SUPPORTING INFORMATION

Sulfination of alcohols with sodium sulfinates promoted by $BF_3 \cdot OEt_2$: an unexpected access

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1. General Information

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 500/125 MHz spectrometer at 20-25 ^{o}C. ^{1}H NMR chemical shifts were reported in ppm using tetramethylsilane (TMS, $\delta = 0.00$ ppm) as the internal standard. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J* value) in Hz and integration. ^{13}C NMR spectra were reported in parts per million using solvent $CDCl_3$ ($\delta = 77.2$ ppm) as an internal standard. All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified. Dichloromethane purchased from chemical supplier was firstly dried over 4Å molecular sieve for one week. Column chromatographys were performed using silica gel, and analytical thin-layer chromatography (TLC) was used to monitor the reactions, performed on silica gel plates.

2. Preparation for starting materials

***p*-Toluenesulfinic acid**[1]: To a 100 mL round flask that was equipped with a stirring bar, sodium *p*-toluenesulfinate (1.78 g, 10 mmol) was dissolved in H_2O (12.5 mL), then added diethyl ether (12.5 mL) and HCl (37%, 0.9 mL). The reaction mixture was stirred during 1 h at room temperature and extracted with diethyl ether (3x 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered with diethyl ether. About half of the diethyl ether was removed to get thick residue under reducing pressure and petroleum ether (20 mL) was added. Then the mixture was filtered to afford *p*-toluenesulfinic acid. Yield: 1.50 g, 96%. The white product was kept at -20 ^{o}C under nitrogen.

Sodium 4-chlorobenzene sulfinate 2d[2]: To a 100 mL round flask that was equipped with a stirring bar, 4-chlorobenzenesulfonyl chloride (2.11 g, 10 mmol), sodium sulfite (2.52 g, 20 mmol) and sodium bicarbonate (1.68 g, 20 mmol) were took in water (10.0 mL) at 80 ^{o}C. After 4 h, the stiring stoped, reaction mixture cooled to room temperature, water was removed to get thick residue under vacuum and the residue was extracted in ethanol. Then recrystallization from ethanol afforded Sodium 4-chlorobenzene sulfinate **2d** (1.39 g, 70%).

The other sodium sulfinates **2c**, **2e**, **2f** and **2g** were also prepared their sulfonyl chlorides using the similar methods.

3. Experimental Procedures

Procedure for sulfination of alcohols with sodium sulfinates

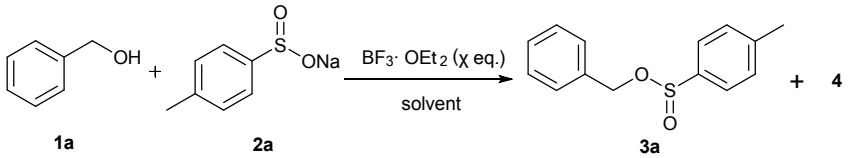
To a 50 mL round flask that was equipped with a stirring bar, sodium *p*-toluenesulfinate (0.65 mmol, 115.8 mg, 1.3 equiv) was dissolved in 1.5 mL of dichloromethane in the atmosphere. Then alcohols (0.5 mmol, 1 equiv) and $BF_3{\cdot}OEt_2$ (0.9 mmol, 113.5 μL 1.8 equiv) were added in the round flask. Then the reaction mixture was heated in oil bath of 50 °C and the stiring was turned on. After 3 h, the stiring stoped, reaction mixture cooled to room temperature, and the dichloromethane was removed to get thick residue under reducing pressure. The resulting residue was purified by thin column chromatography on silica gel column using EtOAc−petroleum ether solution as eluent to afford sulfinates.

Procedure for sulfination of alcohols with benzenesulfinic acid

To a 50 mL round flask that was equipped with a stirring bar, *p*-toluenesulfinic acid (0.65 mmol, 101.5 mg, 1.3 equiv) was dissolved in 1.5 mL of dichloromethane in the atmosphere. Then benzyl alcohols **1a** (0.5 mmol, 52.0 μL, 1 equiv) and $BF_3{\cdot}OEt_2$ (0.1 mmol, 12.3 μL 0.2 equiv) were added in the round flask. Then the reaction mixture was heated in oil bath of 50 °C and the stiring was turned on. After 3 h, the stiring stoped, reaction mixture cooled to room temperature, and the dichloromethane was removed to get thick residue under reducing pressure. The resulting residue was purified by thin column chromatography on silica gel column using EtOAc−petroleum ether solution as eluent to afford sulfinate **3a** (99.7 mg, 81%).

4. Experimental data

Table S1. Optimization of reaction conditions.[a]



Entry	χ	**2a** (eq)	Solvent	V (mL)	*T*(°C)	*t*(h)	**3a** Conv.[b] (%)	**3a** Yield[b] (%)	**4** Yield[c] (%)
1	1.2	1.2	CH_2Cl_2	1.0	45	3	47	44	12
2	1.2	1.2	CH_2Cl_2	1.5	45	3	55	54	10
3	1.2	1.2	CH_2Cl_2	2.0	45	3	51	49	9
4	1.8	1.0	CH_2Cl_2	1.5	45	3	54	52	< 1
5	1.8	1.2	CH_2Cl_2	1.5	45	3	72	70	10
6	1.8	1.3	CH_2Cl_2	1.5	45	3	83	80	12
7	18	1.4	CH_2Cl_2	1.5	45	3	75	72	17
8	1.8	1.6	CH_2Cl_2	1.5	45	3	70	68	26

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (specified), $BF_3{\cdot}OEt_2$ (specified), solvent (specified). [b] Determined by ^{1}H NMR spectroscopy using anisole as an internal standard and on the basis of **1a**. [c] Determined by ^{1}H NMR spectroscopy using anisole as an internal standard and on the basis of **2a**.

5. X-ray structure of 3D (CCDC 1439352)

Table S2. Crystallographic data

	3D
Empirical formula	$C_{26}H_{34}O_3S$
M	426.61
Crystal system	Orthorhombic
Space group	$\boldsymbol{P}2_12_12$
a (Å)	9.7748 (10)
b (Å)	36.406 (3)
c (Å)	6.5704 (6)
α (°)	90.00
β(°)	90.00
γ(°)	90.00
V/Å^3	2338.2 (4)
Z	4
D_c/g cm^{-3}	1.212
μ/mm^{-1}	0.162

θ (max) (°)	27.46
h, k, l, max	12, 47, 8
F(000)	920
R_1,[a] wR_2[b] [$I>2\sigma(I)$]	0.0566, 0.1695

[a] $R = \Sigma(||Fo| - |Fc||)/\Sigma|Fo|$. [b]$Rw = \{\Sigma w[(Fo^2 - Fc^2)^2]/\Sigma w[(Fo^2)^2]\}^{1/2}$.

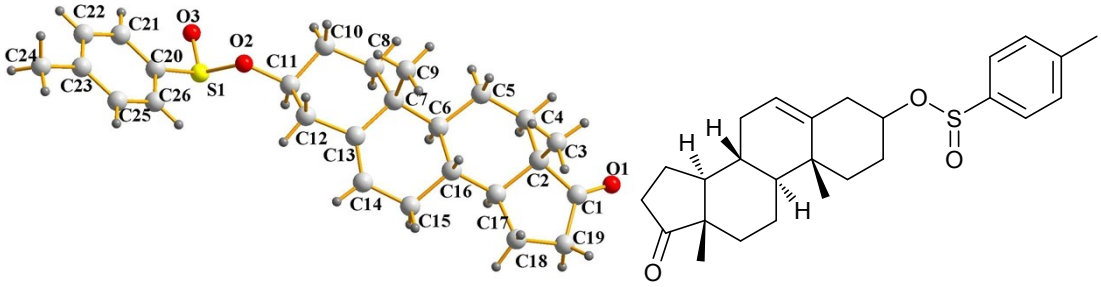
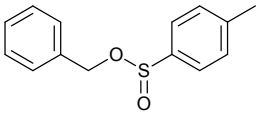
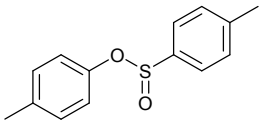


Figure S1. X-ray structure of **3D** (CCDC 1439352)

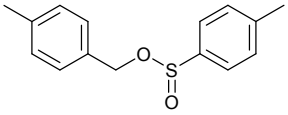
6. Characterizations of Compounds



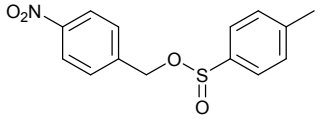
Benzyl 4-methylbenzenesulfinate (3a): Yellow liquid; 87% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.35-7.26 (m, 7H), 5.03 (d, J = 11.0 Hz, 1H), 4.55 (d, J = 11.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 141.8, 135.7, 129.9, 129.9, 128.7, 128.6, 125.5, 65.8, 21.7.



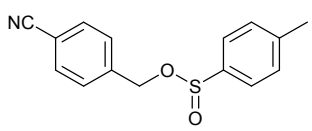
4-Methylphenyl *p*-toluenesulfinate (4): White solid; m.p. 121.3-123.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 142.2, 140.7, 136.7, 130.4, 129.5, 127.8, 124.8, 21.8, 21.7.



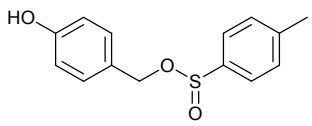
4-Methylbenzyl 4-methylbenzenesulfinate (3b): Yellow liquid; 83% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.15 (q, J = 8.0 Hz, 4H), 4.99 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 11 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 141.9, 138.5, 132.7, 129.9, 129.4, 128.9, 125.5, 65.9, 21.7, 21.3.



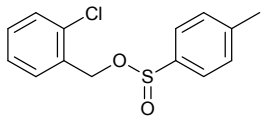
4-Nitrobenzyl 4-methylbenzenesulfinate (3c): Yellow liquid; 73% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dt, *J* = 9.0 Hz, 2.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 11.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.09 (d, *J* = 13.0 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 143.6, 143.3, 141.2, 130.1, 128.8, 125.5, 123.9, 63.5, 21.7.



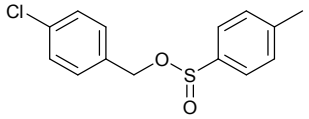
4-Cyanobenzyl 4-methylbenzenesulfinate (3d): Yellow liquid; 65% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.61 (m, 4H), 7.37 (t, *J* = 8.0 Hz, 4H), 5.04 (d, *J* = 12.5 Hz, 1H), 4.56 (d, *J* = 12.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 141.23, 141.20, 132.4, 130.1, 128.7, 125.4, 118.7, 112.2, 63.9, 21.7.



4-Hydroxybenzyl 4-methylbenzenesulfinate (3e): White solid; 37% Yield; m.p. 186.9-188.9 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.95 (dt, *J* = 8.5, 3 Hz, 2H), 6.72 (dt, *J* = 8.5, 3 Hz, 2H), 5.53 (s, 1H), 4.22 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 144.8, 135.1, 132.4, 129.7, 128.8, 120.2, 115.7, 62.4, 21.8.

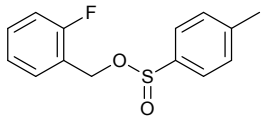


2-Chlorobenzyl 4-methylbenzenesulfinate (3f): Yellow liquid; 82% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.39-7.34 (m, 4H), 7.26-7.24 (m, 2H), 5.14 (d, *J* = 12 Hz, 1H), 4.72 (d, *J* = 12.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 141.6, 133.9, 133.7, 130.1, 129.95, 129.90, 129.7, 127.1, 125.5, 63.3, 21.7.

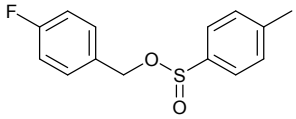


4-Chlorobenzyl 4-methylbenzenesulfinate (3g): Yellow liquid; 95% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 4.97 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H),

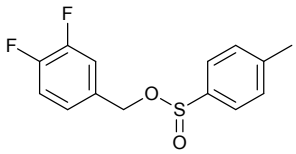
2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 141.7, 134.5, 134.3, 130.04, 129.99, 128.9, 125.5, 64.7, 21.7.



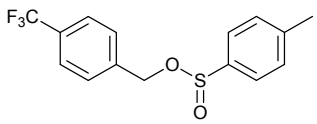
2-Fluorobenzyl 4-methylbenzenesulfinate (3h): Yellow liquid; 78% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.35-7.28 (m, 4H), 7.11 (t, J = 7.0 Hz, 1H), 7.03 (t, J = 8.5 Hz, 1H), 7.03 (d, J = 8.5 Hz, 1H), 5.08 (d, J = 11.5 Hz, 1H), 4.67 (d, J = 11.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1 (d, $J_{C\text{-}F}$ = 247.3 Hz, 1C), 143.1, 141.6, 131.1 (d, $J_{C\text{-}F}$ = 3.6 Hz, 1C), 130.6 (d, $J_{C\text{-}F}$ = 8.1 Hz, 1C), 129.9, 125.5, 124.4 (d, $J_{C\text{-}F}$ = 3.6 Hz, 1C), 123.1 (d, $J_{C\text{-}F}$ = 14.3 Hz, 1C), 115.6 (d, $J_{C\text{-}F}$ = 21.0 Hz, 1C), 59.7 (d, $J_{C\text{-}F}$ = 4.1 Hz, 1C), 21.7.



4-Fluorobenzyl 4-methylbenzenesulfinate (3i): Yellow liquid; 90% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H), 7.25-7.23 (m, 2H), 7.01 (t, J = 8.5 Hz, 2H), 4.98 (d, J = 11.5 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 245.9 Hz, 1C), 143.1, 141.6, 131.55 (d, $J_{C\text{-}F}$ = 3.1 Hz, 1C), 130.66 (d, $J_{C\text{-}F}$ = 8.3 Hz, 1C), 129.9, 125.5, 115.7 (d, $J_{C\text{-}F}$ = 21.5 Hz, 1C), 64.9, 21.7.

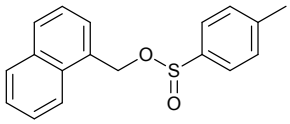


3,4-Difluorobenzyl 4-methylbenzenesulfinate (3j): Yellow liquid; 49% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.13-7.06 (m, 2H), 7.02-6.95 (m, 1H), 4.94 (d, J = 12 Hz, 1H), 4.48 (d, J = 12 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5 (dd, $J_{C\text{-}F}$ = 12.4 Hz, 5.8 Hz, 1C), 149.5 (dd, $J_{C\text{-}F}$ = 12.4 Hz, 7.4 Hz, 1C), 143.4, 141.5, 132.9 (dd, $J_{C\text{-}F}$ = 5.6 Hz, 3.9 Hz, 1C), 123.0, 125.5, 124.7 (dd, $J_{C\text{-}F}$ = 6.5 Hz, 3.6 Hz, 1C), 117.6 (dd, $J_{C\text{-}F}$ = 21.8 Hz, 17.6 Hz, 2C), 64.1, 21.7.

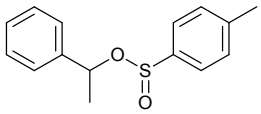


4-(Trifluoromethyl)benzyl 4-methylbenzenesulfinate (3k): Yellow liquid; 52% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.05 (d, J = 12.0 Hz, 1H), 4.58 (d, J

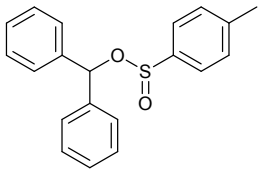
= 12.0 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 141.5, 139.9, 130.8, 130.5, 130.0, 128.6, 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz 1C), 125.5, 64.3, 21.7.



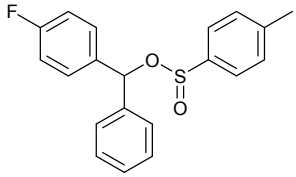
Naphthalen-1-ylmethyl 4-methylbenzenesulfinate (3l): Yellow liquid; 22% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.87-7.83 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.55-7.49 (m, 2H), 7.41-7.38 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 5.51 (d, *J* = 11.5 Hz, 1H), 4.97 (d, *J* = 11.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 141.6, 133.9, 131.8, 131.2, 129.93, 129.87, 128.8, 128.2, 126.8, 126.2, 125.5, 125.4, 123.8, 63.9, 21.7.



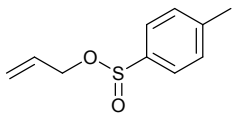
1-Phenylethyl 4-methylbenzenesulfinate (3m): White solid; m.p. 127.1-129.2 ^{o}C; 39% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.31-7.24 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 4.22 (q, *J* = 7.0 Hz, 1H), 2.40 (s, 3H), 1.76 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 134.1, 129.6, 129.43, 129.40, 128.9, 128.5, 66.2, 21.8, 14.3.



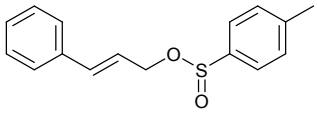
Benzhydryl 4-methylbenzenesulfinate (3n): White solid; m.p. 186.2-191.4 ^{o}C; 92% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 3.5 Hz, 4H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.32-7.31 (m, 6H), 7.15 (d, *J* = 7.5 Hz, 2H), 5.26 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 135.5, 133.3, 130.1, 129.4, 129.2, 128.84, 128.76, 76.7, 21.8.



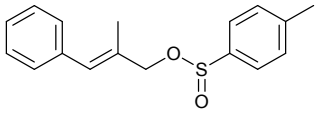
(4-Fluorophenyl)(phenyl)methyl 4-methylbenzenesulfinate (3o): White solid; m.p. 155.7-158.0 ^{o}C; 80% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.48 (m, 6H), 7.32-7.31 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 5.25 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 242.1 Hz, 1C), 162.0, 144.8, 135.3, 133.1, 131.9 (d, $J_{C\text{-}F}$ = 8.3 Hz, 1C), 130.0, 129.5, 129.19, 129.16 (d, $J_{C\text{-}F}$ = 2.9 Hz, 1C), 128.94, 128.89, 115.9 (d, $J_{C\text{-}F}$ = 21.5 Hz, 1C), 75.8, 21.8.



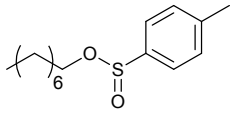
Allyl 4-methylbenzenesulfinate (3p): White liquid; 83% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 5.90-5.82 (m, 1H), 5.30 (dq, *J* = 17.0, 1.5 Hz, 1H), 5.23 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.50 (qt, *J* = 6.0, 1.5 Hz, 1H), 4.12 (qt, *J* = 6.0, 1.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 141.9, 132.6, 129.9, 125.4, 119.4, 65.2, 21.7.



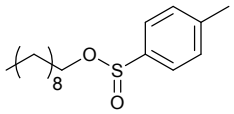
Cinnamyl 4-methylbenzenesulfinate (3q): Yellow liquid; 22% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.34-7.30 (m, 7H), 6.39 (d, *J* = 15.5 Hz, 2H), 6.11 (d, *J* = 16.0, 7.5 Hz, 2H), 3.94 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 139.2, 136.0, 135.7, 129.9, 128.8, 128.71, 128.69, 126.8, 115.5, 60.7, 21.8.



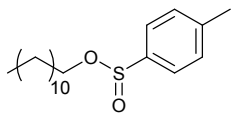
(E)-2-methyl-3-phenylallyl 4-methylbenzenesulfinate (3r): Yellow liquid; 33% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.34-7.30 (m, 4H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.08 (s, 1H), 3.88 (s, 2H), 2.44 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 136.8, 135.5, 134.9, 129.8, 128.9, 128.8, 128.3, 127.3, 126.4, 67.3, 21.8, 18.8.



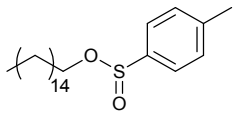
Octyl 4-methylbenzenesulfinate (3s): White liquid; 92% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.03-3.99 (m, 1H), 3.62-3.57 (m, 1H), 2.43 (s, 3H), 1.61 (dt, *J* = 13.5, 6.5 Hz, 2H), 1.30-1.24 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 141.8, 129.7, 125.2, 64.6, 31.7, 29.7, 29.10, 29.06, 25.7, 22.6, 21.5, 14.1.



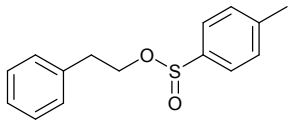
Decyl 4-methylbenzenesulfinate (3t): White liquid; 91% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 4.04-3.99 (m, 1H), 3.62-3.57 (m, 1H), 2.43 (s, 3H), 1.61 (dt, *J* = 14.0, 7.0 Hz, 2H), 1.30-1.24 (m, 14H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 142.0, 129.8, 125.4, 64.7, 32.0, 29.8, 29.7, 29.6, 29.4, 29.3, 25.9, 22.8, 21.7, 14.3.



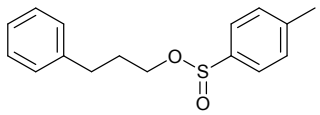
Dodecyl 4-methylbenzenesulfinate (3u): White liquid; 84% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.01 (dt, *J* = 9.5, 7.0 Hz, 1H), 3.60 (dt, *J* = 10.0, 6.0 Hz, 1H), 2.43 (s, 3H), 1.64-1.59 (m, 2H), 1.31-1.24 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 142.0, 129.8, 125.4, 64.8, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 25.9, 22.9, 21.7, 14.3.



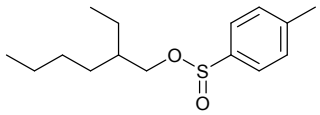
Hexadecyl 4-methylbenzenesulfinate (3v): White liquid; 80% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 4.01 (dt, *J* = 10.0, 6.5 Hz, 1H), 3.60 (dt, *J* = 9.5, 6.5 Hz, 1H), 2.43 (s, 3H), 1.64-1.58 (m, 2H), 1.31-1.23 (m, 26H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 142.1, 129.8, 125.4, 64.8, 32.1, 29.88, 29.87, 29.84, 29.81, 29.7, 29.6, 29.5, 29.3, 25.9, 22.9, 21.7, 14.3.



Phenethyl 4-methylbenzenesulfinate (3w): White liquid; 76% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 4H), 7.23-7.20 (m, 1H), 7.14 (d, *J* = 7.0 Hz, 2H), 4.23 (dt, *J* = 10.0, 7.0 Hz, 1H), 3.80 (dt, *J* = 10.0, 7.0 Hz, 1H), 2.94-2.91 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 141.7, 137.5, 129.8, 129.1, 128.6, 126.8, 125.4, 64.9, 36.4, 21.6.

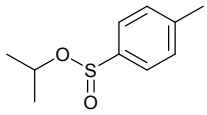


3-Phenylpropyl 4-methylbenzenesulfinate (3x): White liquid; 83% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H) , 7.18 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 4.04 (dt, *J* = 10.0, 6.5 Hz, 1H), 3.63 (dt, *J* = 10.0, 6.5 Hz, 1H), 2.66 (td, *J* = 7.5, 2.0 Hz, 2H), 2.43 (s, 3H), 1.96-1.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 141.9, 141.2, 129.9, 128.59, 128.58, 126.2, 125.4, 63.8, 32.1, 31.5, 21.7.

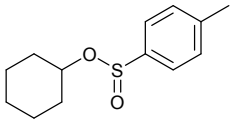


2-Ethylhexyl 4-methylbenzenesulfinate (3y): Foure isomers; White liquid; 94% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.93 (td, *J* = 9.5, 5.5 Hz, 1H), 3.46 (ddd, *J* = 12.5, 5.5 Hz, 1H), 2.43 (s, 3H), 1.51 (dt, *J* = 12.0, 6.0 Hz, 1H), 1.40-1.12 (m, 8H), 0.86 (t, *J* = 6.5 Hz, 1H), 0.82 (td, *J* = 7.5,

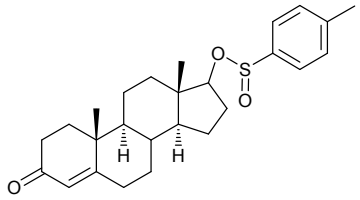
3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 141.89, 141.87, 129.8, 125.4, 66.3, 66.2, 39.70, 39.66, 30.3, 30.2, 29.0, 28.9, 23.6, 23.1, 23.0, 21.6 14.2, 11.03, 10.98.



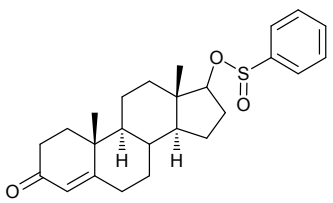
Isopropyl 4-methylbenzenesulfinate (3z): White liquid; 91% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.0 Hz, 2H), 4.61-4.59 (m, 1H), 2.42 (s, 3H), 1.38 (d, *J* = 5.5 Hz, 3H), 1.25 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 142.6, 129.8, 125.2, 72.8, 24.1, 23.9, 21.7.



Cyclohexyl 4-methylbenzenesulfinate (3A): White liquid; 63% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 4.35-4.30 (m, 1H), 2.42 (s, 3H), 2.01 (dd, *J* = 12.5, 3.5 Hz, 1H), 1.81-1.70 (m, 3H), 1.62-1.44 (m, 3H), 1.38-1.19 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 142.5, 129.7, 125.2, 77.9, 33.85, 33.76, 25.3, 24.00, 23.97, 21.6.

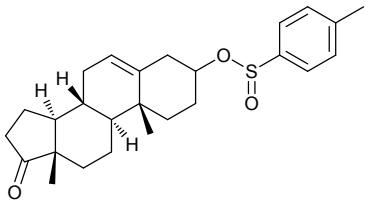


(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-methylbenzenesulfinate (3B): Two isomers; White solid; m.p. 158.5-163.3 °C; 82% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 5.72 (s, 1H), 4.10 (dt, *J* = 40.5 Hz, 8 Hz, 1H), 2.42-2.14 (m, 8H), 2.05-1.95 (m, 2H), 1.81-1.26 (m, 9H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.02-0.87 (m, 3H), 0.83 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 171.04, 171.00, 142.93, 142.87, 142.66, 142.63, 129.75, 129.71, 125.4, 125.3, 124.09, 124.05, 87.3, 85.4, 53.9, 53.8, 50.12, 50.07, 43.2, 43.1, 38.7, 36.5, 36.0, 35.85, 35.83, 35.59, 35.55, 34.1, 32.8, 31.6, 31.5, 29.4, 28.7, 23.7, 23.6, 21.7, 20.6, 20.5, 17.53, 17.50, 12.1, 12.0.

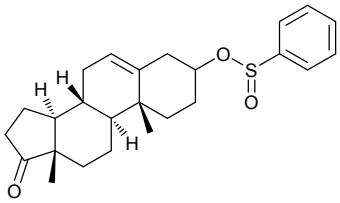


(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl benzenesulfinate (3C): Two isomers; White solid; m.p. 144.5-149.0 °C; 82% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.69 (m, 2H), 7.57-7.51 (m, 3H), 5.72 (s, 1H), 4.12 (dt, *J* = 42.0, 8.5 Hz, 1H), 2.46-2.16 (m, 4H), 2.06-1.95 (m, 1H), 1.85-1.49

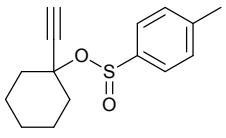
(m, 9H), 1.45-1.25 (m, 2H), 1.18 (d, *J* = 9.0 Hz, 3H), 1.00-0.86 (m, 3H), 0.83 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 171.1, 171.0, 145.9, 145.8, 132.1, 129.13, 129.09, 125.5, 125.4, 124.14, 124.10, 87.5, 85.7, 53.9, 53.8, 50.2, 50.1, 43.2, 43.1, 38.77, 38.76, 36.5, 36.0, 35.9, 35.62, 35.58, 34.1, 32.9, 31.6, 31.5, 29.4, 28.7, 23.7, 23.6, 20.6, 20.5, 17.6, 17.5, 12.1, 12.0.



(8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-methylbenzenesulfinate (3D): Two isomers; White solid; m.p. 153.2-155.7 °C; 81% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.33 (q, *J* = 4 Hz, 2H), 5.38 (dd, *J* = 60.5, 5 Hz, 1H), 4.24-4.16 (m, 1H), 2.51-2.45 (m, 2H), 2.42 (d, *J* = 3.0 Hz, 3H), 2.14-2.02 (m, 2H), 1.98-1.56 (m, 9H), 1.55-1.42 (m, 2H), 1.30-1.24 (m, 2H), 1.17-1.05 (m, 1H), 1.02 (d, *J* = 1.0 Hz, 3H), 1.00-0.97 (m, 1H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 142.9, 142.7, 140.06, 140.04, 129.8, 125.2, 125.1, 122.3, 122.2, 79.1, 78.7, 51.9, 50.2, 47.7, 40.5, 40.3, 37.3, 37.2, 36.8, 36.0, 31.6, 31.5, 30.94, 30.91, 30.1, 29.9, 22.0, 21.7, 20.49, 20.47, 19.4, 13.7.

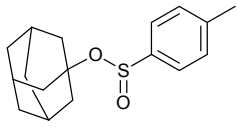


(8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl benzenesulfinate (3E): Two isomers; White solid; m.p. 166.4-172.1 °C; 80% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.56-7.52 (m, 2H), 5.38 (dd, *J* = 68.0 Hz, 5Hz, 1H), 4.25-4.18 (m, 1H), 2.54-2.43 (m, 2H), 2.14-2.04 (m, 2H), 1.98-1.62 (m, 8H), 1.59 (s, 3H), 1.56-1.42 (m, 2H), 1.31-1.24 (m, 2H), 1.18-1.06 (m, 1H), 1.02 (s, 3H), 1.01-0.97 (m, 1H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 145.8, 140.03, 140.00, 132.2, 129.2, 125.24, 125.21, 122.4, 122.3, 79.3, 79.0, 51.9, 50.3, 47.7, 40.5, 40.3, 37.31, 37.27, 36.83, 36.81, 36.0, 31.62, 31.57, 30.97, 30.93, 30.1, 30.0, 22.0, 20.5, 19.5, 13.7.

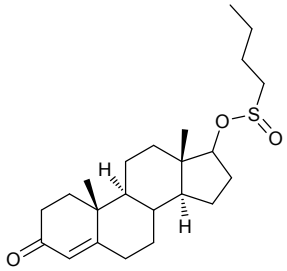


1-Ethynylcyclohexyl 4-methylbenzenesulfinate (3F): Yellow liquid; 48% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.83 (s, 1H), 2.42 (s, 3H), 2.25-

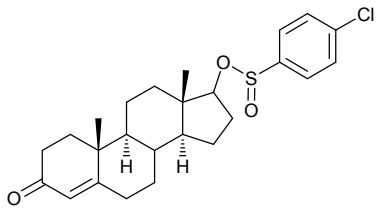
2.23 (m, 1H), 2.05-1.96 (m, 2H), 1.83-1.76 (m, 2H), 1.74-1.69 (m, 1H), 1.66-1.61 (m, 2H), 1.59-1.54 (m, 1H), 1.33-1.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 142.5, 129.8, 125.2, 84.1, 79.3, 39.3, 39.2, 24.9, 23.0, 22.9, 21.7.



Adamantan-1-yl 4-methylbenzenesulfinate (3G): Yellow solid; m.p. 104.5-108.6 °C; 52% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 2.26 (m, 3H), 2.14-2.07 (m, 6H), 1.69 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 142.2, 129.8, 125.1, 82.1, 44.0, 36.0, 31.3, 21.6.

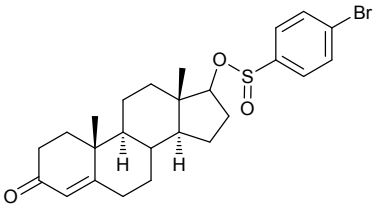


(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl butane-1-sulfinate (3H): Two isomers; White solid; m.p. 75.4-78.0 °C; 42% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (s, 1H), 4.14-4.07 (m, 1H), 2.81-2.67 (m, 2H), 2.44-2.26 (m, 4H), 2.17-2.11 (m, 1H), 2.07-1.99 (m, 2H), 1.89-1.77 (m, 2H), 1.89-1.77 (m, 2H), 1.74-1.55 (m, 8H), 1.50-1.35 (m, 4H), 1.19 (s, 1H), 1.04-1.01 (m, 1H), 0.97-0.92 (m, 4H), 0.84 (d, J = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 171.1, 171.0, 124.2, 124.1, 89.0, 88.4, 57.6, 57.5, 54.0, 53.90, 53.85, 50.5, 50.2, 43.5, 43.1, 38.80, 38.77, 36.8, 36.3, 35.92, 35.89, 35.87, 35.7, 35.6, 34.1, 32.9, 31.6, 31.5, 29.0, 28.6, 23.8, 23.7, 23.5, 22.20, 22.15, 20.64, 20.59, 17.6, 13.9, 12.00, 11.98.

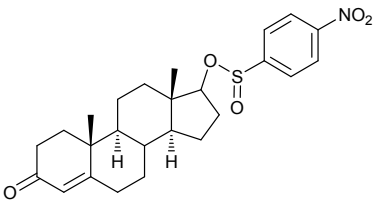


(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-chlorobenzenesulfinate (3I): Two isomers; White solid; m.p. 167.1-171.9 °C; 72% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.62 (m, 2H), 7.52-7.50 (m, 2H), 5.72 (s, 1H), 4.11 (dt, *J* = 38.0 Hz, 8 Hz, 1H), 2.45-2.25 (m, 4H), 2.06-2.00 (m, 1H), 1.85-1.77 (m, 2H), 1.71-1.52 (m, 6H), 1.44-1.29 (m, 2H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.02-0.85 (m, 4H), 0.83 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.60, 199.58, 170.93, 170.89, 144.42, 144.38, 138.53, 138.52,

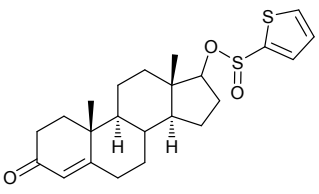
129.5, 129.4, 126.96, 126.90, 124.18, 124.15, 87.9, 85.9, 53.9, 53.8, 50.14, 50.05, 43.2, 43.1, 38.8, 36.5, 36.1, 35.89, 35.87, 35.61, 35.58, 34.1, 32.8, 31.6, 31.5, 29.3, 28.8, 23.7, 23.6, 20.6, 20.5, 17.56, 17.55, 12.1, 12.0.



(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-bromobenzenesulfinate (3J): Two isomers; White solid; m.p. 176.0-177.2 °C; 69% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.59-7.55 (m, 2H), 5.72 (s, 1H), 4.10 (dt, *J* = 37.0 Hz, 8.5 Hz, 1H), 2.46-2.25 (m, 4H), 2.06-2.00 (m, 1H), 1.85-1.78 (m, 2H), 1.75-1.52 (m, 6H), 1.44-1.29 (m, 2H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.04-0.86 (m, 4H), 0.83 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.61, 199.59, 170.93, 170.91, 144.94, 144.89, 132.4, 132.3, 127.11, 127.06, 126.95, 126.92, 124.2, 124.1, 88.0, 86.0, 53.9, 53.8, 50.1, 50.0, 43.2, 43.1, 38.7, 36.5, 36.1, 35.88, 35.86, 35.60, 35.57, 34.1, 32.8, 31.55, 31.51, 29.3, 28.7, 23.7, 23.6, 20.6, 20.5, 17.56, 17.55, 12.1, 12.0.



(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-nitrobenzenesulfinate (3K): Two isomers; Yellow solid; m.p. 175.6-178.0 °C; 45% Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41-8.38 (m, 2H), 7.92-7.88 (m, 2H), 5.72 (s, 1H), 4.16 (dt, *J* = 34.0 Hz, 8.0 Hz, 1H), 2.43-2.25 (m, 4H), 2.06-2.00 (m, 1H), 1.86-1.79 (m, 2H), 1.71-1.54 (m, 6H), 1.43-1.40 (m, 1H), 1.26 (s, 1H), 1.18 (d, *J* = 7.5 Hz, 3H), 1.02-0.86 (m, 4H), 0.84 (d, *J* = 4.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 199.5, 170.8, 170.7, 152.2, 150.24, 150.21, 126.83, 126.78, 124.39, 124.35, 124.21, 124.19, 89.1, 87.0, 53.84, 53.76, 50.1, 50.0, 43.4, 43.2, 38.75, 38.73, 36.6, 36.1, 35.89, 35.87, 35.58, 35.57, 34.08, 34.07, 32.8, 31.52, 31.49, 29.3, 28.8, 23.7, 23.6, 20.6, 20.5, 17.6, 12.2, 12.1.



(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl thiophene-2-sulfinate (3L): Two isomers; White solid; m.p. 124.6-127.8 °C; 87%

Yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 1H), 7.47 (dt, *J* = 4.0 Hz, 1.0 Hz, 1H), 7.15 (dd, *J* = 5.0 Hz, 4.0 Hz, 1H), 5.72 (s, 1H), 4.25 (dt, *J* = 52.0 Hz, 8.0 Hz, 1H), 2.43-2.25 (m, 4H), 2.06-1.99 (m, 1H), 1.86-1.78 (m, 2H), 1.72-1.54 (m, 6H), 1.45-1.33 (m, 2H), 1.18 (d, *J* = 6.0 Hz, 3H), 1.04-0.88 (m, 4H), 0.87 (d, *J* = 3.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 170.99, 170.95, 131.5, 131.4, 129.8, 129.7, 127.8, 124.2, 124.1, 87.2, 85.9, 53.9, 53.8, 50.13, 50.12, 43.3, 43.2, 38.79, 38.78, 36.5, 36.0, 35.90, 35.88, 35.7, 35.6, 34.1, 32.9, 31.59, 31.56, 29.4, 28.8, 23.8, 23.7, 20.63, 20.57, 17.58, 17.56, 12.2, 12.1.

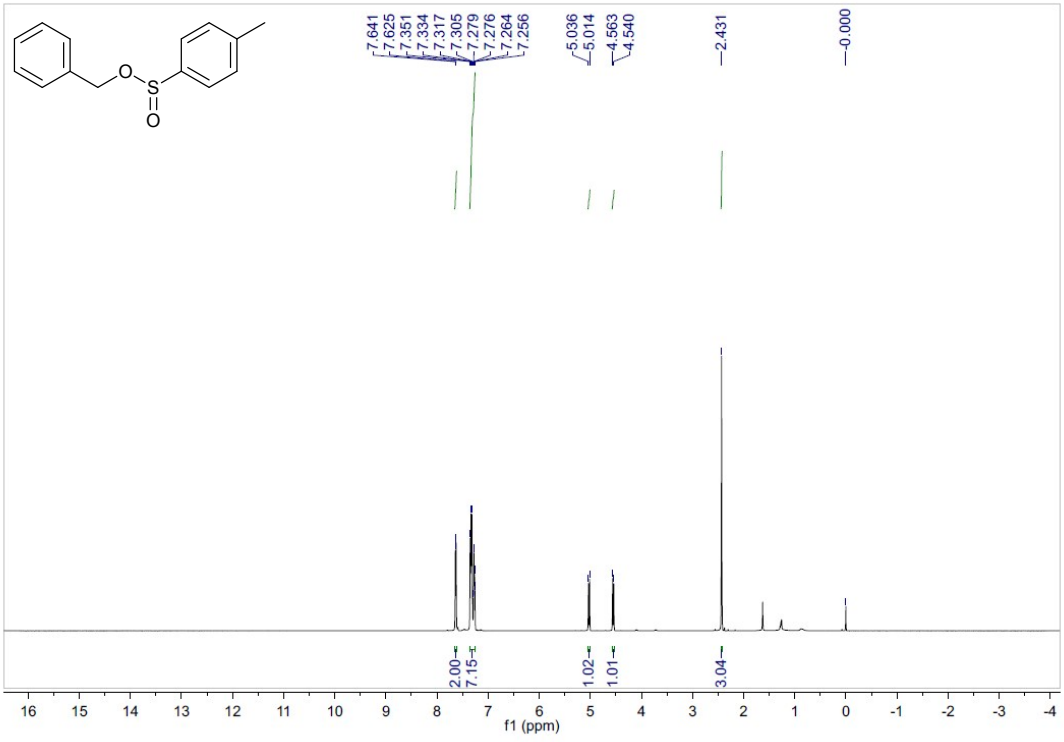
7. References

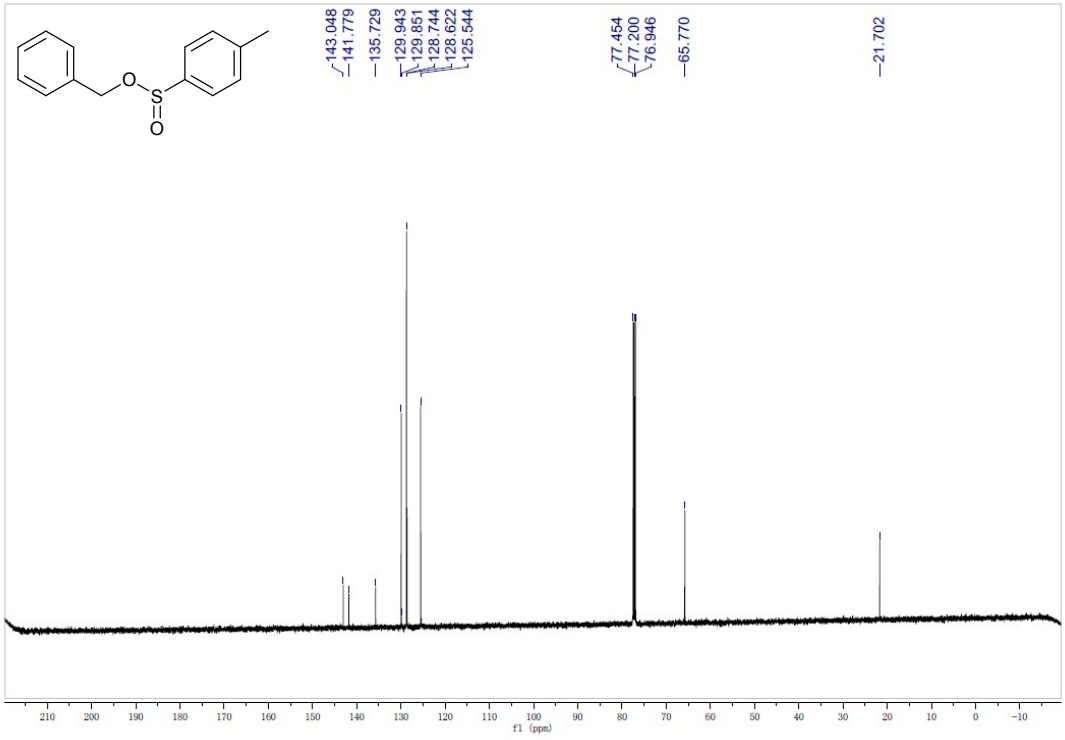
1 F. J. Arroyo, P. L. Alvarado, A. Ganesan and J. C. Menéndez, *Eur. J. Org. Chem.*, 2014, **33**, 5720.

2 (*a*) V. G. Pandya and S. B. Mhaske, *Org. Lett.*, 2014, **16**, 3836; (*b*) N. Umierski and G. Manolikakes, *Org. Lett.*, 2013, **15**, 188.

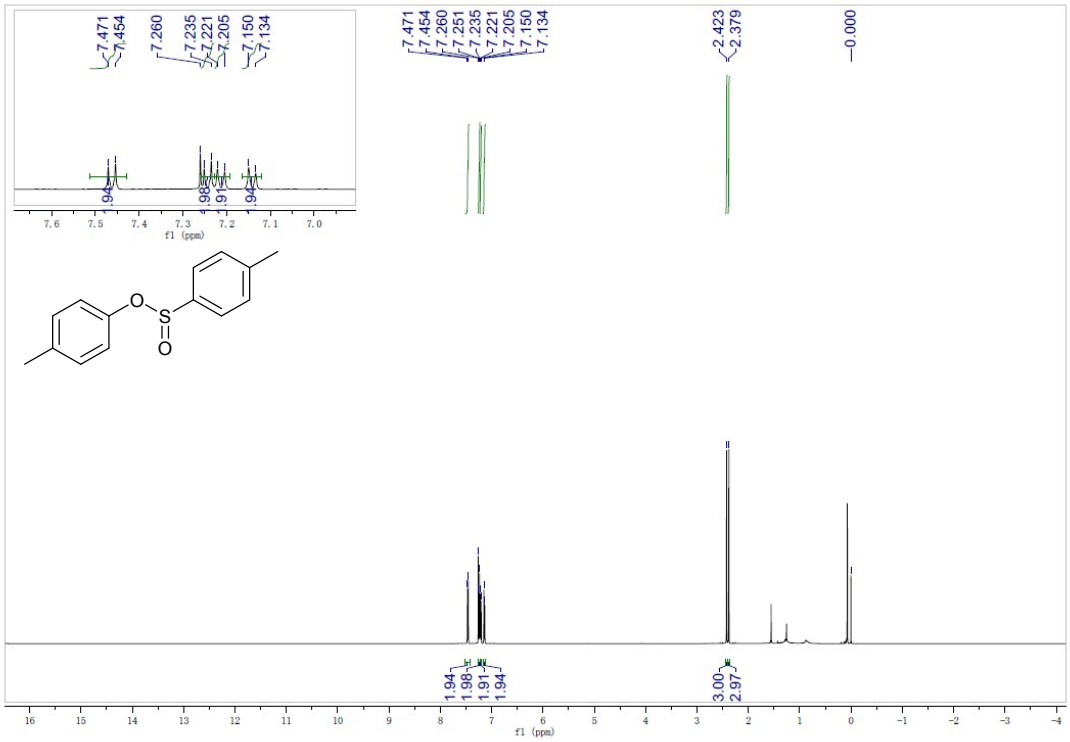
8. Copies of ^{1}H- and ^{13}C-NMR

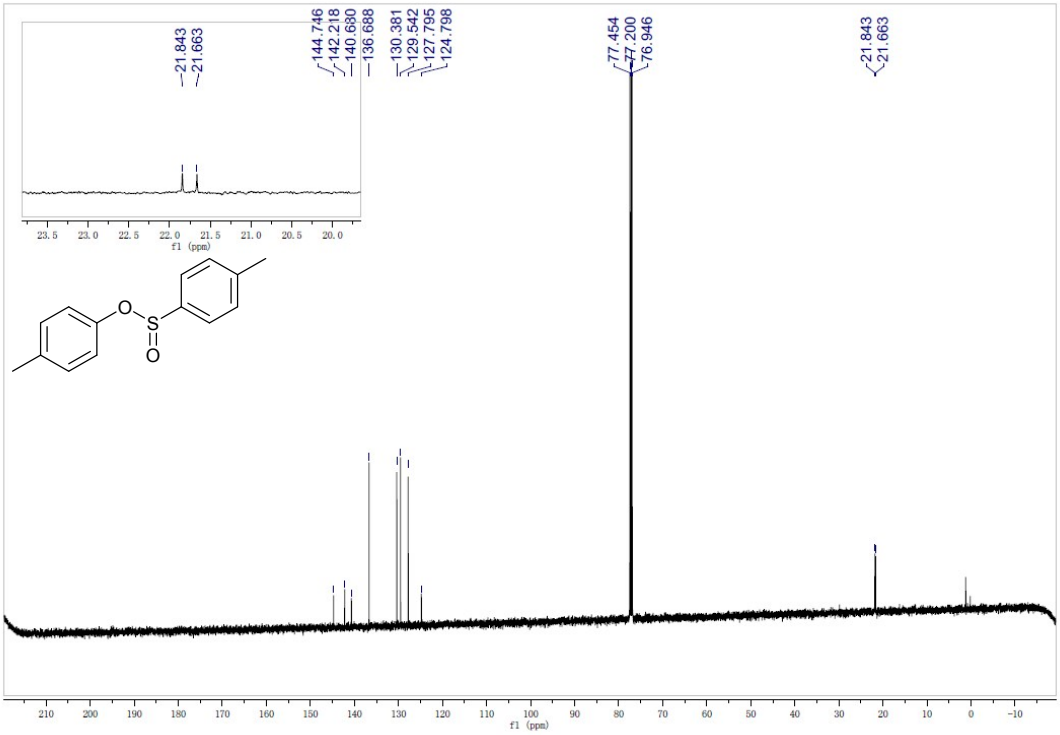
Benzyl 4-methylbenzenesulfinate (3a)



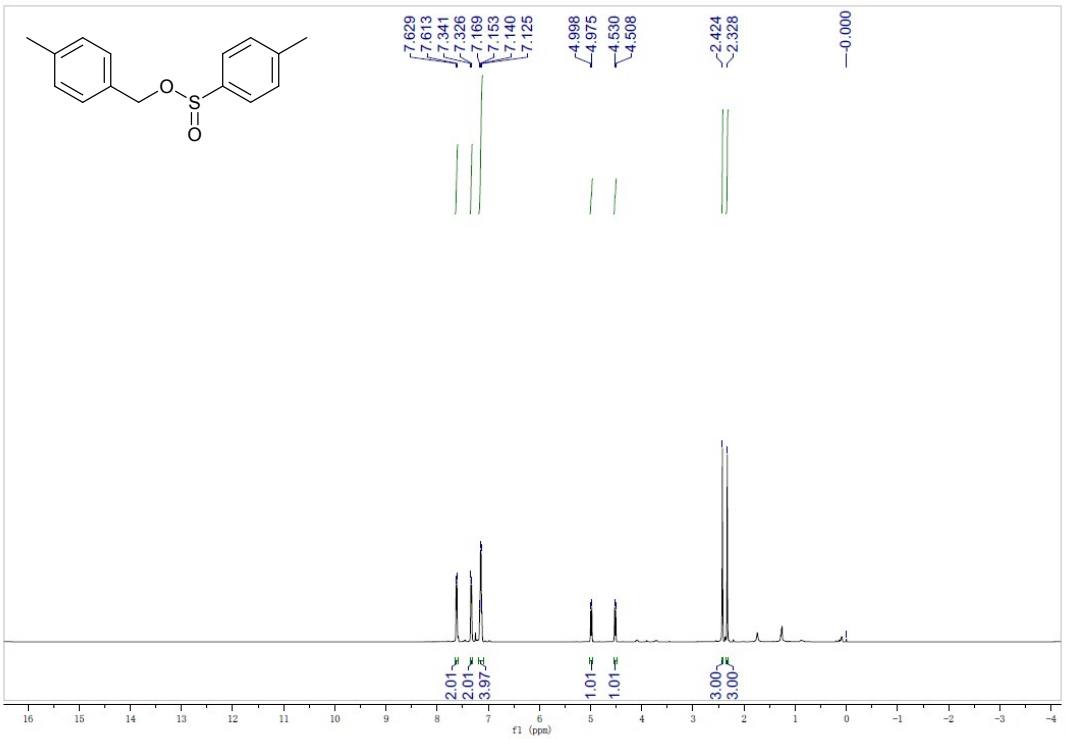


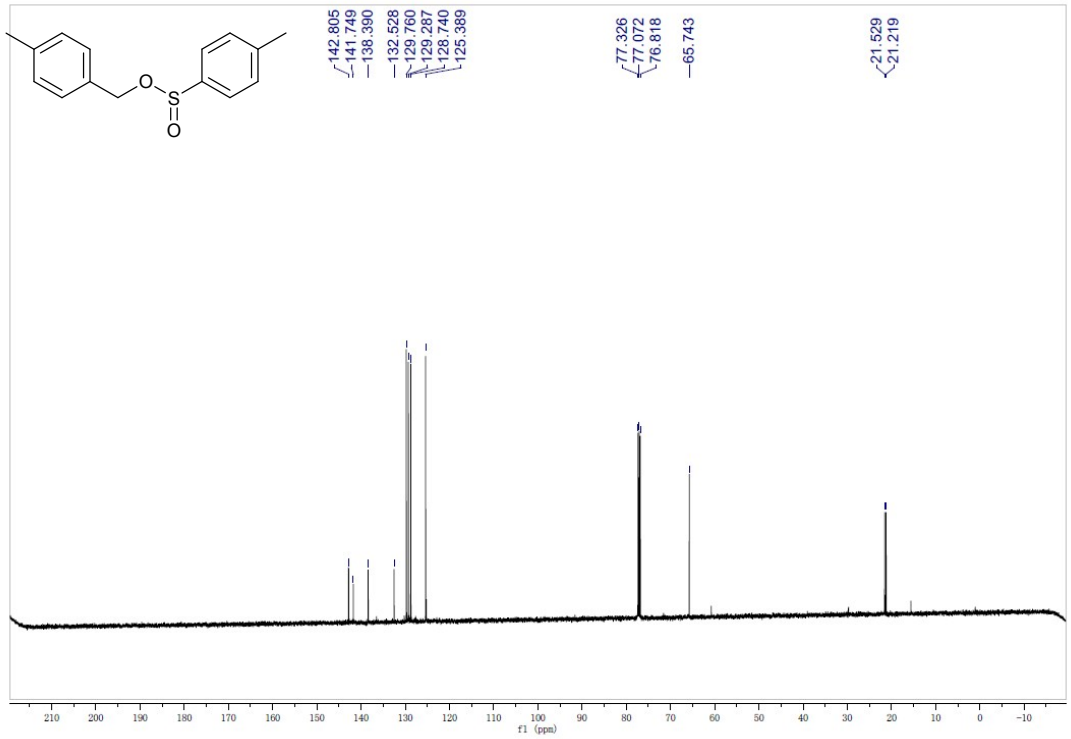
4-Methylphenyl *p*-toluenesulfinate (4)



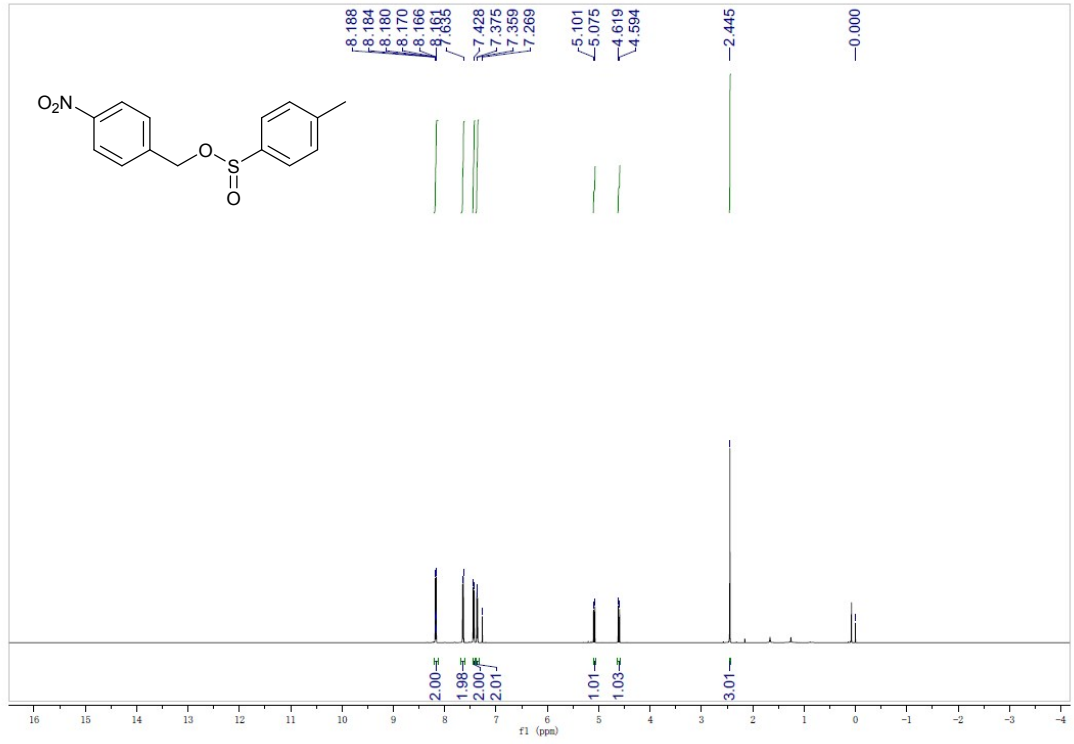


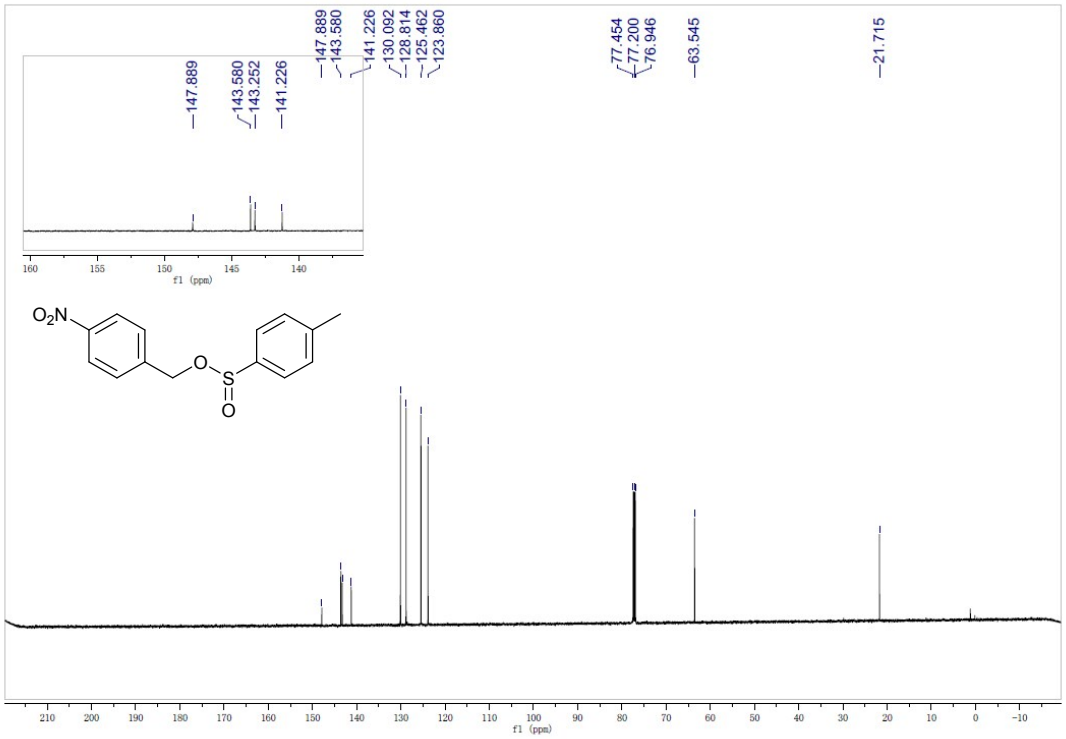
4-Methylbenzyl 4-methylbenzenesulfinate (3b)



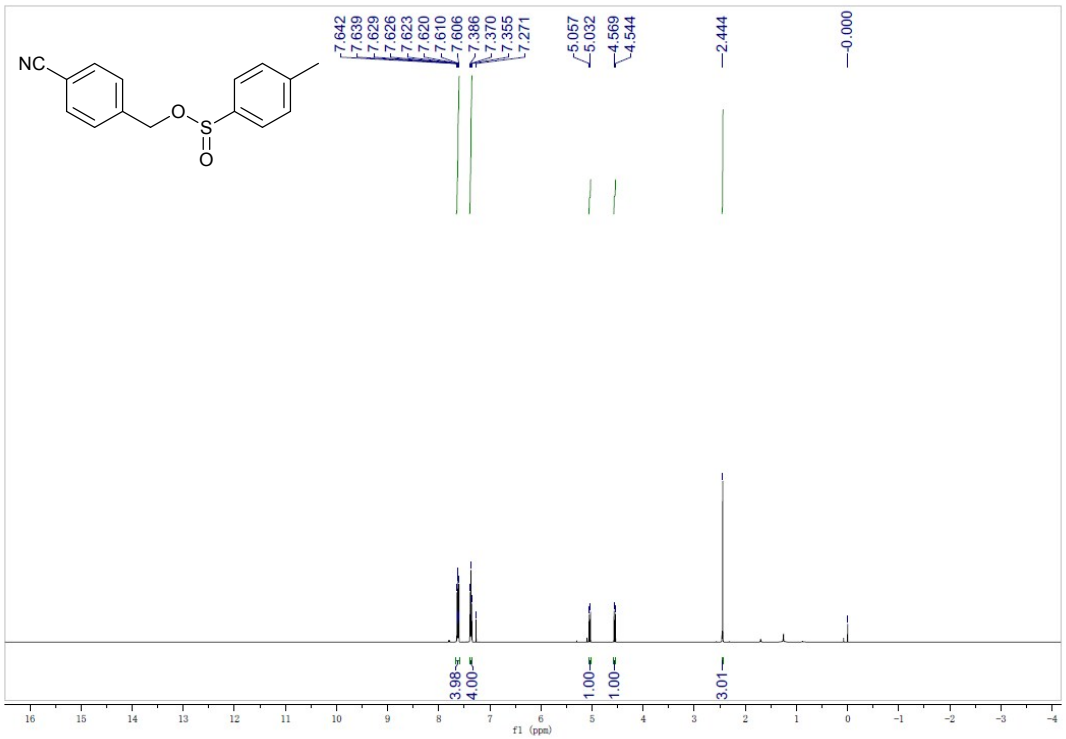


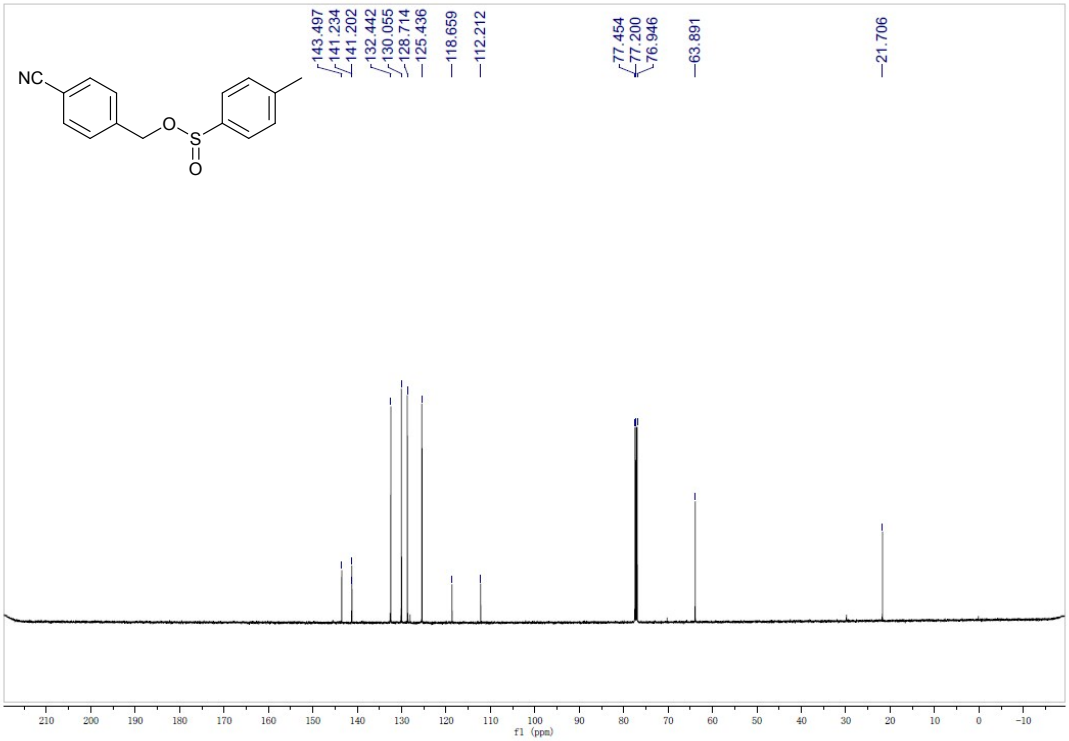
4-Nitrobenzyl 4-methylbenzenesulfinate (3c)



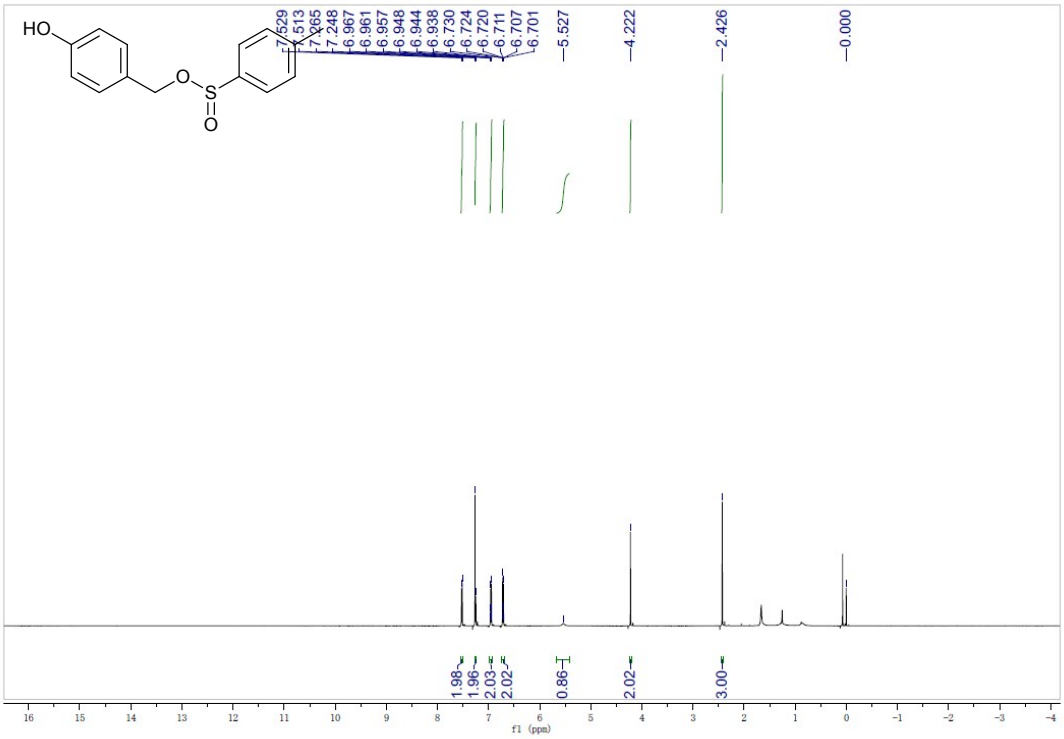


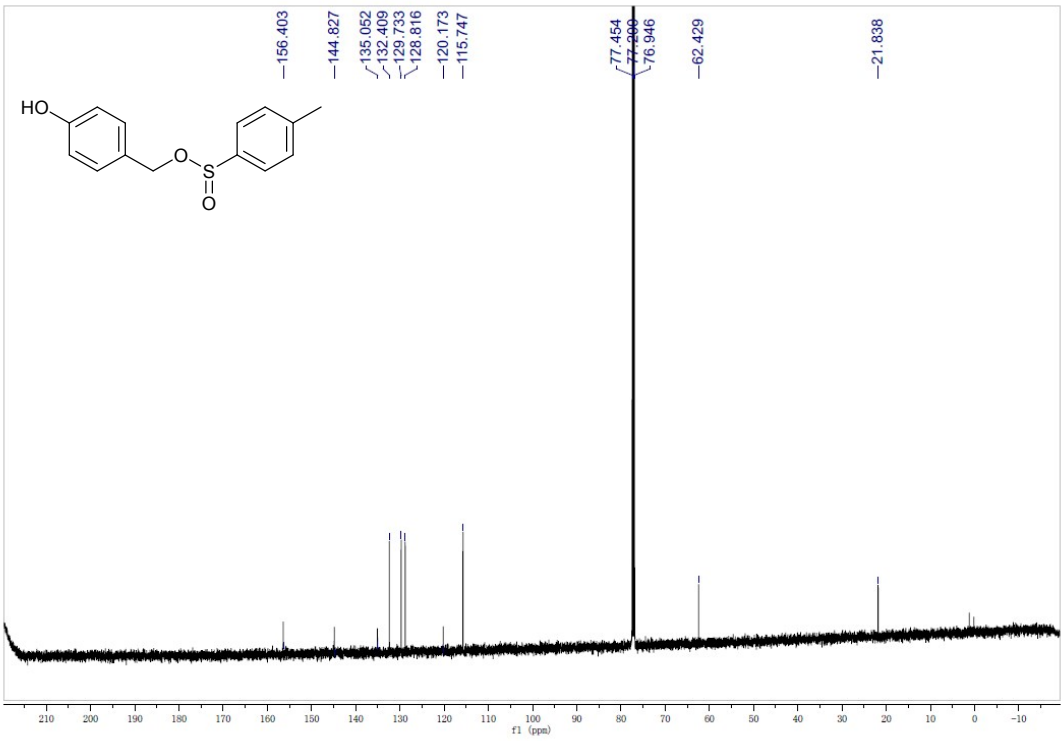
4-Cyanobenzyl 4-methylbenzenesulfinate (3d)



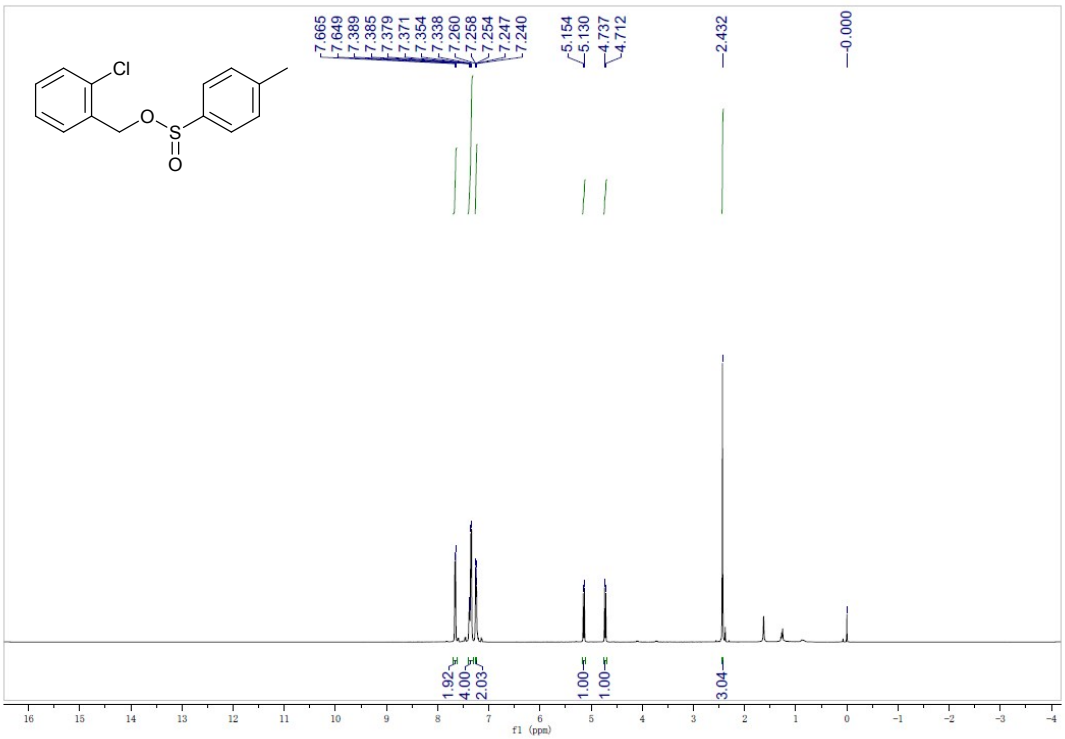


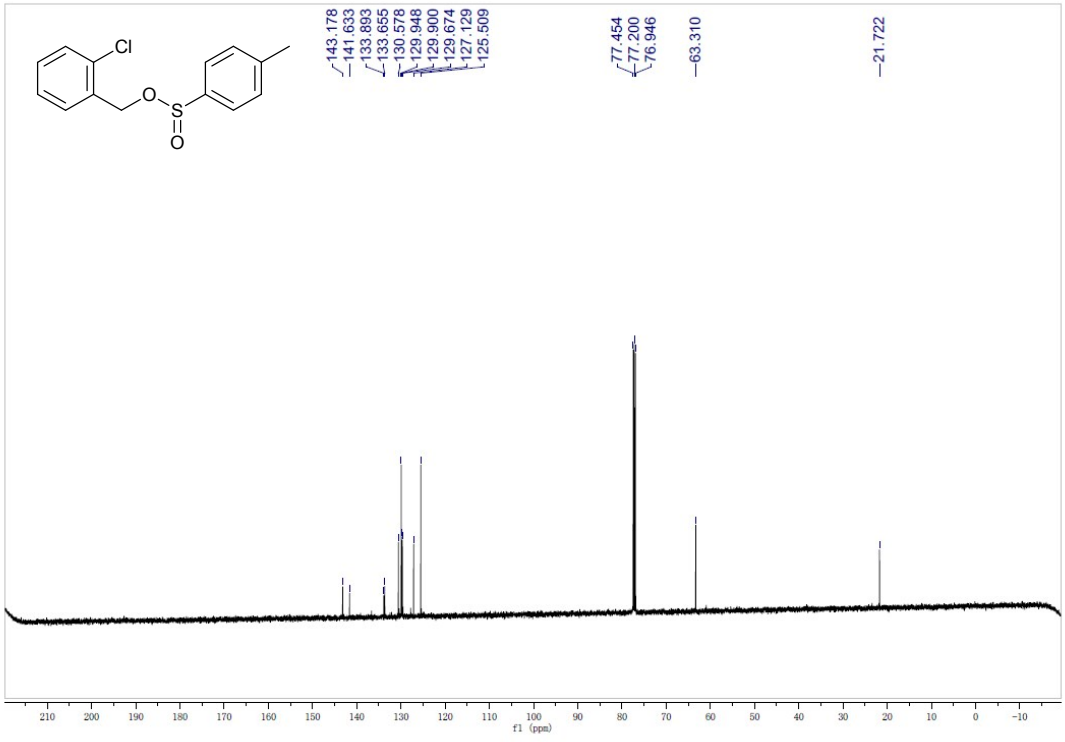
4-Hydroxybenzyl 4-methylbenzenesulfinate (3e)



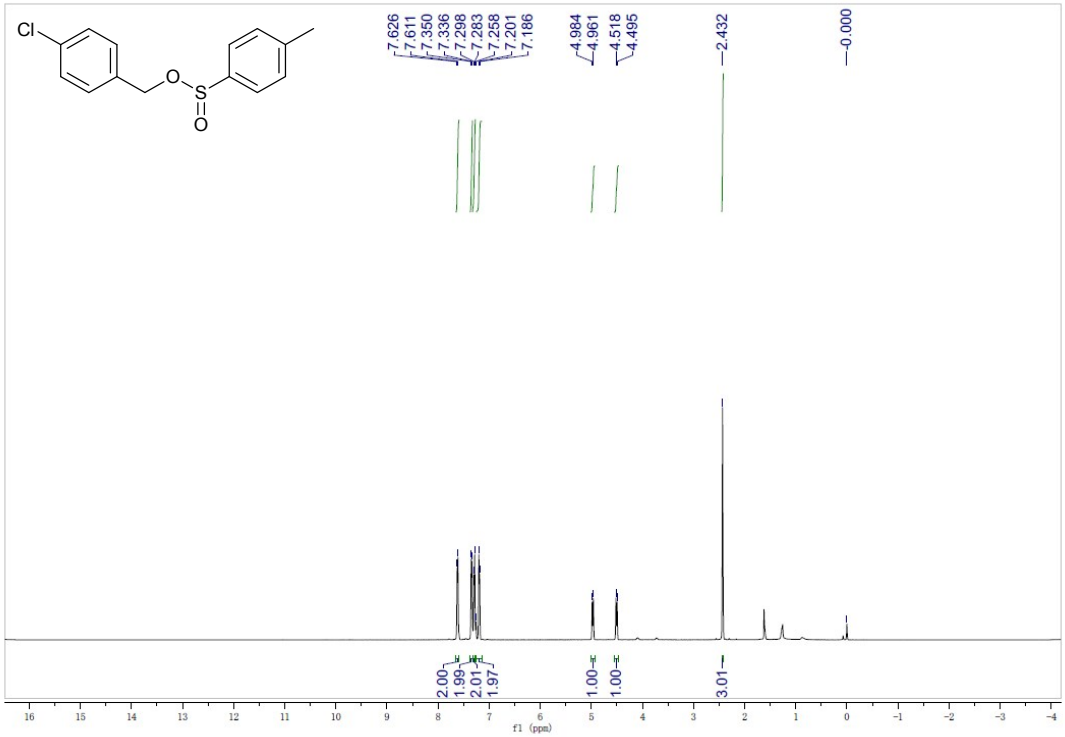


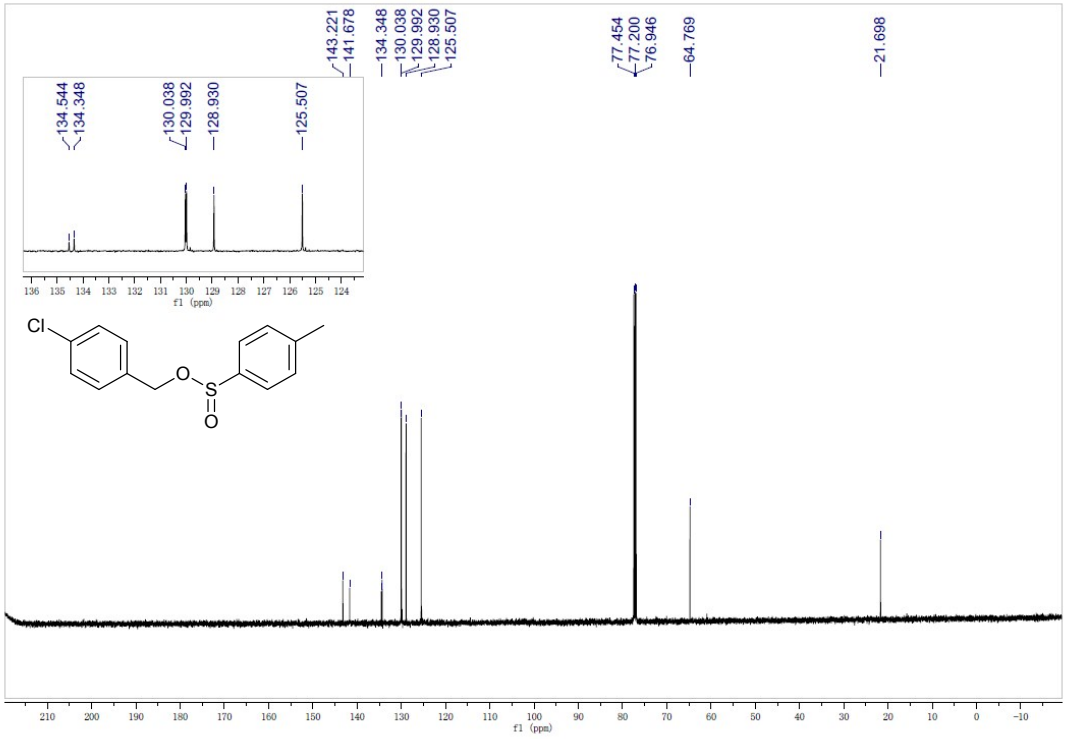
2-Chlorobenzyl 4-methylbenzenesulfinate (3f)



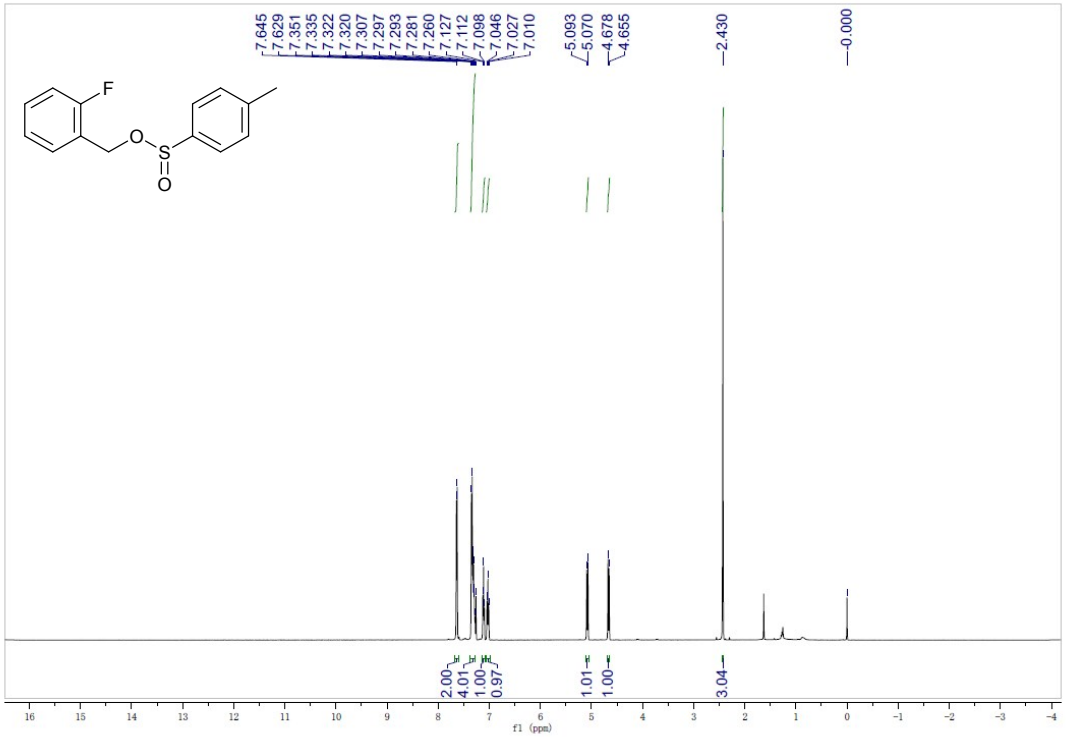


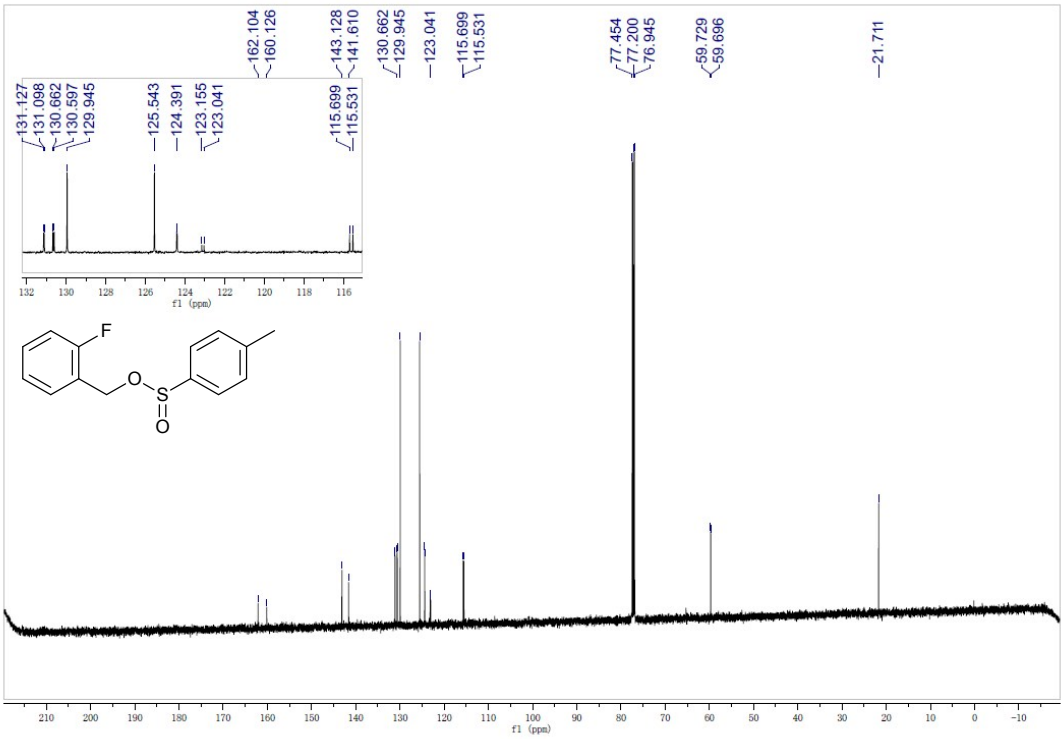
4-Chlorobenzyl 4-methylbenzenesulfinate (3g)



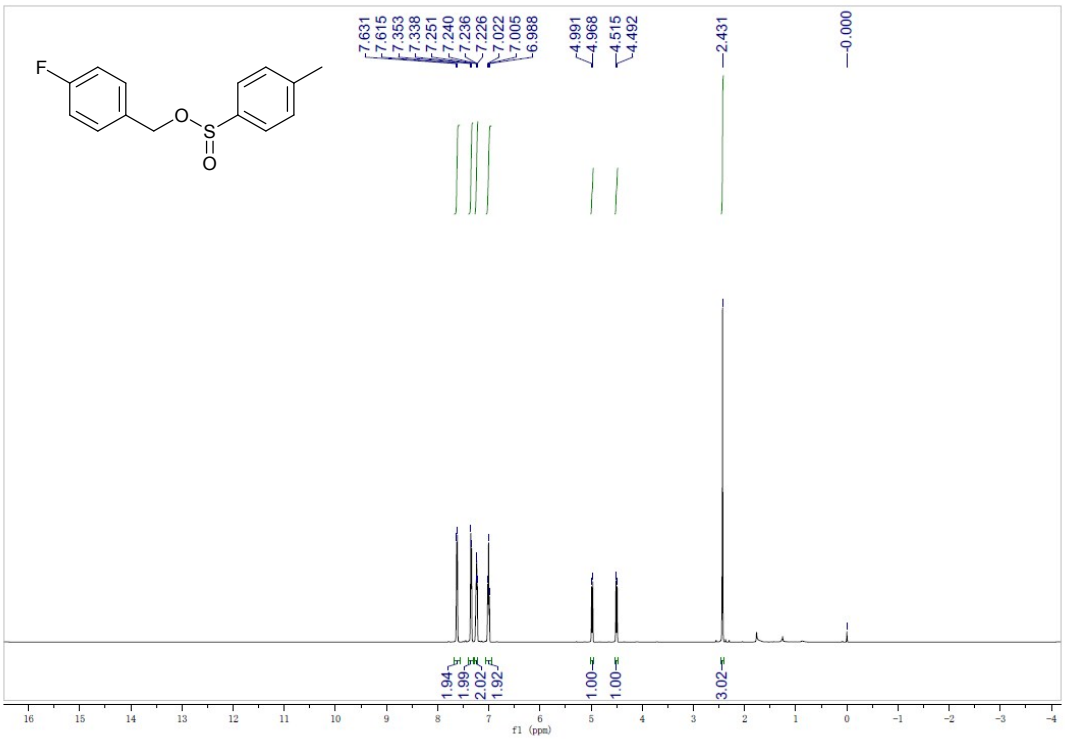


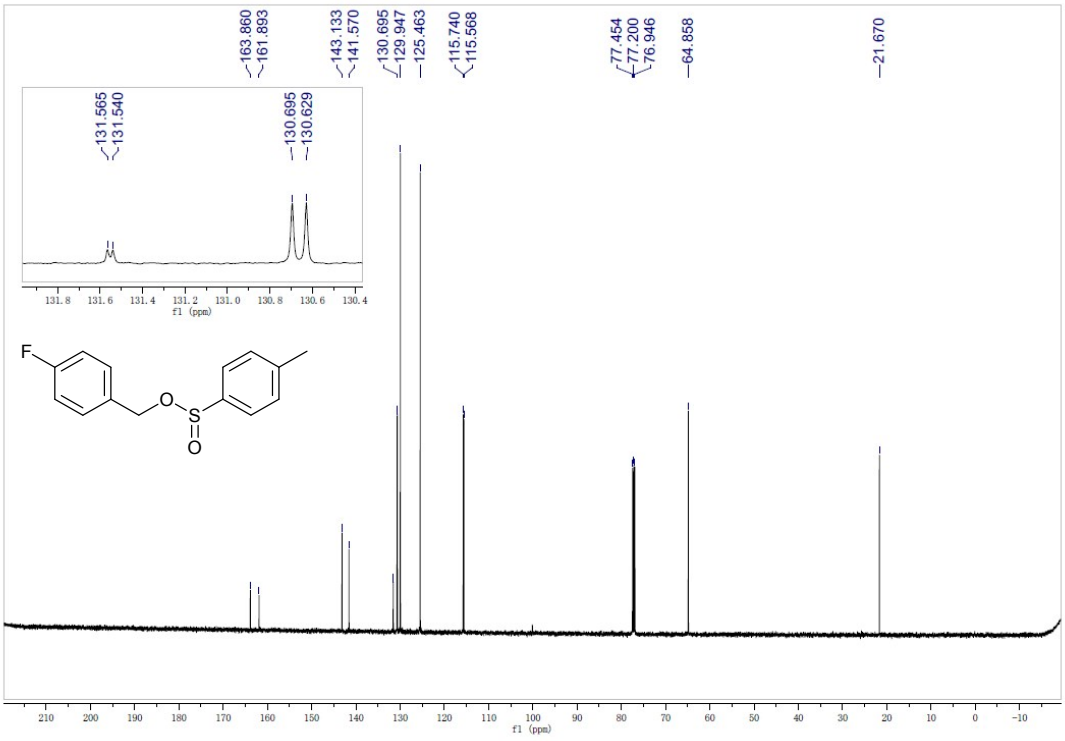
2-Fluorobenzyl 4-methylbenzenesulfinate (3h)



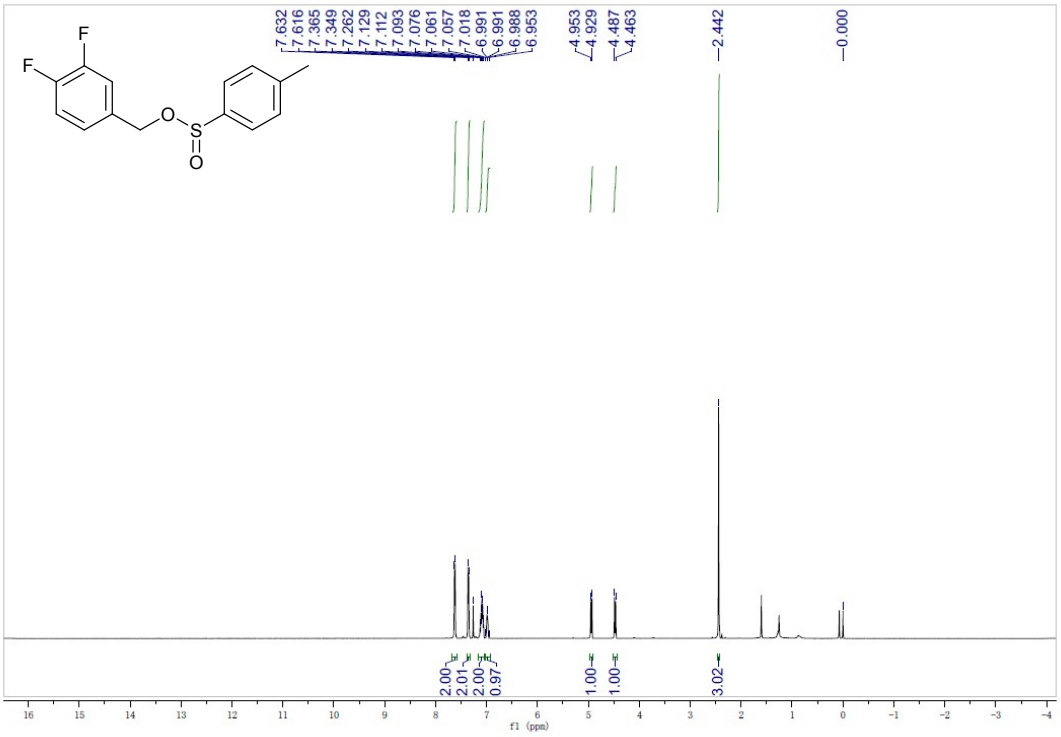


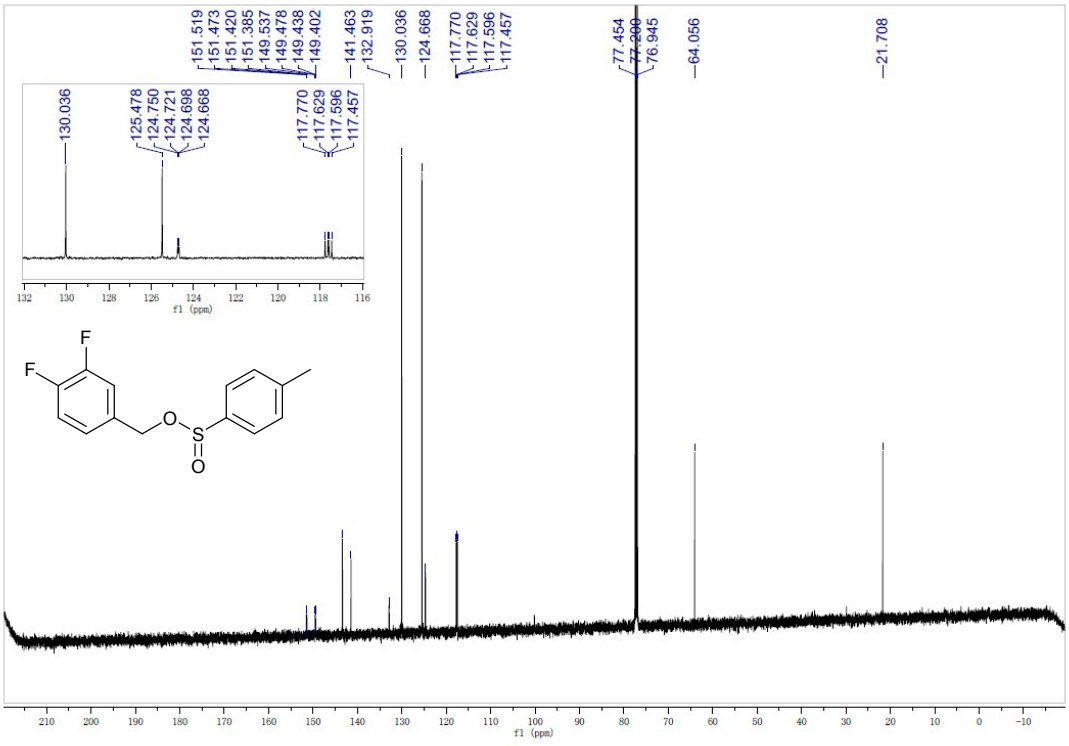
4-Fluorobenzyl 4-methylbenzenesulfinate (3i)



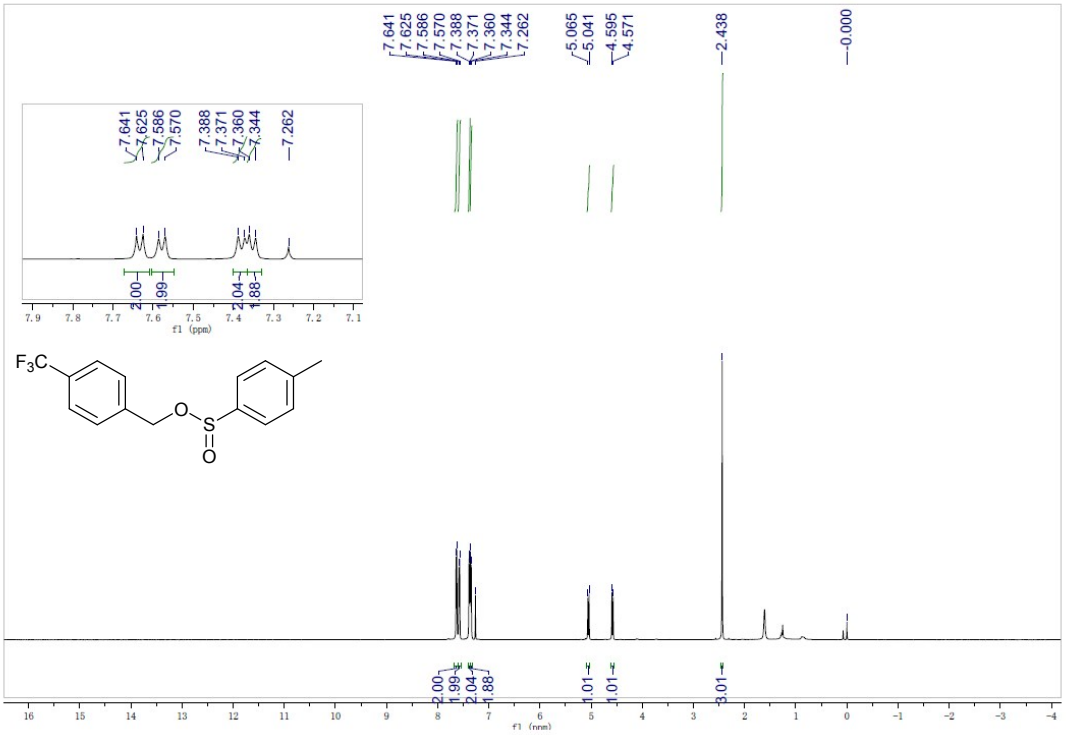


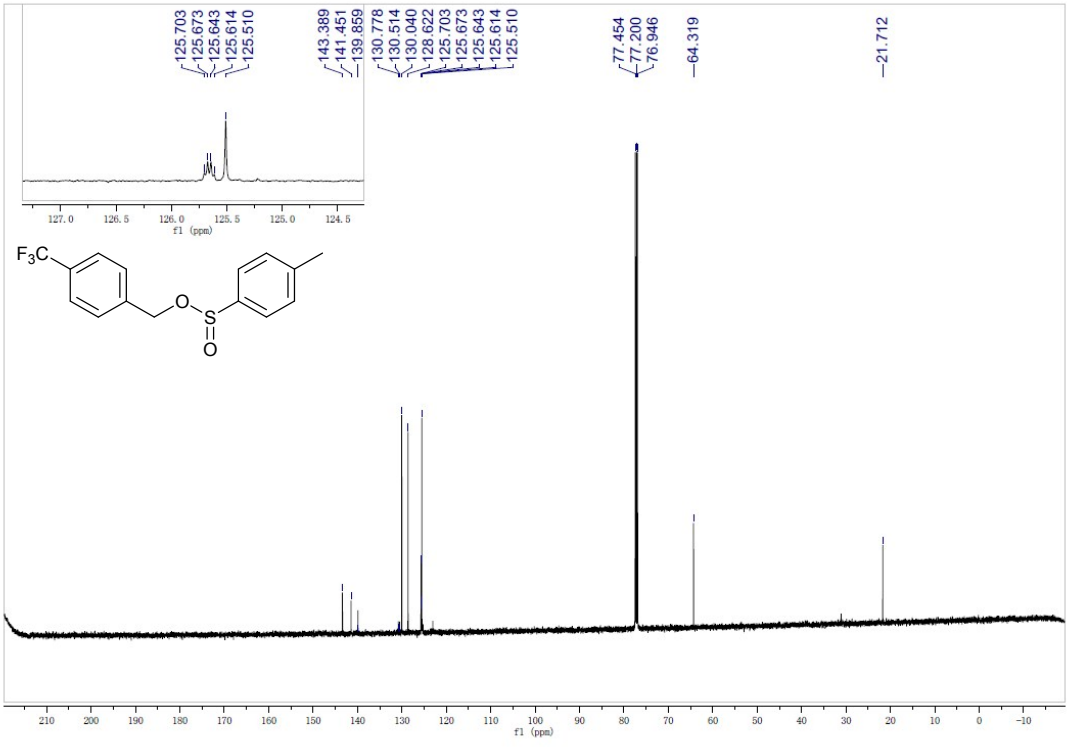
3,4-Difluorobenzyl 4-methylbenzenesulfinate (3j)



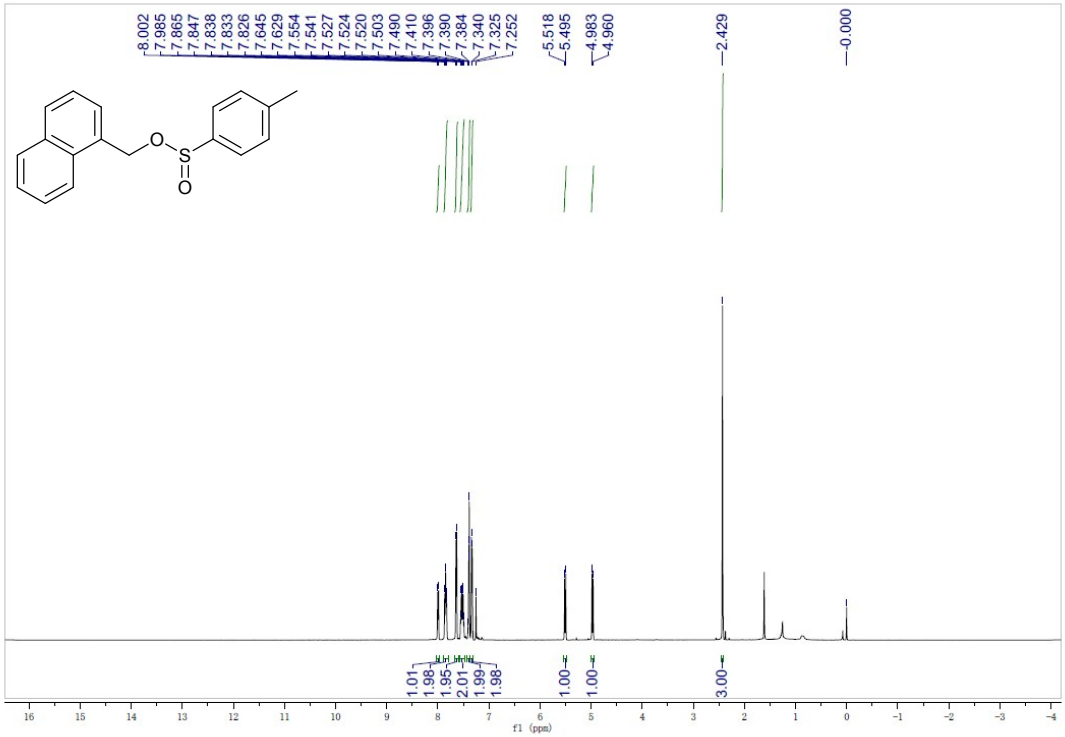


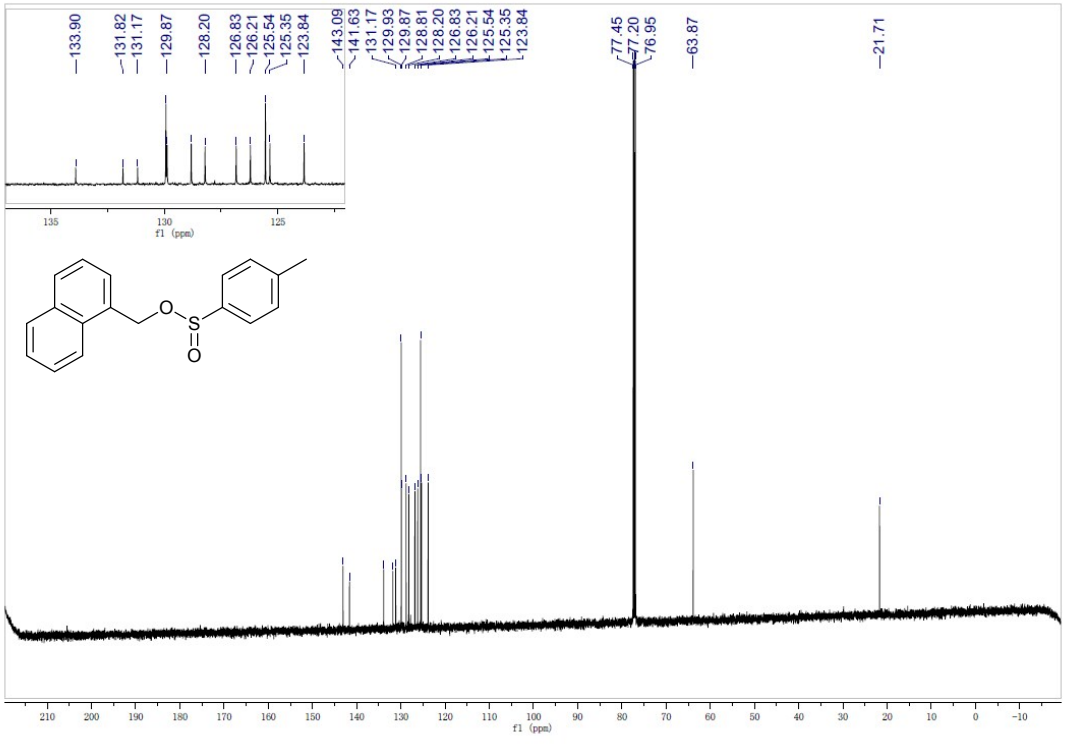
4-(Trifluoromethyl)benzyl 4-methylbenzenesulfinate (3k)



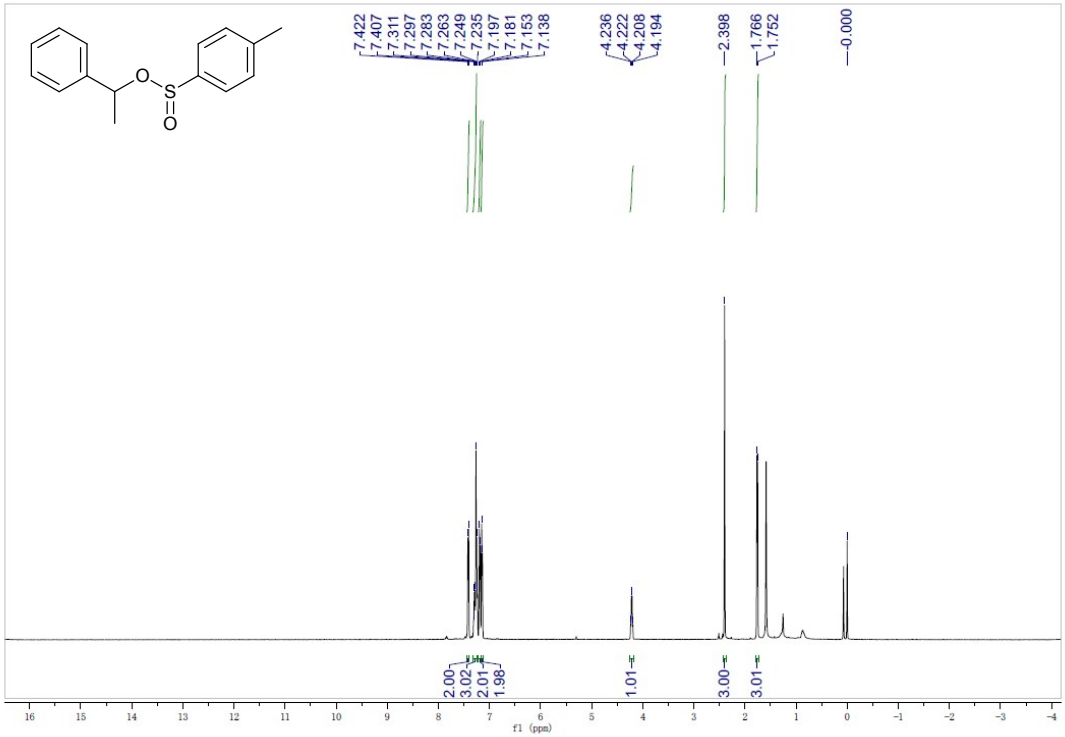


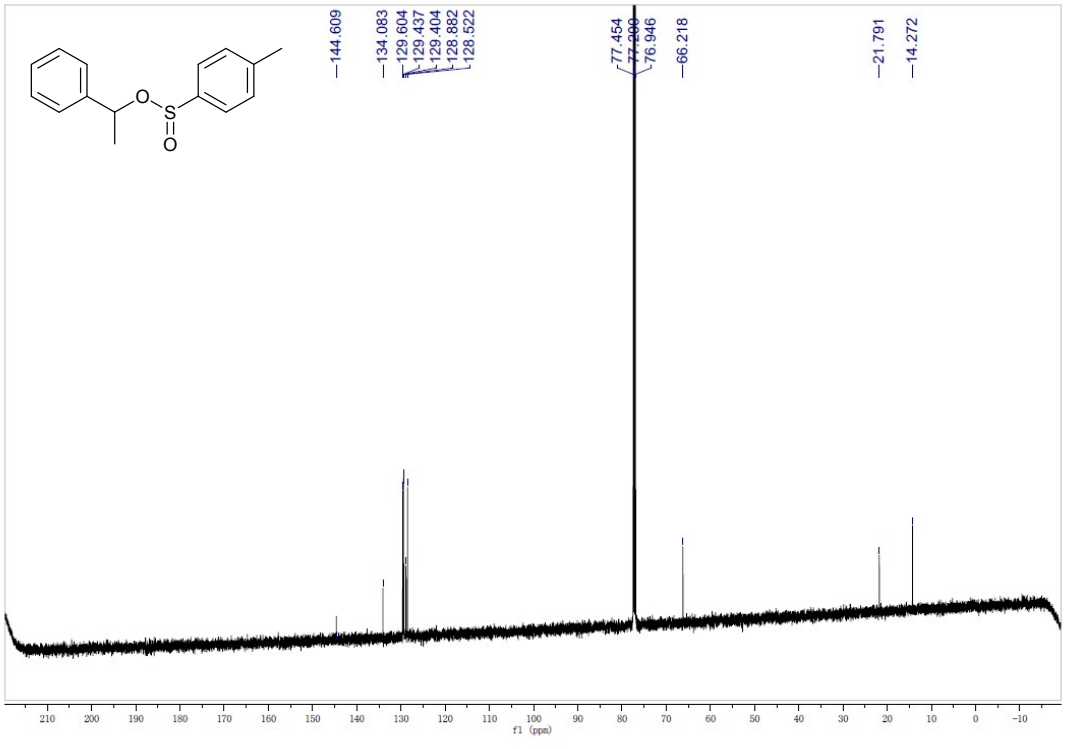
Naphthalen-1-ylmethyl 4-methylbenzenesulfinate (3l)



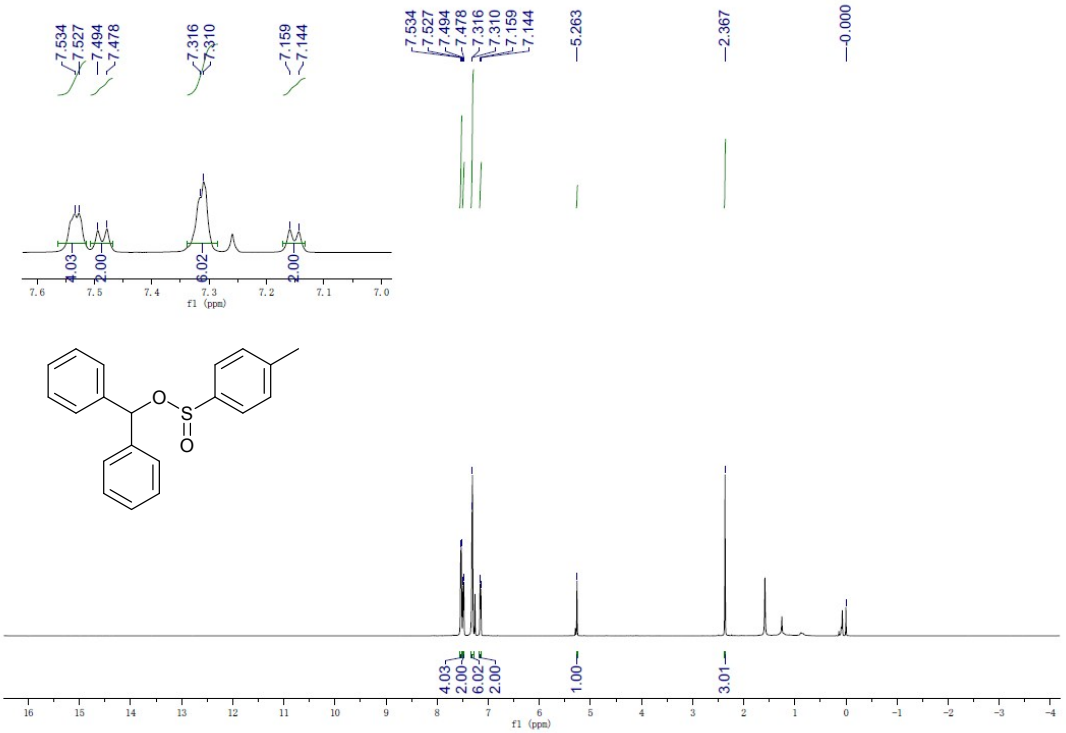


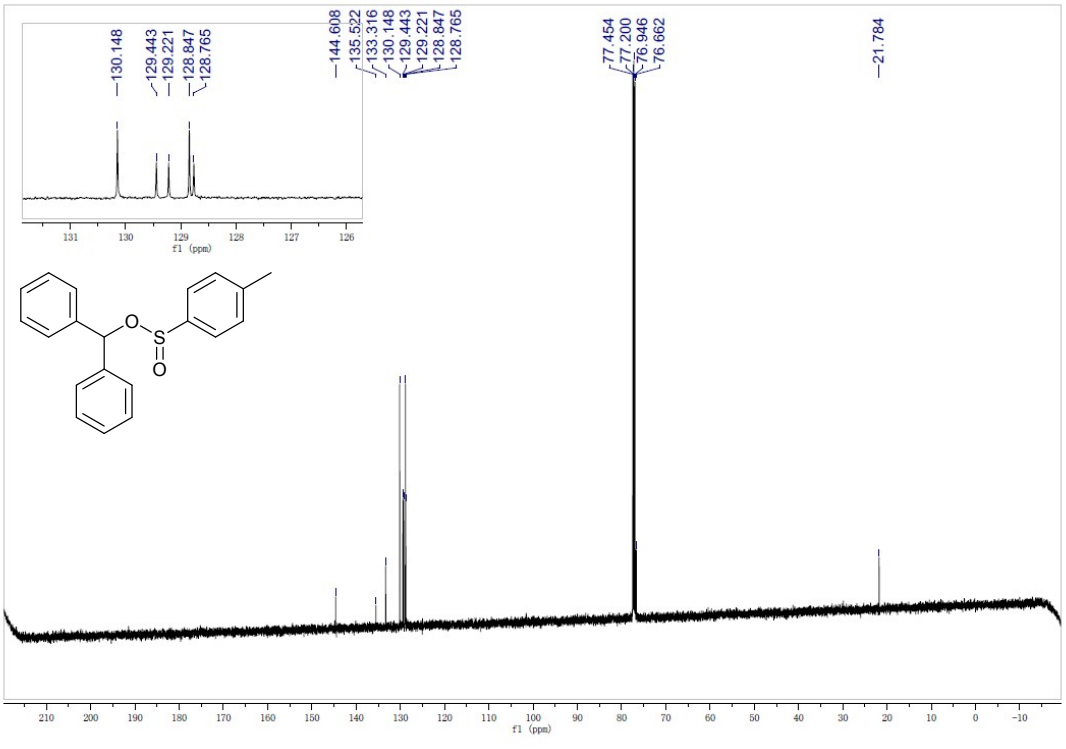
1-Phenylethyl 4-methylbenzenesulfinate (3m)



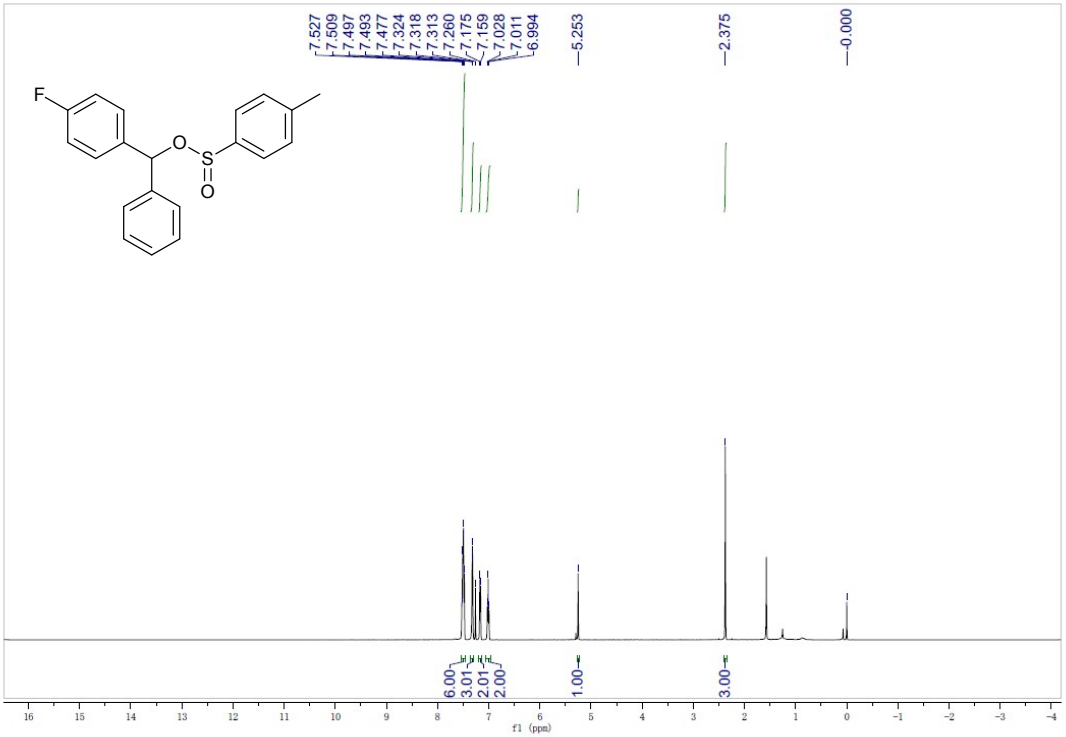


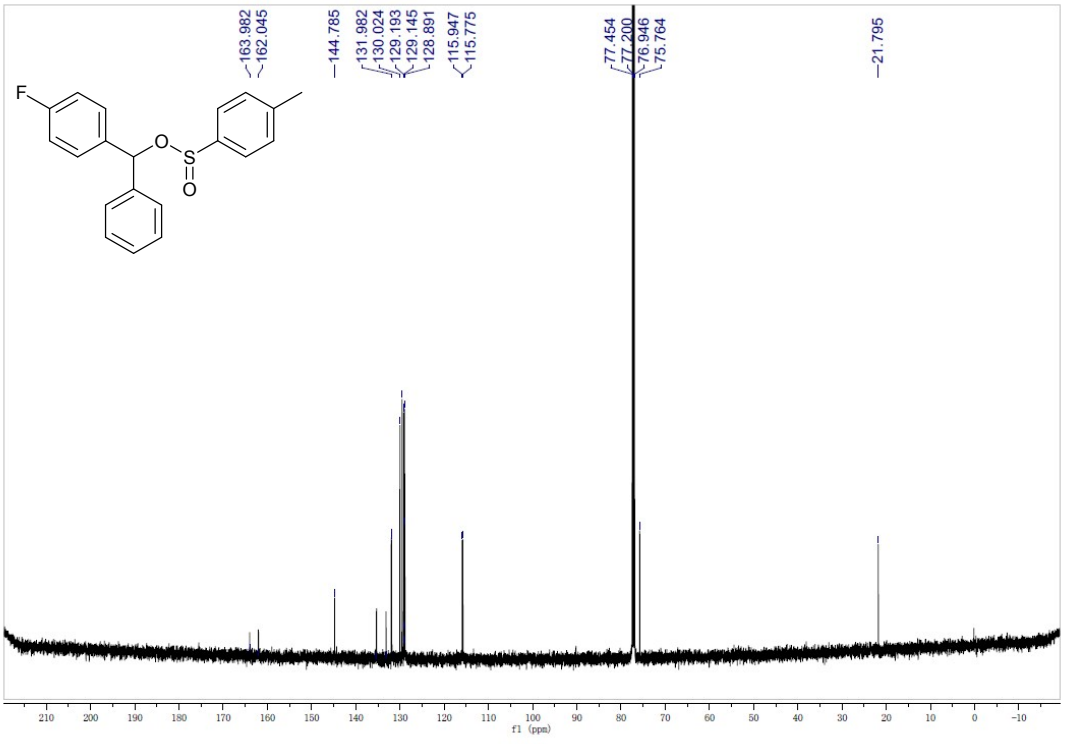
Benzhydryl 4-methylbenzenesulfinate (3n)



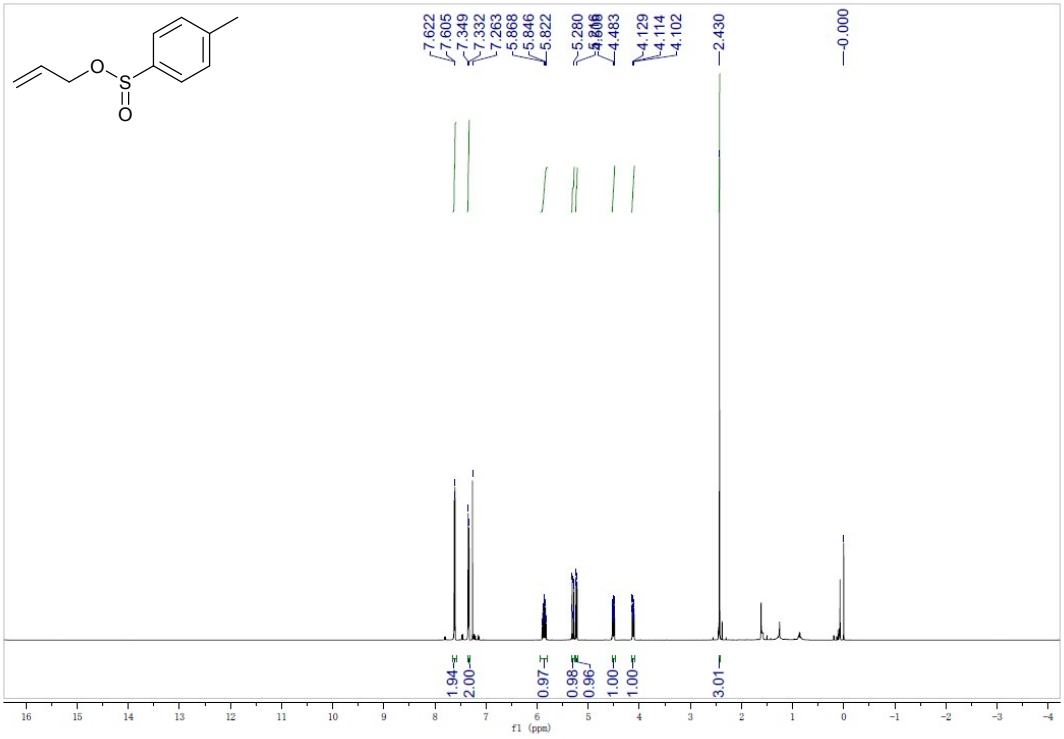


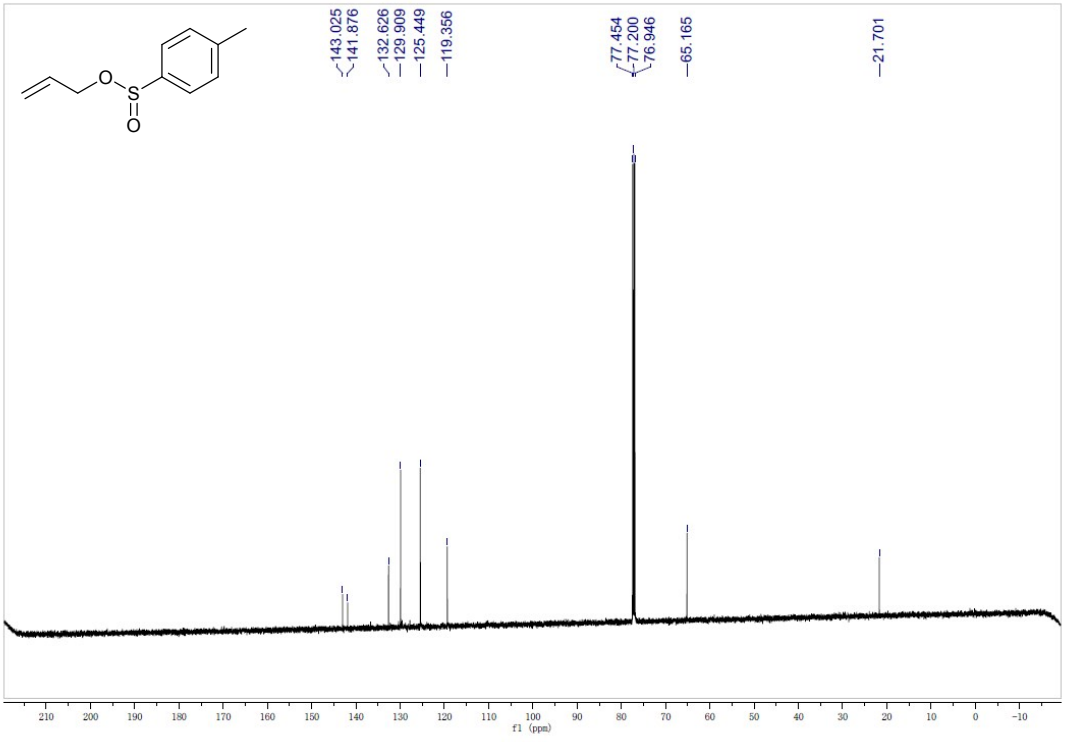
(4-Fluorophenyl)(phenyl)methyl 4-methylbenzenesulfinate (3o)



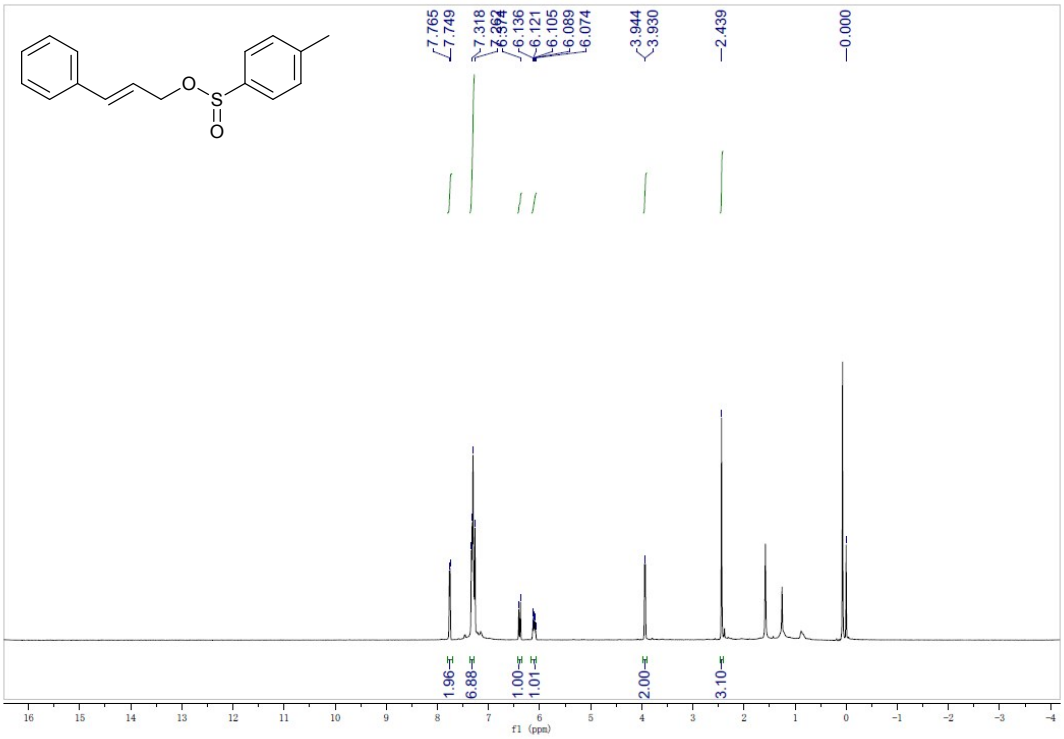


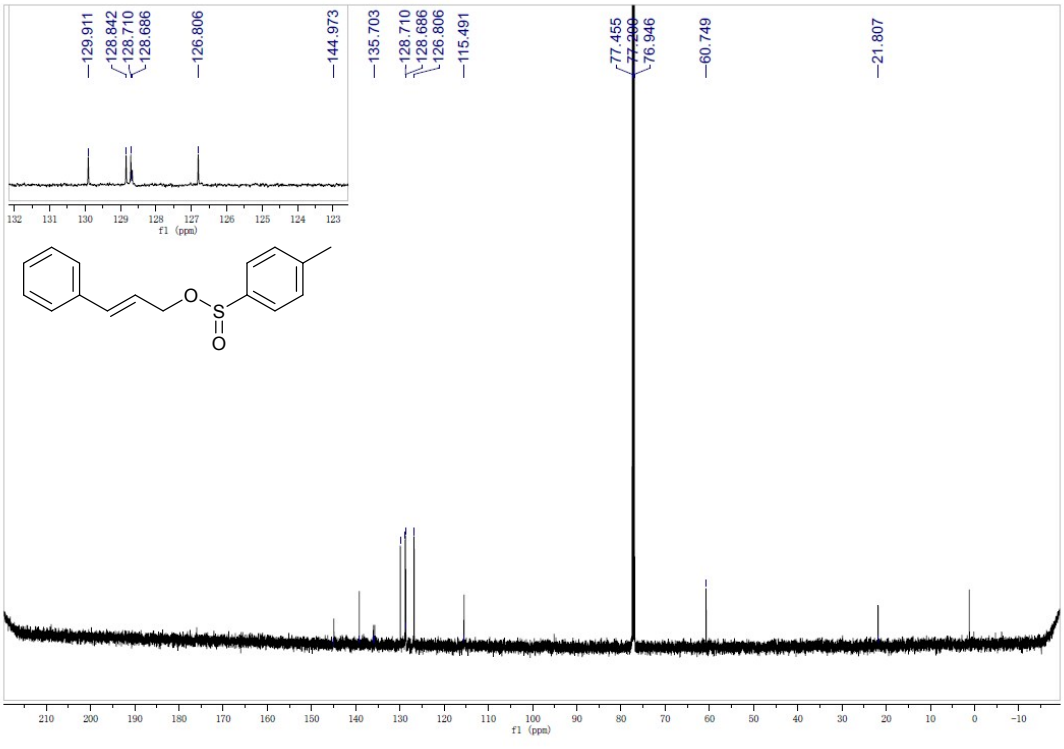
Allyl 4-methylbenzenesulfinate (3p)



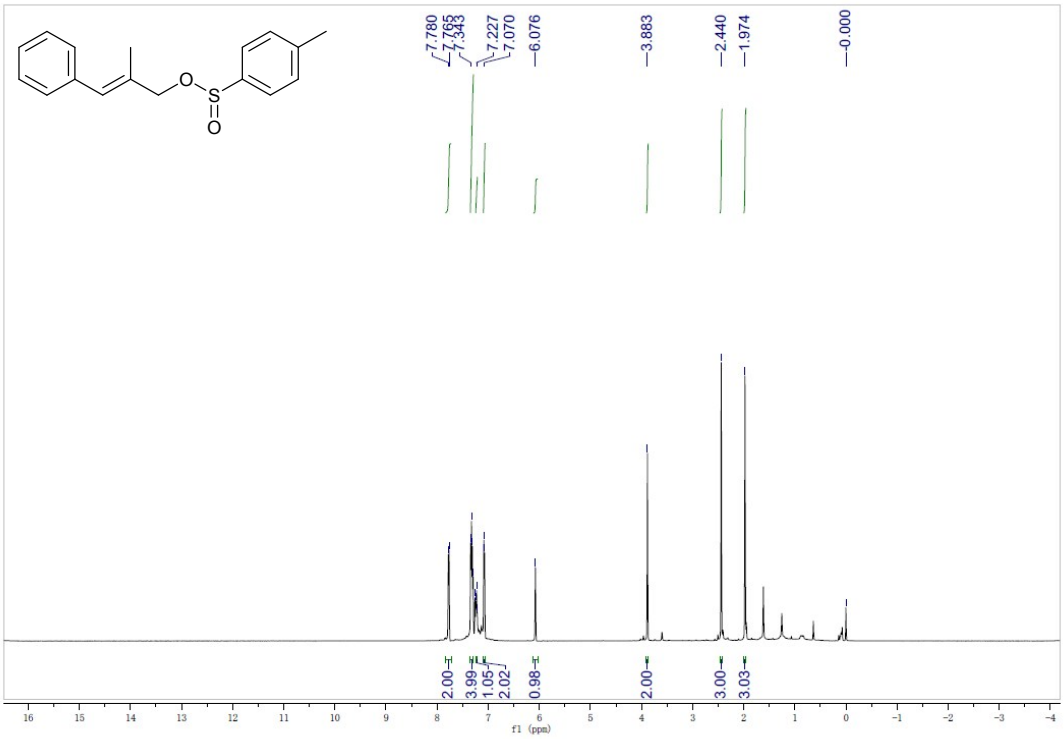


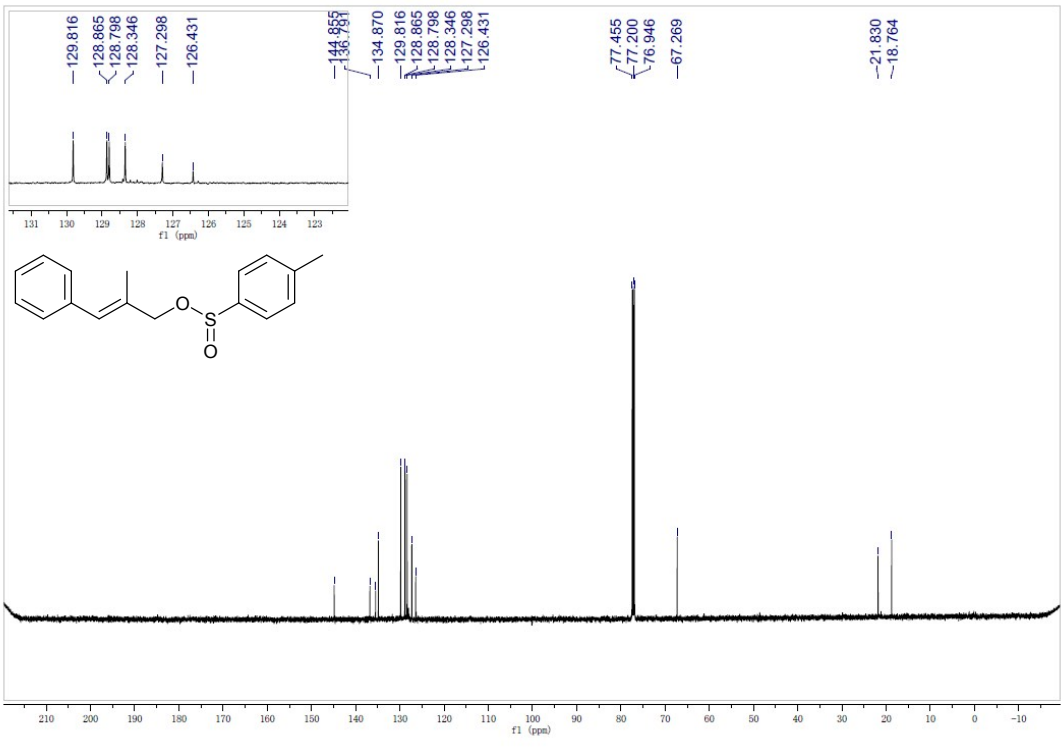
Cinnamyl 4-methylbenzenesulfinate (3q)



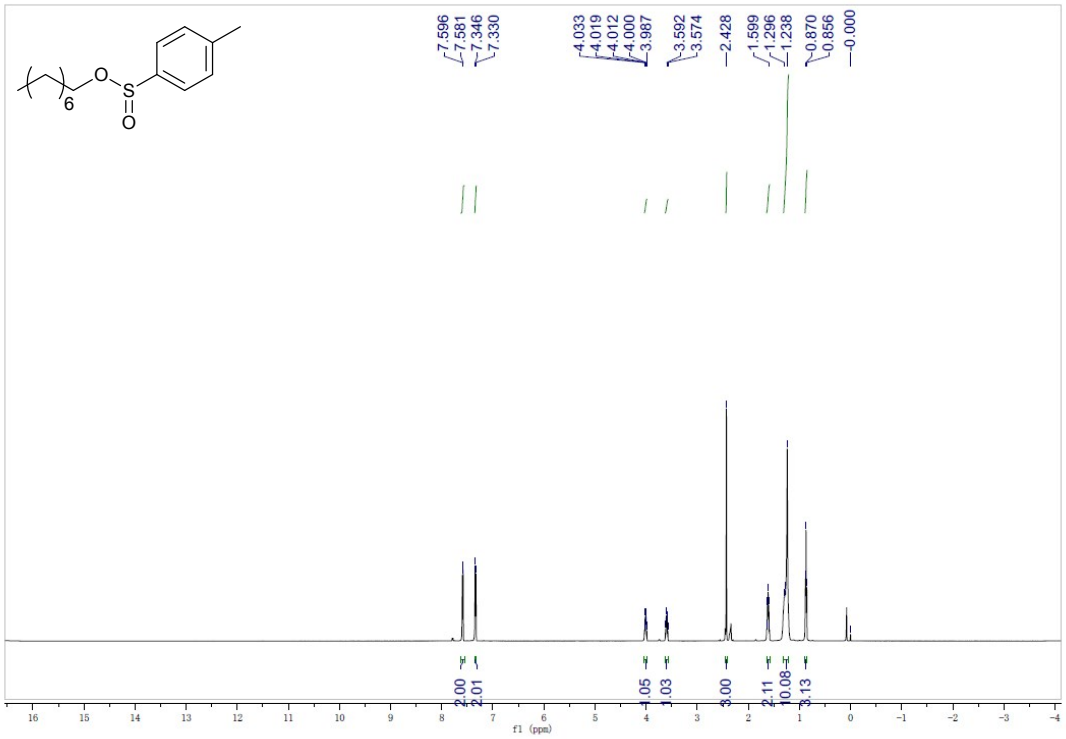


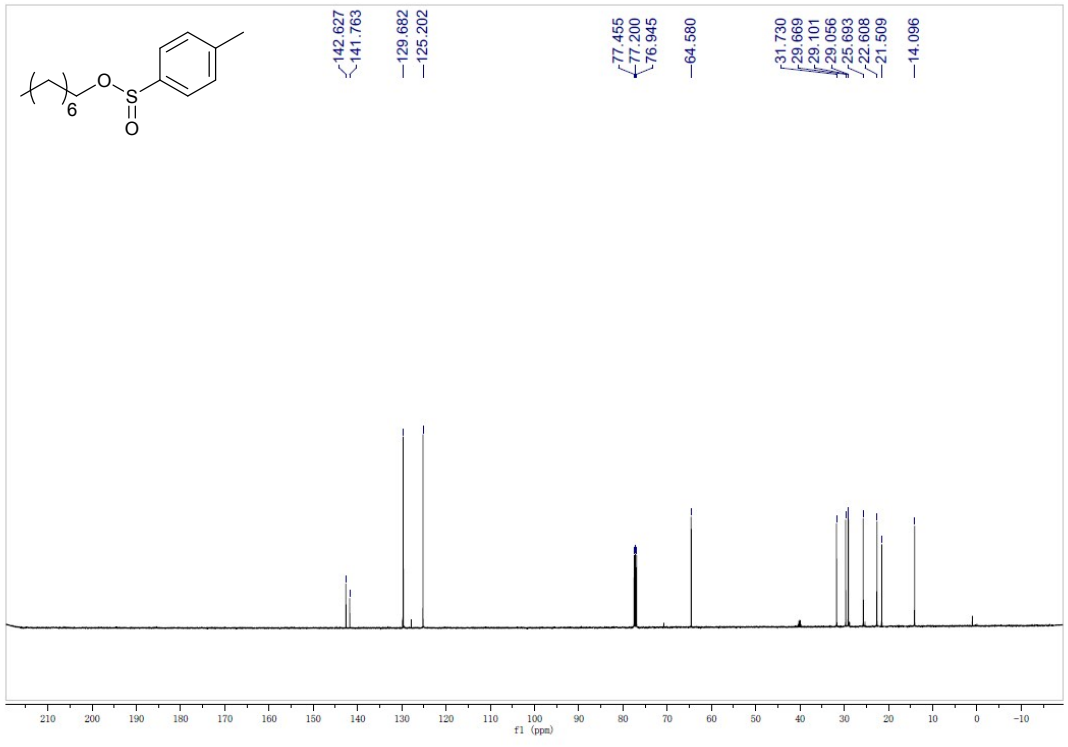
(E)-2-methyl-3-phenylallyl 4-methylbenzenesulfinate (3r)



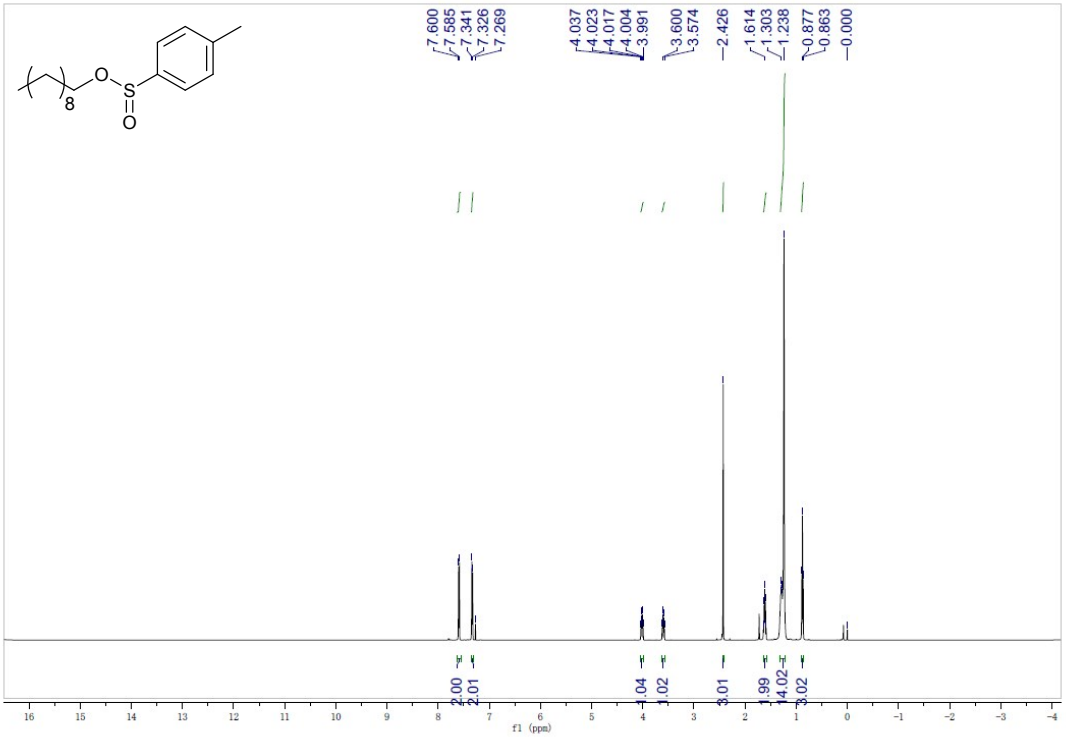


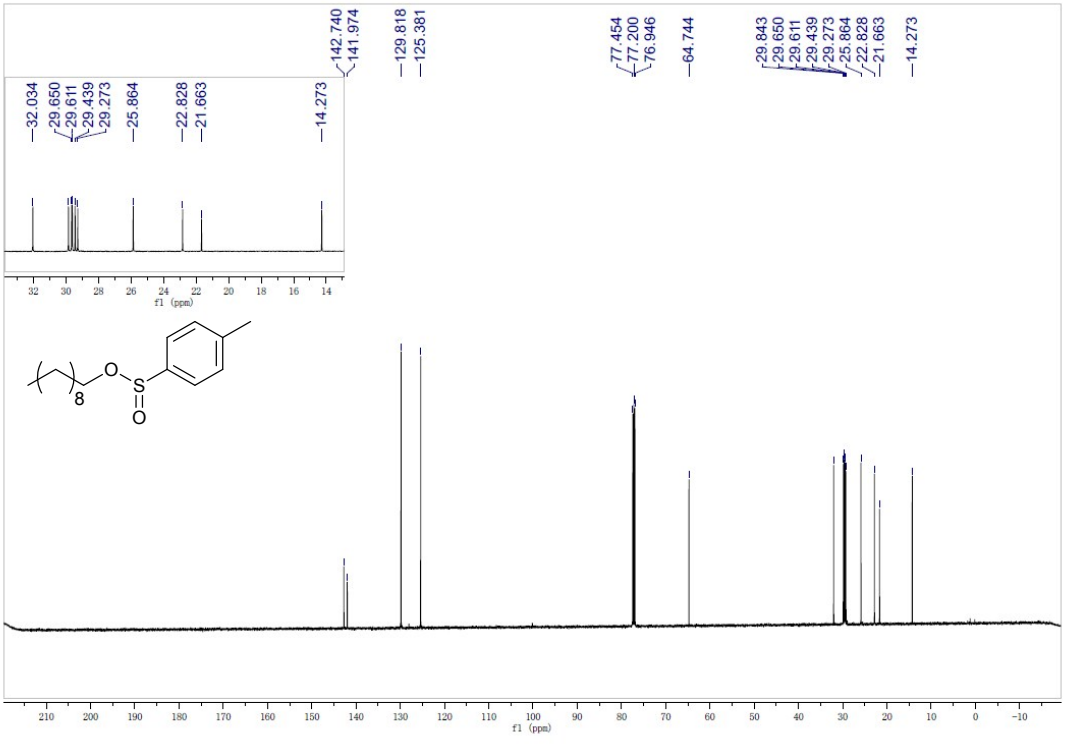
Octyl 4-methylbenzenesulfinate (3s)



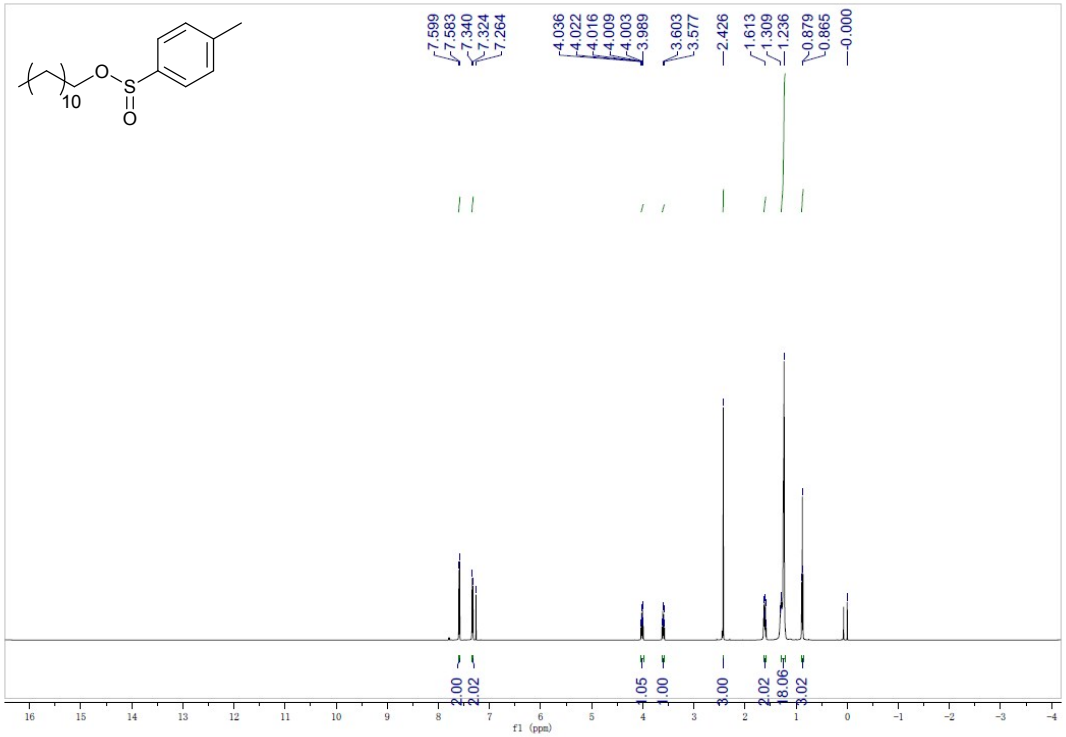


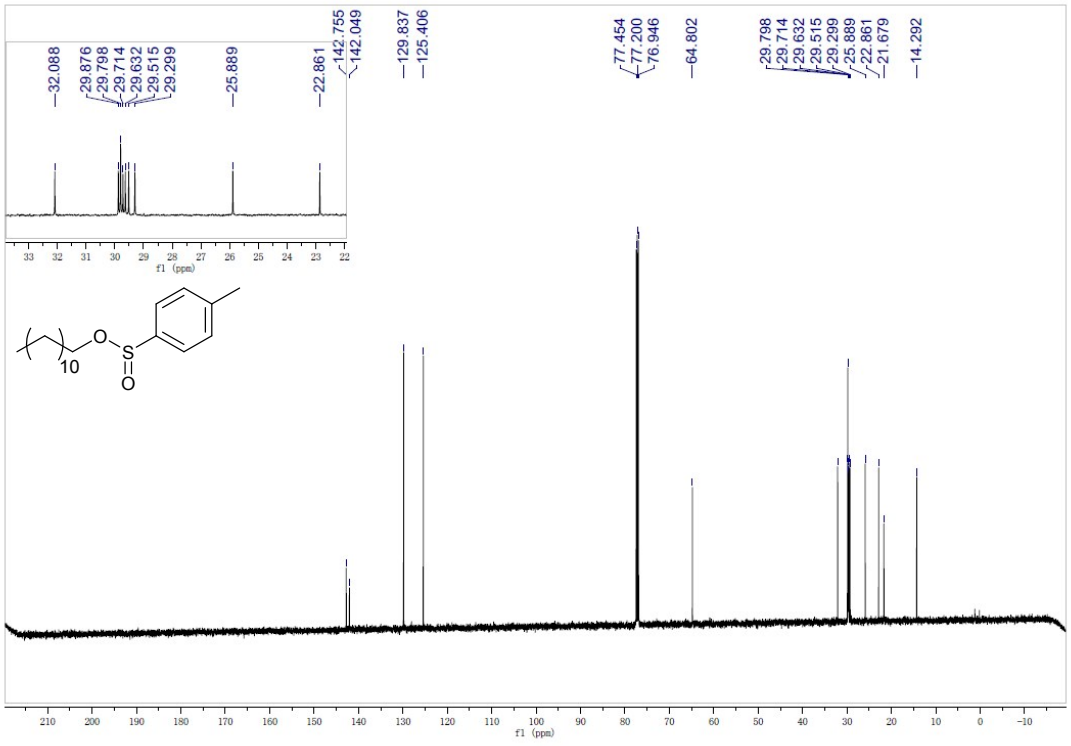
Decyl 4-methylbenzenesulfinate (3t)



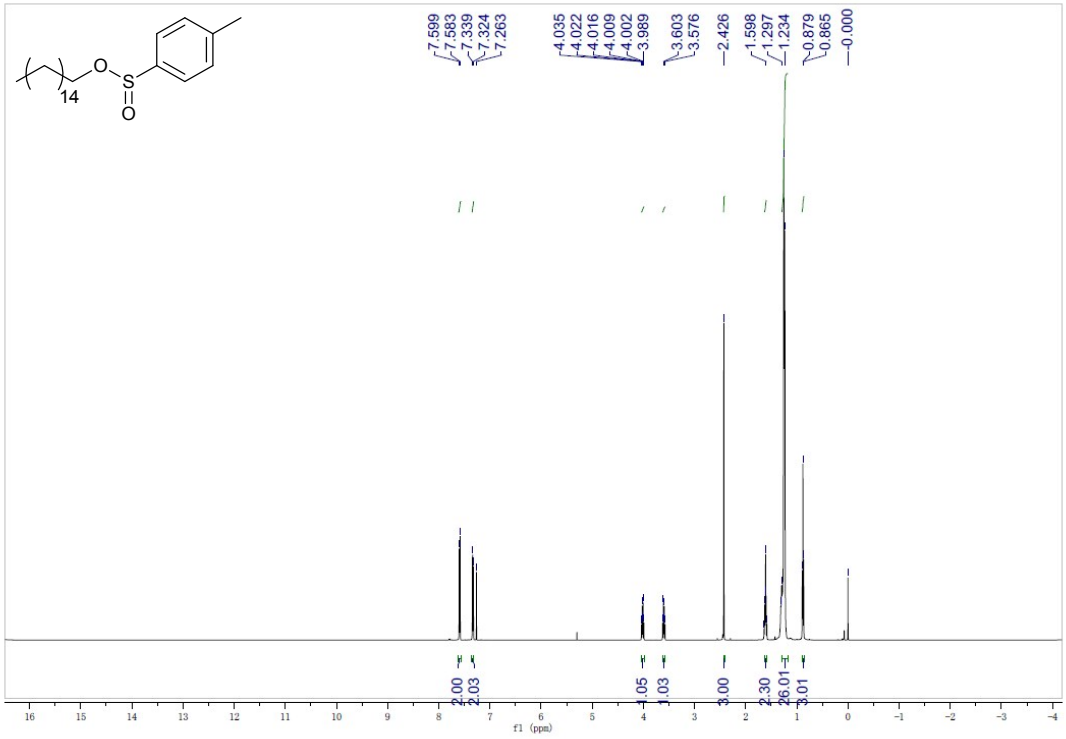


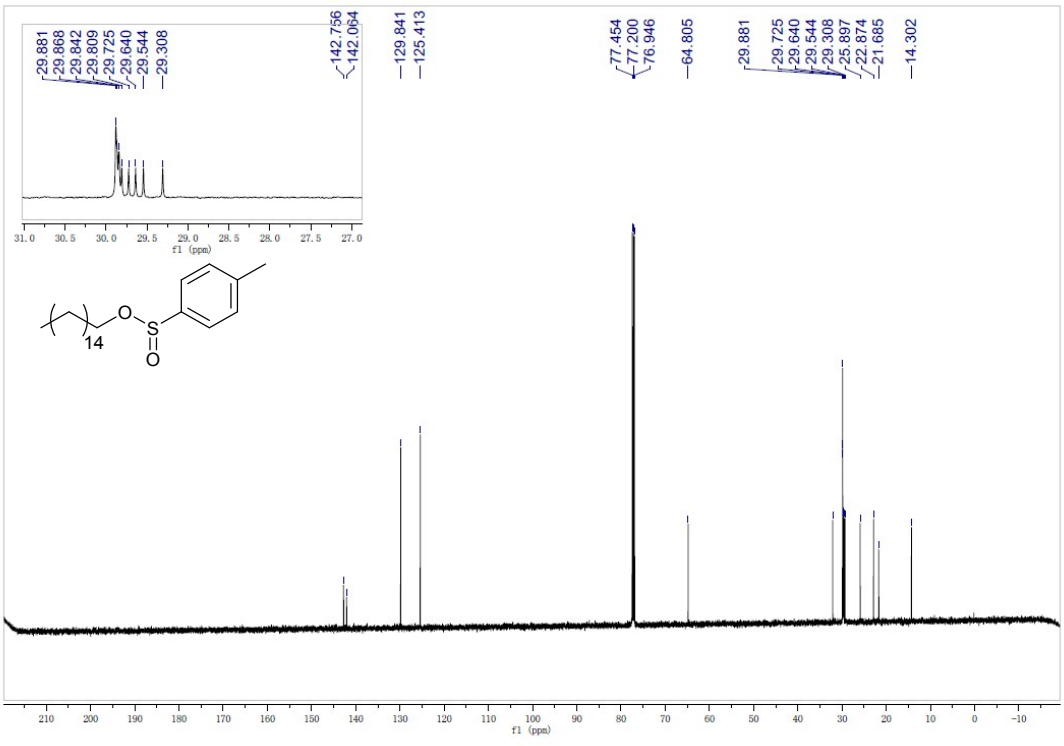
Dodecyl 4-methylbenzenesulfinate (3u)



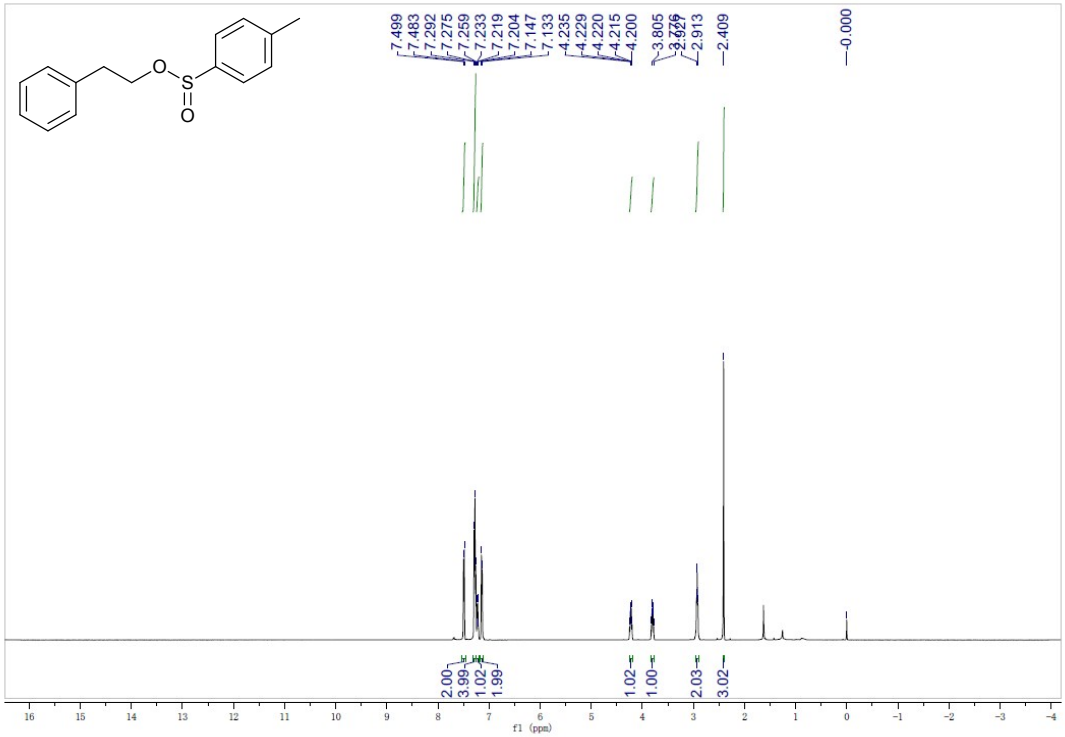


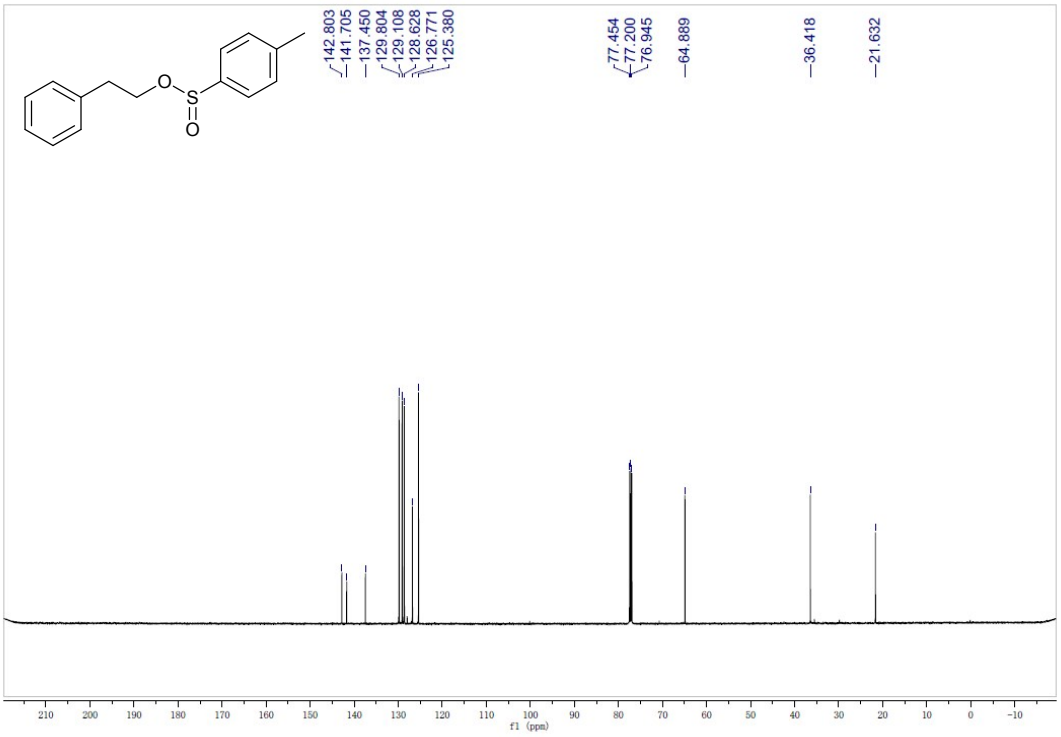
Hexadecyl 4-methylbenzenesulfinate (3v)



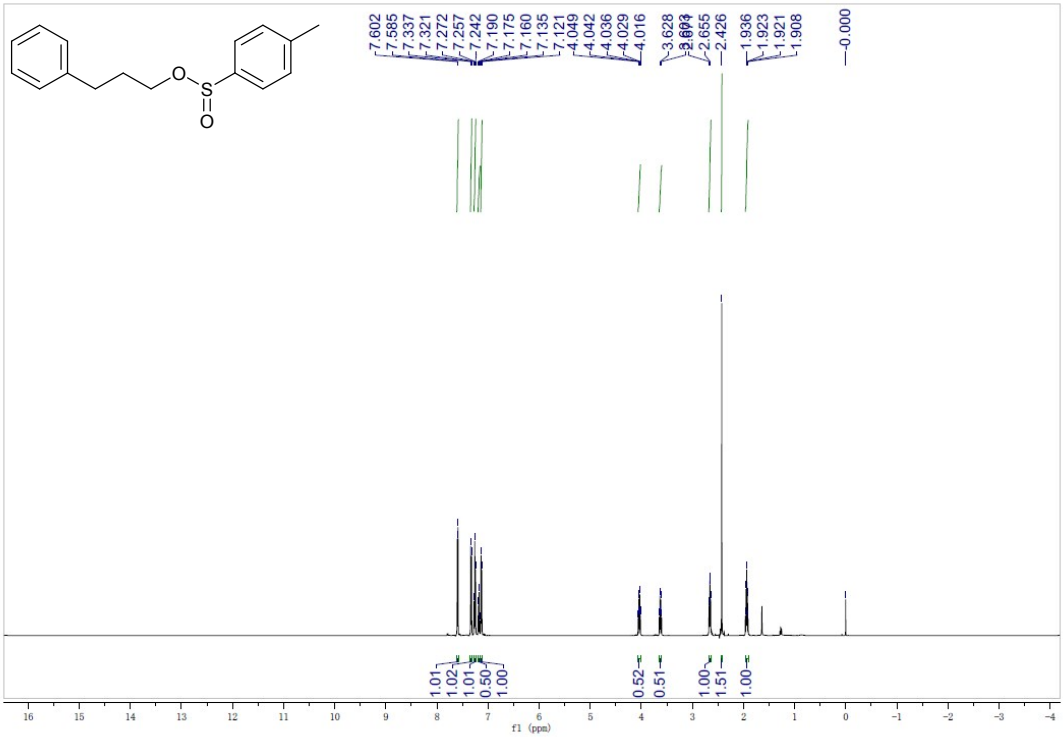


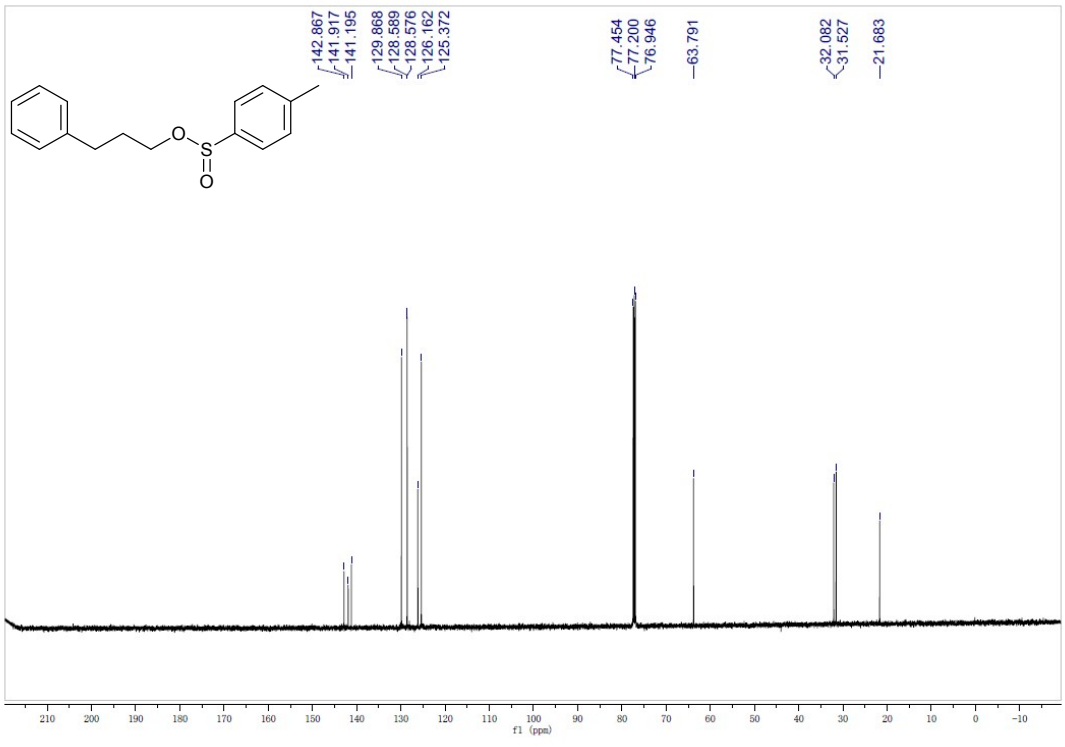
Phenethyl 4-methylbenzenesulfinate (3w)



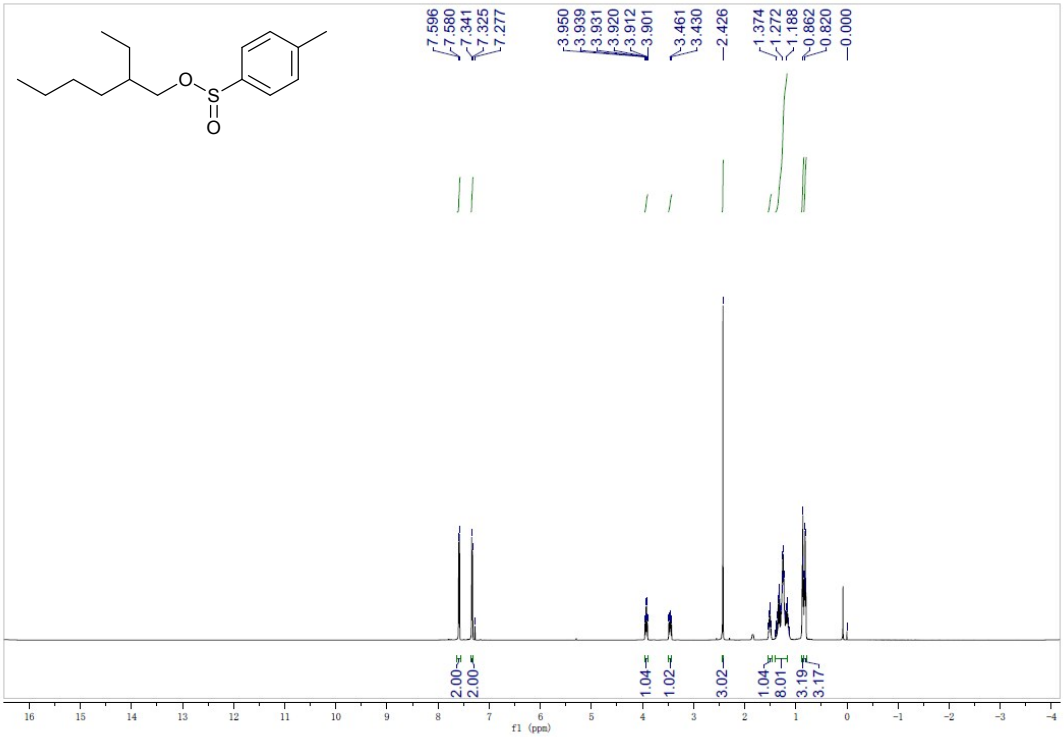


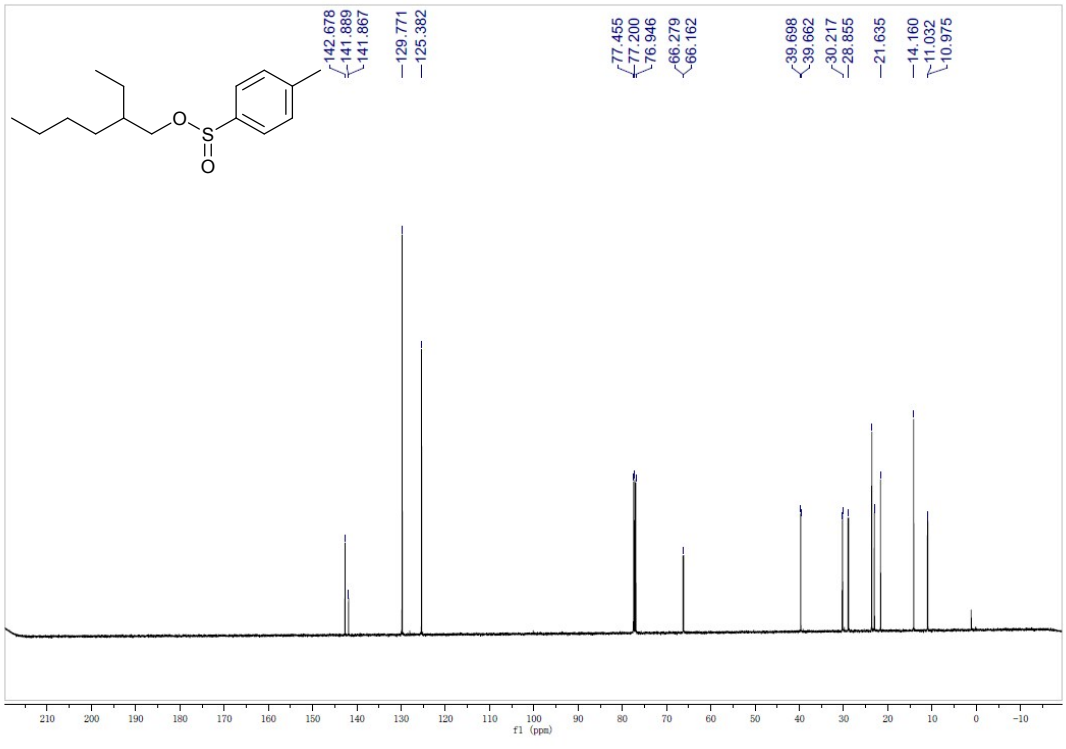
3-Phenylpropyl 4-methylbenzenesulfinate (3x)



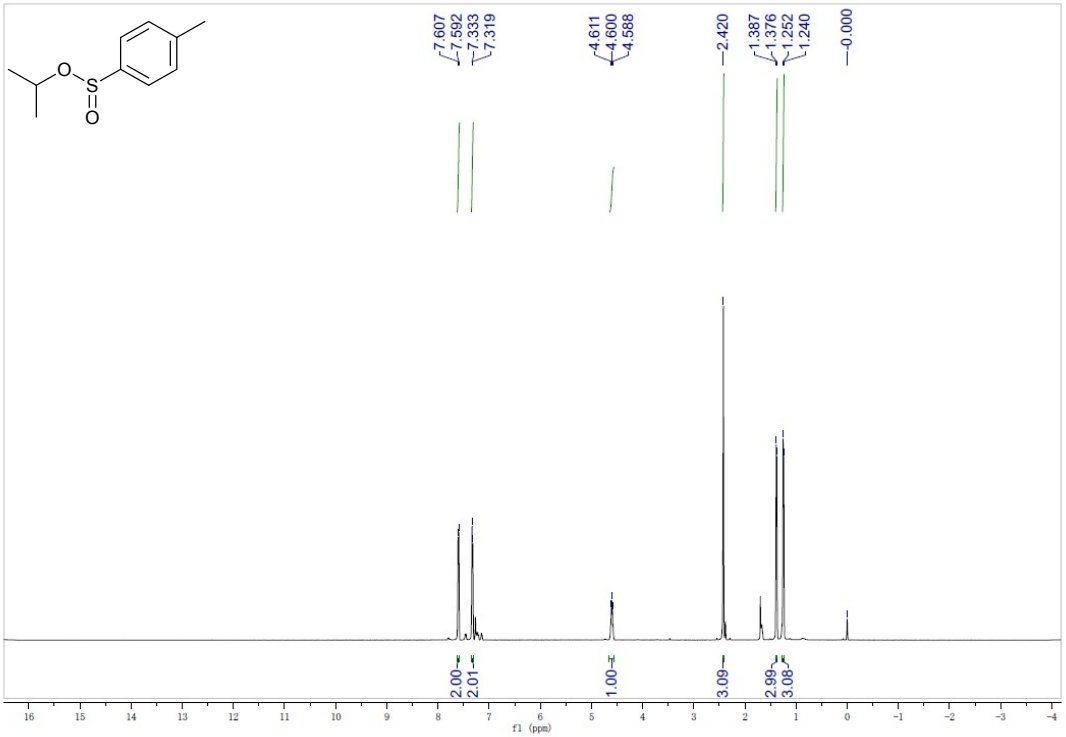


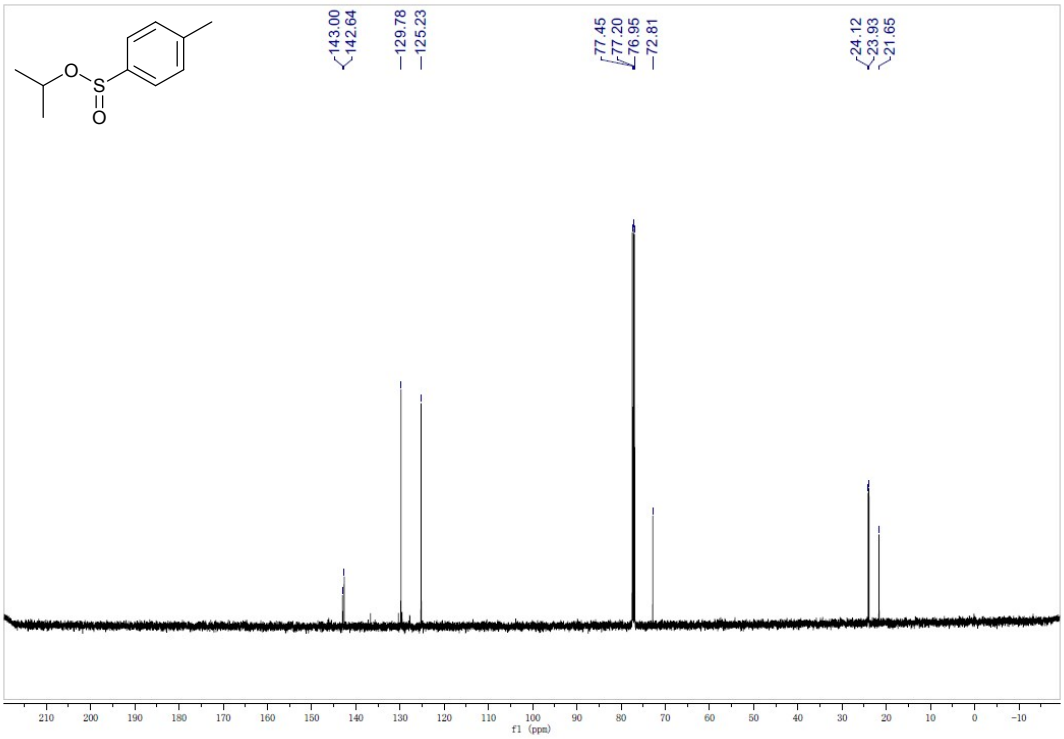
2-Ethylhexyl 4-methylbenzenesulfinate (3y)



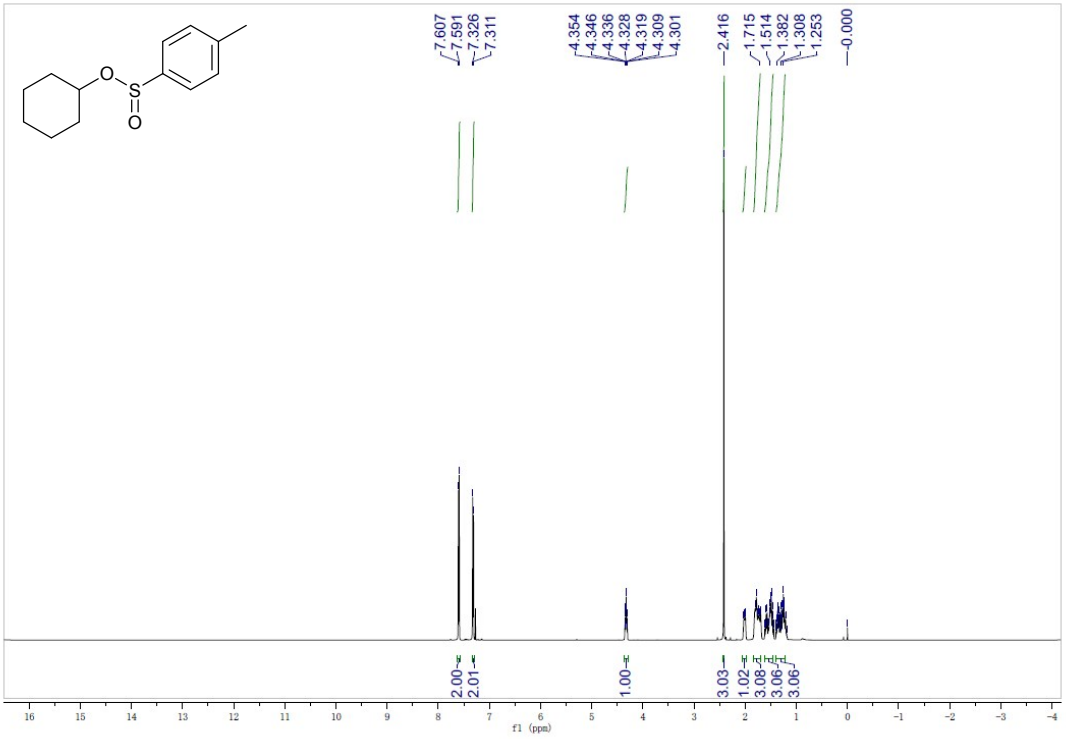


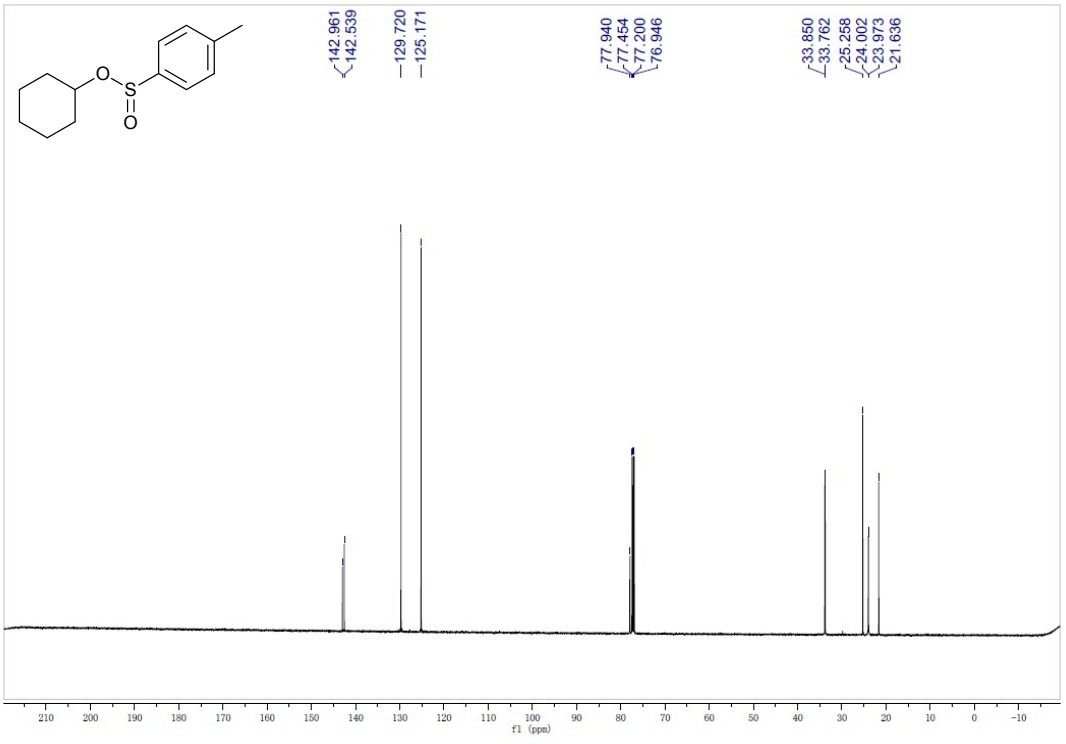
Isopropyl 4-methylbenzenesulfinate (3z)



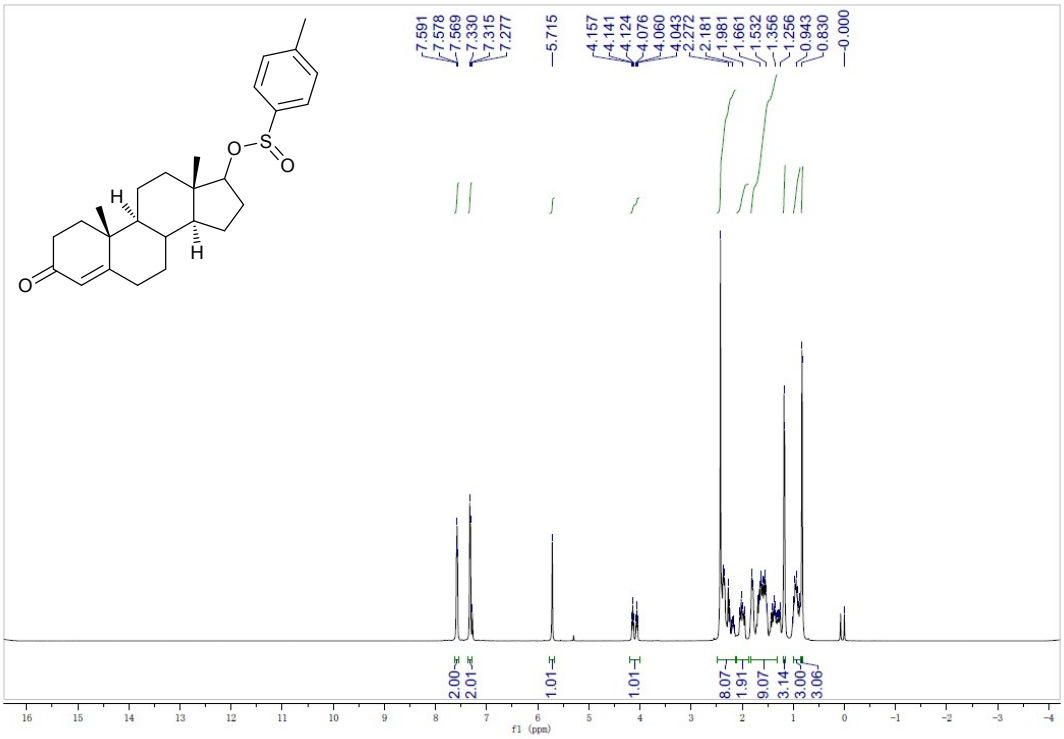


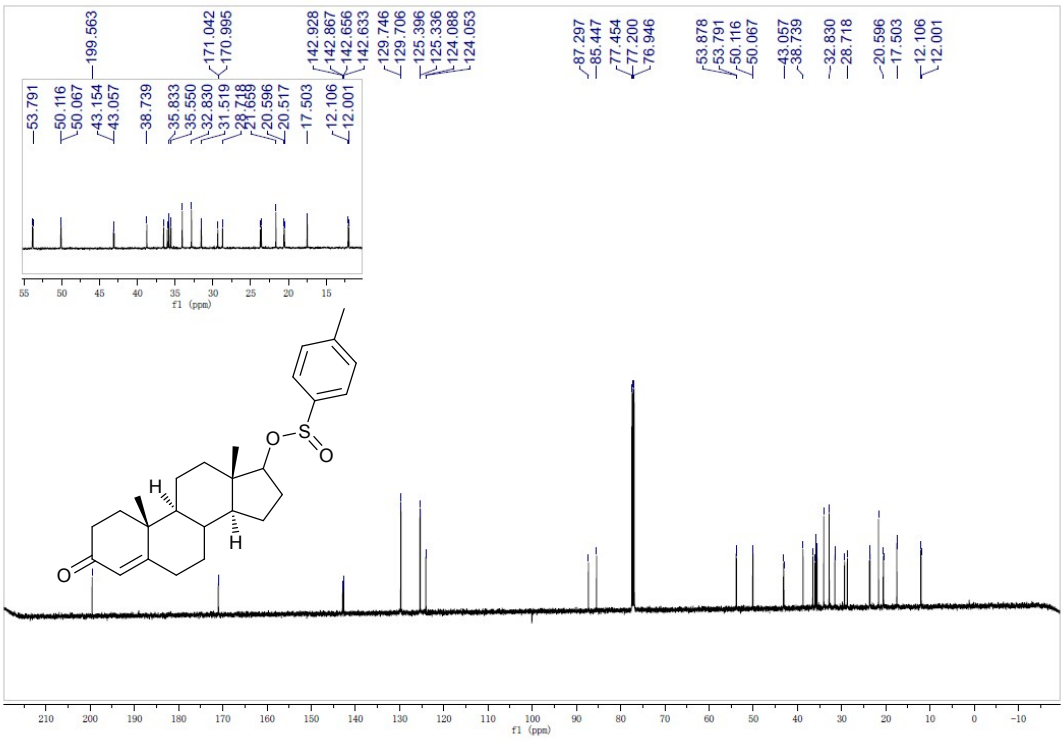
Cyclohexyl 4-methylbenzenesulfinate (3A)



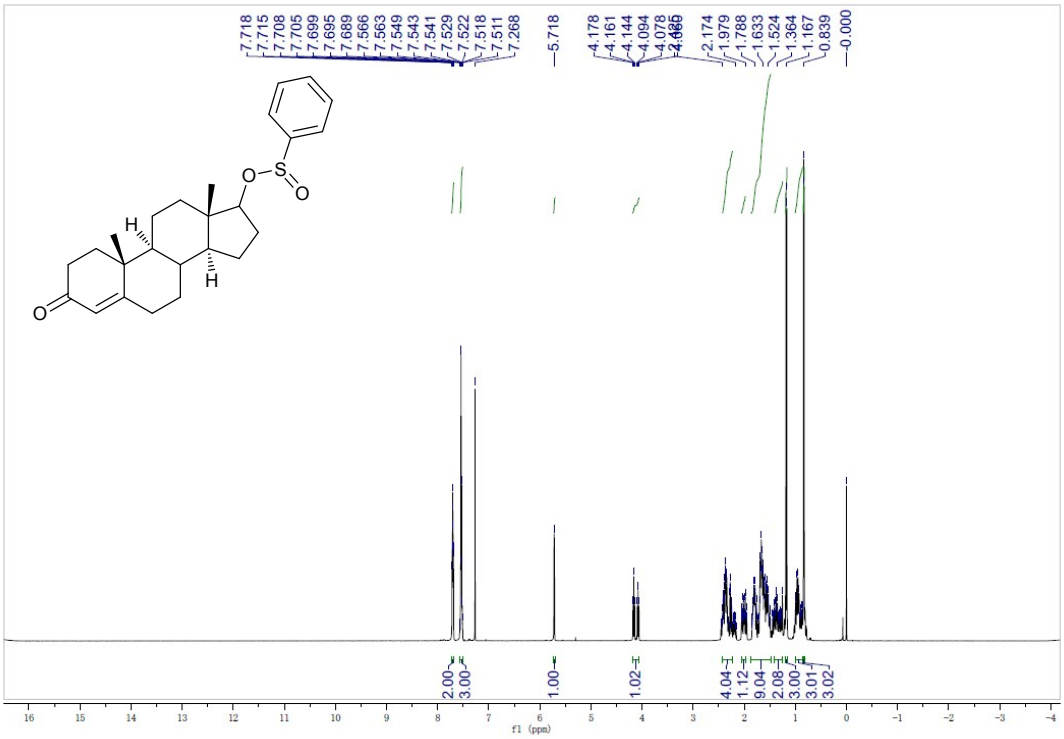


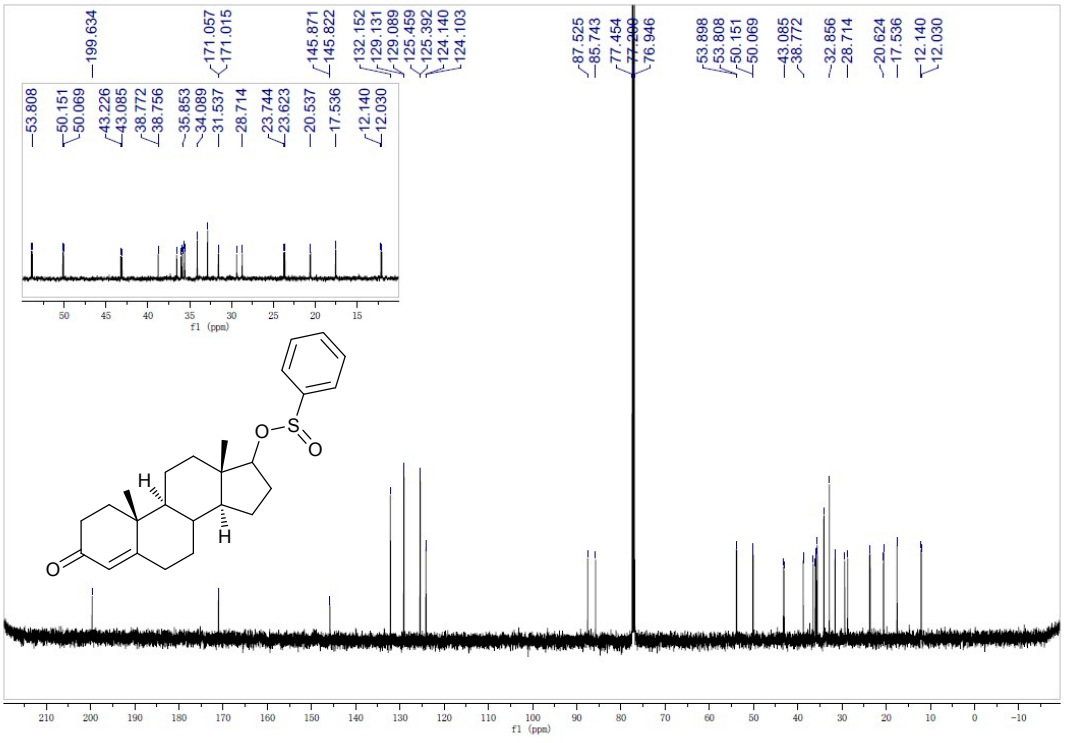
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-methylbenzenesulfinate (3B)



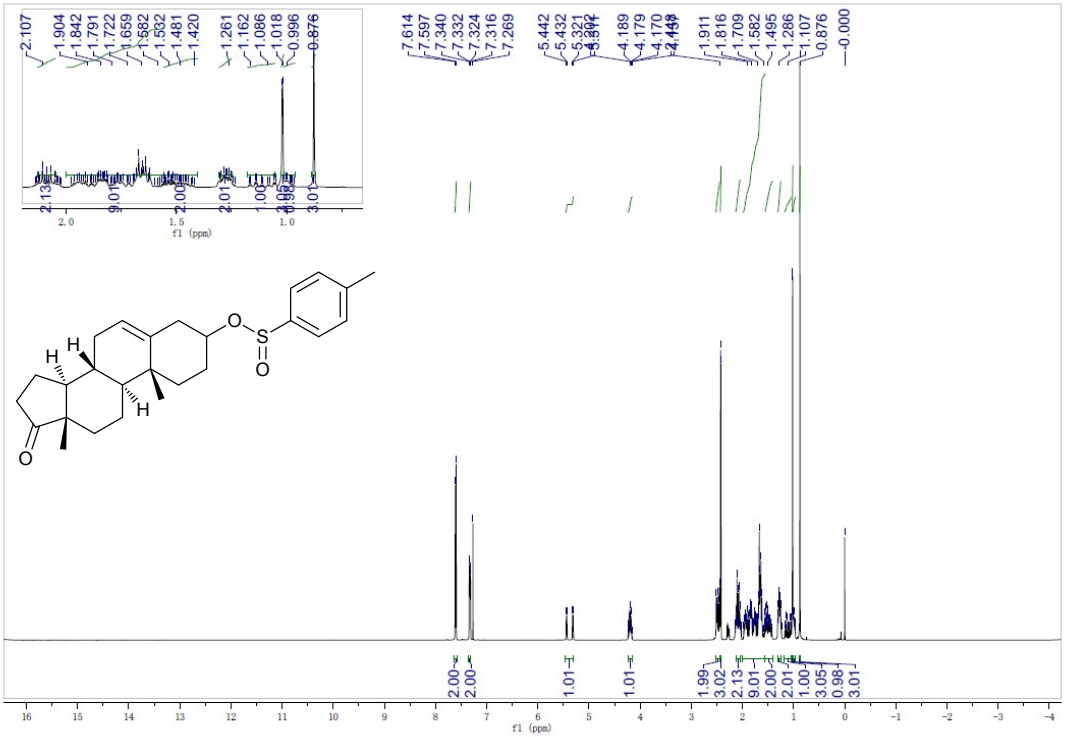


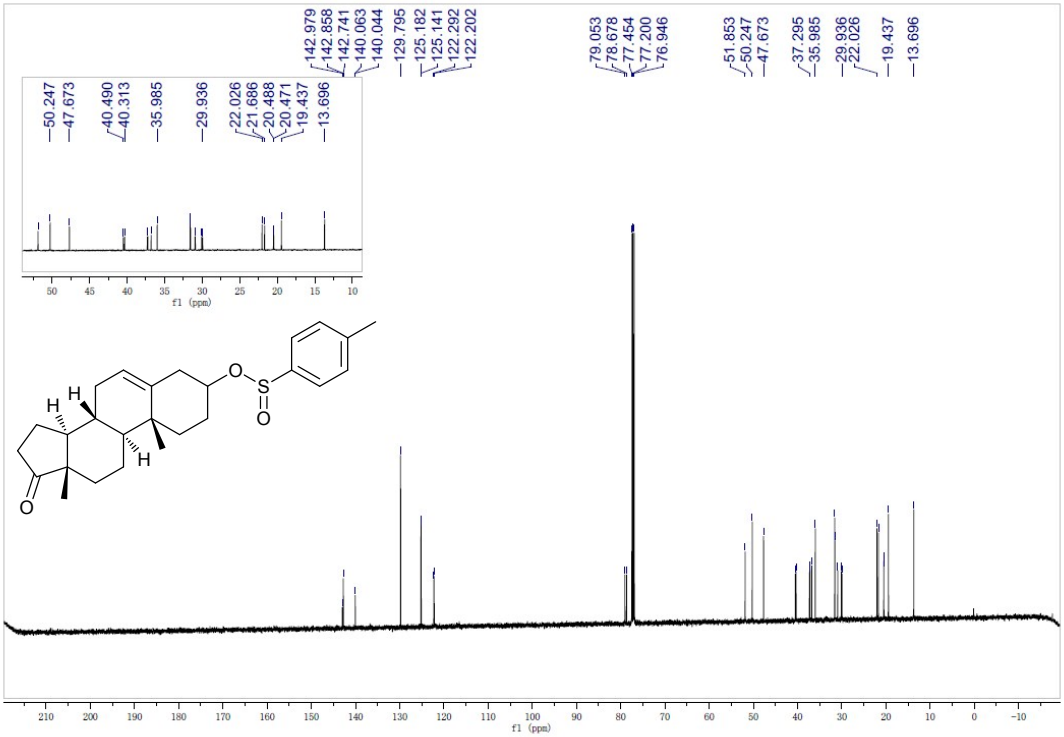
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl benzenesulfinate (3C)



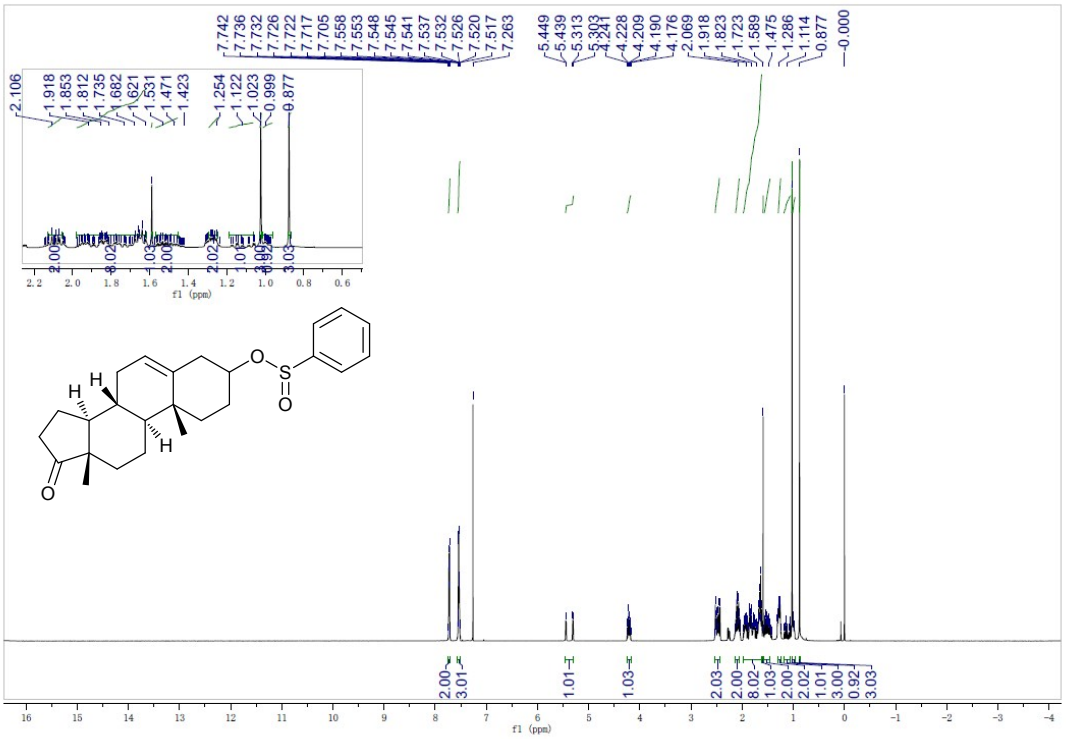


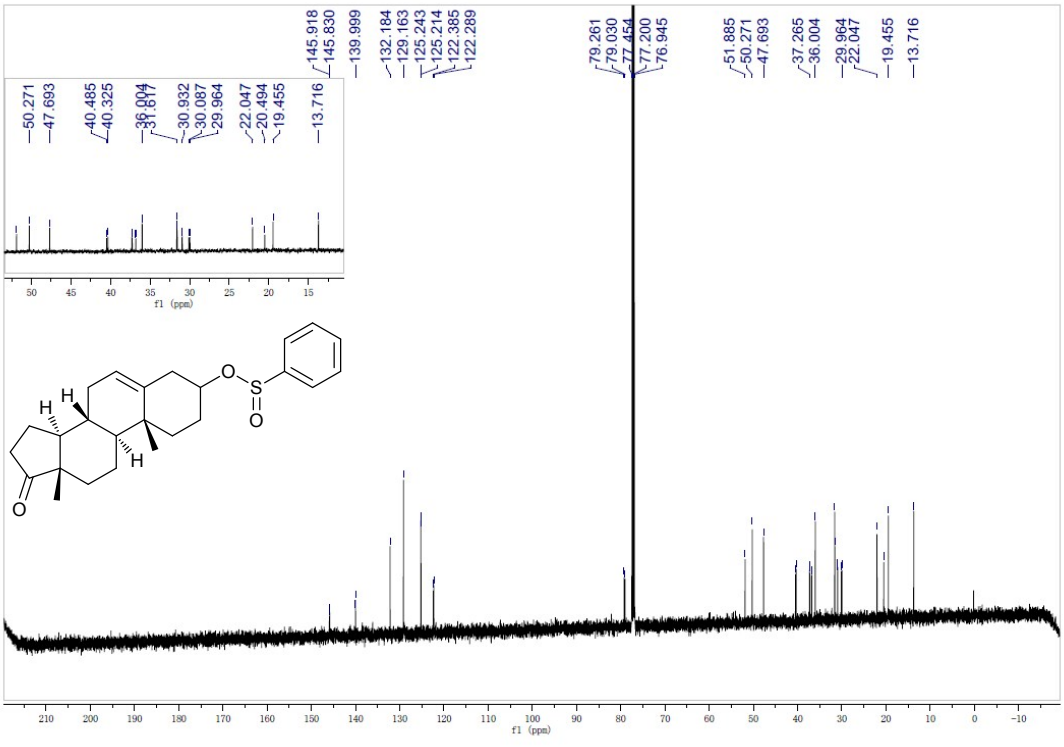
(8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-methylbenzenesulfinate (3D)



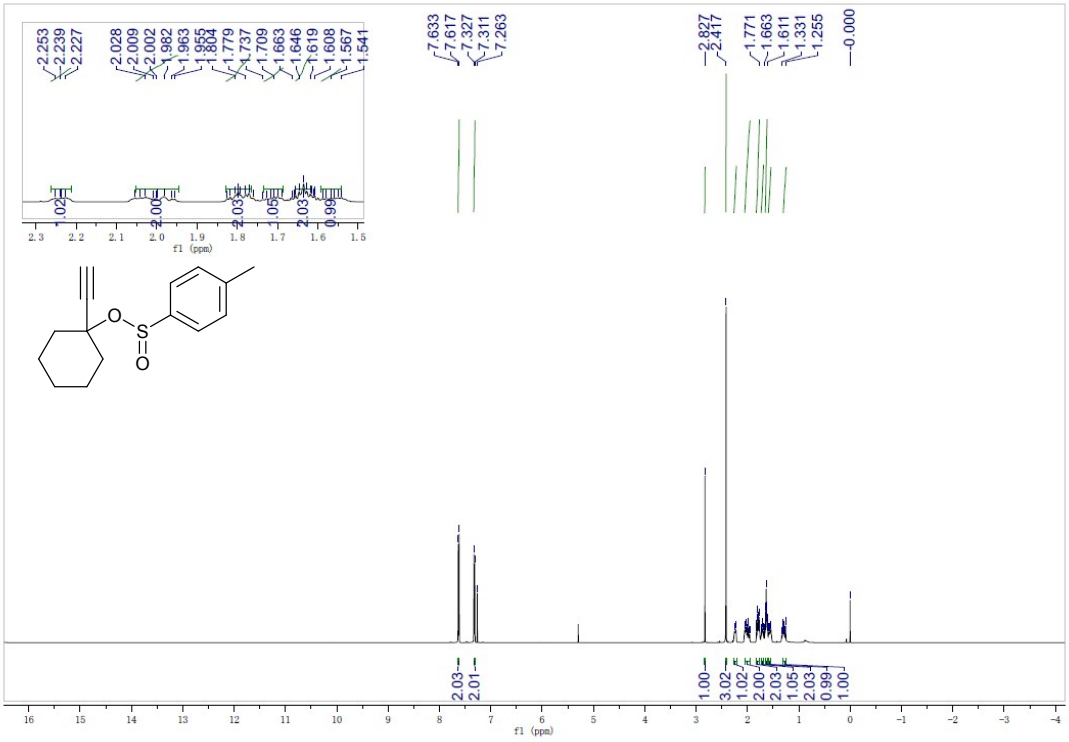


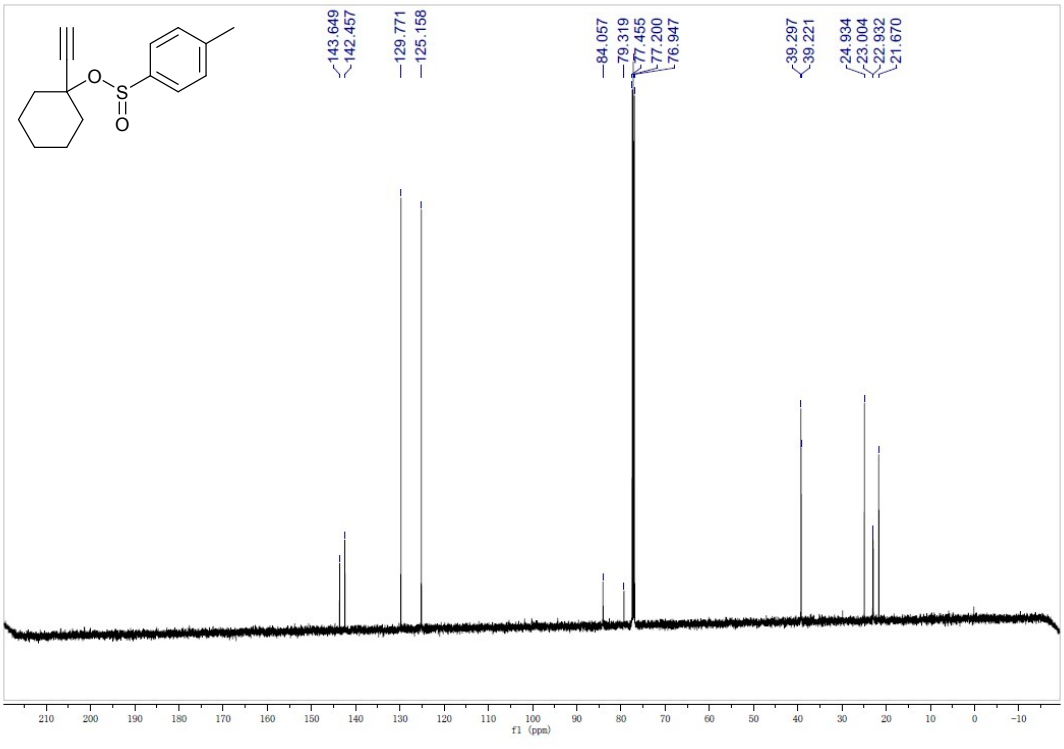
(8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl benzenesulfinate (3E)



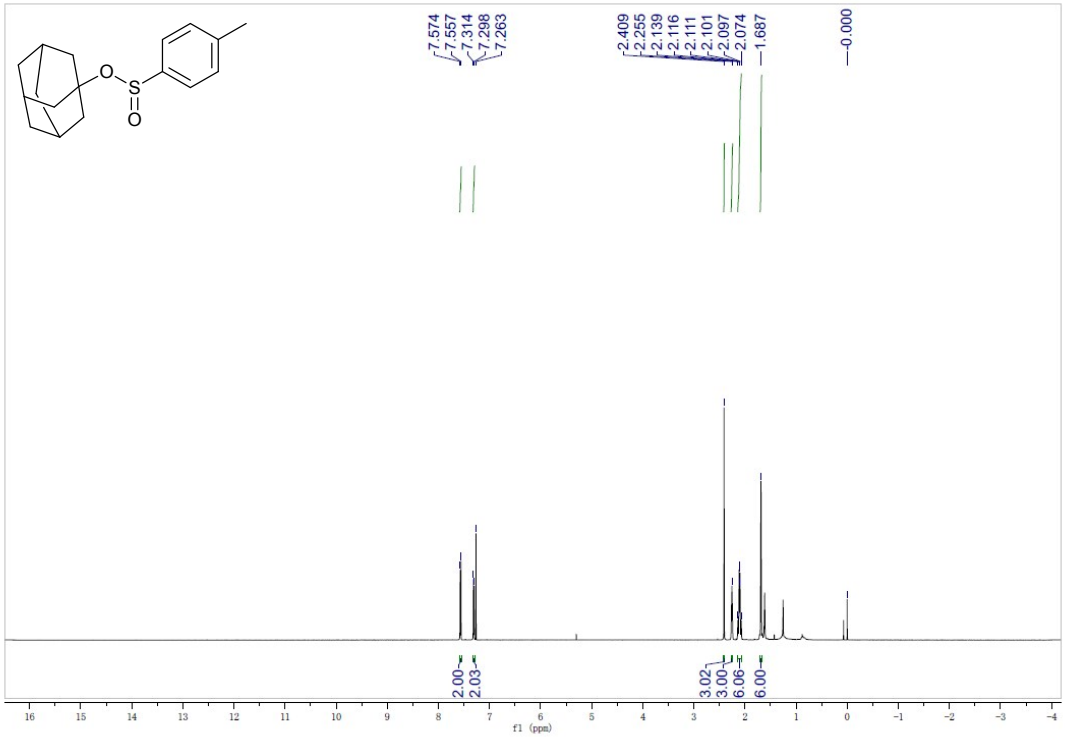


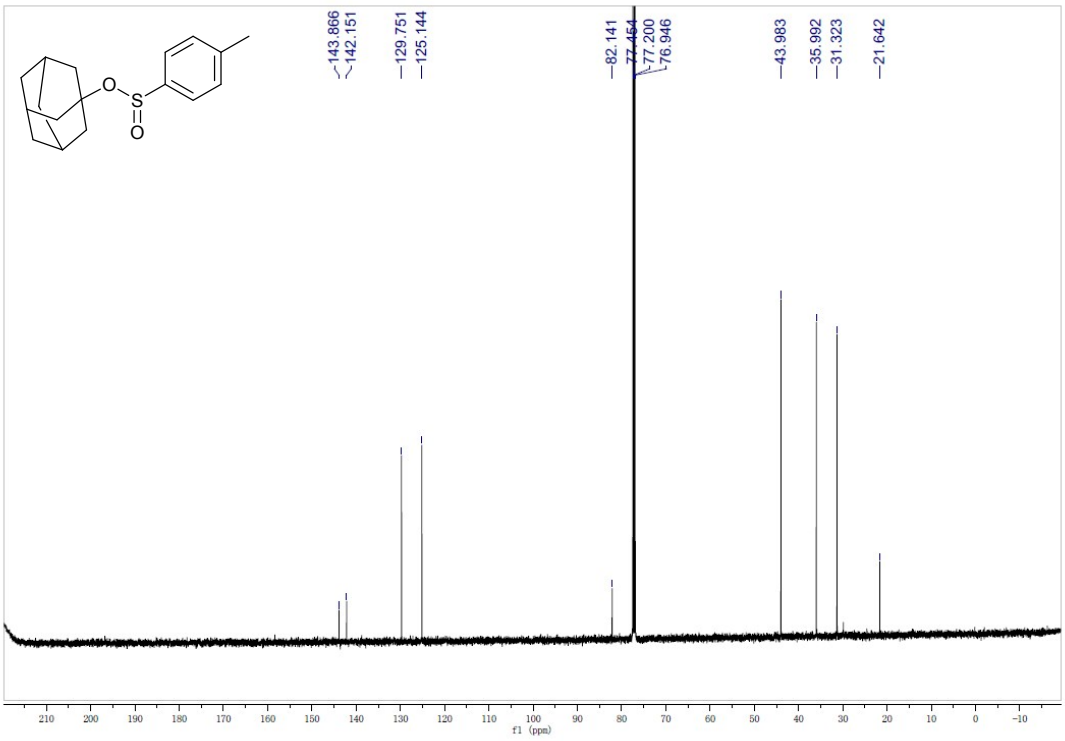
1-Ethynylcyclohexyl 4-methylbenzenesulfinate (3F)



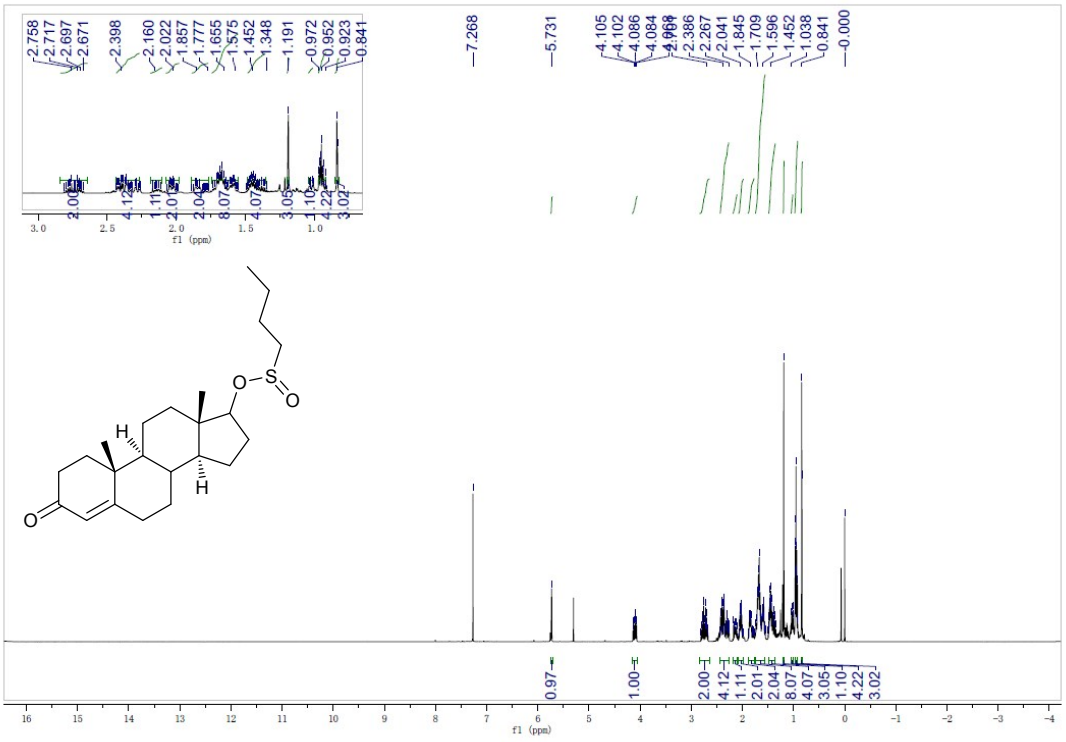


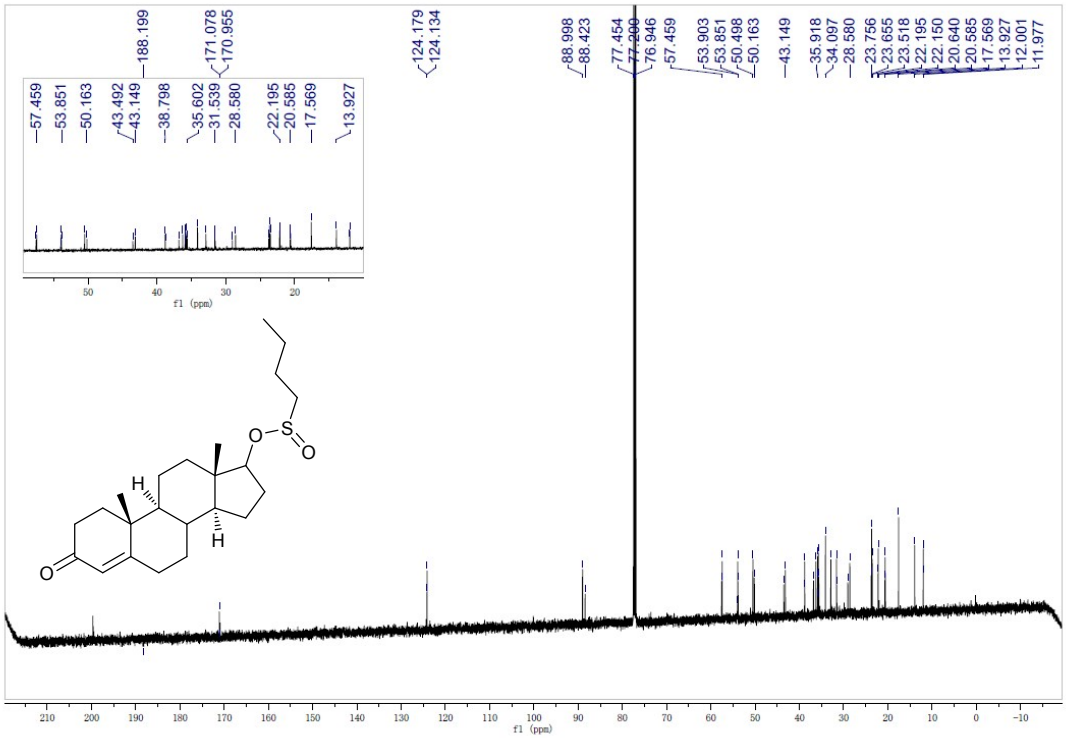
Adamantan-1-yl 4-methylbenzenesulfinate (3G)



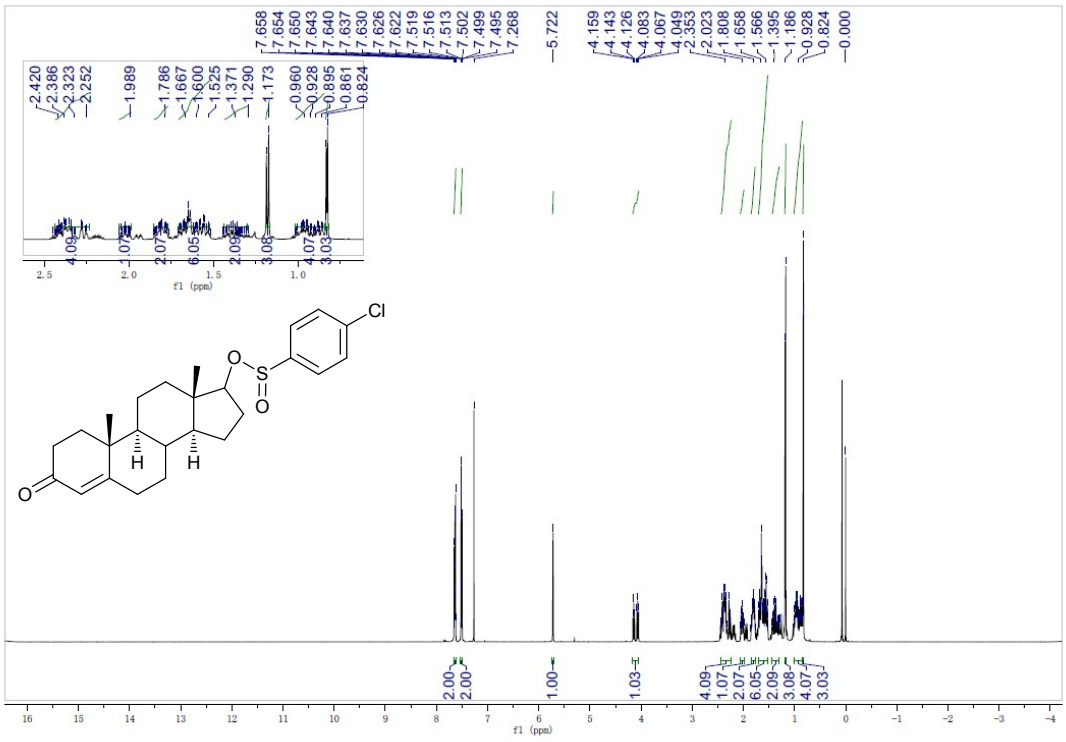


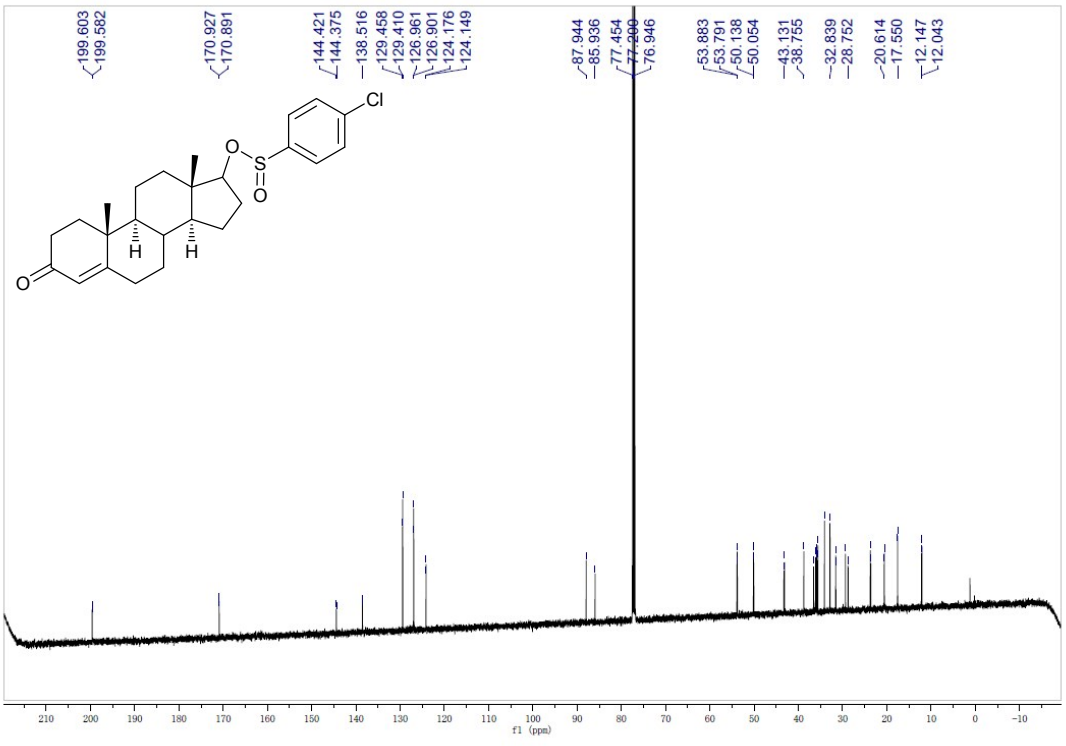
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl butane-1-sulfinate (3H)



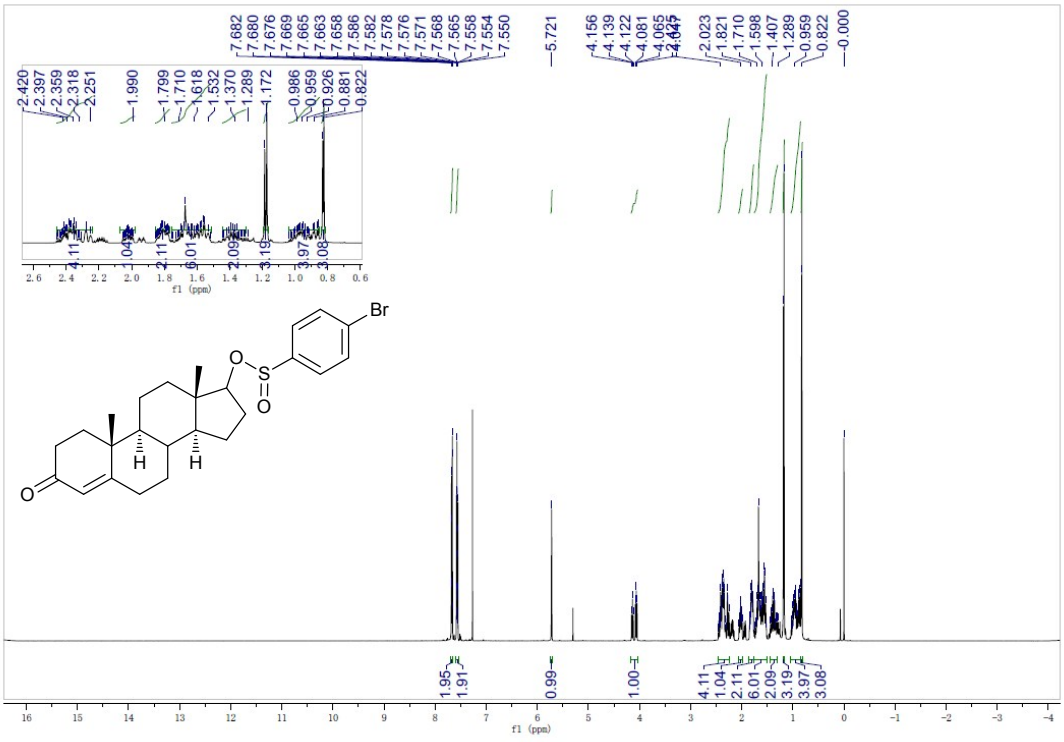


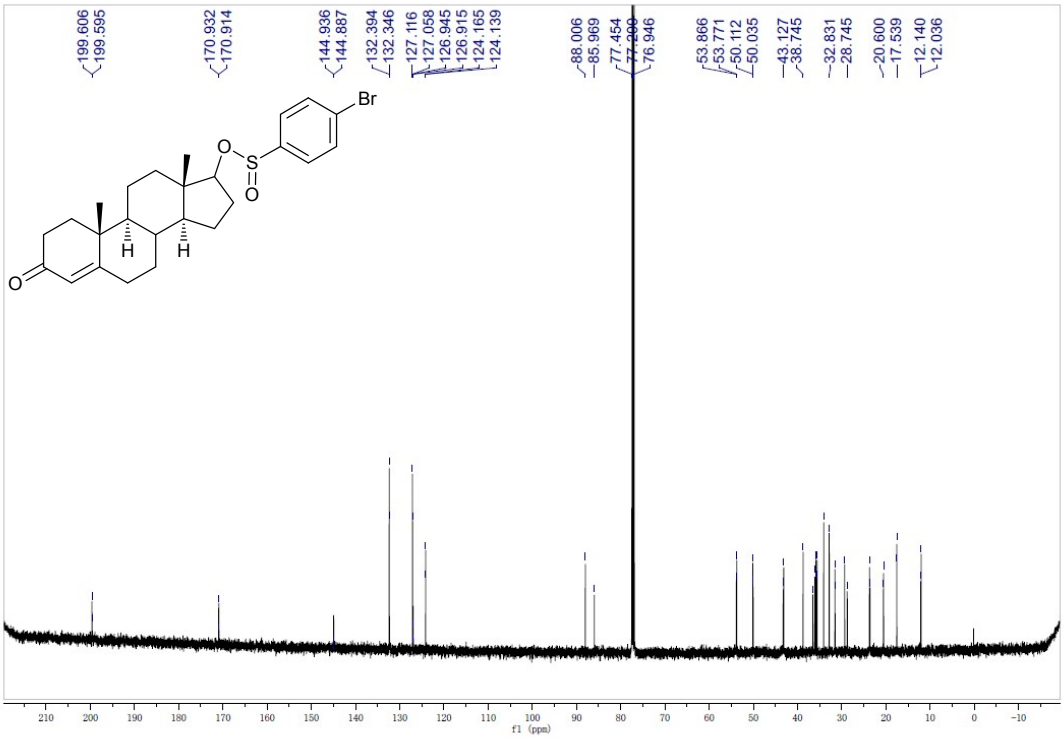
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-chlorobenzenesulfinate (3I)



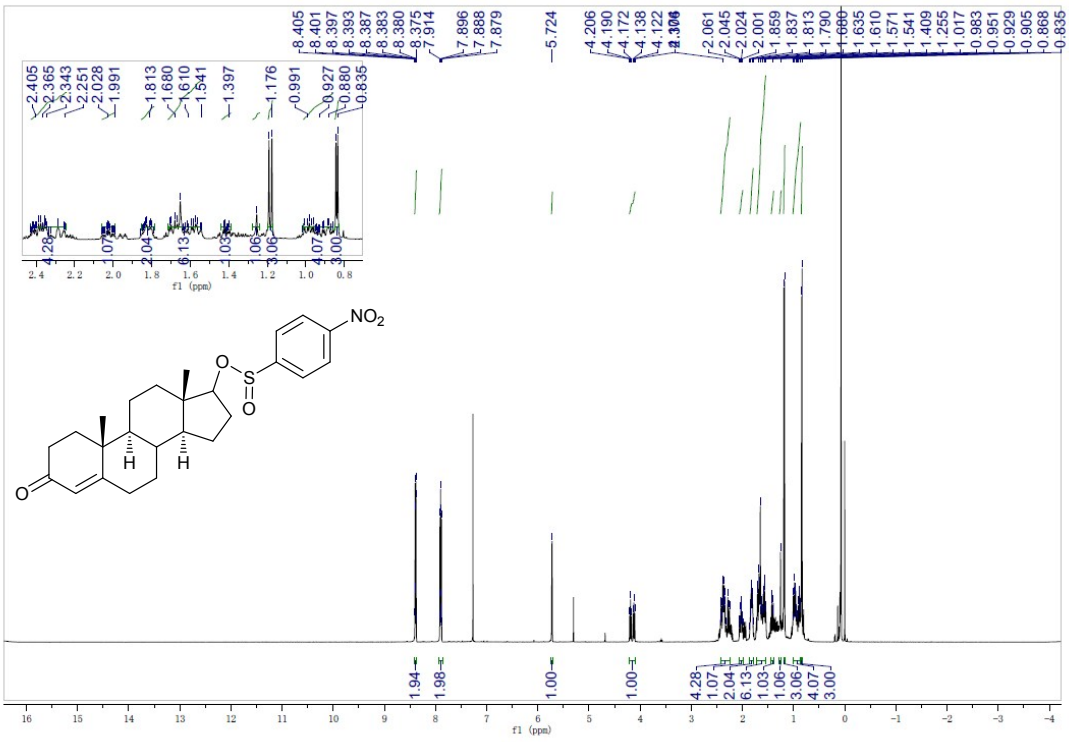


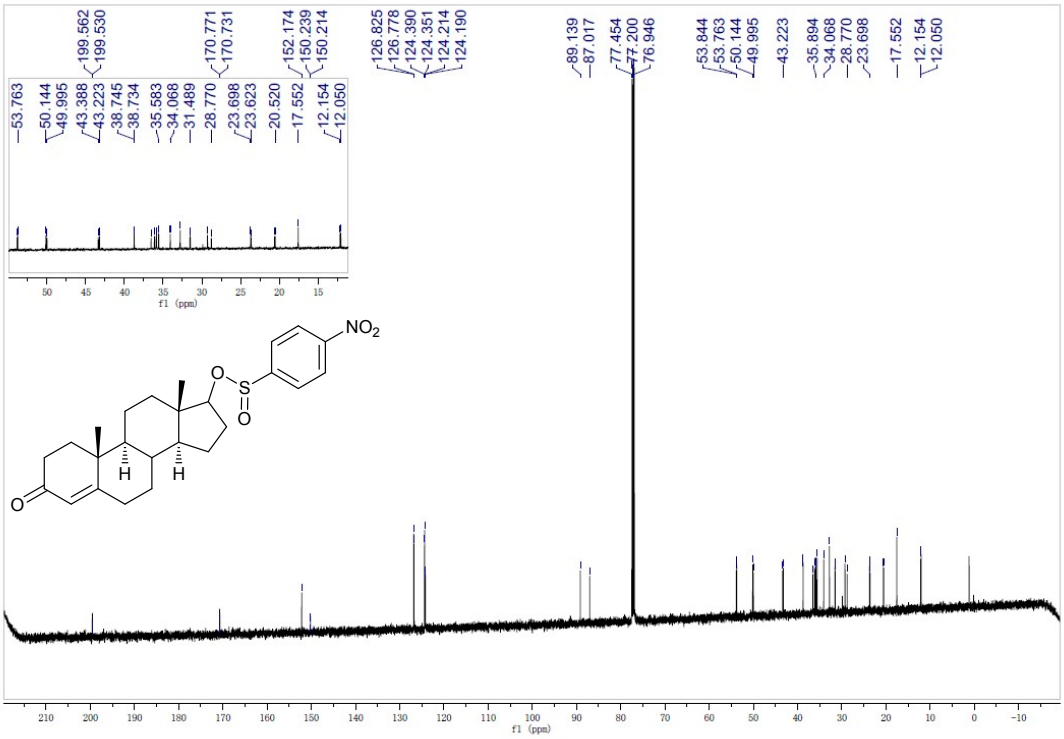
(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-bromobenzenesulfinate (3J)





(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-nitrobenzenesulfinate (3K)





(9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl thiophene-2-sulfinate (3L)