Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Generation of (*Z*)-*β*-alkenyl alkylsulfones via a copper-catalyzed decarboxylative alkylsulfonylation

Tonghao Zhu,[a] Pornchai Rojsitthisak[b] and Jie Wu *[a,c]

[a] *School of Pharmaceutical and Chemical Engineering & Institute for Advanced Studies, Taizhou University, 1139 Shifu Avenue, Taizhou 318000, China*

[b] *Department of Food and Pharmaceutical Chemistry, Faculty of Pharmaceutical Sciences, Chulalongkorn University, 254 Phayathai Road, Patumwan, Bangkok 10330, Thailand.*

[c] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*

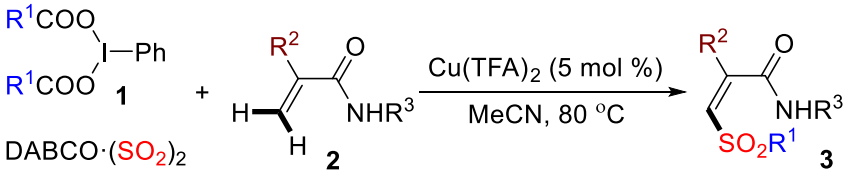
*E-mail: jie_wu@fudan.edu.cn

Supporting Information

General information.

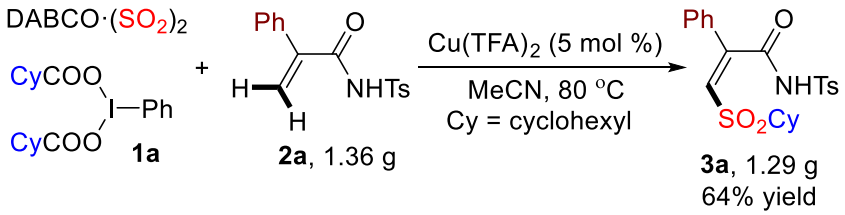
All reactions were carried out in oven dried Schlenk tubes under nitrogen atmosphere. All of *N*-tosyl acrylamides were prepared as reported in the reference.[1] DABCO·$(SO_2)_2$ was prepared according to the reported method.[2] Phenyliodine(III) dicarboxylates were freshly prepared according to the literature.[3] Dry acetonitrile (MeCN) was purchased from Energy Chemical, and copper trifluoroacetate ($Cu(TFA)_2$) was purchased from Adamas-beta. ^1H, ^{19}F, ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on Bruker Avance 400 MHz spectrometers. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI Source). Electrospray–ionisation HRMS data were acquired on a Q–Tof mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF. NMR spectra were taken using TMS (^1H, δ = 0), $CDCl_3$ (^1H, δ = 7.26), $CDCl_3$ (^{13}C, CPD δ = 77.0), DMSO-d_6 (^1H, δ = 2.50) and DMSO-d_6 (^{13}C, CPD δ = 40.0) as the internal standards, respectively. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

General procedures for the synthesis of (Z)-vinyl sulfone derivatives



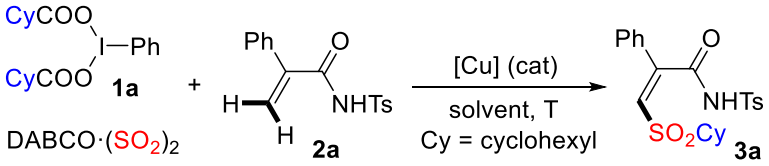
Phenyliodine(III) dicarboxylate **1** (0.6 mmol, 2.0 equiv), acrylamide **2** (0.3 mmol), DABCO·$(SO_2)_2$ (0.6 mmol, 2.0 equiv), and copper trifluoroacetate (0.015 mmol, 5 mol %) were added sequentially into Schlenk tube under nitrogen. Then MeCN (1.5 mL) was added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours as monitored by TLC. Upon completion, solvent was concentrated under vacuum and the residue was purified by flash column chromatography using *n*-hexane/acetone as eluent to afford pure product **3**.

Gram-scale experiment



Phenyliodine(III) dicarboxylate **1a** (9.0 mmol, 2.0 equiv), *N*-tosyl acrylamide **2a** (4.5 mmol, 1.36 g), DABCO·$(SO_2)_2$ (9.0 mmol, 2.0 equiv), and copper trifluoroacetate (0.225 mmol, 5 mol %) were added sequentially into Schlenk tube under nitrogen. Then MeCN (20 mL) was added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours as monitored by TLC. Upon completion, the mixture was cooled to room temperature. Then, the mixture was filtered through a Celite pad eluted with dichloromethane and concentrated under vacuum. The residue was purified by flash column chromatography using *n*-hexane/acetone (10:1 to 3:1) as eluent to afford pure product **3a** (1.29 g, 64%).

Table S1. Optimization of reaction conditions [a]



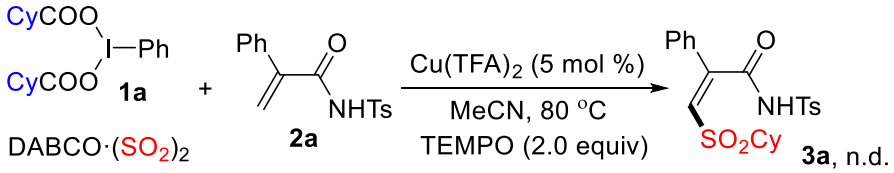
Entry	[Cu] catalyst (mol %)	Solvent	Temperature (°C)	Yield (%) [b]
1	CuCl (10)	MeCN	80	21
2	CuBr (10)	MeCN	80	trace
3	CuI (10)	MeCN	80	trace
4	CuOAc (10)	MeCN	80	57
5	CuTc (10)	MeCN	80	52
6	CuOTf (10)	MeCN	80	42
7	$Cu(MeCN)_4BF_4$ (10)	MeCN	80	55
8	$Cu(MeCN)_4PF_6$ (10)	MeCN	80	54
9	$Cu(OAc)_2$ (10)	MeCN	80	58
10	$Cu(OTf)_2$ (10)	MeCN	80	57
11	$Cu(acac)_2$ (10)	MeCN	80	60
12	$CuCl_2$(10)	MeCN	80	11
13	$CuBr_2$ (10)	MeCN	80	trace
14	$Cu(TFA)_2$ (10)	MeCN	80	63
13	$Cu(TFA)_2$ (10)	DCE	80	17
14	$Cu(TFA)_2$ (10)	EA	80	30
15	$Cu(TFA)_2$ (10)	toluene	80	trace
16	$Cu(TFA)_2$ (10)	DMF	80	19
17	$Cu(TFA)_2$ (10)	DMSO	80	43
18	$Cu(TFA)_2$ (10)	1,4-dioxane	80	23
19 [c]	$Cu(TFA)_2$ (10)	MeCN	80	14
20	$Cu(TFA)_2$ (5)	MeCN	80	65
21	$Cu(TFA)_2$ (15)	MeCN	80	58
22	$Cu(TFA)_2$ (20)	MeCN	80	57

23	$Cu(TFA)_2$ (5)	MeCN	50	14
24	$Cu(TFA)_2$ (5)	MeCN	rt	n.d.
25 [d]	$Cu(TFA)_2$ (5)	MeCN	80	45
26 [e]	$Cu(TFA)_2$ (5)	MeCN	80	80
27	$Cu(TFA)_2$ (0)	MeCN	80	trace

[a] Reaction conditions: phenyliodine(III) dicyclohexylcarboxylate **1a** (0.3 mmol, 1.5 equiv), *N*-tosyl acrylamide **2a** (0.2 mmol), DABCO·$(SO_2)_2$ (0.3 mmol, 1.5 equiv), copper catalyst, solvent (1.0 mL), sealed tube, N_2, 12 h. [b] ^1H NMR yield using mesitylene as internal standard. [c] $K_2S_2O_5$ was used as the sulfur dioxide surrogate. [d] Phenyliodine(III) dicyclohexylcarboxylate **1a** (0.24 mmol, 1.2 equiv) and DABCO·$(SO_2)_2$ (0.24 mmol, 1.2 equiv) were used. [e] Phenyliodine(III) dicyclohexylcarboxylate **1a** (0.4 mmol, 2.0 equiv) and DABCO·$(SO_2)_2$ (0.4 mmol, 2.0 equiv) were used.

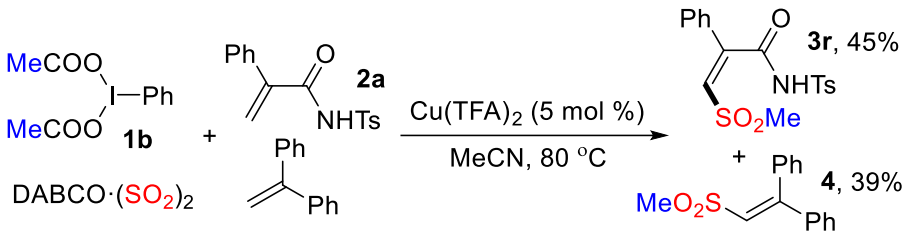
Mechanistic studies

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

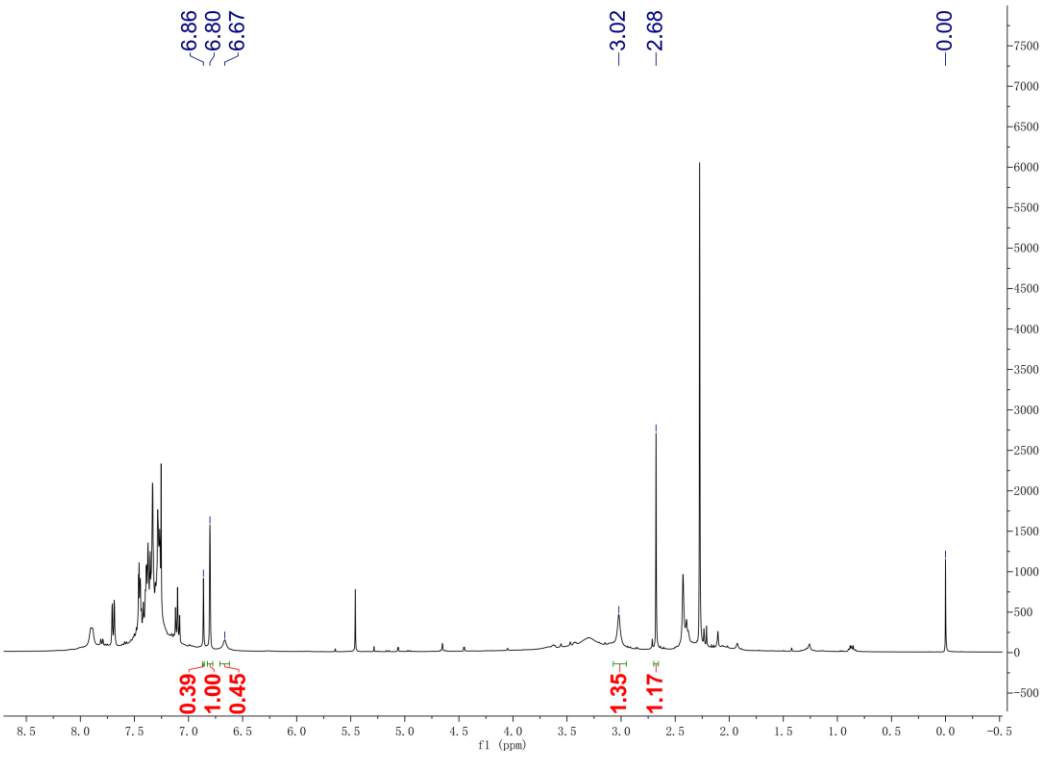


Phenyliodine(III) dicarboxylate **1a** (0.4 mmol, 2.0 equiv), *N*-tosyl acrylamide **2a** (0.2 mmol), DABCO·$(SO_2)_2$ (0.4 mmol, 2.0 equiv), $Cu(TFA)_2$ (0.01 mmol, 5 mol %), and TEMPO (0.4 mmol, 2.0 equiv) were added sequentially into Schlenk tube under nitrogen. Then MeCN (1 mL) was added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours. The resulting mixture was filtered through a Celite pad eluted with dichloromethane. The mixture was concentrated, and the crude was determined by NMR analysis using mesitylene as the internal standard.

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



Phenyliodine(III) dicarboxylate **1b** (0.4 mmol, 2.0 equiv), *N*-tosyl acrylamide **2a** (0.2 mmol), DABCO·$(SO_2)_2$ (0.4 mmol, 2.0 equiv) and $Cu(TFA)_2$ (0.01 mmol, 5 mol %) were added sequentially into Schlenk tube under nitrogen. Then ethene-1,1-diyldibenzene (0.2 mmol) and MeCN (1 mL) were added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours. The resulting mixture was filtered through a Celite pad eluted with dichloromethane. The mixture was concentrated, and the crude was determined by NMR analysis using mesitylene as the internal standard.



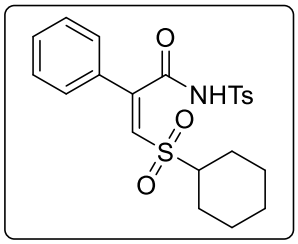
References

1. Feng, C.; Loh, T.-P. *Angew. Chem., Int. Ed*. **2013**, *52*, 12414 -12417.

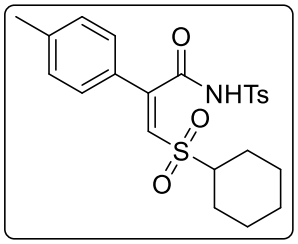
2. Mileghem, S. V.; De Borggraeve, W. M. *Org. Process Res. Dev*. **2017**, *21*, 785.

3. Liang, Y.; Zhang X.; MacMillan, D. W. C. *Nature*, **2018**, *559*, 83.

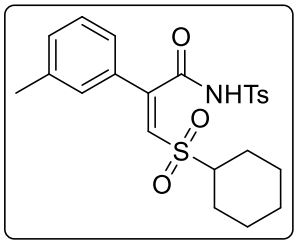
Characterization data for products



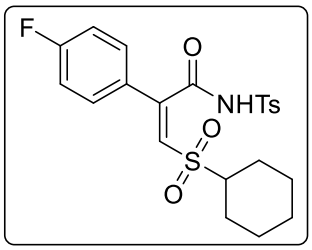
(*Z*)-3-(cyclohexylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3a**): 100.1 mg, yield: 75%, light yellow solid, m.p.: 197.4 – 199.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.46 (br, 1H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.42 (m, 1H), 7.40 – 7.30 (m, 6H), 6.59 (s, 1H), 2.83 (tt, *J* = 11.7, 2.8 Hz, 1H), 2.46 (s, 3H), 1.99 – 1.91 (m, 2H), 1.87 – 1.76 (m, 2H), 1.69 – 1.60 (m, 1H), 1.43 – 1.29 (m, 2H), 1.26 – 1.09 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.6, 149.7, 144.8, 135.1, 131.7, 131.4, 129.2, 129.1, 128.8, 127.2, 123.8, 63.1, 24.9, 24.7, 24.6, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{25}NNaO_5S_2^+$ 470.1066, found 470.1074.



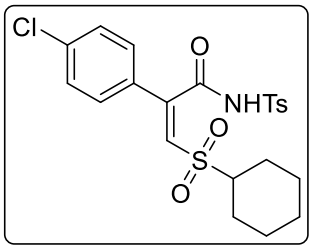
(*Z*)-3-(cyclohexylsulfonyl)-2-(*p*-tolyl)-*N*-tosylacrylamide (**3b**): 85.8 mg, yield: 62%, light yellow solid, m.p.: 202.7 – 204.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.32 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.55 (s, 1H), 2.81 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H), 1.98 – 1.90 (m, 2H), 1.85 – 1.78 (m, 2H), 1.68 – 1.60 (m, 1H), 1.44 – 1.29 (m, 2H), 1.26 – 1.07 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.8, 149.5, 144.8, 142.2, 135.1, 129.9, 129.1, 128.9, 128.8, 127.2, 122.6, 63.2, 24.9, 24.75, 24.69, 21.7, 21.4. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{27}NNaO_5S_2^+$ 484.1223, found 484.1231.



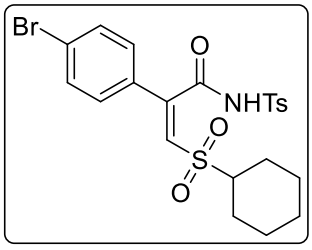
(*Z*)-3-(cyclohexylsulfonyl)-2-(*m*-tolyl)-*N*-tosylacrylamide (**3c**): 96.5 mg, yield: 70%, light yellow solid, m.p.: 225.3 – 227.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 12.78 (s, 1H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.31 -7.23 (m, 2H), 7.18 – 7.08 (m, 2H), 6.96 (s, 1H), 3.02 (t, *J* = 11.4 Hz, 1H), 2.44 (s, 3H), 2.19 (s, 3H), 2.02 – 1.90 (m, 2H), 1.85 – 1.73 (m, 2H), 1.67 – 1.56 (m, 1H), 1.42 – 1.06 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 164.5, 148.1, 144.9, 138.8, 136.4, 132.5, 132.1, 129.9, 129.4, 128.4, 127.7, 124.6, 123.8, 61.9, 25.3, 24.9, 24.8, 21.6, 21.3. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{27}NNaO_5S_2^+$ 484.1223, found 484.1232.



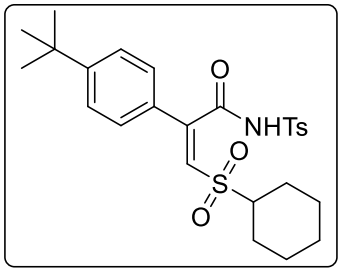
(*Z*)-3-(cyclohexylsulfonyl)-2-(4-fluorophenyl)-*N*-tosylacrylamide (**3d**): 94.1 mg, yield: 67%, light yellow solid, m.p.: 170.0 – 172.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.69 (br, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.56 (s, 1H), 2.84 (tt, *J* = 12.0, 3.2 Hz, 1H), 2.46 (s, 3H), 2.00 – 1.92 (m, 2H), 1.87 – 1.79 (m, 2H), 1.70 – 1.60 (m, 1H), 1.45 – 1.09 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 164.49 (d, *J* = 252.0Hz), 163.6, 148.7, 144.9, 135.1, 129.54 (d, *J* = 8.0Hz), 129.2, 128.8, 127.86 (d, *J* = 4.0Hz), 123.4, 116.38 (d, *J* = 22.0Hz), 63.1, 24.9, 24.73, 24.66, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -107.65 - -107.35 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{24}FNNaO_5S_2^+$ 488.09723, found 488.0984.



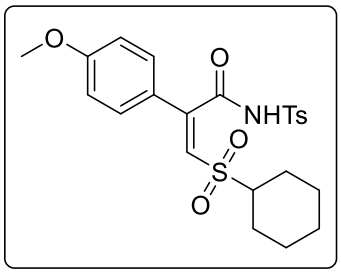
(*Z*)-2-(4-chlorophenyl)-3-(cyclohexylsulfonyl)-*N*-tosylacrylamide (**3e**): 92.5 mg, yield: 64%, light yellow solid, m.p.: 203.8 – 205.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.67 (br, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.28 (m, 6H), 6.59 (s, 1H), 2.84 (tt, *J* = 12.0, 3.2 Hz, 1H), 2.47 (s, 3H), 2.01 – 1.92 (m, 2H), 1.88 – 1.77 (m, 2H), 1.70 – 1.59 (m, 1H), 1.44 – 1.31 (m, 2H), 1.27 – 1.08 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.4, 148.6, 145.0, 137.8, 135.1, 130.1, 129.5, 129.2, 128.8, 128.6, 124.1, 63.2, 24.9, 24.75, 24.69, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{24}Cl^{35}NNaO_5S_2^+$ 504.0677, found: 504.0687; calcd for $C_{22}H_{24}Cl^{37}NNaO_5S_2^+$ 506.0647, found 506.0660.



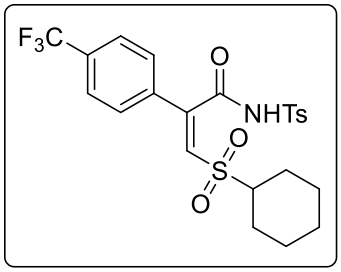
(*Z*)-2-(4-bromophenyl)-3-(cyclohexylsulfonyl)-*N*-tosylacrylamide (**3f**): 71.2 mg, yield: 45%, light yellow solid, m.p.: 204.1 – 205.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.70 (br, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.60 (s, 1H), 2.85 (tt, *J* = 11.9, 3.2 Hz, 1H), 2.47 (s, 3H), 2.00 – 1.92 (m, 2H), 1.88 – 1.78 (m, 2H), 1.72 – 1.62 (m, 1H), 1.46 – 1.29 (m, 2H), 1.18 (dt, J = 20.9, 14.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.4, 148.7, 145.0, 135.0, 132.4, 130.6, 129.2, 128.8, 128.7, 126.2, 124.1, 63.2, 24.9, 24.75, 24.69, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{24}Br^{79}NNaO_5S_2^+$ 548.0171, found: 548.0175; calcd for $C_{22}H_{24}Br^{81}NNaO_5S_2^+$ 550.0151, found 550.0160.



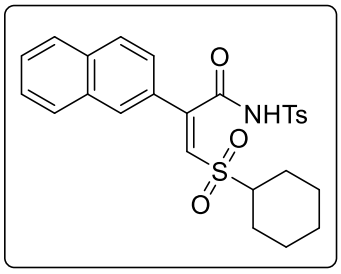
(*Z*)-2-(4-(*tert*-butyl)phenyl)-3-(cyclohexylsulfonyl)-*N*-tosylacrylamide (**3g**): 116.9 mg, yield: 77%, light yellow solid, m.p.: 173.5 – 175.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.21 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.29 (m, 6H), 6.56 (s, 1H), 2.80 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.46 (s, 3H), 2.00 - 1.88(m, 2H), 1.86 – 1.76 (m, 2H), 1.68 – 1.89 (m, 1H), 1.42 – 1.28 (m, 11H), 1.24 – 1.07 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.7, 155.2, 149.5, 144.7, 135.2, 129.1, 128.9, 128.7, 127.0, 126.2, 122.6 63.2, 34.9, 31.0, 24.9, 24.75, 24.71, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{33}NNaO_5S_2^+$ 526.1692, found: 526.1694.



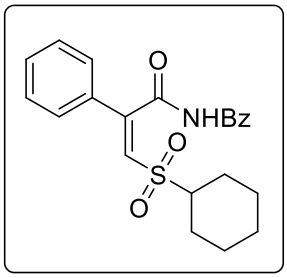
(*Z*)-3-(cyclohexylsulfonyl)-2-(4-methoxyphenyl)-*N*-tosylacrylamide (**3h**): 96.9 mg, yield: 68%, light yellow solid, m.p.: 174.8 – 176.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.20 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.31 (m, 4H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.49 (s, 1H), 3.84 (s, 3H), 2.79 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.46 (s, 3H), 1.98 – 1.89 (m, 2H), 1.86 – 1.77 (m, 2H), 1.68 – 1.60 (m, 1H), 1.41 – 1.09 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 164.0, 162.2, 149.1, 144.8, 135.1, 129.1, 129.0, 128.9, 123.8, 121.0, 114.7, 63.2, 55.5, 24.9, 24.8, 24.7, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{27}NNaO_6S_2^+$ 500.1172, found: 500.1182.



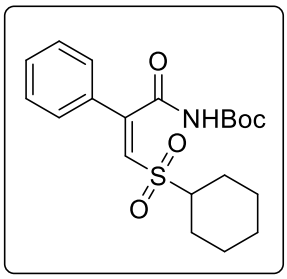
(*Z*)-3-(cyclohexylsulfonyl)-*N*-tosyl-2-(4-(trifluoromethyl)phenyl)acrylamide (**3i**): 85.4 mg, yield: 55%, light yellow solid, m.p.: 189.4 – 191.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.84 (br, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.68 (s, 1H), 2.88 (t, *J* = 11.9 Hz, 1H), 2.46 (s, 3H), 2.03 – 1.94 (m, 2H), 1.88 – 1.78 (m, 2H), 1.71 – 1.61 (m, 1H), 1.45 – 1.07 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.1, 148.5, 145.1, 135.2, 135.0, 132.89 (q, *J* = 32.7 Hz), 129.3, 128.7, 127.7, 126.10 (q, *J* = 3.7 Hz), 125.9, 123.45 (q, *J* = 271.0 Hz), 63.1, 24.9, 24.72, 24.68, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -63.03 (s). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{24}F_3NNaO_5S_2^+$ 538.0940, found 538.0952.



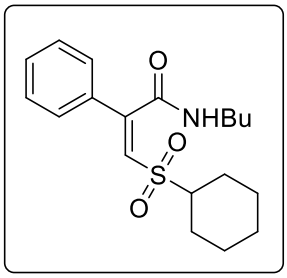
(*Z*)-3-(cyclohexylsulfonyl)-2-(naphthalen-2-yl)-*N*-tosylacrylamide (**3j**): 84.8 mg, yield: 57%, light yellow solid, m.p.: 248.7 – 250.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 12.88 (s, 1H), 8.02 – 7.80 (m, 4H), 7.69 – 7.39 (m, 7H), 7.30 (s, 1H), 3.08 (t, *J* = 11.5 Hz, 1H), 2.50 (s, 4H), 2.10 – 1.95 (m, 2H), 1.87 – 1.74 (m, 2H), 1.67 – 1.57 (m, 1H), 1.47 – 1.09 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 164.5, 147.9, 145.1, 136.5, 134.1, 132.6, 130.0, 129.3, 128.9, 128.5, 128.4, 128.2, 127.7, 124.3, 124.0, 61.9, 25.3, 24.9, 24.8, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{27}NNaO_5S_2^+$ 520.1223, found: 520.1222.



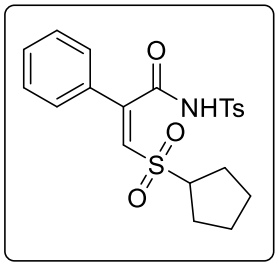
(*Z*)-*N*-(3-(cyclohexylsulfonyl)-2-phenylacryloyl)benzamide (**3m**): 24.7 mg, yield: 21%, white solid, m.p.: 181.7 – 183.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.15 (s, 1H), 7.86 – 7.78 (m, 2H), 7.62 – 7.53 (m, 3H), 7.49 – 7.39 (m, 5H), 6.55 (s, 1H), 2.98 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.26 – 2.14 (m, 2H), 1.94 – 1.82 (m, 2H), 1.73 – 1.65 (m, 1H), 1.53 (qd, *J* = 12.4, 3.1 Hz, 2H), 1.36 – 1.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 167.6, 164.4, 151.7, 133.4, 132.5, 131.7, 130.8, 129.1, 128.9, 127.9, 127.3, 121.6, 63.4, 25.1, 25.02, 25.01. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{23}NNaO_4S^+$ 420.1240, found: 420.1243.



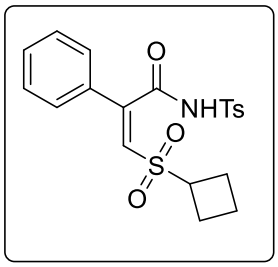
tert-butyl (*Z*)-(3-(cyclohexylsulfonyl)-2-phenylacryloyl)carbamate (**3n**): 27.5 mg, yield: 23%, white solid, m.p.: 161.9 – 163.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (s, 1H), 7.56 – 7.49 (m, 2H), 7.47 – 7.39 (m, 3H), 6.51 (s, 1H), 3.00 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.25 – 2.14 (m, 2H), 1.95 – 1.85 (m, 2H), 1.74 – 1.66 (m, 1H), 1.60 – 1.49 (m, 2H), 1.41 (s, 9H), 1.36 – 1.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 167.0, 151.1, 149.3, 132.4, 130.9, 129.1, 127.1, 121.8, 83.7, 63.4, 27.8, 25.1, 24.98, 24.96. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{27}NNaO_5S^+$ 416.1502, found: 416.1514.



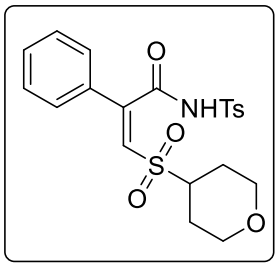
(*Z*)-*N*-butyl-3-(cyclohexylsulfonyl)-2-phenylacrylamide (**3o**): 27.5 mg, yield: 26%, (*Z/E* = 93/7), light yellow solid, m.p.: 126.9 – 128.1 °C. For major (*Z*)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 – 7.50 (m, 2H), 7.49 – 7.39 (m, 3H), 6.55 (s, 1H), 5.87 (t, *J* = 5.4 Hz, 1H), 3.41 (td, *J* = 7.3, 5.9 Hz, 2H), 3.14 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.24 – 2.14 (m, 2H), 1.95 – 1.85 (m, 2H), 1.78 – 1.64 (m, 1H), 1.63 – 1.53 (m, 2H), 1.43 – 1.14 (m, 7H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.4, 152.0, 133.6, 131.0, 129.1, 127.1, 123.6, 63.3, 39.8, 31.0, 25.1, 24.93, 24.91, 20.1, 13.6. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{27}NNaO_3S^+$ 372.1604, found: 372.1613.



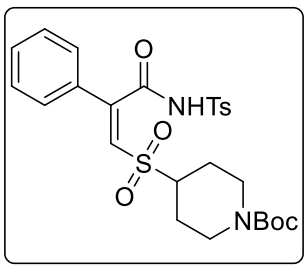
(*Z*)-3-(cyclopentylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3q**): 91.5 mg, yield: 70%, light yellow solid, m.p.: 156.4 – 158.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.48 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.41 – 7.34 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.63 (s, 1H), 3.45 – 3.32 (m, 1H), 2.45 (s, 3H), 2.02 – 1.90 (m, 2H), 1.89 – 1.78 (m, 2H), 1.72 – 1.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.7, 148.8, 144.9, 135.0, 131.6, 131.4, 129.22, 129.18, 128.9, 127.2, 124.7, 63.5, 26.5, 25.7, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{23}NNaO_5S_2^+$ 456.0910, found: 456.0925.



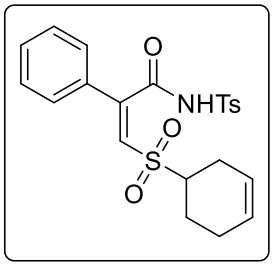
(*Z*)-3-(cyclobutylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3r**): 84.7 mg, yield: 67%, light yellow solid, m.p.: 154.1 – 155.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.54 (br, 1H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.38 – 7.30 (m, 6H), 6.58 (s, 1H), 3.77 (quint, *J* = 8.1 Hz, 1H), 2.47 – 2.34 (m, 5H), 2.21 – 2.10 (m, 2H), 1.99 – 1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.7, 149.4, 144.9, 135.0, 131.6, 131.4, 129.22, 129.20, 128.8, 127.2, 123.7, 56.1, 22.1, 21.7, 17.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{21}NNaO_5S_2^+$ 442.0753, found: 442.0760.



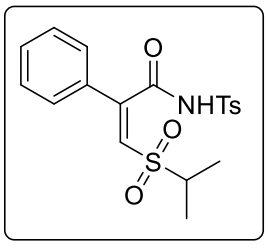
(*Z*)-2-phenyl-3-((tetrahydro-2H-pyran-4-yl)sulfonyl)-*N*-tosylacrylamide (**3s**): 69.8 mg, yield: 52%, light yellow solid, m.p.: 155.1 – 157.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.53 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.41 – 7.31 (m, 6H), 6.58 (s, 1H), 4.04 – 3.94 (m, 2H), 3.35 – 3.24 (m, 2H), 3.16 – 3.03 (m, 1H), 2.46 (s, 3H), 1.85 – 1.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.5, 150.6, 145.1, 135.0, 131.8, 131.4, 129.4, 129.3, 128.9, 127.3, 123.1, 66.2, 60.2, 24.7, 21.8. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{23}NNaO_6S_2^+$ 472.0859, found: 472.0864.



tert-butyl (*Z*)-4-((3-((4-methylphenyl)sulfonamido)-3-oxo-2-phenylprop-1-en-1-yl)sulfonyl)piperidine-1-carboxylate (**3t**): 88.9 mg, yield: 54%, light yellow solid, m.p.: 121.1 – 122.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.84 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.50 – 7.42 (m, 1H), 7.41 – 7.29 (m, 6H), 6.60 (s, 1H), 4.25 – 3.97 (m, 2H), 3.09 – 2.94 (m, 1H), 2.76 – 2.56 (m, 2H), 2.46 (s, 3H), 1.92 – 1.82 (m, 2H), 1.65 – 1.52 (m, 2H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.6, 154.3, 150.6, 145.0, 135.0, 131.7, 131.4, 129.3, 129.2, 128.8, 127.2, 123.1, 80.2, 61.2, 28.3, 24.2, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{32}N_2NaO_7S_2^+$ 571.1543, found: 571.1559.

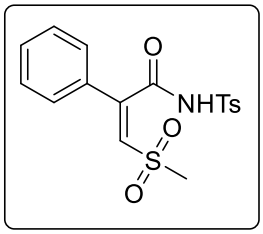


(*Z*)-3-(cyclohex-3-en-1-ylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3u**): 80.9 mg, yield: 61%, light yellow solid, m.p.: 169.0 – 171.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.53 (br, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.40 – 7.29 (m, 6H), 6.62 (s, 1H), 5.63 (dd, J = 23.3, 9.5 Hz, 2H), 3.17 – 3.04 (m, 1H), 2.46 (s, 3H), 2.31 – 1.98 (m, 5H), 1.66 – 1.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.6, 150.0, 144.9, 135.0, 131.5, 129.3, 129.2, 128.8, 127.2, 126.7, 123.4, 123.3, 59.8, 24.0, 23.7, 21.7, 21.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{23}NNaO_5S_2^+$ 468.0910, found: 468.0920.

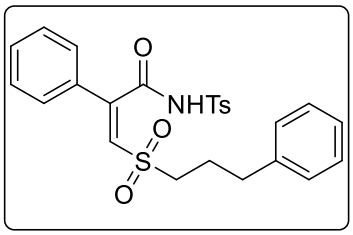


(*Z*)-3-(isopropylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3v**): 72.9 mg, yield: 60%, light yellow solid, m.p.: 136.4 – 137.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.29 (br, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.42 (m, 1H), 7.42 – 7.36 (m, 4H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.62 (s, 1H), 3.17 – 3.04 (m, 1H), 2.46 (s, 3H), 1.23 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100

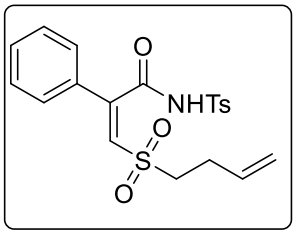
MHz, $CDCl_3$) δ ppm 163.6, 149.9, 144.9, 135.0, 131.6, 129.3, 129.2, 128.9, 127.2, 123.8, 55.5, 21.7, 15.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{21}NNaO_5S_2^+$ 430.0753, found: 430.0764.



(*Z*)-3-(methylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3w**): 84.2 mg, yield: 74%, light yellow solid, m.p.: 215.7 – 216.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 12.87 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.54 – 7.38 (m, 5H), 7.34 (*d*, J = 7.5 Hz, 2H), 7.29 (s, 1H), 3.10 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 164.7, 146.1, 144.8, 136.5, 132.6, 131.6, 129.9, 129.7, 128.4, 127.3, 126.9, 43.6, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{17}H_{17}NNaO_5S_2^+$ 402.0440, found: 402.0447.



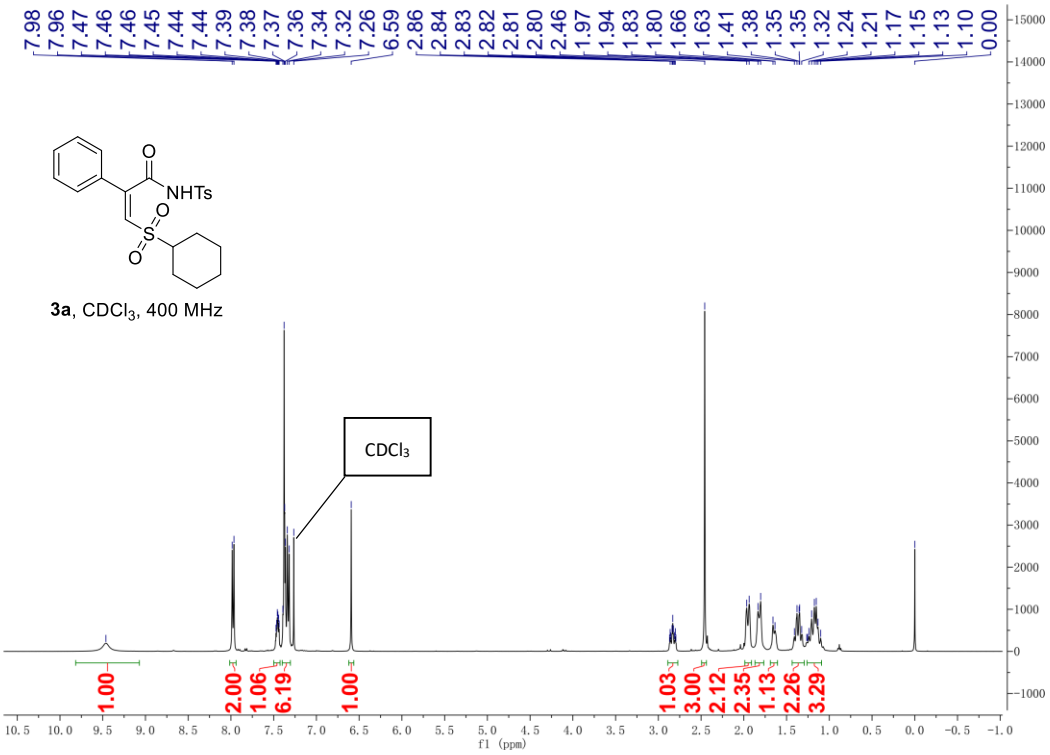
(*Z*)-2-phenyl-3-((3-phenylpropyl)sulfonyl)-*N*-tosylacrylamide (**3x**): 95.3 mg, yield: 66%, light yellow solid, m.p.: 192.1 – 193.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 12.90 (s, 1H), 7.87 (d, J = 7.0 Hz, 2H), 7.55 – 7.14 (m, 13H), 3.26 – 3.07 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.40 (s, 3H), 2.02 – 1.87 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 164.6, 147.4, 144.9, 141.2, 136.4, 132.6, 131.6, 129.8, 129.6, 128.93, 128.92, 128.5, 127.4, 126.6, 125.5, 54.3, 33.9, 23.9, 21.6. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S_2^+$ 506.1066, found: 506.1074.

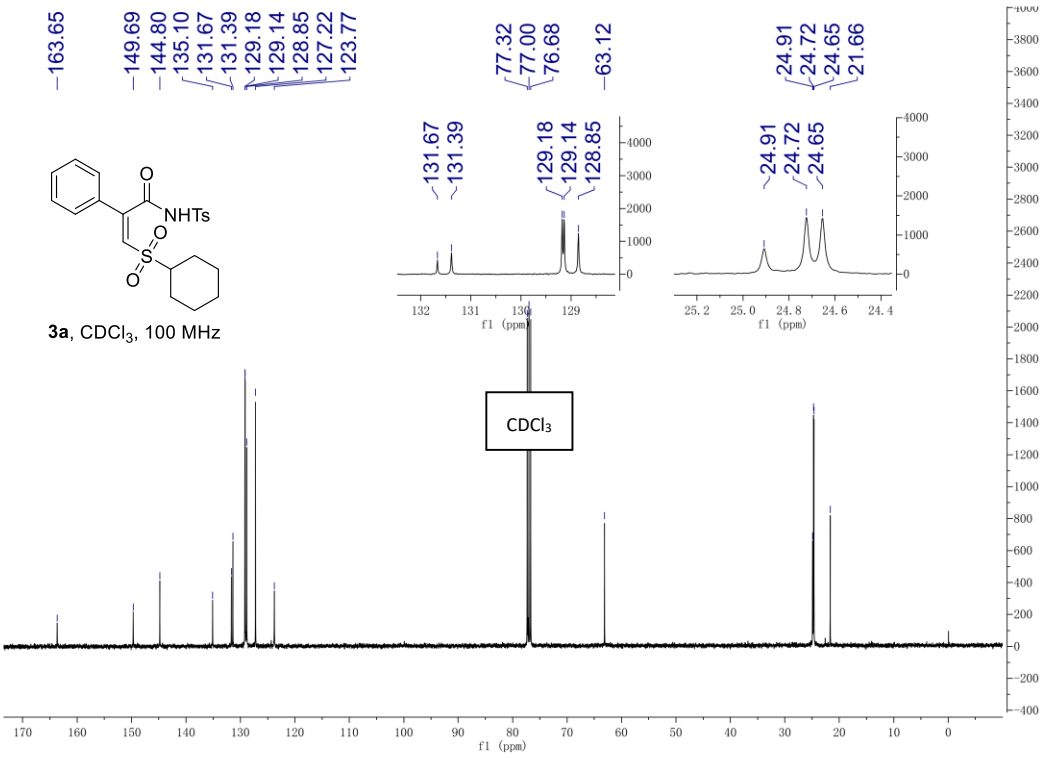


(*Z*)-3-(but-3-en-1-ylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3y**): 54.6 mg, yield: 43%, light yellow solid, m.p.: 166.4 – 168.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.47 (br, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.42 (m, 1H), 7.41 – 7.30 (m, 6H), 6.63 (s, 1H), 5.76 – 5.60 (m, 1H), 5.11 – 4.96 (m, 2H), 3.15 – 3.03 (m, 2H), 2.49 – 2.37 (m, 5H).^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.6, 149.4, 145.0, 135.0, 133.7, 131.6, 131.3, 129.30, 129.27, 128.8, 127.3, 125.4, 117.3, 55.0, 26.0, 21.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{21}NNaO_5S_2^+$ 442.0753, found: 442.0758.

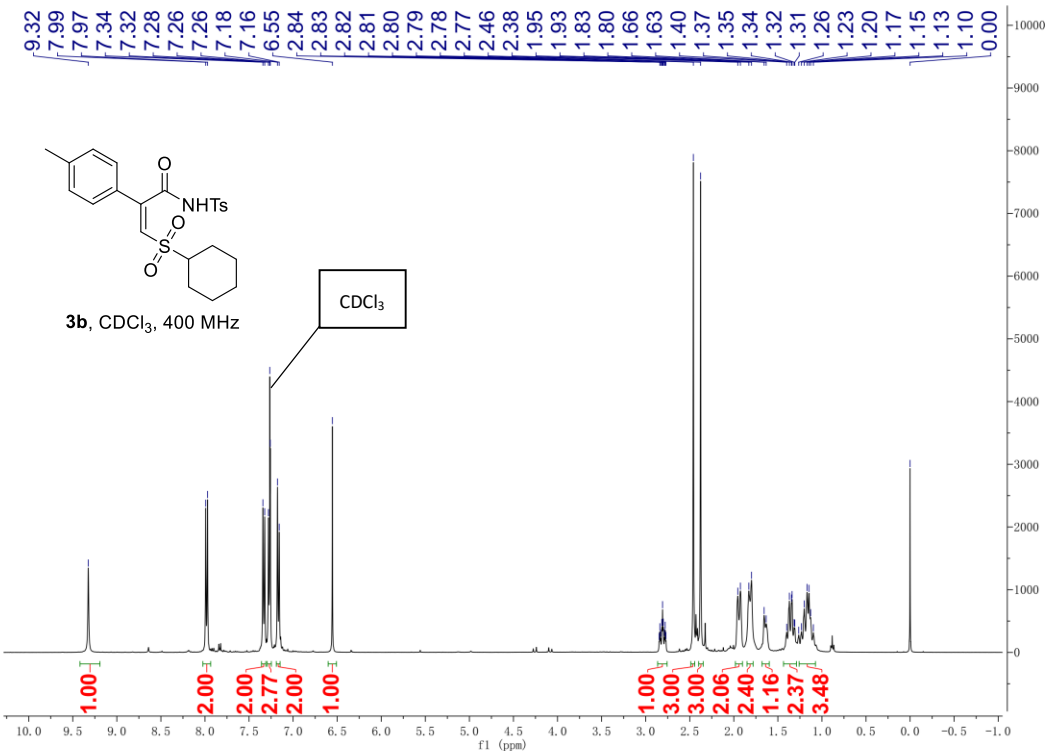
^{1}H, ^{19}F and ^{13}C NMR spectra of products

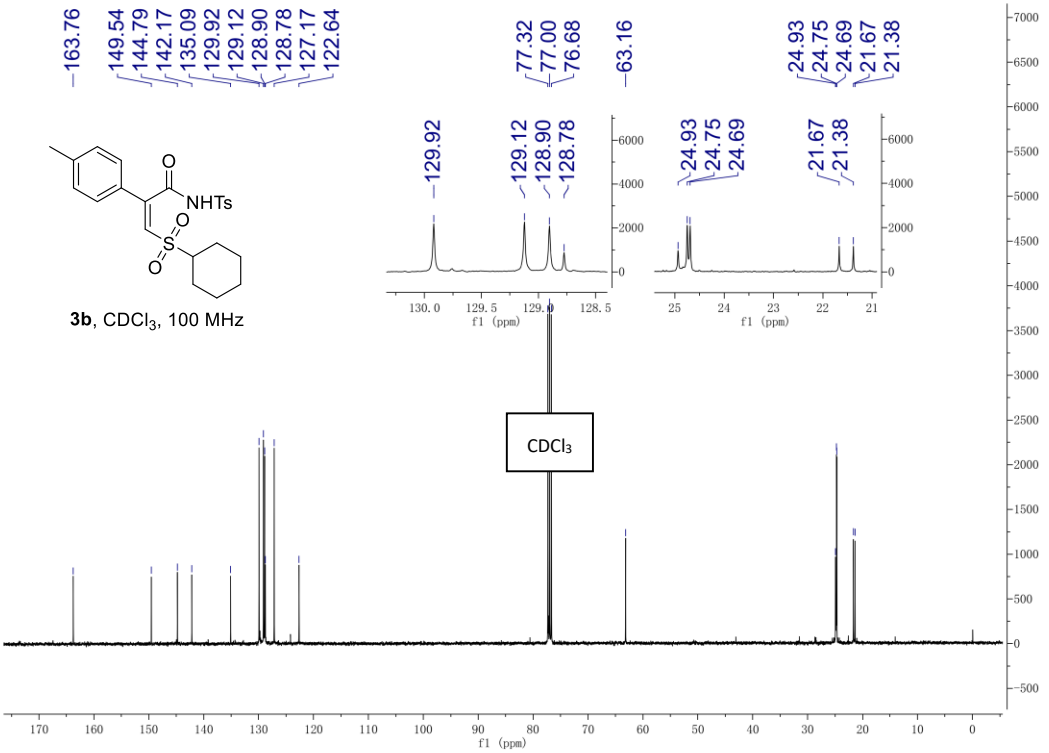
(*Z*)-3-(cyclohexylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3a**)



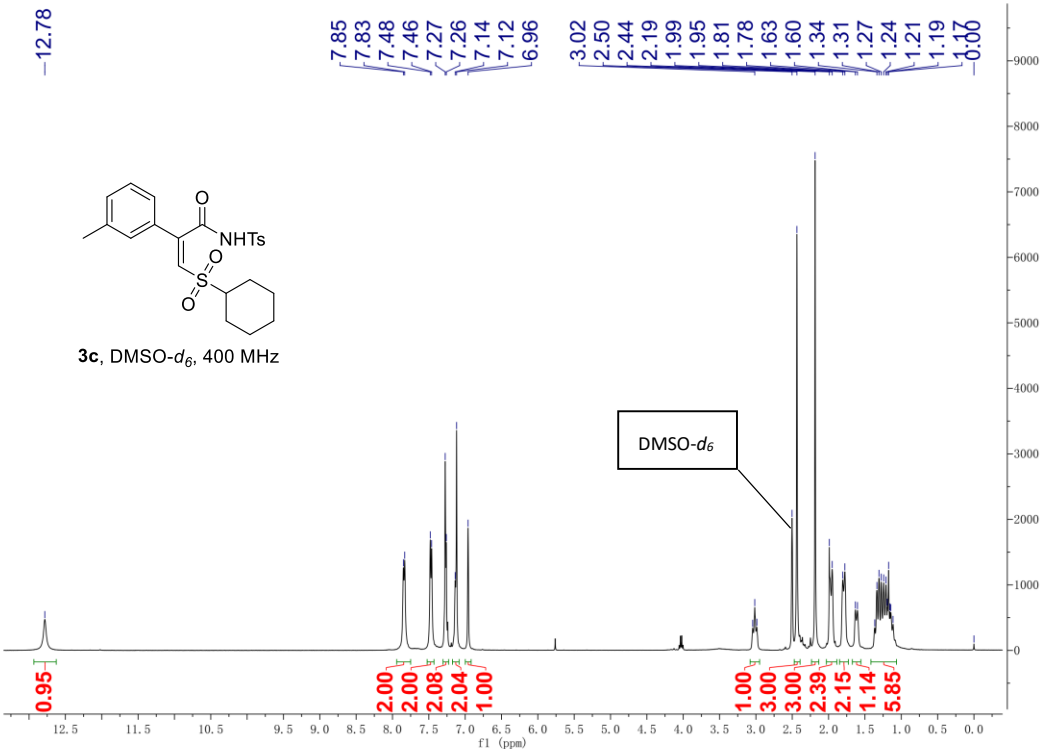


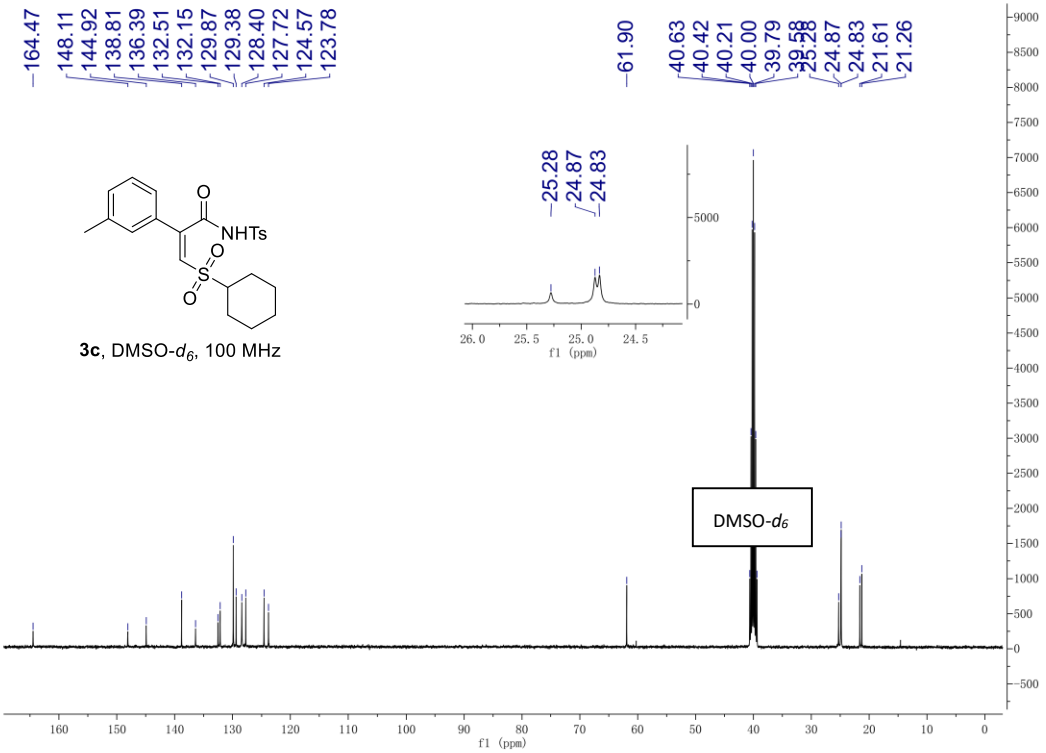
(*Z*)-3-(cyclohexylsulfonyl)-2-(*p*-tolyl)-*N*-tosylacrylamide (**3b**)



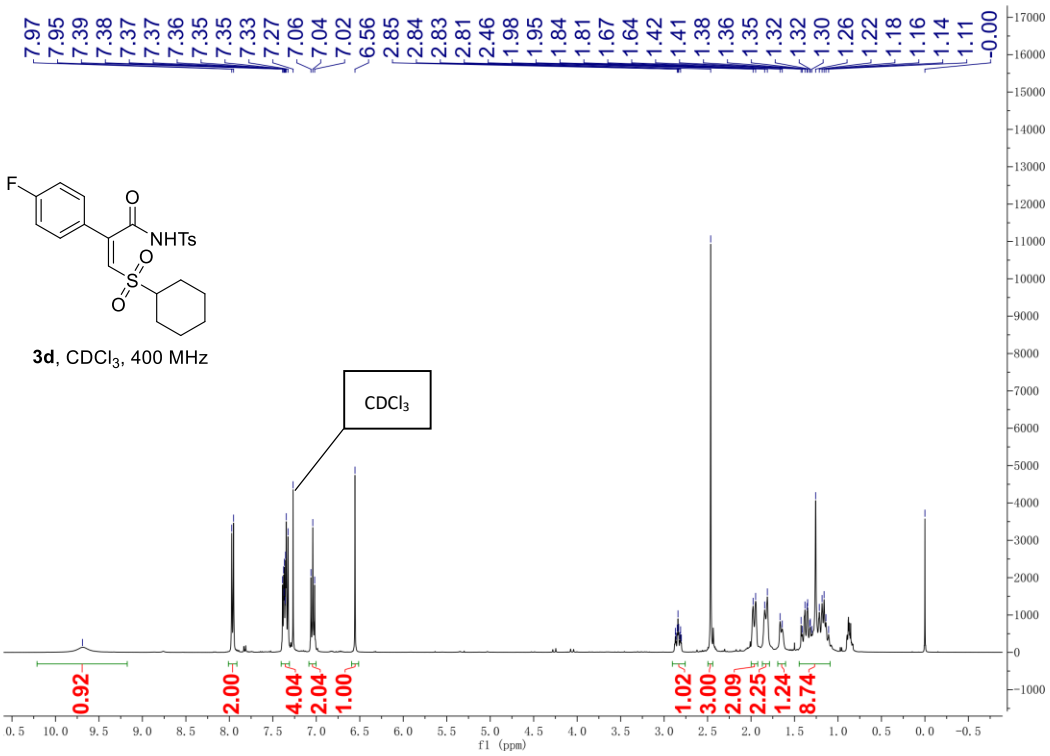


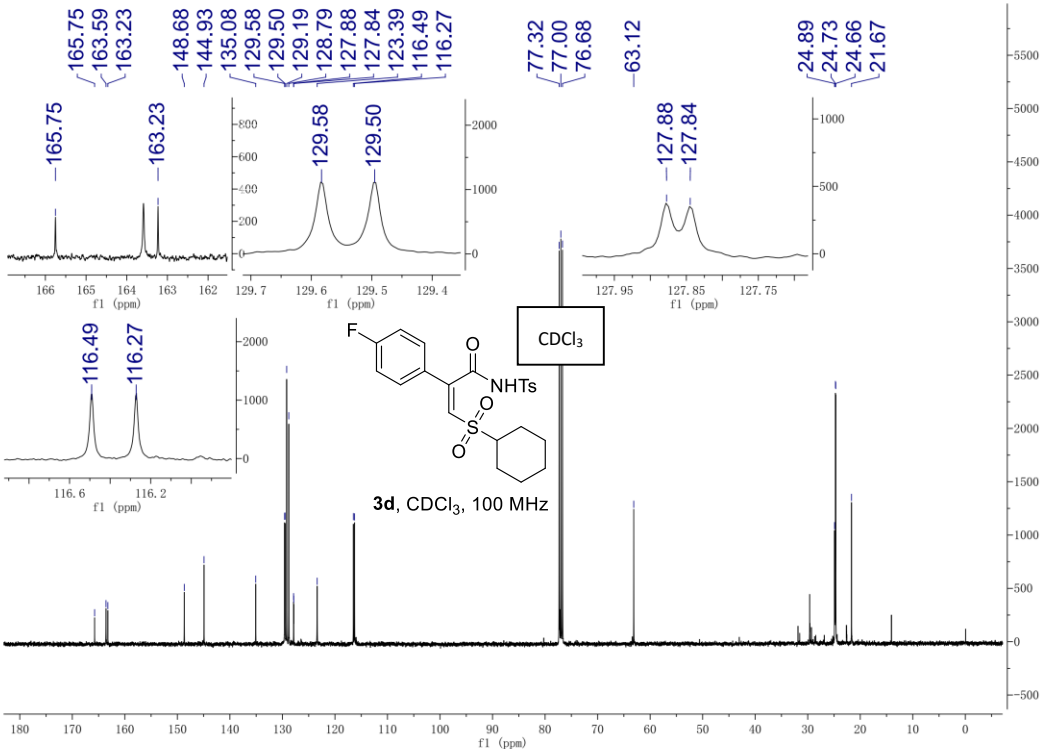
(*Z*)-3-(cyclohexylsulfonyl)-2-(*m*-tolyl)-*N*-tosylacrylamide (**3c**)

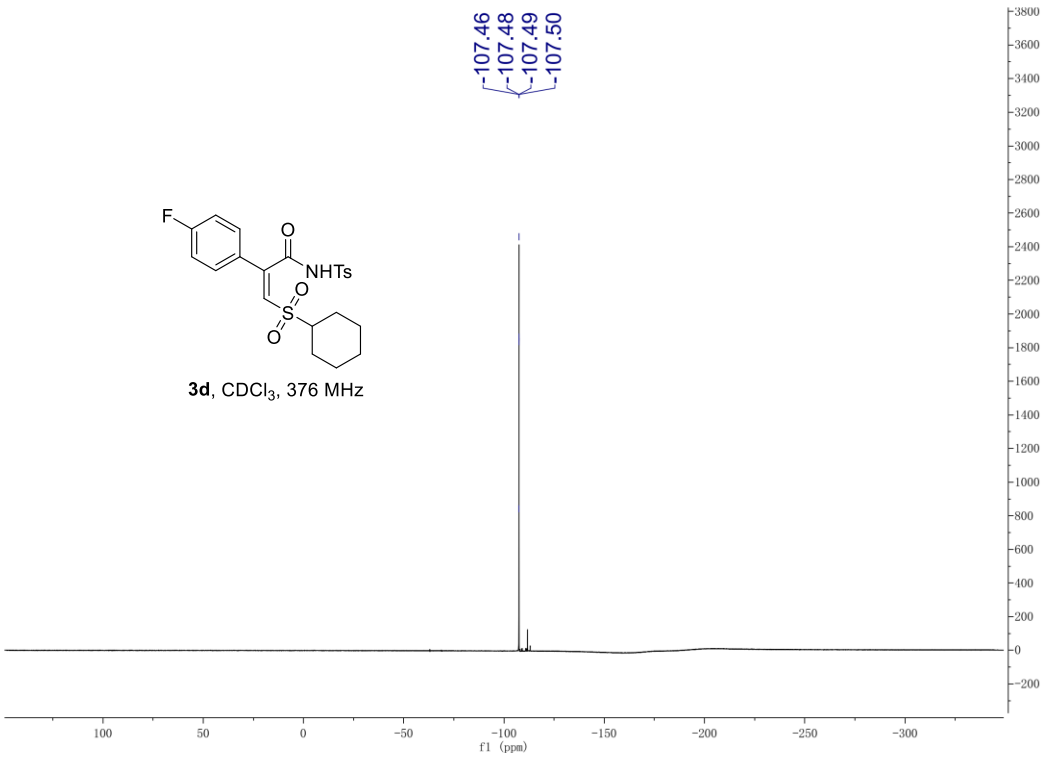




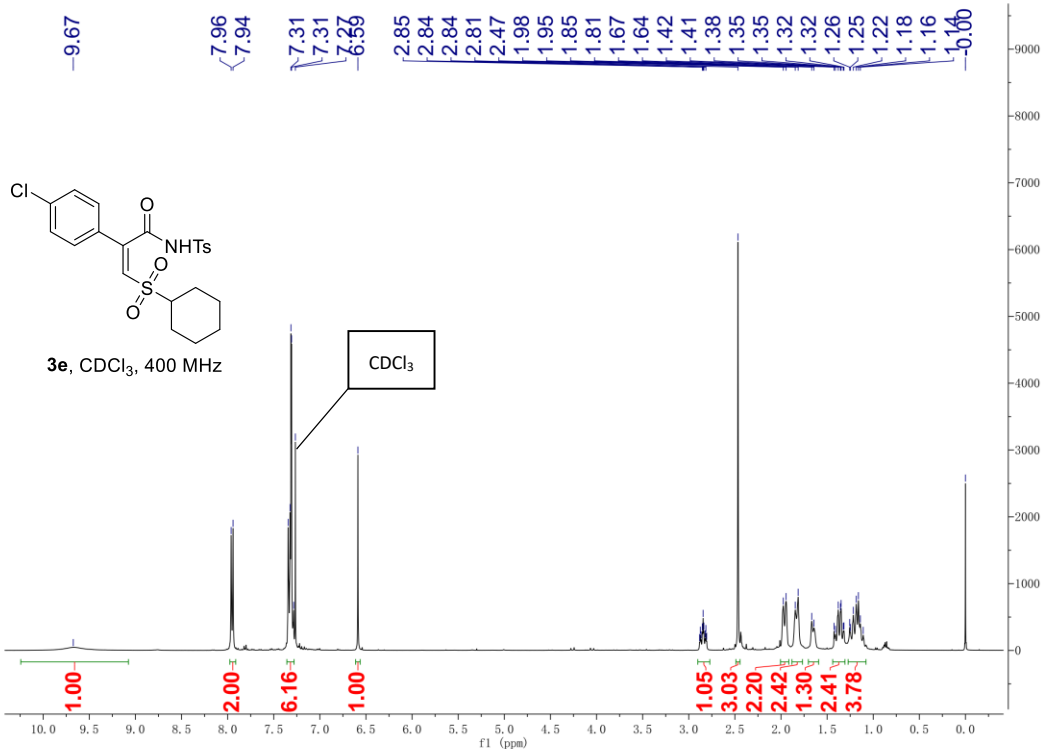
(*Z*)-3-(cyclohexylsulfonyl)-2-(4-fluorophenyl)-*N*-tosylacrylamide (**3d**)

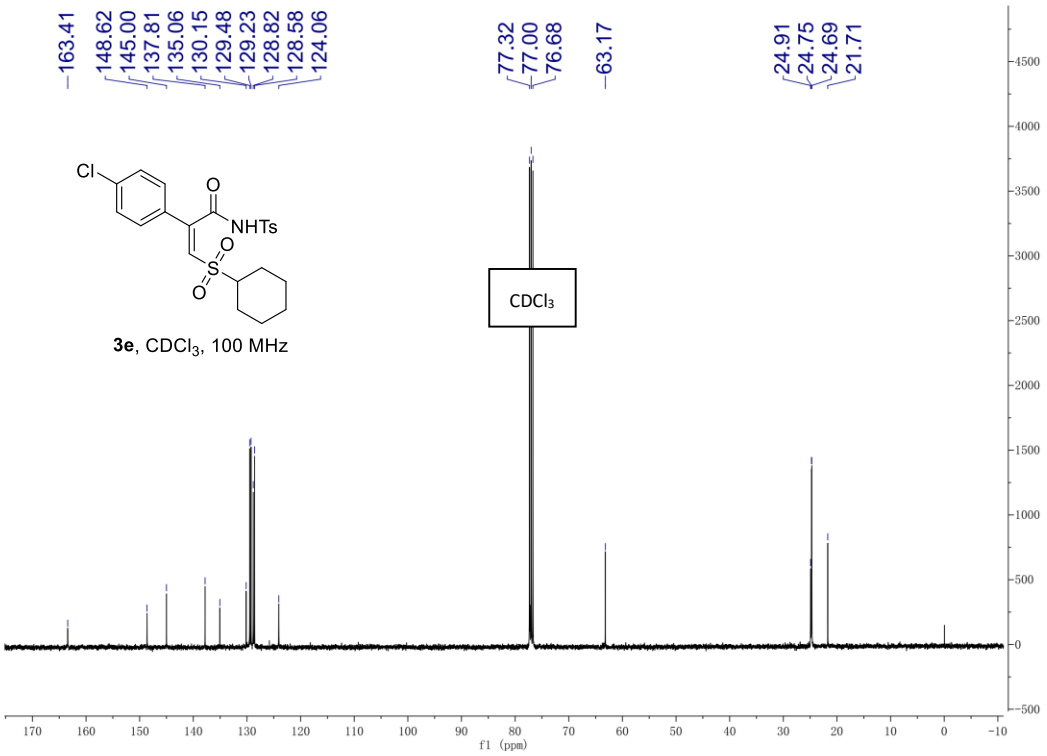




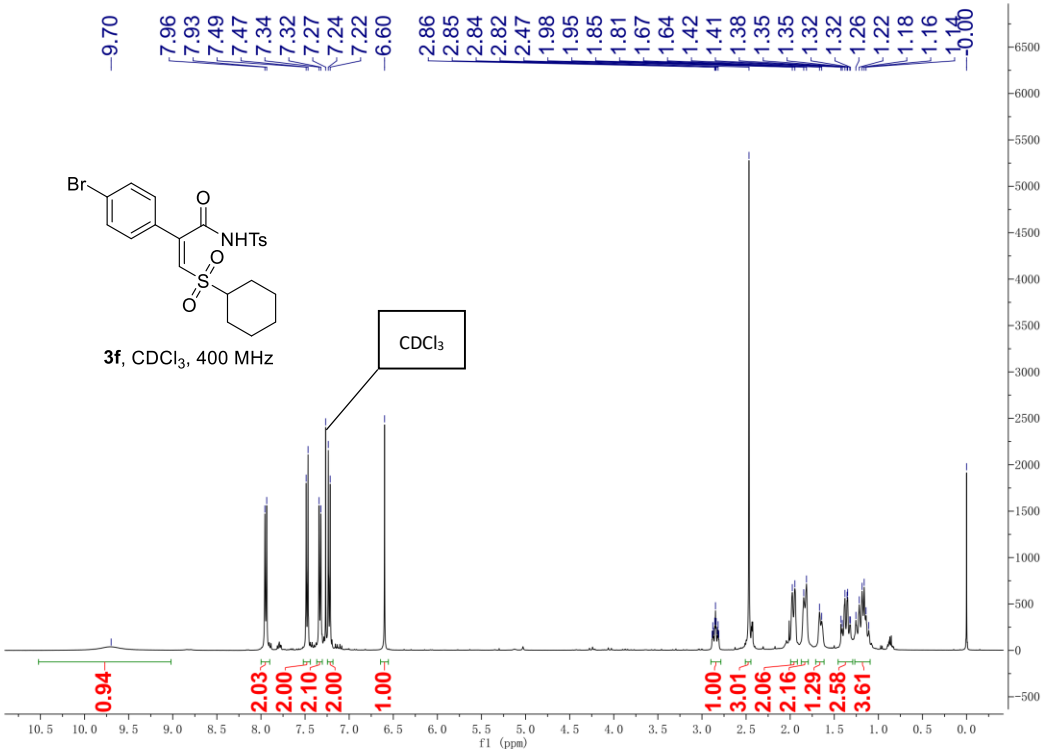


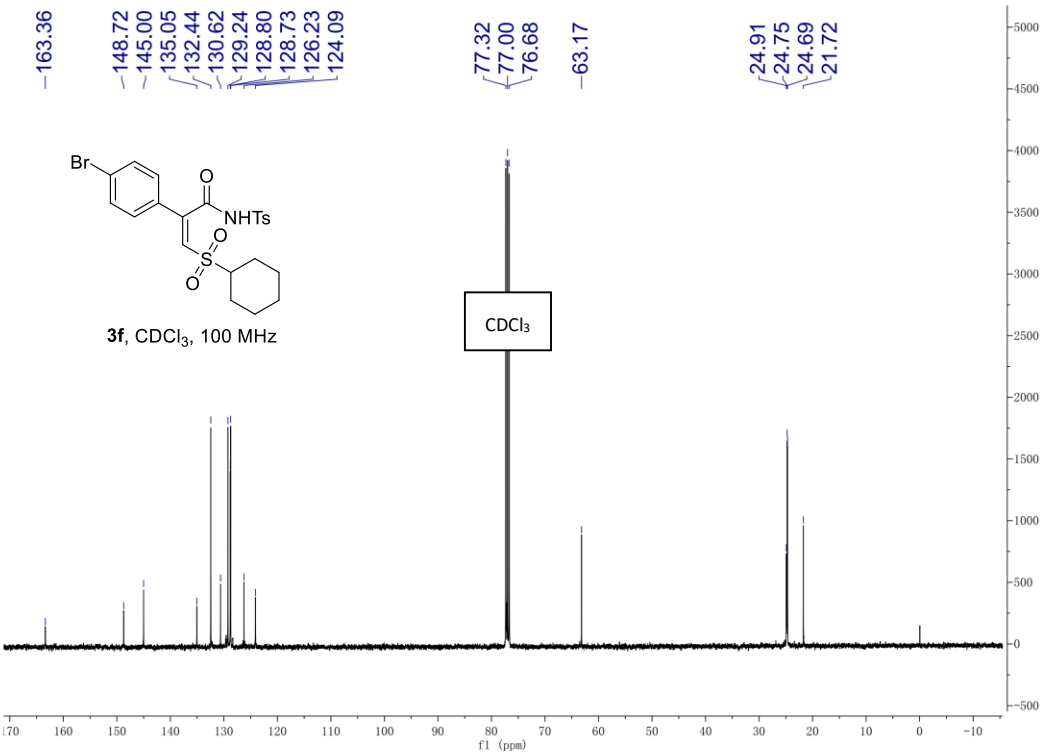
(*Z*)-2-(4-chlorophenyl)-3-(cyclohexylsulfonyl)-*N*-tosylacrylamide (**3e**)





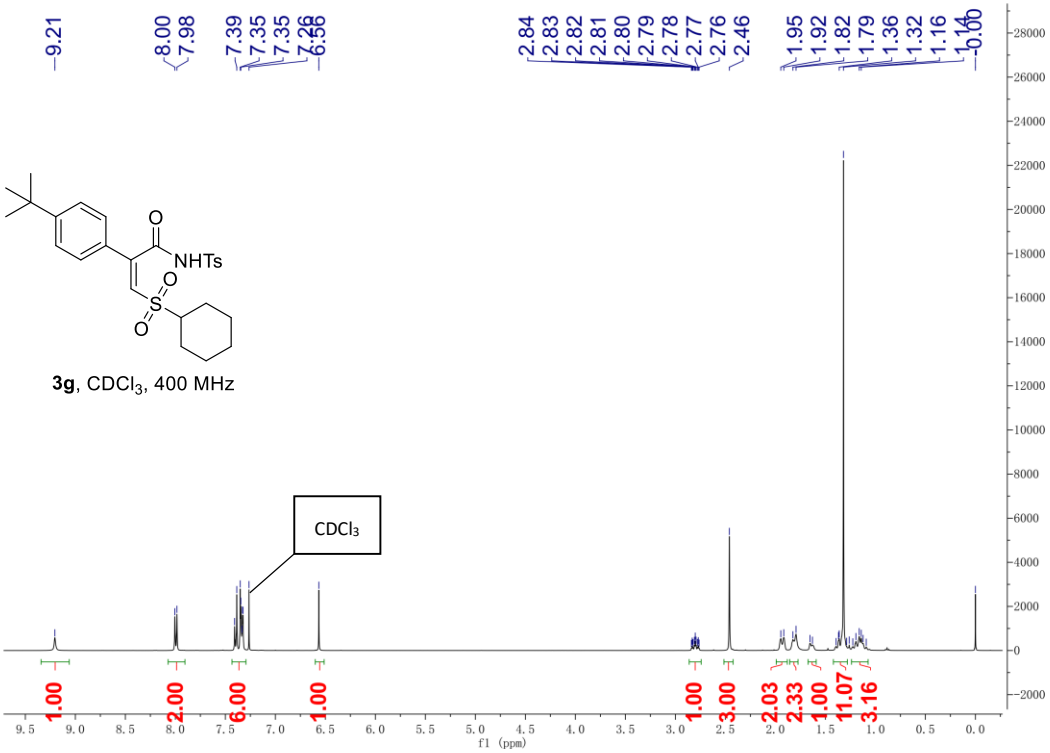
(*Z*)-2-(4-bromophenyl)-3-(cyclohexylsulfonyl)-*N*-tosylacrylamide (**3f**)



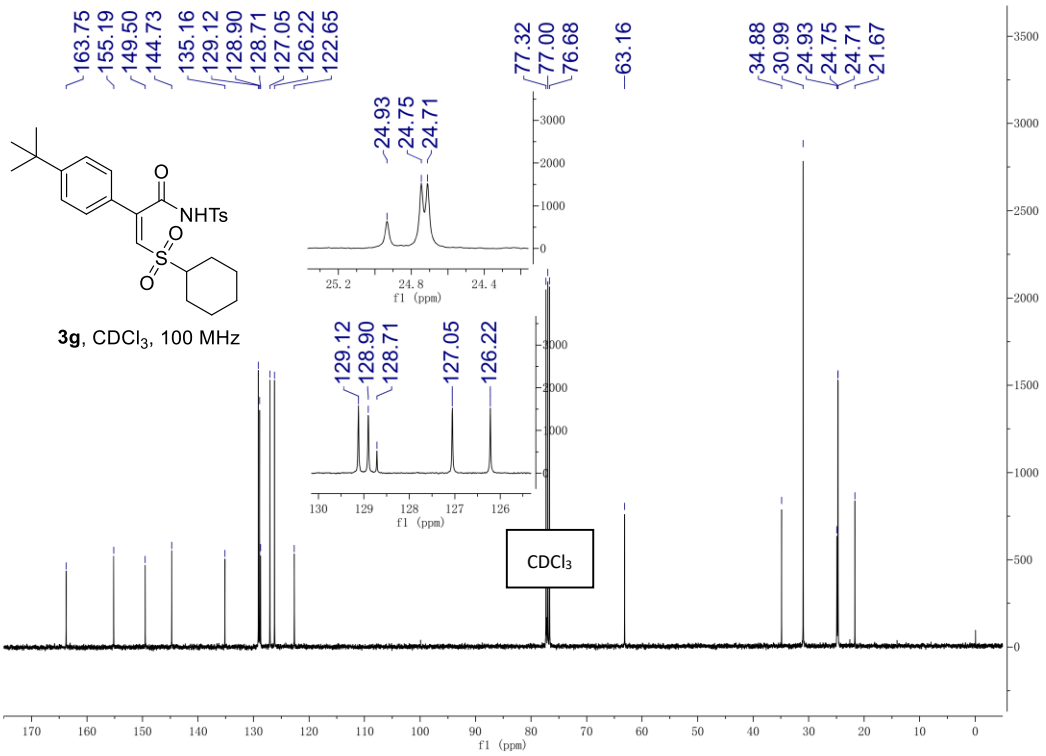


3f, $CDCl_3$, 100 MHz

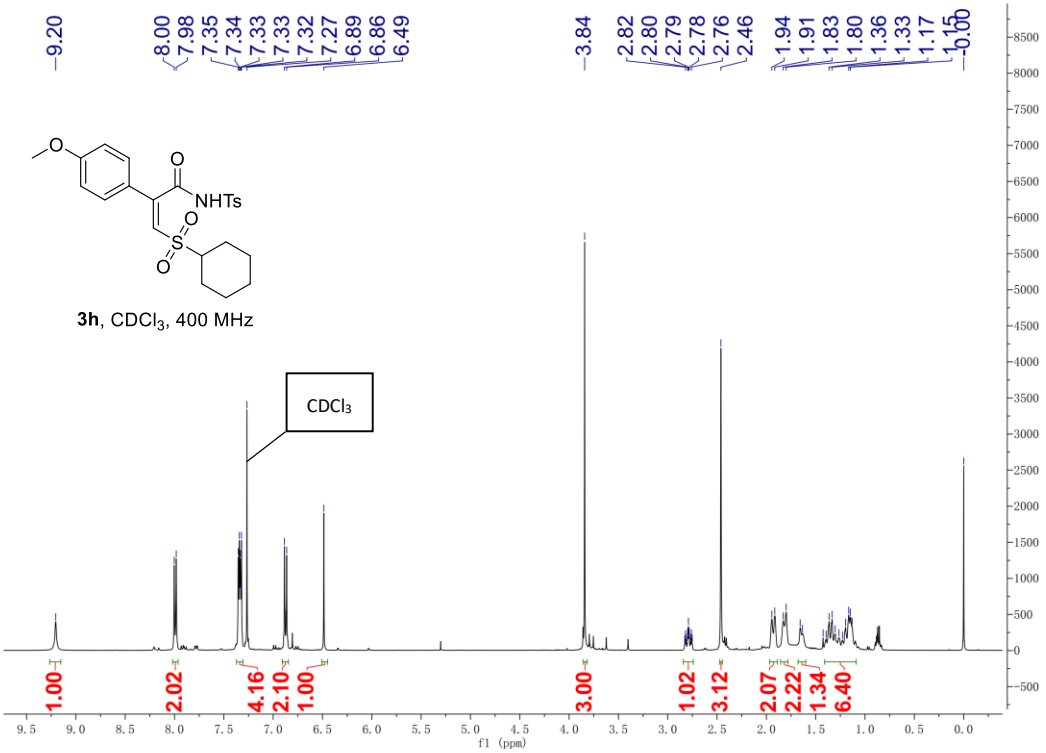
(*Z*)-2-(4-(*tert*-butyl)phenyl)-3-(cyclohexylsulfonyl)-*N*-tosylacrylamide (**3g**)

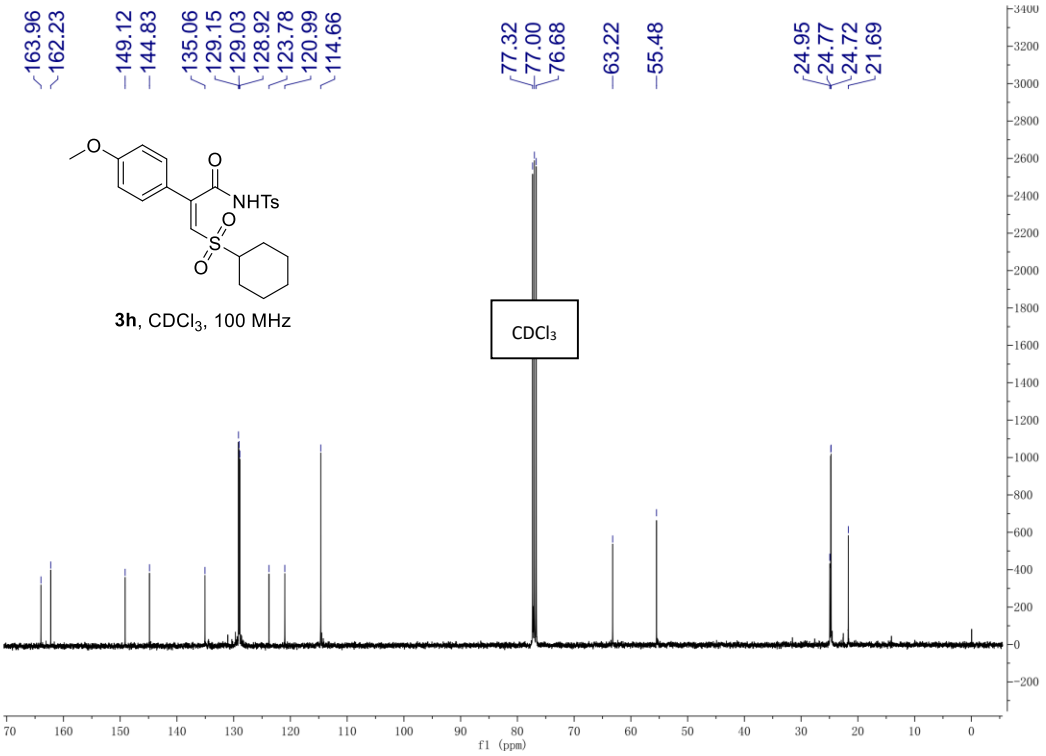


3g, $CDCl_3$, 400 MHz

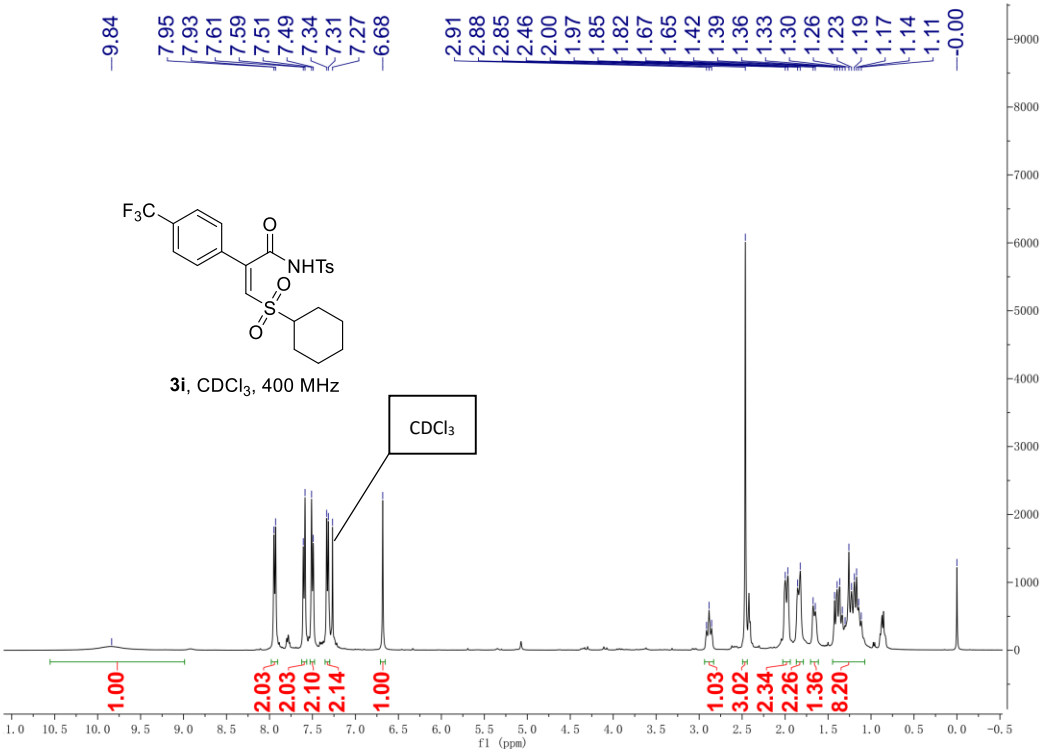


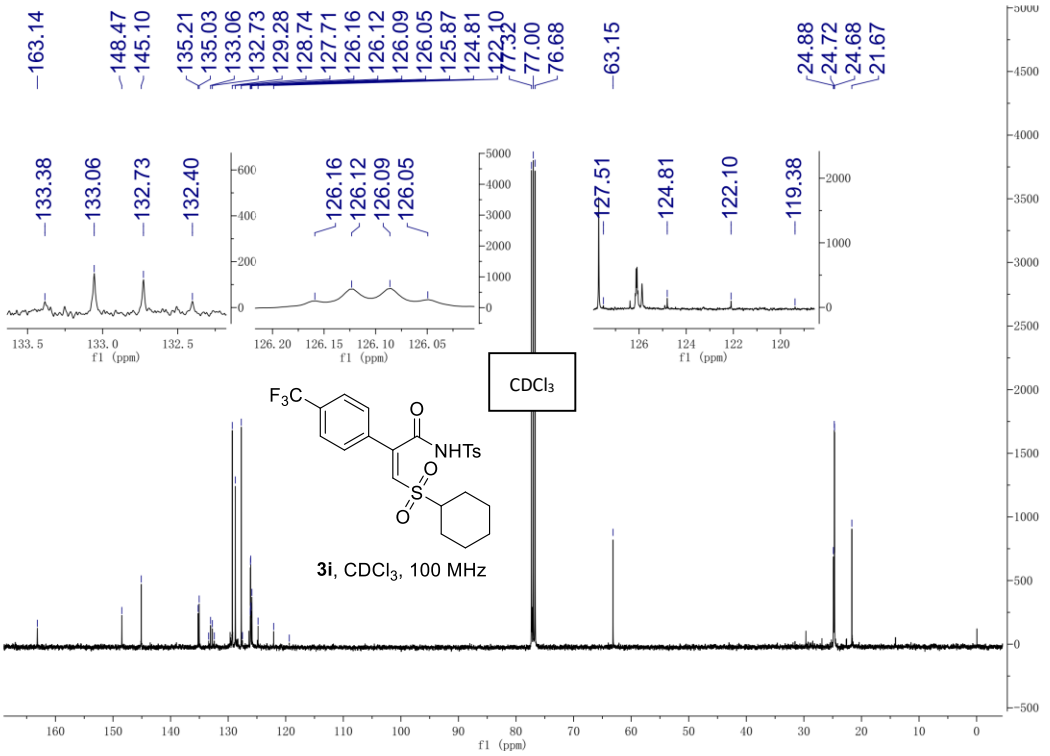
(*Z*)-3-(cyclohexylsulfonyl)-2-(4-methoxyphenyl)-*N*-tosylacrylamide (**3h**)

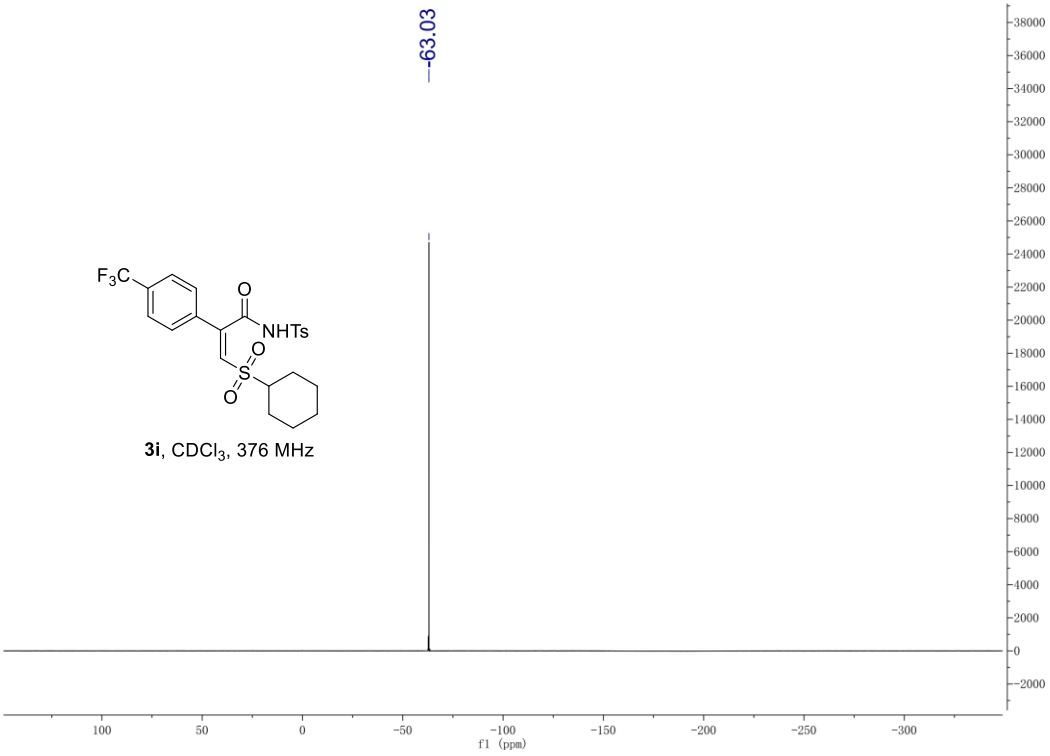




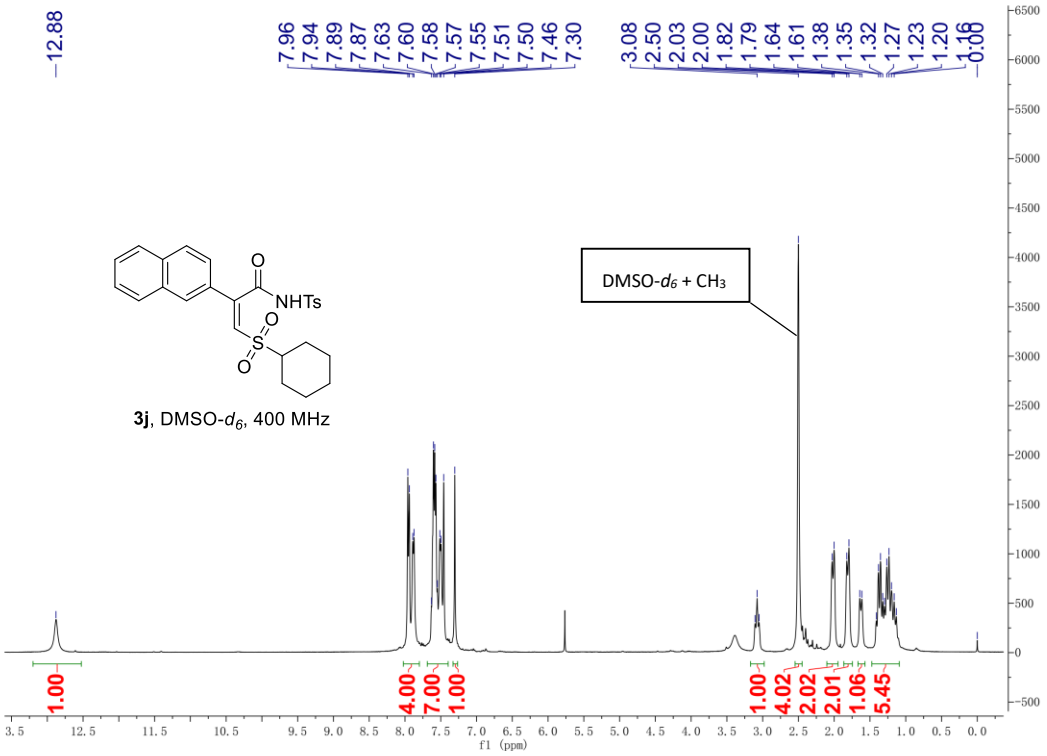
(*Z*)-3-(cyclohexylsulfonyl)-*N*-tosyl-2-(4-(trifluoromethyl)phenyl)acrylamide (**3i**)

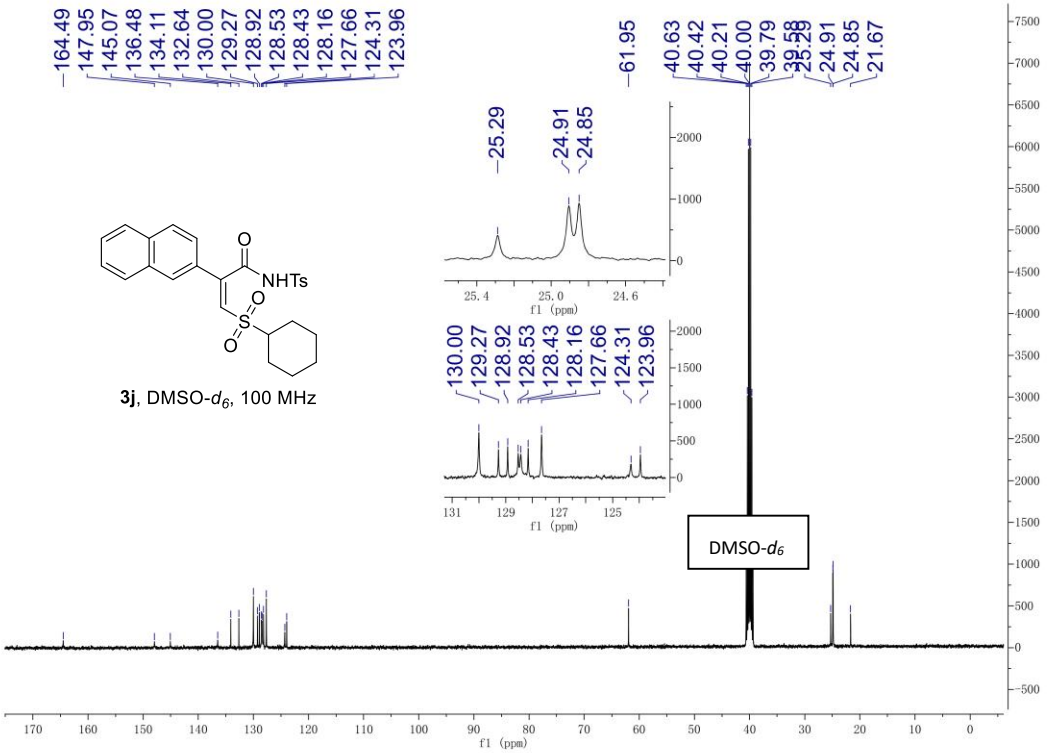



163.14
148.47
145.10
135.21
135.03
133.06
132.73
129.28
128.74
127.71
126.16
126.12
126.09
126.05
125.87
124.81
122.10
77.32
77.00
76.68
63.15
24.88
24.72
24.68
21.67
133.38
133.06
132.73
132.40
126.16
126.12
126.09
126.05
127.51
124.81
122.10
119.38
CDCl3
F3C
O
NHTs
O
S
O
O
3i, CDCl3, 100 MHz
f1 (ppm)

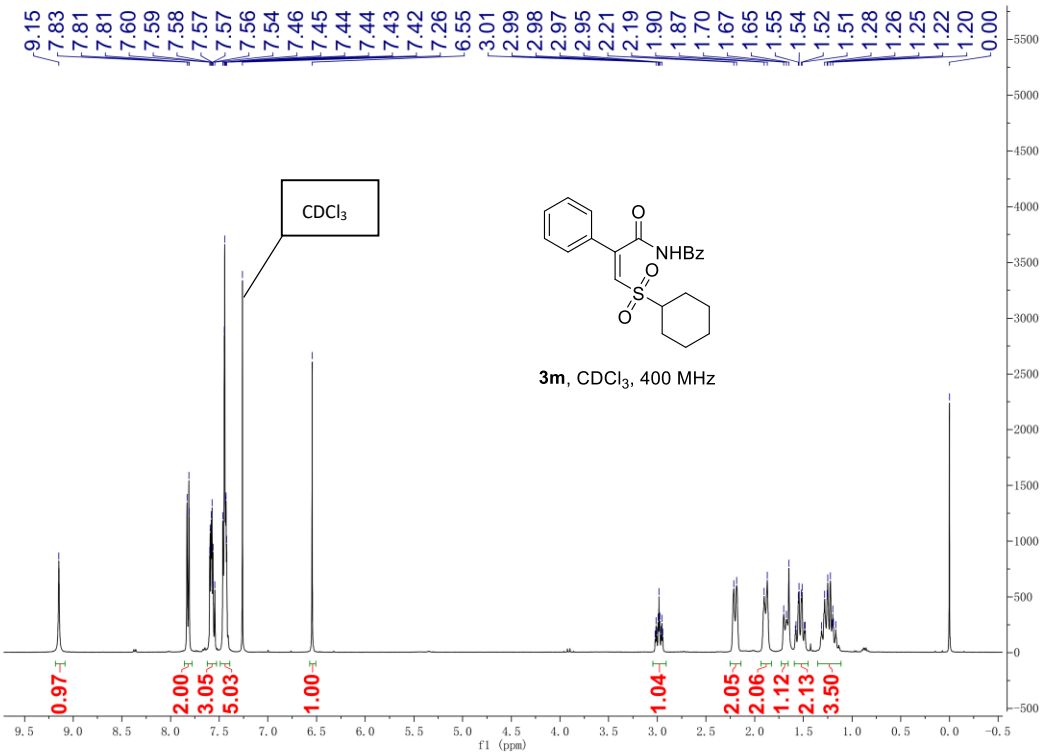

63.03
F3C
O
NHTs
O
S
O
O
3i, CDCl3, 376 MHz
f1 (ppm)

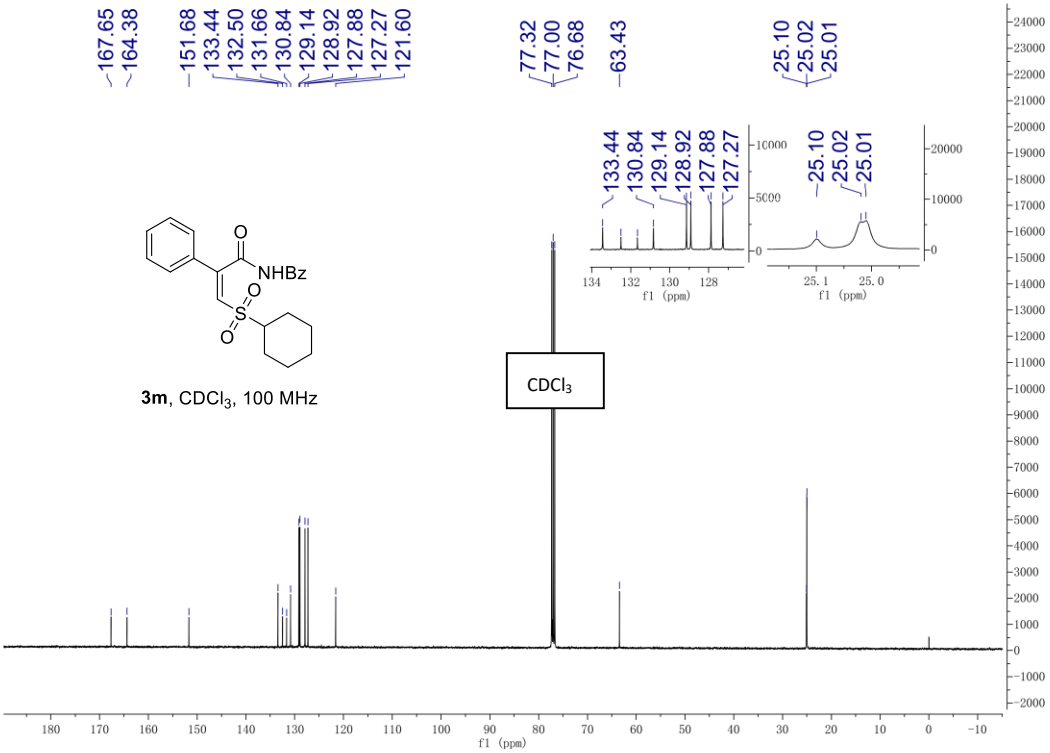
(*Z*)-3-(cyclohexylsulfonyl)-2-(naphthalen-2-yl)-*N*-tosylacrylamide (**3j**)



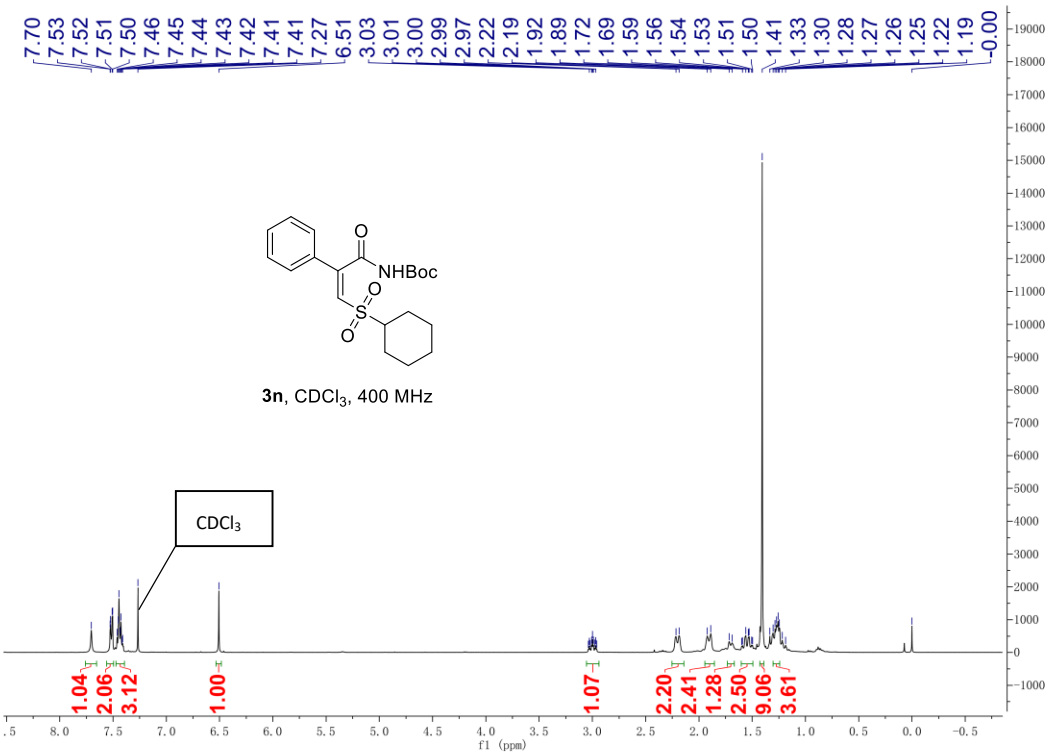


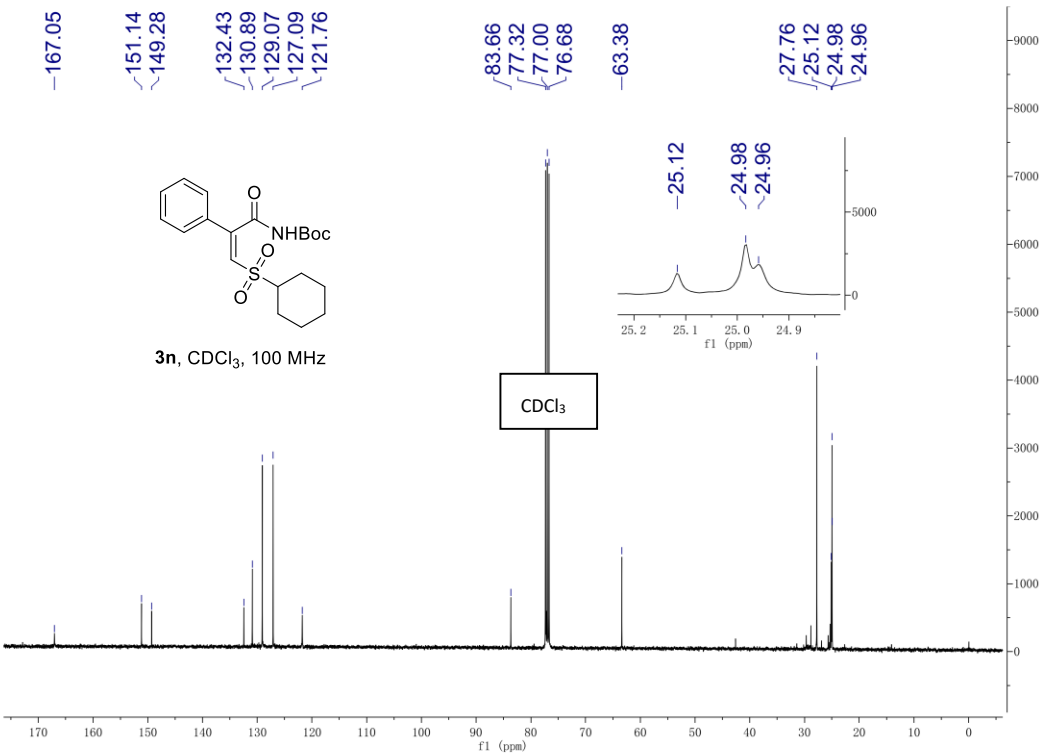
(*Z*)-*N*-(3-(cyclohexylsulfonyl)-2-phenylacryloyl)benzamide (**3m**)



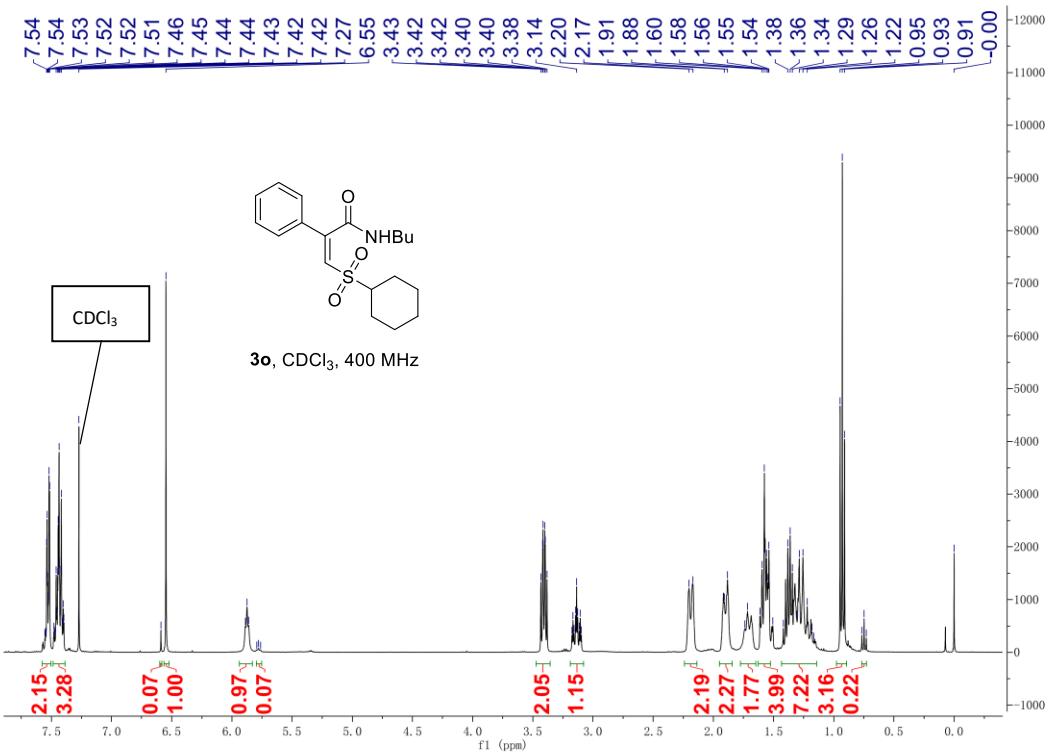


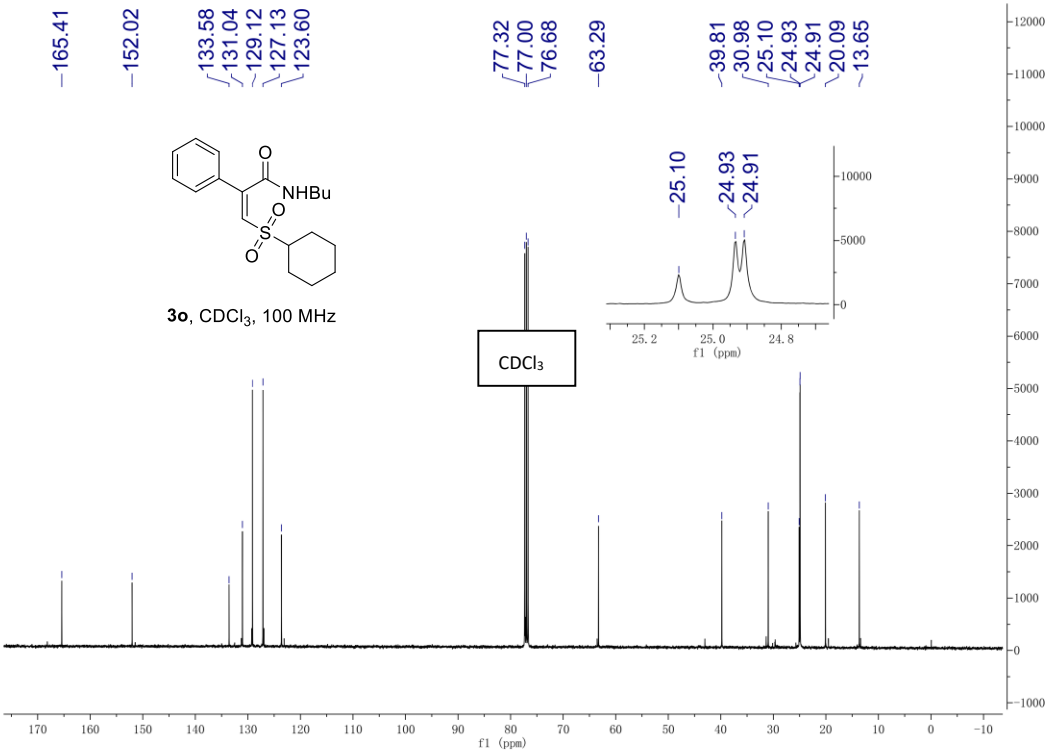
tert-butyl (*Z*)-(3-(cyclohexylsulfonyl)-2-phenylacryloyl)carbamate (**3n**)



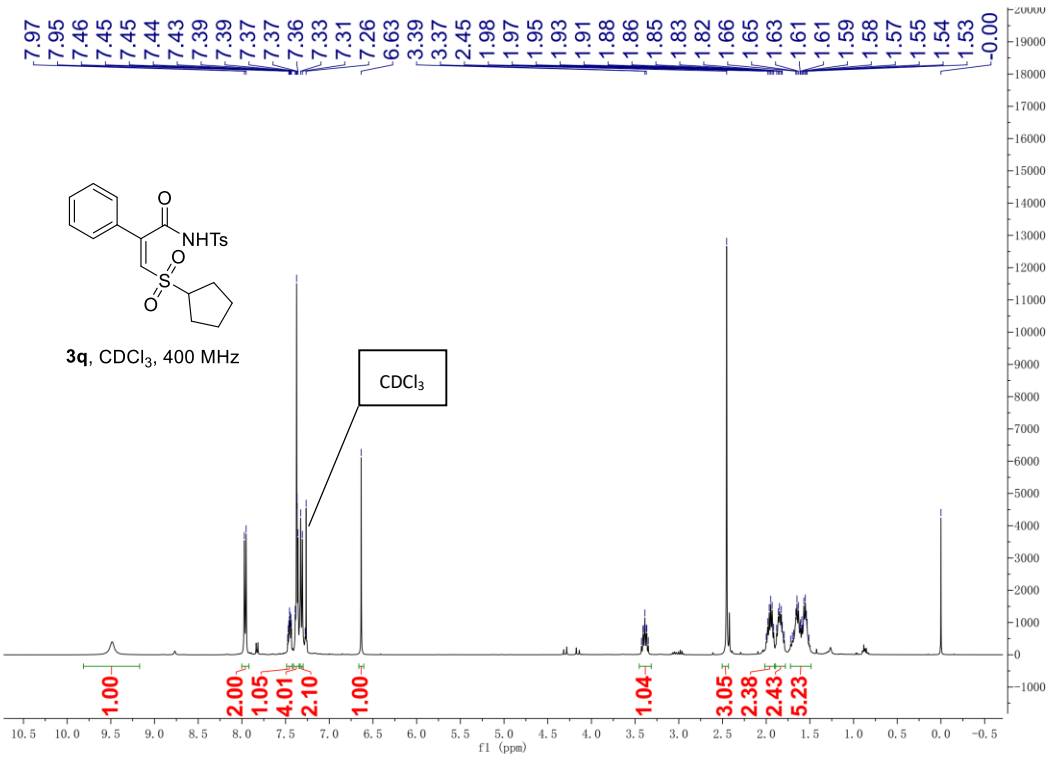


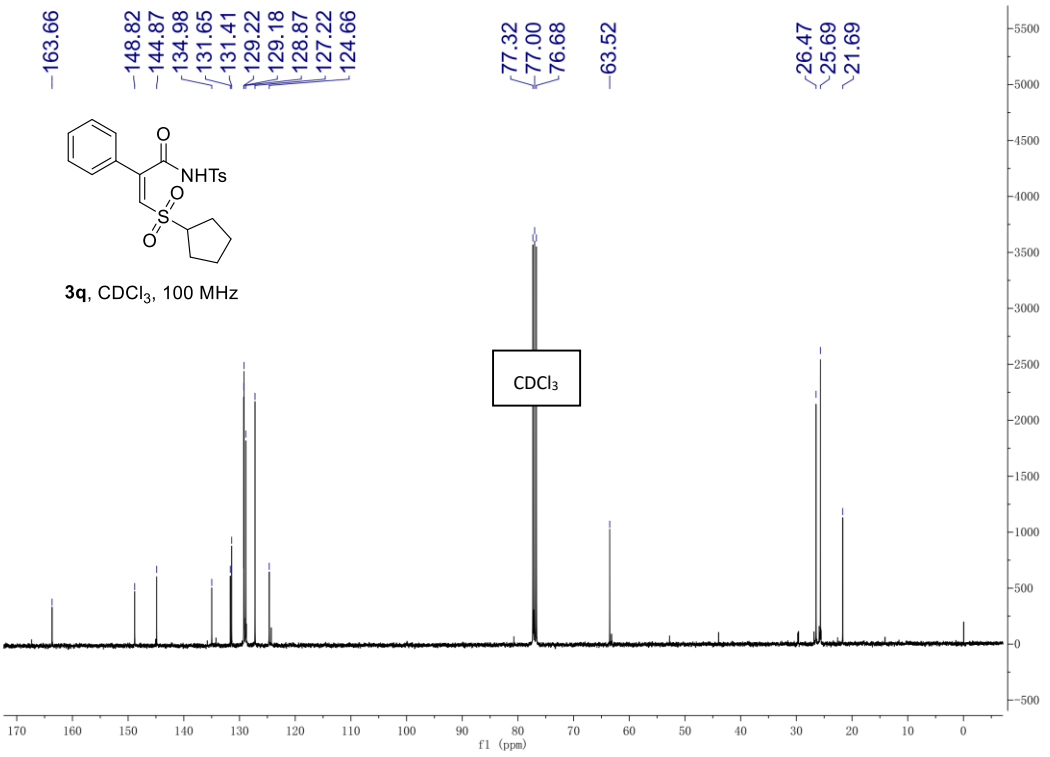
(Z)-N-butyl-3-(cyclohexylsulfonyl)-2-phenylacrylamide (**3o**)



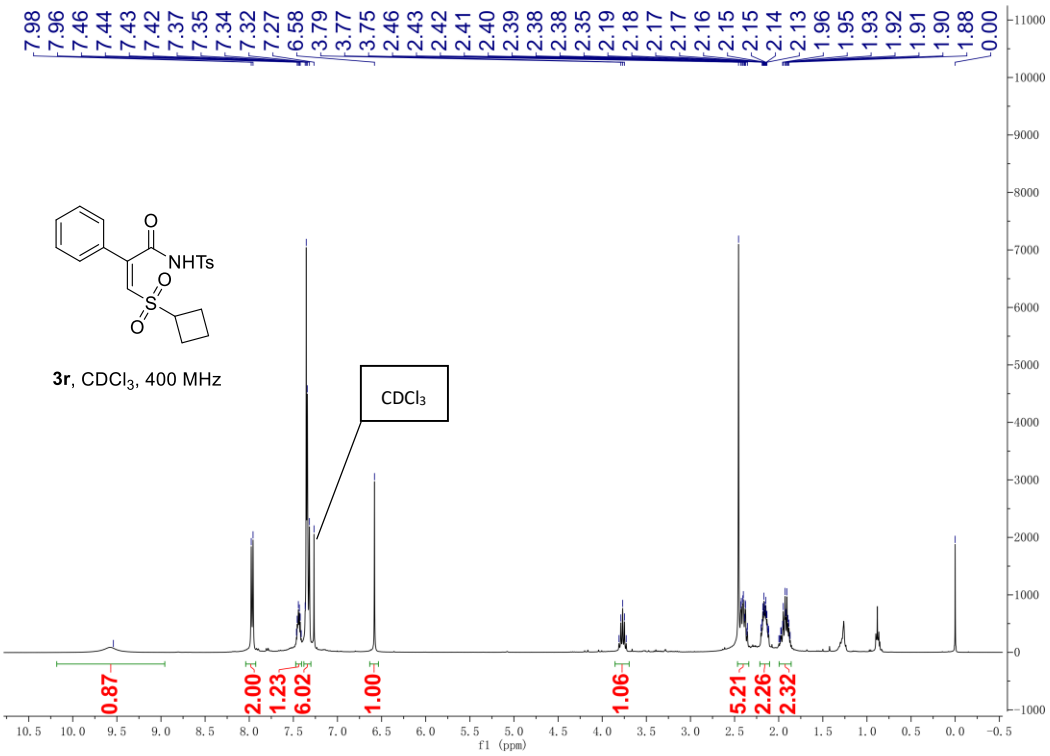


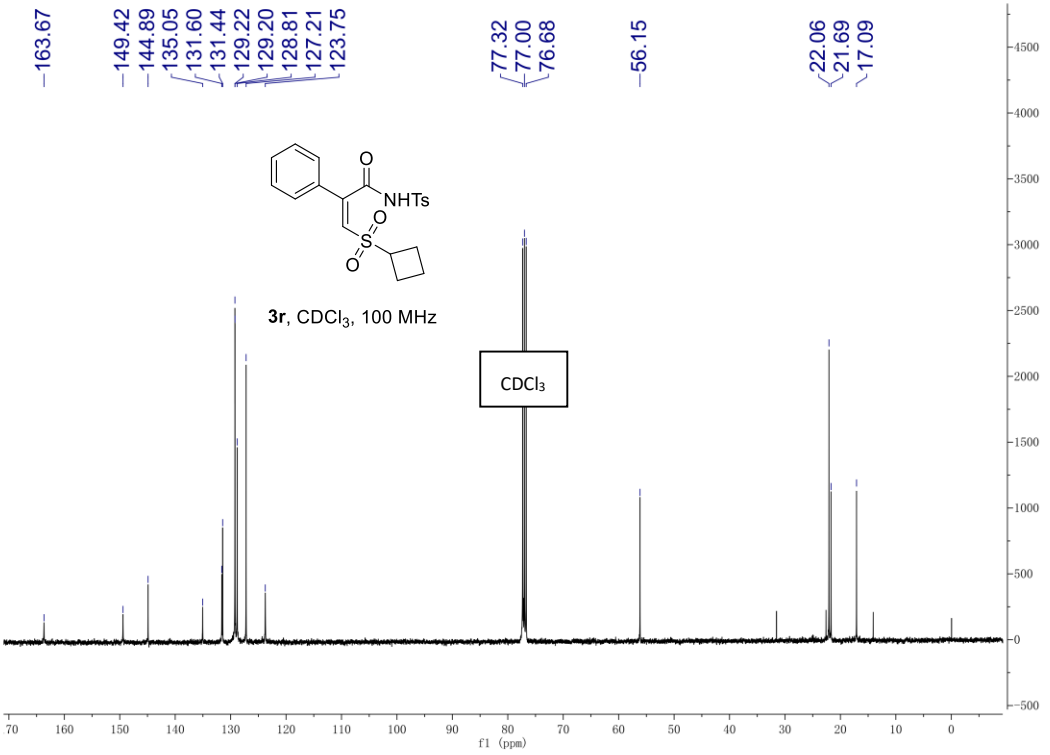
(*Z*)-3-(cyclopentylsulfonyl)-2-phenyl-N-tosylacrylamide (**3q**)



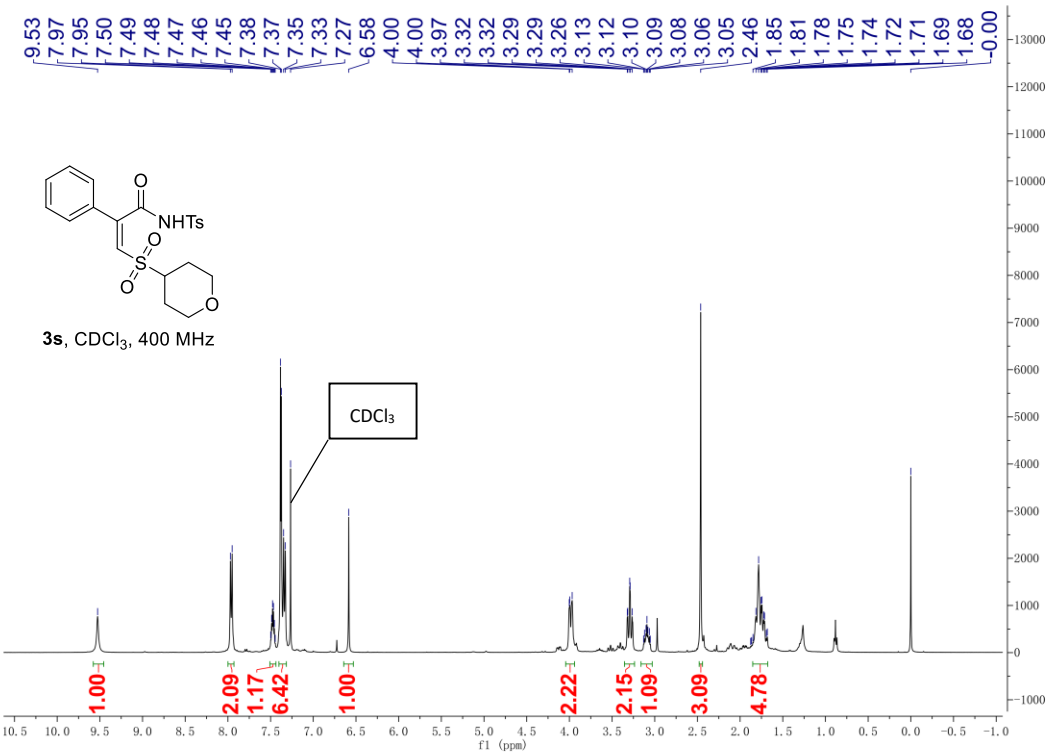


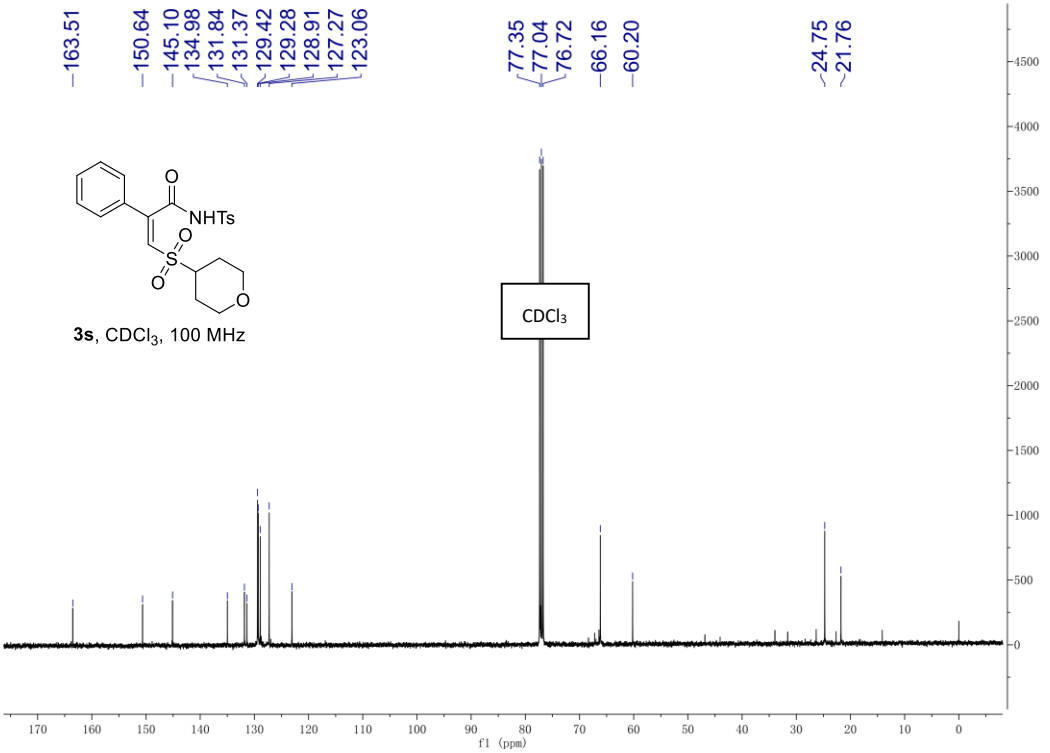
(*Z*)-3-(cyclobutylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3r**)



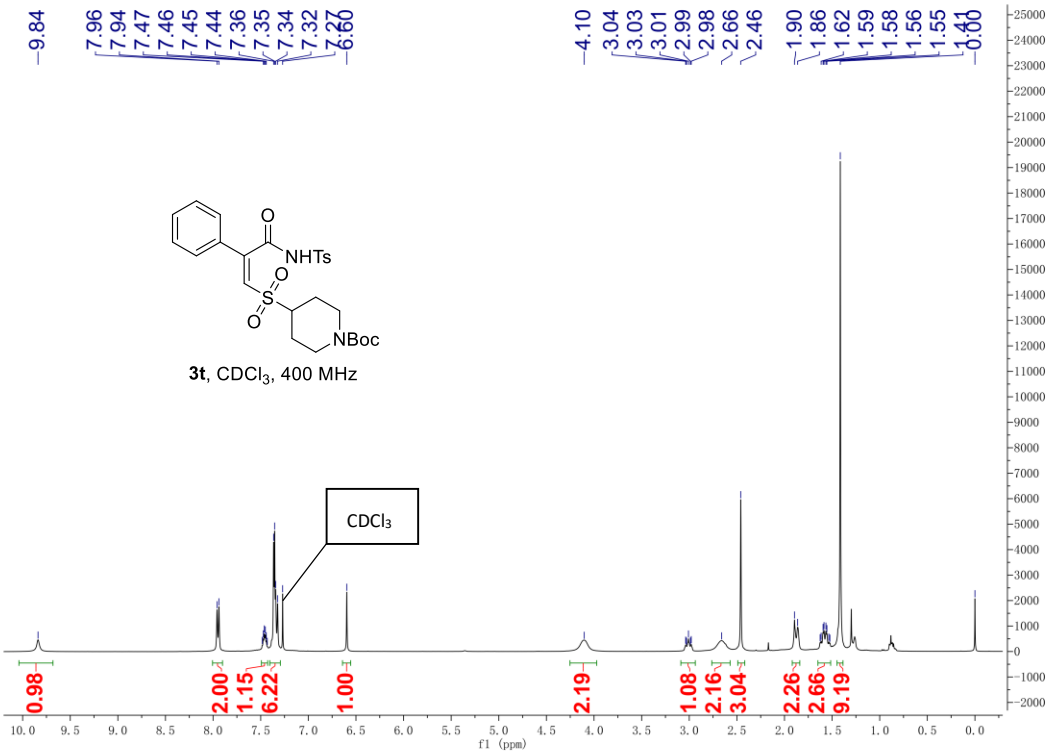


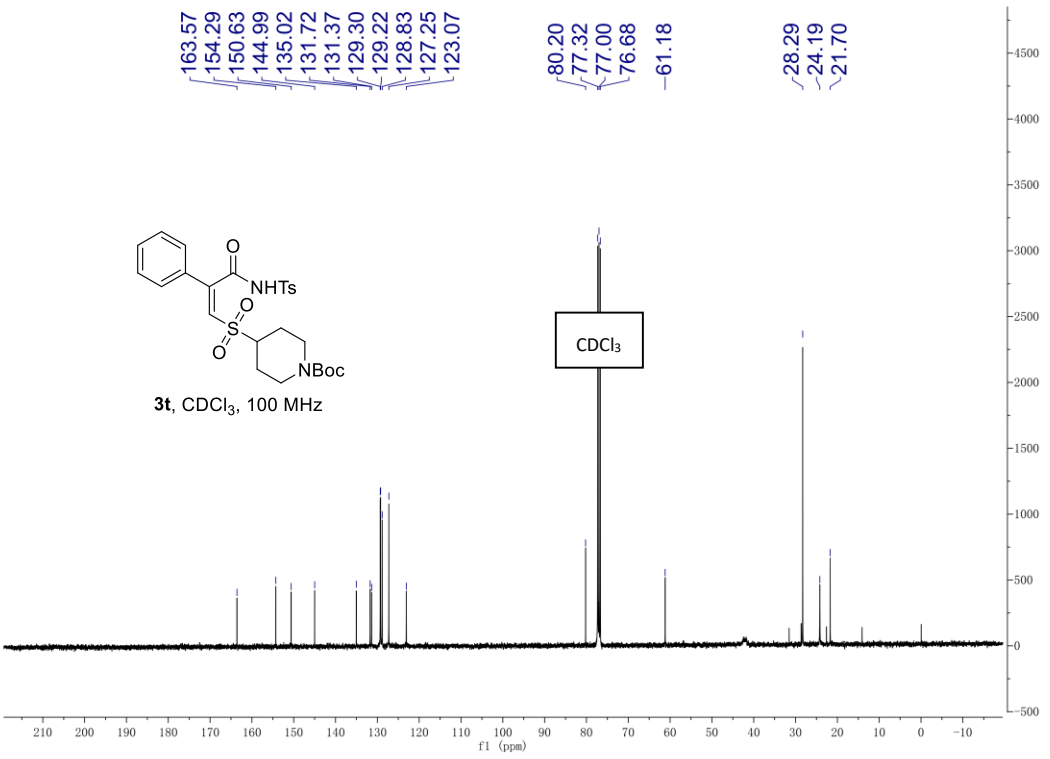
(*Z*)-2-phenyl-3-((tetrahydro-2H-pyran-4-yl)sulfonyl)-*N*-tosylacrylamide (**3s**)



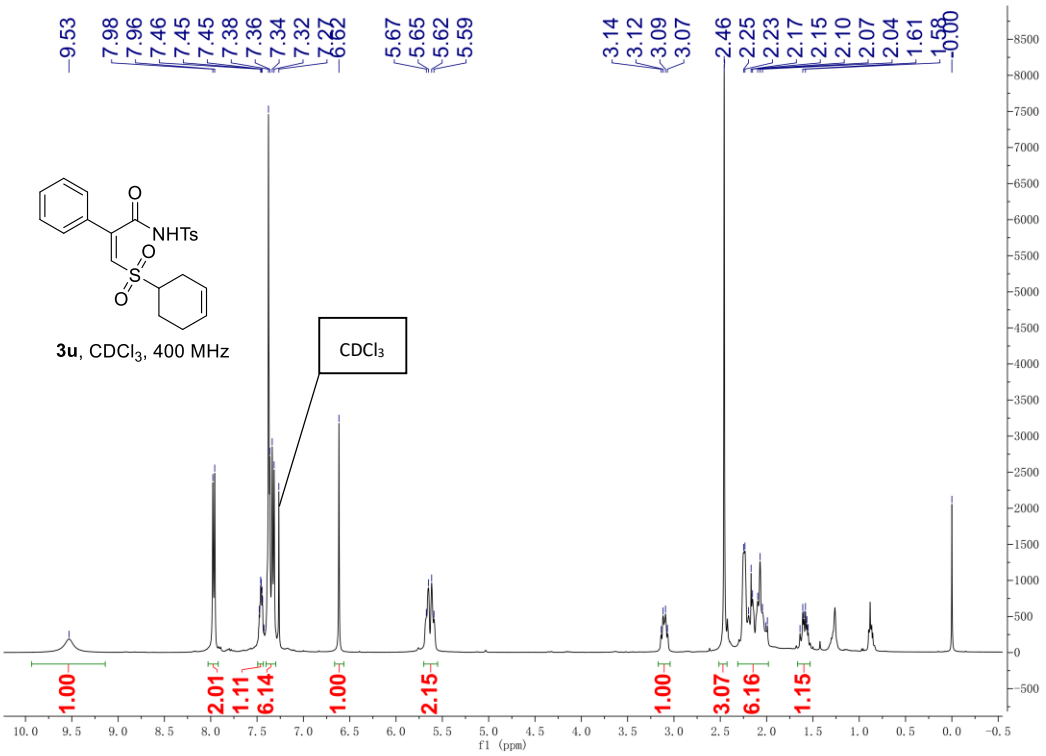


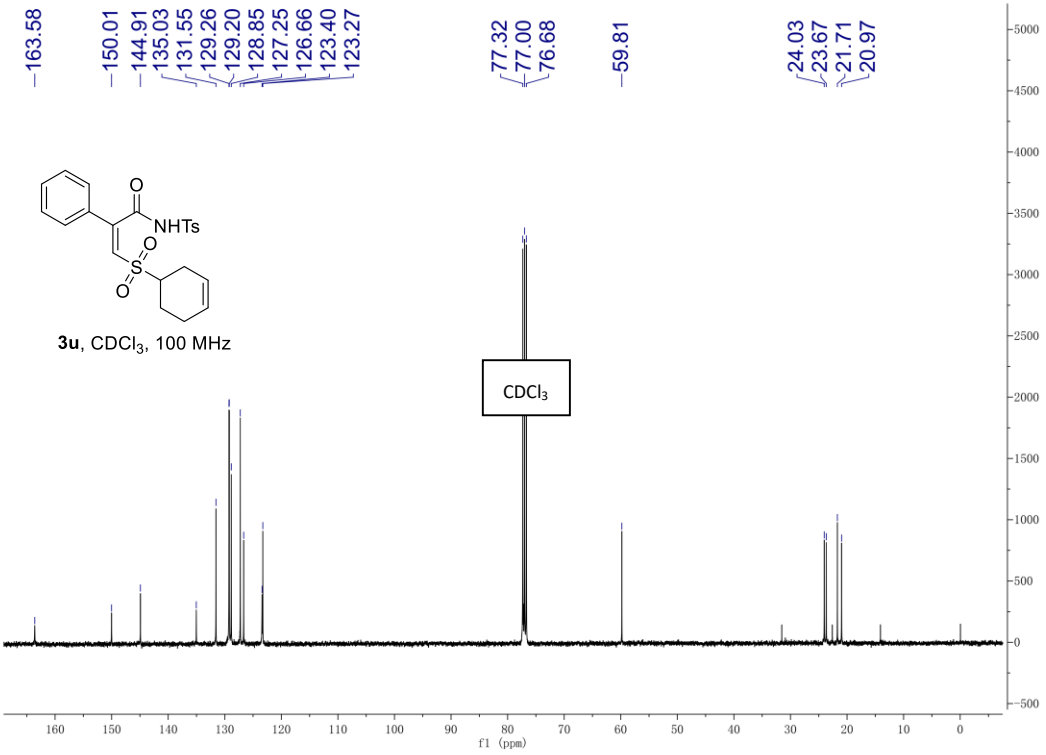
tert-butyl (*Z*)-4-((3-((4-methylphenyl)sulfonamido)-3-oxo-2-phenylprop-1-en-1-yl)sulfonyl)piperidine-1-carboxylate (**3t**)



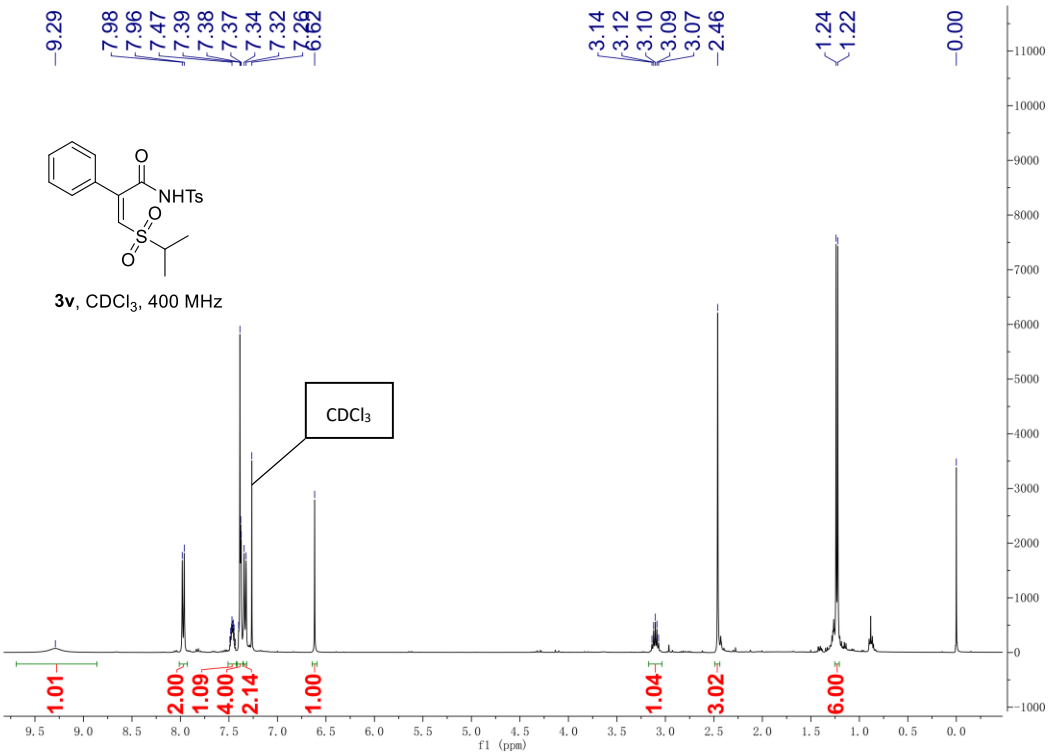


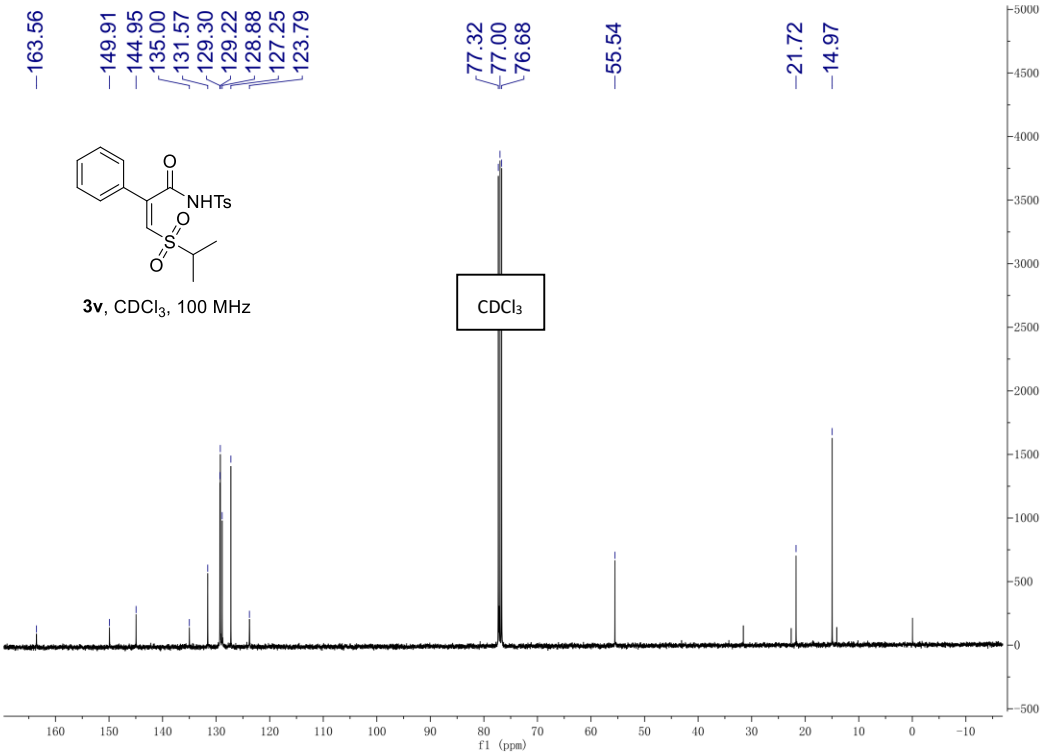
(*Z*)-3-(cyclohex-3-en-1-ylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3u**)



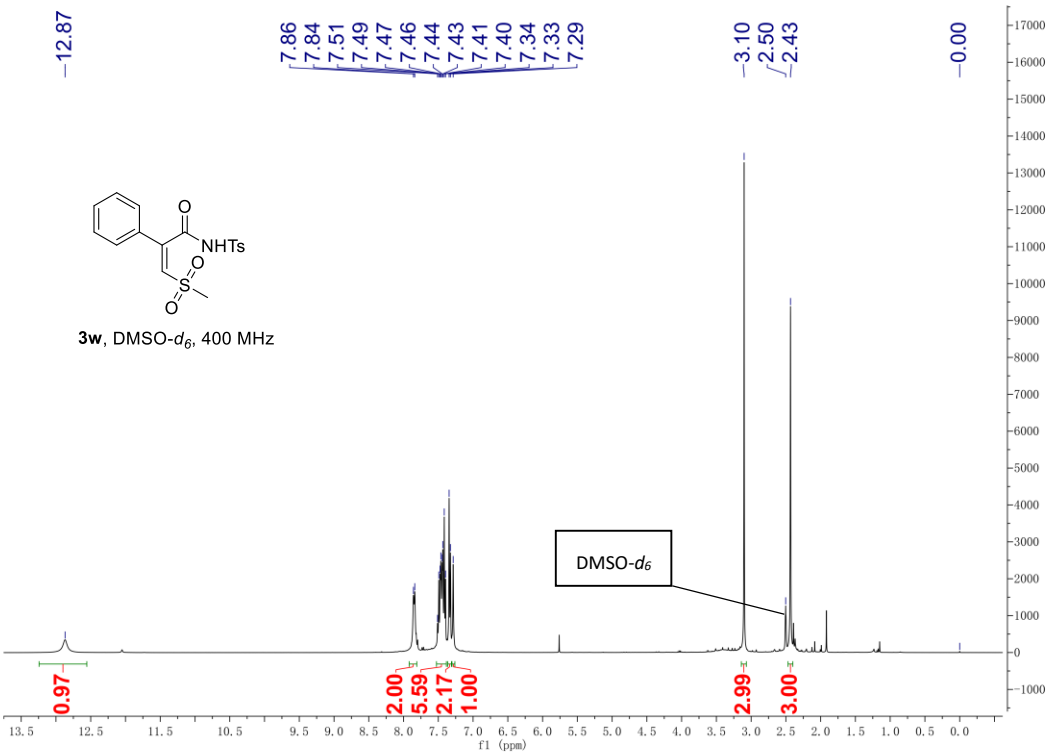


(*Z*)-3-(isopropylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3v**)

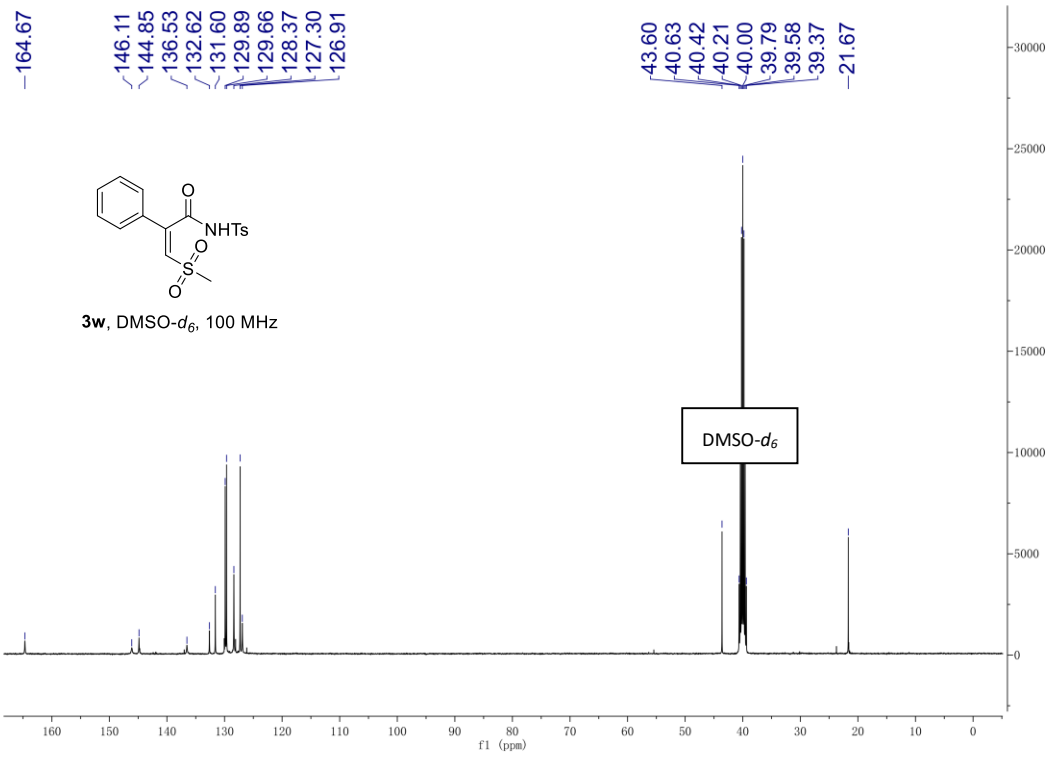




(*Z*)-3-(methylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3w**)

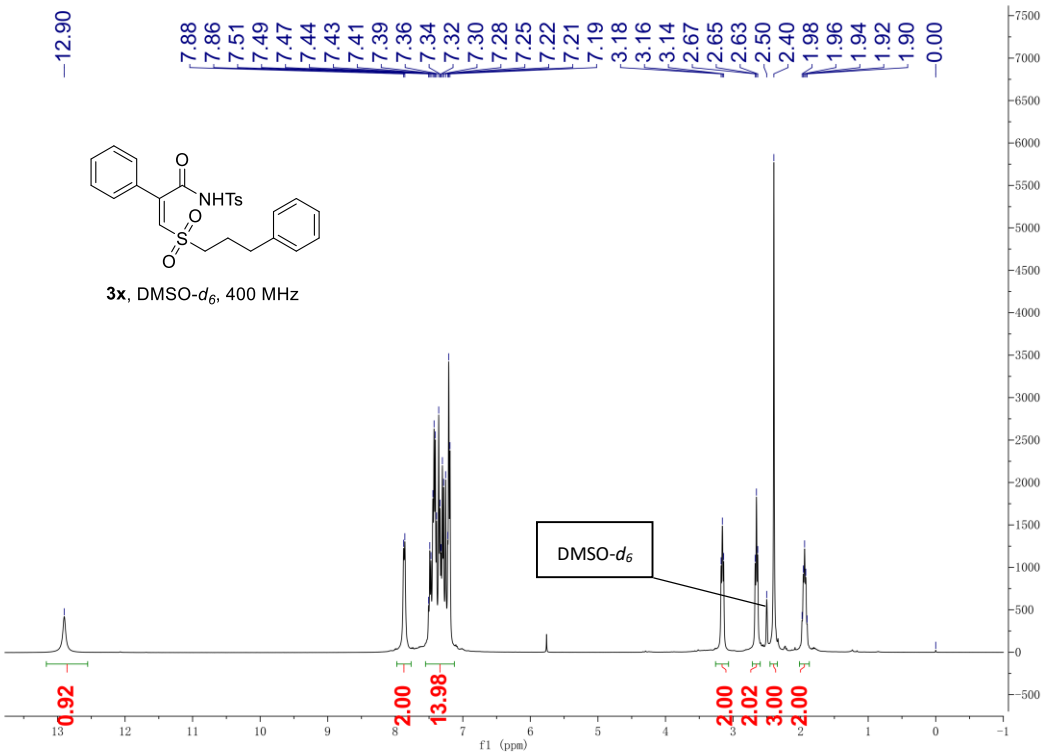


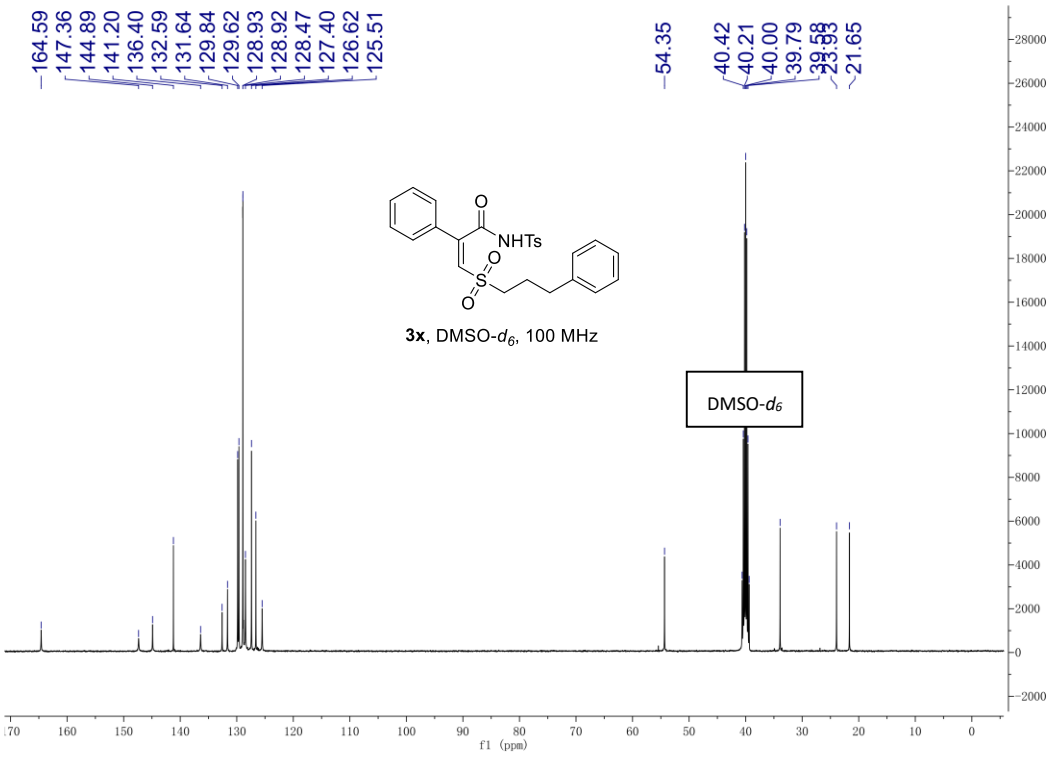
3w, DMSO-d_6, 400 MHz



3w, DMSO-d_6, 100 MHz

(*Z*)-2-phenyl-3-((3-phenylpropyl)sulfonyl)-*N*-tosylacrylamide (**3x**)





(*Z*)-3-(but-3-en-1-ylsulfonyl)-2-phenyl-*N*-tosylacrylamide (**3y**)