Supporting information

Dual roles of sulfonyl hydrazides in the catalyst-free sulfonylation of unsaturated benzylic alcohols in water

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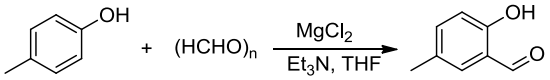
Part I Experimental Section

1.1 General information

^{1}H NMR and ^{13}C NMR were recorded on a Bruker-400MHz Spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz respectively. Commercially available compounds were used without further purification. All solvents were purified according to the standard procedures unless otherwise noted. Substrate **1a-1f,**[1,2] **1g-1i**,[2] **4**,[2] **5**,[3] **7**,[4] $TsNDND_2$ (**11**)[5] was prepared according to the literature procedures.

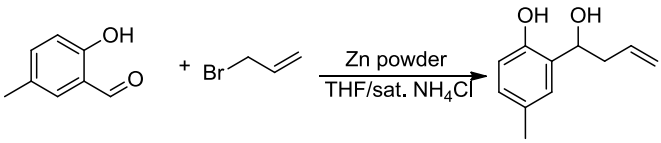
1.2 Preparation of substrates 1a-1f (1b as an example)

a) Preparation of 2-hydroxybenzaldehyde [1]



p-Methyl phenol (2.1 g, 20 mmol), paraformaldehyde (4.2 g), Et_3N (10.6 mL, 76 mmol) and $MgCl_2$ (2.8 g, 30 mmol) were mixed in THF (60 mL). After being refluxed for 24 h, the reaction mixture was cooled to room temperature, and its pH was adjusted to 3 with concentrated hydrochloric acid. The resulting aqueous solution was extracted with ethyl acetate (50 mL × 3). The organic layers were separated, combined and dried with Na_2SO_4. Removal of the solvent gave a crude product which was purified using flash chromatography on a silica gel column with ethyl acetate/petroleum ether = 1/10 as eluent to give a pale yellow solid.

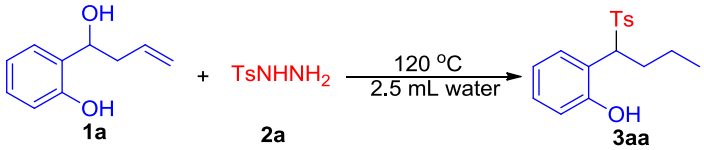
b) Preparation of homoallylic alcohols[2]



To a mixture of 2-hydroxy-5-methylbenzaldehyde (4 mmol) in 8 mL of THF and 16 mL of saturated NH_4Cl solution was added zinc powder (0.520 g, 8mmol) and allyl bromide (700 μL, 8 mmol) at room temperature. After the mixture was stirred for 4 h and it was extracted with ethyl acetate for three times. The combined organic extracts were dried using anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was then purified by column chromatography over silica gel to afford the product **1b** as a light yellow oil.

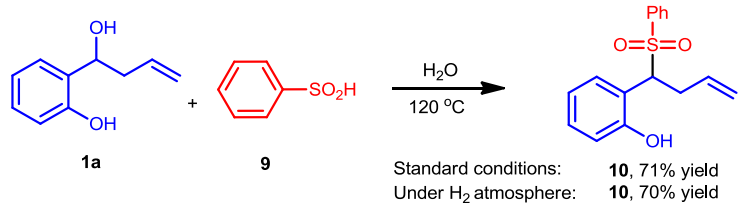
1.3 General working procedure for the sulfonylation and control experiments

a) General working procedure for the sulfonylation (3aa as example)

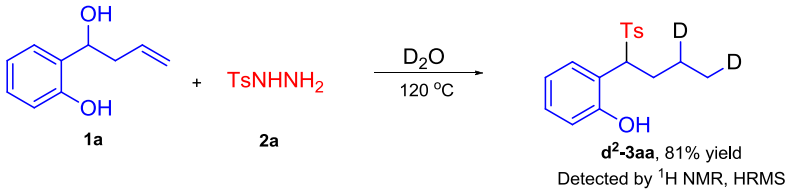


To the mixture of **1a** (82 mg, 0.5 mmol) in 2.5 mL water was added tosylhydrazide (186 mg, 1mmol) in a sealed tube. After the mixture was stirred for 12 h at 120 ^{o}C, it was extracted with ethyl acetate for three times. The combined organic phase was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by column chromatography (PE/EA = 10/1 - 6/1) to afford the product **3aa** as a colorless oil (125 mg, 82% yield).

b)The procedure of control experiments



To the mixture of **1a** (82 mg, 0.5 mmol) in 2.5 mL water was added benzene sulfinic acid (142 mg, 1mmol) in a sealed tube. After the mixture was stirred for 12 h at 120 °C, it was extracted with ethyl acetate for three times. The combined organic phase was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by column chromatography (PE/EA = 10/1 - 6/1) to afford the product **10** as a colorless oil (102 mg, 71% yield).



To the mixture of **1a** (82 mg, 0.5 mmol) in 2.5 mL deuterated water was added tosylhydrazide (186 mg, 1mmol) in a sealed tube. After the mixture was stirred for 12 h at 120 °C, it was extracted with ethyl acetate for three times. The combined organic phase was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by column chromatography (PE/EA = 10/1 - 6/1) to afford the product **d²-3aa** as a colorless oil (123 mg, 81% yield).

d²-3aa HRMS

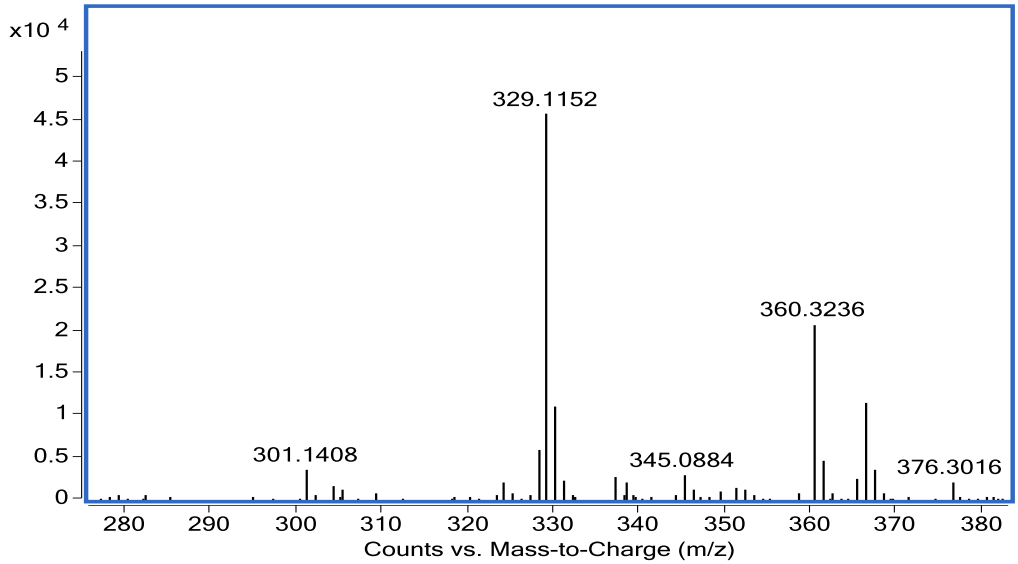
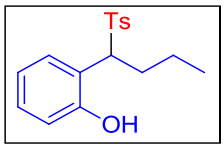


Figure S1. HRMS spectra of d²-3aa

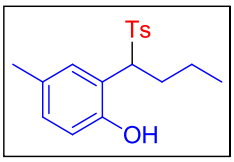
m/z	Relative	Theo.Mass	Delta(mmu)	PPM	Composition
329.1152	100	329.1156	0.4	0.8	C17H18D2NaO3S

1.4 Experimental date of the products

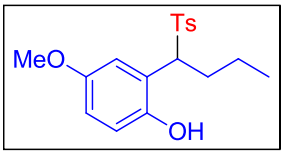
2-(1-tosylbutyl)phenol (3aa): Colorless oil in 82% yield (63% yield, with **4** as substrate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (d, *J* = 8.0 Hz, 2H), 7.21-7.14 (m, 3H), 6.86-6.81 (m, 3H), 4.58 (s, 1H), 2.39 (s, 3H), 2.30-2.21 (m, 2H), 1.24-1.14 (m, 2H), 0.88-0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 144.6, 133.9, 129.8, 129.2, 128.9, 120.7, 118.8, 116.9, 62.6, 28.7, 21.5, 19.9, 13.4; HRMS (ESI) m/z calcd for $C_{17}H_{20}O_3S$ $[M+H]^+$ 305.1211, found 305.1206. Spectral data correspond to those described in the literature.[6]



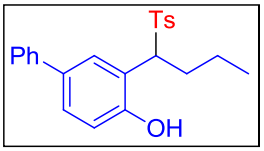
4-methyl-2-(1-tosylbutyl)phenol (3ba): White solid in 78% yield, m.p. 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.50(d, *J* = 6.8 Hz, 2H), 7.22-7.21(d, *J* = 7.7 Hz, 2H), 6.97-6.95(d, *J* = 7.8 Hz, 1H), 6.74(m, 2H), 4.70(s, 1H), 2.40(s, 3H), 2.17(m, 4H), 2.04-2.02(m, 1H), 1.21-1.12(m, 2H), 0.87-0.84(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 144.6, 133.7, 130.5, 130.2, 129.2, 129.0, 118.7, 117.2, 62.5, 29.3, 21.6, 20.5, 20.0, 13.5; HRMS (ESI) m/z calcd for $C_{18}H_{22}O_3S$ $[M+Na]^+$ 341.1187, found 341.1193.



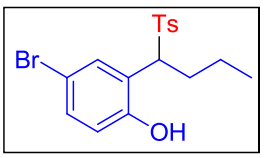
4-methoxy-2-(1-tosylbutyl)phenol (3ca)： Colorless oil in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50(d, *J* = 7.6 Hz, 2H), 7.22-7.20(d, *J* = 7.7 Hz, 2H), 6.71(m, 3H), 6.33(s, 1H), 4.81(s, 1H), 3.66(s, 3H), 2.38(s, 3H), 2.21-2.19(m, 2H), 1.26-1.13(m, 2H), 0.87-0.83(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 149.3, 144.6, 133.7, 129.2, 128.9, 119.8, 117.8, 115.4, 113.6, 62.5, 55.6, 29.2, 21.5, 19.8, 13.5; HRMS (ESI) m/z calcd for $C_{18}H_{22}O_4S$ $[M+Na]^+$ 357.1136, found 357.1128.



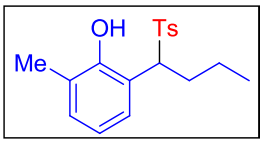
3-(1-tosylbutyl)-[1,1'-biphenyl]-4-ol (3da): White solid in 70% yield, m.p. 137-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53(d, *J* = 7.0 Hz, 2H), 7.37-7.29(m, 6H), 7.25-7.22(m, 3H), 6.92(s, 1H), 6.59(s, 1H), 4.89(s, 1H), 2.39(s, 3H), 2.28-2.26(m, 1H), 2.07-1.85(m, 1H), 1.30-1.16(m, 2H), 0.88-0.84(t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 144.8, 140.3, 133.9, 133.4, 129.3, 129.2, 128.7, 126.8, 126.6, 119.3, 117.6, 62.8, 29.3, 21.6, 19.9, 13.5; HRMS (ESI) m/z calcd for $C_{23}H_{24}O_3S$ $[M+Na]^+$ 403.1344, found 403.1333.



4-bromo-2-(1-tosylbutyl)phenol (3ea): Colorless oil in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53(d, *J* = 7.9 Hz, 2H), 7.27-7.25(d, *J* = 8.0 Hz, 2H), 7.21-7.19(d, *J* = 8.3 Hz, 1H), 7.14(s, 1H), 6.66(s, 1H), 4.81(s, 1H), 2.41(s, 3H), 2.14-2.13(m, 1H), 1.97(m, 1H), 1.28-1.08(m, 2H), 0.85-0.82(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 145.0, 133.3, 132.6, 131.3, 129.4, 129.0, 120.9, 118.2, 112.4, 62.1, 29.2, 21.6, 19.7, 13.4; HRMS (ESI) m/z calcd for $C_{17}H_{19}BrO_3S$ $[M+H]^+$ 383.0317, found 383.0326.

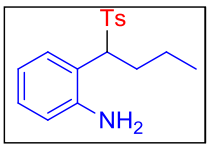


2-methyl-6-(1-tosylbutyl)phenol (3fa): Colorless oil in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$):



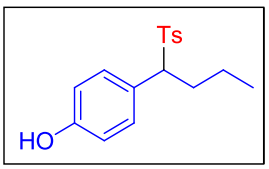
δ 7.46(s, 2H), 7.21-7.19(d, *J* = 7.8 Hz, 2H), 7.08-7.06(d, *J* = 7.2 Hz, 1H), 6.71(s, 2H), 6.11(s, 1H), 4.76(s, 1H), 2.40(s, 3H), 2.23(m, 4H), 2.07-2.01(m, 1H), 1.26-1.12(m, 2H), 0.87-0.84(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 144.8, 133.1, 131.4, 129.2, 126.2, 120.7, 118.9, 63.4, 29.2, 21.6, 19.9, 16.3, 13.5; HRMS (ESI) m/z calcd for $C_{18}H_{22}O_3S$ $[M+Na]^+$ 341.1187, found 341.1178.

2-(1-tosylbutyl)aniline (3ga): Colorless oil in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ



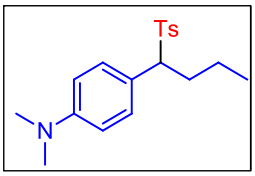
7.50-7.48 (d, *J* = 6.6 Hz, 2H), 7.24-7.22 (d, *J* = 7.2 Hz, 2H), 7.09 (s, 1H), 6.74-6.69 (m, 3H), 4.54-4.52 (d, *J* = 9.6 Hz, 1H), 3.98 (br, 2H), 2.41 (s, 3H), 2.22-2.14 (m, 1H), 1.93-1.91 (m, 1H), 1.23-1.10 (m, 2H), 0.84-0.82 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 144.6, 133.3, 129.5, 129.2, 128.6, 119.3, 118.1, 64.7, 30.2, 21.6, 19.6, 13.4; HRMS (ESI) m/z calcd for $C_{17}H_{21}NO_2S$ $[M+Na]^+$ 326.1191, found 326.1192.

4-(1-tosylbutyl)phenol (3ha): White solid in 73% yield, m.p. 134-136 ^{o}C. ^{1}H NMR (400 MHz,



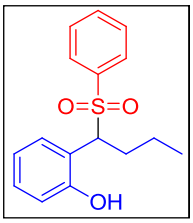
$CDCl_3$): δ 7.45-7.43(d, *J* = 7.9 Hz, 2H), 7.22-7.20(d, *J* = 7.8 Hz, 2H), 6.96-6.94(d, *J* = 8.0 Hz, 2H), 6.71-6.69(d, *J* = 8.0 Hz, 2H), 6.45(s, 1H), 4.01-3.98(m, 1H), 2.40(s, 3H), 2.28-2.22(m, 1H), 2.11-2.02(m, 1H), 1.25-1.12(m, 2H), 0.86-0.83(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 144.5, 134.0, 131.1, 129.3, 129.0, 123.1, 115.5, 70.7, 29.3, 21.6, 19.9, 13.5; HRMS (ESI) m/z calcd for $C_{17}H_{20}O_3S$ $[M+Na]^+$ 327.1031, found 327.1021.

***N,N*-dimethyl-4-(1-tosylbutyl)aniline (3ia):** White solid in 75% yield, m.p. 150-152 ^{o}C. ^{1}H



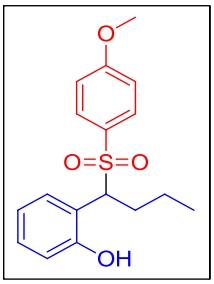
NMR (400 MHz, $CDCl_3$): δ 7.42-7.40(d, *J* = 8.0 Hz, 2H), 7.19-7.17(d, *J* = 7.9 Hz, 2H), 6.95-6.93(d, *J* = 8.4 Hz, 2H), 6.58-6.56(d, *J* = 8.4 Hz, 2H), 3.96-3.93(dd, *J* = 3.2 Hz, 11.8 Hz, 1H), 2.93(s, 6H), 2.39(s, 3H), 2.29-2.26(m, 1H), 2.07-2.04(m, 1H), 1.28-1.16(m, 2H), 0.88-0.84(t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 143.9, 134.7, 130.5, 129.1, 118.8, 111.9, 70.7, 40.3, 29.2, 21.5, 20.0, 13.6; HRMS (ESI) m/z calcd for $C_{19}H_{25}NO_2S$ $[M+Na]^+$ 354.1504, found 354.1513.

2-(1-(phenylsulfonyl)butyl)phenol (3ab): Colorless oil in 78% yield. ^{1}H NMR (400 MHz,

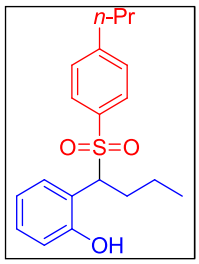


$CDCl_3$): δ 7.62-7.54 (m, 3H), 7.41-7.38 (t, *J* = 7.3 Hz, 2H), 7.17-7.13 (t, *J* = 7.6 Hz, 1H), 6.99-6.81 (m, 3H), 4.68(s, 1H), 2.29-2.10 (m, 2H), 1.30-1.13 (m, 2H), 0.88-0.85 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 136.9, 133.5, 129.8, 128.8, 128.4, 120.6, 118.5, 116.5, 62.4, 28.7, 19.8, 13.4; HRMS (ESI) m/z calcd for $C_{16}H_{18}O_3S$ $[M+Na]^+$ 313.0874, found 313.0864.

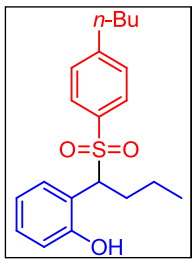
2-(1-((4-methoxyphenyl)sulfonyl)butyl)phenol (3ac): Colorless oil in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50(d, *J* = 8.2 Hz, 2H), 7.17-7.13(t, *J* = 7.5 Hz, 1H), 6.86-6.84(m, 5H), 4.59(s, 1H), 3.83(s, 3H), 2.27-2.14(m, 2H), 1.26-1.14(m, 2H), 0.88-0.84(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 155.4, 131.0, 129.8, 128.2, 120.6, 119.0, 116.6, 113.7, 62.8, 55.5, 28.8, 19.9, 13.4; HRMS (ESI) m/z calcd for $C_{17}H_{20}O_4S$ $[M+H]^+$ 321.1161, found 321.1163.



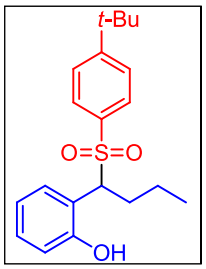
2-(1-((4-propylphenyl)sulfonyl)butyl)phenol (3ad): White solid in 80% yield, m.p. 121-123 °C.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50 (d, *J* = 7.9 Hz, 2H), 7.20-7.13 (m, 3H), 6.84-6.82 (m, 3H), 4.62 (s, 1H), 2.63-2.59 (t, *J* = 7.5 Hz, 2H), 2.26-2.09 (m, 2H), 1.67-1.57 (m, 2H), 1.31-1.14 (m, 2H), 0.91-0.73(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 149.2, 133.9, 132.8, 129.9, 129.0, 128.6, 120.8, 119.0, 117.4, 63.3, 37.8, 28.5, 24.0, 19.9, 13.48, 13.45; HRMS (ESI) m/z calcd for $C_{19}H_{24}O_3S$ $[M+Na]^+$ 355.1344, found 355.1334.



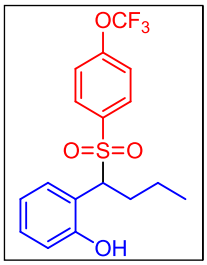
2-(1-((4-butylphenyl)sulfonyl)butyl)phenol (3ae): White solid in 71% yield, m.p. 138-140 °C.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50 (d, *J* = 7.5 Hz, 2H), 7.21-7.12(m, 3H), 7.00-6.81 (m, 3H), 4.68 (s, 1H), 2.65-2.62 (t, *J* = 7.6 Hz, 2H), 2.25-2.14 (m, 2H), 1.61-1.53 (m, 2H), 1.35-1.12(m, 4H), 0.93-0.84(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 149.5, 133.8, 132.8, 129.9, 129.0, 128.6, 120.9, 119.1, 117.6, 63.1, 35.5, 33.0, 28.6, 22.1, 20.0, 13.8, 13.5; HRMS (ESI) m/z calcd for $C_{20}H_{26}O_3S$ $[M+H]^+$ 347.1681, found 347.1673.



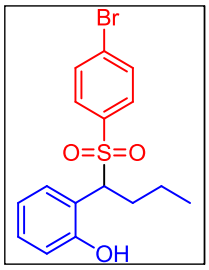
2-(1-((4-(tert-butyl)phenyl)sulfonyl)butyl)phenol (3af): Colorless oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (d, *J* = 8.2 Hz, 2H), 7.42-7.40 (d, *J* = 8.4 Hz, 2H), 7.14-7.10 (t, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.80 (s, 2H), 4.73 (s, 1H), 2.22-2.04(m, 2H), 1.30 (s, 9H), 1.22-1.14(m, 2H), 0.86-0.83(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 155.5, 133.7, 129.9, 128.8, 125.6, 120.7, 118.9, 117.3, 62.8, 35.1, 30.9, 28.8, 19.9, 13.4; HRMS (ESI) m/z calcd for $C_{20}H_{26}O_3S$ $[M+H]^+$ 347.1681, found 347.1675.



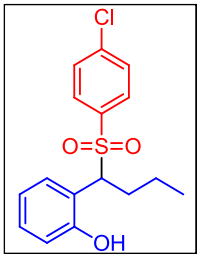
2-(1-((4-(trifluoromethoxy)phenyl)sulfonyl)butyl)phenol (3ag): Colorless oil in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (d, *J* = 8.4 Hz, 2H), 7.19-7.17 (d, *J* = 8.2 Hz, 2H), 7.15-7.11 (t, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.69 (s, 1H), 6.23 (s, 1H), 4.82 (s, 1H), 2.35-2.15 (m, 2H), 1.39-1.14 (m, 2H), 0.90-0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 152.8, 135.4, 131.2, 130.1, 129.2, 124.0-116.2 (q, J_{F-C} = 258.1 Hz), 120.9, 120.1, 118.5, 116.2, 62.6, 28.5, 19.9, 13.4; HRMS (ESI) m/z calcd for $C_{17}H_{17}F_3O_4S$ $[M+H]^+$ 375.0878, found 375.0888.



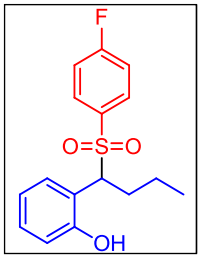
2-(1-((4-bromophenyl)sulfonyl)butyl)phenol (3ah): Colorless oil in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.49 (d, *J* = 8.4 Hz, 2H), 7.44-7.42 (d, *J* = 8.4 Hz, 2H), 7.17-7.10 (m, 2H), 6.86 (s, 1H), 6.70 (s, 1H), 4.83 (s, 1H), 2.29-2.14 (m, 2H), 1.35-1.14 (m, 2H), 0.88-0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 136.2, 131.7, 130.4, 130.0, 128.8, 120.8, 118.3, 116.1, 62.2, 28.6, 19.8, 13.4; HRMS (ESI) m/z calcd for $C_{16}H_{17}BrO_3S$ $[M+H]^+$ 369.0160, found 369.0153.



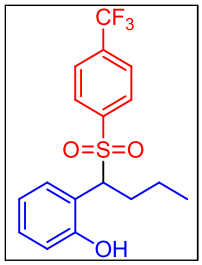
2-(1-((4-chlorophenyl)sulfonyl)butyl)phenol (3ai): Colorless oil in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50 (d, *J* = 8.2 Hz, 2H), 7.36-7.34 (d, *J* = 8.4 Hz, 2H), 7.17-7.13 (m, 2H), 6.86 (s, 1H), 6.74 (s, 1H), 4.76 (s, 1H), 2.34-2.14 (m, 2H), 1.34-1.14 (m, 2H), 0.89-0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 140.3, 135.6, 130.4, 130.1, 128.8, 121.1, 118.6, 116.7, 62.4, 28.4, 19.9, 13.5; HRMS (ESI) m/z calcd for $C_{16}H_{17}ClO_3S$ $[M+Na]^+$ 347.0485, found 347.0487.



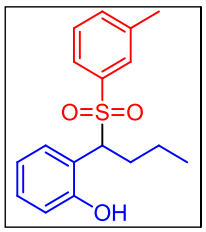
2-(1-((4-fluorophenyl)sulfonyl)butyl)phenol (3aj): Colorless oil in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.28-7.14 (m, 2H), 7.07-7.03 (t, *J* = 8.4 Hz, 2H), 6.87 (s, 1H), 6.71 (s, 1H), 6.40 (s, 1H), 4.86 (s, 1H), 2.31-2.29 (m, 1H), 2.20-2.14 (m, 1H), 1.31-1.17 (m, 2H), 0.90-0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9-164.4 (d, J_{F-C} = 254.5 Hz), 155.1, 132.9, 131.8-131.7 (d, J_{F-C} = 9.5 Hz), 130.0, 128.8, 120.8, 118.5, 115.8-115.6 (d, J_{F-C} = 22.8 Hz), 62.2, 28.5, 19.8, 13.5; HRMS (ESI) m/z calcd for $C_{16}H_{17}FO_3S$ $[M+Na]^+$ 331.0780, found 331.0787.



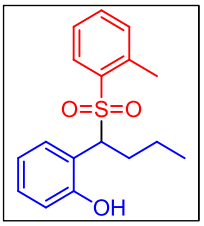
2-(1-((4-(trifluoromethyl)phenyl)sulfonyl)butyl)phenol (3ak): Colorless oil in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.62 (m, 4H), 7.17-7.13 (t, *J* = 7.6 Hz, 2H), 6.88 (s, 1H), 6.69 (s, 1H), 4.81 (s, 1H), 2.37-2.17 (m, 2H), 1.35-1.16 (m, 2H), 0.90-0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 141.0 135.5-134.5 (q, J_{F-C} = 32.4 Hz), 130.2, 129.5, 129.3, 127.2-119.0 (q, J_{F-C} = 271.4 Hz), 125.4, 120.9, 118.1, 116.0, 62.3, 28.5, 19.8, 13.4; HRMS (ESI) m/z calcd for $C_{17}H_{17}F_3O_3S$ $[M+H]^+$ 359.0929, found 359.0938.



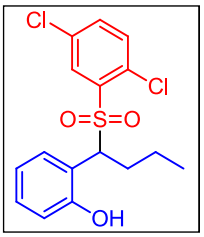
2-(1-(*m*-tolylsulfonyl)butyl)phenol (3al): Colorless oil in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.32 (m, 3H), 7.28-7.24 (t, *J* = 7.6 Hz, 1H), 7.13-7.10 (t, *J* = 7.4 Hz, 1H), 6.82 (m, 1H), 6.76 (m, 1H), 4.76 (s, 1H), 2.29 (s, 3H), 2.25-2.13 (m, 2H), 1.31-1.13 (m, 2H), 0.87-0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 138.8, 136.7, 134.4, 129.9, 129.4, 128.4, 126.1, 120.7, 118.8, 116.9, 62.7, 28.7, 21.1, 19.9, 14.1, 13.5; HRMS (ESI) m/z calcd for $C_{17}H_{20}O_3S$ $[M+H]^+$ 305.1211, found 305.1206.



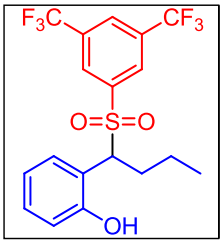
2-(1-(*o*-tolylsulfonyl)butyl)phenol (3am): Colorless oil in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (d, *J* = 7.9 Hz, 1H), 7.39-7.35 (t, *J* = 7.4 Hz, 1H), 7.20-7.12 (m, 3H), 7.07-7.04 (t, *J* = 7.4 Hz, 1H), 6.83 (m, 1H), 6.65 (s, 1H), 4.91 (s, 1H), 2.60 (s, 3H), 2.19-2.17 (m, 2H), 1.31-1.13 (m, 2H), 0.86-0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 139.0, 135.4, 133.4, 132.3, 131.0, 129.7, 125.8, 120.6, 118.2, 116.2, 61.5, 28.7, 20.3, 19.8, 13.4; HRMS (ESI) m/z calcd for $C_{17}H_{20}O_3S$ $[M+H]^+$ 305.1211, found 305.1217.



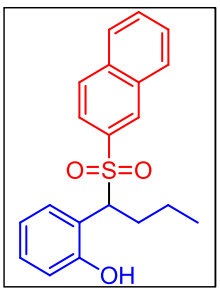
2-(1-((2,5-dichlorophenyl)sulfonyl)butyl)phenol (3an): Colorless oil in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.42-7.33 (m, 3H), 7.13-7.09 (t, *J* = 7.5 Hz, 1H), 6.89 (s, 1H), 6.69 (s, 1H), 5.34 (s, 1H), 2.23-2.11 (m, 2H), 1.35-1.17 (m, 2H), 0.89-0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 136.8, 134.5, 133.2, 132.8, 132.0, 131.5, 130.3, 121.0, 117.3, 116.5, 62.0, 28.6, 19.8, 13.4; HRMS (ESI) m/z calcd for $C_{16}H_{16}Cl_2O_3S$ $[M+H]^+$ 359.0275, found 359.0269.



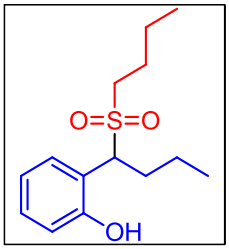
2-(1-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)butyl)phenol (3ao): Colorless oil in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.90 (s, 2H), 7.39 (s, 1H), 7.14-7.10 (t, *J* = 7.6 Hz, 1H), 6.97-6.95 (m, 1H), 6.52 (s, 1H), 5.88 (s, 1H), 4.90 (s, 1H), 2.46-2.38 (m, 1H), 2.21-2.16 (m, 1H), 1.42-1.24 (m, 2H), 0.94-0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 140.2, 132.4-131.4 (q, $J_{F\text{-}C}$ = 34.1 Hz), 130.5, 129.4, 128.8, 126.7, 126.4-118.2 (q, $J_{F\text{-}C}$ = 271.7 Hz), 121.3, 117.7, 115.2, 62.3, 27.6, 19.8, 13.3; HRMS (ESI) m/z calcd for $C_{18}H_{16}F_6O_3S$ $[M+Na]^+$ 449.0622, found 449.0629.



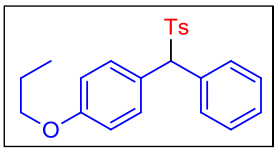
2-(1-(naphthalen-2-ylsulfonyl)butyl)phenol (3ap): Colorless oil in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.85-7.79 (m, 3H), 7.63-7.54 (m, 3H), 7.13-7.09 (m, 2H), 6.80-6.74 (m, 2H), 4.84 (s, 1H), 2.29-2.08 (m, 2H), 1.26-1.12 (m, 2H), 0.86-0.82 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 135.1, 134.0, 131.7, 130.9, 129.9, 129.3, 129.1, 128.5, 127.8, 127.3, 123.5, 120.7, 118.7, 116.9, 62.8, 28.8, 19.8, 13.4; HRMS (ESI) m/z calcd for $C_{20}H_{20}O_3S$ $[M+H]^+$ 341.1211, found 341.1203.



2-(1-(butylsulfonyl)butyl)phenol (3aq): Colorless oil in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 1H), 7.24-7.20 (t, *J* = 7.4 Hz, 1H), 6.97-6.93 (m, 2H), 4.71 (s, 1H), 2.91-2.71 (m, 2H), 2.34-2.32 (m, 1H), 2.16 (m, 1H), 1.84-1.65 (m, 2H), 1.40-1.19 (m, 4H), 0.91-0.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 130.0, 121.0, 119.0, 116.4, 60.2, 50.2, 27.6, 23.1, 21.6, 19.7, 13.42, 13.36; HRMS (ESI) m/z calcd for $C_{14}H_{22}O_3S$ $[M+Na]^+$ 293.1187, found 293.1181.

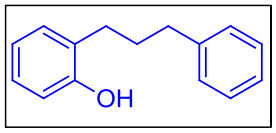


1-methyl-4-((phenyl(4-propoxyphenyl)methyl)sulfonyl)benzene (6): Colorless oil in 71% yield.



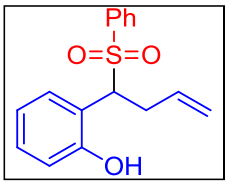
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H), 7.50-7.48 (d, *J* = 7.9 Hz, 2H), 7.43-7.41 (d, *J* = 8.2 Hz, 2H), 7.29 (m, 3H), 7.15-7.14 (d, *J* = 7.6 Hz, 2H), 6.84-6.82 (d, *J* = 8.2 Hz, 2H), 5.22 (s, 1H), 3.90-3.86 (t, *J* = 6.3 Hz, 2H), 2.36 (s, 3H), 1.81-1.75 (m, 2H), 1.03-0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 144.2, 135.4, 133..4, 131.1, 129.8, 129.2, 129.0, 128.6, 128.4, 124.6, 114.5, 75.8, 69.4, 22.4, 21.6, 10.5; HRMS (ESI) m/z calcd for $C_{23}H_{24}O_3S$ $[M+Na]^+$ 403.1344, found 403.1346.

2-(3-phenylpropyl)phenol (8): Colorless oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ



7.29-7.25 (t, *J* = 7.4 Hz, 2H), 7.20-7.15 (m, 3H), 7.11-7.04 (m, 2H), 6.87-6.84 (t, *J* = 7.4 Hz, 1H), 6.73-6.71 (d, *J* = 7.9 Hz, 1H), 4.83 (br, 1H) 2.69-2.62 (m, 4H), 1.99-1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 142.3, 130.2, 128.4, 128.3, 128.1, 127.1, 125.7, 120.8, 115.2, 36.6, 31.2, 29.4; ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[7]

2-(1-(phenylsulfonyl)but-3-en-1-yl)phenol (10): Colorless oil in 71% yield. ^{1}H NMR (400 MHz,



$CDCl_3$): δ 7.62-7.60 (d, *J* = 7.6 Hz, 2H), 7.57-7.54 (t, *J* = 7.4 Hz, 1H), 7.41-7.31 (m, 2H), 7.15-7.11 (t, *J* = 7.5 Hz, 2H), 6.84 (m, 1H), 6.74 (m, 1H), 6.47 (br, 1H), 5.58-5.48 (m, 1H), 5.07-5.02 (d, *J* = 17.0 Hz, 1H), 5.00-4.93 (d, *J* = 10.1 Hz, 1H), 4.83 (s, 1H), 3.10-3.07 (m, 1H), 2.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 136.6, 133.7, 132.6, 130.1, 129.4, 129.0, 128.6, 120.8, 118.3, 116.9, 62.4, 31.0; HRMS (ESI) m/z calcd for $C_{16}H_{16}O_3S$ $[M+Na]^+$ 311.0718, found 311.0727. Spectral data correspond to those described in the literature.[5]

Reference:

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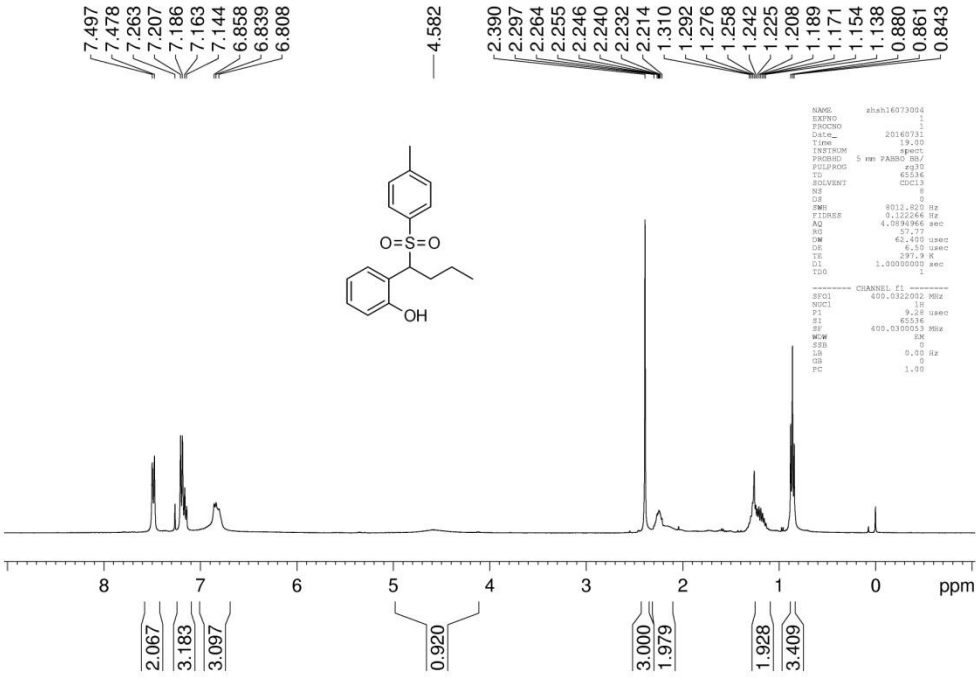
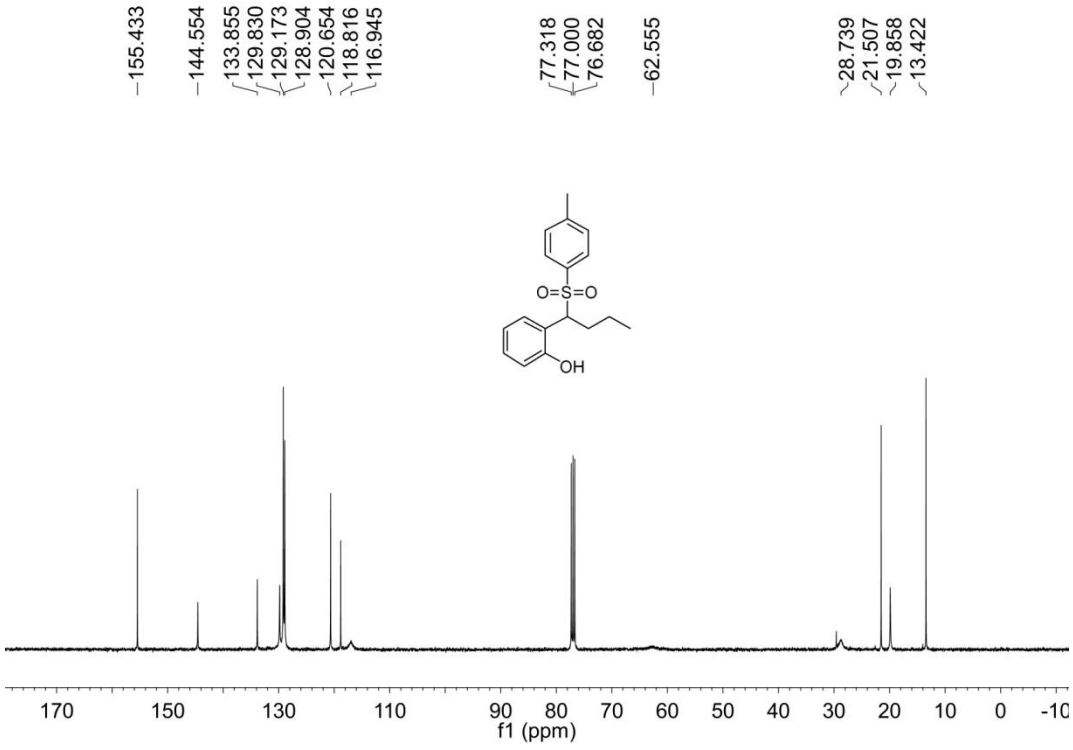
6. P. Chen, K. Wang, W.-G. Guo, X.-H. Liu, Y. Liu and C. Li, *Angew. Chem. Int. Ed.*, 2017, **56**, 3689.
7. N. Kalutharage, and C. S. Yi, *J. Am. Chem. Soc.*, 2015, **137**, 11105.

Part II NMR Spectra

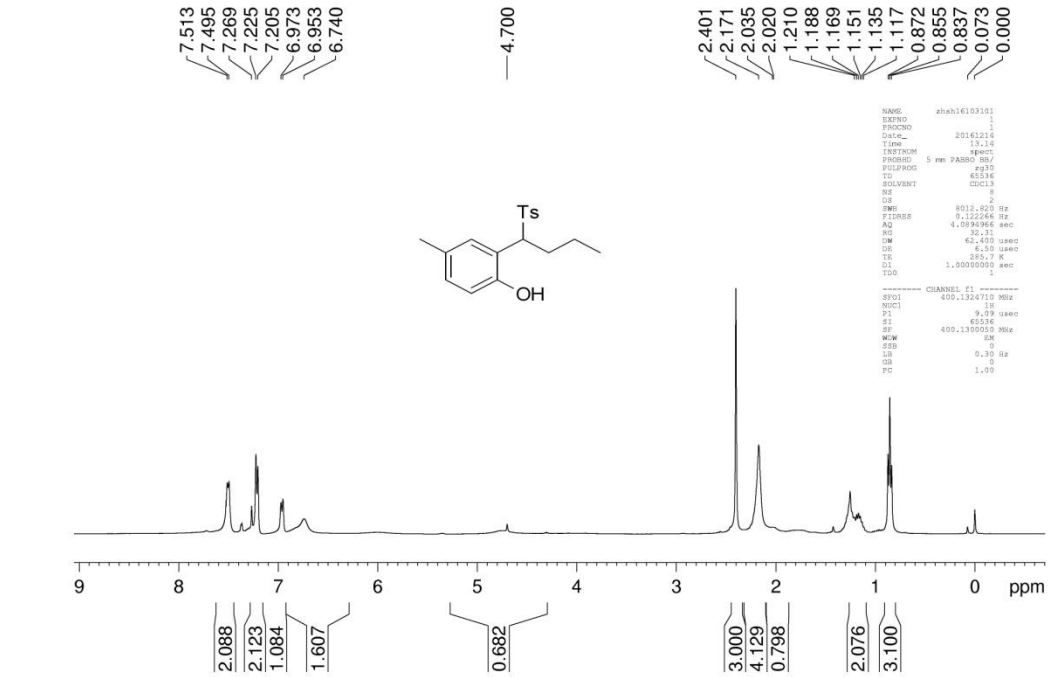
3aa ^{1}H NMR



3aa ^{13}C NMR



3ba ^{1}H NMR



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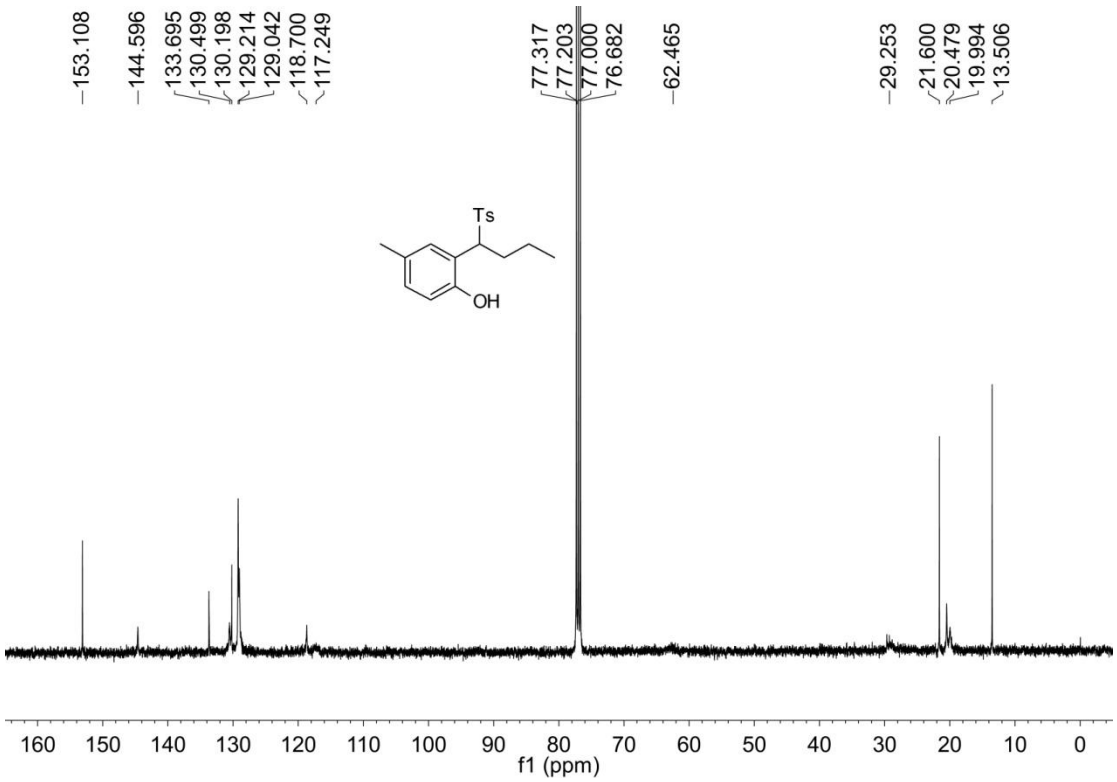
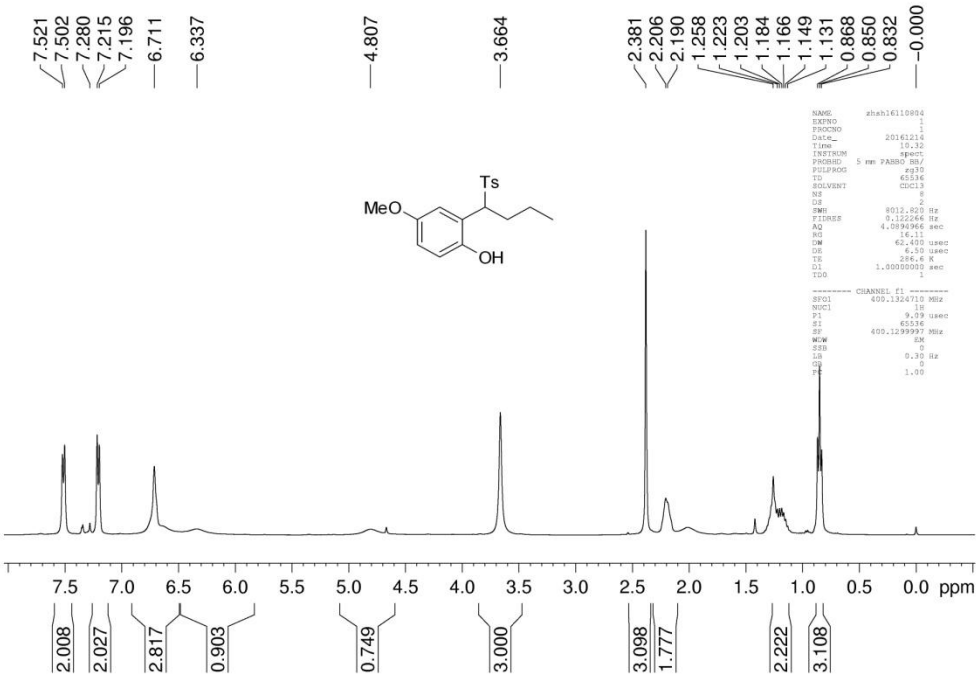
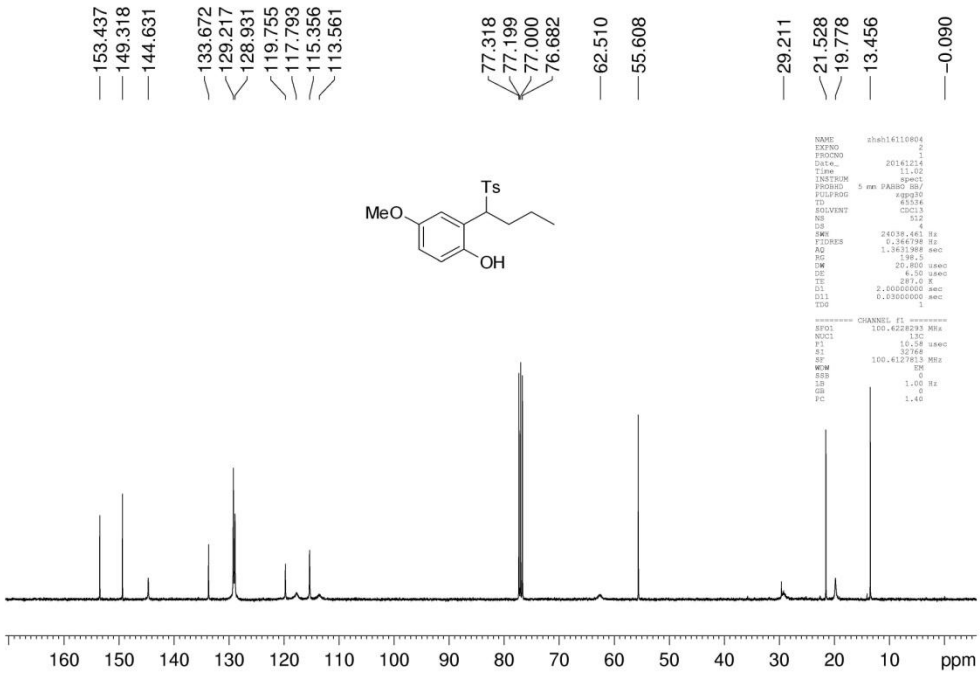


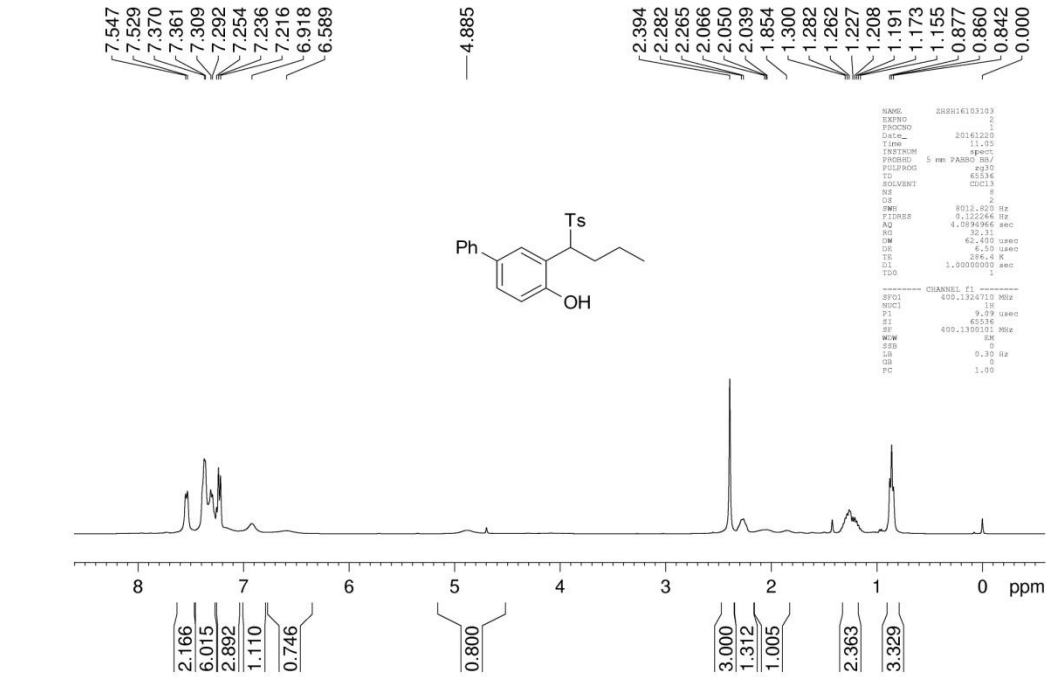
3ca ^{1}H NMR



3ca ^{13}C NMR



3da ^{1}H NMR



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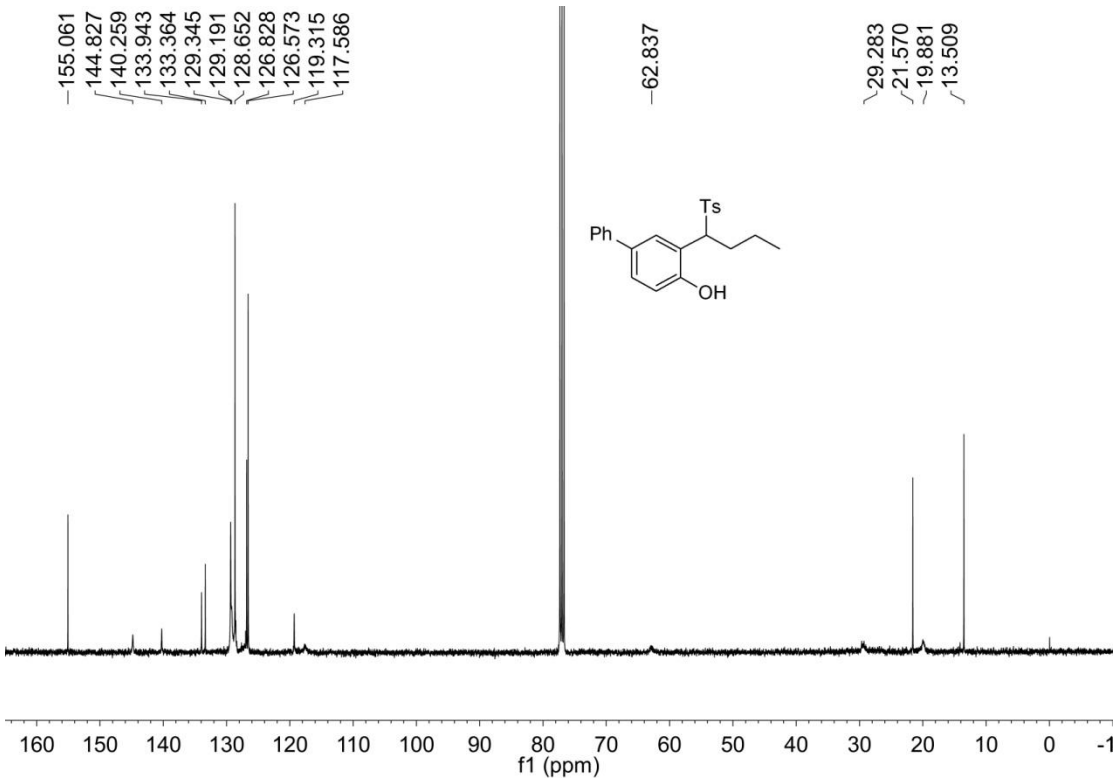

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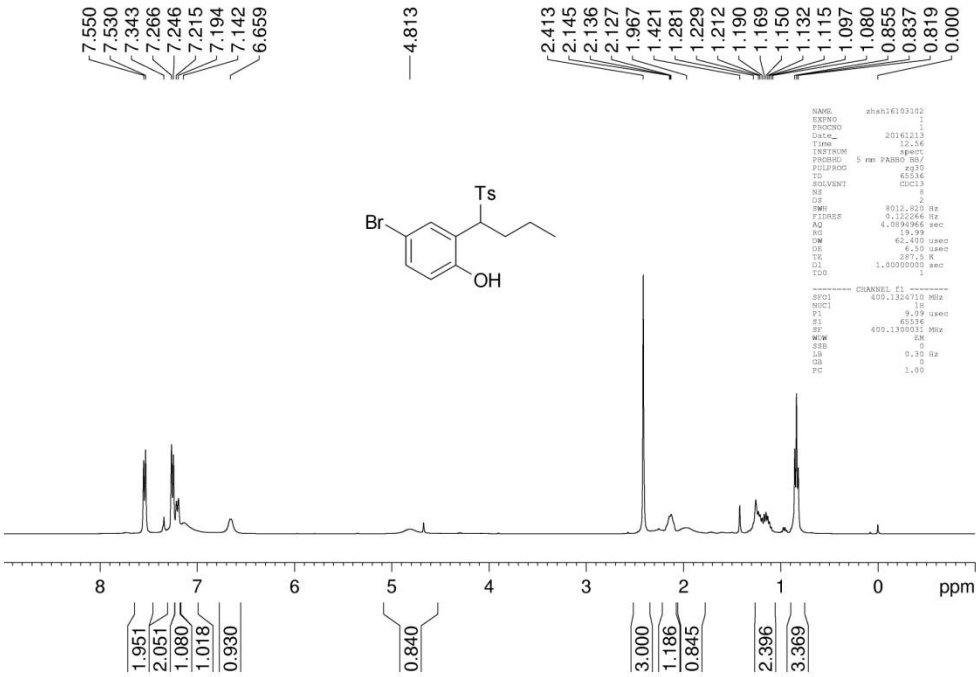
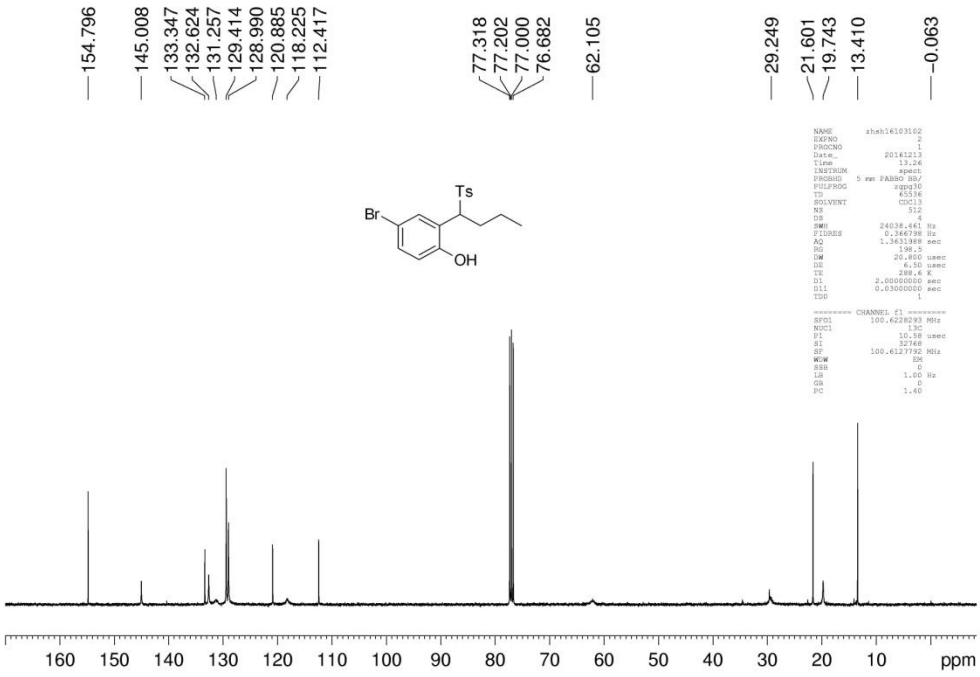


3ea ^{13}C NMR



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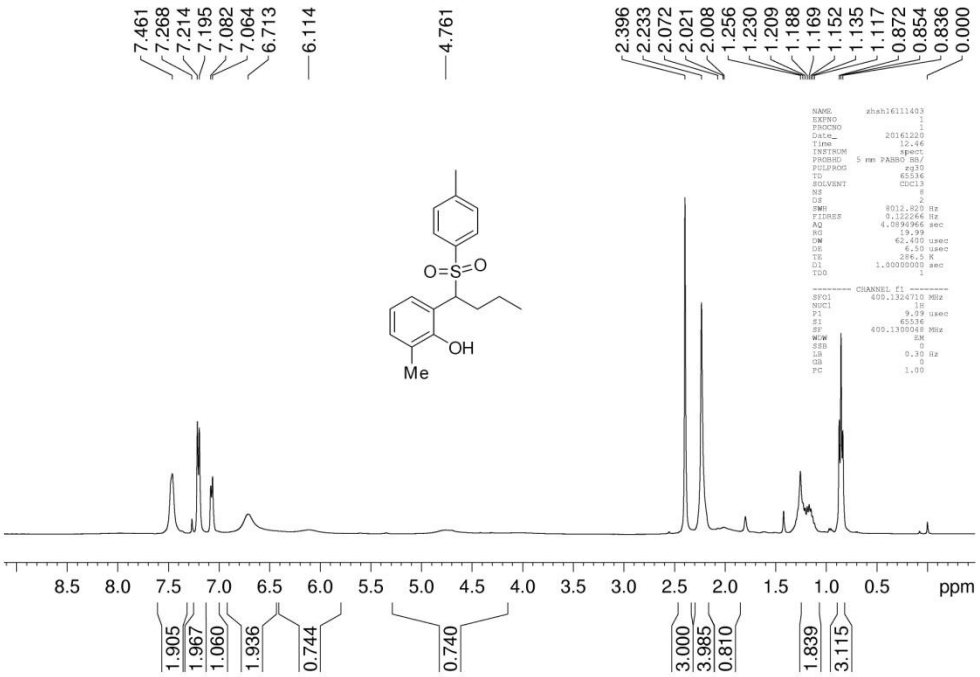

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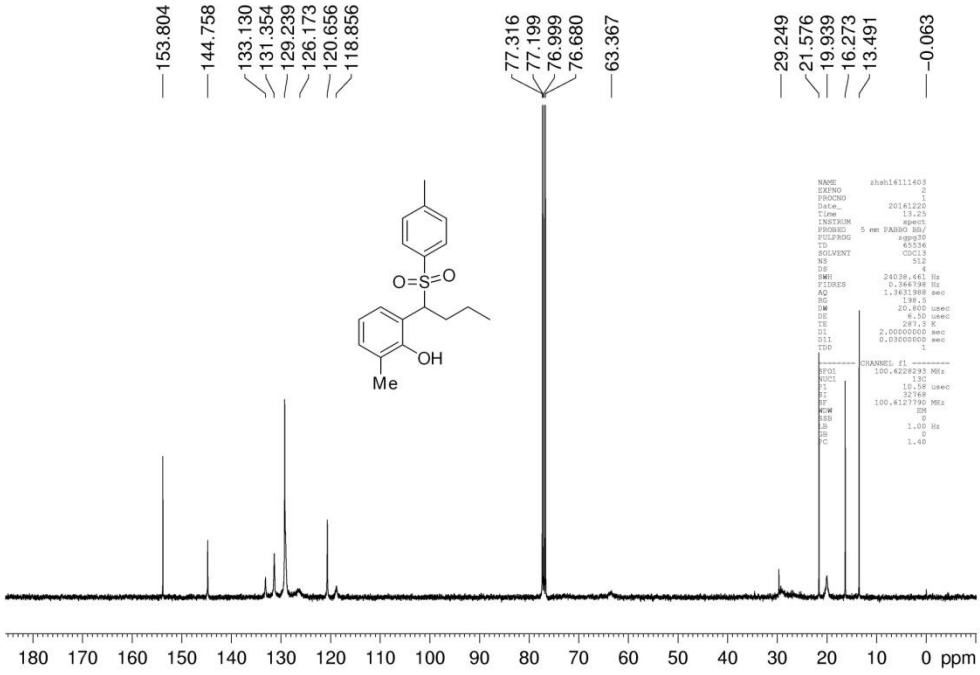

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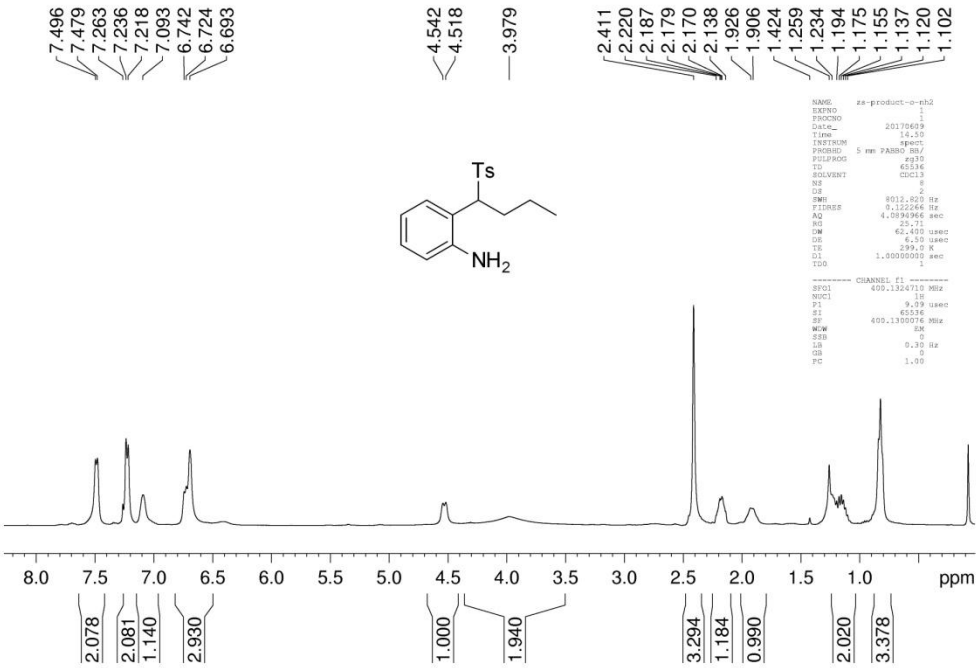

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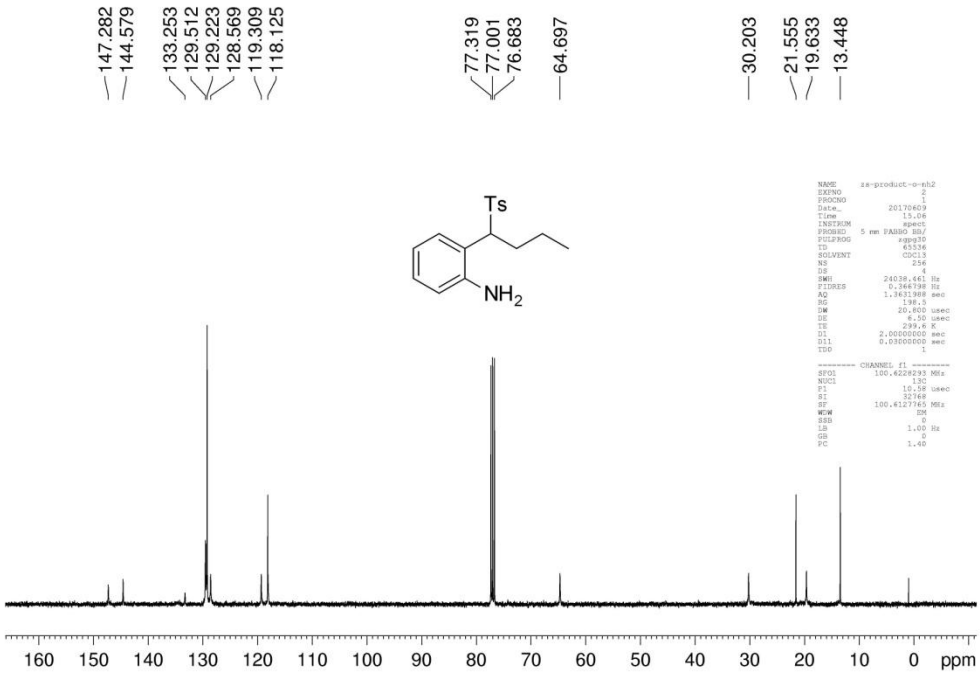

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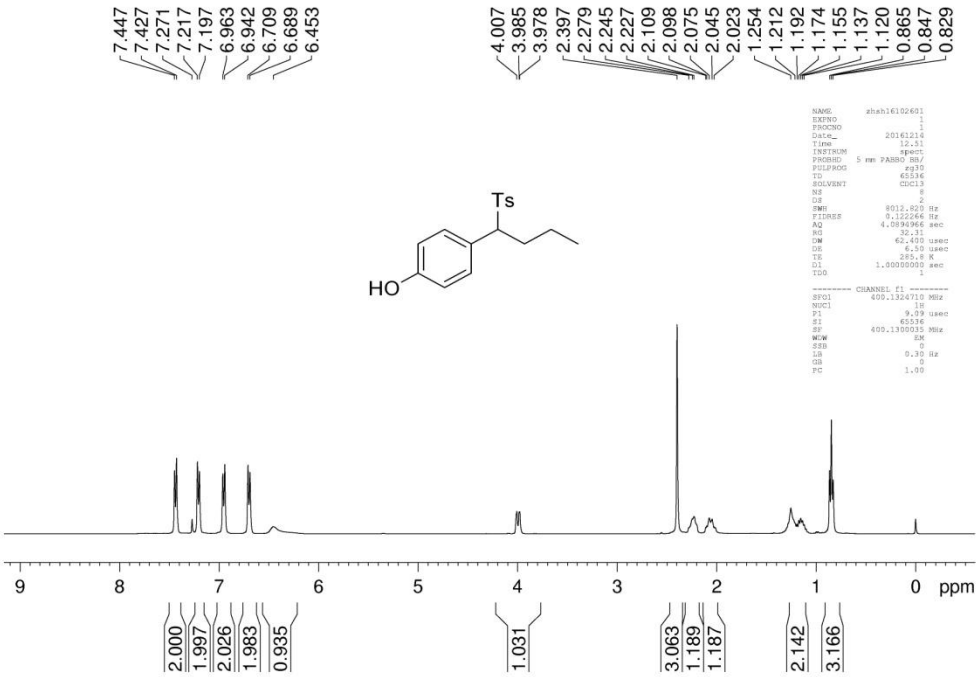

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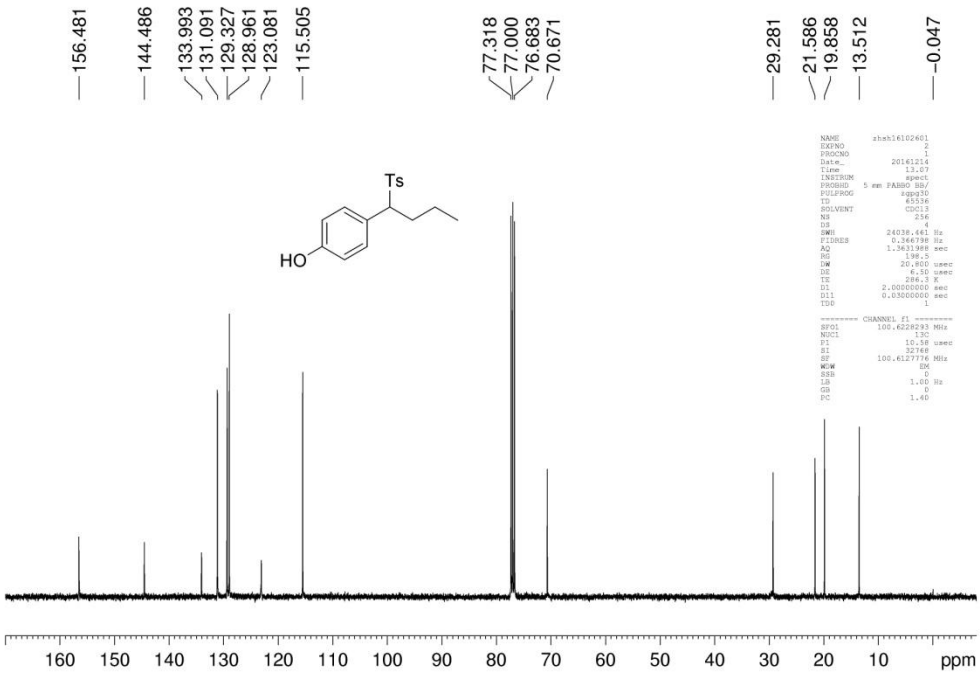

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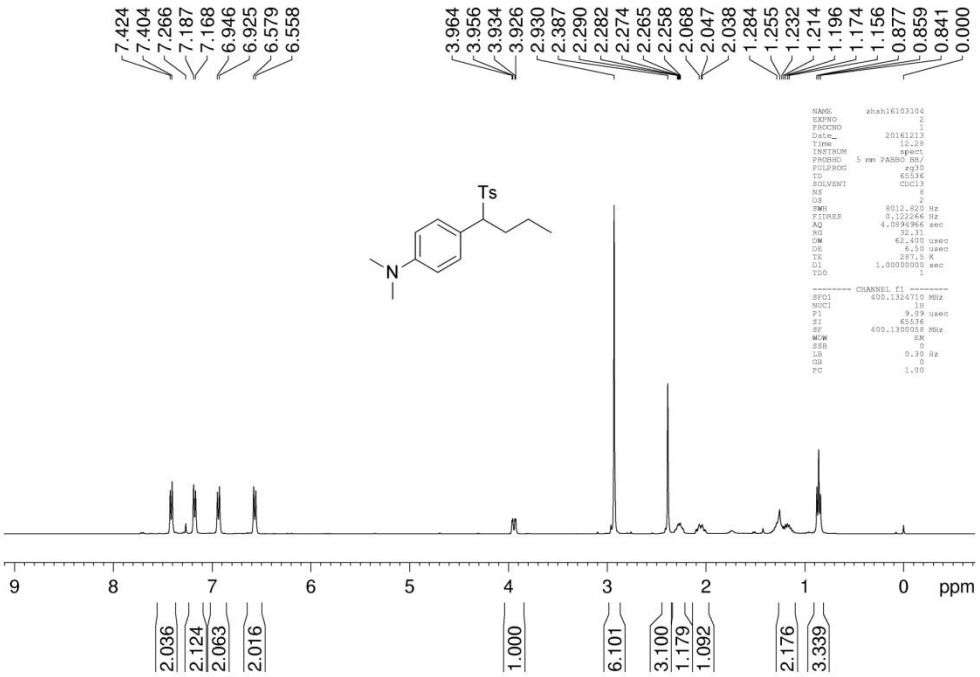

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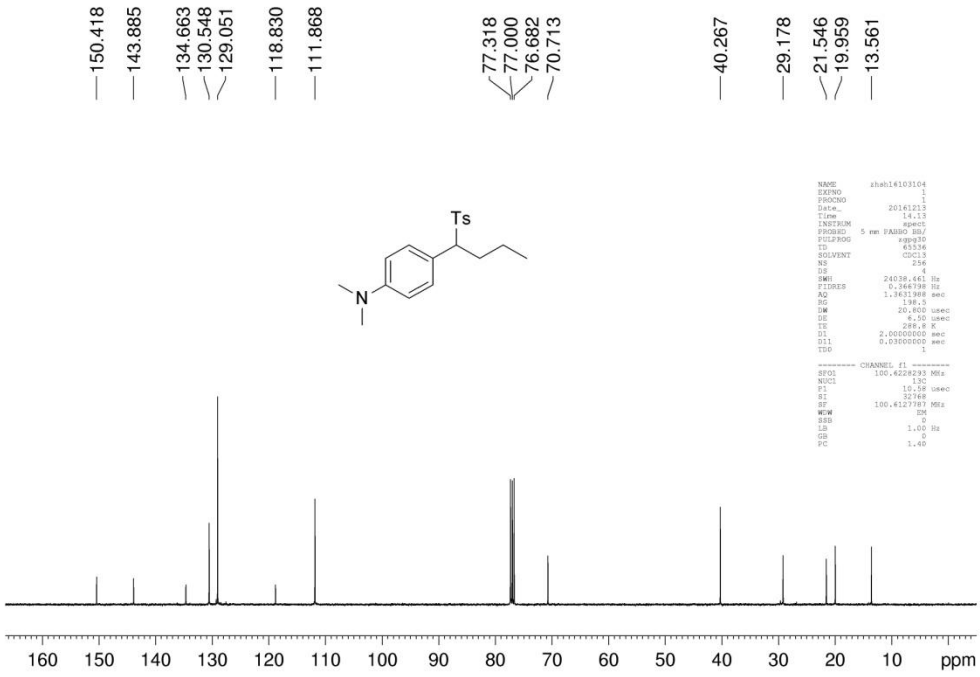

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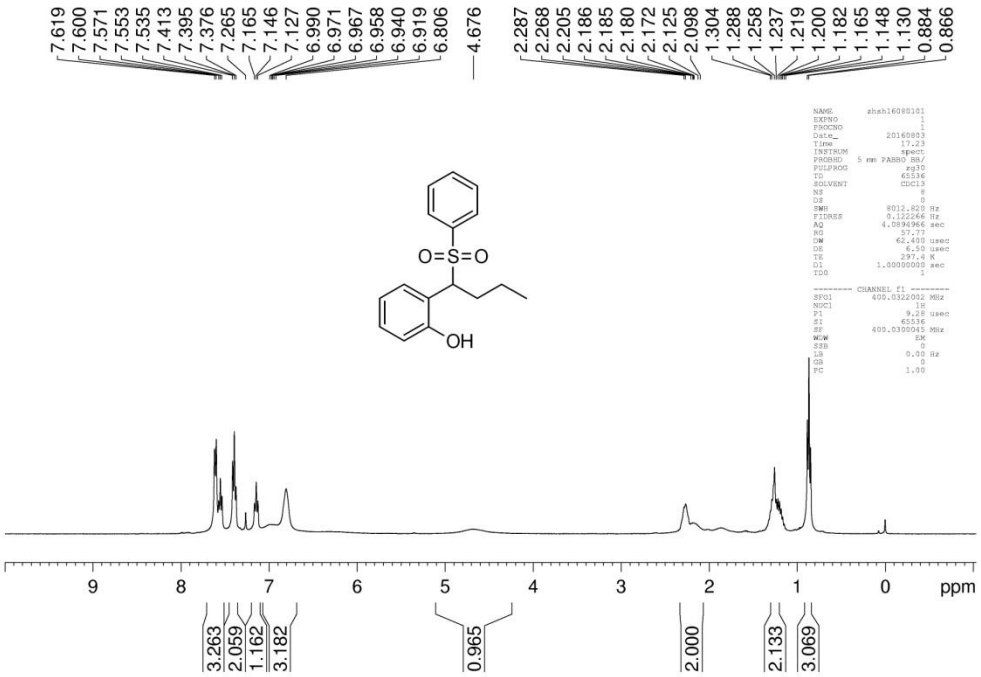
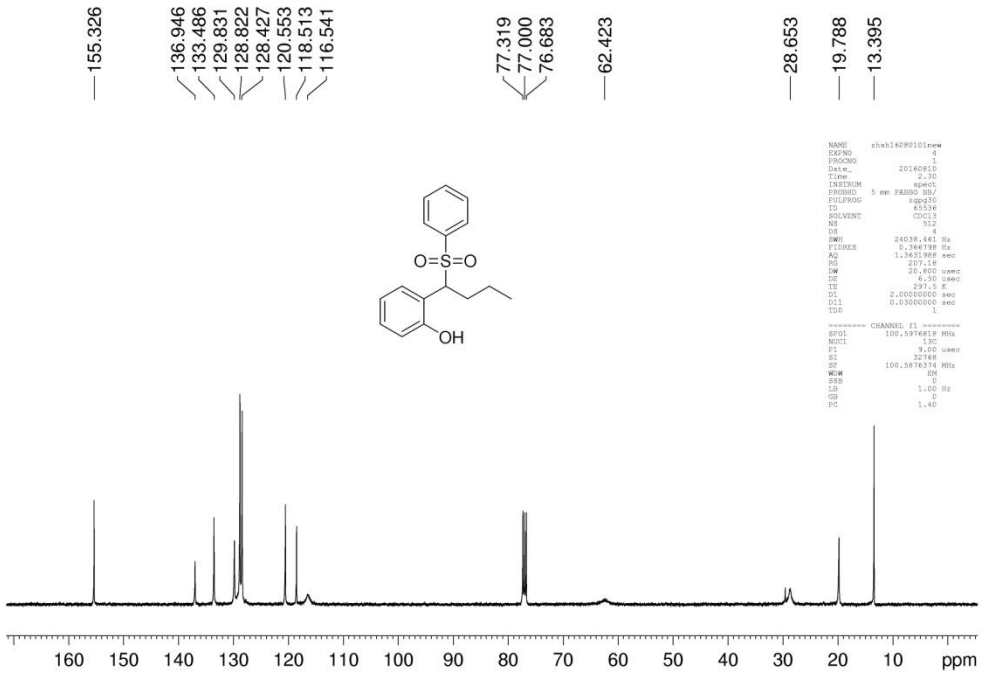


3ab ^{13}C NMR



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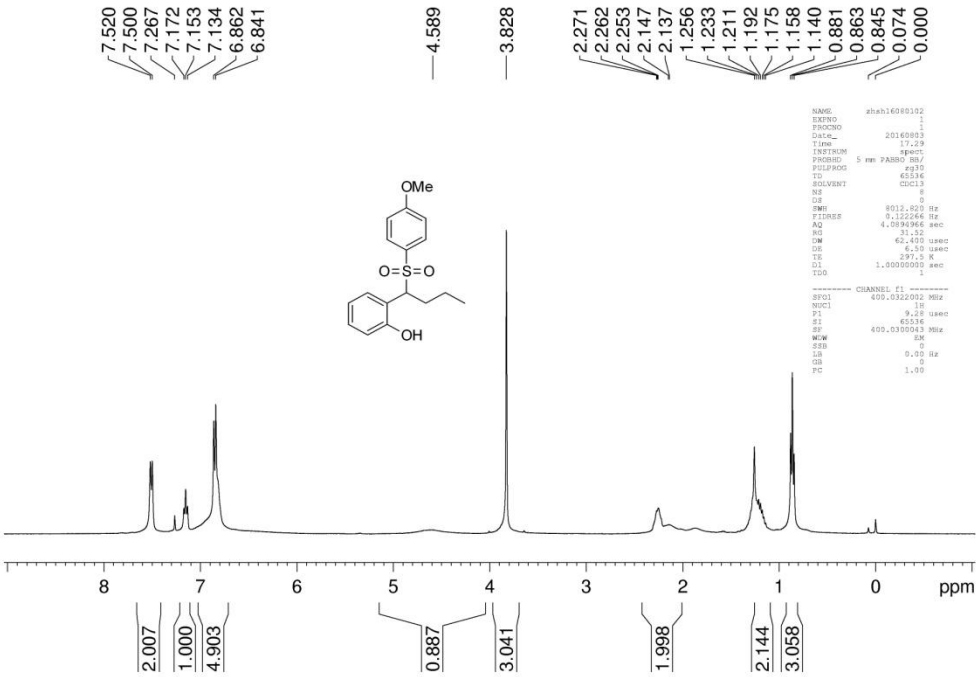

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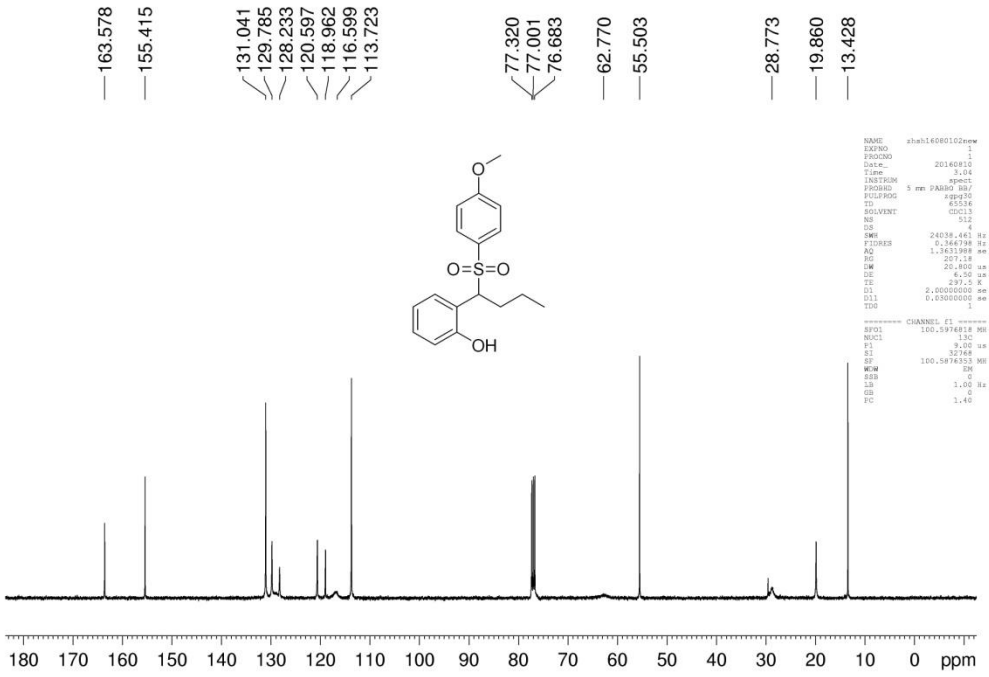

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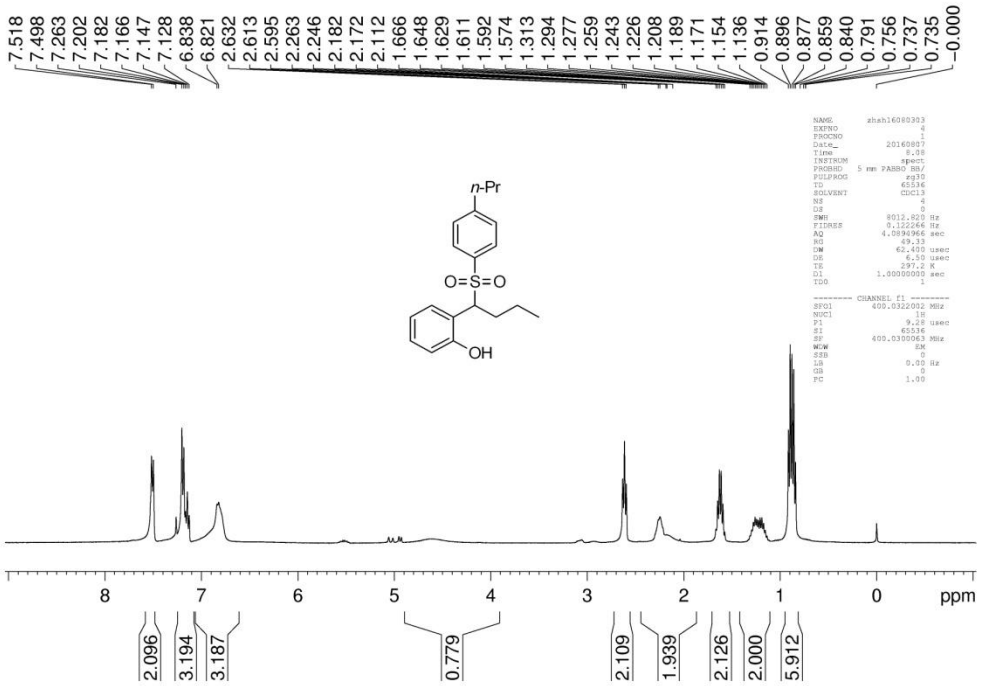

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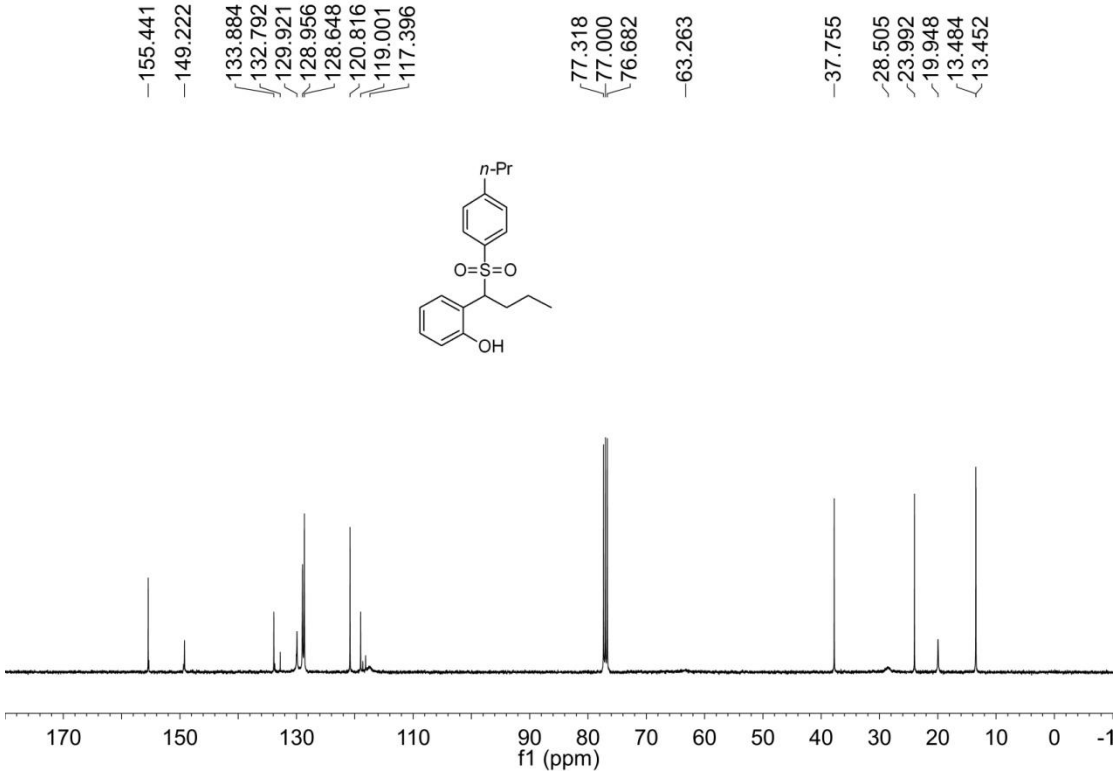
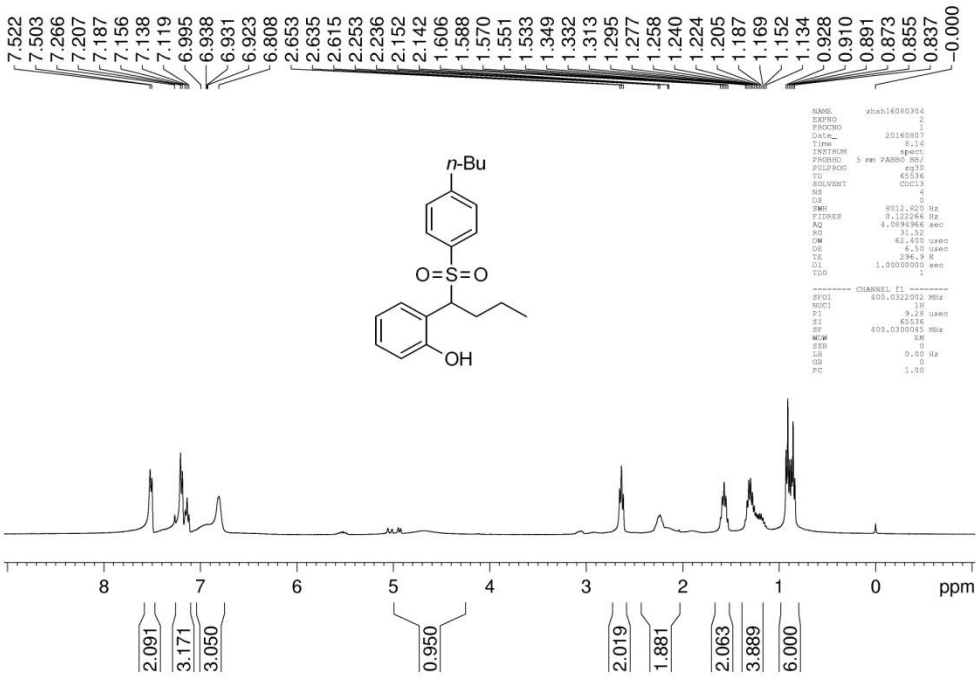


3ae ^{1}H NMR



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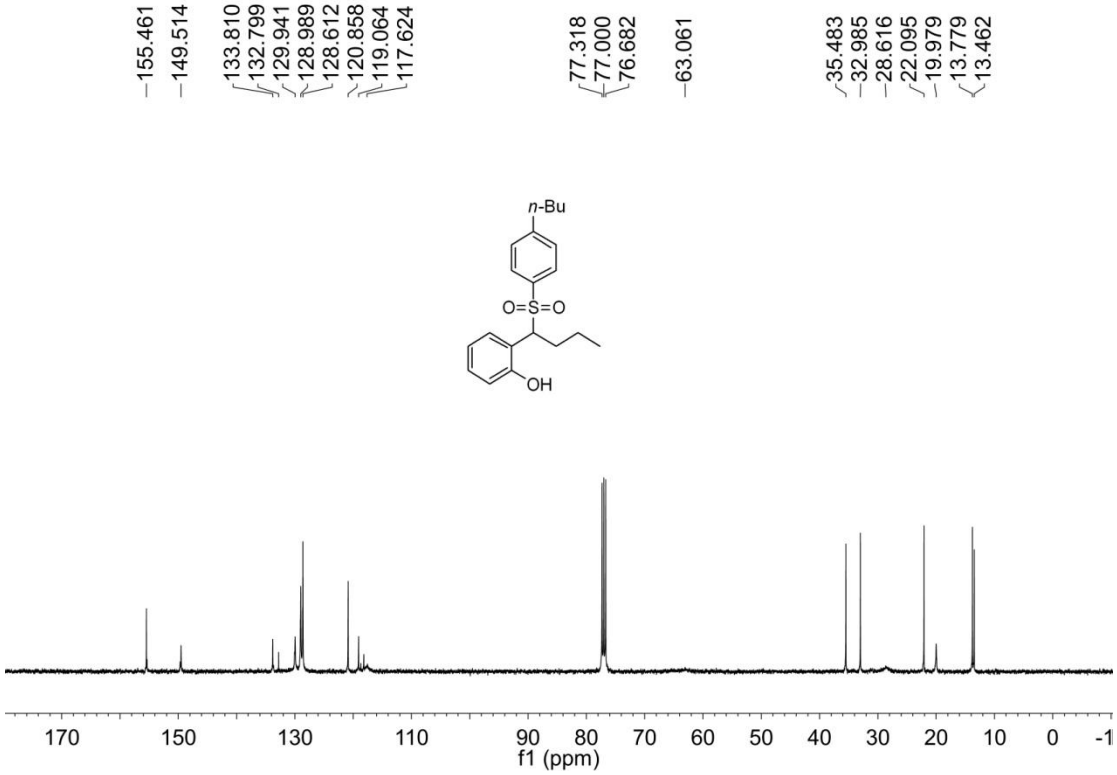

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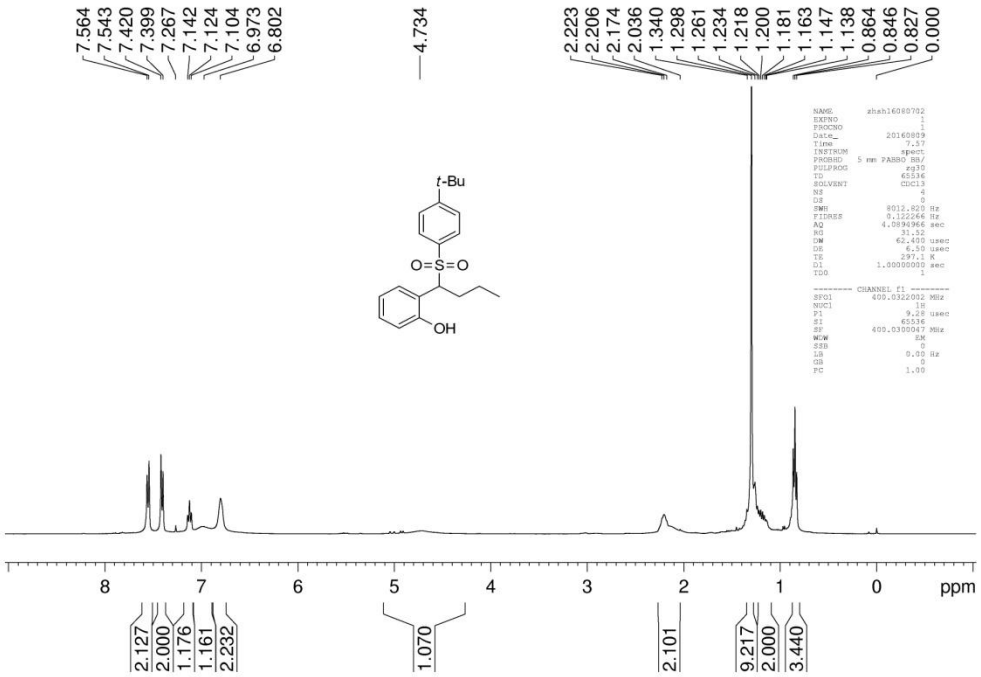

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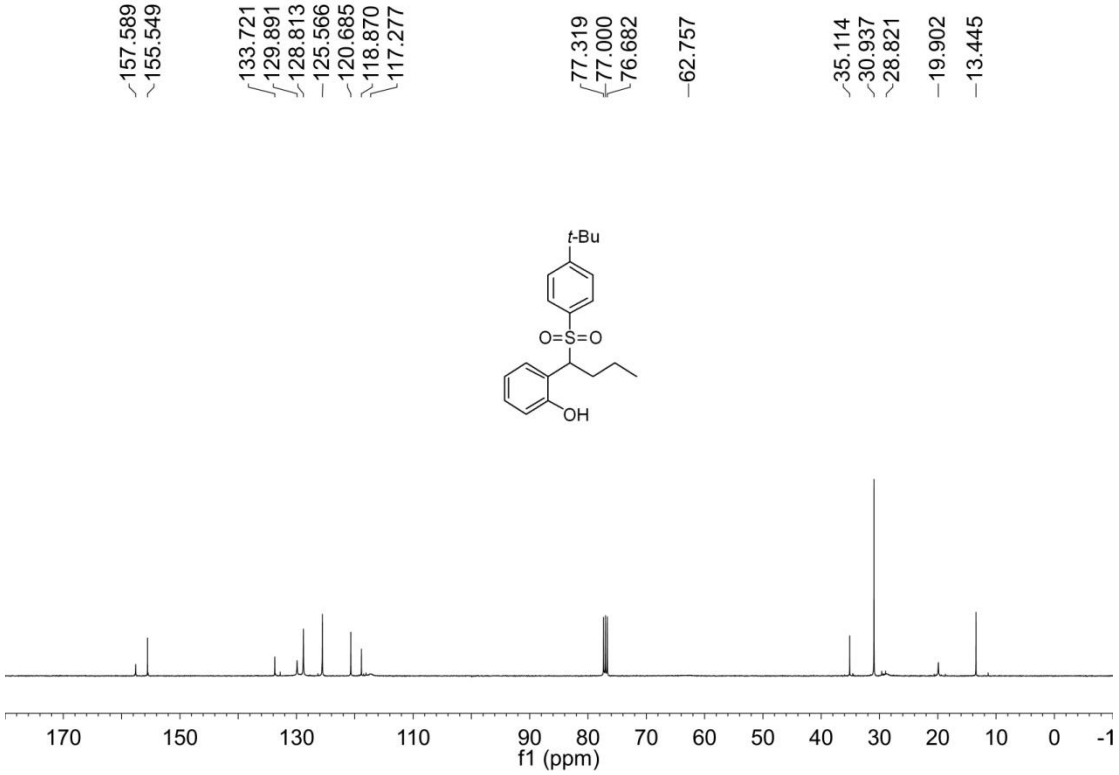

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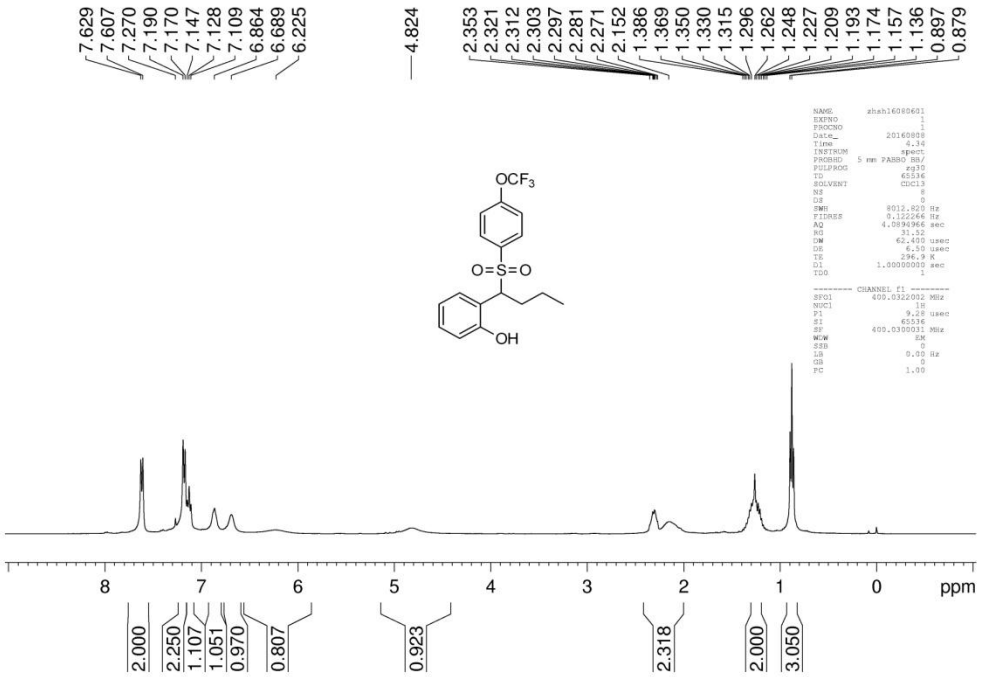

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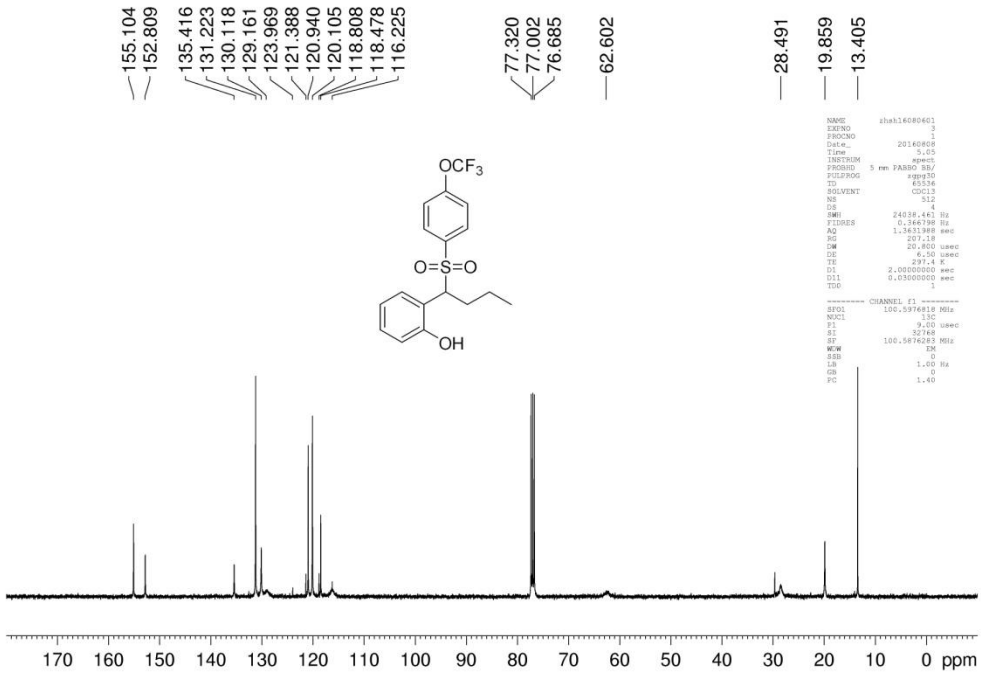

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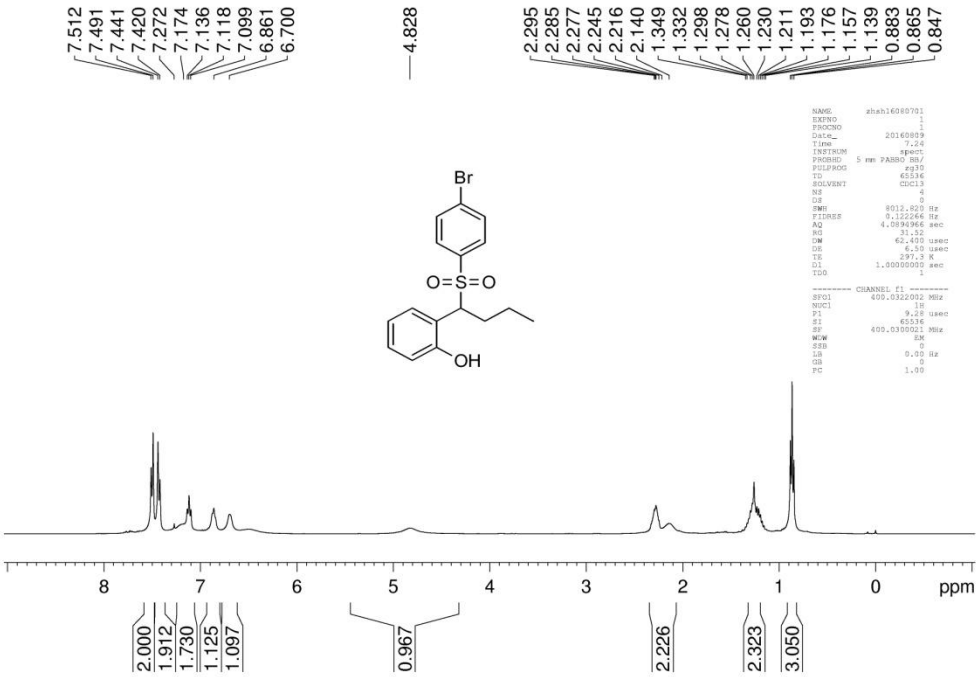

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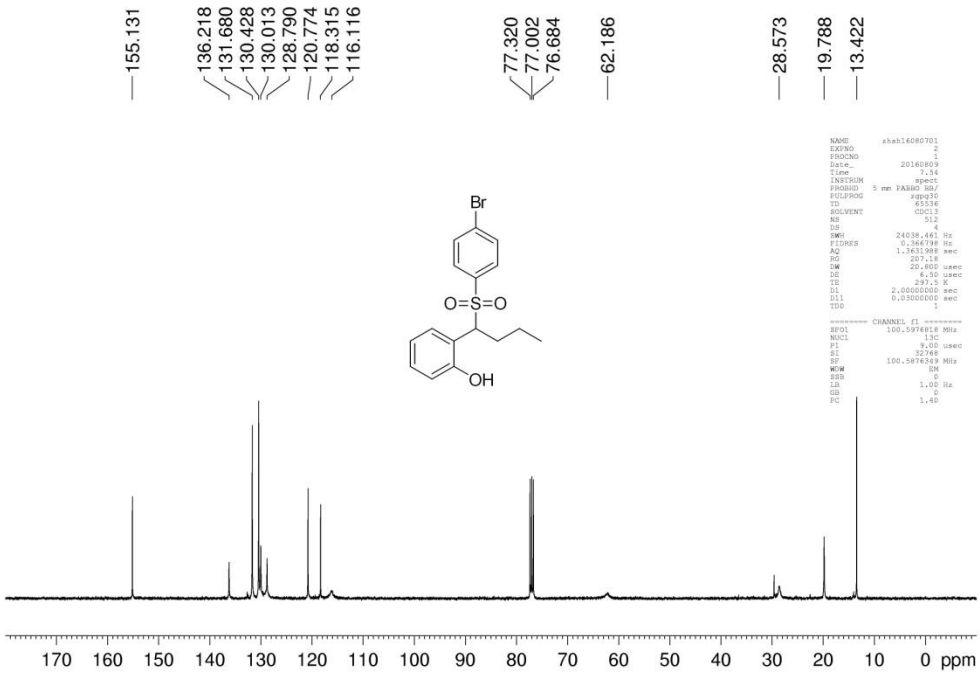

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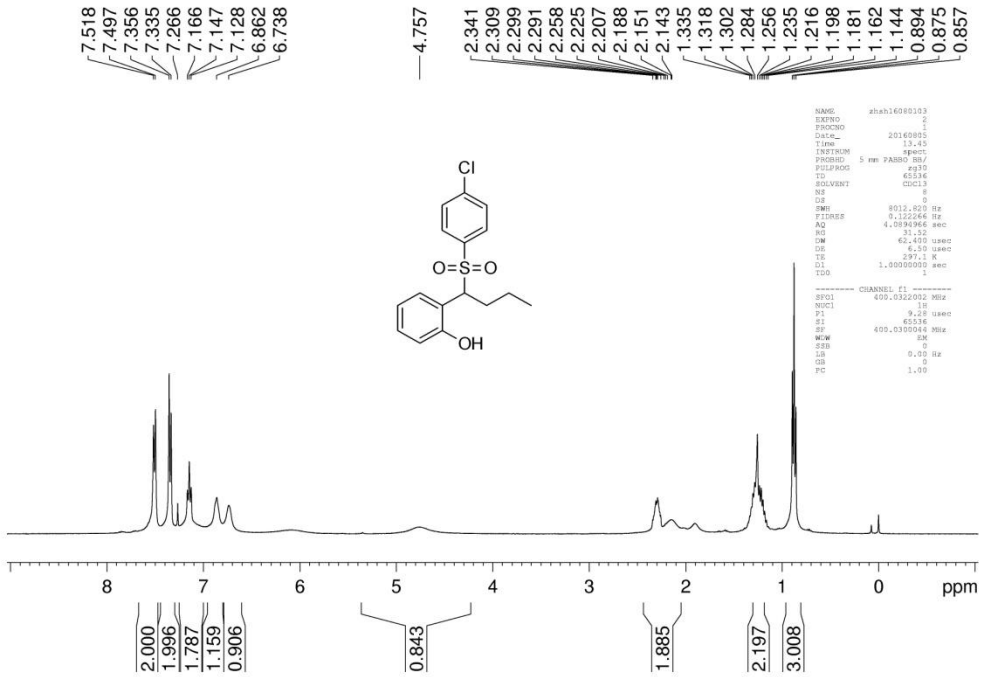

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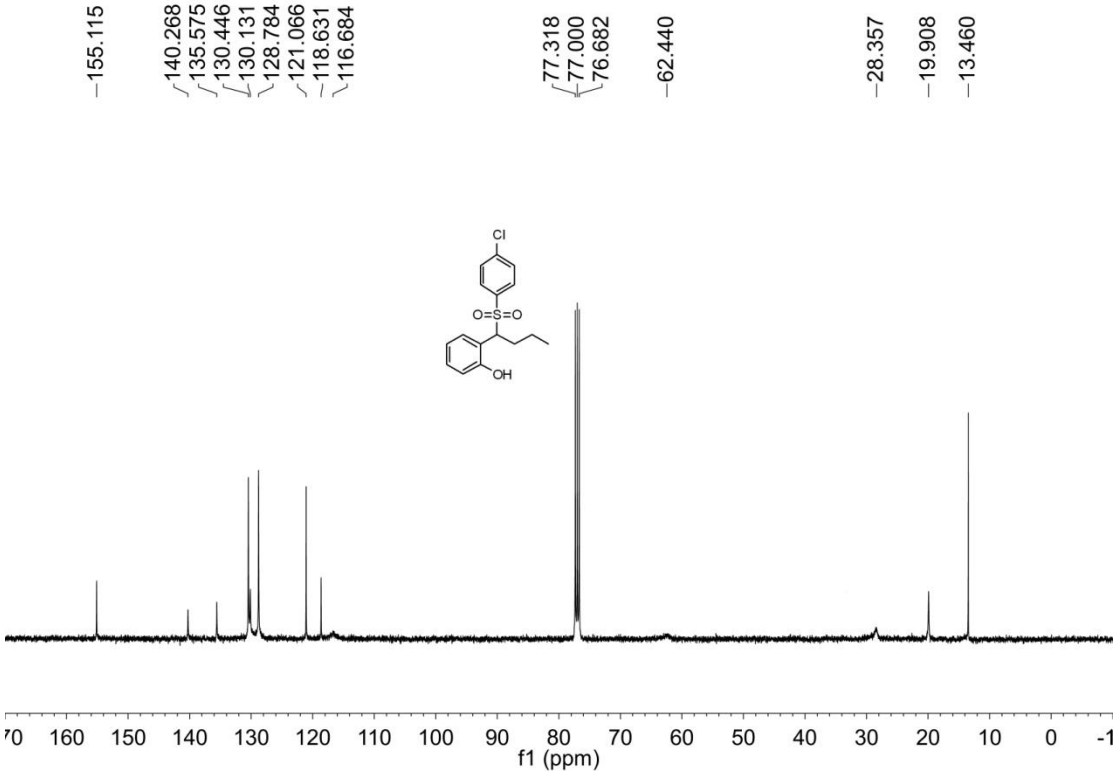

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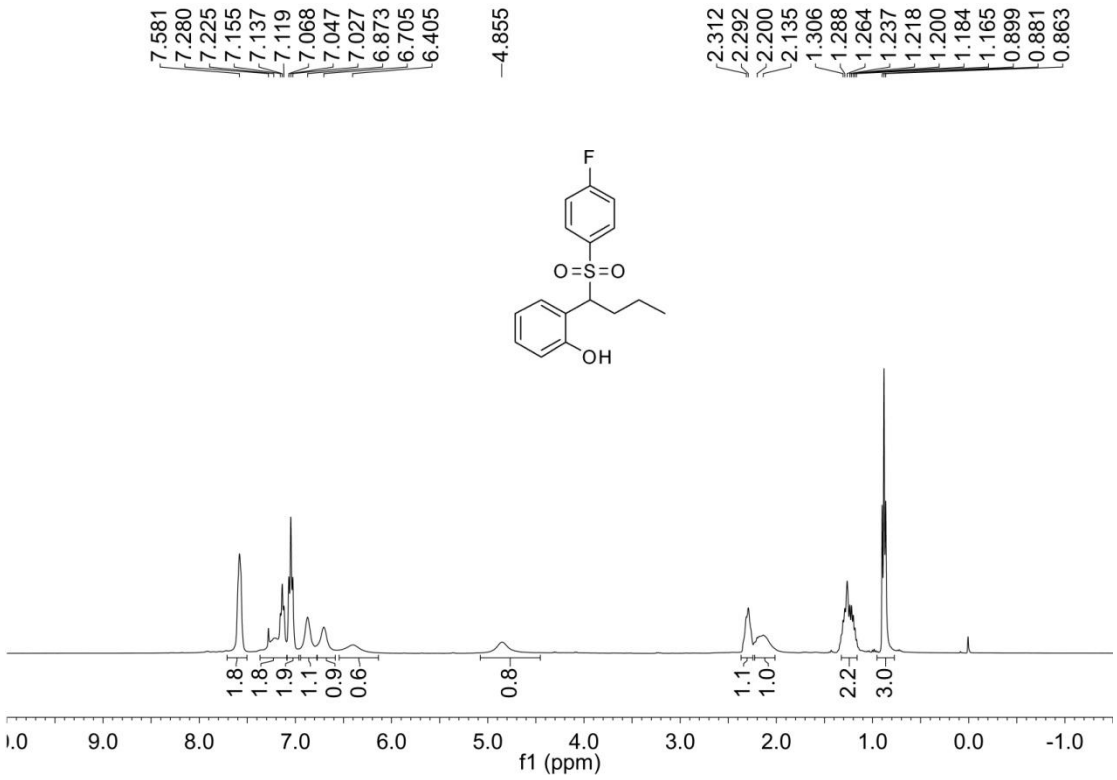

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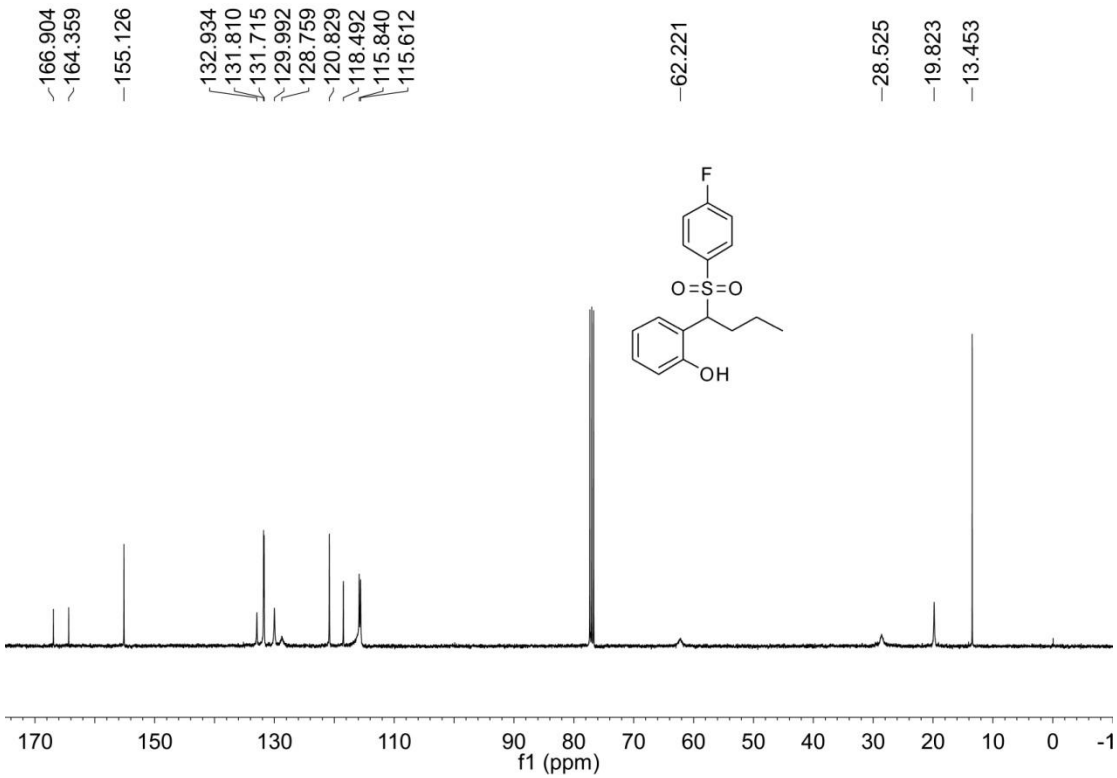

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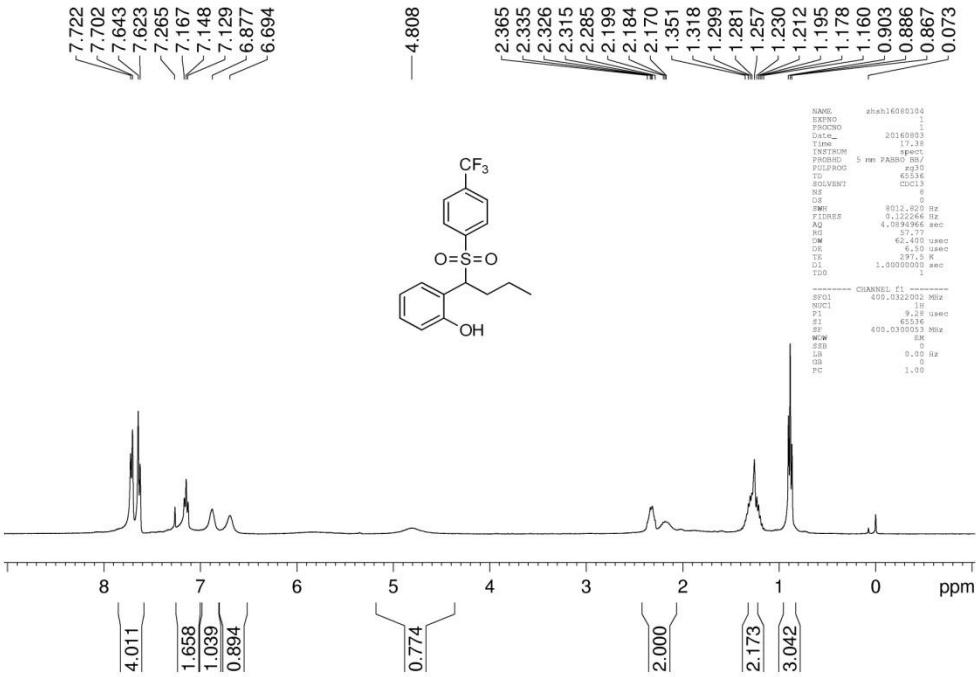

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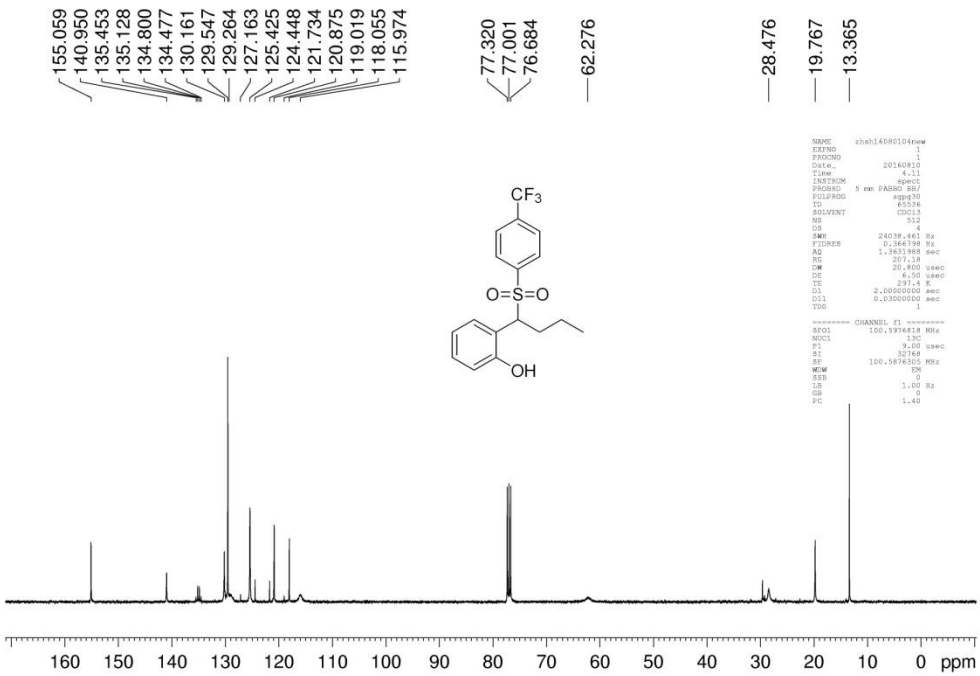

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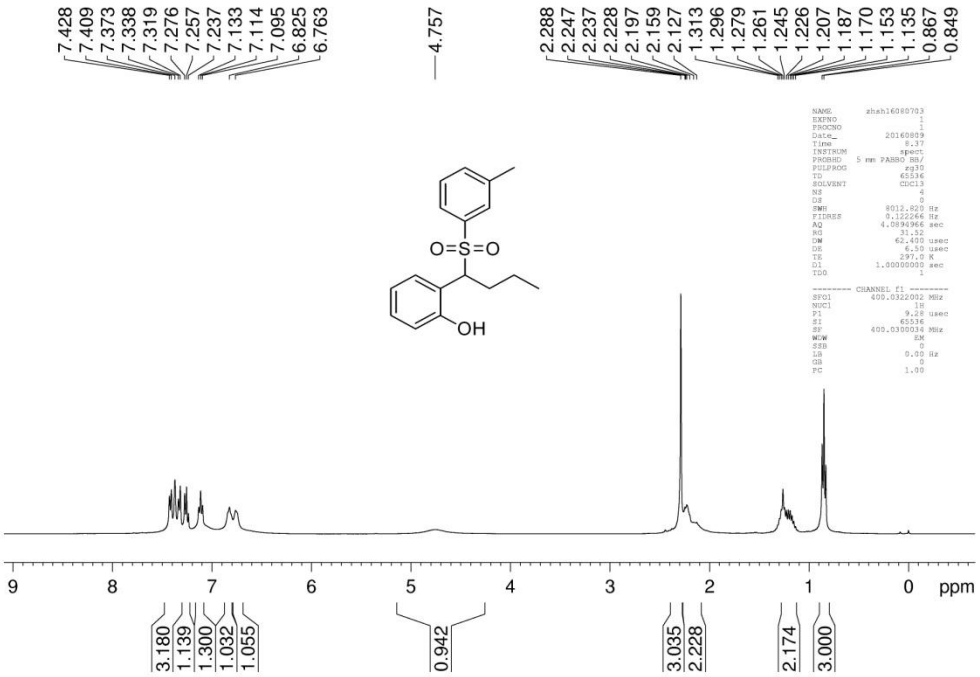

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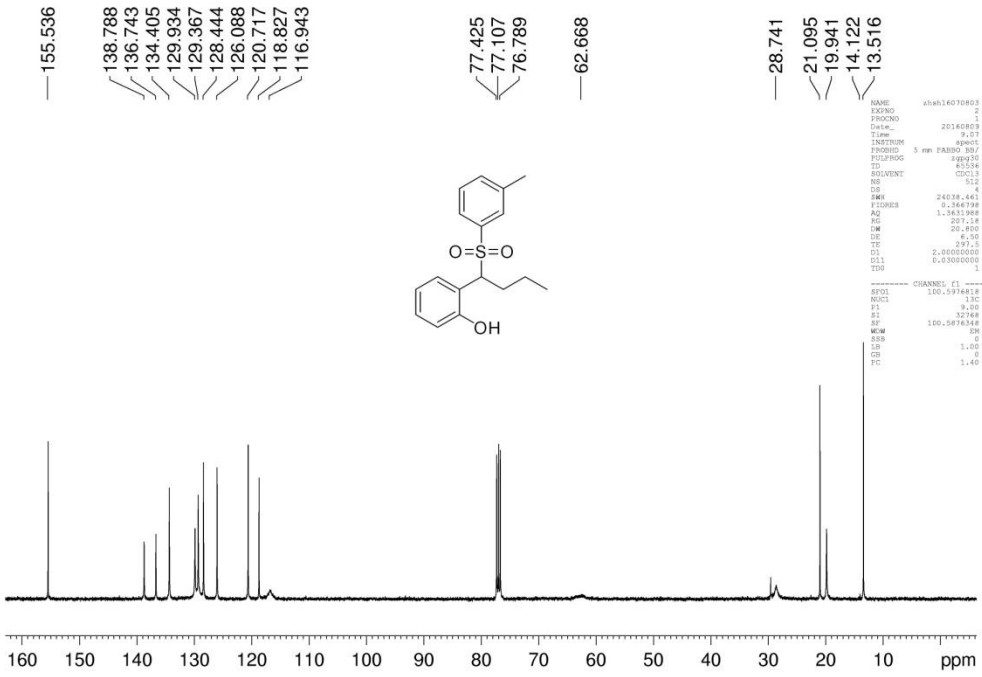

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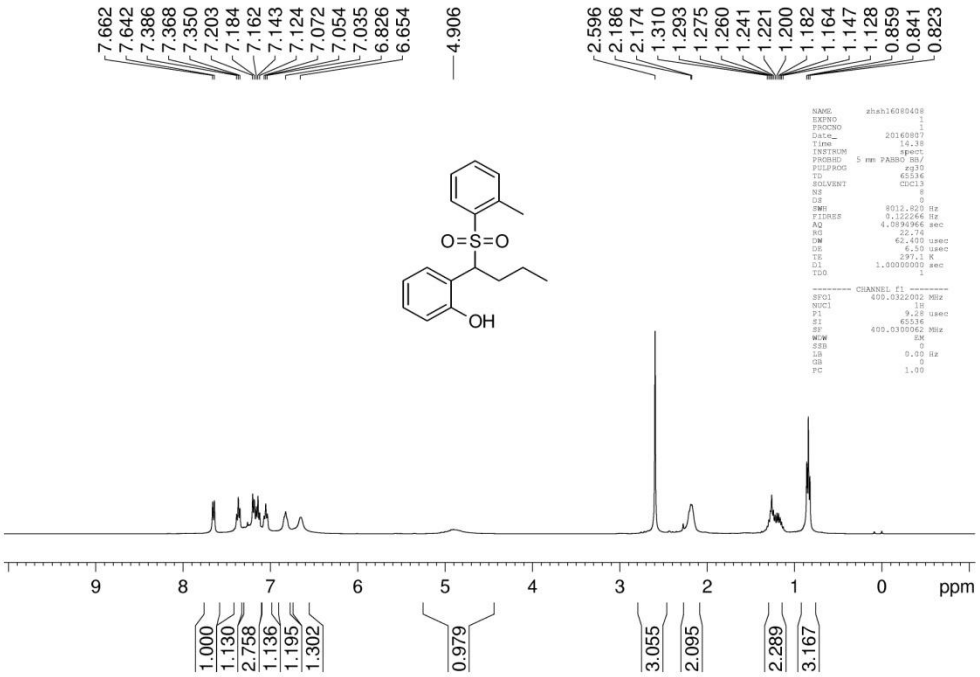

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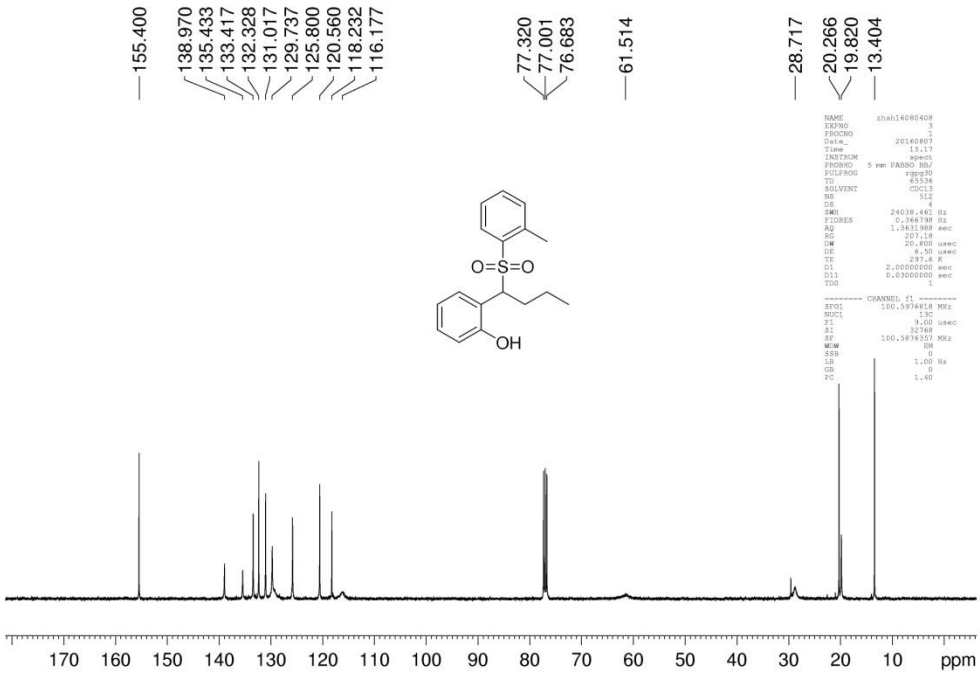

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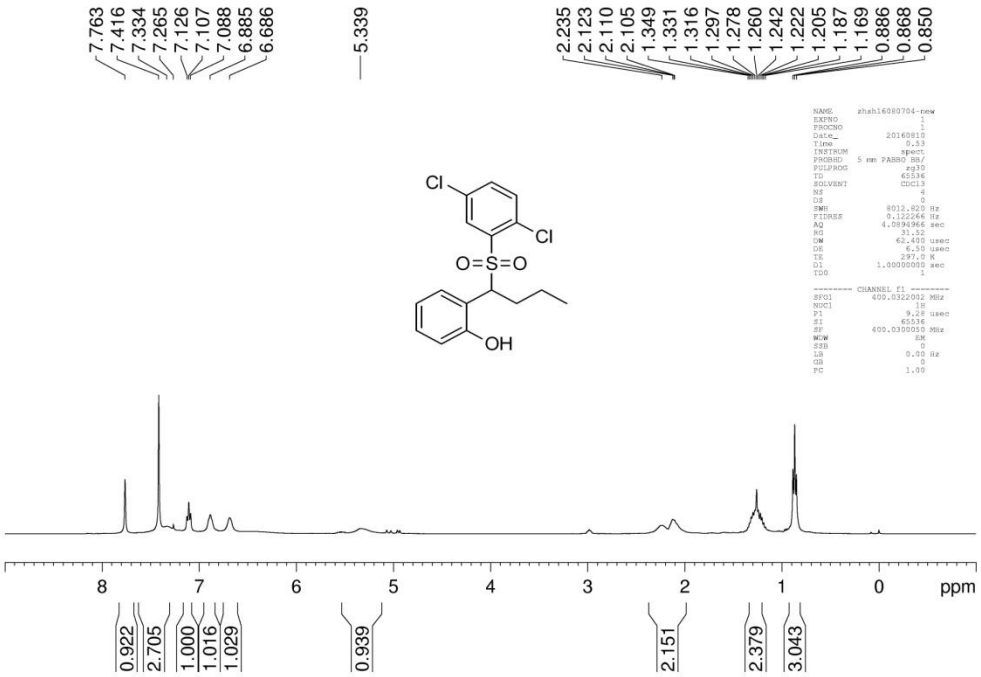

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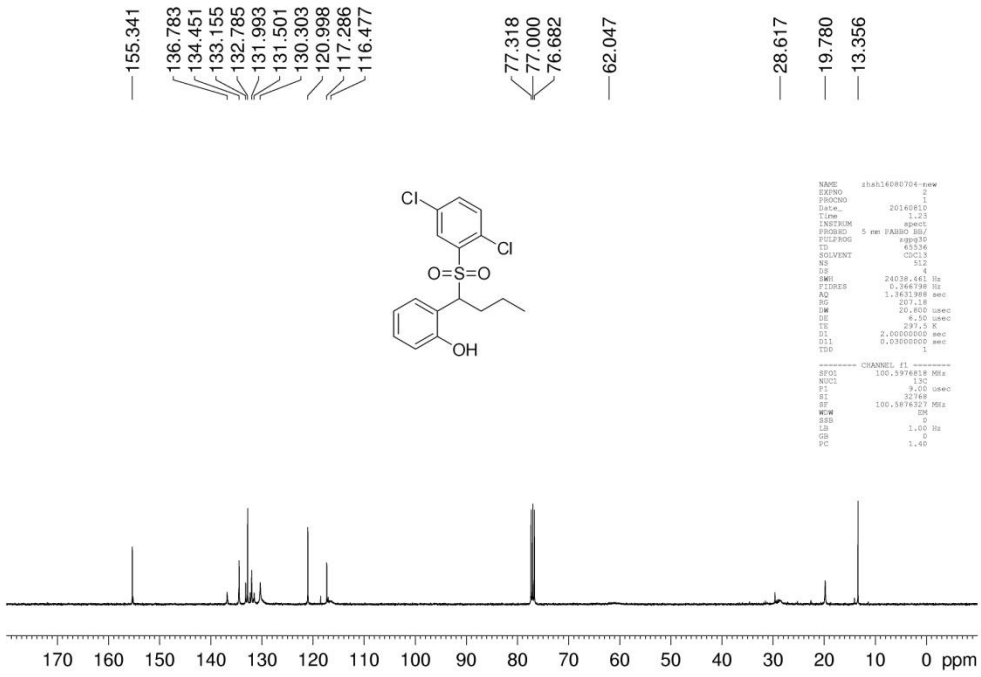

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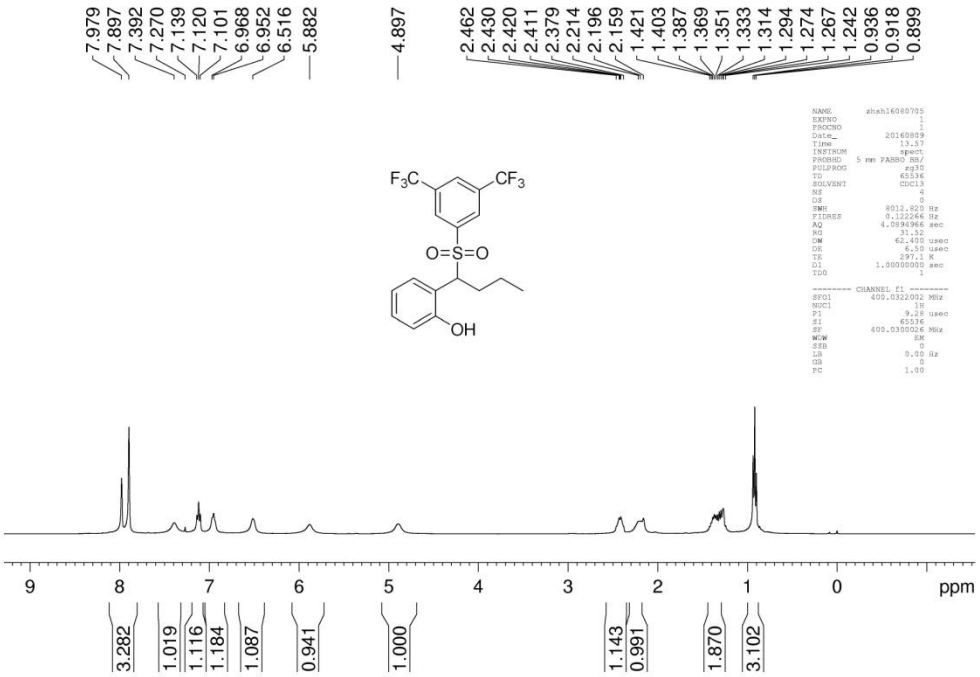

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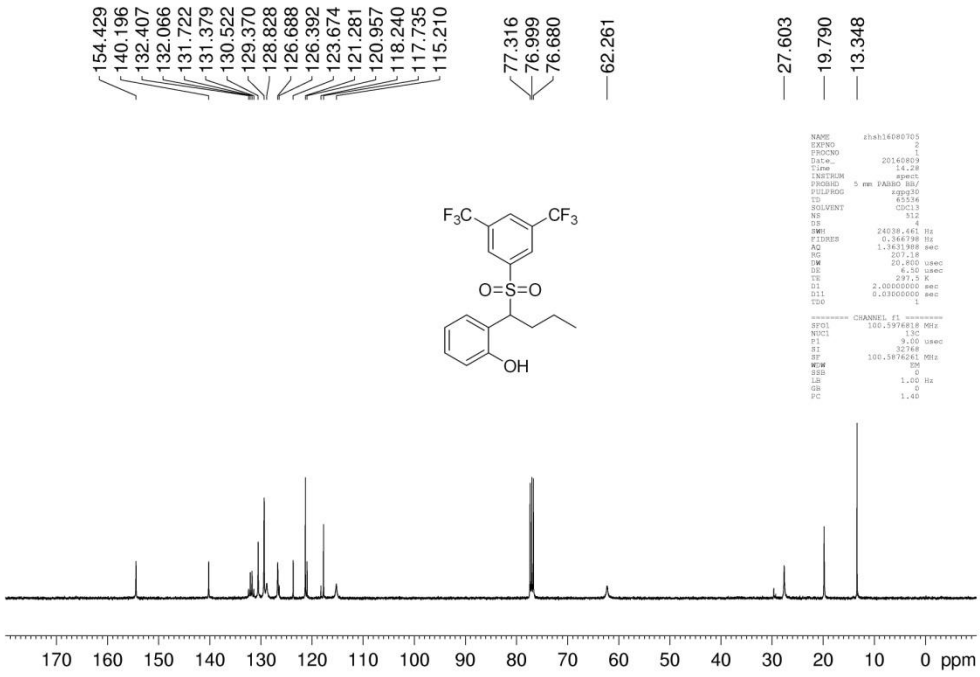
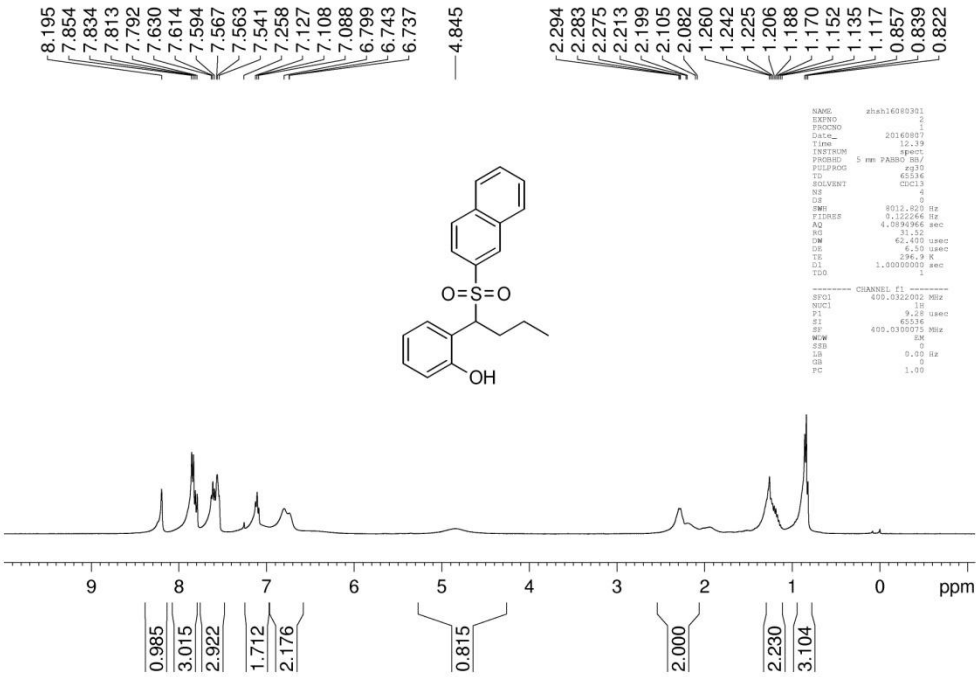
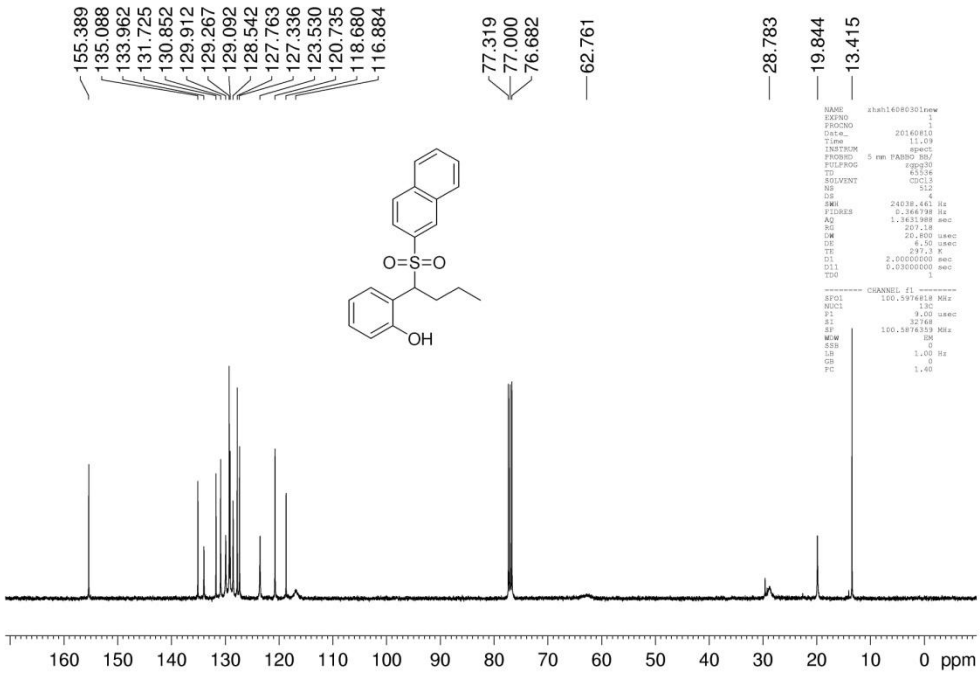


3ap ^{1}H NMR



3ap ^{13}C NMR



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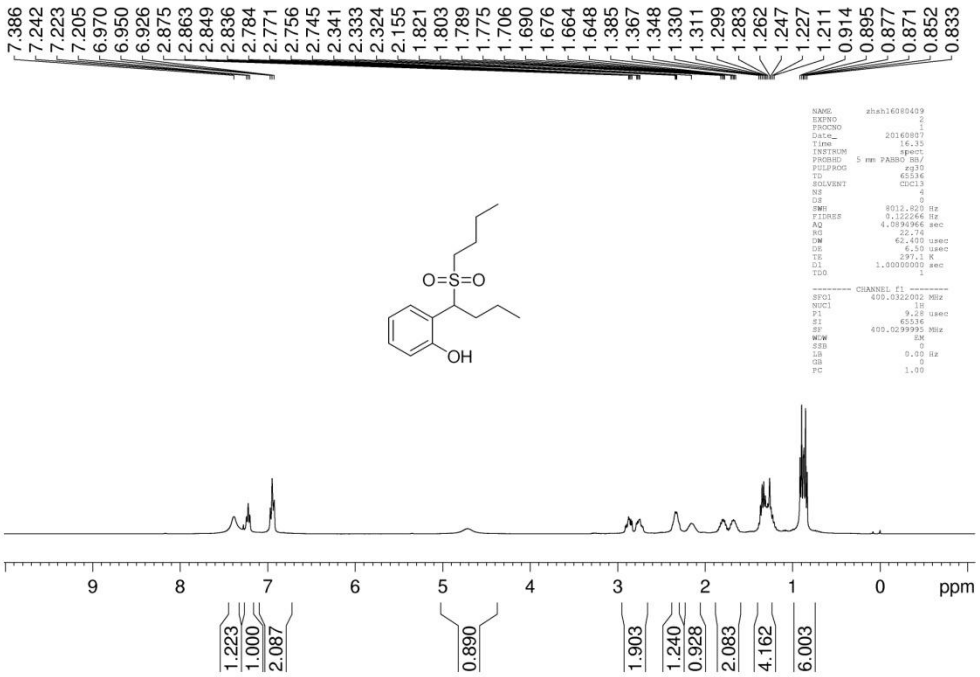

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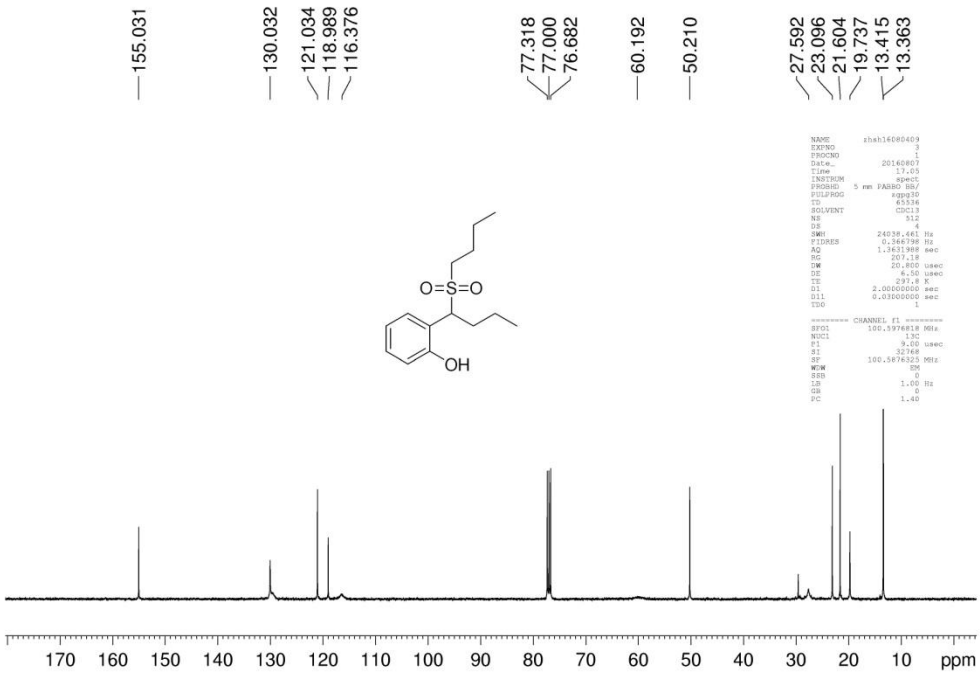
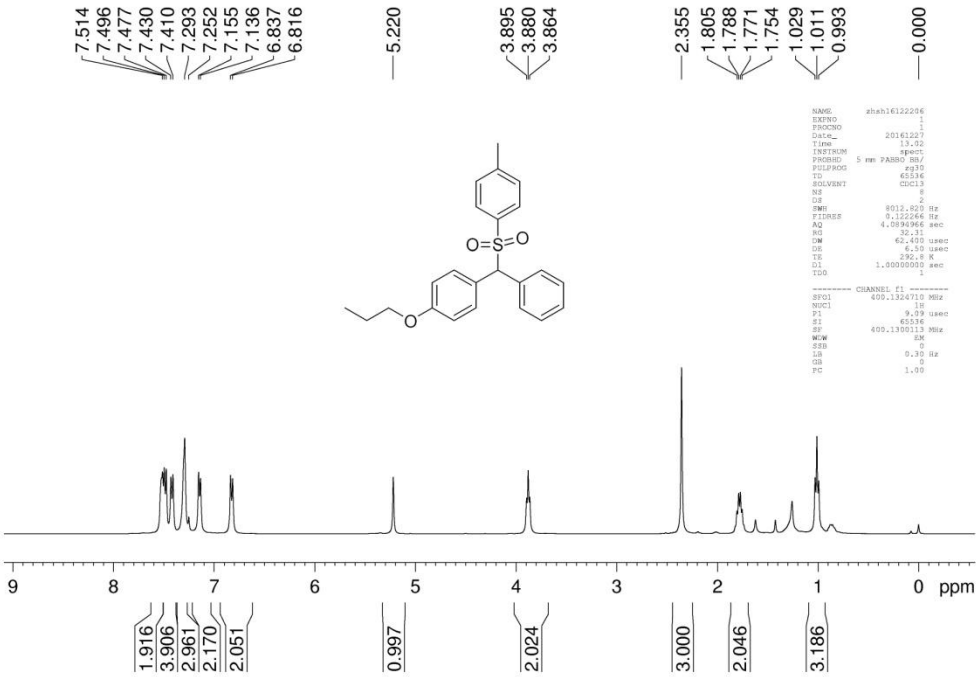


6 ^{1}H NMR



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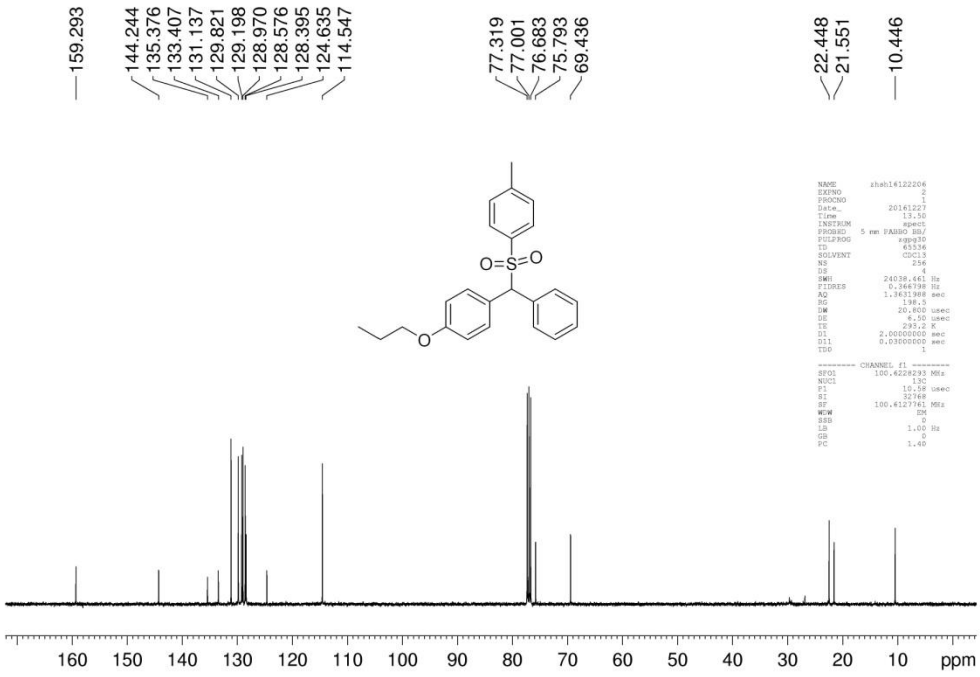
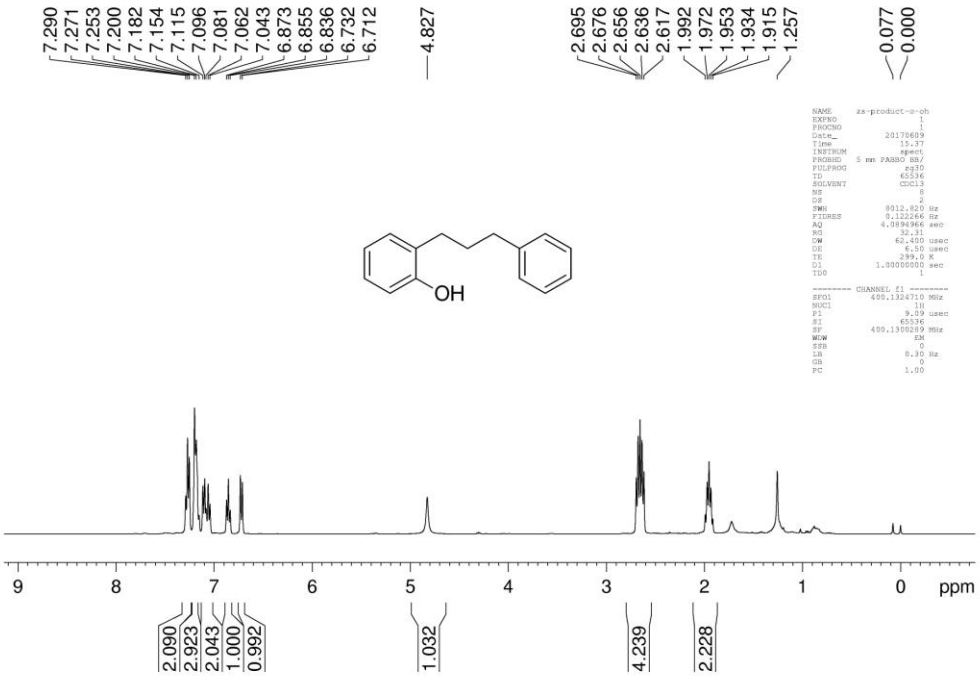
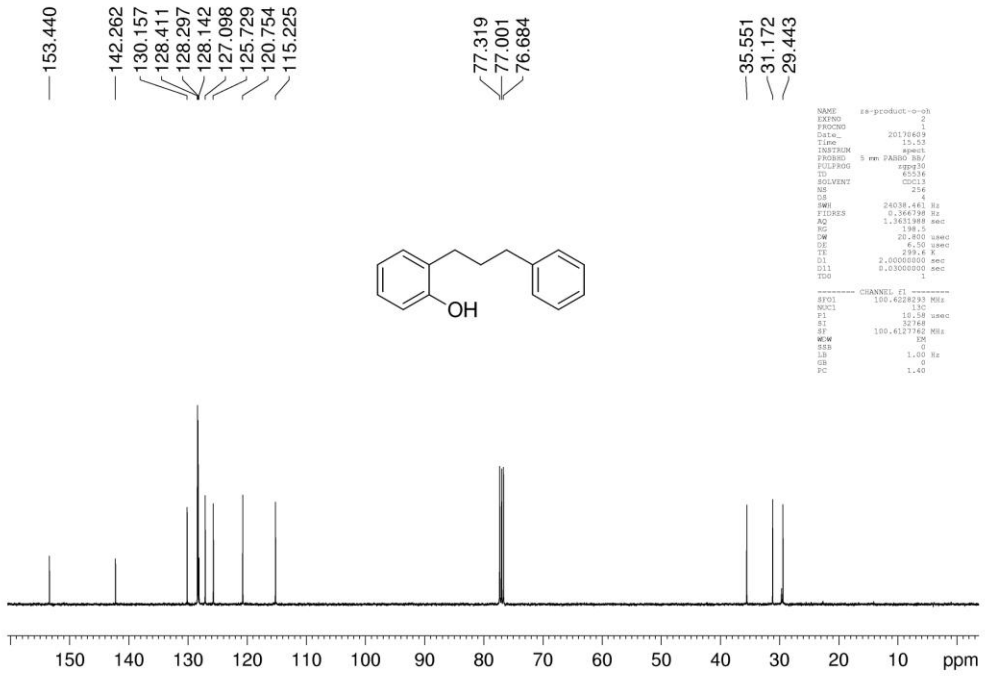


8 ^{1}H NMR



8 ^{13}C NMR



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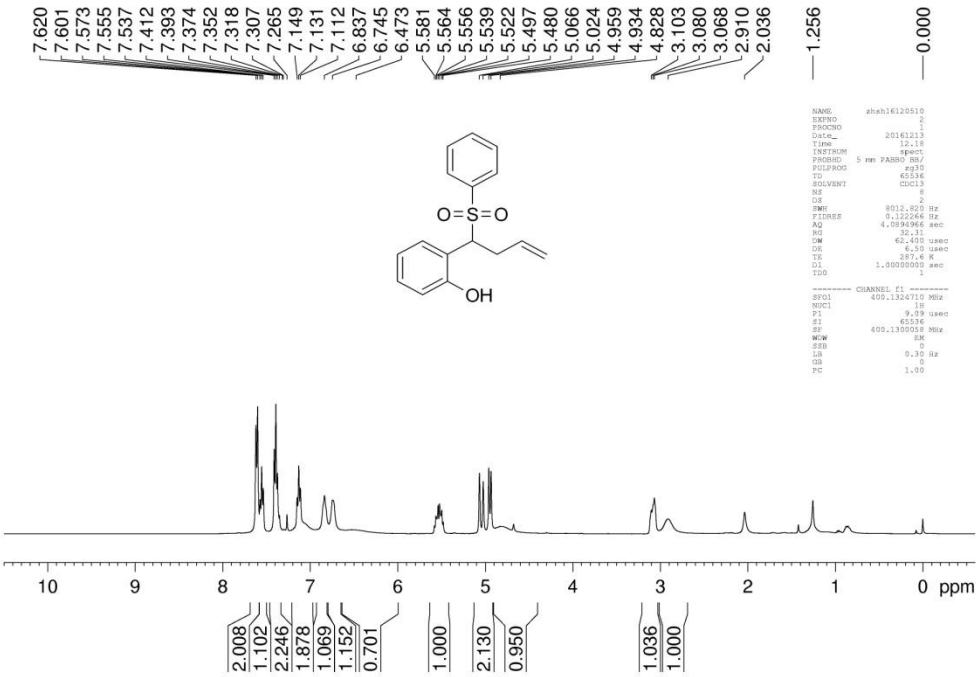
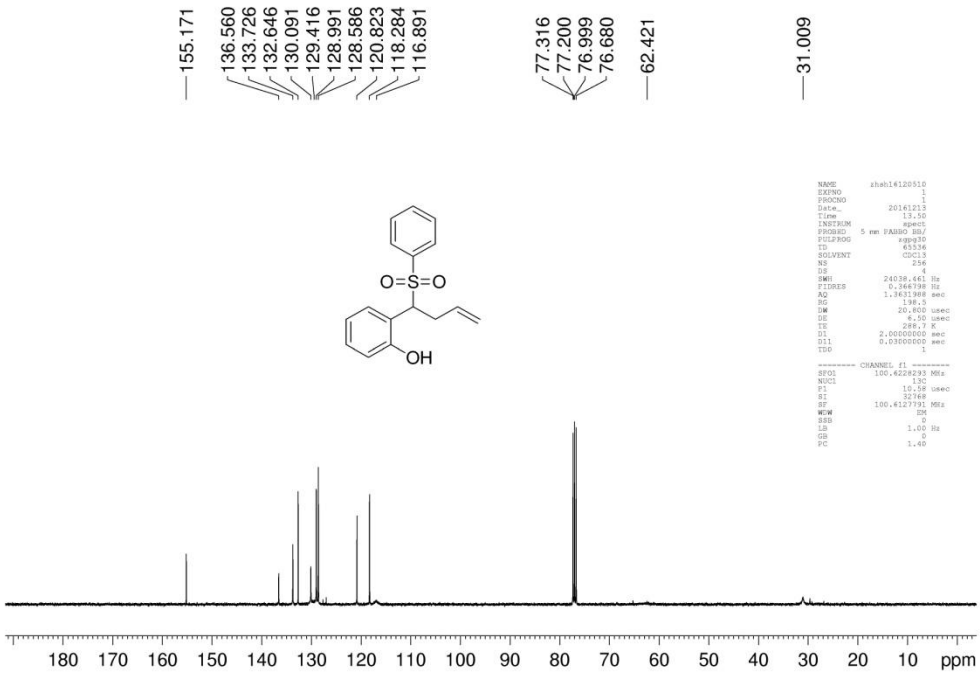
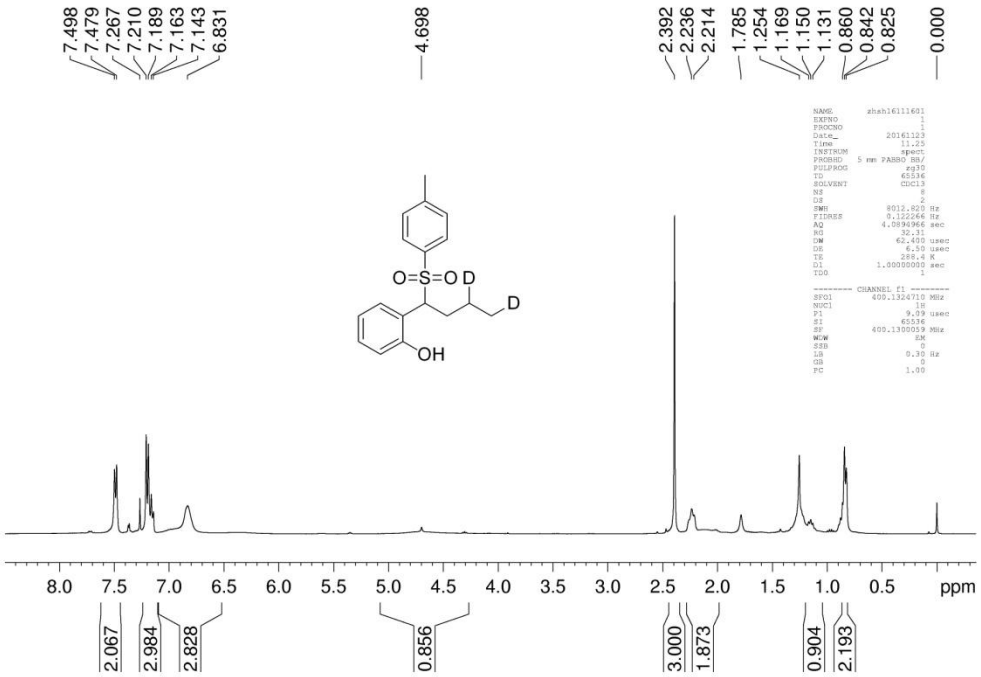


10 ^{13}C NMR



d^2-3aa ^{1}H NMR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1.254
1.169
1.150
1.131
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0.000
O=S=O D
D
OH
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