Silver-mediated radical cascade cyclization of *N*-allylamides with sodium sulfinates to access sulfonated oxazolines

Zhichao Chen,*[,a] Mu He,[a] Hongmei Zheng,[b] Wenting Weng,*[,a] Lidan Sun,*[,a] and Xiaolan Xie[a]

[a] *College of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou, Fujian 362000, P. R. China.*

[b] *Quanzhou Hospital of Traditional Chinese Medicine, Quanzhou, Fujian 362000, P. R. China.*

Corresponding Author: Zhichao Chen, Wenting Weng, and Lidan Sun

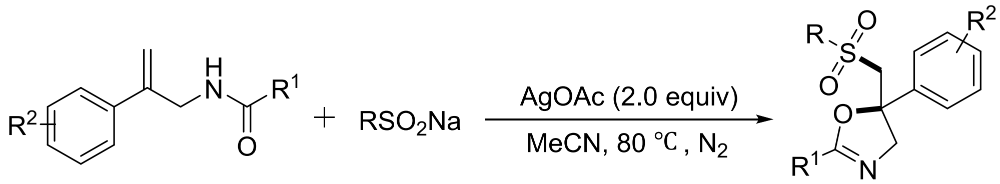
Email: zcchen@qztc.edu.cn, wendywwt@163.com, sunlidan@pku.org.cn.

1. General information

Unless otherwise stated, all commercial materials and solvents were used directly without further purification. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400MHz, ^{13}C 100MHz, ^{19}F NMR 376 MHz), using $CDCl_3$ (spectra were referenced to the solvent peaks ^{1}H: residual $CDCl_3$ = 7.26 ppm, ^{13}C: $CDCl_3$ = 77.0 ppm) as the solvent. High-resolution mass spectra (HRMS) were measured on ESI-TOF. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluent. Thin-layer chromatography (TLC) was carried out on 4×5 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). Reactions were performed with parallel synthesis reactor (WATTCAS WP-TEC-1020H). Starting materials sodium sulfinates **2,** *N*-allylamides **1** were prepared according to the literatures.[S1, S2]

2. General catalytic procedure for the synthesis of 3

Figure 1 The WP-TEC-1020H reaction system

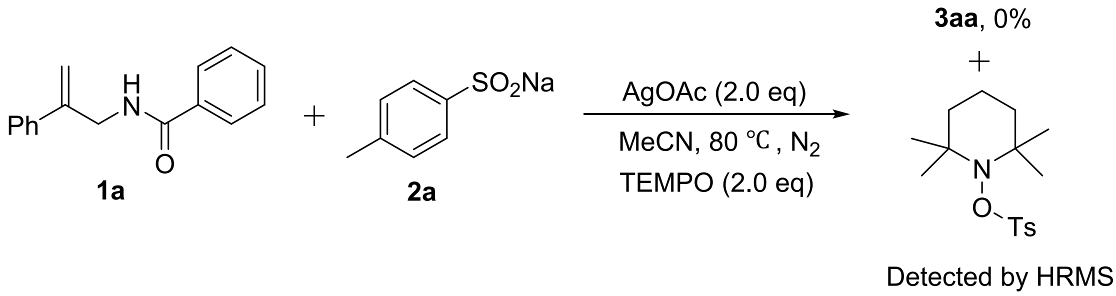


1 **2** **3**

N-Allylamides **1** (0.2 mmol), sodium sulfinates **2** (0.4 mmol, 2 equiv), AgOAc (0.4 mmol, 2 equiv) and 2 mL MeCN were added in a Schlenk tube. Then the mixture was stirred at 80℃ for 12 h under N_2 atmosphere. After completion of the *N*-allylamides, the solvent was removed under reduced pressure by rotary evaporator. Then, the residue was purified by silica gel column chromatography to give the desired products **3**.

3. Mechanism Exploration

(1) Trapping experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)



N-Allylamide **1a** (0.2 mmol), sodium sulfinate **2a** (0.4 mmol), AgOAc (0.4 mmol, 2 equiv), TEMPO (0.4 mmol, 2 equiv) and 2 mL MeCN were added in a schlenk tube. Then the mixture was stirred at 80℃ for 12 h under N_2 atmosphere. The resulting mixture was monitored by TLC, and TEMPO adduct to sulfuryl radical was detected by HRMS (Figure 2). HRMS (ESI) m/z calcd for $C_{16}H_{25}NO_3S$ $[M+Na]^+$ 334.1447, found 334.1445.

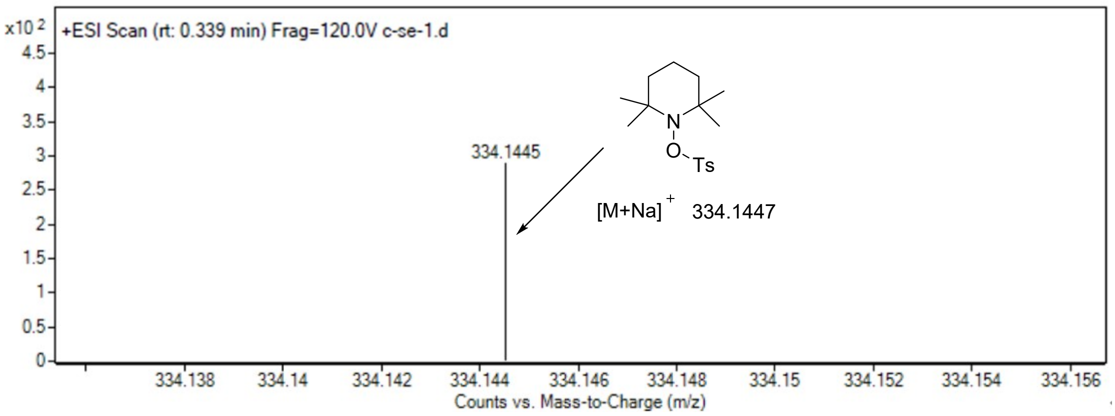
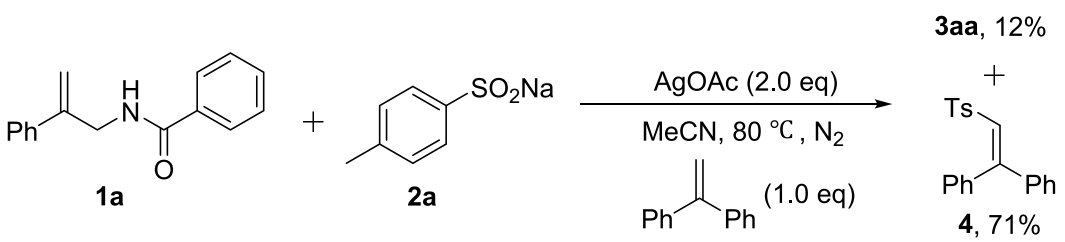


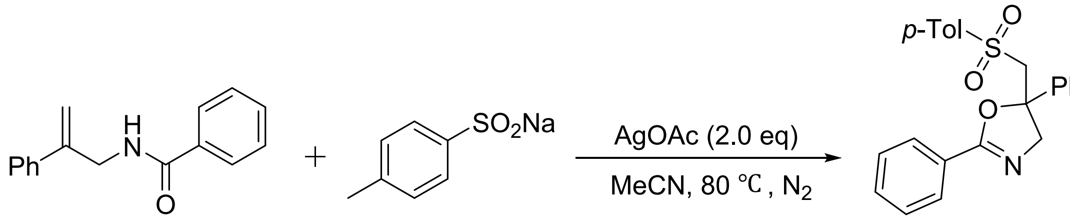
Figure 2

(2) Trapping experiment with ethene-1,1-diyldibenzene



N-Allylamide **1a** (0.2 mmol), sodium sulfinate **2a** (0.4 mmol), AgOAc (0.4 mmol, 2 equiv), TEMPO (0.4 mmol, 2 equiv) and 2 mL MeCN were added in a Schlenk tube. Then the mixture was stirred at 80℃ for 12 h under N_2 atmosphere. The solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give the corresponding compounds **3aa** and **4**.

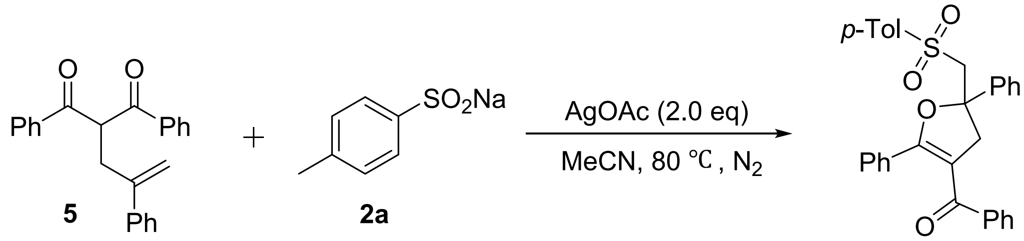
4. The synthetic utility of this methodology



1a **2a** **3aa**

1 g, 4.2 mmol 1.5 g, 8.4 mmol 72%, 0.91 g

N-Allylamide **1a** (4.2 mmol), sodium sulfinate **2a** (8.4 mmol), AgOAc (8.4 mmol, 2 equiv) and 10 mL MeCN were added in a Schlenk tube. Then the mixture was stirred at 80℃ for 24 h under N_2 atmosphere. After completion of the *N*-allylamides, the solvent was removed under reduced pressure by rotary evaporator. Then, the residue was purified by silica gel column chromatography to give the desired product **3aa**.



0.2 mmol 0.4 mmol **6**, 82%

1,3-Diphenyl-2-(2-phenylallyl)propane-1,3-dione **5** (0.2 mmol), sodium sulfinate **2a** (0.4 mmol), AgOAc (0.4 mmol, 2 equiv) and 2 mL MeCN were added in a Schlenk tube. Then the mixture was stirred at 80℃ for 12 h under N_2 atmosphere. The solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give the corresponding compound **6**.

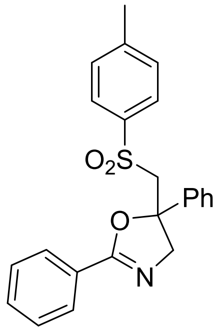
5. References

[S1] (a) *Org. Lett.,* 2017, **19**, 2825; (b) *Org. Chem. Front.,* 2017, **4**, 26.

[S2] (a) *Angew. Chem. Int. Ed.,* 2010, **49**, 4047; (b) *Adv. Synth. Catal.,* 2014, **356**, 3669.

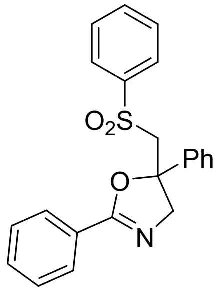
6. Characterization of compounds 3, 4 and 6.

2,5-Diphenyl-5-(tosylmethyl)-4,5-dihydrooxazole (3aa)



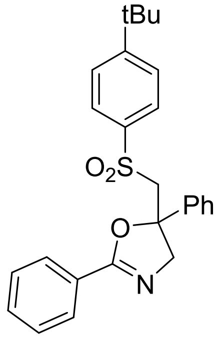
White solid. 68.9 mg, Yield: 88%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.11 (d, *J* = 7.7 Hz, 2H), 4.84 (d, *J* = 15.1 Hz, 1H), 4.19 (d, *J* = 15.1 Hz, 1H), 3.97 (d, *J* = 15.1 Hz, 1H), 3.85 (d, *J* = 15.1 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2, 144.4, 142.3, 137.2, 131.5, 129.6, 128.7, 128.2, 128.1, 128.0, 128.0, 126.9, 124.3, 85.0, 66.6, 64.2, 21.4. HRMS (ESI) *m/z* calcd for $C_{23}H_{21}NO_3S$ $[M+H]^+$ 392.1315, found 392.1317.

2,5-Diphenyl-5-((phenylsulfonyl)methyl)-4,5-dihydrooxazole (3ab)



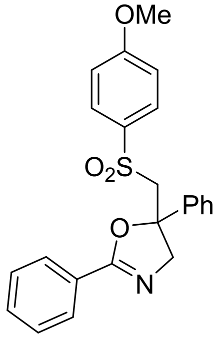
White solid. 68.7 mg, Yield: 91%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 13.8, 7.9 Hz, 4H), 7.47 (q, *J* = 7.1 Hz, 2H), 7.40 – 7.26 (m, 9H), 4.79 (d, *J* = 15.1 Hz, 1H), 4.21 (d, *J* = 15.1 Hz, 1H), 3.99 (d, *J* = 15.1 Hz, 1H), 3.89 (d, *J* = 15.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3, 142.0, 140.3, 133.3, 131.6, 128.9, 128.7, 128.2, 128.2, 128.1, 127.9, 126.9, 124.4, 85.0, 66.9, 64.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{19}NO_3S$ $[M+Na]^+$ 400.0978, found 400.0979.

5-(((4-(Tert-butyl)phenyl)sulfonyl)methyl)-2,5-diphenyl-4,5-dihydrooxazole (3ac)



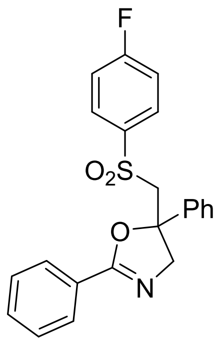
White solid. 68.5 mg, Yield: 79%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.38 (dd, *J* = 18.5, 7.9 Hz, 4H), 7.32 – 7.24 (m, 5H), 4.84 (d, *J* = 15.1 Hz, 1H), 4.23 (d, *J* = 15.1 Hz, 1H), 4.00 (d, *J* = 15.1 Hz, 1H), 3.89 (d, *J* = 15.1 Hz, 1H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3, 157.2, 142.1, 137.2, 131.5, 128.7, 128.3, 128.2, 128.1, 127.8, 127.0, 125.9, 124.4, 85.1, 66.8, 64.1, 35.1, 30.9. HRMS (ESI) *m/z* calcd for $C_{26}H_{27}NO_3S$ $[M+H]^+$ 434.1784, found 434.1785.

5-(((4-Methoxyphenyl)sulfonyl)methyl)-2,5-diphenyl-4,5-dihydrooxazole (3ad)



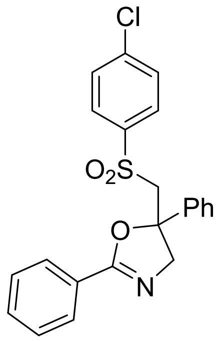
White solid. 66.8 mg, Yield: 82%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 8.9 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.24 (m, 5H), 6.75 (d, *J* = 8.9 Hz, 2H), 4.84 (d, *J* = 15.1 Hz, 1H), 4.18 (d, *J* = 15.1 Hz, 1H), 3.95 (d, *J* = 15.1 Hz, 1H), 3.84 (d, *J* = 15.1 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.4, 162.1, 142.3, 131.6, 131.5, 130.1, 128.7, 128.1, 128.1, 128.0, 126.9, 124.3, 114.1, 85.0, 66.5, 64.3, 55.4. HRMS (ESI) *m/z* calcd for $C_{23}H_{21}NO_4S$ $[M+H]^+$ 408.1264, found 408.1265.

5-(((4-Fluorophenyl)sulfonyl)methyl)-2,5-diphenyl-4,5-dihydrooxazole (3ae)



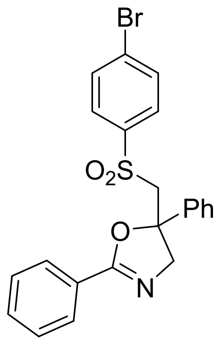
White solid. 68.8 mg, Yield: 87%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.25 (m, 5H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.78 (d, *J* = 15.1 Hz, 1H), 4.20 (d, *J* = 15.1 Hz, 1H), 3.99 (d, *J* = 15.2 Hz, 1H), 3.89 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.5 (d, *J* = 256.3 Hz), 162.1, 141.9, 136.2 (d, *J* = 3.1 Hz), 131.7, 130.9 (d, *J* = 9.7 Hz), 128.8, 128.3, 128.2, 128.1, 126.8, 124.3, 116.2 (d, *J* = 22.7 Hz), 84.9, 67.0, 64.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.74. HRMS (ESI) *m/z* calcd for $C_{22}H_{18}FNO_3S$ $[M+H]^+$ 396.1064, found 392.1067.

5-(((4-Chlorophenyl)sulfonyl)methyl)-2,5-diphenyl-4,5-dihydrooxazole (3af)



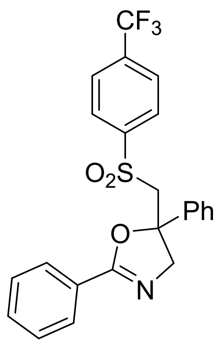
White solid. 65.9 mg, Yield: 80%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.24 (m, 7H), 4.78 (d, *J* = 15.1 Hz, 1H), 4.18 (d, *J* = 15.1 Hz, 1H), 4.00 (d, *J* = 15.2 Hz, 1H), 3.89 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1, 141.8, 140.1, 138.5, 131.7, 129.4, 129.2, 128.8, 128.3, 128.2, 128.0, 126.6, 124.3, 84.8, 67.0, 64.2. HRMS (ESI) *m/z* calcd for $C_{22}H_{18}ClNO_3S$ $[M+H]^+$ 412.0769, found 412.0770.

5-(((4-Bromophenyl)sulfonyl)methyl)-2,5-diphenyl-4,5-dihydrooxazole (3ag)



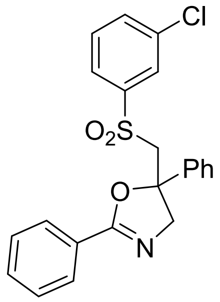
White solid. 71.2 mg, Yield: 78%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.46 – 7.37 (m, 4H), 7.35 – 7.24 (m, 5H), 4.77 (d, *J* = 15.1 Hz, 1H), 4.18 (d, *J* = 15.1 Hz, 1H), 3.99 (d, *J* = 15.3 Hz, 1H), 3.89 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1, 141.8, 139.0, 132.2, 131.8, 129.5, 128.8, 128.4, 128.1, 128.0, 126.6, 124.3, 84.8, 67.0, 64.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{18}BrNO_3S$ $[M+H]^+$ 456.0264, found 456.0262.

2,5-Diphenyl-5-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)-4,5-dihydrooxazole (3ah)



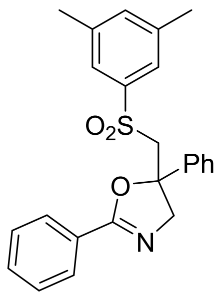
White solid. 65.0 mg, Yield: 73%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.25 (m, 5H), 4.79 (d, *J* = 15.1 Hz, 1H), 4.21 (d, *J* = 15.1 Hz, 1H), 4.06 (d, *J* = 15.3 Hz, 1H), 3.95 (d, *J* = 15.3 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1, 143.4, 141.6, 134.9 (q, *J* = 32.9 Hz), 131.8, 128.8, 128.6, 128.4, 128.3, 127.9, 126.5, 126.0 (q, *J* = 3.4 Hz), 124.3, 122.9 (q, *J* = 273.8 Hz), 84.7, 67.1, 64.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.16. HRMS (ESI) *m/z* calcd for $C_{23}H_{18}F_3NO_3S$ $[M+H]^+$ 446.1032, found 446.1034.

5-(((3-Chlorophenyl)sulfonyl)methyl)-2,5-diphenyl-4,5-dihydrooxazole (3ai)



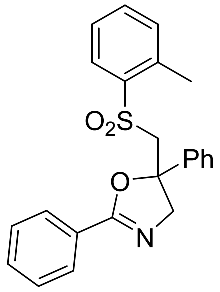
White solid. 66.7 mg, Yield: 81%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.68 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 3H), 7.36 – 7.28 (m, 6H), 4.78 (d, *J* = 15.1 Hz, 1H), 4.23 (d, *J* = 15.1 Hz, 1H), 4.04 (d, *J* = 15.2 Hz, 1H), 3.94 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2, 141.7, 141.5, 135.1, 133.4, 131.7, 130.2, 128.7, 128.3, 128.1, 126.6, 126.0, 124.3, 84.8, 67.1, 64.2. HRMS (ESI) *m/z* calcd for $C_{22}H_{18}ClNO_3S$ $[M+Na]^+$ 434.0588, found 434.0587.

5-(((3,5-Dimethylphenyl)sulfonyl)methyl)-2,5-diphenyl-4,5-dihydrooxazole (3aj)



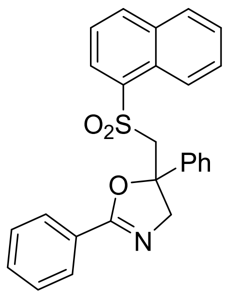
White solid. 69.7 mg, Yield: 86%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.24 (m, 7H), 7.04 (s, 1H), 4.87 (d, *J* = 15.1 Hz, 1H), 4.20 (d, *J* = 15.1 Hz, 1H), 3.98 (d, *J* = 15.1 Hz, 1H), 3.86 (d, *J* = 15.1 Hz, 1H), 2.19 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2, 142.4, 140.0, 139.1, 135.1, 131.6, 128.7, 128.2, 128.2, 128.2, 127.0, 125.5, 124.4, 85.0, 66.6, 64.2, 21.0. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}NO_3S$ $[M+Na]^+$ 428.1291, found 428.1293.

2,5-Diphenyl-5-((*o*-tolylsulfonyl)methyl)-4,5-dihydrooxazole (3ak)



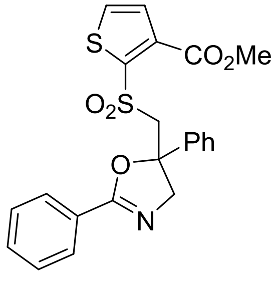
White solid. 53.2 mg, Yield: 68%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.27 (m, 8H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 15.1 Hz, 1H), 4.21 (d, *J* = 15.1 Hz, 1H), 4.02 (d, *J* = 15.1 Hz, 1H), 3.90 (d, *J* = 15.1 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1, 142.2, 138.3, 137.5, 133.4, 132.4, 131.5, 130.1, 128.7, 128.1, 128.1, 126.8, 126.4, 124.3, 85.0, 66.7, 63.4, 20.3. HRMS (ESI) *m/z* calcd for $C_{23}H_{21}NO_3S$ $[M+H]^+$ 392.1315, found 392.1317.

5-((Naphthalen-1-ylsulfonyl)methyl)-2,5-diphenyl-4,5-dihydrooxazole (3al)



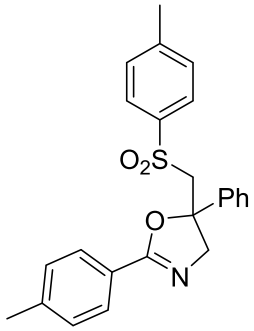
White solid. 60.7 mg, Yield: 71%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.90 (t, *J* = 8.7 Hz, 2H), 7.70 – 7.56 (m, 4H), 7.48 (t, *J* = 7.1 Hz, 1H), 7.38 – 7.20 (m, 8H), 4.84 (d, *J* = 15.1 Hz, 1H), 4.36 – 3.98 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3, 141.9, 135.0, 134.9, 134.1, 131.5, 130.8, 129.3, 128.8, 128.6, 128.2, 128.1, 126.8, 126.8, 124.4, 124.3, 123.8, 85.2, 66.9, 63.9. HRMS (ESI) *m/z* calcd for $C_{26}H_{21}NO_3S$ $[M+H]^+$ 428.1315, found 428.1314.

Methyl 2-(((2,5-diphenyl-4,5-dihydrooxazol-5-yl)methyl)sulfonyl)thiophene-3-carboxylate (3am)



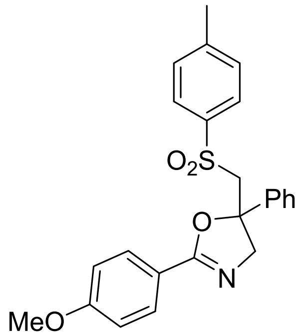
White solid. 52.9 mg, Yield: 60%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.51 (t, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.24 (m, 6H), 7.22 (d, *J* = 5.2 Hz, 1H), 4.81 (d, *J* = 15.0 Hz, 1H), 4.73 (d, *J* = 15.3 Hz, 1H), 4.35 (d, *J* = 15.2 Hz, 1H), 4.24 (d, *J* = 15.0 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3, 160.1, 144.4, 141.8, 133.6, 131.7, 131.5, 129.4, 128.6, 128.3, 128.2, 127.0, 124.5, 85.1, 67.3, 63.0, 53.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{19}NO_5S_2$ $[M+Na]^+$ 464.0597, found 464.0598.

5-Phenyl-2-(p-tolyl)-5-(tosylmethyl)-4,5-dihydrooxazole (3ba)



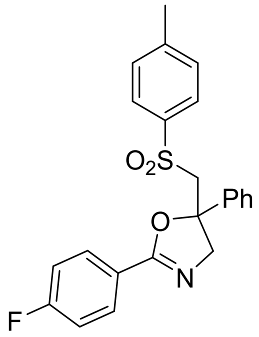
White solid. 68.9 mg, Yield: 85%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 7.4, 3.7 Hz, 4H), 7.37 – 7.29 (m, 5H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.83 (d, *J* = 15.0 Hz, 1H), 4.20 (d, *J* = 15.0 Hz, 1H), 3.99 (d, *J* = 15.1 Hz, 1H), 3.88 (d, *J* = 15.1 Hz, 1H), 2.42 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.4, 144.3, 142.3, 141.9, 137.2, 129.5, 128.9, 128.7, 128.2, 128.0, 128.0, 124.4, 124.1, 84.9, 66.5, 64.2, 21.5, 21.4. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}NO_3S$ $[M+Na]^+$ 428.1291, found 428.1294.

2-(4-Methoxyphenyl)-5-phenyl-5-(tosylmethyl)-4,5-dihydrooxazole (3ca)



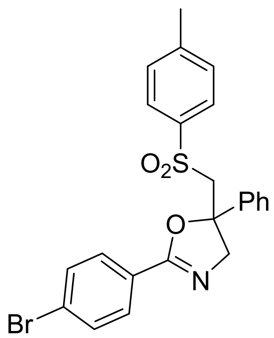
White solid. 68.3 mg, Yield: 81%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.26 (m, 5H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 4.77 (d, *J* = 14.9 Hz, 1H), 4.15 (d, *J* = 14.9 Hz, 1H), 3.95 (d, *J* = 15.1 Hz, 1H), 3.87 – 3.83 (m, 4H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2, 162.1, 144.3, 142.3, 137.3, 130.0, 129.6, 128.7, 128.0, 124.4, 119.4, 113.5, 84.9, 66.6, 64.2, 55.4, 21.5. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}NO_4S$ $[M+Na]^+$ 444.1240, found 444.1244.

2-(4-Fluorophenyl)-5-phenyl-5-(tosylmethyl)-4,5-dihydrooxazole (3da)



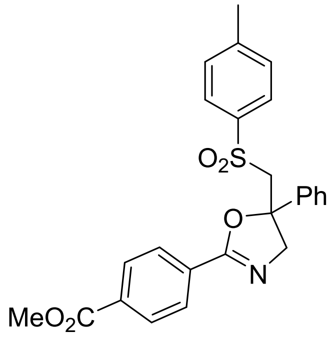
White solid. 73.7 mg, Yield: 90%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.72 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 8.2 Hz, 2H), 4.82 (d, *J* = 15.1 Hz, 1H), 4.18 (d, *J* = 15.1 Hz, 1H), 3.95 (d, *J* = 15.1 Hz, 1H), 3.83 (d, *J* = 15.1 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.7 (d, *J* = 252.3 Hz), 161.3, 144.4, 142.2, 137.3, 130.5 (d, *J* = 8.9 Hz), 129.6, 128.8, 128.1, 128.0, 124.3, 123.2 (d, *J* = 3.2 Hz), 115.3 (d, *J* = 22.0 Hz), 85.3, 66.6, 64.2, 21.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.59. HRMS (ESI) *m/z* calcd for $C_{23}H_{20}FNO_3S$ $[M+Na]^+$ 432.1040, found 432.1043.

2-(4-Bromophenyl)-5-phenyl-5-(tosylmethyl)-4,5-dihydrooxazole (3ea)



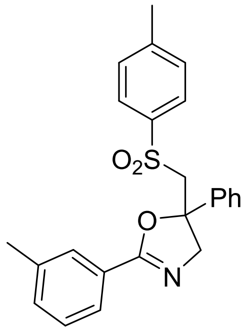
White solid. 75.3 mg, Yield: 80%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 4H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.84 (d, *J* = 15.2 Hz, 1H), 4.17 (d, *J* = 15.2 Hz, 1H), 3.94 (d, *J* = 15.1 Hz, 1H), 3.82 (d, *J* = 15.1 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4, 144.5, 142.2, 137.2, 131.4, 129.7, 129.6, 128.8, 128.2, 127.9, 126.2, 125.9, 124.3, 85.3, 66.4, 64.1, 21.5. HRMS (ESI) *m/z* calcd for $C_{23}H_{20}BrNO_3S$ $[M+H]^+$ 470.0420, found 470.0423.

Methyl 4-(5-phenyl-5-(tosylmethyl)-4,5-dihydrooxazol-2-yl)benzoate (3fa)



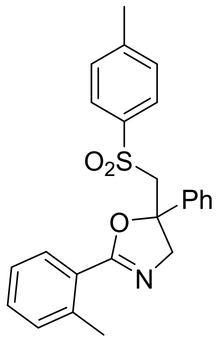
White solid. 67.4 mg, Yield: 75%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.14 (d, *J* = 7.5 Hz, 2H), 4.92 (d, *J* = 15.4 Hz, 1H), 4.25 (d, *J* = 15.4 Hz, 1H), 4.10 – 3.78 (m, 5H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.4, 161.5, 144.6, 142.2, 137.2, 132.7, 131.0, 129.7, 129.4, 128.9, 128.3, 128.2, 128.0, 124.3, 85.5, 66.5, 64.2, 52.5, 21.5. HRMS (ESI) *m/z* calcd for $C_{25}H_{23}NO_5S$ $[M+Na]^+$ 472.1189, found 472.1191.

5-Phenyl-2-(m-tolyl)-5-(tosylmethyl)-4,5-dihydrooxazole (3ga)



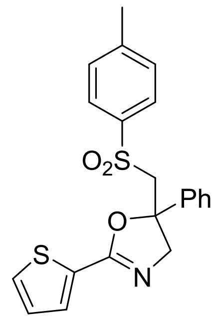
White solid. 70.6 mg, Yield: 87%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.60 (s, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.37 – 7.28 (m, 7H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.86 (d, *J* = 15.1 Hz, 1H), 4.21 (d, *J* = 15.1 Hz, 1H), 4.00 (d, *J* = 15.1 Hz, 1H), 3.89 (d, *J* = 15.2 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.4, 144.4, 142.4, 137.9, 137.2, 132.3, 129.5, 128.7, 128.7, 128.1, 128.0, 126.8, 125.3, 124.3, 84.9, 66.5, 64.1, 21.5, 21.2. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}NO_3S$ $[M+Na]^+$ 428.1291, found 428.1293.

5-Phenyl-2-(o-tolyl)-5-(tosylmethyl)-4,5-dihydrooxazole (3ha)



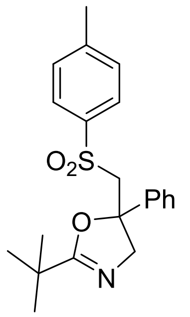
White solid. 68.1 mg, Yield: 84%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.7 Hz, 3H), 7.37 – 7.21 (m, 7H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 4.83 (d, *J* = 15.1 Hz, 1H), 4.25 (d, *J* = 15.1 Hz, 1H), 3.94 (d, *J* = 15.1 Hz, 1H), 3.84 (d, *J* = 15.0 Hz, 1H), 2.58 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3, 144.4, 142.3, 139.3, 137.3, 131.3, 130.7, 130.0, 129.5, 128.7, 128.0, 127.8, 125.9, 125.3, 124.5, 83.9, 67.2, 64.3, 22.2, 21.5. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}NO_3S$ $[M+Na]^+$ 428.1291, found 428.1292.

5-phenyl-2-(thiophen-2-yl)-5-(tosylmethyl)-4,5-dihydrooxazole (3ia)



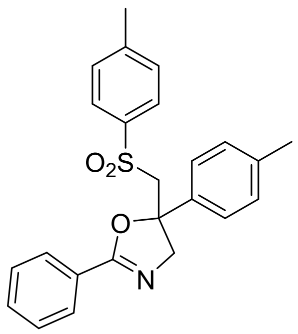
White solid. 55.7 mg, Yield: 70%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 3.7 Hz, 1H), 7.34 – 7.28 (m, 6H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.03 (s, 1H), 4.84 (d, *J* = 15.0 Hz, 1H), 4.17 (d, *J* = 15.0 Hz, 1H), 3.95 (d, *J* = 15.1 Hz, 1H), 3.84 (d, *J* = 15.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.1, 144.5, 142.1, 137.1, 130.6, 130.2, 129.6, 129.5, 128.8, 128.2, 128.0, 127.4, 124.4, 85.6, 66.2, 64.1, 21.5. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}NO_3S_2$ $[M+Na]^+$ 420.0699, found 420.0701.

2-(Tert-butyl)-5-phenyl-5-(tosylmethyl)-4,5-dihydrooxazole (3ja)



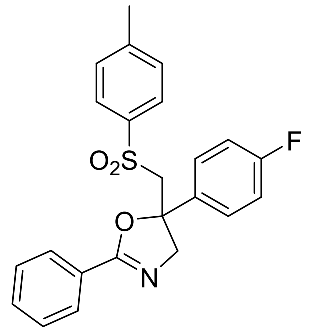
White solid. 55.0 mg, Yield: 74%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.21 (m, 7H), 4.37 (d, *J* = 14.5 Hz, 1H), 4.01 (d, *J* = 14.5 Hz, 1H), 3.82 (d, *J* = 14.7 Hz, 1H), 3.72 (d, *J* = 14.8 Hz, 1H), 2.41 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.8, 144.4, 141.9, 137.6, 129.6, 128.5, 127.9, 127.8, 124.6, 84.7, 67.3, 64.9, 33.2, 27.5, 21.5. HRMS (ESI) *m/z* calcd for $C_{21}H_{25}NO_3S$ $[M+Na]^+$ 394.1447, found 394.14450.

2-Phenyl-5-(*p*-tolyl)-5-(tosylmethyl)-4,5-dihydrooxazole (3ka)



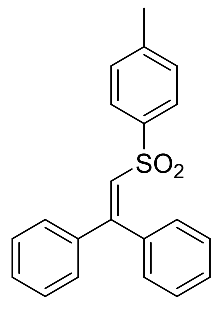
White solid. 69.7 mg, Yield: 86%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 4H), 4.80 (d, *J* = 15.0 Hz, 1H), 4.18 (d, *J* = 15.1 Hz, 1H), 3.94 (d, *J* = 15.1 Hz, 1H), 3.84 (d, *J* = 15.1 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3, 144.4, 139.3, 138.0, 137.3, 131.5, 129.6, 129.4, 128.2, 128.2, 128.1, 127.0, 124.4, 85.1, 66.6, 64.3, 21.5, 21.1. HRMS (ESI) *m/z* calcd for $C_{24}H_{23}NO_3S$ $[M+Na]^+$ 428.1291, found 428.1292.

5-(4-Fluorophenyl)-2-phenyl-5-(tosylmethyl)-4,5-dihydrooxazole (3la)



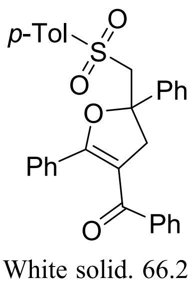
White solid. 72.9 mg, Yield: 89%. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 8.2 Hz, 2H), 4.76 (d, *J* = 15.1 Hz, 1H), 4.16 (d, *J* = 15.1 Hz, 1H), 3.92 (d, *J* = 15.0 Hz, 1H), 3.83 (d, *J* = 15.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3 (d, *J* = 248.0 Hz), 162.2, 144.6, 137.8 (d, *J* = 3.1 Hz), 137.1, 131.6, 129.6, 128.2, 128.2, 127.9, 126.7, 126.4 (d, *J* = 8.3 Hz), 115.6 (d, *J* = 21.7 Hz), 84.7, 66.9, 64.2, 21.5. HRMS (ESI) *m/z* calcd for $C_{23}H_{20}FNO_3S$ $[M+Na]^+$ 432.1040, found 432.1041.

(2-Tosylethene-1,1-diyl)dibenzene (4)



White solid. 47.5 mg, Yield: 71%. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.33 (m, 6H), 7.24 – 7.12 (m, 6H), 7.03 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.8, 143.8, 139.2, 138.6, 135.6, 130.3, 129.8, 129.4, 129.0, 128.9, 128.6, 128.2, 127.8, 127.7, 21.6.

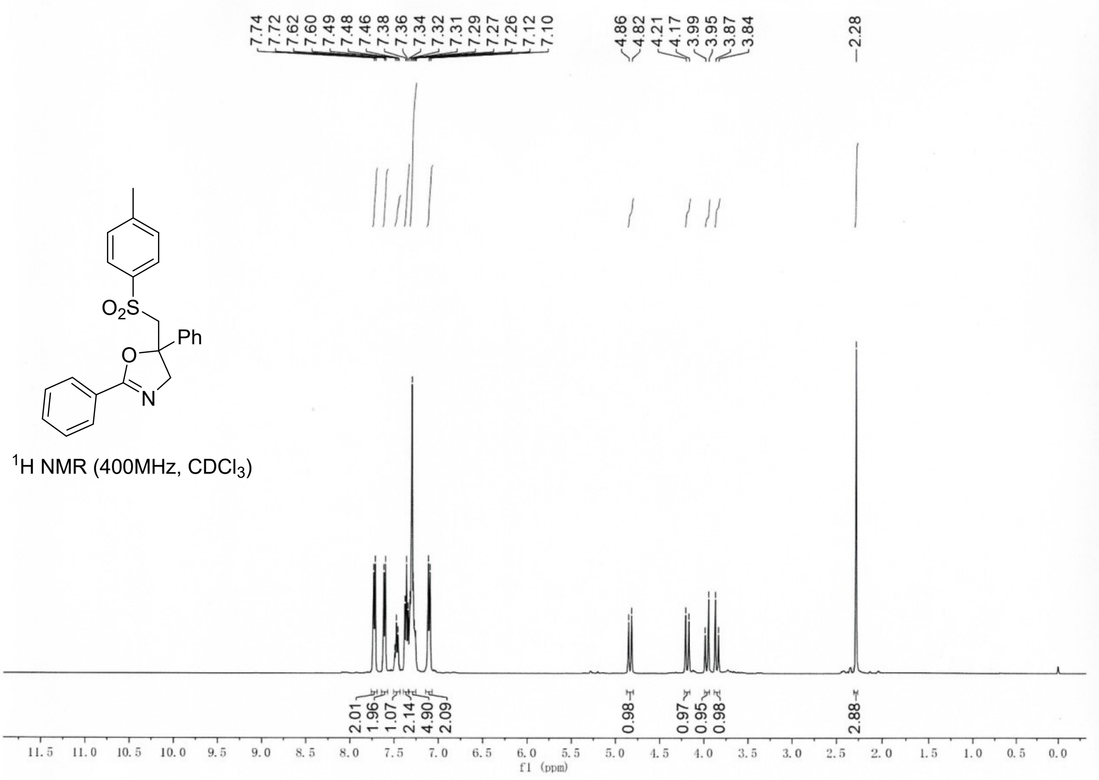
Sulfonated dihydrofuran (6)



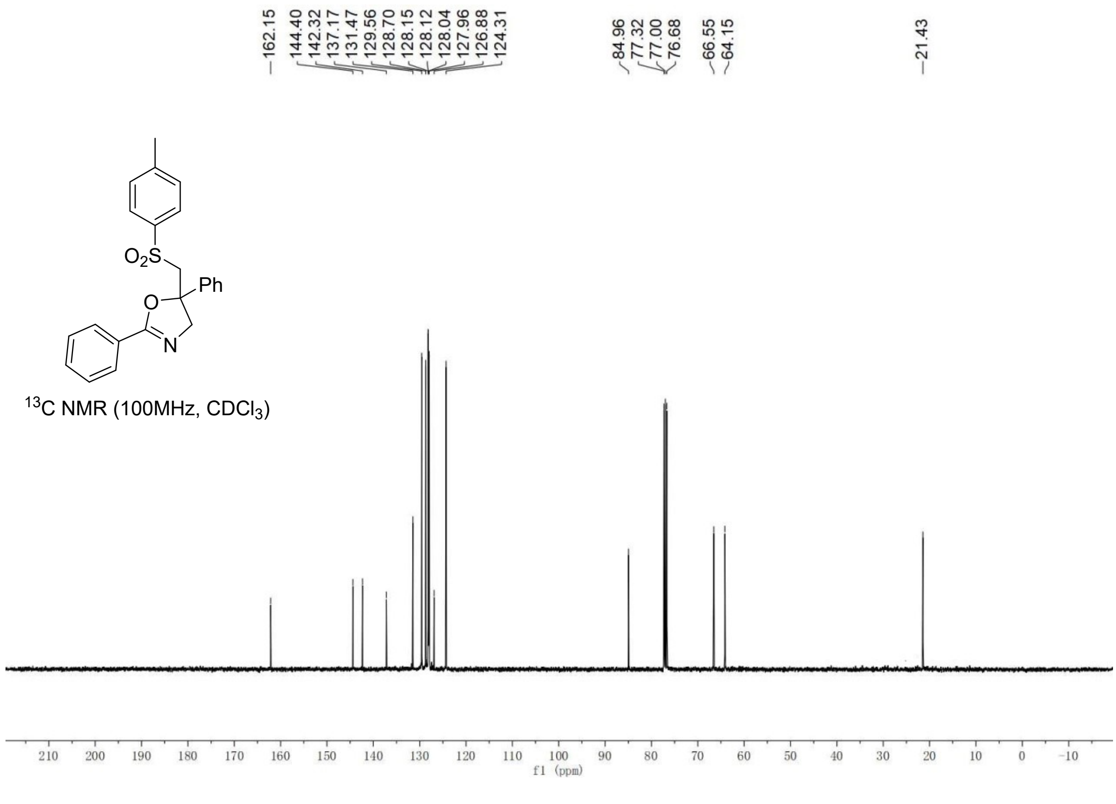
White solid. 66.2 mg, Yield: 82%, mp 165-166 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.32 (m, 3H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.18 – 7.07 (m, 6H), 4.16 (d, *J* = 15.4 Hz, 1H), 3.91 (s, 2H), 3.64 (d, *J* = 15.4 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.0, 163.2, 144.4, 143.1, 138.6, 137.6, 131.4, 130.1, 129.6, 129.5, 129.4, 129.0, 128.7, 128.0, 127.9, 127.7, 127.5, 124.5, 111.7, 86.5, 65.0, 44.9, 21.5. HRMS (ESI): Calcd for $C_{24}H_{20}O_4S$ $[M+H]^+$: 404.1077; found: 404.1073.

9. Copies of the ^{1}H, ^{13}C and ^{19}F NMR Spectra

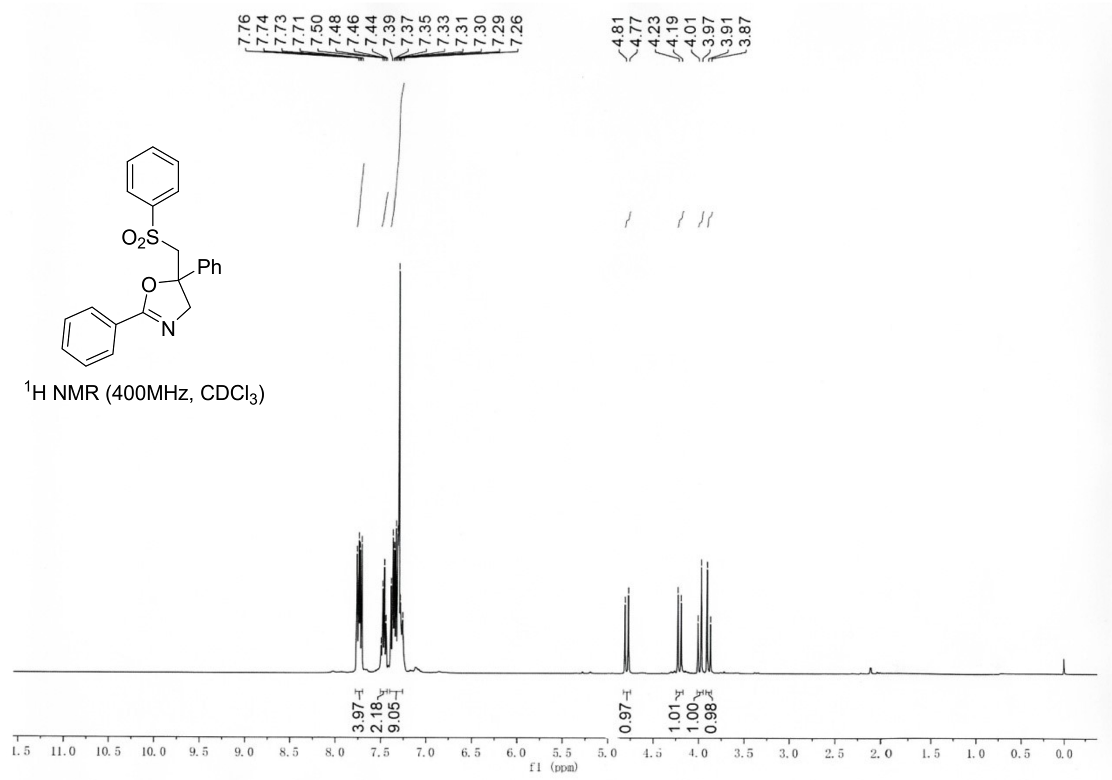
^{1}H NMR spectrum of **3aa**



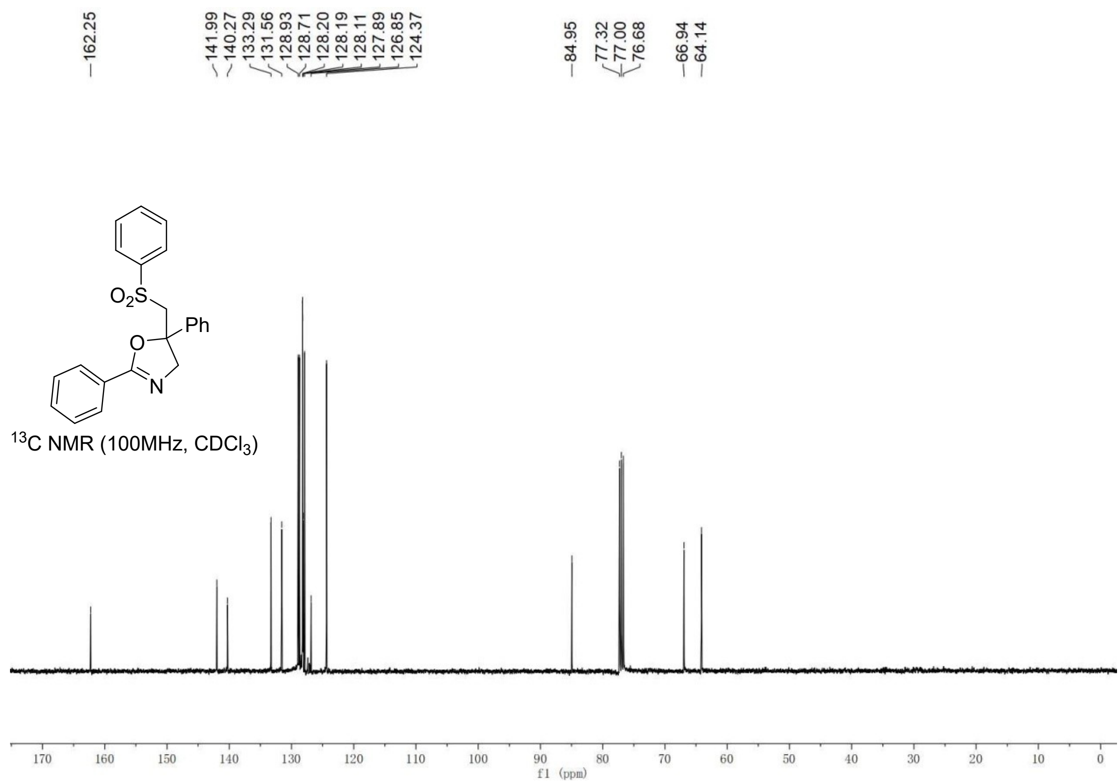
^{13}C NMR spectrum of **3aa**



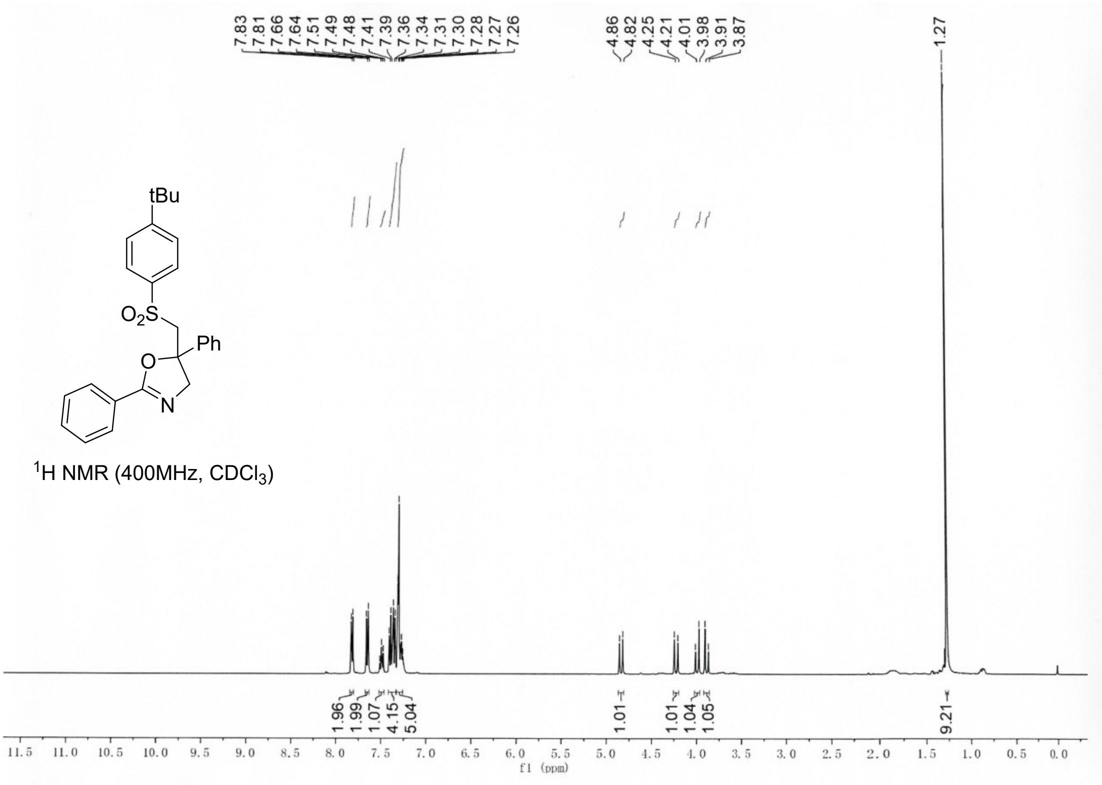
[1]H NMR spectrum of **3ab**



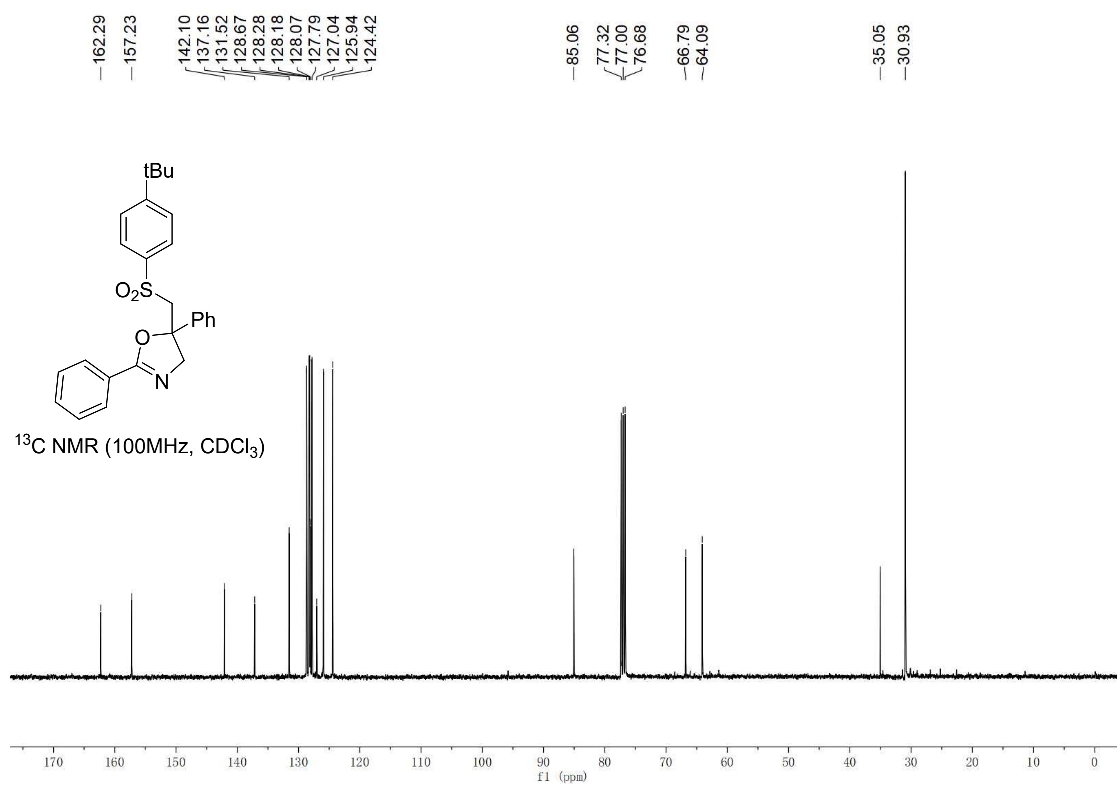
[13]C NMR spectrum of **3ab**



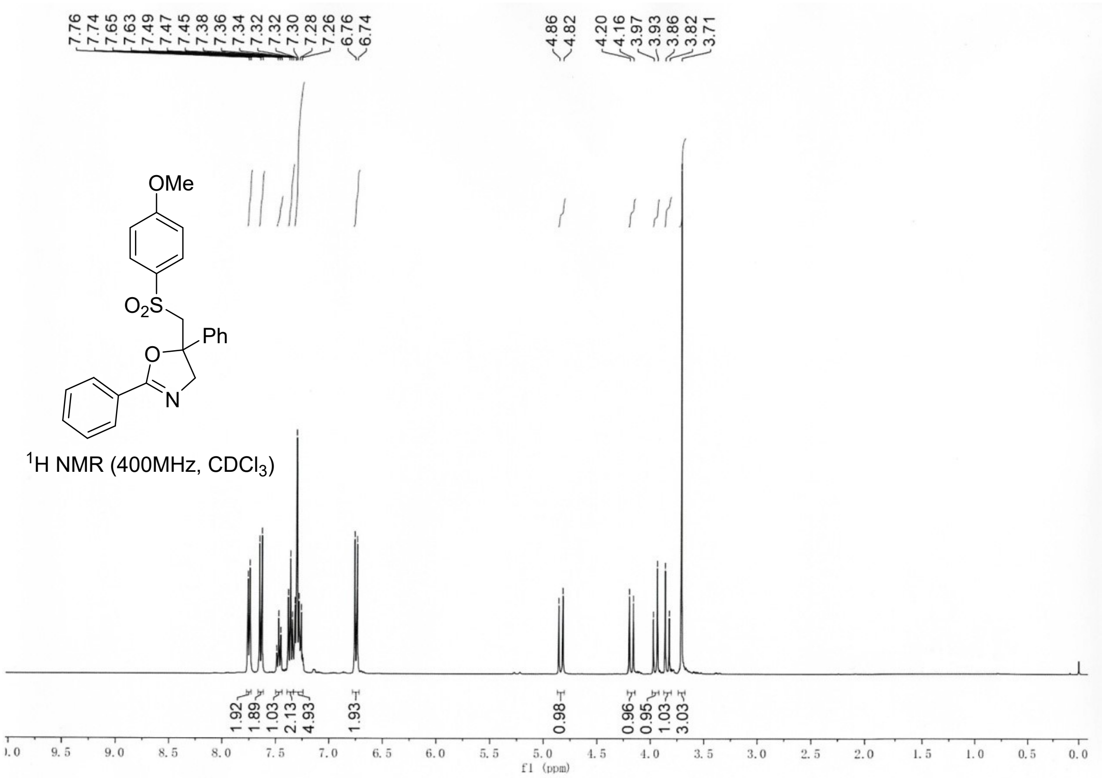
[1]H NMR spectrum of **3ac**



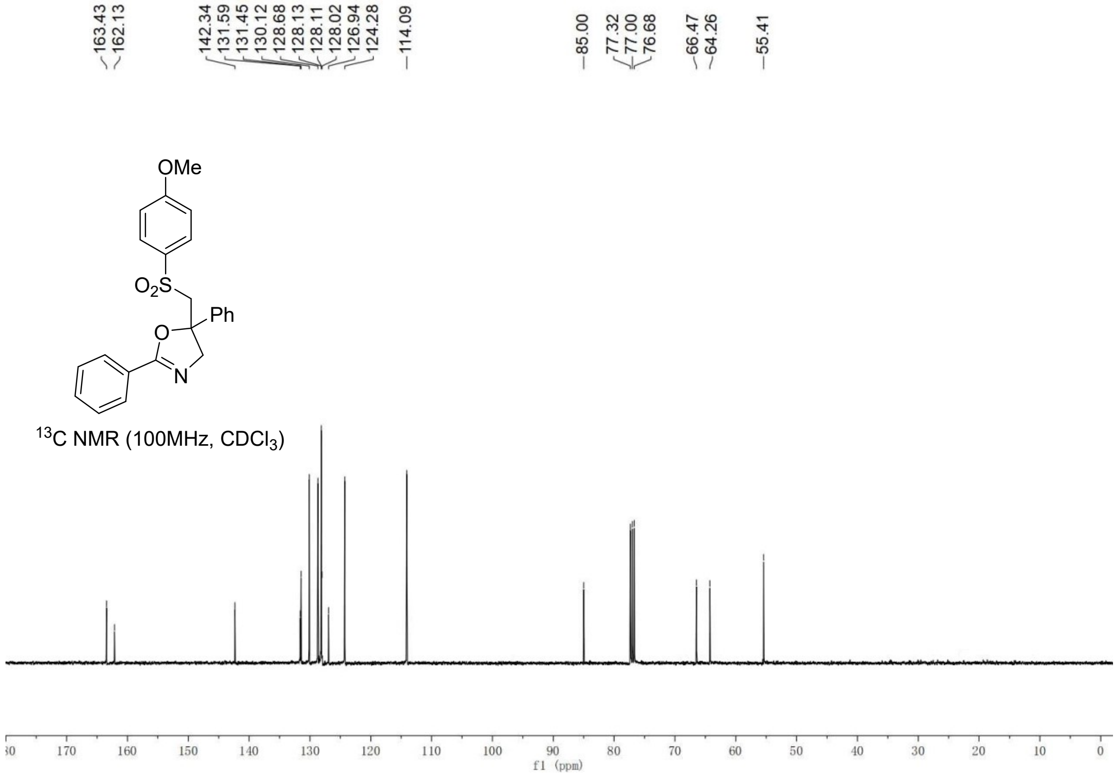
[13]C NMR spectrum of **3ac**



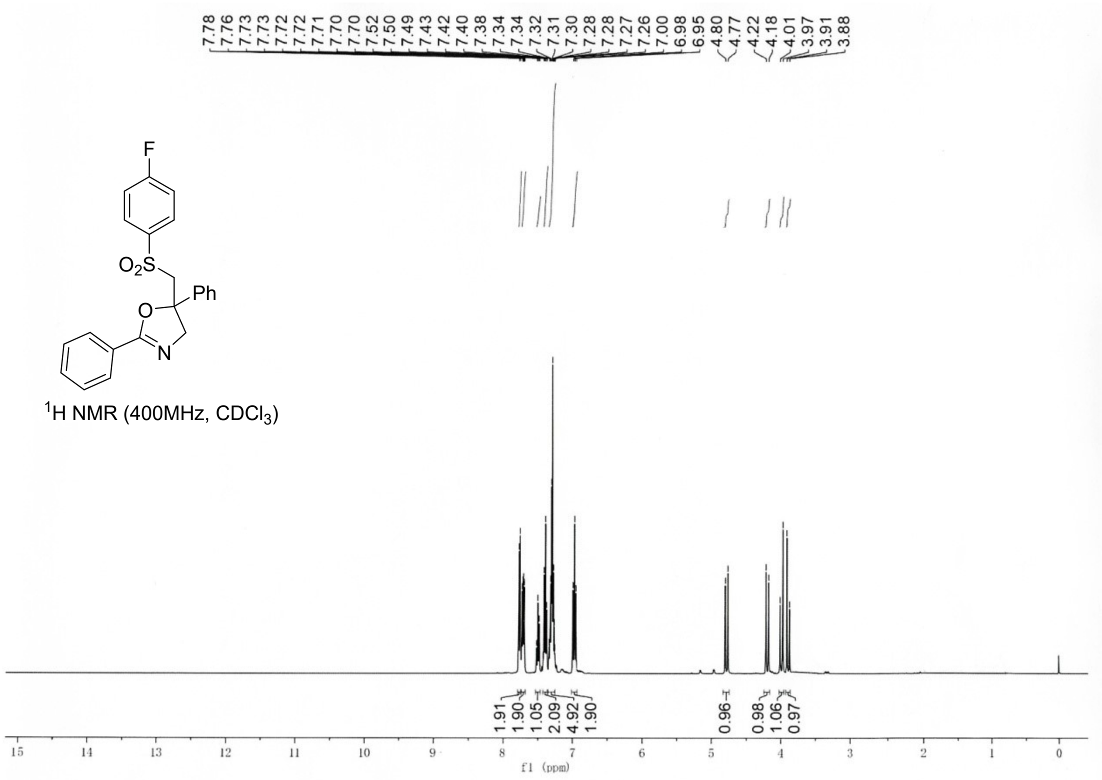
^{1}H NMR spectrum of **3ad**



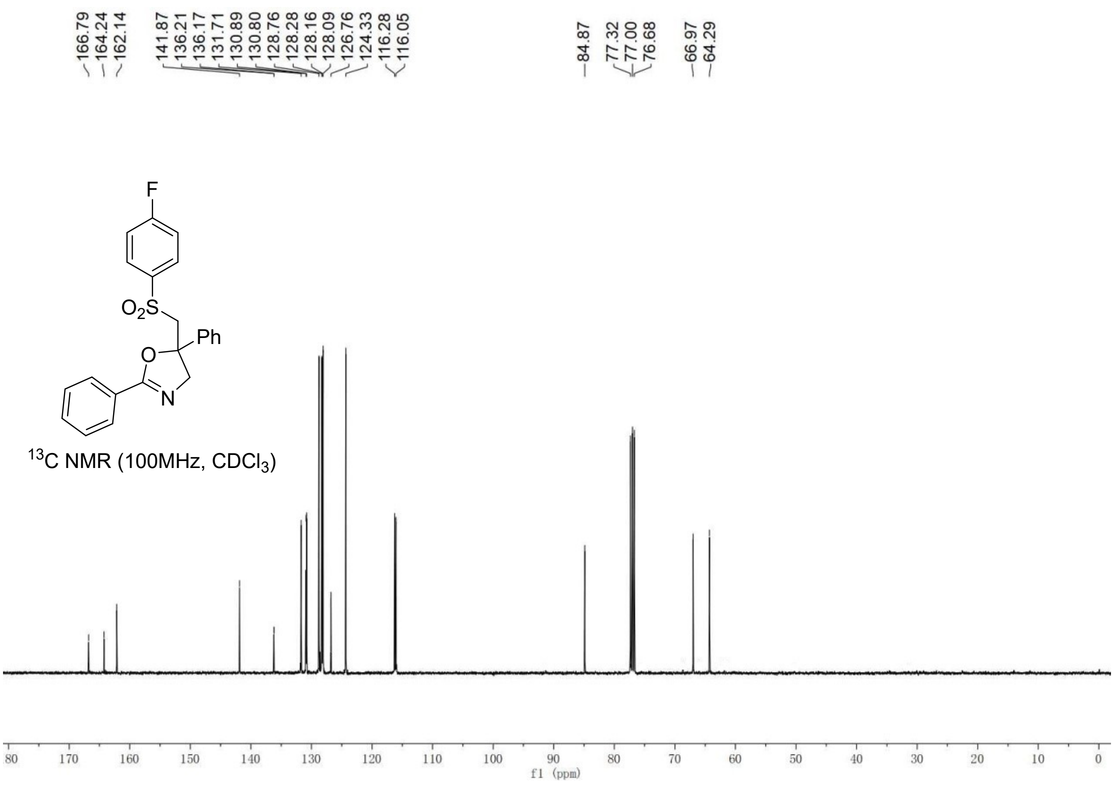
^{13}C NMR spectrum of **3ad**



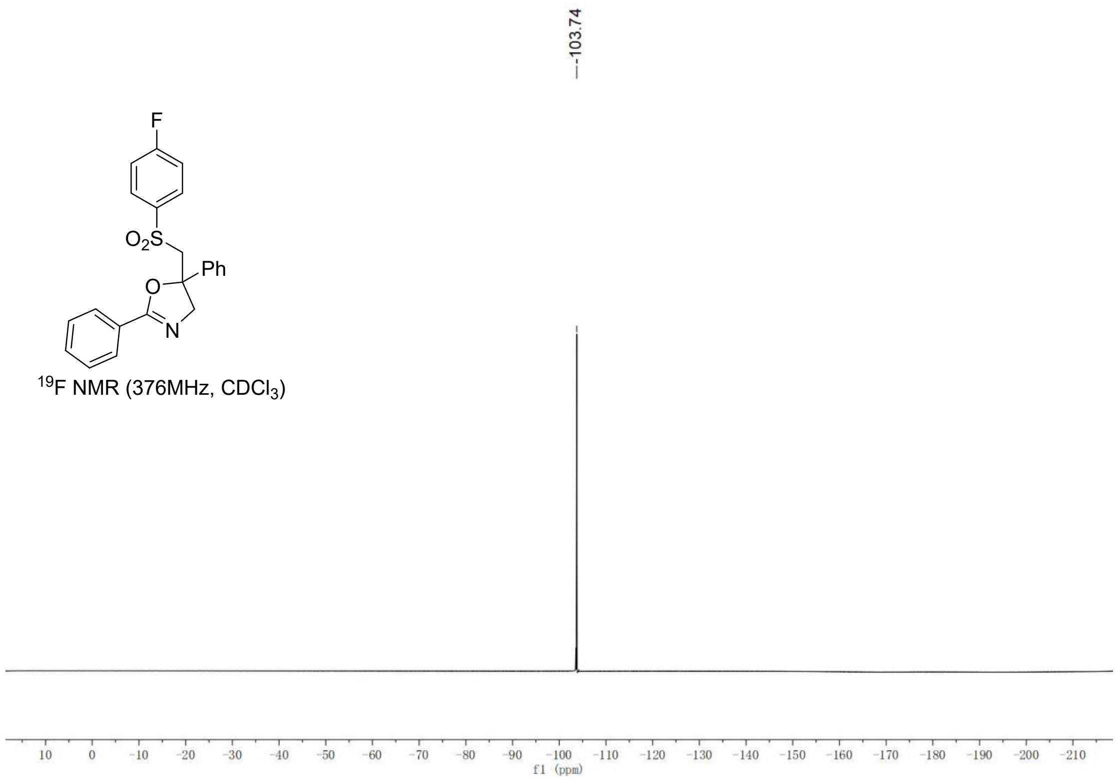
^{1}H NMR spectrum of **3ae**



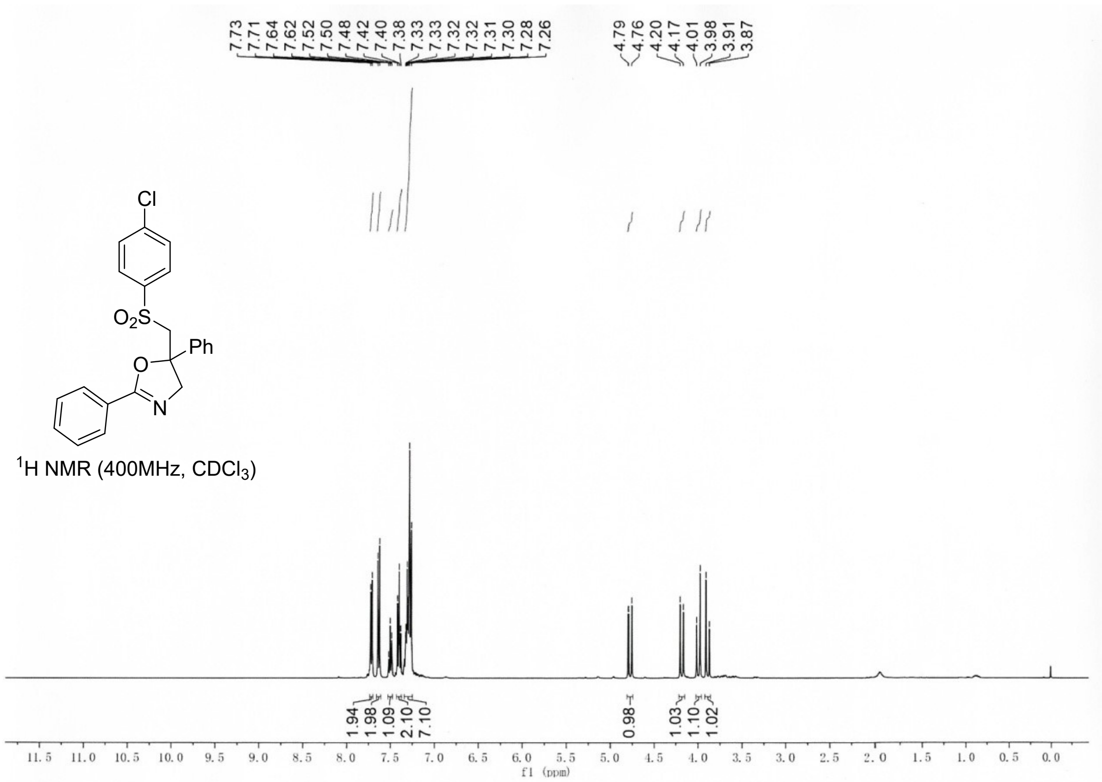
^{13}C NMR spectrum of **3ae**



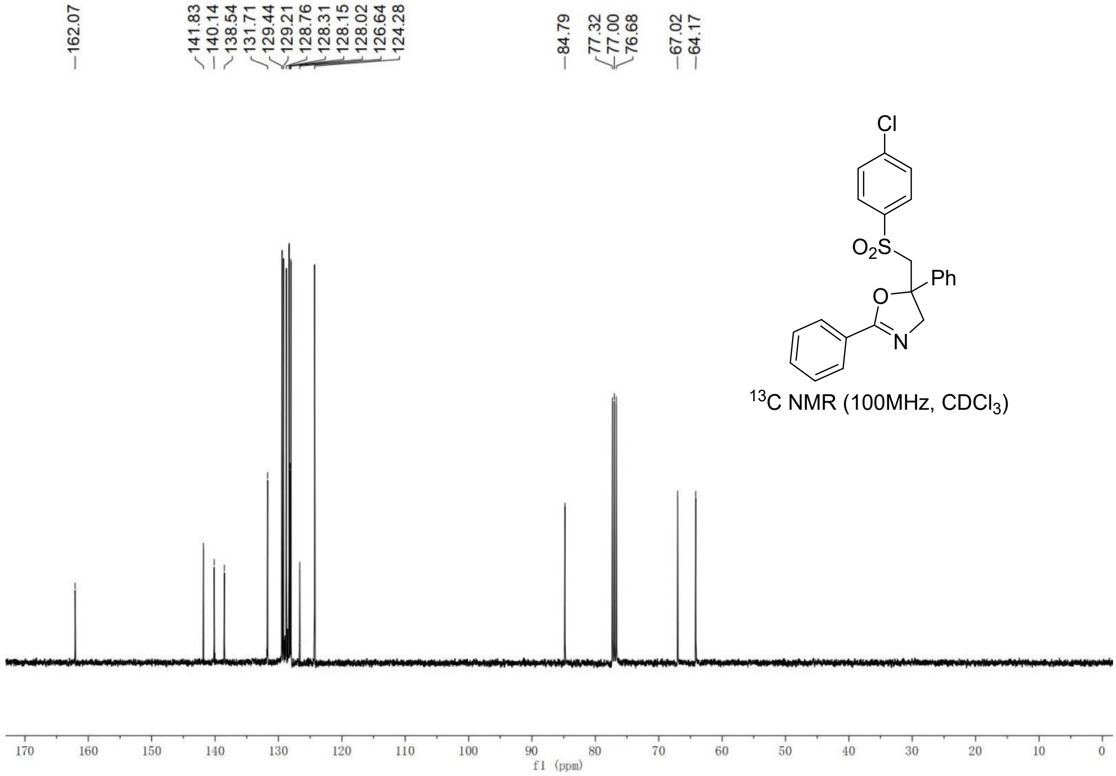
^{19}F NMR spectrum of **3ae**



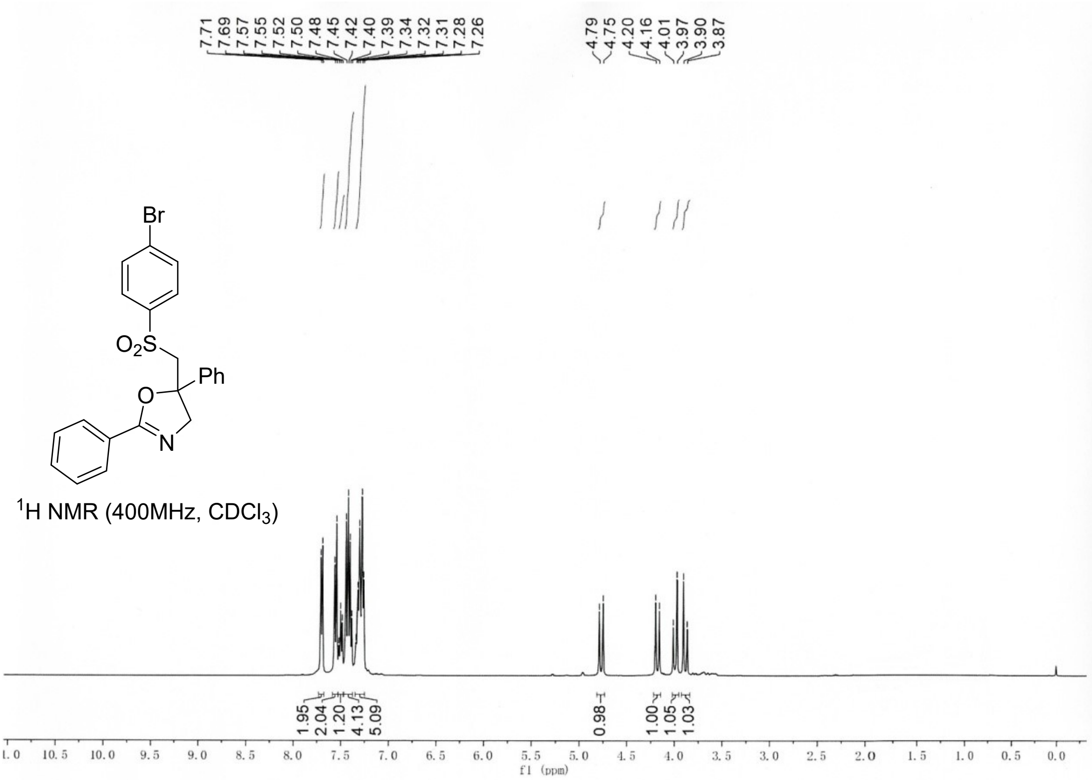
^{1}H NMR spectrum of **3af**



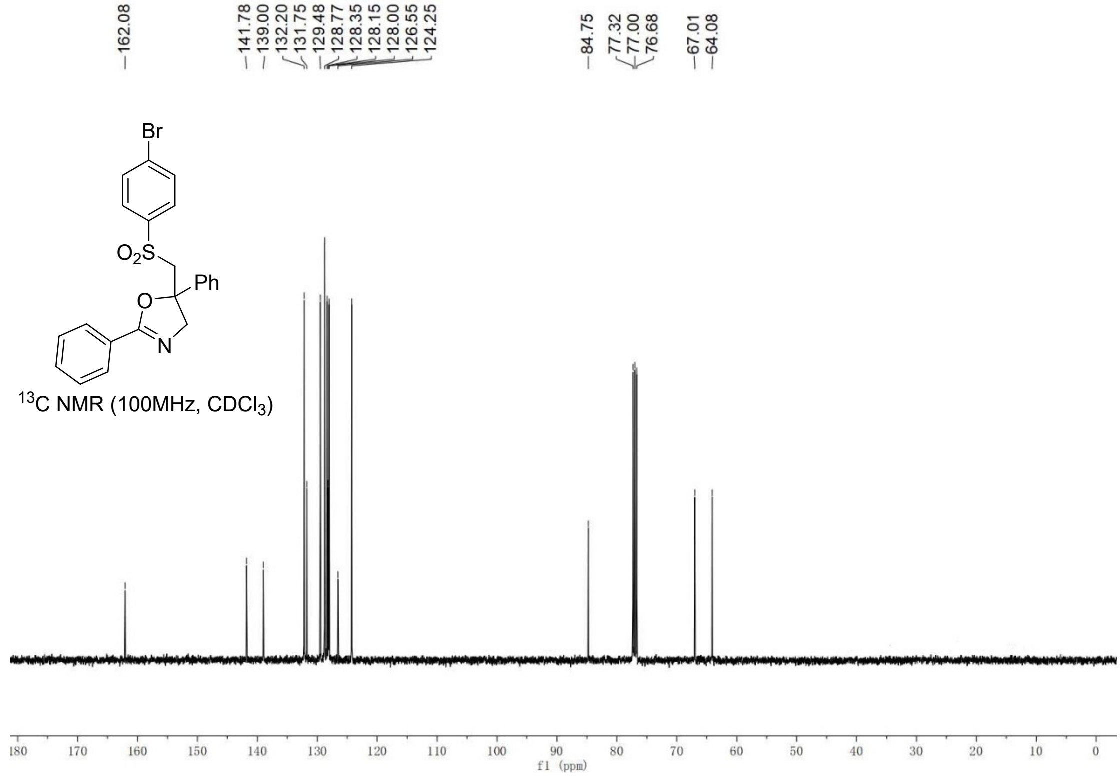
^{13}C NMR spectrum of **3af**



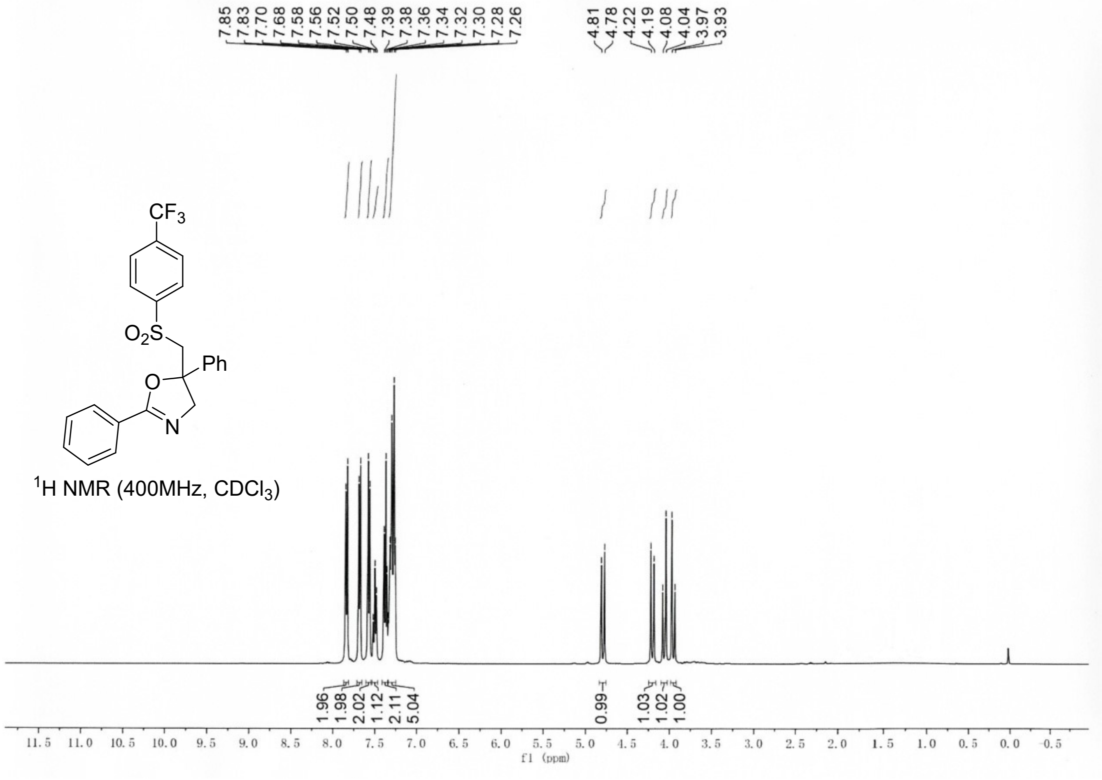
^{1}H NMR spectrum of **3ag**



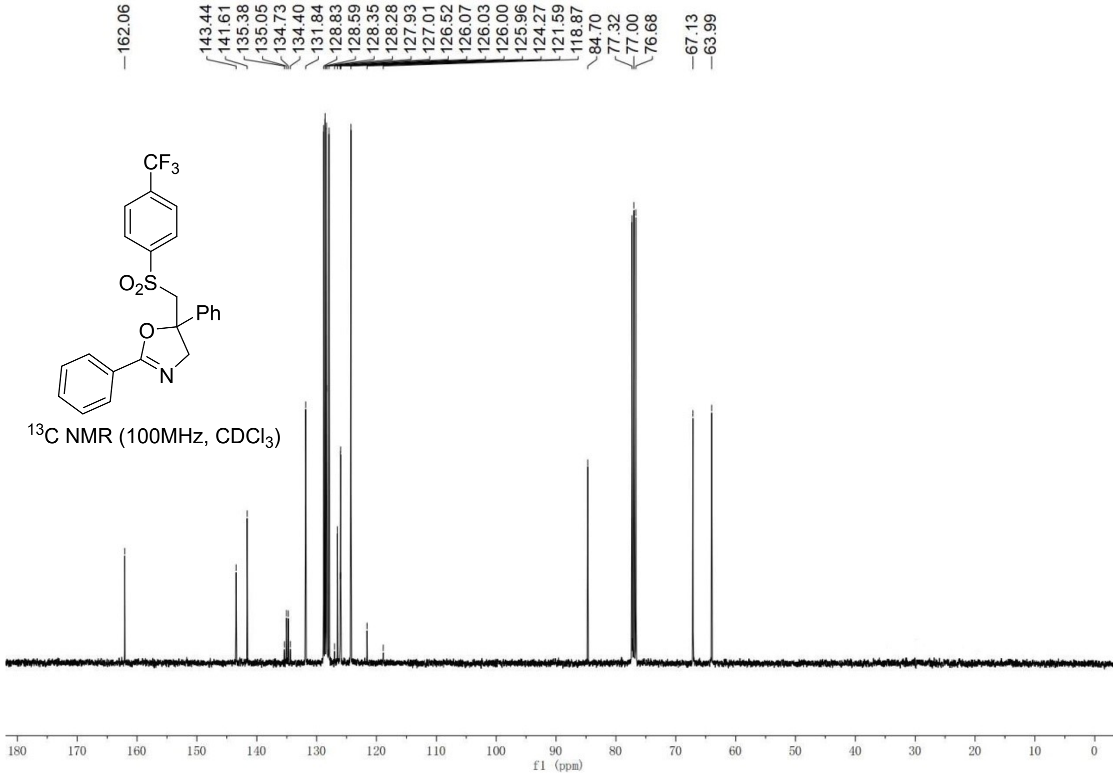
^{13}C NMR spectrum of **3ag**



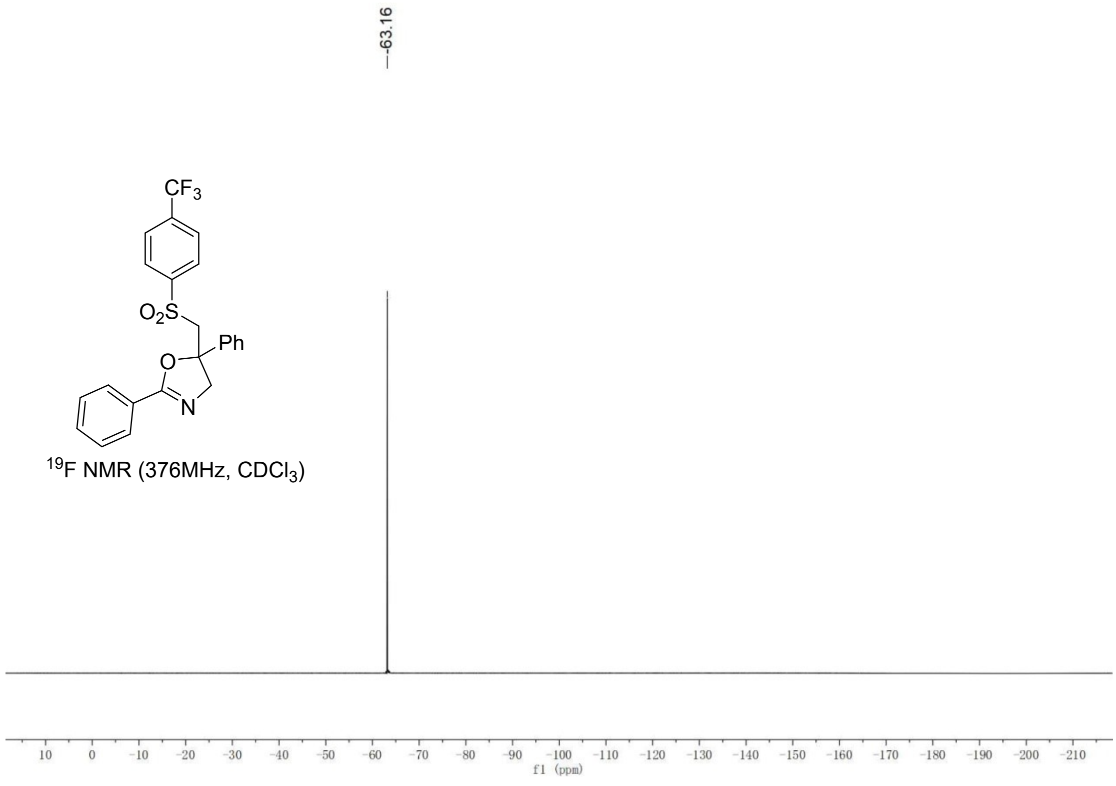
^{1}H NMR spectrum of **3ah**



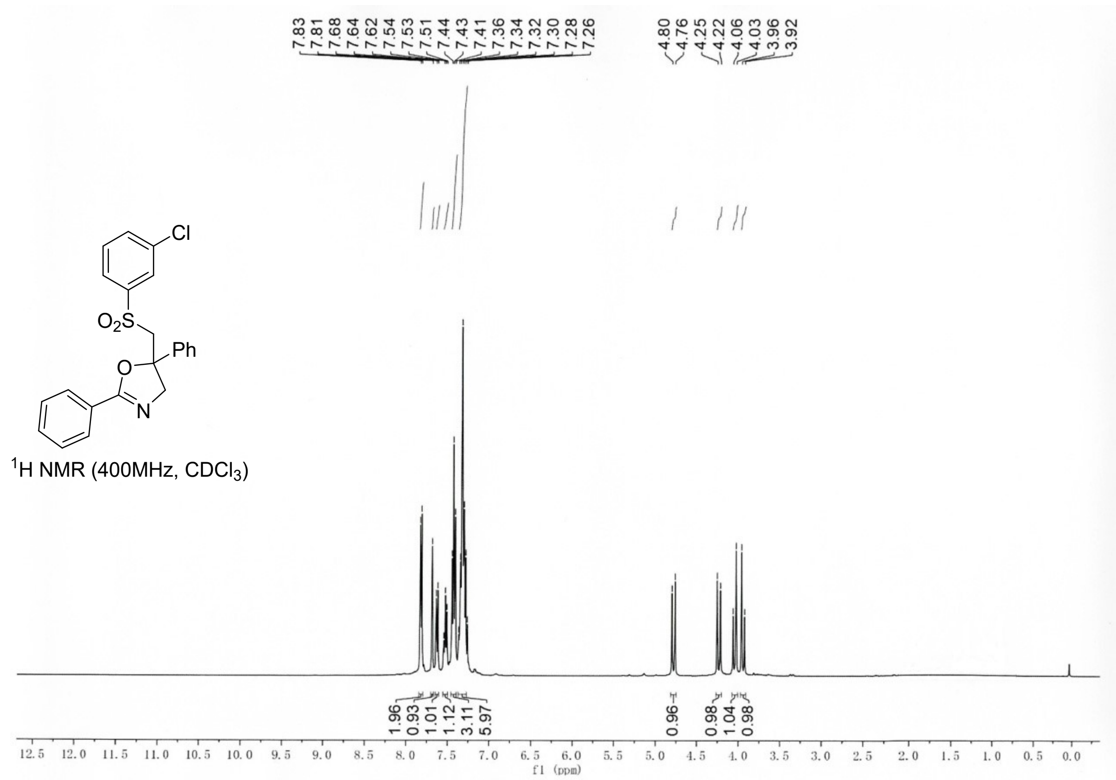
^{13}C NMR spectrum of **3ah**



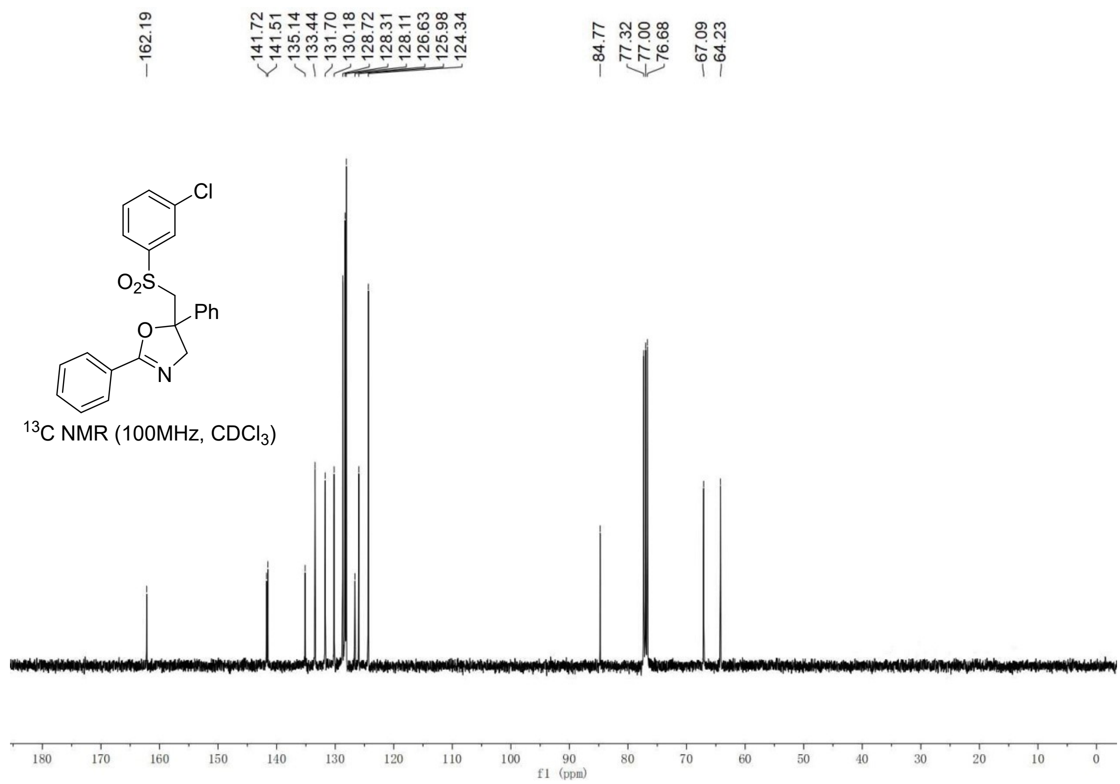
^{19}F NMR spectrum of **3ah**



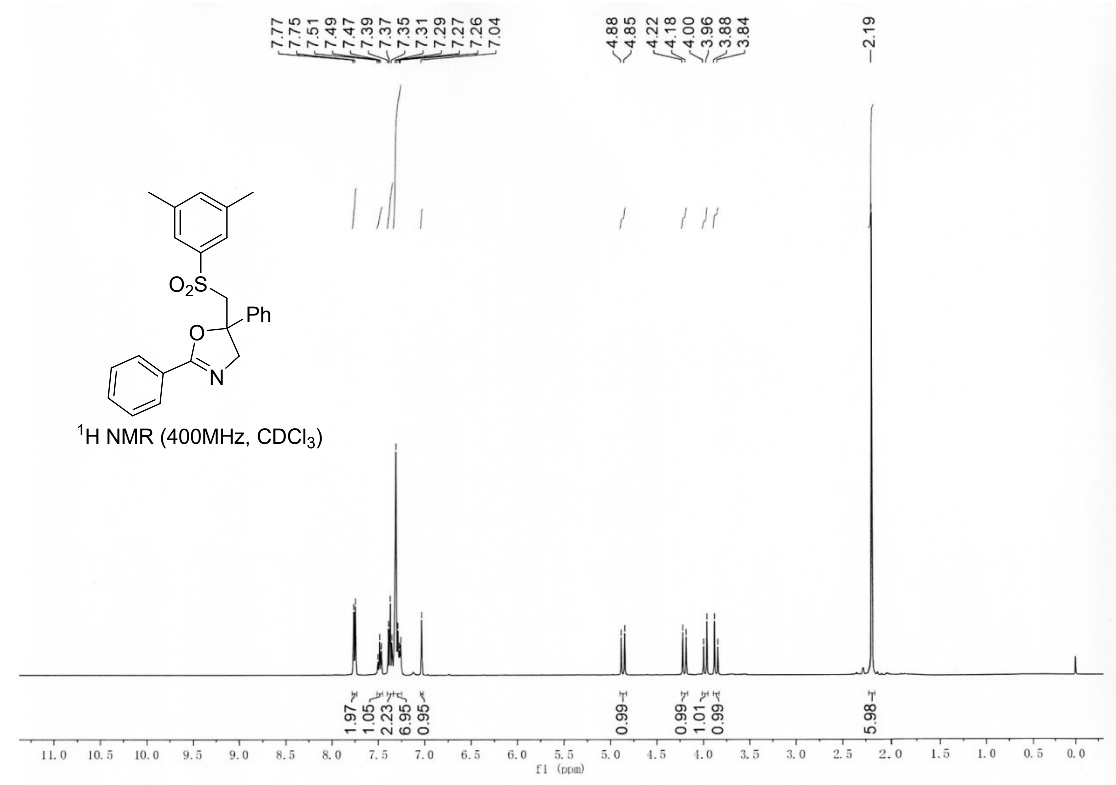
[1]H NMR spectrum of **3ai**



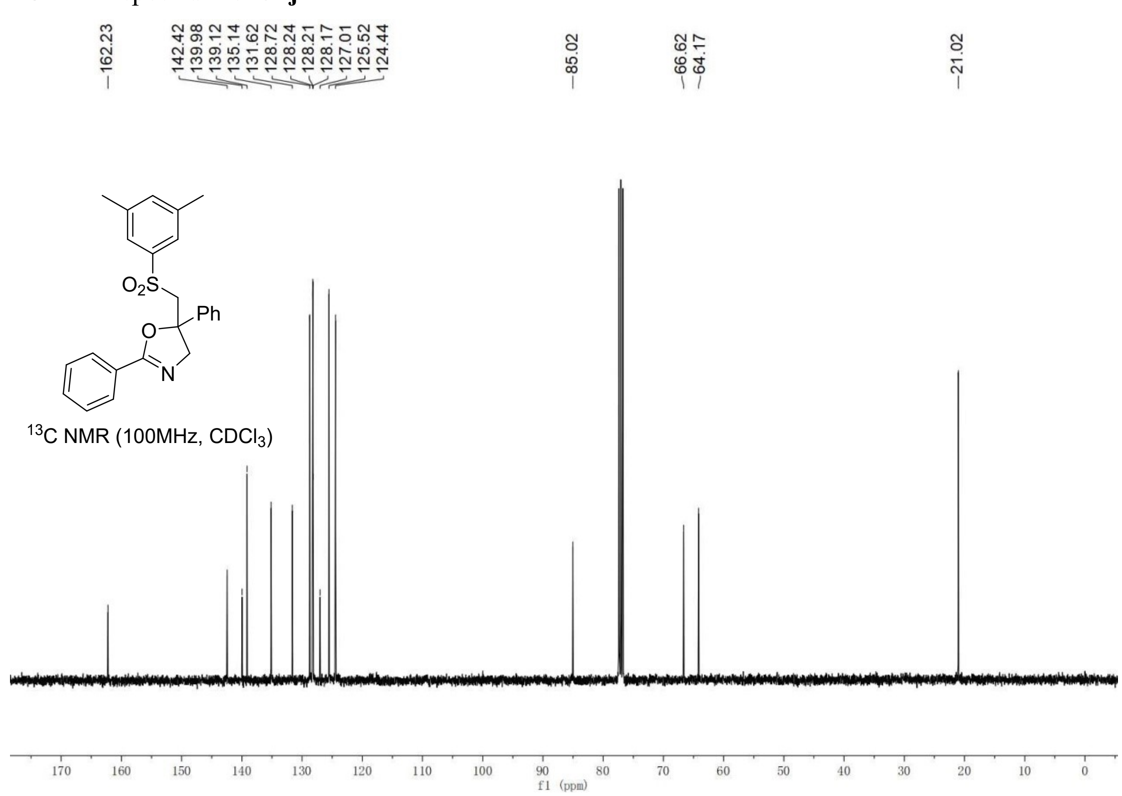
[13]C NMR spectrum of **3ai**



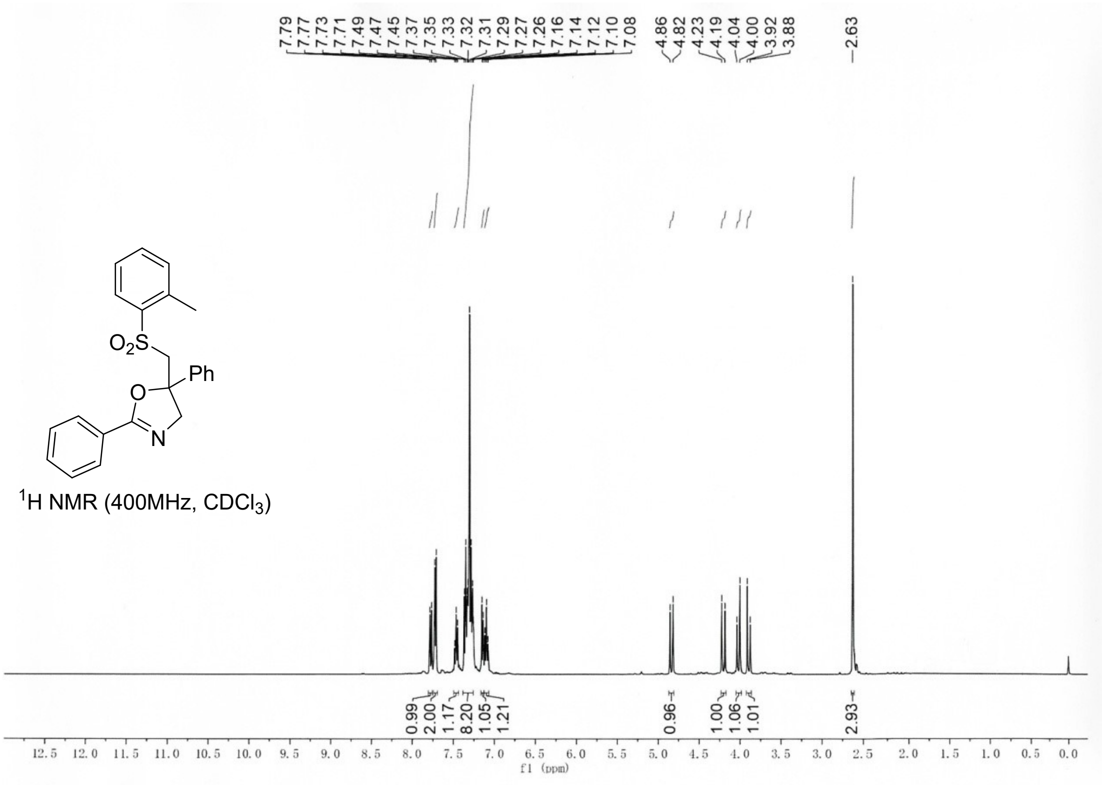
[1]H NMR spectrum of **3aj**



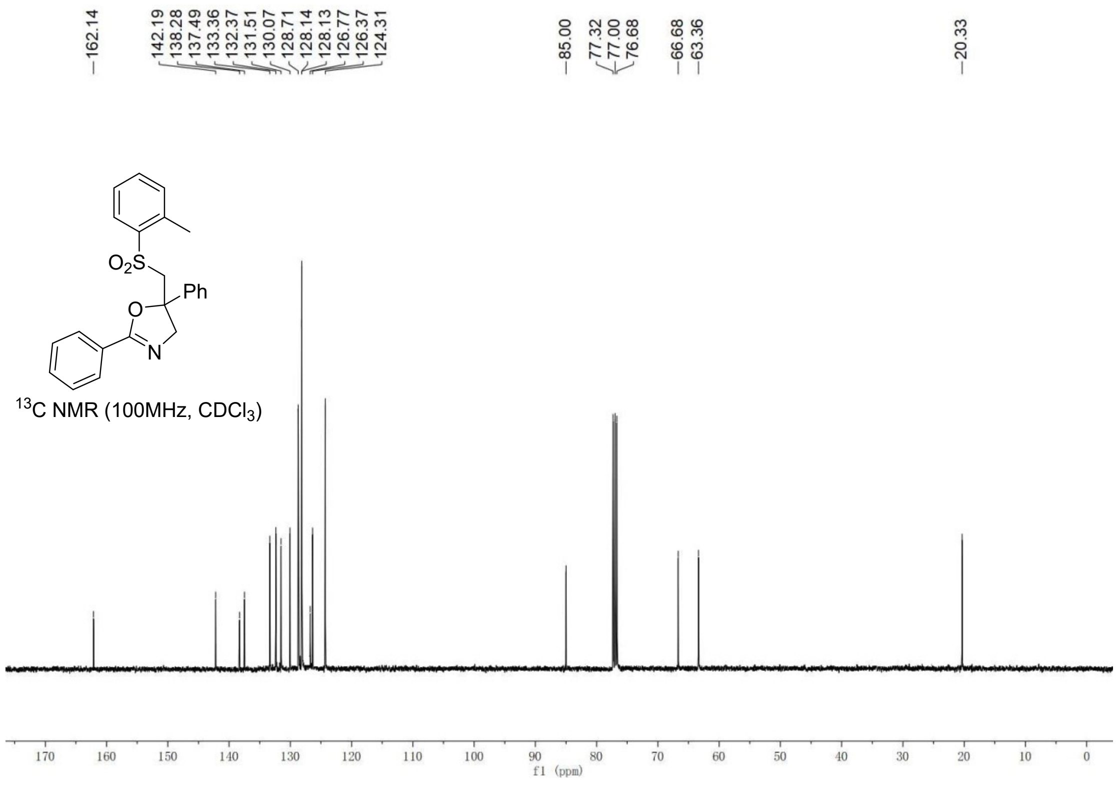
[13]C NMR spectrum of **3aj**



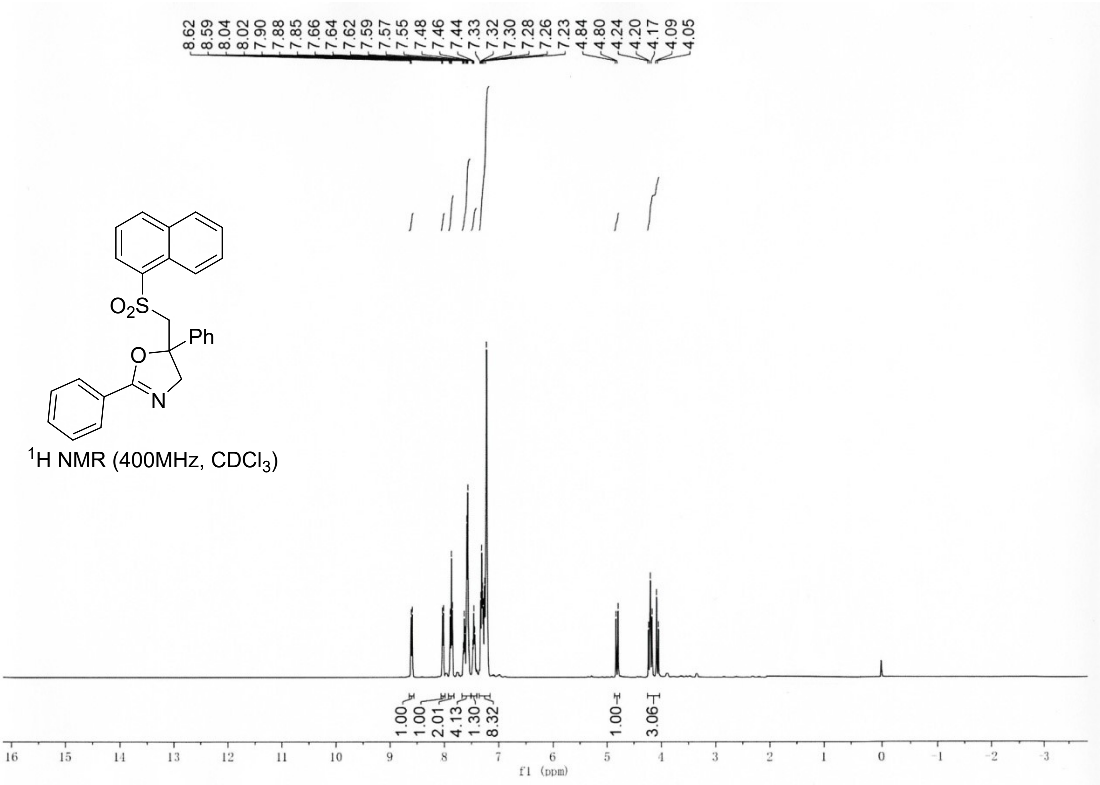
^{1}H NMR spectrum of **3ak**



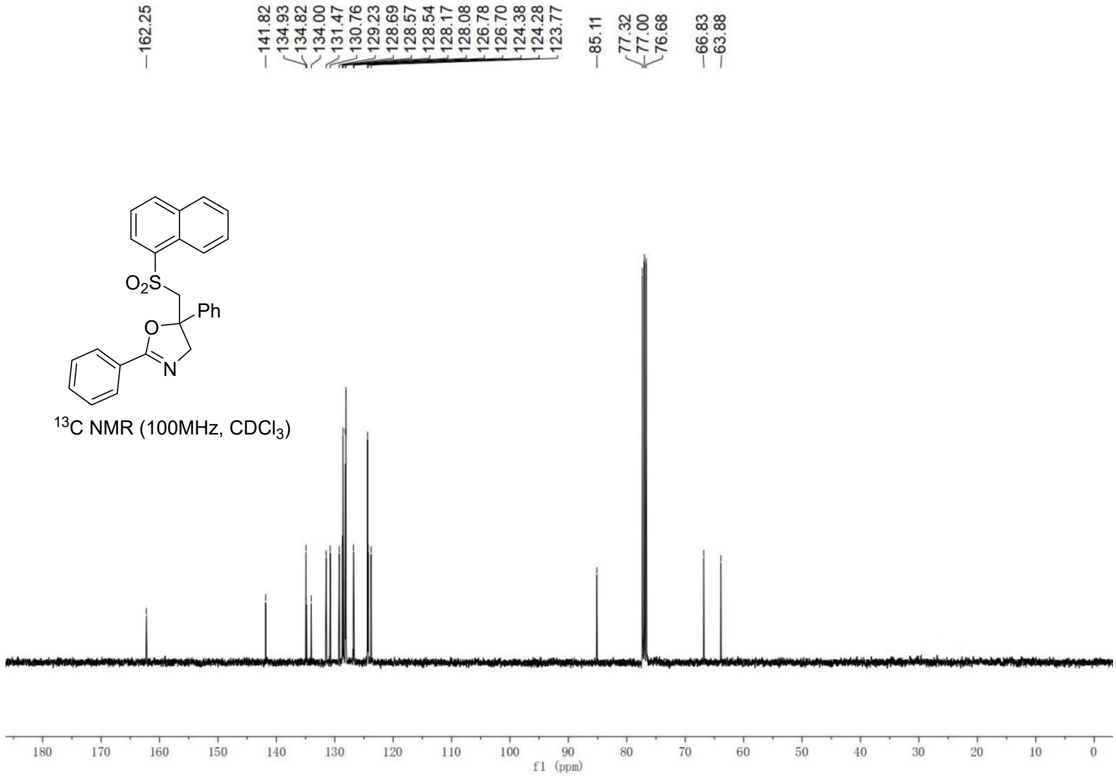
^{13}C NMR spectrum of **3ak**



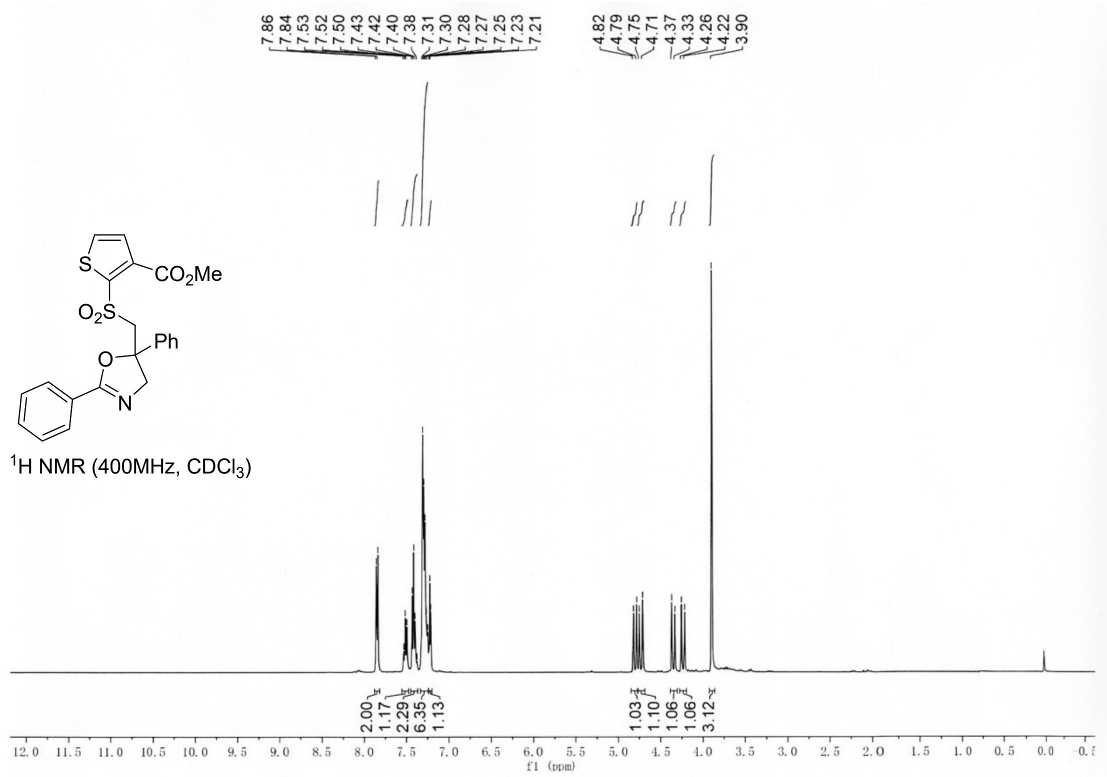
^{1}H NMR spectrum of **3al**



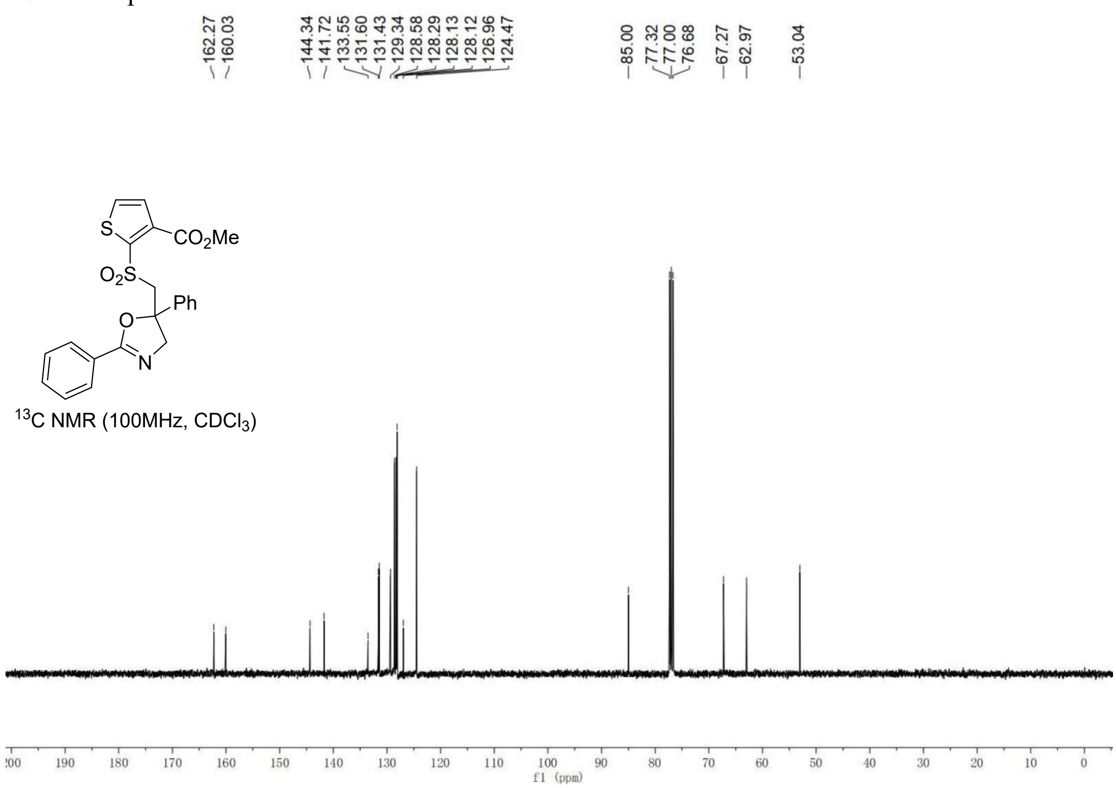
^{13}C NMR spectrum of **3al**



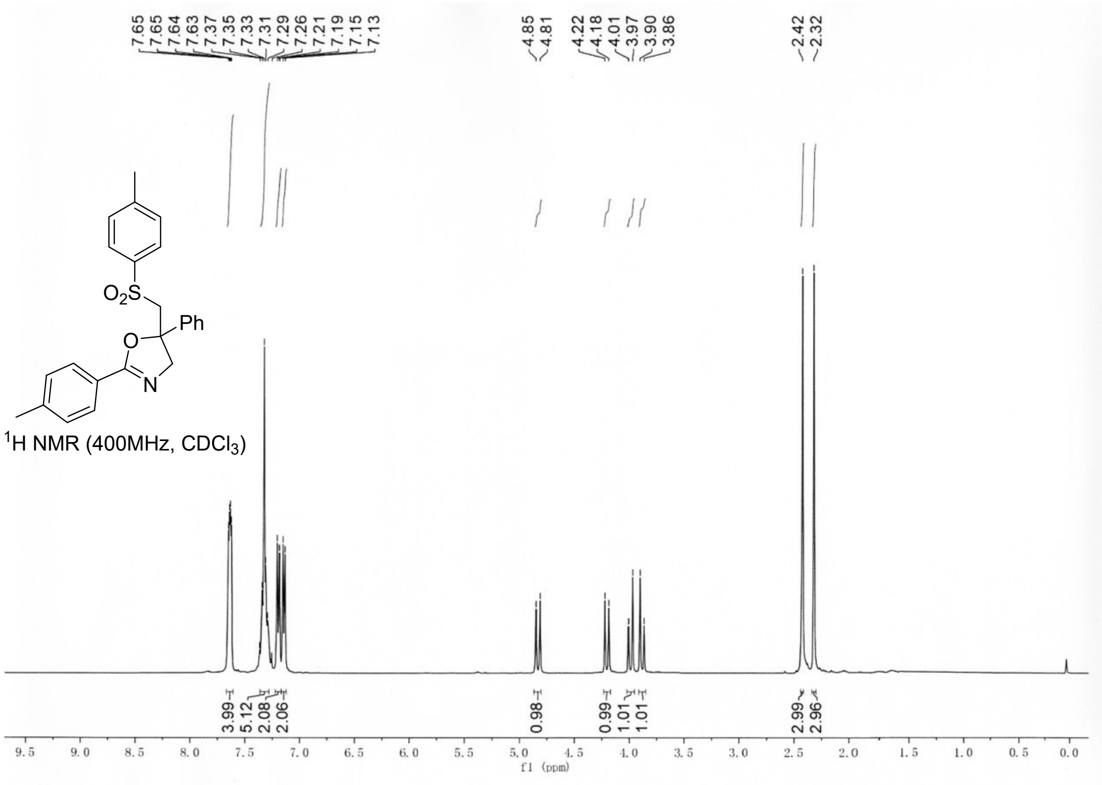
^{1}H NMR spectrum of **3am**



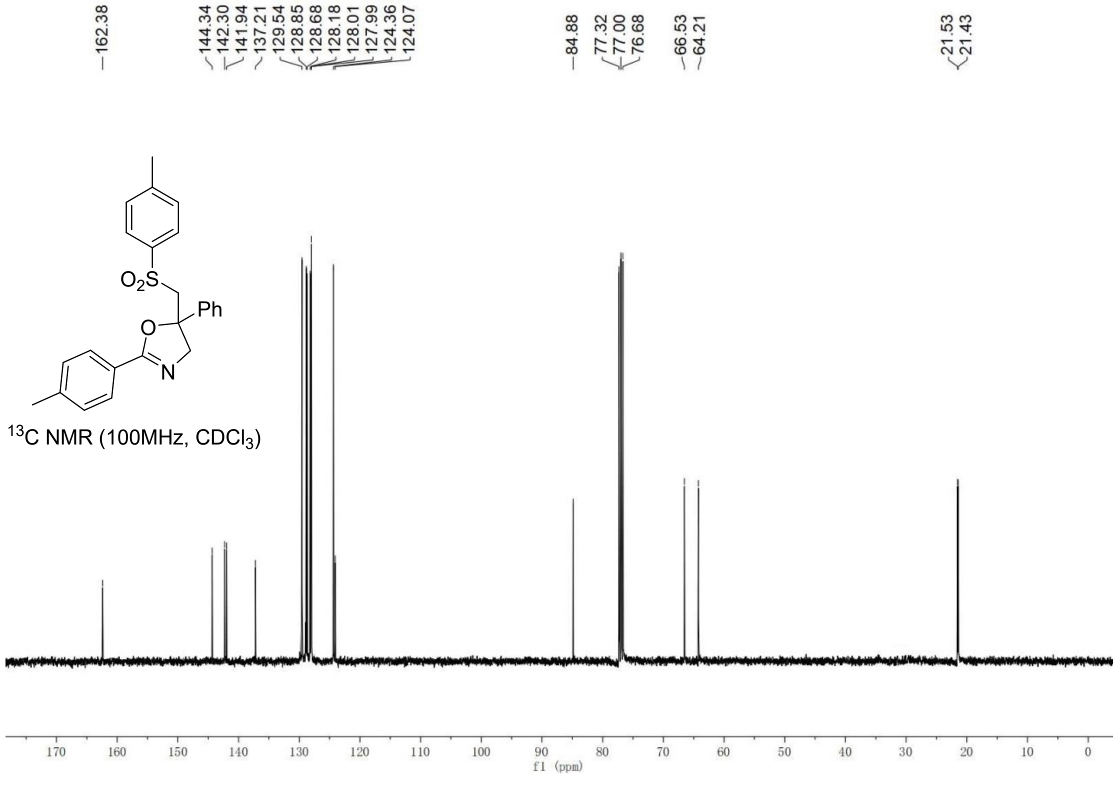
^{13}C NMR spectrum of **3am**



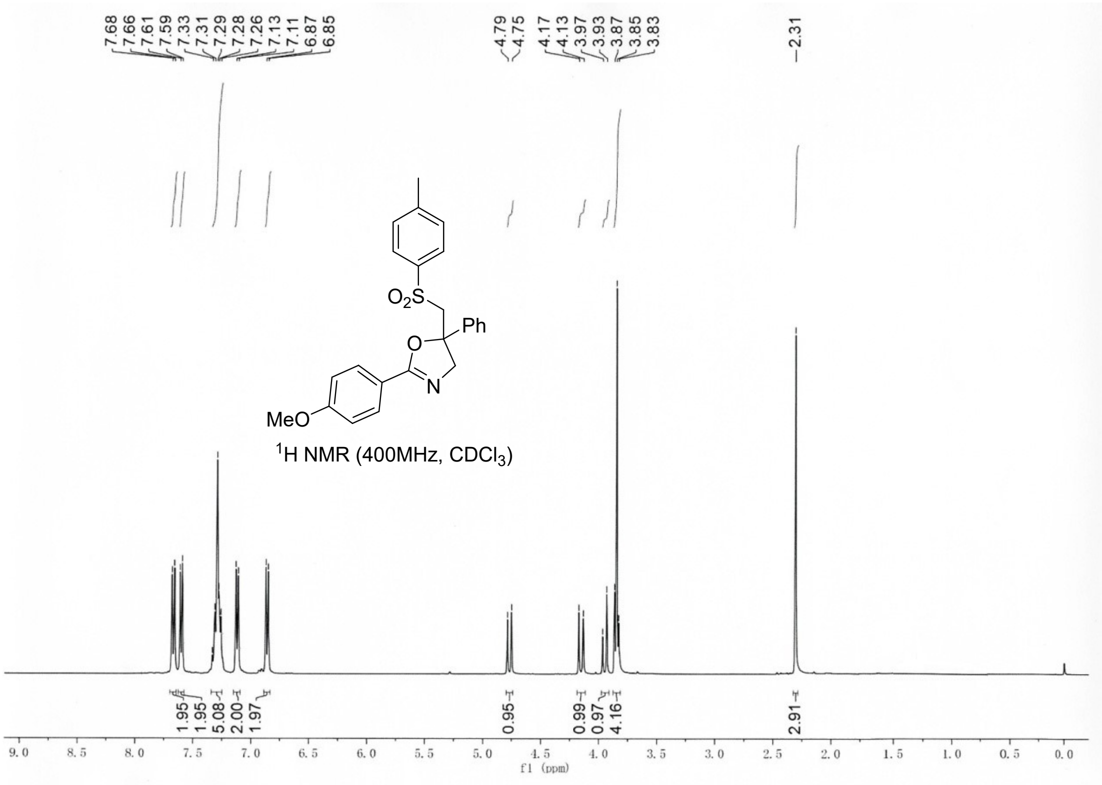
^{1}H NMR spectrum of **3ba**



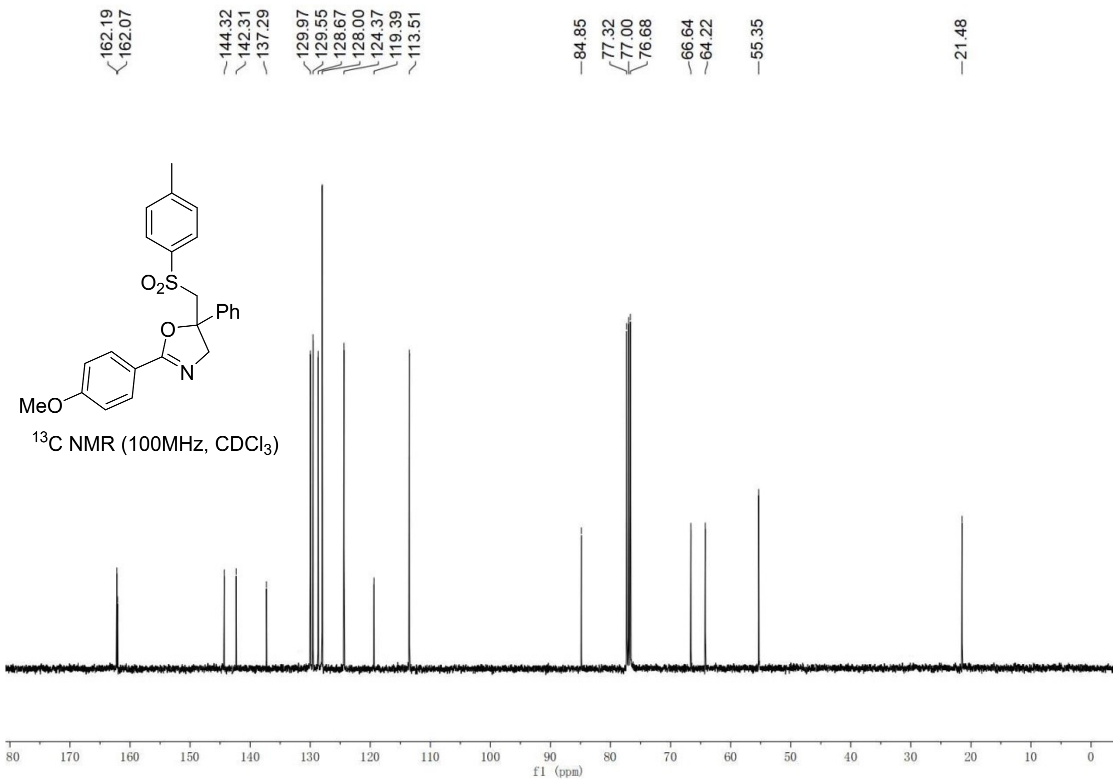
^{13}C NMR spectrum of **3ba**



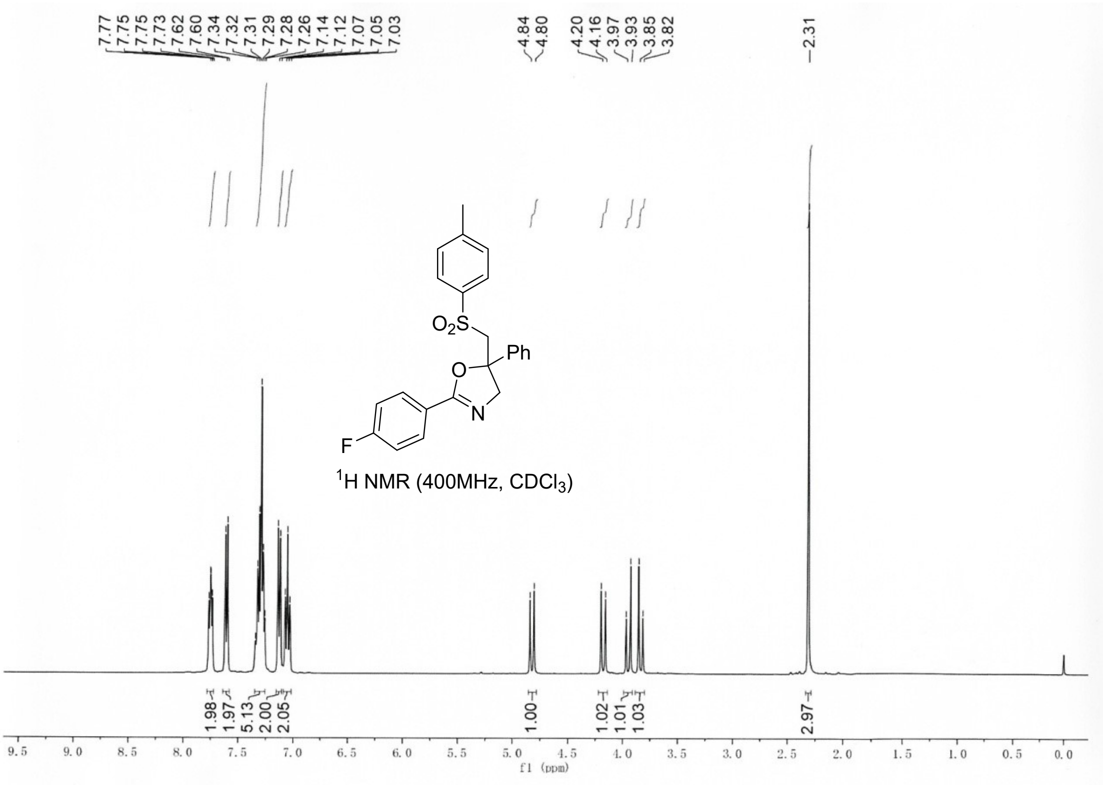
^{1}H NMR spectrum of **3ca**



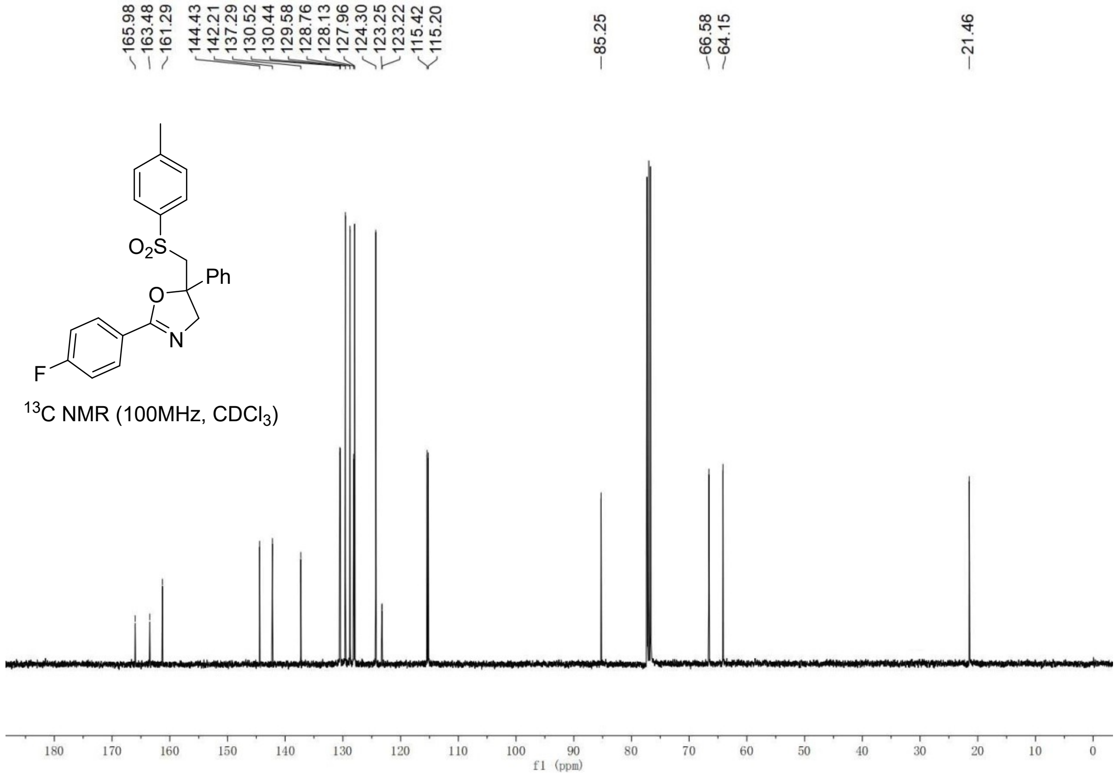
^{13}C NMR spectrum of **3ca**



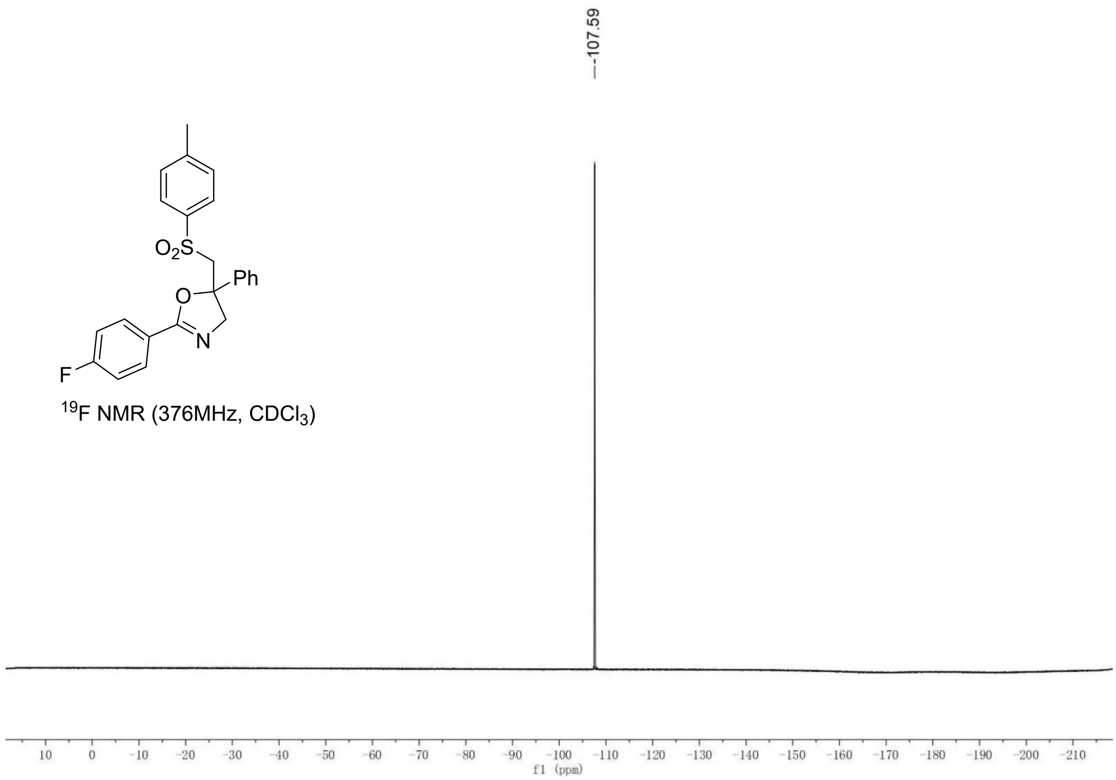
^{1}H NMR spectrum of **3da**



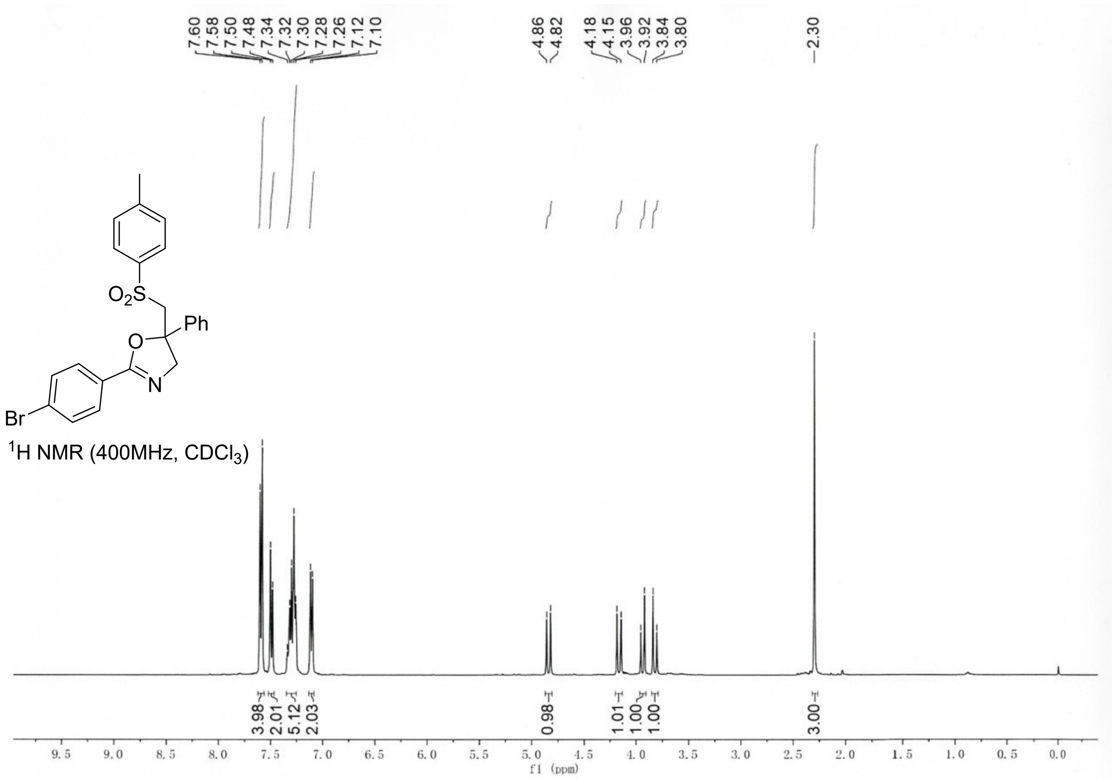
^{13}C NMR spectrum of **3da**



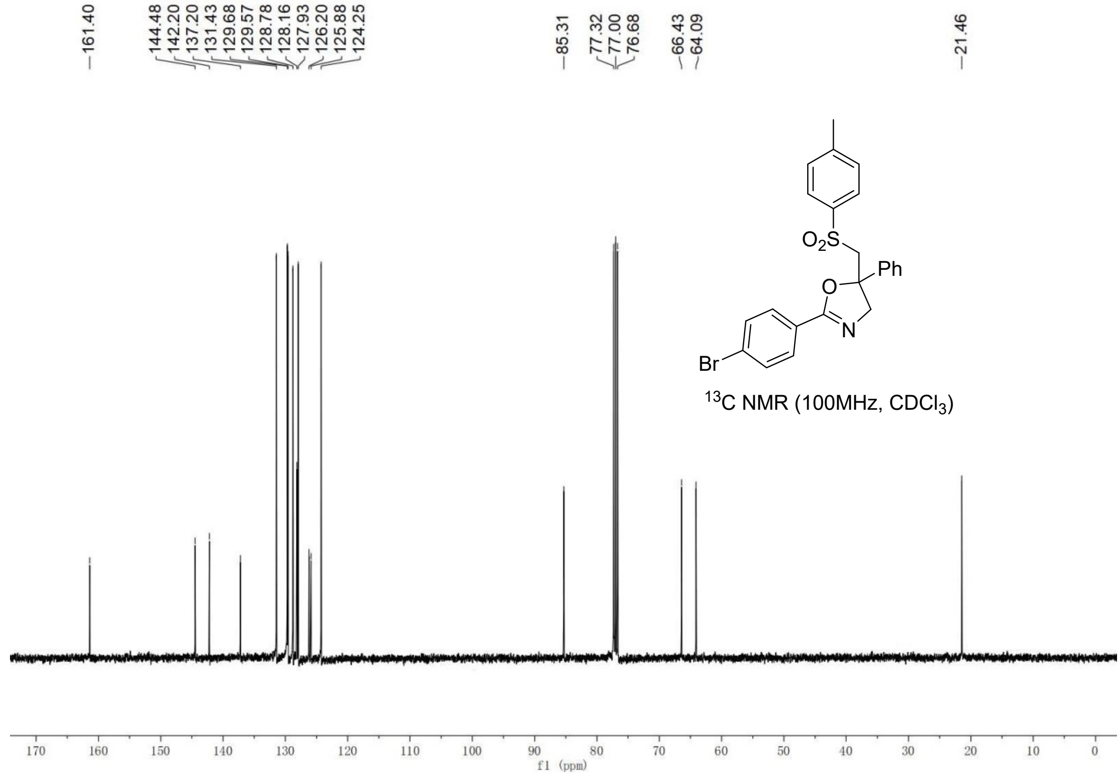
^{19}F NMR spectrum of **3da**



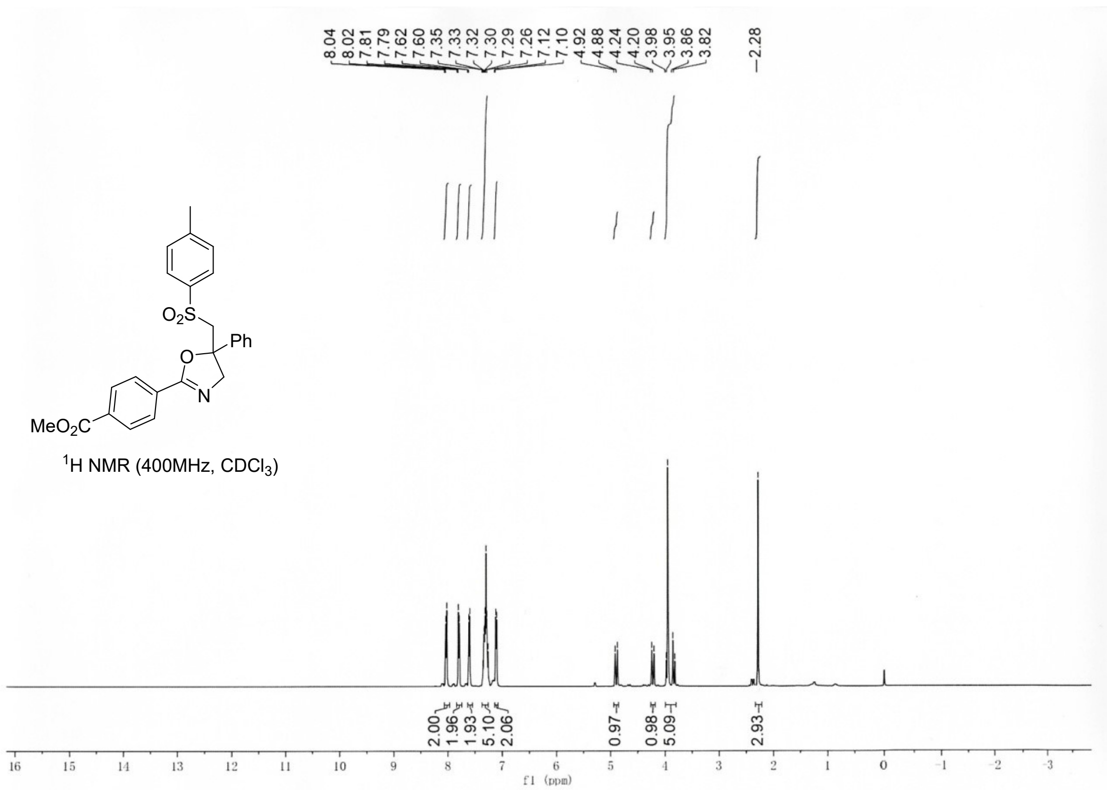
^{1}H NMR spectrum of **3ea**



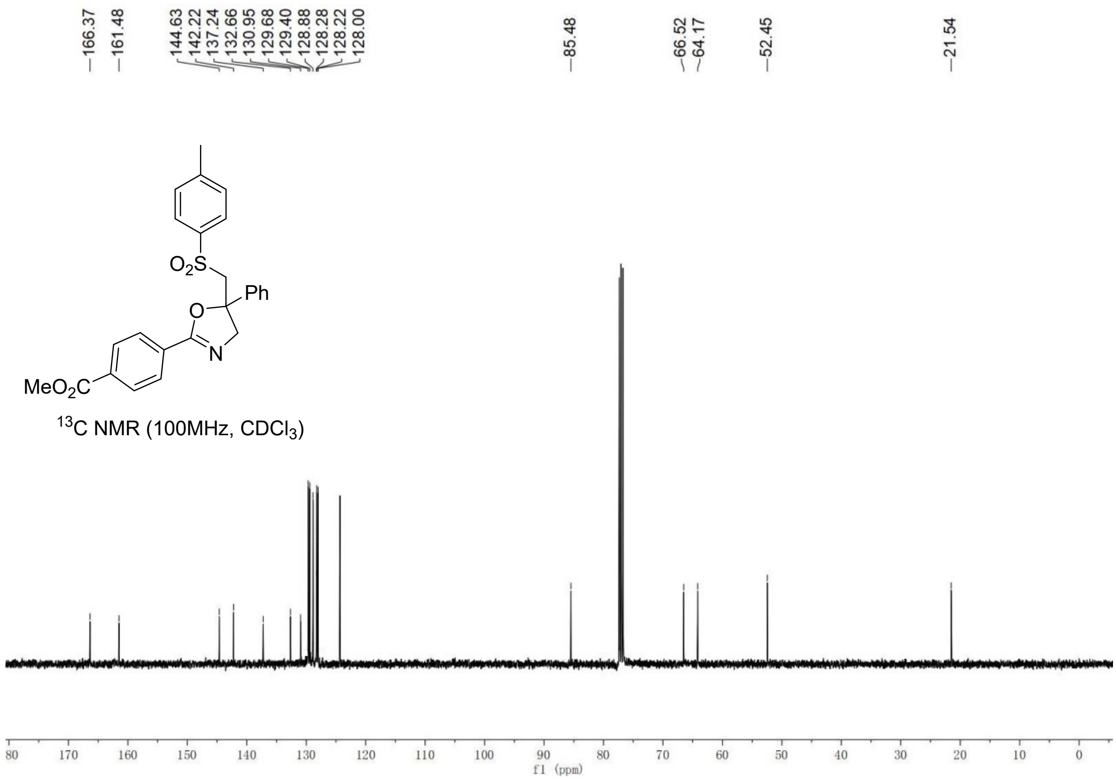
^{13}C NMR spectrum of **3ea**



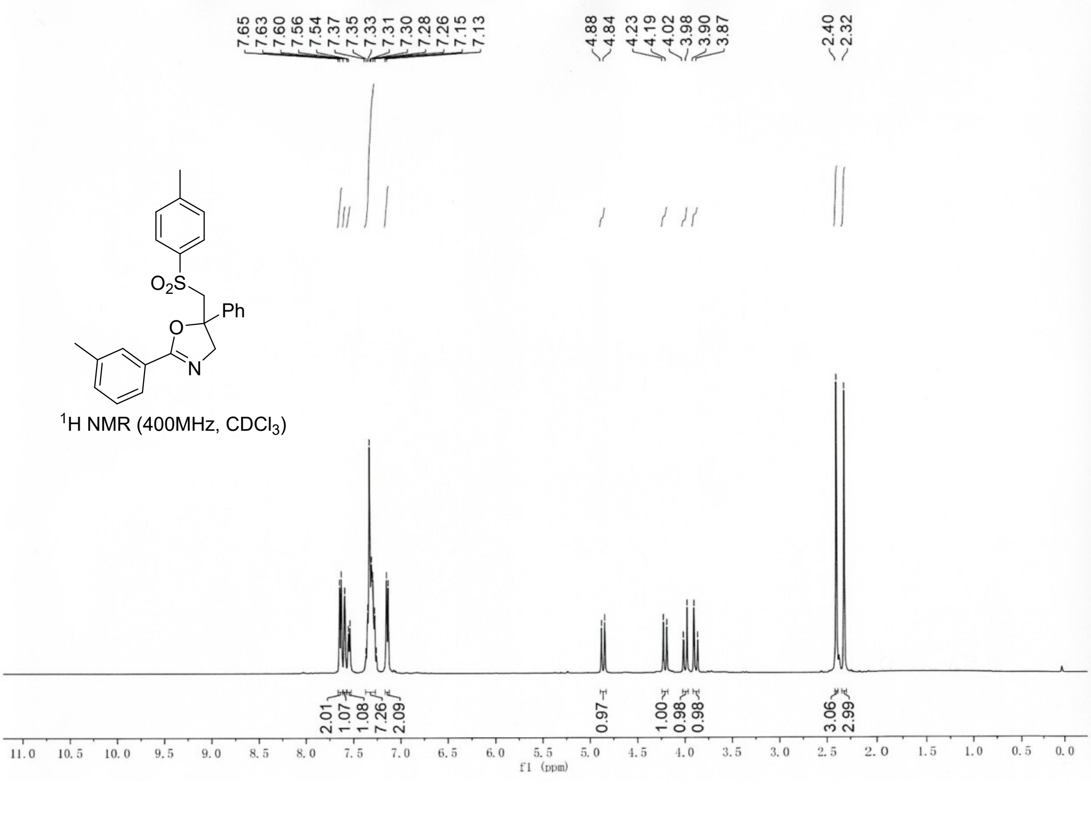
^{1}H NMR spectrum of **3fa**



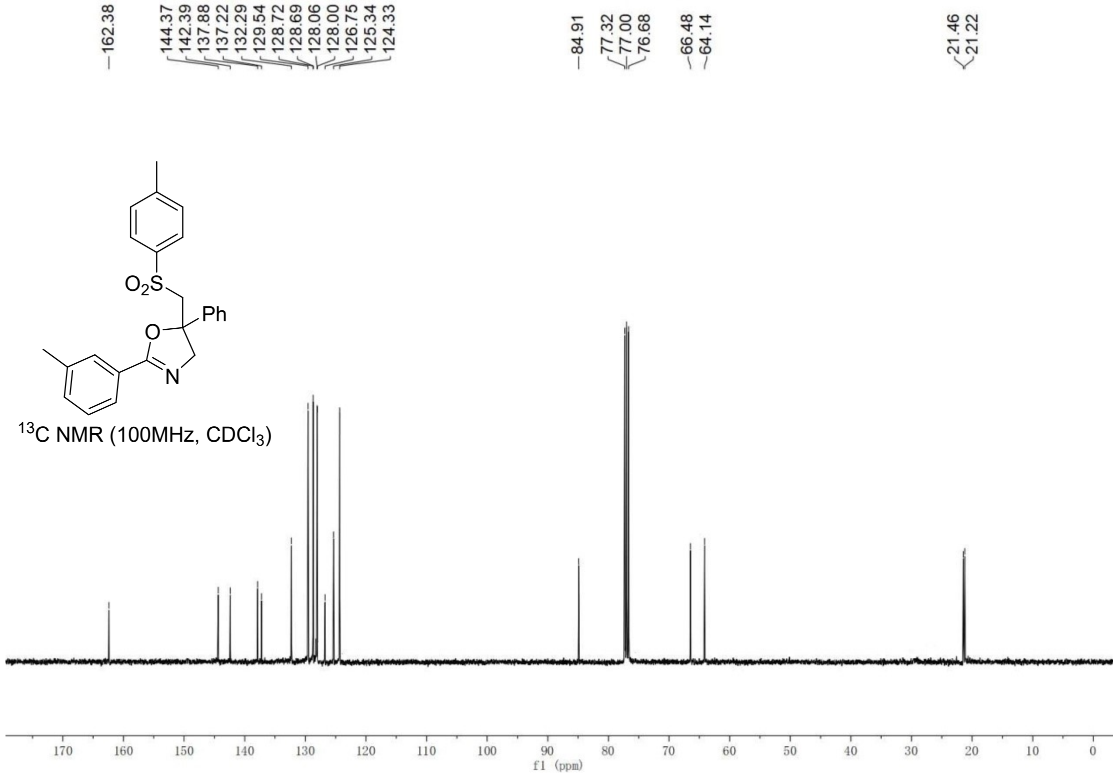
^{13}C NMR spectrum of **3fa**



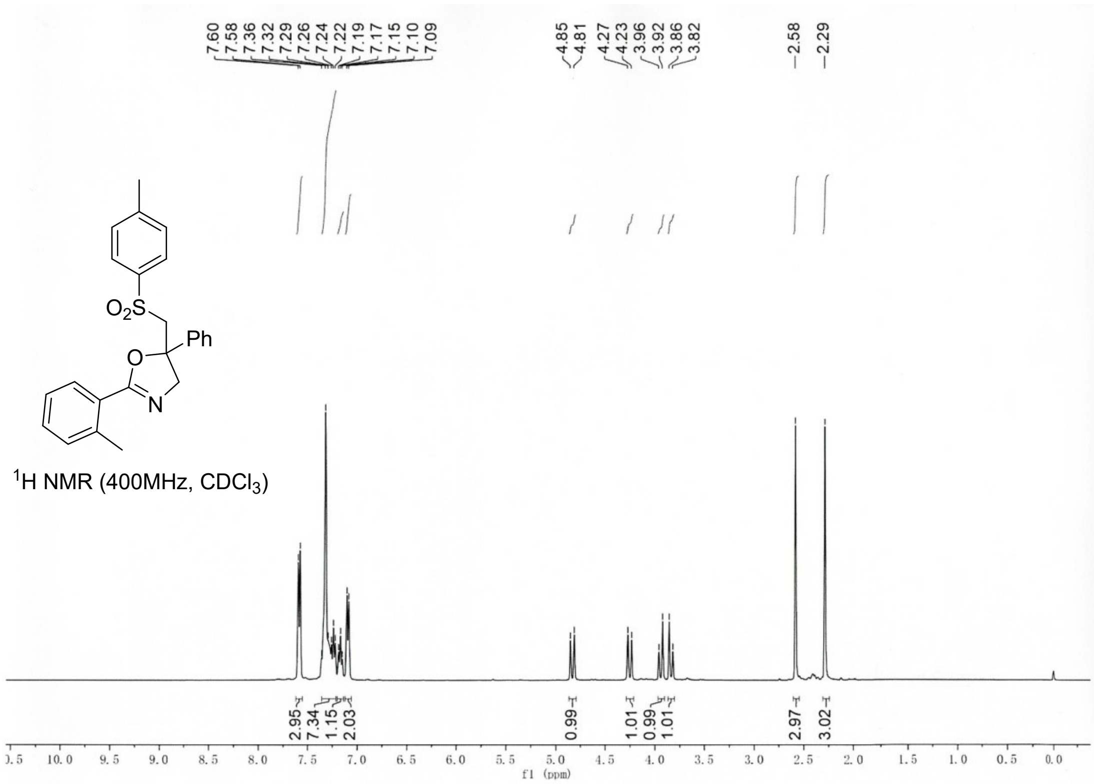
^{1}H NMR spectrum of **3ga**



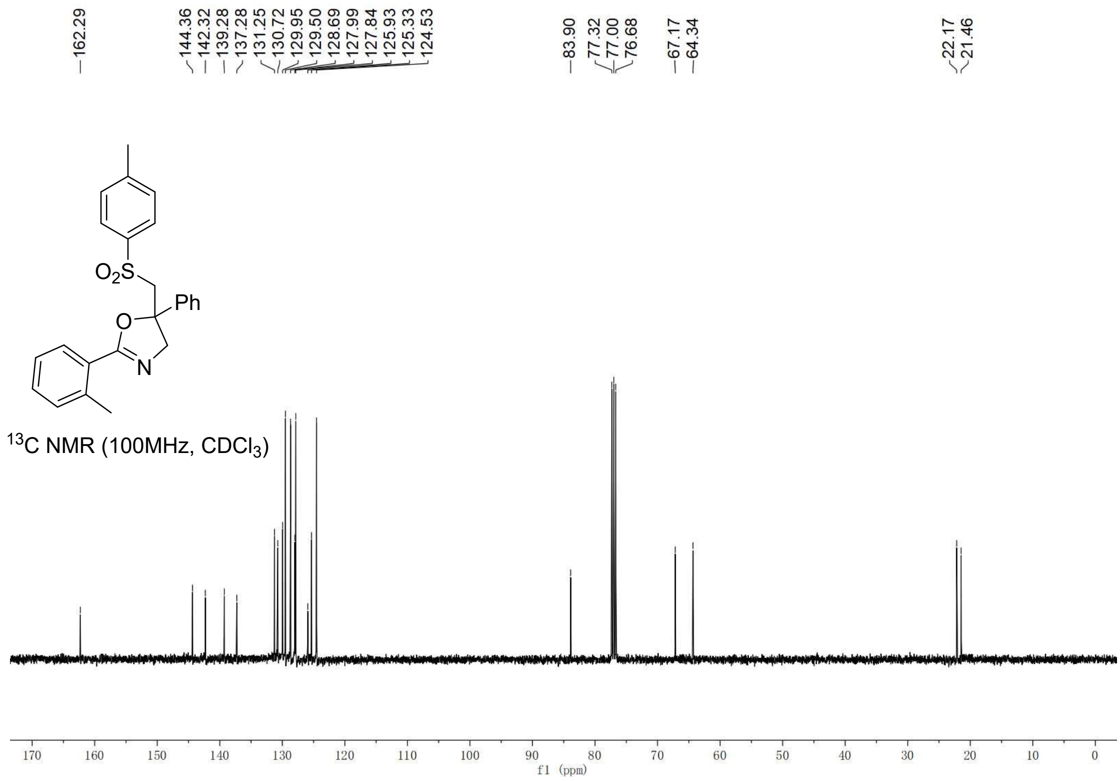
^{13}C NMR spectrum of **3ga**



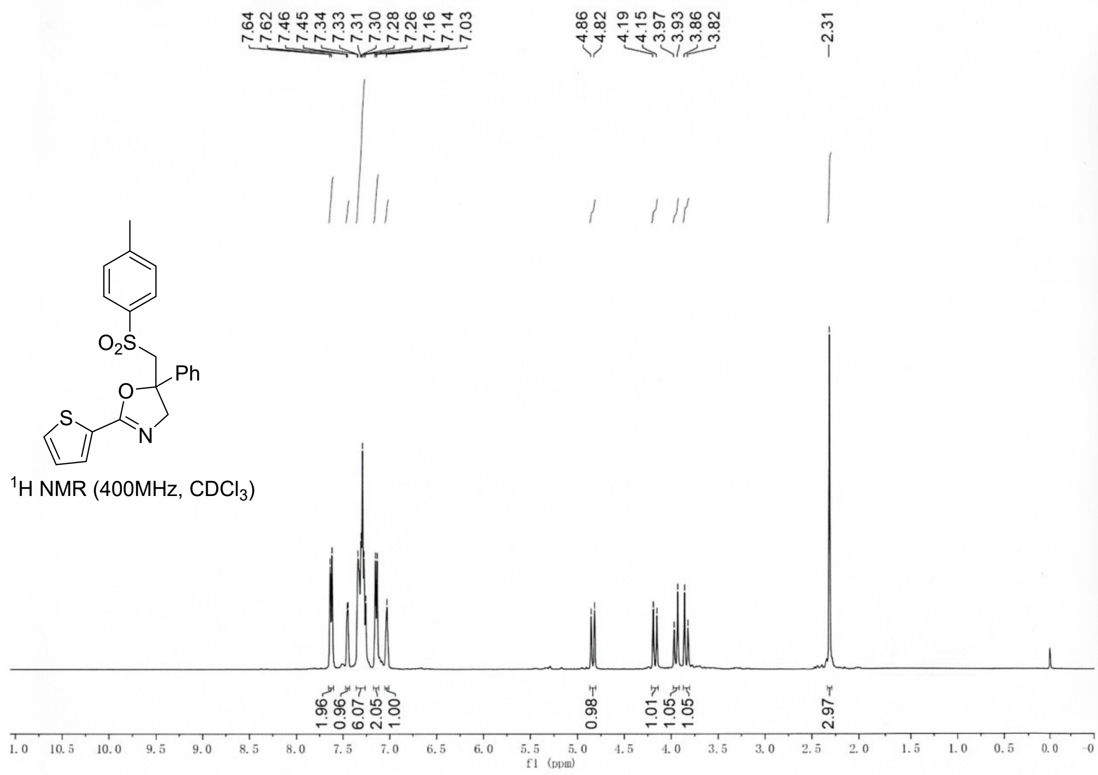
^{1}H NMR spectrum of **3ha**



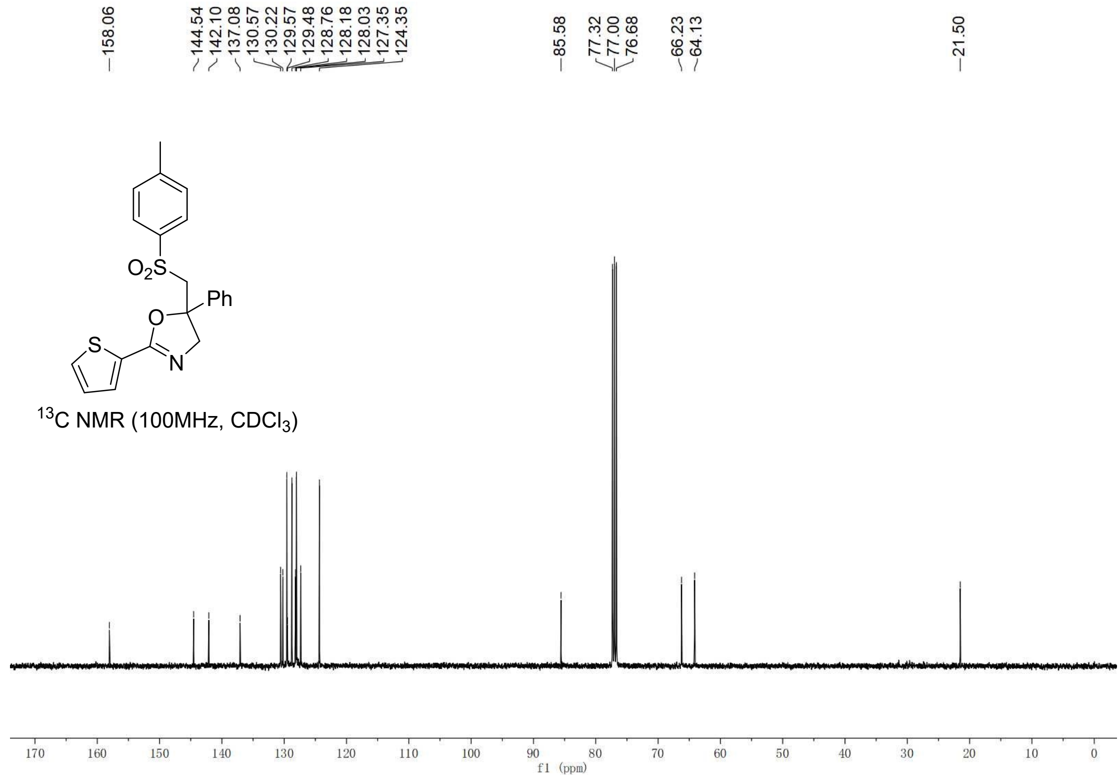
^{13}C NMR spectrum of **3ha**



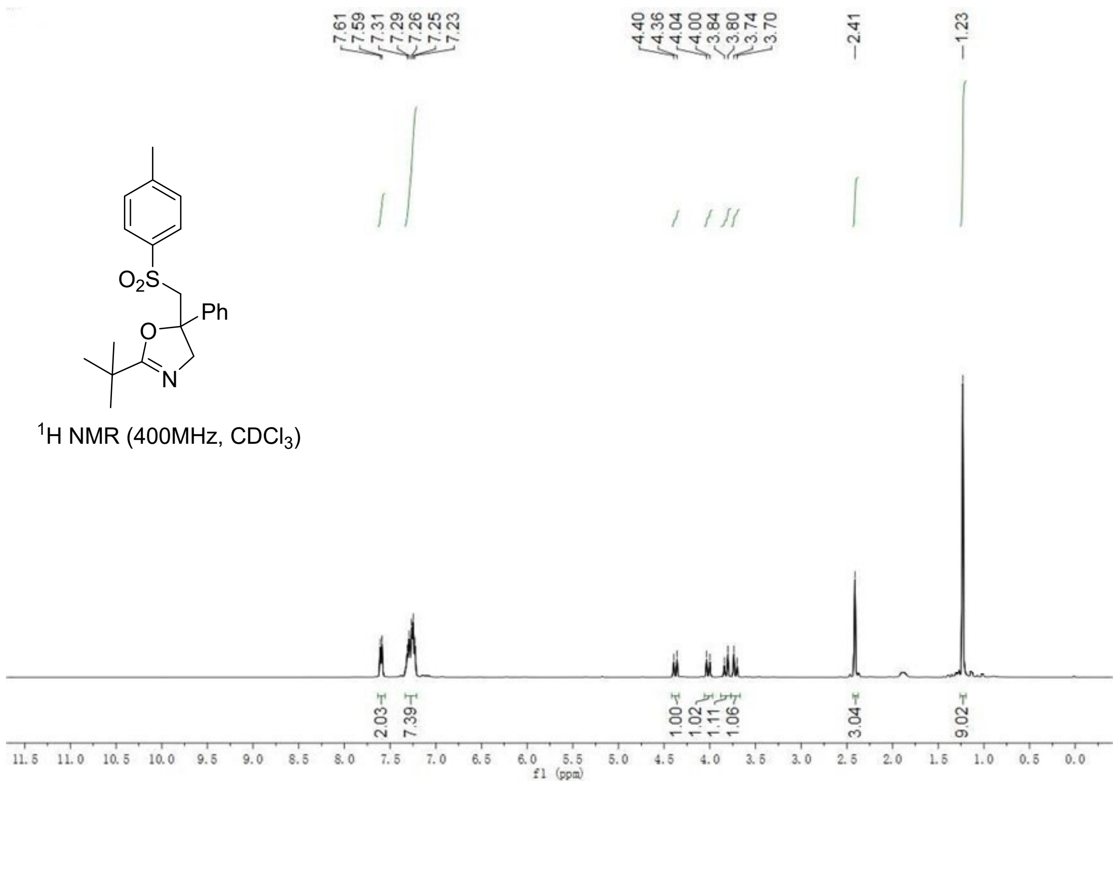
^{1}H NMR spectrum of **3ia**



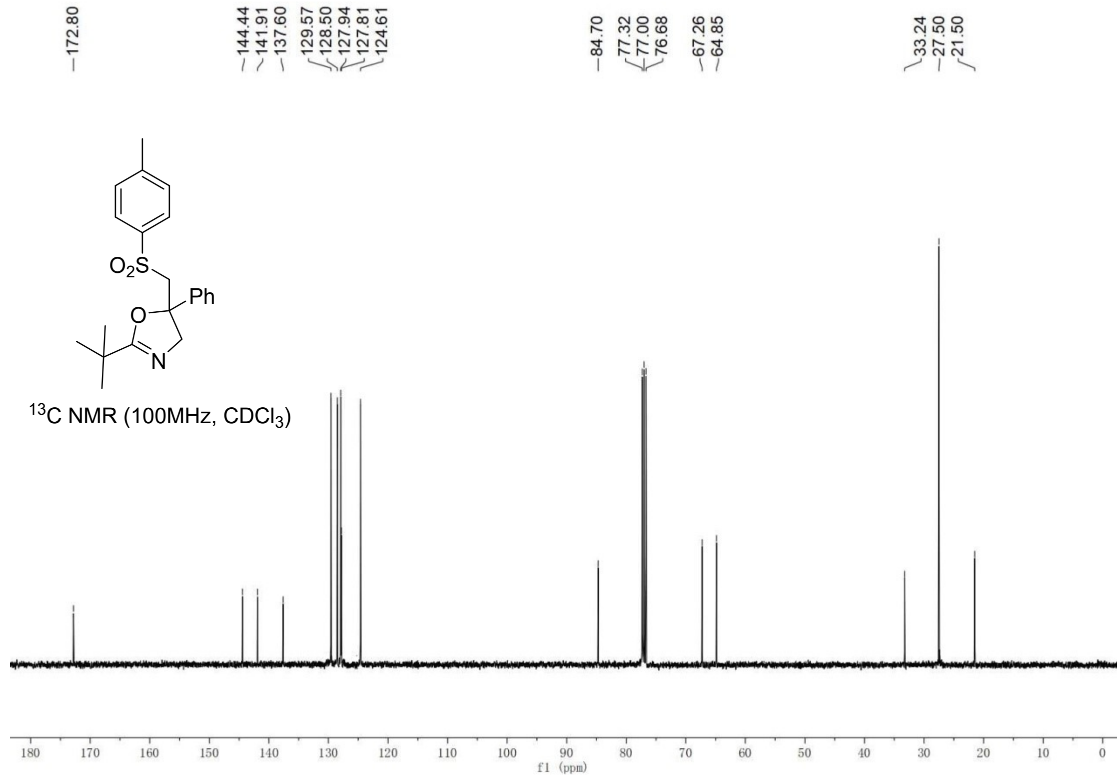
^{13}C NMR spectrum of **3ia**



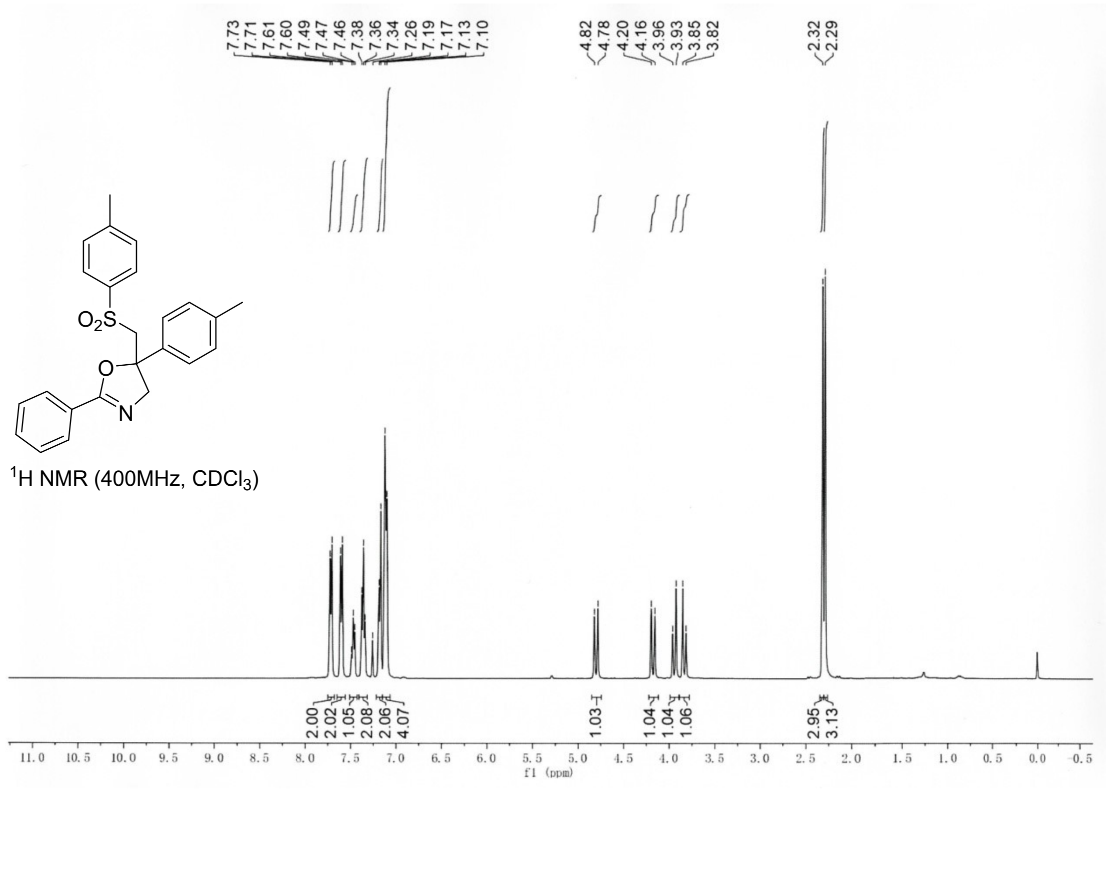
^{1}H NMR spectrum of **3ja**



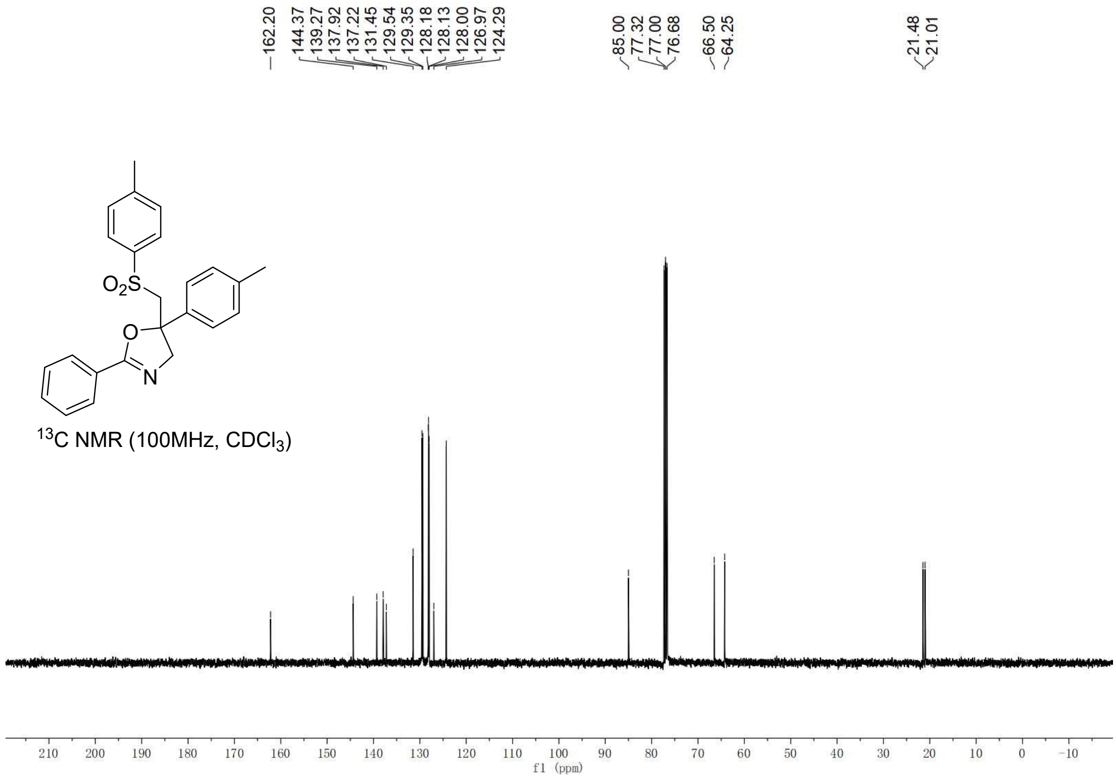
^{13}C NMR spectrum of **3ja**



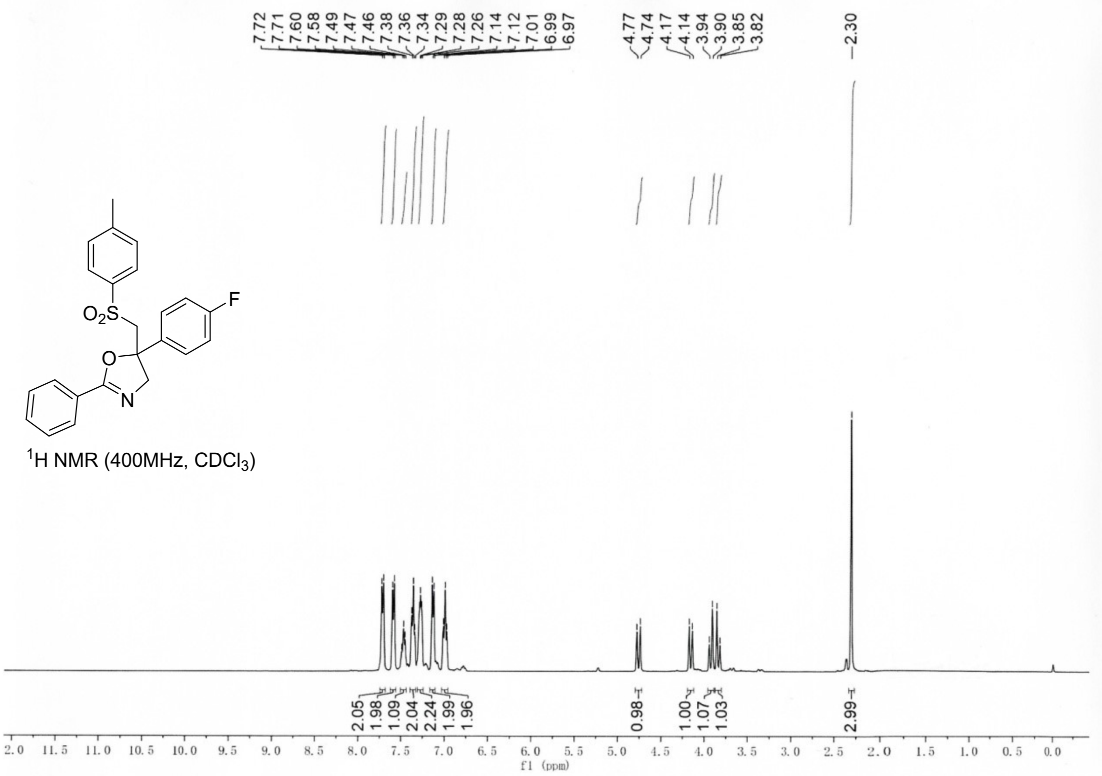
^{1}H NMR spectrum of **3ka**



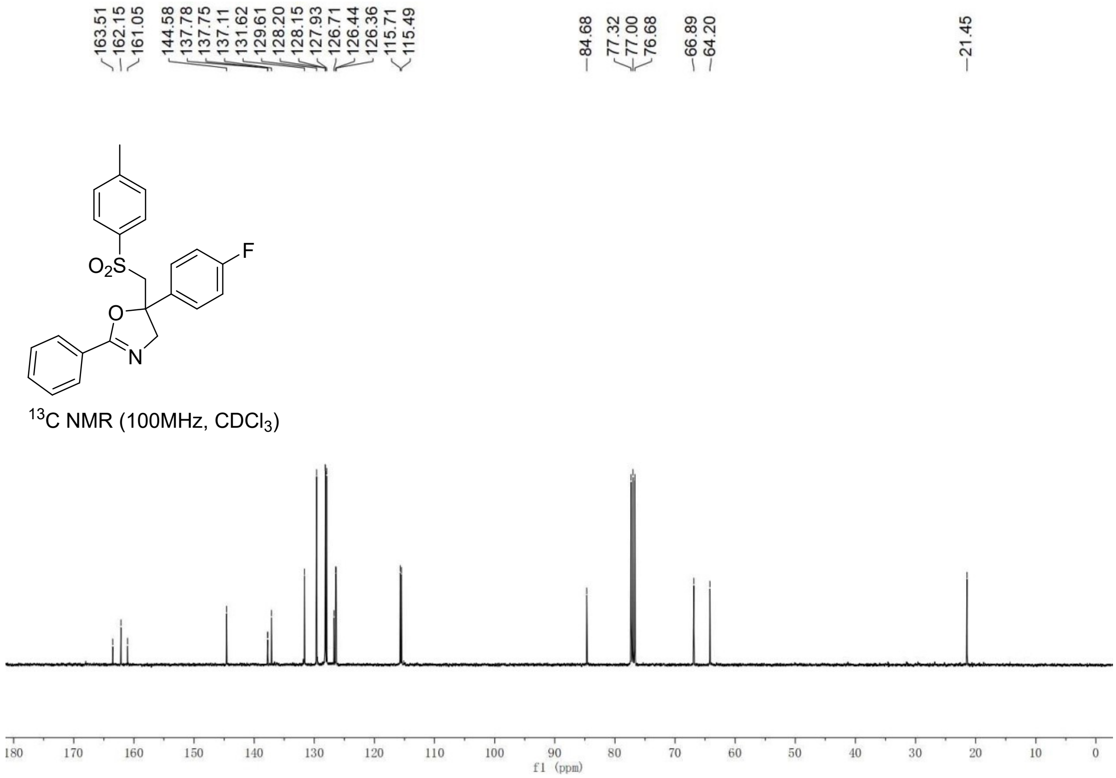
^{13}C NMR spectrum of **3ka**



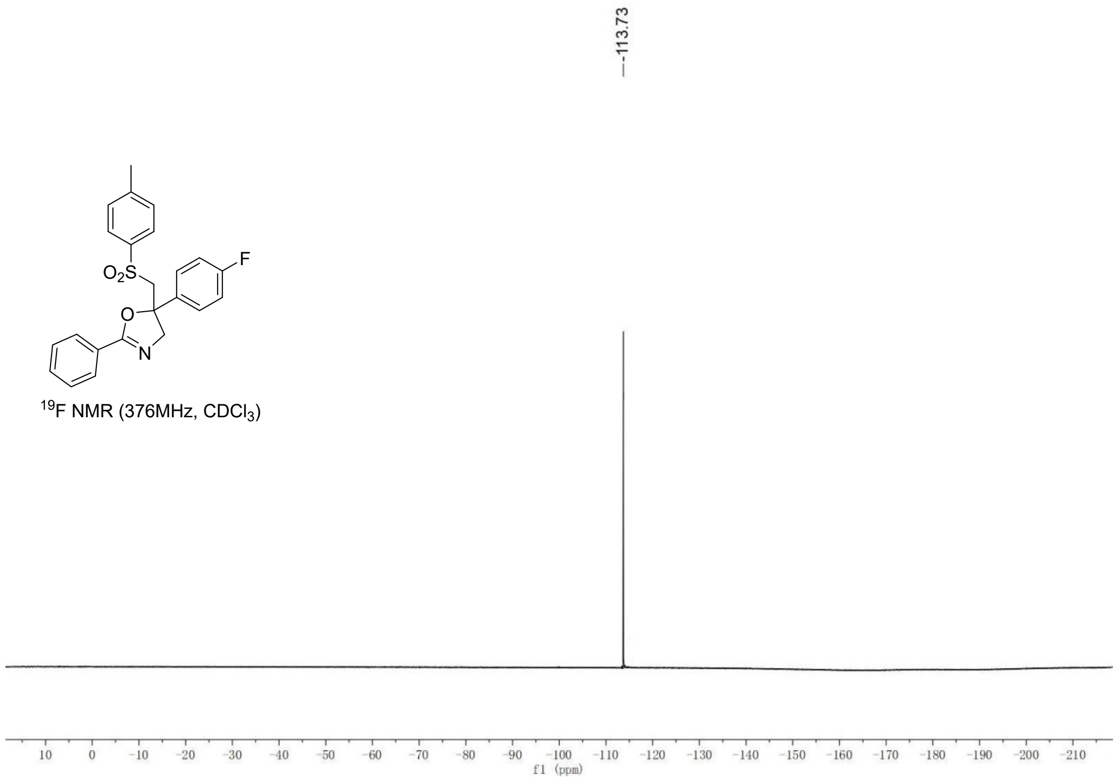
^{1}H NMR spectrum of **3la**



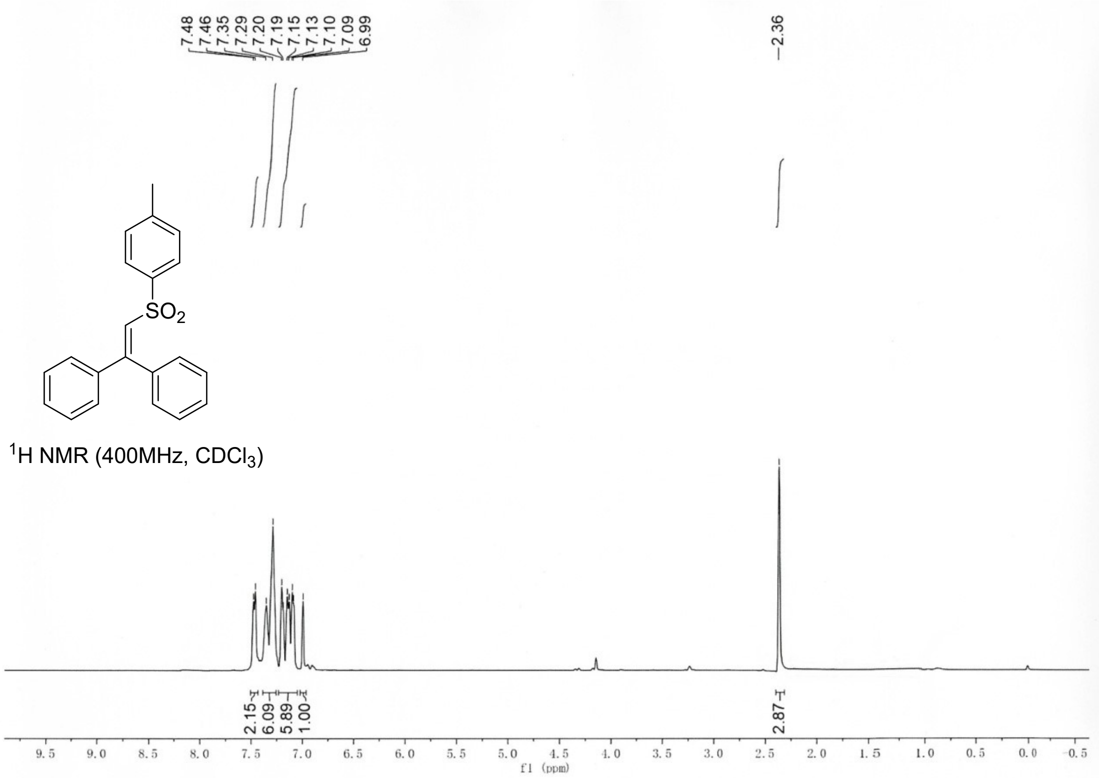
^{13}C NMR spectrum of **3la**



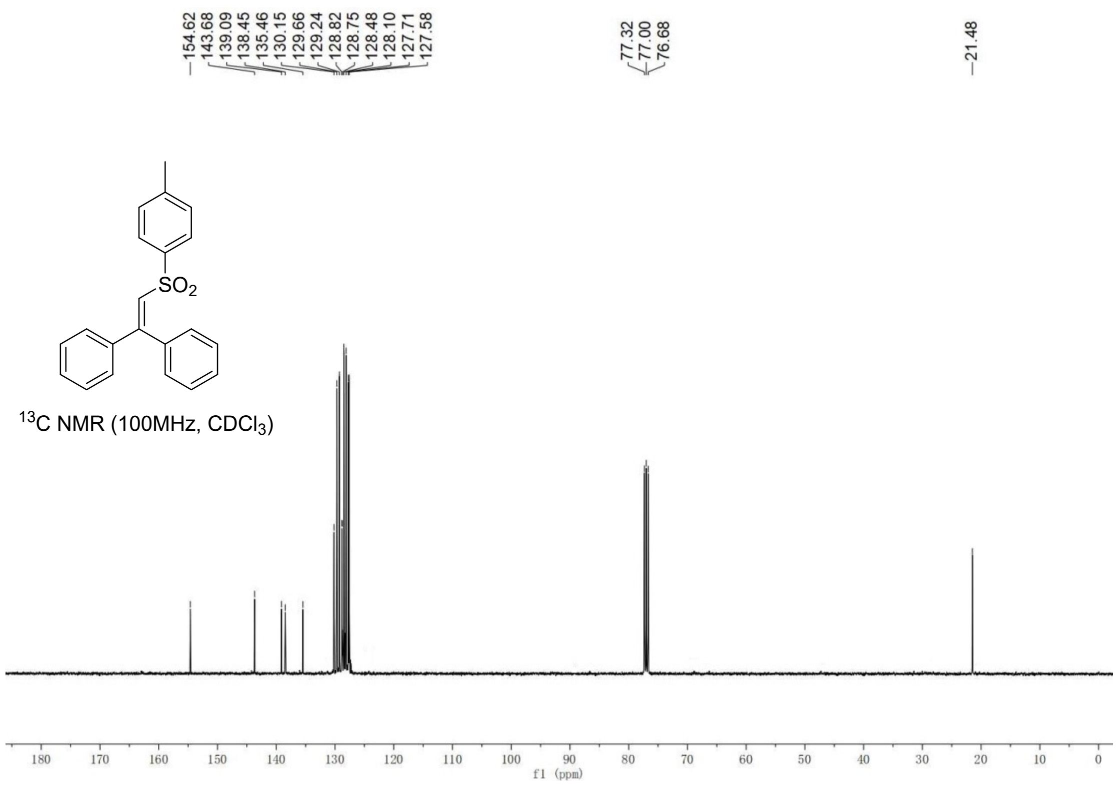
^{19}F NMR spectrum of **3la**



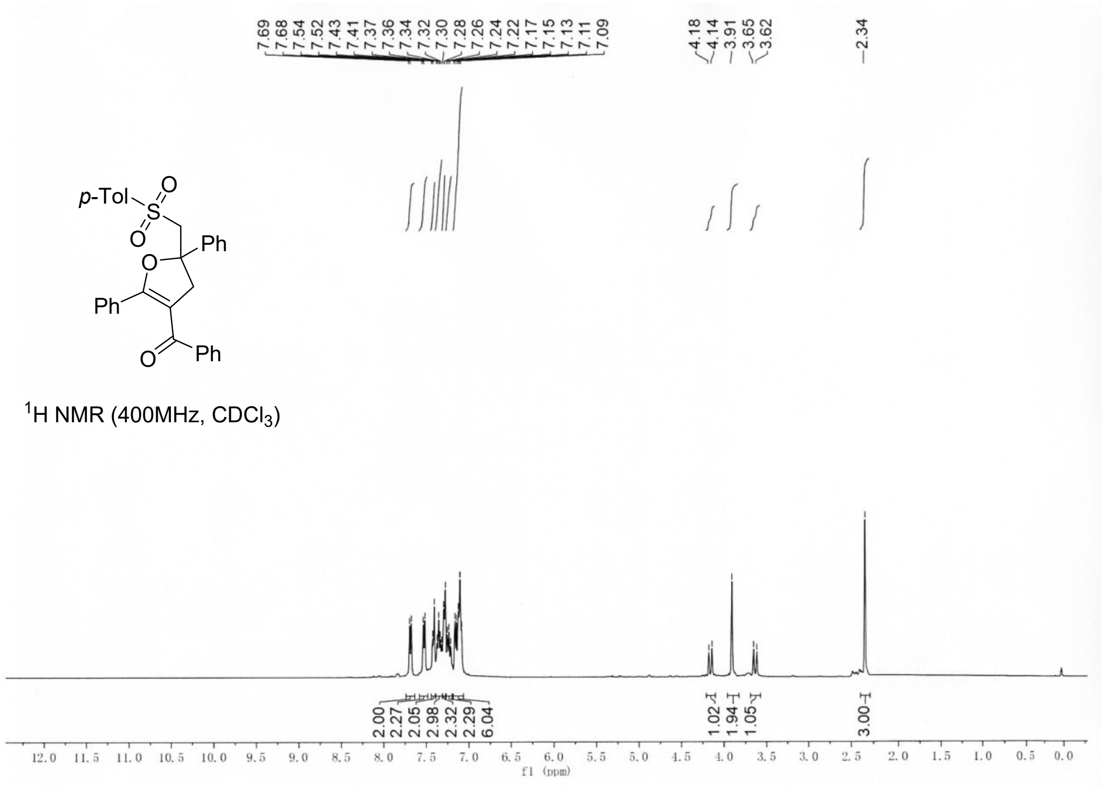
[1]H NMR spectrum of **4**



[13]C NMR spectrum of **4**



^{1}H NMR spectrum of **6**



^{13}C NMR spectrum of **6**