Supporting Information

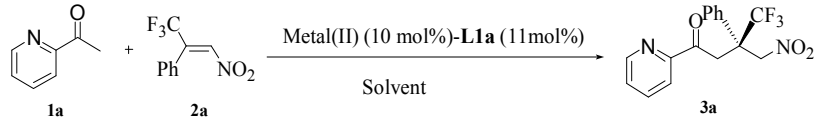
An Efficient Approach to The Construction of Trifluoromethylated All-carbon Quaternary Stereocenters: Enantioselective Ni(II)-Catalyzed Michael Addition of 2-Acetyl Azaarene to β, β-Disubstituted Nitroalkenes

Xuhe Hou, Hongli Ma, Zhenhua Zhang, Lei Xie, Zhaohai Qin, Bin Fu*
Department of Applied Chemistry, China Agricultural University,
No. 2 Yuanmingyuan West Road, Beijing 100193 (China)
fubinchem@cau.edu.cn

Experimental Section

^{1}H NMR, ^{13}C NMR spectra were recorded with a Bruker Avance DPX300 spectrometer with tetramethylsilane as the internal standard. Mass spectra were obtained on Bruker APEX II FT-ICRMS mass spectrometer. Optical rotations were measured on a Perkin–Elmer 341 LC polarimeter. The enantiomeric ratios were determined by HPLC analysis over a chiral column (Daicel Chiralcel OD-H, AD-H, OJ-H or AS-H; eluted with hexane-*iso*-propanol; UV detector). The absolute configuration of the major enantiomer was assigned by comparison with literatures. Solvents were purified and dried by standard procedures.

Table S1. The screening for the reaction of 2-acetyl pyridine with β-trifluoromethyl nitroalkene[a]

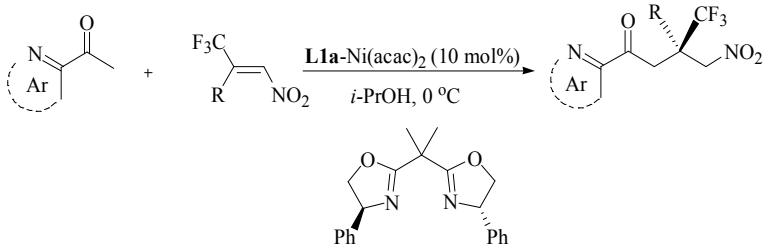


1a **2a** **3a**

Entry	Ligand	Metal	Solvent	T(°C)	Time(h)	Yield (%)[b]	Ee (%)[c]
1	**L1a**	$Fe(OAc)_2$	EtOH	25	72	n.d	-
2	**L1a**	$Fe(OAc)_2$	DCM	25	72	n.d	-
3	**L1a**	$Fe(OAc)_2$	THF	25	72	n.d	
4	**L1a**	$Pd(OAc)_2$	EtOH	25	72	n.d	
5	**L1a**	$Pd(OAc)_2$	DCM	25	72	n.d	
6	**L1a**	$Pd(OAc)_2$	THF	25	72	n.d	
7	**L1a**	$Cu(OAc)_2$	EtOH	25	72	28	24
8	**L1a**	$Cu(OAc)_2$	DCM	25	72	12	15
9	**L1a**	$Cu(OAc)_2$	THF	25	72	26	17
10	**L1a**	$Cu(OTf)_2$	EtOH	25	72	18	21
11	**L1a**	$Cu(OTf)_2$	DCM	25	72	n.d	-
13	**L1a**	$Ni(OAc)_2$	EtOH	25	24	43	89
14	**L1a**	$Ni(acac)_2$	i-PrOH	25	24	95	97
14	**L1a**	$Ni(acac)_2$	i-PrOH	0	24	95	99
15	**L1a**	$Ni(acac)_2$	i-PrOH	35	12	96	90
16	**L1a** (5.5mol%)	$Ni(acac)_2$ (5mol%)	i-PrOH	0	24	76	98
17	**L1a** ((2.75mol%))	$Ni(acac)_2$ (2.5 mol%)	i-PrOH	0	24	52	94

[a]All reactions were performed in different solvent at room temperature under N_2 atmosphere using the complex of 10mol% metal salt and 11mol% **L1a,** and the reaction process was monitored by TLC; [b] The isolated yield; [c] Determined by HPLC.

General procedure for the optimal conditions:



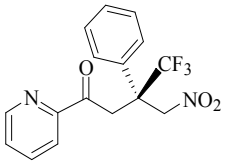
L1a

To a Schlenk tube were added $Ni(acac)_2$ (6.5mg, 0.025mmol) and ligand **L1a**(9.2mg，0.0275mmol) under N_2, 1.0 mL 2-Propanol was then added through syringe. The resulting mixture was stirred at room temperature for 30 min, after which a solution of 2-acetylazaarene (0.25mmol) in 2-propanol (0.4mL) was added and stirred at 0°C for 30 min, then a solution of nitroalkene in 2-propanol (0.6mL) was added. The mixture was stirred at 0 °C until the reaction was completed (monitored by TLC). The solvent was removed under vacuum and the residue was purified by chromatography on silica gel (eluting with ethyl acetate/petroleum ether [1:10~1:4 (v/v)] to afford the product.

Products

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-3-phenyl-1-(pyridin-2-yl)butan-1-one

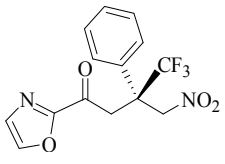
2a



White solid; 95% yield; m.p.:148-149°C; [α] = –76.7 (*c* 0.46, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 19.92 min, t_R (major) = 24.18 min];^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80–8.67 (m, 1H), 7.98 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.84 (td, *J* = 7.7, 1.7 Hz, 1H), 7.53 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.37 (d, *J* = 4.9 Hz, 5H), 5.67 (dd, *J* = 33.5, 12.3 Hz, 2H), 4.49 (dd, *J* = 89.1, 19.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.81, 152.58, 148.86, 136.85, 133.27, 128.76, 127.57, 126.55, 125.66 (q, *J* = 282.75 Hz), 121.65, 74.59, 49.85 (q, *J* = 25.5 Hz), 35.26; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.84. ESI-HRMS Calcd. for $C_{16}H_{14}F_3N_2O_3$([M+H]$^+$): 339.0951, Found 339.0953.

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-1-(oxazol-2-yl)-3-phenylbutan-1-one

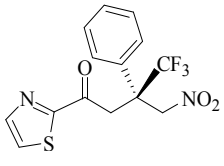
2a



White solid; 59% yield; m.p.:143-145°C; [α] = –58.9 (c 0.47, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) =26.82 min, t_R (minor) = 28.50 min];^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 0.6 Hz, 1H), 7.42 (dd, *J* = 2.1, 1.3 Hz, 5H), 7.28 (s, 1H), 5.71–5.58 (m, 2H), 4.45–4.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.79, 157.28, 142.13, 132.51, 129.12, 129.05, 128.95, 126.37, 125.33(q, *J* = 282.75Hz), 74.11, 49.66 (q, *J* = 25.8 Hz), 36.72; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.86(s, 3F); ESI-HRMS Calcd. for $C_{14}H_{12}F_3N_2O_4$ ([M+H]$^+$): 329.0744, Found 329.0742 .

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-3-phenyl-1-(thiazol-2-yl)butan-1-one

2a

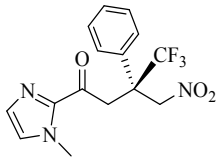


White solid; 99% yield; m.p.:168-170°C; [α] = –47.4(c 0.53, CH_2Cl_2);

99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) = 21.13 min, t_R (minor) = 32.48 min];^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, *J* = 3.0 Hz, 1H), 7.74 (d, *J* = 3.0 Hz, 1H), 7.39 (s, 5H), 5.64 (s, 2H), 4.41 (q, *J* = 19.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.74, 165.92, 144.71, 132.83, 128.95, 128.89, 126.90, 126.43, 125.43(q, *J* = 283.5 Hz), 74.34, 49.76(q, *J* = 25.6 Hz), 36.19(d, *J* = 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.80(s, 3F); ESI-HRMS Calcd. for $C_{14}H_{12}F_3N_2O_3S([M+H]^+)$: 345. 0515, Found 345.0514.

(*S*)-4, 4, 4-trifluoro-1-(1-methyl-1H-imidazol-2-yl)-3-(nitromethyl)-3-phenylbutan-1-one

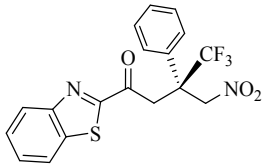
1Ω



White solid; 81% yield; m.p.:174-177°C; [α] = –75.5 (c 0.49, CH_2Cl_2); 96% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 0.80 mL/min, 254 nm; t_R (minor) = 10.87 min ,t_R (major) =15.45 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.33 (m, 5H), 7.22 (d, *J* = 0.9 Hz, 1H), 7.09 (s, 1H), 5.68 (q, *J* = 12.6 Hz, 2H), 4.40 (dd, *J* = 76.3, 18.8 Hz, 2H), 3.93 (s, 3H) ppm;^{13}C NMR (75 MHz, $CDCl_3$): δ 187.28, 142.43, 133.22 , 129.23, 128.76, 127.44, 126.55, 125.52(q, *J* = 282.75Hz), 123.63, 119.86, 49.84 (q, *J* = 25.5 Hz) 36.12, 35.85; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.78(s, 3F). ESI-HRMS Calcd. for $C_{15}H_{15}F_3N_3O_3$ ($[M+H]^+$): 342.1060, Found 342.1061.

(*S*)-1-(benzo[d]thiazol-2-yl)-4, 4, 4-trifluoro-3-(nitromethyl)-3-phenylbutan-1-one

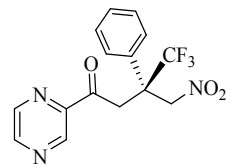
2Ω



White solid; 71% yield; m.p.:95-96°C; [α] = –144.9 (c 0.47, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) =18.38 min, t_R (minor) = 24.88 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37–8.20 (m, 1H), 8.08–7.95 (m, 1H), 7.63 (tdd, *J* = 14.9, 7.2, 1.4 Hz, 2H), 7.51–7.37 (m, 5H), 5.68 (s, 2H), 4.56 (dd, *J* = 44.5, 19.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.32, 165.10, 153.13, 137.30, 132.72, 129.04, 128.97, 127.94 , 127.10, 126.46, 125.50 , 125.44 (q, *J* = 282.75Hz), 122.27, 74.38, 49.78 (q, *J* = 25.7 Hz), 36.33;^{19}FNMR (282 MHz, $CDCl_3$): δ -72.75(s, 3F); ESI-HRMS Calcd. for $C_{18}H_{13}F_3N_2NaO_3S([M+Na]^+)$: 417.0491, Found 417.0495.

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-3-phenyl-1-(pyrazin-2-yl)butan-1-one

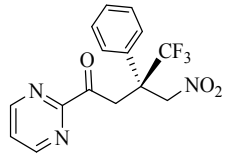
3Ω



White solid; 92% yield; m.p.:74-77°C; [α] = –59.3 (c 0.57, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 18.30 min t_R (major) = 24.42 min];^{1}H NMR (300 MHz, $CDCl_3$) δ 9.18 (d, *J* = 1.4 Hz, 1H), 8.81 (d, *J* = 2.5 Hz, 1H), 8.70 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.44–7.32 (m, 5H), 5.63 (p, *J* = 12.6 Hz, 2H), 4.42 (dd, *J* = 49.2, 19.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.16, 148.30, 146.76, 143.45, 143.34, 132.91, 128.93, 128.88, 126.40, 125.57 (q, *J* =282.75 Hz), 74.37, 49.69 (q, *J* = 25.6 Hz), 35.50; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.93(s, 3F); ESI-HRMS Calcd. for $C_{15}H_{13}F3N_3O_3([M+H]^+)$: 340.0904, Found 340.0904.

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-3-phenyl-1-(pyrimidin-2-yl)butan-1-one

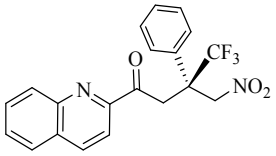
3a



Pale yellow oil; 67% yield; [α] = –38.9 (c 0.47, CH_2Cl_2); 85% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 85:15, 0.80 mL/min, 254 nm; t_R (major) = 50.51 min, t_R (minor) = 112.78 min];^{1}H NMR (300 MHz, $CDCl_3$): δ 8.96 (d, J = 4.9 Hz, 1H), 7.52 (t, J = 4.9 Hz, 1H), 7.38 (s, 3H), 5.66 (q, J = 12.5 Hz, 1H), 4.47 (dd, J = 47.8, 19.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.16, 159.21, 157.57, 132.84, 128.83, 126.49, 125.60 (q, J = 282.75Hz), 123.27, 74.25, 49.80 (q, J = 25.5 Hz), 36.73; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.85(s, 3F); ESI-HRMS Calcd. for $C_{15}H_{13}F_3N_3O_3$ ([M+H]$^+$): 340.0904, Found 340.0906.

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-3-phenyl-1-(quinolin-2-yl)butan-1-one

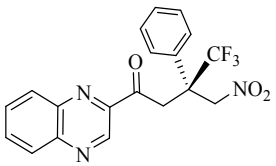
3b



White solid; 71% yield; m.p.:132-133^{o}C; [α] =–174.6 (c 0.46, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) =18.19 min, t_R(minor) = 27.38 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (dd, J = 8.5, 1.9 Hz, 2H), 8.08 (d, J = 8.5 Hz, 1H), 7.97–7.80 (m, 2H), 7.72 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.56–7.34 (m, 5H), 5.85–5.61 (m, 2H), 4.96–4.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.18, 152.14, 146.90, 136.98, 133.33 , 130.51, 130.05, 129.71, 128.78, 128.76, 127.46, 126.62, 126.61, 125.76(q, J = 282.75 Hz), 117.68, 74.68, 49.99 (q, J = 25.4 Hz), 35.01(d, J = 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.75 (s, 3F). ESI-HRMS Calcd. for $C_{20}H_{16}F_3N_2O_3$([M+H]$^+$): 389.1108, Found 389.1109.

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-3-phenyl-1-(quinoxalin-2-yl)butan-1-one

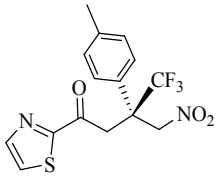
3c



Pale yellow oil; 72% yield; [α] = –148.5 (c 0.39, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) =20.65 min, t_R (minor) = 34.17 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.43 (s, 1H), 8.35–8.12 (m, 2H), 8.05–7.84 (m, 2H), 7.41 (s, 5H), 5.68 (dd, J = 28.4, 12.4 Hz, 2H), 4.60 (dd, J = 67.3, 19.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.44, 145.55, 144.12, 142.62, 140.64, 132.99, 132.47, 130.83, 130.37, 129.31, 128.94, 128.90, 126.46, 125.63(q, J = 282.75Hz), 74.50, 49.79(q, J = 25.5 Hz), 35.23; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.83(s, 3F); ESI-HRMS Calcd. for $C_{19}H_{15}F_3N_3O_3$ ([M+H]+): 390.1060, Found 390.1063.

(*S*)-4, 4, 4-trifluoro-3-(4-methylphenyl)-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one

3d

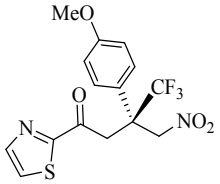


White solid; 97% yield; m.p.:110-112^{o}C; [α] = –50.2 (c 0.46, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.80 mL/min, 254 nm; t_R(major)= 19.12 min, t_R (minor) = 20.98 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, J = 3.0 Hz, 1H), 7.76 (d, J = 3.0 Hz, 1H), 7.26 (dd, J = 23.8, 8.5 Hz, 4H), 5.65 (s, 2H), 4.43 (q, J = 19.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.84, 165.97, 144.71,

138.99, 129.78, 129.61, 126.92, 126.30, 125.52(q, J = 282.75Hz), 74.42, 49.54 (q, J = 25.6 Hz), 36.16 (d, J = 1.5 Hz), 20.63; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.96(s, 3F); ESI-HRMS Calcd. for $C_{15}H_{14}F_3N_2O_3S([M+H]^+)$: 359.0672, Found 359.0672.

(*S*)-4, 4, 4-trifluoro-3-(4-methoxyphenyl)-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one

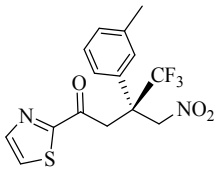
2u



White solid; 81% yield; m.p.:74-76^{o}C; [α] = –48.5(c 0.48, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 23.26 min, t_R (major) = 30.07 min];^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, J =3.0 Hz, 1H), 7.76 (d, J = 3.0 Hz, 1H), 7.38–7.24 (m, 2H), 6.98–6.87 (m, 2H), 5.63 (s, 2H), 4.40 (q, J = 19.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.84, 165.99, 159.70, 144.70, 127.72, 126.92, 125.51(q, J = 282.75 Hz), 124.46, 114.24, 74.40, 55.02, 49.32 (q, J = 25.7 Hz). 36.12; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.13(s, 3F); ESI-HRMS Calcd. for $C_{15}H_{14}F_3N_2O_4S([M+H]^+)$: 375.0621, Found 375.0624.

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-1-(thiazol-2-yl)-3-(*m*-tolyl)butan-1-one

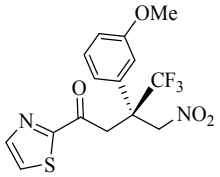
2v



Colourless oil; 85% yield; [α] =-53.6 (c 0.52, CH_2Cl_2); 96% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 11.69 min, t_R (major) = 12.30 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, J = 3.0 Hz, 1H), 7.76 (d, J = 3.0 Hz, 1H), 7.40–7.14 (m, 4H), 5.66 (s, 2H), 4.43 (q, J = 19.0 Hz, 2H), 2.36 (d, J = 5.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.83, 166.00, 144.69, 138.62, 132.77, 129.73, 128.71, 127.09, 126.89, 125.47 (q, J = 282.75 Hz), 123.51, 74.37, 49.68 (q, J = 25.6 Hz), 36.20 (d, J = 1.5 Hz), 21.41; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.75(s, 3F); ESI-HRMS Calcd. for $C_{15}H_{14}F_3N_2O_3S([M+H]^+)$: 359.0672, Found 359.0672.

(*S*)-4, 4, 4-trifluoro-3-(3-methoxyphenyl)-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one

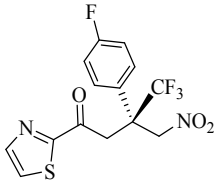
2w



White solid; 91% yield; m.p.:83-84^{o}C; [α] = -41.7 (c 0.52, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 16.60 min , t_R (major) = 20.02 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (t, J = 3.6 Hz, 1H), 7.75 (t, J = 2.7 Hz, 1H), 7.34 (dd, J = 12.2, 4.3 Hz, 1H), 7.03–6.87 (m, 3H), 5.65 (q, J = 12.8 Hz, 2H), 4.42 (dd, J = 45.6, 19.0 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.74, 165.92, 159.71, 144.70, 134.31, 129.85, 126.94 , 125.40 (d, J =282.75 Hz), 118.63, 113.75, 113.40, 74.37, 55.06, 49.73(q, J = 25.7 Hz), 36.23 (d, J = 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.72(s, 3F); ESI-HRMS Calcd. for $C_{15}H_{14}F_3N_2O_4S([M+H]^+)$: 375.0621 , Found 375.0619.

(*S*)-4, 4, 4-trifluoro-3-(4-fluorophenyl)-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one

2x

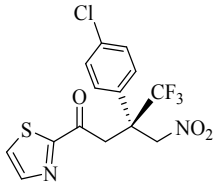


White solid; 71% yield; m.p.:129-131^{o}C; [α] = -59.1 (c 0.54, CH_2Cl_2);

97% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 20.04 min, t_R (major) = 21.59 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, *J* = 3.0 Hz, 1H), 7.78 (d, *J* = 3.0 Hz, 1H), 7.41 (dd, *J* = 8.5, 4.9 Hz, 2H), 7.17–7.06 (m, 2H), 5.69–5.56 (m, 2H), 4.49–4.34 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.60, 165.76, 164.27, 160.95, 144.76, 128.65 (d, *J* = 2.7 Hz), 128.45 (d, *J* = 8.3 Hz), 127.16, 127.08, 125.47(q, *J* = 282.75 Hz), 115.97 (d, *J* = 21.7 Hz), 74.22, 49.32 (q, *J* =25.8 Hz), 36.27; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.97(s, 3F), -111.91(s, 1F); ESI-HRMS Calcd. for $C_{14}H_{11}F_4N_2O_3S([M+H]^+)$: 363.0421, Found 363.0421.

(*S*)-3-(4-chlorophenyl)-4, 4, 4-trifluoro-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one

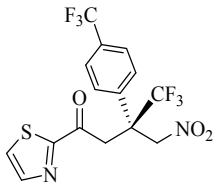
1Ω



White solid; 86% yield; m.p.:111-113°C; [α] = -47.8 (c 0.46, CH_2Cl_2); 94% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 20.22 min , t_R (major) = 28.67 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 3.0 Hz, 1H), 7.79 (d, *J* = 3.0 Hz, 1H), 7.47 – 7.31 (m, 4H), 5.74 – 5.52 (m, 2H), 4.53 – 4.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.53, 165.70, 144.77, 135.31, 131.41, 129.13, 127.89(d, *J* = 0.8Hz), 127.11, 125.21(q, *J* = 282.75 Hz), 74.10, 49.53 (q, *J* = 25.8 Hz), 36.21; ^{19}F NMR(282 MHz, $CDCl_3$): δ -72.83(s, 3F); ESI-HRMS Calcd. for $C_{14}H_{11}F_3ClN_2O_3S([M+H]^+)$: 379.0126, Found 379.0128.

(*S*)-4, 4, 4-trifluoro-3-(4-(trifluoromethyl)phenyl)-3-(nitromethyl)- 1-(thiazol-2-yl) butan-1-one

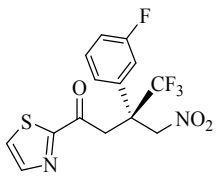
1Ω



White solid; 80% yield; m.p.:76-78°C; [α] = –50.6 (c 0.65, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) = 23.00 min, t_R (minor) = 24.25 min]; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.11 (d, *J* = 3.0 Hz, 1H), 7.80 (d, *J* = 3.0 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.29 (s, 2H), 5.75–5.58 (m, 2H), 4.46 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.41, 165.52, 144.83, 136.91, 131.26 (q, *J* =33.3 Hz), 127.23, 127.09, 128.87 (dd, *J* = 7.1, 3.5 Hz), 125.12(q, *J* = 282.75Hz), 123.27(q, *J* = 270.75Hz), 74.05, 49.32 (q, *J* = 25.7 Hz), 36.34; ^{19}F NMR (282 MHz, $CDCl_3$): *δ* -63.03(s, 3F), -72.55(s, 3F); ESI-HRMS Calcd. for $C_{15}H_{11}F_6N_2O_3S([M+H]^+)$: 413.0389, Found 413.0388.

(*S*)-4, 4, 4-trifluoro-3-(3-fluorophenyl)-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one

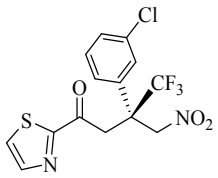
1Ω



White solid; 76% yield; m.p.:131-133°C; [α] = -49.6 (c 0.49, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 14.39 min , t_R (major) = 17.32 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 3.0 Hz, 1H), 7.79 (d, *J* = 3.0 Hz, 1H), 7.42 (td, *J* = 8.2, 6.1 Hz, 1H), 7.26–7.07 (m, 3H), 5.63 (s, 2H), 4.41 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.48, 165.66, 164.30, 161.02, 144.78, 135.33 (d, *J* = 7.0 Hz), 130.42 (d, *J* = 8.3 Hz), 127.07, 125.18 (q, *J* = 282.75 Hz), 122.15 ,

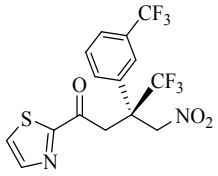
116.13 (d, J = 20.9 Hz), 114.24 (d, J = 24.0 Hz), 49.63 (qd, J = 25.9, 1.7 Hz), 36.34 (d, J = 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -110.54 (s, 1F), -72.71(s, 3F); ESI-HRMS Calcd. for $C_{14}H_{11}F_4N_2O_3S([M+H]^+)$: 363.0421, Found 363.0423.

(*S*)-3-(3-chlorophenyl)-4, 4, 4-trifluoro-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one



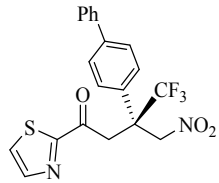
White solid; 65% yield; m.p.:79-80^{o}C; [α] = -44.7 (c 0.63, CH_2Cl_2); >99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 14.07min, t_R (major) = 16.49 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, J = 3.0 Hz, 1H), 7.78 (d, J = 3.0 Hz, 1H), 7.54–7.22 (m, 4H), 5.64 (d, J = 12.9 Hz, 2H), 4.57–4.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.46, 165.64, 144.79, 135.06, 134.95, 130.05, 129.28, 127.13, 126.96, 125.18 (q, J = 282.75 Hz), 124.68, 74.02, 49.65 (q, J = 25.8 Hz), 36.26(d, J = 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.62(s, 3F); ESI-HRMS Calcd. for $C_{14}H_{11}ClF_3N_2O_3S$ ($[M+H]^+$): 379.0126, Found 379.0128.

(*S*)-4, 4, 4-trifluoro-3-(3-(trifluoromethyl)phenyl)-3-(nitromethyl)-1-(thiazol-2-yl) butan-1-one



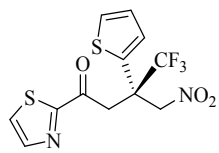
Colourless oil; 79% yield; [α] -42.2 (c 0.52, CH_2Cl_2); 98% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) = 9.88 min, t_R (minor) = 10.48]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (t, J = 3.1 Hz, 1H), 7.79 (t, J = 2.3 Hz, 1H), 7.73–7.50 (m, 4H), 5.76–5.54 (m, 2H), 4.46 (s, 2H);^{13}C NMR (75 MHz, $CDCl_3$): δ 188.45, 165.53, 144.84, 131.43 (dd, J = 65.4, 32.7Hz), 29.91, 128.53, 128.17 (dd, J = 232.7, 161.7Hz), 127.24, 125.97 (q, J = 3.7 Hz), 125.12(q, J = 282.75 Hz), 123.43(q, J =3.0Hz), 123.33(q, J = 270.75 Hz), 74.04, 49.83 (q, J = 25.9 Hz), 36.18 (d, J = 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.67(s,3F), -62.75 (s, 3F); ESI-HRMS Calcd. for $C_{15}H_{10}F_6N_2O_3S([M+H]^+)$: 413.0389 , Found 413.0391.

(*S*)-3-([1, 1'-biphenyl]-4-yl)-4, 4, 4-trifluoro-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one



Colourless oil; 62% yield; [α] =-36.7 (c 0.64, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) = 28.19 min, t_R (minor) = 39.79 min];^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 3.0 Hz, 1H), 7.78 (d, J = 3.0 Hz, 1H), 7.69–7.55 (m, 4H), 7.53–7.34 (m, 5H), 5.80–5.62 (m, 2H), 4.49 (q, J = 19.0 Hz, 2H);^{13}C NMR (75 MHz, $CDCl_3$): δ 188.80, 165.90, 144.76, 141.79, 139.39, 131.62, 128.66, 127.68, 127.48, 127.03, 126.87, 125.48(q, J = 282.75 Hz), 123.59, 74.36, 49.67 (q, J = 25.7 Hz), 36.23; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.71(s,3F); ESI-HRMS Calcd. for $C_{20}H_{15}F_3N_2NaO_3S([M+H]^+)$: 443.0648, Found 443.0646 .

(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-1-(thiazol-2-yl)-3-(thiophen-2-yl)butan-1-one

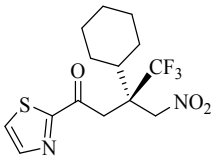


Pale yellow solid; 72% yield; m.p.:172-174^{o}C; [α] = -33.2(c = 0.5, CH_2Cl_2); 93% ee, determined by HPLC analysis [Daicel Chiralcel OD-H

column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 27.38min , t_R (major) = 28.90 min];^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, *J* = 3.0 Hz, 1H), 7.78 (d, *J* = 3.0 Hz, 1H), 7.46–7.30 (m, 2H), 7.13 (d, *J* = 5.1 Hz, 1H), 5.60 (dd, *J* = 43.7, 12.7 Hz, 2H), 4.38 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.74, 165.91, 144.72, 133.46, 126.96, 126.66, 125.51(d, *J* = 0.75Hz), 125.13(q, *J* = 282.75Hz), 123.99(d, *J* = 0.75Hz), 74.09, 48.41 (q, *J* = 26.5 Hz), 37.04 (d, *J* = 1.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): *δ* -73.42(s, 3F); ESI-HRMS Calcd. for $C_{12}H_{10}F_3N_2O_3S_2$([M+H]$^+$): 351.0079 , Found 351.0078.

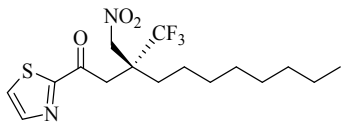
.

(*S*)-3-cyclohexyl-4, 4, 4-trifluoro-3-(nitromethyl)-1-(thiazol-2-yl)butan-1-one



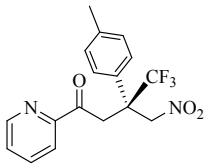
White solid; 72% yield; m.p.:80-84^{o}C; [α] = -17.8 (*c* 0.49, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.80 mL/min, 254 nm; t_R (minor) = 9.80 min, t_R (major) = 10.34 min], ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, *J* = 3.0 Hz, 1H), 7.76 (d, *J* = 3.0 Hz, 1H), 5.15 (dd, *J* = 63.2, 12.5 Hz, 2H), 3.86 (q, *J* = 18.9 Hz, 2H), 2.07 (t, *J* = 11.5 Hz, 1H), 1.84 (t, *J* = 10.8 Hz, 4H), 1.70 (d, *J* = 8.1 Hz, 1H), 1.25 (dt, *J* = 17.3, 9.7 Hz, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 189.62, 166.11, 144.67, 126.78, 126.71(q, *J* = 285.75 Hz), 74.52, 74.49, 49.94(q, *J* = 23.4 Hz), 41.28, 34.86, 34.83, 27.99 (dd, *J* = 3.7,1.8 Hz), 26.91(d, *J* = 26.91 Hz), 25.77; ^{19}F NMR (282 MHz, $CDCl_3$): *δ* -67.42(s,3F); ESI-HRMS Calcd. for $C_{14}H_{18}F_3N_2O_3S$ ([M+H]$^+$): 351.0985, Found 351.0981.

(*R*)-3-(trifluoromethyl)-3-(nitromethyl)-1-(thiazol-2-yl)-undecan-1-one



Colourless oil; 79% yield; [α] -3.39 (*c* 0.56, CH_2Cl_2); 96% ee, determined by HPLC analysis [Daicel Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) = 9.41 min, t_R (minor) = 10.98 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, *J* = 3.0 Hz, 1H), 7.73 (d, *J* = 3.0 Hz, 1H), 4.99 (dd, *J* = 72.5, 12.6 Hz, 2H), 3.76 (dd, *J* = 85.1, 18.7 Hz, 2H), 1.85 (t, *J* = 7.7 Hz, 2H), 1.45–1.17 (m, 12H), 0.85 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 189.53, 165.99, 144.69, 126.84, 126.55(q, *J*=283.5 Hz), 74.63, 46.86(q, *J*=24.5 Hz), 35.68, 31.60, 31.45, 31.01, 29.43(d, *J* = 25.3 Hz), 28.79, 23.21, 22.24 (d, *J* = 10.7Hz), 13.68 (d, *J* = 8.4Hz); ^{19}F NMR (282 MHz, $CDCl_3$): *δ* -72.72(s, 3F); ESI-HRMS Calcd. for $C_{16}H_{24}F_3N_2O_3S$([M+H]$^+$): 381.1454, Found 381.1458.

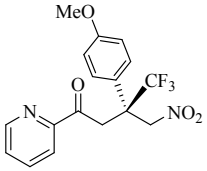
(*S*)-4, 4, 4-trifluoro-3-(nitromethyl)-1-(pyridin-2-yl)-3-(*p*-tolyl)butan-1-one



White solid; 94% yield; m.p.:75-77^{o}C; [α] = -76.6 (c 0.47, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 15.97min , t_R (major) =17.20 min]; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.77 (d, *J* = 4.7 Hz, 1H), 7.91 (ddd, *J* = 22.4, 9.4, 4.8 Hz, 2H), 7.56 (ddd, *J* = 7.4, 4.8, 1.0 Hz, 1H), 7.25 (dd, *J* = 24.7, 8.3 Hz, 4H), 5.67 (dd, *J* = 36.4, 12.3 Hz, 2H), 4.49 (dd, *J* = 91.7, 19.5 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 196.95, 152.68, 148.89, 138.75, 136.87, 130.26, 129.53, 127.57, 126.43, 125.77 (q, *J* = 284.4 Hz), 121.69, 74.67 (d, *J* = 1.2 Hz), 49.64 (q, *J* = 25.5 Hz), 35.25 (d, *J* =1.4

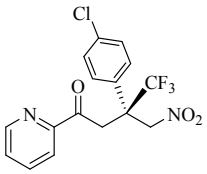
Hz), 20.70; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.04 (s, 3F); ESI-HRMS Calcd. for $C_{17}H_{16}F_3N_2O_3$([M+H]$^+$): 353.1108, Found 353.1103.

(*S*)-4, 4, 4-trifluoro-3-(4-methoxyphenyl)-3-(nitromethyl)-1-(pyridin-2-yl)butan-1-one



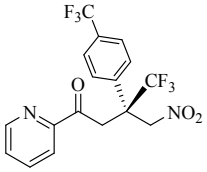
Colourless oil; 95% yield; [α] = -71.1 (c 0.46, CH_2Cl_2); 96% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.80 mL/min, 254 nm; t_R (minor) = 38.97min, t_R (major) = 40.77 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.57–7.49 (m, 1H), 7.35 – 7.22 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.63 (dd, *J* = 37.5, 12.3 Hz, 2H), 4.44 (dd, *J* = 91.3, 19.4 Hz, 2H), 3.77 (d, *J* = 5.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.97, 159.59, 152.69, 148.88, 136.88, 127.84, 125.78 (q, *J* = 284.0 Hz), 127.56, 125.00, 121.69, 114.16, 74.65, 55.04, 49.43 (q, *J* = 25.6 Hz), 35.19; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.21(s, 3F); ESI-HRMS Calcd. for $C_{17}H_{16}F_3N_2O_4$([M+H]$^+$): 369.1057, Found 369.1062.

(*S*)-3-(4-chlorophenyl)-4, 4, 4-trifluoro-3-(nitromethyl)-1-(pyridin-2-yl)butan-1-one



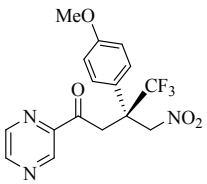
White solid; 93% yield; m.p.:79-80^{o}C; [α] = -72.0 (c 0.5, CH_2Cl_2); 91% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 22.14min , t_R (major) =25,21min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79–8.67 (m, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.85 (td, *J* = 7.7, 1.7 Hz, 1H), 7.53 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.44–7.27 (m, 4H), 5.61 (dd, *J* = 29.4, 12.4 Hz, 2H), 4.45 (dd, *J* = 65.6, 19.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.70, 152.48, 148.93, 136.95, 135.09, 131.92, 129.04, 128.05, 127.73, 125.49 (q, *J* = 284.6 Hz), 121.72, 74.40, 49.65 (q, *J* = 25.7 Hz), 35.34; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.90 (s, 3F); ESI-HRMS Calcd. for $C_{16}H_{13}ClF_3N_2O_3$([M+H]$^+$): 373.0561, Found 373.0564.

(*S*)-4, 4, 4-trifluoro-3-(4-(trifluoromethyl)phenyl)-3-(nitromethyl)-1-(pyridin-2-yl) butan-1-one



White solid; 86% yield; m.p.:97-99^{o}C; [α] = -64.9 (c 0.47, CH_2Cl_2); 94% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 14.31min , t_R (major) =16.56 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.6 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.85 (td, *J* = 7.7, 1.6 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.54 (t, *J* = 6.4 Hz, 3H), 5.66 (q, *J* = 12.4 Hz, 2H), 4.51 (dd, *J* = 62.1, 19.5 Hz, 2H) ppm ;^{13}C NMR (75 MHz, $CDCl_3$): δ 196.60, 152.38, 148.96, 137.44, 136.98, 131.07 (q, *J* =33.0 Hz), 127.81, 127.23, 125.76 (q, *J* = 3.7 Hz), 125.39 (q, *J* = 284.7 Hz), 123.38 (q, *J* = 272.2 Hz), 121.75, 74.34, 49.98 (q, *J* =25.6 Hz), 35.52 (d, *J* =1.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.63 (s, 3F), -62.99 (s, 3F); ESI-HRMS Calcd. for $C_{17}H_{13}F_6N_2O_3$ ([M+H]$^+$): 407.0825, Found407.0828.

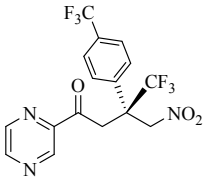
(*S*)-4, 4, 4-trifluoro-3-(4-methoxyphenyl)-3-(nitromethyl)-1-(pyrazin-2-yl)butan-1-one



White solid; 78% yield; m.p.: 69-72^{o}C; [α] = -79.4 (c 0.49, CH_2Cl_2); 99%

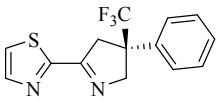
ee; determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R(minor) = 19.80 min, t_R (major) = 42.99min];^{1}H NMR (300 MHz, $CDCl_3$): δ 9.21 (d, J = 1.4 Hz, 1H), 8.84 (d, J = 2.5 Hz, 1H), 8.72 (dd, J = 2.3, 1.6 Hz, 1H), 7.36–7.24 (m, 2H), 6.99–6.85 (m, 2H), 5.62 (q, J = 12.5 Hz, 2H), 4.57–4.23 (m, 2H), 3.80 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.30, 159.82, 148.31, 146.85, 143.51, 143.37, 127.71, 125.66 (q, J = 282.0Hz), 124.59, 114.27, 74.44, 55.07, 49.27 (q, J = 25.7 Hz), 35.45; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.30(s, 3F); ESI-HRMS Calcd. for $C_{16}H_{14}F_3N_3O_4$([M+H]$^+$): 370.1009, Found 370.0999.

(*S*)-4, 4, 4-trifluoro-3-(4-(trifluoromethyl)phenyl)-3-(nitromethyl)-1-(pyrazin-2-yl) butan-1-one



White solid; 90% yield; m.p.:72-75°C; [α] =-67.11(c = 0.52, CH_2Cl_2); 98% ee; determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R(major) = 16.25min, t_R (minor) =37.08 min]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.21 (d, J = 1.5 Hz, 1H), 8.87 (d, J = 2.5 Hz, 1H), 8.74 (dd, J = 2.5, 1.5 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 5.66 (s, 2H), 4.67–4.26 (m, 2H).;13C NMR (75 MHz, CDCl3) δ 195.89 , 148.50 , 146.54 , 143.47 , 143.38 , 137.02 , 131.24 (q, J = 33.2 Hz) ,127.05, 125.84 (q, J = 3.7 Hz) ,125.23(q, J = 285.0 Hz), 123.26 (q, J = 272.4 Hz), 74.04, 49.76 (q, J = 25.8 Hz), 35.68; ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.02(s, 3F), -72.71(s, 3F); ESI-HRMS Calcd. for $C_{16}H_{12}F_6N_3O_3$([M+H]$^+$): 408.0777, Found 408.0775.

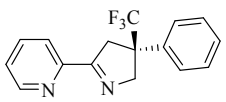
(*S*)-2-(3-phenyl-3-(trifluoromethyl)-3, 4-dihydro-2H-pyrrol-5-yl)thiazole



To a solution of **5a** (103.2mg, 0.3mmol) in 3 mL of MeOH/THF (MeOH/THF(V/V)=1:2), iron (753mg, 13.4mmol) and Acetic acid (270μL, 4.8mmol) was added under N_2, The mixture was stirred for 3h at 65°C, then poured into ethyl acetate(10mL) and filtered, the filtrate was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified with flash chromatography using a mixture of petroleum ether and ethyl acetate (5:1, V/V) to afford white solid **13** (70.7mg, 80%yield). m.p.:116-118°C; [α] = -18.78 (c 0.49, CH_2Cl_2); 99% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (major) = 9.05min, t_R (minor) =9.83min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, J = 3.2 Hz, 1H), 7.50 (d, J = 3.2 Hz, 1H), 7.38 (m, 5H), 5.00(d, J = 18.0Hz, 1H), 4.56(d, J = 15.0Hz, 1H), 4.07(d, J =18.0Hz, 1H), 3.70 (d, J = 21.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.87, 162.53, 143.86, 137.55(d, J = 1.4 Hz), 128.49, 128.24, 128.10, 122.58, 127.39 (q, J =282.2 Hz), 68.52, 55.38 (q, J = 25.4 Hz), 43.53; ^{19}F NMR (282 MHz, $CDCl_3$): δ -76.41(s,3F) ppm; ESI-HRMS Calcd. for $C_{14}H_{12}F_3N_2S$([M+H]$^+$): 297.0688, Found 297.0672.

(*S*)-2-(3-phenyl-3-(trifluoromethyl)-3, 4-dihydro-2H-pyrrol-5-yl)pyridine

Only using **3a** instead of **5a**, the other experimental procedure was the same as **5a**.

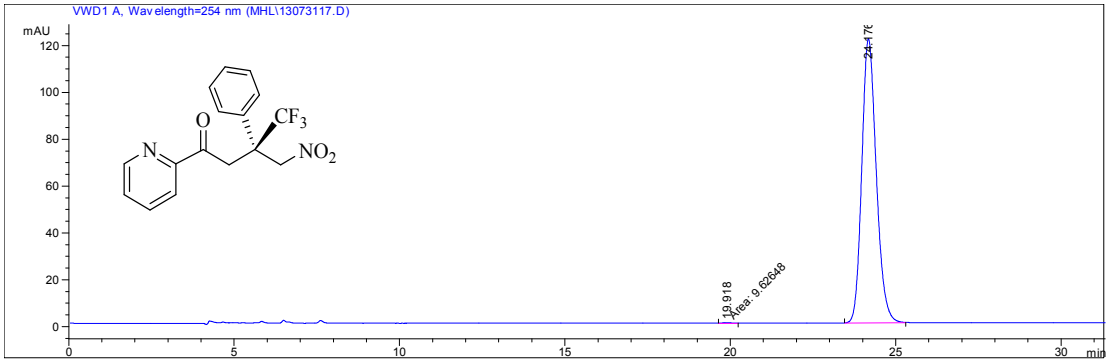


White solid; 66% yield; m.p.:44-45°C; [α] =-74.0 (c 0.5 CH_2Cl_2); 98%ee; determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-

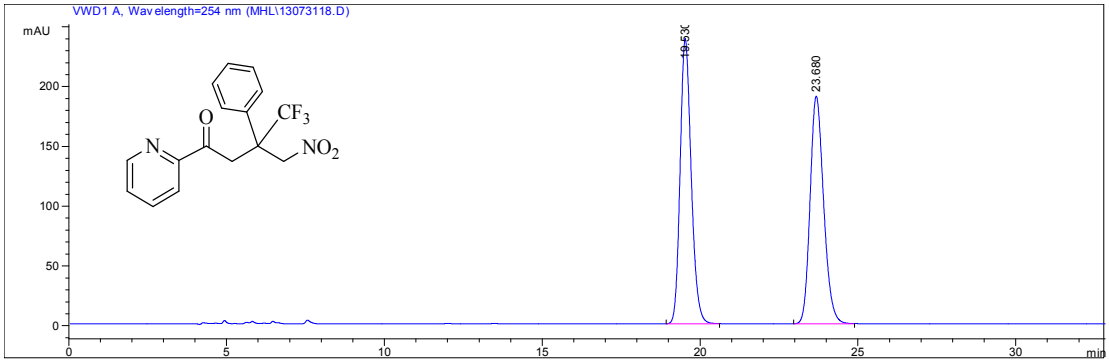
hexane/*i*-PrOH = 90:10, 0.80 mL/min, 254 nm; t_R (minor) = 11.2min, t_R (major) =12.24min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (d, J = 4.8 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.77 (td, J = 7.7, 1.7 Hz, 1H), 7.48–7.30 (m, 6H), 5.01(dd, J = 15.0, 3.0 Hz, 1H), 4.59 (d, J = 75.0,Hz, 1H), 4.09 (dd, J =15.0, 3.0Hz, 1H), 3.70 (d, J = 21.0Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.72, 152.00, 148.93, 138.10, 136.28, 128.37, 127.90, 127.62 (q, J=281.3 Hz), 124.93, 121.67, 68.80, 55.07(q, J=25.1Hz), 43.31; ESI-HRMS Calcd. for $C_{16}H_{14}F_3N_2$([M+H]$^+$): 291.1104, Found 291.1104

HPLC chromatograms for Michael addition adducts

Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) = 19.92 min, t_R (major) = 24.18 min; 99% ee.

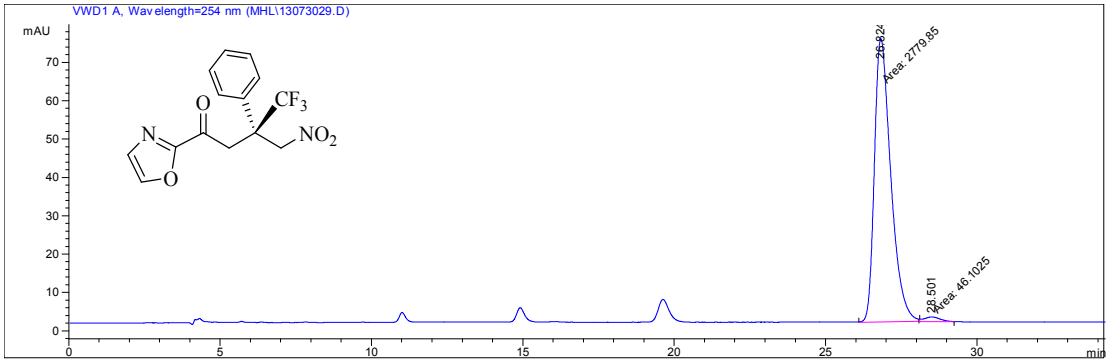


#	Time	Area	Height	Width	Area%	Symmetry
1	19.918	9.6	3.1E-1	0.5218	0.260	0.878
2	24.176	3689.1	121.3	0.467	99.740	0.801

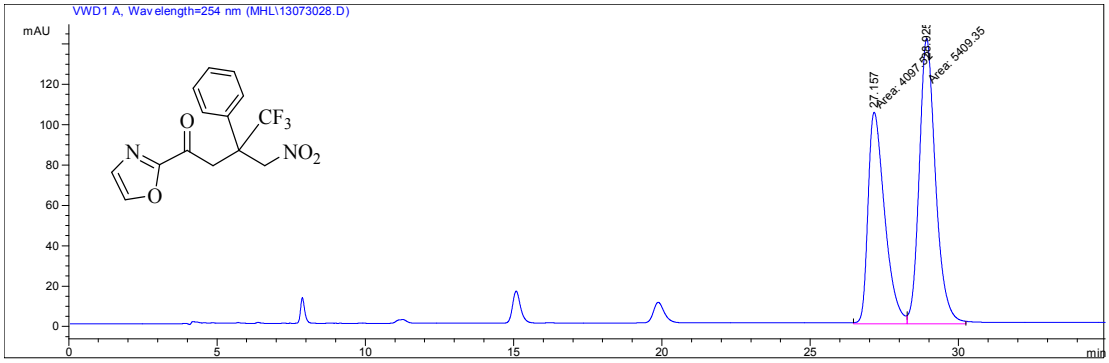


#	Time	Area	Height	Width	Area%	Symmetry
1	19.53	5803.4	238.4	0.3742	50.524	0.803
2	23.68	5683.1	190.4	0.4589	49.476	0.786

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80:20, 0.8 mL/min, 254 nm; t_R (major) = 26.82min, t_R (minor) = 28.50 min; 97% ee.

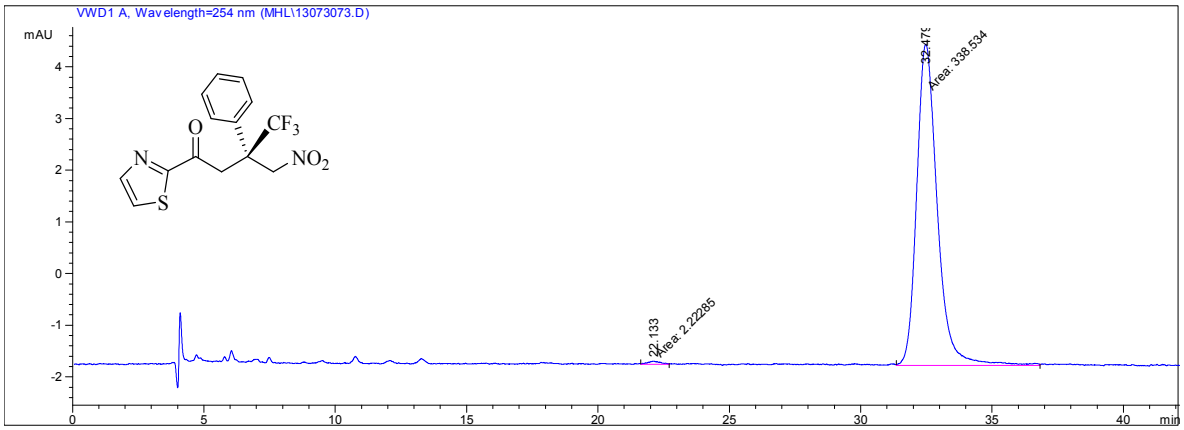


#	Time	Area	Height	Width	Area%	Symmetry
1	26.824	2779.8	73.9	0.627	98.369	0.615
2	28.501	46.1	1.2	0.6179	1.631	0.856

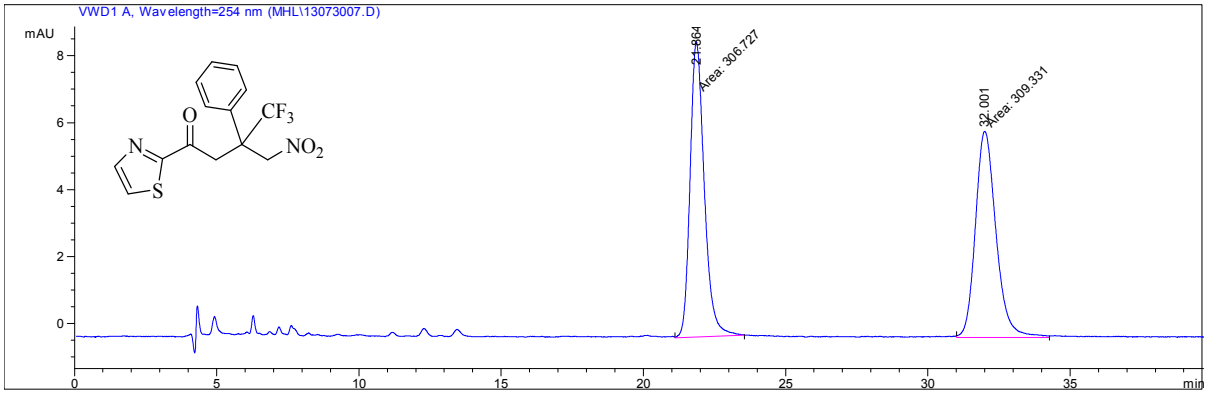


#	Time	Area	Height	Width	Area%	Symmetry
1	27.157	4097.5	104.8	0.6515	43.101	0.566
2	28.925	5409.4	141.3	0.638	56.899	0.789

Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) = 21.88 min, t_R (major) = 31.93 min; 99% ee.

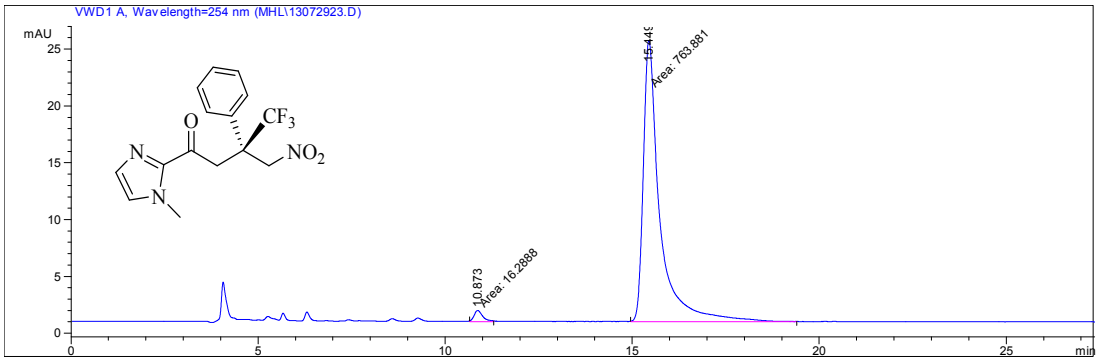


#	Time	Area	Height	Width	Area%	Symmetry
1	22.133	2.2	6.3E-2	0.5842	0.652	0.913
2	32.479	338.5	6.2	0.9086	99.348	0.749

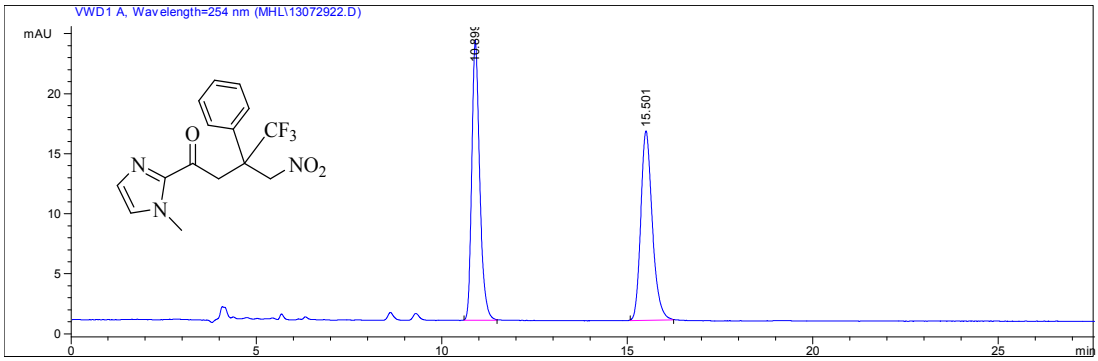


#	Time	Area	Height	Width	Area%	Symmetry
1	21.864	306.7	8.8	0.5801	49.789	0.758
2	32.001	309.3	6.2	0.8382	50.211	0.79

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 80:20, 0.8 mL/min, 254 nm; t_R (minor) = 10.87min, t_R (major) = 15.45 min; 96% ee.

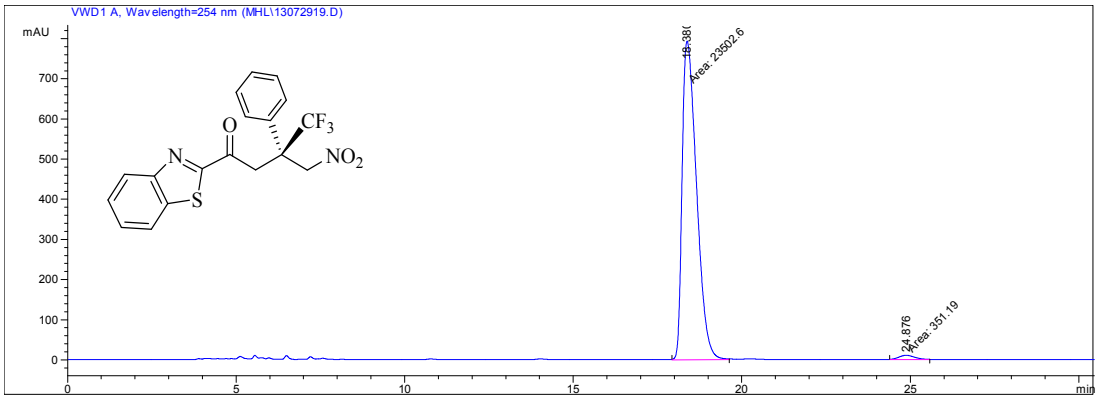


#	Time	Area	Height	Width	Area%	Symmetry
1	10.873	16.3	9.9E-1	0.2746	2.088	0.699
2	15.449	763.9	24.8	0.5143	97.912	0.483

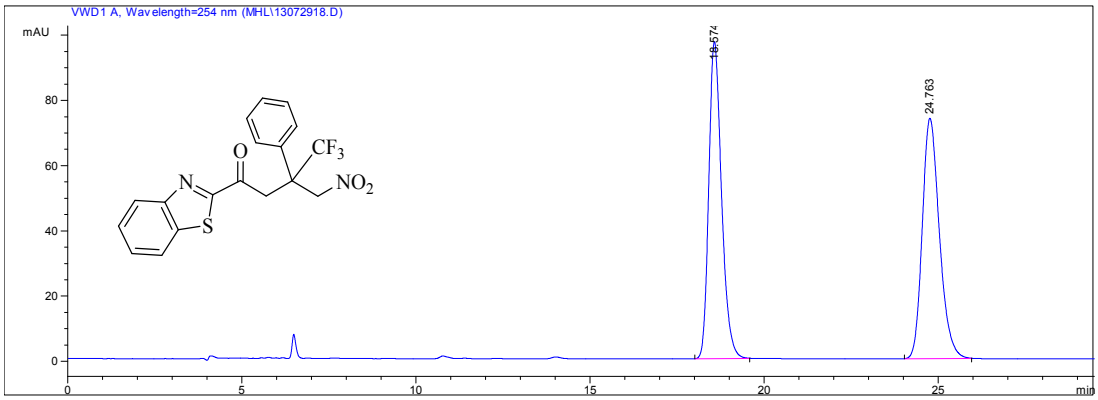


#	Time	Area	Height	Width	Area%	Symmetry
1	10.899	347.2	23.3	0.2263	50.405	0.743
2	15.501	341.6	15.8	0.3299	49.595	0.773

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (major) = 18.38min, t_R (minor) = 24.88 min; 97% ee.

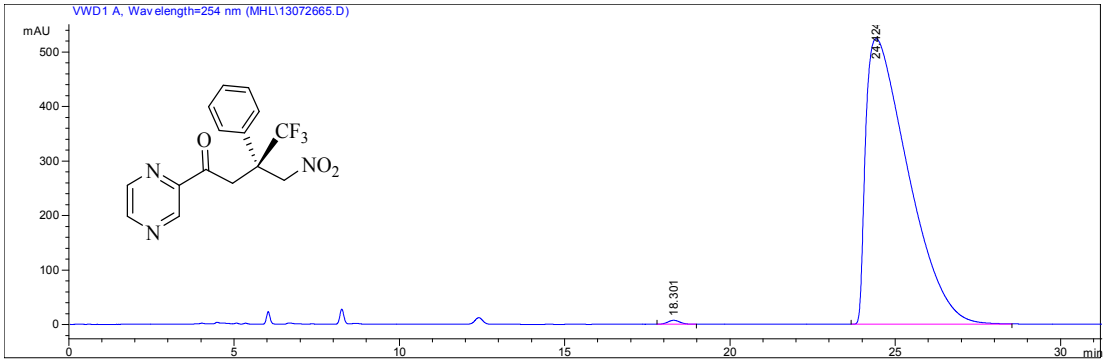


#	Time	Area	Height	Width	Area%	Symmetry
1	18.38	23502.6	793.6	0.4936	98.528	0.511
2	24.876	351.2	10.6	0.551	1.472	0.817

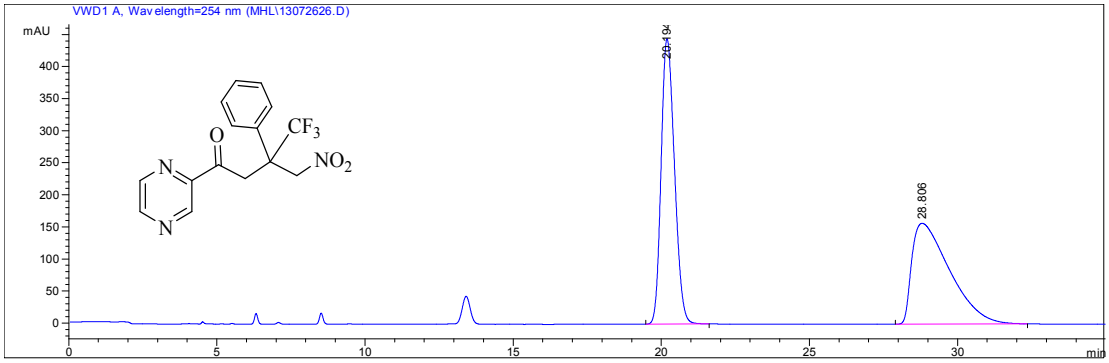


#	Time	Area	Height	Width	Area%	Symmetry
1	18.574	2471	97.2	0.3898	49.573	0.739
2	24.763	2513.6	73.7	0.5231	50.427	0.761

Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) = 18.30min, t_R (major) = 24.42 min; 99% ee.

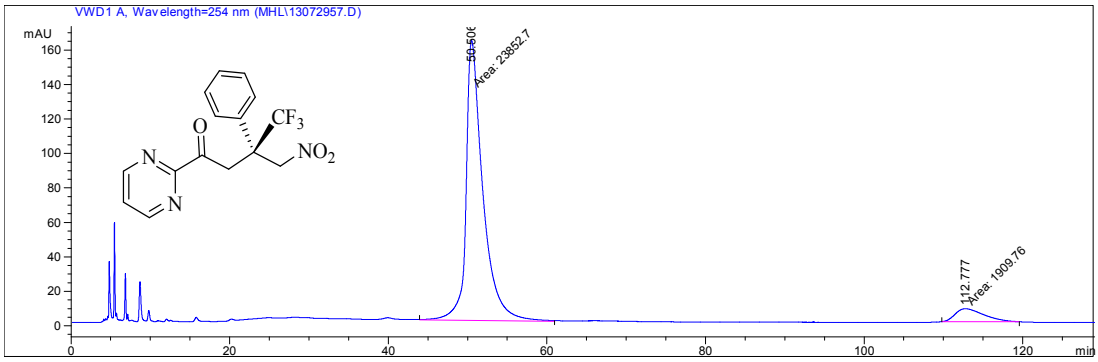


#	Time	Area	Height	Width	Area%	Symmetry
1	18.301	191.2	7.3	0.4055	0.409	0.919
2	24.424	46573.7	523.6	1.3625	99.591	0.298

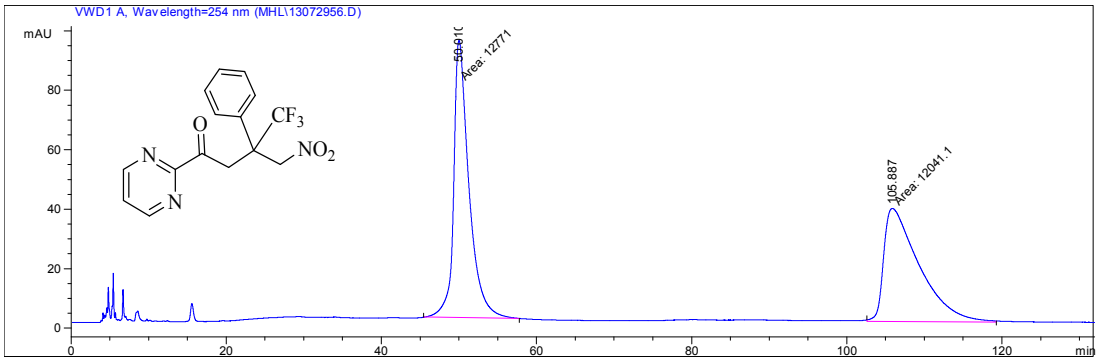


#	Time	Area	Height	Width	Area%	Symmetry
1	20.194	13941.8	445.1	0.4907	49.934	0.752
2	28.806	13978.7	157.3	1.3645	50.066	0.348

Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 85:15, 0.8 mL/min, 254 nm; t_R (major) = 50.51min, t_R (minor) =112.78 min; 85% ee.

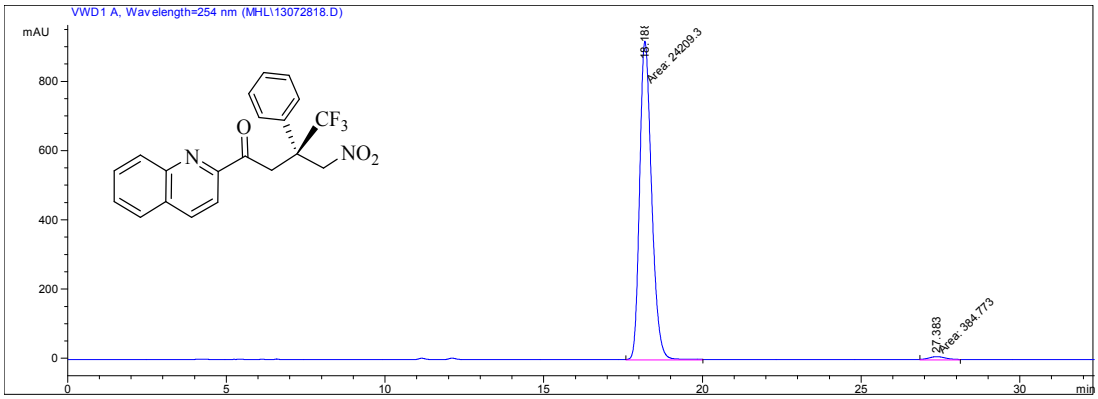


#	Time	Area	Height	Width	Area%	Symmetry
1	50.506	23852.7	162.4	2.4485	92.587	0.489
2	112.777	1909.8	7.6	4.2066	7.413	0.546

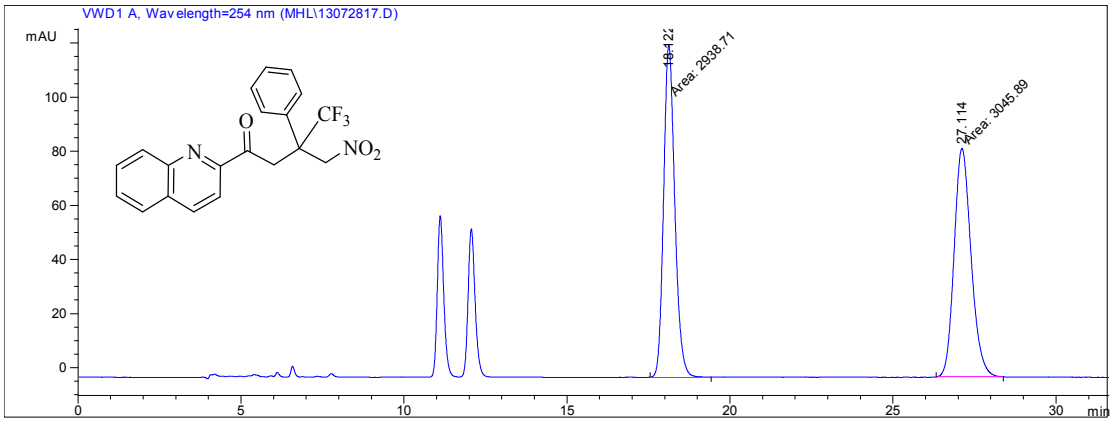


#	Time	Area	Height	Width	Area%	Symmetry
1	50.01	12771	93.2	2.2834	51.471	0.529
2	105.887	12041.1	38	5.2874	48.529	0.317

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (major) = 18.19min, t_R (minor) = 27.38 min; 97% ee.

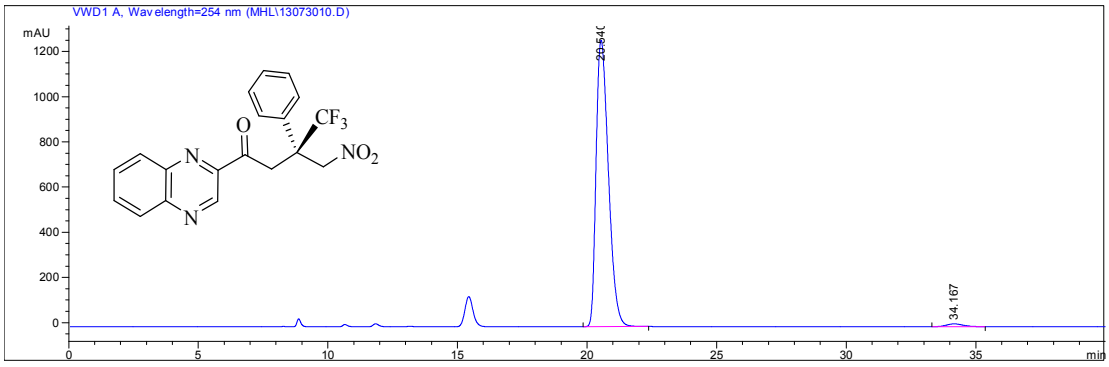


#	Time	Area	Height	Width	Area%	Symmetry
1	18.188	24209.3	921.2	0.438	98.436	0.744
2	27.383	384.8	9.6	0.6705	1.564	0.825

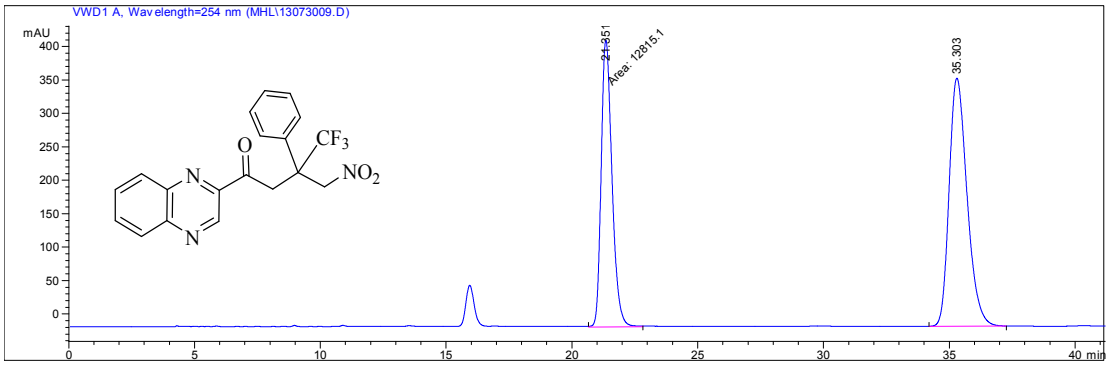


#	Time	Area	Height	Width	Area%	Symmetry
1	18.122	2938.7	122.9	0.3986	49.104	0.822
2	27.114	3045.9	84.4	0.6018	50.896	0.824

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (major) = 20.54min, t_R (minor) =34.17 min; 97% ee.

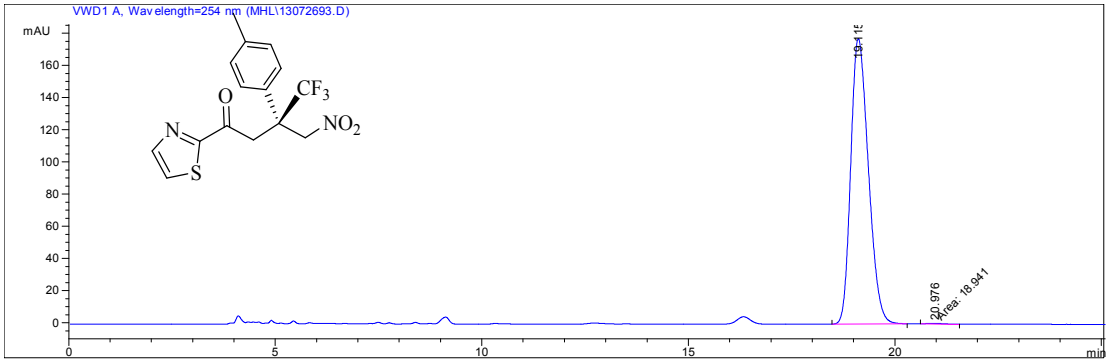


#	Time	Area	Height	Width	Area%	Symmetry
1	20.54	41760.1	1267.7	0.5197	98.640	0.629
2	34.167	575.9	12.7	0.6895	1.360	0.83

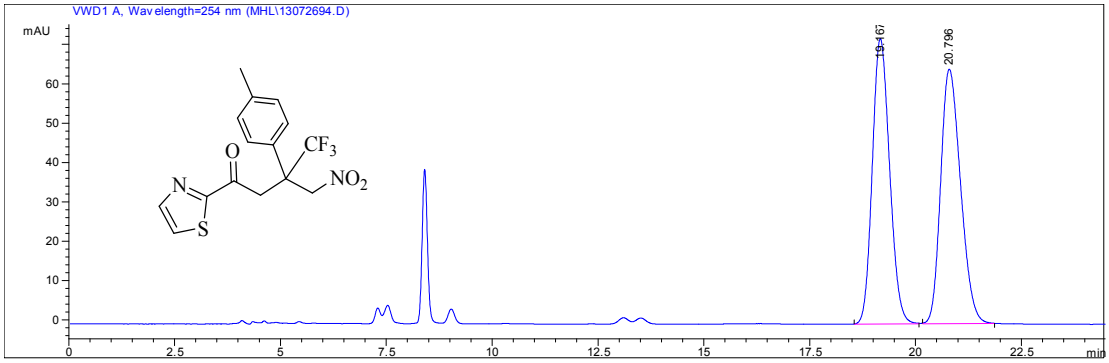


#	Time	Area	Height	Width	Area%	Symmetry
1	21.351	12815.1	428.8	0.4981	41.134	0.733
2	35.303	18339.4	370.9	0.7646	58.866	0.719

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 95:5, 0.8 mL/min, 254 nm; t_R (major) = 19.12min, t_R (minor) =20.98 min; 99% ee.

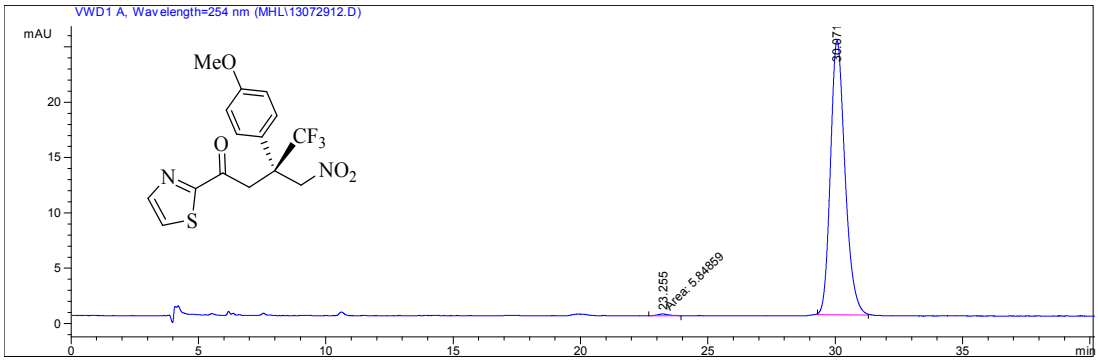


#	Time	Area	Height	Width	Area%	Symmetry
1	19.115	5265.5	177.4	0.4641	99.642	0.714
2	20.976	18.9	5.1E-1	0.6176	0.358	0.425

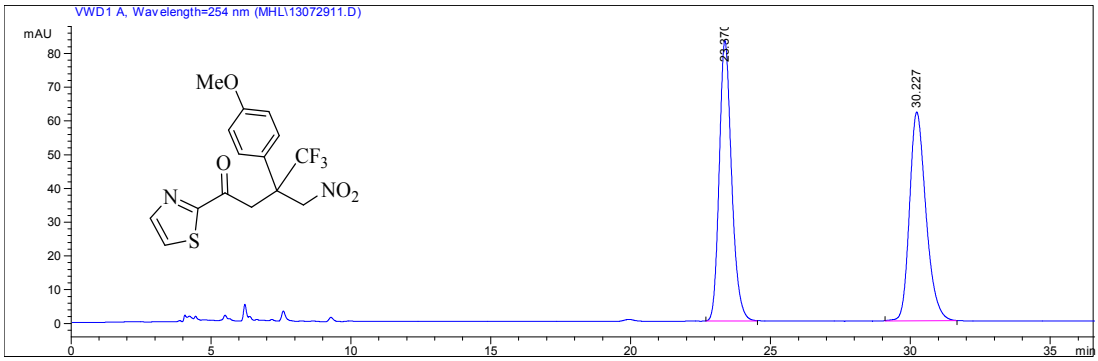


#	Time	Area	Height	Width	Area%	Symmetry
1	19.167	2061.4	72.5	0.4438	49.360	0.821
2	20.796	2114.8	64.7	0.5095	50.640	0.727

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) = 23.26min, t_R (major) =30.07 min; 99% ee.

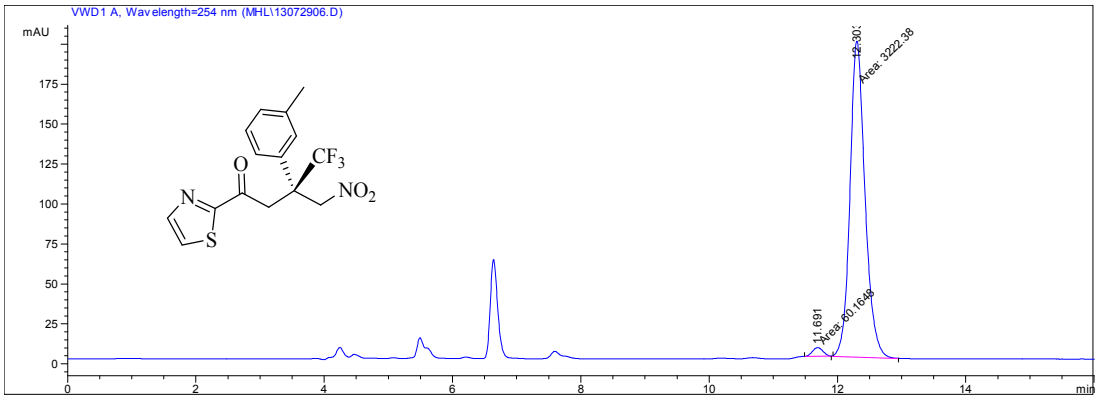


#	Time	Area	Height	Width	Area%	Symmetry
1	23.255	5.8	1.7E-1	0.5755	0.591	0.939
2	30.071	984.4	24.8	0.6059	99.409	0.782

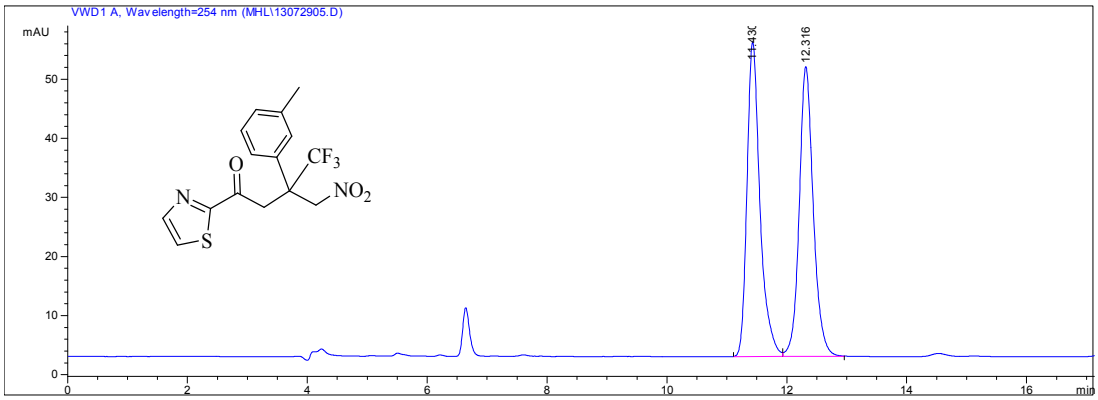


#	Time	Area	Height	Width	Area%	Symmetry
1	23.37	2552.6	83.2	0.4688	50.183	0.796
2	30.227	2534	61.9	0.6292	49.817	0.741

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =11.69min, t_R (major) =12.30 min; 96% ee.

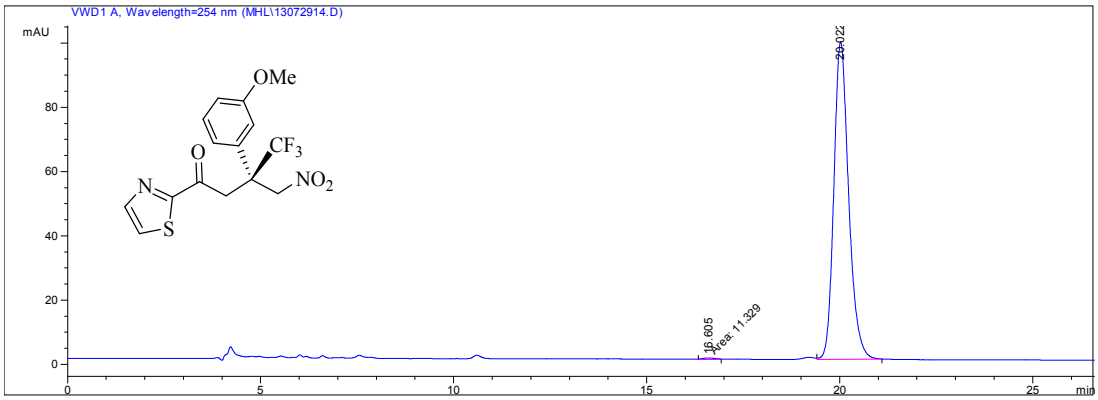


#	Time	Area	Height	Width	Area%	Symmetry
1	11.691	60.2	5.4	0.1872	1.833	0.982
2	12.303	3222.4	197.8	0.2715	98.167	0.814

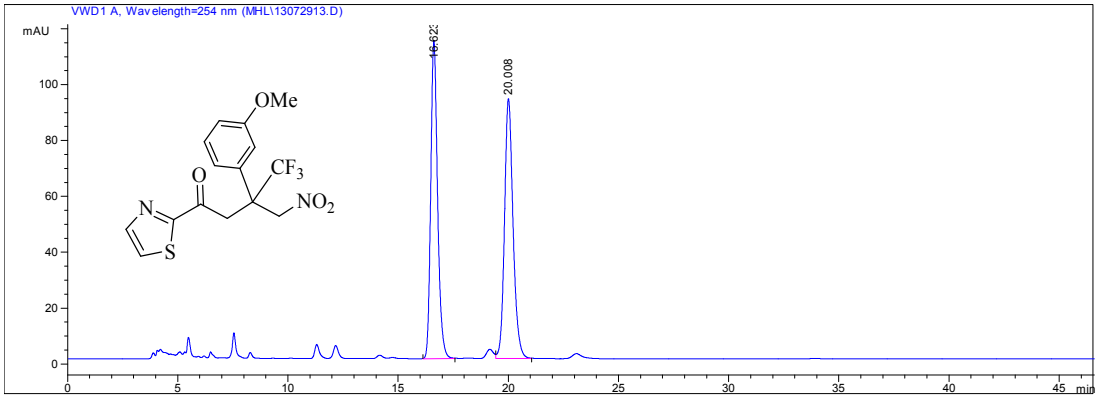


#	Time	Area	Height	Width	Area%	Symmetry
1	11.43	800.7	53.3	0.2263	50.054	0.715
2	12.316	799	49	0.2455	49.946	0.837

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =16.61min, t_R (major) =20.02 min; 99% ee.

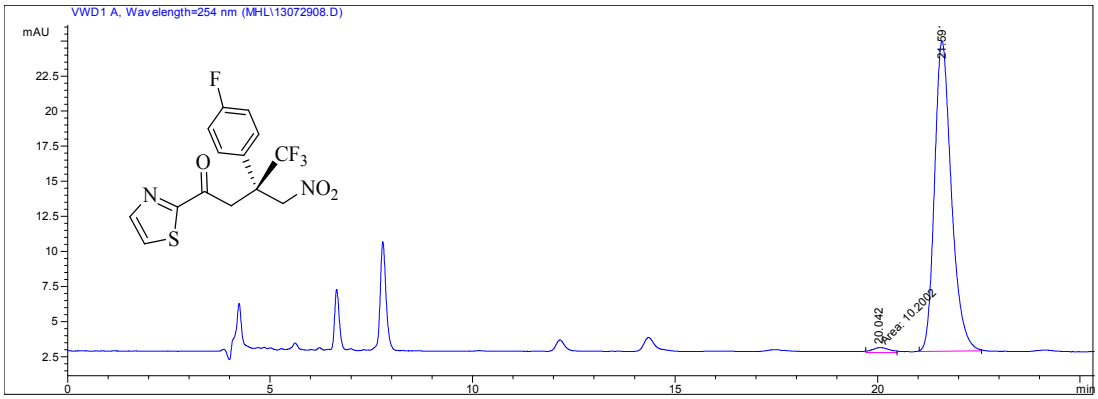


#	Time	Area	Height	Width	Area%	Symmetry
1	16.605	11.3	4.8E-1	0.3944	0.428	0.809
2	20.022	2637.4	98.8	0.406	99.572	0.782

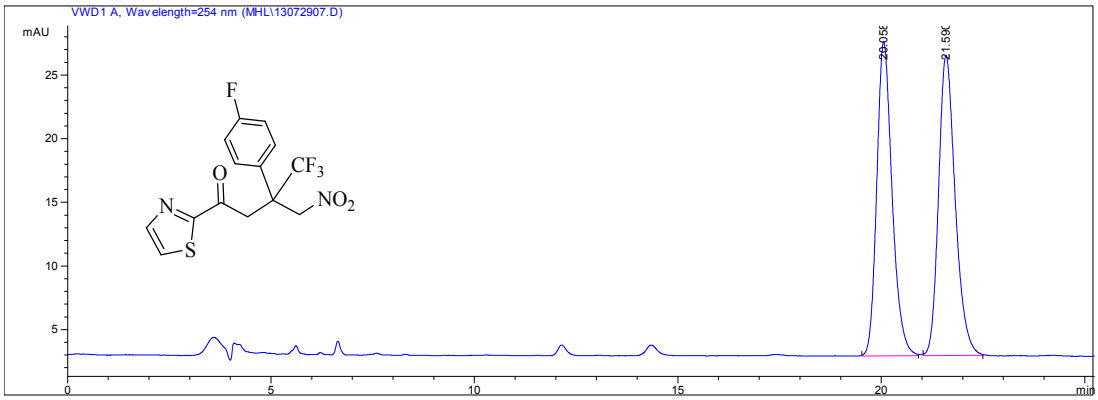


#	Time	Area	Height	Width	Area%	Symmetry
1	16.623	2452.2	113.9	0.3268	49.412	0.791
2	20.008	2510.5	93	0.4095	50.588	0.812

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =20.04min, t_R (major) =21.59 min; 97% ee.

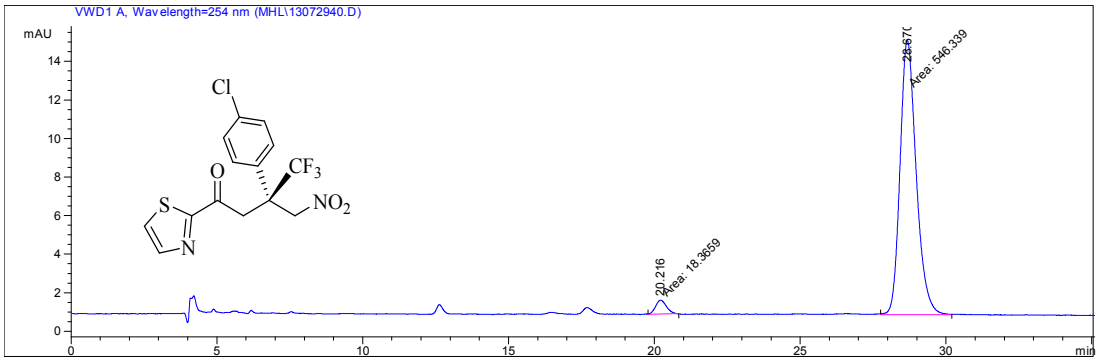


#	Time	Area	Height	Width	Area%	Symmetry
1	20.042	10.2	3.4E-1	0.4991	1.570	0.7
2	21.591	639.4	22.1	0.4393	98.430	0.739

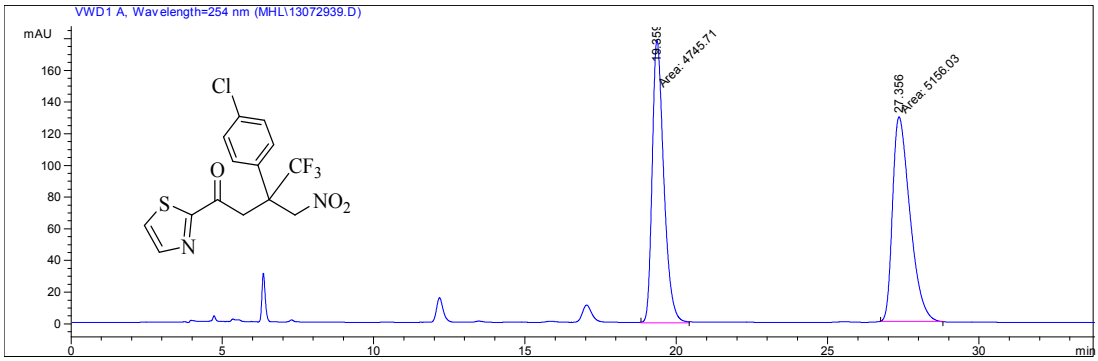


#	Time	Area	Height	Width	Area%	Symmetry
1	20.058	646.5	24.7	0.3988	49.068	0.77
2	21.59	671.1	23.6	0.4339	50.932	0.758

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =20.22min, t_R (major) =28.67 min; 94% ee.

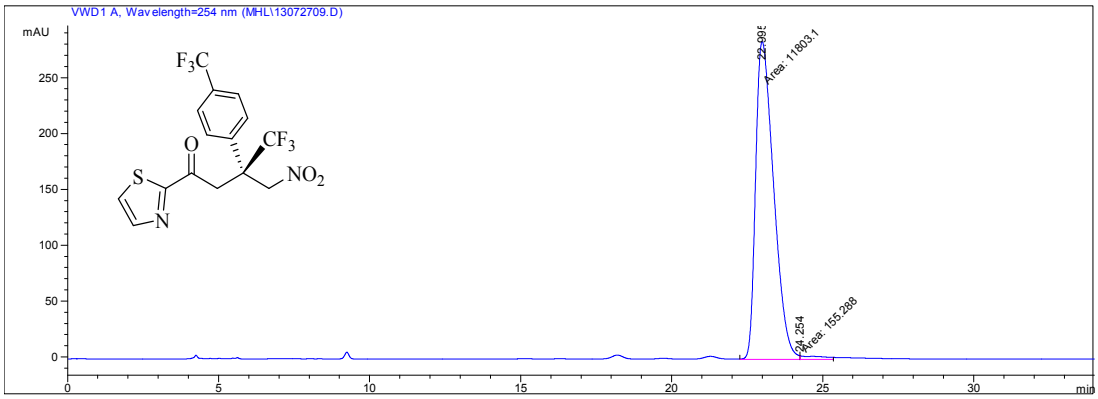


#	Time	Area	Height	Width	Area%	Symmetry
1	20.216	18.4	7.2E-1	0.4264	3.252	0.866
2	28.67	546.3	14.2	0.6401	96.748	0.774

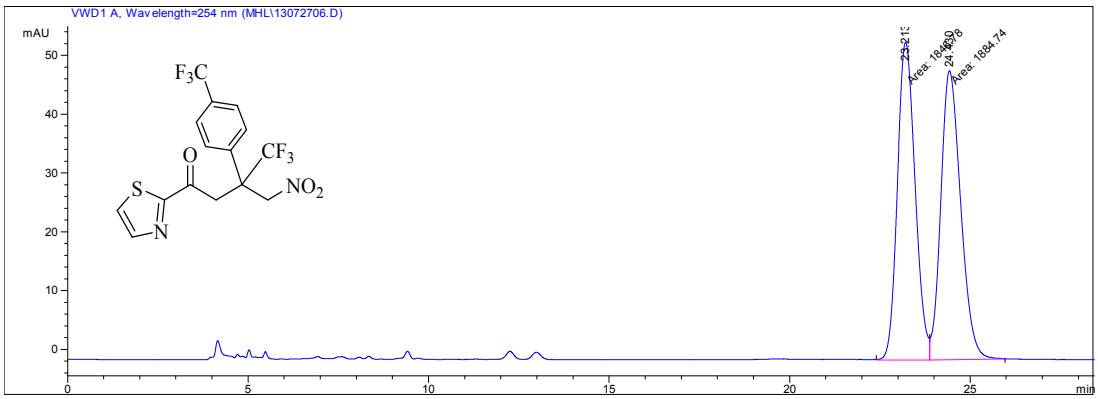


#	Time	Area	Height	Width	Area%	Symmetry
1	19.359	4745.7	178.2	0.4438	47.928	0.67
2	27.356	5156	129.1	0.6656	52.072	0.572

Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 97:3, 0.8 mL/min, 254 nm; t_R (minor) =23.00min, t_R (major) =24.25 min; 98% ee.

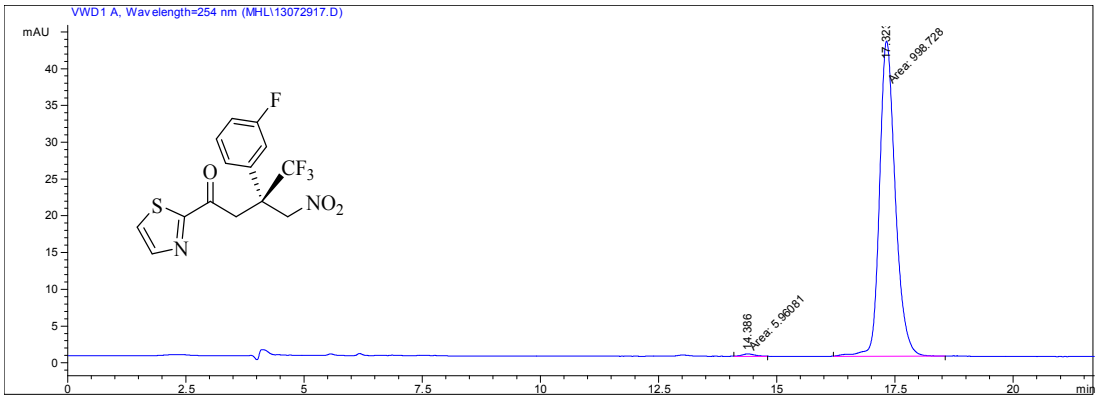


#	Time	Area	Height	Width	Area%	Symmetry
1	22.995	11803.1	284.4	0.6916	98.701	0.548
2	24.254	155.3	3.1	0.6447	1.299	0

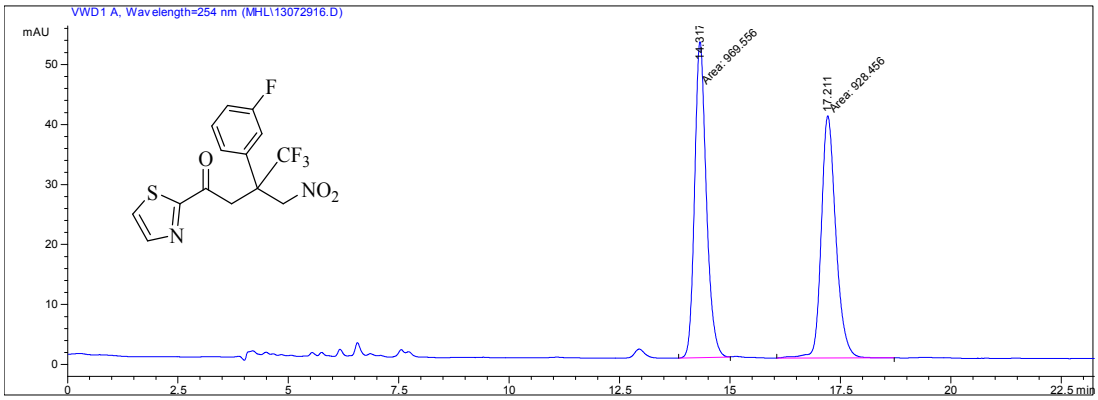


#	Time	Area	Height	Width	Area%	Symmetry
1	23.213	1846.8	54	0.5698	49.491	0.833
2	24.43	1884.7	49.1	0.6398	50.509	0.756

Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =14.37min, t_R (major) =17.32 min; 99% ee.

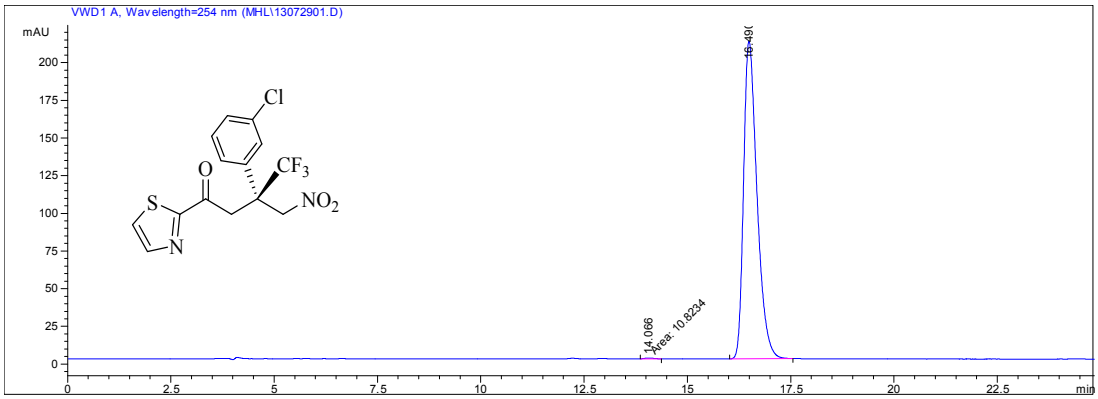


#	Time	Area	Height	Width	Area%	Symmetry
1	14.386	6	3.2E-1	0.3057	0.593	0.777
2	17.323	998.7	42.9	0.3882	99.407	0.785

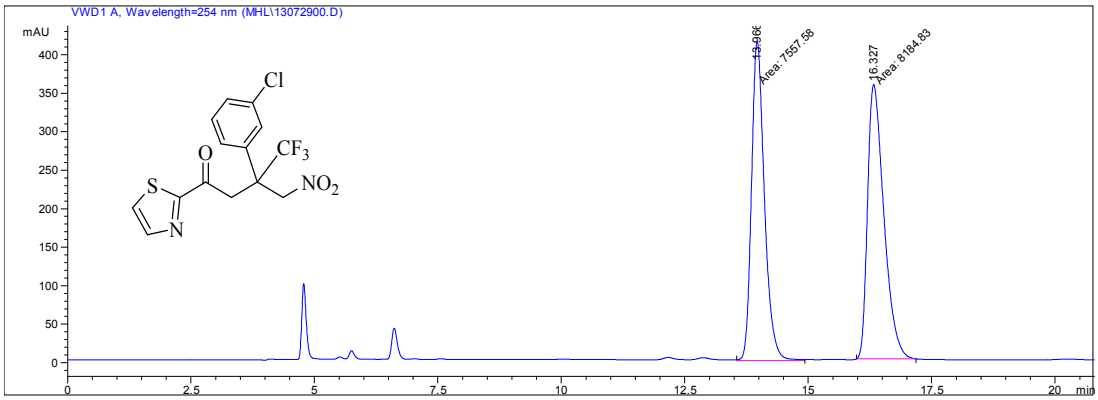


#	Time	Area	Height	Width	Area%	Symmetry
1	14.317	969.6	52.7	0.3068	51.083	0.801
2	17.211	928.5	40.4	0.3835	48.917	0.788

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =14.07min, t_R (major) =16.49 min; 99% ee.

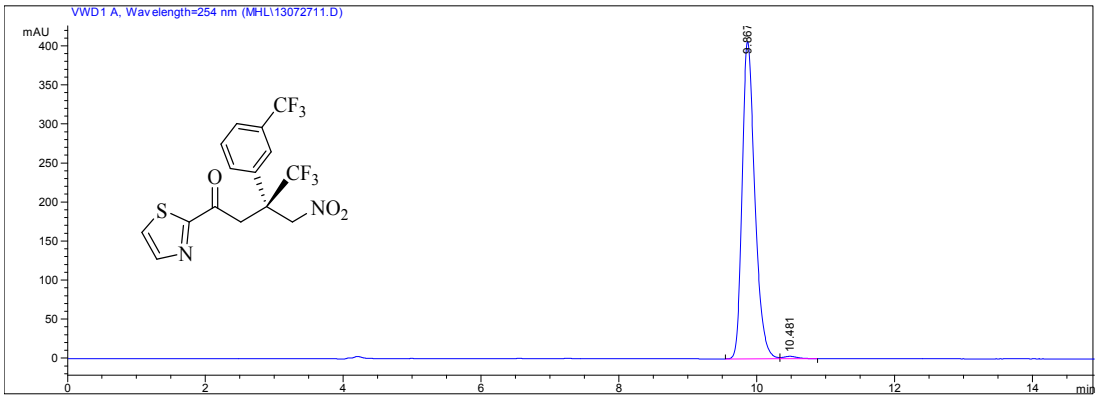


#	Time	Area	Height	Width	Area%	Symmetry
1	14.066	10.8	6.5E-1	0.2795	0.227	0.793
2	16.49	4764.7	210.9	0.3451	99.773	0.625

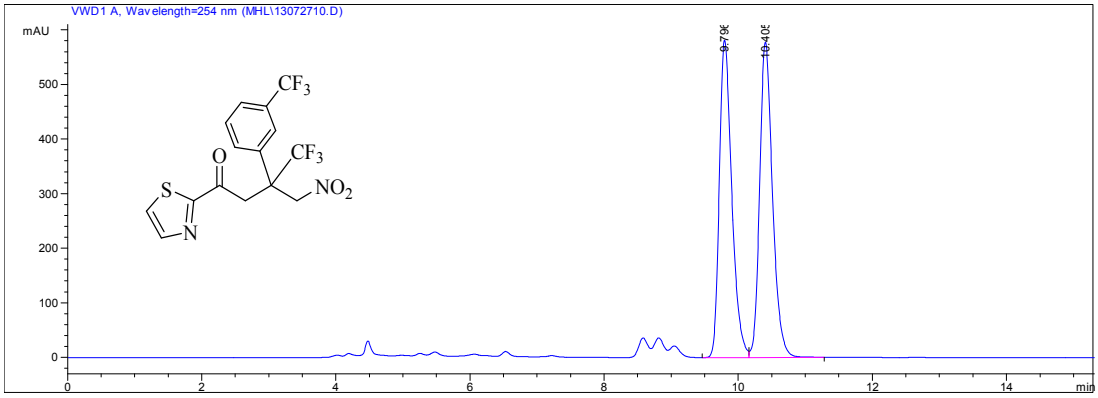


#	Time	Area	Height	Width	Area%	Symmetry
1	13.966	7557.6	414.2	0.3041	48.008	0.743
2	16.327	8184.8	356.1	0.383	51.992	0.578

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (major) =9.87min, t_R (minor) =10.48 min; 98% ee.

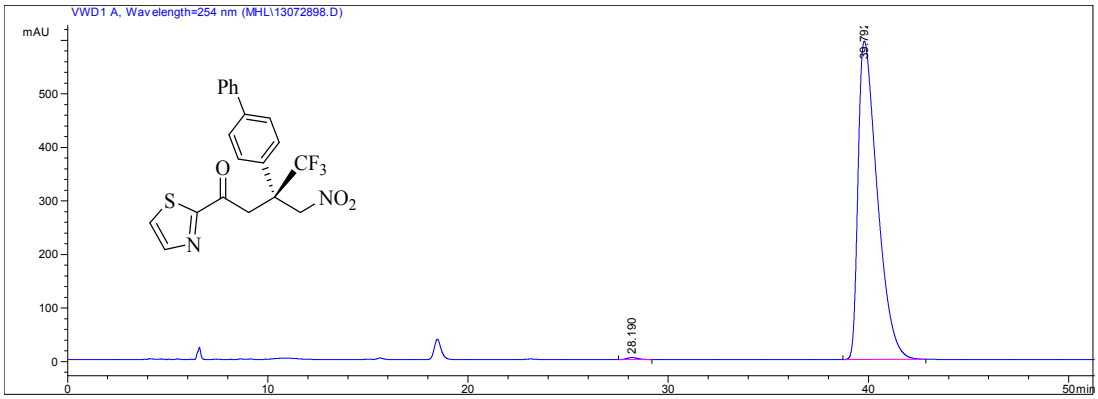


#	Time	Area	Height	Width	Area%	Symmetry
1	9.867	5195.4	406.4	0.1943	99.160	0.705
2	10.481	44	3.1	0.2127	0.840	0.778

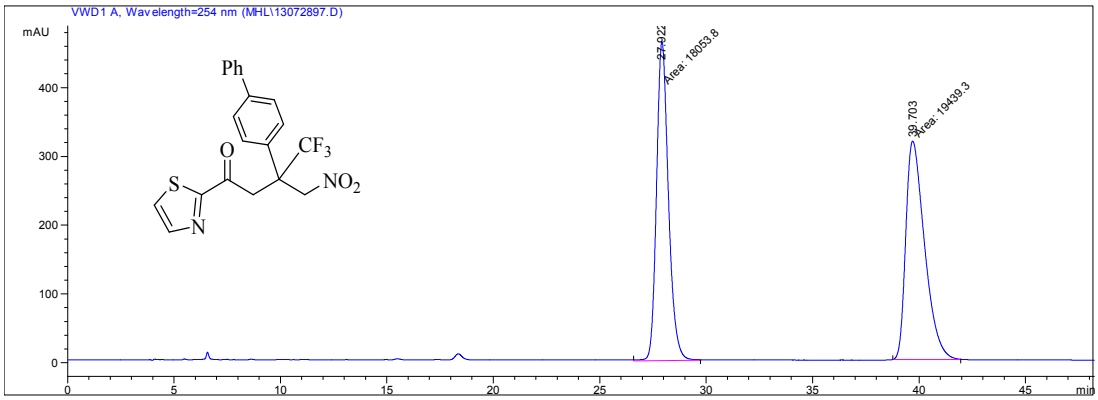


#	Time	Area	Height	Width	Area%	Symmetry
1	9.796	7497.2	581.7	0.197	49.304	0.681
2	10.405	7709	577.8	0.2037	50.696	0.746

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =28.19min, t_R (major) =39.79 min; 99% ee.

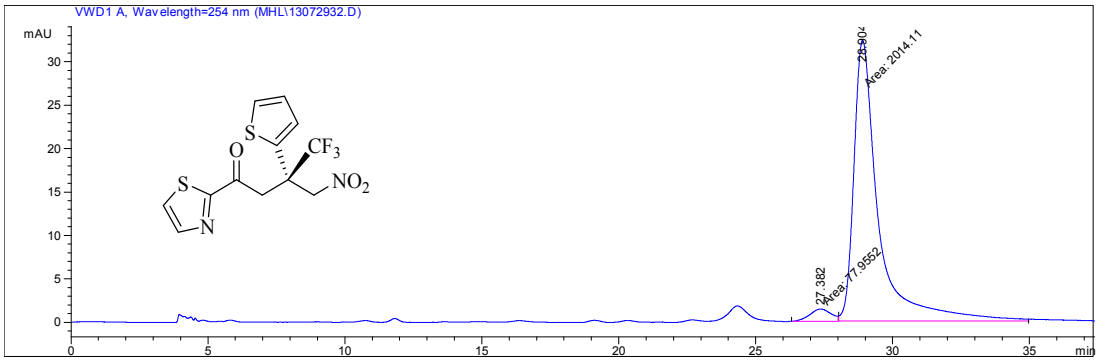


#	Time	Area	Height	Width	Area%	Symmetry
1	28.19	145.1	3.8	0.5658	0.365	0.812
2	39.792	39583.2	594.7	1.0153	99.635	0.445

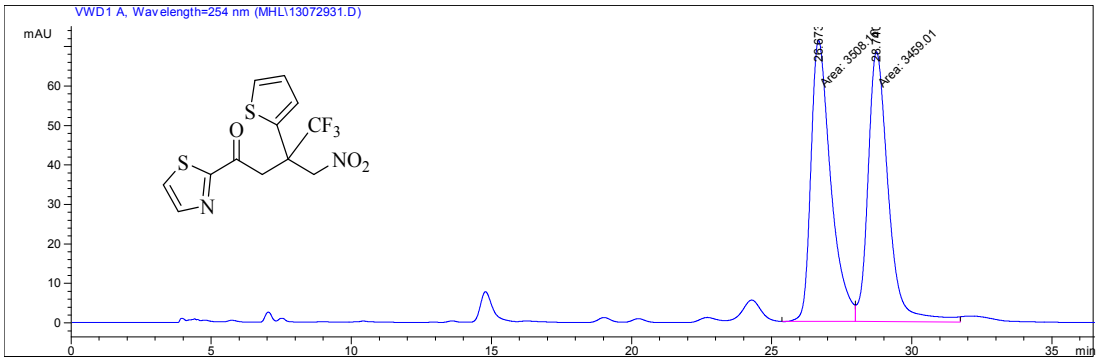


#	Time	Area	Height	Width	Area%	Symmetry
1	27.922	18053.8	463.7	0.6489	48.152	0.796
2	39.703	19439.3	317.4	1.0207	51.848	0.563

Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =27.38min, t_R (major) =28.90min; 93% ee.

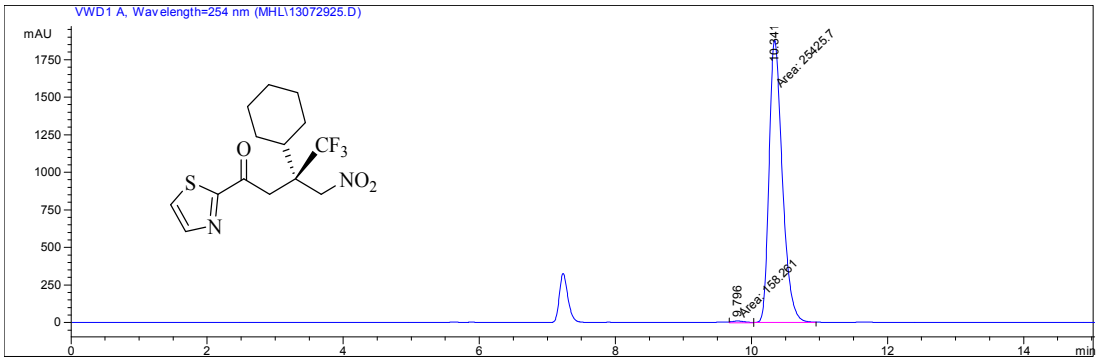


#	Time	Area	Height	Width	Area%	Symmetry
1	27.382	78	1.4	0.9077	3.726	1.051
2	28.904	2014.1	32.3	1.0401	96.274	0.517

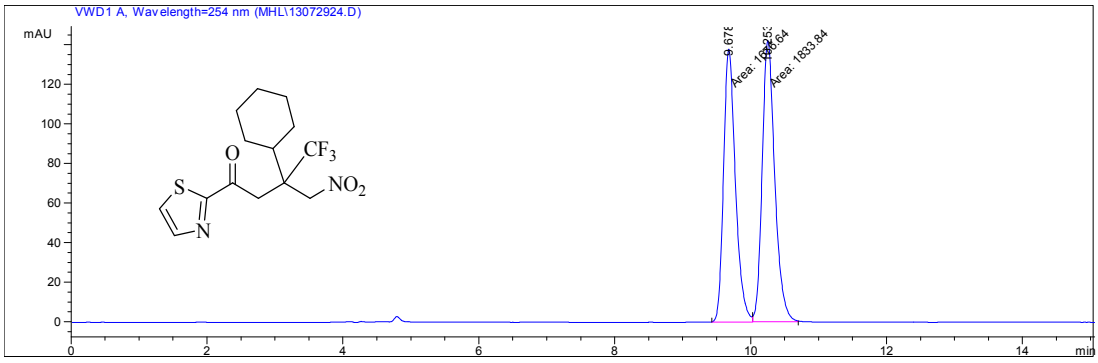


#	Time	Area	Height	Width	Area%	Symmetry
1	26.673	3508.2	71.1	0.822	50.353	0.6
2	28.74	3459	68.3	0.8439	49.647	0.67

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 95:5, 0.8 mL/min, 254 nm; t_R (minor) =9.80min, t_R (major) =10.34min; 99% ee.

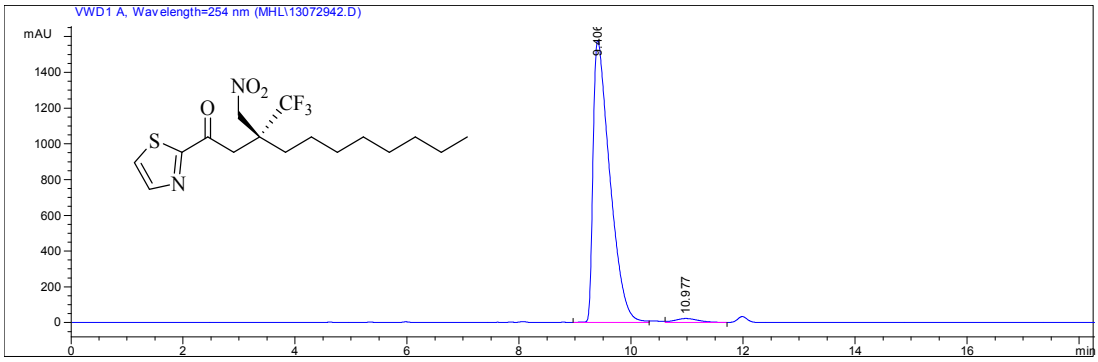


#	Time	Area	Height	Width	Area%	Symmetry
1	9.796	158.3	12	0.2195	0.619	0.694
2	10.341	25425.7	1878.3	0.2256	99.381	0.698

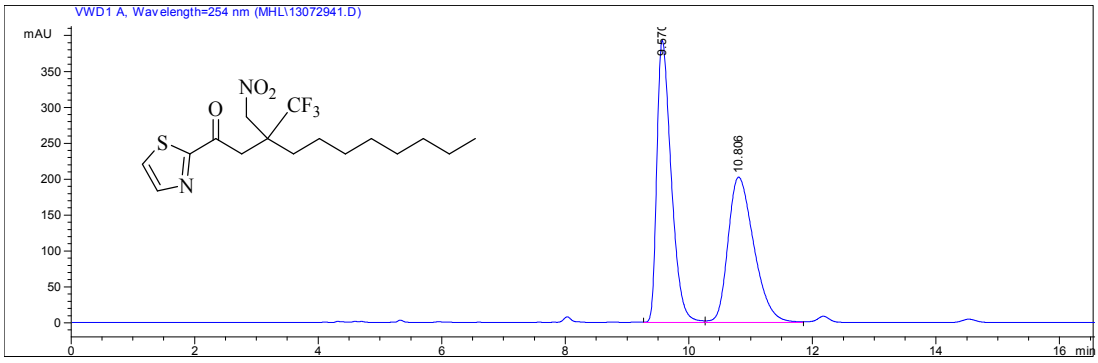


#	Time	Area	Height	Width	Area%	Symmetry
1	9.678	1676.6	138	0.2025	47.761	0.752
2	10.253	1833.8	142.3	0.2147	52.239	0.769

Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (major) =9.41min, t_R (minor) =10.98min; 96% ee.

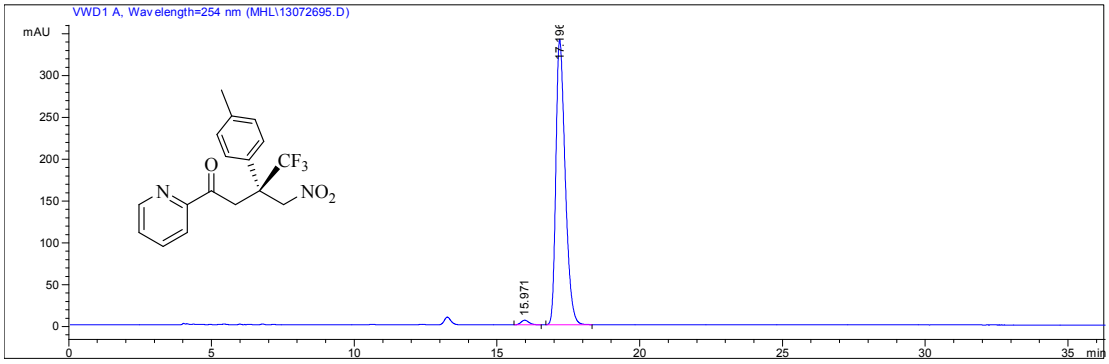


#	Time	Area	Height	Width	Area%	Symmetry
1	9.406	32736.5	1578	0.3075	97.980	0.359
2	10.977	674.8	22.4	0.4559	2.020	0.818

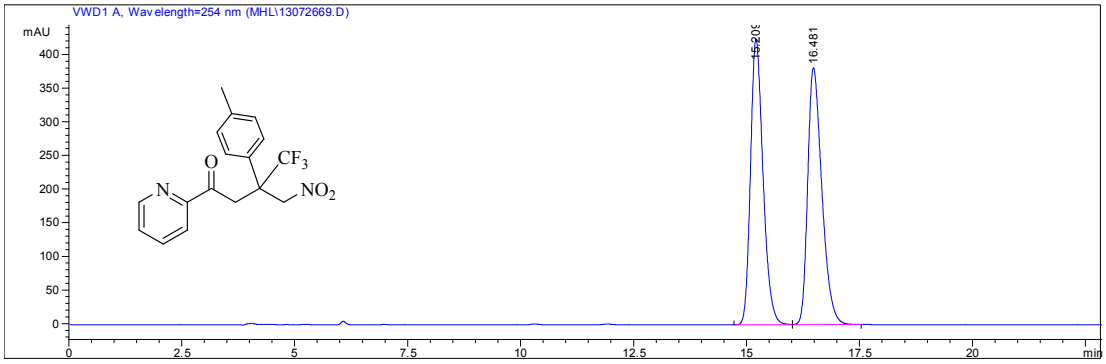


#	Time	Area	Height	Width	Area%	Symmetry
1	9.57	6340.2	392.7	0.2466	51.909	0.56
2	10.806	5873.8	202.4	0.4477	48.091	0.663

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =15.97min, t_R (major) =17.20min; 97% ee.

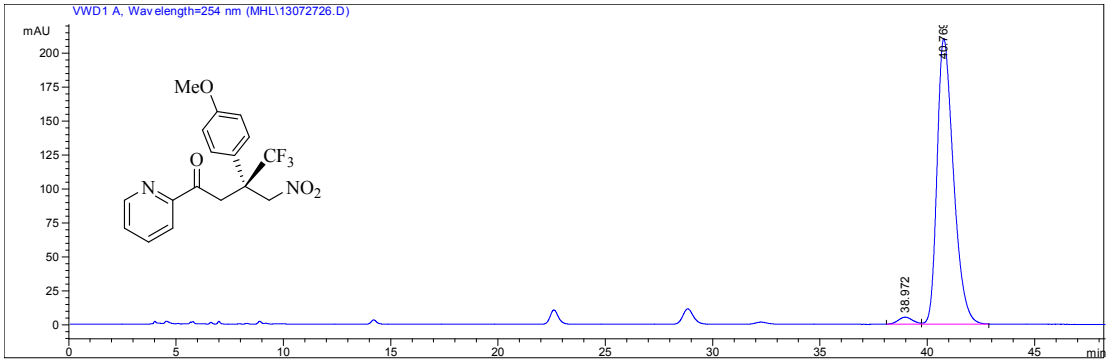


#	Time	Area	Height	Width	Area%	Symmetry
1	15.971	109.8	5.6	0.3023	1.400	0.826
2	17.196	7729.7	341.3	0.3472	98.600	0.644

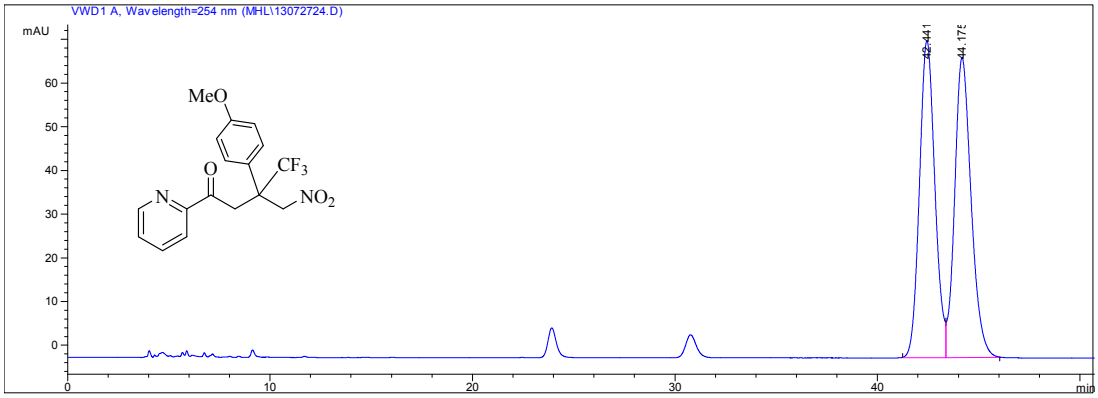


#	Time	Area	Height	Width	Area%	Symmetry
1	15.209	8187	424.4	0.2964	49.610	0.733
2	16.481	8315.8	381.9	0.3341	50.390	0.64

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 95:5, 0.8 mL/min, 254 nm; t_R (minor) =38.97min, t_R (major) =40.77min; 96% ee.

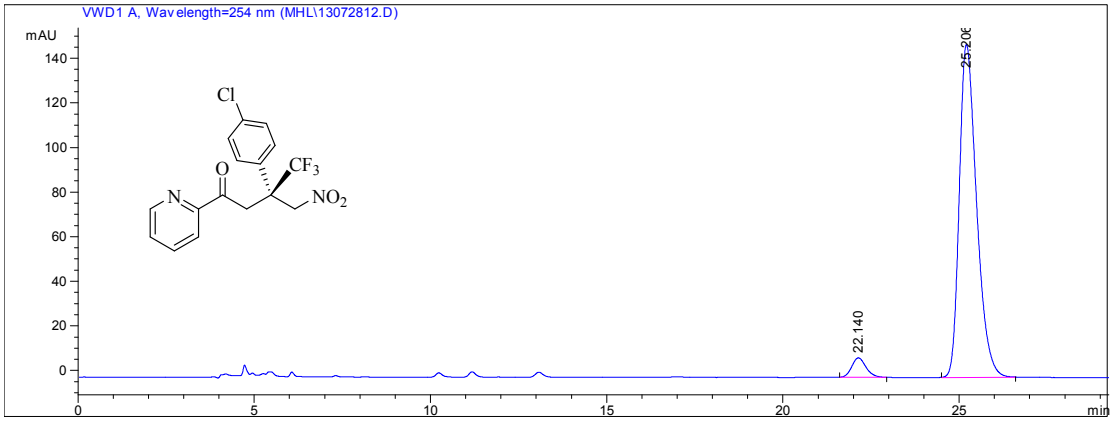


#	Time	Area	Height	Width	Area%	Symmetry
1	38.972	245.1	5.2	0.7202	2.148	0.915
2	40.769	11167	210.3	0.8145	97.852	0.65

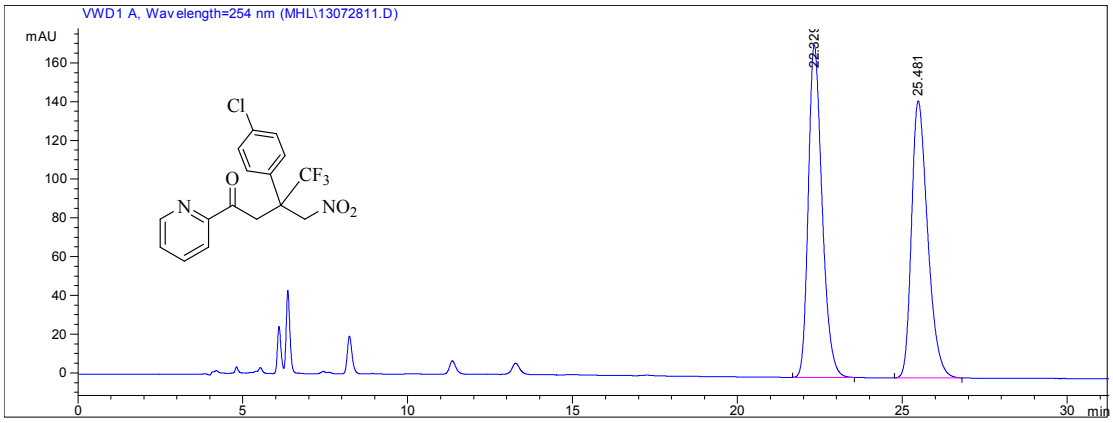


#	Time	Area	Height	Width	Area%	Symmetry
1	42.441	3842.8	72.6	0.813	49.670	0.895
2	44.175	3893.9	68.7	0.8653	50.330	0.77

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =22.14min, t_R (major) =25.21min; 91% ee.

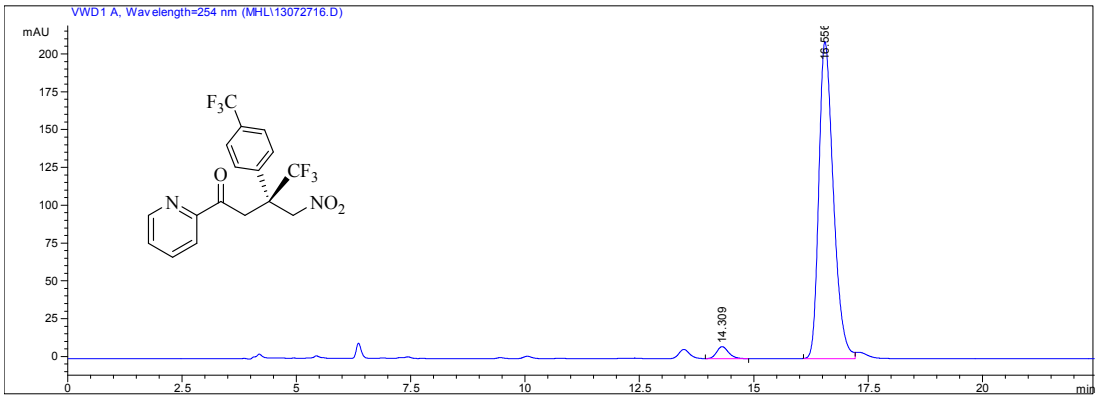


#	Time	Area	Height	Width	Area%	Symmetry
1	22.14	247.2	8.8	0.4294	4.637	0.828
2	25.206	5084.6	149.3	0.5226	95.363	0.661

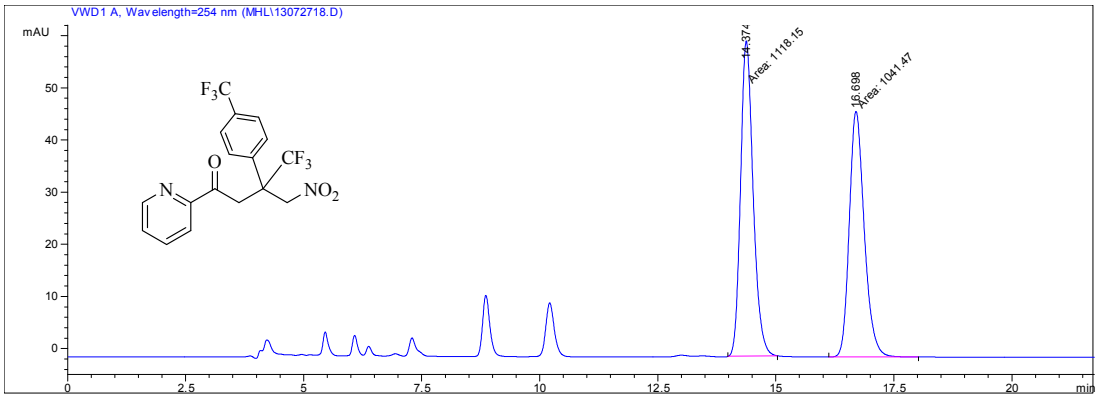


#	Time	Area	Height	Width	Area%	Symmetry
1	22.329	4988.3	171.5	0.4441	50.636	0.714
2	25.481	4863	143	0.5204	49.364	0.665

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =14.31min, t_R (major) =16.56min; 94% ee.

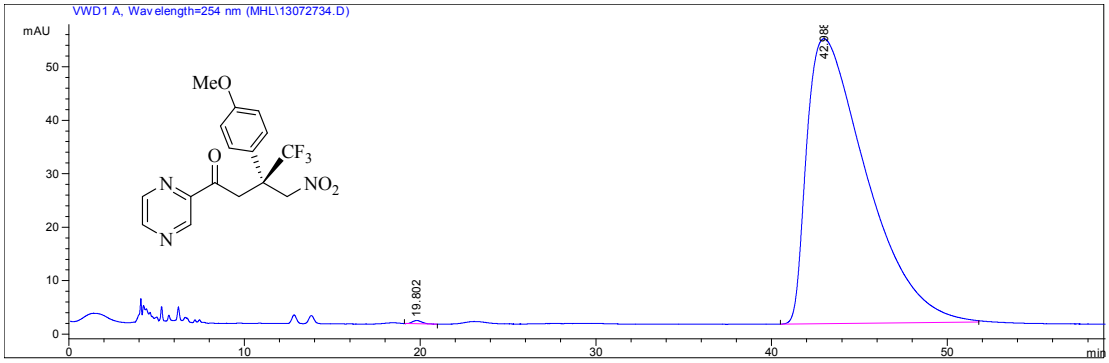


#	Time	Area	Height	Width	Area%	Symmetry
1	14.309	146	8	0.2783	3.054	0.808
2	16.556	4635	209.5	0.3381	96.946	0.679

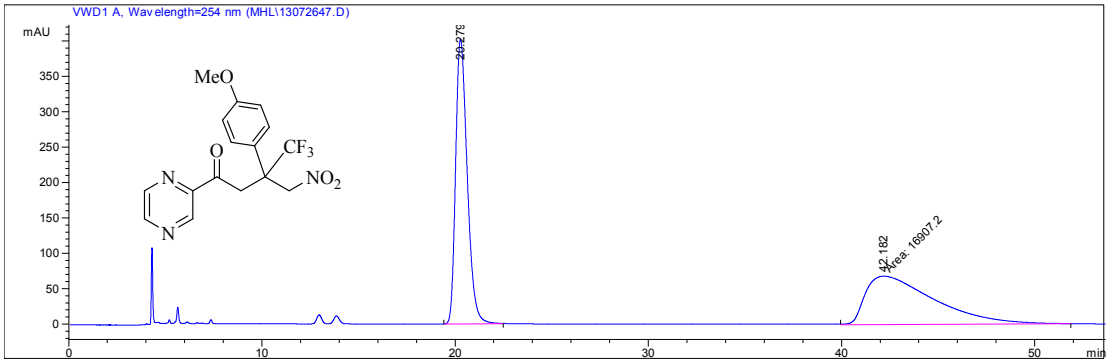


#	Time	Area	Height	Width	Area%	Symmetry
1	14.374	1118.1	60.5	0.3083	51.775	0.8
2	16.698	1041.5	47.1	0.3684	48.225	0.779

Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (minor) =19.80min, t_R (major) =42.99min; 99% ee.

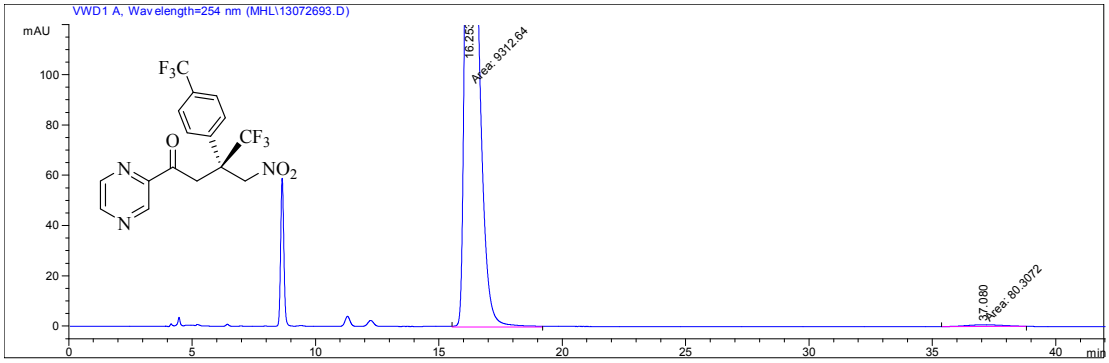


#	Time	Area	Height	Width	Area%	Symmetry
1	19.802	22.4	6.1E-1	0.5823	0.177	0.79
2	42.988	12632.6	53.3	3.3479	99.823	0.375

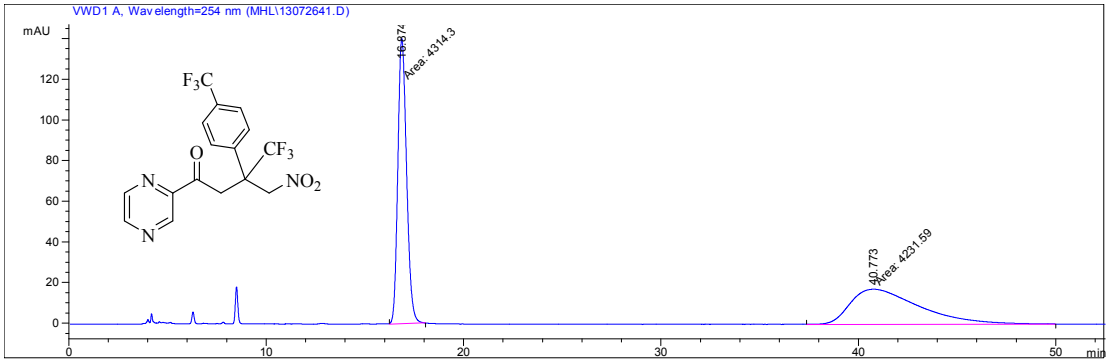


#	Time	Area	Height	Width	Area%	Symmetry
1	20.279	16744.3	402.2	0.6444	49.758	0.674
2	42.182	16907.2	68.4	4.1204	50.242	0.352

Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (major) =16.25min, t_R (minor) =37.08min; 98% ee.

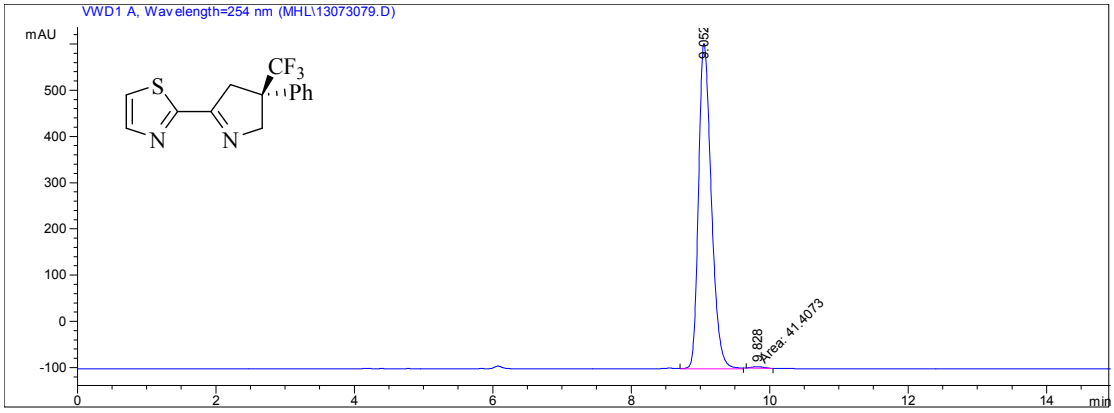


#	Time	Area	Height	Width	Area%	Symmetry
1	16.253	9312.6	263	0.5902	99.145	0.552
2	37.08	80.3	7.3E-1	1.8279	0.855	0.908

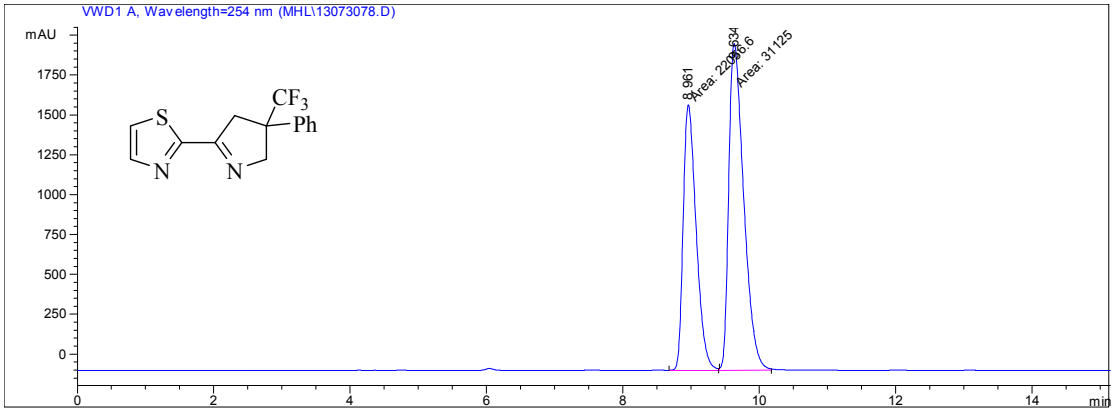


#	Time	Area	Height	Width	Area%	Symmetry
1	16.874	4314.3	140.2	0.5128	50.484	0.794
2	40.773	4231.6	17.3	4.0674	49.516	0.495

Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (major) =9.05min, t_R (minor) =9.83min; 99% ee.

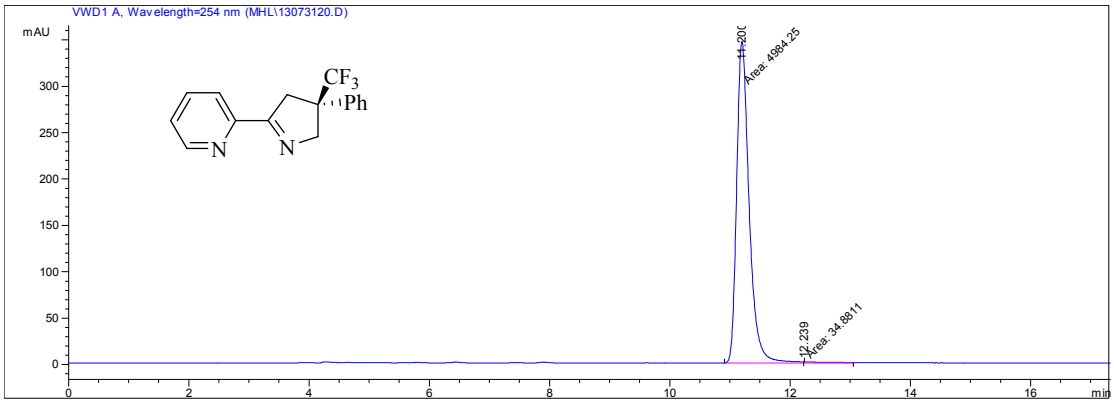


#	Time	Area	Height	Width	Area%	Symmetry
1	9.052	9012.5	703.7	0.1989	99.543	0.7
2	9.828	41.4	3.5	0.1988	0.457	0.736

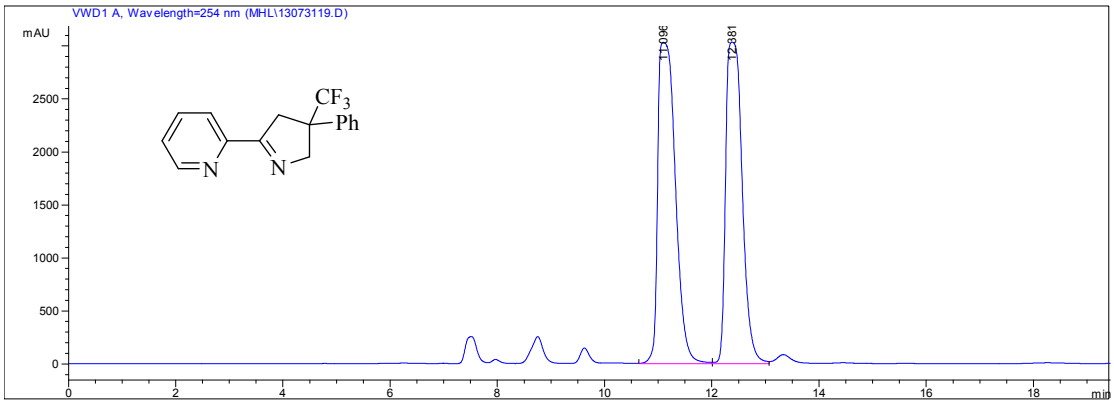


#	Time	Area	Height	Width	Area%	Symmetry
1	8.961	22056.6	1665.8	0.2207	41.474	0.633
2	9.634	31125	2048.8	0.2532	58.526	0.549

Daicel Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t_R (major) =9.05min, t_R (minor) =9.83min; 99% ee.

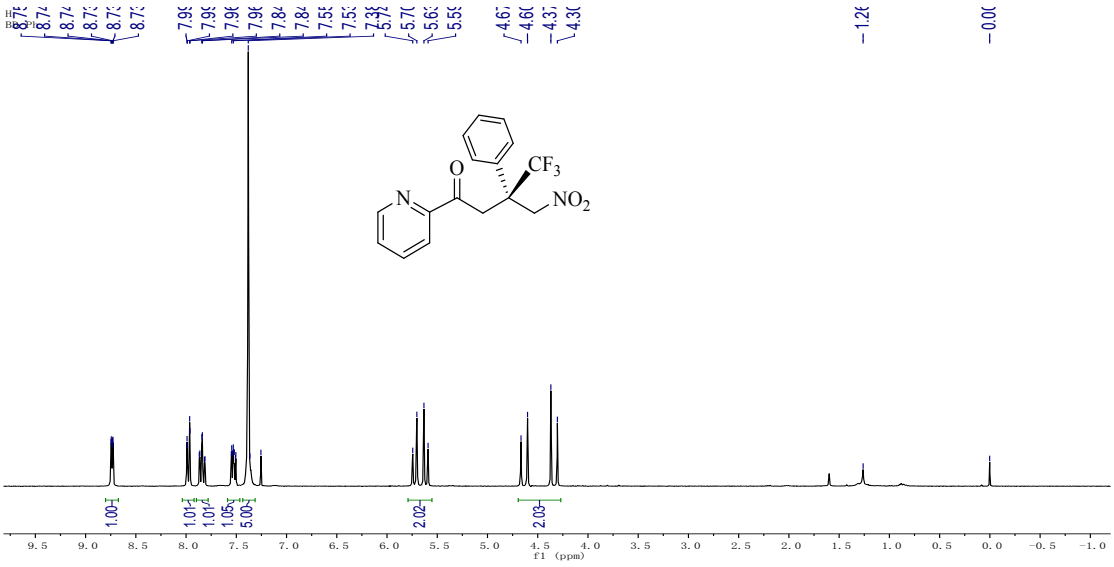


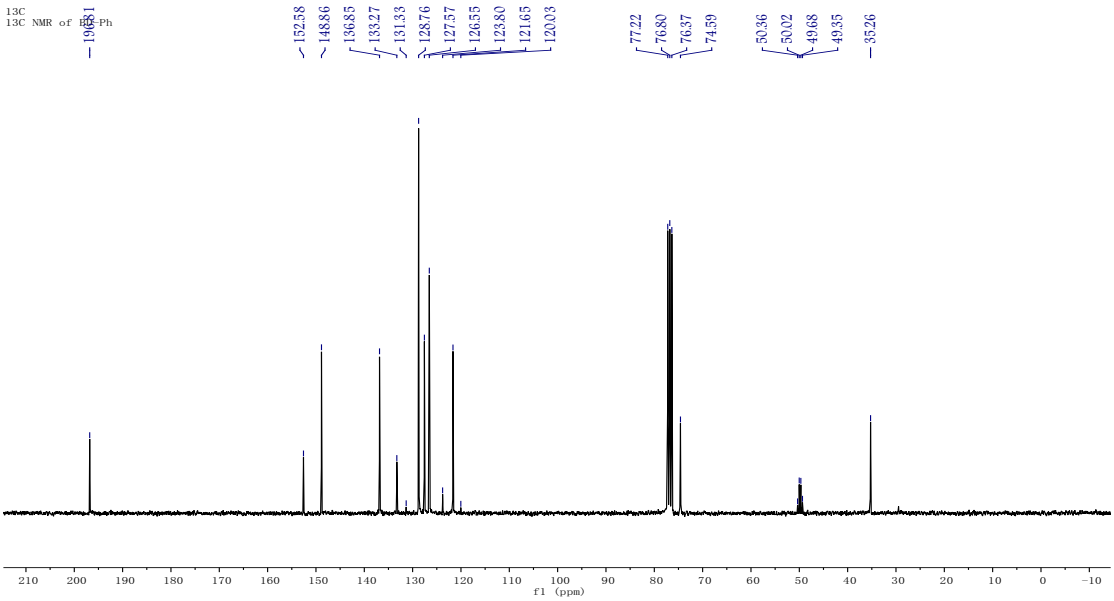
#	Time	Area	Height	Width	Area%	Symmetry
1	11.2	4984.3	346.6	0.2397	99.305	0.688
2	12.239	34.9	1.1	0.3702	0.695	0

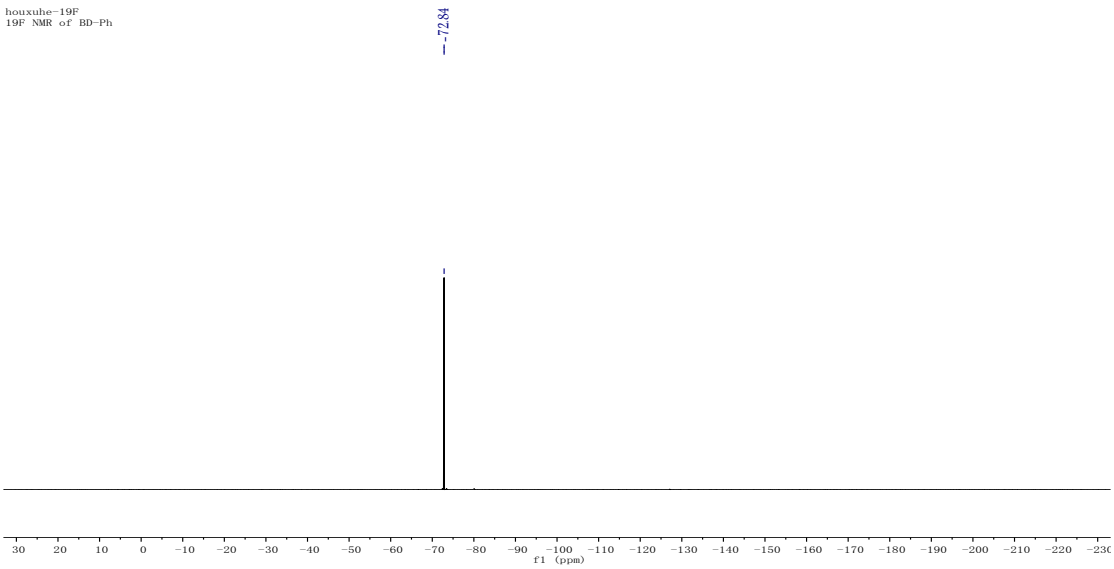


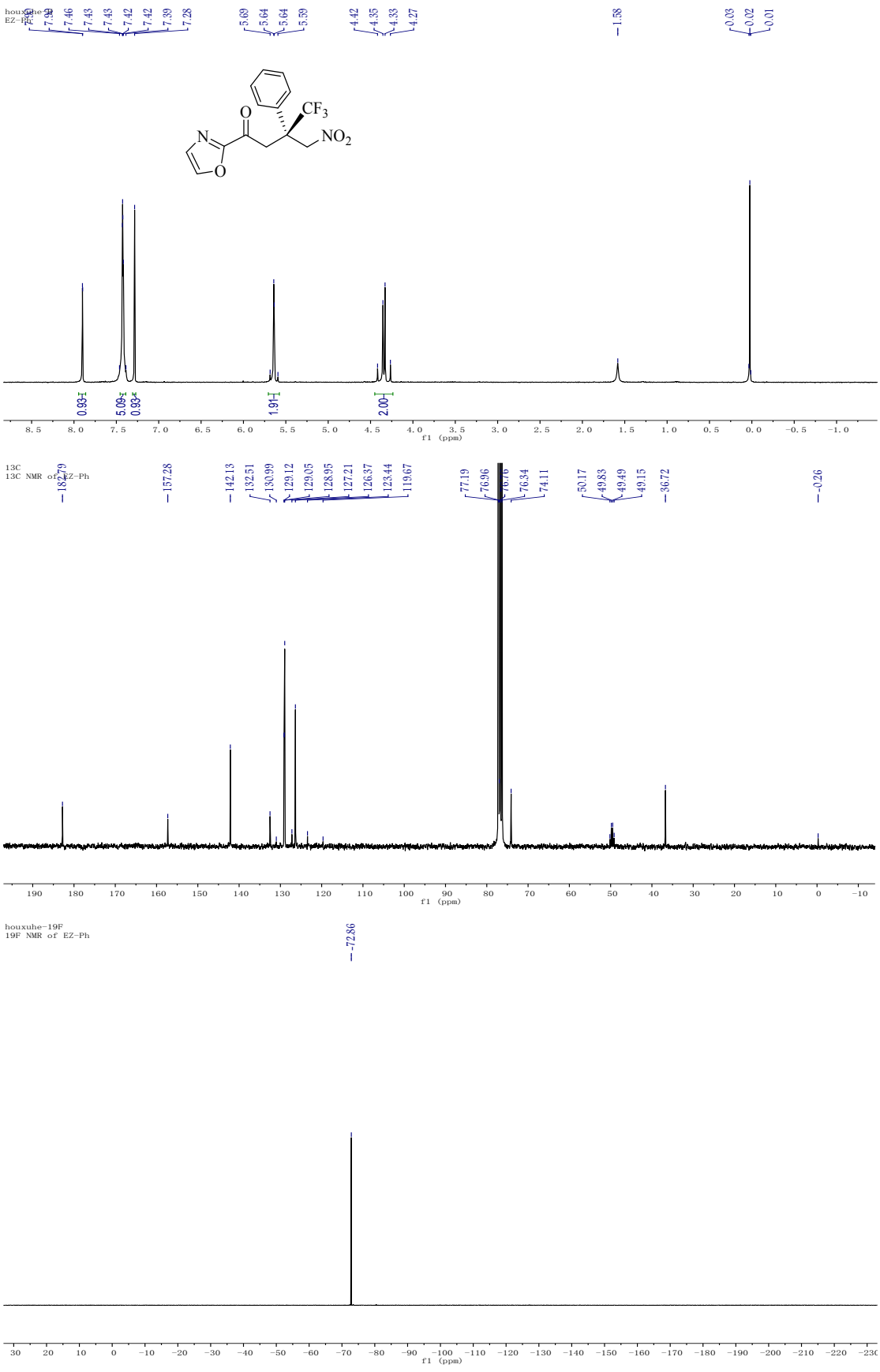
#	Time	Area	Height	Width	Area%	Symmetry
1	11.096	69077.9	3031.9	0.359	51.626	0.454
2	12.381	64727.8	3034.2	0.3348	48.374	0.62

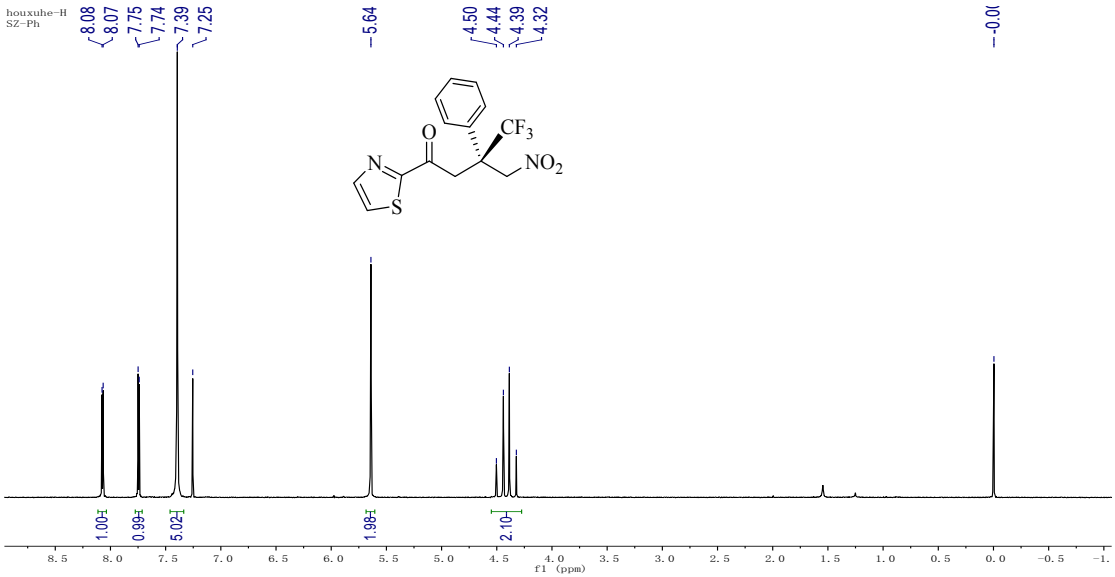
^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectrum for Michael addition products

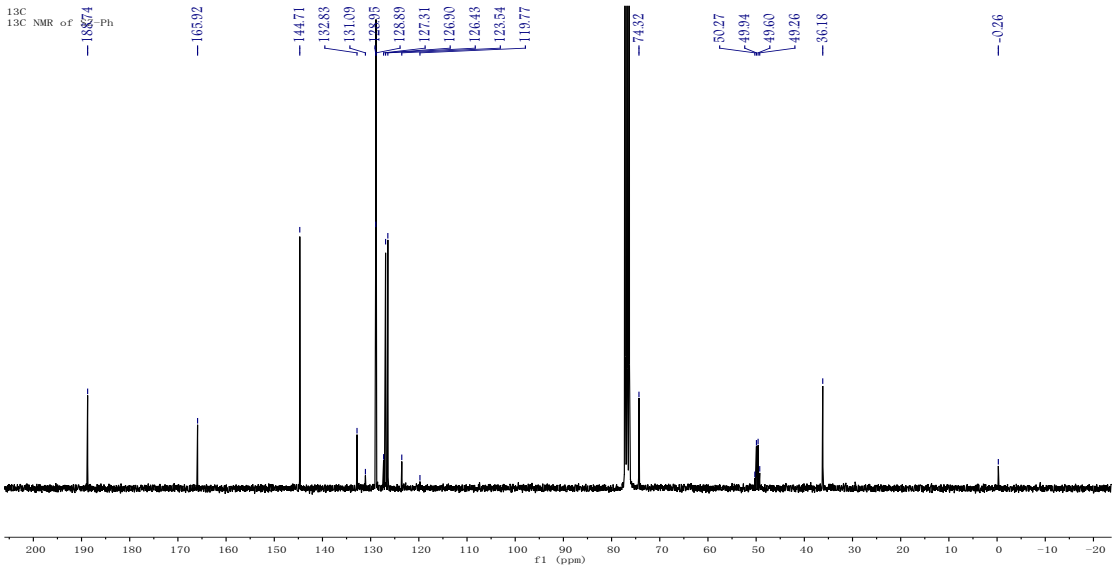

O
CF3
N
NO2
1.00
1.01
1.01
1.05
5.00
2.02
2.03
f1 (ppm)

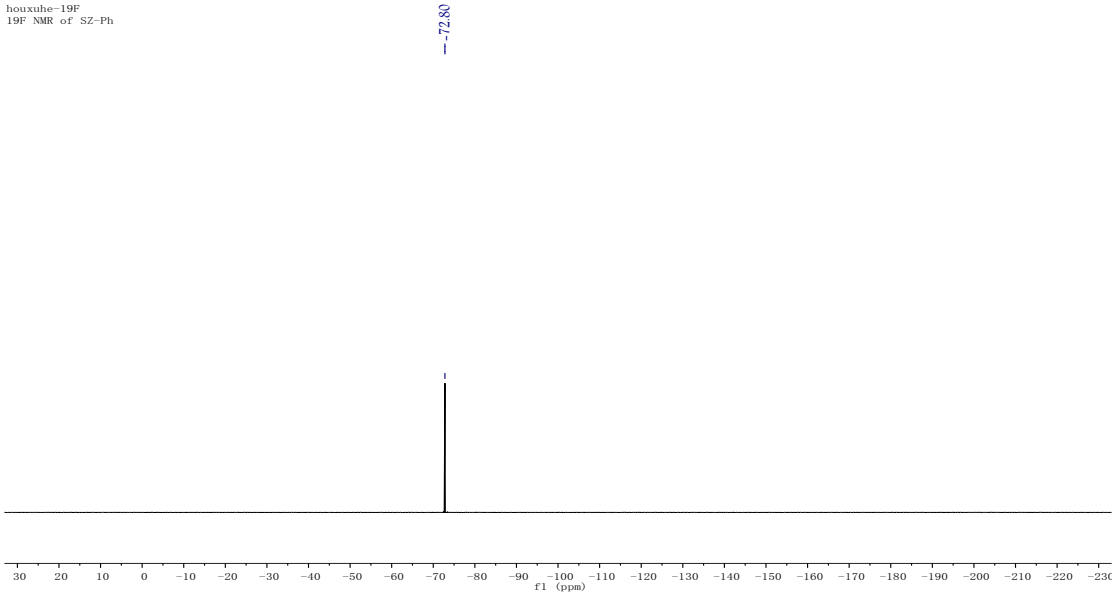

13C
13C NMR of BD-Ph
190.81
152.58
148.86
136.85
133.27
131.33
128.76
127.57
126.55
123.80
121.65
120.03
77.22
76.80
76.37
74.59
50.36
50.02
49.68
49.35
35.26
f1 (ppm)

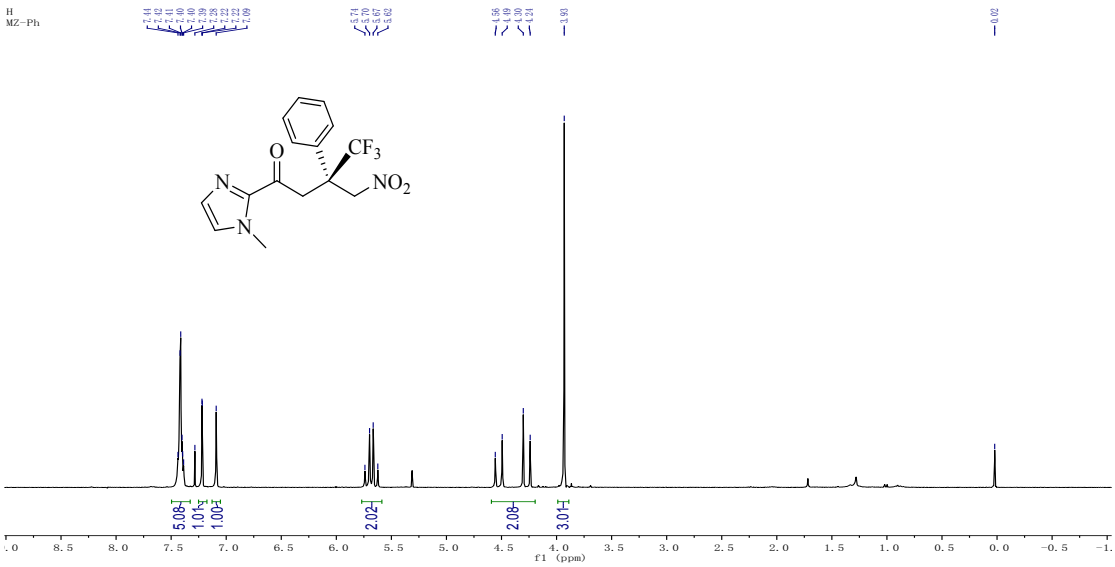

houxuhe-19F
19F NMR of BD-Ph
-72.84
f1 (ppm)

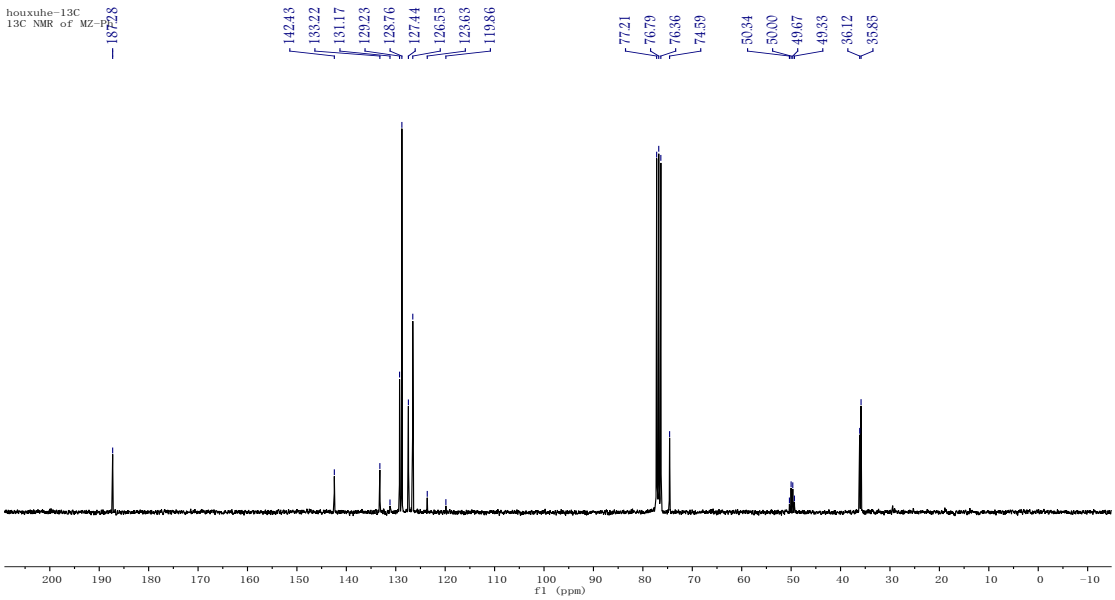

houxuhe-1H
EZ-Ph
7.49
7.46
7.43
7.43
7.42
7.42
7.39
7.28
5.69
5.64
5.64
5.59
4.42
4.35
4.33
4.27
1.58
0.03
0.02
0.01
O
CF3
N
NO2
O
0.93
5.09
0.93
1.91
2.00
f1 (ppm)
13C
13C NMR of EZ-Ph
182.79
157.28
142.13
132.51
130.99
129.12
129.05
128.95
127.21
126.37
123.44
119.67
77.19
76.96
76.76
76.34
74.11
50.17
49.83
49.49
49.15
36.72
-0.26
f1 (ppm)
houxuhe-19F
19F NMR of EZ-Ph
-72.86
f1 (ppm)

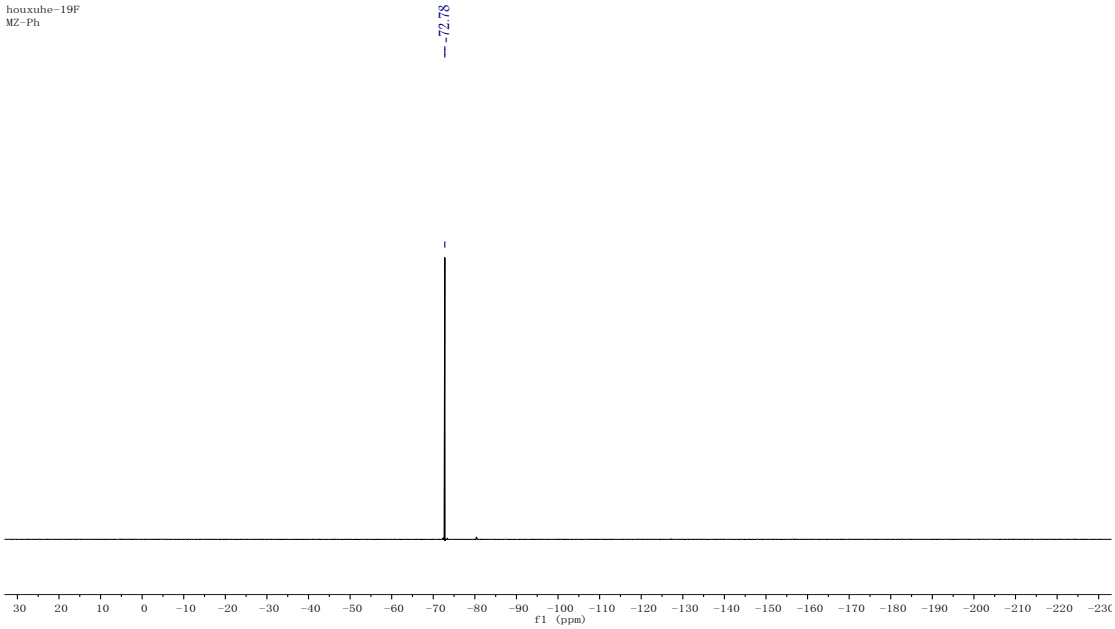

houxuhe-H
SZ-Ph
8.08
8.07
7.75
7.74
7.39
7.25
5.64
4.50
4.44
4.39
4.32
0.00
O
N
S
CF3
NO2
1.00
0.99
5.02
1.98
2.10
f1 (ppm)

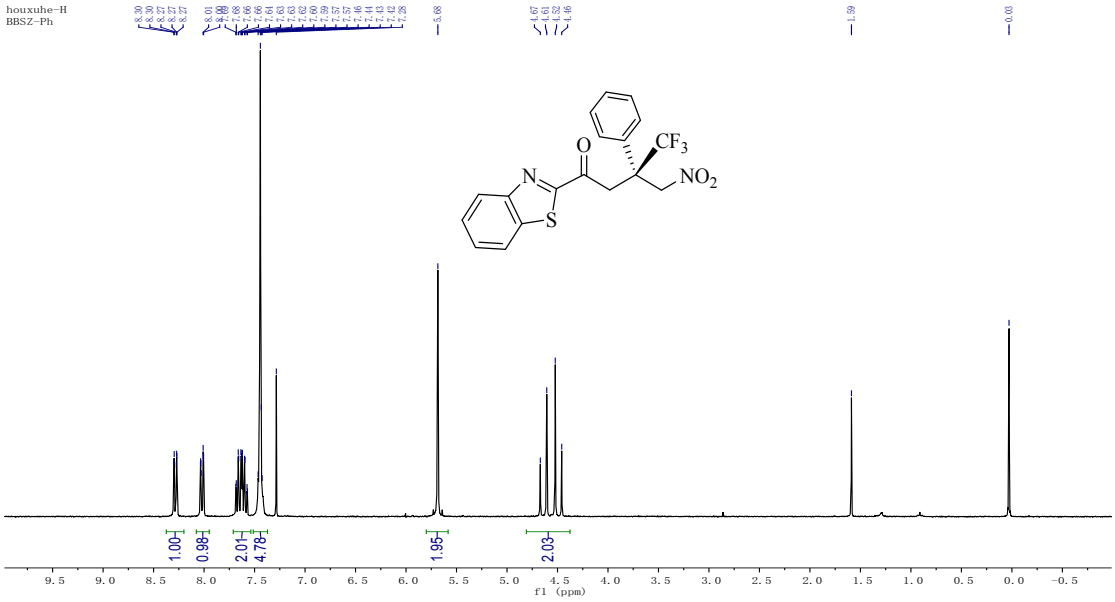

13C
13C NMR of SZ-Ph
188.74
165.92
144.71
132.83
131.09
128.95
128.89
127.31
126.90
126.43
123.54
119.77
74.32
50.27
49.94
49.60
49.26
36.18
0.26
f1 (ppm)

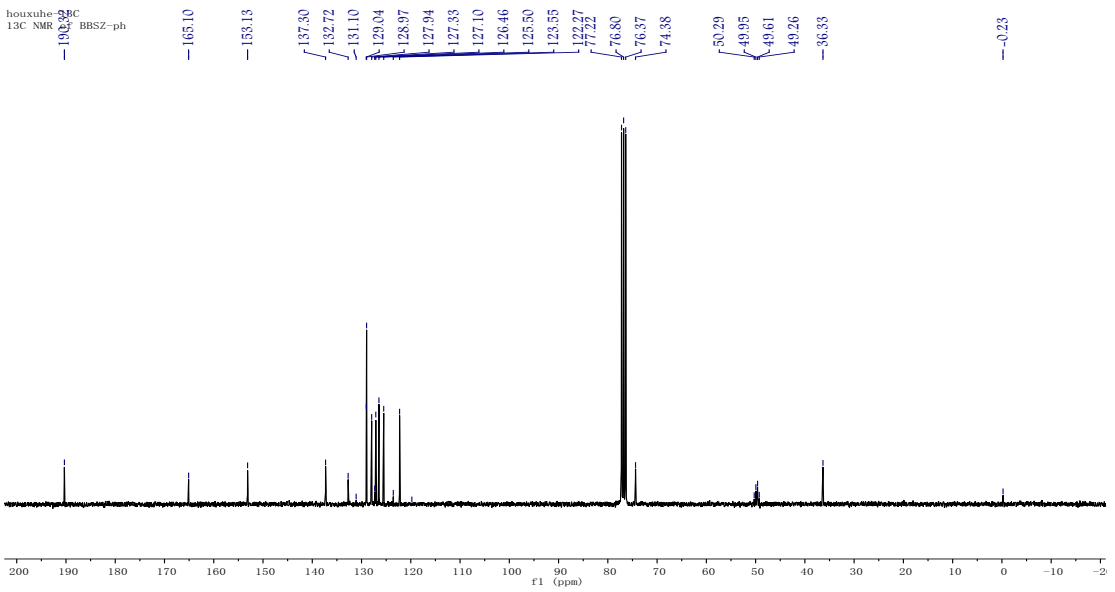

houxuhe-19F
19F NMR of SZ-Ph
-72.80
f1 (ppm)

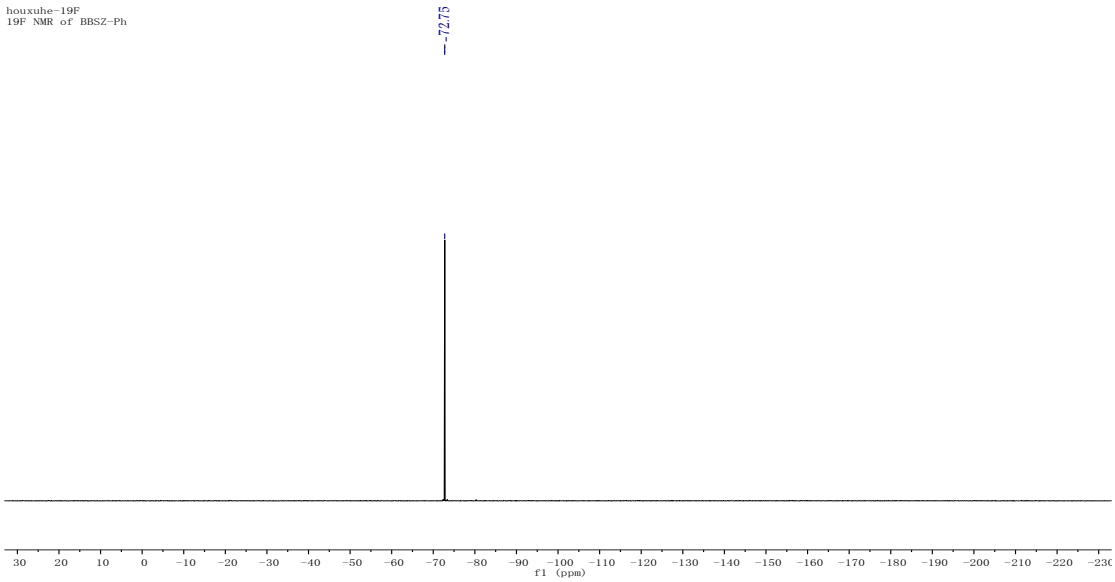

H
MZ-Ph
7.44
7.42
7.41
7.40
7.40
7.39
7.25
7.23
7.22
7.09
5.71
5.70
5.67
5.62
4.56
4.49
4.30
4.21
3.93
0.02
O
CF3
NO2
N
N
5.08
1.01
1.00
2.02
2.08
3.01
f1 (ppm)

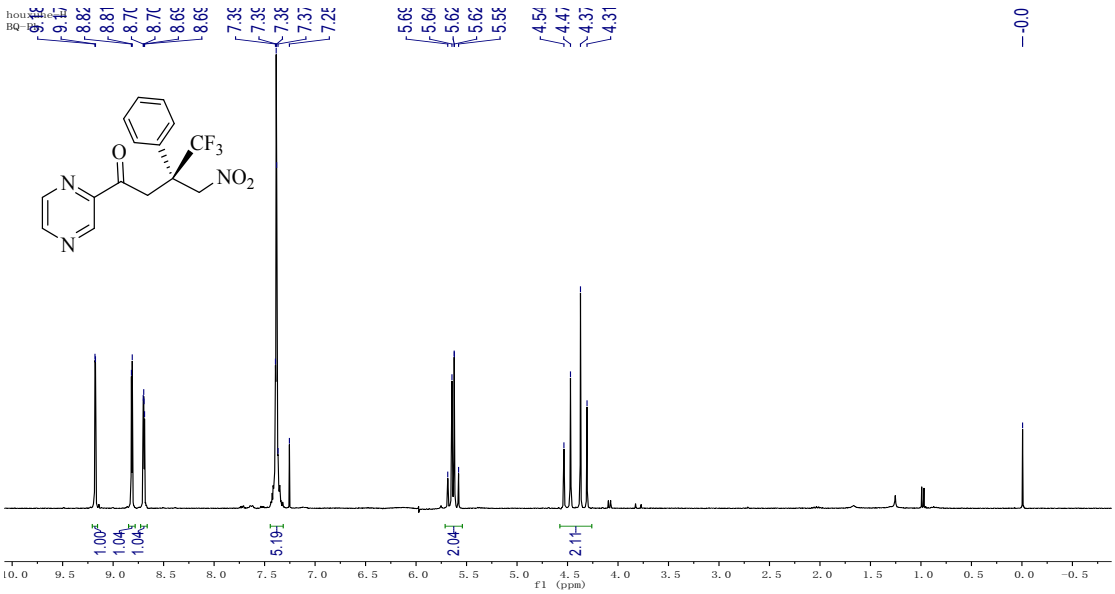

houxuhe-13C
13C NMR of MZ-Ph
187.28
142.43
133.22
131.17
129.23
128.76
127.44
126.55
123.63
119.86
77.21
76.79
76.36
74.59
50.34
50.00
49.67
49.33
36.12
35.85
f1 (ppm)

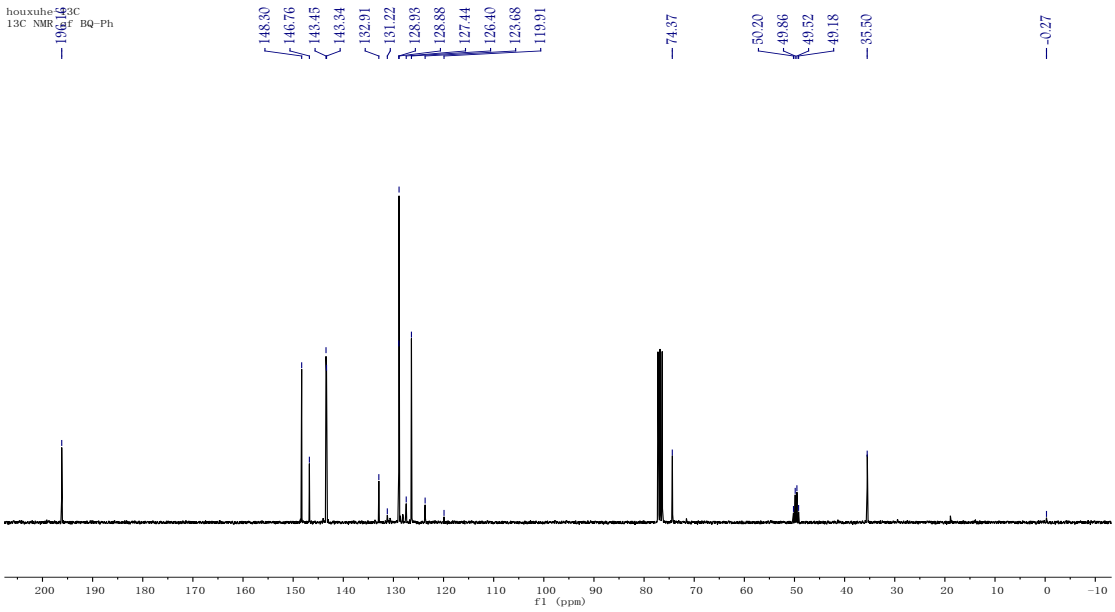

houxuhe-19F
MZ-Ph
-72.78
f1 (ppm)

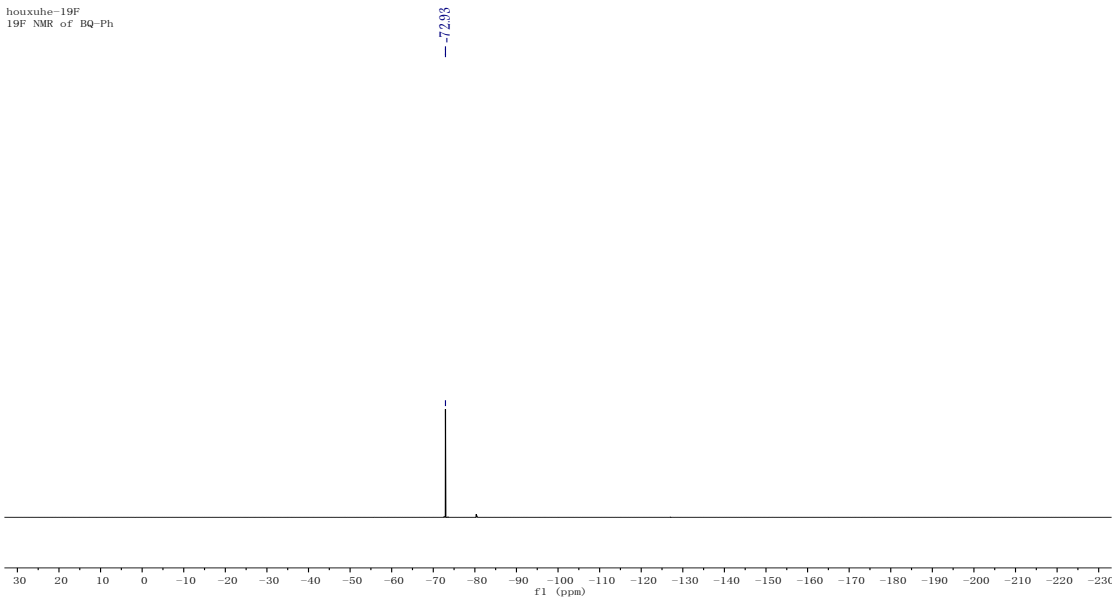

houxuhe-H
BBSZ-Ph
O
CF3
N
NO2
S
1.00
0.98
2.01
4.78
1.95
2.03
f1 (ppm)

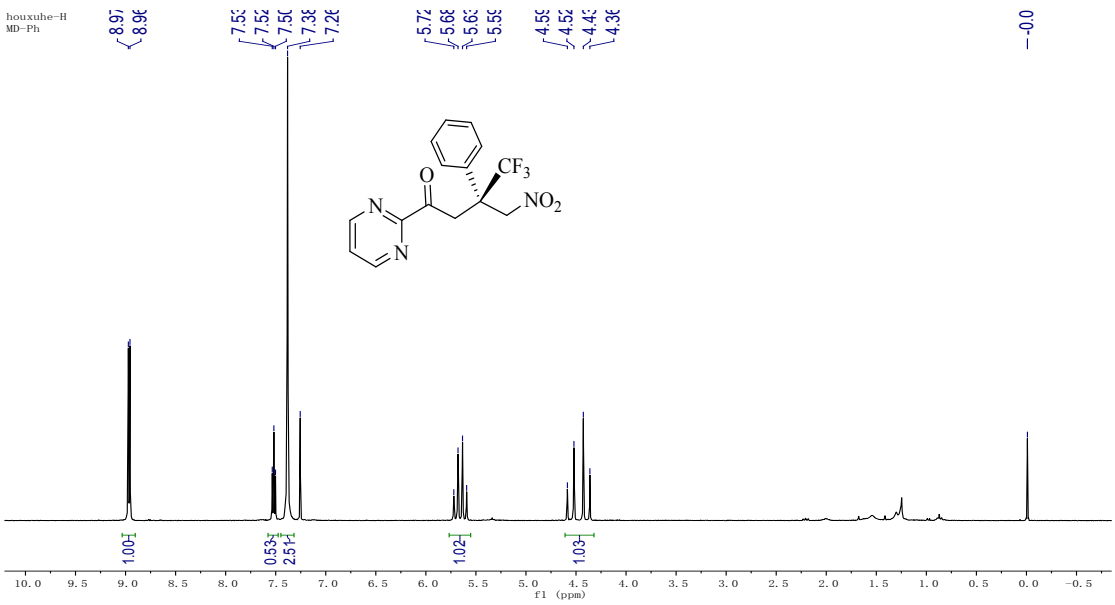

houxuhe-13C
13C NMR of BBSZ-ph
165.10
153.13
137.30
132.72
131.10
129.04
128.97
127.94
127.33
127.10
126.46
125.50
123.55
122.27
77.22
76.80
76.37
74.38
50.29
49.95
49.61
49.26
36.33
-0.23
f1 (ppm)

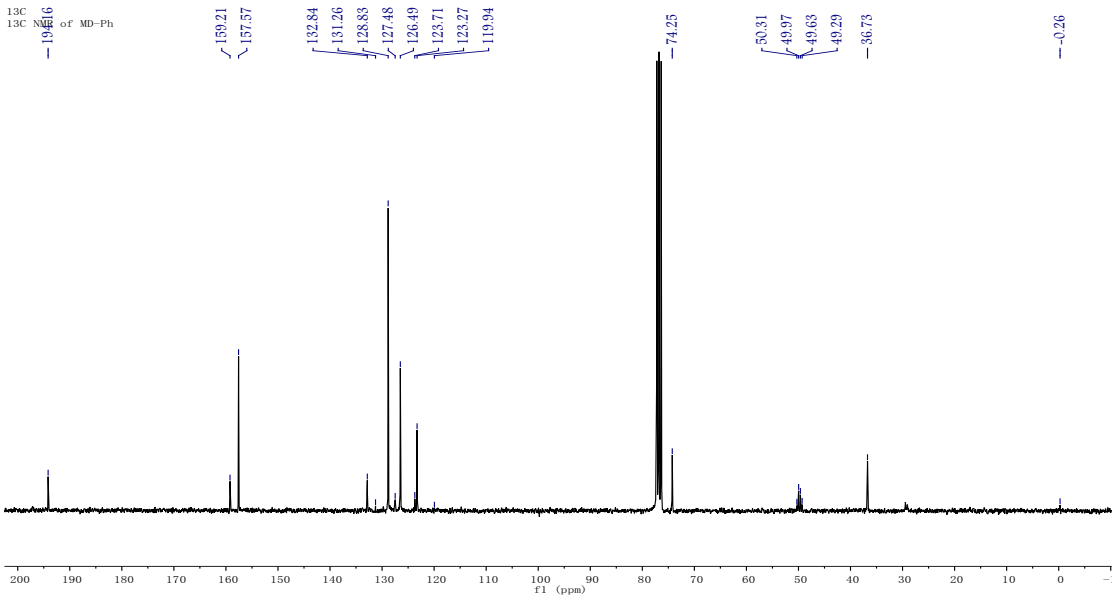

houxuhe-19F
19F NMR of BBSZ-Ph
-72.75
f1 (ppm)

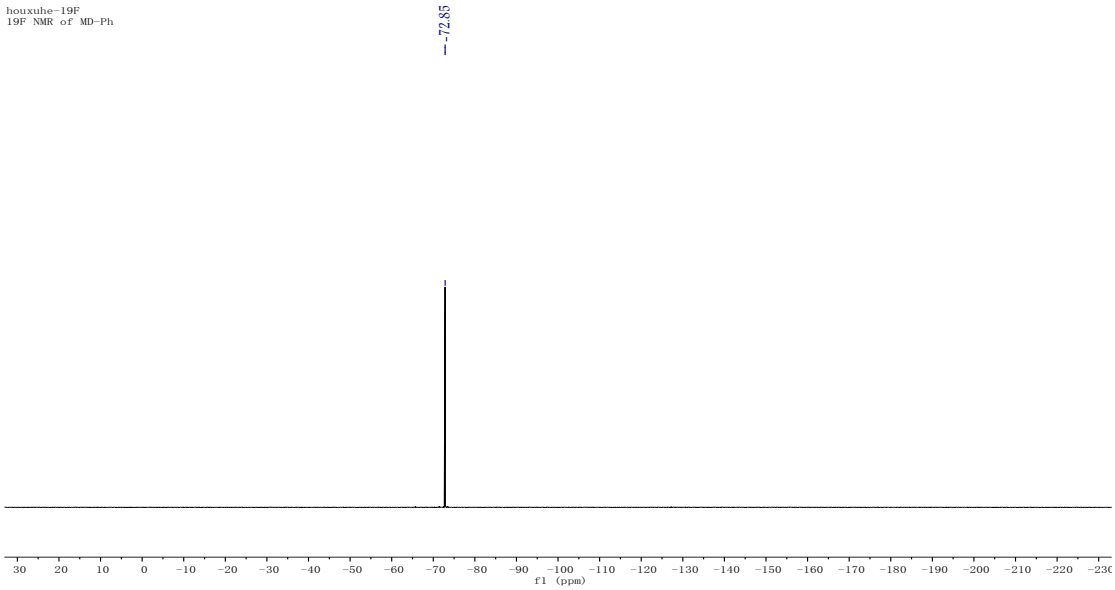

O
CF3
NO2
N
N
1.00
1.04
1.04
5.19
2.04
2.11
f1 (ppm)

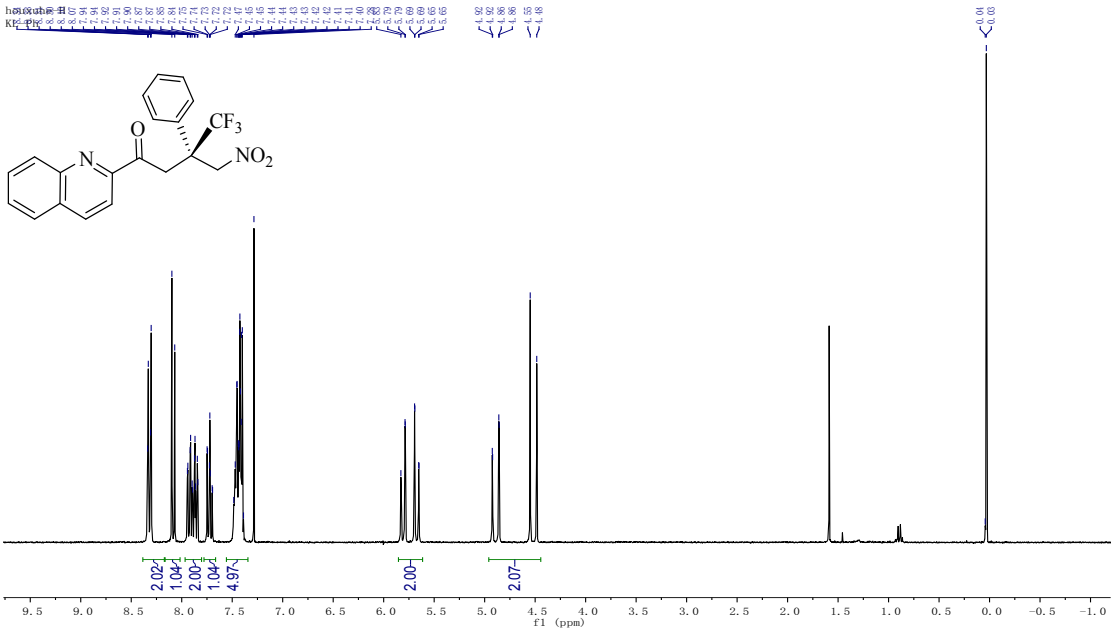

houxuhe-13C
13C NMR of BQ-Ph
148.30
146.76
143.45
143.34
132.91
131.22
128.93
128.88
127.44
126.40
123.68
119.91
74.37
50.20
49.86
49.52
49.18
35.50
-0.27
f1 (ppm)

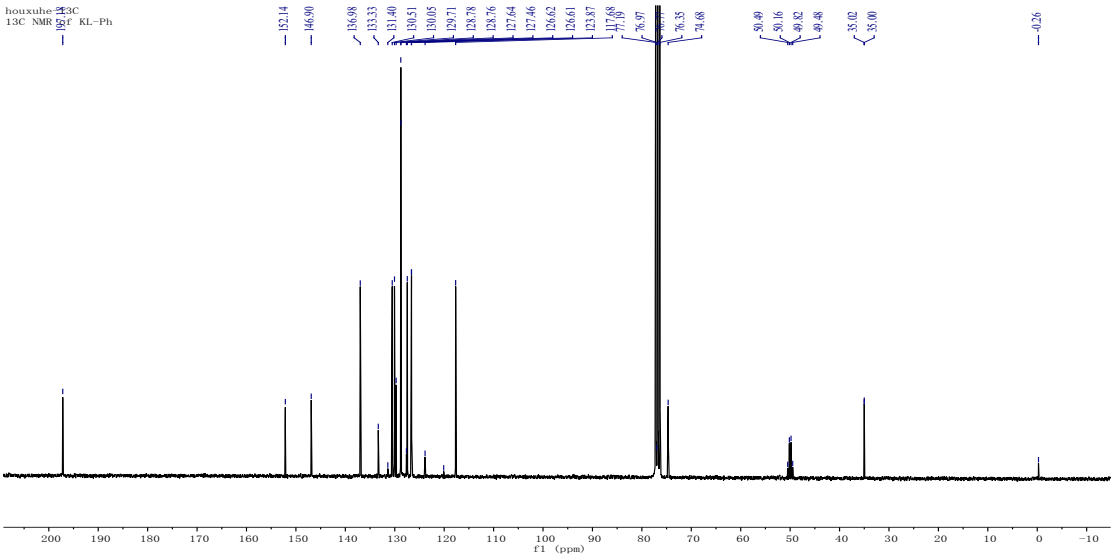

houxuhe-19F
19F NMR of BQ-Ph
-72.93
f1 (ppm)

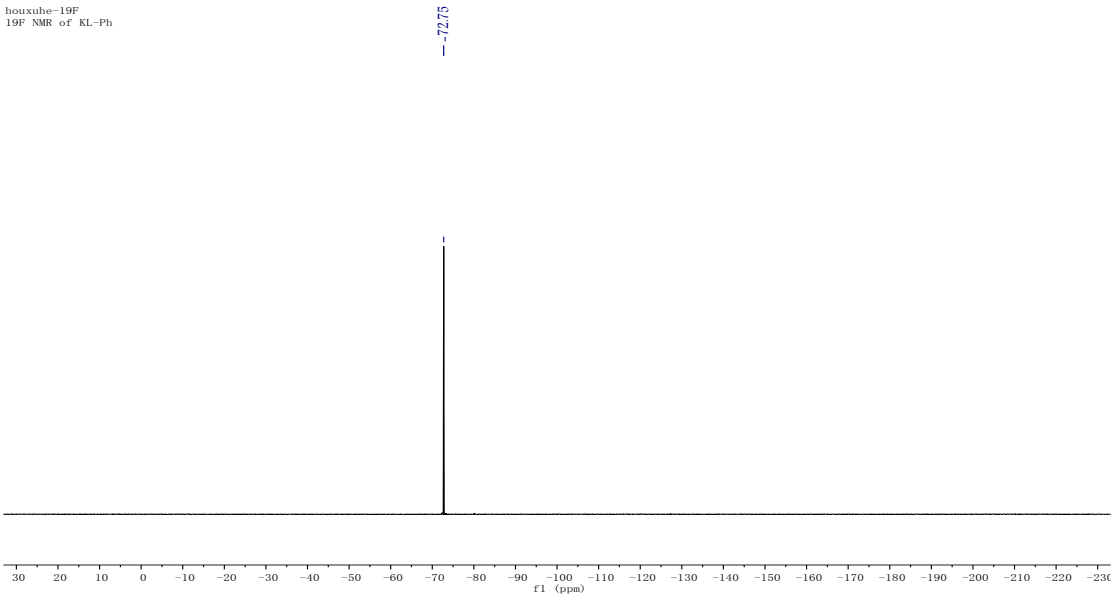

houxuhe-H
MD-Ph
8.97
8.96
7.53
7.52
7.51
7.38
7.28
5.72
5.68
5.63
5.58
4.55
4.52
4.43
4.36
0.00
O
CF3
NO2
N
N
1.00
0.53
2.51
1.02
1.03
f1 (ppm)

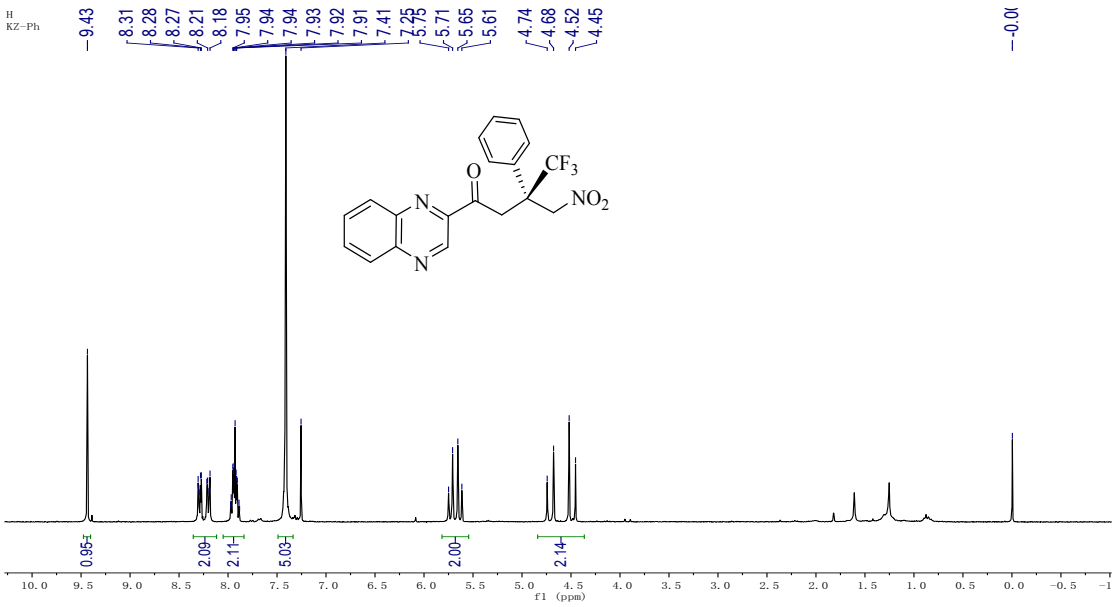

13C
13C NMR of MD-Ph
159.21
157.57
132.84
131.26
128.83
127.48
126.49
123.71
123.27
119.94
74.25
50.31
49.97
49.63
49.29
36.73
0.26
f1 (ppm)

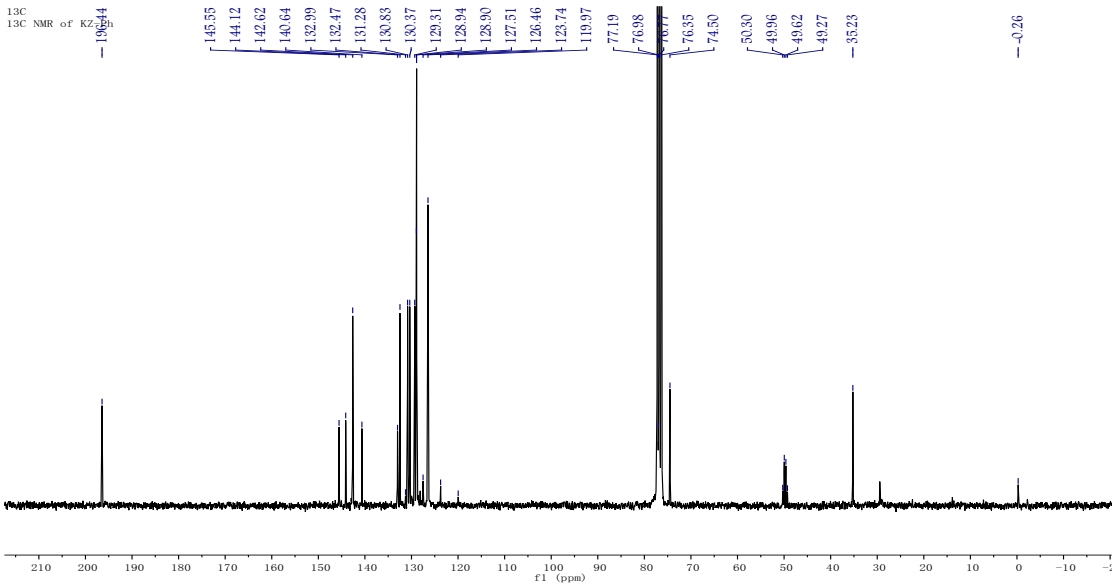

houxuhe-19F
19F NMR of MD-Ph
-72.85
f1 (ppm)

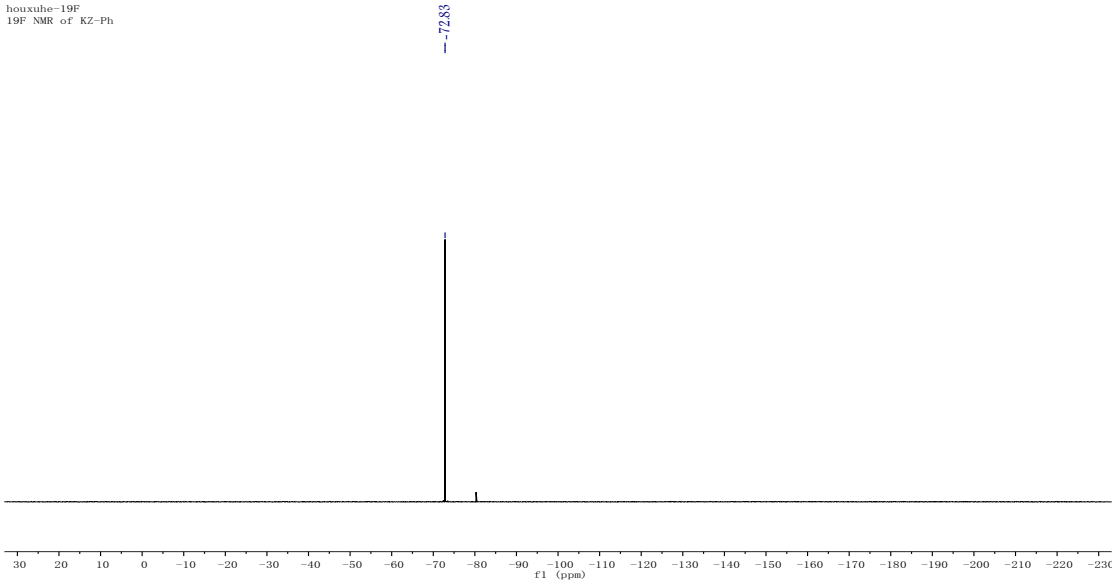

houxuhe-1H
KL-Ph
O
N
CF3
NO2
2.02
1.04
2.00
1.04
4.97
2.00
2.07
f1 (ppm)

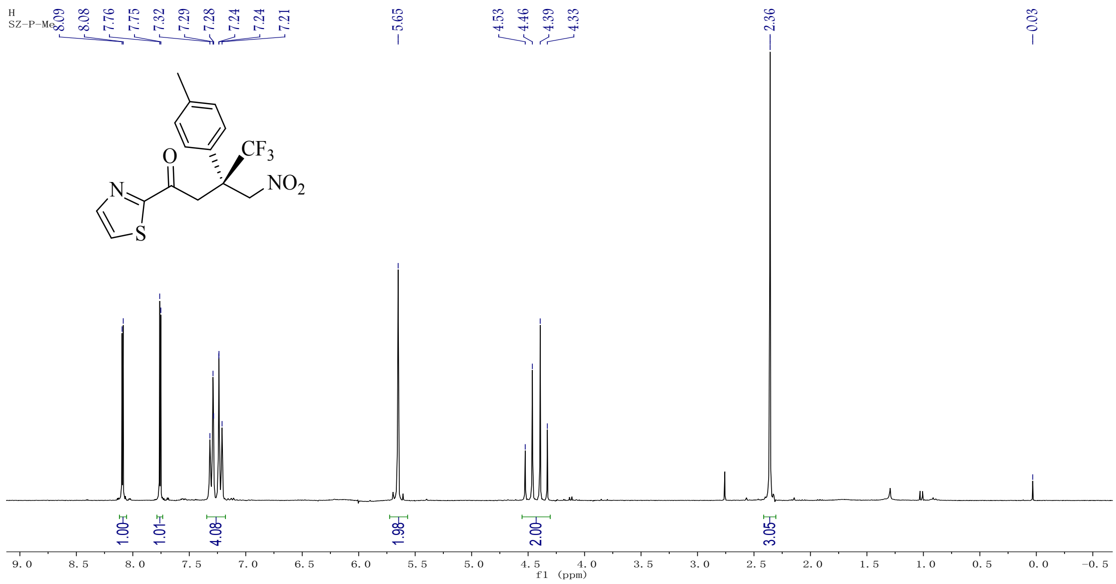

houxuhe-13C
13C NMR of KL-Ph
152.14
146.90
136.98
133.33
131.40
130.51
130.05
129.71
128.78
128.76
127.64
127.46
126.62
126.61
123.87
117.68
77.19
76.97
76.35
74.68
50.49
50.16
49.82
49.48
35.02
35.00
-0.26
f1 (ppm)

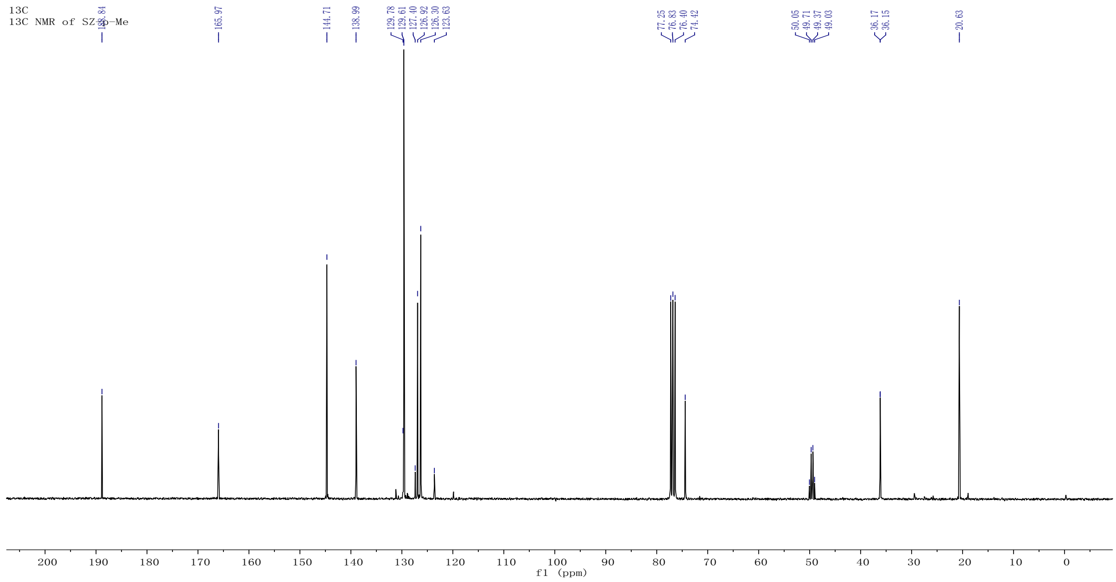

houxuhe-19F
19F NMR of KL-Ph
-72.75
f1 (ppm)

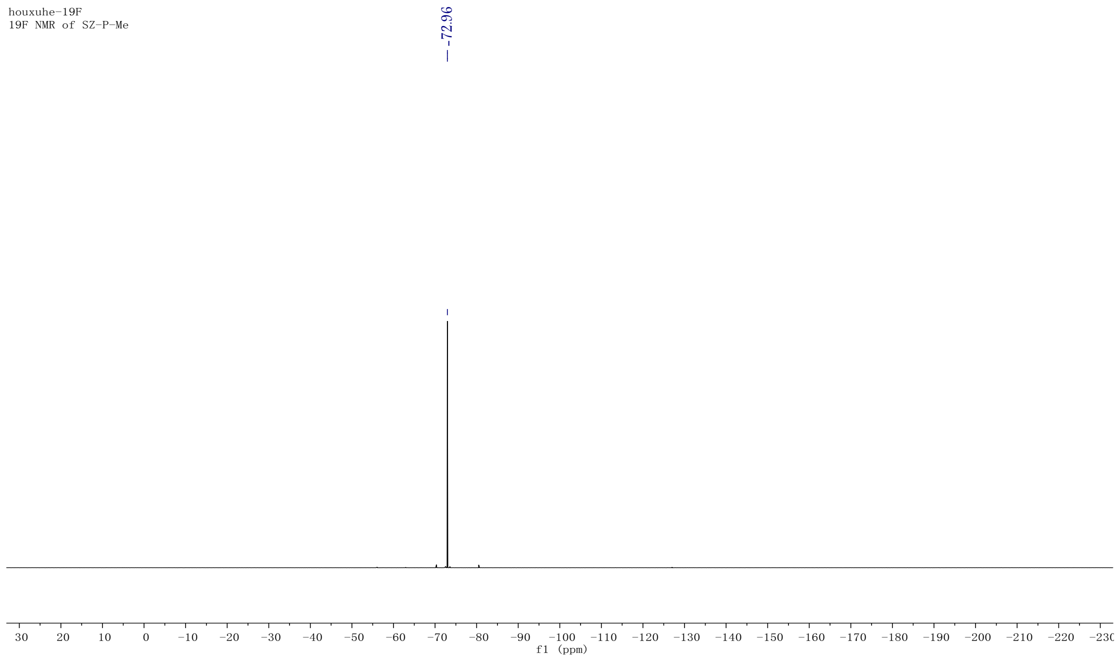

H
KZ-Ph
9.43
8.31
8.28
8.27
8.21
8.18
7.95
7.94
7.94
7.93
7.92
7.91
7.41
5.71
5.65
5.61
4.74
4.68
4.52
4.45
0.00
O
CF3
NO2
N
N
0.95
2.09
2.11
5.03
2.00
2.14
f1 (ppm)

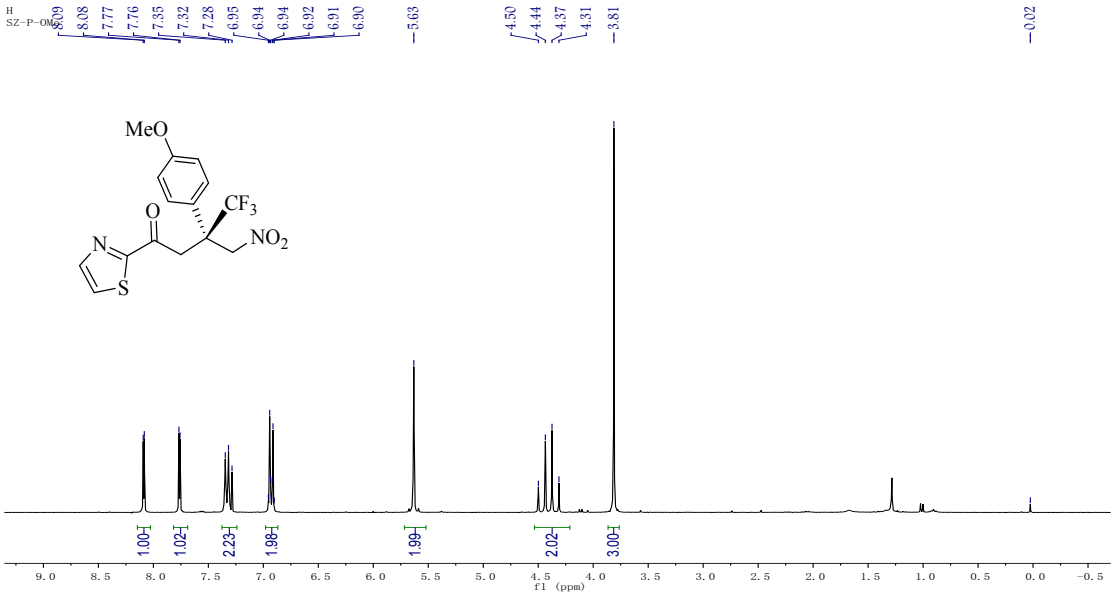

13C
13C NMR of KZ-Ph
190.44
145.55
144.12
142.62
140.64
132.99
132.47
131.28
130.83
130.37
129.31
128.94
128.90
127.51
126.46
123.74
119.97
77.19
76.98
76.77
76.35
74.50
50.30
49.96
49.62
49.27
35.23
0.26
f1 (ppm)

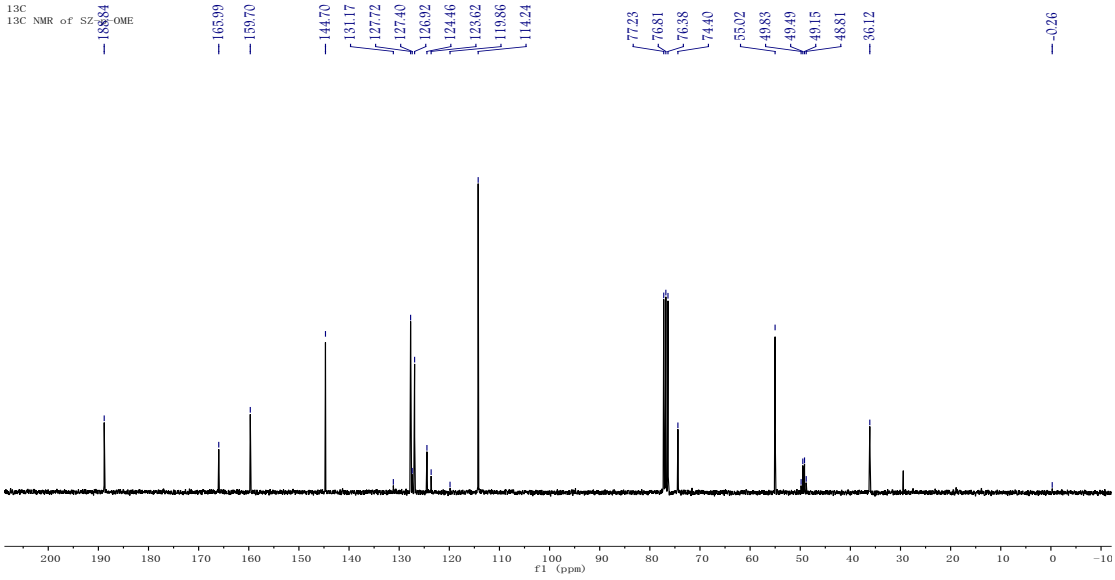

houxuhe-19F
19F NMR of KZ-Ph
-72.83
f1 (ppm)

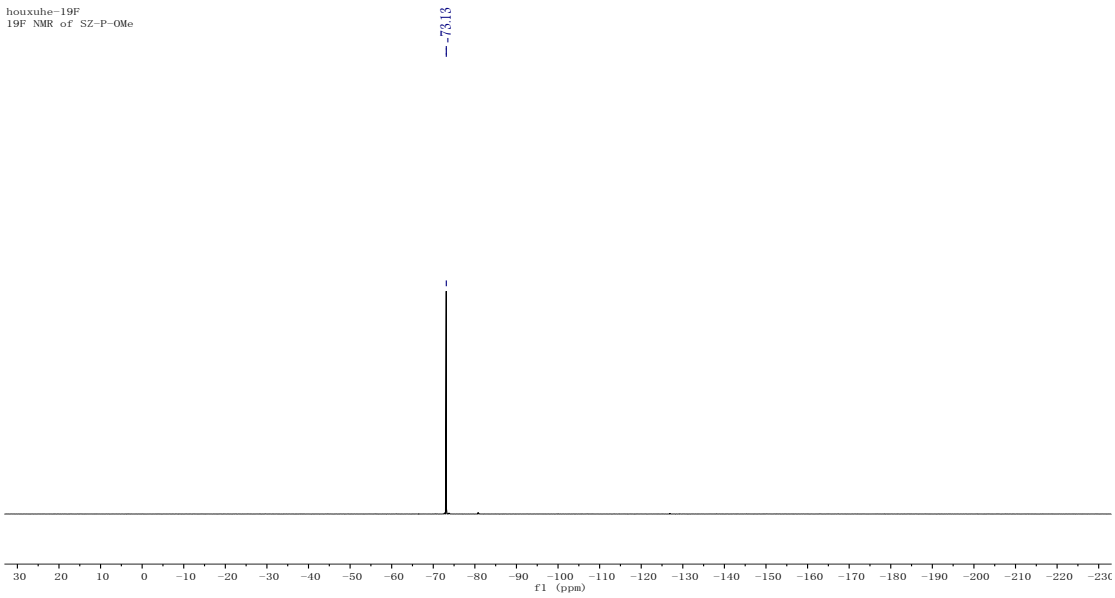

H
SZ-P-Me
8.09
8.08
7.76
7.75
7.32
7.29
7.28
7.24
7.24
7.21
5.65
4.53
4.46
4.39
4.33
2.36
-0.03
CF3
NO2
O
N
S
1.00
1.01
4.08
1.98
2.00
3.05
f1 (ppm)

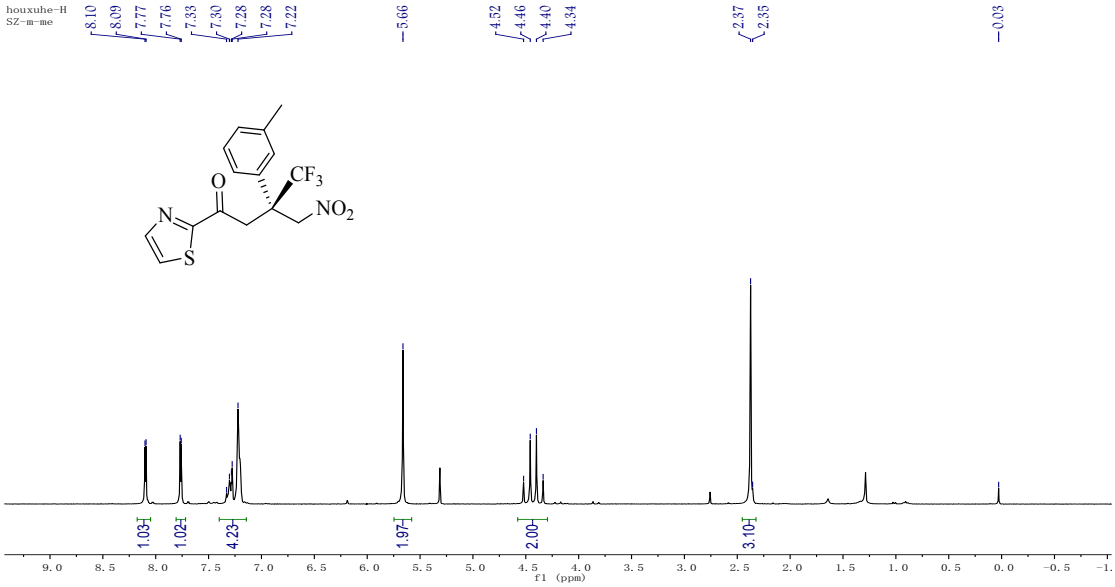

13C
13C NMR of SZ-P-Me
165.97
144.71
138.99
129.78
129.61
127.40
126.92
126.30
123.63
77.25
76.83
76.40
74.42
50.05
49.71
49.37
49.03
36.17
36.15
20.63
f1 (ppm)

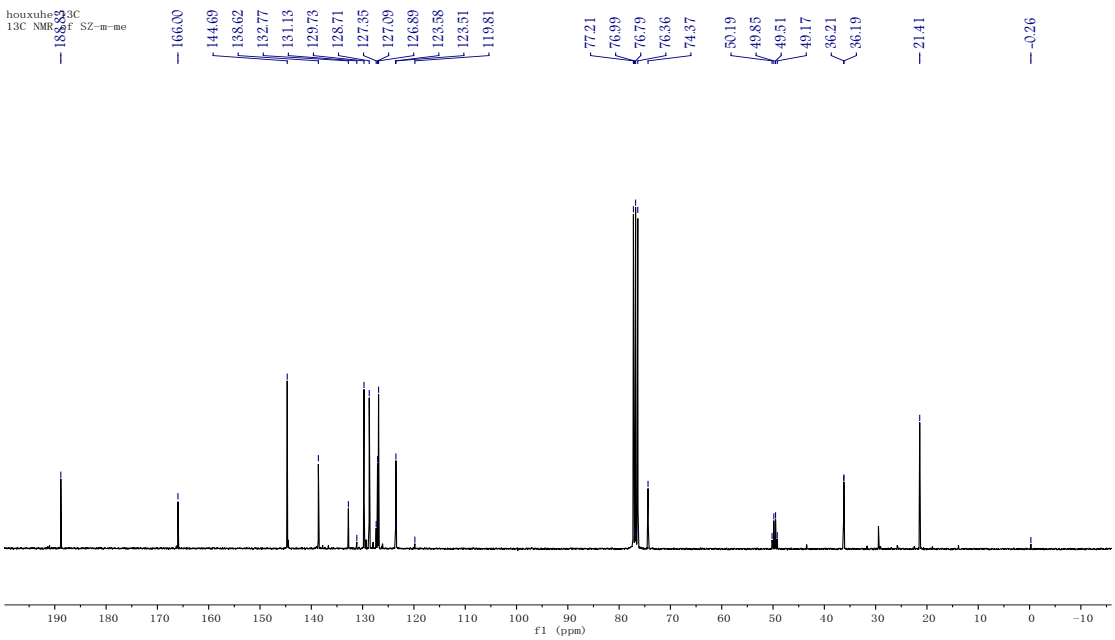

houxuhe-19F
19F NMR of SZ-P-Me
-72.96
f1 (ppm)

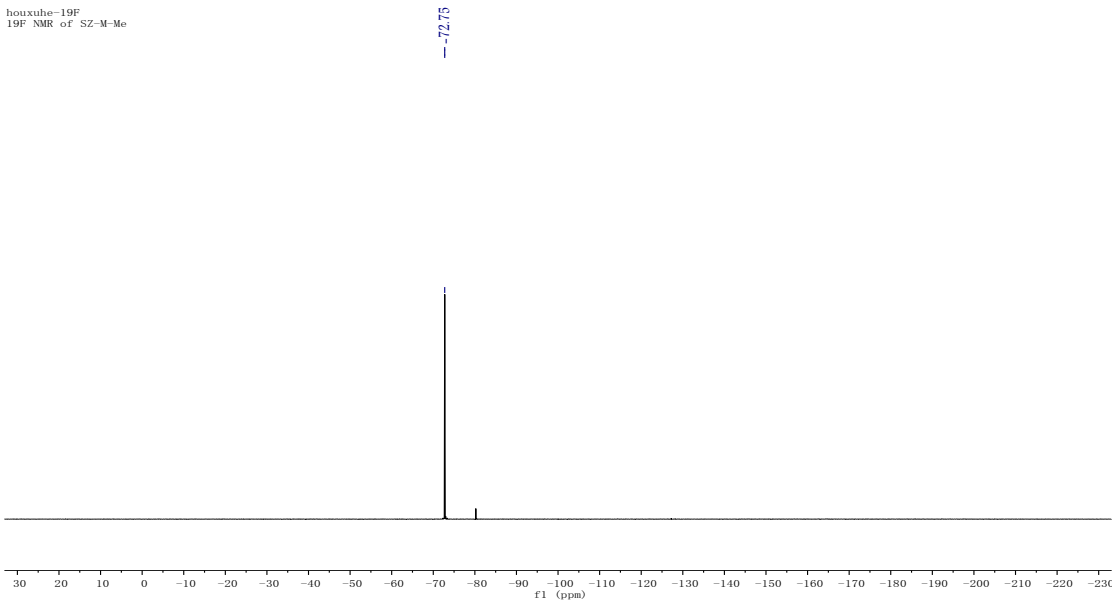

H
SZ-P-OMe
8.09
8.08
7.77
7.76
7.35
7.32
7.28
6.95
6.94
6.94
6.92
6.91
6.90
5.63
4.50
4.44
4.37
4.31
3.81
0.02
MeO
O
CF3
NO2
N
S
1.00
1.02
2.23
1.98
1.99
2.02
3.00
f1 (ppm)

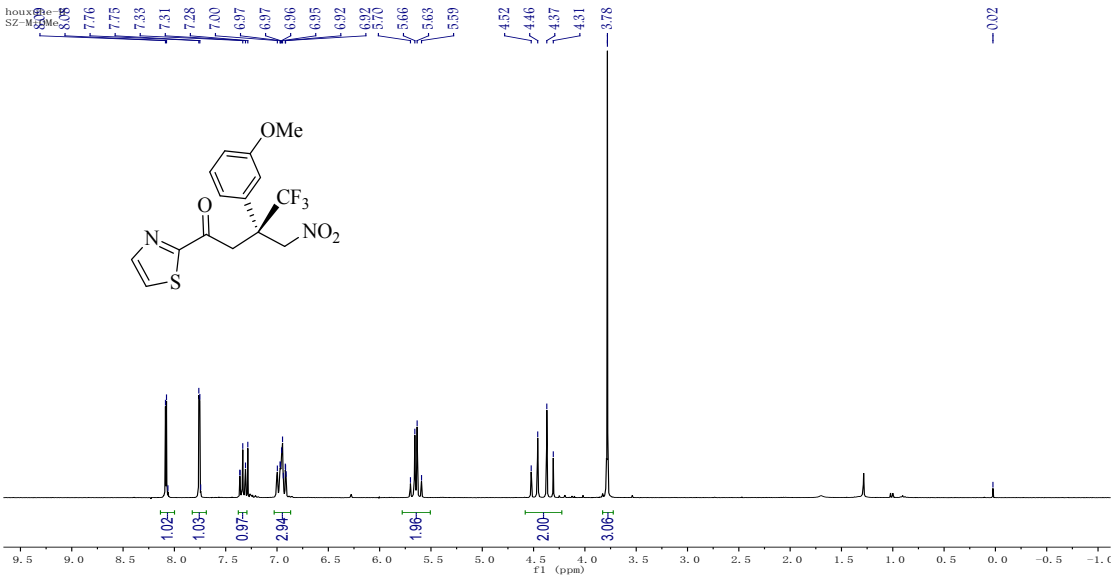

13C
13C NMR of SZ-P-OME
188.84
165.99
159.70
144.70
131.17
127.72
127.40
126.92
124.46
123.62
119.86
114.24
77.23
76.81
76.38
74.40
55.02
49.83
49.49
49.15
48.81
36.12
0.26
f1 (ppm)

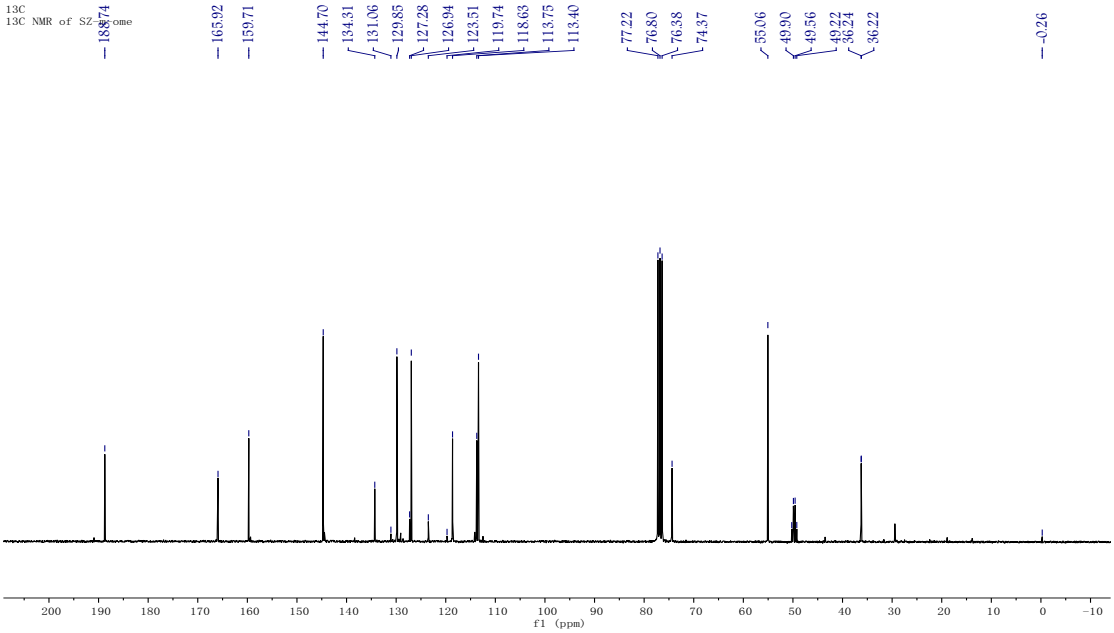

houxuhe-19F
19F NMR of SZ-P-OMe
-73.13
f1 (ppm)

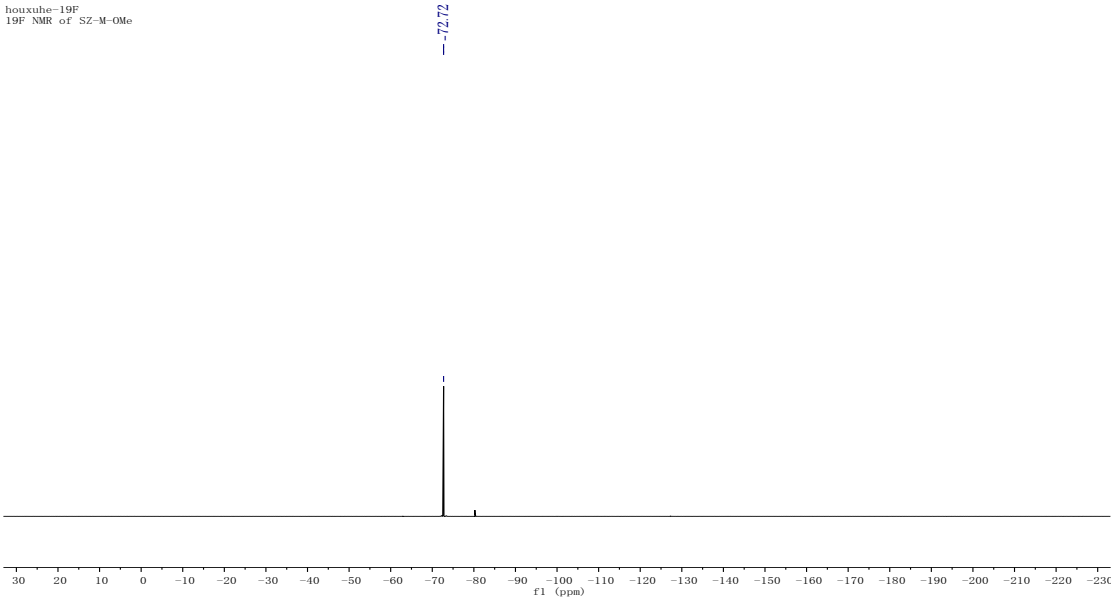

houxuhe-H
SZ-m-me
8.10
8.09
7.77
7.76
7.33
7.30
7.28
7.28
7.22
5.66
4.52
4.46
4.40
4.34
2.37
2.35
0.03
O
CF3
NO2
N
S
1.03
1.02
4.23
1.97
2.00
3.10
f1 (ppm)

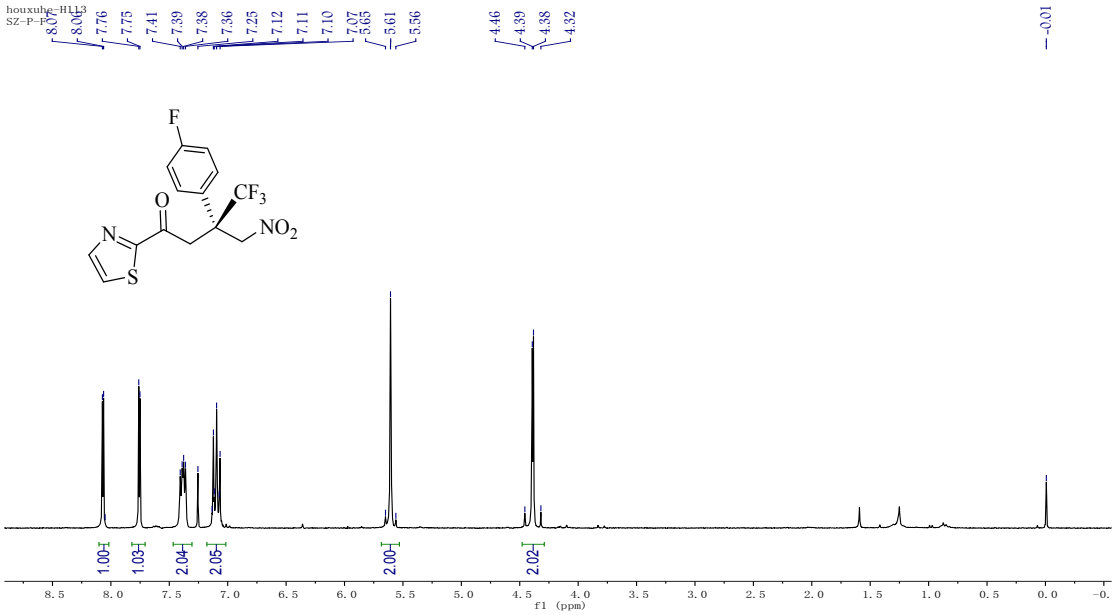

houxuhe-13C
13C NMR of SZ-m-me
166.00
144.69
138.62
132.77
131.13
129.73
128.71
127.35
127.09
126.89
123.58
123.51
119.81
77.21
76.99
76.79
76.36
74.37
50.19
49.85
49.51
49.17
36.21
36.19
21.41
0.26
f1 (ppm)

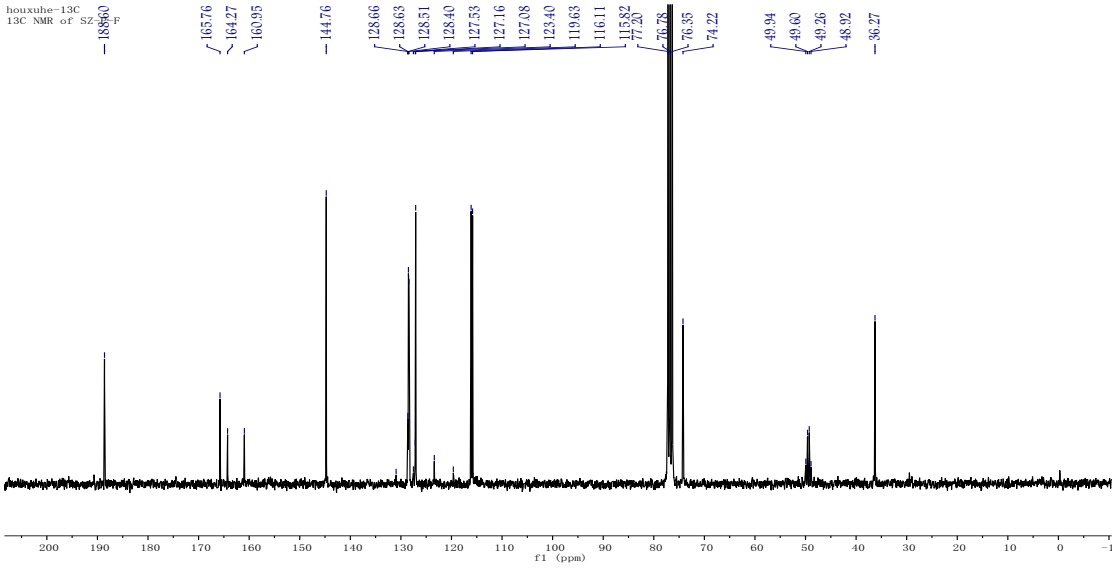

houxuhe-19F
19F NMR of SZ-M-Me
-72.75
f1 (ppm)

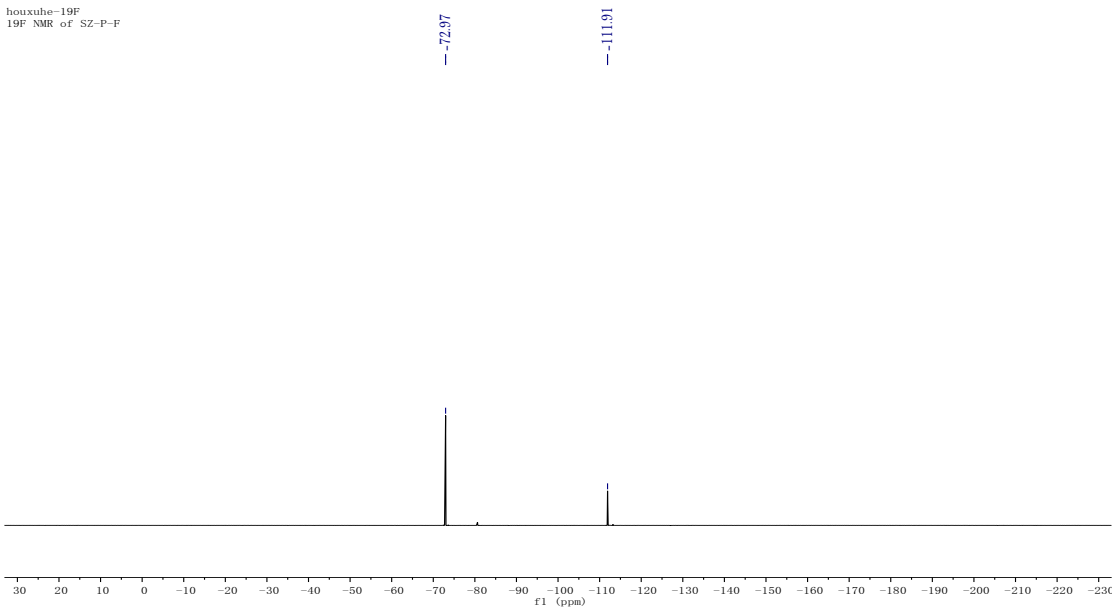

houxuhe-1H
SZ-M-OMe
8.08
7.76
7.75
7.33
7.31
7.28
7.00
6.97
6.97
6.96
6.95
6.92
6.92
5.70
5.66
5.63
5.59
4.52
4.46
4.37
4.31
3.78
0.02
OMe
CF3
O
NO2
N
S
1.02
1.03
0.97
2.94
1.96
2.00
3.06
f1 (ppm)

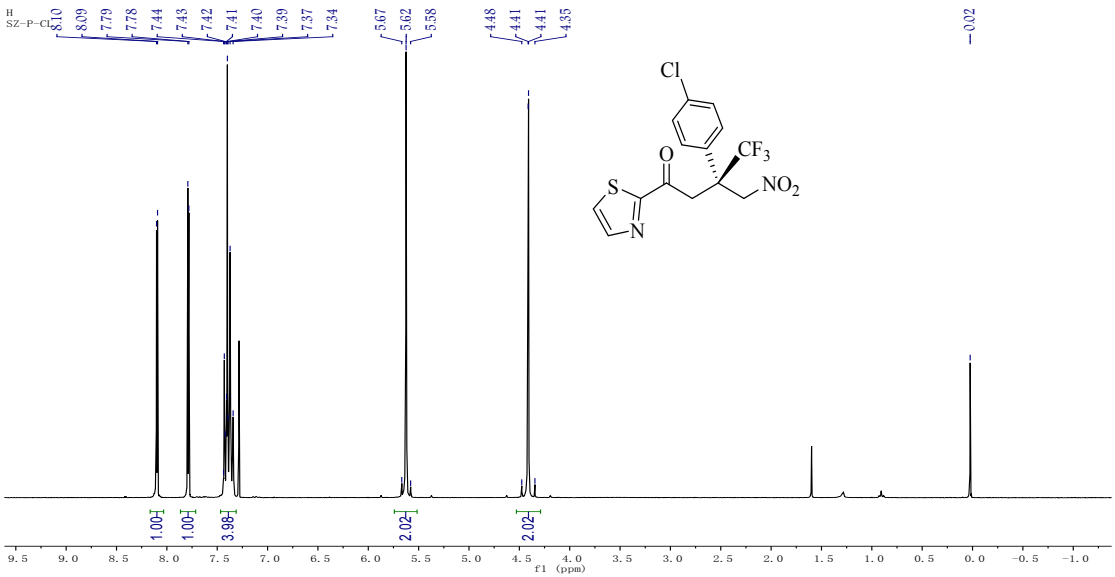

13C
13C NMR of SZ-M-OMe
188.74
165.92
159.71
144.70
134.31
131.06
129.85
127.28
126.94
123.51
119.74
118.63
113.75
113.40
77.22
76.80
76.38
74.37
55.06
49.90
49.56
49.22
36.24
36.22
-0.26
f1 (ppm)

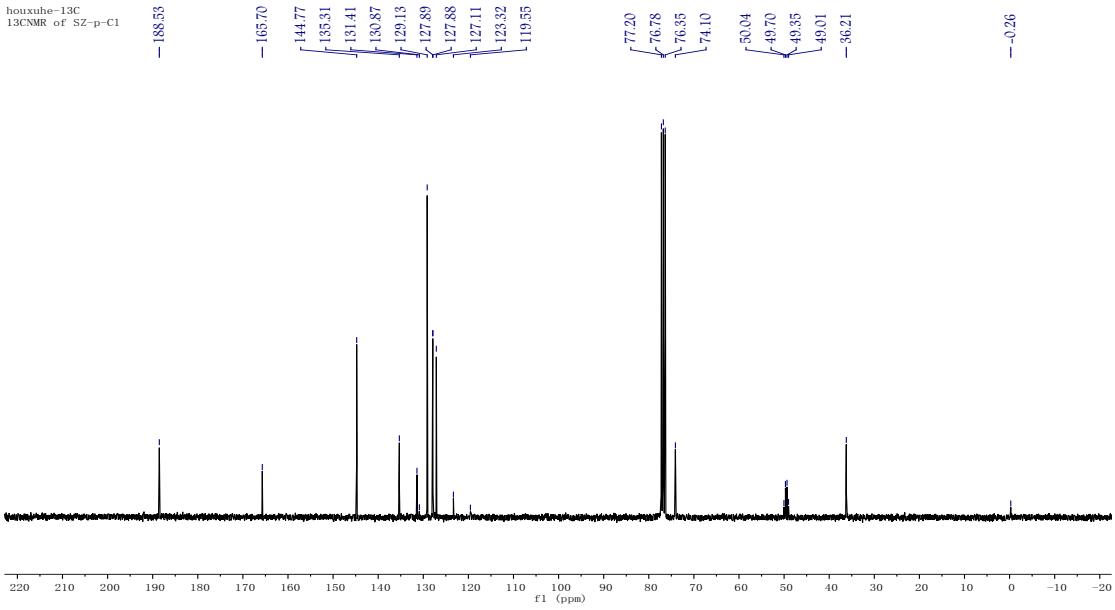

houxuhe-19F
19F NMR of SZ-M-OMe
-72.72
f1 (ppm)

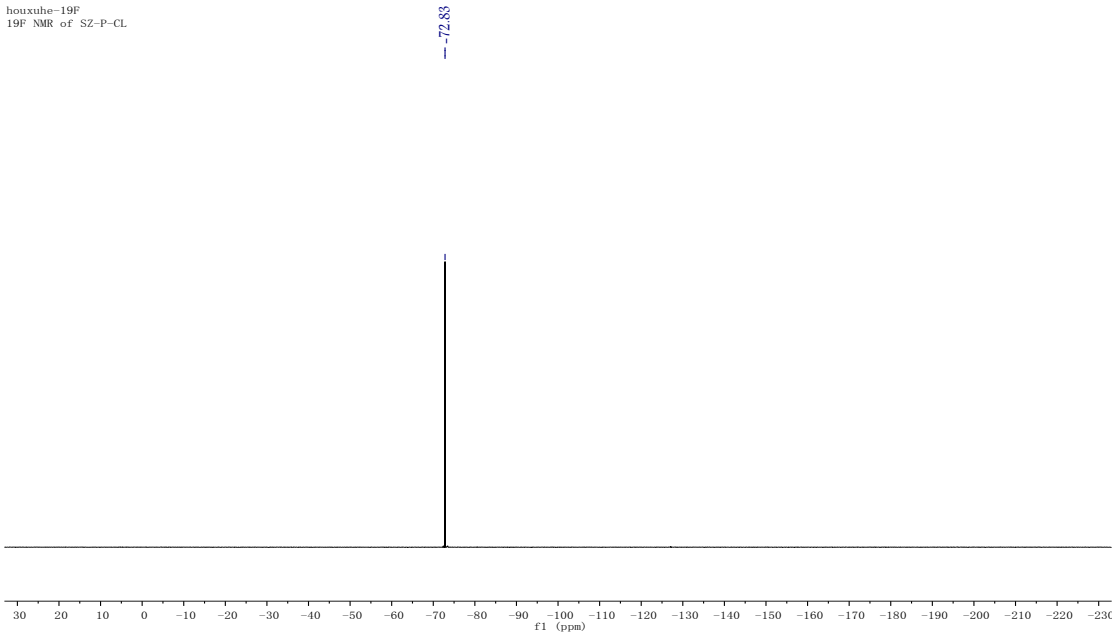

houxuhe-HLL3
SZ-P-F
8.07
8.06
7.76
7.75
7.41
7.39
7.38
7.36
7.25
7.12
7.11
7.10
7.07
5.65
5.61
5.56
4.46
4.39
4.38
4.32
-0.01
F
O
CF3
NO2
N
S
1.00
1.03
2.04
2.05
2.00
2.02
f1 (ppm)

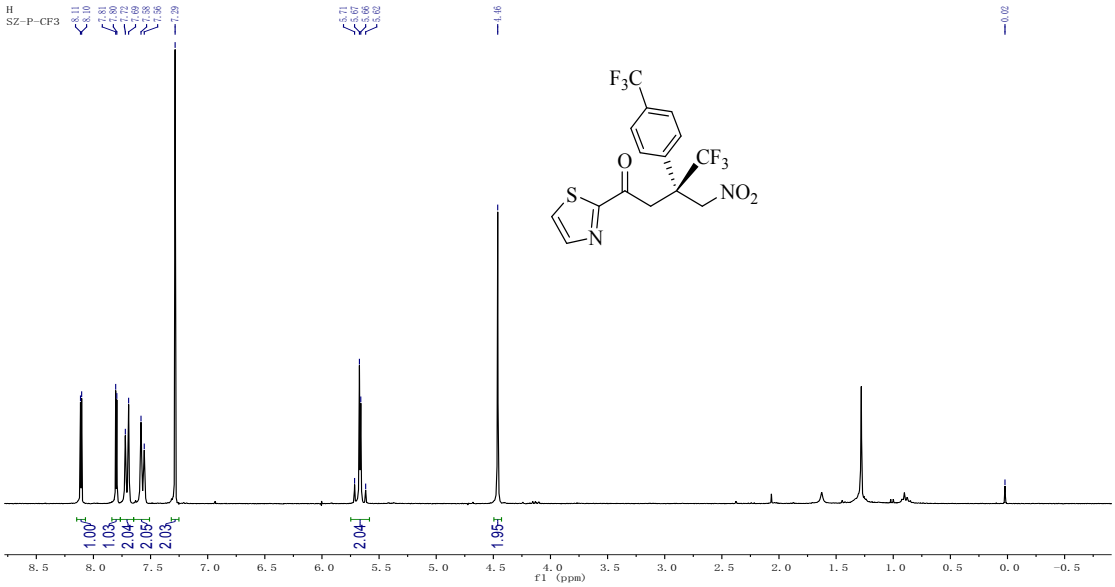

houxuhe-13C
13C NMR of SZ-P-F
188.60
165.76
164.27
160.95
144.76
128.66
128.63
128.51
128.40
127.53
127.16
127.08
123.40
119.63
116.11
115.82
77.20
76.78
76.35
74.22
49.94
49.60
49.26
48.92
36.27
f1 (ppm)

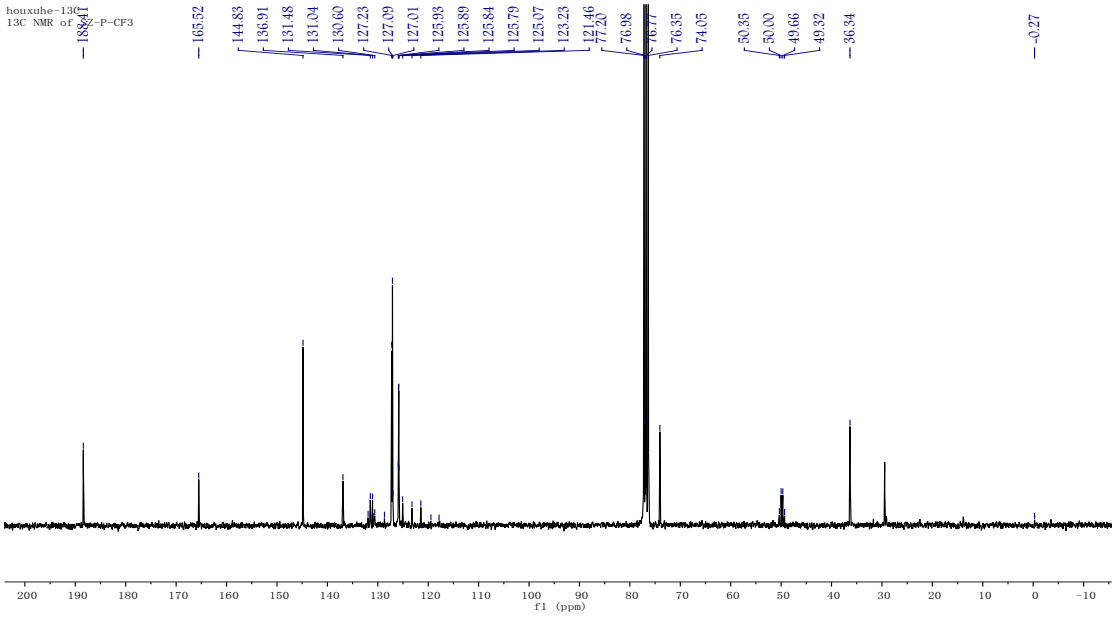

houxuhe-19F
19F NMR of SZ-P-F
-72.97
-111.91
f1 (ppm)

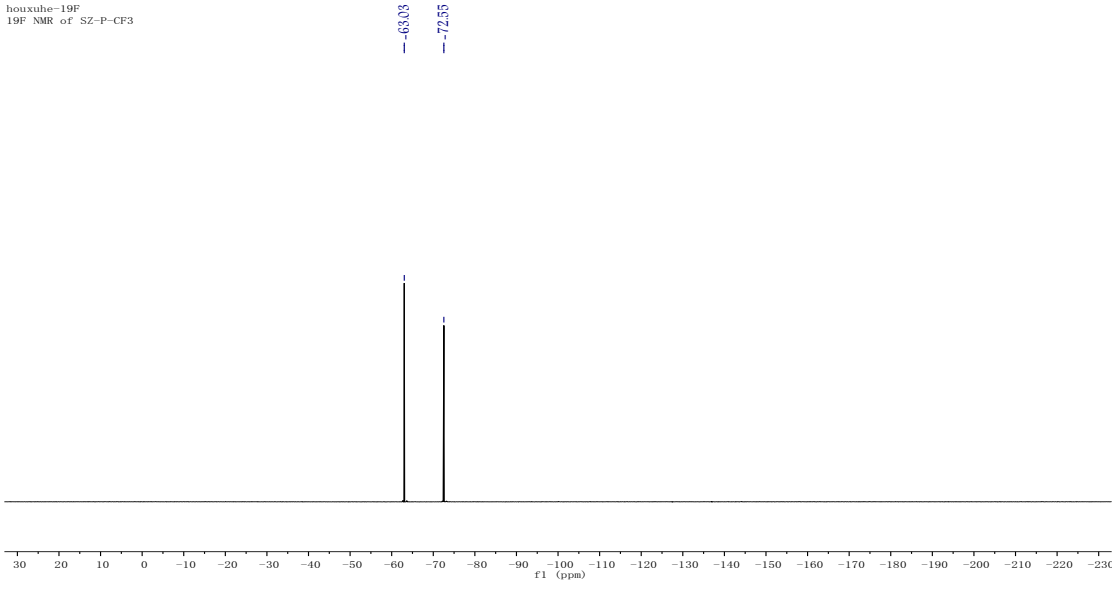

H
SZ-P-CL
8.10
8.09
7.79
7.78
7.44
7.43
7.42
7.41
7.40
7.39
7.37
7.34
5.67
5.62
5.58
4.48
4.41
4.41
4.35
0.02
Cl
O
CF3
NO2
S
N
1.00
1.00
3.99
2.02
2.02
f1 (ppm)

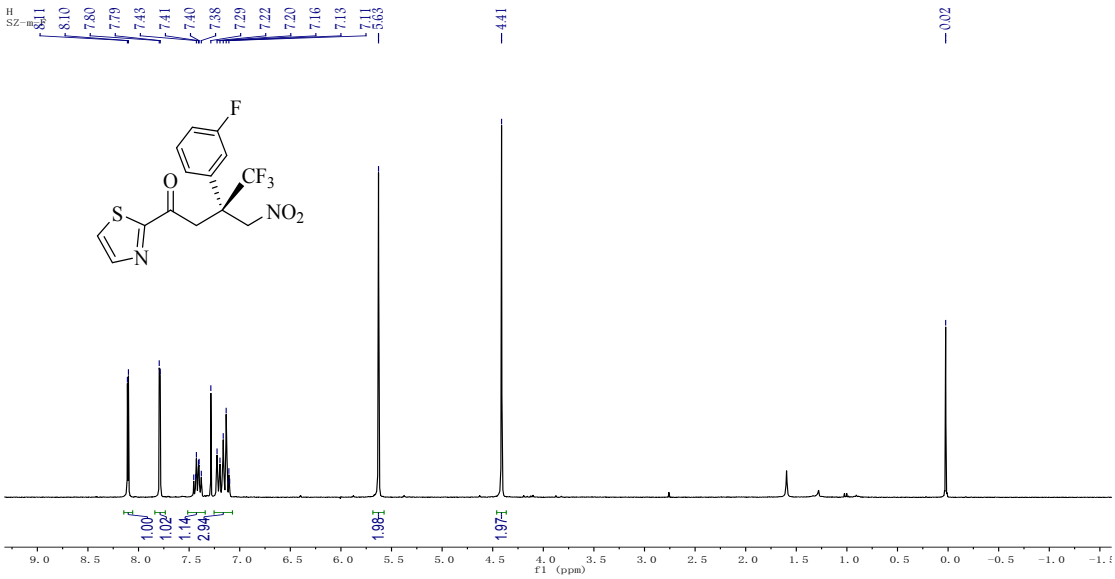

houxuhe-13C
13CNMR of SZ-p-Cl
188.53
165.70
144.77
135.31
131.41
130.87
129.13
127.89
127.88
127.11
123.32
119.55
77.20
76.78
76.35
74.10
50.04
49.70
49.35
49.01
36.21
-0.26
f1 (ppm)

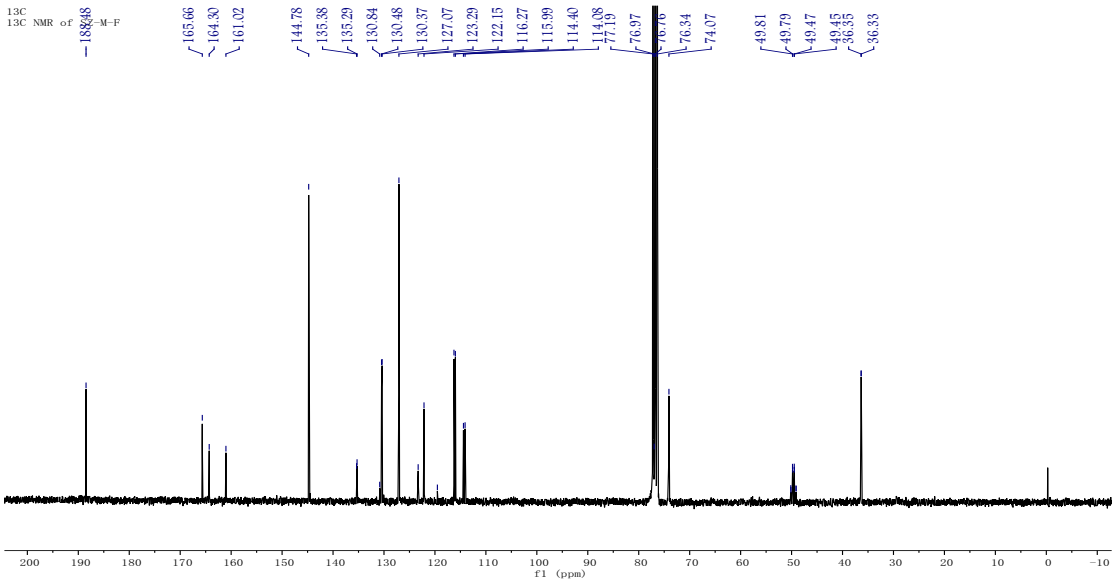

houxuhe-19F
19F NMR of SZ-P-CL
-72.83
f1 (ppm)

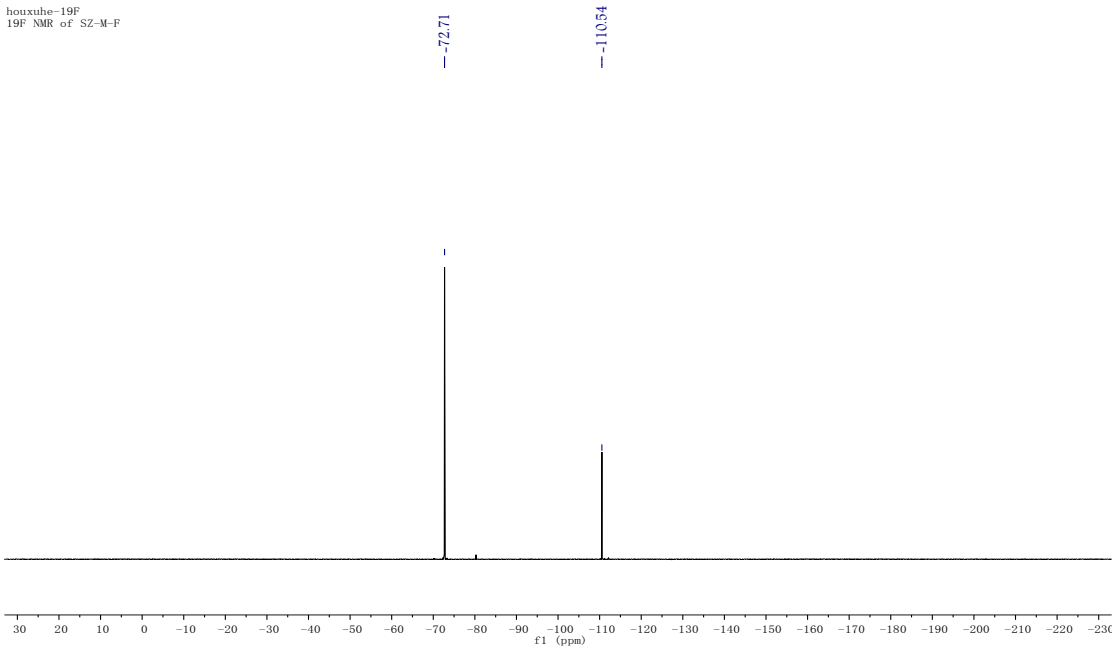

H
SZ-P-CF3
F3C
CF3
NO2
O
S
N
1.00
1.03
2.04
2.05
2.03
2.04
1.95
f1 (ppm)

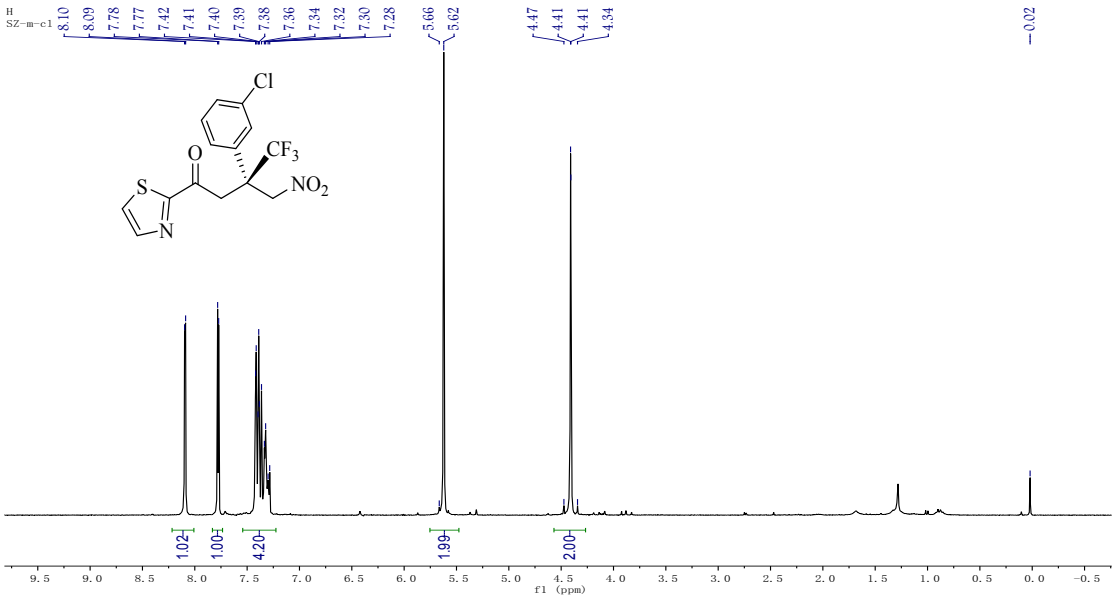

houxuhe-13C
13C NMR of SZ-P-CF3
188.41
165.52
144.83
136.91
131.48
131.04
130.60
127.23
127.09
127.01
125.93
125.89
125.84
125.79
125.07
123.23
121.46
77.20
76.98
76.77
76.35
74.05
50.35
50.00
49.66
49.32
36.34
-0.27
f1 (ppm)

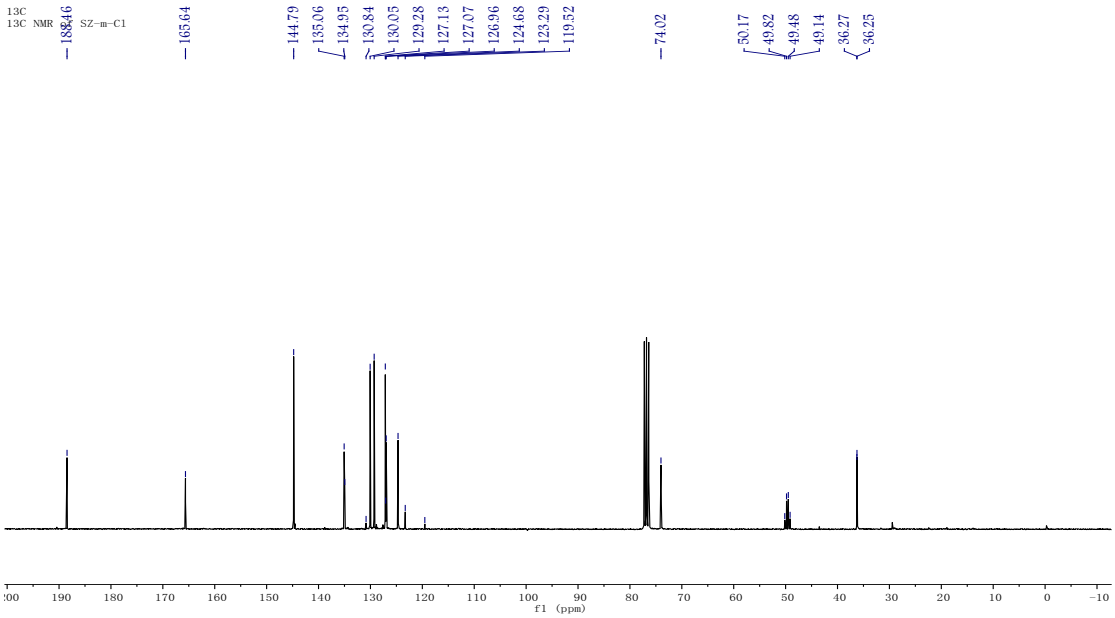

houxuhe-19F
19F NMR of SZ-P-CF3
-63.03
-72.55
f1 (ppm)

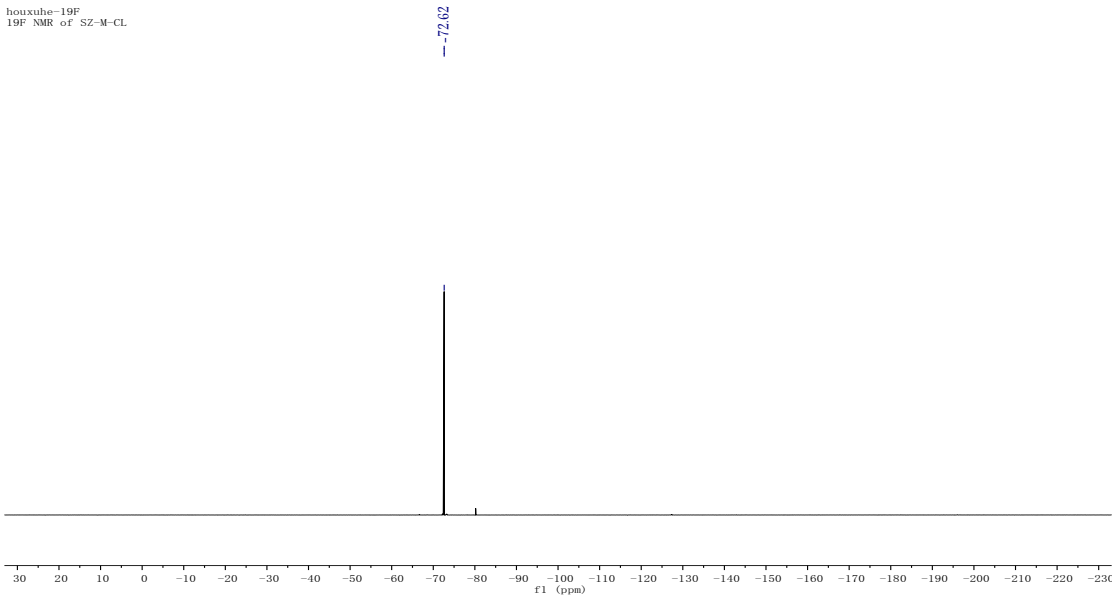

F
CF3
O
S
N
NO2
8.11
8.10
7.80
7.79
7.43
7.41
7.40
7.38
7.29
7.22
7.20
7.16
7.13
7.11
5.63
4.41
0.02
1.00
1.02
1.14
2.94
1.98
1.97
f1 (ppm)

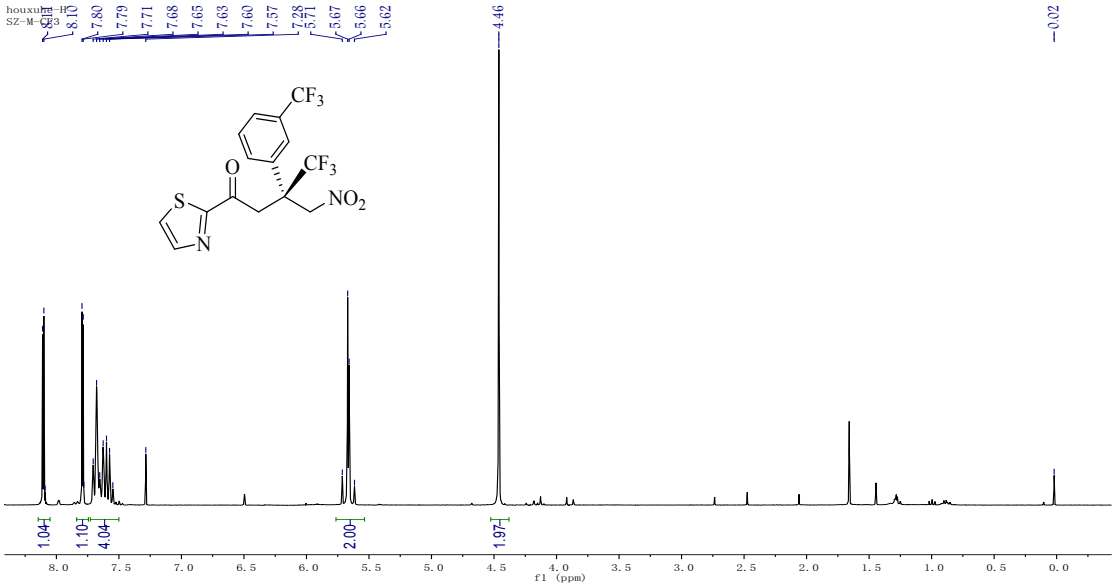

13C
13C NMR of SZ-M-F
188.48
165.66
164.30
161.02
144.78
135.38
135.29
130.84
130.48
130.37
127.07
123.29
122.15
116.27
115.99
114.40
114.08
77.19
76.97
76.76
76.34
74.07
49.81
49.79
49.47
49.45
36.35
36.33
f1 (ppm)

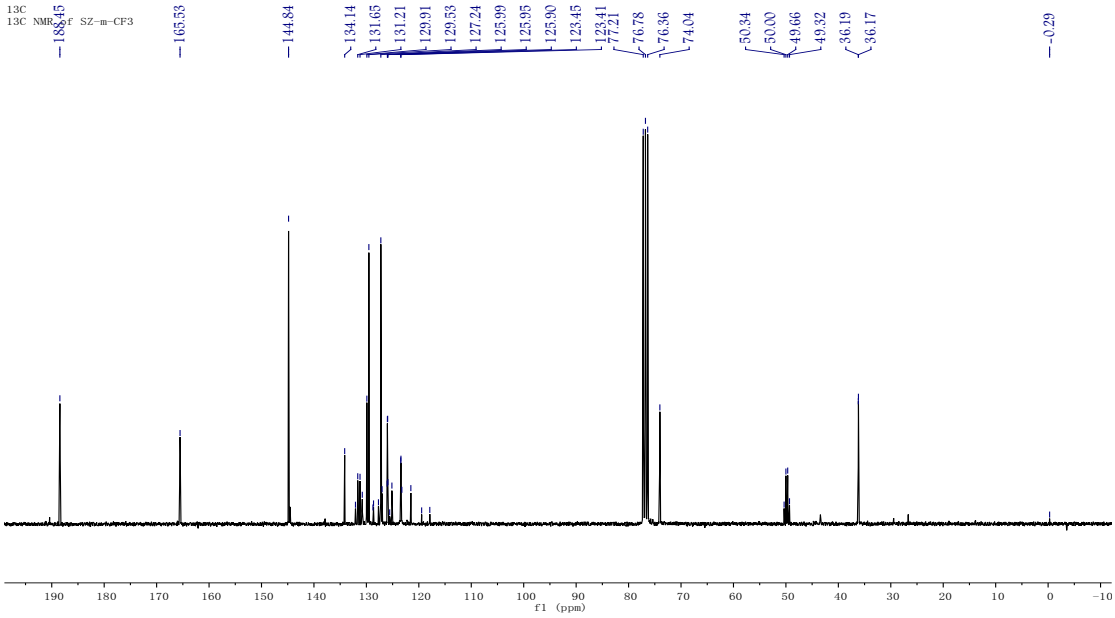

houxuhe-19F
19F NMR of SZ-M-F
-72.71
-110.54
f1 (ppm)

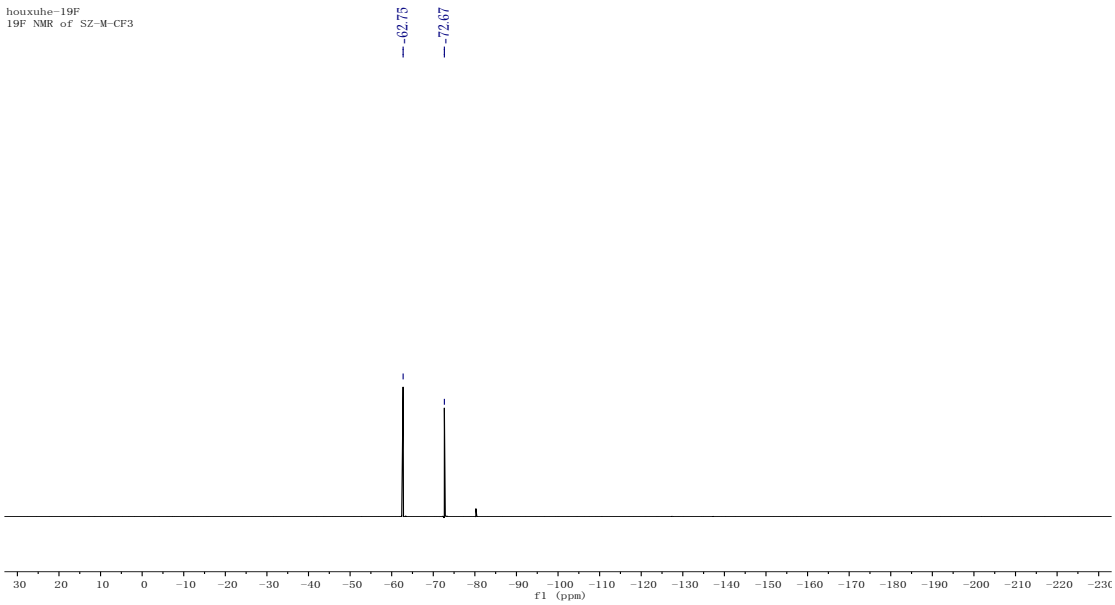

H
SZ-m-c1
8.10
8.09
7.78
7.77
7.42
7.41
7.40
7.39
7.38
7.36
7.34
7.32
7.30
7.28
5.66
5.62
4.47
4.41
4.41
4.34
0.02
Cl
O
CF3
NO2
S
N
1.02
1.00
4.20
1.99
2.00
f1 (ppm)

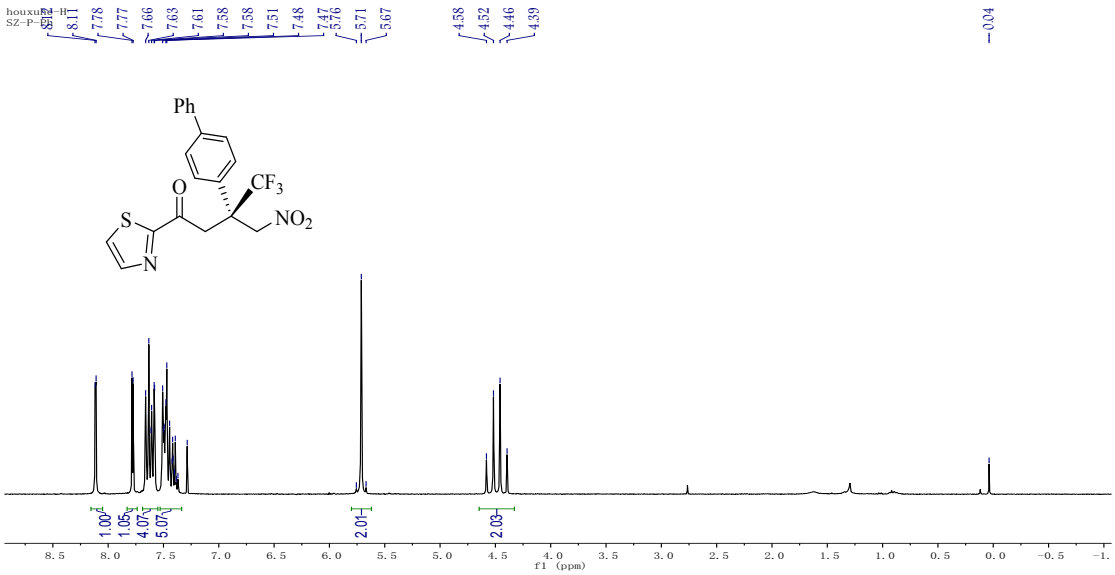

13C
13C NMR SZ-m-C1
188.46
165.64
144.79
135.06
134.95
130.84
130.05
129.28
127.13
127.07
126.96
124.68
123.29
119.52
74.02
50.17
49.82
49.48
49.14
36.27
36.25
f1 (ppm)

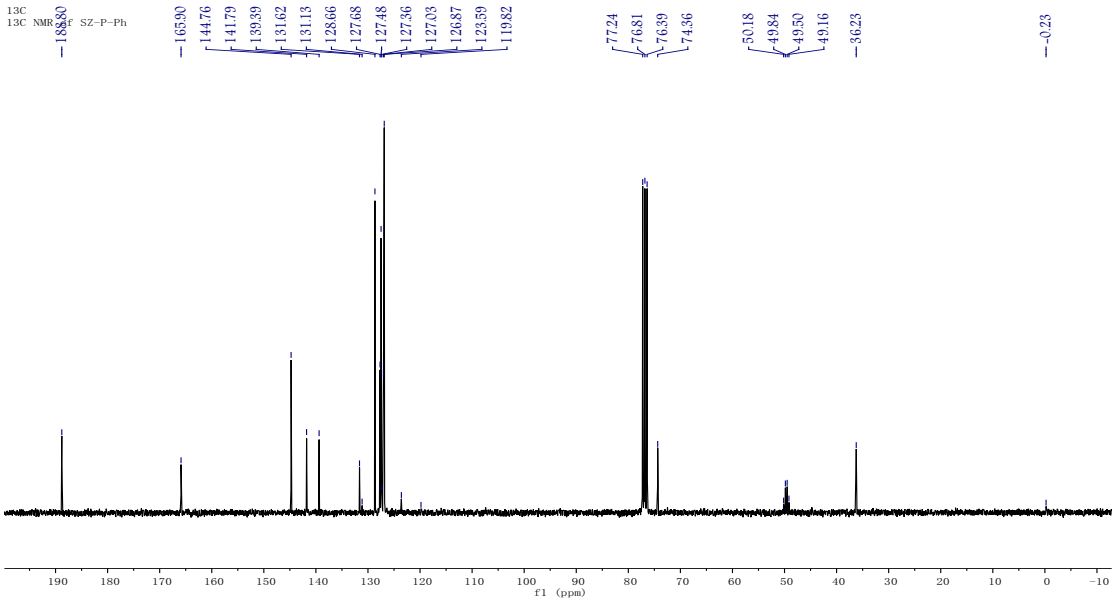

houxuhe-19F
19F NMR of SZ-M-CL
-72.62
f1 (ppm)

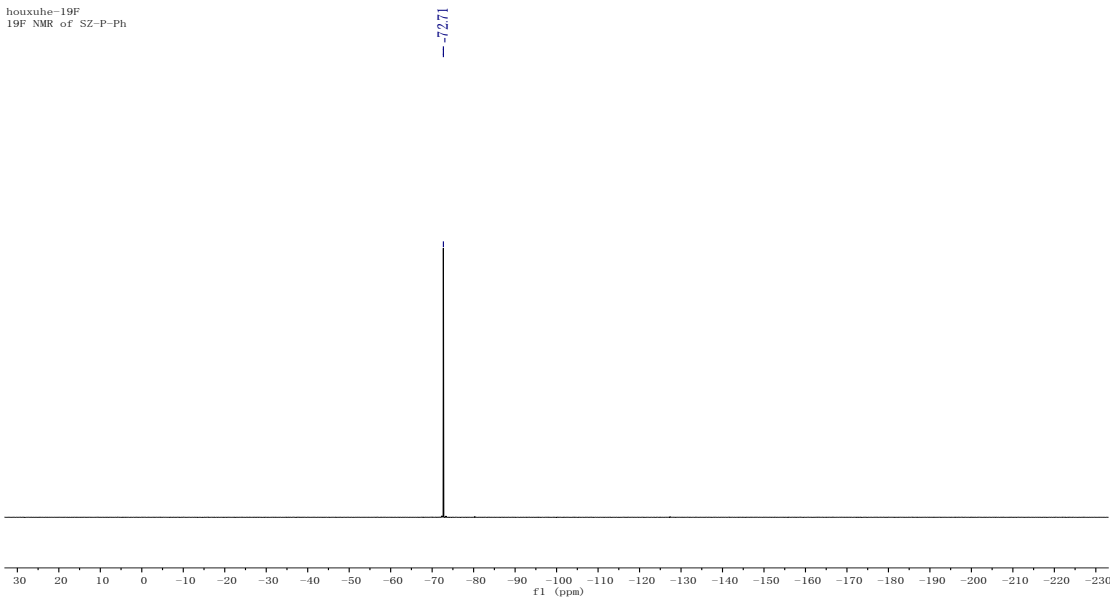

houxuhe-H
SZ-M-CF3
8.10
7.80
7.79
7.71
7.68
7.65
7.63
7.60
7.57
7.28
5.71
5.67
5.66
5.62
4.46
0.02
CF3
CF3
O
S
N
NO2
1.04
1.10
4.04
2.00
1.97
f1 (ppm)

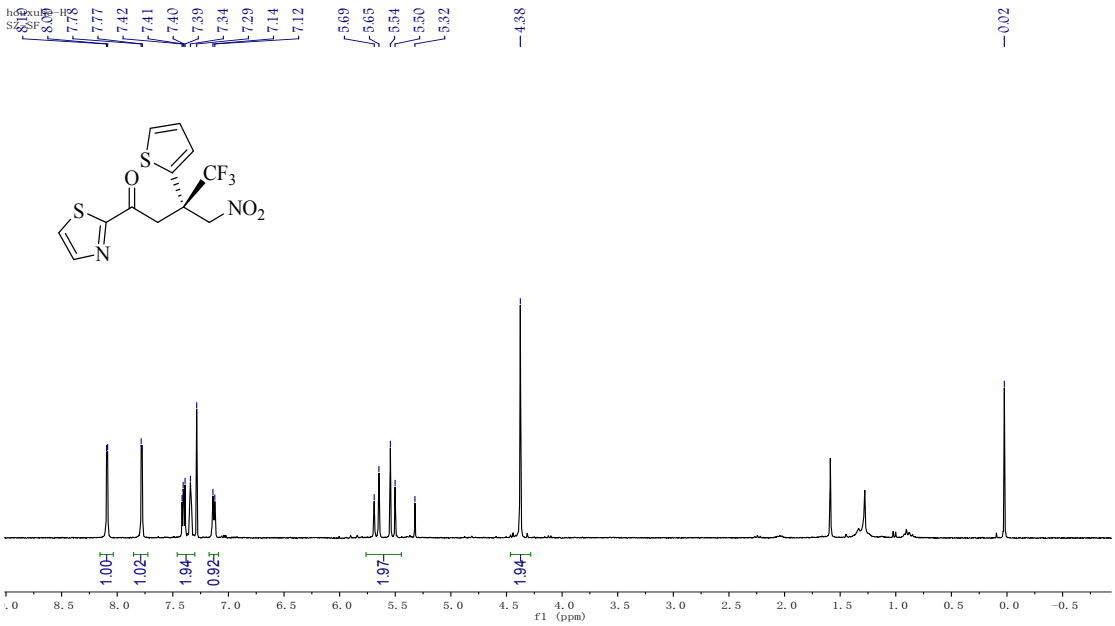

13C
13C NMR of SZ-m-CF3
188.45
165.53
144.84
134.14
131.65
131.21
129.91
129.53
127.24
125.99
125.95
125.90
123.45
123.41
77.21
76.78
76.36
74.04
50.34
50.00
49.66
49.32
36.19
36.17
0.29
f1 (ppm)

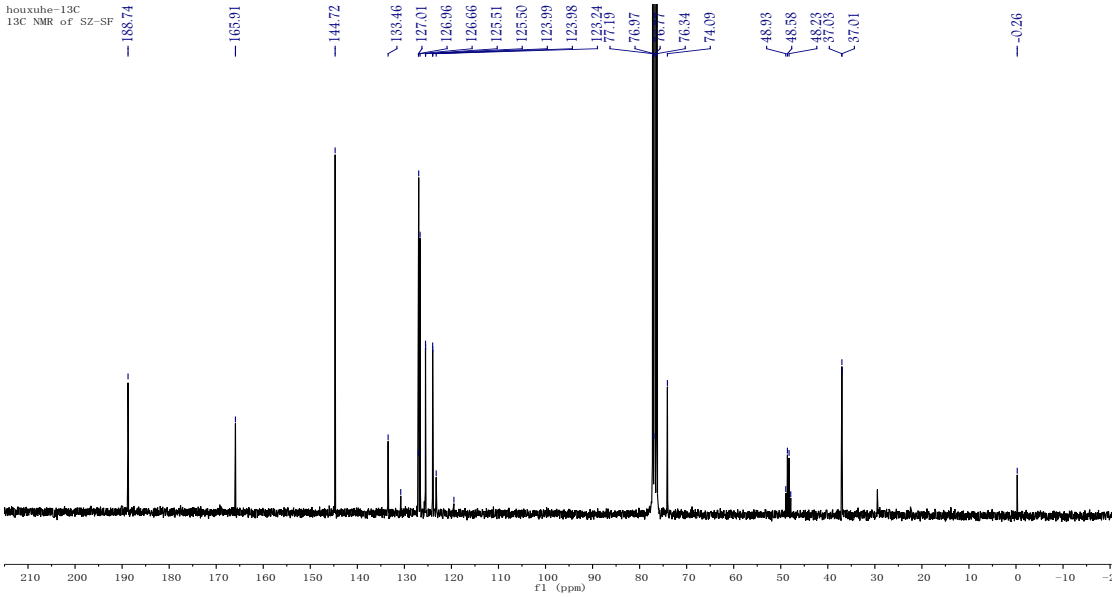

houxuhe-19F
19F NMR of SZ-M-CF3
-62.75
-72.67
f1 (ppm)

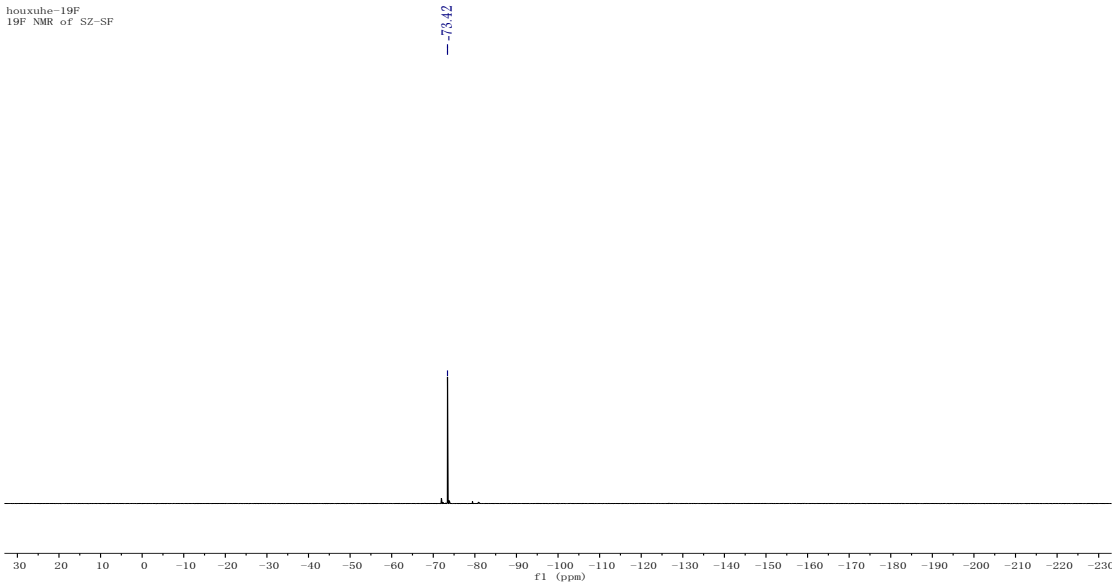

houxuhe-H
SZ-P-Ph
8.11
7.78
7.77
7.66
7.63
7.61
7.58
7.58
7.51
7.48
7.47
7.76
5.71
5.67
4.58
4.52
4.46
4.39
0.04
Ph
O
CF3
NO2
S
N
1.00
1.05
4.07
5.07
2.01
2.03
f1 (ppm)

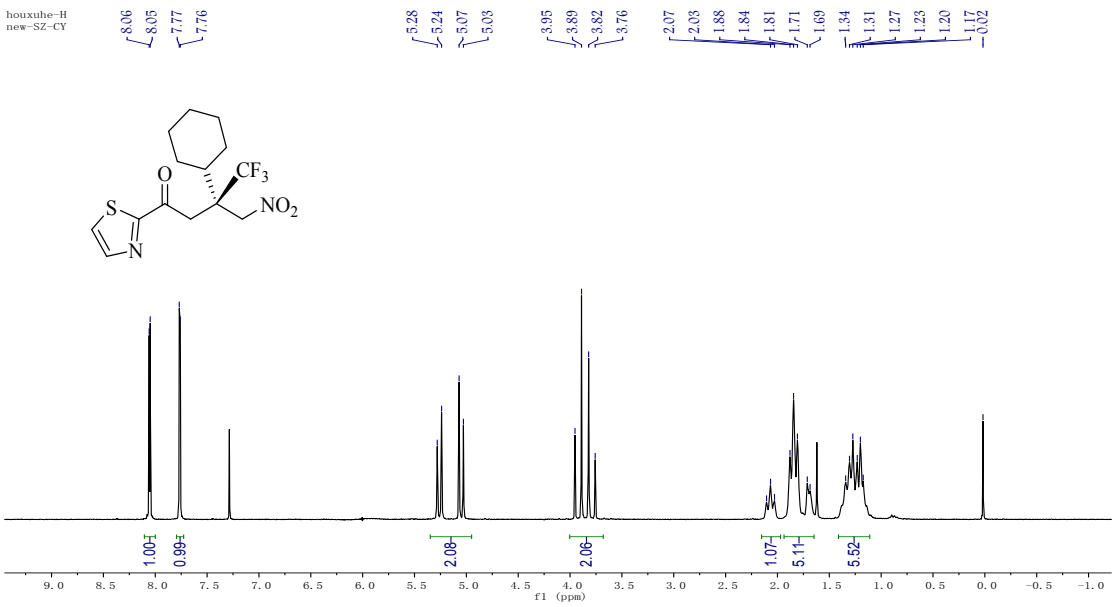

13C
13C NMR of SZ-P-Ph
188.80
165.90
144.76
141.79
139.39
131.62
131.13
128.66
127.68
127.48
127.36
127.03
126.87
123.59
119.82
77.24
76.81
76.39
74.36
50.18
49.84
49.50
49.16
36.23
-0.23
f1 (ppm)

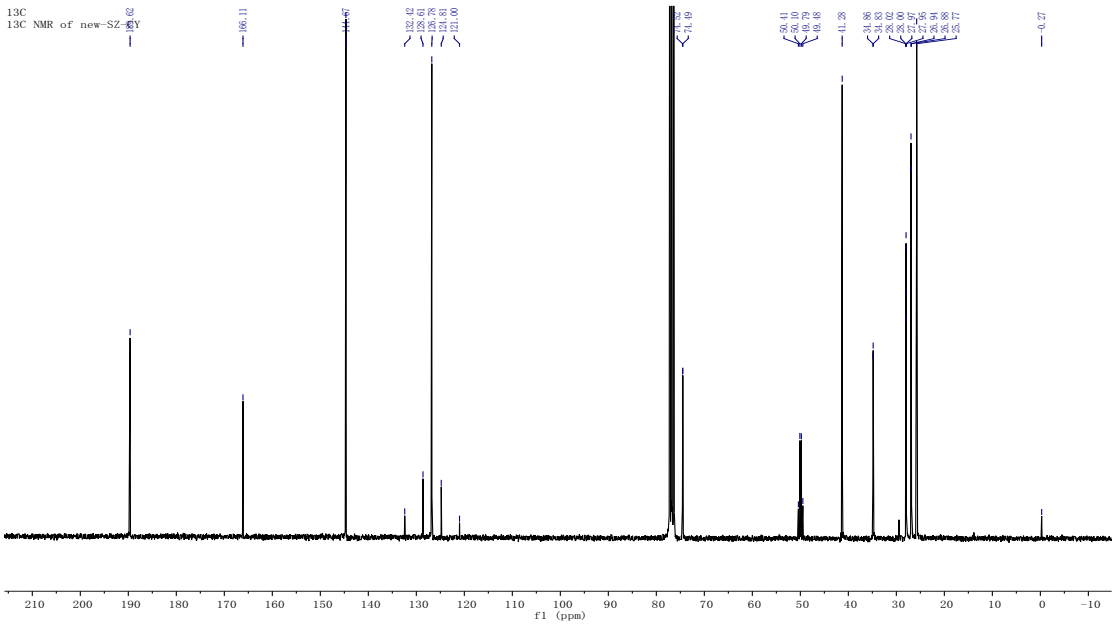

houxuhe-19F
19F NMR of SZ-P-Ph
-72.71
f1 (ppm)

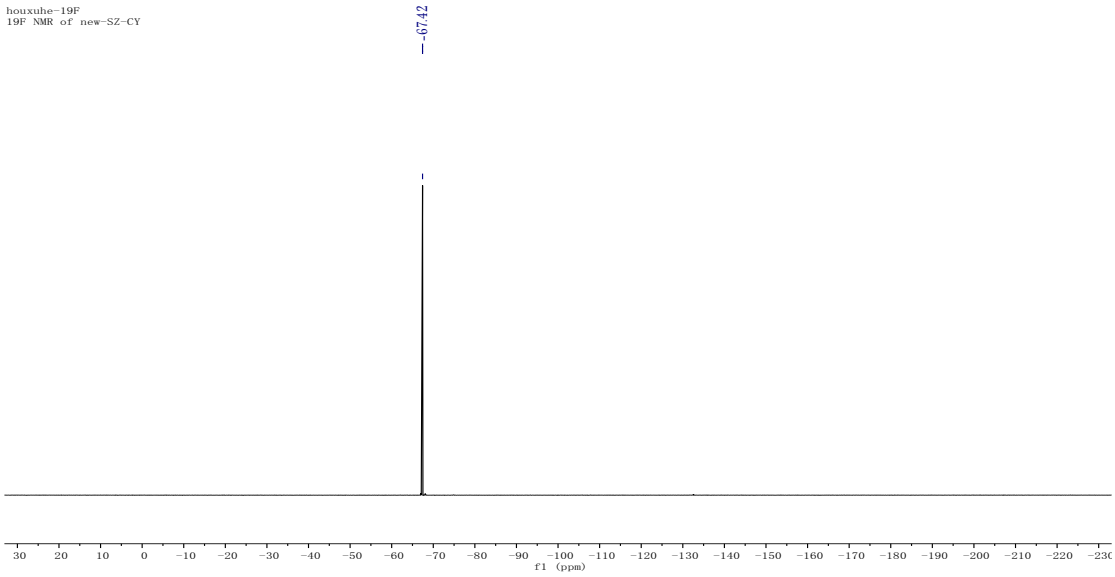

houxuhe-H
SZ-SF
8.08
7.78
7.77
7.42
7.41
7.40
7.39
7.34
7.29
7.14
7.12
5.69
5.65
5.54
5.50
5.32
4.38
0.02
S
O
CF3
NO2
S
N
1.00
1.02
1.94
0.92
1.97
1.94
f1 (ppm)

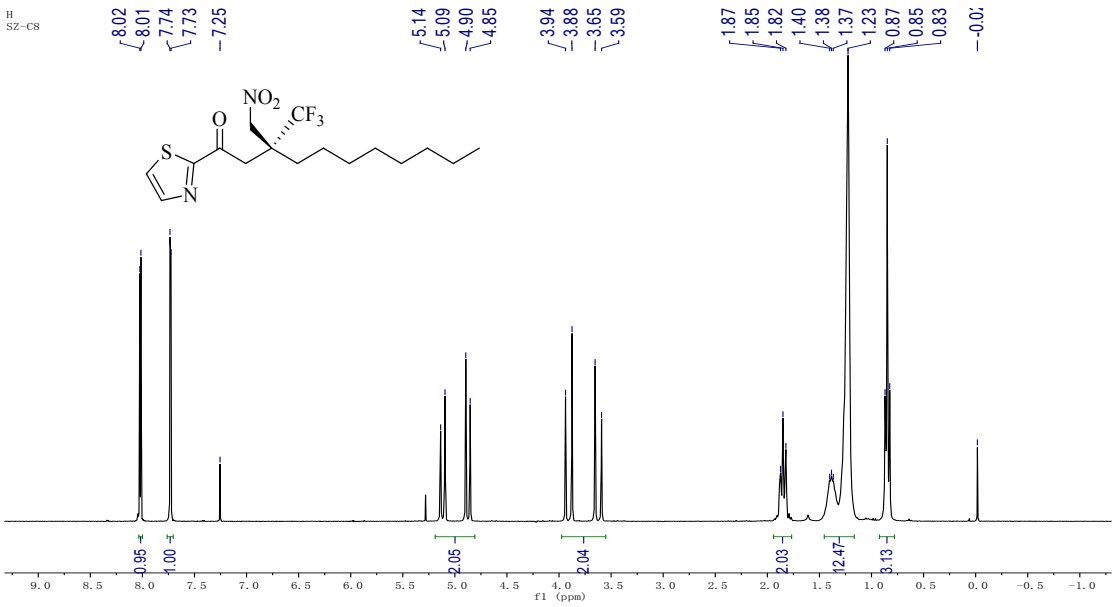

houxuhe-13C
13C NMR of SZ-SF
188.74
165.91
144.72
133.46
127.01
126.96
126.66
125.51
125.50
123.99
123.98
123.24
77.19
76.97
76.77
76.34
74.09
48.93
48.58
48.23
37.03
37.01
-0.26
f1 (ppm)

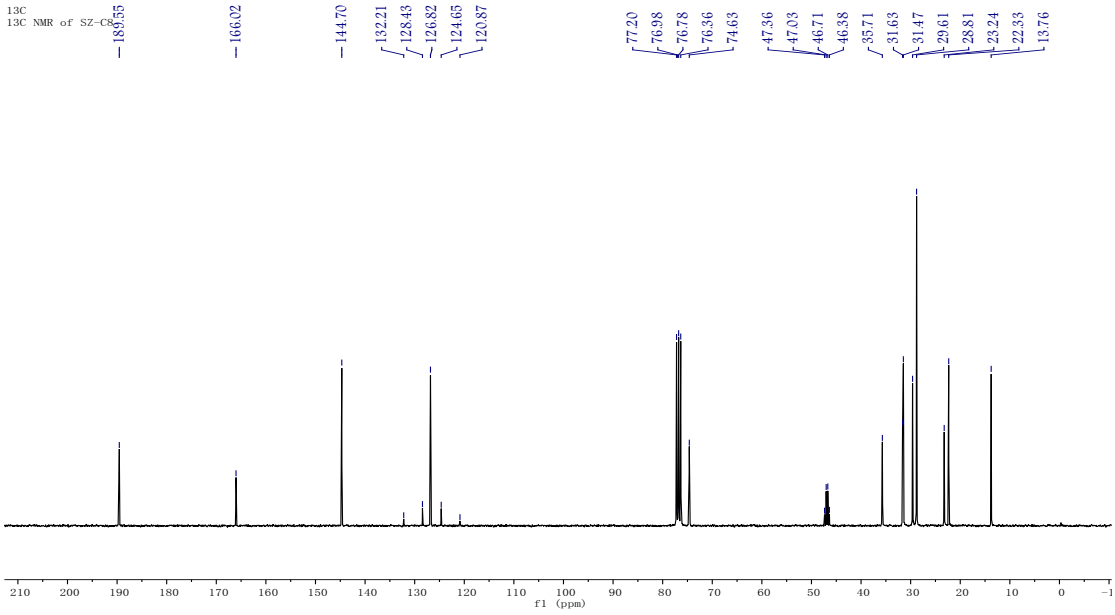

houxuhe-19F
19F NMR of SZ-SF
-73.42
f1 (ppm)

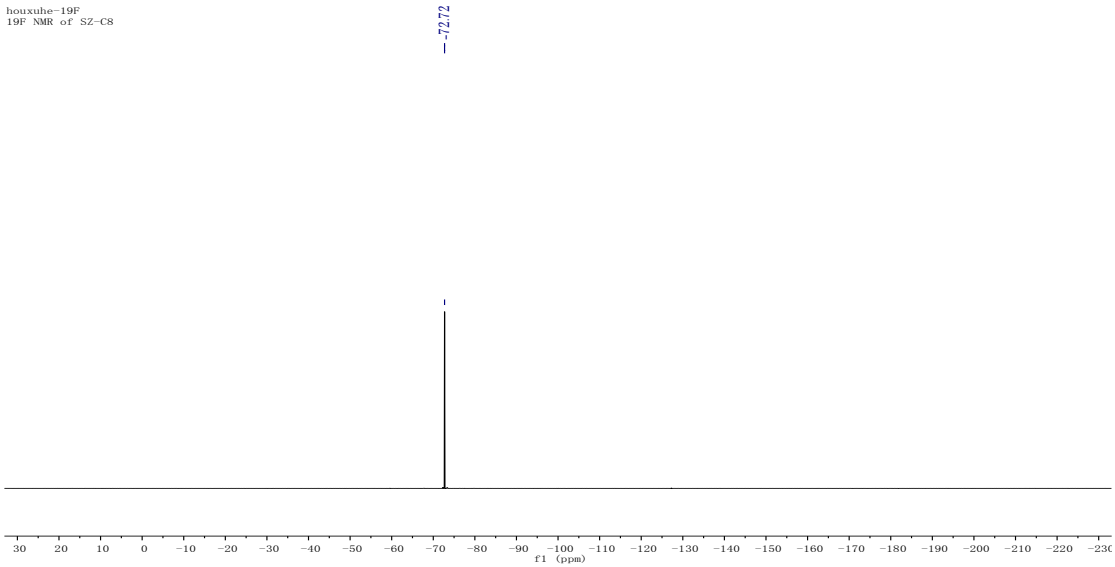

houxuhe-H
new-SZ-CY
8.06
8.05
7.77
7.76
5.28
5.24
5.07
5.03
3.95
3.89
3.82
3.76
2.07
2.03
1.88
1.84
1.81
1.71
1.69
1.34
1.31
1.27
1.23
1.20
1.17
0.02
O
CF3
NO2
S
N
1.00
0.99
2.08
2.06
1.07
5.11
5.52
f1 (ppm)

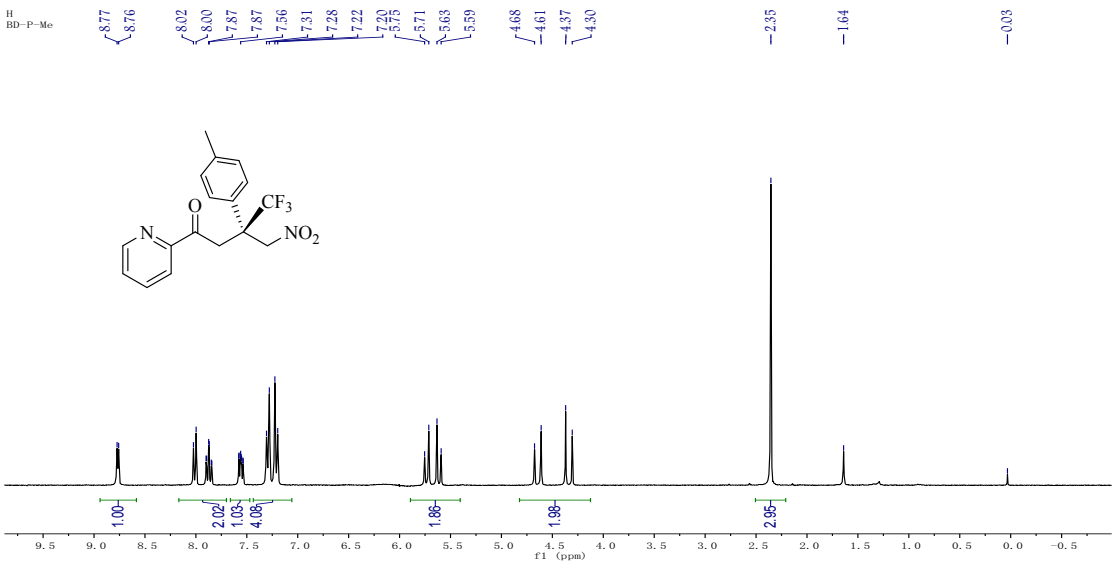

13C
13C NMR of new-SZ-CY
190.62
166.11
144.67
132.42
130.63
128.78
124.81
121.00
74.32
74.49
50.41
50.10
49.79
49.48
41.25
34.86
34.83
28.02
26.00
25.57
25.45
25.94
25.88
25.77
0.27
f1 (ppm)

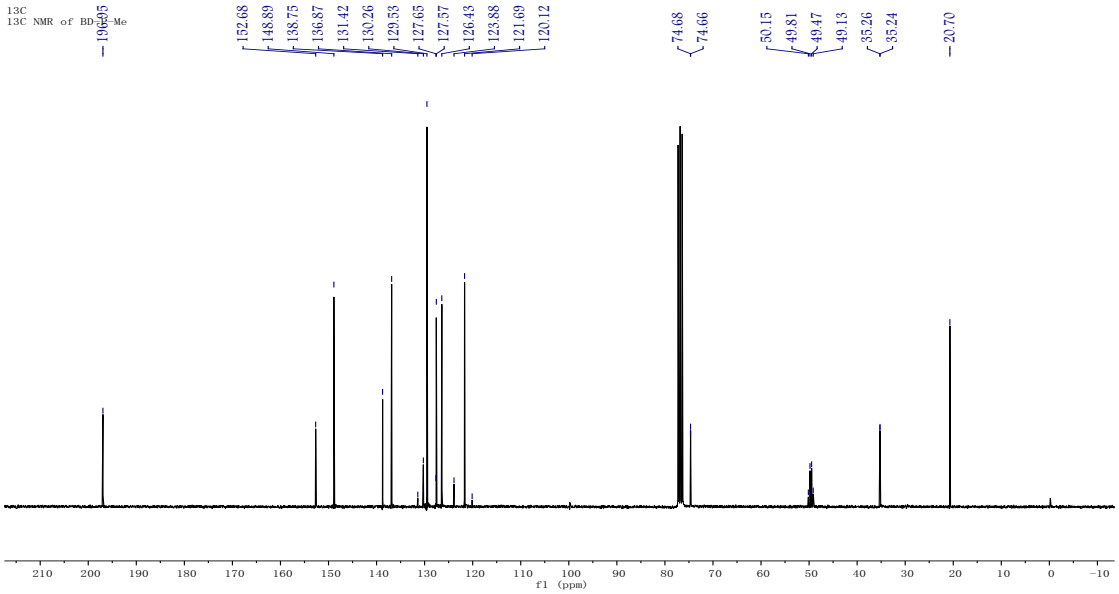

houxuhe-19F
19F NMR of new-SZ-CY
-67.42
f1 (ppm)

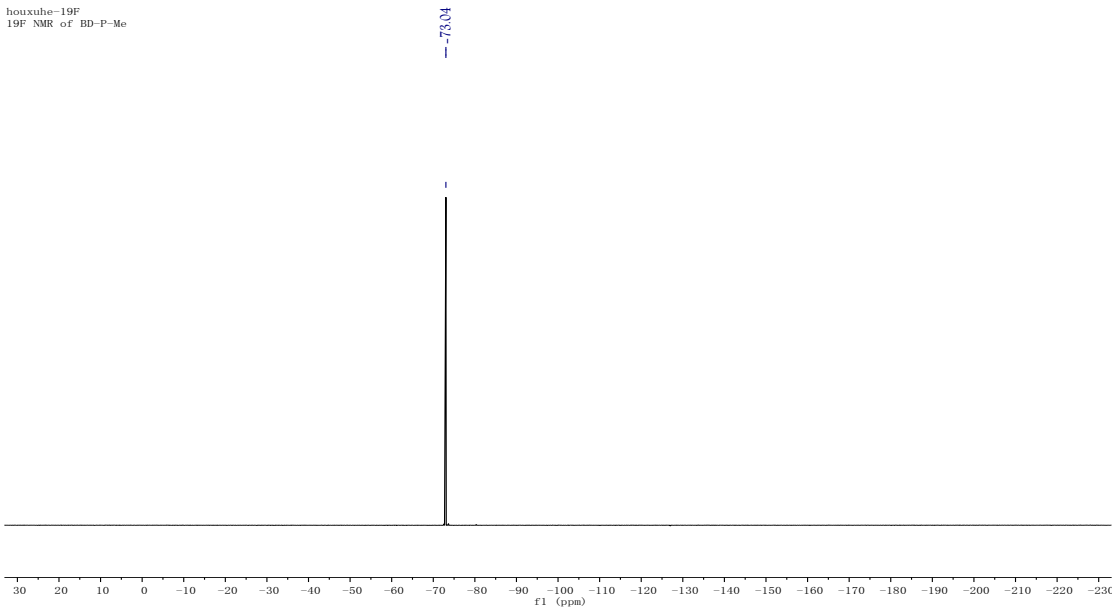

H
SZ-C8
8.02
8.01
7.74
7.73
7.25
5.14
5.09
4.90
4.85
3.94
3.88
3.65
3.59
1.87
1.85
1.82
1.40
1.38
1.37
1.23
0.87
0.85
0.83
NO2
CF3
O
S
N
0.95
1.00
2.05
2.04
2.03
12.47
3.13
f1 (ppm)

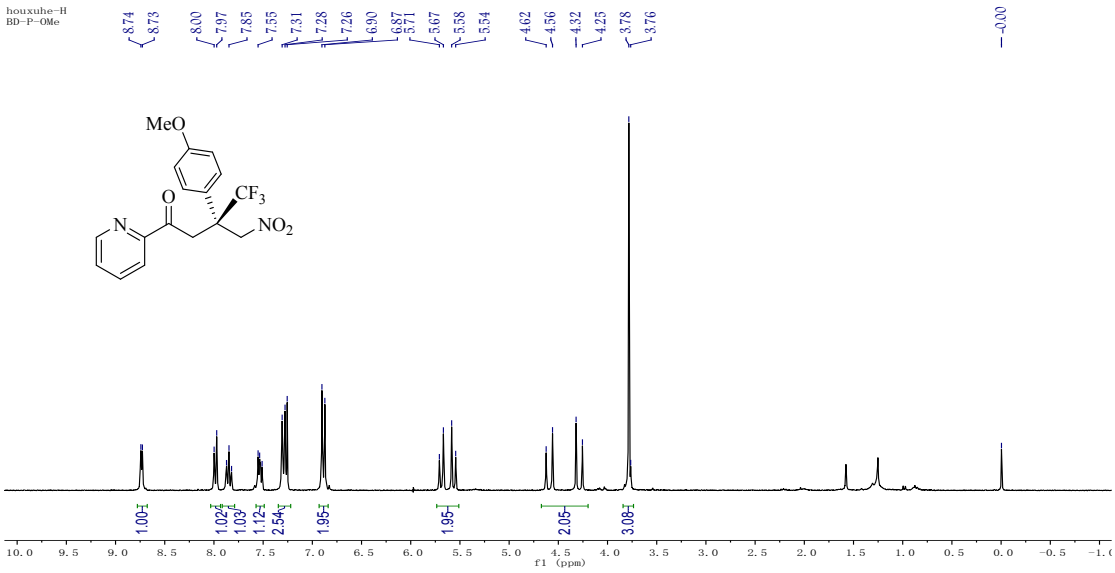

13C
13C NMR of SZ-C8
189.55
166.02
144.70
132.21
128.43
126.82
124.65
120.87
77.20
76.98
76.78
76.36
74.63
47.36
47.03
46.71
46.38
35.71
31.63
31.47
29.61
28.81
23.24
22.33
13.76
f1 (ppm)

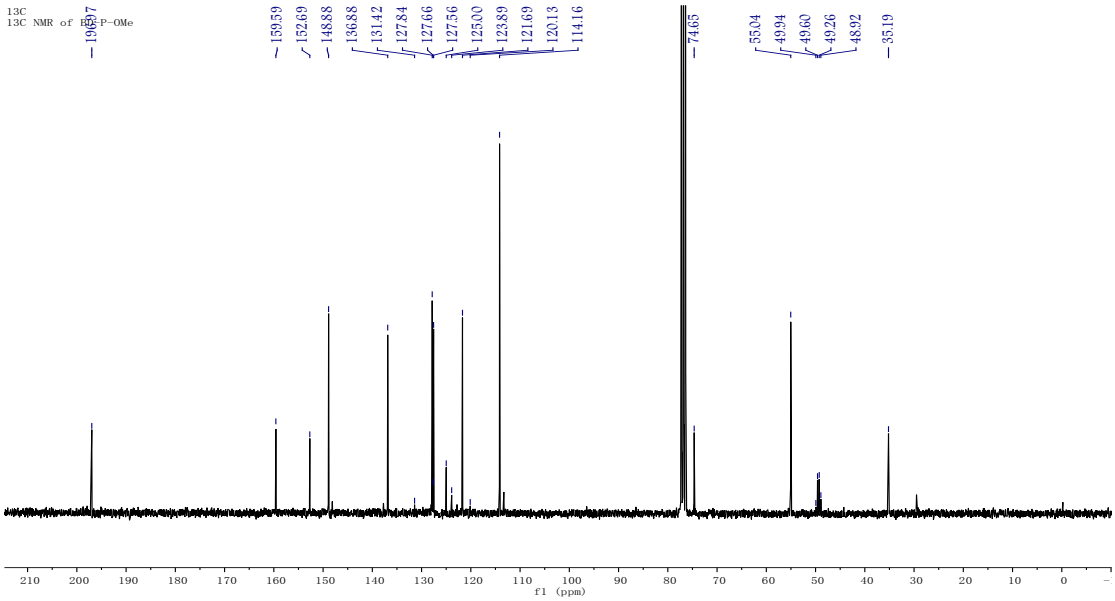

houxuhe-19F
19F NMR of SZ-C8
-72.72
f1 (ppm)

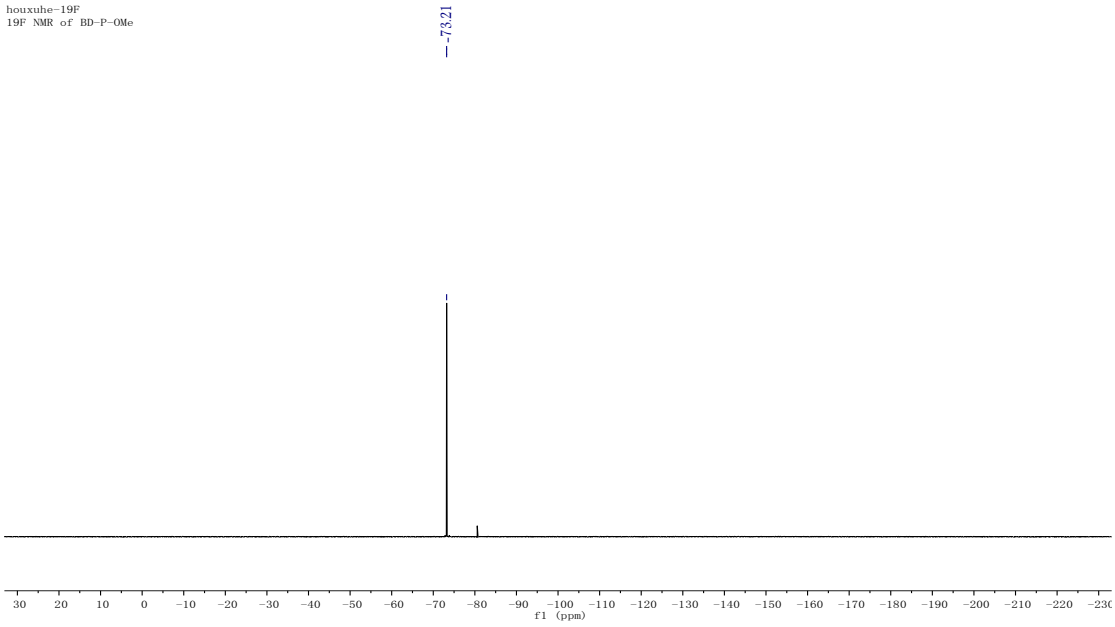

H
BD-P-Me
8.77
8.76
8.02
8.00
7.87
7.87
7.56
7.31
7.28
7.22
7.20
5.75
5.71
5.63
5.59
4.68
4.61
4.37
4.30
2.35
1.64
0.03
O
CF3
N
NO2
1.00
2.02
1.03
4.08
1.86
1.98
2.95
f1 (ppm)

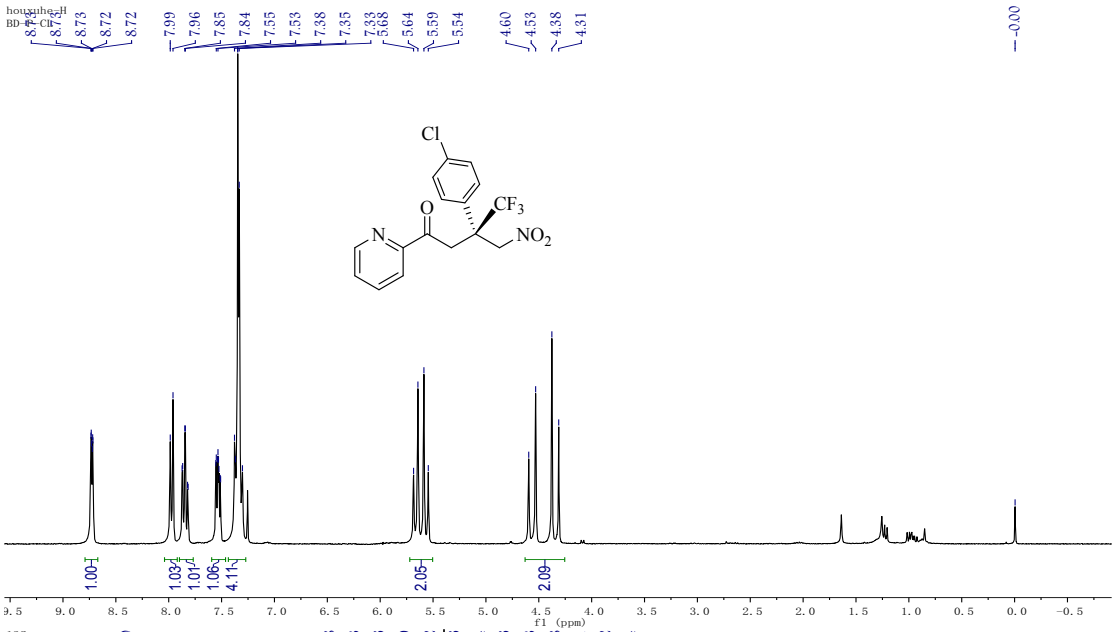

13C
13C NMR of BD-P-Me
196.35
152.68
148.89
138.75
136.87
131.42
130.26
129.53
127.65
127.57
126.43
123.88
121.69
120.12
74.68
74.66
50.15
49.81
49.47
49.13
35.26
35.24
20.70
f1 (ppm)

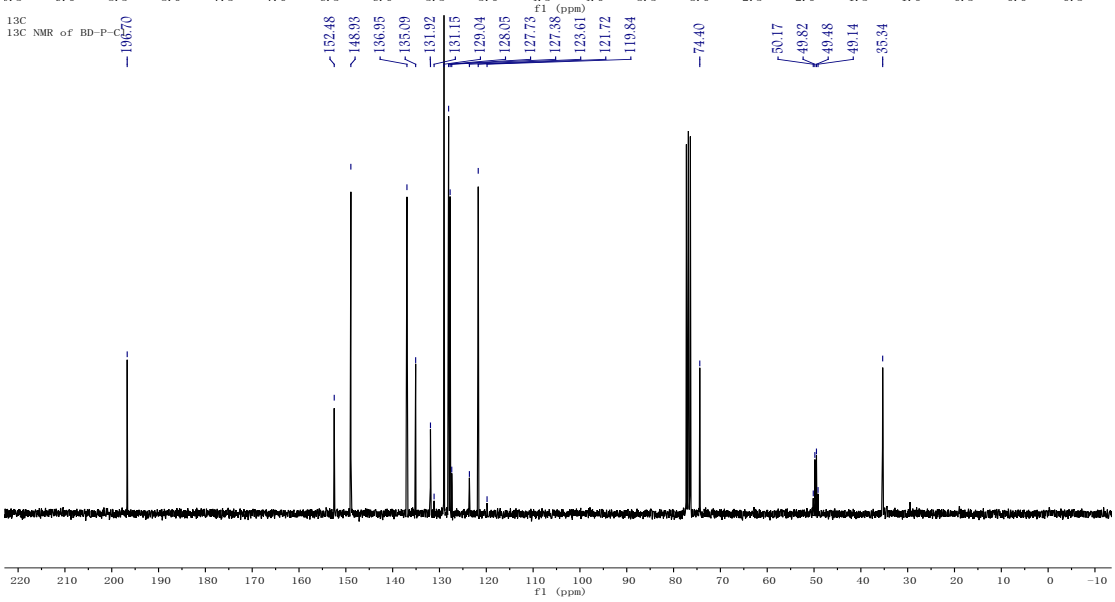

houxuhe-19F
19F NMR of BD-P-Me
-73.04
f1 (ppm)

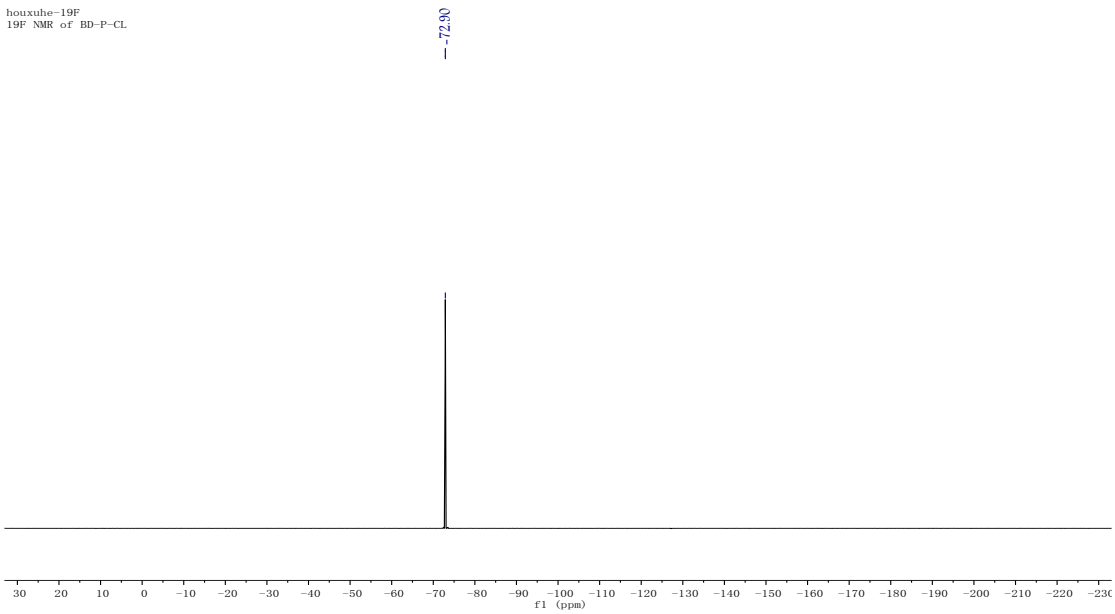

houxuhe-H
BD-P-OMe
8.74
8.73
8.00
7.97
7.85
7.55
7.31
7.28
7.26
6.90
6.87
5.71
5.67
5.58
5.54
4.62
4.56
4.32
4.25
3.78
3.76
0.00
MeO
O
CF3
N
NO2
1.00
1.02
1.09
1.12
2.54
1.95
1.95
2.05
3.08
f1 (ppm)


13C
13C NMR of BD-P-OMe
190.97
159.59
152.69
148.88
136.88
131.42
127.84
127.66
127.56
125.00
123.89
121.69
120.13
114.16
74.65
55.04
49.94
49.60
49.26
48.92
35.19
f1 (ppm)


houxuhe-19F
19F NMR of BD-P-OMe
-73.21
f1 (ppm)

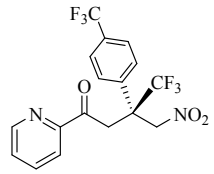

houxuhe-H
8.74
8.73
8.72
8.72
7.99
7.96
7.85
7.84
7.55
7.53
7.38
7.35
7.33
5.68
5.64
5.59
5.54
4.60
4.53
4.38
4.31
-0.00
Cl
O
CF3
N
NO2
1.00
1.03
1.01
1.06
4.11
2.05
2.09
f1 (ppm)

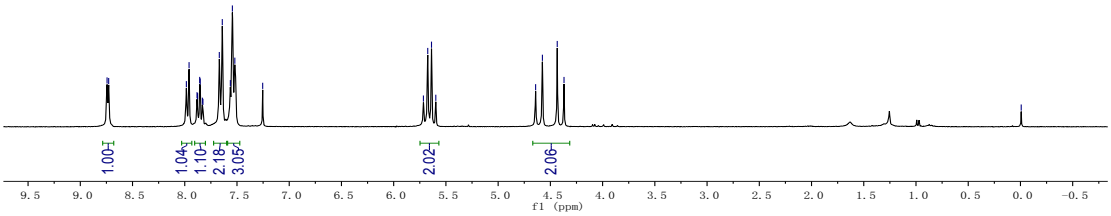

13C
13C NMR of BD-P-CL
196.70
152.48
148.93
136.95
135.09
131.92
131.15
129.04
128.05
127.73
127.38
123.61
121.72
119.84
74.40
50.17
49.82
49.48
49.14
35.34
f1 (ppm)


houxuhe-19F
19F NMR of BD-P-CL
-72.90
f1 (ppm)

houxuhe-H
BD-P-CF3

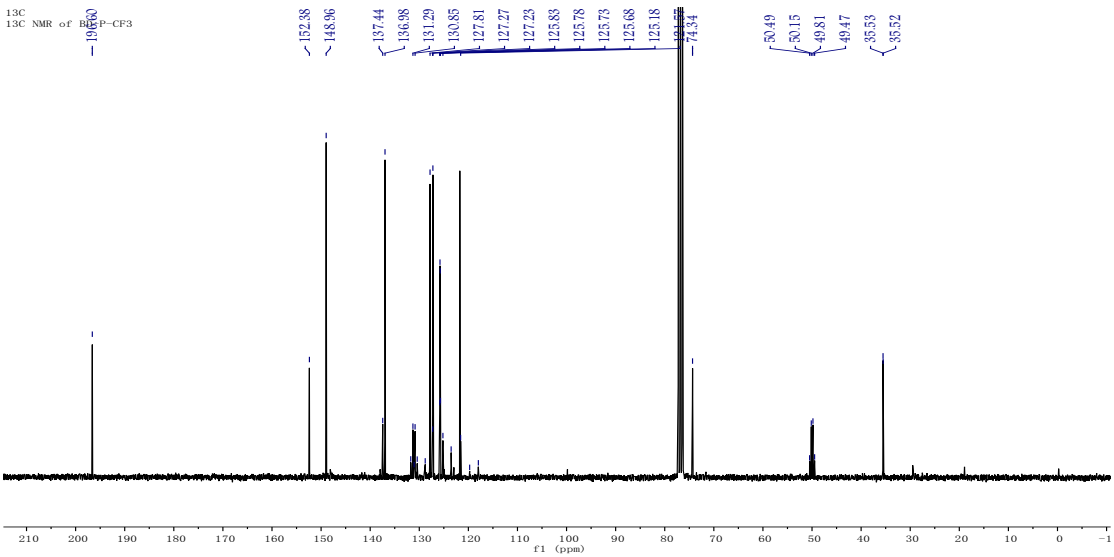
8.74 8.73 7.98 7.96 7.86 7.85 7.67 7.64 7.56 7.54 7.52 5.72 5.67 5.64 5.60 4.64 4.58 4.43 4.37 -0.01





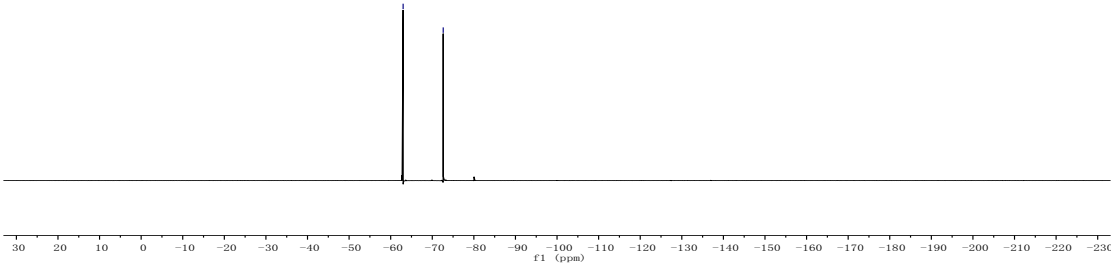
13C
13C NMR of BD-P-CF3

196.60 152.38 148.96 137.44 136.98 131.29 130.85 127.81 127.27 127.23 125.83 125.78 125.73 125.68 125.18 74.34 50.49 50.15 49.81 49.47 35.53 35.52

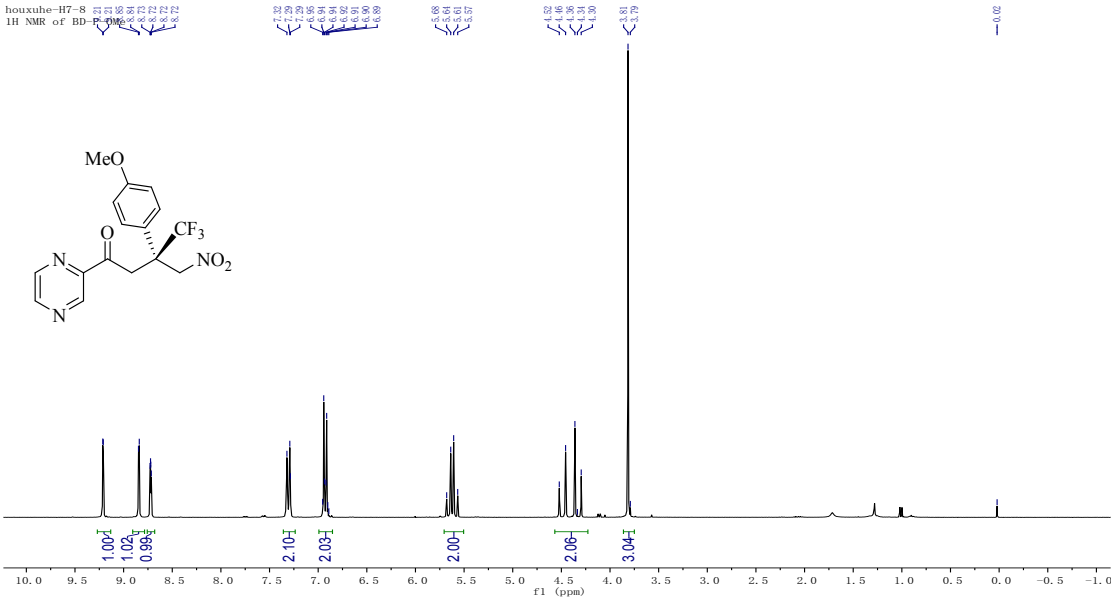


houxuhe-19F
19F NMR of BD-P-CF3

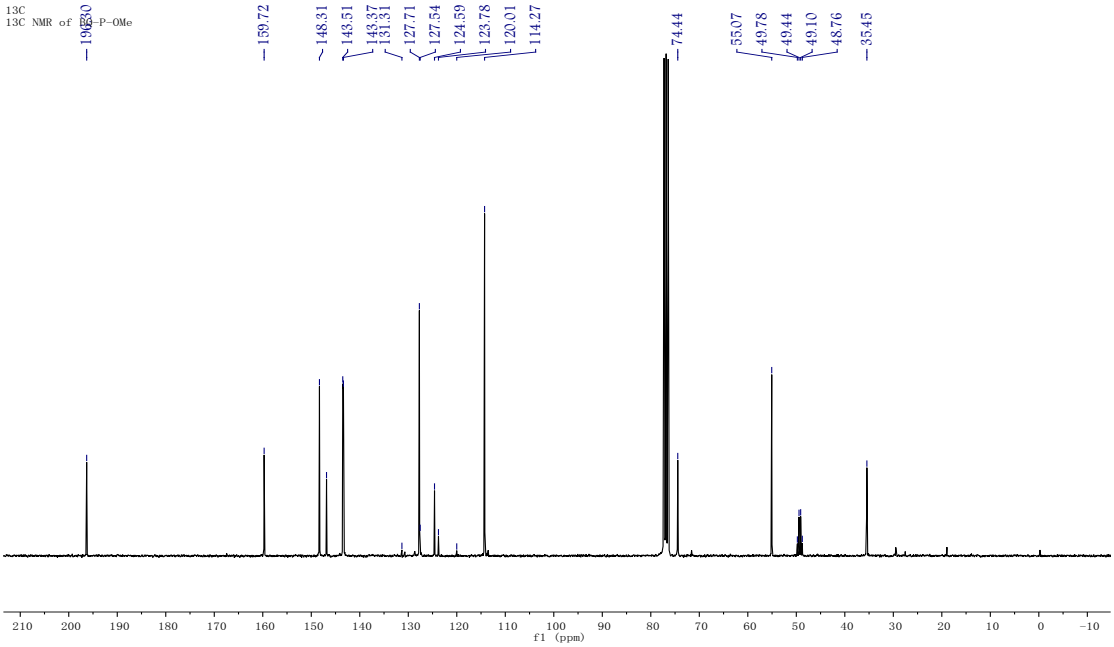
-62.99 -72.63



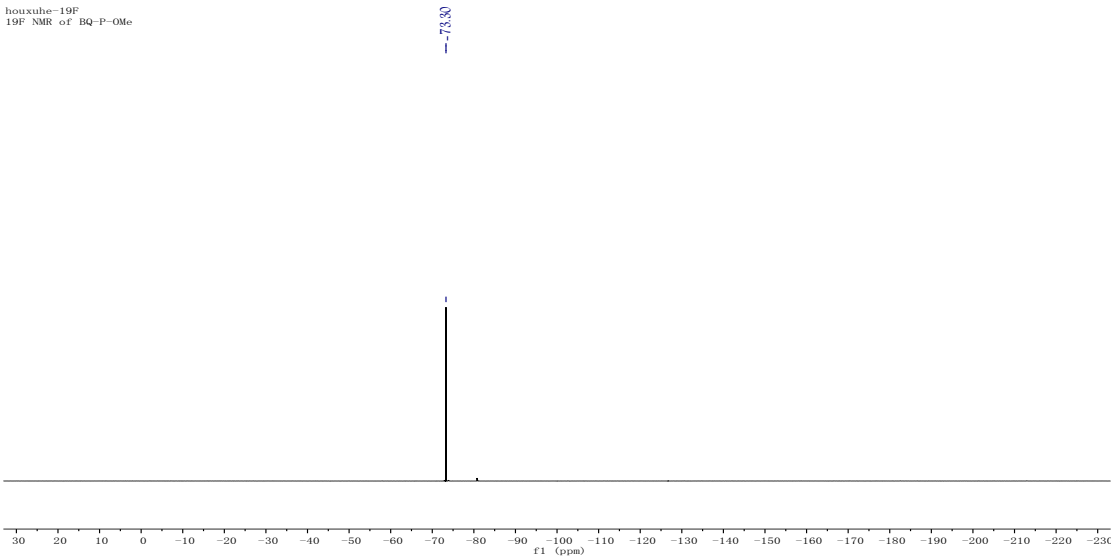
houxuhe-H7-8
1H NMR of BD-P-OMe



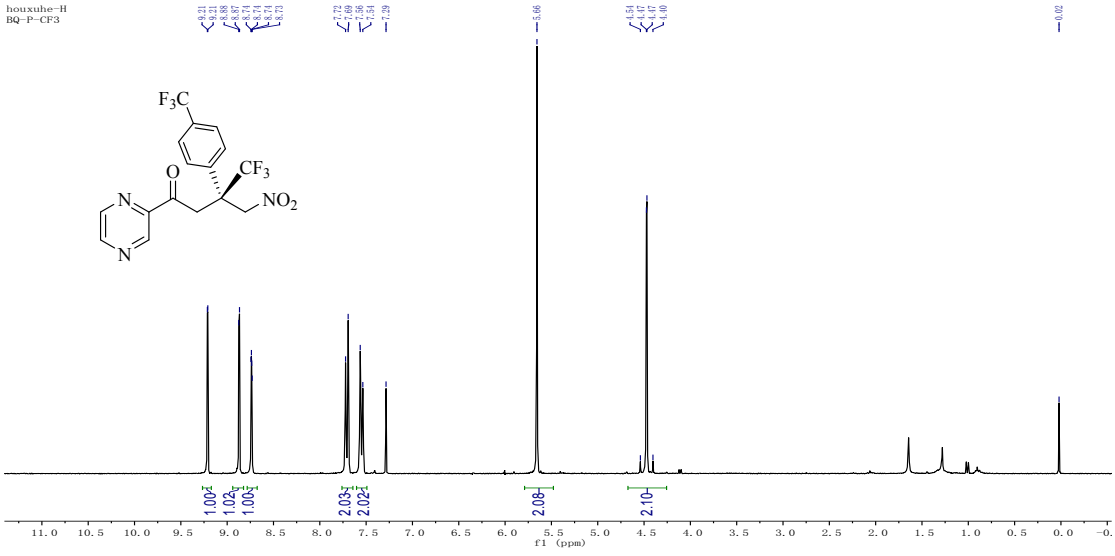
13C
13C NMR of BQ-P-OMe



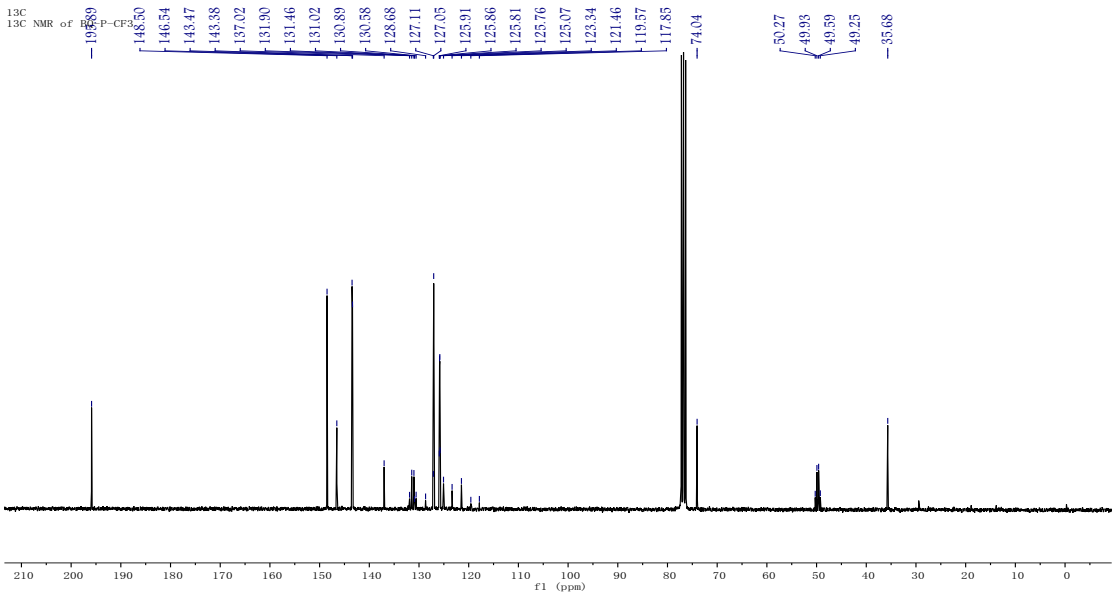
houxuhe-19F
19F NMR of BQ-P-OMe



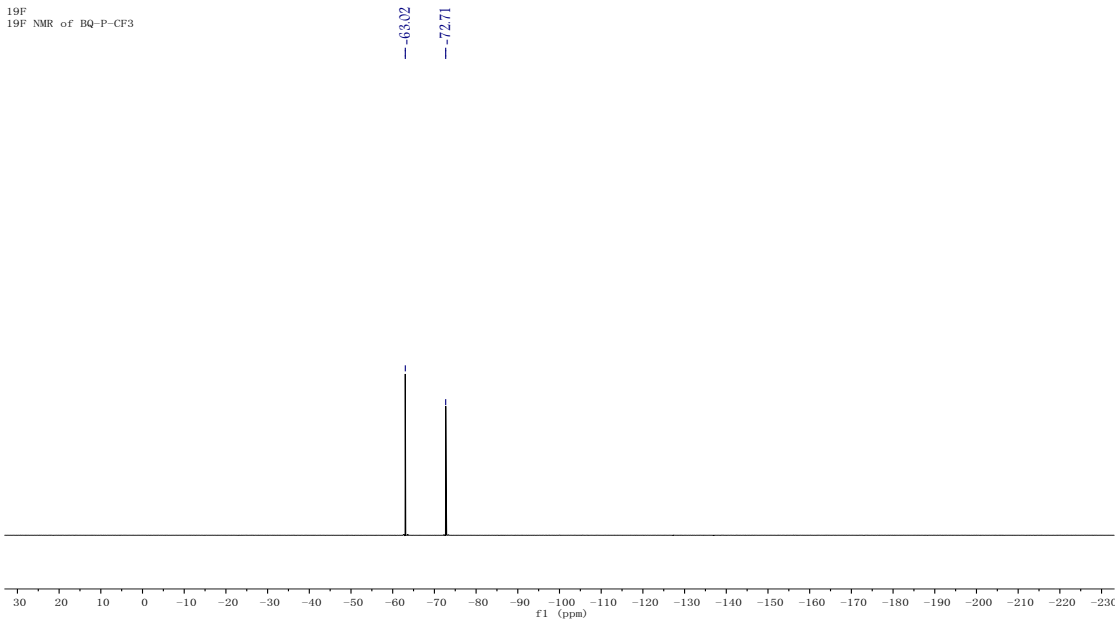
houxuhe-H
BQ-P-CF3



13C
13C NMR of BQ-P-CF3



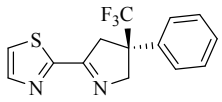
19F
19F NMR of BQ-P-CF3

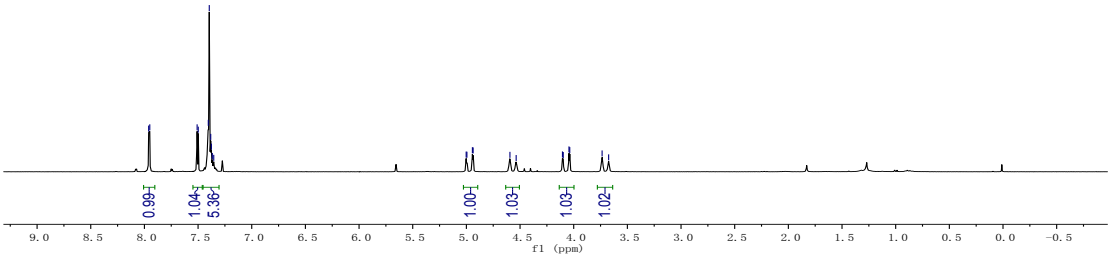


houxuhe-F
SZ-YS

7.96 7.95 7.51 7.50 7.40 7.40 7.38 7.38 7.37 7.35

5.00 5.00 4.94 4.94 4.59 4.54 4.10 4.10 4.04 4.04 3.74 3.67

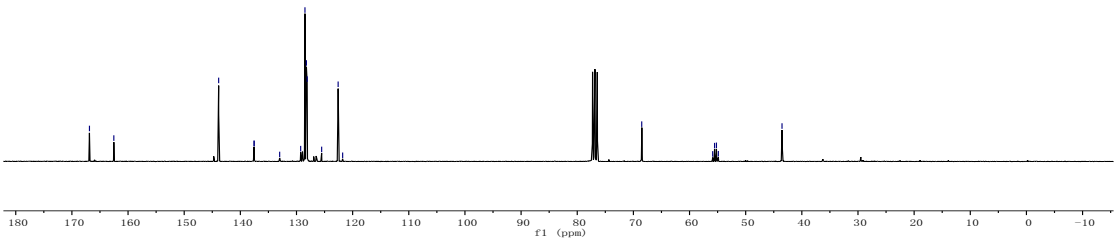




13C
13C NMR of SZ-YS

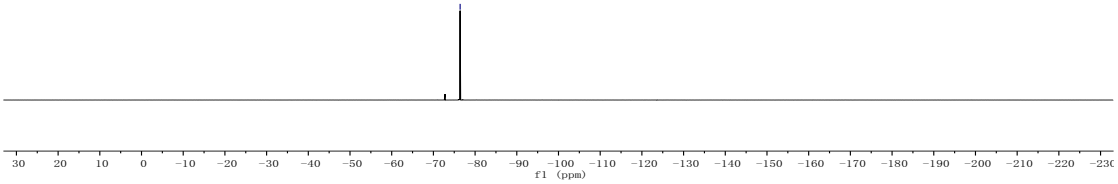
166.87 162.53 143.86 137.56 137.54 133.00 129.26 128.49 128.24 128.10 125.52 122.58 121.78

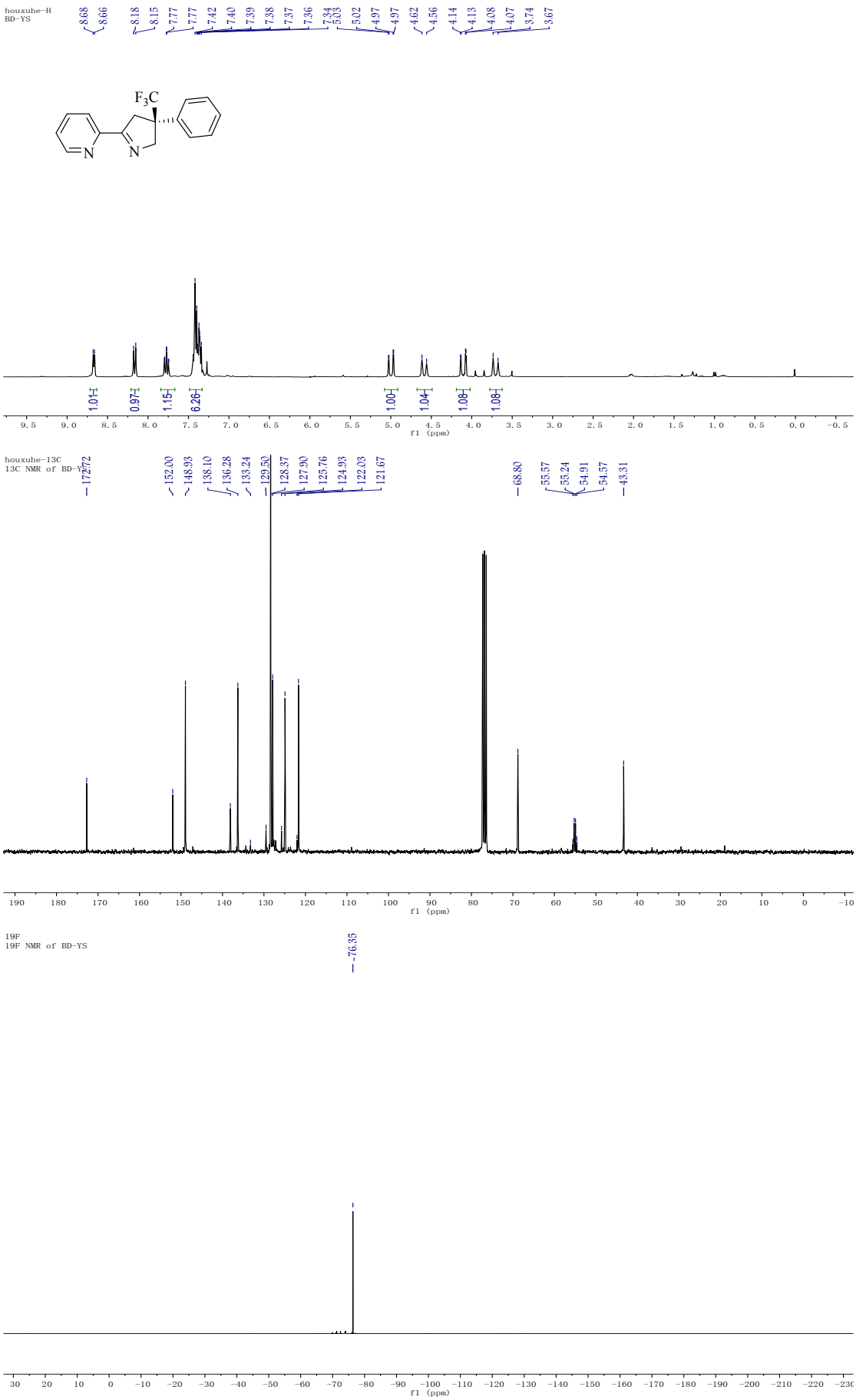
68.52 55.88 55.54 55.21 54.87 43.53



19F
19F NMR of SZ-YS

-76.41




houxuhe-H
BD-YS
houxuhe-13C
13C NMR of BD-YS
19F
19F NMR of BD-YS
f1 (ppm)