Copper-Catalyzed Ring-Open Sulfonylation of Cyclopropanols via the Insertion of Sulfur Dioxide toward the Synthesis of γ-Keto Aryl Sulfones

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Supporting Information

Contents

General information.

All reactions were carried out in oven dried two-chamber under argon atmosphere glovebox (Vigor, SGI800-750TS-F). All of Aryl diazonium salts were prepared according to the literature[1]. Unless otherwise stated, all commercially available compounds were purchased from the reagent company. ^{1}H, ^{19}F, ^{13}C NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2SO$ on Bruker Avance 400 MHz spectrometers. NMR spectra were taken using TMS ($\delta = 0$), $CDCl_3$ ($\delta = 7.26$), and $CDCl_3$ (^{13}C, CPD $\delta = 77.0$) as the internal standards, respectively. High-resolution mass spectrometric measurements were provided by School of Chemistry, Sichuan University, The molecular ion $[M+H]^+$, $[M]^+$ and $[M+Na]^+$ are given in m/z units. Flash column chromatography was performed on silica gel (particle size 200-300 mesh) and eluted with petroleum ether/ethyl acetate.

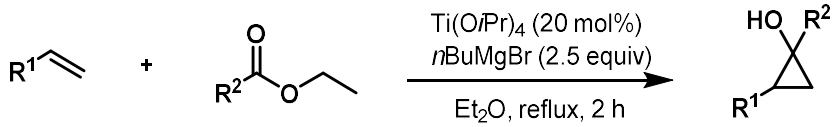
General procedures for the synthesis of diazonium salts 1

1

Substrates 1 were synthesized according to the literature procedures[1]: In a 50 mL round-bottom flask, the aniline (5 mmol) was dissolved in a mixture of absolute ethanol (1.5 mL) and an aqueous solution of HBF_4 (48% aq, 1.25 mL), followed by dropwise addition of *t*BuONO (1.35 mL) at 0 ℃. After stirring at room temperature for 1 h, diethyl ether (5 mL) was added to precipitate the arenediazonium tetrafluoroborates (Note: If there is no solid formed after adding diethyl ether, put the flask in the refrigerator overnight). The solids were filtered off and washed with diethyl ether (3×5 mL), dried in vacuo for 25 minutes, and stored in refrigerator.

General procedures for the synthesis of Cyclopropanols 2

General procedure A



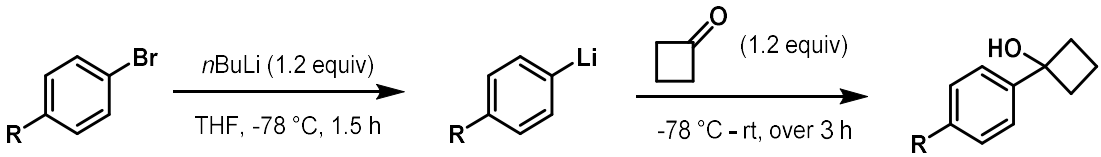
2

Substrates **2** were synthesized according to the literature procedures[2]: To a solution of ester (10 mmol), styrene (11 mmol, 1.1 equiv) and $Ti(OiPr)_4$ (2 mmol, 0.35 ml, 0.2 equiv) in Et_2O (15 mL), a solution of *n*BuMgBr (25 mmol, 2.5 equiv) in Et_2O (12 mL)

was added dropwisely over 1 h at reflux. The mixture was stirred for an additional 1 h, and then poured into ice-cold aqueous solution of hydrochloric acid (50 mL, 1M). The organic layer was separated and the aqueous layer was extracted with ether (2×20 mL). The combined organic extracts were washed with saturated $NaHCO_3$ aq., dried over Na_2SO_4 and concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate (~ 10: 1) to give the desired product **2**.

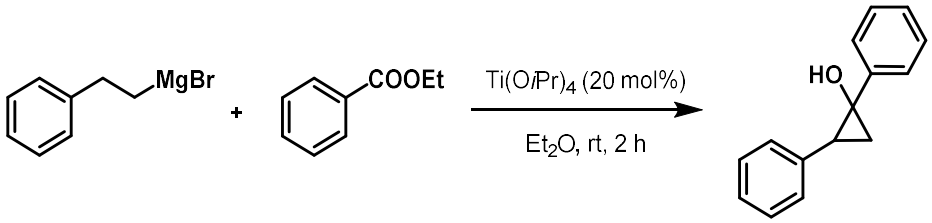
Notes: Cyclopropanols are not stable when chromatography on silica gel, so products were purified by column chromatography quickly, and stored in glovebox at a –20 ºC freezer.

General procedure B



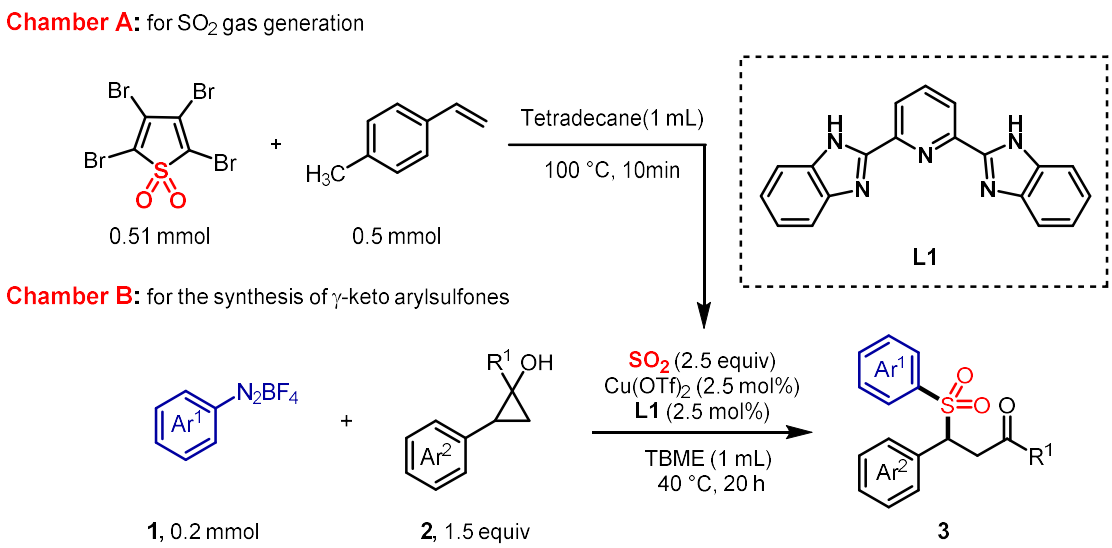
Following the literature procedure[3], a flame-dried round bottom flask charged with 5 mmol of aryl/alkyl bromide (commercially available reagents were used without further purification) in 15 mL THF was cooled to -78 °C and 2.4 mL of *n*BuLi (2.5 M in hexane, 6 mmol, 1.2 equiv) was added dropwise via syringe. The mixture was stirred for 0.5 h at -78 °C before the addition of the corresponding ketone (5 mmol, 1.0 equiv), then the mixture was warmed to room temperature and stirred over 3 h. The ammonium chloride solution was then added to quench the reaction and extracted with ethyl acetate (3 x 30 mL), washed with sodium chloride solution, and dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography (PE/EA) to afford the products.

General procedure C



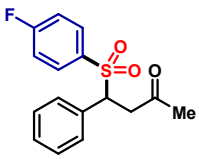
Following the literature procedure[4], a flame-dried round bottom flask charged with 5 mmol of ethyl benzoate and 1 mmol of titanium tetraisopropanolate in 10 mL Et_2O, then 10 mL of Grignard reagent (0.5 M in THF, 5 mmol, 1.0 equiv) was added dropwise via syringe. The mixture was stirred for 2 h at room temperature. The 1.0 M hydrochloric acid solution was then added to quench the reaction and extracted with ethyl acetate (3 x 30 mL), washed with sodium chloride solution, and dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography (PE/EA) to afford the products.

General procedures for the synthesis of γ-keto aryl sulfones 3



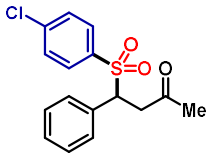
In an argon fulfilled glovebox, tetrabromothiophene S, S-dioxides (0.51 mmol, 237.4 mg) and 1-methyl-4-vinylbenzene (0.5 mmol, 66 uL) were added into chamber A with a magnetic stirring bar, followed by addition of tetradecane (1.0 mL). Diazonium salts **1** (0.2 mmol), Cyclopropanols **2** (0.3 mmol, 1.5 equiv.), $Cu(OTf)_2$ (2.5 mol%, 1.8 mg) and **L1** (1.6 mg, 2.5 mol%) were added into chamber B with a magnetic stirring bar, followed by addition of MTBE (1.0 mL). The two-chamber was sealed and removed out of the glovebox, then chamber A was allowed to heated to 100 °C in heat block. About ten minutes later, the sulfur dioxide was completely released since the system in chamber A became clear. Then chamber B was heated to 40 °C in heat block. Upon completion, the mixture in chamber B was passed through a short silica gel pad with ethyl acetate. The filtrate was washed by ethyl acetate and H_2O (15 mL×3), dried by Na_2SO_4, then concentrated and the residue was purified by flash column chromatography to afford pure products **3**.

Characterization data of products

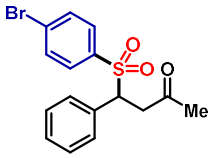


4-((4-fluorophenyl)sulfonyl)-4-phenylbutan-2-one (3a) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (51 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 - 7.40 (m, 2H), 7.20 - 7.13 (m, 3H), 7.04 – 7.03 (m, 2H), 6.99 – 6.95 (m, 2H), 4.64 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.54 (dd, *J* = 18.0, 4.4 Hz, 1H), 3.21 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.10 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.2. ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 165.8 (d, J = 257.6 Hz), 132.8 (d, J = 3.0 Hz), 132.4, 131.9 (d, J = 9.1 Hz), 129.7, 129.0, 128.6, 116.1 (d, J = 23.2 Hz), 66.3, 41.3, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for

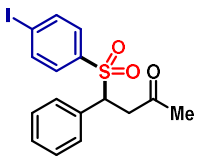
$C_{16}H_{15}FO_3SNa$ 329.0618; Found:329.0620.



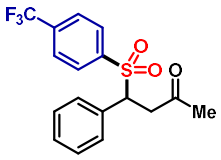
4-((4-chlorophenyl)sulfonyl)-4-phenylbutan-2-one (3b) Prepared by general procedure; isolated as a white solid using petroleum/ethyl acetate (5:1) as eluent (50 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.14 (m, 3H), 7.04 (d, *J* = 6.8 Hz, 2H), 4.65 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.53 (dd, *J* = 18.0, 4.4 Hz, 1H), 3.20 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 140.6, 135.4, 132.2, 130.4, 129.7, 129.1, 129.1, 128.7, 66.3, 41.3, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}ClO_3SNa$ 345.0323; Found: 345.0319.



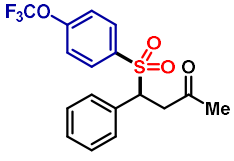
4-((4-bromophenyl)sulfonyl)-4-phenylbutan-2-one (3c) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (62 mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.21 – 7.14 (m, 3H), 7.04 (d, *J* = 7.2 Hz, 2H), 4.65 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.52 (dd, *J* = 18.0, 4.4 Hz, 1H), 3.20 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 135.9, 132.2, 132.0, 130.5, 129.7, 129.2, 129.1, 128.7, 66.2, 41.3, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}BrO_3SNa$ 388.9817; Found: 388.9818.



4-((4-iodophenyl)sulfonyl)-4-phenylbutan-2-one (3d) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (77 mg, 94%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.14 (m, 3H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 6.8 Hz, 2H), 4.65 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.52 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.20 (dd, *J* = 18.0, 9.2 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 138.0, 136.6, 132.2, 130.3, 129.7, 129.1, 128.7, 101.9, 66.0, 41.3, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{23}IO_3SNa$ 541.0305; Found:541.0300.

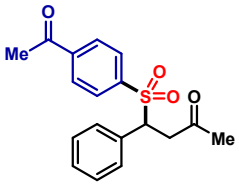


4-phenyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-one (3e) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (51mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 4H), 7.32 – 7.22 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.79 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.65 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.31 (dd, *J* = 18.0, 9.2 Hz, 1H), 2.20 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2. ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 140.5, 135.3 (q, J = 33.3 Hz), 132.0, 129.7, 129.6, 129.2, 128.7, 125.8 (q, J = 4.0 Hz), 123.1 (q, J = 274.7 Hz), 66.2, 41.2, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}F_3O_3SNa$ 379.0586; Found:379.0588.

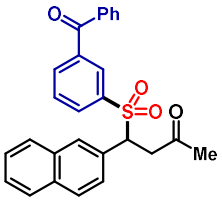


4-phenyl-4-((4-(trifluoromethoxy)phenyl)sulfonyl)butan-2-one (3f) Prepared by general procedure; isolated as a white solid using petroleum/ethyl acetate (5:1) as eluent (53 mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.25 – 7.19 (m, 4H), 7.12 (d, *J* = 7.2 Hz, 2H), 4.75 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.63 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.31 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.20

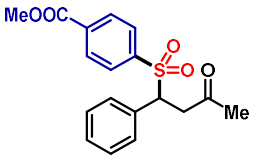
(s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8. ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 153.0 (q, J = 2 Hz), 135.0, 132.2, 131.3, 129.7, 129.1, 128.7, 120.4, 120.1 (d, J = 261.6 Hz), 66.4, 41.2, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}F_3O_4SNa$ 395.0535; Found:395.0536.



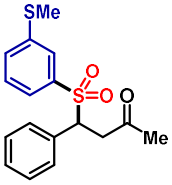
4-((4-acetylphenyl)sulfonyl)-4-phenylbutan-2-one (3g) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (55mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.04 (d, J = 6.4 Hz, 2H), 4.69 (dd, J = 8.8, 4.4 Hz, 1H), 3.56 (dd, J = 18.0, 4.4 Hz, 1H), 3.22 (dd, J = 18.0, 8.8 Hz, 1H), 2.55 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 195.7, 139.7, 131.0, 128.7, 128.4, 128.1, 127.4, 127.4, 65.1, 40.2, 29.5, 25.9, 0.0. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{19}O_4S$ 331.1004; Found: 331.0999.



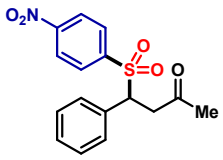
4-((3-benzoylphenyl)sulfonyl)-4-(naphthalen-2-yl)butan-2-one (3h) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (65mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, J = 4.6 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.69 – 7.60 (m, 8H), 7.53 – 7.44 (m, 4H), 7.32 (d, J = 8.4 Hz, 1H), 5.00 (dd, J = 8.8, 4.4 Hz, 1H), 3.75 (dd, J = 18.0, 4.4 Hz, 1H), 3.47 (dd, J = 18.0, 9.2 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 195.2, 142.1, 139.9, 136.3, 133.3, 133.2, 132.9, 130.1, 129.8, 129.7, 129.6, 129.0, 128.6, 128.5, 128.0, 127.7, 127.0, 126.6, 126.5, 66.5, 41.4, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{23}O_4S$ 443.1312; Found: 443.1315.



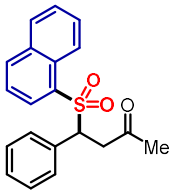
methyl (S)-4-((3-oxo-1-phenylbutyl)sulfonyl)benzoate (3i) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (60 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.19 – 7.11 (m, 3H), 7.03 (d, J = 7.2 Hz, 2H), 4.69 (dd, J = 9.2, 4.4 Hz, 1H), 3.86 (s, 3H), 3.55 (dd, J = 17.6, 4.4 Hz, 1H), 3.22 (dd, J = 18.0, 8.8 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 165.5, 140.8, 134.7, 132.0, 129.8, 129.7, 129.1, 128.7, 66.2, 52.7, 41.2, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}O_5SNa$ 369.0767; Found:369.0762.



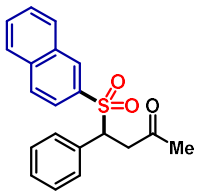
4-((3-(methylthio)phenyl)sulfonyl)-4-phenylbutan-2-one (3j) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (39 mg, 58%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.30 (m, 1H), 7.22 – 7.18 (m, 4H), 7.17 – 7.14 (m, 1H), 7.09 (s, 1H), 7.05 (d, J = 6.8 Hz, 2H), 4.64 (dd, J = 9.2, 4.4 Hz, 1H), 3.54 (dd, J = 17.6, 4.4 Hz, 1H), 3.21 (dd, J = 18.0, 9.2 Hz, 1H), 2.25 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 140.7, 137.4, 132.5, 131.4, 129.8, 129.0, 128.9, 128.5, 125.6, 125.0, 66.3, 41.3, 30.5, 15.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}O_3S_2$ 335.0776; Found: 335.0770.



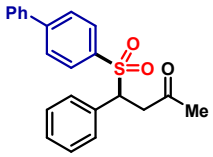
N-(3,3-dimethyl-1-tosylbut-1-en-2-yl)acetamide (3k) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (1:1) as eluent (41 mg, 62%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.22 – 7.14 (m, 3H), 7.04 (d, *J* = 7.2 Hz, 2H), 4.72 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.58 (dd, *J* = 18.0, 4.0 Hz, 1H), 3.24 (dd, *J* = 18.0, 8.8 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 150.7, 142.7, 131.7, 130.4, 129.7, 129.4, 128.9, 123.8, 66.3, 41.0, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_5S$ 334.0749; Found: 334.0748.



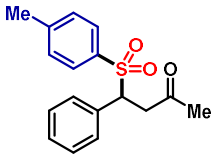
4-(naphthalen-1-ylsulfonyl)-4-phenylbutan-2-one (3l) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (36 mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.56 – 7.53 (m, 1H), 7.27 – 7.23 (m, 1H), 7.10 – 7.06 (m, 1H), 7.01 – 6.98 (m, 2H), 6.86 (d, J = 7.6 Hz, 2H), 5.00 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.63 (dd, *J* = 18.0, 4.8 Hz, 1H), 3.26 (dd, *J* = 18.0, 8.4 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 138.1, 136.7, 135.3, 134.8, 134.7, 132.2, 132.1, 131.9, 131.7, 131.6, 131.2, 127.1, 126.7, 68.2, 44.1, 33.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{18}O_3SNa$ 361.0869; Found: 361.0865.



4-(naphthalen-2-ylsulfonyl)-4-phenylbutan-2-one (3m) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (34 mg, 50%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.81 – 7.73 (m, 3H), 7.60 – 7.55 (m, 1H), 7.53 – 7.49 (m, 1H), 7.39 – 7.36 (m, 1H), 7.17 – 7.15 (m, 1H), 7.12 – 7.08 (m, 2H), 7.05 – 7.03 (m, 2H), 4.75 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.58 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.24 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 135.2, 133.8, 132.4, 131.9, 131.1, 129.8, 129.4, 129.3, 128.9, 128.8, 128.5, 127.9, 127.6, 123.5, 66.3, 41.6, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{18}O_3SNa$ 361.0869; Found: 361.0870.

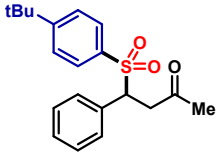


4-([1,1'-biphenyl]-4-ylsulfonyl)-4-phenylbutan-2-one (3n) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (52 mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 6H), 7.42 – 7.34 (m, 3H), 7.21 – 7.13 (m, 3H), 7.10 – 7.07 (m, 2H), 4.70 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.56 (dd, *J* = 18.0, 4.4 Hz, 1H), 3.23 (dd, *J* = 18.0, 9.2 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 145.5, 138.0, 134.3, 131.4, 128.7, 128.5, 128.0, 127.9, 127.7, 127.5, 126.3, 126.2, 65.3, 40.5, 29.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}IO_3SNa$ 387.1025; Found: 387.1021.

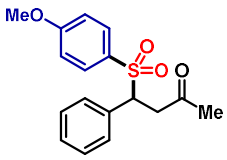


4-phenyl-4-tosylbutan-2-one (3o) Prepared by general procedure; isolated as a yellow solid using petroleum/ethyl acetate (5:1) as eluent (47 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 6.4 Hz, 2H), 4.72 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.60 (dd, *J* = 17.6,

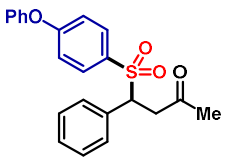
4.4 Hz, 1H), 3.28 (dd, J = 17.6, 8.8 Hz, 1H), 2.39 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 144.8, 133.9, 132.6, 129.7, 129.4, 129.0, 128.8, 128.5, 66.2, 41.6, 30.5, 21.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{18}O_3SNa$ 325.0869; Found:325.0867.



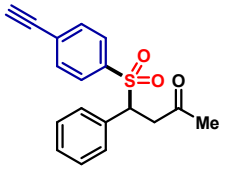
4-((4-(tert-butyl)phenyl)sulfonyl)-4-phenylbutan-2-one (3p) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (59 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 4H), 7.19 – 7.10 (m, 3H), 7.04 (d, J = 6.8 Hz, 2H), 4.64 (dd, J = 9.2, 4.4 Hz, 1H), 3.49 (dd, J = 17.6, 4.4 Hz, 1H), 3.20 (dd, J = 17.6, 9.2 Hz, 1H), 2.08 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 157.8, 133.8, 132.5, 129.7, 128.9, 128.8, 128.4, 125.7, 66.2, 41.6, 35.2, 31.0, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{24}O_3SNa$ 367.1338; Found: 367.1336.



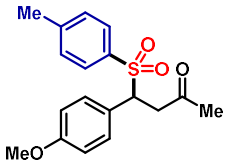
4-((4-methoxyphenyl)sulfonyl)-4-phenylbutan-2-one (3q) Prepared by general procedure; isolated as a yellow solid using petroleum/ethyl acetate (5:1) as eluent (38 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, J = 8.8 Hz, 2H), 7.20 – 7.13 (m, 3H), 7.05 (d, J = 7.2 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 4.62 (dd, J = 9.2, 4.4 Hz, 1H), 3.76 (s, 3H), 3.52 (dd, J = 18.0, 4.4 Hz, 1H), 3.19 (dd, J = 18.0, 9.2 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 163.8, 132.7, 131.2, 129.7, 128.8, 128.5, 128.3, 113.9, 66.4, 55.6, 41.7, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{19}O_4S$ 319.0999; Found: 319.0996.



4-((4-phenoxyphenyl)sulfonyl)-4-phenylbutan-2-one (3r) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (40 mg, 52%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 4H), 7.20 – 7.12 (m, 4H), 7.07 (d, J = 7.2 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 7.6 Hz, 2H), 4.64 (dd, J = 8.8, 4.4 Hz, 1H), 3.52 (dd, J = 18.0, 4.4 Hz, 1H), 3.20 (dd, J = 18.0, 8.8 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 162.5, 155.0, 132.6, 131.3, 130.3, 130.2, 129.7, 128.9, 128.5, 125.1, 120.2, 117.3, 66.4, 41.6, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{20}O_4SNa$ 403.0975; Found:403.0974.

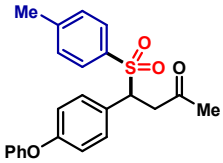


4-((4-ethynylphenyl)sulfonyl)-4-phenylbutan-2-one (3s) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (27mg, 44%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 4H), 7.20 – 7.13 (m, 3H), 7.04 (d, J = 7.2 Hz, 2H), 4.65 (dd, J = 9.2, 4.4 Hz, 1H), 3.53 (dd, J = 18.0, 4.4 Hz, 1H), 3.24 – 3.17 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 136.8, 132.3, 132.2, 129.7, 129.1, 129.0, 128.6, 127.9, 81.8, 81.3, 66.2, 41.3, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{17}O_3S$ 313.0898; Found: 313.0890.

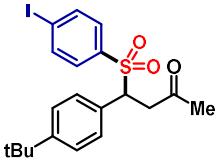


4-(4-methoxyphenyl)-4-tosylbutan-2-one (3t) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (41mg, 62%). 1H NMR (400 MHz, Chloroform-d) δ 7.32 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz,

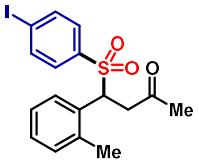
2H), 6.97 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 4.58 (dd, J = 9.2, 4.0 Hz, 1H), 3.70 (s, 3H), 3.47 (dd, J = 17.6, 4.0 Hz, 1H), 3.14 (dd, J = 17.6, 9.2 Hz, 1H), 2.32 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 203.5, 159.9, 144.7, 134.0, 130.9, 129.4, 129.1, 124.3, 113.9, 65.5, 55.3, 41.7, 30.5, 21.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{20}O_4SNa$ 355.0975; Found: 355.0975.



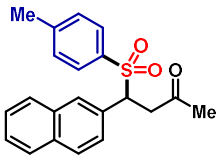
(4-phenoxyphenyl)-4-tosylbutan-2-one (3u) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (62mg, 79%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.06 – 6.99 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.61 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.49 (dd, *J* = 17.6, 4.0 Hz, 1H), 3.16 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.32 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 157.9, 156.6, 144.9, 133.9, 131.1, 129.8, 129.4, 129.1, 127.0, 123.8, 119.2, 118.5, 65.5, 41.7, 30.5, 21.7. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}O_4SNa$ 417.1131; Found: 417.1128.



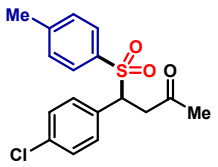
4-(4-(tert-butyl)phenyl)-4-((4-iodophenyl)sulfonyl)butan-2-one (3v) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (68mg, 72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 4.63 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.48 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.18 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.09 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 152.4, 137.9, 136.7, 130.3, 129.3, 128.9, 125.6, 101.7, 65.9, 41.4, 34.6, 31.2, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{24}IO_3S$ 471.0485; Found: 471.0480.



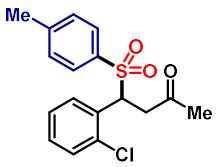
4-((4-iodophenyl)sulfonyl)-4-(o-tolyl)butan-2-one (3w) Prepared by general procedure; isolated as a yellow solid using petroleum/ethyl acetate (5:1) as eluent (68mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.16 – 7.09 (m, 4H), 6.92 (d, *J* = 8.8 Hz, 1H), 4.95 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.52 (dd, *J* = 18.0, 4.0 Hz, 1H), 3.25 (dd, *J* = 18.0, 9.2 Hz, 1H), 2.07 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 137.6, 136.9, 136.0, 129.7, 129.5, 129.3, 127.9, 127.0, 125.4, 100.9, 60.1, 41.3, 29.4, 18.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{18}IO_3S$ 429.0021; Found: 429.0022.



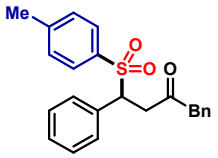
4-(naphthalen-2-yl)-4-tosylbutan-2-one (3x) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (59mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.61 (s, 1H), 7.52 – 7.45 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.91 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.69 (dd, *J* = 17.6, 4.0 Hz, 1H), 3.40 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.36 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 144.8, 133.9, 133.2, 132.9, 130.0, 129.4, 129.0, 128.3, 128.1, 127.6, 126.8, 126.7, 126.4, 66.3, 41.9, 30.5, 21.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{20}O_3SNa$ 375.1025; Found: 375.1026.



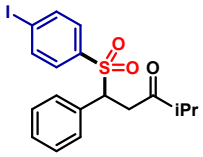
4-(4-chlorophenyl)-4-tosylbutan-2-one (3y) Prepared by general procedure; isolated as a white solid using petroleum/ethyl acetate (5:1) as eluent (47mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 6.8 Hz, 2H), 7.23 – 7.20 (m, 4H), 7.08 (d, *J* = 7.2 Hz, 2H), 4.69 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.59 (dd, *J* = 18.0, 4.4 Hz, 1H), 3.23 (dd, *J* = 18.0, 9.2 Hz, 1H), 2.41 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 145.1, 134.9, 133.7, 131.2, 131.0, 129.6, 129.0, 128.7, 65.4, 41.6, 30.5, 21.7. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}ClO_3SNa$ 359.0479; Found: 359.0479.



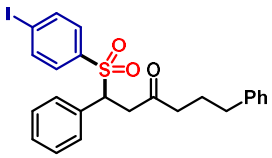
4-(2-chlorophenyl)-4-tosylbutan-2-one (3z) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (41mg, 61%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.25 – 7.18 (m, 4H), 5.45 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.66 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.31 (dd, *J* = 17.6, 9.6 Hz, 1H), 2.41 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 144.8, 133.9, 133.2, 130.0, 129.4, 129.0, 128.1, 127.6, 126.7, 126.4, 66.3, 41.9, 30.5, 21.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}ClO_3SNa$ 359.0479; Found: 359.0476.



1,4-diphenyl-4-tosylbutan-2-one (**3aa**) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (48 mg, 63%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.18 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.10 – 7.06 (m, 4H), 6.99 (d, *J* = 8 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 4.61 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.62 – 3.56 (m, 2H), 3.47 (dd, *J* = 17.6, 4.4 Hz, 1H), 3.23 (dd, *J* = 17.6, 9.6 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 144.7, 133.9, 133.0, 132.3, 129.7, 129.5, 129.4, 129.0, 128.9, 128.7, 128.4, 127.3, 66.3, 50.6, 39.8, 21.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}O_3SNa$ 401.1182; Found: 401.1184.

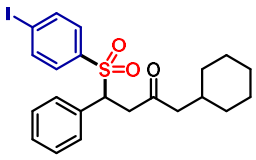


1-((4-iodophenyl)sulfonyl)-4-methyl-1-phenylpentan-3-one (3ab) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (62 mg, 70%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.10 (m, 5H), 7.05 (d, *J* = 7.2 Hz, 2H), 4.66 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.51 (dd, *J* = 17.6, 4.0 Hz, 1H), 3.27 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.56 – 2.49 (m, 1H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 138.0, 136.7, 132.3, 130.3, 129.7, 129.0, 128.6, 101.8, 66.3, 41.4, 38.2, 17.9. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}IO_3S$ 443.0178; Found: 443.0171.

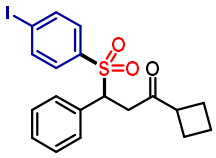


1-((4-iodophenyl)sulfonyl)-1,6-diphenylhexan-3-one (3ac) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (72 mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.08 (m, 8H), 7.04 – 6.99 (m, 4H), 4.65 (dd, J = 8.8, 4.4 Hz, 1H), 3.44 (dd, J = 17.6, 4.4 Hz, 1H), 3.13 (dd, J = 17.6, 9.2 Hz, 1H), 2.46 – 2.37 (m, 3H), 2.31 – 2.23 (m, 1H), 1.79 – 1.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2,

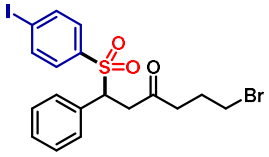
141.2, 138.0, 136.6, 132.2, 130.3, 129.7, 129.1, 128.7, 128.5, 126.1, 101.9, 66.2, 42.5, 40.5, 34.8, 24.9. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{23}IO_3SNa$ 541.0305; Found: 541.0300.



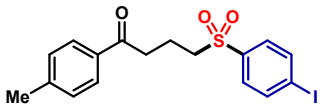
1-cyclohexyl-4-((4-iodophenyl)sulfonyl)-4-phenylbutan-2-one (3ad) Prepared by general procedure; isolated as a white solid using petroleum/ethyl acetate (5:1) as eluent (84 mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 6.4 Hz, 2H), 7.22 – 7.09 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.65 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.43 (dd, *J* = 17.6, 4.0 Hz, 1H), 3.19 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.26 – 2.14 (m, 2H), 1.68 – 1.63 (m, 1H), 1.55 – 1.52 (m, 2H), 1.45 – 1.37 (m, 2H), 1.18 – 0.98 (m, 4H), 0.81 – 0.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2, 138.0, 136.7, 132.2, 130.3, 129.7, 129.0, 128.6, 101.8, 66.2, 51.1, 40.9, 33.8, 33.1, 32.9, 26.1. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{25}IO_3SNa$ 519.0461; Found: 519.0452.



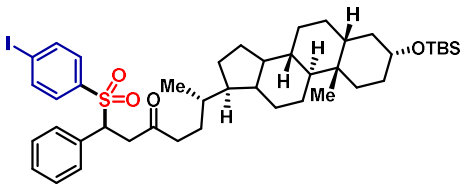
1-cyclobutyl-3-((4-iodophenyl)sulfonyl)-3-phenylpropan-1-one (3ae) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (64 mg, 71%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.09 (m, 5H), 7.04 (d, *J* = 6.8 Hz, 2H), 4.66 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.41 (dd, *J* = 17.6, 4.0 Hz, 1H), 3.22 – 3.10 (m, 2H), 2.21 – 2.11 (m, 1H), 2.10 – 2.00 (m, 2H), 1.95 – 1.82 (m, 2H), 1.72 – 1.62 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 138.0, 136.7, 132.3, 130.3, 129.7, 129.1, 128.6, 101.8, 66.2, 45.7, 37.8, 24.2, 23.9, 17.6. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}IO_3S$ 455.0178; Found: 455.0177.



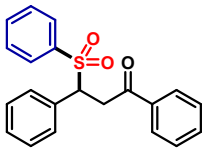
6-bromo-1-((4-iodophenyl)sulfonyl)-1-phenylhexan-3-one (3af) Prepared by general procedure; isolated as a pale yellow solid using petroleum/ethyl acetate (5:1) as eluent (56 mg, 54%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.15 (m, 3H), 7.12 – 7.03 (m, 4H), 4.66 (dd, *J* = 8.8, 4.8 Hz, 1H), 3.52 (dd, *J* = 17.6, 4.8 Hz, 1H), 3.29 – 3.14 (m, 2H), 3.18 (dd, *J* = 17.6, 8.4 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.54 – 2.46 (m, 1H), 2.03 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 138.1, 136.5, 132.1, 130.3, 129.7, 129.2, 128.7, 102.0, 66.2, 41.3, 40.7, 32.8, 26.1. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{19}BrIO_3S$ 520.9283; Found:520.9278.



4-((4-iodophenyl)sulfonyl)-1-(p-tolyl)butan-1-one (3ag) Prepared by general procedure; isolated as a white solid using petroleum/ethyl acetate (5:1) as eluent (26 mg, 30%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 3.07 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 2.11 – 2.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 144.4, 138.7, 138.6, 133.9, 129.5, 129.4, 128.1, 101.7, 55.2, 36.0, 21.7, 17.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{18}IO_3S$ 429.0021; Found: 429.0025.



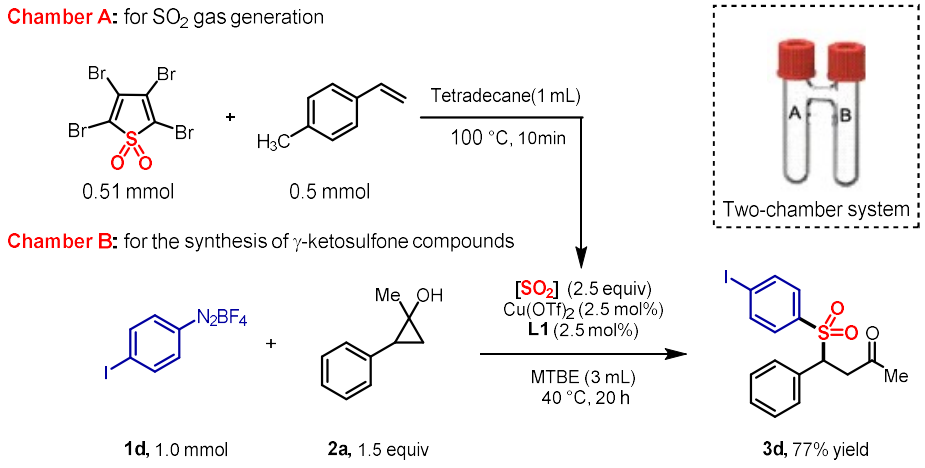
(6S)-6-((3R,5R,8S,9S,10S,17R)-3-((tert-butyldimethylsilyl)oxy)-10-methylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-1-((4-iodophenyl)sulfonyl)-1-phenylheptan-3-one (3ah) Prepared by general procedure; isolated as a yellow solid using petroleum/ethyl acetate (5:1) as eluent (88 mg, 53%).[1]H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.09 (m, 4H), 7.06 – 7.03 (m, 2H), 4.65 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.08 – 4.02 (m, 1H), 3.57 – 3.44 (m, 2H), 3.24 – 3.14 (m, 1H), 2.45 – 2.15 (m, 2H), 2.00 - 1.90 (s, 2H), 1.87 – 1.41 (m, 13H), 1.35 – 0.74 (m, 29H), 0.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 171.2, 138.0, 136.7, 132.2, 130.3, 129.7, 129.1, 128.7, 101.8, 71.9, 66.2, 60.4, 56.5, 55.9, 42.7, 42.1, 40.5, 40.4, 40.3, 40.2, 36.5, 35.8, 35.4, 35.2, 35.1, 34.6, 30.6, 29.5, 28.2, 27.2, 26.4, 24.2, 23.4, 21.1, 20.8, 18.3, 14.2, 12.0. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{43}H_{63}IO_4SSiNa$ 853.3159; Found: 853.3155.



1,3-diphenyl-3-(phenylsulfonyl)propan-1-one (3ai) Prepared by general procedure; isolated as a white solid using petroleum/ethyl acetate (5:1) as eluent (22 mg, 32%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.84 (m, 2H), 7.64 – 7.50 (m, 4H), 7.49 – 7.41 (m, 2H), 7.41 – 7.32 (m, 2H), 7.23 – 7.14 (m, 5H), 4.92 (dd, *J* = 9.7, 3.6 Hz, 1H), 4.18 – 4.11 (m, 1H), 3.94 (dd, *J* = 17.9, 9.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 137.0, 136.2, 133.8, 133.8, 132.6, 129.9, 129.1, 128.9, 128.9, 128.8, 128.6, 128.2, 66.6, 37.0. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{18}O_3SNa$ 373.0869; Found:373.0865.

Gram-Scale Reaction and Transformation of γ-keto aryl sulfones.

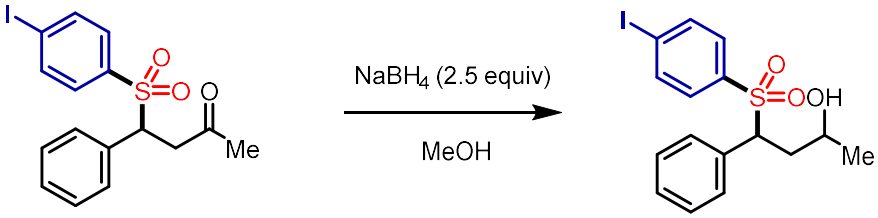
Gram-Scale Reaction



In an argon fulfilled glovebox, tetrabromothiophene S, S-dioxides (2.55 mmol, 1187 mg) and 1-methyl-4-vinylbenzene (2.5 mmol, 330 uL) were added into chamber A with a magnetic stirring bar, followed by addition of tetradecane (3.0 mL). Diazonium salts **1** (1.0 mmol), Cyclopropanols **2** (1.5 mmol, 1.5 equiv.), $Cu(OTf)_2$ (2.5 mol%, 9.0 mg)

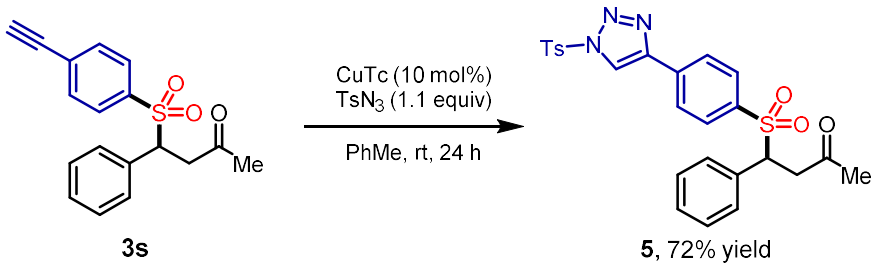
and **L1** (8.0 mg, 2.5 mol%) were added into chamber B with a magnetic stirring bar, followed by addition of MTBE (3.0 mL). The two-chamber was sealed and removed out of the glovebox, then chamber A was allowed to heated to 100 °C in heat block. About ten minutes later, the sulfur dioxide was completely released since the system in chamber A became clear. Then chamber B was heated to 40 °C in heat block. Upon completion, the mixture in chamber B was passed through a short silica gel pad with ethyl acetate. The filtrate was washed by ethyl acetate and H_2O (15 mL×3), dried by Na_2SO_4, then concentrated and the residue was purified by flash column chromatography to afford pure products **3d** in 77% yield.

Transformation of γ-keto arylsulfone



3d **4,** 85% yield

According to the literature[5], to a mixture of **3d** (82.9 mg, 0.2 mmol) in MeOH (3 mL) was added $NaBH_4$ (18.9 mg, 0.5 mmol) at 0 °C. After stirring for 24 hours, the mixture was washed by ethyl acetate and H_2O (15 mL×3), dried by Na_2SO_4, then concentrated and the residue was purified by flash column chromatography to afford pure products **4** (70.7 mg, 85% yield). ^{1}H NMR (400 MHz, Chloroform-d) 7.69 – 7.57 (m, 2H), 7.28 – 7.11 (m, 4H), 7.11 – 6.98 (m, 3H), 4.36 (dd, J = 11.6, 3.5Hz, 1H), 3.49-3.38 (m, 1H), 2.61 – 2.55 (m, 1H), 2.18 – 2.08 (m, 1H), 1.57 (br, 1H), 1.12 (d, J = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 136.9, 133.2, 130.3, 129.7, 129.0, 128.7, 101.6, 68.4, 65.7, 37.8, 23.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{17}IO_3SNa$ 438.9835; Found: 438.9837.

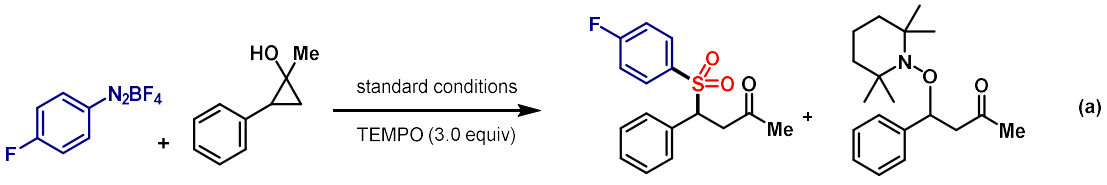


3s **5**, 72% yield

According to the literature[6], copper(I) thiophene-2-carboxylate hydrate (CuTc) (1.9 mg, 0.01 mmol, 10 mol%) and **3s** (37.0 mg, 0.1 mmol, 1.0 equiv) were added to PhMe (1.0 mL) in a 15 mL vial. Then TsN_3 (21.7 mg, 0.11 mmol, 1.1 equiv) were slowly injected into the flask. The reaction was stirred at room temperature for one day. After terminal alkynes were completely reacted (monitored by TLC analysis). The reaction mixture was filtered to remove inorganic compound, the solvent was dried over and purified by flash column chromatography to get N1-sulfonyl-1,2,3-triazoles **5**. Isolated as a white solid using petroleum/ethyl acetate (5/1) as eluent (73.4 mg, 72% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.10 (m, 3H), 7.11 – 6.99 (m, 2H), 4.68 (dd, *J* = 9.0, 4.3 Hz, 1H), 3.56 (dd, *J* = 17.8, 4.3 Hz, 1H), 3.22 (dd, *J* = 17.8, 9.0 Hz, 1H), 2.39 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 146.8, 144.3, 136.0, 133.1, 131.7, 131.2, 129.6, 128.8, 128.7, 128.0, 127.9, 127.6, 125.0, 119.3, 65.2, 40.4, 29.5, 28.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}N_3O_5S_2$ 510.1152; Found: 510.1155.

Mechanistic studies

(a) Radical trapping experiment with TEMPO

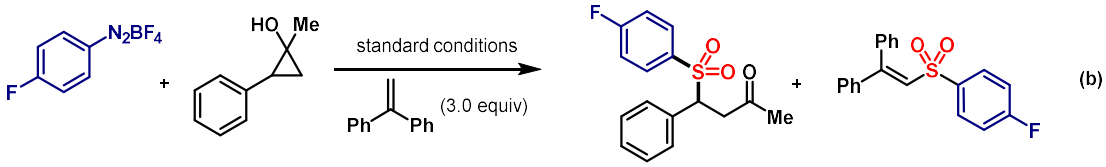


1a **2a** **3a**, 0% **6**, detected by LC-MS

In an argon fulfilled glovebox, tetrabromothiophene S, S-dioxides (0.51 mmol, 237.4 mg) and 1-methyl-4-vinylbenzene (0.5 mmol, 66 uL) were added into chamber A with a magnetic stirring bar, followed by addition of tetradecane (1.0 mL). Diazonium salt

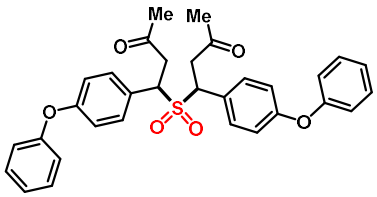
1a (0.2 mmol, 1.0 equiv), Cyclopropanol **2a** (0.3 mmol, 1.5 equiv), $Cu(OTf)_2$ (2.5 mol%, 1.8 mg), **L1** (2.5 mol%,1.6 mg) and TEMPO (0.6 mmol, 3.0 equiv.) were added into chamber B with a magnetic stirring bar, followed by addition of MTBE (1.0 mL). The two-chamber was sealed and removed out of the glovebox, then chamber A was allowed to heated to 100 °C in heat block. About ten minutes later, the sulfur dioxide was completely released since the system in chamber A became clear. Then chamber B was heated to 40 °C in heat block. The yields were determined by ^{19}F-NMR analysis using trifluorotoluene as an internal standard. The benzyl radical combined with TEMPO were detected by LCMS m/z: $[M+H]^+$ calcd for $C_{19}H_{30}NO_2$ 304.2271; found: 304.3362.

(b) Radical trapping experiment with 1,1-Diphenylethylene

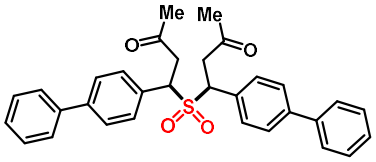


In an argon fulfilled glovebox, tetrabromothiophene S, S-dioxides (0.51 mmol, 237.4 mg) and 1-methyl-4-vinylbenzene (0.5 mmol, 66 uL) were added into chamber A with a magnetic stirring bar, followed by addition of tetradecane (1.0 mL). Diazonium salt **1a** (0.2 mmol, 1.0 equiv), Cyclopropanol **2a** (0.3 mmol, 1.5 equiv), $Cu(OTf)_2$ (2.5 mol%, 1.8 mg), **L1** (2.5 mol%,1.6 mg) and 1,1-Diphenylethylene (0.6 mmol, 3.0 equiv) were added into chamber B with a magnetic stirring bar, followed by addition of MTBE (1.0 mL). The two-chamber was sealed and removed out of the glovebox, then chamber A was allowed to heated to 100 °C in heat block. About ten minutes later, the sulfur dioxide was completely released since the system in chamber A became clear. Then chamber B was heated to 40 °C in heat block. The yields were determined by ^{19}F-NMR analysis using trifluorotoluene as an internal standard. The aryl radical combined with 1,1-Diphenylethylene were detected by LCMS m/z: $[M+Na]^+$ calcd for $C_{20}H_{15}FO_2SNa$ 361.0669; found: 361.2886.

(c) homo-coupling products 8



4-((3-oxo-1-(4-phenoxyphenyl)butyl)sulfonyl)-4-(4-phenoxyphenyl)butan-2-one (8a) Isolated as a side product of the corresponding γ-ketone aryl sulfone. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.19 (m, 2H), 7.09 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.37 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.33 (dd, *J* = 17.8, 3.6 Hz, 1H), 2.98 (dd, *J* = 17.8, 9.7 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 203.1, 158.6, 156.0, 131.4, 130.0, 126.5, 124.2, 119.9, 118.2, 59.8, 42.0, 30.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{32}H_{31}O_6S$ 543.1836; Found: 543.1840.



4-([1,1'-biphenyl]-4-yl)-4-((1-([1,1'-biphenyl]-4-yl)-3-oxobutyl)sulfonyl)butan-2-one (8b) Isolated as a side product of the corresponding γ-ketone aryl sulfone. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 4H), 7.49 – 7.39 (m, 4H), 7.37 – 7.30 (m, 1H), 5.20 (dd, *J* = 8.9, 3.5 Hz, 2H), 2.99 – 2.77 (m, 2H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.3, 141.8, 140.9, 140.8, 128.9, 127.4, 127.2, 126.2, 69.7, 52.0, 30.91. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{32}H_{31}O_4S$ 511.1938; Found: 511.1939.

References

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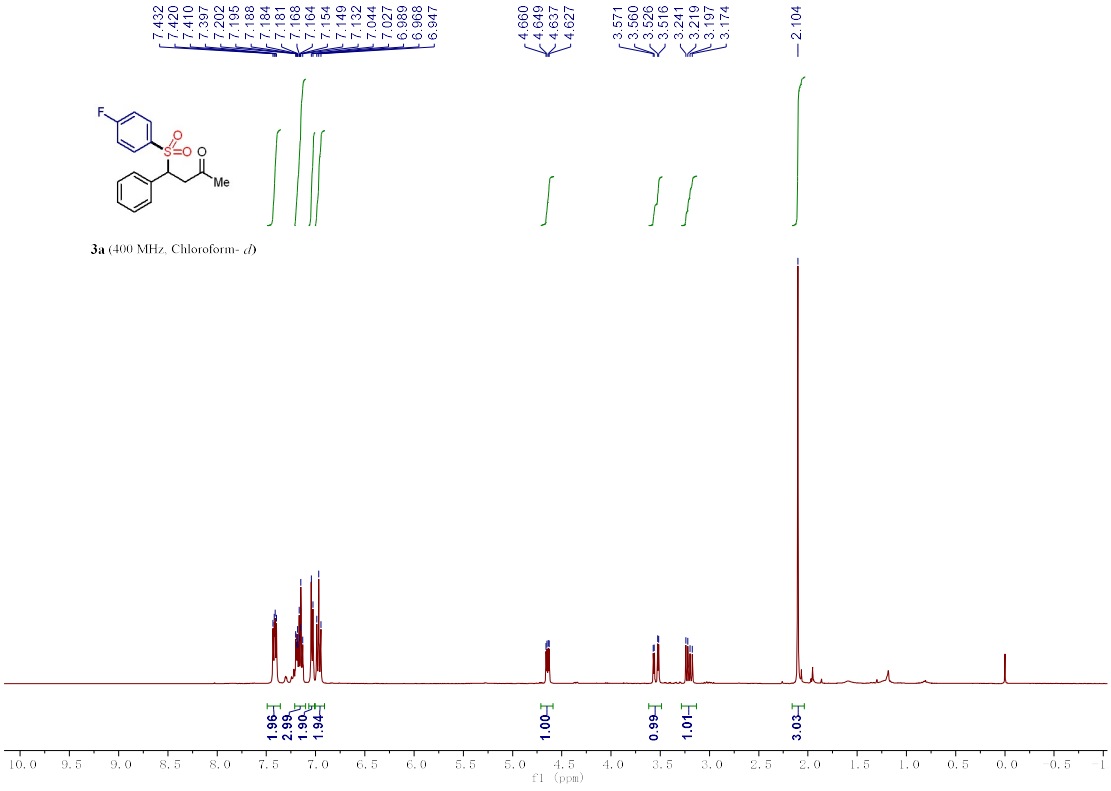
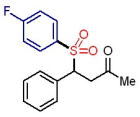
6. Wang, T.; Tang, Z.; Luo, H.; Tian, Y.; Xu, M.; Lu, Q.; Li, B. Access to (Z)-β-Substituted Enamides from N1-H-1,2,3-Triazoles. *Org. Lett.*, **2021**, *23*, 6293-6298.

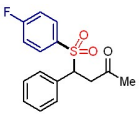
Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra of Products



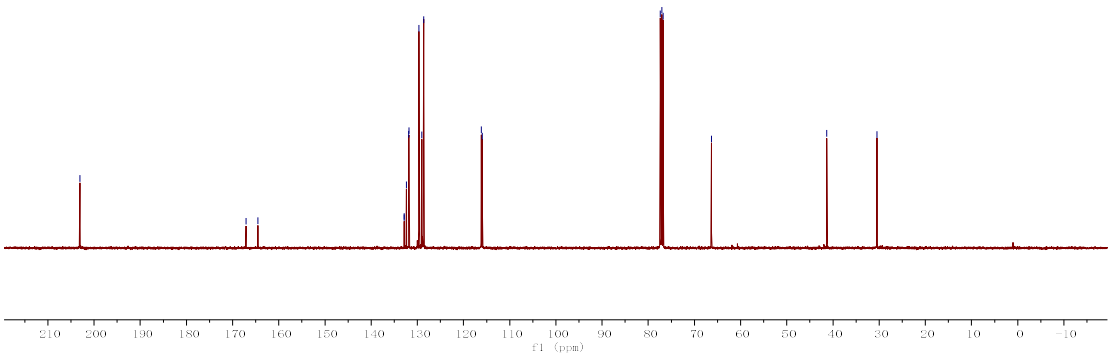
3a (400 MHz, Chloroform-*d*)

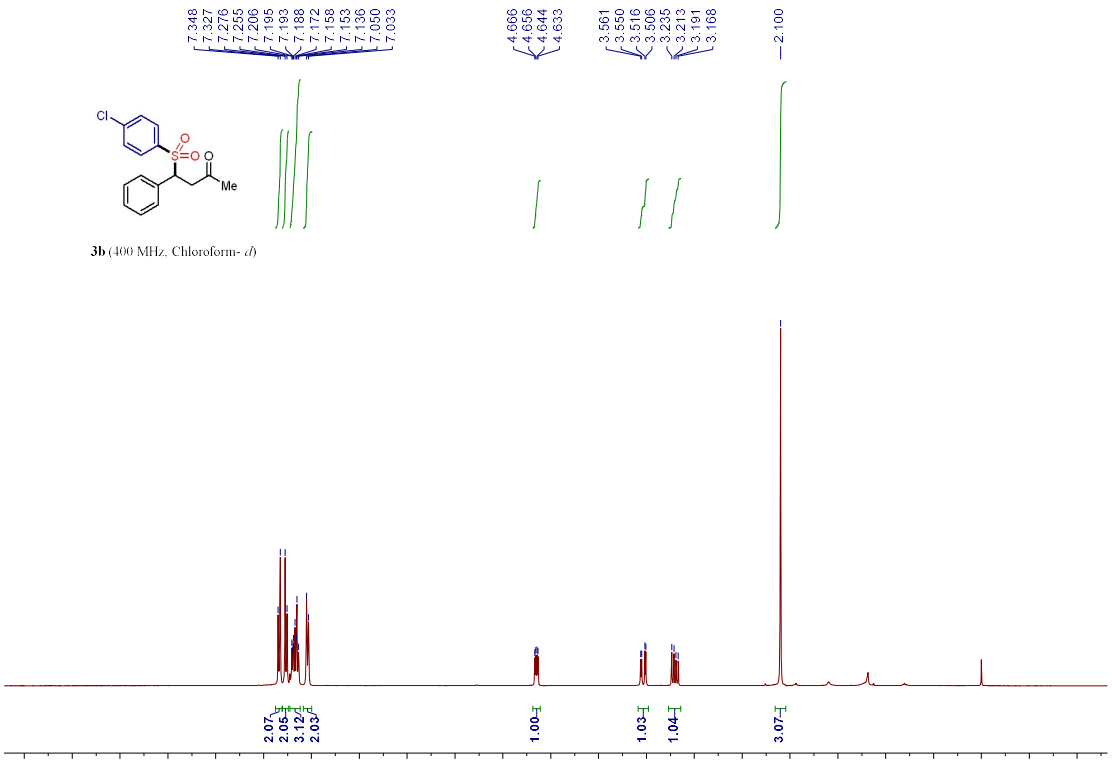


3a (376 MHz, , Chloroform-*d*)



3a (101 MHz, Chloroform-*d*)





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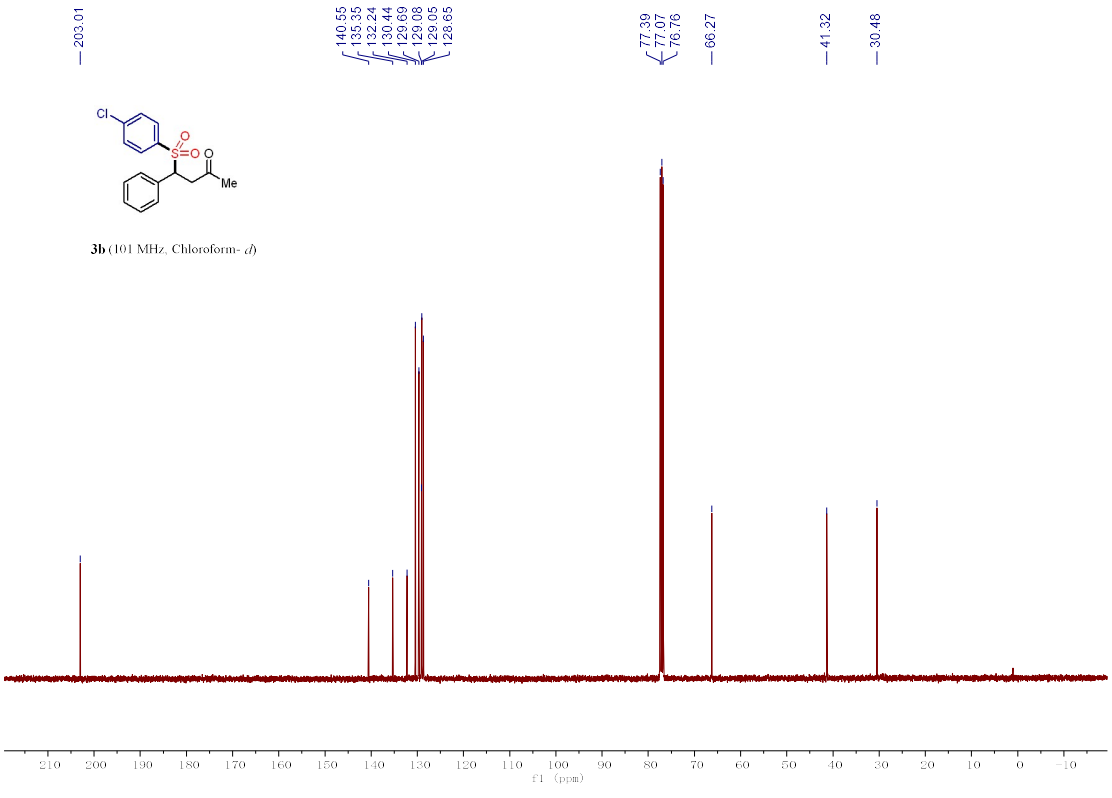

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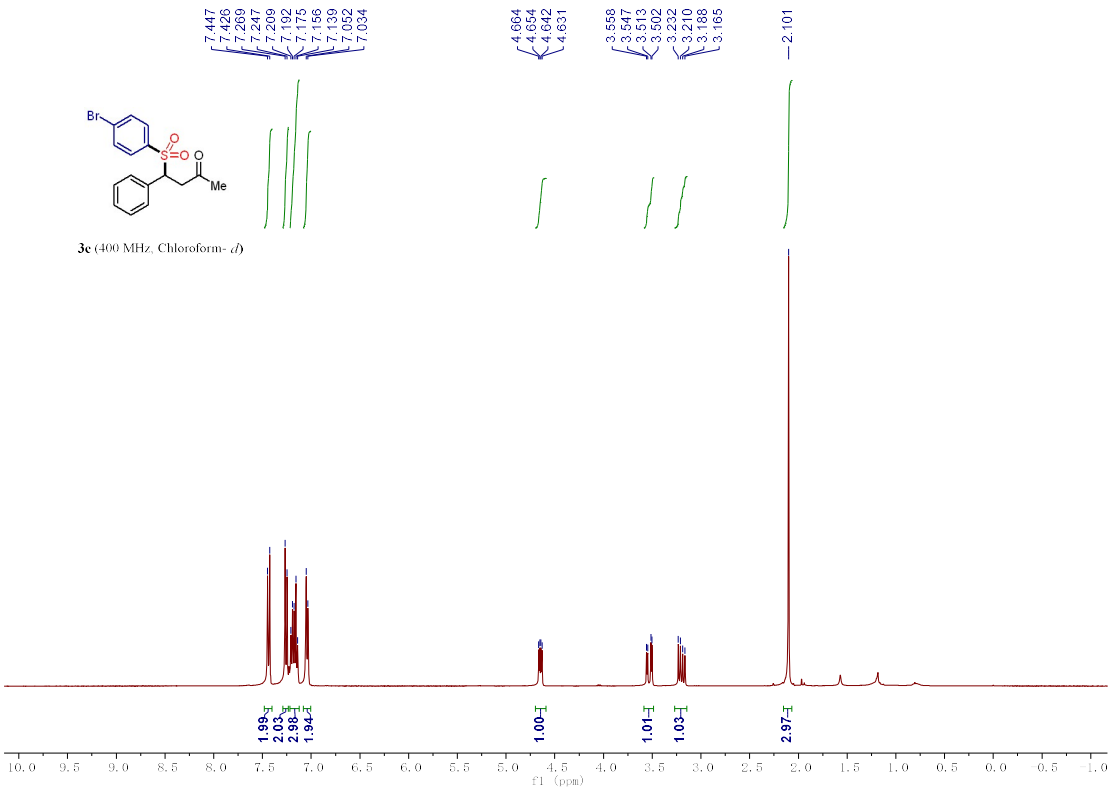

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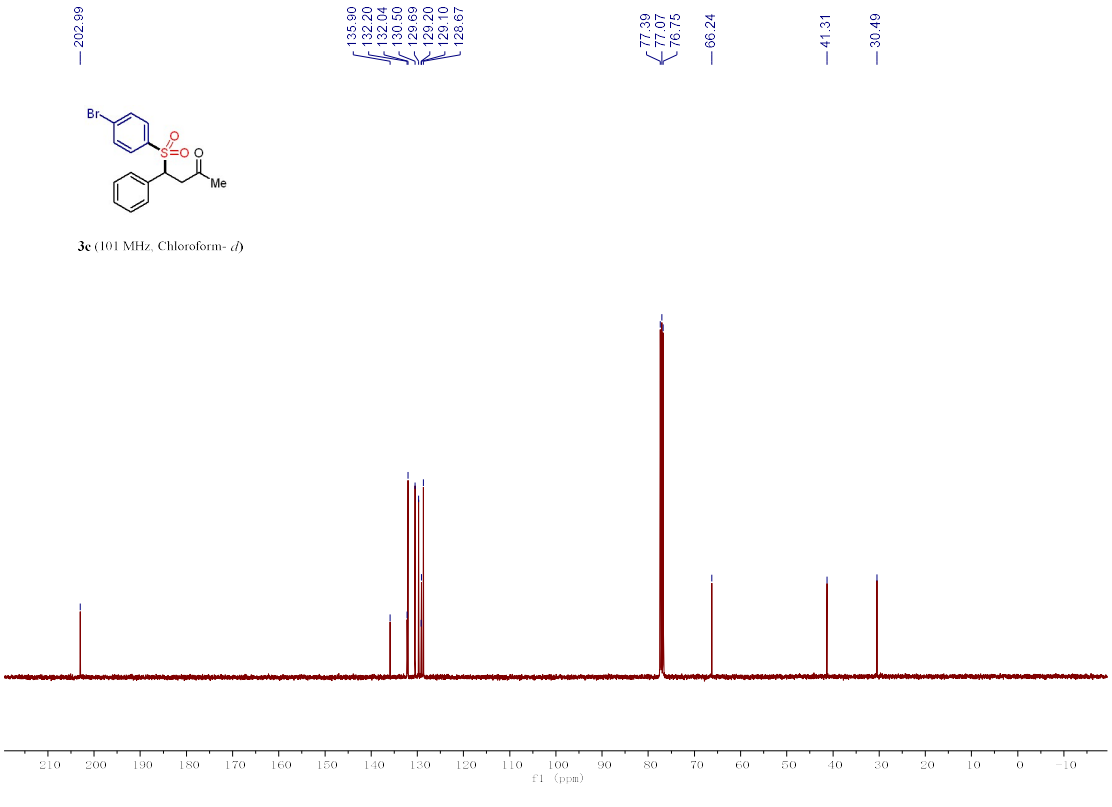

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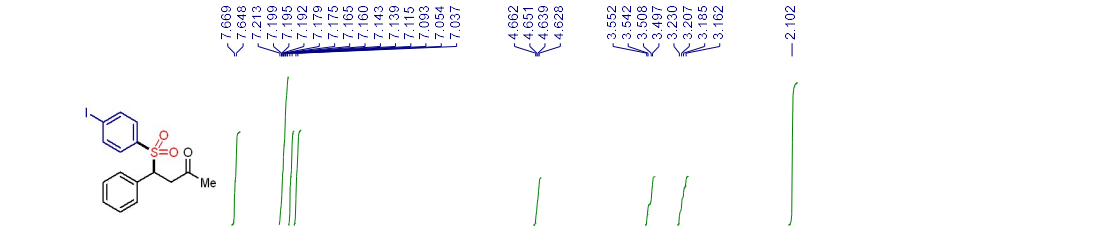

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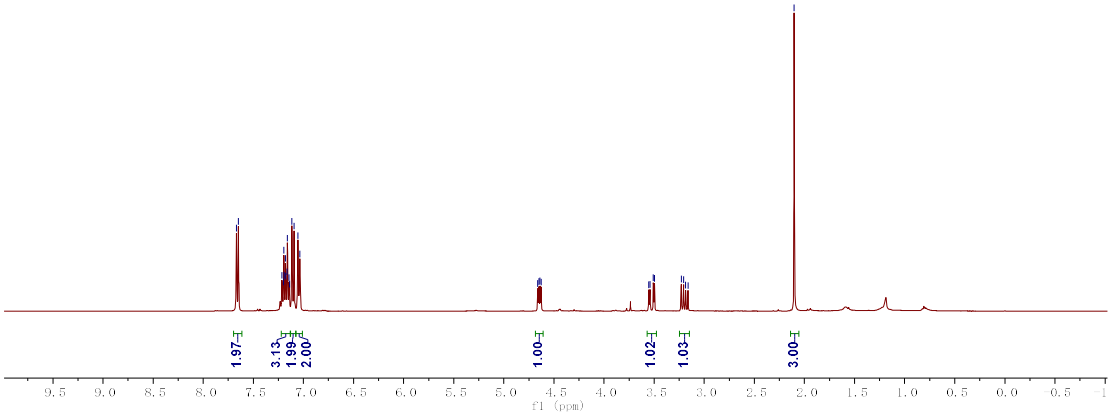

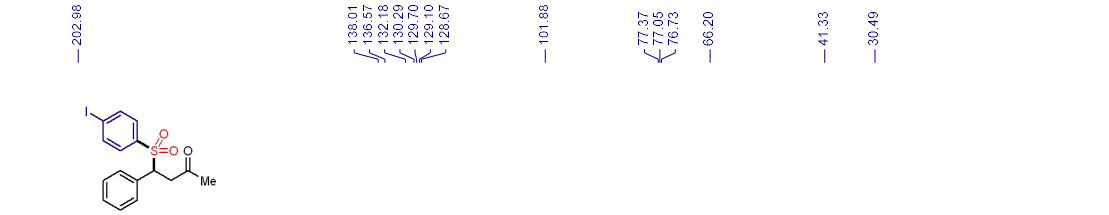

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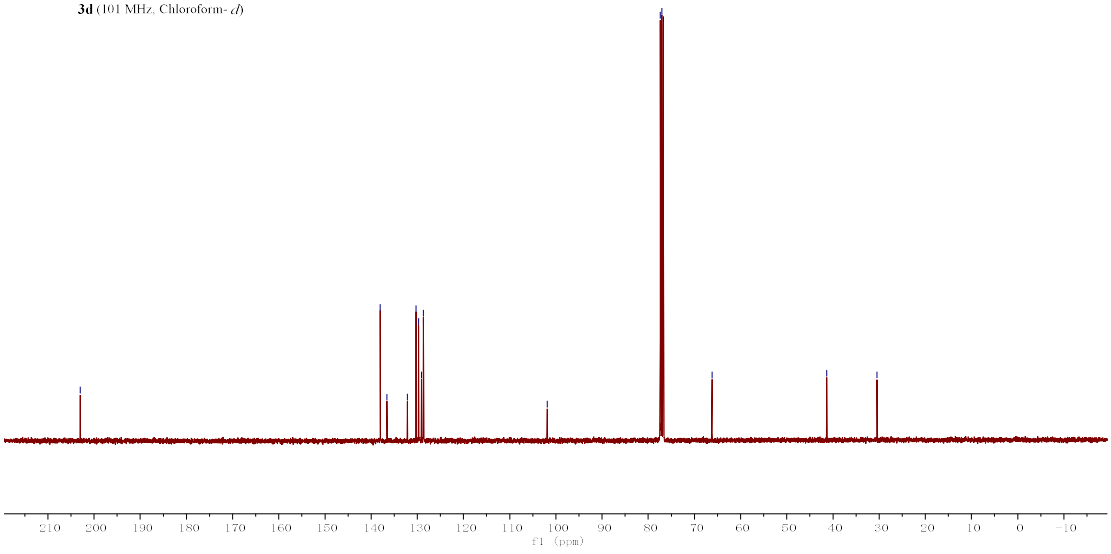

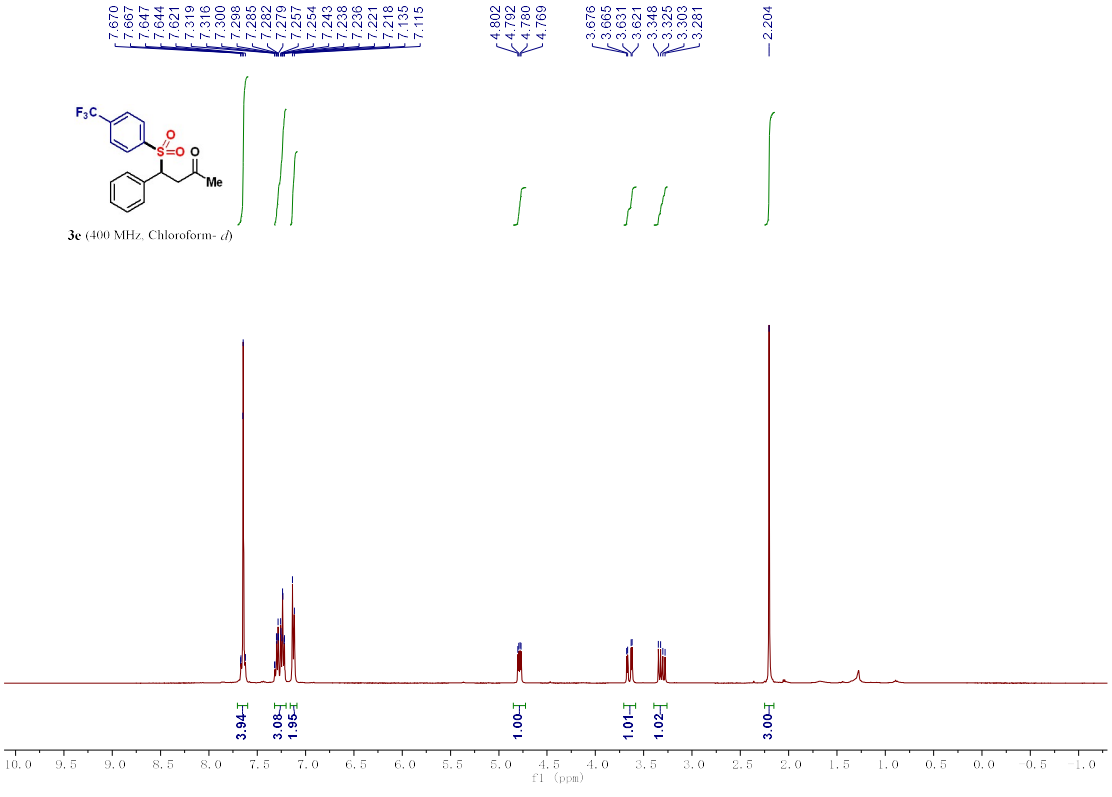

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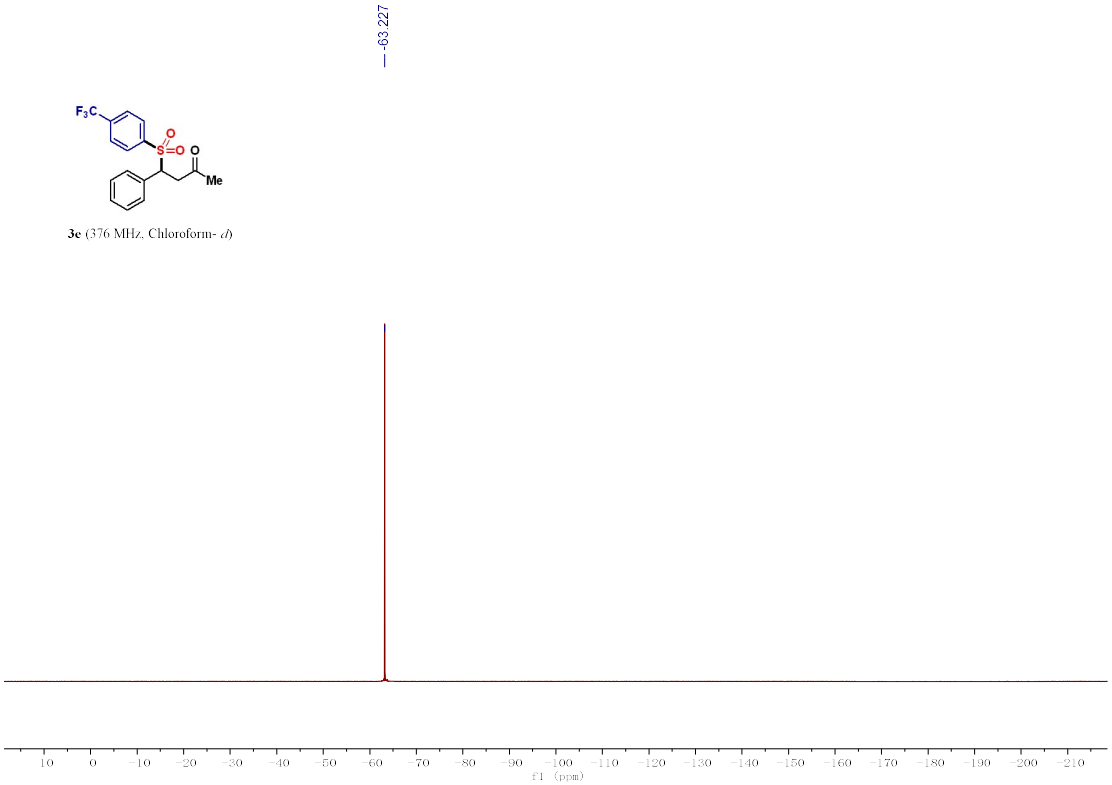

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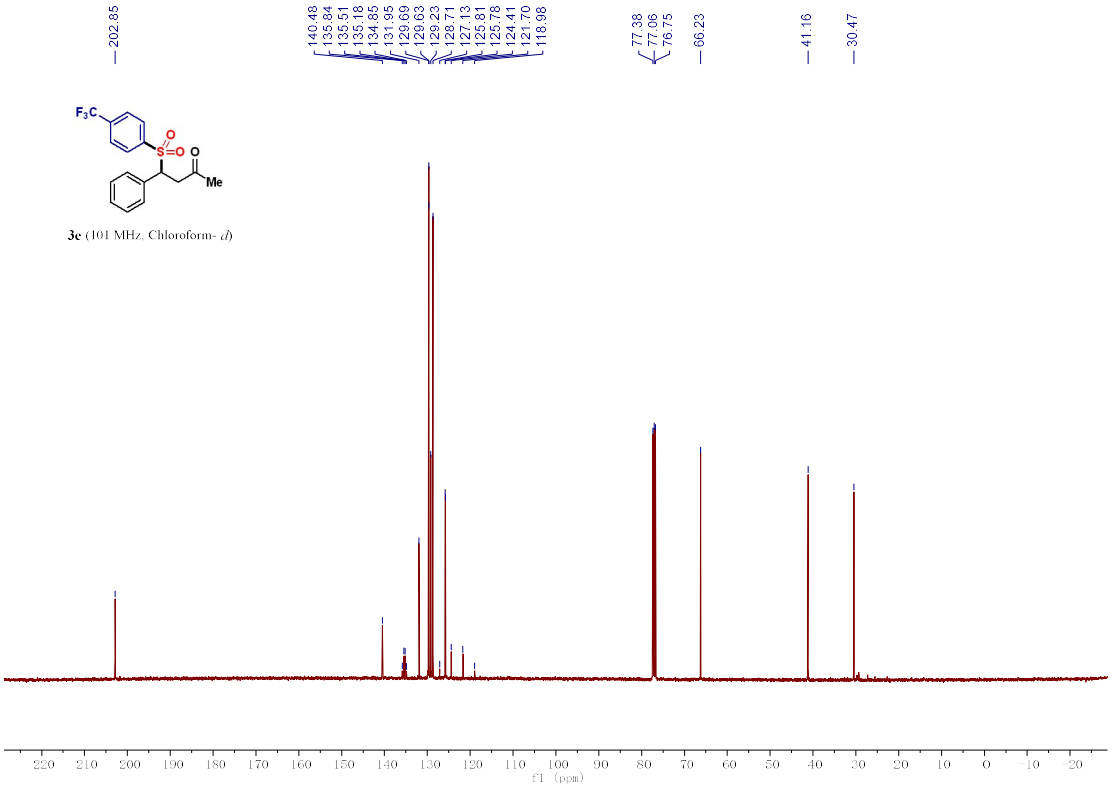

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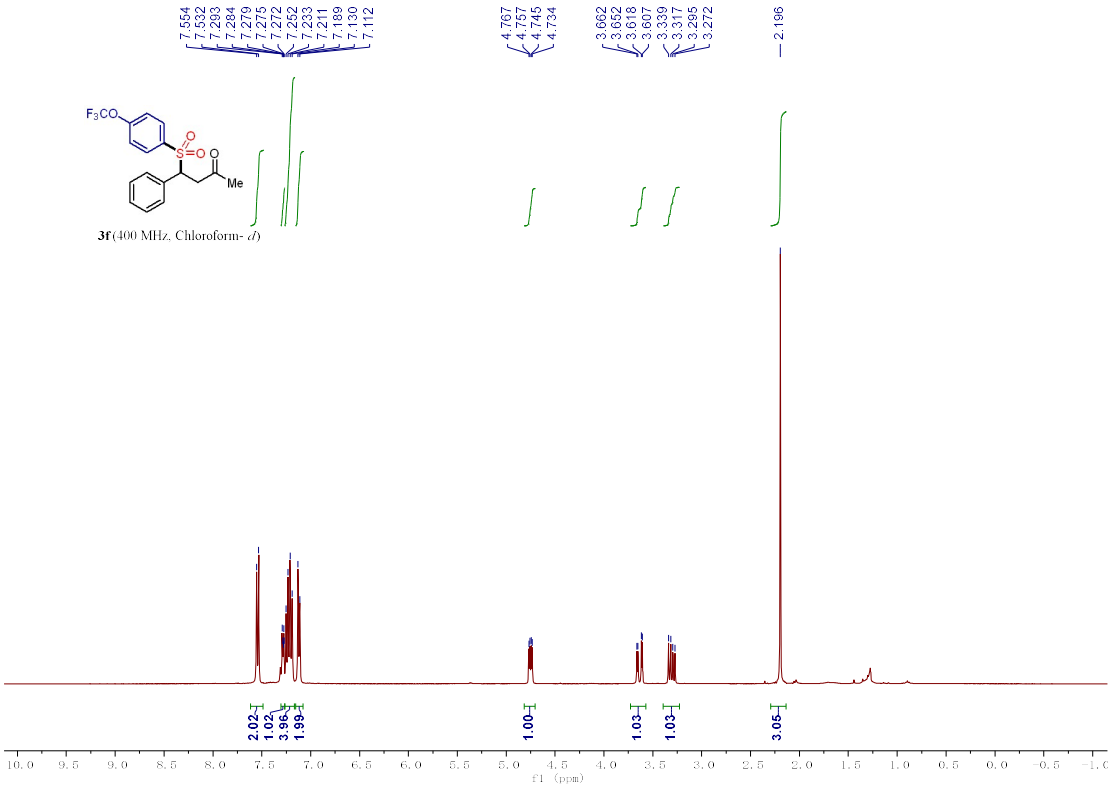

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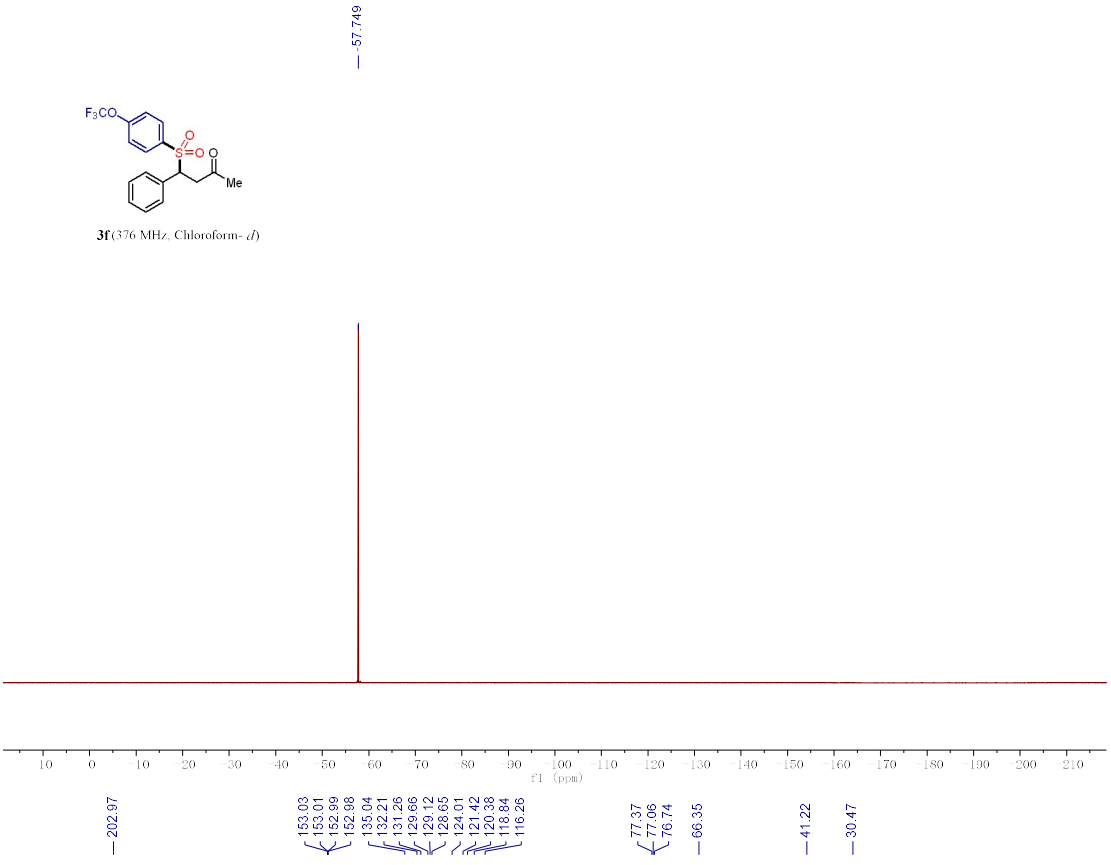
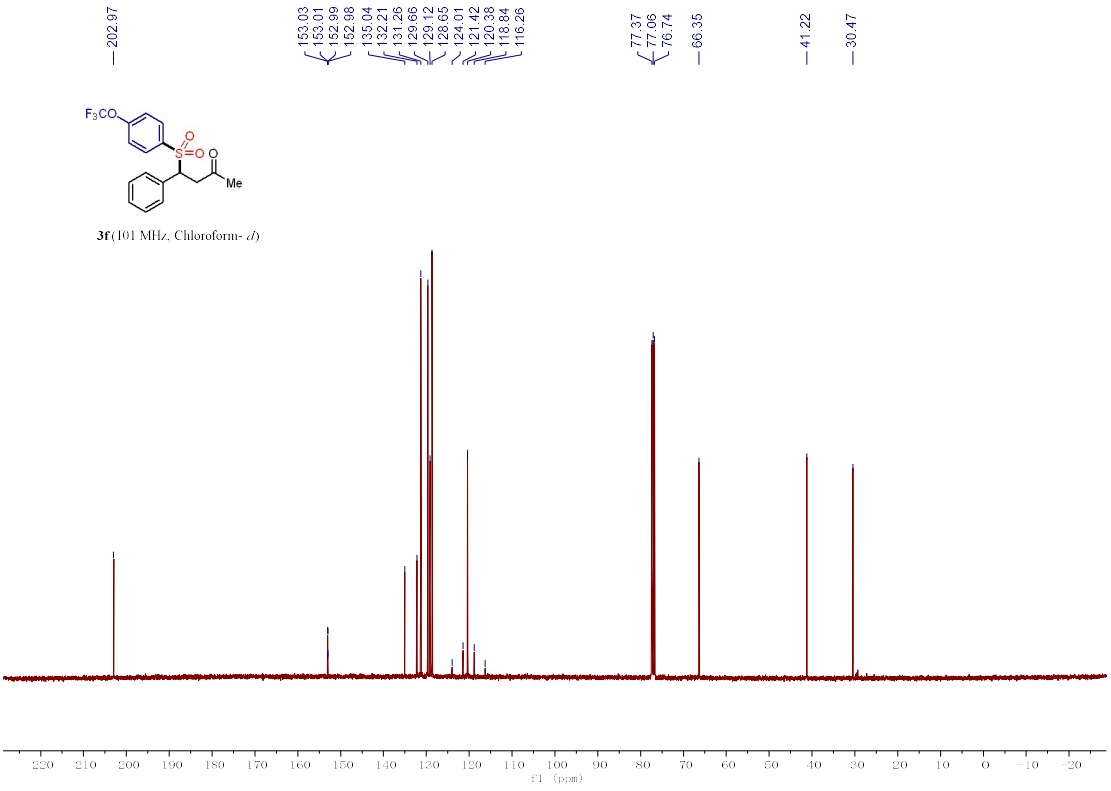


3f(376 MHz, Chloroform-*d*)



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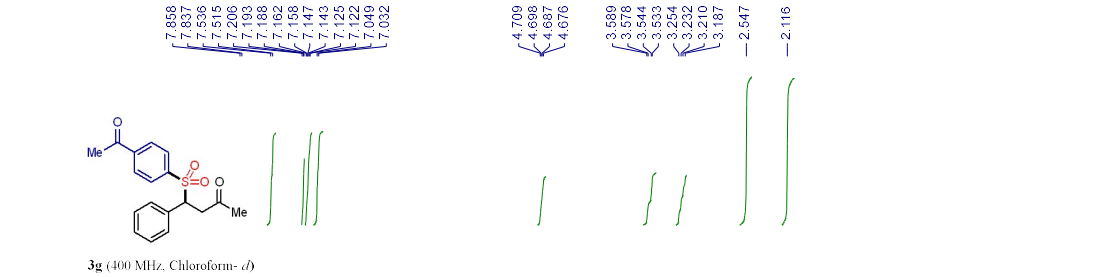
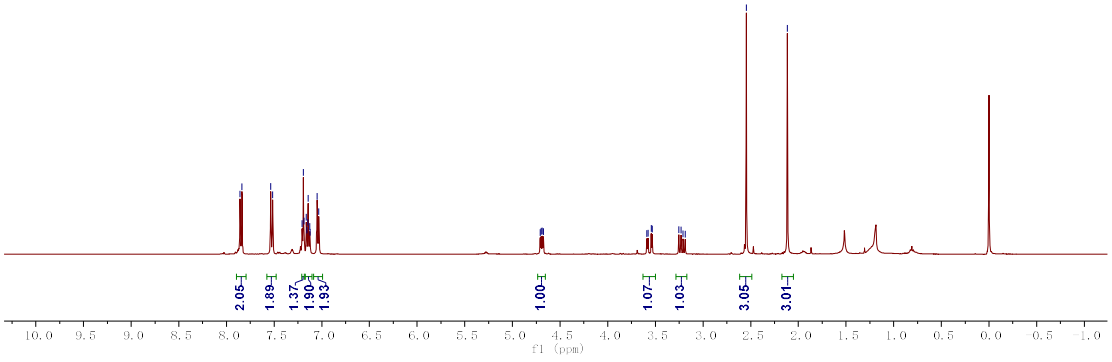
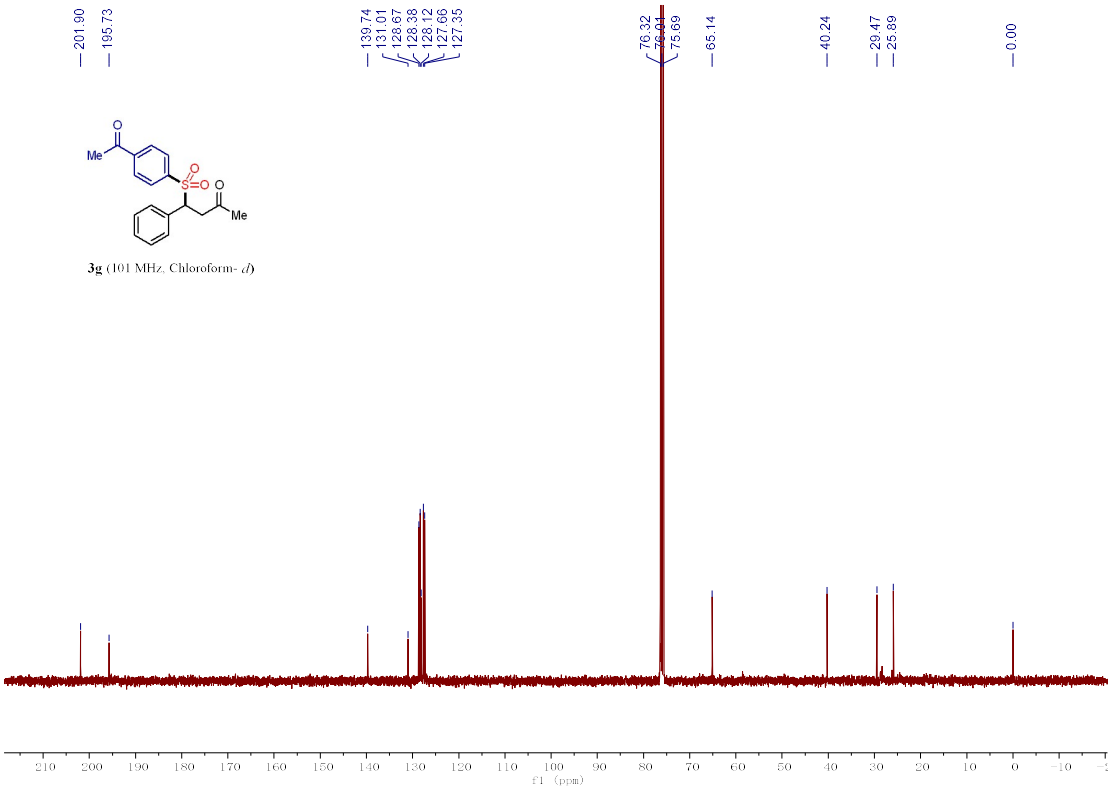


3g (400 MHz, Chloroform- *d*)





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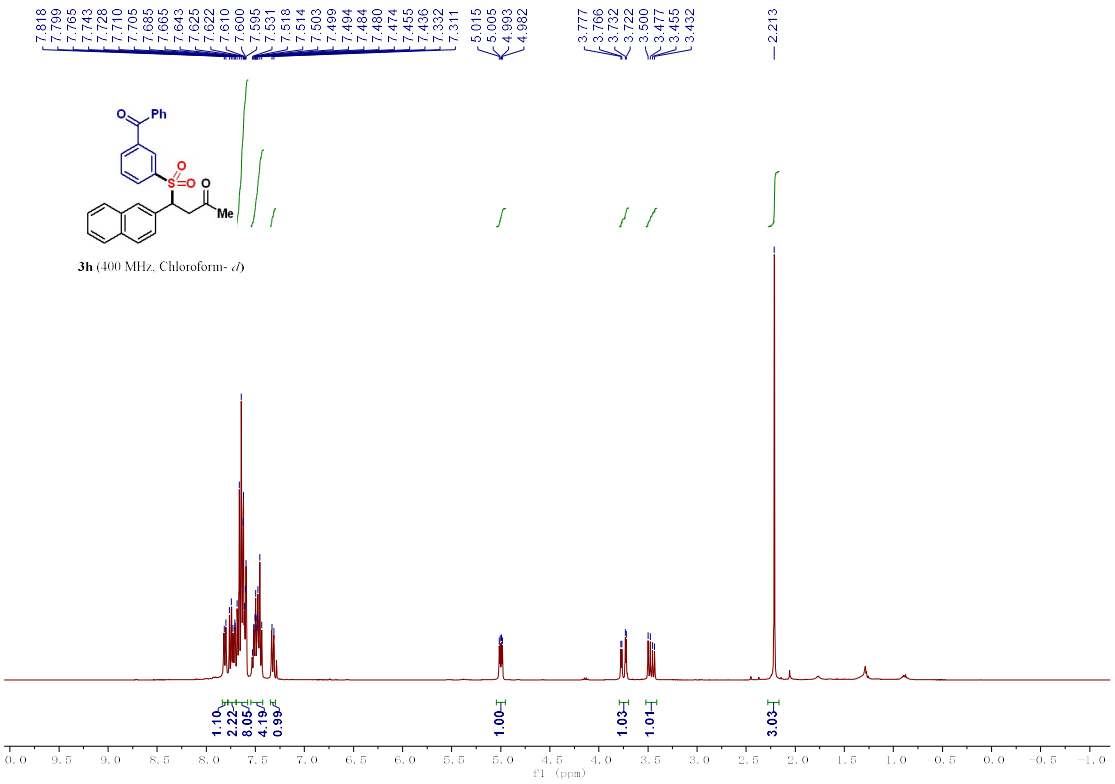

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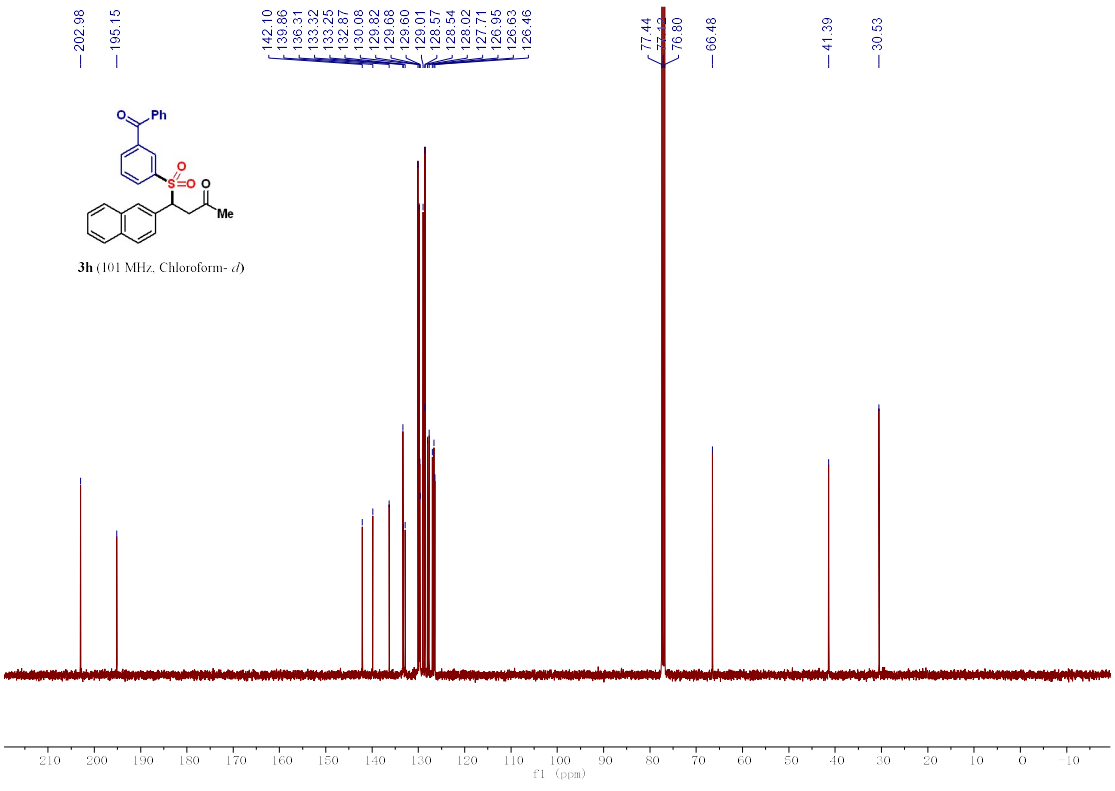

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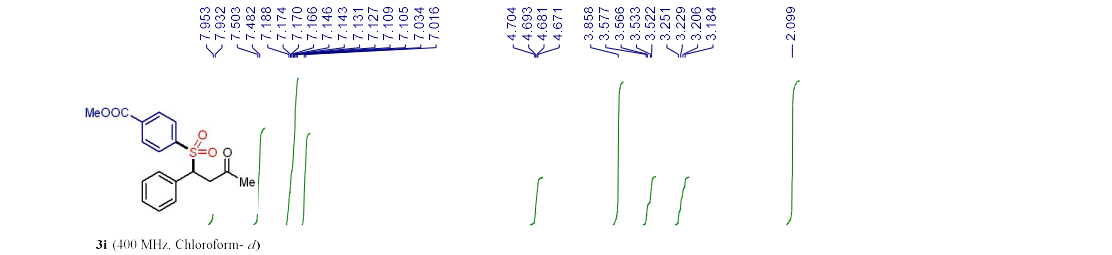

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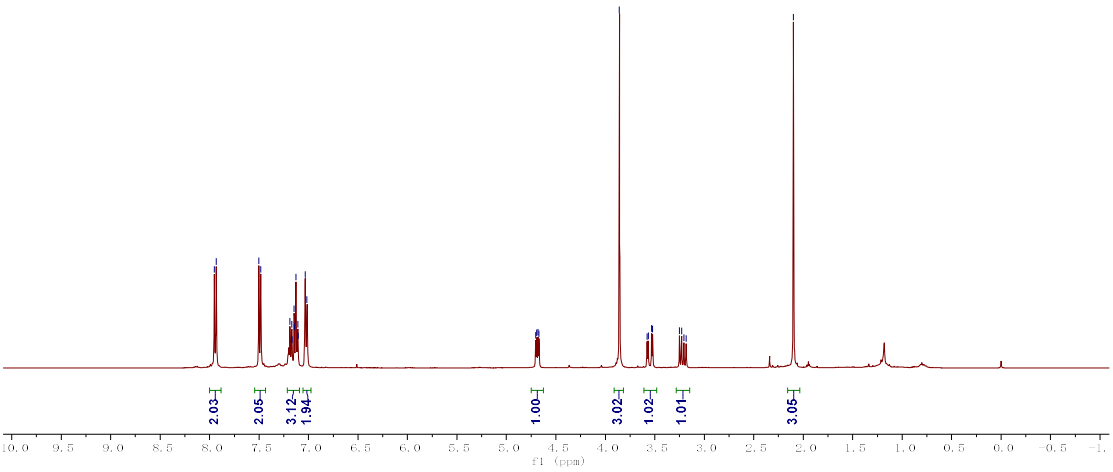

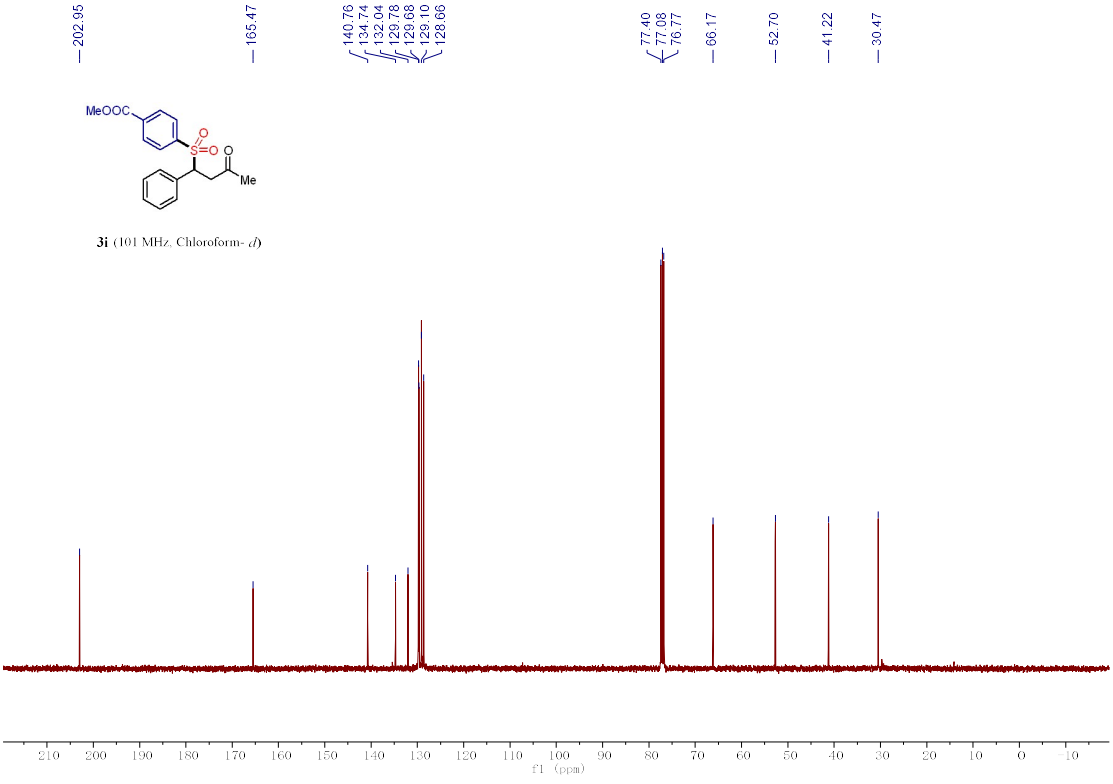

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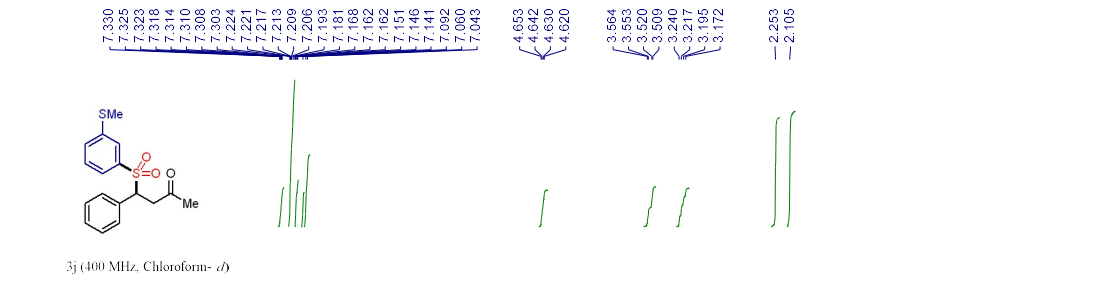

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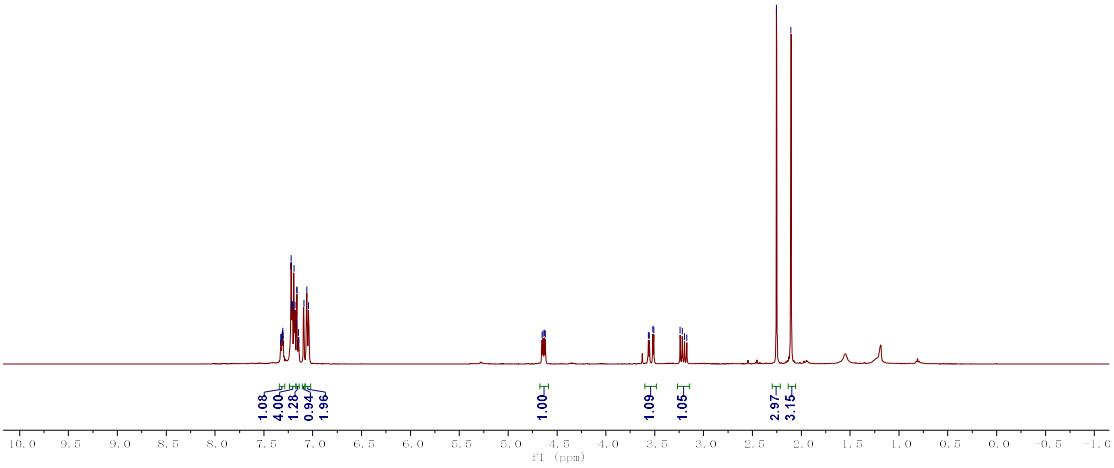

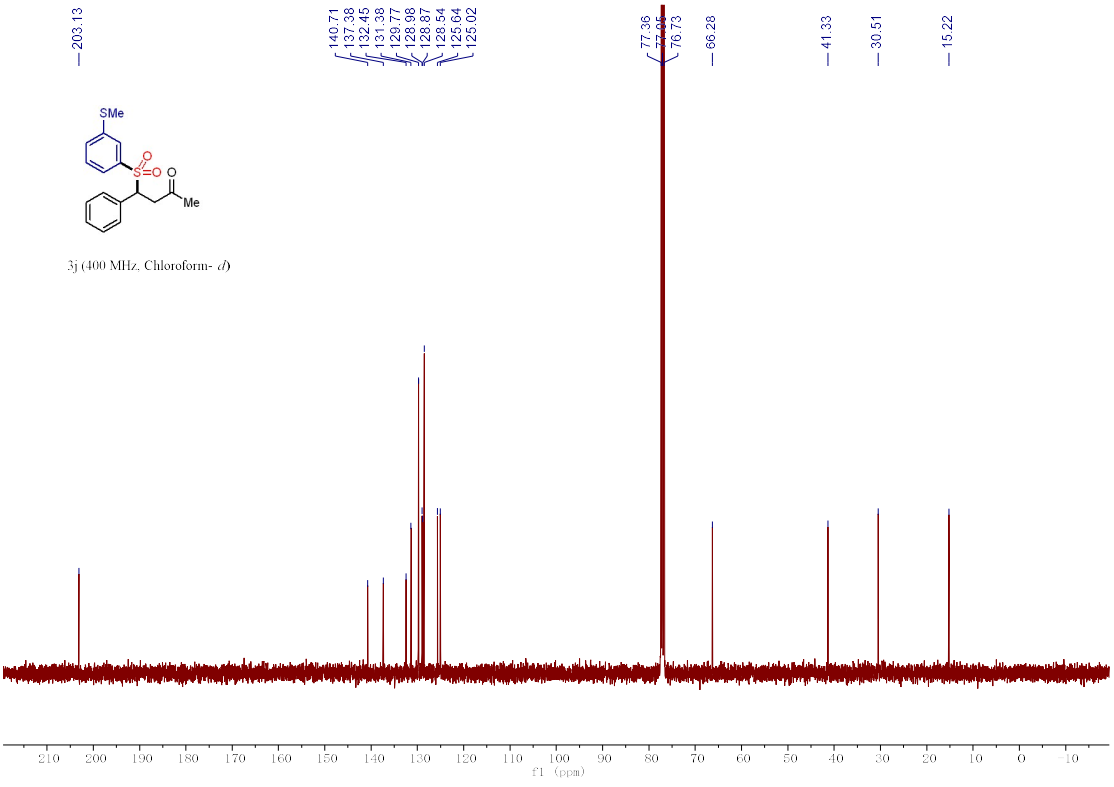

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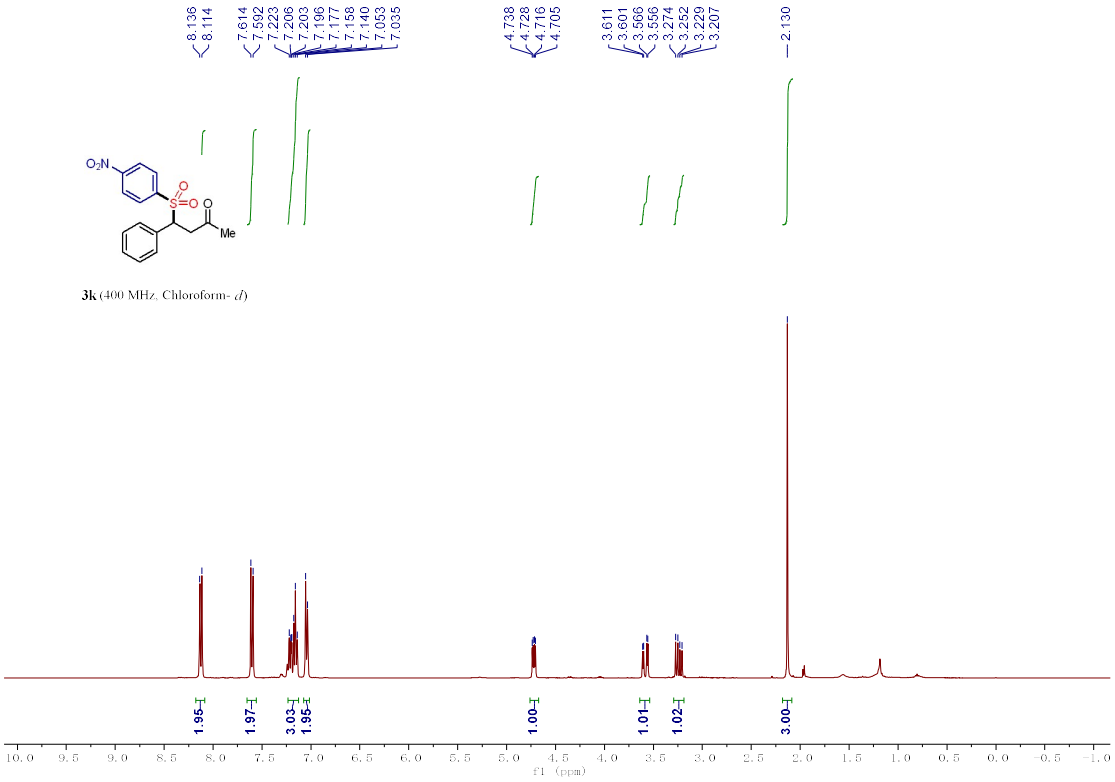

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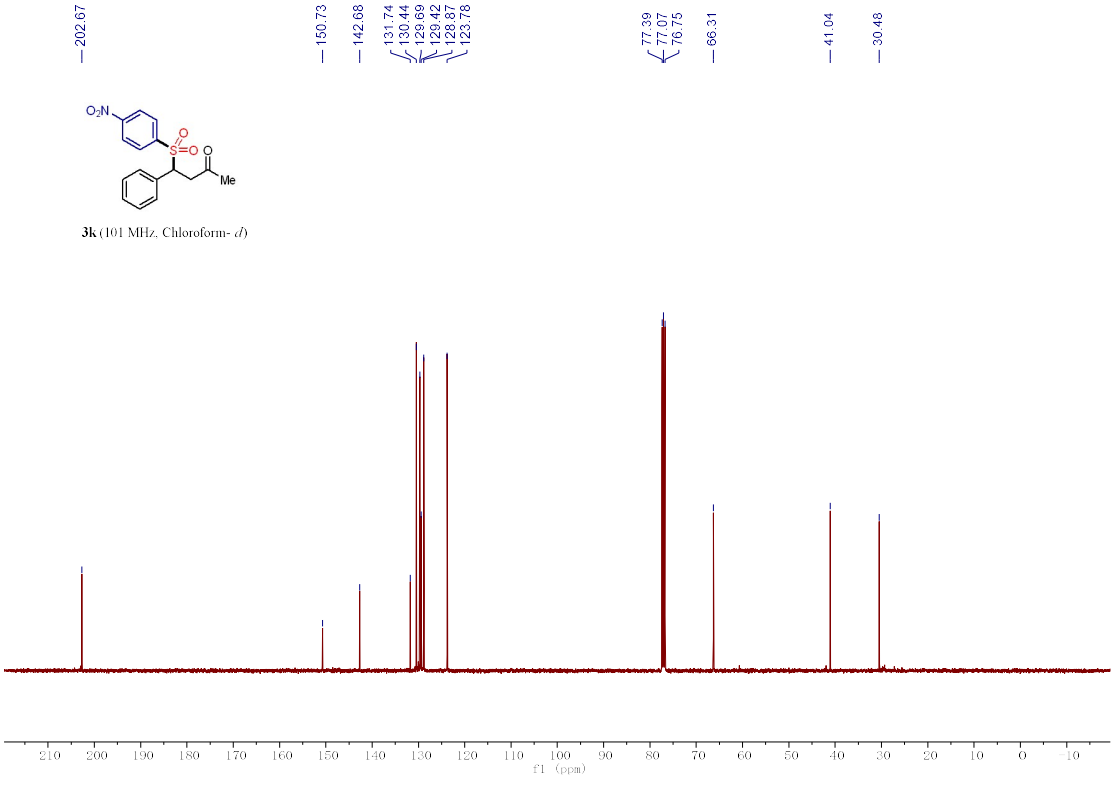

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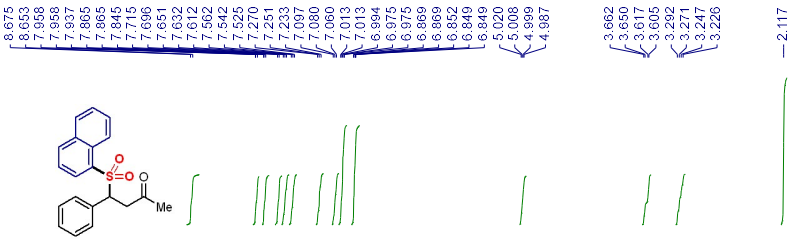
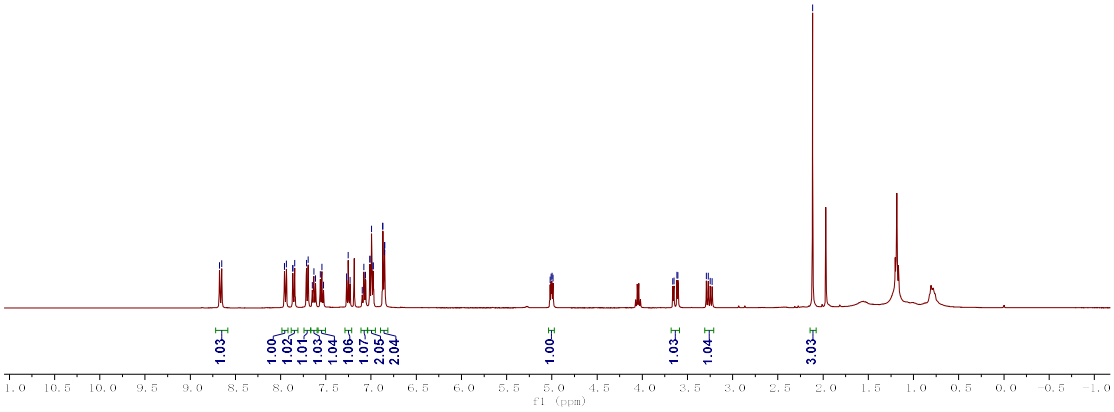
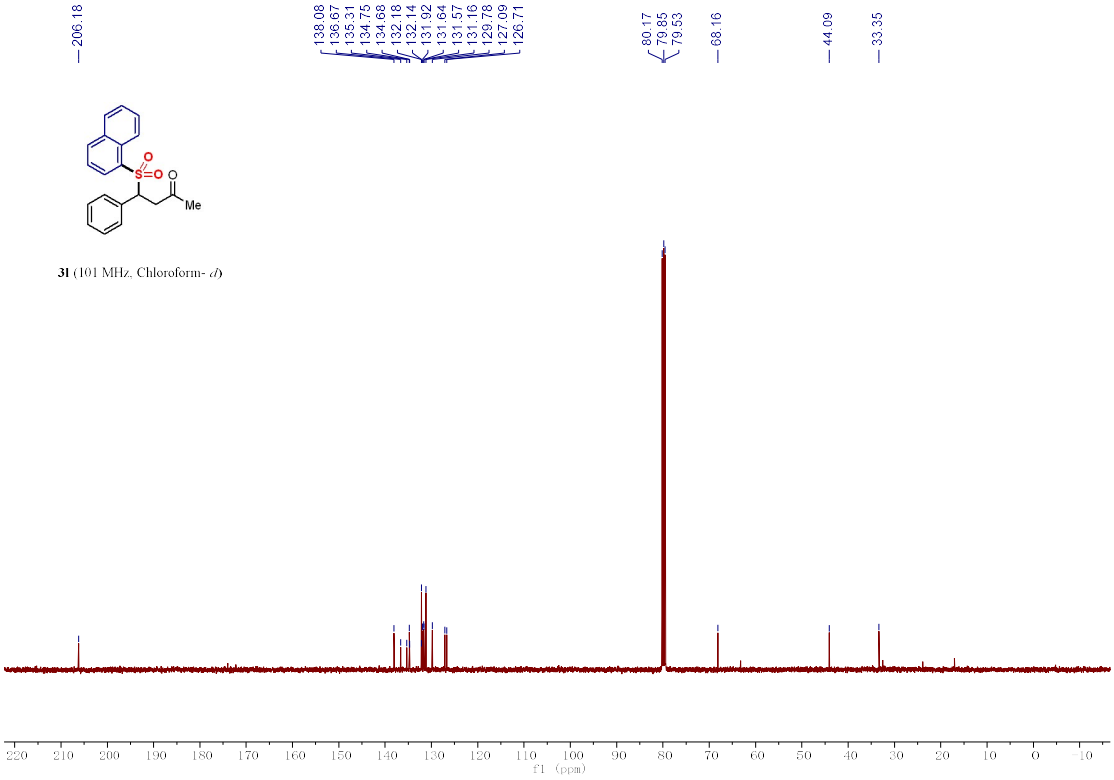
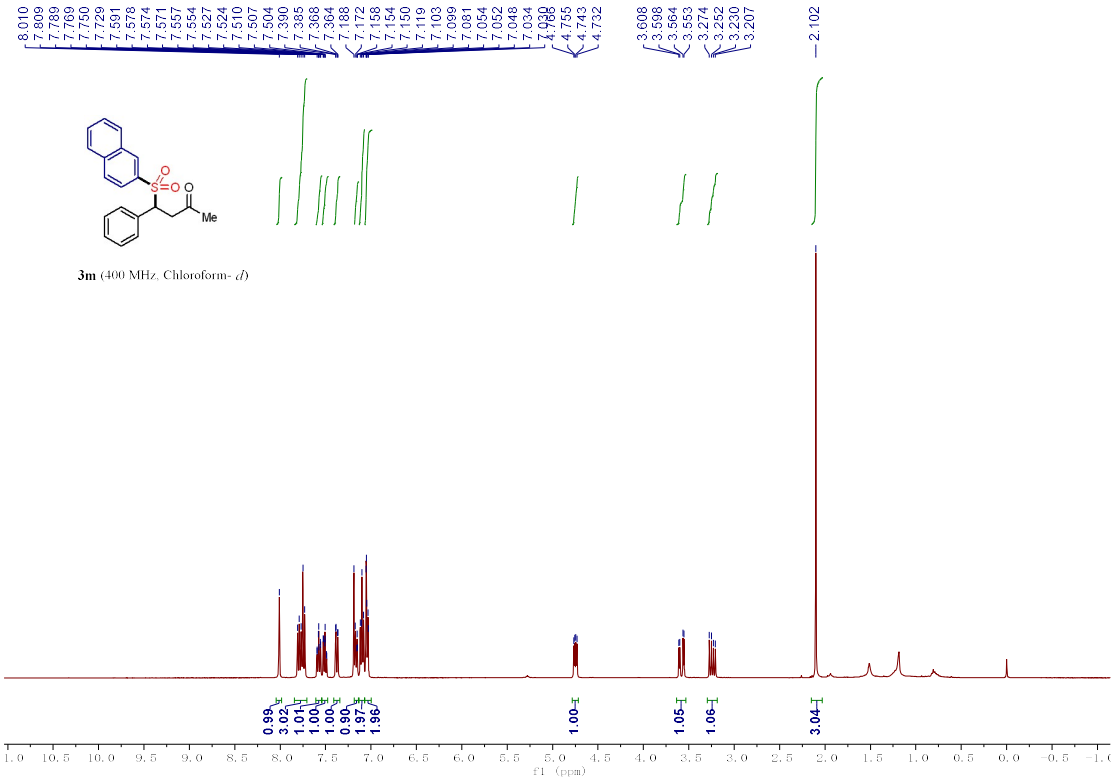


31 (400 MHz, Chloroform-*d*)

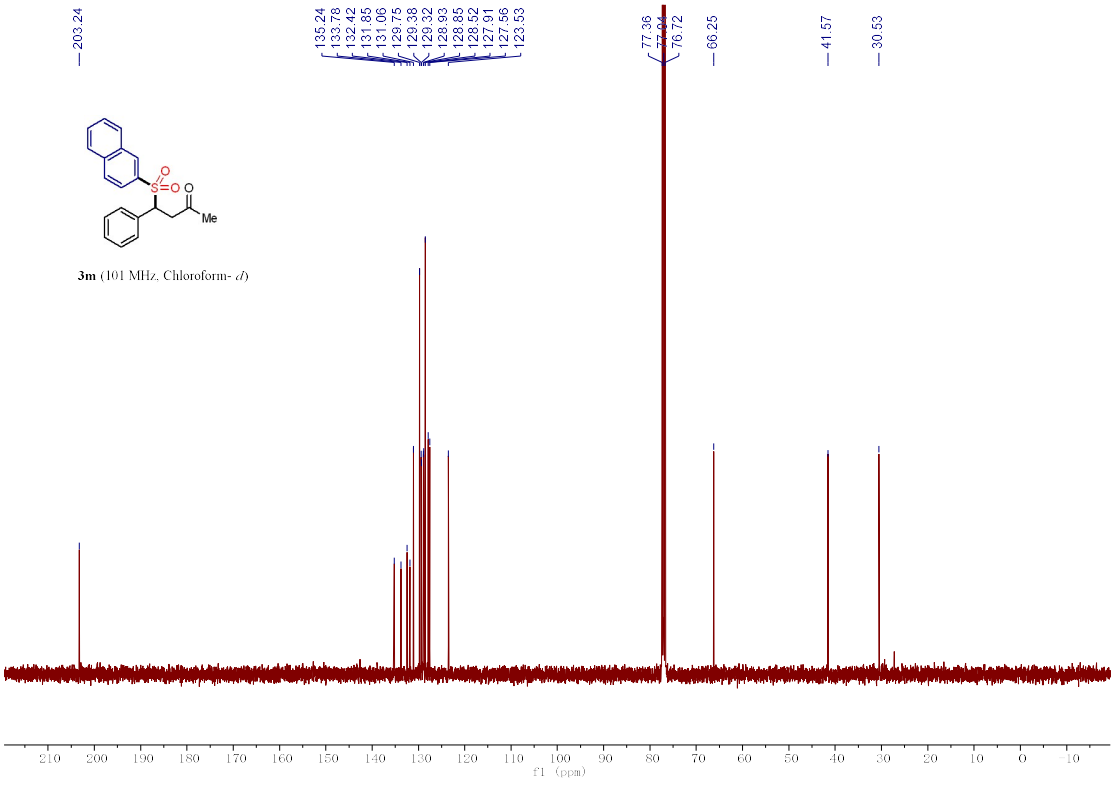




31 (101 MHz, Chloroform-*d*)



3m (400 MHz, Chloroform-*d*)



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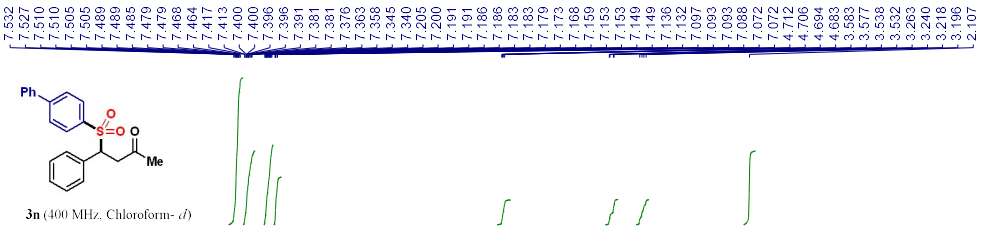

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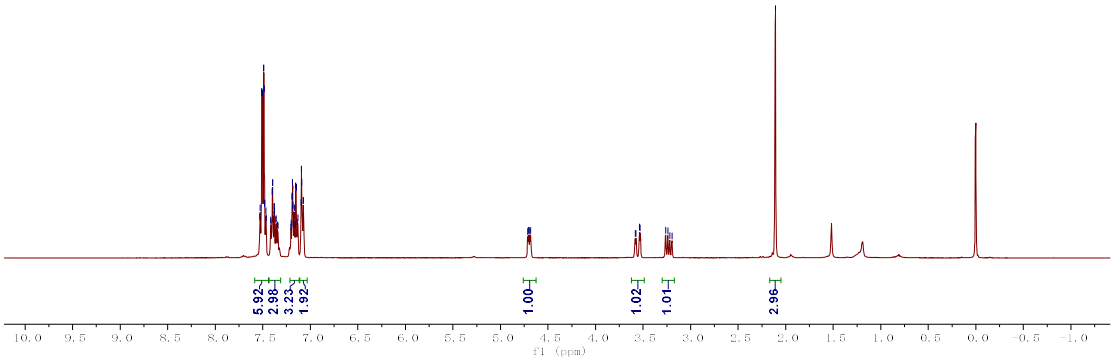

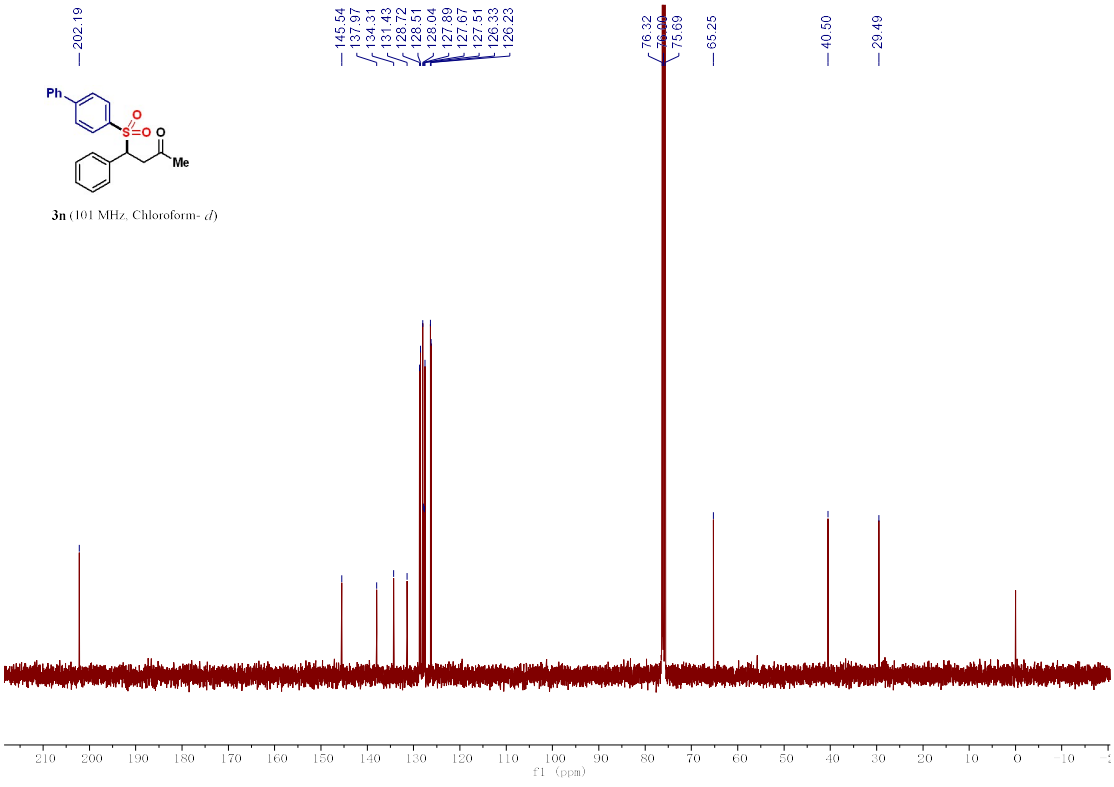

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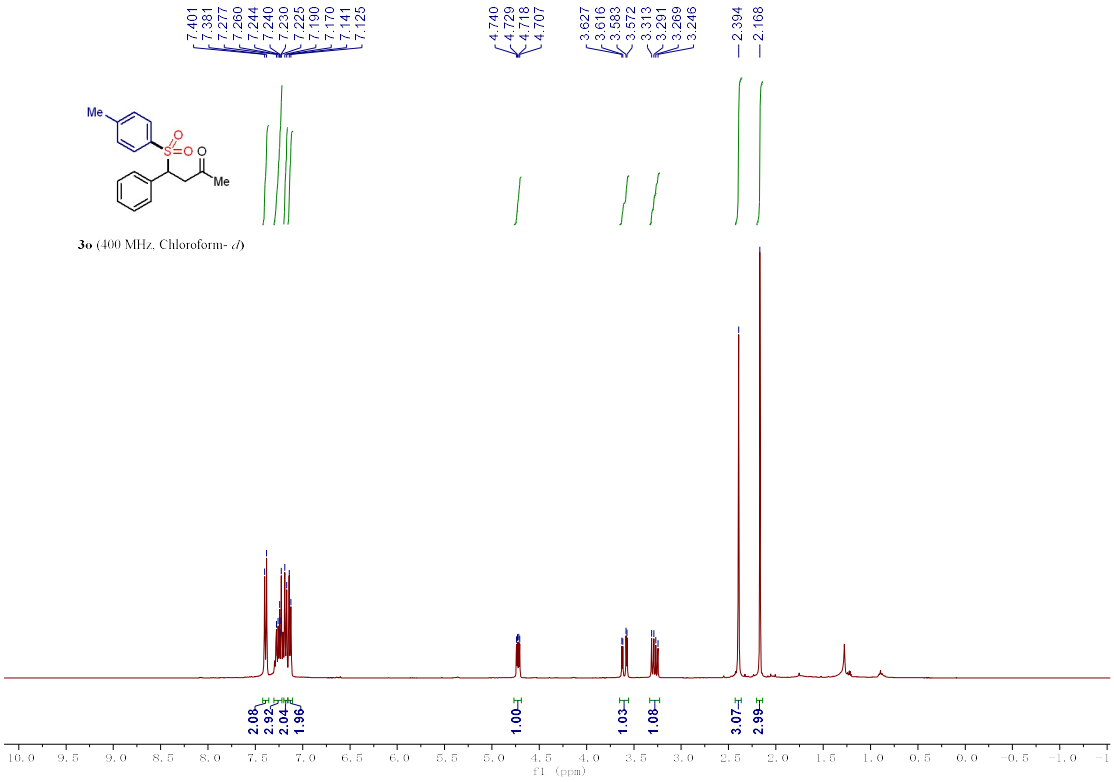

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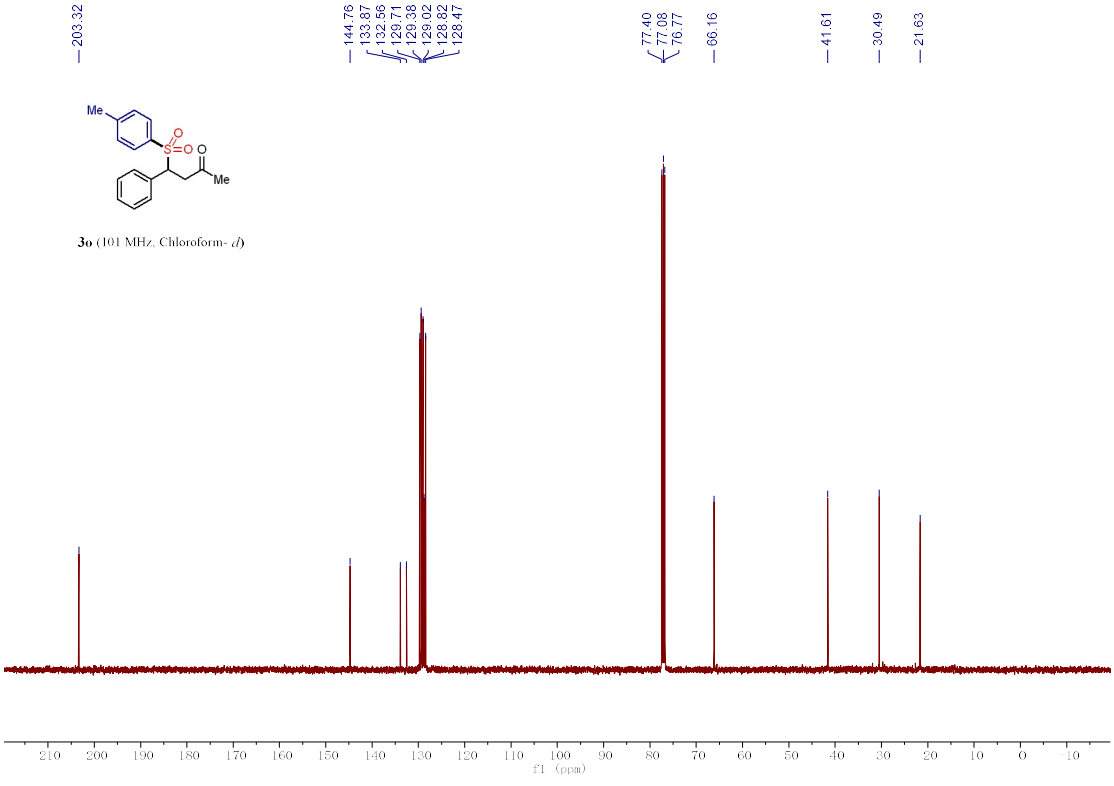

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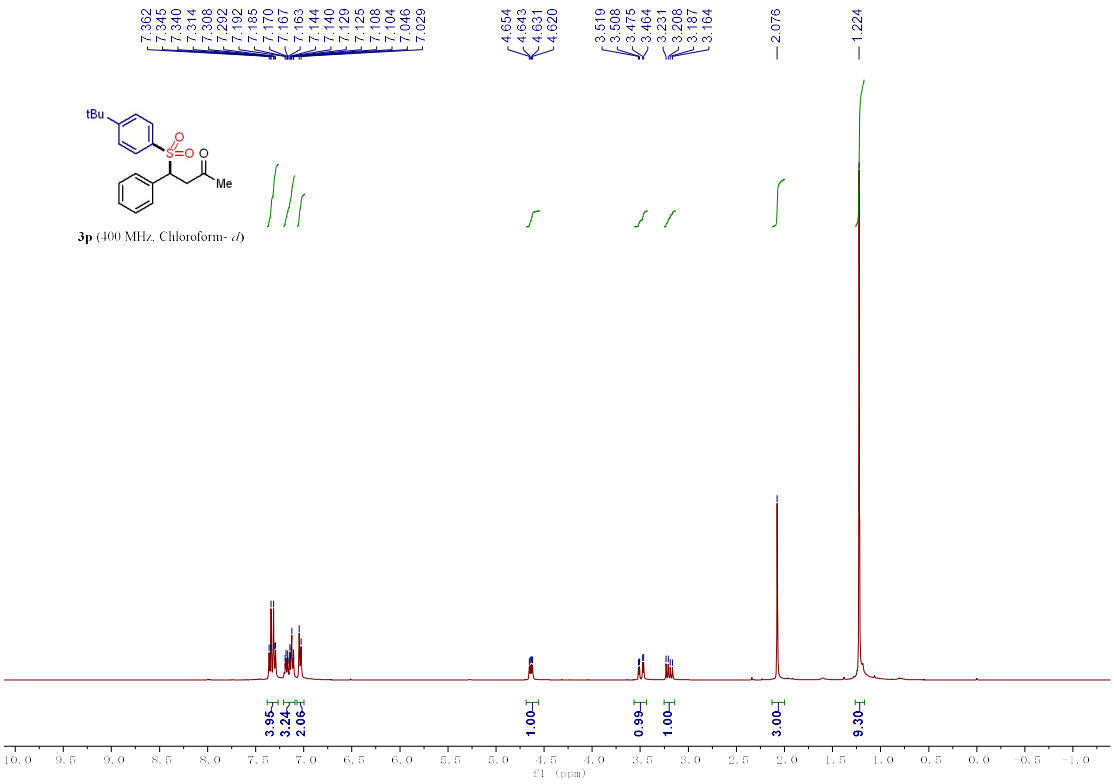

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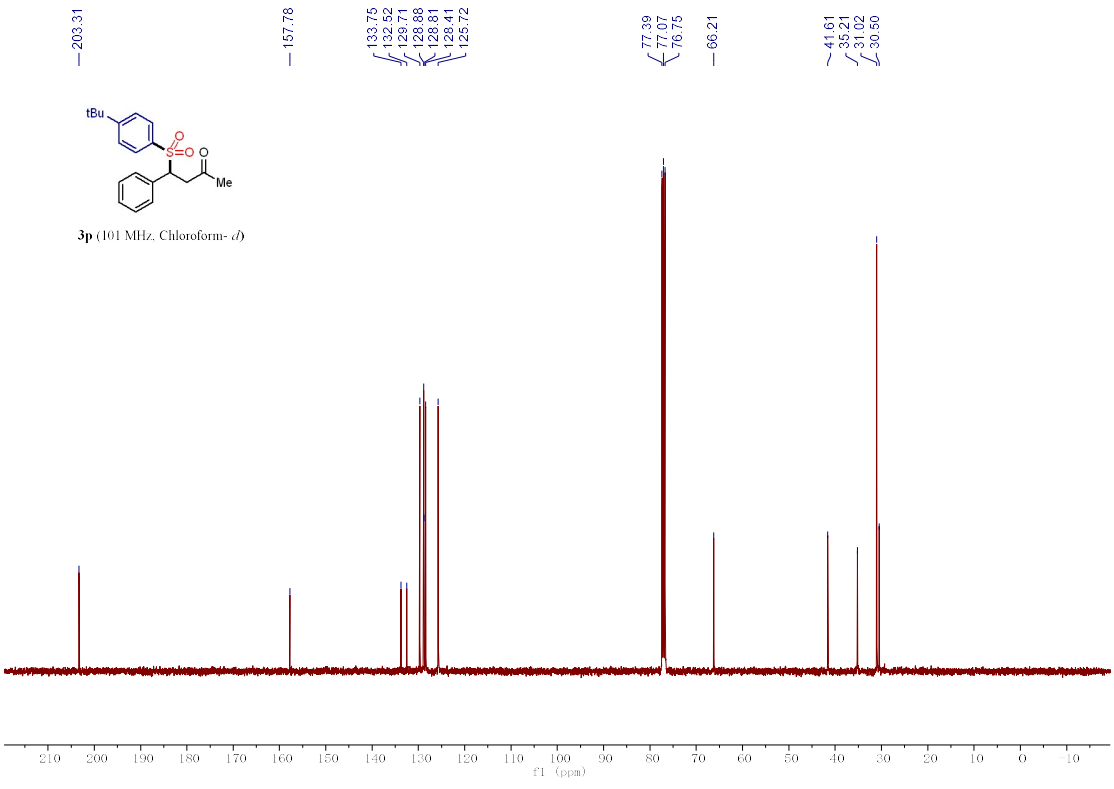
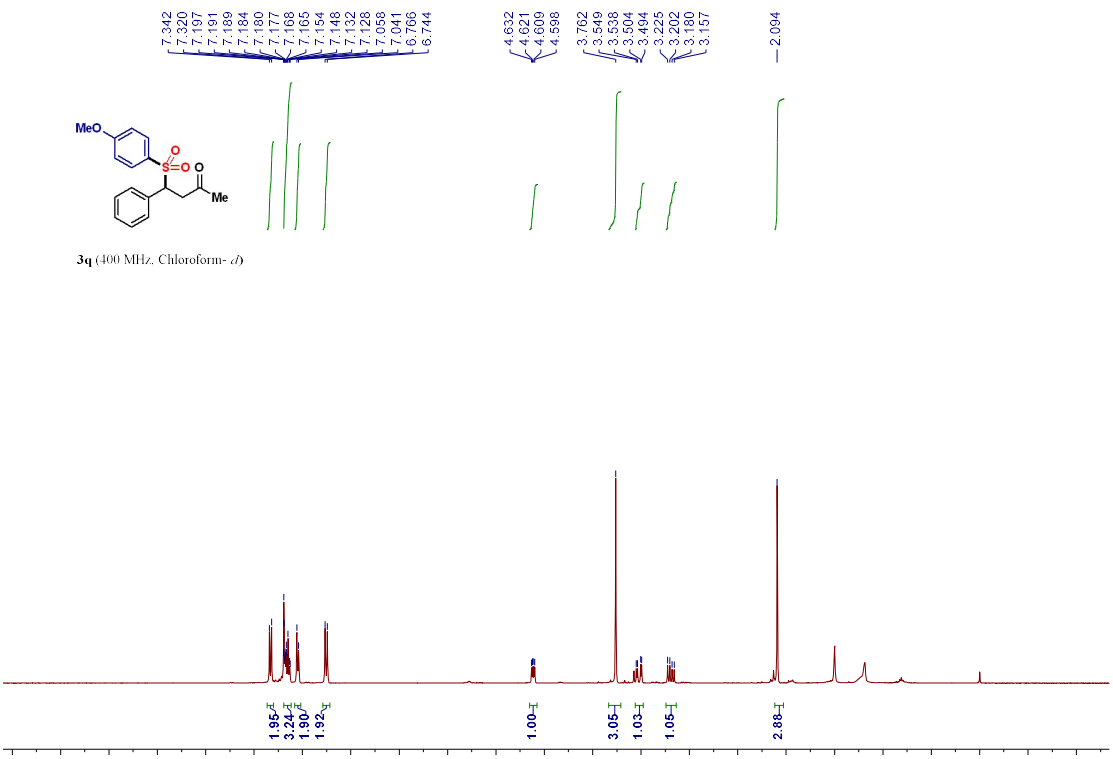


3p (101 MHz, Chloroform-*d*)



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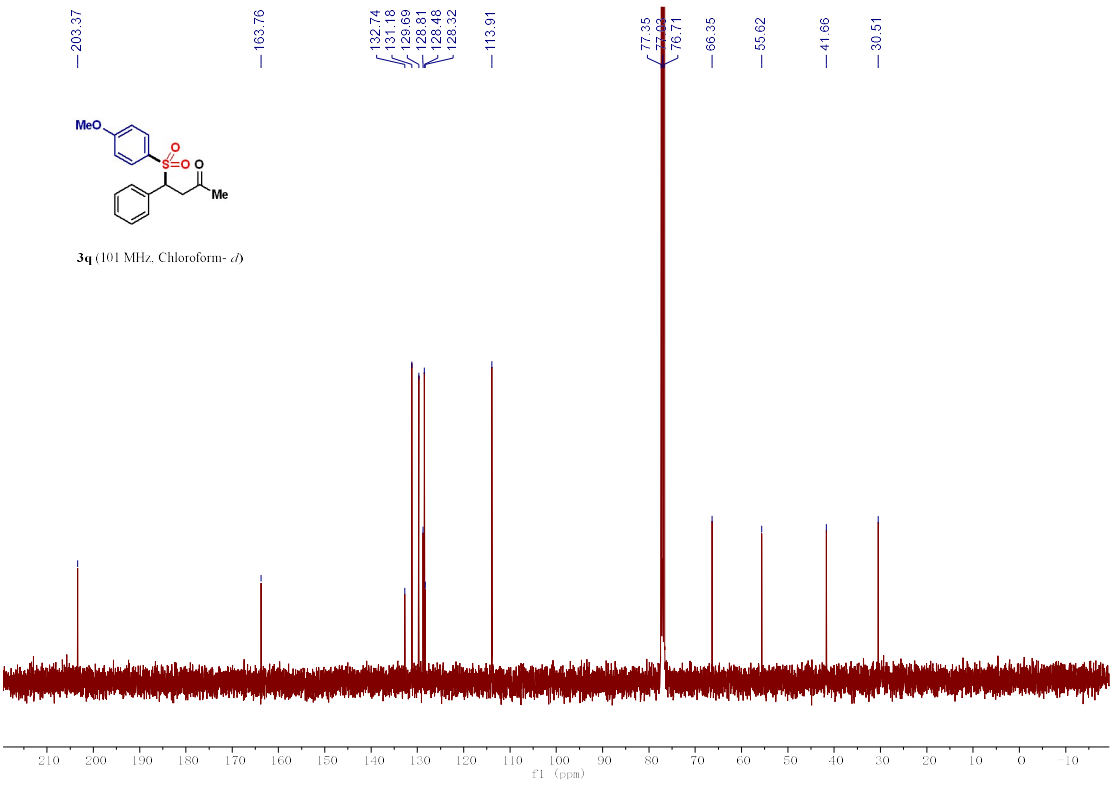
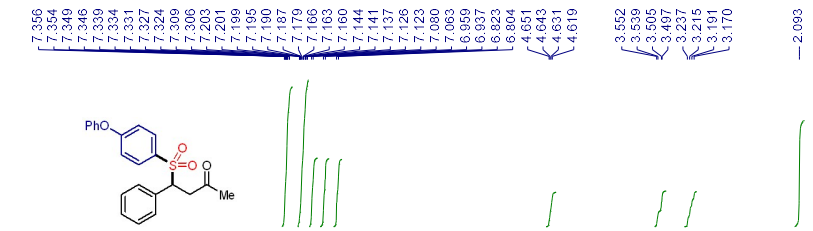
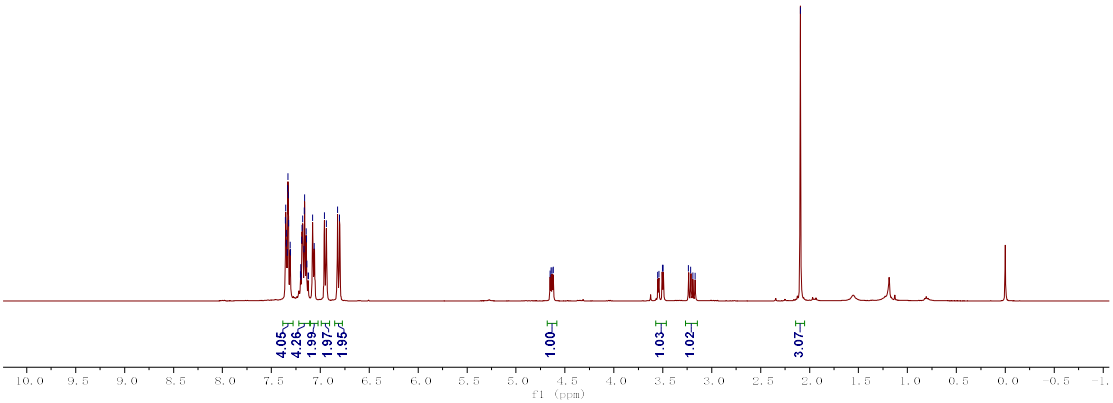
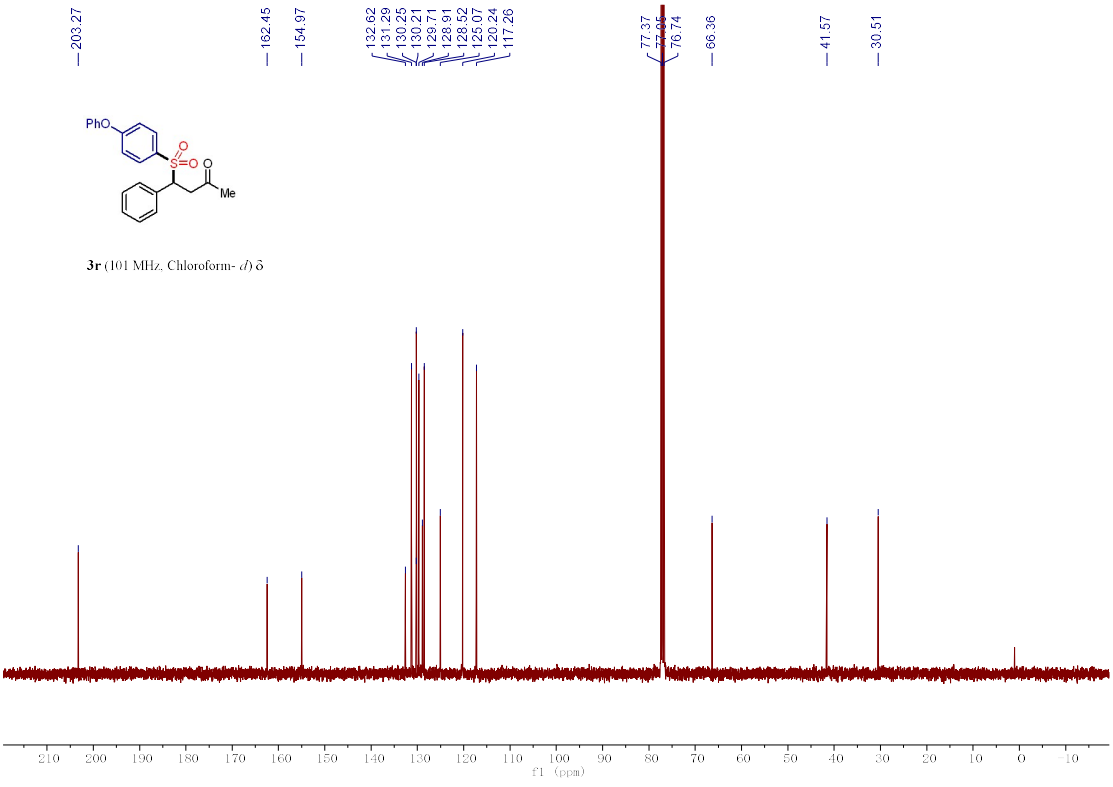


3q (101 MHz, Chloroform-*d*)

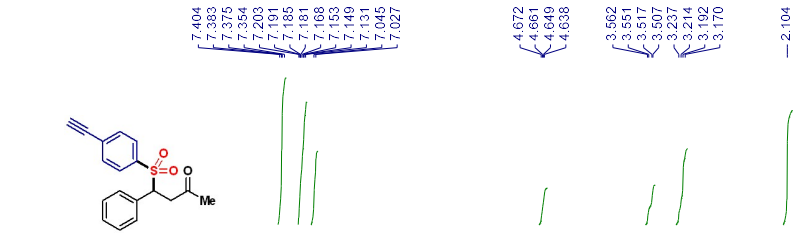


3r (400 MHz, Chloroform-*d*) δ





3r (101 MHz, Chloroform-*d*) δ



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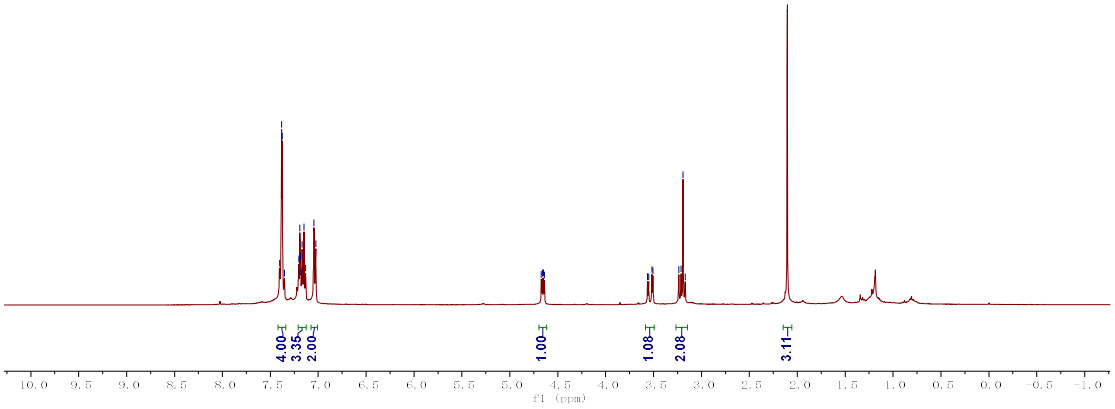

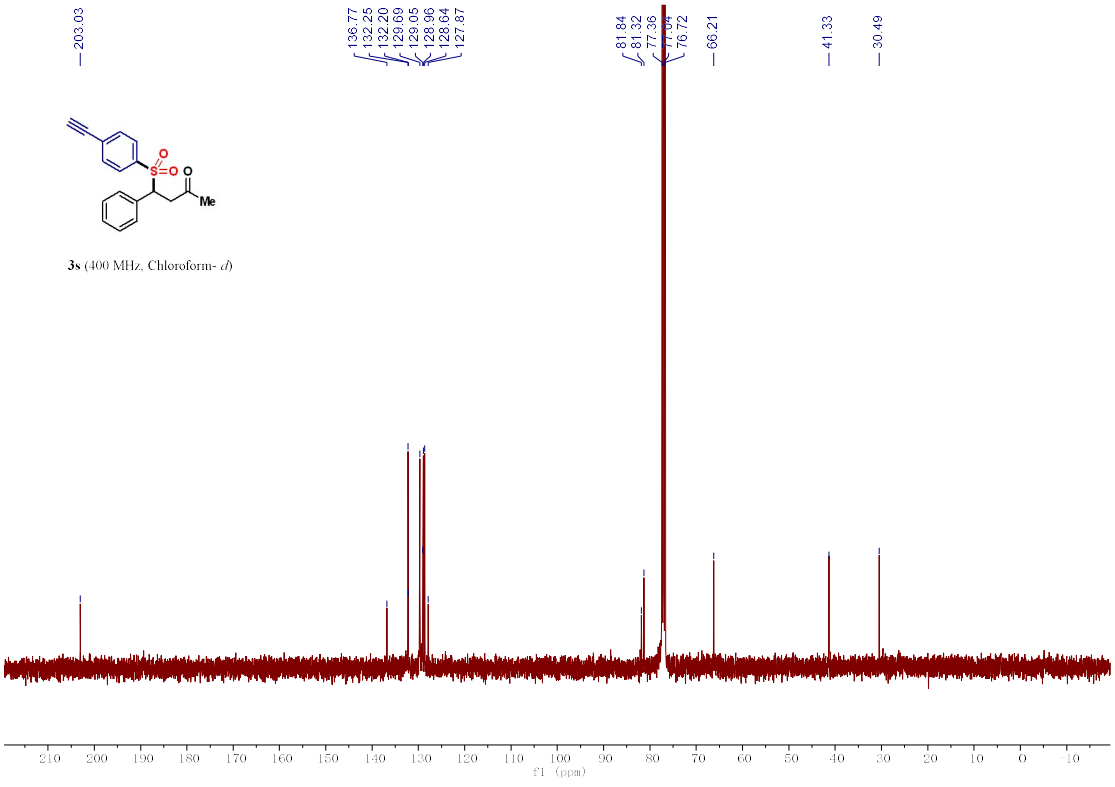

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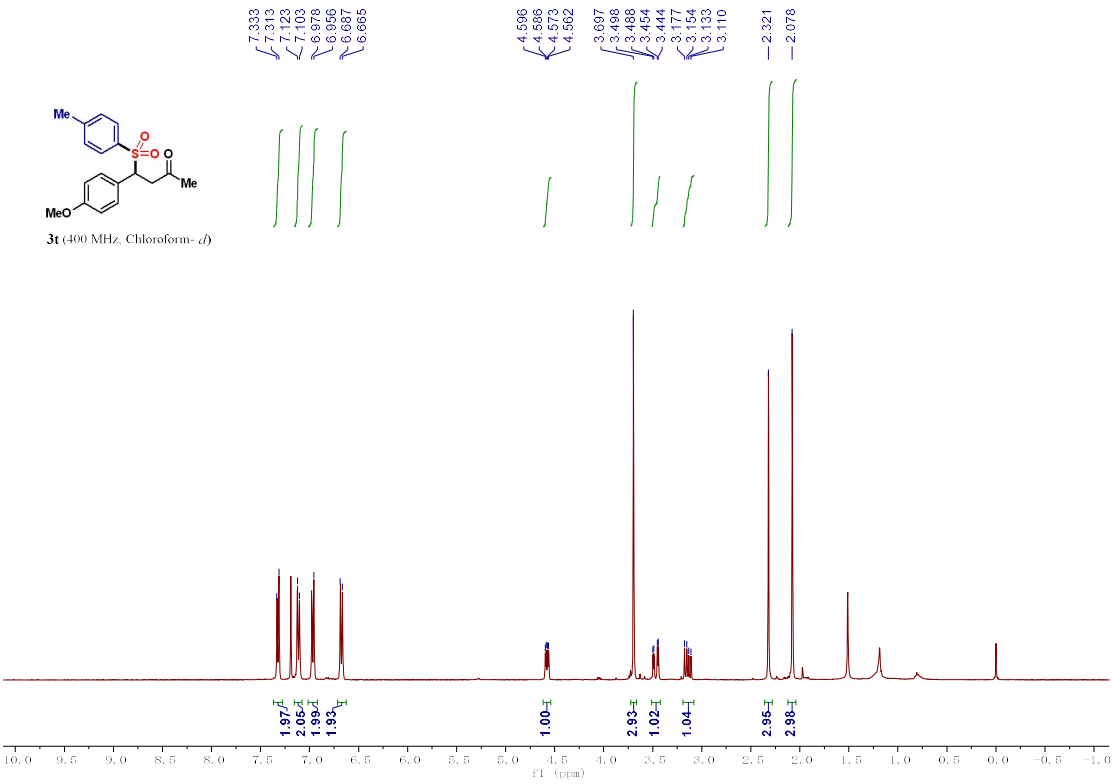

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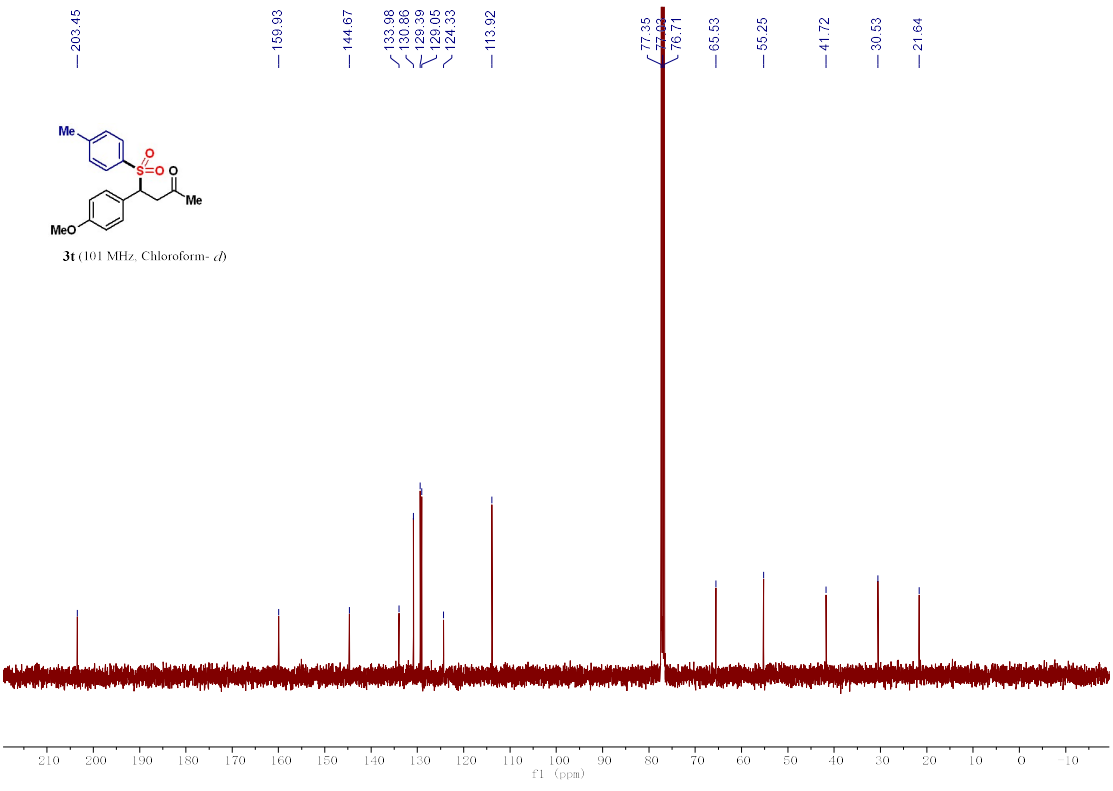

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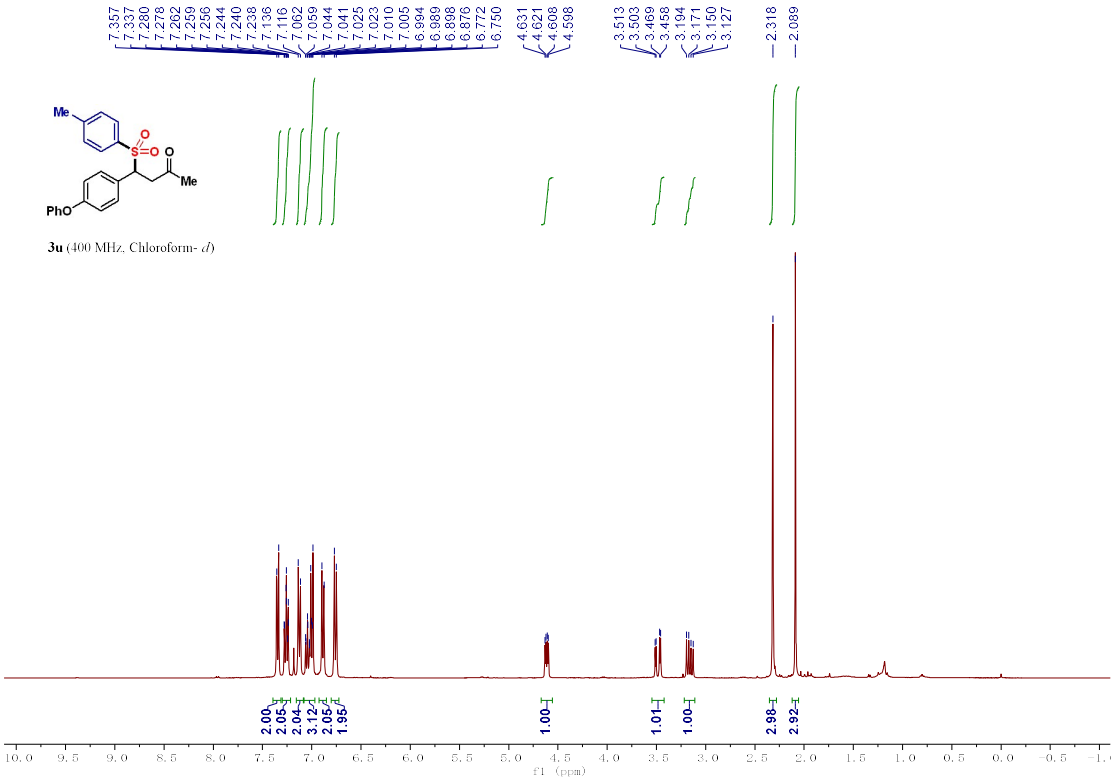

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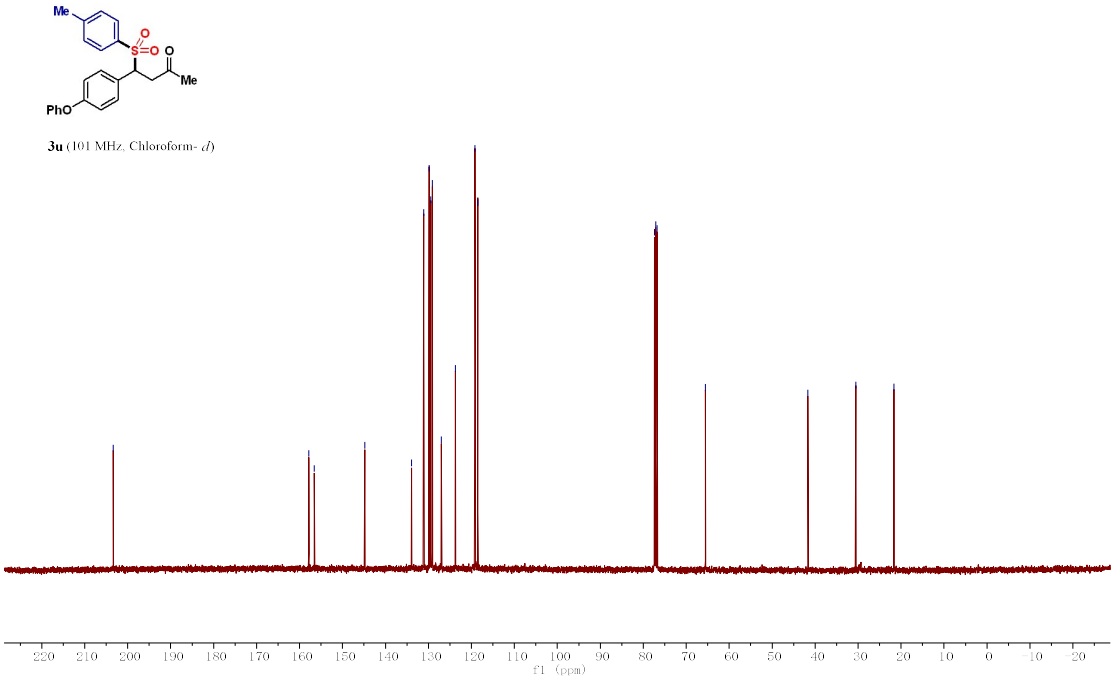

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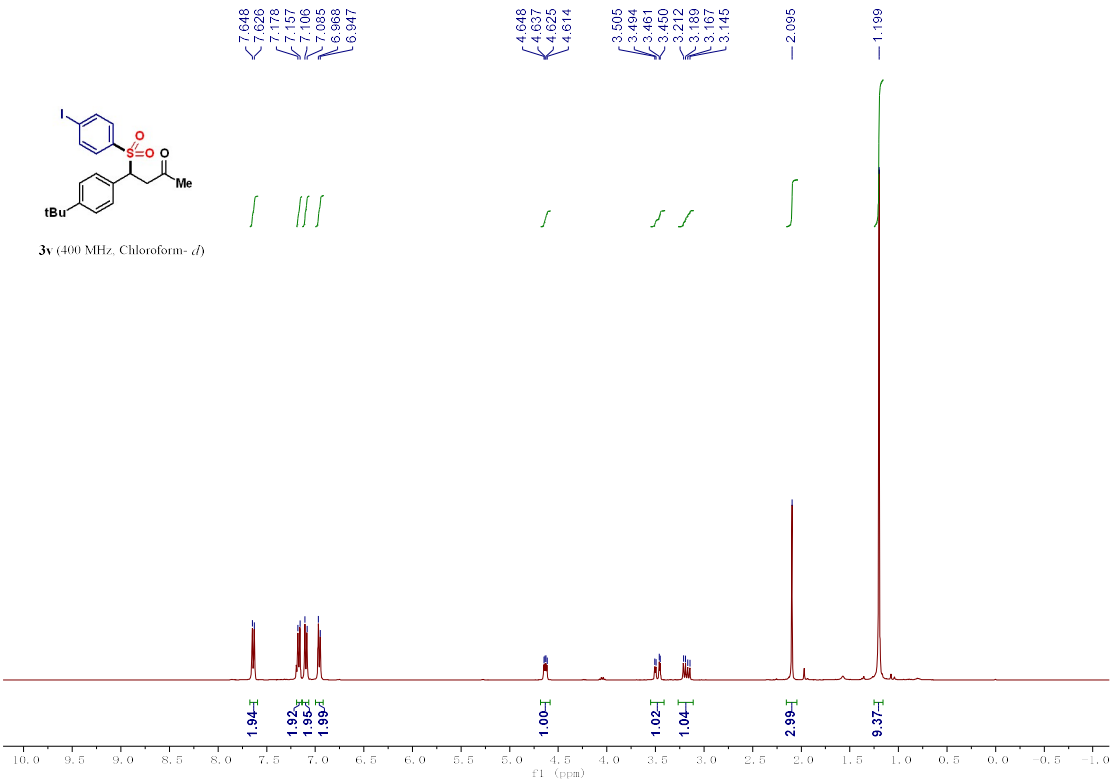
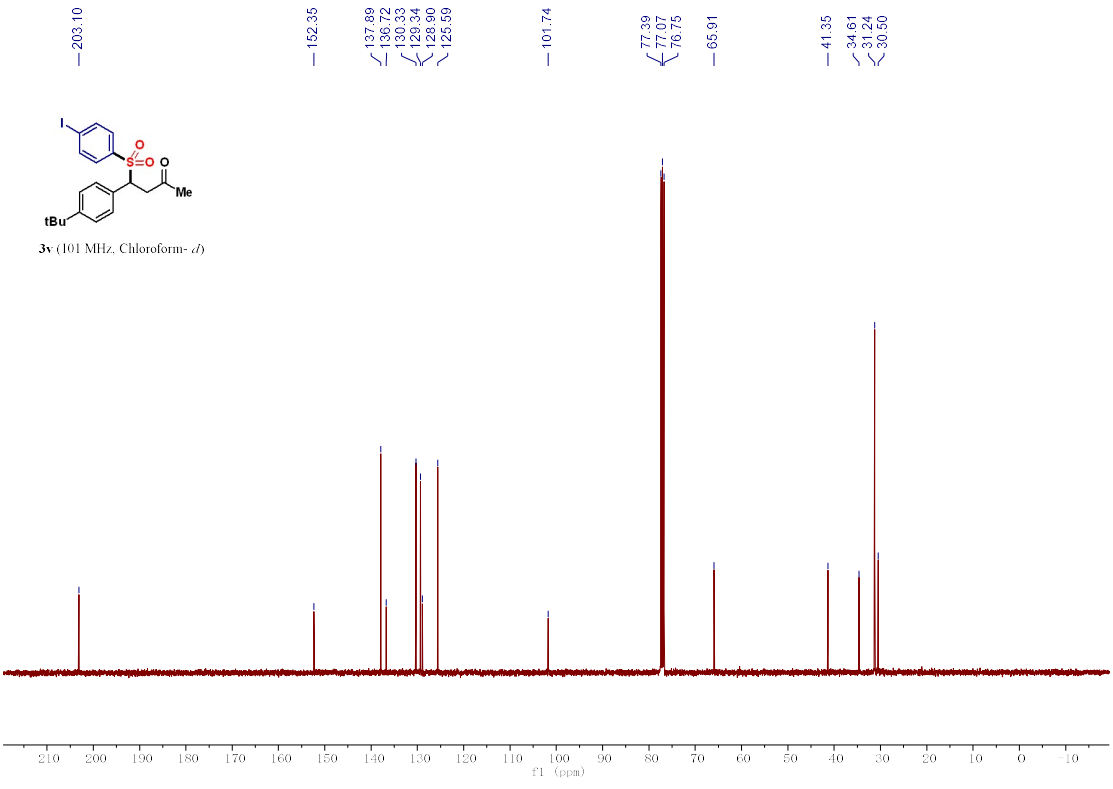
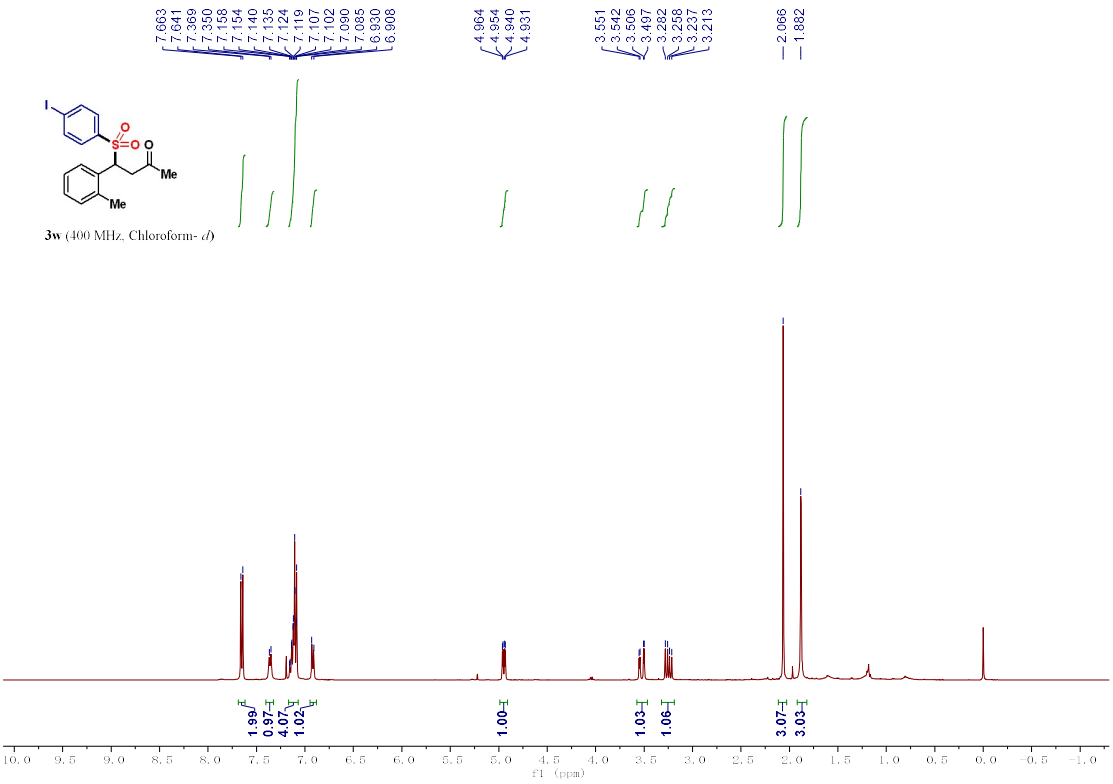


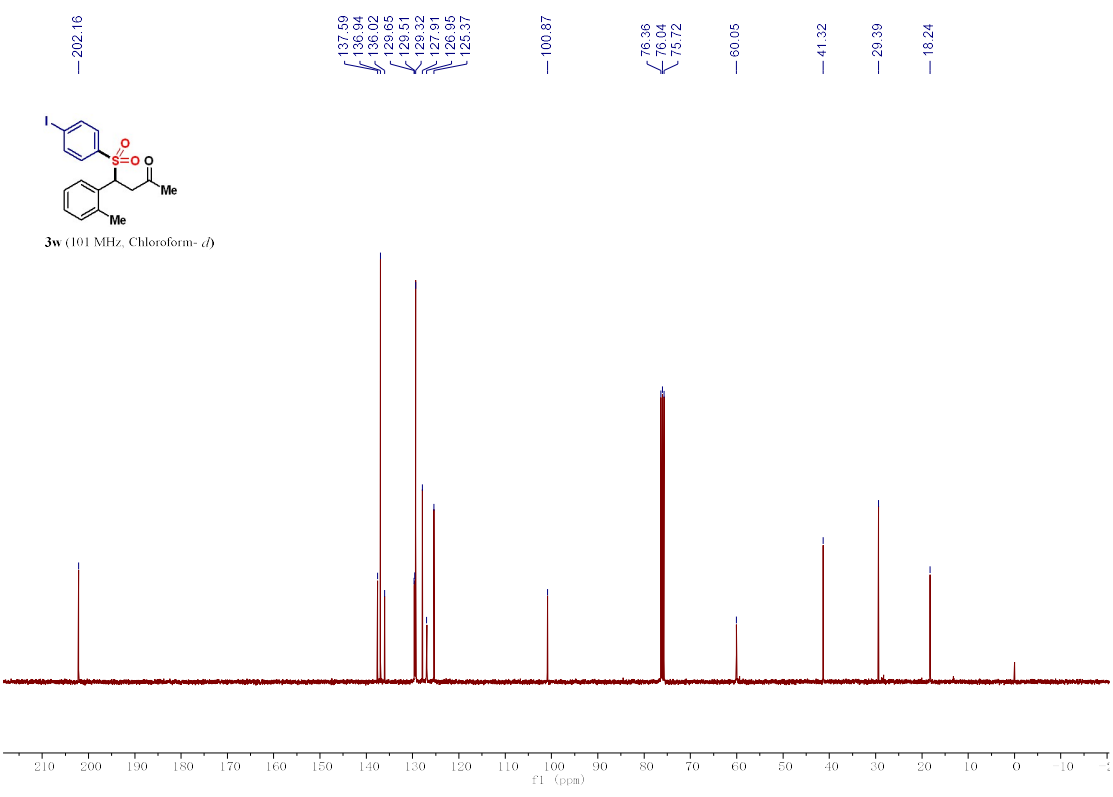
3v (400 MHz, Chloroform-*d*)



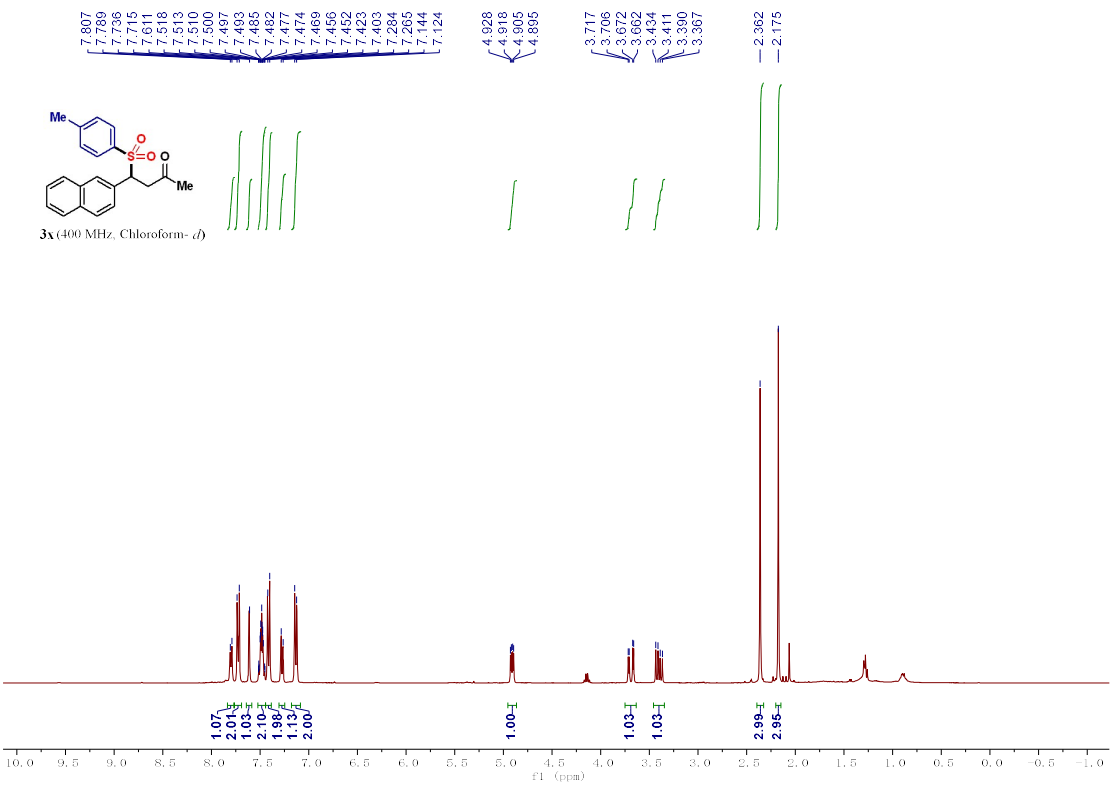
3v (101 MHz, Chloroform-*d*)



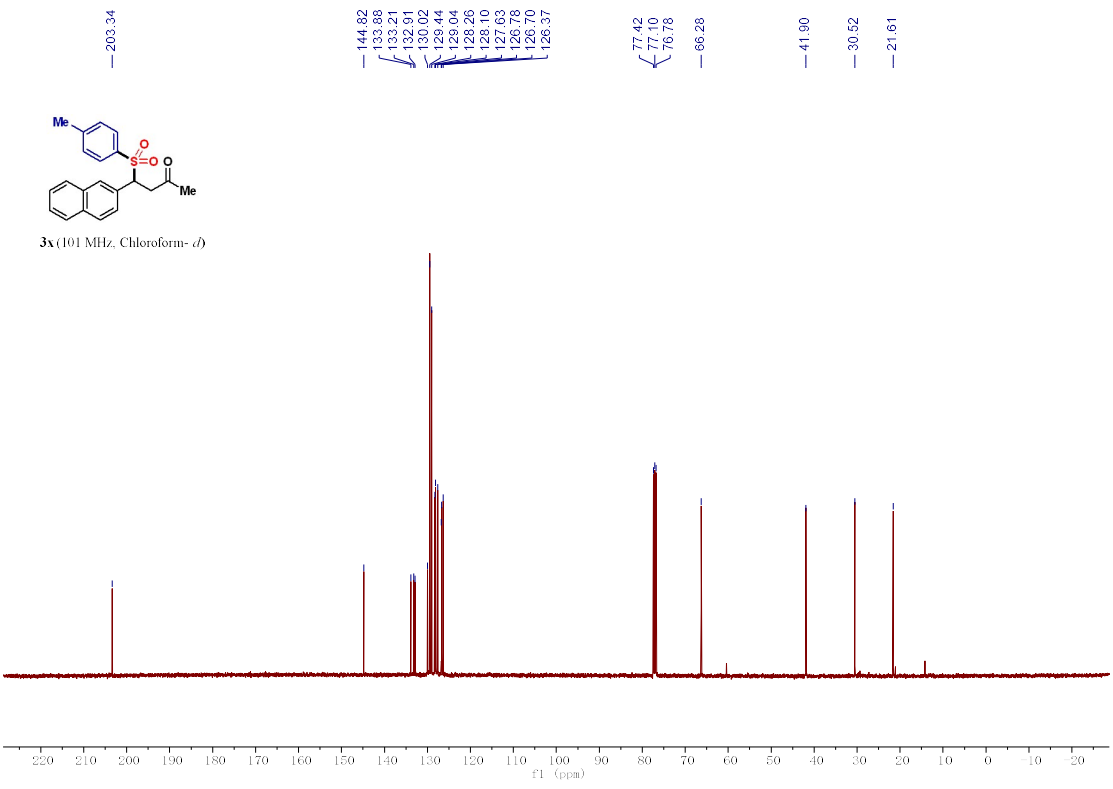
3w (400 MHz, Chloroform- *d*)



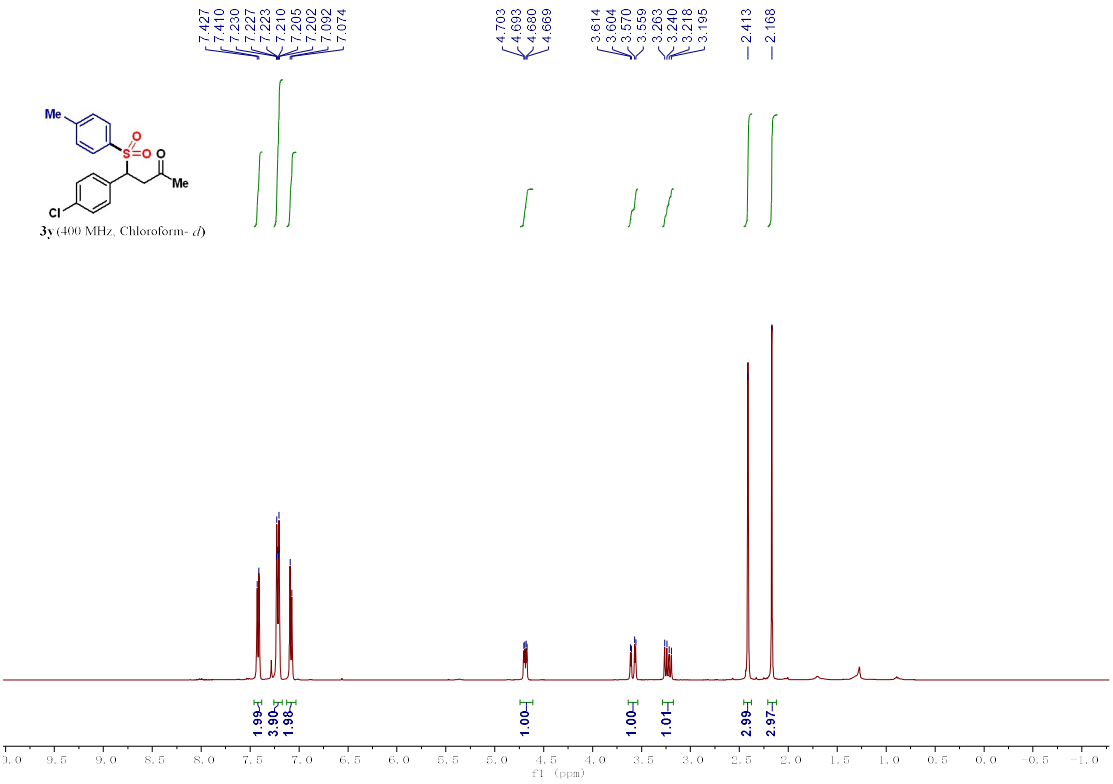
3w (101 MHz, Chloroform- *d*)



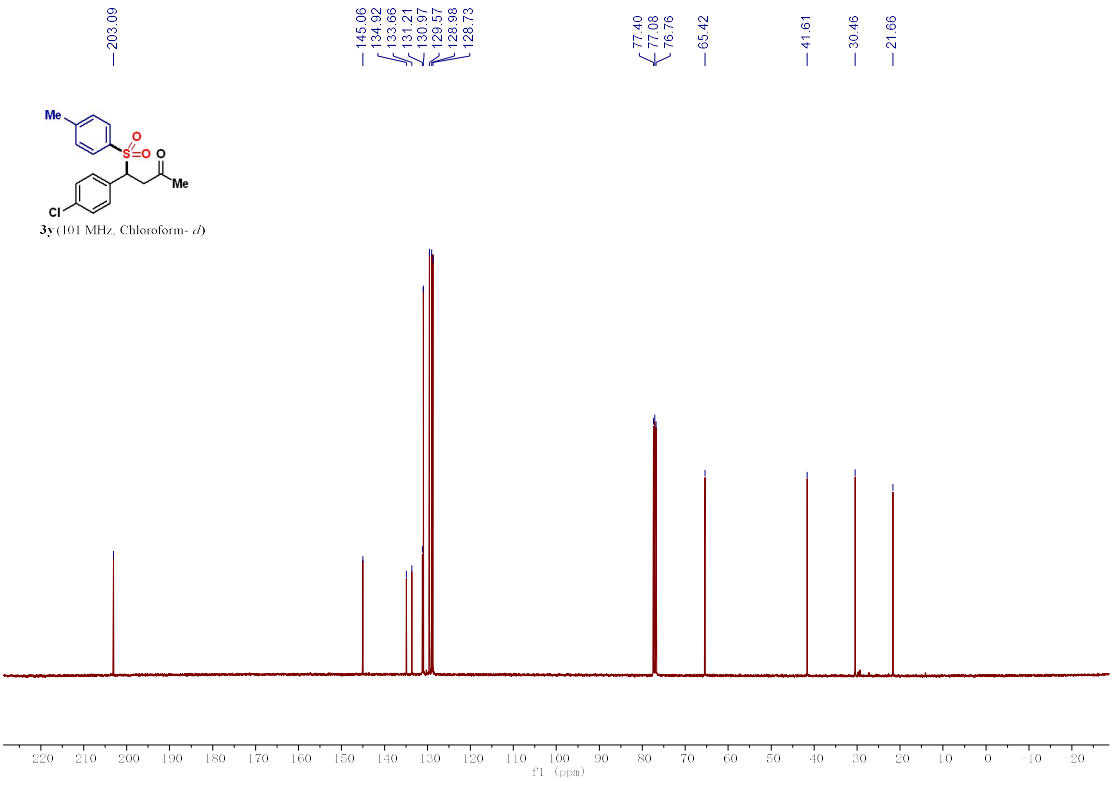
3x (400 MHz, Chloroform- *d*)



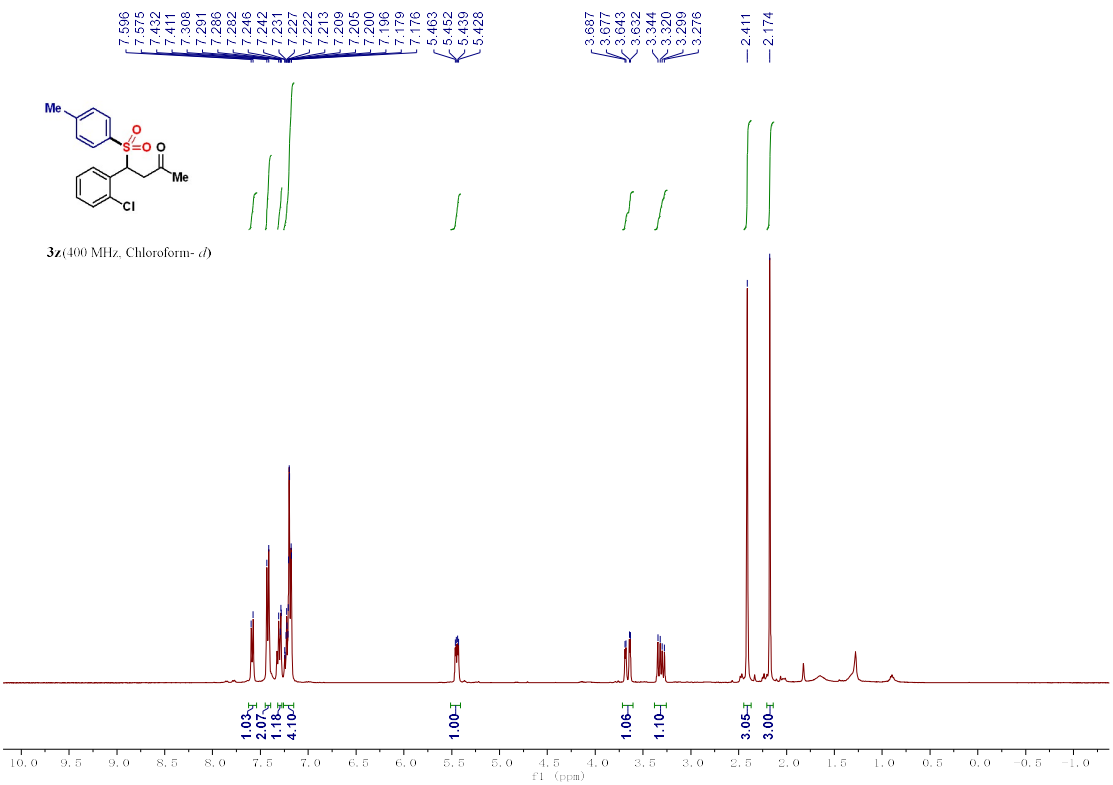
3x (101 MHz, Chloroform- *d*)



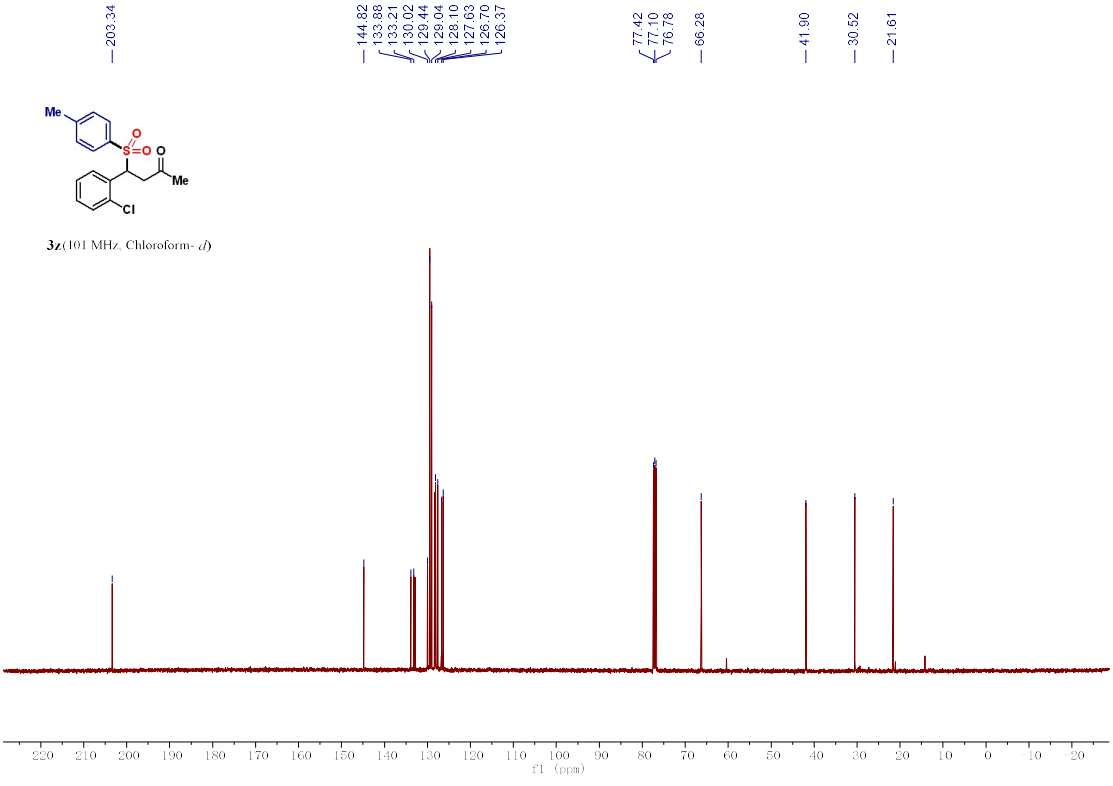
3y (400 MHz, Chloroform- *d*)



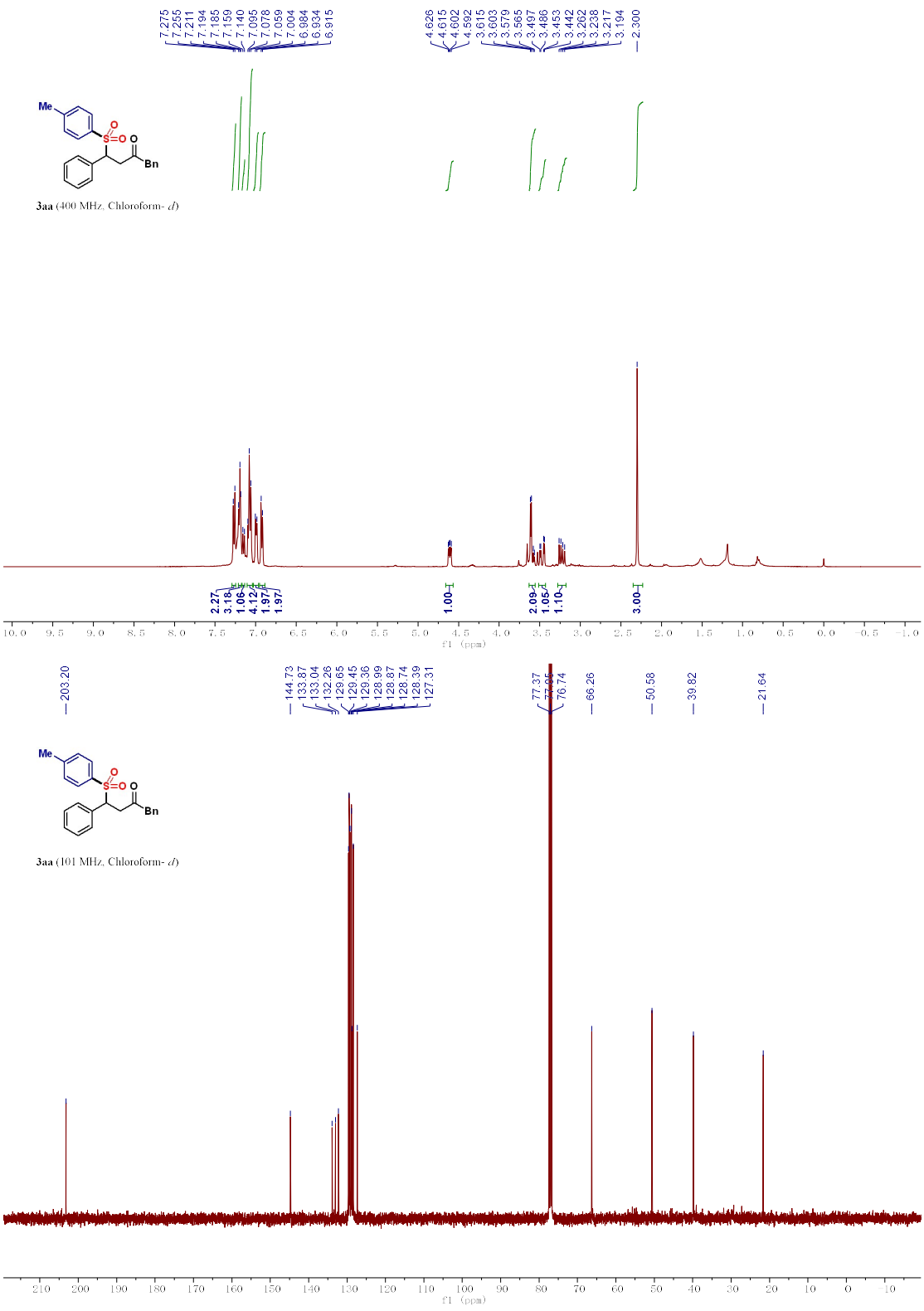
3y (101 MHz, Chloroform- *d*)



3z(400 MHz, Chloroform- *d*)

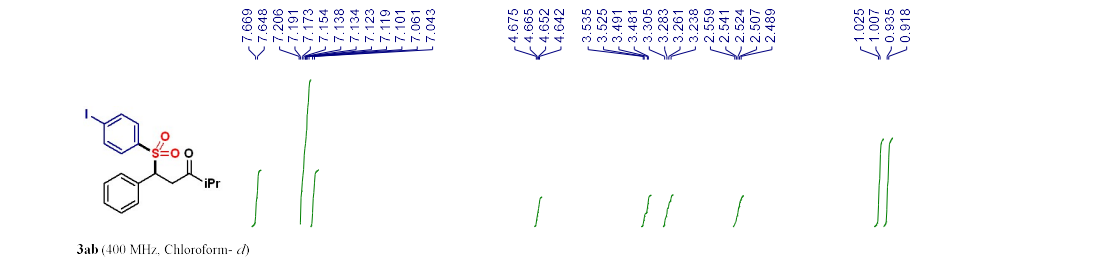


3z(101 MHz, Chloroform- *d*)

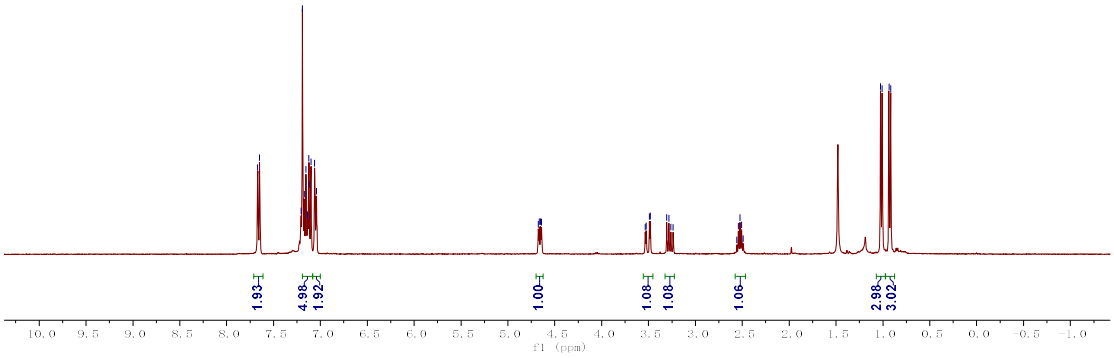


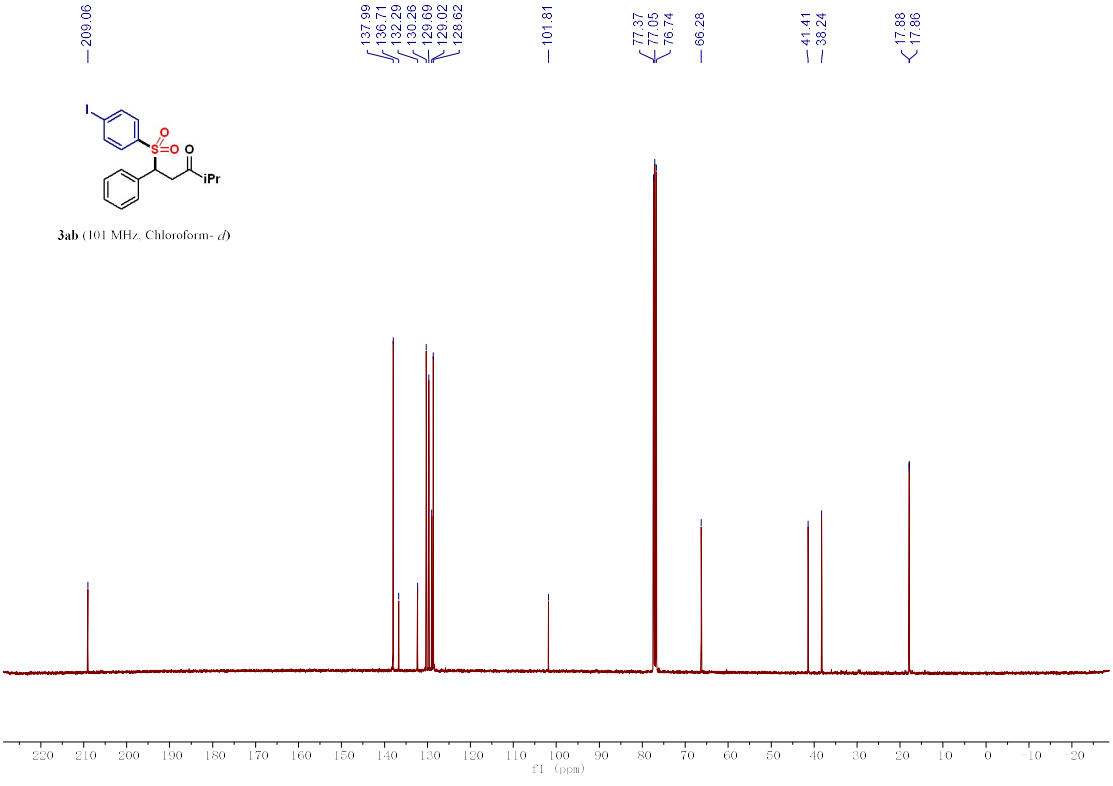
3aa (400 MHz, Chloroform- *d*)

3aa (101 MHz, Chloroform- *d*)

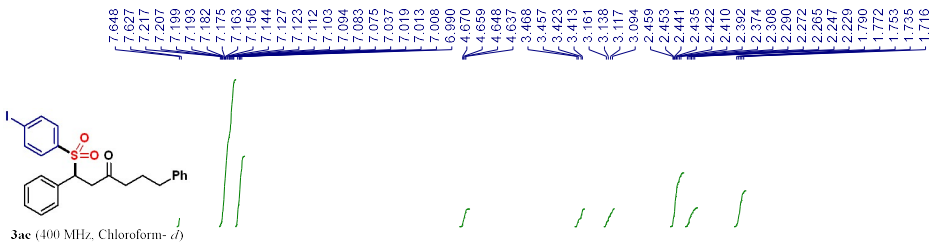


3ab (400 MHz, Chloroform- *d*)

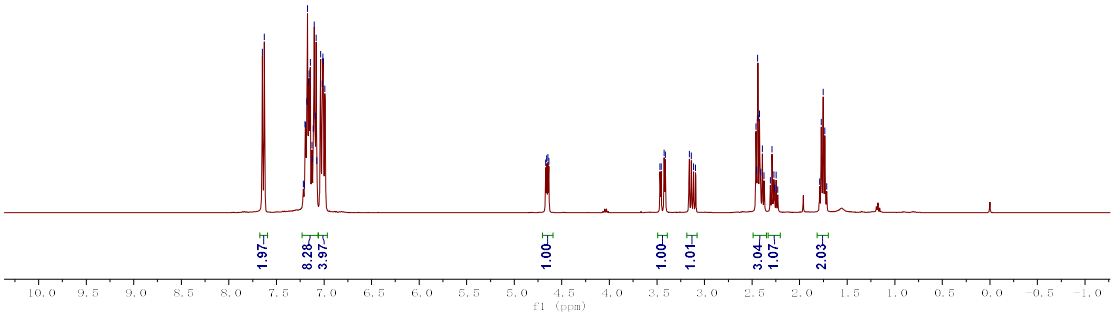


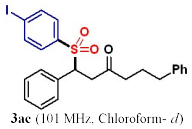


3ab (101 MHz, Chloroform- *d*)

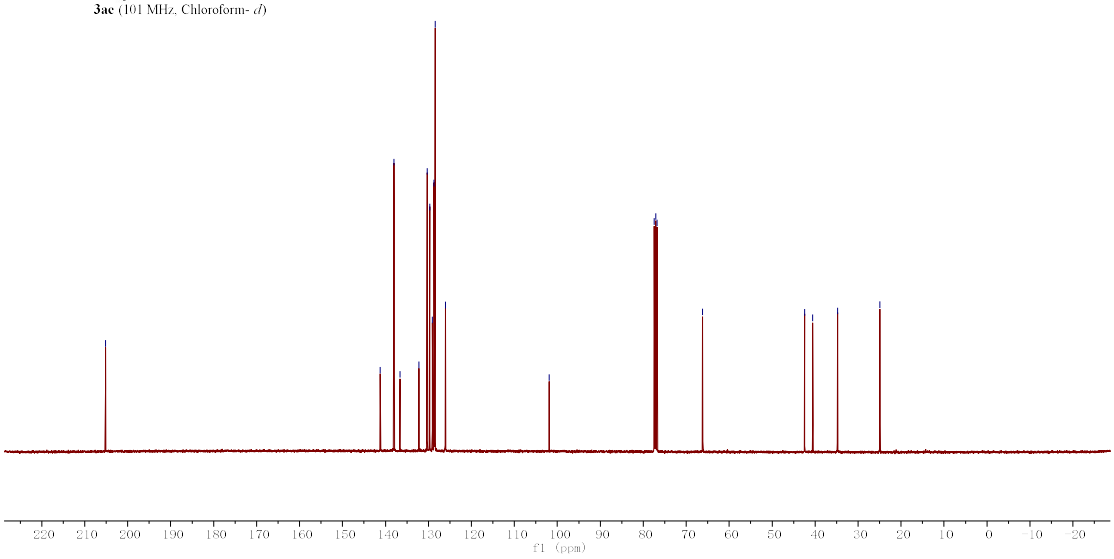


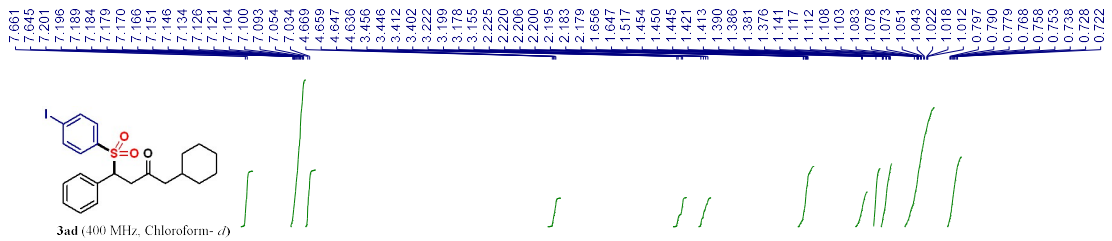
3ae (400 MHz, Chloroform-*d*)



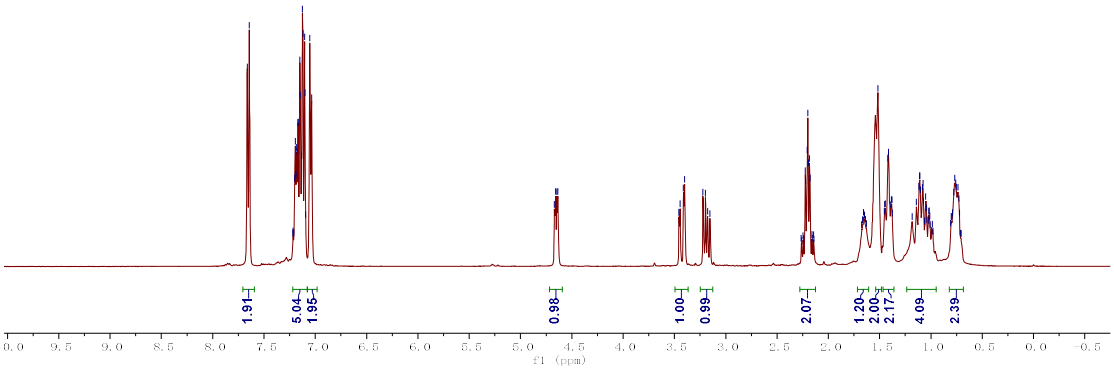


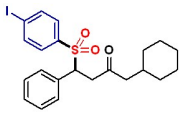
3ae (101 MHz, Chloroform-*d*)



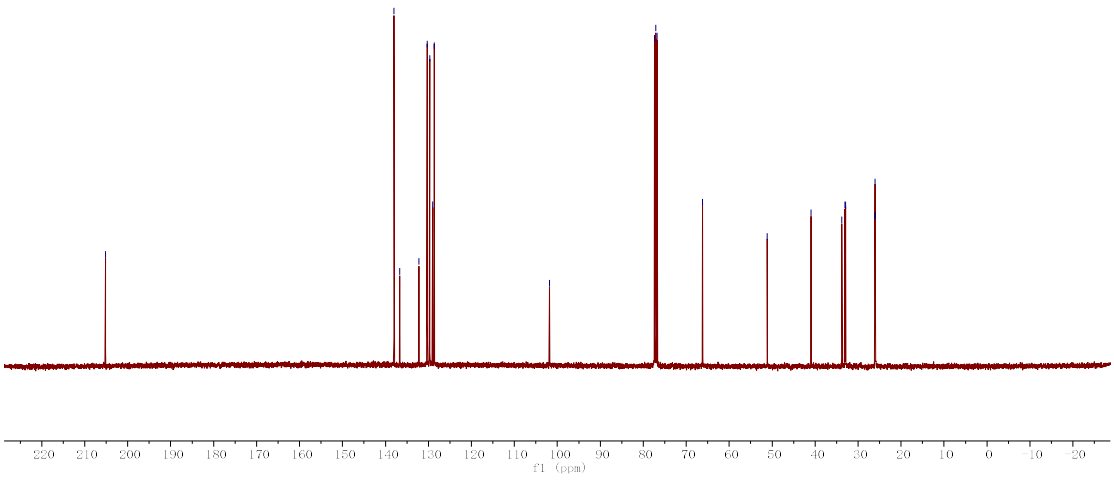


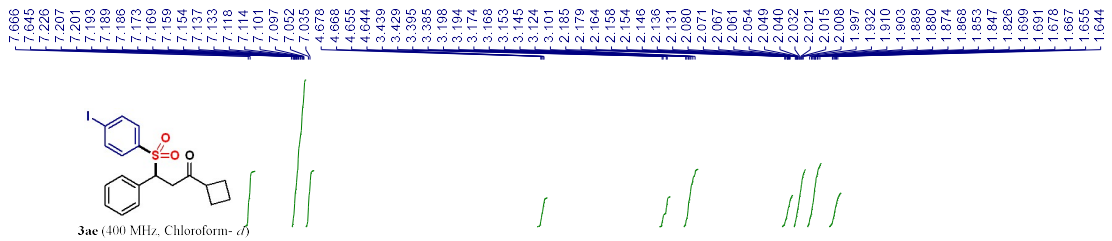
3ad (400 MHz, Chloroform-*d*)



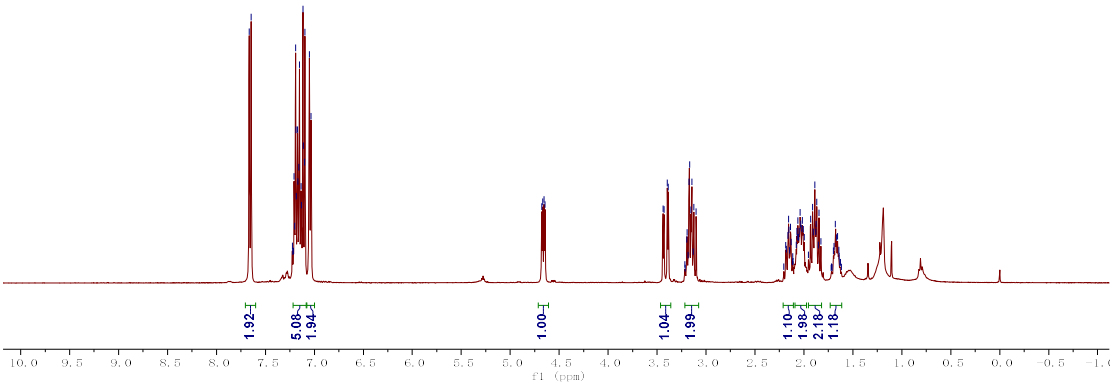


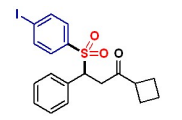
3ad (101 MHz, Chloroform-*d*)



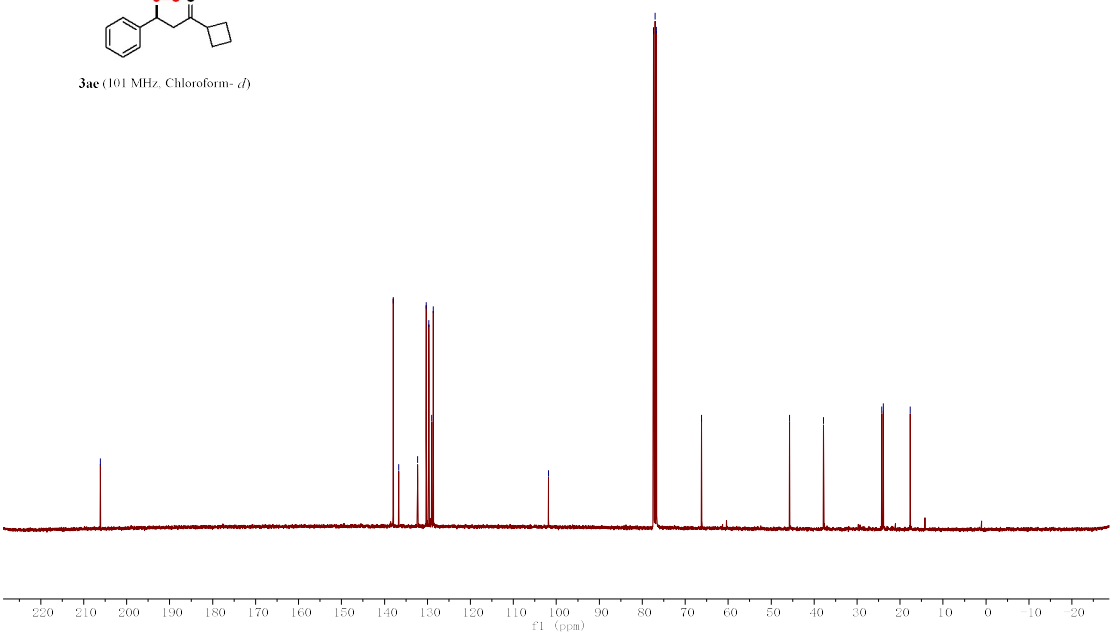


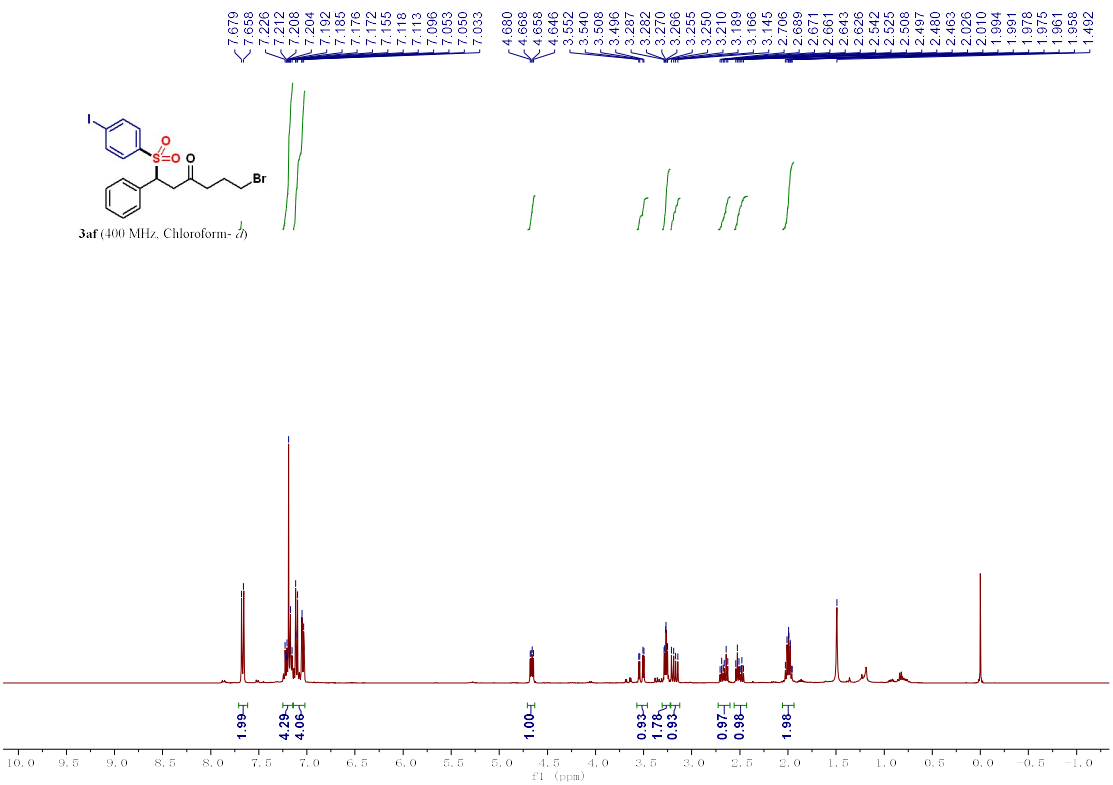
3ae (400 MHz, Chloroform-*d*)



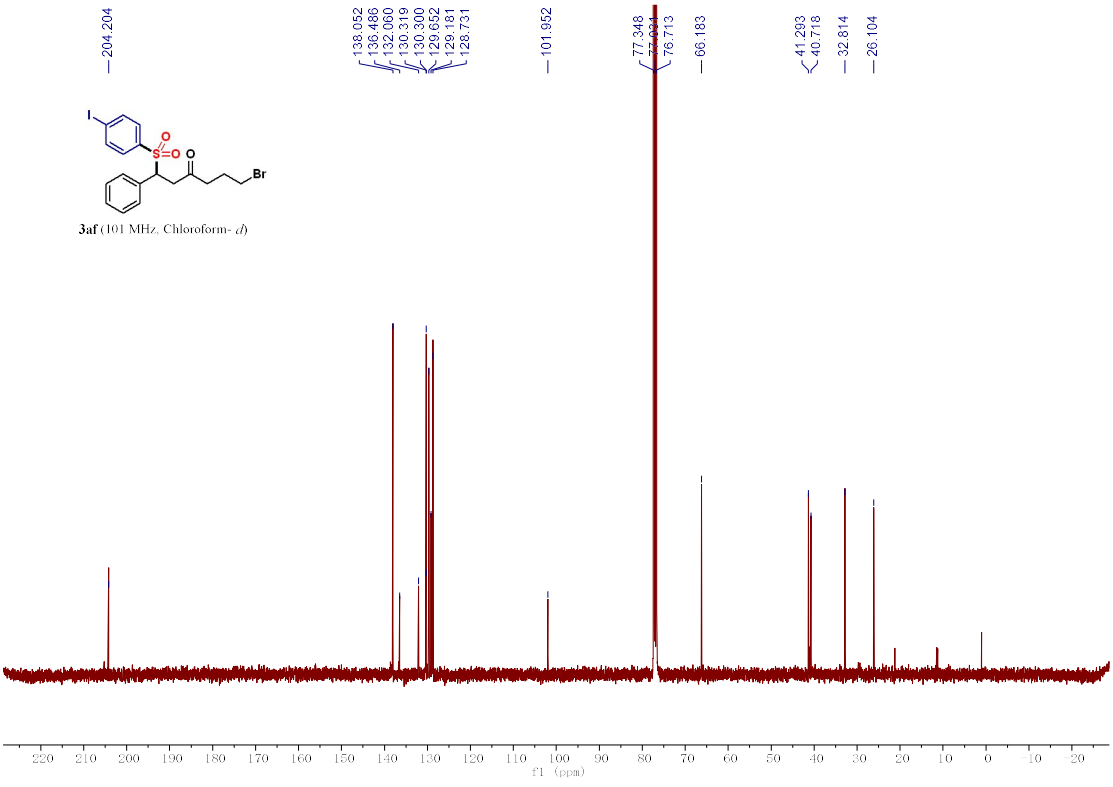


3ae (101 MHz, Chloroform-*d*)

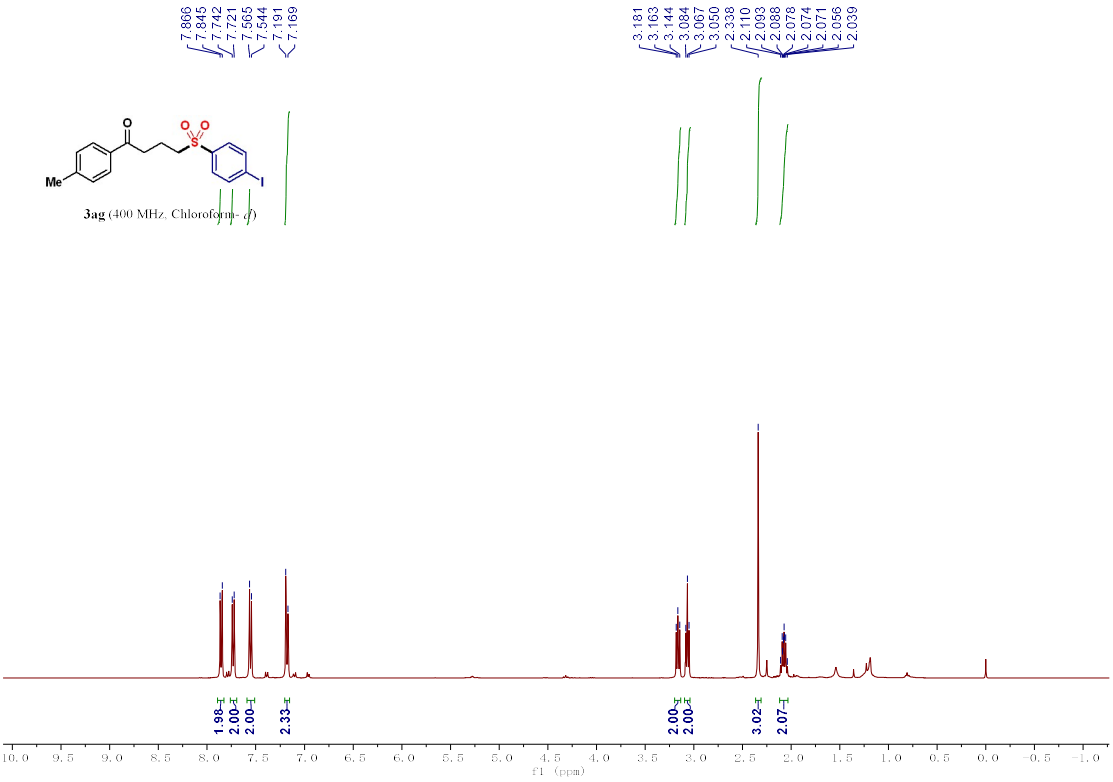




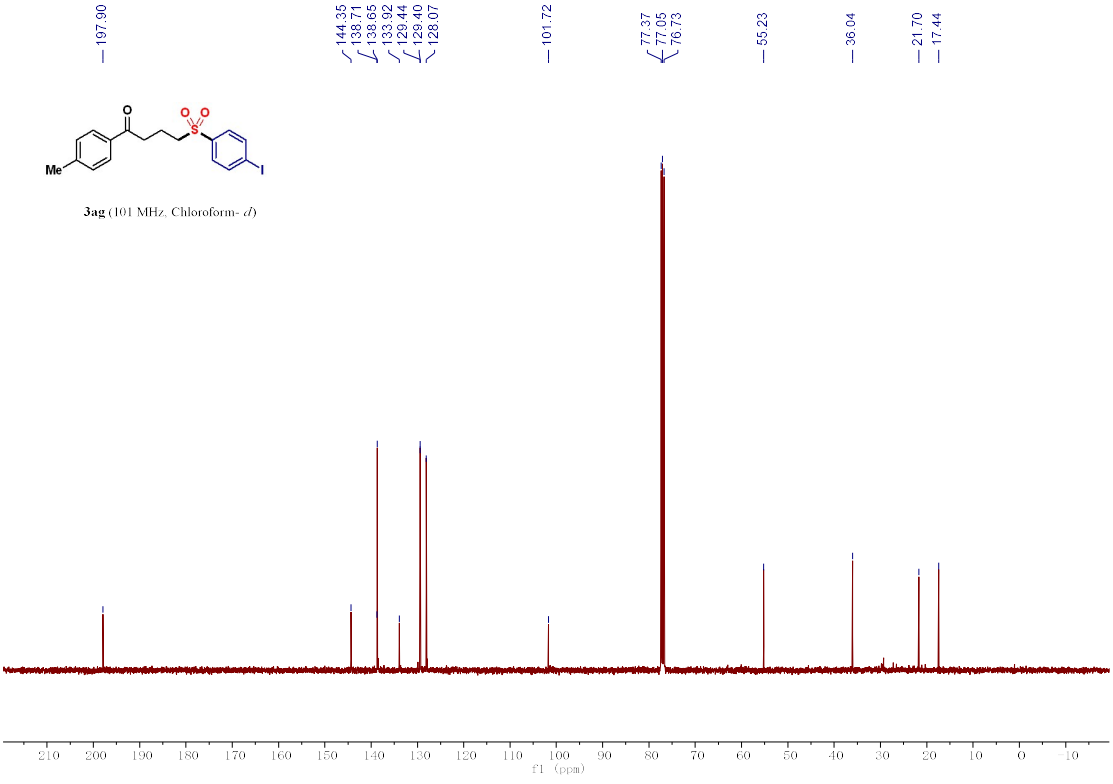
3af (400 MHz, Chloroform-*d*)



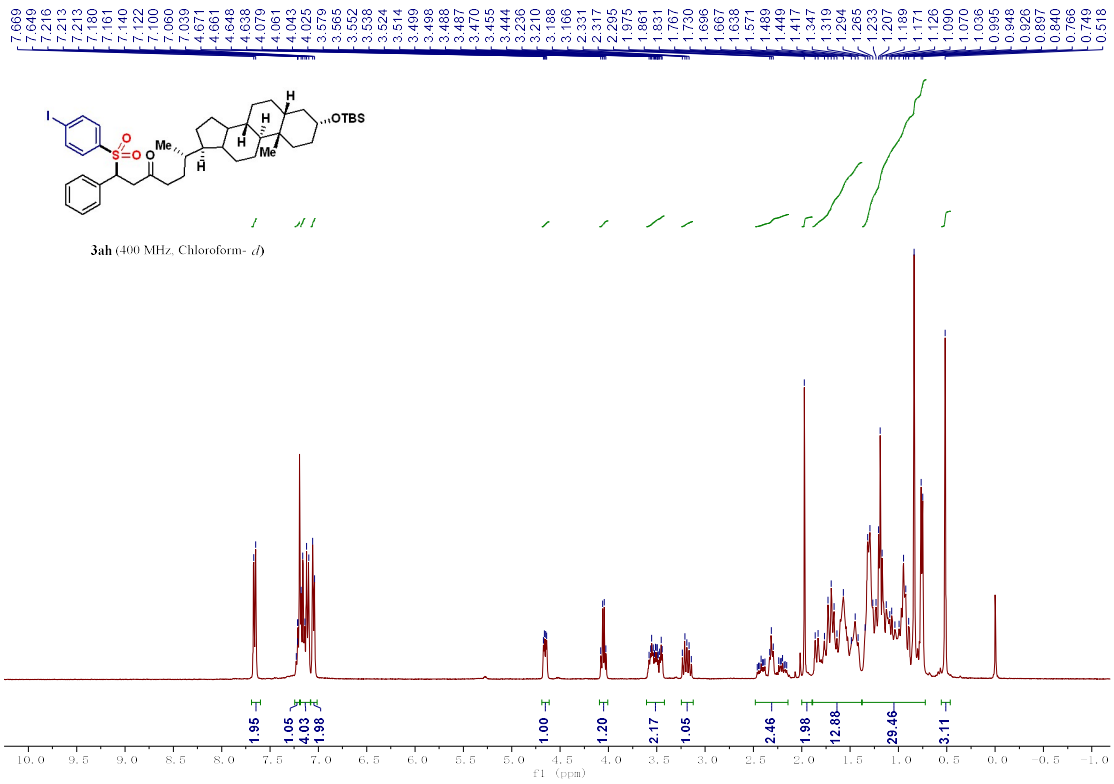
3af (101 MHz, Chloroform-*d*)



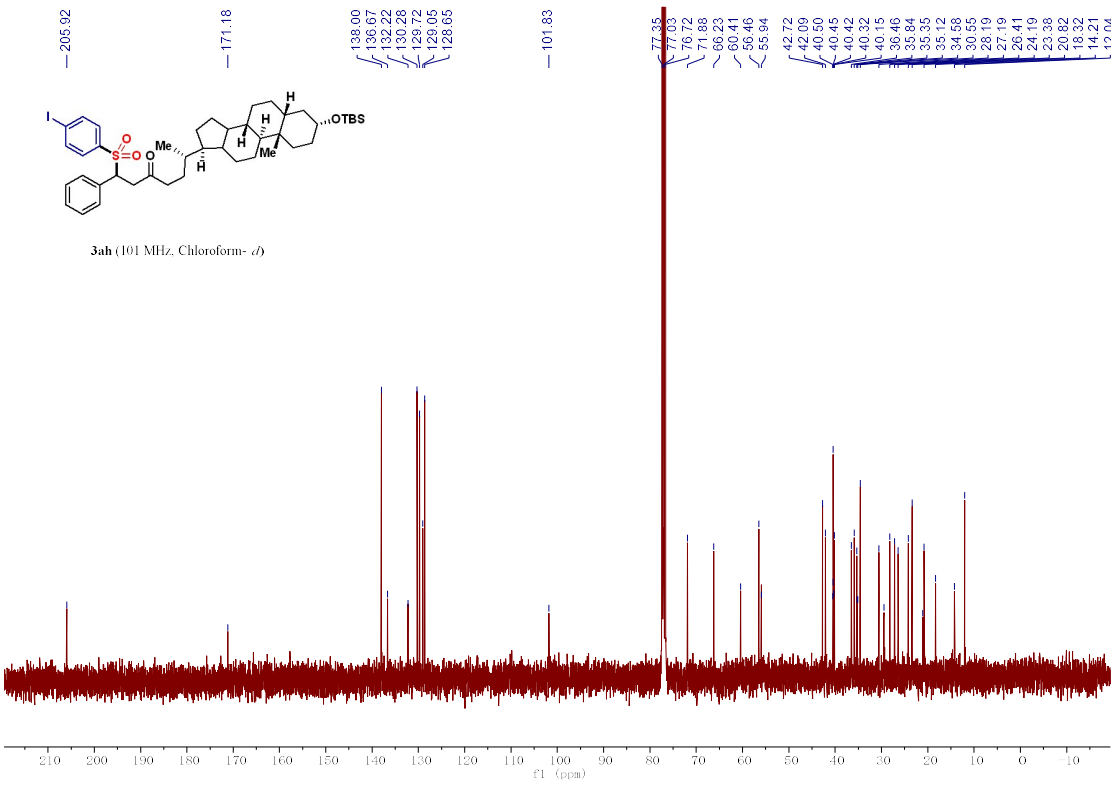
3ag (400 MHz, Chloroform- *d*)



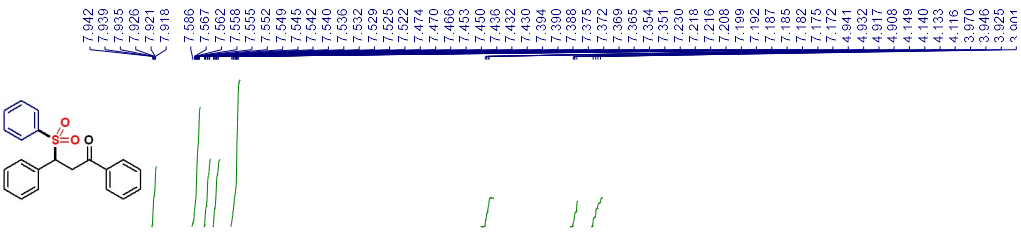
3ag (101 MHz, Chloroform- *d*)



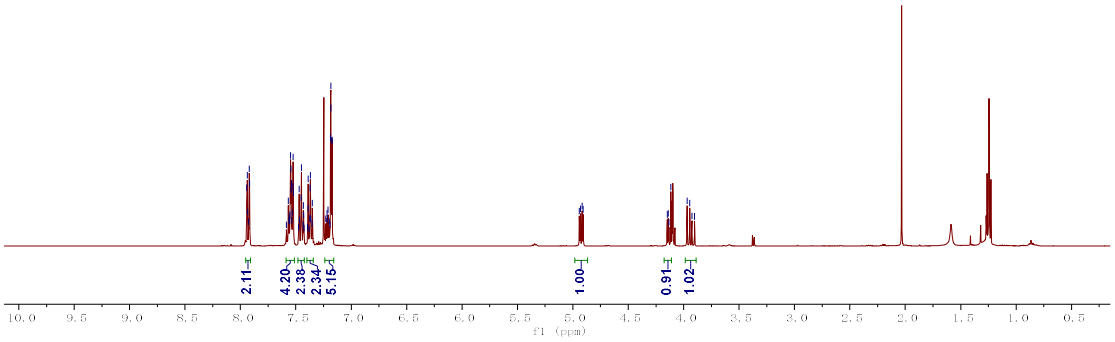
3ah (400 MHz, Chloroform-*d*)

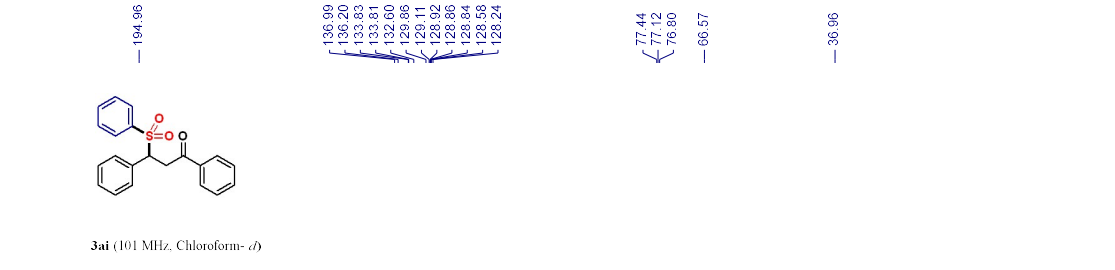


3ah (101 MHz, Chloroform-*d*)



3ai (400 MHz, Chloroform-*d*)





3ai (101 MHz, Chloroform-*d*)