Supporting Information

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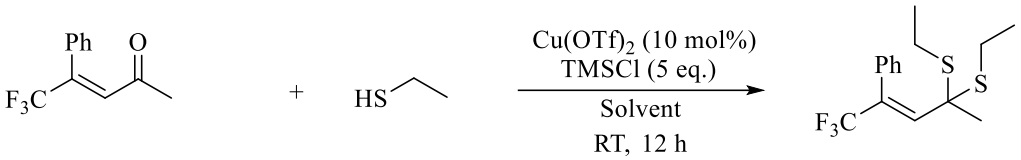
General Information

All commercially available reagents were used without further purification. Column chromatography was performed on silica gel (200-300 mesh). Thin-layer chromatography (TLC) was performed on silica gel plates. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (471 MHz) spectra were recorded on a JEOL ECZ500R NMR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Micro TOF ESI mass spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (*J*) were given in Hertz (Hz). Data were reported as s – singlet, d – doublet, t – triplet, q – quartet, dd – doublet of doublets, m – multiplet, dm – doublet of multiplets.

Experimental Section

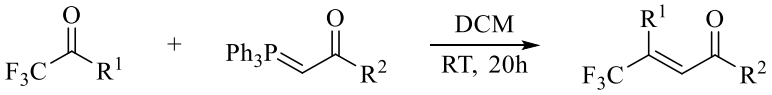
Table S1. Optimization of solvent on 3q



1b **2a** **3q**

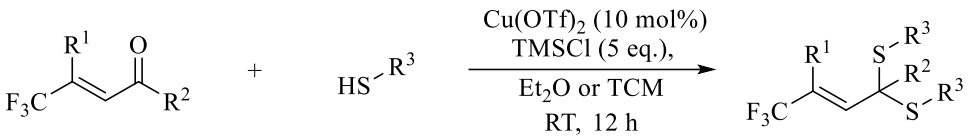
Entry	Catalyst	Solvent	Yield [%]
1	$Cu(OTf)_2$	DCM	15
2	$Cu(OTf)_2$	TCM	18
3	$Cu(OTf)_2$	Et_2O	79
4	$Cu(OTf)_2$	THF	74
5	$Cu(OTf)_2$	MTBE	76
6	$Cu(OTf)_2$	DMF	0

A typical procedure for β-CF_3-substituted enones synthesis[1]:



To a well-stirred solution of trifluoromethyl ketone (5 mmol) in DCM (15 ml) under N_2 α-(triphenylphosphoranylidene)acetophenone (2.28g, 1.2 eq.) or (acetylmethylene)triphenylphosphorane (1.91g, 1.2eq.) was added. The resulting mixture was stirred at room temperature for 20 hours. Then, the reaction mixture was quenched with H_2O (10ml), and extracted with dichloromethane (15 mL×3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The residual was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to afford product **1**.

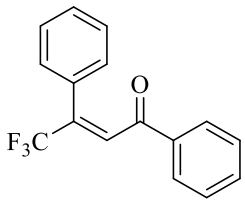
A typical procedure for product synthesis：



To a dry glass tube was added 1 mL solvent, $Cu(OTf)_2$ (10 mol%), β-CF_3-enone (1 eq.) and mercaptan (2 eq.), followed by TMSCl (5 eq.). The mixture was stirred under N_2 atmosphere for 12 hours. After the reaction was complete (monitored by TLC), the residual was quenched with saturated NH_4Cl (aq.) and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over $MgSO_4$, concentrated by rotary evaporation. The crude was further purified by silica gel column chromatography (petroleum ether/DCM = 10/1) to afford product **3.**

Characterization data

(*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one (1a)

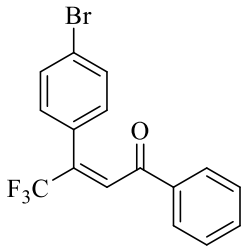


Yellow oil (1.20g, 87%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.85 – 7.77 (m, 2H, Ar-*H*), 7.56 – 7.48 (m, *J* = 6.1, 5.2 Hz, 1H, C*H*CO), 7.40 (td, *J* = 7.7, 2.9 Hz, 2H, Ar-*H*), 7.31 – 7.19 (m, 6H Ar-*H*); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 192.2, 139.0 (q, $J_{C\text{-}F}$ = 30.7 Hz), 136.1, 134.0, 130.9 (q, $J_{C\text{-}F}$ = 5.2 Hz), 129.5, 129.1 (5C), 128.8 (2C), 128.5 (2C), 123.0 (q, $J_{C\text{-}F}$ = 274.8 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.2 (s, 3F).

HRMS (ESI) calcd for $C_{16}H_{11}F_3O$ $[M+H]^+$: 277.0835, found 277.0833.

This data was concordant with literature values.[1]

(*E*)-3-(4-bromophenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (1b)

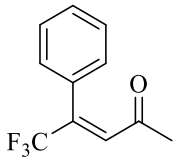


Yellow solid (1.59g, 90%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.85 – 7.81 (m, 2H, Ar-*H*), 7.59 – 7.55 (m, 1H, Ar-*H*), 7.46 – 7.40 (m, 4H, Ar-*H*), 7.33 (q, *J* = 1.4 Hz, 1H, C*H*CO), 7.18 – 7.13 (m, 2H, Ar-*H*); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 191.6, 138.1 (q, J_{C-F} = 31.3 Hz), 136.0, 134.3, 131.8 (2C), 131.3 (q, J_{C-F}= 5.0 Hz), 130.7 (2C), 129.7, 129.0 (4C), 124.1, 122.6 (q, J_{C-F} = 274.8 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.3 (s, 3F).

HRMS (ESI) calcd for $C_{16}H_{10}BrF_3O$ $[M+H]^+$: 354.9940, found 265.354.9941.

This data was concordant with literature values.[2]

(*E*)-5,5,5-trifluoro-4-phenylpent-3-en-2-one (1c)

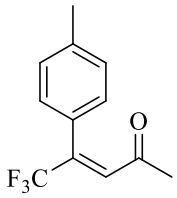


Yellow oil (0.97g, 91%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.50 – 7.39 (m, 3H, Ar-*H*), 7.33 – 7.28 (m, 2H, Ar-*H*), 6.71 (q, *J* = 1.5 Hz, 1H, C*H*CO), 1.90 (d, *J* = 0.6 Hz, 3H, COCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 199.5, 139.1 (q, J_{C-F} = 31.0 Hz)., 132.6 (q, J_{C-F} = 4.9 Hz), 130.9, 130.0, 129.2 (2C), 128.9 (2C), 122.9 (q, J_{C-F} = 274.7 Hz), 30.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -67.1 (s, 3F).

HRMS (ESI) calcd for $C_{11}H_9F_3O$ $[M+H]^+$: 215.0678, found 215.0671.

This data was concordant with literature values.[2]

(*E*)-5,5,5-trifluoro-4-(p-tolyl)pent-3-en-2-one[3] (1d)

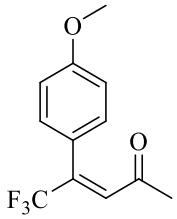


Yellow oil (0.80g, 70%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.25 – 7.21 (m, 2H, Ar-*H*), 7.19 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 6.68 (q, *J* = 1.4 Hz, 1H, C*H*CO), 2.39 (s, 3H, CHCH_3), 1.91 (s, 3H, COCH_3); **^{13}C**

NMR (126 MHz, $CDCl_3$) δ_C/ppm 199.8, 140.3, 139.3 (q, J_{C-F} = 30.5 Hz), 132.4 (q, J_{C-F} = 5.2 Hz), 129.6 (2C), 129.1 (2C), 128.0, 123.0 (q, J_{C-F} = 274.8 Hz)., 30.6, 21.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -67.0 (s, 3F).

HRMS (ESI) calcd for $C_{12}H_{11}F_3O$ $[M+H]^+$: 229.0835, found 229.0834.

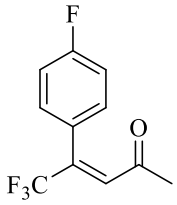
(*E*)-5,5,5-trifluoro-4-(4-methoxyphenyl)pent-3-en-2-one[3] **(1e)**



Yellow oil (0.59g, 48%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.26 – 7.21 (m, 2H, Ar-*H*), 6.97 – 6.92 (m, 2H, Ar-*H*), 6.66 (q, *J* = 1.4 Hz, 1H, C*H*CO), 3.84 (s, 3H, OCH_3), 1.92 (s, 3H, COCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 200.0, 161.0, 138.9 (q, J_{C-F} = 30.7 Hz)., 132.2 (q, J_{C-F} = 4.7 Hz), 130.7 (2C), 123.0 (q, J_{C-F} = 274.9 Hz), 122.9, 114.3 (2C), 55.4, 30.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -67.0 (s, 3F).

HRMS (ESI) calcd for $C_{12}H_{11}F_3O_2$ $[M+H]^+$: 245.0784, found 245.0782.
This data was concordant with literature values.[4]

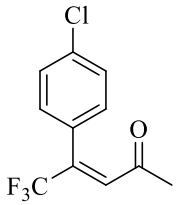
(*E*)-5,5,5-trifluoro-4-(4-fluorophenyl)pent-3-en-2-one[3] **(1f)**



Yellow oil (0.92g, 79%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.32 – 7.27 (m, 2H, Ar-*H*), 7.16 – 7.10 (m, 2H, Ar-*H*), 6.75 (q, *J* = 1.4 Hz, 1H, C*H*CO), 1.98 (s, 3H, COCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 198.9, 163.7 (d, J_{C-F} = 250.5 Hz), 138.0 (q, J_{C-F} = 31.2 Hz), 132.7 (q, J_{C-F} = 4.7 Hz), 131.2 (d, J_{C-F} = 8.5 Hz) (2C), 126.7 (d, J_{C-F} = 3.3 Hz), 122.7 (q, J_{C-F} = 275.0 Hz), 116.2, 116.0, 30.8; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -67.2 (s, 3F), -110.4 (s, 1F).

HRMS (ESI) calcd for $C_{11}H_8F_4O$ $[M+H]^+$: 233.0584, found 233.0579.

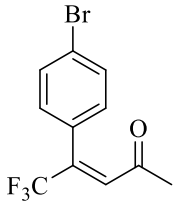
(*E*)-4-(4-chlorophenyl)-5,5,5-trifluoropent-3-en-2-one[3] **(1g)**



Yellow oil (1.12g, 90%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.45 – 7.38 (m, 2H, Ar-*H*), 7.26 – 7.21 (m, 2H, Ar-*H*), 6.76 (q, J = 1.4 Hz, 1H, C*H*CO), 2.00 (s, 3H, COCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 198.7, 137.9 (q, $J_{C\text{-}F}$ = 31.4 Hz), 136.3, 132.6 q, ($J_{C\text{-}F}$ = 4.8 Hz), 130.5 (2C), 129.2 (q, J = 7.6 Hz) (3C), 122.6 (q, $J_{C\text{-}F}$ = 275.0 Hz), 30.9; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -67.1 (s, 3F).

HRMS (ESI) calcd for $C_{11}H_8ClF_3O$ $[M+H]^+$: 249.0289, found 249.0287.

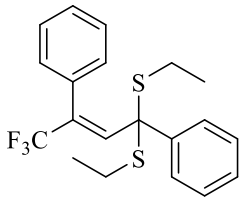
***(E)*-4-(4-bromophenyl)-5,5,5-trifluoropent-3-en-2-one (1h)**



Yellow oil (1.39g, 95%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.60 – 7.54 (m, 2H, Ar-*H*), 7.20 – 7.15 (m, 2H, Ar-*H*), 6.76 (q, J = 1.4 Hz, 1H, C*H*CO), 2.01 (s, 3H, COCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 198.7, 138.0 (q, $J_{C\text{-}F}$ = 31.0 Hz), 132.6 (q, $J_{C\text{-}F}$ = 4.8 Hz), 132.1 (2C), 130.7 (2C), 129.7, 124.5, 122.6 q, $J_{C\text{-}F}$ = 275.0 Hz), 30.9; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -67.1 (s, 3F).

HRMS (ESI) calcd for $C_{11}H_8BrF_3O$ $[M+H]^+$: 292.9784, found 292.9781.

(*E*)-(4,4,4-trifluoro-1,3-diphenylbut-2-ene-1,1-diyl)bis(ethylsulfane) (3a)

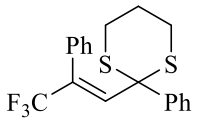


Colorless liquid (53.8mg, 70%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.69 – 7.63 (m, 2H, Ar-*H*), 7.55 – 7.50 (m, 2H, Ar-*H*), 7.45 – 7.33 (m, 6H, Ar-*H*), 6.17 (s, 1H, C*H*CO), 2.92 – 2.70 (m, 2H, CH_2S), 2.20 (qd, J = 7.4, 4.8 Hz, 2H, CH_2S), 1.30 (t, J = 7.5 Hz, 3H, CH_2CH_3), 0.80 (t, J = 7.3 Hz, 3H, CH_2CH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_H/ppm 146.3, 139.5, 135.9, 129.1 (2C), 128.7 (3C), 128.4, 128.3 (2C), 128.1 (2C), 126.3, 125.4, 59.9 (q, $J_{C\text{-}F}$ = 26.1 Hz), 26.9, 25.4, 15.4, 13.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm

-73.0 (s, 3F).

HRMS (ESI) calcd for $C_{20}H_{21}F_3S_2$ $[M+Na]^+$: 405.0929, found 405.0933.

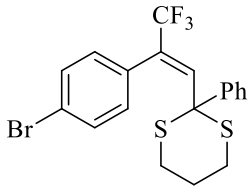
(*E*)-2-phenyl-2-(3,3,3-trifluoro-2-phenylprop-1-en-1-yl)-1,3-dithiane (3b)



Colorless liquid (72.5mg, 99%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.50 – 7.45 (m, 2H, Ar-*H*), 7.18 – 7.07 (m, 4H, Ar-*H*), 7.03 (dd, *J* = 8.6, 6.9 Hz, 2H, Ar-*H*), 6.96 (q, *J* = 1.7 Hz, 1H, C*H*CO), 6.85 – 6.80 (m, 2H, Ar-*H*), 2.80 (ddd, *J* = 14.5, 7.1, 3.2 Hz, 2H, CH_2S), 2.69 (ddd, *J* = 14.5, 9.2, 3.2 Hz, 2H, CH_2S), 2.04 – 1.85 (m, 2H, CH_2CH$_2$S); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 140.1, 138.6 (q, $J_{C\text{-}F}$ = 5.7 Hz), 133.9 (q, $J_{C\text{-}F}$ = 29.1 Hz), 130.4, 130.1 (2C), 128.9 (2C), 128.1 (d, *J* = 6.9 Hz) (3C), 127.4 (d, *J* = 7.3 Hz) (3C), 123.2 (q, $J_{C\text{-}F}$ = 274.5 Hz)., 56.0, 28.3 (2C), 24.0; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.4 (s, 3F).

HRMS (ESI) calcd for $C_{19}H_{17}F_3S_2$ $[M+Na]^+$: 389.0616, found 389.0616.

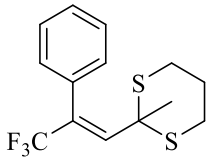
(*E*)-2-(2-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl)-2-phenyl-1,3-dithiane (3c)



Colorless liquid (87.4mg, 98%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.40 – 7.34 (m, 2H, Ar-*H*), 7.09 – 7.01 (m, 5H, Ar-*H*), 6.89 (q, *J* = 1.7 Hz, 1H, C*H*CS), 6.62 – 6.56 (m, 2H, Ar-*H*), 2.71 (ddd, *J* = 14.4, 6.7, 3.4 Hz, 2H, CH_2S), 2.62 (ddd, *J* = 14.5, 9.3, 3.2 Hz, 2H, CH_2S), 1.95 – 1.87 (m, 1H, CH_2CH$_2$S), 1.83 (dtt, *J* = 13.6, 6.6, 3.3 Hz, 1H, CH_2CH$_2$S); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 139.9, 139.4 (q, $J_{C\text{-}F}$ = 5.4 Hz), 132.8 (q, $J_{C\text{-}F}$ = 29.6 Hz), 131.7 (2C), 130.5 (2C), 129.3, 129.0 (2C), 128.2 (2C), 127.5, 122.7, 122.9 (q, $J_{C\text{-}F}$ = 274.4 Hz). 55.8, 28.2 (2C), 23.9; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.5 (s, 3F).

HRMS (ESI) calcd for $C_{19}H_{16}BrF_3S_2$ $[M+H]^+$: 444.9902, found 444.9906.

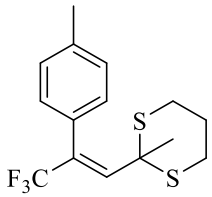
(*E*)-2-methyl-2-(3,3,3-trifluoro-2-phenylprop-1-en-1-yl)-1,3-dithiane (3d)



Colorless liquid (60.1mg, 99%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.41 – 7.33 (m, 3H, Ar-*H*), 7.33 – 7.29 (m, 2H, Ar-*H*), 6.91 (q, *J* = 1.7 Hz, 1H, C*H*C), 3.04 – 2.95 (m, 2H, CH_2S), 2.76 (ddd, *J* = 14.7, 6.1, 3.1 Hz, 2H, CH_2S), 2.08 (dtt, *J* = 14.1, 6.0, 2.8 Hz, 1H, CH_2CH$_2$S), 1.89 (dtt, *J* = 14.0, 10.8, 3.1 Hz, 1H, CH_2CH$_2$S), 1.35 (s, 3H, CCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 137.1 (q, $J_{C\text{-}F}$ = 5.6 Hz), 131.6, 130.4 (2C), 129.3 (q, $J_{C\text{-}F}$ = 29.1 Hz), 129.0, 128.0 (2C), 123.5 (q, $J_{C\text{-}F}$ = 274.3 Hz), 46.7, 28.0, 27.3, 24.3 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.3 (s, 3F)

HRMS (ESI) calcd for $C_{14}H_{15}F_3S_2$ $[M+Na]^+$: 327.0459, found 327.0452.

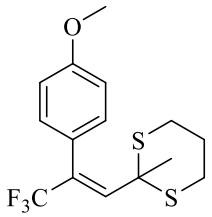
(*E*)-2-methyl-2-(3,3,3-trifluoro-2-(p-tolyl)prop-1-en-1-yl)-1,3-dithiane (3e)



Colorless liquid (63.1mg, 99%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.18 (q, *J* = 8.2 Hz, 4H, Ar-*H*), 6.90 (q, *J* = 1.8 Hz, 1H, C*H*CO), 3.00 (ddd, *J* = 14.8, 10.8, 2.8 Hz, 2H, CH_2S), 2.76 (ddd, *J* = 14.7, 6.1, 3.1 Hz, 2H, CH_2S), 2.37 (s, 3H, CCH_3), 2.08 (dtt, *J* = 16.8, 5.9, 2.8 Hz, 1H, CH_2CH$_2$S), 1.89 (dtt, *J* = 14.0, 10.8, 3.1 Hz, 1H, CH_2CH$_2$S), 1.36 (s, 3H, COCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 138.9, 137.0 (q, $J_{C\text{-}F}$ = 5.2 Hz), 130.2(2C), 129.4 (q, $J_{C\text{-}F}$ = 29.1 Hz)., 128.8 (2C), 128.6, 123.5 (q, $J_{C\text{-}F}$ = 274.4 Hz), 46.8, 28.0, 27.3 (2C), 24.4, 21.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.4 (s, 3F).

HRMS (ESI) calcd for $C_{15}H_{17}F_3S_2$.$[M+Na]^+$: 341.0634, found 341.0619.

(*E*)-2-methyl-2-(3,3,3-trifluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)-1,3-dithiane (3f)

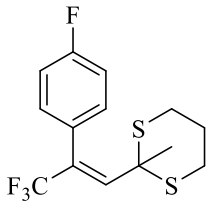


colorless liquid (64.1mg, 96%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.24 – 7.19 (m, 2H, Ar-*H*), 6.90 – 6.88 (m, 2H, Ar-*H*), 6.88 (d, *J* = 2.1 Hz, 1H, C*H*CO), 3.82 (s, 3H, OCH_3), 3.03 – 2.94 (m, 2H, CH_2S),

2.80 – 2.71 (m, 2H, CH_2S), 2.07 (dtt, J = 14.0, 6.0, 2.8 Hz, 1H, CH_2CH$_2$S), 1.89 (dtt, J = 13.9, 10.7, 3.1 Hz, 1H, CH_2CH$_2$S), 1.37 (s, 3H, CCH_3; **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 160.0, 137.2 (q, J_{C-F} = 5.5 Hz), 131.6 (2C), 129.1 (q, J_{C-F} = 29.1 Hz), 123.6 (q, J_{C-F} = 274.3 Hz). 123.5, 113.5 (2C), 55.3, 46.8, 27.9, 27.3 (2C), 24.4; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.51 (3F).

HRMS (ESI) calcd for $C_{15}H_{17}F_3OS_2$ $[M+Na]^+$: 357.0565, found 357.0568.

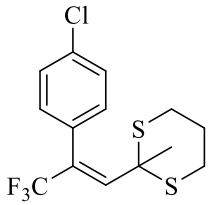
(*E*)-2-methyl-2-(3,3,3-trifluoro-2-(4-fluorophenyl)prop-1-en-1-yl)-1,3-dithiane (3g)



Colorless liquid (42.6mg, 66%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.24 – 7.19 (m, 2H, Ar-H), 7.02 – 6.95 (m, 2H, Ar-H), 6.85 (q, J = 1.8 Hz, 1H, CHCO), 2.96 – 2.85 (m, 2H, CH_2S), 2.74 – 2.63 (m, 2H, CH_2S), 2.00 (dtt, J = 14.0, 6.0, 2.8 Hz, 1H, CH_2CH$_2$S), 1.82 (dtt, J = 13.9, 10.7, 3.1 Hz, 1H, CH_2CH$_2$S), 1.29 (s, 3H, CCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 163.2 (d, J_{C-F} = 248.6 Hz), 137.9, 132.2 (d, J_{C-F} = 8.2 Hz) (2C), 128.4 (q, J_{C-F} = 29.2 Hz), 127.4 (q, J_{C-F} = 3.5 Hz), 123.3 (q, J_{C-F} = 274.2 Hz), 115.3, 115.1, 46.6, 28.1, 27.3 (2C), 24.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.5 (s, 3F), -112.2 (s, 1F)

HRMS (ESI) calcd for $C_{14}H_{14}F_4S_2$.$[M+H]^+$: 323.0546, found 323.0549.

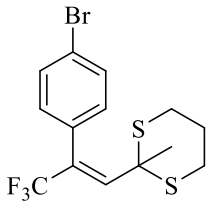
(*E*)-2-(2-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)-2-methyl-1,3-dithiane (3h)



Colorless liquid (50.2mg, 74%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.30 – 7.26 (m, 2H, Ar-H), 7.20 – 7.17 (m, 2H, Ar-H), 6.85 (q, J = 1.7 Hz, 1H, CHCO), 2.94 – 2.86 (m, 2H, CH_2S), 2.69 (ddd, J = 14.7, 6.1, 3.1 Hz, 2H, CH_2S), 2.01 (dtt, J = 13.9, 6.0, 2.8 Hz, 1H, CH_2CH$_2$S), 1.82 (dtt, J = 14.0, 10.8, 3.1 Hz, 1H, CH_2CH$_2$S), 1.30 (s, 3H, CCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 138.1 (q, J_{C-F} = 5.6 Hz), 135.2, 131.7 (2C), 130.0, 128.4 (2C), 128.1 (q, J_{C-F} = 29.4 Hz), 123.2 (q, J_{C-F} = 274.1 Hz)., 46.6, 28.1, 27.4 (2C), 24.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.3 (s, 3F).

HRMS (ESI) calcd for $C_{14}H_{14}ClF_3S_2$ $[M+Na]^+$: 339.0251, found 339.0248.

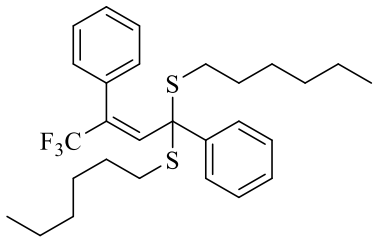
(*E*)-2-(2-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl)-2-methyl-1,3-dithiane (3i)



Colorless liquid (58.0mg, 76%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 2H, Ar-*H*), 7.15 – 7.10 (m, 2H, Ar-*H*), 6.85 (q, *J* = 1.7 Hz, 1H, Ar-*H*), 2.90 (dddd, *J* = 13.7, 10.8, 2.8, 0.9 Hz, 2H, C*H*$_2$S), 2.73 – 2.64 (m, 2H, C*H*$_2$S), 2.01 (dtt, *J* = 13.9, 5.9, 2.8 Hz, 1H, C*H*$_2$CH$_2$S), 1.82 (dtt, *J* = 13.9, 10.8, 3.1 Hz, 1H, C*H*$_2$CH$_2$S), 1.30 (s, 3H, CC*H*$_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 138.1 (q, *J* = 5.4 Hz), 132.0 (2C), 131.3 (2C), 130.5, 128.3 (q, $J_{C\text{-}F}$ = 29.3 Hz), 123.2 (q, $J_{C\text{-}F}$ = 274.0 Hz)., 46.6, 28.2, 27.4 (2C), 24.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.3 (s, 3F).

HRMS (ESI) calcd for $C_{14}H_{14}BrF_3S_2$.$[M+Na]^+$: 404.9564, found 404.9545.

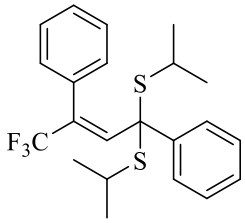
(*E*)-(4,4,4-trifluoro-1,3-diphenylbut-2-ene-1,1-diyl)bis(hexylsulfane) (3j)



Colorless liquid (73.0mg, 74%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.69 – 7.64 (m, 2H, Ar-*H*), 7.52 – 7.48 (m, 2H, Ar-*H*), 7.45 – 7.32 (m, 6H, Ar-*H*), 6.14 (s, 1H, C*H*C), 2.87 – 2.67 (m, 2H, C*H*$_2$S), 2.19 – 2.08 (m, 2H, C*H*$_2$S), 1.69 – 1.60 (m, 2H, C*H*$_2$CH$_2$S), 1.43 (p, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_2$S), 1.31 (tt, *J* = 6.5, 2.7 Hz, 4H, 2×C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.16 – 1.04 (m, 4H, 2×C*H*$_2$CH$_2$CH$_3$), 1.01 – 0.92 (m, 4H, 2× C*H*$_2$CH$_3$), 0.89 (d, *J* = 7.0 Hz, 3H, CH$_2$C*H*$_3$), 0.78 (t, *J* = 7.3 Hz, 3H, CH$_2$C*H*$_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 146.5, 139.7, 135.9, 129.1 (2C), 128.6 (d, *J* = 4.9 Hz) (3C), 128.3 (3C), 128.1 (2C), 126.3, 125.0, 59.8 (q, $J_{C\text{-}F}$ = 25.9 Hz)., 32.7, 31.6, 31.2, 30.4, 29.8, 29.0, 28.8, 28.3, 22.6, 22.4, 14.2, 14.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -73.0 (s, 3F).

HRMS (ESI) calcd for $C_{28}H_{37}F_3S_2$ $[M+Na]^+$: 517.2181, found 517.2188.

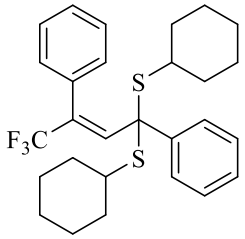
(*E*)-(4,4,4-trifluoro-1,3-diphenylbut-2-ene-1,1-diyl)bis(isopropylsulfane) (3k)



Colorless liquid (49.3mg, 60%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.73 – 7.67 (m, 2H, Ar-*H*), 7.56 – 7.51 (m, 2H, Ar-*H*), 7.44 – 7.32 (m, 6H, Ar-*H*), 6.21 (s, 1H, C*H*CO), 3.23 (hept, *J* = 6.9 Hz, 1H, C*H*S), 2.67 (hept, *J* = 6.7 Hz, 1H, C*H*S), 1.38 (dd, *J* = 13.3, 6.9 Hz, 6H, CH_3CHCH_3), 0.93 (d, *J* = 6.8 Hz, 3H, CH_3CH), 0.74 (d, *J* = 6.6 Hz, 3H, CH_3CH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 146.6, 140.4 (2C), 135.9, 129.4 (2C), 128.6 (2C), 128.5, 128.3 (2C), 127.9 (2C), 126.0 (d, *J* = 11.3 Hz)(2C), 60.1 (q, $J_{C\text{-}F}$ = 26.4 Hz), 36.9, 36.2, 25.6, 25.3, 24.4, 22.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -72.7 (s, 3F).

HRMS (ESI) calcd for $C_{22}H_{25}F_3S_2$ $[M+Na]^+$: 433.1242, found 433.1209.

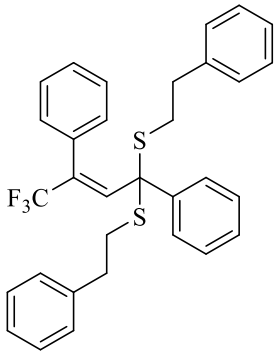
(*E*)-(4,4,4-trifluoro-1,3-diphenylbut-2-ene-1,1-diyl)bis(cyclohexylsulfane) (3l)



Colorless liquid (39.3mg, 40%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.50 – 7.45 (m, 2H, Ar-*H*), 7.18 – 7.07 (m, 4H, Ar-*H*), 7.03 (dd, *J* = 8.6, 6.9 Hz, 2H, Ar-*H*), 6.96 (q, *J* = 1.7 Hz, 1H, C*H*CO), 6.85 – 6.80 (m, 2H, Ar-*H*), 2.80 (ddd, *J* = 14.5, 7.1, 3.2 Hz, 2H, CH_2S), 2.69 (ddd, *J* = 14.5, 9.2, 3.2 Hz, 2H, CH_2S), 2.04 – 1.85 (m, 2H, CH_2CH$_2$S); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 146.3, 140.7, 135.9, 129.4(2C), 128.6(2C), 128.4, 128.2 (d, *J* = 7.7 Hz)(3C), 127.9(2C), 126.1 – 123.1 (m)(2C), 60.0 (q, $J_{C\text{-}F}$ = 26.3 Hz)., 45.3, 44.1, 35.5, 35.3, 34.5, 32.8, 26.6 (d, *J* = 12.0 Hz)(2C), 26.1, 25.8, 25.6, 25.4. **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.4 (s, 3F).

HRMS (ESI) calcd for $C_{28}H_{33}F_3S_2$ $[M+Na]^+$: 513.1868, found 513.1859.

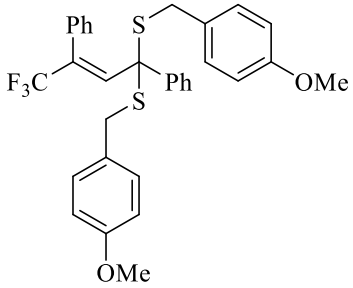
(*E*)-(4,4,4-trifluoro-1,3-diphenylbut-2-ene-1,1-diyl)bis(phenethylsulfane) (3m)



Colorless liquid (40.5mg, 38%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.38 – 7.34 (m, 2H, Ar-*H*), 7.32 – 7.27 (m, 4H, Ar-*H*), 7.25 – 7.16 (m, 3H, Ar-*H*), 7.14 – 7.05 (m, 9H, Ar-*H*), 6.94 – 6.90 (m, 2H, Ar-*H*), 6.75 (q, J = 1.7 Hz, 1H, C*H*C), 2.86 – 2.65 (m, 8H, 4×CH_2); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 141.3, 140.4 (2C), 138.6 (q, $J_{C\text{-}F}$ = 5.4 Hz)., 131.3 (q, $J_{C\text{-}F}$= 29.1 Hz), 130.7, 130.3 (2C), 128.6 (d, J= 9.4 Hz) (8C), 128.3 – 127.8 (m) (5C), 127.5, 127.3 (2C), 126.5 (2C), 123.4 (q, $J_{C\text{-}F}$ = 274.9 Hz), 65.7, 35.0 (2C), 32.2 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.0 (s, 3F).

HRMS (ESI) calcd for $C_{32}H_{29}F_3S_2$ $[M+Na]^+$: 557.1555, found 557.1544.

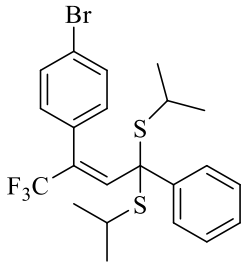
(*E*)-(4,4,4-trifluoro-1,3-diphenylbut-2-ene-1,1-diyl)bis((4-methoxybenzyl)sulfane) (3n)



Colorless liquid (57.5mg, 51%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.40 (ddd, J = 7.1, 5.2, 3.1 Hz, 2H, Ar-*H*), 7.22 – 7.03 (m, 10H, Ar-*H*), 6.97 – 6.92 (m, 2H, Ar-*H*), 6.85 (dd, J = 8.7, 2.6 Hz, 4H, Ar-*H*), 6.74 (h, J = 1.6 Hz, 1H, C*H*C), 3.84 (dd, J = 11.9, 2.5 Hz, 2H, CH_2S), 3.80 (d, J = 2.8 Hz, 6H, 2×OCH_3), 3.65 (dd, J = 12.0, 2.5 Hz, 2H, CH_2S); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 158.9 (2C), 140.9, 138.2 (q, $J_{C\text{-}F}$ = 5.7 Hz), 131.6 (q, $J_{C\text{-}F}$ = 28.9 Hz), 130.6 (d, J = 11.7 Hz) (5C), 130.2 (2C), 128.5 (2C), 128.2 (d, J = 5.4 Hz) (3C), 128.0 (2C), 127.5, 127.4 (2C), 123.3 (q, $J_{C\text{-}F}$ = 274.6 Hz), 114.1 (4C), 66.2, 55.4 (2C), 35.2 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.0 (s, 3F).

HRMS (ESI) calcd for $C_{32}H_{29}F_3O_2S_2$ $[M+Na]^+$: 589.1453, found 589.1426.

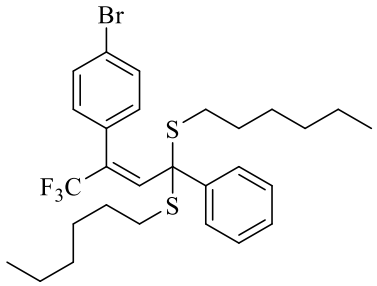
(*E*)-(3-(4-bromophenyl)-4,4,4-trifluoro-1-phenylbut-2-ene-1,1-diyl)bis(isopropylsulfane) (3o)



Colorless liquid (47.6mg, 49%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.57 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.52 – 7.45 (m, 4H, Ar-*H*), 7.44 – 7.36 (m, 3H, Ar-*H*), 6.15 (s, 1H, C*H*CO), 3.21 (hept, *J* = 6.9 Hz, 1H, C*H*S), 2.68 (hept, *J* = 6.8 Hz, 1H, C*H*S), 1.36 (dd, *J* = 12.1, 6.9 Hz, 6H, CH_3CHCH_3), 0.96 (d, *J* = 6.9 Hz, 3H, CH_3CH), 0.77 (d, *J* = 6.6 Hz, 3H, CH_3CH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 147.1, 140.1, 135.0, 131.2 (2C), 131.0 (2C), 128.7 (3C), 128.2 (2C), 126.8 (d, *J* = 282.3 Hz), 125.3, 122.6, 59.7 (q, $J_{C\text{-}F}$ = 26.3 Hz)., 37.0, 36.5, 25.5, 25.2, 24.4, 22.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -72.8 (s, 3F).

HRMS (ESI) calcd for $C_{22}H_{24}BrF_3S_2$ $[M+Na]^+$: 511.0347, found 511.0345.

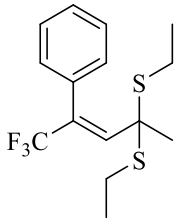
(*E*)-(3-(4-bromophenyl)-4,4,4-trifluoro-1-phenylbut-2-ene-1,1-diyl)bis(hexylsulfane) (3p)



Colorless liquid (66.5mg, 58%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.54 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.51 – 7.46 (m, 4H, Ar-*H*), 7.44 – 7.36 (m, 3H, Ar-*H*), 6.10 (s, 1H, C*H*CO), 2.82 (dt, *J* = 10.5, 7.4 Hz, 1H, CH_2S), 2.70 (ddd, *J* = 10.9, 8.2, 6.7 Hz, 1H, CH_2S), 2.21 – 2.09 (m, 2H, CH_2S), 1.67 – 1.58 (m, 2H, CH_2CH$_2$S), 1.46 – 1.38 (m, 2H, CH_2CH$_2$S), 1.33 – 1.27 (m, 4H, 2×CH_2CH$_2$CH$_2$S), 1.18 – 0.93 (m, 8H, 2×CH_2CH_2CH$_2$CH$_2$CH$_2$S), 0.89 (t, *J* = 6.9 Hz, 3H, CH$_2$CH_3), 0.80 (t, *J* = 7.3 Hz, 3H, CH$_2$CH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 147.0, 139.4, 135.0, 131.2 (2C), 130.8 (2C), 128.7 (d, *J* = 6.0 Hz) (3C), 128.3 (2C), 126.7 (d, *J* = 157.6 Hz), 124.4, 122.7, 59.4 (q, $J_{C\text{-}F}$ = 26.5 Hz), 32.7, 31.6, 31.3 (d, *J* = 12.2 Hz) (2C), 30.3, 28.9, 28.7, 28.3, 22.6 (d, *J* = 19.3 Hz) (2C), 14.1 (d, *J* = 8.4 Hz) (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -73.1 (s, 3F).

HRMS (ESI) calcd for $C_{28}H_{36}BrF_3S_2$ $[M+Na]^+$: 595.1256, found 595.1248.

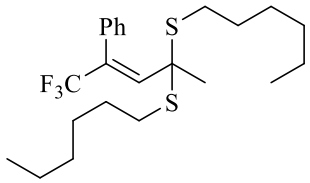
(*E*)-(5,5,5-trifluoro-4-phenylpent-3-ene-2,2-diyl)bis(ethylsulfane) (3q)



colorless liquid (50.6mg, 79%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.41 – 7.33 (m, 3H, Ar-*H*), 7.32 – 7.27 (m, 2H, Ar-*H*), 6.54 (q, *J* = 1.7 Hz, 1H, C*H*C), 2.72 – 2.60 (m, 4H, 2×CH_2S), 1.27 – 1.23 (m, 9H, 2 ×CH_2CH_3, CCH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 137.6 (q, $J_{C\text{-}F}$ = 5.5 Hz), 131.5, 130.5 (2C), 129.2 (q, $J_{C\text{-}F}$ = 29.5 Hz), 129.0, 128.1 (2C), 123.5 (q, $J_{C\text{-}F}$ = 274.3 Hz), 56.8, 27.7, 24.3 (2C), 14.2(2C). **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.4 (s, 3F).

HRMS (ESI) calcd for $C_{15}H_{19}F_3S_2$ $[M+Na]^+$: 343.0772, found 343.0761.

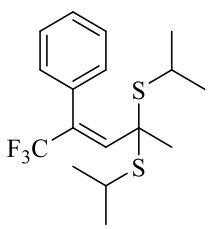
(*E*)-(5,5,5-trifluoro-4-phenylpent-3-ene-2,2-diyl)bis(hexylsulfane) (3r)



Colorless liquid (82.1mg, 95%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.41 – 7.33 (m, 3H, Ar-*H*), 7.32 – 7.27 (m, 2H, Ar-*H*), 6.52 (q, *J* = 1.8 Hz, 1H, C*H*CO), 2.63 (qt, *J* = 11.7, 7.4 Hz, 4H, 2×CH_2S), 1.61 – 1.55 (m, 4H, 2×CH_2CH_2S), 1.40 (ddt, *J* = 12.4, 9.7, 6.0 Hz, 4H, 2×C$H_2CH_2CH_2$S), 1.34 – 1.26 (m, 8H, 2×C$H_2CH_2CH_3$), 1.23 (s, 3H, CCH_3), 0.89 (t, *J* = 6.9 Hz, 6H, 2×CH_2CH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 137.6 (q, $J_{C\text{-}F}$ = 5.6 Hz), 131.6, 130.6 (2C), 129.1 (q, $J_{C\text{-}F}$ = 32.3 Hz) (2C), 128.0 (2C), 123.5 (q, $J_{C\text{-}F}$ = 274.6 Hz), 56.9, 31.5 (2C), 30.3 (2C), 29.2 (2C), 28.9 (2C), 27.7, 22.6 (2C), 14.1 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.4 (s, 3F).

HRMS (ESI) calcd for $C_{23}H_{35}F_3S_2$ $[M+Na]^+$: 455.2024, found 455.2029.

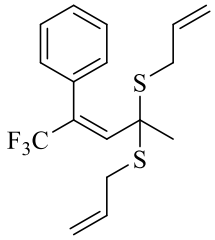
(*E*)-(5,5,5-trifluoro-4-phenylpent-3-ene-2,2-diyl)bis(isopropylsulfane) (3s)



Colorless liquid (24.5mg, 35%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.41 – 7.35 (m, 3H, Ar-*H*), 7.34 – 7.28 (m, 2H, Ar-*H*), 6.64 (q, *J* = 1.8 Hz, 1H, C*H*CO), 3.14 (hept, *J* = 6.9 Hz, 2H, 2×C*H*S), 1.33 (dd, *J* = 6.9, 3.4 Hz, 12H, 4×CHCH_3), 1.26 (s, 3H, CCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 138.9 (q, $J_{C\text{-}F}$ = 5.4 Hz), 131.6, 130.4 (2C), 129.0, 128.2 (q, $J_{C\text{-}F}$ = 28.9 Hz), 128.1 (2C), 123.5 (q, $J_{C\text{-}F}$= 274.4 Hz), 57.7, 35.6 (2C), 28.5, 25.6 (2C), 25.5 (2C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.5 (s, 3F).

HRMS (ESI) calcd for $C_{17}H_{23}F_3S_2$ $[M+Na]^+$: 371.1085, found 371.1083.

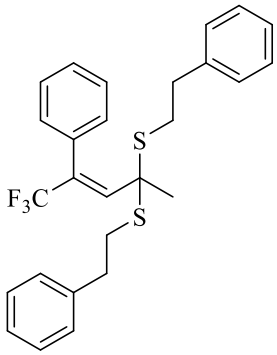
(*E*)-(5,5,5-trifluoro-4-phenylpent-3-ene-2,2-diyl)bis(allylsulfane) (3t)



Colorless liquid (24.1mg, 35%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.40 – 7.34 (m, 3H, Ar-*H*), 7.32 – 7.28 (m, 2H, Ar-*H*), 6.55 (q, *J* = 1.7 Hz, 1H, C*H*CO), 5.85 (ddt, *J* = 17.0, 9.9, 7.0 Hz, 2H, 2×C*H*CH_2), 5.24 (dq, *J* = 16.9, 1.4 Hz, 2H, CHCH_2), 5.12 (dq, *J* = 10.0, 1.1 Hz, 2H, CHCH_2), 3.34 (qdt, *J* = 13.1, 6.9, 1.2 Hz, 4H, 2×CH_2S), 1.27 (s, 3H, CCH_3).; **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 137.2 (q, $J_{C\text{-}F}$ = 5.3 Hz), 133.8 (2C), 131.4, 130.5 (2C), 129.6 (q, $J_{C\text{-}F}$ = 29.0 Hz), 129.0, 128.1 (2C), 123.4 (q, $J_{C\text{-}F}$= 274.2 Hz), 118.2 (2C), 58.0, 33.8 (2C), 27.8; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.5 (s,3F).

HRMS (ESI) calcd for $C_{17}H_{19}F_3S_2$ $[M+Na]^+$: 367.0772, found 367.0770.

(*E*)-(5,5,5-trifluoro-4-phenylpent-3-ene-2,2-diyl)bis(phenethylsulfane) (3u)

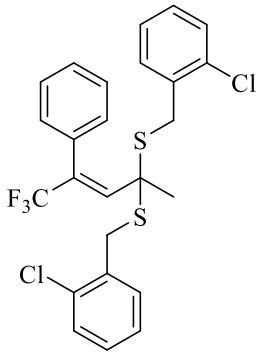


Colorless liquid (79.4mg, 84%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.32 – 7.20 (m, 7H, Ar-*H*), 7.20 – 7.08 (m, 8H, Ar-*H*), 6.45 (q, *J* = 1.7 Hz, 1H, C*H*CO), 2.82 – 2.73 (m, 8H, 2×CH_2CH_2S), 1.17 (s, 3H, CCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 140.3 (2C), 137.3 (q, $J_{C\text{-}F}$ = 5.5 Hz), 131.4, 130.6 (2C),

129. 7 (q, $J_{C\text{-}F}$ = 29.2 Hz), 129.0, 128.6 (d, J = 5.1 Hz) (8C), 128.1 (2C), 126.7 (2C), 123.4 (q, $J_{C\text{-}F}$ = 274.5 Hz), 57.7, 35.7 (2C), 31.8 (2C), 27.8; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.3 (s, 3F).

HRMS (ESI) calcd for $C_{27}H_{27}F_3S_2$.$[M+Na]^+$: 495.1398, found 495.1394.

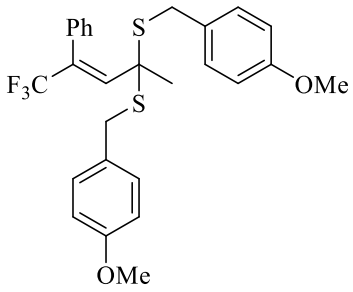
(*E*)-(5,5,5-trifluoro-4-phenylpent-3-ene-2,2-diyl)bis((2-chlorobenzyl)sulfane) (3v)



Colorless liquid (92.1mg, 90%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.43 – 7.34 (m, 7H, Ar-*H*), 7.33 – 7.30 (m, 2H, Ar-*H*), 7.25 – 7.19 (m, 4H, Ar-*H*), 6.60 (q, J = 1.7 Hz, 1H, C*H*CO), 4.09 – 3.99 (m, 4H, 2×CH_2S), 1.34 (s, 3H, CCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 137.0 (q, $J_{C\text{-}F}$= 5.5 Hz), 134.9 (2C), 134.3 (2C), 131.3 (3C), 130.6 (q, $J_{C\text{-}F}$ = 29.3 Hz), 130.5(2C), 129.9 (2C), 129.1, 128.9 (2C), 128.1 (2C), 127.1 (2C), 123.2 (q, $J_{C\text{-}F}$ = 274.6 Hz)., 58.4, 33.0 (2C), 27.4; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.7 (s, 3F).

HRMS (ESI) calcd for $C_{25}H_{21}Cl_2F_3S_2$ $[M+Na]^+$: 535.0306, found 535.0302.

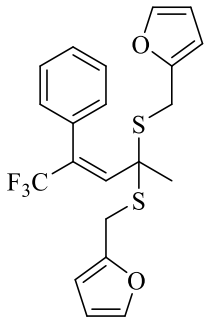
(*E*)-(5,5,5-trifluoro-4-phenylpent-3-ene-2,2-diyl)bis((4-methoxybenzyl)sulfane) (3w)



Colorless liquid (87.8mg, 87%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.32 – 7.24 (m, 3H, Ar-*H*), 7.22 – 7.14 (m, 6H, Ar-*H*), 6.80 – 6.75 (m, 4H, Ar-*H*), 6.43 (q, J = 1.7 Hz, 1H, C*H*CO), 3.78 (q, J = 12.2 Hz, 4H, 2×CH_2S), 3.71 (s, 6H, 2×OC_{H3}), 1.19 (s, 3H, CCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 158.9 (2C), 137.2 (q, $J_{C\text{-}F}$ = 5.4 Hz), 131.5, 130.5 (2C), 130.4 (4C) 129.7 (q, $J_{C\text{-}F}$ = 29.0 Hz), 129.0, 128.8 (2C), 128.1 (2C), 123.3 (q, $J_{C\text{-}F}$ = 274.5 Hz), 114.2 (4C), 58.1, 55.4 (2C), 34.6 (2C), 27.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.4 (s, 3F).

HRMS (ESI) calcd for $C_{27}H_{27}F_3O_2S_2$ $[M+Na]^+$: 527.1297, found 527.1289.

(*E*)-2,2'-(((5,5,5-trifluoro-4-phenylpent-3-ene-2,2-diyl)bis(sulfanediyl))bis(methylene))difuran (3x)



Brown liquid (62.8mg, 74%) **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H/ppm 7.41 – 7.34 (m, 5H, Ar-*H*), 7.32 – 7.27 (m, 2H, 2×C*H*COC), 6.51 (q, *J* = 1.7 Hz, 1H, C*H*CO), 6.32 (dd, *J* = 3.3, 1.9 Hz, 2H, 2×C*H*C), 6.24 – 6.20 (m, 2H, 2×C*H*CHO), 4.01 – 3.87 (m, 4H, 2×CH_2S), 1.27 (s, 3H, CCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C/ppm 150.8 (2C), 142.3 (2C), 136.7 (q, $J_{C\text{-}F}$ = 5.7 Hz), 131.4, 130.5 (2C), 130.3 (q, $J_{C\text{-}F}$ = 29.5 Hz). 129.1, 128.1 (2C), 123.2 (q, $J_{C\text{-}F}$ = 274.3 Hz), 110.7 (2C), 108.1 (2C), 58.4, 27.5 (3C); **^{19}F NMR** (471 MHz, $CDCl_3$) δ_F/ppm -66.6 (s, 3F).

HRMS (ESI) calcd for $C_{21}H_{19}F_3O_2S_2$.$[M+Na]^+$: 447.0671, found 447.0661.

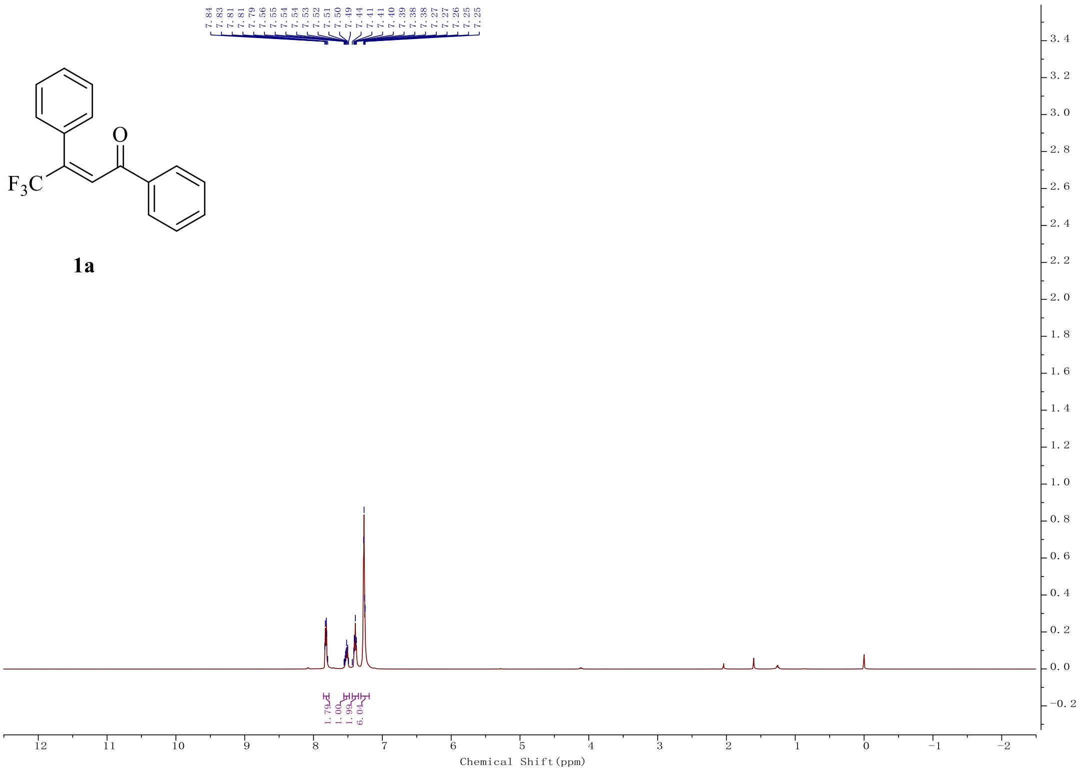
References：

[1] P. Kwiatkowski, A. Cholewiak, A. Kasztelan, *Org. Lett.* **2014**, *16*, 5930–5933.

[2] A. Sanz-Marco, G. Blay, C. Vila, J. R. Pedro, *Org. Lett.* **2016**, *18*, 3538–3541.

[3] J. Chen, S. Meng, L. Wang, H. Tang, Y. Huang, *Chem. Sci.* **2015**, *6*, 4184–4189.

[4] V. Bizet, X. Pannecoucke, J. L. Renaud, D. Cahard, *J. Fluor. Chem.* **2013**, *152*, 56–61.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7.54
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7.51
7.50
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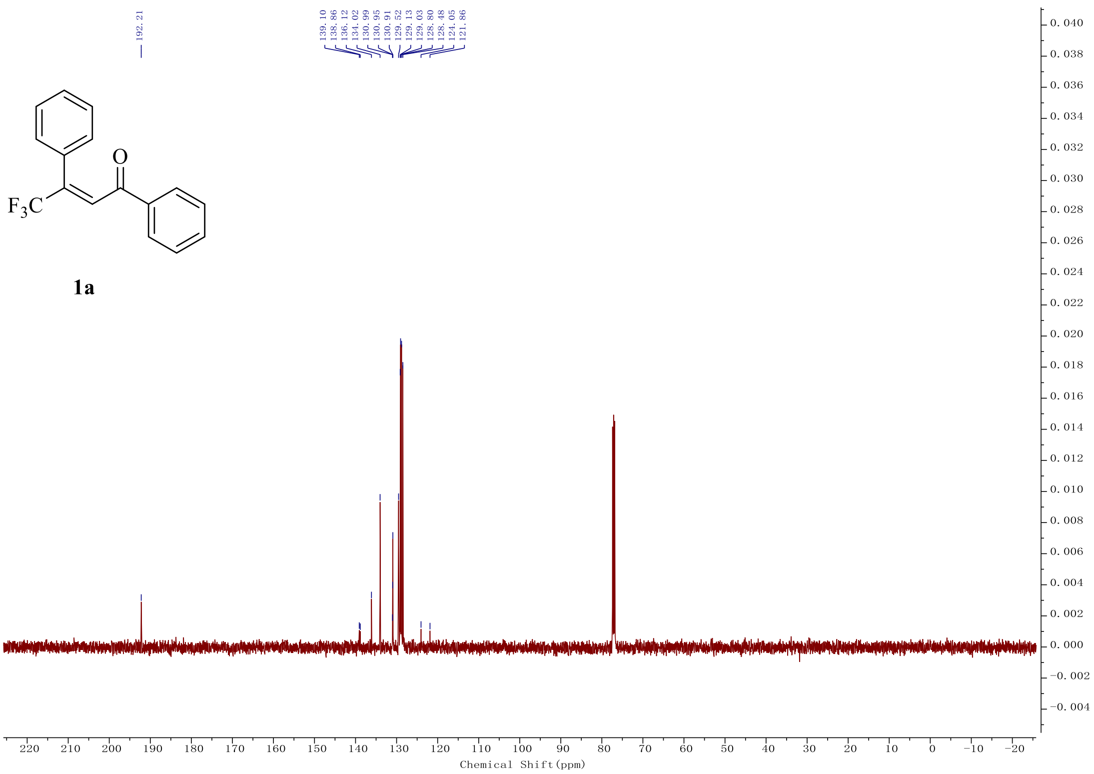
7.44
7.41
7.41
7.40
7.39
7.38
7.38
7.27
7.27
7.26
7.25
7.25
O
F_3C
1a
1.70
1.00
1.99
6.01
Chemical Shift(ppm)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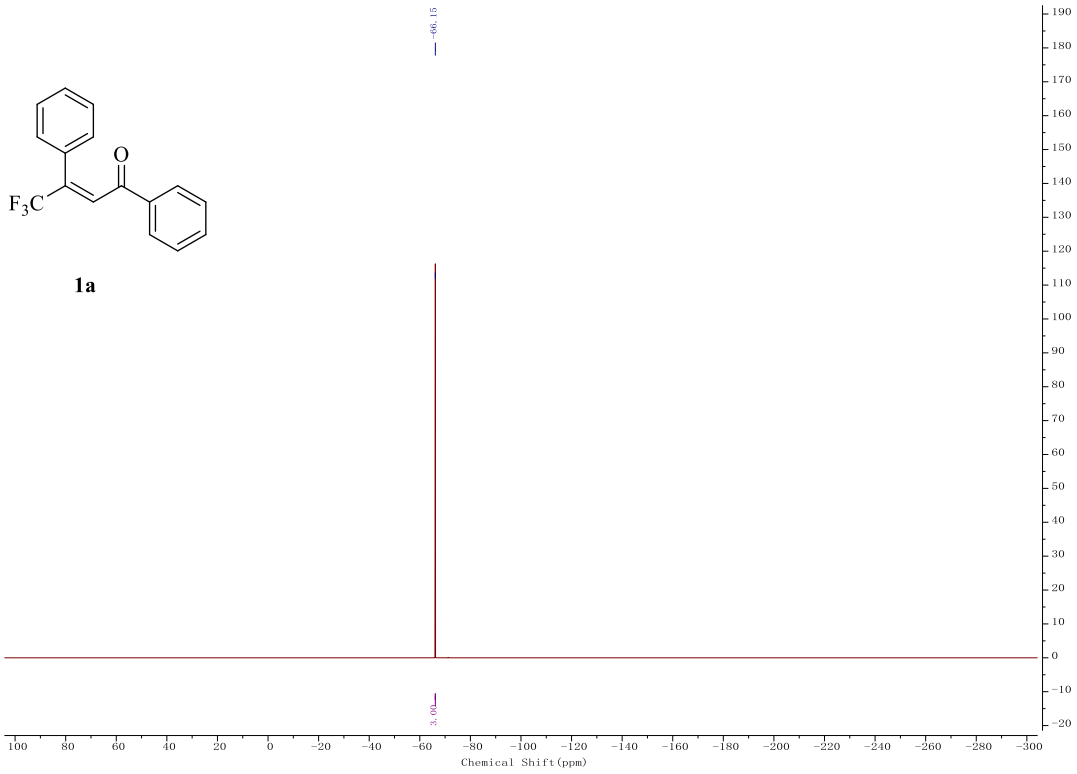
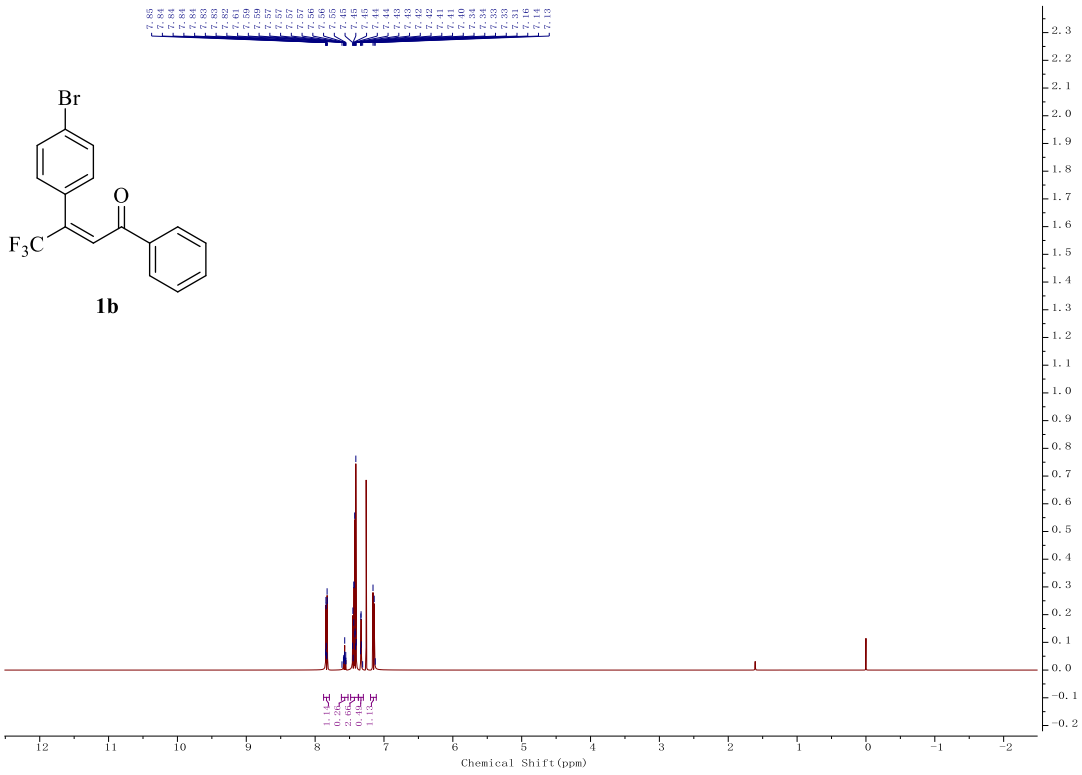
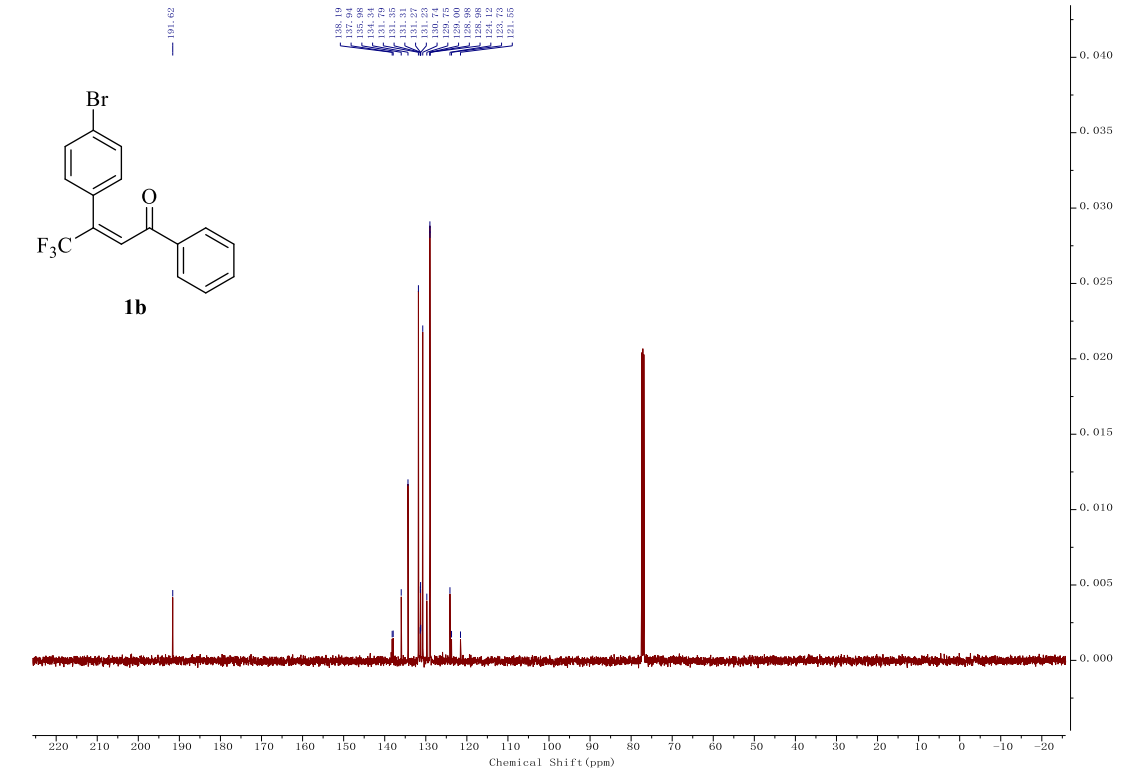
139.10
138.86
136.12
134.02
130.99
130.95
130.91
129.52
129.13
129.03
128.80
128.48
124.05
121.86
O
F_3C
1a
Chemical Shift(ppm)



1a



1b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134.34
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131.31
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131.23
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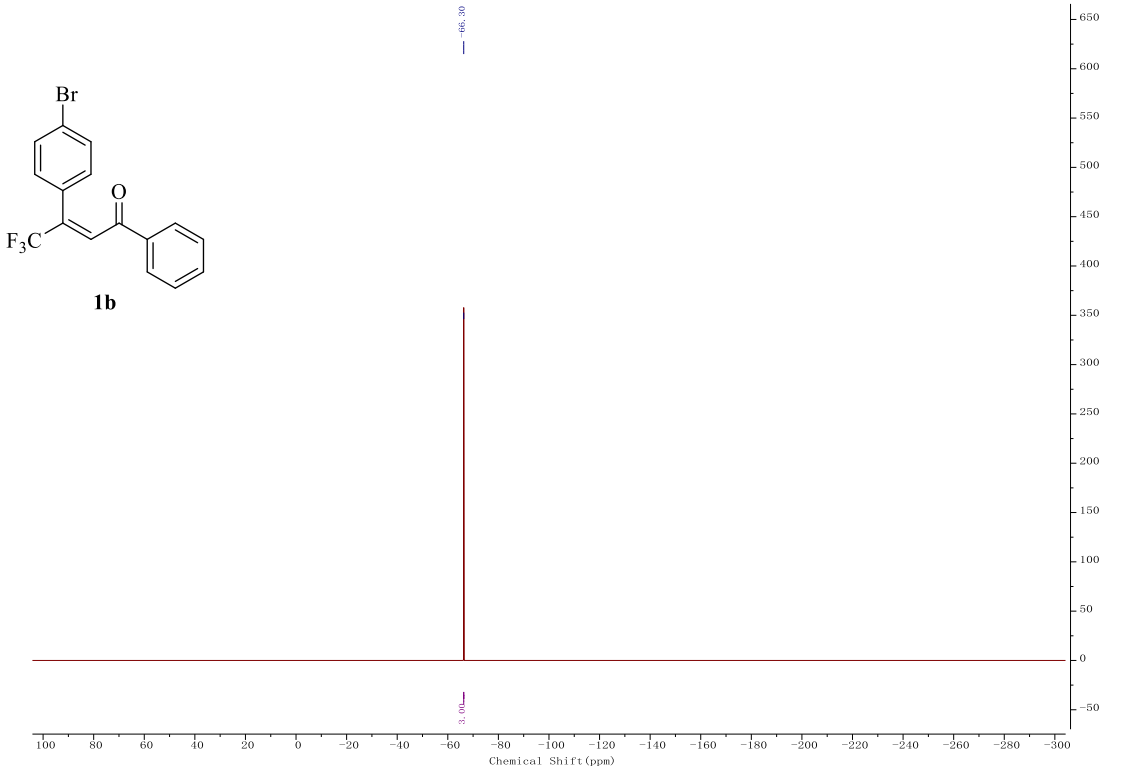
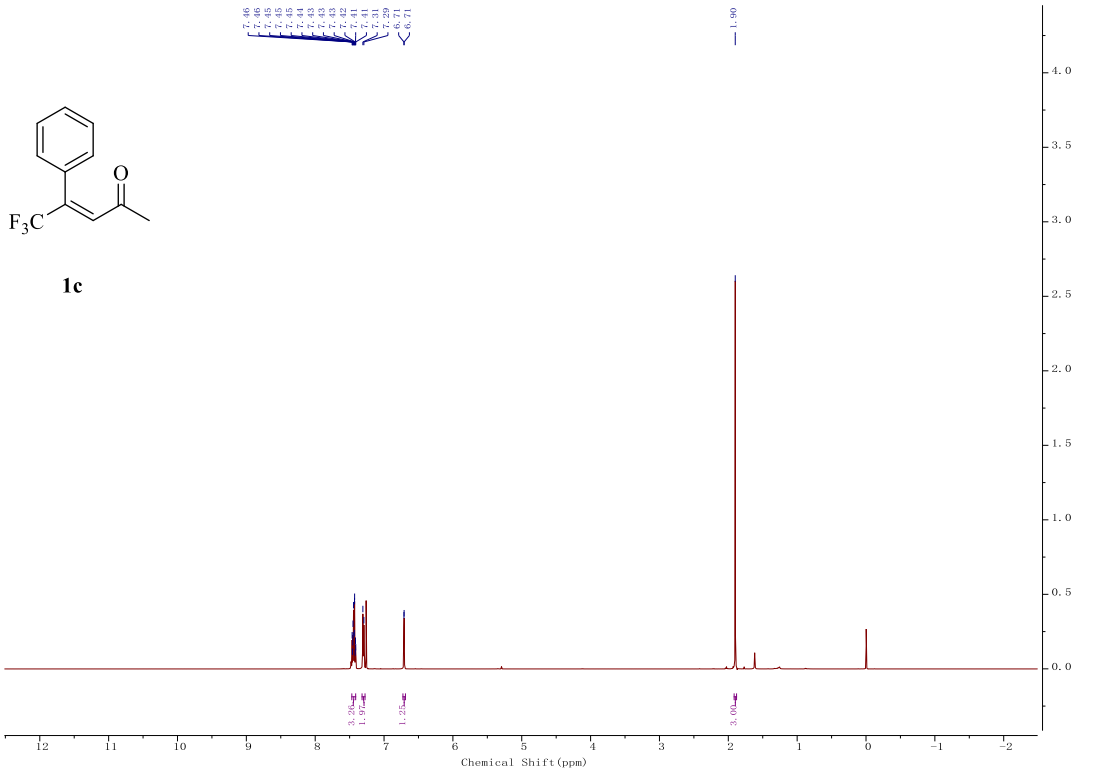
128.98
128.69
124.12
123.73
121.55
Br
O
F3C
1b
Chemical Shift(ppm)


-66.30
Br
O
F3C
1b
3.00
Chemical Shift(ppm)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7.46
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7.45
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7.44
7.43
7.43
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7.41
7.41
7.31
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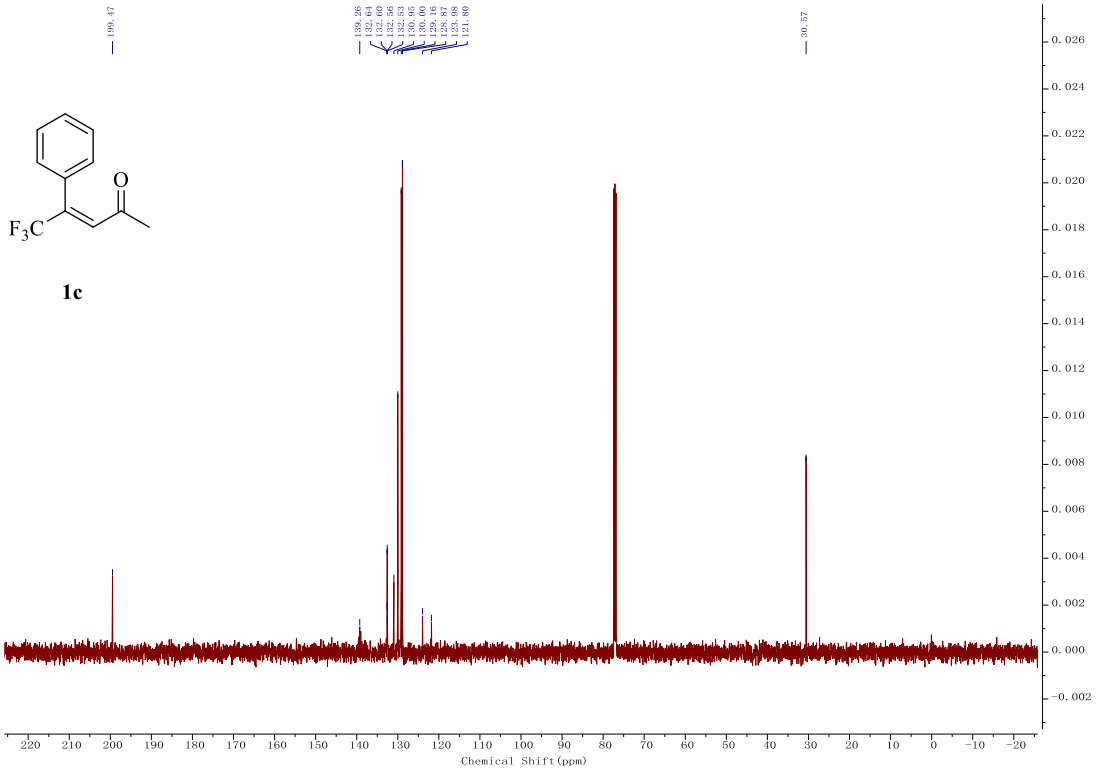
6.71
6.71
1.90
O
F3C
1c
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3.26
1.97
1.25
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
Chemical Shift(ppm)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128.87
123.98
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30.57
O
F3C
1c
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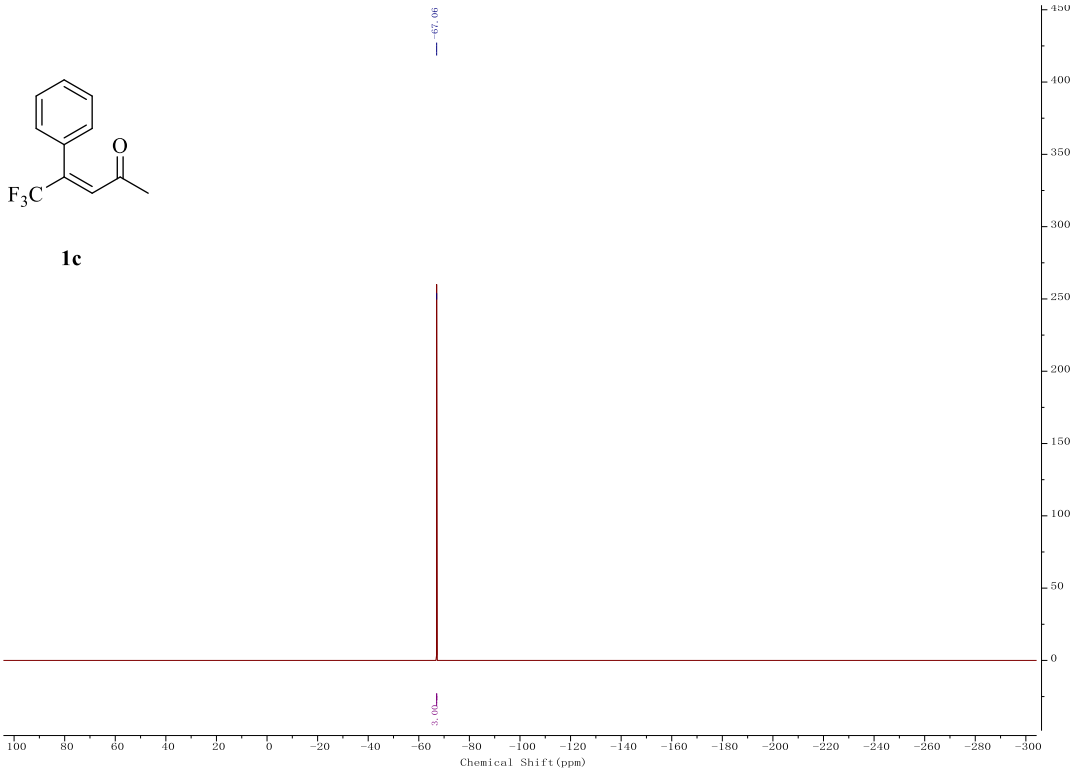
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
−0.002
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
Chemical Shift(ppm)

O
F3C

1c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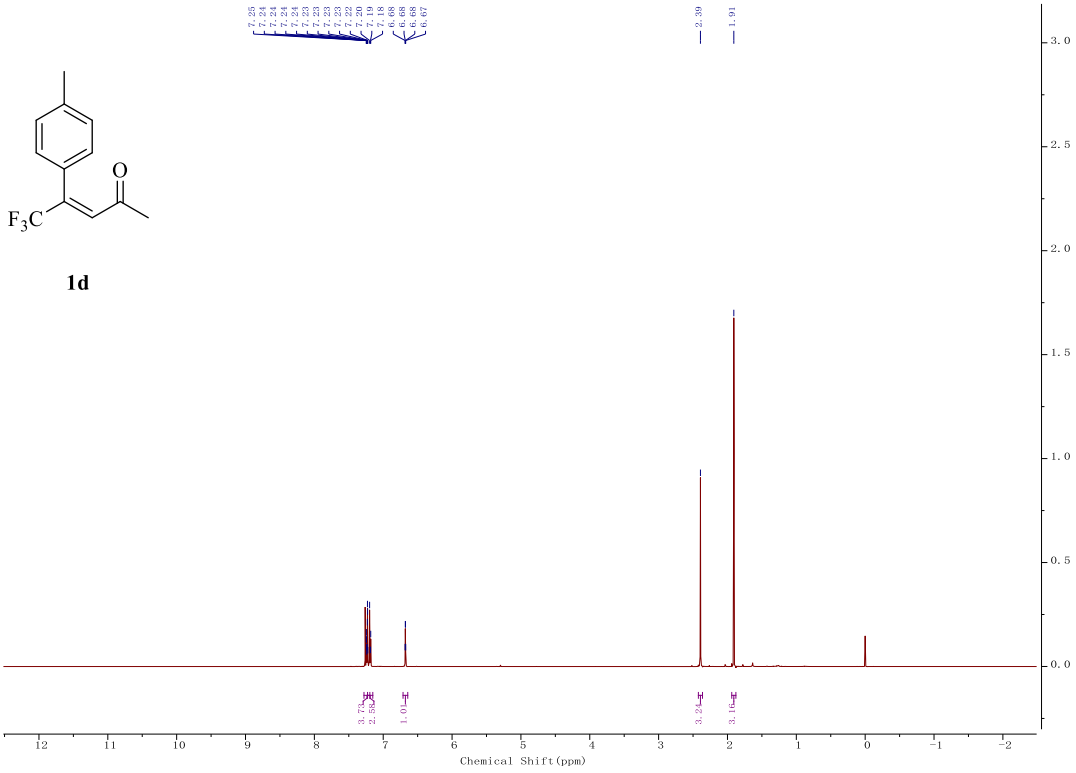
3.00
Chemical Shift(ppm)

O
F3C

1d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7.22
7.20
7.19
7.18
6.68
6.68
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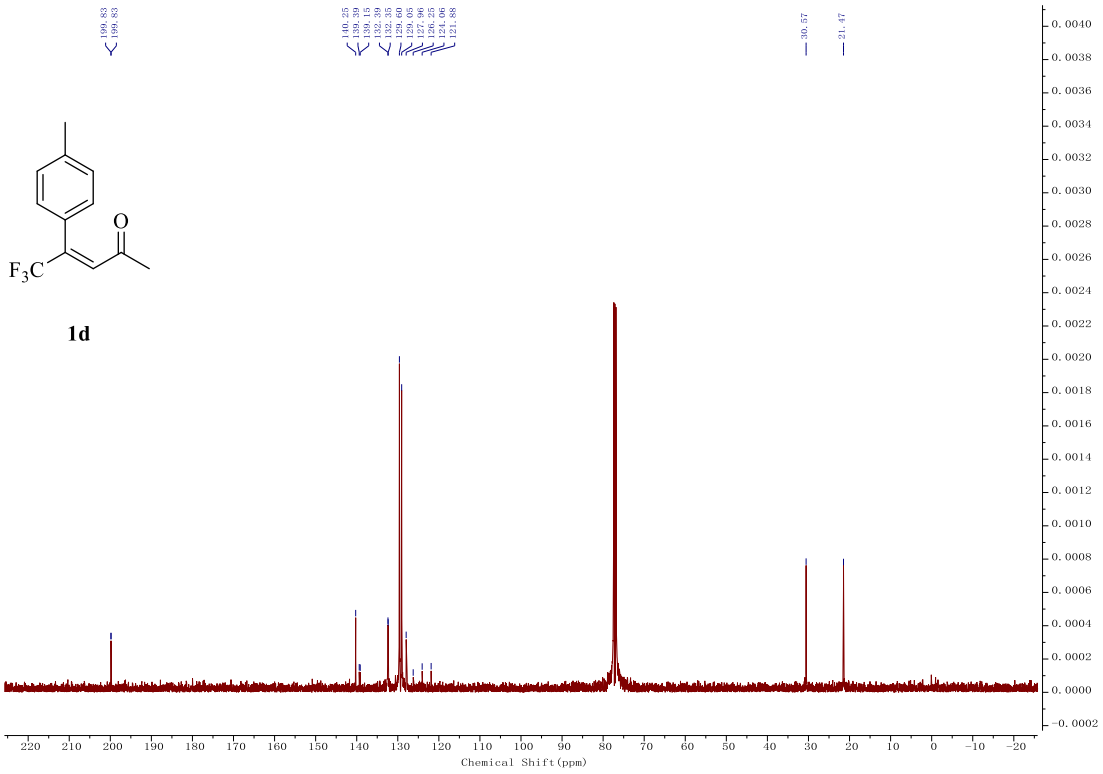
6.67
2.39
1.91
3.73
2.58
1.01
3.24
3.16
Chemical Shift(ppm)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140.25
139.39
139.15
132.39
132.35
129.60
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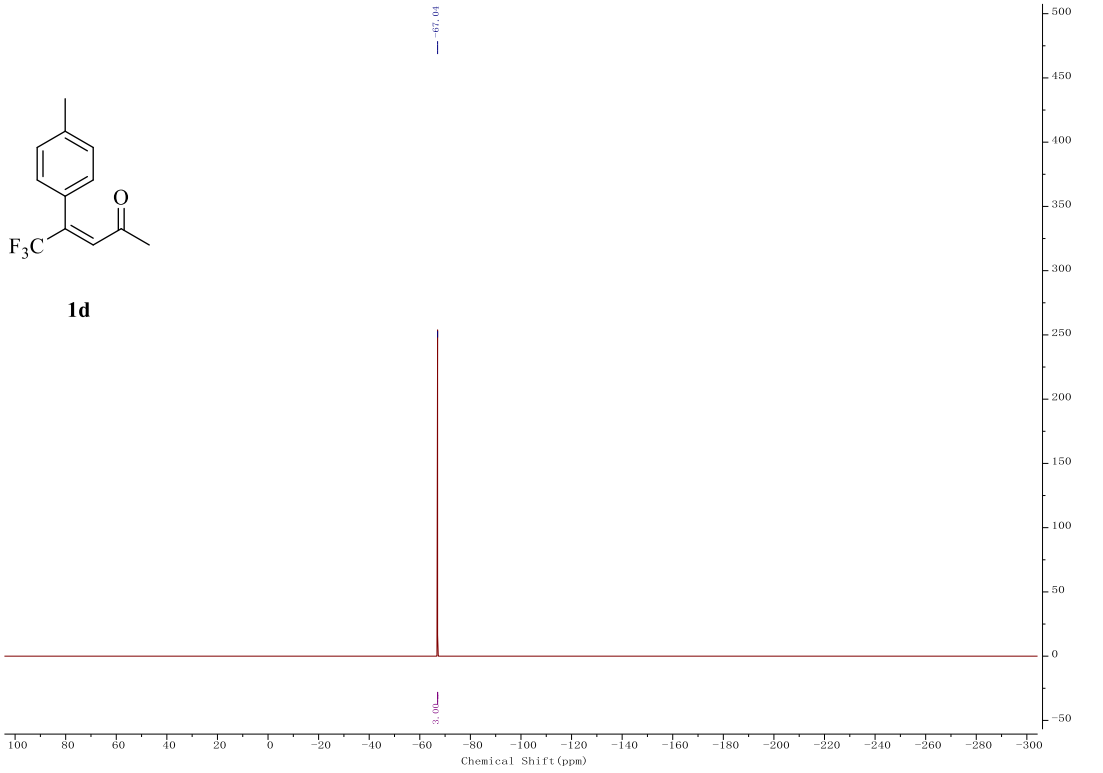
127.96
126.25
124.06
121.88
30.57
21.47
O
F3C
Chemical Shift(ppm)

1d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3.00
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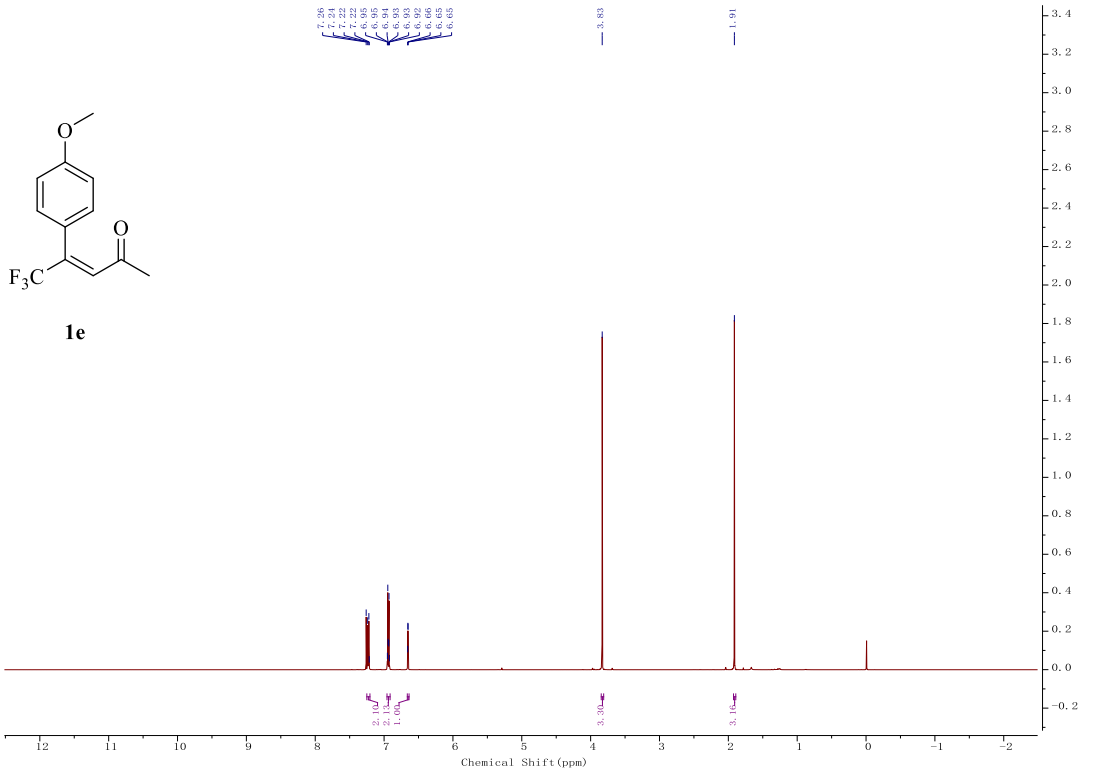
F3C
Chemical Shift(ppm)

1d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6.95
6.94
6.93
6.93
6.92
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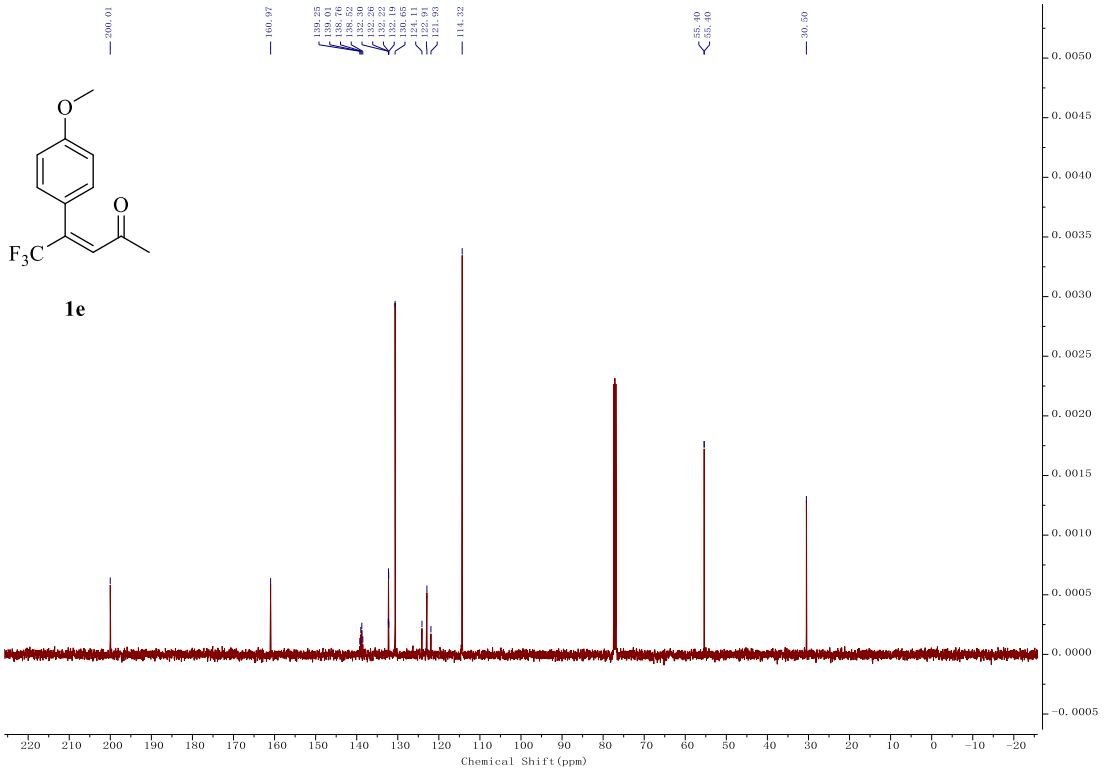
2.10
2.15
1.00
3.30
3.16
Chemical Shift(ppm)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132.26
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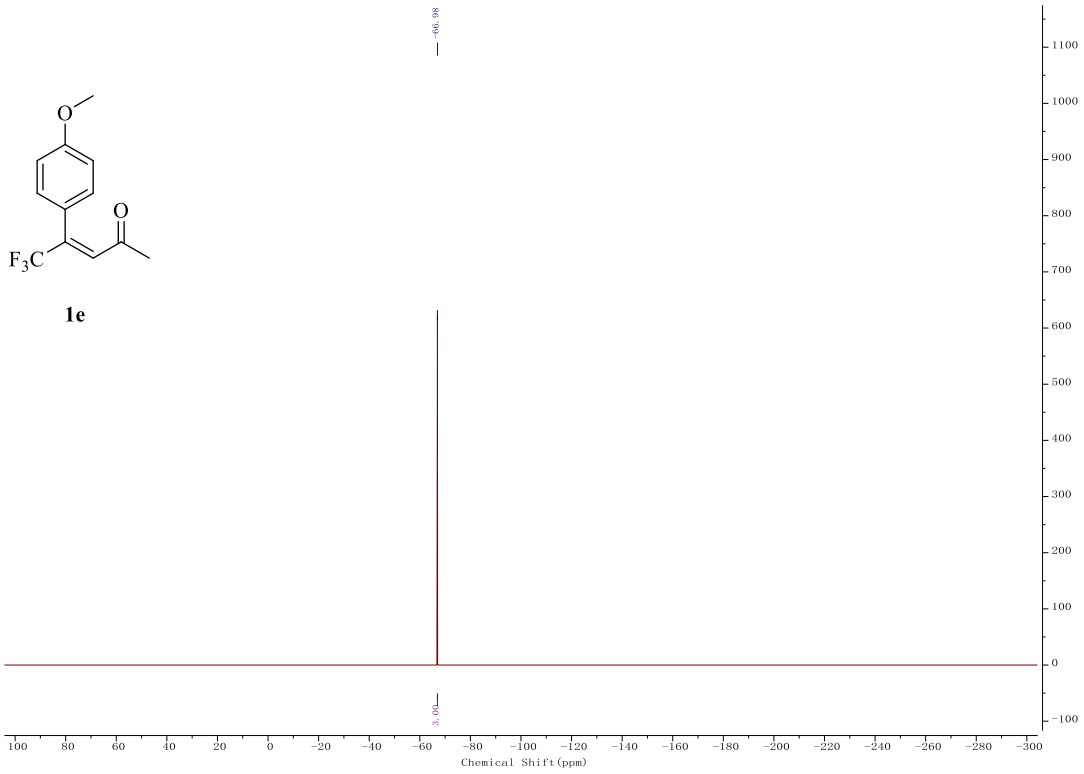
121.93
114.32
55.40
55.40
30.50
Chemical Shift(ppm)

1e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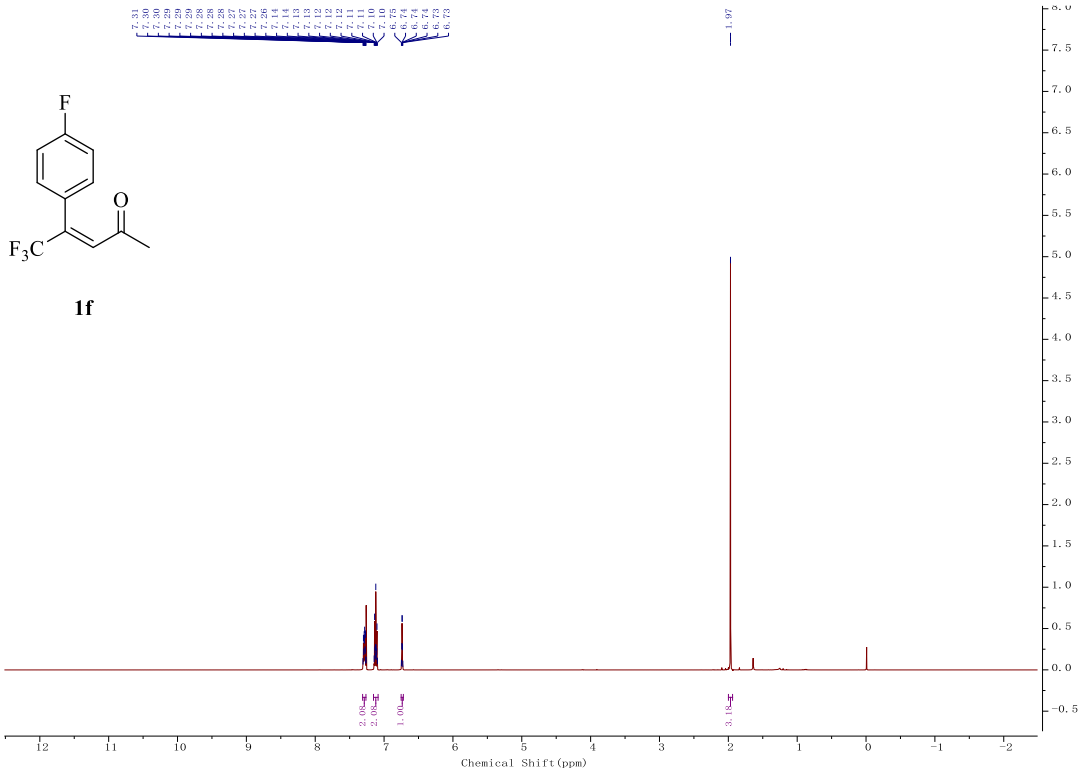
3.00
Chemical Shift(ppm)

1e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7.14
7.14
7.13
7.13
7.12
7.12
7.12
7.11
7.11
7.10
7.10
6.75
6.74
6.74
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6.73
6.73
1.97
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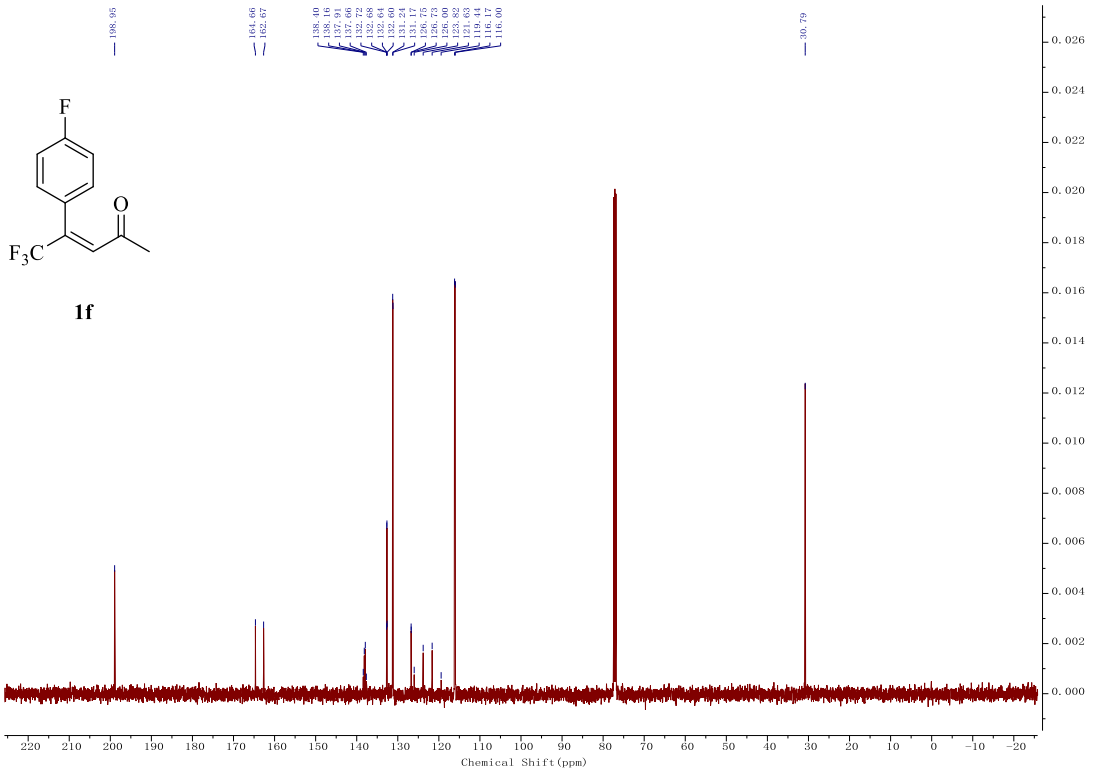
1.00
3.18
Chemical Shift(ppm)

1f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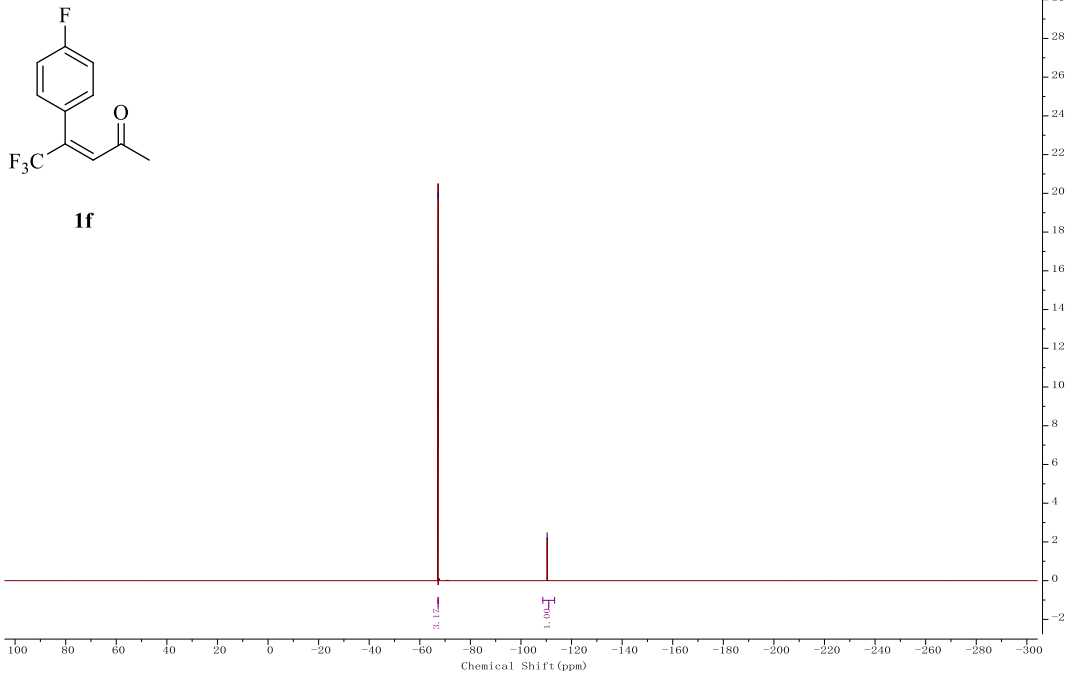
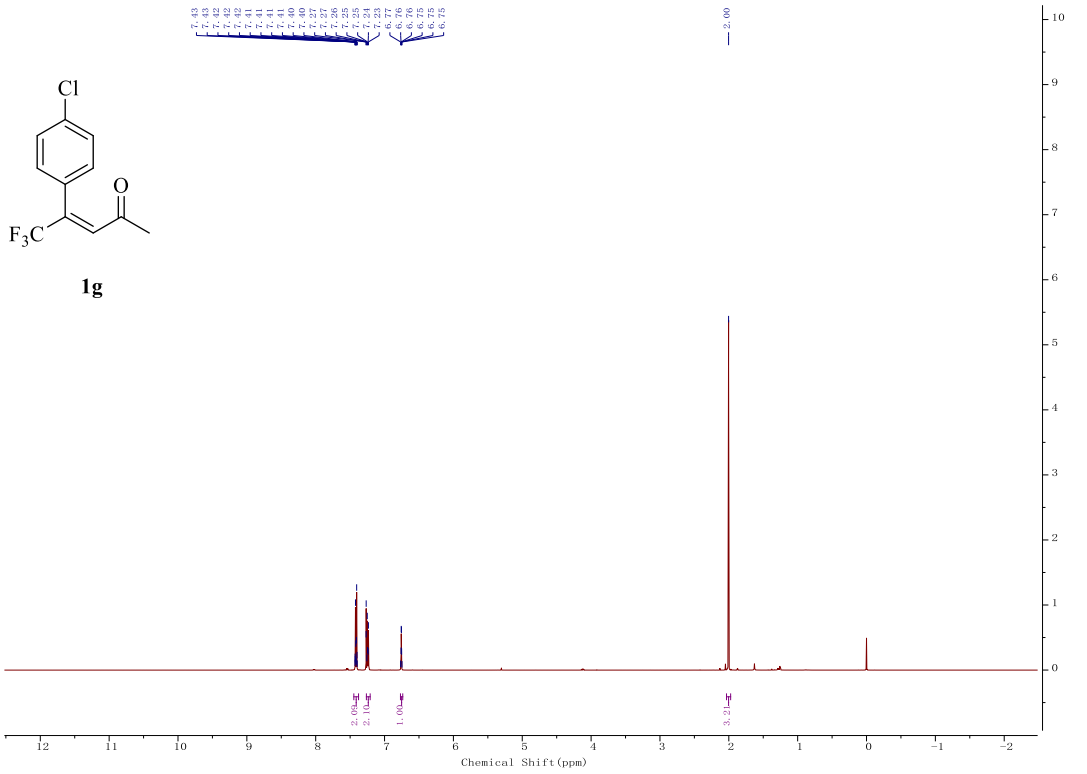
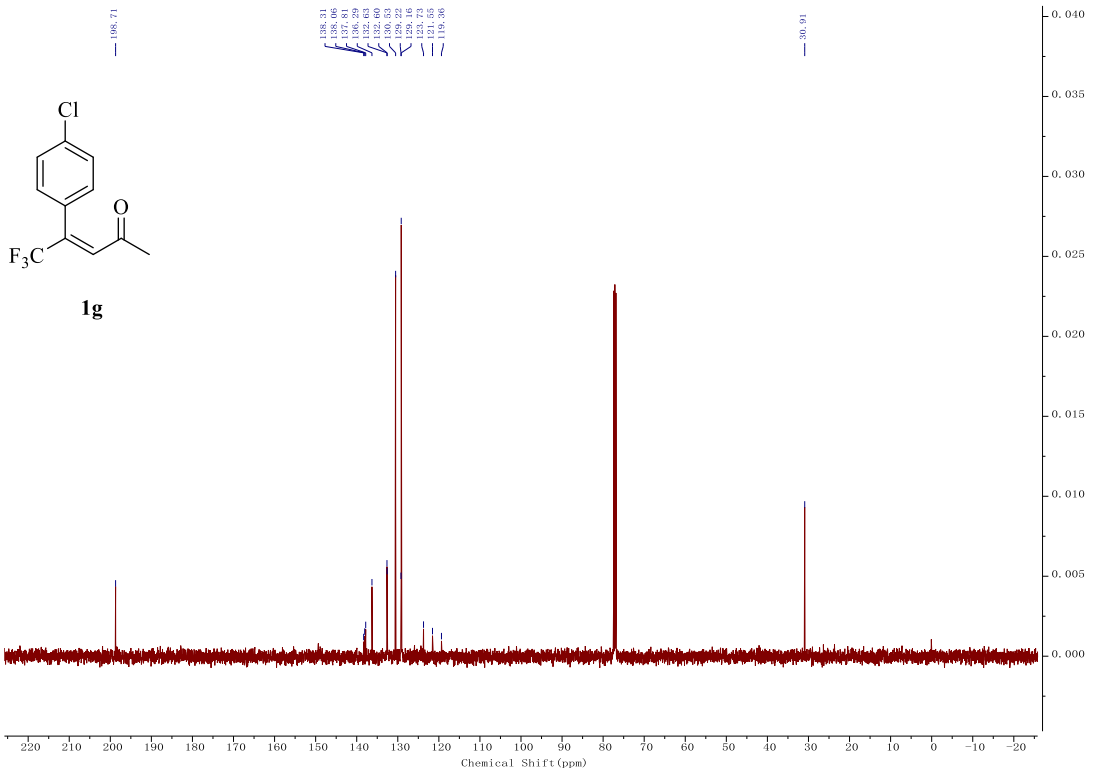
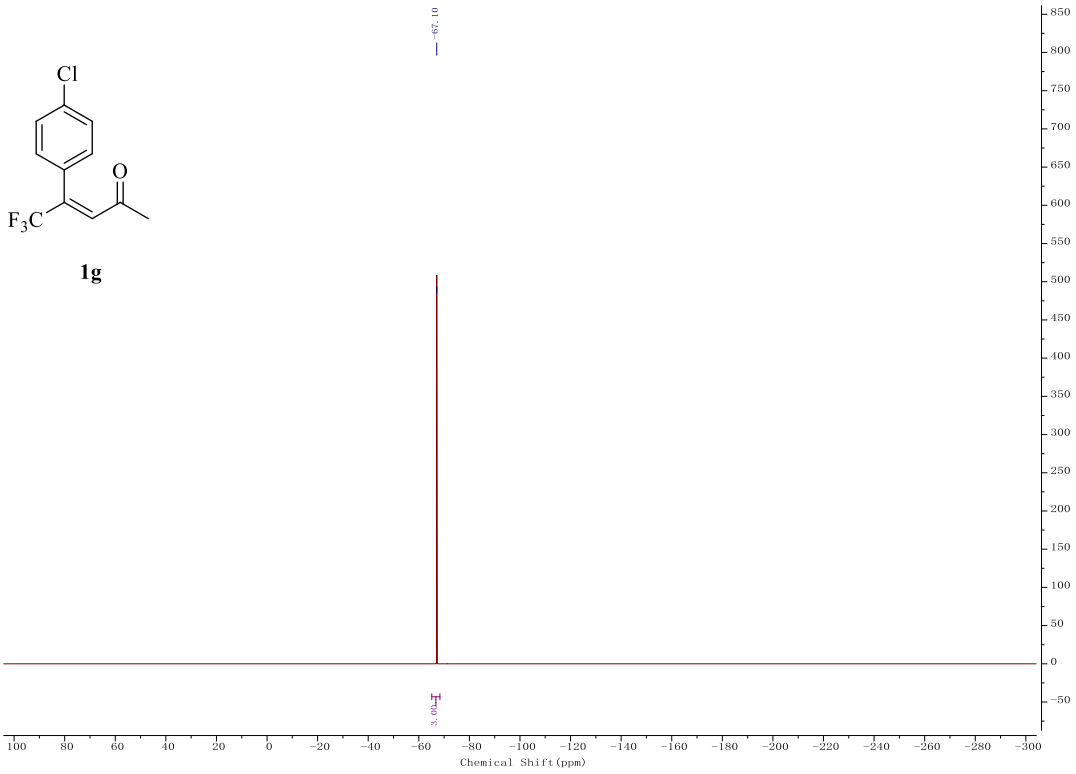
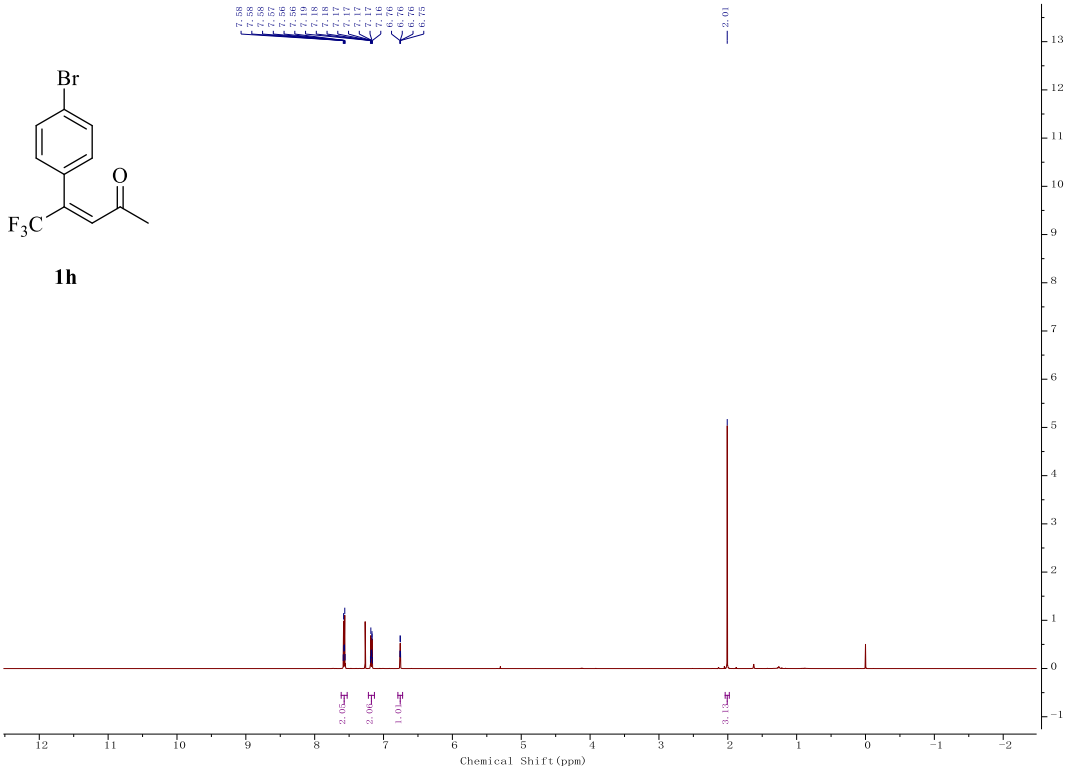
126.00
123.82
121.63
119.44
116.17
116.00
30.79
Chemical Shift(ppm)

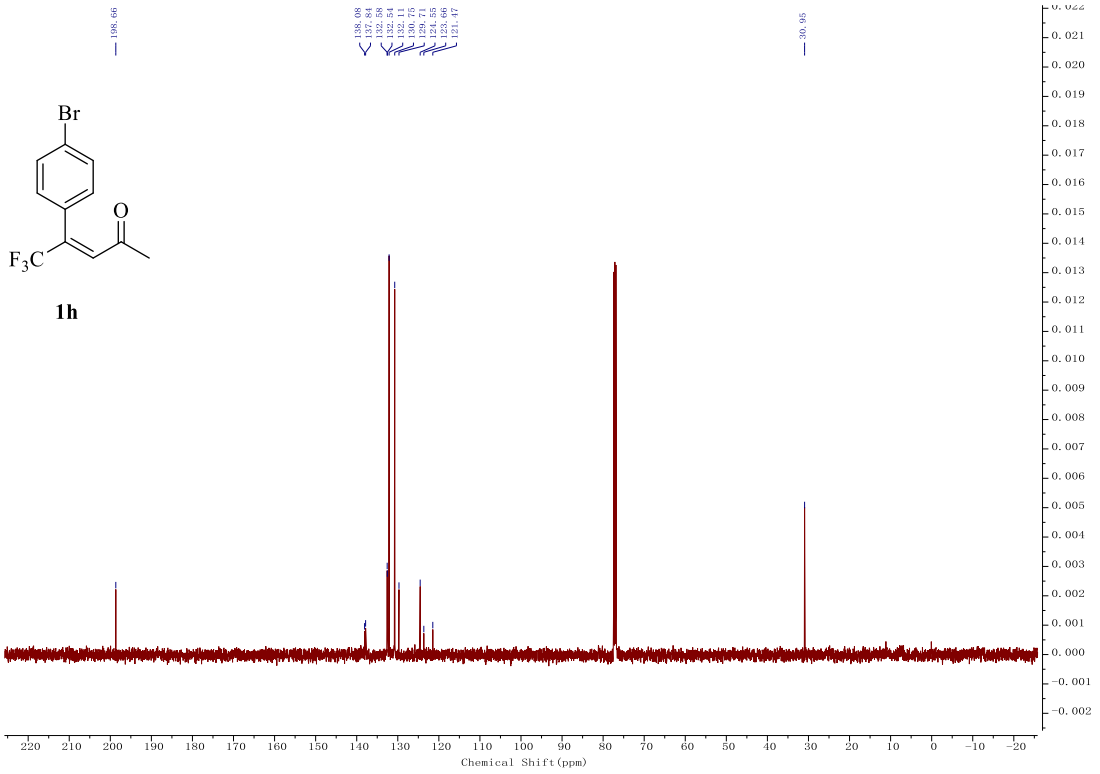

-67.25
-110.35
3.17
1.00
Chemical Shift(ppm)

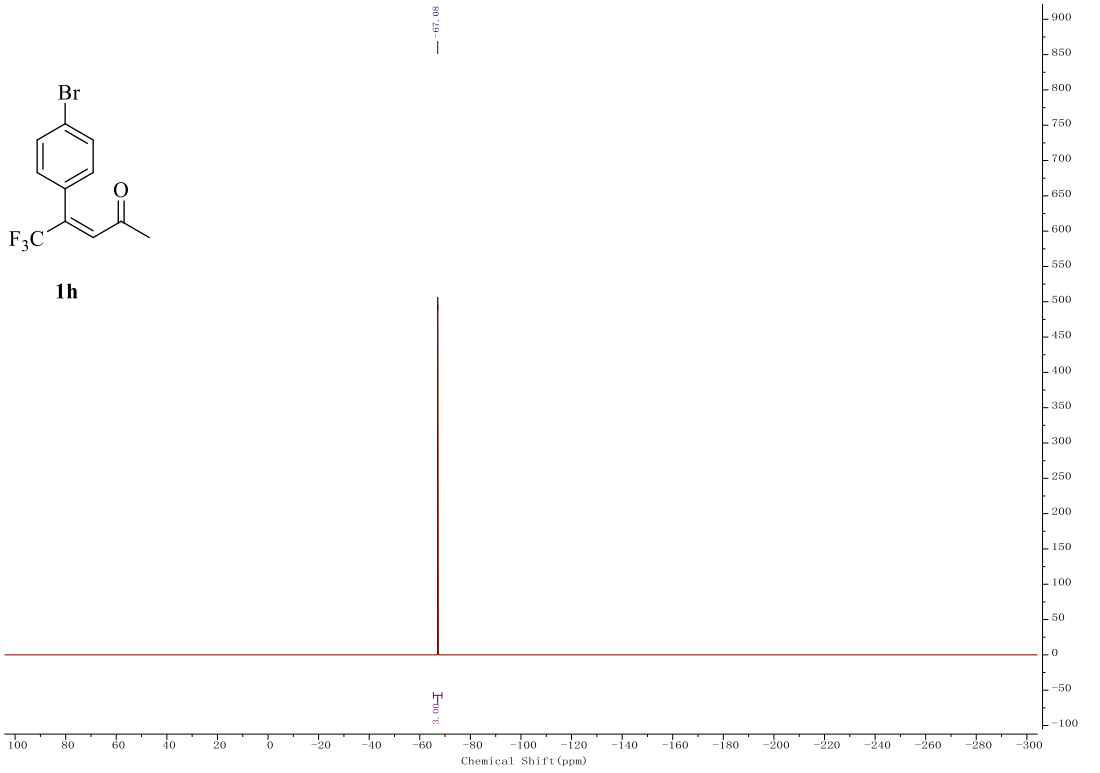

Cl
O
F3C
1g
Chemical Shift(ppm)

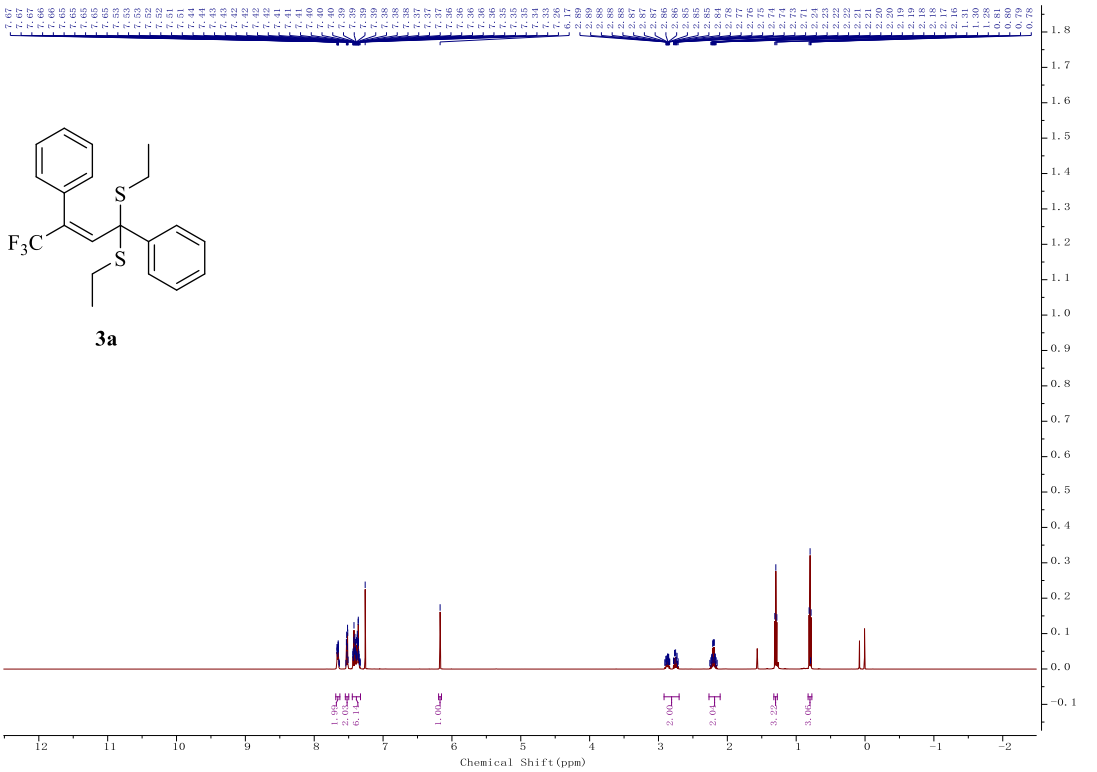

Cl
O
F3C
1g
Chemical Shift(ppm)


Cl
O
F3C
1g
-67.10
3.00
Chemical Shift(ppm)

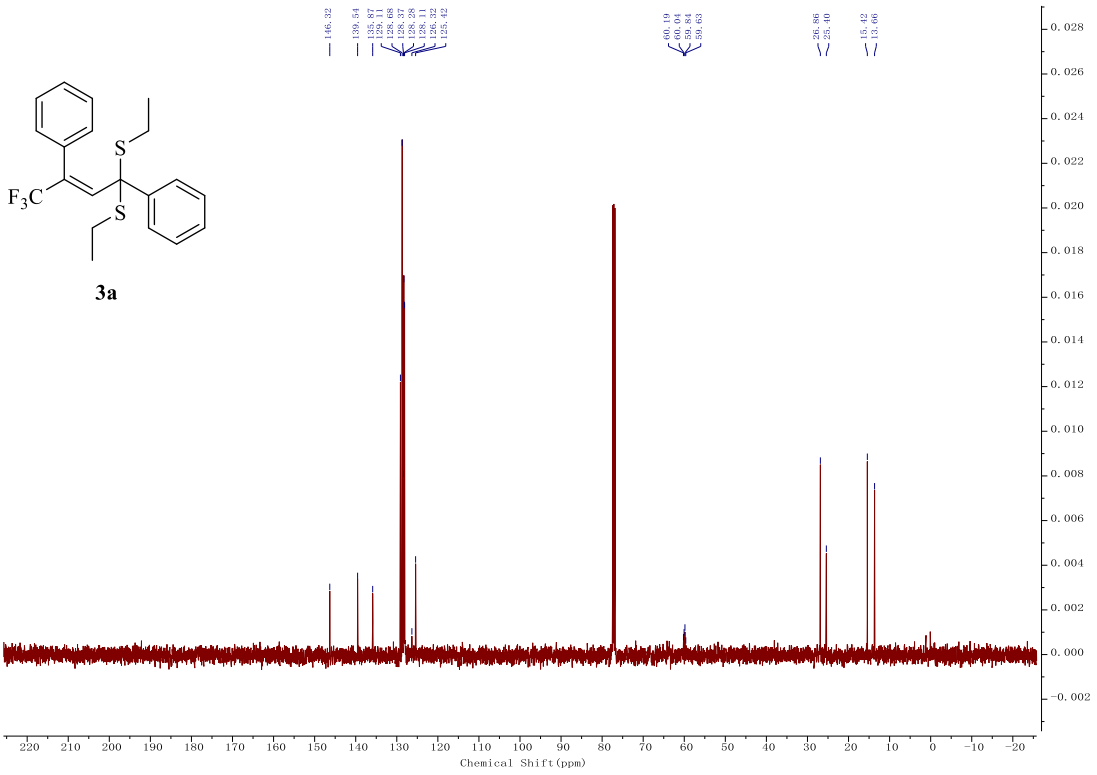

Br
O
F3C
1h
7.58
7.58
7.58
7.57
7.56
7.56
7.56
7.19
7.18
7.18
7.17
7.17
7.17
7.17
7.16
6.76
6.76
6.76
6.75
2.01
2.05
2.06
1.01
3.13
Chemical Shift(ppm)


198.66
138.08
137.84
132.58
132.54
132.11
130.75
130.71
124.55
123.66
121.47
30.95
Br
O
F3C
1h
Chemical Shift(ppm)


-67.08
3.00
Br
O
F3C
1h
Chemical Shift(ppm)



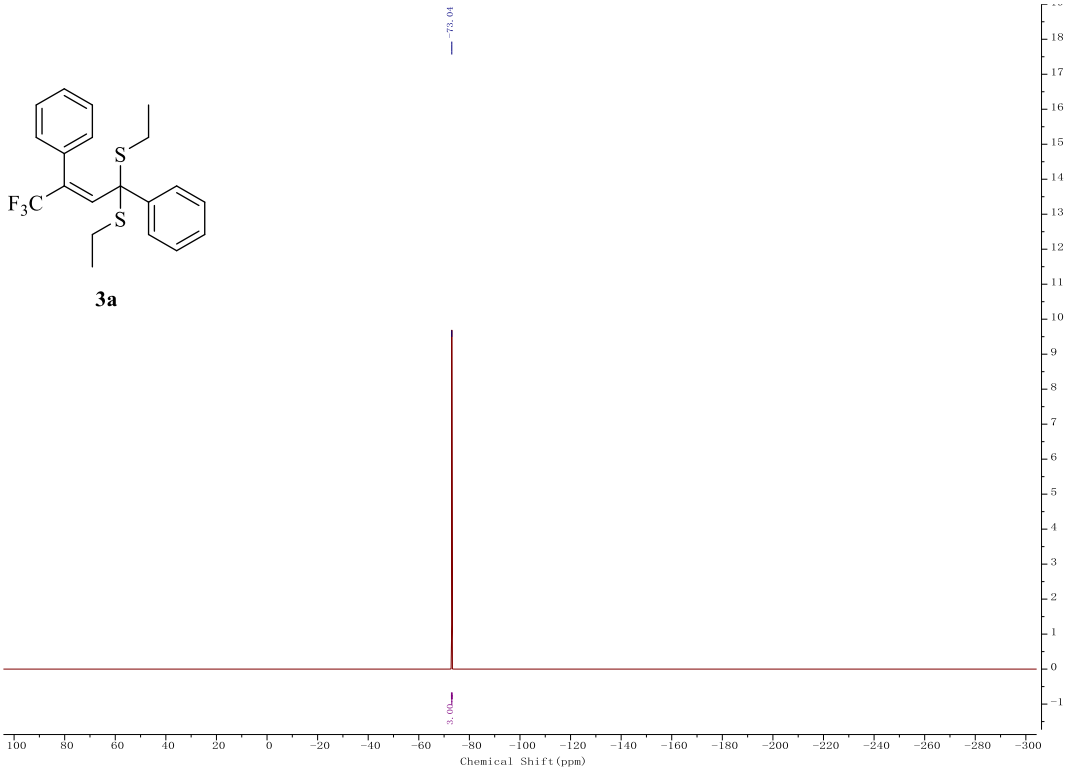
3a



3a

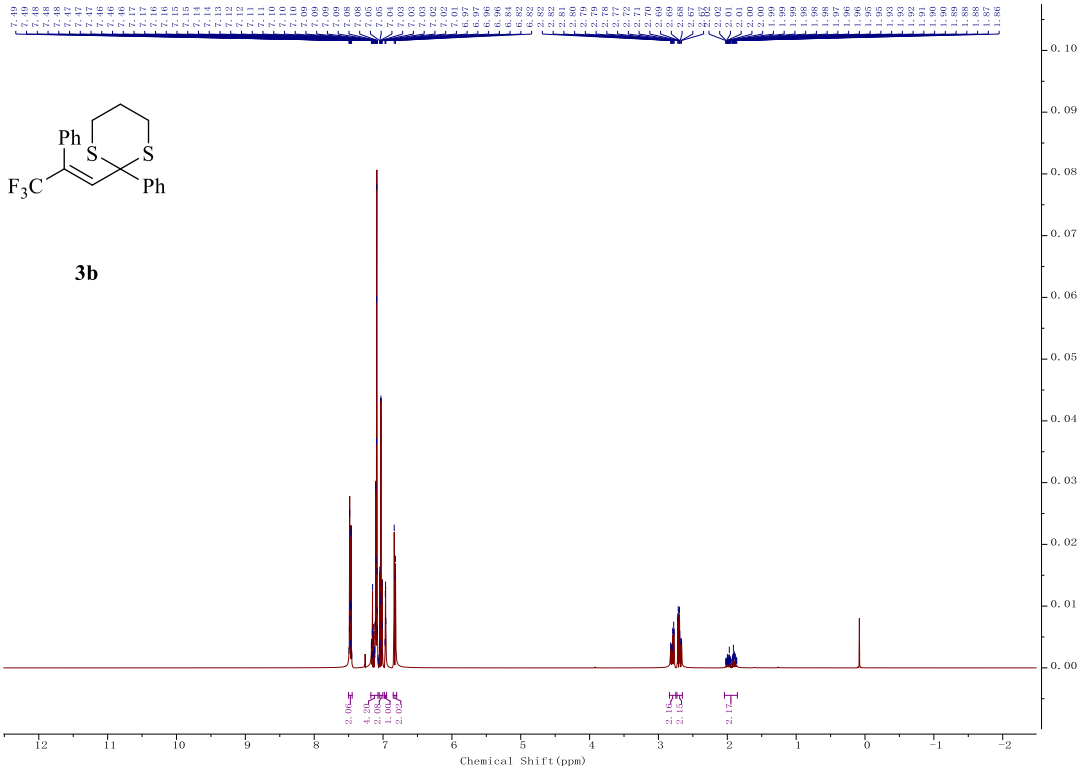
S
S
F3C

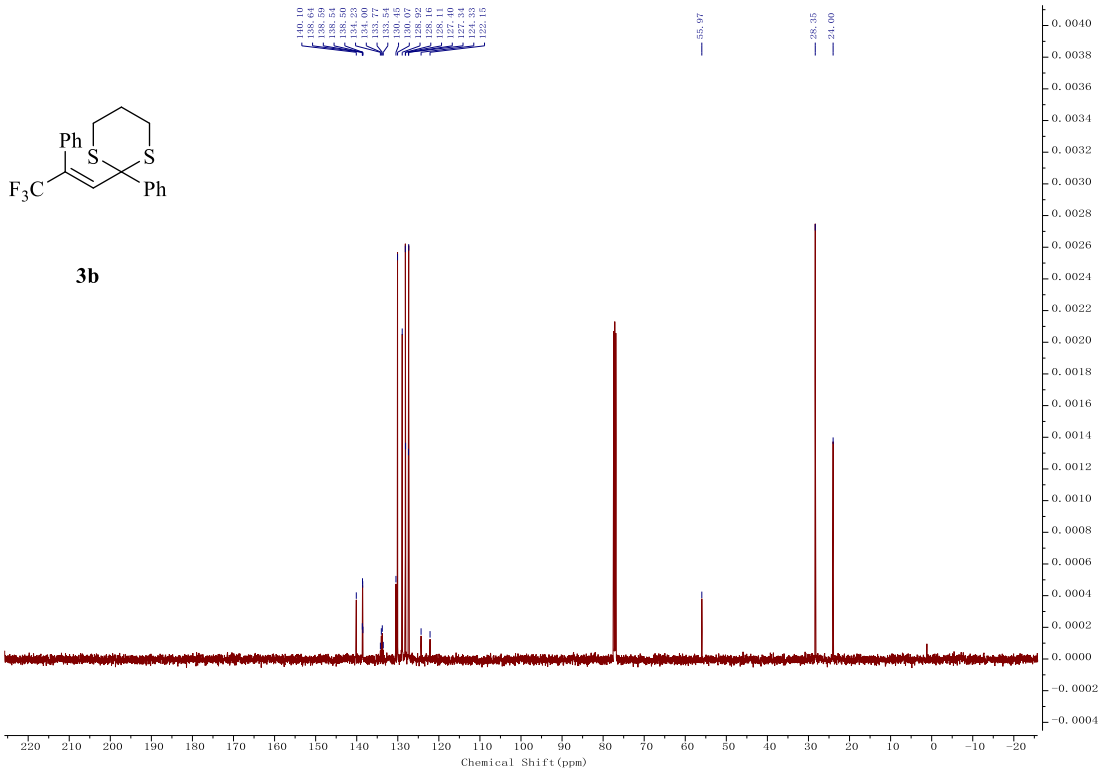
3a

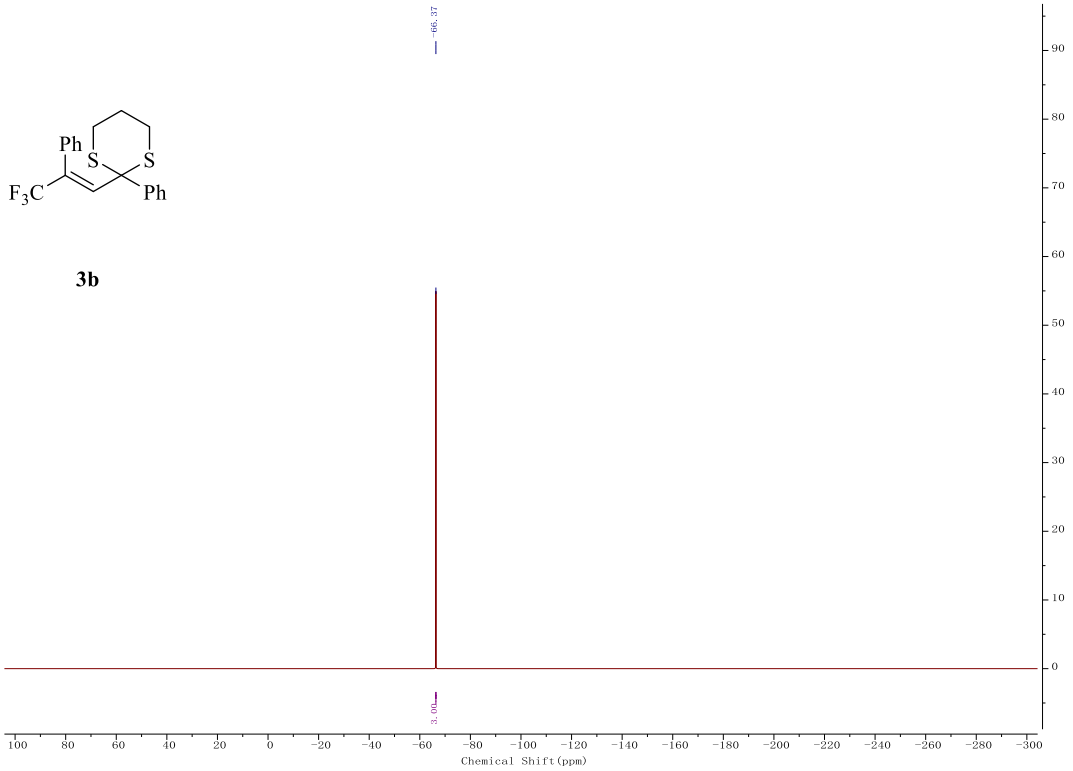

-73.04
3.00
Chemical Shift(ppm)

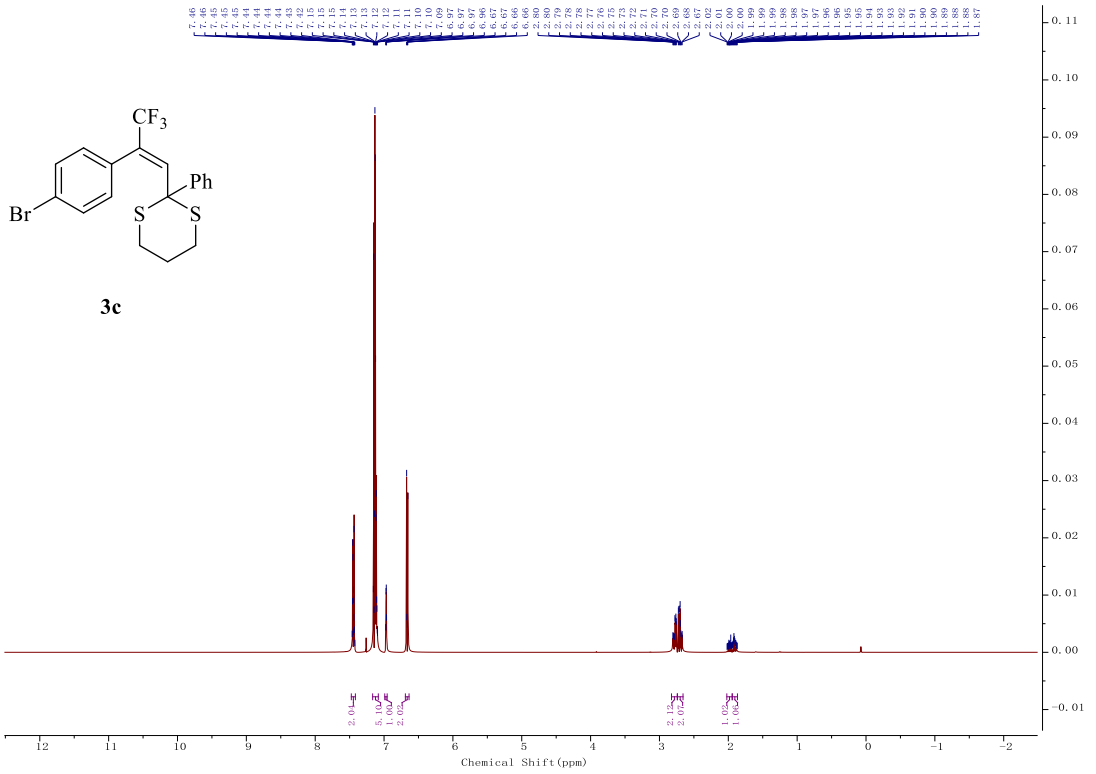
Ph
S
S
F3C
Ph

3b

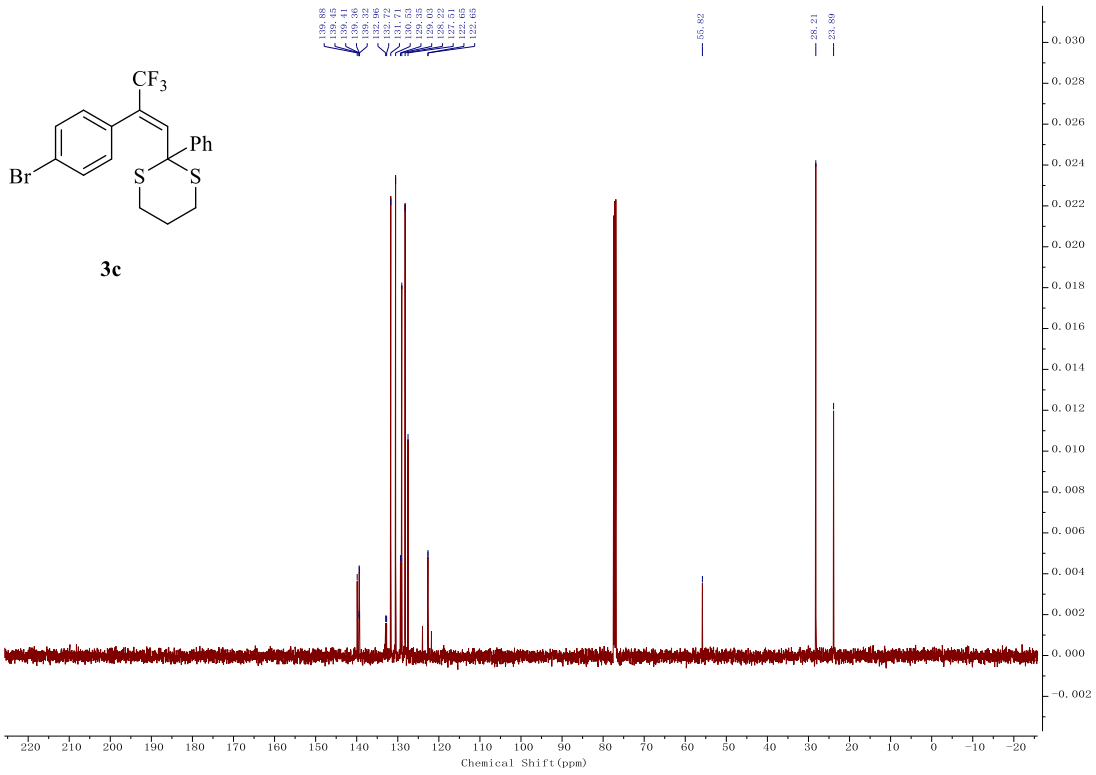

2.06
4.20
2.06
1.00
2.02
2.15
2.15
2.17
Chemical Shift(ppm)


Ph
S
S
F3C
Ph
3b
140.10
139.64
138.95
138.54
138.50
134.23
134.00
133.77
130.45
130.07
128.92
128.16
128.11
127.40
127.34
124.33
122.15
55.97
28.35
24.00
Chemical Shift(ppm)


Ph
S
S
F3C
Ph
3b
-66.37
3.00
Chemical Shift(ppm)


CF3
Ph
Br
S
S
Chemical Shift(ppm)

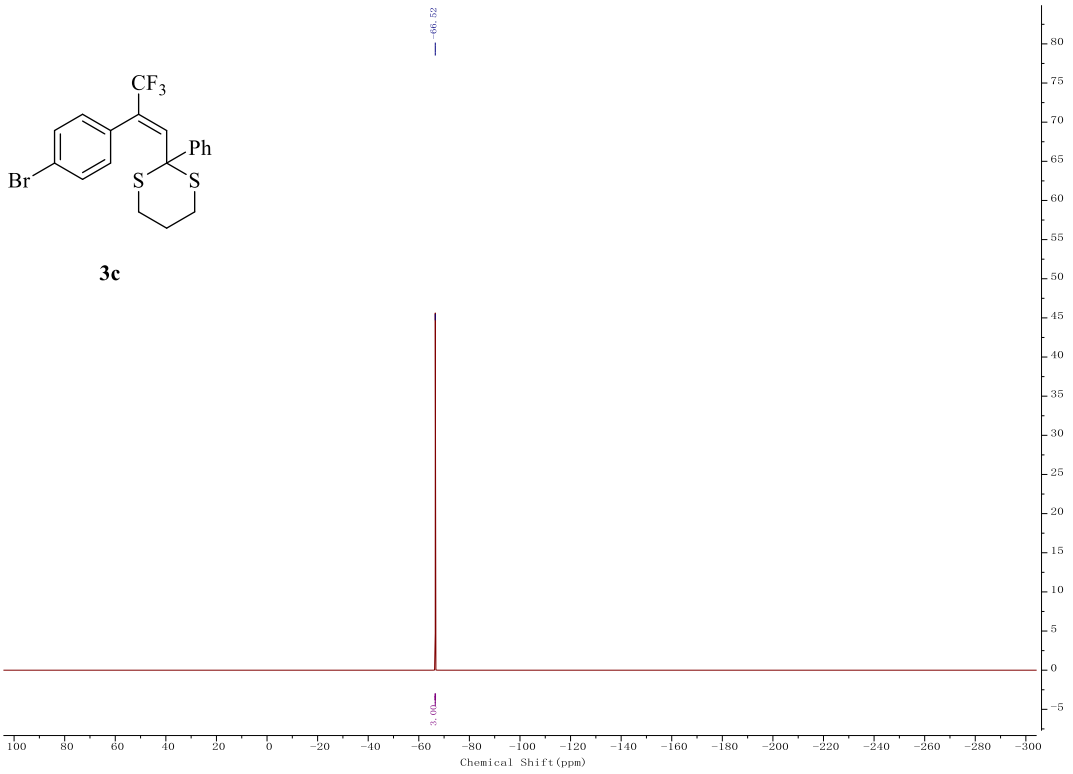
3c


CF3
Ph
Br
S
S
Chemical Shift(ppm)

3c

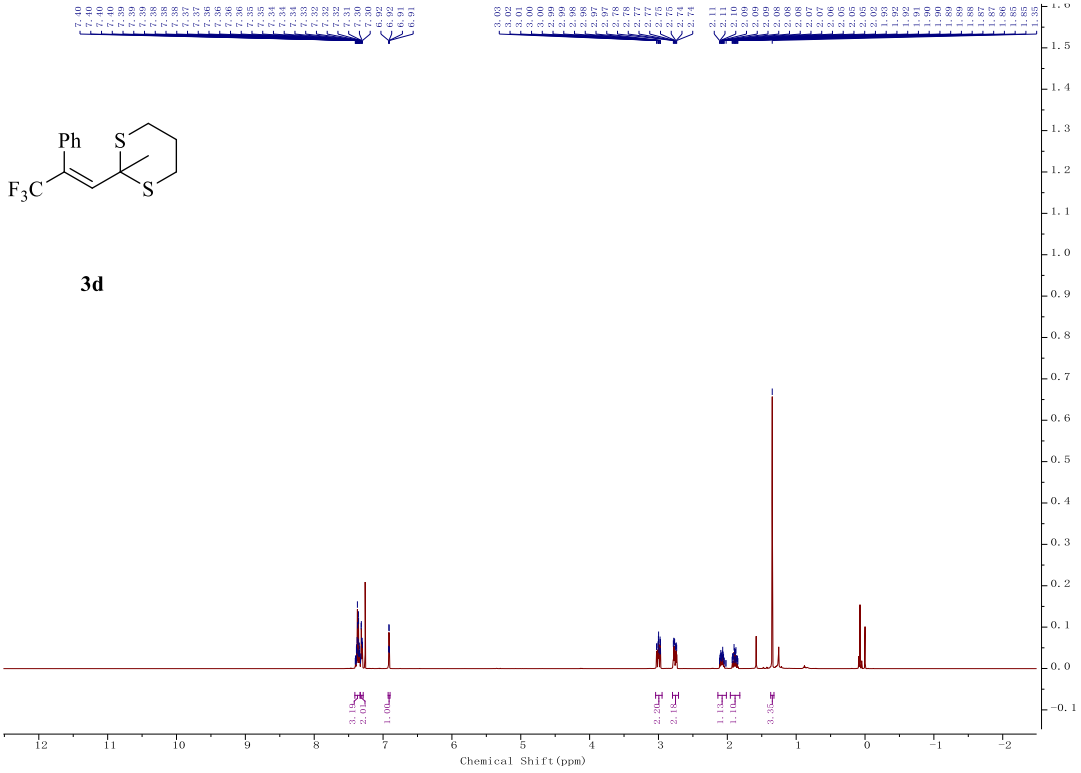
CF3
Ph
Br
S
S

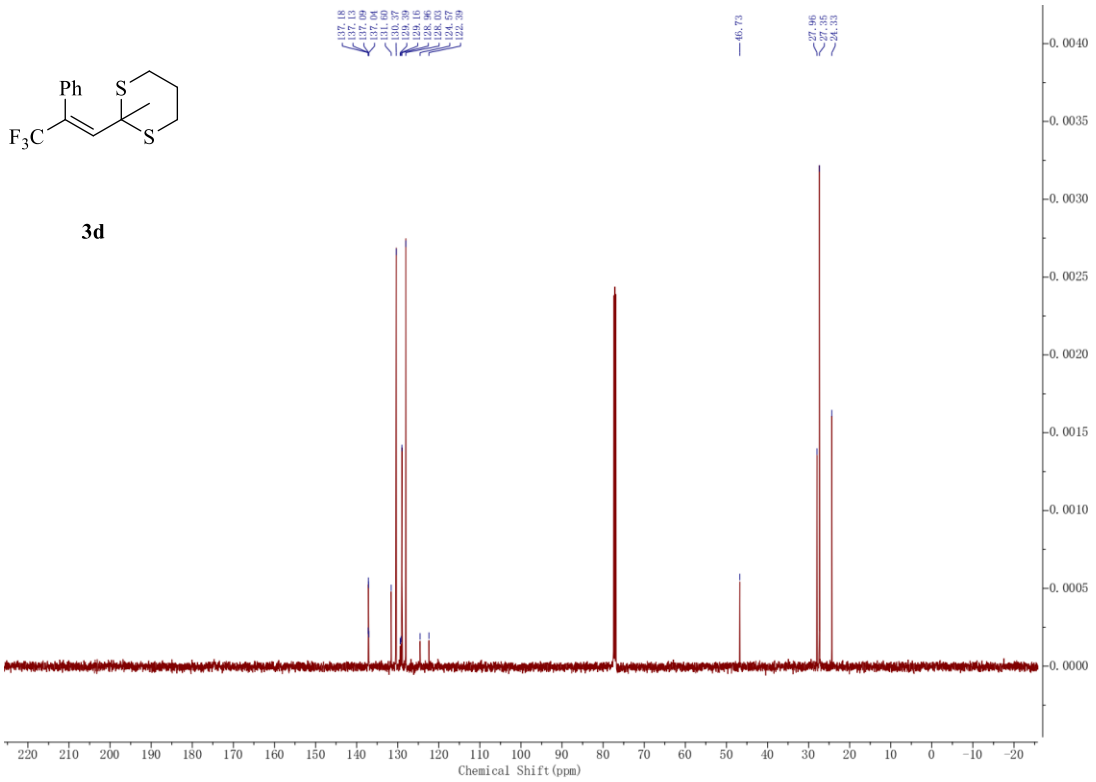
3c


-66.52
3.00
Chemical Shift(ppm)

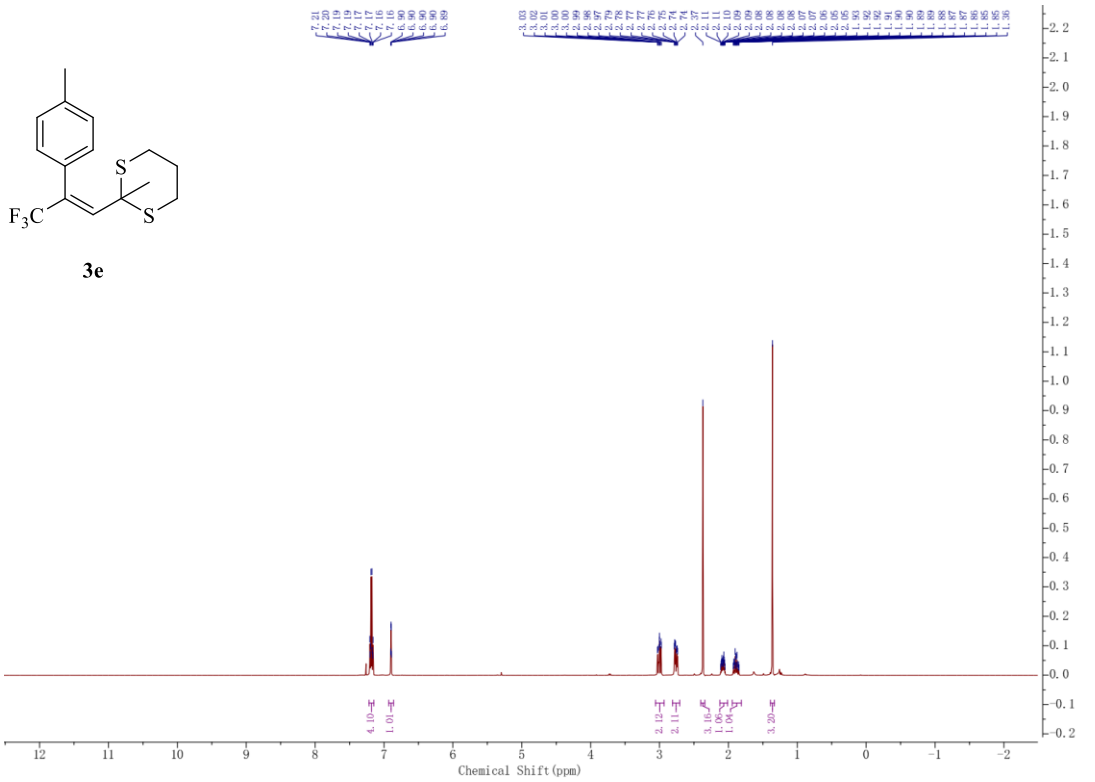
Ph
S
F3C
S

3d

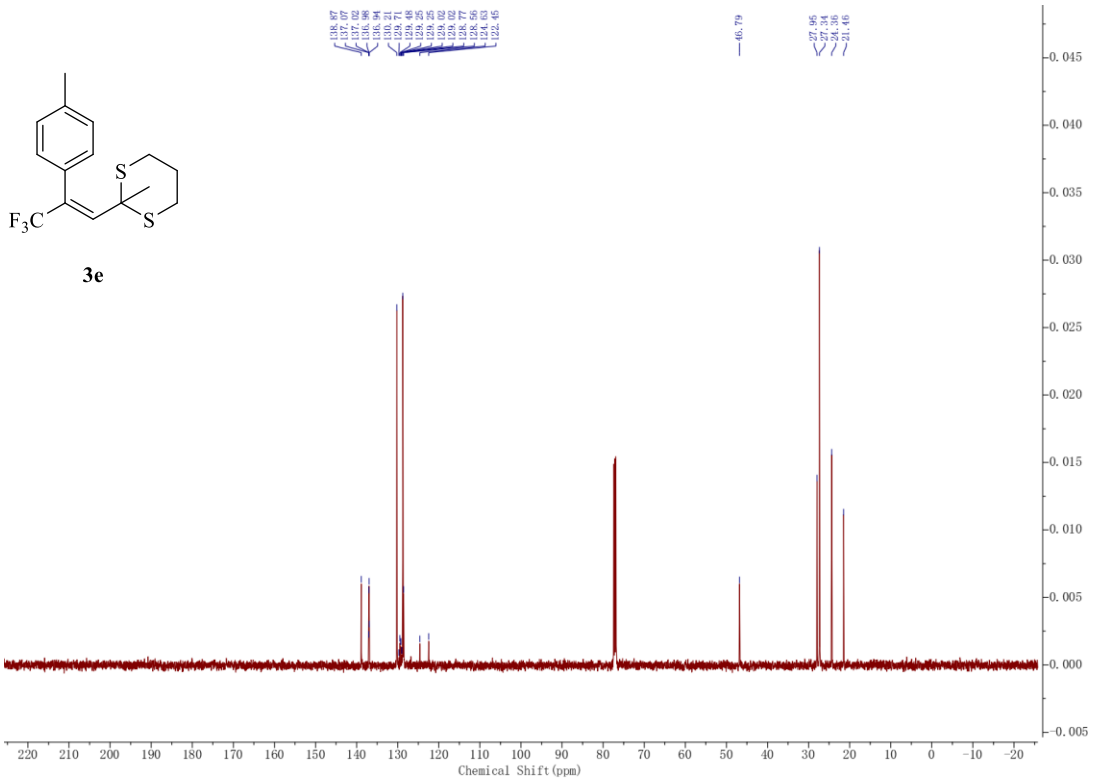

3.15
2.01
1.00
2.20
2.18
1.13
1.10
3.35
Chemical Shift(ppm)


Ph
S
S
F3C
3d
137.18
137.13
137.09
137.04
131.60
130.37
129.38
124.16
128.96
126.03
124.57
122.39
46.73
27.96
27.35
24.33
Chemical Shift(ppm)


Ph
S
S
F3C
3d
-66.30
3.00
Chemical Shift(ppm)



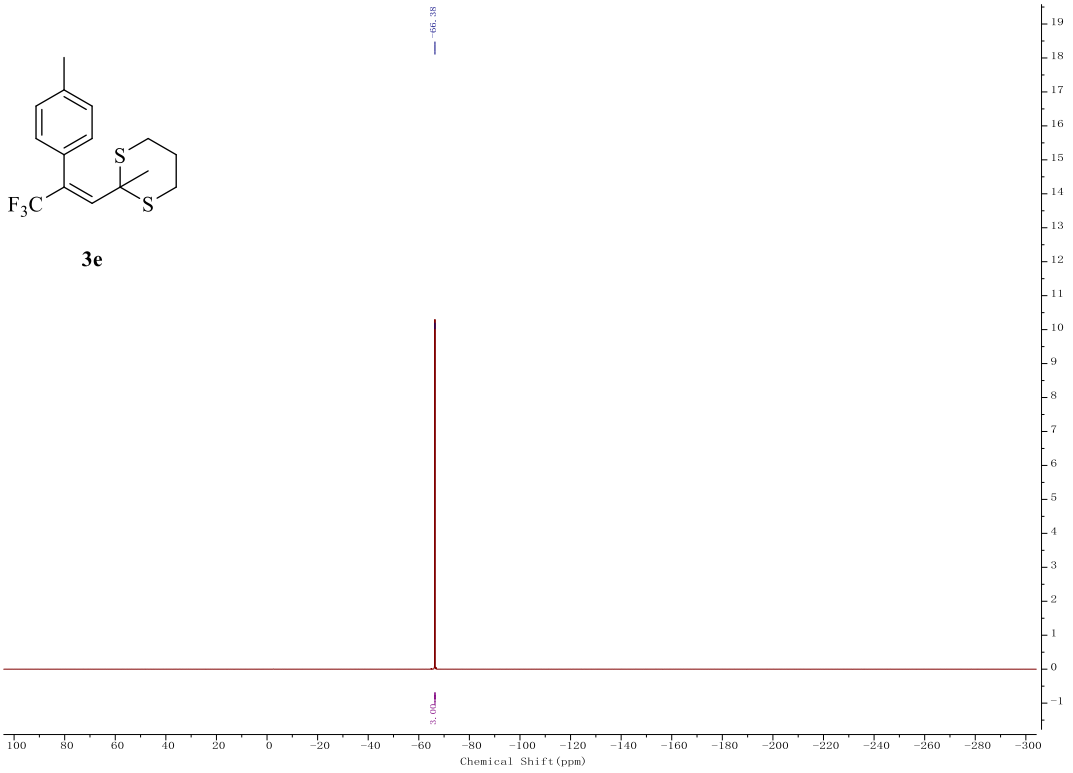
3e



3e

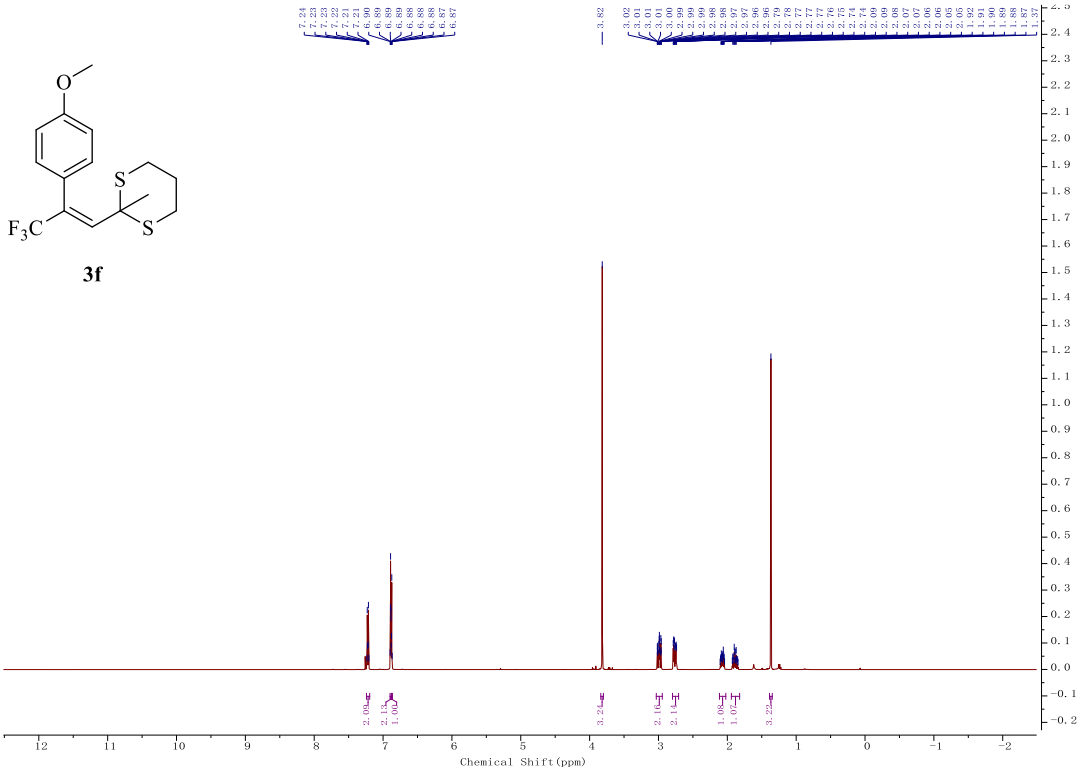
S
S
F3C

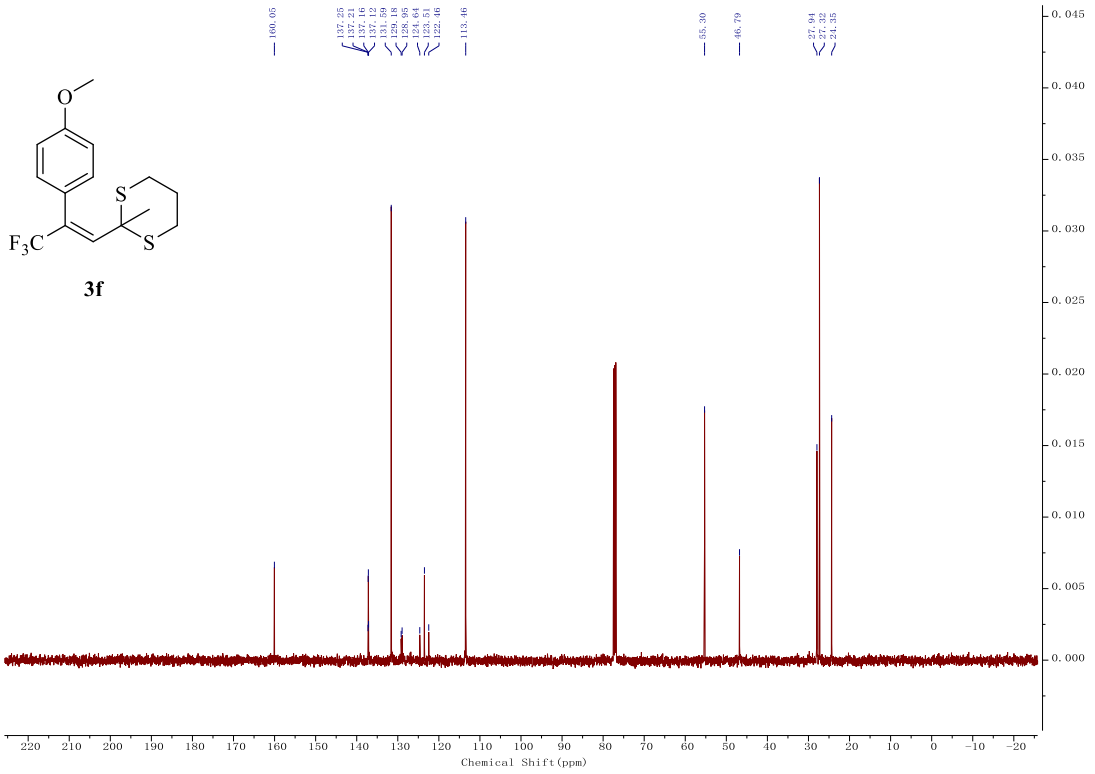
3e


-66.38
3.00
Chemical Shift(ppm)

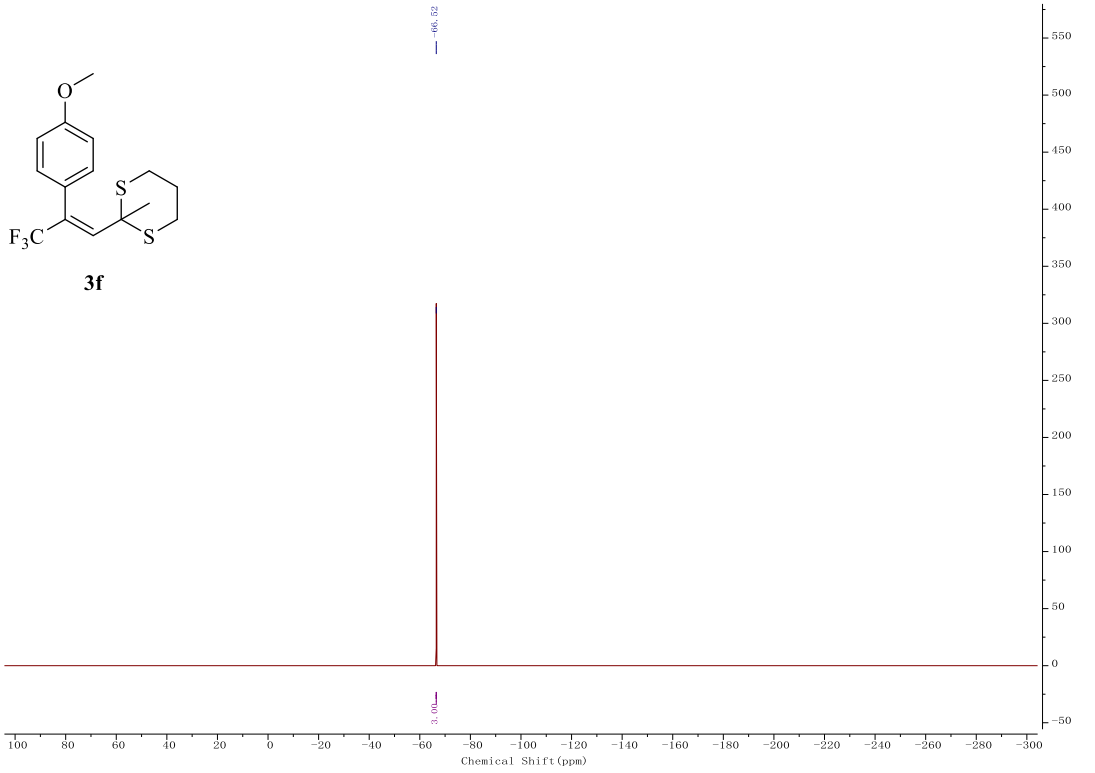
O
S
S
F3C

3f

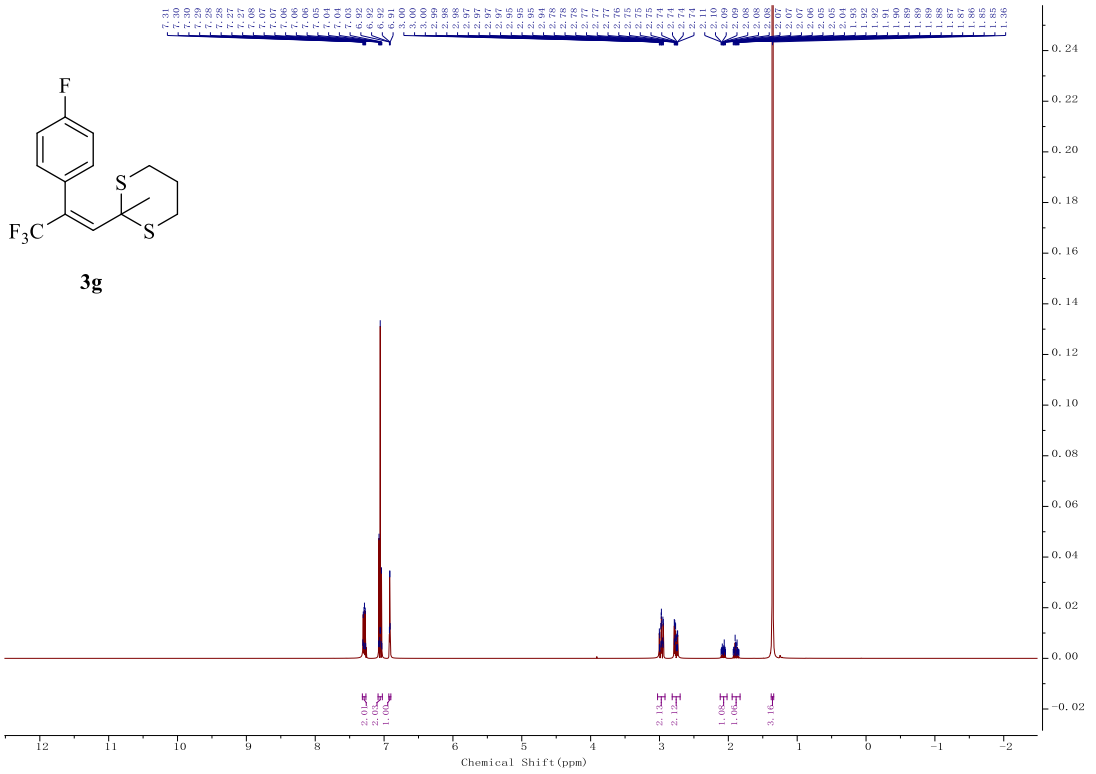

7.24
7.23
7.23
7.22
7.21
7.21
6.90
6.89
6.89
6.89
6.88
6.88
6.88
6.87
6.87
3.82
2.09
2.13
1.00
3.24
2.16
2.14
1.08
1.07
3.22
Chemical Shift(ppm)

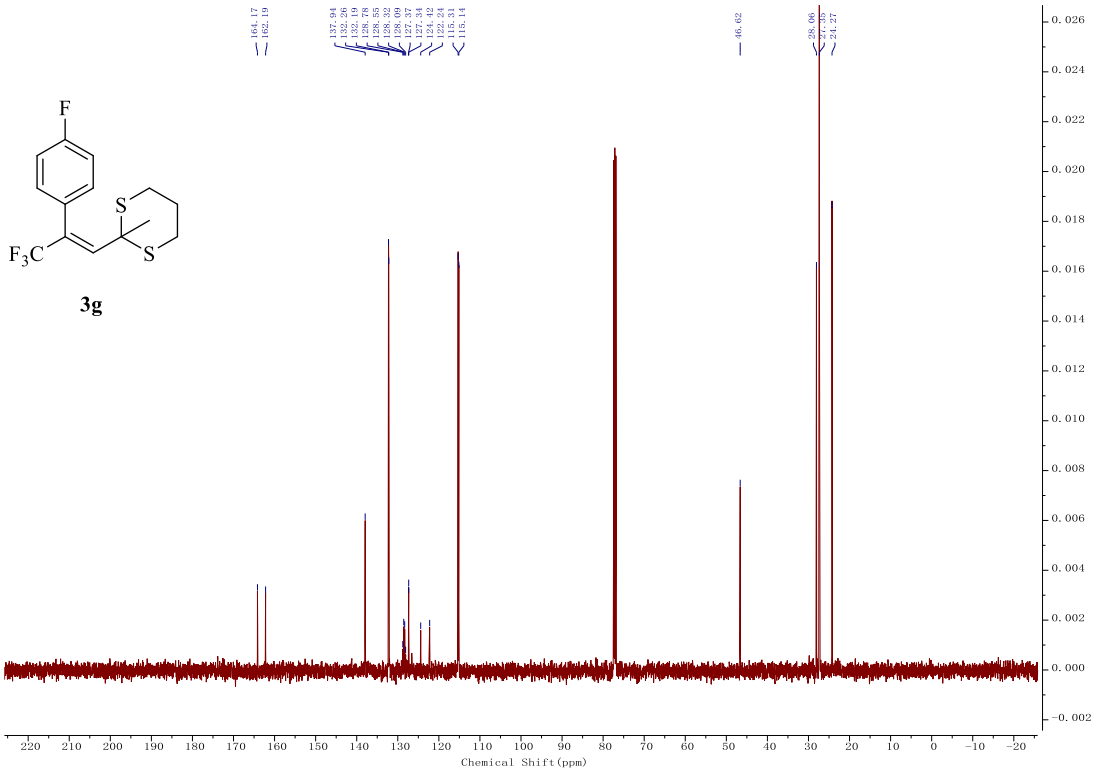

160.05
137.25
132.21
137.16
137.12
131.59
130.18
128.95
124.64
123.51
122.46
113.46
55.30
46.79
27.94
27.32
24.35
Chemical Shift(ppm)

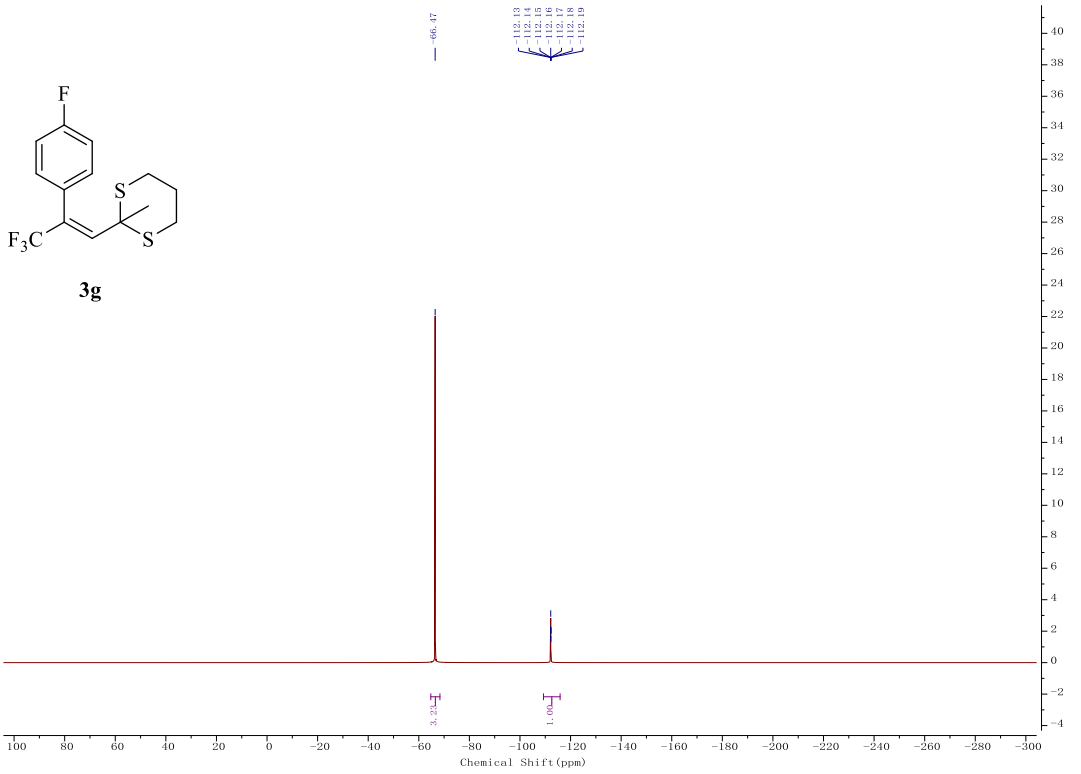
3f


-66.52
3.00
Chemical Shift(ppm)

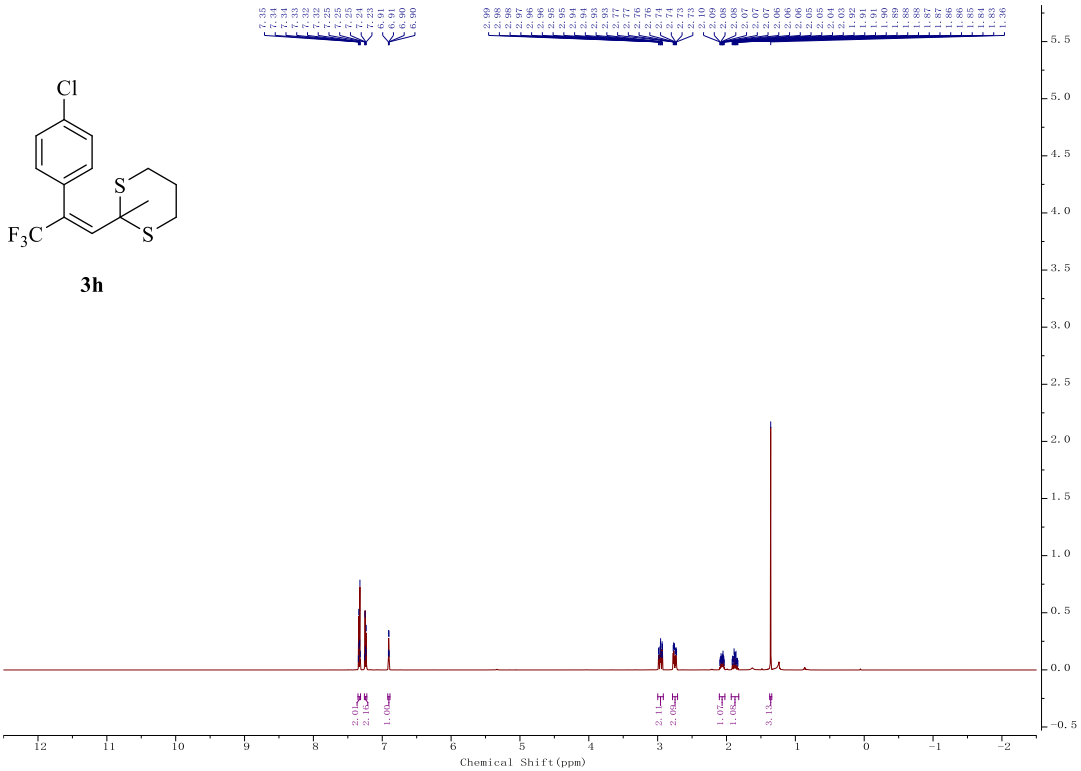
3f


F
S
F3C
S
3g
Chemical Shift(ppm)

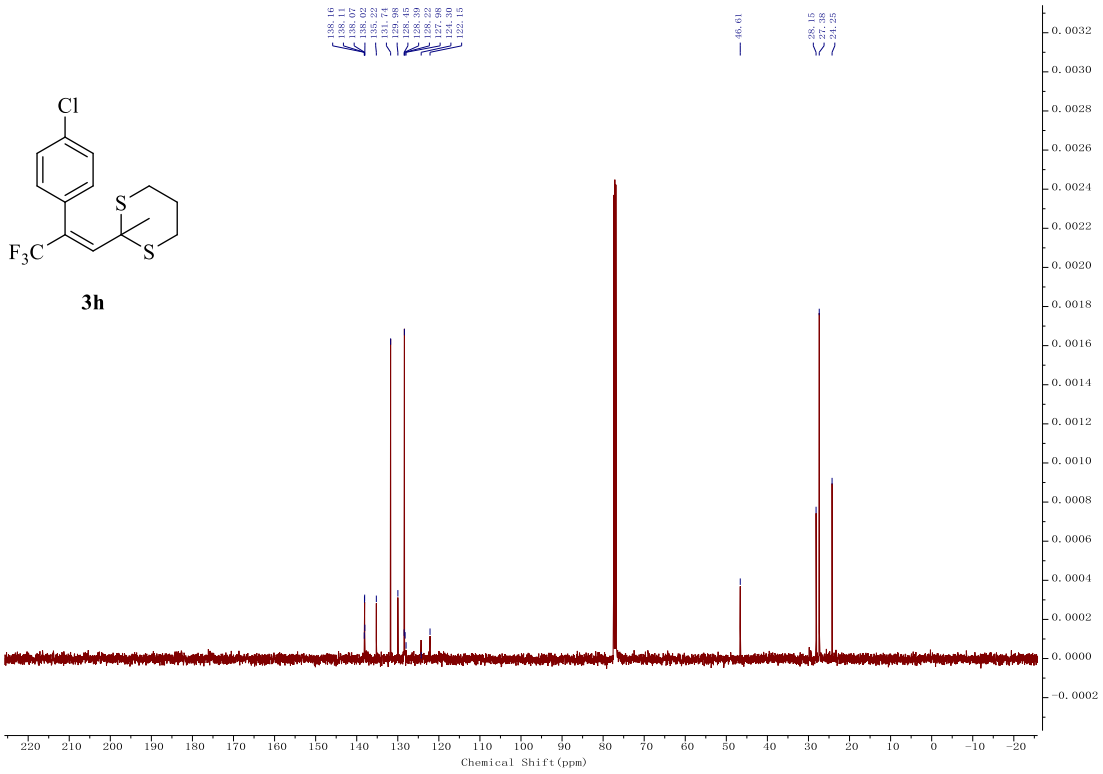

F
S
F3C
S
3g
Chemical Shift(ppm)

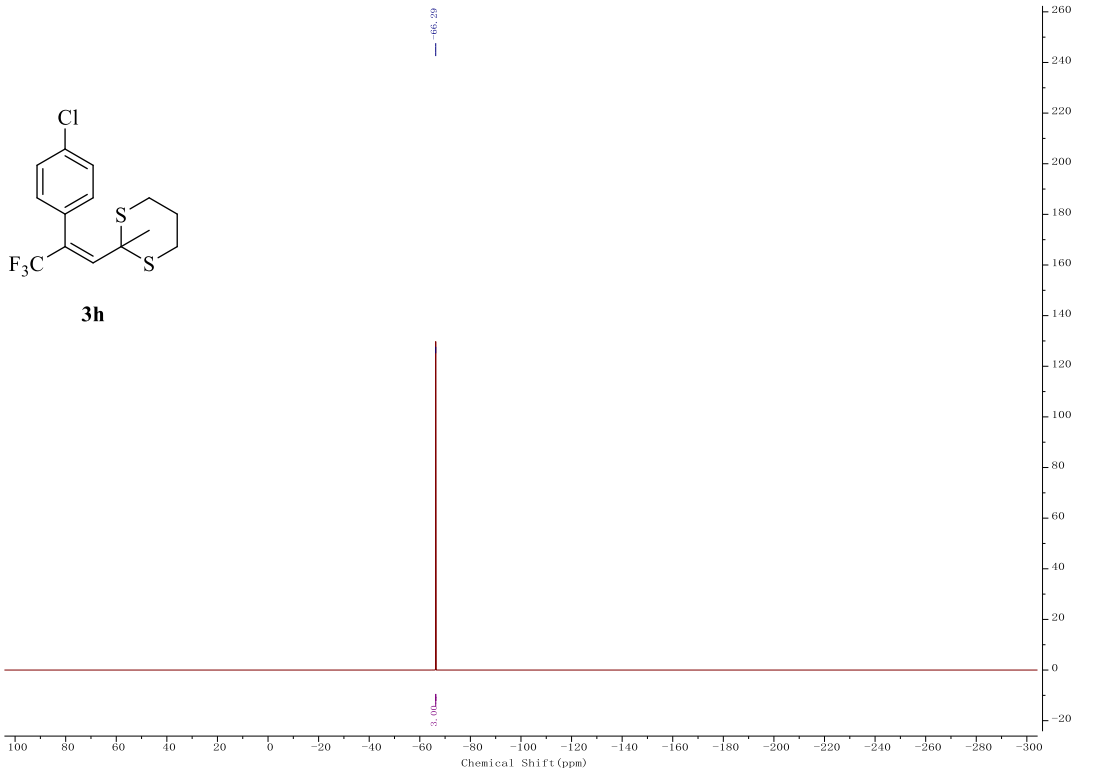

F
S
S
F3C
-66.47
-112.13
-112.14
-112.15
-112.16
-112.17
-112.18
-112.19
3.23
1.00
Chemical Shift(ppm)

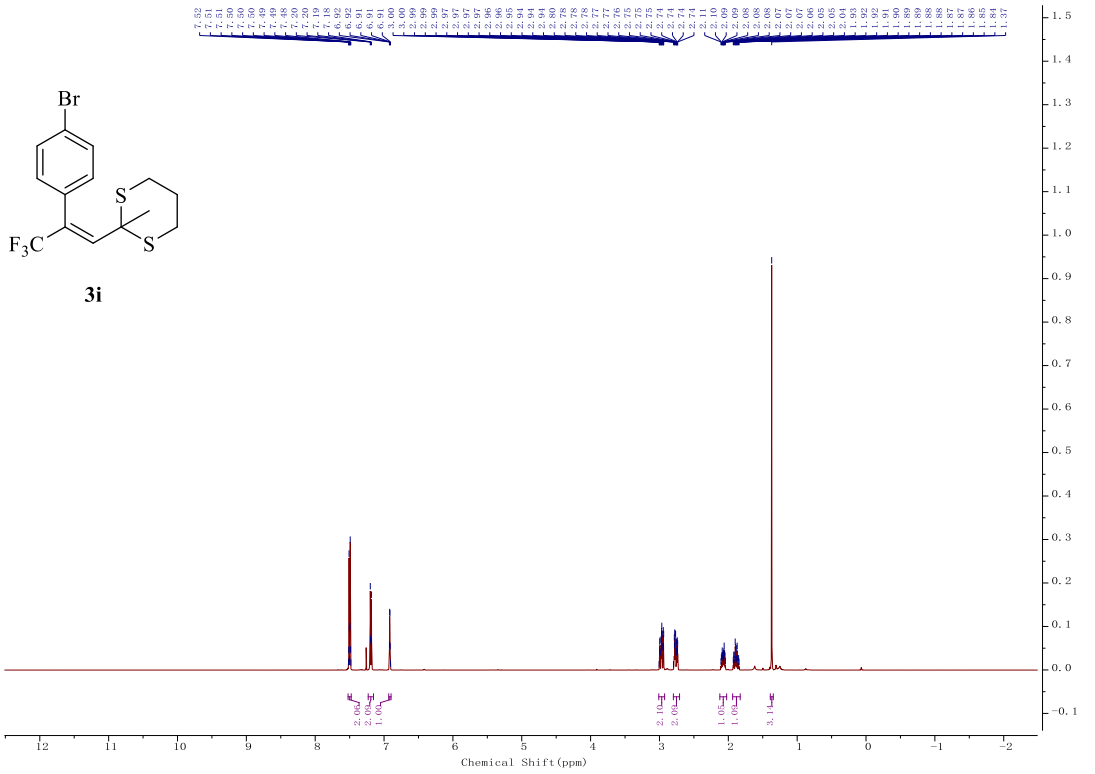
3g

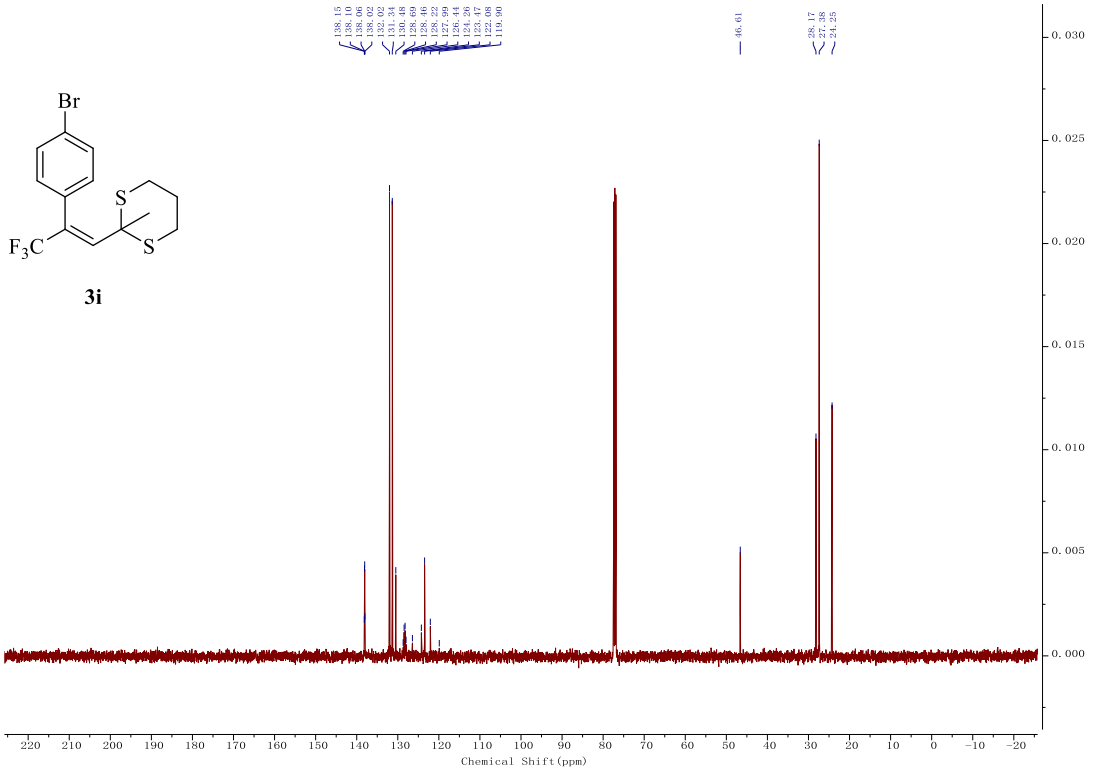

Cl
S
S
F3C
7.35
7.34
7.34
7.33
7.32
7.25
7.25
7.25
7.24
7.23
6.91
6.91
6.90
6.90
2.99
2.98
2.98
2.97
2.96
2.96
2.95
2.95
2.94
2.93
2.93
2.77
2.77
2.76
2.76
2.74
2.74
2.73
2.73
2.10
2.09
2.08
2.08
2.07
2.07
2.07
2.06
2.06
2.06
2.05
2.05
2.04
2.03
2.02
1.91
1.91
1.90
1.89
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.84
1.83
1.36
2.01
2.16
1.00
2.11
2.09
1.07
1.08
3.13
Chemical Shift(ppm)

3h


138.16
138.11
136.07
135.22
131.74
129.98
128.45
128.39
128.22
127.98
124.30
122.15
46.61
28.15
27.38
24.25
Cl
S
S
F3C
3h
Chemical Shift(ppm)

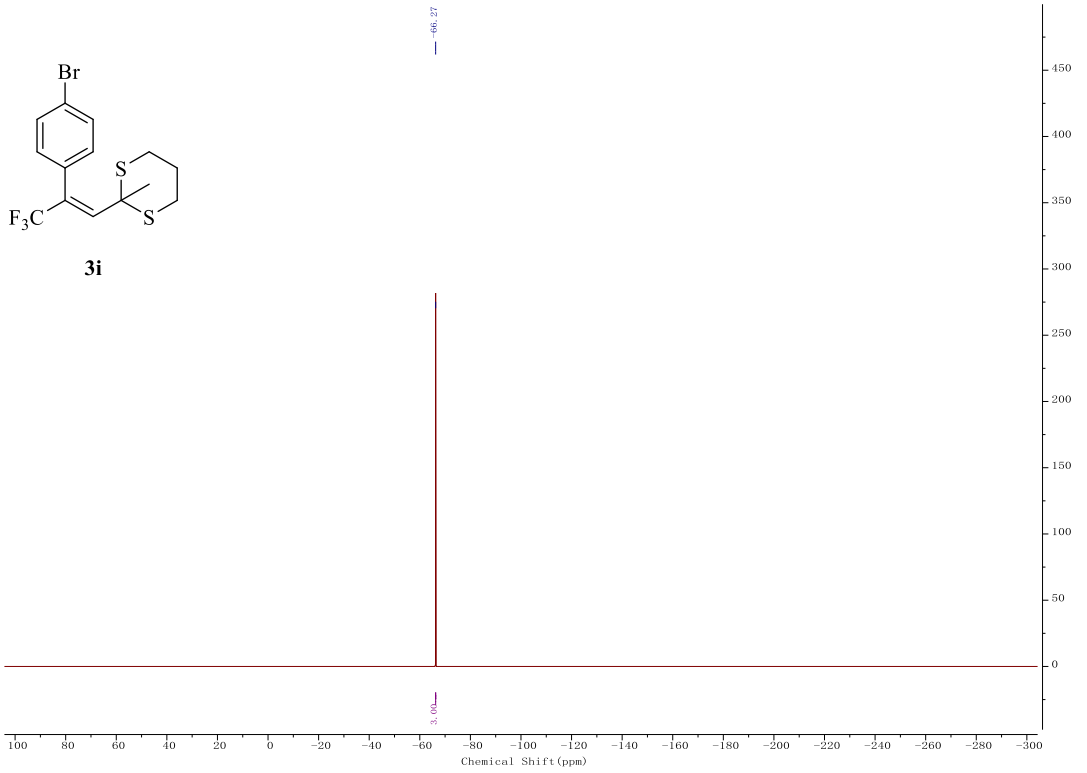

-66.29
3.00
Cl
S
S
F3C
3h
Chemical Shift(ppm)

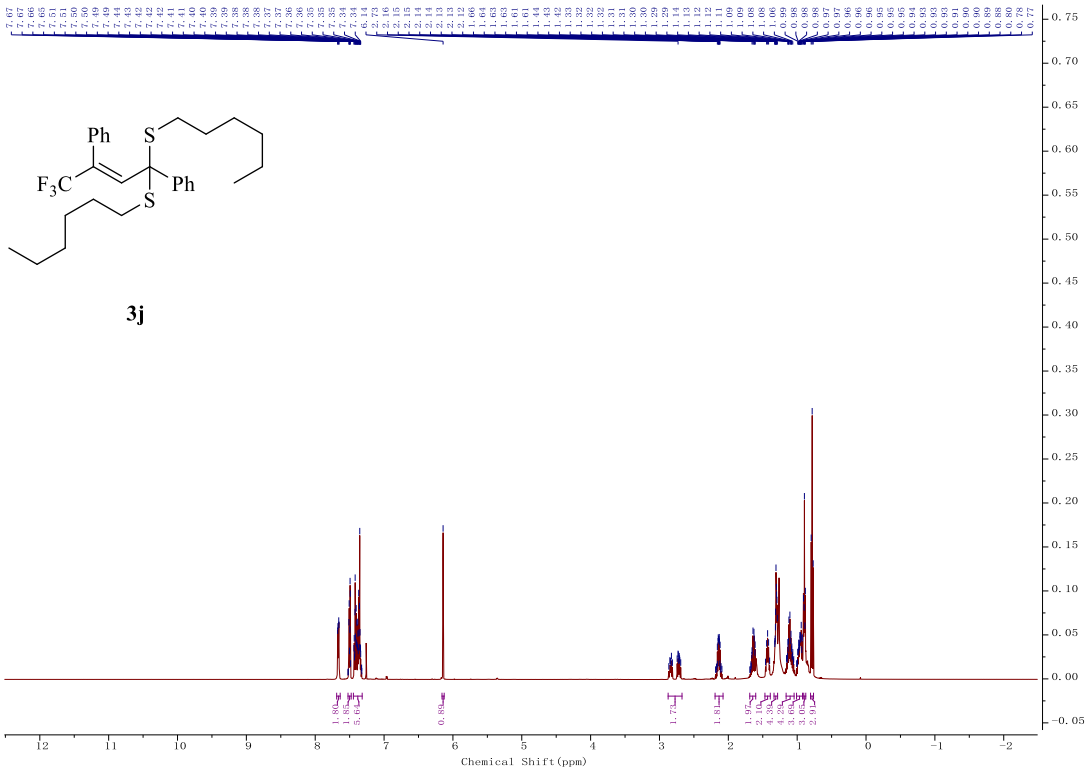

Br
S
S
F3C
3i
Chemical Shift(ppm)


Br
S
S
F3C
3i
Chemical Shift(ppm)

Br
S
S
F3C

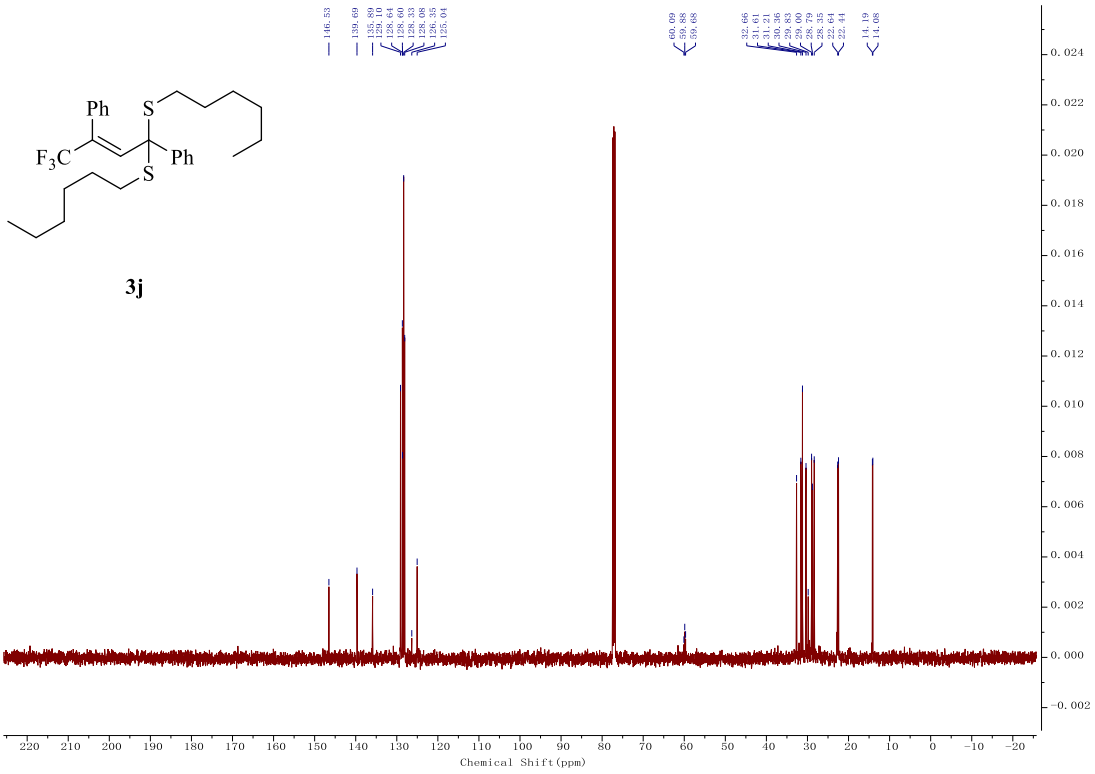
3i

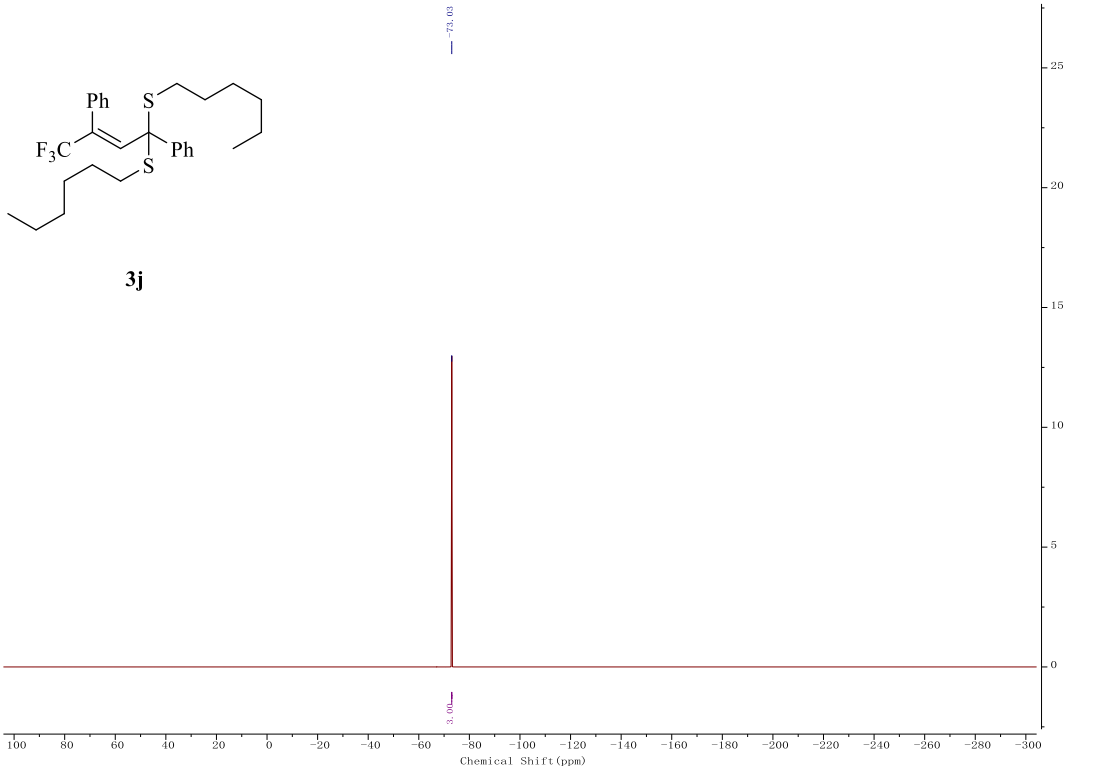

-66.27
3.00
Chemical Shift(ppm)

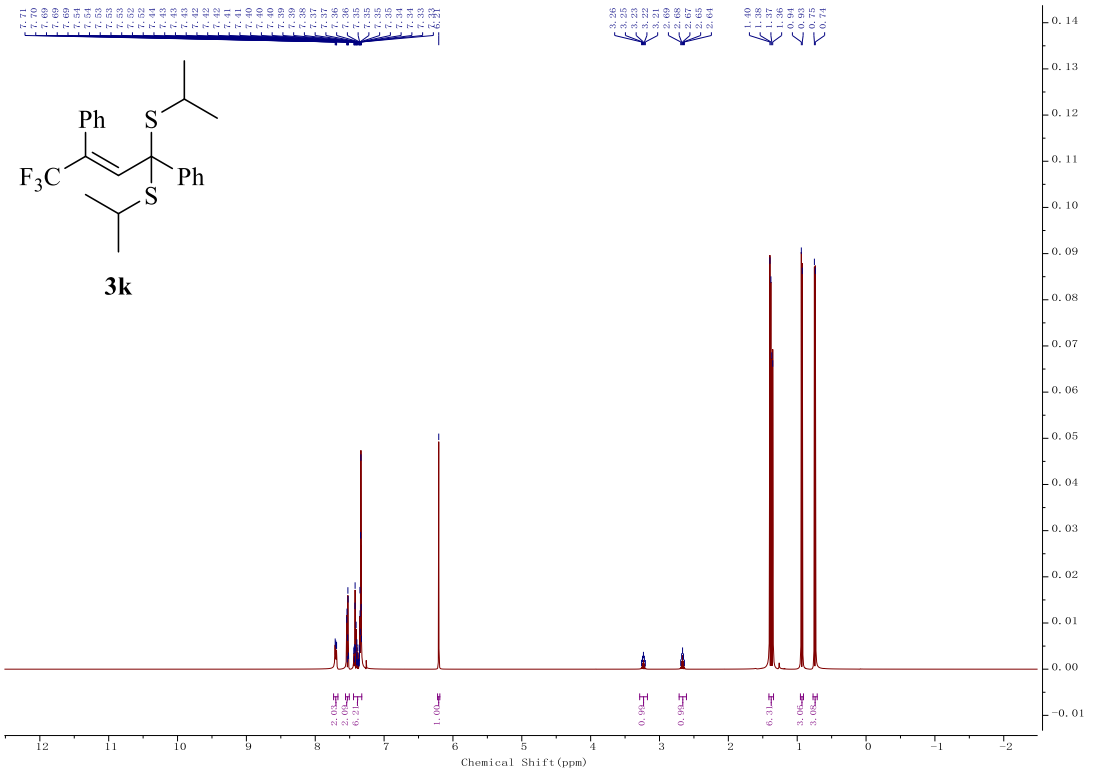

1.80
1.85
5.64
0.83
1.74
1.81
1.97
2.10
4.29
3.68
3.05
2.94
Chemical Shift(ppm)

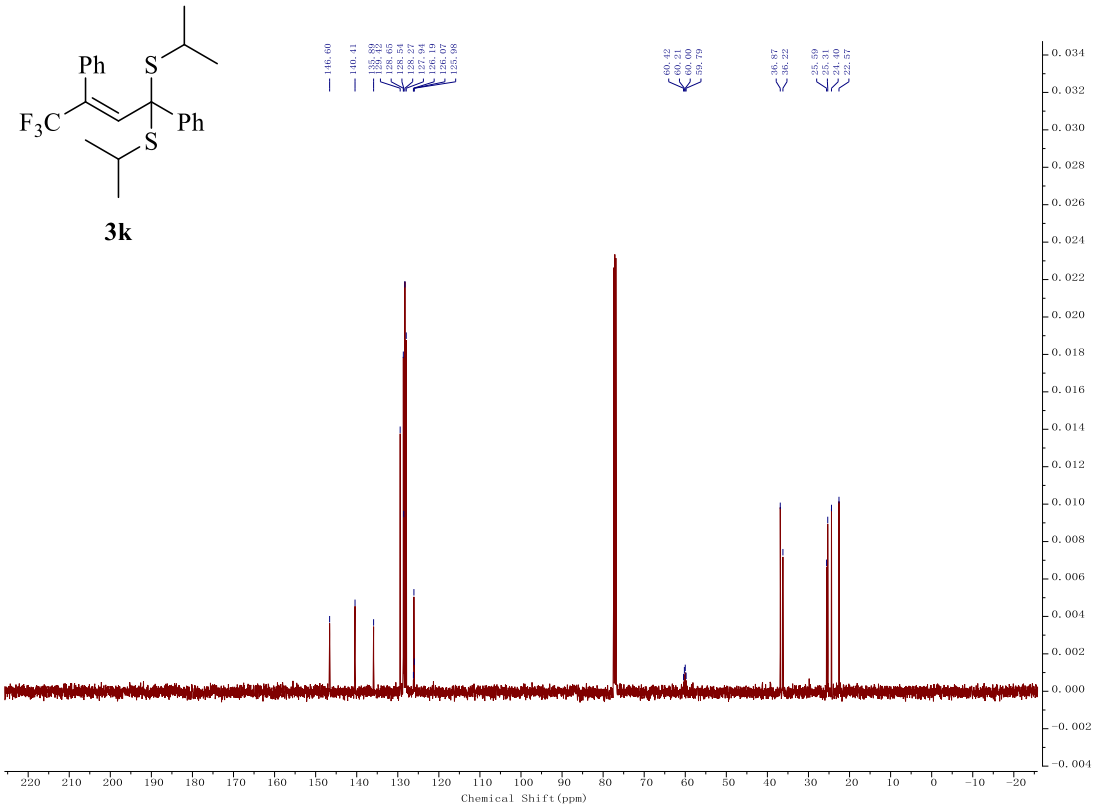
Ph
S
F3C
Ph
S

3j


Ph
S
F3C
Ph
S
3j
146.53
139.69
133.89
130.11
128.64
128.60
128.33
126.68
126.55
125.04
60.09
59.88
59.68
32.66
31.64
31.21
30.36
29.83
29.66
29.00
28.79
28.35
22.64
22.44
14.19
14.08
Chemical Shift(ppm)

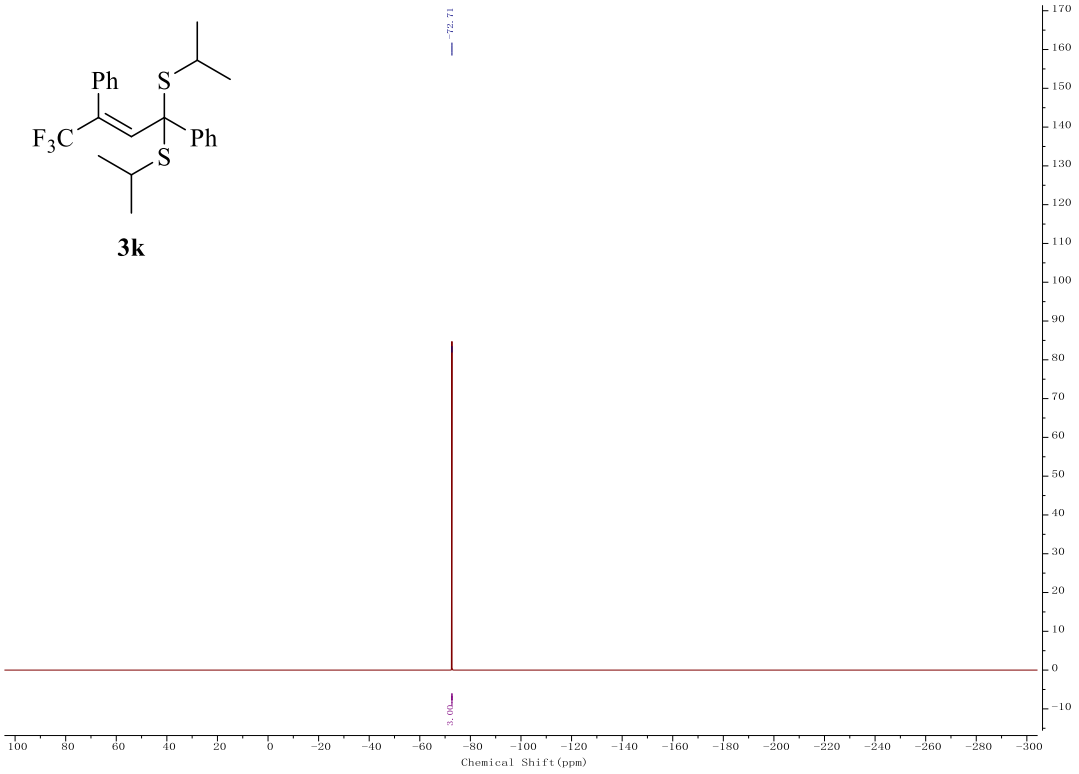

Ph
S
F3C
Ph
S
3j
73.03
3.00
Chemical Shift(ppm)

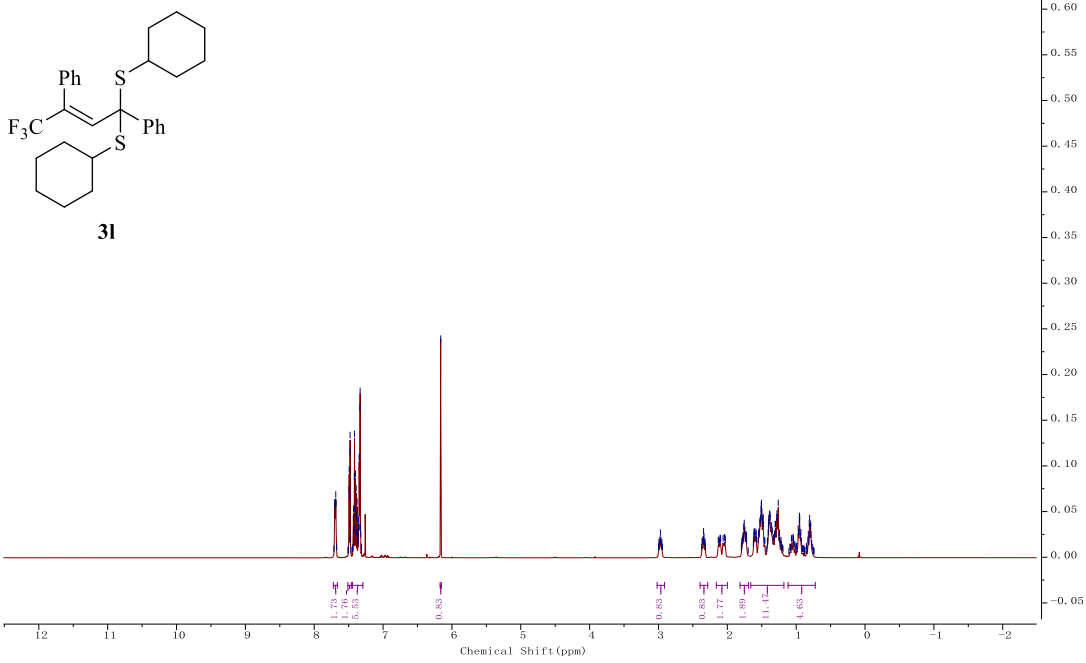

Ph
S
F3C
Ph
S
3k
Chemical Shift(ppm)


Ph
S
F3C
Ph
S
3k
Chemical Shift(ppm)

Ph
S
F3C
Ph
S

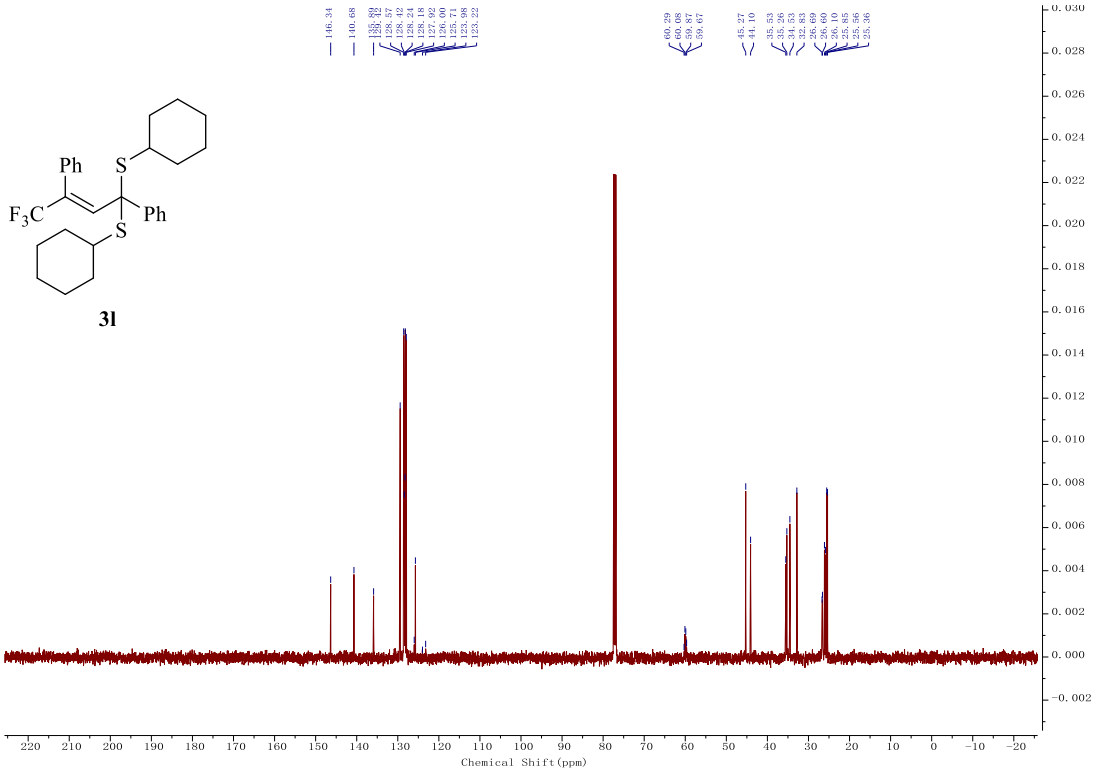
3k

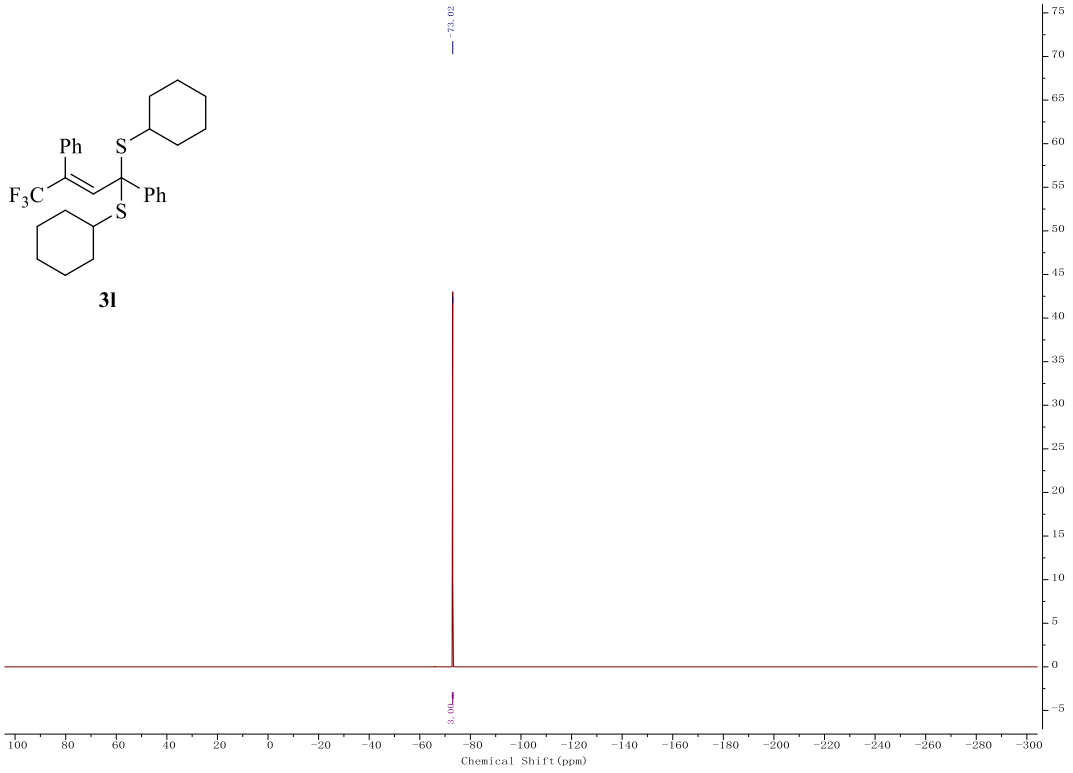

-72.71
3.00
Chemical Shift(ppm)

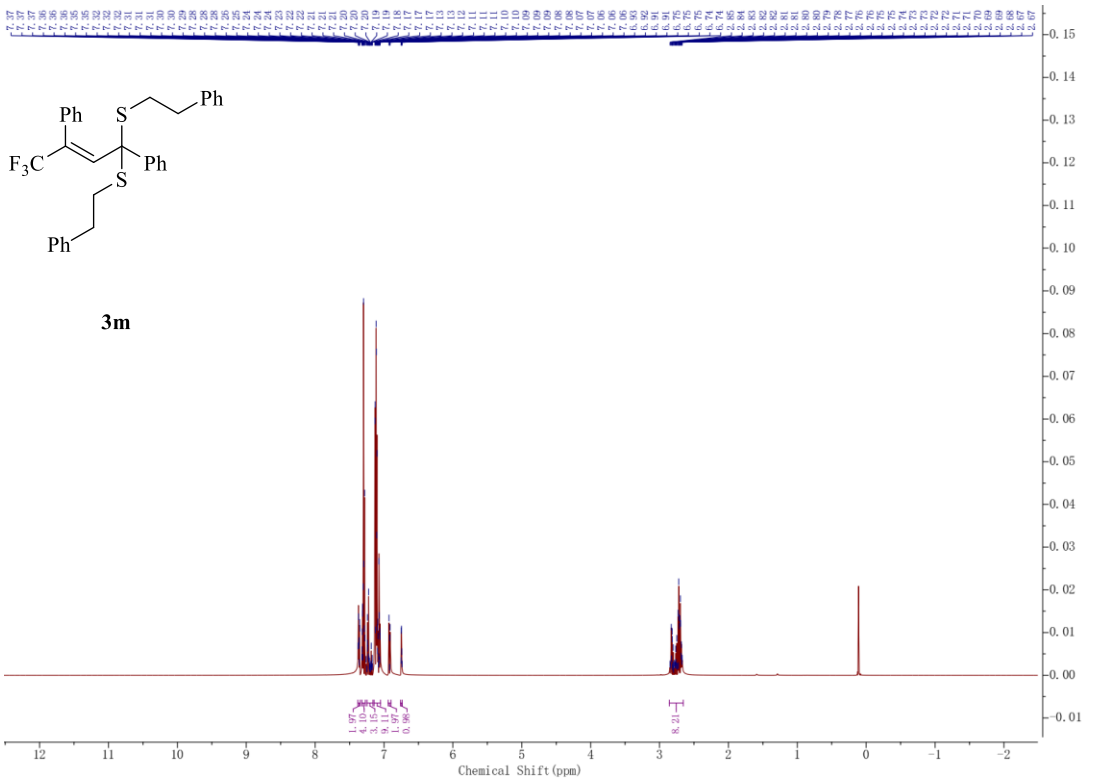

1.73
1.76
5.53
0.83
0.83
0.83
1.77
1.89
11.42
4.63
Chemical Shift(ppm)

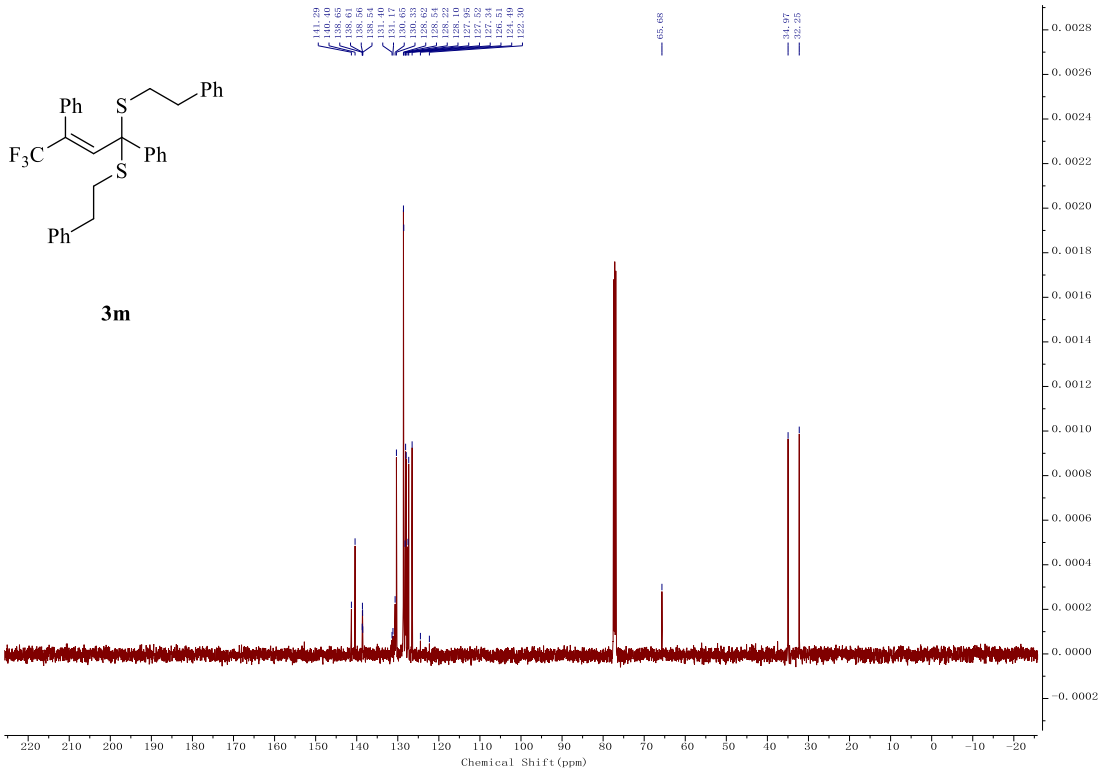
Ph
S
F3C
Ph
S

3l


Ph
S
F3C
Ph
S
3l
Chemical Shift(ppm)

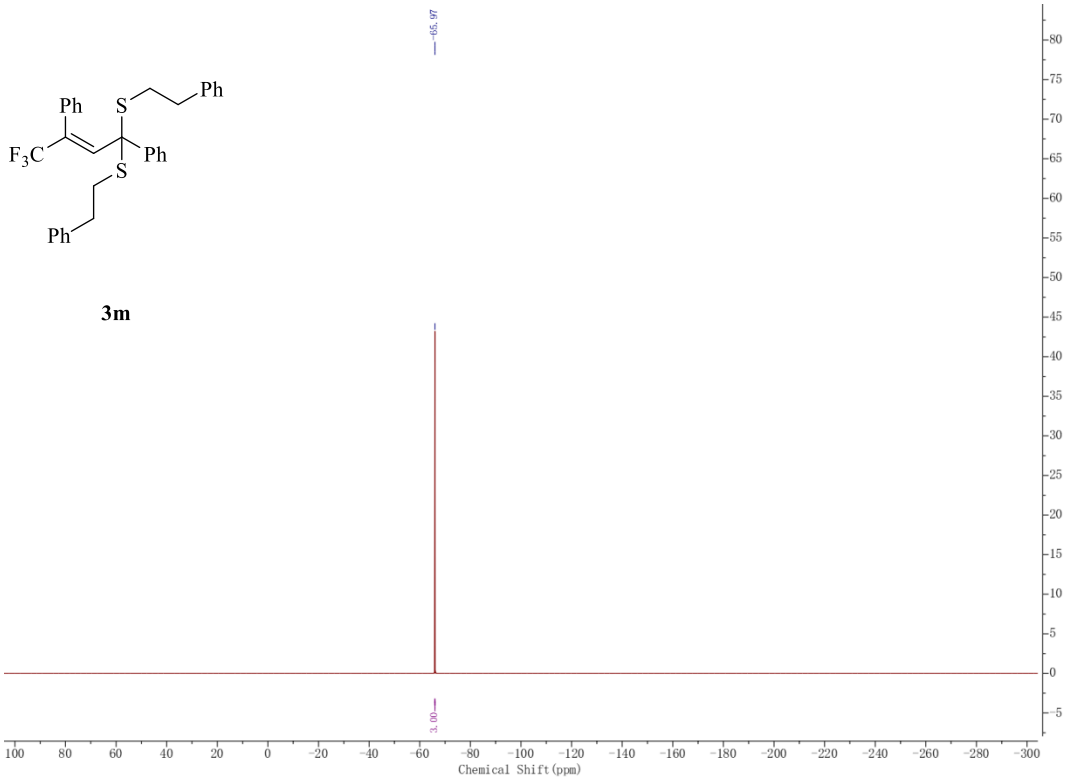

Ph
S
F3C
Ph
S
3l
Chemical Shift(ppm)

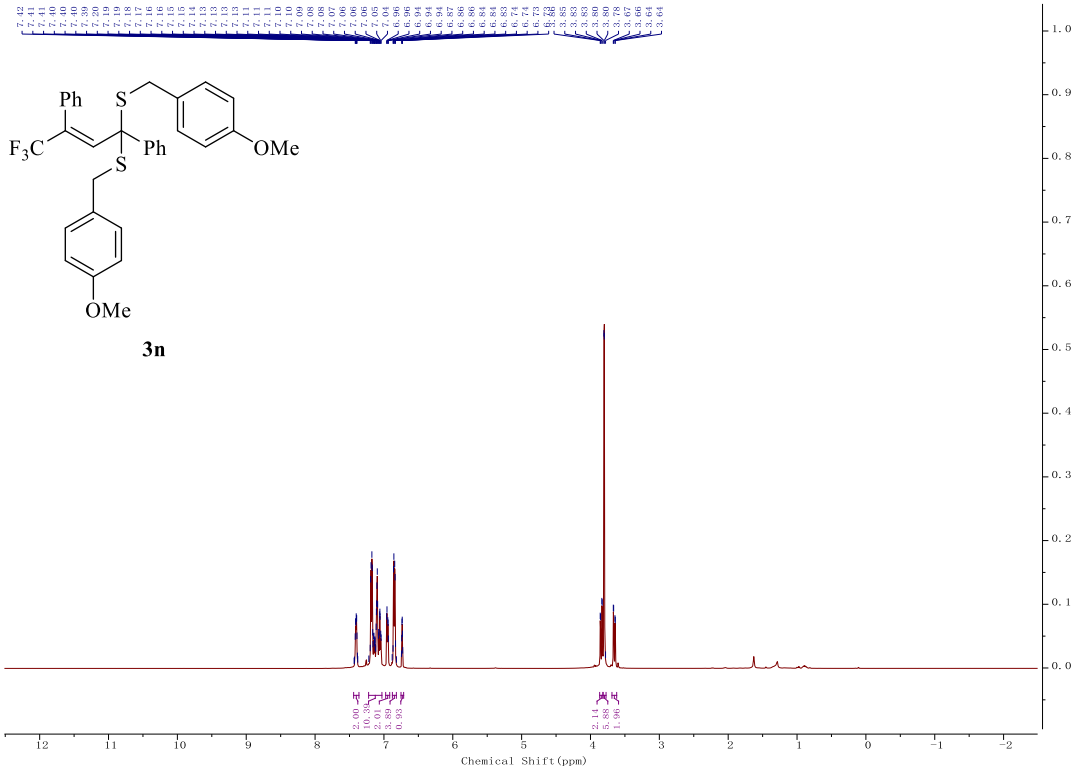

Ph
S
Ph
F3C
Ph
S
Ph
3m
Chemical Shift(ppm)


Ph
S
Ph
F3C
Ph
S
Ph
3m
Chemical Shift(ppm)

Ph
S
Ph
F3C
Ph
S
Ph

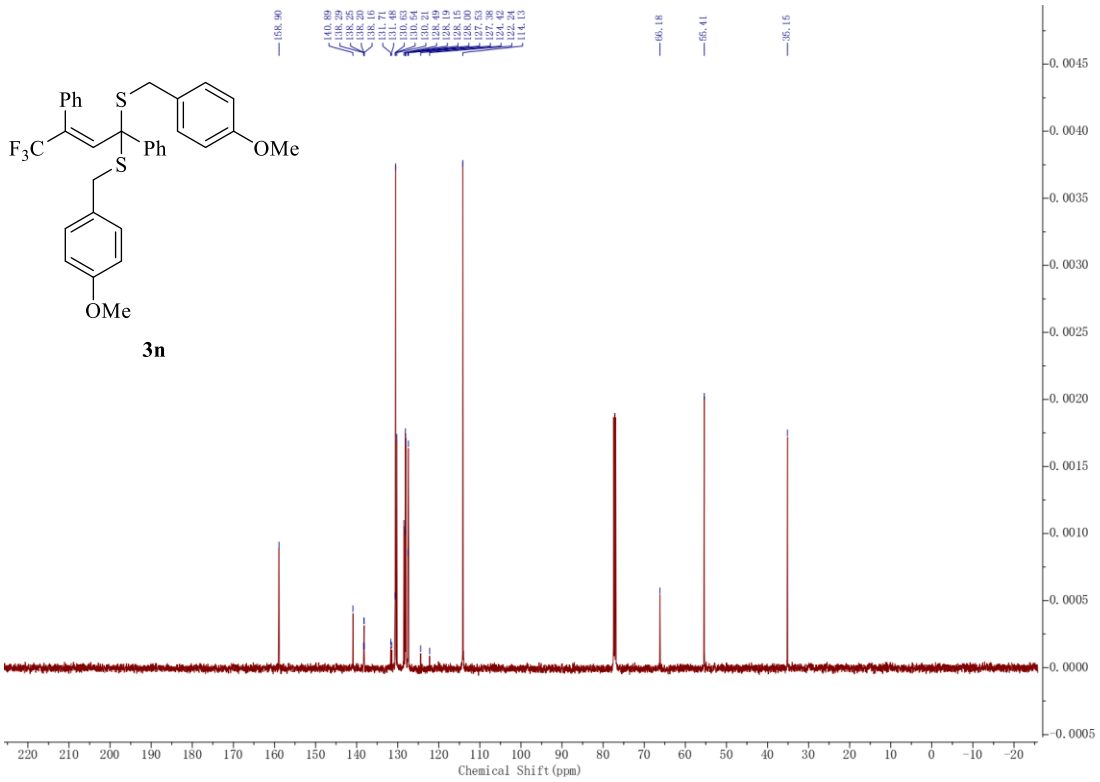
3m


65.97
3.00
Chemical Shift(ppm)

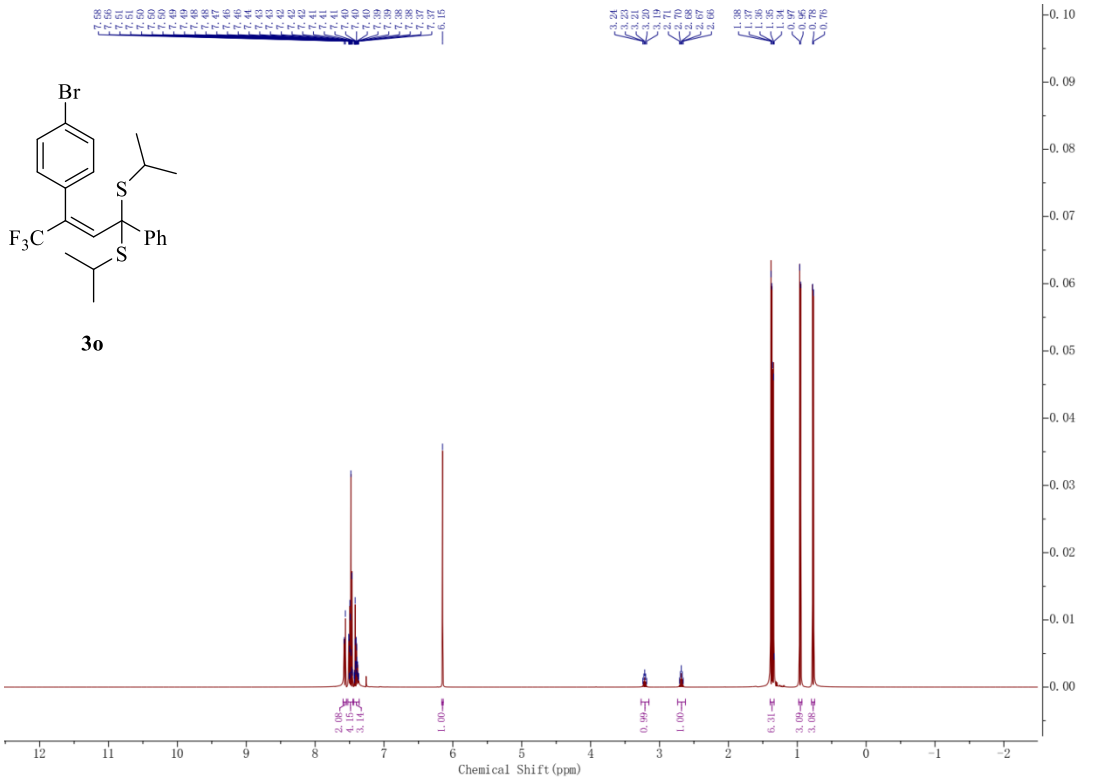

Chemical Shift(ppm)

Ph
S
F3C
Ph
OMe
S
OMe

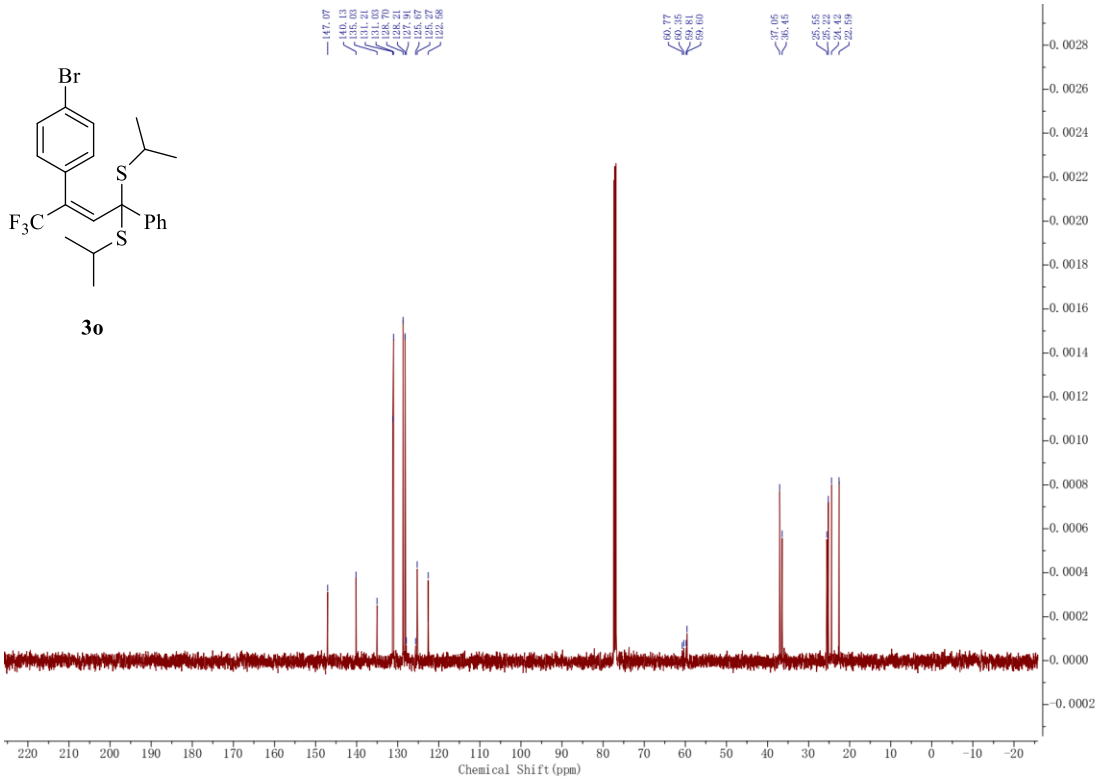
3n


Ph
S
F3C
Ph
OMe
S
OMe
3n
168.90
140.89
138.29
138.25
138.20
138.16
131.71
131.46
130.63
130.54
130.21
128.49
128.19
128.15
128.00
127.53
127.38
124.42
122.24
114.13
66.18
55.41
35.15
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
-0.0005
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift(ppm)


Ph
S
F3C
Ph
OMe
S
OMe
3n
-66.02
1.00
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
Chemical Shift(ppm)


Br
S
S
Ph
F3C
Chemical Shift(ppm)

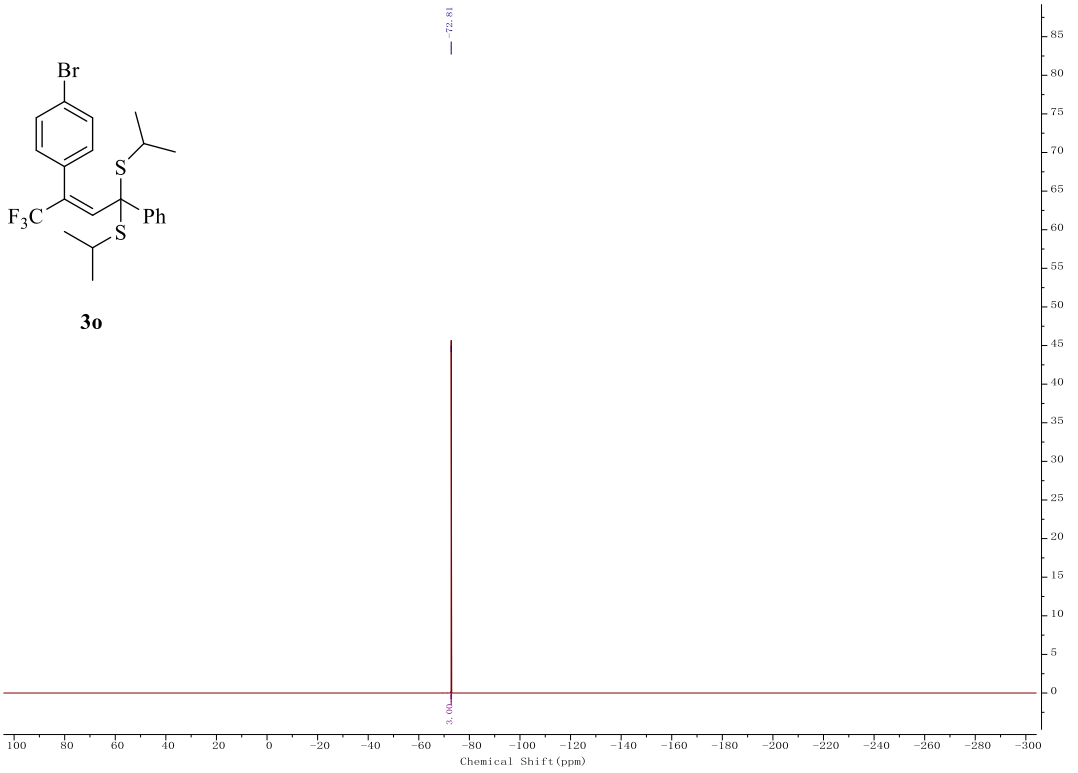
3o

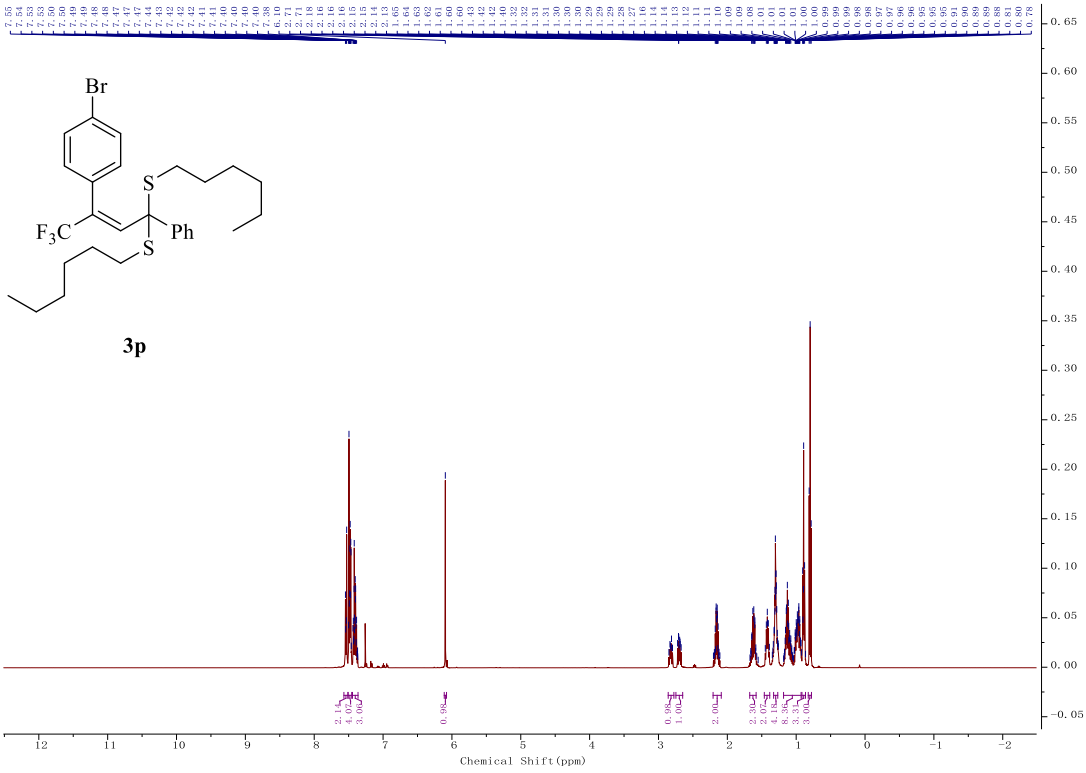

Br
S
S
Ph
F3C
Chemical Shift(ppm)

3o

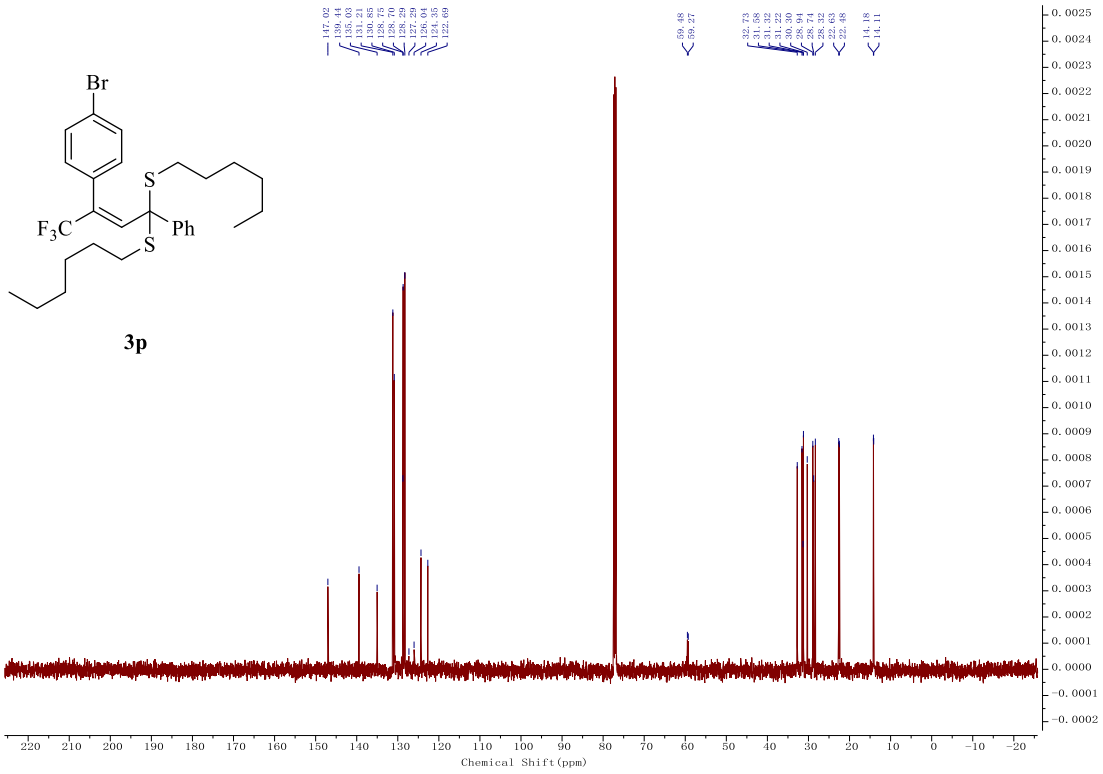
Br
S
F3C
Ph
S

3o

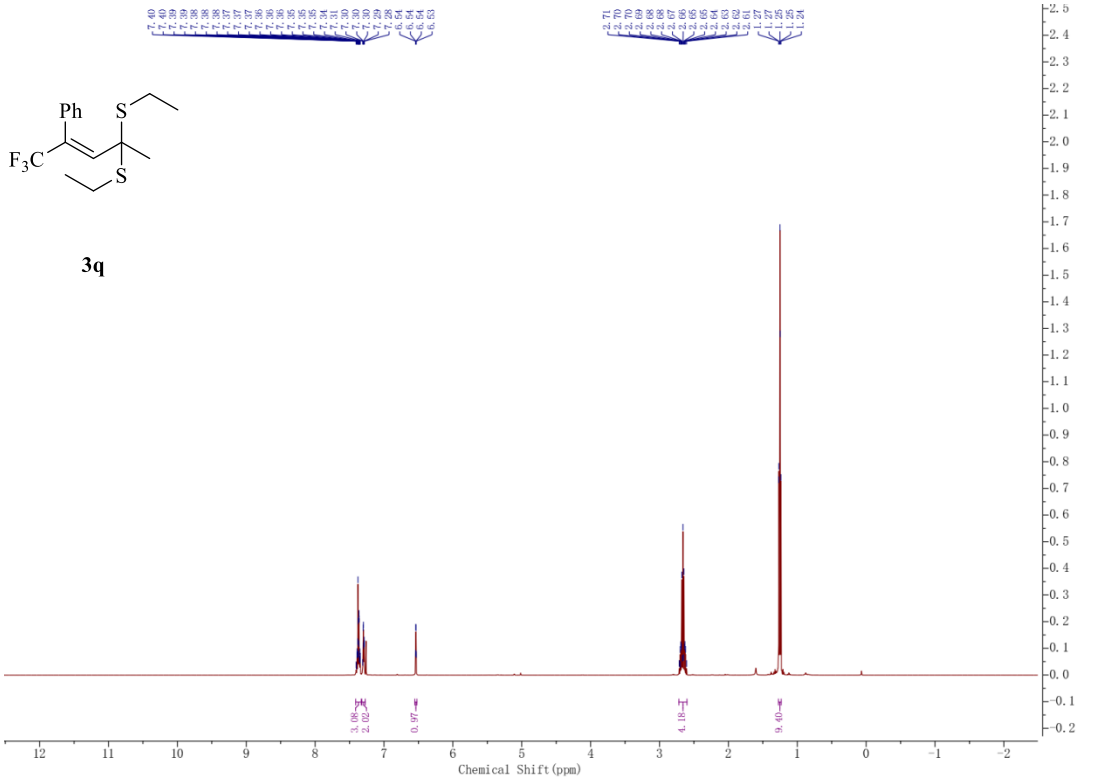

-72.81
3.00
Chemical Shift(ppm)

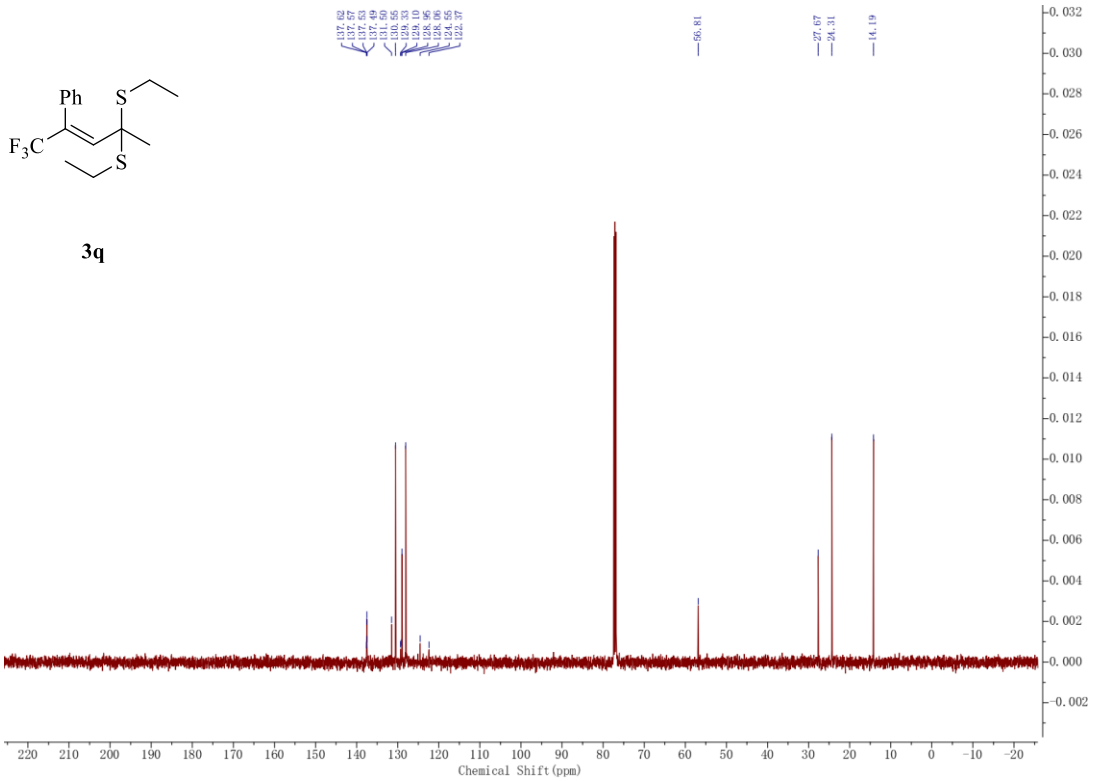

Br
S
F3C
Ph
S
Chemical Shift(ppm)

3p


Br
S
F3C
Ph
S
3p
147.02
140.44
135.03
131.21
130.85
128.75
128.70
128.29
127.29
126.04
124.35
122.69
59.48
59.27
32.73
31.98
31.32
31.22
30.30
29.84
28.74
28.32
22.63
22.48
14.18
14.11
Chemical Shift(ppm)

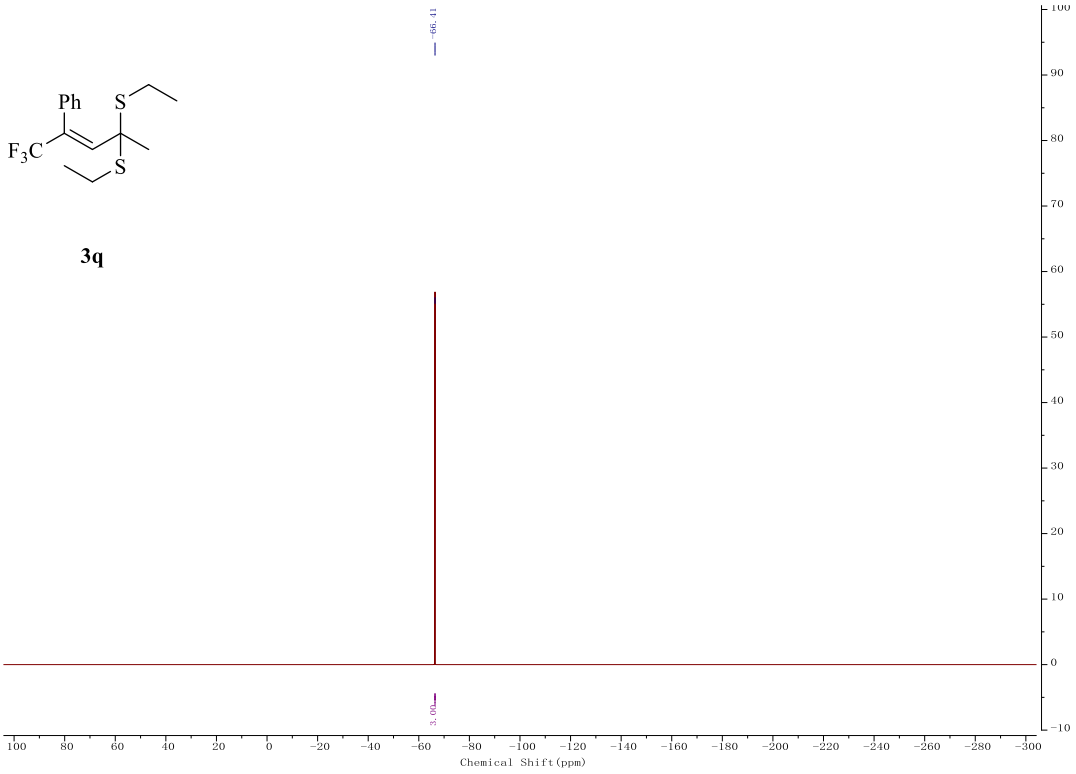

Br
S
F3C
Ph
S
3p
-73.09
3.00
Chemical Shift(ppm)


Ph
S
F3C
S
3q
Chemical Shift (ppm)


Ph
S
F3C
S
3q
Chemical Shift (ppm)

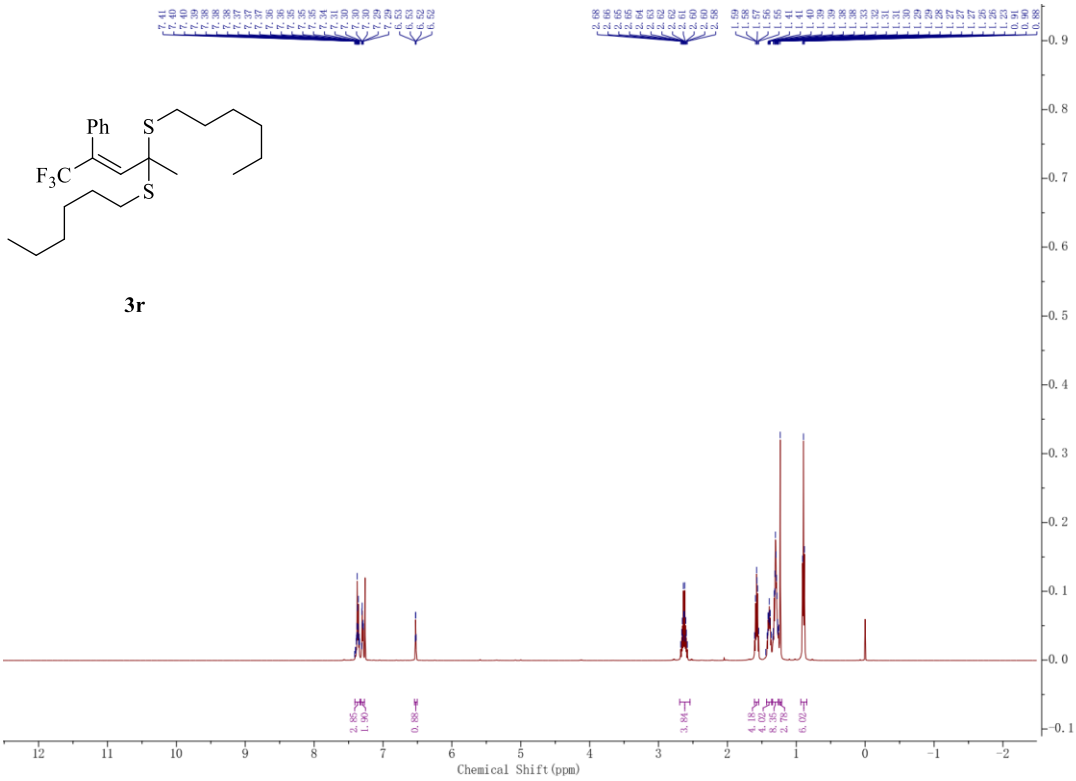
Ph
S
F3C
S

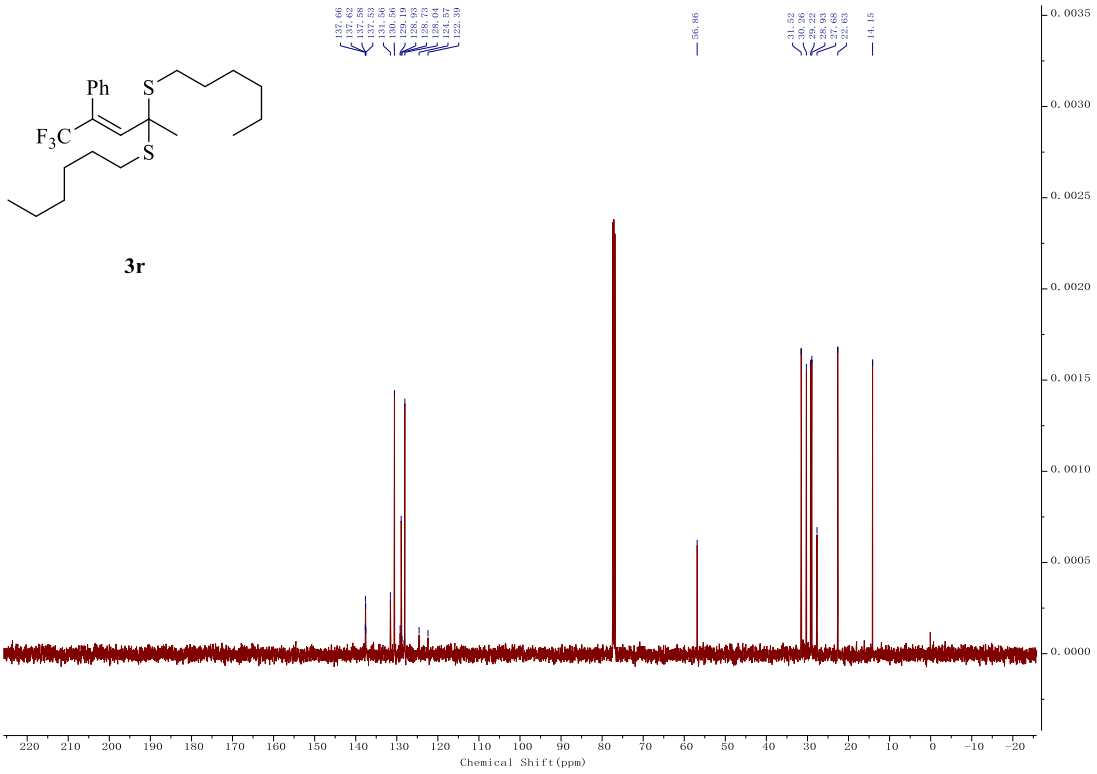
3q

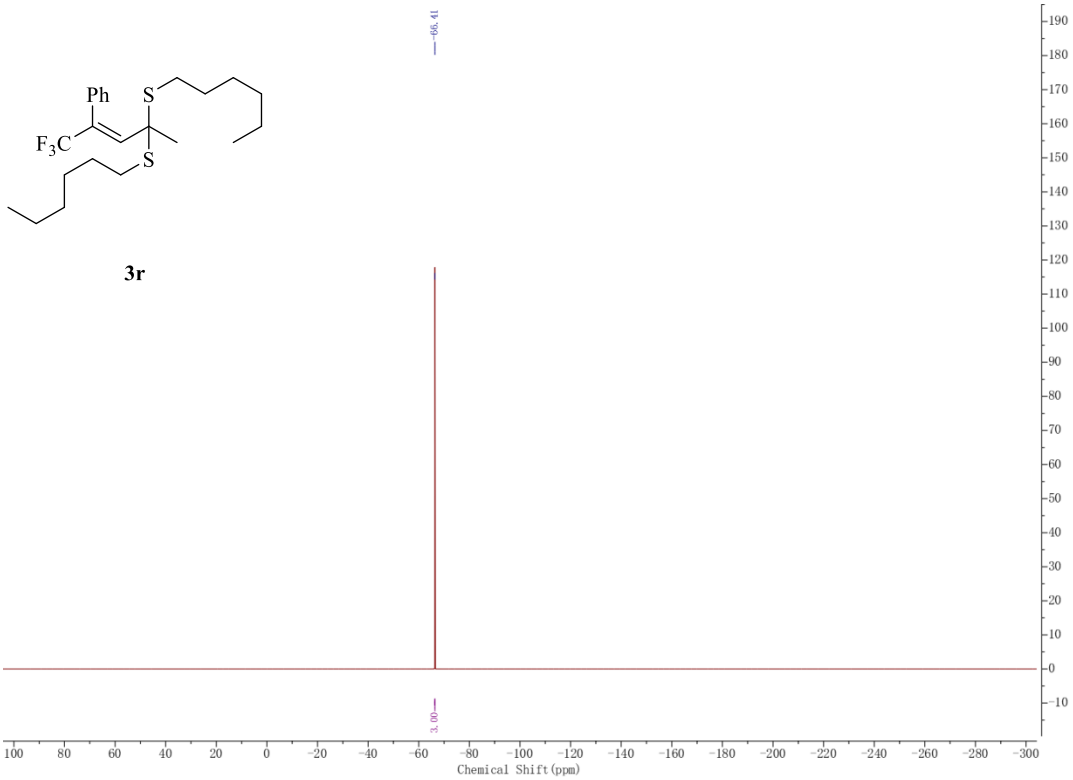

-66.41
3.00
Chemical Shift(ppm)

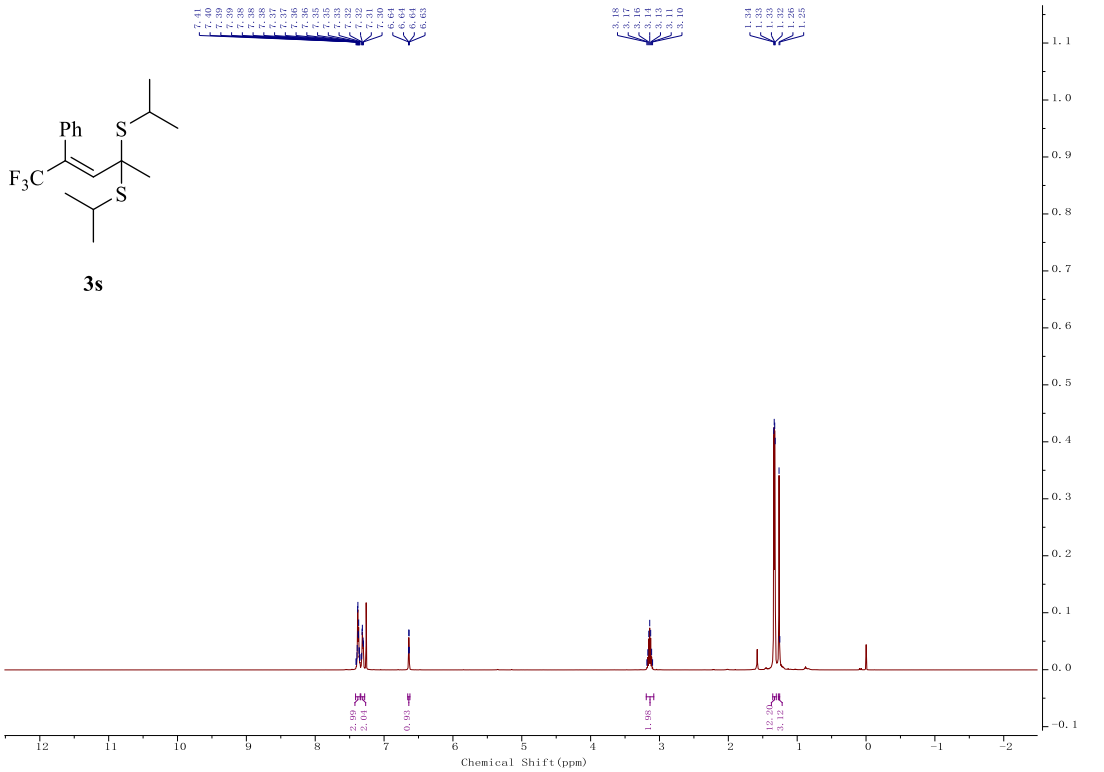
Ph
S
F3C
S

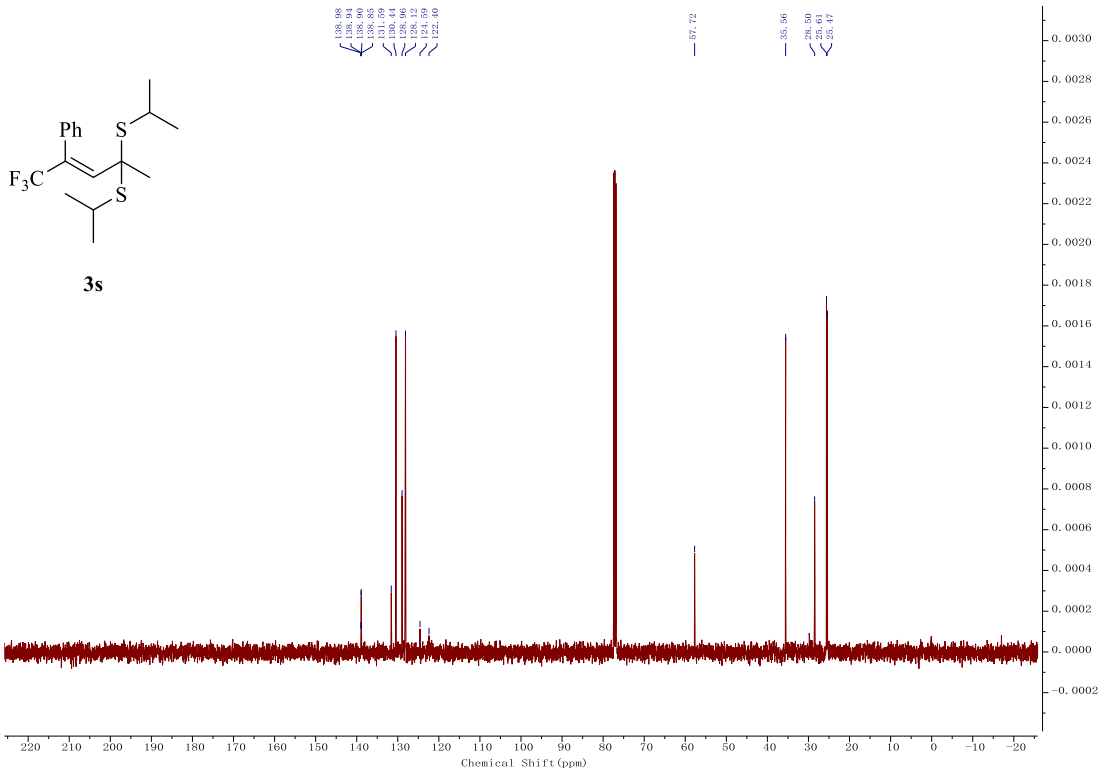
3r


2.05
1.90
0.88
3.84
4.18
4.02
8.35
2.70
6.02
Chemical Shift(ppm)


Ph
S
F3C
S
3r
137.66
137.02
137.58
137.53
131.56
130.55
129.19
128.93
128.73
128.64
124.57
122.39
56.86
31.52
30.26
29.22
28.93
27.68
22.63
14.15
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift(ppm)

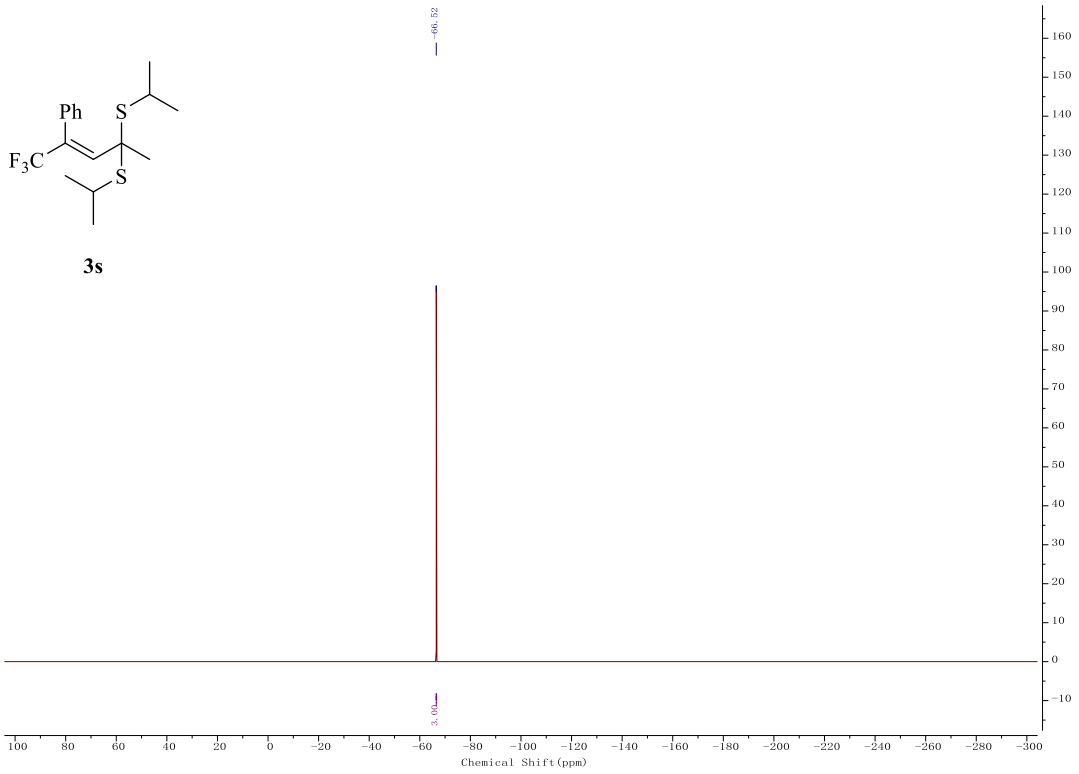

Ph
S
F3C
S
3r
-66.41
3.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
Chemical Shift(ppm)


Ph
S
F3C
S
3s
Chemical Shift(ppm)


Ph
S
F3C
S
3s
Chemical Shift(ppm)

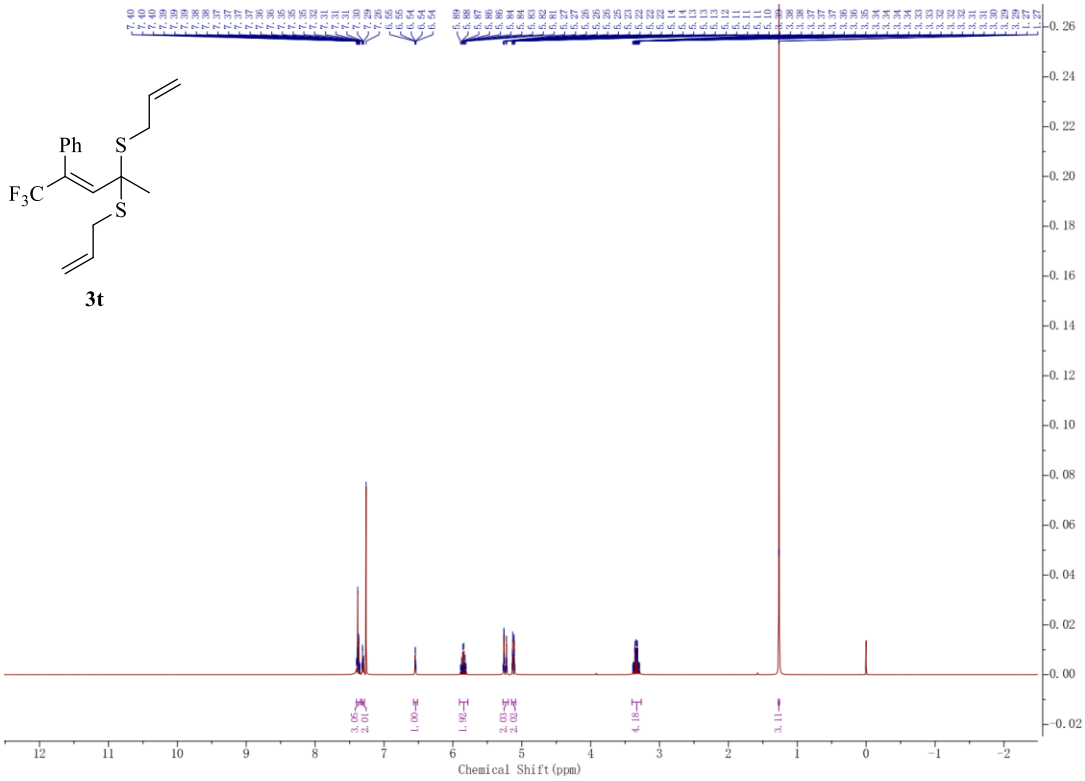
Ph
S
F3C
S

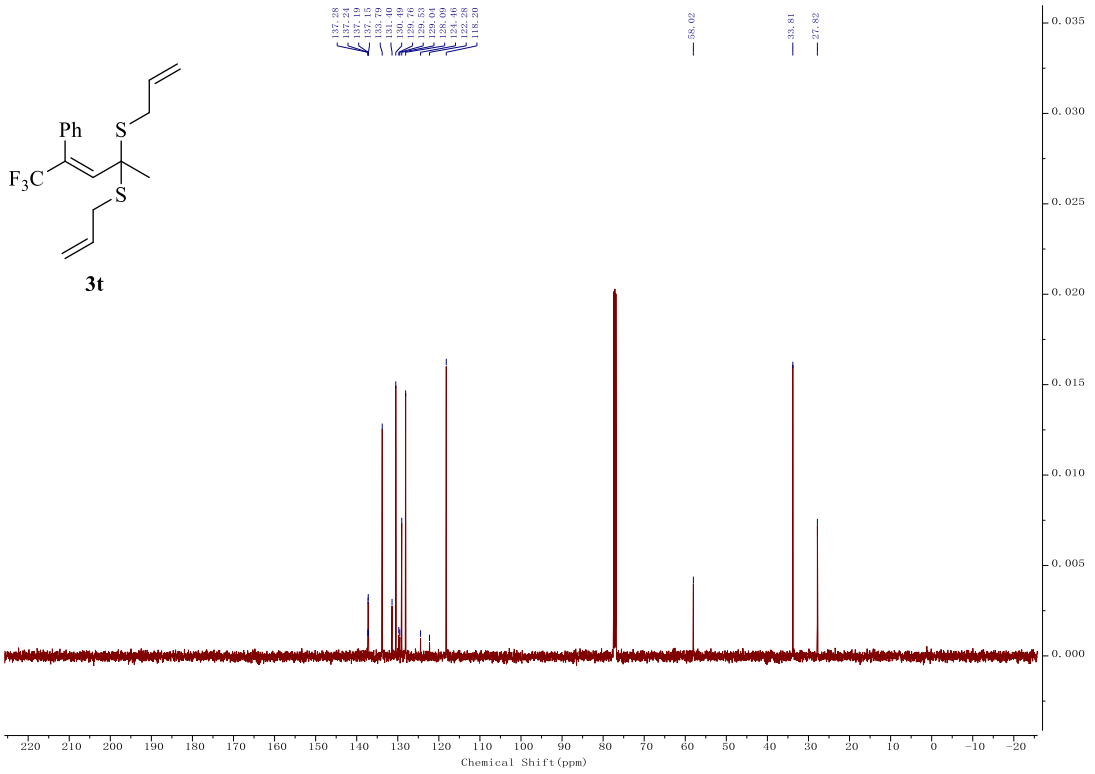
3s

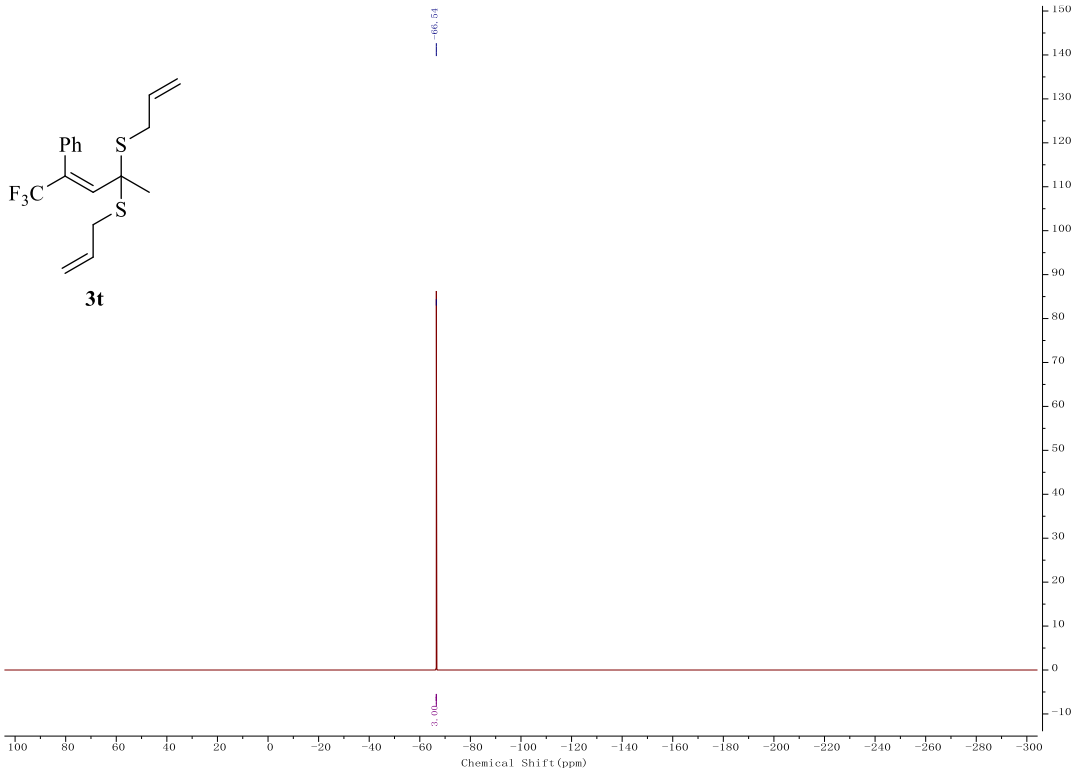

-66.52
3.00
Chemical Shift(ppm)

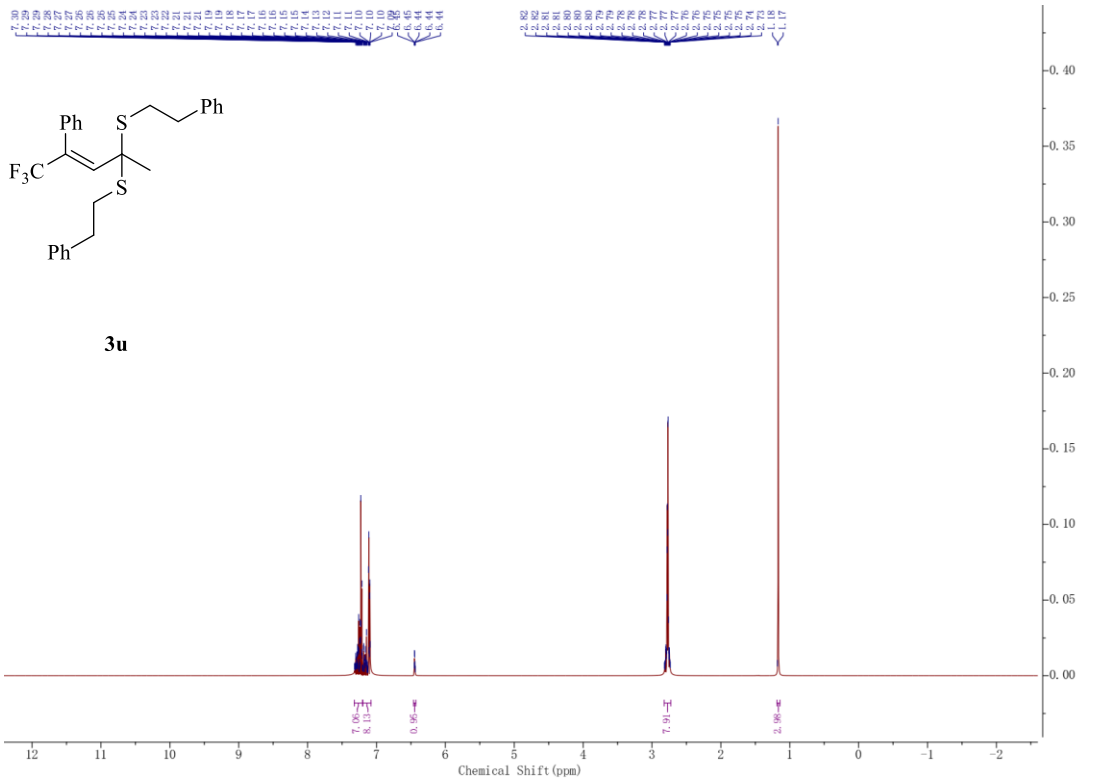
Ph
S
F3C
S

3t

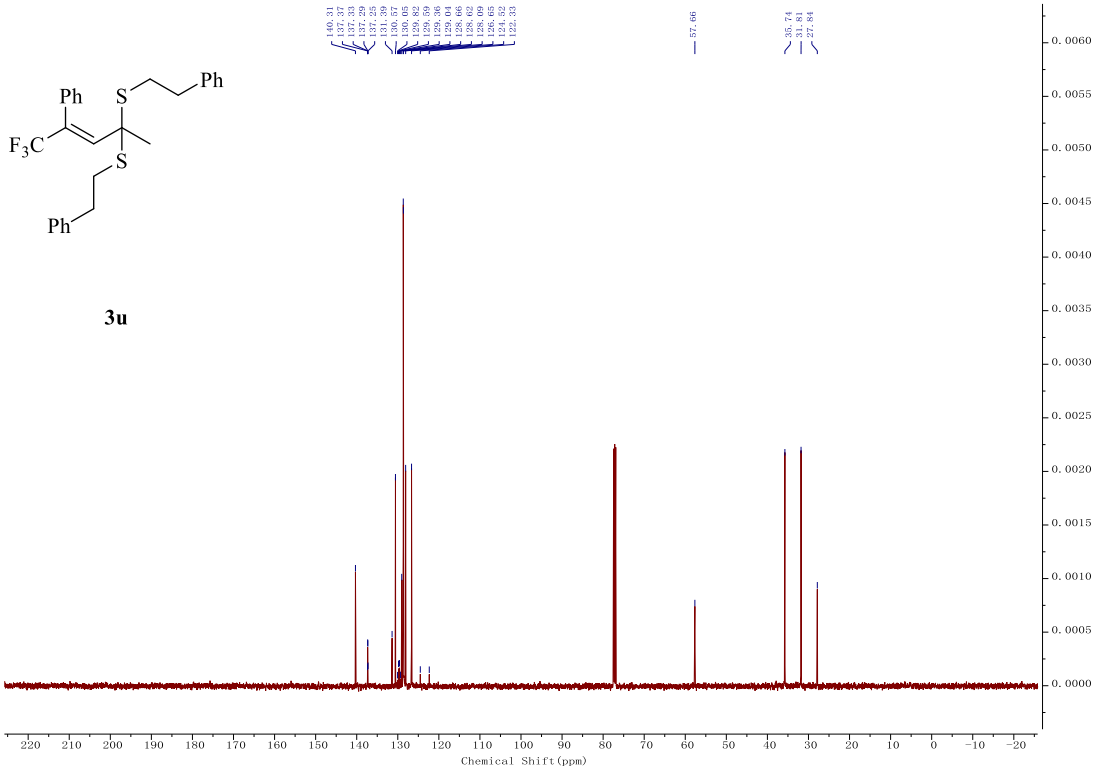

3.05
2.01
1.00
1.92
2.03
2.02
4.18
3.11
Chemical Shift(ppm)


Ph
S
F3C
S
3t
137.28
137.24
137.19
137.15
133.79
131.40
130.49
129.76
129.55
129.04
128.09
124.46
122.28
118.29
58.02
33.81
27.82
Chemical Shift(ppm)

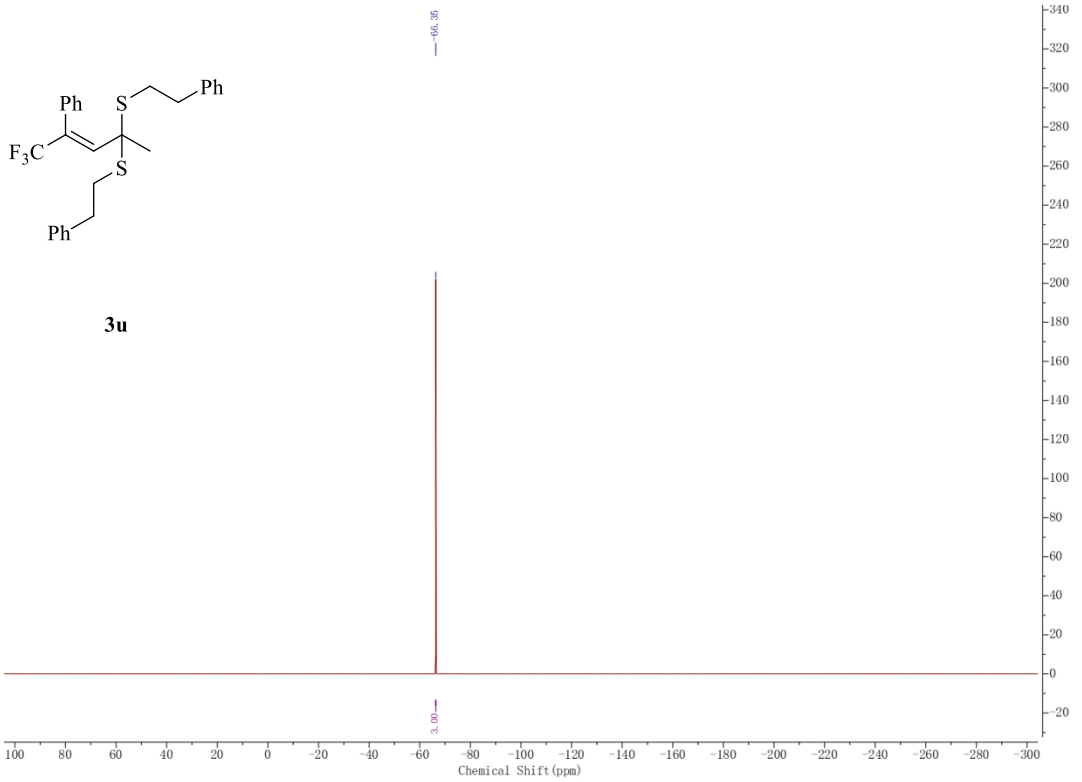

Ph
S
F3C
S
3t
-66.54
3.00
Chemical Shift(ppm)


Ph
S
Ph
F3C
S
Ph
Chemical Shift(ppm)

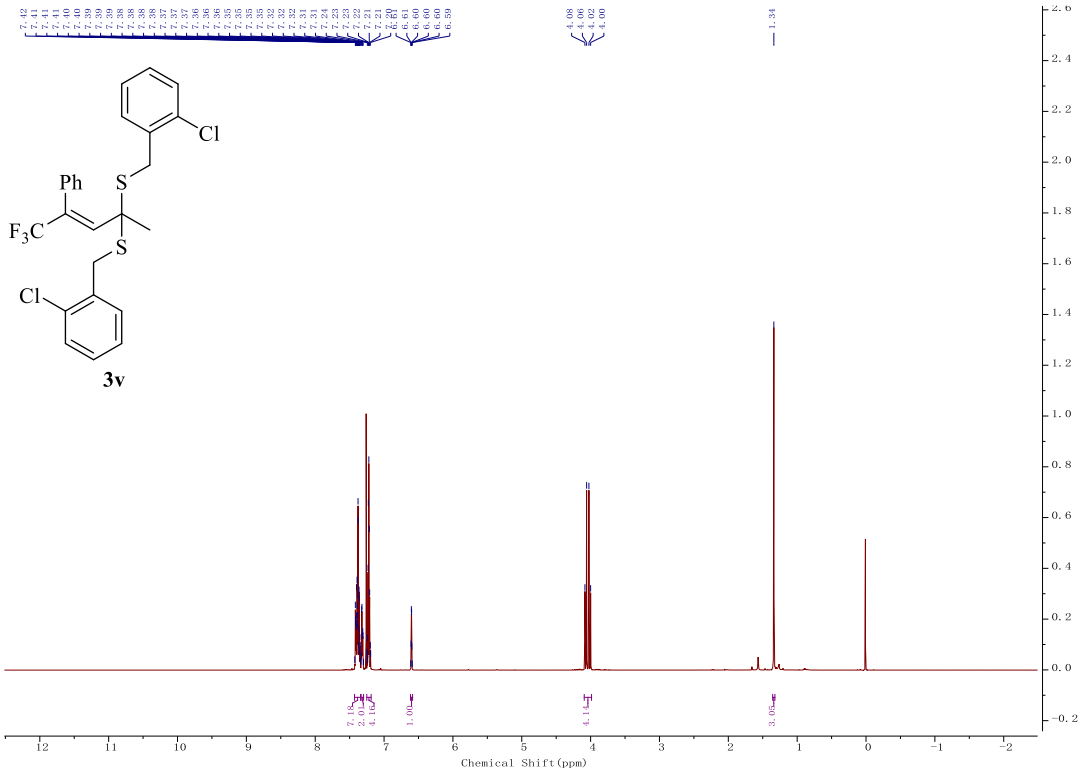
3u


Ph
S
Ph
F3C
S
Ph
Chemical Shift(ppm)

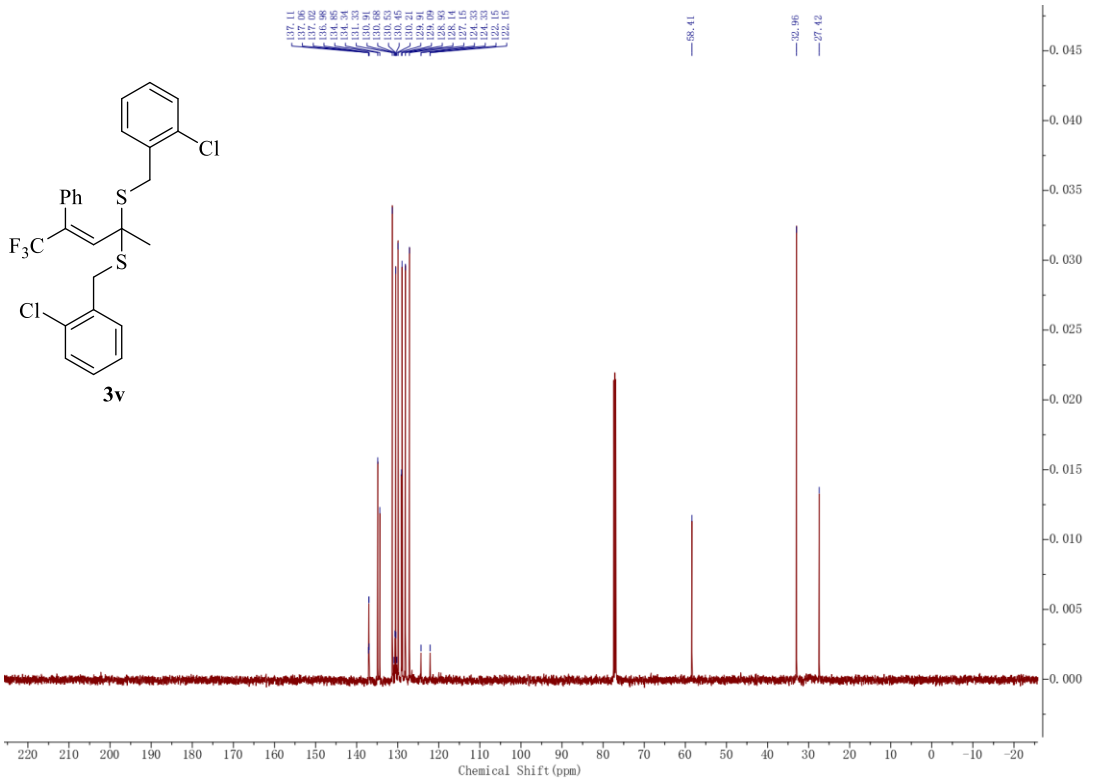
3u

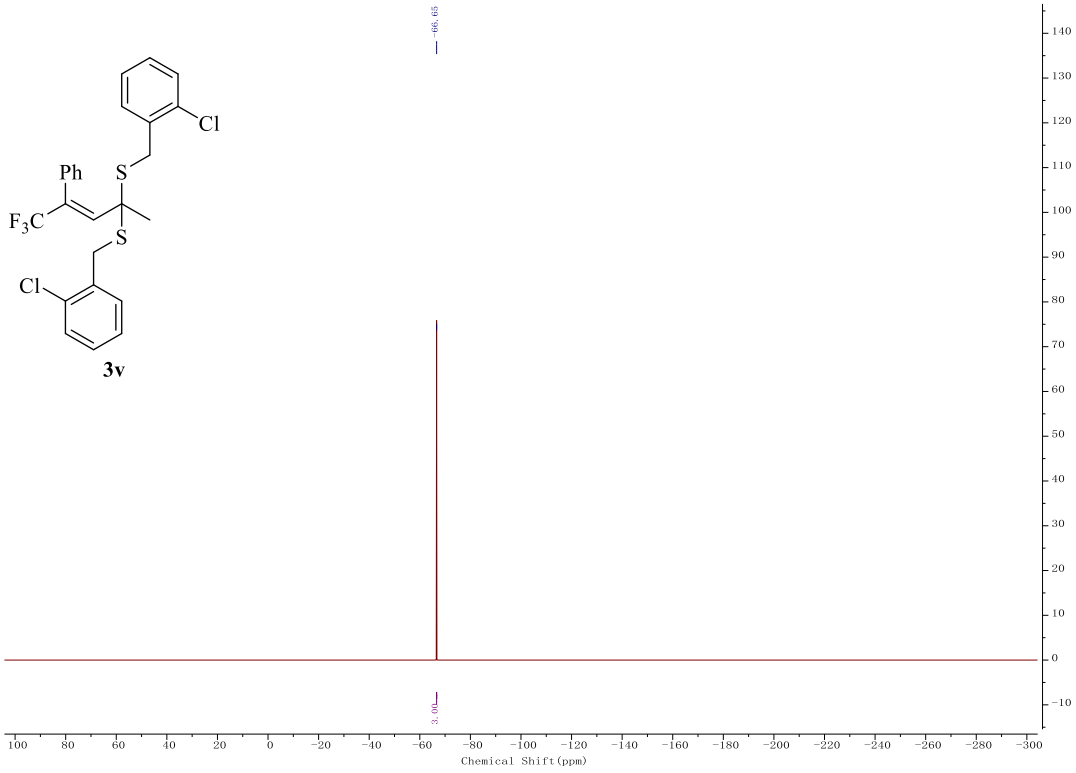

Ph
S
Ph
F3C
S
Ph
-66.35
3.00
Chemical Shift(ppm)

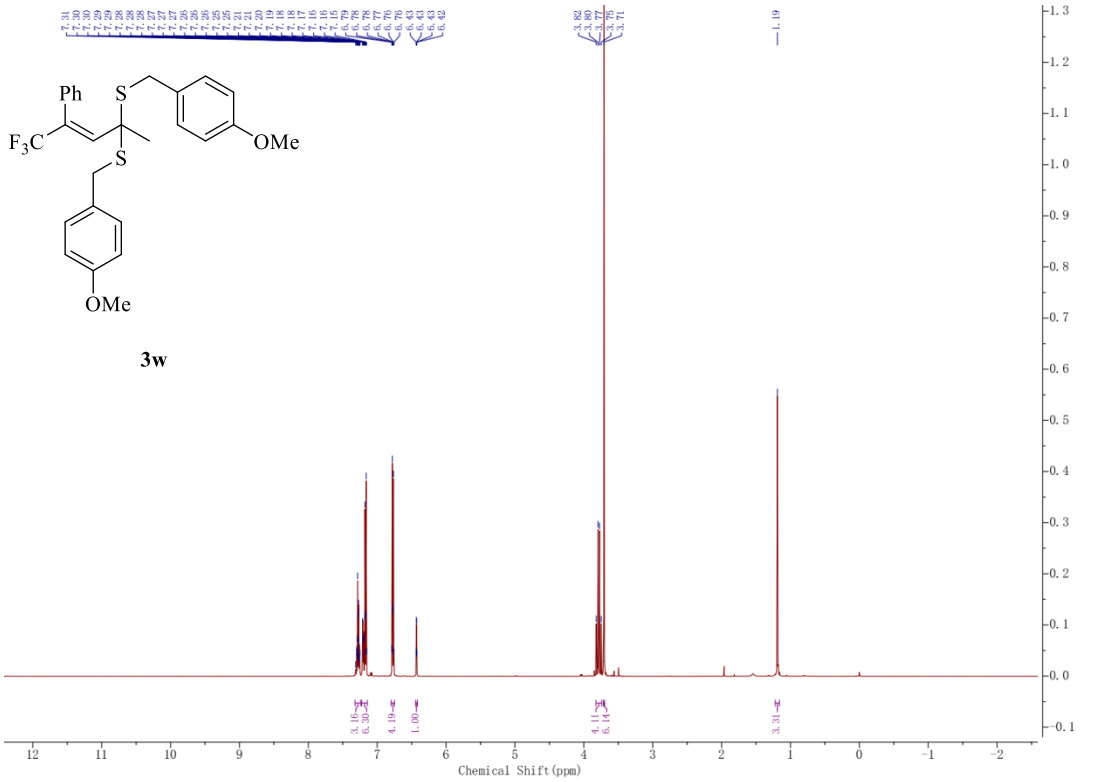
3u


Cl
Ph
S
F3C
S
Cl
1.34
Chemical Shift(ppm)

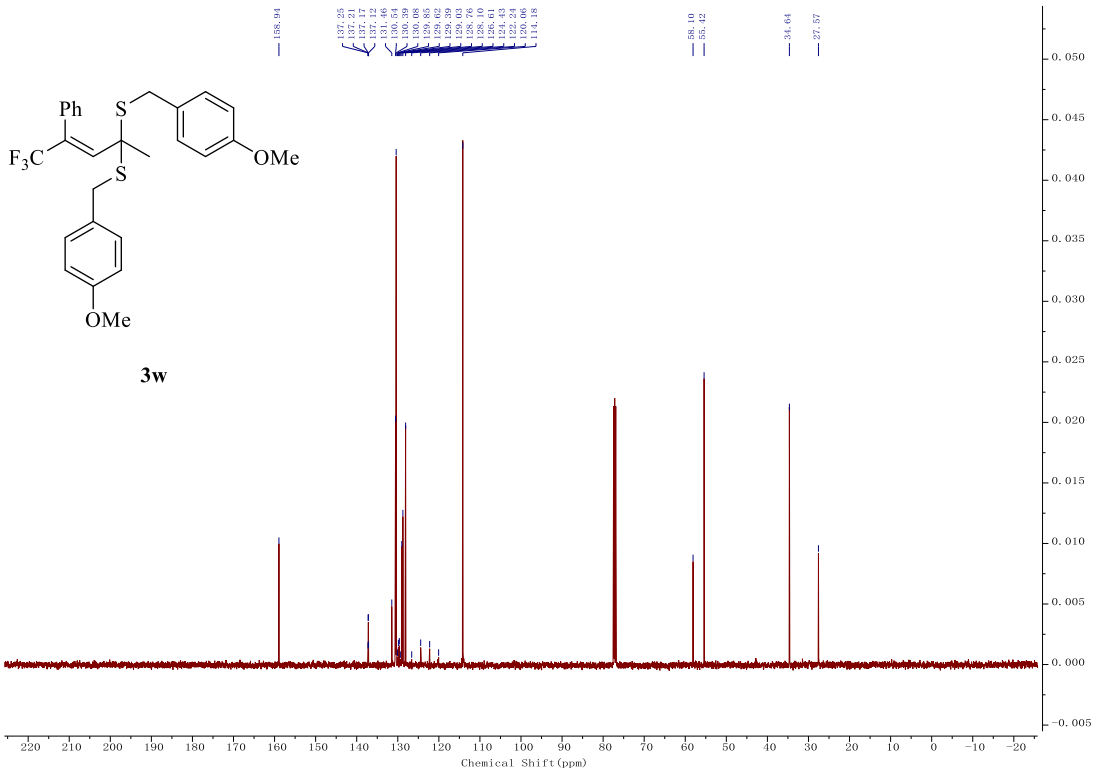
3v


Cl
Ph
S
F3C
S
Cl
3v
137.11
137.06
137.02
135.98
134.85
134.34
131.33
131.04
130.68
130.53
130.45
130.21
129.94
129.09
128.93
128.14
127.15
124.33
122.15
122.15
58.41
32.96
27.42
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift(ppm)


Cl
Ph
S
F3C
S
Cl
3v
-65.65
3.00
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
Chemical Shift(ppm)


Ph
S
F3C
S
OMe
OMe
Chemical Shift(ppm)

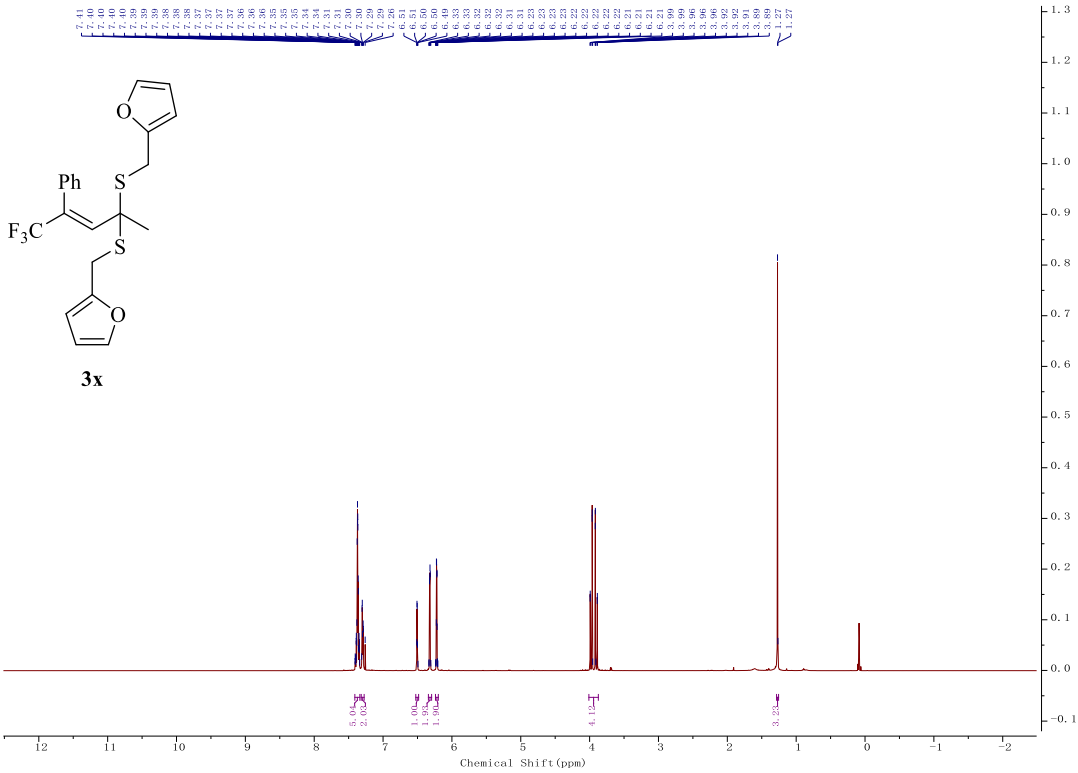
3w


Ph
S
F3C
S
OMe
OMe
Chemical Shift(ppm)

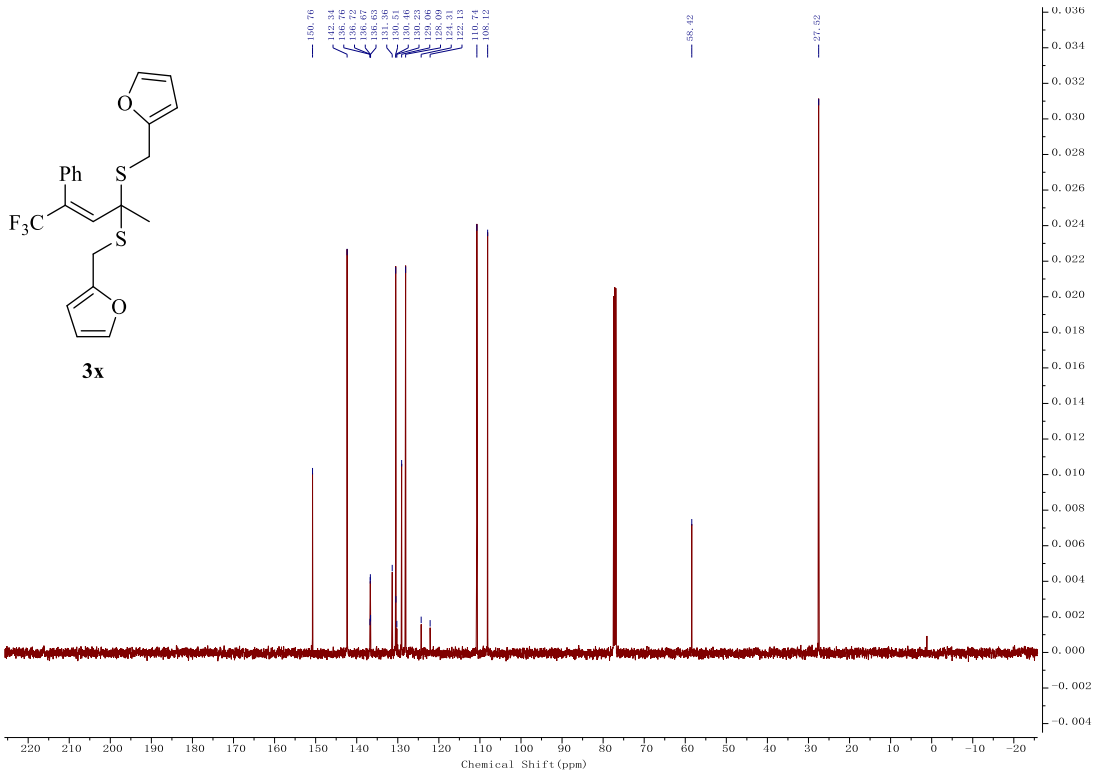
3w

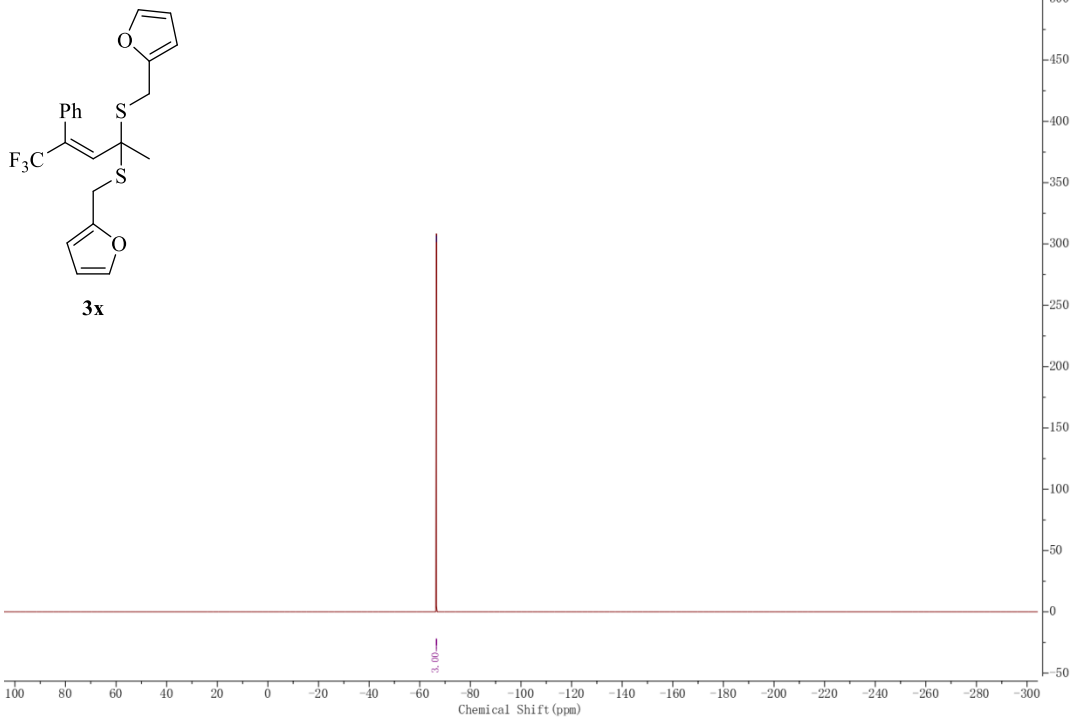

Ph
S
F3C
S
OMe
OMe
-66.42
3.00
Chemical Shift(ppm)

3w


O
Ph
S
F3C
S
O
5.04
2.00
1.00
1.93
1.90
4.12
3.23
Chemical Shift(ppm)

3x


150.76
142.34
136.76
136.72
136.67
136.63
131.36
130.51
130.46
130.23
129.06
128.69
124.31
122.13
110.74
108.12
58.42
27.52
Chemical Shift(ppm)


-66.69
3.00
Chemical Shift(ppm)

3x