Supporting Information

1,3-Dithianes as Acyl Anion Equivalents in Pd-Catalyzed Asymmetric Allylic Substitution

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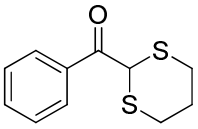
1. General Information

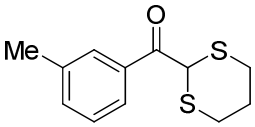
All the reactions were monitored by TLC (thin layer chromatography) using UV light to visualize the course of reaction. Anhydrous THF, DME, Et_2O, 1,4-dioxane, and toluene were prepared by distillation over sodium-benzophenone prior to use. ^1H, ^{19}F, and ^{13}C NMR spectra were obtained using a Varian MERCURY plus-400 spectrometer with TMS as an internal standard. HRMS was performed on a Brucker solariX FTICR Mass Spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. Melting points were measured with SGW X-4 micro melting point apparatus. 2-Aryl-1,3-dithianes **2** were prepared according to literature procedures.[1] All commercially available reagents were used as received.

2. Preparation of 2-Aroyl-1,3-dithianes 4

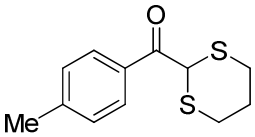
General procedure: To a solution of 1,3-dithiane (601 mg, 5 mmol) in THF (10 mL) at −40 °C was added *n*-BuLi (5 mmol, 2.5 M in hexane), and the solution was stirred for 1 h. This mixture was added dropwise to a solution of ethyl benzoates (6 mmol) in THF (10 mL) at −40 °C. The solution was slowly warmed to RT and stirred overnight. The reaction was quenched with water and diluted with EtOAc (90 mL). The resulting mixture was washed with 1M HCl, H_2O, and brine, dried over Na_2SO_4, and then concentrated in vacuum. The residue was purified by flash column chromatography to give the corresponding 2-aroyl-1,3-dithianes.



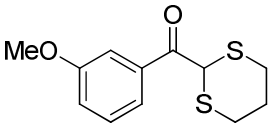
(1,3-Dithian-2-yl)(phenyl)methanone (4a):[2] White solid (448 mg, 40%). mp: 92–93 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98–7.92 (m, 2H), 7.61–7.55 (m, 1H), 7.50–7.45 (m, 2H), 5.15 (s, 1H), 3.45–3.35 (m, 2H), 2.73–2.65 (m, 2H), 2.25–2.00 (m, 2H).



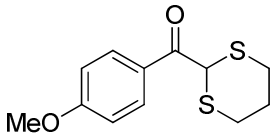
(1,3-Dithian-2-yl)(*m*-tolyl)methanone (4b): Yellow solid (404 mg, 34%). mp: 42–43 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80–7.66 (m, 2H), 7.40–7.26 (m, 2H), 5.14 (s, 1H), 3.43–3.31 (m, 2H), 2.74–2.60 (m, 2H), 2.42 (s, 3H), 2.22–1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.1, 138.8, 134.9, 134.3, 129.4, 128.8, 126.1, 42.9, 26.7, 25.4, 21.6; IR: 2920, 1674, 1275, 656; HRMS (APCI) $[M+H]^+$ calcd for $C_{12}H_{15}OS_2$ 239.0564; found 239.0569.



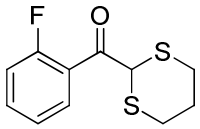
(1,3-Dithian-2-yl)(*p*-tolyl)methanone (4c):[3] Yellow solid (381 mg, 32%). mp: 123–125 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 5.15 (s, 1H), 3.38 (t, J = 12.0 Hz, 2H), 2.68 (ddd, J = 9.2, 6.0, 3.2 Hz, 2H), 2.41 (s, 3H), 2.20–2.00 (m, 2H).



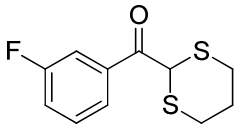
(1,3-Dithian-2-yl)(3-methoxyphenyl)methanone (4d): White solid (520 mg, 41%). mp: 68–69 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.45 (m, 2H), 7.40–7.30 (m, 1H), 7.14–7.04 (m, 1H), 5.12 (s, 1H), 3.84 (s, 3H), 3.42–3.32 (m, 2H), 2.66 (ddd, J = 8.8, 5.6, 2.8 Hz, 2H), 2.18–1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.7, 160.2, 136.2, 129.9, 121.3, 120.0, 113.4, 55.7, 42.8, 26.7, 25.4; IR: 1636, 649; HRMS (APCI) $[M+H]^+$ calcd for $C_{12}H_{15}O_2S_2$ 255.0513; found 255.0513.



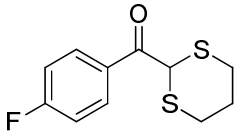
(1,3-Dithian-2-yl)(4-methoxyphenyl)methanone (4e): White solid (493 mg, 38%). mp: 56–57 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.15 (s, 1H), 3.85 (s, 3H), 3.38–3.28 (m, 2H), 2.72–2.64 (m, 2H), 2.20−1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 163.9, 131.3, 127.4, 114.1, 55.7, 43.5, 27.2, 25.5; IR: 2920, 1666, 1262, 1170, 596; HRMS (APCI) $[M+H]^+$ calcd for $C_{12}H_{15}O_2S_2$ 255.0513; found 255.0513.



(1,3-Dithian-2-yl)(2-fluorophenyl)methanone (4f): White solid (423 mg, 35%). mp: 63–64 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96−7.86 (m, 1H), 7.55−7.46 (m, 1H), 7.30–7.18 (m, 1H), 7.13−7.04 (m, 1H), 5.00 (s, 1H), 3.28 (t, J = 12.4 Hz, 2H), 2.61−2.50 (m, 2H), 2.25–1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 160.9 (d, $J_{C\text{-}F}$ = 252.3 Hz), 134.8 (d, $J_{C\text{-}F}$ = 9.1 Hz), 131.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 124.7 (d, d, $J_{C\text{-}F}$ = 3.2 Hz), 123.7 (d, $J_{C\text{-}F}$ = 12.6 Hz), 116.6 (d, $J_{C\text{-}F}$ = 24.1 Hz), 45.6 (d, $J_{C\text{-}F}$ = 8.3 Hz), 25.7, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ –108.5; IR: 2923, 1677, 1608, 1265, 743, 628; HRMS (APCI) $[M+H]^+$ calcd for $C_{11}H_{12}OFS_2$ 243.0314; found 243.0313.

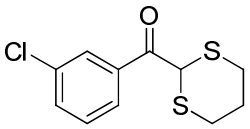


(1,3-Dithian-2-yl)(3-fluorophenyl)methanone (4g): White solid (412 mg, 34%). mp: 76–78 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71−7.58 (m, 2H), 7.49–7.35 (m, 1H), 7.28−7.20 (m, 1H), 5.05 (s, 1H), 3.33 (t, J = 12.0 Hz, 2H), 2.71−2.59 (m, 2H), 2.20–1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 162.8 (d, $J_{C\text{-}F}$ = 246.9 Hz), 136.7 (d, $J_{C\text{-}F}$ = 6.3 Hz), 130.3 (d, $J_{C\text{-}F}$ = 7.7 Hz), 124.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 120.4 (d, $J_{C\text{-}F}$ = 21.4 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22.5 Hz), 42.4, 26.3, 25.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ –111.4; IR: 1654, 673, 496; HRMS (APCI) $[M+H]^+$ calcd for $C_{11}H_{12}OFS_2$ 243.0314; found 243.0313.

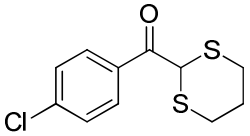


(1,3-Dithian-2-yl)(4-fluorophenyl)methanone (4h): White solid (497 mg, 41%). mp: 88–90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (t, J = 7.2 Hz, 2H), 7.10 (t, J = 8.8 Hz, 2H), 5.09 (s, 1H), 3.31 (t, J = 12.8 Hz, 2H), 2.75–2.60 (m, 2H), 2.20–1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1,

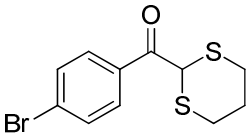
165.7 (d, $J_{C\text{-}F}$ = 254.4 Hz), 131.4 (d, $J_{C\text{-}F}$ = 9.3 Hz), 130.8 (d, $J_{C\text{-}F}$ = 2.9 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.8 Hz), 42.8, 26.6, 25.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ –114.4; IR: 2904, 1642, 596; HRMS (APCI) $[M+H]^+$ calcd for $C_{11}H_{12}OFS_2$ 243.0314; found 243.0318.



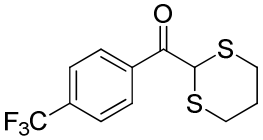
(3-Chlorophenyl)(1,3-dithian-2-yl)methanone (4i): Yellow solid (388 mg, 30%). mp: 88–90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (t, J = 2.0 Hz, 1H), 7.82–7.73 (m, 1H), 7.55−7.50 (m, 1H), 7.40 (t, J = 7.9 Hz, 1H), 5.06 (s, 1H), 3.39−3.30 (m, 2H), 2.67 (ddd, J = 8.8, 5.6, 2.8 Hz, 2H), 2.22–1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 136.6, 135.3, 133.4, 130.2, 129.0, 126.9, 42.7, 26.6, 25.2; IR: 1637, 649; HRMS (APCI) $[M+H]^+$ calcd for $C_{11}H_{12}OS_2Cl$ 259.0018; found 259.0027.



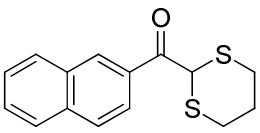
(4-Chlorophenyl)(1,3-dithian-2-yl)methanone (4j): Yellow solid (453 mg, 35%). mp: 97–98 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.81 (m, 2H), 7.47–7.36 (m, 2H), 5.08 (s, 1H), 3.38−3.28 (m, 2H), 2.67 (ddd, J = 8.8, 6.0, 2.8 Hz, 2H), 2.19–1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 140.0, 133.1, 130.4, 129.2, 42.9, 26.8, 25.3; IR: 1642, 610, 413; HRMS (APCI) $[M+H]^+$ calcd for $C_{11}H_{12}OS_2Cl$ 259.0018; found 259.0024.



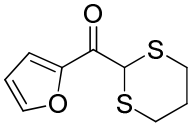
(4-Bromophenyl)(1,3-dithian-2-yl)methanone (4k): White solid (521 mg, 34%). mp: 98–99 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83−7.75 (m, 2H), 7.62−7.55 (m, 2H), 5.07 (s, 1H), 3.49–3.17 (m, 2H), 2.75–2.60 (m, 2H), 2.20–1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 133.6, 132.2, 130.5, 128.7, 42.9, 26.7, 25.3; IR: 1654, 497; HRMS (APCI) $[M+H]^+$ calcd for $C_{11}H_{12}OS_2Br$ 302.9513; found 302.9521.



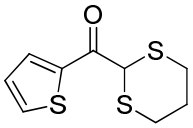
(1,3-Dithian-2-yl)(4-(trifluoromethyl)phenyl)methanone (4l): White solid (585 mg, 40%). mp: 70–72 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H), 5.08 (s, 1H), 3.38−3.28 (m, 2H), 2.73–2.56 (m, 2H), 2.22–1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 137.5, 134.5 (d, $J_{C\text{-}F}$ = 32.7 Hz), 129.0, 126.2 (q, J = 271.7 Hz), 125.7 (q, $J_{C\text{-}F}$ = 3.6 Hz), 42.5, 26.2, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.2; IR: 2925, 1677, 1271, 1067, 668, 648; HRMS (APCI) $[M+H]^+$ calcd for $C_{12}H_{12}OS_2F_3$ 293.0282; found 293.0290.



(1,3-Dithian-2-yl)(naphthalen-2-yl)methanone (4m): Yellow solid (384 mg, 28%). mp: 80–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.05–7.75 (m, 4H), 7.62–7.50 (m, 2H), 5.32 (s, 1H), 3.48−3.36 (m, 2H), 2.80–2.65 (m, 2H), 2.26–2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9, 135.9, 132.7, 132.1, 130.5, 129.9, 128.9, 128.8, 127.9, 127.1, 124.6, 43.1, 26.9, 25.4; IR: 1692, 1384, 610, 408; HRMS (APCI) $[M+H]^+$ calcd for $C_{15}H_{15}OS_2$ 275.0564; found 275.0572.



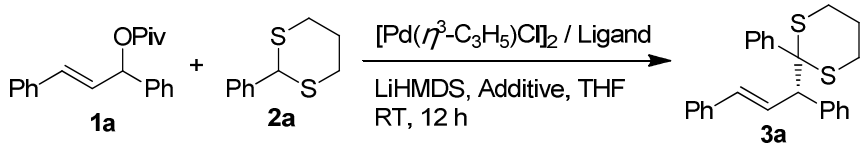
(1,3-Dithian-2-yl)(furan-2-yl)methanone (4n): White solid (396 mg, 37%). mp: 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.55 (m, 1H), 7.28–7.24 (m, 1H), 6.55 (dd, J = 3.6, 1.6 Hz, 1H), 4.89 (s, 1H), 3.50–3.36 (m, 2H), 2.69–2.46 (m, 2H), 2.24−1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.2, 150.3, 146.7, 118.5, 112.9, 40.9, 26.1, 25.3; IR: 1657, 595; HRMS (APCI) $[M+H]^+$ calcd for $C_9H_{11}O_2S_2$ 215.0200; found 215.0206.



(1,3-Dithian-2-yl)(thiophen-2-yl)methanone (4o): White solid (357 mg, 31%). mp: 138–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.62 (m, 2H), 7.15–7.10 (m, 1H), 4.91 (s, 1H), 3.49–3.39 (m, 2H), 2.65 (ddd, J = 8.4, 5.6, 2.8 Hz, 2H), 2.22–2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 141.5, 134.6, 132.8, 128.4, 43.4, 26.7, 25.3; IR: 2922, 2850, 1640, 1384, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_9H_{11}OS_3$ 230.9972; found 230.9977.

3. Optimization of the Reaction Conditions[a]

Table S1 Screening the effect of ligand, additive, and base on the reaction



Entry	Ligand	Additive	Yield (%)[b][4]	Ee (%)[c]
1	**L1**	-	36	25
2	**L2**	-	32	20
3	**L3**	-	NP	-
4	**L4**	-	27	63
5	**L5**	-	33	59
6	**L6**	-	43	73
7	**L6**	LiCl	48	75
8	**L6**	LiBr	46	79
9	**L6**	LiI	47	85
10	**L6**	CaI_2	NP	-
11	BenzP*	-	41	78
12	BenzP*	LiF	42	68
13	BenzP*	LiCl	Trace	72
14	BenzP*	LiBr	34	90

15	**BenzP***	**LiI**	**52**	**92**
16	QuinoxP*	LiI	41	90
17[d]	BenzP*	LiI	NP	-
18[e]	BenzP*	LiI	NP	-
19[f]	BenzP*	LiI	NP	-

[a] Unless otherwise noted, the reaction of **1a** (0.1 mmol) with **2a** (0.2 mmol) was carried out using a catalytic system consisting of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol%) and ligand (5.5 mol%) in the presence of LiHMDS (0.15 mmol) and an additive (0.1 mmol) in THF (3 mL) under a nitrogen atmosphere at RT for 12 h. [b] Isolated yield. [c] Determined by HPLC using a chiral Daicel OD-H column. [d] NaHMDS was used as a base. [e] KHMDS was used as a base. [f] LDA was used as a base.

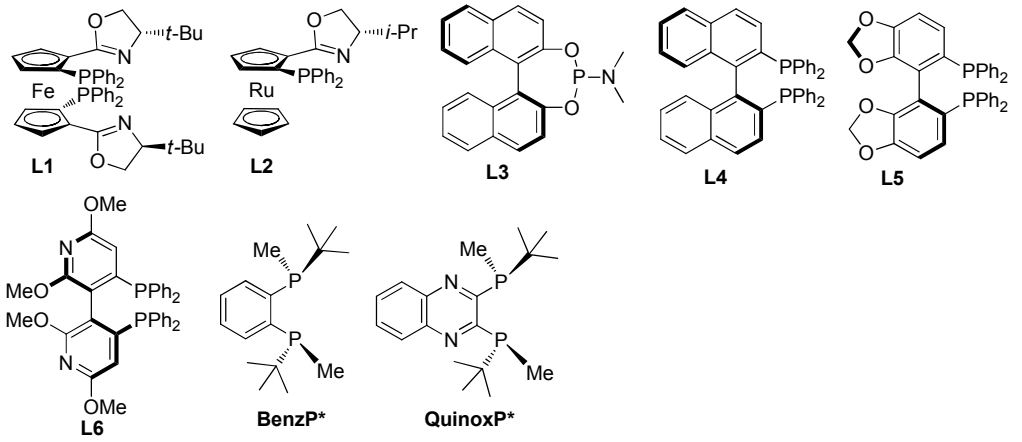
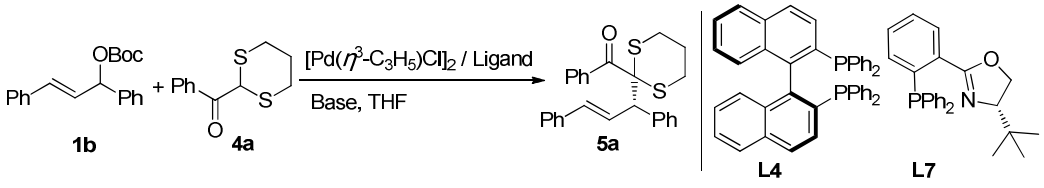


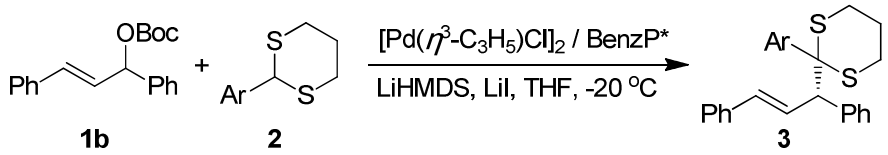
Table S2 Screening the effect of ligand and base on the reaction



Entry	Ligand	Base (equiv)	Yield (%)[b]	Ee (%)[c]
1	**L4**	*t*BuOK (2)	67	27
2	**L7**	*t*BuOK (2)	trace	-
3	BenzP*	*t*BuOK (2)	51	93
4	BenzP*	DBU (2)	trace	92
5	BenzP*	LiHMDS (2)	NP	-
6	BenzP*	*t*BuONa (2)	91	95
7	BenzP*	*t*BuONa (2.5)	33	95
8	BenzP*	*t*BuONa (1.5)	93	95
9	BenzP*	NaH (2)	NP	
10[d]	**BenzP***	**NaH (1.5)**	**96**	**95**

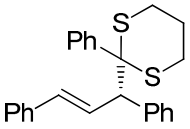
[a] Unless otherwise noted, the reaction of **1b** (0.15 mmol) with **4a** (0.1 mmol) was carried out using a catalytic system consisting of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol%) and ligand (5.5 mol%) in the presence of a base in THF (4 mL) under a nitrogen atmosphere at RT for 12 h. [b] Isolated yield. [c] Determined by HPLC using a chiral Daicel IC-3 column. [d] 15-Crown-5 (0.12 mmol) was used.

4. Pd-Catalyzed Allylic Substitution with 2-Aryl-1,3-dithiane Nucleophiles

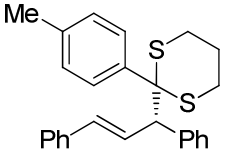


1b **2** **3**

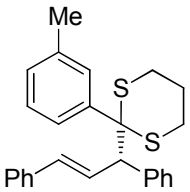
To an oven-dried glassware were added $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.9 mg, 2.5 mol%), BenzP* (1.6 mg, 5.5 mol%), and anhydrous THF (1.0 mL). To another dry glassware were added **2** (0.2 mmol), ultra-dry LiI (0.1 mmol, 13.3 mg), and anhydrous THF (1.0 mL). LiHMDS (1.5 – 5 equiv) was then added to the second glassware. The mixture was stirred at RT under a nitrogen atmosphere for 1 h. Then a solution of allylic carbonate **1b** (31 mg, 0.10 mmol) in anhydrous THF (1.0 mL) was added to the first glassware. The solution in the first glassware was added dropwise to another one. The reaction mixture was stirred at −20 °C for 12 h, quenched with H_2O, and extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated in vacuum. The residue was then purified by preparative TLC (cyclohexane:anisole = 10:1) to give the desired product.



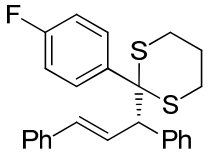
(*S*)-2-(1,3-Diphenylallyl)-2-phenyl-1,3-dithiane (3a): Using 1.5 equiv of LiHMDS to obtain a white solid (36.9 mg, 95%). mp: 102–104 °C; $[\alpha]_D^{20}$ = –1.5 (*c* 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.45–7.08 (m, 11H), 6.91−6.85 (m, 2H), 6.63−6.49 (m, 2H), 4.06 (d, *J* = 8.0 Hz, 1H), 2.71–2.51 (m, 4H), 1.97–1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.3, 137.2, 133.2, 131.0, 130.0, 128.5, 128.1, 127.7, 127.5, 127.4, 127.2, 127.1, 126.5, 64.0, 61.7, 27.7, 27.6, 24.8; IR: 2917, 2850, 1631, 1383, 1265, 738; HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{25}S_2$ 389.1398; found 389.1407; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 6.6 min, t_{minor} = 8.2 min.



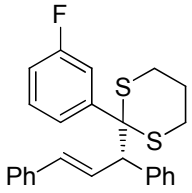
(*S*)-2-(1,3-Diphenylallyl)-2-(*p*-tolyl)-1,3-dithiane (3b): Using 4 equiv of LiHMDS to obtain yellow oil (30.2 mg, 75%). $[\alpha]_D^{20}$ = –4.4 (*c* 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.39–7.06 (m, 10H), 6.85 (d, *J* = 6.8 Hz, 2H), 6.49 (d, *J* = 4.6 Hz, 2H), 4.01 (t, *J* = 4.4 Hz, 1H), 2.68–2.51 (m, 4H), 2.38 (s, 3H), 1.90–1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 137.2, 136.8, 135.1, 133.0, 131.0, 130.00, 128.7, 128.4, 127.8, 127.3, 127.1, 126.5, 63.7, 61.6, 27.6, 27.5, 24.8, 21.0; IR: 2920, 2849, 1633, 1385, 418; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 5.3 min, t_{minor} = 6.7 min.



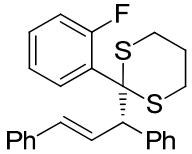
(*S*)-2-(1,3-Diphenylallyl)-2-(*m*-tolyl)-1,3-dithiane (3c): Using 5 equiv of LiHMDS to obtain yellow oil (31.0 mg, 77%); $[\alpha]_D^{20}$ = +1.0 (*c* 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.60–7.44 (m, 2H), 7.38–7.03 (m, 10H), 6.81 (d, *J* = 7.3 Hz, 2H), 6.50−6.46 (m, 2H), 3.97 (d, *J* = 7.2 Hz, 1H), 2.70–2.50 (m, 4H), 2.30 (s, 3H), 1.90–1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.1, 137.6, 137.2, 133.0, 131.6, 130.0, 128.4, 128.0, 127.9, 127.8, 127.7, 127.3, 127.2, 127.1, 126.4, 63.9, 61.5, 27.6, 27.5, 24.8, 21.6; IR: 2920, 2856, 1641, 1384, 629; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{27}S_2$ 403.1554; found 403.1513; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 5.0 min, t_{minor} = 6.2 min.



(*S*)-2-(1,3-Diphenylallyl)-2-(4-fluorophenyl)-1,3-dithiane (3d): Using 5 equiv of LiHMDS to obtain a white solid (33.2 mg, 82%). mp: 134–135 °C; $[\alpha]_D^{20}$ = –5.3 (*c* 0.68, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.39–7.06 (m, 8H), 6.99 (t, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.48 (d, *J* = 4.8 Hz, 2H), 4.02 – 3.92 (t, *J* = 4.4 Hz, 1H), 2.70–2.50 (m, 4H), 2.00–1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9 (d, $J_{C\text{-}F}$ = 246.0 Hz), 138.0, 137.0, 134.2 (d, $J_{C\text{-}F}$ = 2.0 Hz), 133.3, 132.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.9, 128.5, 127.5, 127.4, 127.2, 126.4, 114.8, 114.6, 63.2, 61.6, 27.5, 27.4, 24.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –115.95; IR: 2919, 2849, 1645, 1384, 678, 433; HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{24}S_2F$ 407.1303; found 407.1316; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 99/1, 0.7 mL/min, 254 nm: t_{major} = 6.2 min, t_{minor} = 8.3 min.

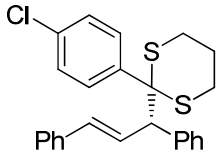


(*S*)-2-(1,3-Diphenylallyl)-2-(3-fluorophenyl)-1,3-dithiane (3e): Using 3 equiv of LiHMDS to obtain a white solid (39.4 mg, 97%). mp: 40–42 °C; $[\alpha]_D^{20}$ = +0.9 (*c* 0.15, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.54−7.44 (m, 2H), 7.38–7.09 (m, 9H), 6.97 (td, *J* = 8.0, 2.4 Hz, 1H), 6.86−6.81 (m, 2H), 6.59–6.42 (m, 2H), 3.96 (d, *J* = 8.6 Hz, 1H), 2.66–2.51 (m, 4H), 1.93–1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, $J_{C\text{-}F}$ = 243.4 Hz), 142.0 (d, $J_{C\text{-}F}$ = 6.7 Hz), 138.0, 137.0, 133.4, 129.9, 129.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.5, 127.5, 127.4, 127.3, 127.2, 126.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 126.5, 117.9 (d, $J_{C\text{-}F}$ = 23.7 Hz), 114.1 (d, $J_{C\text{-}F}$ = 21.1 Hz), 63.4 (d, $J_{C\text{-}F}$ = 1.5 Hz), 61.7, 27.8, 27.5, 24.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ –113.4; IR: 2920, 2850, 1633, 1384, 1265, 963, 869, 698, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{24}S_2F$ 407.1303; found 407.1288; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 5.9 min, t_{minor} = 7.1 min.

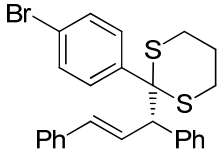


(*S*)-2-(1,3-Diphenylallyl)-2-(2-fluorophenyl)-1,3-dithiane (3f): Using 1.5 equiv of LiHMDS to obtain a white solid (24.9 mg, 61%). mp: 116–117 °C; $[\alpha]_D^{20}$ = +14.9 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (t, *J* = 8.0 Hz, 1H), 7.40–6.81 (m, 14H), 6.40 (d, *J* = 15.6 Hz, 1H), 4.38

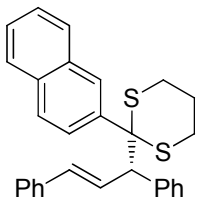
(d, J = 8.8 Hz, 1H), 2.85–2.55 (m, 4H), 1.94–1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0 (d, $J_{C\text{-}F}$ = 250.0 Hz), 138.9, 137.3, 133.7, 132.9, 129.7, 129.5 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.5, 128.4, 128.1 (d, $J_{C\text{-}F}$ = 7.1 Hz), 127.4, 127.2, 127.0, 126.5, 123.3 (d, $J_{C\text{-}F}$ = 3.6 Hz), 117.2 (d, $J_{C\text{-}F}$ = 24.3 Hz), 61.6 (d, $J_{C\text{-}F}$ = 6.3 Hz), 58.4 (d, $J_{C\text{-}F}$ = 1.9 Hz), 28.1, 27.9, 24.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ –101.1; IR: 2920, 2849, 1633, 1384, 697, 963, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{24}S_2F$ 407.1303; found 407.1293; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 99/1, 0.7 mL/min, 254 nm: t_{major} = 10.0 min, t_{minor} = 9.6 min.



(*S*)-2-(4-Chlorophenyl)-2-(1,3-diphenylallyl)-1,3-dithiane (3g): Using 4 equiv of LiHMDS to obtain a white solid (41.5 mg, 98%). mp: 138–140 °C; $[\alpha]_D^{20}$ = –17.5 (*c* 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.8 Hz, 2H), 7.39–7.11 (m, 10H), 6.89–6.82 (m, 2H), 6.55−6.43 (m, 2H), 3.99 (d, J = 8.0 Hz, 1H), 2.66–2.37 (m, 4H), 1.92–1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 137.2, 137.0, 133.5, 133.2, 132.5, 129.9, 128.5, 128.1, 127.5, 127.4 127.3, 127.1, 126.5, 63.3, 61.5, 27.6, 27.5, 24.7; IR: 2921, 2851, 1637, 1481, 1452, 1384, 1093, 617, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{24}S_2Cl$ 423.1008; found 423.0987; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 6.2 min, t_{minor} = 8.8 min.

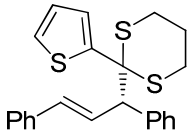


(*S*)-2-(4-Bromophenyl)-2-(1,3-diphenylallyl)-1,3-dithiane (3h): Using 3 equiv of LiHMDS to obtain a white solid (45.8 mg, 98%). mp: 145–146 °C; $[\alpha]_D^{20}$ = −10.4 (*c* 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.40–7.10 (m, 8H), 6.87 (d, J = 6.8 Hz, 2H), 6.59–6.40 (m, 2H), 4.00 (d, J = 7.6 Hz, 1H), 2.74–2.50 (m, 4H), 1.98–1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 137.8, 137.0, 133.5, 133.0, 131.1, 129.9, 128.5, 127.5, 127.3, 127.1, 126.5, 121.6, 63.3, 61.4, 27.6, 27.5, 24.7; IR: 2921, 2850, 1640, 1384, 1093, 619, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{24}S_2Br$ 467.0503; found 467.0490; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 6.1 min, t_{minor} = 8.7 min.

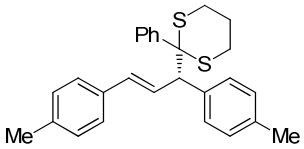


(*S*)-2-(1,3-Diphenylallyl)-2-(naphthalen-2-yl)-1,3-dithiane (3i): Using 3 equiv of LiHMDS to obtain yellow oil (43.1 mg, 98%). $[\alpha]_D^{20}$ = –26.3 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.96–7.76 (m, 4H), 7.51 (dt, J = 14.0, 6.8 Hz, 2H), 7.44–7.02 (m, 8H), 6.85 (d, J = 7.4 Hz, 2H), 6.59−6.51 (m, 2H), 4.14 (d, J = 3.7 Hz, 1H), 2.70−2.58 (m, 4H), 2.00–1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.1, 135.9, 133.2, 133.1, 132.3, 130.9, 130.0, 128.5, 128.4, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.5, 126.4, 126.0, 64.0, 61.6, 27.7, 27.6, 24.8; IR: 2919, 2849, 1633, 1384, 742, 696, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{29}H_{27}S_2$ 439.1554;

found 439.1546; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 6.5 min, t_{minor} = 8.2 min.

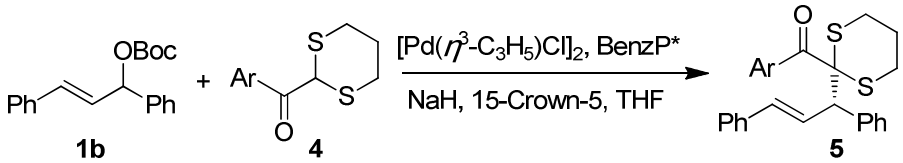


(*S*)-2-(1,3-Diphenylallyl)-2-(thiophen-2-yl)-1,3-dithiane (3j): Using 3 equiv of LiHMDS to obtain a white solid (36.3 mg, 92%). mp: 38–39 °C; $[\alpha]_D^{20}$ = +11.2 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.10 (m, 9H), 7.04–6.90 (m, 4H), 6.77–6.67 (m, 1H), 6.56−6.48 (m, 1H), 4.05 (d, *J* = 9.6 Hz, 1H), 3.04–2.60 (m, 4H), 2.00–1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 138.3, 137.1, 133.4, 130.3, 129.8, 128.5, 127.6, 127.5, 127.4, 127.3, 127.2, 126.9, 126.5, 62.3, 59.5, 28.1, 27.9, 24.6; IR: 2923, 2850, 1640, 1384, 697, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{23}H_{23}S_3$ 395.0962; found 395.0927; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 8.2 min, t_{minor} = 10.7 min.

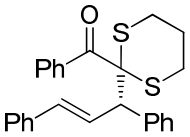


(*S*)-2-(1,3-Di-*p*-tolylallyl)-2-phenyl-1,3-dithiane (3k): Using 3 equiv of LiHMDS to obtain yellow oil (38.7 mg, 93%). $[\alpha]_D^{20}$ = –2.0 (*c* 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.18 (m, 5H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.48 – 6.34 (m, 2H), 3.97 (d, *J* = 7.2 Hz, 1H), 2.66 – 2.51 (m, 4H), 2.32 (s, 3H), 2.25 (s, 3H), 1.91 – 1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 137.0, 136.7, 135.3, 134.5, 132.8, 131.0, 129.8, 129.1, 128.1, 127.9, 127.0, 126.7, 126.4, 64.0, 61.3, 27.6, 27.5, 24.8, 21.2, 21.1; IR: 2933, 2838, 1645, 1184, 419; Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 5.4 min, t_{minor} = 6.7 min.

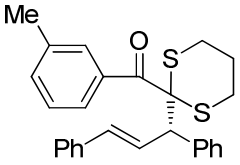
5. Pd-Catalyzed Allylic Substitution with 2-Aroyl-1,3-dithiane Nucleophiles



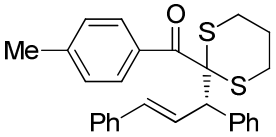
To an oven-dried glassware were added $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.9 mg, 2.5 mol%), BenzP* (1.6 mg, 5.5 mol%), and anhydrous THF (1 mL). To another dry glassware were added **4** (0.1 mmol), NaH (6 mg of 60% in mineral oil, 0.15 mmol), 15-crown-5 (24 μL, 0.12 mmol), and anhydrous THF (2 mL). The mixture was stirred at RT under a nitrogen atmosphere for 1 h. Then a solution of allylic carbonate **1b** (46.5 mg, 0.15 mmol) in anhydrous THF (1 mL) was added to the first glassware. The resulting solution was added dropwise to the second glassware. The reaction mixture was stirred for 12 h, quenched with H_2O, and extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated in vacuum. The residue was then purified by flash column chromatography (SiO_2; petroleum ether:EtOAc = 30:1) to give the corresponding product.



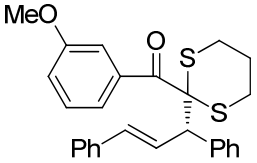
(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(phenyl)methanone (5a): White solid (40.1 mg, 96%). mp: 125–126 °C; $[\alpha]_D^{20}$ = +63.4 (*c* 0.70, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.08–7.98 (m, 2H), 7.53–7.45 (m, 1H), 7.45–7.08 (m, 12H), 6.79 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.11 (d, *J* = 15.6 Hz, 1H), 4.41 (d, *J* = 8.5 Hz, 1H), 3.32–3.12 (m, 2H), 2.76–2.66 (m, 2H), 2.08–1.98 (m, 1H), 1.86–1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 138.5, 138.4, 137.1, 133.5, 131.7, 130.2, 130.1, 128.7, 128.2, 128.1, 127.8, 127.7, 127.6, 126.8, 66.1, 56.5, 28.4, 24.3; IR: 1642, 1384, 497; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{25}OS_2$ 417.1347; found 417.1342; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 10.1 min, t_{minor} = 11.1 min.



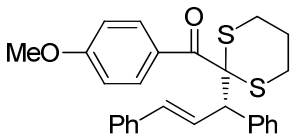
(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(*m*-tolyl)methanone (5b): Yellow oil (40.5 mg, 94%). $[\alpha]_D^{20}$ = +70.7 (*c* 0.20, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.68 (s, 1H), 7.40–7.10 (m, 12H), 6.79 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 4.40 (d, *J* = 8.4 Hz, 1H), 3.32–3.08 (m, 2H), 2.80–2.59 (m, 2H), 2.34 (s, 3H), 2.10–1.95 (m, 1H), 1.90–1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 138.6, 138.5, 137.9, 137.1, 133.5, 132.5, 130.8, 130.2, 128.7, 128.1, 127.9, 127.8, 127.7, 127.6, 127.1, 126.8, 66.2, 56.5, 28.4, 24.3, 21.7; IR: 2923, 2847 1691, 1658, 1383, 496, 434; HRMS (APCI) $[M+H]^+$ calcd for $C_{27}H_{27}OS_2$ 431.1503; found 431.1514; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 9.7 min, t_{minor} = 10.8 min.



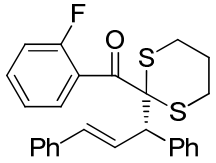
(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(*p*-tolyl)methanone (5c): White solid (41.8 mg, 97%). mp: 136–138 °C; $[\alpha]_D^{20}$ = +79.0 (*c* 0.18, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.43–7.12 (m, 12H), 6.79 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.14 (d, *J* = 15.6 Hz, 1H), 4.46 (d, *J* = 8.4 Hz, 1H), 3.29–3.06 (m, 2H), 2.79–2.60 (m, 2H), 2.41 (s, 3H), 2.06–1.97 (m, 1H), 1.87–1.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 148.0, 142.5, 138.4, 137.1, 135.5, 133.4, 130.4, 130.1, 128.8, 128.7, 128.1, 127.7, 127.6, 126.8, 66.6, 56.5, 28.4, 24.3, 21.7; IR: 2920, 2849 1637, 1471, 1384, 1117, 518, 446; HRMS (APCI) $[M+H]^+$ calcd for $C_{27}H_{27}OS_2$ 431.1503; found 431.1520; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 97/3, 0.5 mL/min, 254 nm: t_{major} = 17.8 min, t_{minor} = 18.6 min.



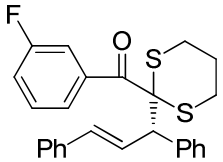
(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(3-methoxyphenyl)methanone (5d): Yellow oil (42.4 mg, 95%). $[\alpha]_D^{20}$ = +60.1 (*c* 0.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.65 (m, 1H), 7.43–7.36 (m, 1H), 7.35–7.10 (m, 11H), 7.03 (ddd, *J* = 8.4, 2.8, 0.8 Hz, 1H), 6.77 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.09 (d, *J* = 15.6 Hz, 1H), 4.40 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 3.32–3.10 (m, 2H), 2.76–2.64 (m, 2H), 2.08–1.98 (m, 1H), 1.90–1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 159.2, 139.8, 138.5, 137.0, 133.5, 130.2, 129.1, 128.7, 128.1, 127.8, 127.6, 126.8, 122.4, 118.2, 114.9, 66.1, 56.5, 55.5, 28.4 24.2; IR: 2920, 2849 1677, 1584, 1272, 955, 404; HRMS (APCI) $[M+H]^+$ calcd for $C_{27}H_{27}O_2S_2$ 447.1452; found 447.1456; Daicel Chiralpak IE column, *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm: t_{major} = 17.0 min, t_{minor} = 11.5 min.



(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(4-methoxyphenyl)methanone (5e): Yellow oil (43.8 mg, 98%). $[\alpha]_D^{20}$ = +69.4 (*c* 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–8.07 (m, 2H), 7.51–7.10 (m, 10H), 6.94–6.73 (m, 3H), 6.18 (d, *J* = 16.0 Hz, 1H), 4.48 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 3.29–3.01 (m, 2H), 2.79–2.60 (m, 2H), 2.10–1.92 (m, 1H), 1.90–1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 162.6, 138.4, 137.1, 133.4, 132.7, 130.0, 128.7, 128.1, 128.0, 127.8, 127.7, 127.6, 126.8, 113.3, 66.9, 56.7, 55.6, 28.5, 24.4; IR: 2919, 2848 1665, 1598, 1420, 1260, 742, 696; HRMS (APCI) $[M+H]^+$ calcd for $C_{27}H_{27}O_2S_2$ 447.1452; found 447.1462; Daicel Chiralpak IE column, *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm: t_{major} = 25.3 min, t_{minor} = 17.0 min.

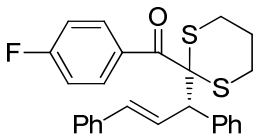


(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(2-fluorophenyl)methanone (5f): White solid (26.1 mg, 66%). mp: 114–115 °C; $[\alpha]_D^{20}$ = +37.0 (*c* 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (t, *J* = 6.4 Hz, 1H), 7.63–6.88 (m, 13H), 6.76 (dd, *J* = 15.6, 8.0 Hz, 1H), 6.15 (d, *J* = 15.6 Hz, 1H), 4.18 (d, *J* = 8.0 Hz, 1H), 3.32–2.86 (m, 2H), 2.75–2.52 (m, 2H), 2.09–1.93 (m, 1H), 1.87–1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 159.8 (d, $J_{C\text{-}F}$ = 252.8 Hz), 138.2, 136.8, 133.4, 131.9 (d, $J_{C\text{-}F}$ = 8.5 Hz), 130.2, 129.5, 128.4, 128.0, 127.5, 127.4, 126.5, 123.2, 122.9 (d, $J_{C\text{-}F}$ = 3.9 Hz), 116.4 (d, $J_{C\text{-}F}$ = 21.9 Hz), 64.8, 55.9, 27.9, 27.7, 23.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –110.8; IR: 2920, 2848 1644, 1384, 543, 418, 404; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{24}OS_2F$ 435.1253; found 435.1241; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 97/3, 1 mL/min, 254 nm: t_{major} = 11.3 min, t_{minor} = 12.5 min.

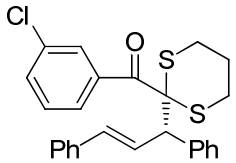


(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(3-fluorophenyl)methanone (5g): Using *t*BuONa (0.15 mmol) and 15-crown-5 (0.12 mmol) as base to obtain yellow oil (42.1 mg, 97%). $[\alpha]_D^{20}$ =

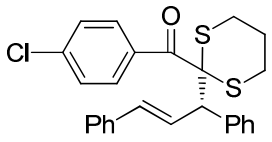
+28.5 (*c* 0.57, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.63 (m, 2H), 7.40–7.04 (m, 12H), 6.75 (dd, *J* = 16.0, 8.4 Hz, 1H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.29 (d, *J* = 8.4 Hz, 1H), 3.34–3.16 (m, 1H), 3.16–3.02 (m, 1H), 2.76–2.59 (m, 2H), 2.16–1.89 (m, 1H), 1.89–1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 161.7 (d, $J_{C\text{-}F}$ = 245.7 Hz), 140.2, 140.1, 137.9, 136.6, 133.3, 129.8, 129.5 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.5, 128.0, 127.6 (d, $J_{C\text{-}F}$ = 9.0 Hz), 127.2, 126.5, 125.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 118.5 (d, $J_{C\text{-}F}$ = 21.1 Hz), 116.9 (d, $J_{C\text{-}F}$ = 23.7 Hz), 65.7, 56.3, 28.2, 23.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –50.0; IR: 2920, 2849 1645, 1507, 1488, 1384, 634, 442, 418; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{24}OS_2F$ 435.1253; found 435.1254; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 98/2, 0.3 mL/min, 254 nm: t_{major} = 21.6 min, t_{minor} = 22.4 min.



(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(4-fluorophenyl)methanone (5h): Using *t*BuONa (0.15 mmol) and 15-crown-5 (0.12 mmol) as base to obtain yellow solid (43.1 mg, 99%); mp: 146–147 °C; $[\alpha]_D^{20}$ = +71.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–7.93 (m, 2H), 7.44–7.10 (m, 10H), 7.00 (t, *J* = 8.8 Hz, 2H), 6.76 (dd, *J* = 16.0, 8.4 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 4.30 (d, *J* = 8.4 Hz, 1H), 3.24 (t, *J* = 13.2 Hz, 1H), 3.09 (t, *J* = 12.8 Hz, 1H), 2.83–2.56 (m, 2H), 2.10–1.93 (m, 1H), 1.92–1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 164.6 (d, $J_{C\text{-}F}$ = 252.2 Hz), 138.0, 136.7, 134.3 (d, $J_{C\text{-}F}$ = 3.3 Hz), 133.2, 132.5 (d, $J_{C\text{-}F}$ = 8.6 Hz), 129.7, 128.5, 128.0, 127.6, 127.5, 127.3, 126.5, 114.9 (d, $J_{C\text{-}F}$ = 21.4 Hz), 66.0, 56.5, 28.2, 23.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –107.1; IR: 2920, 2848, 1645, 1555, 1417, 442, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{24}OS_2F$ 435.1253; found 435.1266; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 7.3 min, t_{minor} = 7.8 min.

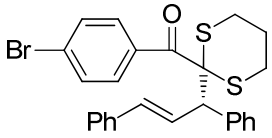


(*S*)-(3-Chlorophenyl)(2-(1,3-diphenylallyl)-1,3-dithian-2-yl)methanone (5i): Yellow oil (42.9 mg, 95%). $[\alpha]_D^{20}$ = +27.3 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.38–7.16 (m, 11H), 6.76 (dd, *J* = 16.0, 8.4 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 4.27 (d, *J* = 8.4 Hz, 1H), 3.34–3.17 (m, 1H), 3.17–3.03 (m, 1H), 2.82–2.59 (m, 2H), 2.17–1.98 (m, 1H), 1.98–1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 140.2, 138.2, 136.9, 134.0, 133.6, 131.6, 130.1, 130.0, 129.4, 128.7, 128.3, 128.1, 127.8, 127.7, 127.5, 126.8, 66.0, 56.6, 28.4, 24.1; IR: 2914, 2844, 1677, 1658, 1650 1641, 1631, 1383, 531, 464, 401; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{24}OS_2Cl$ 451.0957; found 451.0958; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm: t_{major} = 8.2 min, t_{minor} = 8.6 min.

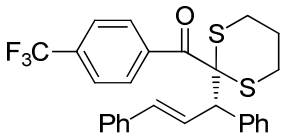


(*S*)-(4-Chlorophenyl)(2-(1,3-diphenylallyl)-1,3-dithian-2-yl)methanone (5j): White solid (43.3 mg, 96%). mp: 128–130 °C; $[\alpha]_D^{20}$ = +50.3 (*c* 0.59, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d,

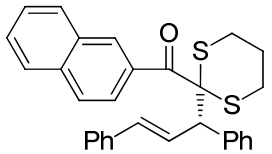
J = 8.8 Hz, 2H), 7.49–7.03 (m, 12H), 6.78 (dd, J = 16.0, 8.4 Hz, 1H), 6.14 (d, J = 16.0 Hz, 1H), 4.31 (d, J = 8.4 Hz, 1H), 3.33–3.17 (m, 1H), 3.17–3.02 (m, 1H), 2.81–2.61 (m, 2H), 2.15–1.90 (m, 1H), 1.90–1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 138.2, 138.1, 136.9, 136.8, 133.6, 131.6, 130.0, 128.7, 128.4, 128.3, 127.9, 127.8, 127.5, 126.8, 66.2, 56.7, 28.4, 24.2; IR: 1658, 1650 1641, 1631, 649, 496; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{24}OS_2Cl$ 451.0957; found 451.0960; Daicel Chiralpak IE column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 13.8 min, t_{minor} = 10.7 min.



(*S*)-(4-Bromophenyl)(2-(1,3-diphenylallyl)-1,3-dithian-2-yl)methanone (5k): White solid (44.6 mg, 90%). mp: 143–145 °C; $[\alpha]_D^{20}$ = +43.0 (*c* 0.46, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.84 (m, 2H), 7.54–7.44 (m, 2H), 7.37–7.08 (m, 10H), 6.77 (dd, J = 15.6, 8.4 Hz, 1H), 6.13 (d, J = 16.0 Hz, 1H), 4.30 (d, J = 8.4 Hz, 1H), 3.31–3.17 (m, 1H), 3.17–3.02 (m, 1H), 2.79–2.55 (m, 2H), 2.15–1.94 (m, 1H), 1.94–1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 138.2, 137.2, 136.9, 133.6, 131.7, 131.3, 130.0, 128.7, 128.3, 127.9, 127.8, 127.5, 126.8, 126.6, 66.2, 56.7, 28.4, 24.2; IR: 2922, 2853, 1643, 1384 744, 526, 518, 501; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{24}OS_2Br$ 495.0452; found 495.0459; Daicel Chiralpak IE column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 14.5 min, t_{minor} = 11.3 min.

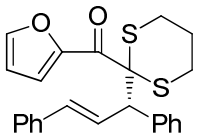


(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(4-(trifluoromethyl)phenyl)methanone (5l): Yellow oil (44.6 mg, 92%). $[\alpha]_D^{20}$ = +30.2 (*c* 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.35–6.96 (m, 10H), 6.74 (dd, J = 15.6, 8.0 Hz, 1H), 6.08 (d, J = 16.0 Hz, 1H), 4.20 (d, J = 8.4 Hz, 1H), 3.34–3.19 (m, 1H), 3.18–3.04 (m, 1H), 2.81–2.61 (m, 2H), 2.16–1.94 (m, 1H), 1.94–1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 141.9, 138.2, 136.8, 133.7, 133.0 (q, $J_{C\text{-}F}$ = 32.6 Hz), 130.2, 130.0, 128.7, 128.3, 127.9, 127.8, 127.3, 126.8, 126.6 (q, $J_{C\text{-}F}$ = 271.0 Hz), 125.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 65.6, 56.6, 28.4, 24.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.0; IR: 2922, 2850, 1639, 1507, 1471, 1384, 739, 704, 517, 457, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{27}H_{24}OS_2F_3$ 485.1221; found 485.1218; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 99/1, 0.6 mL/min, 254 nm: t_{major} = 9.4 min, t_{minor} = 9.9 min.

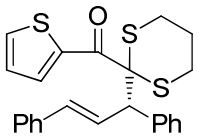


(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(naphthalen-2-yl)methanone (5m): Yellow oil (45.7 mg, 98%). $[\alpha]_D^{20}$ = +65.8 (*c* 0.66, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.01–7.48 (m, 7H), 7.38–7.11 (m, 9H), 6.82 (dd, J = 15.6, 8.4 Hz, 1H), 6.11 (d, J = 15.6 Hz, 1H), 4.51 (d, J = 8.8 Hz, 1H), 3.38–3.09 (m, 2H), 2.90–2.57 (m, 2H), 2.12–1.98 (m, 1H), 1.96–1.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 138.4, 137.0, 135.7, 134.8, 133.6, 132.4, 131.0, 130.2, 129.8, 128.7, 128.3, 128.2, 127.9, 127.8, 127.7, 126.8, 66.7, 56.7, 28.5, 24.3; IR: 2920, 2847, 1650, 1641,

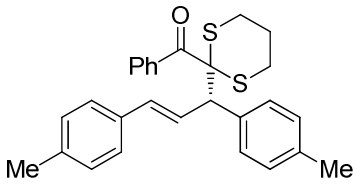
1631, 1384, 610, 408; HRMS (APCI) $[M+H]^+$ calcd for $C_{30}H_{27}OS_2$ 467.1503; found 467.1516; Daicel Chiralpak IE column, *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm: t_{major} = 17.2 min, t_{minor} = 12.4 min.



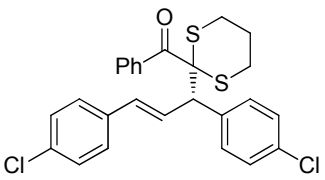
(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(furan-2-yl)methanone (5n): Yellow oil (40.2 mg, 99%). $[\alpha]_D^{20}$ = +38.7 (*c* 0.46, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.73–7.13 (m, 12H), 6.84 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.50 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 4.71 (d, *J* = 8.4 Hz, 1H), 3.22–3.03 (m, 1H), 3.00–2.80 (m, 1H), 2.74–2.54 (m, 2H), 2.01–1.87 (m, 1H), 1.87–1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.3, 151.1, 145.4, 138.1, 136.9, 133.1, 129.4, 128.5, 128.0, 127.7, 127.6, 127.5, 126.6, 120.5, 112.0, 66.4, 55.3, 28.2, 28.0, 24.0; IR: 2920, 2847, 1631, 1384, 496; HRMS (APCI) $[M+H]^+$ calcd for $C_{24}H_{23}O_2S_2$ 407.1139; found 407.1149; Daicel Chiralpak IE column, *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm: t_{major} = 24.8 min, t_{minor} = 16.2 min.



(*S*)-(2-(1,3-Diphenylallyl)-1,3-dithian-2-yl)(thiophen-2-yl)methanone (5o): White solid (41.8 mg, 99%). mp: 108–110 °C; $[\alpha]_D^{20}$ = +45.7 (*c* 0.28, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.20–8.07 (m, 1H), 7.67–7.53 (m, 1H), 7.44–7.12 (m, 10H), 7.13–7.09 (m, 1H), 6.80 (dd, *J* = 15.6, 8.8 Hz, 1H), 6.28 (d, *J* = 15.6 Hz, 1H), 4.49 (d, *J* = 8.4 Hz, 1H), 3.19–2.82 (m, 2H), 2.81–2.48 (m, 2H), 2.05–1.91 (m, 1H), 1.90–1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.9, 140.3, 138.0, 137.0, 135.6, 133.7, 133.6, 129.9, 128.7, 128.2, 127.9, 127.8, 127.6, 127.4, 126.8, 68.4, 57.1, 28.5, 28.4, 24.3; IR: 2922, 2850, 1640, 1384 457, 441, 409; HRMS (APCI) $[M+H]^+$ calcd for $C_{24}H_{23}OS_3$ 423.0911; found 423.0927; Daicel Chiralpak IE column, *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm: t_{major} = 22.8 min, t_{minor} = 13.6 min.

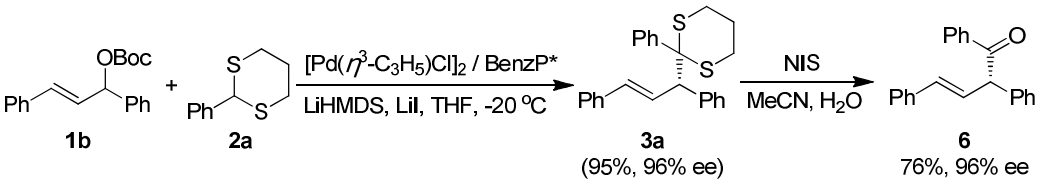


(*S*)-(2-(1,3-Di-*p*-tolylallyl)-1,3-dithian-2-yl)(phenyl)methanone (5p): Yellow oli (40.9 mg, 92%). $[\alpha]_D^{20}$ = +17.4 (*c* 0.46, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.43 (m, 1H), 7.41 – 7.31 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.69 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.03 (d, *J* = 16.0 Hz, 1H), 4.37 (d, *J* = 8.4 Hz, 1H), 3.36 – 3.02 (m, 2H), 2.79 – 2.54 (m, 2H), 2.30 (s, 3H), 2.28 (s, 3H),2.05 – 1.92 (m, 1H), 1.86 – 1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 138.2, 137.3, 137.1, 135.2, 134.0, 133.1, 131.6, 130.1, 129.7, 129.1, 128.6, 127.9, 126.4, 126.2, 66.2, 55.7, 28.1, 24.0, 21.2, 21.1; IR: 3011, 2797, 1867, 1640, 1338, 457, 441, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{28}H_{29}OS_2$ 445.1660; found 445.1664; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 8.8 min, t_{minor} = 10.9 min.



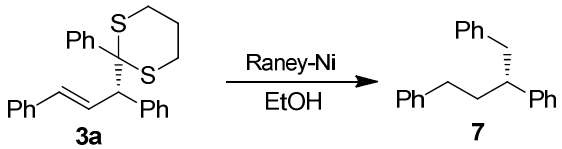
(*S*)-(2-(1,3-Dis(4-chlorophenyl)allyl)-1,3-dithian-2-yl)(phenyl)methanone (5q): Yellow oli (46.6 mg, 96%). $[\alpha]_D^{20}$ = +15.3 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.38 – 7.31 (m, 2H), 7.23 – 7.09 (m, 8H), 6.68 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.97 (d, *J* = 16.0 Hz, 1H), 4.34 (d, *J* = 8.4 Hz, 1H), 3.33 – 3.09 (m, 2H), 2.79 – 2.61 (m, 2H), 2.06 – 1.97 (m, 1H), 1.89 – 1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 138.0, 136.4, 135.1, 133.4, 133.3, 132.2, 131.8, 131.2, 129.9, 128.6, 128.1, 128.0, 127.7, 127.6, 65.4, 55.5, 28.1, 23.9; IR: 3566, 2922, 2850, 1868, 1637, 1385 456, 419; HRMS (APCI) $[M+H]^+$ calcd for $C_{26}H_{23}OS_2Cl_2$ 485.0567; found 485.0577; Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 8.1 min, t_{minor} = 8.7 min.

6. Large Scale Synthesis of 3a and the Derivatization of 3a and 5a

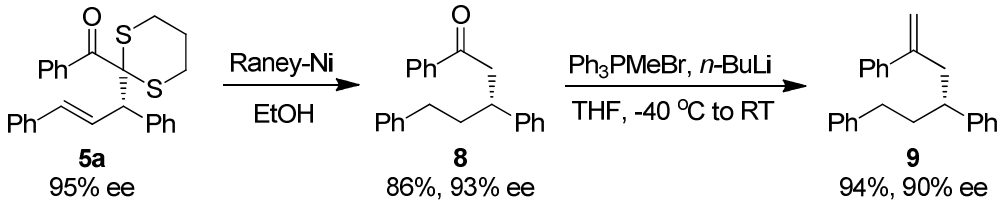


To an oven-dried glassware were added $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (36 mg, 2.5 mol%), BenzP* (64 mg, 5.5 mol%), and anhydrous THF (20.0 mL). To another dry glassware were added **2a** (8 mmol, 1.57 g), ultra-dry LiI (4 mmol, 532 mg), and anhydrous THF (20 mL). Then LiHMDS (1M in THF, 6 mL) was added to the second glassware. The mixture was stirred at RT under a nitrogen atmosphere for 1 h. Then a solution of allylic carbonate **1b** (4 mmol, 1.24 g) in anhydrous THF (20 mL) was added to the first glassware. The solution in the first glassware was added to another one. The reaction mixture was stirred at −20 °C for 12 h, quenched with H_2O, and extracted with EtOAc (80 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated in vacuum. The residue was purified by preparative HPLC (*n*-hexane/*i*-PrOH = 10:1) to give the product **3a** as a white solid (1.48 g, 95%, 96% ee).

To a solution of **3a** (77.6 mg, 0.2 mmol) in MeCN (9.0 mL) and water (0.5 mL) at −20 °C was added NIS (112.5 mg, 0.5 mmol), and the mixture was stirred and warmed to RT. The reaction was monitored by TLC until full consumption of **3a**. The reaction mixture was diluted with DCM, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash column chromatography to give the compound **6** as a white solid (45.3 mg, 76%, 96% ee, the column chromatography purification should be quickly carried out to avoid the racemization of **6**). mp: 43–45 °C; $[\alpha]_D^{20}$ = +24.4 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.65–7.07 (m, 13H), 6.76 (dd, *J* = 15.6, 8.0 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 5.45 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 138.9, 137.0, 136.6, 133.4, 132.3, 129.3, 129.1, 128.9, 128.8, 128.7, 128.6, 127.8, 127.5, 126.7, 57.5; IR: 2921, 2850, 1644, 1384 696, 517, 456; HRMS (APCI) $[M+H]^+$ calcd for $C_{22}H_{19}O$ 299.1436; found 299.1449; Daicel Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 24.8 min, t_{minor} = 28.4 min.



To a solution of **3a** (38.8 mg, 0.1 mmol) in EtOH (15 mL) was added Raney-Ni (water slurry, 2 mL). The reaction was monitored by TLC until full consumption of **3a**. The reaction mixture was filtrated, dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash column chromatography to give the compound **7** as yellow oil (26.1 mg, 91%, 83% ee). $[\alpha]_D^{20}$ = -29.9 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.08 (m, 11H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 2.99–2.76 (m, 3H), 2.55–2.32 (m, 2H), 2.10–1.85 (m, 2H);[5] Daicel Chiralpak OD-H column, *n*-hexane, 1 mL/min, 220 nm: t_{major} = 46.8 min, t_{minor} = 30.7 min.



To a solution of **5a** (83.1 mg, 0.2 mmol) in EtOH (8.0 mL) was added Raney-Ni (water slurry, 6 mL), and the mixture was stirred at RT for 2 h. The reaction mixture was filtrated, dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash column chromatography to give the compound **8** as a white solid (54.1 mg, 86%, 93% ee).[6] $[\alpha]_D^{20}$ = –5.0 (*c* 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.55–6.98 (m, 13H), 3.45–3.15 (m, 3H), 2.52−2.41 (m, 2H), 2.15–2.03 (m, 1H), 2.03–1.85 (m, 1H); Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm: t_{major} = 12.3 min, t_{minor} = 16.3 min.

To a solution of Ph_3PMeBr (107.1 mg, 0.3 mmol) in anhydrous THF (2 mL) was added *n*-BuLi (0.25 mmol, 2.5 M in hexane) dropwise at −40 °C, and the mixture was stirred for 1 h. Then a solution of **8** (31.4 mg, 0.1 mmol) in anhydrous THF (2.0 mL) was added dropwise to the above solution. The reaction mixture was warmed to RT and stirred overnight, filtrated through celite, and concentrated in vacuum. The residue was purified by flash column chromatography to give the compound **9** as colorless oil (29.2 mg, 94%, 90% ee).[7] $[\alpha]_D^{20}$ = −2.0 (*c* 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.00 (m, 15H), 5.15 (d, *J* = 1.6 Hz, 1H), 4.89 (d, *J* = 1.2 Hz, 1H), 2.88−2.75 (m, 2H), 2.73–2.63 (m, 1H), 2.46–2.28 (m, 2H), 2.10–1.98 (m, 1H), 1.94–1.81 (m, 1H); Daicel Chiralpak OD-H column, *n*-hexane, 1 mL/min, 254 nm: t_{major} = 44.0 min, t_{minor} = 32.0 min.

7. Reference

[1] Samajdar, S.; Basu, M. K.; Becker, F. F.; Banik, B. K. *Tetrahedron Lett.* **2001**, *42*, 4425.

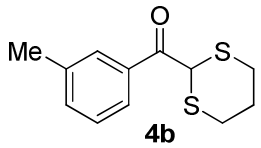
[2] Page, P. C. B.; Wilkes, R. D.; Namwindwa, E. S.; Witty, M. J. *Tetrahedron* **1996**, *52*, 2125.

[3] Balasubramaniam, S.; Kommidi, H.; Aidhen, I. S. *Tetrahedron Lett.* **2011**, *52*, 2683.

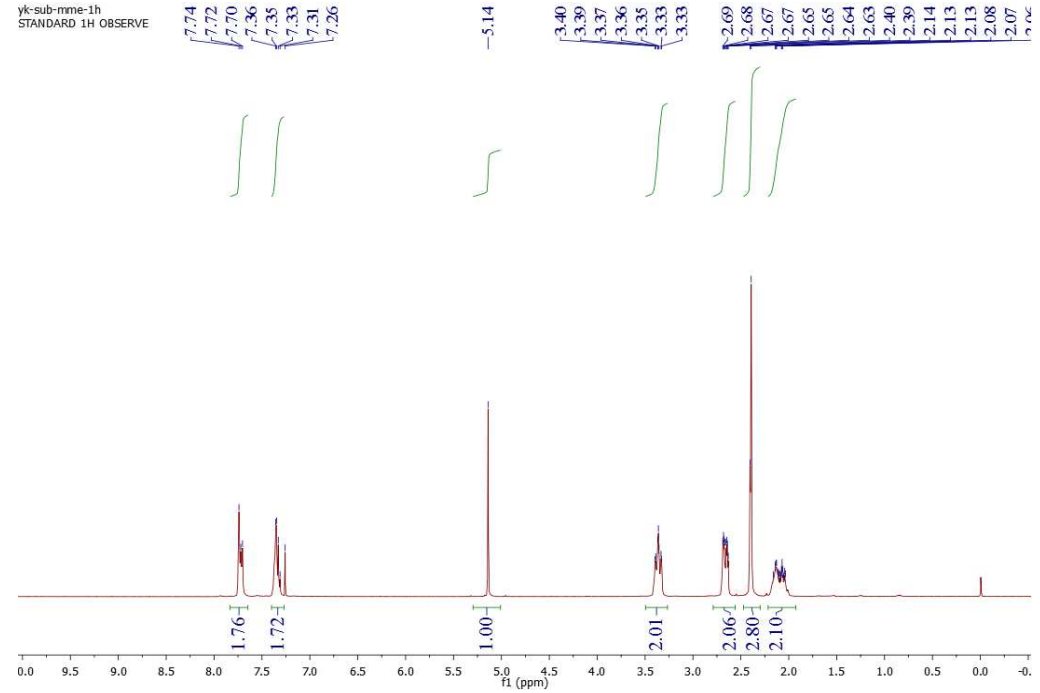
[4] A byproduct was also formed and identified as hexa-1,5-diene-1,3,4,6-tetrayltetrabenzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.05 (m, 20H), 6.53 (dd, *J* = 15.6, 5.6 Hz, 1H), 6.42 (d, *J* = 16 Hz, 1H), 6.33 (dd, *J* = 15.6, 5.2 Hz,1H), 6.22 (d, *J* = 16 Hz, 1H), 3.94–3.83 (m, 2H). The spectrum is consistent with the published data, see: Shirakawa. E.; Hironaka. K.; Otsuka. H.; Hayashi.T. *Chem. Commun.* 2006, 3927.

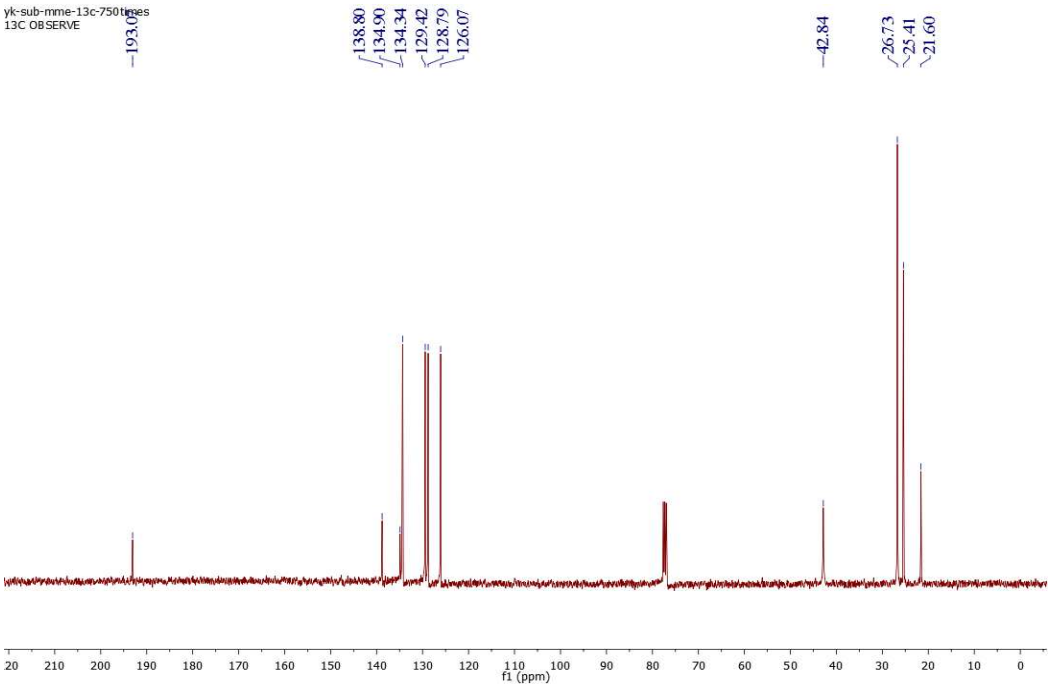
[5] Prementine, G. S.; Tirrell, D. A. *Macromolecules* **1989**, *22*, 52.
[6] Totleben, M. J.; Curran, D. P.; Wipf, P. *J. Org. Chem*. **1992**, *57*, 1740.
[7] Ellis, G. A.; T. Wyche, P.; Fry, C. G.; Braun, D. R.; Bugni, T. S. *Mar. Drugs* **2014**, *12*, 1013.

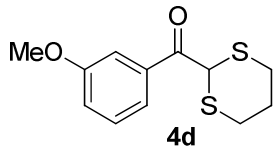
8. NMR Spectra



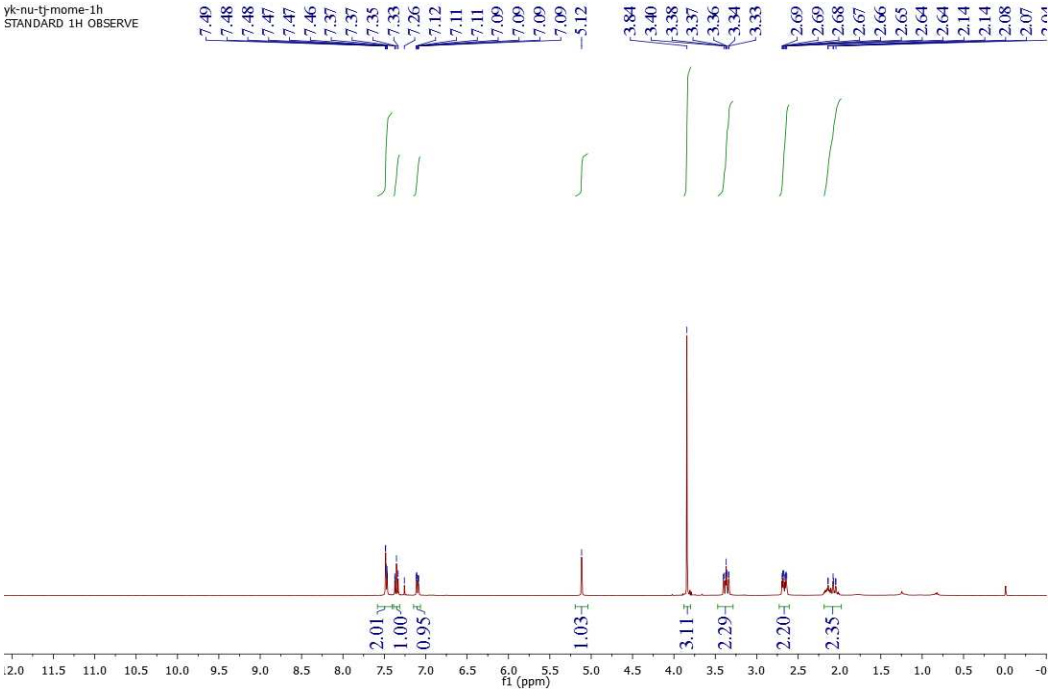
4b






MeO
O
S
S

4d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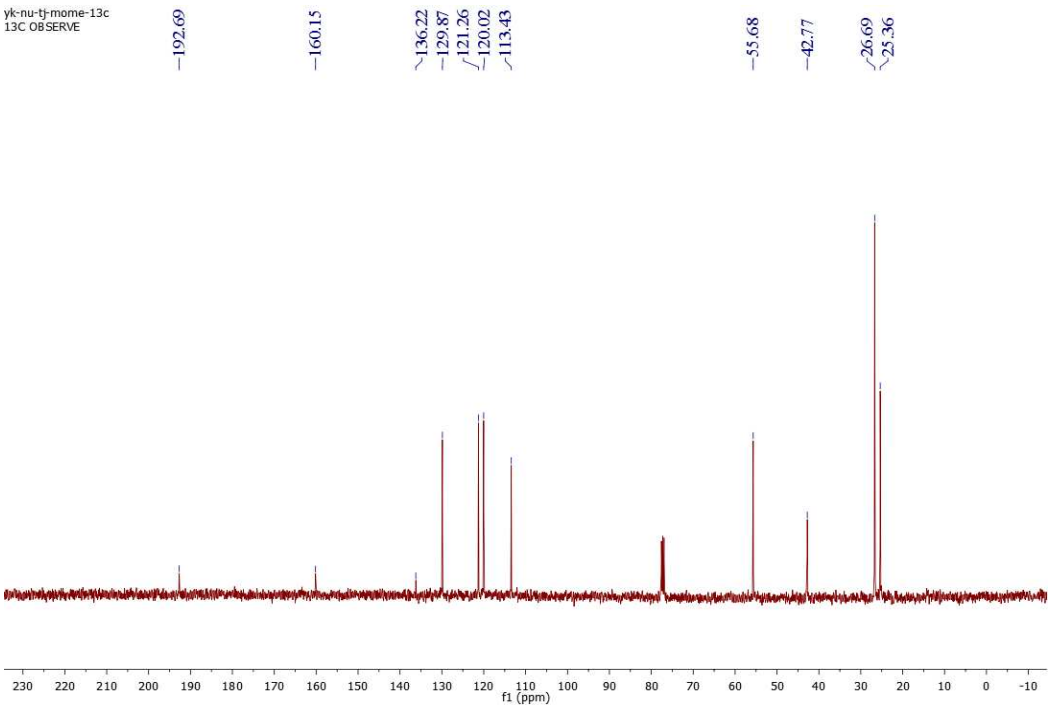
STANDARD 1H OBSERVE
7.49 7.48 7.48 7.47 7.47 7.46 7.37 7.37 7.35 7.33 7.26 7.12 7.11 7.11 7.09 7.09 7.09 7.09 5.12
3.84 3.40 3.38 3.37 3.36 3.34 3.33
2.69 2.69 2.68 2.67 2.66 2.65 2.64 2.64 2.14 2.14 2.08 2.07
2.01 1.00 0.95 1.03 3.11 2.29 2.20 2.35
f1 (ppm)


yk-nu-tj-mome-13c
13C OBSERVE
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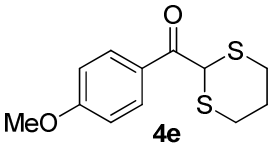
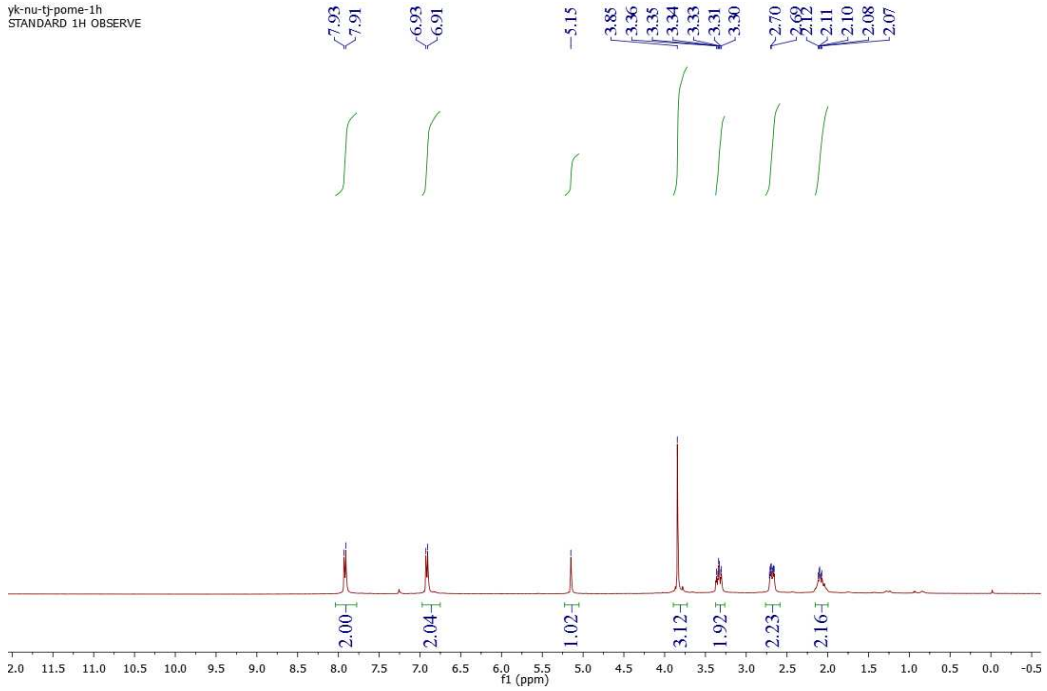
f1 (ppm)


O
S
S
MeO

4e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STANDARD 1H OBSERVE
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7.91
6.93
6.91
5.15
3.85
3.36
3.35
3.34
3.33
3.31
3.30
2.70
2.69
2.12
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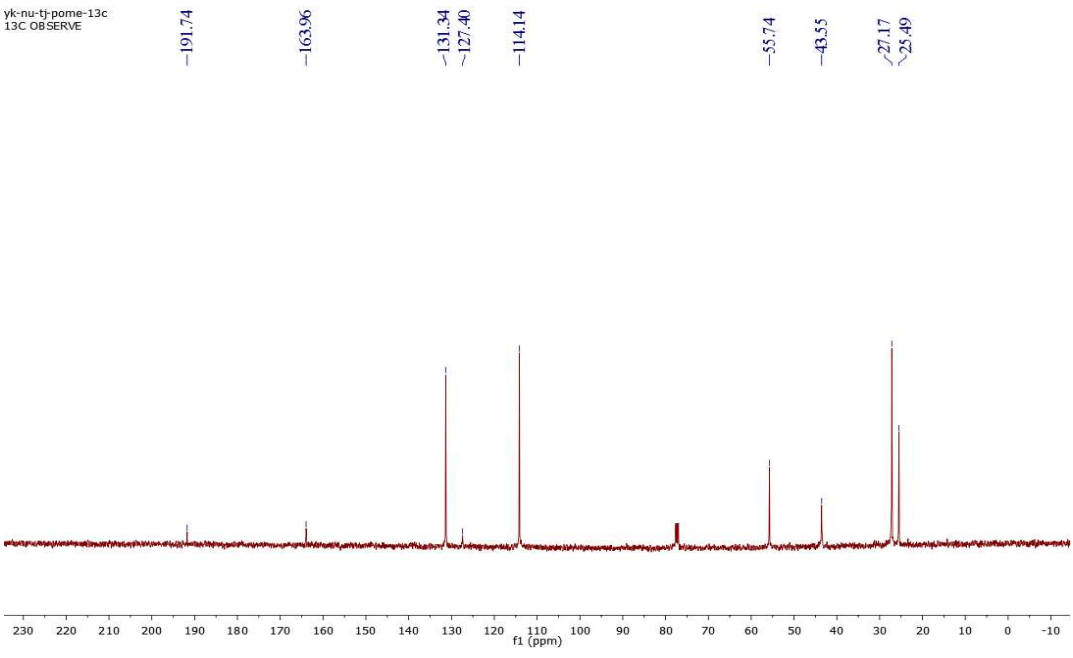
1.02
3.12
1.92
2.23
2.16
f1 (ppm)


yk-nu-tj-pome-13c
13C OBSERVE
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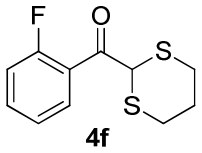
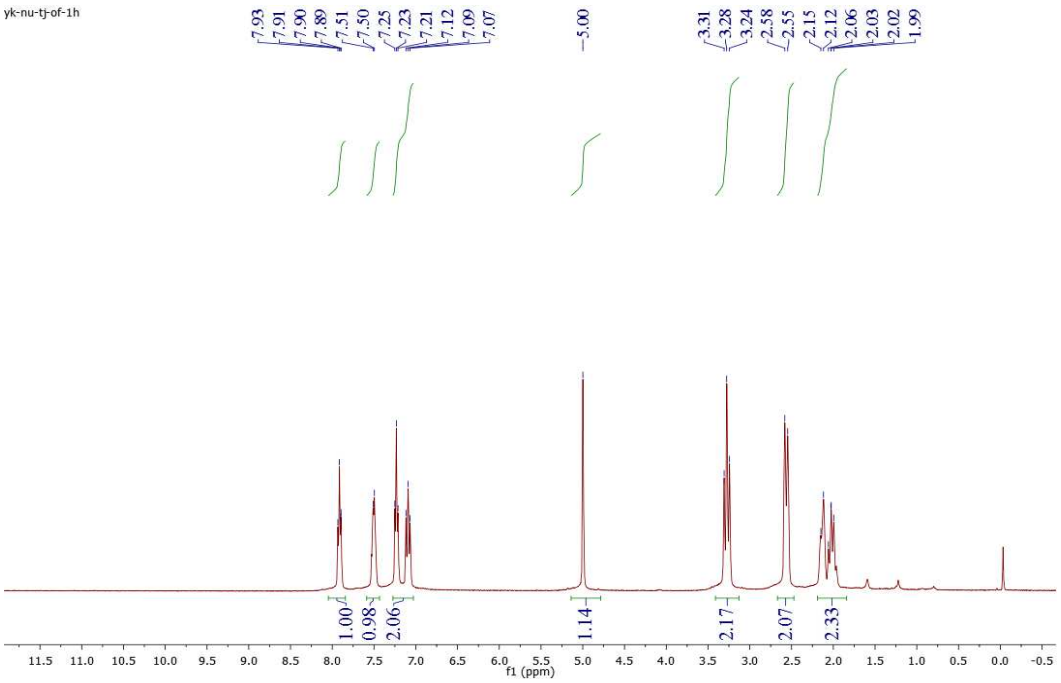
131.34
127.40
114.14
55.74
43.55
27.17
25.49
f1 (ppm)


F
O
S
S

4f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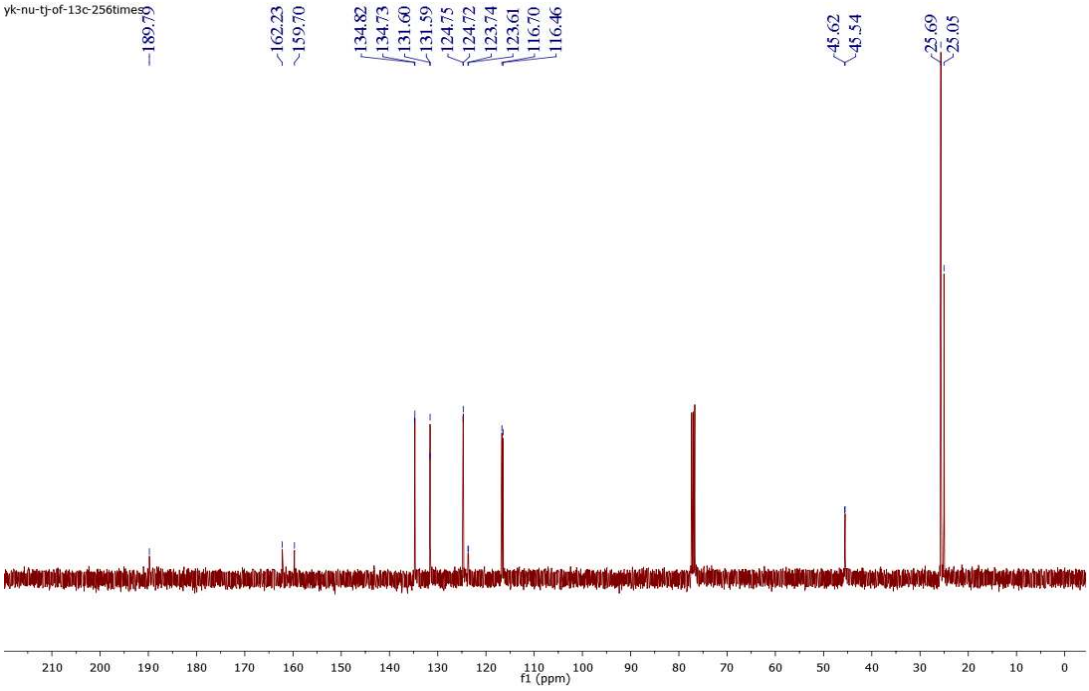
7.93
7.91
7.90
7.89
7.51
7.50
7.25
7.23
7.21
7.12
7.09
7.07
5.00
3.31
3.28
3.24
2.58
2.55
2.15
2.12
2.06
2.03
2.02
1.99
1.00
0.98
2.06
1.14
2.17
2.07
2.33
f1 (ppm)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162.23
159.70
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131.59
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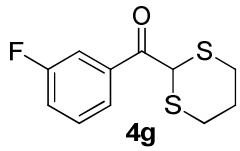
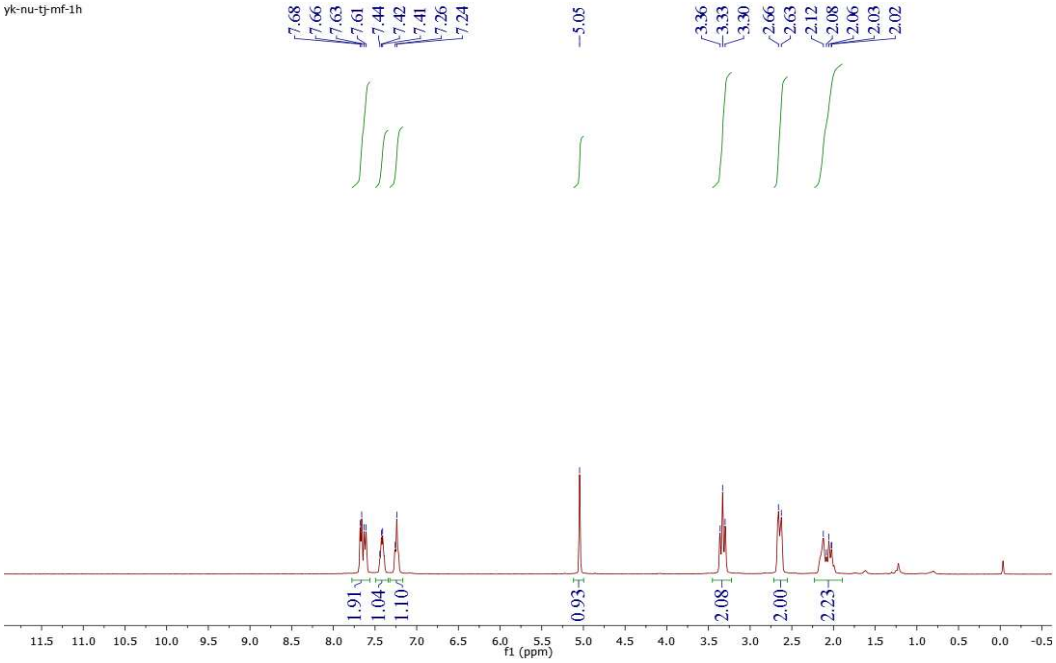
116.46
45.62
45.54
25.69
25.05
f1 (ppm)

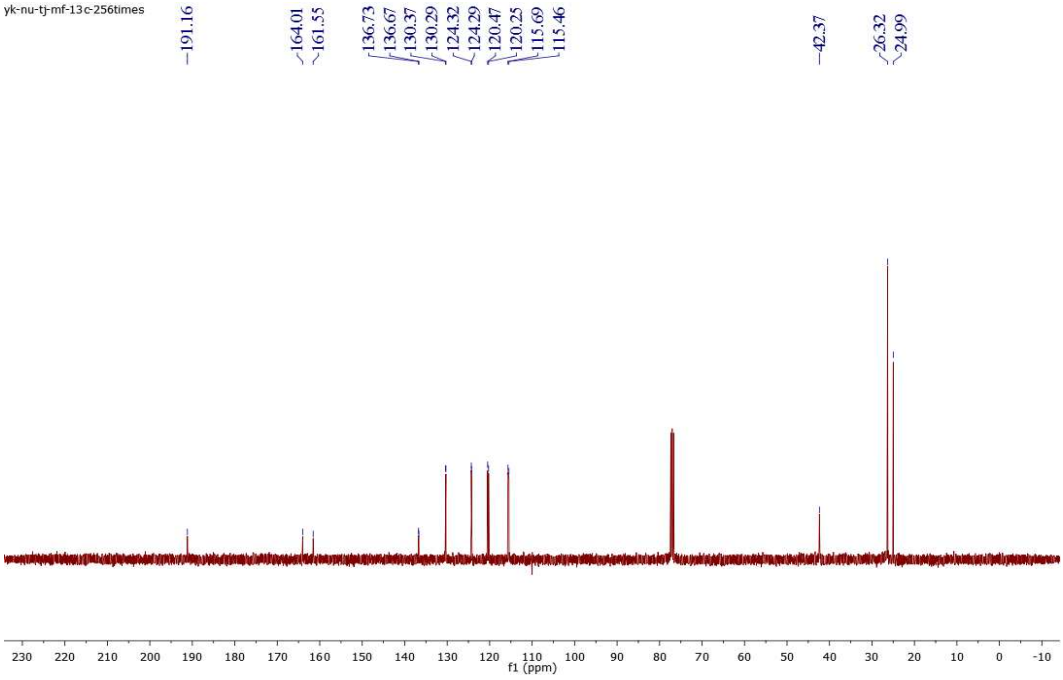


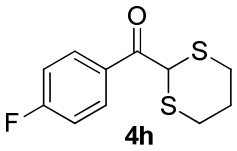
4g

yk-nu-tj-mf-1h

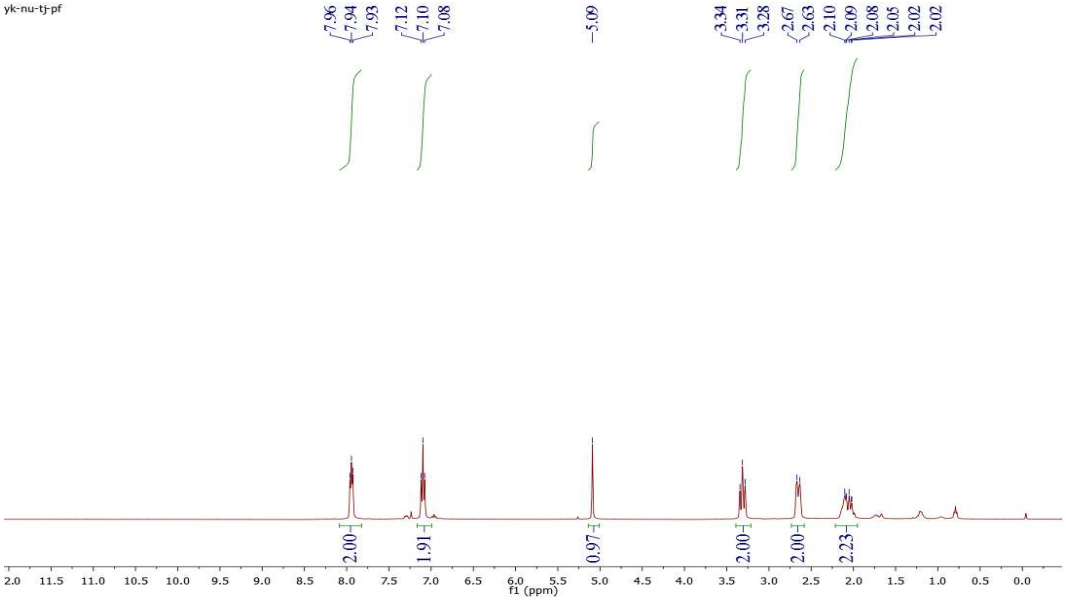


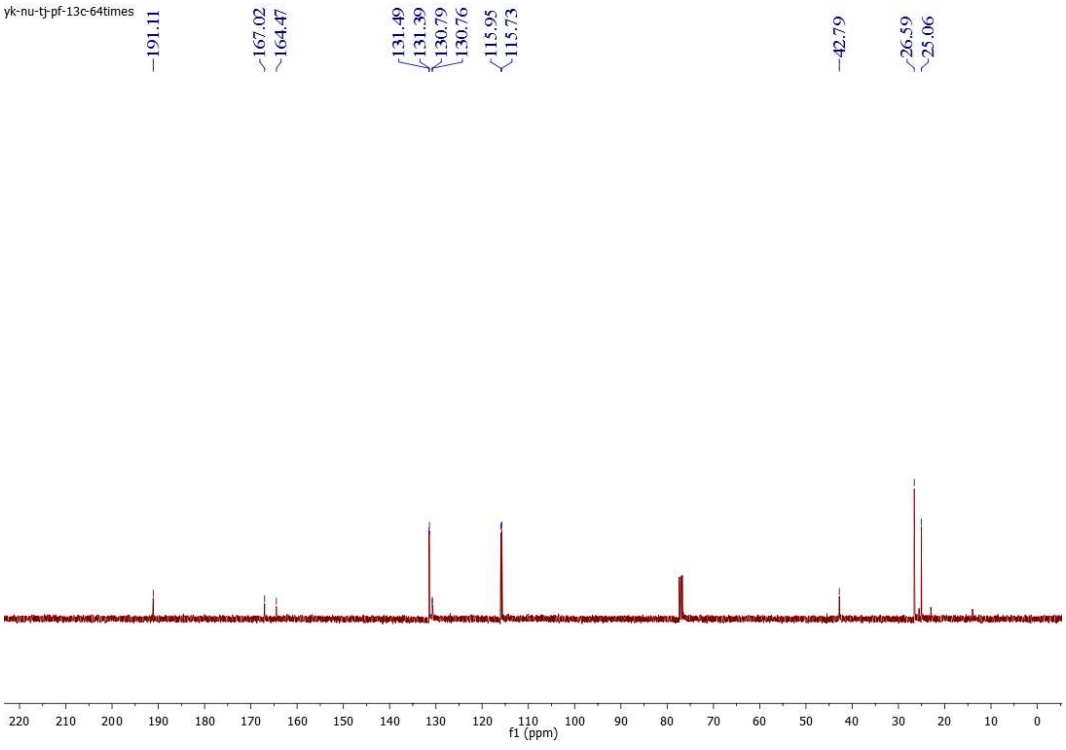
yk-nu-tj-mf-13c-256times

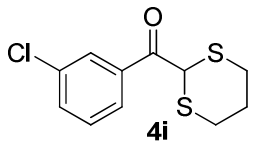



O
S
S
F

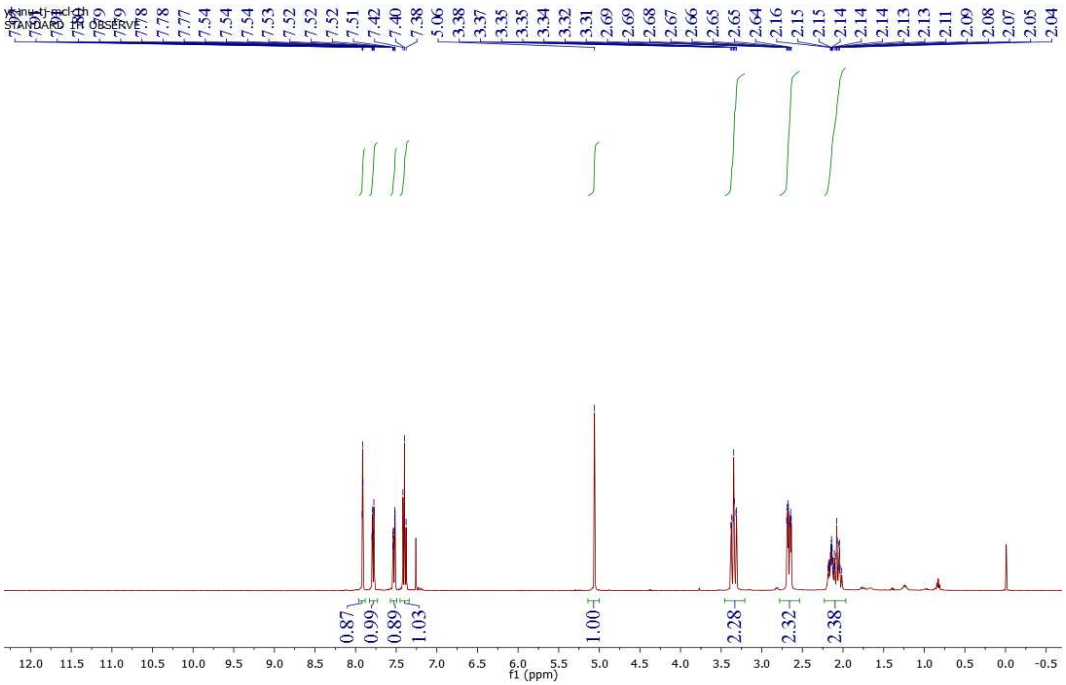
4h

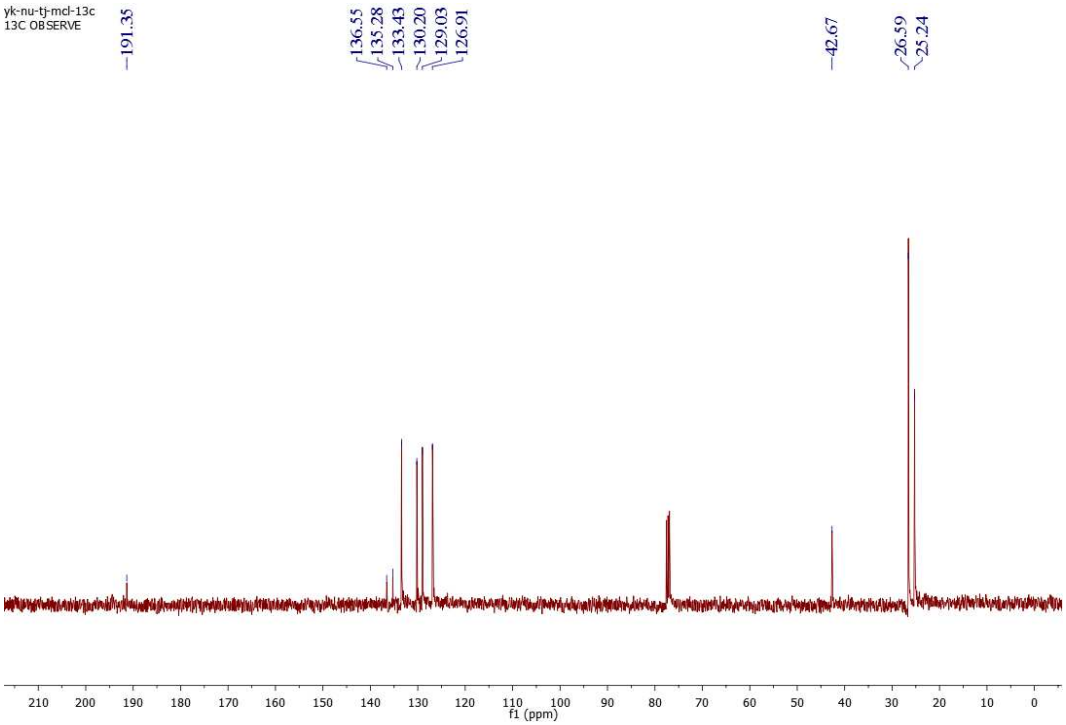

yk-nu-tj-pf
7.96
7.94
7.93
7.12
7.10
7.08
5.09
3.34
3.31
3.28
2.67
2.63
2.10
2.09
2.08
2.05
2.02
2.02
2.00
1.91
0.97
2.00
2.00
2.23
f1 (ppm)

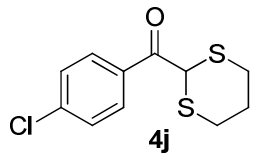

yk-nu-tj-pf-13c-64times
191.11
167.02
164.47
131.49
131.39
130.79
130.76
115.95
115.73
42.79
26.59
25.06
f1 (ppm)


O
Cl
S
S

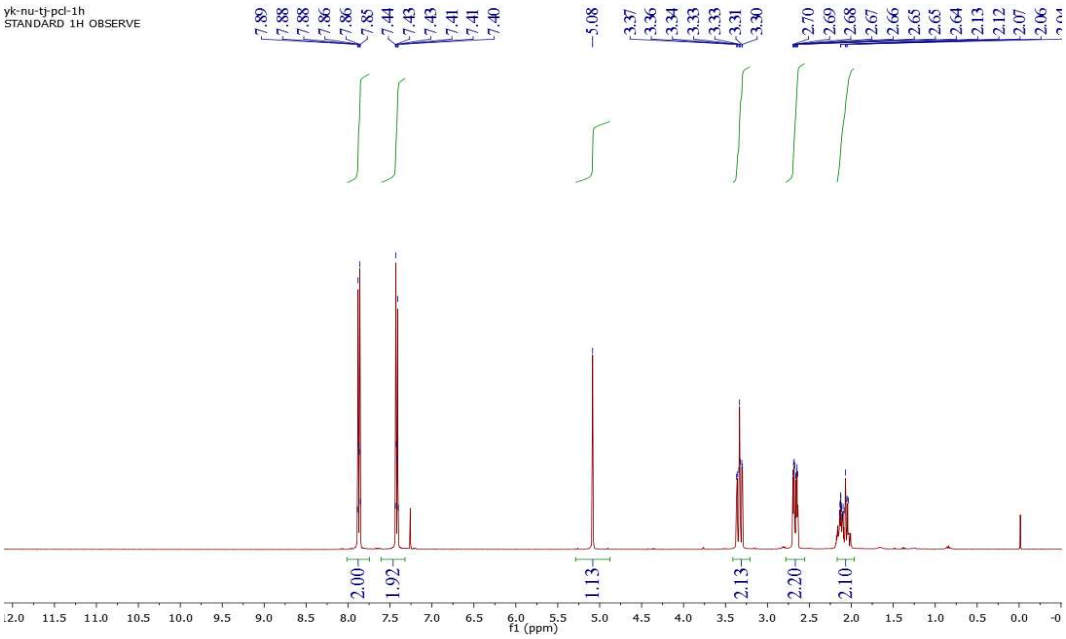
4i

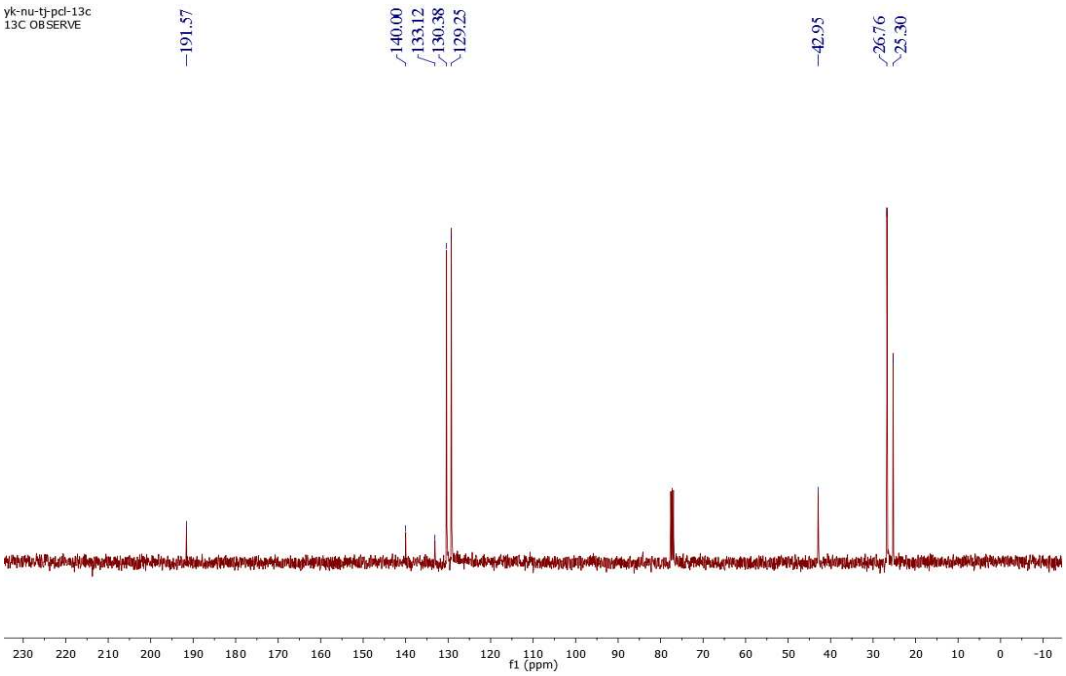

STANDARD 1H OBSERVE
0.87
0.99
0.89
1.03
1.00
2.28
2.32
2.38
f1 (ppm)

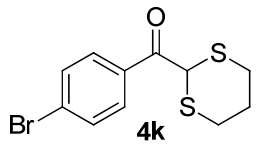

yk-nu-tj-mcl-13c
13C OBSERVE
191.35
136.55
135.28
133.43
130.20
129.03
126.91
42.67
26.59
25.24
f1 (ppm)


O
S
S
Cl

4j

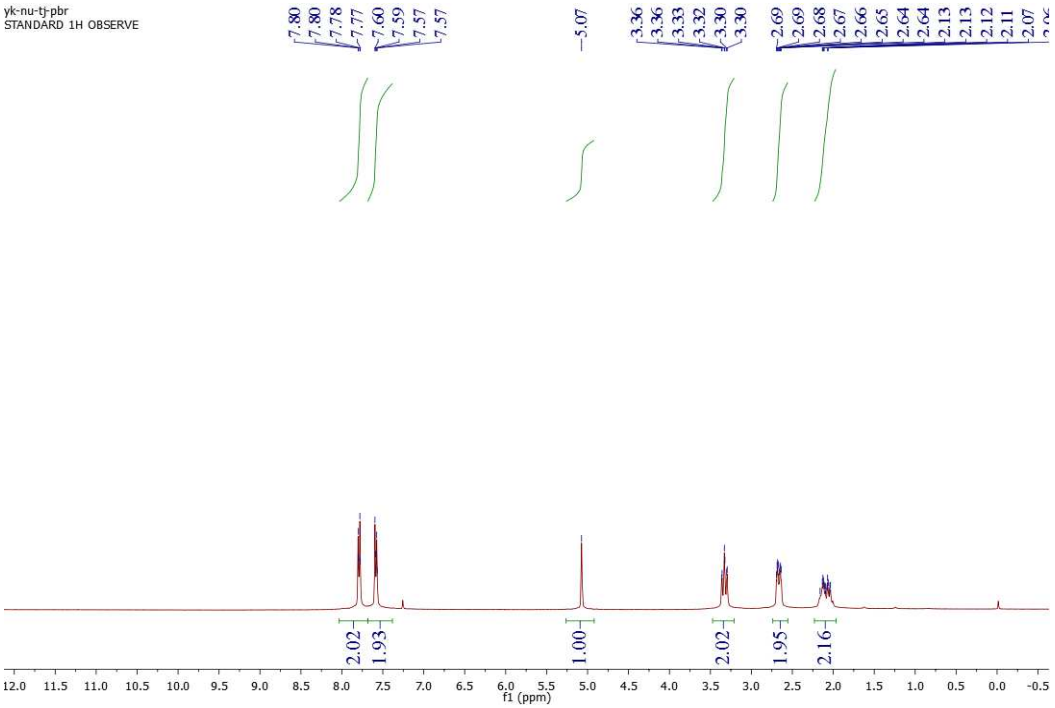

yk-nu-tj-pcl-1h
STANDARD 1H OBSERVE
7.89
7.88
7.88
7.86
7.86
7.85
7.44
7.43
7.43
7.41
7.41
7.40
5.08
3.37
3.36
3.34
3.33
3.33
3.31
3.30
2.70
2.69
2.68
2.67
2.66
2.65
2.65
2.64
2.13
2.12
2.07
2.06
2.00
1.92
1.13
2.13
2.20
2.10
f1 (ppm)


yk-nu-tj-pcl-13c
13C OBSERVE
191.57
140.00
133.12
130.38
129.25
42.95
26.76
25.30
f1 (ppm)

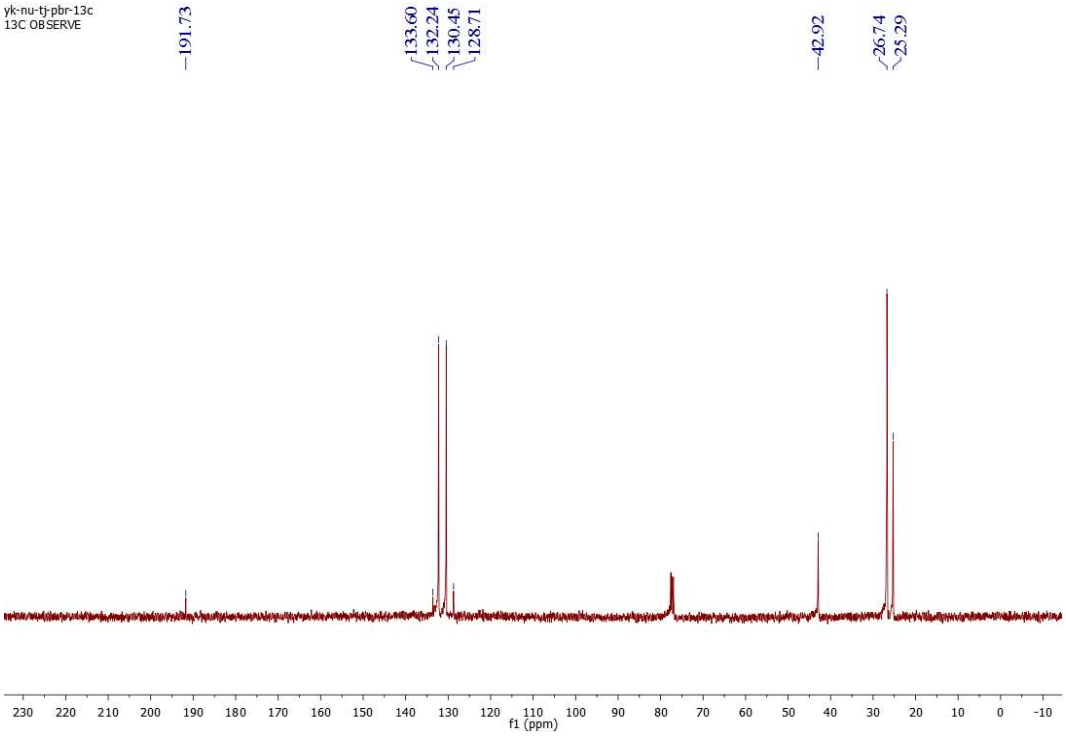


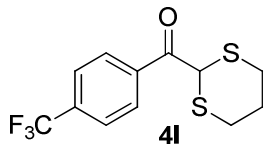
4k

yk-nu-tj-pbr
STANDARD 1H OBSERVE

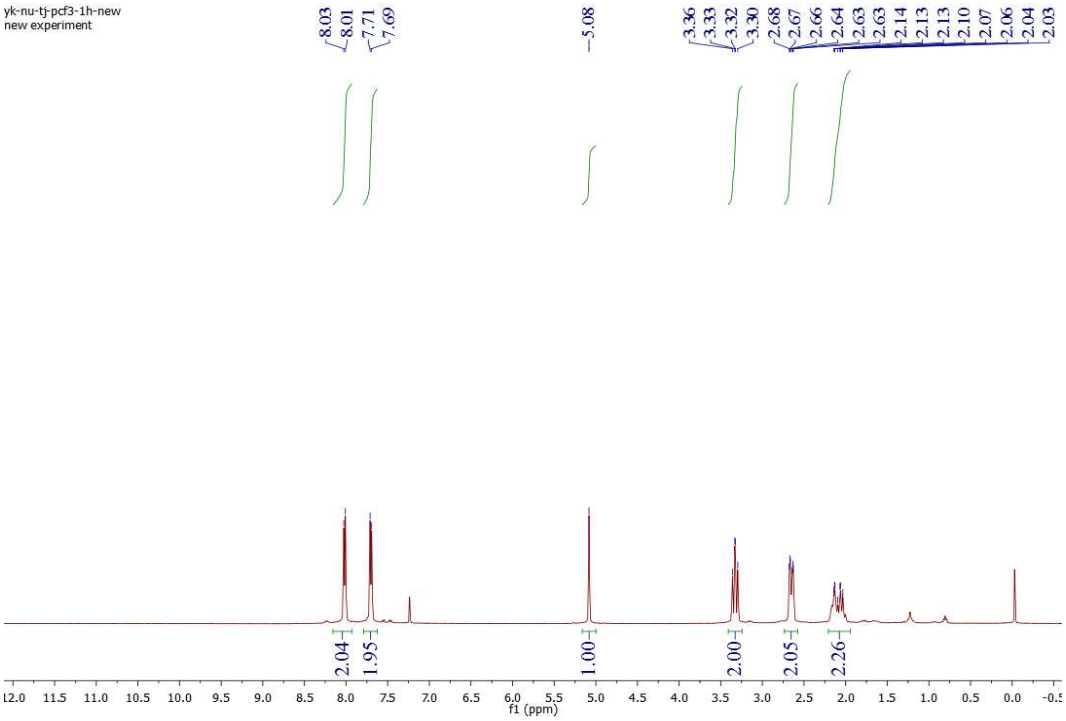


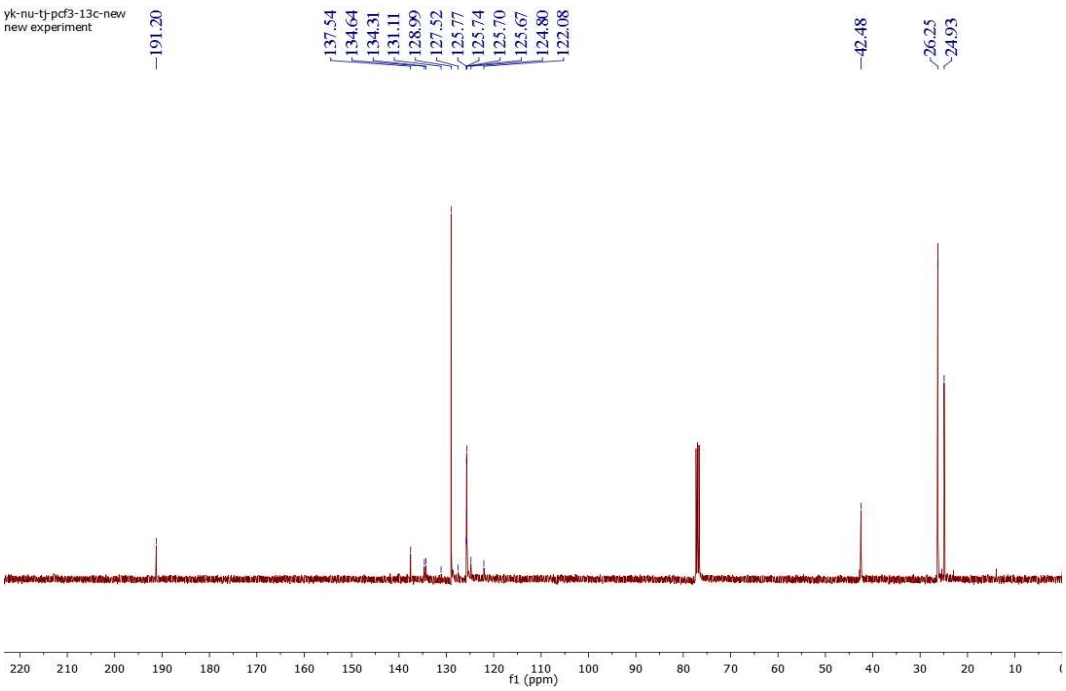
yk-nu-tj-pbr-13c
13C OBSERVE

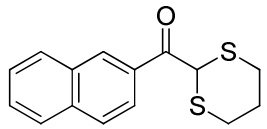



O
S
S
F3C

4l


yk-nu-tj-pcf3-1h-new
new experiment
8.03
8.01
7.71
7.69
5.08
3.36
3.33
3.32
3.30
2.68
2.67
2.66
2.64
2.63
2.63
2.14
2.13
2.13
2.10
2.07
2.06
2.04
2.03
2.04
1.95
1.00
2.00
2.05
2.26
f1 (ppm)

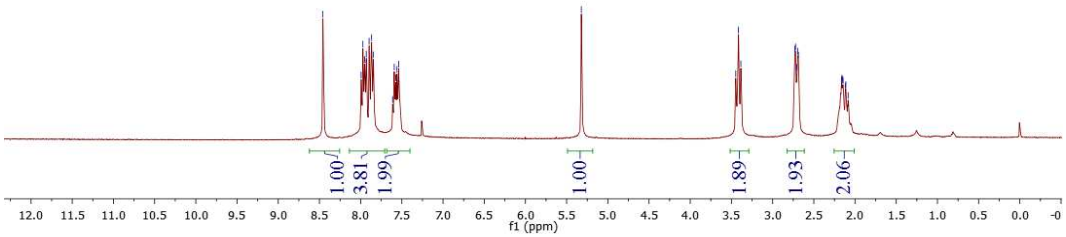

yk-nu-tj-pcf3-13c-new
new experiment
191.20
137.54
134.64
134.31
131.11
128.99
127.52
125.77
125.74
125.70
125.67
124.80
122.08
42.48
26.25
24.93
f1 (ppm)



4m

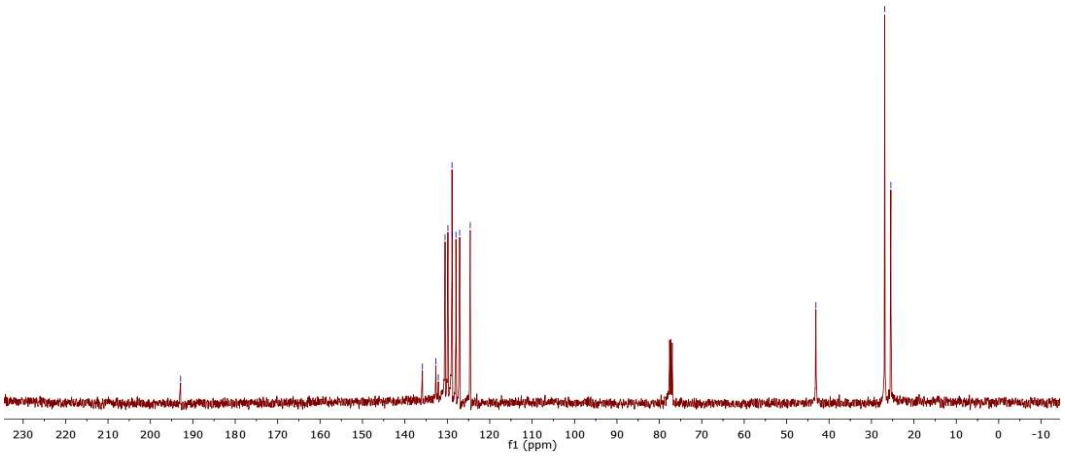
yk-nu-tj-2-naph-1h
STANDARD 1H OBSERVE

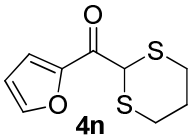
8.46 7.99 7.97 7.95 7.93 7.90 7.87 7.85 7.61 7.59 7.57 7.56 7.54 5.32 3.45 3.41 3.39 2.73 2.17 2.16 2.15 2.12 2.11 2.08



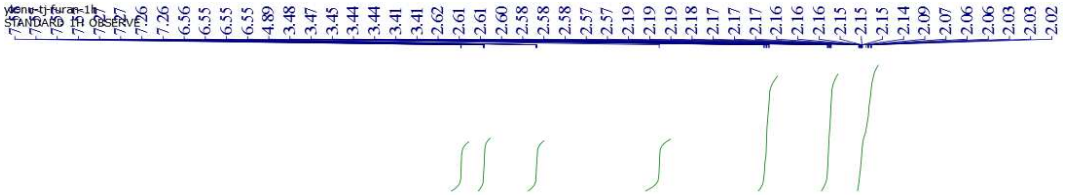
yk-nu-tj-2-naph-13c
13C OBSERVE

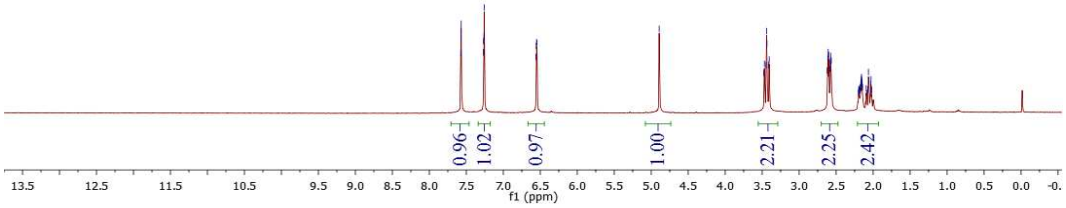
192.88 135.86 132.70 132.12 130.53 129.85 128.89 128.83 127.97 127.09 124.59 43.10 26.87 25.42

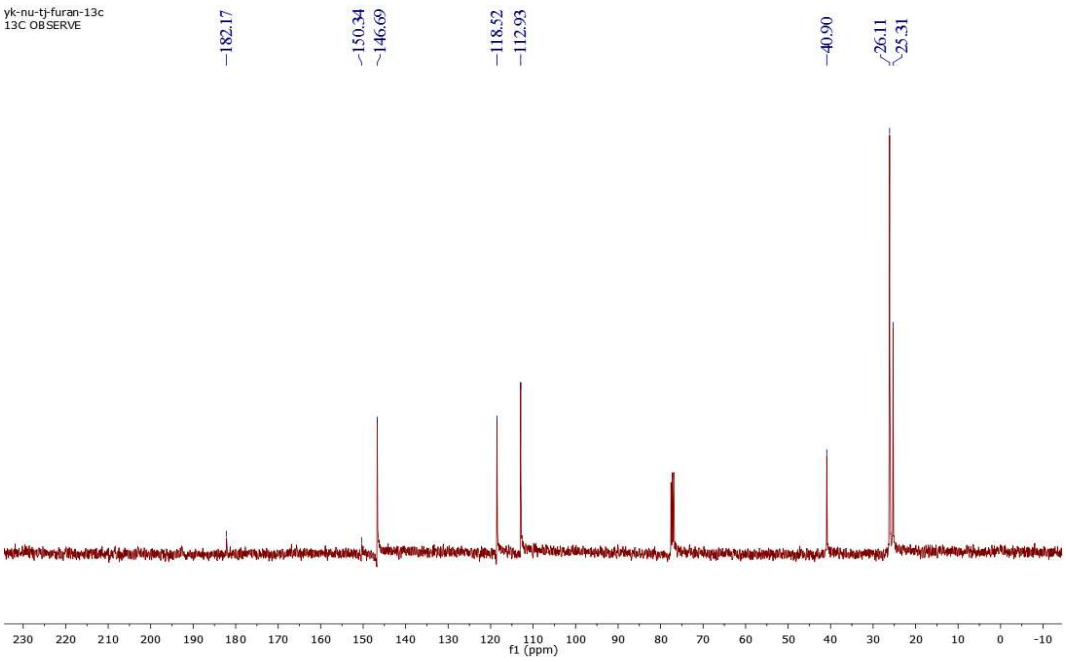


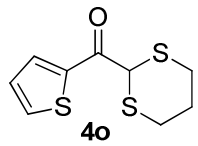

O
S
O
S

4n

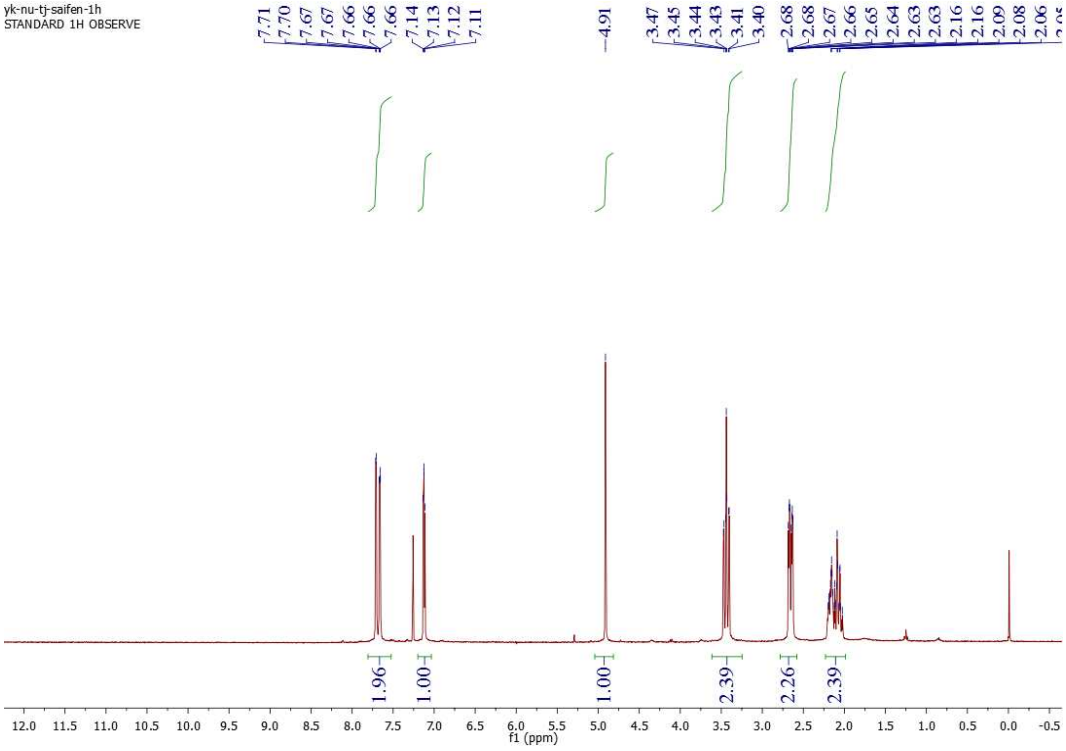


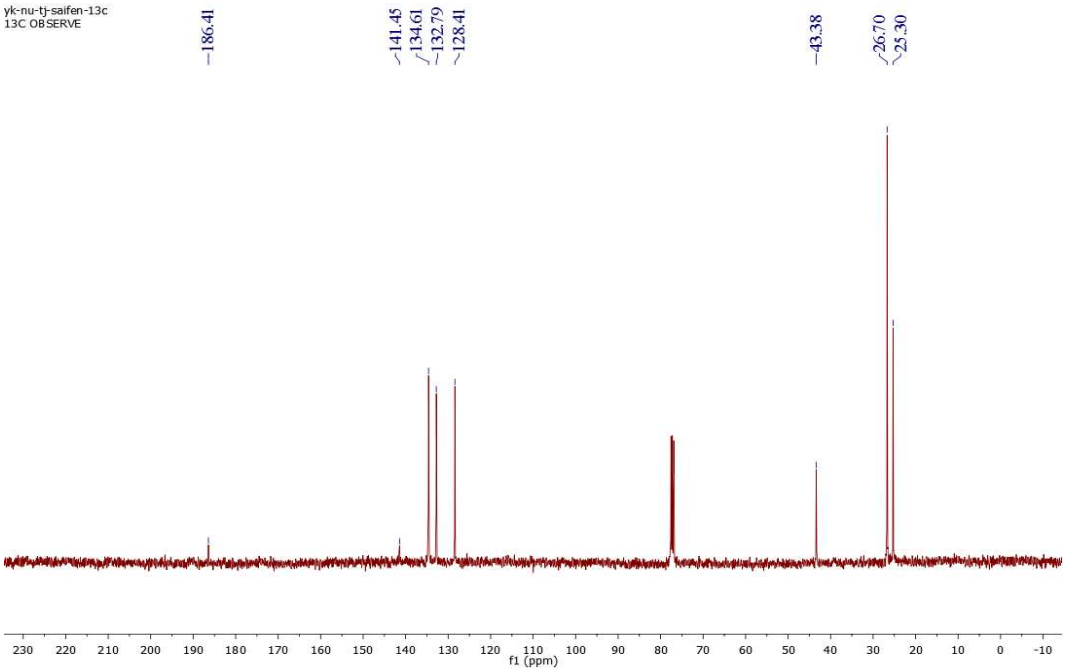

0.96
1.02
0.97
1.00
2.21
2.25
2.42
f1 (ppm)

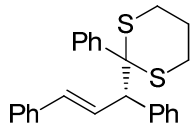

182.17
150.34
146.69
118.52
112.93
40.90
26.11
25.31
f1 (ppm)


O
S
S
S

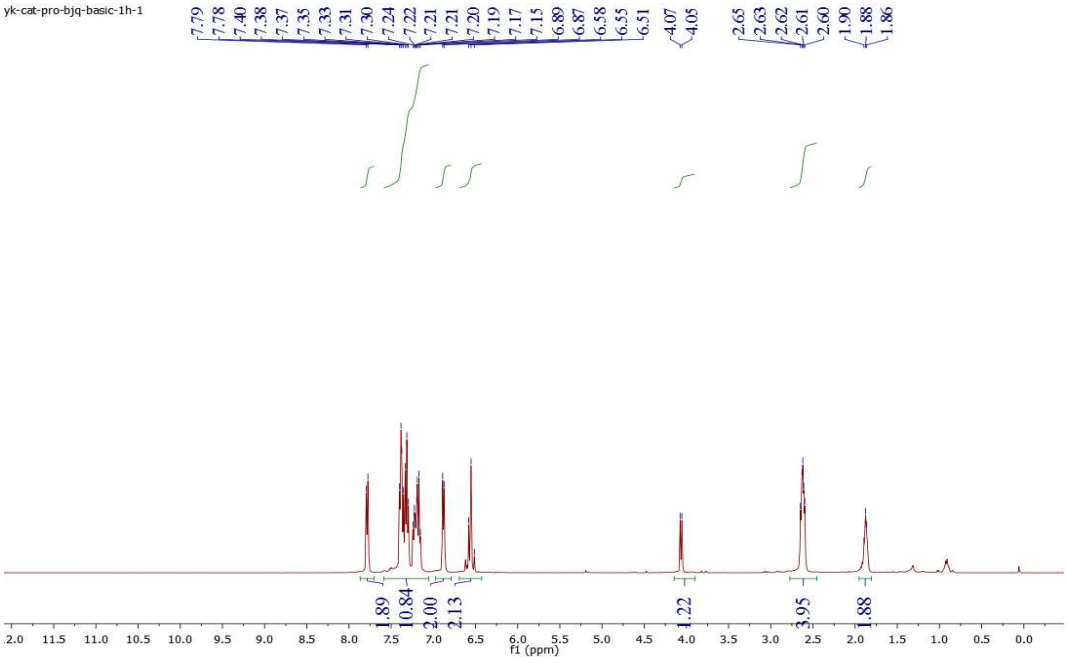
4o

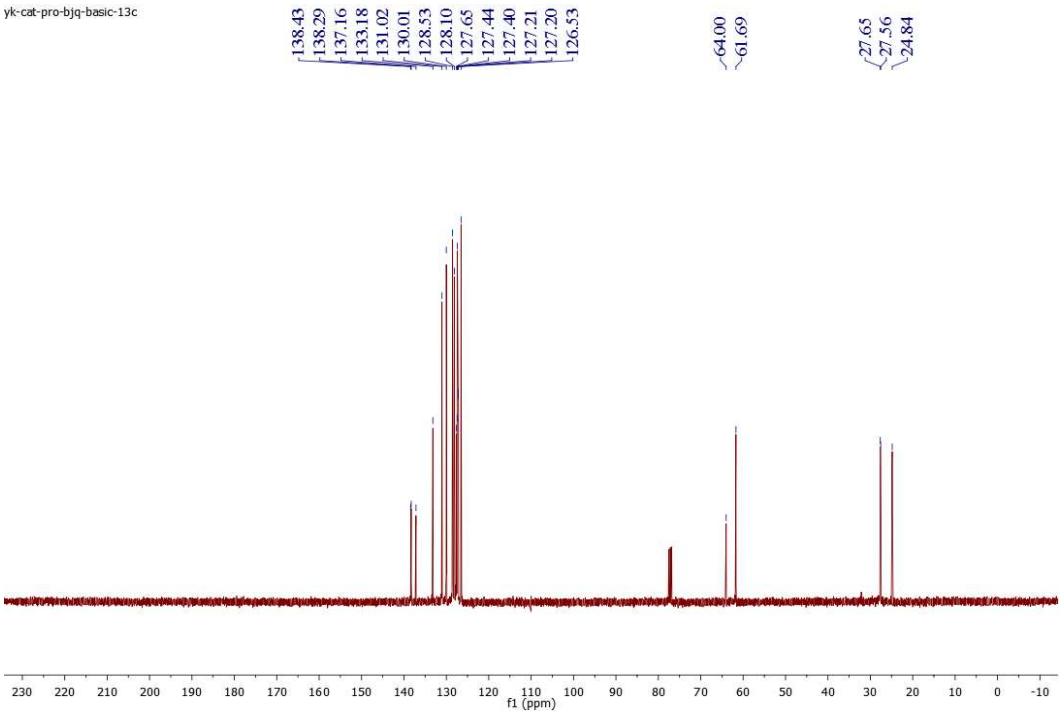

yk-nu-tj-saifen-1h
STANDARD 1H OBSERVE
7.71
7.70
7.67
7.67
7.66
7.66
7.66
7.14
7.13
7.12
7.11
4.91
3.47
3.45
3.44
3.43
3.41
3.40
2.68
2.68
2.67
2.66
2.65
2.64
2.63
2.63
2.16
2.16
2.09
2.08
2.06
1.96
1.00
1.00
2.39
2.26
2.39
f1 (ppm)

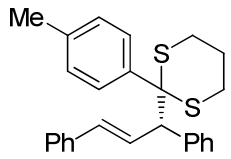

yk-nu-tj-saifen-13c
13C OBSERVE
186.41
141.45
134.61
132.79
128.41
43.38
26.70
25.30
f1 (ppm)


Ph
S
S
Ph
Ph

3a

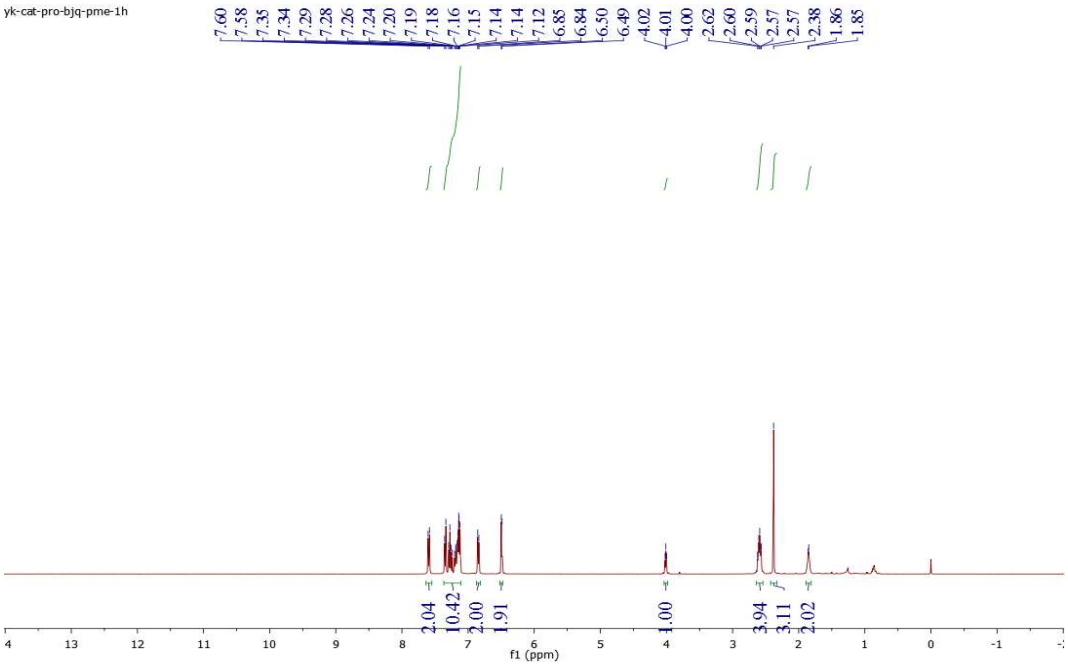

yk-cat-pro-bjq-basic-1h-1
7.79
7.78
7.40
7.38
7.37
7.35
7.33
7.31
7.30
7.24
7.22
7.21
7.21
7.20
7.19
7.17
7.15
6.89
6.87
6.58
6.55
6.51
4.07
4.05
2.65
2.63
2.62
2.61
2.60
1.90
1.88
1.86
1.89
10.84
2.00
2.13
1.22
3.95
1.88
f1 (ppm)


yk-cat-pro-bjq-basic-13c
138.43
138.29
137.16
133.18
131.02
130.01
128.53
128.10
127.65
127.44
127.40
127.21
127.20
126.53
64.00
61.69
27.65
27.56
24.84
f1 (ppm)

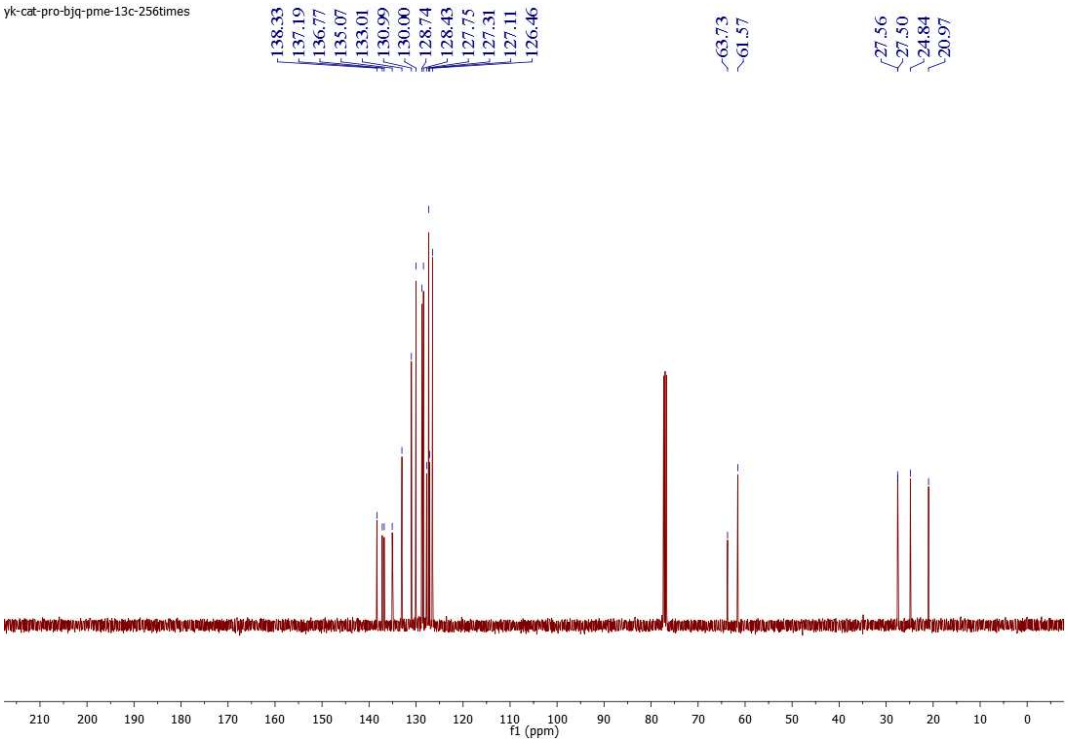


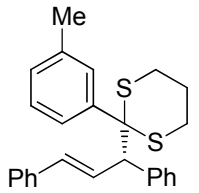
3b

yk-cat-pro-bjq-pme-1h

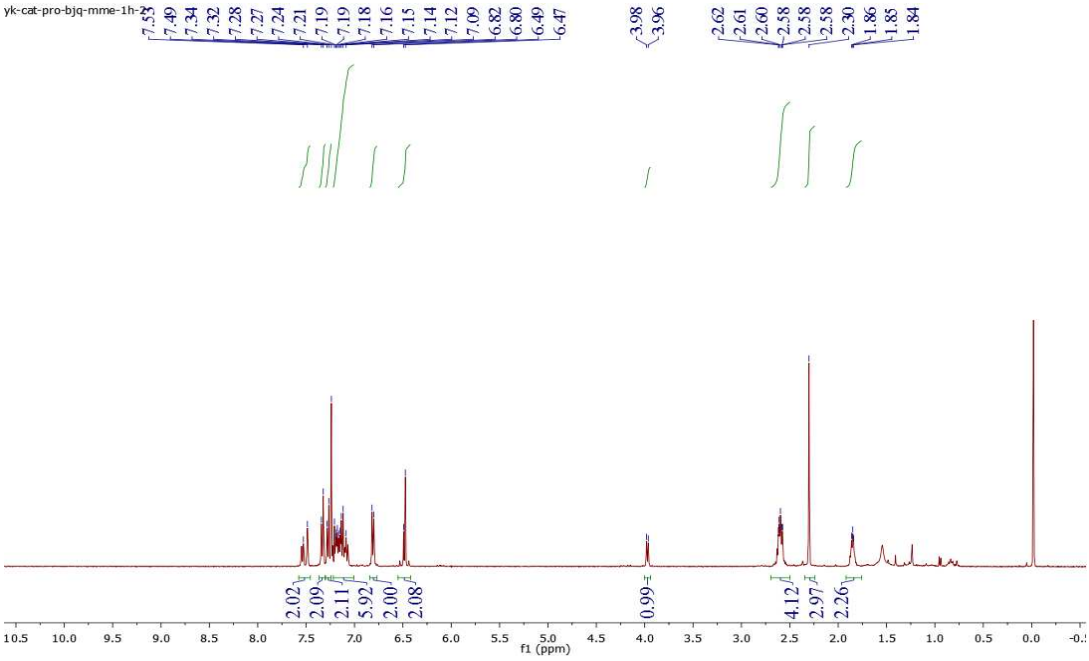


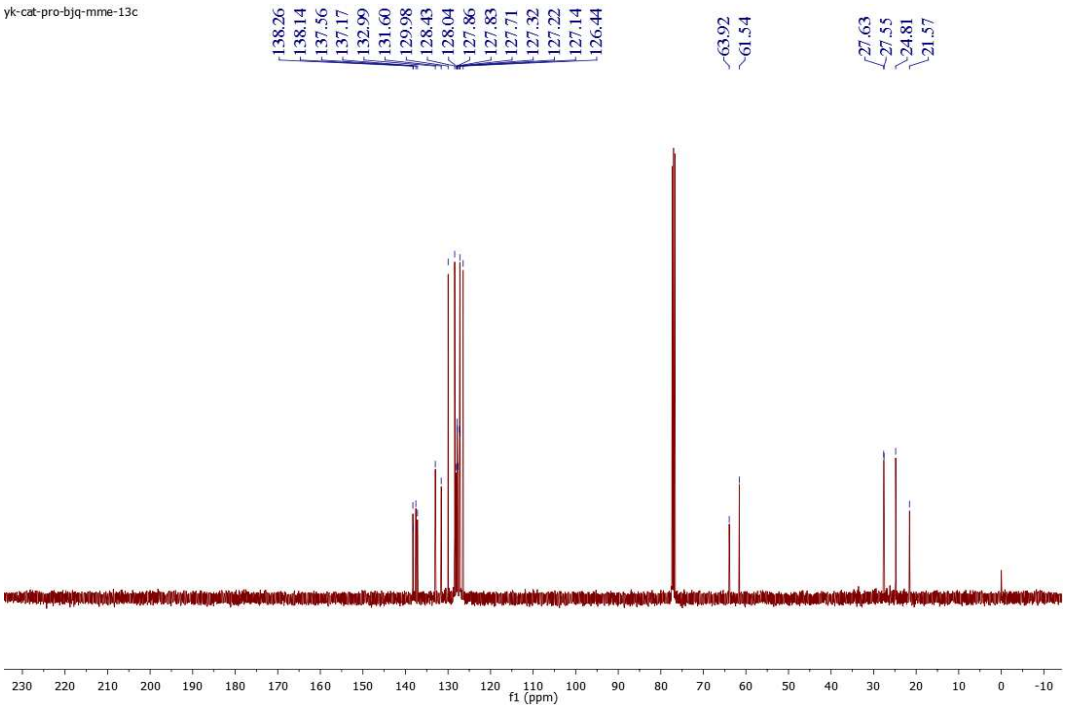
yk-cat-pro-bjq-pme-13c-256times

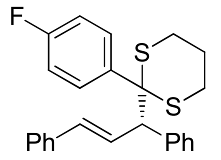



Me
S
S
Ph
Ph

3c

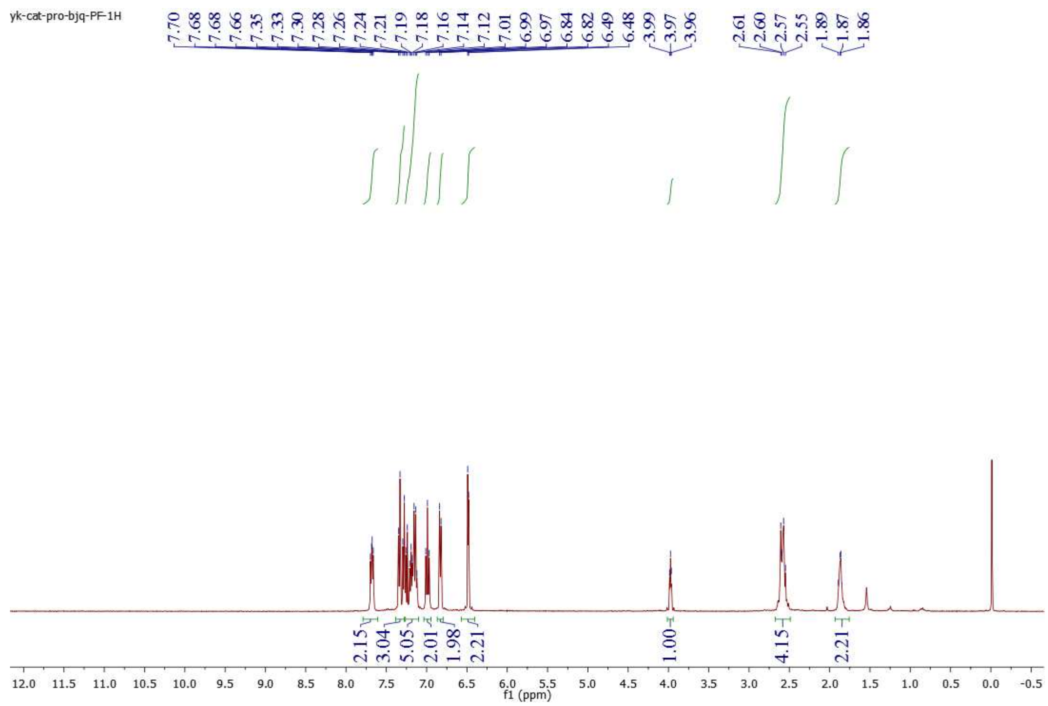

yk-cat-pro-bjq-mme-1h-2
7.53
7.49
7.34
7.32
7.28
7.27
7.24
7.21
7.19
7.19
7.18
7.16
7.15
7.14
7.12
7.09
6.82
6.80
6.49
6.47
3.98
3.96
2.62
2.61
2.60
2.58
2.58
2.58
2.30
1.86
1.85
1.84
2.02
2.09
2.11
5.92
2.00
2.08
0.99
4.12
2.97
2.26
f1 (ppm)


yk-cat-pro-bjq-mme-13c
138.26
138.14
137.56
137.17
132.99
131.60
129.98
128.43
128.04
127.86
127.83
127.71
127.32
127.22
127.14
126.44
63.92
61.54
27.63
27.55
24.81
21.57
f1 (ppm)

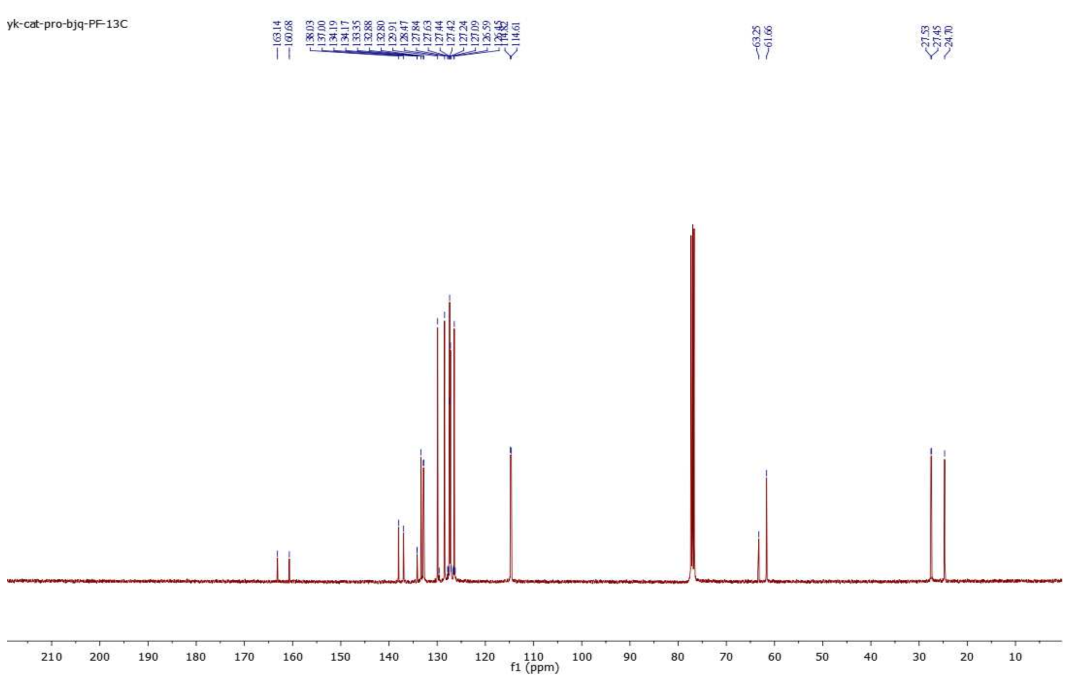


F
S
S
Ph
Ph

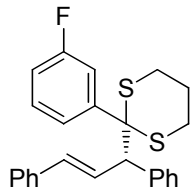
3d



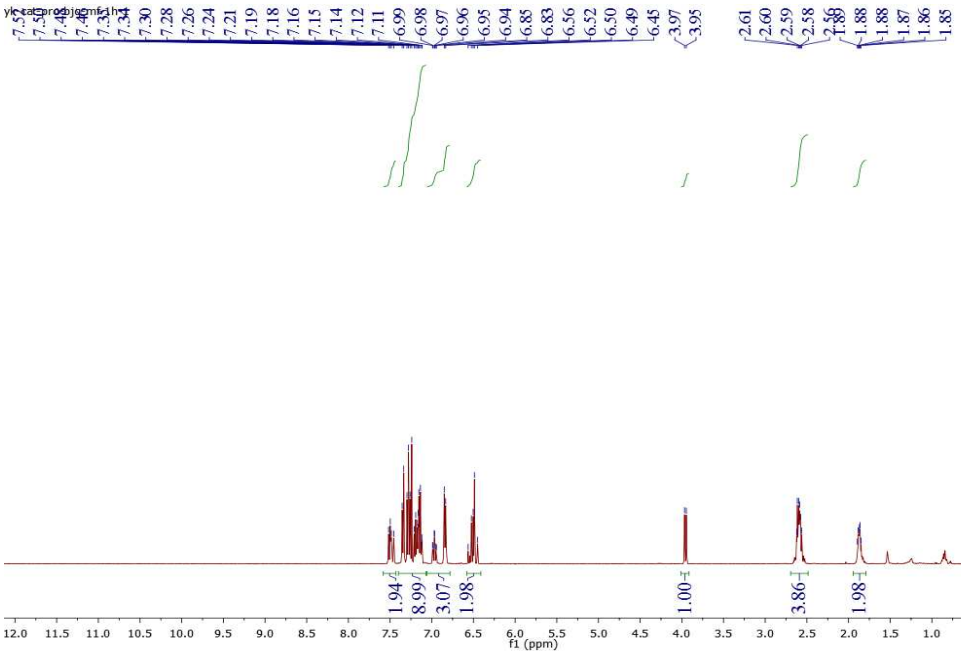
yk-cat-pro-bjq-PF-1H
7.70
7.68
7.68
7.66
7.35
7.33
7.30
7.28
7.26
7.24
7.21
7.19
7.18
7.16
7.14
7.12
7.01
6.99
6.97
6.84
6.82
6.49
6.48
3.99
3.97
3.96
2.61
2.60
2.57
2.55
1.89
1.87
1.86
2.15
3.04
5.05
2.01
1.98
2.21
1.00
4.15
2.21
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

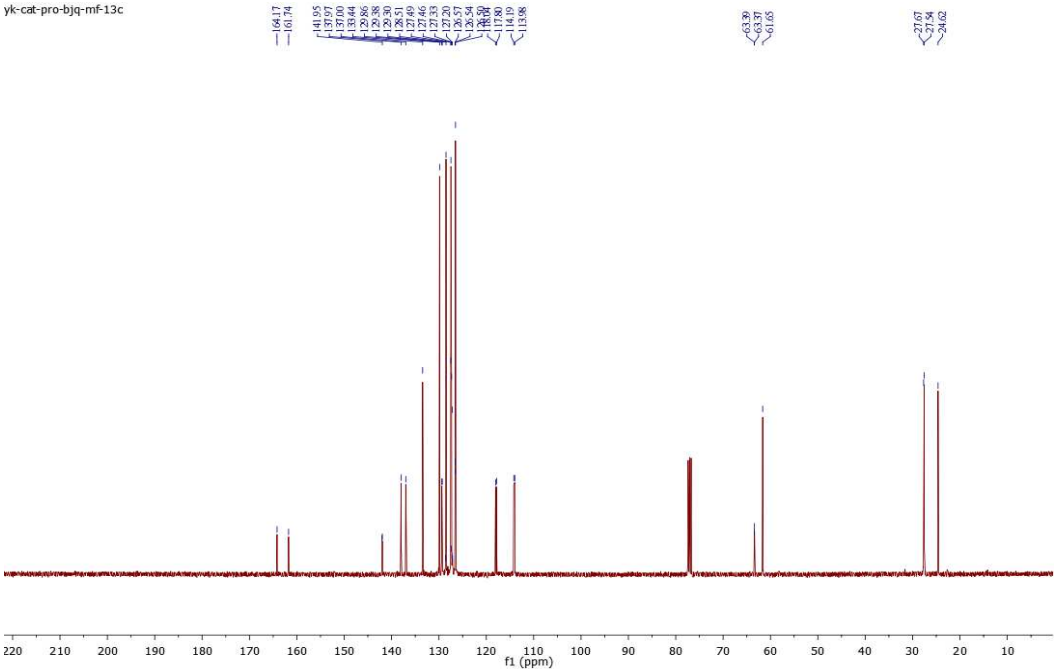


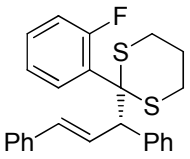
yk-cat-pro-bjq-PF-13C
163.14
160.68
138.03
137.00
134.19
134.17
133.35
132.88
132.80
129.91
128.47
127.84
127.63
127.44
127.42
127.24
127.09
126.59
126.45
114.82
114.61
63.25
61.66
27.53
27.45
24.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


F
S
S
Ph
Ph

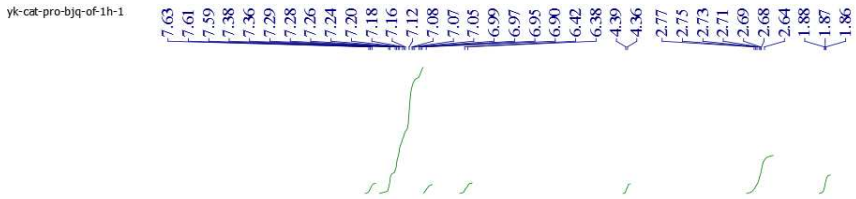
3e

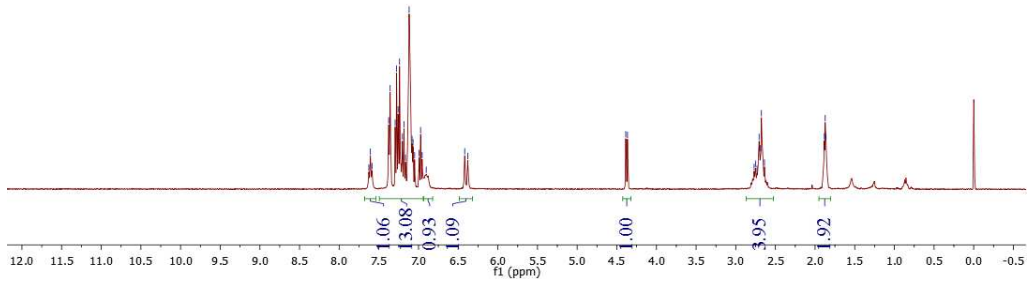

1.94
8.99
3.07
1.98
1.00
3.86
1.98
f1 (ppm)


yk-cat-pro-bjq-mf-13c
f1 (ppm)

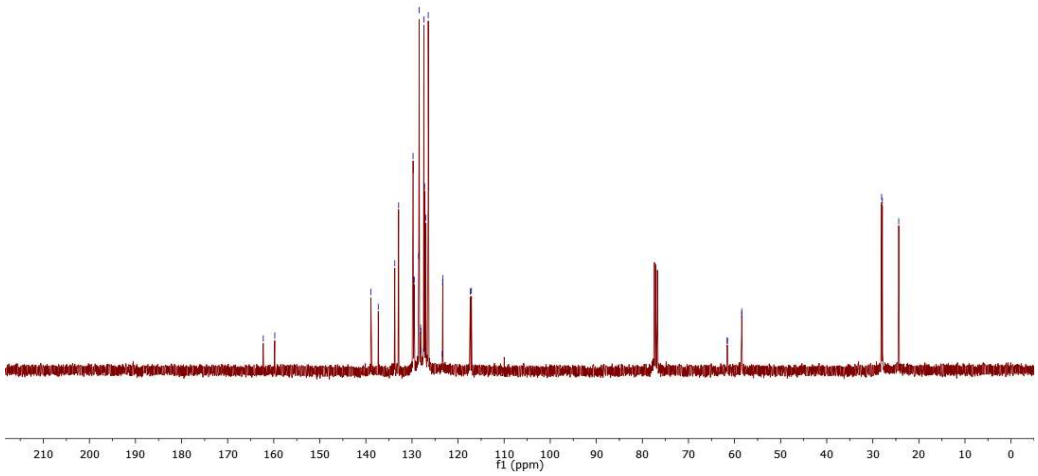

F
S
S
Ph
Ph

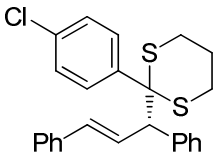
3f


yk-cat-pro-bjq-of-1h-1
7.63
7.61
7.59
7.38
7.36
7.29
7.28
7.26
7.24
7.20
7.18
7.16
7.12
7.08
7.07
7.05
6.99
6.97
6.95
6.90
6.42
6.38
4.39
4.36
2.77
2.75
2.73
2.71
2.69
2.68
2.64
1.88
1.87
1.86

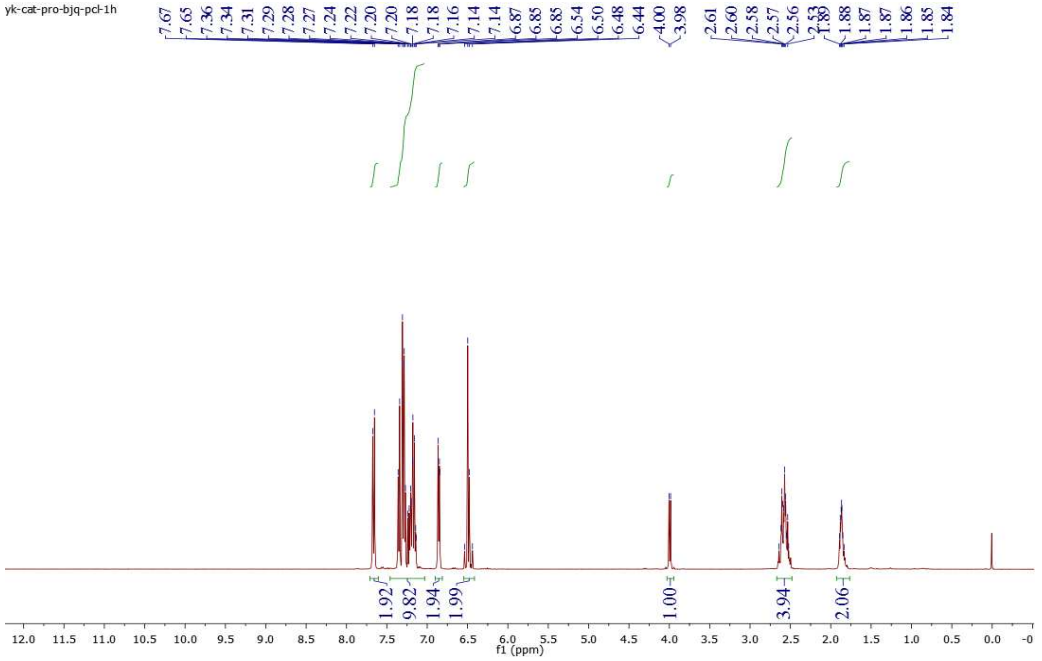

1.06
13.08
0.93
1.09
1.00
3.95
1.92
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

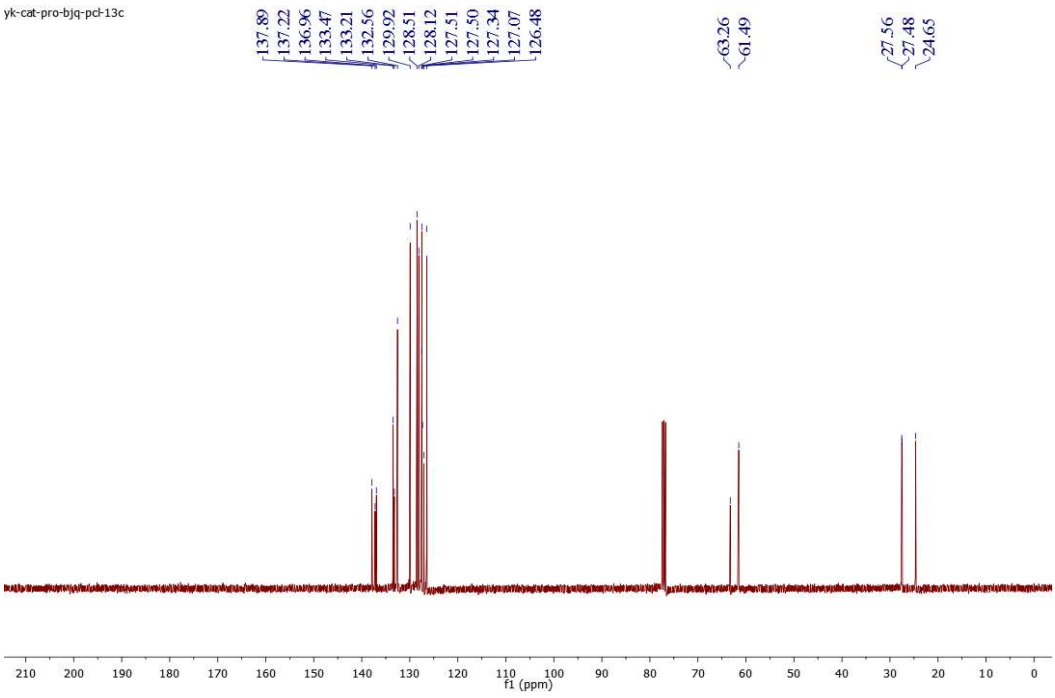

yk-cat-pro-bjq-of-13c
new experiment
162.28
159.78
138.93
137.32
133.73
132.90
129.76
129.60
129.51
128.54
128.42
128.14
128.07
127.43
127.26
127.03
126.47
123.36
123.32
117.34
117.10
61.60
61.54
58.45
58.43
28.09
27.92
24.37

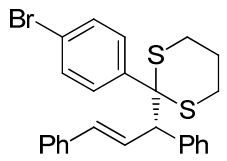

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
S
S
Ph
Ph

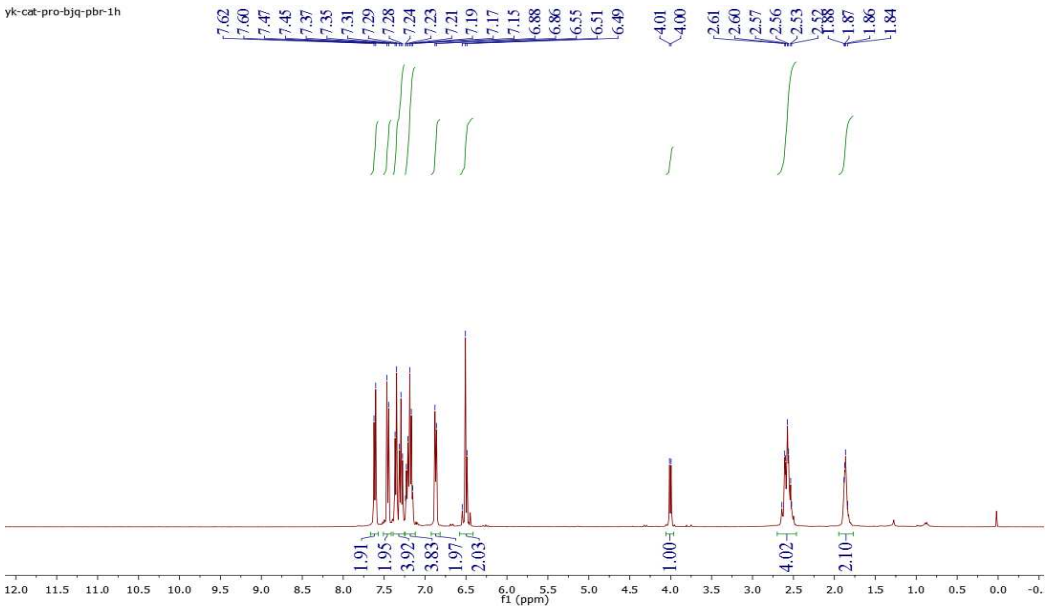
3g

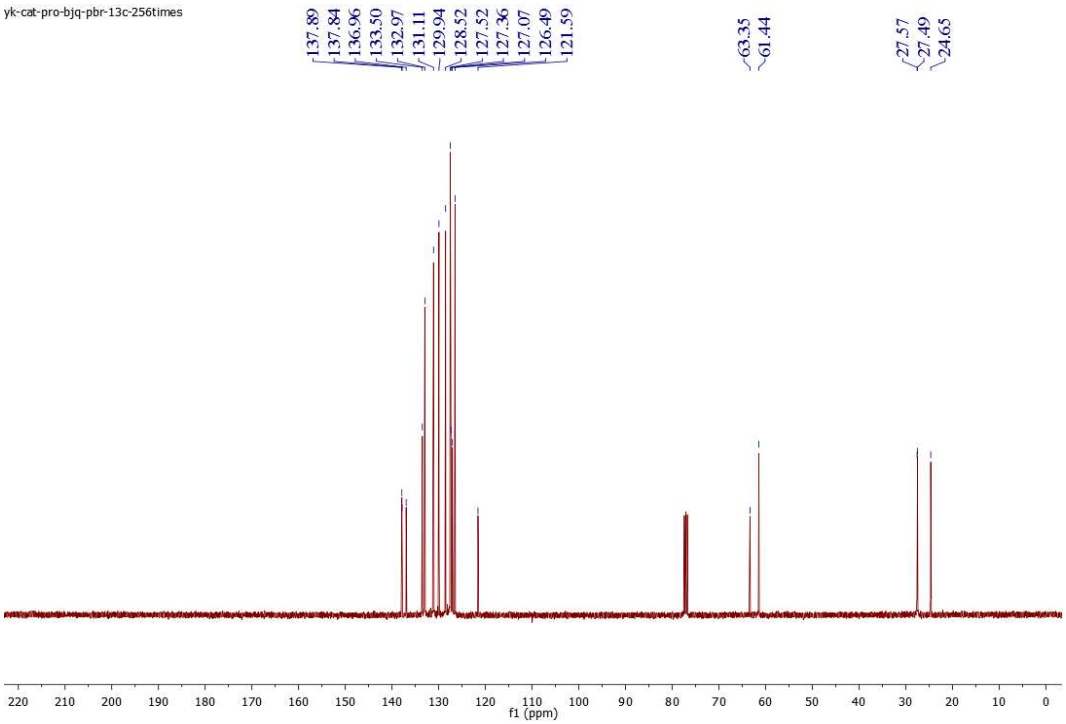

yk-cat-pro-bjq-pcl-1h
7.67
7.65
7.36
7.34
7.31
7.29
7.28
7.27
7.24
7.22
7.20
7.20
7.18
7.18
7.16
7.14
7.14
6.87
6.85
6.85
6.54
6.50
6.48
6.44
4.00
3.98
2.61
2.60
2.58
2.57
2.56
1.88
1.87
1.87
1.86
1.85
1.84
1.92
9.82
1.94
1.99
1.00
3.94
2.06
f1 (ppm)

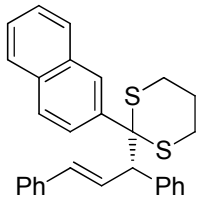

yk-cat-pro-bjq-pcl-13c
137.89
137.22
136.96
133.47
133.21
132.56
129.92
128.51
128.12
127.51
127.50
127.34
127.07
126.48
63.26
61.49
27.56
27.48
24.65
f1 (ppm)


Br
S
S
Ph
Ph

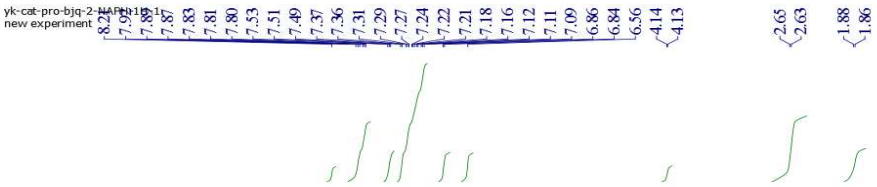
3h

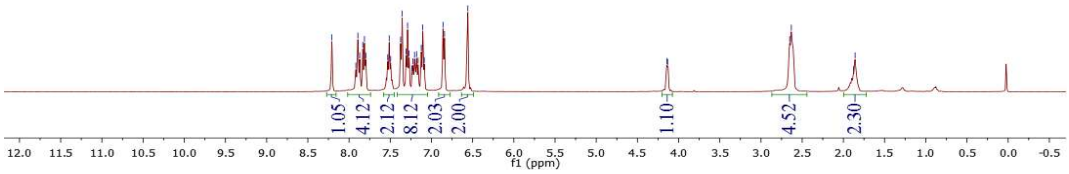

yk-cat-pro-bjq-pbr-1h
7.62
7.60
7.47
7.45
7.37
7.35
7.31
7.29
7.28
7.24
7.23
7.21
7.19
7.17
7.15
6.88
6.86
6.55
6.51
6.49
4.01
4.00
2.61
2.60
2.57
2.56
2.53
1.88
1.87
1.86
1.84
1.91
1.95
3.92
3.83
1.97
2.03
1.00
4.02
2.10
f1 (ppm)


yk-cat-pro-bjq-pbr-13c-256times
137.89
137.84
136.96
133.50
132.97
131.11
129.94
128.52
127.52
127.36
127.07
126.49
121.59
63.35
61.44
27.57
27.49
24.65
f1 (ppm)

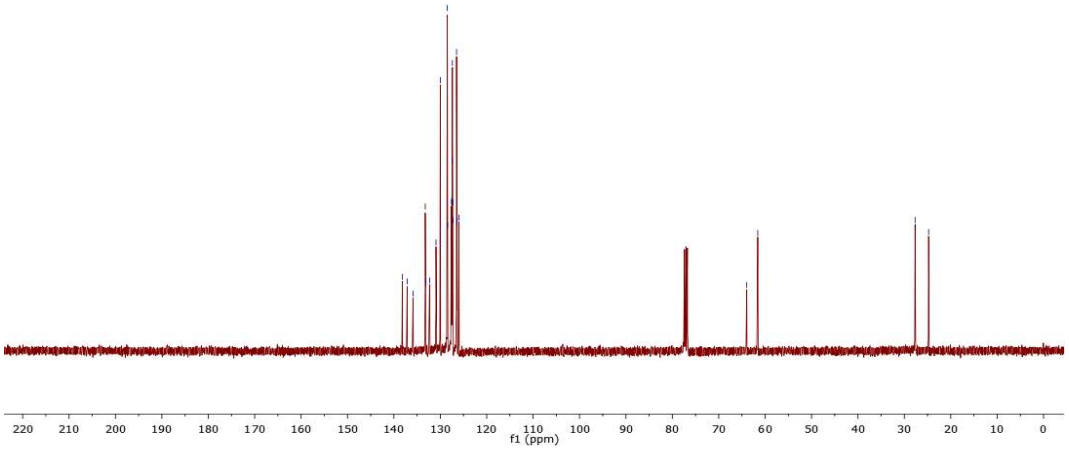

S
S
Ph
Ph

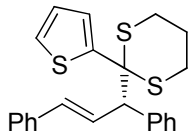
3i


yk-cat-pro-bjq-2-NAPH-1H
new experiment
8.27
7.92
7.89
7.87
7.83
7.81
7.80
7.53
7.51
7.49
7.37
7.36
7.31
7.29
7.27
7.24
7.22
7.21
7.18
7.16
7.12
7.11
7.09
6.86
6.84
6.56
4.14
4.13
2.65
2.63
1.88
1.86

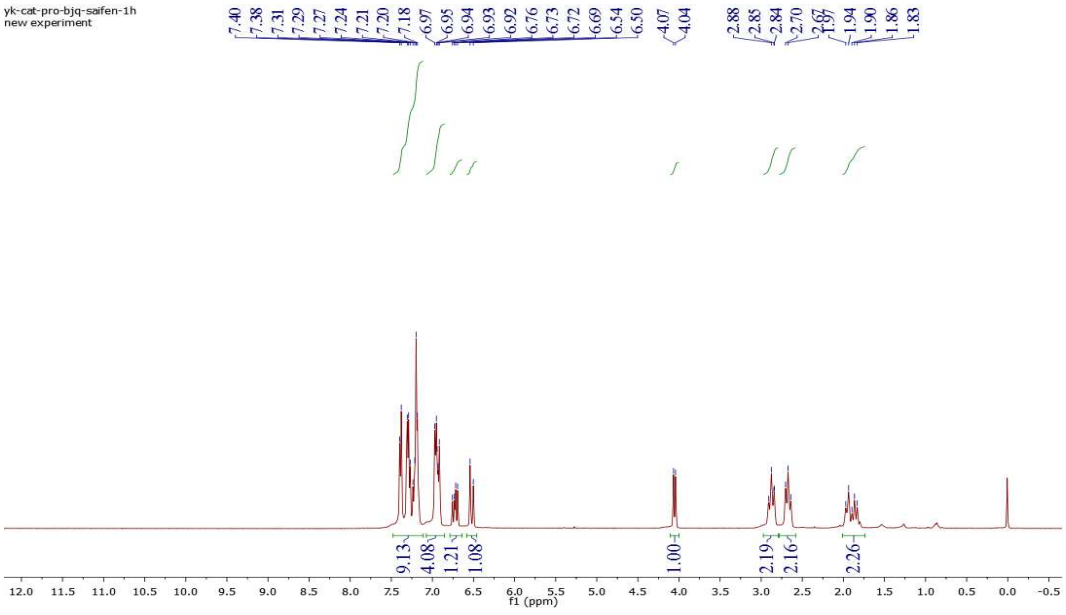

1.05
4.12
2.12
8.12
2.03
2.00
1.10
4.52
2.30
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

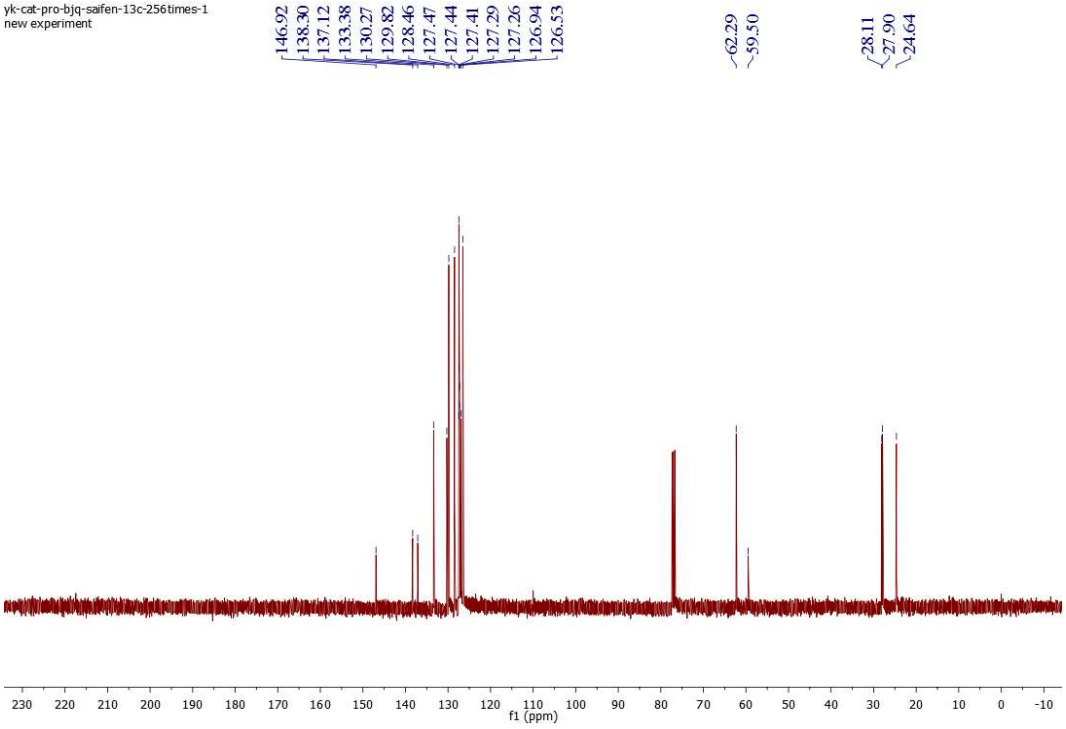

yk-cat-pro-bjq-2-NAPH-13C
new experiment
138.18
137.13
135.87
133.24
133.16
132.31
130.93
130.00
128.49
128.42
127.58
127.51
127.42
127.39
127.31
127.26
126.50
126.37
125.99
63.96
61.59
27.69
27.61
24.77

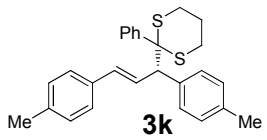

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


S
S
S
Ph
Ph

3j

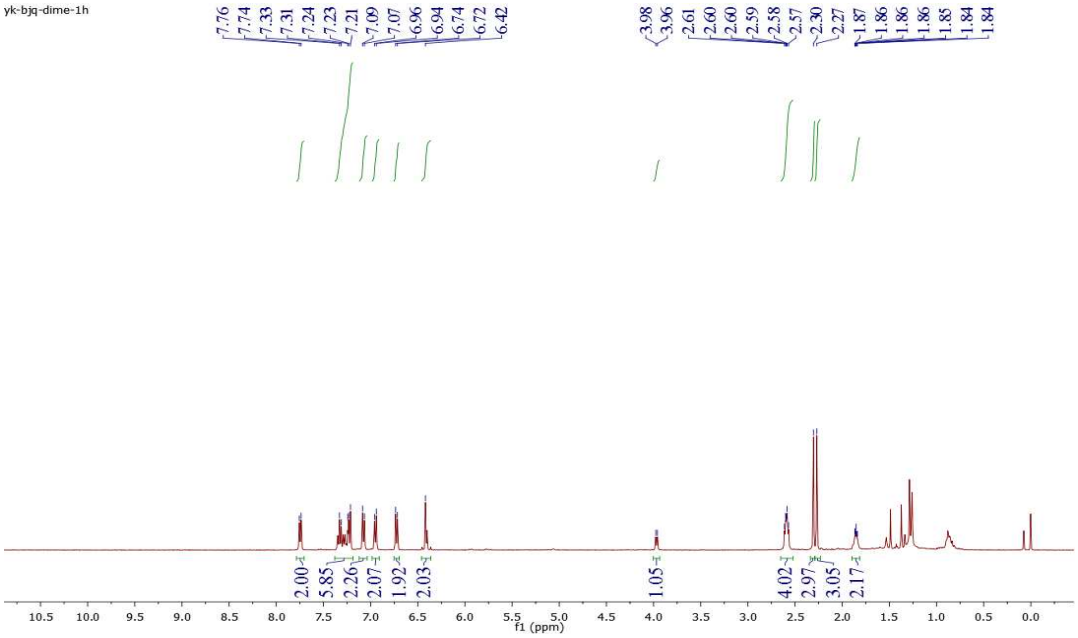

yk-cat-pro-bjq-saifen-1h
new experiment
7.40
7.38
7.31
7.29
7.27
7.24
7.21
7.20
7.18
6.97
6.95
6.94
6.93
6.92
6.76
6.73
6.72
6.69
6.54
6.50
4.07
4.04
2.88
2.85
2.84
2.70
2.67
1.97
1.94
1.90
1.86
1.83
9.13
4.08
1.21
1.08
1.00
2.19
2.16
2.26
f1 (ppm)


yk-cat-pro-bjq-saifen-13c-256times-1
new experiment
146.92
138.30
137.12
133.38
130.27
129.82
128.46
127.47
127.44
127.41
127.29
127.26
126.94
126.53
62.29
59.50
28.11
27.90
24.64
f1 (ppm)

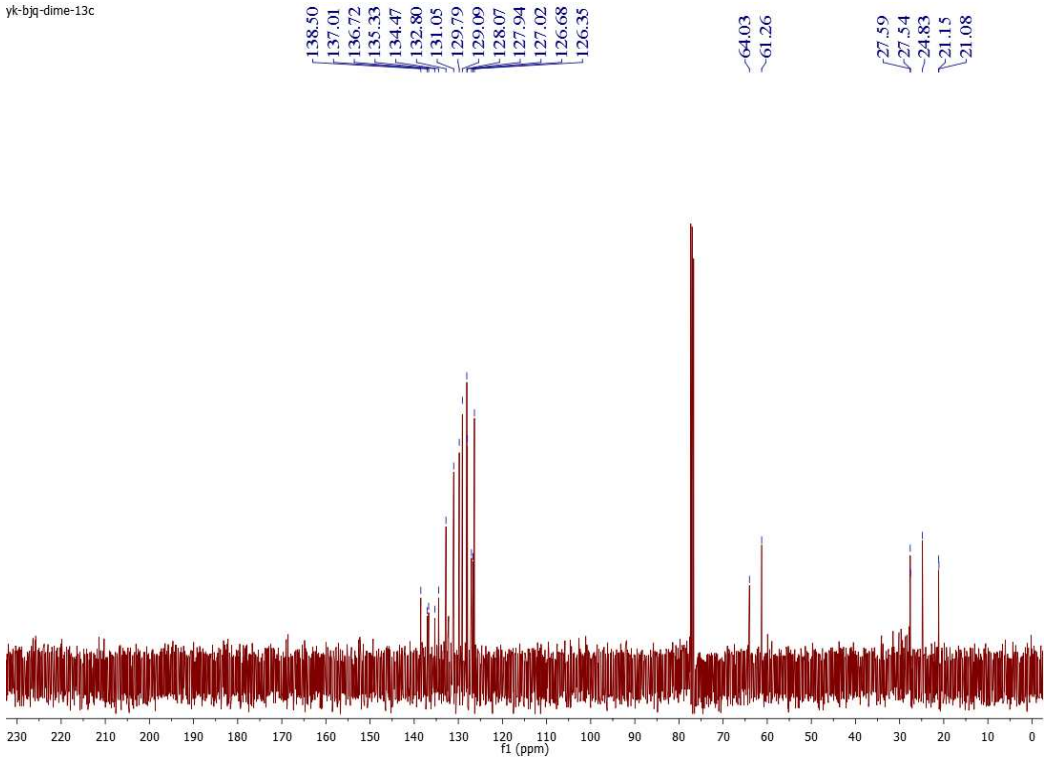


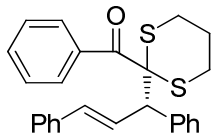
3k

yk-bjq-dime-1h

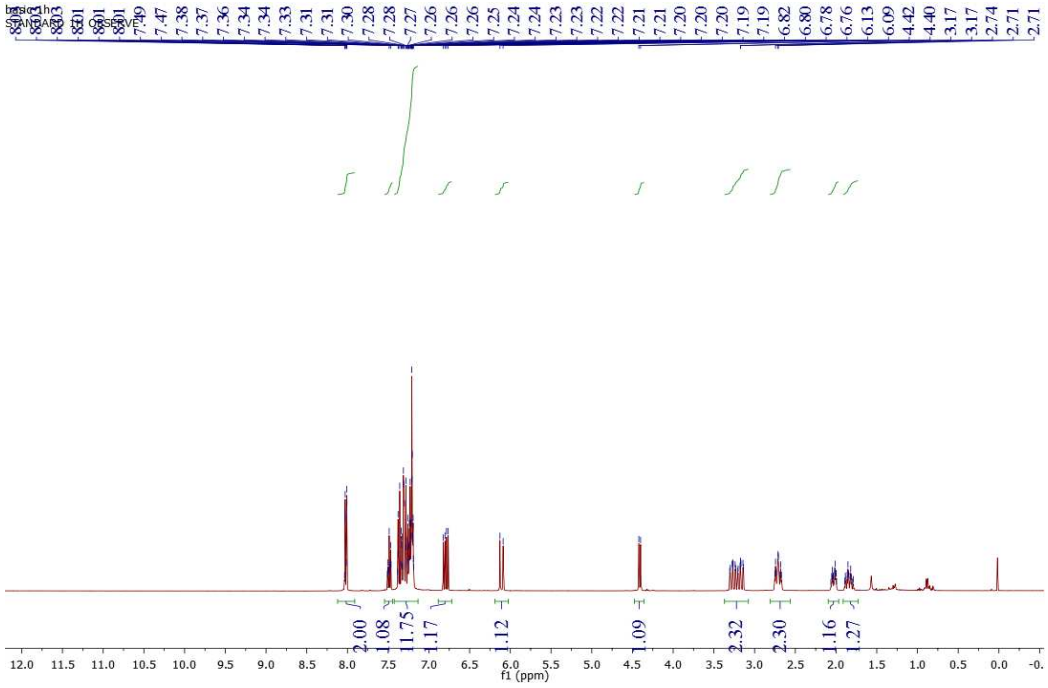


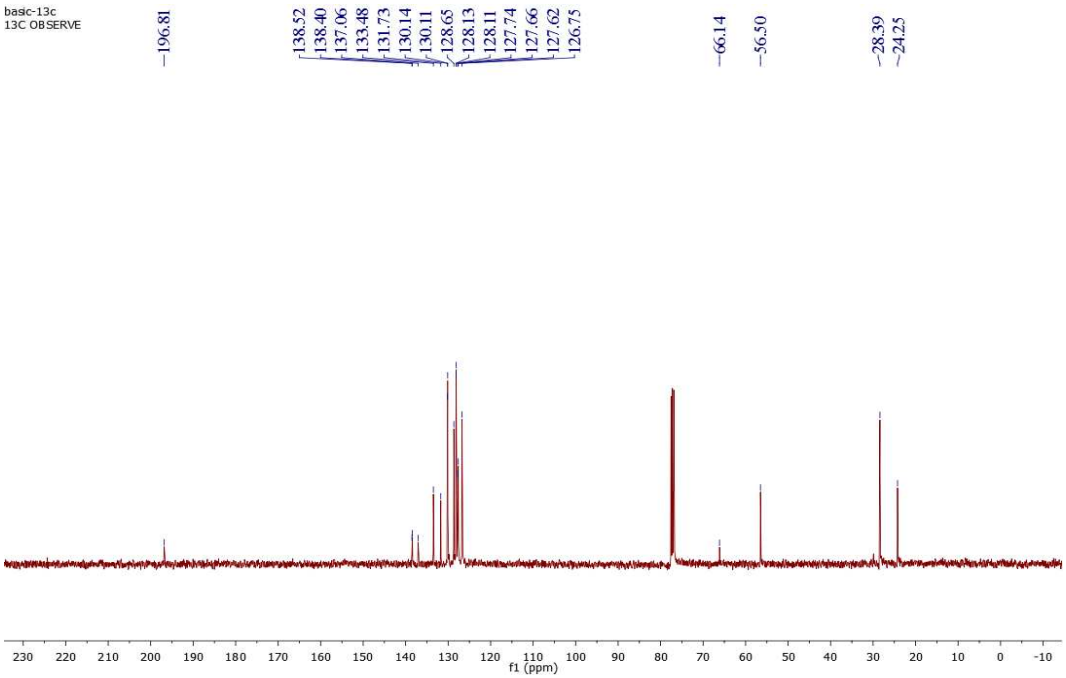
yk-bjq-dime-13c

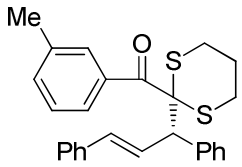



O
S
S
Ph
Ph

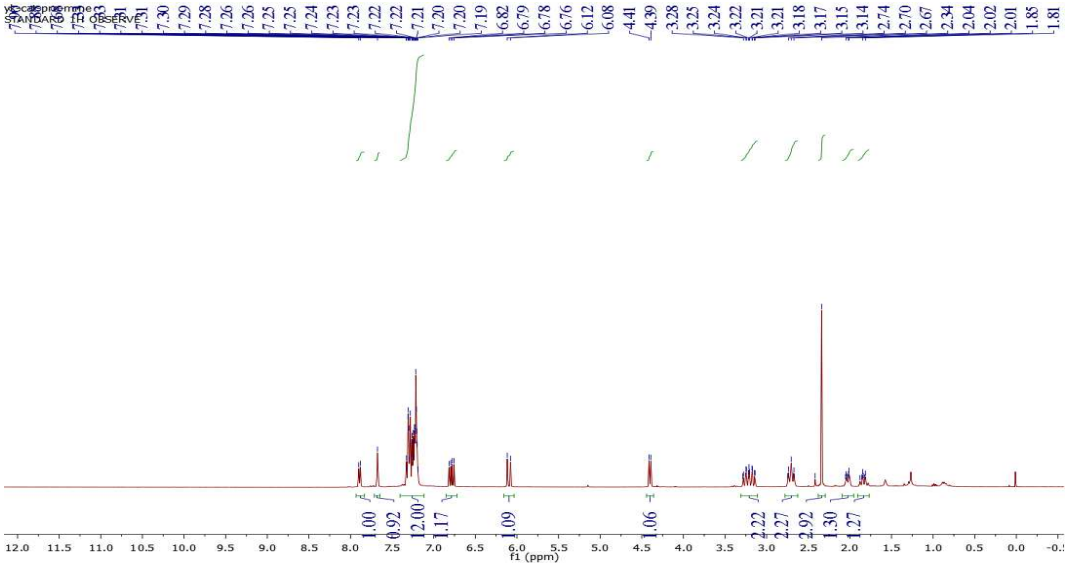
5a

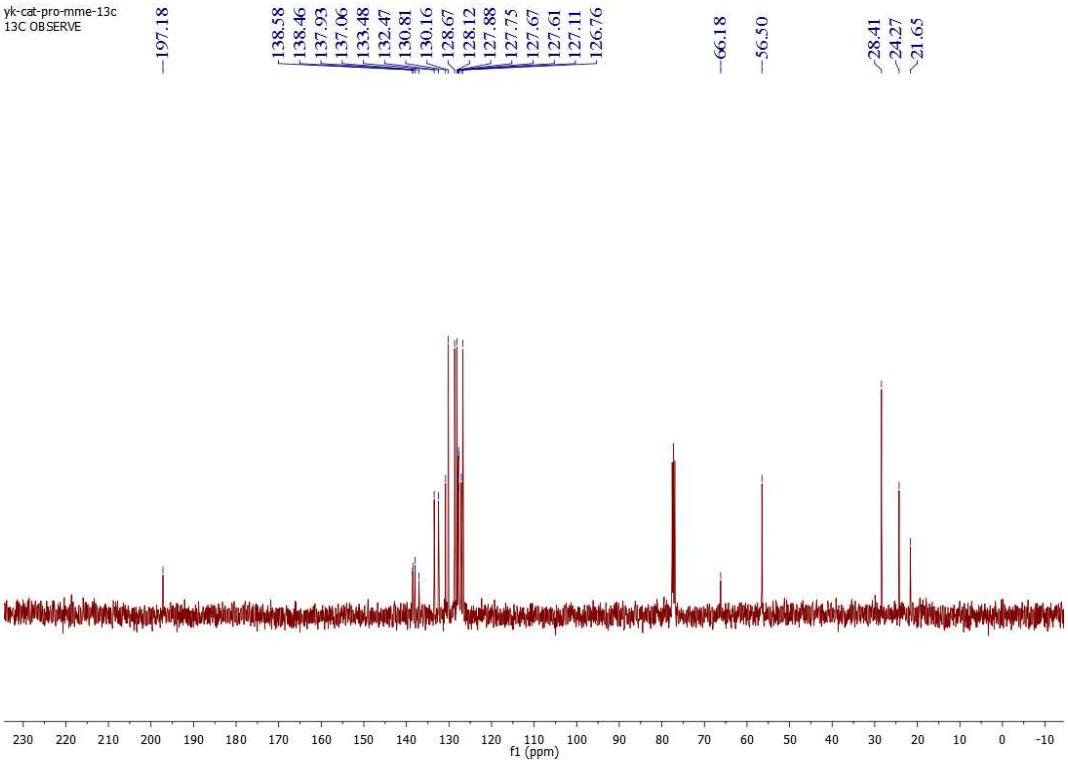

7.47
7.38
7.37
7.36
7.34
7.34
7.33
7.31
7.31
7.30
7.28
7.28
7.27
7.26
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.20
7.19
7.19
6.82
6.80
6.78
6.76
6.13
6.09
4.42
4.40
3.17
3.17
2.74
2.71
2.71
2.00
1.08
11.75
1.17
1.12
1.09
2.32
2.30
1.16
1.27
f1 (ppm)

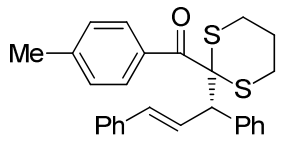

basic-13c
13C OBSERVE
196.81
138.52
138.40
137.06
133.48
131.73
130.14
130.11
128.65
128.13
128.11
127.74
127.66
127.62
126.75
66.14
56.50
28.39
24.25
f1 (ppm)


Me
O
S
S
Ph
Ph

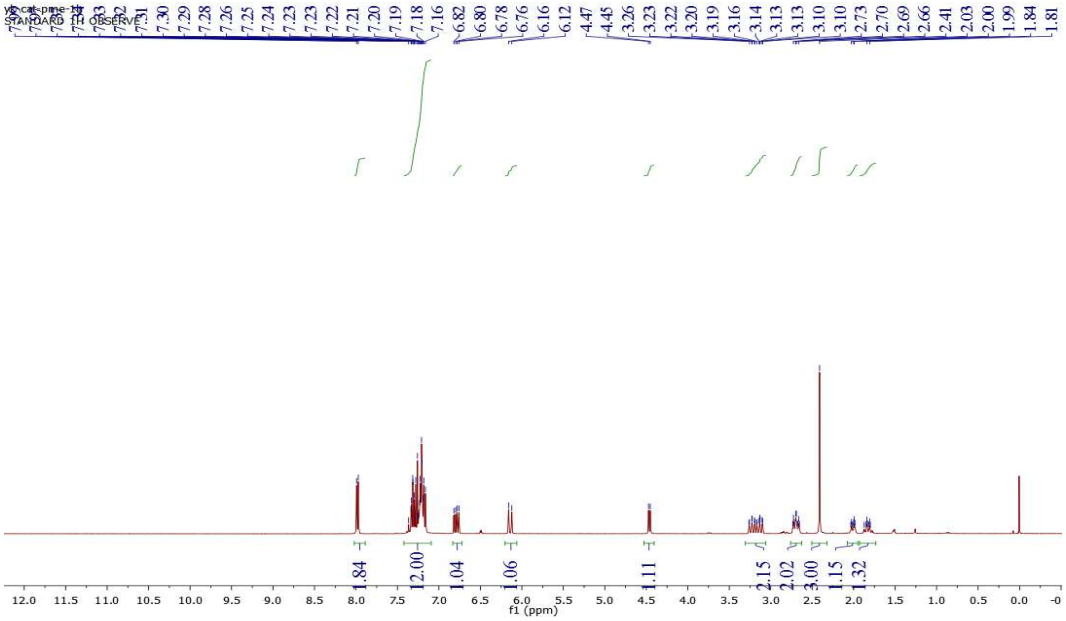
5b

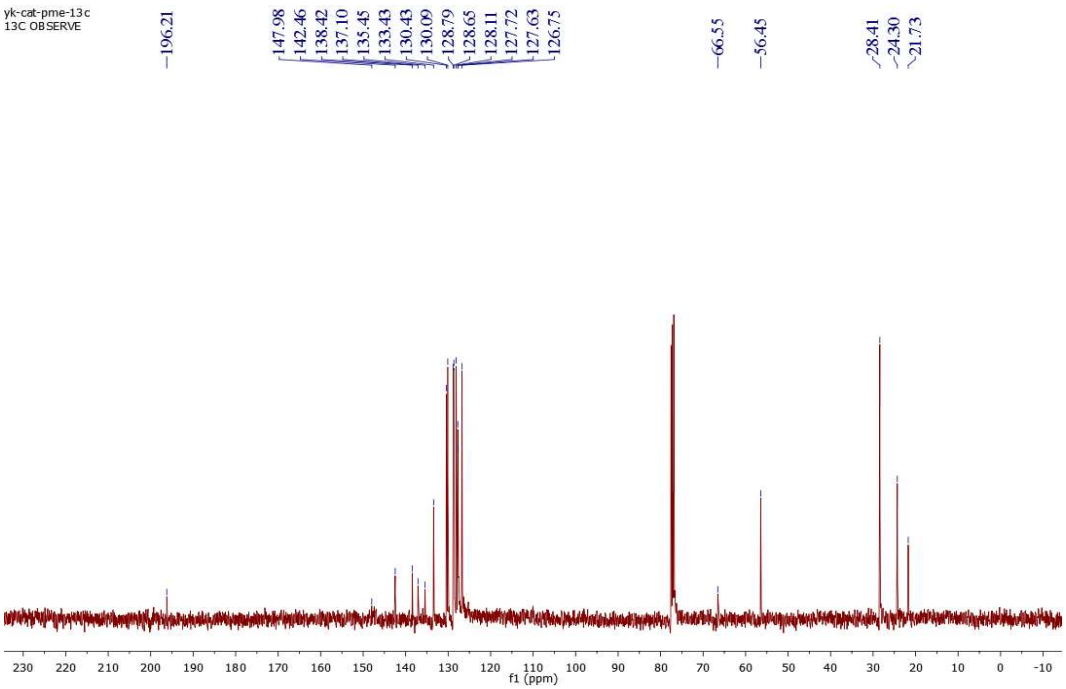

STANDARD 1H OBSERVE
7.30
7.29
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
6.82
6.79
6.78
6.76
6.12
6.08
4.41
4.39
3.28
3.25
3.24
3.22
3.21
3.18
3.17
3.15
3.14
2.74
2.70
2.67
2.34
2.04
2.02
2.01
1.85
1.81
1.00
0.92
2.00
1.17
1.09
1.06
2.22
2.27
2.92
1.30
1.27
f1 (ppm)

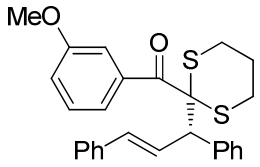

yk-cat-pro-mme-13c
13C OBSERVE
197.18
138.58
138.46
137.93
137.06
133.48
132.47
130.81
130.16
128.67
128.12
127.88
127.75
127.67
127.61
127.11
126.76
66.18
56.50
28.41
24.27
21.65
f1 (ppm)


Me
O
S
S
Ph
Ph

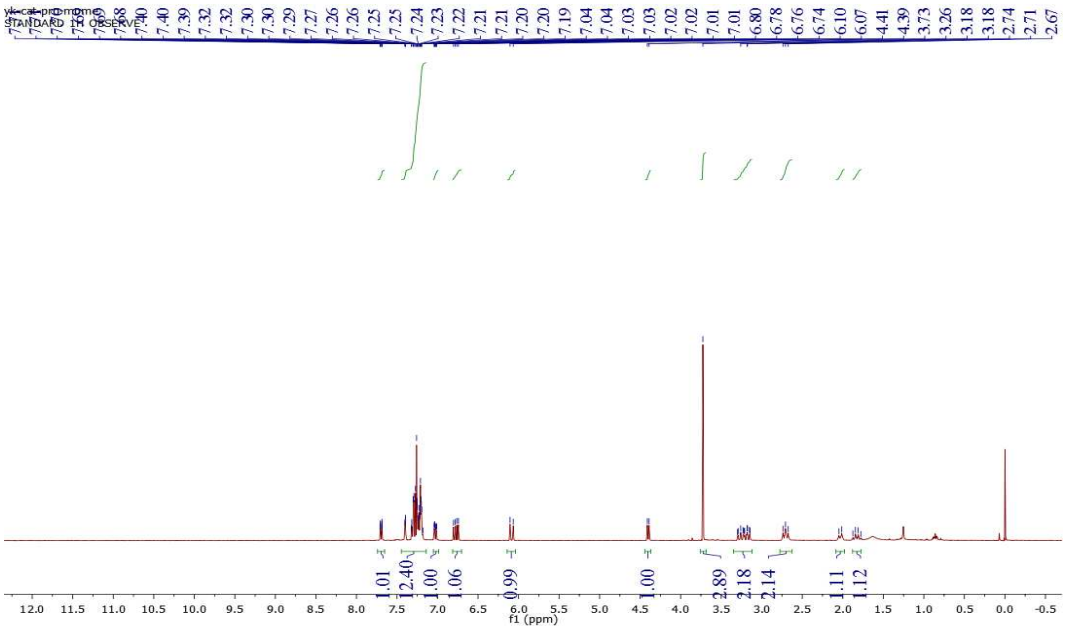
5c

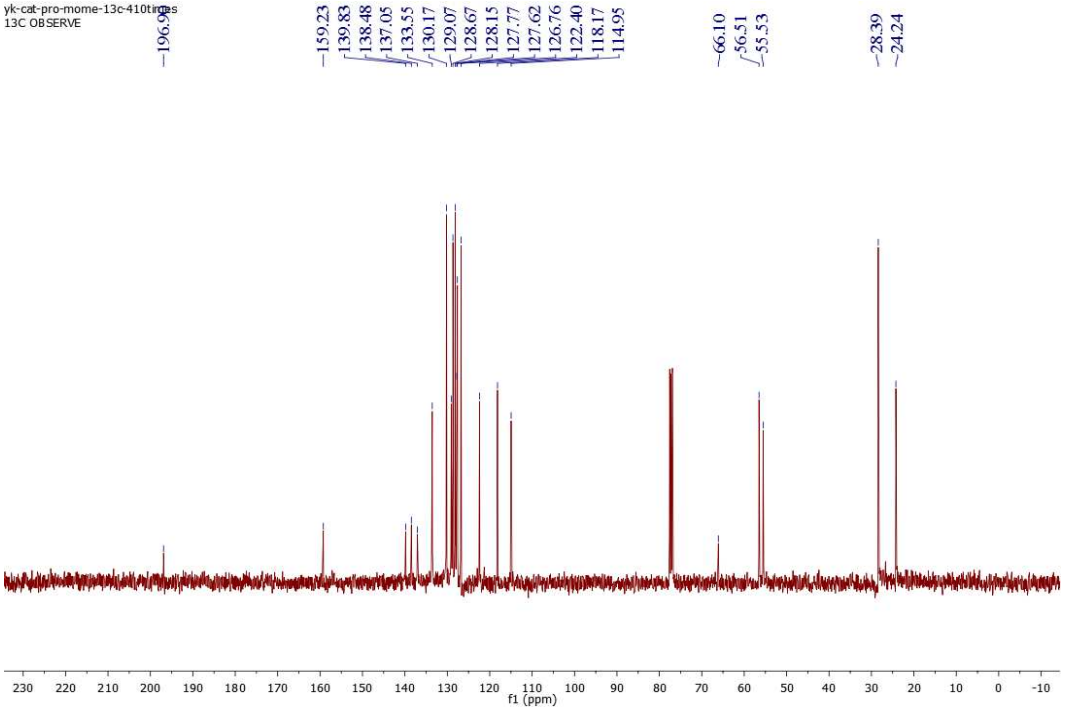

yk-cat-pme-1H
STANDARD 1H OBSERVE
7.33
7.32
7.31
7.30
7.29
7.28
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.19
7.18
7.16
6.82
6.80
6.78
6.76
6.16
6.12
4.47
4.45
3.26
3.23
3.22
3.20
3.19
3.16
3.14
3.13
3.13
3.10
3.10
2.73
2.70
2.69
2.66
2.41
2.03
2.00
1.99
1.84
1.81
1.84
12.00
1.04
1.06
1.11
2.15
2.02
3.00
1.15
1.32
f1 (ppm)

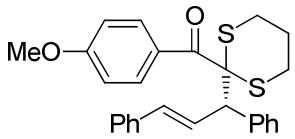

yk-cat-pme-13c
13C OBSERVE
196.21
147.98
142.46
138.42
137.10
135.45
133.43
130.43
130.09
128.79
128.65
128.11
127.72
127.63
126.75
66.55
56.45
28.41
24.30
21.73
f1 (ppm)


MeO
O
S
S
Ph
Ph

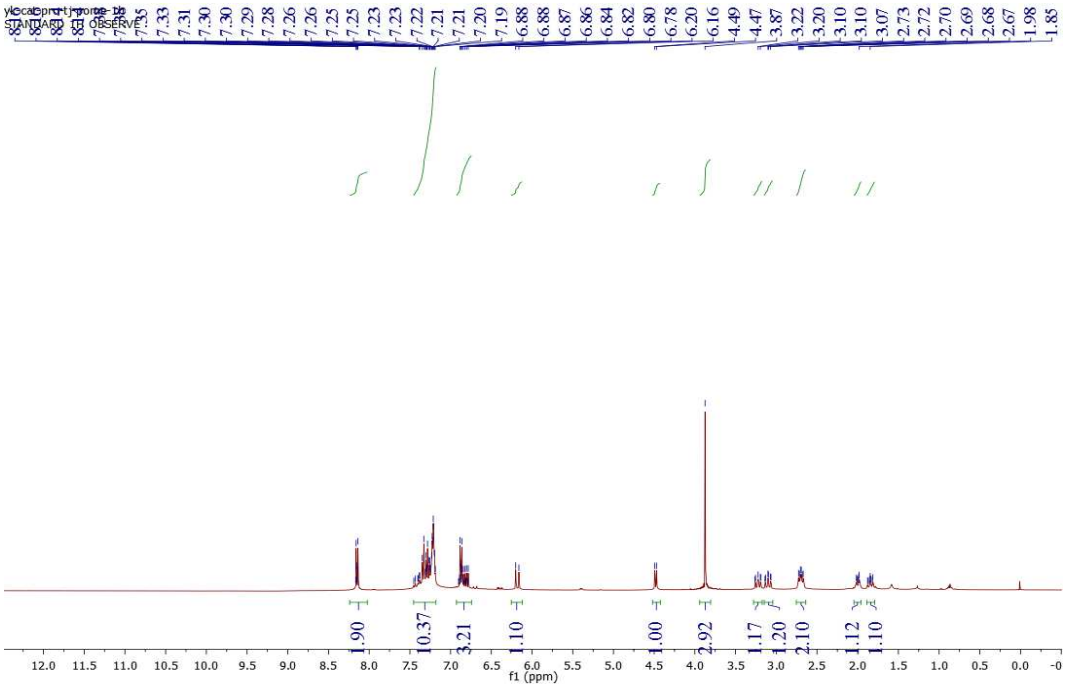
5d

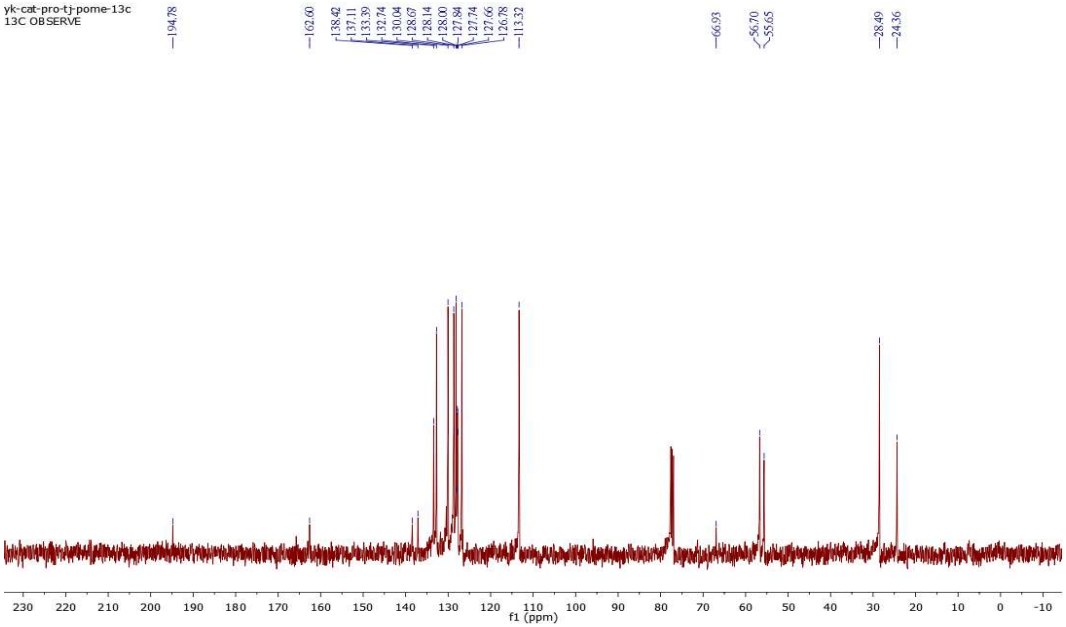

yk-cat-pro-mome
STANDARD 1H OBSERVE
7.40
7.40
7.39
7.32
7.32
7.30
7.30
7.29
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.04
7.04
7.03
7.03
7.02
7.02
7.01
7.01
6.80
6.78
6.76
6.74
6.10
6.07
4.41
4.39
3.73
3.26
3.18
3.18
2.74
2.71
2.67
1.01
2.40
1.00
1.06
0.99
1.00
2.89
2.18
2.14
1.11
1.12
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

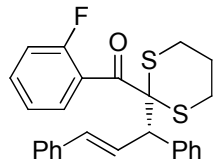

yk-cat-pro-mome-13c-410times
13C OBSERVE
196.94
159.23
139.83
138.48
137.05
133.55
130.17
129.07
128.67
128.15
127.77
127.62
126.76
122.40
118.17
114.95
66.10
56.51
55.53
28.39
24.24
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
MeO
S
S
Ph
Ph

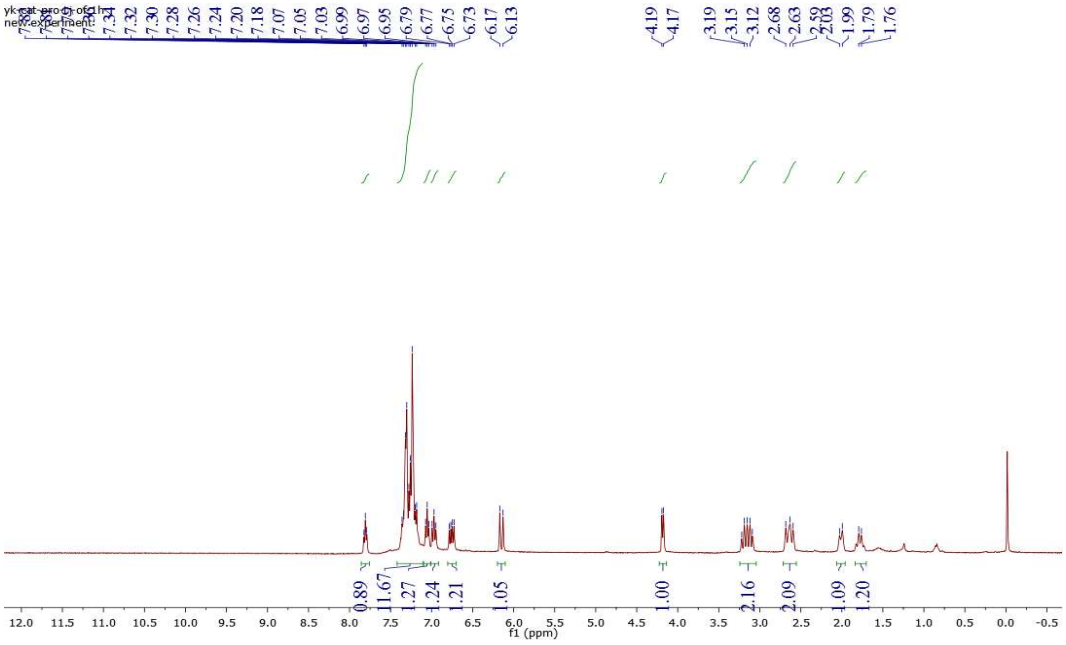
5e

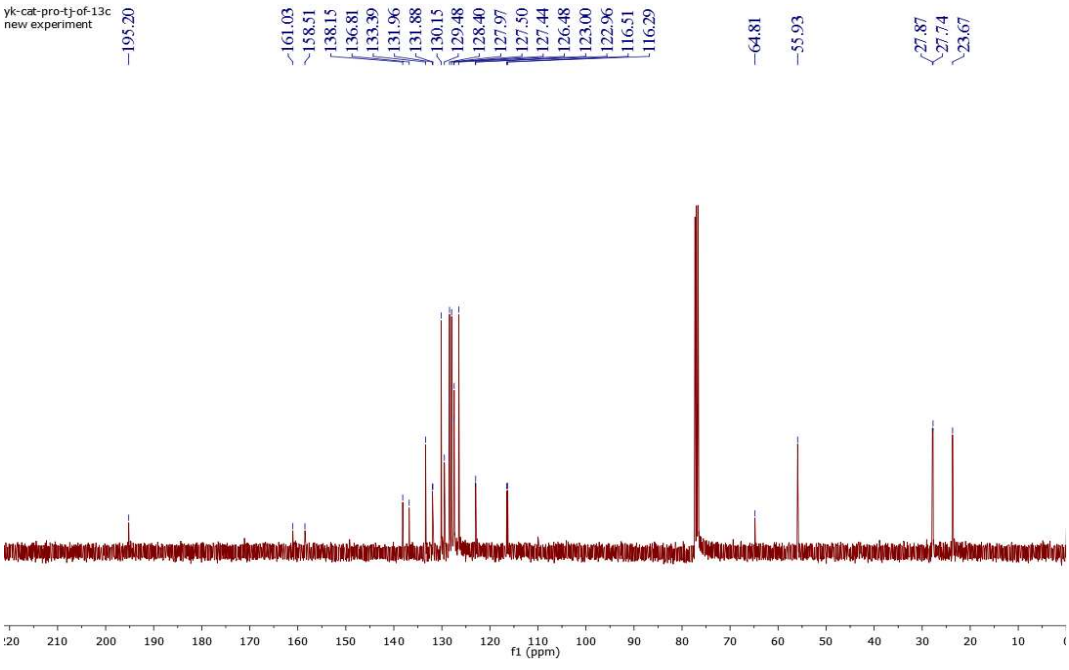

STANDARD 1H OBSERVE
1.90
10.37
3.21
1.10
1.00
2.92
1.17
1.20
2.10
1.12
1.10
f1 (ppm)

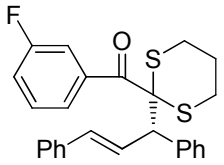

yk-cat-pro-tj-pome-13c
13C OBSERVE
194.78
162.60
138.42
137.11
133.39
132.74
130.04
128.67
128.14
128.00
127.84
127.74
127.66
126.78
113.32
66.93
56.70
55.65
28.49
24.36
f1 (ppm)


F
O
S
S
Ph
Ph

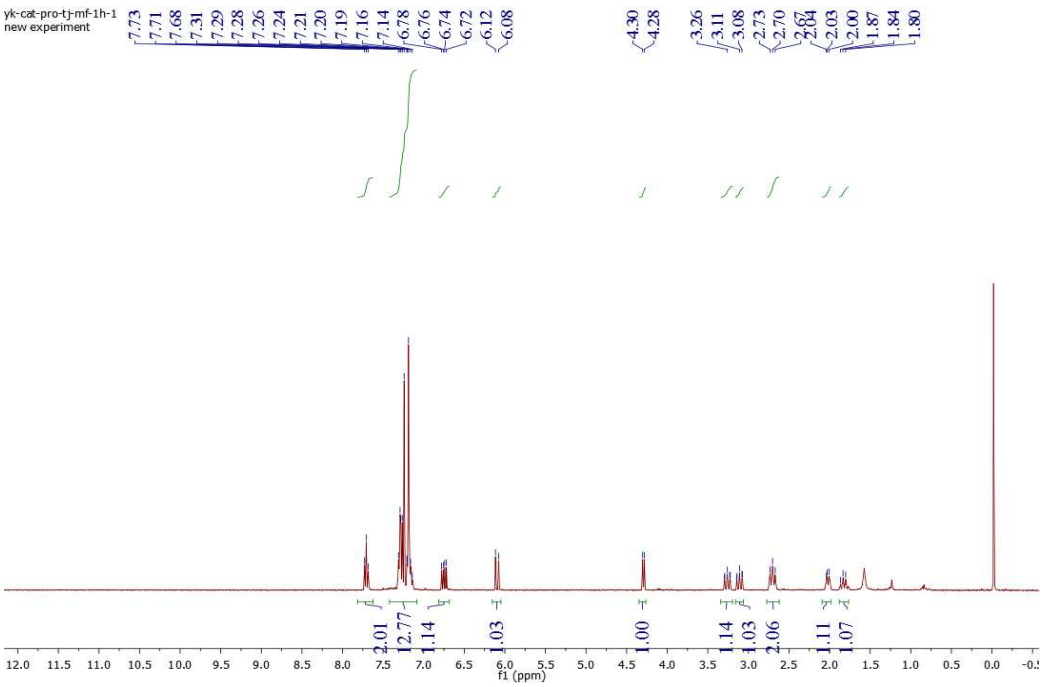
5f

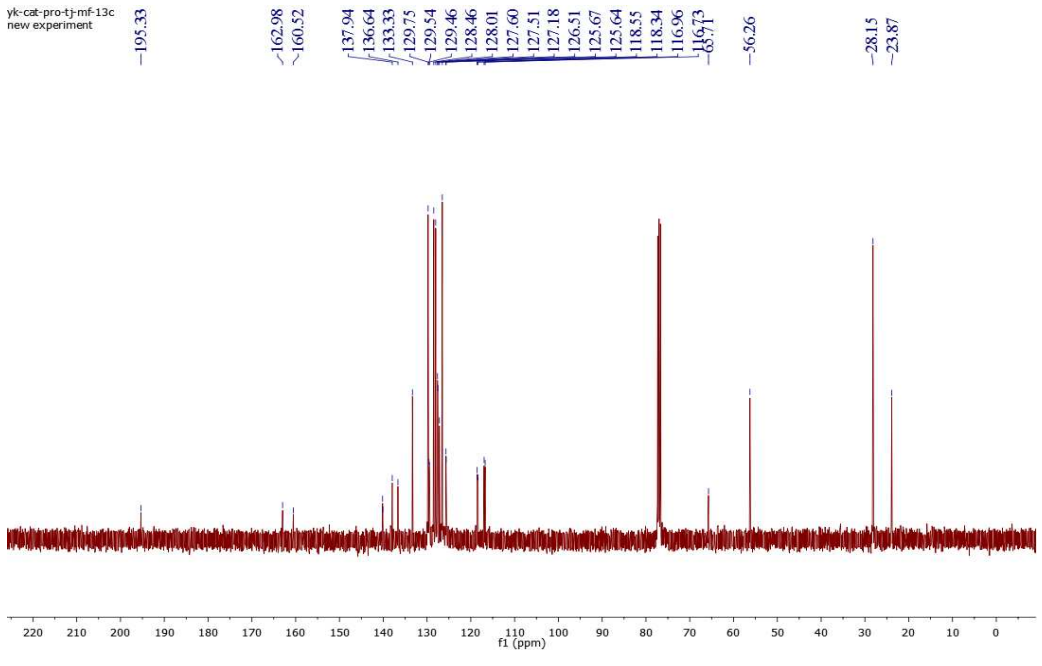

7.34
7.32
7.30
7.28
7.26
7.24
7.20
7.18
7.07
7.05
7.03
6.99
6.97
6.95
6.79
6.77
6.75
6.73
6.17
6.13
4.19
4.17
3.19
3.15
3.12
2.68
2.63
2.59
2.03
1.99
1.79
1.76
0.89
11.67
1.27
1.24
1.21
1.05
1.00
2.16
2.09
1.09
1.20
f1 (ppm)

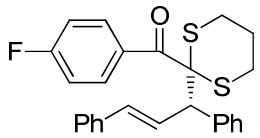

yk-cat-pro-tj-of-13c
new experiment
195.20
161.03
158.51
138.15
136.81
133.39
131.96
131.88
130.15
129.48
128.40
127.97
127.50
127.44
126.48
123.00
122.96
116.51
116.29
64.81
55.93
27.87
27.74
23.67
f1 (ppm)


F
O
S
S
Ph
Ph

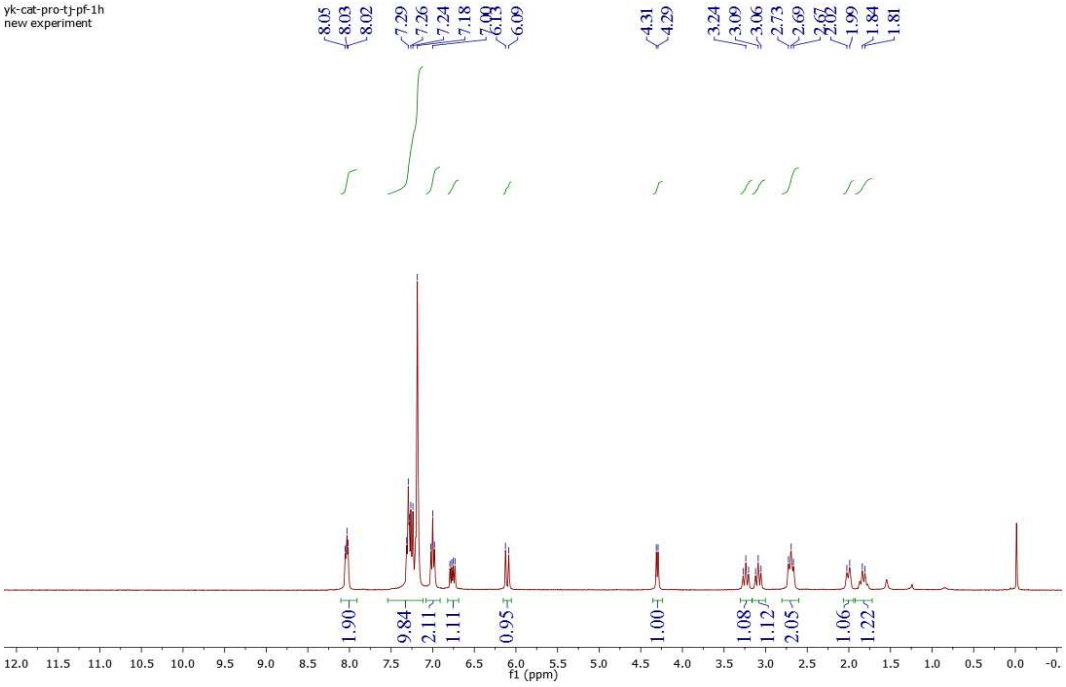
5g

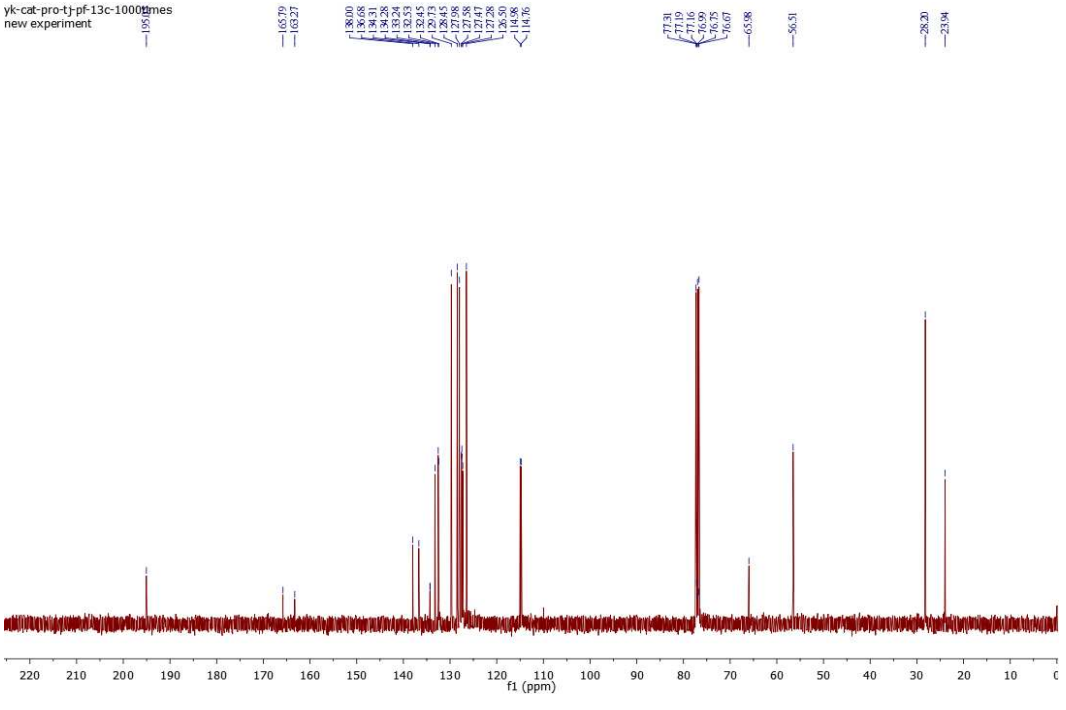

yk-cat-pro-tj-mf-1h-1
new experiment
7.73
7.71
7.68
7.31
7.29
7.28
7.26
7.24
7.21
7.20
7.19
7.16
7.14
6.78
6.76
6.74
6.72
6.12
6.08
4.30
4.28
3.26
3.11
3.08
2.73
2.70
2.67
2.64
2.03
2.00
1.87
1.84
1.80
2.01
12.77
1.14
1.03
1.00
1.14
1.03
2.06
1.11
1.07
f1 (ppm)

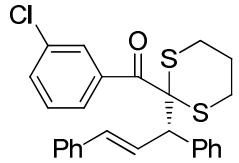

yk-cat-pro-tj-mf-13c
new experiment
195.33
162.98
160.52
137.94
136.64
133.33
129.75
129.54
129.46
128.46
128.01
127.60
127.51
127.18
126.51
125.67
125.64
118.55
118.34
116.96
116.73
63.71
56.26
28.15
23.87
f1 (ppm)


O
S
S
F
Ph
Ph

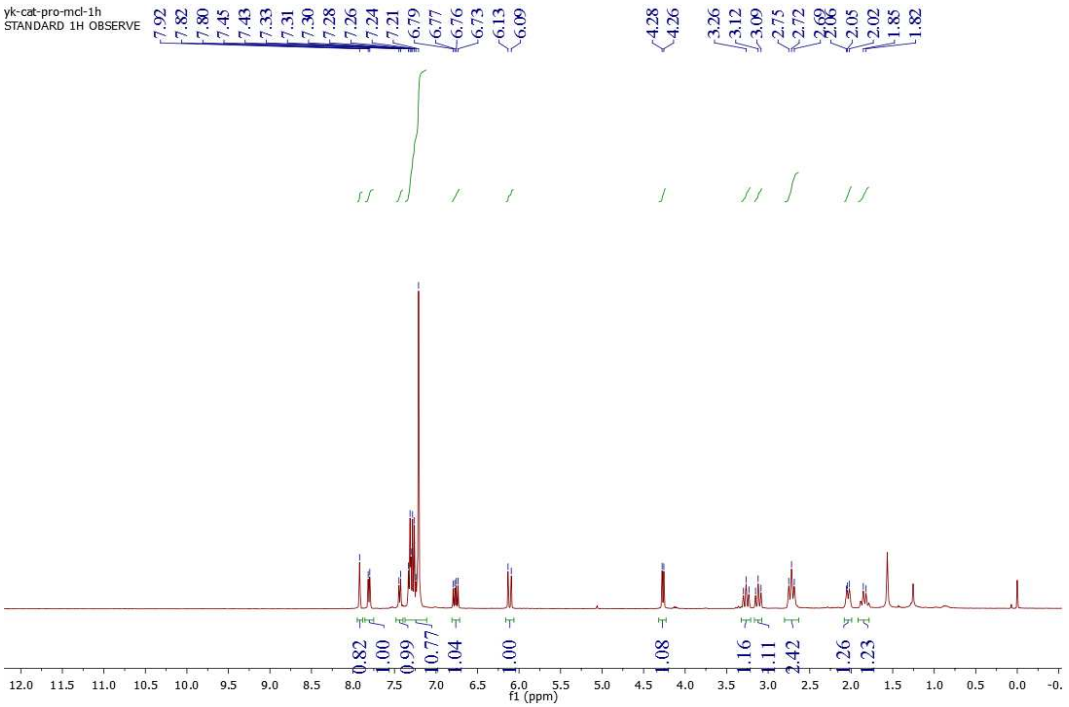
5h

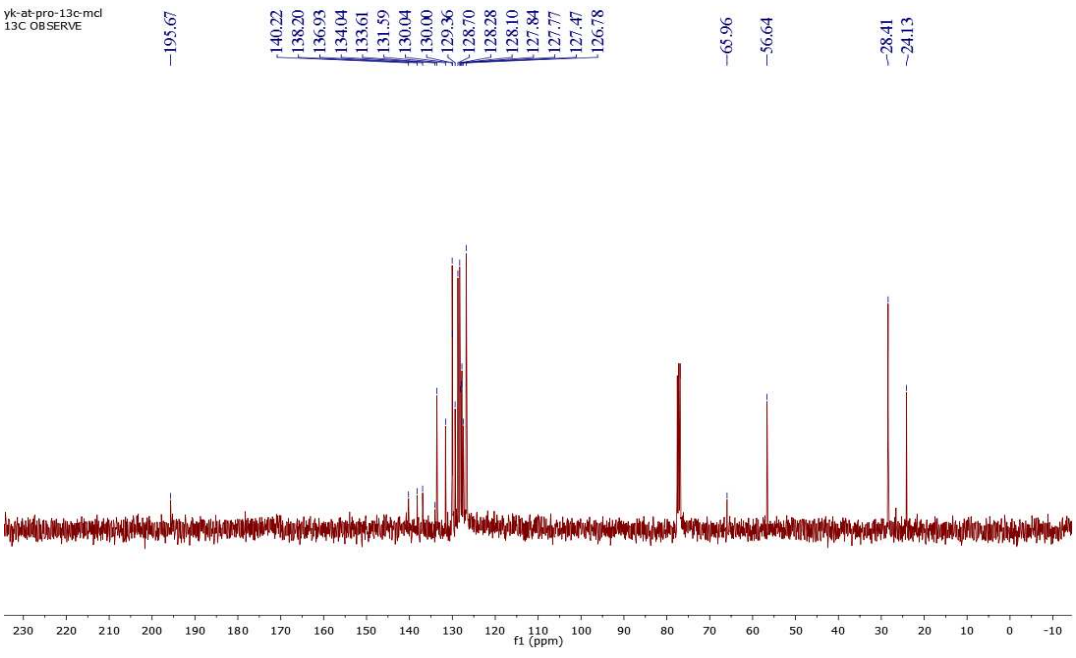

yk-cat-pro-tj-pf-1h
new experiment
8.05
8.03
8.02
7.29
7.26
7.24
7.18
7.00
6.13
6.09
4.31
4.29
3.24
3.09
3.06
2.73
2.69
2.67
2.62
1.99
1.84
1.81
1.90
9.84
2.11
1.11
0.95
1.00
1.08
1.12
2.05
1.06
1.22
f1 (ppm)

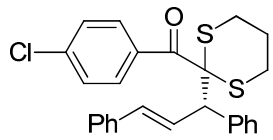

yk-cat-pro-tj-pf-13c-10000times
new experiment
195.01
165.79
163.27
138.00
136.68
134.31
134.28
132.74
132.53
132.45
129.73
128.45
127.98
127.96
127.47
127.28
126.50
114.98
114.76
77.31
77.19
77.16
76.99
76.75
76.67
65.38
56.51
28.20
23.94
f1 (ppm)


Cl
O
S
S
Ph
Ph

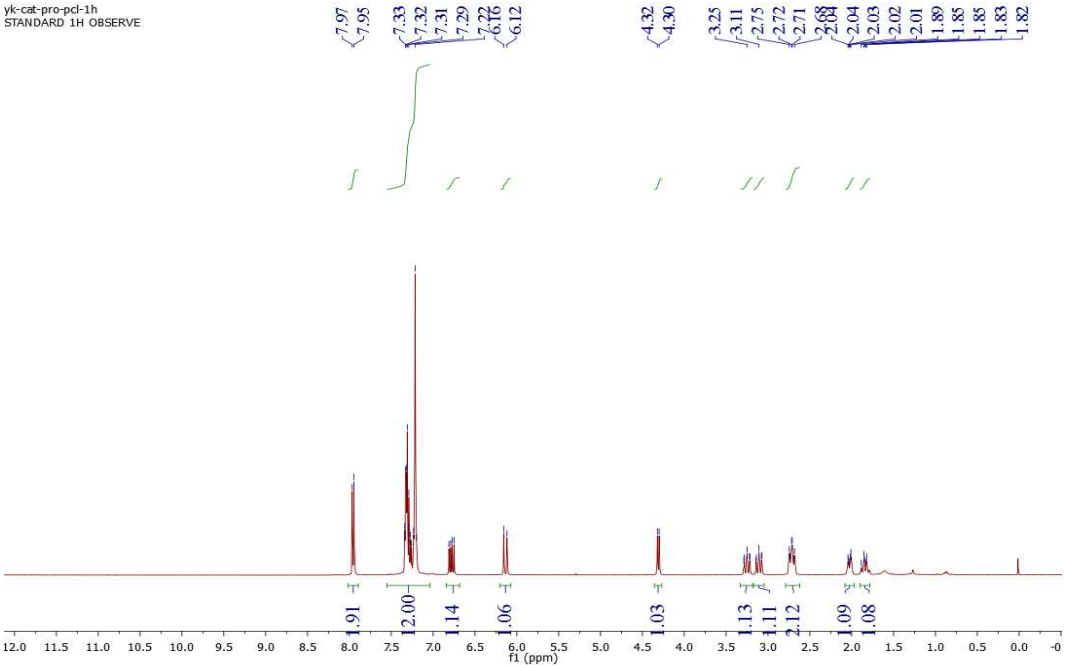
5i

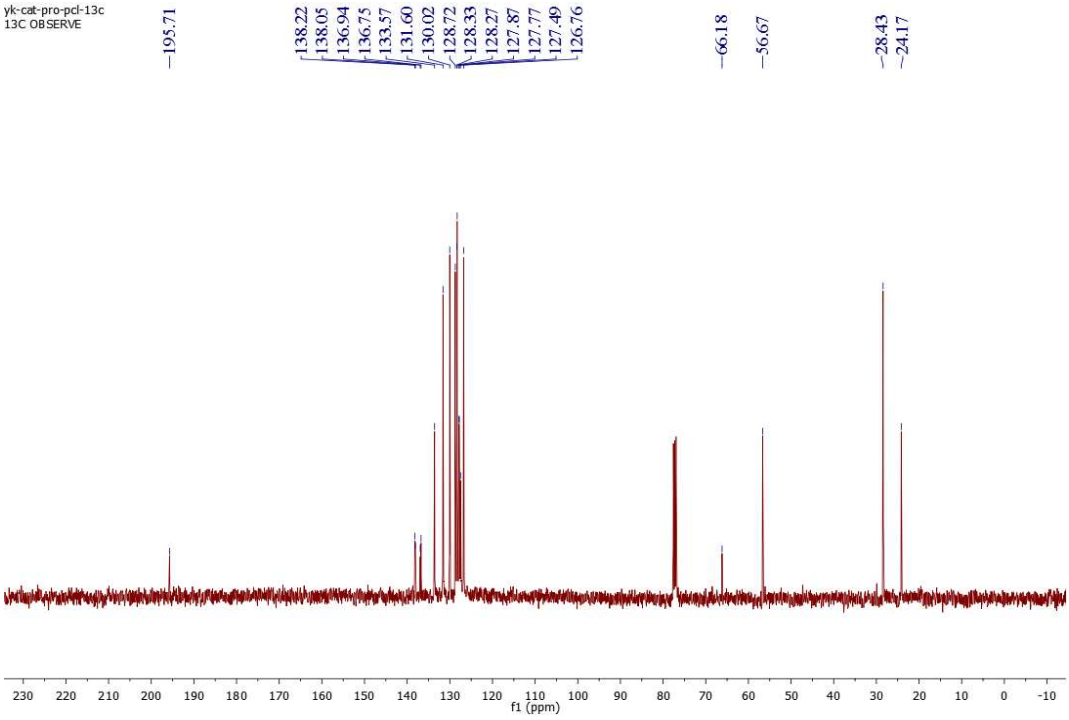

yk-cat-pro-mcl-1h
STANDARD 1H OBSERVE
7.92
7.82
7.80
7.45
7.43
7.33
7.31
7.30
7.28
7.26
7.24
7.21
6.79
6.77
6.76
6.73
6.13
6.09
4.28
4.26
3.26
3.12
3.09
2.75
2.72
2.68
2.66
2.05
2.02
1.85
1.82
0.82
1.00
0.99
10.77
1.04
1.00
1.08
1.16
1.11
2.42
1.26
1.23
f1 (ppm)

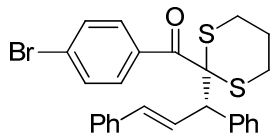

yk-at-pro-13c-mcl
13C OBSERVE
195.67
140.22
138.20
136.93
134.04
133.61
131.59
130.04
130.00
129.36
128.70
128.28
128.10
127.84
127.77
127.47
126.78
65.96
56.64
28.41
24.13
f1 (ppm)


O
S
S
Cl
Ph
Ph

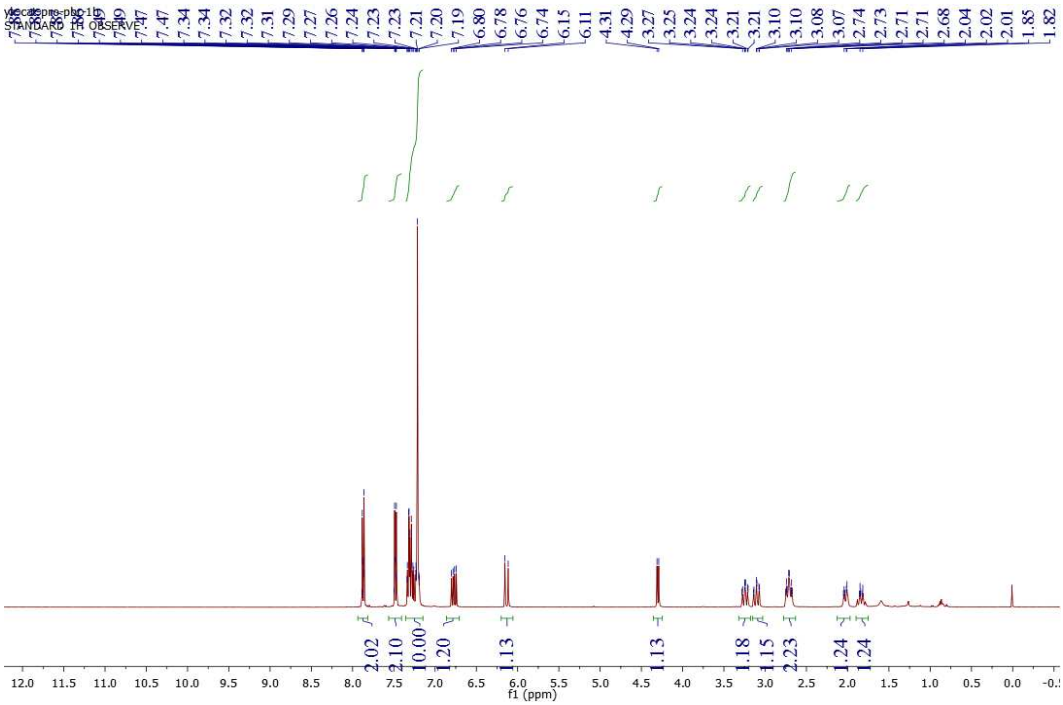
5j

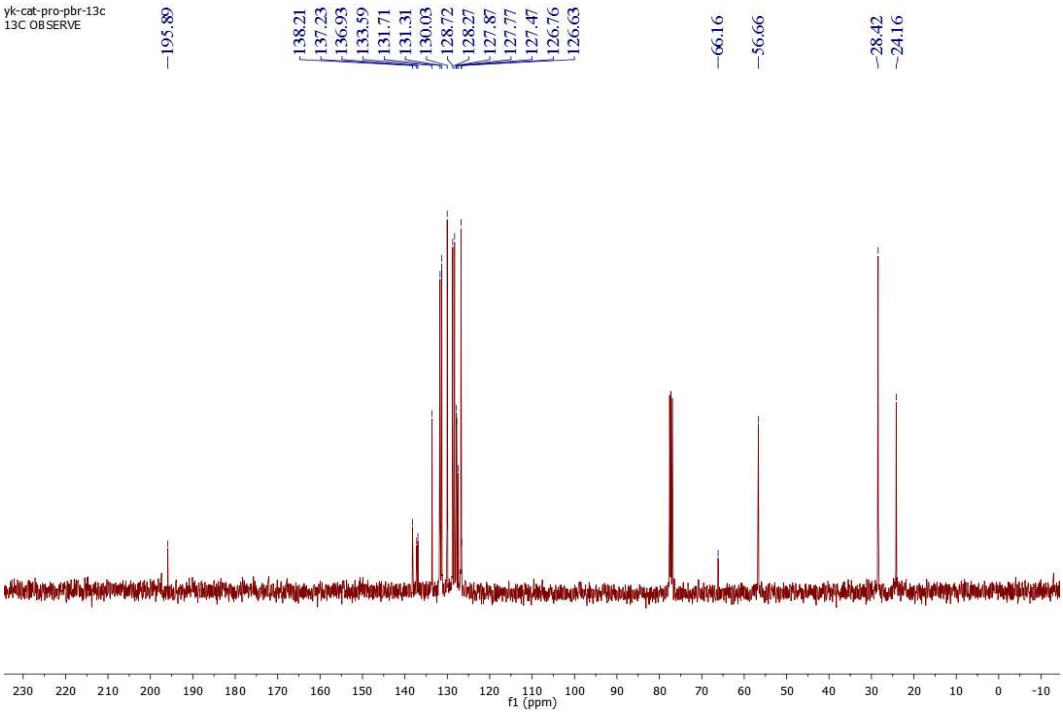

yk-cat-pro-pcl-1h
STANDARD 1H OBSERVE
7.97
7.95
7.33
7.32
7.31
7.29
6.16
6.12
4.32
4.30
3.25
3.11
2.75
2.72
2.71
2.04
2.03
2.02
2.01
1.89
1.85
1.83
1.82
1.91
12.00
1.14
1.06
1.03
1.13
1.11
2.12
1.09
1.08
f1 (ppm)

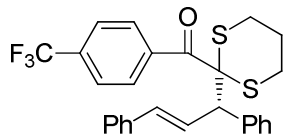

yk-cat-pro-pcl-13c
13C OBSERVE
195.71
138.22
138.05
136.94
136.75
133.57
131.60
130.02
128.72
128.33
128.27
127.87
127.77
127.49
126.76
66.18
56.67
28.43
24.17
f1 (ppm)


O
S
S
Br
Ph
Ph

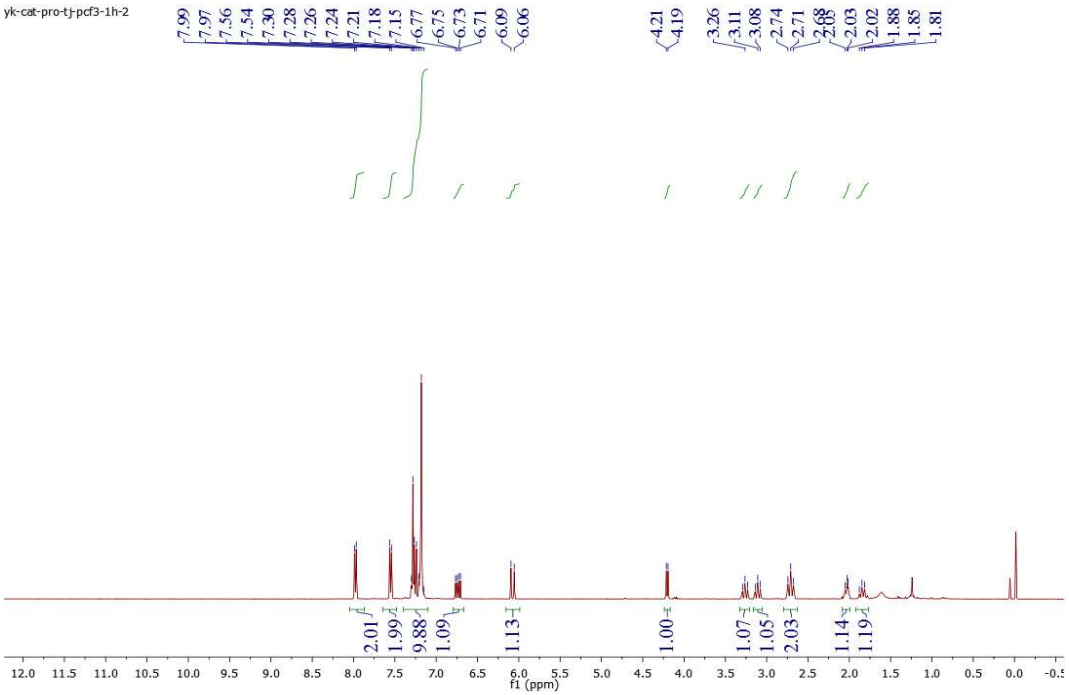
5k

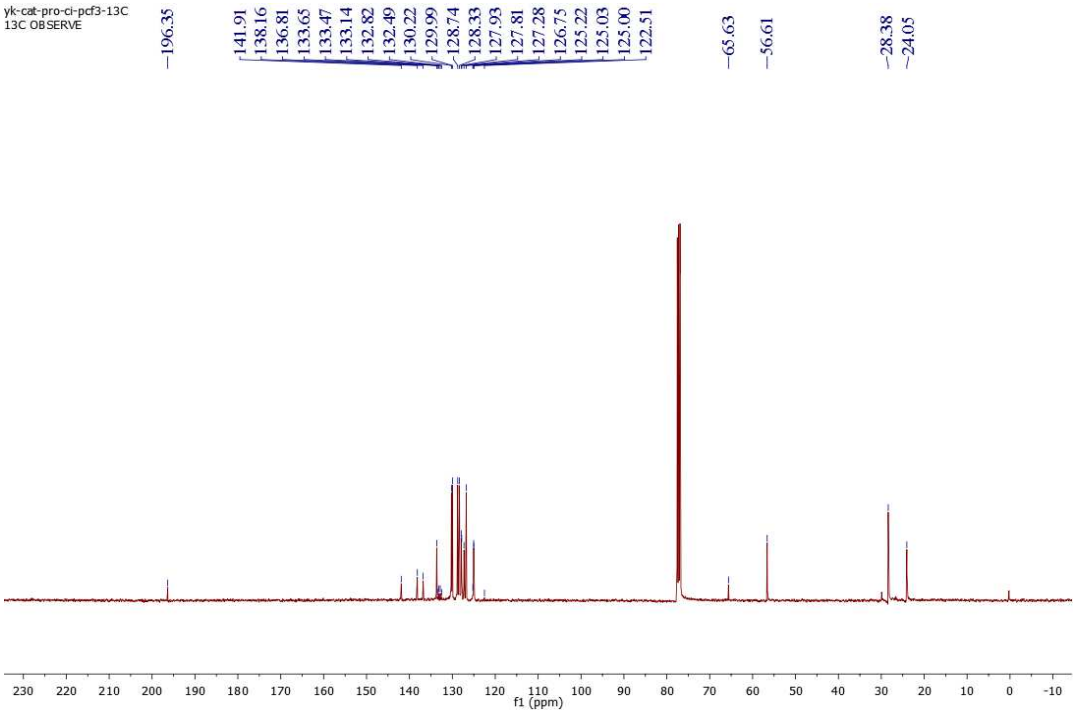

yk-cat-pro-pbr-1h
STANDARD 1H OBSERVE
7.47
7.34
7.34
7.32
7.31
7.29
7.27
7.26
7.24
7.23
7.23
7.21
7.20
7.19
6.80
6.78
6.76
6.74
6.15
6.11
4.31
4.29
3.27
3.25
3.24
3.24
3.21
3.21
3.10
3.10
3.08
3.07
2.74
2.73
2.71
2.71
2.68
2.04
2.02
2.01
1.85
1.82
2.02
2.10
10.00
1.20
1.13
1.13
1.18
1.15
2.23
1.24
1.24
f1 (ppm)

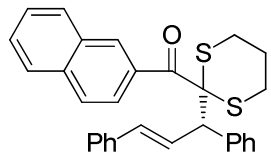

yk-cat-pro-pbr-13c
13C OBSERVE
195.89
138.21
137.23
136.93
133.59
131.71
131.31
130.03
128.72
128.27
127.87
127.77
127.47
126.76
126.63
66.16
56.66
28.42
24.16
f1 (ppm)


O
S
S
F3C
Ph
Ph

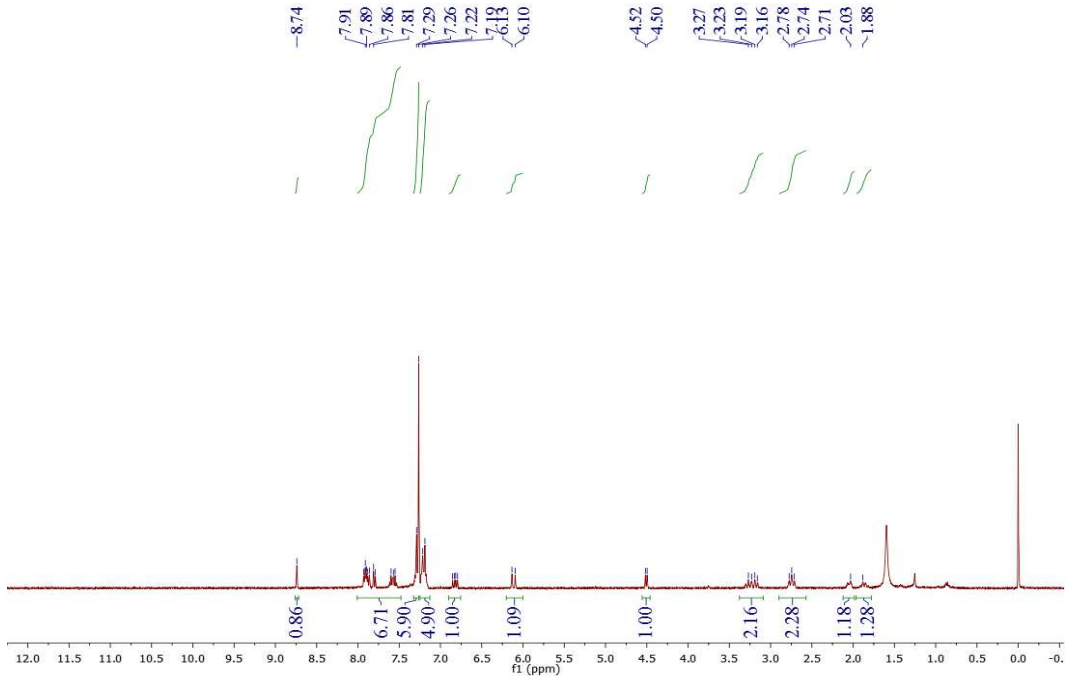
5l

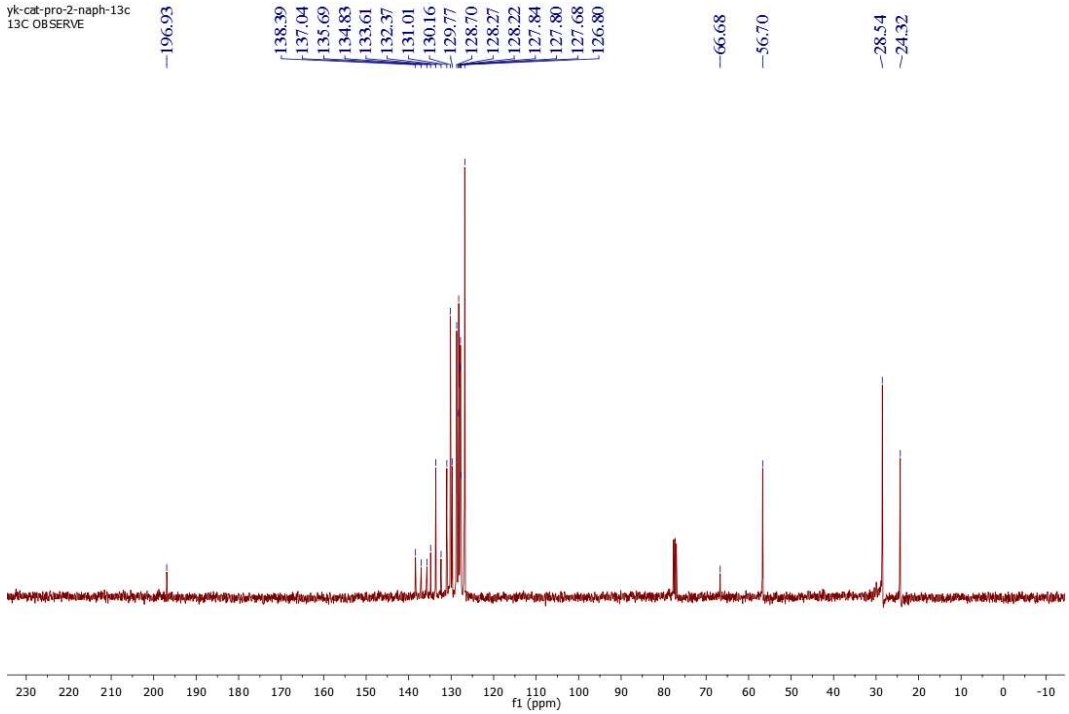

yk-cat-pro-tj-pcf3-1h-2
7.99
7.97
7.56
7.54
7.30
7.28
7.26
7.24
7.21
7.18
7.15
6.77
6.75
6.73
6.71
6.09
6.06
4.21
4.19
3.26
3.11
3.08
2.74
2.71
2.68
2.65
2.03
2.02
1.88
1.85
1.81
2.01
1.99
9.88
1.09
1.13
1.00
1.07
1.05
2.03
1.14
1.19
f1 (ppm)

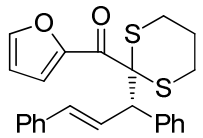

yk-cat-pro-ci-pcf3-13C
13C OBSERVE
196.35
141.91
138.16
136.81
133.65
133.47
133.14
132.82
132.49
130.22
129.99
128.74
128.33
127.93
127.81
127.28
126.75
125.22
125.03
125.00
122.51
65.63
56.61
28.38
24.05
f1 (ppm)


O
S
S
Ph
Ph

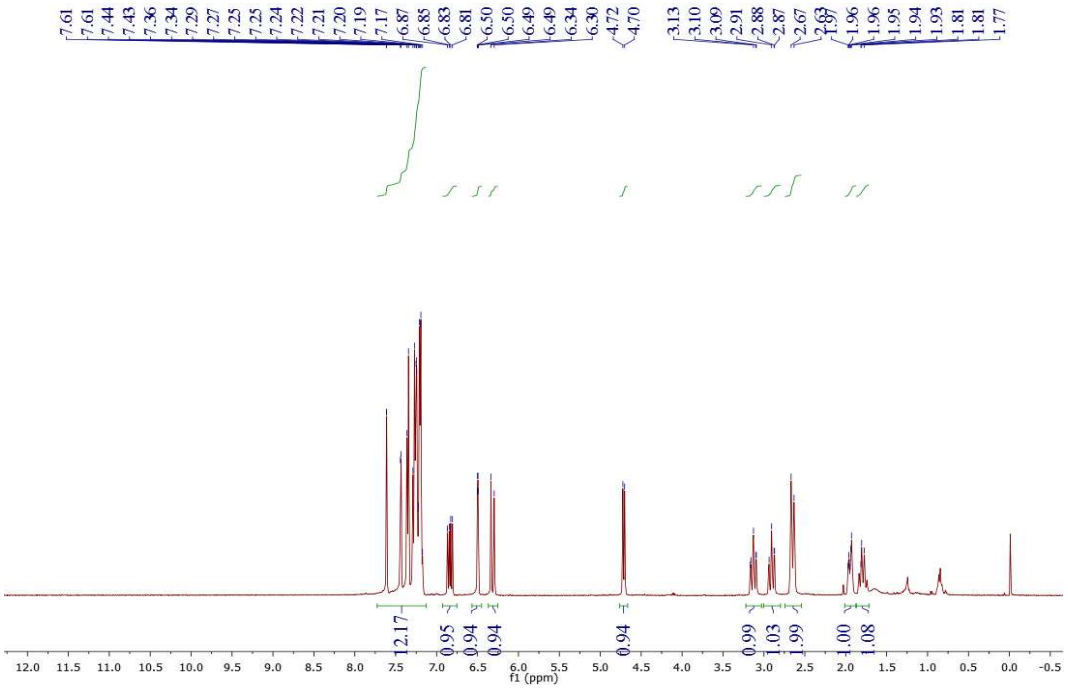
5m

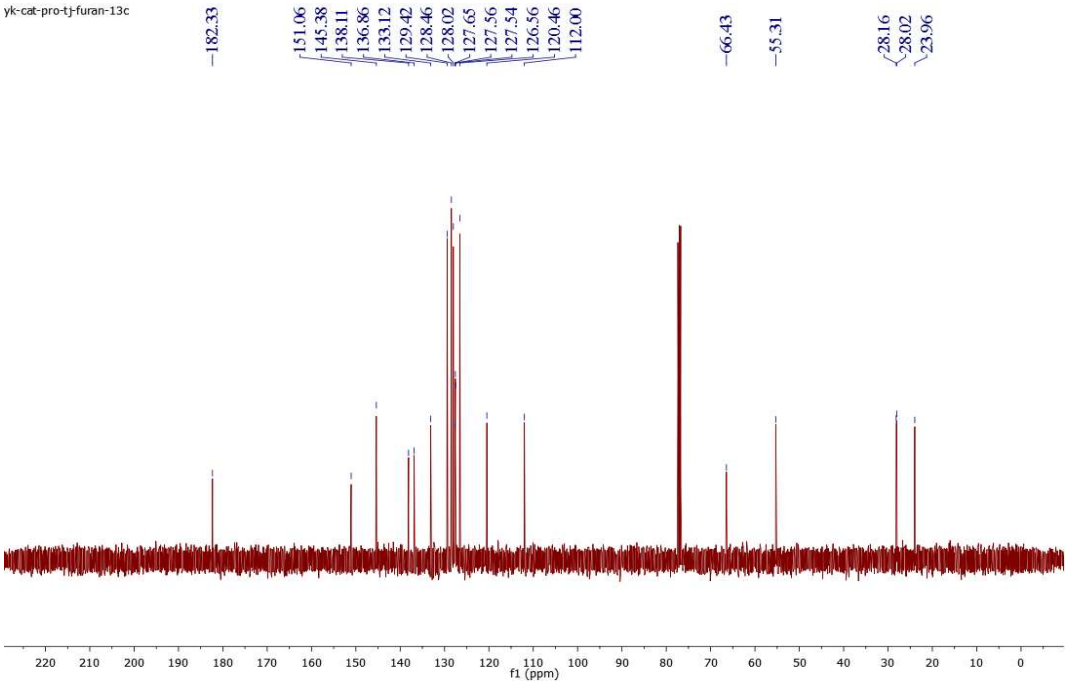

8.74
7.91
7.89
7.86
7.81
7.29
7.26
7.22
7.19
7.13
6.10
4.52
4.50
3.27
3.23
3.19
3.16
2.78
2.74
2.71
2.03
1.88
0.86
6.71
5.90
4.90
1.00
1.09
1.00
2.16
2.28
1.18
1.28
f1 (ppm)

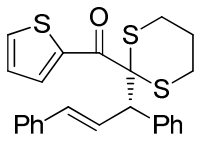

yk-cat-pro-2-naph-13c
13C OBSERVE
196.93
138.39
137.04
135.69
134.83
133.61
132.37
131.01
130.16
129.77
128.70
128.27
128.22
127.84
127.80
127.68
126.80
66.68
56.70
28.54
24.32
f1 (ppm)


O
O
S
S
Ph
Ph

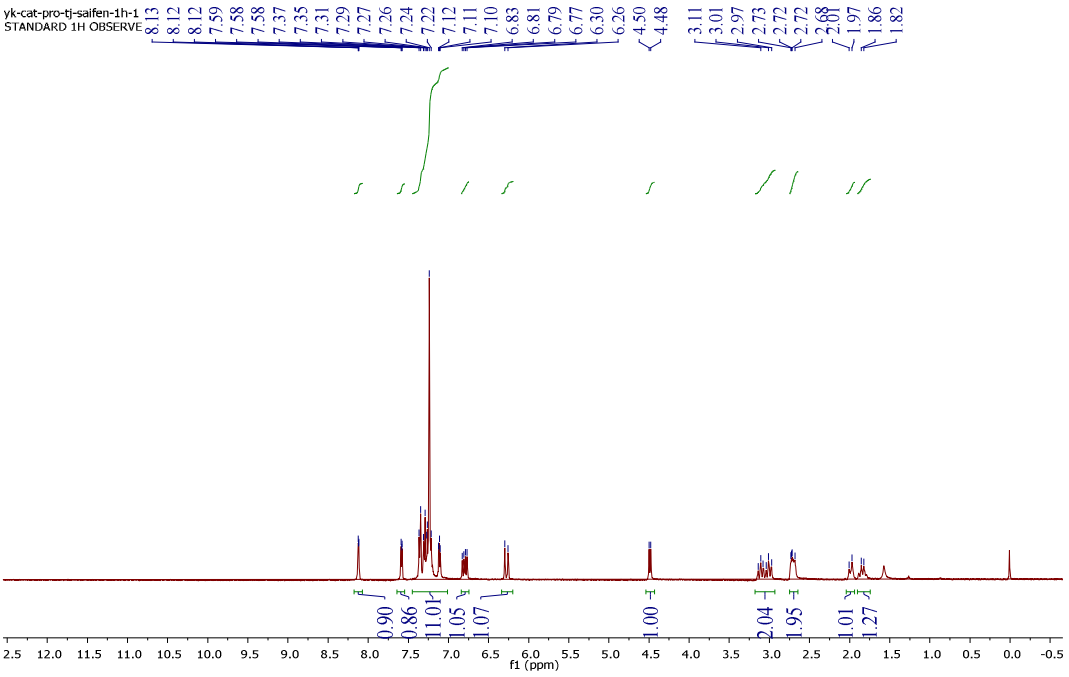
5n

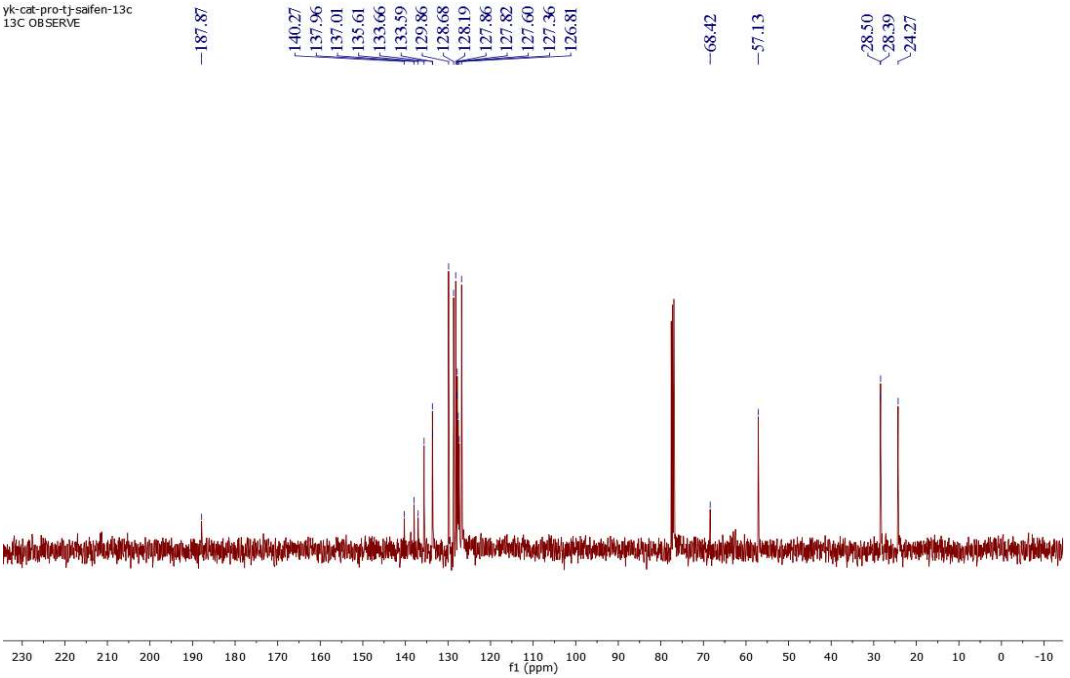

7.61 7.61 7.44 7.43 7.36 7.34 7.29 7.27 7.25 7.25 7.24 7.22 7.21 7.20 7.19 7.17 6.87 6.85 6.83 6.81 6.50 6.50 6.49 6.49 6.34 6.30 4.72 4.70 3.13 3.10 3.09 2.91 2.88 2.87 2.67 2.63 1.97 1.96 1.96 1.95 1.94 1.93 1.81 1.81 1.77
12.17 0.95 0.94 0.94 0.94 0.99 1.03 1.99 1.00 1.08
f1 (ppm)


yk-cat-pro-tj-furan-13c
182.33 151.06 145.38 138.11 136.86 133.12 129.42 128.46 128.02 127.65 127.56 127.54 126.56 120.46 112.00 66.43 55.31 28.16 28.02 23.96
f1 (ppm)


S
O
S
S
Ph
Ph

5o


yk-cat-pro-tj-saifen-1h-1
STANDARD 1H OBSERVE
8.13
8.12
8.12
7.59
7.58
7.58
7.37
7.35
7.31
7.29
7.27
7.26
7.24
7.22
7.12
7.11
7.10
6.83
6.81
6.79
6.77
6.30
6.26
4.50
4.48
3.11
3.01
2.97
2.73
2.72
2.72
2.68
2.01
1.97
1.86
1.82
0.90
0.86
11.01
1.05
1.07
1.00
2.04
1.95
1.01
1.27
f1 (ppm)


yk-cat-pro-tj-saifen-13c
13C OBSERVE
187.87
140.27
137.96
137.01
135.61
133.66
133.59
129.86
128.68
128.19
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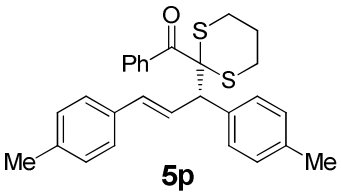
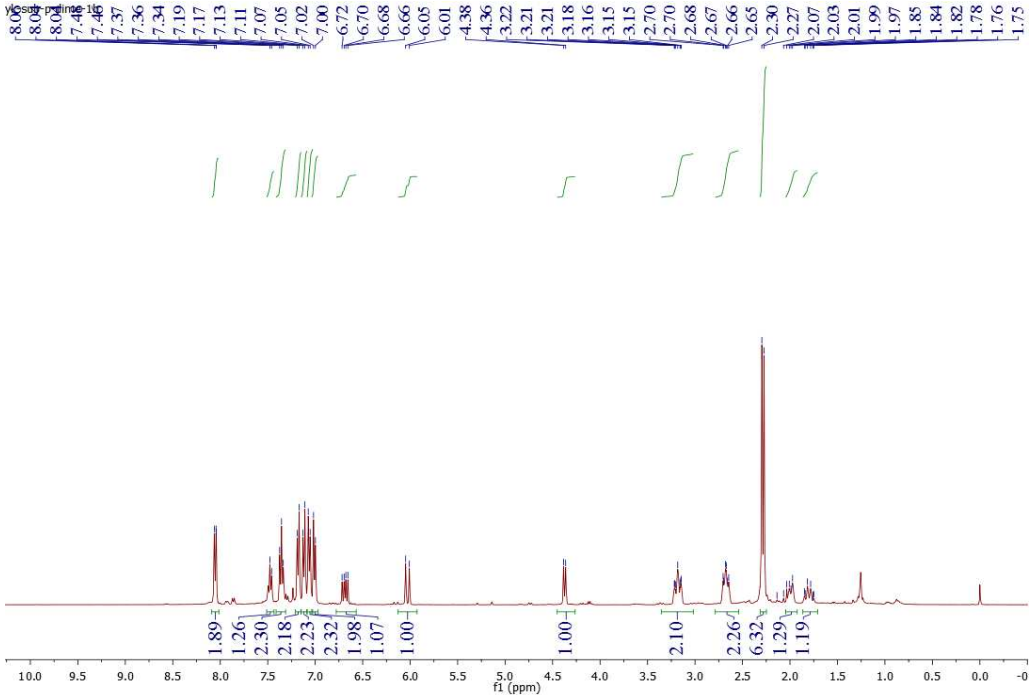
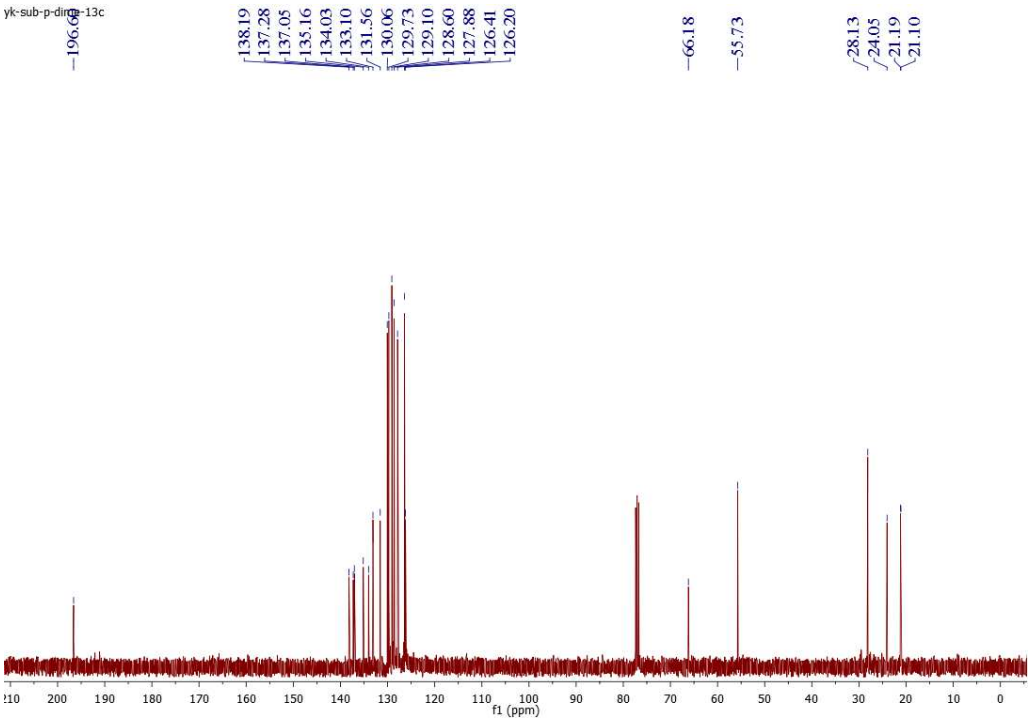
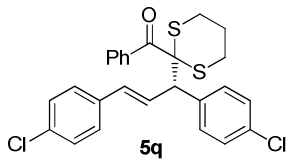
126.81
68.42
57.13
28.50
28.39
24.27
f1 (ppm)


O
S
Ph
S
Me
Me

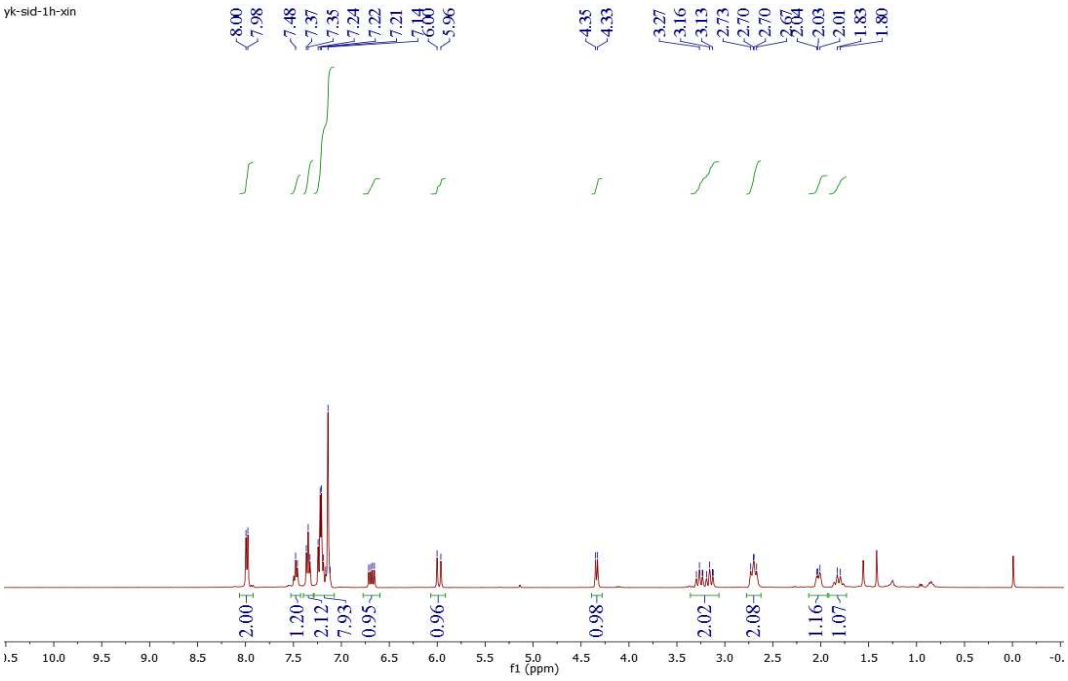
5p

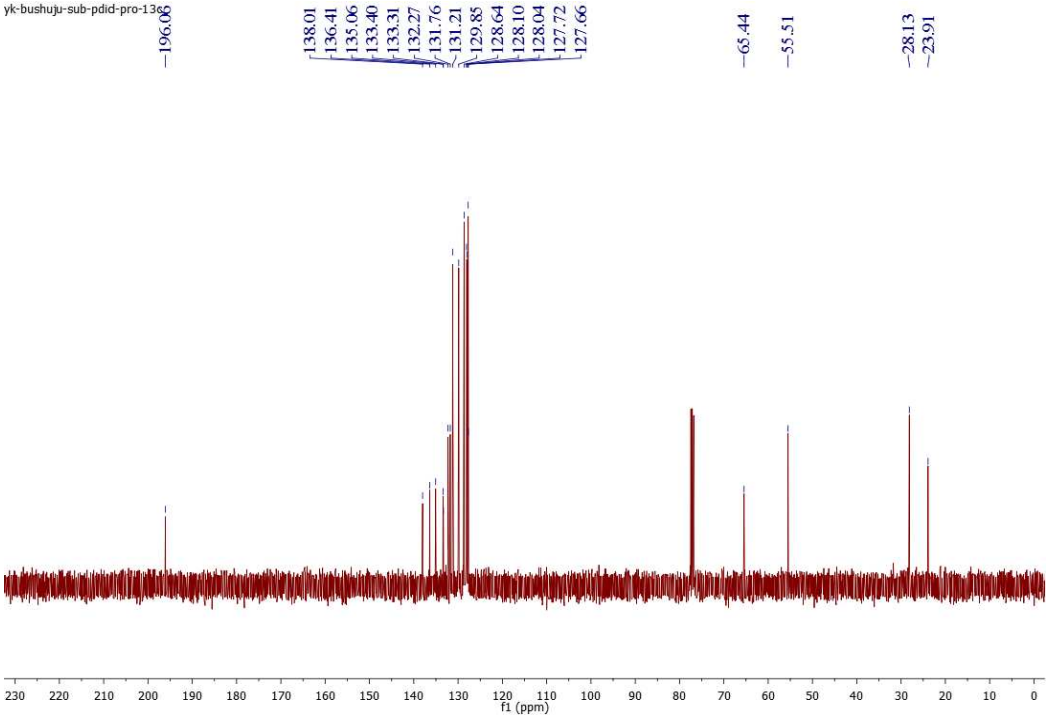

8.05
8.03
8.01
7.48
7.46
7.37
7.36
7.34
7.19
7.17
7.13
7.11
7.07
7.05
7.02
7.00
6.72
6.70
6.68
6.66
6.05
6.01
4.38
4.36
3.22
3.21
3.21
3.18
3.16
3.15
3.15
2.70
2.70
2.68
2.67
2.66
2.65
2.30
2.27
2.07
2.03
2.01
1.99
1.97
1.85
1.84
1.82
1.78
1.76
1.75
1.89
1.26
2.30
2.18
2.23
2.32
1.98
1.07
1.00
1.00
2.10
2.26
6.32
1.29
1.19
f1 (ppm)

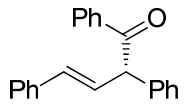

196.62
138.19
137.28
137.05
135.16
134.03
133.10
131.56
130.06
129.73
129.10
128.60
127.88
126.41
126.20
66.18
55.73
28.13
24.05
21.19
21.10
f1 (ppm)


O
S
Ph
S
Cl
Cl

5q

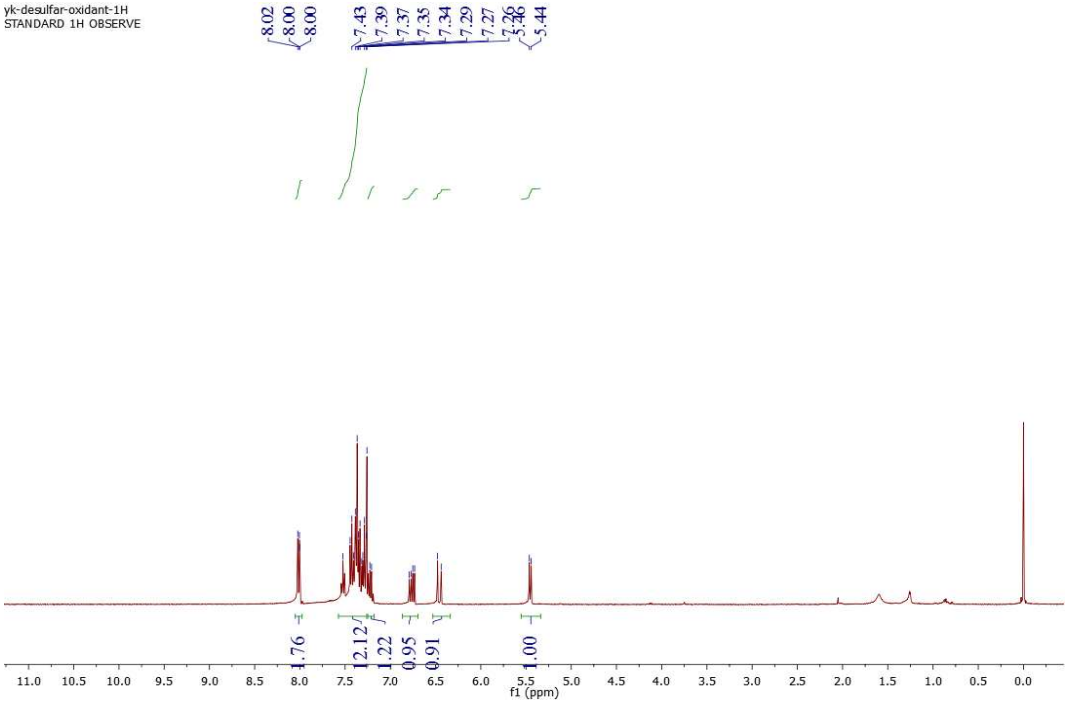

yk-sid-1h-xin
8.00
7.98
7.48
7.37
7.35
7.24
7.22
7.21
7.14
6.00
5.96
4.35
4.33
3.27
3.16
3.13
2.73
2.70
2.70
2.67
2.64
2.03
2.01
1.83
1.80
2.00
1.20
2.12
7.93
0.95
0.96
0.98
2.02
2.08
1.16
1.07
f1 (ppm)


yk-bushuju-sub-pdid-pro-13c
196.06
138.01
136.41
135.06
133.40
133.31
132.27
131.76
131.21
129.85
128.64
128.10
128.04
127.72
127.66
65.44
55.51
28.13
23.91
f1 (ppm)

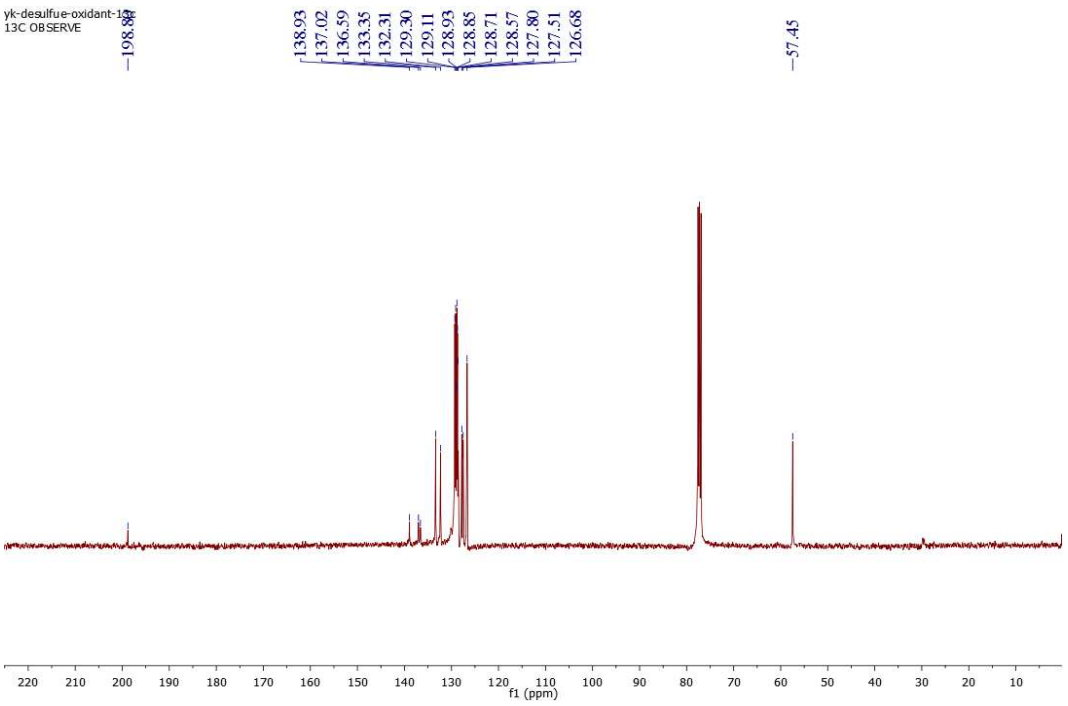


6

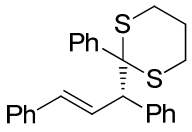
yk-desulfar-oxidant-1H
STANDARD 1H OBSERVE



yk-desulfue-oxidant-1
13C OBSERVE



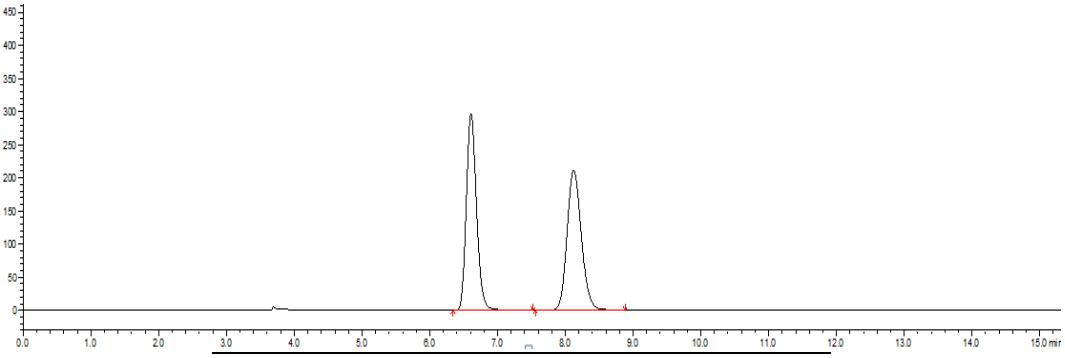
9. HPLC Data



3a

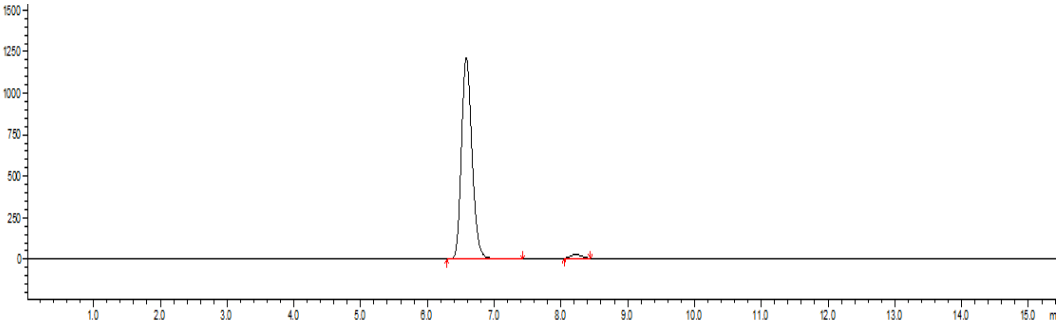
96% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

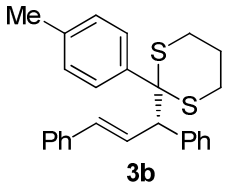


	Retention Time (min)	Area (%)
Peak 1	6.608	50.031
Peak 2	8.123	49.969

Chiral:



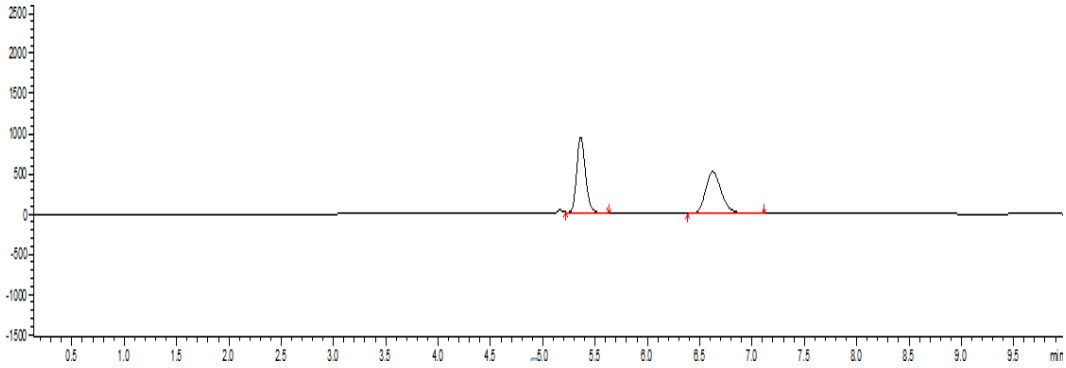
	Retention Time (min)	Area (%)
Peak 1	6.582	97.935
Peak 2	8.225	2.065



3b

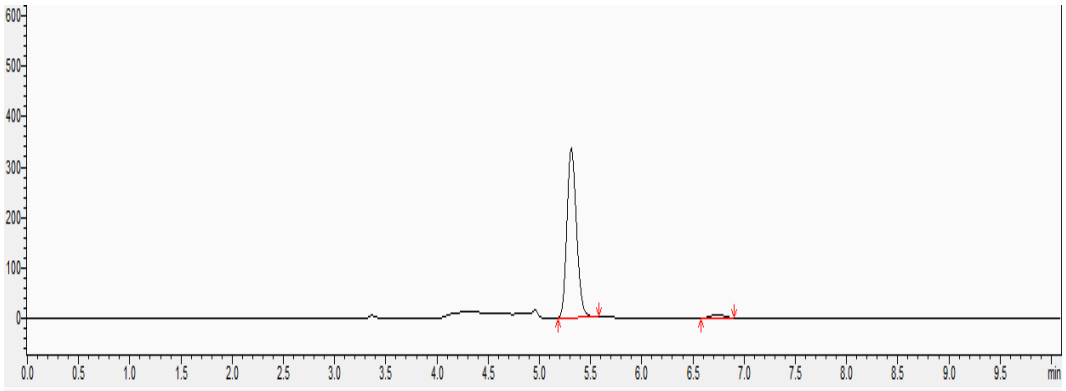
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

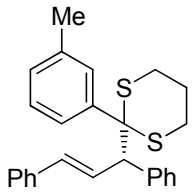


	Retention Time (min)	Area (%)
Peak 1	5.362	49.553
Peak 2	6.624	50.447

Chiral:



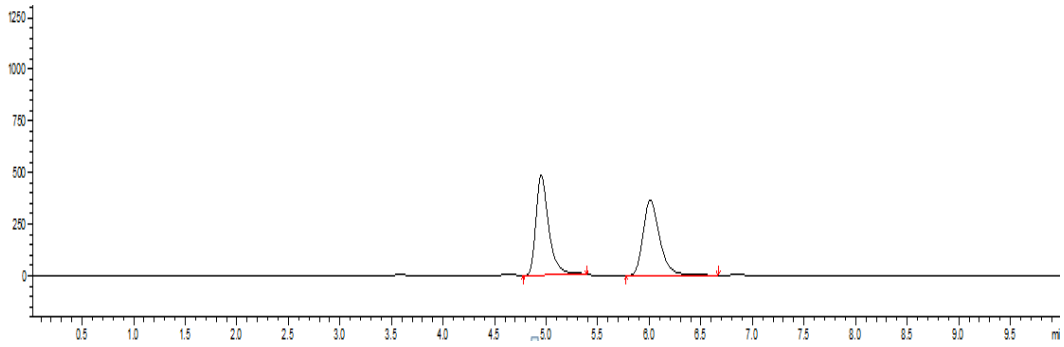
	Retention Time (min)	Area (%)
Peak 1	5.314	97.078
Peak 2	6.734	2.922



3c

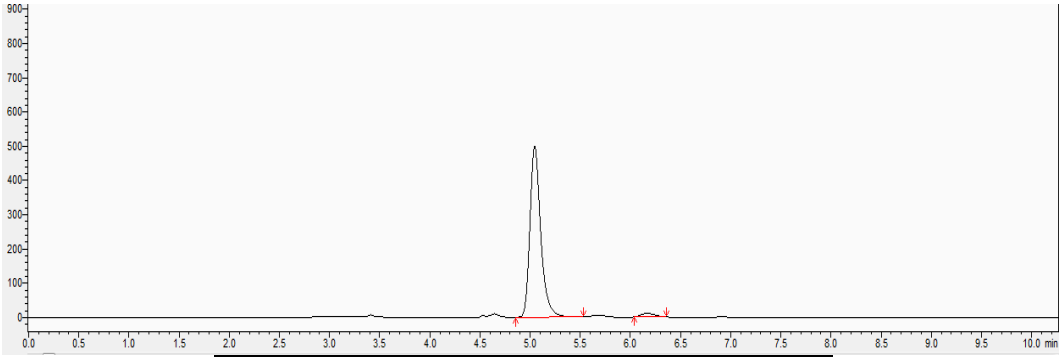
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

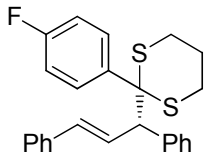


	Retention Time (min)	Area (%)
Peak 1	4.952	50.547
Peak 2	6.009	49.453

Chiral:



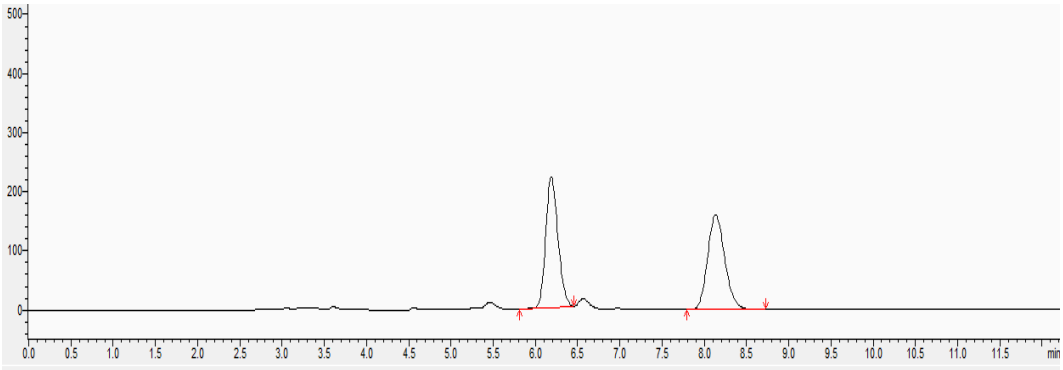
	Retention Time (min)	Area (%)
Peak 1	5.046	97.492
Peak 2	6.172	2.508



3d

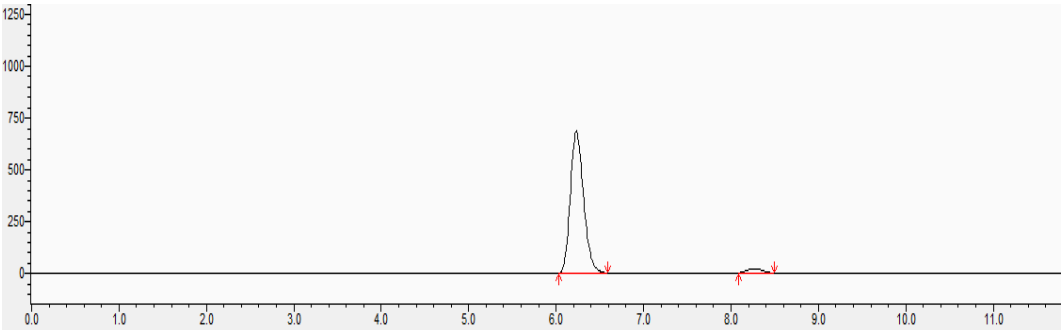
93% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column,*n*-hexane/*i*-PrOH = 99/1, 0.7 mL/min, 254 nm.

Racemate:

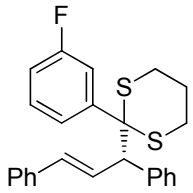


	Retention Time (min)	Area (%)
Peak 1	6.188	49.678
Peak 2	8.134	50.322

Chiral:



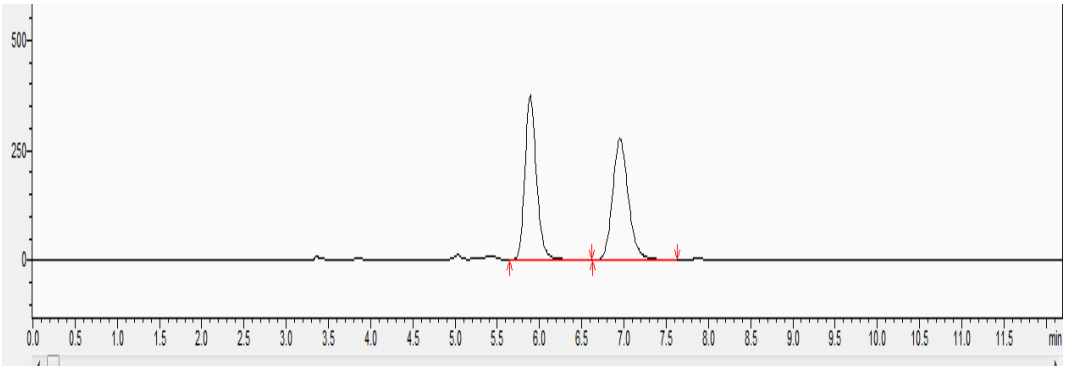
	Retention Time (min)	Area (%)
Peak 1	6.231	96.357
Peak 2	8.262	3.643



3e

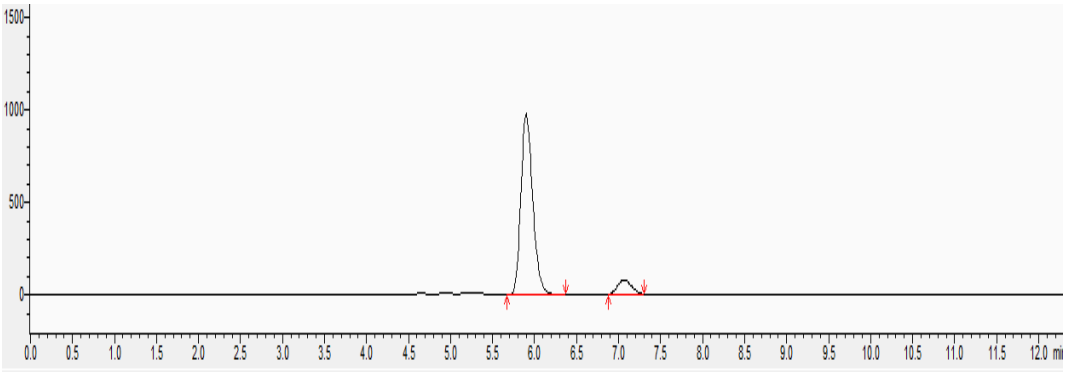
83% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

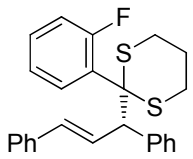


	Retention Time (min)	Area (%)
Peak 1	5.889	49.880
Peak 2	6.952	50.120

Chiral:



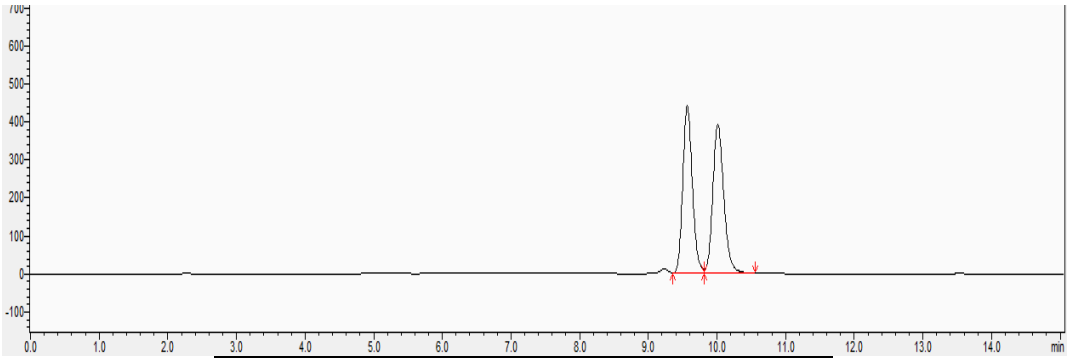
	Retention Time (min)	Area (%)
Peak 1	5.900	91.404
Peak 2	7.065	8.596



3f

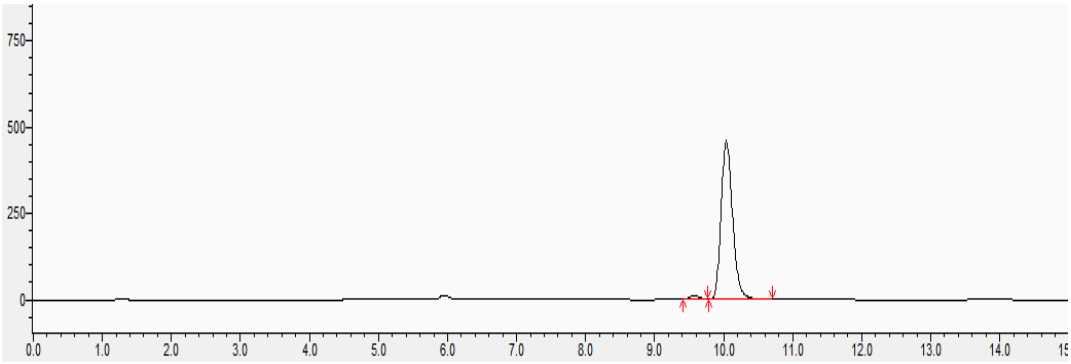
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane/*i*-PrOH = 99/1, 0.7 mL/min, 254 nm.

Racemate:

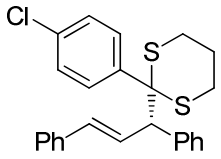


	Retention Time (min)	Area (%)
Peak 1	9.568	49.477
Peak 2	10.013	50.523

Chiral:



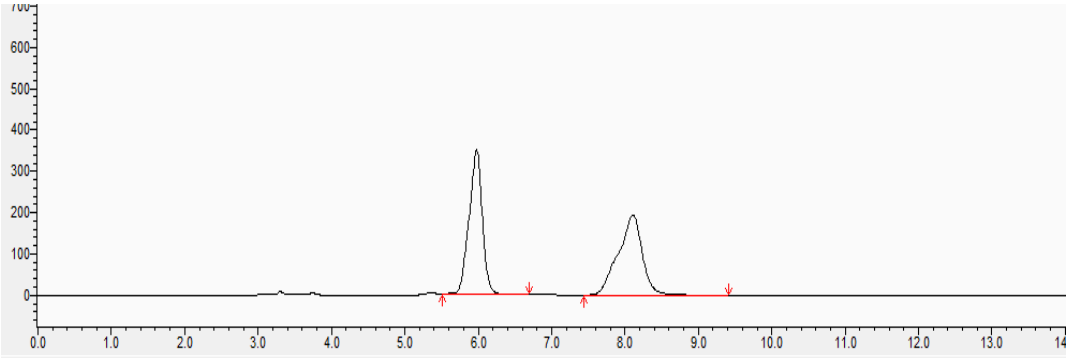
	Retention Time (min)	Area (%)
Peak 1	9.573	2.107
Peak 2	10.038	97.893



3g

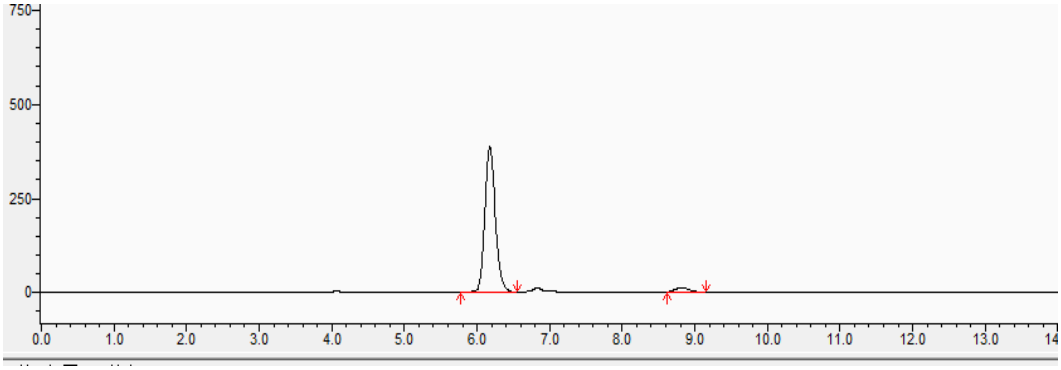
92% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

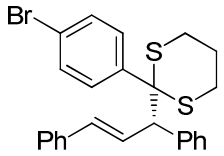


	Retention Time (min)	Area (%)
Peak 1	5.977	50.148
Peak 2	8.109	49.852

Chiral:



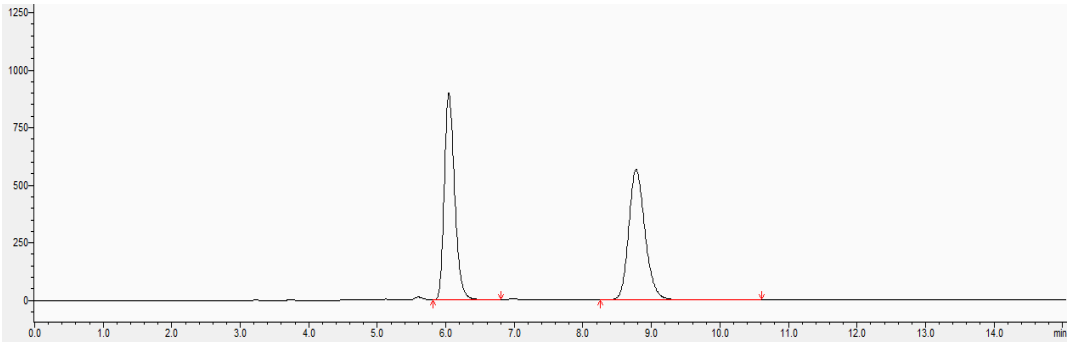
	Retention Time (min)	Area (%)
Peak 1	6.175	95.797
Peak 2	8.816	4.203



3h

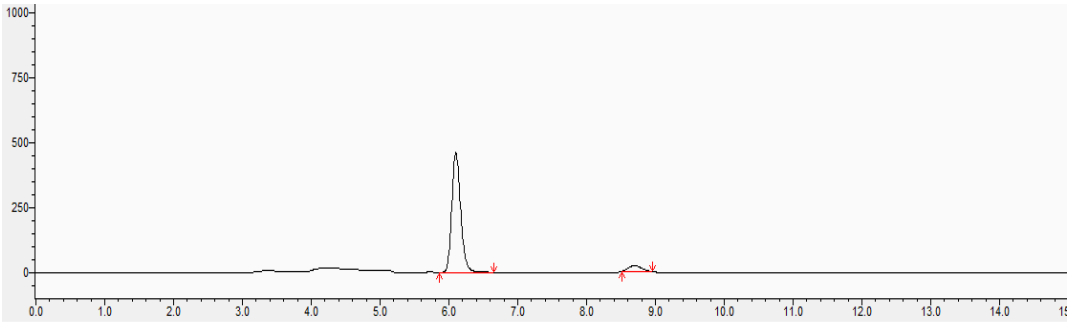
86% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

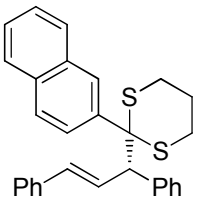


	Retention Time (min)	Area (%)
Peak 1	6.045	49.555
Peak 2	8.777	50.445

Chiral:



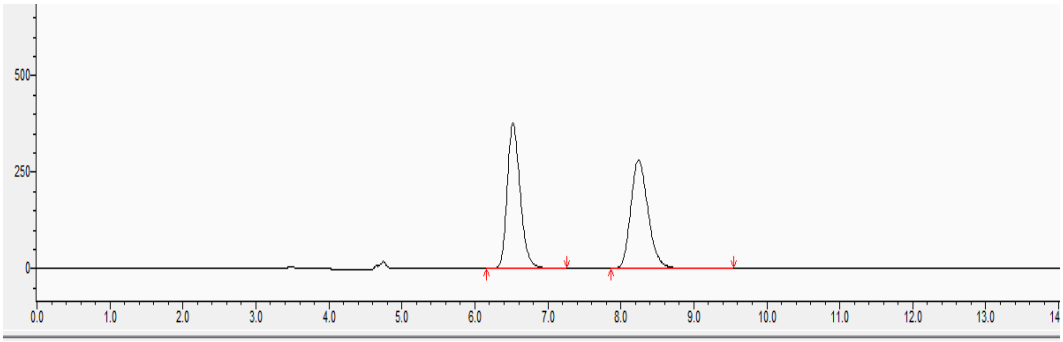
	Retention Time (min)	Area (%)
Peak 1	6.101	92.931
Peak 2	8.697	7.069



3i

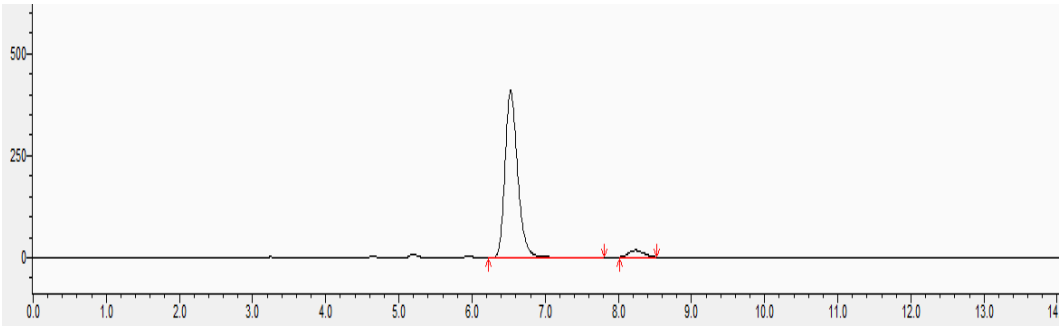
91% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

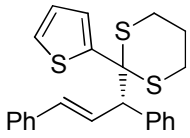


	Retention Time (min)	Area (%)
Peak 1	6.522	49.910
Peak 2	8.243	50.090

Chiral:



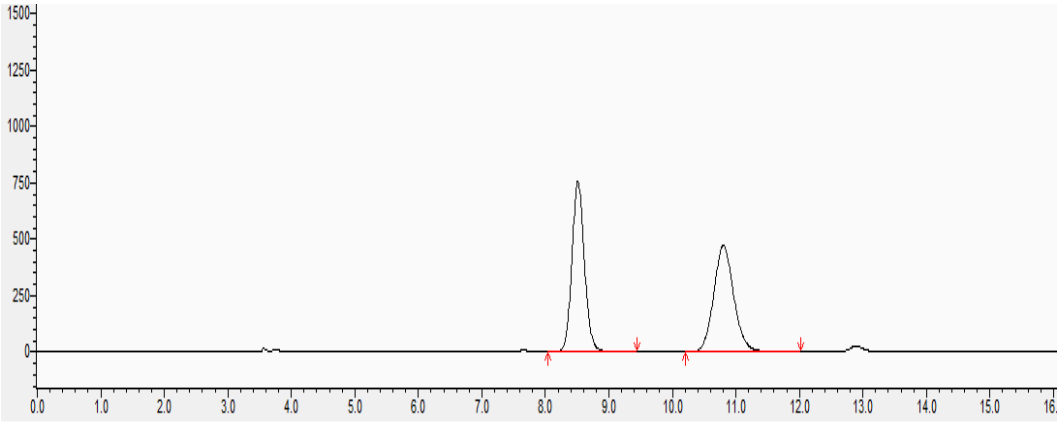
	Retention Time (min)	Area (%)
Peak 1	6.528	95.354
Peak 2	8.237	4.646



3j

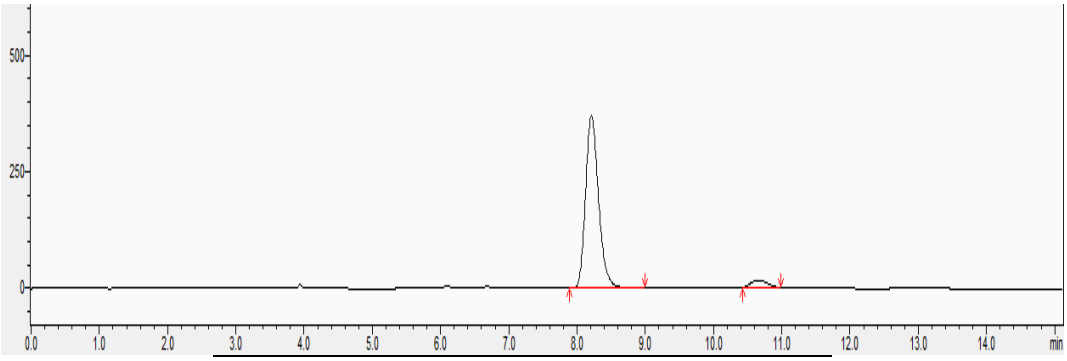
90% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

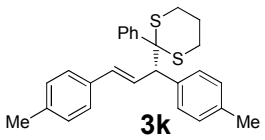


	Retention Time (min)	Area (%)
Peak 1	8.511	49.907
Peak 2	10.803	50.093

Chiral:



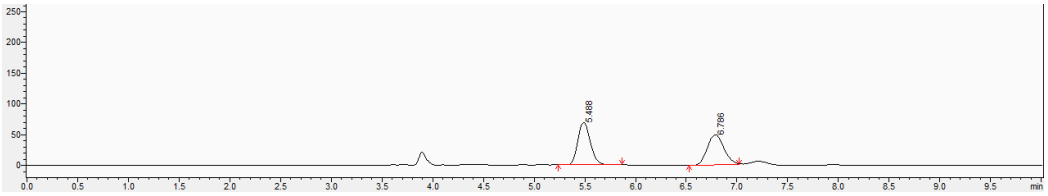
	Retention Time (min)	Area (%)
Peak 1	8.212	94.794
Peak 2	10.660	5.206



3k

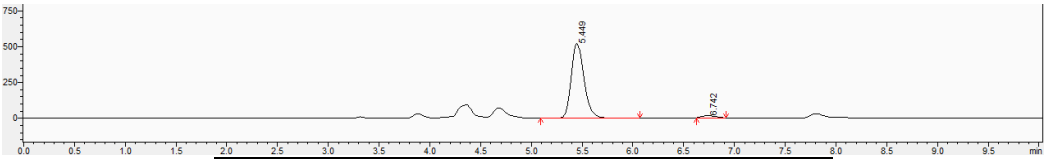
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

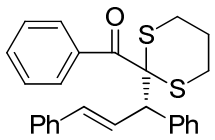


	Retention Time (min)	Area (%)
Peak 1	5.488	50.111
Peak 2	6.786	49.889

Chiral:



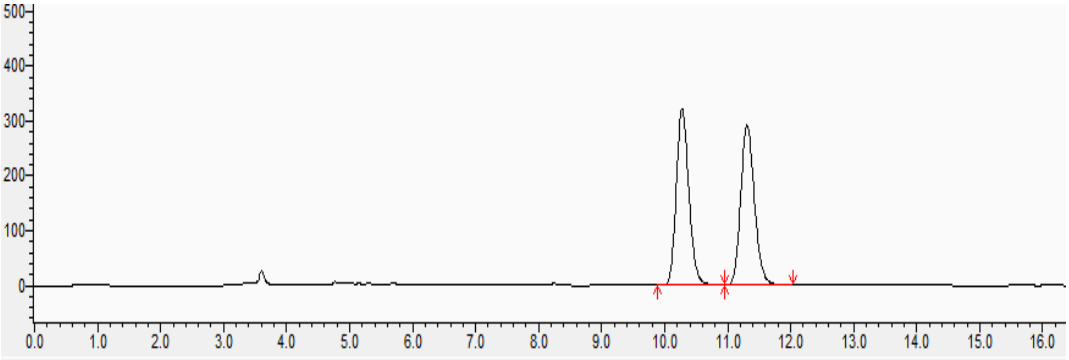
	Retention Time (min)	Area (%)
Peak 1	5.449	97.082
Peak 2	6.742	2.918



5a

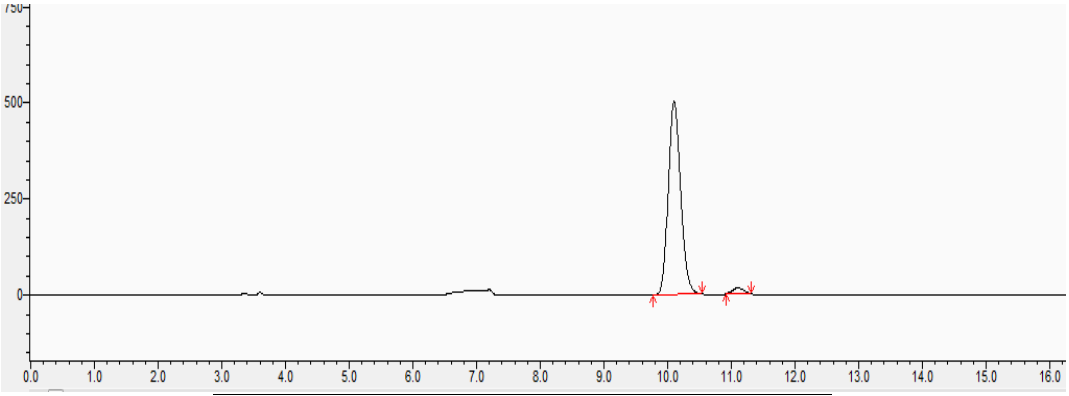
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

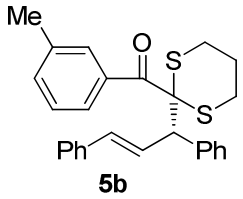


	Retention Time (min)	Area (%)
Peak 1	10.277	50.184
Peak 2	11.308	49.816

Chiral:



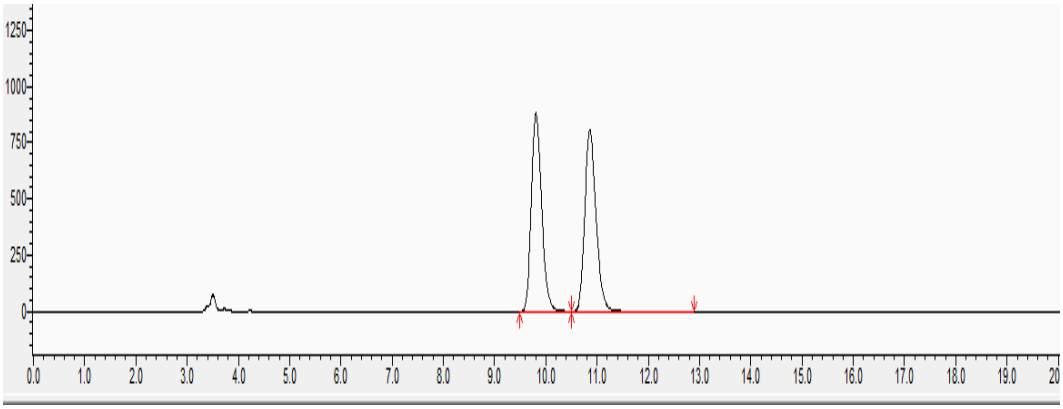
	Retention Time (min)	Area (%)
Peak 1	10.099	97.333
Peak 2	11.103	2.667



5b

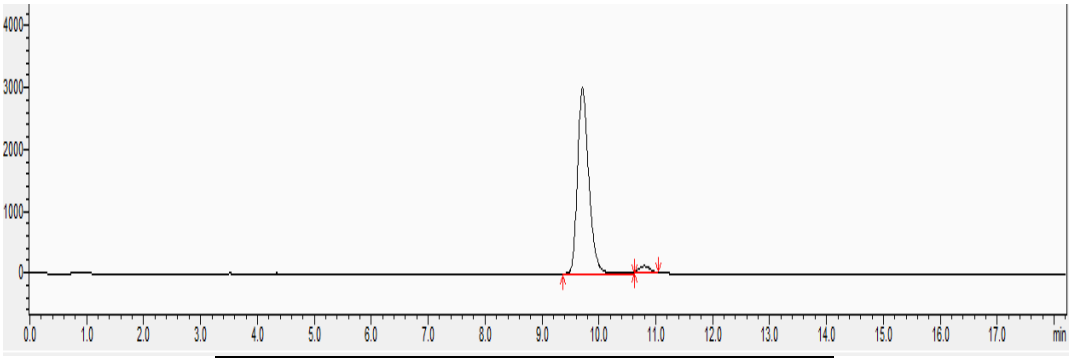
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

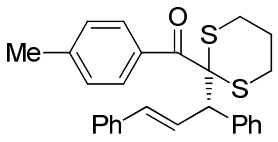


	Retention Time (min)	Area (%)
Peak 1	9.807	49.866
Peak 2	10.859	50.134

Chiral:



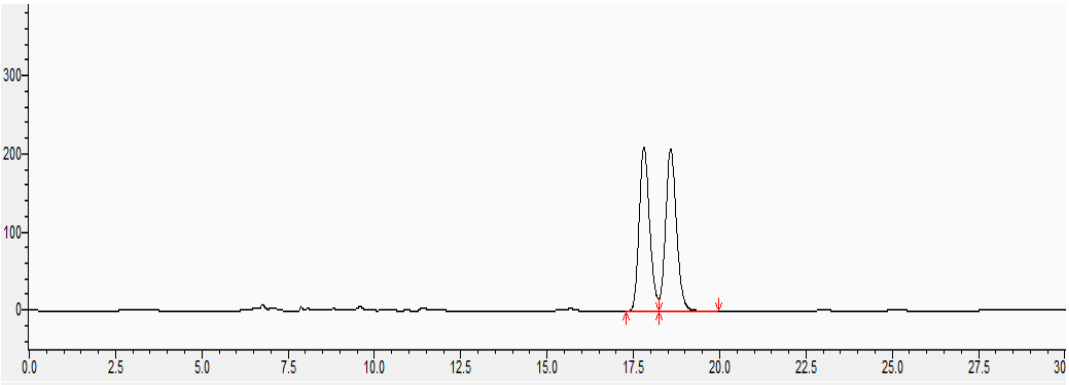
	Retention Time (min)	Area (%)
Peak 1	9.711	96.911
Peak 2	10.795	3.089



5c

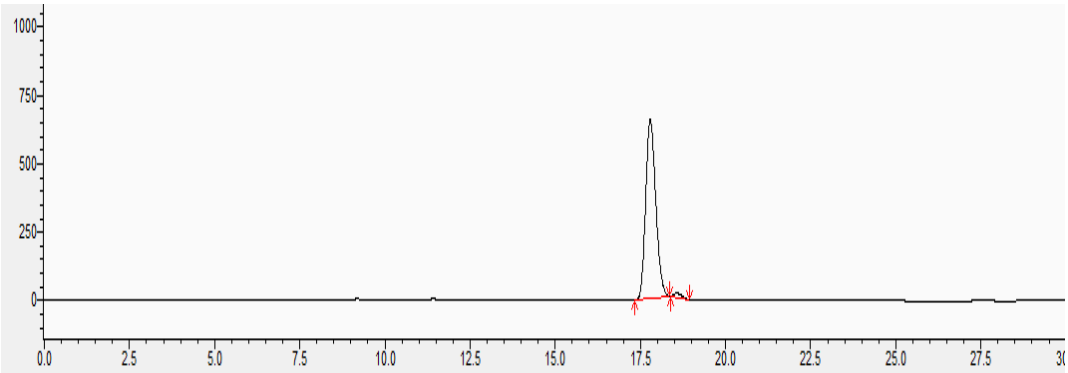
96% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 97/3, 0.5 mL/min, 254 nm.

Racemate:

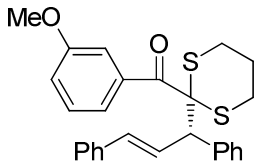


	Retention Time (min)	Area (%)
Peak 1	17.806	49.197
Peak 2	18.581	50.803

Chiral:



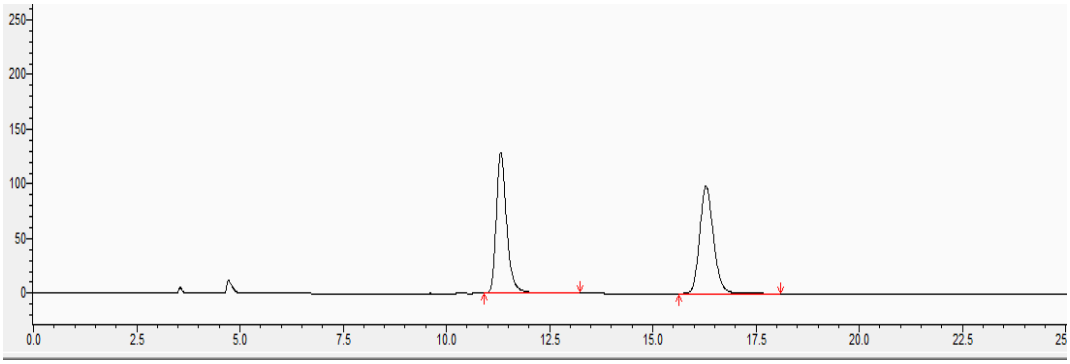
	Retention Time (min)	Area (%)
Peak 1	17.792	98.204
Peak 2	18.570	1.796



5d

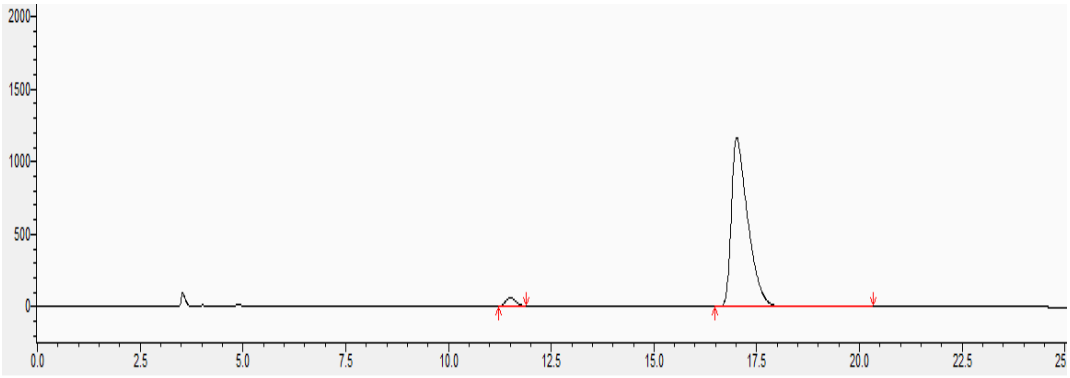
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE column, *n*-hexane /*i*-PrOH = 95/5, 1 mL/min, 254 nm.

Racemate:

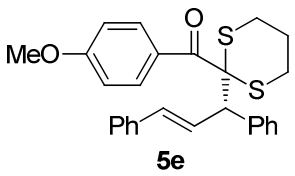


	Retention Time (min)	Area (%)
Peak 1	11.319	49.840
Peak 2	16.288	50.160

Chiral:



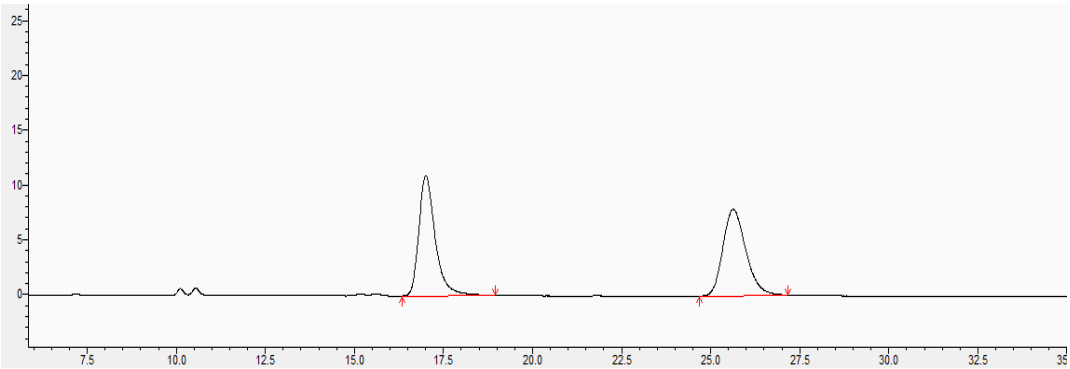
	Retention Time (min)	Area (%)
Peak 1	11.506	3.090
Peak 2	17.013	96.910



5e

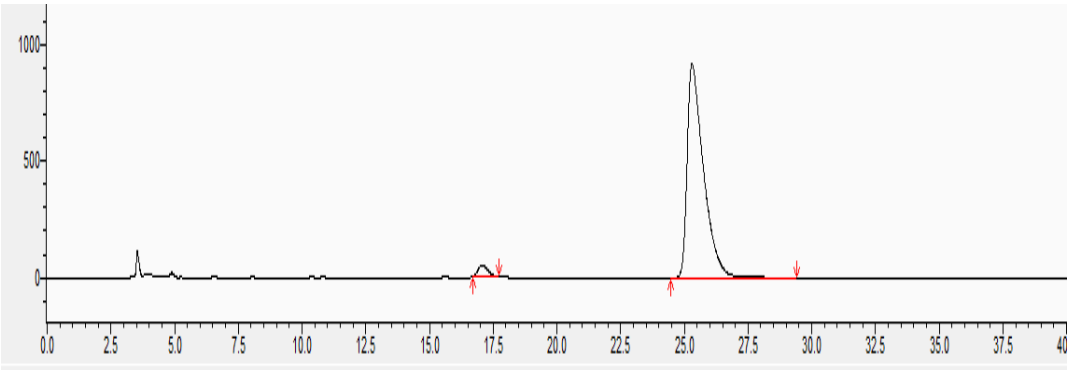
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE column, *n*-hexane /*i*-PrOH = 95/5, 1 mL/min, 254 nm.

Racemate:

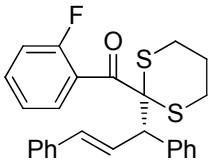


	Retention Time (min)	Area (%)
Peak 1	17.005	49.967
Peak 2	25.629	50.033

Chiral:



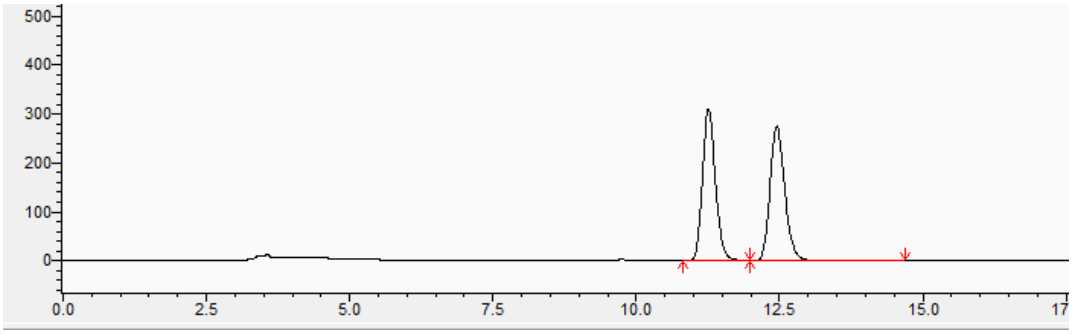
	Retention Time (min)	Area (%)
Peak 1	17.077	3.170
Peak 2	25.302	96.830



5f

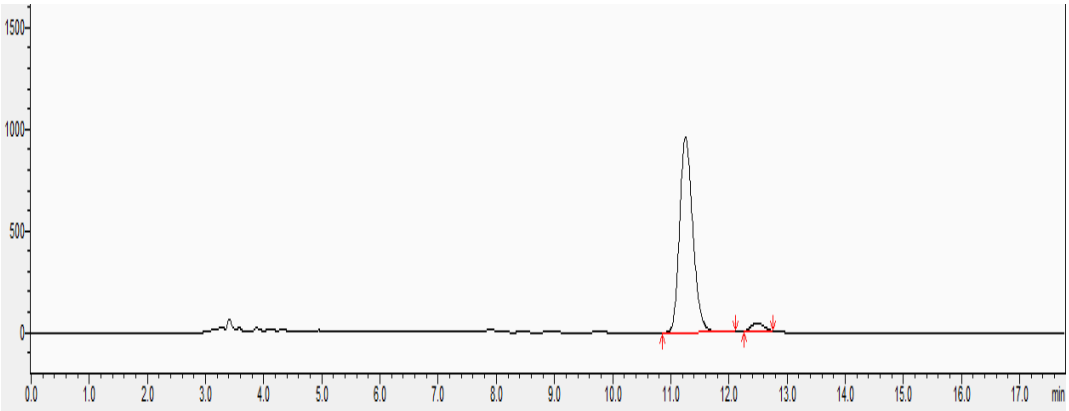
92% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 97/3, 1 mL/min, 254 nm.

Racemate:

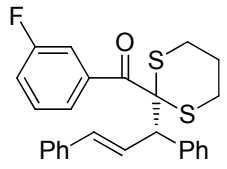


	Retention Time (min)	Area (%)
Peak 1	11.260	49.862
Peak 2	12.452	50.138

Chiral:



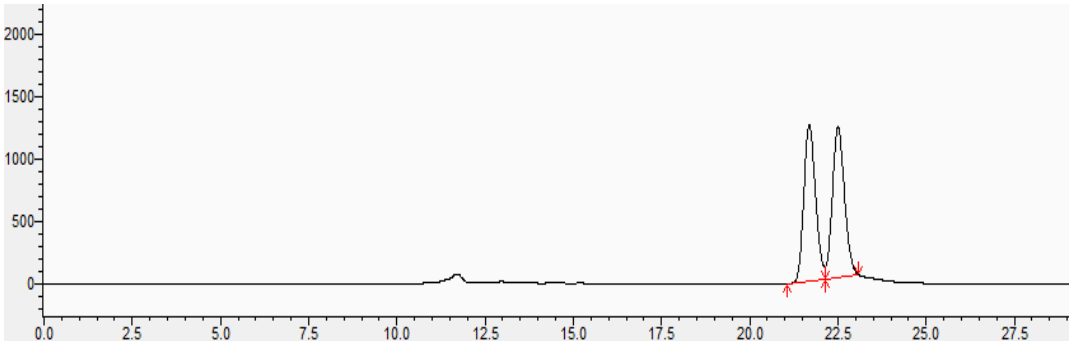
	Retention Time (min)	Area (%)
Peak 1	11.254	96.060
Peak 2	12.486	3.940



5g

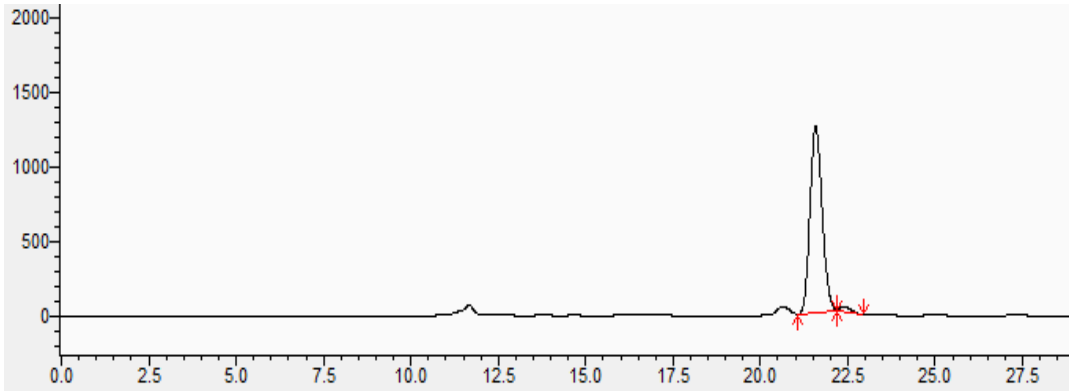
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 98/2, 0.3 mL/min, 254 nm.

Racemate:

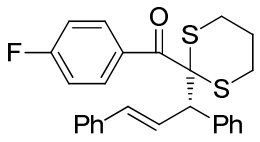


	Retention Time (min)	Area (%)
Peak 1	21.688	49.720
Peak 2	22.503	50.280

Chiral:



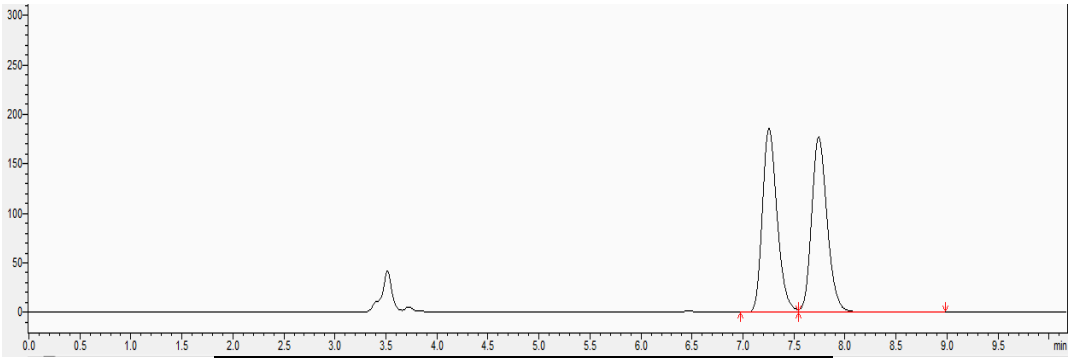
	Retention Time (min)	Area (%)
Peak 1	21.579	97.348
Peak 2	22.404	2.652



5h

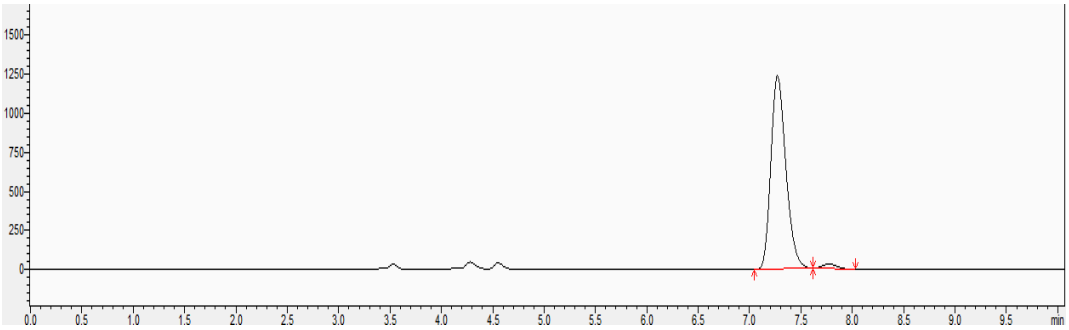
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

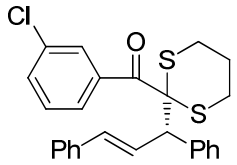


	Retention Time (min)	Area (%)
Peak 1	7.254	49.700
Peak 2	7.739	50.300

Chiral:



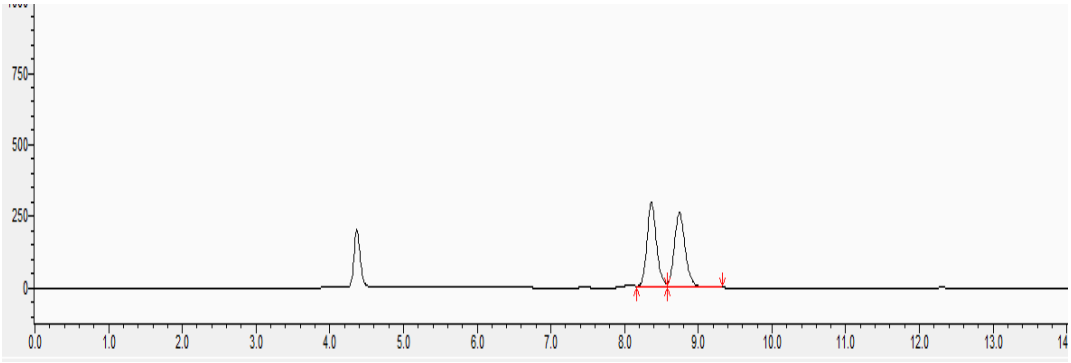
	Retention Time (min)	Area (%)
Peak 1	7.270	97.654
Peak 2	7.771	2.346



5i

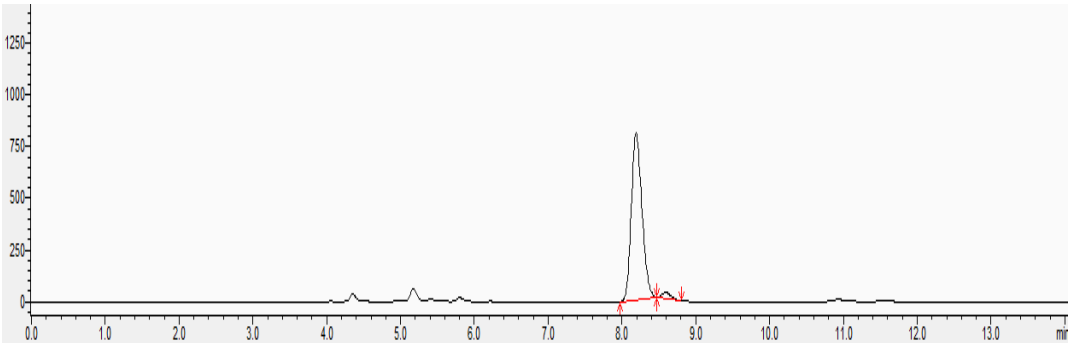
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 98/2, 0.8 mL/min, 254 nm.

Racemate:

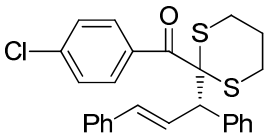


	Retention Time (min)	Area (%)
Peak 1	8.364	50.038
Peak 2	8.743	49.962

Chiral:



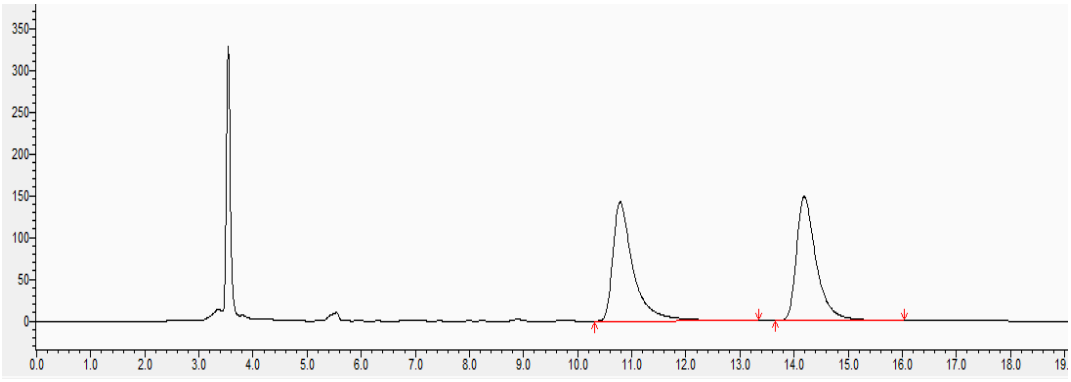
	Retention Time (min)	Area (%)
Peak 1	8.193	96.828
Peak 2	8.592	3.172



5j

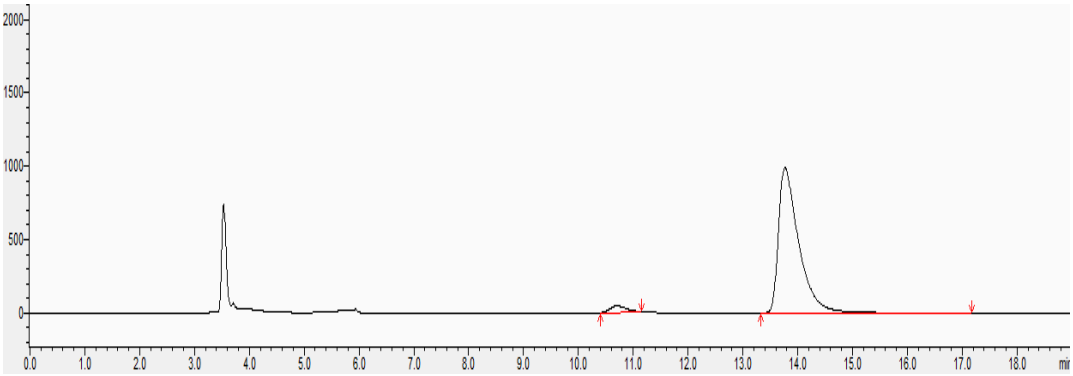
93% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

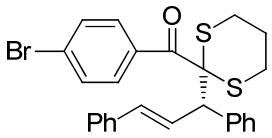


	Retention Time (min)	Area (%)
Peak 1	10.784	49.801
Peak 2	14.186	50.199

Chiral:



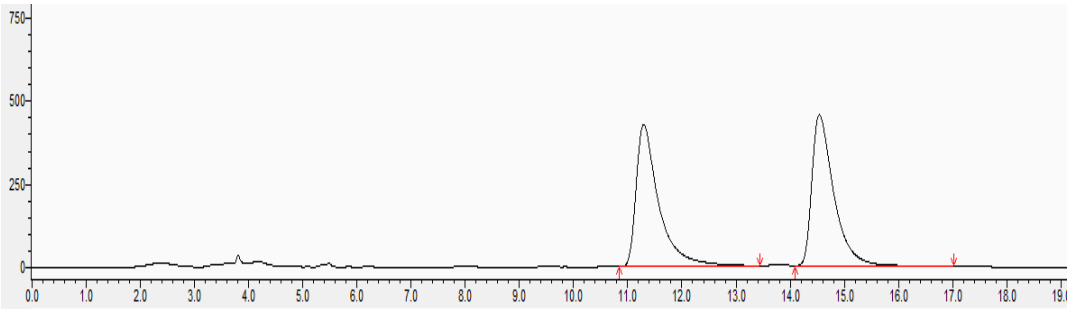
	Retention Time (min)	Area (%)
Peak 1	10.706	3.411
Peak 2	13.768	96.589



5k

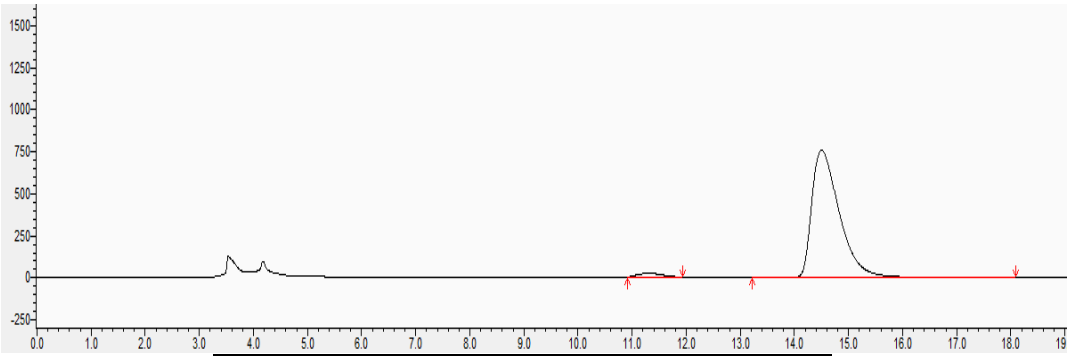
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

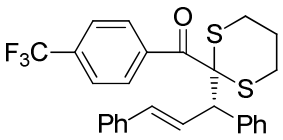


	Retention Time (min)	Area (%)
Peak 1	11.300	49.241
Peak 2	14.538	50.759

Chiral:



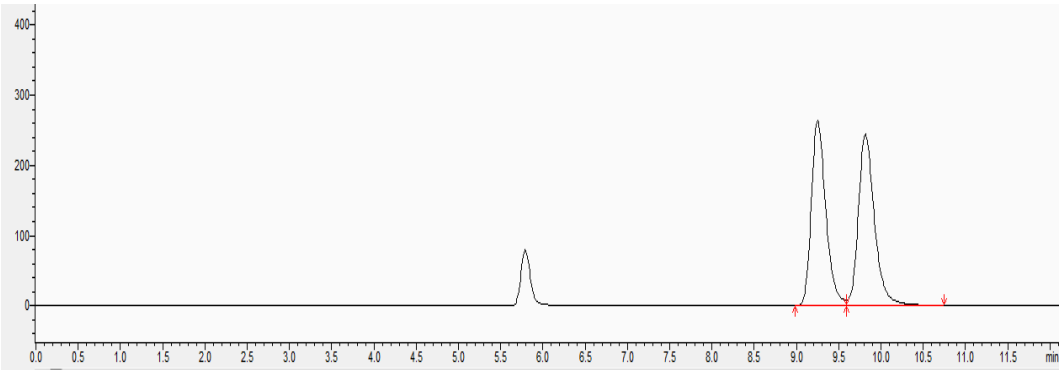
	Retention Time (min)	Area (%)
Peak 1	11.309	2.530
Peak 2	14.503	97.470



5l

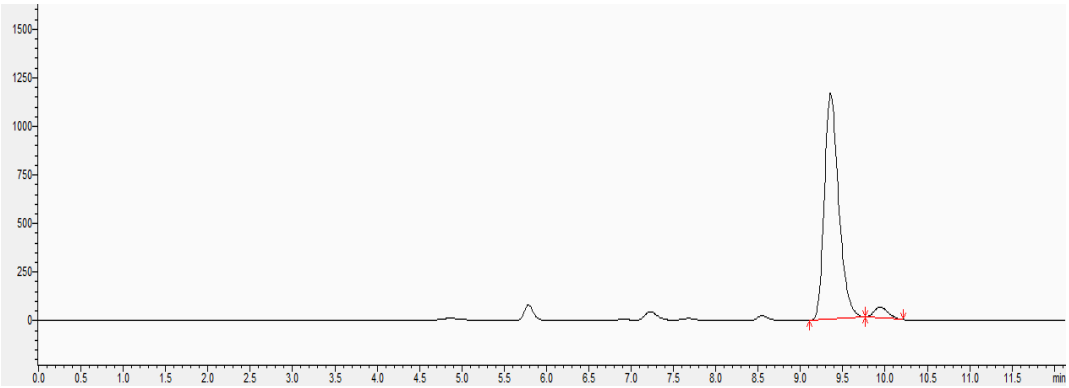
91% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 99/1, 0.6 mL/min, 254 nm.

Racemate:

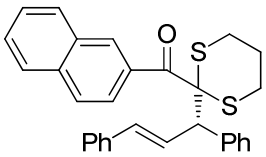


	Retention Time (min)	Area (%)
Peak 1	9.251	49.240
Peak 2	9.816	50.760

Chiral:



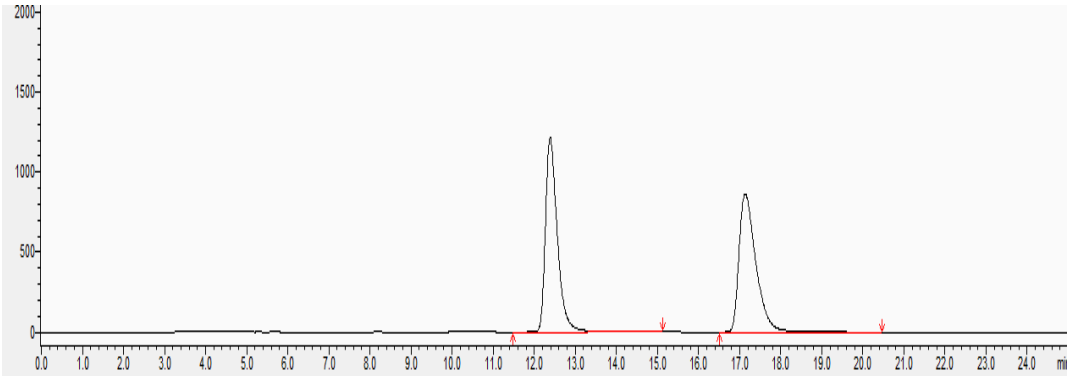
	Retention Time (min)	Area (%)
Peak 1	9.356	95.482
Peak 2	9.942	4.518



5m

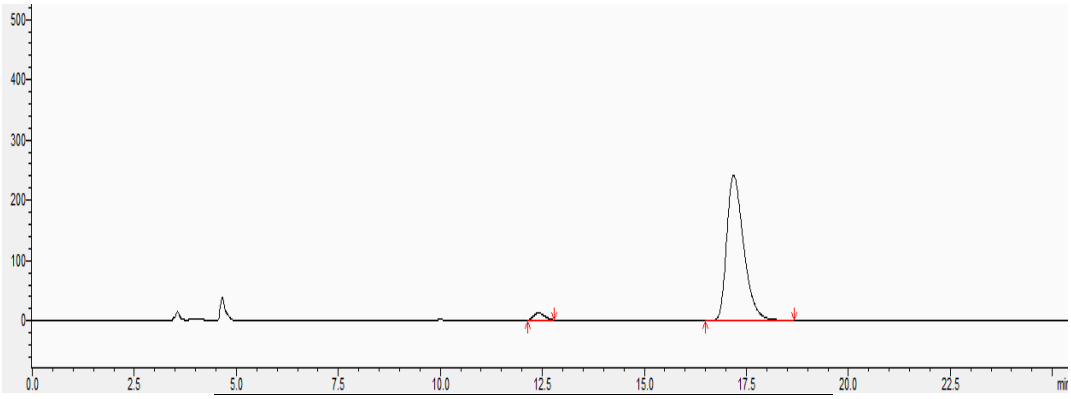
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE column, *n*-hexane /*i*-PrOH = 95/5, 1 mL/min, 254 nm.

Racemate:

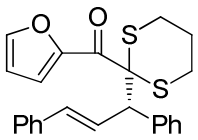


	Retention Time (min)	Area (%)
Peak 1	12.388	49.886
Peak 2	17.136	50.114

Chiral:



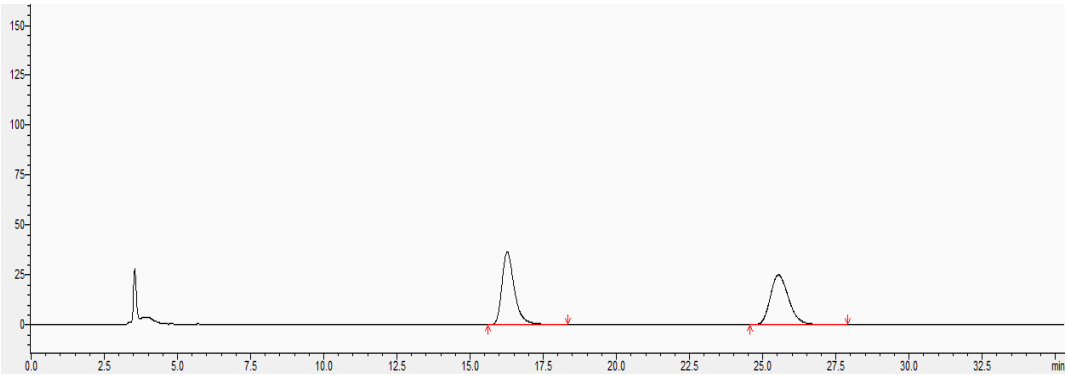
	Retention Time (min)	Area (%)
Peak 1	12.410	3.033
Peak 2	17.190	96.967



5n

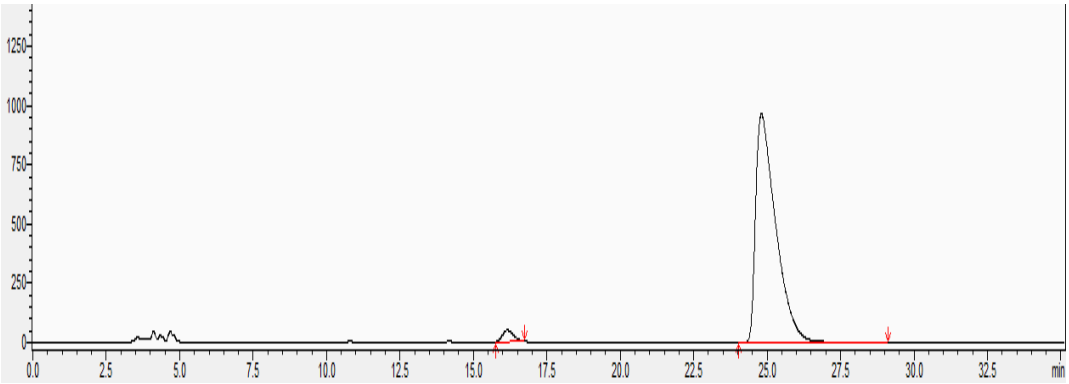
95% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE column, *n*-hexane /*i*-PrOH = 95/5, 1 mL/min, 254 nm.

Racemate:

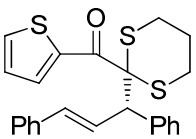


	Retention Time (min)	Area (%)
Peak 1	16.267	49.826
Peak 2	25.539	50.174

Chiral:



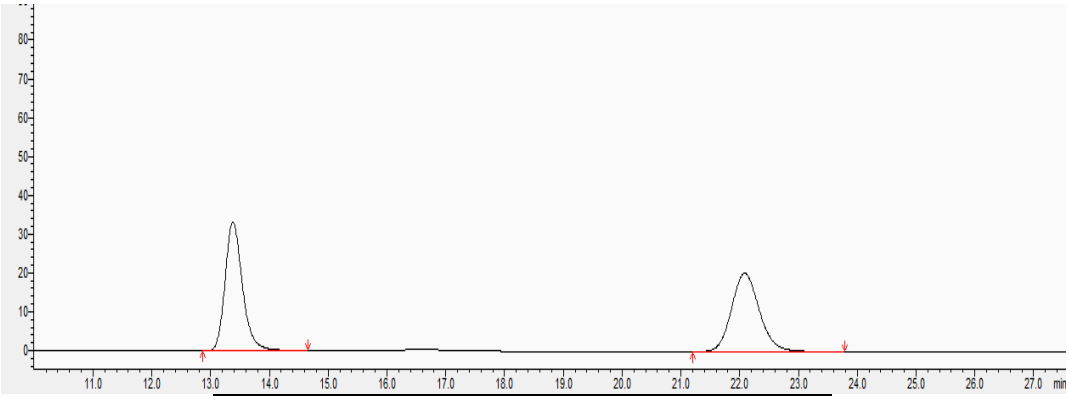
	Retention Time (min)	Area (%)
Peak 1	16.160	2.714
Peak 2	24.806	97.286



5o

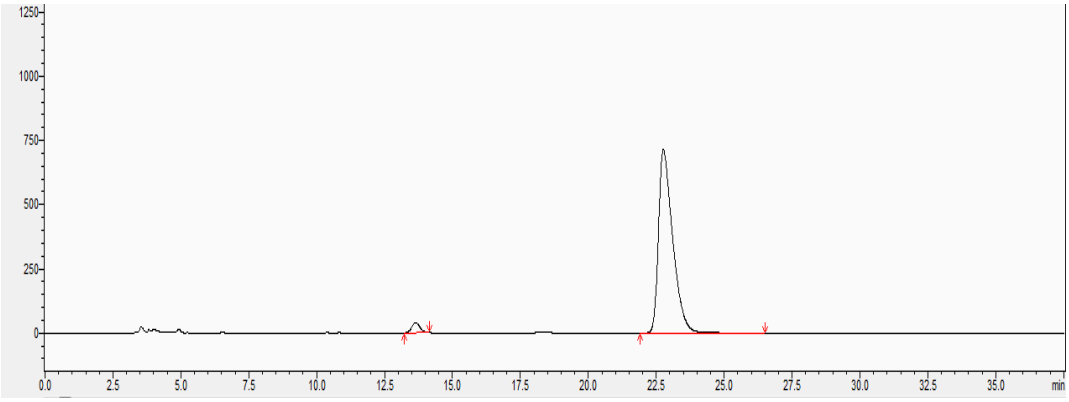
94% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IE column, *n*-hexane /*i*-PrOH = 95/5, 1 mL/min, 254 nm.

Racemate:

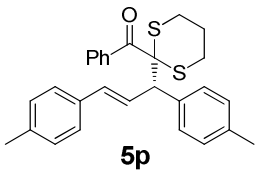


	Retention Time (min)	Area (%)
Peak 1	13.380	50.511
Peak 2	22.085	49.489

Chiral:



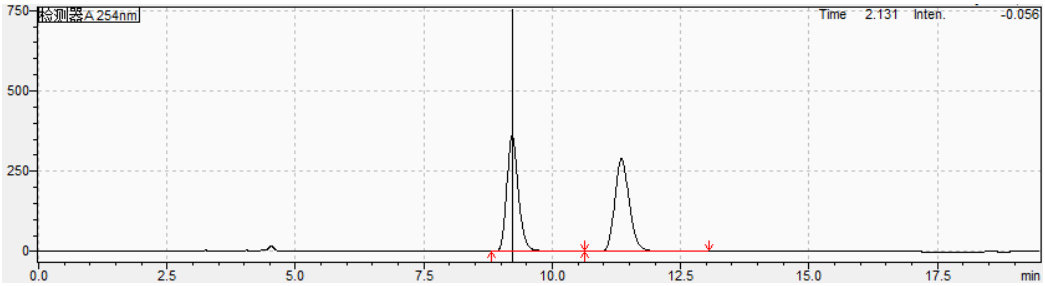
	Retention Time (min)	Area (%)
Peak 1	13.640	3.128
Peak 2	22.767	96.872



5p

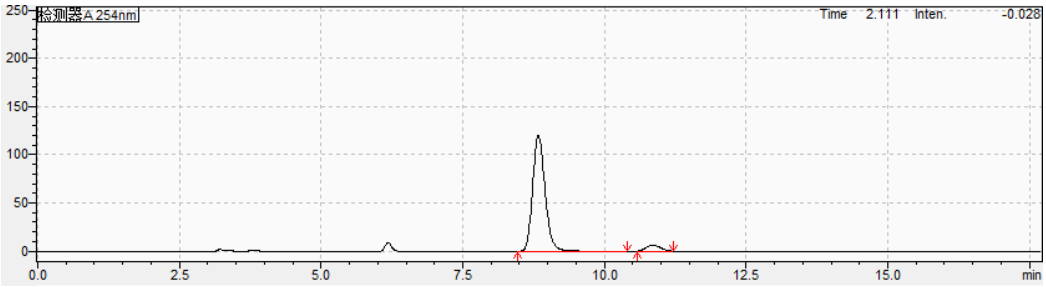
89% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

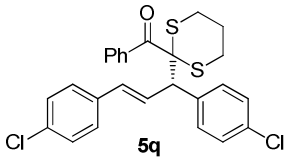


	Retention Time (min)	Area (%)
Peak 1	9.218	50.022
Peak 2	11.348	49.978

Chiral:



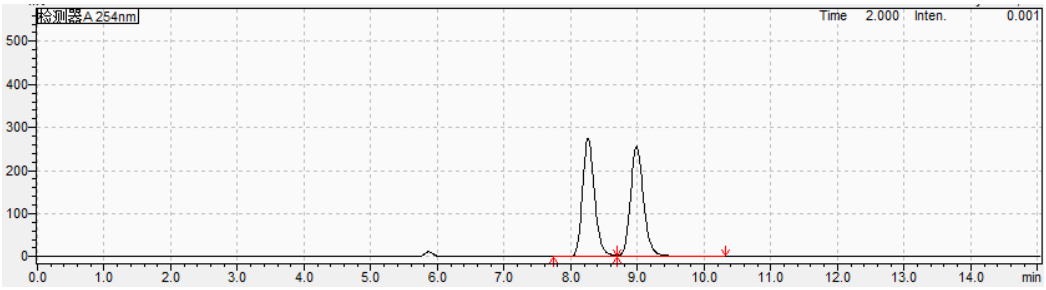
	Retention Time (min)	Area (%)
Peak 1	8.835	94.453
Peak 2	10.853	5.547



5q

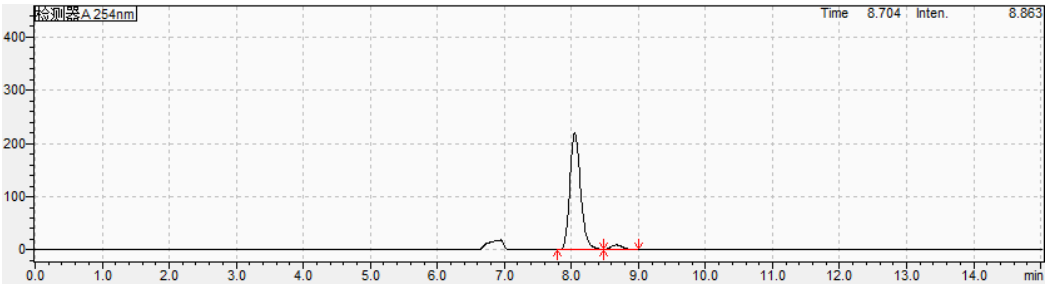
92% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak IC-3 column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

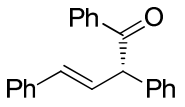


	Retention Time (min)	Area (%)
Peak 1	8.257	49.612
Peak 2	8.985	50.388

Chiral:



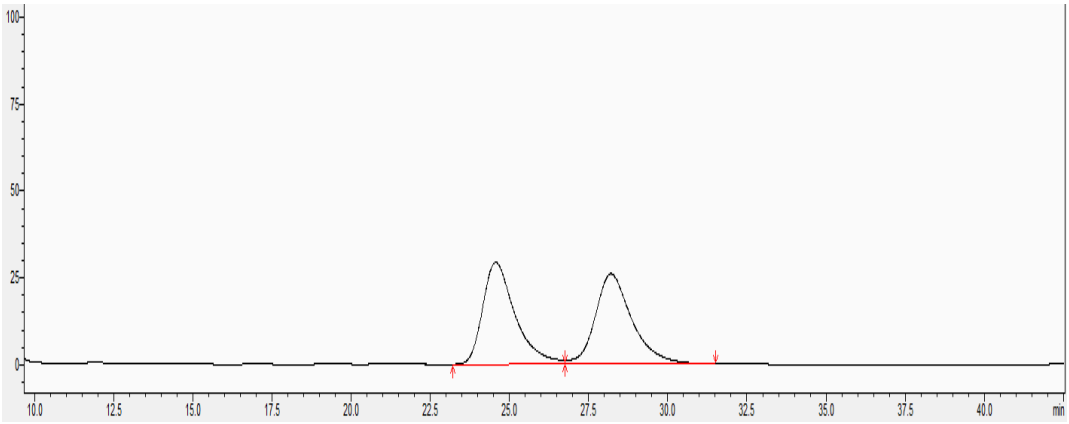
	Retention Time (min)	Area (%)
Peak 1	8.050	96.185
Peak 2	8.673	3.815



6

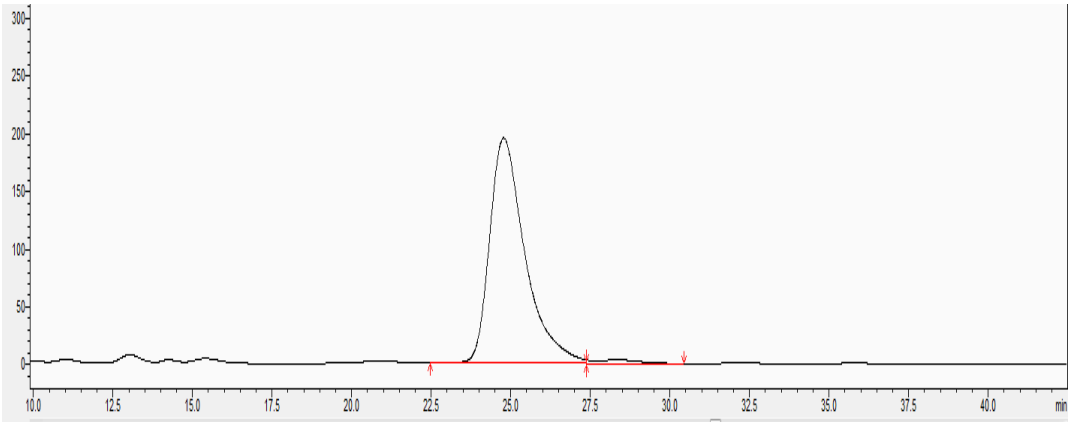
96% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak AD-H column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

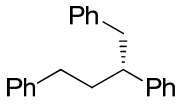


	Retention Time (min)	Area (%)
Peak 1	24.564	49.886
Peak 2	28.205	50.114

Chiral:



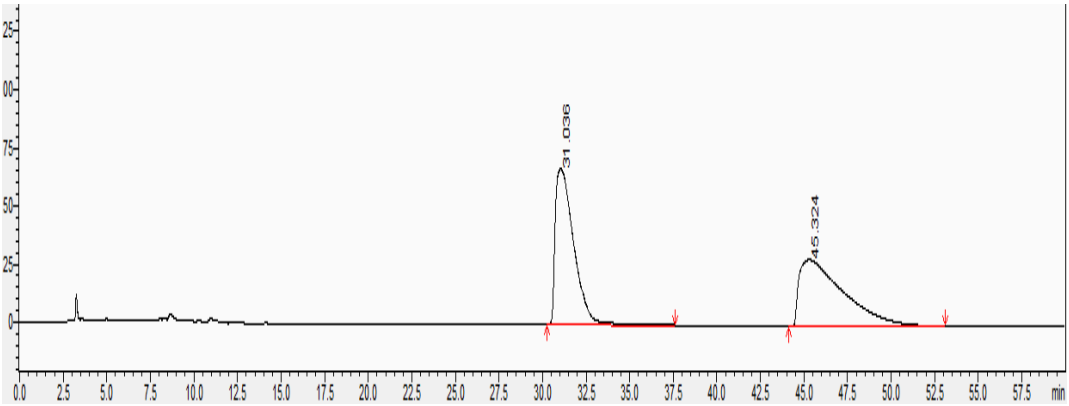
	Retention Time (min)	Area (%)
Peak 1	24.777	97.954
Peak 2	28.359	2.046



7

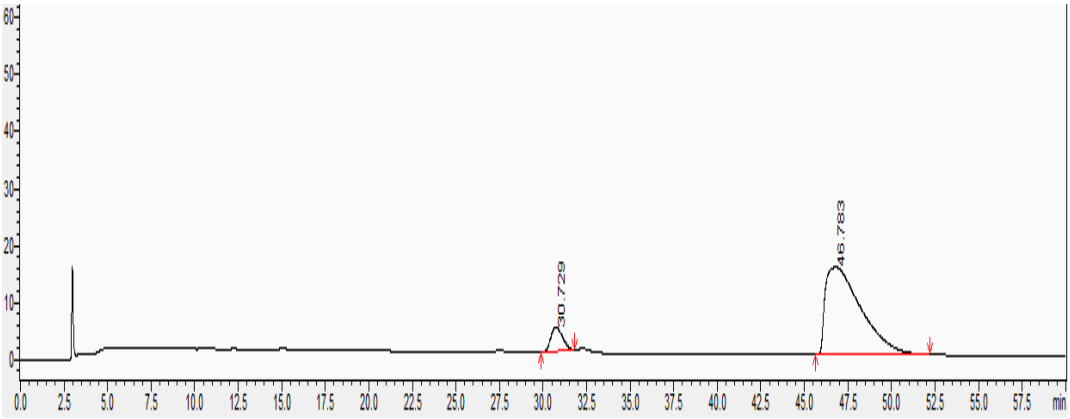
83% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane /*i*-PrOH = 100/0, 1 mL/min, 220 nm.

Racemate:

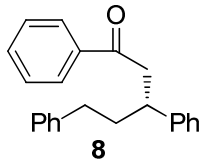


	Retention Time (min)	Area (%)
Peak 1	31.036	49.640
Peak 2	45.324	50.360

Chiral:



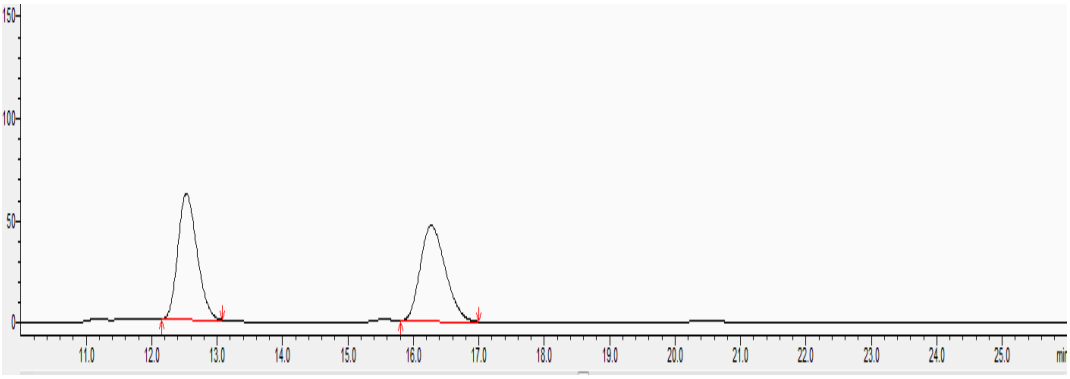
	Retention Time (min)	Area (%)
Peak 1	30.729	8.546
Peak 2	46.783	91.454



8

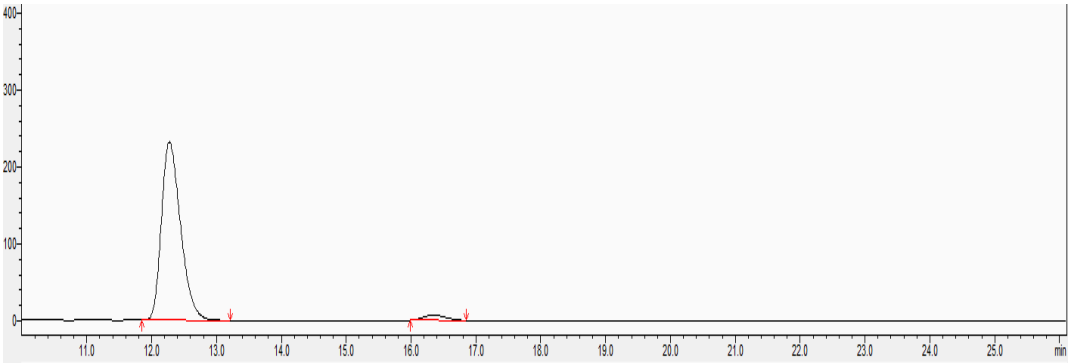
93% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, *n*-hexane /*i*-PrOH = 98/2, 1 mL/min, 254 nm.

Racemate:

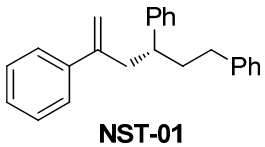


	Retention Time (min)	Area (%)
Peak 1	12.529	50.644
Peak 2	16.273	49.356

Chiral:



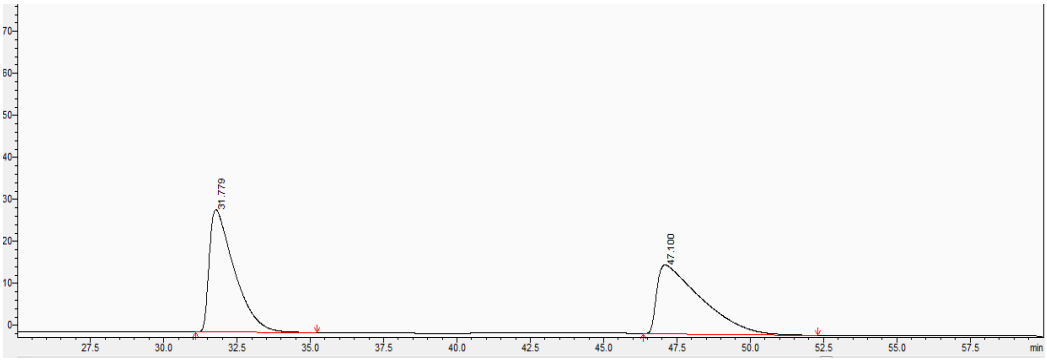
	Retention Time (min)	Area (%)
Peak 1	12.275	96.651
Peak 2	16.345	3.349



NST-01

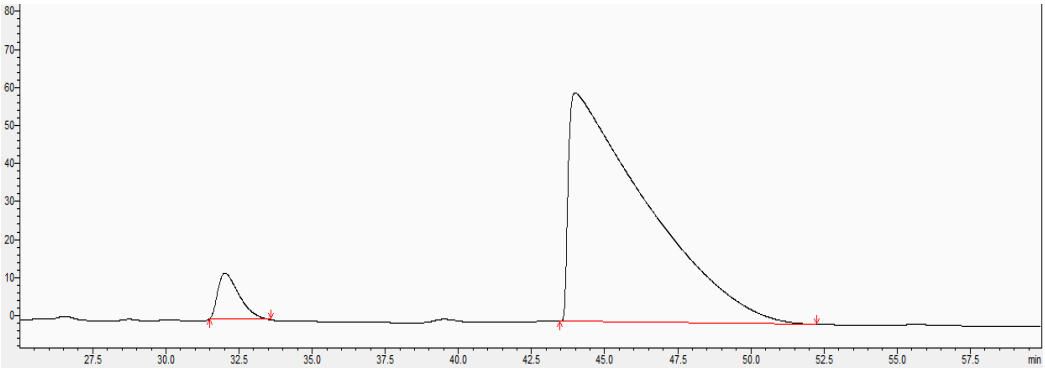
90% *ee*, enantiomeric excess was determined by HPLC, Daicel Chiralpak OD-H column, Hexane/*i*-PrOH = 100/0, 1 mL/min, 254 nm.

Racemate:



	Retention Time (min)	Area (%)
Peak 1	31.779	50.239
Peak 2	47.100	49.761

Chiral:



	Retention Time (min)	Area (%)
Peak 1	32.021	5.138
Peak 2	43.995	94.862