Supporting Information

Copper-catalyzed Redox-neutral Regioselective Chlorosulfonylation of Vinylarenes

Lixia Liu, Chengming Wang*

Department of Chemistry, College of Chemistry and Materials Science
Jinan University
Guangzhou, 511443, China
Email: cmwang2019@jnu.edu.cn

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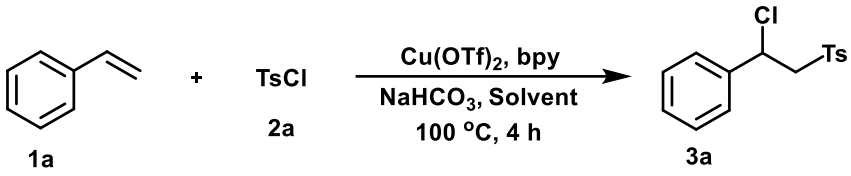
General Methods and Materials:

Unless specified, all reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions. Alkenes starting materials were synthesized according to a previous reported literature.[1] The *BipG*-derived alkene,[2] *fenofibrate*-derived alkene and estrone-derived alkene,[3] *cholesterol*-derived alkene,[4] *(-)menthol*-derived alkene[4] were synthesized according to reported literatures. $Cu(OTf)_2$ (purity: 98%) and acetonitrile (super dry, 99.9%) were purchased from *J&K*; all other reagents were purchased and used without further purification unless specified otherwise. Solvents for chromatography were technical grade and distilled prior to use. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). ^{1}H NMR and ^{13}C NMR data were recorded on Bruker 300 M nuclear resonance spectrometers unless otherwise specified, respectively. Chemical shifts (δ) in ppm are reported as quoted relative to the residual signals of chloroform (^{1}H 7.26 ppm or ^{13}C 77.16 ppm). Multiplicities are described as: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet); and coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded with total proton decoupling. High resolution mass spectrometry (HRMS) analysis was performed using electrospray ionization (ESI) with a quadrupole-time of flight (QTOF) mass analyzer. HRMS (ESI) analysis was performed by The Analytical Instrumentation Center at College of Chemistry and Materials Science, Jinan University, and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units.

Conditions Screening

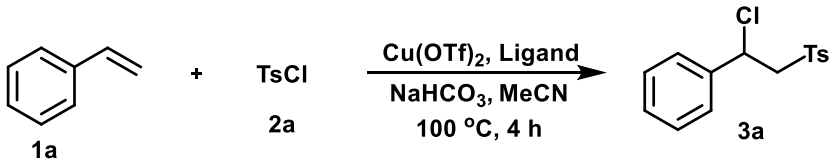
Table 1 Solvent opitimizations[a]



Entry	Solvent	Yield[b]
1	DMSO	20%
2	1, 4-dioxane	72%
3	**MeCN**	**91%**
4	MTBE	4%
5	DMF	4%
6	Isopropanol	0%

[a] Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (2.0 equiv.), $Cu(OTf)_2$ (10 mol%), bpy (10 mol%), $NaHCO_3$ (1.1 equiv.), solvent (1.5 mL), under N_2, 4 h; [b] ^1H NMR yield.

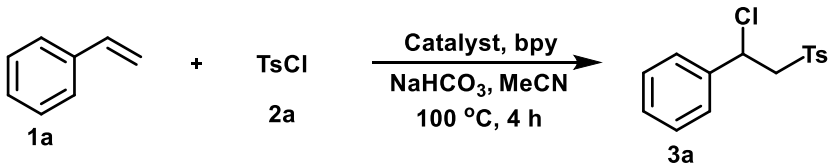
Table 2 Ligand opitimizations[a]



Entry	Ligand	Yield[b]
1	dtbpy	46%
2	2,2'-biquinoline	69%
3	AIBN	28%
4	**bpy**	**91%**
5	tri(*o*-tolyl)-phosphine	41%
6	4,4'-dimethoxy-2,2'-bipyridine	40%
7	2,2'-bi(5-methylpyridine)	31%

[a] Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (2.0 equiv.), $Cu(OTf)_2$ (10 mol%), ligand (10 mol%), $NaHCO_3$ (1.1 equiv.), MeCN (1.5 mL), under N_2, 4 h; [b] ^1H NMR yield.

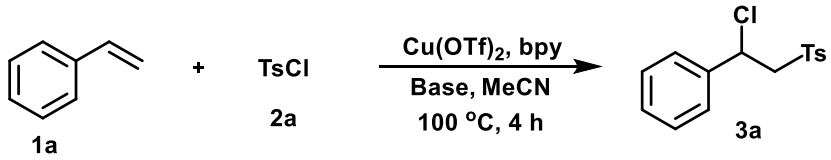
Table 3 Catalyst opitimizations[a]



Entry	Catalyst	Yield[b]
1	$CuBr_2$	25%
2	$Cu(OAc)_2$	33%
3	CuCl	79%
4	$FeSO_4$	4%
5	$Pd(OAc)_2$	17%
6	**$Cu(OTf)_2$**	**91%**
7	$Pd(TFA)_2$	0%

[a] Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (2.0 equiv.), catalyst (10 mol%), bpy (10 mol%), $NaHCO_3$ (1.1 equiv.), MeCN (1.5 mL), under N_2, 4 h; [b] ^1H NMR yield.

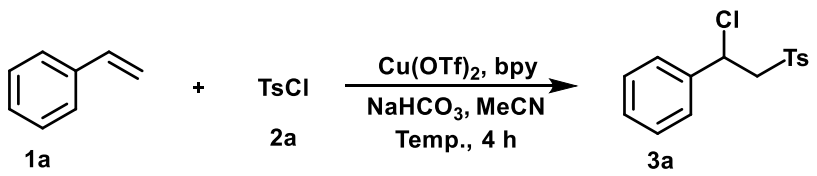
Table 4 Base opitimizations[a]



Entry	Base	Yield[b]
1	Na_2CO_3	8%
2	K_3PO_4	9%
3	Li_2CO_3	56%
4	CH_3COOK	44%
5	Et_3N	21%
6	K_2CO_3	25%
7	$KHCO_3$	50%
8	Cs_2CO_3	9%
9	CsF	ND
10	NaOH	56%
11	LiO^tBu	88%
12	DIPEA	81%
13	DABCO	22%
14	DMAP	39%
15	DBU	86%
16	TMG	55%
17	**$NaHCO_3$**	**91%**

[a] Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (2.0 equiv.), $Cu(OTf)_2$ (10 mol%), bpy (10 mol%), base (1.1 equiv.), MeCN (1.5 mL), under N_2, 4 h; [b] ^1H NMR yield.

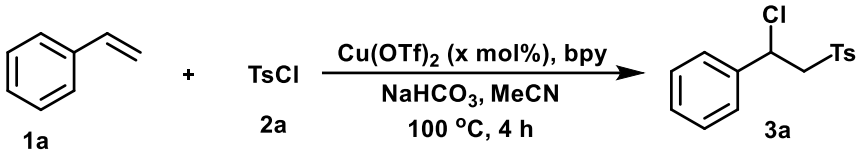
Table 5 Temperature opitimizations[a]



Entry	Temperature (°C)	Yield[b]
1	**100**	**91%**
2	80	70%
3	60	9%
4	40	ND
5	rt	ND

[a] Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (2.0 equiv.), $Cu(OTf)_2$ (10 mol%), bpy (10 mol%), $NaHCO_3$ (1.1 equiv.), MeCN (1.5 mL), under N_2, 4 h; [b] ^1H NMR yield.

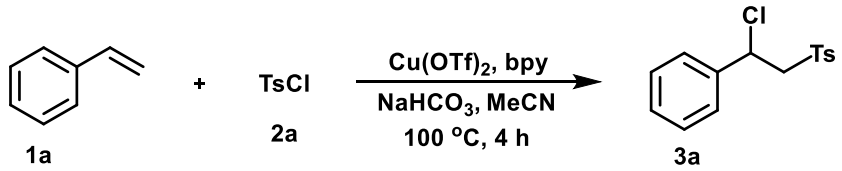
Table 6 Amounts of $Cu(OTf)_2$ opitimizations[a]



Entry	Catalyst (mol%)	Yield[b]
1	**10 mol%**	**91%**
2	5mol%	79%
3	1mol%	24%

[a] Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (2.0 equiv.), $Cu(OTf)_2$ (x mol%), bpy (10 mol%), $NaHCO_3$ (1.1 equiv.), MeCN (1.5 mL), under N_2, 4 h; [b] ^1H NMR yield.

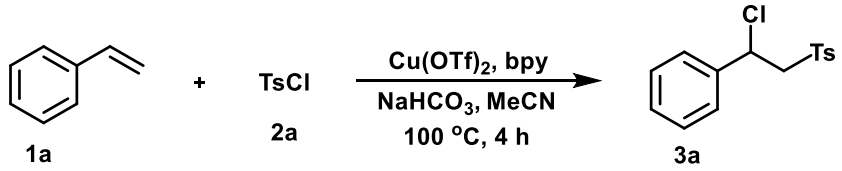
Table 7 Amounts of TsCl opitimizations[a]



Entry	TsCl (equiv.)	Yield[b]
1	1.0 (equiv.)	18%
2	1.2 (equiv.)	38%
3	1.5 (equiv.)	71%
4	**2.0 (equiv.)**	**91%**

[a] Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (x equiv.), $Cu(OTf)_2$ (10 mol%), bpy (10 mol%), $NaHCO_3$ (1.1 equiv.), MeCN (1.5 mL), under N_2, 4 h; [b] ^1H NMR yield.

Table 8 Control experiments[a]



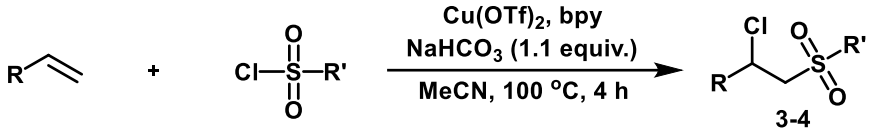
Entry	Conditions	Yield[b]
1	without $Cu(OTf)_2$	ND
2	without bpy	<5%
3	without $NaHCO_3$	ND
4	under air	31%

[a] Reaction on a 0.2 mmol scale, using **1a** (1.0 equiv.), **2a** (2.0 equiv.), $Cu(OTf)_2$ (10 mol%), bpy (10 mol%), $NaHCO_3$ (1.1 equiv.), MeCN (1.5 mL), under N_2, 4 h; [b] ^1H NMR yield.

Note:

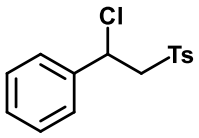
MTBE = *tert*-butyl methyl ether; dtbpy = 4,4'-di-*tert*-butyl-2,2'-dipyidyl; AIBN = 2,2'-azobis(2-methylpropionitrile); bpy = 2,2'-bipyridine; DIPEA = N,N-diisopropylethylamine; DABCO = 1,4-diaza[2.2.2]bicyclooctane; DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene; TMG = 1,1,3,3-tetramethyl guanidine; ND = Not Detected.

General Procedure for Chlorosulfonylation

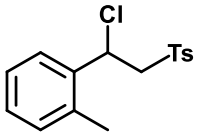


Sulfonyl chloride **2** (0.4 mmol, 2.0 equiv.), $Cu(OTf)_2$ (10 mol%) and $NaHCO_3$ (0.22 mmol, 1.1 equiv.) were weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then alkene **1** (0.2 mmol, 1.0 equiv.) in MeCN (1.5 mL) was added through the side-arm by syringe. The reaction was stirred under nitrogen at 100 °C for 4 h. After reaction, the mixture was cooled to room temperature. Volatile solvent and reagents were removed by rotary evaporation and the residue was purified by silica gel flash chromatography using petroleum ether/EtOAc (50:1 to 15:1) to afford the desired product **3** or **4**.

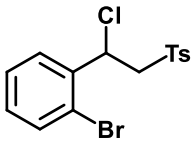
Characterization of Products



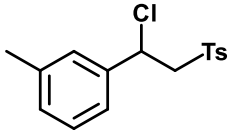
1-((2-chloro-2-phenylethyl)sulfonyl)-4-methylbenzene (3a).[5] yield: 93%, white solid, melting point: 76-77 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.28-7.23 (m, 7H), 5.34 (t, *J* = 6.9 Hz, 1H), 3.99-3.82 (m, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.9, 138.6, 136.2, 129.8, 129.1, 128.9, 128.2, 127.2, 64.1, 55.2, 21.6. IR (ATR): 3061, 2977, 2830, 1599, 1320, 1139, 693 cm^{-1}. HRMS (ESI) m/z: found: 295.0558, calcd. for $C_{15}H_{16}ClO_2S$ $[M+H]^+$: 295.0554.



1-(1-chloro-2-tosylethyl)-2-methylbenzene (3b).[6] yield: 80%, white solid, melting point: 89-90 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.07-7.01 (m, 3H), 5.29 (t, *J* = 6.9 Hz, 1H), 3.98-3.80 (m, 2H), 2.40 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.8, 138.7, 138.4, 136.2, 129.9, 129.7, 128.8, 128.2, 127.7, 124.4, 64.0, 55.2, 21.6, 21.3. IR (ATR): 3102, 2815, 1608, 1573, 1312, 897, 679 cm^{-1}. HRMS (ESI) m/z: found: 309.0717, calcd. for $C_{16}H_{18}ClO_2S$ $[M+H]^+$: 309.0711.

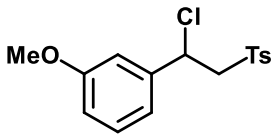


1-bromo-2-(1-chloro-2-tosylethyl)benzene (3c). yield: 37%, white solid, melting point: 75-76 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.28 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 1H), 5.76 (t, *J* = 7.5 Hz, 1H), 3.94-3.80 (m, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.5, 145.2, 137.0, 136.0, 132.5, 130.1, 129.8, 128.9, 128.0, 121.2, 63.9, 54.2, 21.5. IR (ATR): 2917, 2849, 1511, 1322, 1264, 1213, 1156, 920, 810, 792 cm^{-1}. HRMS (ESI): found: 394.9482, calcd. for $C_{15}H_{14}BrClO_2SNa$ $[M+Na]^+$: 394.9479.

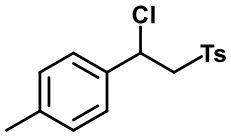


1-(1-chloro-2-tosylethyl)-3-methylbenzene (3d).[7] yield: 81%, white solid, melting point: 109-110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.25-7.02 (m, 6H), 5.63 (t, *J* =

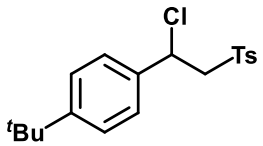
5.6 Hz, 1H), 4.01-3.84 (m, 2H), 2.40 (d, *J* = 2.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.9, 136.6, 136.2, 135.5, 130.9, 129.8, 128.9, 128.1, 126.8, 126.7, 63.4, 51.4, 21.6, 19.1. IR (ATR): 3059, 2990, 1598, 1316, 914, 760, 553 cm^{-1}. HRMS (ESI) m/z: found: 309.0719, calcd. for $C_{16}H_{18}ClO_2S$ $[M+H]^+$: 309.0711.



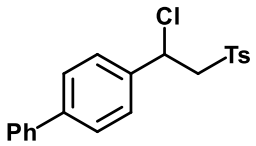
1-(1-chloro-2-tosylethyl)-3-methoxybenzene (3e).[6] yield: 97%, white solid, melting point: 105-106 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.23-7.14 (m, 3H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.81-6.74 (m, 2H), 5.28 (t, *J* = 6.9 Hz, 1H), 3.96-3.79 (m, 2H), 3.73 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.8, 144.9, 139.9, 136.2, 130.0, 129.7, 128.2, 119.5, 114.7, 112.6, 64.1, 55.3, 55.1, 21.6. IR (ATR): 2996, 2832, 1592, 1491, 1190, 940, 772 cm^{-1}. HRMS (ESI) m/z: found: 325.0663, calcd. for $C_{16}H_{18}ClO_3S$ $[M+H]^+$: 325.0660.



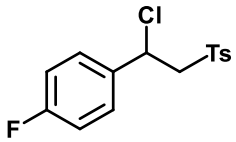
1-((2-chloro-2-(p-tolyl)ethyl)sulfonyl)-4-methylbenzene (3f).[6] yield: 88%, yellow solid, melting point: 116-118 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 5.30 (t, *J* = 5.7 Hz, 1H), 3.97-3.80 (m, 2H), 2.41 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.83, 139.2, 136.3, 135.6, 129.7, 129.5, 128.2, 127.1, 64.1, 55.1, 21.6, 21.2. IR (ATR): 3014, 2983, 1594, 1387, 872, 634 cm^{-1}. HRMS (ESI) m/z: found: 331.0537, calcd. for $C_{16}H_{17}ClNaO_2S$ $[M+Na]^+$: 331.0530.



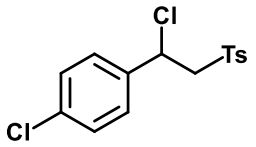
1-(*tert*-butyl)-4-(1-chloro-2-tosylethyl)benzene (3g).[6] yield: 74%, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.3 (t, *J* = 7.0 Hz, 1H), 3.99-3.85 (m, 2H), 2.38 (s, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.3, 144.6, 136.3, 135.4, 129.7, 128.2, 126.9, 125.8, 64.0, 55.1, 34.6, 31.3, 21.6. IR (ATR): 3085, 2932, 2893, 1582, 1372, 932, 534 cm^{-1}. HRMS (ESI) m/z: found: 373.0992, calcd. for $C_{19}H_{23}ClNaO_2S$ $[M+Na]^+$: 373.0999.



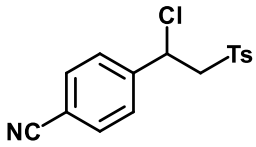
4-(1-chloro-2-tosylethyl)-1,1'-biphenyl (3h). yield: 81%, white solid, melting point: 98-99 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.54-7.51 (m, 2H), 7.47-7.37 (m, 5H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.39 (t, *J* = 8.6 Hz, 1H), 4.03-3.89 (m, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.9, 142.1, 140.1, 137.3, 136.2, 129.8, 128.9, 128.2, 127.8, 127.7, 127.5, 127.1, 64.0, 55.0, 21.6. IR (ATR): 2937, 1595, 1486, 1318, 1135, 759, 693 cm^{-1}. HRMS (ESI): found: 357.0915, calcd. for $C_{21}H_{18}O_2SNa$ [M-HCl+Na]$^+$: 357.0920.



1-((2-chloro-2-(4-fluorophenyl)ethyl)sulfonyl)-4-methylbenzene (3i).[7] yield: 92%, white solid, melting point: 103-104 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.29-7.24 (m, 4H), 6.95 (t, *J* = 8.6 Hz, 2H), 5.34 (t, *J* = 7.1 Hz, 1H), 3.98-3.80 (m, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.9 (d, *J* = 247.6 Hz), 145.1, 136.2, 134.4 (d, *J* = 3.3 Hz), 129.8, 129.2 (d, *J* = 8.5 Hz), 128.1, 115.9 (d, *J* = 21.8 Hz), 64.1, 54.4, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ -111.8 (s, 1F). IR (ATR): 3071, 2932, 1592, 1071, 883, 654 cm^{-1}. HRMS (ESI): found: 335.0284, calcd. for $C_{15}H_{14}ClFO_2SNa$ [M+Na]$^+$: 335.0279.

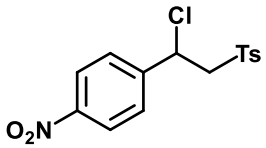


1-chloro-4-(1-chloro-2-tosylethyl)benzene (3j).[6] yield: 98%, white solid, melting point: 115-116 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.24-7.19 (m, 6H), 5.29 (t, *J* = 7.2 Hz, 1H), 3.95-3.79 (m, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.1, 136.9, 136.0, 135.1, 129.8, 129.0, 128.7, 128.1, 63.9, 54.3, 21.6. IR (ATR): 3015, 2812, 1653, 1587, 1091, 872, 684 cm^{-1}. HRMS (ESI): found: 329.0169, calcd. for $C_{15}H_{15}Cl_2O_2S$ [M+H]$^+$: 329.0164.

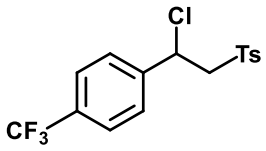


4-(1-chloro-2-tosylethyl)benzonitrile (3k).[6] yield: 73%, white solid, melting point: 108-109 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62-7.55 (m, 4H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.28-7.25 (m, 2H), 5.35 (t, *J* = 6.6 Hz, 1H), 3.95-3.78 (m, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.5, 143.4, 136.0, 132.6, 130.0, 128.2, 128.1, 118.0, 113.0, 63.6, 53.9, 21.7. IR (ATR): 2956, 2871, 1607, 1592, 1087, 897, 614 cm^{-1}. HRMS (ESI): found: 342.0321, calcd. for $C_{16}H_{14}ClNO_2S$ Na[M+Na]$^+$:

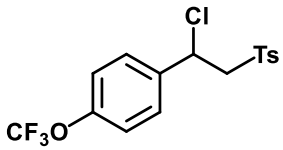
342.0326.



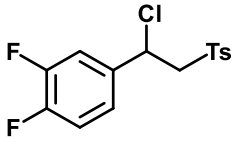
1-((2-chloro-2-(4-nitrophenyl)ethyl)sulfonyl)-4-methylbenzene (3l).[6] yield: 79%, white solid, melting point: 120-121 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.11 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.39 (t, *J* = 6.4 Hz, 1H), 3.97-3.81 (m, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.0, 145.5, 145.2, 135.9, 130.0, 128.5, 128.1, 124.1, 63.6, 53.5, 21.6. IR (ATR): 2934, 2715, 1593, 1364, 1139, 1085, 774, 551 cm^{-1}. HRMS (ESI): found: 340.0409, calcd. for $C_{15}H_{15}ClNO_2S$ $[M+H]^+$: 340.0405.



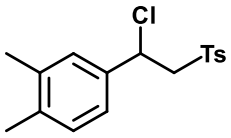
1-((2-chloro-2-(4-(trifluoromethyl)phenyl)ethyl)sulfonyl)-4-methylbenzene (3m). yield: 57%, white solid, melting point: 115-116 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 5.35 (t, *J* = 7.7 Hz, 1H), 3.99-3.84 (m, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.2, 142.0, 135.9, 131.3 (q, *J* = 32.3 Hz), 129.8, 128.0, 127.8, 125.8 (q, *J* = 3.8 Hz), 63.7, 54.1, 21.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.9 (s, 3F). IR (ATR): 2918, 2850, 1596, 1321, 1162, 1138, 1068, 912, 780, 548, 515 cm^{-1}. HRMS (ESI): found: 385.0248, calcd. for $C_{16}H_{14}ClF_3O_2SNa$ $[M+Na]^+$: 385.0247.



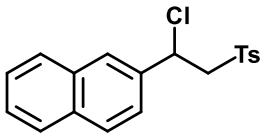
1-((2-chloro-2-(4-(trifluoromethoxy)phenyl)ethyl)sulfonyl)-4-methylbenzene (3n). yield: 61%, white solid, melting point: 100-101 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.1 Hz, 2H), 5.34 (t, *J* = 6.9 Hz, 1H), 3.97-3.82 (m, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.1, 137.5, 135.9, 131.8 (d, *J* = 222.5 Hz), 129.9, 128.9, 128.4, 128.1, 122.9, 62.9, 53.8, 21.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ -57.8 (s, 3F). IR (ATR): 2879, 1733, 1596, 1319, 1140, 755, 548 cm^{-1}. HRMS (ESI): found: 401.0206, calcd. for $C_{16}H_{14}ClF_3O_3SNa$ $[M+Na]^+$: 401.0196.



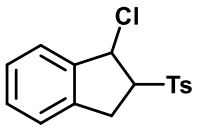
4-(1-chloro-2-tosylethyl)-1,2-difluorobenzene (3o). yield: 33%, white solid, melting point: 126-127 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.08-7.03 (m, 3H), 5.27 (t, *J* = 6.9 Hz, 1H), 3.93-3.76 (m, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.8, 145.3, 143.2, 136.0, 135.4 (t, *J* = 4.3 Hz), 129.9, 128.1, 123.8 (d, *J* = 6.7, 3.8 Hz), 117.7 (d, *J* = 17.4 Hz), 116.5 (d, *J* = 17.9 Hz), 63.9, 53.8, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ -135.8 (d, *J* = 20.1 Hz, 1F), -136.1 (d, *J* = 20.1 Hz, 1F). IR (ATR): 2918, 1730, 1521, 1317, 1133, 755, 552 cm^{-1}. HRMS (ESI): found: 353.0184, calcd. for $C_{15}H_{13}ClF_2O_2SNa$ $[M+Na]^+$: 353.0185.



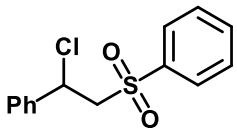
4-(1-chloro-2-tosylethyl)-1,2-dimethylbenzene (3p). yield: 95%, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.00-6.96 (m, 3H), 5.27 (t, *J* = 6.9 Hz, 1H), 3.97-3.82 (m, 2H), 2.40 (s, 3H), 2.20 (s, 3H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.7, 137.9, 137.2, 136.3, 135.8, 130.0, 129.6, 128.2, 128.2, 124.7, 64.0, 55.2, 21.6, 19.7, 19.5. IR (ATR): 2879, 1733, 1596, 1319, 1140, 755, 548, 514 cm^{-1}. HRMS (ESI): found: 287.1105, calcd. for $C_{17}H_{19}O_2S$ $[M-HCl+H]^+$: 287.1100.



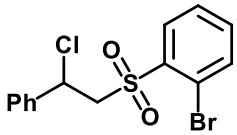
2-(1-chloro-2-tosylethyl)naphthalene (3q).[6] yield: 97%, white solid, melting point: 118-119 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78-7.71 (m, 2H), 7.67 (d, *J* = 9.3 Hz, 2H), 7.52-7.47 (m, 4H), 7.30 (dd, *J* = 6.3, 1.5 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 2H), 5.50 (t, *J* = 7.1 Hz, 1H), 4.08-3.95 (m, 2H), 2.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.8, 135.9, 135.3, 133.4, 132.8, 129.5, 129.1, 128.1, 128.1, 127.6, 126.9, 126.7, 124.0, 63.8, 55.6, 21.4. IR (ATR): 2854, 1592, 1352, 1074, 782, 673 cm^{-1}. HRMS (ESI): found: 345.0717, calcd. for $C_{19}H_{18}ClO_2S$ $[M+H]^+$: 345.0711.



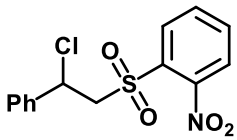
1-chloro-2-tosyl-2,3-dihydro-1H-indene (3r).[6] yield: 90%, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 3H), 7.28 (d, *J* = 4.0 Hz, 2H), 7.20-7.19 (m, 1H), 5.70 (d, *J* = 4.7 Hz, 1H), 4.20-4.13 (m, 1H), 3.59-3.40 (m, 2H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.4, 140.3, 138.9, 134.8, 130.1, 129.7, 128.8, 128.1, 125.3, 124.6, 72.7, 60.6, 31.9, 21.7. IR (ATR): 2932, 2752, 1587, 1318, 1052, 814, 678 cm^{-1}. HRMS (ESI): found: 307.0559, calcd. for $C_{16}H_{16}ClO_2S$ $[M+H]^+$: 307.0554.



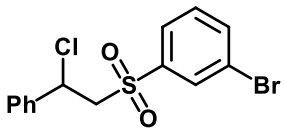
(1-chloro-2-(phenylsulfonyl)ethyl)benzene (4a).[8] yield: 98%, white solid, melting point: 92-93 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.29-7.23 (m, 5H), 5.35 (t, *J* = 6.9 Hz, 1H), 4.01-3.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.2, 138.4, 133.8, 129.2, 129.2, 128.9, 128.1, 127.2, 64.1, 55.1. IR (ATR): 3063, 2961, 2926, 1599, 1407, 1319, 748, 552 cm^{-1}. HRMS (ESI): found: 281.0391, calcd. for $C_{14}H_{14}ClO_2S$ $[M+H]^+$: 281.0398.



1-bromo-2-((2-chloro-2-phenylethyl)sulfonyl)benzene (4b).[5] yield: 57%, white solid, melting point: 87-88 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.64 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.35-7.19 (m, 6H), 5.35 (t, *J* = 7.1 Hz, 1H), 4.37-4.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.3, 137.9, 135.1, 134.7, 132.1, 129.3, 128.9, 127.9, 127.2, 120.7, 61.2, 55.3. IR (ATR): 3077, 2831, 1597, 1365, 1142, 1095, 759, 528 cm^{-1}. HRMS (ESI): found: 358.9500, calcd. for $C_{14}H_{13}BrClO_2S$ $[M+H]^+$: 358.9504.

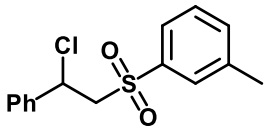


1-((2-chloro-2-phenylethyl)sulfonyl)-2-nitrobenzene (4c). yield: 65%, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.65 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.33 (td, *J* = 6.6, 2.0 Hz, 2H), 7.26 (s, 2H), 7.21-7.19 (m, 3H), 5.35 (t, *J* = 7.1 Hz, 1H), 4.36-4.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.0, 134.9, 133.3, 132.6, 132.4, 129.5, 129.0, 127.3, 125.0, 64.4, 55.3. IR (ATR): 3032, 2935, 1595, 1303, 1144, 770, 553 cm^{-1}. HRMS (ESI): found: 326.0245, calcd. for $C_{14}H_{13}ClNO_4S$ $[M+H]^+$: 326.0248.

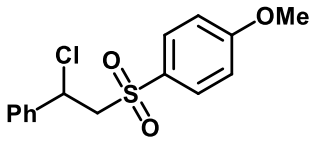


1-bromo-3-((2-chloro-2-phenylethyl)sulfonyl)benzene (4d).[5] yield: 94%, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.32-7.26 (m, 6H), 5.35 (t, *J* = 7.1 Hz, 1H), 4.03-3.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.0, 137.9, 136.8, 131.1, 130.6, 129.5, 128.9, 127.2, 126.6, 123.1, 64.0, 55.0. IR (ATR): 3072, 2926, 1600, 1138, 915, 524 cm^{-1}. HRMS

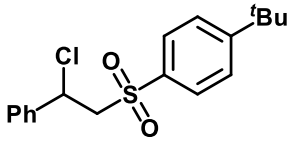
(ESI): found: 358.9508, calcd. for $C_{14}H_{13}BrClO_2S$ $[M+H]^+$: 358.9503.



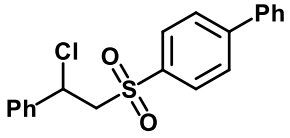
1-((2-chloro-2-phenylethyl)sulfonyl)-3-methylbenzene (4e).[5] yield: 98%, white solid, melting point: 95-96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56 (d, *J* = 6.9 Hz, 1H), 7.47 (s, 1H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.29-7.24 (m, 5H), 5.35 (t, *J* = 7.0 Hz, 1H), 4.00-3.84 (m, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.4, 139.0, 138.4, 134.6, 129.2, 129.1, 128.8, 128.5, 127.2, 125.2, 64.0, 55.1, 21.2. IR (ATR): 2962, 2831, 1599, 1365, 1134, 685, 573 cm^{-1}. HRMS (ESI): found: 295.0554, calcd. for $C_{15}H_{16}ClO_2S$ $[M+H]^+$: 295.0554.



1-((2-chloro-2-phenylethyl)sulfonyl)-4-methoxybenzene (4f).[5] yield: 97%, white solid, melting point: 97-98 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65 (d, *J* = 8.9 Hz, 2H), 7.32-7.21 (m, 5H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.31 (t, *J* = 6.9 Hz, 1H), 3.97-3.79 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.9, 138.7, 130.6, 130.4, 129.1, 128.9, 127.2, 114.4, 64.2, 55.7, 55.3. IR (ATR): 3003, 2927, 1594, 1262, 832, 765 cm^{-1}. HRMS (ESI): found: 333.0329, calcd. for $C_{15}H_{15}ClNaO_3S$ $[M+Na]^+$: 333.0323.

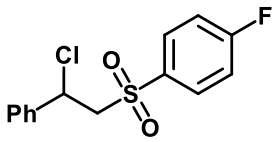


1-(tert-butyl)-4-((2-chloro-2-phenylethyl)sulfonyl)benzene (4g). yield: 95%, white solid, melting point: 110-111 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.27-7.22 (m, 5H), 5.35 (t, *J* = 6.9 Hz, 1H), 4.00-3.85 (m, 2H), 1.31 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.7, 138.4, 136.0, 129.1, 128.9, 127.9, 127.2, 126.1, 63.9, 55.2, 35.2, 31.0. IR (ATR): 2987, 1728, 1573, 1313, 1277, 1173, 806, 697, 565 cm^{-1}. HRMS (ESI): found: 375.0575, calcd. for $C_{18}H_{21}ClO_2SK$ $[M+K]^+$: 375.0582.

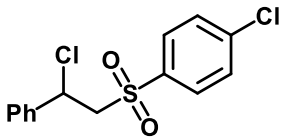


4-((2-chloro-2-phenylethyl)sulfonyl)-1,1'-biphenyl (4h).[9] yield: 78%, white solid, melting point: 95-96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.62-7.56 (m, 4H), 7.51-7.43 (m, 3H), 7.29-7.23 (m, 5H), 5.33 (t, *J* = 7.0 Hz, 1H), 4.01-3.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.7, 139.1, 138.4, 137.6, 129.2, 128.9, 128.8, 128.7, 127.7, 127.4, 127.3, 64.1, 55.2.

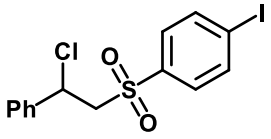
IR (ATR): 3062, 2925, 1595, 1173, 837, 692, 533 cm^{-1}. HRMS (ESI): found: 379.0532, calcd. for $C_{20}H_{17}ClNaO_2S$ $[M+Na]^+$: 379.0530.



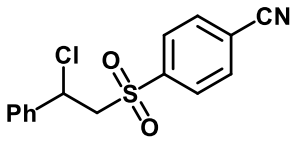
1-((2-chloro-2-phenylethyl)sulfonyl)-4-fluorobenzene (4i).[5] yield: 94%, white solid, melting point: 87-88 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73 (q, *J* = 5.1 Hz, 2H), 7.33-7.21 (m, 5H), 7.08 (t, *J* = 8.5 Hz, 2H), 5.33 (t, *J* = 7.0 Hz, 1H), 4.01-3.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.8 (d, *J* = 254.9 Hz), 138.3, 135.2 (d, *J* = 3.1 Hz), 131.1 (d, *J* = 9.7 Hz), 129.3, 129.0, 127.2, 116.4 (d, *J* = 22.6 Hz), 64.2, 55.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.0 (s, 1F). IR (ATR): 2989, 2937, 1592, 1492, 1233, 1138, 696 cm^{-1}. HRMS (ESI): found: 321.0127, calcd. for $C_{14}H_{12}ClFNaO_2S$ $[M+Na]^+$: 321.0127.



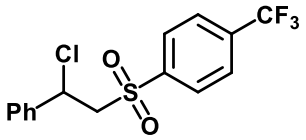
1-chloro-4-((2-chloro-2-phenylethyl)sulfonyl)benzene (4j).[5] yield: 85%, white solid, melting point: 108-109 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.29-7.22 (m, 5H), 5.34 (t, *J* = 7.0 Hz, 1H), 4.01-3.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.6, 138.2, 137.6, 129.7, 129.4, 129.3, 129.0, 127.2, 64.1, 55.1. IR (ATR): 3067, 2827, 1599, 1457, 742, 518 cm^{-1}. HRMS (ESI): found: 336.9821, calcd. for $C_{14}H_{12}Cl_2NaO_2S$ $[M+Na]^+$: 336.9827.



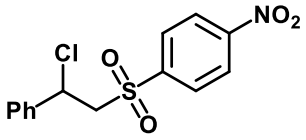
1-((2-chloro-2-phenylethyl)sulfonyl)-4-iodobenzene (4k).[5] yield: 94%, white solid, melting point: 103-104 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.31-7.26 (m, 5H), 5.35 (t, *J* = 7.0 Hz, 1H), 4.02-3.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.8, 138.4, 138.1, 129.5, 129.3, 129.0, 127.2, 101.9, 64.0, 55.0. IR (ATR): 2872, 1525, 1325, 775, 562 cm^{-1}. HRMS (ESI): found: 428.9187, calcd. for $C_{14}H_{12}ClINaO_2S$ $[M+Na]^+$: 428.9183.



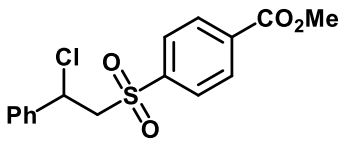
4-((2-chloro-2-phenylethyl)sulfonyl)benzonitrile (4l).[5] yield: 63%, white solid, melting point: 117-118 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.28-7.23 (m, 5H), 5.37 (t, *J* = 7.0 Hz, 1H), 4.08-3.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.2, 137.8, 132.8, 129.5, 129.1, 128.9, 127.3, 117.4, 117.1, 63.9, 54.6. IR (ATR): 2988, 1600, 1457, 1019, 596 cm^{-1}. HRMS (ESI): found: 306.0357, calcd. for $C_{15}H_{13}ClNO_2S$ $[M+H]^+$: 306.0350.



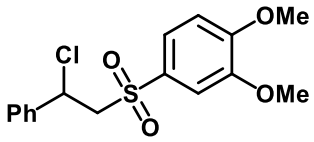
1-((2-chloro-2-phenylethyl)sulfonyl)-4-(trifluoromethyl)benzene (4m).[6] yield: 90%, white solid, melting point: 116-117 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.26-7.20 (m, 5H), 5.36 (t, *J* = 7.2 Hz, 1H), 4.06-3.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.6, 137.8, 135.3 (q, *J* = 33.0 Hz), 129.4, 129.0, 128.8, 127.2, 126.2 (q, *J* = 3.7 Hz), 123.0 (q, *J* = 271.5 Hz), 63.9, 54.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.3 (s, 3F). IR (ATR): 2988, 2830, 1603, 1326, 1138, 703, 546 cm^{-1}. HRMS (ESI): found: 349.0278, calcd. for $C_{15}H_{13}ClF_3O_2S$ $[M+H]^+$: 349.0271.



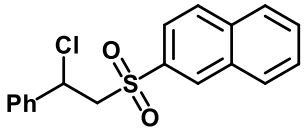
1-((2-chloro-2-phenylethyl)sulfonyl)-4-nitrobenzene (4n).[6] yield: 97%, white solid, melting point: 87-88 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 2H), 7.26-7.23 (m, 5H), 5.37 (t, *J* = 7.1 Hz, 1H), 4.09-3.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.7, 144.7, 137.8, 129.7, 129.5, 129.1, 127.3, 124.2, 64.1, 54.9. IR (ATR): 3062, 2936, 1581, 1321, 771, 633 cm^{-1}. HRMS (ESI): found: 326.0251, calcd. for $C_{14}H_{13}ClNO_4S$ $[M+H]^+$: 326.0248.



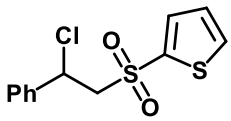
methyl 4-((2-chloro-2-phenylethyl)sulfonyl)benzoate (4o).[5] yield: 96%, white solid, Melting Point: 110-111 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.28-7.20 (m, 5H), 5.34 (t, *J* = 7.0 Hz, 1H), 4.04-3.86 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.4, 143.0, 138.1, 134.8, 130.2, 129.3, 129.0, 128.3, 127.2, 63.9, 55.0, 52.8. IR (ATR): 2984, 2940, 2832, 1726, 1459, 1327, 854 cm^{-1}. HRMS (ESI): found: 339.0458, calcd. for $C_{16}H_{16}ClO_4S$ $[M+H]^+$: 339.0452.



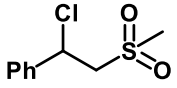
4-((2-chloro-2-phenylethyl)sulfonyl)-1,2-dimethoxybenzene (4p). yield: 97%, white solid, melting point: 126-127 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.27-7.21 (m, 5H), 7.13 (d, *J* = 1.8 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 5.31 (t, *J* = 6.9 Hz, 1H), 3.99-3.83 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.5, 149.0, 138.6, 130.7, 129.1, 128.9, 127.2, 122.4, 110.7, 110.3, 64.3, 56.3, 56.2, 55.2. IR (ATR): 2931, 1586, 1507, 1260, 1126, 1017, 758, 696, 516 cm^{-1}. HRMS (ESI): found: 363.0428, calcd. for $C_{16}H_{17}ClO_4SNa$ $[M+Na]^+$: 363.0428.



2-((2-chloro-2-phenylethyl)sulfonyl)naphthalene (4q). yield: 95%, white solid, melting point: 120-121 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.25 (s, 1H), 7.87 (t, *J* = 8.1 Hz, 3H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.67-7.56 (m, 3H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.17-7.10 (m, 3H), 5.39 (t, *J* = 6.9 Hz, 1H), 4.09-3.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.3, 135.9, 135.3, 131.9, 130.4, 129.5, 129.5, 129.5, 129.2, 128.8, 127.9, 127.7, 127.2, 122.4, 63.9, 55.2. IR (ATR): 3060, 2976, 1594, 1313, 1123, 799, 548 cm^{-1}. HRMS (ESI): found: 331.0559, calcd. for $C_{18}H_{16}ClO_2S$ $[M+H]^+$: 331.0554.

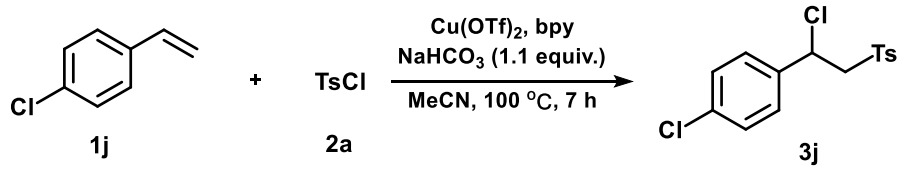


2-((2-chloro-2-phenylethyl)sulfonyl)thiophene (4r).[5] yield: 83%, yellow solid, melting point: 107-108 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.66 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.48 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.32-7.26 (m, 5H), 7.01 (td, *J* = 4.1, 0.7 Hz 1H), 5.36 (t, *J* = 6.9 Hz, 1H), 4.10-3.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.0, 138.5, 134.9, 134.7, 129.3, 129.0, 127.9, 127.2, 65.3, 55.1. IR (ATR): 3097, 3060, 2967, 2868, 1600, 1501, 1364, 854, 695 cm^{-1}. HRMS (ESI): found: 308.9782, calcd. for $C_{12}H_{11}ClNaO_2S_2$ $[M+Na]^+$: 308.9781.



(1-chloro-2-(methylsulfonyl)ethyl)benzene (4s).[5] yield: 78%, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42-7.36 (m, 5H), 5.38 (t, *J* = 6.1 Hz, 1H), 3.85 (dd, *J* = 15.2 Hz, 7.7 Hz, 1H), 3.64 (dd, *J* = 15.1 Hz, 5.9 Hz, 1H), 2.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.6, 129.6, 129.3, 127.2, 63.5, 55.6, 42.7. IR (ATR): 2967, 2868, 1600, 1501, 1364, 854, 695 cm^{-1}. HRMS (ESI): found: 219.0246, calcd. for $C_9H_{12}ClO_2S$ $[M+H]^+$: 219.0241.

General Procedure for Scale-up Reaction



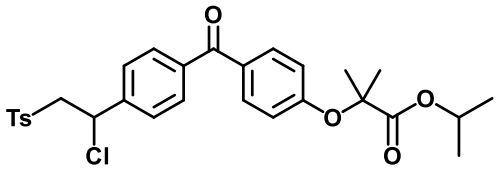
For Chlorosulfonylation:

Tosyl chloride **2a** (20.0 mmol, 3.8 g), $Cu(OTf)_2$ (1.0 mol, 360 mg) and $NaHCO_3$ (11.0 mmol, 0.92 g) were weighed into a 100 mL Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then 4-chlorostyrene **1j** (10.0 mmol, 1.39 g) in MeCN (50 mL) was added through the side-arm by syringe. The reaction was stirred under nitrogen at 100 °C for 7 h. After reaction, the mixture was cooled to room temperature. Volatile solvent and reagents were removed by rotary evaporation and the residue was purified by silica gel flash chromatography using petroleum ether/EtOAc (50:1 to 15:1) to afford the desired product **3j** as a white solid, got: 3.02 g, 92% yield.

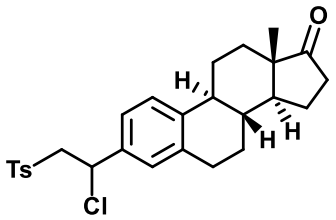
Late-stage Modification of Bioactive Molecules

Procedures

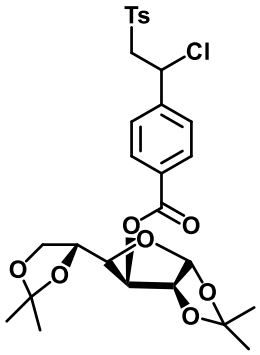
For all the chlorosulfonylation reactions, follow *the General Procedure for Chlorosulfonylation***.**



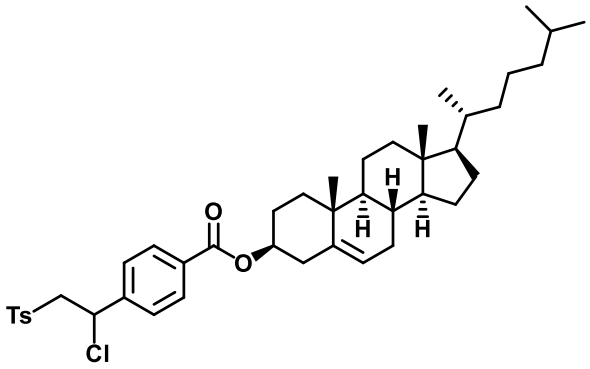
ethyl 2-(4-(4-(1-chloro-2-tosylethyl)benzoyl)phenoxy)-2-methylpropanoate (5a). yield: 77%, yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, *J* = 6.2 Hz, 2H), 7.58 (d, *J* = 5.7 Hz, 4H), 7.34 (d, *J* = 5.8 Hz, 2H), 7.19 (d, *J* = 5.8 Hz, 2H), 6.83 (d, *J* = 6.1 Hz, 2H), 5.35 (t, *J* = 5.0 Hz, 1H), 5.08-5.02 (m, 2H), 3.97-3.85 (m, 2H), 2.35 (s, 3H), 1.63 (s, 6H), 1.17 (d, *J* = 4.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.3, 173.0, 159.8, 145.2, 142.0, 138.7, 136.0, 132.0, 130.2, 130.0, 129.8, 128.1, 127.2, 117.2, 69.3, 63.7, 60.4, 54.5, 25.4, 21.6, 21.5. IR (ATR): 2985, 1713, 1597, 1280, 1141, 1101, 829, 763, 553 cm^{-1}. HRMS (ESI): found: 543.1596, calcd. for $C_{29}H_{32}ClO_6S$ $[M+H]^+$: 543.1603.



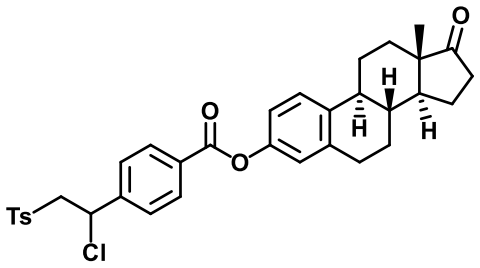
(8R,9S,13S,14S)-3-(1-chloro-2-tosylethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5b). yield: 77%, dr = 1:1, white solid, melting point: 118-119 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.56 (m, 2H), 7.21-7.14 (m, 3H), 7.04-7.02 (m, 1H), 6.92 (s, 1H), 5.27-5.23 (m, 1H), 3.96-3.81 (m, 2H), 2.88-2.64 (m, 2H), 2.53-2.21 (m, 6H), 2.19-1.94 (m, 4H), 1.17 (d, *J* = 4.4 Hz, 6H), 0.89 (d, *J* = 2.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 220.6, 144.6, 140.9, 137.1, 136.3, 135.8, 135.8, 129.6, 128.2, 127.6, 125.9, 124.6, 63.9, 55.1, 55.0, 50.4, 47.9, 44.4, 38.0, 37.9, 35.8, 31.5, 29.2, 26.3, 25.6, 25.6, 21.7, 21.6, 21.6, 13.8. IR (ATR): 2928, 1736, 1711, 1317, 1219, 1137, 1085, 773, 551, 515 cm^{-1}. HRMS (ESI): found: 493.1565, calcd. for $C_{27}H_{31}ClO_3SNa$ $[M+Na]^+$: 493.1575.



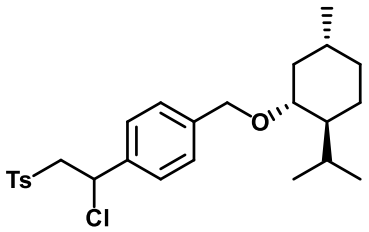
(3aS,5S,6aS)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-(1-chloro-2-tosylethyl)benzoate (5c). yield: 95%, dr = 1:1, white solid, melting point: 120-121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.37-7.33 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 5.91 (d, *J* = 3.2 Hz, 1H), 5.45 (s, 1H), 5.32 (t, *J* = 6.8 Hz, 1H), 4.58 (d, *J* = 2.8 Hz, 1H), 4.35-4.24 (m, 2H), 4.09-4.04 (m, 2H), 3.93-3.78 (m, 2H), 2.36 (d, *J* = 6.4 Hz, 3H), 1.52 (s, 3H), 1.38 (s, 3H), 1.28 (s, 3H), 1.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.4, 164.4, 145.3, 145.2, 143.9, 143.6, 136.0, 135.9, 130.3, 130.2, 130.1, 129.9, 129.9, 128.2, 128.1, 127.6, 127.5, 112.4, 109.5, 109.4, 105.1, 105.1, 83.3, 79.9, 79.9, 76.9, 72.5, 72.5, 67.3, 67.3, 63.6, 63.5, 54.2, 26.9, 26.9, 26.7, 26.2, 25.3, 21.6, 21.6. IR (ATR): 2987, 1716, 1267, 1217, 1085, 1016, 773, 554, 514 cm^{-1}. HRMS (ESI): found: 603.1417, calcd. for $C_{28}H_{33}ClO_9SNa$ $[M+Na]^+$: 603.1426.



(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(1-chloro-2-tosylethyl)benzoate (5d). yield: 68%, white solid, melting point: 128-129 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.43 (d, *J* = 3.9 Hz, 1H), 5.35 (t, *J* = 7.2 Hz, 1H), 4.90-4.82 (m, 1H), 3.94 (dd, *J* = 14.7, 6.4 Hz, 1H), 3.85 (dd, *J* = 14.7, 7.6 Hz, 1H), 2.46 (d, *J* = 7.7 Hz, 2H), 2.40 (s, 3H), 2.05-1.75 (m, 6H), 1.61-1.46 (m, 6H), 1.34-0.99 (m, 17H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.1, 145.1, 142.8, 139.5, 136.0, 131.5, 130.1, 129.8, 128.2, 127.2, 123.0, 74.9, 63.8, 56.7, 56.2, 54.4, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 32.0, 31.9, 29.7, 29.4, 28.3, 28.0, 27.9, 24.3, 23.9, 22.9, 22.7, 22.6, 21.6, 21.1, 19.4, 18.8, 11.9. IR (ATR): 2936, 1706, 1275, 1138, 903, 758, 557 cm^{-1}. HRMS (ESI): found: 745.3446, calcd. for $C_{43}H_{59}ClO_4SK$ $[M+K]^+$: 745.3454.



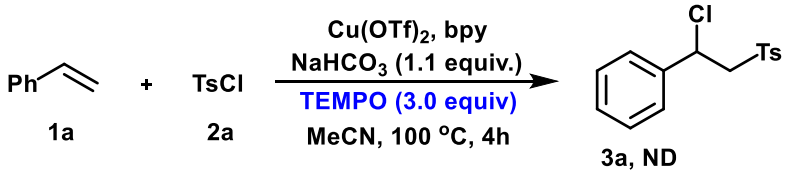
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-(1-chloro-2-tosylethyl)benzoate (5e). yield: 64%, white solid, melting point: 115-116 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.10 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 15.4 Hz, 1H), 7.29-7.26 (m, 3H), 7.00-6.95 (m, 2H), 5.40 (t, *J* = 7.0 Hz, 1H), 3.97 (dd, *J* = 14.7, 6.5 Hz, 1H), 3.88 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.97-2.94 (m, 2H), 2.57-2.44 (m, 5H), 2.37-2.31 (m, 1H), 2.23 -1.98 (m, 4H), 1.70 -1.46 (m, 6H), 0.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 220.8, 164.6, 148.7, 145.2, 143.8, 138.2, 137.7, 136.0, 130.7, 130.3, 129.9, 128.2, 127.5, 126.6, 121.6, 118.7, 63.8, 54.3, 50.5, 48.0, 44.2, 38.0, 35.9, 31.6, 29.5, 26.4, 25.8, 21.7, 21.6, 13.9. IR (ATR): 2923, 1735, 1321, 1139, 1069, 914, 762, 553 cm^{-1}. HRMS (ESI): found: 629.1517, calcd. for $C_{34}H_{35}ClO_5SK$ $[M+K]^+$: 629.1525.



((2-chloro-2-(4-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)ethyl)sulfonyl)-4-methylbenzene (5f). yield: 73%, white solid, melting point: 89-90 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.31-7.20 (m, 6H), 5.34 (t, *J* = 6.8 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 3.96 (dd, *J* = 14.7, 6.9 Hz, 1H), 3.84 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.19 (td, *J* = 10.4, 3.8 Hz, 1H), 2.43 (s, 3H), 2.30-2.18 (m, 2H), 1.70-1.64 (m, 2H), 1.36-1.29 (m, 1H), 1.02-0.89 (m, 10H), 0.76 (dd, *J* = 6.8, 2.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.9, 140.5, 140.5, 137.6, 137.6, 136.2, 129.8, 128.2, 128.1, 128.0, 127.1, 79.2, 79.1, 69.8, 69.7, 64.2, 55.0, 48.4, 40.3, 34.6, 31.6, 25.6, 23.3, 22.4, 21.6, 21.0, 16.2. IR (ATR): 2923, 2868, 1713, 1598, 1320, 1138, 1085, 812, 552 cm^{-1}. HRMS (ESI): found: 485.1914, calcd. for $C_{28}H_{33}ClO_9SNa$ $[M+Na]^+$: 485.1888.

Mechanistic Study

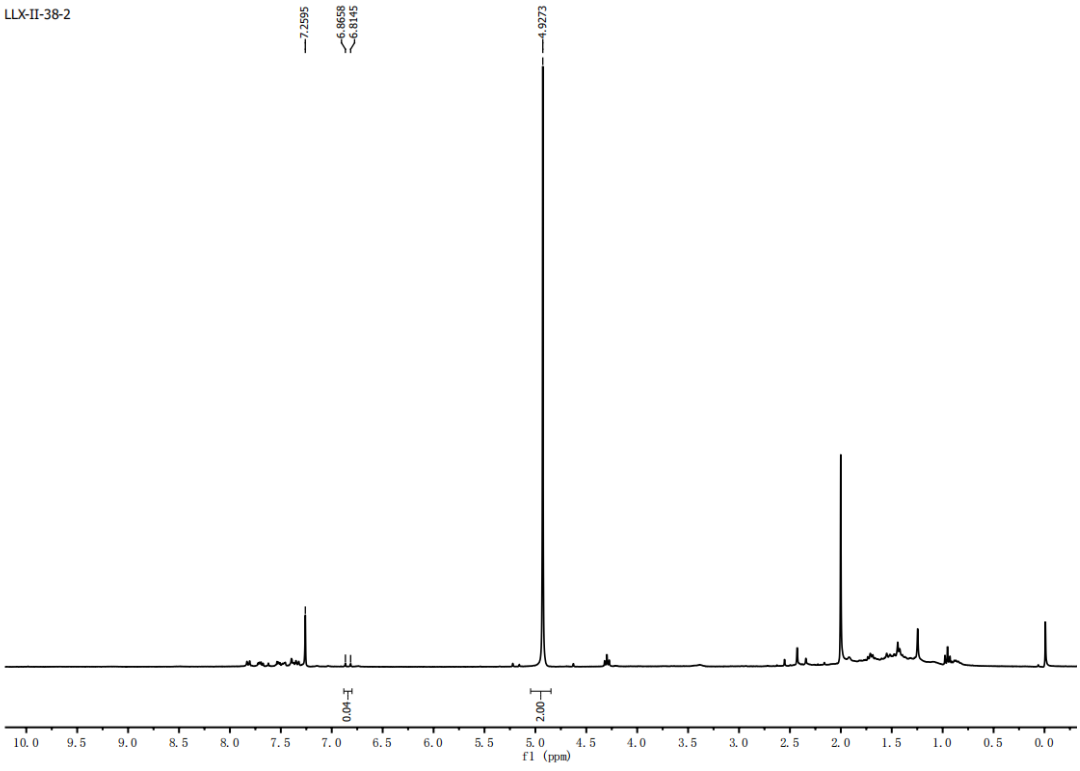
Scheme 1 Radical capture experiments



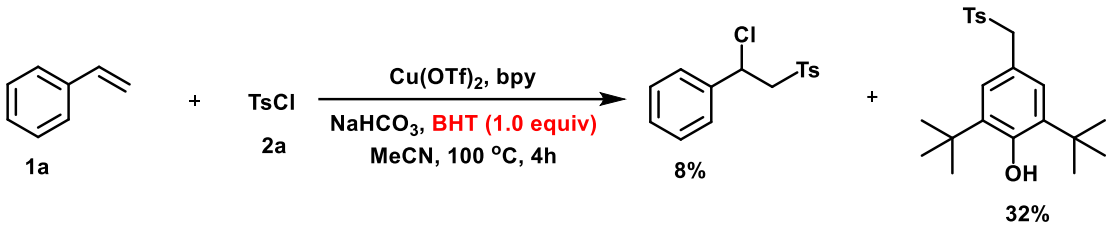
Procedures:

(a) TEMPO

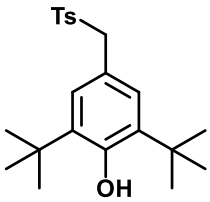
Tosyl chloride **2a** (0.4 mmol, 76.3 mg, 2.0 equiv.), $Cu(OTf)_2$ (7.2 mg, 10 mol%, 0.1 equiv.), **TEMPO** (93.8 mg, 0.6 mmol, 3.0 equiv.) and $NaHCO_3$ (0.22 mmol, 18.5 mg, 1.1 equiv.) were weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then styrene **1a** (0.2 mmol, 20.8 mg, 1.0 equiv.) in MeCN (1.5 mL) was added through the side-arm by syringe. The reaction was stirred under nitrogen at 100 °C for 4 h. After reaction, the mixture was cooled to room temperature. It was extracted with EtOAc and the solvent was then removed by rotary evaporation and the residue was submitted to ^1H NMR (0.2 mmol CH_2Br_2 was added as an internal standard).



(b) BHT

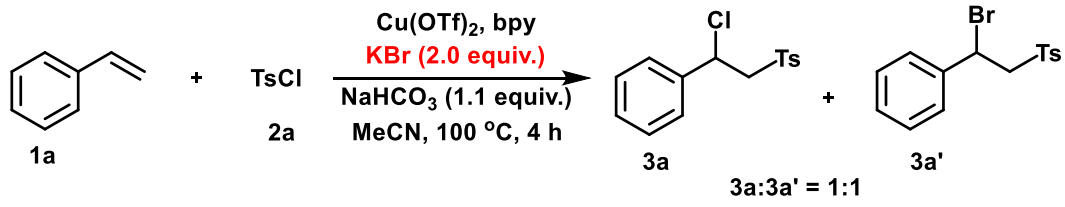


Tosyl chloride **2a** (0.4 mmol, 76.3 mg, 2.0 equiv.), $Cu(OTf)_2$ (7.2 mg, 10 mol%, 0.1 equiv.), **BHT** (44.1 mg, 0.2 mmol, 1.0 equiv.) and $NaHCO_3$ (0.22 mmol, 18.5 mg, 1.1 equiv.) were weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then styrene **1a** (0.2 mmol, 20.8 mg, 1.0 equiv.) in MeCN (1.5 mL) was added through the side-arm by syringe. The reaction was stirred under nitrogen at 100 °C for 4 h. After reaction, the mixture was cooled to room temperature. Volatile solvent and reagents were removed by rotary evaporation and the residue was purified by silica gel flash chromatography using petroleum ether/EtOAc (50:1 to 15:1) to directly afford the chlorosulfonylation product **3a** (4.8 mg, 8% yield) and the BHT-adduct **6a** (24 mg, 32% yield).



2,6-di-*tert*-butyl-4-(tosylmethyl)phenol (6a).[10] yield: 32%, yellow solid, melting point: 106-107 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.73 (s, 2H), 5.24 (s, 1H), 4.20 (s, 2H), 2.40 (s, 3H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.2, 144.3, 136.0, 134.9, 129.3, 128.9, 127.7, 119.0, 63.4, 34.1, 30.1, 21.5. IR (ATR): 3415, 2816, 2546, 1594, 1325, 889, 673 cm^{-1}. HRMS (ESI): found: 375.1987, calcd. for $C_{22}H_{31}O_3S$ $[M+H]^+$: 375.1988.

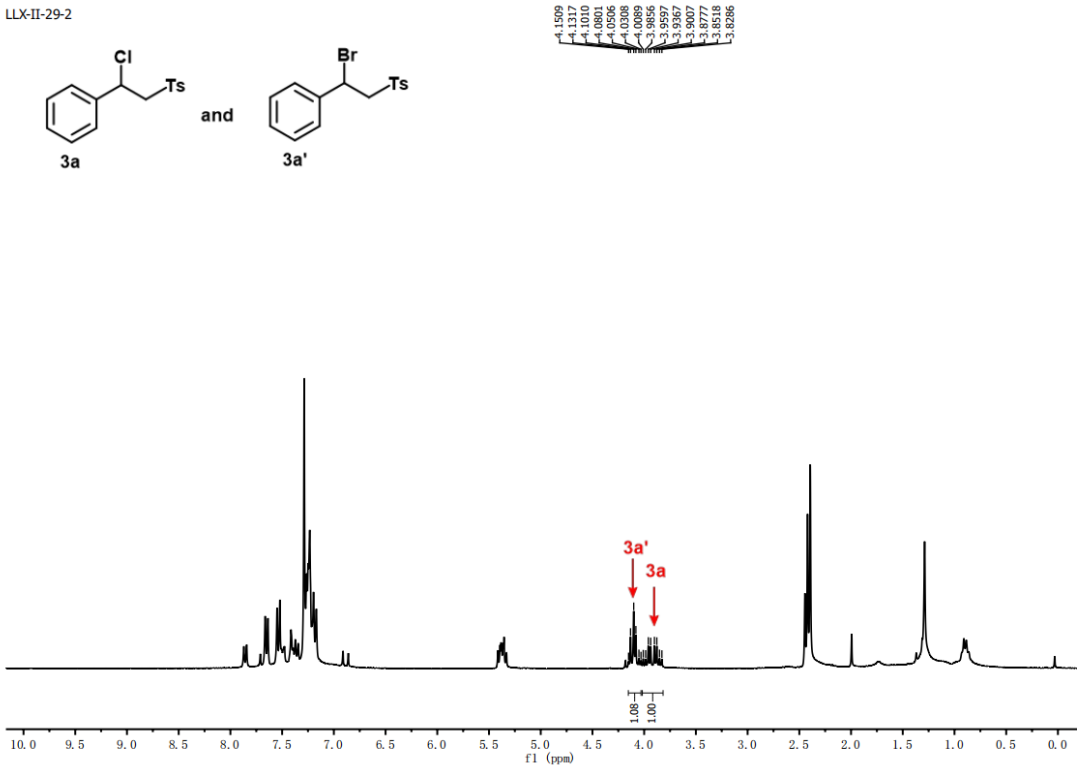
Scheme 2 Carbon cation capture experiment



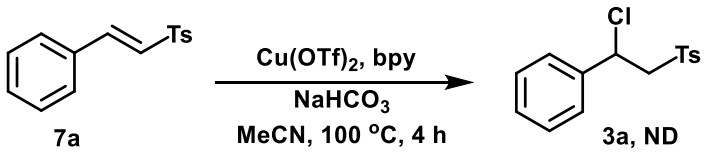
Procedures:

Tosyl chloride **2a** (0.4 mmol, 76.3 mg, 2.0 equiv.), $Cu(OTf)_2$ (7.2 mg, 10 mol%, 0.1 equiv.), **KBr** (47.6 mg, 0.4 mmol, 2.0 equiv.) and $NaHCO_3$ (0.22 mmol, 18.5 mg, 1.1 equiv.) were weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then styrene **1a** (0.2 mmol, 20.8 mg, 1.0 equiv.) in MeCN (1.5 mL) was added through the side-arm by syringe. The reaction was stirred under argon at 100 °C for 4 h. After reaction, the mixture was cooled to room

temperature. It was extracted with EtOAc and the solvent was then removed by rotary evaporation and the residue was submitted to ^{1}H NMR The ratio of the products **3a** and **3a'** were detected as **3a** : **3a'** = 1 : 1.

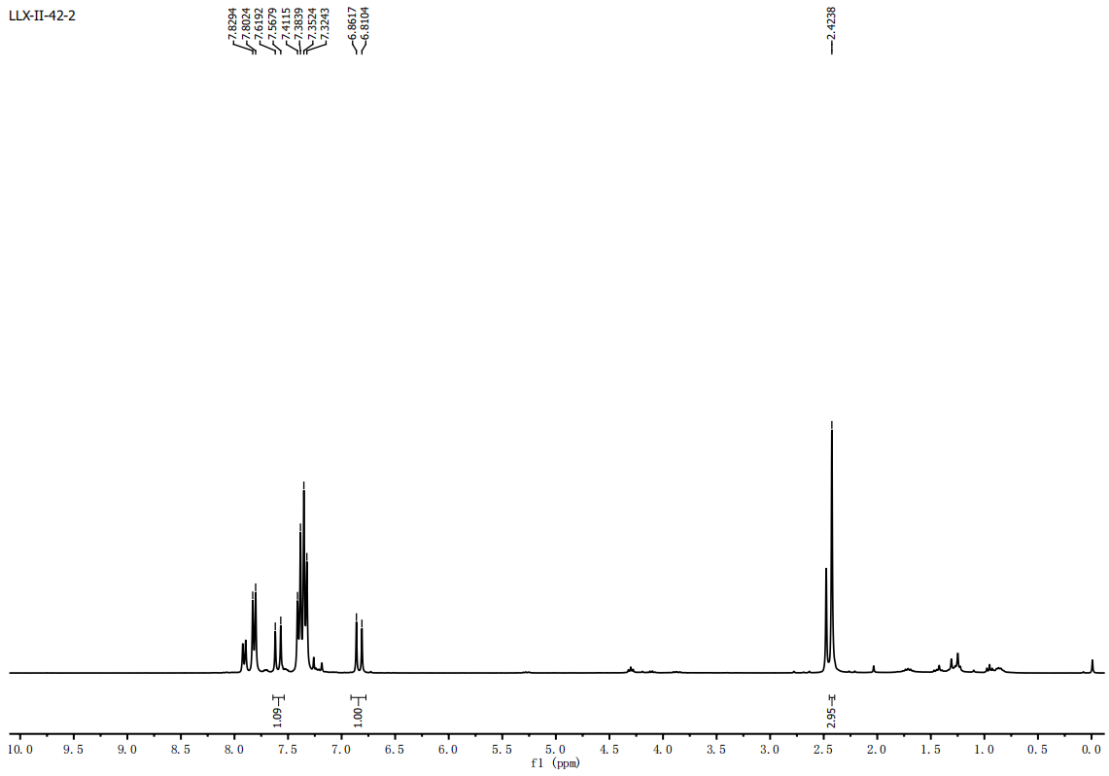


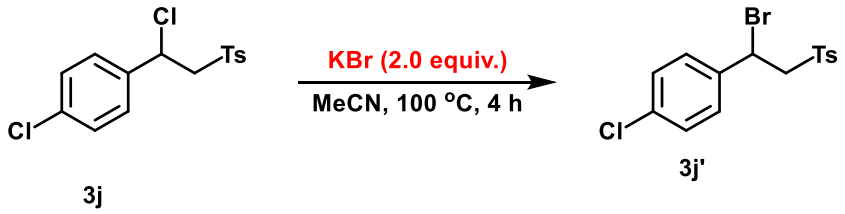
Scheme 3 From sulfonylation product to chlorosulfonylation product



Procedures:

(*E*)-1-methyl-4-(styrylsulfonyl)benzene **7a** (0.2 mmol, 65.9 mg, 1.0 equiv.), $Cu(OTf)_2$ (7.2 mg, 10 mol%, 0.1 equiv.), and $NaHCO_3$ (0.6 mmol, 50.4 mg, 3.0 equiv.) were weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then MeCN (1.5 mL) was added through the side-arm by syringe. The reaction was stirred under nitrogen at 100 °C for 4 h. After reaction, the mixture was cooled to room temperature. It was extracted with EtOAc and the solvent was then removed by rotary evaporation and the residue was submitted to ^{1}H NMR, no product **3a** was detected.



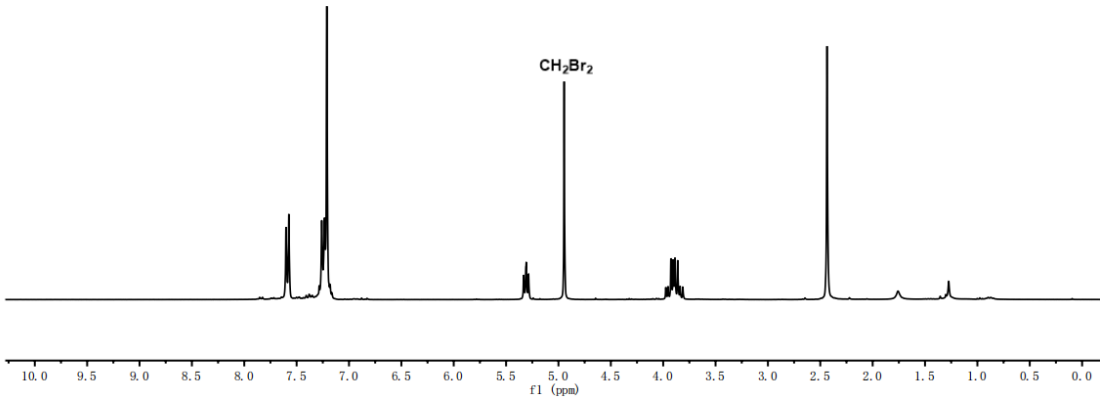


3j 3j'

Procedures:

1-chloro-4-(1-chloro-2-tosylethyl)benzene **3j** (0.2 mmol, 65.9 mg, 1.0 equiv.), KBr (0.4 mmol, 47.6 mg, 2.0 equiv.) were weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then MeCN (1.5 mL) was added through the side-arm by syringe. The reaction was stirred under nitrogen at 100 °C for 4 h. After reaction, the mixture was cooled to room temperature. It was extracted with EtOAc and the solvent was then removed by rotary evaporation and the residue was submitted to ^{1}H NMR, no product **3j'** was detected.

LLX-KBr
LLX-KBr-H



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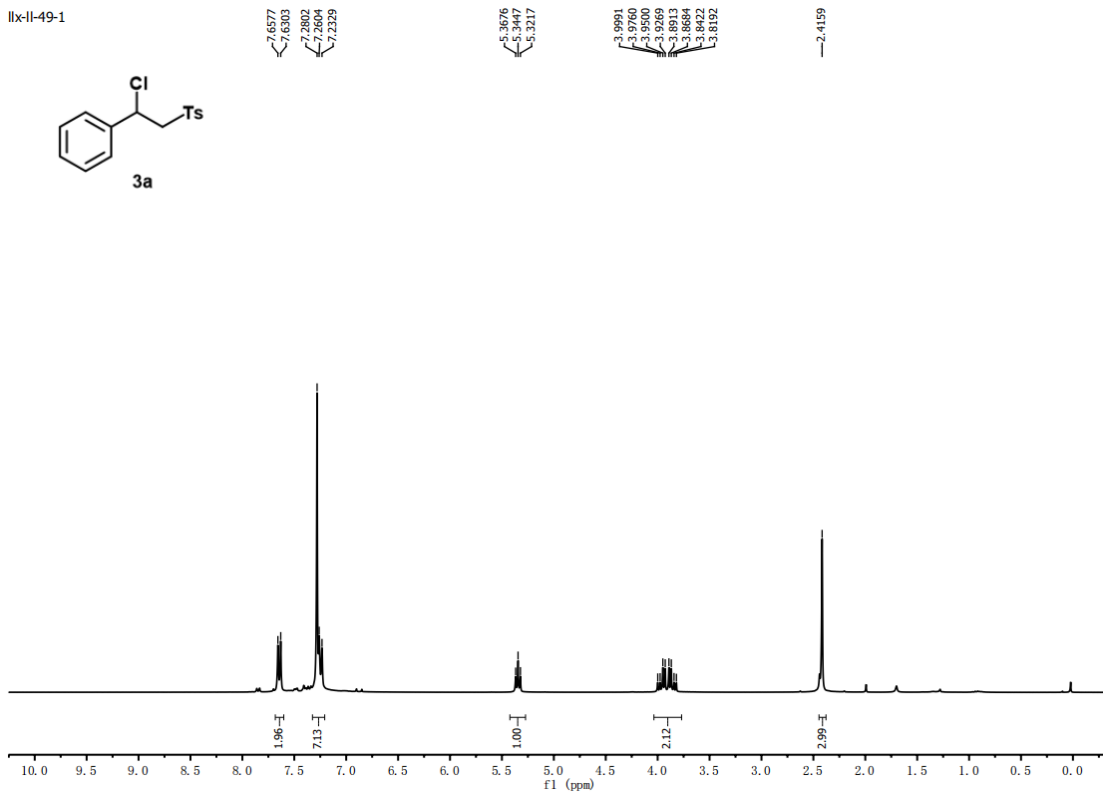
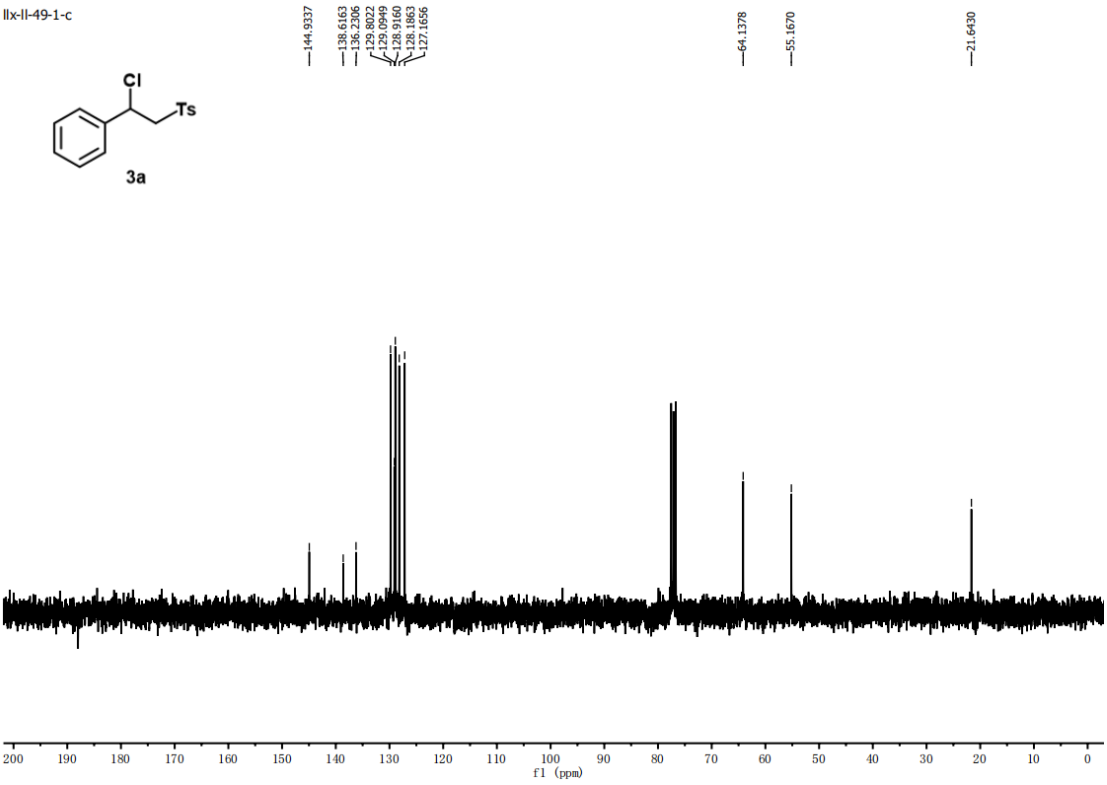
NMR Spectra Images of Products





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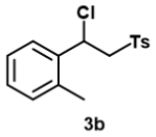
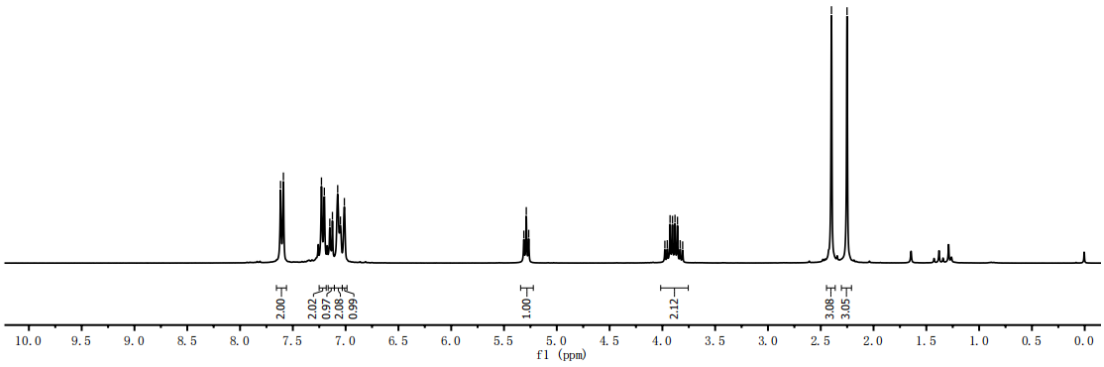
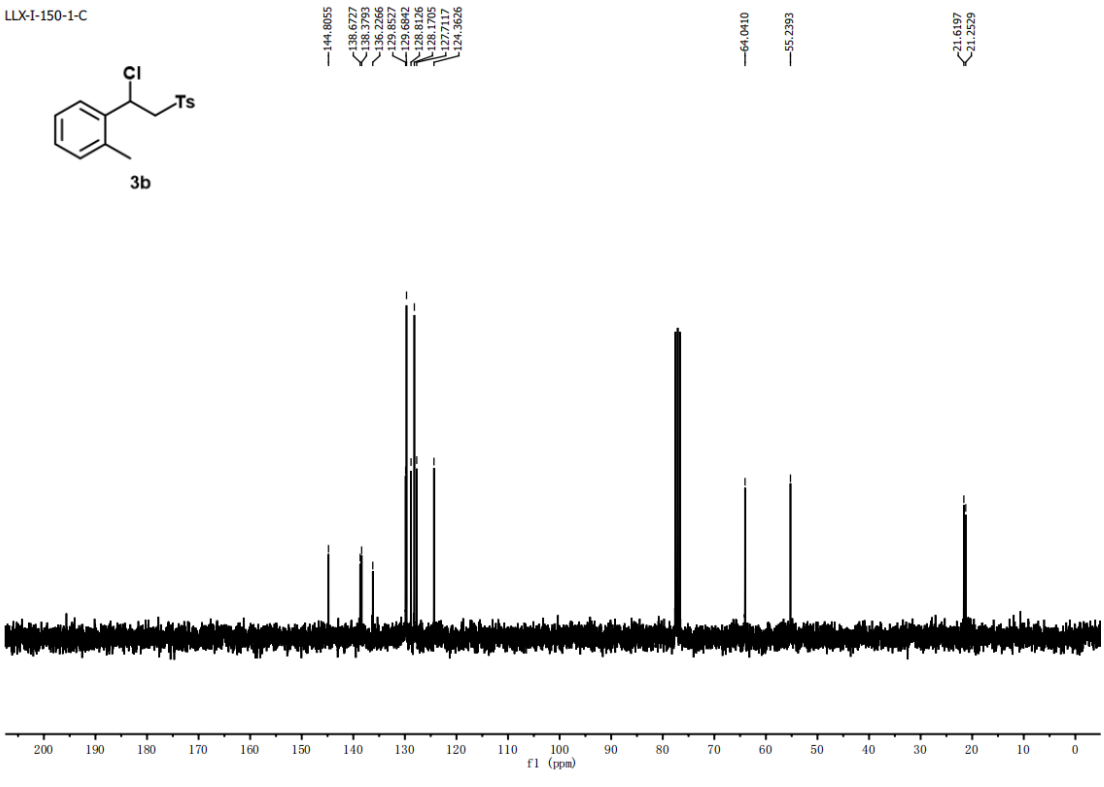


3b



LLX-I-150-1-C

3b



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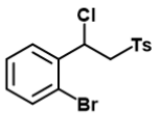

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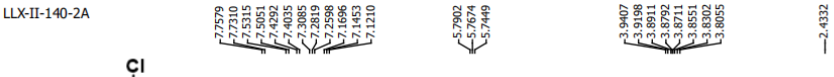
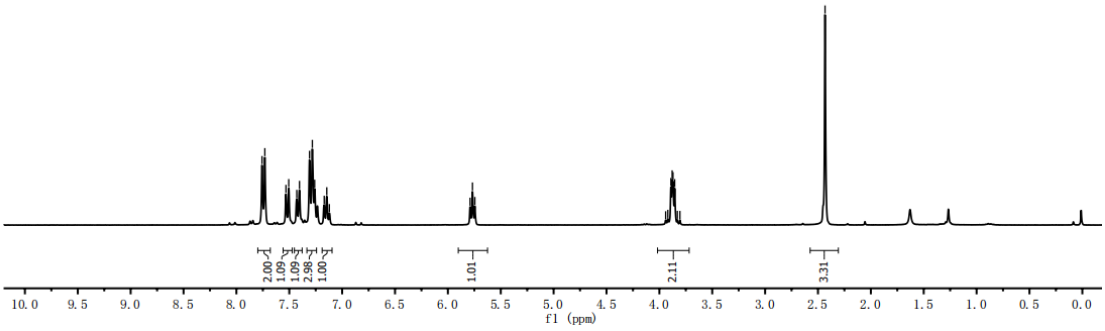
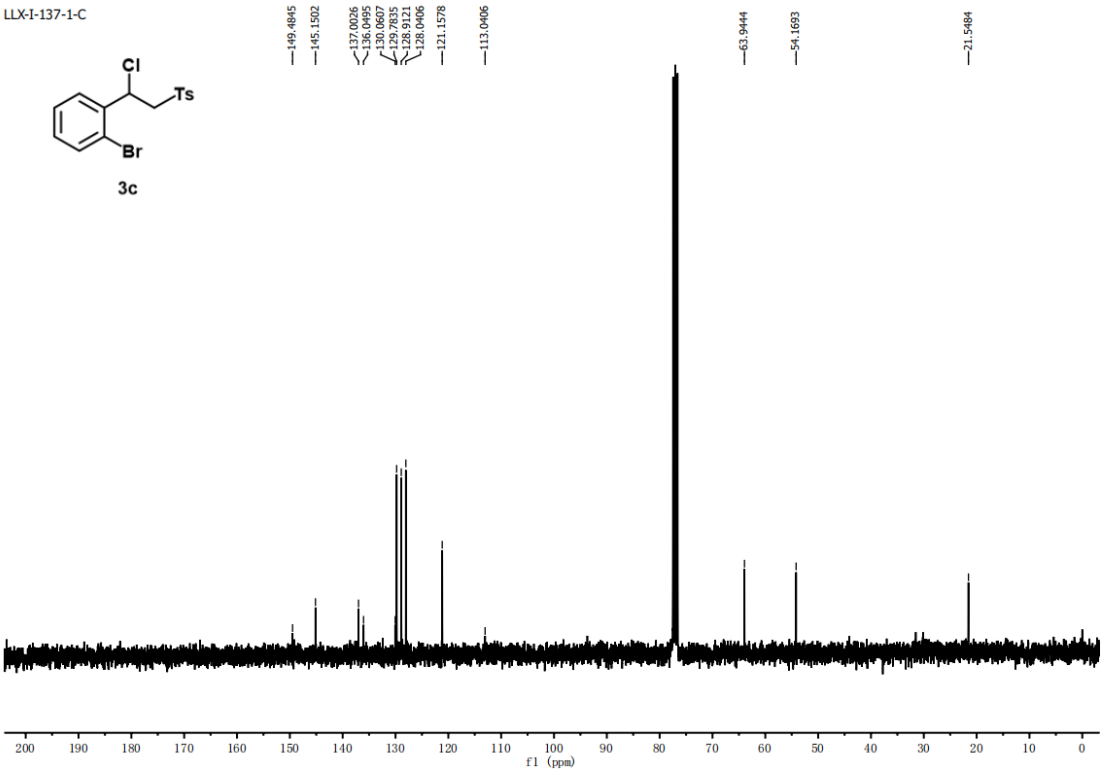




LLX-I-137-1-C

3c



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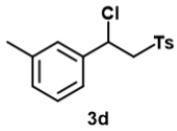
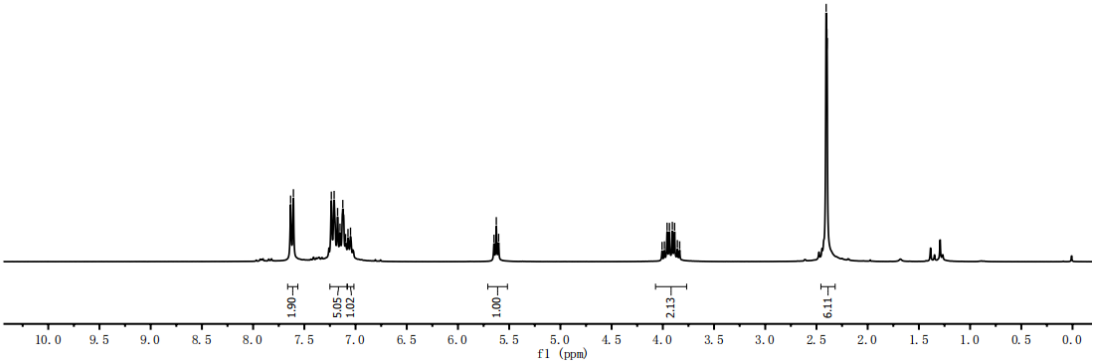
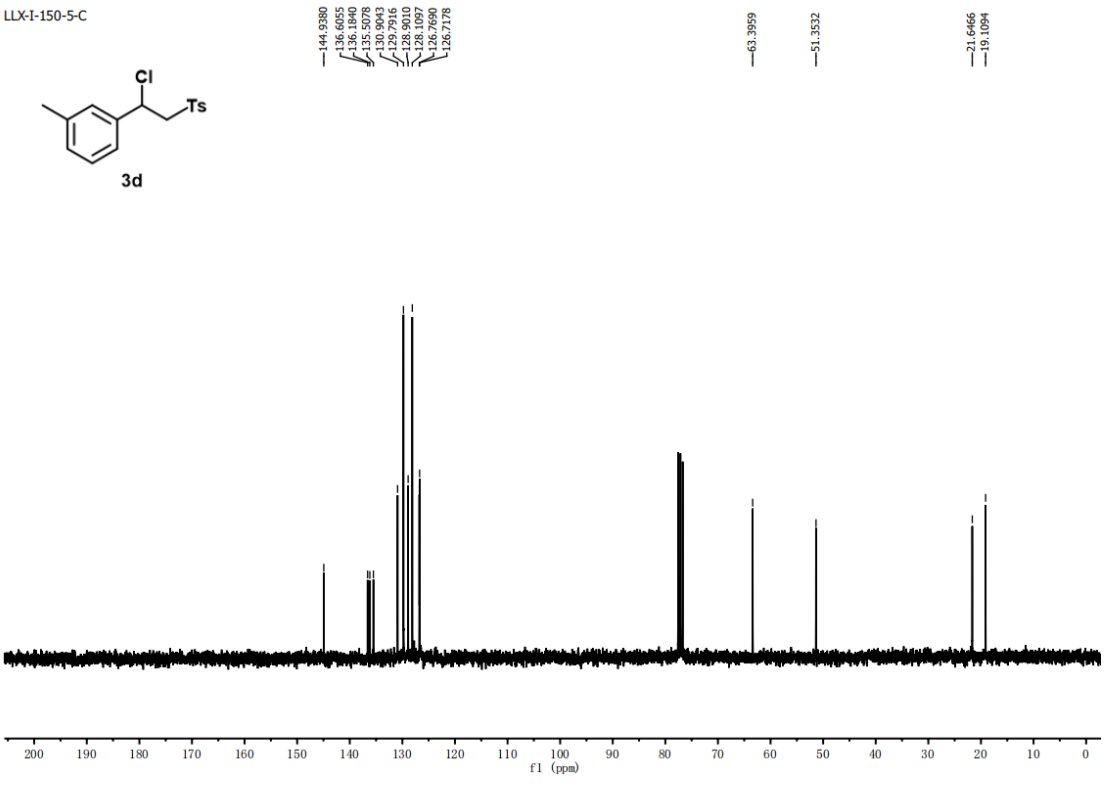


3d



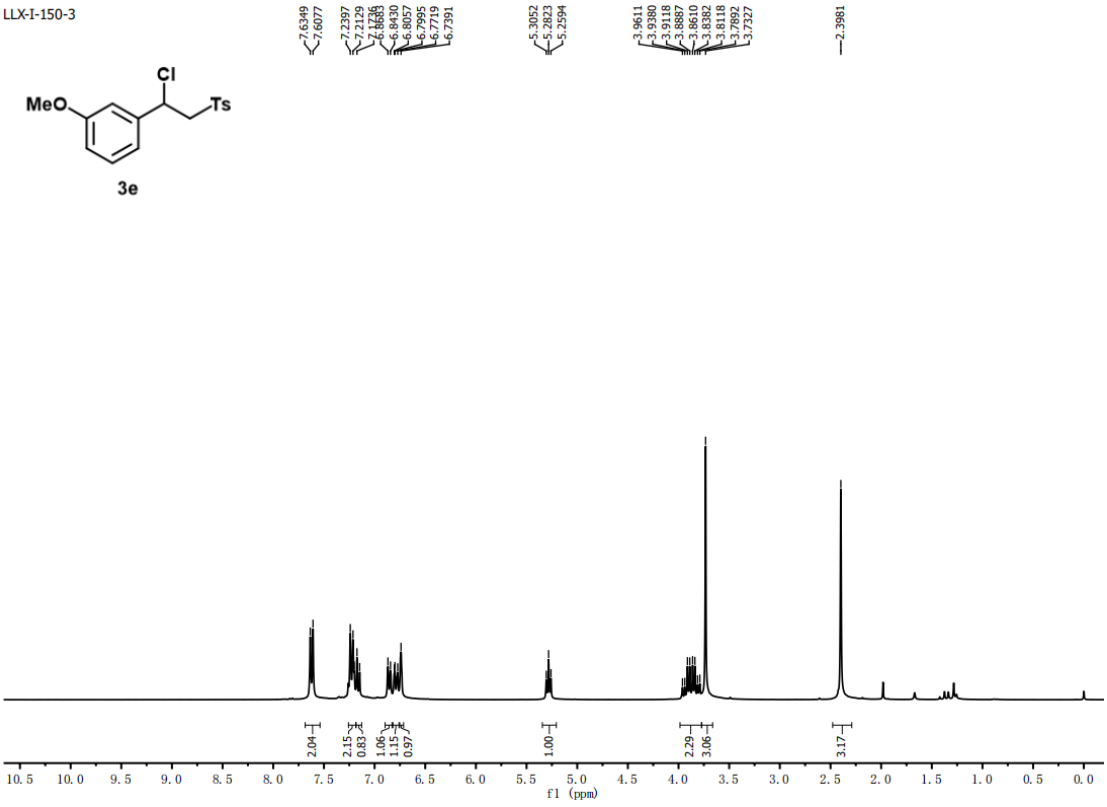
LLX-I-150-5-C

3d



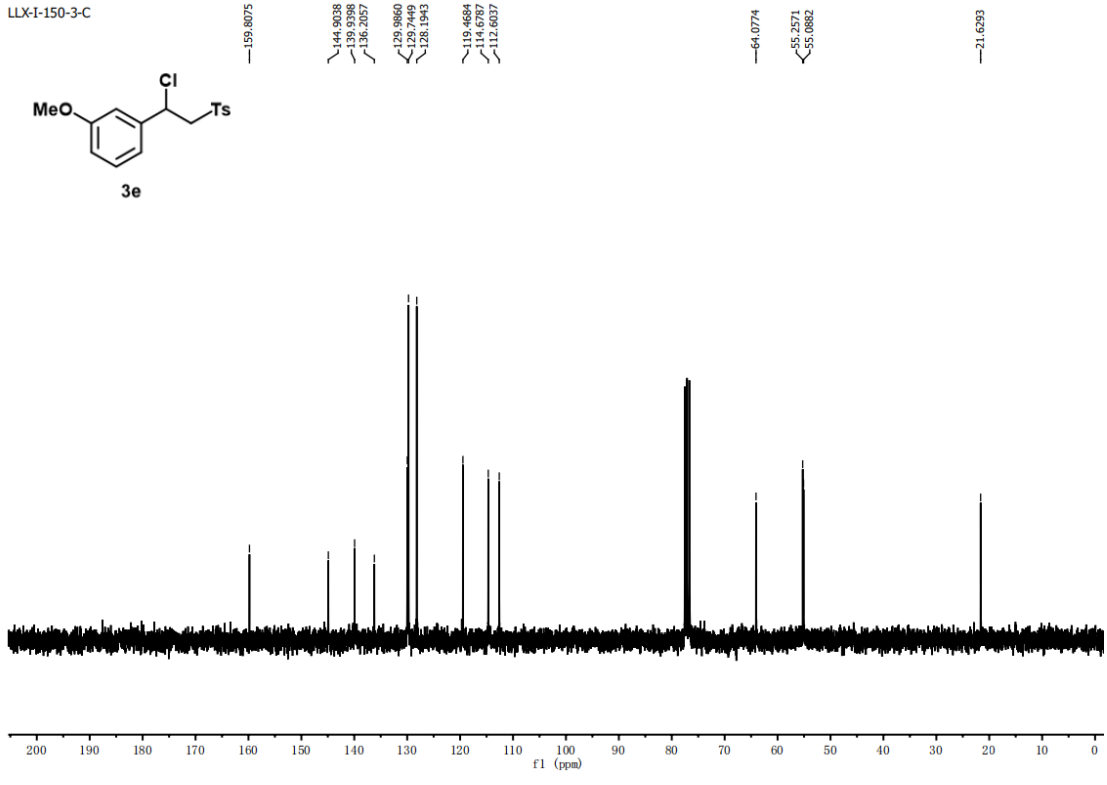
LLX-I-150-3

3e

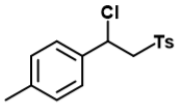


LLX-I-150-3-C

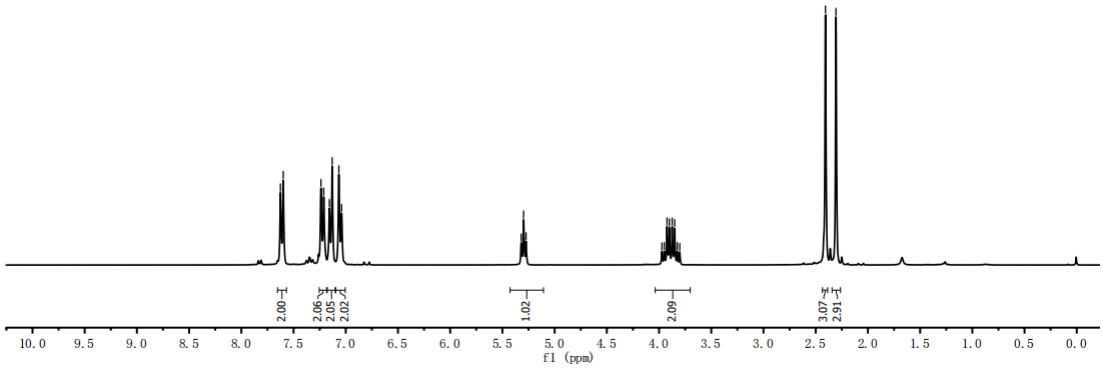
3e



LLX-II-140-3A

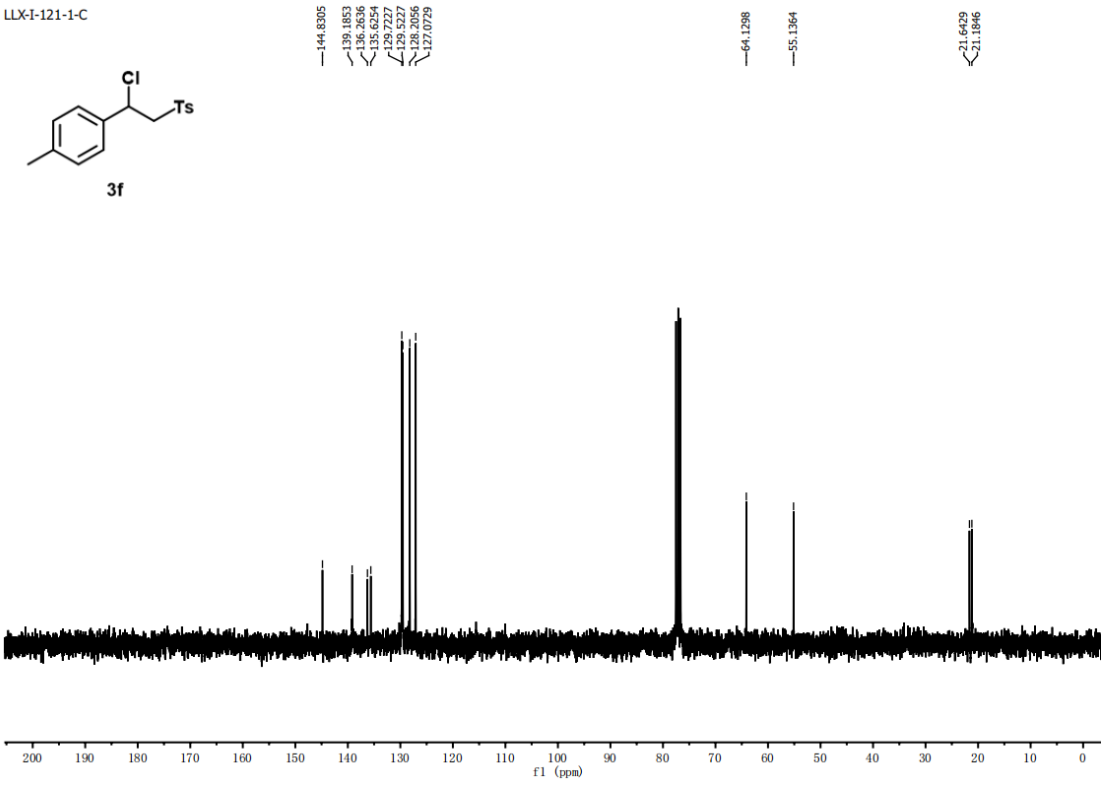


3f



LLX-I-121-1-C

3f



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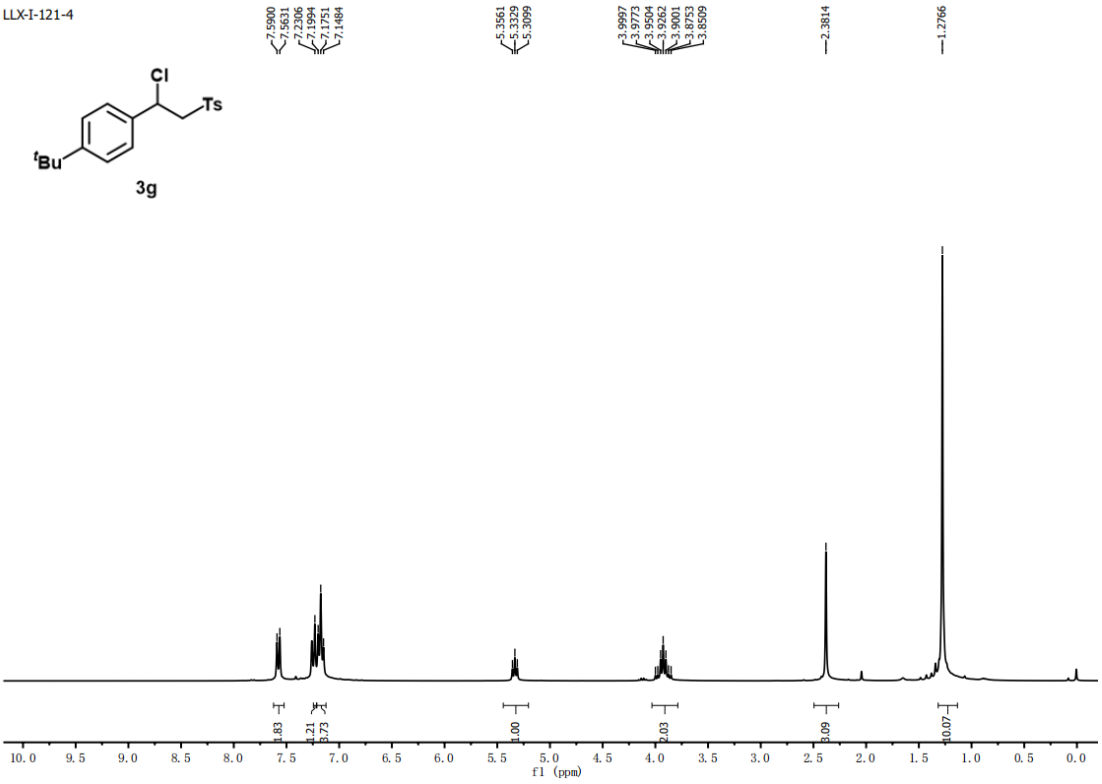
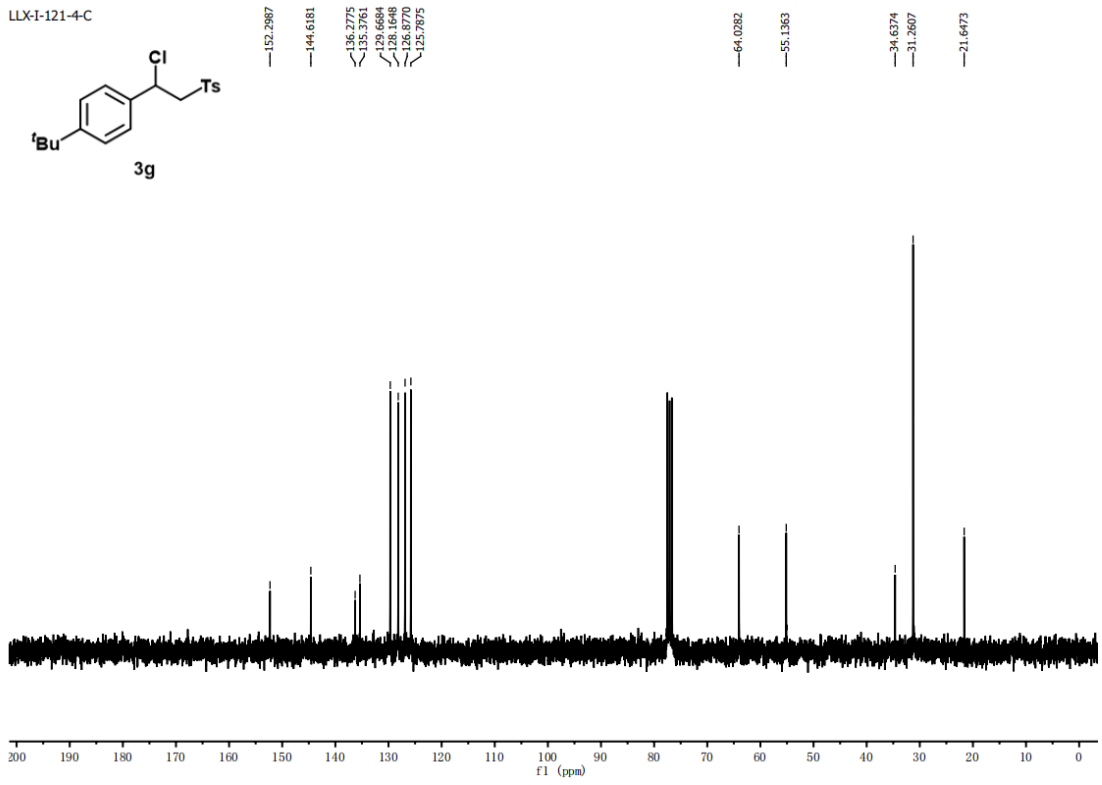
3g



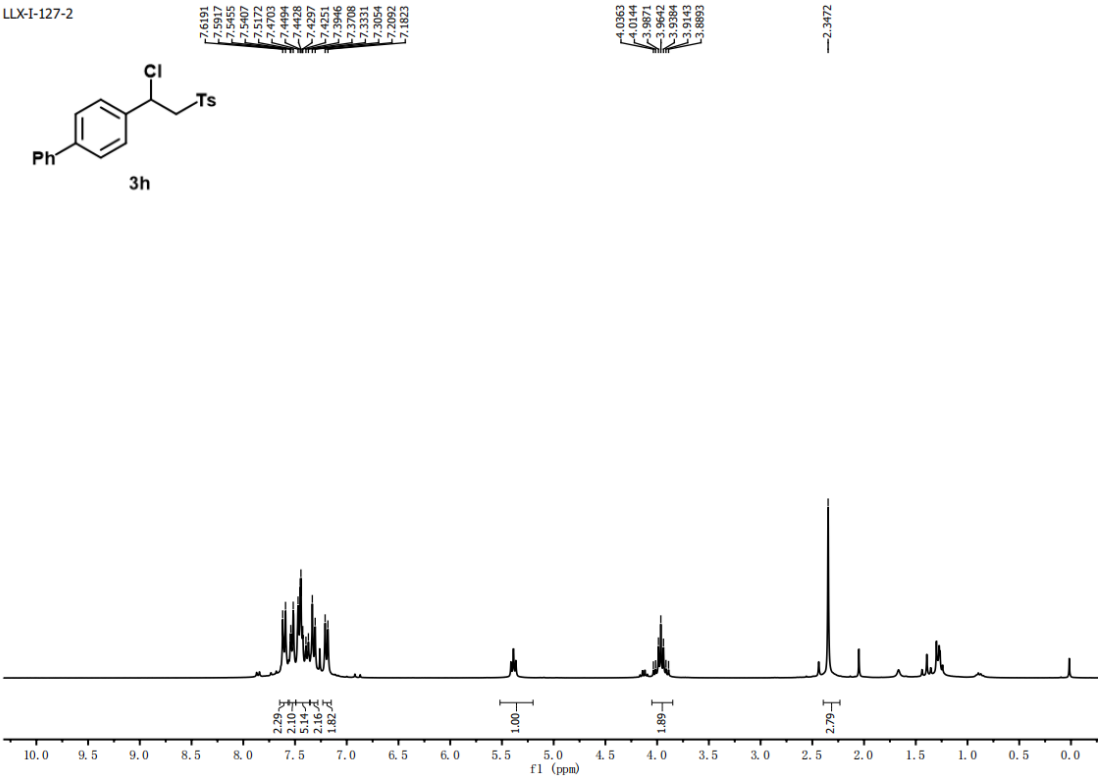
LLX-I-121-4-C

3g



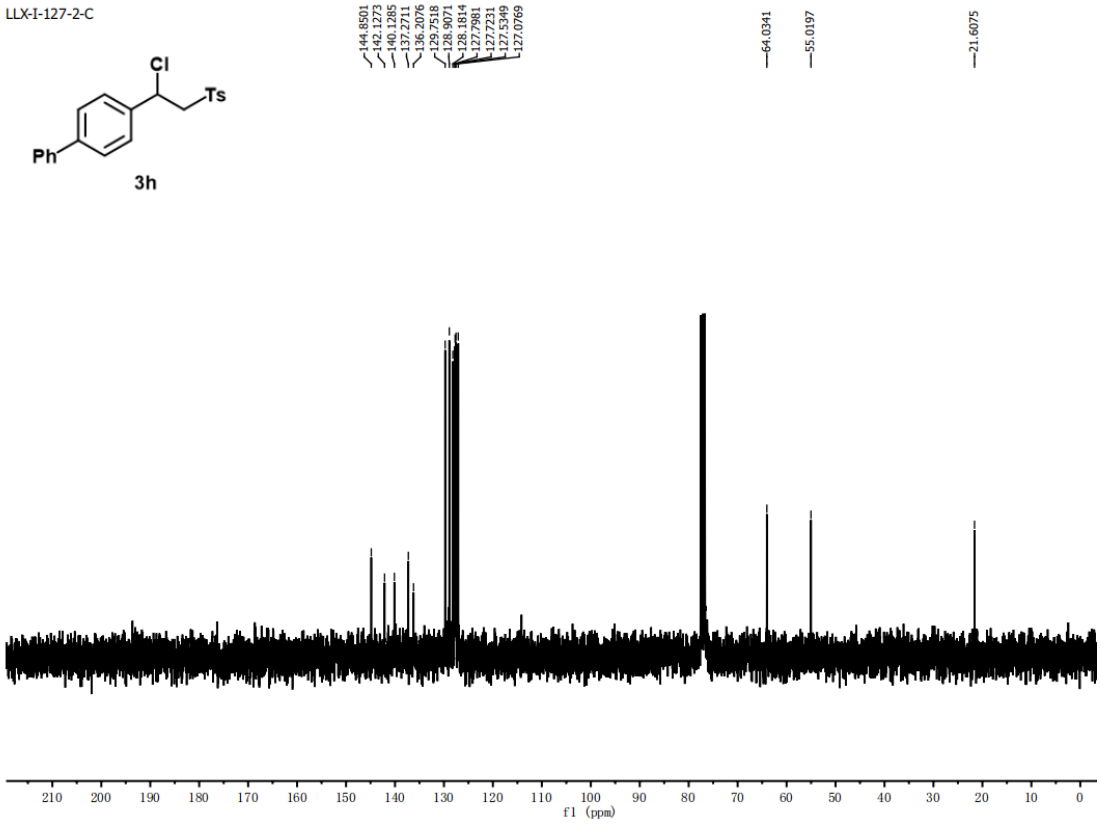
LLX-I-127-2

3h



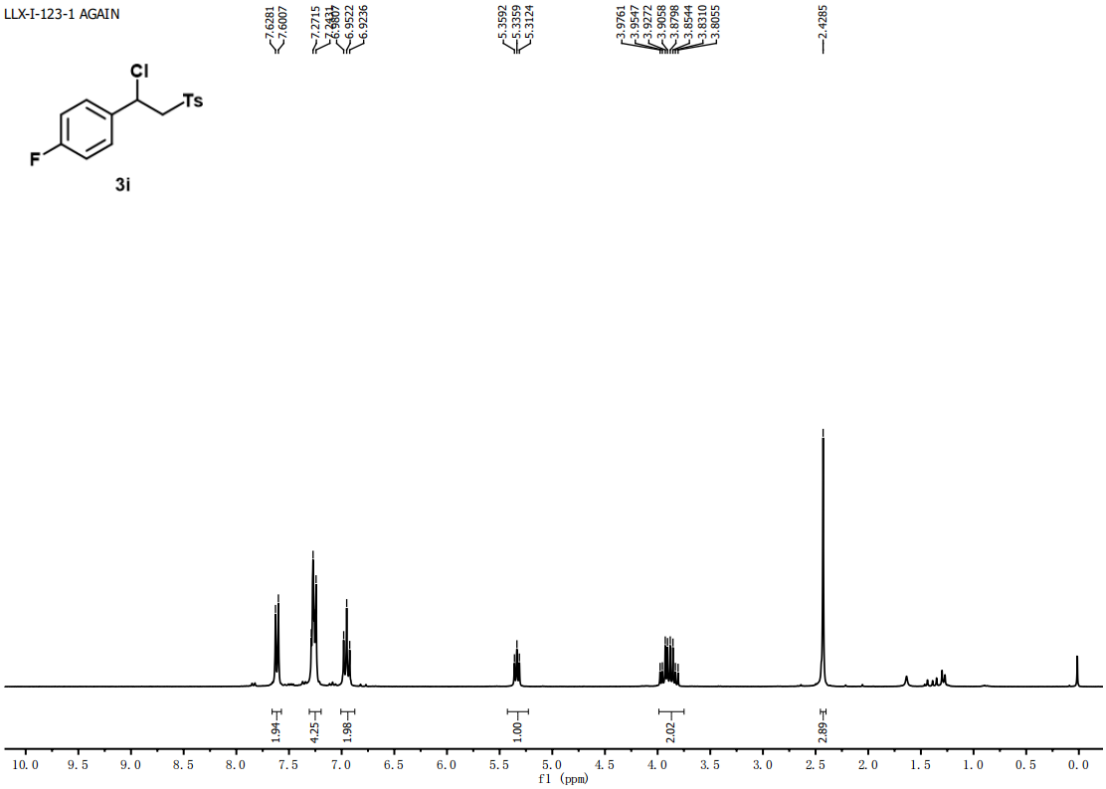
LLX-I-127-2-C

3h



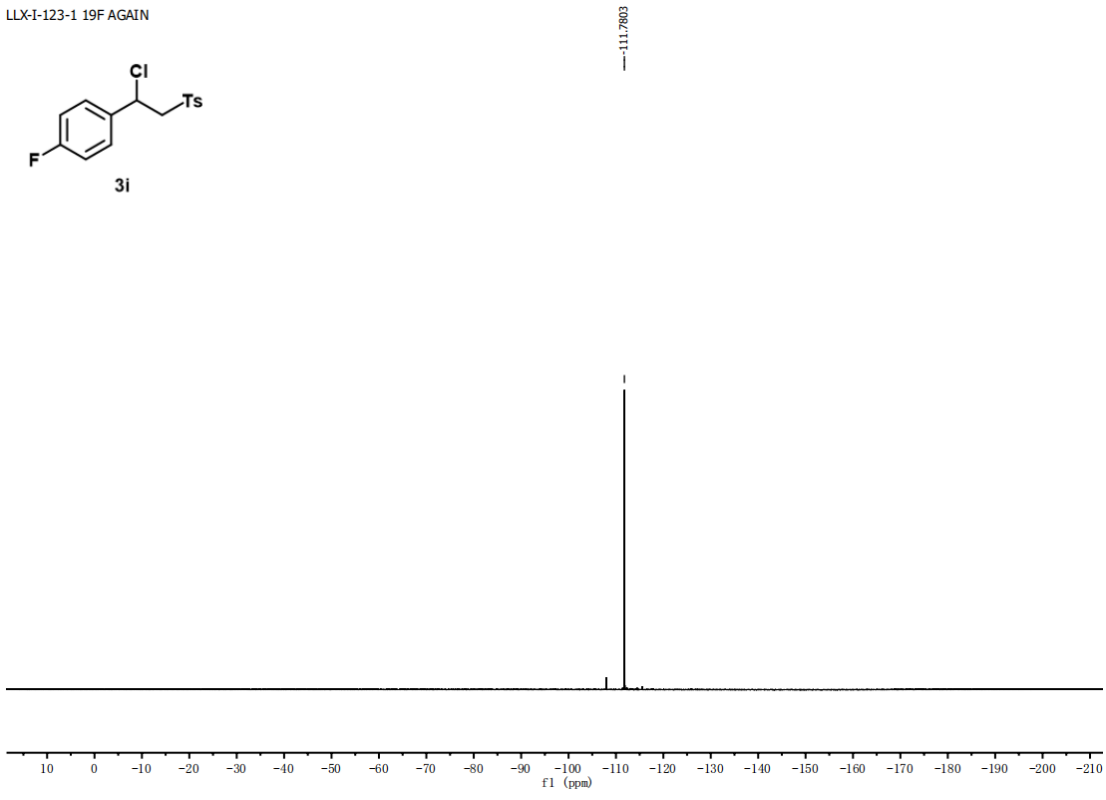
LLX-I-123-1 AGAIN

3i



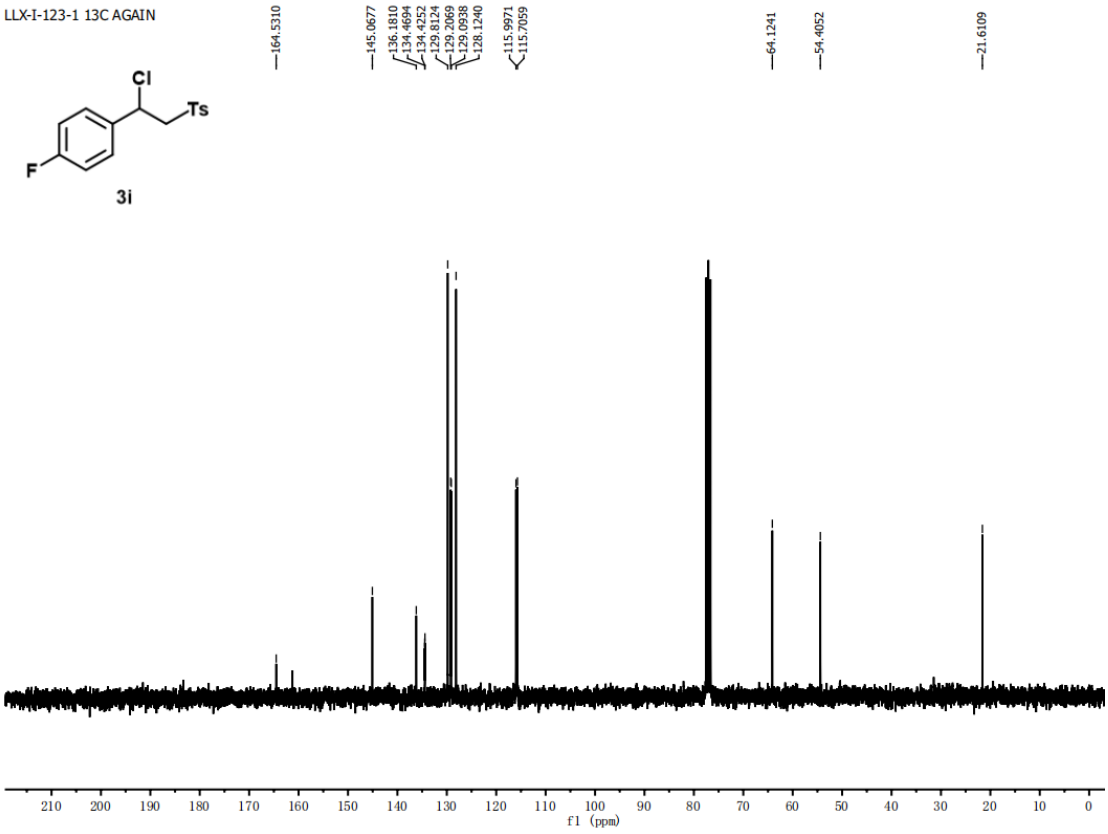
LLX-I-123-1 19F AGAIN

3i



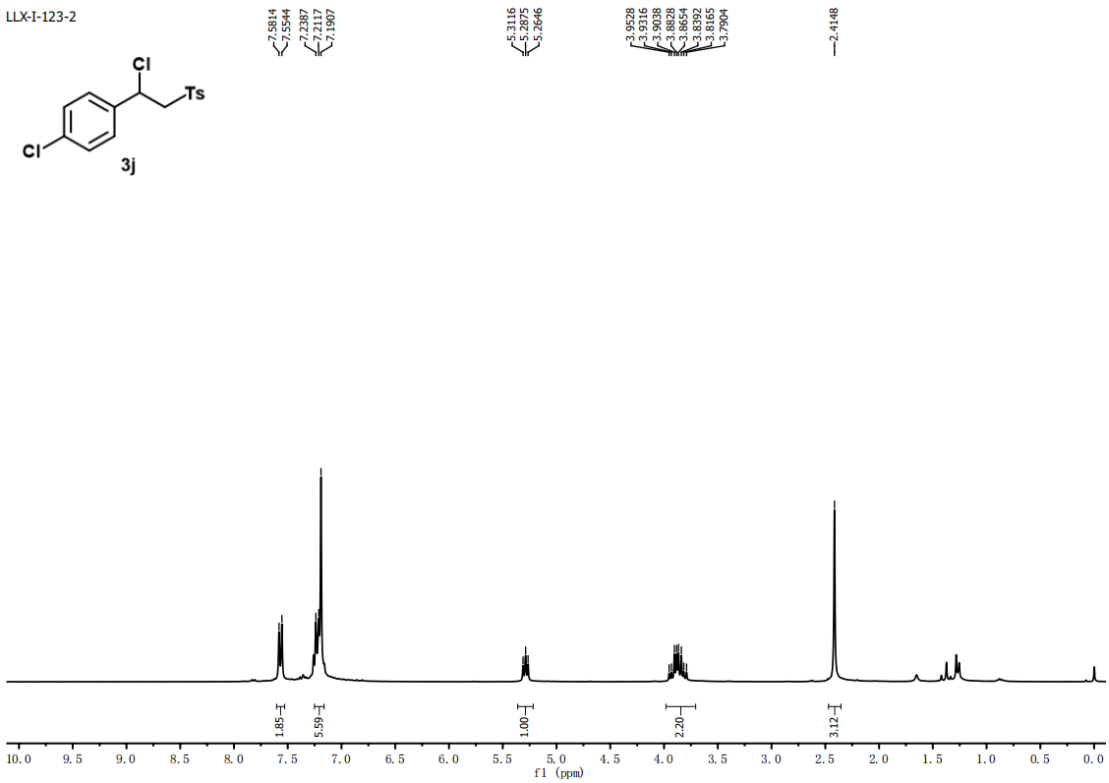
LLX-I-123-1 13C AGAIN

3i



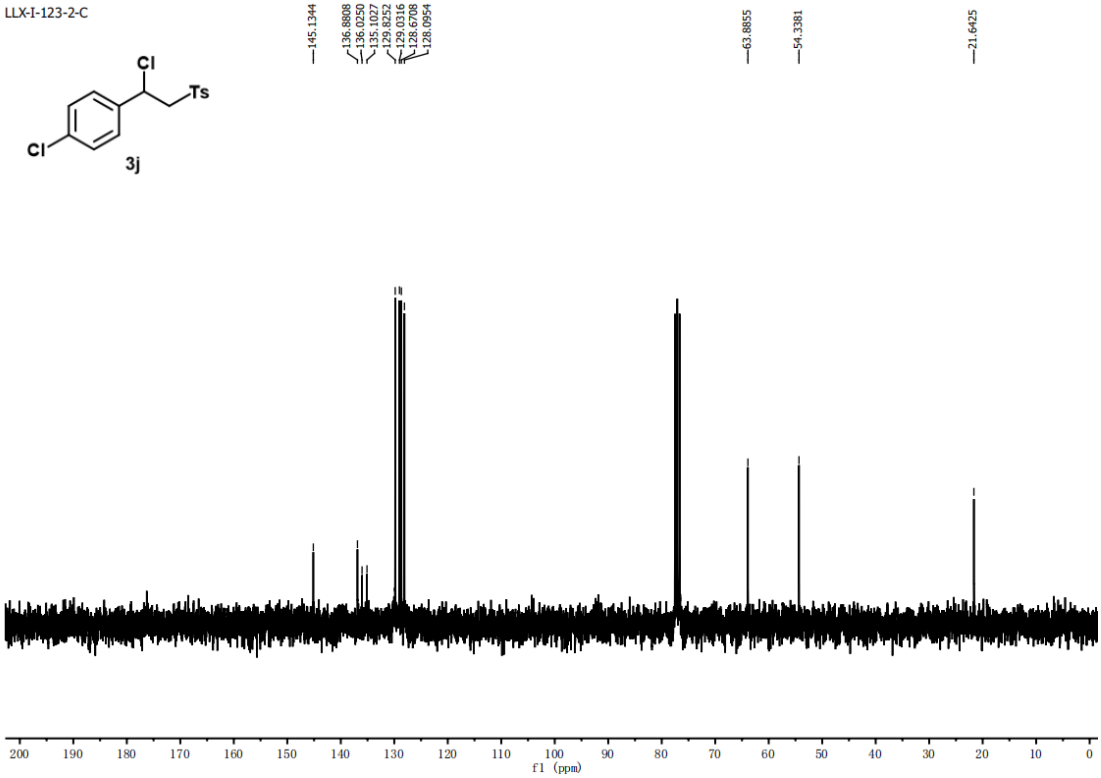
LLX-I-123-2

3j



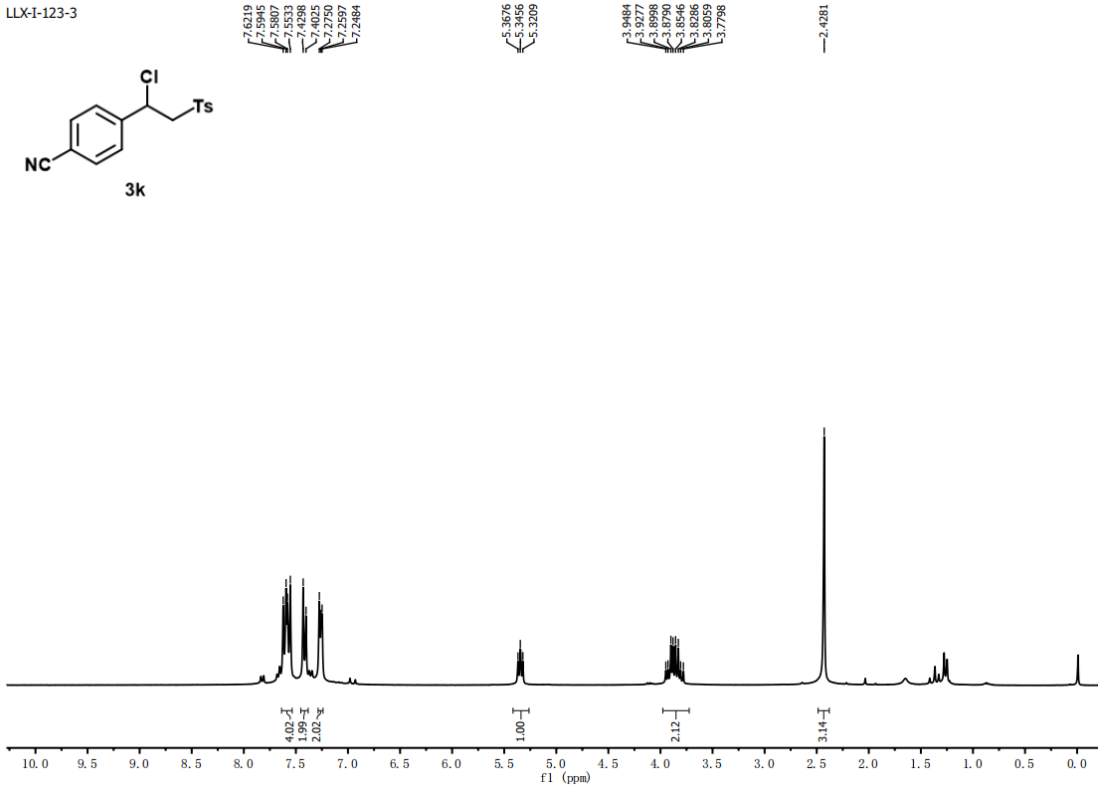
LLX-I-123-2-C

3j



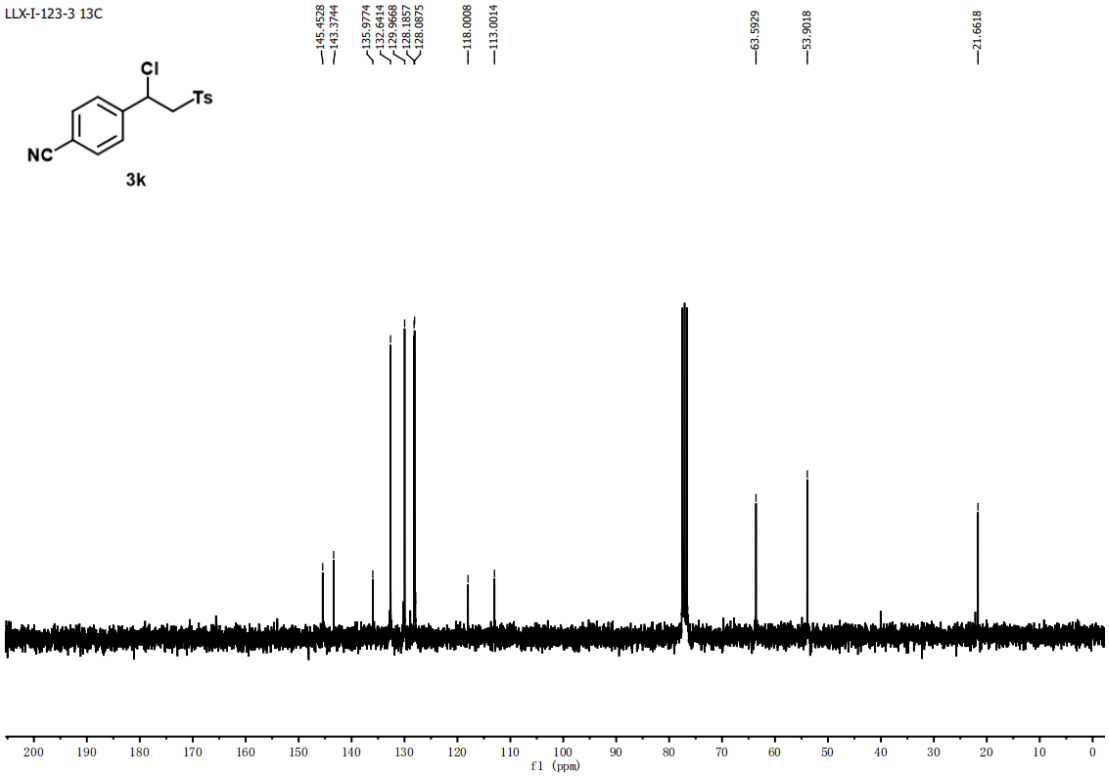
LLX-I-123-3

3k



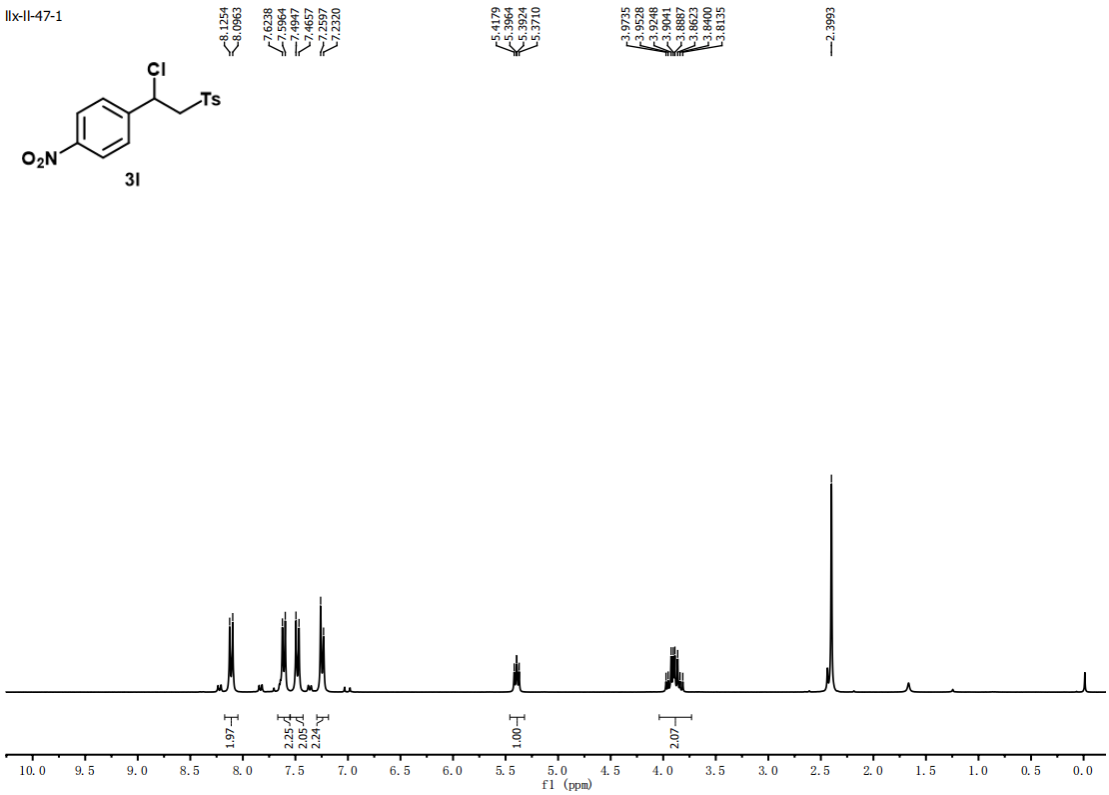
LLX-I-123-3 13C

3k



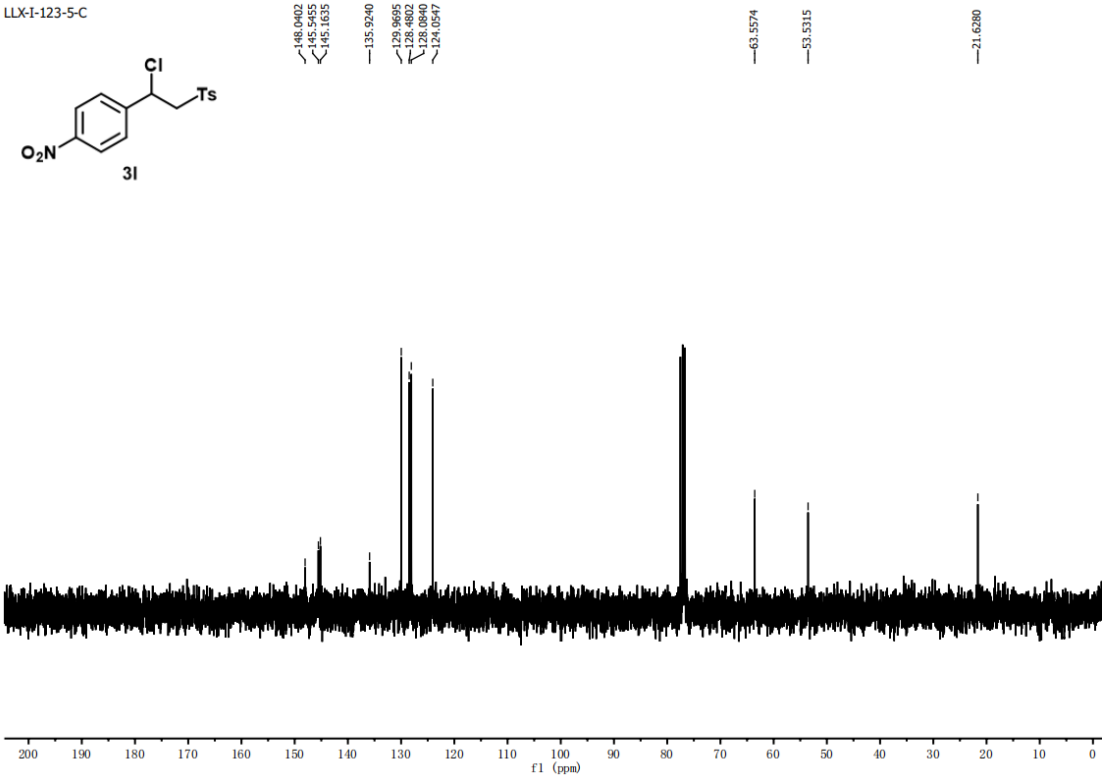
llx-ll-47-1

3l



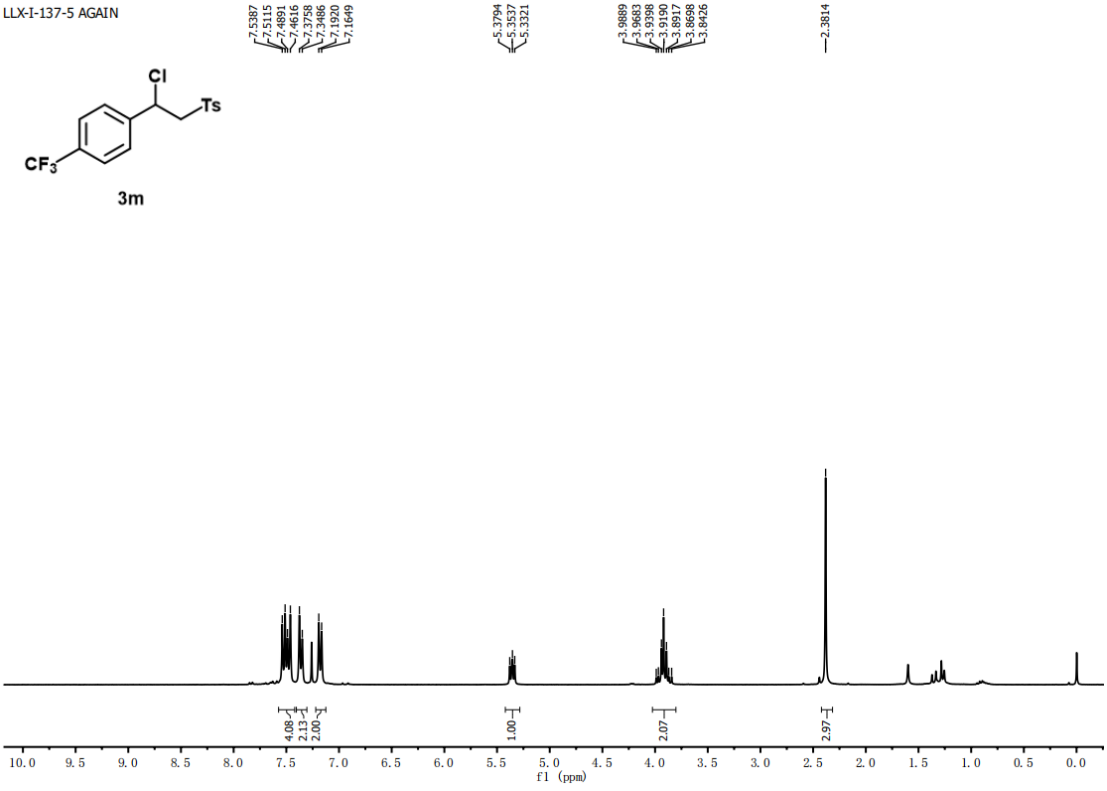
LLX-I-123-5-C

3l



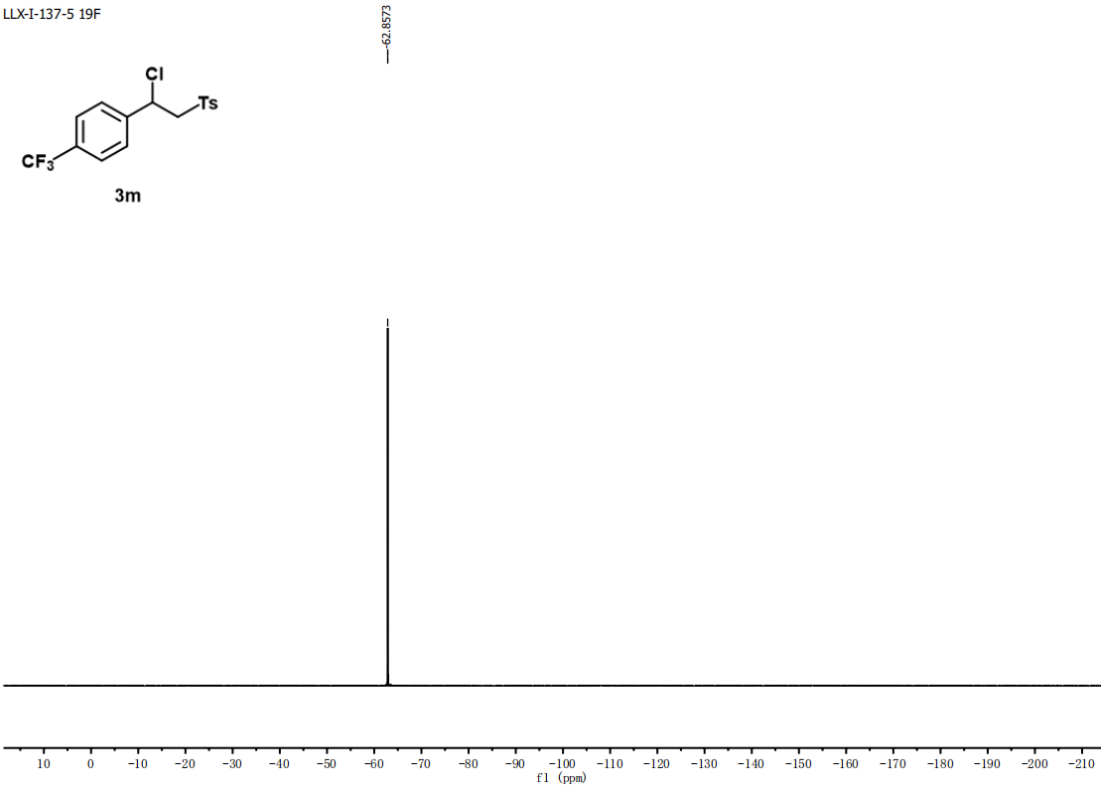
LLX-I-137-5 AGAIN

3m



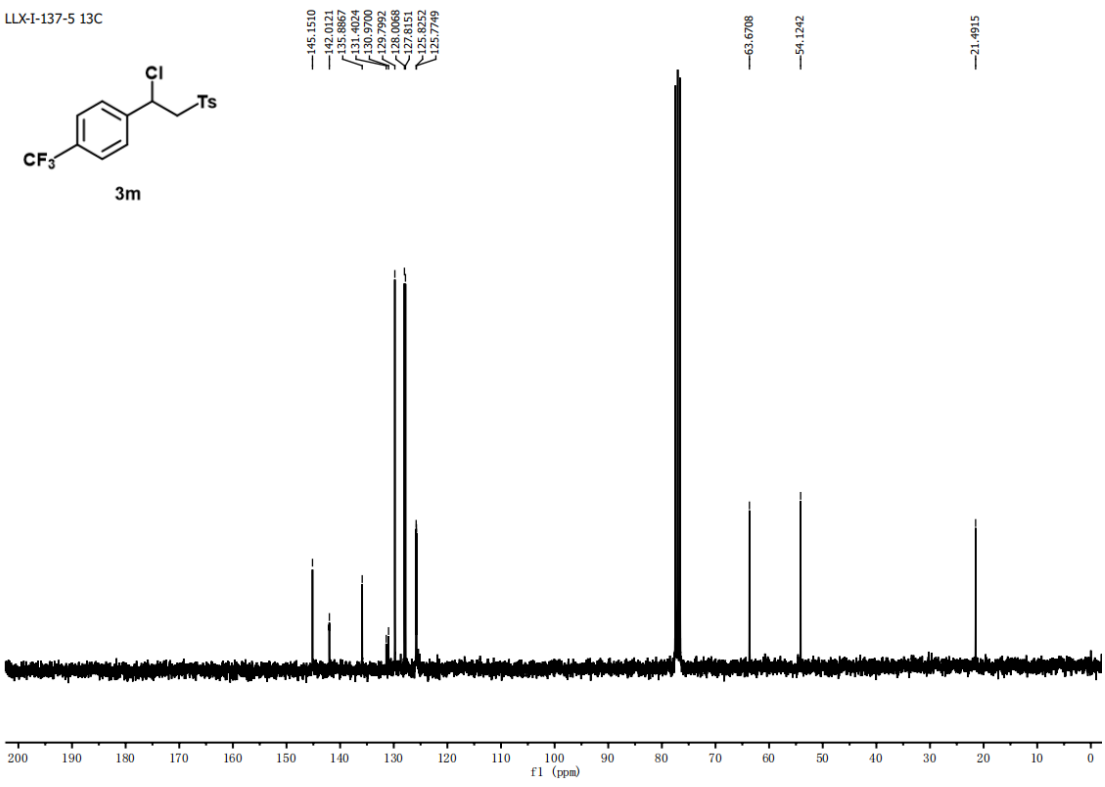
LLX-I-137-5 19F

3m

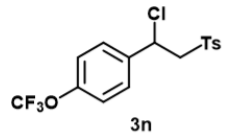


LLX-I-137-5 13C

3m



llx-ii-144-4



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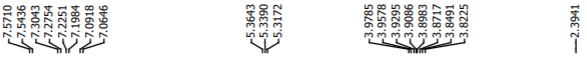
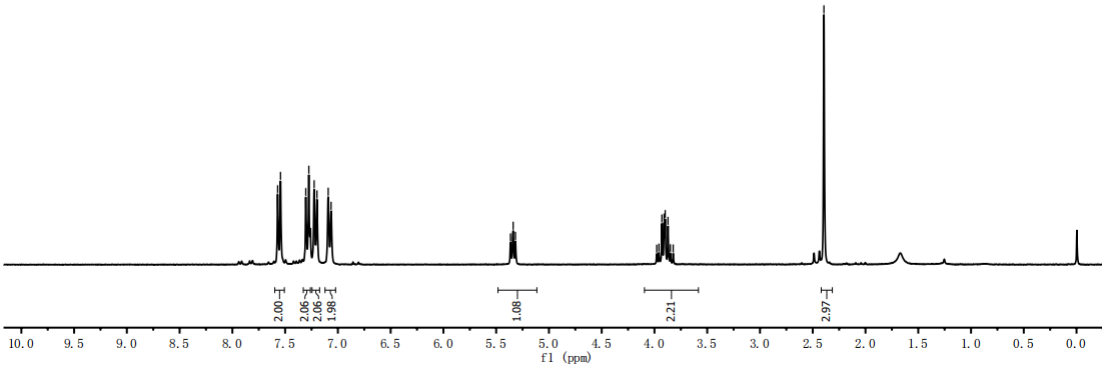
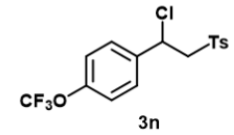




LLX-I-137-2-C



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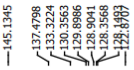

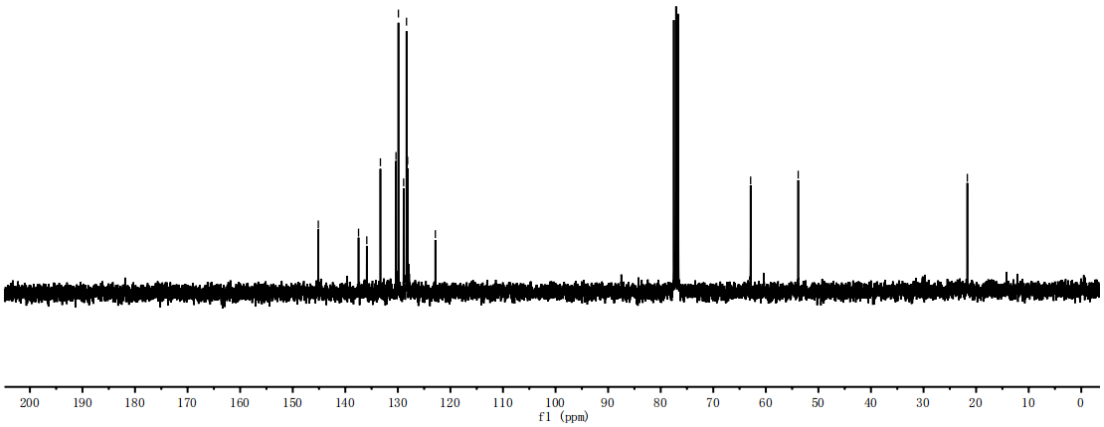

LLX-I-137-2-A-F

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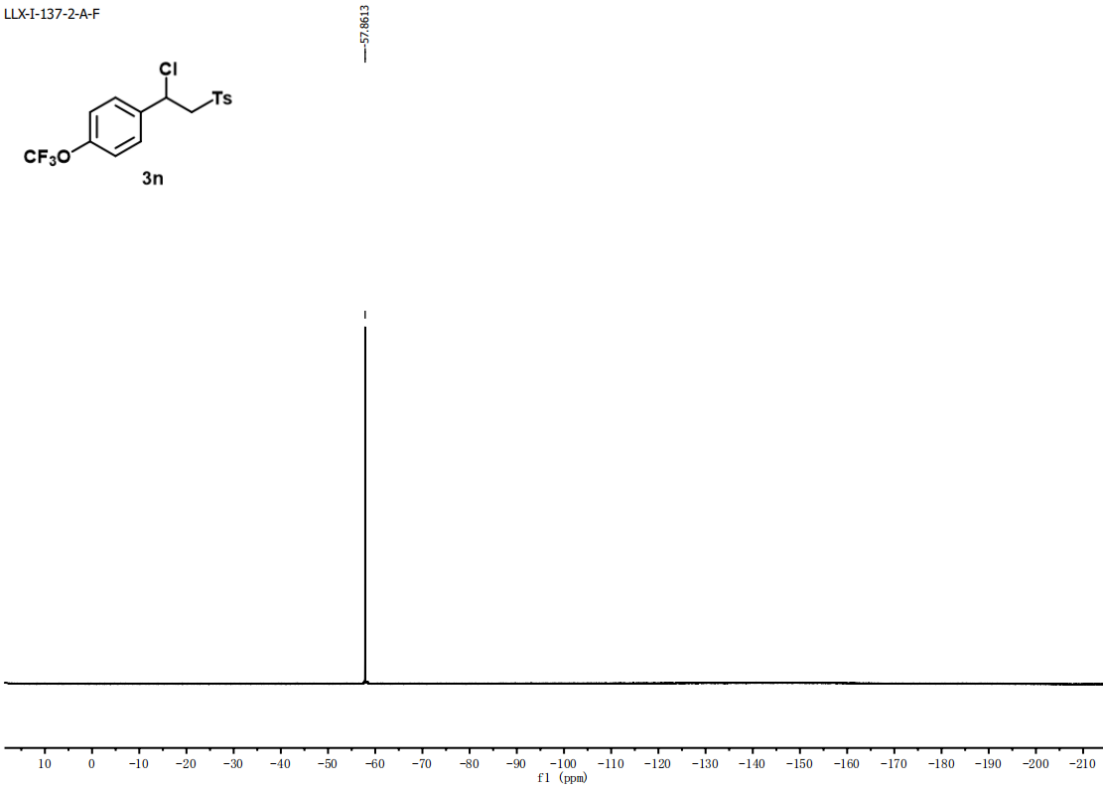
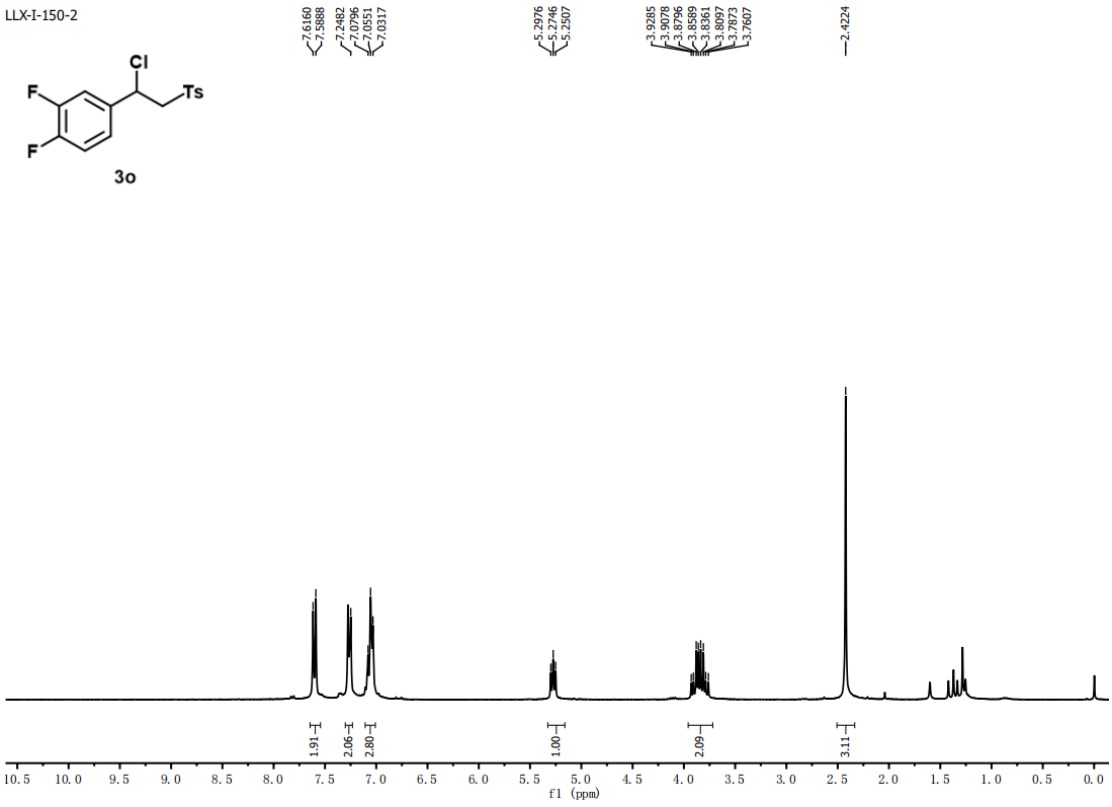
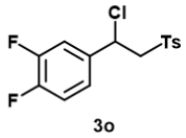


LLX-I-150-2

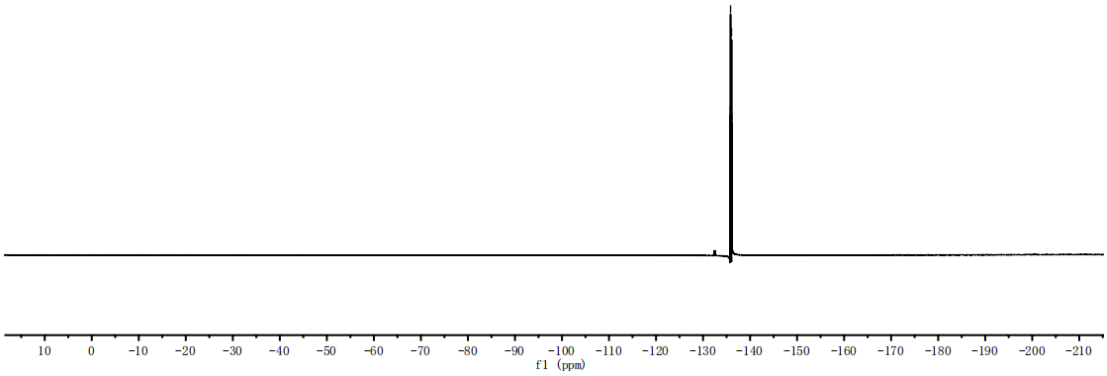
3o



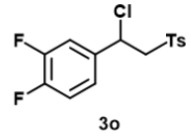
LLX-I-150-2-F



3o



LLX-I-150-2-C



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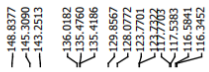
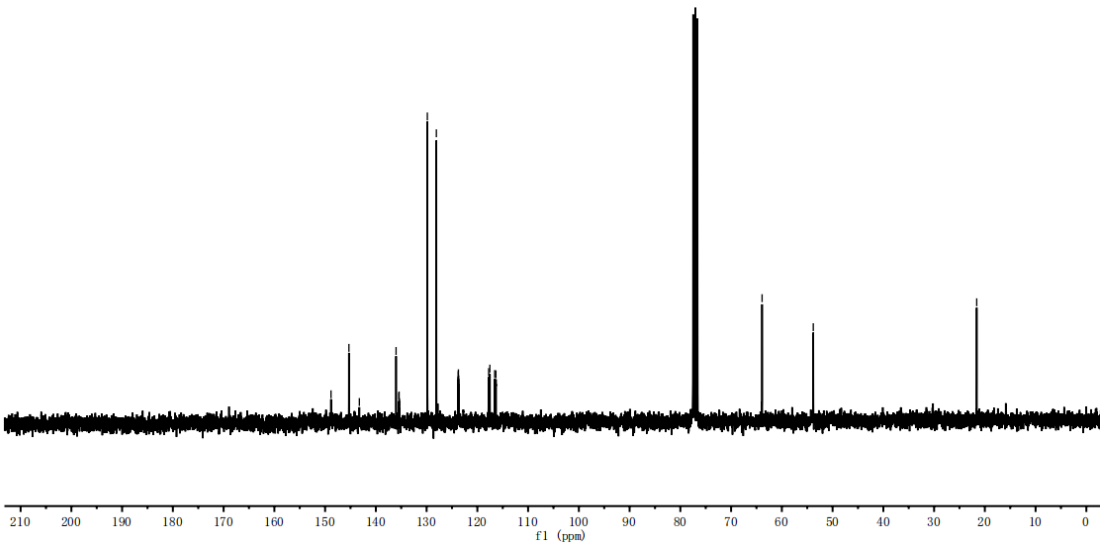
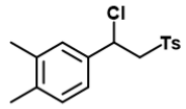




LLX-I-121-5



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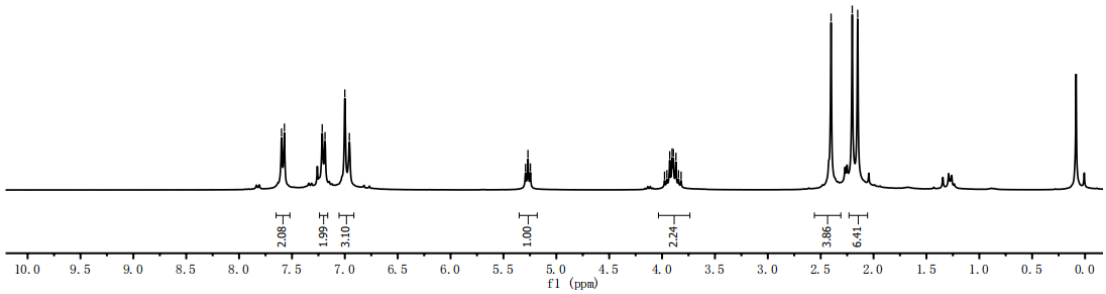
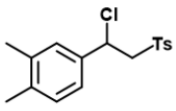
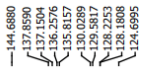
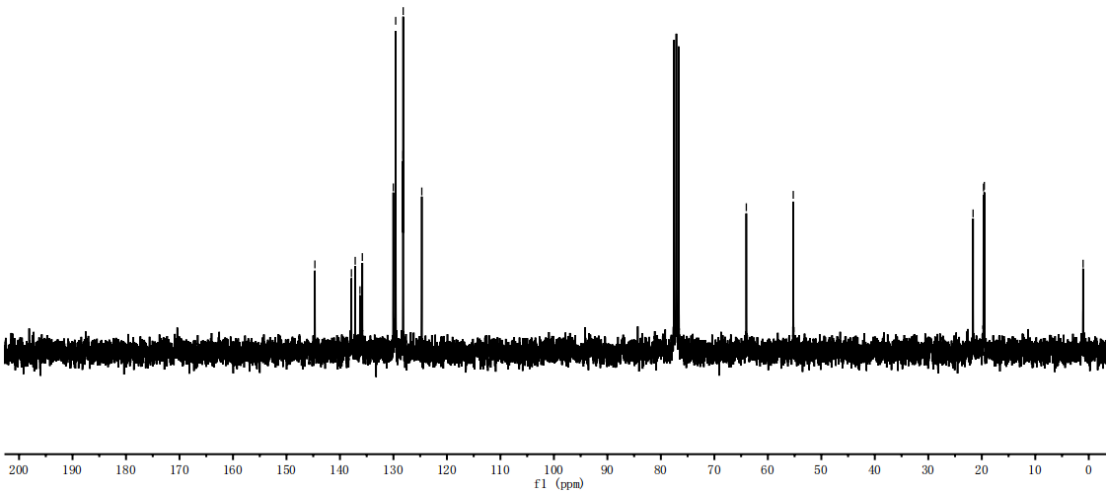


LLX-I-121-5-C

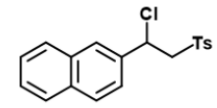


3p





LLX-I-121-2



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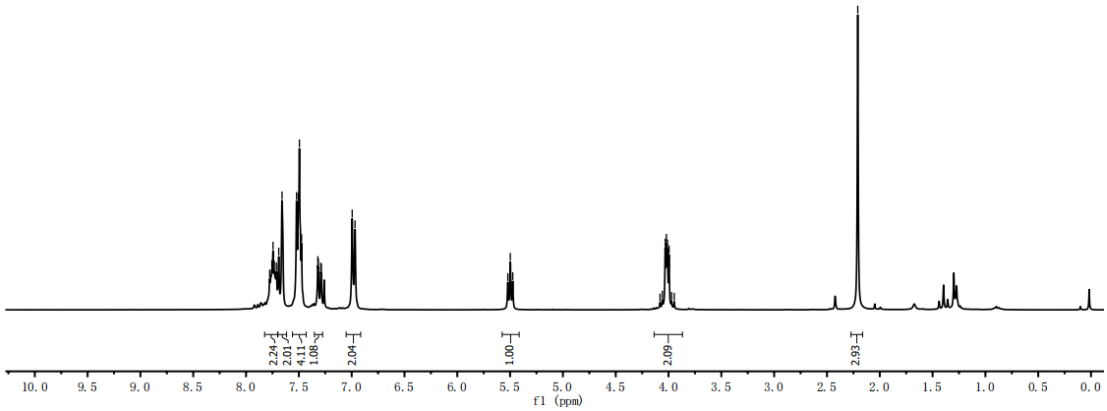
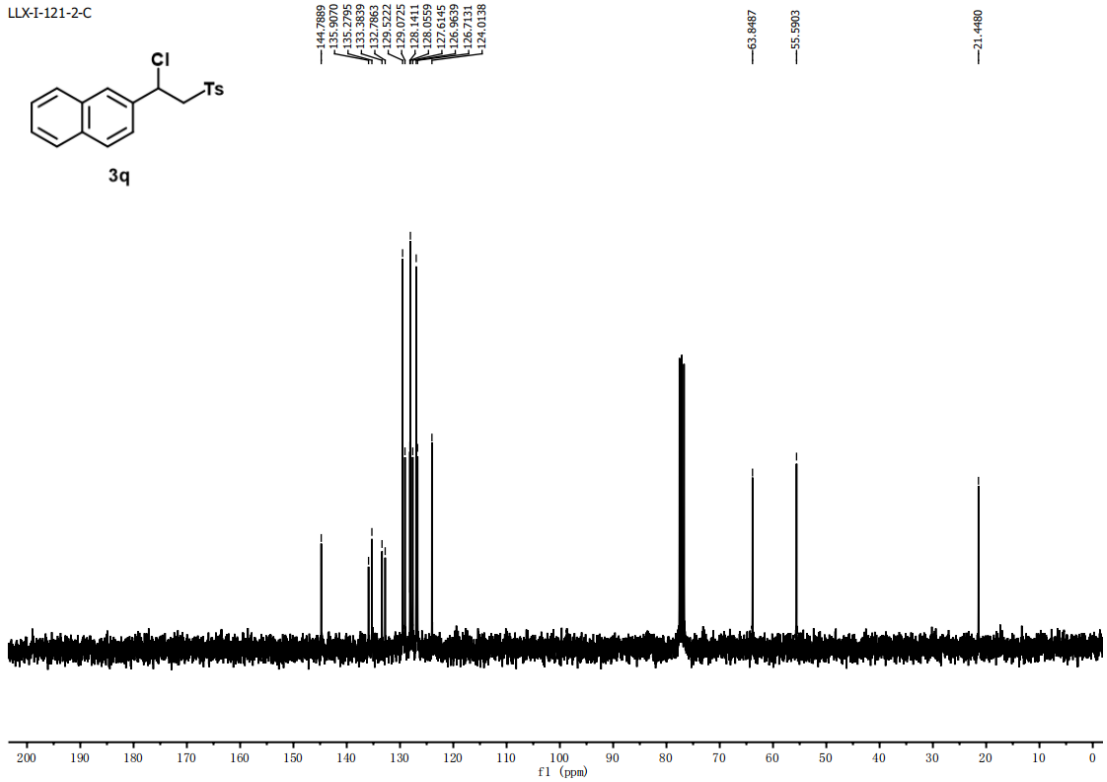
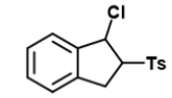


LLX-I-121-2-C

3q



LLX-I-127-5



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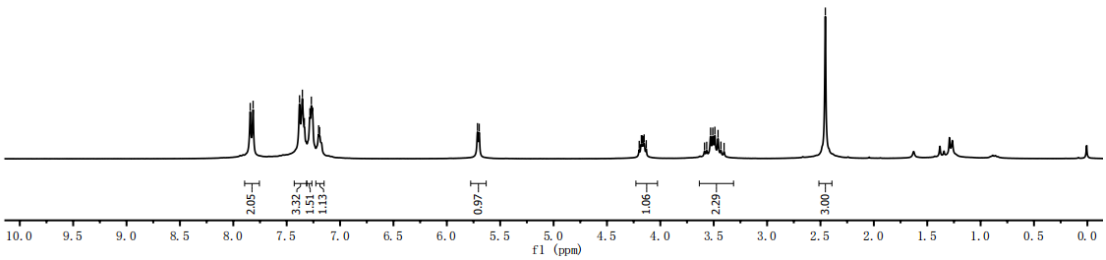
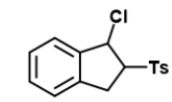
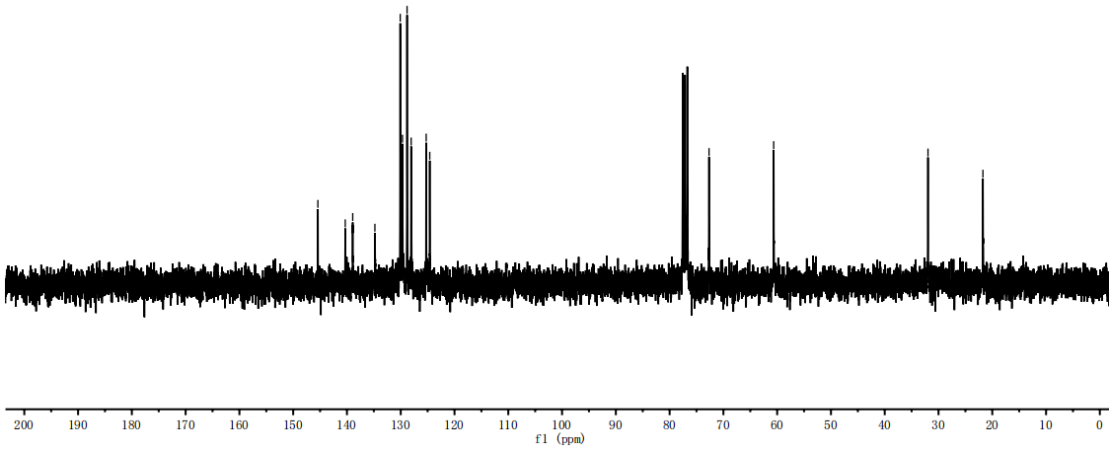


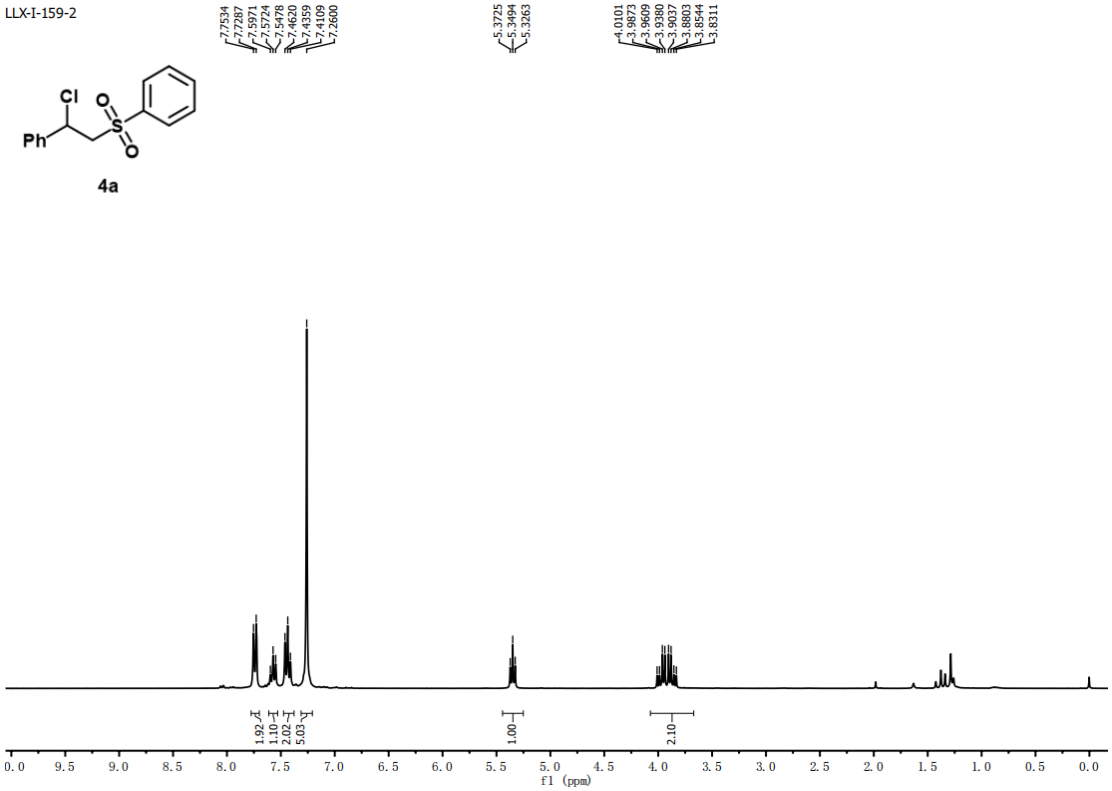
LLX-I-127-5-C



3r

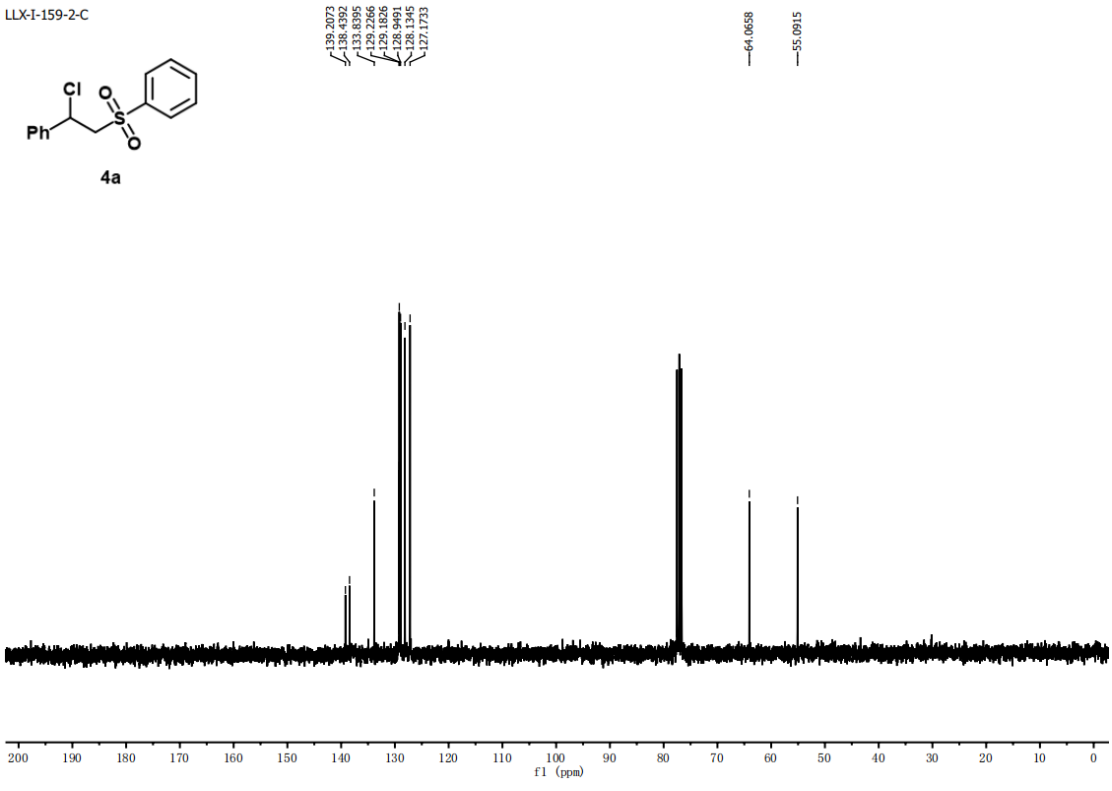


LLX-I-159-2



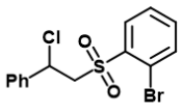
4a

LLX-I-159-2-C



4a

LLX-I-152-6



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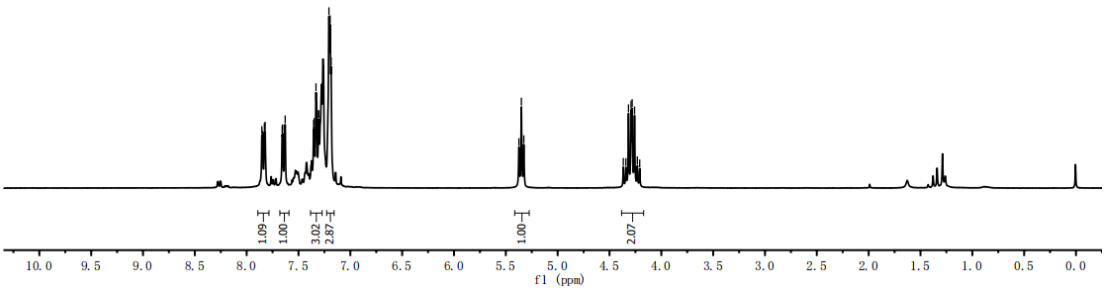

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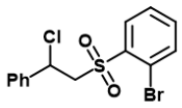

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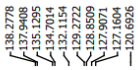
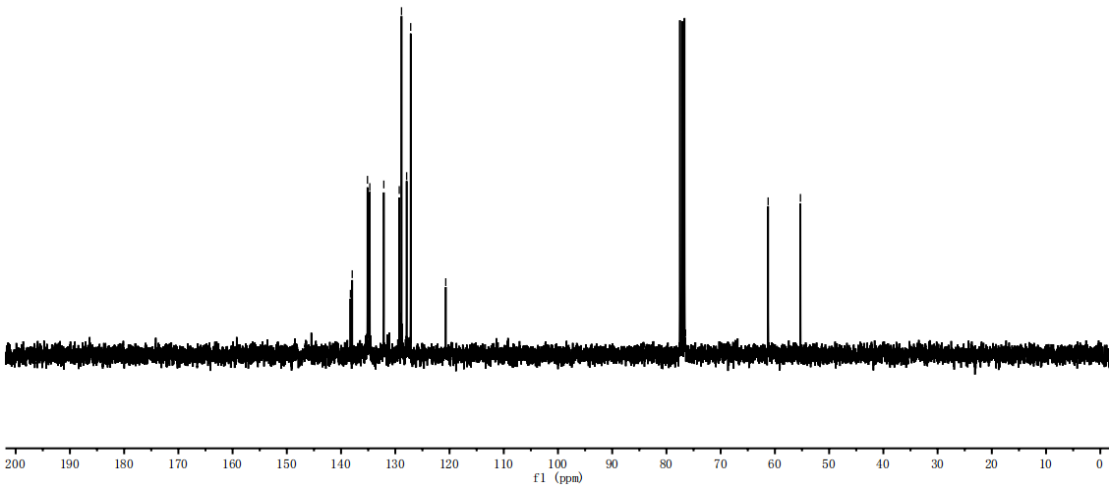
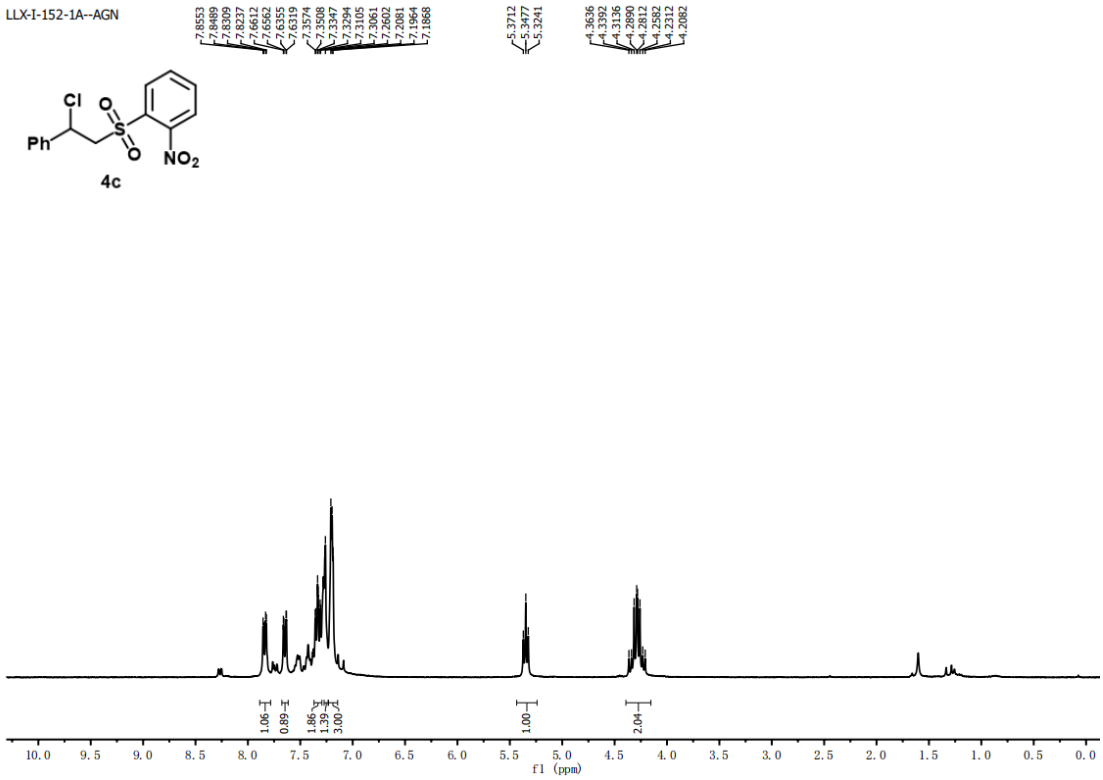




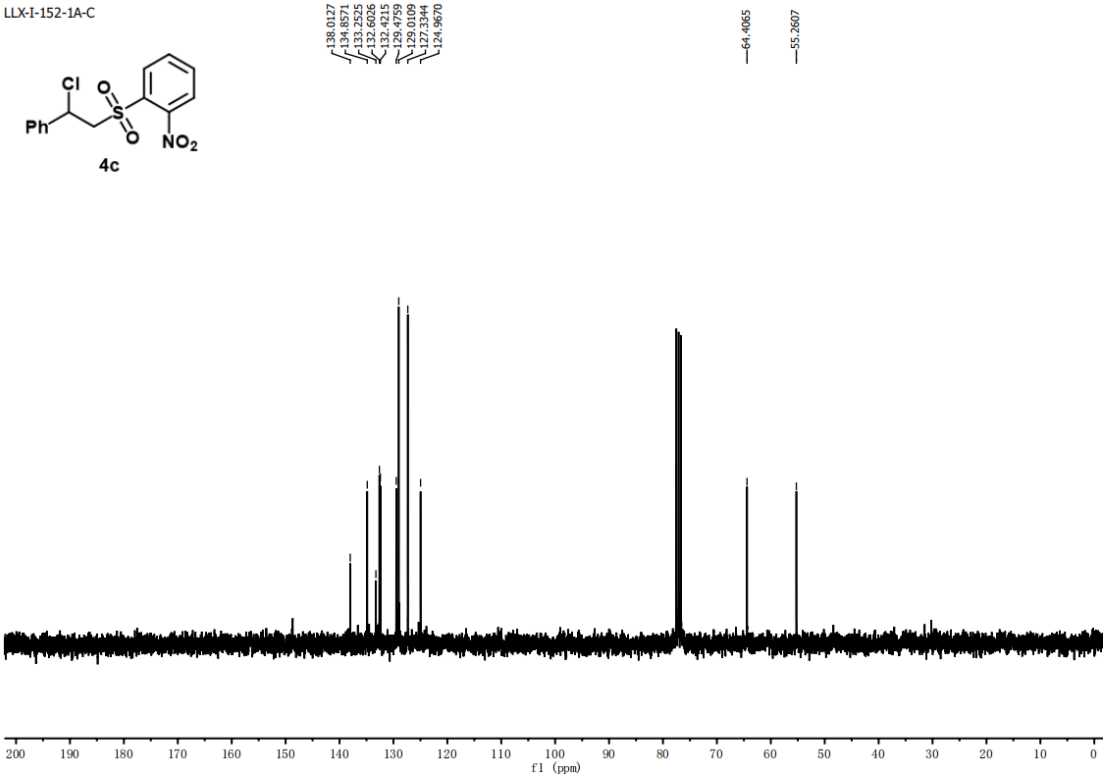
LLX-I-152-1A--AGN

4c



LLX-I-152-1A-C

4c

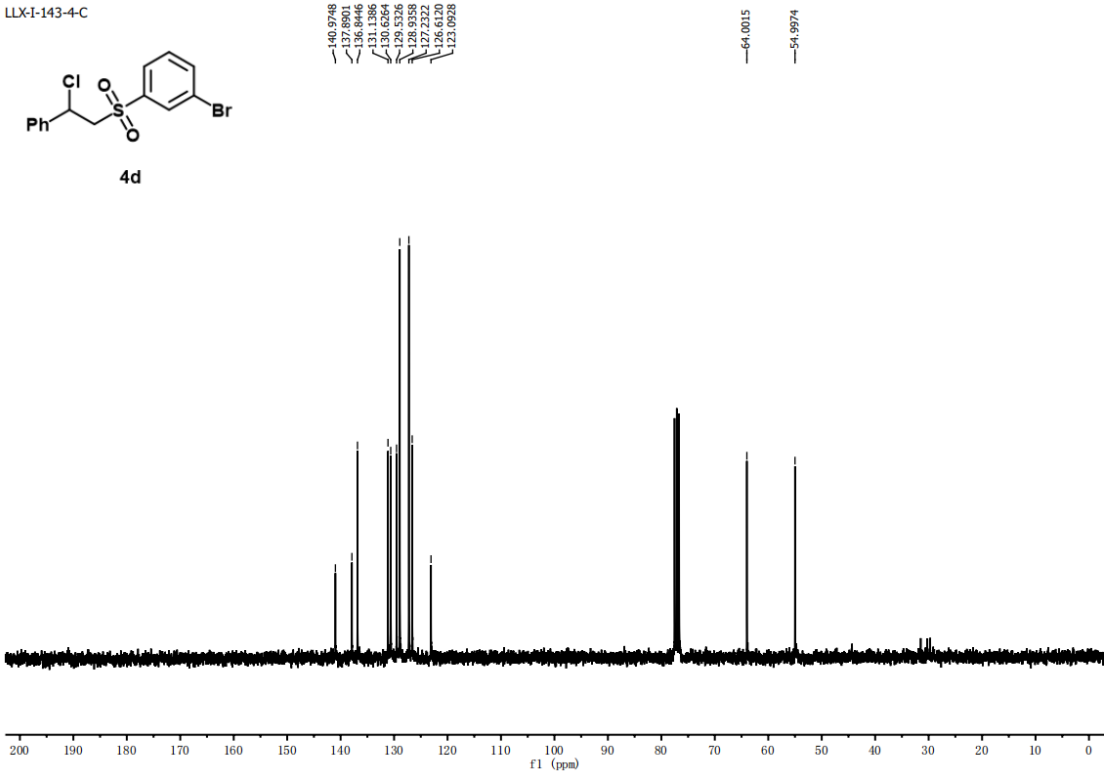


LLX-I-143-4

4d

LLX-I-143-4-C

4d



LLX-I-152-4

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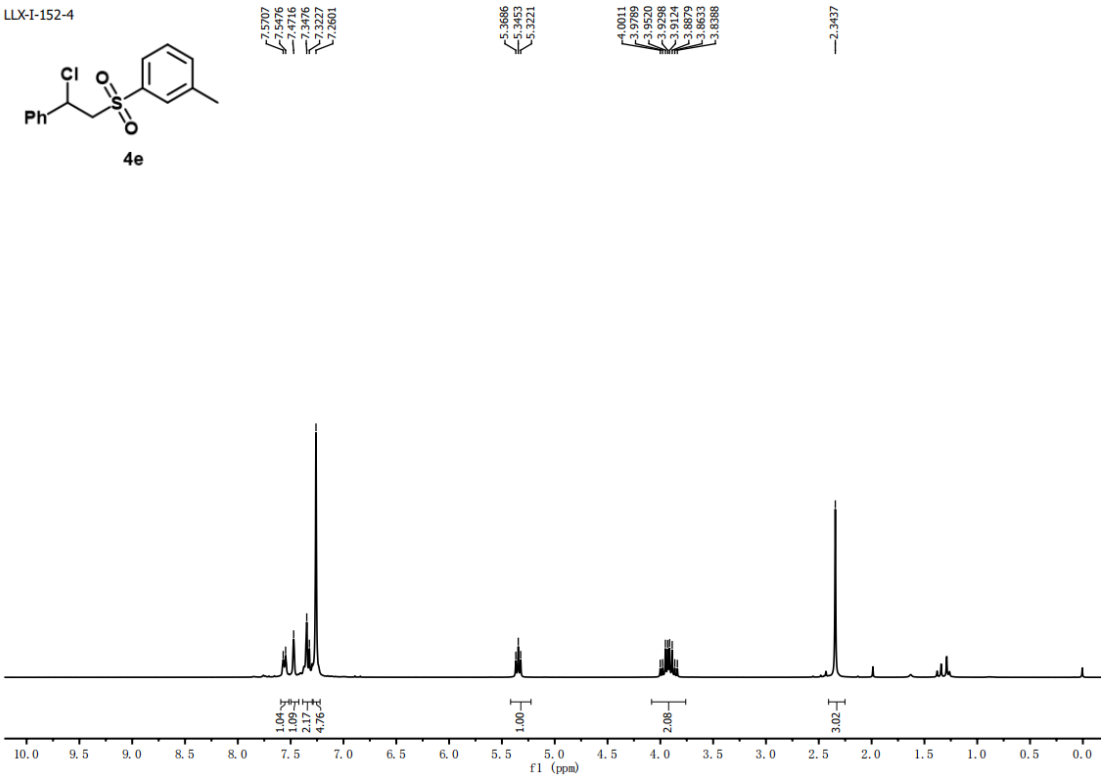
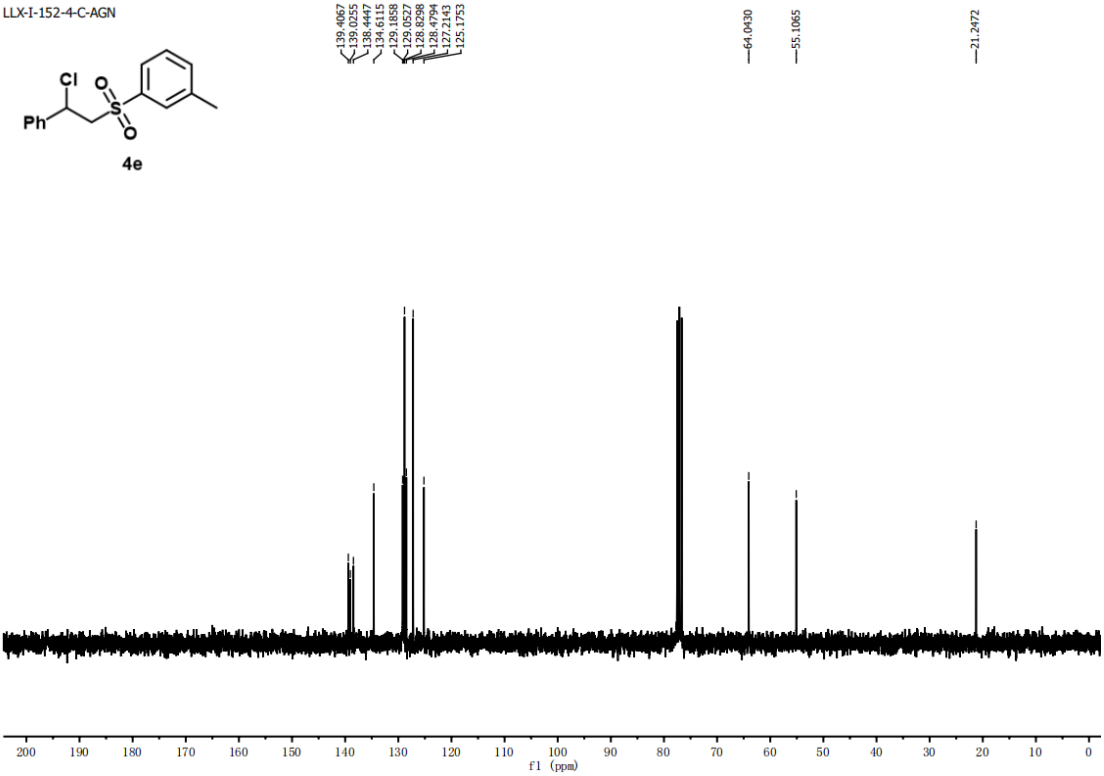


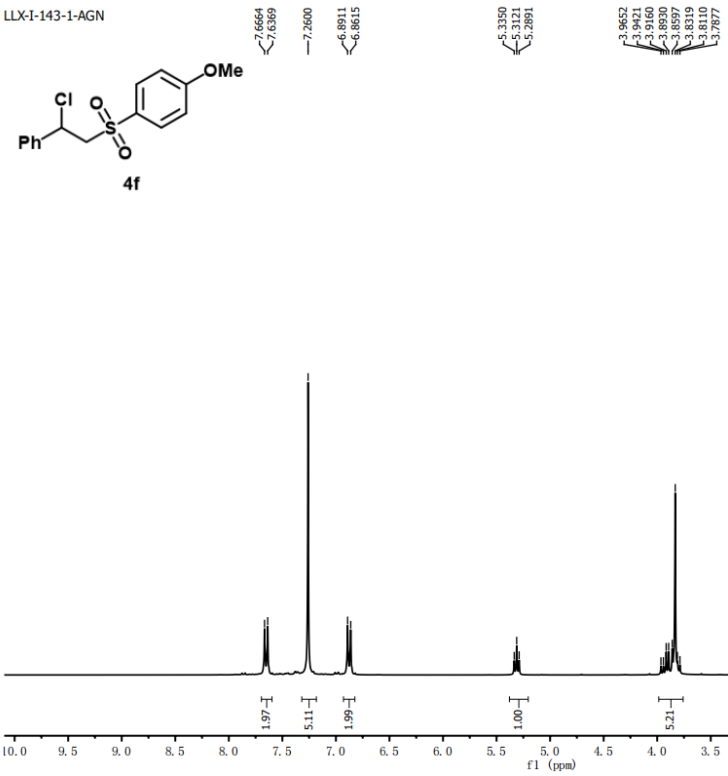
LLX-I-152-4-C-AGN

4e



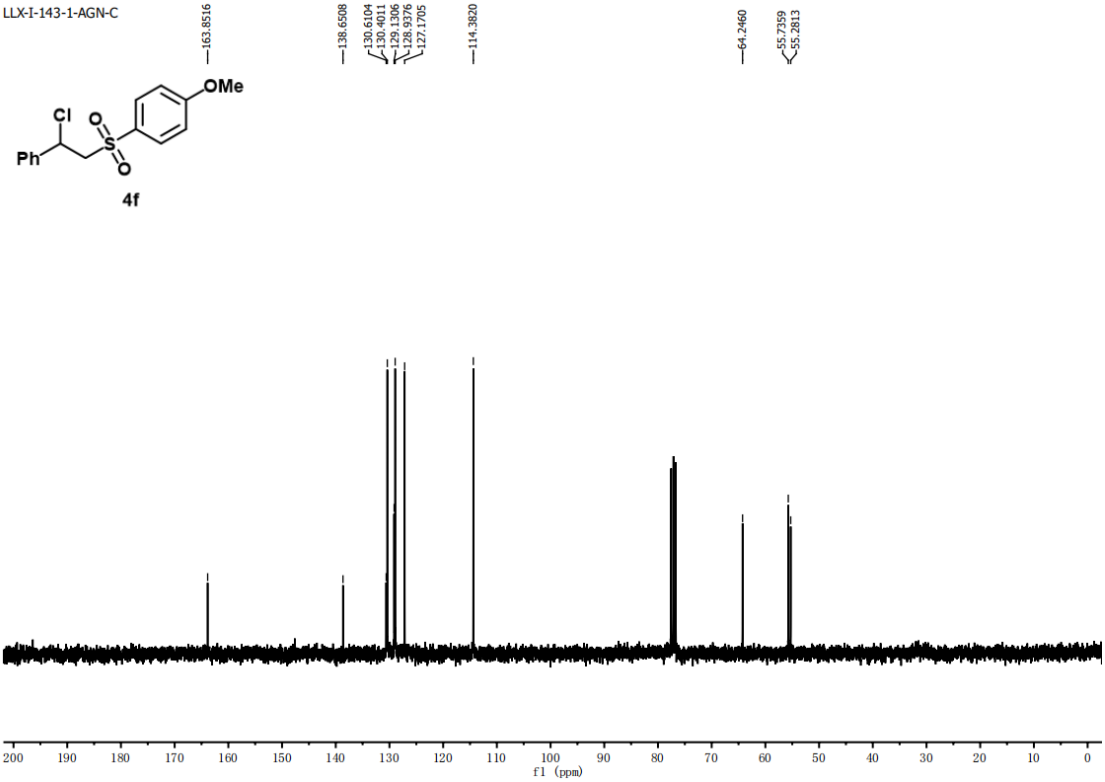
LLX-I-143-1-AGN

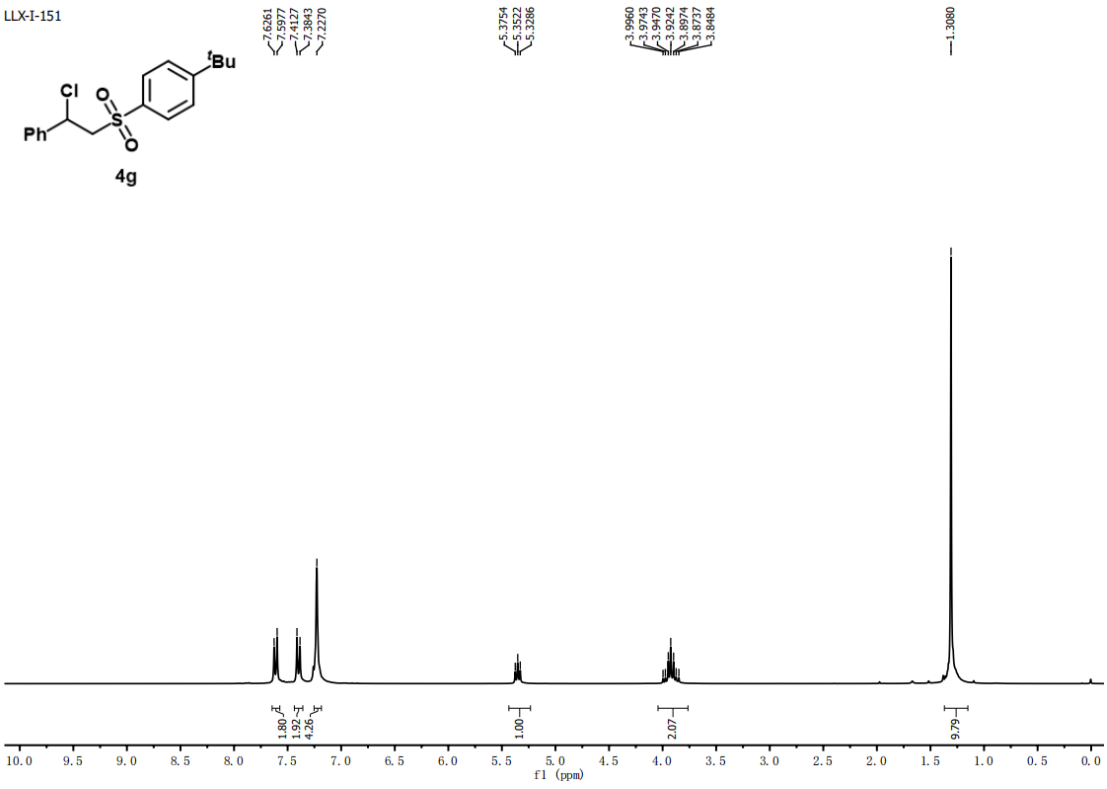
4f



LLX-I-143-1-AGN-C

4f




LLX-I-151
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5.3522
5.3286
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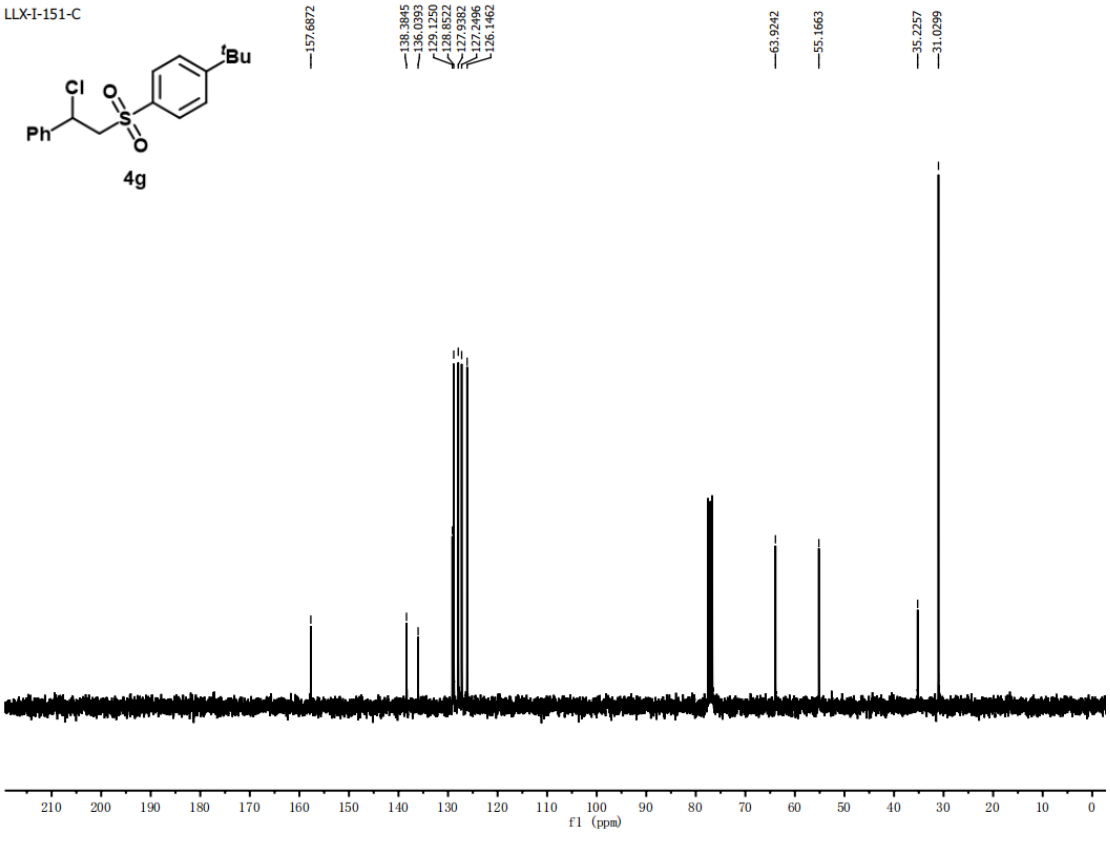
3.9743
3.9470
3.9242
3.8974
3.8737
3.8484
1.3080
Cl
Ph
O
S
O
tBu
4g
1.80
1.92
4.26
1.00
2.07
9.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


LLX-I-151-C
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136.0393
129.1250
128.8522
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127.2496
126.1462
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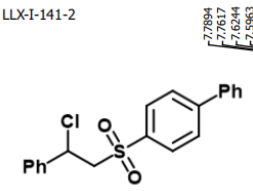
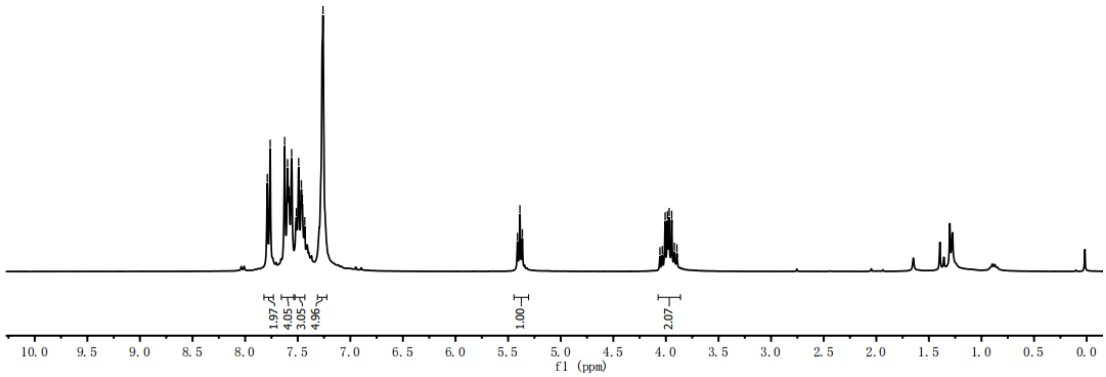
55.1663
35.2257
31.0299
Cl
Ph
O
S
O
tBu
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

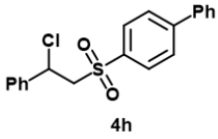
LLX-I-141-2



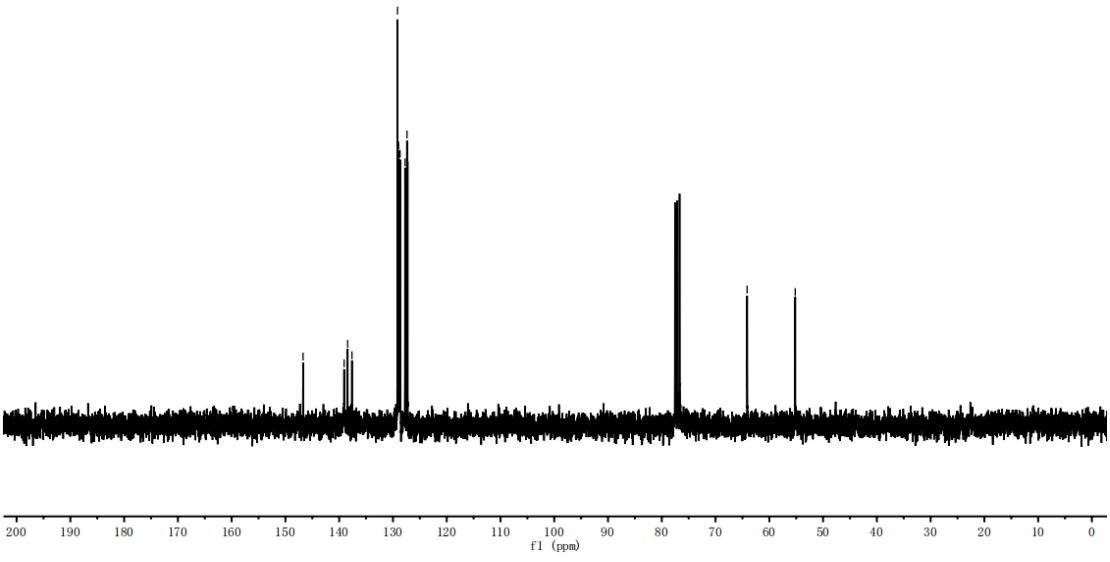
4h



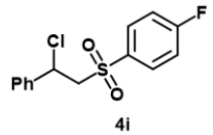
LLX-I-141-2-C



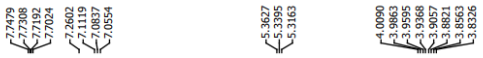
4h

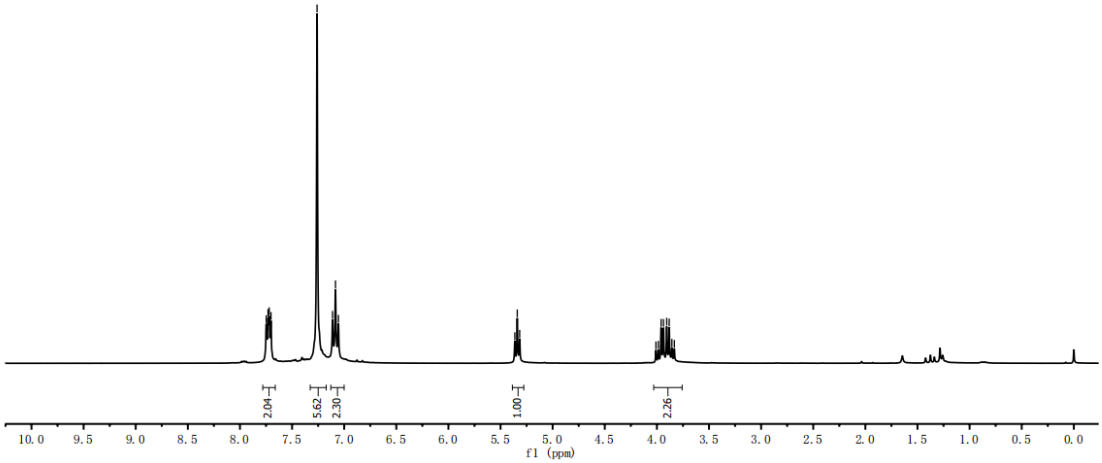


LLX-I-143-5

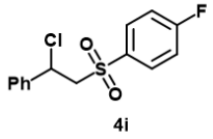


4i

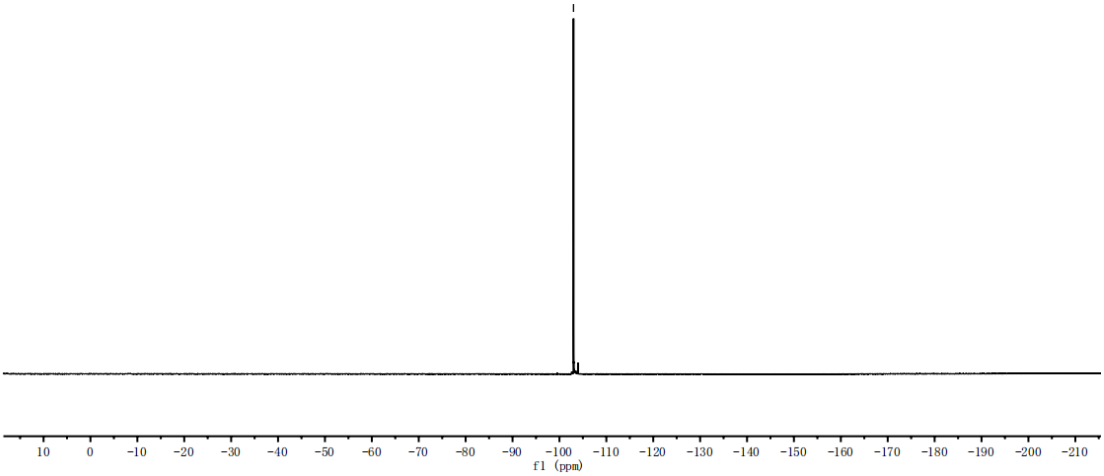




LLX-I-143-5-F

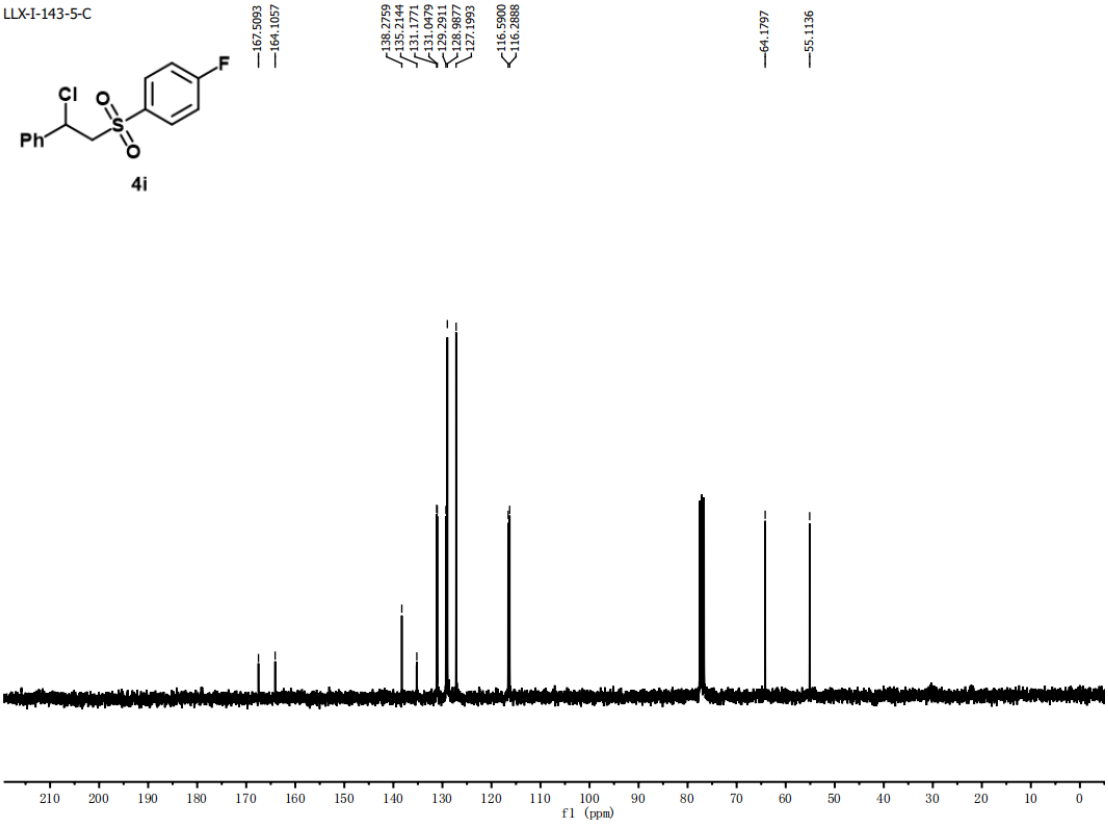


4i



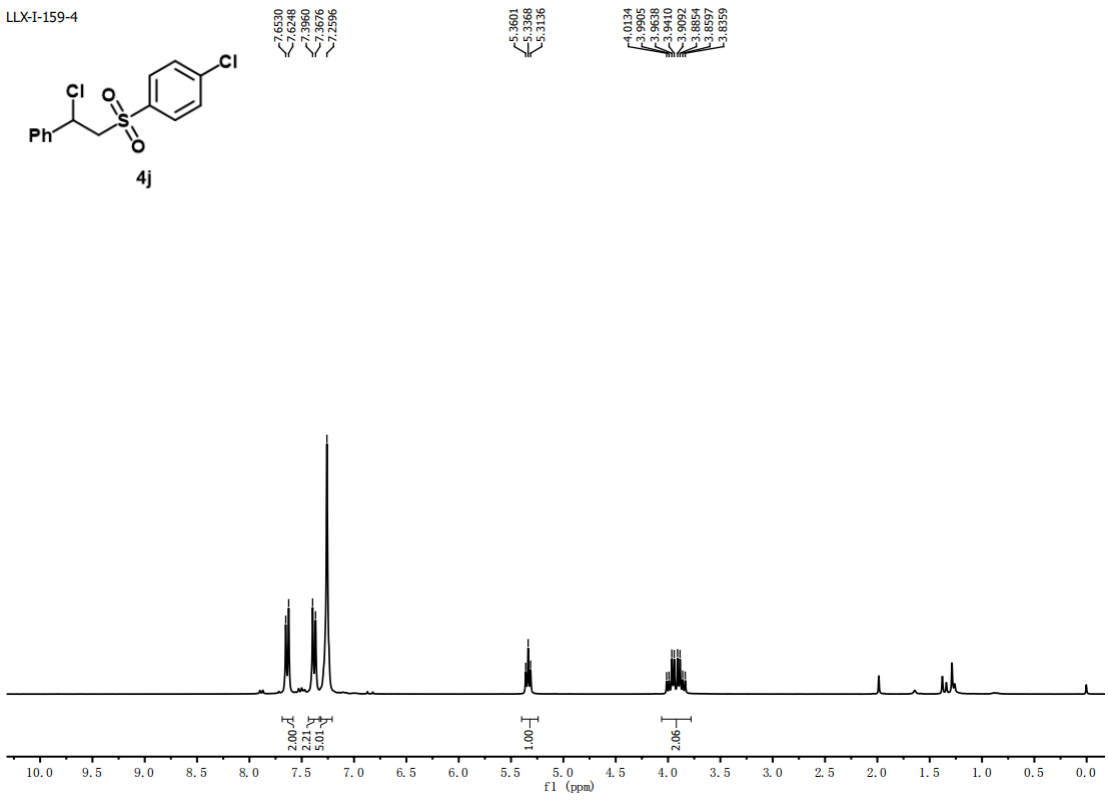
LLX-I-143-5-C

4i



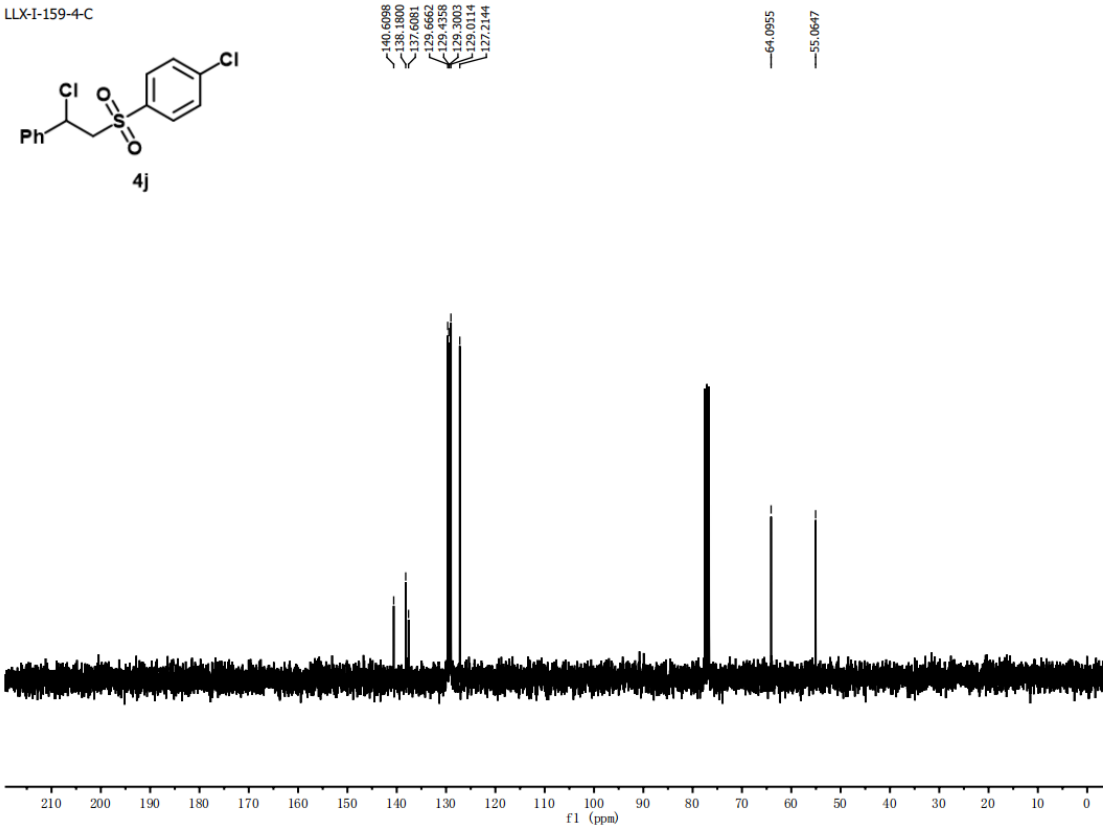
LLX-I-159-4

4j



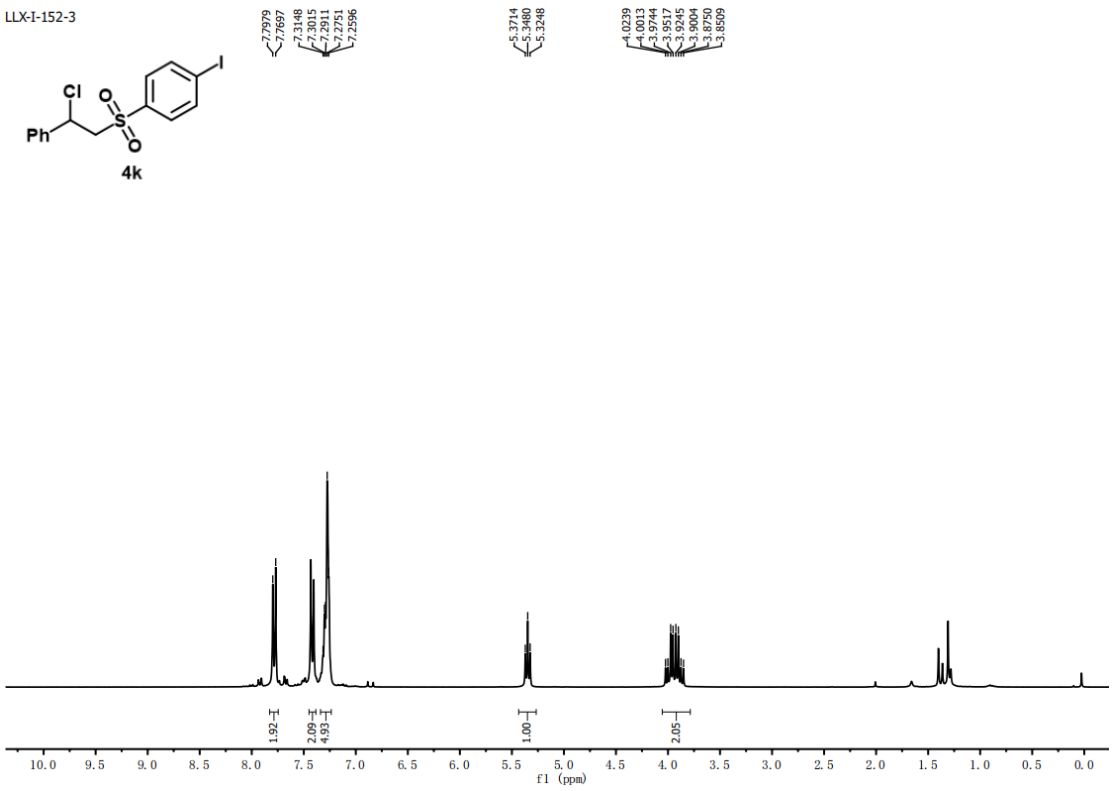
LLX-I-159-4-C

4j



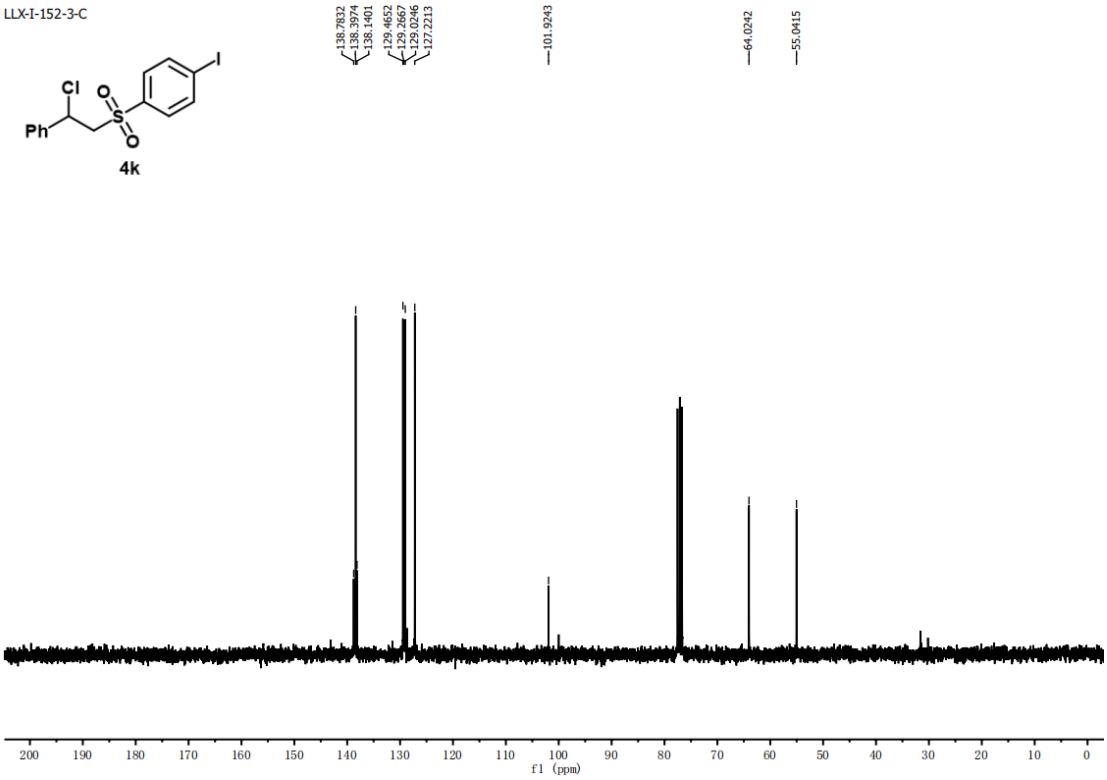
LLX-I-152-3

4k



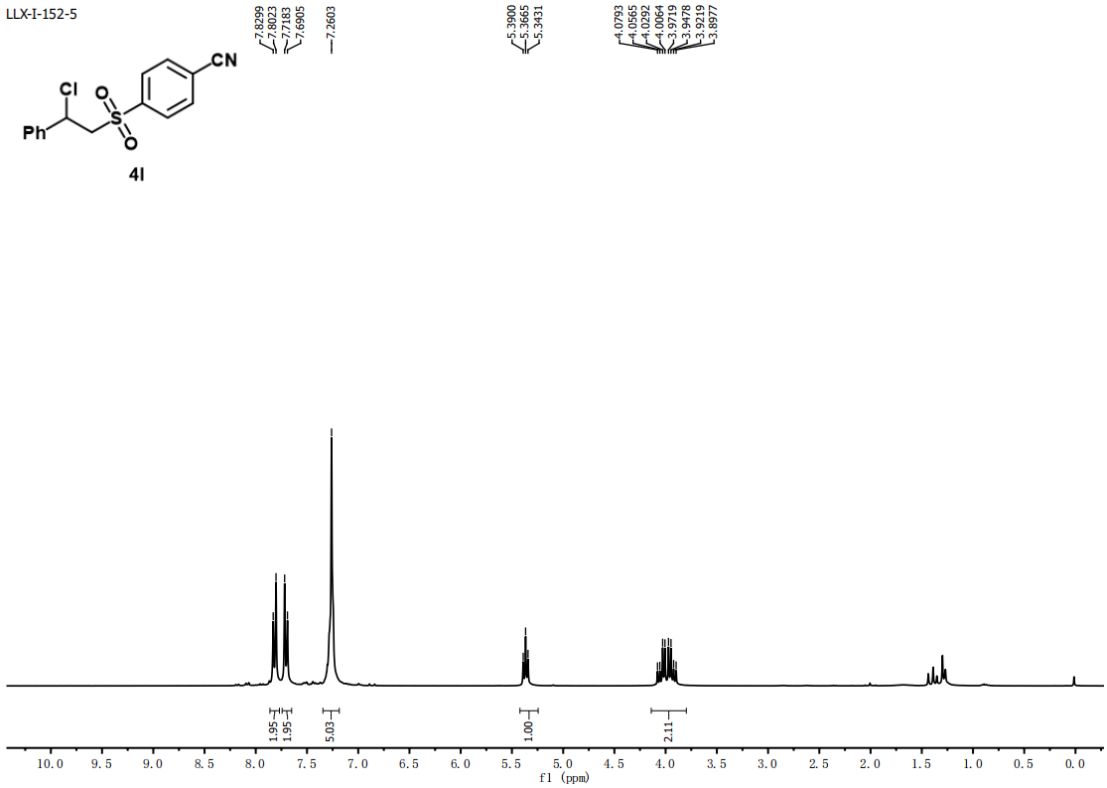
LLX-I-152-3-C

4k



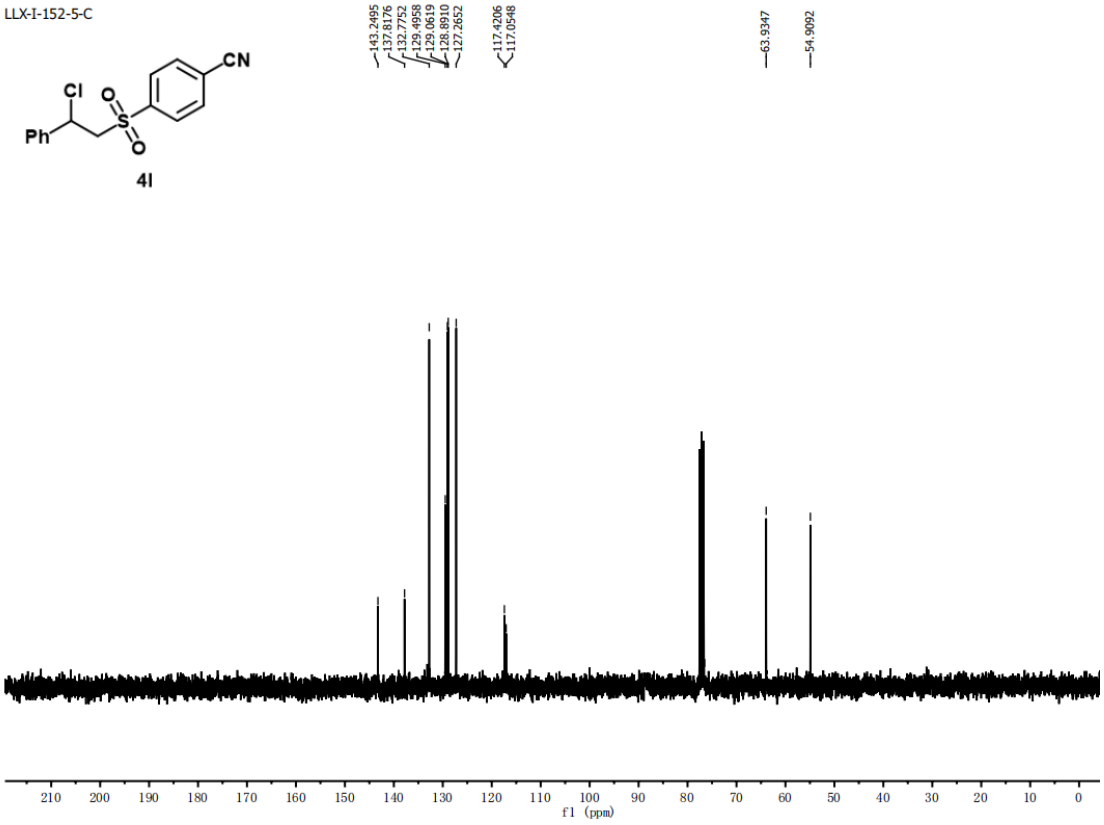
LLX-I-152-5

4l



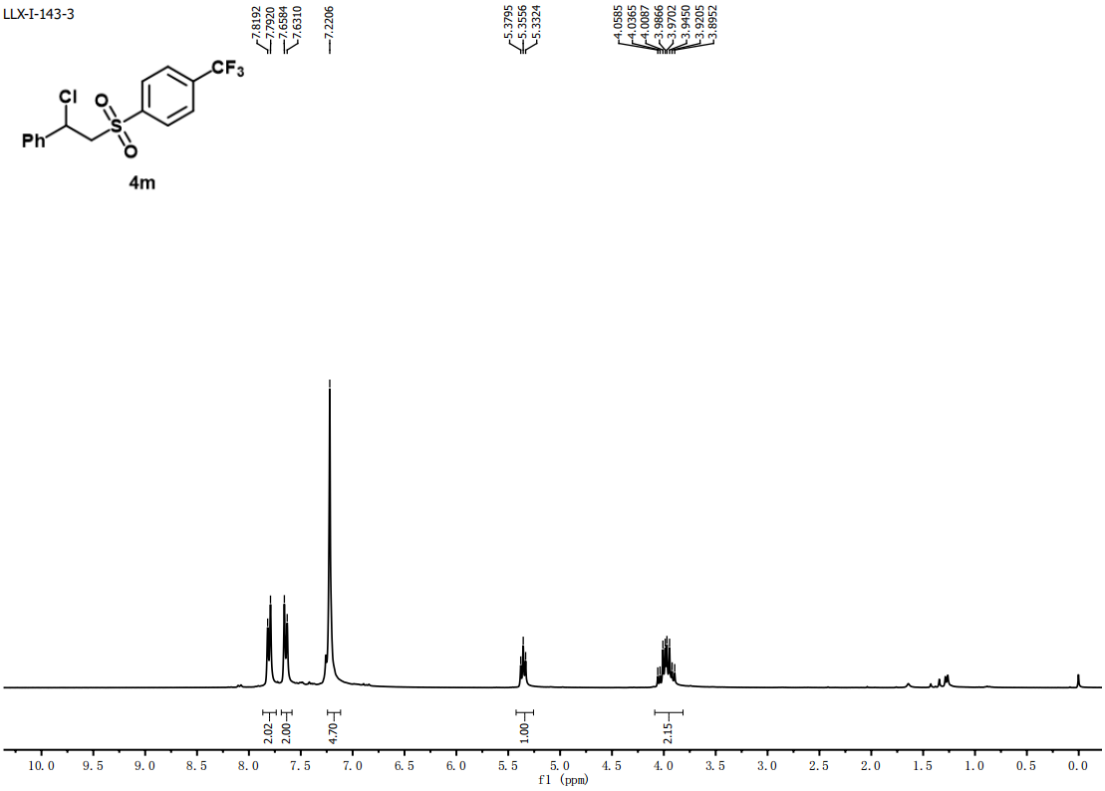
LLX-I-152-5-C

4l



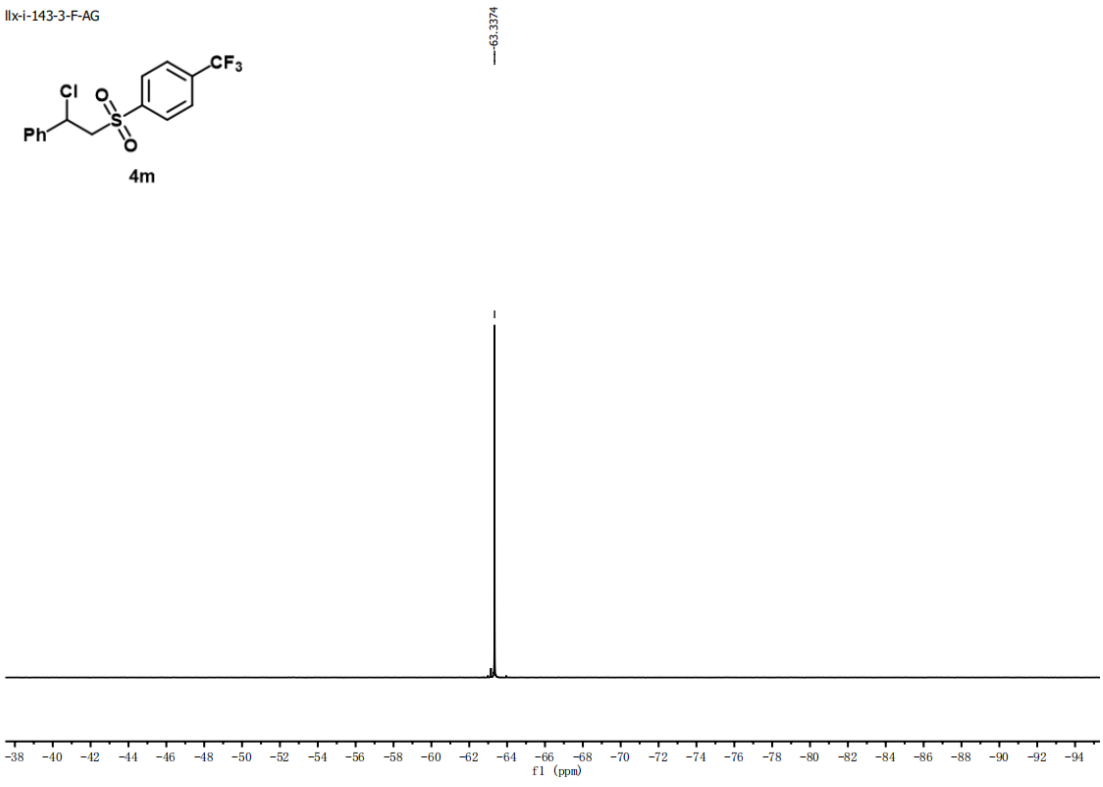
LLX-I-143-3

4m



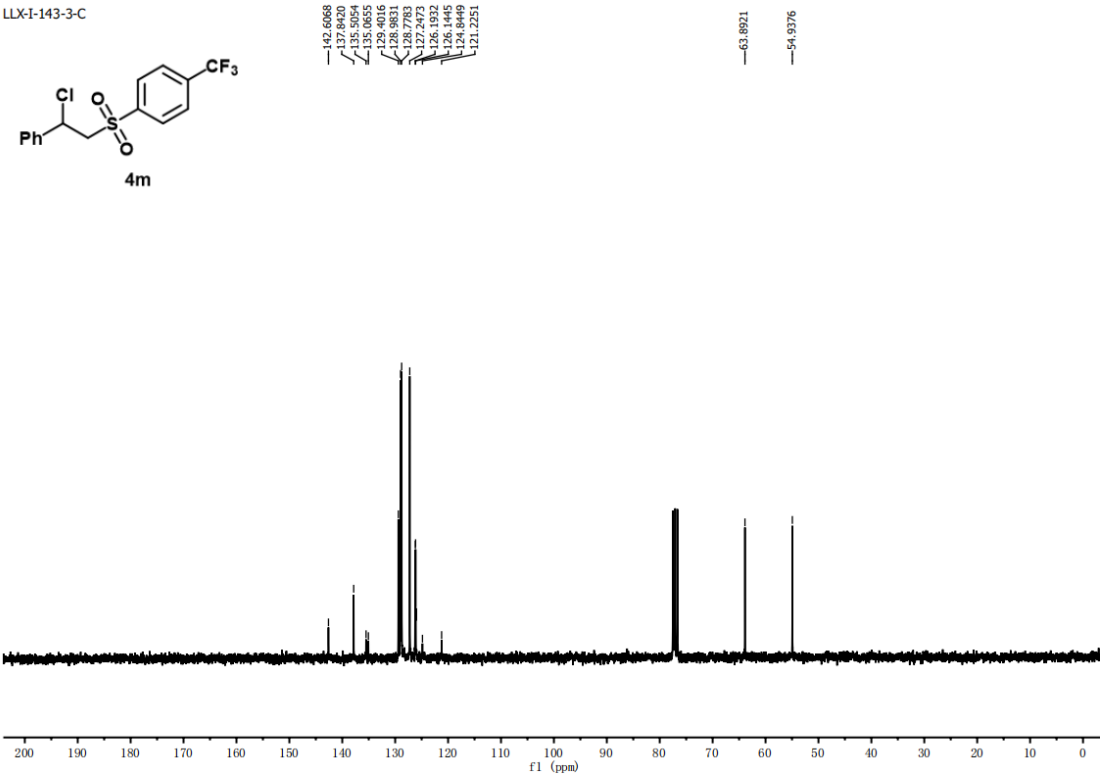
llx-i-143-3-F-AG

4m



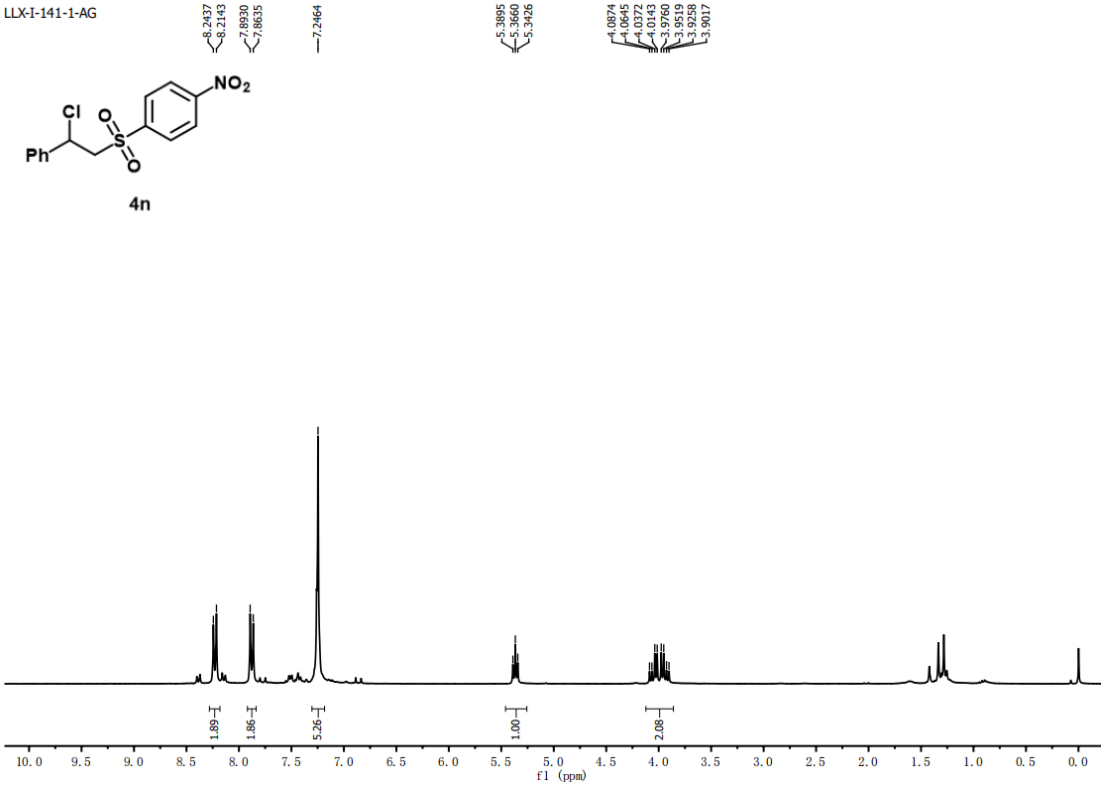
LLX-I-143-3-C

4m



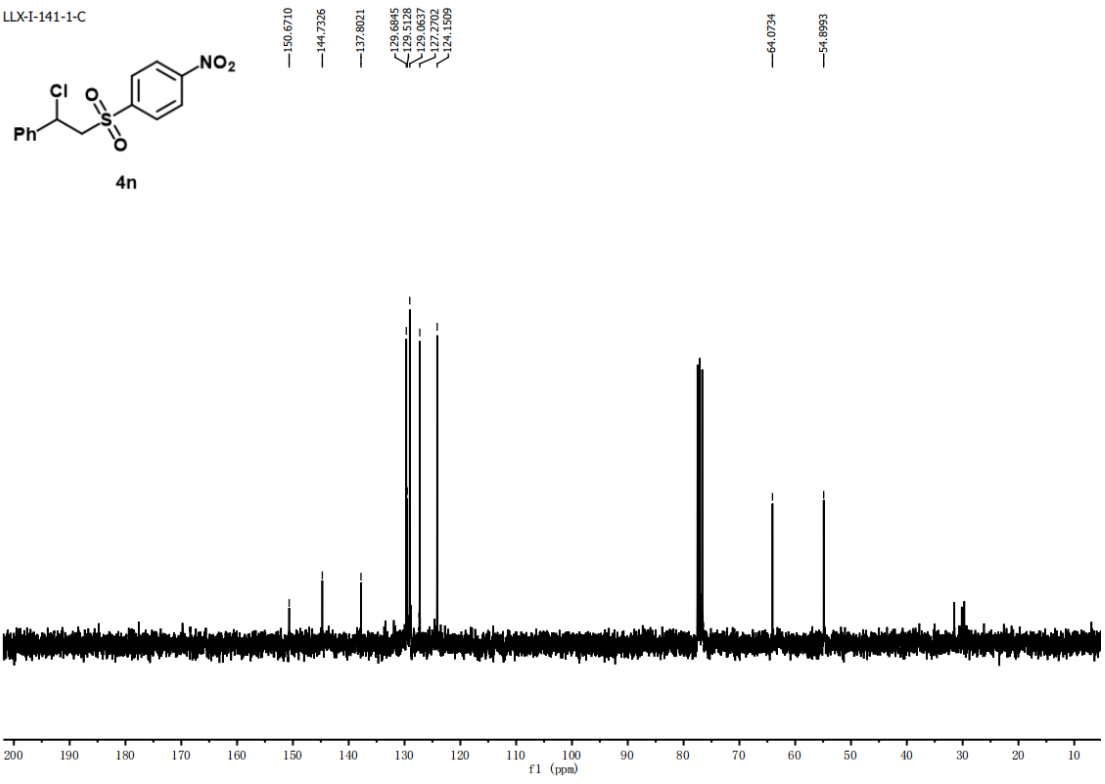
LLX-I-141-1-AG

4n

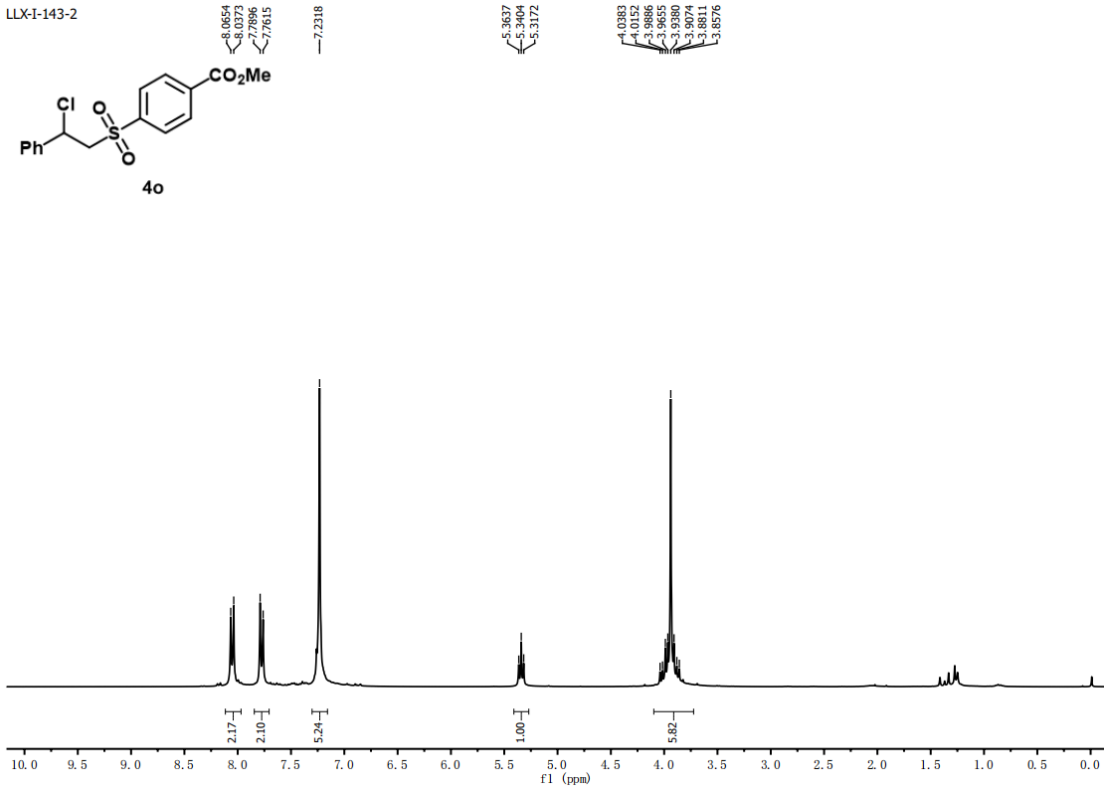


LLX-I-141-1-C

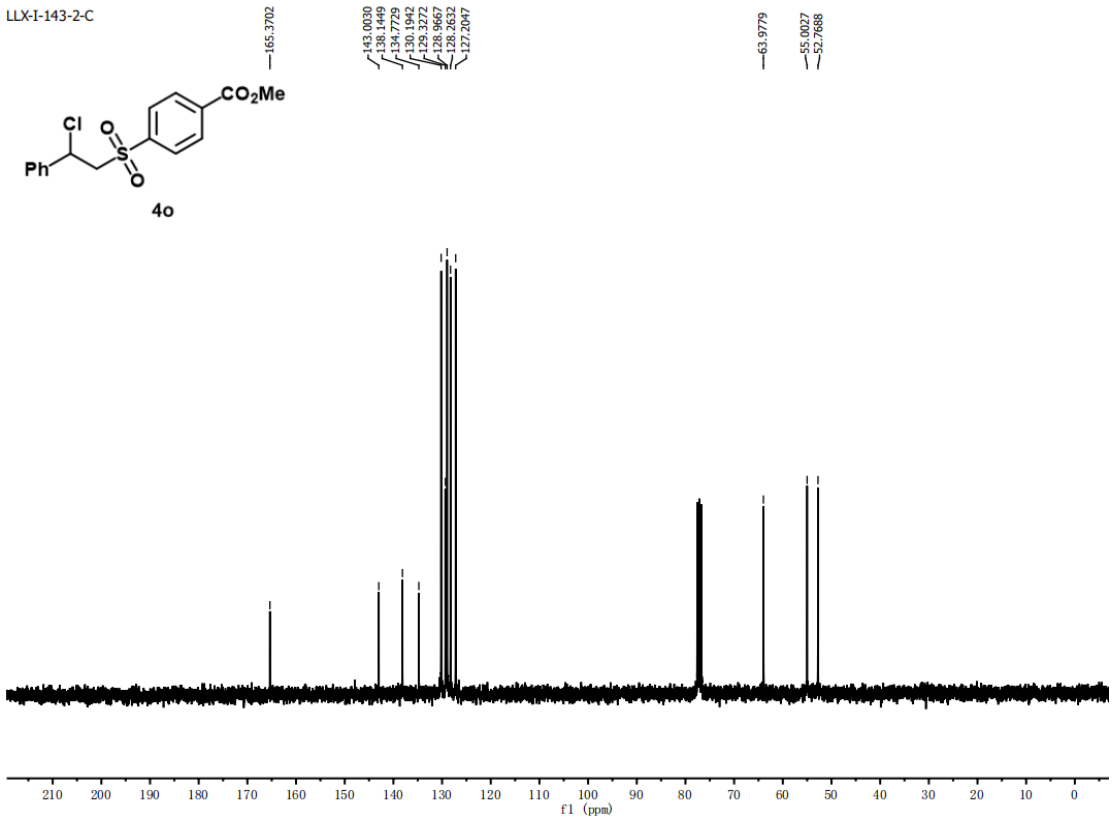
4n



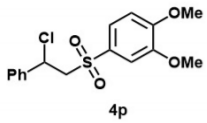
LLX-I-143-2



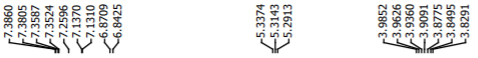
LLX-I-143-2-C

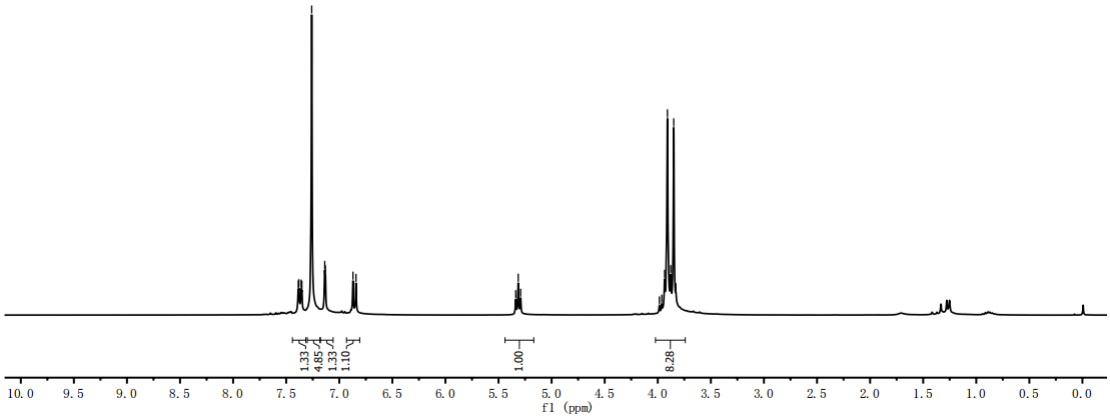


LLX-I-141-3

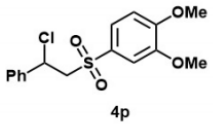


4p

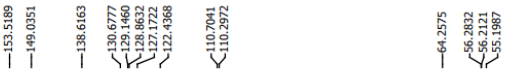


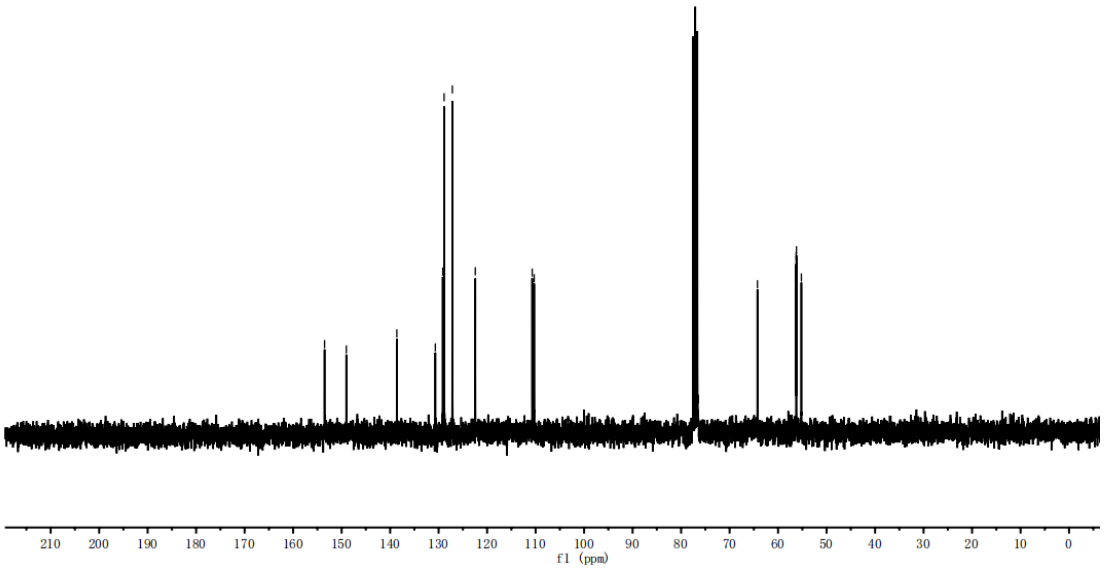


llx-i-141-3-C-A



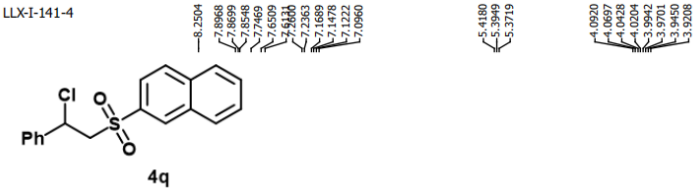
4p

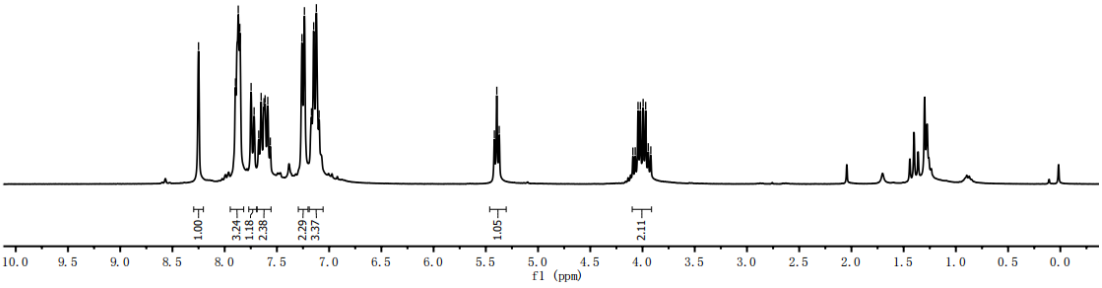




LLX-I-141-4

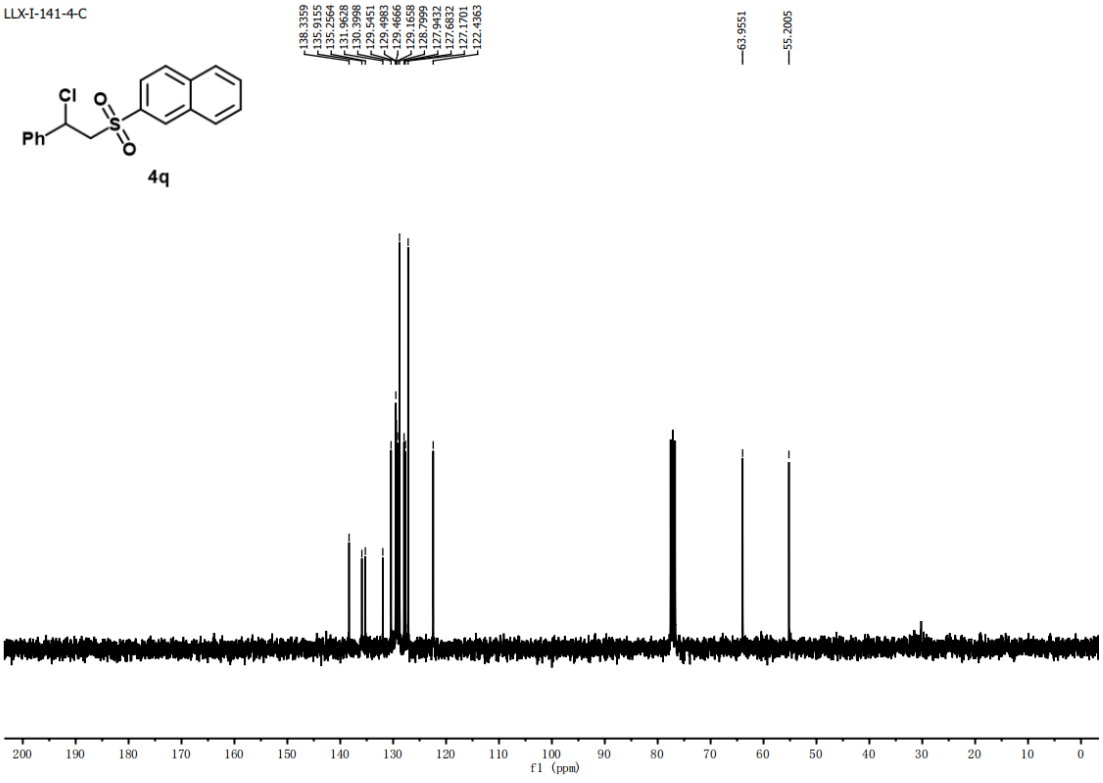
4q





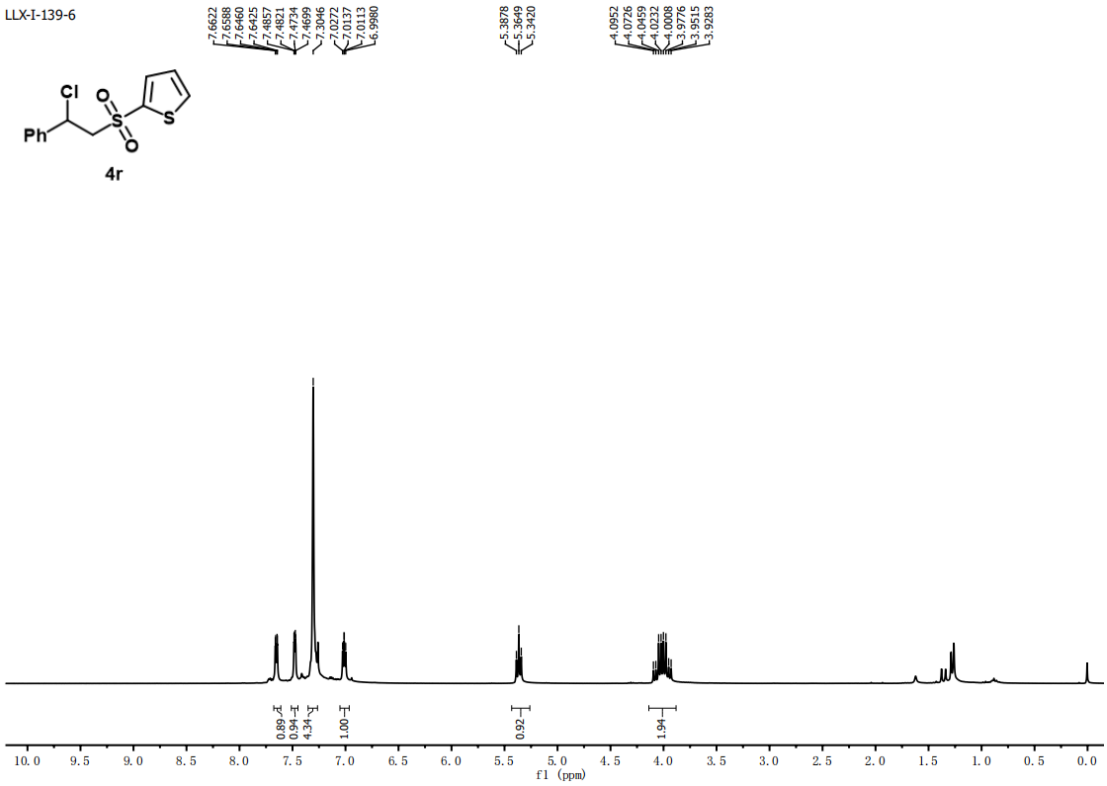
LLX-I-141-4-C

4q



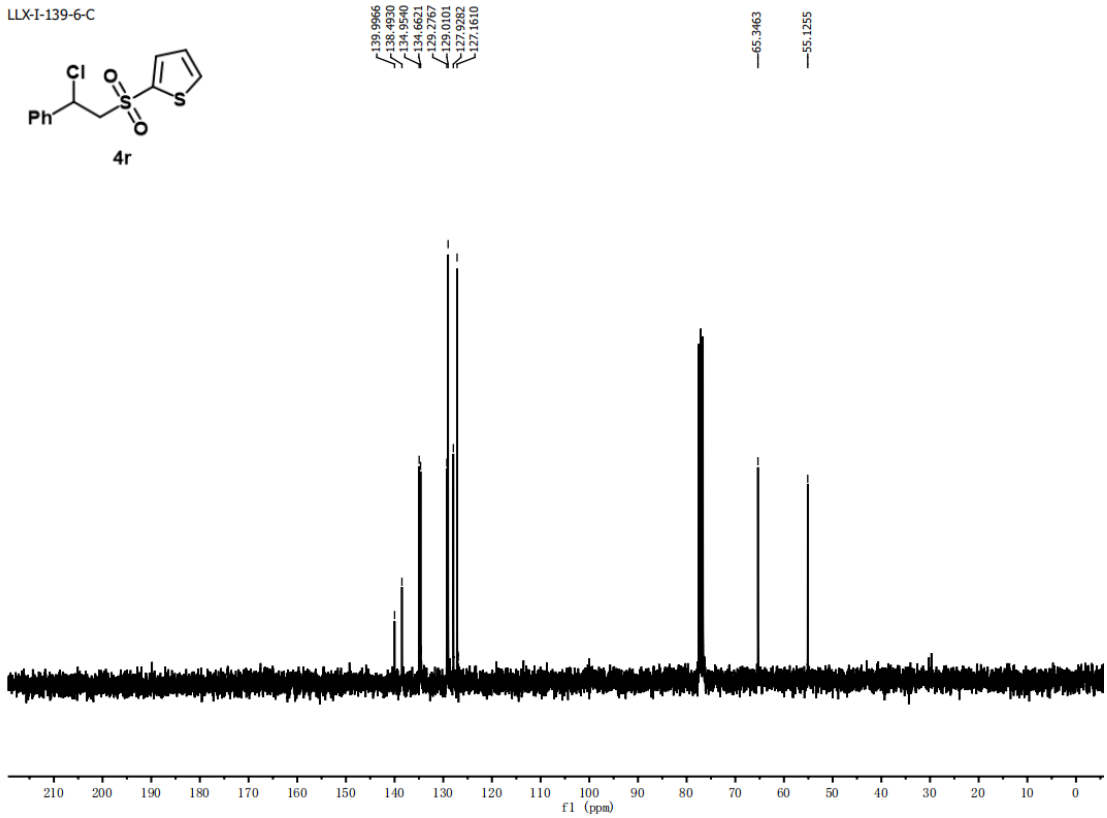
LLX-I-139-6

4r

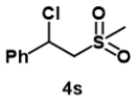


LLX-I-139-6-C

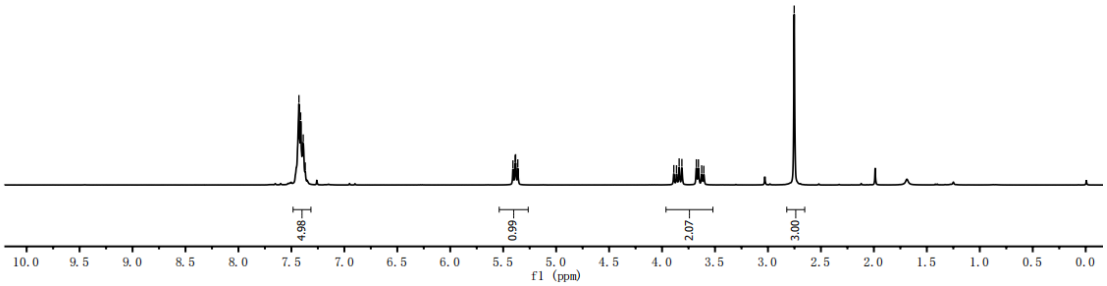
4r



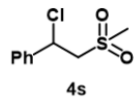
llx-ii-144-5



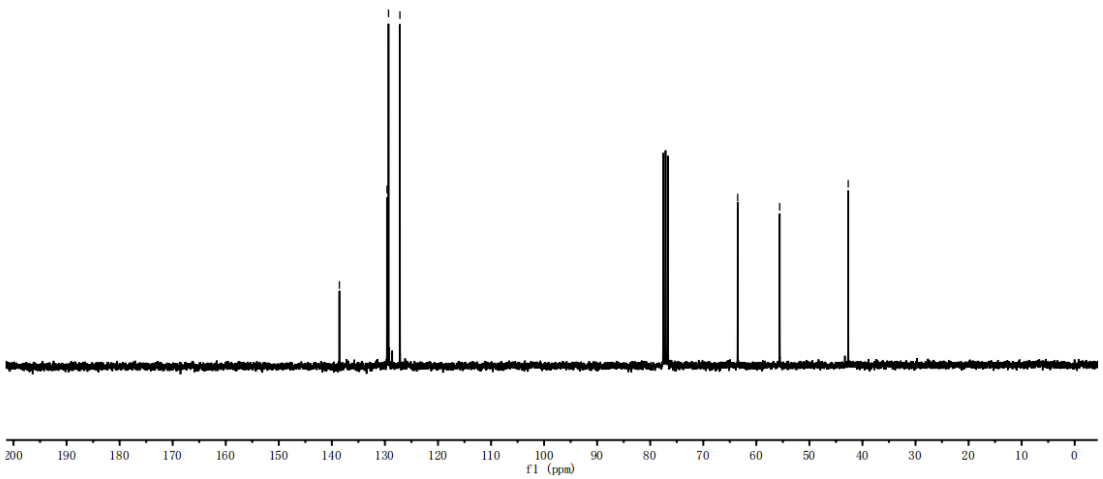
4s

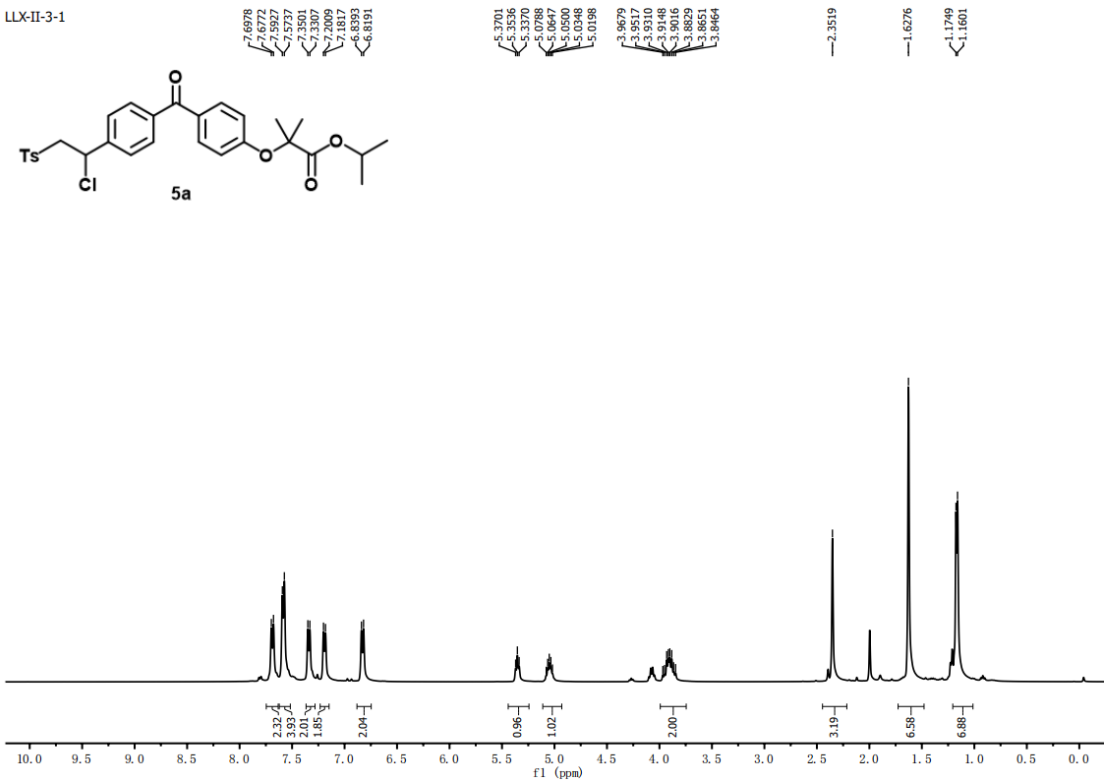


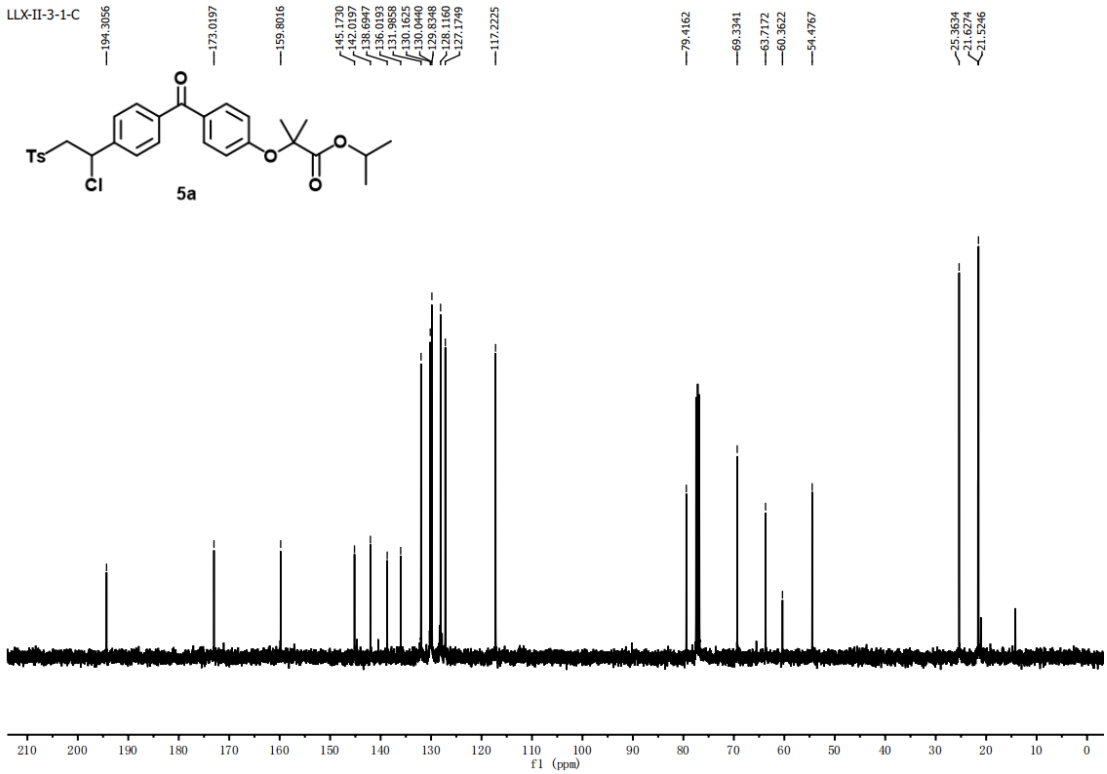
LLX-II-144-5
LLX-II-144-5-C

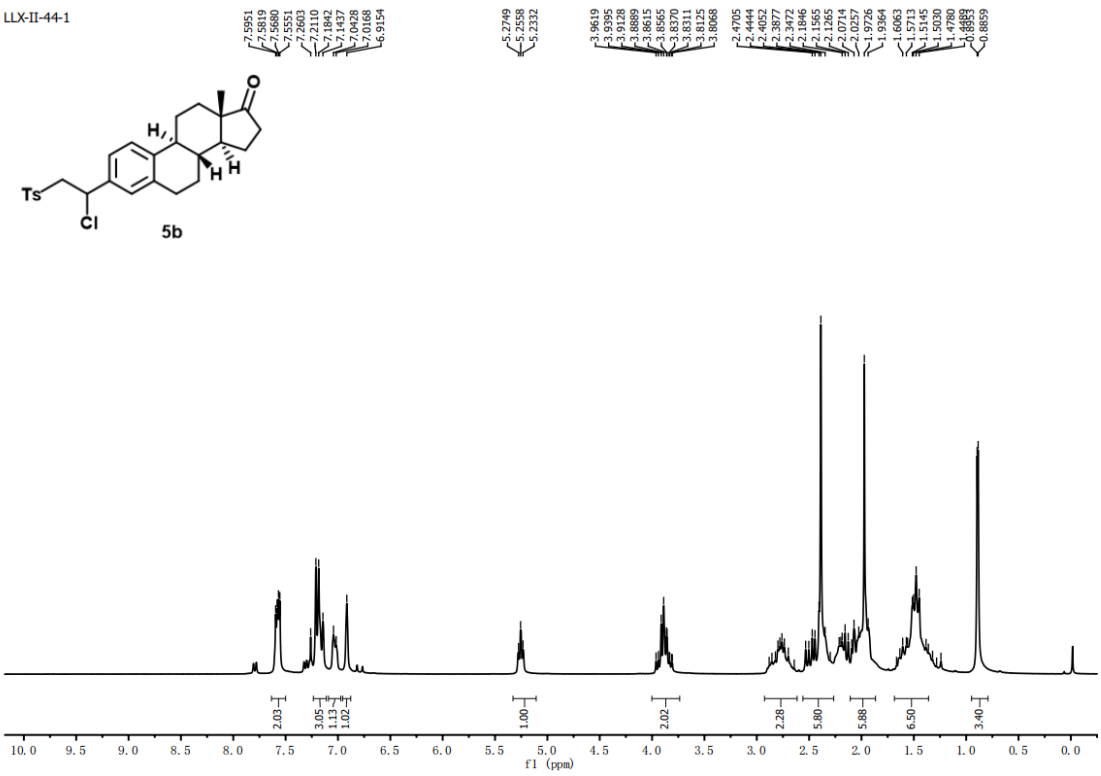


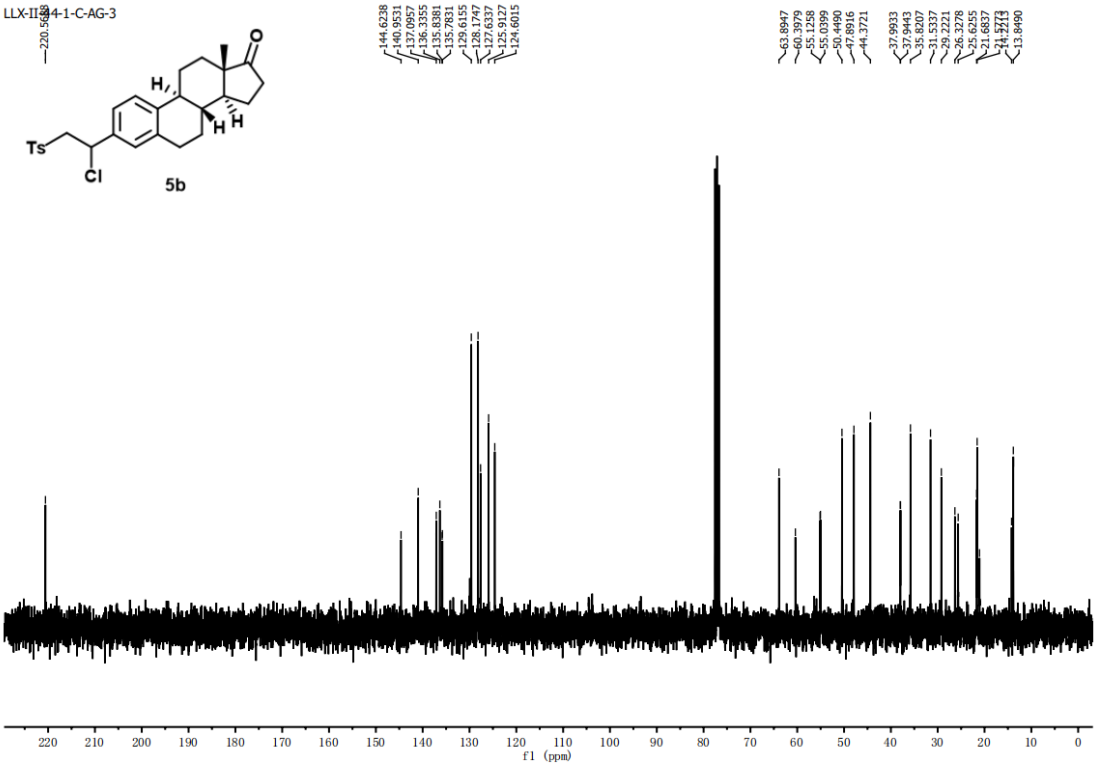
4s




LLX-II-3-1
7.6978
7.6772
7.5927
7.5737
7.3501
7.3300
7.2009
7.1817
6.8393
6.8191
5.3701
5.3556
5.3370
5.0788
5.0647
5.0500
5.0348
5.0198
3.9679
3.9517
3.9310
3.9148
3.9016
3.8829
3.8651
3.8464
2.3519
1.6276
1.1749
1.1601
Ts
Cl
O
O
O
5a
2.32
3.93
2.01
1.85
2.04
0.96
1.02
2.00
3.19
6.58
6.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


LLX-II-3-1-C
194.3056
173.0197
159.8016
145.1730
142.0197
138.6947
136.0193
131.9858
130.1625
130.0440
129.8348
128.1160
127.1749
117.2225
79.4162
69.3341
63.7172
60.3622
54.4767
25.3634
21.6274
21.5246
Ts
Cl
O
O
O
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


LLX-II-44-1
7.5951
7.5819
7.5680
7.5551
7.2603
7.2110
7.1842
7.1437
7.0428
7.0168
6.9154
5.2749
5.2558
5.2332
3.9619
3.9395
3.9128
3.8889
3.8645
3.8515
3.8370
3.8311
3.8125
3.8068
2.4705
2.4444
2.4052
2.3877
2.3472
2.1946
2.1565
2.1365
2.0714
2.0257
1.9726
1.9364
1.6063
1.5713
1.5145
1.5030
1.4780
1.4489
1.4353
0.8859
Ts
Cl
5b
2.03
3.05
1.13
1.02
1.00
2.02
2.28
5.80
5.88
6.50
3.40
f1 (ppm)


LLX-II-44-1-C-AG-3
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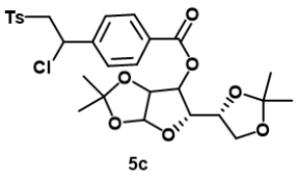
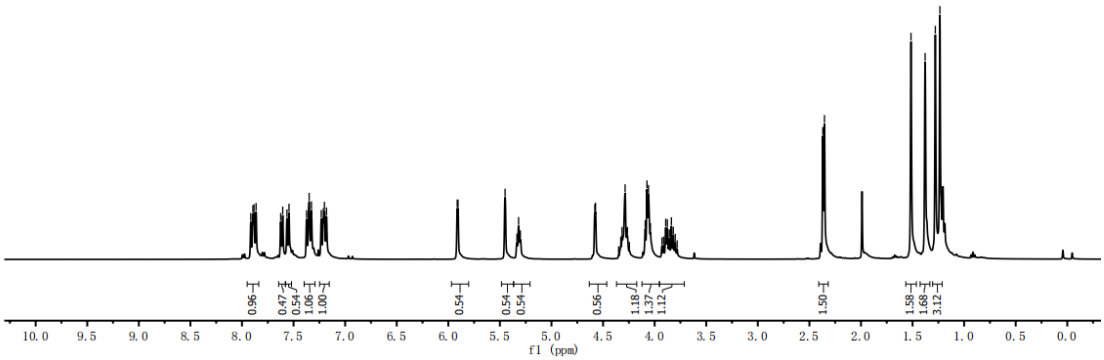
144.6238
140.9531
137.9957
136.3355
135.8381
135.7831
129.6155
128.1747
127.6337
125.9127
124.6015
63.8947
60.3979
55.1258
55.0399
50.4490
47.8916
44.3721
37.9933
37.9443
35.8207
31.5337
29.2221
26.3278
25.6255
21.6837
14.5213
14.2773
13.8490
Ts
Cl
5b
f1 (ppm)

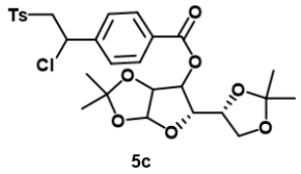
LLX-II-6-2



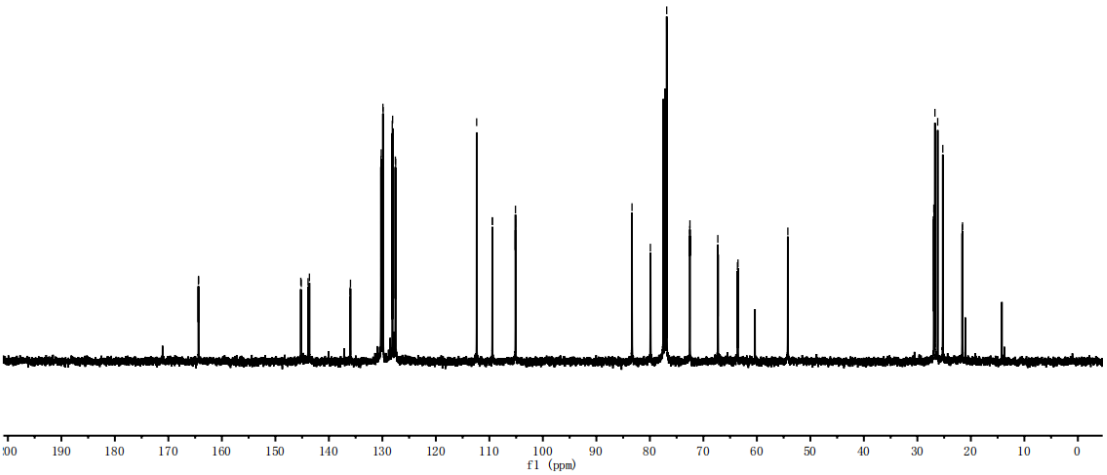
5c

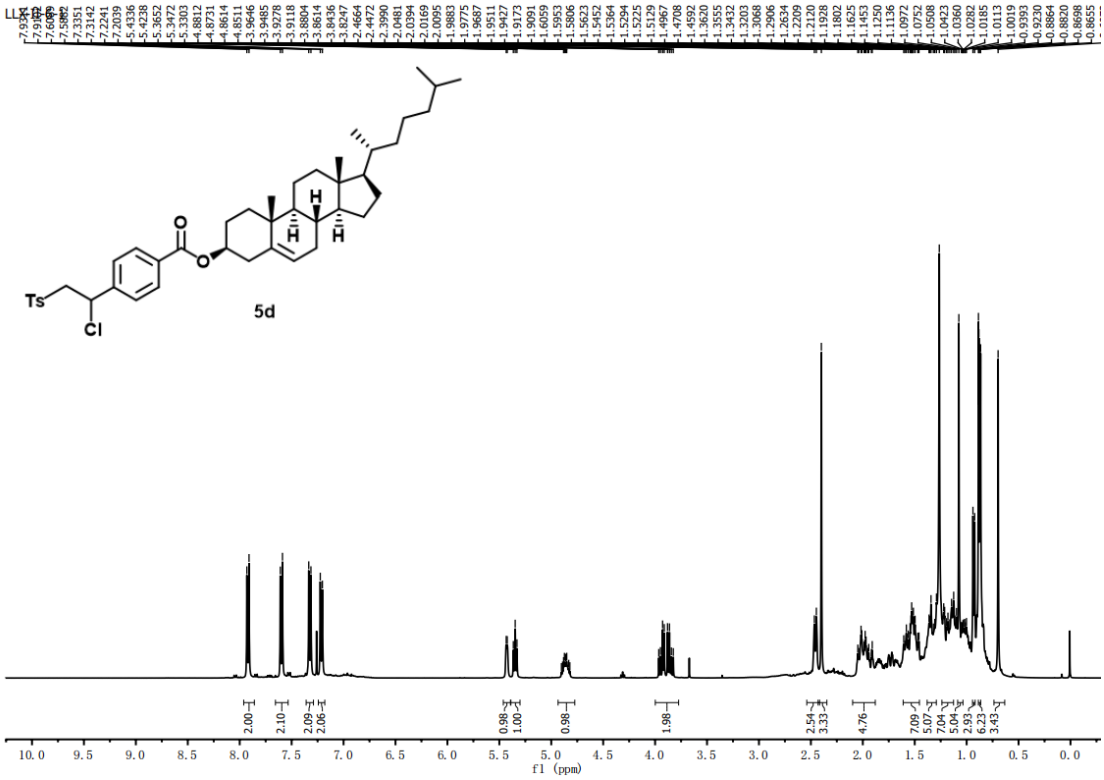


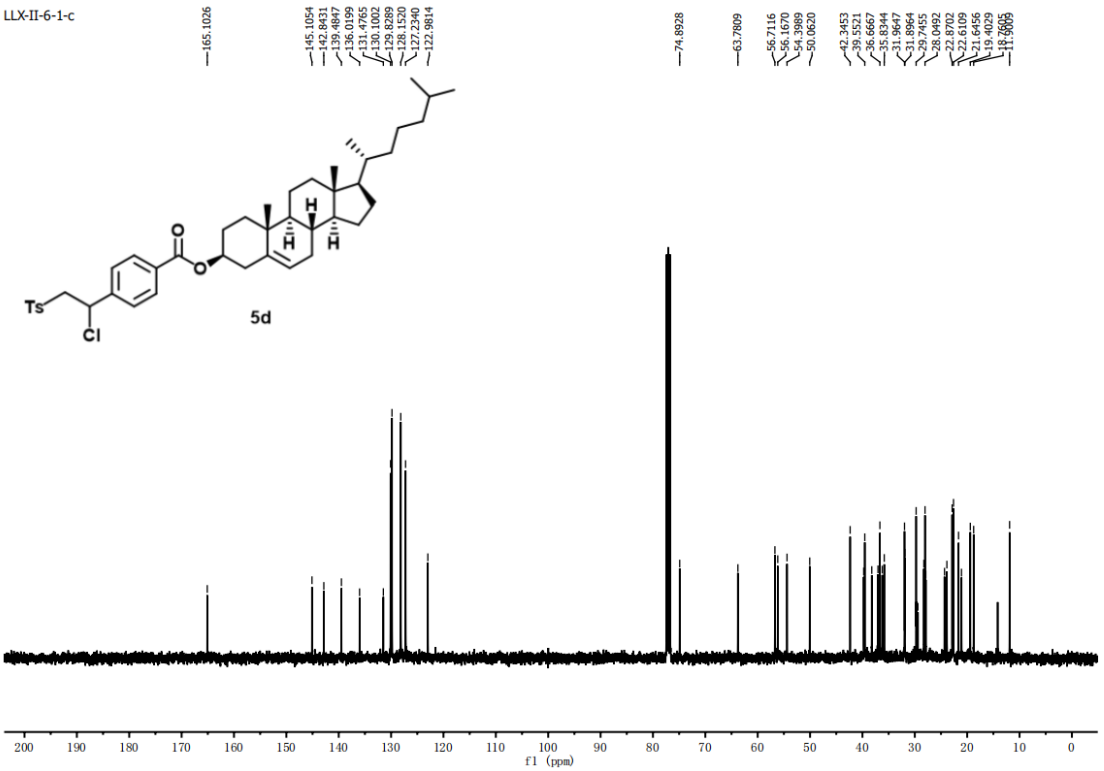
LLX-II-6-2-C

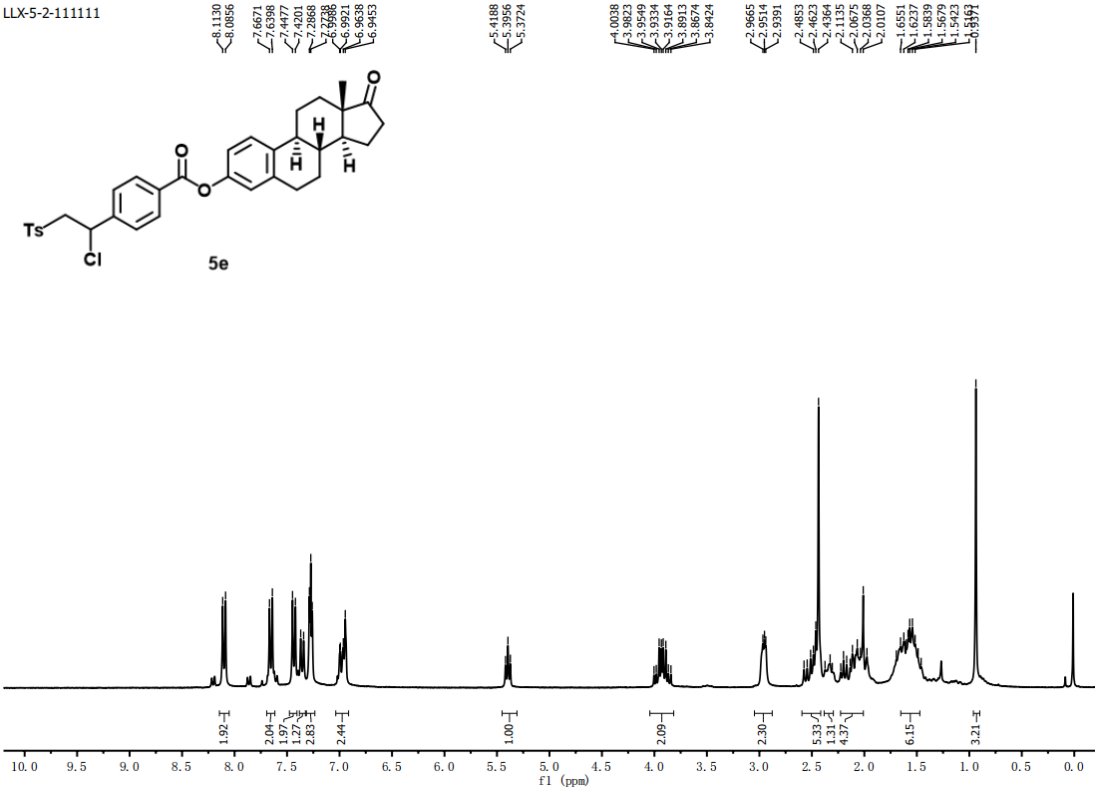


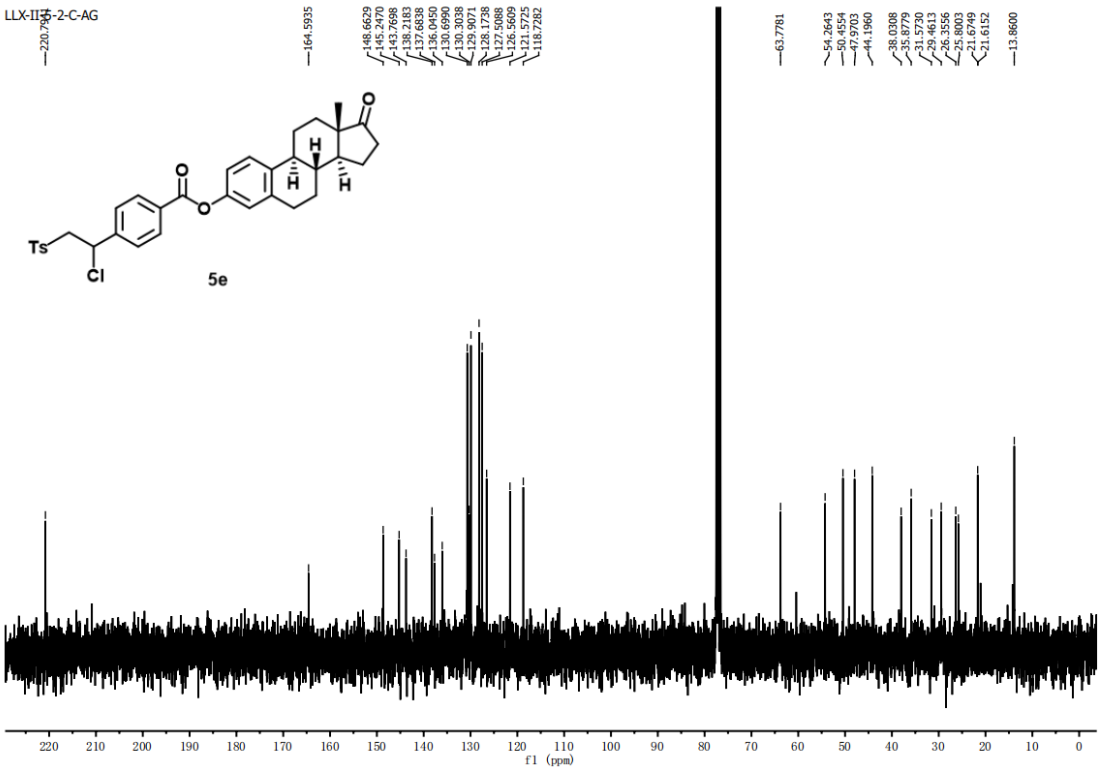
5c



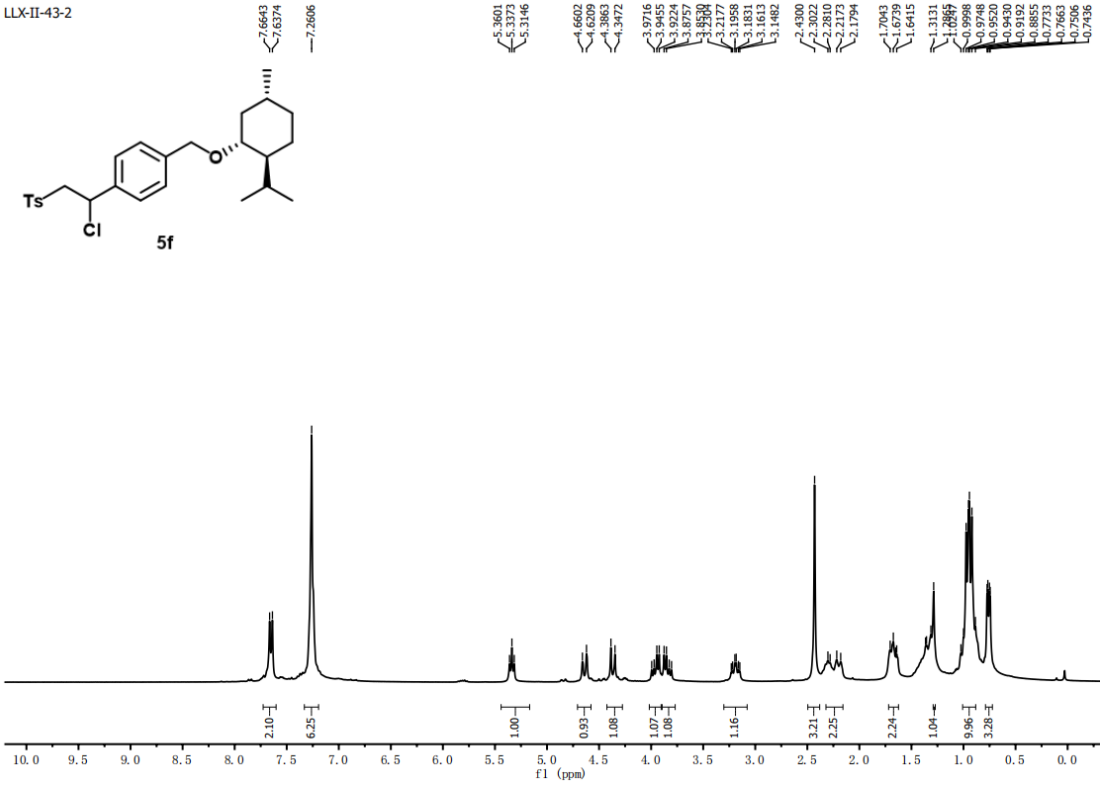

Ts
Cl
5d
f1 (ppm)


LLX-II-6-1-c
Ts
Cl
5d
f1 (ppm)


LLX-5-2-111111
8.1130
8.0856
7.6671
7.6398
7.4477
7.4201
7.2868
6.9921
6.9638
6.9453
5.4188
5.3956
5.3724
4.0038
3.9823
3.9549
3.9334
3.9164
3.8913
3.8674
3.8424
2.9665
2.9514
2.9391
2.4853
2.4623
2.4364
2.1135
2.0775
2.0568
2.0107
1.6551
1.6237
1.5839
1.5679
1.5423
Ts
Cl
5e
1.92
2.04
1.97
1.27
2.83
2.44
1.00
2.09
2.30
5.33
1.31
4.37
6.15
3.21
f1 (ppm)


LLX-III-5-2-C-AG
220.7945
164.5935
148.6629
145.2470
143.7698
138.2183
137.6838
136.0450
130.6990
130.3038
129.9071
128.1738
127.5088
126.5609
121.5725
118.7282
63.7781
54.2643
50.4554
47.9703
44.1960
38.0308
35.8779
31.5730
29.4613
26.3556
25.8003
21.6749
21.6152
13.8600
Ts
Cl
5e
f1 (ppm)

LLX-II-43-2



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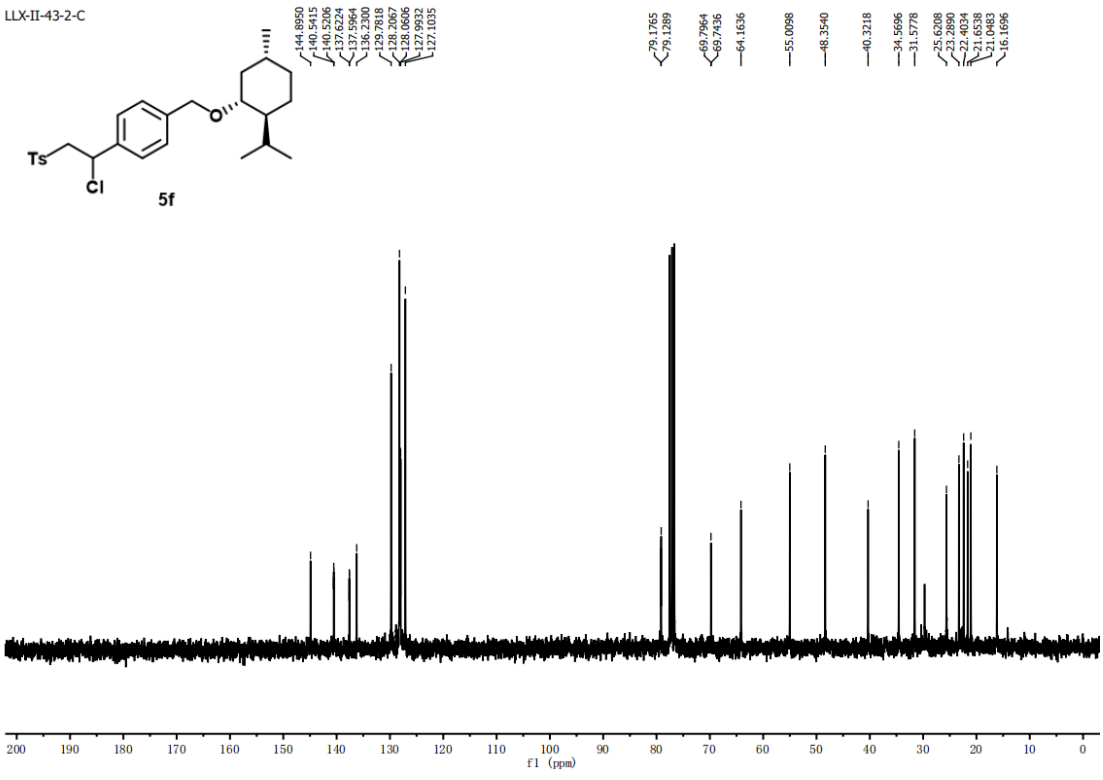
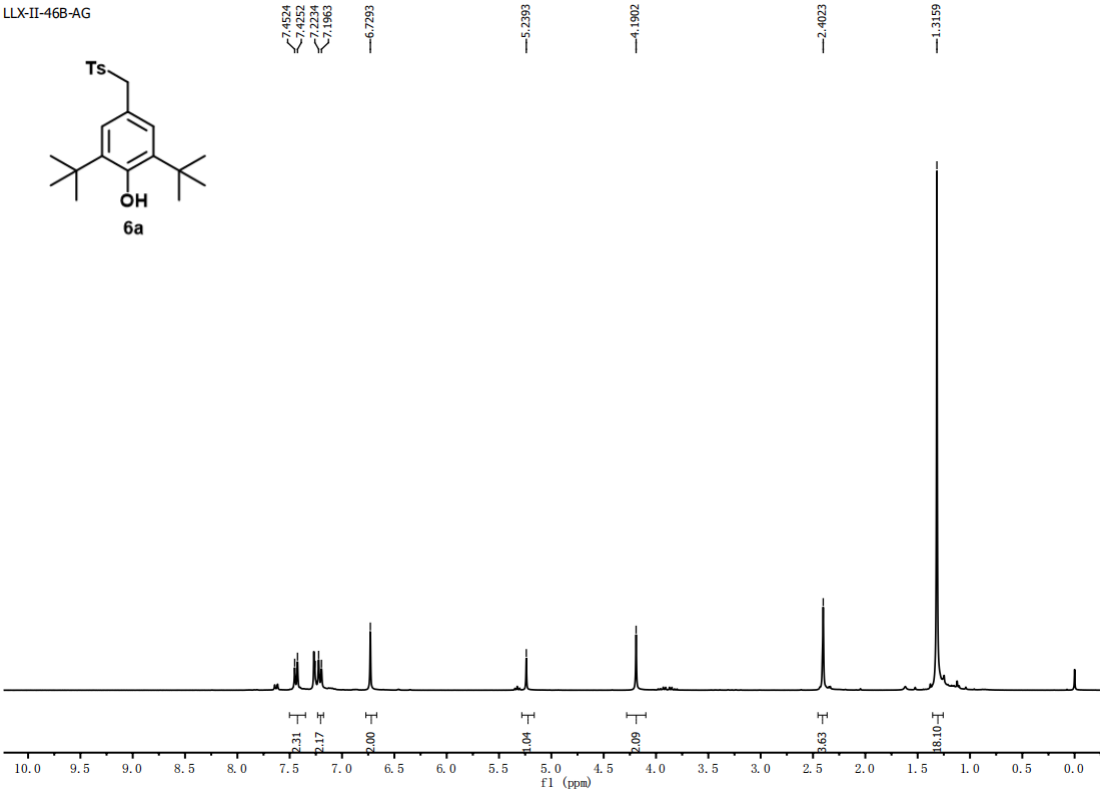


LLX-II-46B-AG

6a



LLX-II-46B-AG-C

6a