Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-Light-Promoted Hydroxysulfonylation of Alkylidenecyclopropanes: Synthesis of Cyclopropane-Containing β-Hydroxysulfones

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I. General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using $CDCl_3$ or DMSO as a solvent on a 400 MHz spectrometer at 298 K. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained via ESI mode with a TOF mass analyzer. The intensity data were recorded on a Bruker D8 QUEST with Mo-Kα radiation (λ = 0.71073 Å). The crystal structure was solved by means of direct methods and refined by employing full-matrix least squares on F2 (SHELXTL-2014). All solvents were obtained from commercial sources and were used as received. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

II. Experimental Section and Characterization Data

ACPs 1 was synthesized according to the literatures.[1-11]

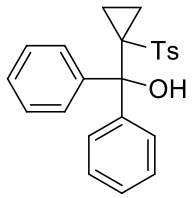
Method 1: KO^{t}Bu (2.53 g, 22.5 mmol) was added at room temperature in three portions (7.5 mmol each) to a stirred suspension of 3-bromopropyltriphenylphosphonium bromide (4.64 g, 10 mmol) in dry THF (45 mL). After the solution was stirred at room temperature for 30 min. The orange solution was then refluxed for 2 h before aryl ketones (10 mmol) was added and stirring was continued at 65 °C for overnight. The reaction mixture was quenched by brine (20 mL) at room temperature, the aqueous layer was extracted with hexane (3 × 10 mL). The combined organic layers were washed with brine (4 × 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography over silica gel with PE / EA to afford the corresponding product **1**.

Method 2: To a suspension of 0.85 g of NaH (53% suspension in mineral oil) in 20 ml 1,2-dimethoxyethane, 3-bromopropyltriphenylphosphonium bromide (4.64 g, 10 mmol) was added at room temp under N_2, and then two drops of EtOH were added. This mixture was stirred for 6 h at 60-70 °C. Aryl ketones (10 mmol) was added and

the mixture was stirred at 70 ℃ for an additional 5 h. The mixture was poured into ice-water and extracted with hexane. The hexane extract was dried and concentrated. The crude reaction mixture was purified by flash column chromatography over silica gel with PE / EA to afford the corresponding product **1**.

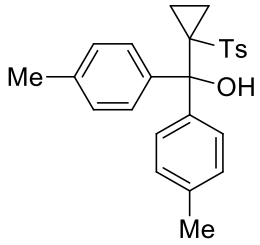
Synthesis of *β*-Hydroxysulfones 3

ACPs (**1**, 0.2 mmol), TsCl (**2a**, 0.3 mmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (2 mol %), and K_2HPO_4 (1.5 equiv) was added in CH_3CN:H_2O=30:1 (1 mL) at room temperature and 12 W blue LED light irradiation for 3 h under N_2 atmosphere. After the reaction, CH_3CN was removed under reduced pressure, purification was finally performed by flash column chromatography on silica gel using EtOAc and petroleum ether to give the desired product **3**.



Diphenyl(1-tosylcyclopropyl)methanol (**3aa**)

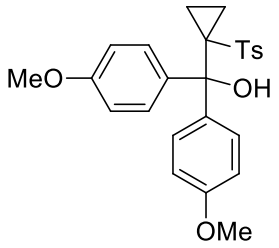
White solid; m.p. 181-182 °C; yield: 68.2 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 4H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.14-7.05 (m, 6H), 7.00 (d, *J* = 8.0 Hz, 2H), 5.78 (s, 1H), 2.37 (s, 3H), 1.71-1.67 (m, 2H), 1.05-0.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.4, 137.5, 129.2, 128.6, 127.7, 127.5, 127.2, 79.0, 49.1, 21.5, 10.5. HRMS (ESI): calcd for $C_{23}H_{22}O_3S$ ($[M+Na]^+$) 401.1182, found 401.1191.



Di-*p*-tolyl(1-tosylcyclopropyl)methanol (**3ba**)

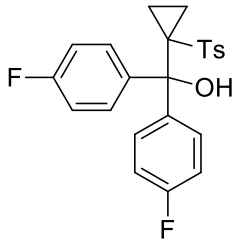
White solid; m.p. 225-226 °C; yield: 56.2 mg (69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 4H), 5.67 (s, 1H), 2.39 (s, 3H), 2.24 (s, 6H), 1.68-1.65 (m, 2H), 1.05-1.01 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.5, 137.7, 136.9, 129.1, 128.6, 128.1, 127.5, 78.7, 49.4, 21.6, 20.9, 10.4. HRMS (ESI): calcd for $C_{25}H_{26}O_3S$ ($[M+Na]^+$) 429.1495, found 429.1496.



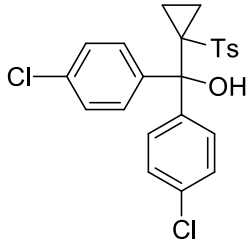
Bis(4-methoxyphenyl)(1-tosylcyclopropyl)methanol (**3ca**)

White solid; m.p. 173-174 °C; yield: 57.7 mg (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 9.2 Hz, 4H), 5.68 (s, 1H), 3.73 (s, 6H), 2.38 (s, 3H), 1.69-1.66 (m, 2H), 1.03-1.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 143.6, 137.7, 134.7, 129.1, 128.8, 128.6, 112.7, 78.5, 55.2, 49.6, 21.5, 10.4. HRMS (ESI): calcd for $C_{25}H_{26}O_5S$ ($[M+Na]^+$) 461.1393, found 461.1399.



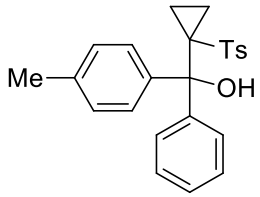
Bis(4-fluorophenyl)(1-tosylcyclopropyl)methanol (**3da**)

White solid; m.p. 200-201 °C; yield: 44.1 mg (53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 4H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.78-6.74 (m, 4H), 5.86 (s, 1H), 2.41 (s, 3H), 1.73-1.70 (m, 2H), 0.99-0.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.9 Hz), 144.3, 138.0 (d, *J* = 3.2 Hz), 137.3, 129.4, 129.3, 128.6, 114.4 (d, *J* = 21.2 Hz), 78.4, 49.1, 21.5, 10.4. HRMS (ESI): calcd for $C_{23}H_{20}F_2O_3S$ ($[M+Na]^+$) 437.0993, found 437.0997.



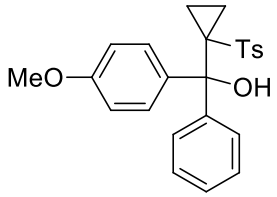
Bis(4-chlorophenyl)(1-tosylcyclopropyl)methanol (**3ea**)

White solid; m.p. 260-261 °C; yield: 55.0 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.08-7.02 (m, 6H), 5.89 (s, 1H), 2.45 (s, 3H), 1.75-1.71 (m, 2H), 0.99-0.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 140.4, 137.1, 133.7, 129.4, 128.9, 128.5, 127.7, 78.3, 48.9, 21.6, 10.2. HRMS (ESI): calcd for $C_{23}H_{20}Cl_2O_3S$ ($[M+Na]^+$) 469.0402, found 469.0413.



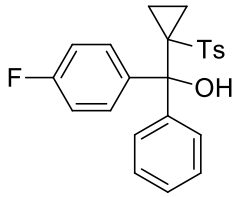
Phenyl(*p*-tolyl)(1-tosylcyclopropyl)methanol (**3fa**)

White solid; m.p. 182-183 °C; yield: 53.0 mg (68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.26-7.23 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.13-7.04 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.70-1.66 (m, 2H), 1.05-1.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.5, 139.4, 137.6, 137.0, 129.2, 128.6, 128.2, 127.6, 127.6, 127.5, 127.2, 78.9, 49.3, 21.6, 20.9, 10.5, 10.4. HRMS (ESI): calcd for $C_{24}H_{24}O_3S$ ($[M+Na]^+$) 415.1338, found 415.1344.



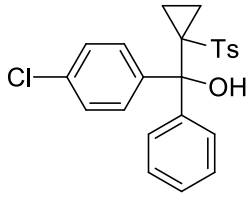
(4-Methoxyphenyl)(phenyl)(1-tosylcyclopropyl)methanol (**3ga**)

White solid; m.p. 138-139 °C; yield: 46.8 mg (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7. 27 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11-7.06 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 9.2 Hz, 2H), 5.73 (s, 1 H), 3.72 (s, 3H), 2.37 (s, 3H), 1.70-1.66 (m, 2H), 1.04-1.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 143.7, 142.7, 137.6, 134.5, 129.2, 128.9, 128.6, 127.6, 127.5, 127.2, 112.8, 78.8, 55.2, 49.3, 21.5, 10.5, 10.3. HRMS (ESI): calcd for $C_{24}H_{24}O_4S$ ($[M+Na]^+$) 431.1288, found 431.1295.



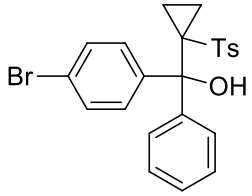
(4-Fluorophenyl)(phenyl)(1-tosylcyclopropyl)methanol (**3ha**)

White solid; m.p. 195-196 °C; yield: 56.0 mg (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 4H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.15-7.07 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.76-6.71 (m, 2H), 5.83 (s, 1H), 2.39 (s, 3H), 1.71-1.68 (m, 2H), 1.04-0.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.6 Hz), 144.1, 142.0, 138.4 (d, *J* = 3.2 Hz), 137.4, 129.4, 129.3, 129.2, 128.6, 127.6, 127.4, 114.2 (d, *J* = 21.3 Hz), 78.7, 49.1, 21.5, 10.7, 10.2. HRMS (ESI): calcd for $C_{23}H_{21}FO_3S$ ($[M+H]^+$) 397.1268, found 397.1268.



(4-Chlorophenyl)(phenyl)(1-tosylcyclopropyl)methanol (**3ia**)

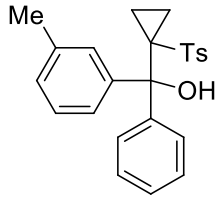
White solid; m.p. 187-188 °C; yield: 50.9 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16-7.08 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.85 (s, 1H), 2.41 (s, 3H), 1.75-1.67 (m, 2H), 1.05-0.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.6, 141.2, 137.3, 133.4, 129.3, 128.9, 128.6, 127.7, 127.6, 127.6, 127.5, 78.6, 49.0, 21.6, 11.0, 9.7. HRMS (ESI): calcd for $C_{23}H_{21}ClO_3S$ ($[M+Na]^+$) 435.0792, found 435.0799.



(4-Bromophenyl)(phenyl)(1-tosylcyclopropyl)methanol (**3ja**)

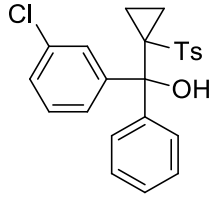
White solid; m.p. 188-189 °C; yield: 66.5 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.23-7.20 (m, 4H), 7.15-7.09 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.85 (s, 1H), 2.42 (s, 3H), 1.76-1.66 (m, 2H), 1.06-0.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.8, 141.4, 137.3, 130.5, 129.4, 129.3, 128.5, 127.7, 127.6, 127.5,

121.7, 78.6, 48.97, 21.6, 11.1, 8.5. HRMS (ESI): calcd for $C_{23}H_{21}BrO_3S$ ($[M+H]^+$) 457.0468, found 457.0461.



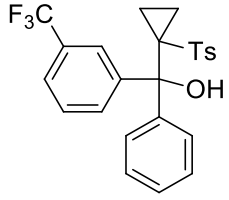
Phenyl(*m*-tolyl)(1-tosylcyclopropyl)methanol (**3ka**)

White solid; m.p. 153-154 °C; yield: 51.2 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.18-7.16 (m, 2H), 7.12-7.06 (m, 3H), 7.01-6.95 (m, 3H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.79 (s, 1H), 2.37 (s, 3H), 2.14 (s, 3H), 1.74-1.64 (m, 2H), 1.08-1.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.4, 142.2, 137.5, 137.0, 129.2, 128.6, 128.4, 128.0, 127.7, 127.5, 127.4, 127.3, 124.9, 78.9, 49.2, 21.5, 10.9, 10.2. HRMS (ESI): calcd for $C_{24}H_{24}O_3S$ ($[M+Na]^+$) 415.1338, found 415.1321.



(3-Chlorophenyl)(phenyl)(1-tosylcyclopropyl)methanol (**3la**)

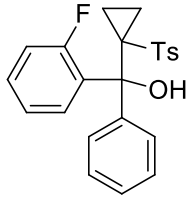
White solid; m.p. 167-168 °C; yield: 56.2 mg (68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 3H), 7.14-7.12 (m, 3H), 7.09-7.00 (m, 4H), 5.92 (s, 1H), 2.39 (s, 3H), 1.78-1.66 (m, 2H), 1.09-0.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 144.4, 141.4, 137.0, 133.6, 129.4, 129.0, 128.5, 127.9, 127.7, 127.6, 127.4, 125.7, 78.6, 48.8, 21.6, 11.1, 9.6. HRMS (ESI): calcd for $C_{23}H_{21}ClO_3S$ ($[M+Na]^+$) 435.0792, found 435.0795.



Phenyl(1-tosylcyclopropyl)(3-(trifluoromethyl)phenyl)methanol (**3ma**)

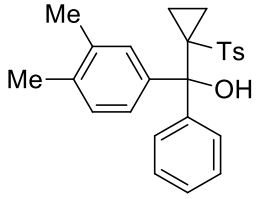
White solid; m.p. 174-175 °C; yield: 55.8 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.38-7.34 (m, 3H), 7.22-7.10 (m, 6H), 7.00 (d,

J = 8.4 Hz, 2H), 6.00 (s, 1H), 2.36 (s, 3H), 1.79-1.70 (m, 2H), 1.06-0.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 143.9, 141.3, 137.0, 130.9 (q, *J* = 2.2 Hz), 129.9 (q, *J* = 32.1 Hz), 129.4, 128.6, 128.1, 127.8, 127.7, 127.6, 124.3-124.1 (m), 123.9 (q, *J* = 270.8 Hz), 78.7, 48.8, 21.5, 10.9, 9.8. HRMS (ESI): calcd for $C_{24}H_{21}F_3O_3S$ ($[M+Na]^+$) 469.1056, found 469.1041.



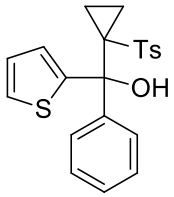
(2-Fluorophenyl)(phenyl)(1-tosylcyclopropyl)methanol (**3na**)

White solid; m.p. 164-165 °C; yield: 55.0 mg (69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 1H), 7.48-7.46 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.23-7.18 (m, 3H), 7.10-7.07 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.41-6.35 (m, 1H), 5.70 (s, 1H), 2.37 (s, 3H), 1.84-1.78 (m, 1H), 1.68-1.60 (m, 1H), 1.20-1.14 (m, 1H), 1.07-1.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J* = 243.0 Hz), 143.7, 140.8, 136.6, 131.8 (d, *J* = 13.0 Hz), 129.6 (d, *J* = 8.6 Hz), 129.4 (d, *J* = 4.1 Hz), 129.0, 128.9, 127.9, 127.8 (d, *J* = 3.7 Hz), 127.6, 124.4 (d, *J* = 2.9 Hz), 116.0 (d, *J* = 24.4 Hz), 78.3 (d, *J* = 3.2 Hz), 48.7 (d, *J* = 2.1 Hz), 21.6, 13.7 (d, *J* = 8.6 Hz), 9.7 (d, *J* = 2.9 Hz). HRMS (ESI): calcd for $C_{23}H_{21}FO_3S$ ($[M+Na]^+$) 419.1088, found 419.1099.



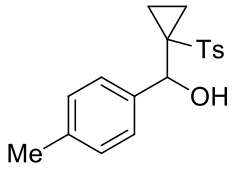
(3,4-Dimethylphenyl)(phenyl)(1-tosylcyclopropyl)methanol (**3oa**)

White solid; m.p. 142-143 °C; yield: 43.2 mg (53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.11-7.07 (m, 5H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.74 (s, 1H), 2.37 (s, 3H), 2.14 (s, 3H), 2.05 (s, 3H), 1.73-1.63 (m, 2H), 1.08-1.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.4, 139.9, 137.6, 135.7, 135.4, 129.0, 128.9, 128.6, 127.7, 127.5, 127.2, 125.1, 78.8, 49.4, 21.6, 20.0, 19.3, 10.8, 10.2. HRMS (ESI): calcd for $C_{25}H_{26}O_3S$ ($[M+Na]^+$) 429.1495, found 429.1504.



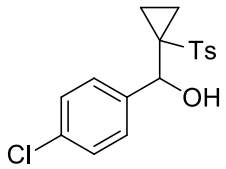
Phenyl(thiophen-2-yl)(1-tosylcyclopropyl)methanol (**3pa**)

White solid; m.p. 174-175 °C; yield: 26.3 mg (34%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13-7.09 (m, 2H), 7.06-7.00 (m, 4H), 6.68 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.61 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.12 (s, 1H), 2.37 (s, 3H), 1.82-1.65 (m, 2H), 1.29-1.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 143.7, 142.5, 137.3, 129.2, 128.4, 127.8, 127.5, 126.6, 126.4, 125.4, 78.3, 49.5, 21.5, 12.0, 9.4. HRMS (ESI): calcd for $C_{21}H_{20}O_3S_2$ ($[M+Na]^+$) 407.0746, found 407.0746.



p-Tolyl(1-tosylcyclopropyl)methanol (**3qa**)

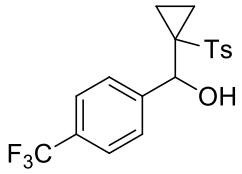
White solid; m.p. 94-95 °C; yield: 29.9 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.27 (s, 1H), 3.70 (s, 1H), 2.49 (s, 3H), 2.28 (s, 3H), 1.68-1.62 (m, 1H), 1.37-1,31 (m, 1H), 1.12-1.07 (m, 1H), 0.41-0.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 137.9, 135.4, 134.5, 130.0, 128.8, 128.7, 126.5, 70.9, 47.1, 21.7, 21.1, 12.9, 6.5. HRMS (ESI): calcd for $C_{18}H_{20}O_3S$ ($[M+Na]^+$) 339.1025, found 339.1014.



(4-Chlorophenyl)(1-tosylcyclopropyl)methanol (**3ra**)

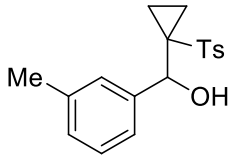
Yellow oil; yield: 35.0 mg (52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.22 (d, *J* = 1.6 Hz, 1H), 3.80 (d, *J* = 2.4 Hz, 1H), 2.49 (s, 3H), 1.72-1.66 (m, 1H), 1.44-1.38 (m, 1H), 1.09-1.04 (m,1H), 0.46-0.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ 145.0, 136.2, 135.2, 133.9, 130.0, 128.7, 128.3, 127.9, 70.7, 47.0, 21.7, 12.8, 6.9. HRMS (ESI): calcd for $C_{17}H_{17}ClO_3S$ ([M+Na]$^+$) 359.0479, found 359.0491.



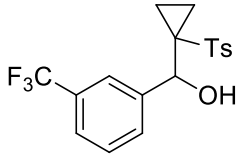
(1-Tosylcyclopropyl)(4-(trifluoromethyl)phenyl)methanol (**3sa**)

White solid; m.p. 67-68 °C; yield: 42.0 mg (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.23 (s, 1H), 3.87 (s, 1H), 2.46 (s, 3H), 1.75-1.69 (m, 1H), 1.53-1.47 (m, 1H), 1.15-1.09 (m, 1H), 0.53-0.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 142.0, 135.3, 130.2 (q, *J* = 32.3 Hz), 130.0, 128.6, 126.9, 125.0 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.5 Hz), 71.2, 46.9, 21.6, 12.8, 7.7. HRMS (ESI): calcd for $C_{18}H_{17}F_3O_3S$ ([M+Na]$^+$) 393.0743, found 393.0752.



m-Tolyl(1-tosylcyclopropyl)methanol (**3ta**)

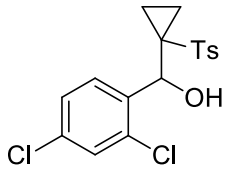
White solid; m.p. 117-118 °C; yield: 41.1 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.12-7.08 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H), 3.70 (s, 1H), 2.49 (s, 3H), 2.25 (s, 3H), 1.69-1.62 (m, 1H), 1.39-1.34 (m, 1H), 1.15-1.09 (m, 1H), 0.44-0.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 137.8, 137.5, 135.4, 129.9, 128.8, 128.7, 128.0, 127.0, 123.8, 71.1, 47.1, 21.7, 21.4, 13.0, 6.7. HRMS (ESI): calcd for $C_{18}H_{20}O_3S$ ([M+Na]$^+$) 339.1025, found 339.1025.



(1-Tosylcyclopropyl)(3-(trifluoromethyl)phenyl)methanol (**3ua**)

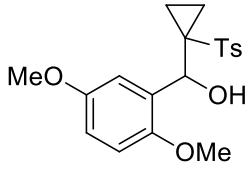
Yellow oil; yield: 39.5 mg (53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.37-7.33 (m, 3H), 7.29 (s, 1H), 7.26 (d, *J* = 8.0 Hz,

1H), 5.26 (d, *J* = 3.2 Hz, 1H), 3.88 (d, *J* = 3.2 Hz, 1H), 2.48 (s, 3H), 1.76-1.70 (m, 1H), 1.51-1.45 (m, 1H), 1.12-1.07 (m, 1H), 0.48-0.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.0, 135.2, 130.6 (q, *J* = 32.3 Hz), 130.0, 128.6, 124.9 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 270.7 Hz), 123.3 (q, *J* = 3.8 Hz), 71.1, 46.9, 21.7, 12.8, 7.3. HRMS (ESI): calcd for $C_{18}H_{17}F_3O_3S$ ($[M+Na]^+$) 393.0743, found 393.0751.



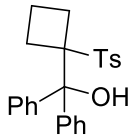
(2,4-Dichlorophenyl)(1-tosylcyclopropyl)methanol (**3va**)

White solid; m.p. 132-133 °C; yield: 43.8 mg (59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.24 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 5.58 (s, 1H), 3.99 (d, *J* = 1.6 Hz, 1H), 2.49 (s, 3H), 1.75-1.71 (m, 1H), 1.42-1.36 (m, 1H), 0.95-0.90 (m, 1H), 0.24-0.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.6, 134.5, 133.5, 133.2, 129.9, 129.2, 128.8, 128.7, 127.3, 67.3, 45.8, 21.7, 13.9, 5.9. HRMS (ESI): calcd for $C_{17}H_{16}Cl_2O_3S$ ($[M+Na]^+$) 393.0089, found 393.0089.



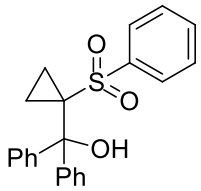
(2,5-Dimethoxyphenyl)(1-tosylcyclopropyl)methanol (**3wa**)

White solid; m.p. 168-169 °C; yield: 36.0 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 3.2 Hz, 1H), 6.71 (dd, *J* = 3.2 Hz, 8.8 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 5.59 (s, 1H), 3.74 (s, 3H), 3.68 (d, *J* = 2.0 Hz, 1H), 3.24 (s, 3H), 2.50 (s, 3H), 1.70-1.64 (m, 1H), 1.33-1.26 (m, 1H), 1.05-0.99 (m, 1H), 0.27-0.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 149.9, 144.4, 135.7, 129.5, 129.0, 126.6, 113.7, 112.4, 110.6, 65.6, 55.7, 55.1, 46.2, 21.7, 13.8, 6.3. HRMS (ESI): calcd for $C_{19}H_{22}O_5S$ ($[M+Na]^+$) 385.1080, found 385.1080.



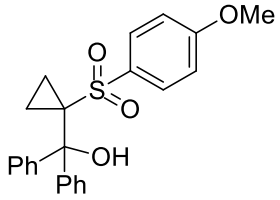
Diphenyl(1-tosylcyclobutyl)methanol (**3xa**)

White solid; m.p. 170-171 °C; yield: 26.3 mg (34%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.45 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.16-7.09 (m, 6H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.40 (s, 1H), 3.03-2.95 (m, 2H), 2.85-2.77 (m, 2H), 2.38 (s, 3H), 1.82-1.71 (m, 1H), 0.96-0.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 142.9, 135.8, 129.5, 129.3, 127.7, 127.5, 127.1, 79.3, 74.7, 27.1, 21.6, 15.1. HRMS (ESI): calcd for $C_{24}H_{24}O_3S$ ($[M+H]^+$) 393.1519, found 393.1522.



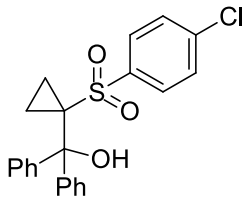
Diphenyl(1-(phenylsulfonyl)cyclopropyl)methanol (**3ab**)

White solid; m.p. 201-202 °C; yield: 56.6 mg (78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 1H), 7.40-7.37 (m, 4H), 7.36-7.32 (m, 2H), 7.24-7.20 (m, 2H), 7.13-7.05 (m, 6H), 5.76 (s, 1H), 1.74-1.71 (m, 2H), 1.08-1.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 140.6, 132.8, 128.6, 128.5, 127.6, 127.5, 127.4, 79.0, 49.2, 10.6. HRMS (ESI): calcd for $C_{22}H_{20}O_3S$ ($[M+H]^+$) 365.1206, found 365.1209.



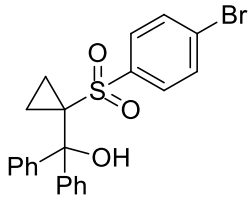
(1-((4-Methoxyphenyl)sulfonyl)cyclopropyl)diphenylmethanol (**3ac**)

White solid; m.p. 145-146 °C; yield: 57.4 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 4H), 7.27-7.23 (m, 2H), 7.12-7.06 (m, 6H), 6.68-6.64 (m, 2H), 5.83 (s, 1H), 3.83 (s, 3H), 1.69-1.66 (m, 2H), 1.04-1.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 142.4, 131.9, 130.7, 127.7, 127.5, 127.3, 113.9, 79.0, 55.7, 49.0, 10.5. HRMS (ESI): calcd for $C_{23}H_{22}O_4S$ ($[M+Na]^+$) 417.1131, found 417.1132.



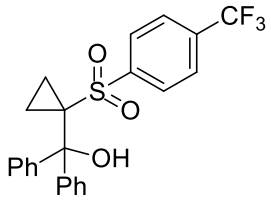
(1-((4-Chlorophenyl)sulfonyl)cyclopropyl)diphenylmethanol (**3ad**)

White solid; m.p. 204-205 °C; yield: 56.4 mg (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 4H), 7.26-7.24 (m, 2H), 7.19-7.08 (m, 8H), 5.66 (s, 1H), 1.73-1.69 (m, 2H), 1.09-1.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.7, 139.0, 130.0, 128.9, 127.7, 127.6, 127.5, 78.8, 49.3, 10.6. HRMS (ESI): calcd for $C_{22}H_{19}ClO_3S$ ($[M+Na]^+$) 421.0636, found 421.0636.



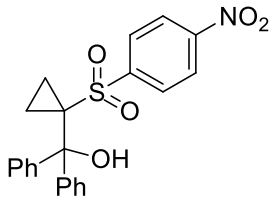
(1-((4-Bromophenyl)sulfonyl)cyclopropyl)diphenylmethanol (**3ae**)

White solid; m.p. 180-181 °C; yield: 71.4 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 6H), 7.19-7.08 (m, 8H), 5.65 (s, 1H), 1.73-1.69 (m, 2H), 1.09-1.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.5, 131.8, 130.0, 128.3, 127.7, 127.6, 127.5, 78.8, 49.3, 10.6. HRMS (ESI): calcd for $C_{22}H_{19}BrO_3S$ ($[M+Na]^+$) 465.0130, found 465.0119.



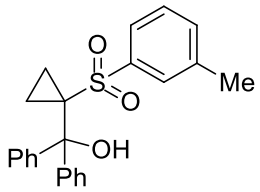
Diphenyl(1-((4-(trifluoromethyl)phenyl)sulfonyl)cyclopropyl)methanol (**3af**)

White solid; m.p. 161-162 °C; yield: 68.1 mg (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 4H), 7.38-7.36 (m, 4H), 7.15-7.05 (m, 6H), 5.62 (s, 1H), 1.78-1.75 (m, 2H), 1.13-1.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.9, 134.3 (q, J = 32.8 Hz), 129.0, 127.7, 127.6, 125.6 (q, J = 3.7 Hz), 123.2 (q, J = 271.4 Hz), 78.7, 49.4, 10.6. HRMS (ESI): calcd for $C_{23}H_{19}F_3O_3S$ ($[M+Na]^+$) 455.0899, found 455.0902.



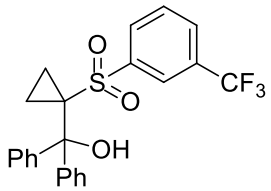
(1-((4-Nitrophenyl)sulfonyl)cyclopropyl)diphenylmethanol (**3ag**)

White solid; m.p. 191-192 °C; yield: 74.6 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 9.2 Hz, 2H), 7.40-7.37 (m, 4H), 7.17-7.07 (m, 6H), 5.48 (s, 1H), 1.80-1.76 (m, 2H), 1.17-1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 146.2, 141.9, 129.9, 127.8, 127.7, 123.5, 78.7, 49.8, 10.9. HRMS (ESI): calcd for $C_{22}H_{19}NO_5S$ ($[M+Na]^+$) 432.0876, found 432.0878.



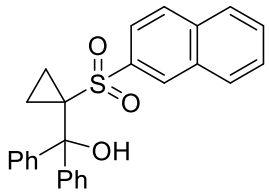
Diphenyl(1-(m-tolylsulfonyl)cyclopropyl)methanol (**3ah**)

White solid; m.p. 169-170 °C; yield: 55.7 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 4H), 7.27-7.24 (m, 2H), 7.19-7.15 (m, 1H), 7.13-7.05 (m, 6H), 6.98 (s, 1H), 5.80 (s, 1H), 2.19 (s,3H), 1.74-1.71 (m, 2H), 1.07-1.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 140.3, 138.8, 133.9, 129.4, 128.5, 127.6, 127.4, 125.7, 78.9, 49.3, 21.2, 10.5. HRMS (ESI): calcd for $C_{23}H_{22}O_3S$ ($[M+Na]^+$) 401.1182, found 401.1188.



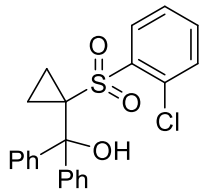
Diphenyl(1-((3-(trifluoromethyl)phenyl)sulfonyl)cyclopropyl)methanol (**3al**)

White solid; m.p. 162-163 °C; yield: 65.1 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.59-7.55 (m, 2H), 7.42-7.37 (m, 5H), 7.14-7.05 (m, 6H), 5.59 (s, 1H), 1.80-1.77 (m, 2H), 1.15-1.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 141.8, 131.7, 131.3 (q, *J* = 33.3 Hz), 129.7 (q, *J* = 3.4 Hz), 129.4, 127.8, 127.7, 127.6, 125.6 (q, *J* = 4.0 Hz), 123.0 (q, *J* = 271.4 Hz), 78.7, 49.5, 10.7. HRMS (ESI): calcd for $C_{23}H_{19}F_3O_3S$ ($[M+Na]^+$) 455.0899, found 455.0892.



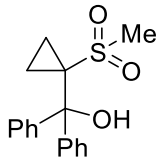
(1-(Naphthalen-2-ylsulfonyl)cyclopropyl)diphenylmethanol (**3aj**)

White solid; m.p. 199-200 °C; yield: 56.0 mg (68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J*= 8.4 Hz, 1H), 7.78 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67-7.60 (m, 2H), 7.55-7.51 (m, 1H), 7.46 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.39-7.36 (m, 4H), 6.97-6.90 (m, 6H), 5.83 (s, 1H), 1.81-1.78 (m, 2H), 1.10-1,07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 137.3, 134.8, 131.9, 131.0, 129.7, 129.2, 128.7, 127.6 (2C), 127.4 (2C), 127.2, 123.2, 79.0, 49.2, 10.6. HRMS (ESI): calcd for $C_{26}H_{22}O_3S$ ($[M+Na]^+$) 437.1182, found 437.1161.



(1-((2-Chlorophenyl)sulfonyl)cyclopropyl)diphenylmethanol (**3ak**)

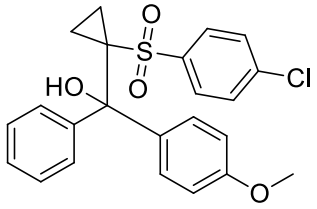
White solid; m.p. 156-157 °C; yield: 37.8 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 4H), 7.39-7.36 (m, 2H), 7.30-7.25 (m, 1H), 7.10-7.05 (m, 6H), 6.95-6.91 (m, 1H), 5.76 (s, 1H), 2.01-1.98 (m, 2H), 1.15-1.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 138.6, 133.8, 133.3, 132.1, 131.4, 127.6, 127.5, 127.4, 127.1, 78.9, 49.6, 10.1. HRMS (ESI): calcd for $C_{22}H_{19}ClO_3S$ ($[M+Na]^+$) 421.0636, found 421.0640.



(1-(Methylsulfonyl)cyclopropyl)diphenylmethanol (**3al**)

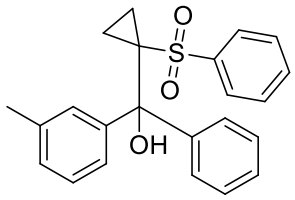
White solid; m.p. 96-97 °C; yield: 55.0 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 4H), 7.36-7.25 (m, 6H), 4.71 (s, 1H), 2.64 (s, 3H), 1.59-1.55 (m, 2H), 1.03-0.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 128.1, 128.0, 127.9, 78.9, 47.8, 43.1, 10.5. HRMS (ESI): calcd for $C_{17}H_{18}O_3S$ ($[M+Na]^+$) 325.0869, found

325.0862.



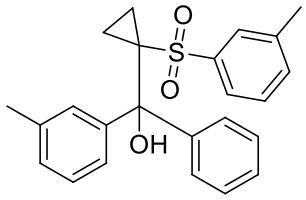
(1-((4-Chlorophenyl)sulfonyl)cyclopropyl)(4-methoxyphenyl)(phenyl)methanol (**3gd**)

White solid; m.p. 61-62 °C; yield: 53.1 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.29-7.23 (m, 4H), 7.20-7.07 (m, 5H), 6.61 (d, *J* = 9.2 Hz, 2H), 5.61 (s, 1H), 3.74 (s, 3H), 1.72-1.69 (m, 2H), 1.08-1.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 142.3, 139.5, 139.1, 134.1, 129.9, 128.9, 128.8, 127.6, 127.5, 127.4, 112.8, 78.6, 55.2, 49.6, 10.6, 10.5. HRMS (ESI): calcd for $C_{23}H_{21}ClO_4S$ ($[M+Na]^+$) 451.0741, found 451.0756.



Phenyl(1-(phenylsulfonyl)cyclopropyl)(*m*-tolyl)methanol (**3kb**)

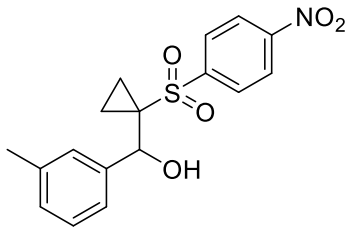
White solid; m.p. 112-113 °C; yield: 62.3 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 1H), 7.41-7.38 (m, 2H), 7.35-7.32 (m, 2H), 7.25-7.19 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.12-7.06 (m, 3H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.93-6.90 (m, 1H), 5.76 (s, 1H), 2.16 (s, 3H), 1.76-1.68 (m, 2H), 1.02-1.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 142.1, 140.6, 137.1, 132.8, 128.6, 128.5, 128.3, 128.2, 127.7, 127.6, 127.5, 127.4, 124.8, 78.9, 49.3, 21.6, 10.8, 10.4. HRMS (ESI): calcd for $C_{23}H_{22}O_3S$ ($[M+Na]^+$) 401.1182, found 401.1187.



Phenyl(*m*-tolyl)(1-(*m*-tolylsulfonyl)cyclopropyl)methanol (**3kh**)

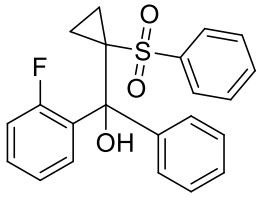
White solid; m.p. 134-135 °C; yield: 66.5 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.26-7.21 (m, 3H), 7.18-7.15 (m, 2H), 7.11-7.05 (m, 3H),

6.98-6.89 (m, 3H), 5.81 (s, 1H), 2.18 (s, 3H), 2.15 (s, 3H), 1.77-1.67 (m, 2H), 1.10-1.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 142.1, 140.4, 138.7, 137.0, 133.9, 129.4, 128.4, 128.3, 128.2, 127.7, 127.4, 127.3, 125.7, 124.8, 78.9, 49.4, 21.6, 21.2, 10.8, 10.2. HRMS (ESI): calcd for $C_{24}H_{24}O_3S$ ($[M+Na]^+$) 415.1338, found 415.1141.



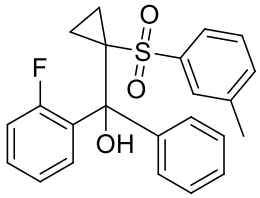
(1-((4-Ntrophenyl)sulfonyl)cyclopropyl)(*m*-tolyl)methanol (**3kg**)

White solid; m.p. 119-120 °C; yield: 43.1 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.87-6.85 (m, 2H), 5.24 (s, 1H), 3.31 (br, 1H), 2.23 (s, 3H), 1.69-1.56 (m, 2H), 1.31-1.24 (m, 1H), 0.73-0.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.1, 138.2, 137.9, 130.0, 129.2, 128.3, 127.1, 124.0, 123.7, 71.7, 47.0, 21.3, 12.5, 8.4. HRMS (ESI): calcd for $C_{17}H_{17}NO_5S$ ($[M+Na]^+$) 370.0720, found 370.0733.



(2-Fluorophenyl)(phenyl)(1-(phenylsulfonyl)cyclopropyl)methanol (**3nb**)

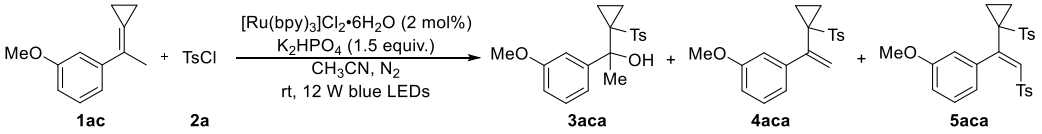
White solid; m.p. 159-160 °C; yield: 53.6 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.80 (m, 1H), 7.48-7.43 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25-7.18 (m, 5H), 7.12-7.04 (m, 2H), 6.38-6.33 (m, 1H), 5.67 (s, 1H), 1.89-1.83 (m, 1H), 1.74-1.68 (m, 1H), 1.23-1.16 (m, 1H), 1.10-1.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J* = 242.9 Hz), 140.7, 139.7, 132.8, 131.6 (d, *J* = 13.0 Hz), 129.9 (d, *J* = 8.6 Hz), 129.3 (d, *J* = 4.1 Hz), 128.9, 128.2, 128.0, 127.8 (d, *J* = 3.8 Hz), 127.7, 124.4 (d, *J* = 2.8 Hz), 116.1 (d, *J* = 24.5 Hz), 78.2 (d, *J* = 3.1 Hz), 48.8, 13.8 (d, *J* = 8.5 Hz), 9.6 (d, *J* = 2.9 Hz). HRMS (ESI): calcd for $C_{22}H_{19}FO_3S$ ($[M+Na]^+$) 405.0931, found 405.0937.



(2-Fluorophenyl)(phenyl)(1-(m-tolylsulfonyl)cyclopropyl)methanol (**3nh**)

White solid; m.p. 132-133 °C; yield: 64.2 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.81 (m, 1H), 7.49-7.46 (m, 2H), 7.29-7.26 (m, 2H), 7.24-7.15 (m, 4H), 7.12-7.05 (m, 3H), 6.40-6.34 (m, 1H), 5.73 (s, 1H), 2.21 (s, 3H), 1.90-1.84 (m, 1H), 1.72-1.66 (m, 1H), 1.23-1.16 (m, 1H), 1.10-1.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (d, *J* = 243.2 Hz), 140.6, 139.4, 138.3, 133.8, 131.6 (d, *J* = 13.2 Hz), 129.8 (d, *J* = 8.6 Hz), 129.4, 129.3 (d, *J* = 4.1 Hz), 128.1, 127.9, 127.8 (d, *J* = 3.9 Hz), 127.7, 126.2, 124.2 (d, *J* = 2.9 Hz), 115.9 (d, *J* = 24.5 Hz), 78.1 (d, *J* = 3.4 Hz), 48.9 (d, *J* = 2.3 Hz), 21.2, 13.8 (d, *J* = 8.7 Hz), 9.5 (d, *J* = 3.2 Hz). HRMS (ESI): calcd for $C_{23}H_{21}FO_3S$ ($[M+Na]^+$) 419.1088, found 419.1096.

Table S1. Optimization of Reaction Conditions[a,b]



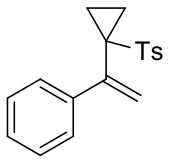
entry	**1ac**/**2a**	*t*/h	solvent	Yield (%) **3aca**/**4aca**/**5aca**
1	1/1.5	3	CH_3CN:H_2O=30:1	0/15%/8%
2[c]	1/1.5	3	CH_3CN:H_2O=30:1	0/21%/4%
3[d]	1/1.5	3	CH_3CN:H_2O=30:1	0/36%/0
4	1/1.5	3	CH_3CN	0/29%/0
5	1/1.5	12	CH_3CN	0/38%/5%
6[e]	1/3	30	CH_3CN	0/0/39%
7[f]	1/3	30	CH_3CN	0/0/24%

8	1/1.05	12	CH_3CN	0/59%/5%
9	1.5/1	12	CH_3CN	0/46%/0
10	1.5/1	16	CH_3CN	0/63%/0
11	1.5/1	20	CH_3CN	0/60%/0
12 [g)]	1.5/1	16	CH_3CN	0/60%/0

[a)] Reactions were carried out using **1** (0.3 mmol), **2a** (0.2 mmol), $[Ru(bpy)_3]Cl_2•6H_2O$ (2 mol%), base (0.3 mmol) and in a solvent (1 mL) at room temperature and 12 W blue LEDs light irradiation for 16 h under N_2 atmosphere. [b)] Isolated yield. [c)] $NaHCO_3$ (1.5 equiv.) was applied as the base. [d)] 50 °C. [e)] $[Ru(bpy)_3]Cl_2•6H_2O$ (5 mol%). [f)] $[Ru(bpy)_3]Cl_2•6H_2O$ (5 mol%) and K_2HPO_4 (3.0 equiv.). [g)] $[Ru(bpy)_3]Cl_2$ (2 mol%).

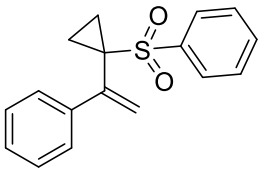
Synthesis of cyclopropyl styrenes 4

ACPs (**1**, 0.3 mmol), TsCl (**2a**, 0.2 mmol), $[Ru(bpy)_3]Cl_2•6H_2O$ (2 mol %), and K_2HPO_4 (1.5 equiv.) was added in CH_3CN (1 mL) at room temperature and 12 W blue LEDs light irradiation for 16 h under N_2 atmosphere. After the reaction, CH_3CN was removed under reduced pressure, purification was finally performed by flash column chromatography on silica gel using EtOAc and petroleum ether to give the desired product **4**.



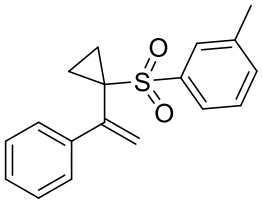
1-Methyl-4-((1-(1-phenylvinyl)cyclopropyl)sulfonyl)benzene (**4ya**)

White solid; m.p. 112-113 °C; yield: 50.0 mg (84%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.45-7.40 (m, 2H), 7.25-7.22 (m, 5H), 5.71 (s, 1H), 5.06 (s, 1H), 2.41 (s, 3H), 1.97-1.94 (m, 2H), 1.15-1.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.2, 138.2, 135.2, 129.5, 129.3, 128.1, 127.9, 126.9, 123.2, 46.6, 21.6, 14.6. HRMS (ESI): calcd for $C_{18}H_{18}O_2S$ ($[M+H]^+$) 299.1100, found 299.1082.



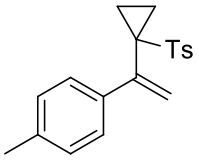
(1-(1-(Phenylsulfonyl)cyclopropyl)vinyl)benzene (**4yb**)

White solid; m.p. 68-69 °C; yield: 39.7 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.60-7.55 (m, 1H), 7.47-7.39 (m, 4H), 7.25-7.21 (m, 3H), 5.72 (s, 1H), 5.06 (s, 1H), 2.00-1.97 (m, 2H), 1.18-1.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 138.1, 133.4, 129.4, 128.7, 128.1, 128.0, 126.9, 123.3, 46.6, 14.7. HRMS (ESI): calcd for $C_{17}H_{16}O_2S$ ($[M+Na]^+$) 307.0763, found 307.0775.



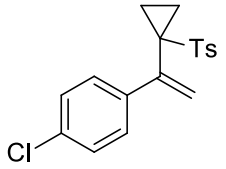
1-Methyl-3-((1-(1-phenylvinyl)cyclopropyl)sulfonyl)benzene (**4yh**)

Yellow liquid; yield: 38.6 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 1H), 7.54 (s, 1H), 7.43-7.39 (m, 2H), 7.37-7.30 (m, 2H), 7.24-7.21 (m, 3H), 5.72 (s, 1H), 5.09 (s, 1H), 2.35 (s, 3H), 1.99-1.95 (m, 2H), 1.18-1.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 138.8, 138.2, 138.0, 134.2, 129.8, 128.5, 128.0, 127.9, 126.9, 126.5, 123.2, 46.6, 21.3, 14.6. HRMS (ESI): calcd for $C_{18}H_{18}O_2S$ ($[M+Na]^+$) 321.0920, found 321.0932.



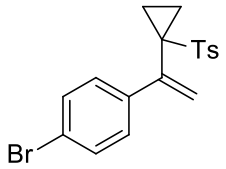
1-Methyl-4-((1-(1-(*p*-tolyl)vinyl)cyclopropyl)sulfonyl)benzene (**4za**)

White solid; m.p. 115-116 °C; yield: 38.8 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.66 (s, 1H), 4.99 (s, 1H), 2.41 (s, 3H), 2.31 (s, 3H), 1.96-1.92 (m, 2H), 1.15-1.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 142.0, 137.8, 135.4, 135.2, 129.4, 129.2, 128.8, 126.8, 122.2, 46.6, 21.6, 21.1, 14.6. HRMS (ESI): calcd for $C_{19}H_{20}O_2S$ ($[M+Na]^+$) 335.1076, found 335.1068.



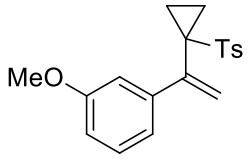
1-Chloro-4-(1-(1-tosylcyclopropyl)vinyl)benzene (**4aaa**)

White solid; m.p. 141-142 °C; yield: 42.7 mg (64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.39-7.35 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.22-7.18 (m, 2H), 5.69 (s, 1H), 5.05 (s, 1H), 2.43 (s, 3H), 1.97-1.94 (m, 2H), 1.15-1.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.2, 136.7, 135.0, 133.9, 129.4, 129.3, 128.2, 123.5, 46.6, 21.6, 14.5. HRMS (ESI): calcd for $C_{18}H_{17}ClO_2S$ ($[M+H]^+$) 333.0711, found 333.0704.



1-Bromo-4-(1-(1-tosylcyclopropyl)vinyl)benzene (**4aba**)

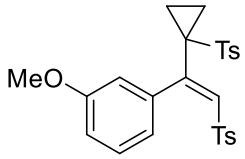
White solid; m.p. 135-136 °C; yield: 46.3 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.38-7.34 (m, 2H), 7.32-7.28 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.70 (s, 1H), 5.06 (s, 1H), 2.43 (s, 3H), 1.97 (s, 3H), 1.97-1.94 (m, 2H), 1.15-1.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.3, 137.2, 135.0, 131.2, 129.4, 129.3, 128.5, 123.5, 122.2, 46.5, 21.6, 14.5. HRMS (ESI): calcd for $C_{18}H_{17}BrO_2S$ ($[M+H]^+$) 377.0205, found 377.0220.



1-Methoxy-3-(1-(1-tosylcyclopropyl)vinyl)benzene (**4aca**)

Yellow oil; yield: 41.0 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.01-6.98 (m, 1H), 6.95-6.94 (m, 1H), 6.80-6.77 (m, 1H), 5.71 (s, 1H), 5.09 (s, 1H), 3.76 (s, 3H), 2.41 (s, 3H), 1.97-1.93 (m, 2H), 1.15-1.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 144.3, 142.1, 139.8, 135.2, 129.4, 129.3, 129.0, 123.6, 119.5, 113.4, 112.7, 55.2, 46.7, 21.6,

14.7. HRMS (ESI): calcd for $C_{19}H_{20}O_3S$ ([M+H]$^+$) 329.1206, found 329.1218.

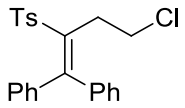


(*E*)-1-methoxy-3-(2-tosyl-1-(1-tosylcyclopropyl)vinyl)benzene (**5aca**)

White solid; m.p. 115-116 °C; yield: 8.0 mg (8%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.89 (s, 1H), 6.82-6.79 (m, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 6.12 (s, 1H), 3.63 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H), 1.87-1.83 (m, 2H), 1.03-1.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 148.0, 145.1, 144.3, 138.4, 137.6, 135.3, 135.2, 129.9, 129.4, 129.2, 128.9, 128.0, 121.2, 115.1, 113.1, 55.1, 48.1, 21.7, 21.6, 15.0. HRMS (ESI): calcd for $C_{26}H_{26}O_5S_2$ ([M+Na]$^+$) 505.1114, found 505.1116.

III. Derivatization of product 3aa.

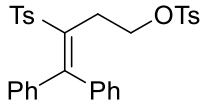
A stired solution of *β*-Hydroxysulfones (0.2 mmol, 75.6 mg) and $SnCl_4$ (0.2 mmol, 52.1 mg) in CH_2Cl_2 (1 mL) was refluxed for 1 h. After cooling to room temperature, the solution was washed with 10 % $NaHCO_3$ and with brine, dried (Na_2SO_4) and evaporated to remove the solvent. The residue was chromatographed on silica gel with acetic ether-light petroleum 1:5 as eluent.



(4-Chloro-2-tosylbut-1-ene-1,1-diyl)dibenzene (**6aa**)

White solid; m.p. 149-150 °C; yield: 69.3 mg (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 5H), 7.19-7.15 (m, 1H), 7.11-7.03 (m, 6H), 6.95-6.93 (m, 2H), 3.82 (t, *J* = 7.2 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 143.4, 140.7, 139.2, 138.9, 138.1, 129.1, 129.0, 128.7, 128.4, 128.0, 127.8, 127.7, 127.5, 43.1, 33.9, 21.5. HRMS (ESI): calcd for $C_{23}H_{21}ClO_2S$ ([M+Na]$^+$) 419.0843, found 419.0861.

β-Hydroxysulfones (0.2 mmol, 75.6 mg) and *p*-toluenesulfonic acid (0.2 mmol, 34.4 mg) in dry methylbenzene (2 mL) was refluxed for 1 h. After cooling to room temperature, the methylbenzene solution was washed with 10 % $NaHCO_3$ and with brine, dried (Na_2SO_4) and evaporated to remove the solvent. The mixture was chromatographed on silica gel with acetic ether-light petroleum 1:5 as eluent.

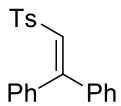


4,4-Diphenyl-3-tosylbut-3-en-1-yl 4-methylbenzenesulfonate (**7aa**)

White solid; m.p. 149-150 °C; yield: 90.2 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.29-7.23 (m, 5H), 7.15-7.13 (m, 1H), 7.09-7.03 (m, 6H), 6.91-6.88 (m, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 144.8, 143.6, 140.5, 138.8, 137.9, 137.5, 132.9, 129.9, 129.2, 128.8, 128.7, 128.3, 128.0, 127.9, 127.7, 127.6, 127.5, 68.6, 30.4, 21.7, 21.6. HRMS (ESI): calcd for $C_{30}H_{28}O_5S_2$ ($[M+Na]^+$) 555.1270, found 555.1262.

IV. Control experiments.

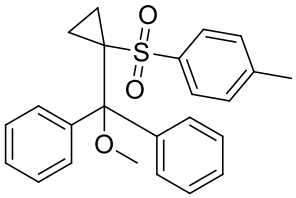
MCPs (**1a**, 0.2 mmol, 41.2 mg), TsCl (**2a**, 0.3 mmol, 57.3 mg), diphenylethene (3.0 equiv., 108.0 mg), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (2 mol%, 3.0 mg), and K_2HPO_4 (1.5 equiv., 52.2 mg) was added in CH_3CN:H_2O=30:1 (1 mL) at room temperature and 12 W blue LEDs light irradiation for 3 h under N_2 atmosphere. After the reaction, CH_3CN was removed under reduced pressure, purification was finally performed by flash column chromatography on silica gel using EtOAc and petroleum ether to give the product **8aa**.



4,4'-(4,4-Diphenylbut-3-ene-1,3-diyldisulfonyl)bis(methylbenzene)[12] (**8aa**)

White solid; m.p. 97-98 °C; yield: 29.2 mg (29%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.39-7.34 (m, 2H), 7.32-7.28 (m, 4H), 7.21-7.19 (m, 2H),

7.15 (d, J = 8.0 Hz, 2H), 7.11-7.09 (m, 2H), 6.99 (s, 1H), 2.38 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 143.8, 139.2, 138.6, 135.6, 130.2, 129.8, 129.3, 129.0, 128.8, 128.6, 128.2, 127.8, 127.7, 21.6.



(Methoxy(1-tosylcyclopropyl)methylene)dibenzene (**9aaa**)

White solid; m.p. 115-116 °C; yield: 61.2 mg (78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 4H), 7.33 (d, J = 8.0 Hz, 2H), 7.31-7.28 (m, 6H), 7.09 (d, J = 8.4 Hz, 2H), 2.84 (s, 3H), 2.37 (s, 3H), 1.74-1.71 (m, 2H), 1.26-1.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 140.0, 138.6, 130.6, 128.7, 128.2, 128.0, 127.4, 84.6, 51.3, 50.8, 21.5, 13.4. HRMS (ESI): calcd for $C_{24}H_{24}O_3S$ ([M+Na]$^+$) 415.1338, found 415.1347.

V. Crystal structure of 3aa.

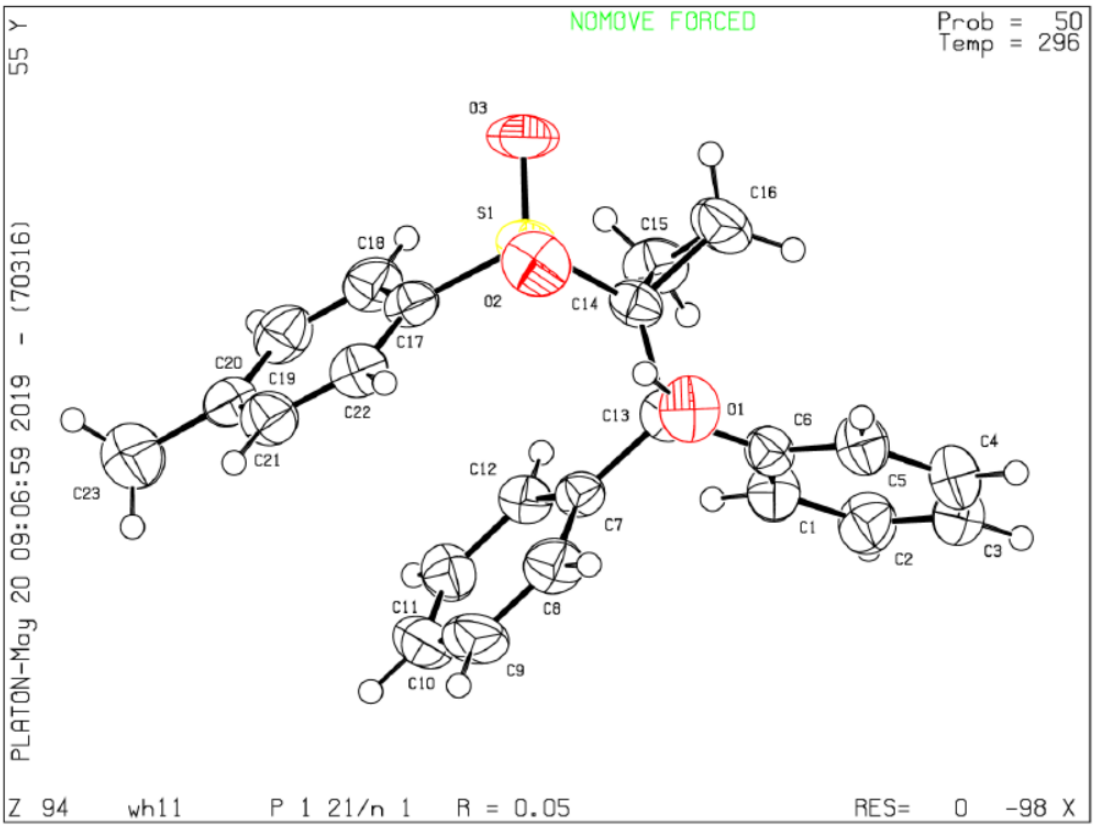


Table 1. Single crystal data for wh11.

Identification code	wh11	
Chemical formula	$C_{23}H_{22}O_3S$	
Formula weight	378.46 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.230 x 0.250 x 0.500 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.3828(19) Å	α = 90°
	b = 11.548(2) Å	β = 91.392(10)°
	c = 14.490(3) Å	γ = 90°
Volume	1904.1(6) $Å^3$	
Z	4	
Density (calculated)	1.320 g/cm^3	
Absorption coefficient	0.191 mm^{-1}	
F(000)	800	

Table 2. Data collection and structure refinement for wh11.

Theta range for data collection	2.25 to 25.12°
Index ranges	-13<=h<=13, -13<=k<=13, -17<=l<=17
Reflections collected	14632
Independent reflections	3376 [R(int) = 0.0572]
Coverage of independent reflections	99.1%
Absorption correction	Multi-Scan

Max. and min. transmission	0.9570 and 0.9110
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3376 / 0 / 246
Goodness-of-fit on F^2	1.032
Δ/σ_{max}	0.001
Final R indices	2216 data; I>2σ(I) R1 = 0.0495, wR2 = 0.1031
	all data R1 = 0.0940, wR2 = 0.1198
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0517P)^2+0.4169P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.156 and -0.306 eÅ^{-3}
R.M.S. deviation from mean	0.044 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for wh11.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S1	0.41686(5)	0.48660(5)	0.74423(5)	0.0505(2)
O1	0.58872(14)	0.37657(15)	0.59971(12)	0.0564(5)
O2	0.53092(15)	0.53685(14)	0.72874(13)	0.0628(5)
O3	0.31751(16)	0.56300(15)	0.74648(14)	0.0713(6)
C1	0.3968(2)	0.1307(2)	0.54575(17)	0.0527(7)
C2	0.3698(2)	0.0680(2)	0.4671(2)	0.0627(8)
C3	0.4097(3)	0.1019(3)	0.3828(2)	0.0672(8)
C4	0.4761(3)	0.2002(3)	0.37782(19)	0.0681(8)

C5	0.5018(2)	0.2644(2)	0.45578(18)	0.0573(7)
C6	0.4625(2)	0.2312(2)	0.54149(16)	0.0429(6)
C7	0.53381(18)	0.22680(19)	0.70753(15)	0.0382(6)
C8	0.6525(2)	0.2125(2)	0.72775(18)	0.0544(7)
C9	0.6908(2)	0.1425(3)	0.7998(2)	0.0643(8)
C10	0.6120(3)	0.0851(2)	0.8524(2)	0.0628(8)
C11	0.4941(2)	0.0975(2)	0.83318(18)	0.0532(7)
C12	0.4553(2)	0.16772(19)	0.76206(16)	0.0414(6)
C13	0.49430(18)	0.3043(2)	0.62727(16)	0.0416(6)
C14	0.39026(19)	0.38426(19)	0.65369(16)	0.0414(6)
C15	0.2641(2)	0.3480(2)	0.64254(19)	0.0569(7)
C16	0.3123(2)	0.4339(3)	0.5776(2)	0.0643(8)
C17	0.4248(2)	0.41366(19)	0.85034(17)	0.0439(6)
C18	0.3244(2)	0.3723(2)	0.89066(19)	0.0541(7)
C19	0.3334(2)	0.3138(2)	0.97301(19)	0.0580(7)
C20	0.4413(2)	0.2977(2)	0.01762(17)	0.0520(7)
C21	0.5398(2)	0.3421(2)	0.97685(18)	0.0532(7)
C22	0.5328(2)	0.3993(2)	0.89399(18)	0.0489(7)
C23	0.4498(3)	0.2330(3)	0.1075(2)	0.0790(9)

Table 4. Bond lengths (Å) for wh11.

S1-O3	1.4354(17)	S1-O2	1.4446(17)
S1-C17	1.754(3)	S1-C14	1.786(2)
O1-C13	1.425(2)	O1-H1	0.82
C1-C2	1.379(3)	C1-C6	1.383(3)
C1-H1A	0.93	C2-C3	1.370(4)
C2-H2	0.93	C3-C4	1.367(4)
C3-H3	0.93	C4-C5	1.377(4)
C4-H4	0.93	C5-C6	1.384(3)
C5-H5	0.93	C6-C13	1.538(3)
C7-C8	1.385(3)	C7-C12	1.387(3)
C7-C13	1.527(3)	C8-C9	1.383(4)

C8-H8	0.93	C9-C10	1.363(4)
C9-H9	0.93	C10-C11	1.371(3)
C10-H10	0.93	C11-C12	1.376(3)
C11-H11	0.93	C12-H12	0.93
C13-C14	1.557(3)	C14-C15	1.501(3)
C14-C16	1.511(3)	C15-C16	1.482(4)
C15-H15A	0.97	C15-H15B	0.97
C16-H16A	0.97	C16-H16B	0.97
C17-C22	1.379(3)	C17-C18	1.381(3)
C18-C19	1.373(4)	C18-H18	0.93
C19-C20	1.386(3)	C19-H19	0.93
C20-C21	1.379(3)	C20-C23	1.502(4)
C21-C22	1.371(3)	C21-H21	0.93
C22-H22	0.93	C23-H23A	0.96
C23-H23B	0.96	C23-H23C	0.96

Table 5. Bond angles (°) for wh11.

O3-S1-O2	117.92(12)	O3-S1-C17	107.39(12)
O2-S1-C17	107.58(11)	O3-S1-C14	107.69(11)
O2-S1-C14	106.78(11)	C17-S1-C14	109.29(11)
C13-O1-H1	109.5	C2-C1-C6	120.9(3)
C2-C1-H1A	119.5	C6-C1-H1A	119.5
C3-C2-C1	121.0(3)	C3-C2-H2	119.5
C1-C2-H2	119.5	C4-C3-C2	118.7(3)
C4-C3-H3	120.7	C2-C3-H3	120.7
C3-C4-C5	120.7(3)	C3-C4-H4	119.6

C5-C4-H4	119.6	C4-C5-C6	121.4(3)
C4-C5-H5	119.3	C6-C5-H5	119.3
C1-C6-C5	117.3(2)	C1-C6-C13	122.8(2)
C5-C6-C13	119.9(2)	C8-C7-C12	117.4(2)
C8-C7-C13	119.9(2)	C12-C7-C13	122.71(19)
C9-C8-C7	121.1(3)	C9-C8-H8	119.4
C7-C8-H8	119.4	C10-C9-C8	120.5(2)
C10-C9-H9	119.8	C8-C9-H9	119.8
C9-C10-C11	119.3(3)	C9-C10-H10	120.4
C11-C10-H10	120.4	C10-C11-C12	120.6(3)
C10-C11-H11	119.7	C12-C11-H11	119.7
C11-C12-C7	121.1(2)	C11-C12-H12	119.4
C7-C12-H12	119.4	O1-C13-C7	110.27(18)
O1-C13-C6	105.00(18)	C7-C13-C6	110.67(19)
O1-C13-C14	107.76(18)	C7-C13-C14	111.85(18)
C6-C13-C14	111.03(18)	C15-C14-C16	58.96(16)
C15-C14-C13	122.7(2)	C16-C14-C13	118.8(2)
C15-C14-S1	114.10(18)	C16-C14-S1	111.75(18)
C13-C14-S1	117.17(15)	C16-C15-C14	60.86(16)
C16-C15-H15A	117.7	C14-C15-H15A	117.7
C16-C15-H15B	117.7	C14-C15-H15B	117.7
H15A-C15-H15B	114.8	C15-C16-C14	60.18(16)
C15-C16-H16A	117.8	C14-C16-H16A	117.8
C15-C16-H16B	117.8	C14-C16-H16B	117.8
H16A-C16-H16B	114.9	C22-C17-C18	120.1(2)
C22-C17-S1	119.1(2)	C18-C17-S1	120.78(19)

C19-C18-C17	119.5(2)	C19-C18-H18	120.3
C17-C18-H18	120.3	C18-C19-C20	121.2(3)
C18-C19-H19	119.4	C20-C19-H19	119.4
C21-C20-C19	118.1(3)	C21-C20-C23	121.4(2)
C19-C20-C23	120.6(3)	C22-C21-C20	121.6(2)
C22-C21-H21	119.2	C20-C21-H21	119.2
C21-C22-C17	119.5(2)	C21-C22-H22	120.3
C17-C22-H22	120.3	C20-C23-H23A	109.5
C20-C23-H23B	109.5	H23A-C23-H23B	109.5
C20-C23-H23C	109.5	H23A-C23-H23C	109.5
H23B-C23-H23C	109.5		

Table 6. Anisotropic atomic displacement parameters (Å^2) for wh11.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S1	0.0475(4)	0.0385(4)	0.0651(5)	-0.0010(3)	-0.0070(3)	0.0020(3)
O1	0.0472(10)	0.0616(12)	0.0608(12)	0.0057(9)	0.0095(9)	-0.0197(9)
O2	0.0580(11)	0.0496(11)	0.0805(14)	0.0039(9)	-0.0043(10)	-0.0216(9)
O3	0.0704(13)	0.0495(11)	0.0934(15)	-0.0052(10)	-0.0119(11)	0.0257(10)
C1	0.0582(17)	0.0527(16)	0.0472(16)	-0.0001(13)	0.0008(13)	-0.0057(14)
C2	0.075(2)	0.0539(17)	0.059(2)	-0.0053(15)	-0.0047(15)	-0.0062(15)
C3	0.086(2)	0.065(2)	0.0498(19)	-0.0106(15)	-0.0107(16)	0.0149(18)
C4	0.085(2)	0.076(2)	0.0439(18)	0.0092(16)	0.0011(15)	0.0083(18)
C5	0.0625(17)	0.0604(17)	0.0490(17)	0.0077(15)	0.0025(14)	-0.0035(14)
C6	0.0393(13)	0.0473(15)	0.0420(15)	0.0042(12)	-0.0002(11)	0.0012(12)
C7	0.0307(13)	0.0399(13)	0.0438(14)	-0.0041(11)	-0.0016(11)	0.0016(11)
C8	0.0334(14)	0.0666(17)	0.0632(18)	-0.0026(15)	0.0027(12)	0.0027(13)
C9	0.0435(16)	0.0680(19)	0.080(2)	-0.0050(17)	-0.0170(15)	0.0179(15)
C10	0.074(2)	0.0483(16)	0.065(2)	0.0020(14)	-0.0226(16)	0.0097(15)
C11	0.0654(18)	0.0416(14)	0.0523(16)	0.0035(13)	-0.0046(14)	-0.0079(13)

C12	0.0352(13)	0.0389(13)	0.0499(15)	0.0005(12)	-0.0022(11)	-0.0024(11)
C13	0.0313(13)	0.0449(14)	0.0487(15)	0.0051(12)	0.0049(11)	-0.0080(11)
C14	0.0344(13)	0.0397(13)	0.0498(15)	0.0034(11)	-0.0068(11)	-0.0007(11)
C15	0.0334(14)	0.0610(17)	0.0759(19)	-0.0069(15)	-0.0073(13)	-0.0020(13)
C16	0.0575(17)	0.0695(19)	0.0649(19)	0.0062(16)	-0.0188(14)	0.0128(15)
C17	0.0385(14)	0.0400(14)	0.0529(15)	-0.0099(12)	-0.0026(12)	0.0034(11)
C18	0.0328(14)	0.0681(18)	0.0615(18)	-0.0095(15)	0.0006(12)	0.0059(13)
C19	0.0479(16)	0.0673(18)	0.0593(18)	-0.0075(15)	0.0132(14)	0.0022(14)
C20	0.0536(17)	0.0508(16)	0.0516(17)	-0.0079(13)	0.0018(14)	0.0110(14)
C21	0.0416(16)	0.0585(17)	0.0589(18)	-0.0061(14)	-0.0075(13)	0.0029(13)
C22	0.0390(14)	0.0484(15)	0.0593(18)	-0.0072(13)	-0.0018(12)	-0.0043(12)
C23	0.087(2)	0.082(2)	0.069(2)	0.0086(18)	0.0042(17)	0.0098(18)

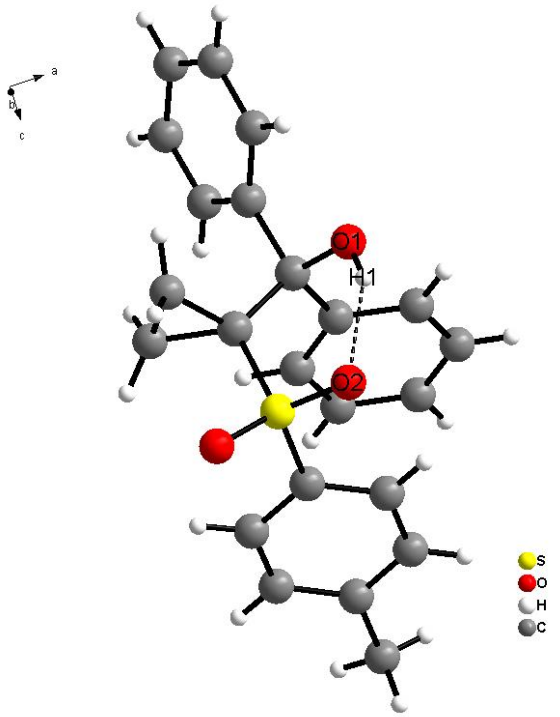
Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for wh11.

	x/a	y/b	z/c	U(eq)
H1	0.5961	0.4308	0.6360	0.085
H1A	0.3705	0.1051	0.6025	0.063
H2	0.3239	0.0017	0.4714	0.075
H3	0.3919	0.0588	0.3301	0.081
H4	0.5043	0.2239	0.3212	0.082
H5	0.5464	0.3315	0.4507	0.069
H8	0.7074	0.2507	0.6923	0.065
H9	0.7708	0.1345	0.8125	0.077
H10	0.6379	0.0379	0.9008	0.075
H11	0.4399	0.0582	0.8686	0.064
H12	0.3750	0.1757	0.7503	0.05
H15A	0.2482	0.2707	0.6193	0.068
H15B	0.2093	0.3755	0.6879	0.068
H16A	0.2872	0.5138	0.5835	0.077
H16B	0.3260	0.4089	0.5149	0.077
H18	0.2512	0.3841	0.8622	0.065
H19	0.2660	0.2844	0.9993	0.07
H21	0.6128	0.3330	1.0063	0.064
H22	0.6003	0.4281	0.8674	0.059
H23A	0.5185	0.1849	1.1083	0.119

H23B	0.3812	0.1856	1.1140	0.119
H23C	0.4550	0.2872	1.1576	0.119

Table 8. Hydrogen bond parameters (Å, °) for compound 3aa.

D–H···A	D(D)···H)	d(H)···A)	d(D)···A)	∠(DHA)	Symmetry transformation for A
O(1)–H(1)···O(2)	0.82	1.98	2.7229(6)	151	x,y,z
C(5)–H(5)···O(1)	0.93	2.26	2.6279(5)	103	x,y,z
C(8)–H(8)···O(1)	0.93	2.38	2.7370(6)	103	x,y,z
C(12)–H(12)···O(3)	0.93	2.55	3.3316(7)	142	3/2-x,1/2-y,1/2-z
C(16)–H(16A)···O(3)	0.97	2.44	2.8645(6)	106	x,y,z
C(22)–H(22)···O(2)	0.93	2.48	2.8733(6)	105	x,y,z



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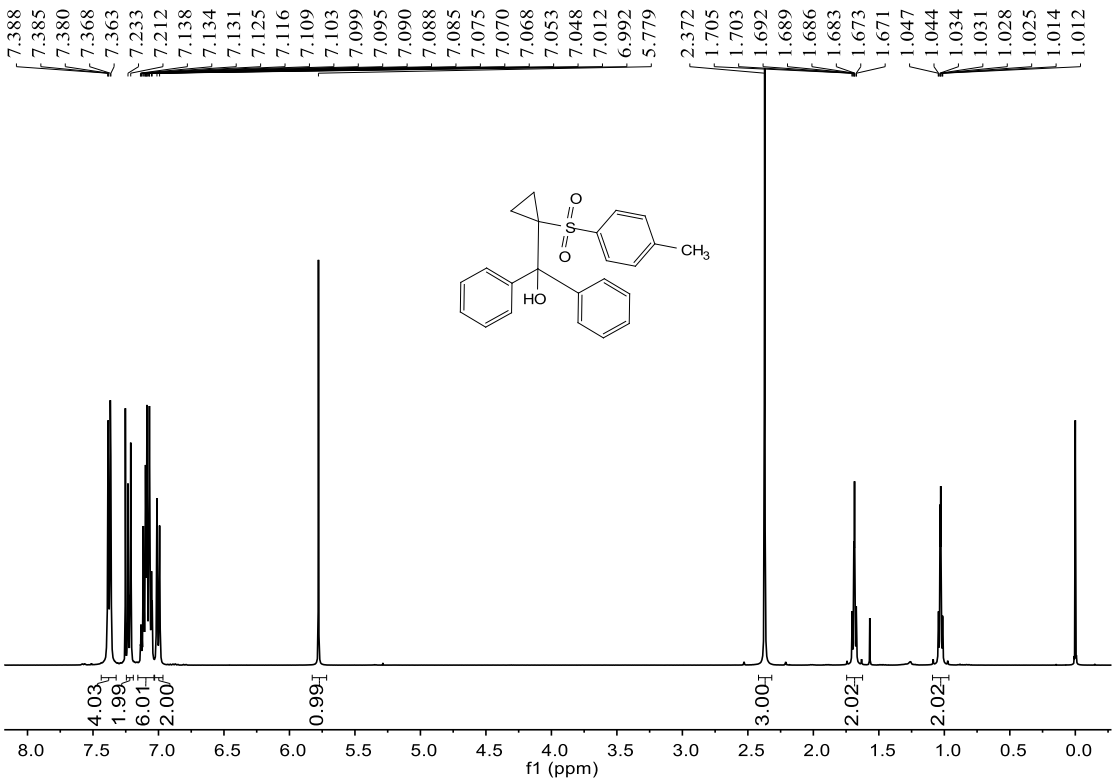
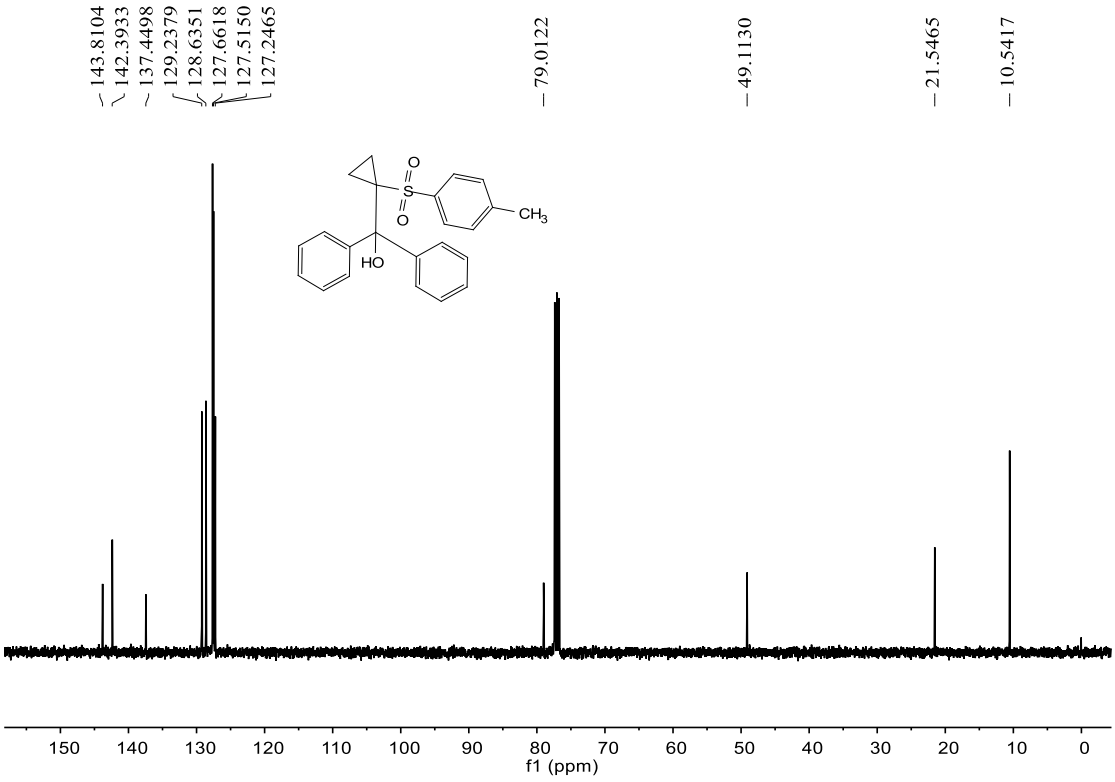
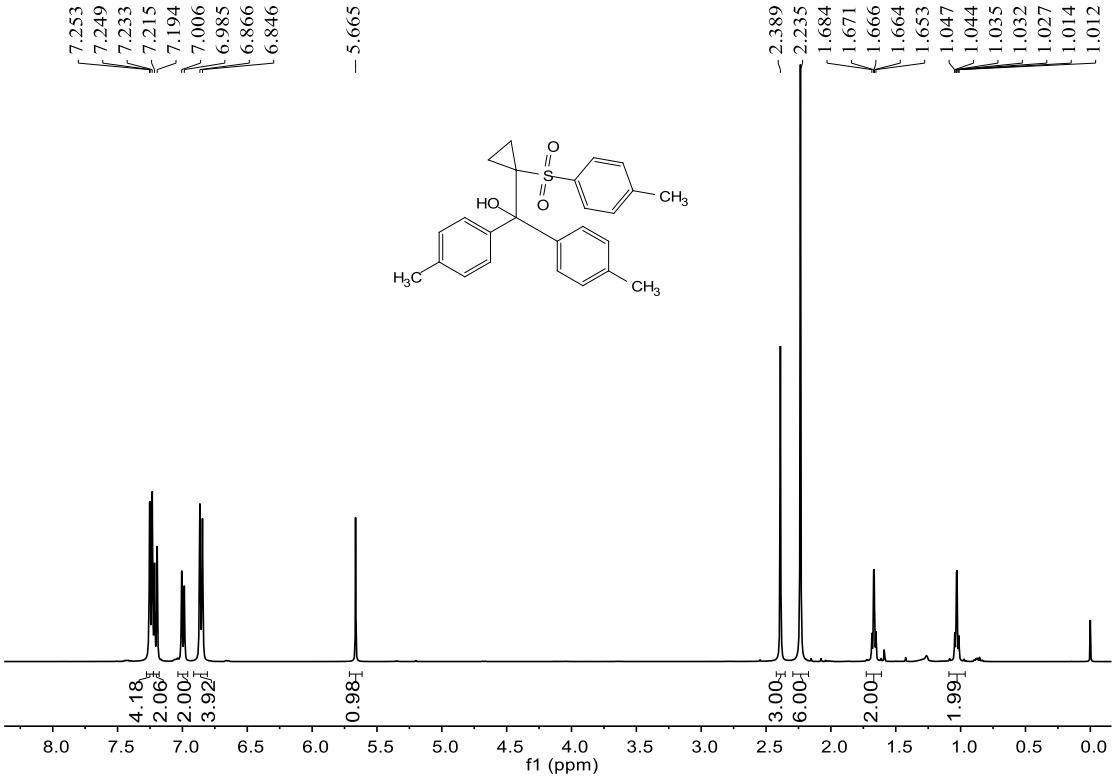
VI. NMR Spectra

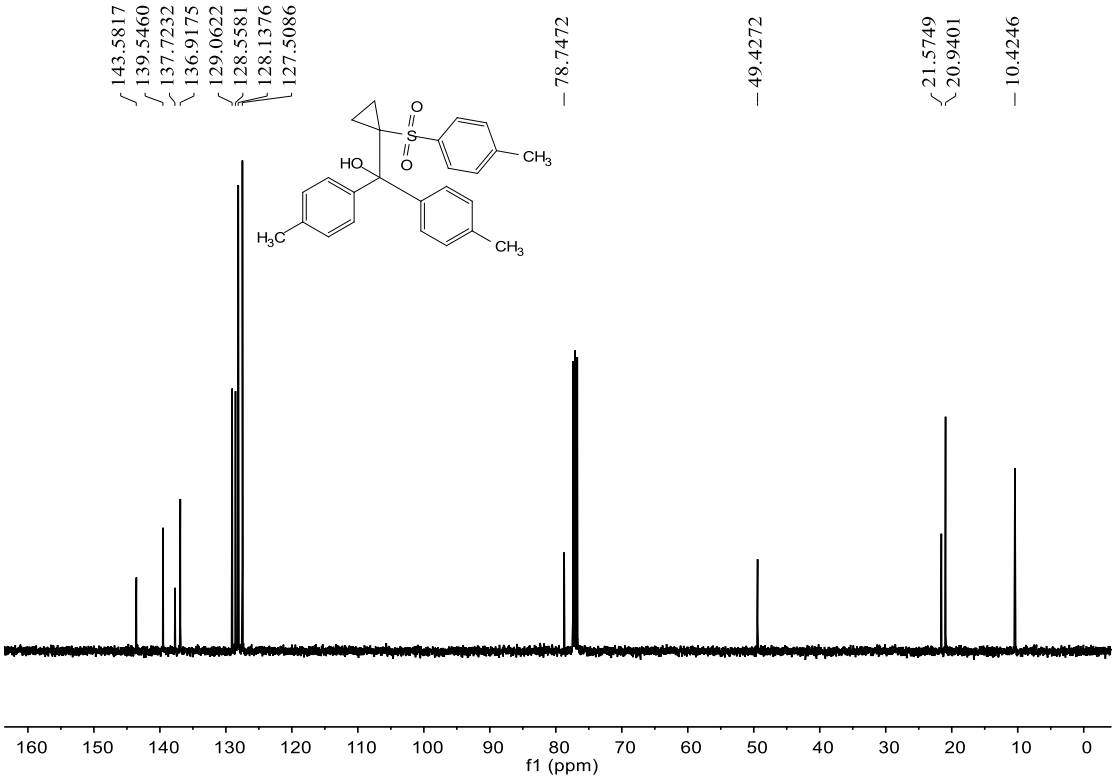
^{1}H NMR and ^{13}C NMR spectra of compound **3aa**





^{1}H NMR and ^{13}C NMR spectra of compound **3ba**





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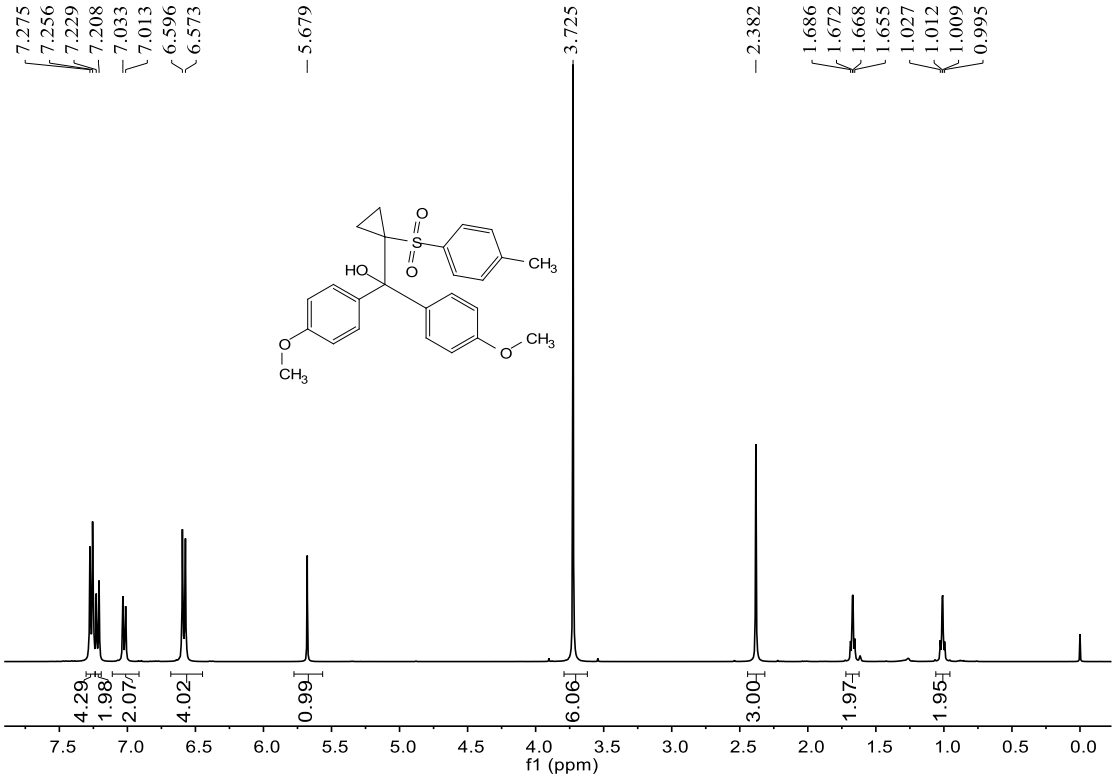

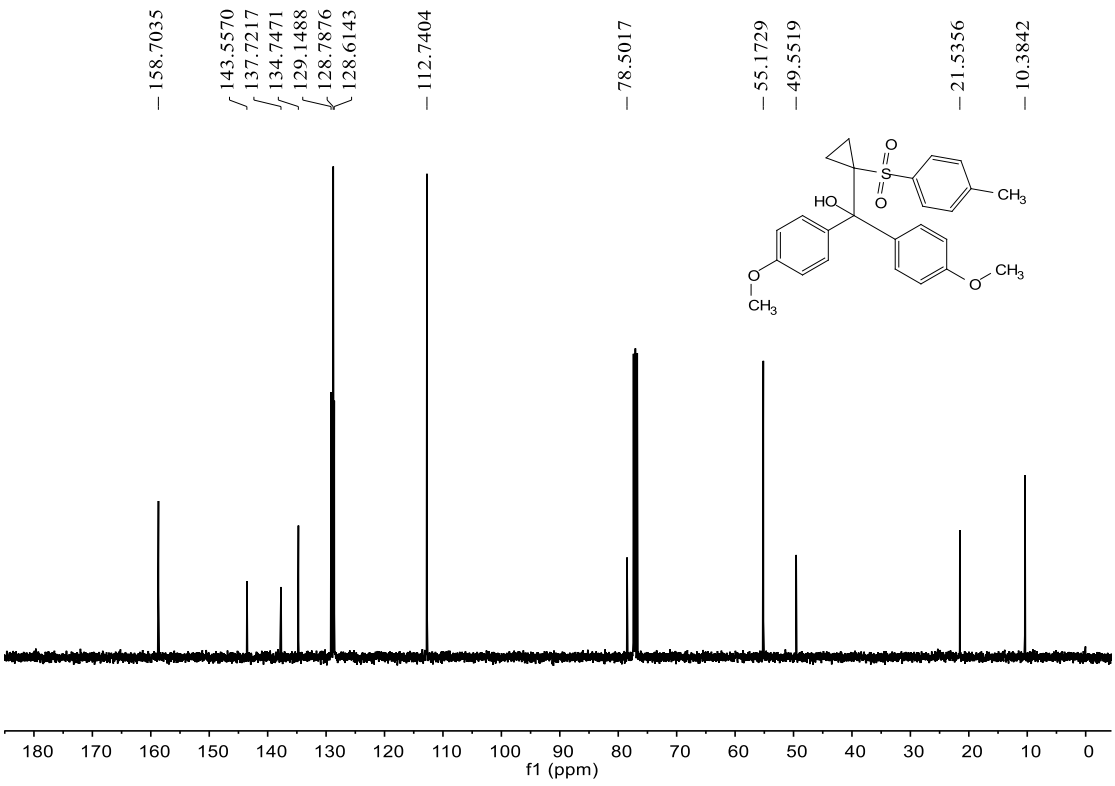

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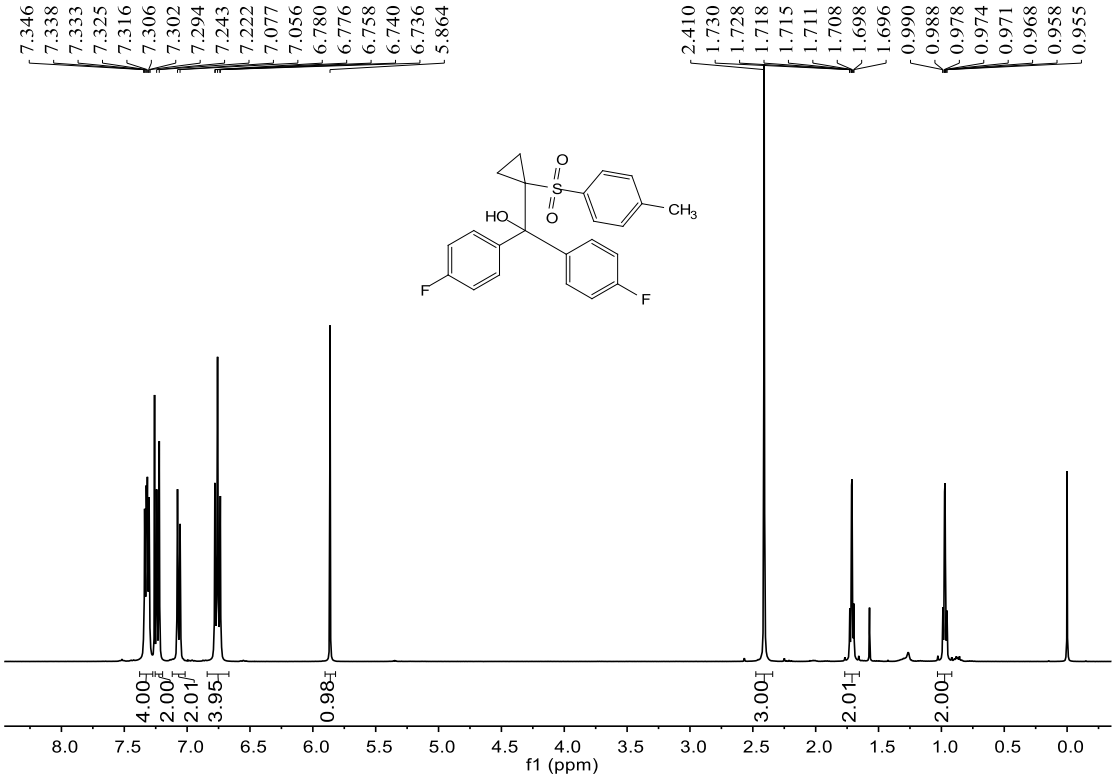

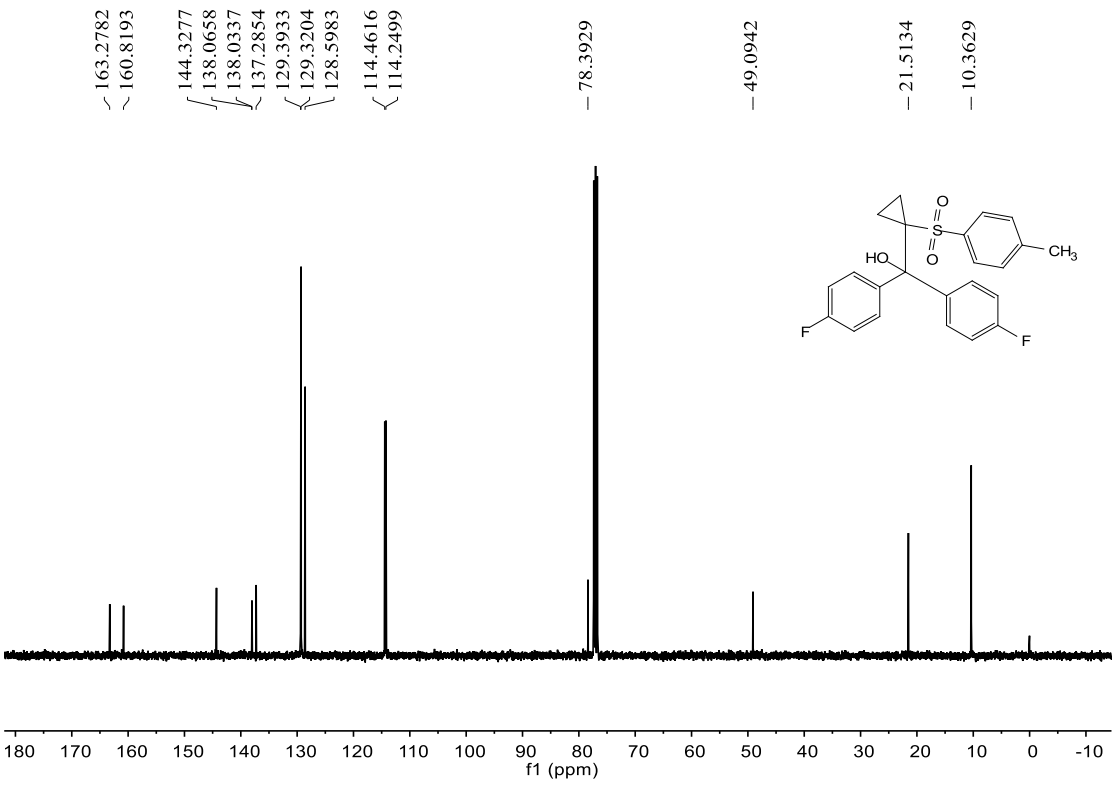

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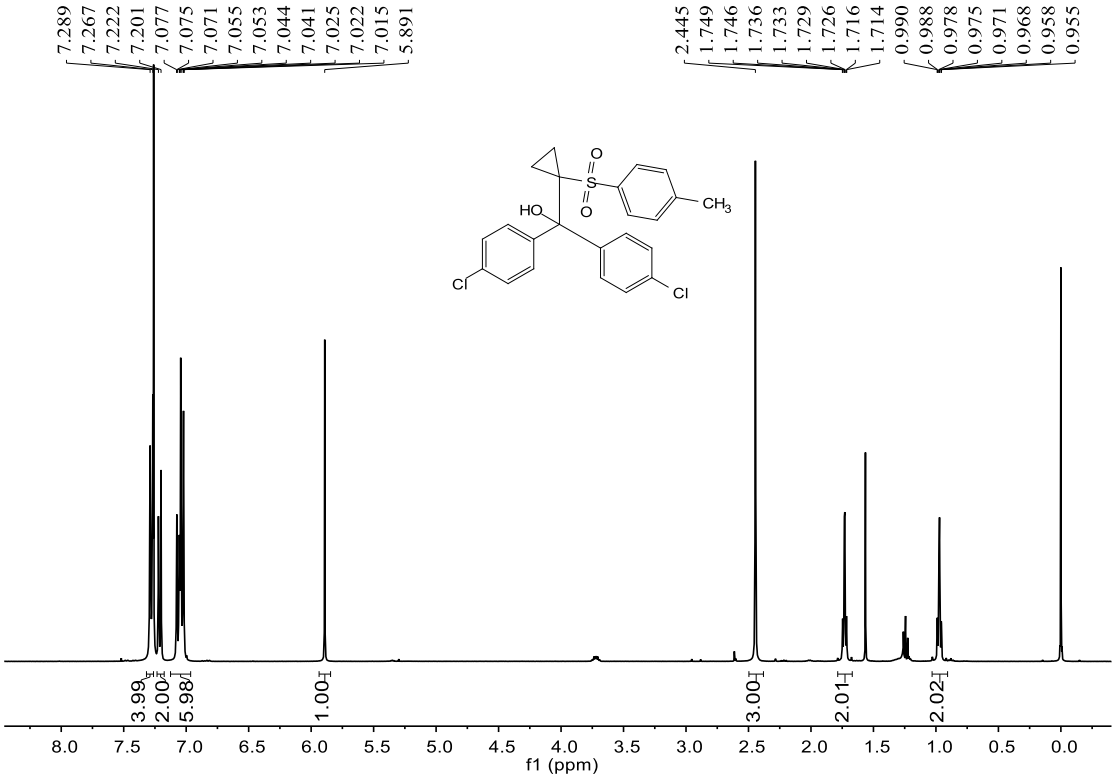
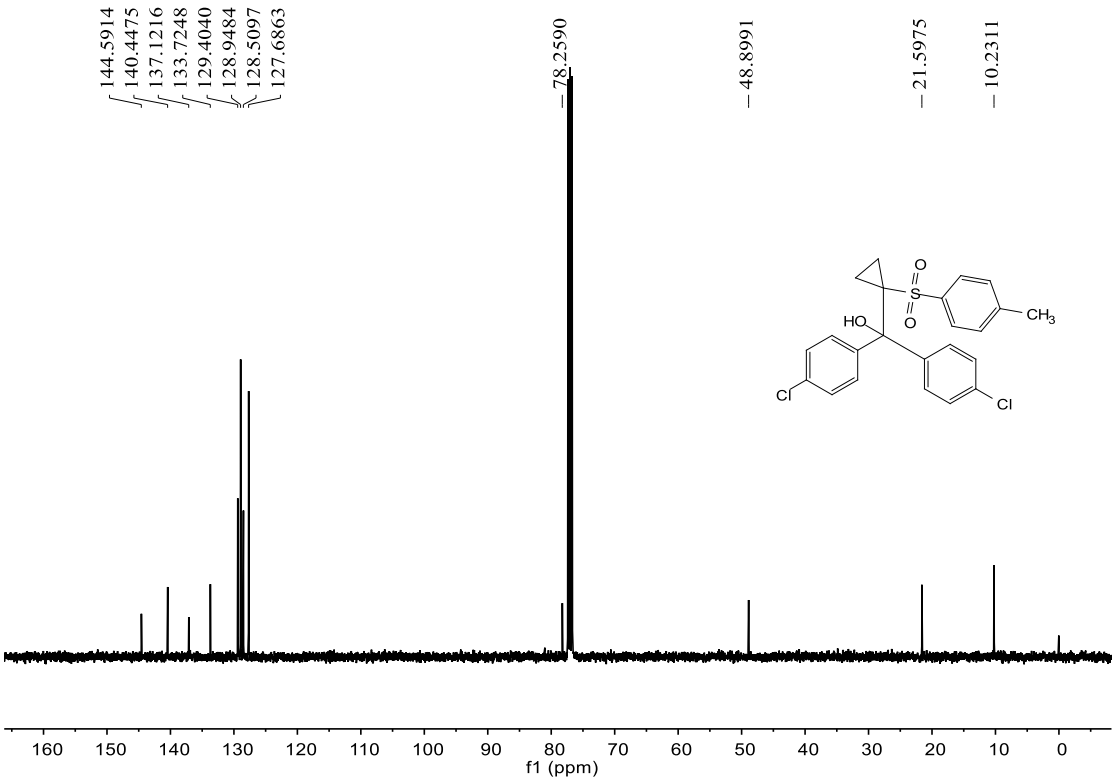
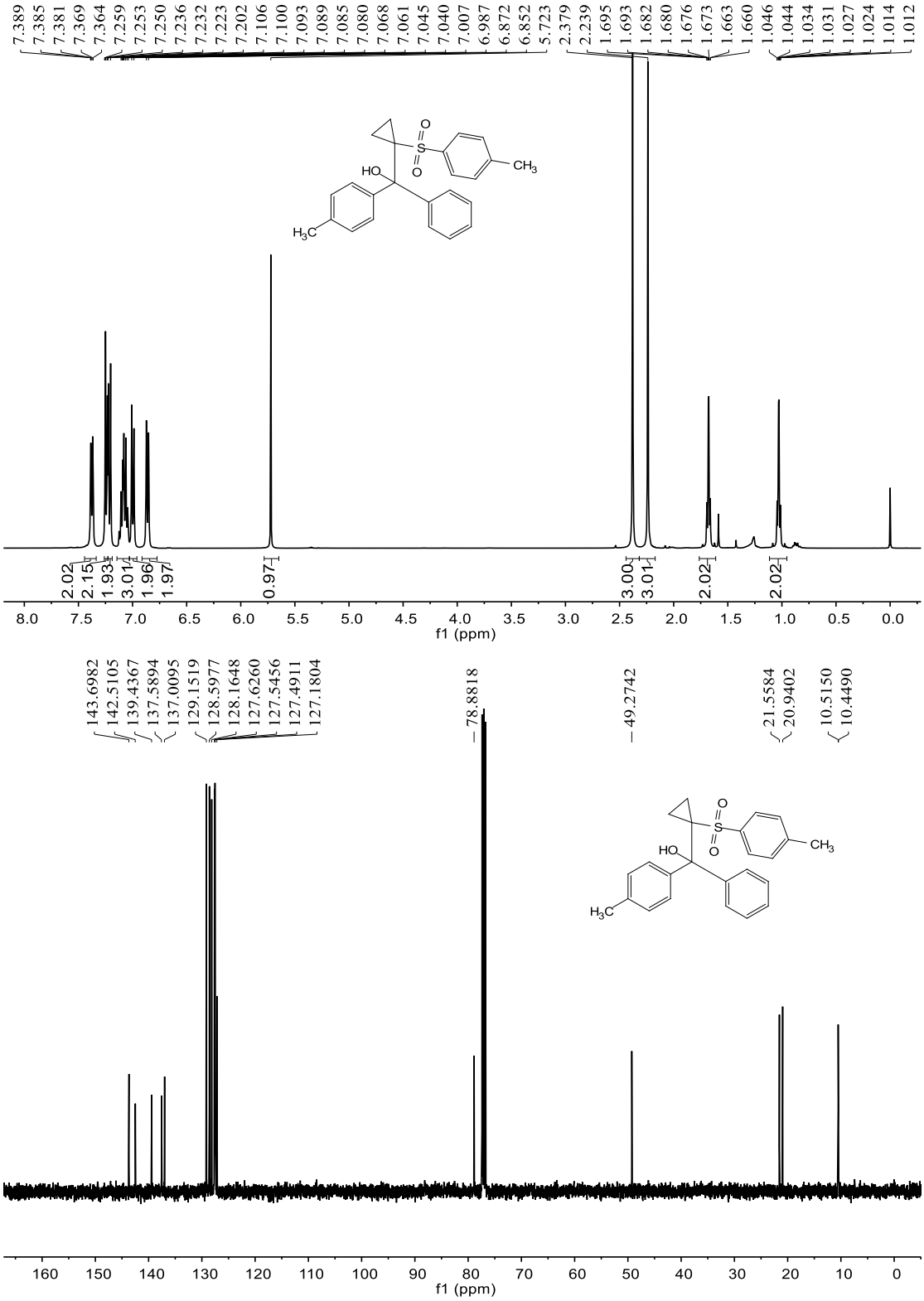
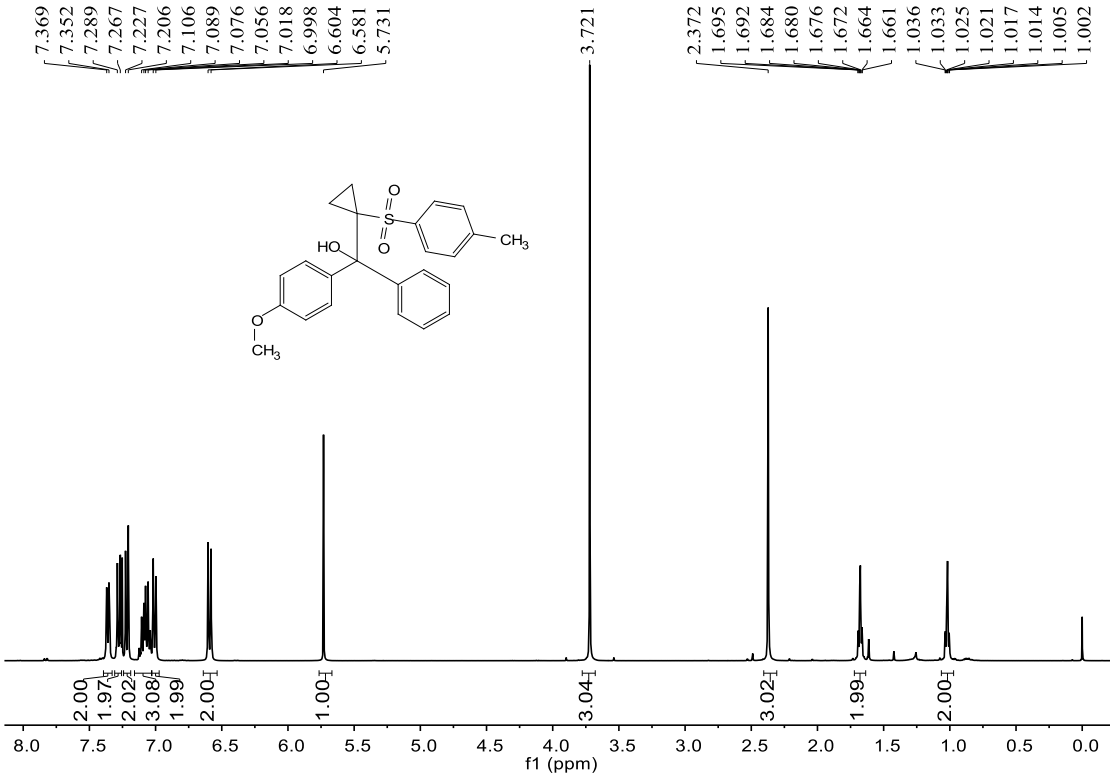


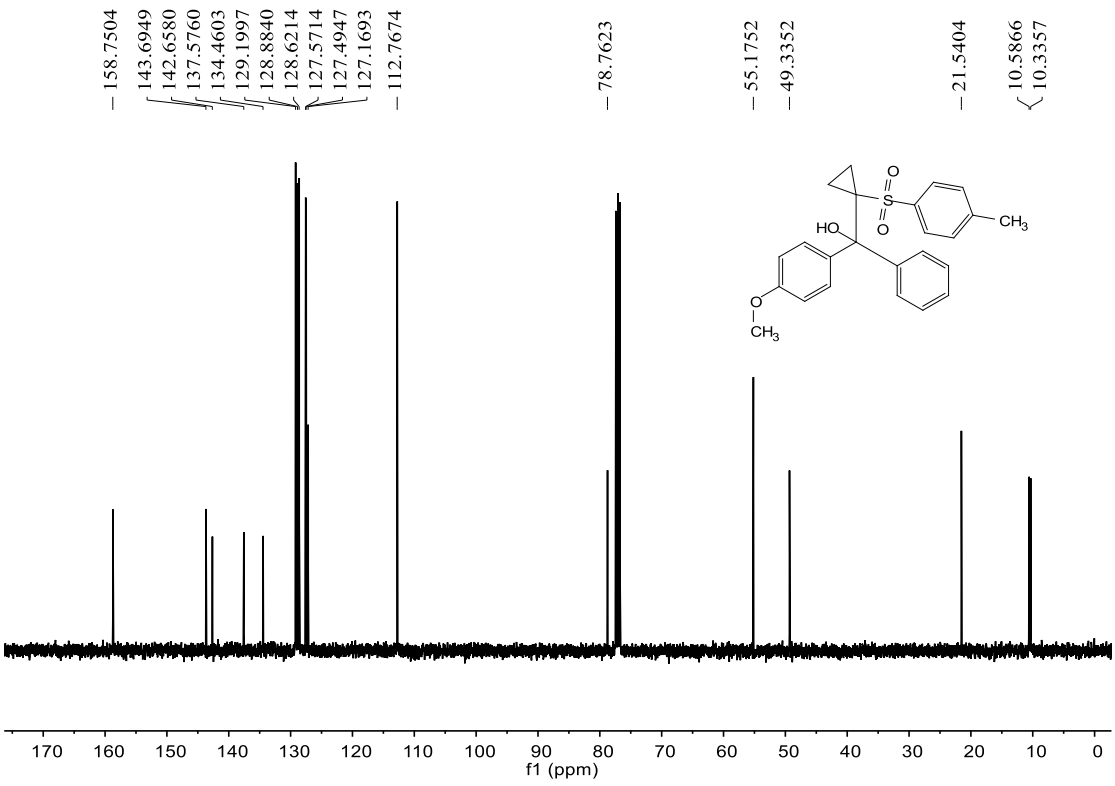


^{1}H NMR and ^{13}C NMR spectra of compound **3fa**

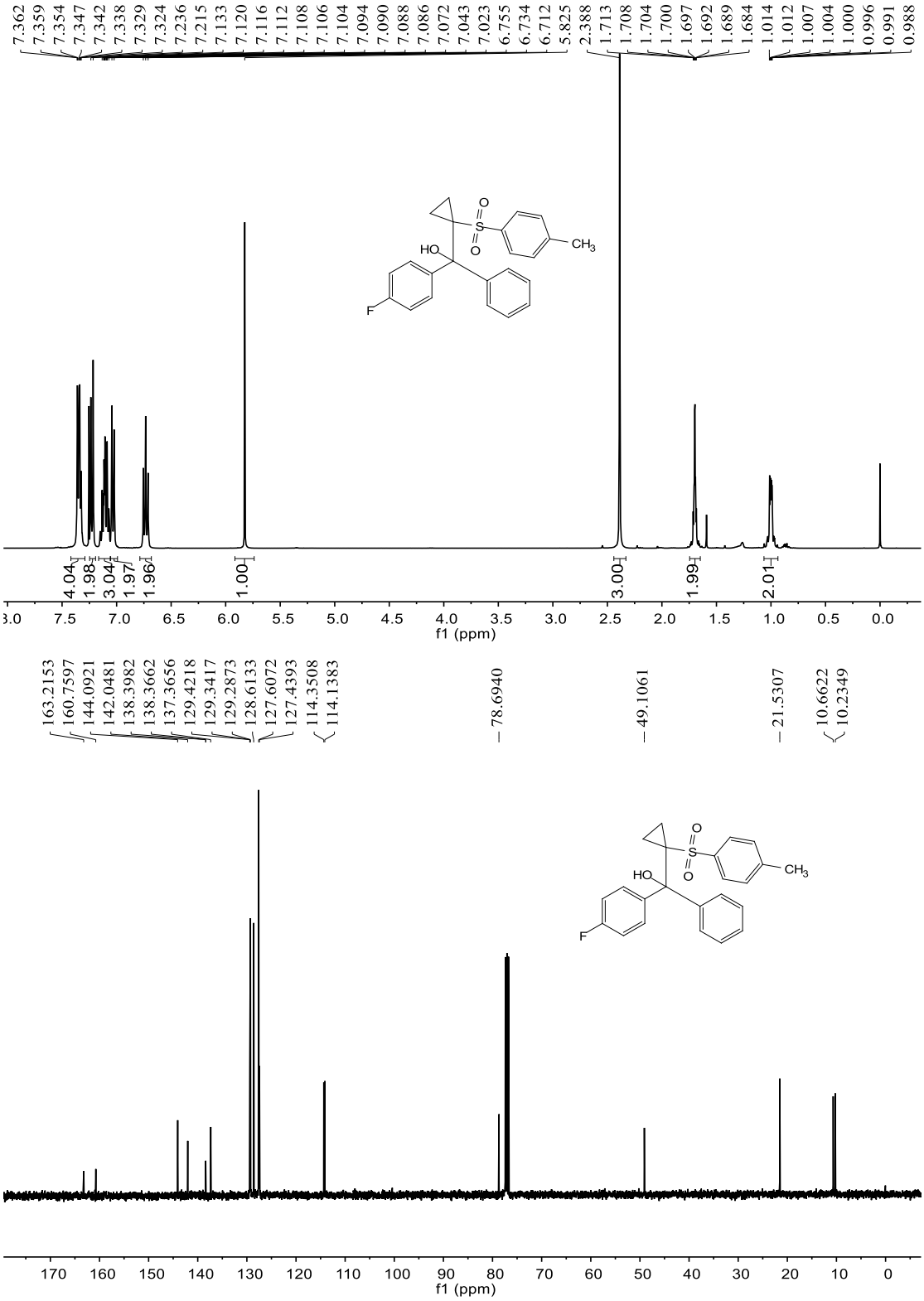


^{1}H NMR and ^{13}C NMR spectra of compound **3ga**





^{1}H NMR and ^{13}C NMR spectra of compound **3ha**



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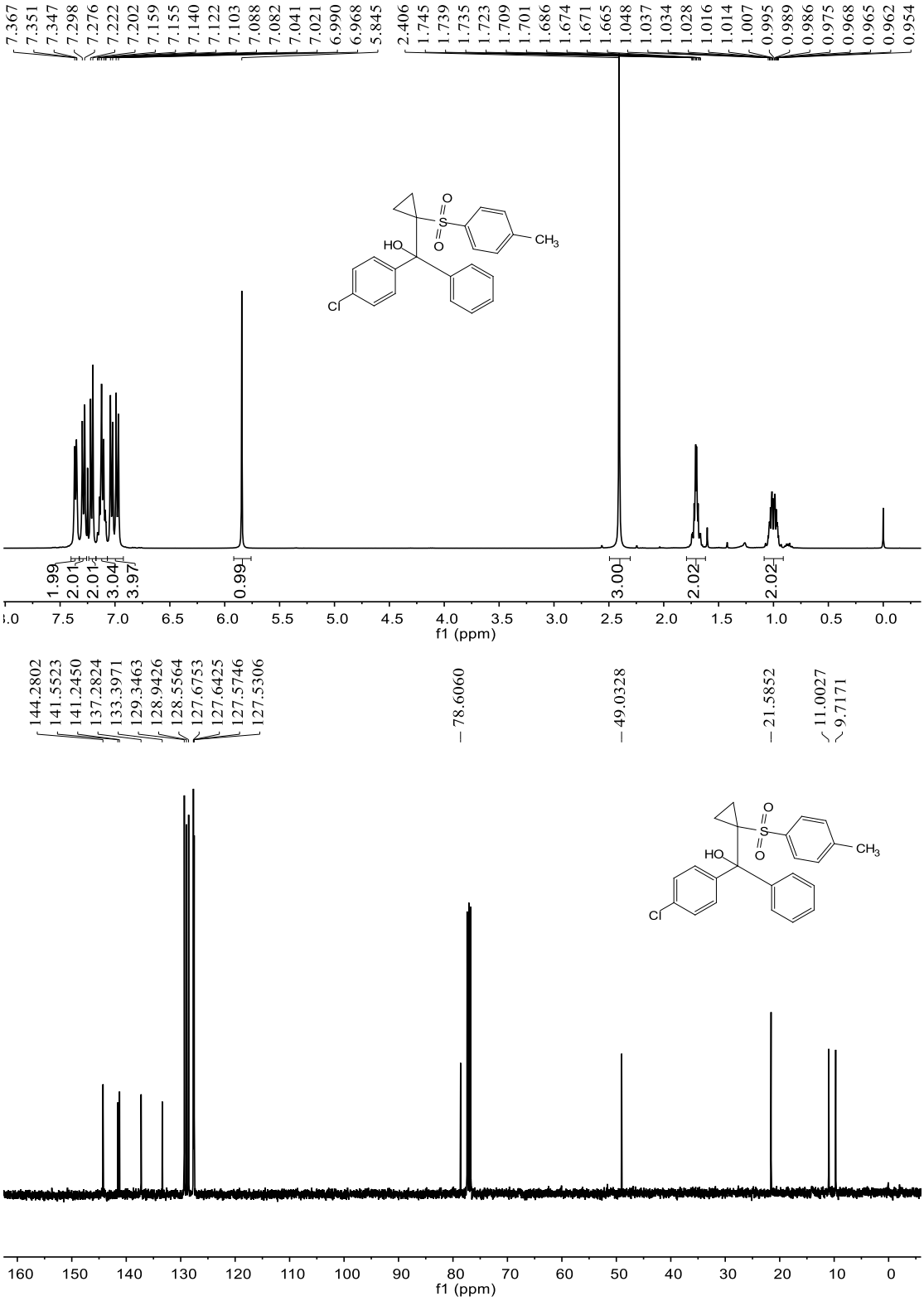
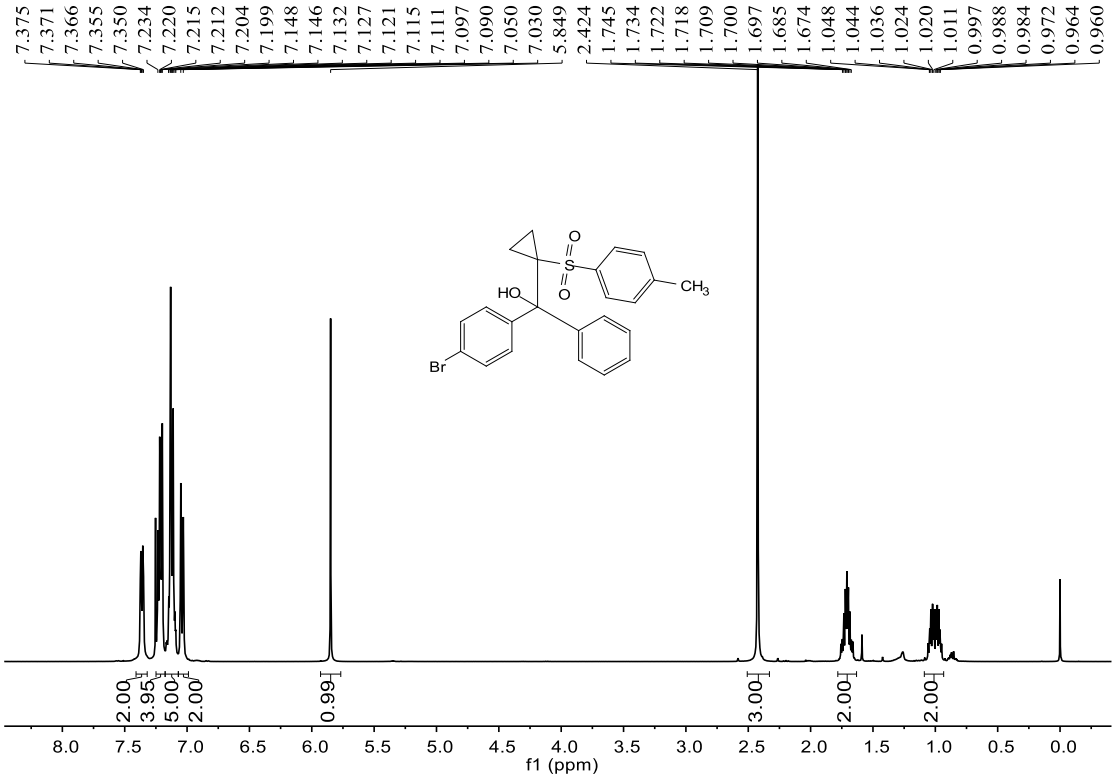
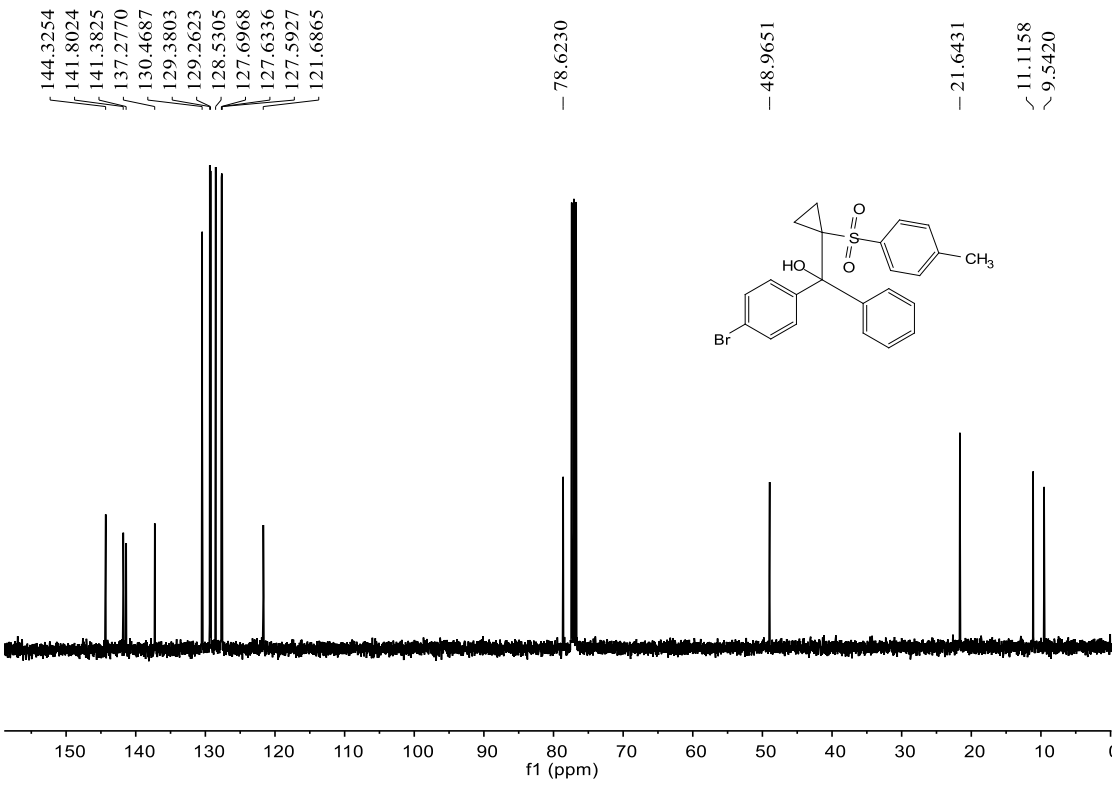
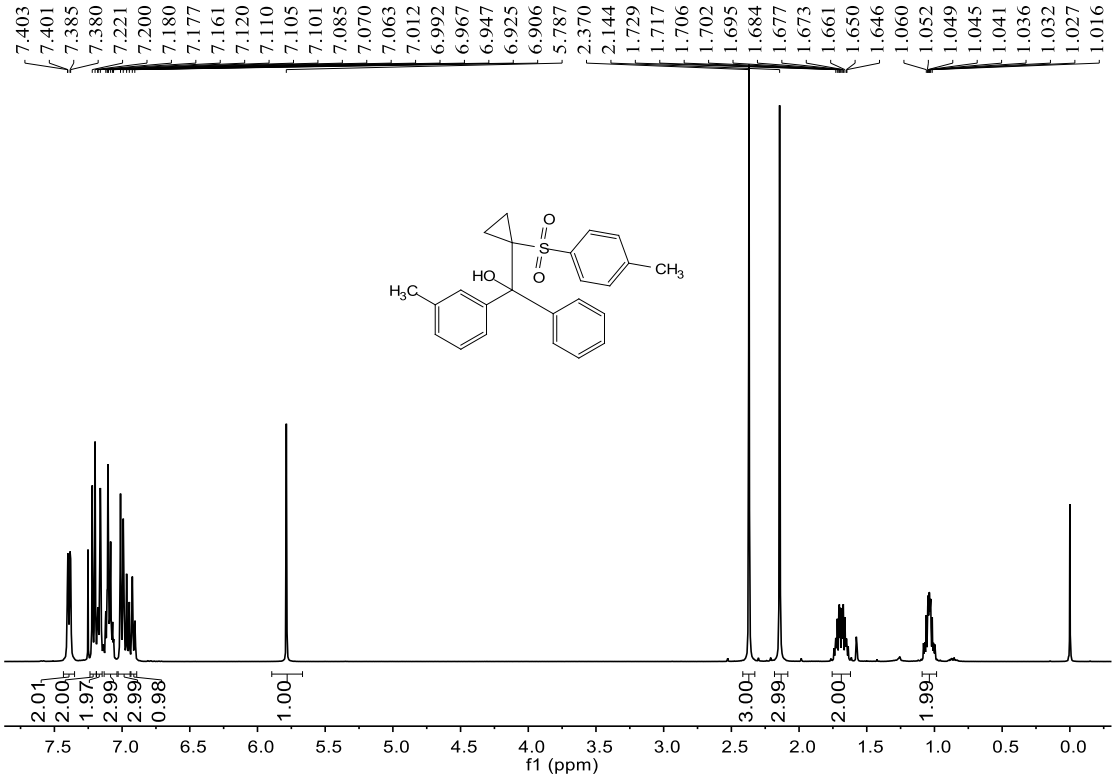


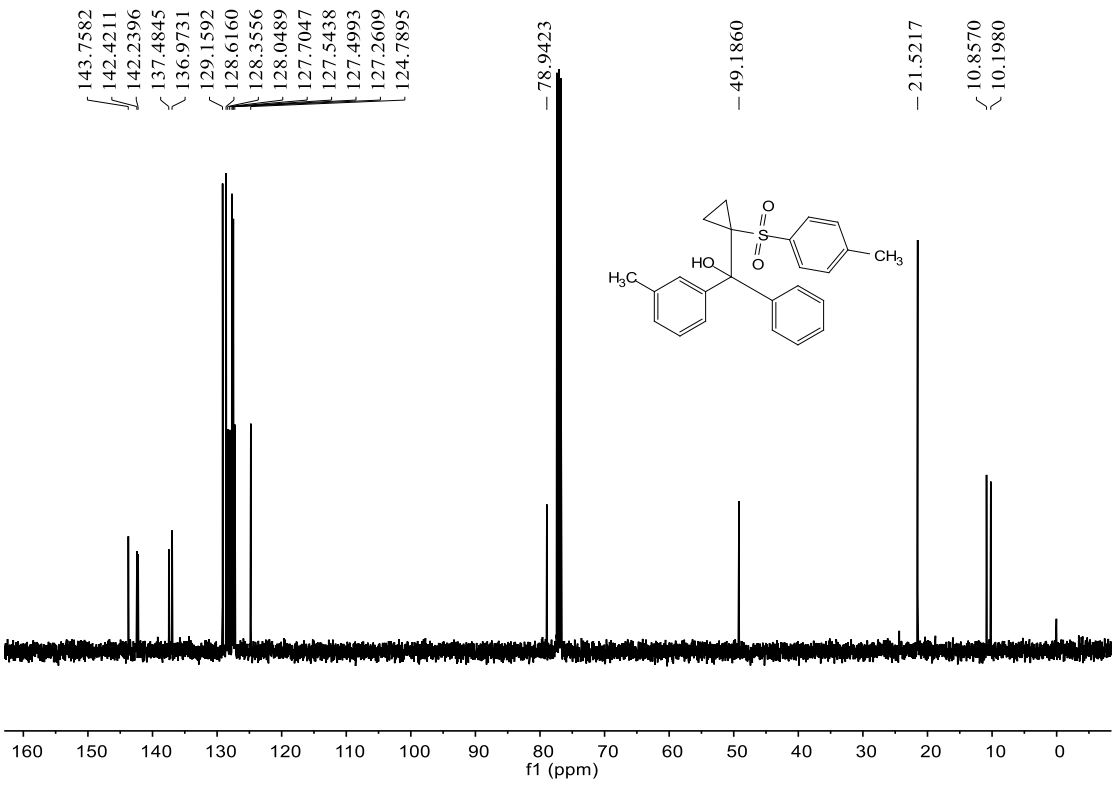
^{1}H NMR and ^{13}C NMR spectra of compound **3ja**





^{1}H NMR and ^{13}C NMR spectra of compound **3ka**





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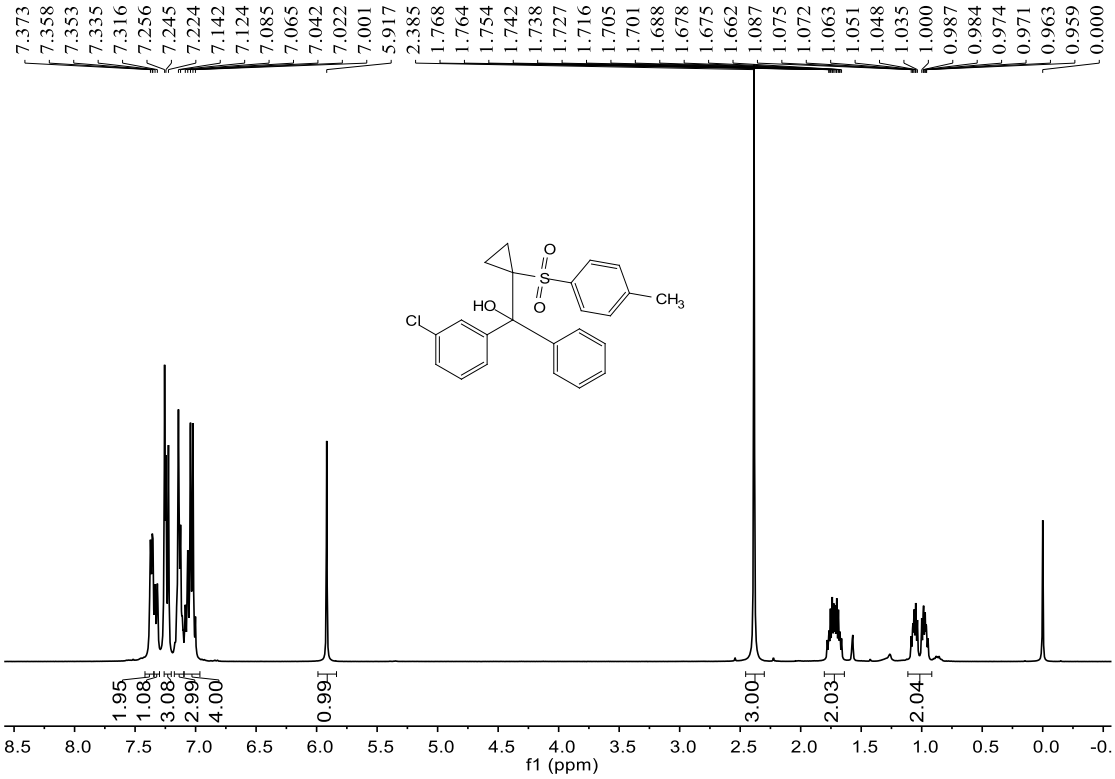
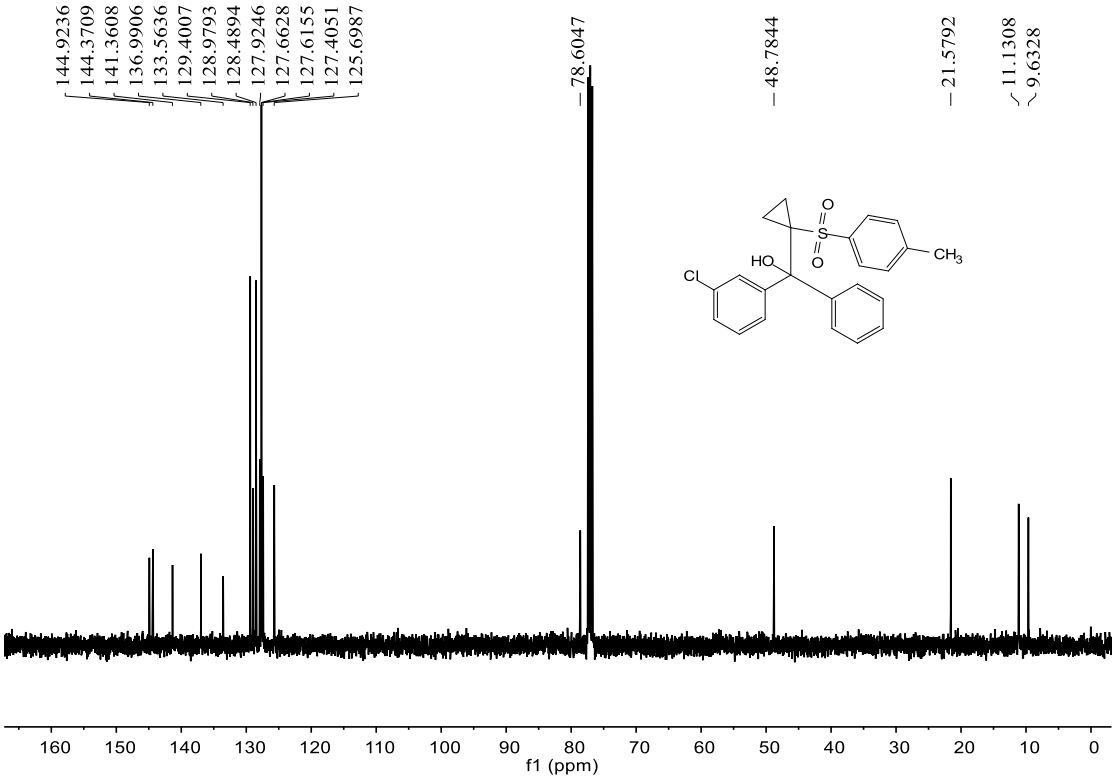
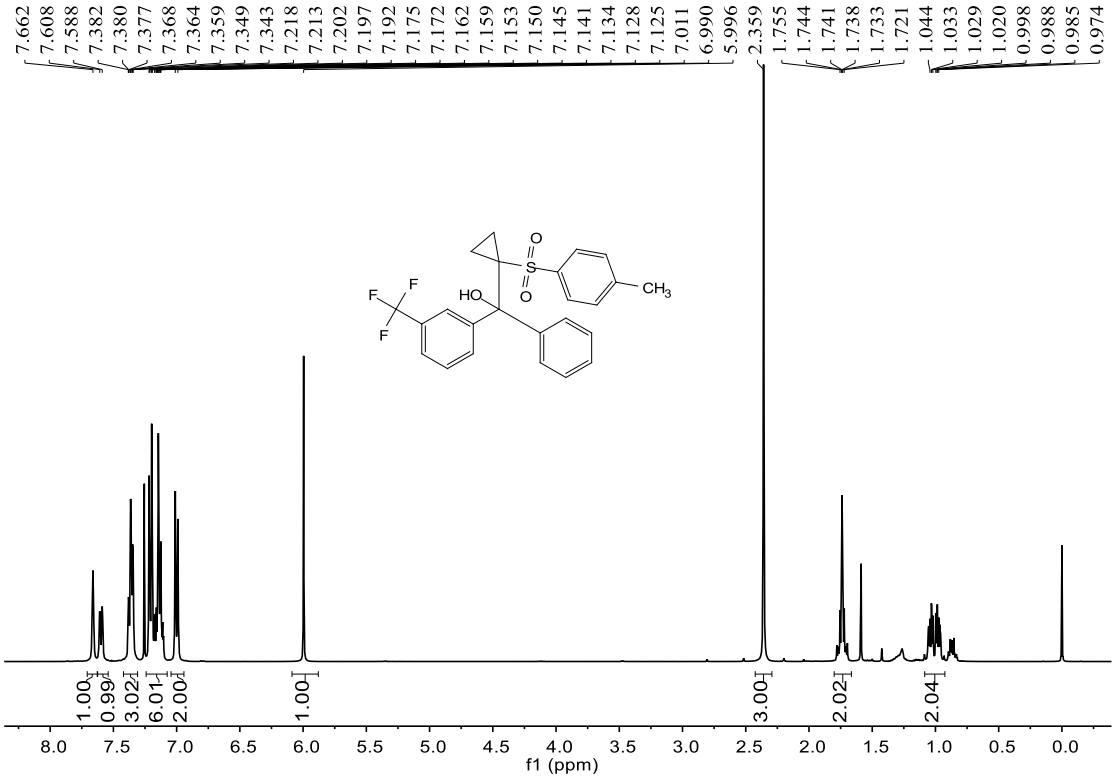
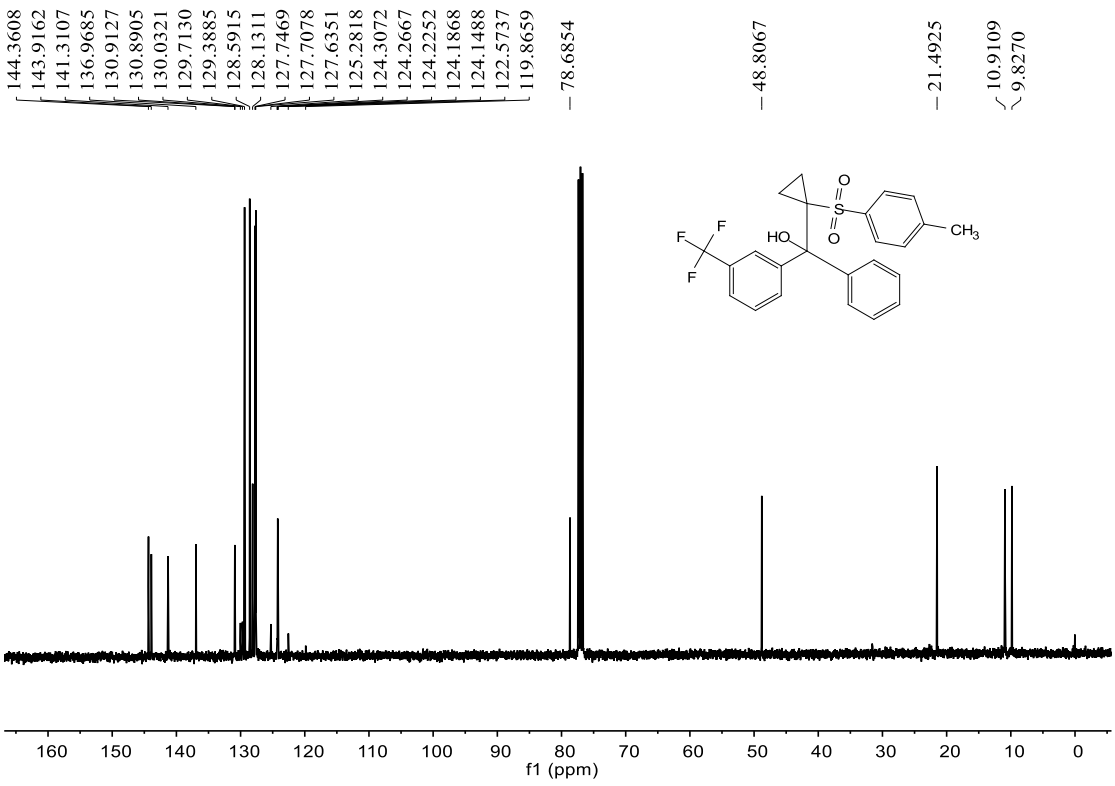


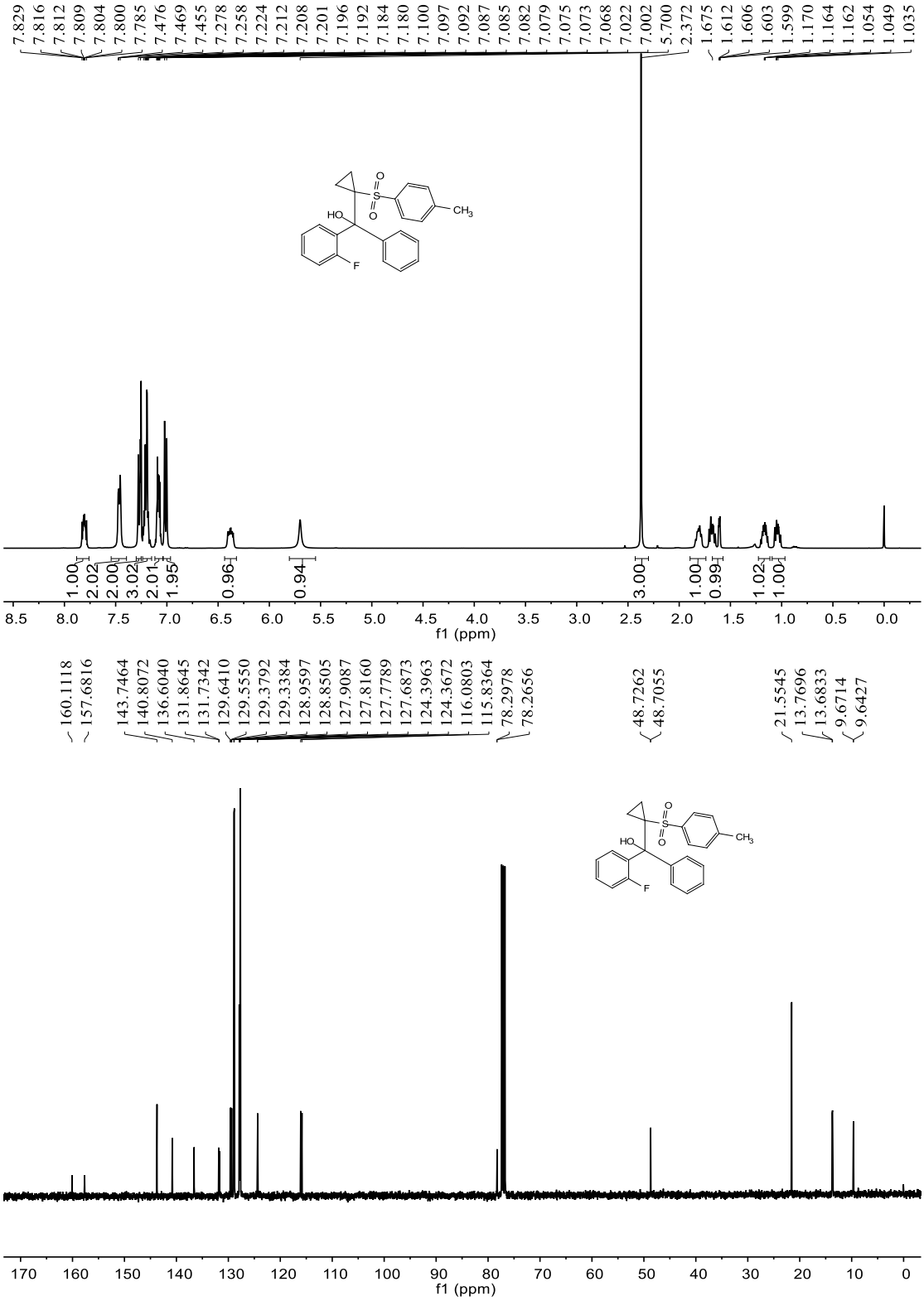


^{1}H NMR and ^{13}C NMR spectra of compound **3ma**

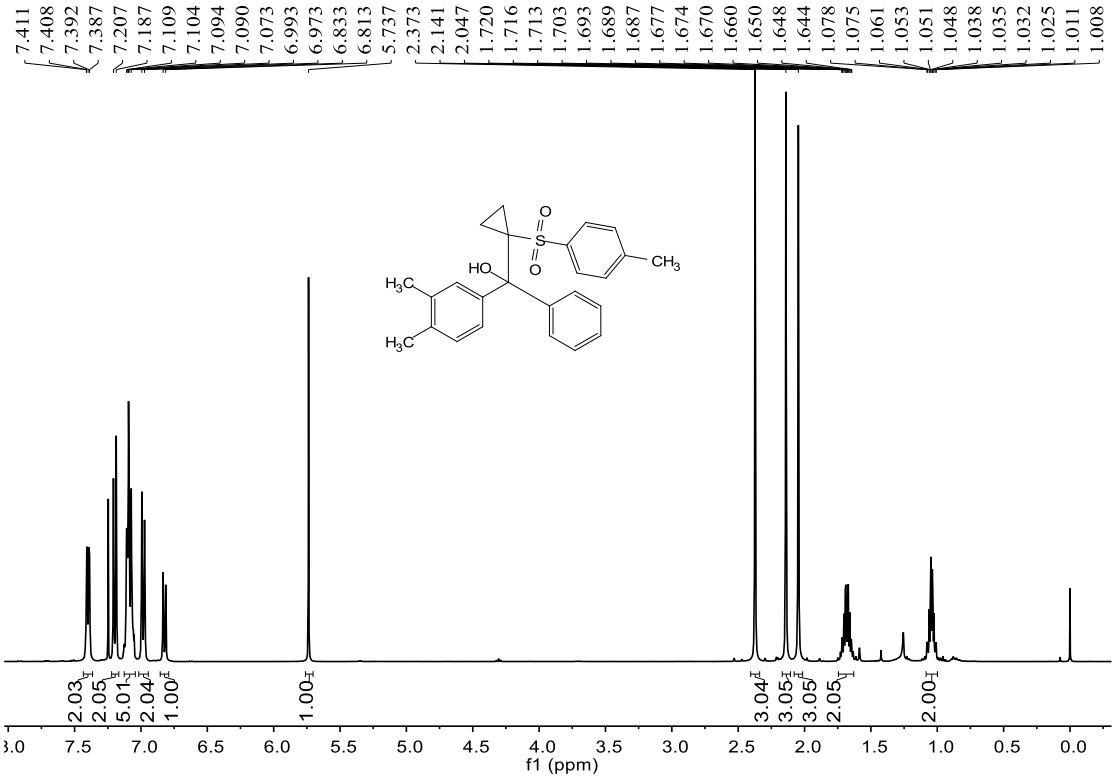


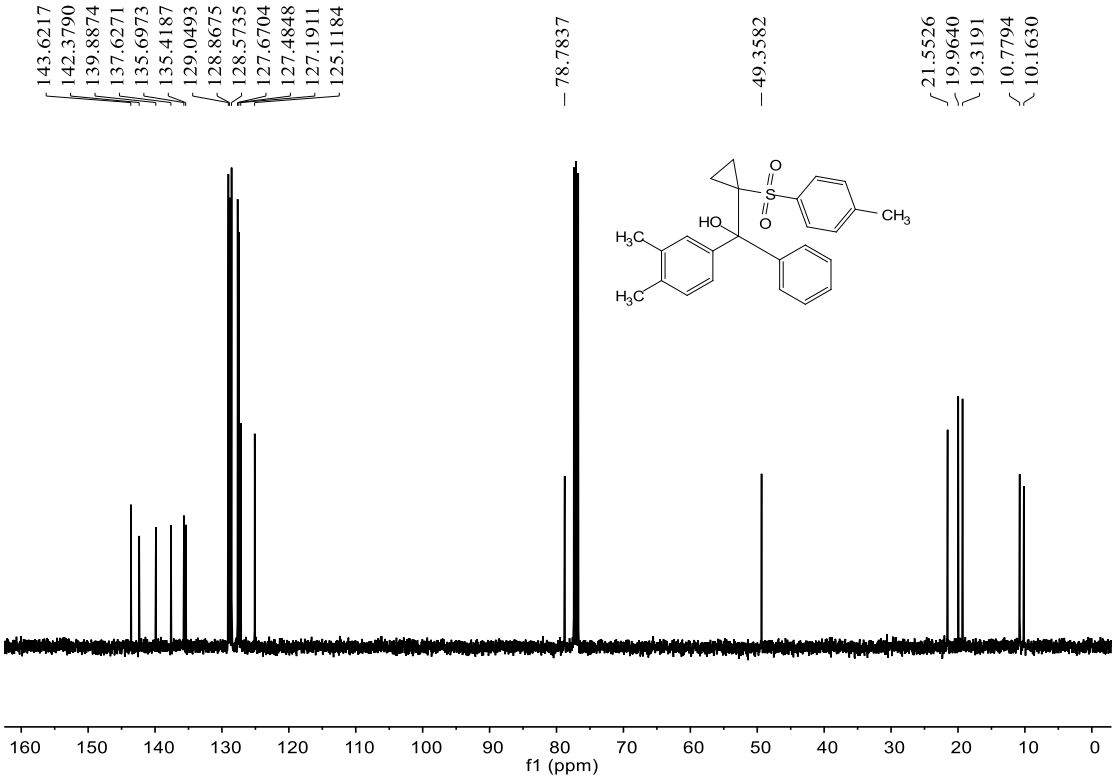


^{1}H NMR and ^{13}C NMR spectra of compound **3na**

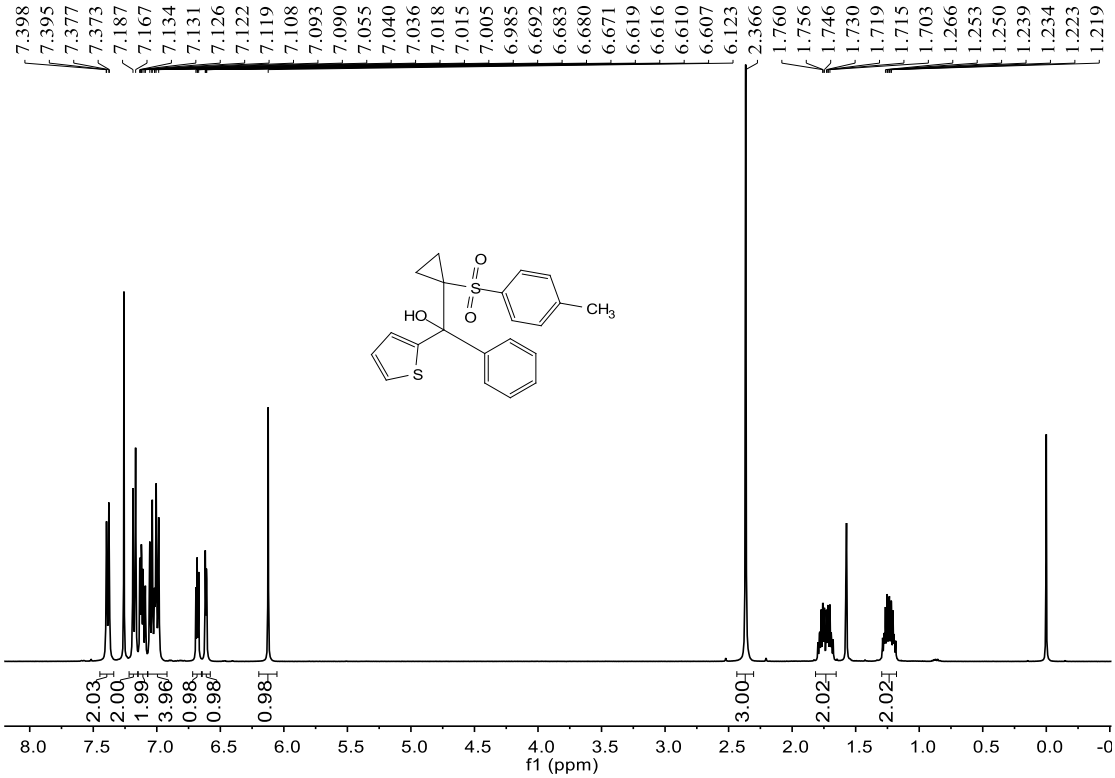


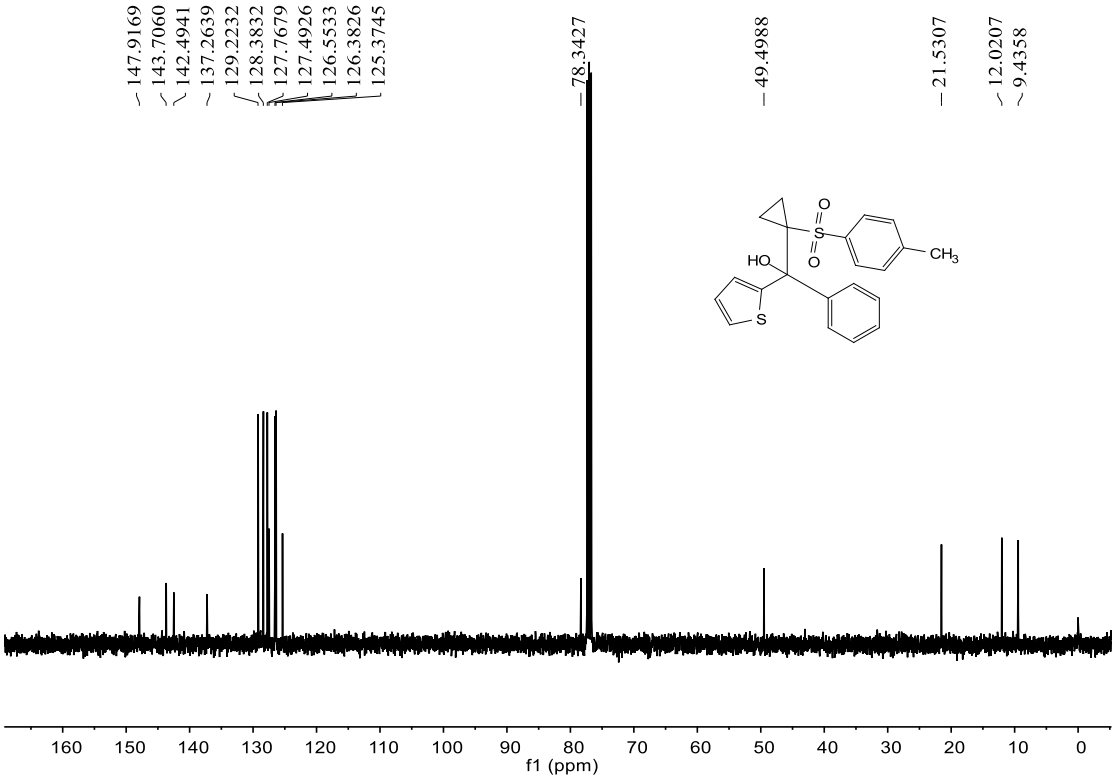
^{1}H NMR and ^{13}C NMR spectra of compound **3oa**



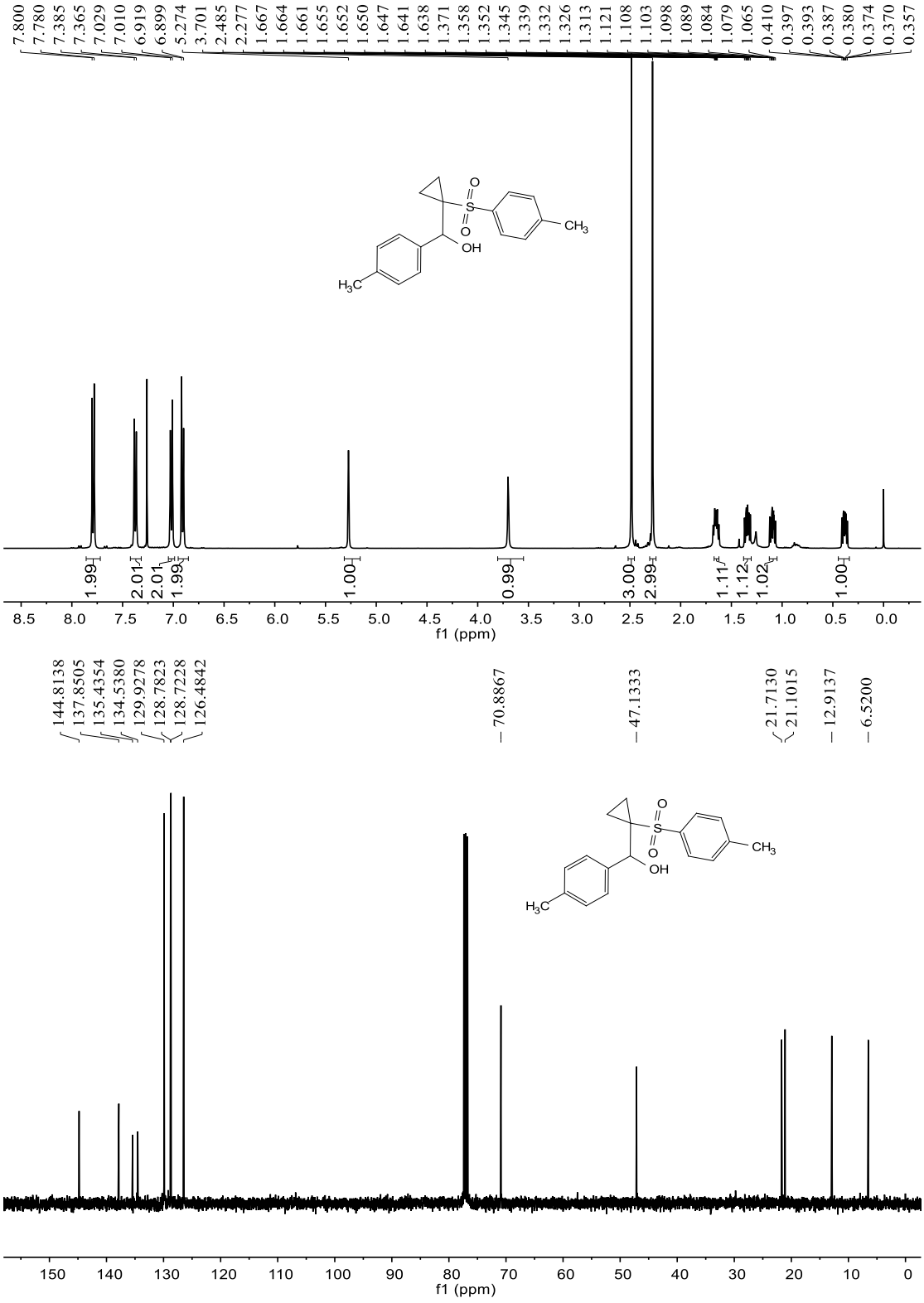


^{1}H NMR and ^{13}C NMR spectra of compound **3pa**





^{1}H NMR and ^{13}C NMR spectra of compound **3qa**



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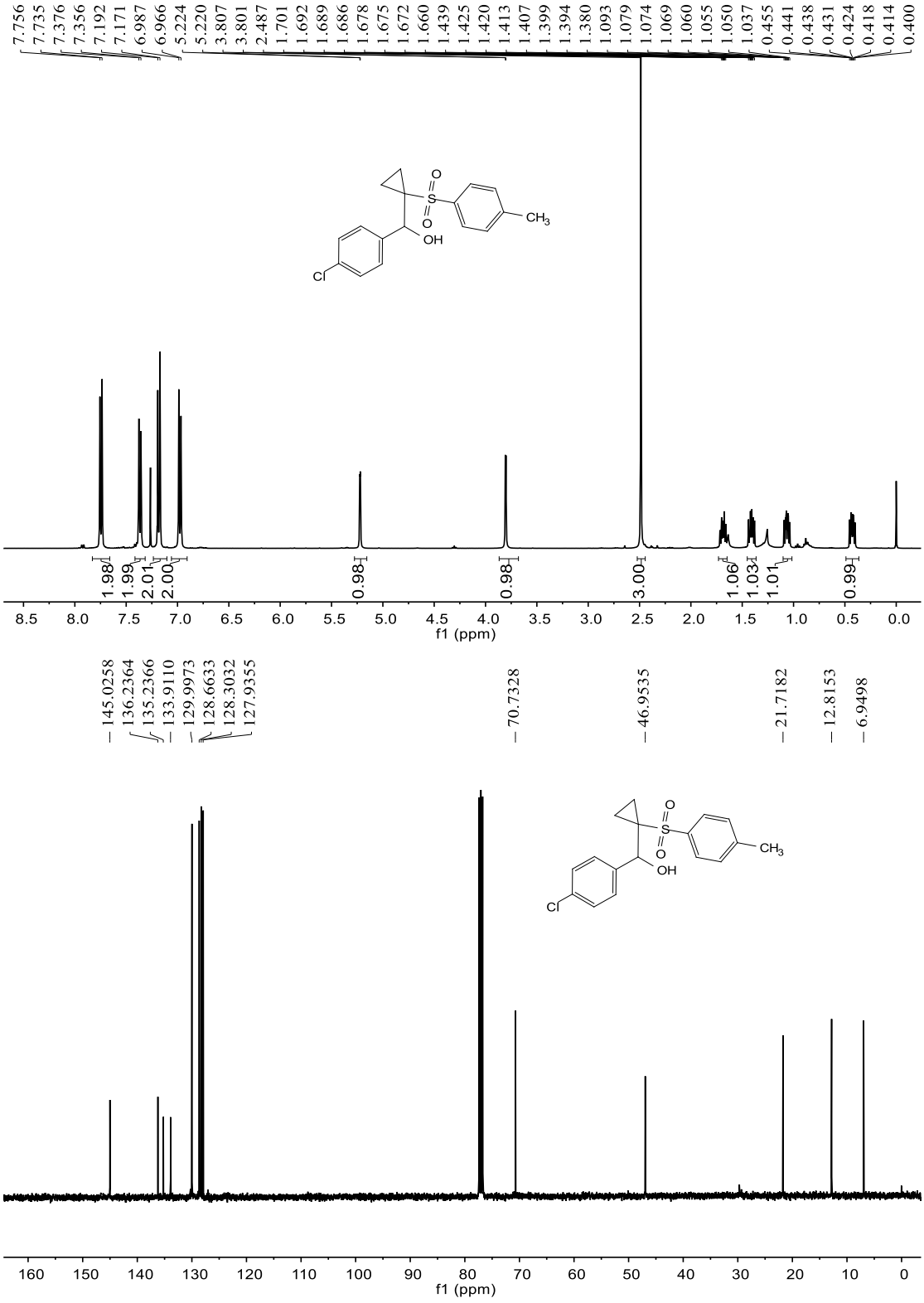

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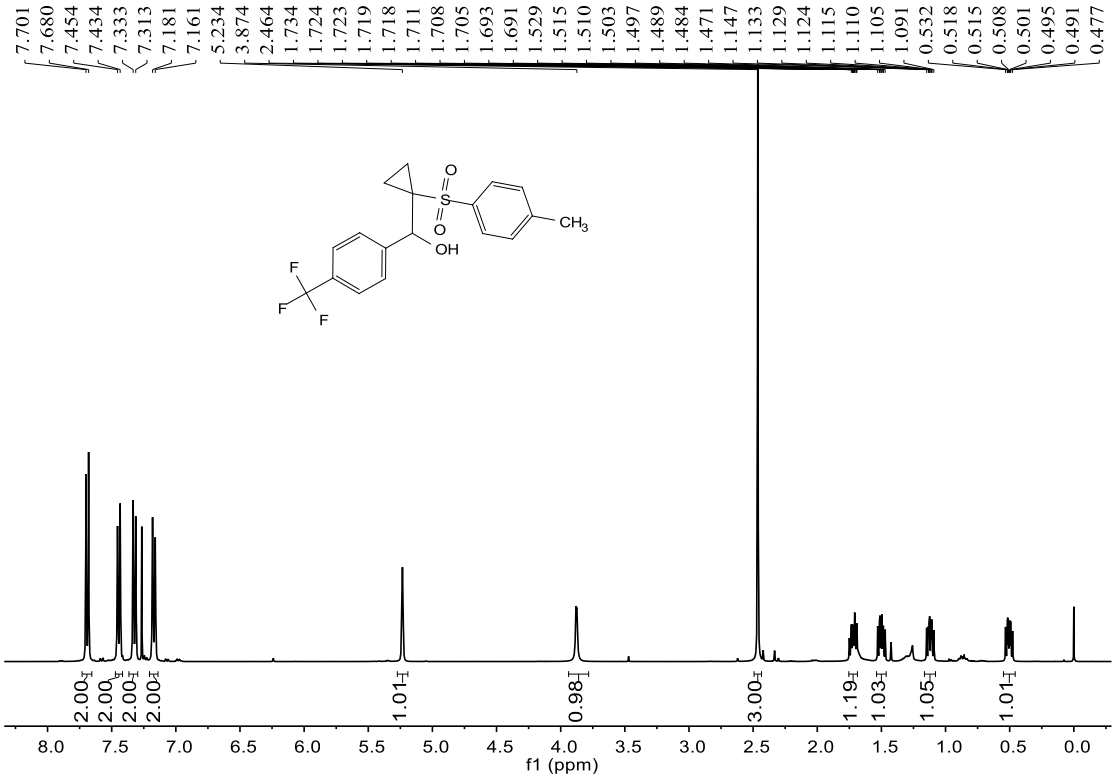
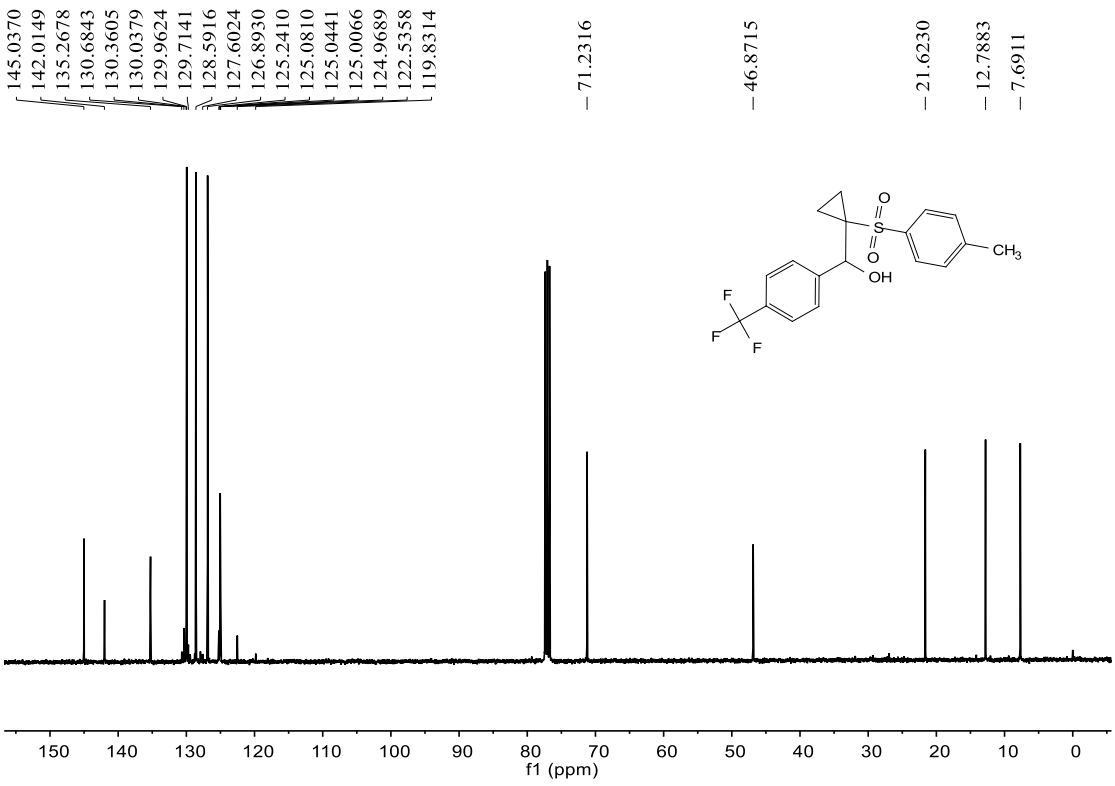
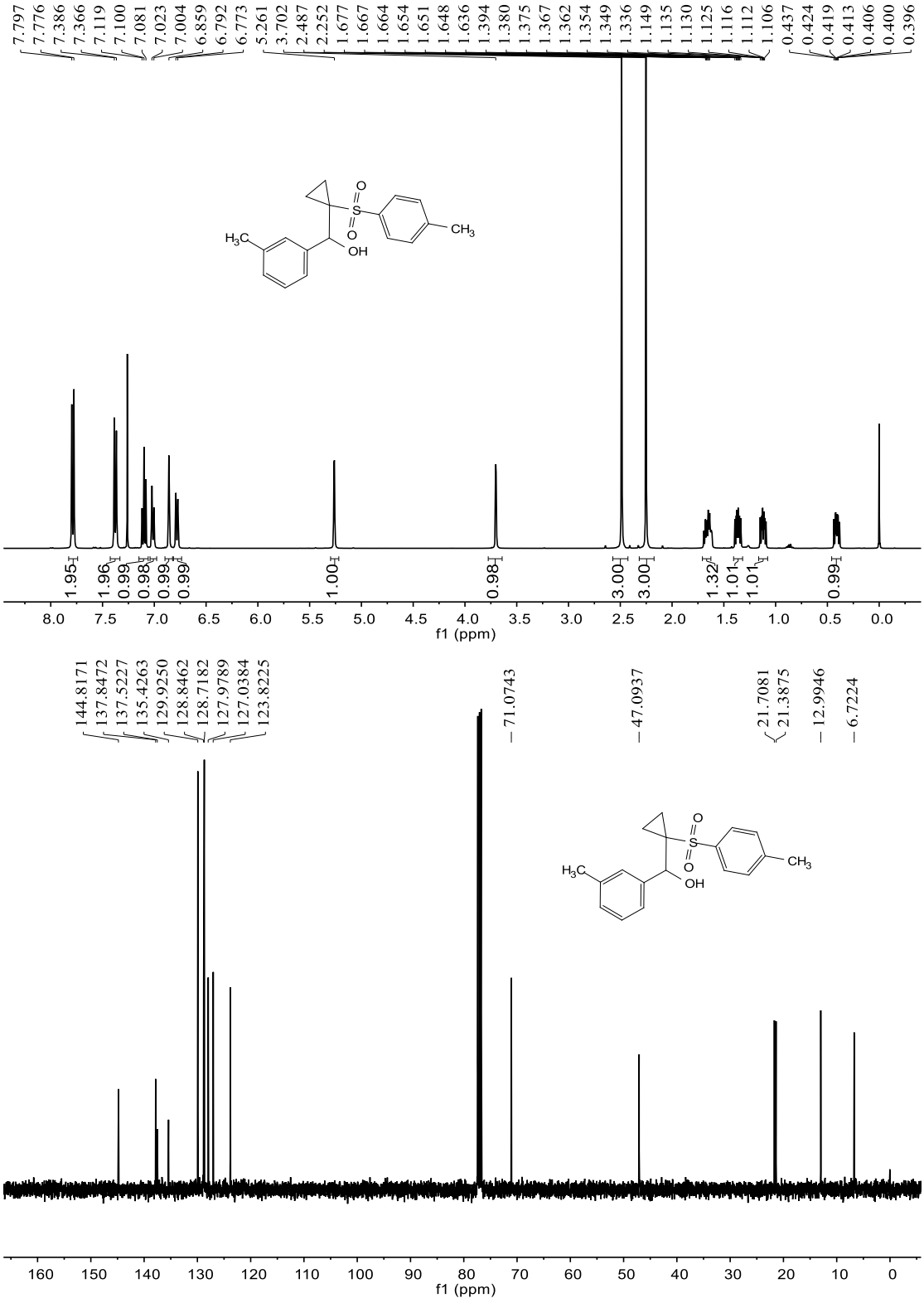




^{1}H NMR and ^{13}C NMR spectra of compound **3ta**



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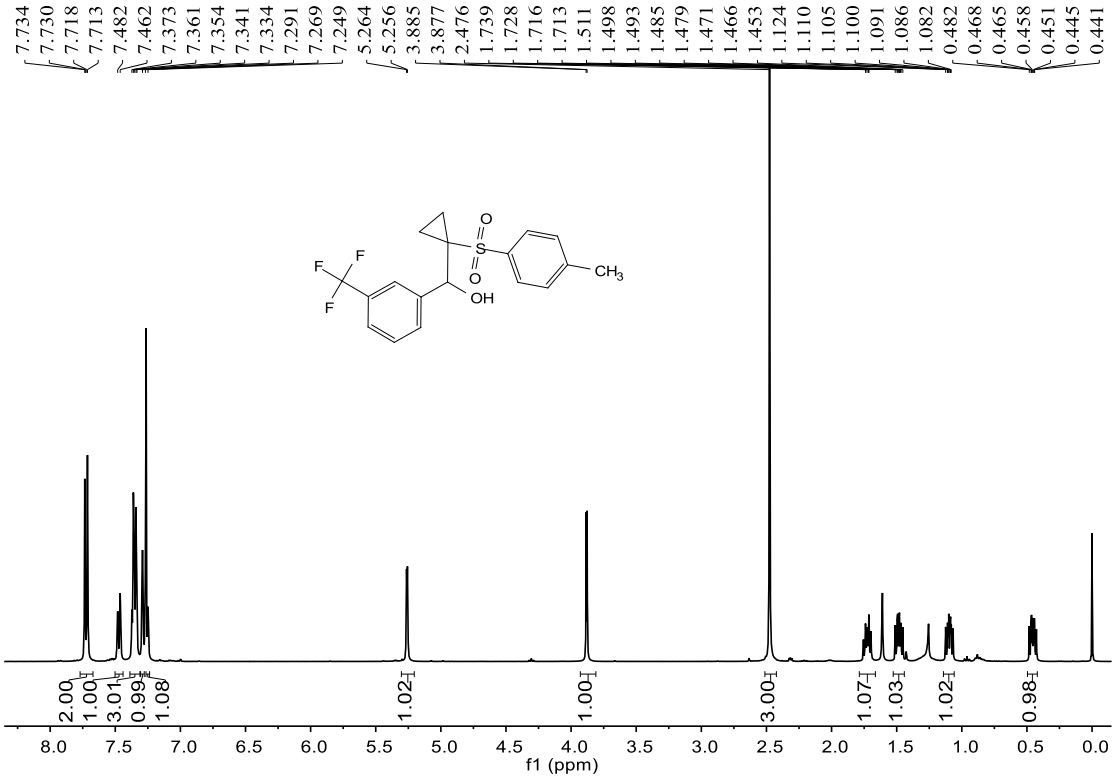

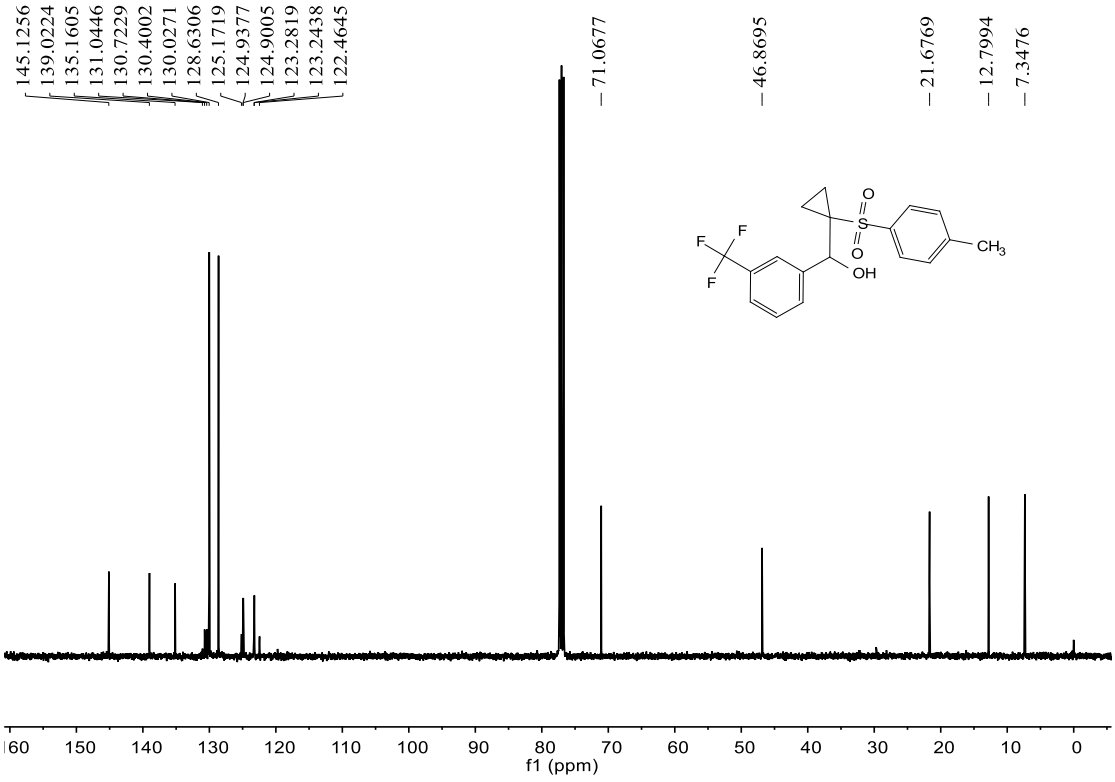

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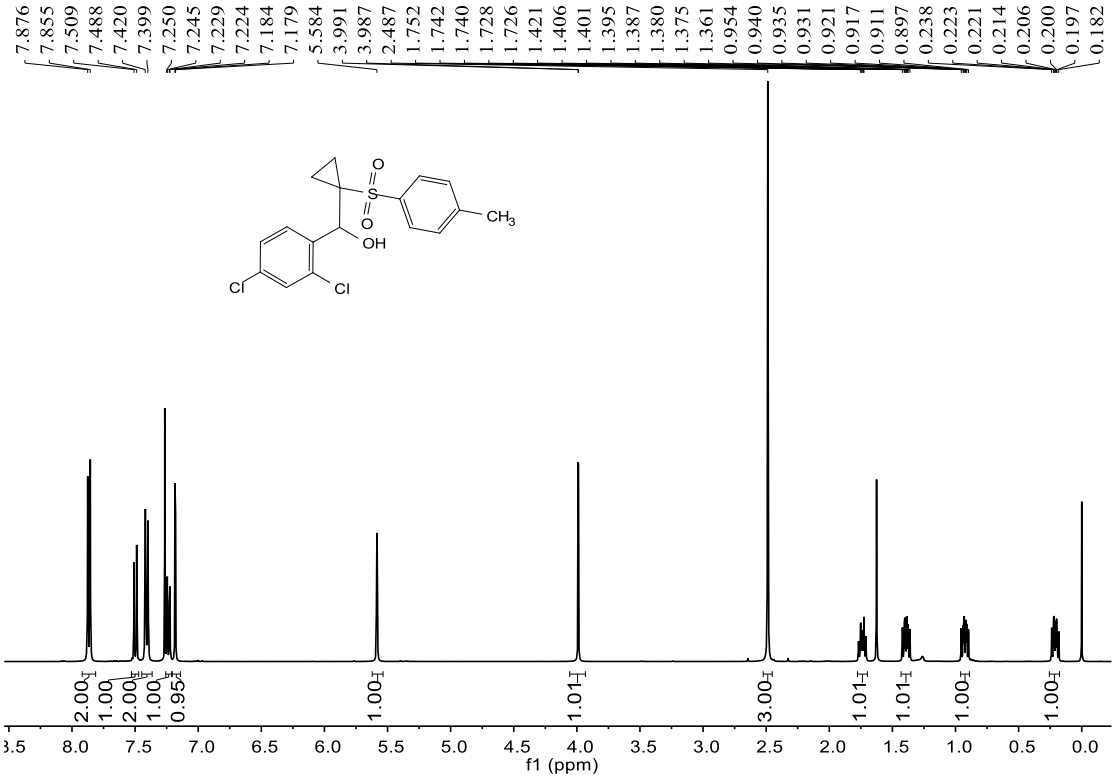
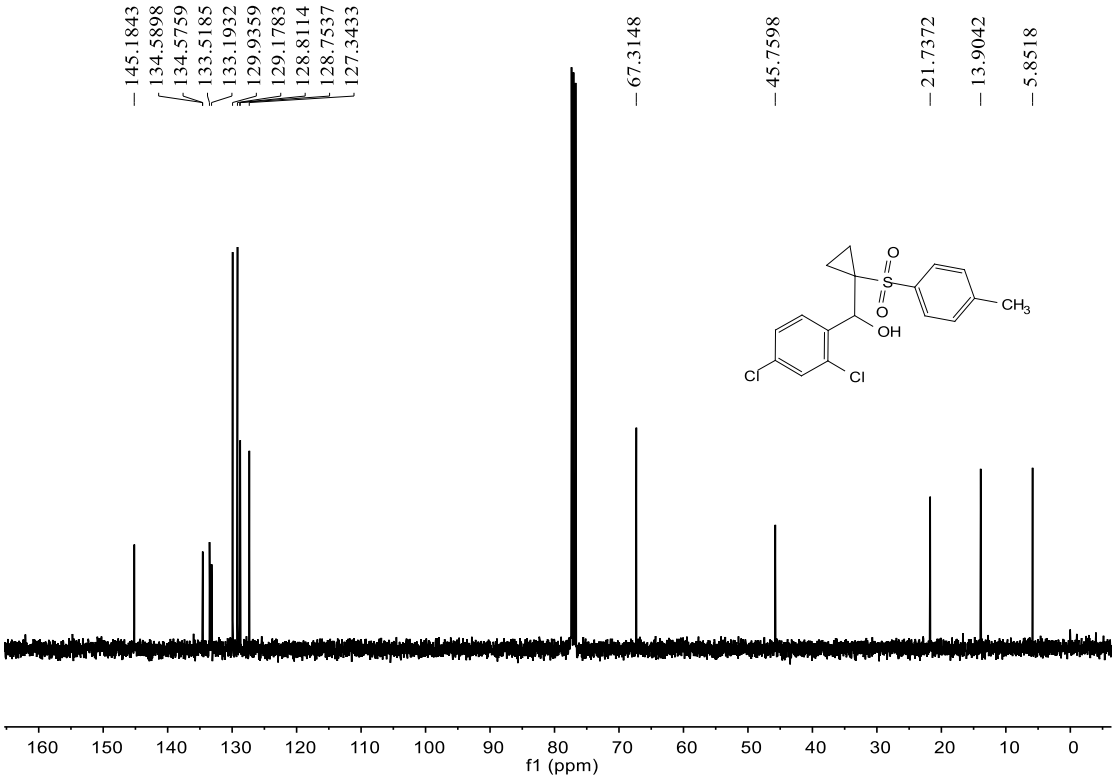
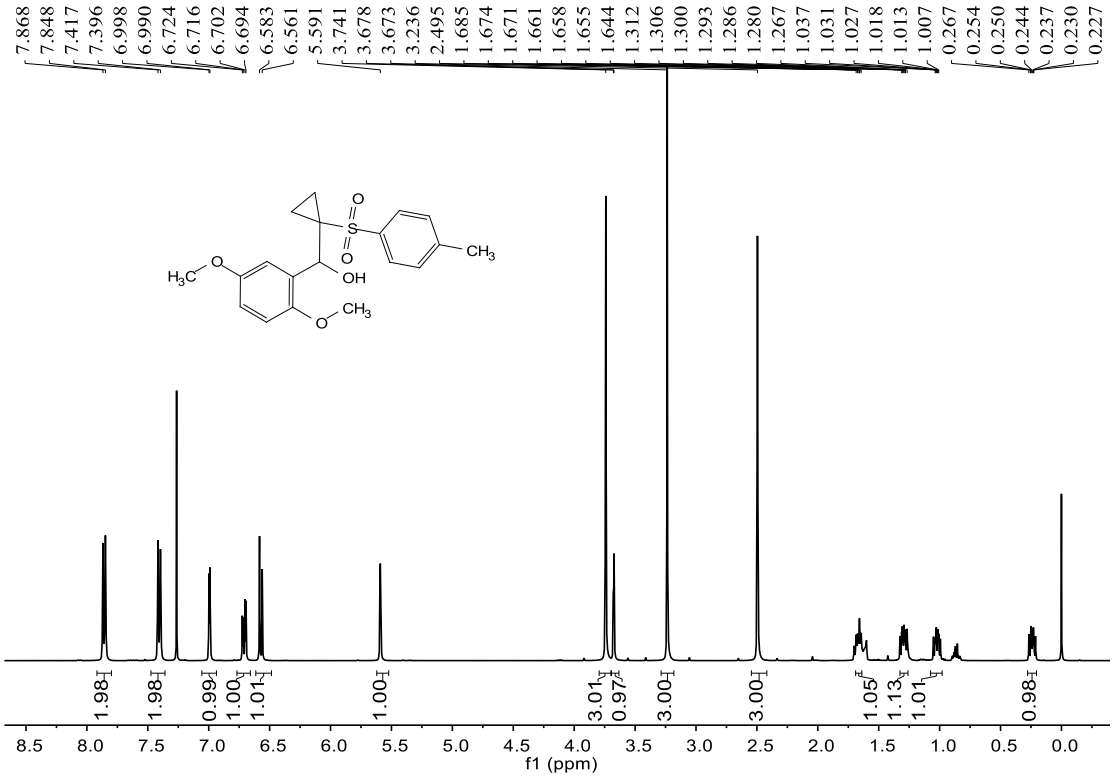
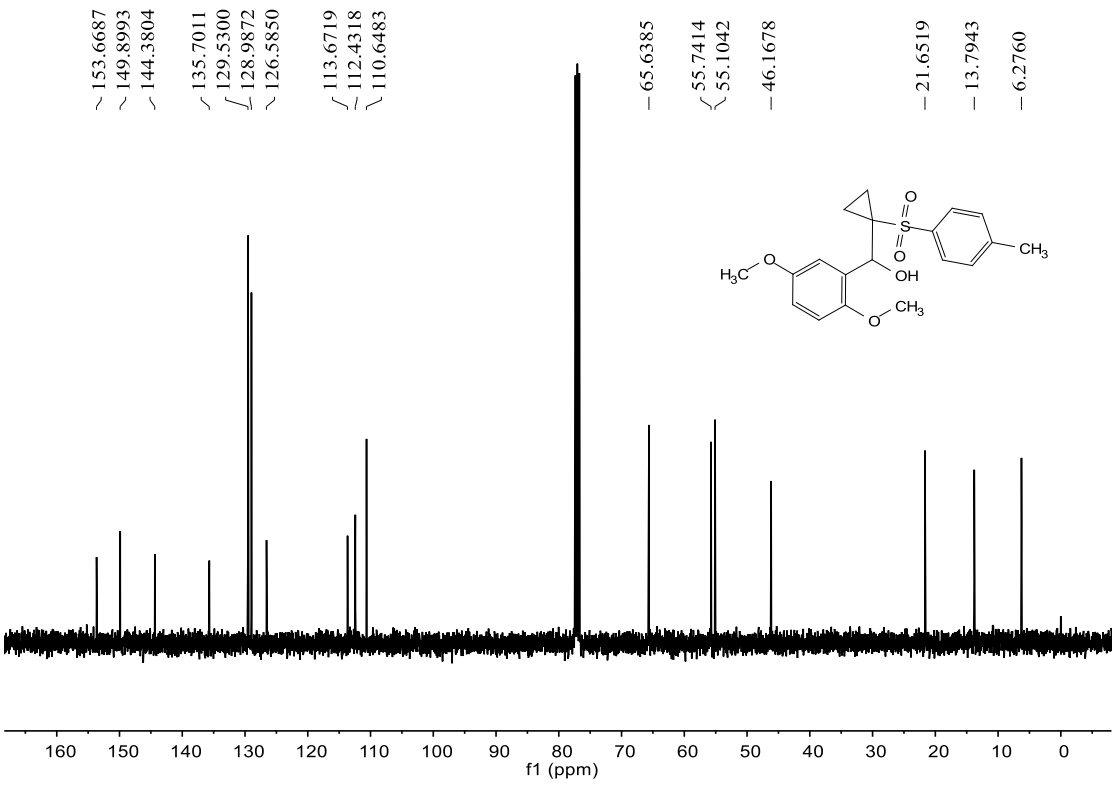


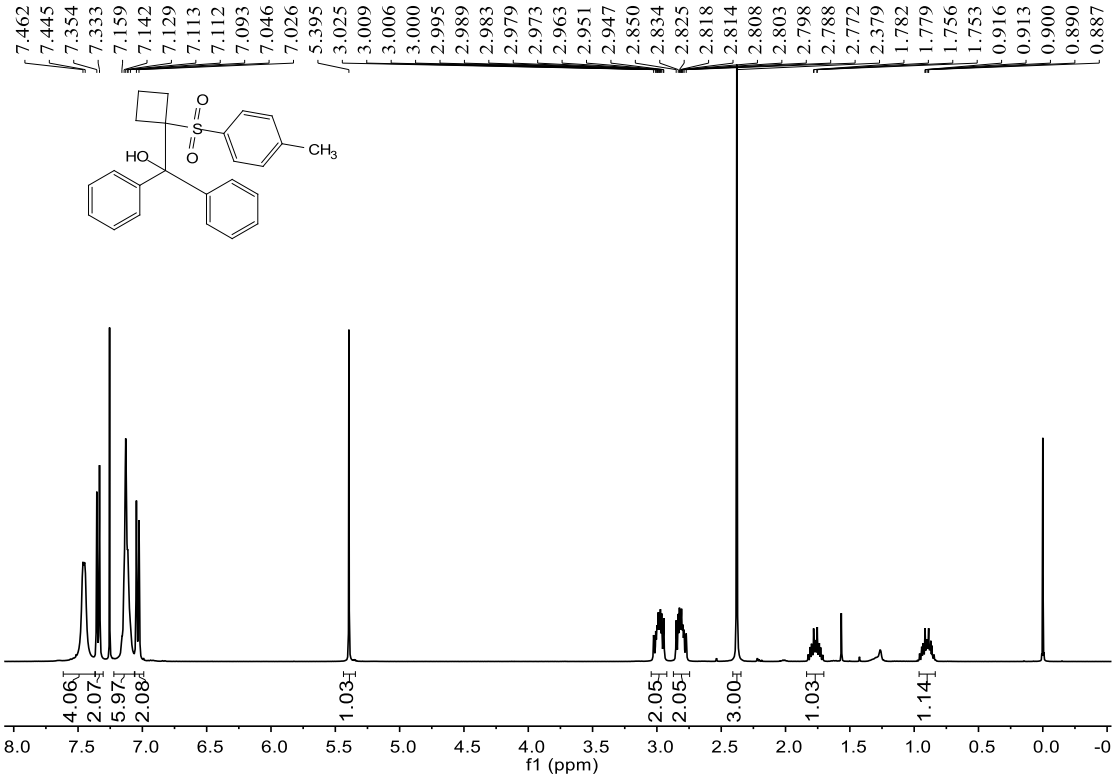


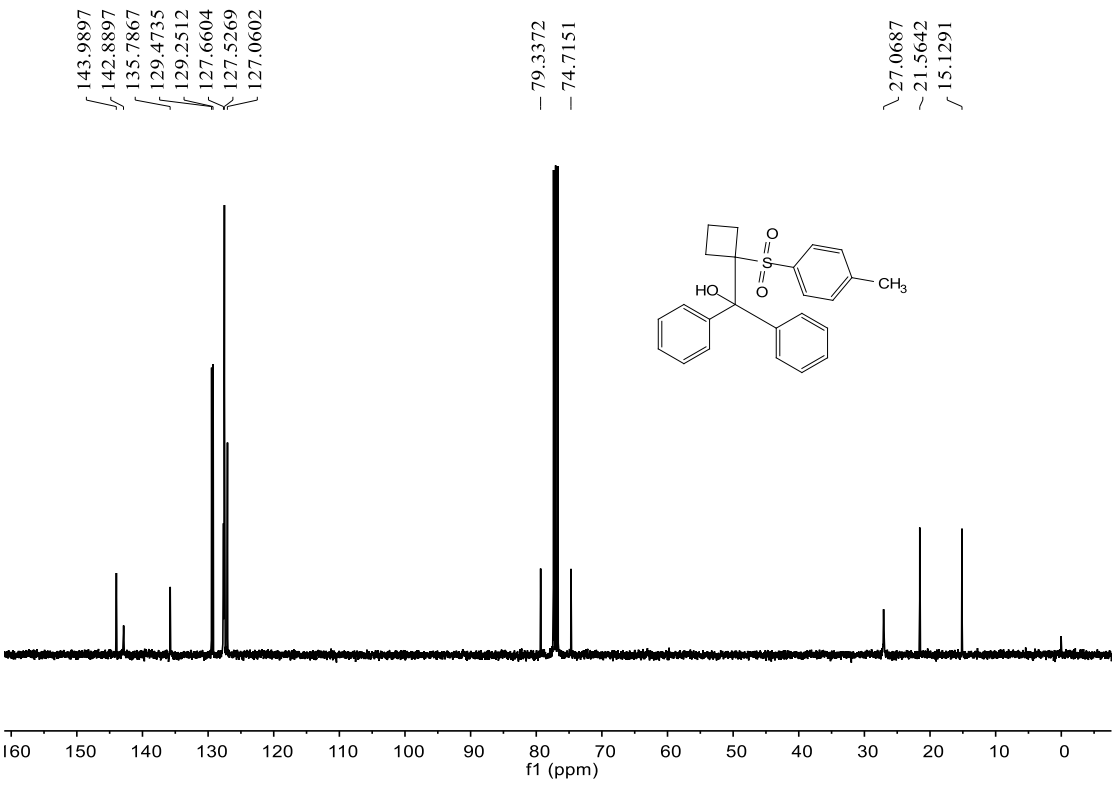
^{1}H NMR and ^{13}C NMR spectra of compound **3wa**



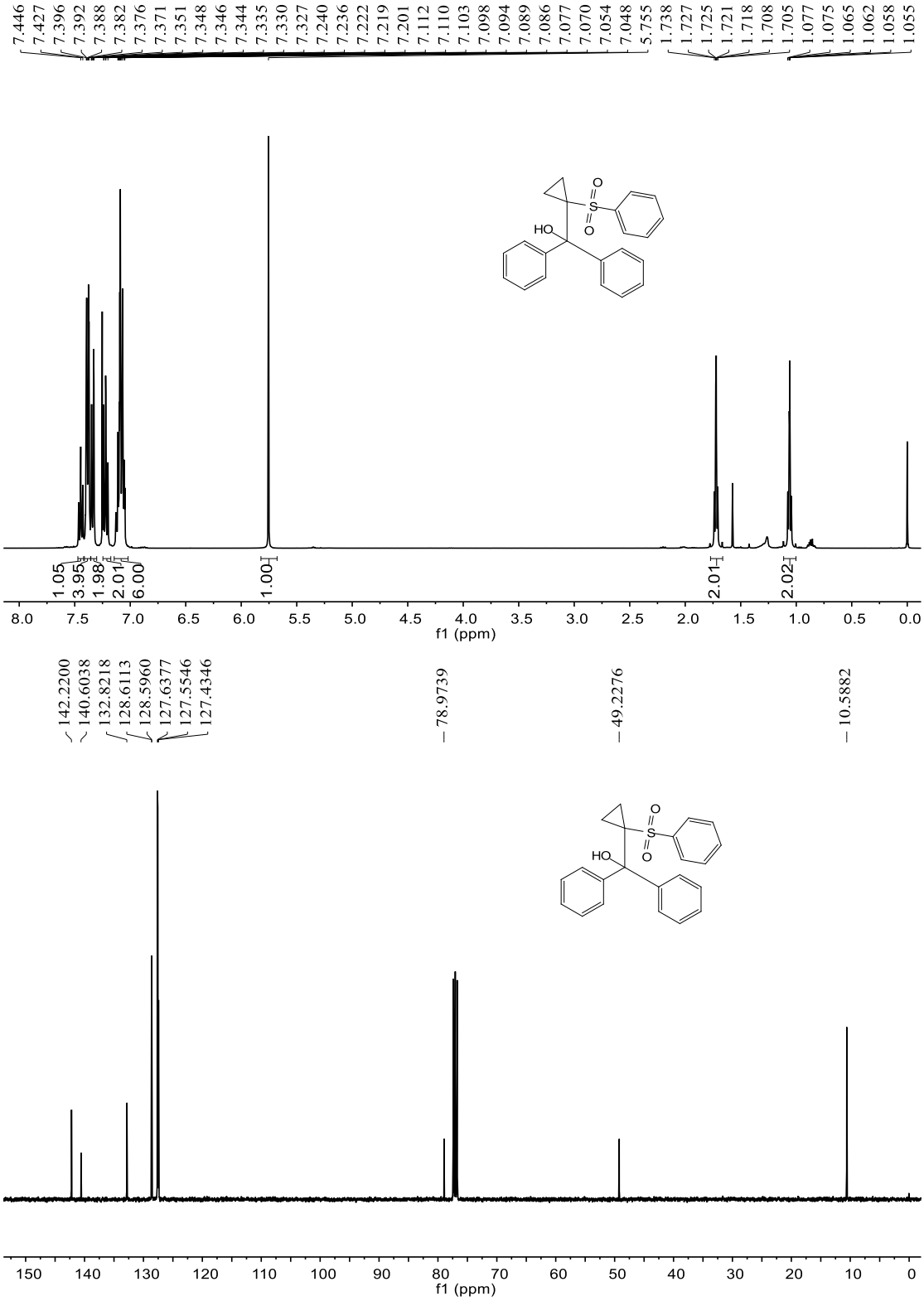


^{1}H NMR and ^{13}C NMR spectra of compound **3xa**





^{1}H NMR and ^{13}C NMR spectra of compound **3ab**



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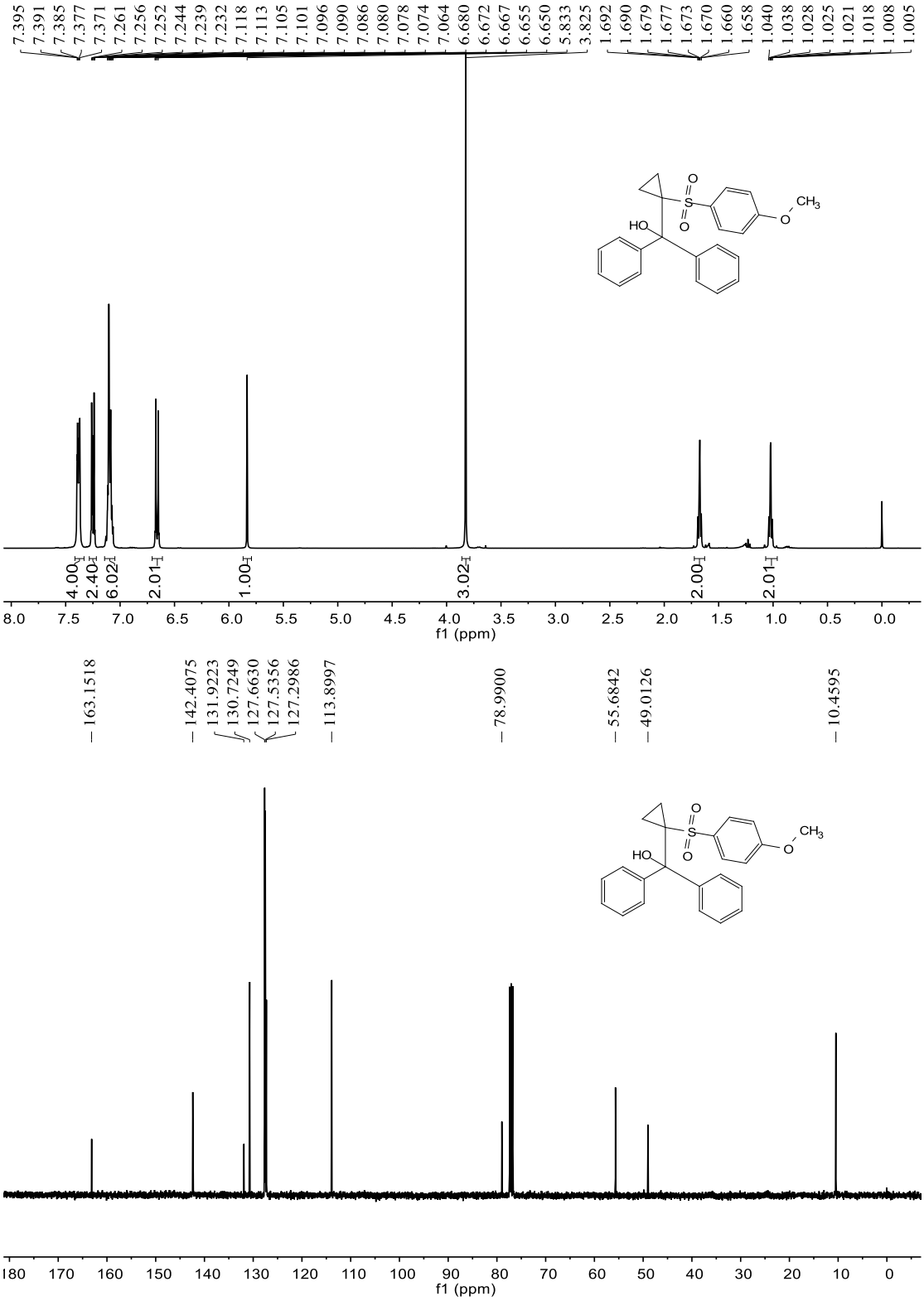

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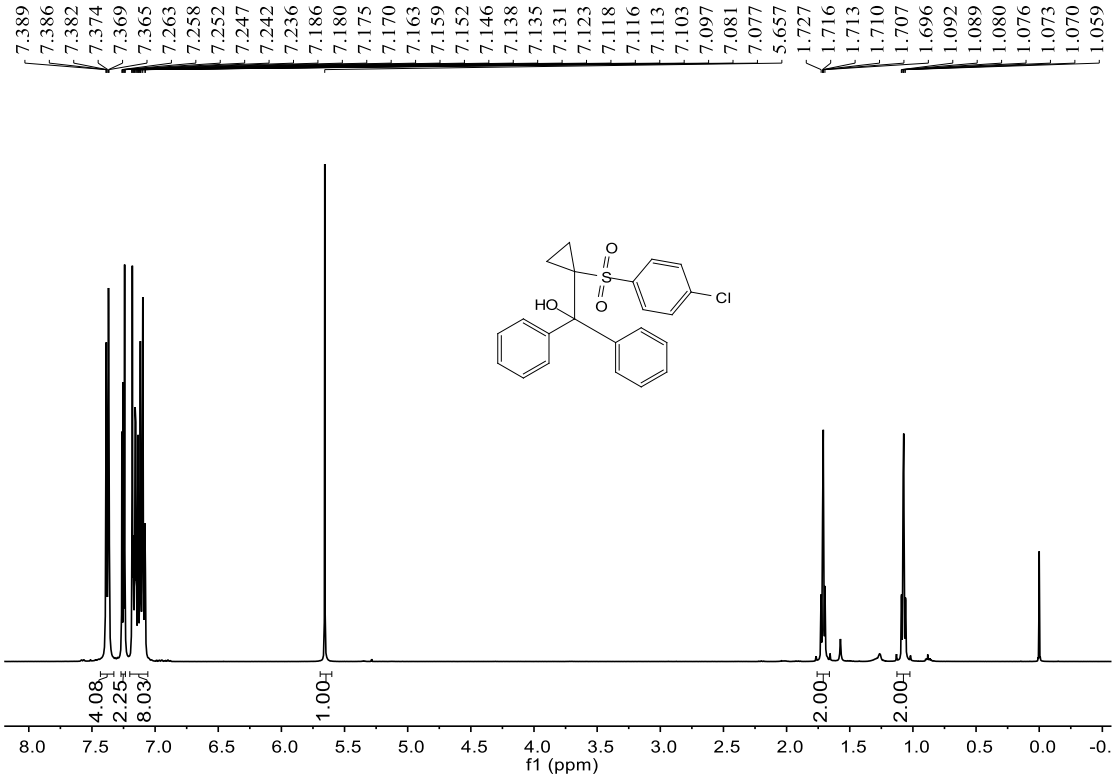
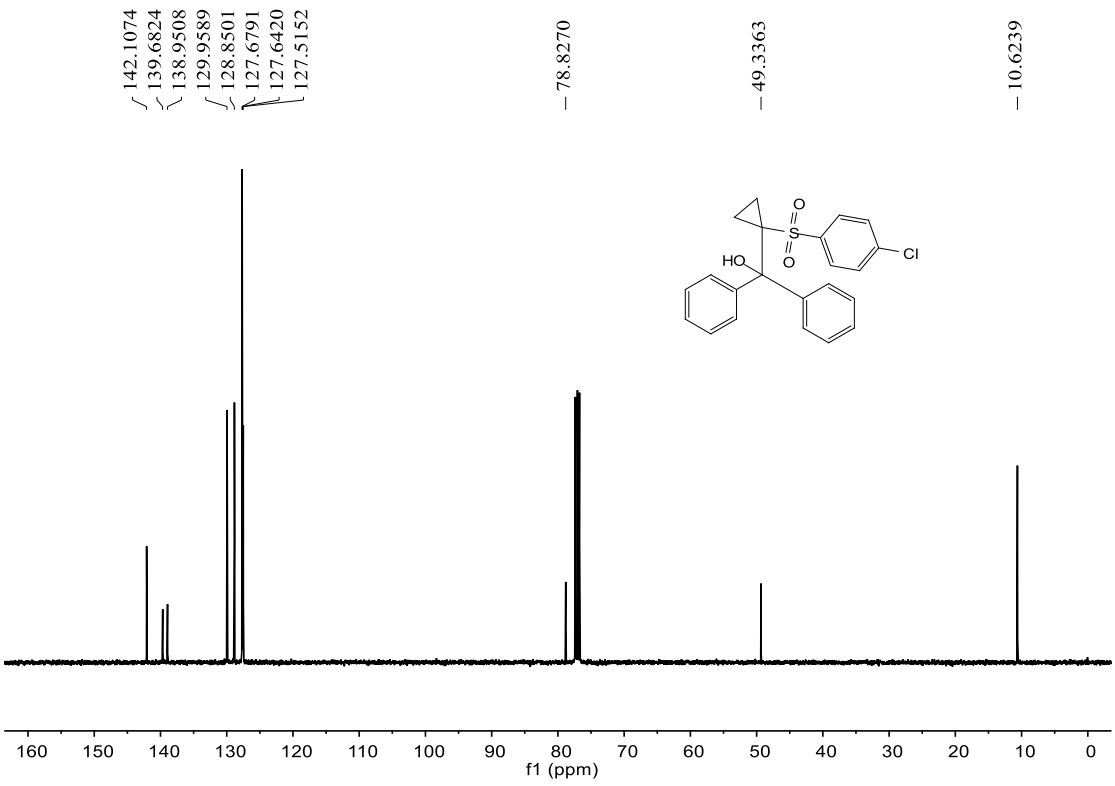
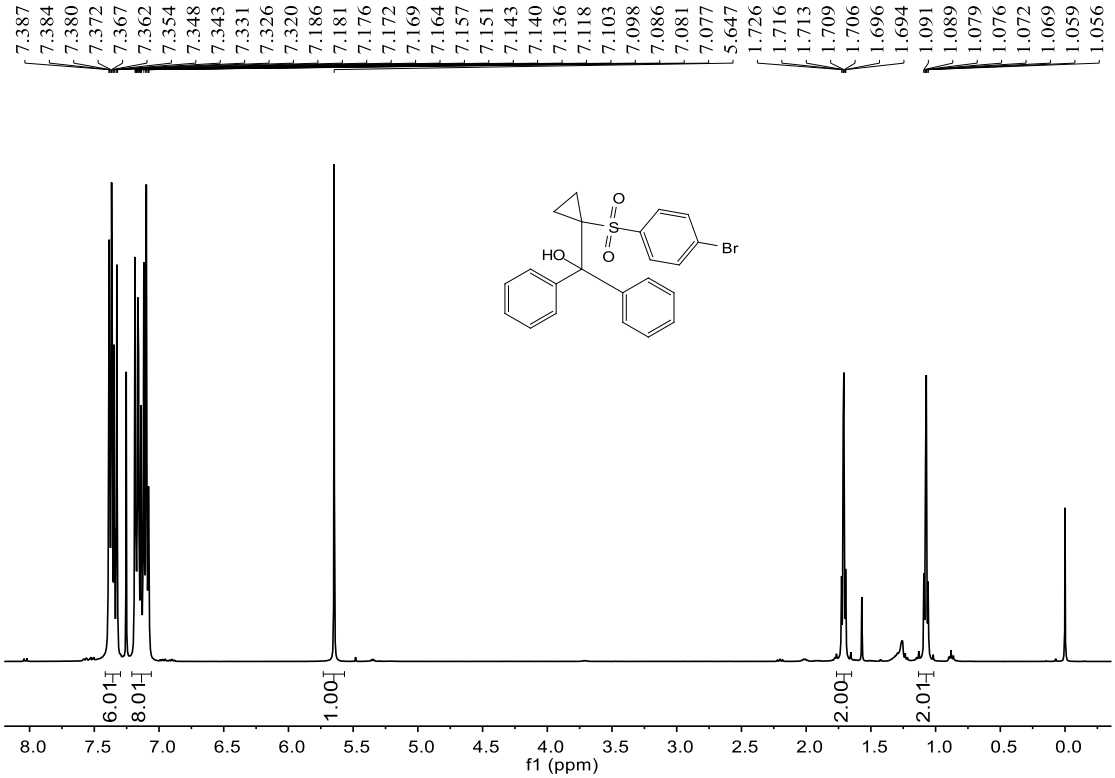
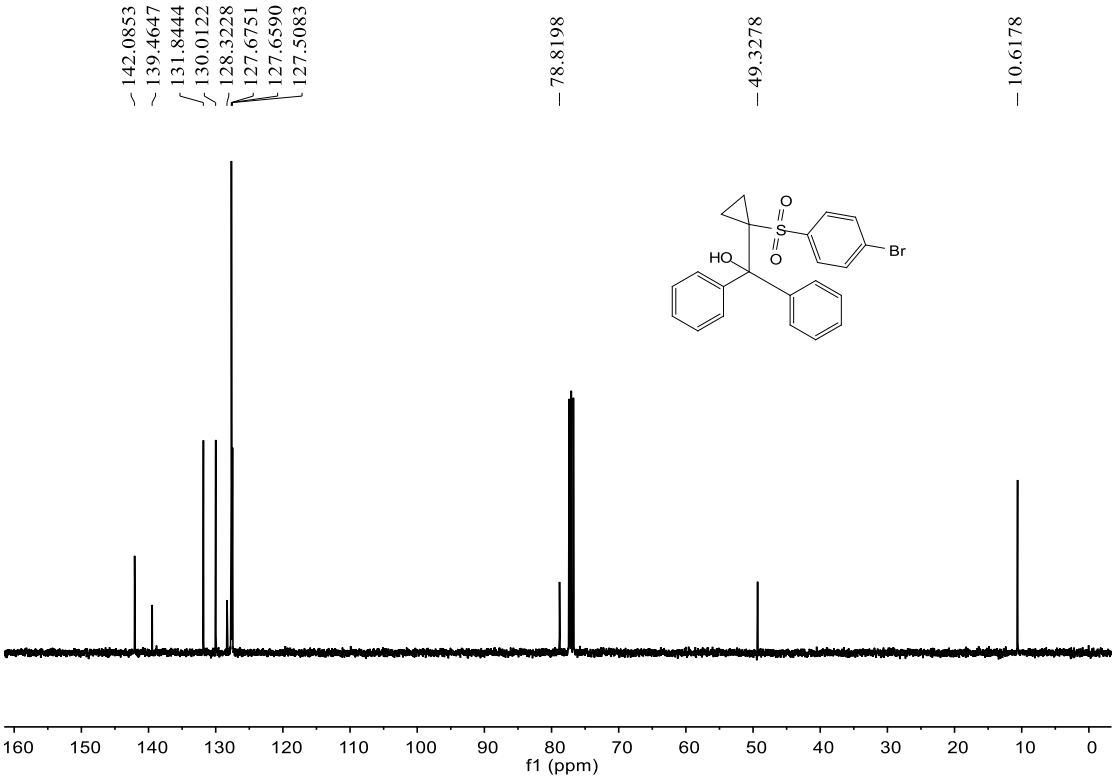


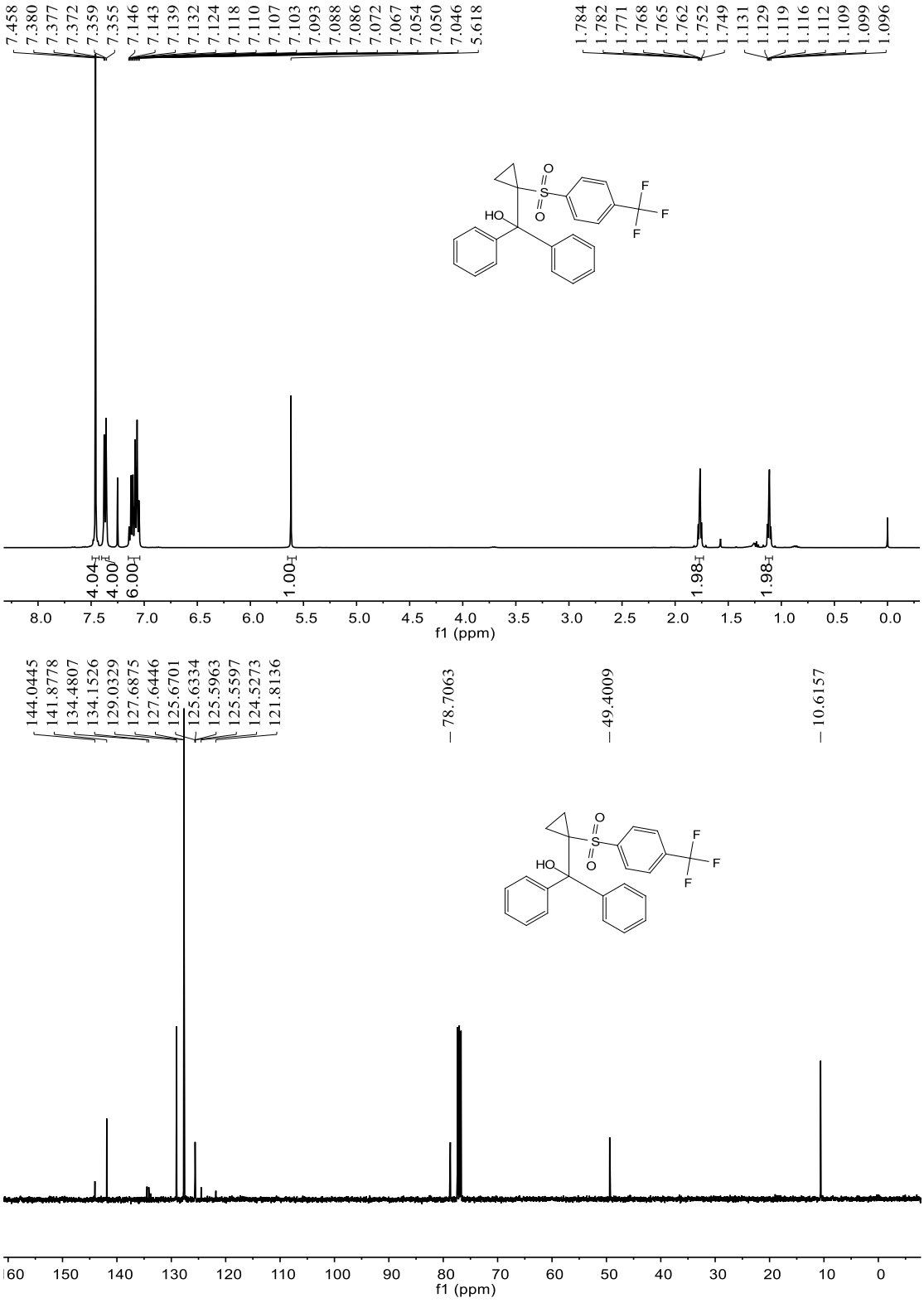


^{1}H NMR and ^{13}C NMR spectra of compound **3ae**

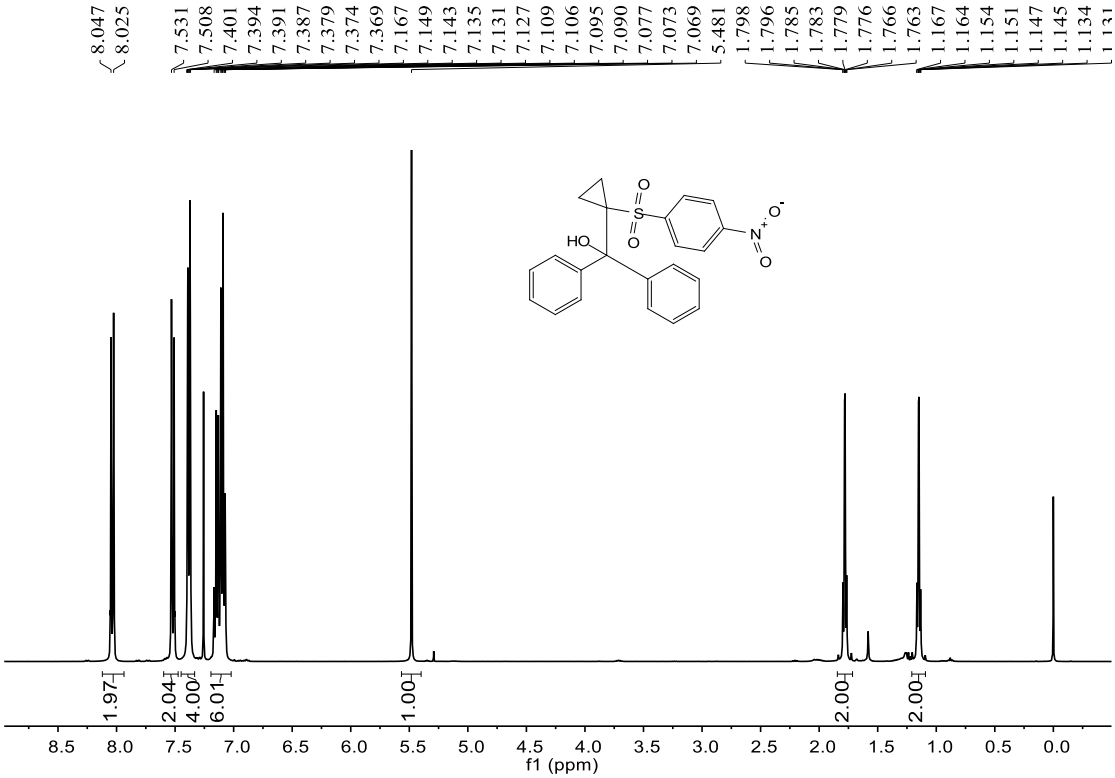


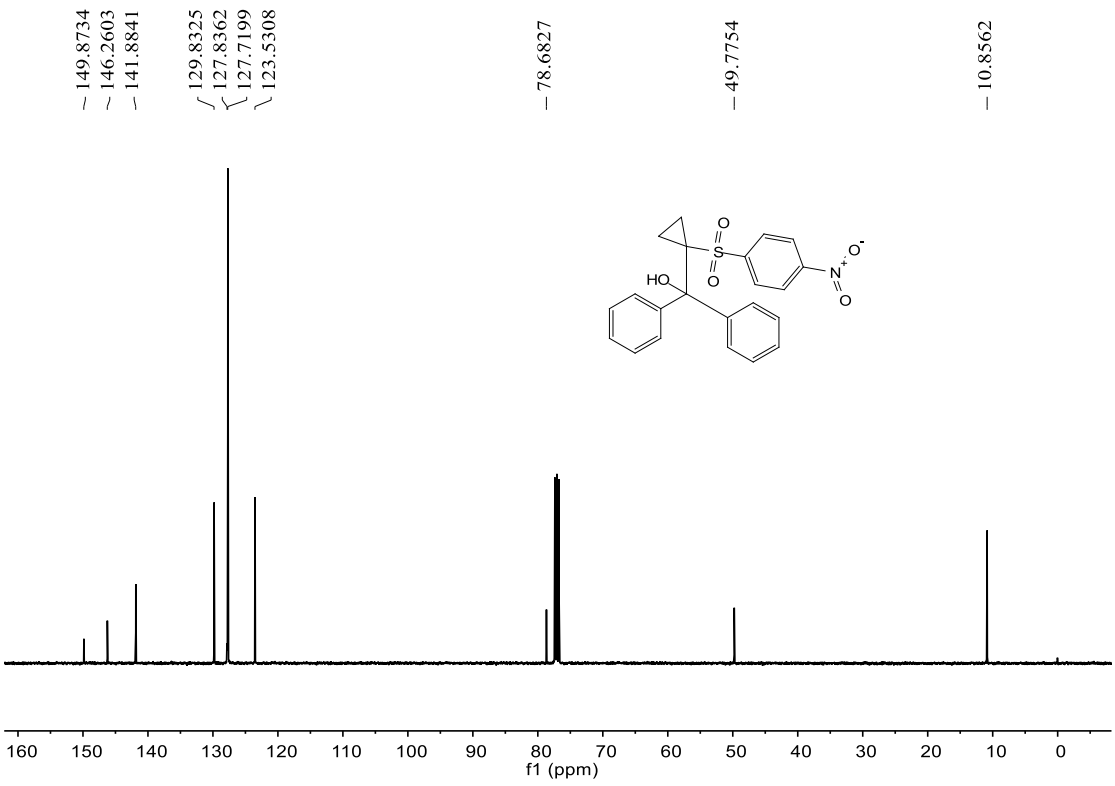


^{1}H NMR and ^{13}C NMR spectra of compound **3af**

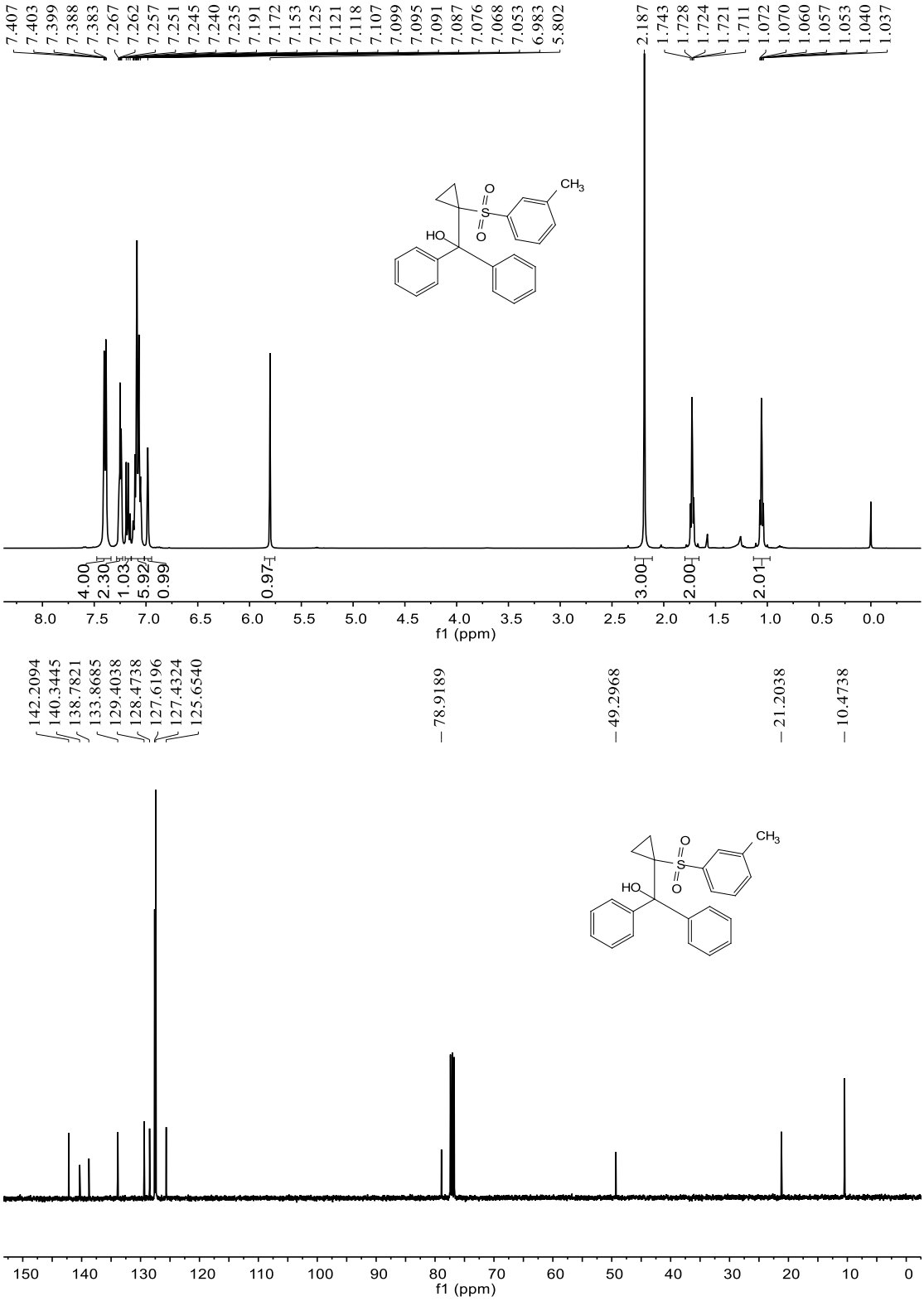


^{1}H NMR and ^{13}C NMR spectra of compound **3ag**

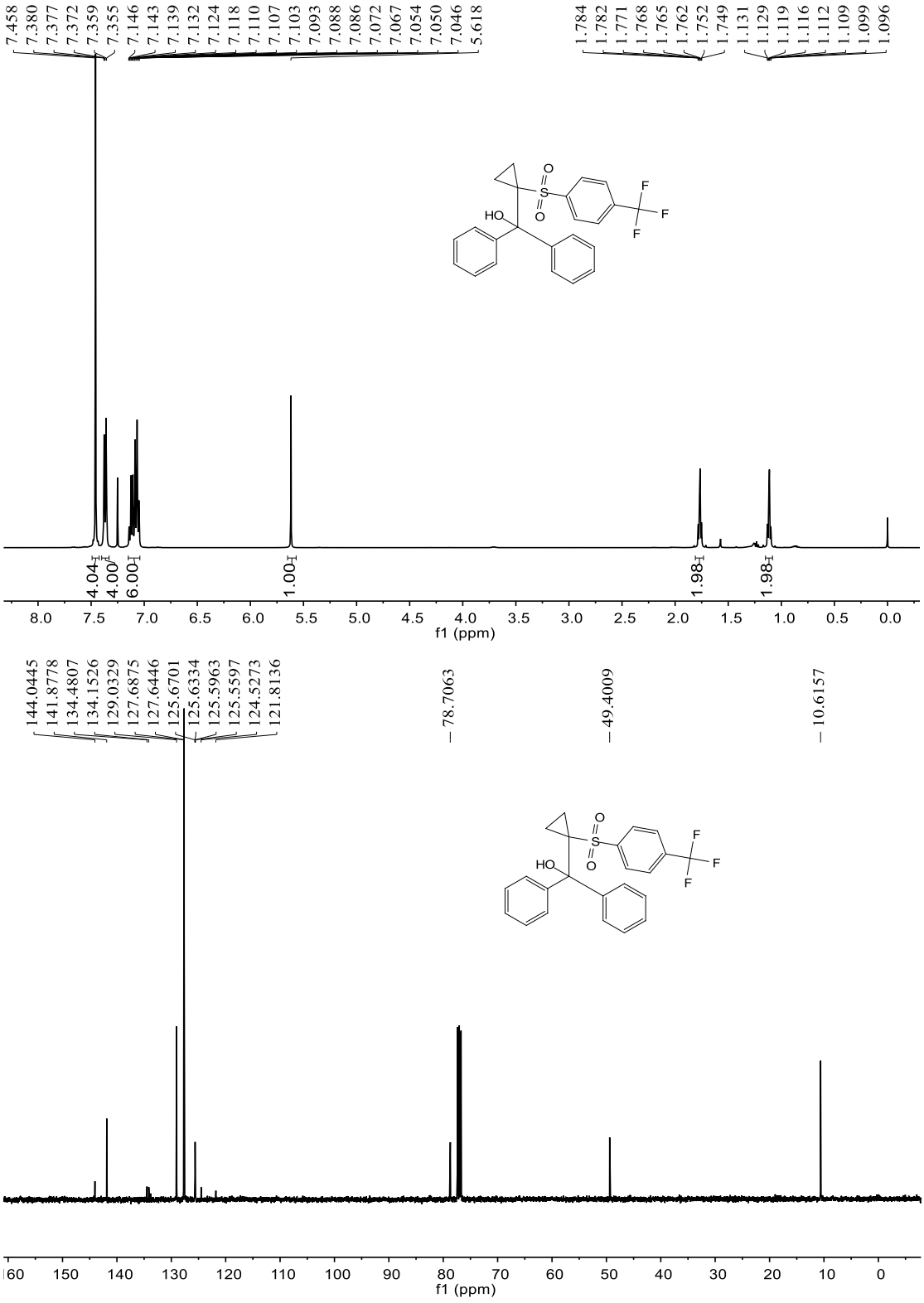




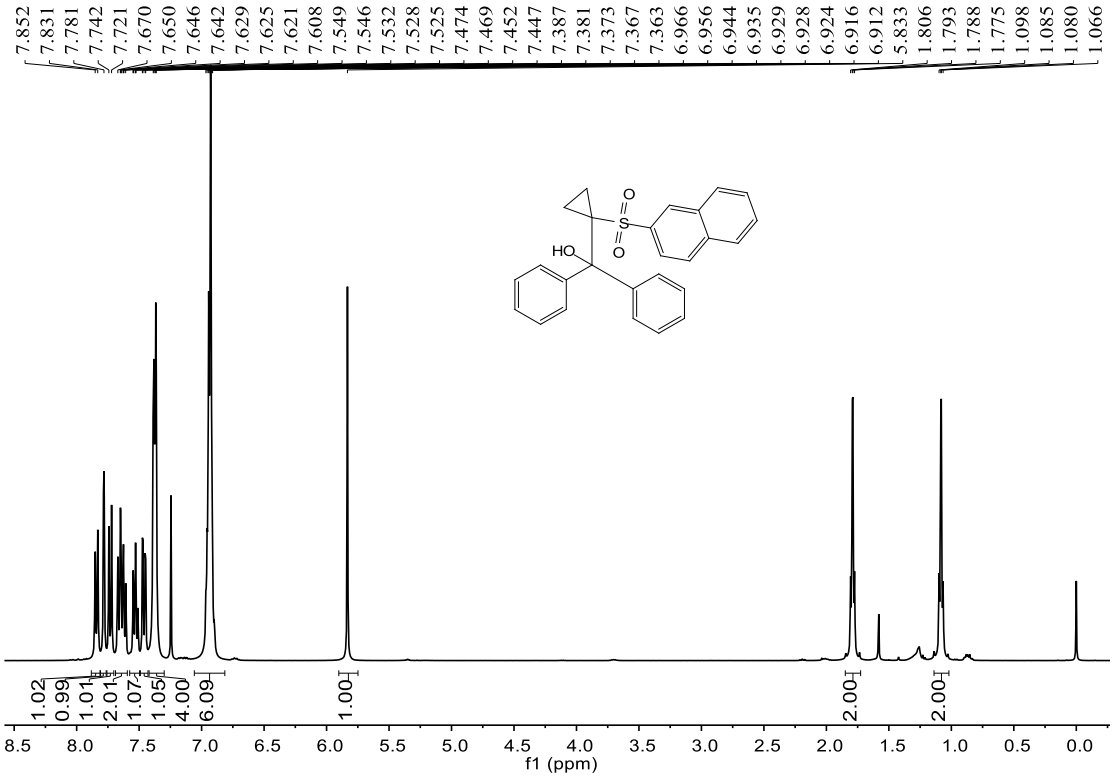
^{1}H NMR and ^{13}C NMR spectra of compound **3ah**

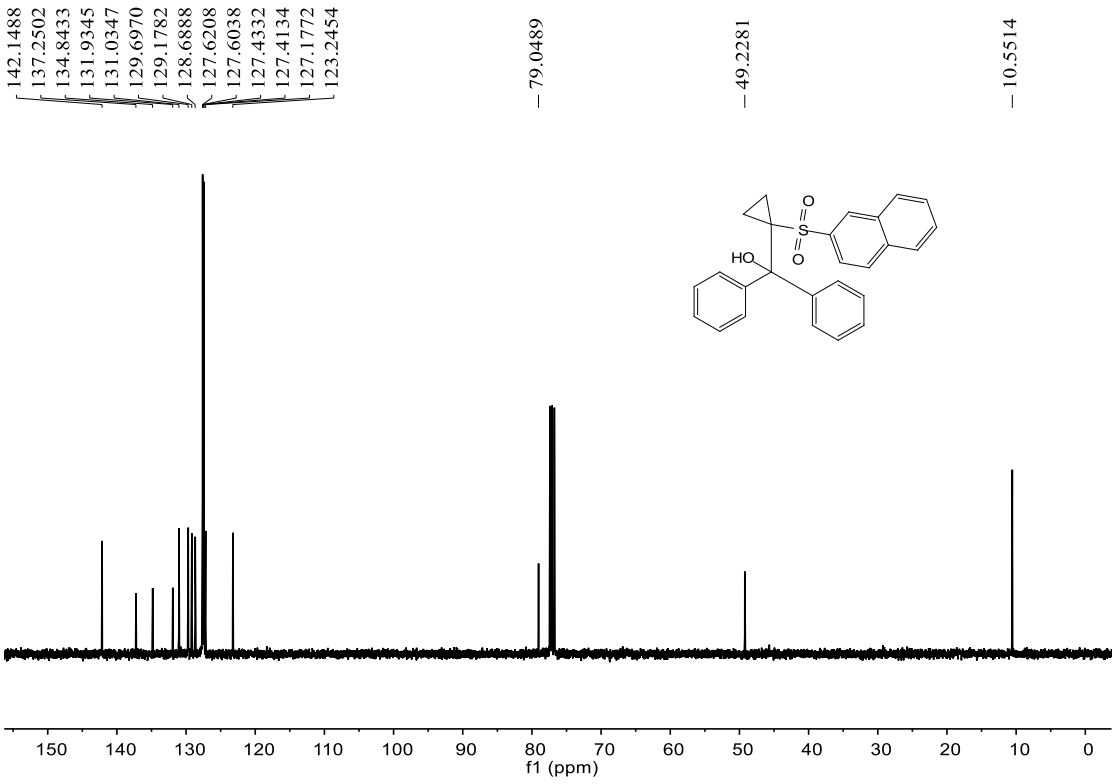


^{1}H NMR and ^{13}C NMR spectra of compound **3ai**

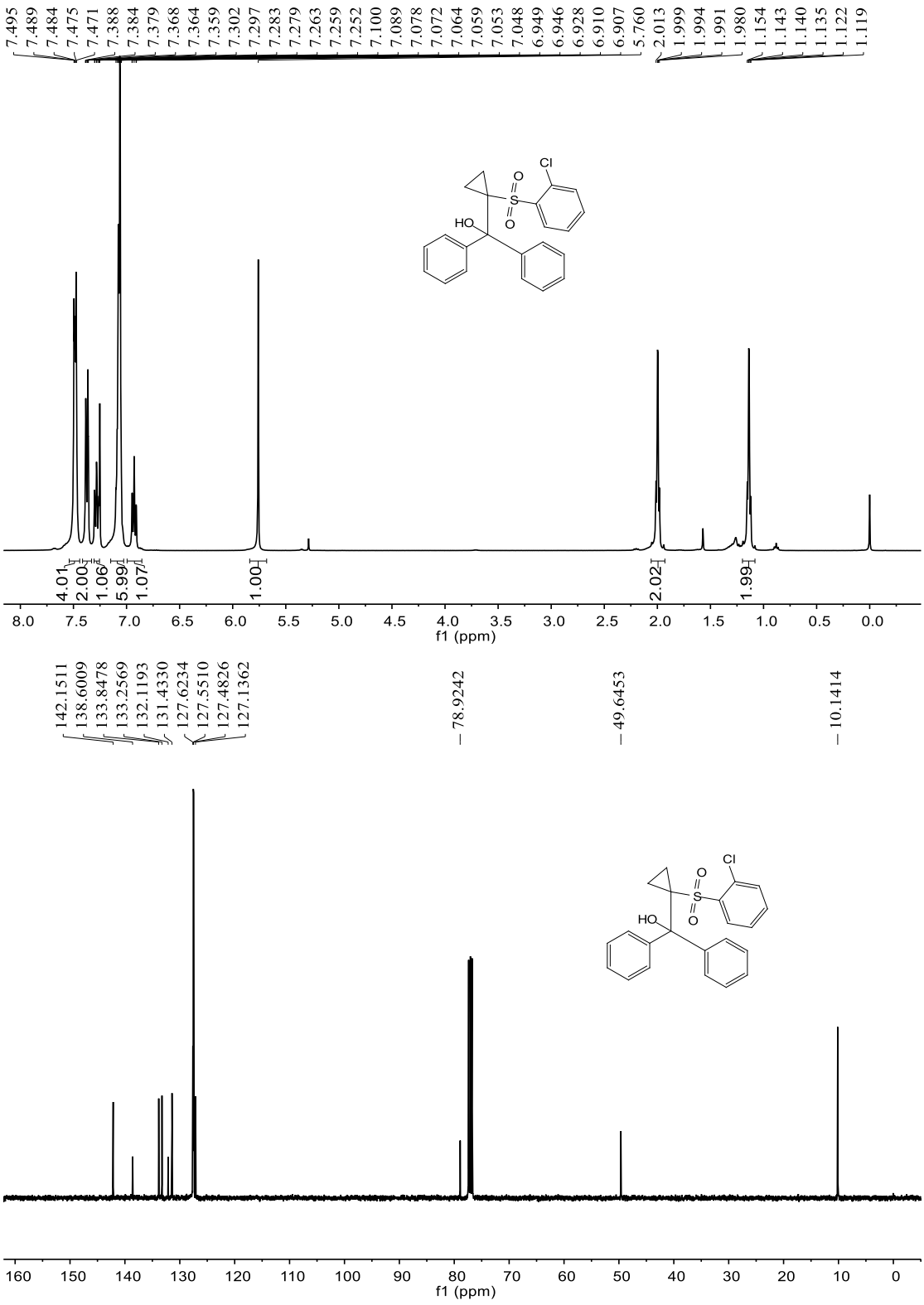


^{1}H NMR and ^{13}C NMR spectra of compound **3aj**

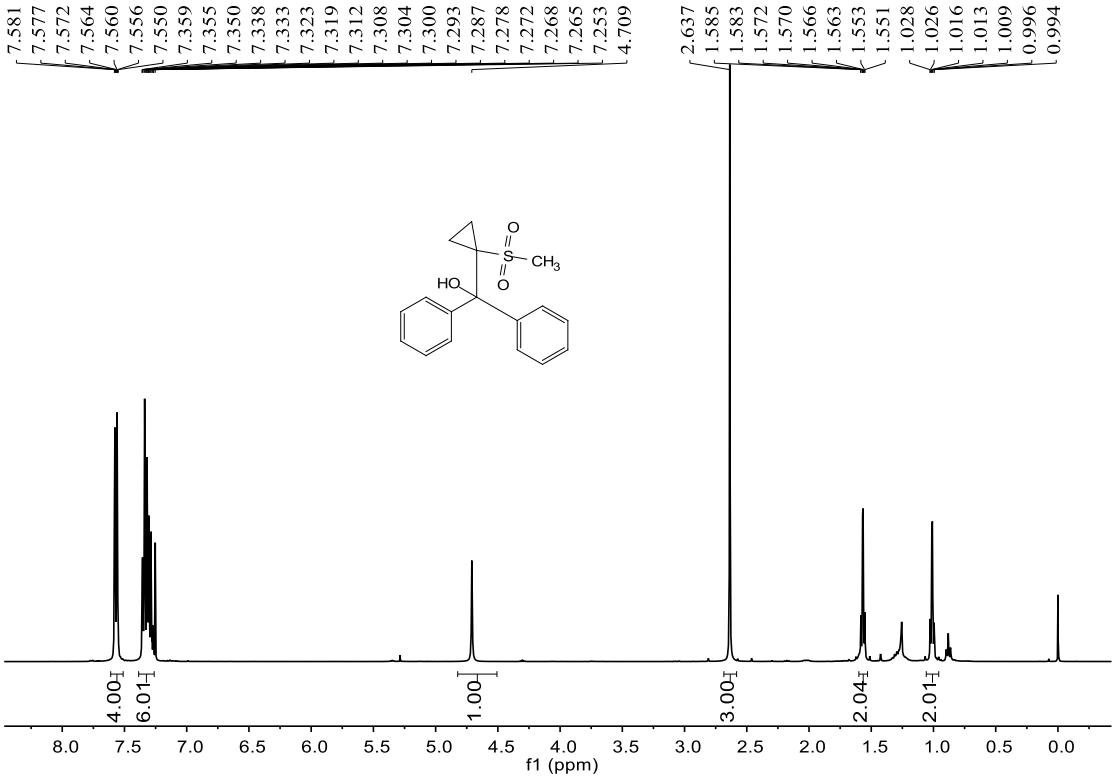


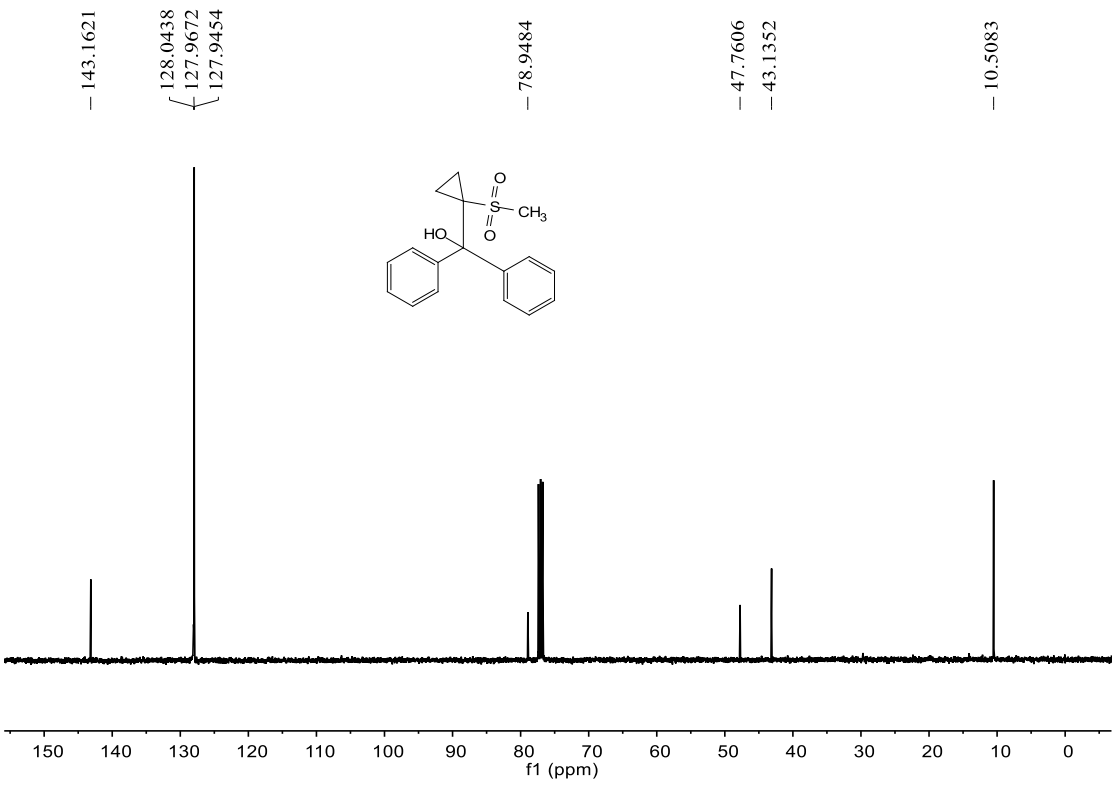


^{1}H NMR and ^{13}C NMR spectra of compound **3ak**

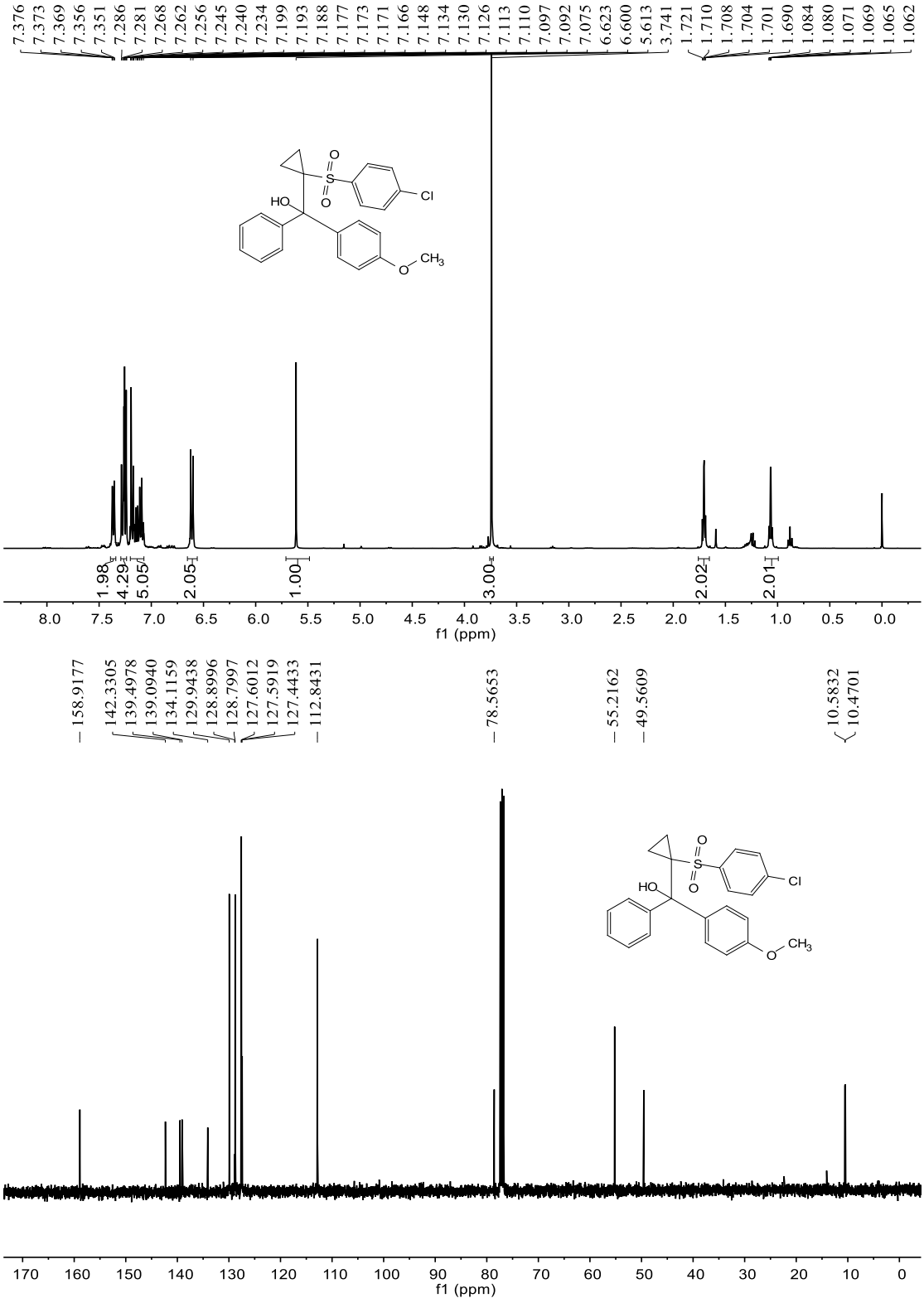


^{1}H NMR and ^{13}C NMR spectra of compound **3al**

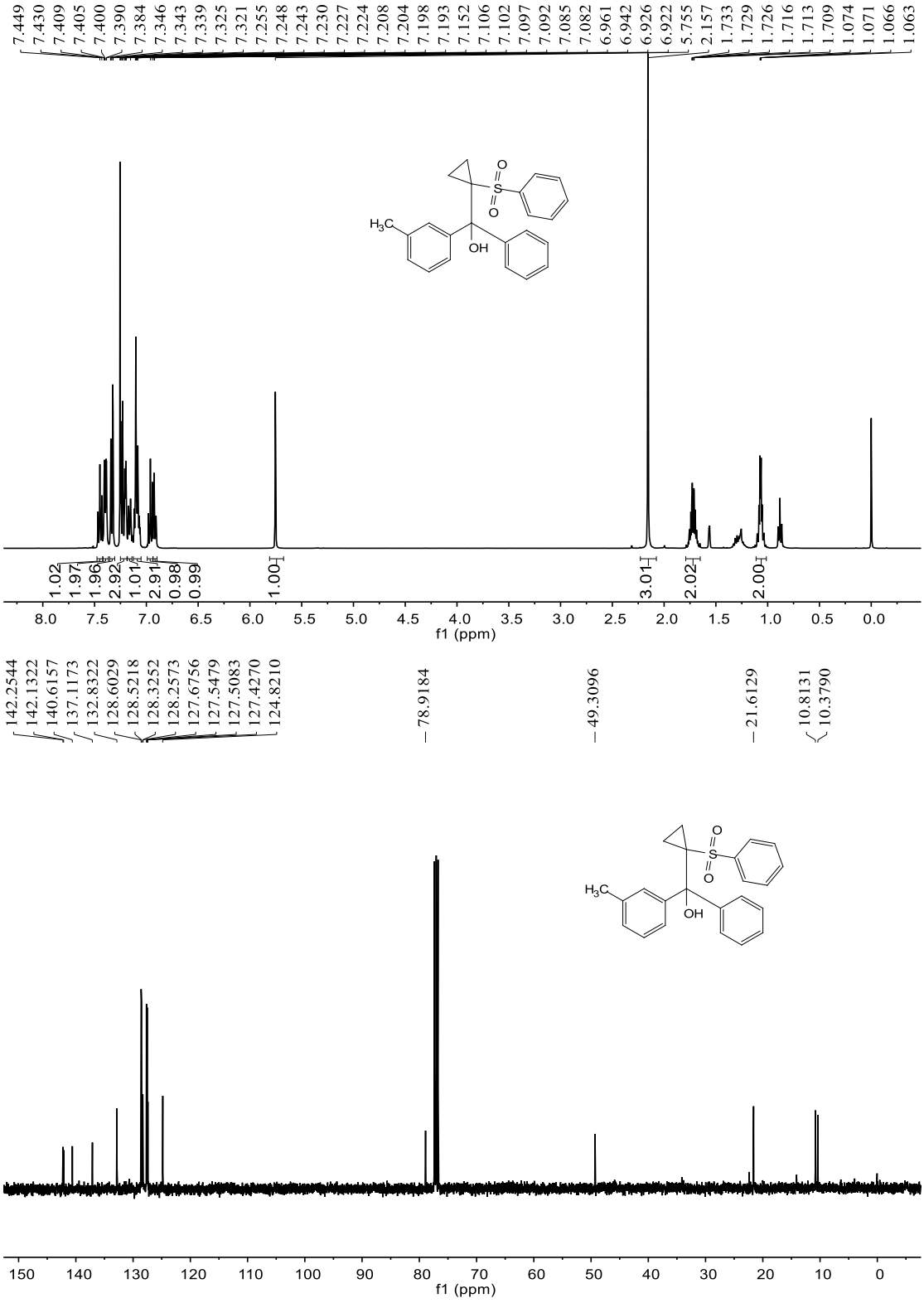




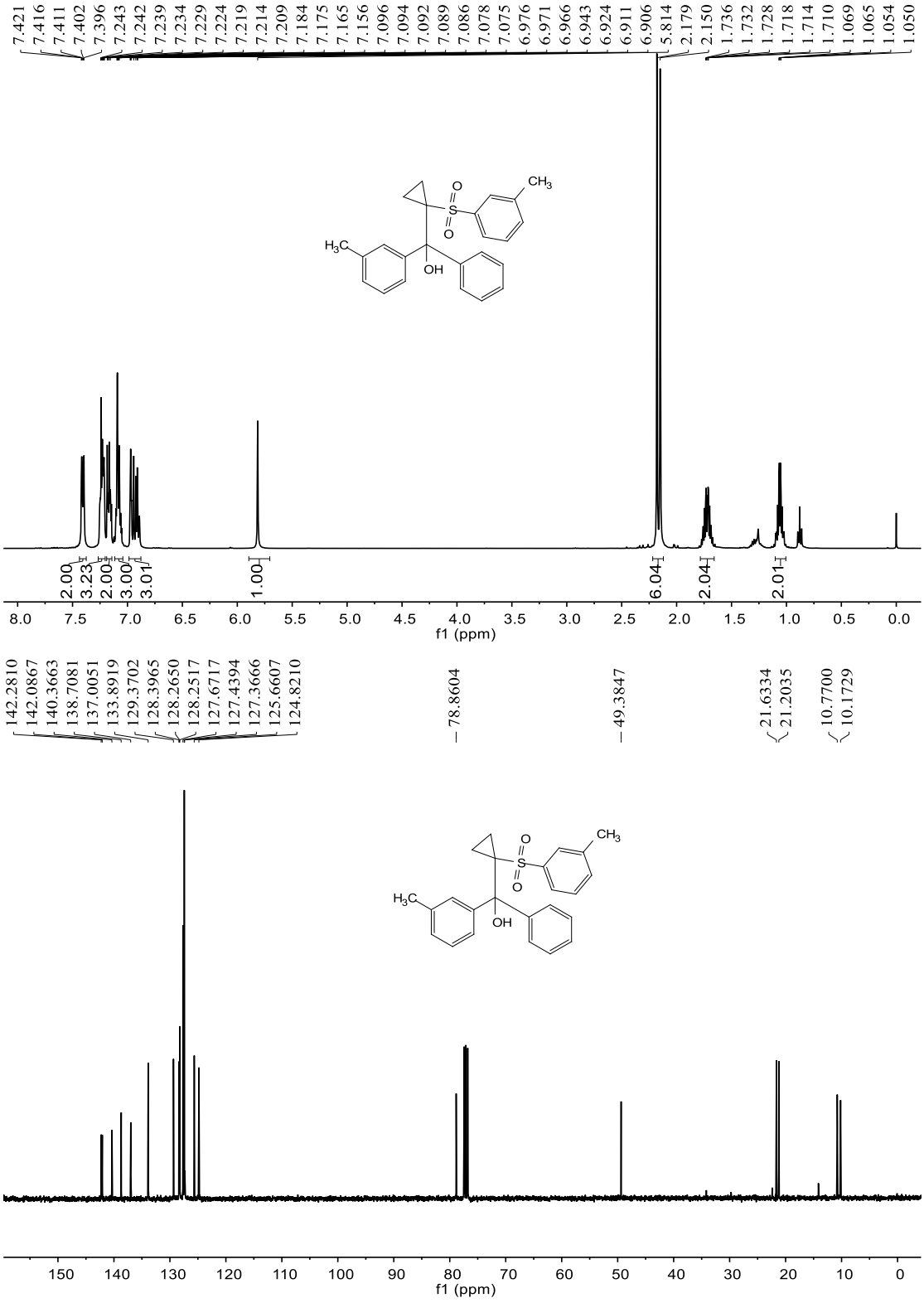
^{1}H NMR and ^{13}C NMR spectra of compound **3gd**



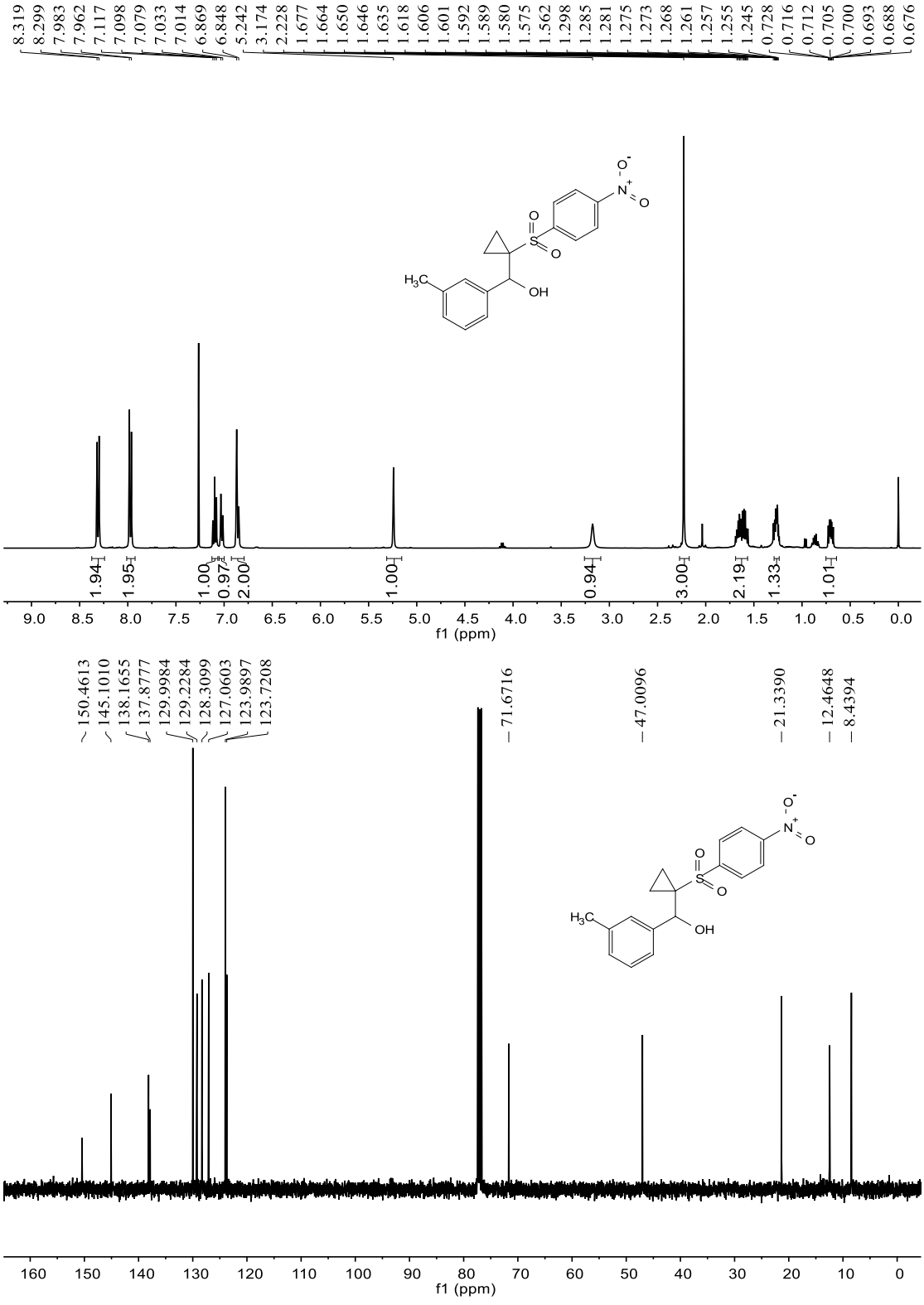
^{1}H NMR and ^{13}C NMR spectra of compound **3kb**



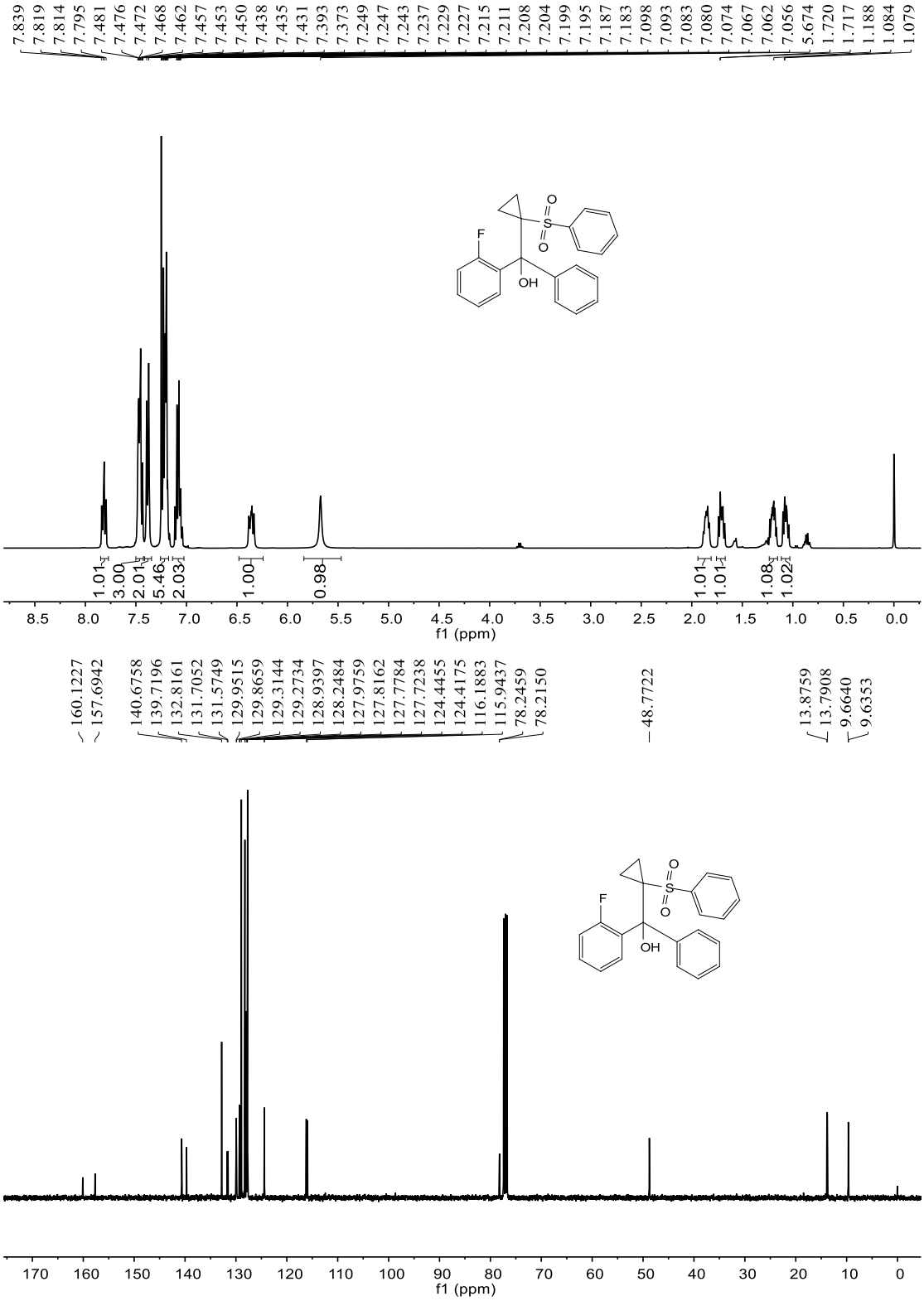
^{1}H NMR and ^{13}C NMR spectra of compound **3kh**



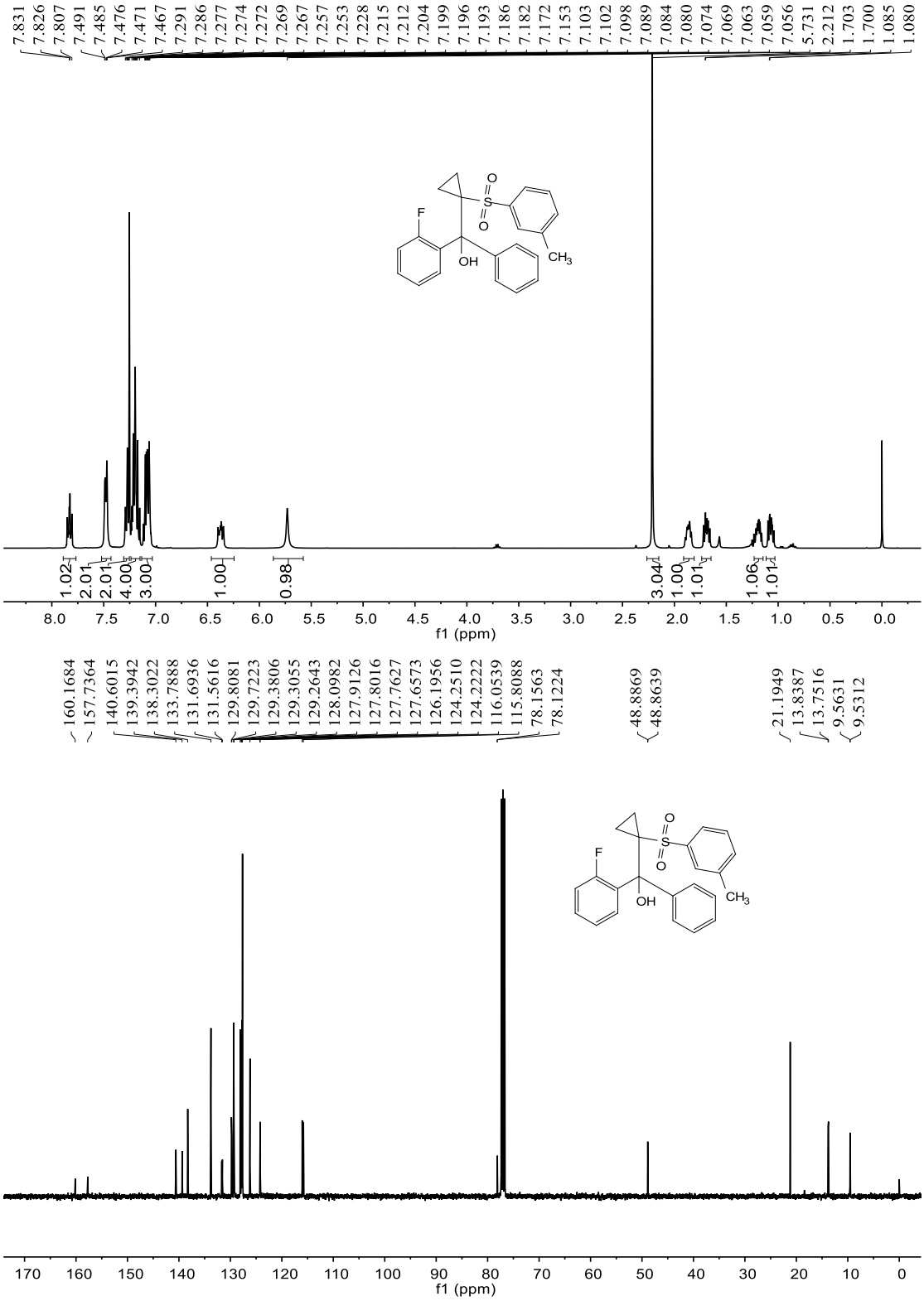
^{1}H NMR and ^{13}C NMR spectra of compound **3kg**



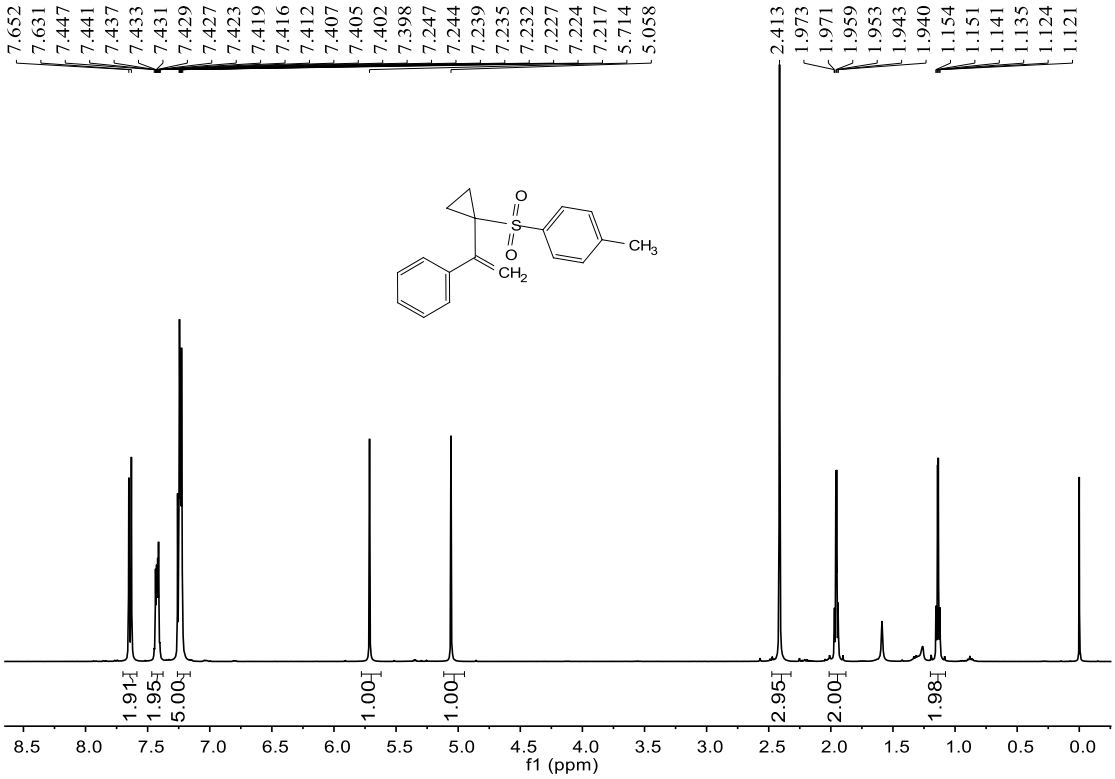
^{1}H NMR and ^{13}C NMR spectra of compound **3nb**

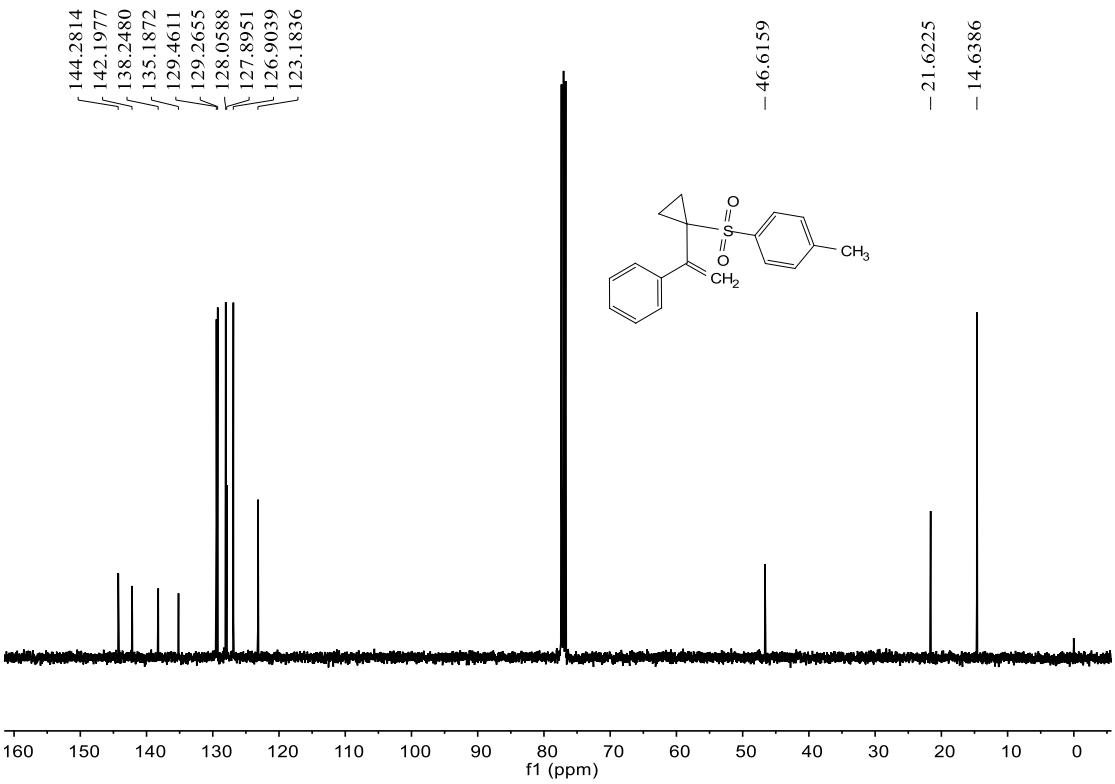


^{1}H NMR and ^{13}C NMR spectra of compound **3nh**

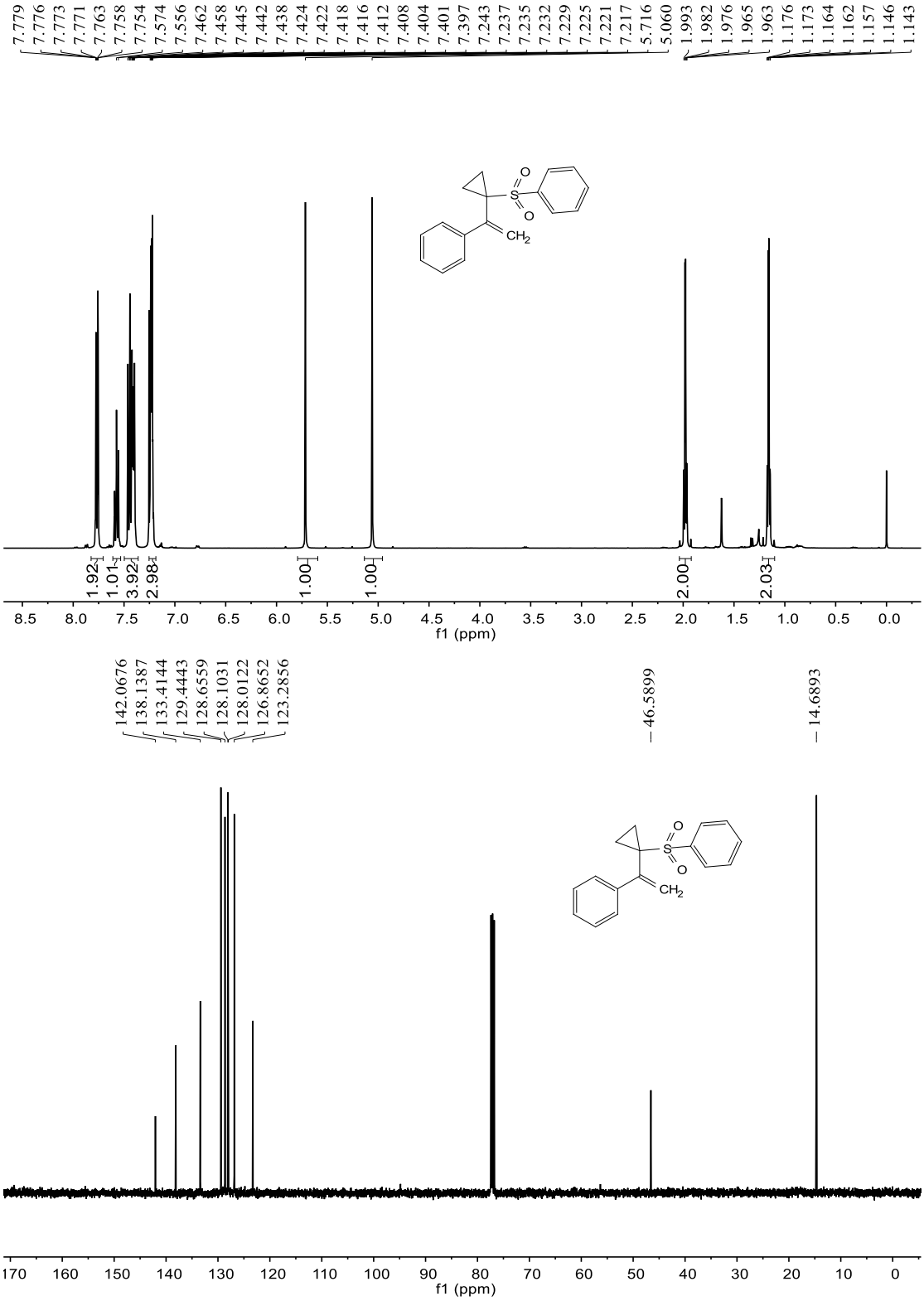


^{1}H NMR and ^{13}C NMR spectra of compound **4ya**

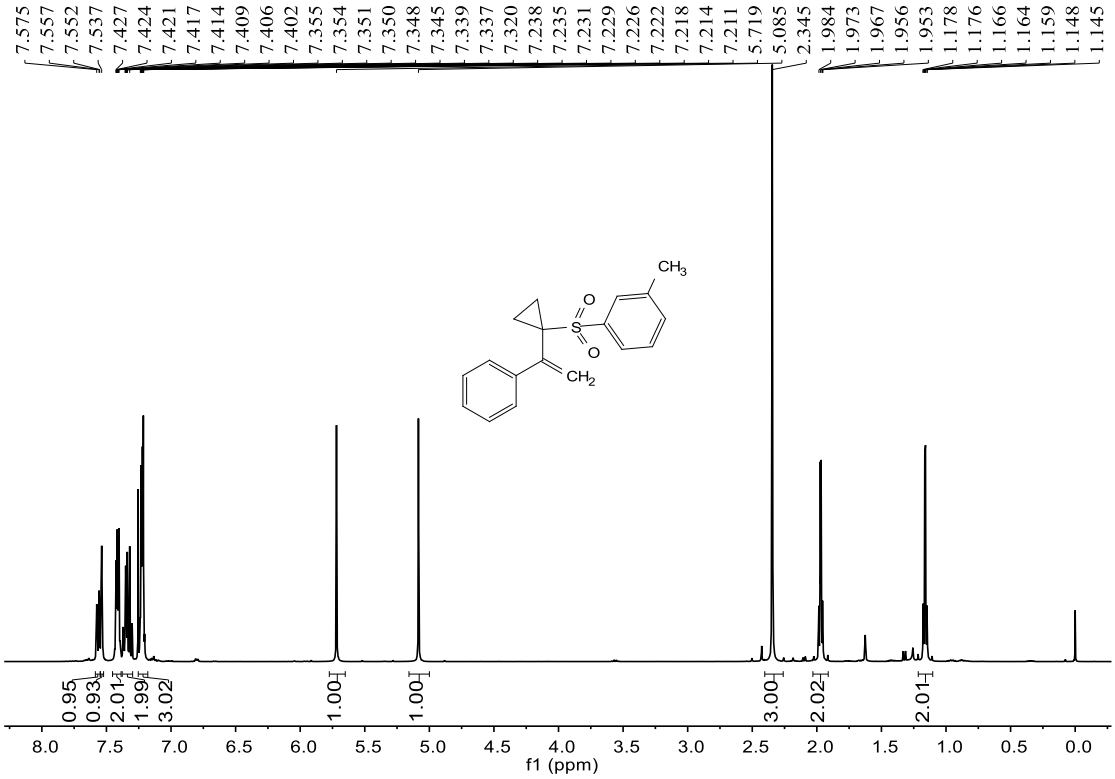


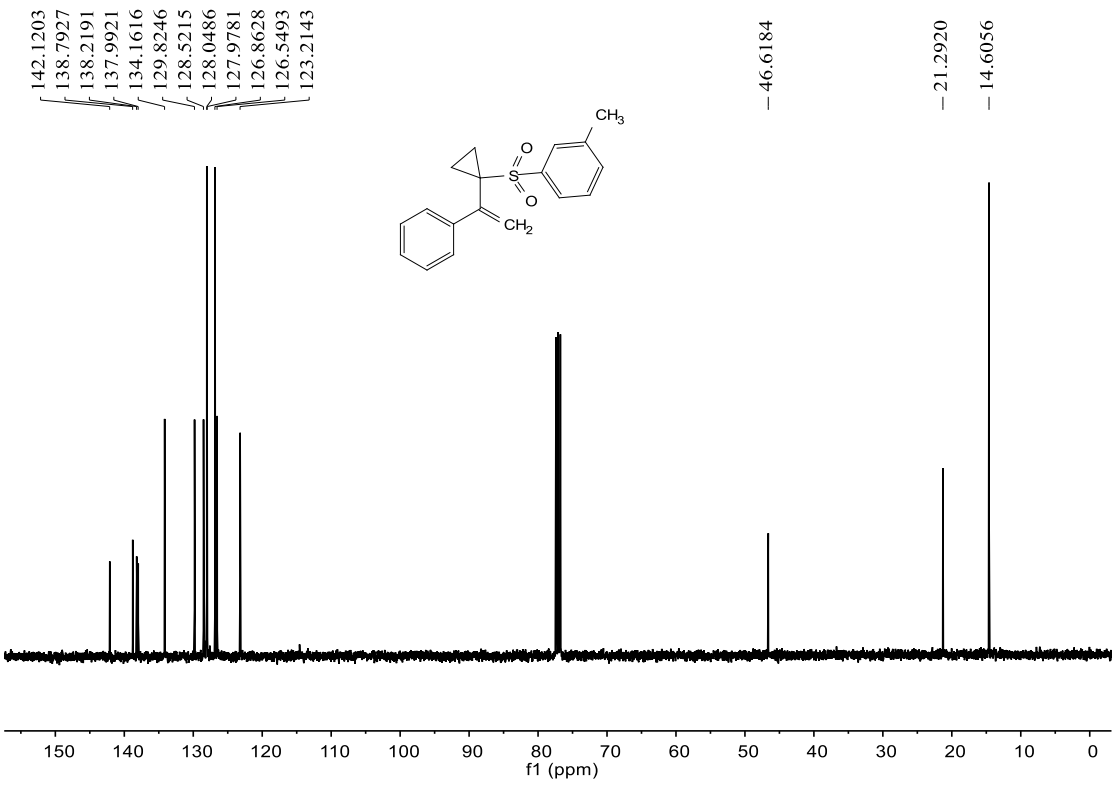


^{1}H NMR and ^{13}C NMR spectra of compound **4yb**

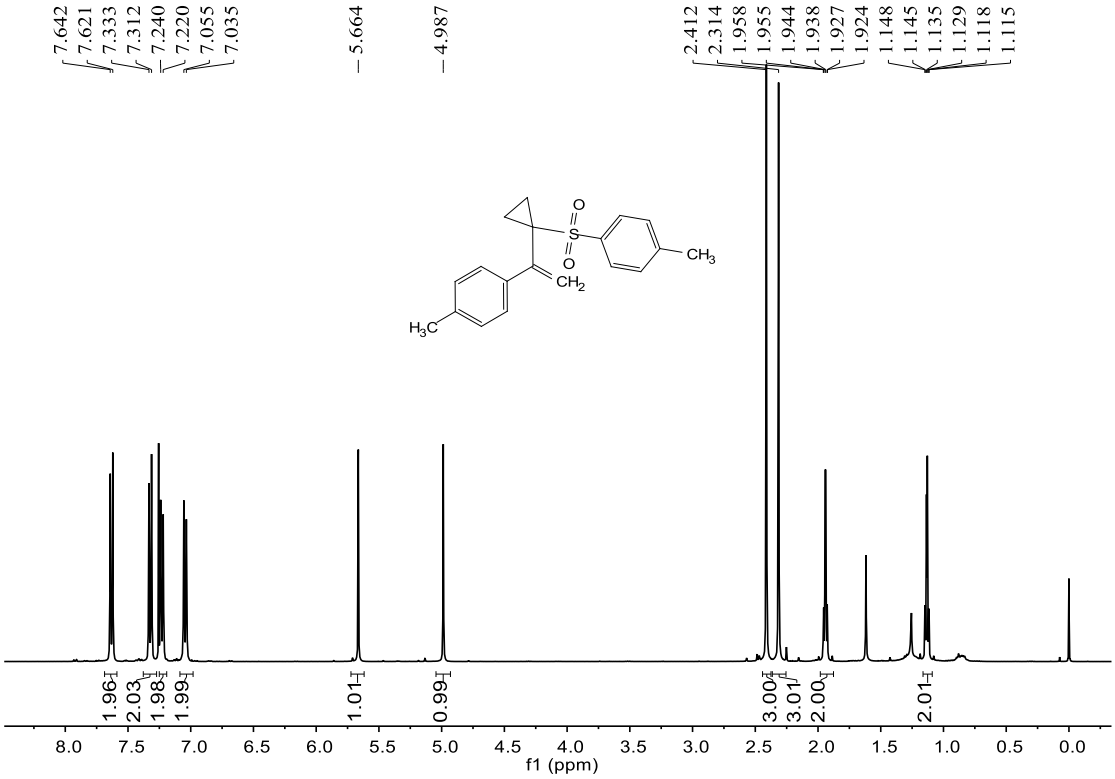


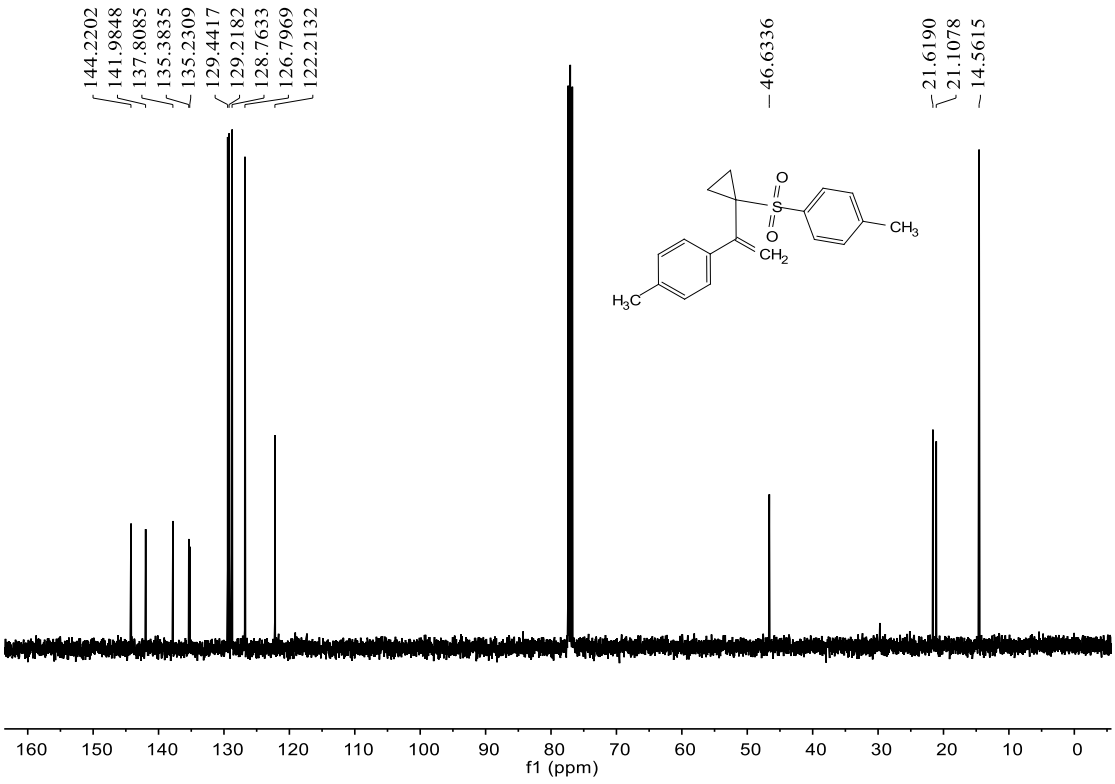
^{1}H NMR and ^{13}C NMR spectra of compound **4yh**



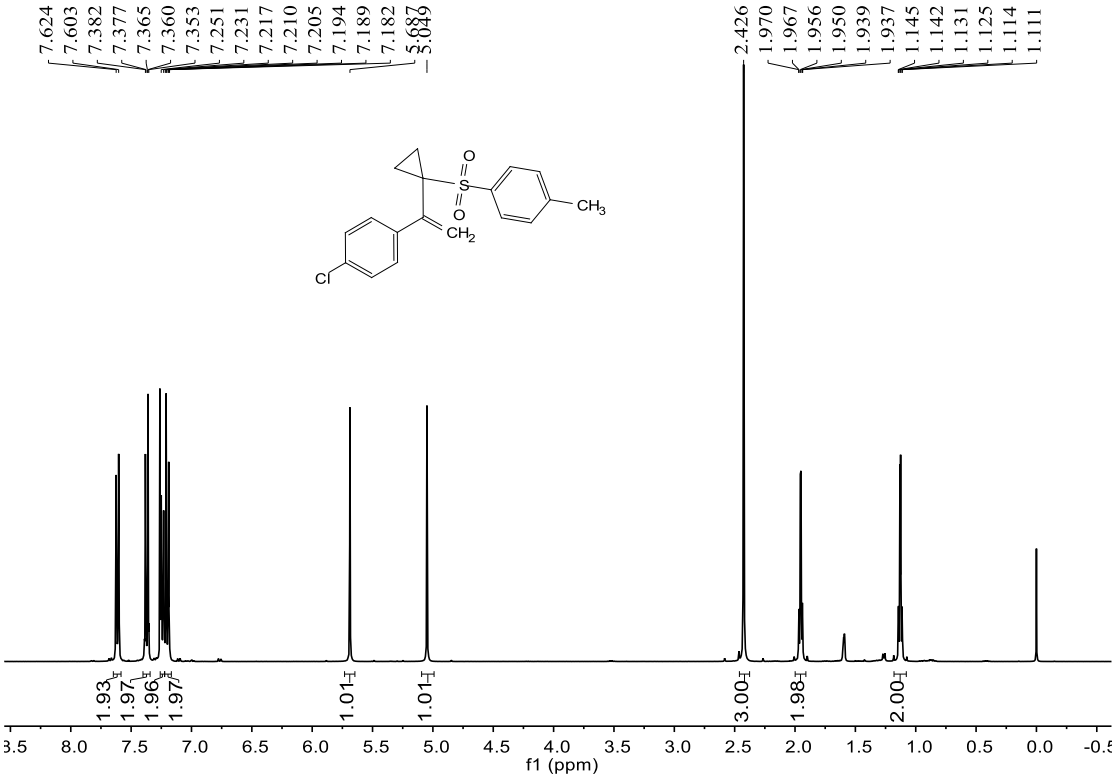


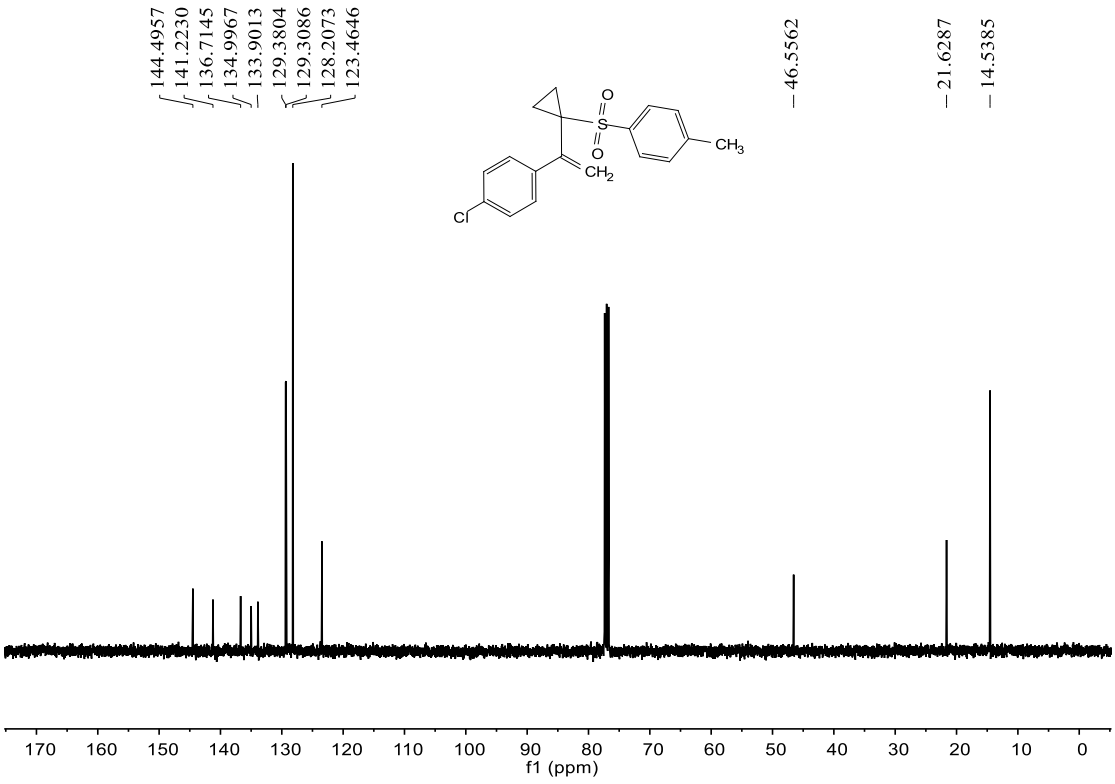
^{1}H NMR and ^{13}C NMR spectra of compound **4za**



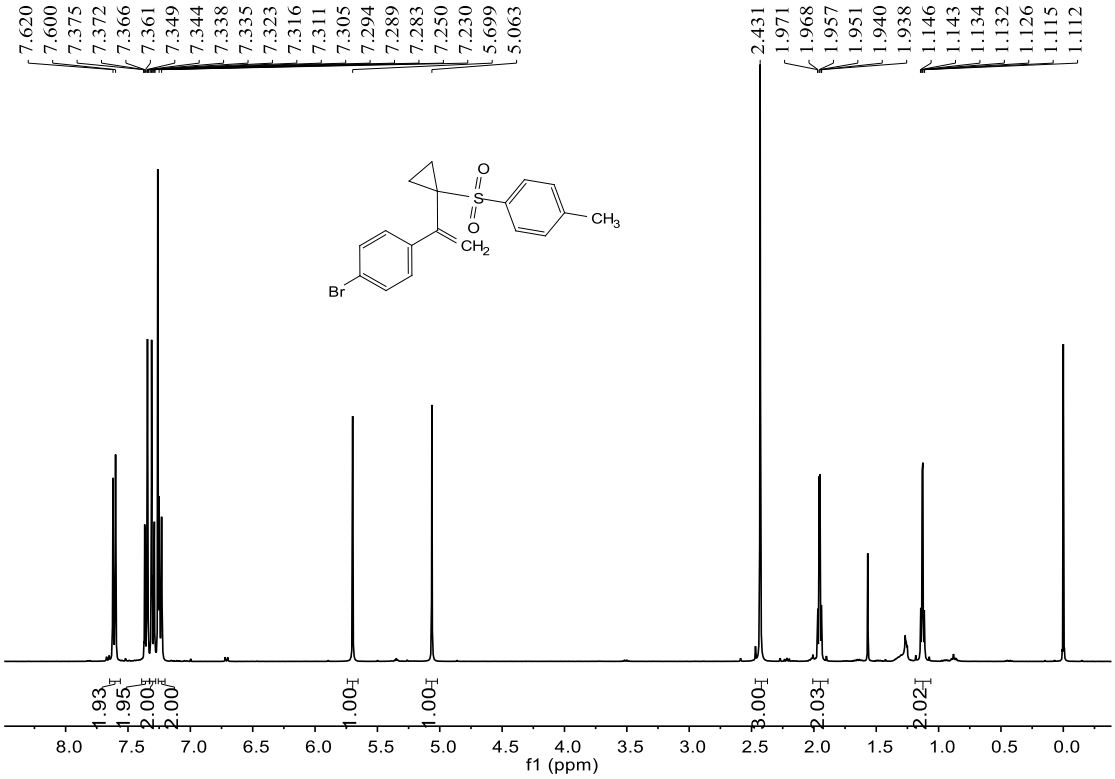


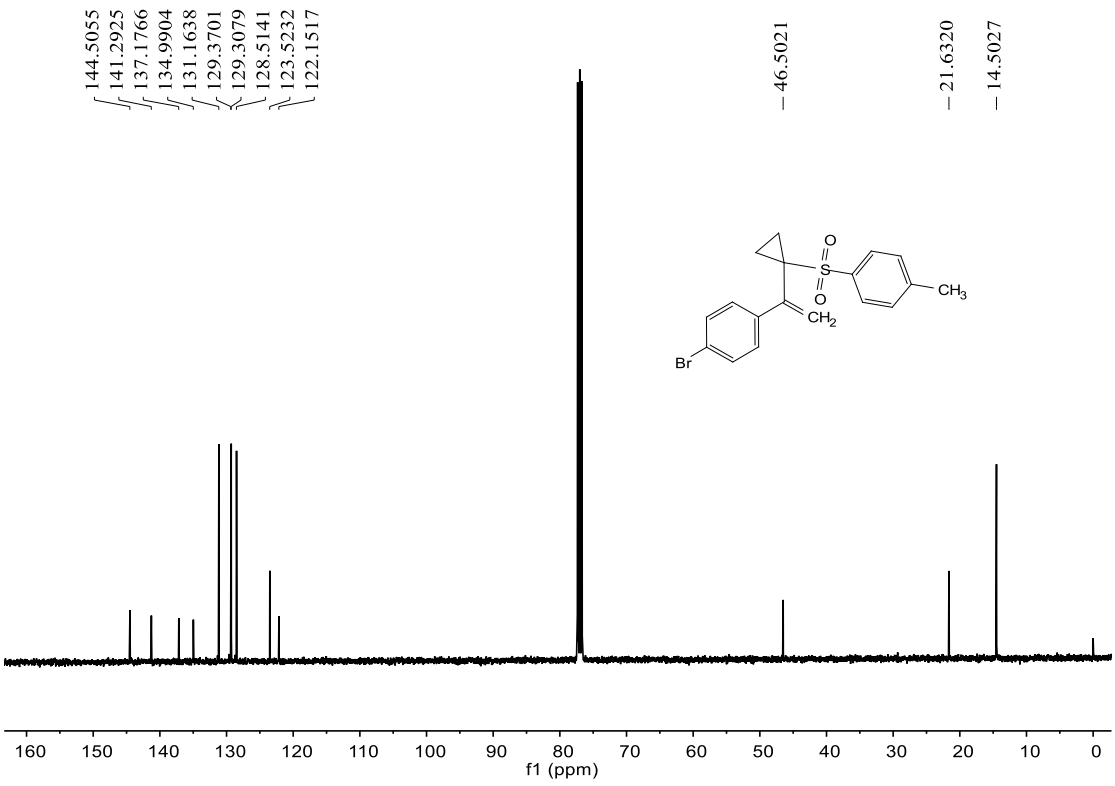
^{1}H NMR and ^{13}C NMR spectra of compound **4aaa**



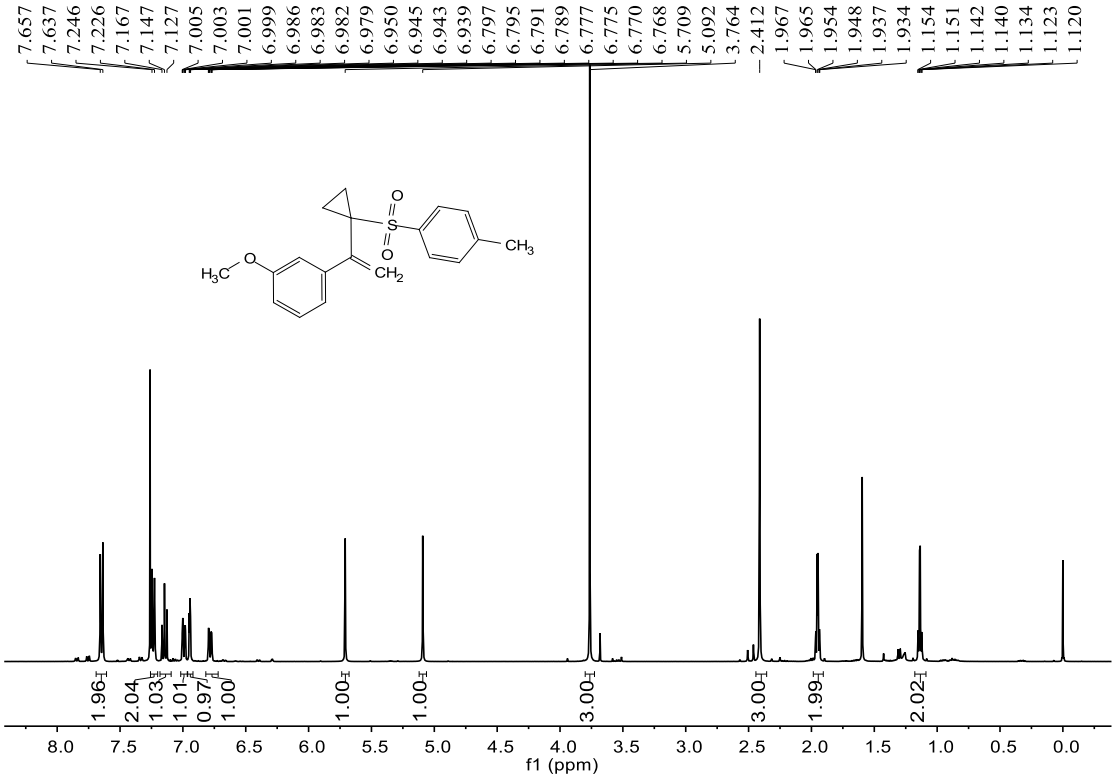


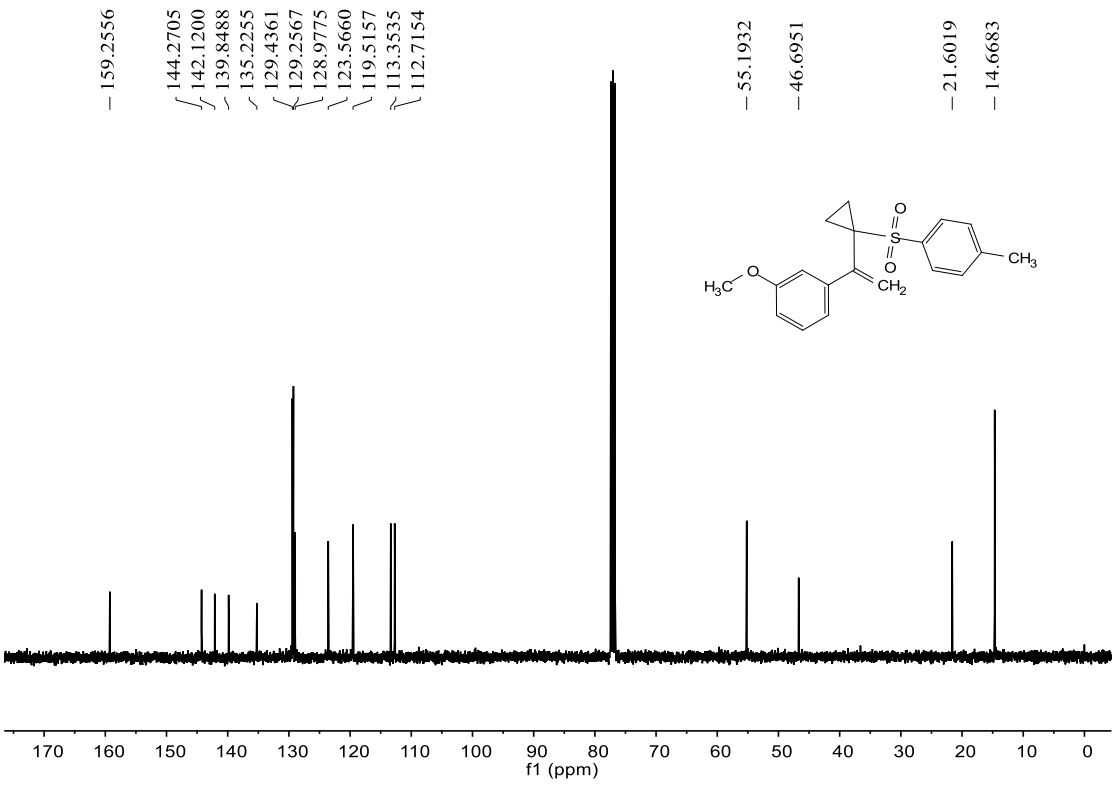
^{1}H NMR and ^{13}C NMR spectra of compound **4aba**



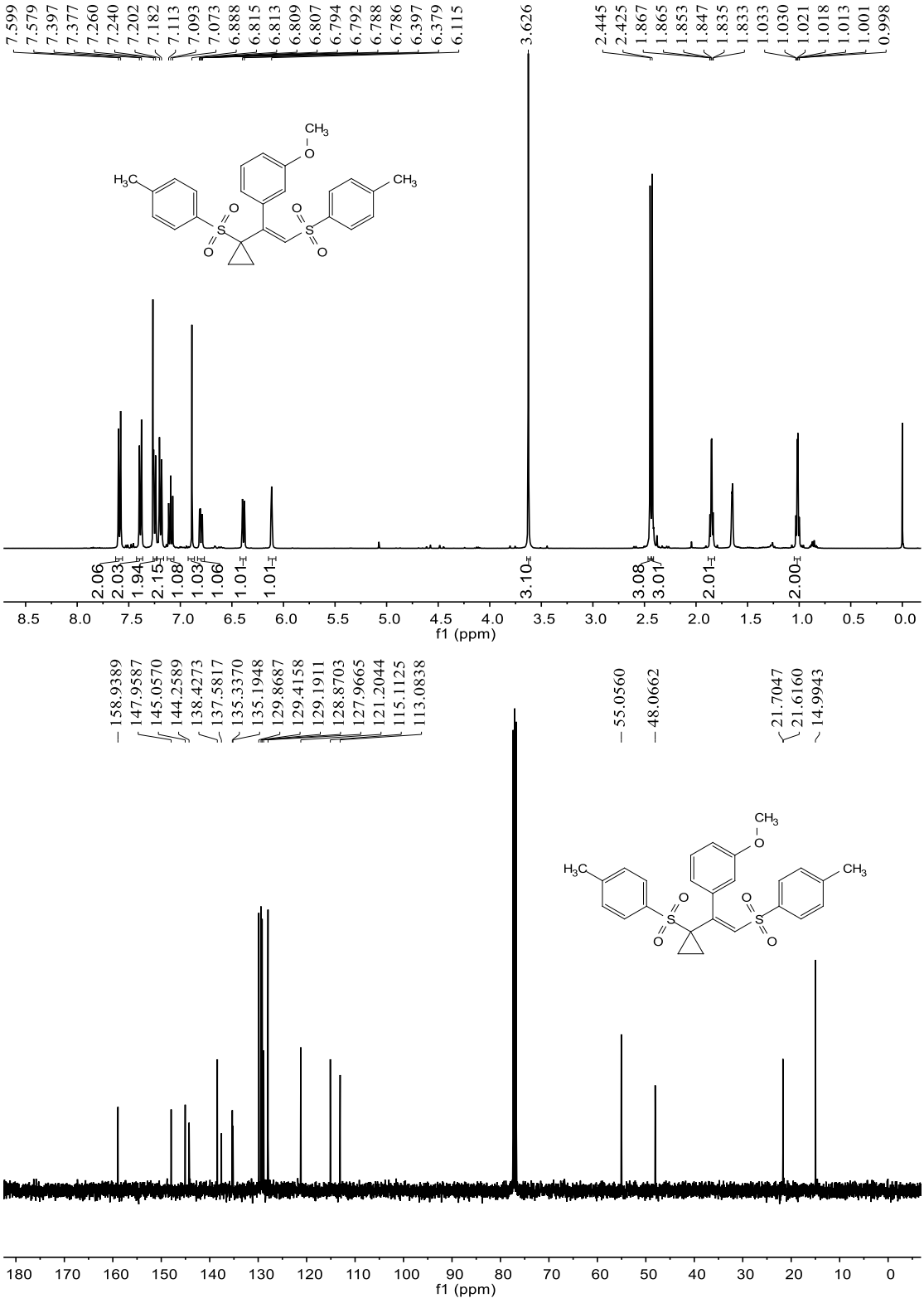


^{1}H NMR and ^{13}C NMR spectra of compound **4aca**

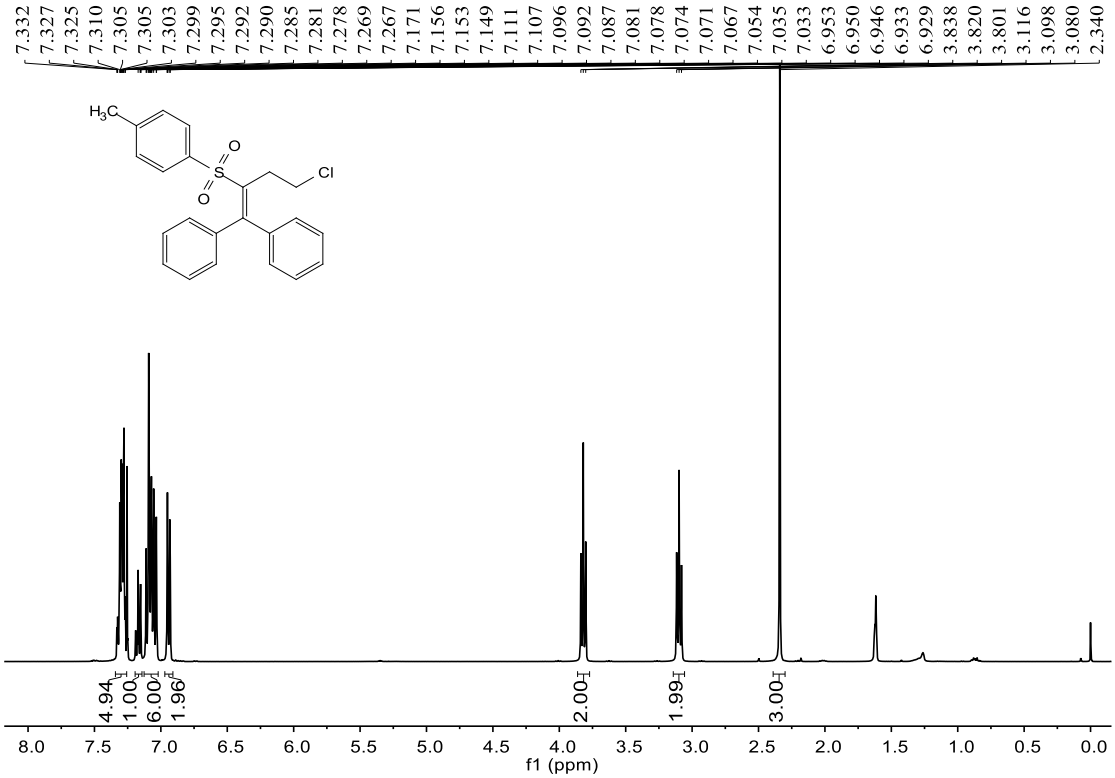


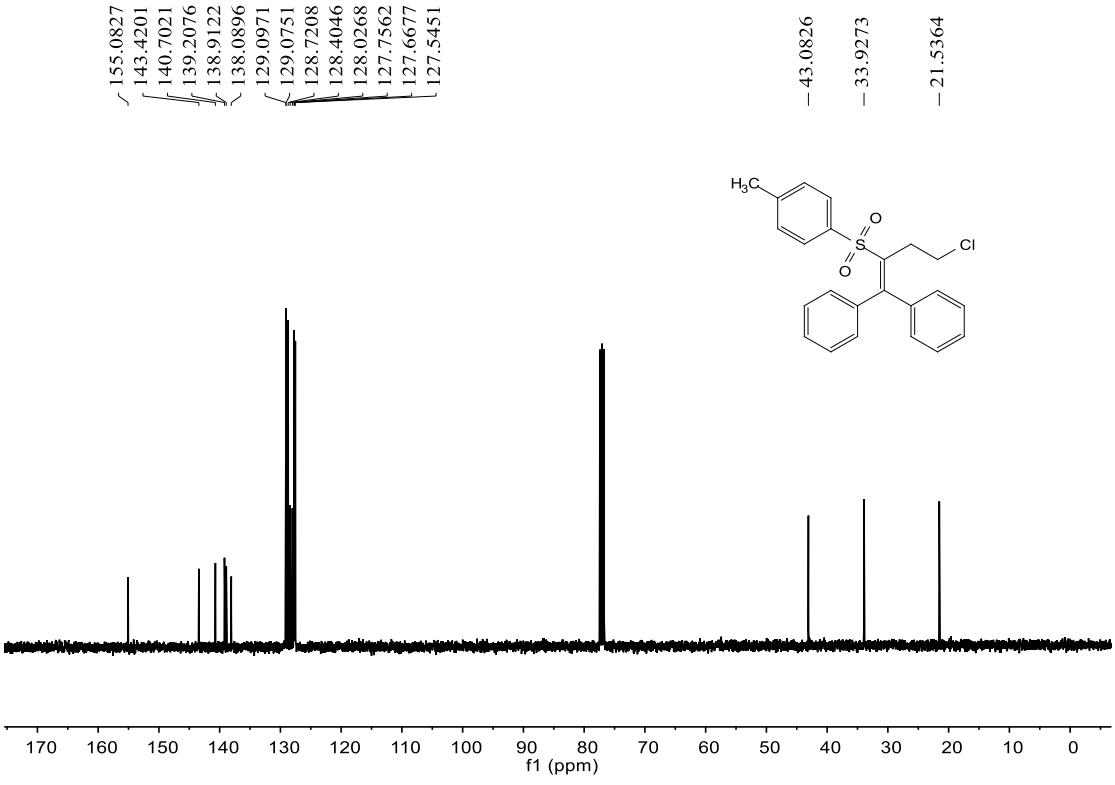


^{1}H NMR and ^{13}C NMR spectra of compound **5aca**

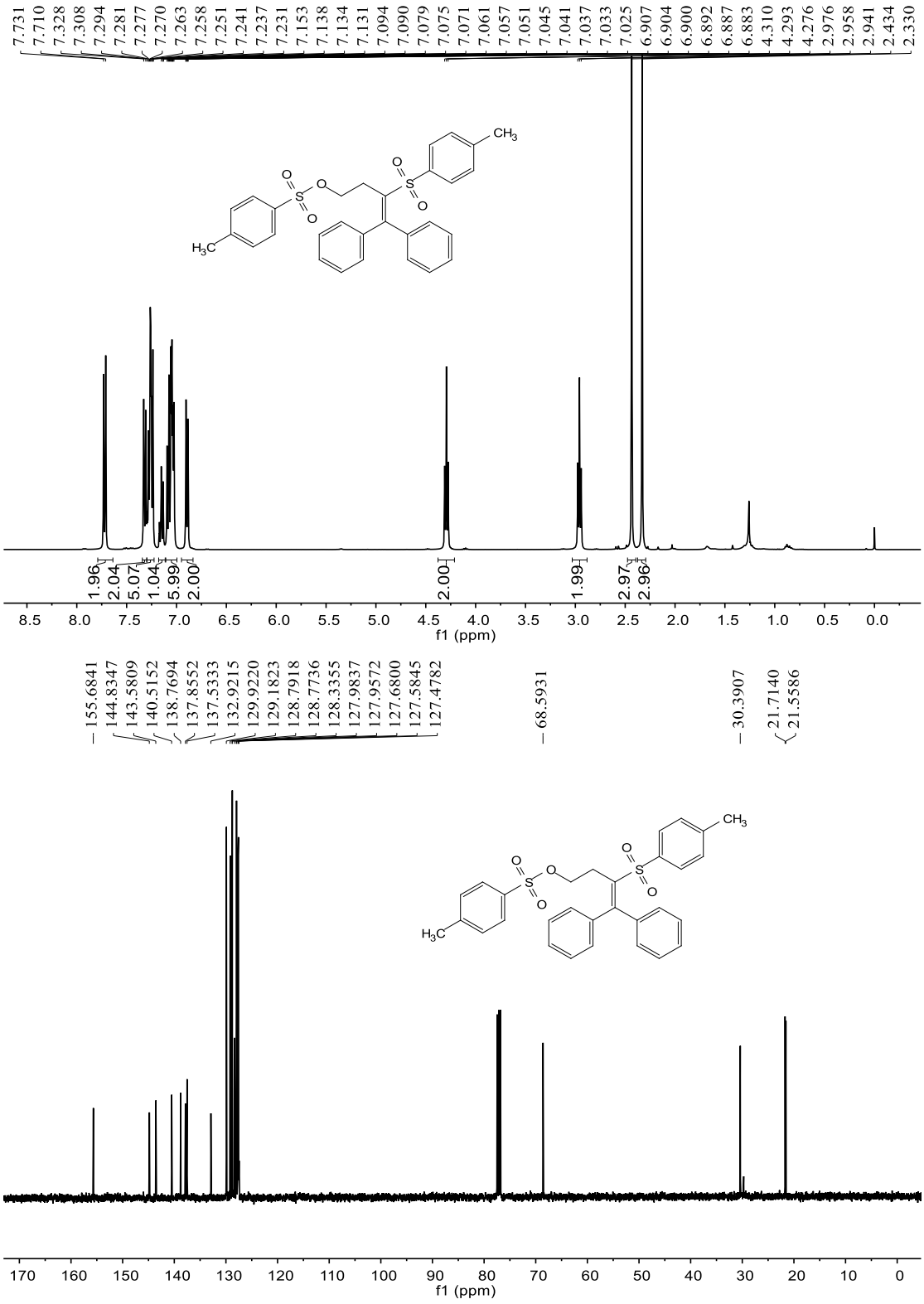


^{1}H NMR and ^{13}C NMR spectra of compound **6aa**

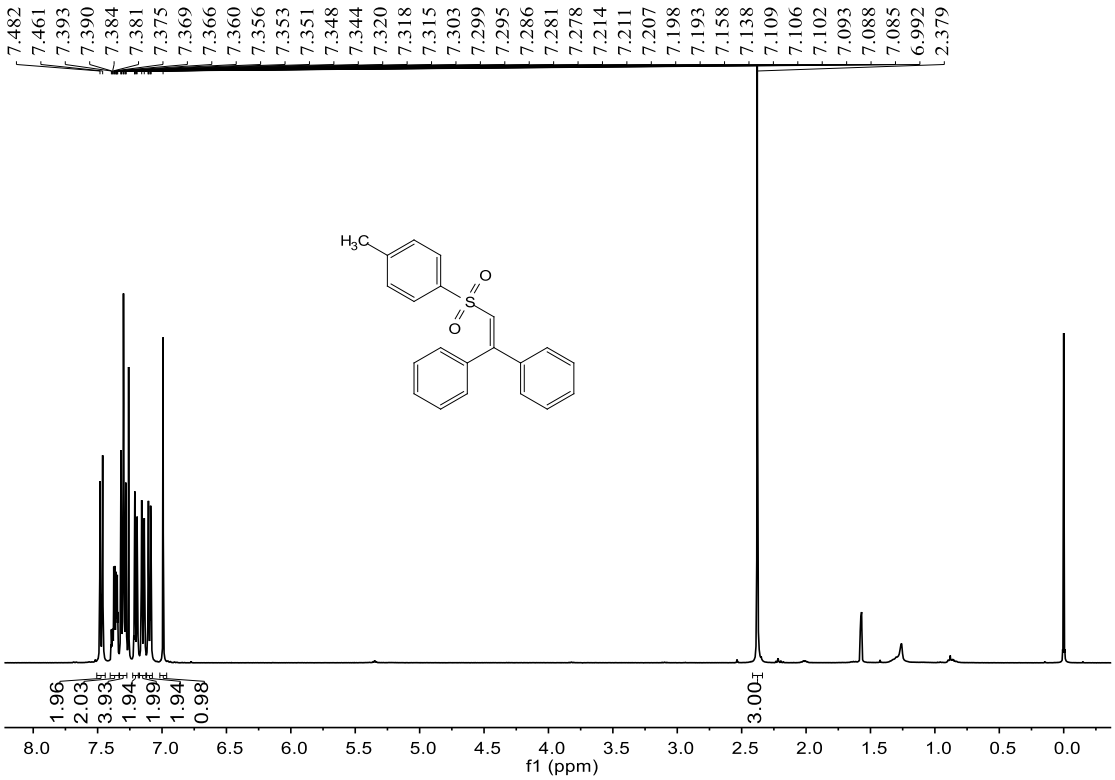


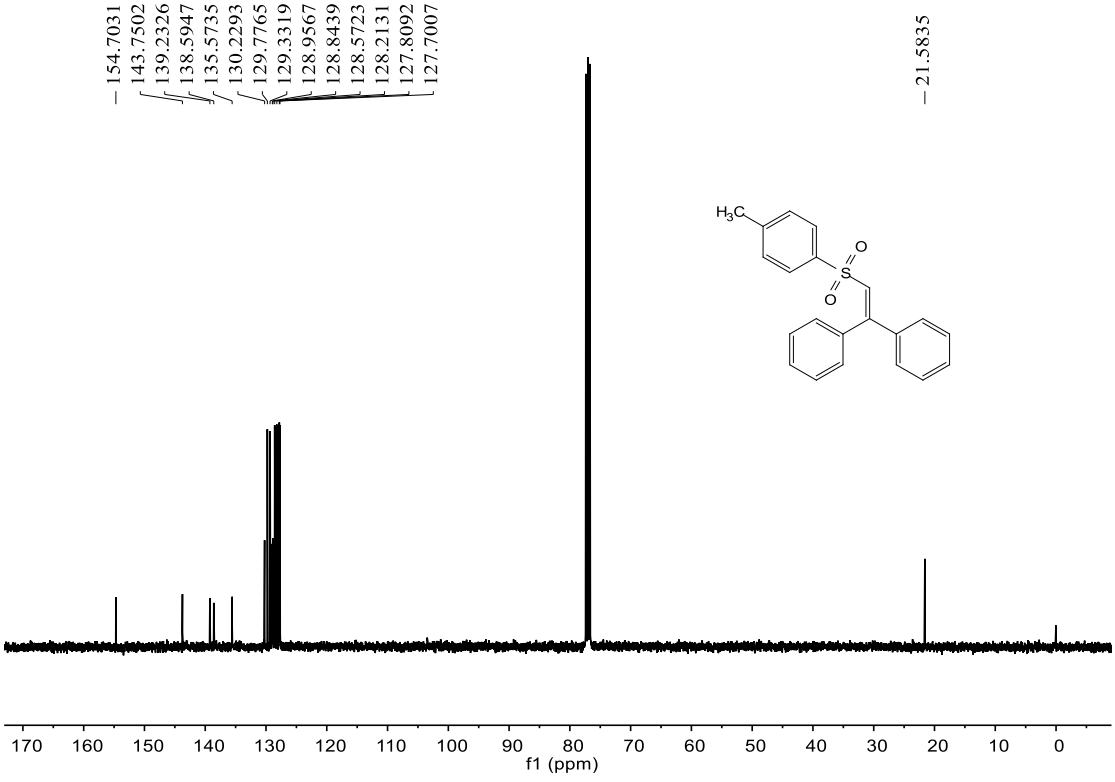


^{1}H NMR and ^{13}C NMR spectra of compound **7aa**



^{1}H NMR and ^{13}C NMR spectra of compound **8aa**





^{1}H NMR and ^{13}C NMR spectra of compound **9aa**