

Supporting Information

Palladium-catalyzed regioselective hydrosulfonylation of allenamides with arylsulfonic acids

Luan-Ying Li,^{‡a} Bo-Rong Leng,^{‡ab} Jia-Zhuo Li,^a Qing-Quan Liu,^a Jianguang Yu,^{*a} Ping Wei,^a De-Cai Wang,^{*a} Yi-Long Zhu^{*a}

^aSchool of Pharmaceutical Sciences, Nanjing Tech University, Nanjing 211816, P. R. China. E-mail: zhuyilong_88@njtech.edu.cn, dcwang@njtech.edu.cn, yjg@njtech.edu.cn

^bCollege of Life and Health, Nanjing Polytechnic Institute, Nanjing 210048, P. R. China.

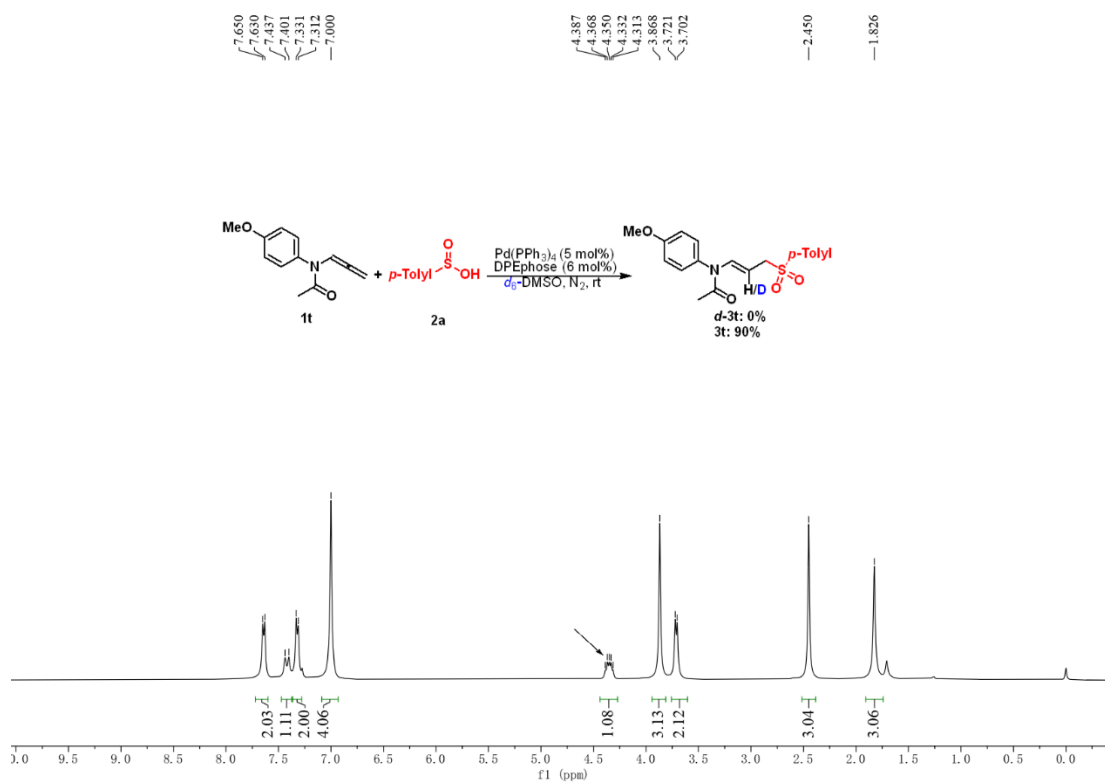
Context

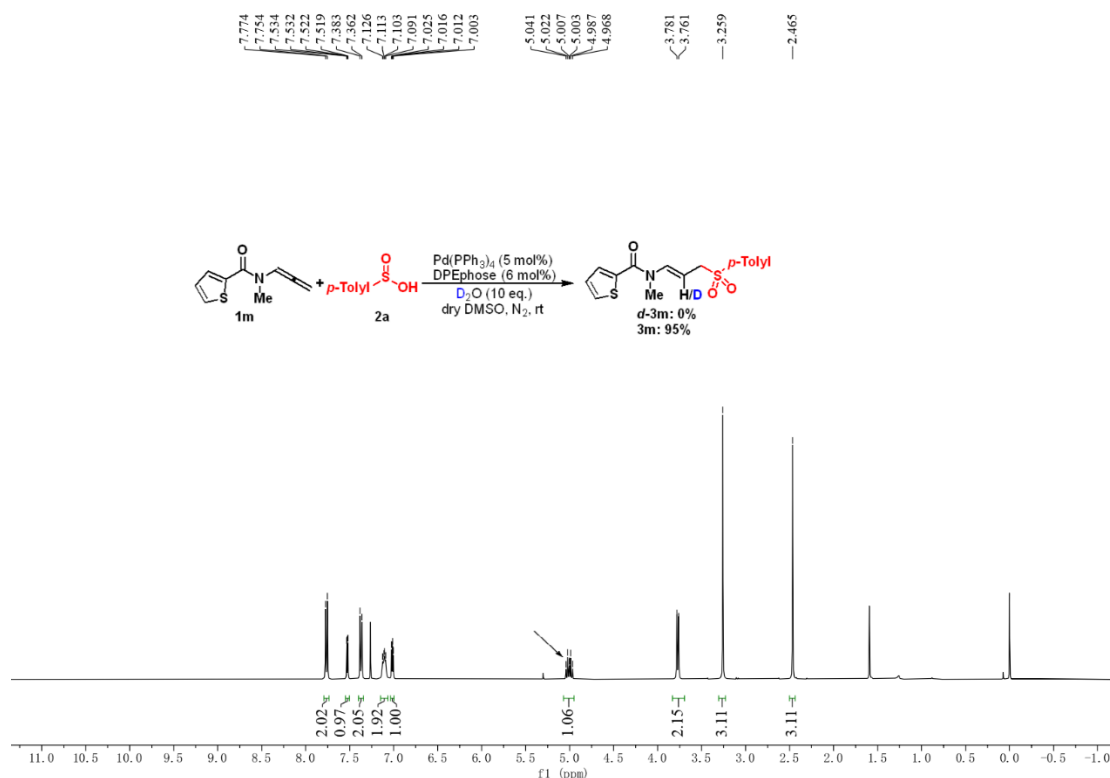
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General Information

^1H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl_3 with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored with thinlayer chromatography (TLC) using 254 nm UV light. The melting points were measured with digital melting point detector.

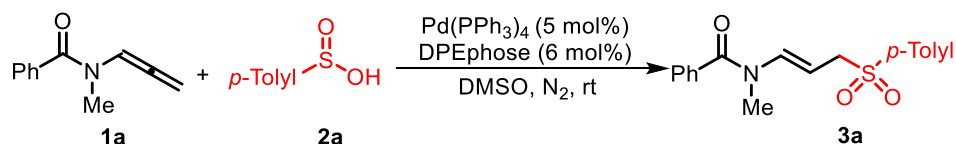
Deuterium-Labeling Experiment Result





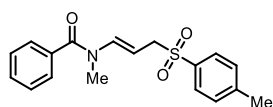
General Procedure for the Synthesis of Compound 3 and 4

Example for the synthesis of 3a



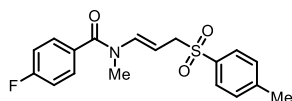
In a flame-dried Schlenk tube along with a stir bar under nitrogen conditions, allenamide (**1a**, 0.2 mmol, 34.6 mg), *p*-methylbenzenesulfonic acid (**2a**, 0.24 mmol, 37.5 mg) and Pd(PPh₃)₄ (11.55 mg, 0.01 mmol), DPEphos (6.45 mg, 0.012 mmol) was added into the tube and then dry DMSO (2 mL) was injected into the reaction system. Subsequently, the tube was stirred at room temperature. The reaction was stirred for 6h and monitored by TLC. Upon completion, the reaction mixture was concentrated by vacuum distillation and purified by flash column chromatography to afford the desired pure product **3a** (eluent: ethyl acetate/petroleum ether = 1:6).

Characterization Data of Compounds 3a-3z and 3aa-3ab



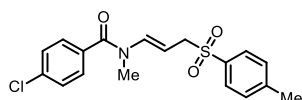
(E)-*N*-methyl-*N*-(3-tosylprop-1-en-1-yl)benzamide (**3a**)

Light yellow solid; 63.2mg, 96 % yield; mp: 123-125°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.49-7.41 (m, 1H), 7.41-7.32 (m, 4H), 7.30-7.19 (m, 2H), 6.61 (s, 1H), 5.04-4.85 (m, 1H), 3.69 (d, *J* = 7.6 Hz, 2H), 3.20 (s, 3H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 170.3, 144.8, 135.4, 134.3, 130.7, 129.8, 128.5, 128.5, 128.0, 58.5, 21.7. HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₉NO₃S [M+Na]⁺ 352.0983; found, 352.0974.



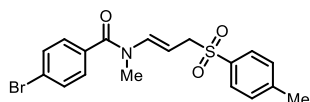
(E)-4-fluoro-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3b)

White solid; 64.5mg, 93% yield; mp: 128-130°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.35-7.25 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 5.09-4.85 (m, 2H), 3.70 (d, *J* = 6.8 Hz, 2H), 3.20 (s, 1H), 2.48 (s, 1H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 169.3, 163.9 (d, *J* = 250.4 Hz), 162.7, 144.8, 135.4, 130.6, 130.5, 130.4, 129.8, 128.5, 115.7 (d, *J* = 21.7 Hz), 58.4, 21.7.; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -108.16. HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈FNO₃S [M+Na]⁺ 370.0889; found, 370.0880.



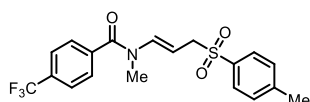
(E)-4-chloro-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3c)

White solid; 67.5mg, 93 % yield; mp: 159-161°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.4 Hz, 4H), 7.30-7.21 (m, 2H), 6.60 (s, 1H), 5.07-4.88 (m, 1H), 3.69 (d, *J* = 7.6 Hz, 2H), 3.20 (s, 3H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 169.2, 144.8, 137.0, 135.5, 135.1, 132.7, 129.8, 129.6, 128.8, 128.5, 108.2, 58.4, 21.7; HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈ClNO₃S [M+Na]⁺ 386.0594; found, 386.0598.



(E)-4-bromo-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3d)

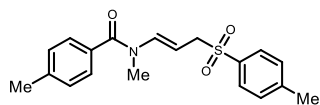
White solid; 76.5mg, 94 % yield; mp: 165-167°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.57 (s, 1H), 5.10-4.89 (m, 1H), 3.70 (s, 2H), 3.20 (s, 3H), 2.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 169.3, 144.9, 135.4, 133.1, 131.8, 130.1, 129.8, 129.7, 128.5, 128.5, 125.3, 58.3, 21.7; HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈FNO₃S [M+Na]⁺ 430.0086; found, 430.0080.



(E)-N-methyl-N-(3-tosylprop-1-en-1-yl)-4-(trifluoromethyl)benzamide (3e)

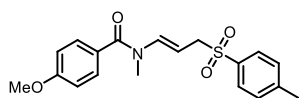
White solid; 65.1mg, 82 % yield; mp: 149-151°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.51-7.33 (m, 4H), 6.48 (s, 1H), 5.02 (s, 1H), 3.68 (s, 2H), 3.24 (s, 3H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.8, 144.9, 137.9, 135.5, 132.5 (*J* =

32.6 Hz), 129.9, 128.5, 125.6 ($J = 3.9$ Hz), 123.5 ($J = 272.5$ Hz), 58.2, 30.4, 21.7. ^{19}F NMR (376 MHz, Chloroform- d) δ -63.04. HR-MS (ESI-TOF, m/z) calcd for $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 420.0857; found, 420.0854.



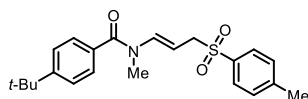
(E)-N,4-dimethyl-N-(3-tosylprop-1-en-1-yl)benzamide (3f)

White solid, 62.4mg, 91% yield; mp: 110-112°C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.24-7.10 (m, 4H), 6.69 (s, 1H), 5.00-4.83 (m, 1H), 3.69 (d, $J = 7.6$ Hz, 2H), 3.19 (s, 3H), 2.48 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) δ 170.5, 144.8, 141.2, 135.4, 131.4, 129.8, 129.1, 128.6, 128.2, 58.5, 21.7, 21.5.; HR-MS (ESI-TOF, m/z) calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 366.1140; found, 366.1132.



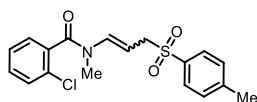
(E)-4-methoxy-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3g)

White solid; 66.7mg, 93 % yield; mp: 162-164°C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.32-7.19 (m, 2H), 6.94-6.82 (m, 3H), 4.99-4.83 (m, 1H), 3.85 (s, 3H), 3.71 (d, $J = 7.6$ Hz, 2H), 3.20 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) δ 170.2, 161.6, 144.8, 135.4, 130.4, 130.1, 129.8, 128.6, 126.3, 113.7, 94.9, 58.6, 55.4, 21.7. HR-MS (ESI-TOF, m/z) calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_4\text{S}$ $[\text{M}+\text{Na}]^+$ 382.1089; found, 382.1082.



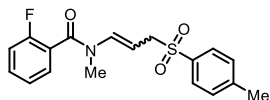
(E)-4-(tert-butyl)-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3h)

White solid; 71.6mg, 93 % yield; mp: 95-97°C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) δ 7.74 (d, $J = 8.0$ Hz, 2H), 7.37 (dd, $J = 8.4, 3.6$ Hz, 4H), 7.21 (d, $J = 7.6$ Hz, 2H), 6.76 (s, 1H), 5.09-4.78 (m, 1H), 3.72 (d, $J = 5.2$ Hz, 2H), 3.20 (s, 3H), 2.49 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 ; δ , ppm) δ 170.5, 154.2, 144.8, 135.4, 131.2, 129.8, 128.6, 128.1, 125.4, 58.5, 34.9, 31.2, 21.7.; HR-MS (ESI-TOF, m/z) calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 408.1609; found, 408.1614.



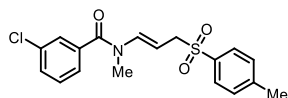
2-chloro-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3i)

Light yellow solid, 68.2mg, 94 % yield; mp: 118-119°C; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) δ 7.66 (d, $J = 8.0$ Hz, 2H), 7.45-7.09 (m, 6H), 6.16 (s, 1H), 5.17-4.91 (m, 1H), 3.86 (d, $J = 7.6$ Hz, 2H), 3.25 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) δ 167.4, 144.8, 136.2, 133.8, 131.0, 130.6, 129.8, 129.8, 128.4, 128.3, 127.2, 96.6, 58.2, 33.6, 21.7. HR-MS (ESI-TOF, m/z) calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 386.0594; found, 386.0586.



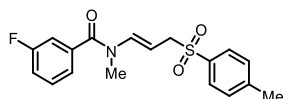
2-fluoro-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3j)

Light yellow solid, 63.1mg, 91% yield; mp: 139-140°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.50-7.30 (m, 4H), 7.23-6.98 (m, 3H), 6.34 (d, *J* = 14.0, 1H), 4.99-4.92 (m, 1H), 3.65 (d, *J* = 7.6 Hz, 2H), 3.24 (s, 3H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.9, 158.27 (*J* = 248.6 Hz), 144.8, 136.7, 135.2, 132.3 (*J* = 8.0 Hz), 129.8, 129.4, 128.4, 124.75 (*J* = 20.1 Hz), 116.1 (*J* = 20.5 Hz), 96.4, 58.2, 33.92, 29.8, 21.7.; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -113.61, 114.09. HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈FNO₃S [M+Na]⁺ 370.0889; found, 370.0887.



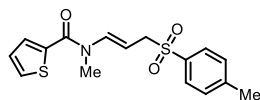
(E)-3-chloro-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3k)

Light yellow solid; 93 % yield; 67.5mg, mp: 128-129°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34-7.26 (m, 2H), 7.13 (s, 1H), 6.53 (s, 1H), 5.19-4.82 (m, 1H), 3.70 (s, 2H), 3.20 (s, 3H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.8, 144.9, 136.1, 135.3, 134.8, 130.8, 129.8, 128.8, 128.5, 128.0, 125.9, 58.3, 21.7.; HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈ClNO₃S [M+Na]⁺ 386.0594; found, 386.0588.



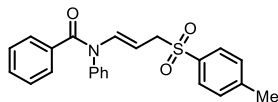
(E)-3-fluoro-N-methyl-N-(3-tosylprop-1-en-1-yl)benzamide (3l)

White solid; 64.5mg, 93 % yield; mp: 136-138°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.42-7.30 (m, 3H), 7.20-7.11 (m, 1H), 7.05 (s, 1H), 6.97 (s, 1H), 6.52 (s, 1H), 5.10-4.88 (m, 1H), 3.70 (s, 2H), 3.20 (s, 3H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.8, 162.4 (*J* = 247.3 Hz), 144.9, 136.4 (d, *J* = 7.0 Hz), 135.3, 130.4 (*J* = 8.0 Hz), 129.8, 128.5, 123.6, 117.8 (d, *J* = 20.9 Hz), 115.1 (*J* = 22.9 Hz), 96.3, 58.4, 41.0, 21.7; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -111.09. HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈FNO₃S [M+Na]⁺ 370.0889; found, 370.0890.



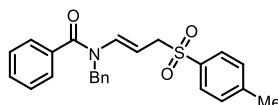
(E)-N-methyl-N-(3-tosylprop-1-en-1-yl)thiophene-2-carboxamide (3m)

White solid; 63mg, 94 % yield; mp: 136-137°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.18-7.06 (m, 2H), 7.01 (dd, *J* = 5.2, 4.0 Hz, 1H), 5.09-4.91 (m, 1H), 3.77 (d, *J* = 7.6 Hz, 2H), 3.26 (s, 3H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 163.4, 144.9, 136.5, 135.4, 131.2, 130.9, 129.9, 128.6, 127.1, 96.3, 58.4, 41.0, 21.7; HR-MS (ESI-TOF, *m/z*) calcd for C₁₆H₁₇NO₃S₂ [M+Na]⁺ 358.0548; found, 358.0546.



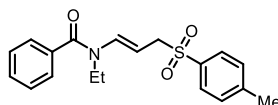
(E)-N-phenyl-N-(3-tosylprop-1-en-1-yl)benzamide (3n)

White solid; 63.3mg, 81 % yield; mp: 141-142°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 14.4 Hz, 1H), 7.37-7.30 (m, 4H), 7.31-7.23 (m, 4H), 7.21-7.13 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 4.70-4.49 (m, 1H), 3.75 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.9, 144.8, 139.1, 136.8, 135.5, 134.6, 130.4, 129.7(4), 129.7(0), 128.9, 128.6, 128.5, 128.4, 127.9, 100.3, 58.6, 21.7. HR-MS (ESI-TOF, *m/z*) calcd for C₂₃H₂₁NO₃S [M+Na]⁺ 414.114; found, 414.1120.



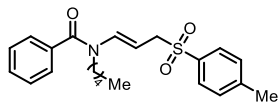
(E)-N-benzyl-N-(3-tosylprop-1-en-1-yl)benzamide (3o)

White solid; 74.5mg, 92 % yield; mp: 108-109°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.48-7.39 (m, 5H), 7.37 (d, *J* = 5.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.31-7.28 (m, 2H), 7.25-7.20 (m, 4H), 6.51 (s, 1H), 4.97 (s, 2H), 4.90-4.82 (m, 1H), 3.56 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 170.6, 144.5, 136.1, 134.9, 134.2, 130.9, 129.6, 128.9, 128.6(1), 128.5(6), 128.0, 127.5, 126.8, 58.6, 21.7; HR-MS (ESI-TOF, *m/z*) calcd for C₂₄H₂₃NO₃S [M+Na]⁺ 428.1296; found, 428.1289.



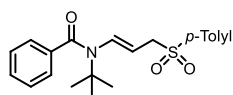
(E)-N-ethyl-N-(3-tosylprop-1-en-1-yl)benzamide (3p)

Light yellow solid; 61.7mg, 90 % yield; mp: 74-75 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.52-7.28 (m, 5H), 7.21 (s, 2H), 6.48 (s, 1H), 5.10-4.82 (m, 1H), 3.77 (s, 2H), 3.68 (d, *J* = 8.0 Hz, 2H), 2.48 (s, 3H), 1.21 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 170.0, 144.8, 135.3, 134.6, 130.6, 129.8, 128.6, 128.5, 127.9, 95.1, 58.7, 38.5, 21.7, 12.0; HR-MS (ESI-TOF, *m/z*) calcd for C₁₉H₂₁NO₃S [M+Na]⁺ 366.1140; found, 366.1136.



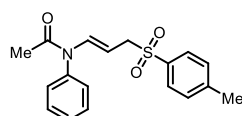
(E)-N-pentyl-N-(3-(p-tolylsulfinyl)prop-1-en-1-yl)benzamide (3q)

Light yellow oli, 68.5mg, 89 % yield; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.39-7.20 (m, 4H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.47 (s, 1H), 5.00-4.82 (m, 1H), 3.79-3.59 (m, 2H), 2.49 (s, 3H), 1.66-1.54 (m, 2H), 1.37-1.23 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 170.2, 144.8, 135.3, 134.6, 130.6, 129.8, 128.6, 128.4, 127.9, 58.7, 29.7, 29.1, 26.4, 22.4, 21.7, 14.0. HR-MS (ESI-TOF, *m/z*) calcd for C₂₂H₂₇NO₃S [M+Na]⁺ 408.1609; found, 408.1616.



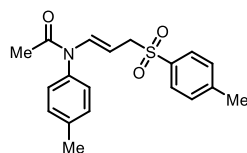
(E)-N-(tert-butyl)-N-(3-tosylprop-1-en-1-yl)benzamide (3r)

White solid; 59.4mg, 80 % yield; mp: 101-102°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.51-7.43 (m, 4H), 7.39-7.31 (m, 3H), 7.30-7.25 (m, 2H), 6.27 (d, *J* = 13.6 Hz, 1H), 4.82-4.65 (m, 1H), 3.52 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.38 (s, 9H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 171.8, 144.8, 137.6, 137.6, 135.4, 130.3, 129.9, 128.9, 128.2, 128.1, 117.5, 58.7, 57.6, 27.6, 21.6. R-MS (ESI-TOF, m/z) calcd for C₂₁H₂₅NO₃S [M+Na]⁺ 394.1453; found, 394.1461.



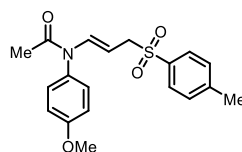
(E)-N-phenyl-N-(3-tosylprop-1-en-1-yl)acetamide (3s)

White solid; 59.8mg, 91 % yield; mp: 173-175°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.55-7.40 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 6.8 Hz, 2H), 4.39-4.22 (m, 1H), 3.71 (d, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 1.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.8, 144.8, 138.9, 135.2(3), 135.2(8), 130.3, 129.7, 129.2, 128.6, 128.5, 99.2, 58.6, 23.1, 21.7; HR-MS (ESI-TOF, m/z) calcd for C₁₈H₁₉NO₃S [M+Na]⁺ 352.0983; found, 352.0979.



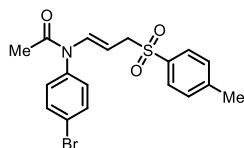
(E)-N-(p-tolyl)-N-(3-tosylprop-1-en-1-yl)acetamide (3t)

White solid; 63.8mg, 93 % yield; mp: 132-135°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.63 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 14.4 Hz, 1H), 7.34-7.26 (m, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.38-4.27 (m, 1H), 3.71 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.45 (s, 3H), 2.42 (s, 3H), 1.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 169.0, 144.7, 139.3, 136.2, 135.2, 130.9, 129.6, 128.5, 128.2, 99.1, 58.6, 23.1, 21.7, 21.2; HR-MS (ESI-TOF, m/z) calcd for C₁₉H₂₁NO₃S [M+Na]⁺ 366.1140; found, 366.1136.



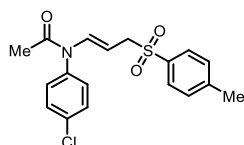
(E)-N-(4-methoxyphenyl)-N-(3-tosylprop-1-en-1-yl)acetamide (3u)

White solid; 65.3mg, 91 % yield; mp: 121-123°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 14.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.05-6.95 (m, 4H), 4.38-4.28 (m, 1H), 3.86 (s, 3H), 3.72 (dd, *J* = 7.6, 1.0 Hz, 2H), 2.44 (s, 3H), 1.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 169.2, 159.8, 144.7, 135.4, 135.2, 131.4, 129.6, 129.5, 128.5, 115.4, 99.0, 58.6, 55.5, 23.1, 21.6; HR-MS (ESI-TOF, m/z) calcd for C₁₉H₂₁NO₄S [M+Na]⁺ 382.1089; found, 382.1092.



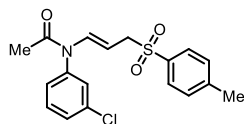
(E)-N-(4-bromophenyl)-N-(3-tosylprop-1-en-1-yl)acetamide (3v)

White solid; 70.8mg, 87% yield; mp: 147-148°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.64 (dd, *J* = 8.4, 2.0 Hz, 4H), 7.44 (d, *J* = 14.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.04-6.98 (m, 2H), 4.34-4.21 (m, 1H), 3.71 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.45 (s, 3H), 1.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.3, 144.9, 137.9, 135.3, 135.0, 133.7, 130.3, 129.7, 128.4, 123.3, 99.4, 58.4, 23.1, 21.7; HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈BrNO₃S [M+Na]⁺ 430.0088; found, 430.0080.



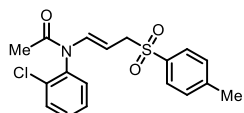
(E)-N-(4-chlorophenyl)-N-(3-tosylprop-1-en-1-yl)acetamide (3w)

White solid; 60.2mg, 83 % yield; mp: 129-131°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.67-7.61 (m, 2H), 7.54-7.38 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.10-7.03 (m, 2H), 4.34-4.25 (m, 1H), 3.71 (dd, *J* = 8.0, 1.2 Hz, 2H), 2.45 (s, 3H), 1.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.4, 144.9, 137.4, 135.3, 135.1, 130.7, 130.0, 129.7, 128.4, 99.4, 58.4, 23.1, 21.7; HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈ClNO₃S [M+Na]⁺ 386.0594; found, 386.0585.



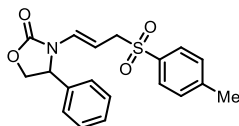
(E)-N-(3-chlorophenyl)-N-(3-tosylprop-1-en-1-yl)acetamide (3x)

White solid; 59.5mg, 82 % yield; mp: 159-160°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.49-7.38 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.11 (s, 1H), 7.07-6.99 (m, 1H), 4.38-4.22 (m, 1H), 3.82-3.61 (m, 2H), 2.46 (s, 3H), 1.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.3, 144.9, 140.0, 135.8, 135.2, 135.0, 131.3, 129.7, 129.6, 129.0, 128.5, 127.0, 99.7, 58.5, 23.1, 21.7; HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈ClNO₃S [M+Na]⁺ 386.0594; found, 386.0589.



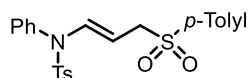
(E)-N-(2-chlorophenyl)-N-(3-tosylprop-1-en-1-yl)acetamide (3y)

White solid; 62.4mg, 86 % yield; mp: 151-152°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.61-7.55 (m, 1H), 7.49-7.40 (m, 2H), 7.35 (d, *J* = 14.4 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25-7.16 (m, 1H), 4.30-4.21 (m, 1H), 3.73 (dd, *J* = 8.0, 1.2 Hz, 2H), 2.44 (s, 3H), 1.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 168.4, 144.8, 136.2, 134.9, 133.5, 133.3, 131.2, 130.8, 130.6, 129.6, 128.8, 128.6, 98.7, 58.5, 22.5, 21.7; HR-MS (ESI-TOF, *m/z*) calcd for C₁₈H₁₈ClNO₃S [M+Na]⁺ 386.0594; found, 386.0589.



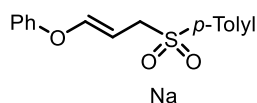
(E)-4-phenyl-3-(3-tosylprop-1-en-1-yl)oxazolidin-2-one (3z)

Clear oil; 43.6mg, 61% yield; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.51-7.40 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.26-7.19 (m, 4H), 6.58 (d, *J* = 14.4 Hz, 1H), 5.00 (dd, *J* = 9.2, 5.2 Hz, 1H), 4.72 (t, *J* = 8.8 Hz, 1H), 4.65-4.50 (m, 1H), 4.14 (dd, *J* = 9.2, 5.2 Hz, 1H), 3.74-3.53 (m, 2H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 155.3, 144.7, 137.5, 134.9, 130.0, 129.7, 129.6, 129.2, 128.3, 126.1, 98.4, 70.8, 58.4, 58.2, 21.7. HR-MS (ESI-TOF, *m/z*) calcd for C₁₉H₁₉NO₄S [M+Na]⁺ 380.0932; found, 380.0937.



(E)-4-methyl-N-phenyl-N-(3-tosylprop-1-en-1-yl)benzenesulfonamide (3aa)

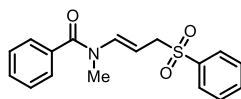
Clear oil; 70.6mg, 80% yield; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.41-7.33 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 14.0 Hz, 1H), 6.89-6.84 (m, 2H), 4.26-4.14 (m, 1H), 3.67 (d, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 144.7, 144.4, 136.5, 135.5, 135.26, 135.2, 130.0, 129.7, 129.7, 129.5, 128.5, 127.5, 96.3, 77.3, 58.2, 21.7, 21.7. HR-MS (ESI-TOF, *m/z*) calcd for C₂₃H₂₃NO₄S₂ [M+Na]⁺ 464.0966; found, 464.0972.



(E)-1-methyl-4-((3-phenoxyallyl)sulfonyl)benzene (3ab)

White solid; 41.5mg, 72% yield; mp: 96-97°C ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.33-7.25 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.45 (d, *J* = 12.4 Hz, 1H), 5.27-5.14 (m, 1H), 3.74 (d, *J* = 9.2 Hz, 2H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 156.4, 149.7, 144.8, 135.2, 129.8, 129.7, 128.7, 123.7, 117.1, 98.4, 56.1, 21.7. HR-MS (ESI-TOF, *m/z*) calcd for C₁₆H₁₆O₃S [M+Na]⁺ 311.0718.0966; found, 311.0725.

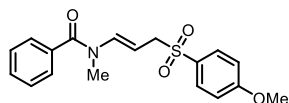
Characterization Data of Compounds 4a-4j



(E)-N-methyl-N-(3-(phenylsulfonyl)prop-1-en-1-yl)benzamide (4a)

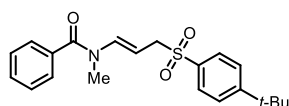
White solid; 59.2mg, 94 % yield; mp: 135-137 °C; ¹ H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31-7.18 (m, 2H), 6.62 (s, 1H), 5.10-4.79 (m, 1H), 3.72 (s, 2H), 3.20 (s, 3H). ¹³C NMR

(100 MHz, CDCl₃; δ , ppm) δ 170.4, 138.3, 134.3, 133.8, 130.7, 129.2, 128.5, 128.5, 128.0, 58.4. HR-MS (ESI-TOF, m/z) calcd for C₁₇H₁₇NO₃S [M+H]⁺ 316.1007; found, 316.1006.



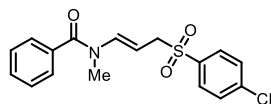
(E)-N-(3-((4-methoxyphenyl)sulfonyl)prop-1-en-1-yl)-N-methylbenzamide (4b)

White solid; 64.2mg, 93% yield; mp 154-156°C; ¹H NMR (400 MHz, CDCl₃; δ , ppm) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.49-7.41 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31-7.23 (m, 2H), 7.08-6.98 (m, 2H), 6.58 (s, 1H), 5.05-4.85 (m, 1H), 3.91 (s, 3H), 3.78-3.57 (m, 2H), 3.21 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ , ppm) δ 170.4, 163.8, 134.3, 130.7(1), 130.6(8), 129.7, 128.5, 128.5, 128.0, 114.3, 58.6, 55.8. HR-MS (ESI-TOF, m/z) calcd for C₁₈H₁₉NO₄S [M+Na]⁺ 368.0932; found, 368.0931.



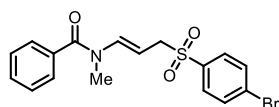
(E)-N-(3-((4-tert-butylphenyl)sulfonyl)prop-1-en-1-yl)-N-methylbenzamide (4c)

White solid; 40.1mg, 54 % yield; mp: 133-135°C; ¹H NMR (400 MHz, CDCl₃; δ , ppm) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.61-7.54 (m, 2H), 7.49-7.42 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.34-7.25 (m, 2H), 6.71 (s, 1H), 5.06-4.89 (m, 1H), 3.71 (d, *J* = 7.6 Hz, 2H), 3.21 (s, 3H), 1.36 (s, 9H). ¹³C NMR (100 MHz, CDCl₃; δ , ppm) δ 170.3, 157.8, 135.5, 134.4, 130.7, 128.5, 128.3, 128.0, 126.2, 58.5, 35.3, 31.1; HR-MS (ESI-TOF, m/z) calcd for C₂₁H₂₅NO₃S [M+Na]⁺ 394.1453; found, 394.1447.



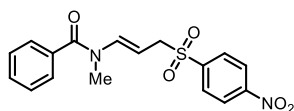
(E)-N-(3-((4-chlorophenyl)sulfonyl)prop-1-en-1-yl)-N-methylbenzamide (4d)

White solid; 41.2mg, 59 % yield; mp: 137-140°C; ¹H NMR (400 MHz, CDCl₃; δ , ppm) δ 8.16 (d, *J* = 8.4 Hz, 2H), 8.01-7.91 (m, 2H), 7.88-7.81 (m, 1H), 7.80-7.73 (m, 2H), 7.69-7.60 (m, 2H), 6.98 (s, 1H), 5.49-5.13 (m, 1H), 4.19-3.99 (m, 2H), 3.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ , ppm) δ 170.4, 140.6, 136.7, 134.2, 130.8, 130.0, 129.5, 128.6, 127.9, 58.4. HR-MS (ESI-TOF, m/z) calcd for C₁₇H₁₆ClNO₃S [M+Na]⁺ 372.0437; found, 372.0437.



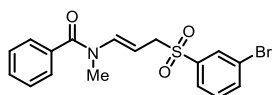
(E)-N-(3-((4-bromophenyl)sulfonyl)prop-1-en-1-yl)-N-methylbenzamide (4e)

White solid; 62.9mg, 80 % yield; mp: 127-128°C; ¹H NMR (400 MHz, CDCl₃; δ , ppm) δ 7.76-7.67 (m, 4H), 7.50-7.44 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.33-7.19 (m, 2H), 6.61 (s, 1H), 5.01-4.85 (m, 1H), 3.71 (s, 2H), 3.21 (s, 3H). ¹³C NMR (100 MHz, CDCl₃; δ , ppm) δ 170.4, 137.2, 134.2, 132.5, 130.8, 130.4, 130.1, 129.4, 129.2, 128.6, 127.9, 58.4, 41.0. HR-MS (ESI-TOF, m/z) calcd for C₁₇H₁₆BrNO₃S [M+Na]⁺ 415.9932; found, 415.9930.



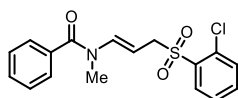
(E)-N-methyl-N-(3-((4-nitrophenyl)sulfonyl)prop-1-en-1-yl)benzamide (4f)

Light yellow solid; 62.6mg, 87 % yield; mp: 169-171°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 8.41 (t, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.82 (s, 1H), 5.00-4.85 (m, 1H), 3.80 (s, 2H), 3.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 170.4, 151.9, 150.9, 144.1, 134.1, 130.9, 130.0, 128.6, 127.9, 124.3, 95.1, 58.4, 26.1; HR-MS (ESI-TOF, *m/z*) calcd for C₁₇H₁₆N₂O₅S [M+Na]⁺ 383.0678; found, 383.0668.



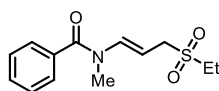
(E)-N-(3-((3-bromophenyl)sulfonyl)prop-1-en-1-yl)-N-methylbenzamide (4g)

White solid; 50.3mg, 64 % yield; mp: 174-175 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 8.13-7.91 (m, 1H), 7.80 (t, *J* = 8.0 Hz, 2H), 7.65-7.17 (m, 7H), 6.67 (s, 1H), 5.02-4.82 (m, 1H), 3.74 (s, 2H), 3.21 (s, 3H), ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 170.4, 140.1, 136.9, 134.3, 131.5, 130.8, 130.7, 128.6, 127.9, 127.1, 123.2, 94.7, 58.5, 40.9; HR-MS (ESI-TOF, *m/z*) calcd for C₁₇H₁₆BrNO₃S [M+Na]⁺ 415.9932; found, 415.9929.



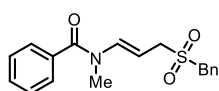
(E)-N-(3-((2-chlorophenyl)sulfonyl)prop-1-en-1-yl)-N-methylbenzamide (4h)

White solid; 62.1mg, 89% yield; mp: 137-140°C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 8.07-8.02 (m, 1H), 7.61-7.50 (m, 2H), 7.49-7.42 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 4.0 Hz, 2H), 6.74 (s, 1H), 5.00-4.81 (m, 1H), 4.04 (s, 2H), 3.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 170.3, 136.0, 134.9, 134.3, 132.6, 132.2, 131.8, 130.8, 128.6, 127.9, 127.4, 94.6, 56.4, 41.0; HR-MS (ESI-TOF, *m/z*) calcd for C₁₇H₁₆ClNO₃S [M+Na]⁺ 372.0437; found, 372.0430.



(E)-N-(3-(ethylsulfonyl)prop-1-en-1-yl)-N-methylbenzamide (4i)

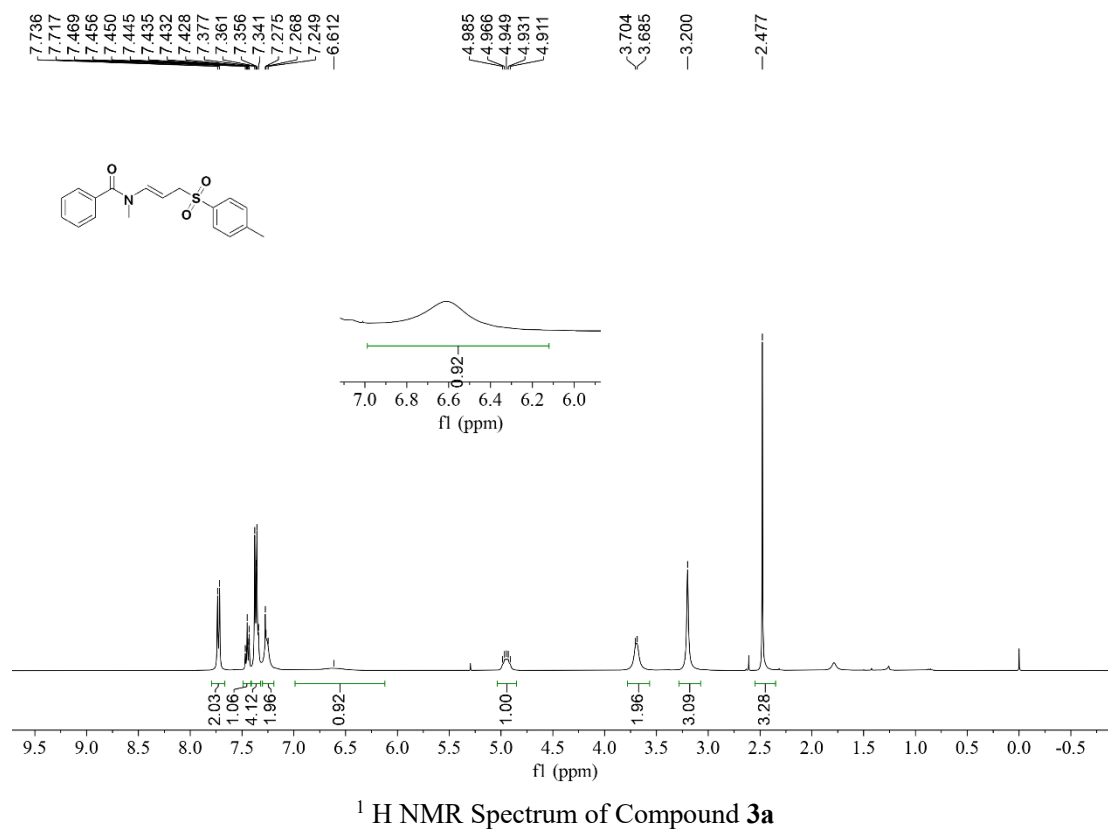
Light yellow oil; 50.2mg, 94 % yield; ¹H NMR (400 MHz, CDCl₃; δ, ppm) δ 7.63-7.03 (m, 6H), 5.08-4.88 (m, 1H), 3.62 (s, 2H), 3.22 (s, 3H), 3.02-2.87 (m, 2H), 1.34 (t, *J* = 8.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃; δ, ppm) δ 170.5, 134.5, 133.0, 130.8, 128.6, 128.0, 113.2, 54.2, 45.6, 29.7, 14.1; HR-MS (ESI-TOF, *m/z*) calcd for C₁₃H₁₇NO₃S [M+Na]⁺ 290.0827; found, 290.0824.

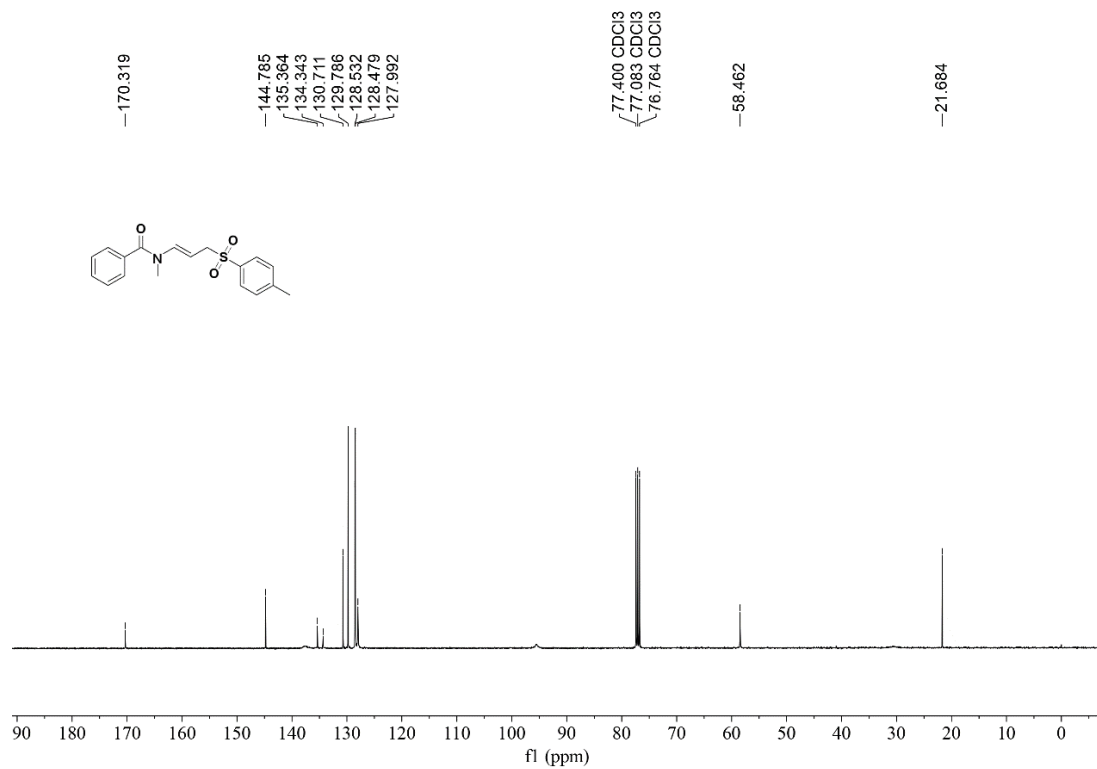


(E)-N-(3-(benzylsulfonyl)prop-1-en-1-yl)-N-methylbenzamide (4j)

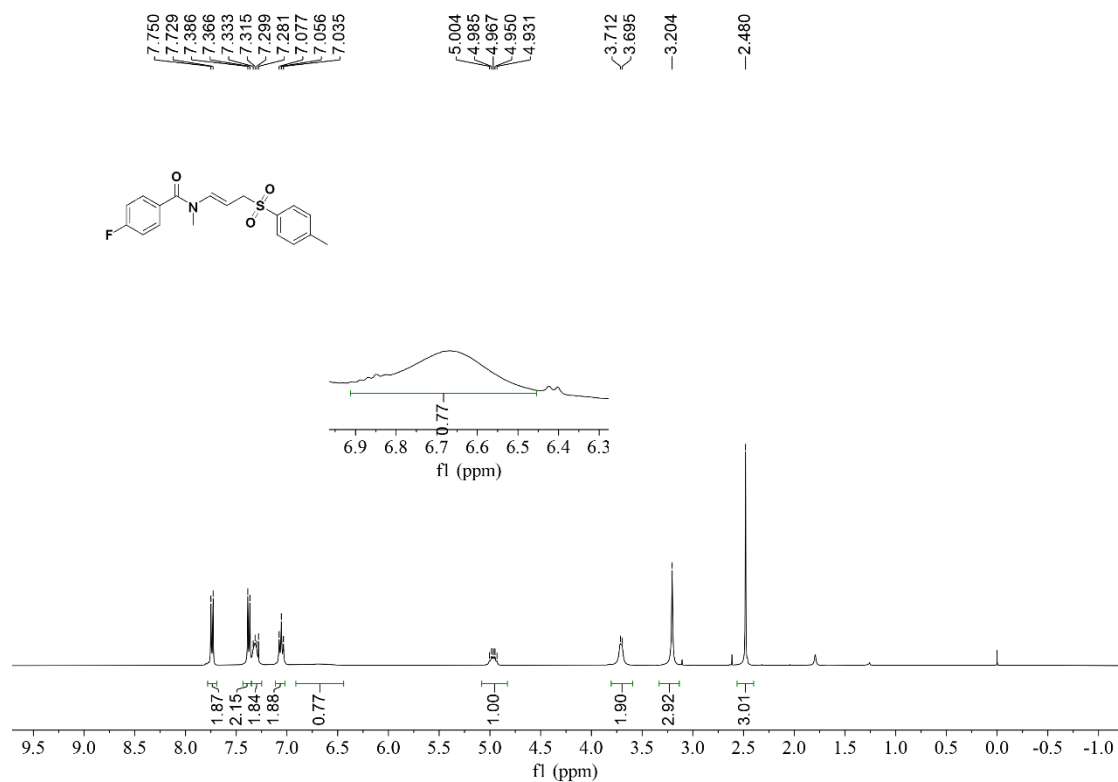
Light yellow oil; 59.2mg, 90 % yield; ^1H NMR (400 MHz, CDCl_3 ; δ , ppm) δ 7.52-7.44 (m, 6H), 7.35 (s, 5H), 5.04-4.78 (m, 1H), 4.21 (s, 2H), 3.51 (s, 2H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm) δ 170.4, 134.5, 130.8, 130.7, 129.1, 129.1, 128.7, 127.9, 127.9, 126.9, 58.2, 53.5, 29.7; HR-MS (ESI-TOF, m/z) calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 352.0983 ; found, 352.0976.

Copies of ^1H , ^{13}C NMR and ^{19}F NMR Spectra of Products 3a-3z and 3aa-3ab

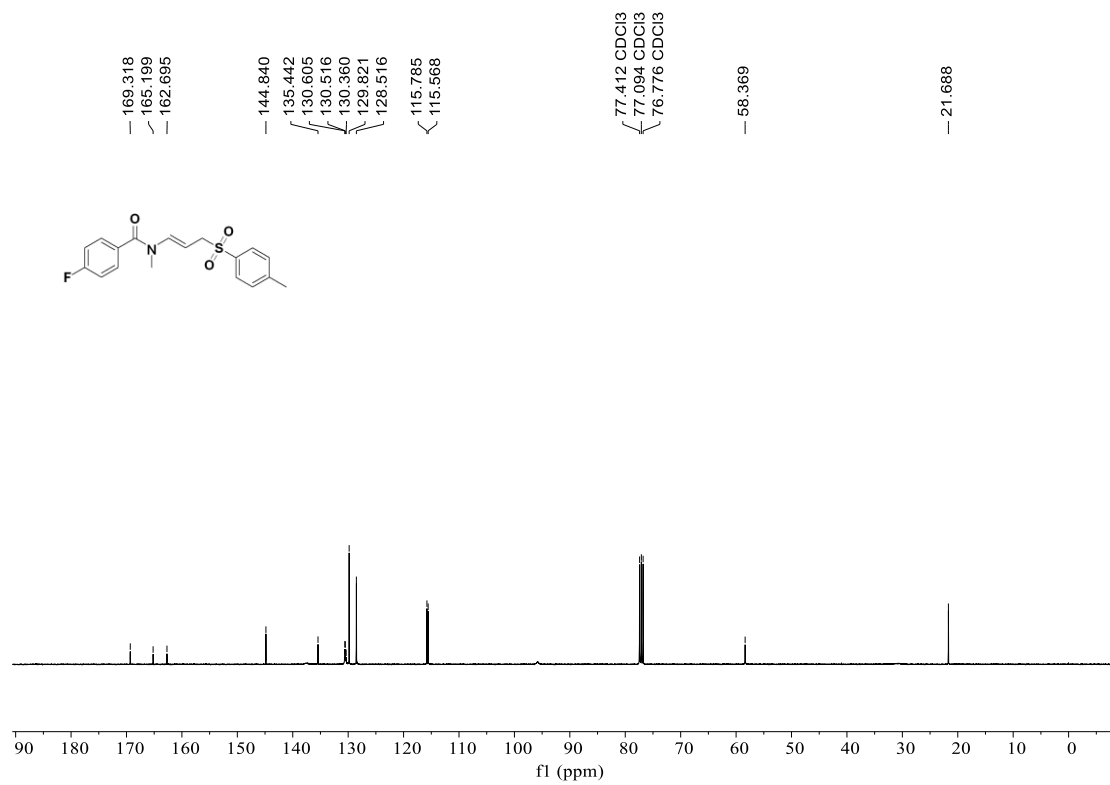




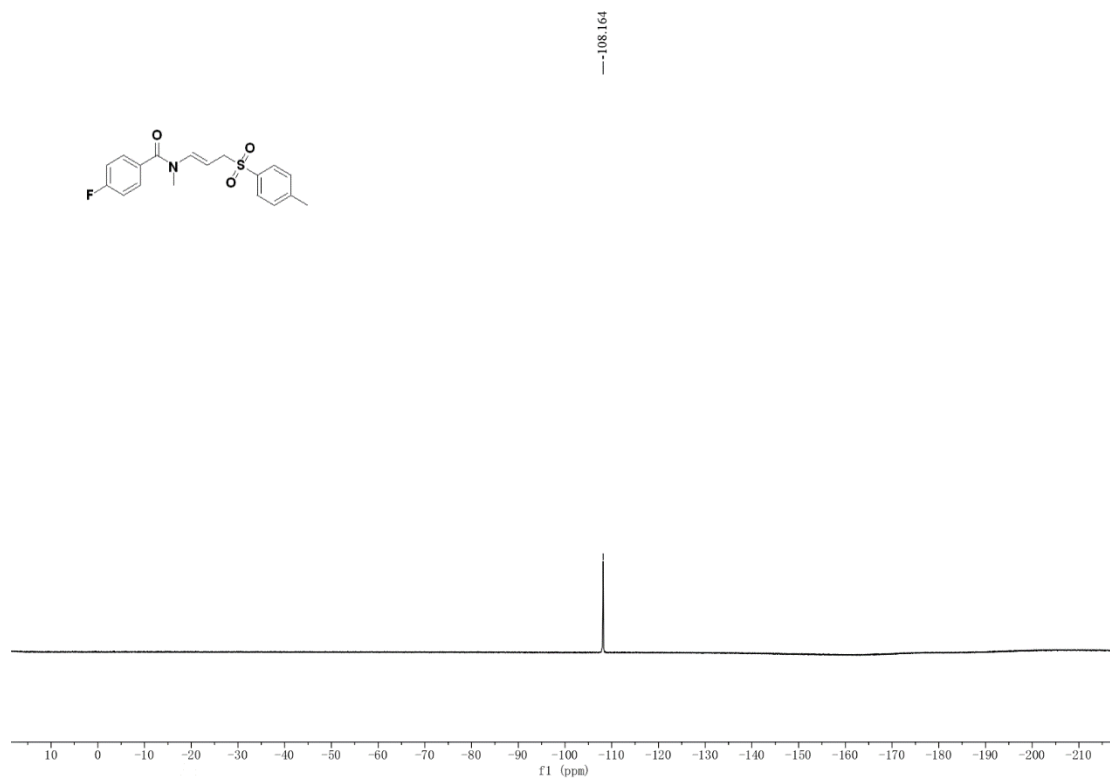
¹³C NMR Spectrum of Compound **3a**



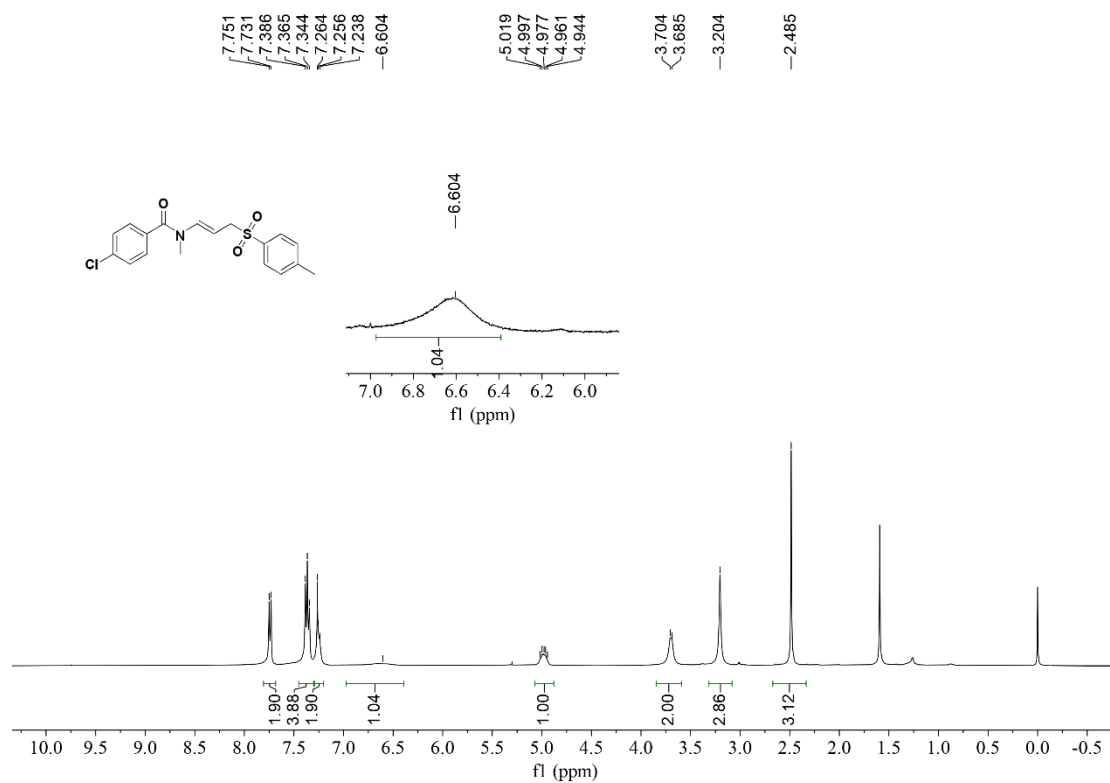
¹H NMR Spectrum of Compound **3b**



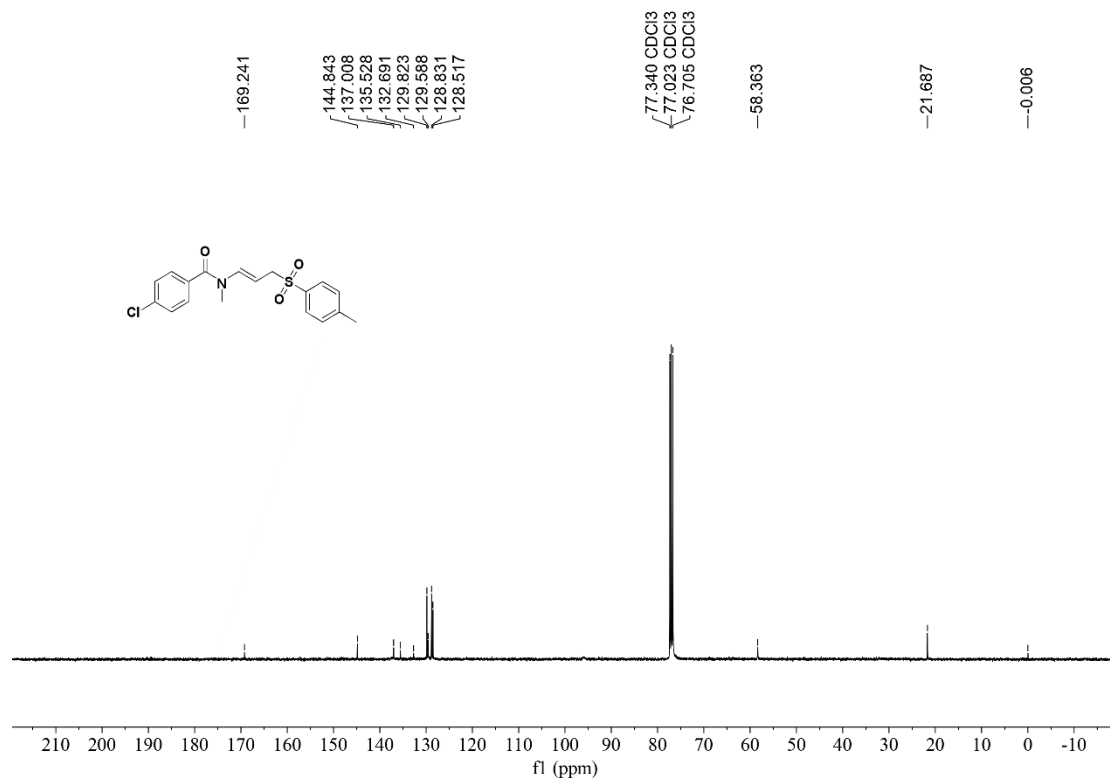
¹³C NMR Spectrum of Compound **3b**



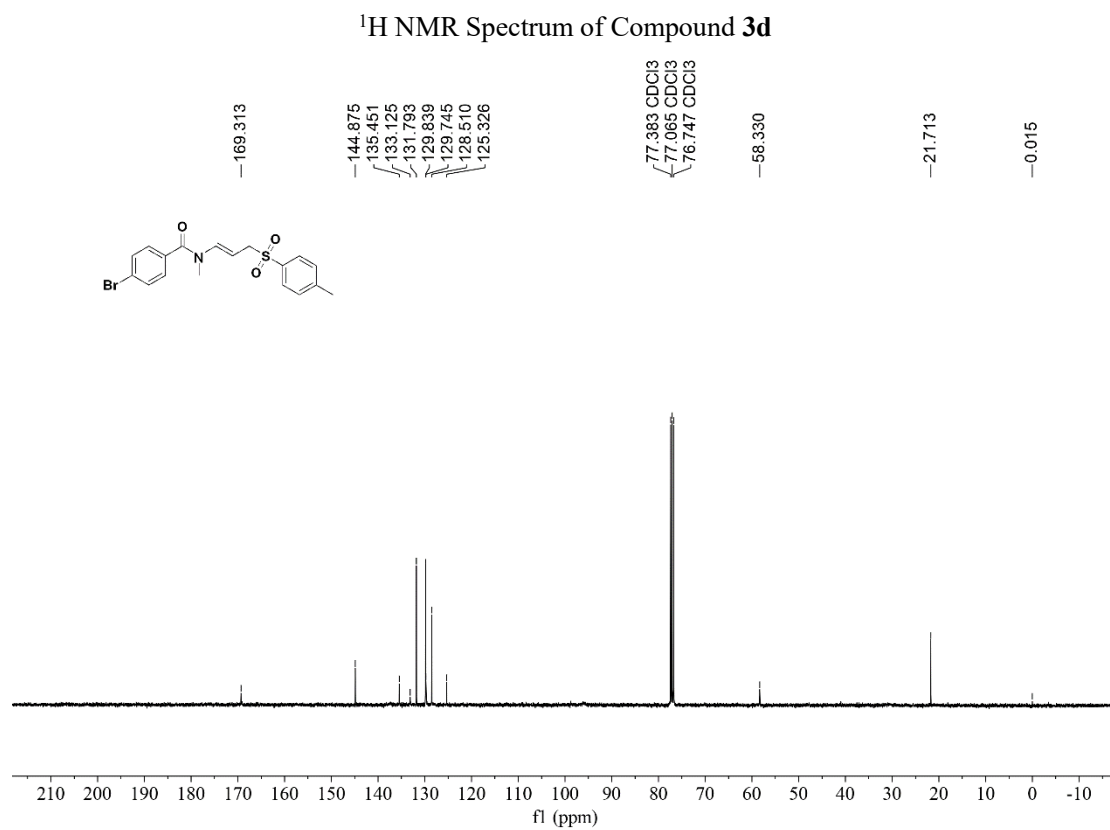
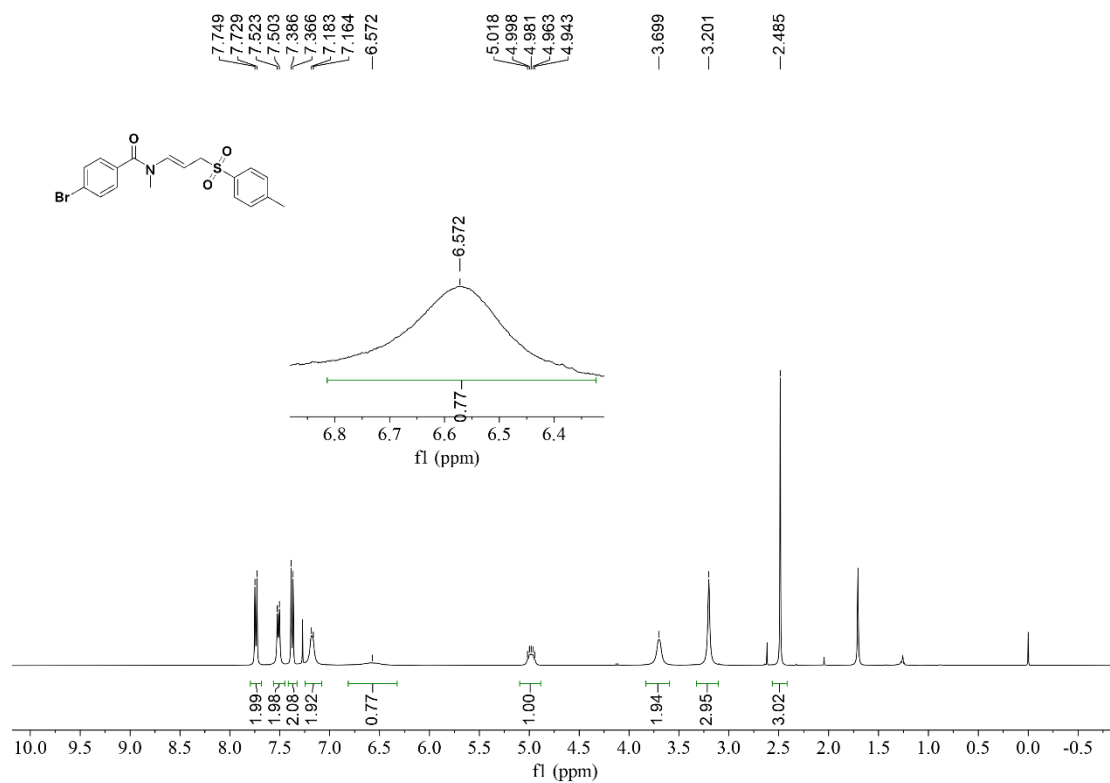
¹⁹F NMR Spectrum of Compound **3b**

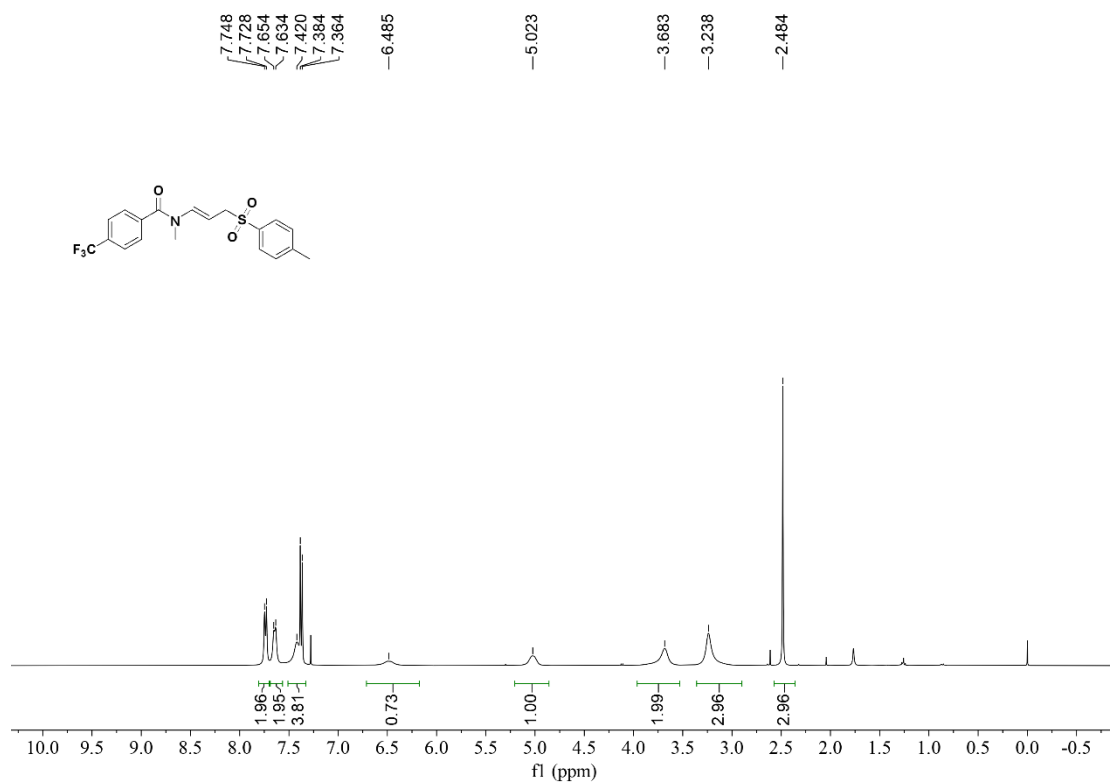


¹H NMR Spectrum of Compound 3c

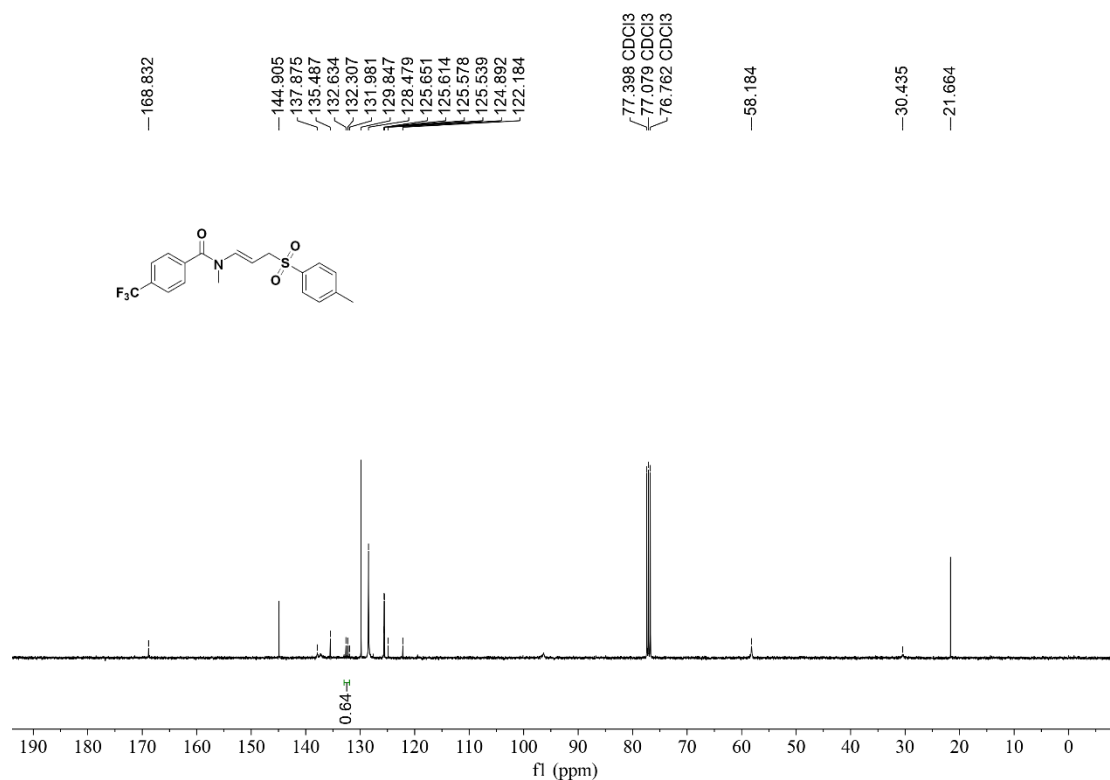


¹³C NMR Spectrum of Compound 3c

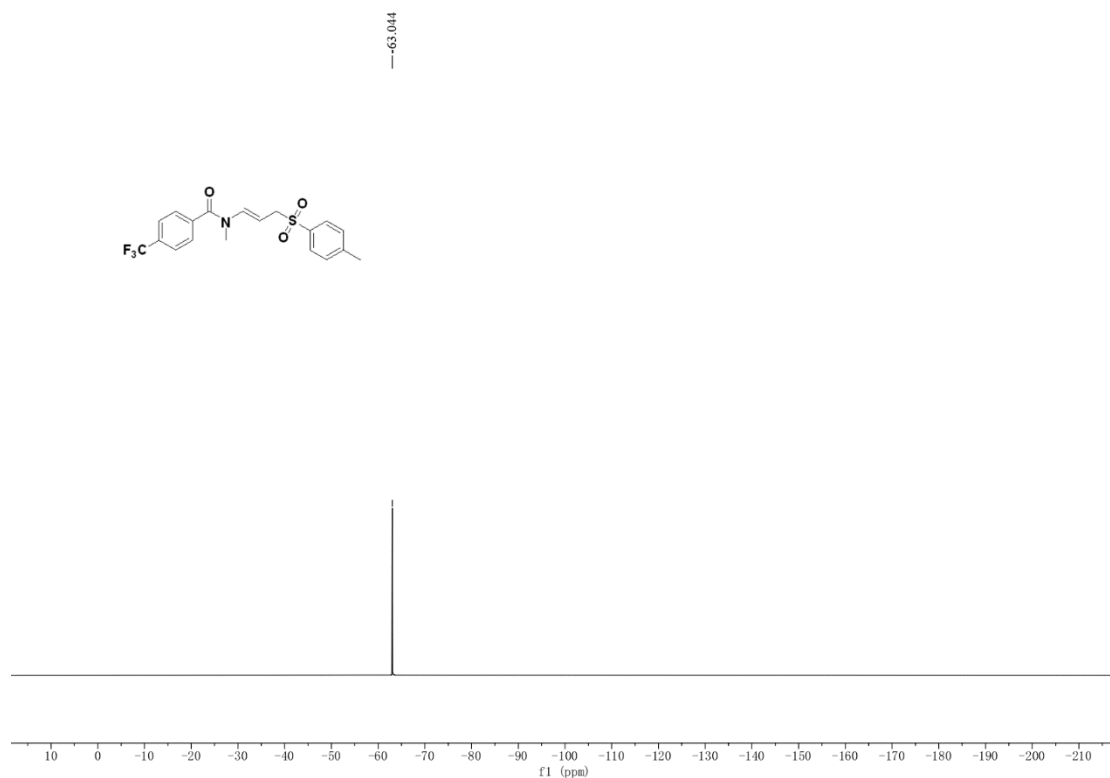




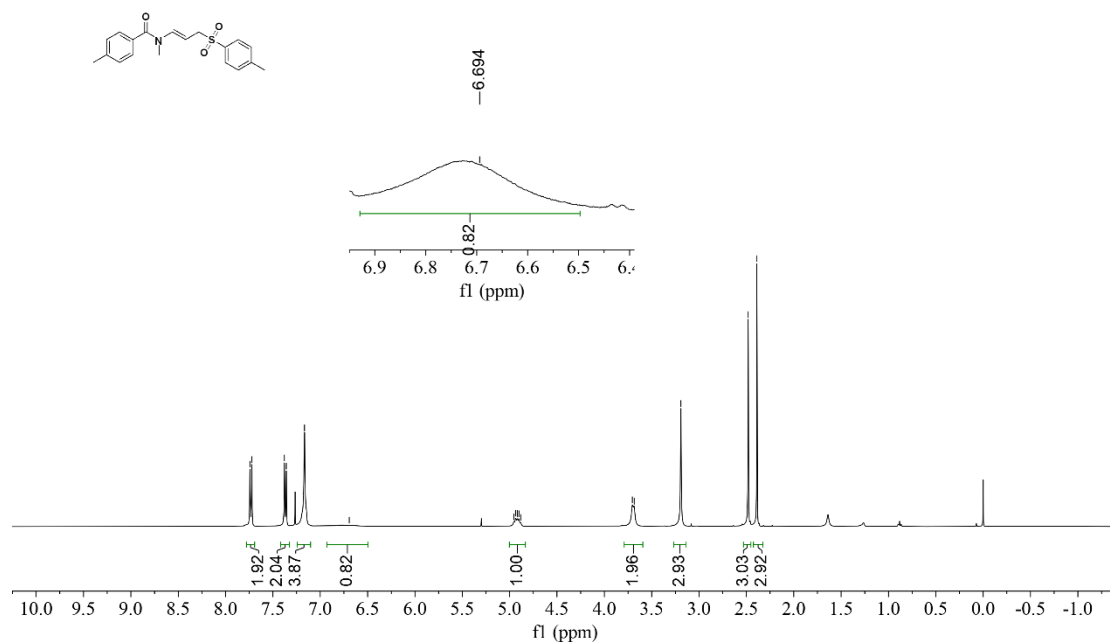
¹H NMR Spectrum of Compound **3e**



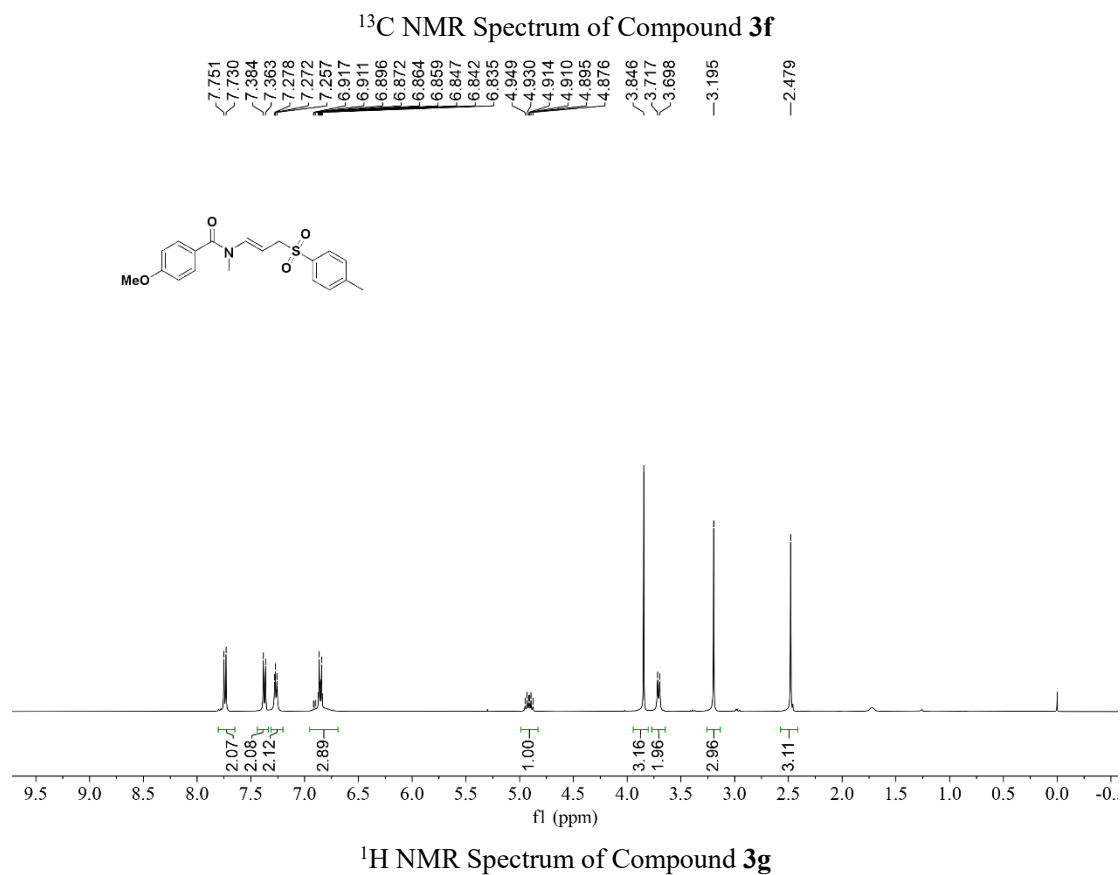
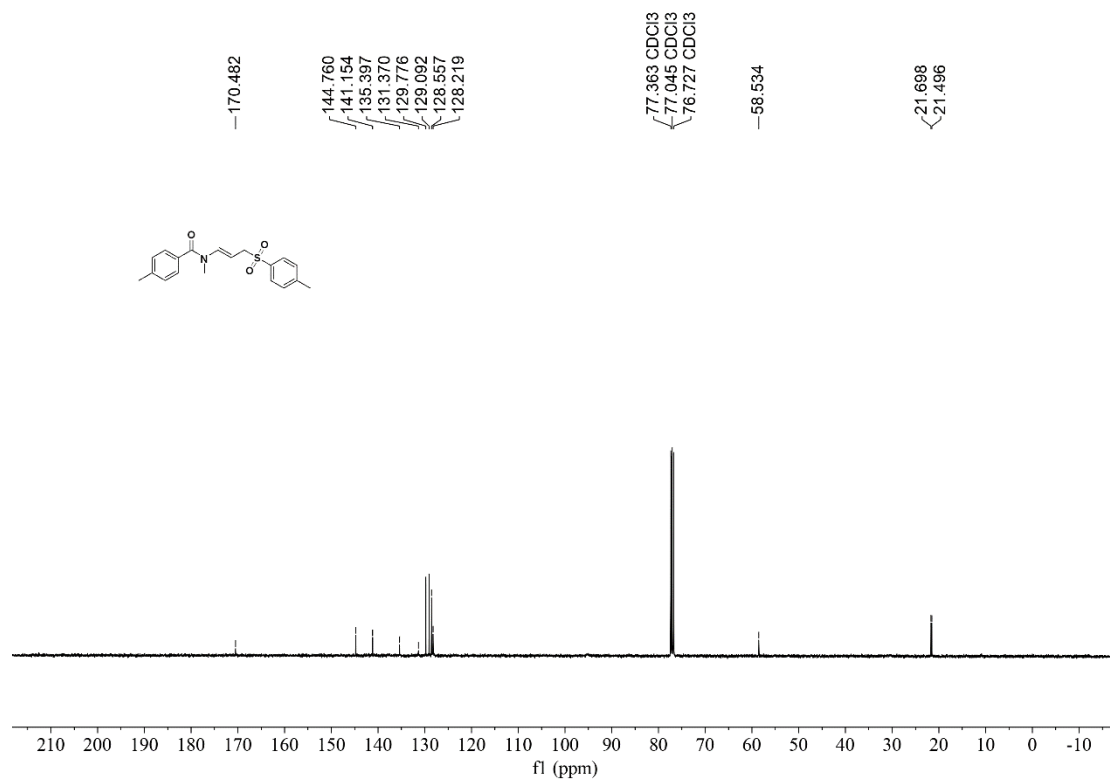
¹³C NMR Spectrum of Compound **3e**

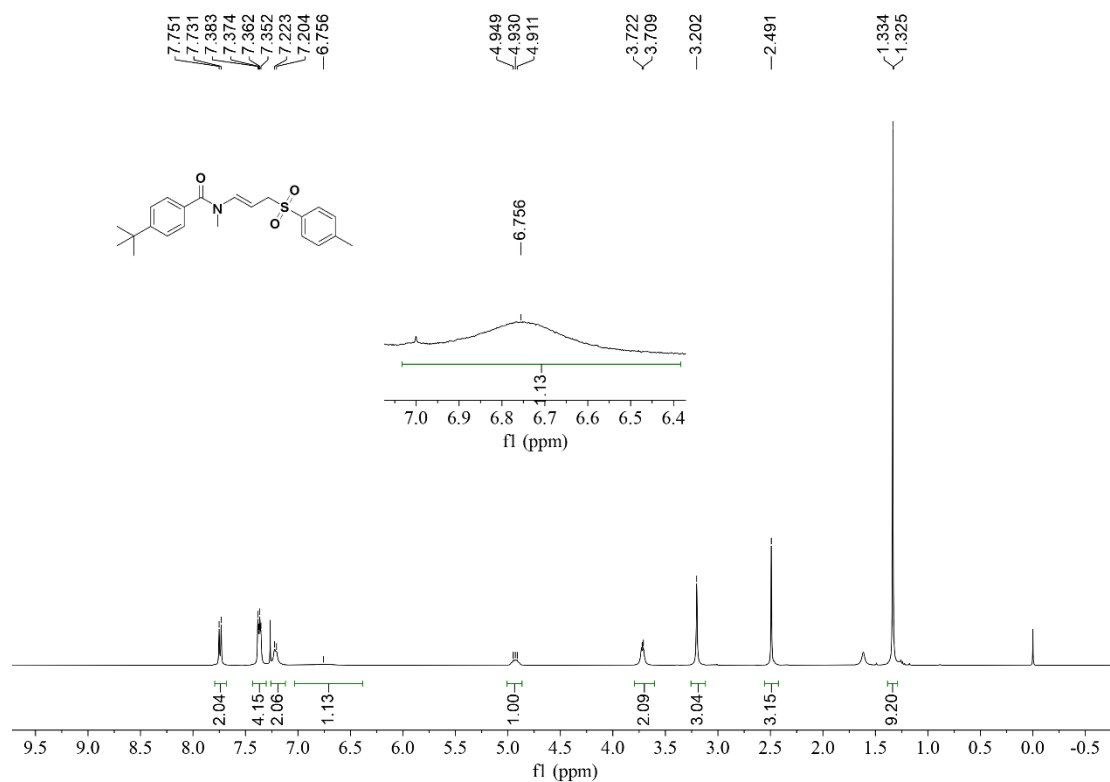
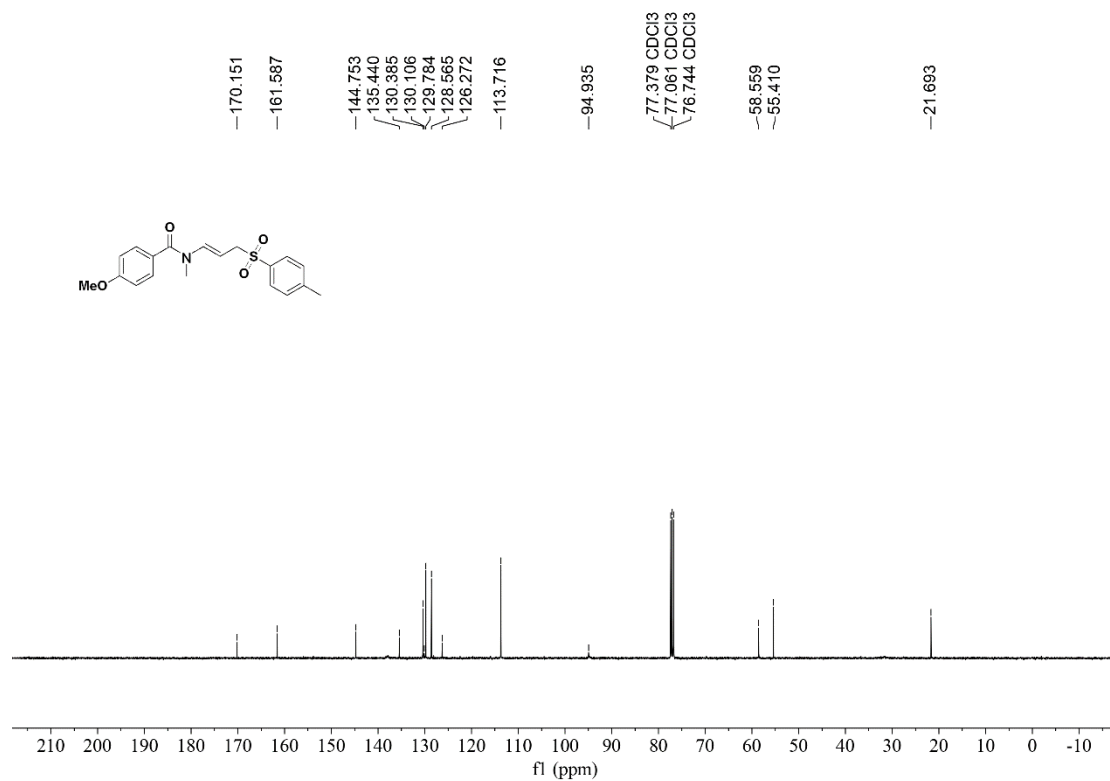


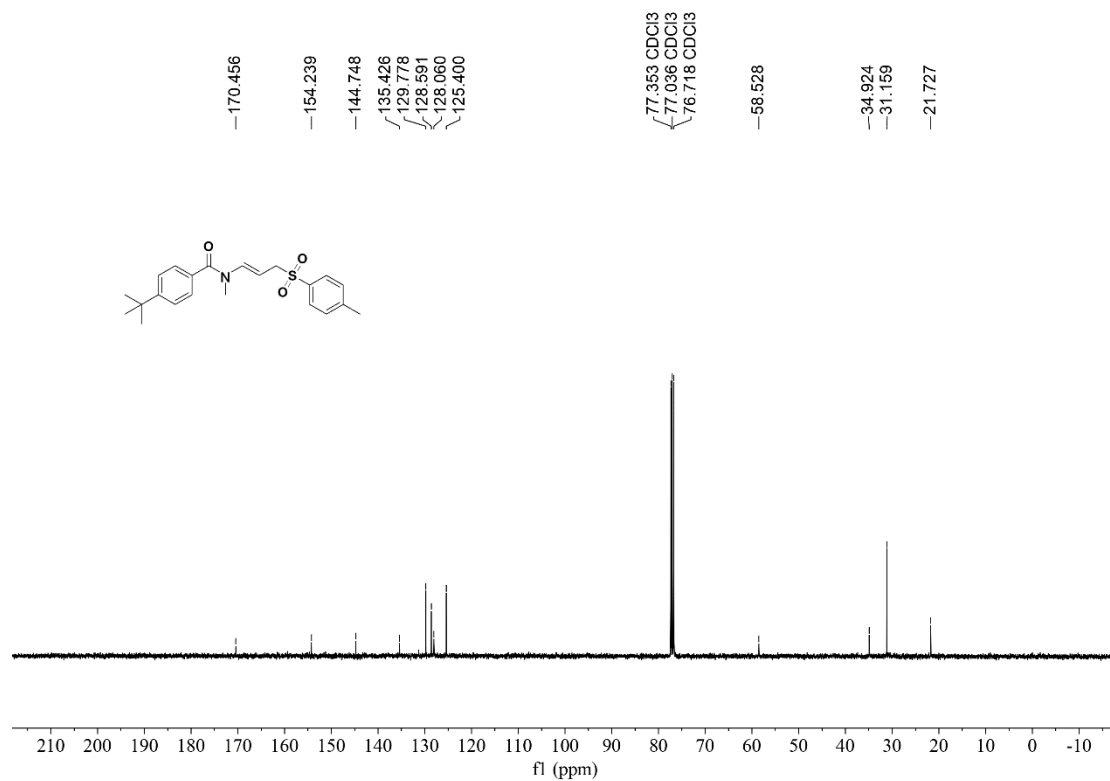
¹⁹F NMR Spectrum of Compound **3e**



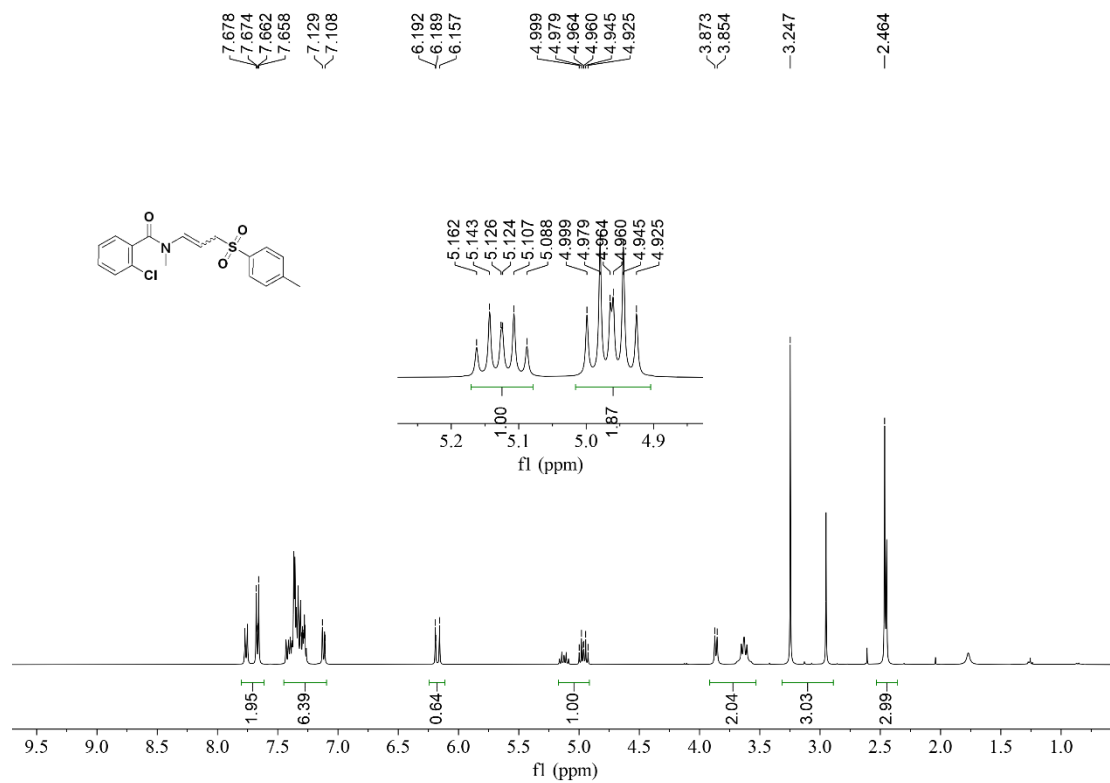
¹H NMR Spectrum of Compound **3f**



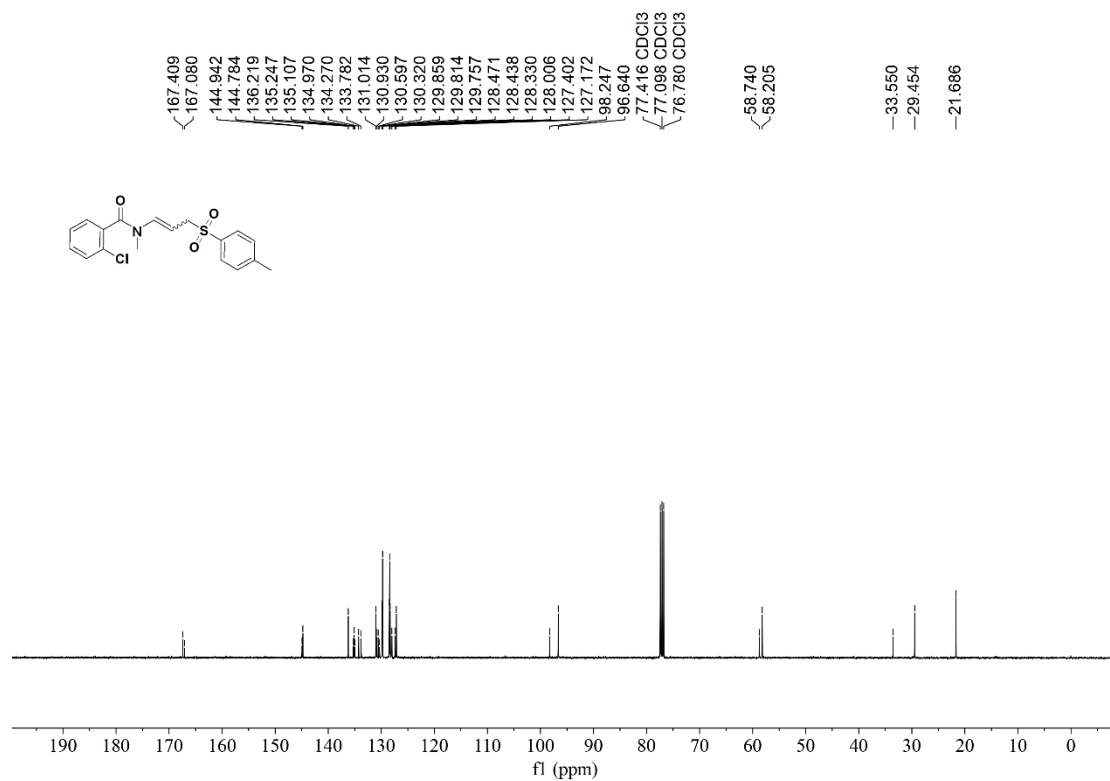




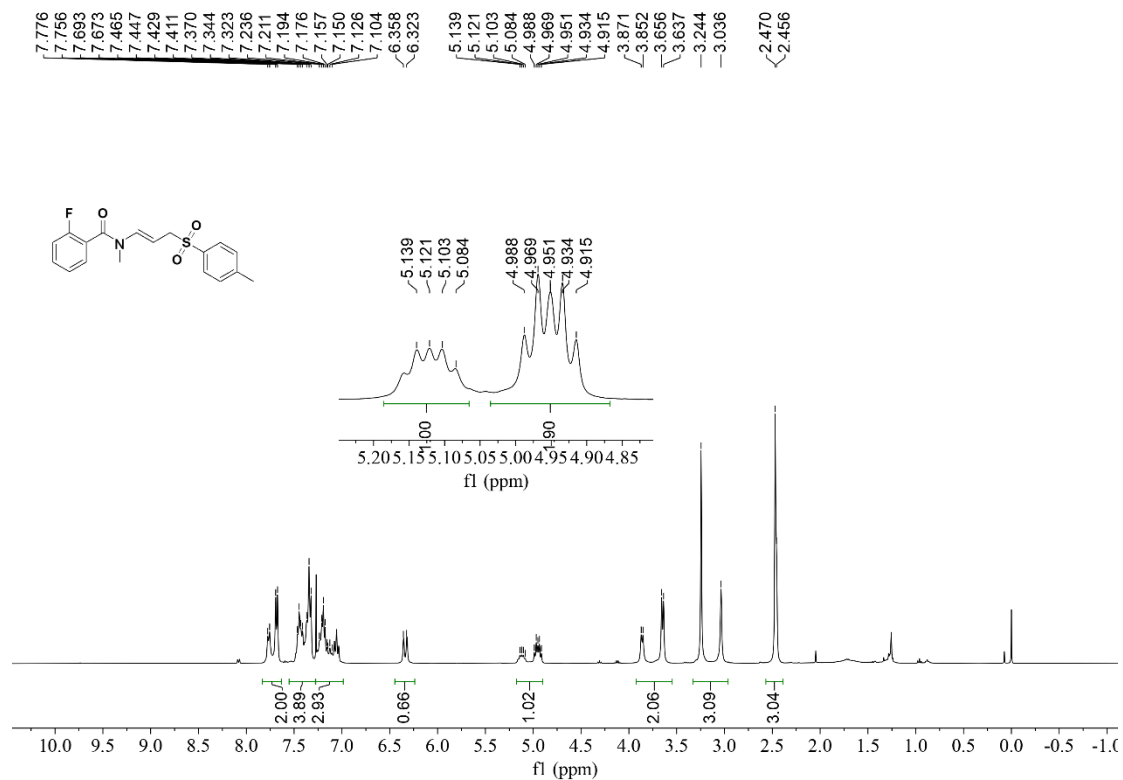
¹³C NMR Spectrum of Compound 3h



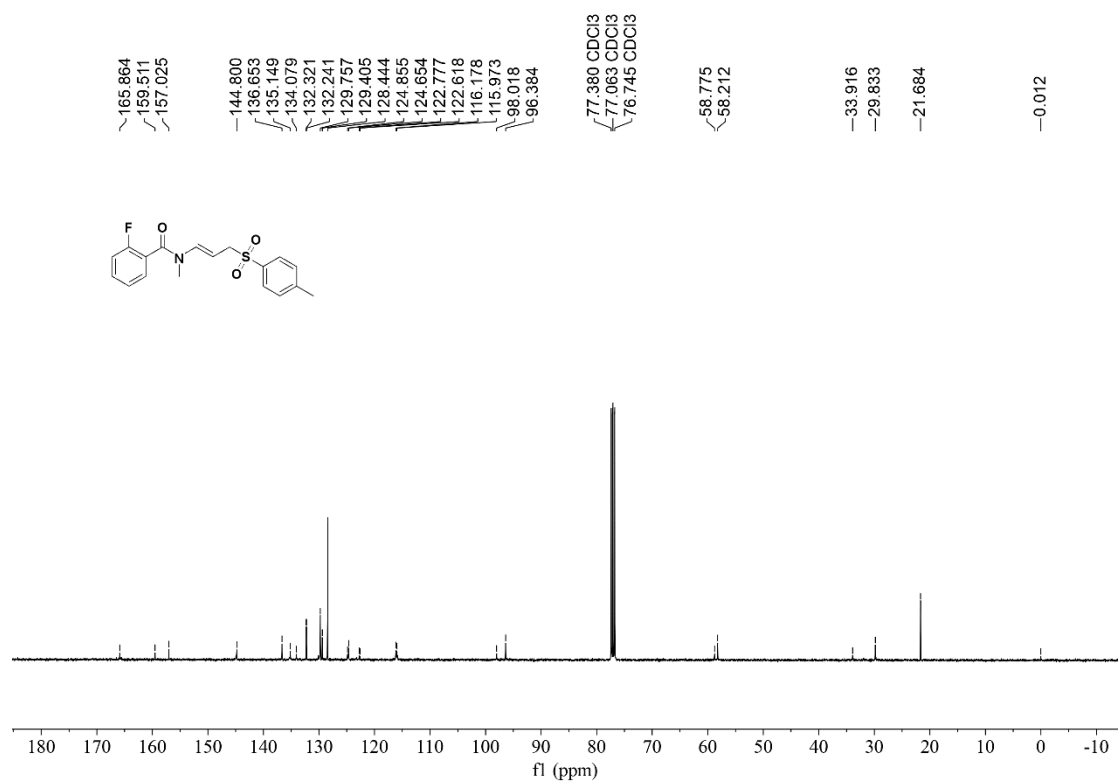
¹H NMR Spectrum of Compound 3i



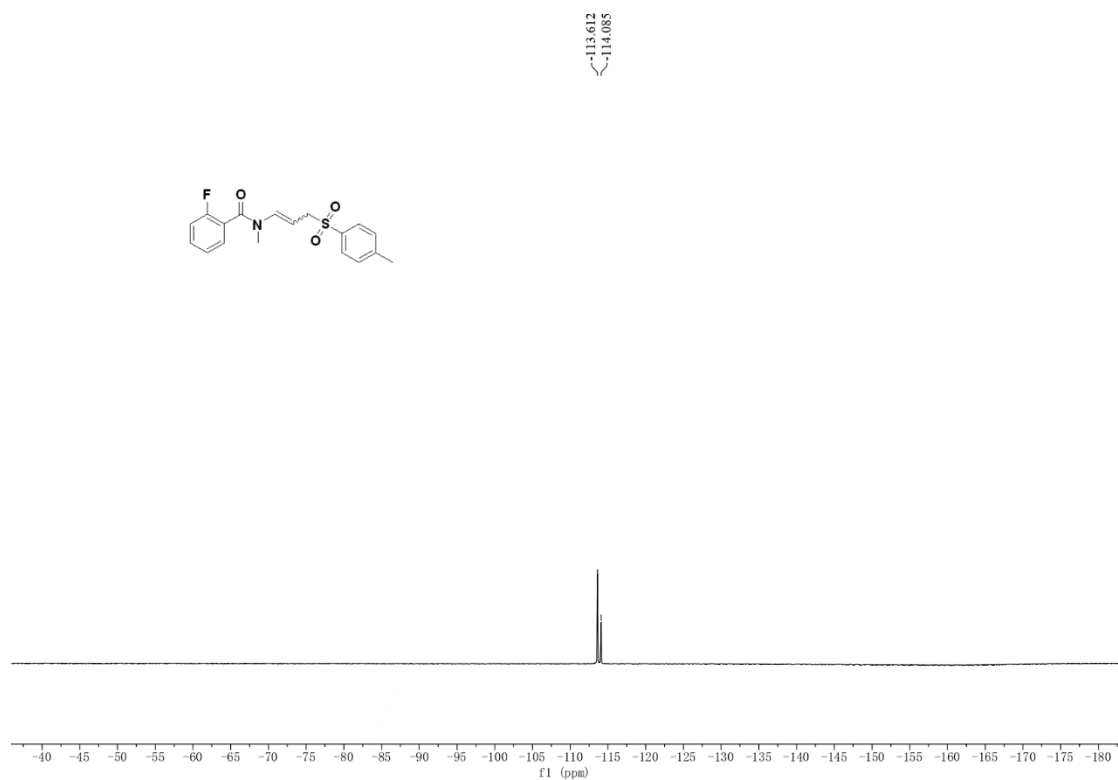
¹³C NMR Spectrum of Compound 3i



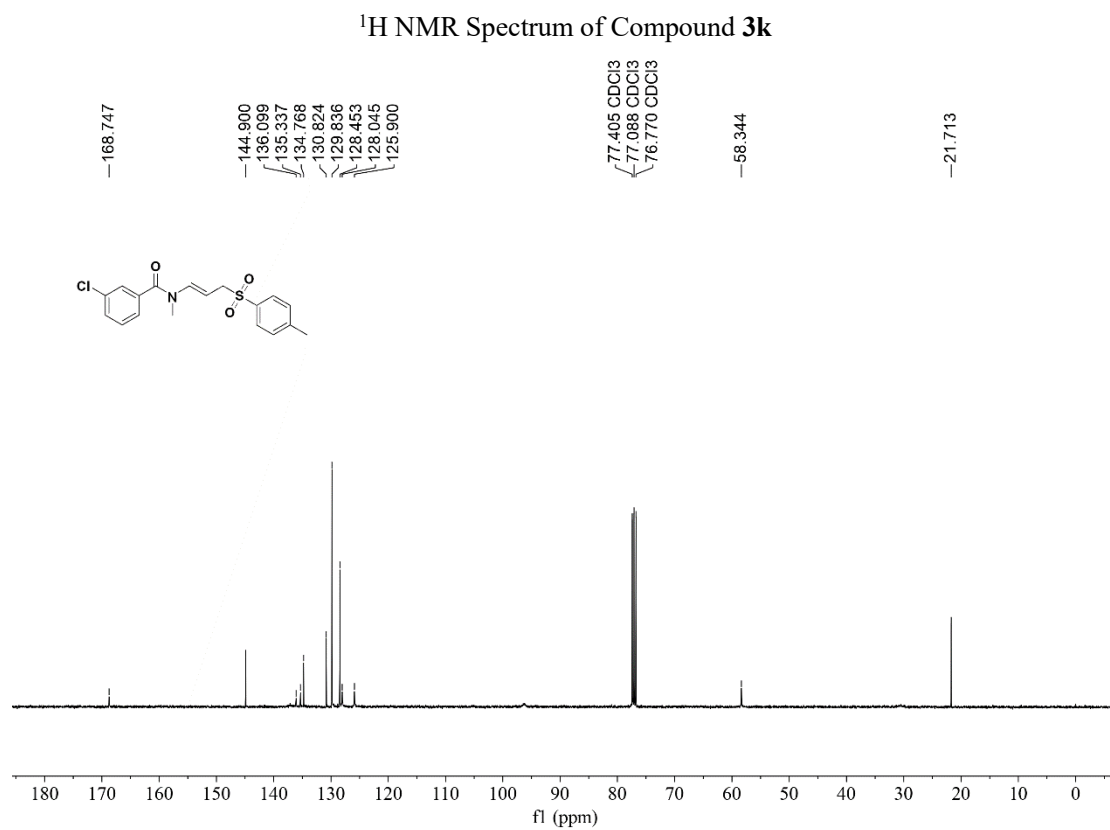
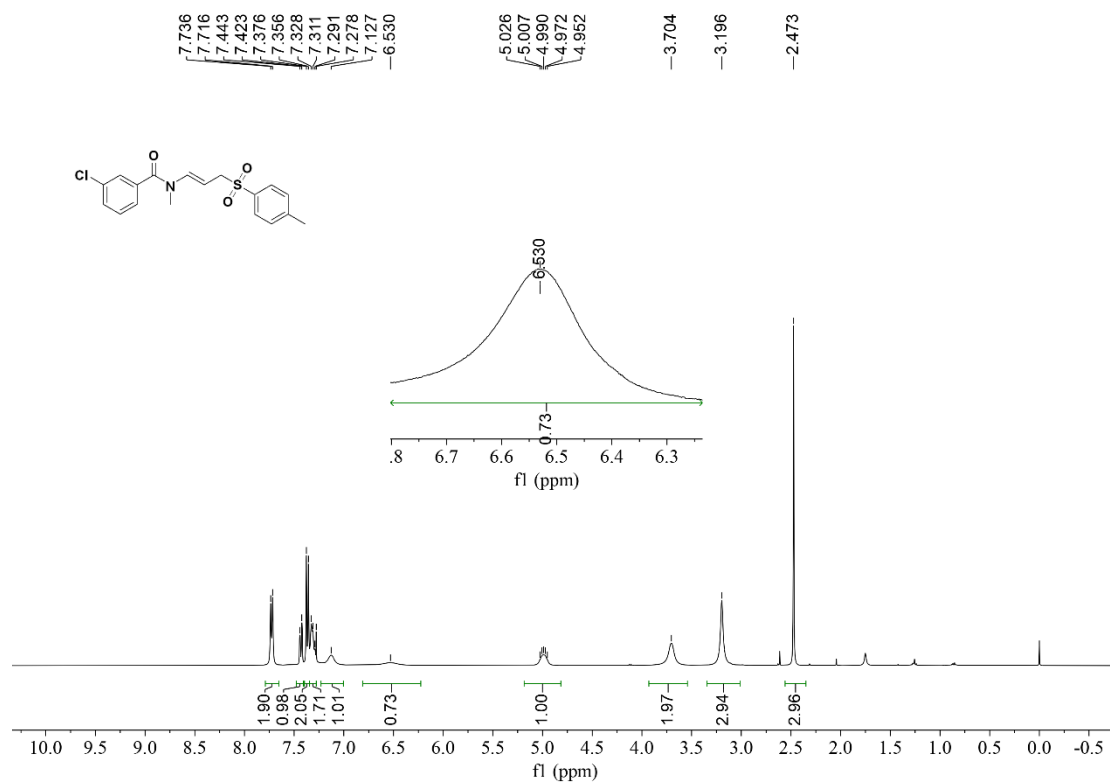
¹H NMR Spectrum of Compound 3j

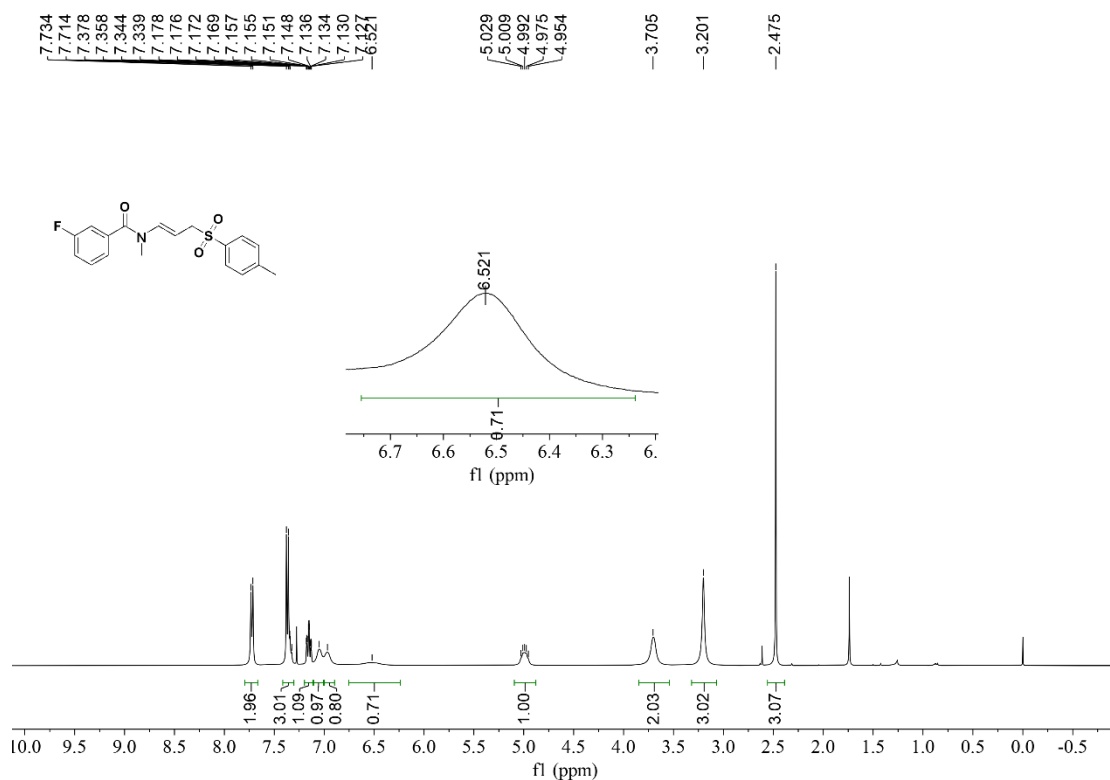


¹³C NMR Spectrum of Compound 3j

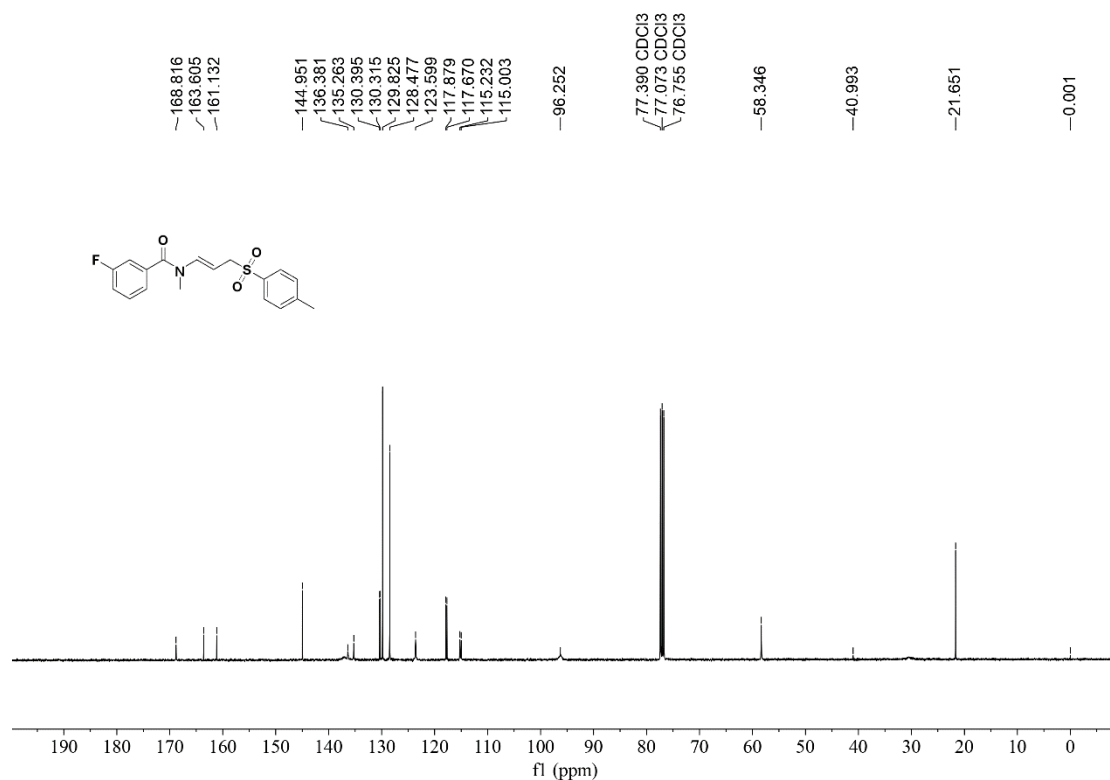


¹⁹F NMR Spectrum of Compound 3j

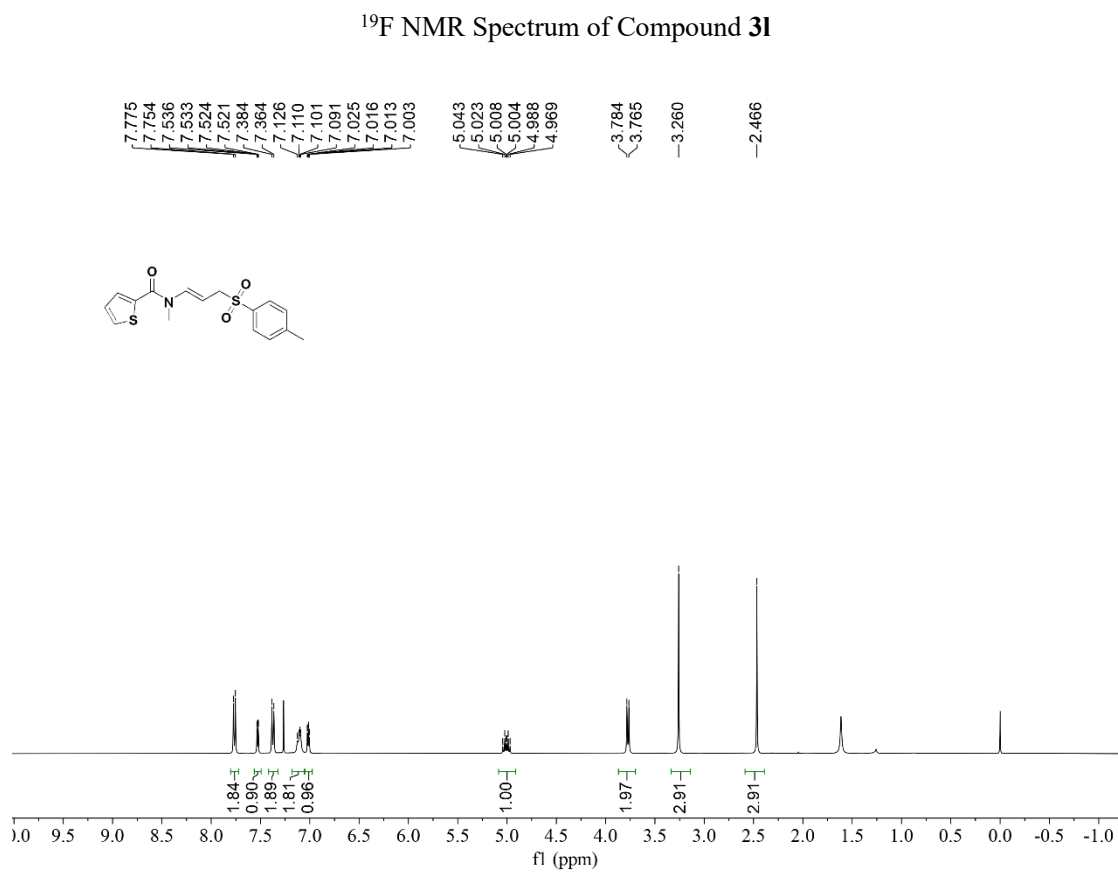
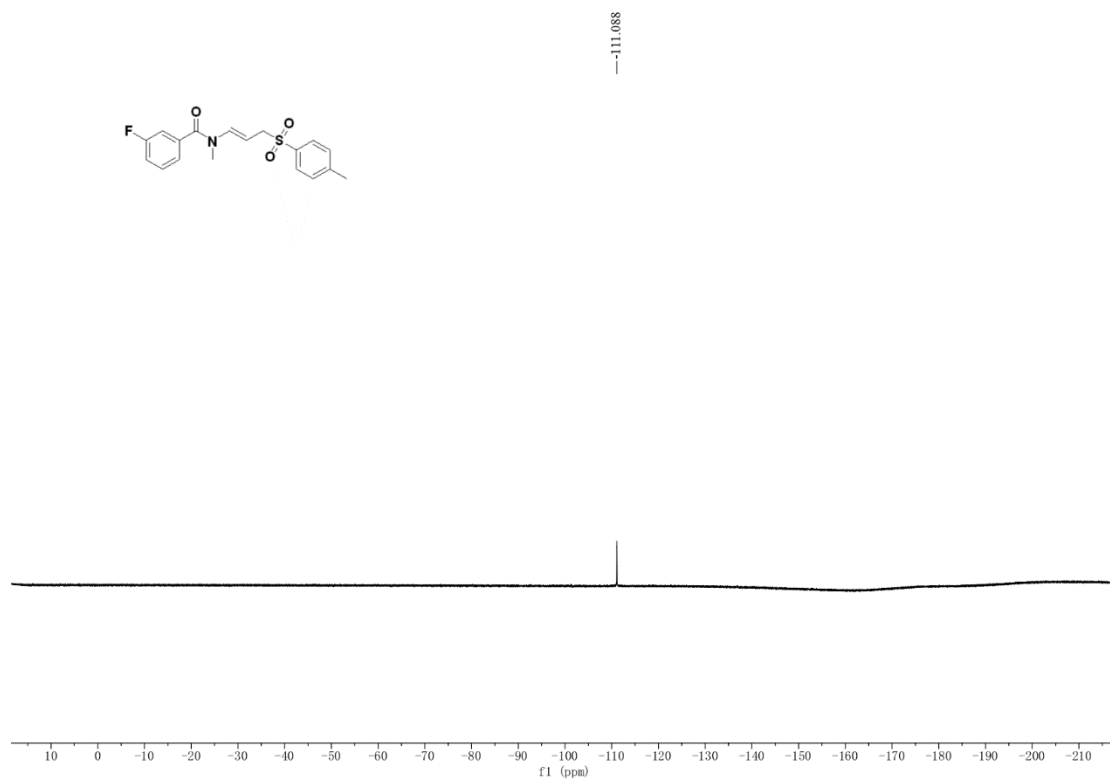


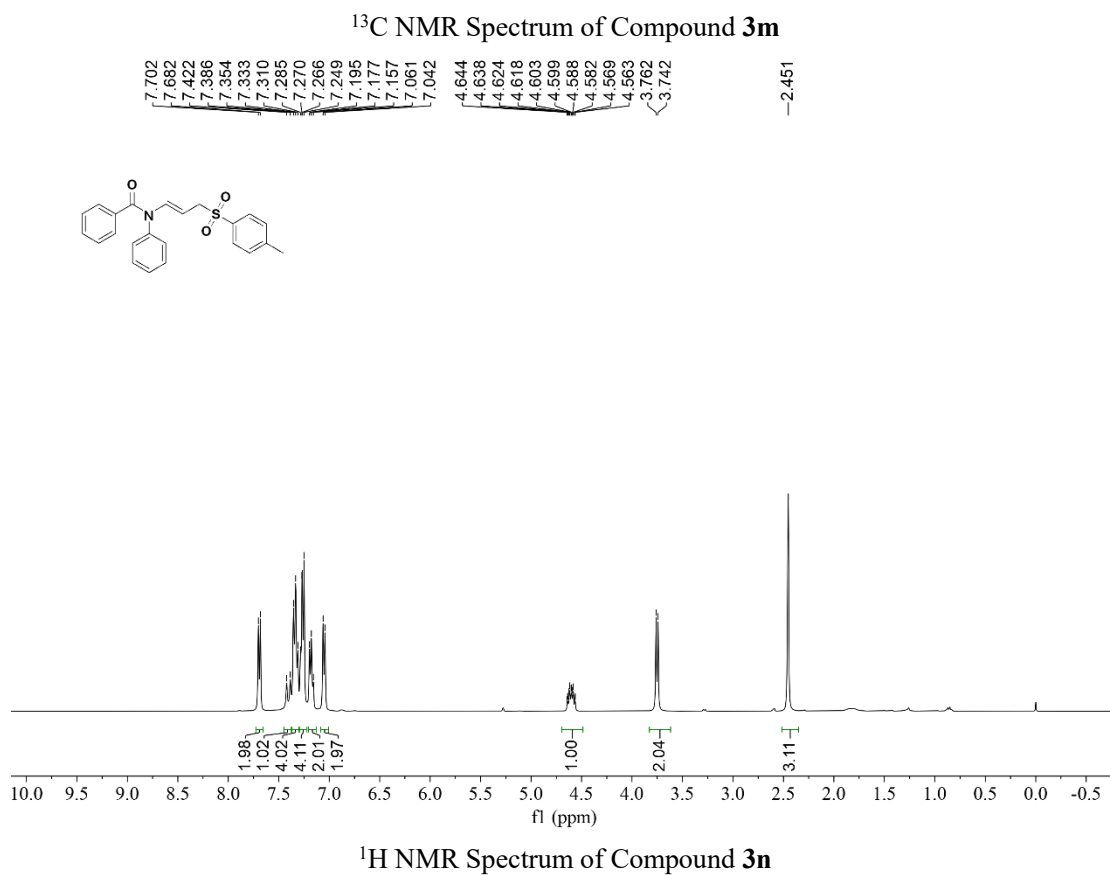
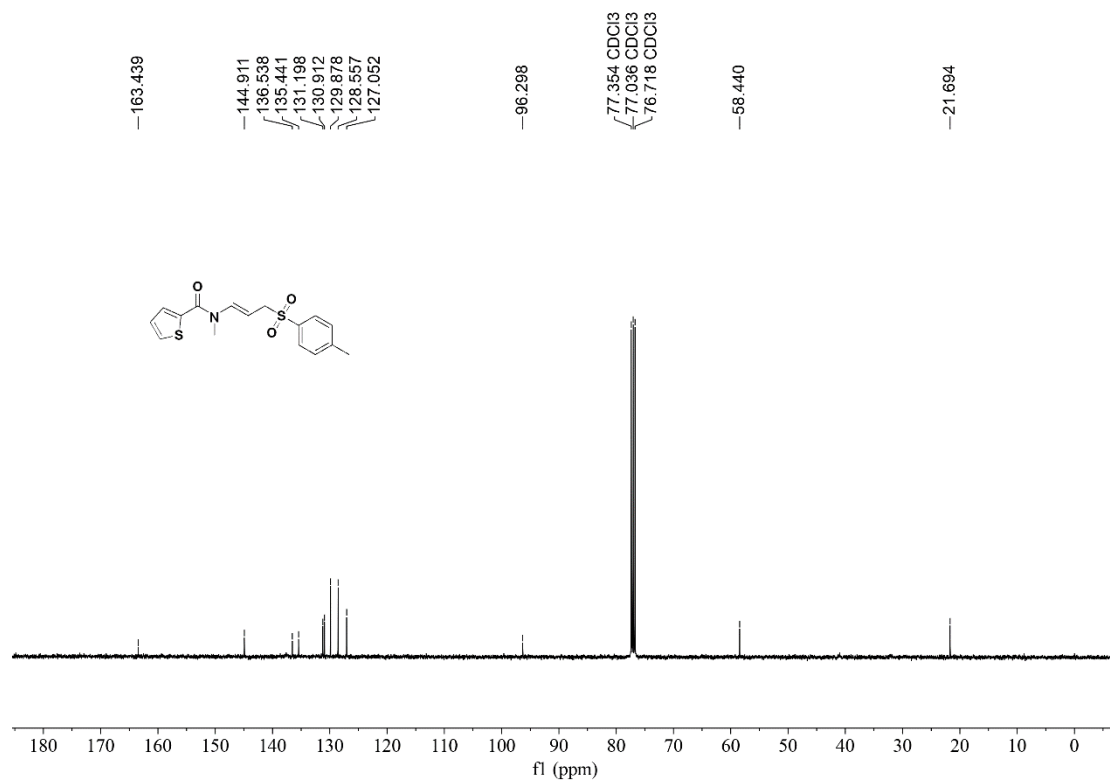


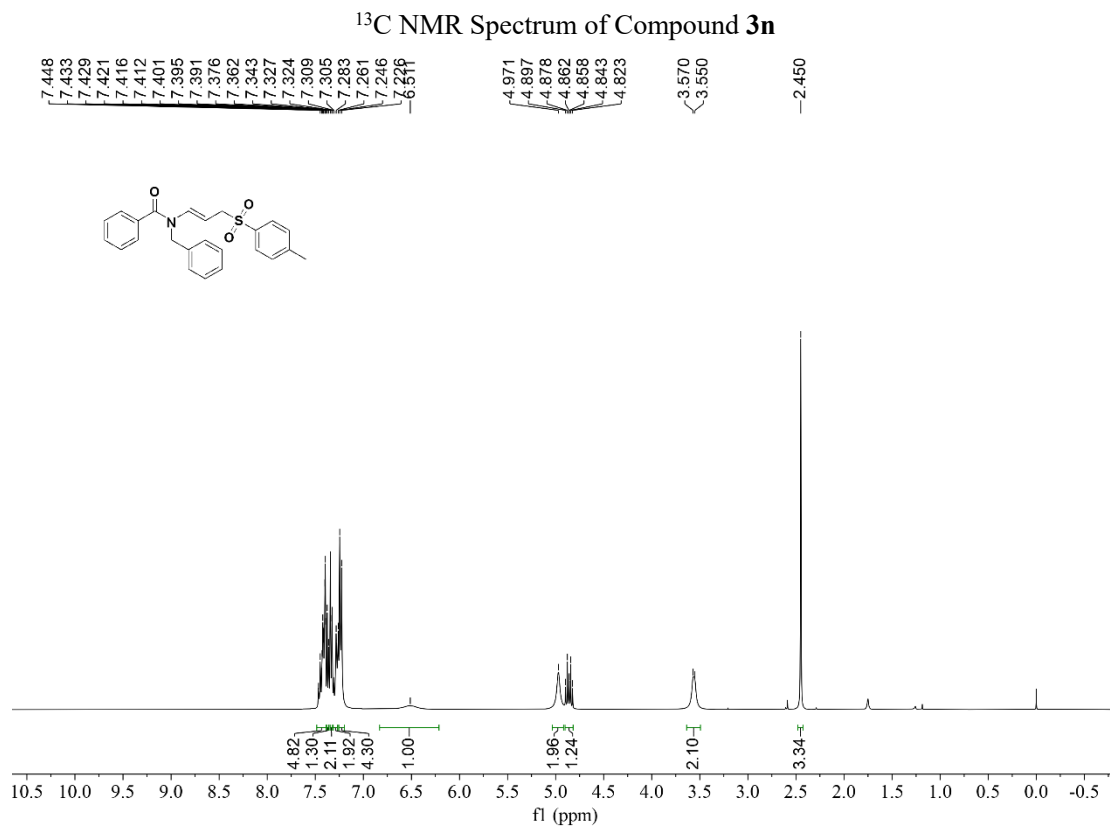
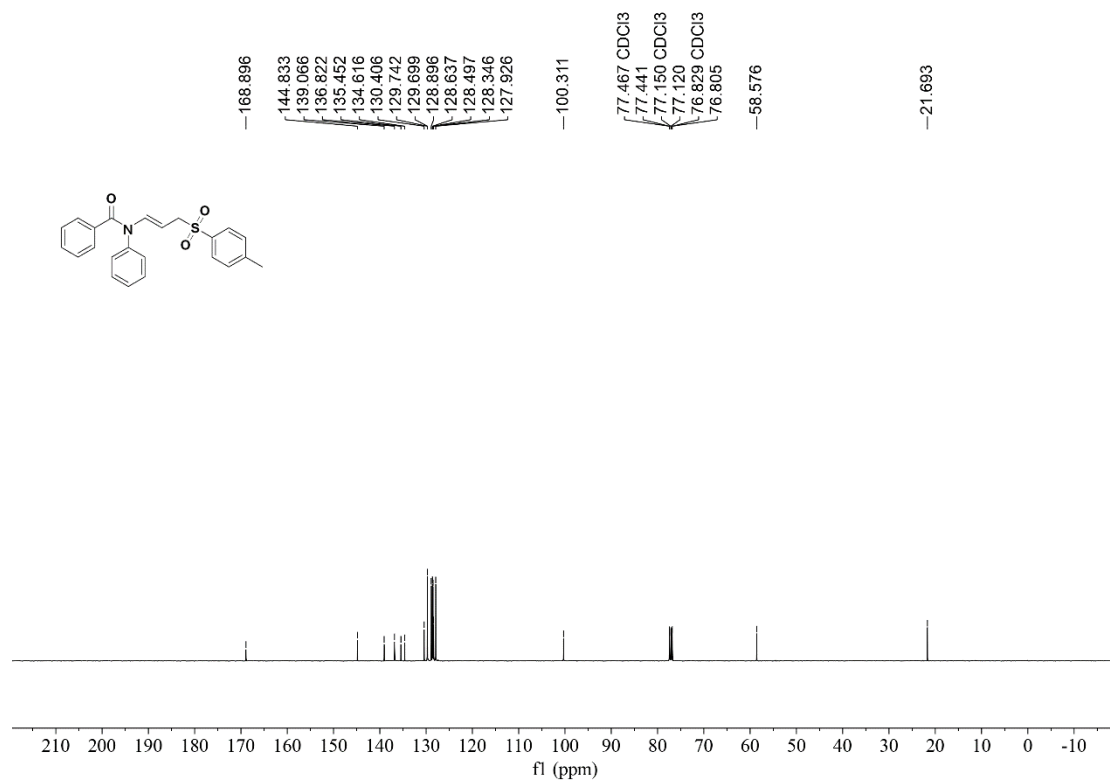
¹H NMR Spectrum of Compound 31

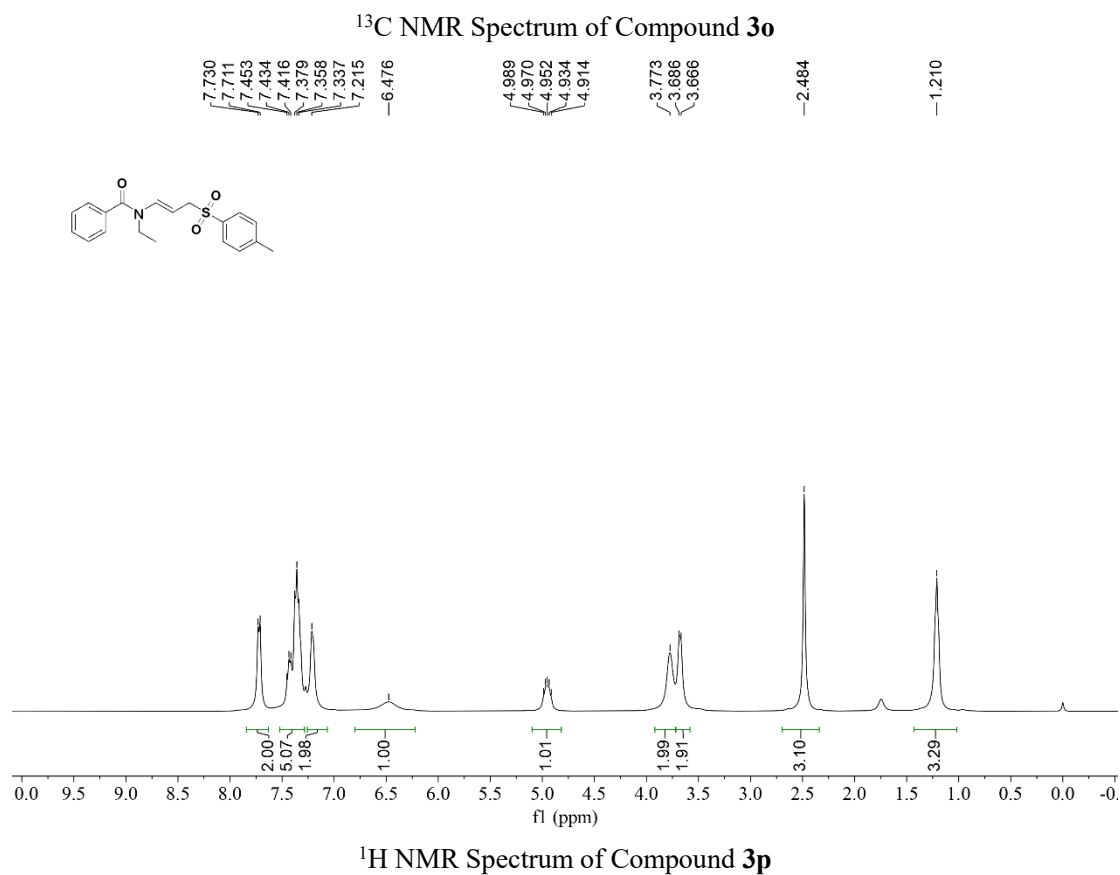
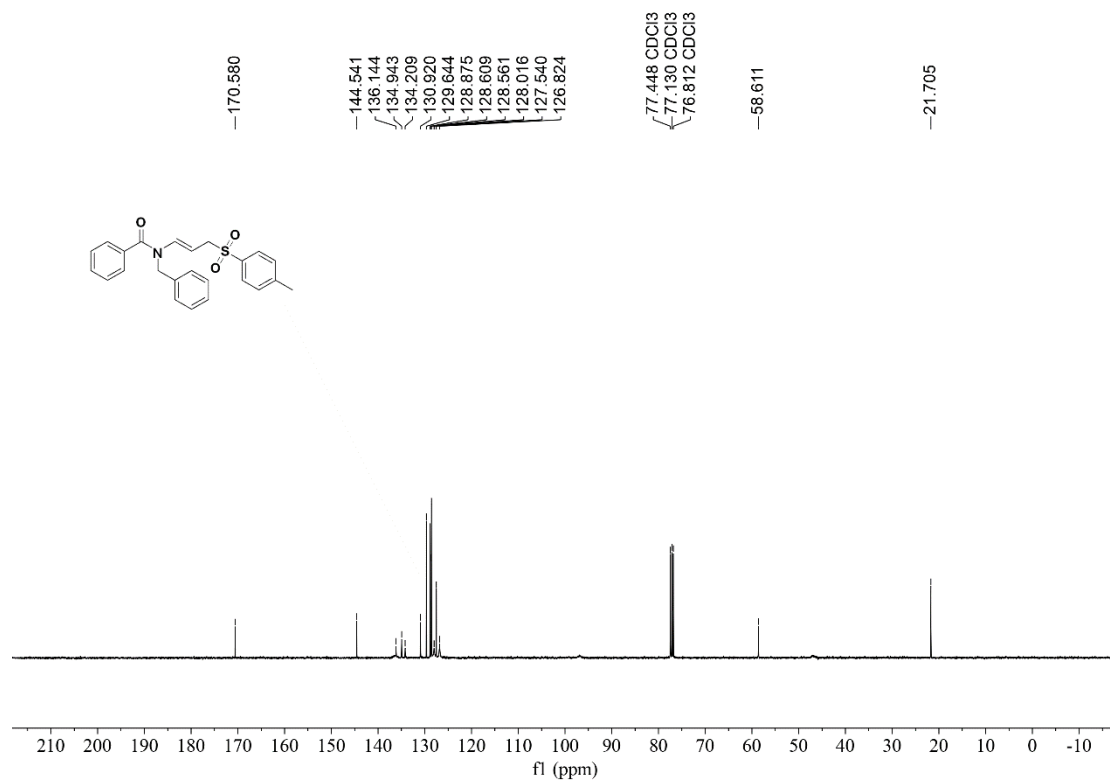


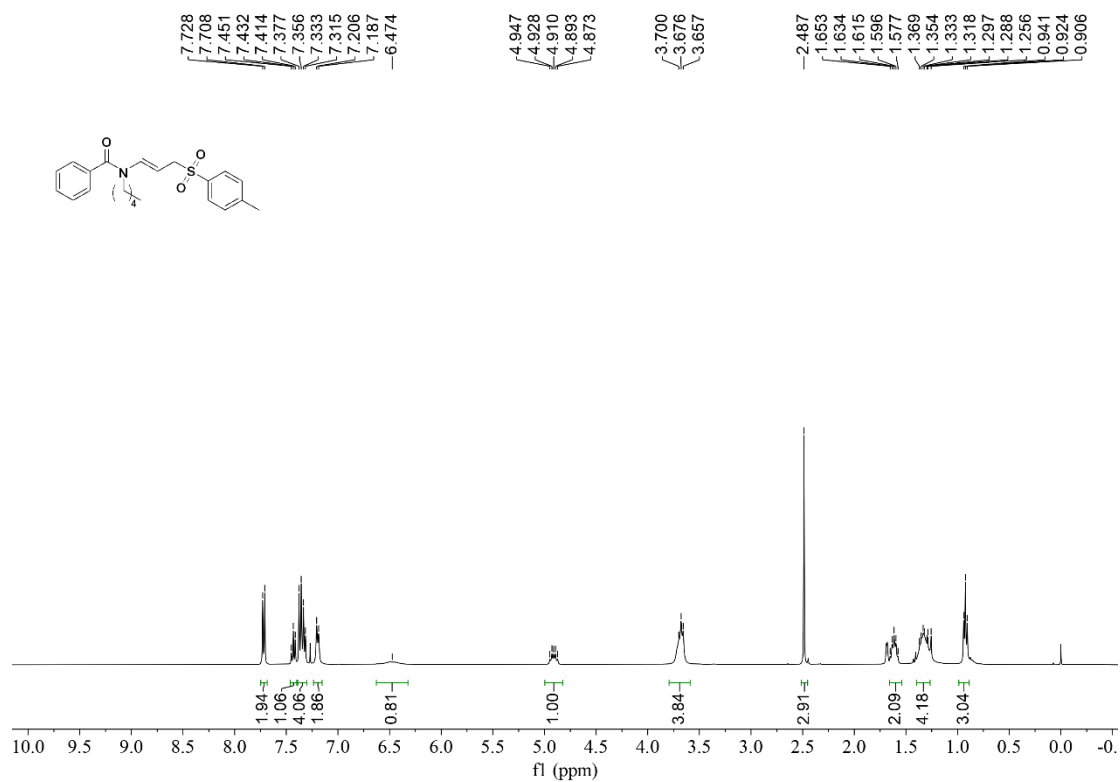
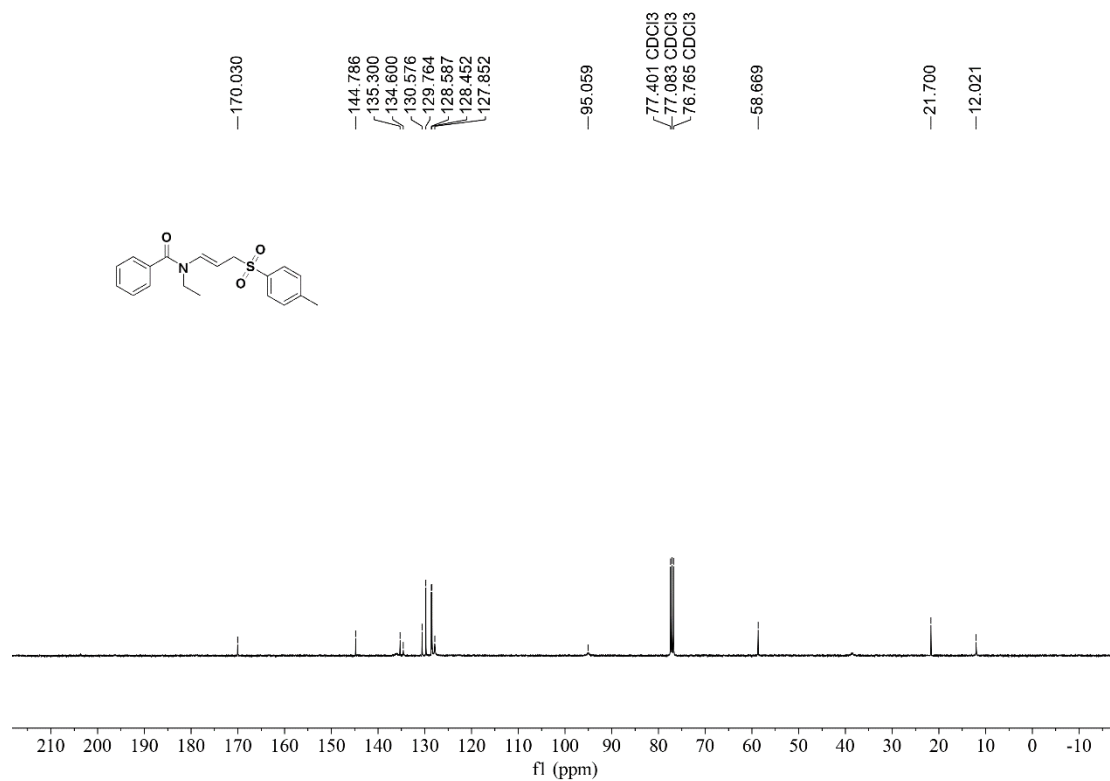
¹³C NMR Spectrum of Compound 31

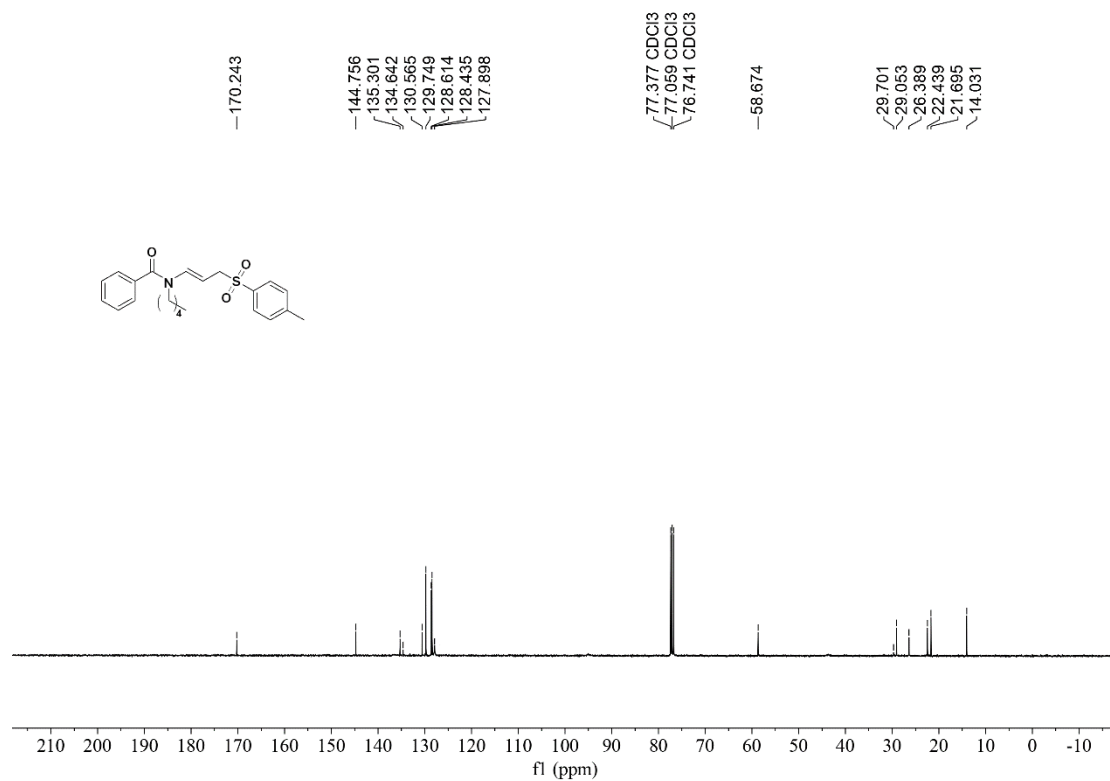




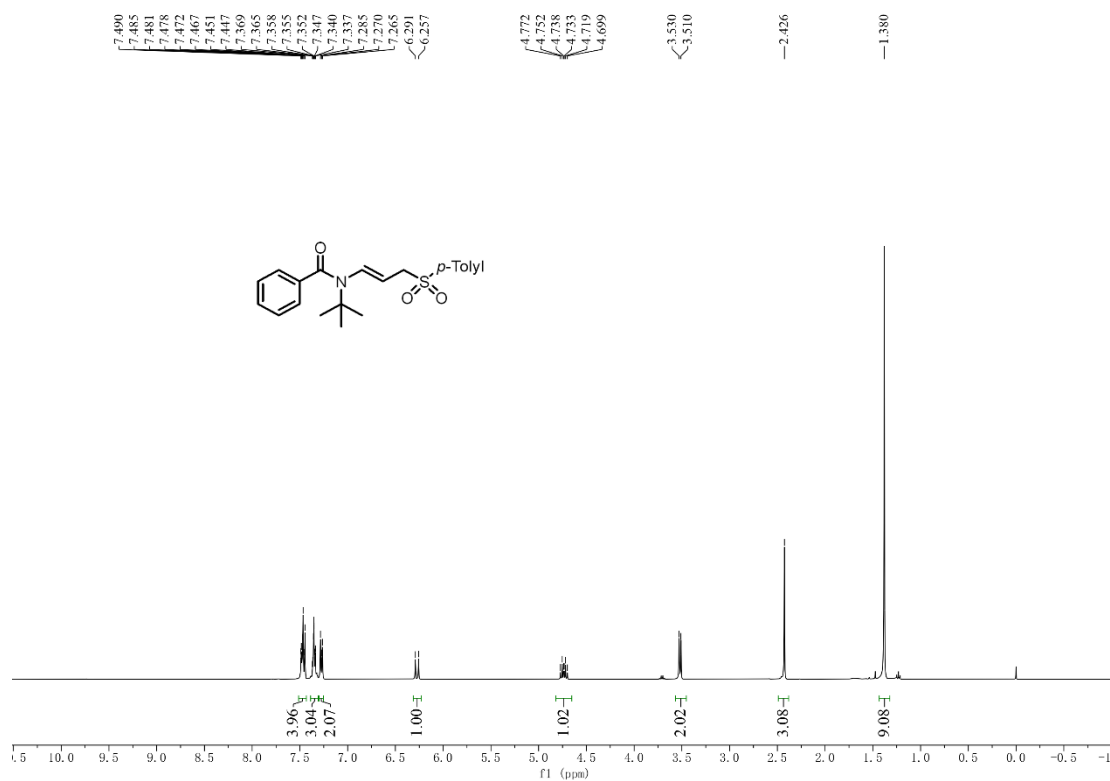




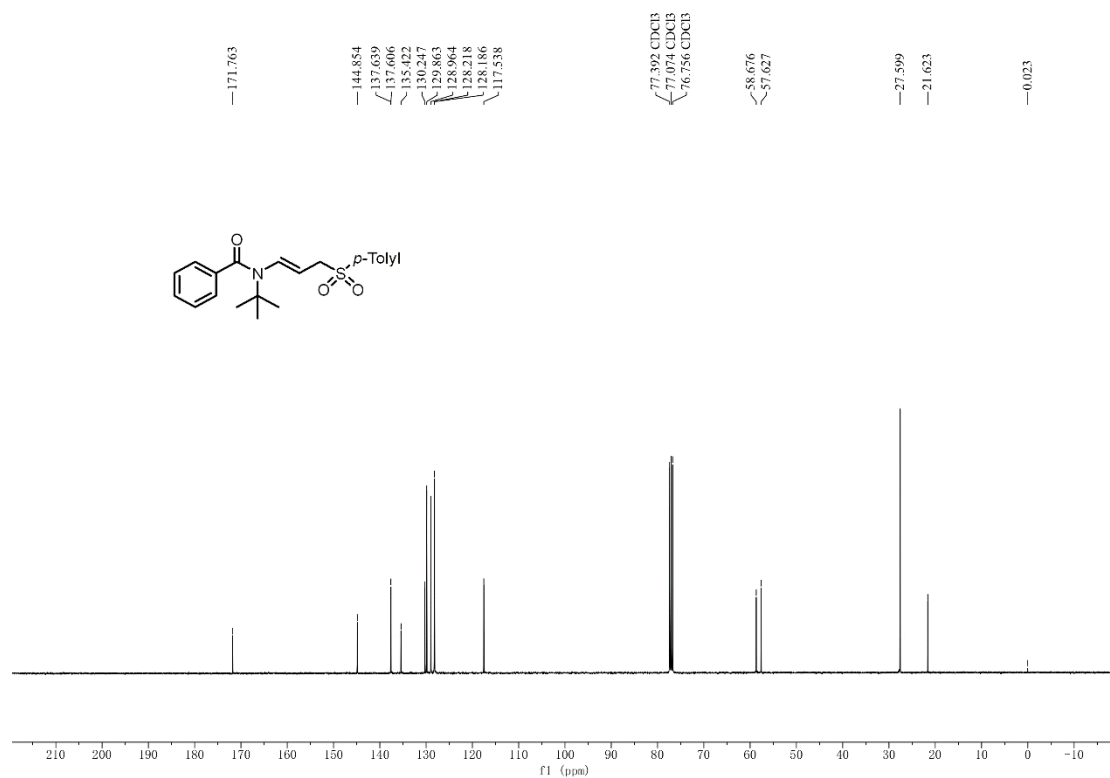




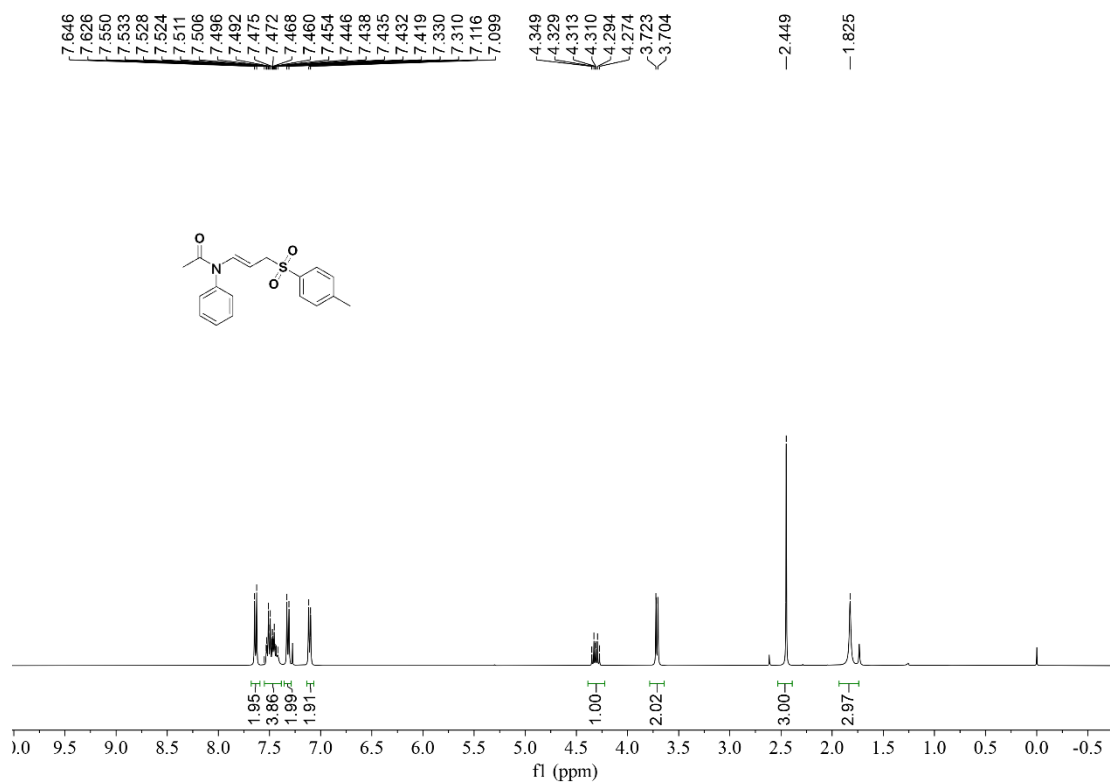
¹³C NMR Spectrum of Compound 3q



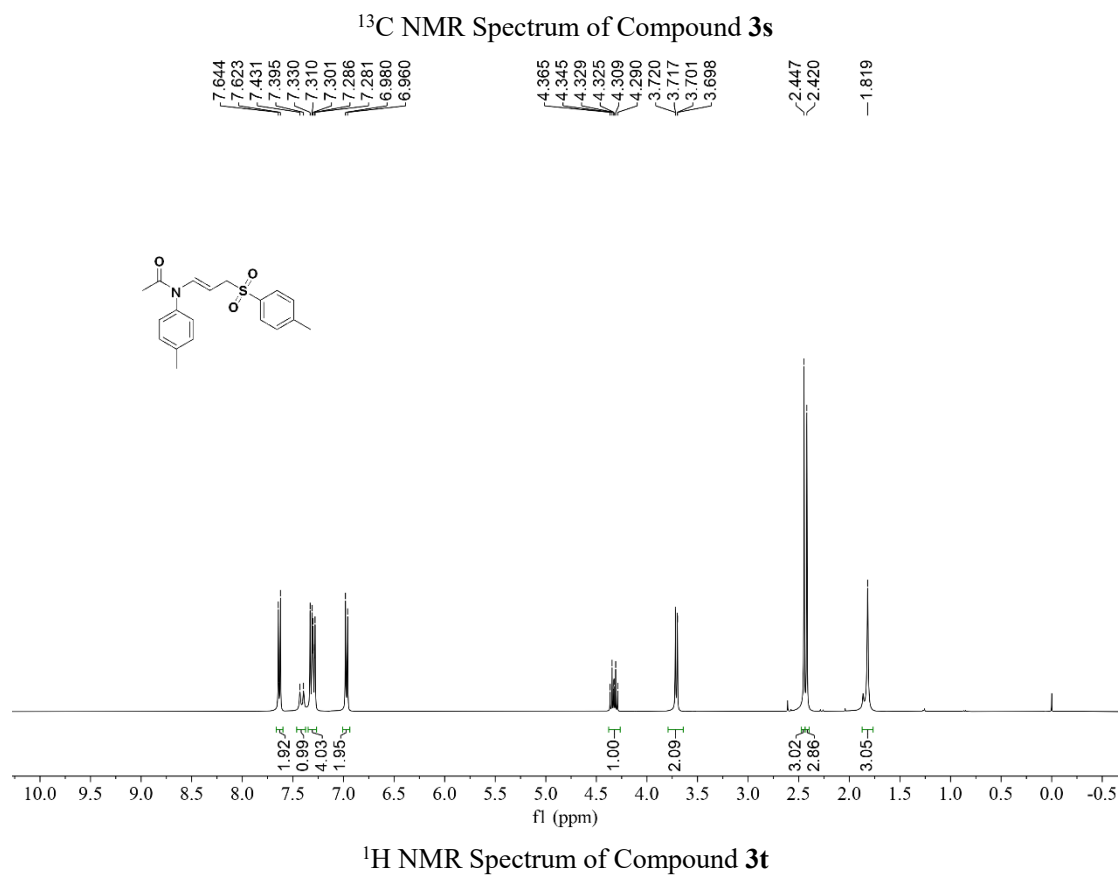
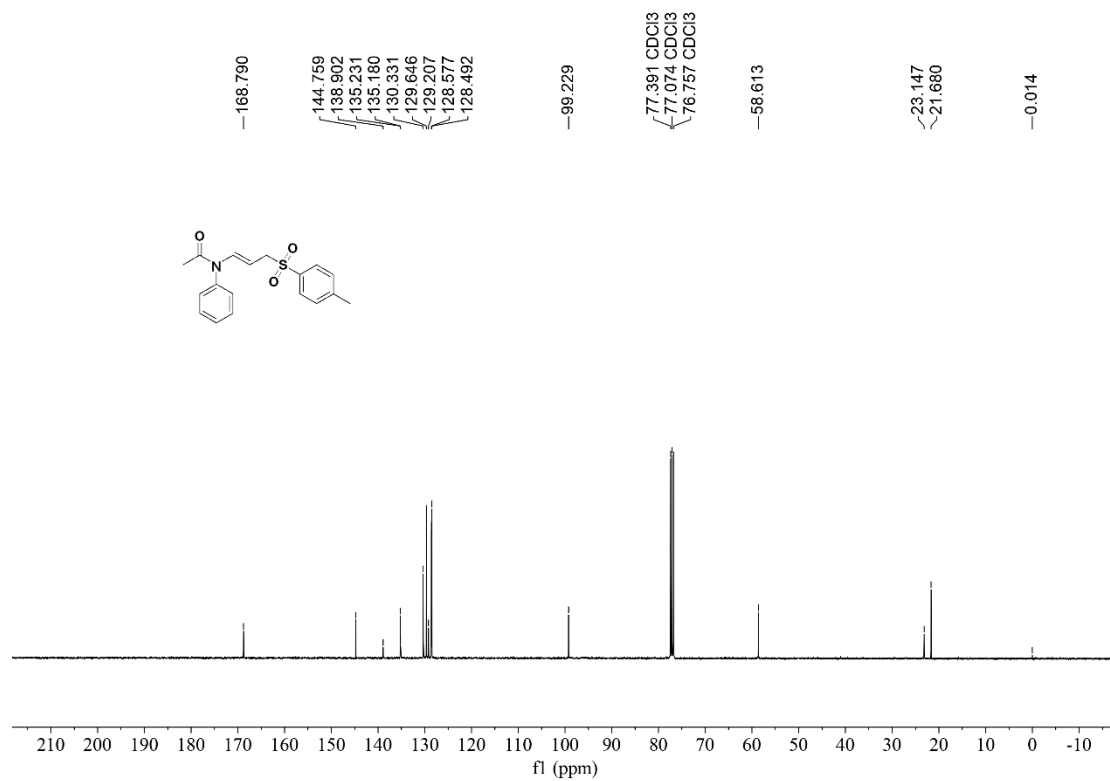
¹H NMR Spectrum of Compound 3r

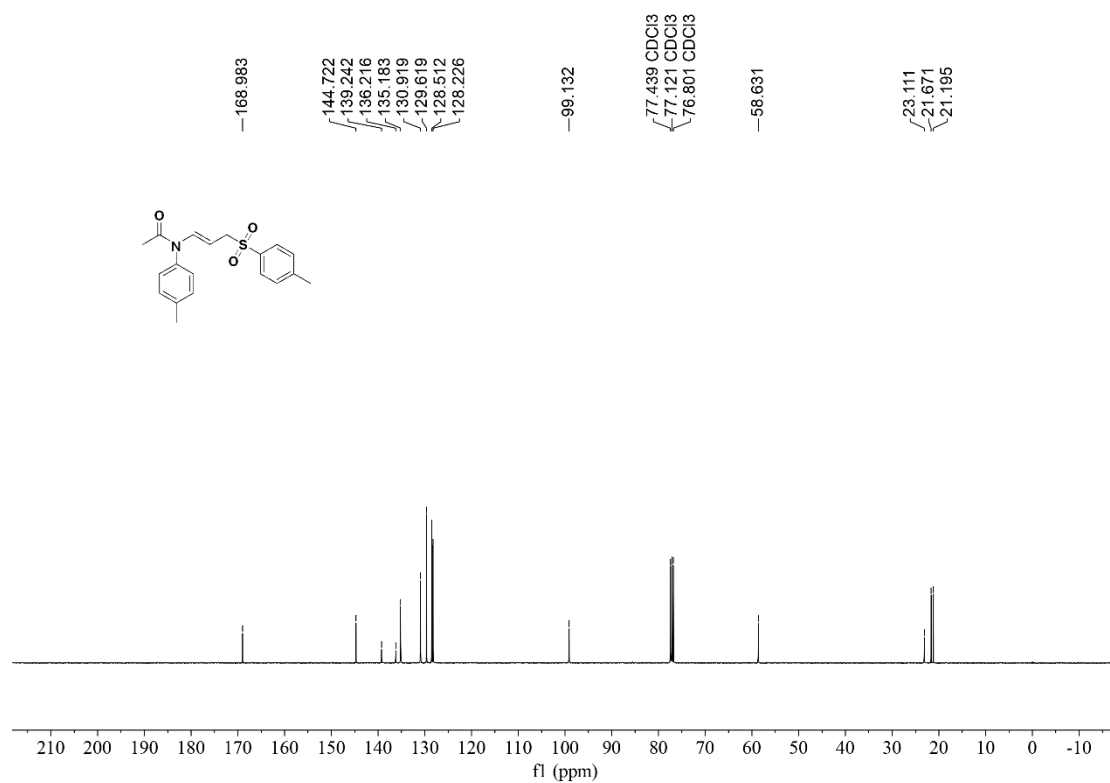


¹³C NMR Spectrum of Compound 3r

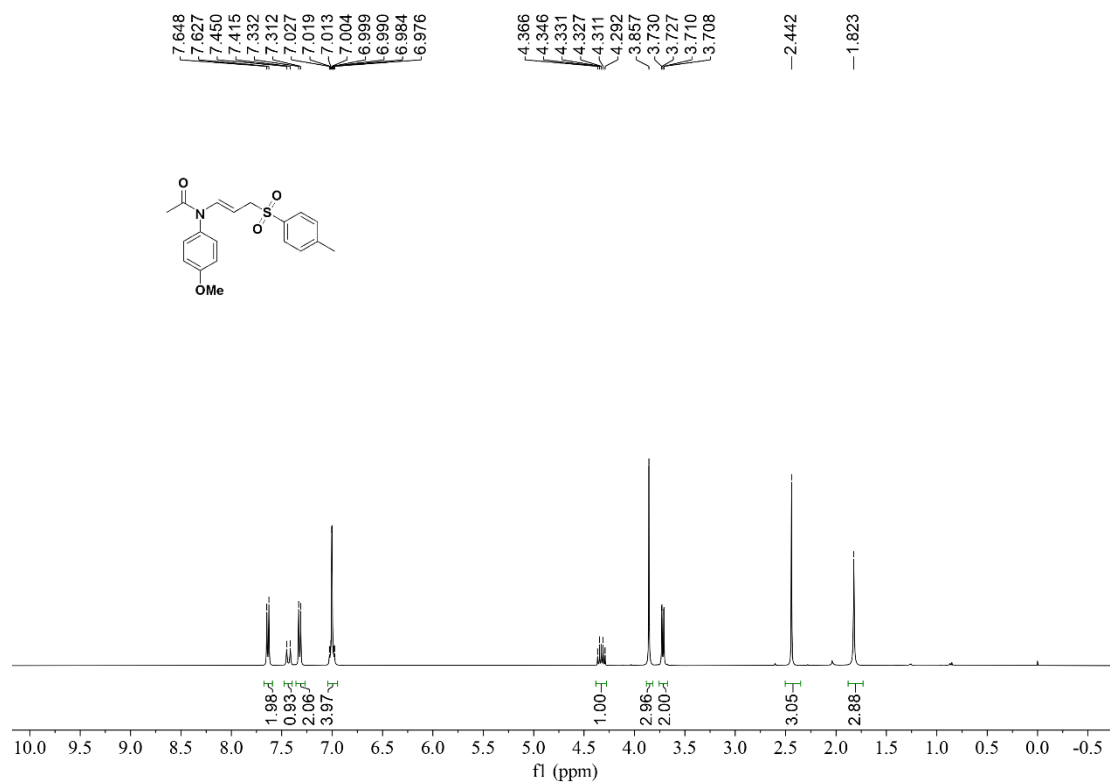


¹H NMR Spectrum of Compound 3s

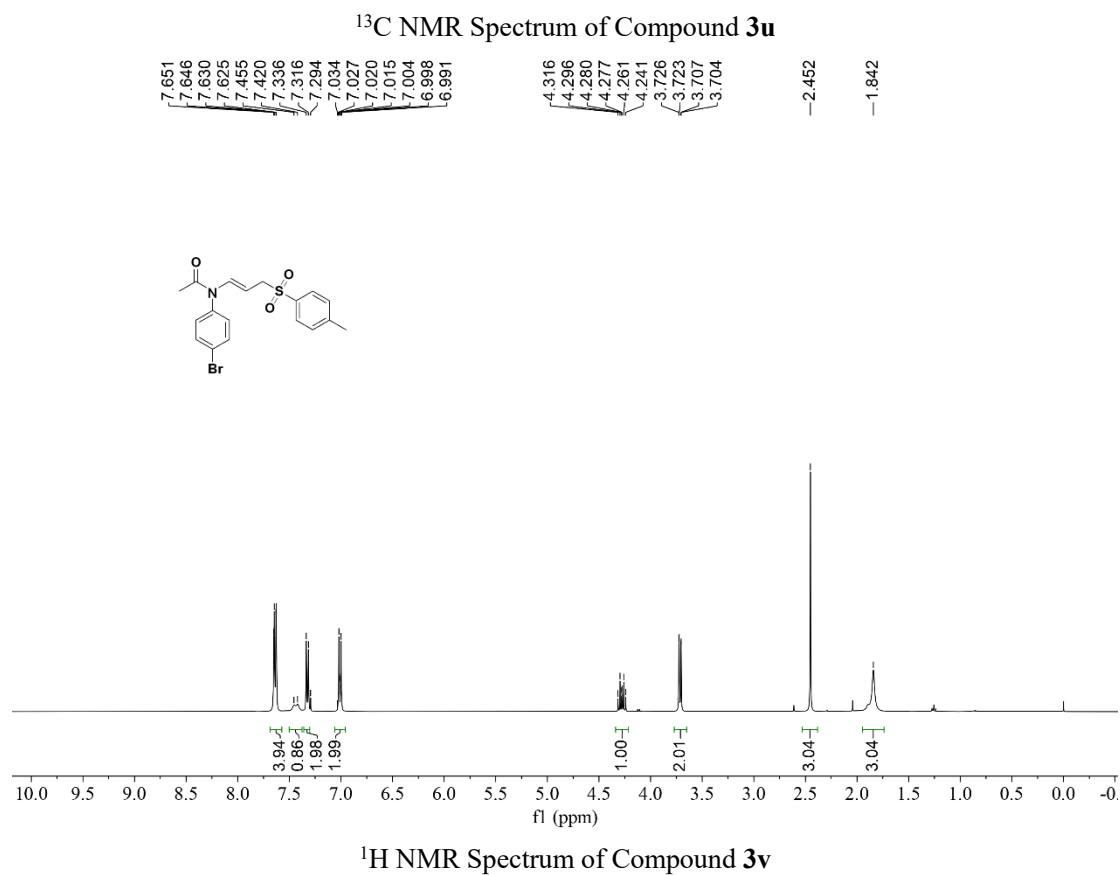
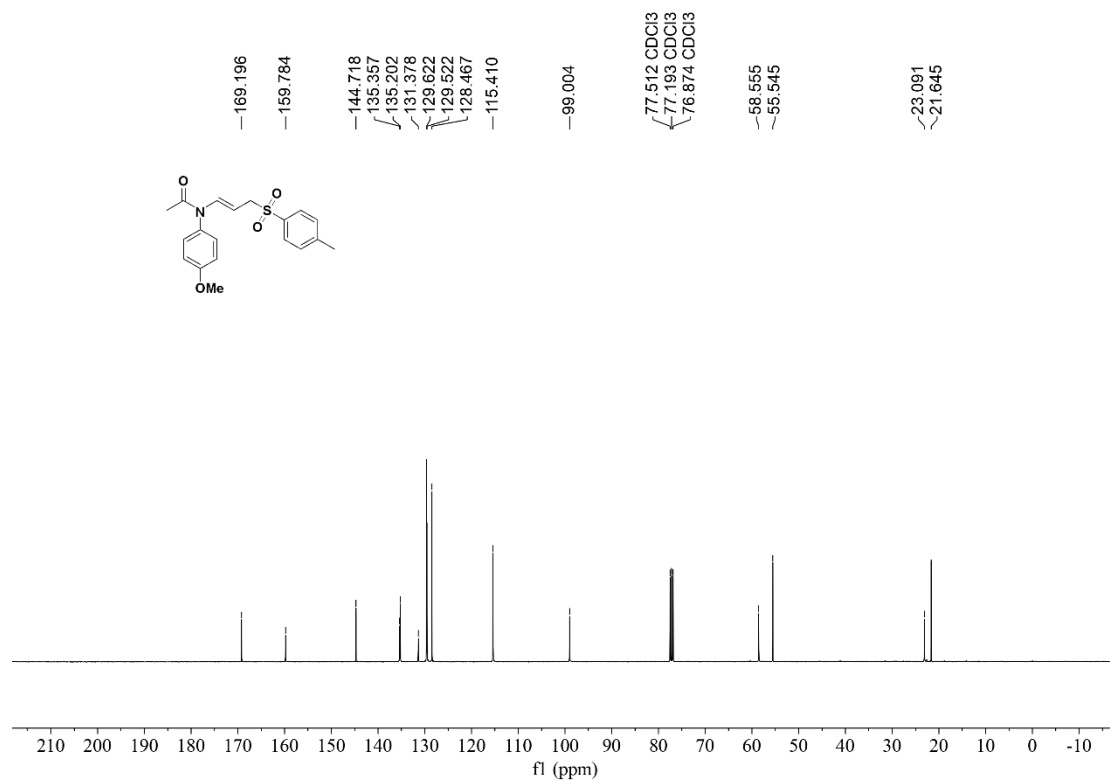


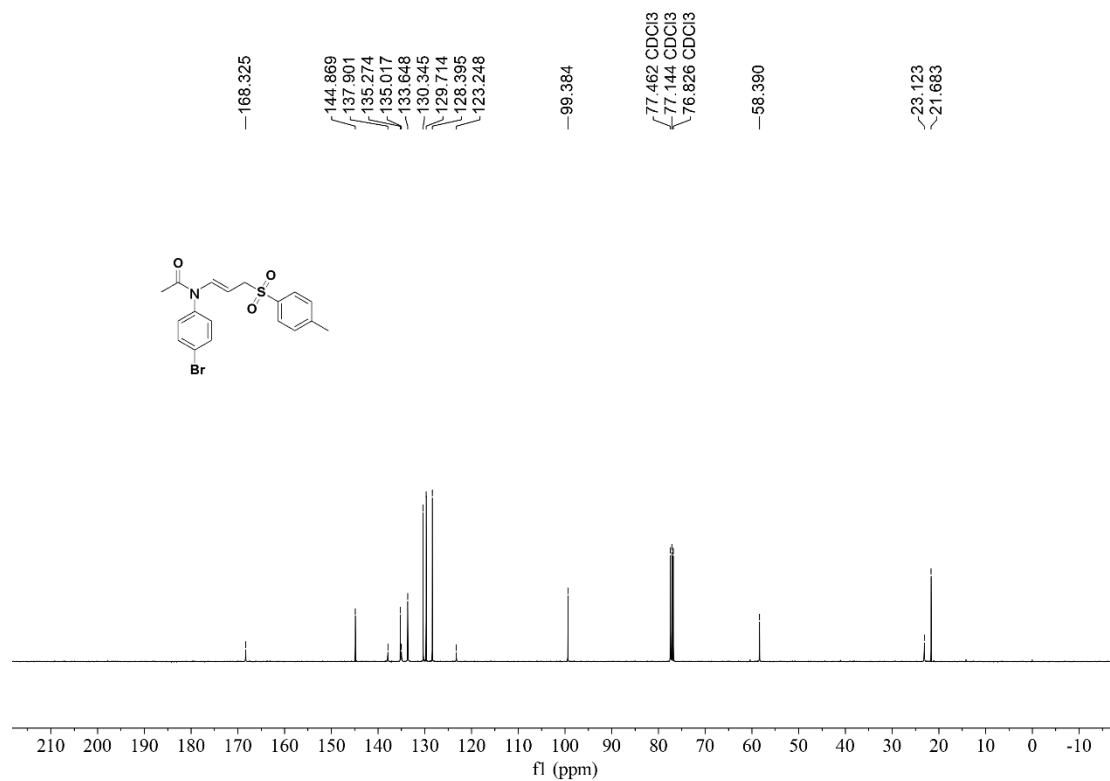


¹³C NMR Spectrum of Compound 3t

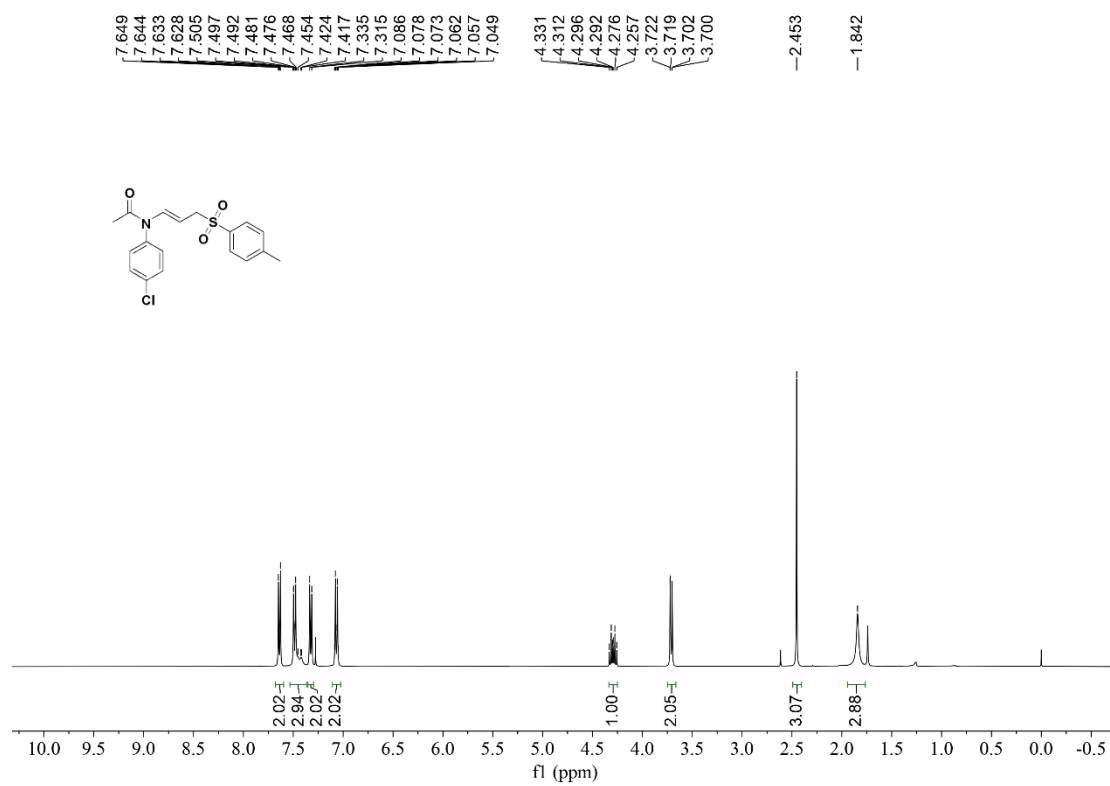


¹H NMR Spectrum of Compound 3u

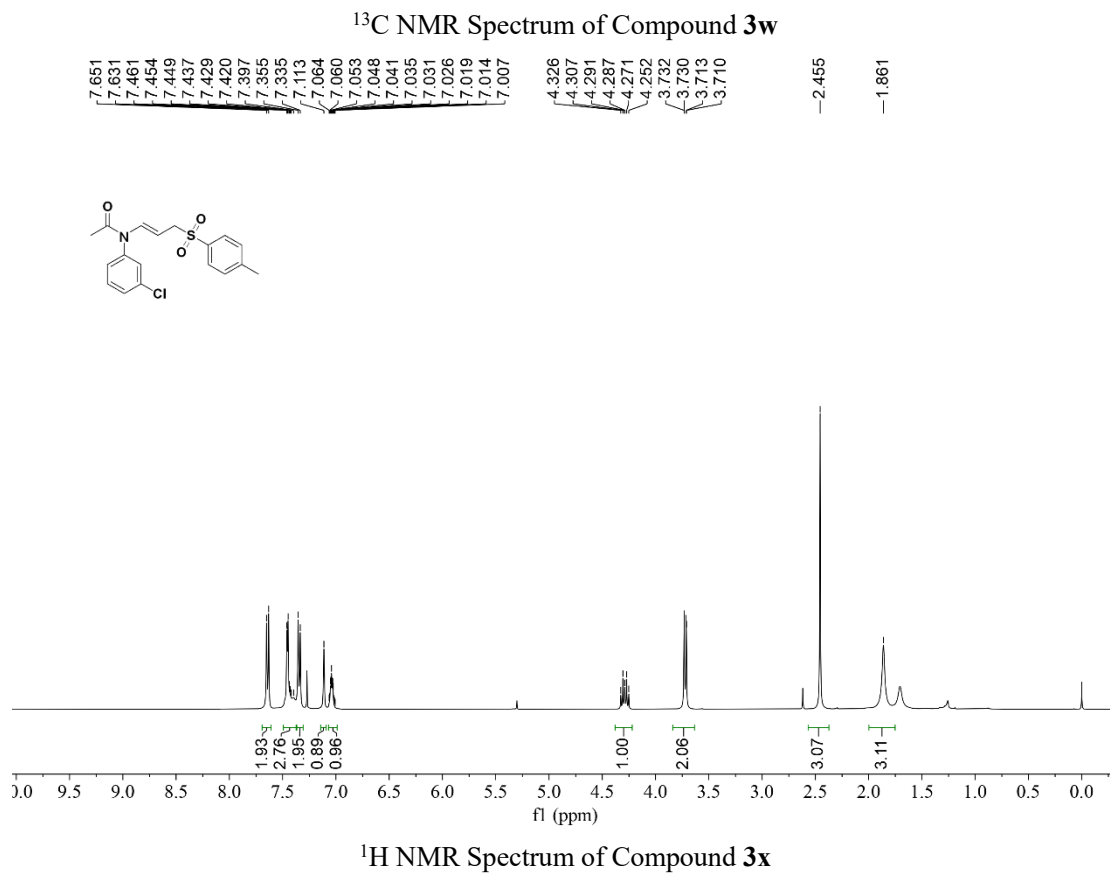
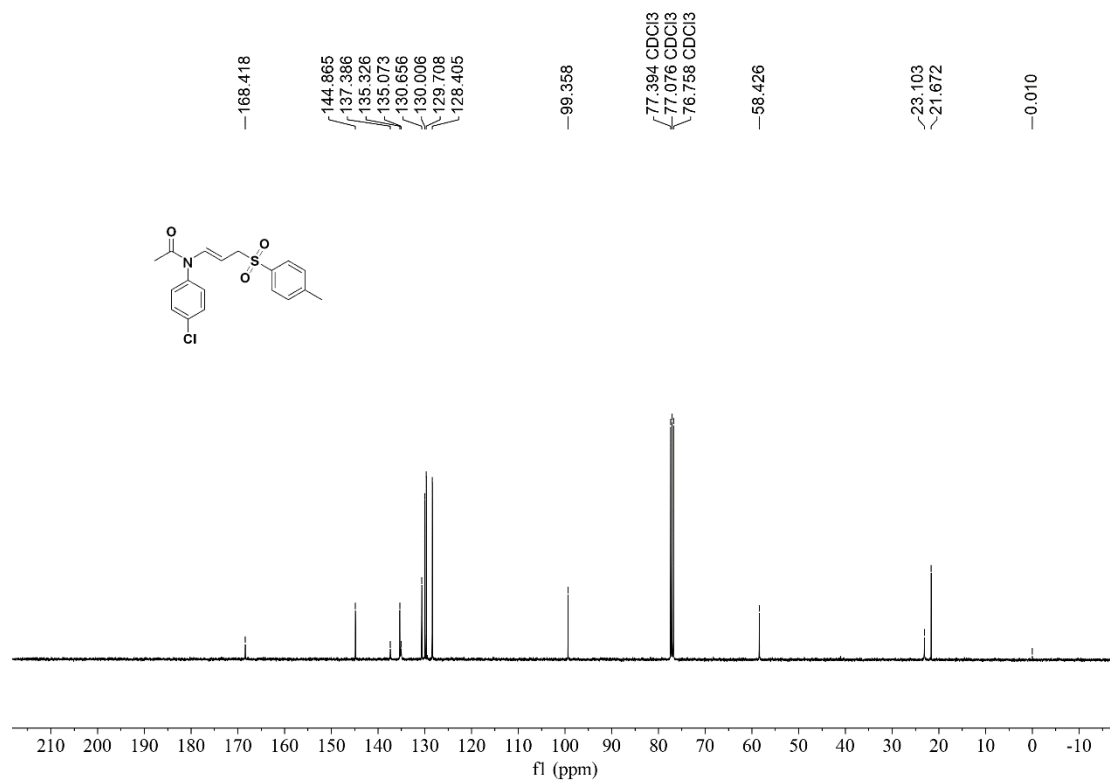


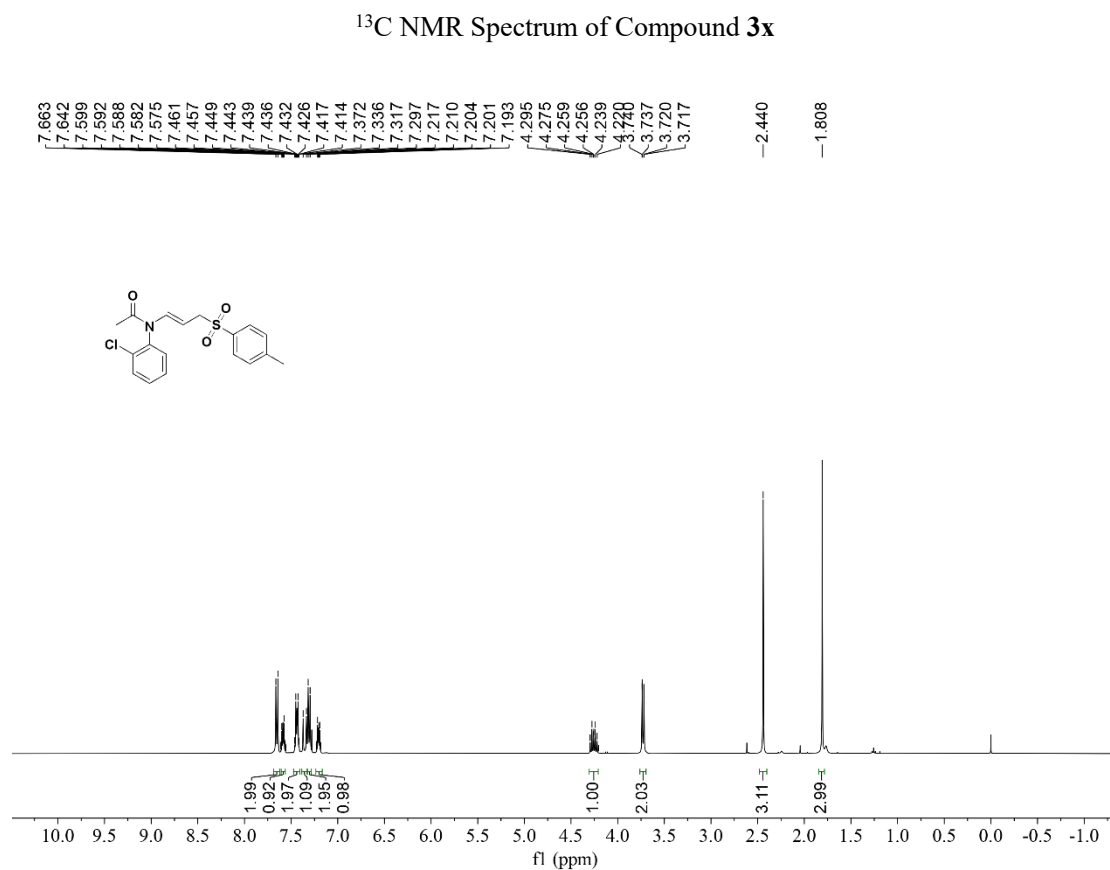
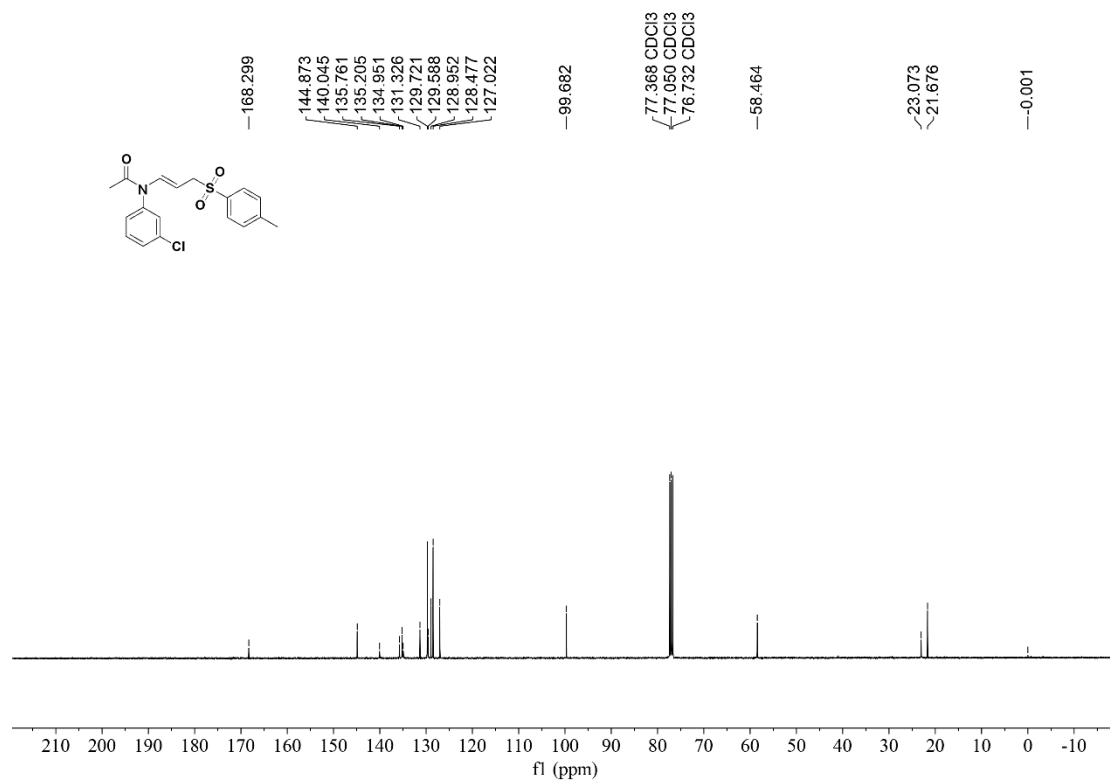


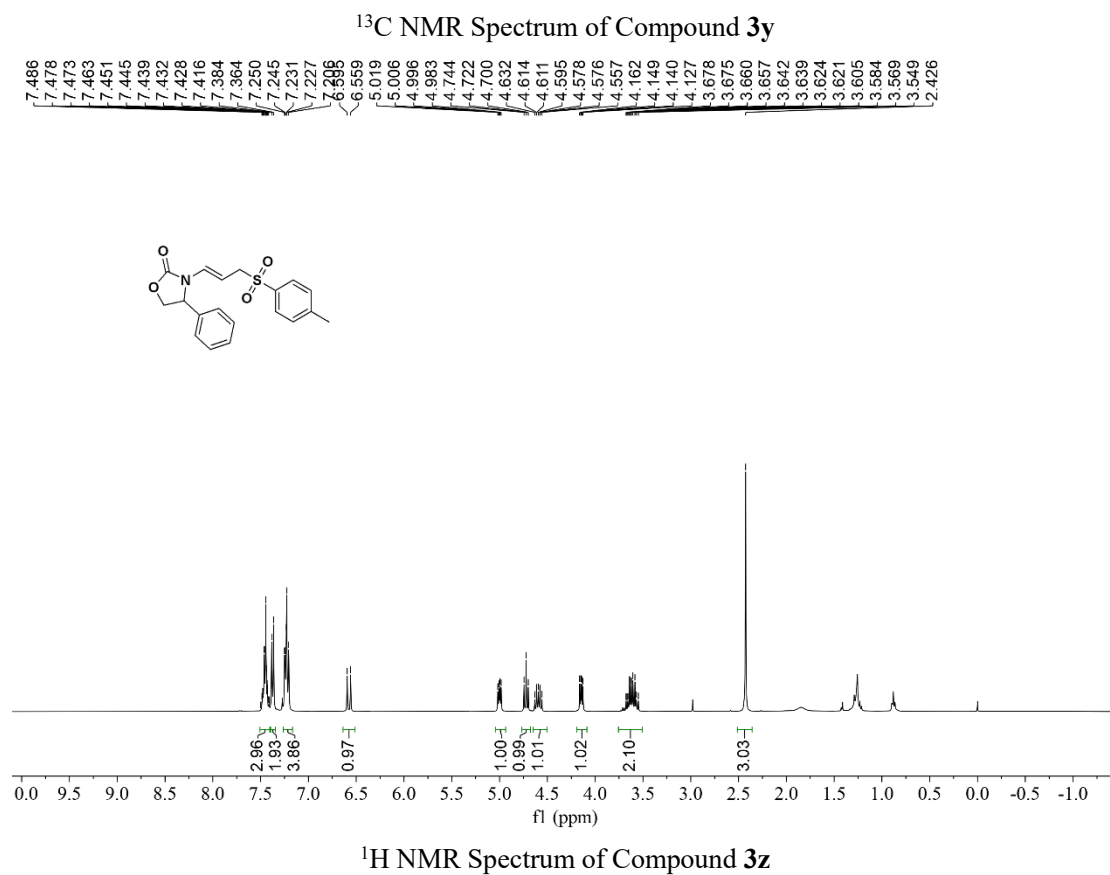
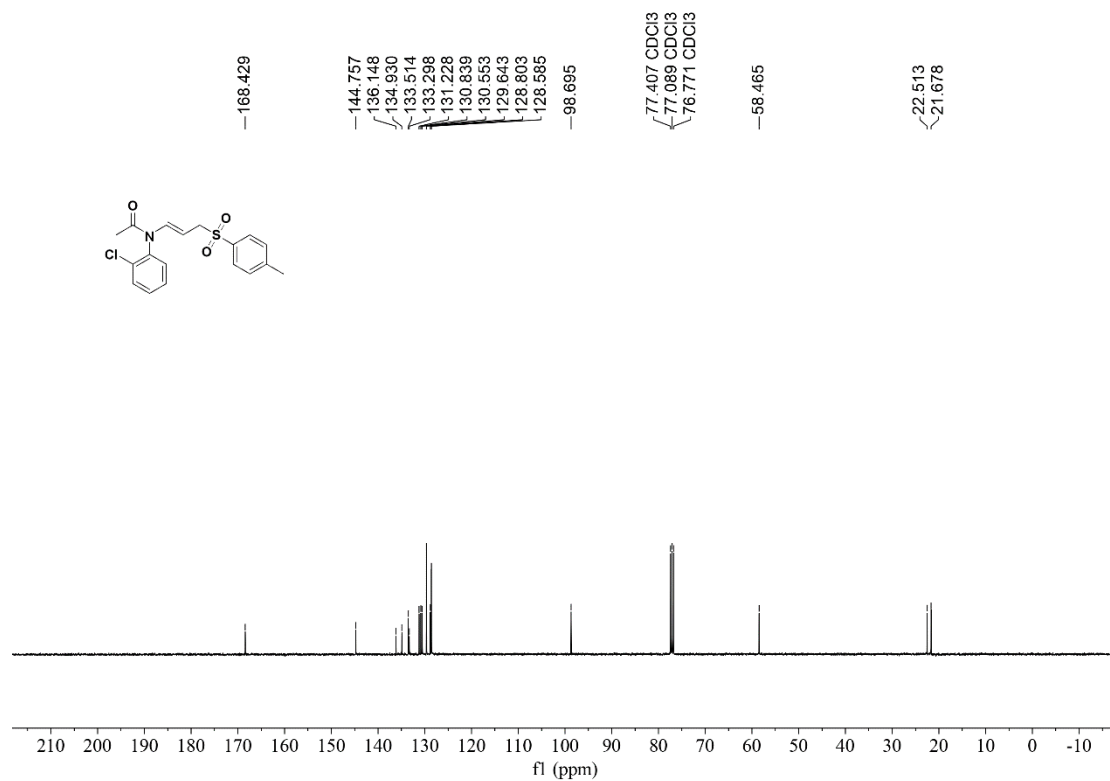
¹³C NMR Spectrum of Compound 3v

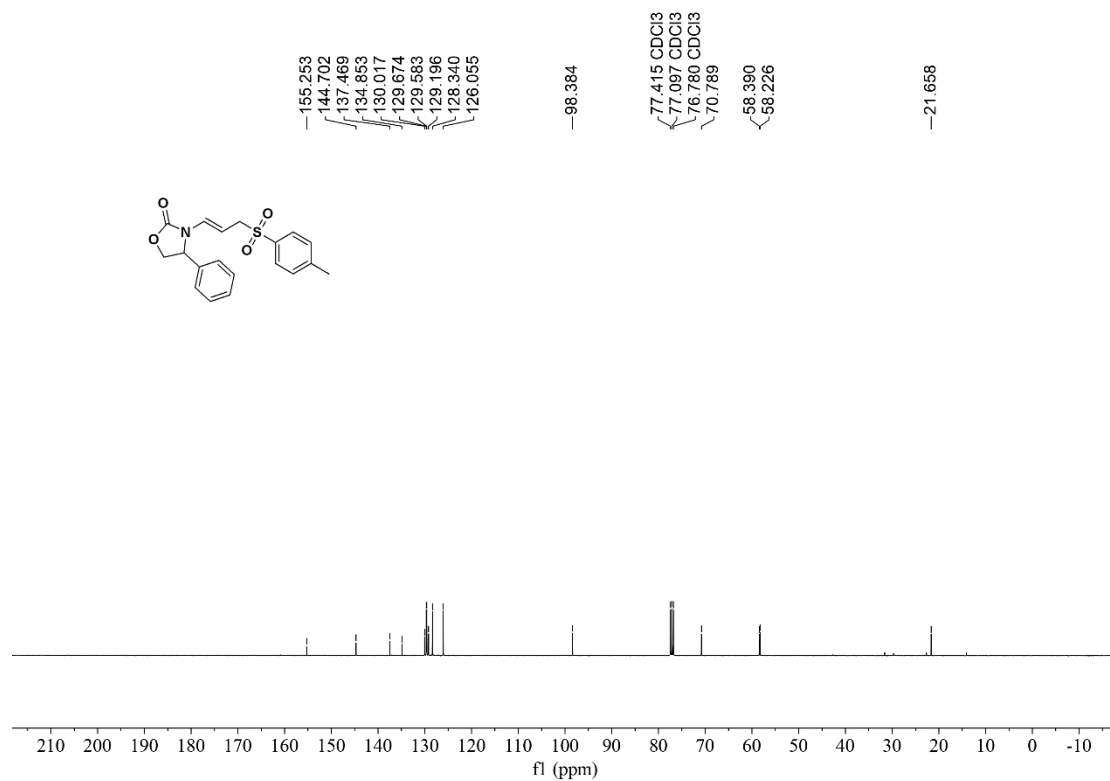


¹H NMR Spectrum of Compound 3w

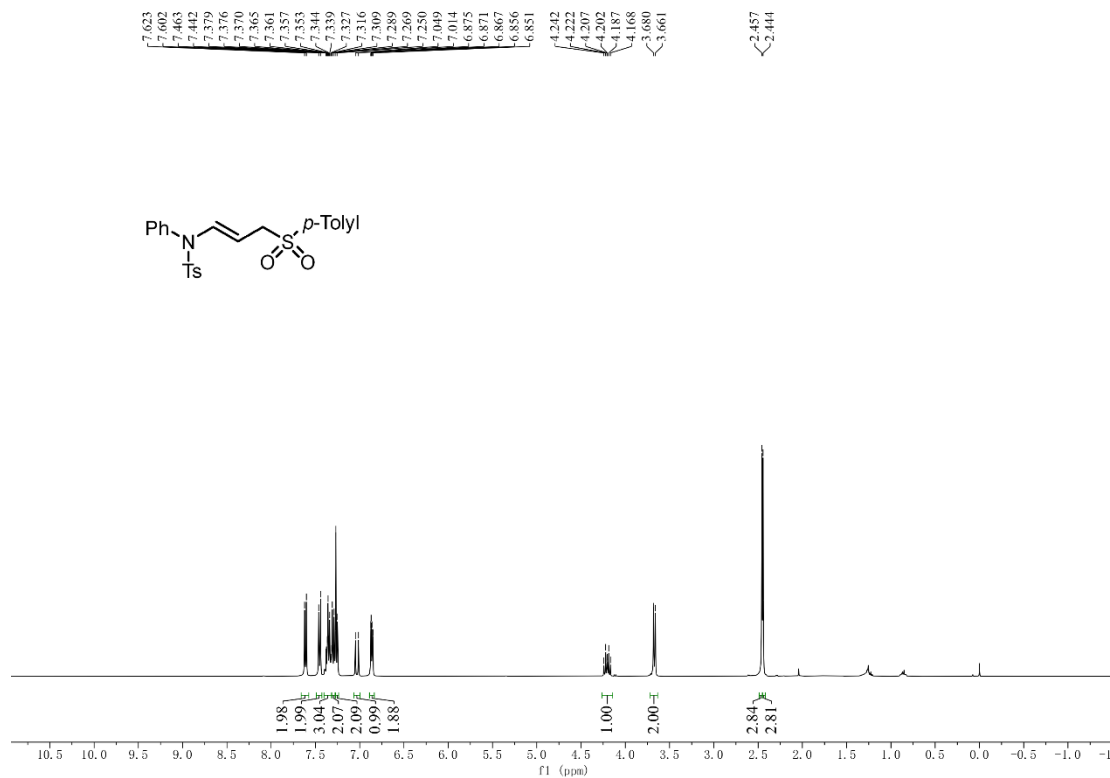




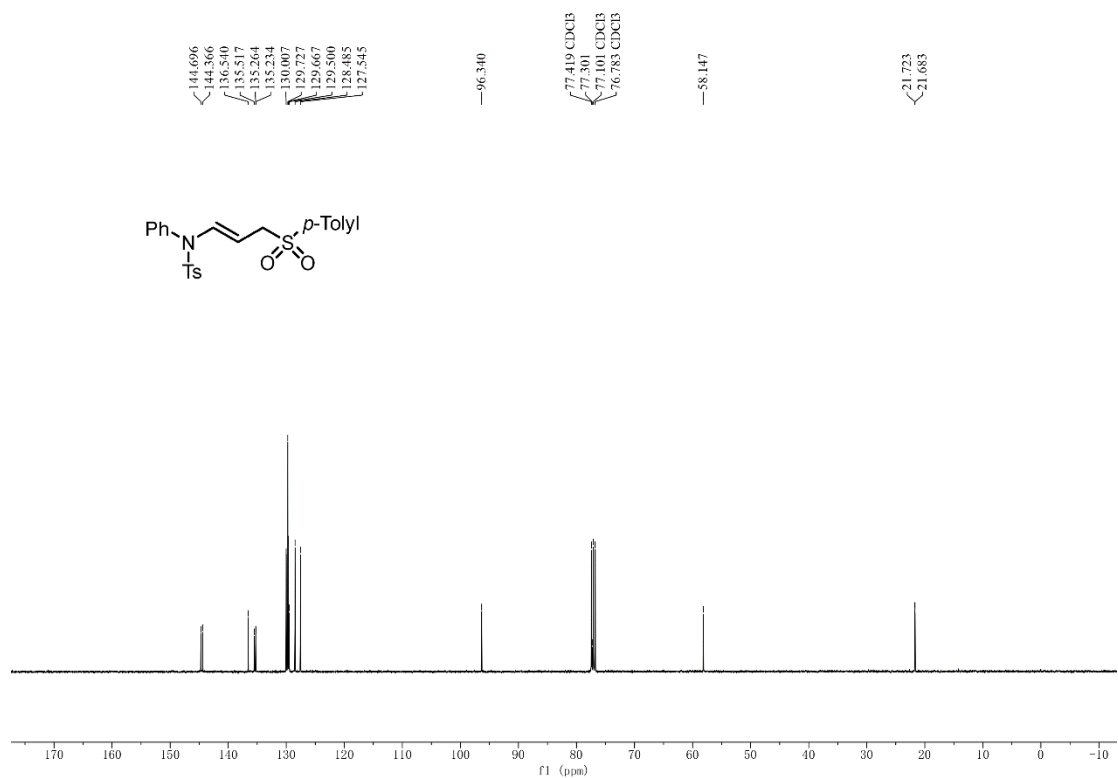




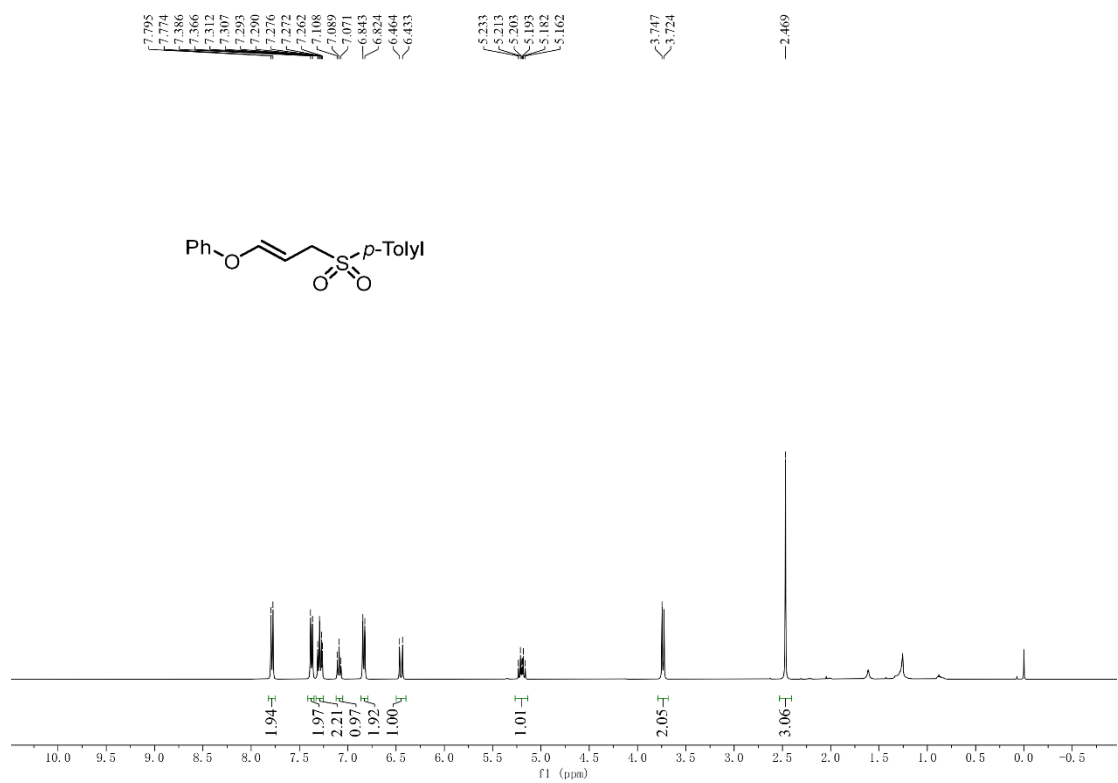
¹³C NMR Spectrum of Compound 3z



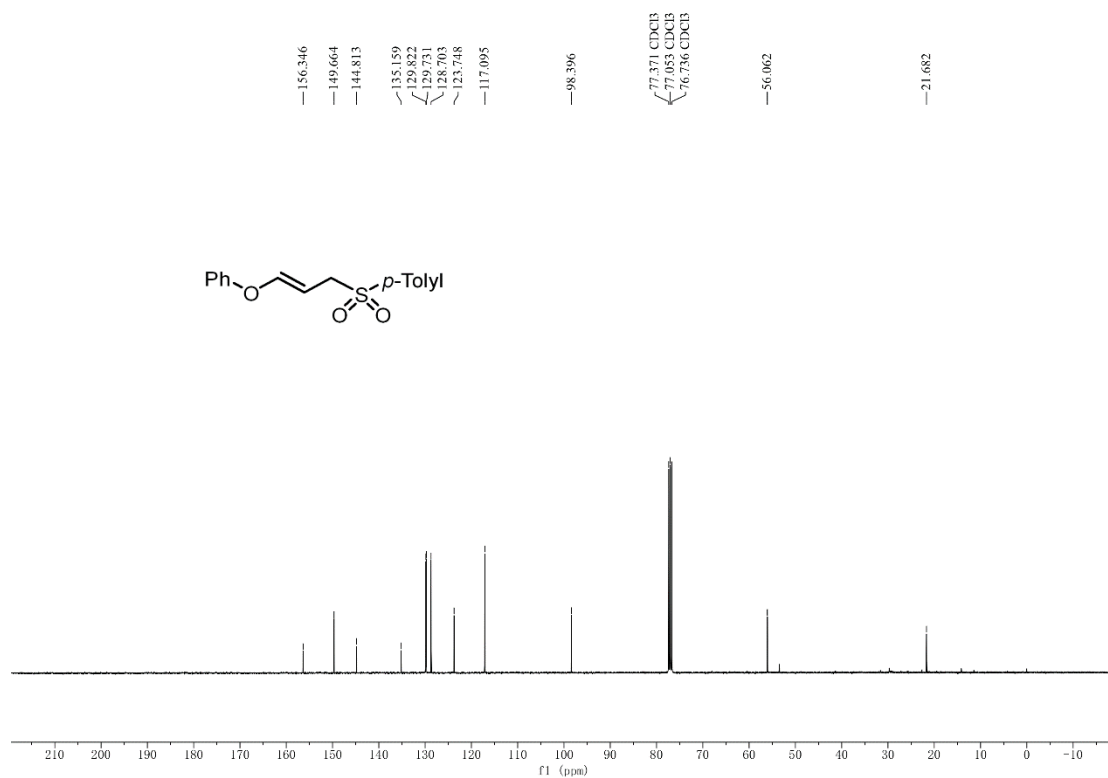
¹H NMR Spectrum of Compound 3aa



¹³C NMR Spectrum of Compound 3aa

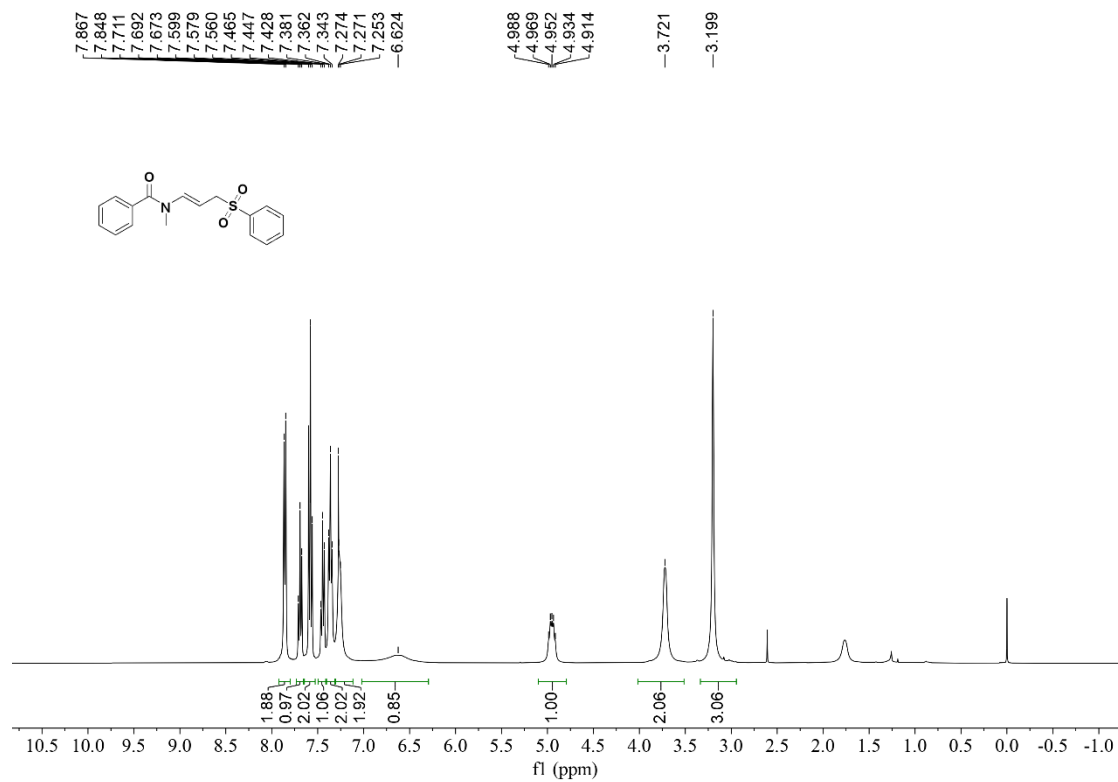


¹H NMR Spectrum of Compound 3ab

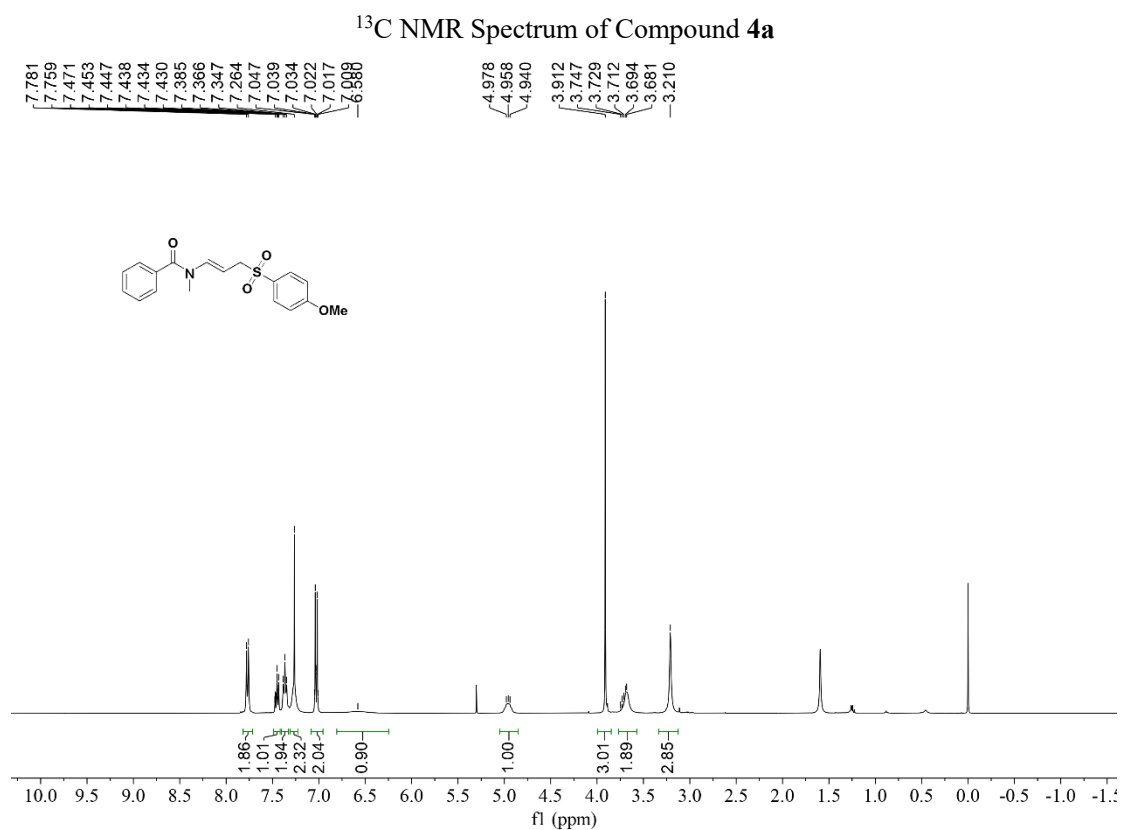
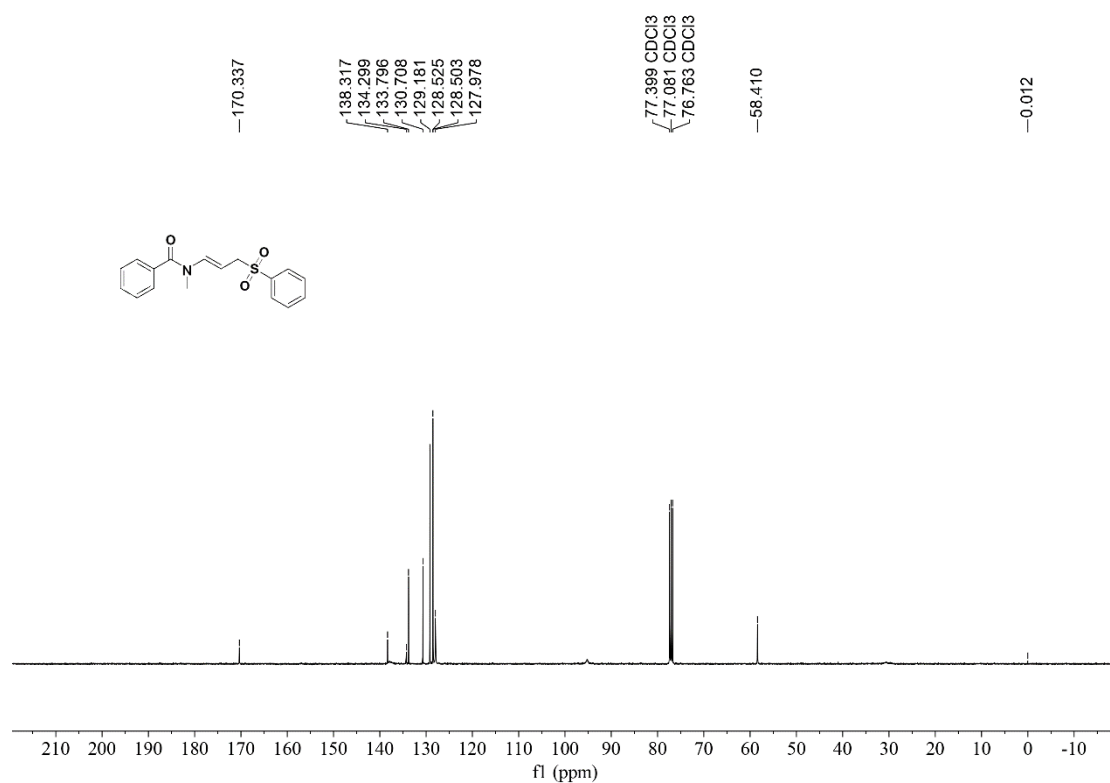


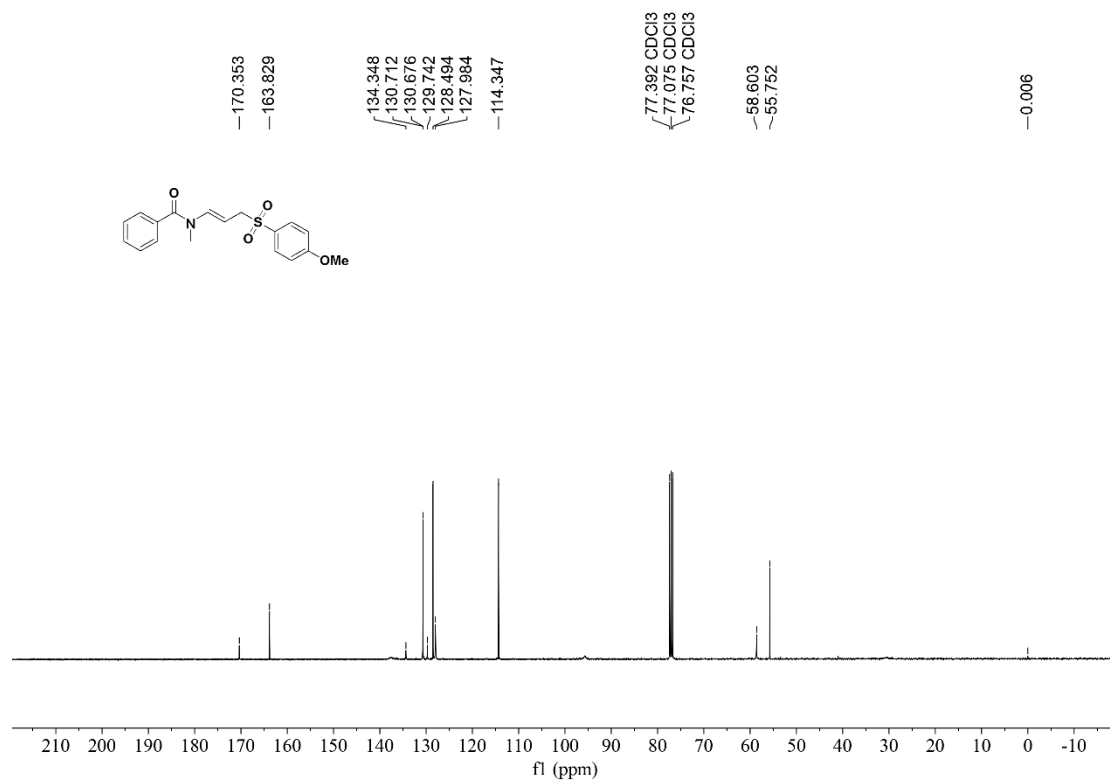
¹³C NMR Spectrum of Compound 3ab

Copies of ¹H, ¹³C NMR and ¹⁹F NMR Spectra of Products 4a-4j

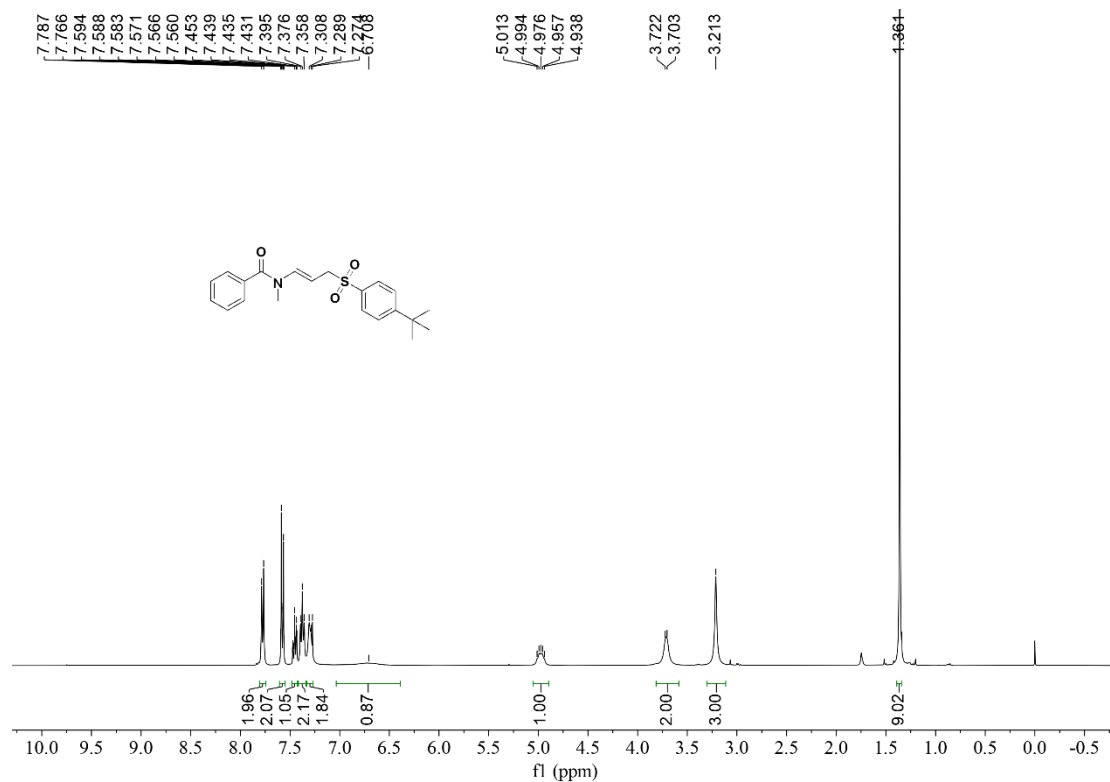


¹H NMR Spectrum of Compound 4a

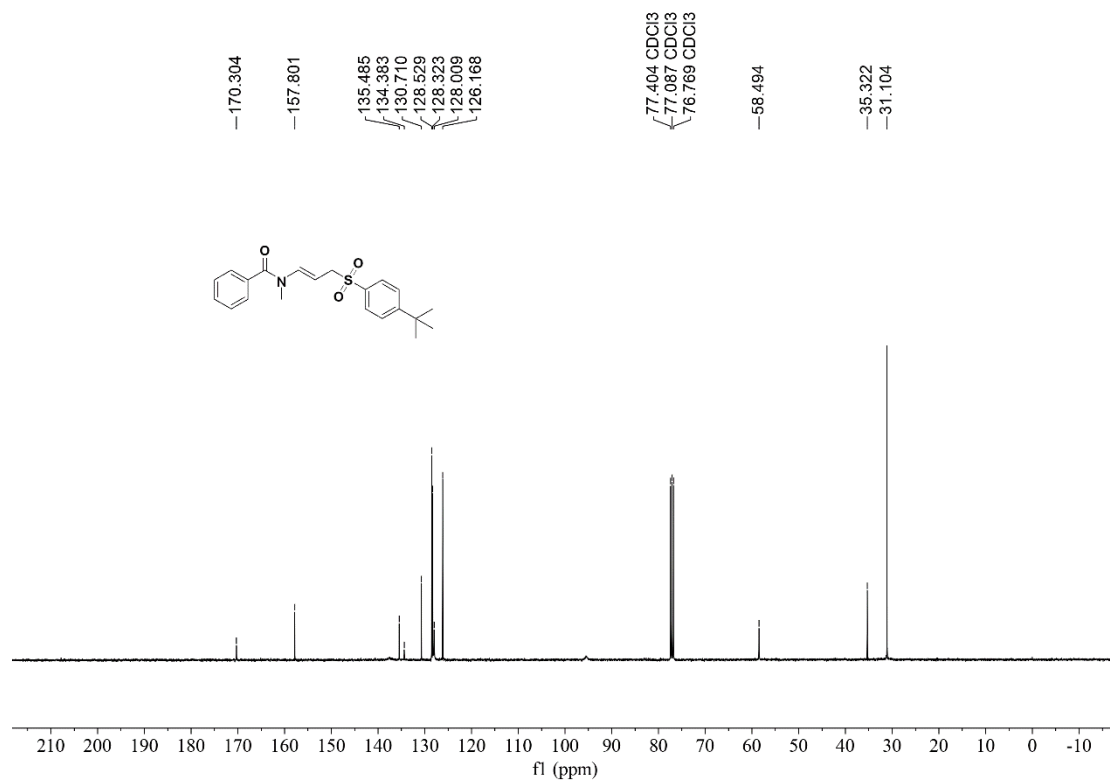




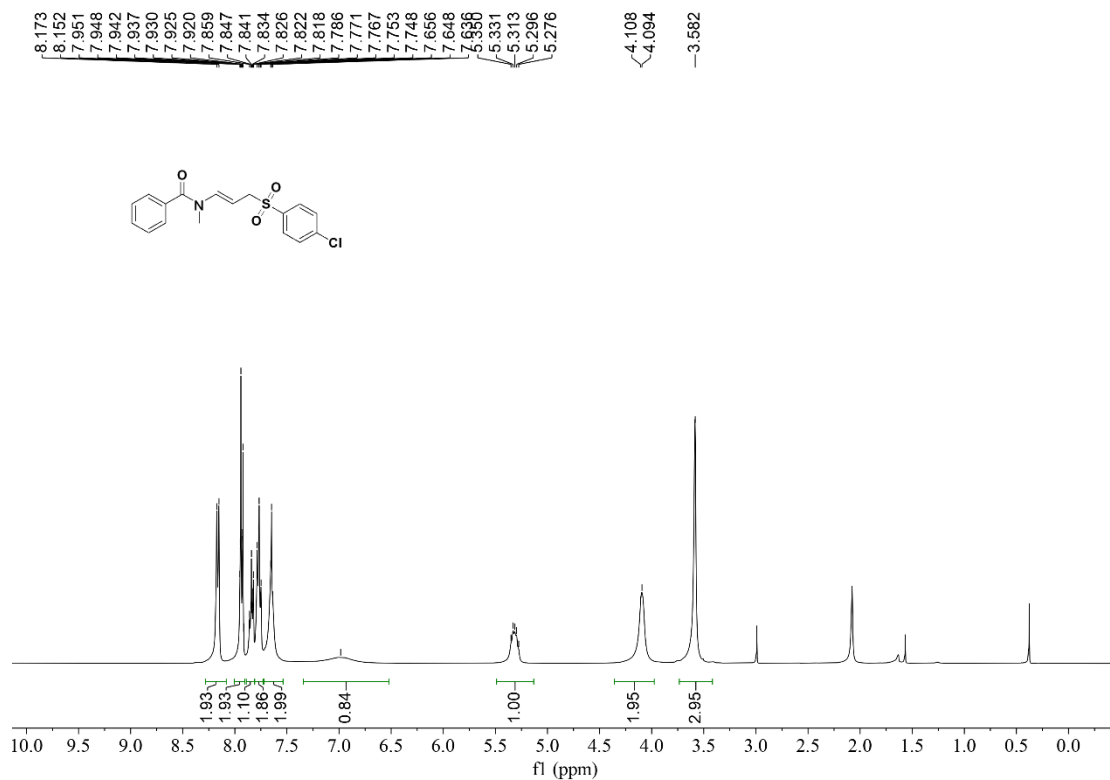
¹³C NMR Spectrum of Compound 4b



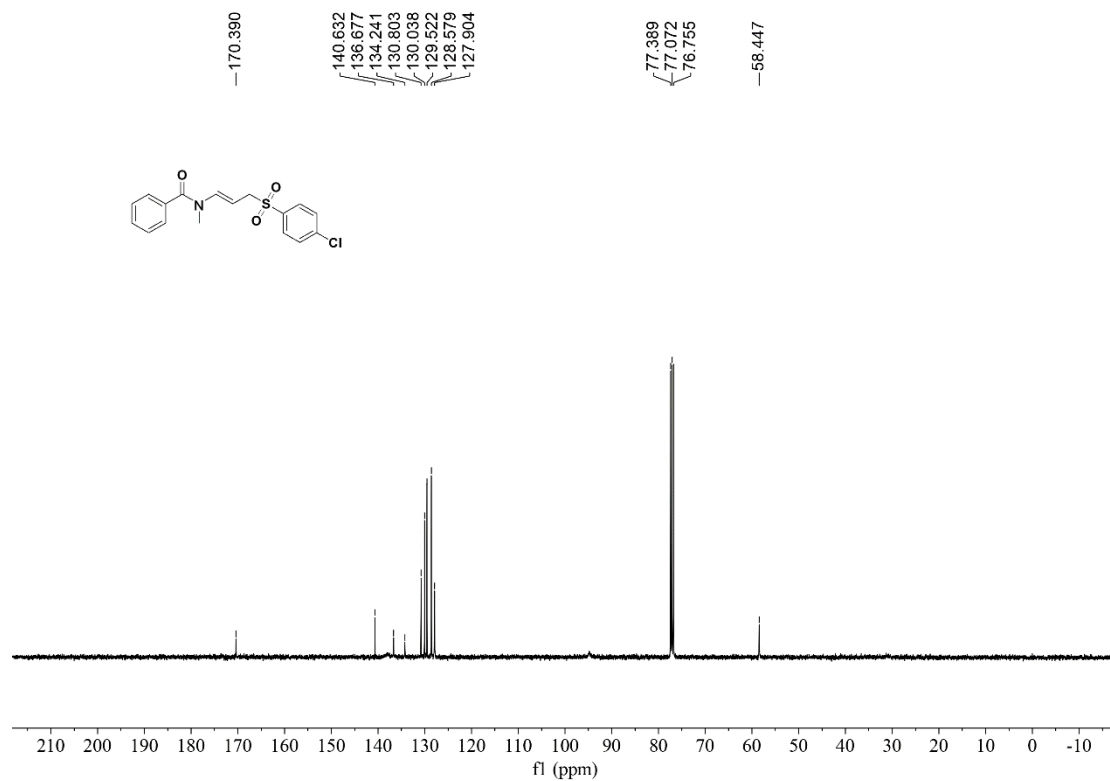
¹H NMR Spectrum of Compound 4c



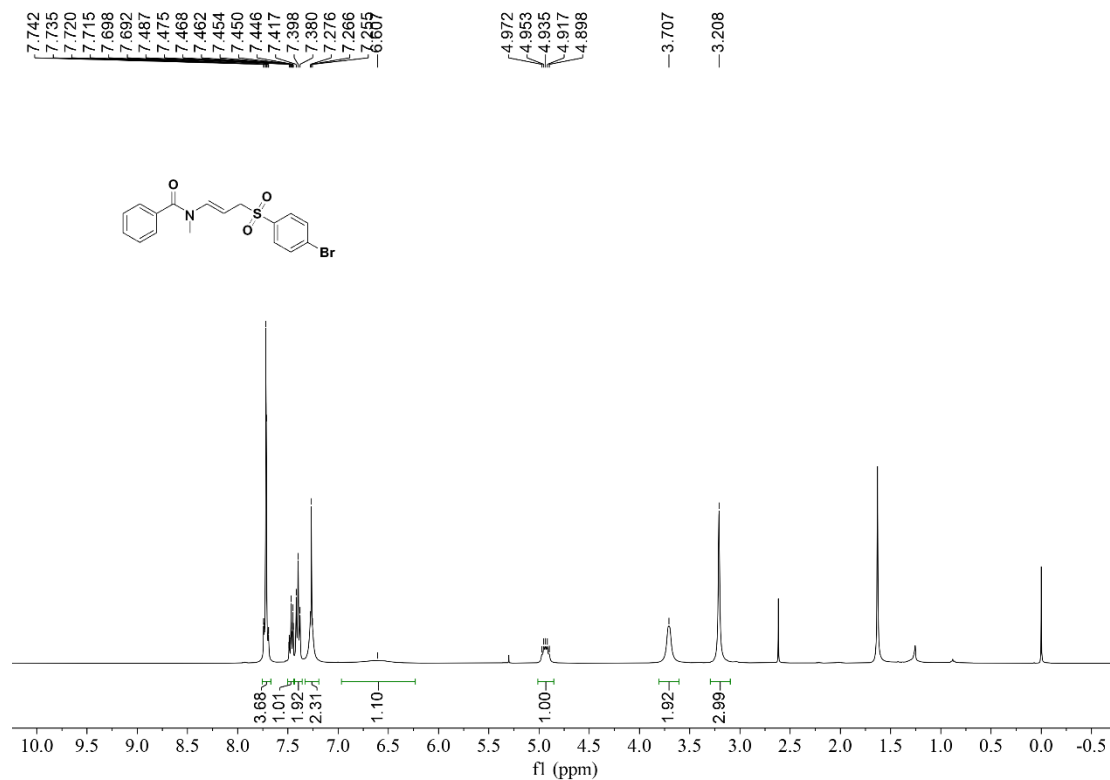
¹³C NMR Spectrum of Compound **4c**



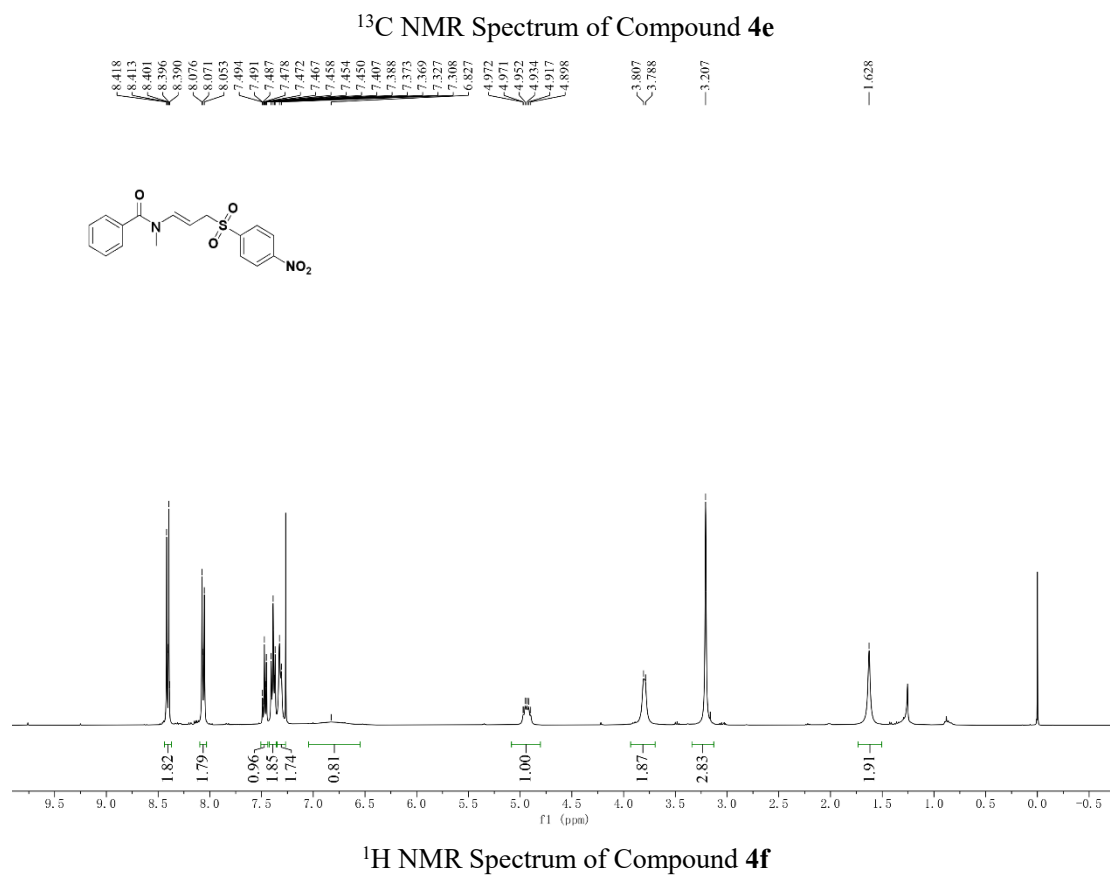
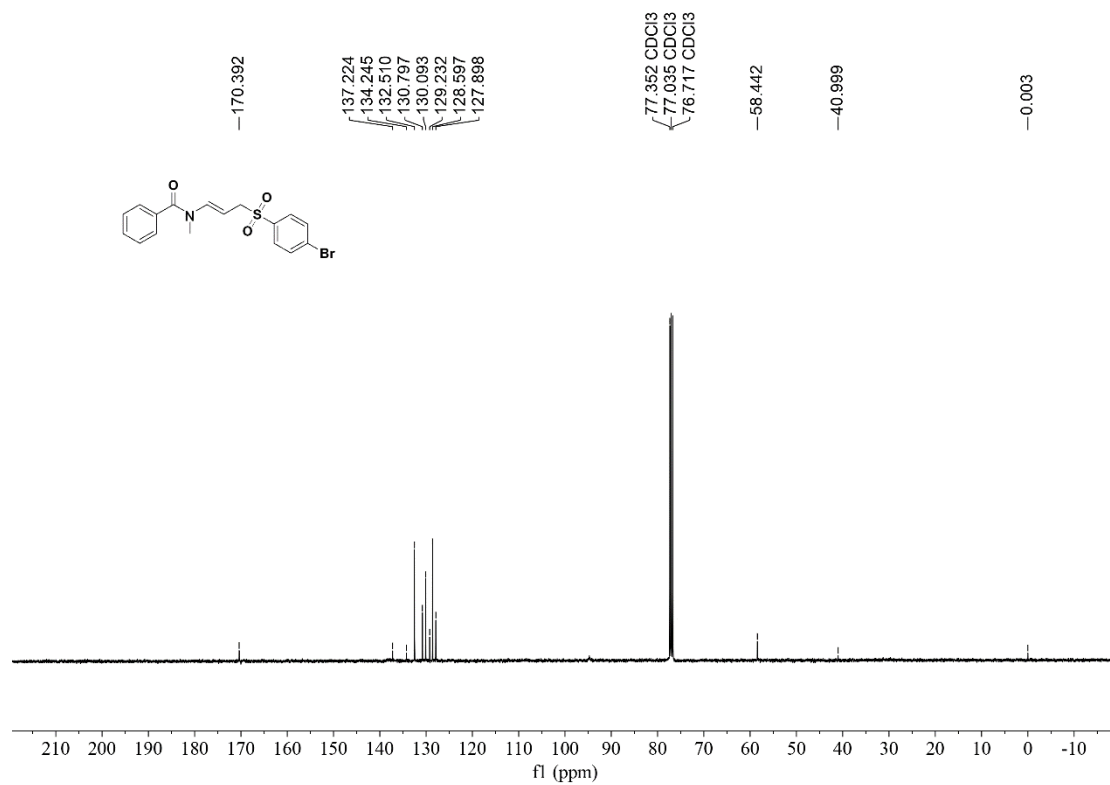
¹H NMR Spectrum of Compound **4d**

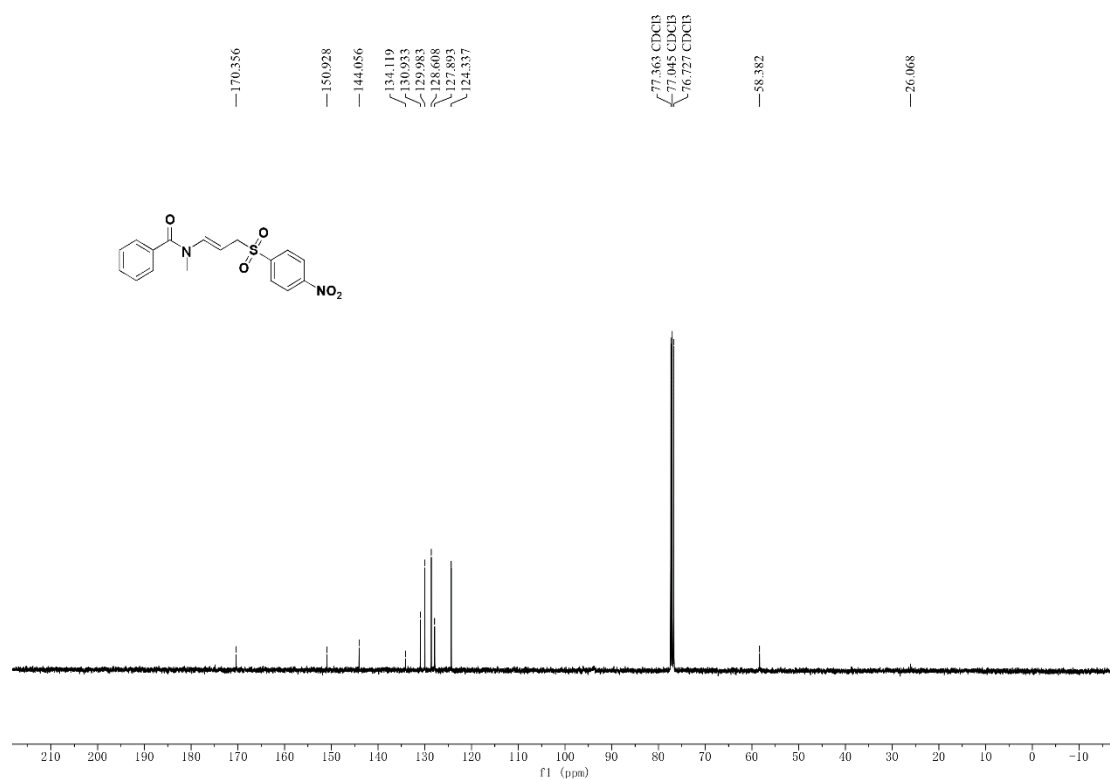


^{13}C NMR Spectrum of Compound 4d

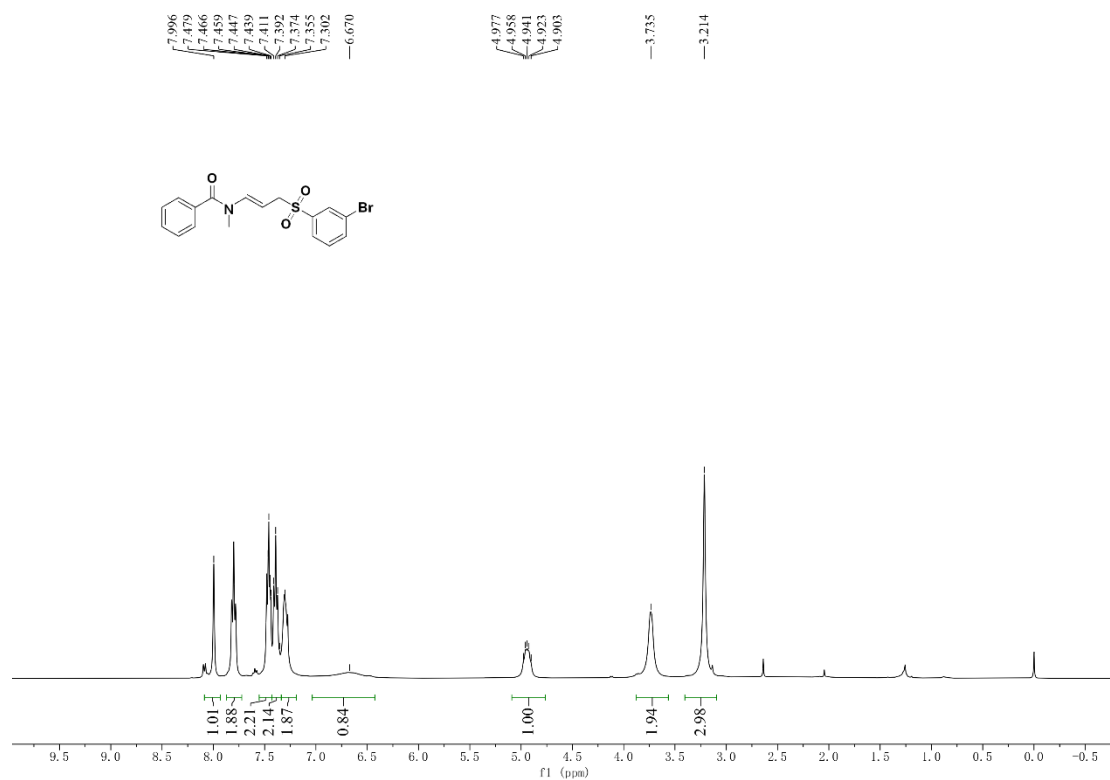


^1H NMR Spectrum of Compound 4e

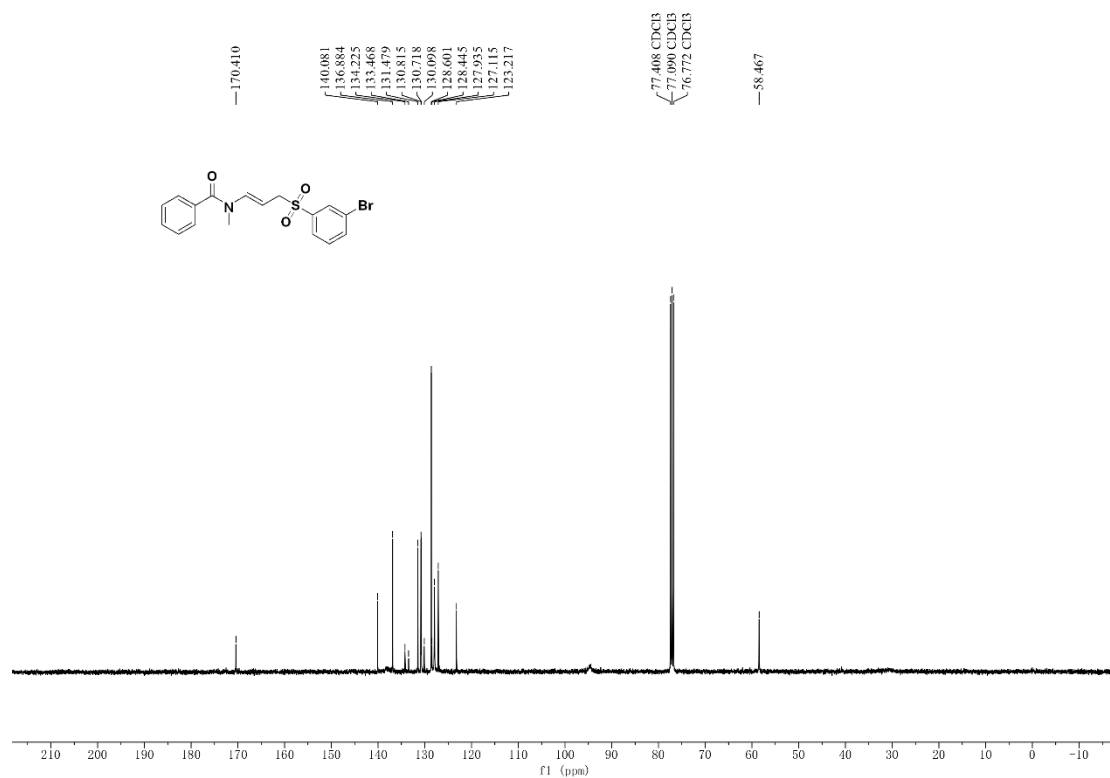




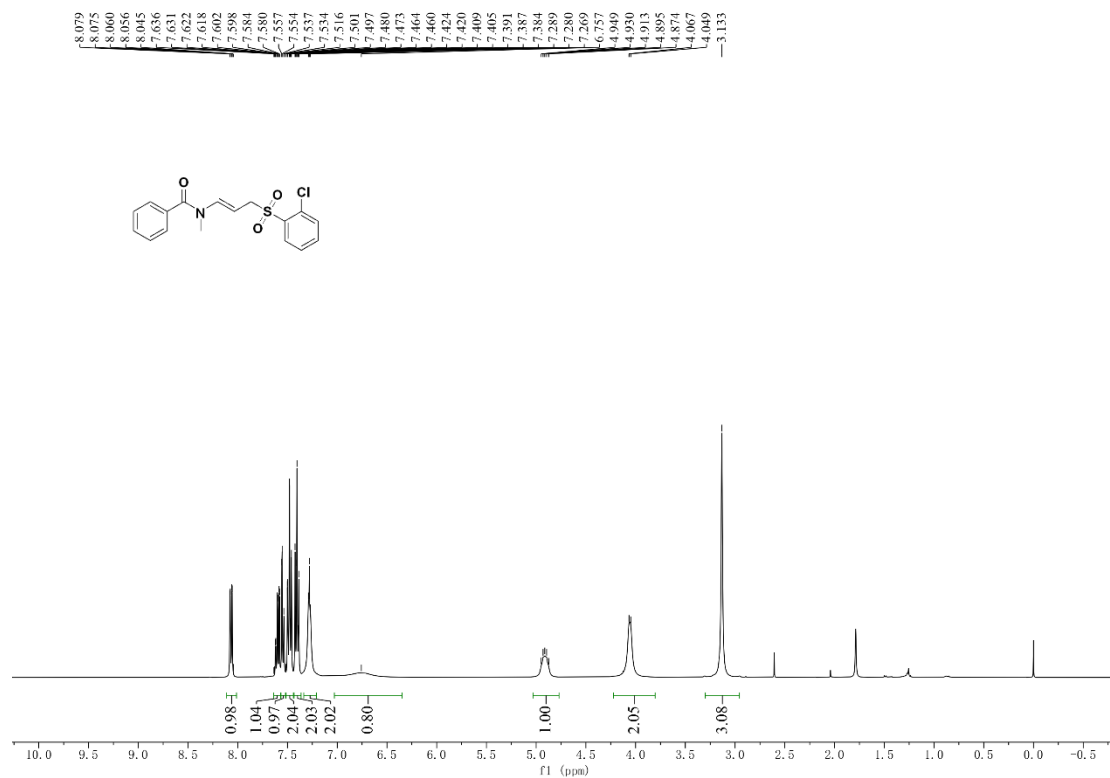
¹³C NMR Spectrum of Compound 4f



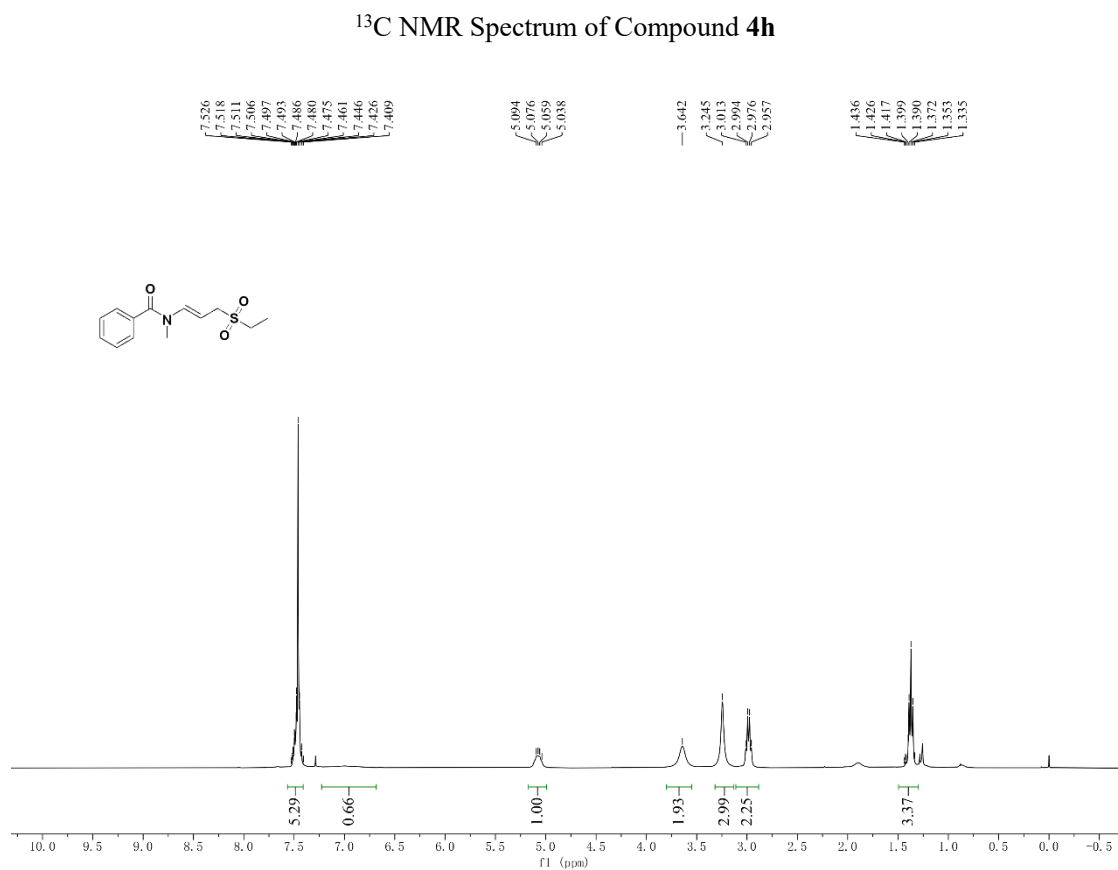
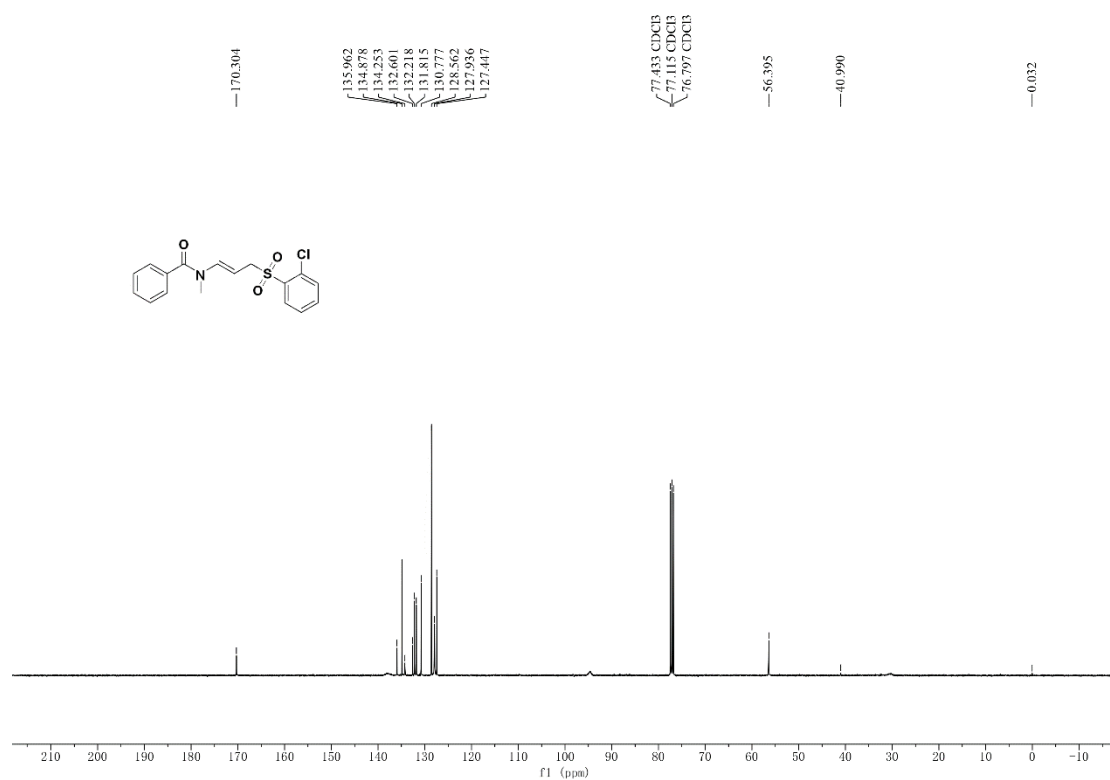
¹H NMR Spectrum of Compound 4g

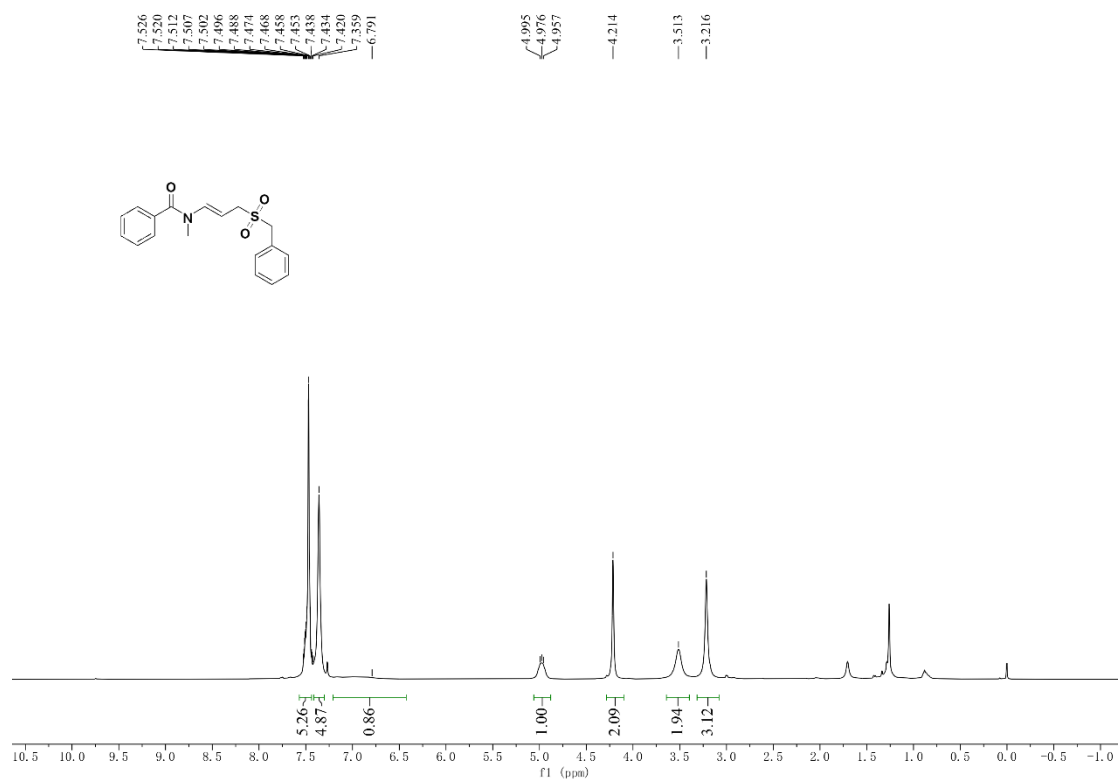
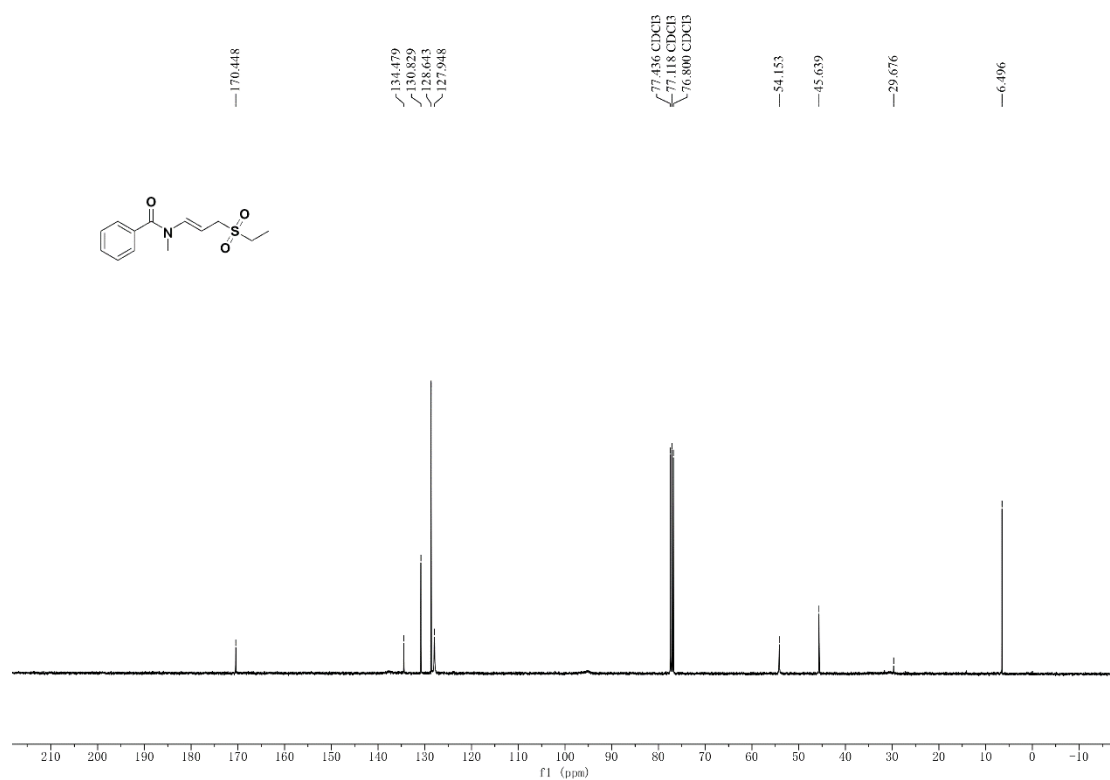


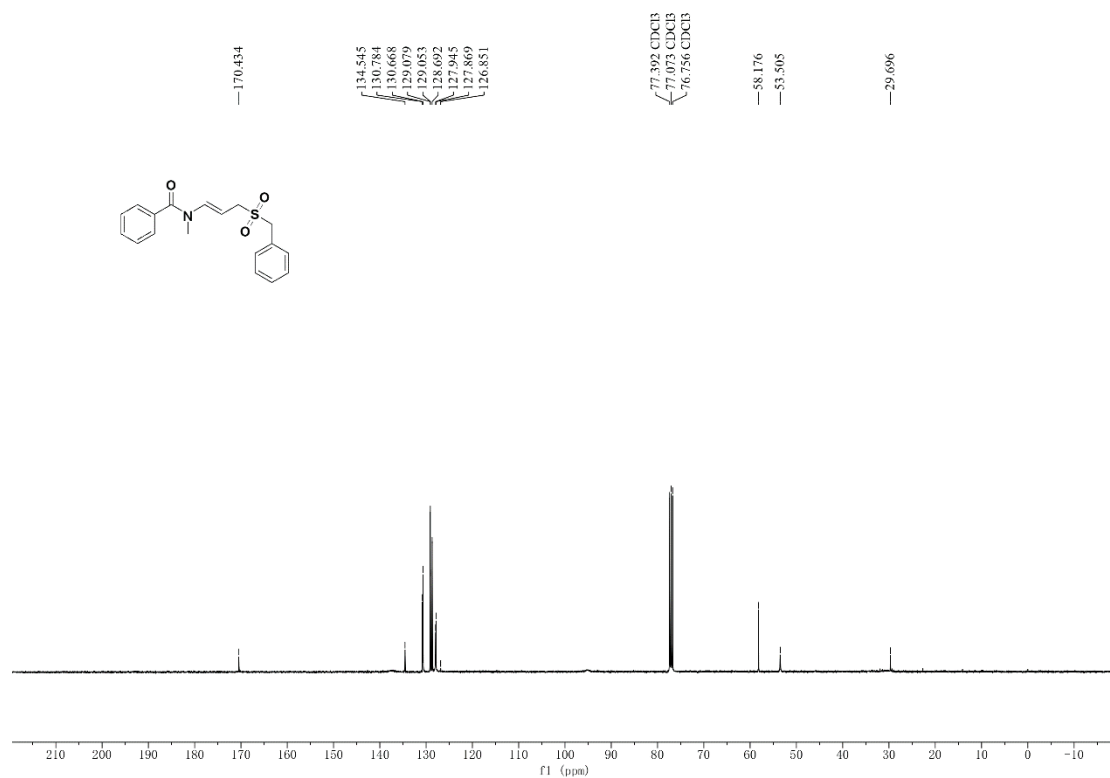
¹³C NMR Spectrum of Compound 4g



¹H NMR Spectrum of Compound 4h







^{13}C NMR Spectrum of Compound 4j