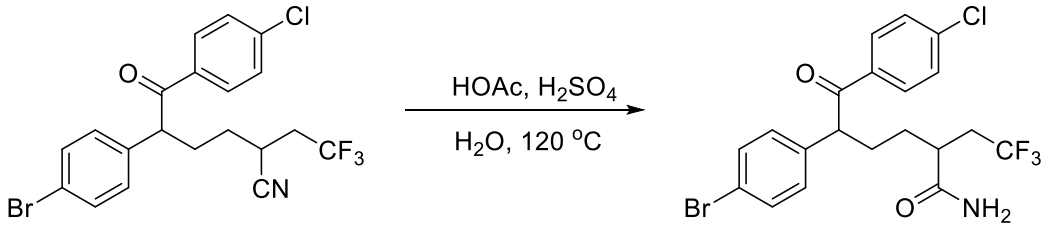
To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added **4a** (100 mg, 0.21 mmol) and $LiAlH_4$ (69.6 mg, 0.4 mmol, 2.0 equiv.). Then, the reaction tube was evacuated and back-filled with nitrogen three times. Subsequently, dry THF (4 mL) was added, The reaction was stirred at 25 ^oC 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 15/1) to afford the desired product **5** in 83% yield.



5-(4-bromophenyl)-6-(4-chlorophenyl)-6-hydroxy-2-(2,2,2-trifluoroethyl)hexanenitrile(5) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 10/1, v/v) as a white liquid (76.0 mg, 83% yield, dr =1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.41 (m, 2H, two isomers), 7.33-7.27 (m, 4H, two isomers), 7.21-7.08 (m, 2H, two isomers), 7.07-6.97 (m,2H, two isomers), 4.75(dd, J =18.7, 6.8 Hz 1H, two isomers), 3.00-2.55 (m, 2H, two isomers),2.52-2.28 (m, 1H, two isomers), 2.20-2.11 (m, 2H, two isomers), 1.96-1.70 (m, 2H, two isomers), 1.67-1.58 (m, 2H, two isomers),1.56-1.34 (m, 2H,two isomers).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5 (overlap, two isomers), 138.4 & 138.3 (two isomers), 133.7 & 133.68 (two isomers), 131.9 & 131.78 (two isomers), 130.6 & 130.5 (overlap, two isomers), 128.6 & 128.5 (overlap, two isomers), 128.0 & 127.90 (overlap, two isomers), 130.4 & 130.34 (two isomers), 129.1 & 129.0 (two isomers), 126.67 (q, $^1J_{C\text{-}F}$ = 282.6 Hz) & 126.65 (q, $^1J_{C\text{-}F}$ = 282.6 Hz) (two isomers), 121.3 &121.28 (overlap, two isomers), 52.9 & 52.7(two isomers), , 36.4 (q, $^2J_{C\text{-}F}$ = 30.3 Hz) & 36.1 (q, $^2J_{C\text{-}F}$ = 30.3 Hz) (two isomers), 36.3 & 36.25 (overlap, two isomers), 30.1 & 30.0 (overlap, two isomers), 29.72 (overlap, two isomers), 29.01 & 28.93 (two isomers), 26.29 (overlap, two isomers), 25.7 (q, $^3J_{C\text{-}F}$ = 3.0Hz) & 25.6 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) (two isomers), 22.72 (two isomers), 14.1 (two isomers). HRMS (ESI) calcd. for

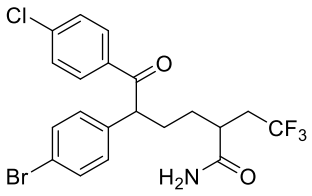
$C_{20}H_{19}BrClF_3NO$ $[M+H]^+$: 460.0286, 462.0265; found: 460.0240, 462.0230.

5. Procedure for hydrolysis of product 4a to produce compound 6



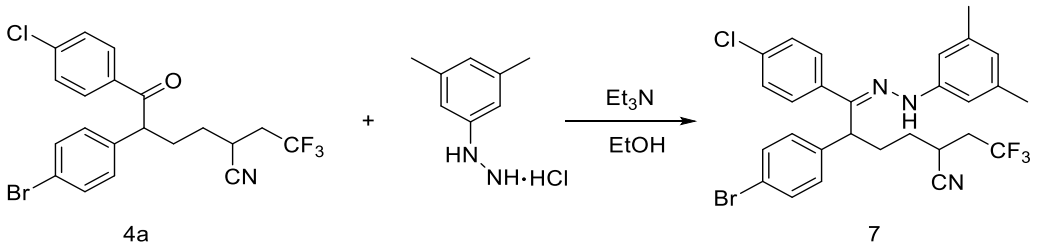
4a 6

To a tube were added **4a** (100 mg, 0.21 mmol) and 1 mL HOAc，1 mL H_2O，1.5 mL 98 % H_2SO_4. The reaction was stirred at 120 °C for 24 hours. Quenching reaction of saturated sodium bicarbonate. The reaction mixture was extracted with ethyl acetate (3×50 mL). The combined organic layers were dried over anhydrous $MgSO_4$. After concentration, and dryness, the resulting crude material was purified by column chromatography on silica gel (petroleum ether / acetone from 15/1) to afford the desired product **6** in the yield 75%.

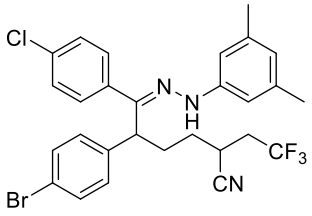


5-5-(4-bromophenyl)-6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanamide(6) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 5/1, v/v) as a white soild (67.0 mg, 75 %yield, dr =1:1).^{1}H NMR (300 MHz, DMSO-*d*6) δ 8.02 (dd, *J* = 8.7, 2.4 Hz, two isomers),7.57-7.42 (m, 4H, two isomers), 7.26(dd, *J*= 8.5, 2.4 Hz, two isomers), 4.84-4.78 (m,1H,two isomers), 2.67-2.49 (m, 2H, two isomers), 2.28-2.18 (m, 1H, two isomers), 2.12-2.94 (m, 2H, two isomers), 1.81- 1.69 (m, 2H, two isomers), 1.59-1.23 (m,2H,two isomers).^{13}C (75 MHz, DMSO-*d*6) δ 199.0 & 198.9 (two isomers), 179.6 & 179.5 (overlap, two isomers), 139.2 & 138.9 (two isomers), 138.78 (two isomers), 138.74 (two isomers), 135.1 & 134.9 (overlap, two isomers), 135.0 (overlap, two isomers), 132.1& 132.08 (overlap, two isomers), 130.9 & 130.8(two isomers), 129.78 & 129.38 (two isomers), 124.69 (q, $^1J_{C\text{-}F}$ = 266.6 Hz) , 120.6 (overlap, two isomers), 119.95 & 119.87 (two isomers), 51.7 & 51.6 (overlap, two isomers),42.79 & 42.2(overlap, two isomers) 36.4 (q, $^2J_{C\text{-}F}$ = 35.0 Hz) (two isomers), 30.88 (overlap, two isomers), 30.19(overlap, two isomers), 26.80(q, $^3J_{C\text{-}F}$ = 3.3 Hz) HRMS (ESI) calcd. for $C_{20}H_{19}BrClF_3NO_2$ $[M+H]^+$: 476.0235, 478.0214; found: 476.0240, 478.0220.

6. Procedure for synthesis of hydrazone 7

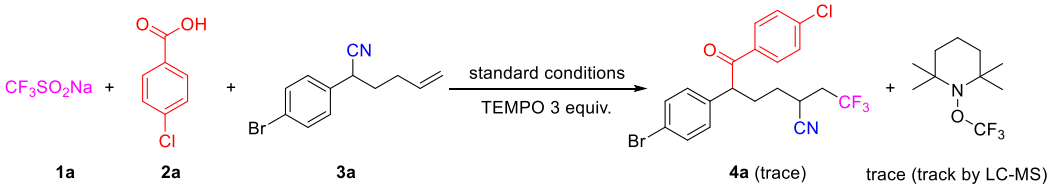


To an oven-dried reaction tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added 4a (100 mg, 0.21 mmol) and 3,5-Dimethylphenylhydrazine hydrochloride (68 mg, 0.42 mmol 2.0 equiv.), triethylamine (40 mg, 0.42 mmol 2.0 equiv.) and EtOH (4 mL). Then, the reaction mixture was stirred at 25 ºC for 8 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 15/1) to afford the desired product 7 in the yield of 80%.



6-**(4-bromophenyl)-6-(4-chlorophenyl)-6-(2-(3,5-dimethylphenyl)hydrazineylidene)-2-(2,2,2-trifluoroethyl)hexanenitrile (7)** The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a white solid (57.0 mg, 54%yield, dr =1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 8.8 ,7.3 Hz, 2H, two isomers), 7.48-7.40 (m, 4H, two isomers), 7.33(dd, *J* = 8.8,7.3 Hz, 2H, two isomers), 7.04 (d, *J*=8.1 Hz, 2H, two isomers), 6.82 (s, 1H, two isomers), 3.11 (td, *J* = 12.7, 3.9 Hz, 1H, two isomers), 2.91 (ddd, J = 12.9,11.1,4.9 Hz, 1H, two isomers), 2.75 – 2.62 (m, 1H, two isomers), 2.62 – 2.45 (m, 1H, two isomers), 2.42 (d, *J* = 2.5 Hz, 3H,two isomers), 2.33 (ddt, *J* = 19.4, 9.7, 4.8 Hz, 1H,two isomers), 2.02 (d, *J* = 8.3 Hz, 3H,two isomers), 1.68 (s, 1H,two isomers), 1.21 – 0.86 (m, 2H,two isomers). ^{13}C NMR (101 MHz, CDCl3) δ 178.8 & 178.7(two isomers), 154.7 & 154.6 (overlap, two isomers), 139.4 & 139.3 (two isomers), 139.2 (two isomers), 137.4 (two isomers), 137.0 (overlap, two isomers), 132.7 (overlap, two isomers), 132.6 (overlap, two isomers), 130.44 & 130.34 (two isomers), 130.16 (two isomers), 129.32 & 129.15 (two isomers), 124.67 (q, $^{1}J_{C\text{-}F}$ = 278.6 Hz) & 124.65 (q, $^{1}J_{C\text{-}F}$ = 278.6 Hz) (two isomers), 121.6 (overlap, two isomers), 119.95 & 119.87 (two isomers), 119.12 & 119.00 (two isomers) 63.95 (overlap, two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.3 Hz) & 36.1 (q, $^{2}J_{C\text{-}F}$ = 30.3 Hz) (two isomers), 36.3 & 36.25 (overlap, two isomers), 28.92 (overlap, two isomers), 28.20 (overlap, two isomers), 26.57(two isomers), 26.29 (overlap, 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), 21.42 & 21.40 (two isomers), 17.27 & 17.22 (two isomers) HRMS (ESI) calcd. for $C_{28}H_{27}BrClF_3N_3$ $[M+H]^+$: 576.1024, 578.1004; found: 576.1056, 578.1000.

7. Radical trapping experiment



To a reaction tube (5 mL) quipped with a Teflon® stir bar and fitted with a rubber septum were added acid (0.2 mmol, 1.0 equiv.), CDI (0.2 mmol, 1.0 equiv.), DCE 1 mL. The mixture was stirred at room temperature for 4 hours.

To another quartz tube (10 mL) equipped with a Teflon® stir bar and fitted with a rubber septum were added NHC-A (9.5 mg, 0.03 mmol, 15 mol%), Cs_2CO_3 (130 mg, 0.4 mmol, 2.0 equiv.), sodium sulfite **1** (0.4 mmol, 2.0 equiv.). The mixture wa charged with the in-situ prepared acylazole via springe**.** Then, the reaction tube was evacuated and back-filled with nitrogen three times. Subsequently, dry 1,2-dichloroethane (DCE) (1 mL), hexenenitrile **3** (0.2 mmol, 1.0 equiv.) TEMPO （0.6 mmol 3 equiv.）were added under the protection of nitrogen. The reaction was stirred at Blue LEDs for 24 hours. The resulting crude material was tested by LC-MS. 2,2,6,6-tetramethyl-1-(trifluoromethoxy)piperidine was tracked by LC-Ms. No product was observed.

8. DFT calculations for activating energy

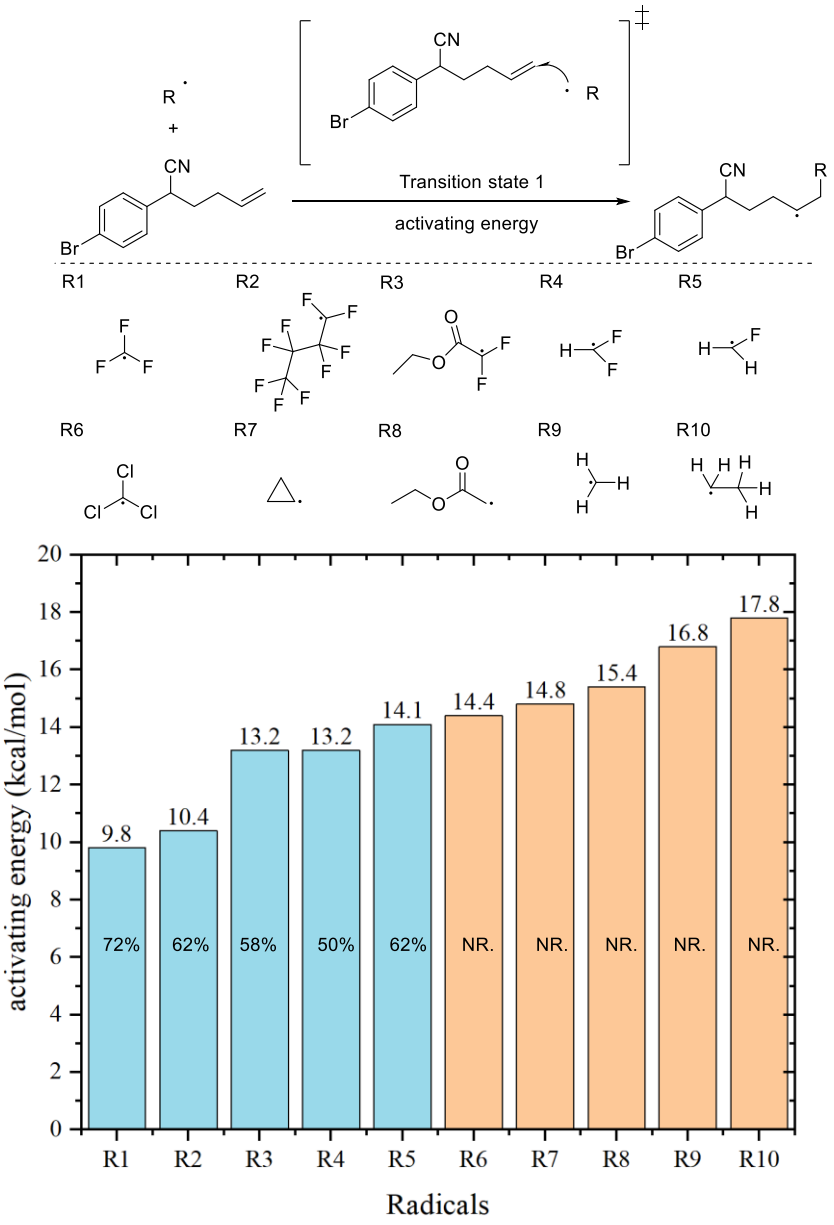
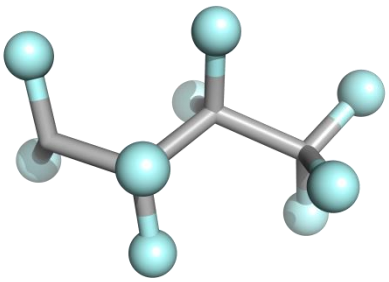


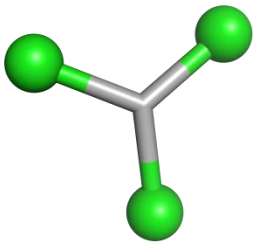
Figure 1. Gibbs free energy activating energy of different radicals(kcal/mol)

We calculated different radical species additions with **S1**. All of the transition states are similar to ^{2}TS1 in Figure 1 and calculated in same level (PCMSMD(dichloroethane)-(U)M06-2X/def2TZVP).

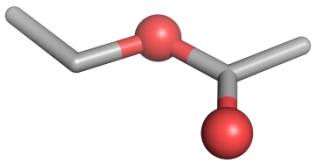
Table 1. thermal correction to Gibbs free energy (G_0, hartree), single point energies (SP-E, hartree),sum of electronic and thermal free energies (Gc, hartree) with the addition of SP-E as well as thermal corrections, and relative Gibbs free energies (ΔG, kcal mol^{-1}) of various species with respect to S1 for radical coupling and radical addition reactions at the PCM-SMD(dichloroethane)-(U)M06-2X/def2TZVP//PCM(dichloroethane)-(U)M06-2X/def2SVP level. IF represents imaginary frequencies (cm^{-1}).

Species	G_0	SP-E	$G_c(G_0+SP-E)$
S1	0.164981	-3093.399738	-3093.234757
r1	0.012226	-1051.045626	-1051.0334
r2	-0.022492	-1418.635734	-1418.658226
r3	0.042326	-117.2025987	-117.1602727
r4	0.074065	-307.0364691	-306.9624041
r5	-0.013958	-337.5969545	-337.6109125
r6	-0.00539	-238.3350136	-238.3404036
r7	0.002373	-139.0726147	-139.0702417
r8	0.009325	-39.82216849	-39.81284349
r9	0.035355	-79.1358502	-79.1004952
r10	0.056325	-505.5379818	-505.4816568

Structure r1				
				
cartesian coordinates of stationary point structure [Å]	C	-4.29060000	-0.11900000	0.01090000
	C	-3.75870000	0.75750000	1.16510000
	C	-2.21460000	0.82790000	1.24260000
	C	-1.71960000	1.37570000	2.56420000
	F	-5.58290000	0.10910000	-0.14780000
	F	-3.65720000	0.18040000	-1.11280000
	F	-4.10970000	-1.39810000	0.28570000
	F	-4.22060000	0.25460000	2.31620000
	F	-4.23050000	1.99500000	1.00710000
	F	-1.72430000	-0.40640000	1.07950000
	F	-1.78540000	1.61880000	0.25490000
	F	-1.78700000	0.53660000	3.56500000
	F	-2.20860000	2.55430000	2.86470000

Structure r2				
				
cartesian coordinates	C	-2.31160000	0.39770000	0.17560000
of stationary point	Cl	-1.61650000	1.38060000	1.39530000
structure [Å]	Cl	-4.00260000	0.53710000	-0.06590000
	Cl	-1.61560000	-1.14930000	-0.06790000

Structure r3				
				
cartesian coordinates	C	0.84920000	-0.19230000	-0.01620000
of stationary point	C	2.37160000	-0.19220000	-0.01620000
structure [Å]	C	1.61030000	1.05900000	-0.08690000
	H	0.32180000	-0.54230000	-0.90930000
	H	0.35550000	-0.45620000	0.92490000
	H	2.89900000	-0.54210000	-0.90930000
	H	2.86530000	-0.45600000	0.92480000
	H	1.61030000	1.85870000	-0.82570000

Structure r4				
				
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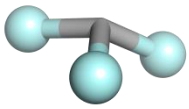
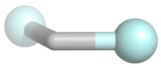
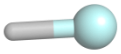
	O	1.11420000	0.73460000	0.05100000
	O	-0.65440000	2.10800000	-0.11240000
	C	0.22490000	3.22620000	0.01570000
	C	-0.61080000	4.48260000	-0.04440000
	H	0.96940000	3.18880000	-0.79370000
	H	0.77260000	3.14190000	0.96630000
	H	0.03430000	5.36570000	0.05090000
	H	-1.14800000	4.54450000	-1.00040000
	H	-1.34560000	4.49770000	0.77190000
	C	-1.04760000	-0.17960000	-0.21550000
	H	-2.10730000	0.03870000	-0.32980000
	H	-0.68220000	-1.20400000	-0.19990000

Structure r5				
				
cartesian coordinates of stationary point structure [Å]	C	-2.25330000	0.47990000	0.03290000
	F	-3.56210000	0.50110000	-0.00390000
	F	-1.79700000	1.12510000	1.07700000
	F	-1.79720000	-0.74680000	-0.00380000

Structure r6				
				
cartesian coordinates of stationary point structure [Å]	C	-1.76908700	1.37788100	-0.05744900
	H	-2.85973300	1.43260600	0.03780200
	F	-1.27266800	0.15629800	0.00238100
	F	-1.27286200	2.04081500	-1.08500500

Structure r7				
				
cartesian coordinates of stationary point structure [Å]	C	-1.80597000	1.35107100	-0.12419200
	H	-1.31026700	1.96901300	-0.87342400
	H	-2.87424700	1.41610900	0.08428500
	F	-1.27720100	0.13941500	0.03968000

Structure r8				
				
cartesian coordinates of stationary point structure [Å]	C	-1.84042200	1.28465200	-0.21883700
	H	-1.32742400	0.37812000	0.09553600
	H	-1.32740100	2.01016800	-0.84673000
	H	-2.86576800	1.46665500	0.09638000

Structure r9				
				
cartesian coordinates of stationary point structure [Å]	C	-4.16024200	2.19606900	-0.18646600
	H	-3.66098100	2.94112300	-0.80706700
	H	-5.18632000	2.40158600	0.12083300
	C	-3.58196800	0.83517000	-0.02721200
	H	-2.48279400	0.85928300	0.00125700
	H	-3.93895200	0.34450900	0.89008400
	H	-3.85784900	0.16713800	-0.86605600

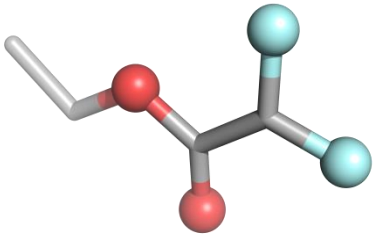
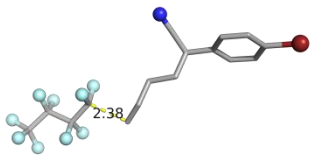
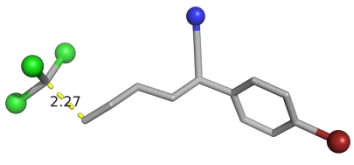
Structure r10				
				
cartesian coordinates of stationary point structure [Å]	C	-1.94267700	1.23214300	-0.08508700
	F	-1.28457600	0.66666000	-1.05372000
	F	-1.26462800	2.14272900	0.55151400
	C	-3.39675100	1.18019000	-0.06769000
	O	-4.03228900	0.46392400	-0.80431900
	O	-3.89640500	1.96497200	0.88160100
	C	-5.32302500	1.93396200	1.03470600
	C	-5.68498400	2.86542800	2.16512600
	H	-5.62984400	0.89746000	1.23670000
	H	-5.78374800	2.23864700	0.08395700
	H	-6.77324400	2.86703800	2.30822800
	H	-5.20993500	2.54188700	3.10075500
	H	-5.36067300	3.89030200	1.94099500

Table 2. thermal correction to Gibbs free energy (G_0, hartree), single point energies (SP-E, hartree),sum of electronic and thermal free energies (Gc, hartree) with the addition of SP-E as well as thermal corrections, and relative Gibbs free energies (ΔG, kcal mol^{-1}) of various species with respect to S1 for radical coupling and radical addition reactions at the PCM-SMD(dichloroethane)-(U)M06-2X/def2TZVP//PCM(dichloroethane)-(U)M06-2X/def2SVP level. IF represents imaginary frequencies (cm^{-1}).

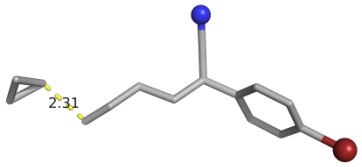
Species	G_0	SP-E	$G_c(G_0+SP-E)$	ΔG	IF
TS1-r1	0.195184	-4144.446762	-4144.251578	10.4	282.73i
TS1-r2	0.161555	-4512.031559	-4511.870004	14.4	446.64i
TS1-r3	0.224678	-3210.596043	-3210.371365	14.8	479.35i
TS1-r4	0.257243	-3400.429793	-3400.17255	15.4	562.19i
TS1-r5	0.167974	-3430.998087	-3430.830113	9.8	296.19i
TS1-r6	0.177126	-3331.731329	-3331.554203	13.1	469.28i
TS1-r7	0.18472	-3232.465663	-3232.280943	15.1	531.72i
TS1-r8	0.192931	-3133.213832	-3133.020901	16.8	592.82i
TS1-r9	0.219204	-3172.526101	-3172.306897	17.8	569.51i
TS1-r10	0.240747	-3598.936076	-3598.695329	13.2	451.95i

Structure TS1-r1				
				
cartesian coordinates of stationary point structure [Å]	C	-1.89710000	-0.31870000	0.13820000
	C	-0.50790000	-0.31340000	0.03370000
	C	0.20780000	0.88730000	0.05440000
	C	-0.48900000	2.09220000	0.17970000
	C	-1.87870000	2.10380000	0.28800000
	C	-2.57010000	0.89480000	0.26580000
	H	-2.44780000	-1.25960000	0.12500000
	H	0.02610000	-1.26140000	-0.06340000
	H	0.05360000	3.04030000	0.20290000
	H	-2.41470000	3.04770000	0.39110000

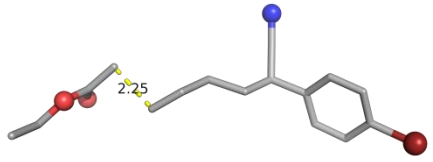
	Br	-4.46080000	0.89920000	0.41820000
	C	1.71490000	0.85140000	-0.13220000
	C	2.10370000	0.93550000	-1.62340000
	H	2.09780000	-0.09790000	0.27390000
	C	3.60760000	0.79810000	-1.86040000
	H	1.56590000	0.12900000	-2.14380000
	H	1.73540000	1.88990000	-2.03230000
	H	4.13190000	1.60430000	-1.31420000
	H	3.96980000	-0.15660000	-1.44730000
	C	3.97130000	0.89810000	-3.30850000
	C	4.74970000	0.00630000	-3.95490000
	H	3.63210000	1.79580000	-3.83810000
	H	4.97340000	0.11690000	-5.01910000
	C	2.37480000	1.92350000	0.62810000
	N	2.89700000	2.77920000	1.19910000
	H	5.03680000	-0.93580000	-3.47770000
	C	6.88230000	0.81500000	-3.27880000
	C	7.94500000	0.21730000	-4.17070000
	F	6.81230000	2.12850000	-3.33720000
	F	6.96260000	0.39660000	-2.02750000
	C	9.38590000	0.42080000	-3.64470000
	F	7.85210000	0.78130000	-5.38350000
	F	7.72940000	-1.10100000	-4.27690000
	C	10.48470000	0.15060000	-4.69460000
	F	9.51440000	1.68590000	-3.22690000
	F	9.58010000	-0.40210000	-2.61160000
	F	11.65830000	0.07120000	-4.09020000
	F	10.24390000	-0.99230000	-5.31970000
	F	10.52350000	1.12940000	-5.58150000

Structure TS1-r2				
cartesian coordinates of stationary point structure [Å]	C	-1.90720000	-0.41680000	-0.10640000
	C	-0.51700000	-0.34380000	-0.05610000
	C	0.13300000	0.89090000	0.03330000
	C	-0.63110000	2.06020000	0.07190000

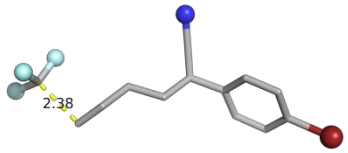
	C	-2.02320000	2.00410000	0.02510000
	C	-2.64830000	0.76270000	-0.06560000
	H	-2.40690000	-1.38370000	-0.17240000
	H	0.06970000	-1.26470000	-0.08530000
	H	-0.14120000	3.03400000	0.14680000
	H	-2.61260000	2.92080000	0.06030000
	Br	-4.54200000	0.67490000	-0.13050000
	C	1.65150000	0.92940000	0.00790000
	C	2.18810000	1.00890000	-1.43710000
	H	2.03700000	0.00820000	0.47230000
	C	3.71450000	0.95510000	-1.51870000
	H	1.75200000	0.16360000	-1.99000000
	H	1.81150000	1.93290000	-1.90410000
	H	4.13360000	1.79980000	-0.94090000
	H	4.08610000	0.03040000	-1.04950000
	C	4.20580000	1.04690000	-2.92780000
	C	5.06890000	0.16780000	-3.49560000
	H	3.88600000	1.92400000	-3.50190000
	H	5.31740000	0.23940000	-4.55740000
	C	2.17470000	2.04660000	0.80840000
	N	2.59270000	2.93700000	1.41130000
	H	5.31590000	-0.77140000	-2.99060000
	C	7.15110000	0.91540000	-2.99040000
	Cl	7.25230000	2.50530000	-3.68170000
	Cl	7.22880000	0.89860000	-1.25420000
	Cl	8.19080000	-0.25270000	-3.75140000

Structure TS1-r3				
cartesian coordinates of stationary point structure [Å]	C	-1.93570000	-0.37060000	0.01620000
	C	-0.54910000	-0.27890000	0.12370000
	C	0.09800000	0.95480000	0.01150000
	C	-0.66440000	2.10460000	-0.21510000
	C	-2.05170000	2.03020000	-0.32350000
	C	-2.67450000	0.78920000	-0.20680000
	H	-2.43310000	-1.33640000	0.11000000

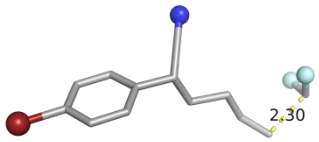
	H	0.03540000	-1.18430000	0.30090000
	H	-0.17570000	3.07820000	-0.30250000
	H	-2.63990000	2.93200000	-0.49590000
	Br	-4.56310000	0.67860000	-0.34930000
	C	1.61540000	1.00880000	0.06040000
	C	2.22810000	0.94990000	-1.35540000
	H	1.98250000	0.14510000	0.63650000
	C	3.75710000	0.91430000	-1.35780000
	H	1.83080000	0.04590000	-1.84100000
	H	1.86430000	1.81490000	-1.93290000
	H	4.13350000	1.81500000	-0.83910000
	H	4.10940000	0.04240000	-0.78320000
	C	4.31890000	0.86880000	-2.74610000
	C	5.17690000	-0.07860000	-3.19080000
	H	4.05100000	1.70080000	-3.40790000
	H	5.47330000	-0.11060000	-4.24200000
	C	2.08200000	2.20920000	0.77100000
	N	2.45450000	3.16250000	1.30350000
	H	5.36810000	-0.97720000	-2.59680000
	C	7.35240000	0.56610000	-2.74360000
	C	8.27540000	0.05870000	-3.77020000
	C	7.86520000	1.52080000	-3.73560000
	H	7.86940000	-0.55470000	-4.58270000
	H	9.29730000	-0.20580000	-3.47950000
	H	7.18560000	1.86680000	-4.52320000
	H	8.60590000	2.26470000	-3.42520000
	H	7.48070000	0.58040000	-1.66130000

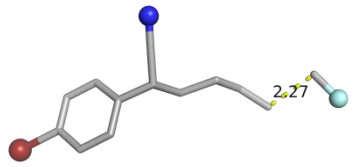
Structure TS1-r4				
cartesian coordinates of stationary point structure [Å]	C	-1.82330000	-0.56060000	-0.48680000
	C	-0.43420000	-0.48160000	-0.41300000
	C	0.19770000	0.71270000	-0.05490000
	C	-0.58330000	1.83670000	0.22860000
	C	-1.97410000	1.77380000	0.16160000
	C	-2.58120000	0.57230000	-0.19740000

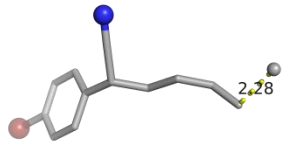
	H	-2.30830000	-1.49750000	-0.76260000
	H	0.16550000	-1.36690000	-0.63640000
	H	-0.10760000	2.77790000	0.51480000
	H	-2.57580000	2.65410000	0.38980000
	Br	-4.47360000	0.47450000	-0.28980000
	C	1.71540000	0.77780000	-0.05810000
	C	2.25680000	1.22180000	-1.43390000
	H	2.11320000	-0.22440000	0.16650000
	C	3.78440000	1.22780000	-1.51090000
	H	1.84540000	0.52680000	-2.18100000
	H	1.85750000	2.22220000	-1.66490000
	H	4.17590000	1.92380000	-0.74570000
	H	4.17690000	0.22750000	-1.26740000
	C	4.28120000	1.65550000	-2.85480000
	C	5.18300000	0.95080000	-3.59050000
	H	3.94290000	2.63300000	-3.21660000
	H	5.43300000	1.26260000	-4.60720000
	C	2.21490000	1.66800000	1.00050000
	N	2.61360000	2.38660000	1.81030000
	H	5.42390000	-0.08090000	-3.31740000
	C	7.21150000	1.59060000	-2.85650000
	C	7.98910000	0.67980000	-3.67970000
	H	7.16230000	2.64130000	-3.13940000
	O	8.32250000	-0.44280000	-3.35840000
	O	8.25620000	1.19060000	-4.89590000
	C	8.97080000	0.34340000	-5.79570000
	C	9.15910000	1.09480000	-7.09090000
	H	8.40140000	-0.58710000	-5.94320000
	H	9.93480000	0.06780000	-5.34160000
	H	9.70980000	0.47090000	-7.80810000
	H	8.18770000	1.35800000	-7.53290000
	H	9.72960000	2.01940000	-6.92410000
	H	7.09950000	1.32200000	-1.80670000

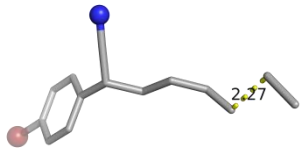
Structure TS1-r5	

cartesian coordinates of stationary point structure [Å]				
	C	-1.88620000	-0.42910000	-0.07230000
	C	-0.49610000	-0.34390000	-0.03930000
	C	0.14450000	0.89700000	0.03030000
	C	-0.62900000	2.06020000	0.06640000
	C	-2.02100000	1.99200000	0.03660000
	C	-2.63670000	0.74460000	-0.03450000
	H	-2.37840000	-1.40080000	-0.12280000
	H	0.09790000	-1.26020000	-0.06640000
	H	-0.14650000	3.03880000	0.12560000
	H	-2.61760000	2.90410000	0.06980000
	Br	-4.53020000	0.64070000	-0.07650000
	C	1.66220000	0.94800000	-0.01470000
	C	2.17900000	1.01760000	-1.46750000
	H	2.06140000	0.03460000	0.45340000
	C	3.70390000	0.97460000	-1.57160000
	H	1.74220000	0.16320000	-2.00570000
	H	1.78740000	1.93350000	-1.93840000
	H	4.12620000	1.82940000	-1.01310000
	H	4.08780000	0.05760000	-1.09680000
	C	4.17230000	1.04580000	-2.99180000
	C	4.96740000	0.12590000	-3.57330000
	H	3.87550000	1.93390000	-3.56150000
	H	5.24730000	0.20440000	-4.62670000
	C	2.18610000	2.07690000	0.76840000
	N	2.60440000	2.97620000	1.35760000
	H	5.21320000	-0.80850000	-3.05860000
	C	7.13170000	0.87330000	-2.91190000
	F	8.10160000	0.01480000	-3.15640000
	F	7.02170000	1.07560000	-1.61420000
	F	7.36520000	2.01250000	-3.52860000

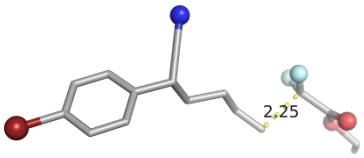
Structure TS1-r6				
cartesian coordinates of stationary point structure [Å]	C	-1.85815500	-0.35214700	0.13600000
	C	-0.46841200	-0.25325300	0.13925500
	C	0.16216100	0.98589900	-0.00386200
	C	-0.62112200	2.13361300	-0.15242700
	C	-2.01235200	2.05183300	-0.15663400
	C	-2.61860700	0.80588600	-0.01328600
	H	-2.34490200	-1.32042800	0.25257500
	H	0.13084500	-1.15870400	0.25687800
	H	-0.14501200	3.11104400	-0.25884200
	H	-2.61886300	2.95043800	-0.26869800
	Br	-4.50993600	0.68454600	-0.01759000
	C	1.67849900	1.04520000	-0.07417000
	C	2.17839900	0.90630200	-1.52809500
	H	2.09431100	0.21482100	0.51824500
	C	3.70163900	0.87958500	-1.64899100
	H	1.75240100	-0.02513000	-1.92993600
	H	1.76085400	1.73361100	-2.12399000
	H	4.11215800	1.81166200	-1.21815400
	H	4.11344400	0.05021500	-1.05214500
	C	4.16079300	0.75925200	-3.06943900
	C	5.07501800	-0.14351600	-3.49155200
	H	3.79093300	1.51582100	-3.76998300
	H	5.34416100	-0.21691700	-4.54726900
	C	2.19450300	2.28407300	0.52932300
	N	2.60123600	3.26714300	0.97562000
	H	5.37711400	-0.97094400	-2.84288800
	C	7.03958100	0.88864900	-2.87666700
	H	7.94847700	0.45097800	-3.30929100
	F	6.84156600	2.15230200	-3.22044300
	F	6.96492900	0.76101200	-1.55724600

Structure TS1-r7				
cartesian coordinates of stationary point structure [Å]	C	-1.86083800	-0.47511900	-0.07336200
	C	-0.47595900	-0.33607600	-0.01868200
	C	0.11599100	0.92897400	0.03902700
	C	-0.70166900	2.06205100	0.03856800
	C	-2.08925200	1.93997700	-0.01461500
	C	-2.65637900	0.66900400	-0.07043000
	H	-2.31741700	-1.46397900	-0.11321000
	H	0.15095000	-1.23038600	-0.01945500
	H	-0.25640800	3.05822600	0.08913200
	H	-2.72282100	2.82688800	-0.01047000
	Br	-4.54213500	0.49147400	-0.13733300
	C	1.63118600	1.03715800	0.02328500
	C	2.17778000	1.08237200	-1.42009700
	H	2.05334800	0.15334900	0.52743800
	C	3.70593900	1.09503400	-1.49423100
	H	1.78516300	0.19835100	-1.94429900
	H	1.76099400	1.96758000	-1.92672200
	H	4.08017600	1.97181100	-0.93528400
	H	4.10720200	0.20037900	-0.99081200
	C	4.20229200	1.14625500	-2.90731900
	C	5.02574700	0.21936500	-3.45740600
	H	3.91332600	2.02394400	-3.49580800
	H	5.26143300	0.24601600	-4.52314700
	C	2.09446900	2.20836200	0.78377400
	N	2.46168300	3.14121100	1.35479600
	H	5.21413400	-0.72707000	-2.94225600
	C	7.21770900	0.65823500	-3.04391700
	H	7.41876300	1.55443600	-3.63556400
	H	7.25676800	0.71550400	-1.95332200
	F	7.78867200	-0.44892500	-3.54088000

Structure TS1-r8				
cartesian coordinates of stationary point structure [Å]	C	-1.90290800	-0.43520500	-0.10523000
	C	-0.51300500	-0.35236000	-0.06202900
	C	0.12878200	0.88563400	0.03555700
	C	-0.64367200	2.04882300	0.08760300
	C	-2.03536400	1.98298400	0.04731700
	C	-2.65266600	0.73807400	-0.04935900
	H	-2.39831700	-1.40342500	-0.17714300
	H	0.07853600	-1.26952900	-0.10342200
	H	-0.15908300	3.02432500	0.16984000
	H	-2.63358800	2.89292400	0.09313000
	Br	-4.54463800	0.63726500	-0.09944500
	C	1.64670100	0.93727900	0.00501200
	C	2.17849500	1.02542700	-1.44187500
	H	2.04068500	0.01696700	0.46455200
	C	3.70494600	0.99939400	-1.53459900
	H	1.75415600	0.17481500	-1.99594500
	H	1.78143500	1.94185500	-1.90719500
	H	4.10913300	1.84681600	-0.95066200
	H	4.08975300	0.07915600	-1.06546200
	C	4.19002300	1.08699600	-2.94940700
	C	5.05263000	0.20210400	-3.51254800
	H	3.87735600	1.96850300	-3.52010400
	H	5.28633600	0.25890900	-4.57693400
	C	2.16166800	2.05580700	0.81037600
	N	2.56866400	2.94844000	1.41757900
	H	5.26385000	-0.74812900	-3.01501100
	C	7.18098700	0.84385200	-3.01561000
	H	7.73519500	0.03487300	-3.49394800
	H	7.22424200	1.82145500	-3.49600500
	H	7.14256200	0.83657400	-1.92579100

Structure TS1-r9	

cartesian coordinates of stationary point structure [Å]				
	C	-1.92699300	-0.43414800	-0.01695700
	C	-0.54406700	-0.29175400	0.07168500
	C	0.04852000	0.97422100	0.06014400
	C	-0.76635900	2.10456000	-0.04407000
	C	-2.15173600	1.97932600	-0.13260000
	C	-2.71958500	0.70743400	-0.11891300
	H	-2.38421500	-1.42348200	-0.00267100
	H	0.08047300	-1.18413900	0.15215900
	H	-0.32055300	3.10181000	-0.04847500
	H	-2.78307500	2.86451200	-0.20956700
	Br	-4.60269700	0.52626700	-0.23624500
	C	1.56347100	1.08326800	0.08145300
	C	2.14999600	1.04846000	-1.34654500
	H	1.97156000	0.23000100	0.64616200
	C	3.67943900	1.05954000	-1.38115200
	H	1.77144300	0.13608800	-1.83112900
	H	1.74688000	1.90324000	-1.91306700
	H	4.03840400	1.96512000	-0.85857300
	H	4.06712700	0.19414300	-0.81910200
	C	4.21492300	1.03447200	-2.78064600
	C	5.07284300	0.09023600	-3.24843700
	H	3.93878300	1.87601000	-3.42561300
	H	5.33306700	0.05635600	-4.30838200
	C	2.00418800	2.29637500	0.78784800
	N	2.35323900	3.26076100	1.31632800
	H	5.24061900	-0.82688700	-2.67617500
	C	7.21766500	0.64830700	-2.77936600
	H	7.26687000	1.60226900	-3.30966300
	H	7.12951300	0.73767000	-1.69356800
	C	8.00177900	-0.49946500	-3.32703500
	H	9.08716300	-0.36684200	-3.16631400
	H	7.72157900	-1.44811800	-2.84499300
	H	7.85113200	-0.61146600	-4.41128300

Structure TS1-r10				
cartesian coordinates of stationary point structure [Å]	C	-1.84471200	-0.48682200	-0.16919200
	C	-0.45399500	-0.40870300	-0.14490500
	C	0.19201400	0.82178100	0.00445000
	C	-0.57628000	1.98230800	0.12821800
	C	-1.96849400	1.92084900	0.10800000
	C	-2.59043200	0.68339400	-0.04123500
	H	-2.34365300	-1.44934800	-0.28177800
	H	0.13439800	-1.32367900	-0.24171400
	H	-0.08793000	2.95155500	0.25203600
	H	-2.56364400	2.82817900	0.21014300
	Br	-4.48304000	0.58885400	-0.06365800
	C	1.70943800	0.87380900	-0.04691100
	C	2.21762200	1.05152900	-1.49365600
	H	2.10928100	-0.07298100	0.34915100
	C	3.74273000	1.02372800	-1.60563800
	H	1.78098600	0.23970600	-2.09409000
	H	1.82011300	1.99794900	-1.89336500
	H	4.16276000	1.82770500	-0.97409200
	H	4.13342200	0.07261000	-1.21106500
	C	4.21121100	1.22150900	-3.01254700
	C	5.07168800	0.38994600	-3.64899000
	H	3.88251500	2.13650600	-3.51709700
	H	5.32864600	0.54902200	-4.69899200
	C	2.23897100	1.94149100	0.81615400
	N	2.65815800	2.79625500	1.46777600
	H	5.32658000	-0.58160500	-3.21382500
	C	7.05245100	1.18471200	-2.93427000
	F	6.91791200	1.05184600	-1.63306500
	F	7.01696100	2.44514900	-3.30332900
	C	7.99897800	0.27184600	-3.59286800
	O	8.33149200	-0.78327300	-3.11046600
	O	8.31685100	0.70352400	-4.80842800
	C	9.13406100	-0.17478200	-5.59635700
	C	9.37242400	0.48993600	-6.92976500

	H	8.61234600	-1.13734100	-5.69959800
	H	10.07178500	-0.36075100	-5.05351400
	H	9.99823500	-0.15643800	-7.55855500
	H	8.42167300	0.66808700	-7.44962500
	H	9.88660400	1.45099300	-6.79643300

9. DFT calculations for transition state

All density functional theory (DFT) calculations were performed with the Gaussian 16 program package. [1]

Full geometry optimizations were operated to locate all of the stationary points, using (U)M06-2X density functional theory method[2-3] with def2SVP [4]basis for all atoms, and a polarized continuum model based on solute electron density (PCM)[5-6] 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 (OSTS4, OSTS5) 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.[7] 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[8-9] 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// PCM(dichloroethane)-(U)M06-2X/def2SVP level.

Unless mentioned otherwise, the Gibbs free energy of formation (ΔG) are obtained at the PCM-SMD(dichloroethane)-(U)M06-2X/def2TZVP// PCM(dichloroethane)-(U)M06-2X/def2SVP level . All 3D graphs of molecules are performed by Pymol10. 3D-isosurfaces of TS1 are performed by Multiwfn and VMD.

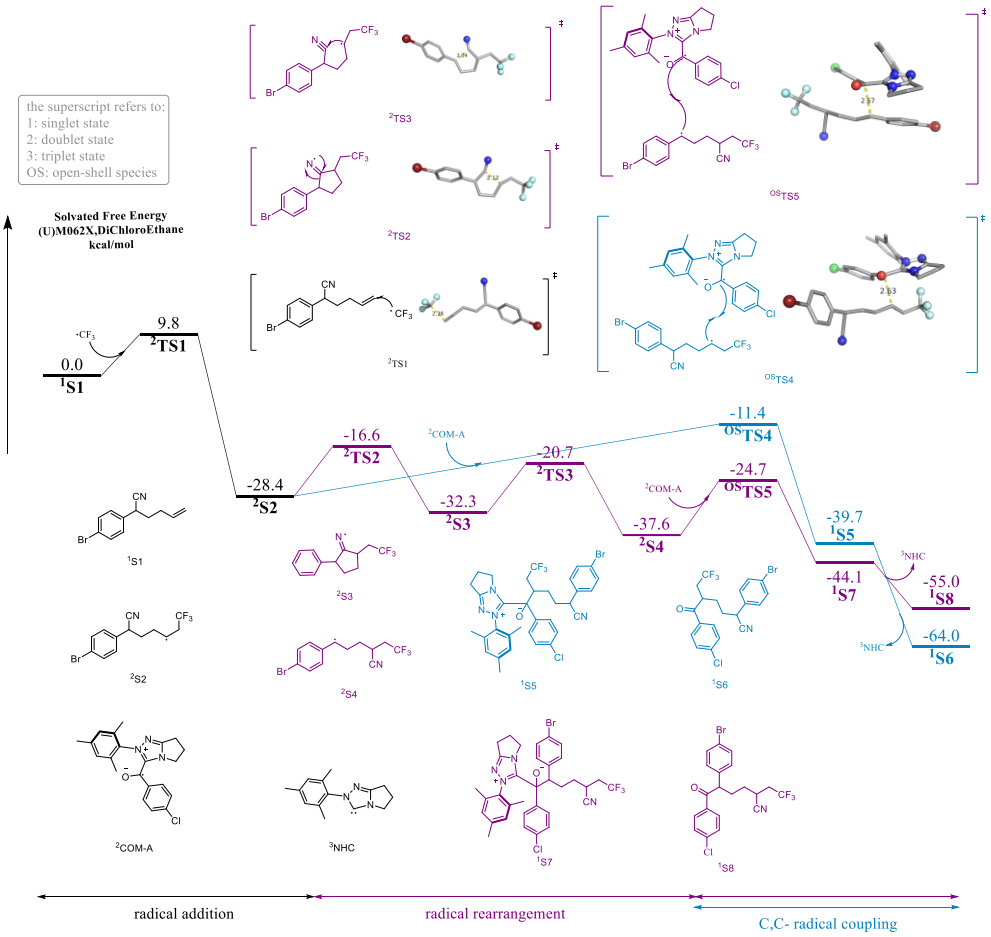
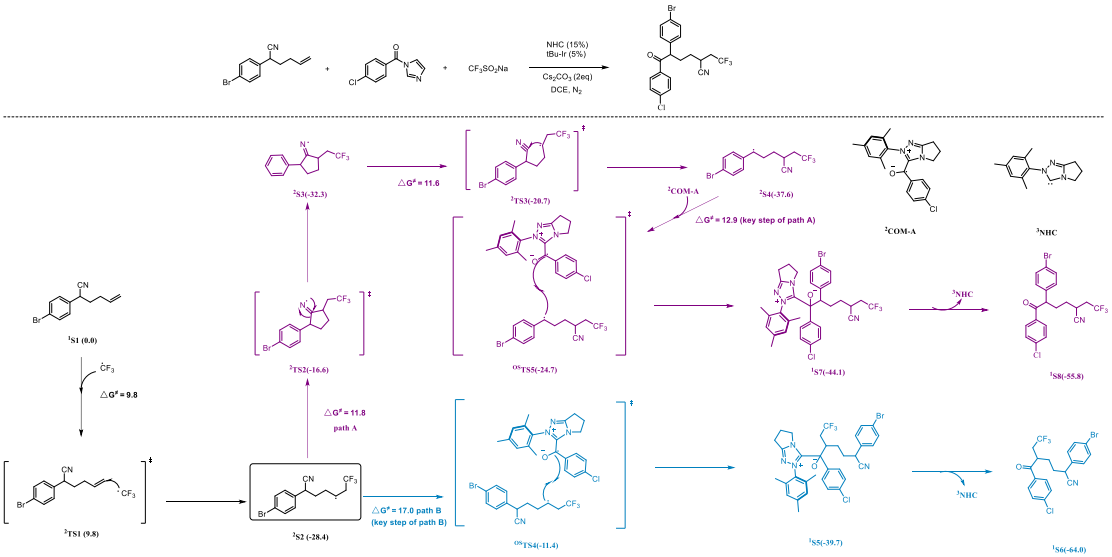


Figure 1. Gibbs free energy profiles for the NHC-catalyzed CN migration.

Scheme 1 Schematic mechanism for the NHC-catalyzed CN migration.[a]



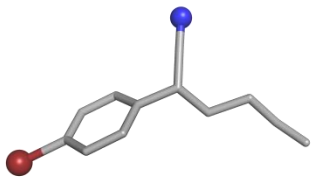
[a] The superscript prefixes '1', '2', '3', and 'OS' are used to indicate the singlet, doublet, triplet, and open-shell species, respectively. Geometries\ of ^{OS}TS4 and ^{OS}TS5, are optimized in the open-shell singlet. Relative Gibbs free energies (ΔG, kcal mol^{-1}) are relative to species I at the PCM-SMD(dichloroethane)-(U)M06-2X/def2TZVP//PCM(dichloroethane)-(U)M06-2X/def2SVP level. DFT-Optimized geometries are provided in structure details section below.

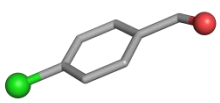
Table 1. thermal correction to Gibbs free energy (G_0, hartree), single point energies (SP-E, hartree),sum of electronic and thermal free energies (Gc, hartree) with the addition of SP-E as well as thermal corrections, and relative Gibbs free energies (ΔG, kcal mol^{-1}) of various species with respect to S1 for radical coupling and radical addition reactions at the PCM-SMD(dichloroethane)-(U)M06-2X/def2TZVP//PCM(dichloroethane)-(U)M06-2X/def2SVP level. IF represents imaginary frequencies (cm^{-1}).

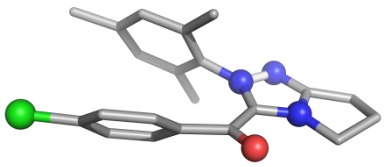
Species	G_0	SP-E	G_c(G_0+SP-E)	ΔG	IF
S1	0.164981	-3093.399738	-3093.234757		
COMA	0.328199	-1512.513655	-1512.185456		
S5	0.536413	-4943.63076	-4943.094347	-39.7	
S7	0.53483	-4943.63621	-4943.10138	-44.1	
TS4	0.530408	-4943.579709	-4943.049301	-11.4	526.42i
TS5	0.532509	-4943.602961	-4943.070452	-24.7	266.71i
S2	0.172127	-3431.063105	-3430.890978	-28.4	
S4	0.174191	-3431.079798	-3430.905607	-37.6	
TS2	0.175915	-3431.048013	-3430.872098	-16.6	537.41i
S3	0.179396	-3431.076483	-3430.897087	-32.3	

TS3	0.177088	-3431.055727	-3430.878639	-20.7	579.15i
S6	0.259195	-4235.71271	-4235.453515	-64.0	
a2	0.055565	-804.516055	-804.46049		
S8	0.258887	-4235.71384	-4235.454953	-55.8	

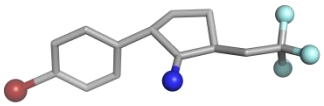
Structure Details

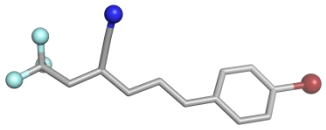
Structure S1				
				
cartesian coordinates of stationary point structure [Å]	C	-1.58740000	-0.43030000	-0.08430000
	C	-0.20450000	-0.28850000	0.00480000
	C	0.38410000	0.97820000	0.05790000
	C	-0.43440000	2.11000000	0.01800000
	C	-1.81980000	1.98520000	-0.07000000
	C	-2.38390000	0.71250000	-0.12090000
	H	-2.04180000	-1.42040000	-0.12020000
	H	0.42320000	-1.18170000	0.03480000
	H	0.00840000	3.10760000	0.06450000
	H	-2.45420000	2.87100000	-0.09660000
	Br	-4.26700000	0.53160000	-0.23610000
	C	1.89900000	1.09020000	0.07980000
	C	2.48060000	1.13290000	-1.34950000
	H	2.31080000	0.20940000	0.59750000
	C	4.00930000	1.15430000	-1.38450000
	H	2.10590000	0.24430000	-1.87930000
	H	2.07070000	2.01350000	-1.86950000
	H	4.36720000	2.03890000	-0.83010000
	H	4.40650000	0.26550000	-0.86900000
	C	4.53440000	1.20520000	-2.78990000
	C	5.30250000	0.27140000	-3.34990000
	H	4.23840000	2.08010000	-3.38100000
	H	5.64900000	0.36190000	-4.38130000
	H	5.61480000	-0.61530000	-2.79060000
	C	2.33950000	2.26570000	0.84740000
	N	2.69020000	3.20180000	1.42340000

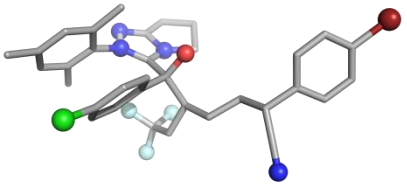
Structure a2				
cartesian coordinates of stationary point structure [Å]	C	2.94330000	0.37490000	0.00050000
	O	3.76050000	-0.47780000	-0.00030000
	C	1.46830000	0.23590000	0.00010000
	C	0.88430000	-1.03980000	0.00010000
	C	0.66860000	1.38200000	-0.00020000
	C	-0.49840000	-1.16760000	0.00000000
	H	1.52430000	-1.92350000	-0.00010000
	C	-0.71780000	1.26370000	0.00000000
	H	1.14050000	2.36580000	0.00010000
	C	-1.28430000	-0.01110000	0.00010000
	H	-0.97500000	-2.14770000	0.00010000
	H	-1.35990000	2.14390000	-0.00010000
	Cl	-3.01160000	-0.16730000	0.00000000

Structure COMA				
cartesian coordinates of stationary point structure [Å]	C	-1.68670000	-0.89660000	-0.56970000
	C	-0.14190000	-0.90480000	-0.54700000
	C	0.30580000	0.34570000	-1.34250000
	C	-0.88490000	1.23750000	-1.18800000
	C	-3.04440000	1.35530000	-0.72230000
	H	-2.10390000	-1.46360000	-1.41580000
	H	-2.15100000	-1.25820000	0.35210000
	H	0.20120000	-0.81610000	0.49260000
	H	1.22730000	0.80060000	-0.96210000
	N	-1.95780000	0.52360000	-0.75180000
	N	-1.17000000	2.48170000	-1.39980000
	N	-2.51030000	2.57630000	-1.09180000

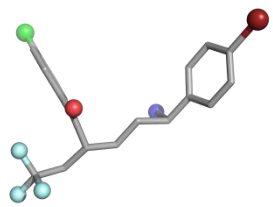
	H	0.26740000	-1.83310000	-0.96020000
	H	0.45150000	0.12200000	-2.40980000
	C	-3.14020000	3.85040000	-1.01130000
	C	-3.60410000	4.30720000	0.23200000
	C	-3.32720000	4.58470000	-2.19220000
	C	-4.35730000	5.48320000	0.25200000
	C	-4.06800000	5.76470000	-2.11680000
	C	-4.62380000	6.20900000	-0.91240000
	H	-4.74630000	5.84200000	1.20860000
	H	-4.24280000	6.33630000	-3.03180000
	C	-3.31360000	3.55950000	1.50550000
	H	-4.05630000	2.76580000	1.68250000
	H	-2.32340000	3.08390000	1.47190000
	H	-3.34510000	4.24410000	2.36250000
	C	-2.78730000	4.08260000	-3.50330000
	H	-1.68860000	4.11560000	-3.51430000
	H	-3.06890000	3.03110000	-3.67020000
	H	-3.16760000	4.68520000	-4.33700000
	C	-5.52210000	7.41640000	-0.87250000
	H	-6.57630000	7.09880000	-0.91370000
	H	-5.38630000	7.98610000	0.05670000
	H	-5.33850000	8.08320000	-1.72490000
	C	-4.34880000	0.93400000	-0.31060000
	O	-4.47480000	-0.18080000	0.25990000
	C	-5.51810000	1.84000000	-0.48990000
	C	-5.72530000	2.58820000	-1.65580000
	C	-6.45410000	1.94080000	0.54890000
	C	-6.78900000	3.47980000	-1.75690000
	H	-5.04070000	2.47760000	-2.49810000
	C	-7.52340000	2.82790000	0.46530000
	H	-6.31620000	1.32740000	1.44130000
	C	-7.66650000	3.60730000	-0.68240000
	H	-6.93610000	4.07680000	-2.65730000
	H	-8.23580000	2.92980000	1.28420000
	Cl	-8.96950000	4.76340000	-0.77840000

Structure S3				
cartesian coordinates of stationary point structure [Å]	C	-2.69910000	-0.85020000	-0.58110000
	C	-1.35510000	-0.51100000	-0.45880000
	C	-0.96050000	0.64420000	0.22810000
	C	-1.94600000	1.45730000	0.79260000
	C	-3.29890000	1.13470000	0.67920000
	C	-3.66220000	-0.01880000	-0.00890000
	H	-2.99770000	-1.75300000	-1.11390000
	H	-0.60060000	-1.16640000	-0.90080000
	H	-1.65730000	2.36040000	1.33400000
	H	-4.06070000	1.77460000	1.12480000
	C	0.49570000	1.02200000	0.31780000
	C	1.43250000	-0.11200000	0.78590000
	C	1.15000000	1.48080000	-0.99830000
	H	0.61240000	1.82420000	1.06420000
	C	2.71950000	-0.07790000	-0.05600000
	C	2.64580000	1.28660000	-0.75510000
	H	0.87460000	2.51210000	-1.25300000
	H	0.81410000	0.82840000	-1.82010000
	H	2.59750000	-0.87050000	-0.81410000
	H	3.02910000	2.06960000	-0.08100000
	H	3.24060000	1.31620000	-1.67650000
	C	3.95820000	-0.37870000	0.77620000
	H	3.84810000	-1.34840000	1.28140000
	H	4.11030000	0.38900000	1.54860000
	C	5.21370000	-0.44740000	-0.04990000
	N	1.19890000	-0.91540000	1.70310000
	Br	-5.49610000	-0.47410000	-0.16920000
	F	5.53030000	0.73660000	-0.59080000
	F	5.09740000	-1.31600000	-1.06160000
	F	6.26120000	-0.83290000	0.68300000

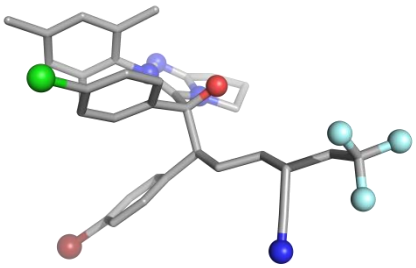
Structure S4				
cartesian coordinates of stationary point structure [Å]	C	4.33390000	0.04890000	0.05210000
	C	3.33700000	-0.88780000	0.33630000
	C	2.00350000	-0.53220000	0.19520000
	C	1.62920000	0.76960000	-0.23330000
	C	2.67360000	1.69140000	-0.51300000
	C	4.00600000	1.34110000	-0.37370000
	H	3.60800000	-1.89100000	0.66620000
	H	1.23520000	-1.27330000	0.41910000
	H	2.41580000	2.69890000	-0.84550000
	H	4.79430000	2.06170000	-0.59270000
	C	0.27150000	1.15360000	-0.38190000
	H	0.06480000	2.17260000	-0.71910000
	C	-0.88030000	0.24520000	-0.10630000
	H	-0.81230000	-0.65250000	-0.74980000
	H	-0.82270000	-0.13640000	0.93070000
	C	-2.22630000	0.92900000	-0.31850000
	H	-2.30970000	1.28370000	-1.35800000
	H	-2.29740000	1.81470000	0.33070000
	C	-3.42770000	0.02500000	0.00180000
	H	-3.34520000	-0.31610000	1.04680000
	C	-4.74770000	0.78780000	-0.16120000
	H	-4.94710000	1.01890000	-1.21660000
	Br	6.15380000	-0.43710000	0.24490000
	H	-4.67890000	1.73600000	0.38860000
	C	-5.94050000	0.05080000	0.38950000
	F	-6.17060000	-1.09590000	-0.25650000
	F	-7.04670000	0.78970000	0.29430000
	F	-5.77480000	-0.25520000	1.68140000
	C	-3.38840000	-1.18340000	-0.84050000
	N	-3.31730000	-2.11420000	-1.51790000

Structure S5				
				
cartesian coordinates of stationary point structure [Å]	C	-1.14540000	-0.31310000	-0.36400000
	C	0.37350000	-0.04250000	-0.28980000
	C	0.65510000	1.09060000	-1.30600000
	C	-0.65990000	1.79600000	-1.30780000
	C	-2.79810000	1.67070000	-0.81470000
	H	-1.39540000	-1.10210000	-1.08420000
	H	-1.61790000	-0.51840000	0.60320000
	H	0.62910000	0.30550000	0.71980000
	H	1.48110000	1.74810000	-1.01450000
	N	-1.64990000	0.97380000	-0.85590000
	N	-1.11380000	2.98270000	-1.55500000
	N	-2.44630000	2.89670000	-1.24950000
	H	0.95510000	-0.94690000	-0.49720000
	H	0.86290000	0.69660000	-2.31190000
	C	-3.22970000	4.10310000	-1.31620000
	C	-3.56300000	4.73060000	-0.10450000
	C	-3.60440000	4.61400000	-2.56170000
	C	-4.39800000	5.84390000	-0.16890000
	C	-4.41990000	5.75120000	-2.56970000
	C	-4.85700000	6.35350000	-1.39020000
	H	-4.69680000	6.33120000	0.76270000
	H	-4.73810000	6.16000000	-3.53210000
	C	-3.01440000	4.23160000	1.20470000
	H	-3.23400000	3.16430000	1.37180000
	H	-1.91860000	4.34850000	1.21910000
	H	-3.43030000	4.81320000	2.03710000
	C	-3.21720000	3.96250000	-3.86230000
	H	-2.30770000	3.35810000	-3.77050000
	H	-4.02290000	3.30360000	-4.22090000
	H	-3.05320000	4.72900000	-4.63100000
	C	-5.81980000	7.50990000	-1.41520000
	H	-6.82940000	7.15740000	-1.15160000
	H	-5.53810000	8.27910000	-0.68300000
	H	-5.86880000	7.97110000	-2.40990000

	C	-4.05100000	1.10150000	-0.07570000
	O	-3.61480000	0.96950000	1.17750000
	C	-5.25910000	2.06070000	-0.21230000
	C	-5.74390000	2.55940000	-1.42600000
	C	-5.88880000	2.45950000	0.96830000
	C	-6.81190000	3.45360000	-1.46480000
	H	-5.25250000	2.30000000	-2.36500000
	C	-6.96430000	3.34610000	0.95310000
	H	-5.48500000	2.07260000	1.90450000
	C	-7.40860000	3.84330000	-0.26860000
	H	-7.16460000	3.86370000	-2.41150000
	H	-7.44610000	3.66510000	1.87770000
	Cl	-8.72140000	4.99440000	-0.30350000
	C	-4.43230000	-0.32390000	-0.67130000
	C	-5.46050000	-0.97470000	0.27750000
	C	-4.92590000	-0.46240000	-2.11800000
	H	-3.51350000	-0.92340000	-0.59830000
	C	-4.80750000	-1.74960000	1.41640000
	H	-6.11150000	-1.65390000	-0.29630000
	H	-6.11940000	-0.19840000	0.69780000
	H	-5.24730000	-1.50330000	-2.26910000
	H	-5.80160000	0.16600000	-2.33170000
	C	-3.90850000	-0.23160000	-3.20180000
	C	-5.82160000	-2.30100000	2.44020000
	H	-4.12610000	-1.06890000	1.94190000
	H	-4.21510000	-2.59190000	1.02150000
	F	-3.55260000	1.05940000	-3.34040000
	F	-2.77200000	-0.90870000	-2.97780000
	F	-4.36790000	-0.62300000	-4.39160000
	C	-5.11970000	-2.99630000	3.59420000
	H	-6.40010000	-1.45290000	2.84070000
	C	-6.79210000	-3.18800000	1.78080000
	C	-4.55980000	-2.21130000	4.60790000
	C	-4.95630000	-4.38230000	3.64290000
	N	-7.53220000	-3.88530000	1.23540000
	C	-3.85100000	-2.79390000	5.65480000
	H	-4.67820000	-1.12580000	4.58140000
	C	-4.24910000	-4.98190000	4.68510000
	H	-5.39020000	-5.01240000	2.86360000
	C	-3.70190000	-4.17990000	5.68250000
	H	-3.42110000	-2.17710000	6.44400000
	H	-4.12740000	-6.06460000	4.71900000
	Br	-2.73980000	-4.98440000	7.10460000

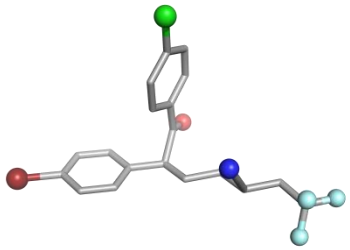
Structure S6				
cartesian coordinates of stationary point structure [Å]	C	2.09650000	-0.70680000	-0.98730000
	O	1.69310000	-0.92060000	-2.10880000
	C	2.52890000	0.68040000	-0.60610000
	C	2.66020000	1.61060000	-1.64740000
	C	2.77330000	1.09690000	0.70850000
	C	3.03540000	2.92270000	-1.39230000
	H	2.46150000	1.28100000	-2.66730000
	C	3.14010000	2.41270000	0.98150000
	H	2.67210000	0.41220000	1.54850000
	C	3.27090000	3.31330000	-0.07300000
	H	3.14420000	3.64500000	-2.20110000
	H	3.32270000	2.73990000	2.00450000
	Cl	3.73190000	4.95310000	0.25980000
	C	2.12790000	-1.86950000	0.01080000
	C	1.05760000	-1.74570000	1.11000000
	C	3.50870000	-2.15490000	0.60780000
	H	1.85230000	-2.73220000	-0.61360000
	C	-0.28860000	-1.27210000	0.57370000
	H	0.94260000	-2.73950000	1.57100000
	H	1.39340000	-1.07630000	1.91590000
	H	3.44050000	-3.01320000	1.29140000
	H	3.91090000	-1.30800000	1.17940000
	C	4.53200000	-2.50460000	-0.43950000
	C	-1.40270000	-1.27460000	1.64100000
	H	-0.61950000	-1.91910000	-0.25300000
	H	-0.20910000	-0.25110000	0.16540000
	F	4.15740000	-3.55530000	-1.17600000
	F	5.71090000	-2.80340000	0.10900000
	F	4.73850000	-1.48790000	-1.28940000
	C	-2.73090000	-0.83170000	1.05120000
	H	-1.51140000	-2.29760000	2.03430000
	C	-1.00960000	-0.42850000	2.77950000
	C	-3.57530000	-1.78610000	0.47750000
	C	-3.09440000	0.51650000	1.00280000

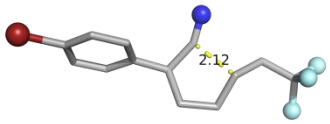
	N	-0.67150000	0.24970000	3.64940000
	C	-4.76750000	-1.40700000	-0.13560000
	H	-3.30310000	-2.84330000	0.50810000
	C	-4.28460000	0.91150000	0.39490000
	H	-2.44780000	1.27470000	1.45060000
	C	-5.11090000	-0.05700000	-0.17060000
	H	-5.42470000	-2.15520000	-0.57880000
	H	-4.56670000	1.96370000	0.36330000
	Br	-6.73160000	0.47140000	-0.99790000

Structure S7				
cartesian coordinates of stationary point structure [Å]	C	-4.44740000	-1.88380000	2.01080000
	C	-3.92020000	-2.79420000	3.14150000
	C	-2.94150000	-3.78720000	2.46840000
	C	-2.47660000	-2.97610000	1.30470000
	C	-2.87070000	-1.23110000	0.02210000
	H	-5.37760000	-2.26710000	1.56780000
	H	-4.57090000	-0.83110000	2.28900000
	H	-3.37080000	-2.18160000	3.86840000
	H	-2.11510000	-4.09740000	3.11670000
	N	-3.35970000	-1.97330000	1.03190000
	N	-1.44870000	-2.91850000	0.51940000
	N	-1.70340000	-1.83280000	-0.27490000
	H	-4.73670000	-3.29960000	3.66780000
	H	-3.45610000	-4.69000000	2.10730000
	C	-0.68840000	-1.43400000	-1.21170000
	C	0.11890000	-0.33570000	-0.88940000
	C	-0.55400000	-2.16520000	-2.39480000
	C	1.03560000	0.08050000	-1.85500000
	C	0.39260000	-1.71920000	-3.31980000
	C	1.17050000	-0.58300000	-3.08020000
	H	1.65840000	0.95420000	-1.64650000
	H	0.50420000	-2.25970000	-4.26280000
	C	0.00450000	0.34710000	0.44690000
	H	-1.03350000	0.63390000	0.68070000

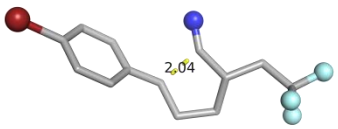
	H	0.34950000	-0.32990000	1.24490000
	H	0.63030000	1.24810000	0.46930000
	C	-1.43280000	-3.35420000	-2.67030000
	H	-1.27490000	-4.14200000	-1.91950000
	H	-2.49880000	-3.07730000	-2.62680000
	H	-1.22630000	-3.76910000	-3.66420000
	C	2.10960000	-0.05000000	-4.12870000
	H	1.66630000	0.83800000	-4.60630000
	H	3.06700000	0.25830000	-3.68660000
	H	2.30590000	-0.79540000	-4.90980000
	C	-3.49000000	0.17420000	-0.30300000
	O	-3.35800000	0.82700000	0.84410000
	C	-2.75870000	0.84960000	-1.48940000
	C	-2.53810000	0.25570000	-2.73780000
	C	-2.28040000	2.14390000	-1.27760000
	C	-1.83740000	0.92170000	-3.74050000
	H	-2.87760000	-0.76180000	-2.93550000
	C	-1.58110000	2.83190000	-2.26880000
	H	-2.44950000	2.58400000	-0.29440000
	C	-1.35820000	2.20530000	-3.49080000
	H	-1.64390000	0.44130000	-4.70010000
	H	-1.19780000	3.83770000	-2.09470000
	Cl	-0.43890000	3.03030000	-4.72620000
	C	-5.03180000	-0.04410000	-0.68930000
	C	-5.26660000	-0.88170000	-1.92530000
	C	-5.74410000	1.31630000	-0.73240000
	H	-5.45490000	-0.60110000	0.15890000
	C	-5.52120000	-0.30680000	-3.17850000
	C	-5.19340000	-2.27950000	-1.85230000
	C	-6.12520000	1.83990000	0.64870000
	H	-5.10420000	2.05790000	-1.24090000
	H	-6.65710000	1.21990000	-1.34150000
	C	-5.66630000	-1.08890000	-4.32230000
	H	-5.58560000	0.77770000	-3.27710000
	C	-5.33500000	-3.08140000	-2.98430000
	H	-5.02870000	-2.76530000	-0.88760000
	H	-6.83390000	1.14650000	1.13220000
	H	-5.21790000	1.87930000	1.26420000
	C	-6.75200000	3.24330000	0.61090000
	C	-5.56140000	-2.47430000	-4.21680000
	H	-5.85420000	-0.62360000	-5.29010000
	H	-5.27290000	-4.16710000	-2.90690000
	C	-7.06610000	3.74010000	2.02670000
	H	-6.03040000	3.93590000	0.14720000

	C	-7.95220000	3.24900000	-0.24390000
	Br	-5.74440000	-3.55040000	-5.76810000
	H	-7.90810000	3.18730000	2.46550000
	H	-6.18440000	3.57680000	2.66060000
	C	-7.38710000	5.20950000	2.09320000
	N	-8.88530000	3.20370000	-0.92080000
	F	-6.38480000	5.95460000	1.61300000
	F	-8.47790000	5.52360000	1.38700000
	F	-7.60360000	5.59950000	3.35100000

Structure S8				
cartesian coordinates of stationary point structure [Å]	C	0.06360000	0.41670000	1.94230000
	O	-0.11170000	0.48360000	3.13880000
	C	0.03000000	1.66380000	1.10670000
	C	-0.46910000	2.82550000	1.71250000
	C	0.46170000	1.72070000	-0.22510000
	C	-0.55440000	4.01860000	1.00660000
	H	-0.79490000	2.77370000	2.75180000
	C	0.38740000	2.91160000	-0.94280000
	H	0.88250000	0.84340000	-0.71520000
	C	-0.12500000	4.04860000	-0.32110000
	H	-0.94860000	4.92200000	1.47140000
	H	0.72570000	2.96180000	-1.97720000
	Cl	-0.22940000	5.53310000	-1.21470000
	C	0.26740000	-0.95160000	1.28460000
	C	1.68500000	-1.09580000	0.75120000
	C	-0.84230000	-1.26720000	0.27470000
	C	1.96700000	-1.61980000	-0.51410000
	C	2.75640000	-0.70410000	1.56530000
	H	-0.71630000	-0.66610000	-0.63890000
	H	-0.74990000	-2.32260000	-0.02590000
	C	-2.23430000	-1.03080000	0.85160000
	C	3.28240000	-1.74650000	-0.96250000
	H	1.16180000	-1.93630000	-1.17780000
	C	4.07400000	-0.82100000	1.13290000

	H	2.55950000	-0.30090000	2.56170000
	H	-2.36080000	0.02580000	1.14100000
	H	-2.37110000	-1.63160000	1.76360000
	C	-3.36040000	-1.40050000	-0.12820000
	C	4.32590000	-1.34320000	-0.13500000
	H	3.48970000	-2.15530000	-1.95150000
	H	4.89770000	-0.50970000	1.77530000
	H	-3.25970000	-2.46360000	-0.40090000
	C	-4.73720000	-1.18430000	0.51020000
	C	-3.20800000	-0.62530000	-1.37230000
	Br	6.11500000	-1.50670000	-0.73820000
	H	-4.94730000	-0.11500000	0.65000000
	H	-4.75210000	-1.66640000	1.49690000
	C	-5.86630000	-1.78340000	-0.28680000
	N	-3.04070000	0.00460000	-2.32390000
	F	-5.97930000	-1.23060000	-1.49810000
	F	-7.03390000	-1.62020000	0.33570000
	F	-5.69260000	-3.09690000	-0.47230000
	H	0.16350000	-1.65200000	2.12840000
Structure TS2				
cartesian coordinates of stationary point structure [Å]	C	-2.89540000	-0.91560000	-0.55170000
	C	-1.52620000	-0.73050000	-0.37710000
	C	-1.03670000	0.35400000	0.35790000
	C	-1.94500000	1.25620000	0.91810000
	C	-3.31890000	1.08680000	0.75190000
	C	-3.78130000	-0.00070000	0.01510000
	H	-3.27100000	-1.76540000	-1.12160000
	H	-0.83140000	-1.45220000	-0.81210000
	H	-1.57860000	2.10710000	1.49630000
	H	-4.02190000	1.79240000	1.19470000
	C	0.44980000	0.60990000	0.49010000
	C	1.22150000	-0.66150000	0.70870000
	C	1.04320000	1.36840000	-0.70470000
	H	0.62740000	1.21000000	1.39780000
	C	2.97690000	-0.06880000	-0.32030000
	C	2.56120000	1.35400000	-0.53740000

	H	0.63130000	2.38510000	-0.74930000
	H	0.75960000	0.85040000	-1.63480000
	H	2.83650000	-0.73640000	-1.17760000
	H	2.85540000	1.97240000	0.32520000
	H	3.05520000	1.77750000	-1.42780000
	C	4.11300000	-0.43110000	0.58360000
	H	4.05140000	-1.49080000	0.87120000
	H	4.10530000	0.17480000	1.50170000
	C	5.45590000	-0.22090000	-0.07210000
	N	1.32970000	-1.74930000	1.14330000
	Br	-5.64660000	-0.24480000	-0.21820000
	F	5.64020000	1.05900000	-0.42330000
	F	5.58720000	-0.95120000	-1.18460000
	F	6.46100000	-0.55380000	0.74090000

Structure TS3				
cartesian coordinates of stationary point structure [Å]	C	-2.85700000	0.88390000	-0.82710000
	C	-1.54110000	1.14980000	-0.46080000
	C	-0.98420000	0.59300000	0.70570000
	C	-1.79610000	-0.25230000	1.48820000
	C	-3.10880000	-0.53020000	1.13110000
	C	-3.63210000	0.04370000	-0.02890000
	H	-3.27860000	1.32720000	-1.72930000
	H	-0.94960000	1.80960000	-1.09570000
	H	-1.37800000	-0.70540000	2.38920000
	H	-3.72460000	-1.18680000	1.74570000
	C	0.39790000	0.81240000	1.11200000
	C	1.48730000	-0.81910000	0.53930000
	C	1.29680000	1.84800000	0.49920000
	H	0.58480000	0.62900000	2.17600000
	C	2.67010000	-0.09390000	-0.04670000

	C	2.72600000	1.31300000	0.54900000
	H	1.21180000	2.80110000	1.04590000
	H	1.02120000	2.04390000	-0.54650000
	H	2.45550000	-0.00690000	-1.12510000
	H	3.08050000	1.25830000	1.59090000
	H	3.42240000	1.95220000	-0.00760000
	C	3.91710000	-0.95880000	0.13890000
	H	3.76580000	-1.94090000	-0.32850000
	H	4.12820000	-1.12060000	1.20530000
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	Br	-5.42250000	-0.32530000	-0.52520000
	F	5.58160000	0.72210000	0.18730000
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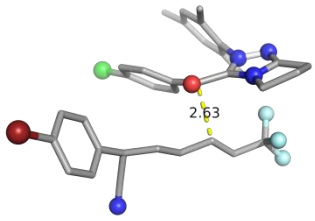
Structure TS4				
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	H	-0.62420000	-0.79520000	-1.11430000
	H	-0.21280000	-0.00840000	0.43350000
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	H	0.63260000	1.04290000	-3.35200000

	C	-3.26270000	4.01130000	-1.10720000
	C	-3.25830000	4.60440000	0.16480000
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	C	-6.28770000	6.89890000	-0.17170000
	H	-7.11530000	6.35220000	0.30780000
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	F	-1.65300000	-0.80370000	-3.15380000
	F	-2.92550000	-0.53430000	-4.86640000
	C	-6.10730000	-2.06340000	3.06300000
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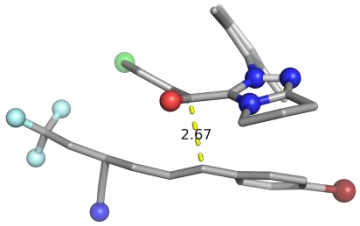
Structure TS5				
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	N	-1.84880000	-1.79250000	-0.42250000
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	H	-0.70950000	0.65870000	1.18410000
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	H	-2.04800000	-2.26010000	-4.28980000
	C	1.45550000	1.32940000	-3.87000000
	H	0.91700000	2.28090000	-4.00520000
	H	2.44020000	1.56660000	-3.44530000
	H	1.59720000	0.87950000	-4.86090000
	C	-3.23590000	0.13840000	0.61450000
	O	-3.64580000	0.42620000	1.76170000
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	H	-5.18650000	-3.27670000	0.05990000
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	C	-5.07940000	-3.88450000	-3.27140000
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	H	-4.85040000	-5.13510000	-1.52240000
	C	-5.85680000	4.25990000	0.51070000
	H	-5.02080000	3.20820000	-1.16510000
	C	-7.05890000	3.41760000	-1.51020000
	Br	-4.81510000	-5.31480000	-4.48710000
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	H	-5.04350000	3.98950000	1.19890000
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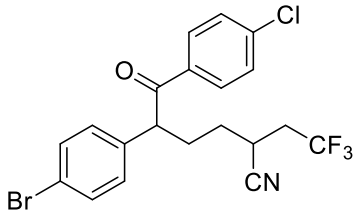
	N	-7.93930000	3.55390000	-2.24320000
	F	-4.43770000	5.62330000	-0.78820000
	F	-6.52840000	6.12060000	-0.78180000
	F	-5.33090000	6.49960000	0.96370000

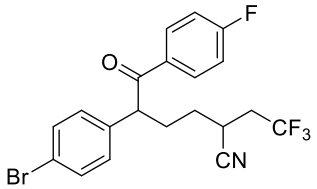
5. Characterization of the products

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 (65 mg, 72% yield, *dr* = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.7, 1.9 Hz, 2H, two isomers), 7.37 (d, *J* = 8.0 Hz, 2H, two isomers), 7.29 (d, *J* = 8.4 Hz, 2H, two isomers), 7.06 (d, *J* = 7.9 Hz, 2H, two isomers), 4.40 (t, *J* = 7.1 Hz, 1H, two isomers), 2.79 (m, 1H, two isomers), 2.56 – 2.21 (m, 3H, two isomers), 1.96 (m, 1H, two isomers), 1.61 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.37 & 197.30 (two isomers), 140.33 & 140.31 (two isomers), 137.5 & 137.3 (two isomers), 134.58 & 134.55 (two isomers), 132.9 (overlap, two isomers), 130.4 (overlap, two isomers), 130.1 & 129.9 (two isomers), 129.4 (overlap, two isomers), 126.74 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) & 126.72 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 123.0 (overlap, two isomers), 119.47 & 119.46 (two isomers), 52.76 & 52.73 (two isomers), 36.9 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.5 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 31.1 & 30.8 (two isomers), 30.1 & 29.9 (two isomers), 25.89 (q, $^{3}J_{C\text{-}F}$ = 2.7 Hz) & 25.86 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz) (two isomers).^{19}F NMR (282 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). The reported data was in accordance with literature. [11]

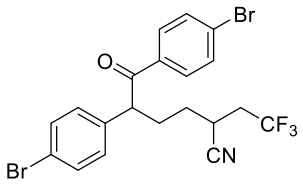
5-(4-bromophenyl)-6-(4-fluorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile



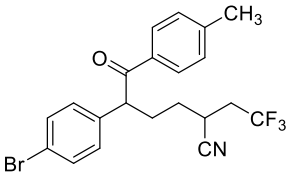
(4b) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (58 mg, 67% yield, *dr* =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H, two isomers), 7.48 – 7.44 (m, 2H, two isomers), 7.16 (dd, *J* = 8.4, 1.9 Hz, 2H, two isomers), 7.10 – 7.06 (m, 2H, two isomers), 4.50 (t, *J* = 7.2 Hz, 1H, two isomers), 2.95 – 2.84 (m, 1H, two isomers), 2.60 – 2.25 (m, 3H, two isomers), 2.13 – 1.95 (m, 1H, two isomers), 1.79 – 1.63 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.73 & 196.66 (two isomers), 167.19 (d, $^{1}J_{C\text{-}F}$ = 257.1 Hz) & 167.17 (d, $^{1}J_{C\text{-}F}$ = 256.9 Hz) (two isomers), 137.44 & 137.40 (two isomers), 132.8 (overlap, two isomers), 131.5 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz) (overlap, two isomers), 129.76

& 129.72 (two isomers), 126.51 (q, $^{1}J_{C\text{-}F}$ = 278.6 Hz) & 126.48 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 121.9 (overlap, two isomers), 119.50 & 119.48 (two isomers), 116.1 (q, $^{2}J_{C\text{-}F}$ = 22.0 Hz) (overlap, two isomers), 52.45 & 52.41 (two isomers), 36.8 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.7 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) (two isomers), 30.9 & 30.7 (two isomers), 30.16 & 29.97 (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 -64.8 (s, one isomer), -64.9 (s, one isomer), -104.0 (s, one isomers), -104.1 (s, one isomers). The reported data was in accordance with literature. [11]

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

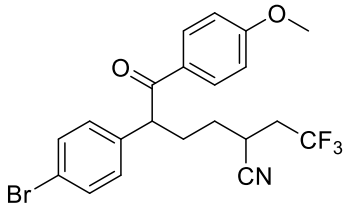


(4c) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (68 mg, 68% yield, *dr* =1:1). 1H NMR (300 MHz, CDCl3) δ 7.78 (dd, *J* = 8.6, 1.8 Hz, 2H two isomers), 7.56 (d, *J* = 8.6 Hz, 2H two isomers), 7.47 (dd, *J* = 8.6, 1.8 Hz, 2H two isomers), 7.15 (dd, *J* = 8.6, 1.8 2H two isomers), 4.49 (t, *J* = 7.1 Hz, 1H two isomers), 2.90 (m, 1H two isomers), 2.66–2.22 (m, 2H two isomers), 2.19–1.91 (m, 1H two isomers), 1.84 – 1.53 (m, 2H two isomers).^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4 & 197.3 (two isomers), 137.3 & 137.3 (two isomers), 134.8 & 134.78 (two isomers), 132.8 (overlap, two isomers), 132.3 (overlap, two isomers), 130.7 (overlap, two isomers), 129.8 & 129.7 (two isomers), 128.95 & 128.93 (two isomers), 127.04 (q, $^{1}J_{C\text{-}F}$ = 275.5 Hz) & 127.08 (q, $^{1}J_{C\text{-}F}$ = 275.8 Hz) (two isomers), 123.0 (overlap, two isomers), 119.57 & 119.55(two isomers), 52.60 & 52.56 (two isomers), 37.4 (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 (282MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature. [11]



5-(4-bromophenyl)-6-oxo-6-(p-tolyl)-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 colorless liquid (63 mg, 70 % yield, *dr* =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.3, 1.8 Hz, 2H, two isomers), 7.46 (d, *J* = 8.4 Hz, 2H, two isomers), 7.25 – 7.11 (m, 4H, two isomers), 4.54 (t, *J* = 7.2 Hz, 1H, two isomers), 2.90 – 2.81 (m, 1H, two isomers), 2.56 – 2.45 (m, 1H, two isomers), 2.35 (s, 3H, two isomers), 2.35 – 2.16 (m, 2H, two isomers), 2.20 – 1.95 (m, 1H, two isomers), 1.82 – 1.69 (m, 1H, two isomers), 1.85-1.63 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.96 & 197.89(two isomers), 144.59 & 144.57 (two isomers), 137.89 & 137.85 (two isomers), 133.61 & 133.58 (two isomers), 132.53 (overlap, two isomers), 129.85 & 129.80 (two isomers), 129.58 (overlap, two isomers), 128.96 (two isomers), 126.56 (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), 121.70 & 119.56 (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). The reported data was in accordance with literature. [11]

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

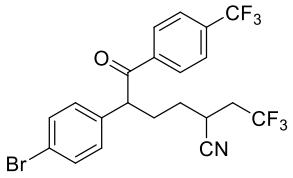


The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow colorless liquid (68 mg, 76% yield, *dr* =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H, two isomers), 7.32 – 7.28 (m, 2H, two isomers), 7.24 – 7.17 (m, 4H, two isomers), 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 (75 MHz, $CDCl_3$) , ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6

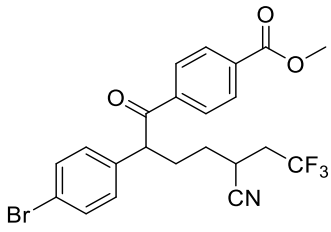
(two isomers), 163.7 (overlap, two isomers), 137.9 (two isomers), 132.4 (overlap, two isomers), 131.1 (overlap, two isomers) 129.6(two isomers), 128.9 & 128.8 (two isomers), 126.8 (q, $^{1}J_{C\text{-}F}$ = 258Hz) & 123.4 (q, $^{1}J_{C\text{-}F}$ = 258 Hz) (two isomers), 121.5 (overlap, two isomers), 119.4 (two isomers), 55.5 (overlap, two isomers), 51.9 & 52.8 (two isomers), 36.5 (q, $^{2}J_{C\text{-}F}$ = 30 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30 Hz) (two isomers),31.0 & 30.6 (two isomers), 30.2 & 30.0 (two isomers), 25.6 (q, $^{3}J_{C\text{-}F}$ = 12 Hz) & 25.5 (q, $^{3}J_{C\text{-}F}$ = 12 Hz) (two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.8 (overlap, one isomers), -64.8 (s, one isomer), -64.9 (s, one isomer)，-64.9 (s, one isomer).HRMS (ESI) calcd. for $C_{21}H_{20}BrF_3NO_2$ $[M+H]^+$: 454.0625, 456.0604; found: 454.0655, 456.0625

6-([1,1'-biphenyl]-4-yl)-5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4f) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (69 mg, 70% 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 & 196.8 (two isomers), 146.3 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz) (overlap, two isomers), 137.7 & 137.70 (two isomers), 134.79 & 134.77 (two isomers), 132.9 (overlap, two isomers), 129.9 (overlap, two isomers), 129.8 (overlap, two isomers), 129.46 & 129.31(two isomers), 126.14 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) & 126.11 (q, $^{1}J_{C\text{-}F}$ = 278.6 Hz) (two isomers), 119.5 (overlap, two isomers), 119.3 (q, $^{1}J_{C\text{-}F}$ = 260.2 Hz) (overlap, two isomers), 119.47 & 119.46 (two isomers), 52.49 & 52.44 (two isomers), 36.93 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.7 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz) (two isomers), 31.9 & 30.7 (two isomers), 30.3 & 30.0 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) (two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature.[11]

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



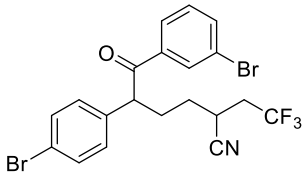
(trifluoromethyl)phenyl)hexanenitrile (4g) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (49 mg, 50 %yield, *dr* = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H, two isomers), 7.66 (d, *J* = 8.2 Hz, 2H, 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 197.47 & 197.40 (two isomers), 138.75 & 138.74 (two isomers), 136.34 & 136.29 (two isomers), 134.81 (q, $^{2}J_{C\text{-}F}$ = 32 Hz) & 134.55 (q, $^{2}J_{C\text{-}F}$ = 32 Hz) (two isomers), 134.1 (overlap, two isomers), 129.8 (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), 119.47 & 119.46 (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 (282 MHz, $CDCl_3$) δ -63.2 (overlap, two isomers), -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature. [11]



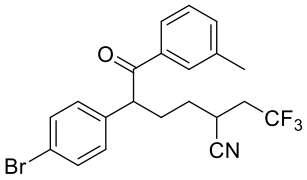
5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)-6-(4-(trifluoromethyl)phenyl)hexanenitrile (4h) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (49 mg, 50 % yield, *dr* = 1:1). 1H NMR (300 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H, two isomers), 7.96 (d, *J* = 8.2 Hz, 2H, two isomers), 7.24-7.10 (m, 2H, two isomers), 4.53 (t, *J* = 7.2 Hz, 1H, two isomers), 3.94(s, 3H, two isomers) 2.90 (m, 1H, two isomers), 2.66 – 2.24 (m, 2H, two isomers), 2.20-1.93 (m, 1H, two isomers),1.69 (m, 2H, two isomers). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8 & 197.7 (two isomers), 165.9

(overlap, two isomers), 139.1 (two isomers), 136.9 (overlap, two isomers), 136.8 (overlap, two isomers) 134.1(two isomers), 129.9 & 129.7 (two isomers), 128.6 (q, $^{1}J_{C\text{-}F}$ = 258Hz) & 121.4 (q, $^{1}J_{C\text{-}F}$ = 258 Hz) (two isomers), 119.5 (overlap, two isomers), 119.3 (two isomers), 52.8 & 52.6 (overlap, two isomers), 41.9 & 41.5 (two isomers), 36.2 (q, $^{2}J_{C\text{-}F}$ = 30 Hz) & 36.0 (q, $^{2}J_{C\text{-}F}$ = 30 Hz) (two isomers),30.61 & 30.69 (two isomers), 30.3 & 30.1 (two isomers), 24.6 (q, $^{3}J_{C\text{-}F}$ = 12 Hz) (two isomers).^{19}F NMR (282 MHz, $CDCl_3$) -64.8 (s, one isomer), -64.9 (s, one isomer). HRMS (ESI) calcd. for $C_{22}H_{19}BrF_3NNaO_3$ $[M+H]^+$: 504.0393 found: 504.0386,

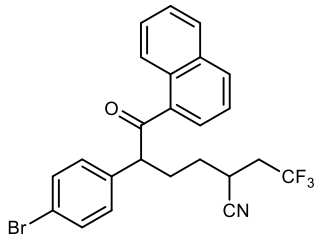
6-(3-bromophenyl)-5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile



(4i) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (61.1 mg, 61% yield, *dr* =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (q, *J* = 1.6 Hz, 1H, two isomers), 7.82 – 7.77 (m, 1H, two isomers), 7.67 – 7.60 (m, 1H, two isomers), 7.52 – 7.44 (m, 2H, two isomers), 7.35– 7.24 (m, 2H, two isomers), 7.16 (dt, *J* = 6.6, 1.8 Hz, 2H, two isomers), 4.48 (t, *J* = 7.2 Hz, 1H, two isomers), 2.10 -1.97 (m, 1H, two isomers)，2.10 – 1.97 (m, 1H, two isomers),1.76 -1.69(m, 1 H, two isomers)1.62 – 1.57 (m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.05 & 196.98 (two isomers), 137.85 & 137.83 (two isomers), 137.04 & 136.99 (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 (282 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature. [11]



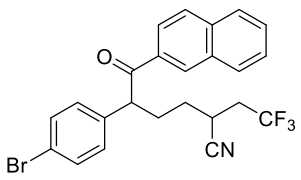
5-(4-bromophenyl)-6-oxo-6-(m-tolyl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4j) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (54.7 mg, 62% yield, dr =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.44 (m, 4H, two isomers), 7.33 (t, J =8.0 Hz, 1H, two isomers), 7.23-7.12 (m, 2H, two isomers), 7.08 (dd, J = 8.2, 2.6 Hz, 1H, two isomers), 4.54 (t, J = 7.2 Hz, 1H, two isomers), 3.84 (s, 3H, two isomers), 2.90 (m, 1H, two isomers), 2.65 – 2.20 (m, 2H, two isomers), 1.69(m, 1H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2 & 198.1 (two isomers), 160.0 (overlap, two isomers), 137.66 & 137.60 (two isomers), 137.50 & 137.47 (two isomers), 132.5 (overlap, two isomers), 129.83 & 129.77 (two isomers), 125.15 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) & 125.12 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 121.7 (overlap, two isomers), 121.3 (overlap, two isomers), 119.9 (overlap, two isomers), 119.51 & 119.48 (two isomers), 113.34 & 113.31 (two isomers), 55.5 (overlap, two isomers), 52.54 & 52.49 (two isomers), 36.5 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 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, $^{3}J_{C\text{-}F}$ = 2.8 Hz) (two isomers).^{19}F NMR (282 MHz, $CDCl_3$) δ -64.86 (s, one isomer), -64.92 (s, one isomer). The reported data was in accordance with literature. [11]



5-(4-bromophenyl)-6-(naphthalen-1-yl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile(4k)

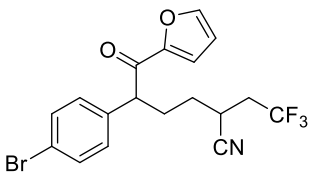
The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (72 mg, 51% yield, dr =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (t, J = 7.7 Hz, 1H, two isomers), 7.97 (d, J = 8.2, 1H, two isomers), 7.97 (d, J = 8.0 Hz, 1H, two isomers), 7.80 (d, J = 7.3Hz, 1H, two isomers), 7.68-7.34 (m, 6H, two isomers), , 7.20 (dd, J = 8.5, 2.4 Hz, 2H, two isomers), 4.59 (t, J = 7.3 Hz, 1H, two isomers), 3.00–2.88 (m, 1H, two isomers), 2.66 – 2.05 (m, 3H, two isomers),1.88-1.63 (m, 3H, two isomers). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.9 (two isomers), 136.81 (two isomers),

135.6 & 135.5 (two isomers), 133.9 (overlap, two isomers), 133.0 (overlap, two isomers), 132.3 (overlap, two isomers), 130.4 (overlap, two isomers), 129.7 (two isomers), 128.5 (overlap, two isomers), 128.2 (overlap, two isomers), 127.3 (q, $^{1}J_{C\text{-}F}$ = 234 Hz, two isomers), 126.8 (overlap, two isomers), 125.3 (two isomers) 124.2(q, $^{1}J_{C\text{-}F}$ = 234 Hz, overlap, two isomers), 121.7 & 119.3 (two isomers), 55.6 (overlap, two isomers), 36.5 (overlap, two isomers), 31.0 & 30.6 (two isomers), 30.5 (q, $^{2}J_{C\text{-}F}$ = 29 Hz) & 30.0 (q, $^{2}J_{C\text{-}F}$ = 29 Hz), 29.73 (overlap, two isomers) (q, $^{4}J_{C\text{-}F}$ = 3 Hz) 25.5 (q, $^{3}J_{C\text{-}F}$ = 7 Hz) (two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.8 (s, one isomer). HRMS (ESI) calcd. for $C_{24}H_{20}BrF_3NO$ $[M+H]^+$: 474.0675, 476.0655; found: 474.0682, 476.0666.

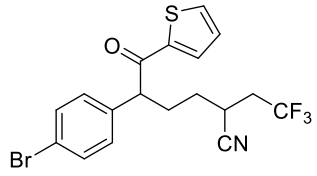


5-(4-bromophenyl)-6-(naphthalen-2-yl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4l) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (72 mg, 77% yield, *dr* =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.2 Hz, 1H, two isomers), 7.96 (dd, *J* = 8.6, 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 198.36 & 198.28 (two isomers), 137.76 & 137.70 (two isomers), 135.73 (overlap, two isomers), 133.59 & 133.48 (two isomers), 132.5 (overlap, two isomers), 132.4 (overlap, two isomers), 130.69 & 130.68 (two isomers), 129.86 & 129.82 (two isomers), 129.7(overlap, two isomers), 128.8 (overlap, two isomers), 127.82 (overlap, two isomers), 126.55 (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), 124.2 (overlap, two isomers), 121.8 (overlap, two isomers), 119.55 &

119.52 (two isomers), 52.46 & 52.41 (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), 31.10 & 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 (282 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature. [11]

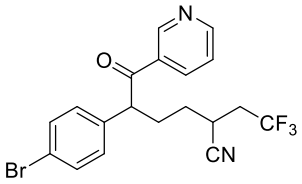


(4-bromophenyl)-6-(furan-2-yl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4m) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 15/1, v/v) as a yellow liquid (49 mg, 61% yield, *dr* =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (m,1H, two isomers), 7.48 – 7.40 (m, 2H, two isomers), 7.26-7.10 (m, 3H, two isomers), 6.52 (dd, *J* = 3.6, 1.7 Hz, 1H, two isomers), 4.39 (t, *J* = 7.4 Hz, 1H, two isomers), 2.90 (m, 1H, two isomers), 2.55 – 2.28 (m, 2H, two isomers), 2.20 – 1.92 (m, 1H, two isomers), 1.84 - 1.55 (m, 3H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.33 & 187.30 (two isomers), 152.10 & 152.09 (two isomers), 146.96 & 146.955 (two isomers), 137.03 & 136.96 (two isomers), 132.3 (overlap, two isomers), 130.0 & 129.97 (two isomers), 126.13 (q, $^{1}J_{C\text{-}F}$ = 278.5 Hz) & 125.10 (q, $^{1}J_{C\text{-}F}$ = 278.4 Hz) (two isomers), 121.8 (overlap, two isomers), 121.0 & 119.45 (two isomers), 118.56 & 118.53 (two isomers), 112.7 (overlap, two isomers), 52.42 & 52.38 (two isomers), 36.8 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 30.1 & 29.97（two isomers), 28.8 & 29.6 (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 (282 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature. [11]



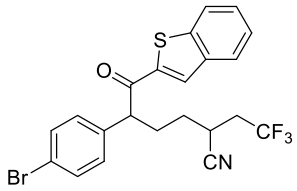
5-(4-bromophenyl)-6-oxo-6-(thiophen-2-yl)-2-(2,2,2-trifluoroethyl)hexanenitrile(4n) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 15/1, v/v) as a yellow liquid (49 mg, 60% yield, *dr* =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.63 (m, 1H, two isomers), 7.64 – 7.63 (m, 1H, two

isomers), 7.48 (d,J= 8.4 Hz, 2H, two isomers), 7.21 (dd, *J* = 8.5, 2.2 Hz, 2H, two isomers), 7.10-7.08 (m, 1H, two isomers), 4.37 (t, *J* = 7.3 Hz, 1H, two isomers), 2.93-2.84 (m, 1H, two isomers), 2.57 – 2.26 (m, 3H, two isomers), 2.13 – 1.99 (m, 1H, two isomers),1.79-1.72 (m, 2H, 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, $^1J_{C\text{-}F}$ = 275.6 Hz) & 125.08 (q, $^1J_{C\text{-}F}$ = 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, $^2J_{C\text{-}F}$ = 29.8 Hz) & 36.2 (q, $^2J_{C\text{-}F}$ = 29.7 Hz) (two isomers), 30.8 & 30.5 (two isomers), 30.2 & 29.9 (two isomers), 25.7 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) & 25.6 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.88 (s, one isomer), -64.95 (s, one isomer). The reported data was in accordance with literature. [11]

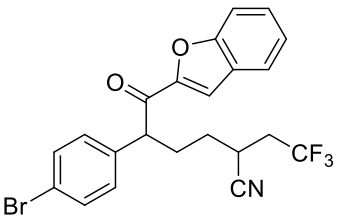


5-(4-bromophenyl)-6-oxo-6-(pyridin-3-yl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4o) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (52 mg, 65% yield, *dr* =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.4 Hz, 1H, two isomers), 8.02 (dt, *J* = 7.9 Hz, 1.1 Hz 1H, two isomers), 7.82 (td, *J* = 7.7 Hz 1.7 Hz 1H, two isomers), 7.60 – 7.35 (m, 3H, two isomers), 7.33-7.22 (m, 2H, two isomers), 5.41 (m, 1H, two isomers), 3.01 – 2.86 (m, 1H, two isomers), 2.61 – 2.45 (m, 1H, two isomers), 2.68-1.68 (m, 3H, two isomers),1.83-1.58 (m, 3H, two isomers), ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9 & 199.8 (two isomers), 152.37 & 152.31 (two isomers), 149.0 (overlap, two isomers), 137.20 & 137.18 (two isomers), 137.01 (overlap, two isomers), 132.0 (overlap, two isomers), 130.688 & 130.65 (two isomers), 127.57 & 127.00 (two isomers), 125.15 (q, $^1J_{C\text{-}F}$ = 275.7 Hz) & 125.13 (q, $^1J_{C\text{-}F}$ = 275.6 Hz) (two isomers), 122.99 & 122.97 (two isomers), 121.4 (overlap, two isomers), 119.5 (overlap, two isomers), 49.48 & 49.32 (two isomers), 36.55 (q, $^2J_{C\text{-}F}$ = 29.8 Hz) &

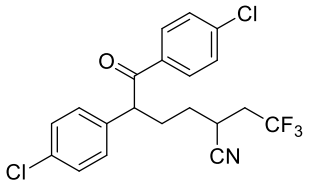
36.3 (q, $^{2}J_{C\text{-}F}$ = 29.7 Hz) (two isomers), 30.19 & 30.15 (two isomers), 29.76 & 29.71 (two isomers), 25.6 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.5 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers). ^{19}F NMR (282MHz, $CDCl_3$) δ -64.9 (s, one isomer), -64.9 (s, one isomer).The reported data was in accordance with literature. [11]



6-(benzo[b]thiophen-2-yl)-5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl) hexanenitrile (4p) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (68.9 mg, 65 % yield, *dr* = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 4.4 Hz, 1H, two isomers), 7.83 (t, *J* = 7Hz, 2H, two isomers), 7.54 – 7.46 (m, 4H, two isomers), 7.32-7.22 (m, 2H, two isomers), 4.52 (t, *J* = 7.3 Hz, 1H, two isomers), 2.97 – 2.86 (m, 1H, two isomers), 2.64 -2.25 (m, 3H, two isomers), 2.21 – 1.99 (m, 1H, two isomers), 1.85 – 1.60 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.79& 192.72 (two isomers), 142.7 (overlap, two isomers), 142.57 & 142.54 (two isomers), 139.0 (overlap, two isomers), 137.35 & 137.31 (two isomers), 132.6 (overlap, two isomers), 130.16 & 130.11 (two isomers), 129.8 & 129.7 (two isomers), 127.9 (overlap, two isomers), 126.5 (overlap, two isomers), 125.3 (overlap, two isomers), 125.13 (q, $^{1}J_{C\text{-}F}$ = 278.4 Hz) & 125.09 (q, $^{1}J_{C\text{-}F}$ = 278.4 Hz) (two isomers), 123.0 (overlap, two isomers), 122.1 (overlap, two isomers), 119.46 & 119.43 (two isomers), 53.79 & 53.73 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 30.9 & 30.5 (two isomers), 30.1 & 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 (282 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature. [11]

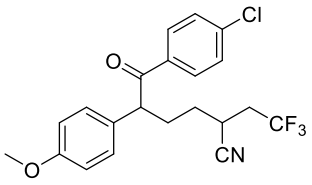


(benzofuran-2-yl)-5-(4-bromophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4q) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (48 mg, 52% yield, *dr* = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H, two isomers), 7.58-7.57 (m, 5H, two isomers), 7.38 – 7.24 (m, 4H, two isomers), 4.55 (t, *J* = 7.4 Hz, 1H, two isomers), 2.99 – 2.89 (m, 1H, two isomers), 2.65 – 2.30 (m, 3H, two isomers),1.85 – 1.61 (m, 3H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.32 & 189.29 (two isomers), 155.7 (overlap, two isomers), 151.87 & 151.86 (two isomers), 136.8 & 136.7 (two isomers), 132.5 (overlap, two isomers), 130.06 & 130.03 (two isomers), 129.0 (overlap, two isomers), 127.0 (overlap, two isomers), 125.14 (q, $^{1}J_{C\text{-}F}$ = 279.3 Hz) & 125.10 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 124.3 (overlap, two isomers), 123.8 (overlap, two isomers), 122.1 (overlap, two isomers), 119.43 & 119.40 (two isomers), 52.9 & 52.8 (two isomers), 36.6 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz) (two isomers), 30.6 & 30.1 (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 (282MHz, $CDCl_3$) δ -64.85 (s, one isomer), -64.92 (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.

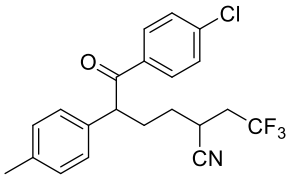


5,6-bis(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4r) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (62.8 mg, 75% yield, *dr* =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz 2H, two isomers), 7.39 (d, *J* = 8.2 Hz, 2H, two isomers), 7.35 – 7.29 (m, 2H, two isomers), 7.21 (d, *J* = 8.1 Hz, 2H, two isomers), 4.51 (t, *J* = 7.3 Hz, 1H, two isomers), 2.94 – 2.83 (m, 1H, two isomers), 2.63 – 2.24 (m, 3H, two isomers), 2.40 – 2.25 (m, 2H, two isomers), 2.16 – 1.94 (m, 1H, two isomers), 1.76 – 1.57 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.19 & 197.13 (two isomers), 140.0 (overlap, two isomers), 136.8 (overlap, two isomers), 134.3 (overlap, two isomers), 133.8 (overlap, two isomers), 129.7 (overlap,

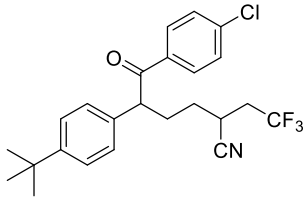
two isomers), 129.4 (overlap, two isomers), 129.1 (overlap, two isomers), 125.04 (q, $^{1}J_{C\text{-}F}$ = 261.0 Hz) & 125.00 (q, $^{1}J_{C\text{-}F}$ = 259.3 Hz) (two isomers), 119.5 (overlap, two isomers), 52.4 (overlap, two isomers), 36.6 (q, $^{2}J_{C\text{-}F}$ = 29.6 Hz) & 36.2(q, $^{2}J_{C\text{-}F}$ = 29.2 Hz) (two isomers), 30.9 & 30.7 (two isomers), 30.1 & 29.9 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 1.7 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 1.9 Hz) (two isomers).^{19}F NMR (282 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature. [11]



5-(4-chlorophenyl)-6-oxo-5-(p-tolyl)-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 (59.8 mg, 70% 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 (75 MHz, $CDCl_3$) δ 197.8 & 197.6 (two isomers), 159.3 (overlap, two isomers), 139.8 (overlap, two isomers), 134.7 (overlap, two isomers), 130.7 (overlap, two isomers), 130.3 & 130.2 (two isomers), 129.3 & 129.2 (two isomers), 129.15 (overlap, two isomers), 125.16 (q, $^{1}J_{C\text{-}F}$ = 276 Hz) & 125.14 (q, $^{1}J_{C\text{-}F}$ = 276 Hz) (two isomers), 119.7 (overlap, two isomers), 115.0 (overlap, two isomers), 55.5 (overlap, two isomers), 52.5(overlap, two isomers), 36.7 (q, $^{2}J_{C\text{-}F}$ = 30 Hz) & 36.0 (q, $^{2}J_{C\text{-}F}$ = 29 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 (282 MHz, $CDCl_3$) δ -64.9 (s, one isomer), -65.0 (s, one isomer). The reported data was in accordance with literature. [11]

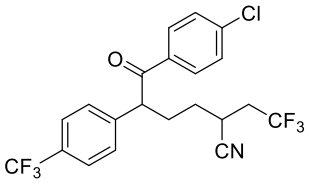


6-(4-chlorophenyl)-5-(4-methoxyphenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4t) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (58 mg, 72% yield, *dr* = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.5, 1.8 Hz, 2H, two isomers), 7.37 (d, *J* = 8.2 Hz, 2H, two isomers), 7.17 (d, *J* = 8.2 Hz 2H, two isomers), 6.86 (d, *J* = 8.2 Hz 2H, two isomers), 4.46 (t, *J* = 7.2 Hz, 1H, two isomers), 3.78 (s, 3H, two isomers), 1.72 – 1.56 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5 & 197.4 (two isomers), 139.56 & 139.54 (two isomers), 137.5 (overlap, two isomers), 135.14 & 135.09 (two isomers), 134.55 & 134.52 (two isomers), 130.17 (overlap, two isomers), 130.13(overlap, two isomers), 129.0 (overlap, two isomers), 127.87 & 127.83 (two isomers), 125.07 (q, $^{1}J_{C\text{-}F}$ = 276 Hz) & 125.04 (q, $^{1}J_{C\text{-}F}$ = 276 Hz) (two isomers), 115.9 (overlap, two isomers), 52.8 (overlap, two isomers), 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 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 (282 MHz, $CDCl_3$) δ -64.90 (s, one isomer), -64.95 (s, one isomer). The reported data was in accordance with literature. [11]

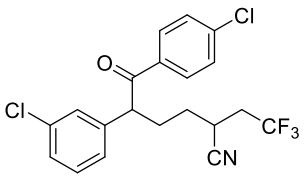


5-(4-(tert-butyl)phenyl)-6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4u) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (50 mg, 60% yield, *dr* = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2Hz, 2H two isomers), 7.43 – 7.31 (m, 4H two isomers), 7.18 (d, J = 8.3Hz, 2H，two isomers), 4.49(t, J = 7.2 Hz, 1H，two isomers), 2.99 – 2.71 (m, 1H，two isomers), 2.66 – 2.24 (m, 4H，two isomers), 2.38 – 2.23 (m, 2H，two isomers), 2.16 – 1.98 (m, 1H，two isomers), 1.77 – 1.59 (m, 2H，two isomers), 1.29 (s, 9H，two isomers).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6 & 197.5 (two isomers), 150.7 (overlap, two isomers), 139.7 (overlap, two isomers), 135.07 & 135.03 (two isomers), 134.70 & 134.68 (two

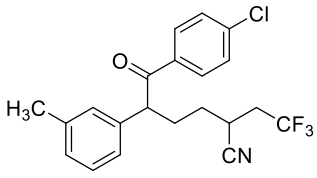
isomers), 130.3 (overlap, two isomers), 129.3 (overlap, two isomers), 127.69 & 127.65 (two isomers), 126.5 (overlap, two isomers), 125.18 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) & 125.15 (q, $^{1}J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 119.6 (overlap, two isomers), 52.74 & 52.72 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 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 -64.90 (s, one isomer), -64.99 (s, one isomer).The reported data was in accordance with literature. [11]



6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)-5-(3-(trifluoromethyl)phenyl)hexanenitrile (4v) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (48 mg, 65% yield, *dr* = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.6, 2.0 Hz, 2H, two isomers), 7.54 (d,J = 3.8 Hz 2H, two isomers), 7.48 (d,J = 5.6 Hz 2H, two isomers), 7.41 (d, *J* = 8.4 Hz, 2H, two isomers), 4.62 (t, *J* = 7.1 Hz, 1H, two isomers), 3.06 – 2.83 (m, 1H, two isomers), 2.61 – 2.28(m, 2H, two isomers), 2.20 – 1.94 (m, 1H, two isomers), 1.87 – 1.55 (m, 2H, two isomers).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 & 196.9 (two isomers), 140.32 & 140.30 (two isomers), 139.34 & 139.29 (two isomers), 134.28 & 134.26 (two isomers), 131.4 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz) (overlap, two isomers), 130.21 & 130.20 (two isomers), 130.1 (overlap, two isomers), 129.3 (overlap, two isomers), 125.11 (q, $^{1}J_{C\text{-}F}$ = 278.4 Hz) & 125.08 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 124.8 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz) (overlap, two isomers), 123.9 (q, $^{1}J_{C\text{-}F}$ = 273.6 Hz) (overlap, two isomers), 119.45 & 119.40 (two isomers), 52.7 (overlap, two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 31.2 & 30.9 (two isomers), 30.2 & 30.0 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz) (two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.63 (s, one isomer), -62.64 (s, one isomer), -64.8 (s, one isomer), -64.9(s, one isomer).The reported data was in accordance with literature. [11]

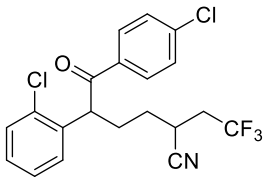


(3-chlorophenyl)-6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4w) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (52 mg, 66% yield, *dr* =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.4, 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), 4.50 (t, *J* = 7.2 Hz, 1H, two isomers), 2.95 – 2.82 (m, 1H, two isomers), 2.60 – 2.23 (m, 3H, two isomers), 1.72 – 1.68 (m, 3H, 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, $^{1}J_{C\text{-}F}$ = 278.4 Hz) & 125.10 (q, $^{1}J_{C\text{-}F}$ = 278.4 Hz) (two isomers), 119.5 & 119.4 (two isomers), 52.72 & 52.70 (two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 31.0 & 30.8 (two isomers), 30.2 & 30.0 (two isomers), 25.8 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) (two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.88 (s, one isomer), -64.94 (s, one isomer).The reported data was in accordance with literature. [11]

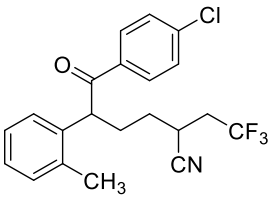


(4-chlorophenyl)-6-oxo-5-(m-tolyl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4x) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (50 mg, 60% yield, *dr* = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.6, 1.7 Hz, 2H, two isomers), 7.38 (d, *J* = 8.4 Hz, 2H, two isomers), 7.24 (t, *J* = 7.8 Hz, 1H, two isomers), 7.07 (d, *J* = 8.0 Hz, 3H, two isomers), 4.46 (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, 2H, two isomers), ^{13}C NMR (101 MHz,

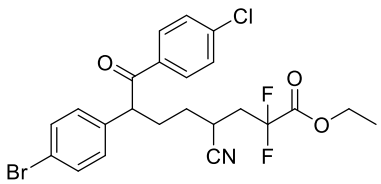
$CDCl_3$) δ 197.58 & 197.51 (two isomers), 139.72 & 139.70 (two isomers), 139.37 (overlap, two isomers), 138.24 & 138.18 (two isomers), 134.66 & 134.64 (two isomers), 130.3 (overlap, two isomers), 129.4 (overlap, two isomers), 128.7 (overlap, two isomers), 128.6 (overlap, two isomers), 128.56 & 128.54 (two isomers), 125.27 & 125.21 (two isomers), 125.10 (q, $^1J_{C\text{-}F}$ = 278.2 Hz) & 125.07 (q, $^1J_{C\text{-}F}$ = 278.3 Hz) (two isomers), 119.6 & 119.5 (two isomers), 53.26 & 53.23(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), 30.14 & 30.11 (two isomers), 25.8 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) & 25.7 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) (two isomers), 21.5 (overlap, two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.93 (s, one isomer), -64.97(s, one isomer).The reported data was in accordance with literature. [11]



(2-chlorophenyl)-6-(4-chlorophenyl)-6-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (4y) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (53.6 mg, 67% yield, *dr* = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H, two isomers), 7.37 (d, *J* = 7.2 Hz, 1H, two isomers), 7.33 (d, *J* = 6 Hz, 2H, two isomers), 7.17-6.91 (m, 3H, two isomers), 4.95(t, *J* = 6.8 Hz, 1H, two isomers), 2.94 – 2.75 (m, 1H, two isomers), 2.59 – 2.16 (m, 3H, two isomers), 2.11 – 2.43 (m, 3H, two isomers), ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.36 & 197.2 (two isomers), 140.05 & 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), 129.23 & 129.20 (two isomers), 128.7 & 128.6 (two isomers), 128.10 & 128.08 (two isomers), 125.17 (q, $^1J_{C\text{-}F}$ = 278.5 Hz) & 125.14 (q, $^1J_{C\text{-}F}$ = 278.6 Hz) (two isomers), 119.49 & 119.45 (two isomers), 48.8 & 48.7 (two isomers), 36.5 (q, $^2J_{C\text{-}F}$ = 30.3 Hz) & 36.3 (q, $^2J_{C\text{-}F}$ = 30.1 Hz) (two isomers), 30.4 & 30.1 (two isomers), 29.9 & 29.8 (two isomers), 25.8 (q, $^3J_{C\text{-}F}$ = 3.0 Hz) & 25.7 (q, $^3J_{C\text{-}F}$ = 2.9 Hz) (two isomers). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.92 (s, one isomer), -64.97 (s, one isomer). The reported data was in accordance with literature. [11]



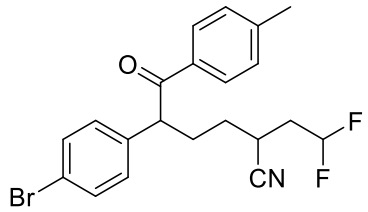
(4-chlorophenyl)-6-oxo-5-(o-tolyl)-2-(2,2,2-trifluoroethyl)hexanenitrile (4z) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a colorless liquid (52 mg, 67% yield, *dr* = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H, two isomers), 7.35 (d, *J* = 8.5 Hz, 2H, two isomers), 7.32-7.05 (m, 3H, two isomers), 6.95 (ddd, *J* = 7.6, 3.7, 1.5 Hz, 1H, two isomers), 4.70 – 4.59 (m, 1H, two isomers), 2.92 – 2.84 (m, 1H, two isomers), 2.61-2.24 (m, 5H, two isomers), 2.10 – 1.60(m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3 & 198.2 (two isomers), 139.6 & 139.5 (two isomers), 137.15 (overlap, two isomers), 137.08 (overlap, two isomers), 134.84 & 134.78 (two isomers), 131.6 (overlap, two isomers), 129.94 & 129.93 (two isomers), 129.0 (overlap, two isomers), 127.7 (overlap, two isomers), 127.3 (overlap, two isomers), 127.3 & 127.2 (two isomers), 125.21 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) & 125.16 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz) (two isomers), 119.7 & 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), 26.0 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) & 25.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) (two isomers), 19.88 & 19.86(two isomers). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). The reported data was in accordance with literature. [11]



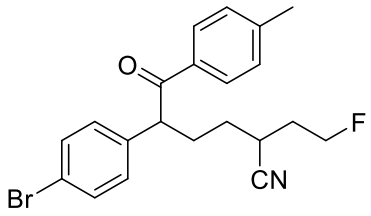
Ethyl-7-(4-bromophenyl)-8-(4-chlorophenyl)-4-cyano-2,2-difluoro-8-oxooctanoate (4aa) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (59 mg, 58% yield, dr =1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.6, 1.8 Hz, 2H, two isomers), 7.47 (d, *J* = 8.3 Hz, 2H, two isomers), 7.39 (d, *J* = 8.4 Hz, 2H, two isomers), 7.21-7.11 (m, 2H, two isomers), 4.49 (t, *J* = 7.2 Hz, 1H, two isomers), 4.43 – 4.31 (m, 2H, two isomers), 2.98 – 2.84 (m, 1H, two isomers), 2.72 – 1.91(m, 1H, two isomers), 1.79-1.68(m, 5H, two isomers) 1.34 (m, 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), 140.03 & 140.02 (two isomers), 137.36 & 137.30 (two isomers), 134.40 & 134.39 (two isomers), 132.7 (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), 114.4 (t, $^1J_{C\text{-}F}$ = 254.1 Hz) (overlap, two isomers), 63.8 (overlap, two isomers), 52.6 (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 & 30.8 (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 (282 MHz, $CDCl_3$) δ -104.3 (d, *J* = 36.8 Hz, one isomer), -104.71 (d, *J* = 36.1 Hz, one isomer), -105.72 (d, *J* = 15.3 Hz, one isomer), -106.45 (d, *J* = 14.6 Hz, one isomer). The reported data was in accordance with literature. [11]

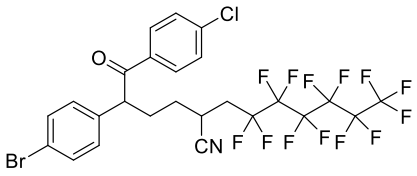
5-(4-bromophenyl)-2-(2,2-difluoroethyl)-6-oxo-6-(p-tolyl)hexanenitrile (4ab) The



title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (41 mg, 50% yield, *dr* =1:1). ^{1}H NMR (300 MHz, 5$CDCl_3$) δ 7.84 (dd, *J* = 8.3, 1.8 Hz, 2H, two isomers), 7.45(d, *J* = 8.4 Hz, 2H, two isomers), 7.25-7.14 (m, 4H, two isomers), 6.22-5.77 (m, 1H, two isomers), 4.54 (t, *J* = 7.2 Hz, 1H, two isomers), 2.90-2.71 (m, 1H, two isomers), 2.47 – 1.92 (m, 5H, two isomers),1.81-1.52 (m, 2H, two isomers), ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8 (two isomers), 144.4 (two isomers),137.8 (overlap, two isomers), 133.50&133.47 (overlap, two isomers), 132.3 (overlap, two isomers), 129.74&129.69 (overlap, two isomers), 129.4 (two isomers), 128.8 (overlap, two isomers), 121.53(overlap, two isomers), 114.7 ($^1J_{C\text{-}F}$ = 232 Hz, two isomers), 52.1 (overlap, two isomers), 36.3 (overlap, two isomers), 31.0 (q, $^2J_{C\text{-}F}$ = 27 Hz) 25.3 (two isomers). 21.6 (overlap, two isomers)^{19}F NMR (282 MHz, $CDCl_3$) δ -115.7 (d, *J* = 49.6 Hz, one isomer), -116.7 (d, *J* = 50.1 Hz, one isomer), -117.1 (d, *J* = 20.4 Hz, one isomer), -118.1 (d, *J* = 20.9 Hz, one isomer). HRMS (ESI) calcd. for $C_{21}H_{21}BrF_2NO$ $[M+H]^+$: 420.0770, 422.0749; found: 420.0750, 422.0660.

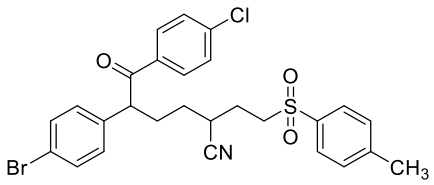


5-(4-bromophenyl)-2-(2-fluoroethyl)-6-oxo-6-(p-tolyl)hexanenitrile(4ac) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid(49 mg, 62% yield, *dr* =1:1) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.3, 1.8 Hz, 2H, two isomers), 7.45 (d, *J* = 8.4 Hz, 2H, two isomers), 7.25-7.14 (m, 4H, two isomers, 4.68 (td, *J* = 5.2, 1.8 Hz, 1H, two isomers), 4.58-4.50 (m, 1H, two isomers), 2.91 – 2.73 (m, 1H, two isomers), 2.47-2.24 (m, 4H, two isomers), 2.15-1.82 (m, 2H, two isomers), 1.77-1.51 (m, 2H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0 (overlap, two isomers) (two isomers), 144.3 (two isomers),137.9 (overlap, two isomers), 133.60 & 133.58 (overlap, two isomers), 132.3 (overlap, two isomers), 129.7 (overlap, two isomers), 129.4 (two isomers), 128.8 & 128.1(overlap, two isomers, 81.5 ($^{1}J_{C\text{-}F}$ = 258 Hz,two isomers) & 79.87($^{1}J_{C\text{-}F}$ = 258 Hz, two isomers), 52.2 & 52.1(overlap, two isomers), 31.2 (overlap, two isomers), 30.9 (overlap, two isomers), 30.1 ($^{2}J_{C\text{-}F}$ = 36 Hz, two isomers)) & 29.7 ($^{2}J_{C\text{-}F}$ = 36 Hz, two isomers), 28.1(q，$^{3}J_{C\text{-}F}$ = 15 Hz, two isomers)) & 27.9 ($^{3}J_{C\text{-}F}$ = 4Hz, two isomers), 21.6 (overlap, two isomers)^{19}F NMR (282 MHz, $CDCl_3$) δ 16.0 (s, one isomer), 15.8 (s, one isomer). HRMS (ESI) calcd. for $C_{21}H_{22}BrFNO$ $[M+H]^+$:402.0869; found: 402.0851.



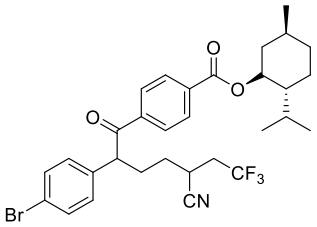
(5-bromophenyl)-4-(4-chlorophenyl)-4-oxobutyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanenitrile (4ad) The title compound was obtained according to the general condition (eluent: petroleum ether / acetone = 20/1, v/v) as a yellow liquid (59.4 mg, 42%yield, dr =1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 & 197.06 (two isomers), 140.15 & 140.13 (two isomers), 137.28 & 137.24 (two isomers), 134.35 & 134.33 (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 (282 MHz, $CDCl_3$) δ -80.8 (t, *J* = 7.3 Hz,), -113.1 – -113.7 (m one isomer), -121.78, (s, isomer), -122.85 (s , isomer), -126.14 (, one isomer). The reported data was in accordance with literature. [11]



7-**(4-bromophenyl)-6-(4-chlorophenyl)-6-oxo-2-(2-tosylethyl)hexanenitrile (4ae)** 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 (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H, two isomers), 7.79 (dd, *J* = 8.3, 2.4 Hz, 2H, two isomers), 7.45 (d, *J* = 8.1 Hz, 2H, two isomers), 7.39 (dd, *J* = 8.0, 5.7 Hz, 4H, two isomers), 7.14 (d, *J* = 8.3 Hz, 2H, two isomers), 4.48 (t, *J* = 7.2 Hz, 1H, two isomers), 3.32 – 3.11 (m, 2H, two isomers), 2.90 – 2.75 (m, 1H, two isomers), 2.48 (s, 3H, two isomers), 2.36 – 1.87 (m, 3H, two isomers), 1.72 – 1.45 (m, 3H, two isomers), ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.21 & 197.19 (two isomers), 145.4 (overlap, two isomers), 140.0 & 139.9 (two isomers), 137.4 (overlap, two isomers), 135.79 & 135.77 (two isomers), 134.38 & 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), 52.42 & 52.38 (two isomers), 31.05 & 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).

The reported data was in accordance with literature. [11]



(1R,2R,5S)-2-isopropyl-5-methylcyclohexyl-4-(2-(4-bromophenyl)-5-cyano-7,7,7-trifluoroheptanoyl)benzoate (4af) 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 (300 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 2H, two isomers), 7.96 (d, J = 8.4 Hz, 2H, two isomers), 7.57-7.41 (m, 2H, two isomers), 7.18-7.13 (m, 2H, two isomers), 4.94 (tdd, J = 10.8, 4.2, 1.8 Hz, 1H, two isomers), 4.55 (t, J = 7.1 Hz, 1H, two isomers), 3.00 – 2.81 (m, 1H, two isomers), 2.58 – 2.45 (m, 2H, two isomers), 2.43 – 2.26 (m, 2H, two isomers), 2.21 – 1.84 (m, 2H, two isomers), 1.85 – 1.48 (m, 2H, two isomers), 1.77 – 1.69 (m, 5H, two isomers), 1.20 – 1.07 (m, 2H, two isomers), 0.92 (t, J = 6.2 Hz, 6H, two isomers), 0.78 (d, J = 6.9 Hz, 3H, two isomers). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 & 197.8 (two isomers), 165.0 (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), 129.85 & 129.81 (two isomers), 128.68 & 128.66 (two isomers), 125.13 (q, $^{1}J_{C\text{-}F}$ = 278.0 Hz) & 125.11 (q, $^{1}J_{C\text{-}F}$ = 278.1 Hz) (two isomers), 122.0 (overlap, two isomers), 119.5 & 119.4 (two isomers), 75.68 (overlap, two isomers), 52.88 & 52.83 (two isomers), 47.32 & 47.31 (two isomers), 41.0 (overlap, two isomers), 36.4 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) & 36.3 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz) (two isomers), 34.3 (overlap, two isomers), 31.6 (overlap, two isomers), 30.58 & 30.54 (two isomers), 30.1 (overlap, two isomers), 29.9 (overlap, two isomers), 26.7 & 26.6 (two isomers), 25.7 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) & 25.6 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz) (two isomers), 23.7 & 23.6 (two isomers), 22.1 (overlap, two isomers), 20.88 & 20.84 (two isomers), 16.63 & 16.60 (two isomers).^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (s, one isomer), -64.9 (s, one isomer). HRMS (ESI) calcd. for $C_{31}H_{36}BrF_3NO_3$ $[M+H]^+$: 606.1826, 608.1805; found: 606.1823, 608.1818.

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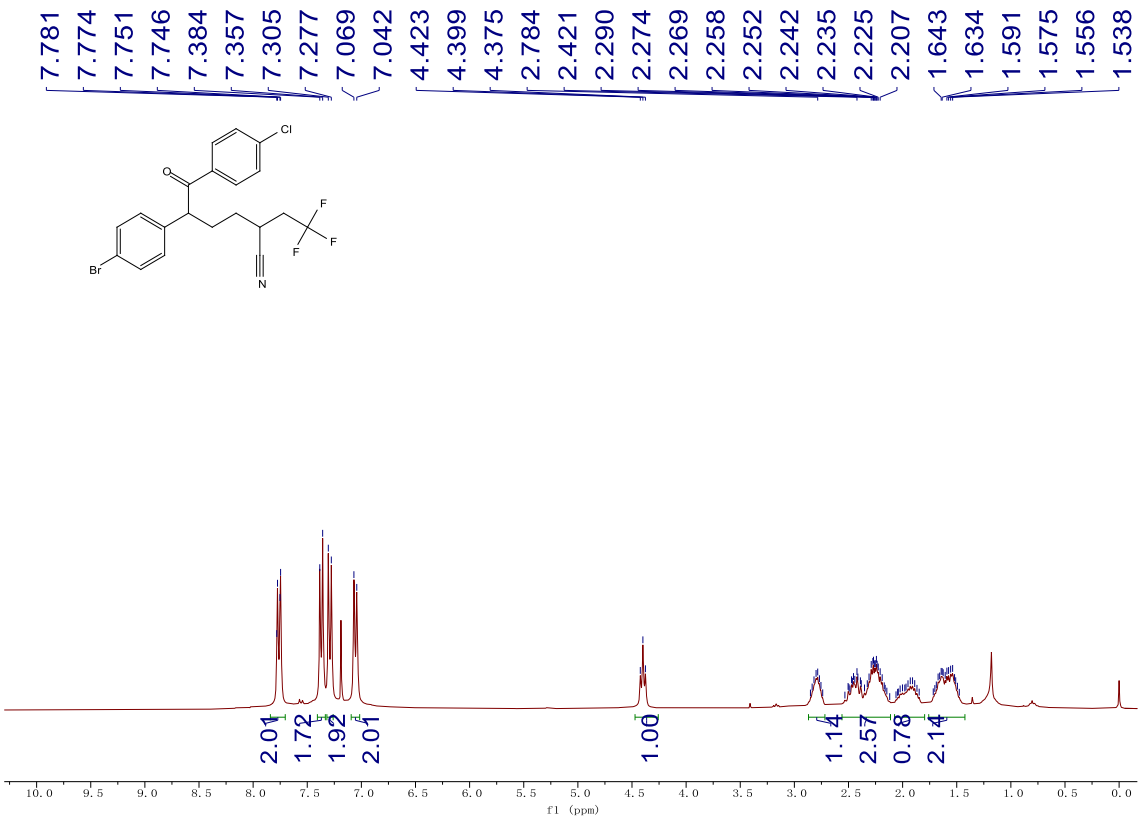
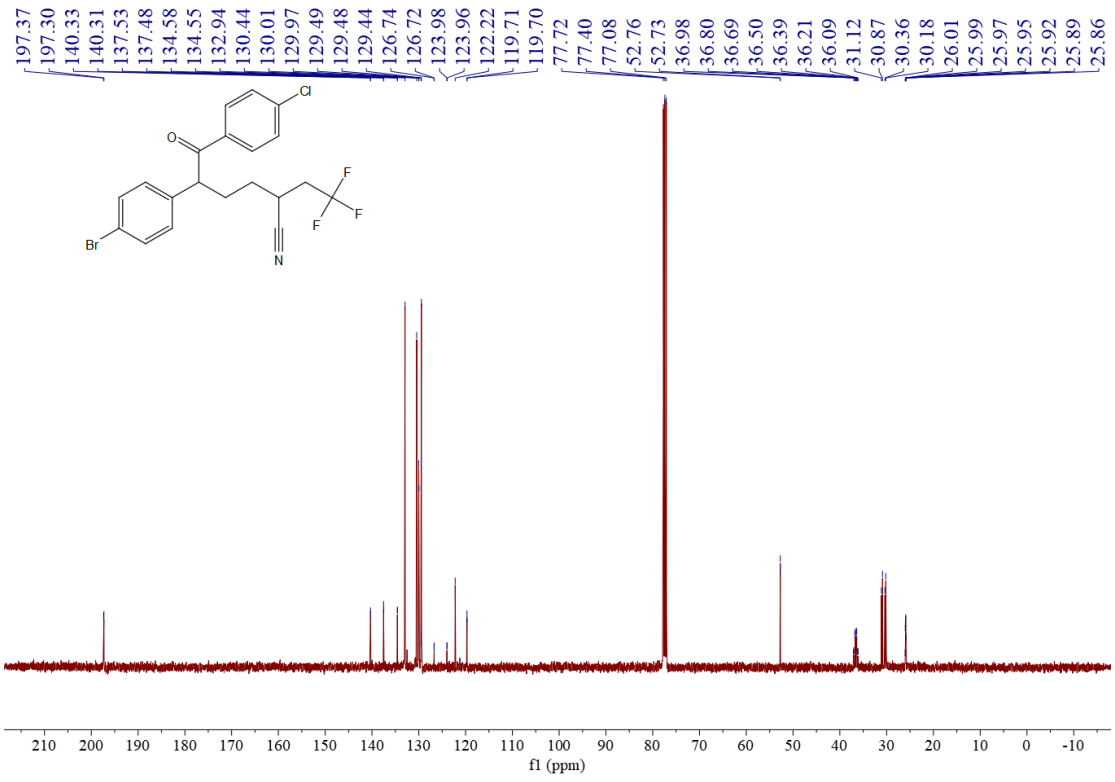
7. Copies of NMR spectra

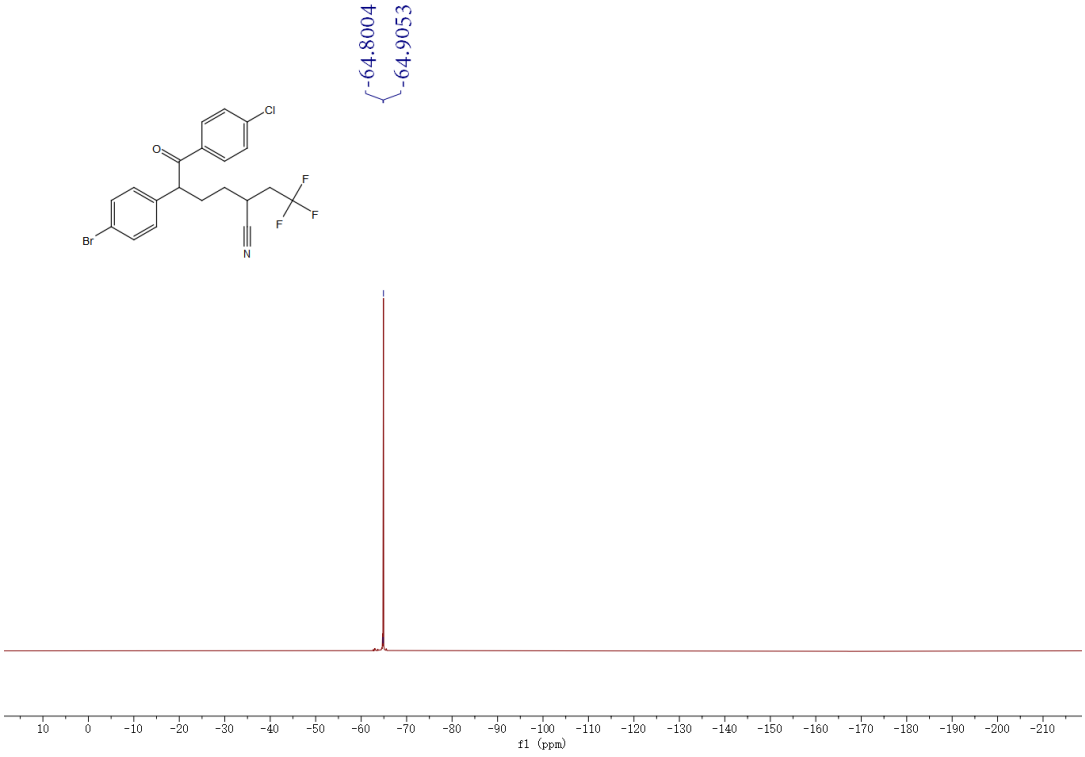
4a ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



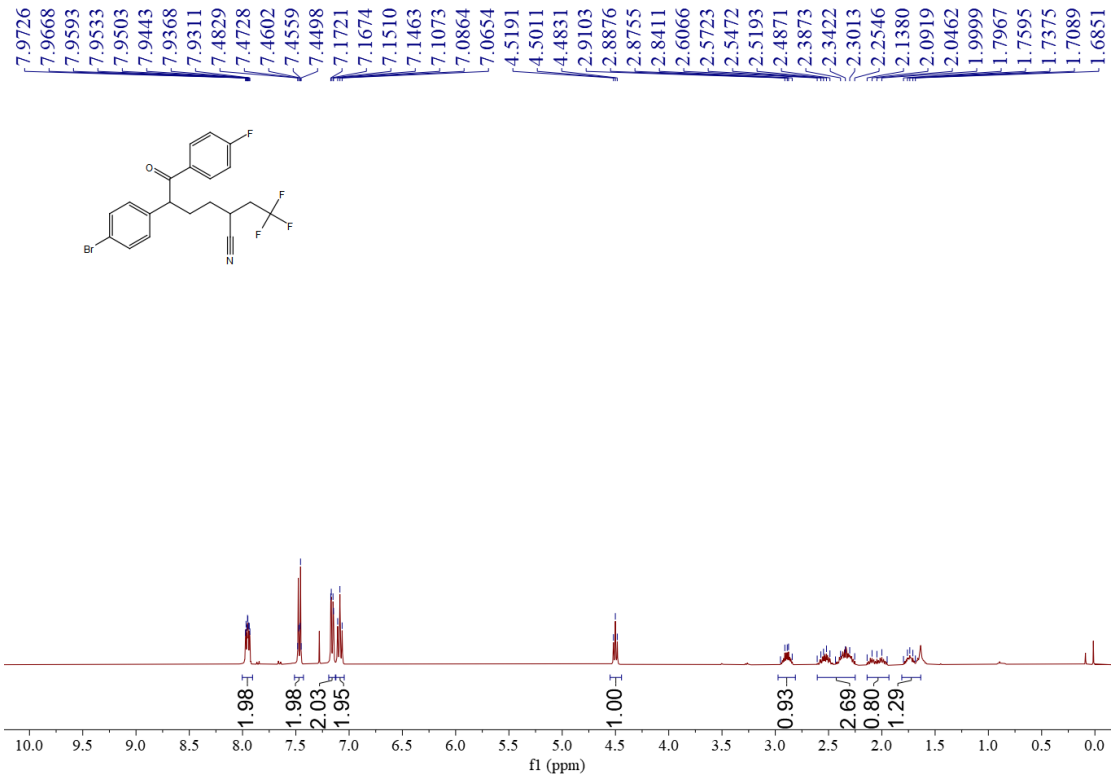
4a ^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



4a ^{19}F NMR (282 MHz, Chloroform-*d*)



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



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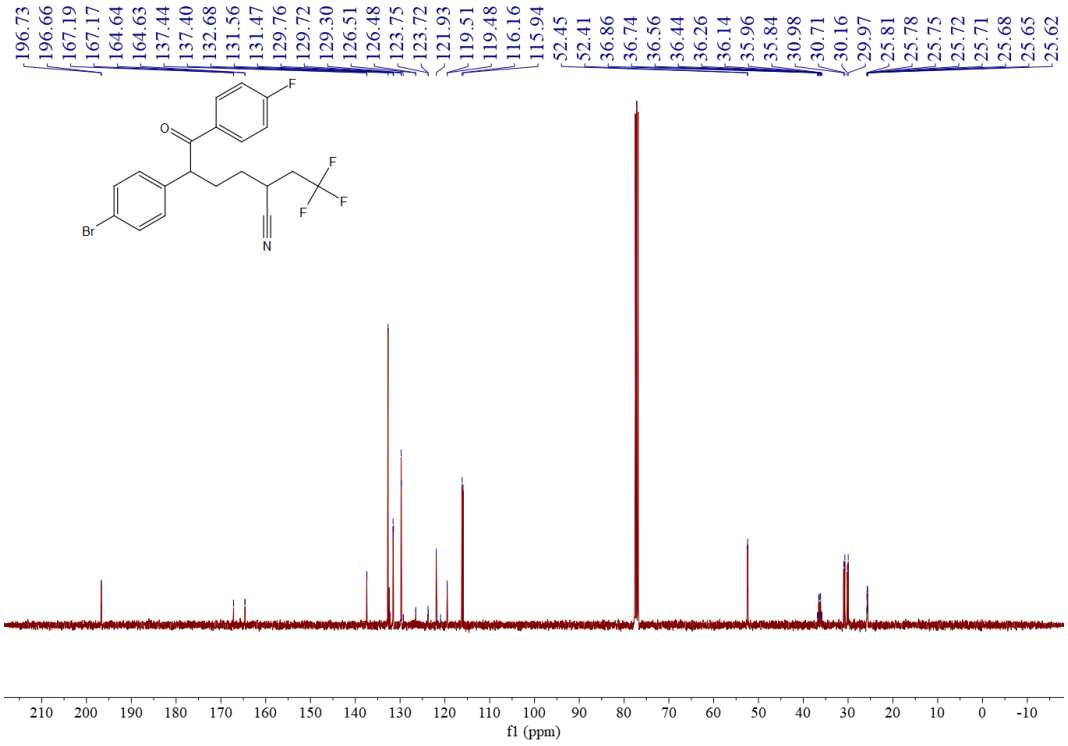

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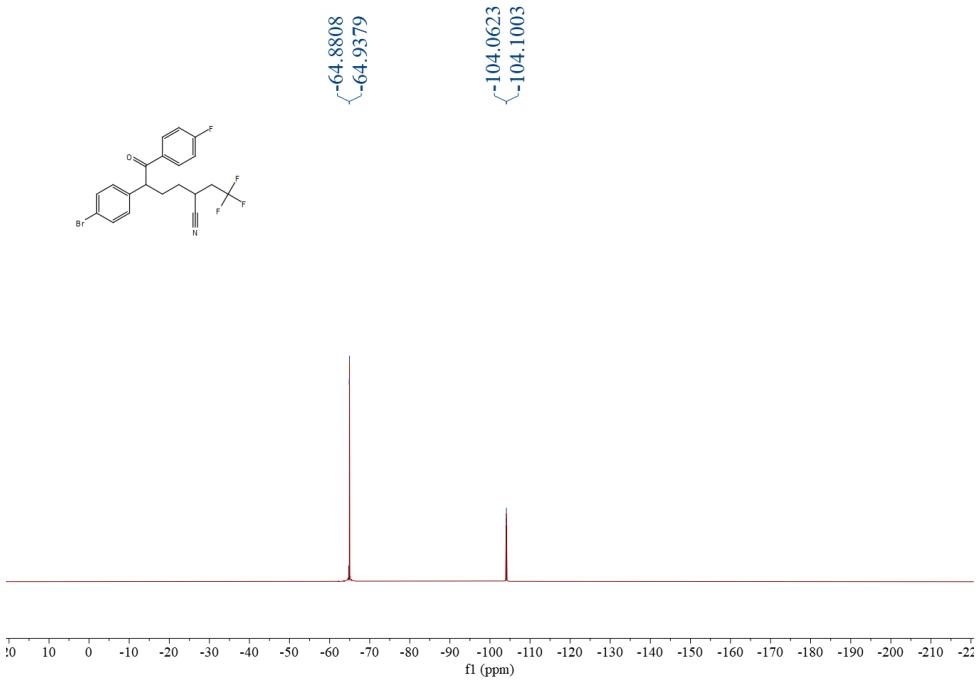
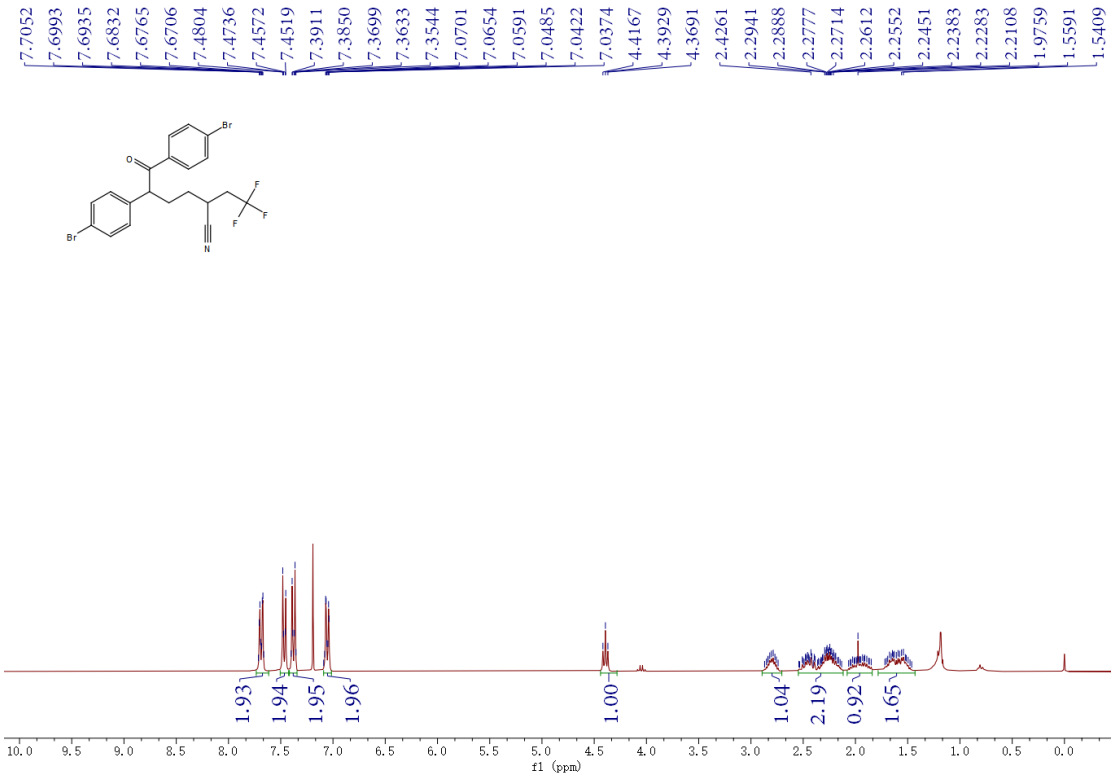
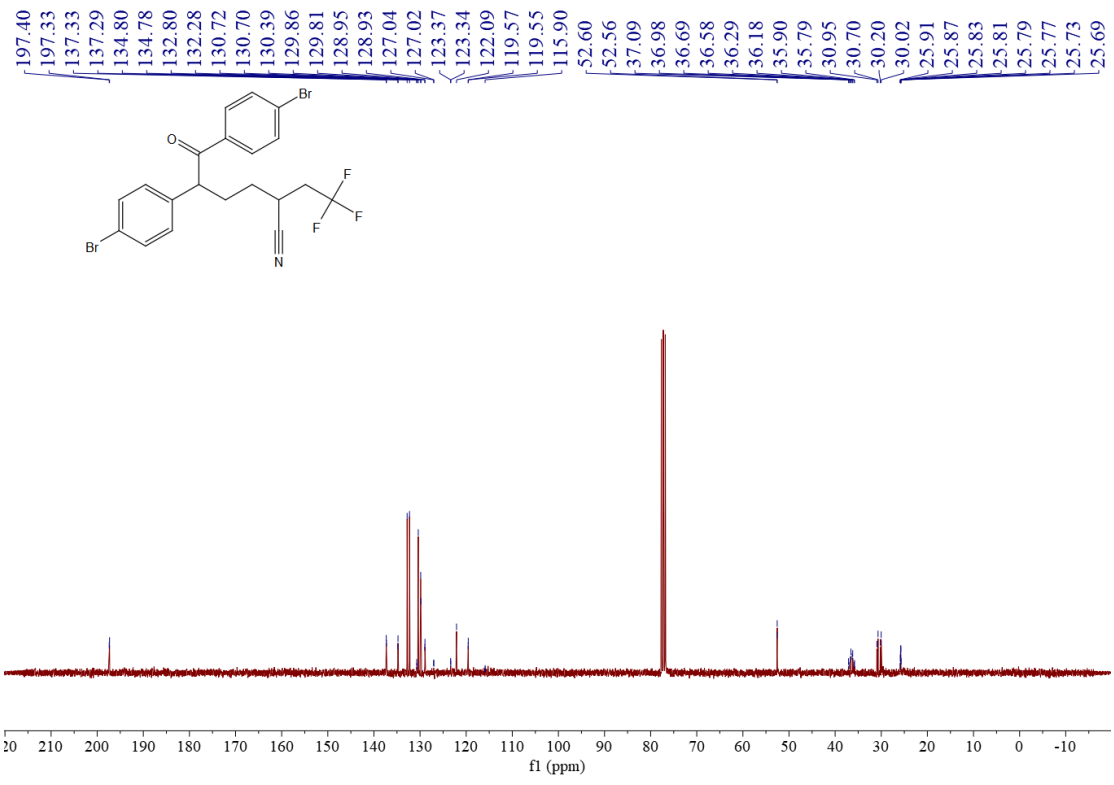


4c ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C {1H}NMR (101 MHz, Chloroform-*d*)



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



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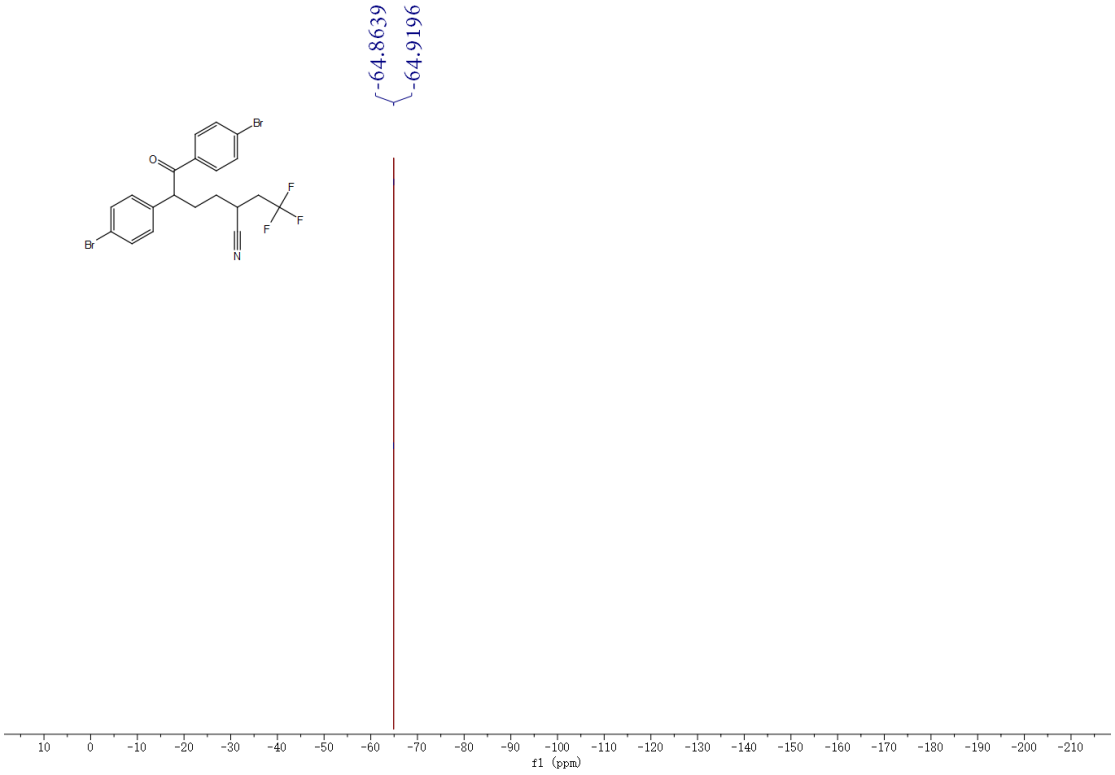
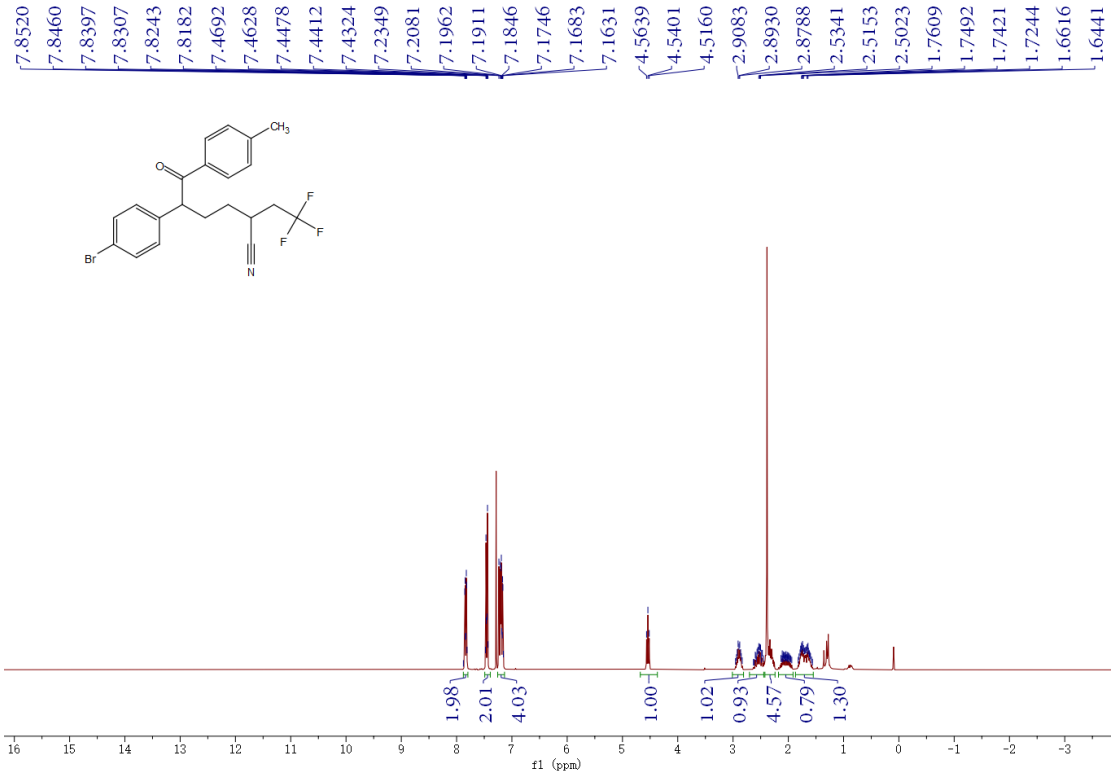
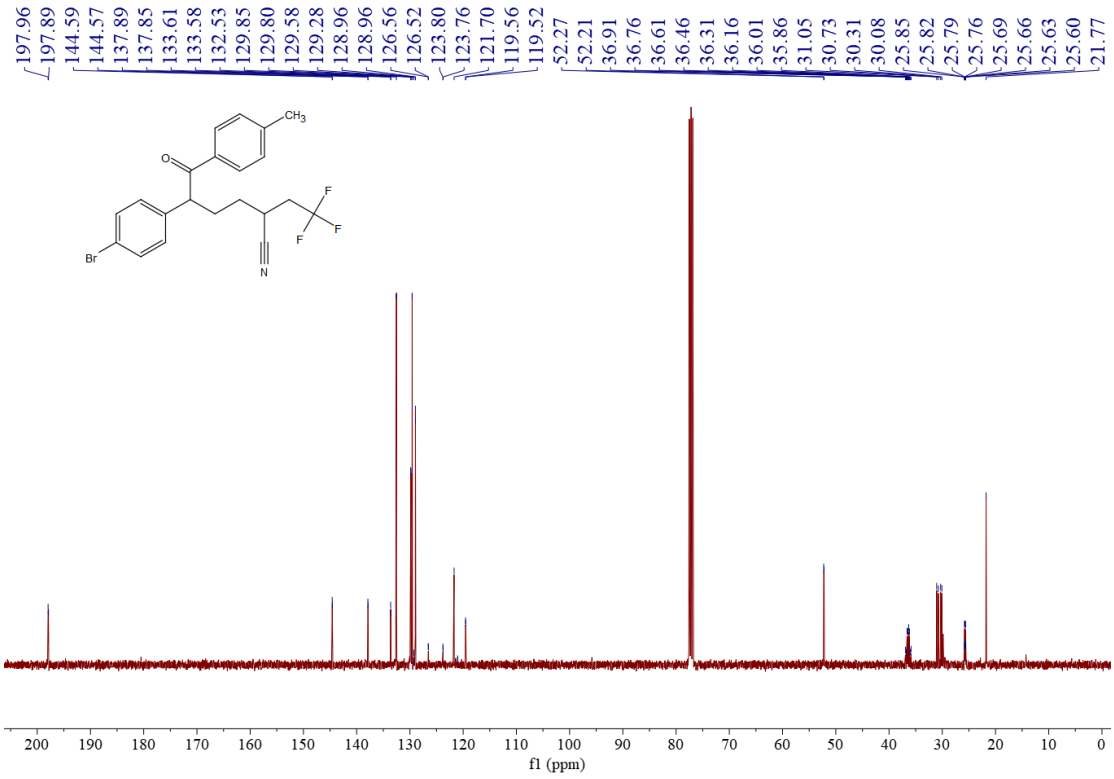


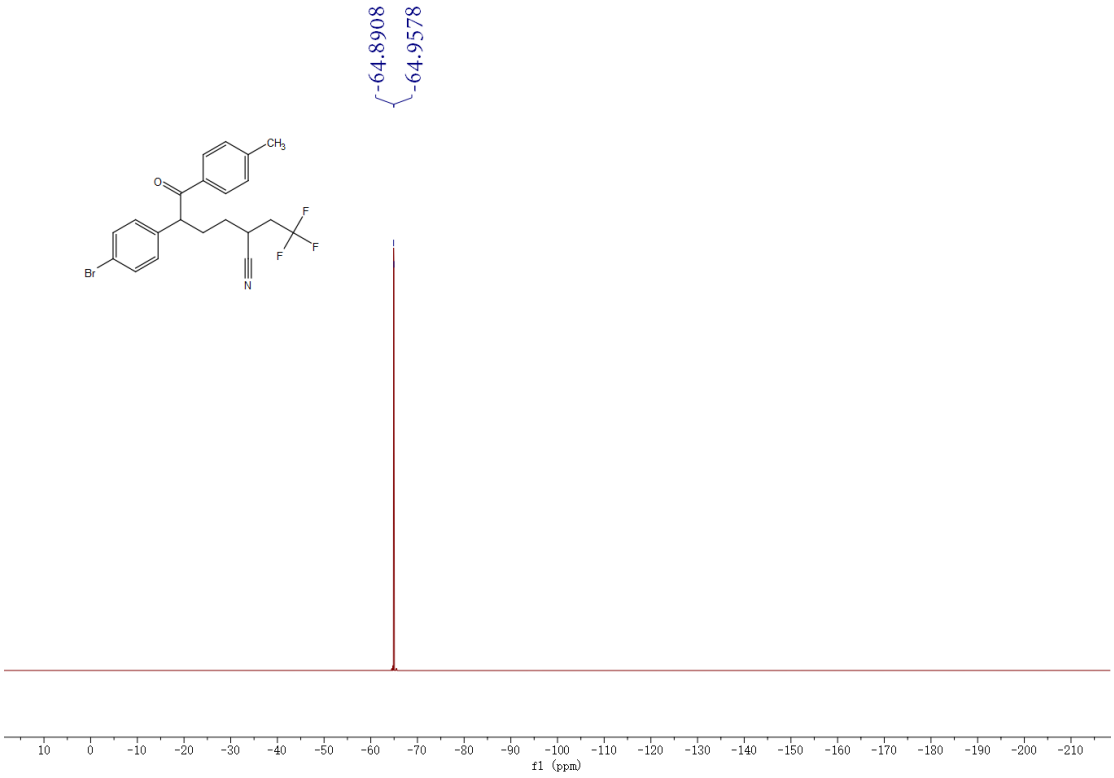
4d ^{1}H NMR (400 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



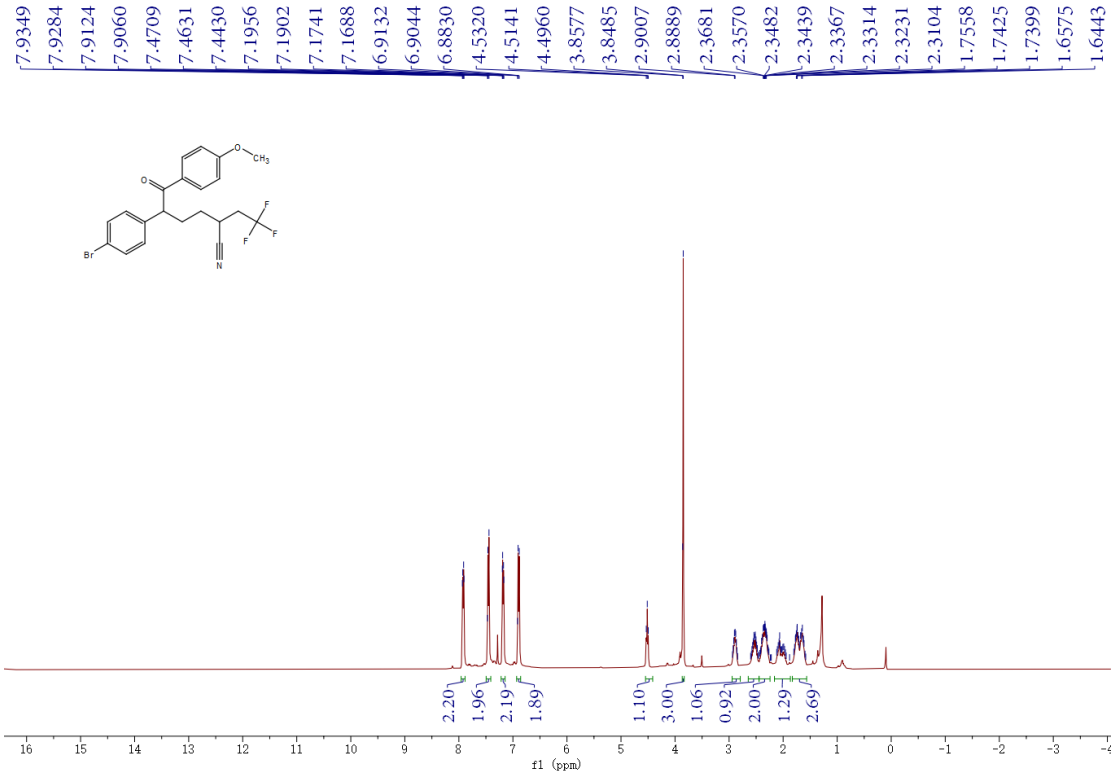
4d ^{13}C NMR (101 MHz, Chloroform-*d*)



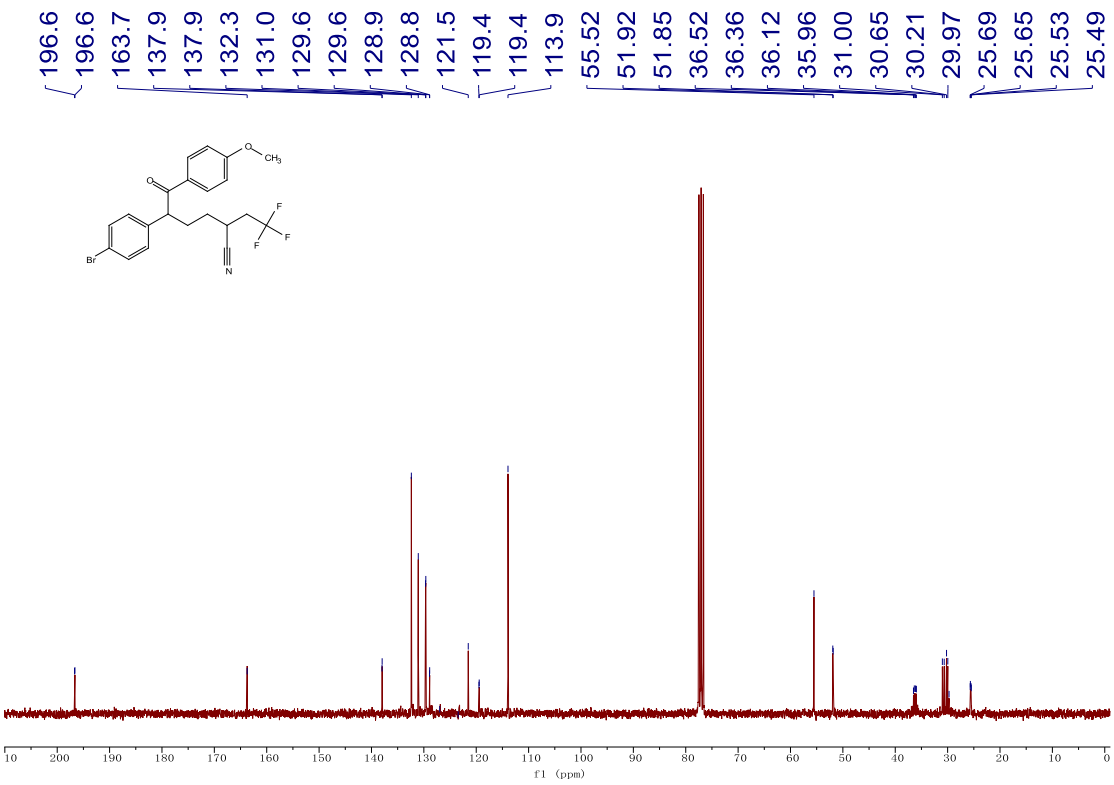
4d ^{19}F NMR (376 MHz, Chloroform-*d*)



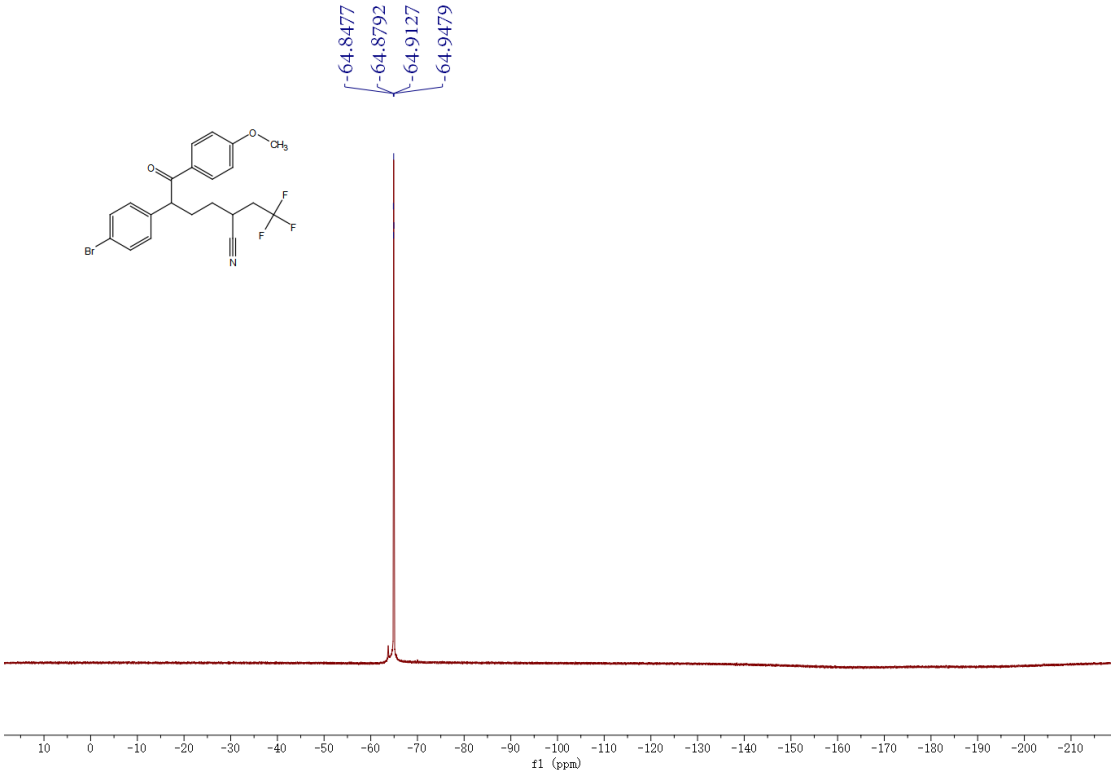
4e ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C {1H}NMR (75 MHz, Chloroform-*d*)



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



4e ^{19}F NMR (282 MHz, Chloroform-*d*)



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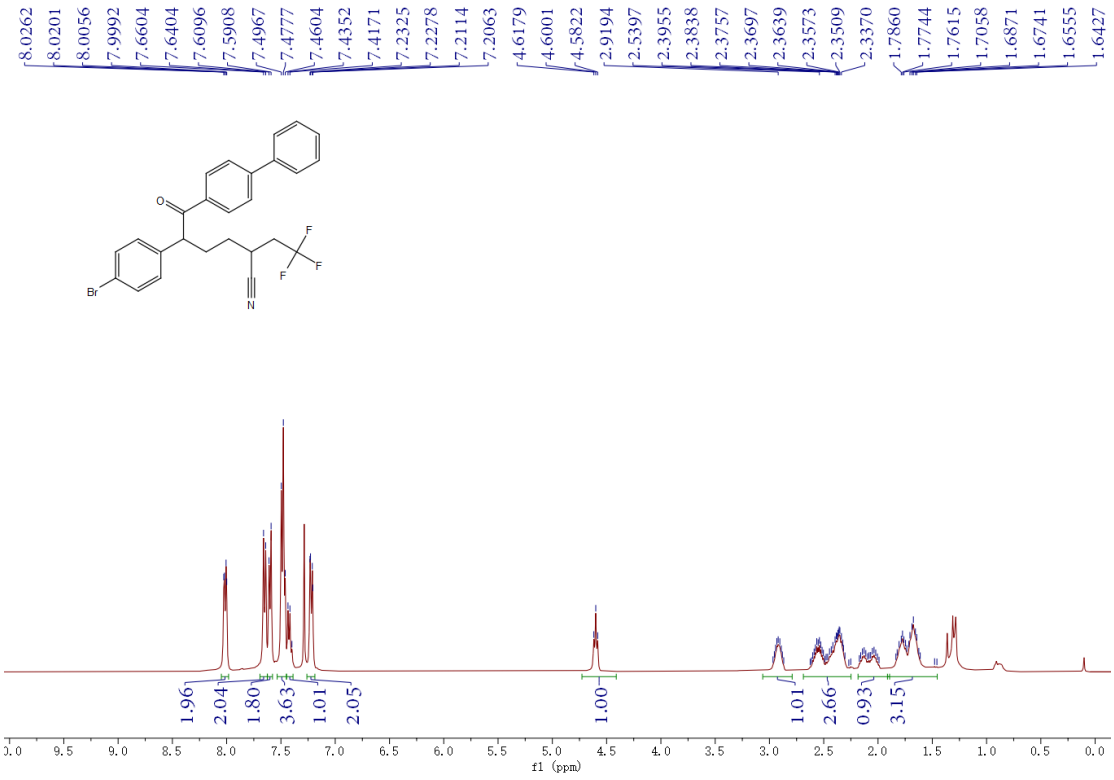
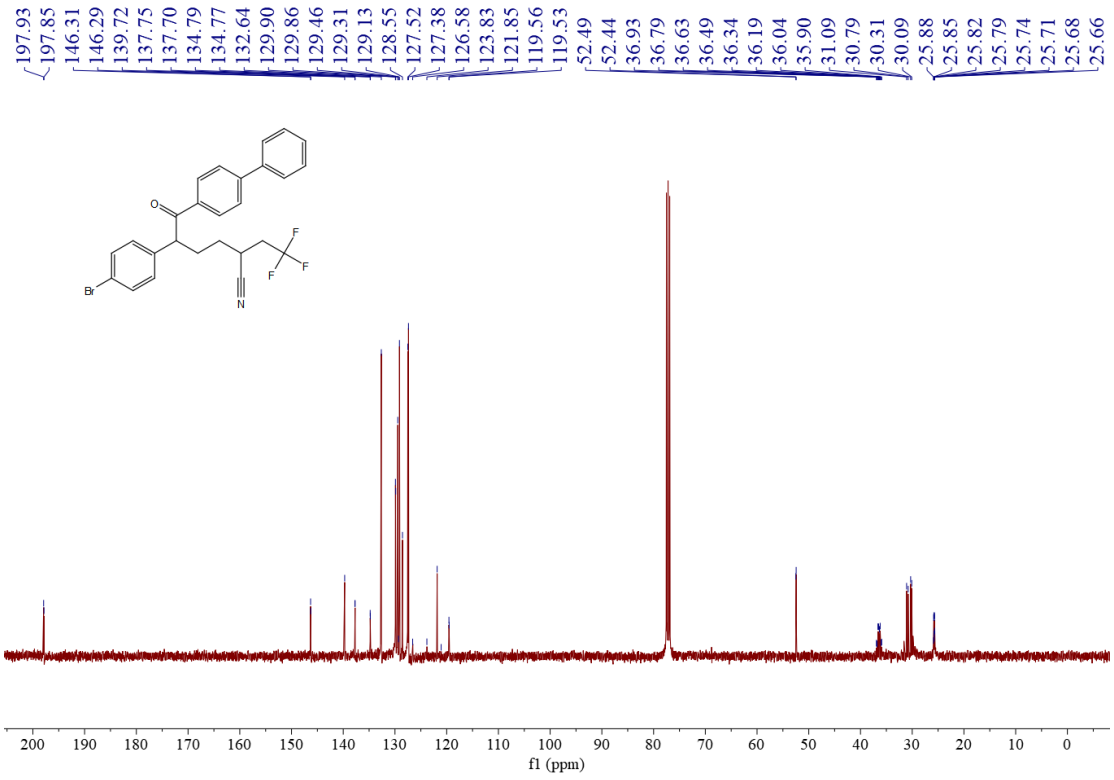
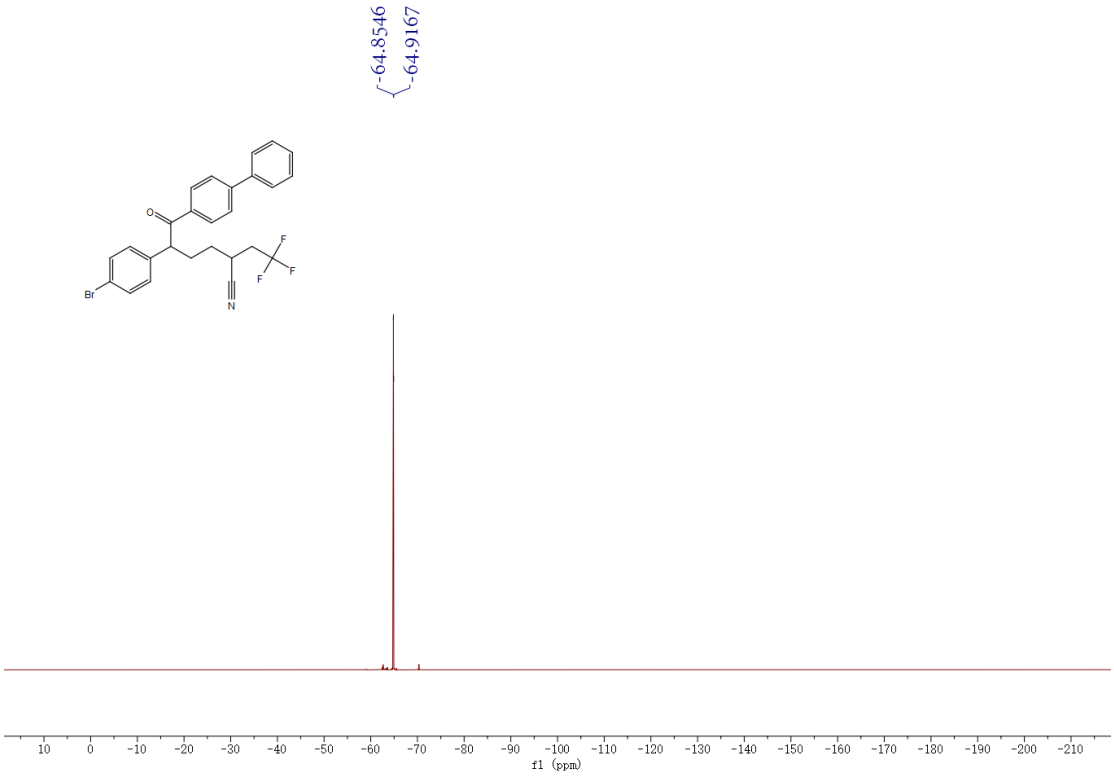


4f ^{13}C NMR (101 MHz, Chloroform-*d*)



4f ^{19}F NMR (282 MHz, Chloroform-*d*)



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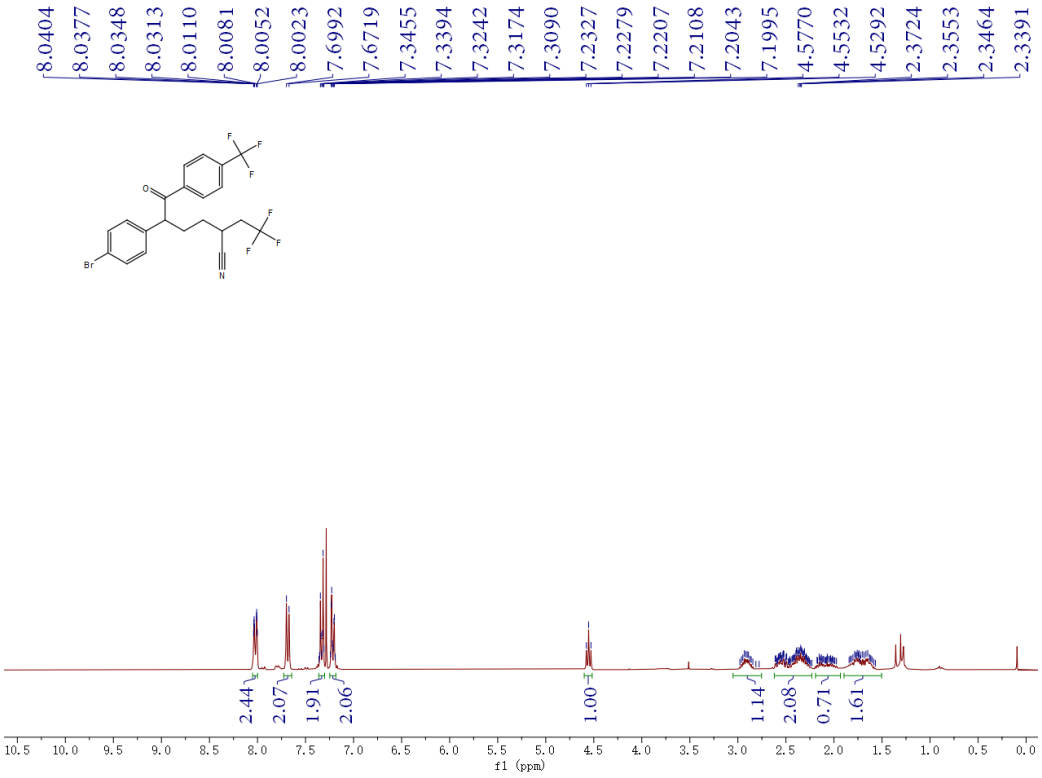
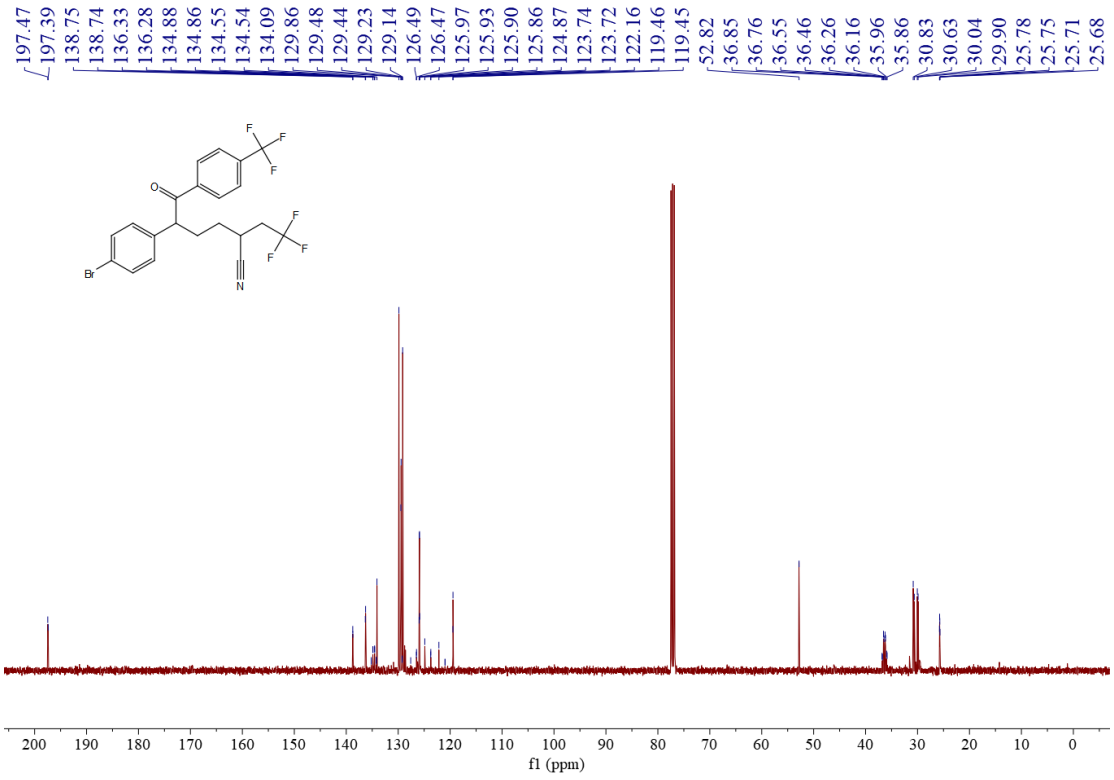
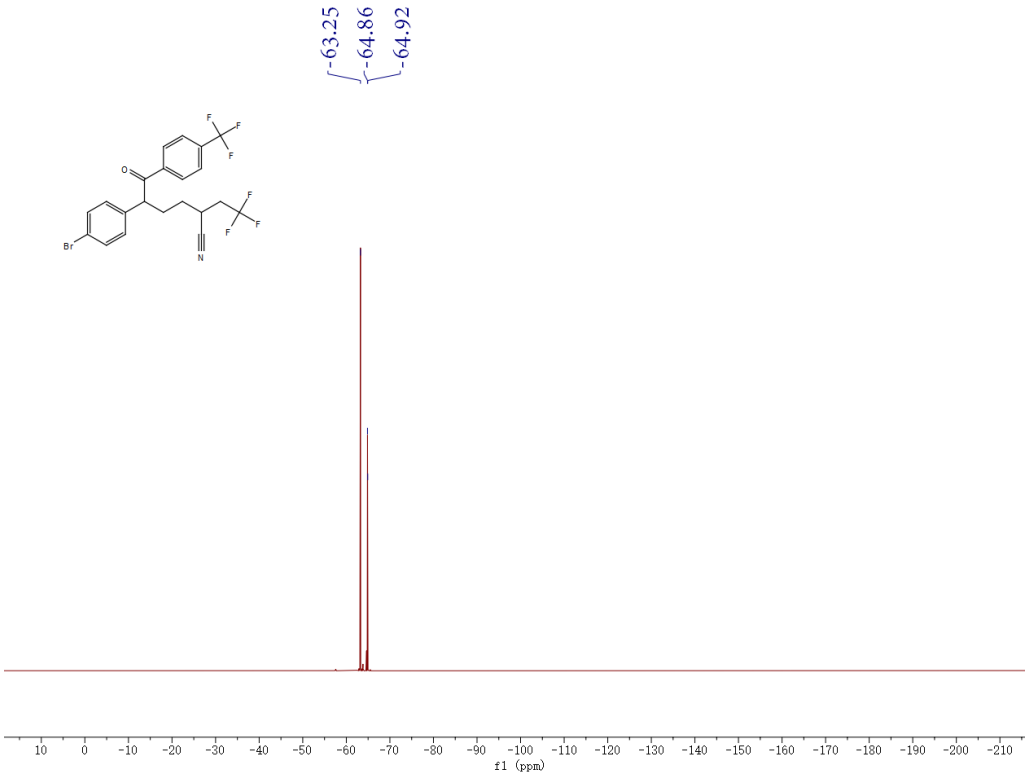


4g ^{13}C NMR (101 MHz, Chloroform-*d*)



4g ^{19}F NMR (282 MHz, Chloroform-*d*)



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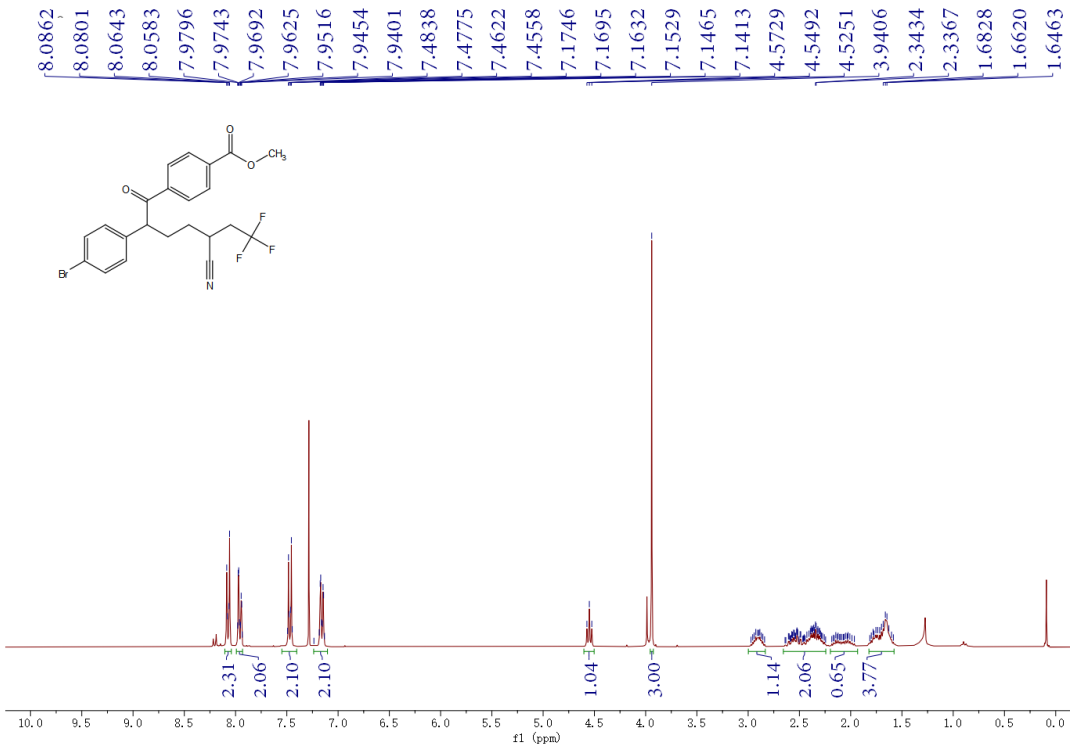
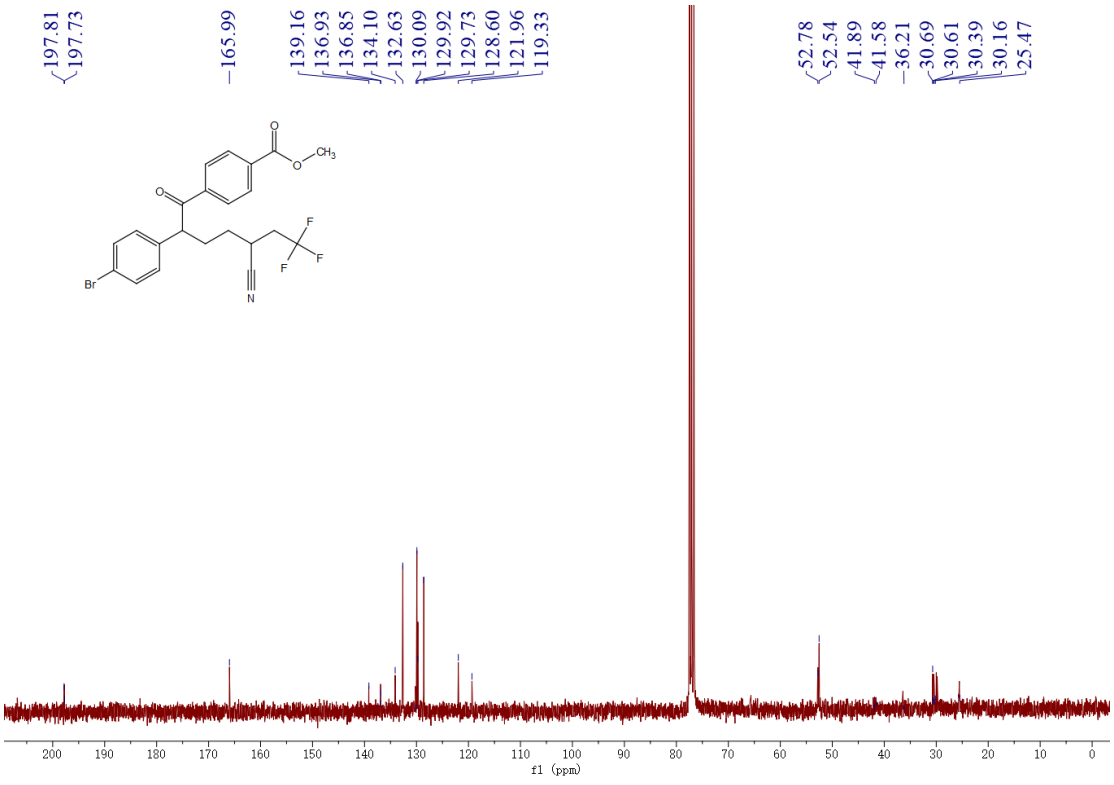
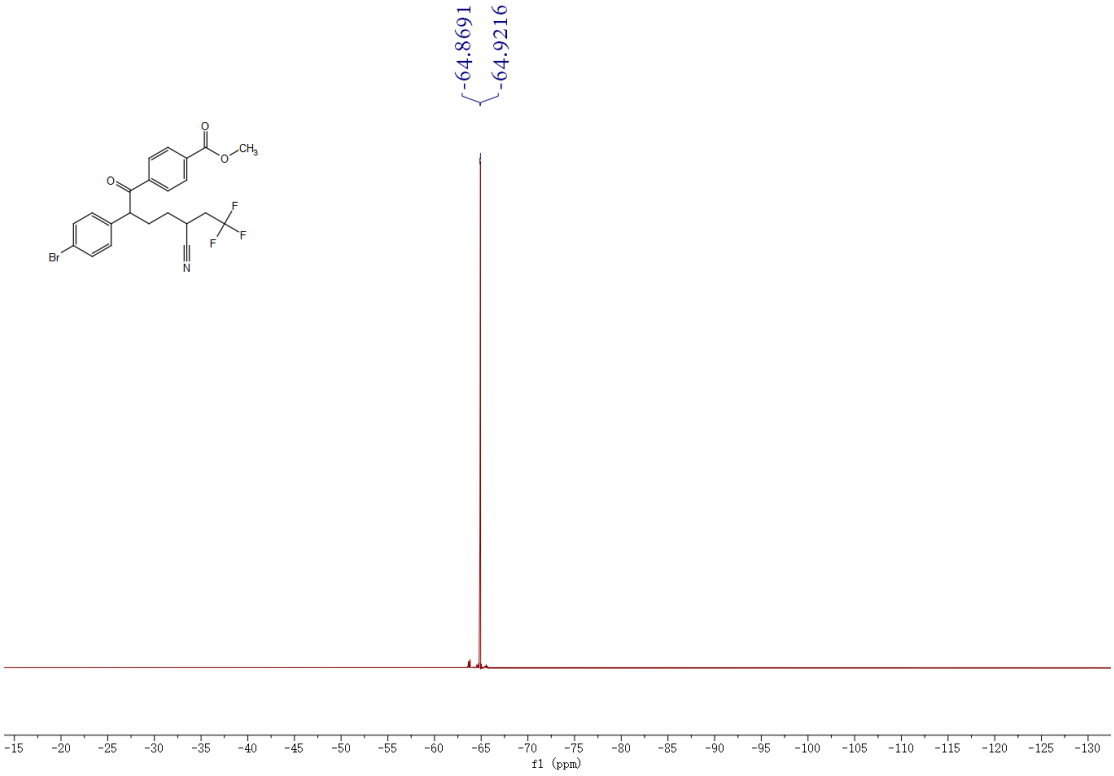


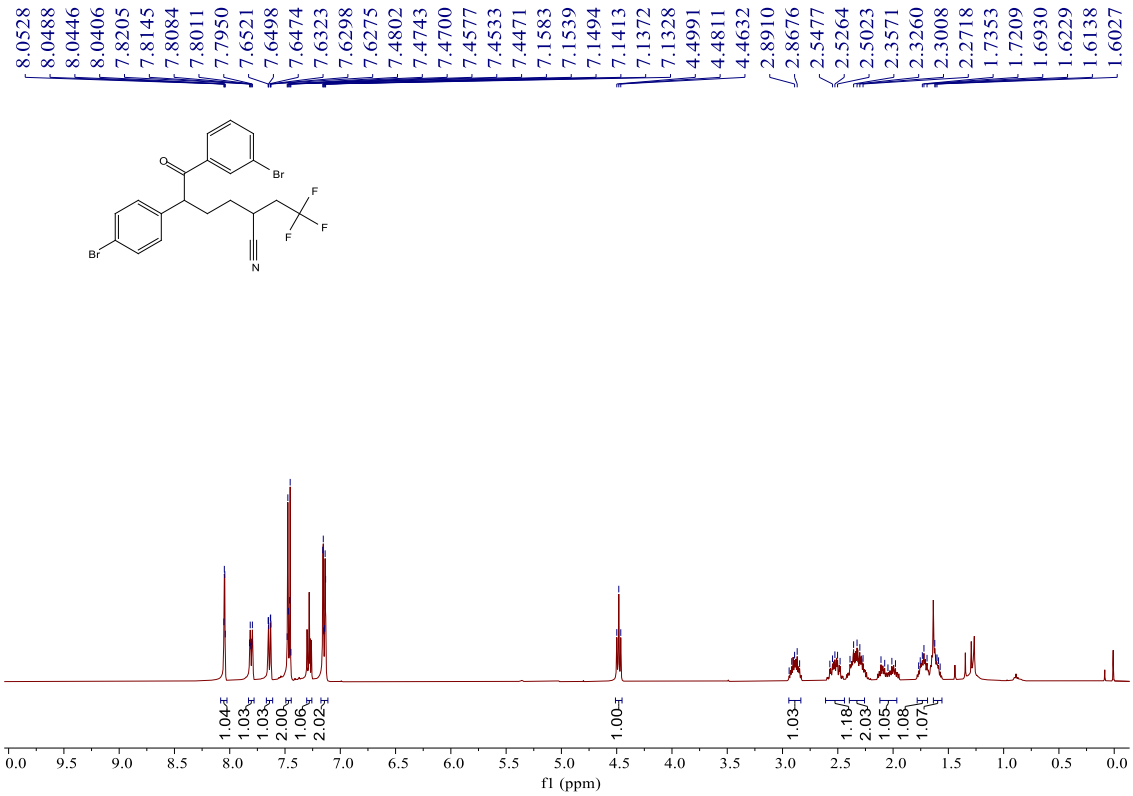
4h ^{13}C NMR(75 MHz，Chloroform-*d*）



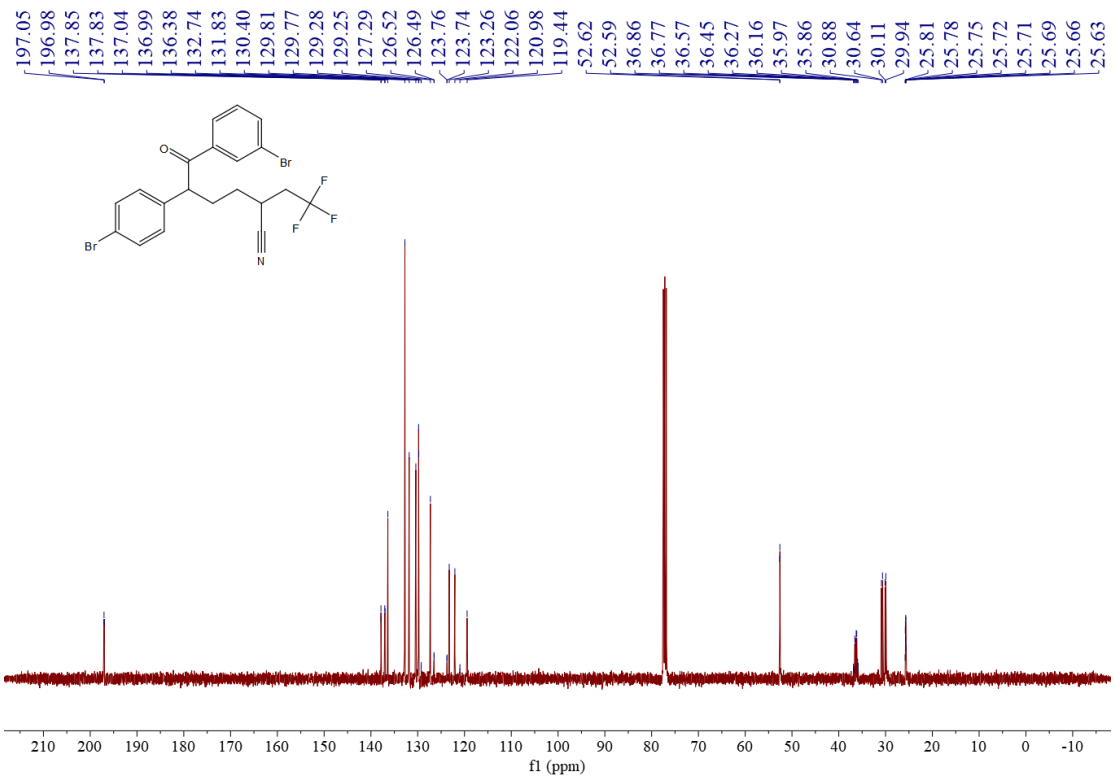
4h ^{19}F NMR (282 MHz, Chloroform-*d*)



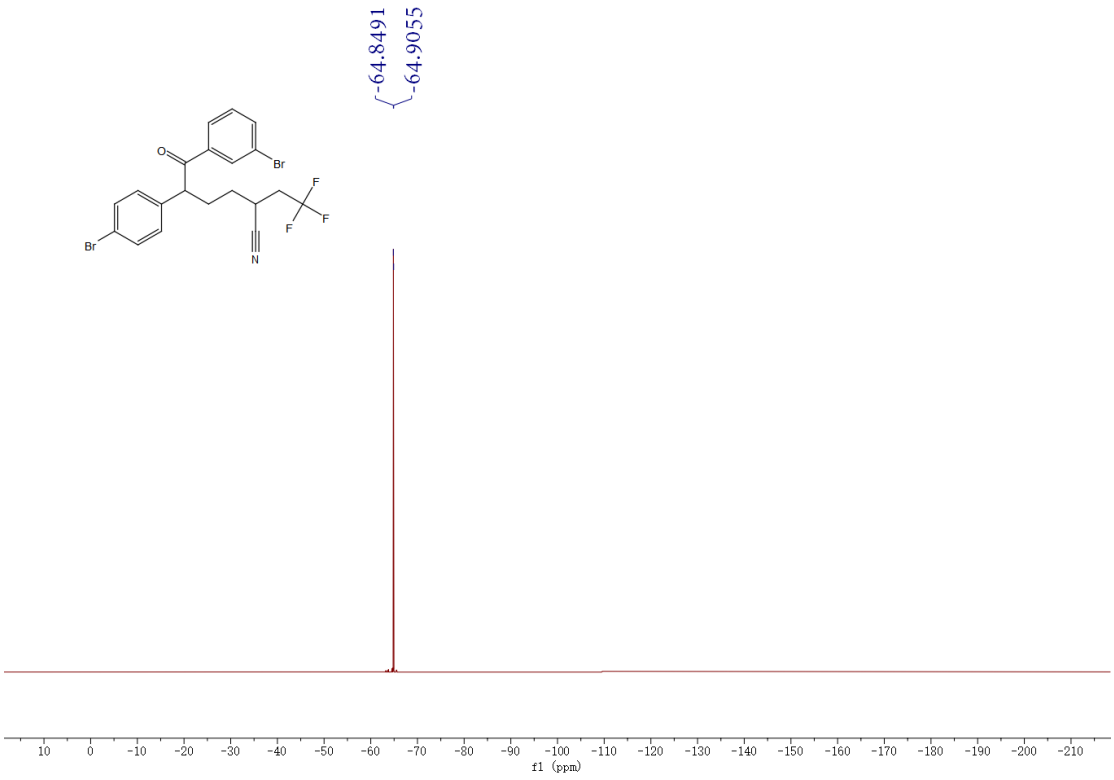
4i ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



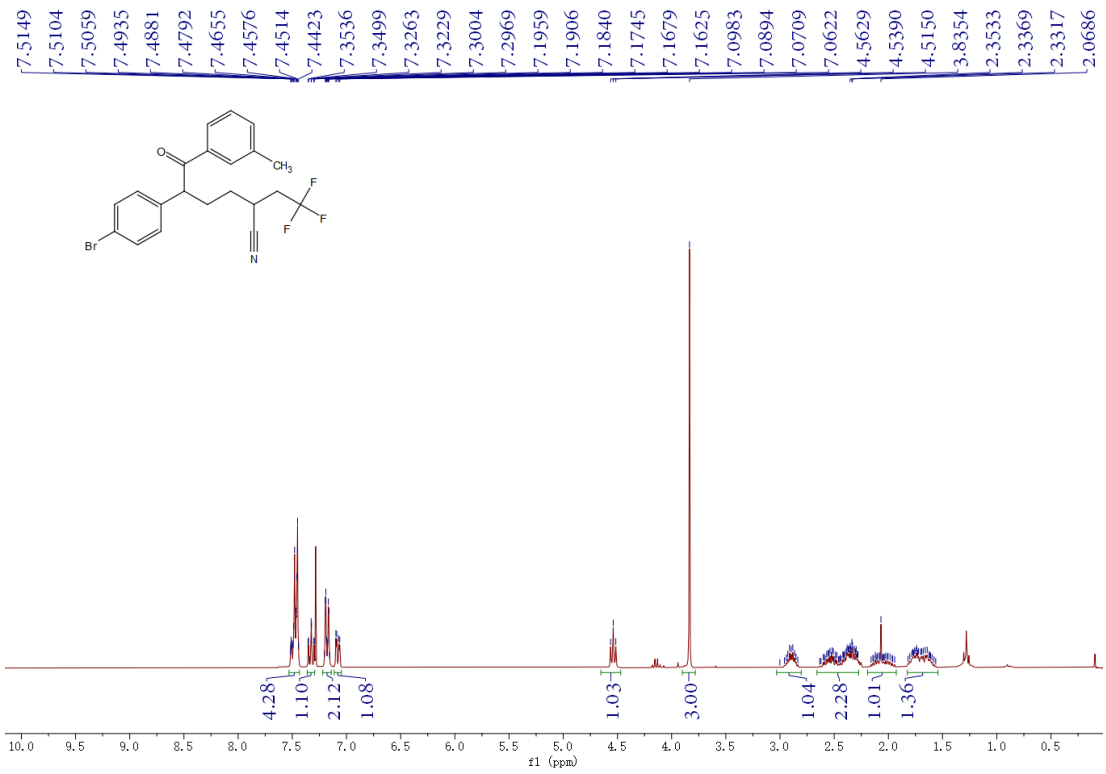
4i ^{13}C NMR (101 MHz, Chloroform-*d*)



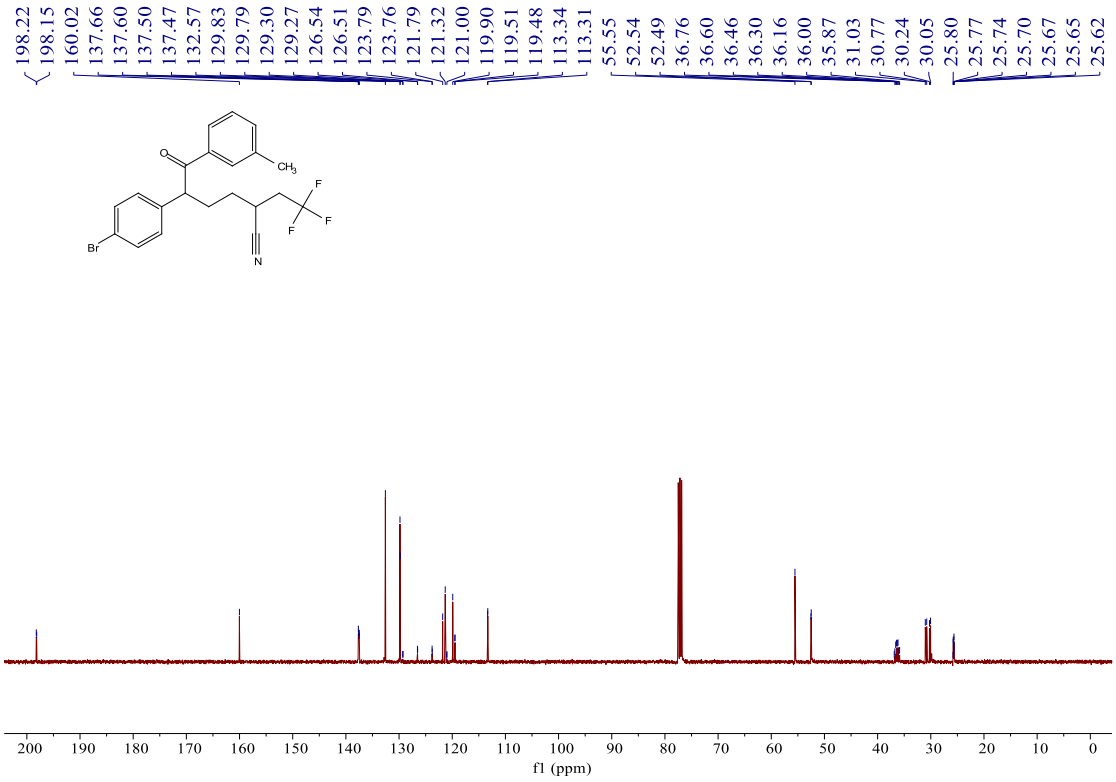
4i ^{19}F NMR (376 MHz, Chloroform-*d*)



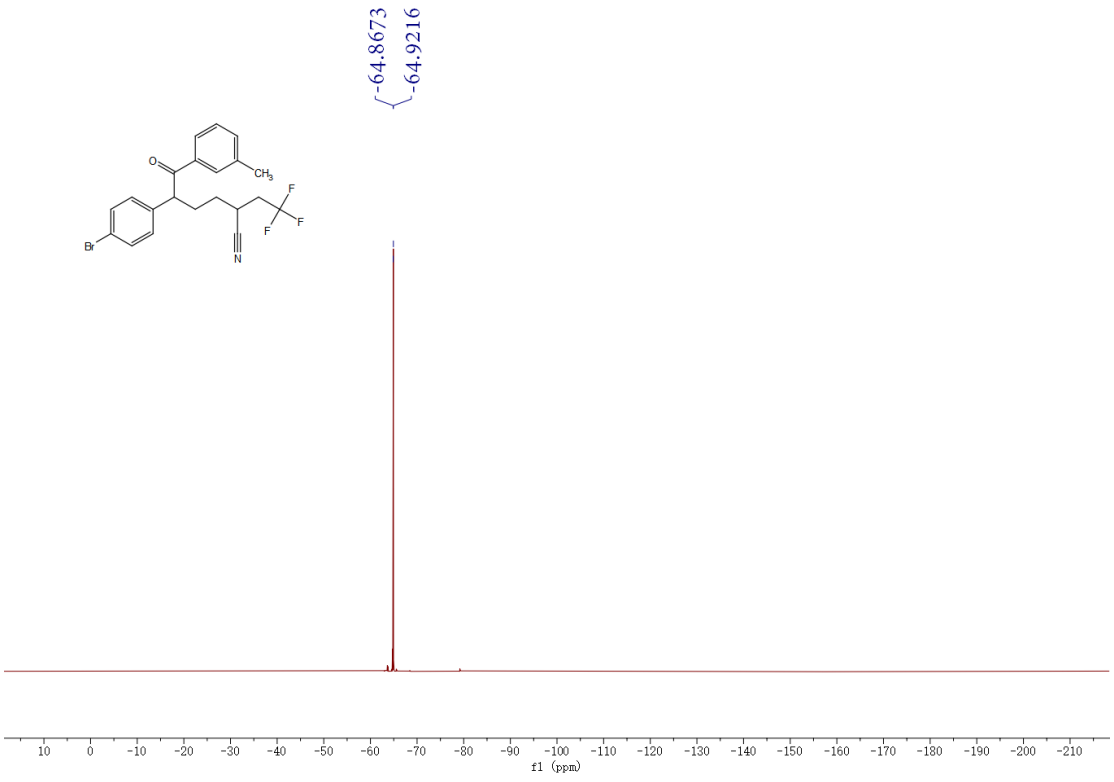
4j ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (101 MHz, Chloroform-*d*)



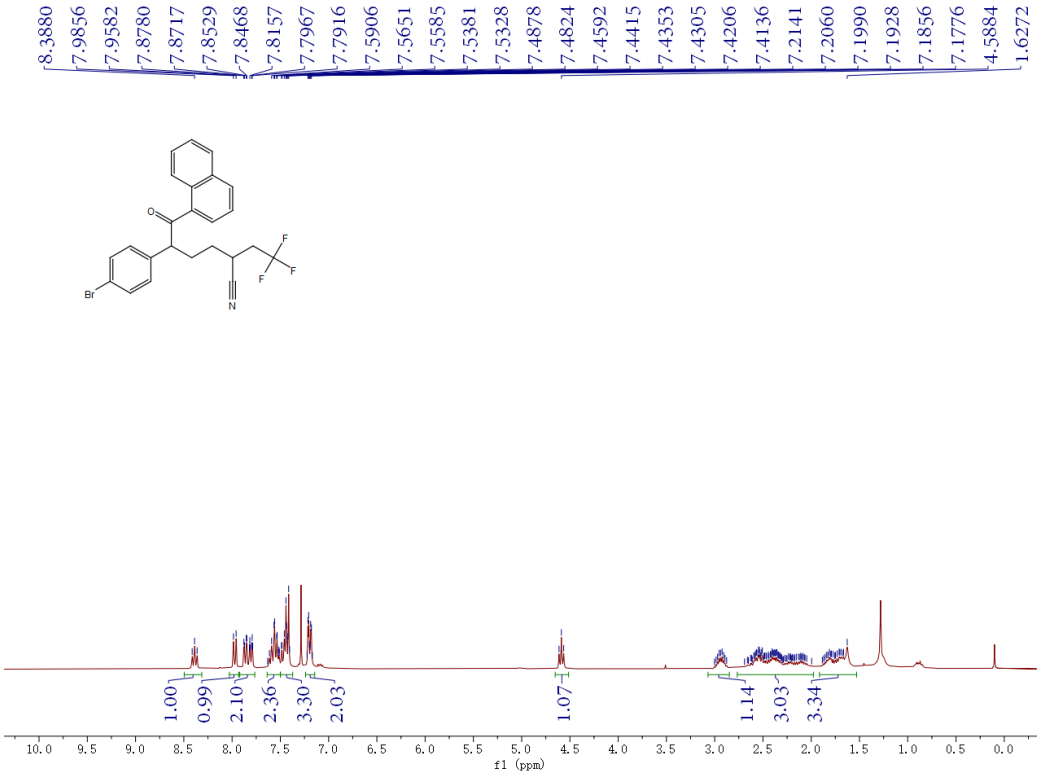
4j ^{13}C NMR (101 MHz, Chloroform-*d*)



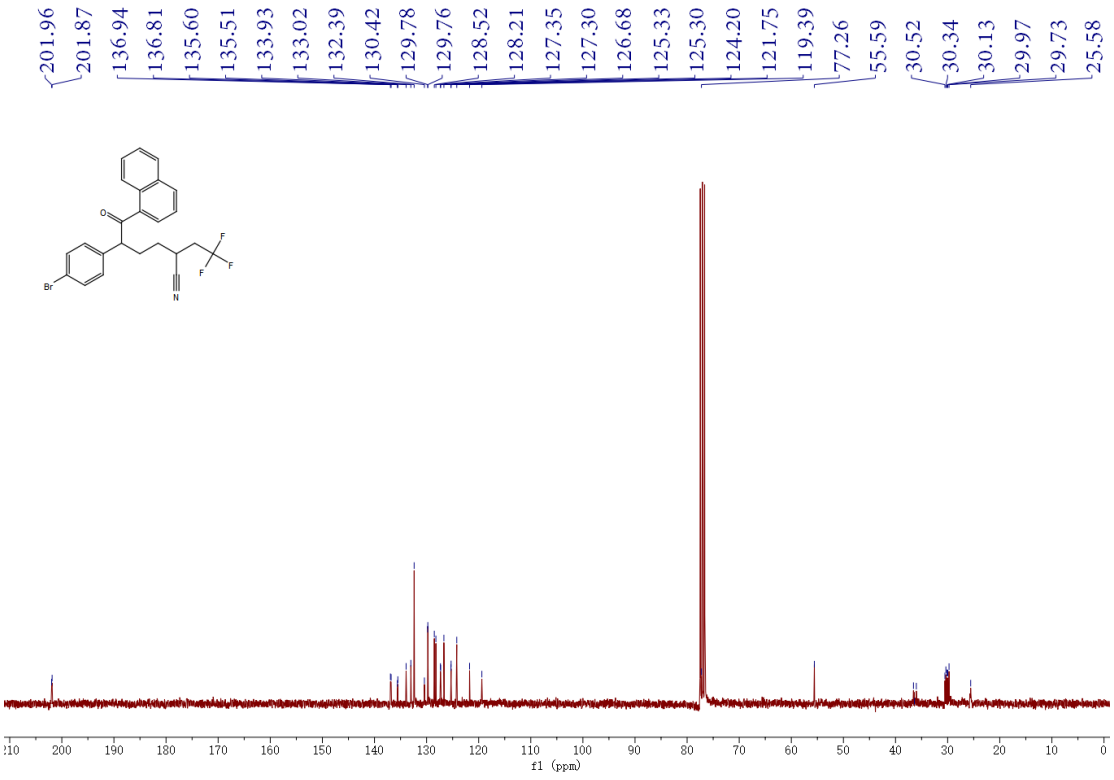
4j ^{19}F NMR (282 MHz, Chloroform-*d*)


-64.8673
-64.9216
O
CH3
F
F
F
Br
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

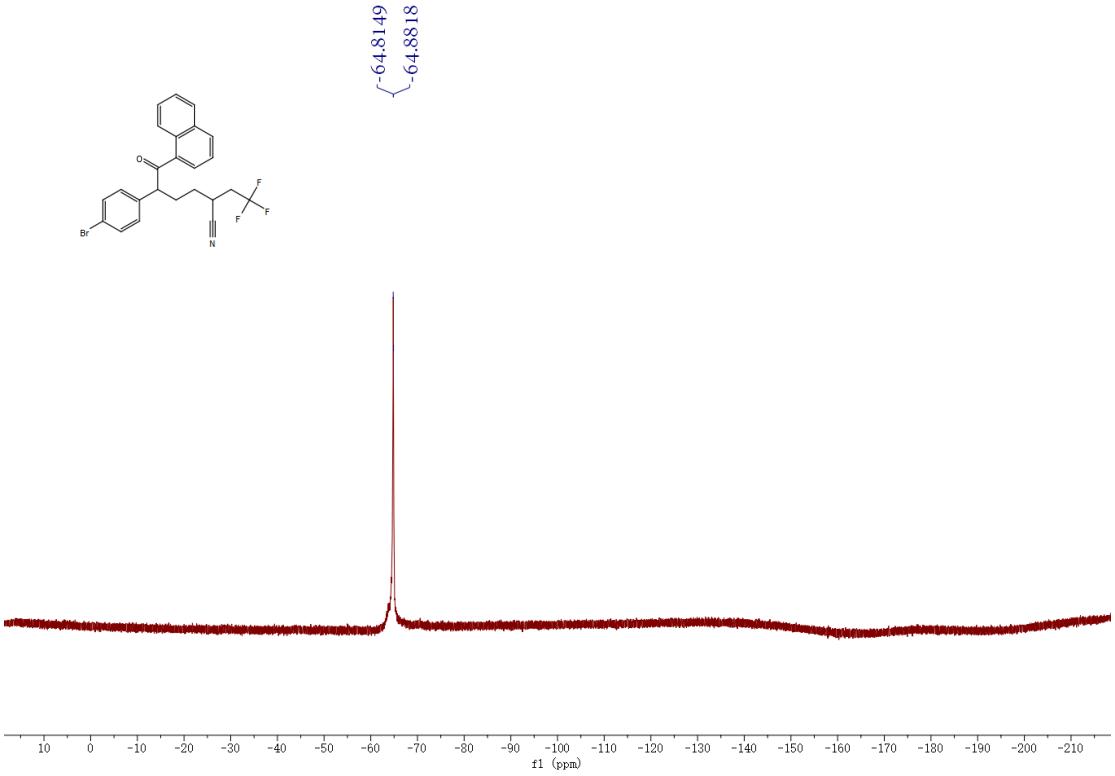
4k ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



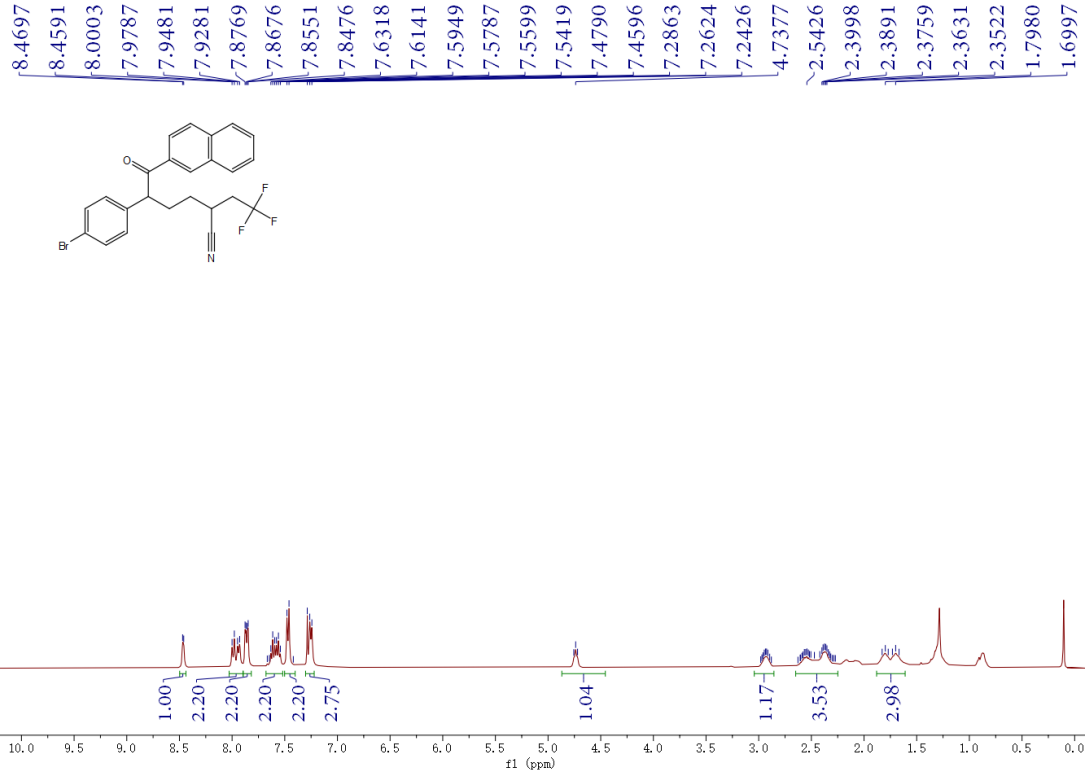
4k ^{13}C NMR (75 MHz, Chloroform-*d*)



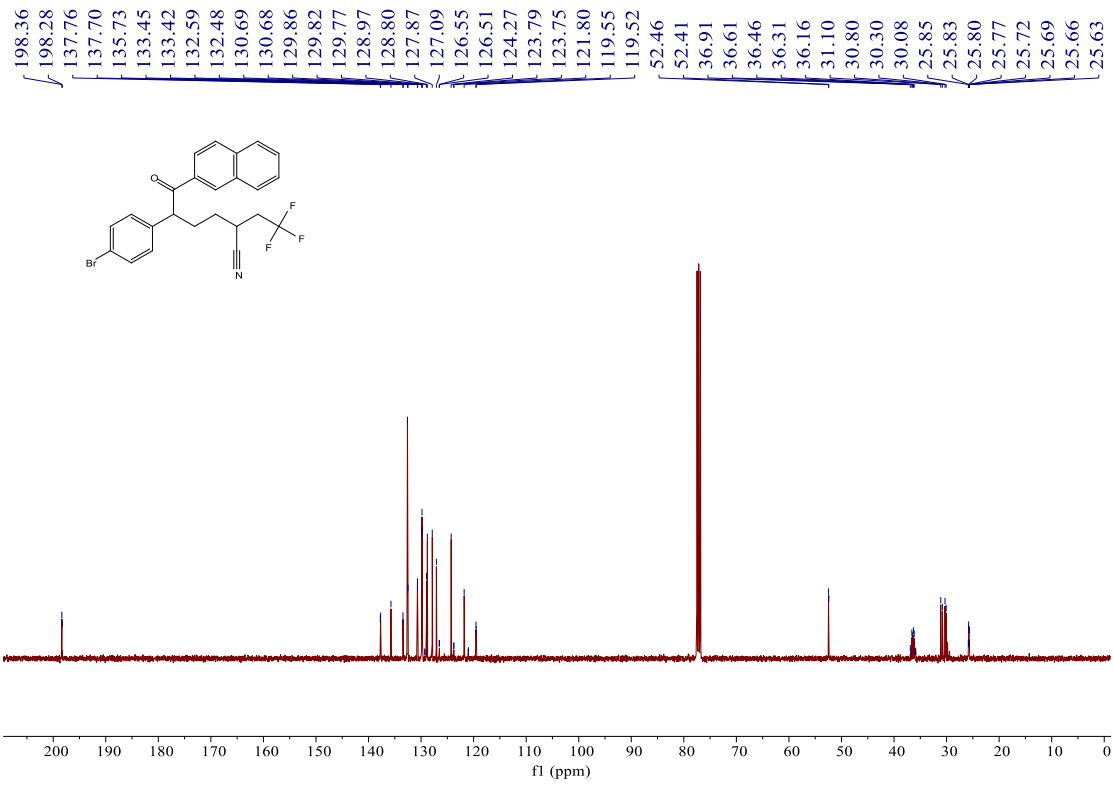
4k ^{19}F NMR (282 MHz, Chloroform-*d*)



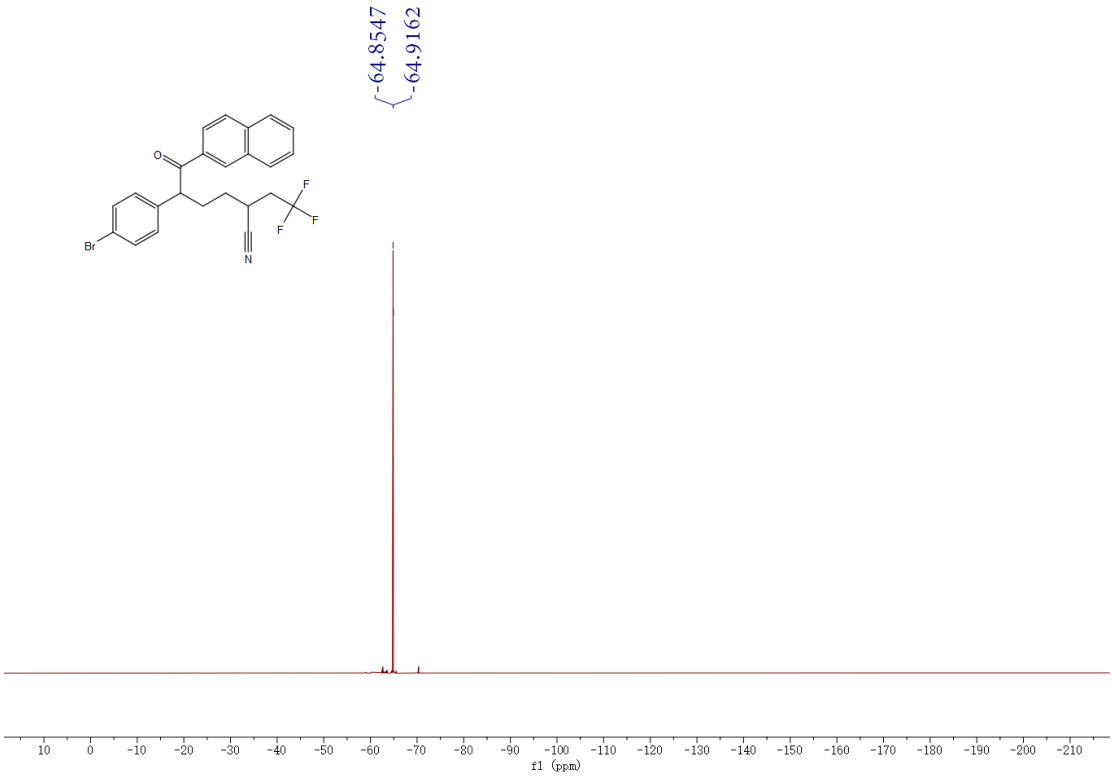
4l ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C NMR (101 MHz, Chloroform-*d)*



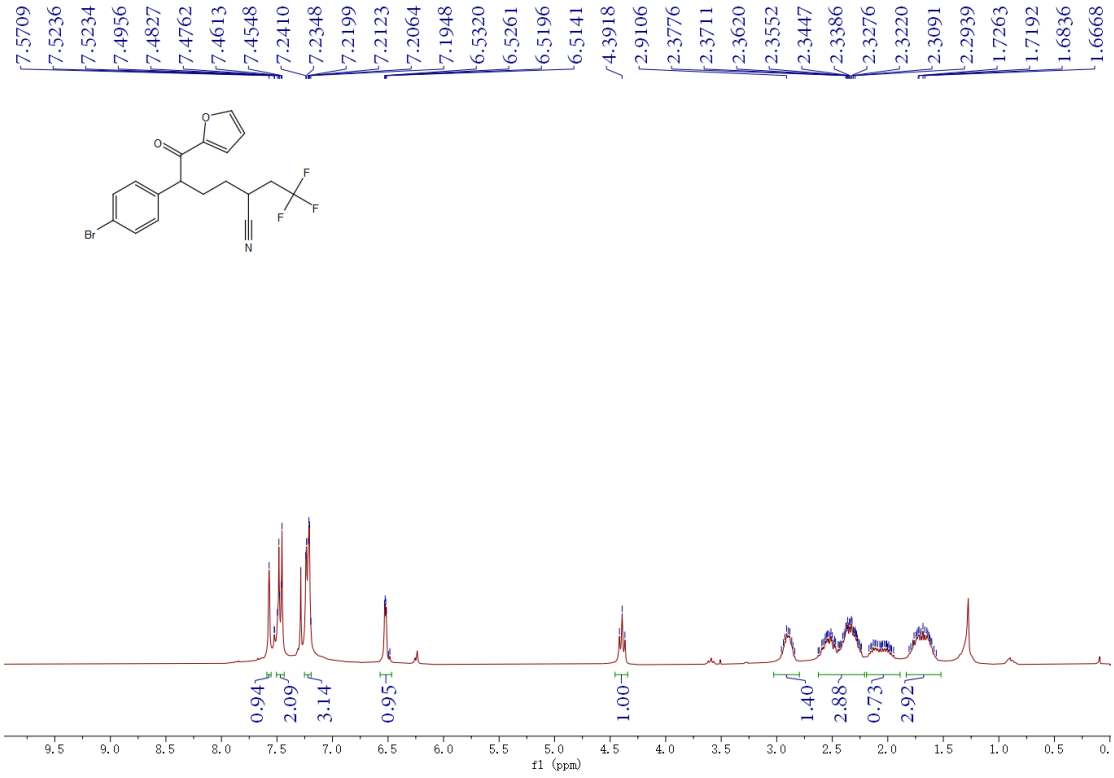
^{13}C NMR (101 MHz, Chloroform-*d)*



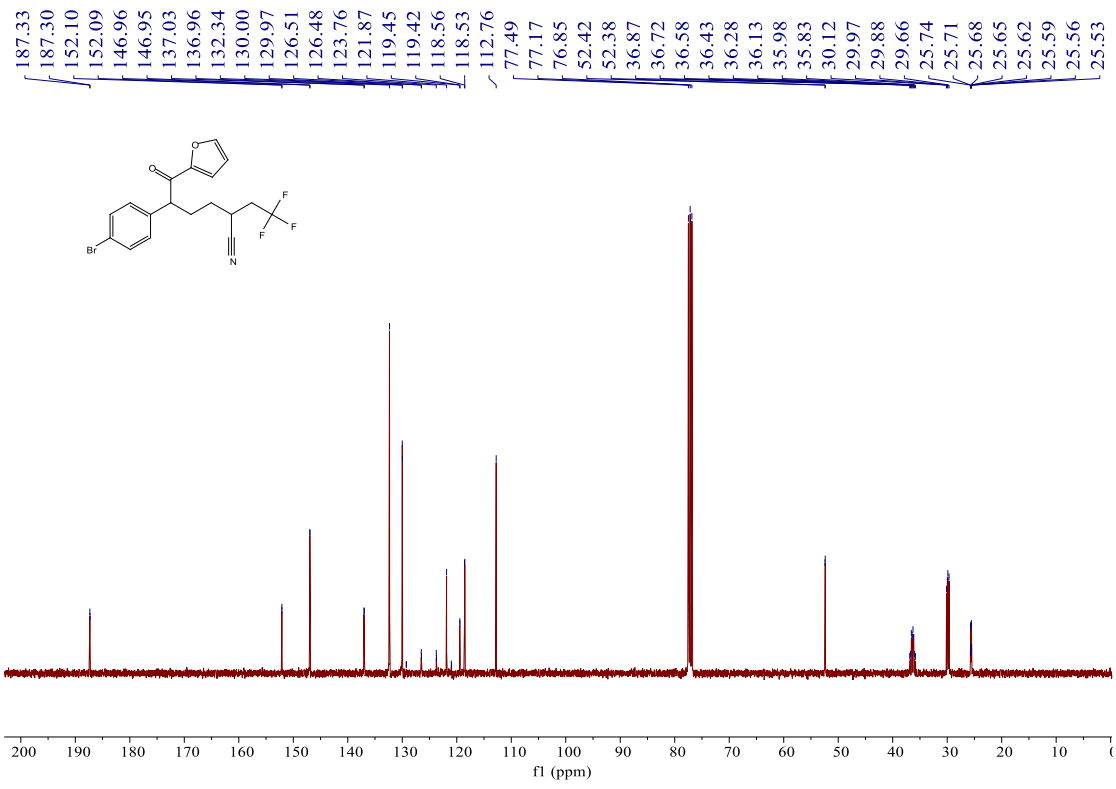
4l ^{19}F NMR (282 MHz, Chloroform-*d*)



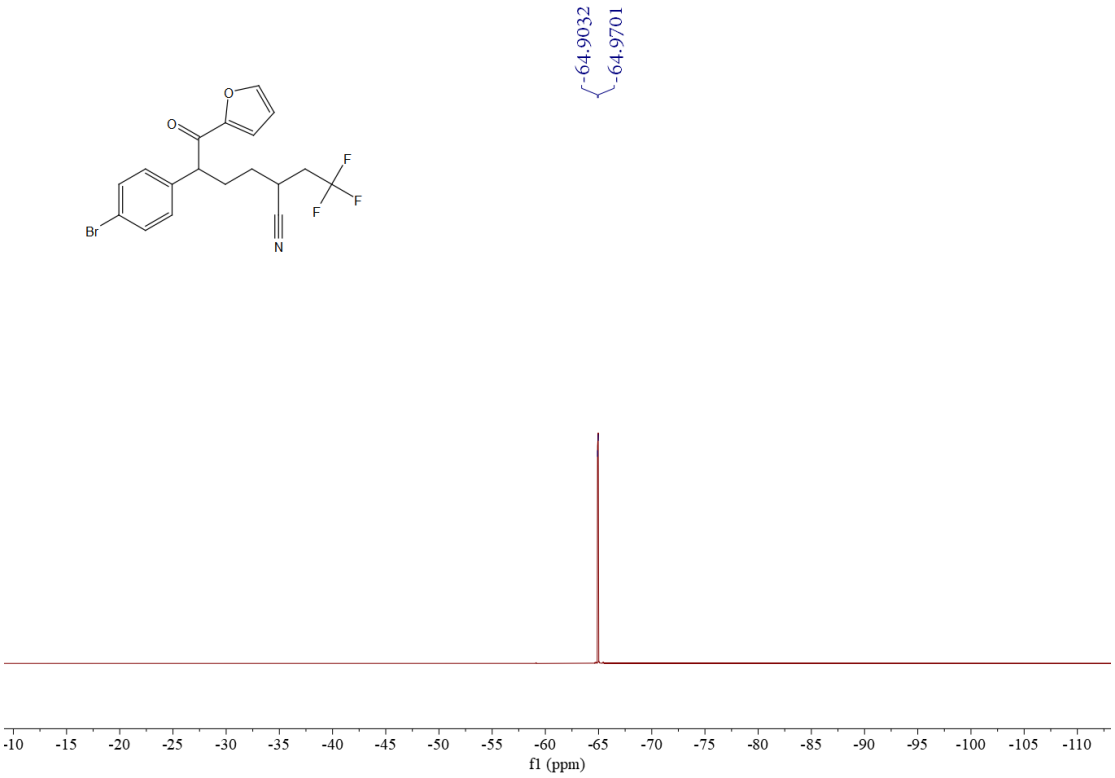
4m ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (101 MHz, Chloroform-*d*)



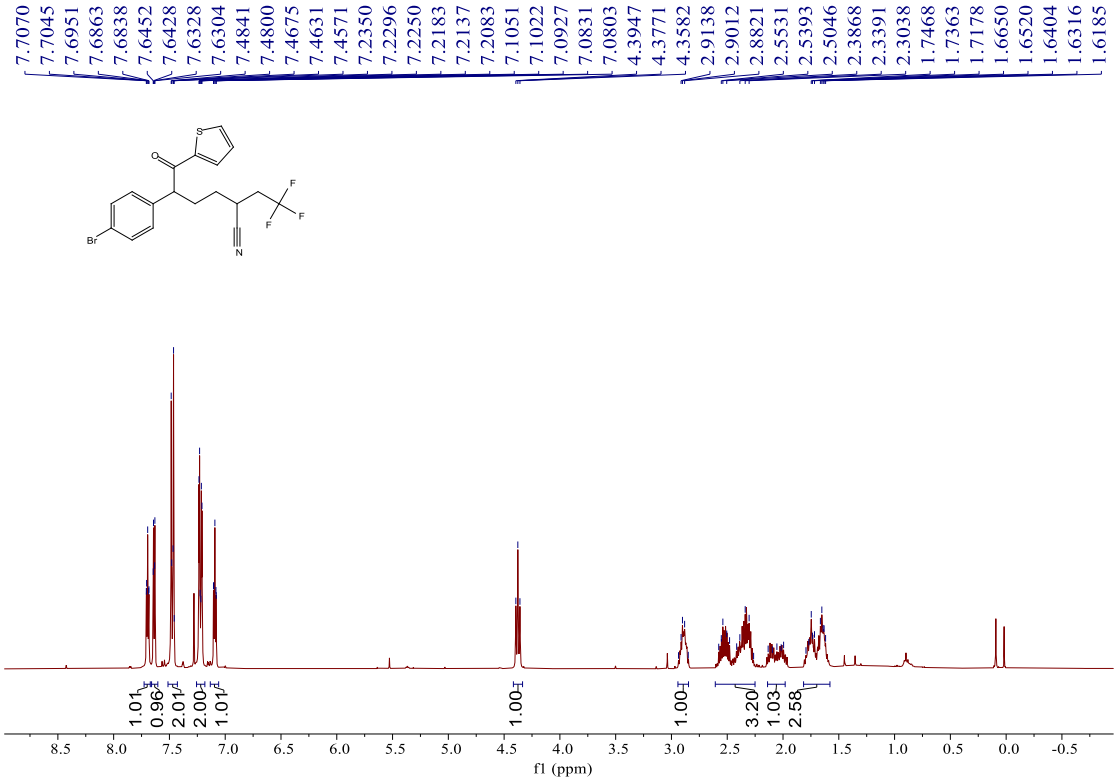
^{13}C NMR (101 MHz, Chloroform-*d*)



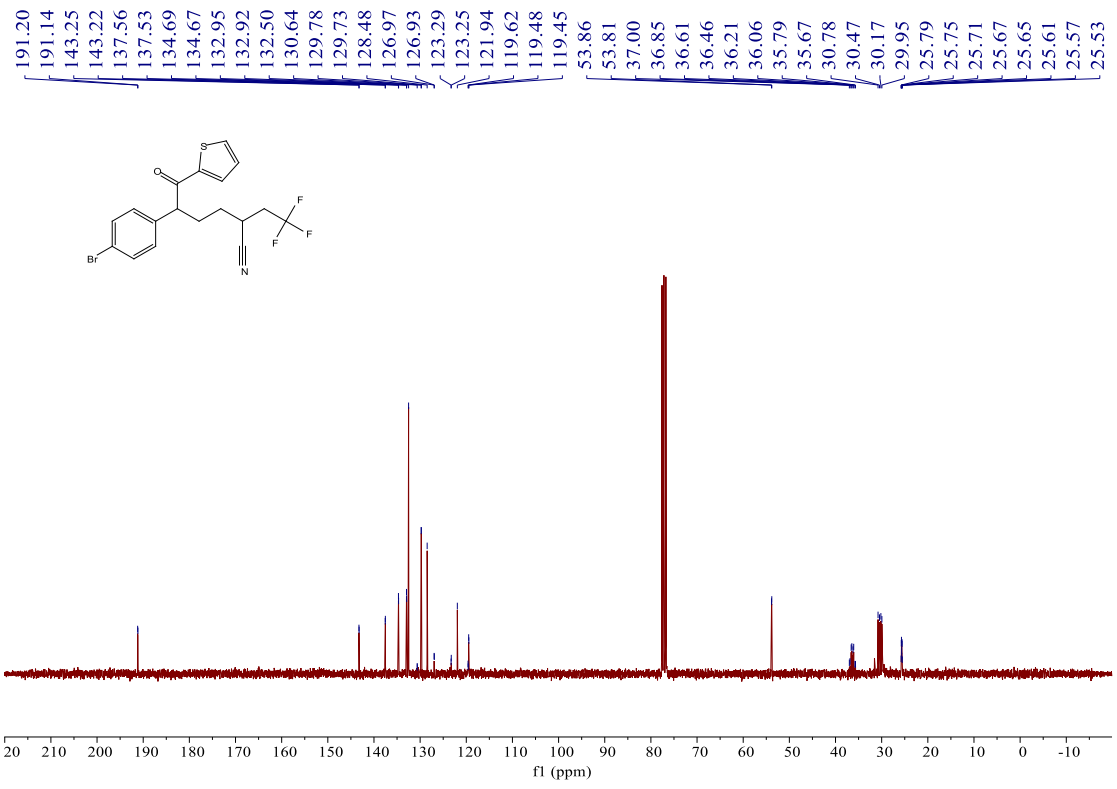
4m ^{19}F NMR (282 MHz, Chloroform-*d*)



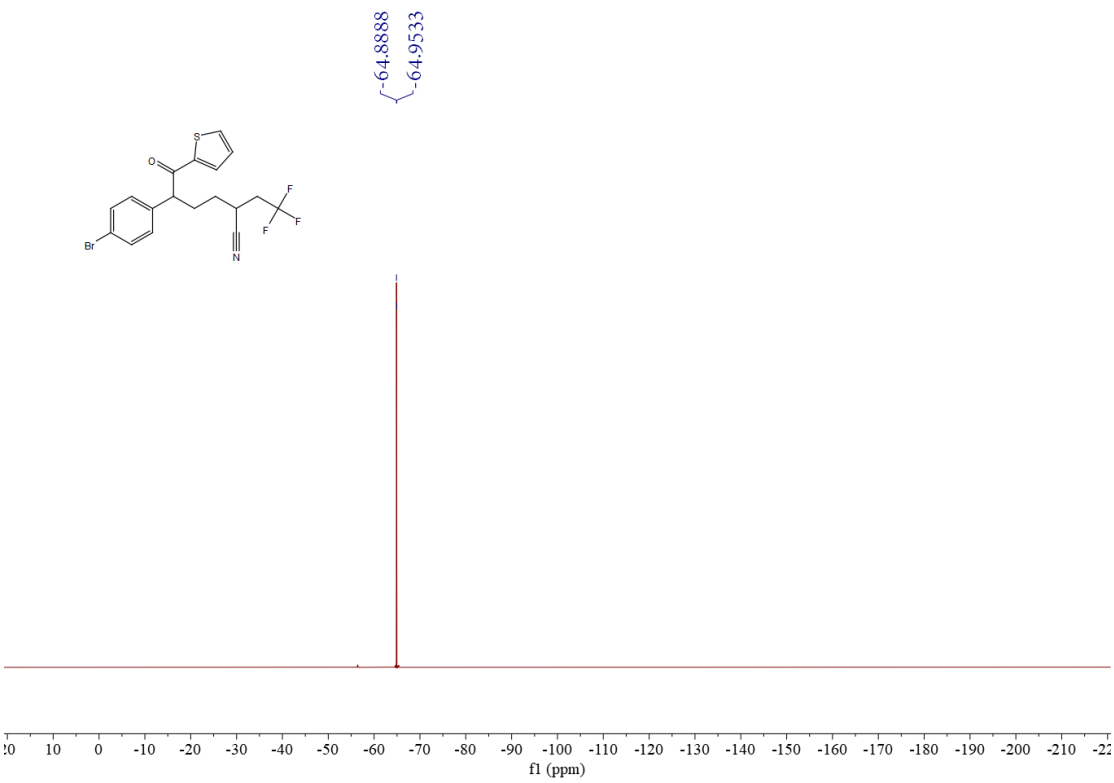
4n ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



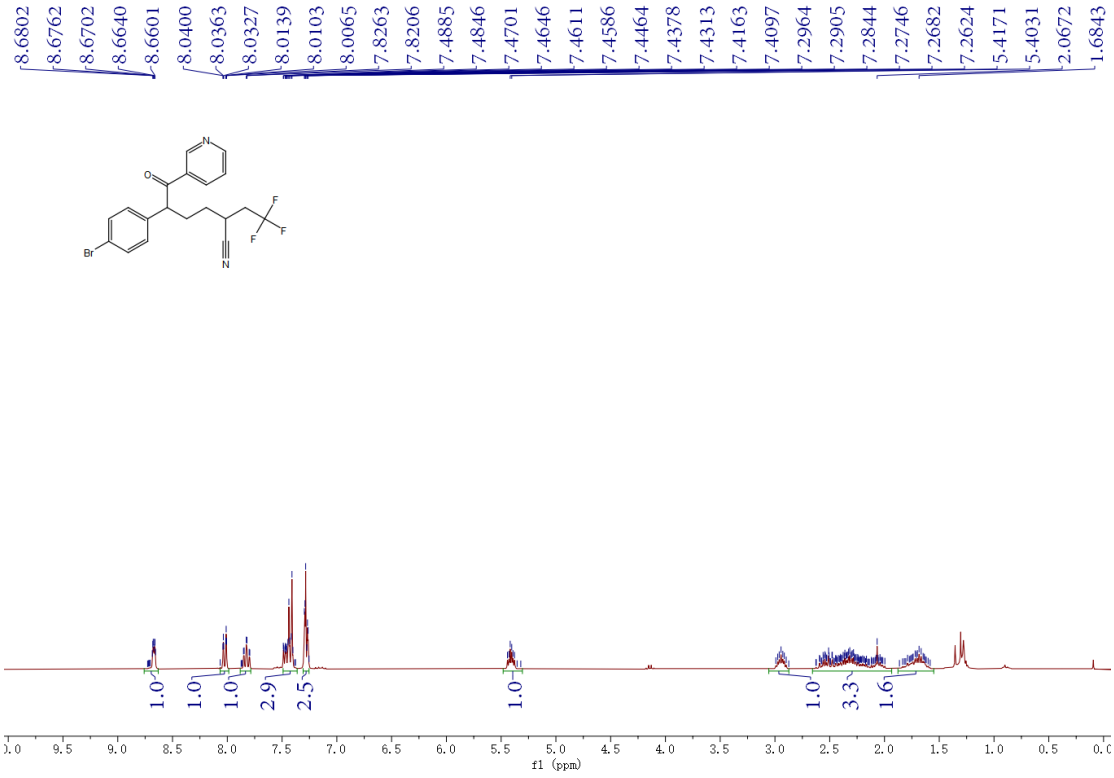
^{13}C NMR (75 MHz, Chloroform-*d*)



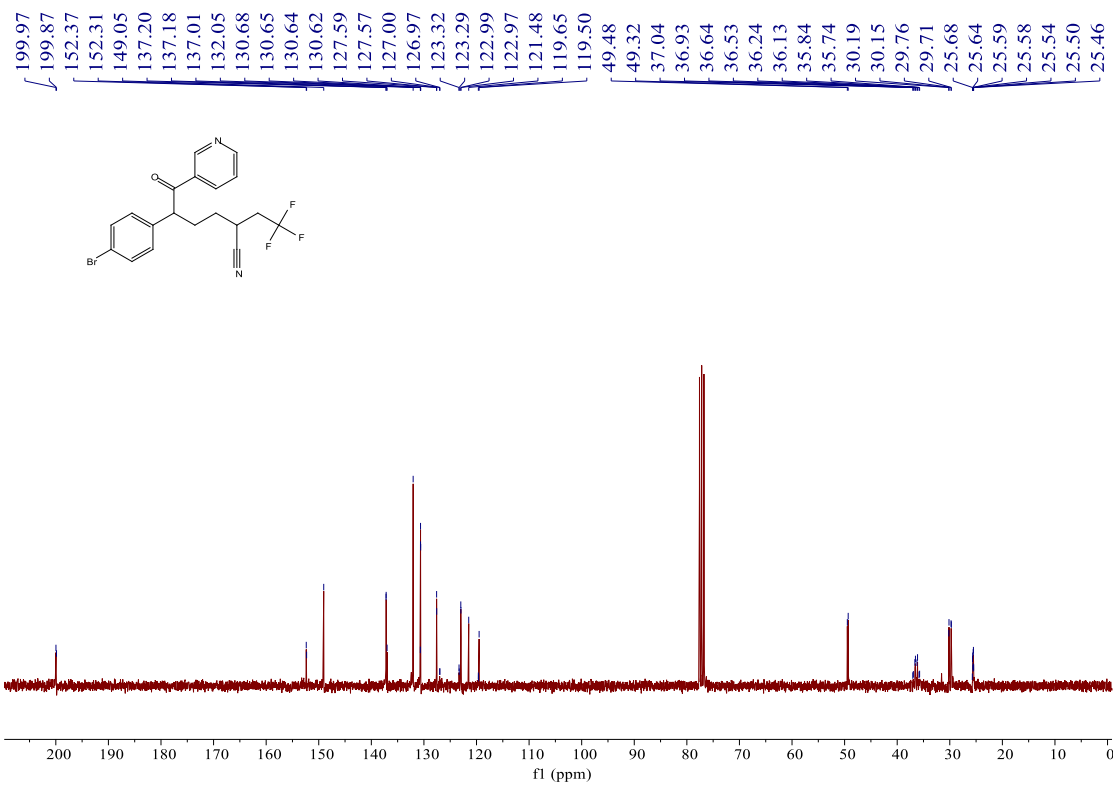
4n ^{19}F NMR (376 MHz, Chloroform-*d*)



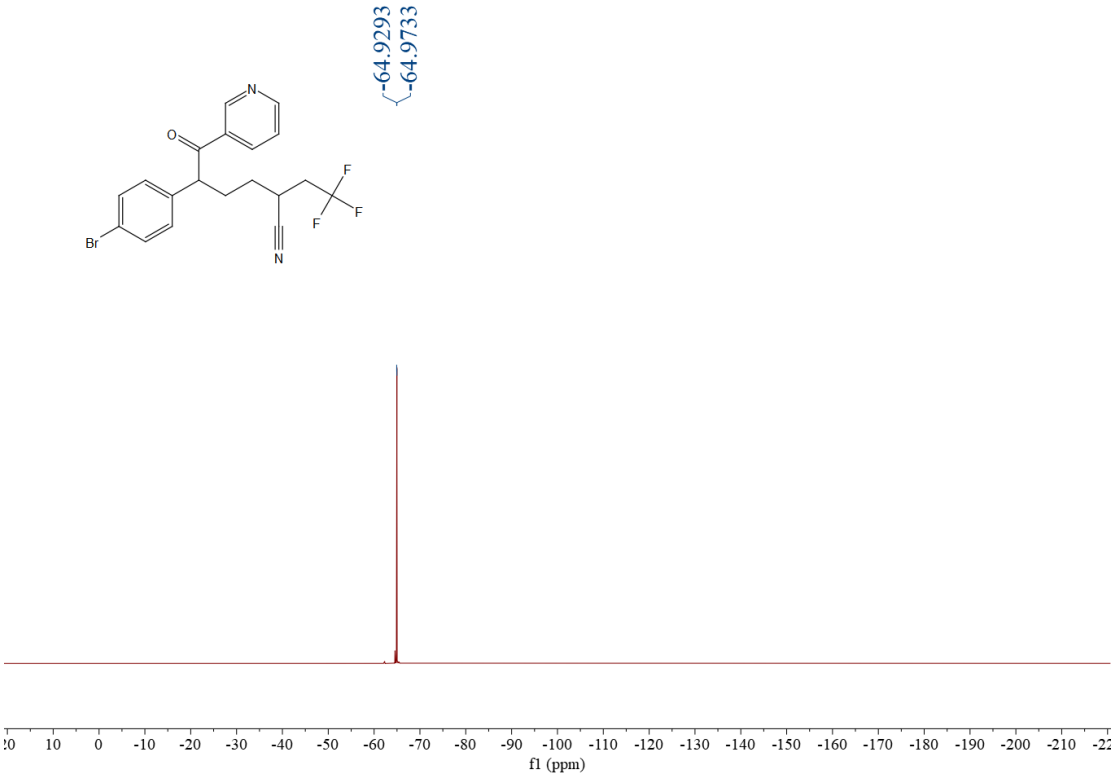
4o ^{1}H NMR (400 MHz, Chloroform-*d*)



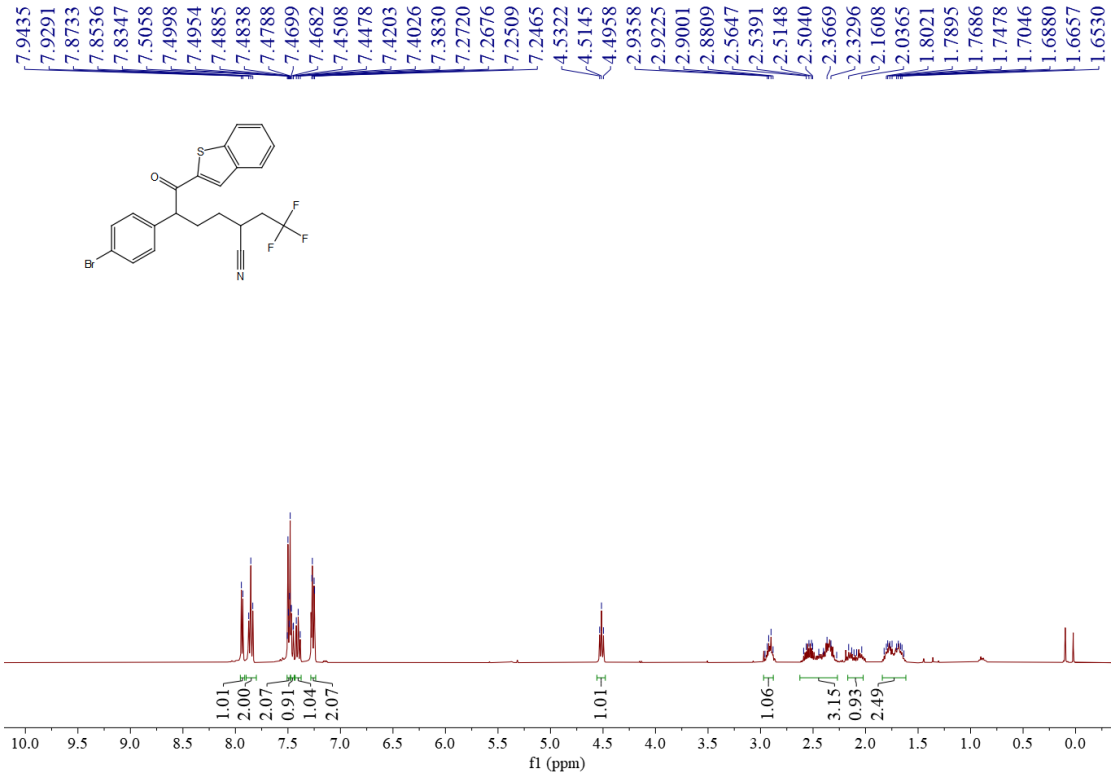
^{13}C NMR (75 MHz, Chloroform-*d*)



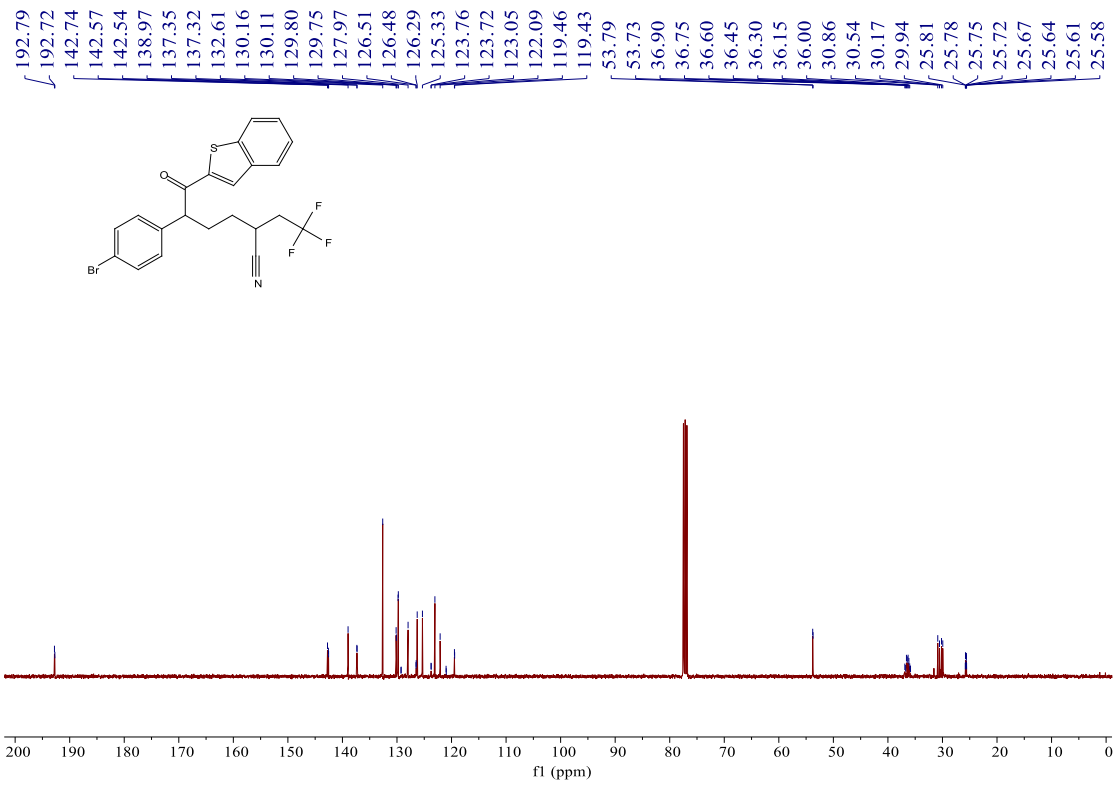
4o ^{19}F NMR (282 MHz, Chloroform-*d*)



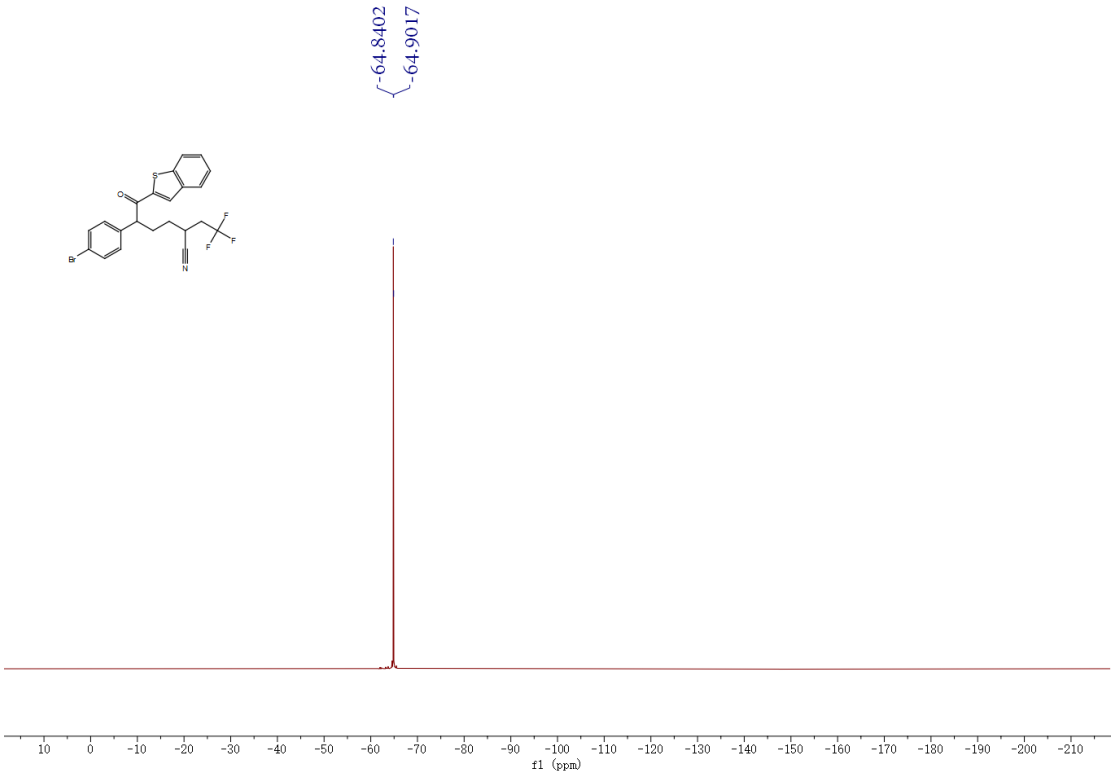
4p ^{1}H NMR (400 MHz, Chloroform-*d*) ^{13}C NMR (101 MHz, Chloroform-*d*)



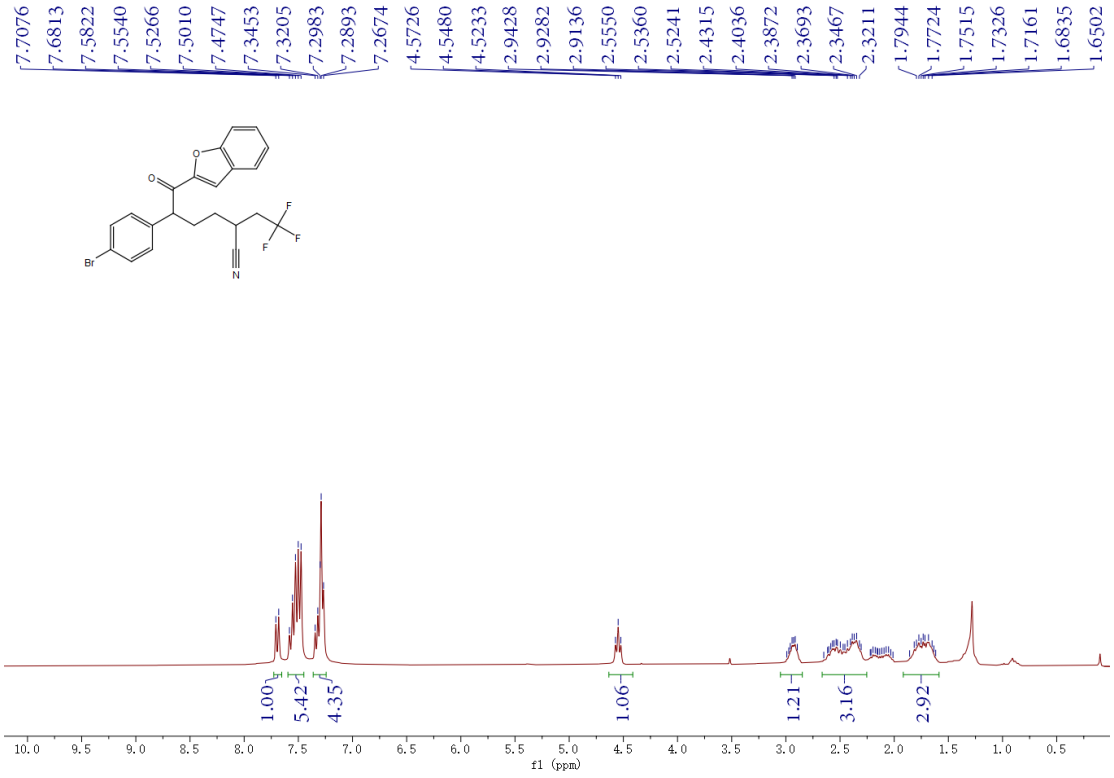
4p ^{13}C NMR (101 MHz, Chloroform-*d*)



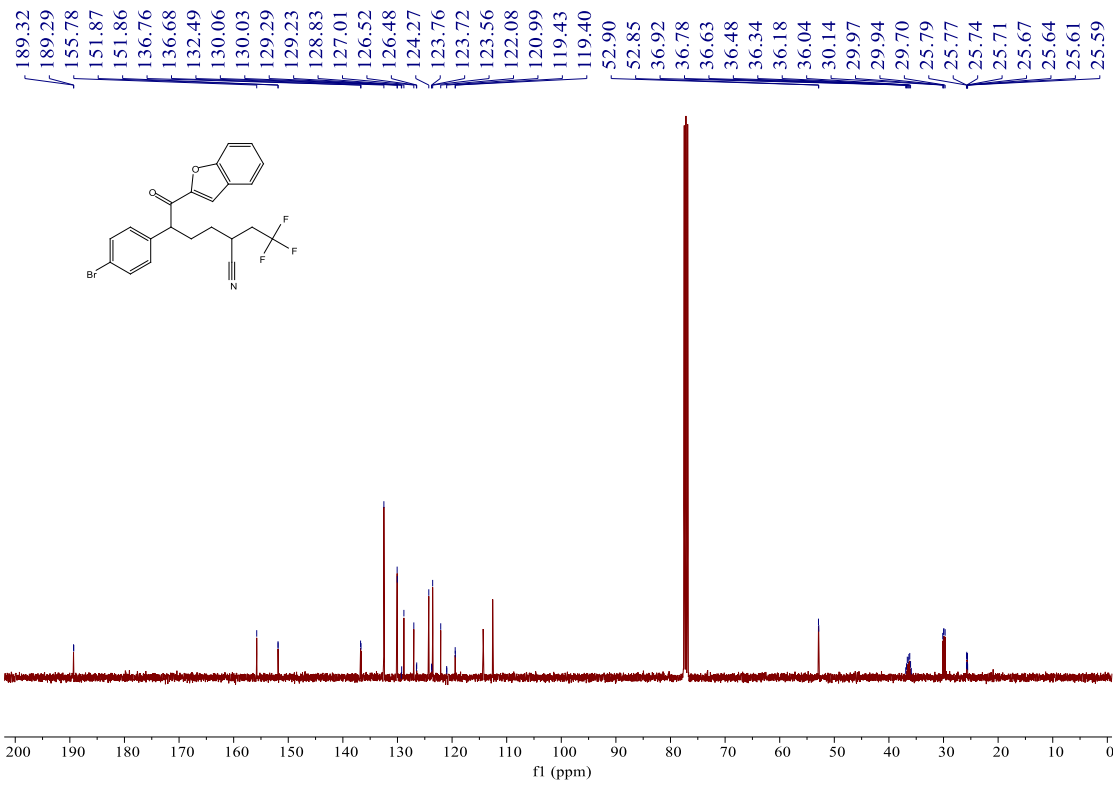
4p ^{19}F NMR (282 MHz, Chloroform-*d*)



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



4q ^{13}C (101 MHz, Chloroform-*d*)



4q ^{19}F NMR (282 MHz, Chloroform-*d*)

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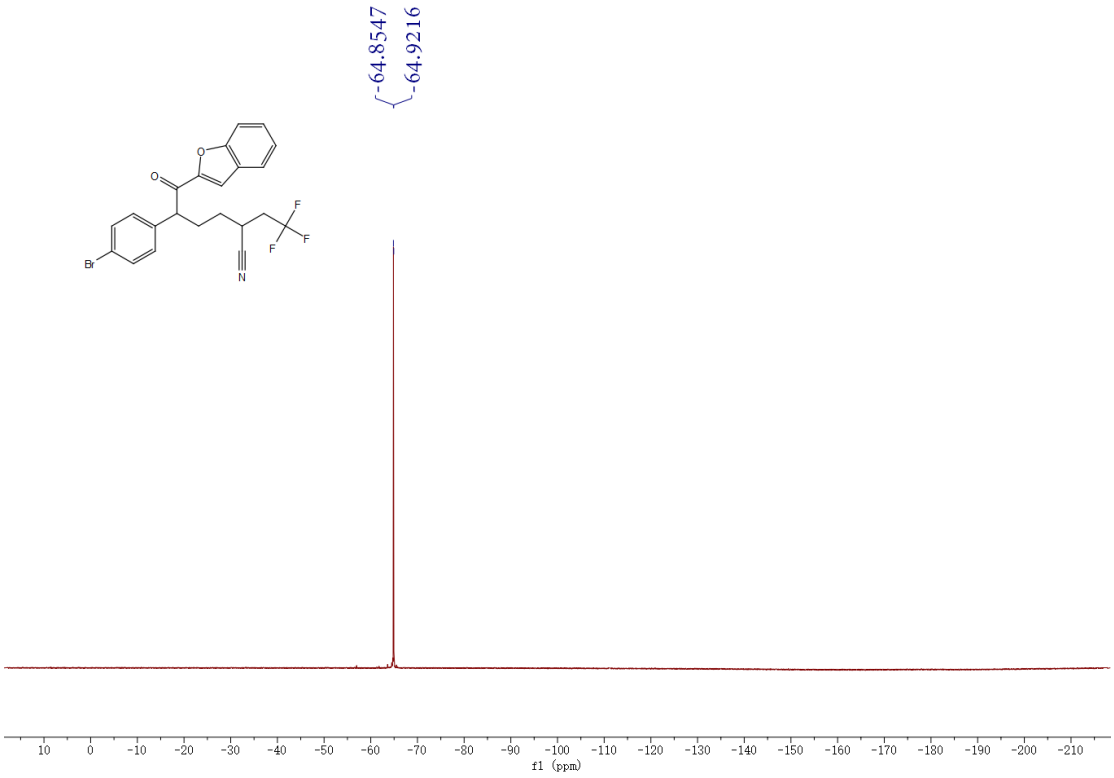
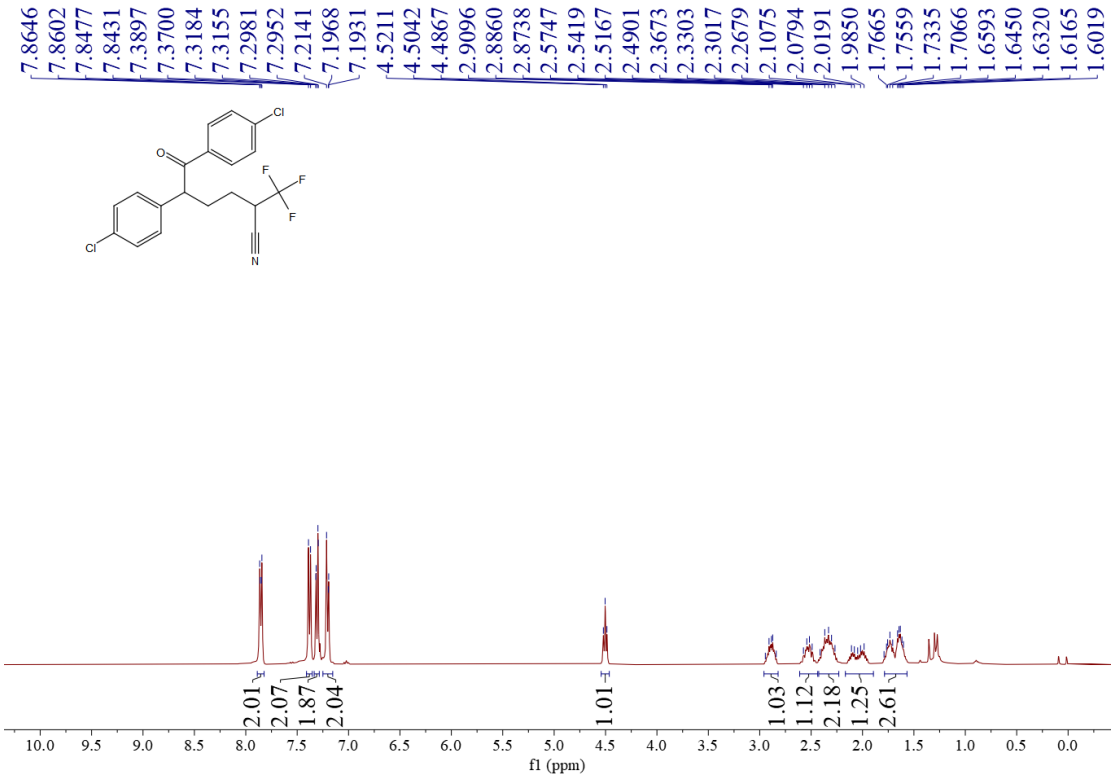
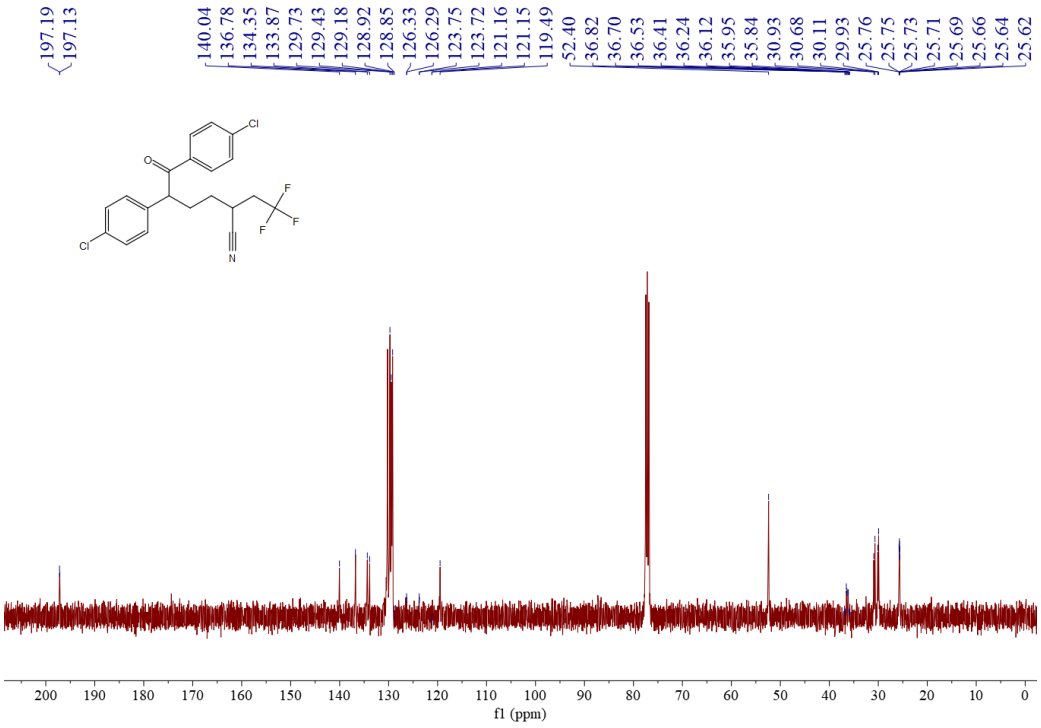


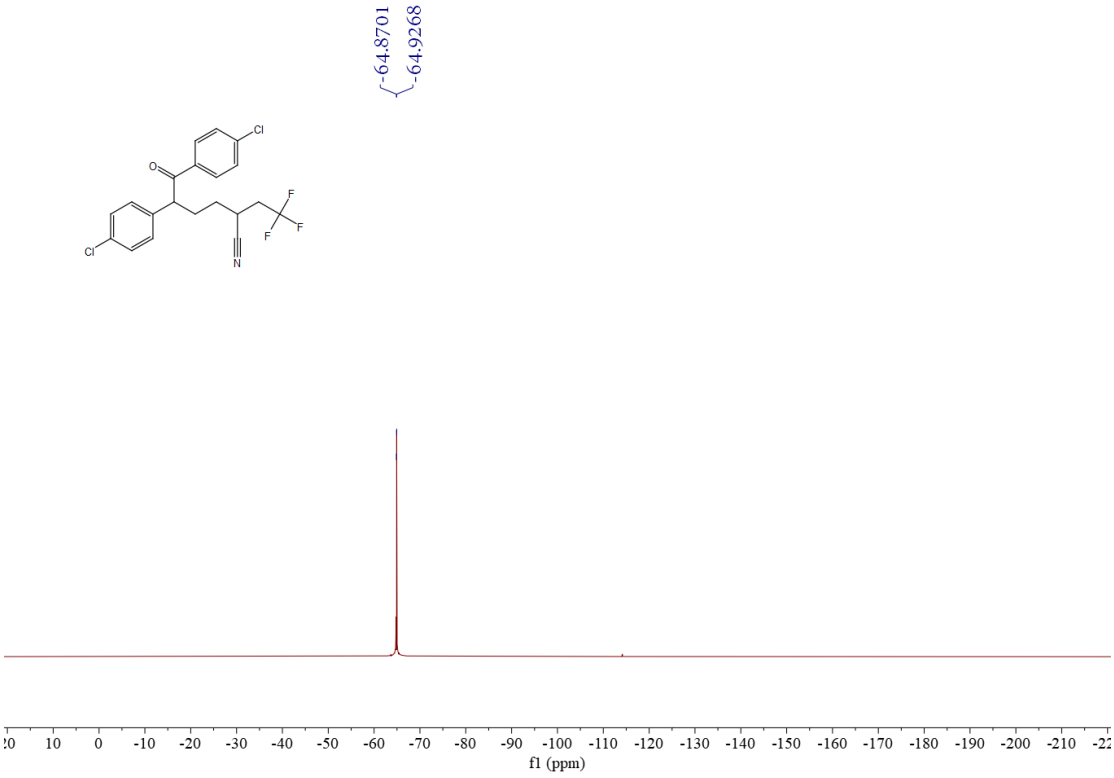
4r ^{1}H NMR(300 MHz,Chloroform-*d*)/^{13}C (101 MHz, Chloroform-*d*)



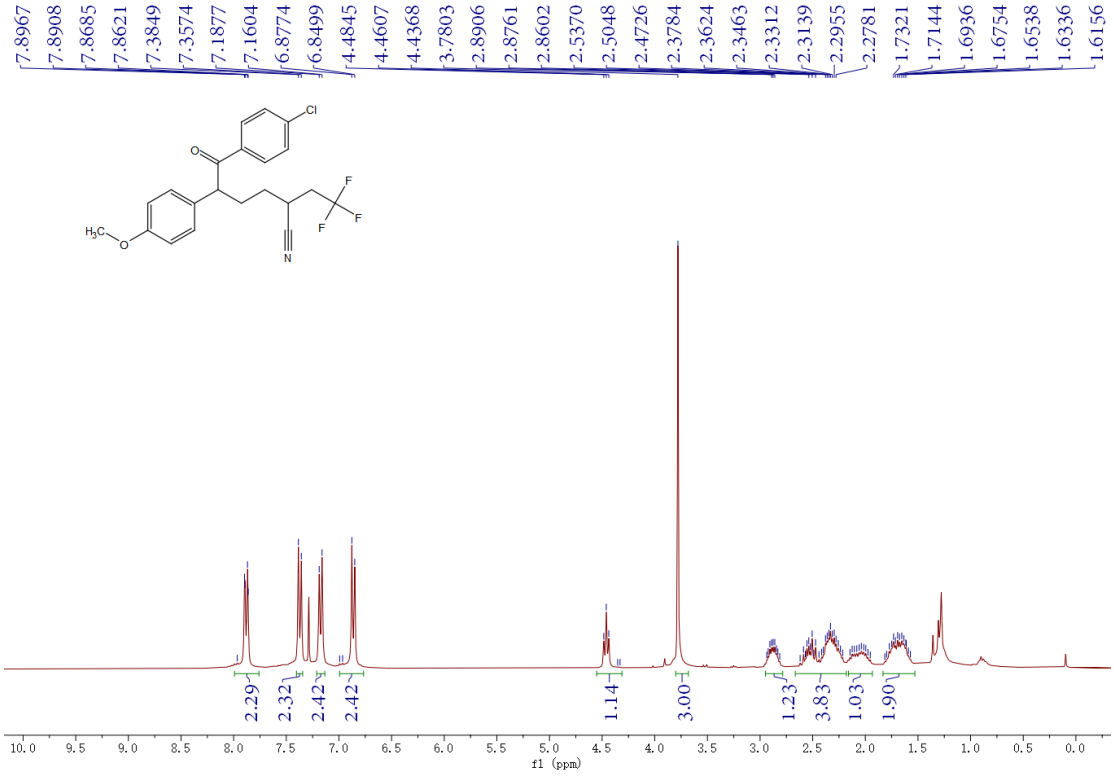
4r ^{13}C (101 MHz, Chloroform-*d*)



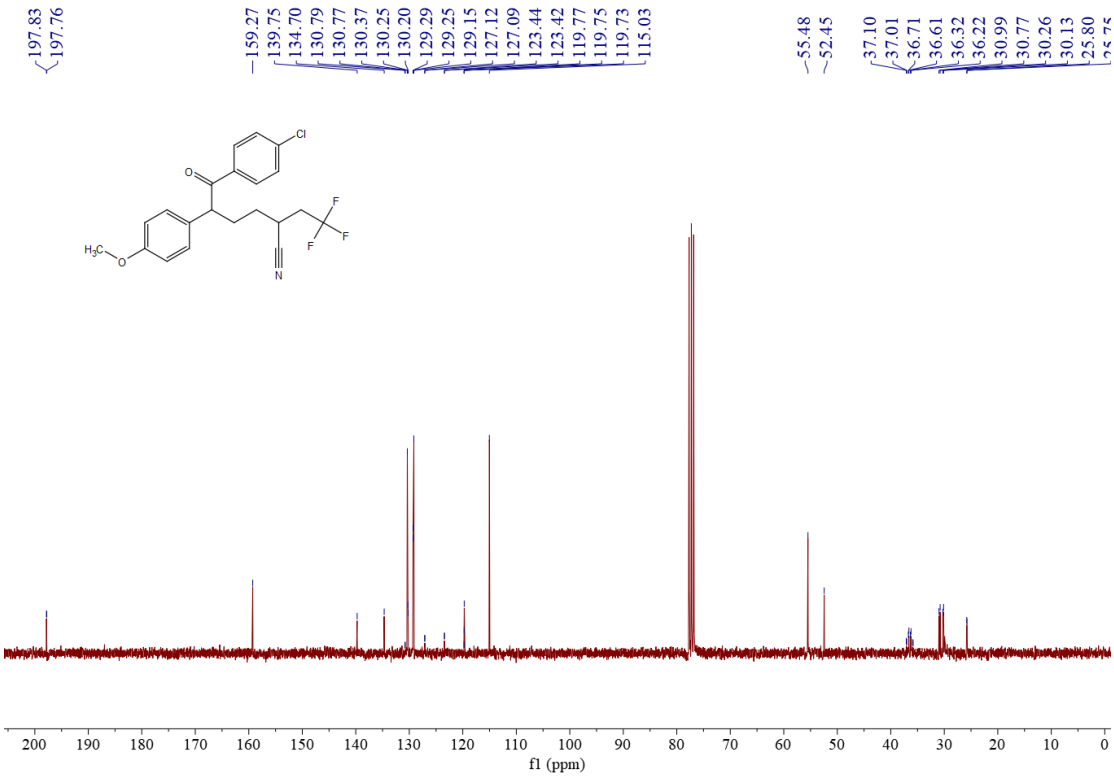
4r ^{19}F NMR (282 MHz, Chloroform-*d*)



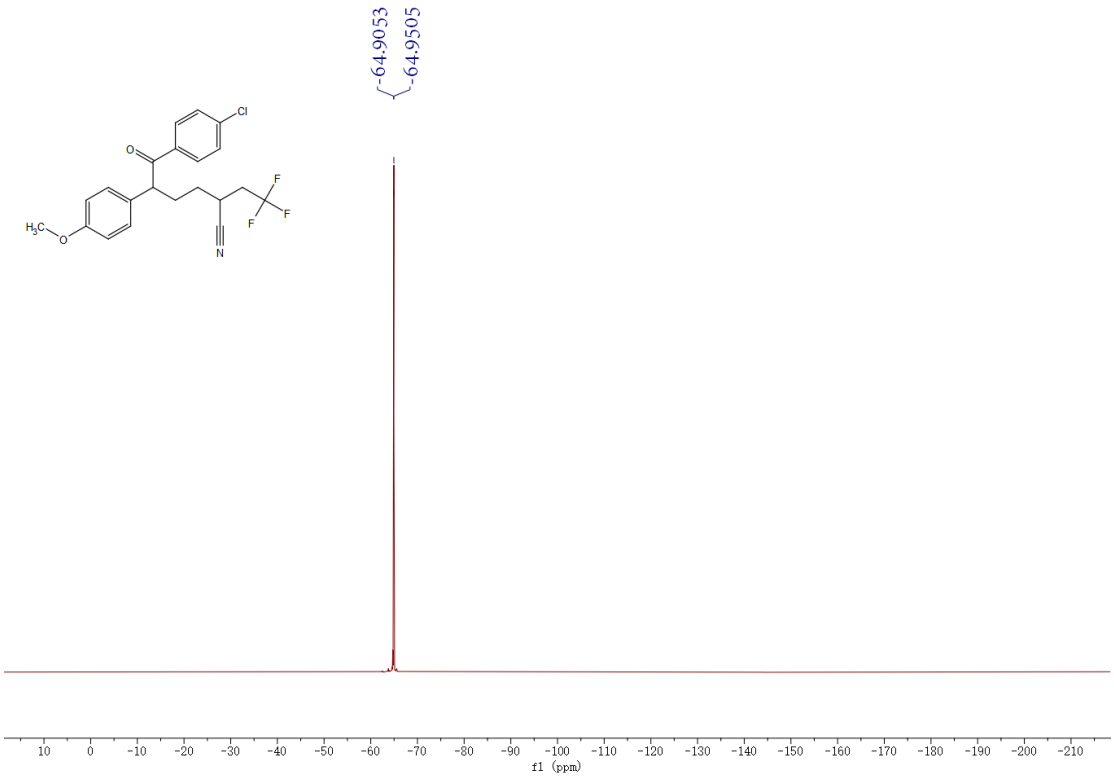
4s ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C (75 MHz, Chloroform-*d*)



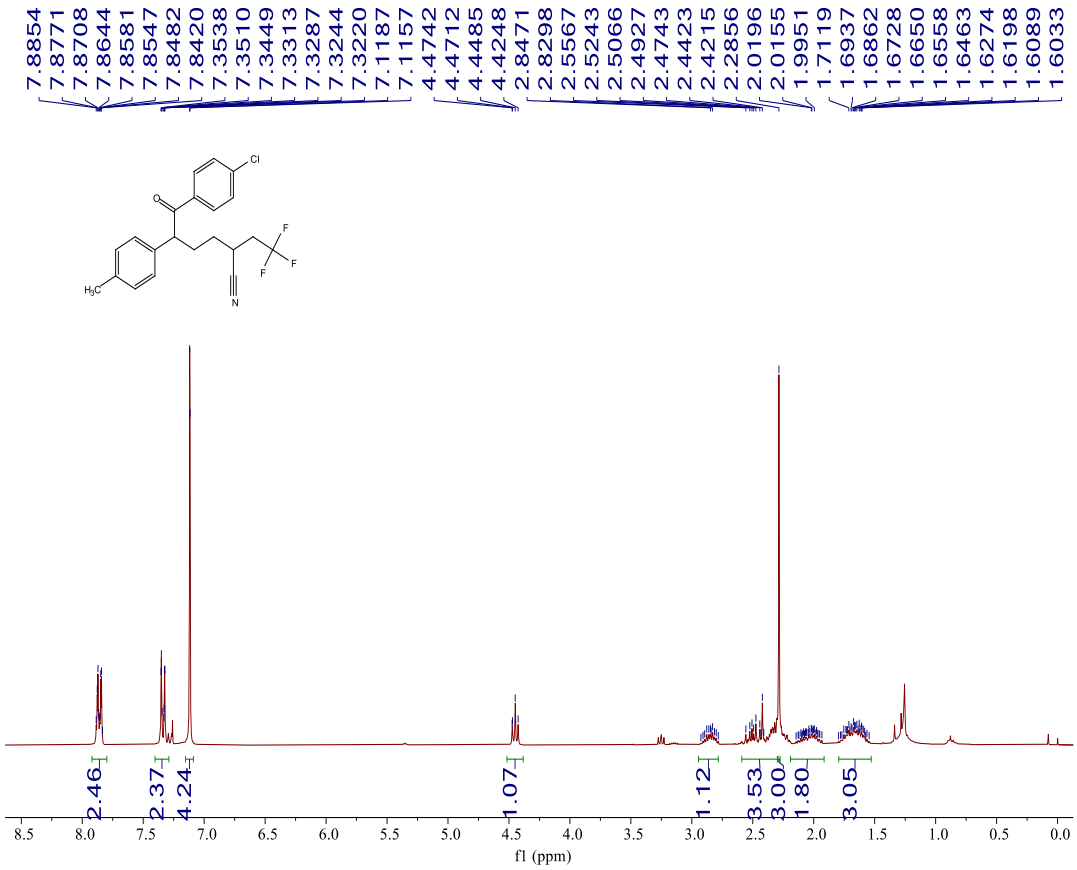
4s ^{13}C (75 MHz, Chloroform-*d*)



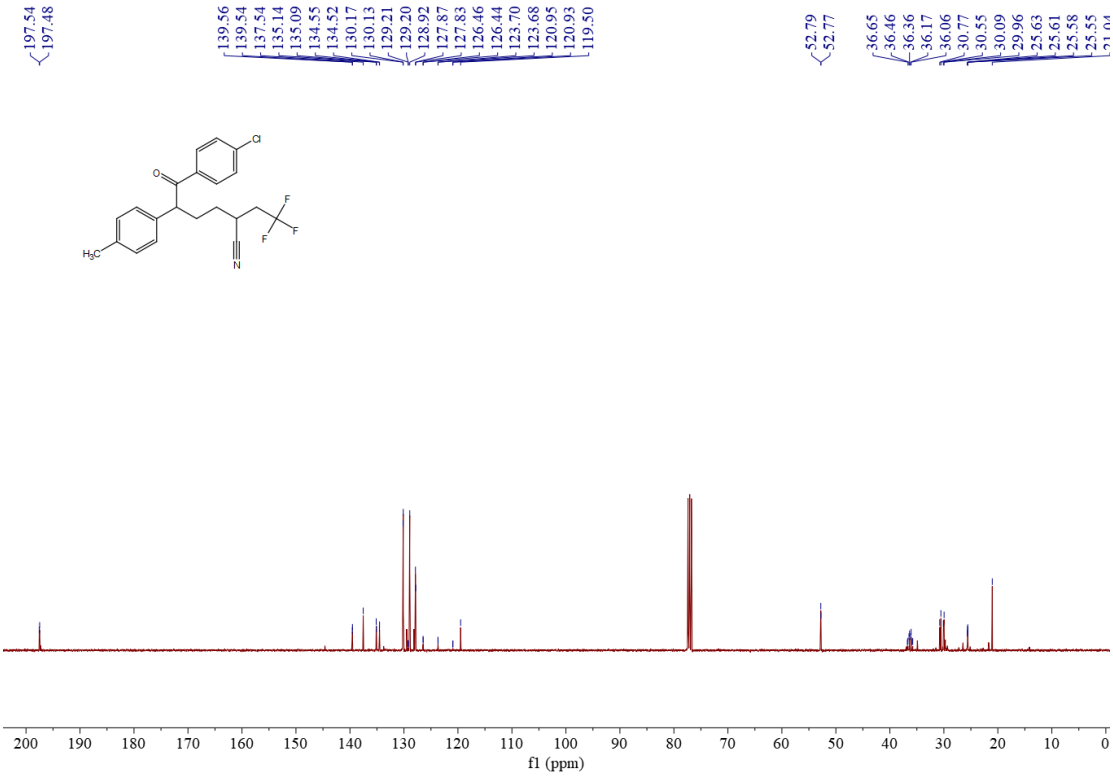
4s ^{19}F NMR (282 MHz, Chloroform-*d*)



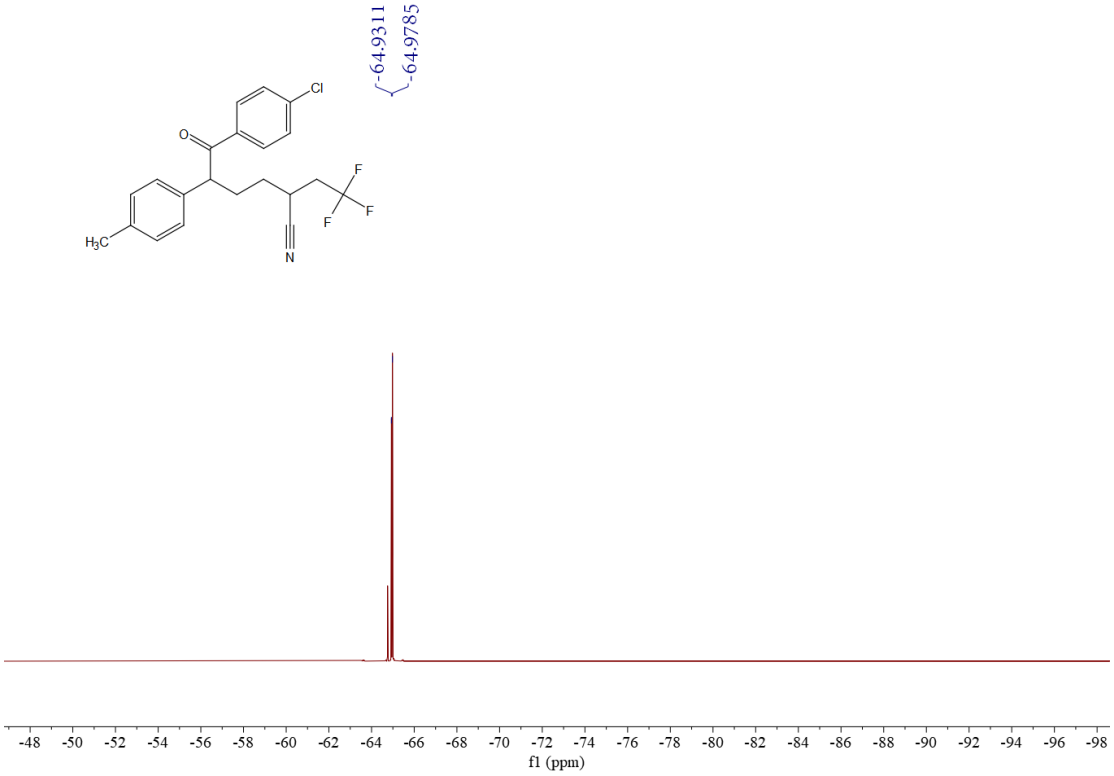
4t ^{1}H NMR (400 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



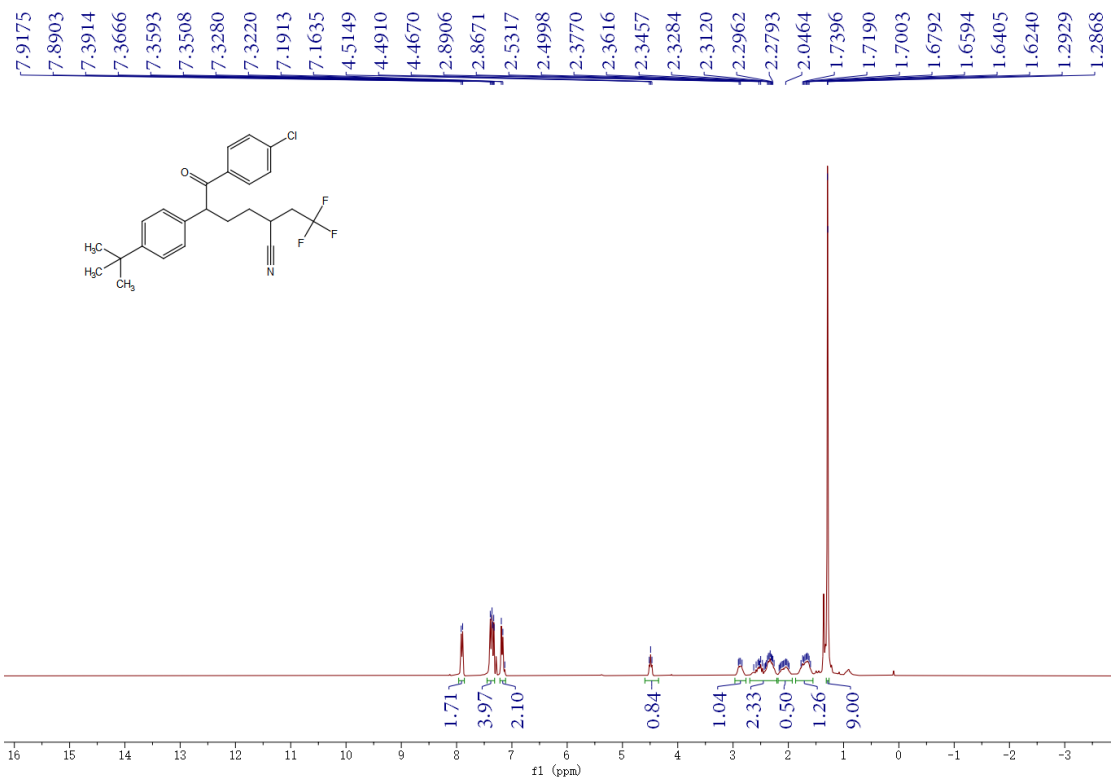
4t ^{13}C NMR (101 MHz, Chloroform-*d*)



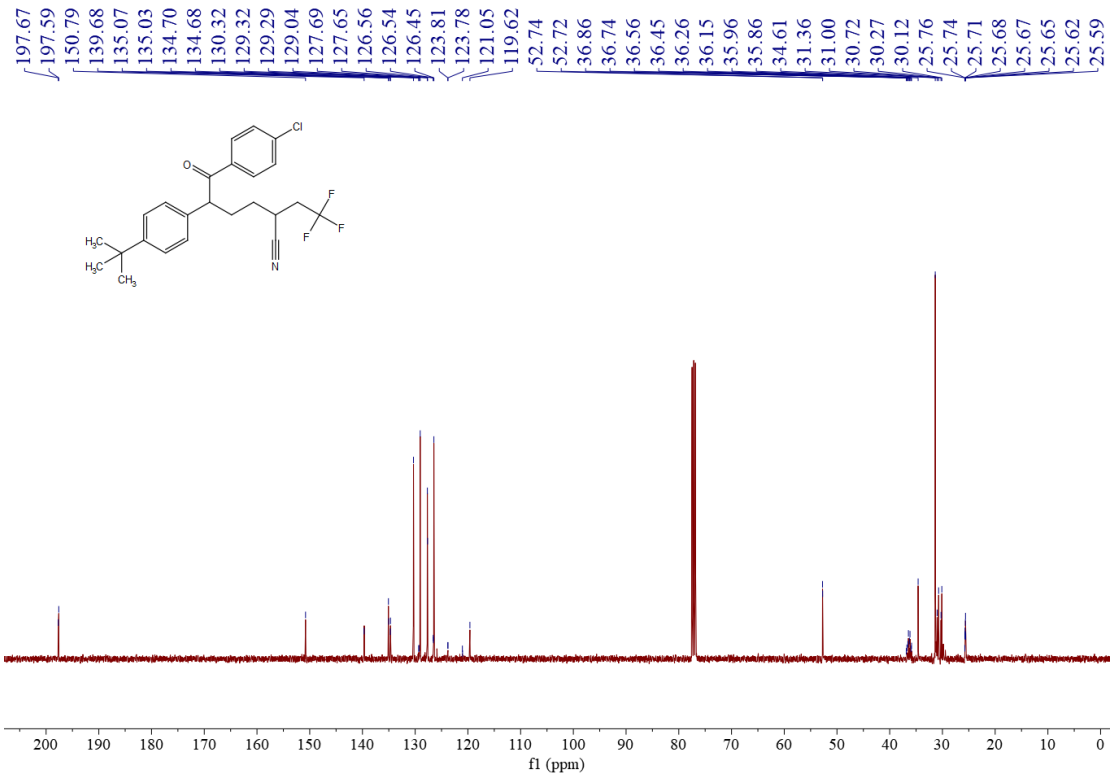
4t ^{19}F NMR (376 MHz, Chloroform-*d*)



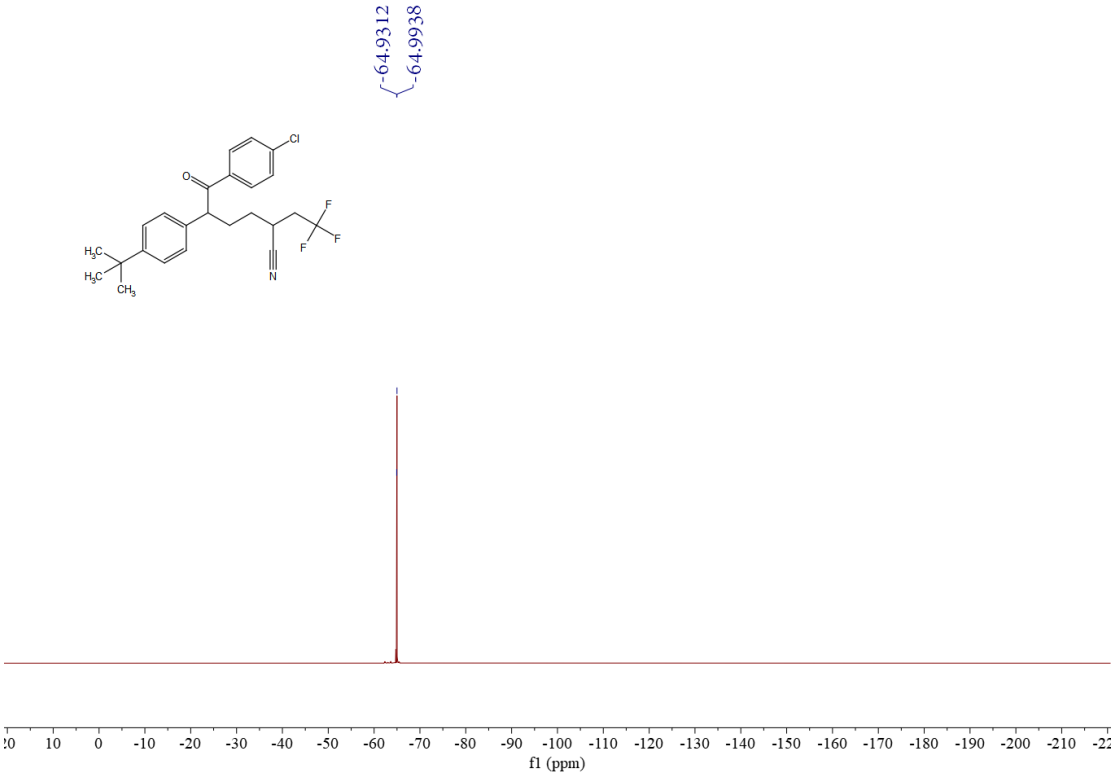
4u ^{1}H NMR (300 MHz, Chloroform-*d*）^{13}C NMR (101 MHz, Chloroform-*d*)



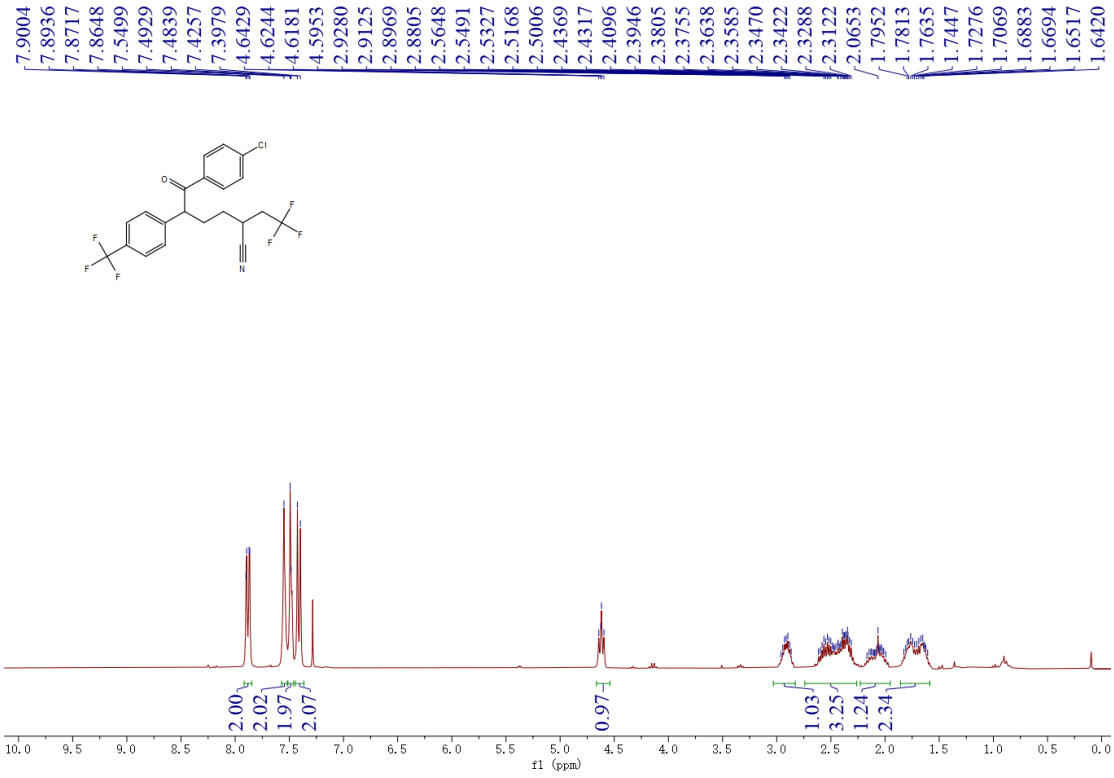
4u ^{13}C NMR (101 MHz, Chloroform-*d*)



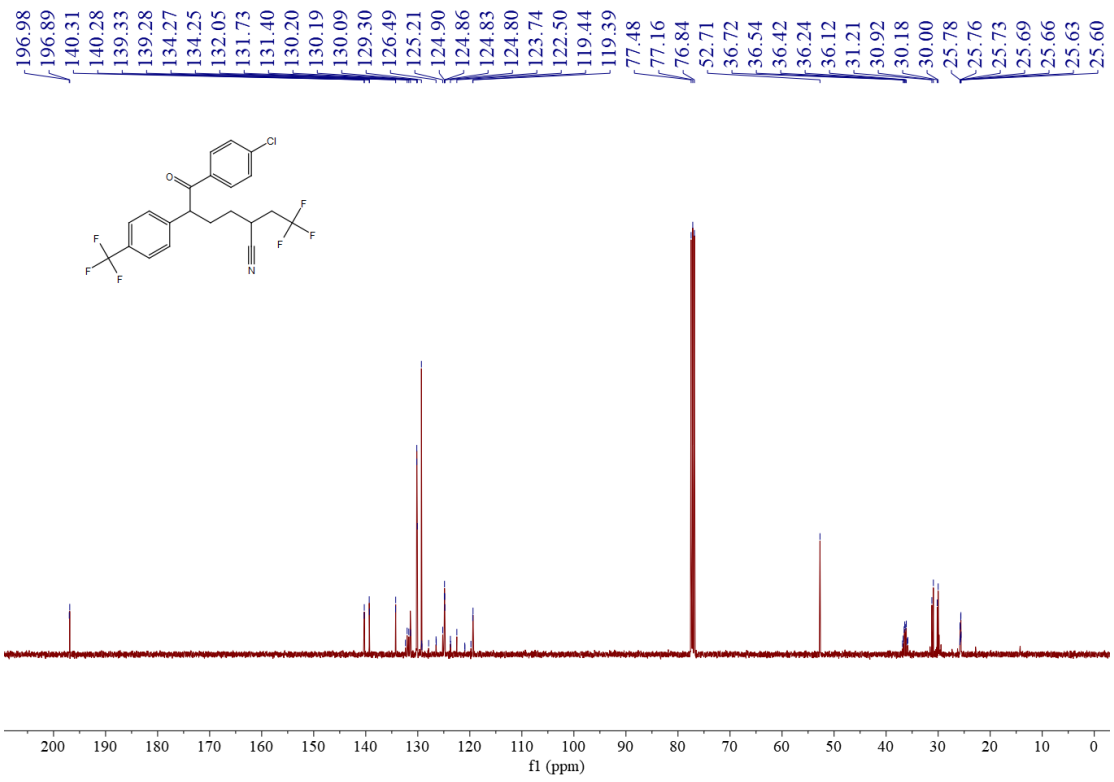
4u ^{19}F NMR (282MHz, Chloroform-*d*)



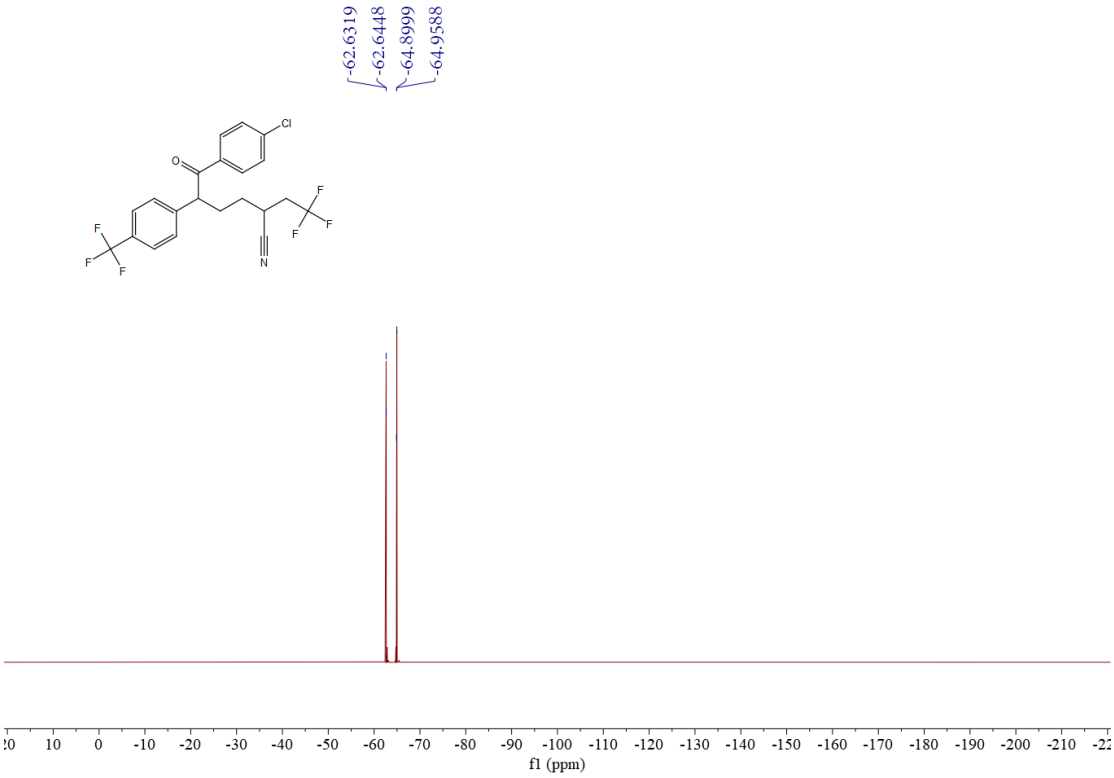
4v ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C NMR (101 MHz, Chloroform-*d*)



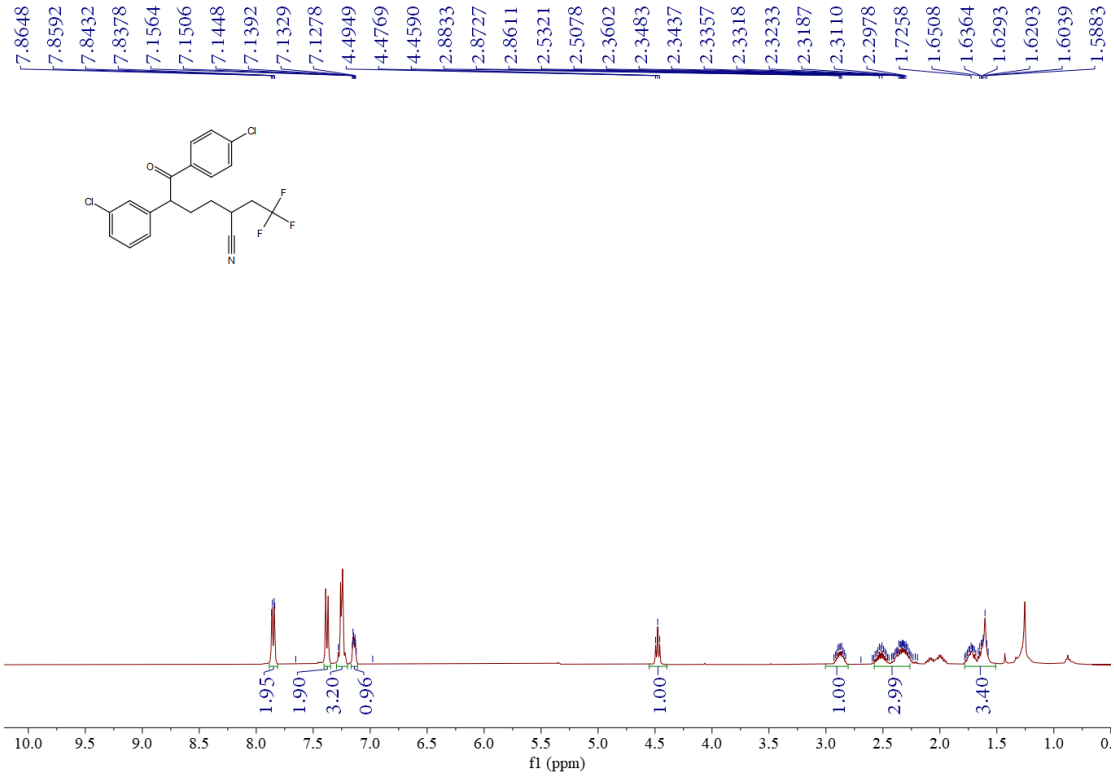
^{13}C NMR (101 MHz, Chloroform-*d*)



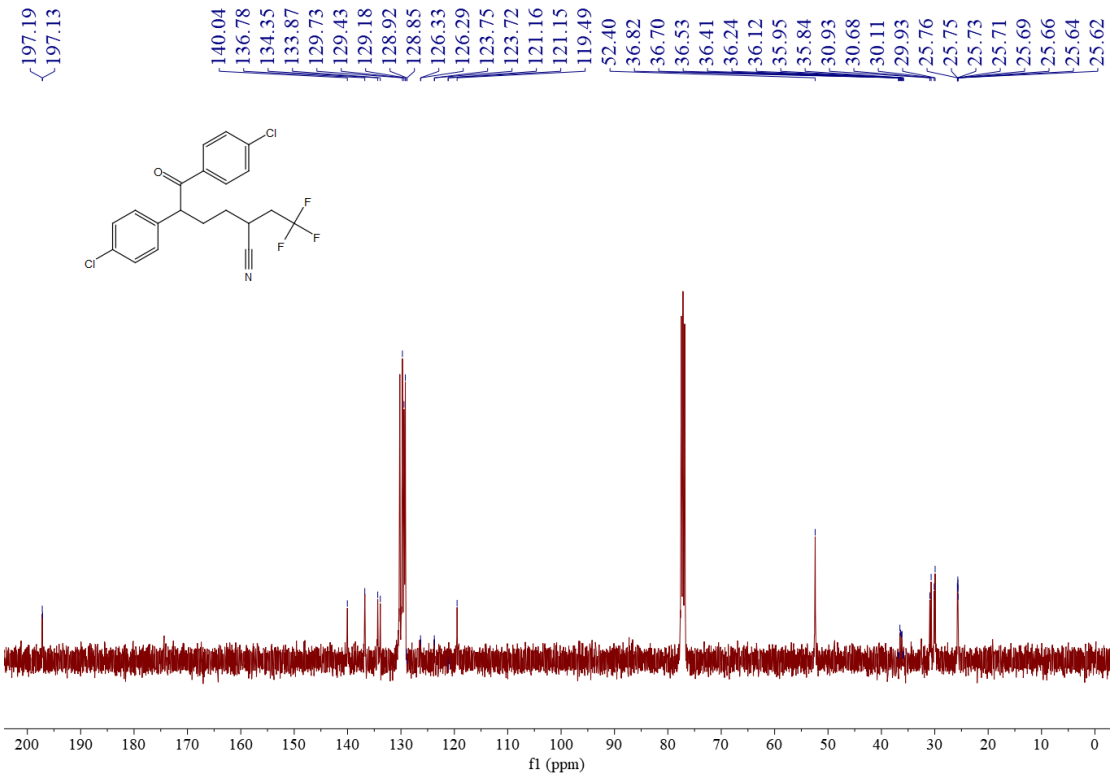
4v ^{19}F NMR (376 MHz, Chloroform-*d*)



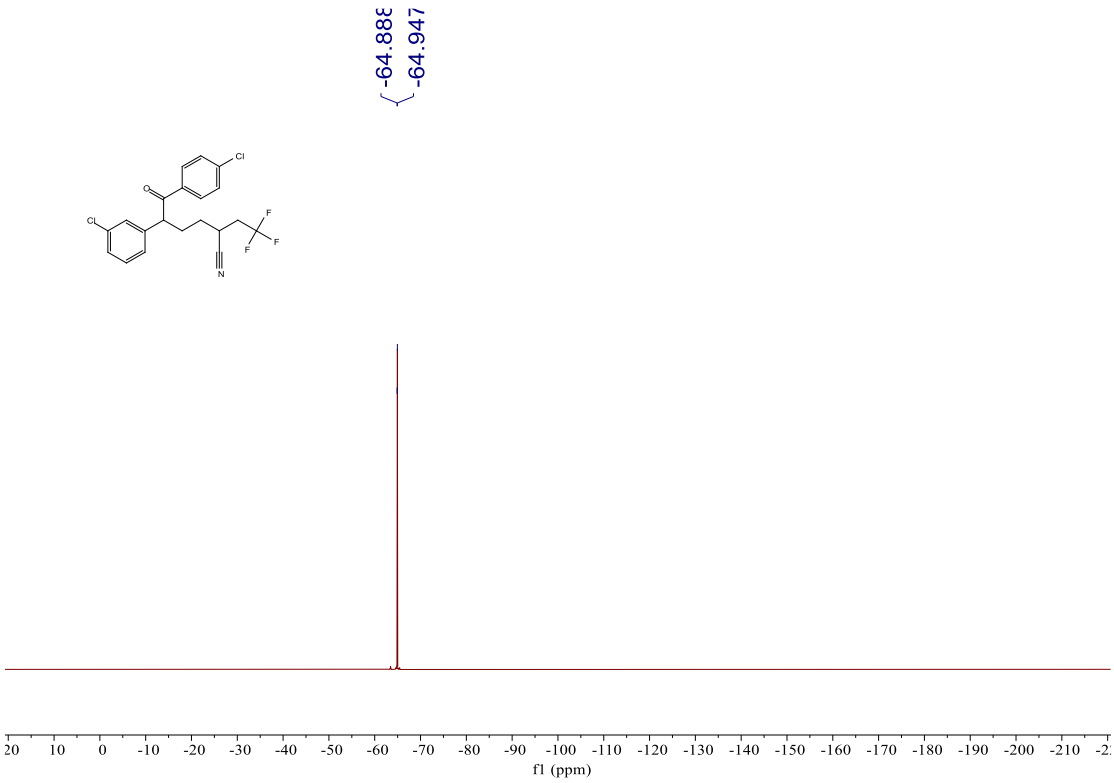
4w ^{1}H NMR 400 MHz, Chloroform-*d*)/ ^{13}C NMR (101 MHz, Chloroform-*d*)



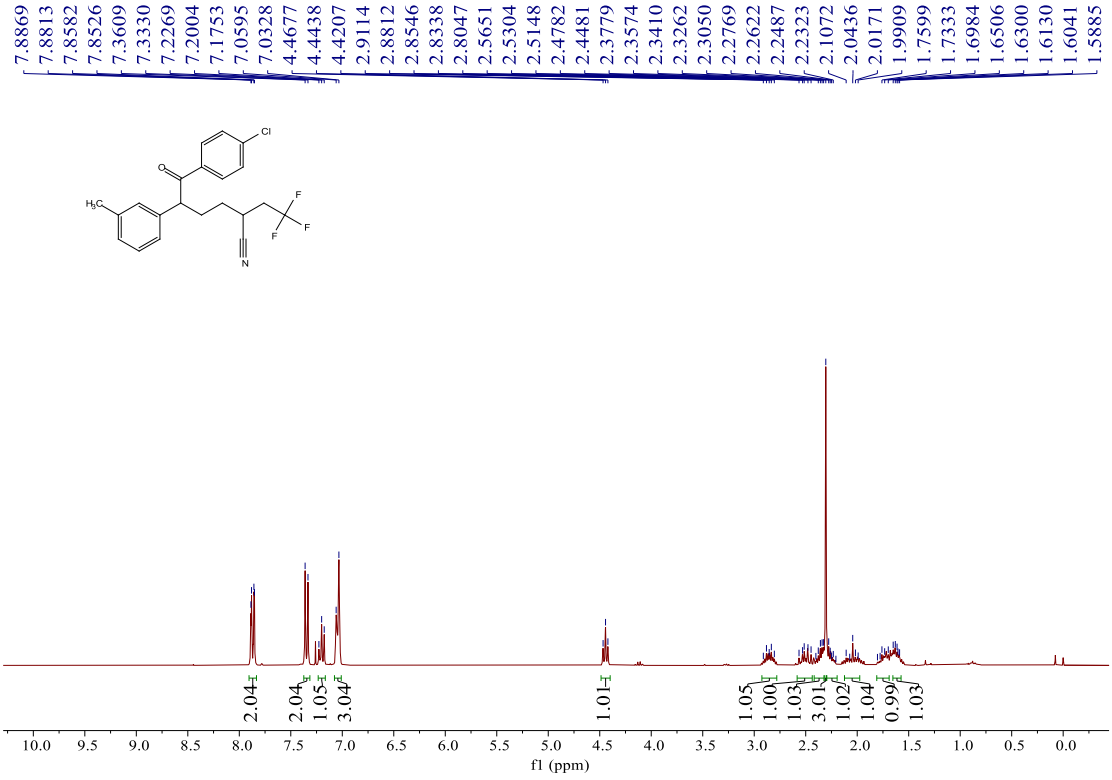
4w ^{13}C NMR (101 MHz, Chloroform-*d*)



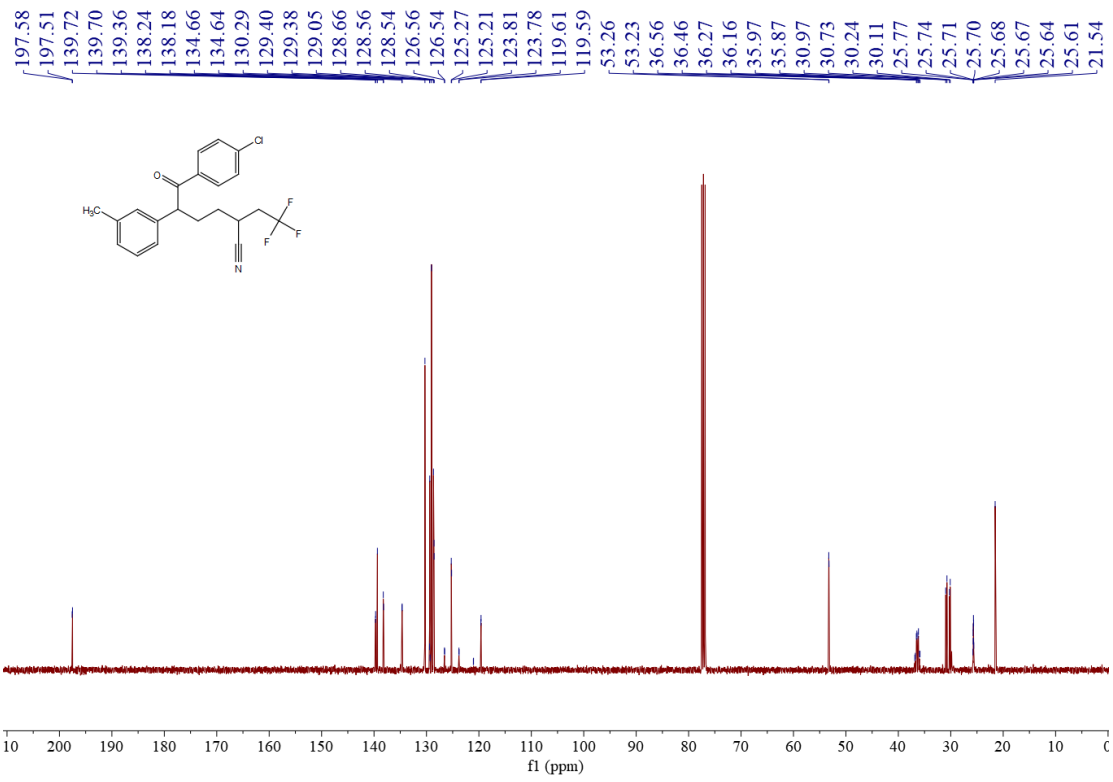
4w ^{19}F NMR (282 MHz, Chloroform-*d*)



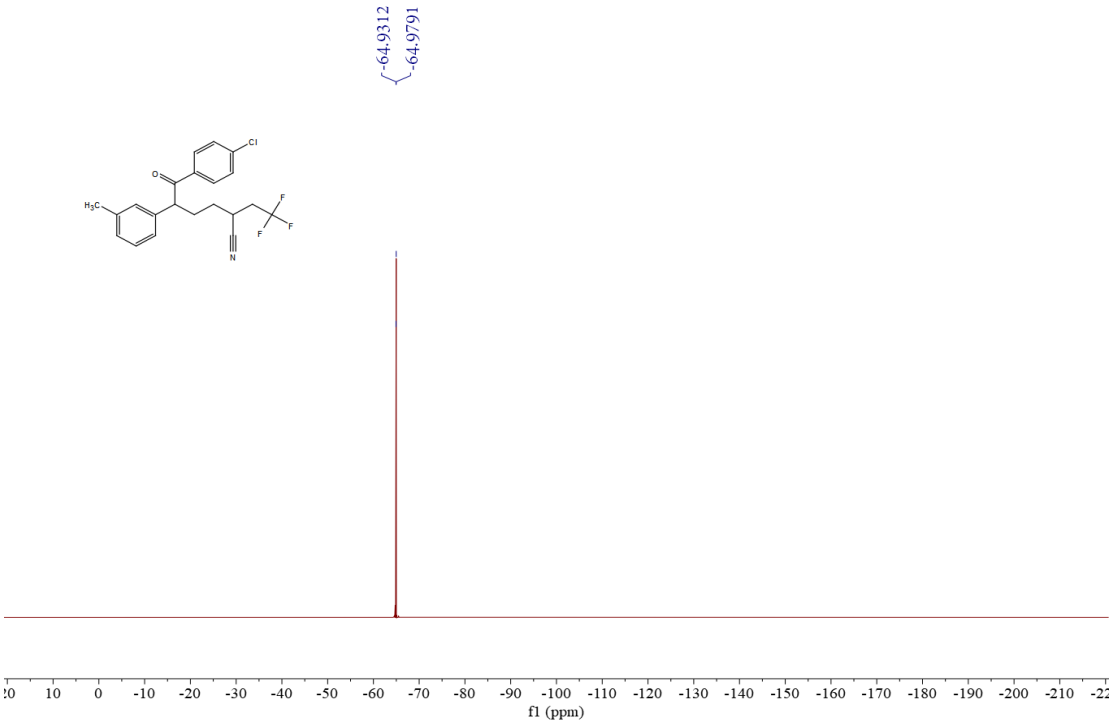
4x ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



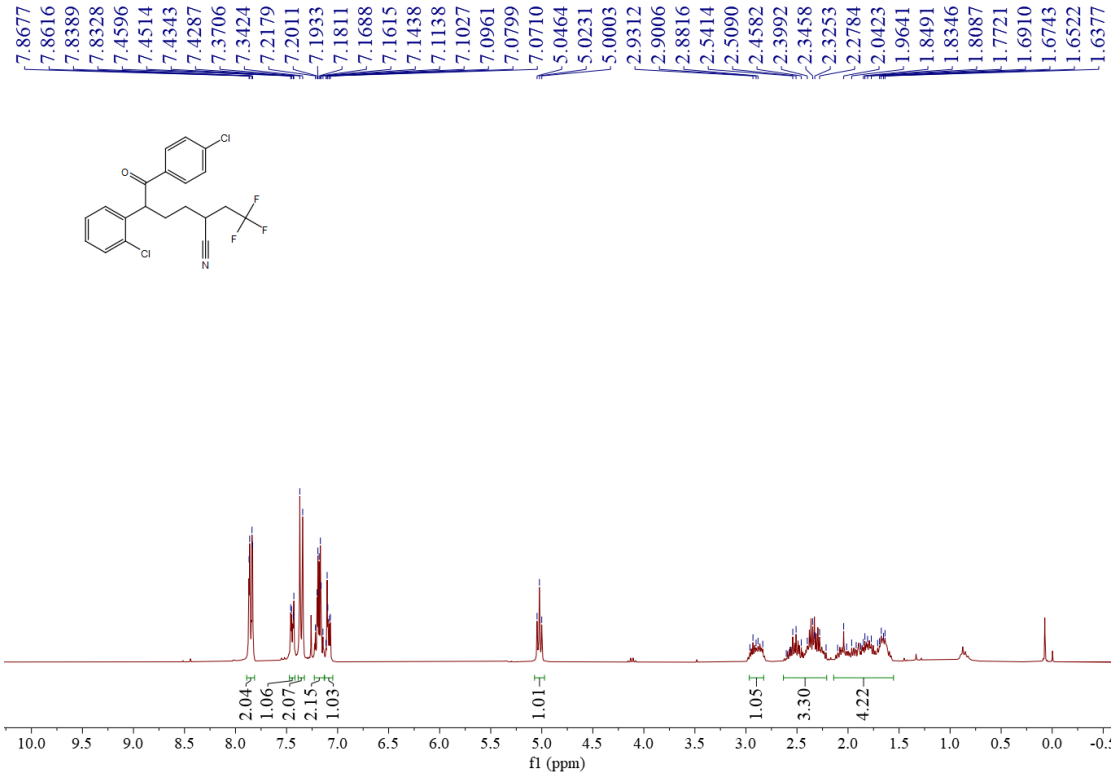
4x ^{13}C NMR (101 MHz, Chloroform-*d*)



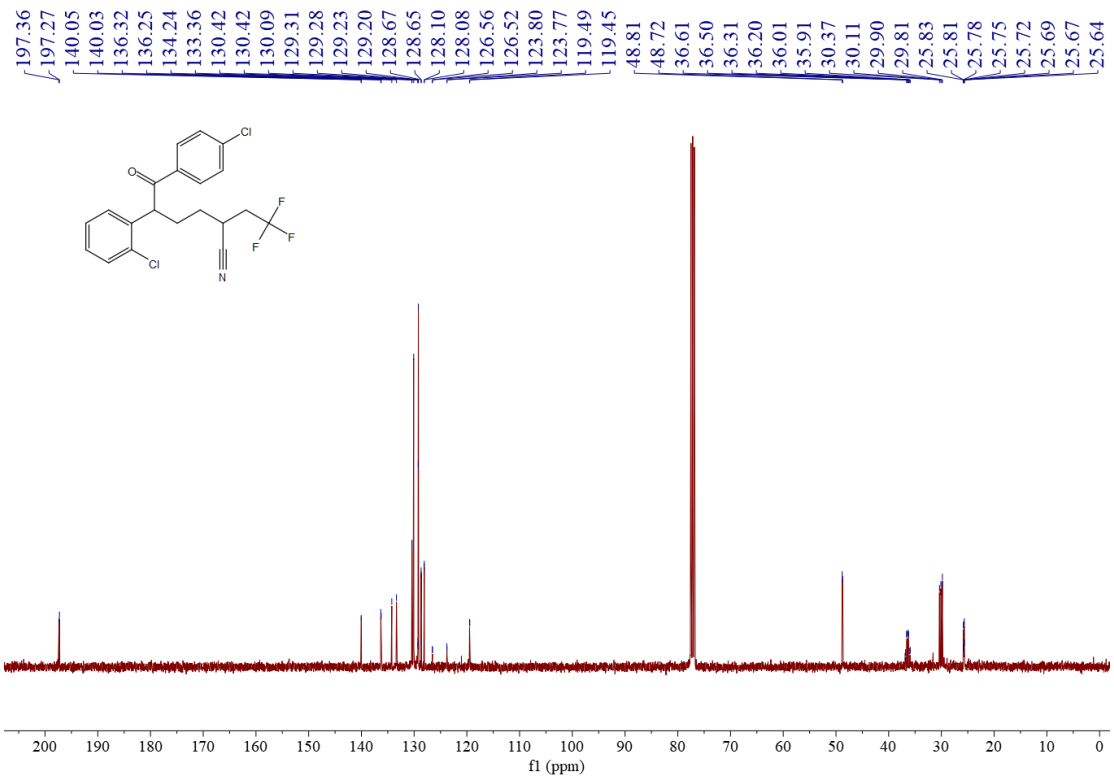
4x ^{19}F NMR (282 MHz, Chloroform-*d*)



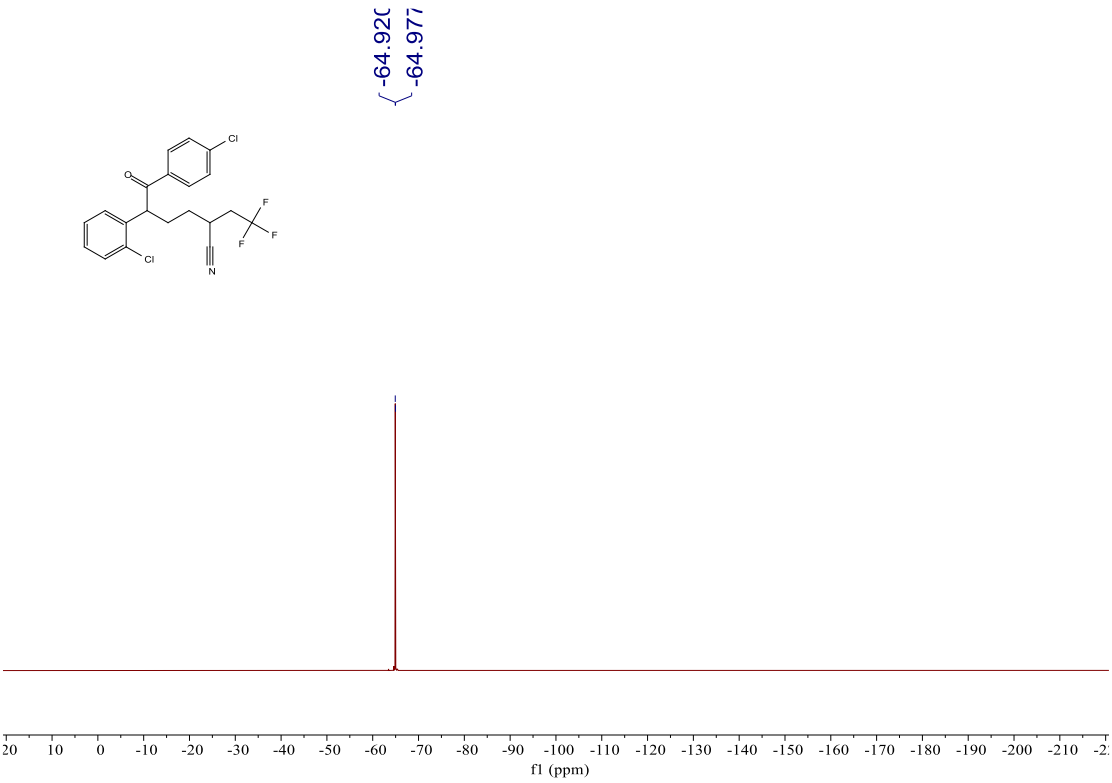
4y ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



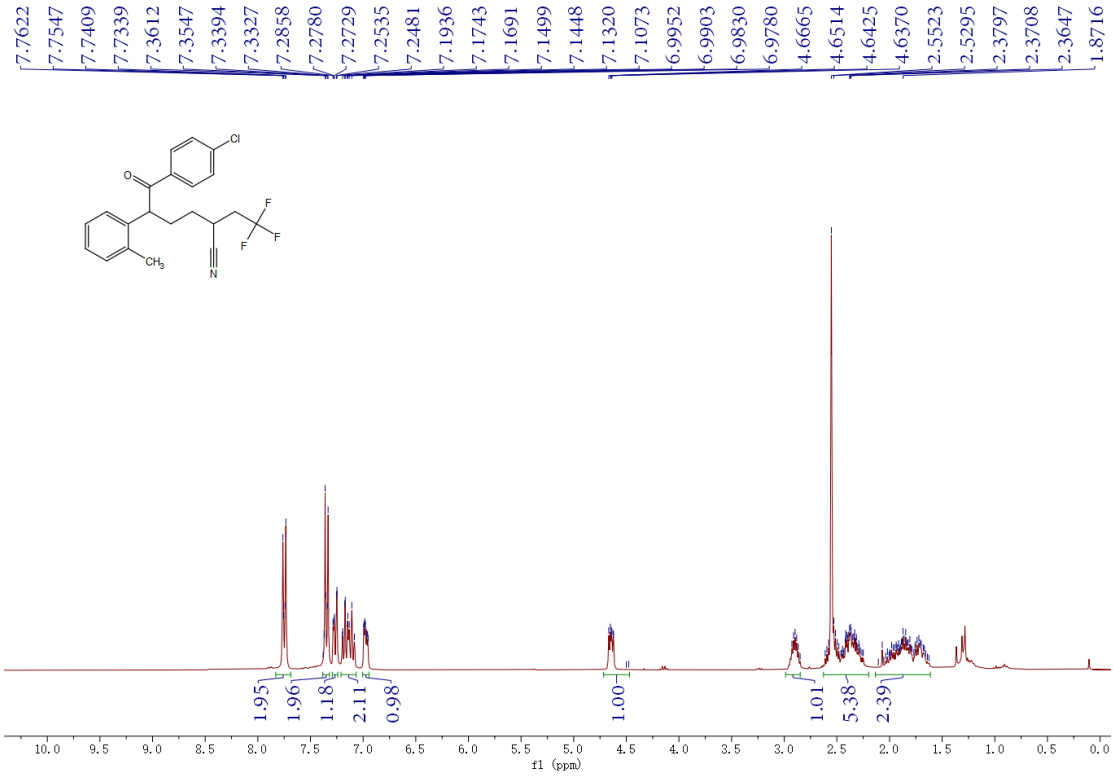
4y ^{13}C NMR (101 MHz, Chloroform-*d*)



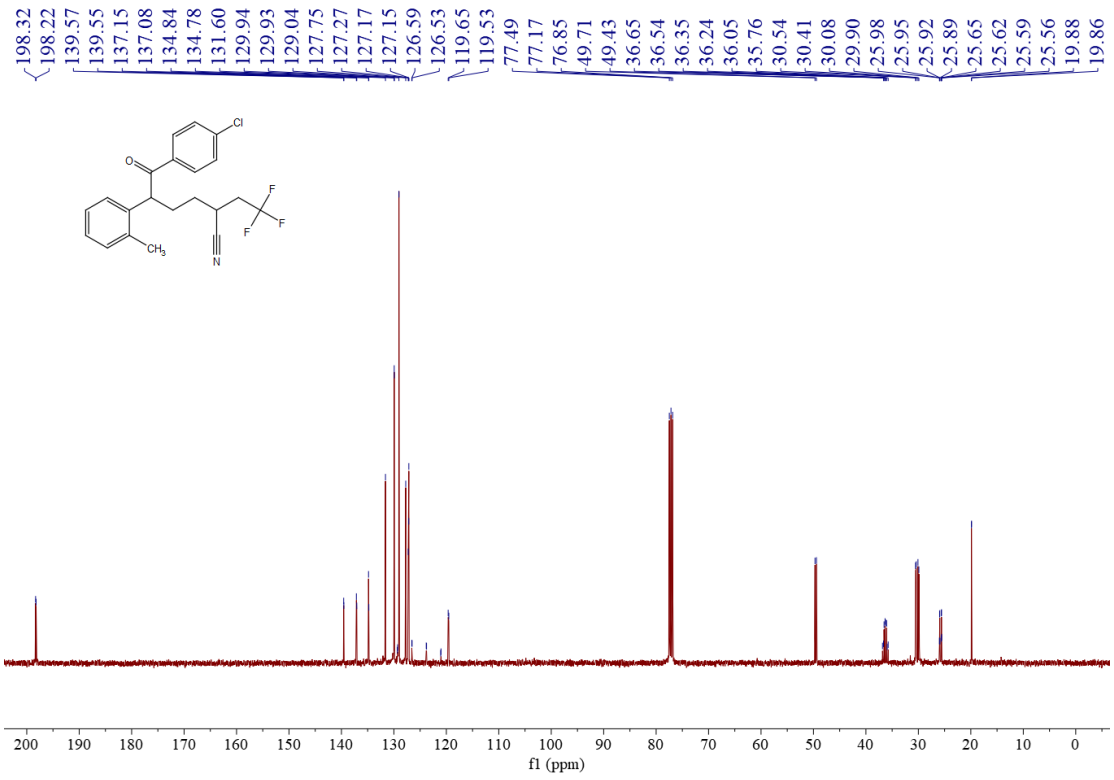
4y ^{19}F NMR (282MHz, Chloroform-*d*)



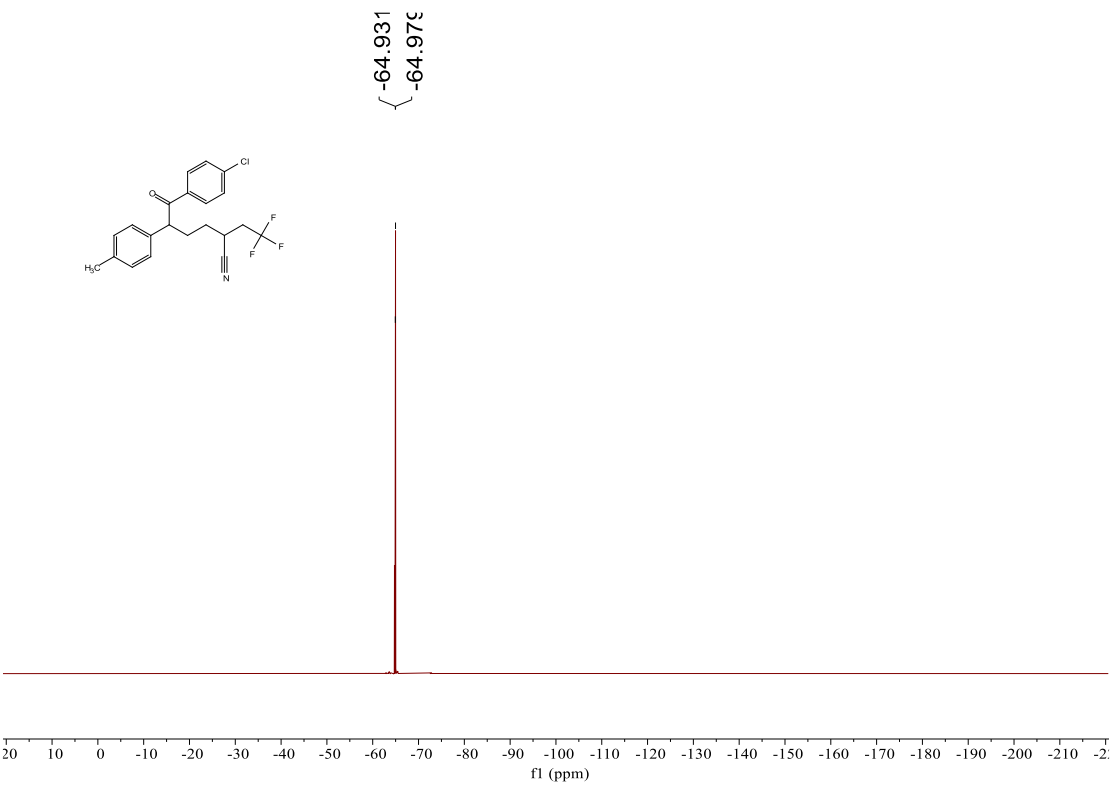
4z ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



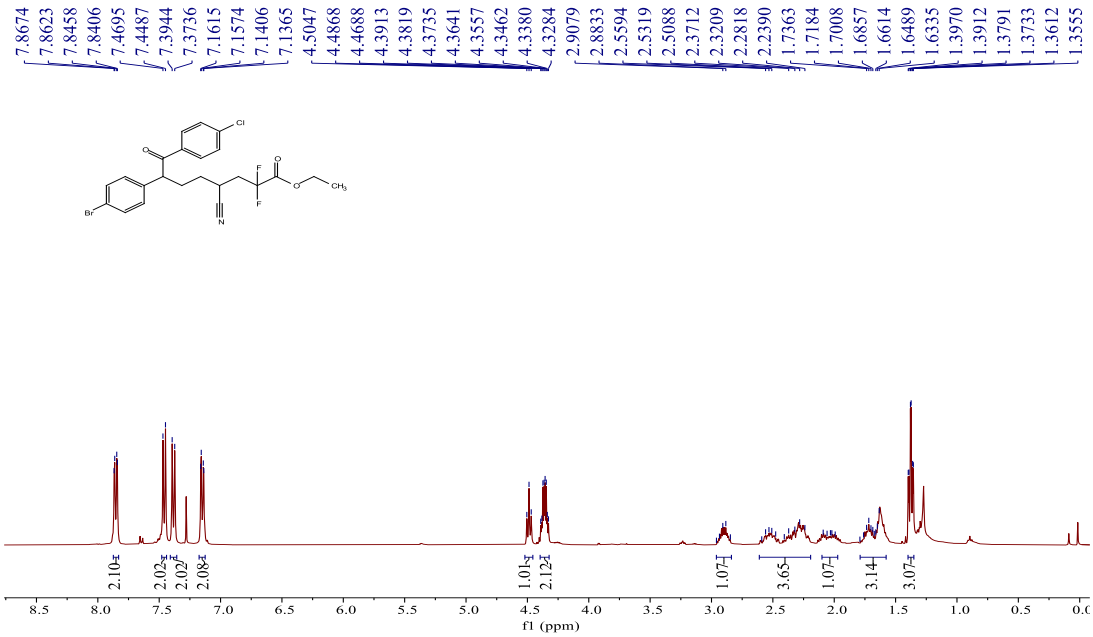
4z ^{13}C NMR (101 MHz, Chloroform-*d*)



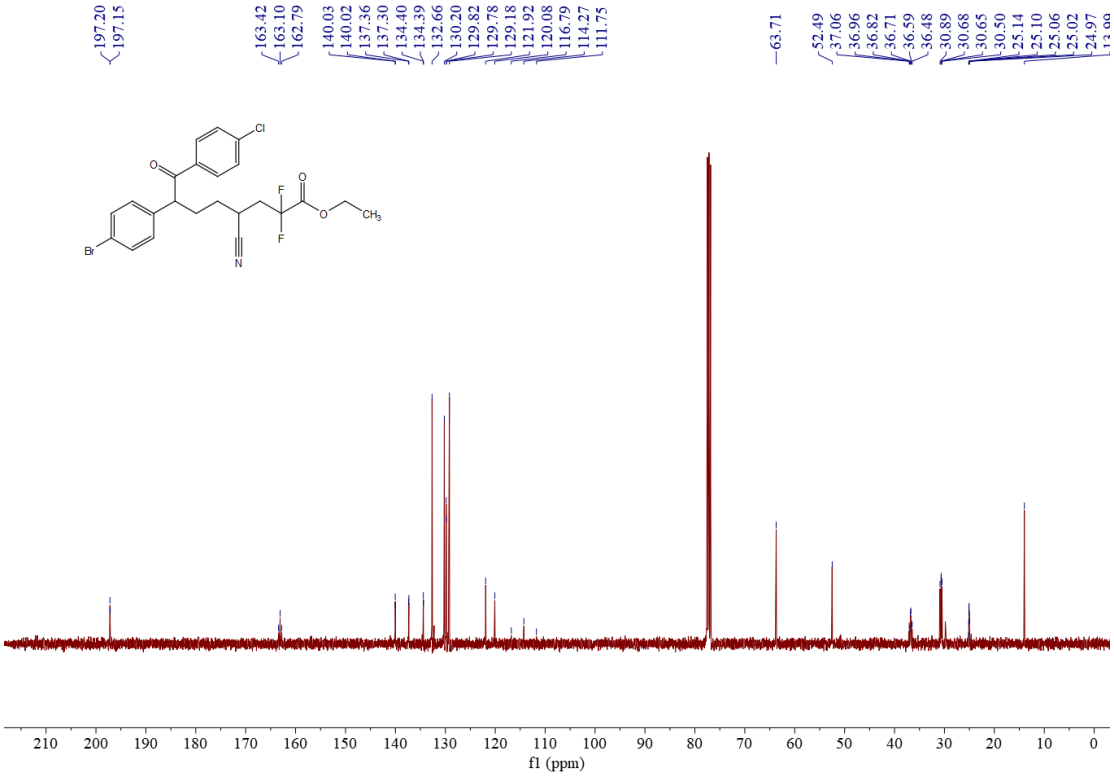
4z ^{19}F NMR (282 MHz, Chloroform-*d*)



4aa[1]H NMR (400 MHz, Chloroform-*d*)



4aa [13]C NMR (101 MHz, Chloroform-*d*)



4aa[19]F NMR (282 MHz, Chloroform-*d*)

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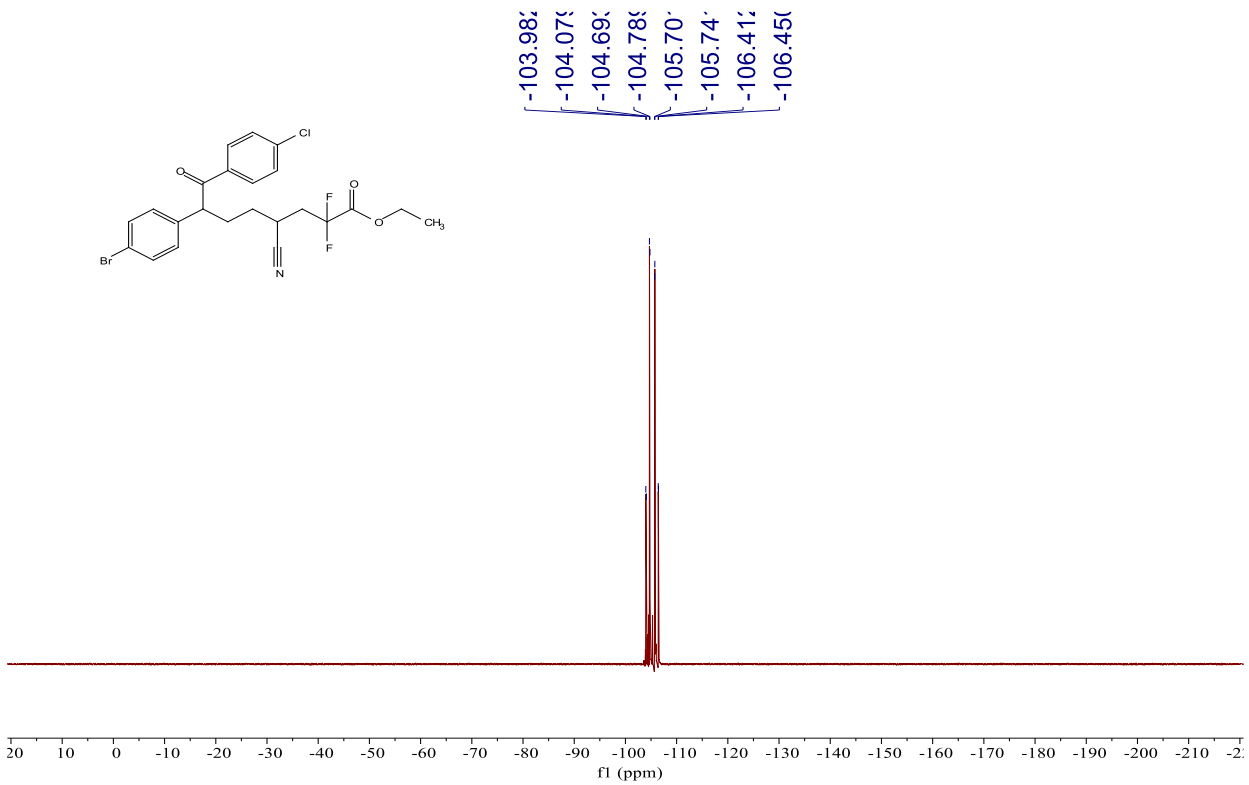
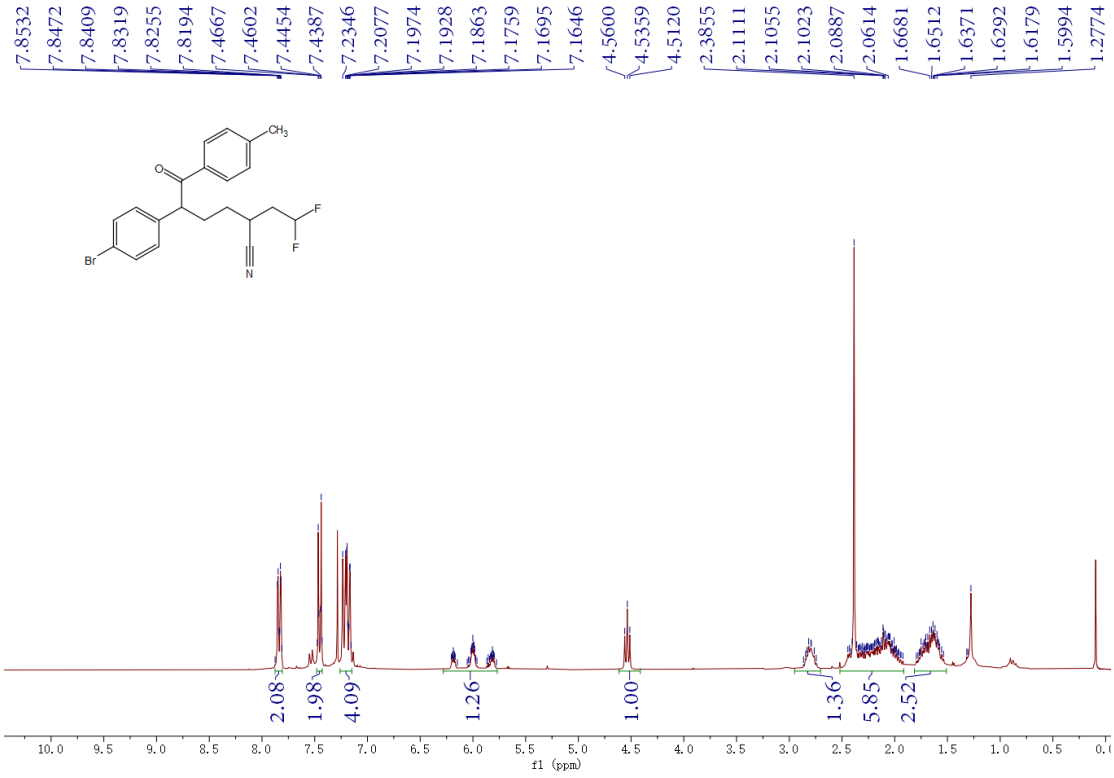
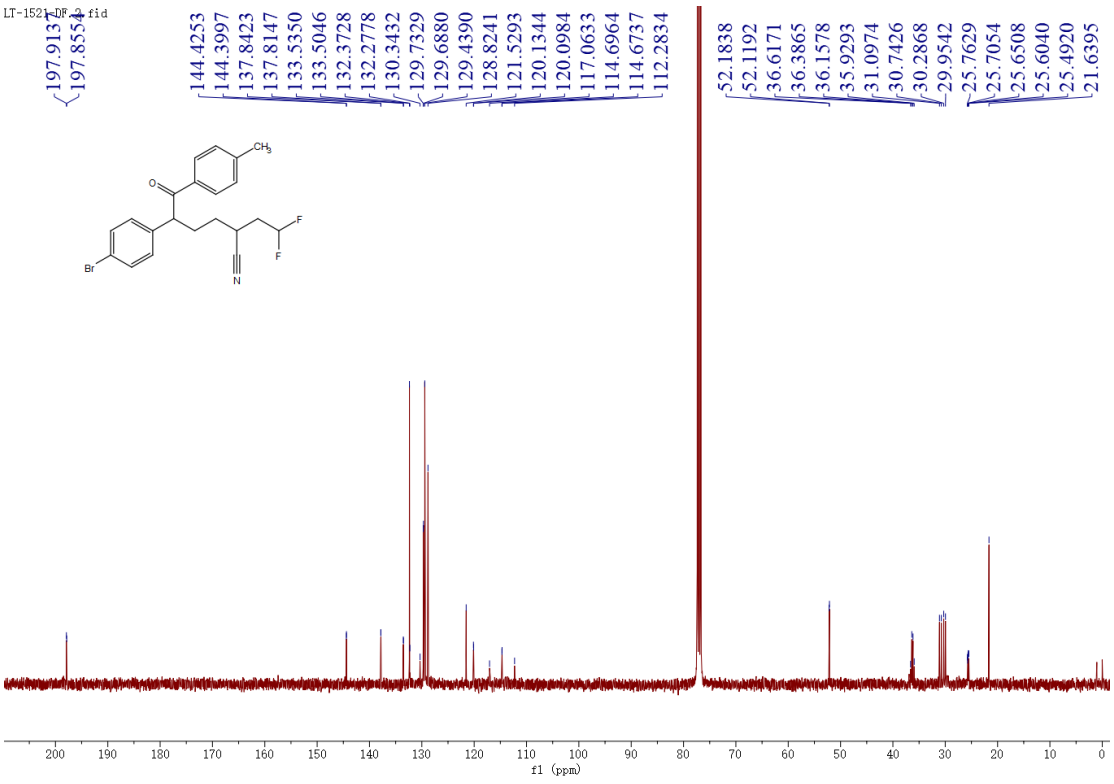

-103.98
-104.07
-104.69
-104.78
-105.70
-105.74
-106.41
-106.45
Cl
O
F
O
O
CH3
Br
F
N
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

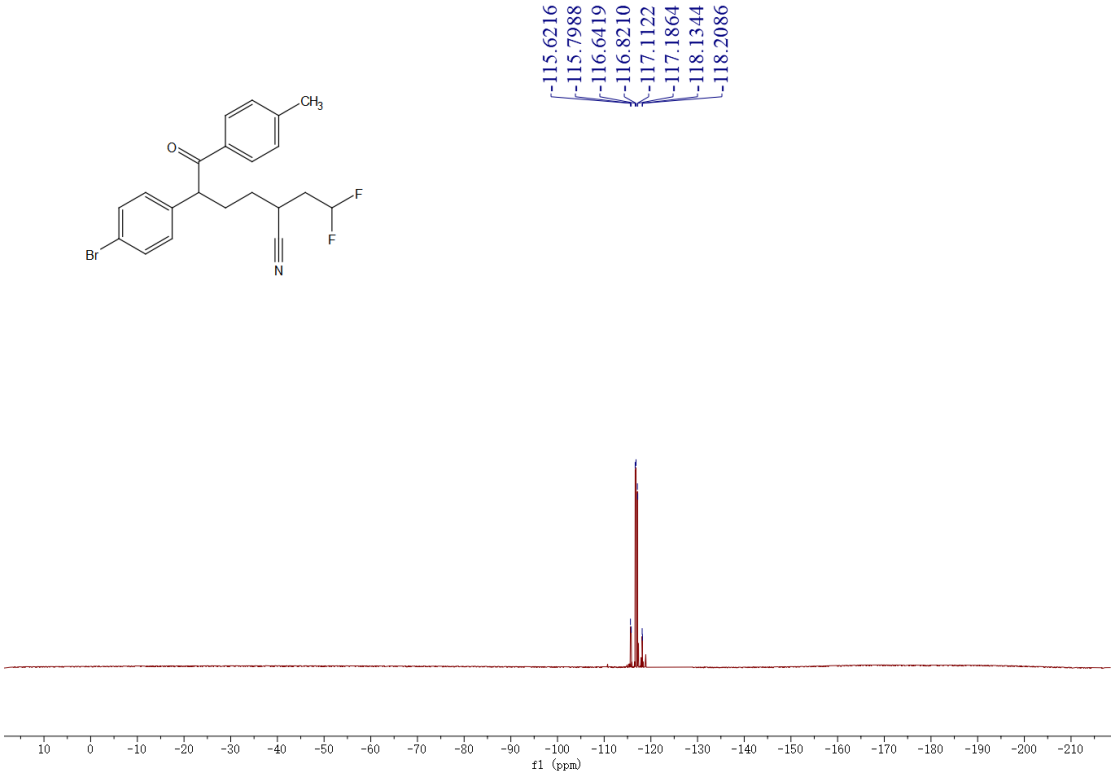
4ab ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C (75 MHz, Chloroform-*d*)



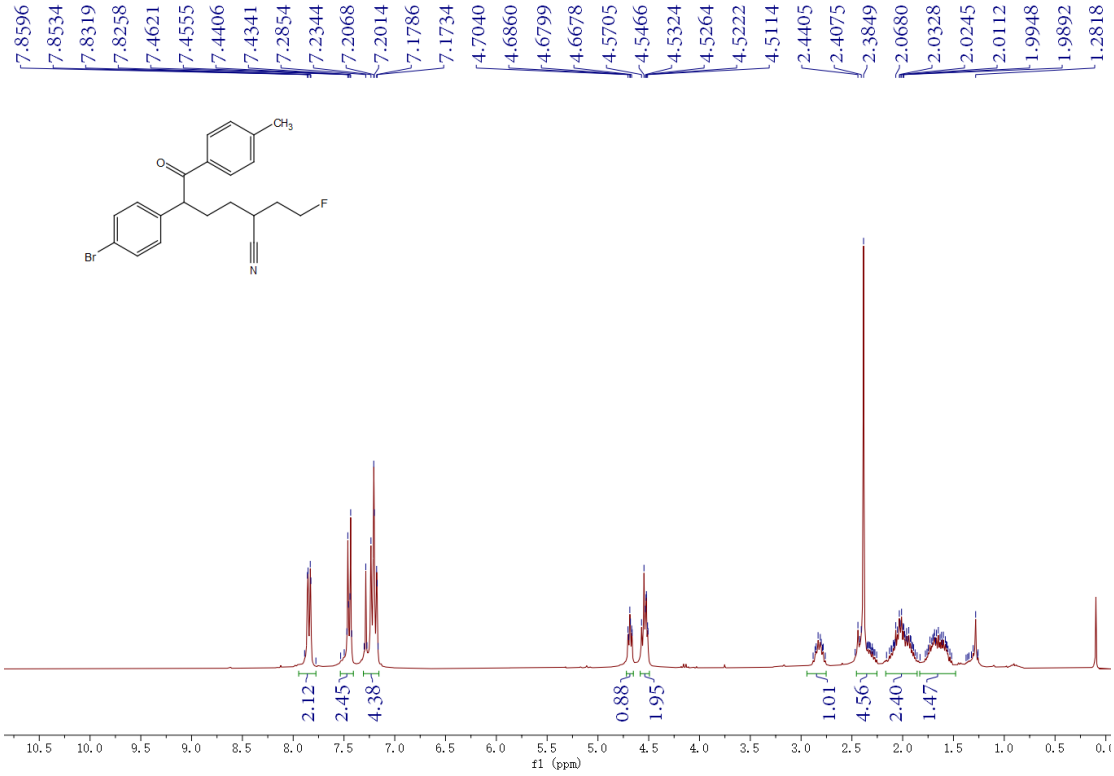
4ab ^{13}C (75 MHz, Chloroform-*d*)



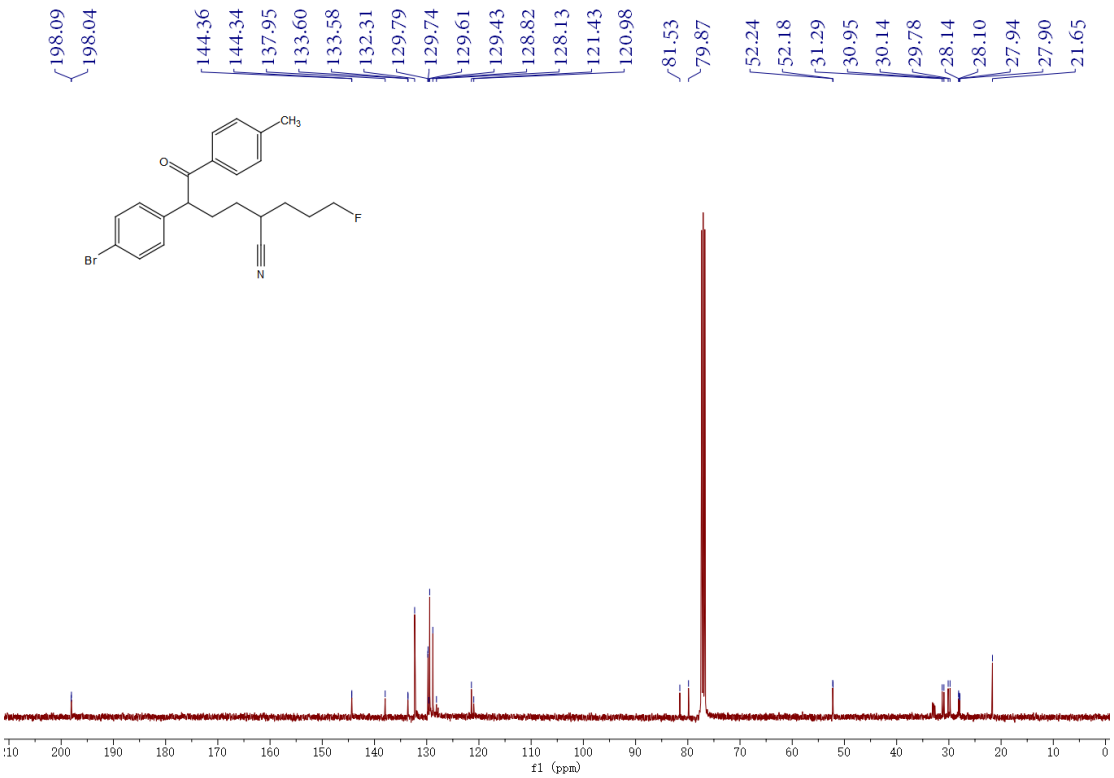
4ab ^{19}F NMR (376 MHz, Chloroform-*d*)



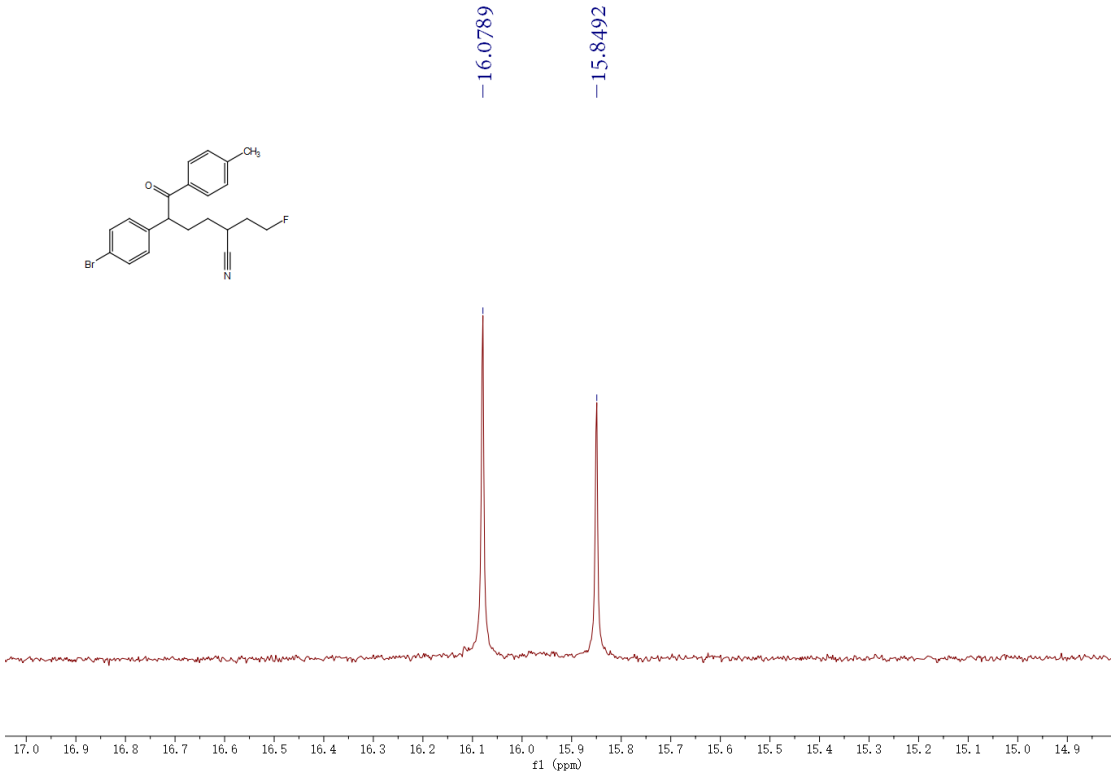
4ac ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C(101 MHz,Chloroform-*d*)



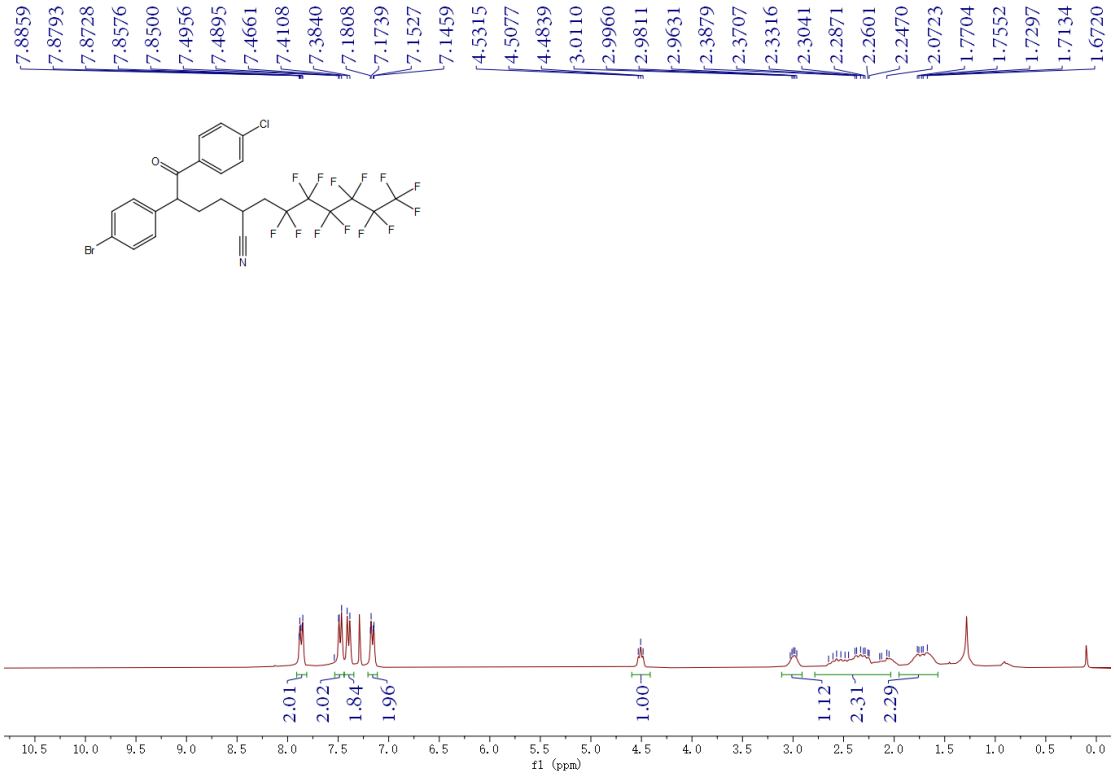
4ac ^{13}C(101 MHz,Chloroform-*d*)



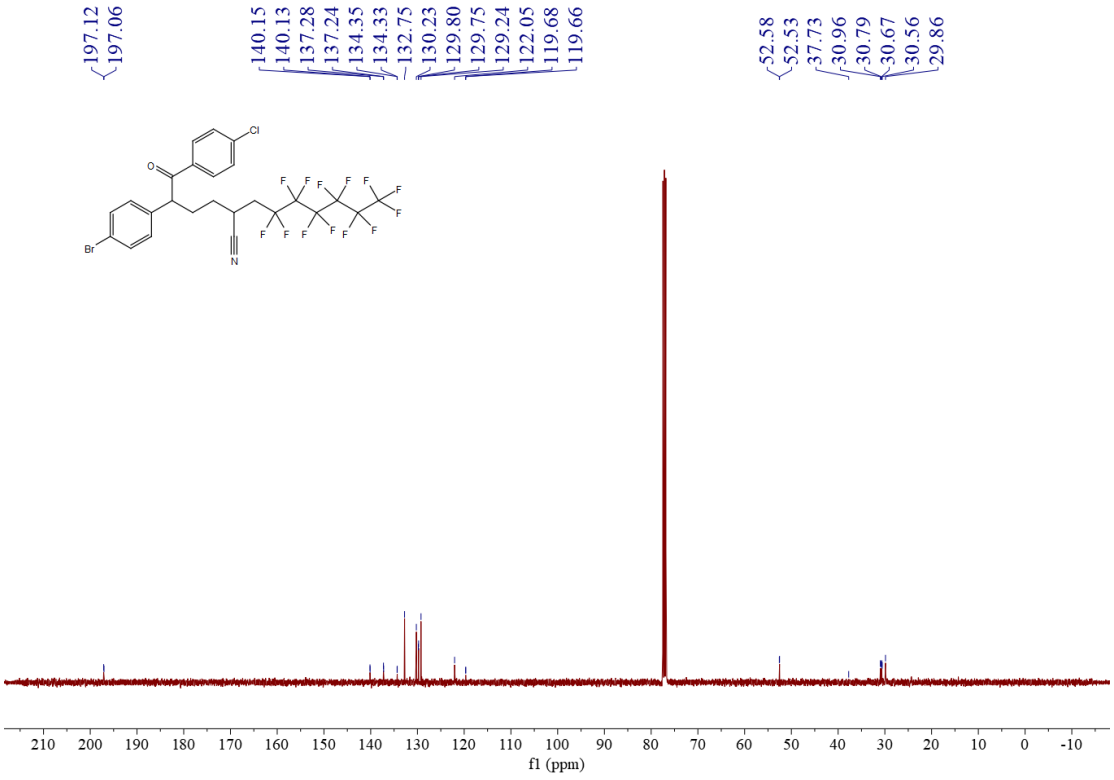
4ac ^{19}F NMR (282 MHz, Chloroform-*d*)



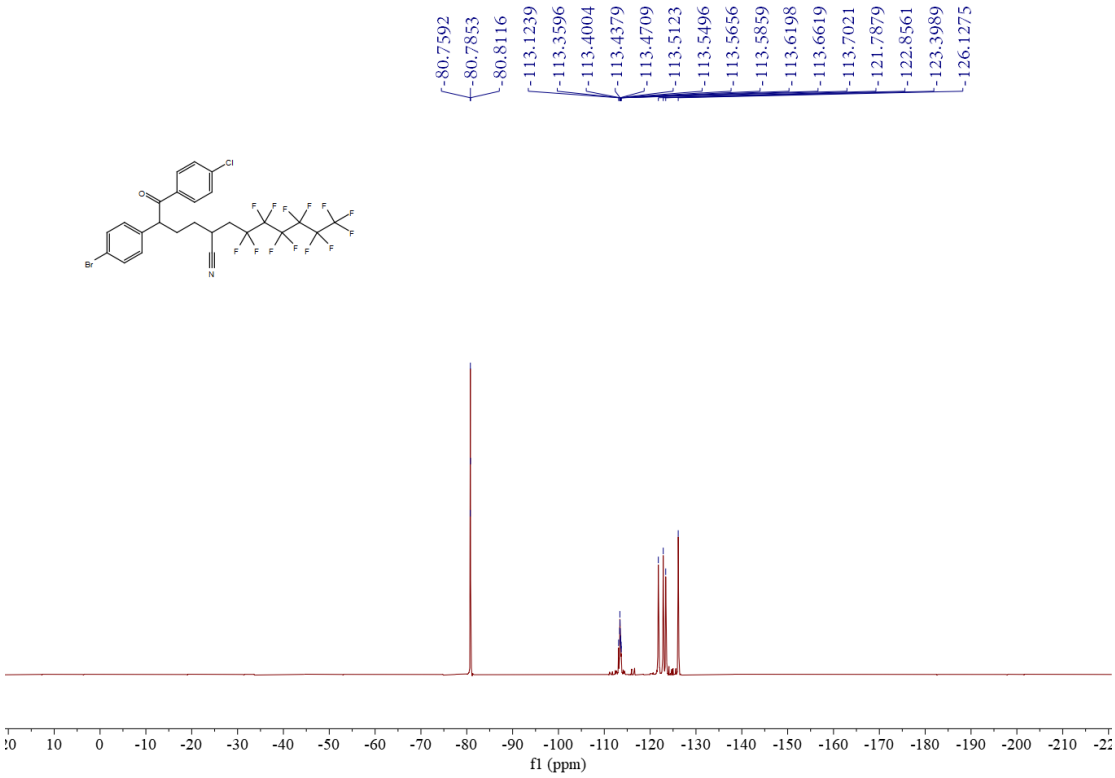
4ad^{1}H NMR (300 MHz, Chloroform-*d*) /^{13}C NMR (101 MHz, Chloroform-*d*)



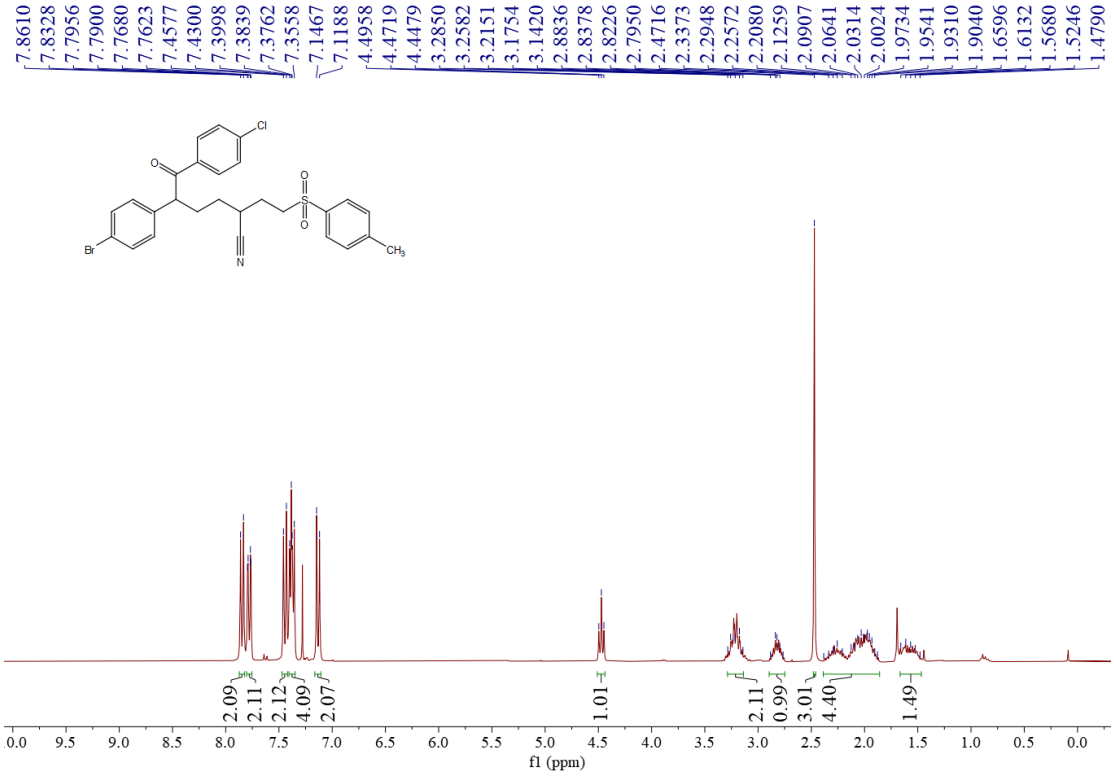
4ad ^{13}C NMR (101 MHz, Chloroform-*d*)



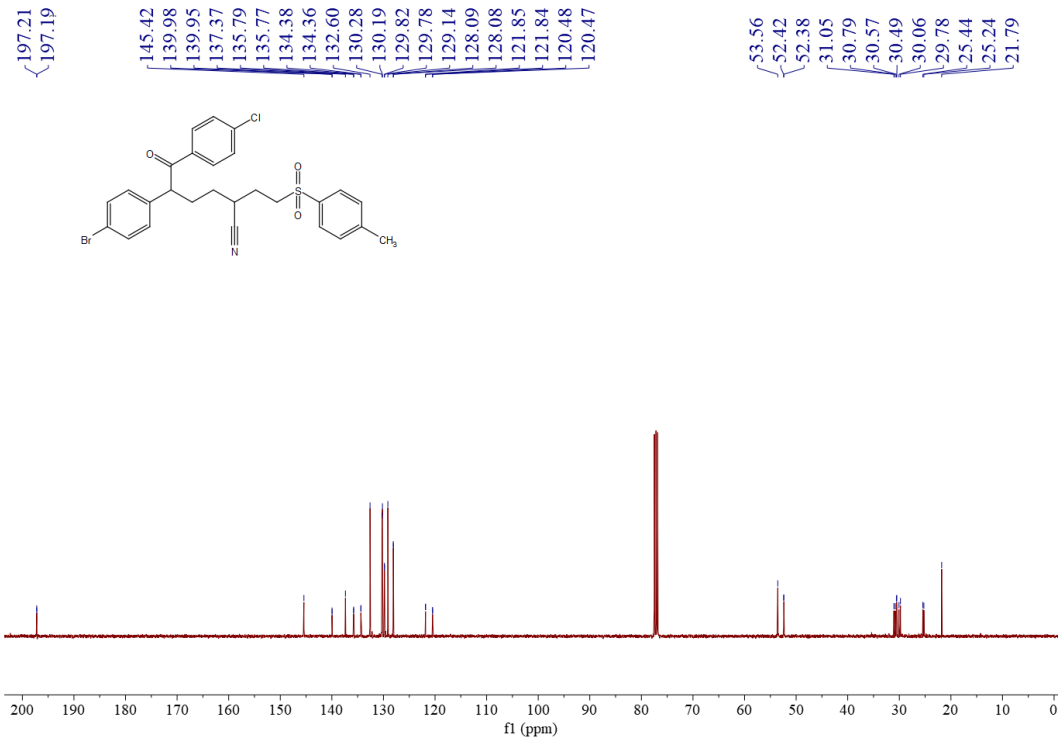
4ad ^{19}F NMR (282 MHz, Chloroform-*d*)



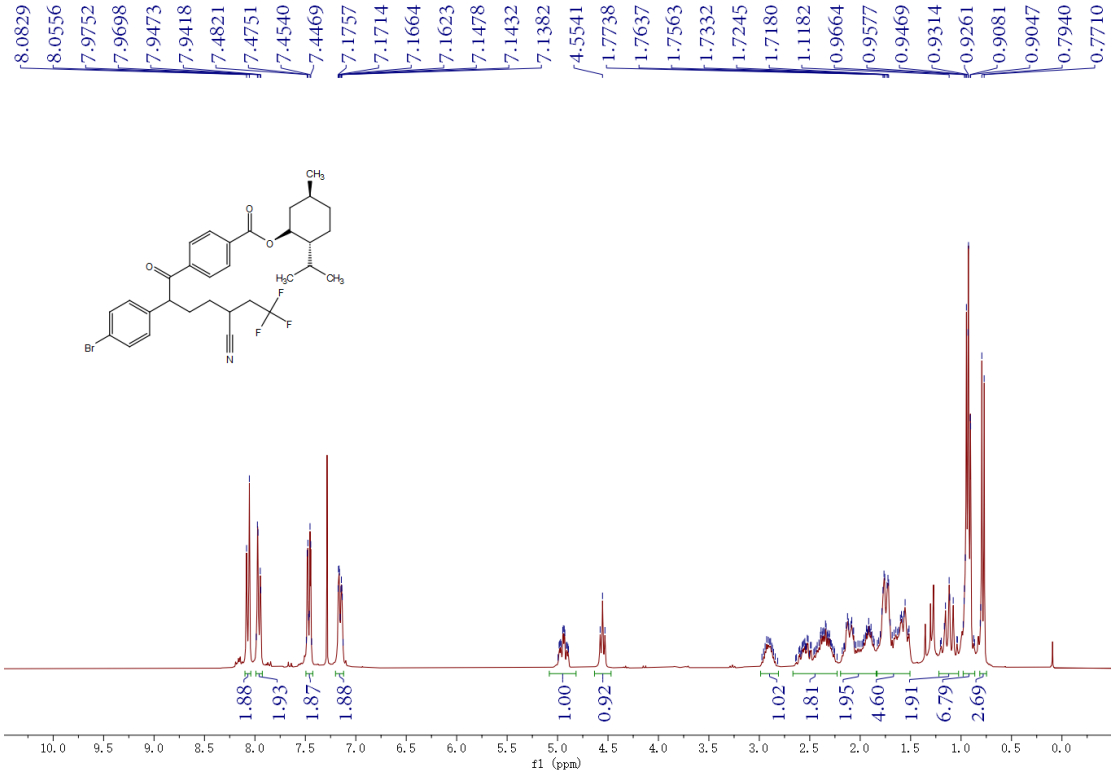
4ae ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



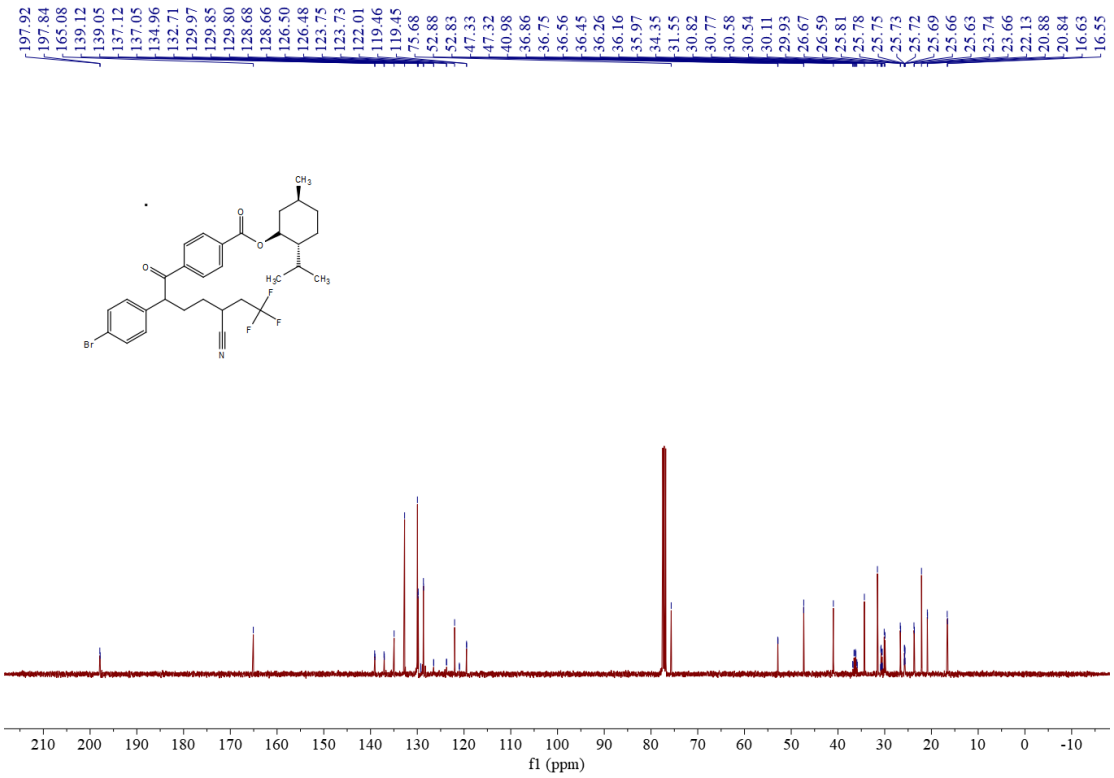
4ae ^{13}C NMR (101 MHz, Chloroform-*d*)



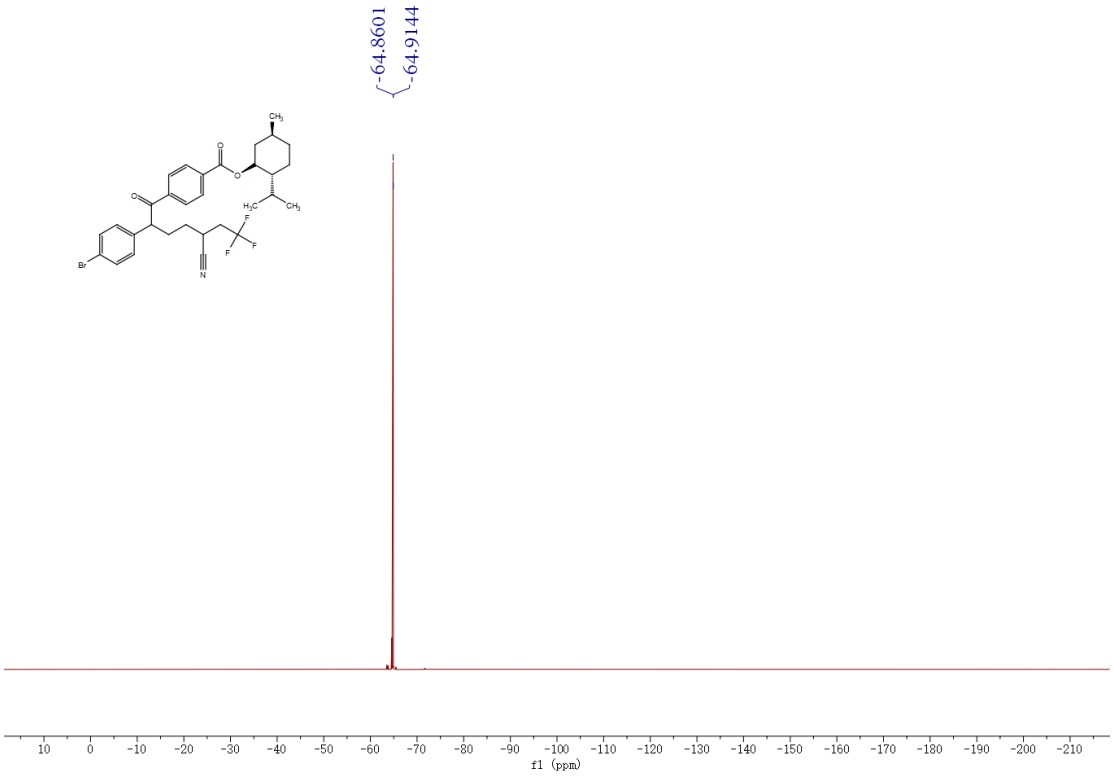
4af ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



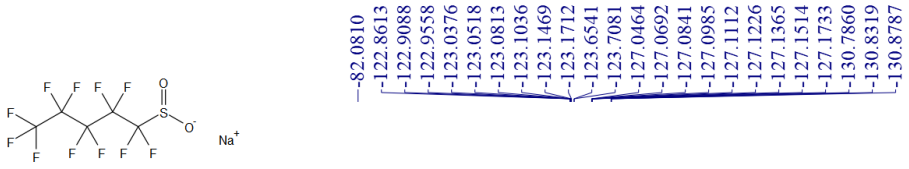
4af ^{13}C NMR (101 MHz, Chloroform-*d*)

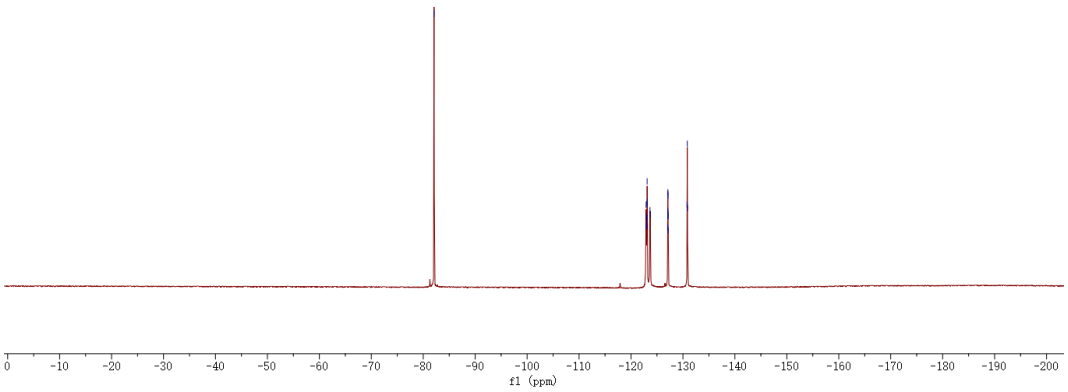


4af ^{19}F NMR (282MHz, Chloroform-*d*)

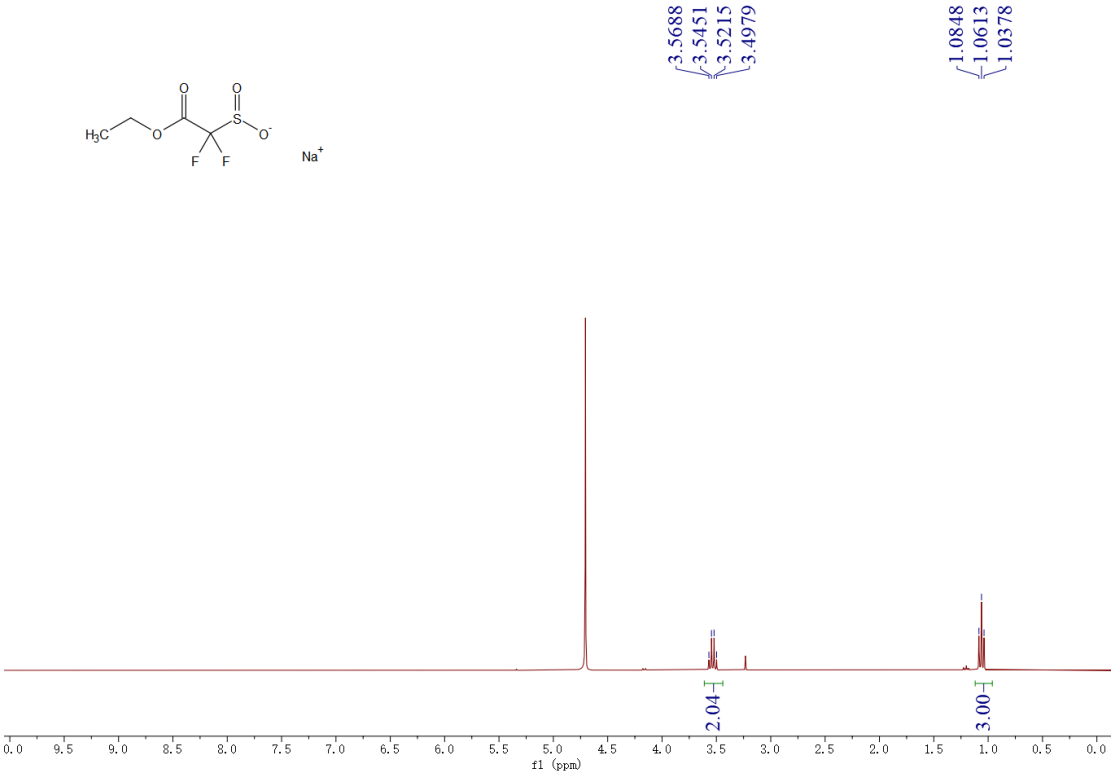


3ad ^{19}F NMR (282M，Deuterium oxide)

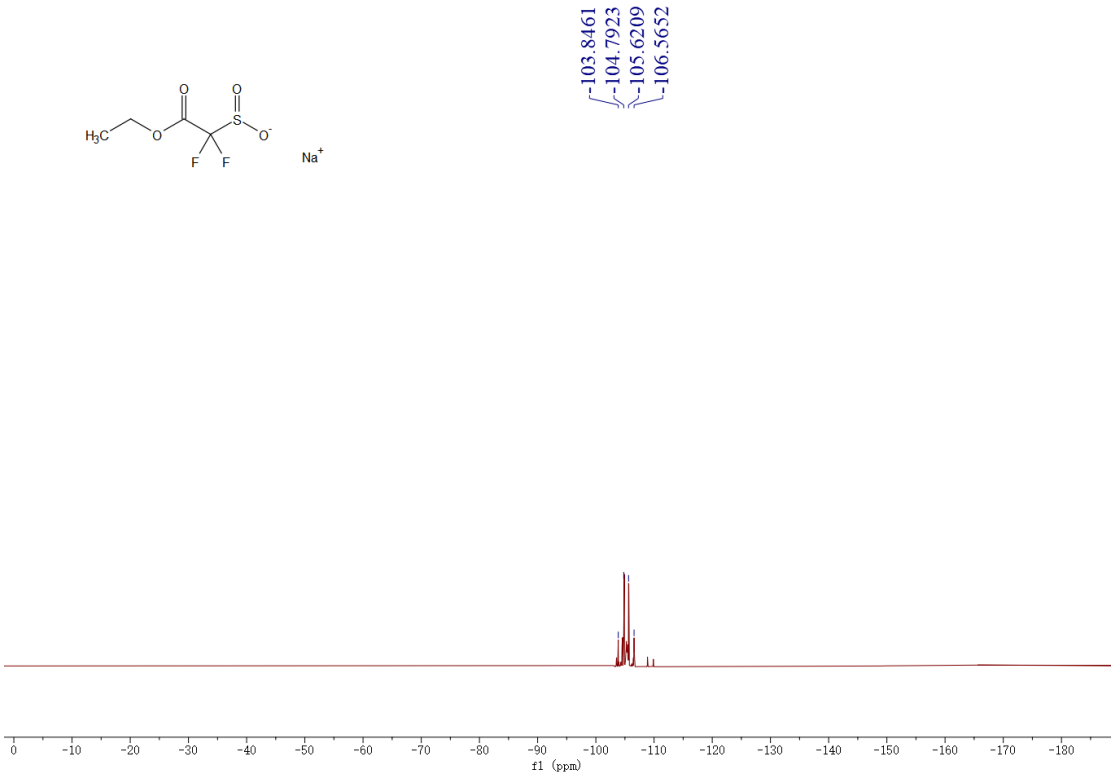




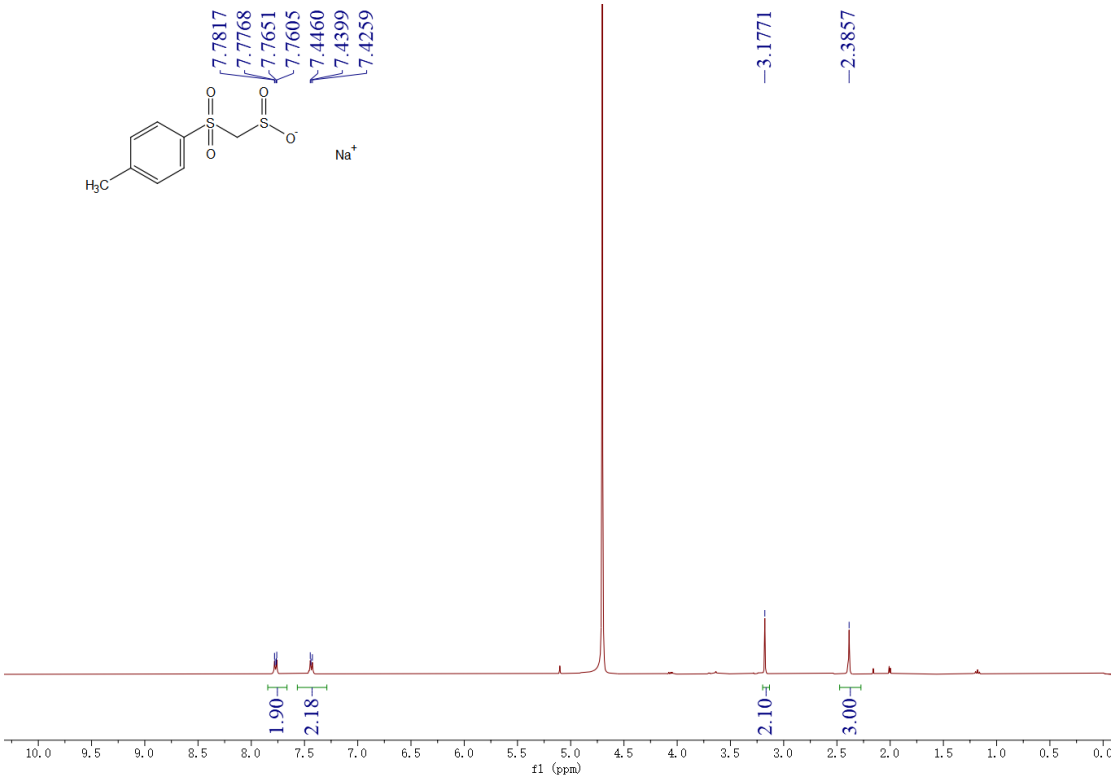
3aa ^{1}H NMR (300 MHz, Deuterium oxide)/^{19}F NMR (282M，Deuterium oxide)



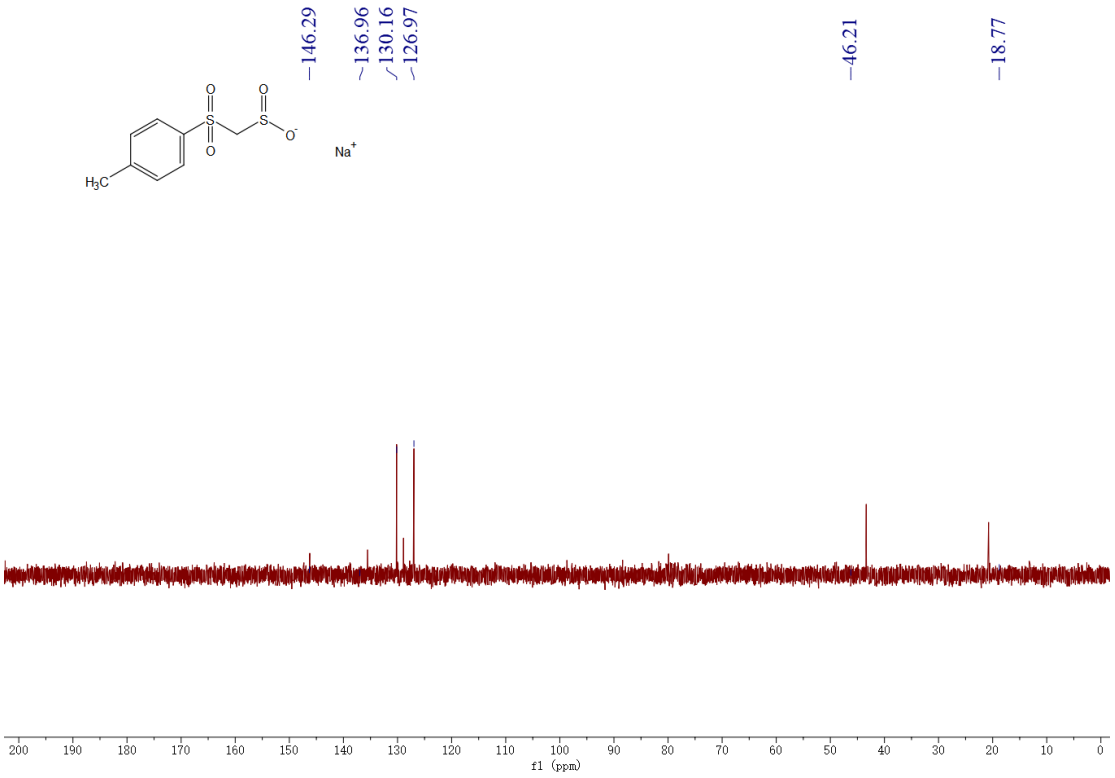
3aa ^{19}F NMR (282M，Deuterium oxide)



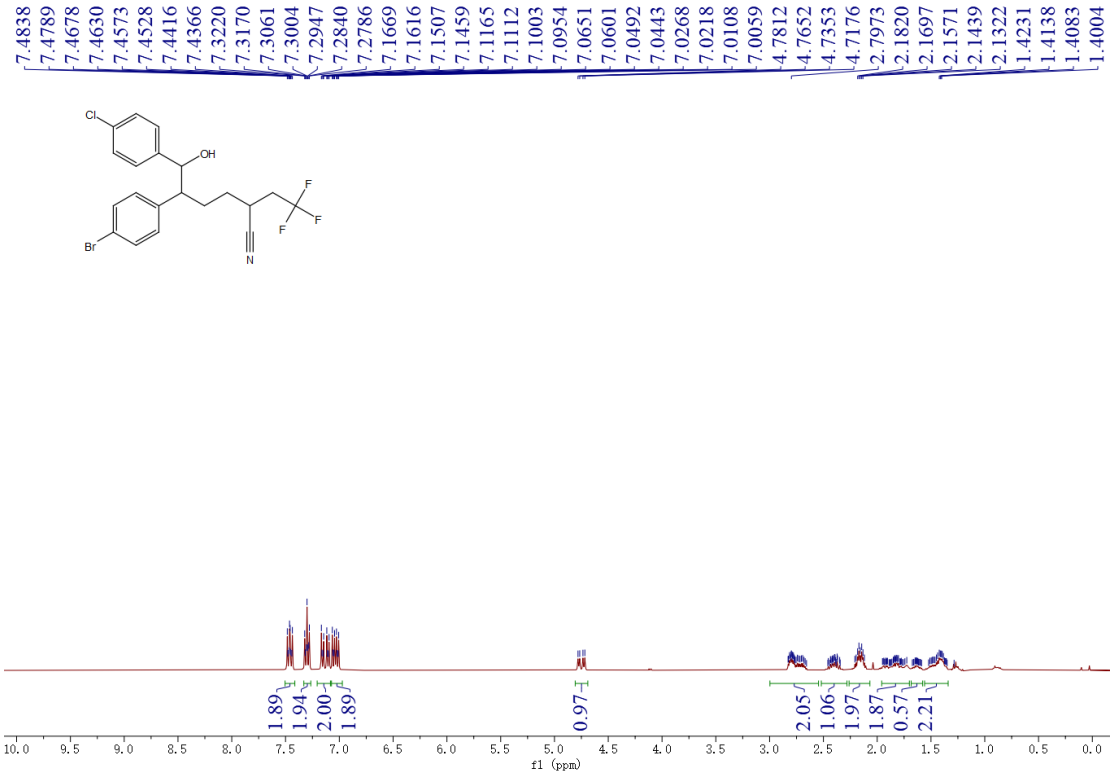
3ae ^{1}H NMR (300 MHz, Deuterium oxide)



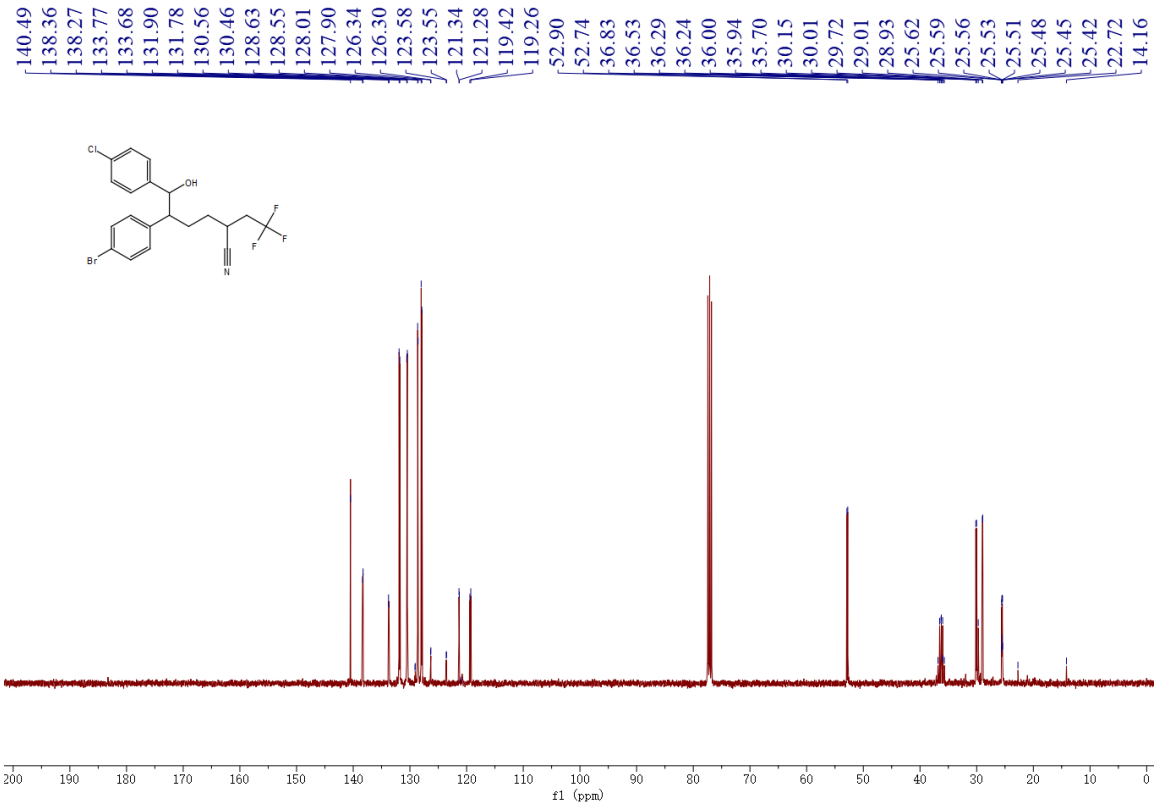
3ae ^{13}C NMR (101 MHz, Deuterium oxide)



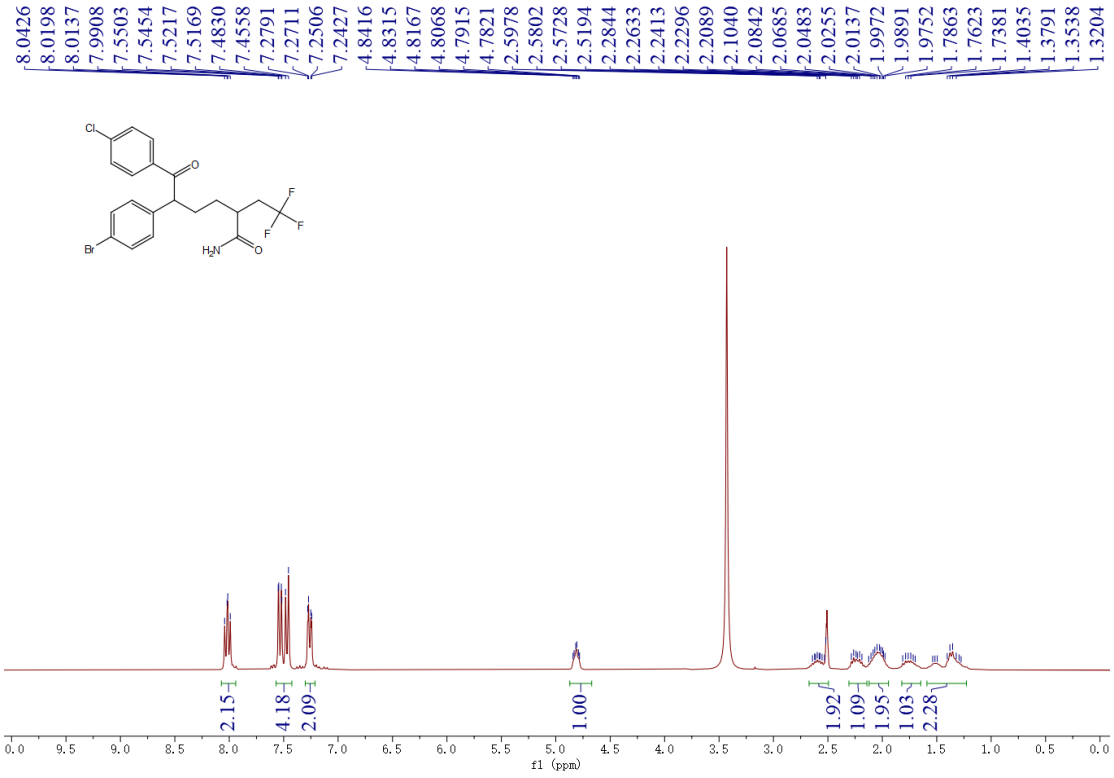
5 ^{1}H NMR (300 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



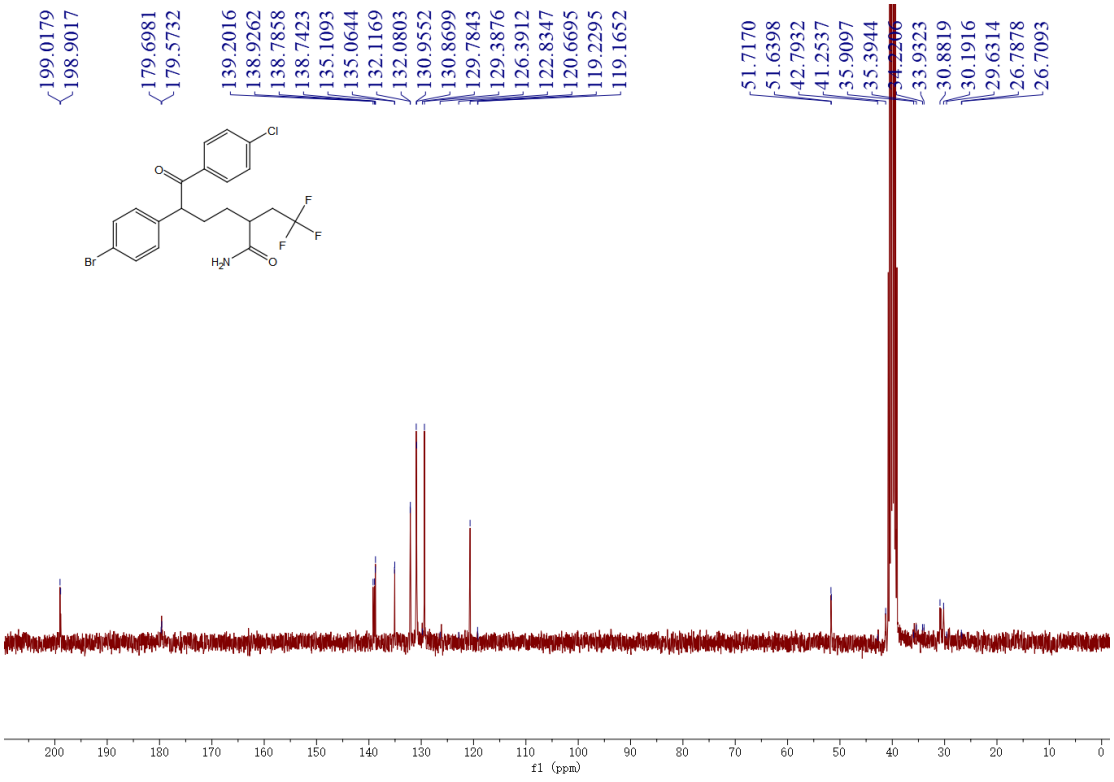
5 ^{13}C NMR (101 MHz, Chloroform-*d*)



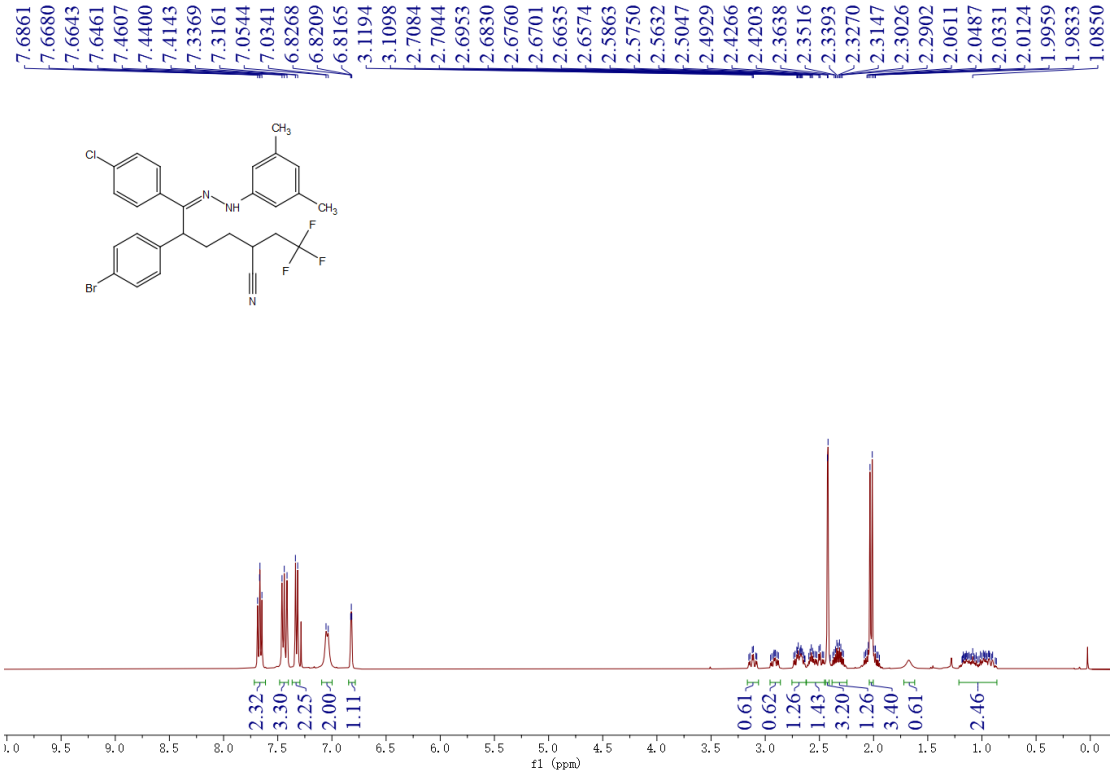
6 ^{1}H NMR (400 MHz, Dimethyl sulfoxide-*d*6)/^{13}C(75 MHz, Dimethyl sulfoxide-*d*6)



6 ^{13}C (75 MHz, Dimethyl sulfoxide-*d*6)



7 ^{1}H NMR (400 MHz, Chloroform-*d*)/^{13}C NMR (101 MHz, Chloroform-*d*)



7 ^{13}C NMR (101 MHz, Chloroform-*d*)