Supporting information

Synthesis of *N*-Sulfonyl Acetamidines Using Calcium Carbide as a Alkyne Source

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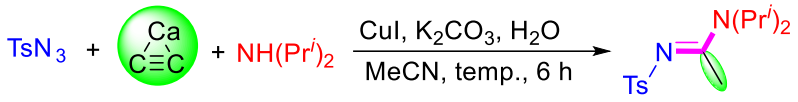
1. Some supplementary experiments

1.1 Supplementary condition optimization

Table S1 Optimization of the other reaction conditions[a].

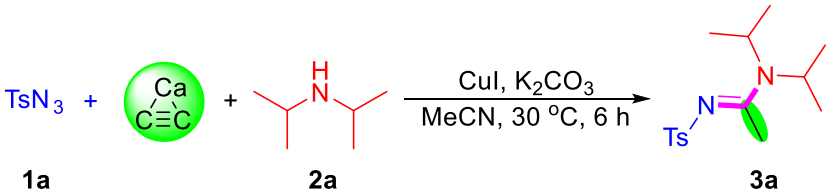


1a **2a** **3a**

Entry	Temp. (°C)	Amount of K_2CO_3 (mmol)	Amount of CaC_2 (mmol)	Amount of H_2O (mmol)	Yield (%)[b]
1	20	0.3	0.6	1.5	73
2	40	0.3	0.6	1.5	76
3	30	0.15	0.6	1.5	86
4	30	0.36	0.6	1.5	87
5	30	0.45	0.6	1.5	82
6	30	0.3	0.45	1.5	86
7	30	0.3	0.75	1.5	85
8	30	0.3	0.6	1.2	82
9	30	0.3	0.6	1.8	73

[a]Reaction condition: 4-methylbenzenesulfonyl azide (**1a**) (0.3 mmol), CaC_2 (appropriate amount), diisopropylamine (**2a**) (0.3 mmol), H_2O (appropriate amount), CuI (3 mL) and K_2CO_3 (0.3 mmol) in MeCN (3 mL) was heated in an oil bath at appropriate temperature for 6 h. [b]Isolated yield.

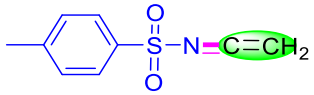
1.2 Reaction Intermediate Detected by HRMS



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

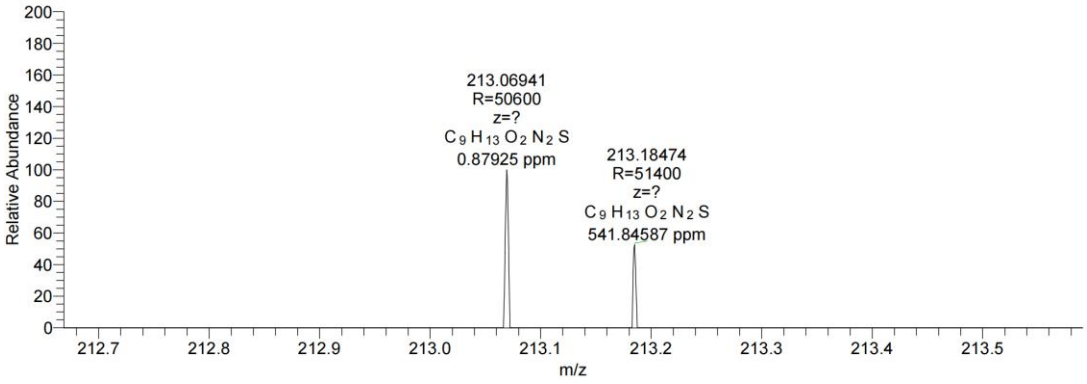
For the reaction of **1a**, **2a** and calcium carbide to synthesize **3a**, when the reaction is carried out under standard conditions for 3 h, an important intermediate **6** can be detected by HRMS.

Intermediate 6 :



HRMS (ESI): *m/z* $(M+NH_4)^+$ calcd for $C_9H_{13}N_2O_2S^+$: 213.0692; Found: 213.0694.

The mass spectrum is as follow:

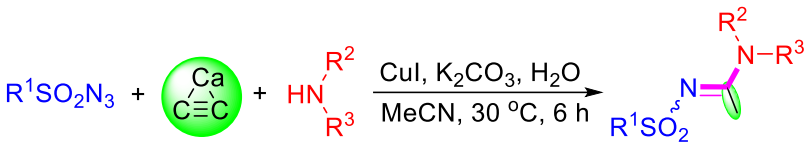


2. Experimental Section

2.1 General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury-600 MB or 400 MB instrument using $CDCl_3$ or DMSO-d_6 as solvents and Me_4Si as internal standard. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltronics APEX II 47e and Orbitrap Elite mass spectrometer. IR spectra were measured by FT-3000 Fourier Transform Infrared spectrometer. Melting points were observed in an electrothermal melting point apparatus (X-5, Beijing Tech Instrument Co. Ltd, China). Calcium carbide was purchased from Macklin Chemical Company (China, purity: 98%), and ground into powder (ca. 50−100 mesh) in a ceramic mortar prior to use. The solvents were all deoxygenated with nitrogen gas for 5 min and dehydrated with molecular sieve for over 12 h prior to use. Unless otherwise noted, the reagents were reagent grade and used without any further purification. Column chromatography was carried out on a flash chromatographic system using silica gel (200−300 mesh) and petroleum ether (60–90 °C) and ethyl acetate as eluent. For thin layer chromatography (TLC), silica gel plates precoated with GF-254 were used. Various amines are commercially available, and purchased from Energy Chemical Company (China) or Bide Pharmatech Company (China). Partial sulfonyl azides were synthesized by reacting the corresponding sulfonyl chlorides with sodium azide according to literature procedure. [1]

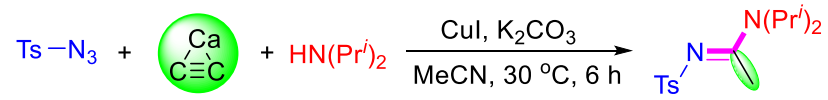
2.2 The general procedure for synthesis of *N*-sulfonyl acetamidines 3a−3p and 4a−4o



The mixture of sulfonyl azide **1** (0.3 mmol), calcium carbide (0.6 mmol, 38.5 mg, 2.0 equiv, purity 98%), amine **2** (0.3 mmol, 1.0 equiv), copper(I) iodide (0.03 mmol, 5.7 mg, 0.1 equiv), potassium carbonate (0.3 mmol, 41.5 mg, 1.0 equiv), and water (1.5 mmol, 27 mg, 5 equiv) in acetonitrile (3 mL) was stirred at 30 °C for 6 h. After the

completion of the reaction, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×10 mL), and washed with saturated brine (3×10 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v = 2:1 to 5:1) as eluent to give the pure product.

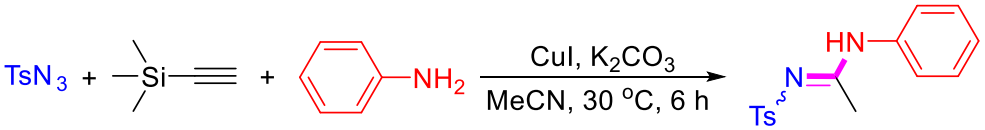
2.3 Gram-scale synthesis of 3a



1a 1.77 g | 1.15 g | **2a** 0.91 g | **3a** 2.24 g 84%

The mixture of 4-methylbenzenesulfonyl azide (**1a**) (9 mmol, 1.77 g), calcium carbide (18 mmol, 1.15 g, 2.0 eq, purity 98%), diisopropylamine (**2a**) (9 mmol, 0.91 g, 1.0 equiv), copper(I) iodide (0.9 mmol, 0.17 g, 0.1 equiv), potassium carbonate (9 mmol, 1.24 g, 1.0 equiv), and water (45 mmol, 0.81 g, 5 equiv) in acetonitrile (90 mL) was stirred at 30 °C for 6 h. After the completion of the reaction, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×60 mL), and washed with saturated brine (3×60 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v 5:1) as eluent to give the pure product **3a** (2.24 g, 84%).

2.4 Synthesis of 4a using ethynyltrimethylsilane as a substitute for calcium carbide

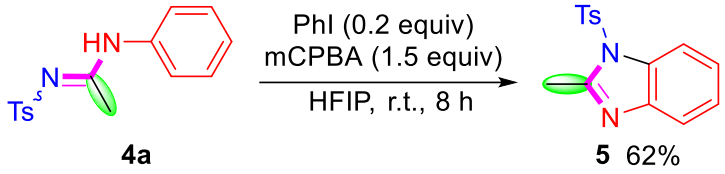


1a **4a** 95% (*E*/*Z*= 60:40)

The mixture of sulfonyl azide **1a** (0.3 mmol, 59.2 mg), ethynyltrimethylsilane (0.6 mmol, 58.9 mg, 2.0 equiv), aniline (0.3 mmol, 27.9 mg, 1.0 equiv), copper(I) iodide (0.03 mmol, 5.7 mg, 0.1 equiv), and potassium carbonate (0.3 mmol, 41.5 mg, 1.0

equiv) in acetonitrile (3 mL) was stirred at 30 °C for 6 h. After the completion of the reaction, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×10 mL), and washed with saturated brine (3×10 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v = 2:1) as eluent to give the pure product **4a** (82.18 mg, 95%).

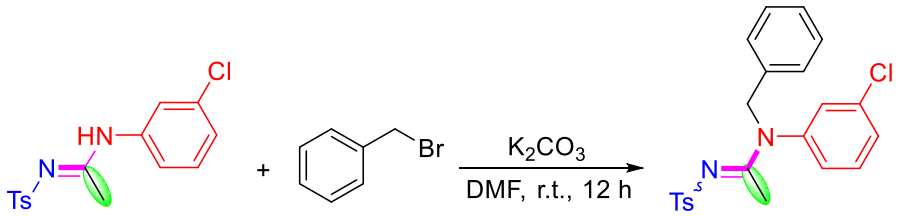
2.5 Synthesis of 2-methyl-1-tosyl-1*H*-benzo[*d*]imidazole (5)



4a **5** 62%

The mixture of (*E*/*Z*)-*N*-phenyl-*N*'-tosylacetimidamide (**4a**) (0.3 mmol, 86.5 mg), phenyliodide (0.06 mmol, 12.2 mg, 0.2 equiv), mCPBA (0.45 mmol, 77.6 mg, 1.5 equiv) in HFIP (2 mL) was stirred at room temperature for 8 h. After the completion of the reaction, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×10 mL), and washed with saturated brine (3×10 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v = 4:1) as eluent to give the pure product **5** (53.3 mg, 62%).

2.6 The synthesis of (*E*)-*N*-benzyl-*N*-(3-chlorophenyl)-*N*'-tosylacetimidamide (6)



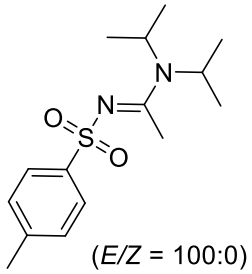
4h **6** 85%

The mixture of (*E*)-*N*-(3-chlorophenyl)-*N*'-tosylacetimidamide (**4h**) (0.3 mmol, 96.84 mg), benzyl bromide (0.9 mmol, 153.94 mg, 3.0 equiv), potassium carbonate (0.6 mmol, 82.93 mg, 2.0 equiv) in DMF (3 mL) was stirred at room temperature for 12 h. After the completion of the reaction, the resulting mixture was filtered to remove the

solid, and the liquor was extracted with ethyl acetate (3×10 mL), and washed with saturated brine (3×10 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v = 2:1) as eluent to give the pure product **6** (105.3 mg, 85%).

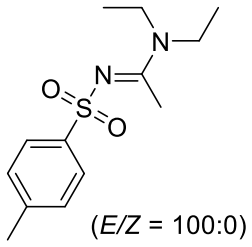
3. Analytical Data of the Products 3a−3p, 4a−4o, 5 and 6

3.1 (E)-N,N-Diisopropyl-N'-tosylacetimidamide (3a)



White solid (78.3 mg, 88%). M.p. 201 − 202 ºC. Purified by column chromatography (petroleum ether/ethyl acetate, 5:1). R_f = 0.58. IR (KBr) 2982, 1545, 1477, 1419, 1262, 1136, 1078, 1013, 965, 830, 778, 671 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.60 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 4.09−4.02 (m, 1H), 3.70 (bs, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 1.19 (d, J = 6.7 Hz, 6H), 1.11 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.8, 142.2, 141.7, 129.6, 125.9, 50.1, 47.5, 21.3, 20.4, 20.1, 19.6 ppm. HRMS (ESI): m/z $(M+H)^+$ calcd for $C_{15}H_{25}N_2O_2S^+$: 297.1631; Found: 297.1618.

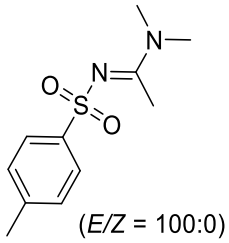
3.2 (E)-N,N-Diethyl-N'-tosylacetimidamide (3b)



Yellow oil (59.6 mg, 74%). Purified by column chromatography (petroleum ether/ethyl acetate, 5:1). R_f = 0.56. IR (KBr) 2968, 1542, 1429, 1371, 1257, 1128, 1079, 1049, 963, 805, 779, 724, 660 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J =

8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.45 (q, *J* = 7.1 Hz, 2H), 3.33 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 2.37 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.6, 141.7, 141.4, 129.1, 126.2, 44.0, 43.8, 21.5, 17.6, 13.8, 12.2 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{13}H_{21}N_2O_2S^+$: 269.1318; Found: 269.1316.

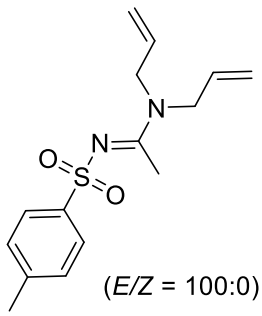
3.3 (E)-N,N-Dimethyl-N'-tosylacetimidamide (3c)[2]



(*E*/*Z* = 100:0)

White solid (51.9 mg, 72%). M.p. 158 − 159 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 5:1). R_f = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.08 (s, 3H), 3.06 (s, 3H), 2.48 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 141.9, 141.3, 129.2, 126.4, 39.0, 39.0, 21.6, 18.1 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{11}H_{17}N_2O_2S^+$: 241.1005; Found: 241.1003.

3.4 (E)-N,N-Diallyl-N'-tosylacetimidamide (3d)

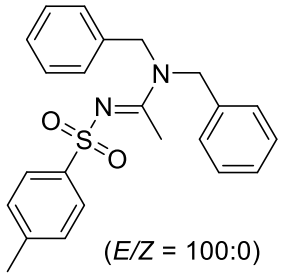


(*E*/*Z* = 100:0)

Yellow oil (73.7 mg, 84%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.78−5.66 (m, 2H), 5.22 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.15−5.06 (m, 3H), 4.05 (d, *J* = 6.1 Hz, 2H), 3.89 (d, *J* = 4.9 Hz, 2H), 2.46 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 14 1.9, 141.0, 131.5, 131.2, 129.1, 126.2, 118.6, 117.7, 51.4, 50.7, 21.4, 17.7 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$

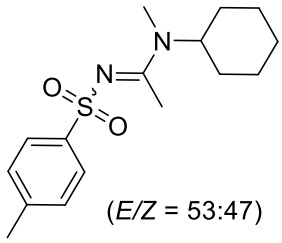
calcd for $C_{15}H_{21}N_2O_2S^+$: 293.1318; Found: 293.1315.

3.5 (E)-N,N-dibenzyl-N'-tosylacetimidamide (3e)



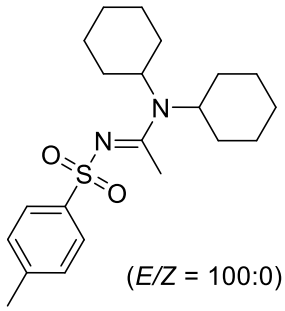
Yellow oil (106.0 mg, 90%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.40−7.32 (m, 3H), 7.30−7.26 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.19−7.17 (m, 2H), 7.12 (d, *J* = 7.1 Hz, 2H), 4.73 (s, 2H), 4.54 (s, 2H), 2.62 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 142.0, 141.0, 135.8, 134.9, 129.3, 129.2, 128.8, 128.4, 128.1, 127.9, 126.3, 126.3, 51.5, 51.5, 21.5, 18.2 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{23}H_{25}N_2O_2S^+$: 393.1631; Found: 393.1628.

3.6 (E/Z)-N-Cyclohexyl-N-methyl-N'-tosylacetimidamide (3f)



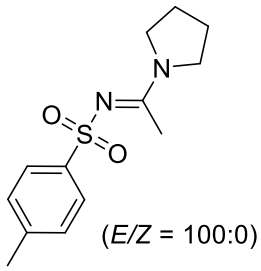
Yellow oil (78.7 mg, 85%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.78 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.87 (s, 3H), 2.54 (s, 1.6H), 2.45 (s, 1.4H), 2.38 (s, 3H), 1.87−1.76 (m, 2H), 1.68−1.63 (m, 3H), 1.56−1.47 (m, 1H), 1.36−1.26 (m, 4H), 1.15−1.03 (m, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 164.8, 141.8, 141.7, 141.6, 141.5, 129.2, 126.3, 126.2, 58.0, 55.9, 40.0, 30.8, 29.4, 25.7, 25.5, 25.5, 25.2, 21.5, 19.1, 18.0 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{25}N_2O_2S^+$: 309.1631; Found: 309.1629.

3.7 (E)-N,N-Dicyclohexyl-N'-tosylacetimidamide (3g)



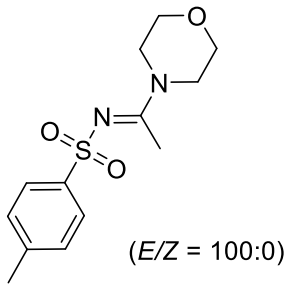
White solid (84.7 mg, 75%). M.p. 191 − 192 ºC. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) 7.77 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.50 (s, 3H), 2.35 (s, 3H), 1.82−1.77 (m, 2H), 1.63 (d, *J* = 9.3 Hz, 6H), 1.49−1.46 (m, 4H), 1.35−1.21 (m, 5H), 1.14−1.05 (m, 4H) 0.86−0.82 (m, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.0, 141.6, 141.4, 128.9, 125.9, 59.3, 58.4, 30.6, 29.1, 26.3, 25.7, 25.2, 25.0, 21.4, 20.1 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{21}H_{33}N_2O_2S^+$: 377.2257; Found: 377.2253.

3.8 (E)-4-Methyl-N-(1-(pyrrolidin-1-yl)ethylidene)benzenesulfonamide (3h)



Yellow oil (66.1 mg, 78%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.45 (t, *J* = 6.7 Hz, 2H), 2.45 (s, 3H), 2.39 (s, 3H), 2.02−1.95 (m, 2H), 1.92−1.85 (m, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9, 141.9, 141.4, 129.2, 126.5, 48.6, 48.3, 25.8, 24.5, 21.6, 19.3 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{13}H_{19}N_2O_2S^+$: 267.1162; Found: 267.1160.

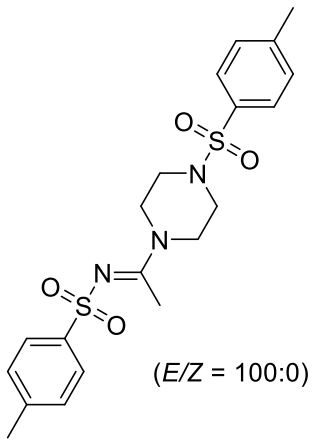
3.9 (E)-4-Methyl-N-(1-morpholinoethylidene)benzenesulfonamide (3i)



(*E*/*Z* = 100:0)

Yellow solid (66.1 mg, 78%). M.p. 121 − 122 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.72 (t, *J* = 4.4 Hz, 2H), 3.69 (t, *J* = 4.8 Hz, 2H), 3.64 (t, *J* = 4.8 Hz, 2H), 3.50 (t, *J* = 5.1 Hz, 2H), 2.51 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 142.2, 140.9, 129.3, 126.4, 66.4, 66.3, 46.7, 44.7, 21.5, 17.7 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{13}H_{19}N_2O_3S^+$: 283.1111; Found: 283.1108.

3.10 (E)-4-Methyl-N-(1-(4-tosylpiperazin-1-yl)ethylidene)benzenesulfonamide (3j)

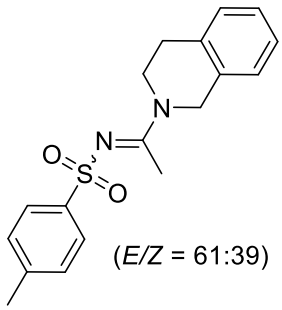


(*E*/*Z* = 100:0)

White solid (80.3 mg, 66%). M.p. 202 − 203 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) 7.74 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.81 (t, *J* = 5.2 Hz, 2H), 3.81 (t, *J* = 5.2 Hz, 2H), 3.59 (t, *J* = 4.5 Hz, 2H), 3.00 (t, *J* = 4.5 Hz, 2H), 2.96 (t, *J* = 5.2 Hz, 2H), 2.46 (s, 6H), 2.39 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.2, 144.5, 140.5, 131.7, 130.0, 129.2, 127.7, 126.3, 110.0,

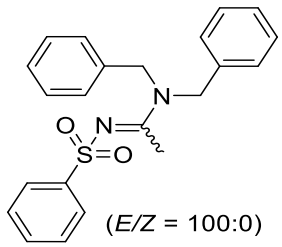
45.9, 45.6, 45.4, 43.5,21.6, 21.4, 17.7 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{26}N_3O_4S_2^+$: 436.1359; Found: 436.1359.

3.11 (E/Z)-N-(1-(3,4-Dihydroisoquinolin-2(1H)-yl)ethylidene)-4-methylbenzenesulfonamide (3k)



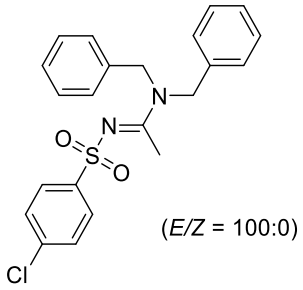
Yellow oil (75.9 mg, 77%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.27−7.09 (m, 6H), 4.78 (s, 1.22H), 4.61 (s, 0.78H), 3.89 (t, *J* = 6.0 Hz, 0.78H), 3.68 (t, *J* = 5.8 Hz, 1.22H), 2.91 (t, *J* = 5.9 Hz, 1.22H), 2.85 (t, *J* = 6.0 Hz, 0.78H), 2.58 (s, 1.17H), 2.55 (s, 1.83H), 2.40 (s, 1.83H), 2.39 (s, 1.17H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 142.1, 142.0, 141.2, 141.1, 134.9, 133.8, 132.4, 131.7, 129.3, 129.2, 128.5, 128.0, 127.6, 127.1, 127.0, 127.7, 127.7, 126.4, 126.4, 126.2, 48.2, 47.1, 44.5, 42.4, 29.2, 28.2, 21.5, 21.5, 18.4, 18.2 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{21}N_2O_2S^+$: 329.1318; Found: 329.1317.

3.12 (E/Z)-N,N-Dibenzyl-N'-(phenylsulfonyl)acetimidamide (3l)



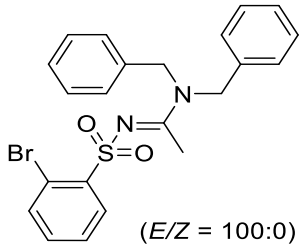
Yellow oil (99.9 mg, 88%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) 7.91 (d, *J* = 7.3 Hz, 2H), 7.49−7.28 (m, 9H), 7.18−7.11 (m, 4H), 4.73 (s, 2H), 4.55 (s, 2H), 2.64 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 143.8, 135.8, 134.9, 131.6, 129.4, 128.8, 128.6, 128.4, 128.2, 128.0, 126.4, 126.3, 51.7, 51.6, 18.4 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{22}H_{23}N_2O_2S^+$: 379.1475; Found: 379.1472.

3.13 (E)-N,N-Dibenzyl-N'-((4-chlorophenyl)sulfonyl)acetimidamide (3m)



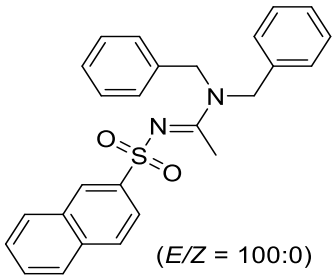
White solid (105.3 mg, 85%). M.p. 151 − 152 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) 7.81 (d, J = 8.4 Hz, 2H), 7.40−7.34 (m, 5H), 7.30−7.29 (m, 3H), 7.16−7.12 (m, 4H), 4.72 (s, 2H), 4.57 (s, 2H), 2.65 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 142.4, 137.8, 135.7, 134.7, 129.4, 128.9, 128.8, 128.3, 128.2, 128.0, 127.9, 126.3, 51.8, 18.5 ppm. HRMS (ESI): m/z $(M+H)^+$ calcd for $C_{22}H_{23}N_2O_2ClS^+$: 413.1085; Found: 413.1082.

3.14 (E)-N,N-Dibenzyl-N'-((2-bromophenyl)sulfonyl)acetimidamide (3n)



Yellow oil (108.4 mg, 79%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) 8.23 (dd, J = 7.8, 1.6 Hz, 1H), 7.68 (dd, J = 7.9, 1.1 Hz, 1H), 7.43−7.36 (m, 6H), 7.25−7.24 (m, 2H), 7.20−7.17 (m, 2H), 7.13 (d, J = 7.0 Hz, 2H), 4.78 (s, 2H), 4.54 (s, 2H), 2.67 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8, 142.5, 135.7, 135.1, 134.8, 132.7, 129.7, 129.4, 128.8, 128.6, 128.2, 128.0, 127.4, 126.3, 120.6, 51.6, 51.3, 18.9 ppm. HRMS (ESI): m/z $(M+H)^+$ calcd for $C_{22}H_{22}N_2O_2BrS^+$: 457.0580; Found: 457.0577.

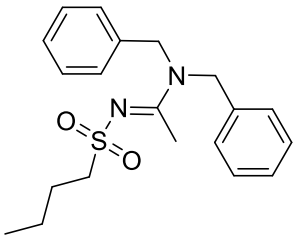
3.15 (E)-N,N-Dibenzyl-N'-(naphthalen-2-ylsulfonyl)acetimidamide (3o)



(*E*/*Z* = 100:0)

White oil (106.7 mg, 83%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.46. IR (KBr) 3034, 1542, 1475, 1362, 1265, 1087, 1010, 857, 754, 696, 665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 8.47 (s, 1H), 7.92−7.86 (m, 4H), 7.61−7.54 (m, 2H), 7.40−7.33 (m, 3H), 7.26−7.25 (m, 3H), 7.18−7.12 (m, 4H) 4.75 (s, 2H), 4.56 (s, 2H), 2.67 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 140.7, 135.8, 134.8, 134.5, 132.2, 129.3, 129.3, 128.9, 128.8, 128.3, 128.2, 128.2, 127.9, 127.9, 127.1, 126.7, 126.3, 122.8, 51.7, 51.7, 18.4 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{26}H_{25}N_2O_2S^+$: 429.1631; Found: 429.1630.

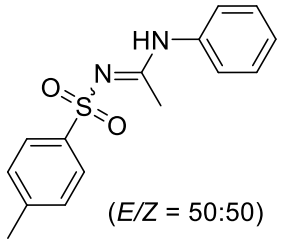
3.16 (E)-N,N-Dibenzyl-N'-(butylsulfonyl)acetimidamide (3p)



(*E*/*Z* = 100:0)

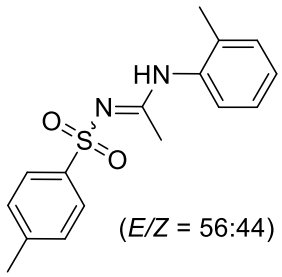
White oil (80.7 mg, 75%). Purified by column chromatography (petroleum ether/ethyl acetate, 5:1). R_f = 0.43. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.35−7.30 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.0 Hz, 2H), 4.74 (s, 2H), 4.54 (s, 2H), 3.07−3.03 (m, 2H), 2.64 (s, 3H), 1.84−1.76 (m, 2H), 1.45−1.35 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 140.3, 135.9, 135.0, 129.2, 128.8, 128.4, 128.1, 128.1, 127.9, 127.8, 126.9, 126.2, 55.1, 51.3, 51.2, 25.9, 21.6, 18.5, 13.6 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{27}N_2O_2S^+$: 359.1788; Found: 359.1787.

3.17 (E/Z)-N-Phenyl-N'-tosylacetimidamide (4a)



Yellow oil (70.9 mg, 82%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 0.5H), 8.09 (s, 0.5H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.42−7.39 (m, 1H), 7.35 (d, *J* = 7.2 Hz, 0.5H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.26−7.20 (m, 2H), 7.12 (m, d, *J* = 7.6 Hz, 1H), 7.11 (m, d, *J* = 7.4 Hz, 0.5H), 2.54 (s, 1.5H), 2.42 (s, 1.5H), 2.39 (s, 1.5H), 2.02 (s, 1.5H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.4, 143.2, 142.4, 140.2, 139.1, 137.3, 136.6, 129.7, 129.4, 129.2, 128.7, 128.1, 126.4, 126.3, 126.2, 125.4, 121.8, 21.9, 21.5, 21.5 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{17}N_2O_2S^+$: 289.1005; Found: 289.1003.

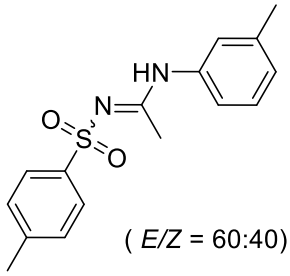
3.18 (E/Z)-N-(o-Tolyl)-N'-tosylacetimidamide (4b)



Yellow oil (67.1 mg, 74%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (m, 0.44H), 8.34 (s, 0.56H), 7.85 (d, *J* = 8.2 Hz, 0.88H), 7.77 (d, *J* = 8.2 Hz, 1.12H), 7.39 (d, *J* = 8.4 Hz, 1.12H), 7.29 (d, *J* = 8.0 Hz, 0.88H), 7.22 (d, *J* = 8.0 Hz, 1.12H), 7.19(d, *J* = 8.0 Hz, 0.88H), 6.99 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 1.68H), 2.41 (s, 1.32H), 2.38 (s, 1.68H), 2.36 (s, 1.32H), 2.26 (s, 1.68H), 1.99 (s, 1.32H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 163.5, 143.2, 142.4, 140.4, 139.2, 138.3, 135.1, 135.0, 134.0, 130.3, 129.5, 129.3, 129.2, 126.5, 126.4, 126.2, 121.9, 21.8, 21.6, 21.5, 21.3, 21.0, 21.0 ppm.

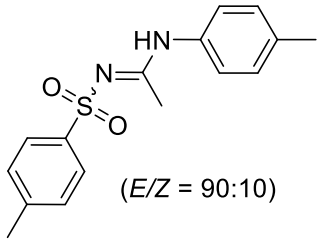
HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{19}N_2O_2S^+$: 303.1162; Found: 303.1160.

3.19 (E/Z)-N-(m-Tolyl)-N'-tosylacetimidamide (4c)



Yellow oil (70.8 mg, 78%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f= 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 0.4H), 7.90 (s, 0.6H), 7.85 (d, *J* = 8.1 Hz, 1.2H), 7.80 (d, *J* = 8.1 Hz, 0.8H), 7.29 (d, *J* = 8.2 Hz, 2.4H), 7.24 (s, 0.6H), 7.22 (s, 0.4H), 7.13 (d, *J* = 8.0 Hz, 0.6H), 7.08 (d, *J* = 7.7 Hz, 0.4H), 6.92−6.88 (m, 1.6H), 2.54 (s, 1.2H), 2.40 (s, 1.8H), 2.38 (s, 1.2H), 2.34 (s, 1.8H), 2.21 (s, 1.2H), 2.00 (s, 1.8H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.2, 143.2, 142.4, 140.5, 140.0, 139.3, 138.6, 137.4, 136.6, 129.6, 129.5, 129.3, 129.0, 128.7, 126.9, 126.6, 126.4, 126.3, 123.4, 122.6, 119.0, 22.2, 21.7, 21.6, 21.5, 21.4 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{19}N_2O_2S^+$: 303.1162; Found: 303.1160.

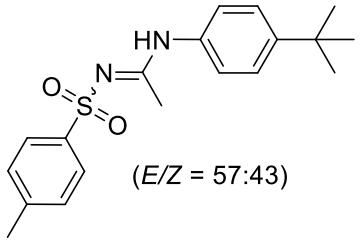
3.20 (E/Z)-N-(p-Tolyl)-N'-tosylacetimidamide (4d)



Yellow oil (72.6 mg, 80%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f= 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (m, 1H), 7.88 (d, *J* = 8.1 Hz, 1.8H), 7.71 (d, *J* = 7.7 Hz, 0.2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.28−7.21 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 1H), 2.63 (s, 0.3H), 2.42 (s, 2.7H), 2.37 (s, 0.3H), 2.24 (s, 2.7H), 2.22 (s, 0.3H), 1.91 (s, 2.7H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 143.2, 139.4, 135.6, 134.9, 131.4, 129.5, 129.2, 128.8, 127.6, 127.3, 126.6, 126.4, 21.7, 17.9 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{19}N_2O_2S^+$: 303.1162; Found:

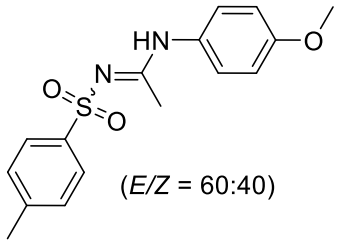
303.1158.

3.21 (E/Z)-N-(4-(tert-Butyl)phenyl)-N'-tosylacetimidamide (4e)



Yellow oil (94.0 mg, 91%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 0.43H), 8.08 (s, 0.57H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.26−7.22 (m, 2H), 7.04 (d, *J* = 8.5, 1H), 2.54 (s, 1.29H), 2.42 (s, 1.71H), 2.40 (s, 1.29H), 2.03 (s, 1.71H), 1.32 (s, 5.13H), 1.26 (s, 3.87H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 163.1, 151.3, 148.3, 143.1, 142.3, 140.3, 139.2, 134.8, 133.8, 129.4, 129.2, 126.5, 126.4, 126.4, 125.8, 125.5, 121.3, 34.7, 34.4, 31.3, 31.2, 22.0, 22.0, 21.5, 21.5 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{19}H_{25}N_2O_2S^+$: 345.1631; Found: 345.1629.

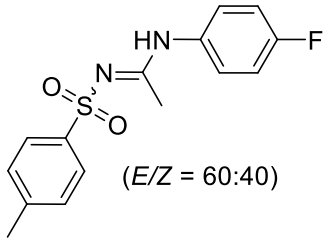
3.22 (E/Z)-N-(4-Methoxyphenyl)-N'-tosylacetimidamide (4f)



Yellow oil (84.1 mg, 88%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 0.4H), 8.11 (s, 0.6H), 7.85 (d, *J* = 8.3 Hz, 1.2H), 7.77 (d, *J* = 8.2 Hz, 0.8H), 7.41 (d, *J* = 9.0 Hz, 0.8H), 7.29 (d, *J* = 8.0 Hz, 1.2H), 7.23 (d, *J* = 8.1 Hz, 0.8H), 7.04 (d, *J* = 8.8 Hz, 1.2H), 6.89 (d, *J* = 8.9 Hz, 1.2H), 6.73 (d, *J* = 9.0 Hz, 0.8H), 3.81 (s, 1.8H), 3.73 (s, 1.2H), 2.50 (s, 1.2H), 2.41 (s, 1.8H), 2.38 (s, 1.2H), 1.96 (s, 1.8H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.2, 159.2, 157.0, 143.1, 142.2, 140.4, 139.2, 130.5, 129.4,

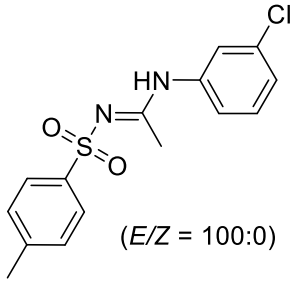
129.2, 129.2, 127.8, 126.4, 126.3, 123.5, 114.7, 113.8, 55.5, 55.4, 21.7, 21.5, 21.4 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{19}N_2O_3S^+$: 319.1111; Found: 319.1110.

3.23 (E/Z)-N-(4-Fluorophenyl)-N'-tosylacetimidamide (4g)



Yellow solid (68.9 mg, 75%). M.p. 180 − 181 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 0.4H), 8.26 (s, 0.6H), 7.85 (d, *J* = 8.2 Hz, 0.8H), 7.76 (d, *J* = 8.2 Hz, 1.2H), 7.47−7.44 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 0.8H), 7.24 (d, *J* = 8.1 Hz, 1.2H), 7.14−7.10 (m, 2H), 7.04 (d, *J* = 8.5 Hz, 1H), 2.51 (s, 1.8H), 2.42 (s, 1.2H), 2.40 (s, 1.8H), 1.98 (s, 1.2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.6, 162.0 (d , *J* = 247.5 Hz), 159.9 (d, *J* = 244.2 Hz), 143.3, 142.6, 140.0, 138.9, 133.3 (d , *J* = 2.8 Hz), 132.5 (d , J = 3.2 Hz), 129.5, 129.3, 128.4 (d , *J* = 8.6 Hz), 126.4, 126.2, 123.8 (d , *J* = 8.0 Hz), 126.7 (d , *J* = 22.8 Hz), 115.4 (d , *J* = 22.4 Hz), 21.7, 21.5, 21.4 ppm. 19F NMR (376 MHz, $CDCl_3$) δ −112.5, 116.1 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{16}N_2O_2FS^+$: 307.0911; Found: 307.0909.

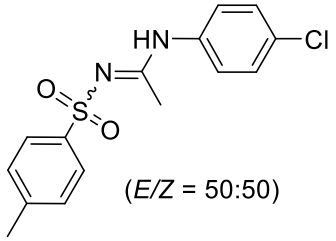
3.24 (E)-N-(3-Chlorophenyl)-N'-tosylacetimidamide (4h)



White solid (69.7 mg, 72%). M.p. 147 − 148 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.42. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.5 (s, 1H), 7.78 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.39−7.34 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.7, 142.2, 140.3, 139.3, 132.9, 130.4, 129.4, 125.9, 124.6, 121.2,

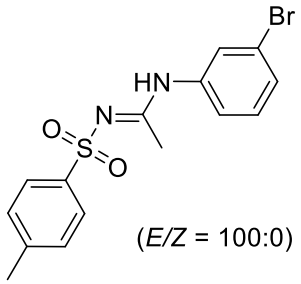
111.9, 20.9, 20.9 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{16}N_2O_2ClS^+$: 323.0616; Found: 323.0615.

3.25 (E/Z)-N-(4-Chlorophenyl)-N'-tosylacetimidamide (4i)



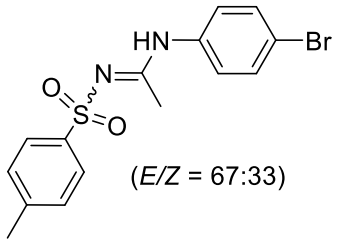
White solid (80.4 mg, 83%). M.p. 182 − 183 ºC. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.43. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.4 (s, 1H), 7.73 (dd, *J* = 8.0, 3.8 Hz, 2H), 7.61 (d, *J* = 8.7, 3.7 Hz, 2H), 7.40−7.34 (m, 4H), 2.47 (s, 1.5H), 2.45 (s, 1.5H), 2.36 (s, 1.5H), 2.35 (s, 1.5H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.7, 142.1, 140.4, 136.8, 129.4, 128.8, 128.6, 125.9, 123.2, 20.9, 20.8 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{16}N_2O_2ClS^+$: 323.0616; Found: 323.0615.

3.26 (E)-N-(3-Bromophenyl)-N'-tosylacetimidamide (4j)



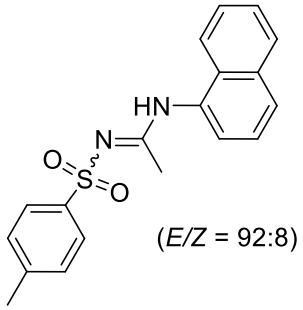
Yellow solid (72.7 mg, 66%). M.p. 192 − 193 ºC. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.44. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.5 (s, 1H), 7.92 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 77.33−7.27 (m, 2H), 2.47 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.6, 142.2, 140.4, 139.4, 130.6, 129.4, 127.5, 125.8, 124.1, 121.3, 120.3, 20.9, 20.9 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{16}N_2O_2BrS^+$: 367.0110; Found: 367.0110.

3.27 (E/Z)-N-(4-Bromophenyl)-N'-tosylacetimidamide (4k)



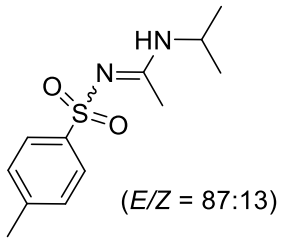
Yellow solid (85.9 mg, 78%). R_f = 0.44. M.p. 172 − 173 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.52. IR (KBr) 3344, 2915, 1529, 1484, 1395, 1264, 1141, 1086, 1005, 822, 746, 707, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 0.33H), 8.11 (s, 0.67H), 7.84 (d, *J* = 7.8 Hz, 0.66H), 7.77 (d, *J* = 8.1 Hz, 1.34H), 7.54 (d, *J* = 8.3 Hz, 0.66H), 7.39 (d, *J* = 8.7 Hz, 1.34H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 1.34H), 7.01 (d, *J* = 8.1 Hz, 0.66H), 2.54 (s, 2.01H), 2.42 (s, 0.99H), 2.41 (s, 2.01H), 2.01 (s, 0.99H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 143.6, 142.9, 140.0, 138.9, 136.5, 133.0, 131.9, 130.9, 129.6, 129.5, 128.0, 126.6, 126.4, 123.5, 118.5, 110.1, 22.1, 22.0, 21.7, 21.6 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{16}N_2O_2BrS^+$: 367.0110; Found: 367.0107.

3.28 (E/Z)-N-(Naphthalen-1-yl)-N'-tosylacetimidamide (4l)



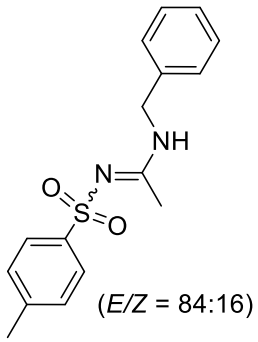
Yellow oil (79.2 mg, 78%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.92−7.87 (m, 2H), 7.82−7.78 (m, 1H), 7.58−7.55 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.35−7.31 (m, 3H), 2.74 (s, 0.24H), 2.45 (s, 2.76H), 2.32 (s, 0.24H), 1.91 (s, 2.76H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 143.4, 143.3, 139.4, 139.2, 134.4, 132.8, 129.9, 129.7, 129.6, 129.2, 128.6, 127.8, 127.1, 126.7, 126.5, 125.4, 125.2, 121.9, 21.7, 21.6 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{19}H_{19}N_2O_2S^+$: 339.1162; Found: 339.1161.

3.29 (E/Z)-N-Isopropyl-N'-tosylacetimidamide (4m)



Yellow oil (52.7 mg, 69%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 0.13H), 7.90 (s, 0.87H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.16−4.07 (m, 0.87H), 3.73−3.68 (m, 0.13H), 2.39 (s, 0.39H), 2.38 (s, 2.61H), 2.30 (s, 0.39H), 2.29 (s, 2.61H), 1.24 (d, *J* = 6.4 Hz, 0.78H), 1.12 (d, *J* = 6.6 Hz, 5.22H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 142.9, 142.1, 140.9, 139.7, 129.4, 129.3, 126.4, 126.4, 46.7, 44.0, 23.4, 22.0, 21.6, 21.6, 21.4 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{12}H_{19}N_2O_2S^+$: 255.1162; Found: 255.1160.

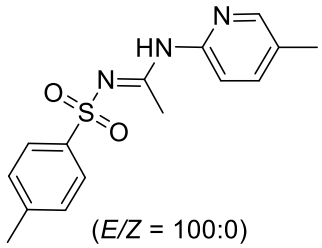
3.30 (E/Z)-N-Benzyl-N'-tosylacetimidamide (4n)



Yellow oil (57.2 mg, 63%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.50. IR (KBr) 3363, 1546, 1425, 1362, 1271, 1139, 1084, 741, 665 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (s, 0.16H), 7.76 (d, *J* = 8.2 Hz, 0.32H), 7.69 (d, *J* = 8.2 Hz, 1.68H), 7.36−7.31 (m, 0.48H), 7.28−7.24 (m, 2.52H), 7.21−7.16 (m, 4H), 6.56 (s, 0.84H), 4.43 (d, *J* = 6.1 Hz, 0.32H), 4.41 (d, *J* = 5.6 Hz, 1.68H), 2.40 (s, 0.42H), 2.38 (s, 2.58H), 2.33 (s, 2.58H), 2.06 (s, 0.42H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 143.1, 142.3, 140.6, 139.3, 136.7, 135.8, 129.5, 129.3, 129.2, 128.8, 128.3, 128.3, 127.9, 126.9, 126.5, 126.4, 48.1, 46.1, 21.6, 21.6,

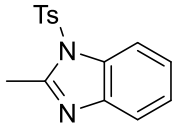
21.1 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{19}N_2O_2S^+$: 303.1162; Found: 303.1159.

3.31 (E)-N-(5-Methylpyridin-2-yl)-N'-tosylacetimidamide (4o)



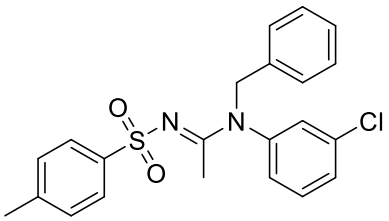
White solid (59.2 mg, 65%). M.p. 197 − 198 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 5:1). R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.06−8.04 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.61 (s, 3H), 2.42 (s, 3H), 2.28 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.7, 148.5, 147.4, 142.6, 139.9, 139.1, 130.4, 129.3, 126.5, 115.6, 22.1, 21.5, 17.8 ppm. HRMS (ESI): *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{18}N_3O_2S^+$: 304.1114; Found: 304.1115.

3.32 2-Methyl-1-tosyl-1H-benzo[d]imidazole (5)[3]



Yellow Soil (53.3 mg, 62%). M.p. 150 − 151 °C. Purified by column chromatography (petroleum ether/ethyl acetate, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.82 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 146.2, 141.8, 135.5, 133.3, 130.4, 126.9, 124.9, 124.8, 119.7, 113.6, 21.8, 17.0 ppm.

3.33 (E)-N-Benzyl-N-(3-chlorophenyl)-N'-tosylacetimidamide (6)



Yellow oil (105.3 mg, 85%). Purified by column chromatography (petroleum ether/ethyl acetate, 2:1). R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 8.6, 4.6 Hz, 2H), 7.35 – 7.18 (m, 7H), 7.09 – 7.07 (m, 2H), 7.00 (s, 1H), 6.83 (s, 1H), 4.93 (s, 2H), 2.41 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 142.6, 142.2, 140.5, 135.4, 130.8, 129.2, 129.1, 128.9, 128.5, 128.2, 127.9, 126.4, 55.5, 21.5, 19.9 ppm. HRMS (ESI): m/z $(M+H)^+$ calcd for $C_{22}H_{22}ClN_2O_2S^+$: 413.1085; Found: 413.1082.

4. References

[1] Keipour, H.; Jalba, A.; Delage-Laurin, L.; Ollevier, T. Copper-Catalyzed Carbenoid Insertion Reactions of α-Diazoesters and α-Diazoketones into Si – H and S – H Bonds. *J. Org. Chem.* **2017**, *82,* 3000−3010.

[2] (a) Chevrier Q.; Pierru T.; Craquelin A.; Maitrejean P.; Jean A.; Bettoni, L. Synthesis of *N*-Sulfonyl Formamidines by Direct Condensationbetween Sulfonamide and Formamide Enabled by a Photogenerated Vilsmeier-Type Reagent. *J. Org. Chem.* **2024**, *89*, 15282−15288; (b) Chow, S. Y.; Odell, L. R. Synthesis of *N*-Sulfonyl Amidines and Acyl Sulfonyl Ureas from Sulfonyl Azides, Carbon Monoxide, and Amides. *J. Org. Chem.* **2017***, 82,* 2515−2522.

[3] Wang, J.; Lu, P.; Wang, Y. Copper-catalyzed multi-component synthesis of acrylamidines and benzimidazoles. *Org. Chem. Front.* **2015**, *2*, 1346−1351.

5. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra for all Products

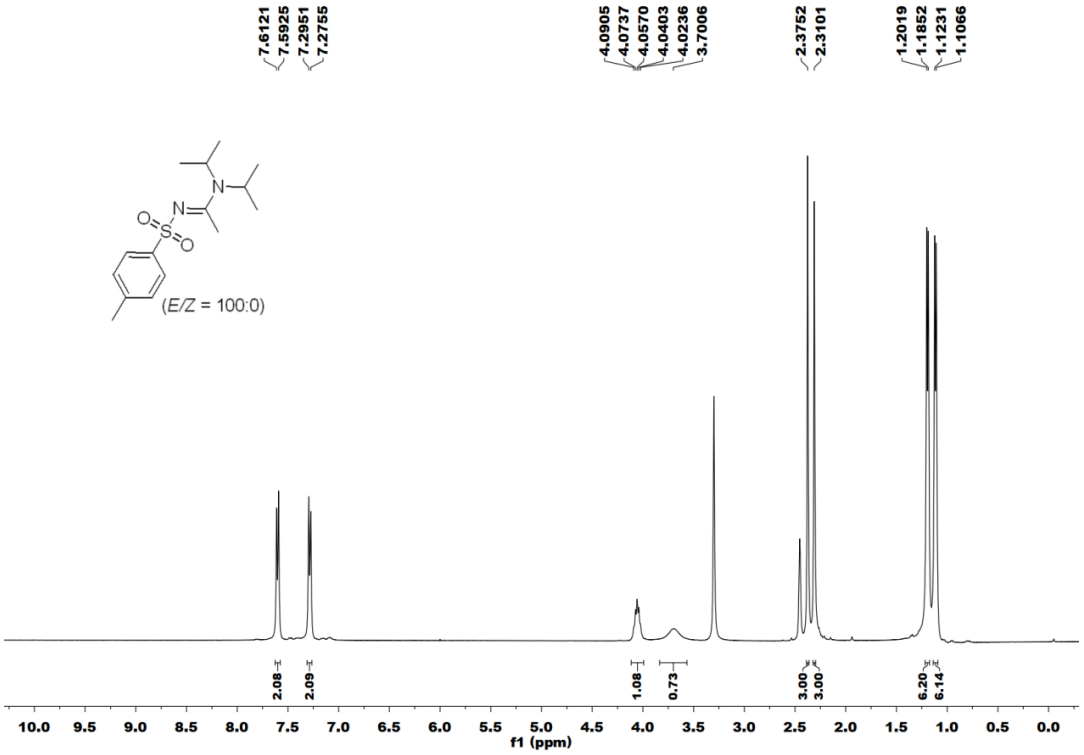


Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6) of *(E)*-*N*,*N*-diisopropyl-*N'*-tosylacetimidamide (3a)

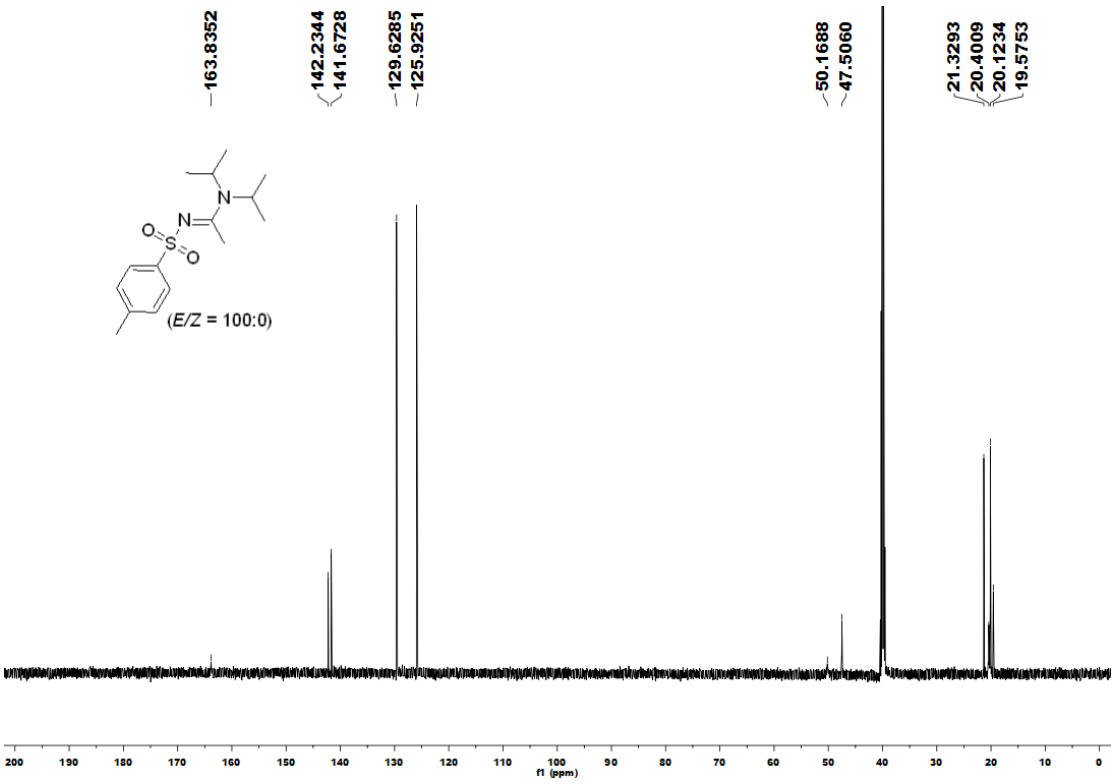


Fig. S2 ^{13}C NMR (150 MHz, DMSO-d_6) of (*E*)-*N*,*N*-diisopropyl-*N'*-tosylacetimidamide (3a)

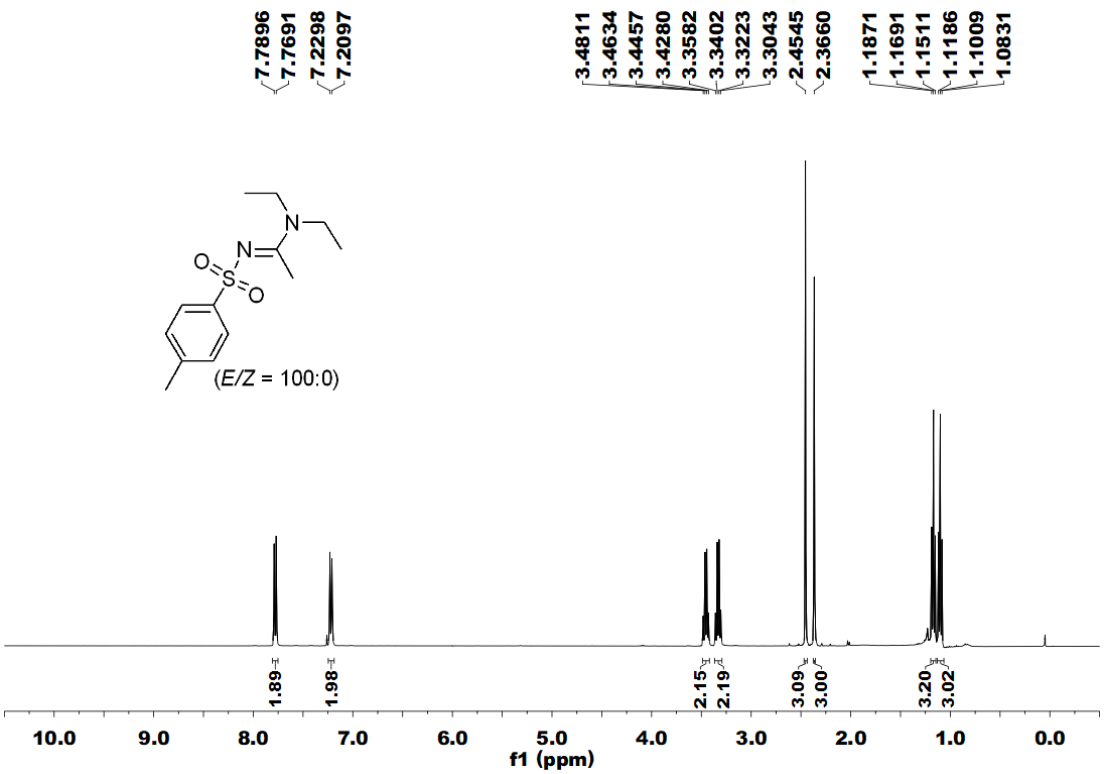


Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$) of *(E)-N,N*-diethyl-*N'*-tosylacetimidamide (3b)

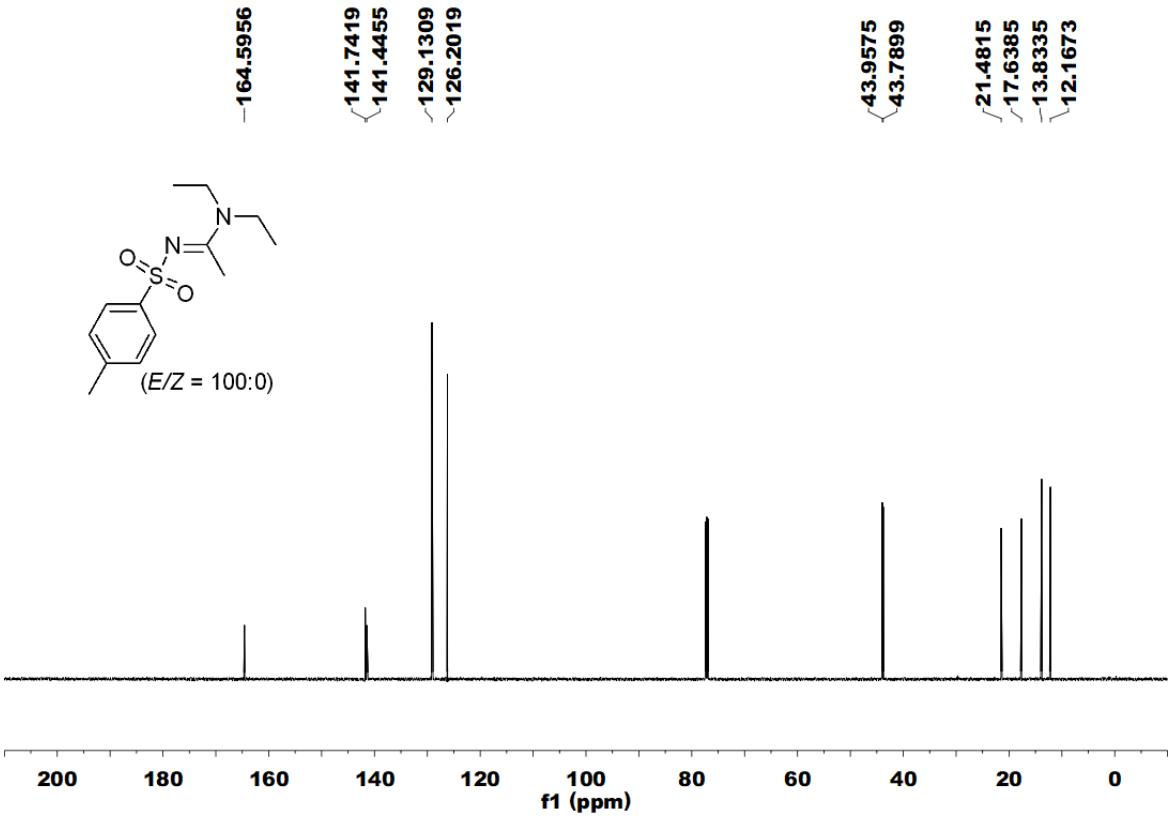


Fig. S4 ^{13}C NMR (150 MHz, $CDCl_3$) of *(E)-N,N*-diethyl-*N'*-tosylacetimidamide (3b)

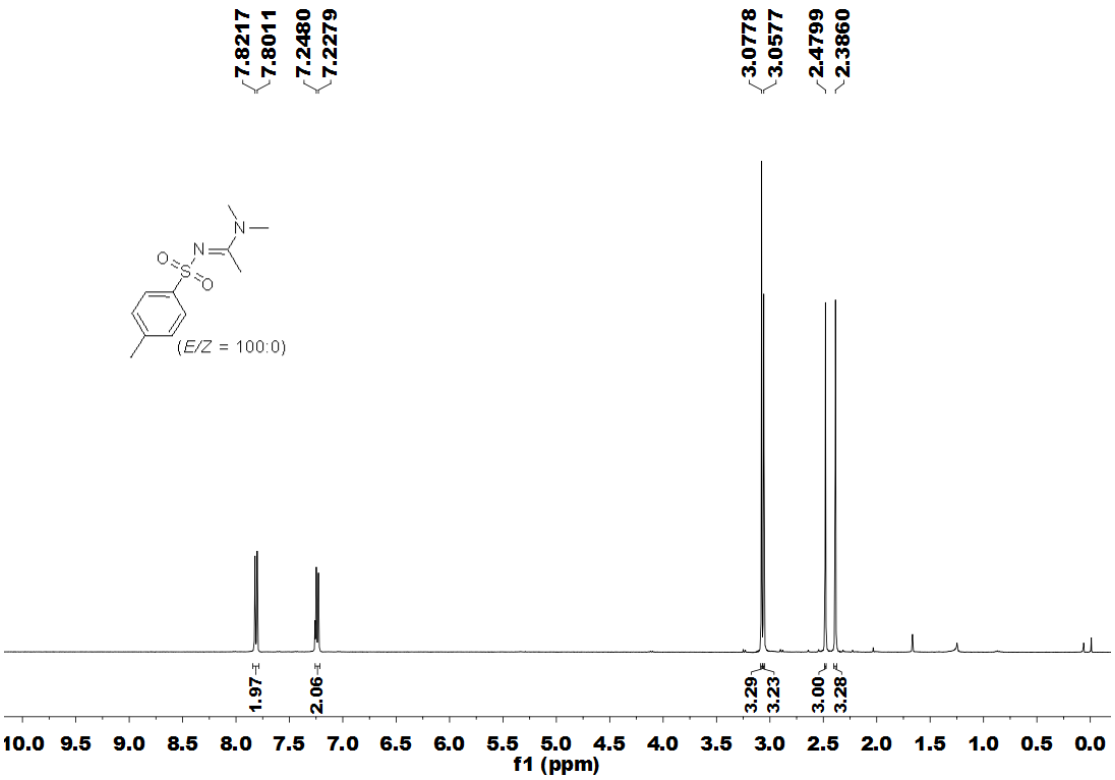


Fig. S5 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dimethyl-*N*'-tosylacetimidamide (3c)

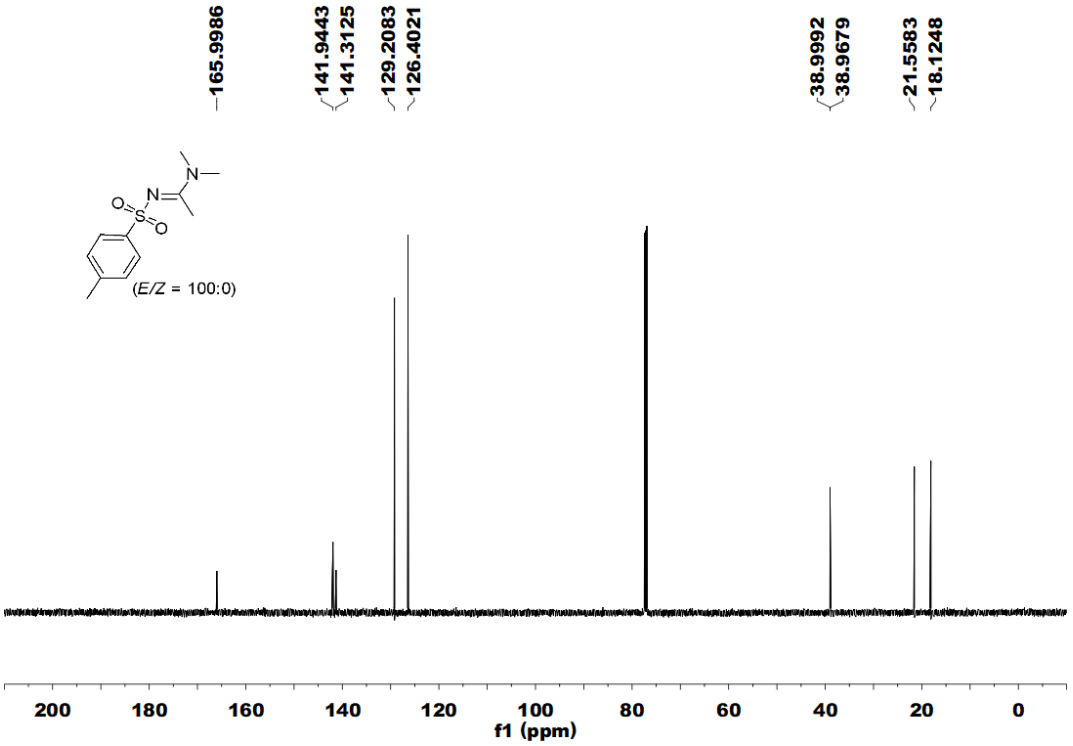


Fig. S6 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dimethyl-*N*'-tosylacetimidamide (3c)

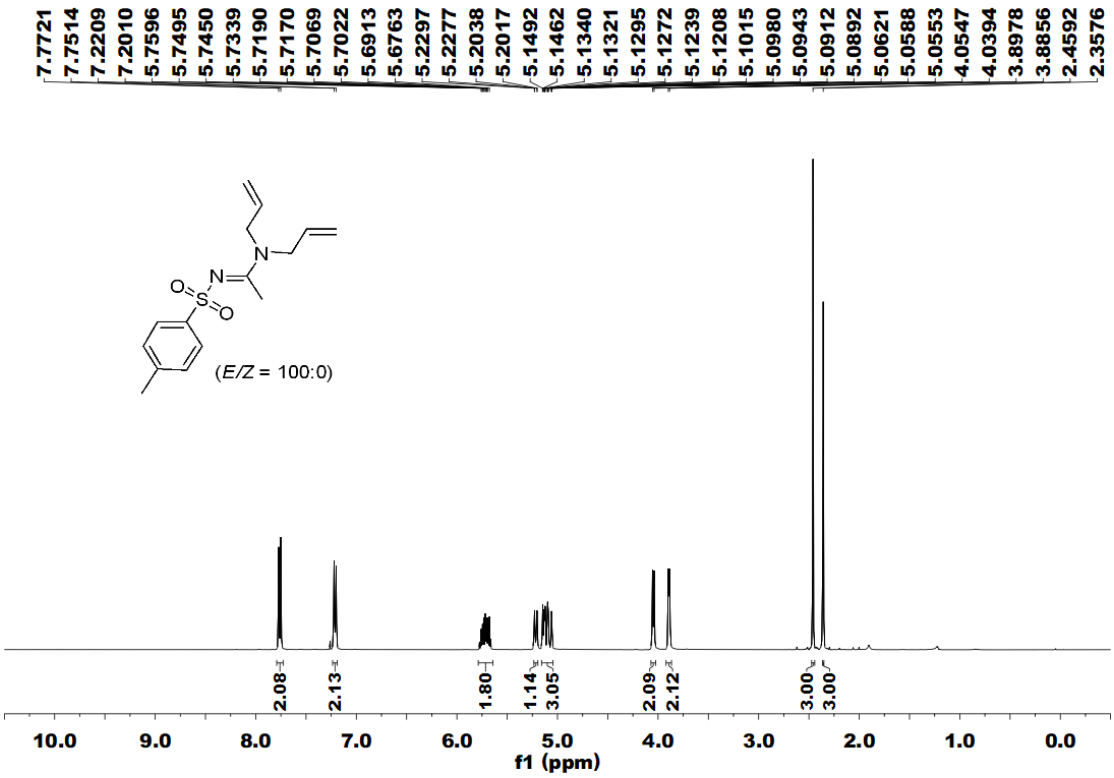


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*,*N*-diallyl-*N*'-tosylacetimidamide (3d)

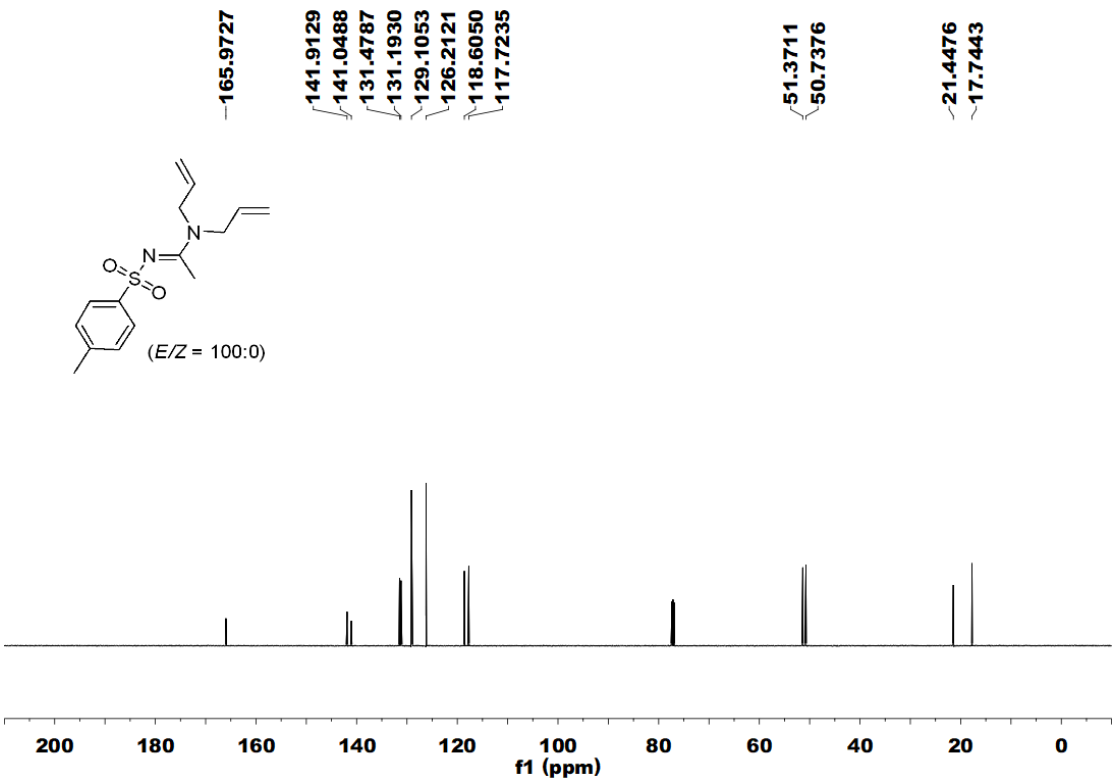


Fig. S8 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*,*N*-diallyl-*N*'-tosylacetimidamide (3d)

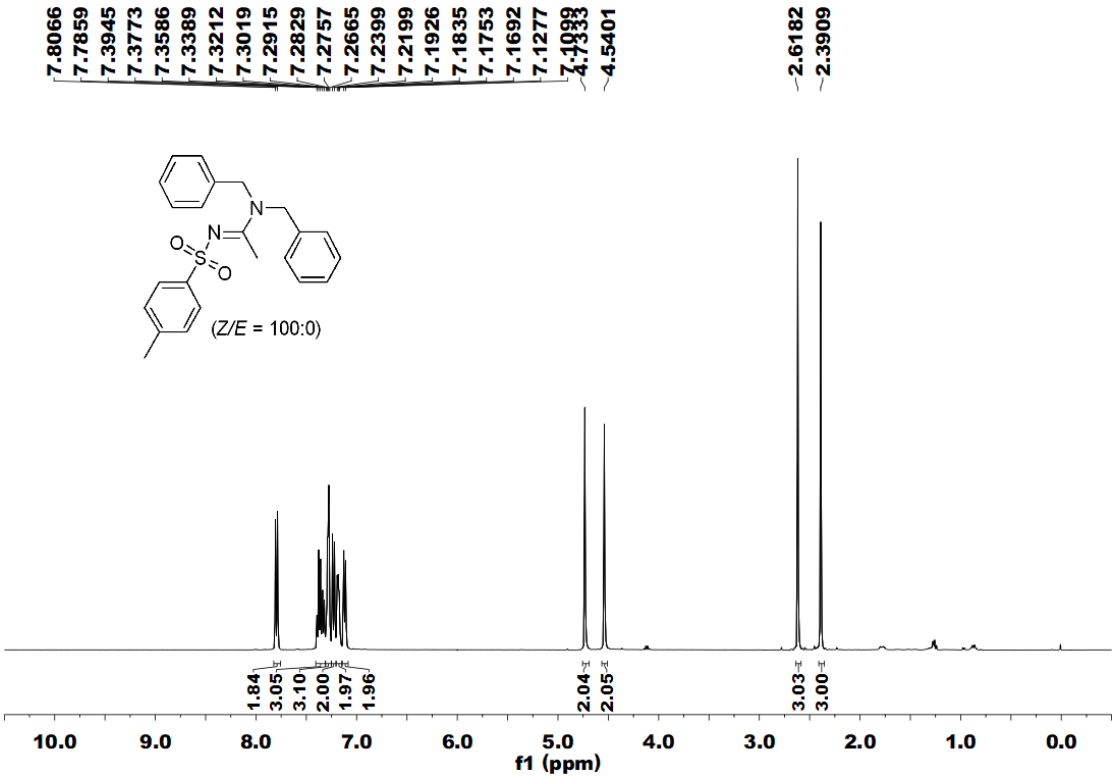


Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N*'-tosylacetimidamide (3e)

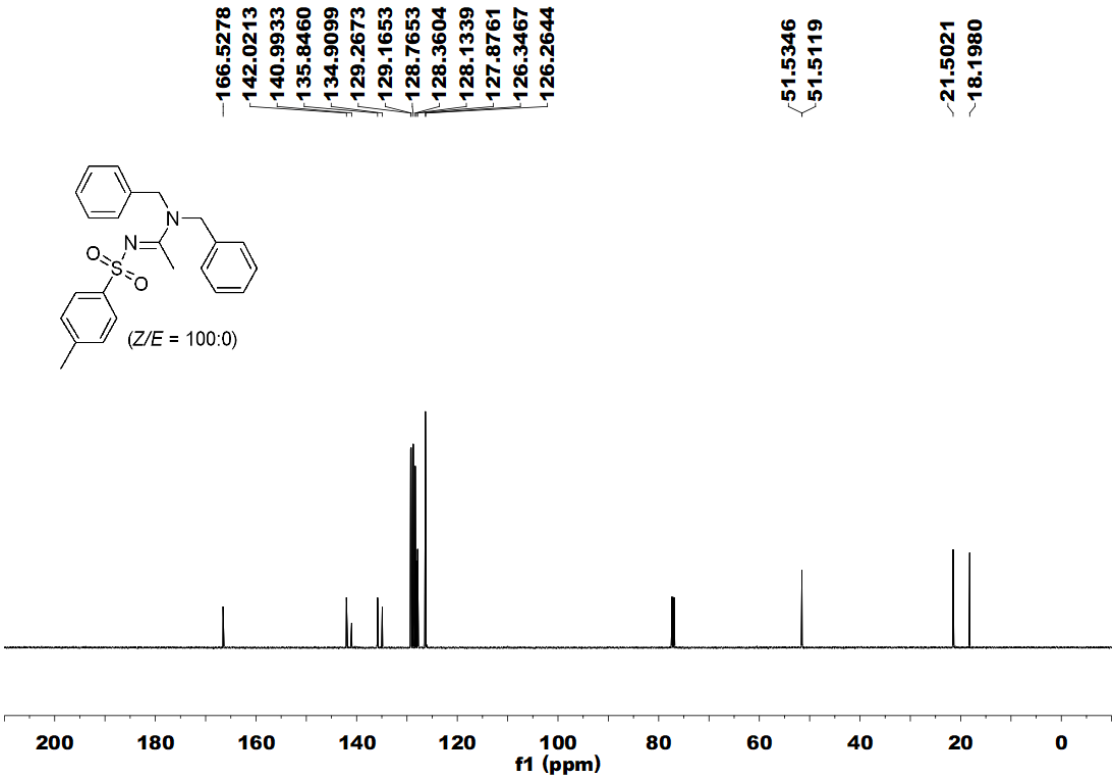


Fig. S10 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N*'-tosylacetimidamide (3e)

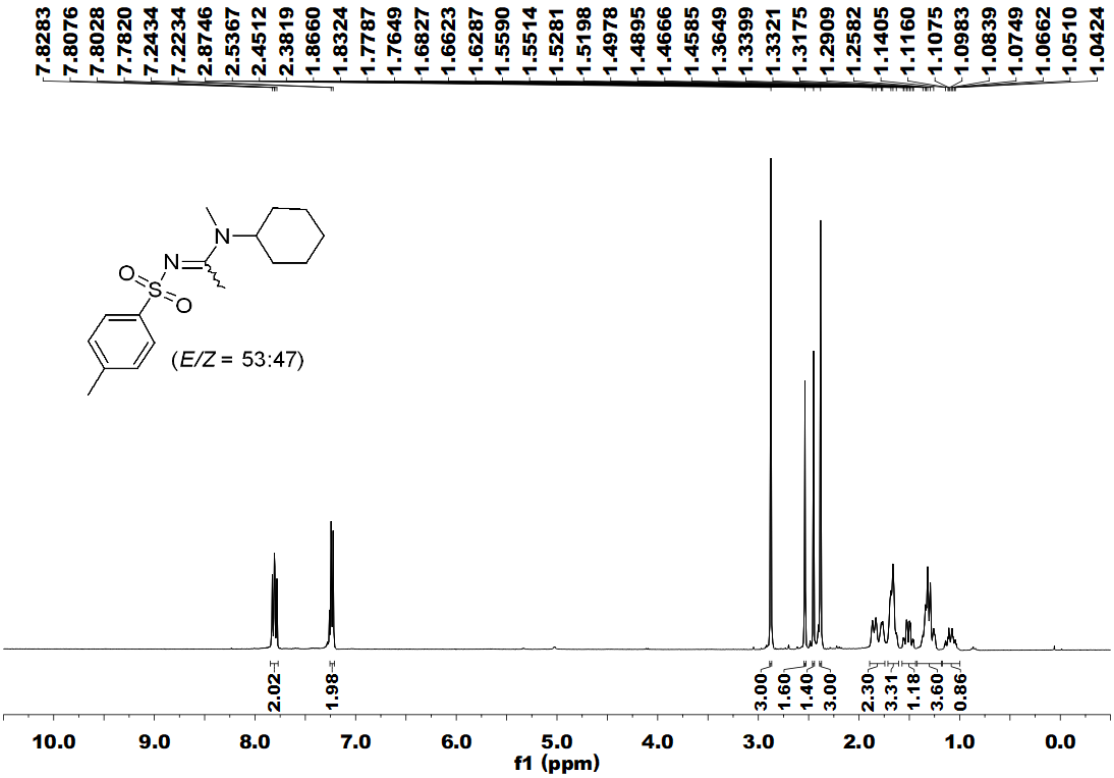


Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-cyclohexyl-*N*-methyl-*N*'-tosylacetimidamide (3f)

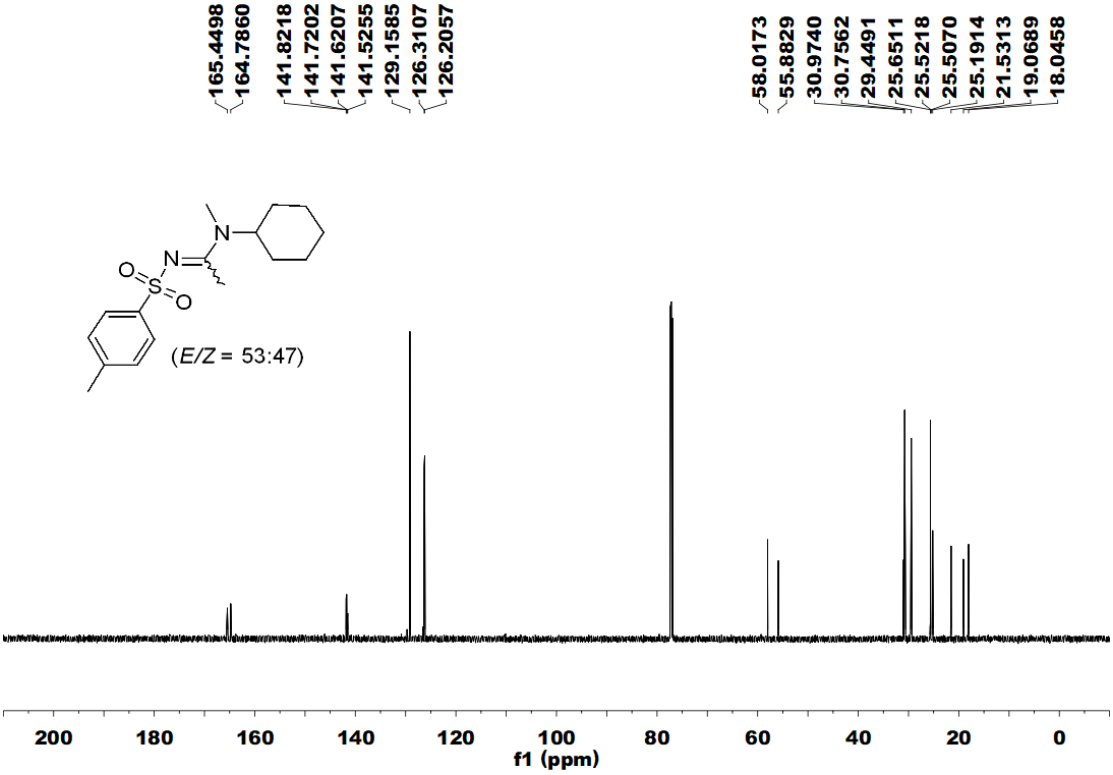


Fig. S12 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-cyclohexyl-*N*-methyl-*N*'-tosylacetimidamide (3f)

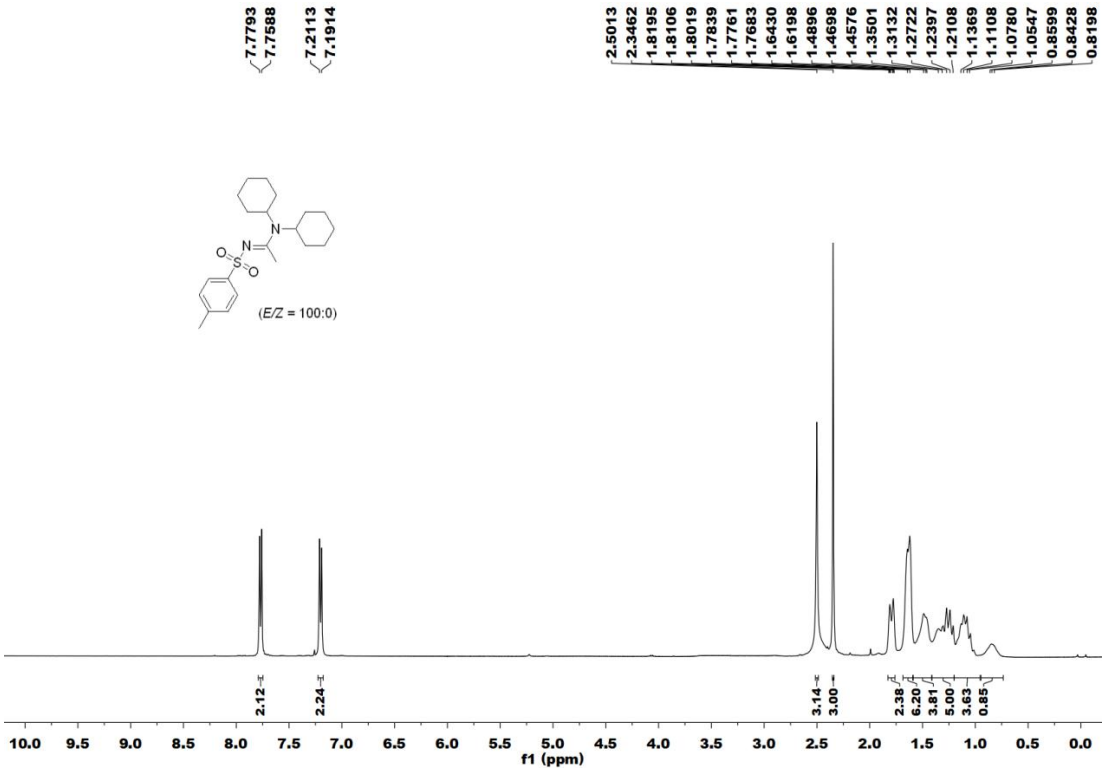


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*,N-dicyclohexyl-*N*'-tosylacetimidamide (3g)

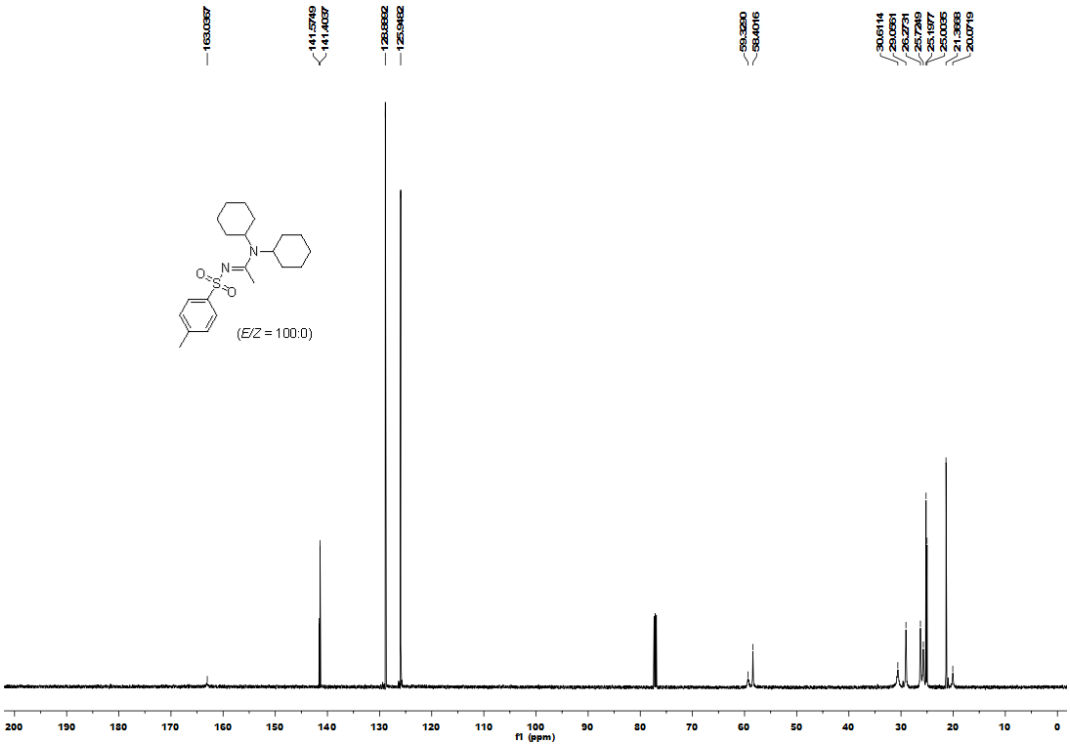


Fig. S14 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*,N-dicyclohexyl-*N*'-tosylacetimidamide (3g)

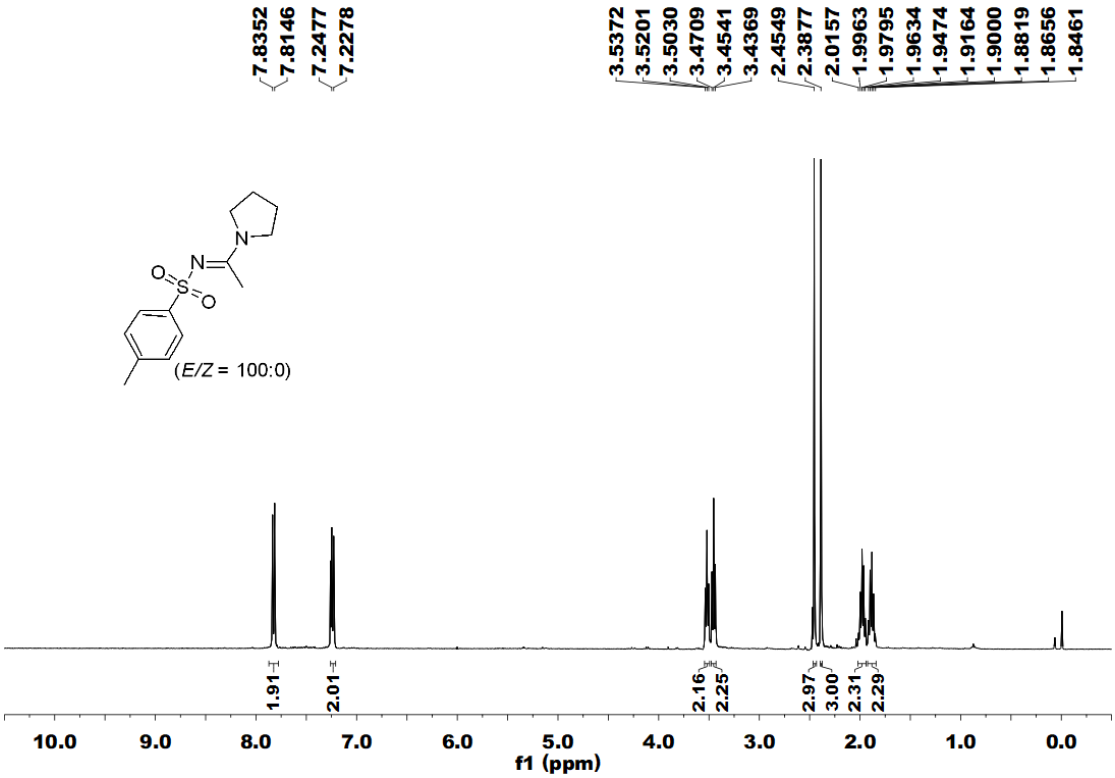


Fig. S15 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-4-methyl-*N*-(1-(pyrrolidin-1-yl) ethylidene)benzenesulfonamide (3h)

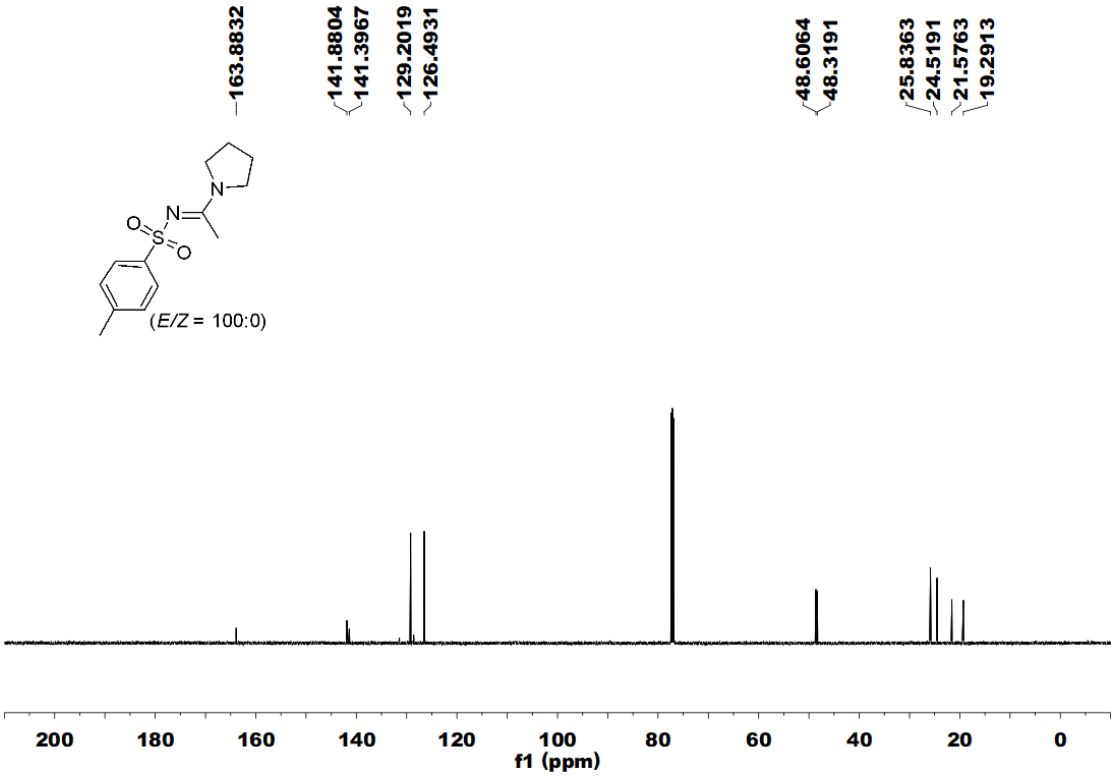


Fig. S16 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-4-methyl-*N*-(1-(pyrrolidin-1-yl) ethylidene)benzenesulfonamide (3h)

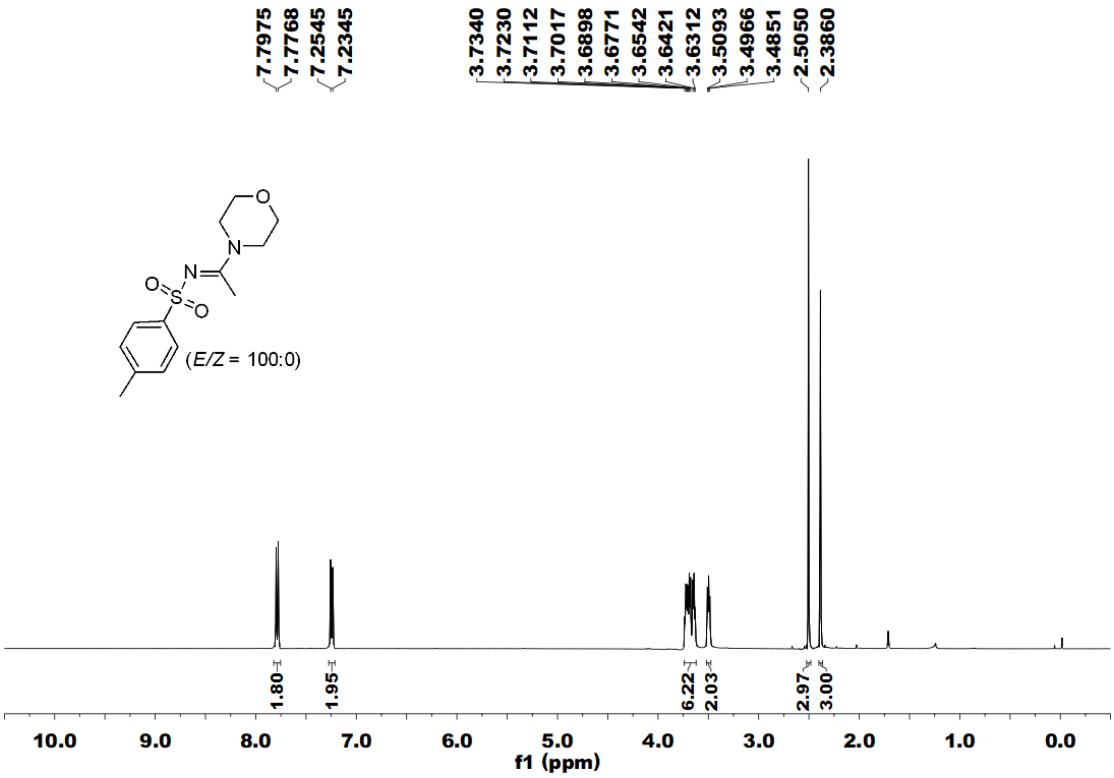


Fig. S17 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-4-methyl-*N*-(1-morpholinoethylidene) benzenesulfonamide (3i)

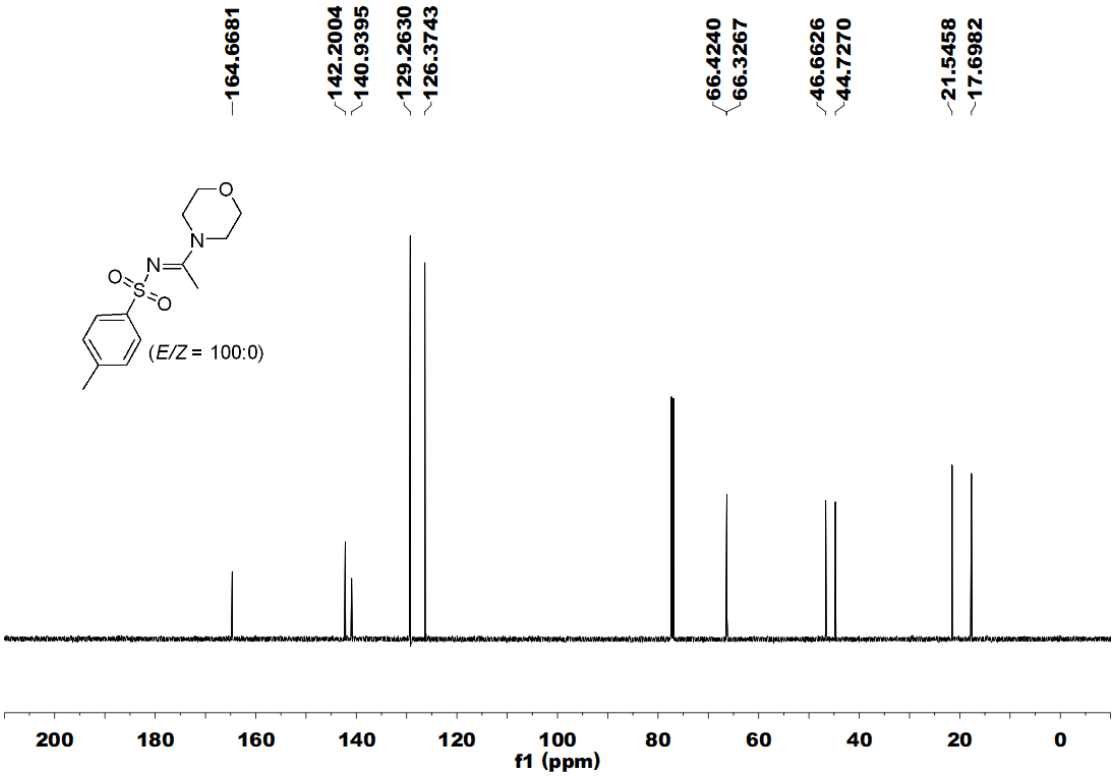


Fig. S18 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-4-methyl-*N*-(1-morpholinoethylidene) benzenesulfonamide (3i)

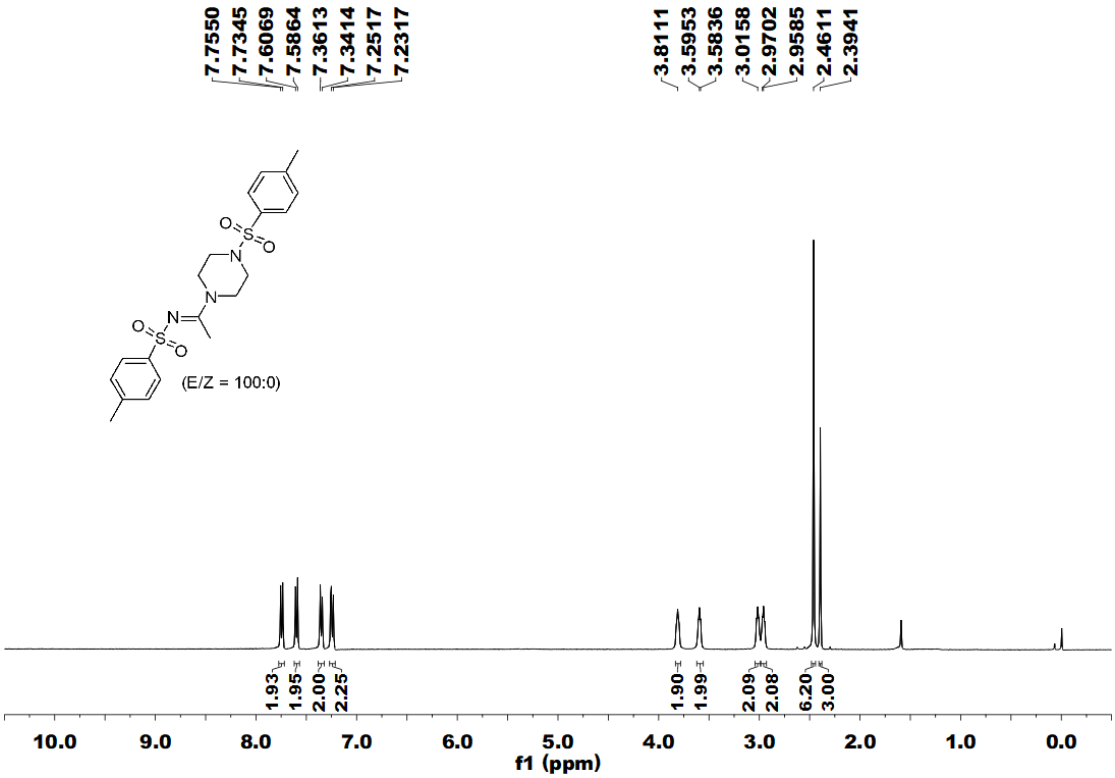


Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$) of *(E)-4-methyl-N-(1-(4-tosylpiperazin-1-yl) ethylidene)benzenesulfonamide* (3j)

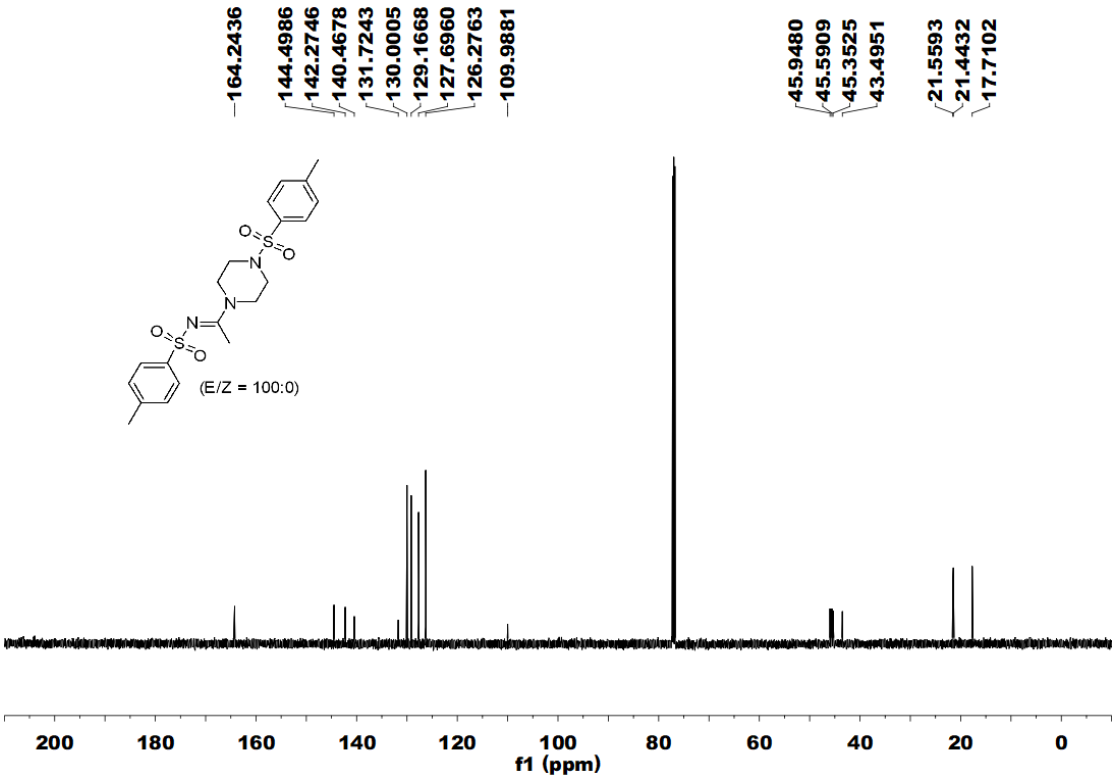


Fig. S20 ^{13}C NMR (150 MHz, $CDCl_3$) of *(E)-4-methyl-N-(1-(4-tosylpiperazin-1-yl) ethylidene)benzenesulfonamide* (3j)

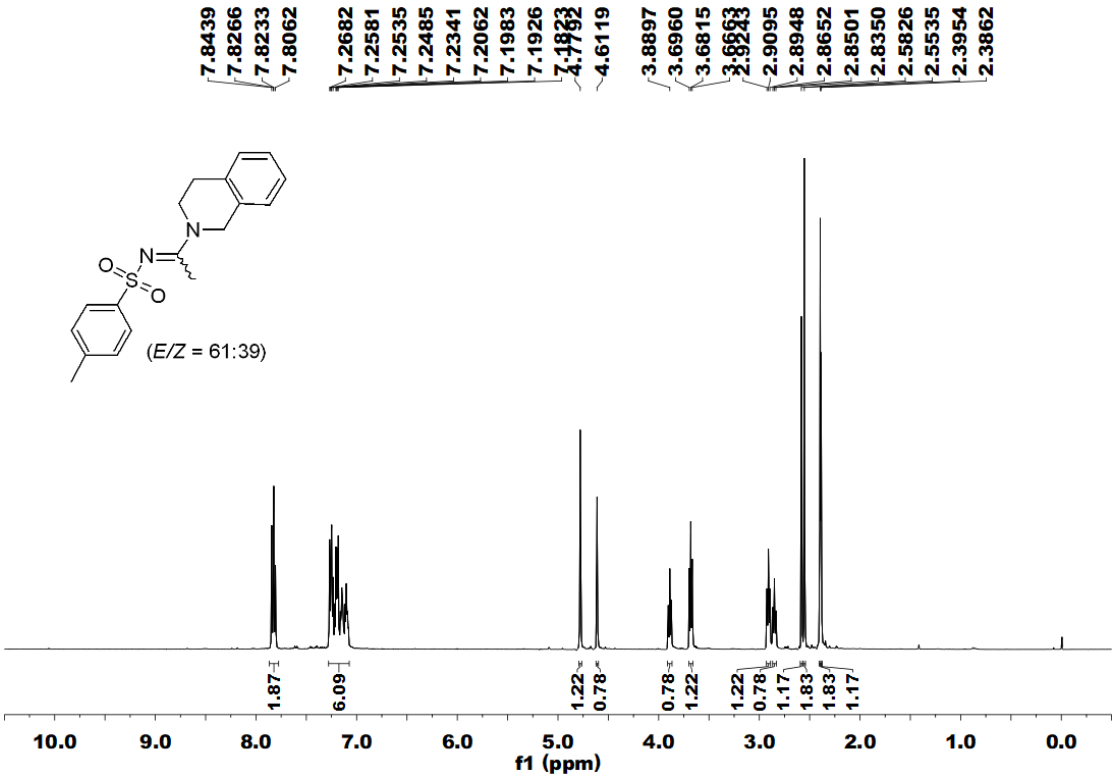


Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(1-(3,4-dihydroisoquinolin-2(*1H*) -yl) ethylidene)-4-methylbenzenesulfonamide (3k)

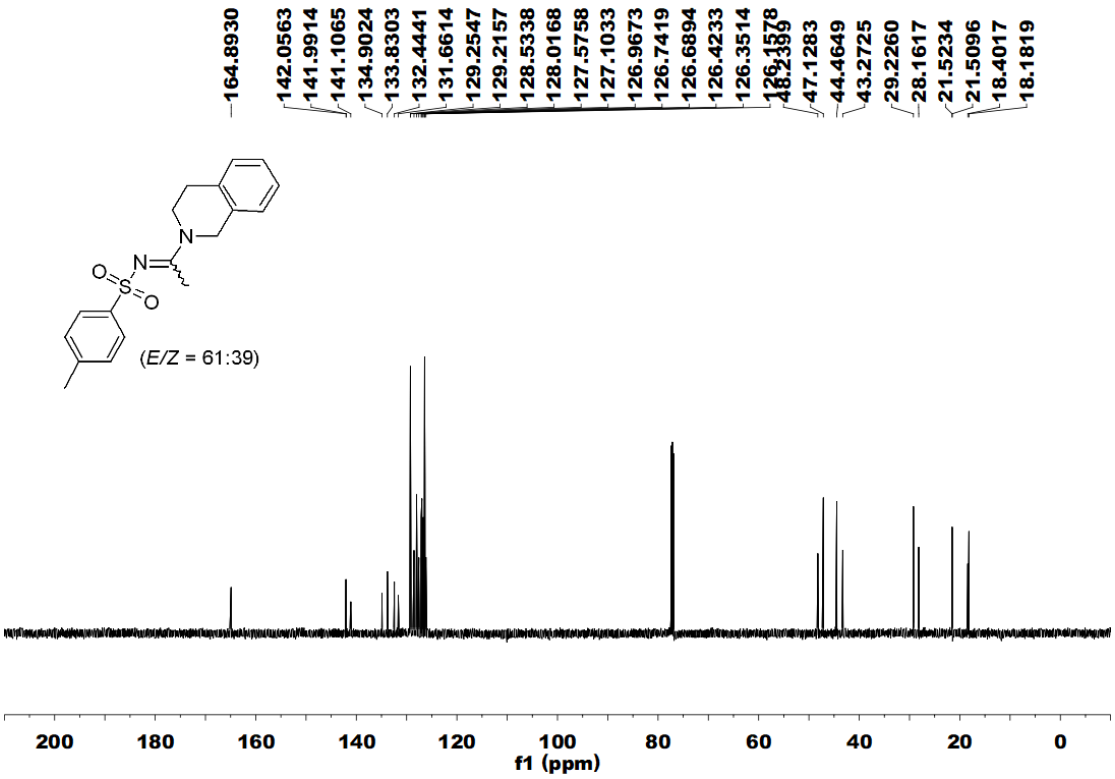


Fig. S22 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(1-(3,4-dihydroisoquinolin-2(*1H*) -yl) ethylidene)-4-methylbenzenesulfonamide (3k)

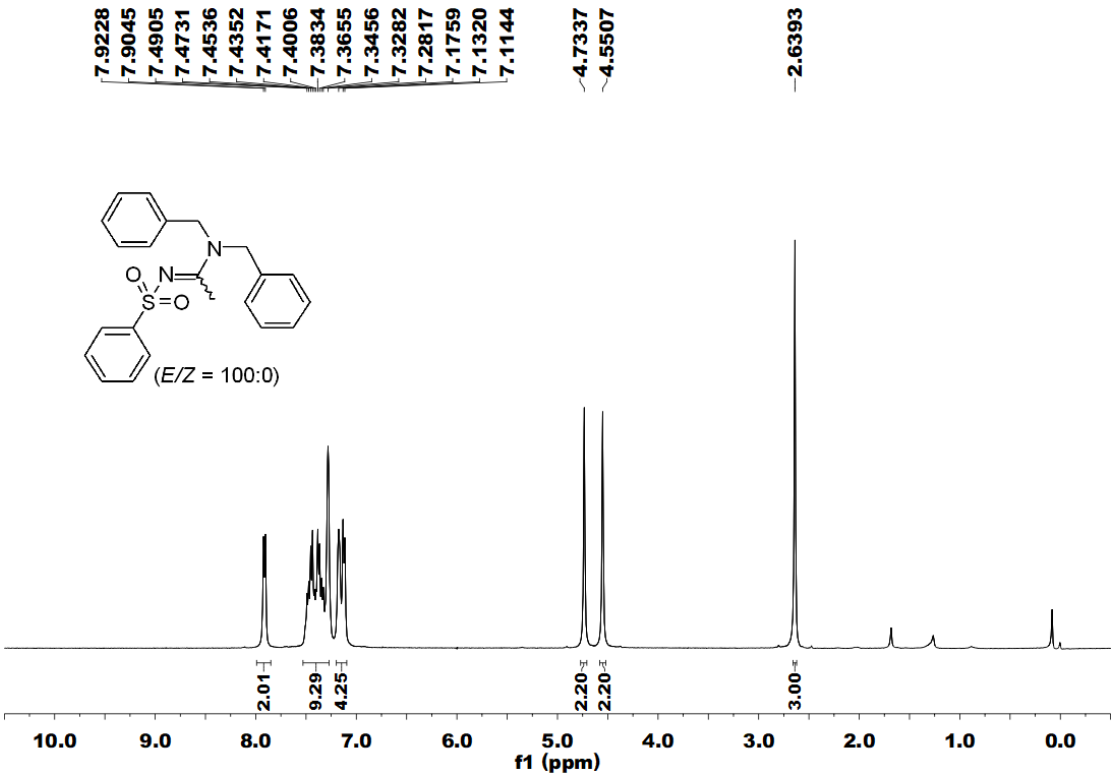


Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*,*N*-dibenzyl-*N*'- (phenylsulfonyl) acetimidamide (3l)

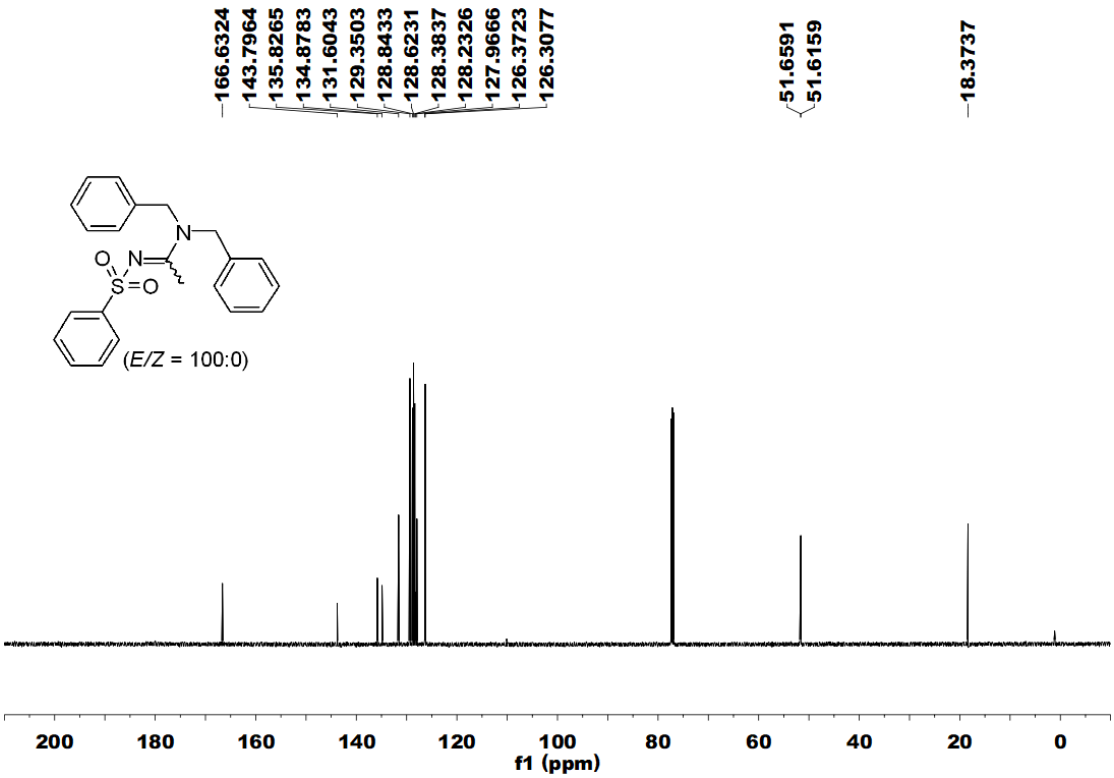


Fig. S24 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*,*N*-dibenzyl-*N*'- (phenylsulfonyl) acetimidamide (3l)

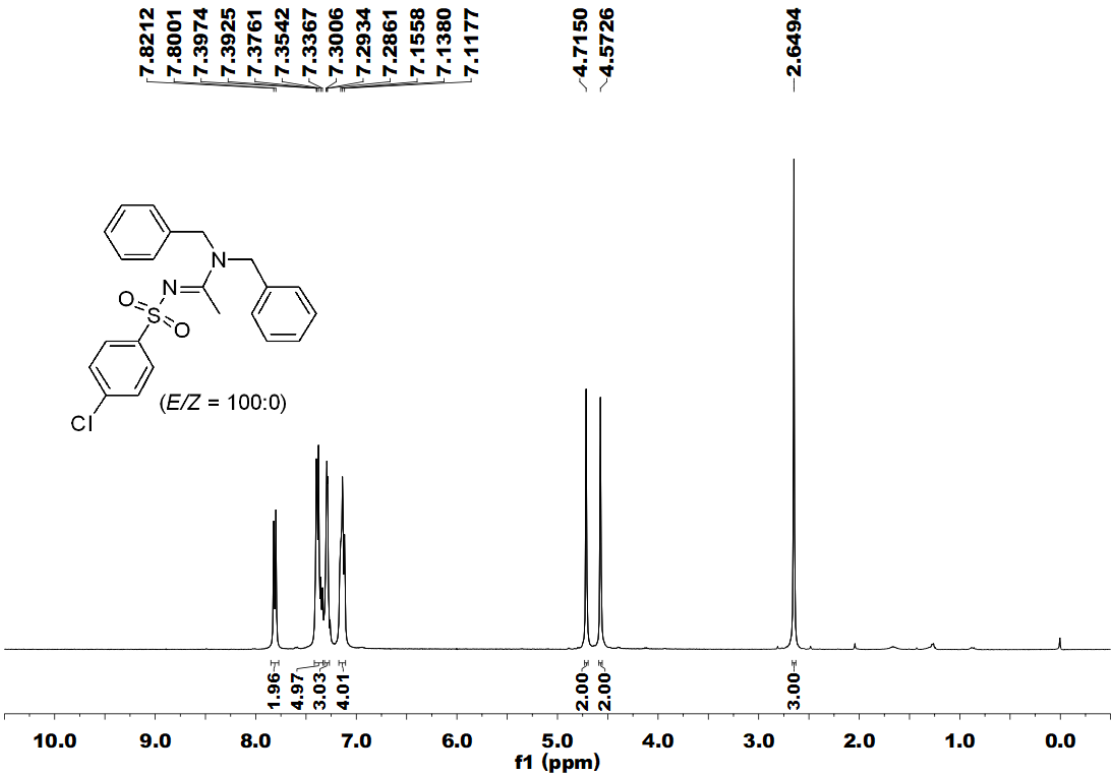


Fig. S25 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N*'-((4-chlorophenyl) sulfonyl)acetimidamide (3m)

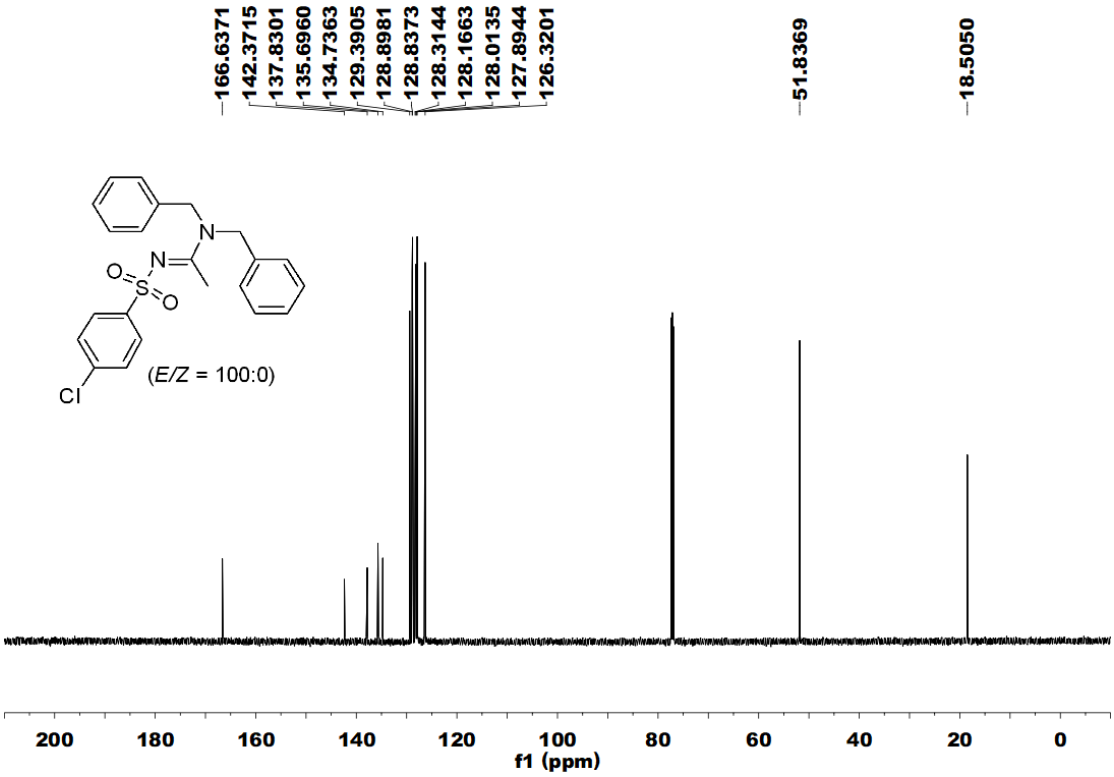


Fig. S26 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N*'-((4-chlorophenyl) sulfonyl)acetimidamide (3m)

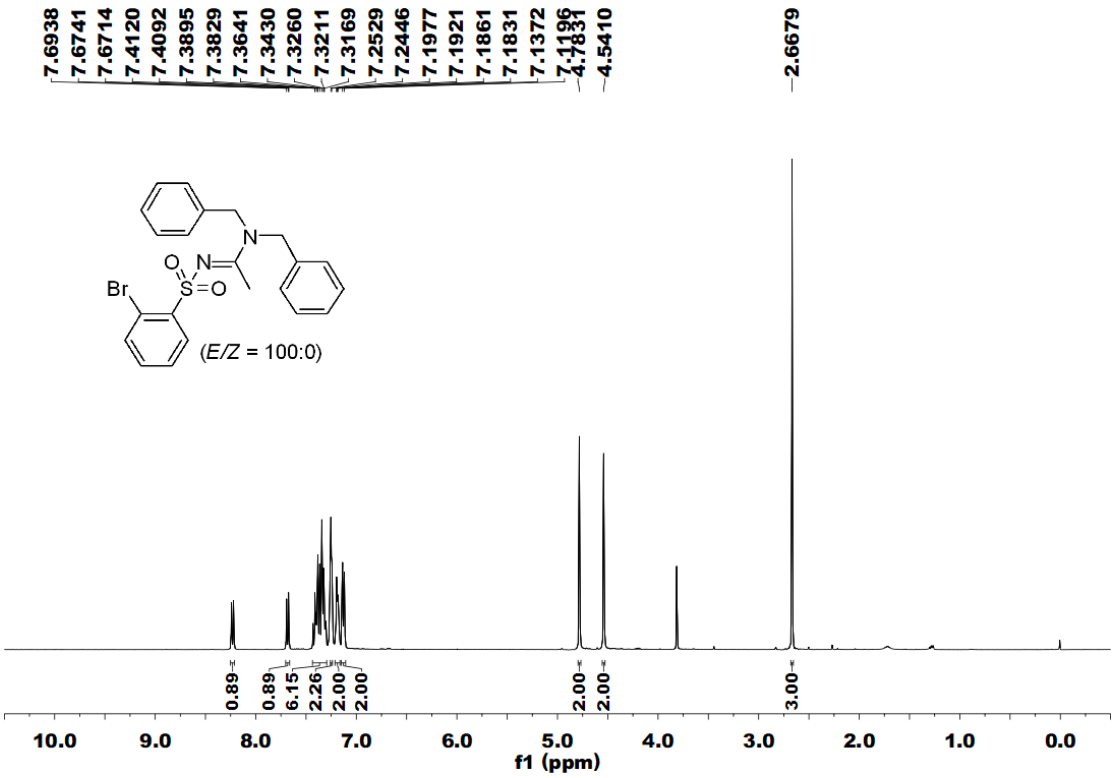


Fig. S27 ^{1}H NMR (600 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N*'-((2-bromophenyl) sulfonyl)acetimidamide (3n)

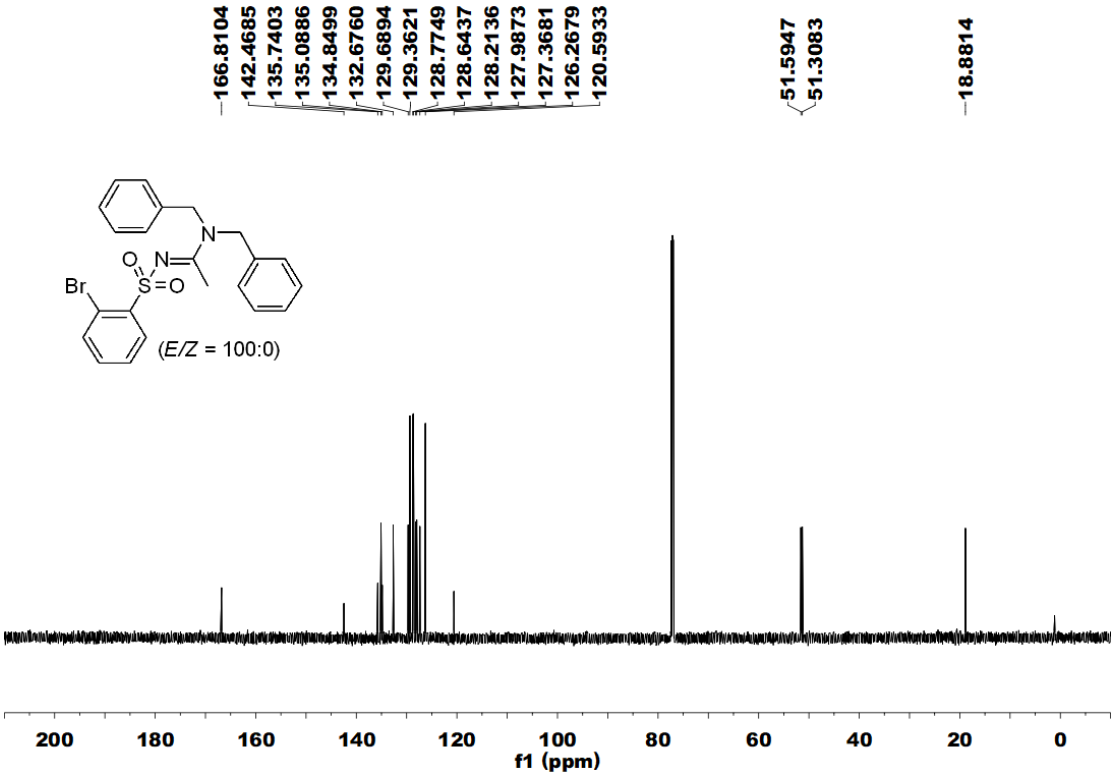


Fig. S28 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N*'-((2-bromophenyl) sulfonyl)acetimidamide (3n)

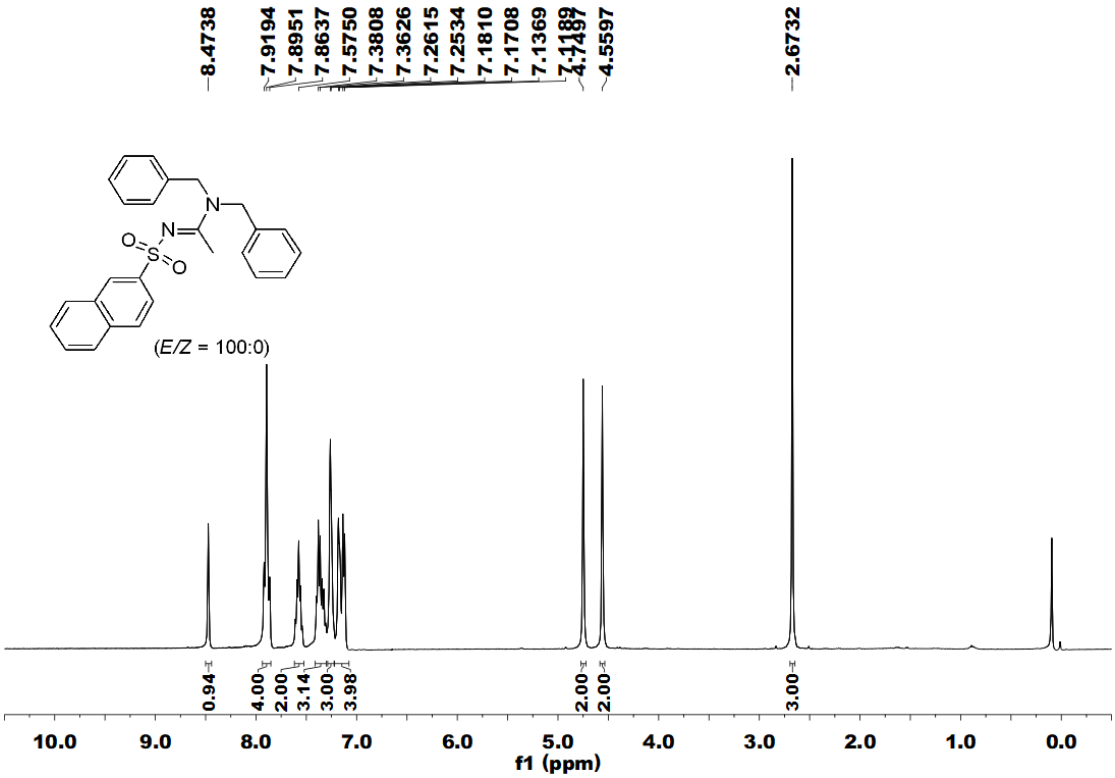


Fig. S29 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N*'-(naphthalen-2-ylsulfonyl)acetimidamide (3o)

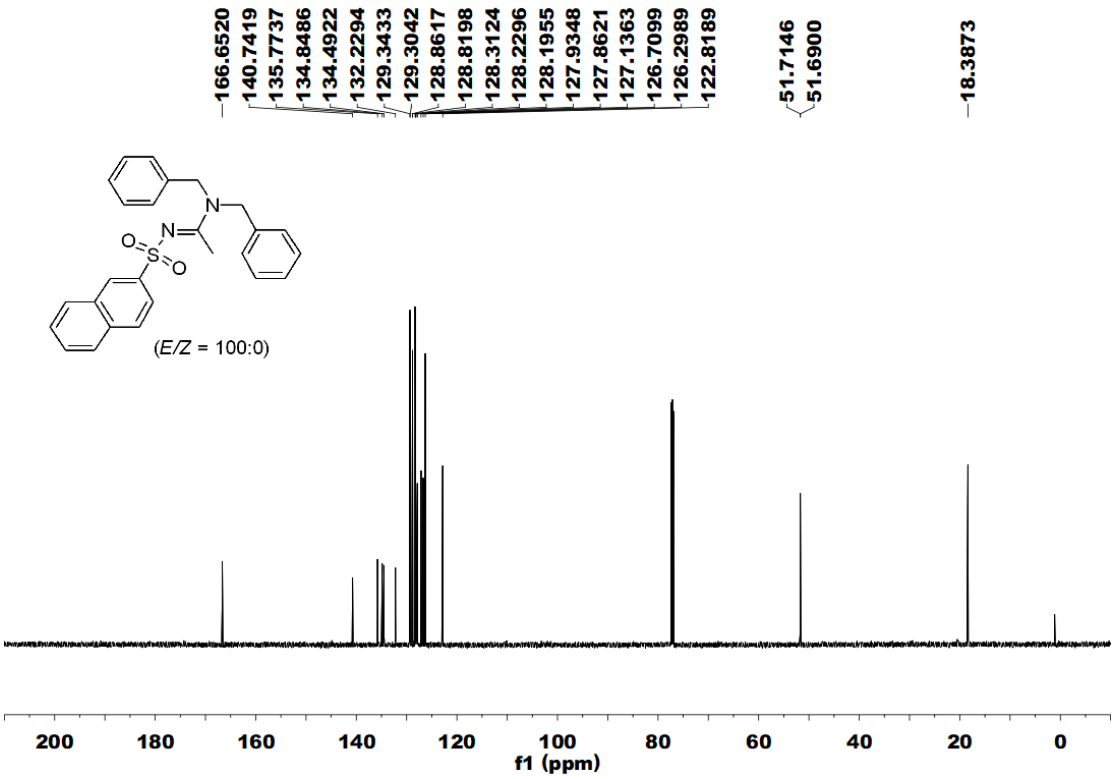


Fig. S30 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N*'-(naphthalen-2-ylsulfonyl)acetimidamide (3o)

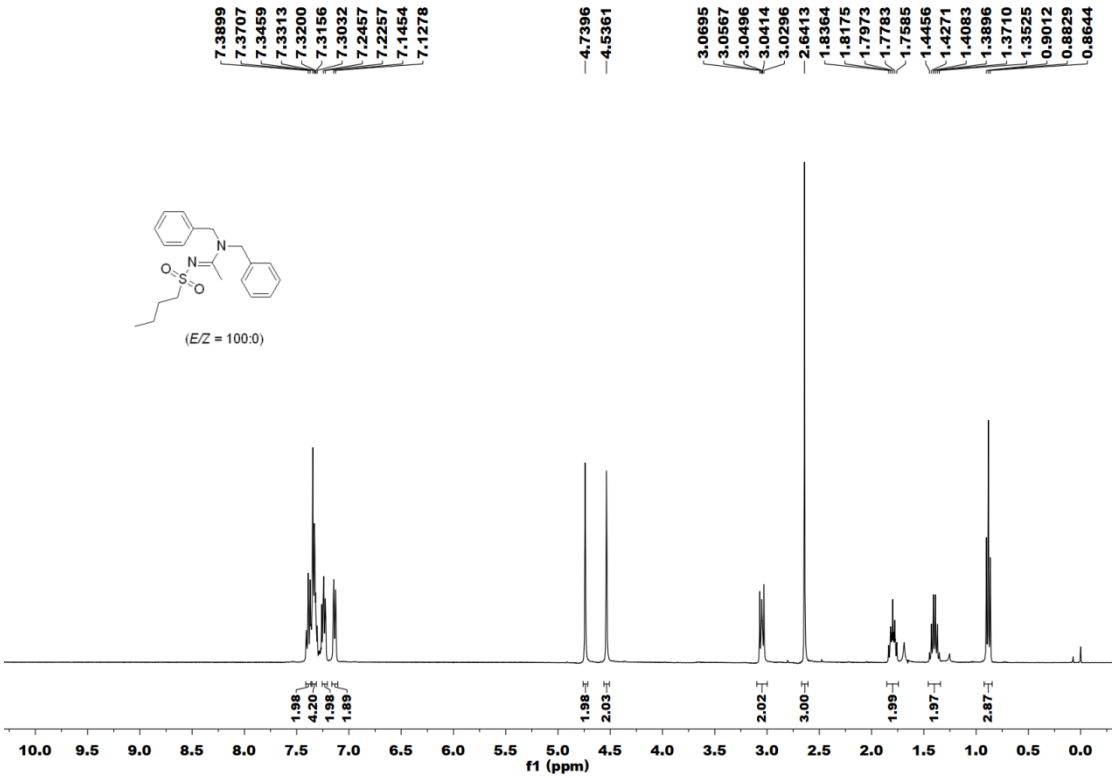


Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N′*-(butylsulfonyl)acetimidamide (3p)

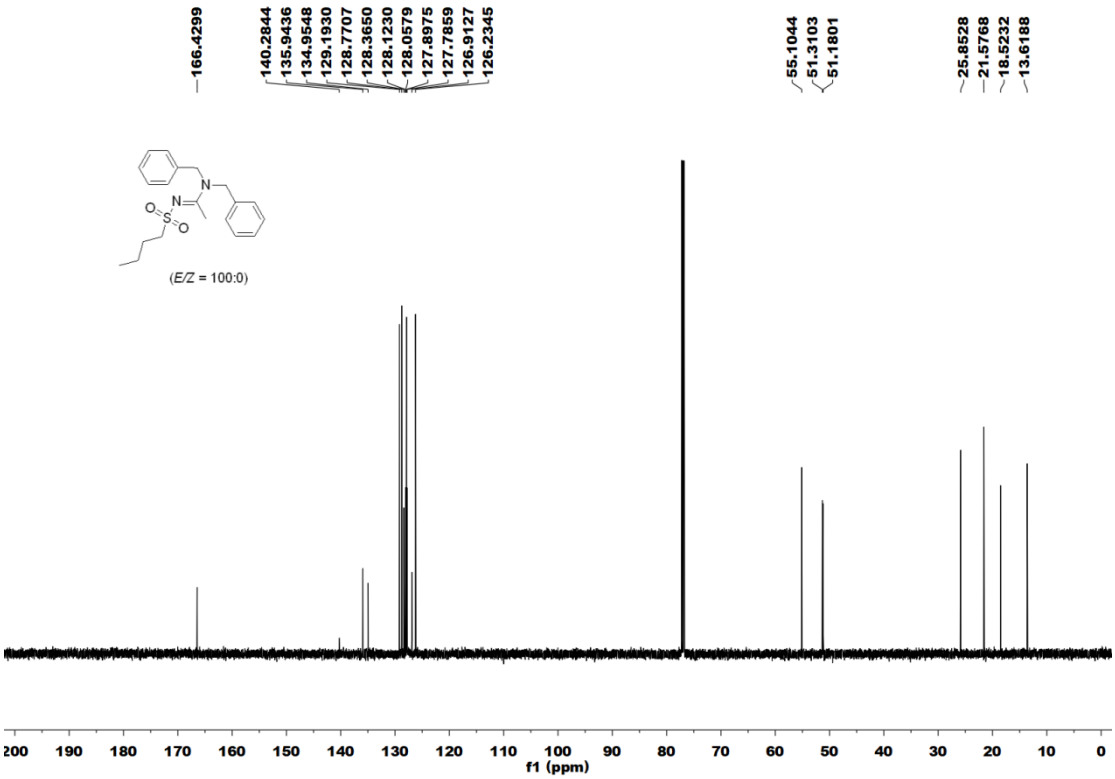


Fig. S32 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*,*N*-dibenzyl-*N′*-(butylsulfonyl)acetimidamide (3p)

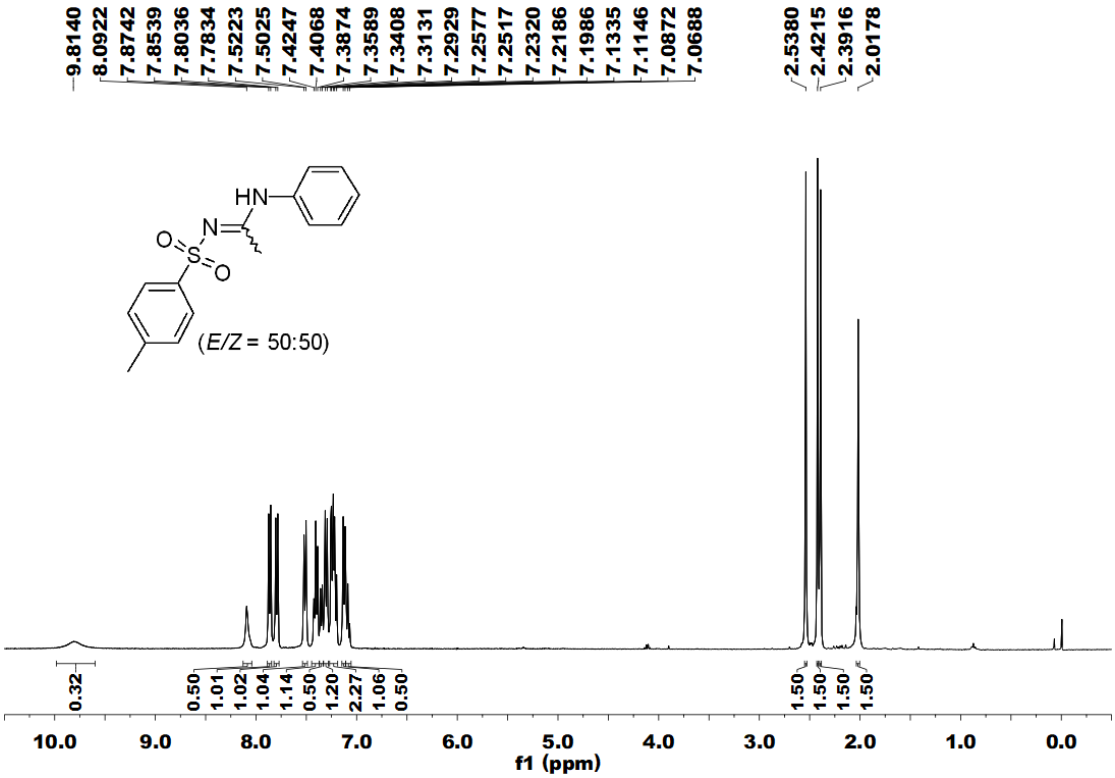


Fig. S33 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-phenyl-*N*'-tosylacetimidamide (4a)

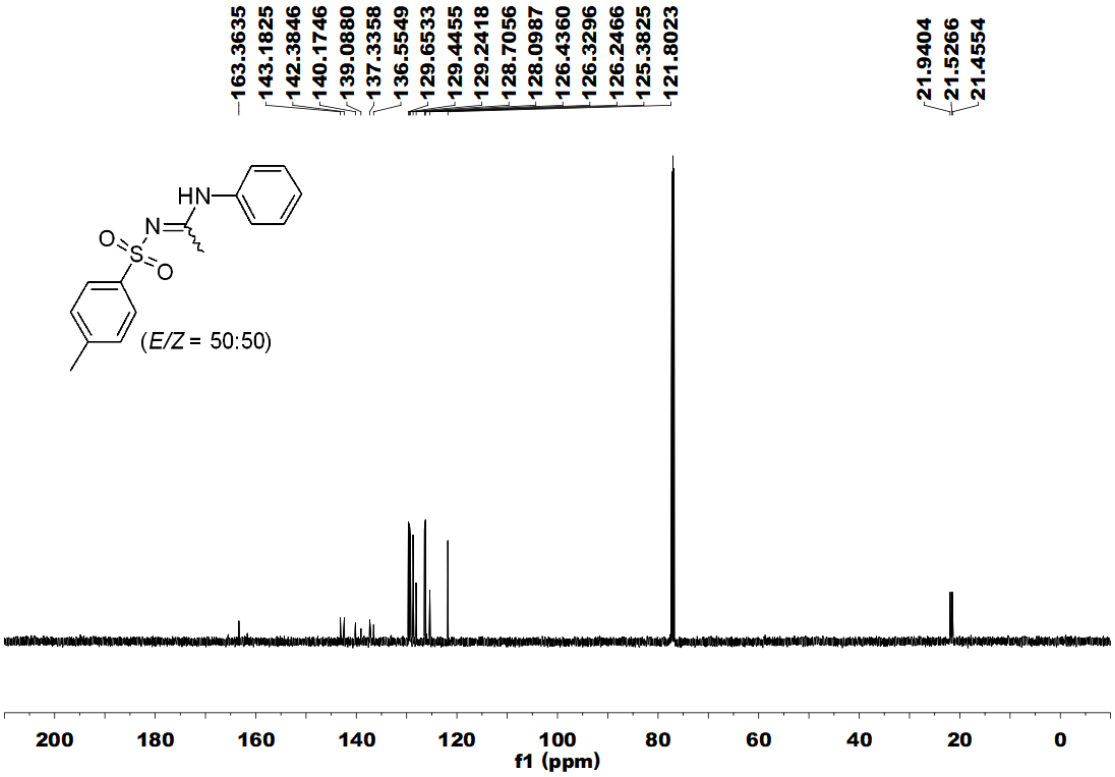


Fig. S34 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-phenyl-*N*'-tosylacetimidamide (4a)

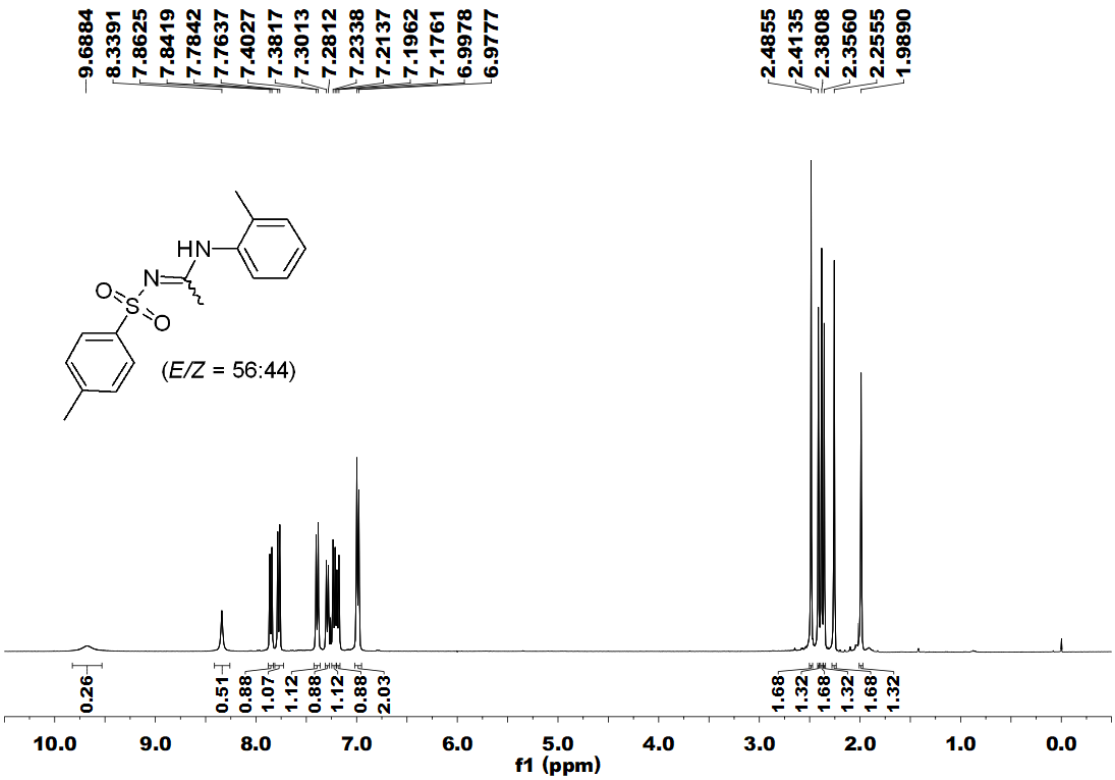


Fig. S35 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(*o*-tolyl)-*N*'-tosylacetimidamide (4b)

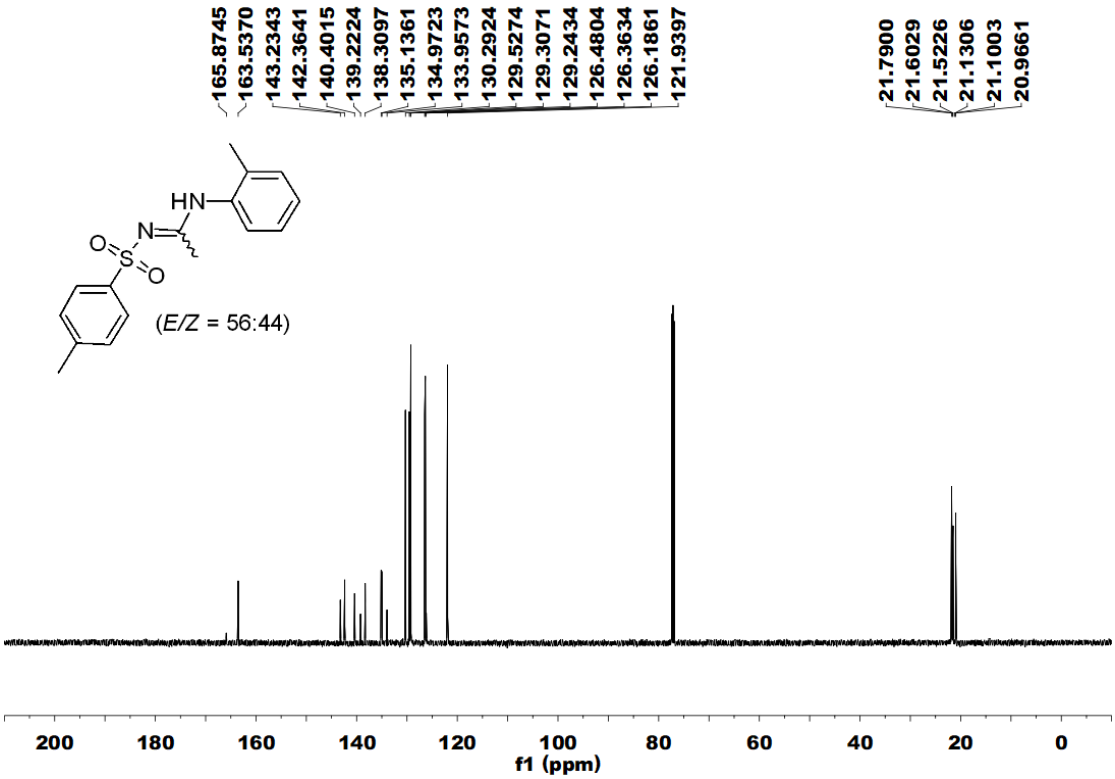


Fig. S36 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(*o*-tolyl)-*N*'-tosylacetimidamide (4b)

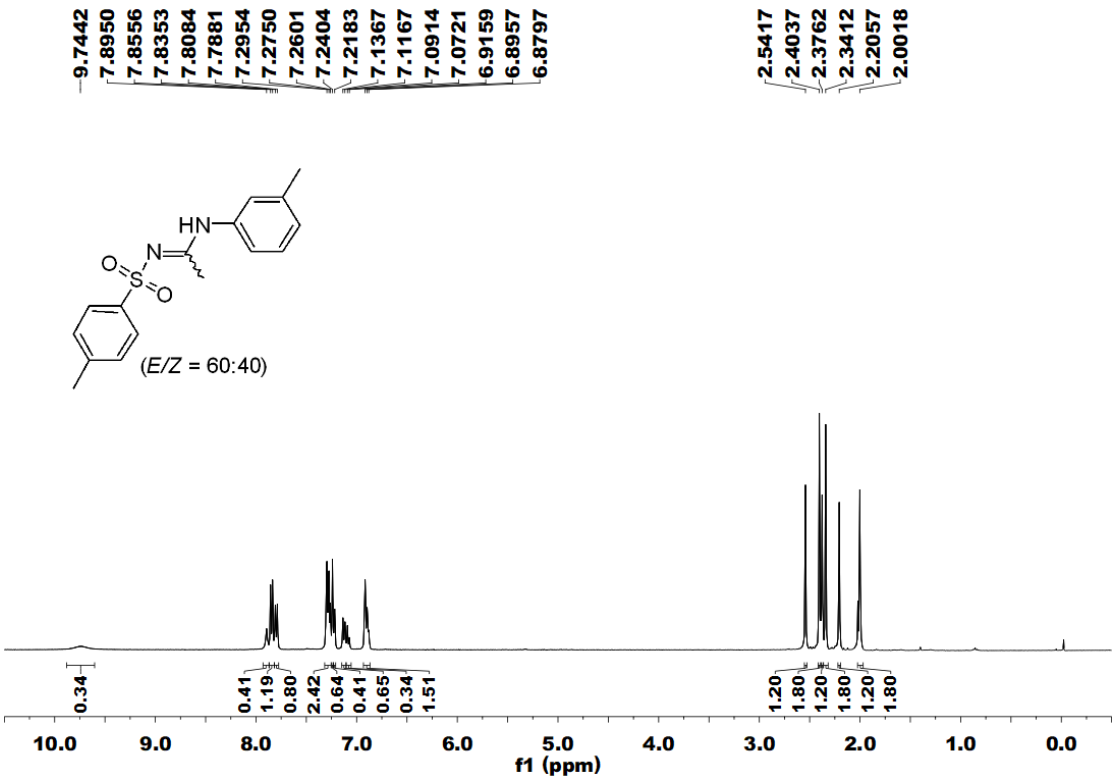


Fig. S37 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(*m*-tolyl)-*N*'-tosylacetimidamide (4c)

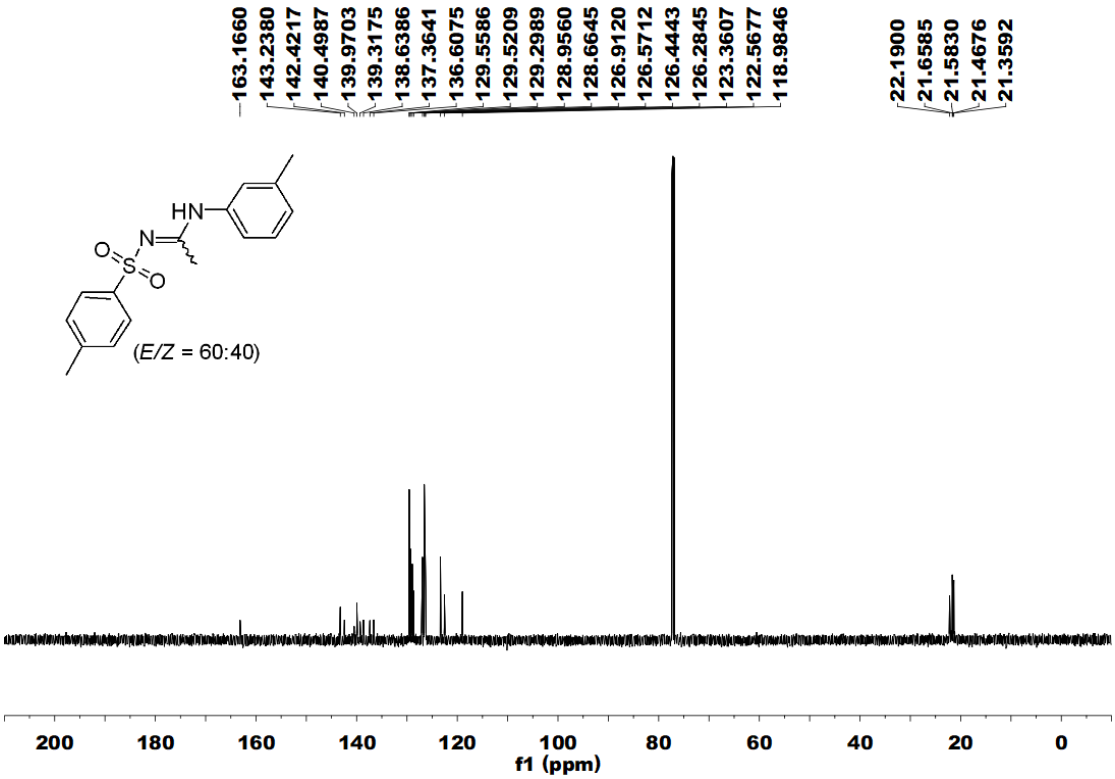


Fig. S38 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(*m*-tolyl)-*N*'-tosylacetimidamide (4c)

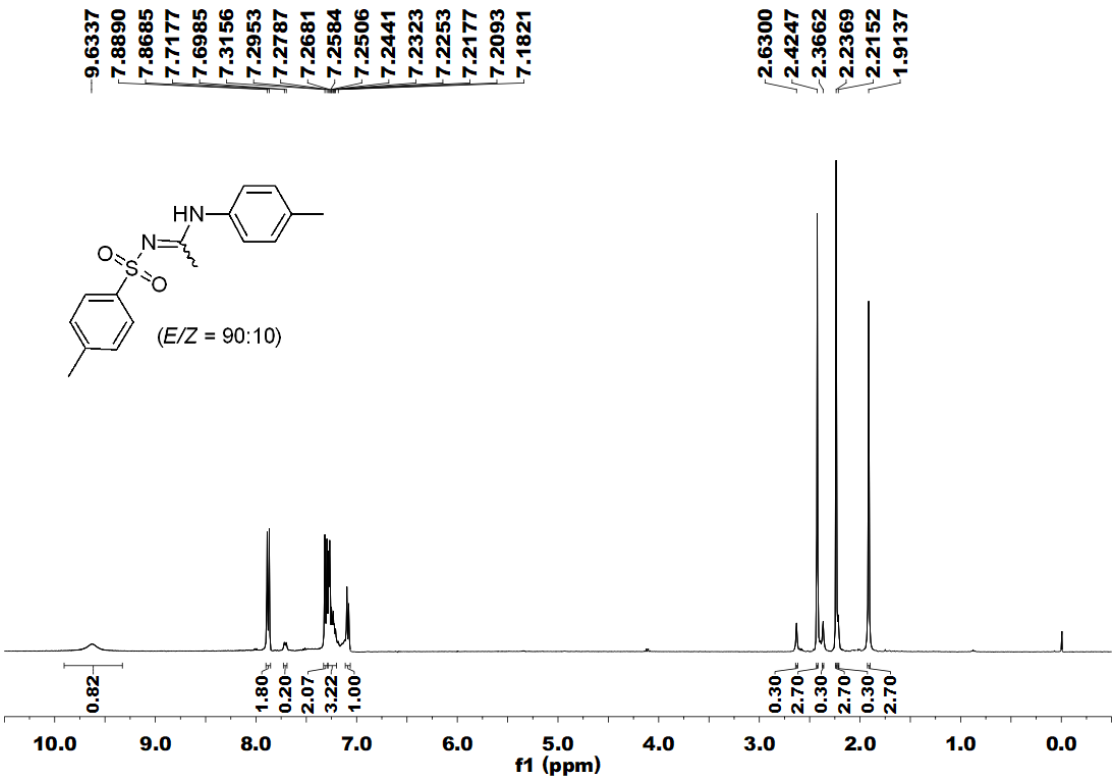


Fig. S39 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(*p*-tolyl)-*N*'-tosylacetimidamide (4d)

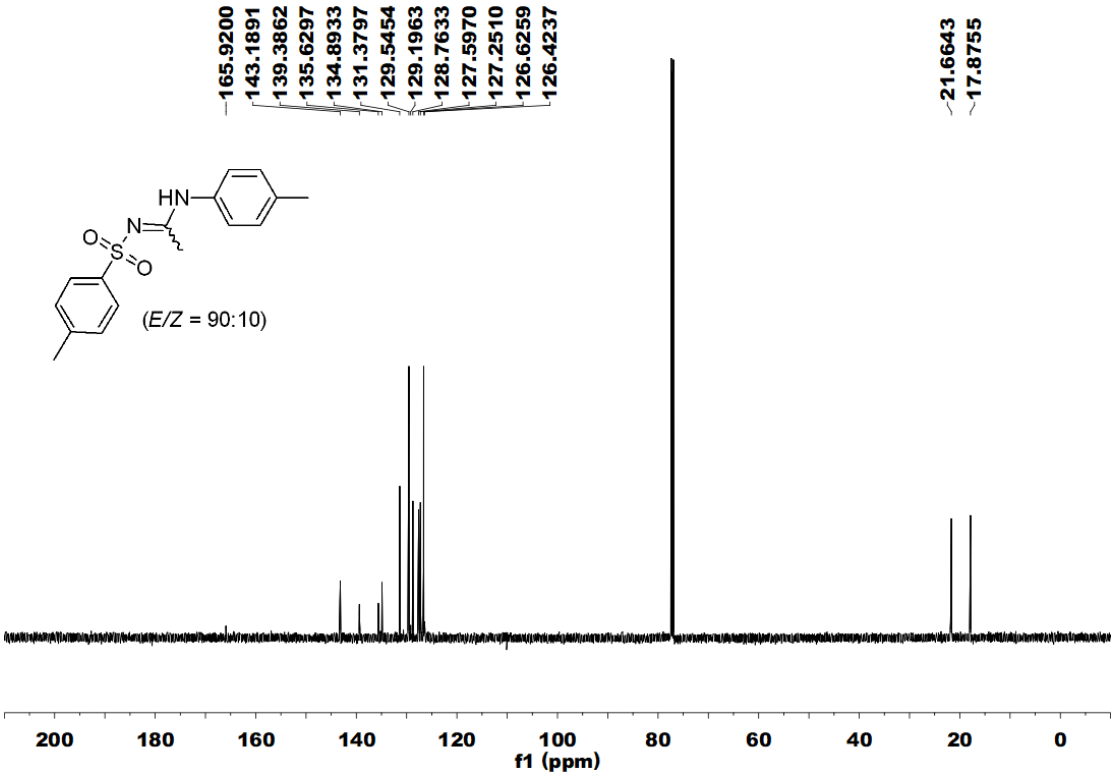


Fig. S40 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(*p*-tolyl)-*N*'-tosylacetimidamide (4d)

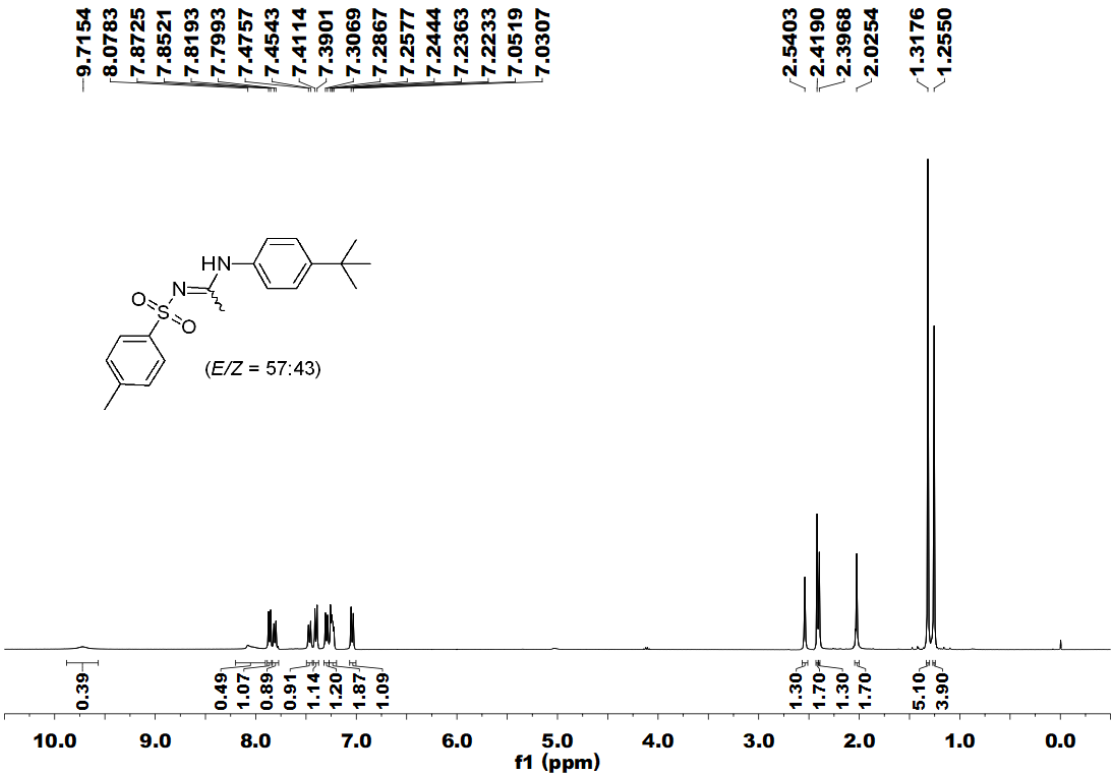


Fig. S41 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-(*tert*-butyl)phenyl)-*N*'-tosylacetimidamide (4e)

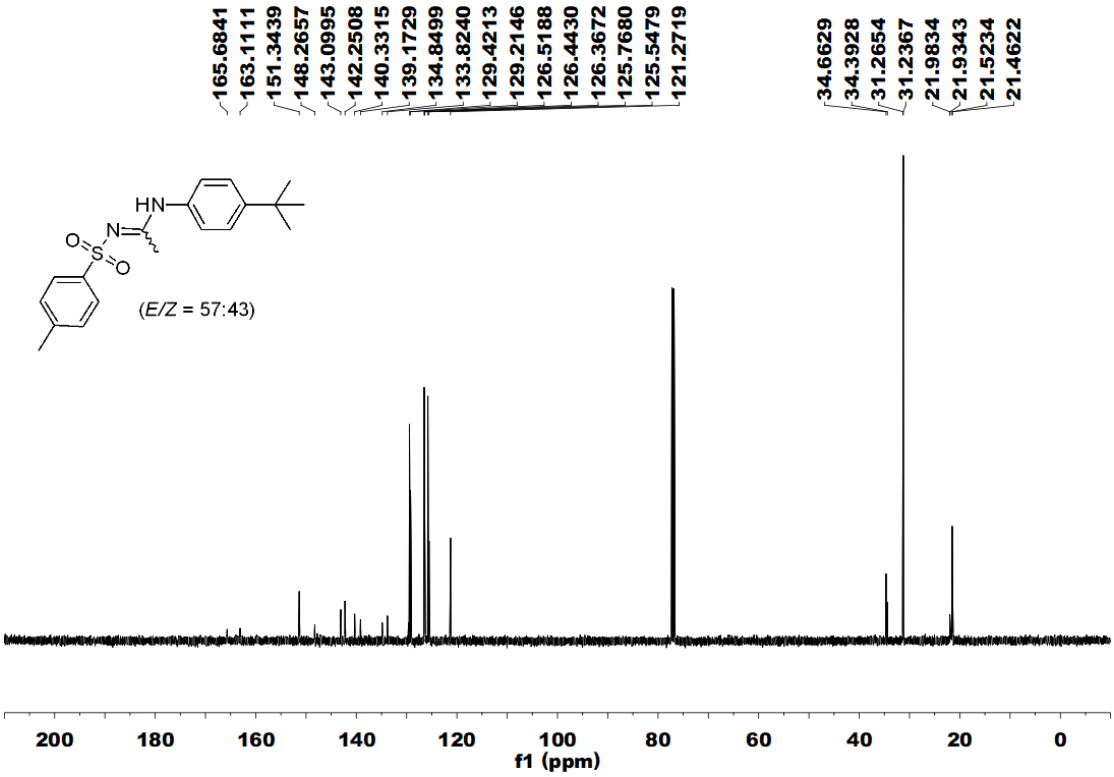


Fig. S42 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-(*tert*-butyl)phenyl)-*N*'-tosylacetimidamide (4e)

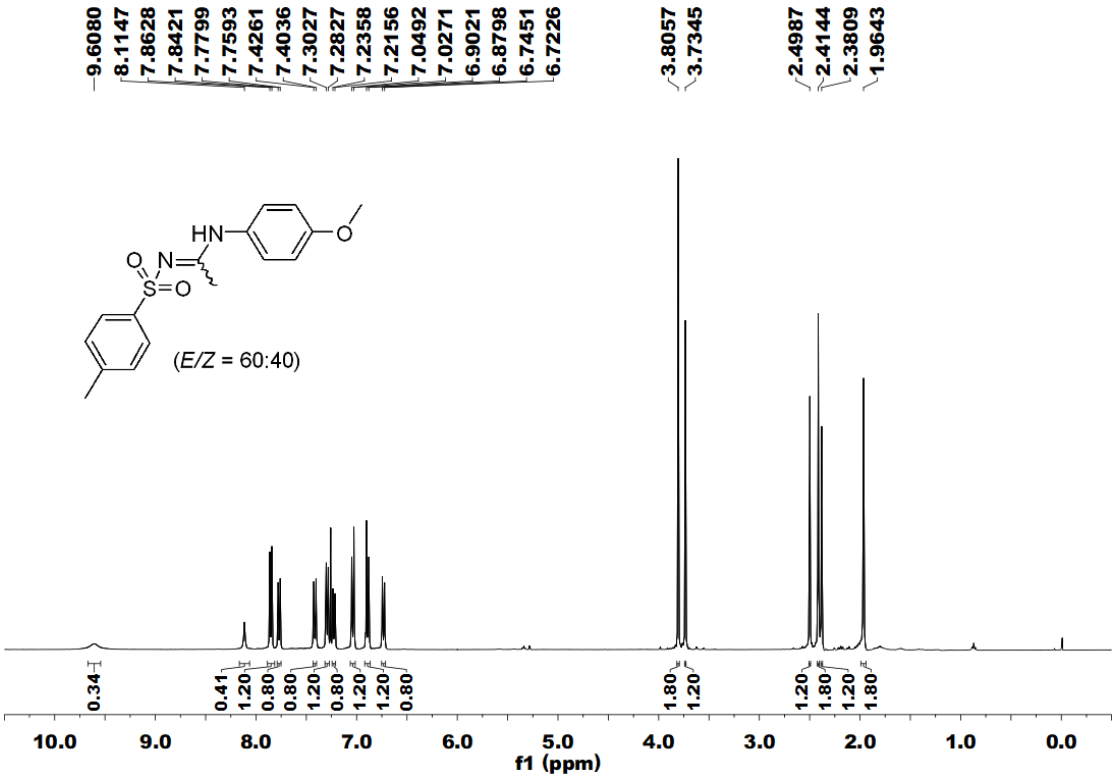


Fig. S43 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-methoxyphenyl)-*N*'-tosylacetimidamide (4f)

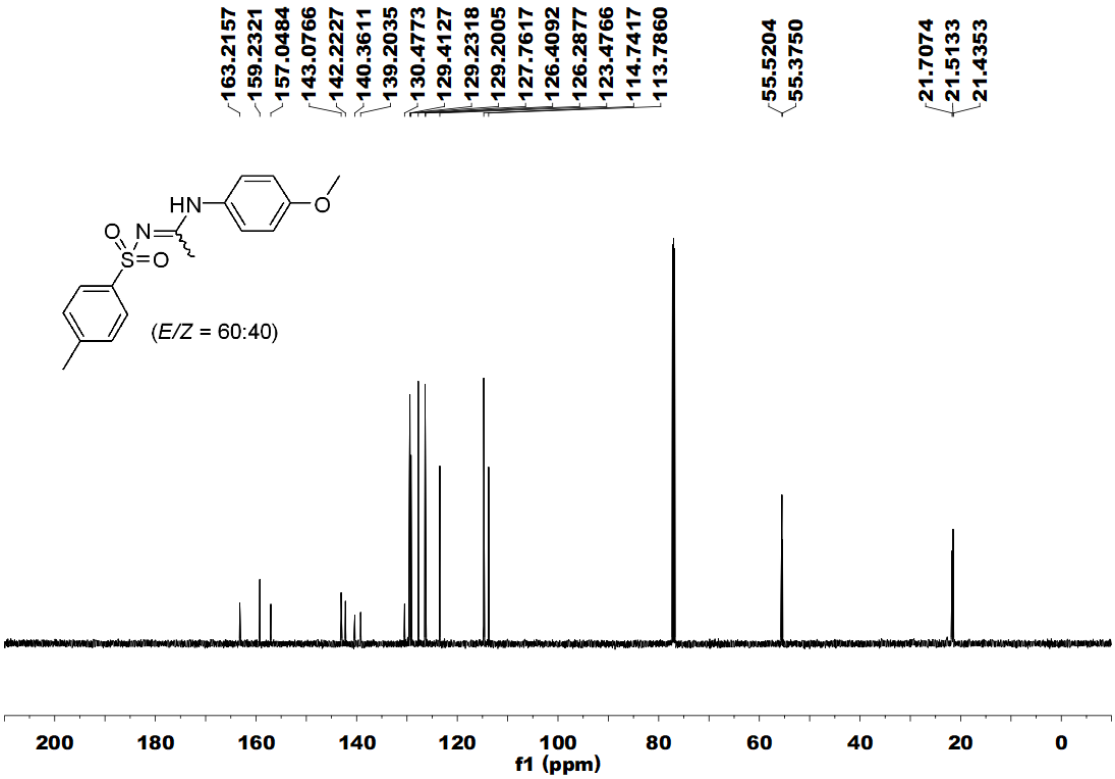


Fig. S44 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-methoxyphenyl)-*N*'-tosylacetimidamide (4f)

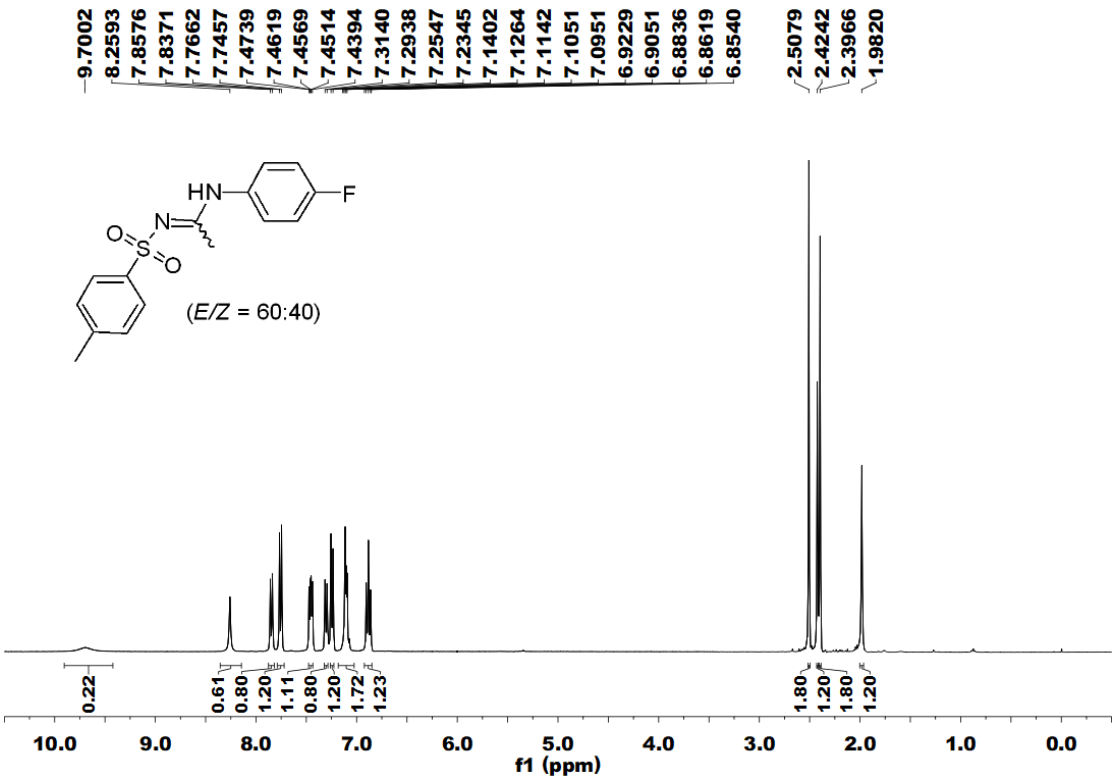


Fig. S45 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-fluorophenyl)-*N*'-tosylacetimidamide (4g)

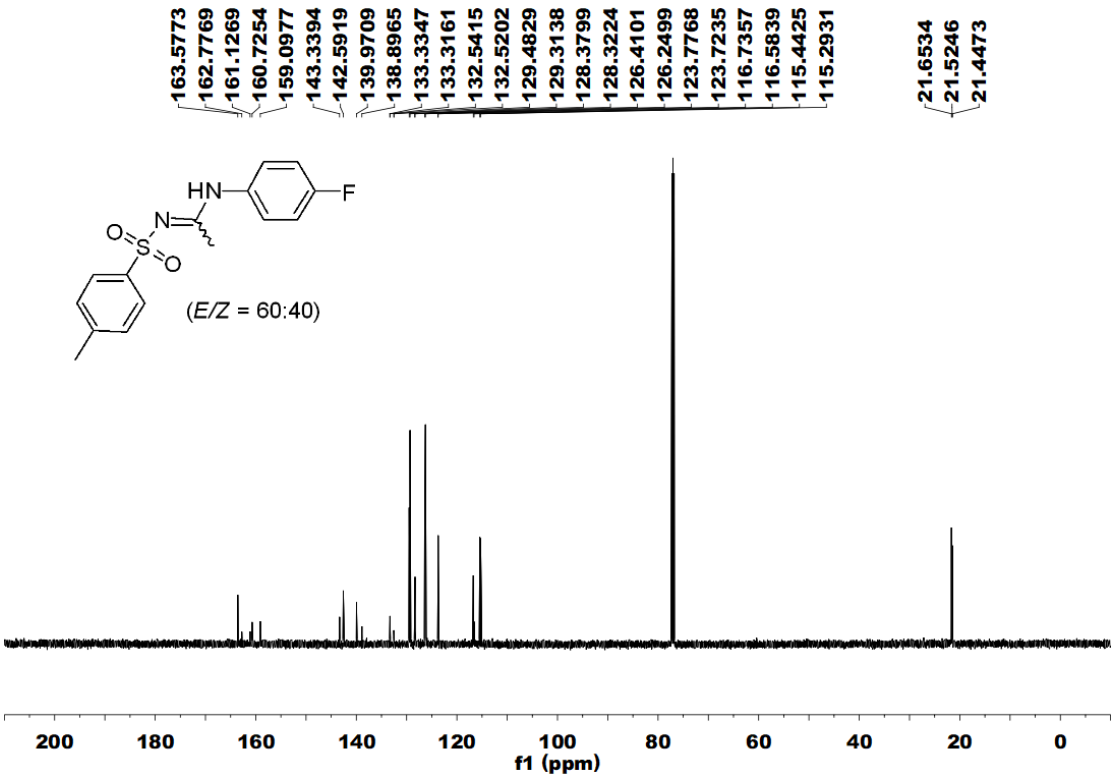


Fig. S46 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-fluorophenyl)-*N*'-tosylacetimidamide (4g)

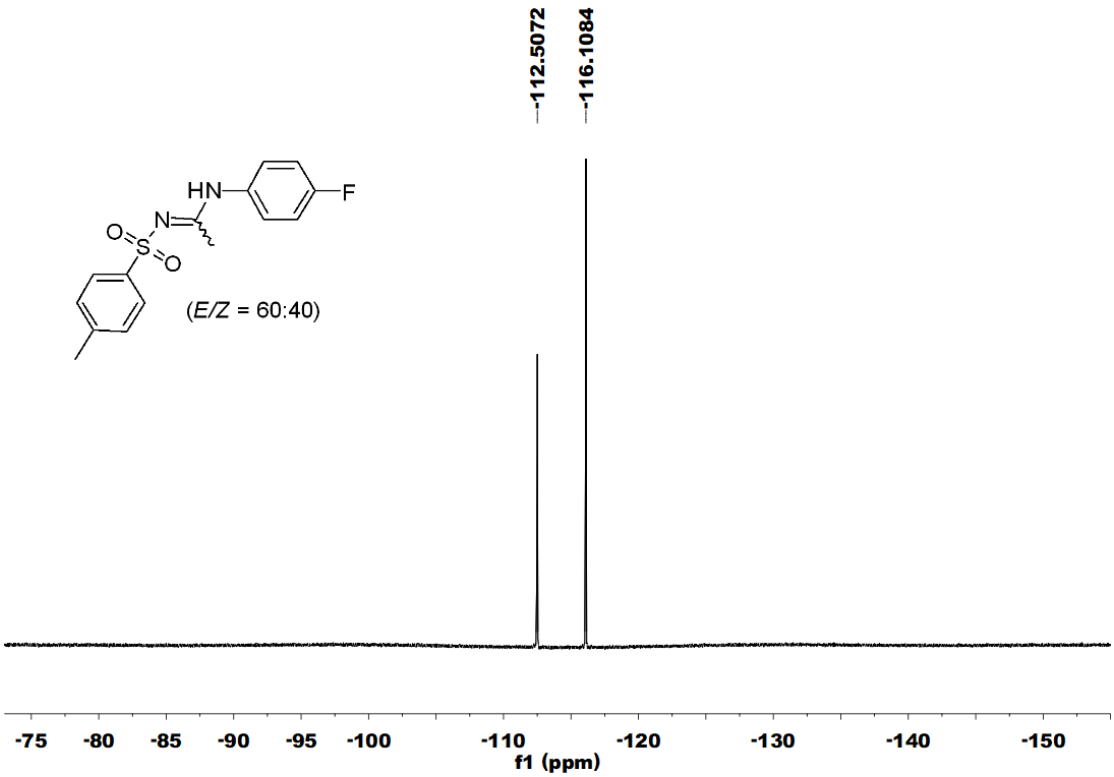


Fig. S47 ^{19}F NMR (376 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-fluorophenyl)-*N*'-tosylacetimidamide (4g)

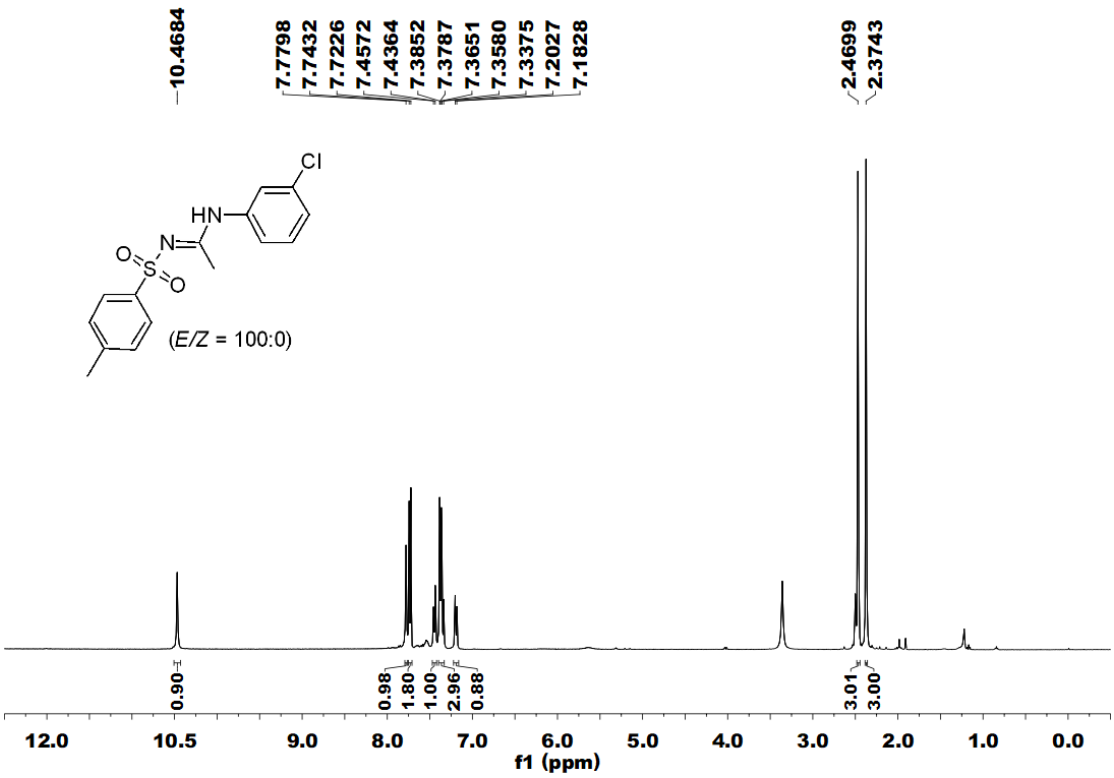


Fig. S48 ^{1}H NMR (400 MHz, DMSO-d_6) of (*E*)-*N*-(3-chlorophenyl)-*N*'-tosylacetimidamide (4h)

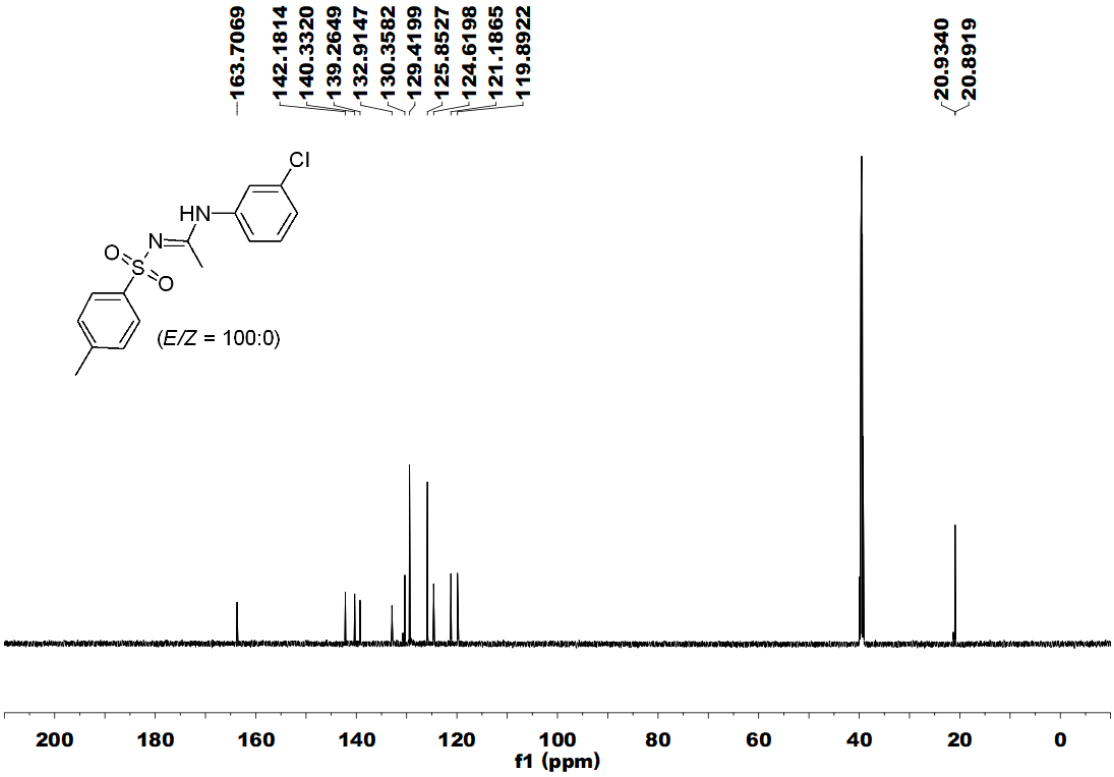


Fig. S49 ^{13}C NMR (150 MHz, DMSO-d_6) of (*E*)-*N*-(3-chlorophenyl)-*N*'-tosylacetimidamide (4h)

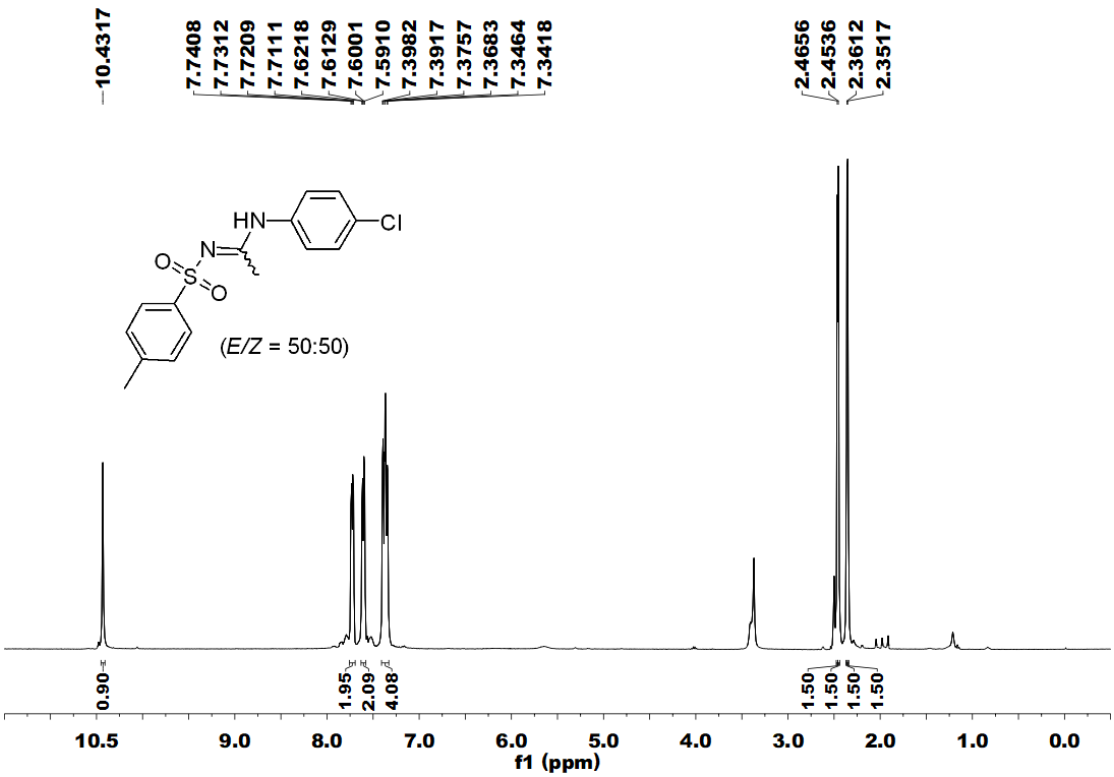


Fig. S50 ^{1}H NMR (400 MHz, DMSO-d_6) of (*E/Z*)-*N*-(4-chlorophenyl)-N'-tosylacetimidamide (4i)

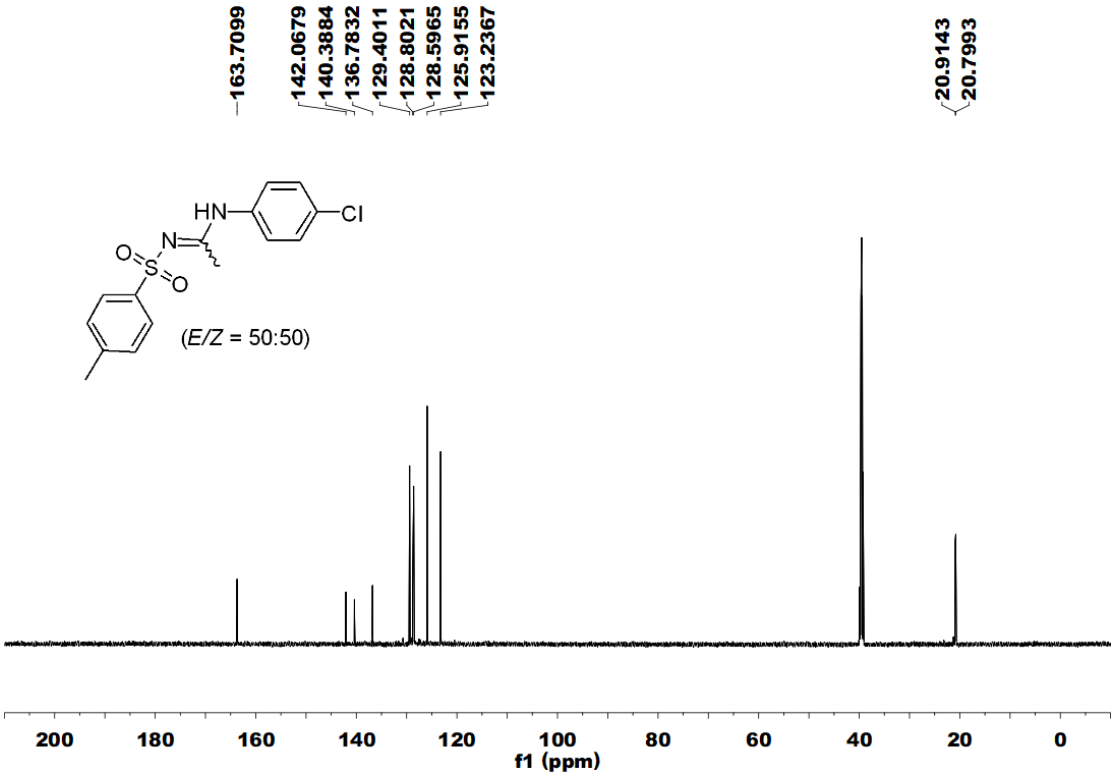


Fig. S51 ^{13}C NMR (150 MHz, DMSO-d_6) of (*E/Z*)-*N*-(4-chlorophenyl)-N'-tosylacetimidamide (4i)

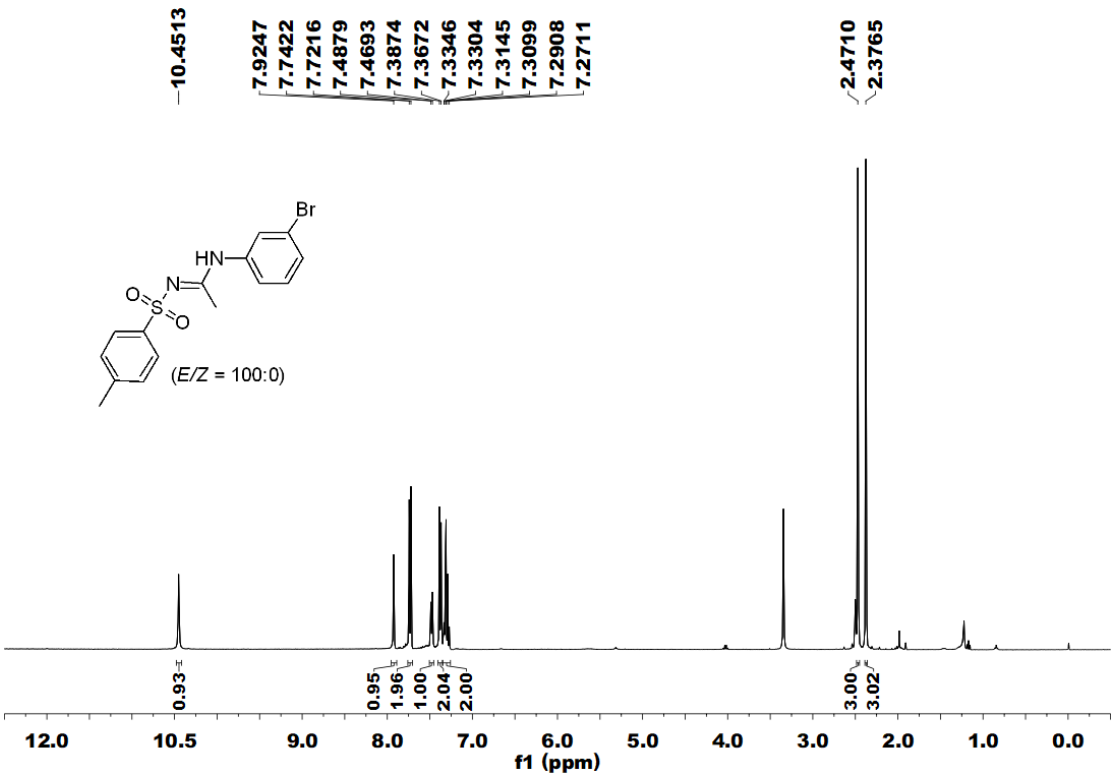


Fig. S52 ^{1}H NMR (400 MHz, DMSO-d_6) of (*E*)-*N*-(3-bromophenyl)-*N*'-tosylacetimidamide (4j)

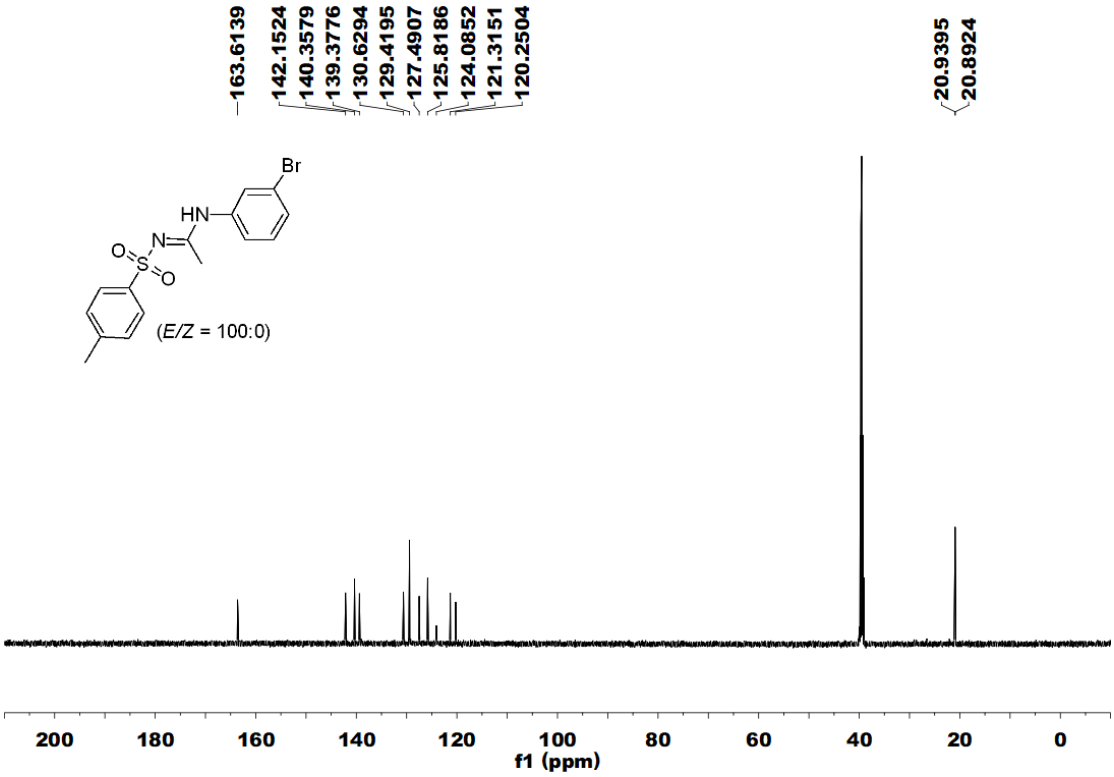


Fig. S53 ^{13}C NMR (150 MHz, DMSO-d_6) of (*E*)-*N*-(3-bromophenyl)-*N*'-tosylacetimidamide (4j)

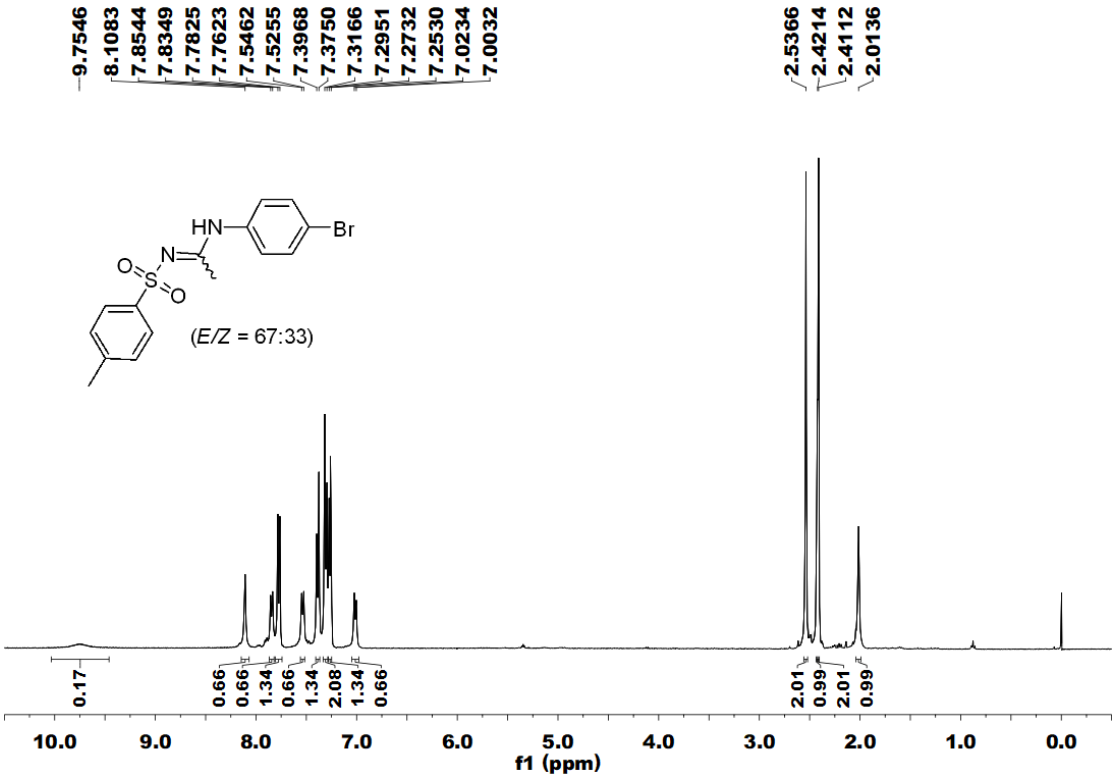


Fig. S54 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-bromophenyl)-*N*'-tosylacetimidamide (4k)

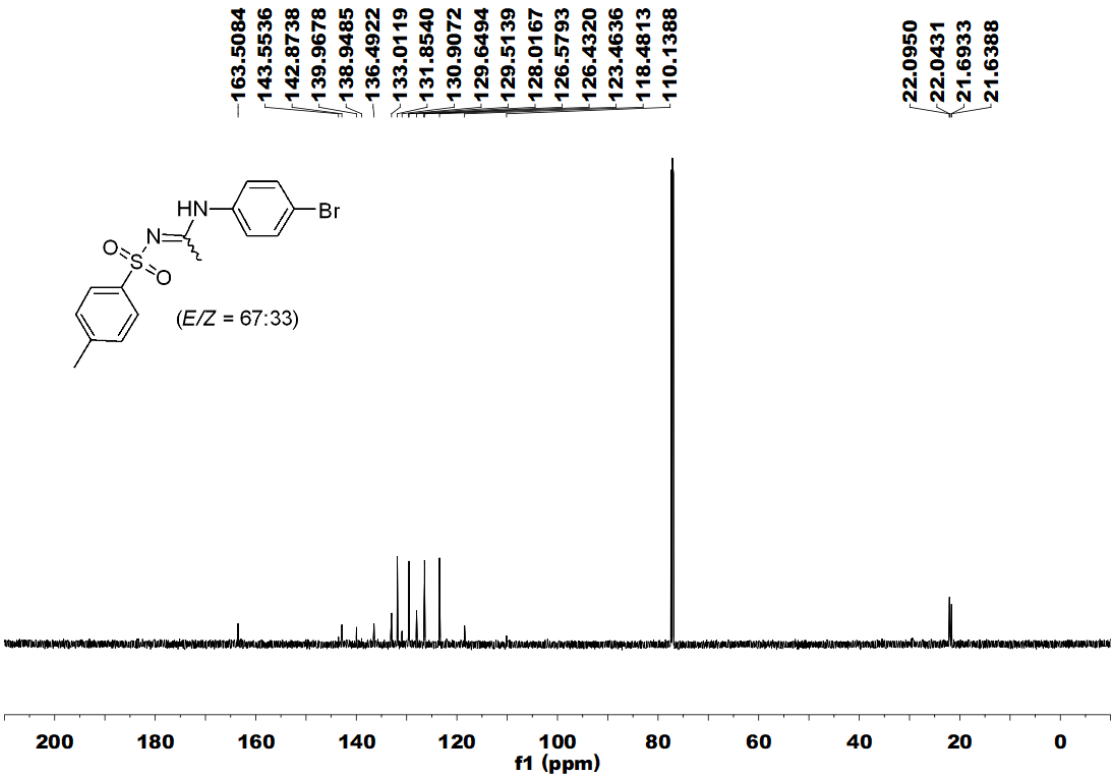


Fig. S55 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(4-bromophenyl)-*N*'-tosylacetimidamide (4k)

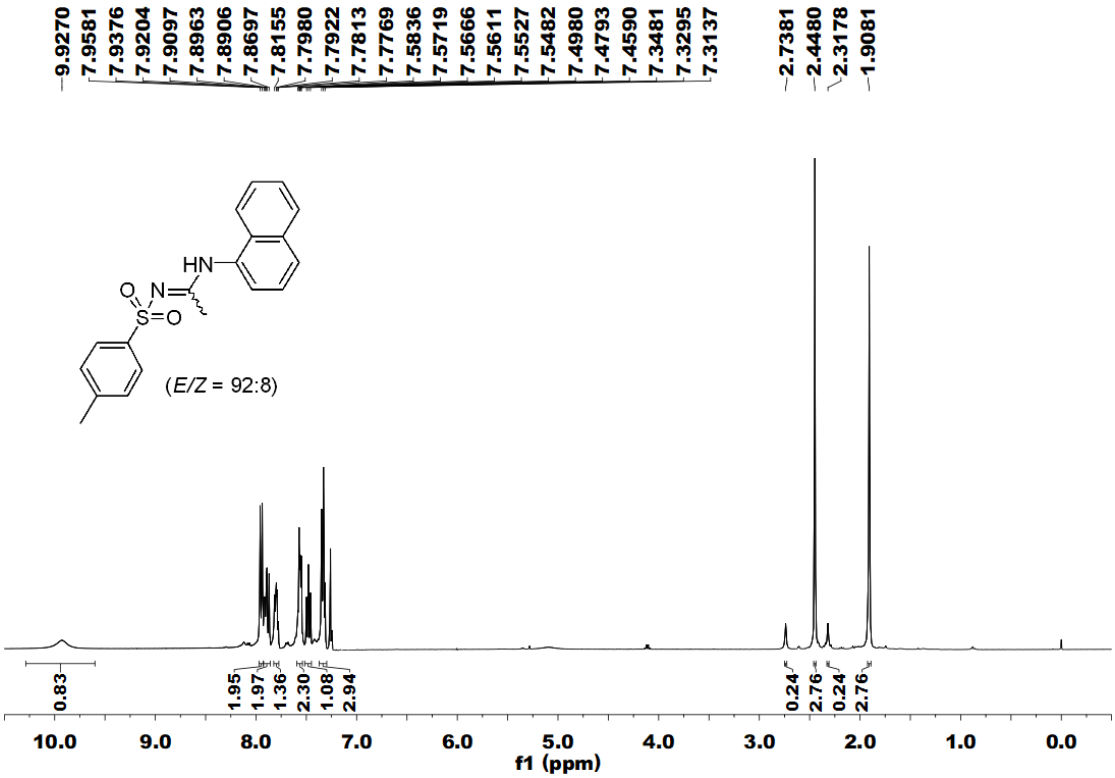


Fig. S56 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-(naphthalen-1-yl)-*N*'-tosylacetimidamide (4l)

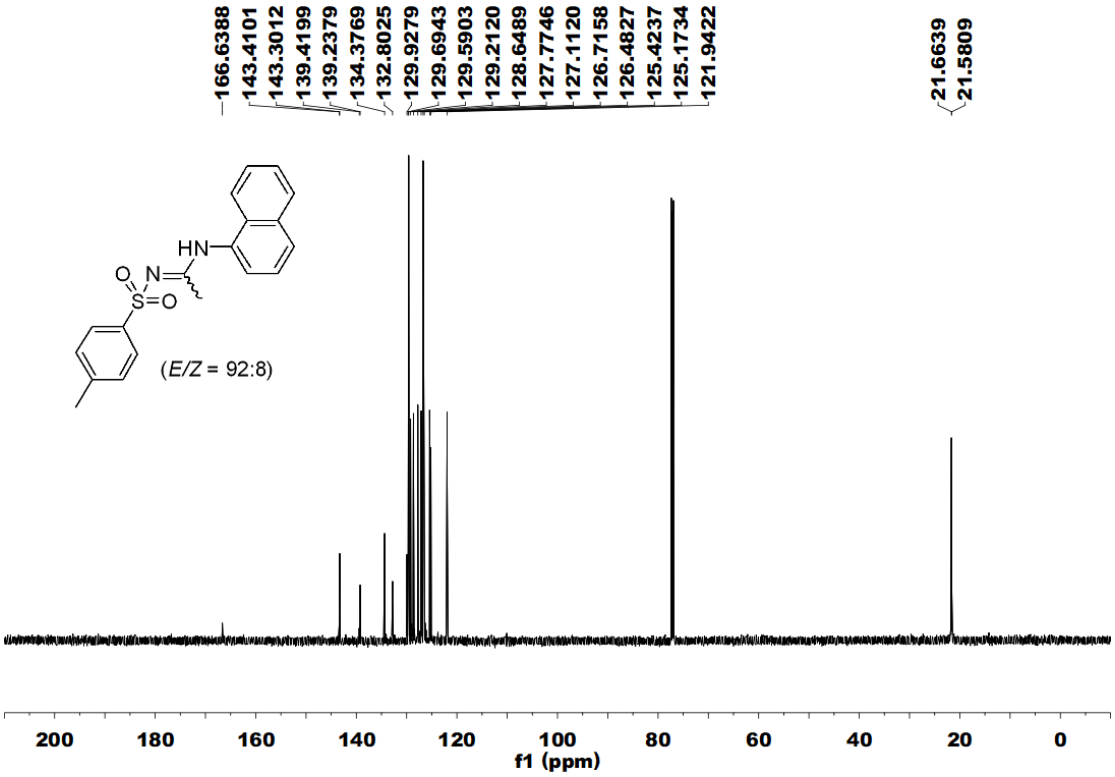


Fig. S57 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-(naphthalen-1-yl)-*N*'-tosylacetimidamide (4l)

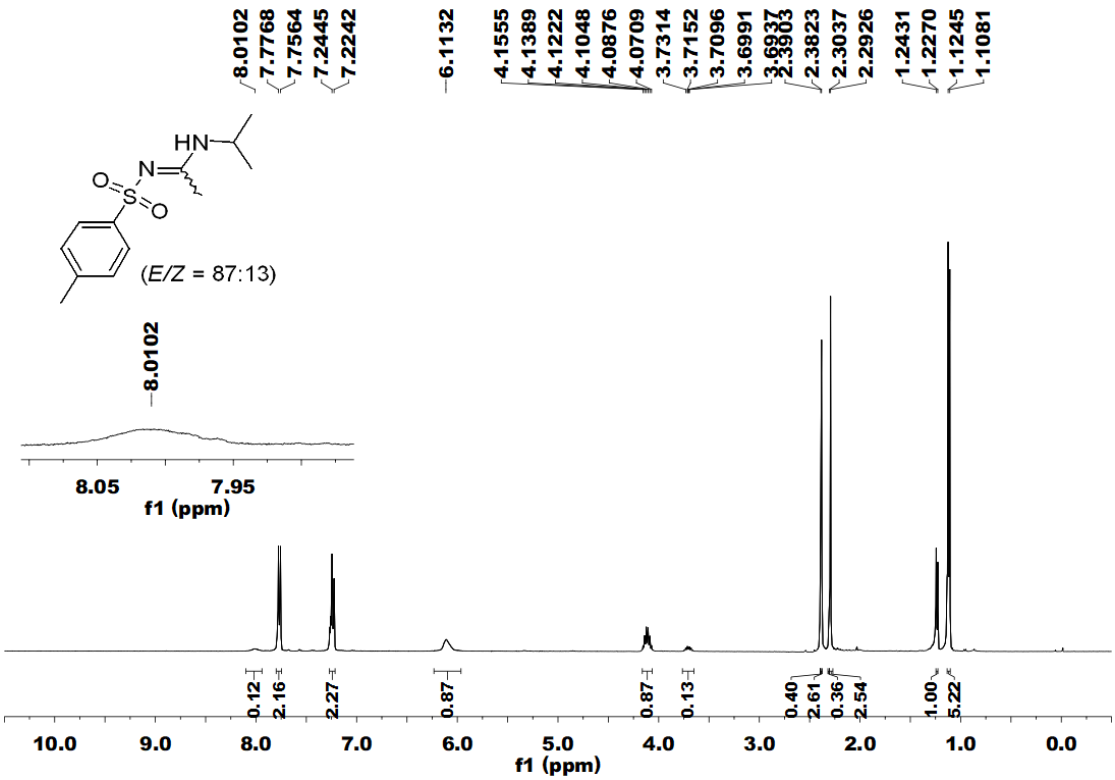


Fig. S58 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E/Z*)-*N*-isopropyl-*N*'-tosylacetimidamide (4m)

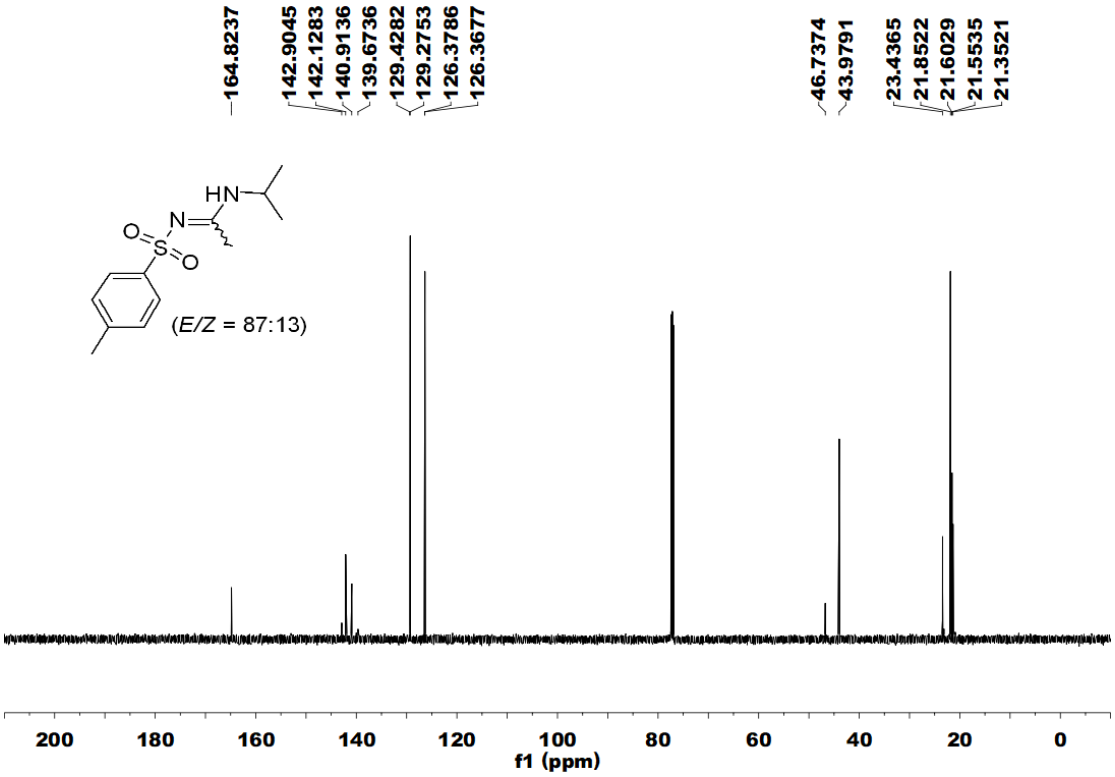


Fig. S59 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-isopropyl-*N*'-tosylacetimidamide (4m)

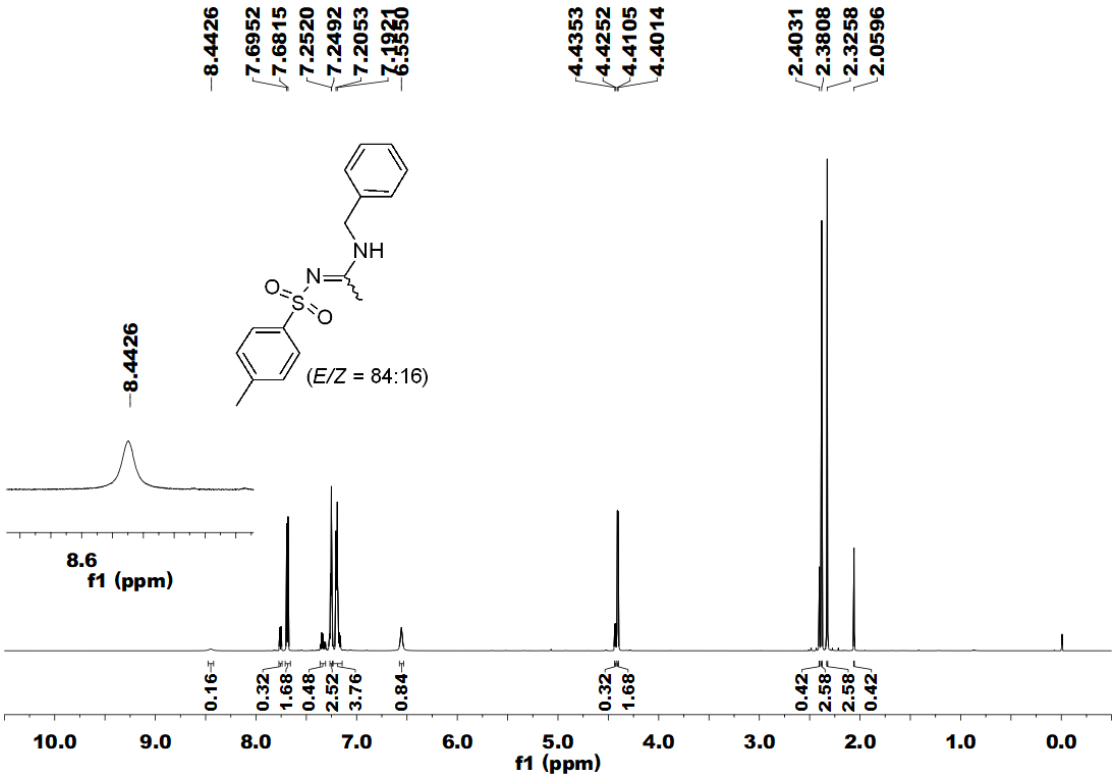


Fig. S60 ^{1}H NMR (600 MHz, $CDCl_3$) of (*E/Z*)-*N*-benzyl-*N*'-tosylacetimidamide (4n)

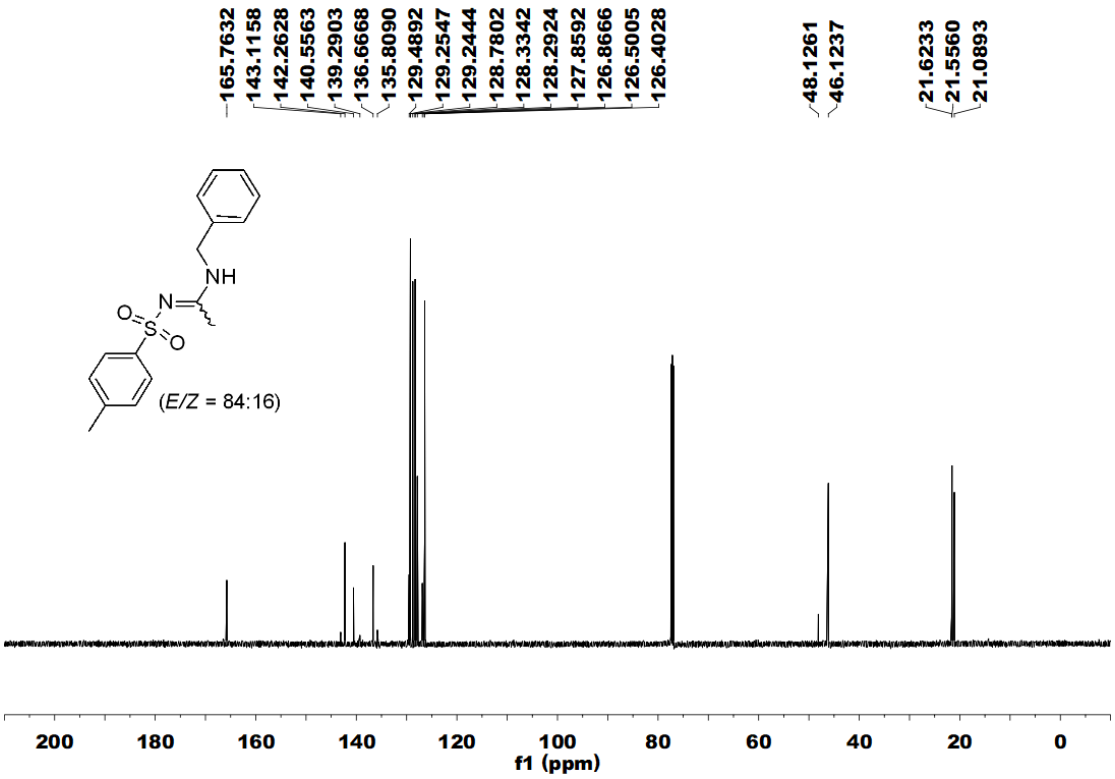


Fig. S61 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E/Z*)-*N*-benzyl-*N*'-tosylacetimidamide (4n)

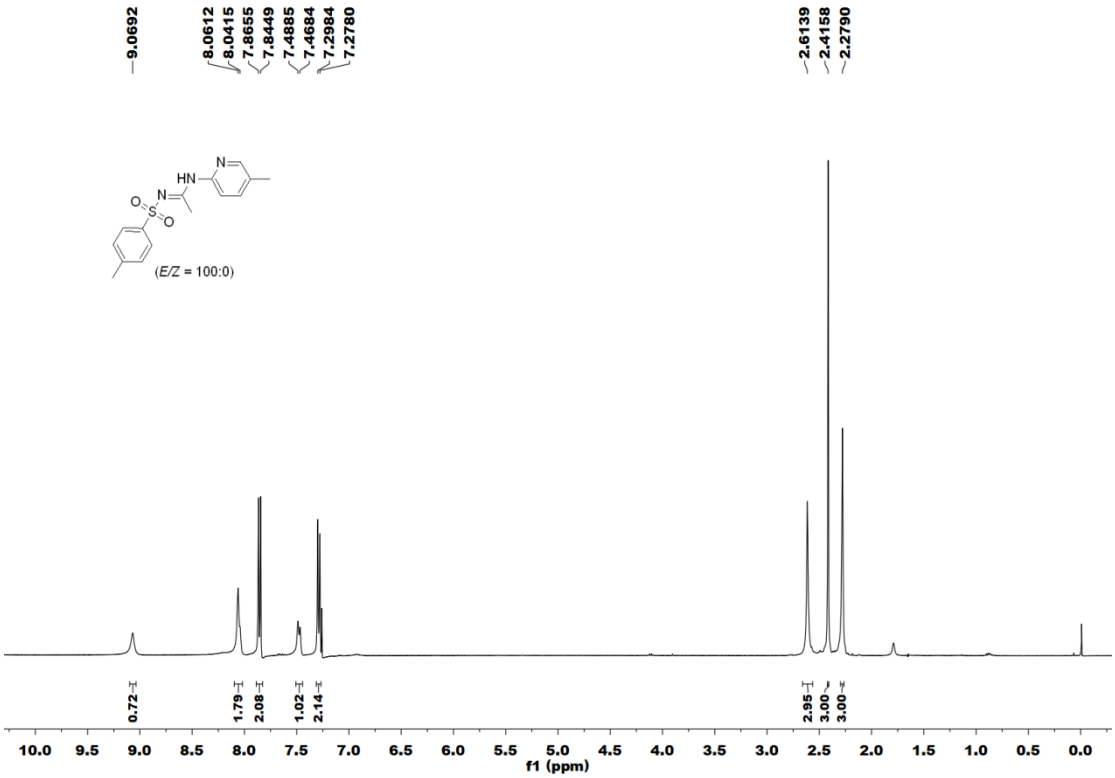


Fig. S62 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*-(5-methylpyridin-2-yl)-*N′*-tosylacetimidamide (4o)

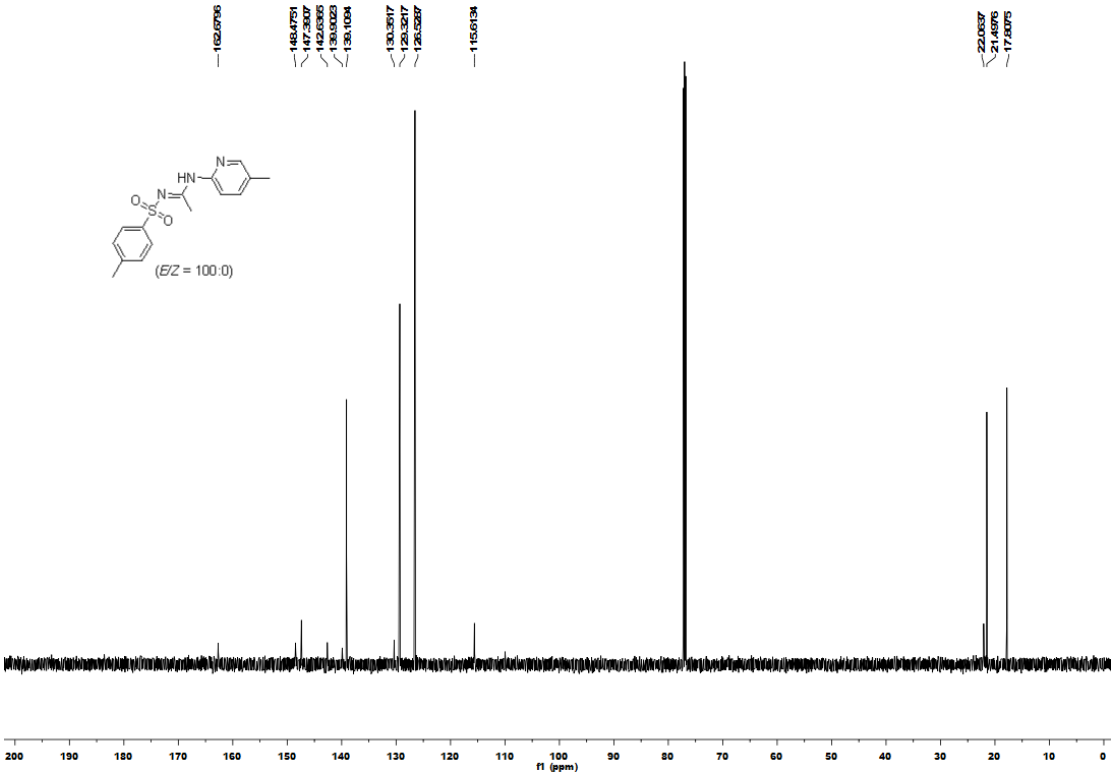


Fig. S63 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*-(5-methylpyridin-2-yl)-*N′*-tosylacetimidamide (4o)

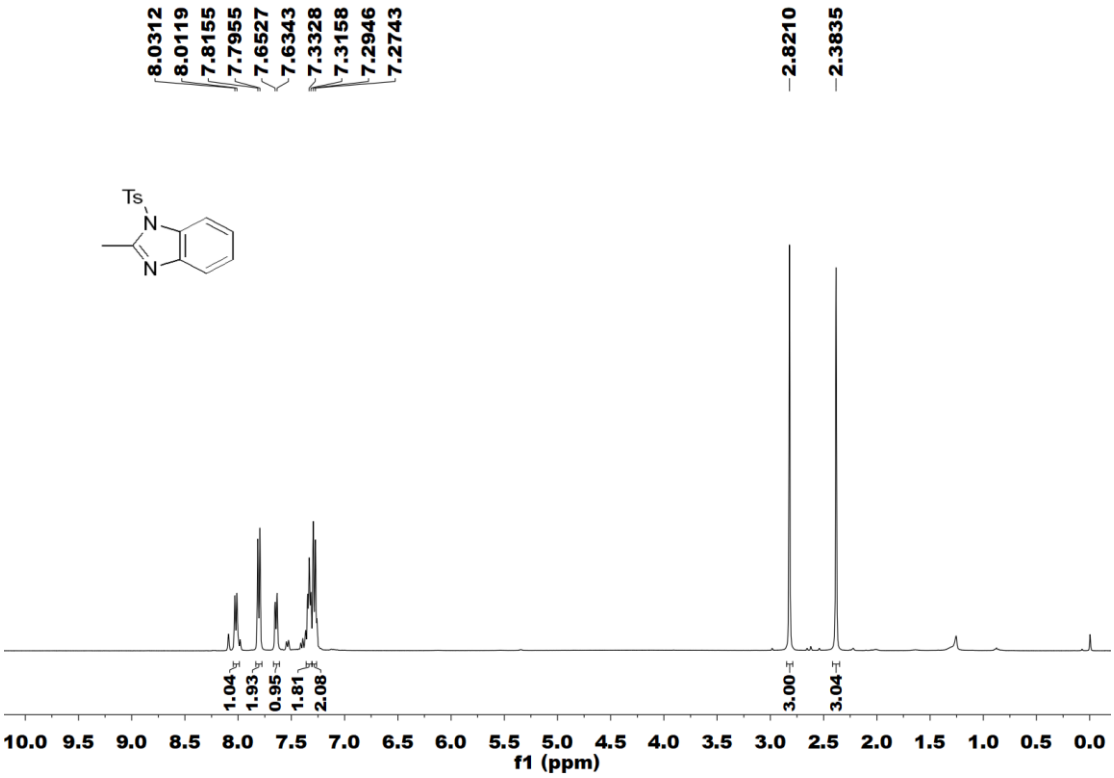


Fig. S64 ^{1}H NMR (400 MHz, $CDCl_3$) of 2-methyl-1-tosyl-1*H*-benzo[*d*]imidazole (5)

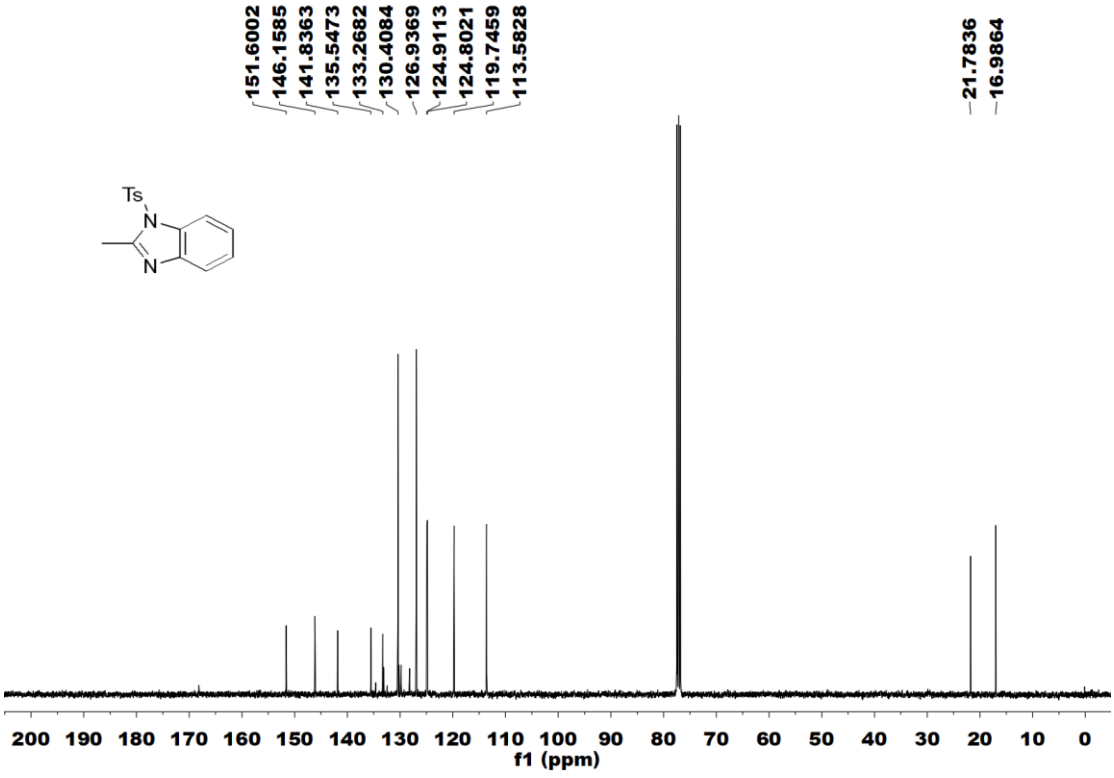


Fig. S65 ^{13}C NMR (150 MHz, $CDCl_3$) of 2-methyl-1-tosyl-1*H*-benzo[*d*]imidazole (5)

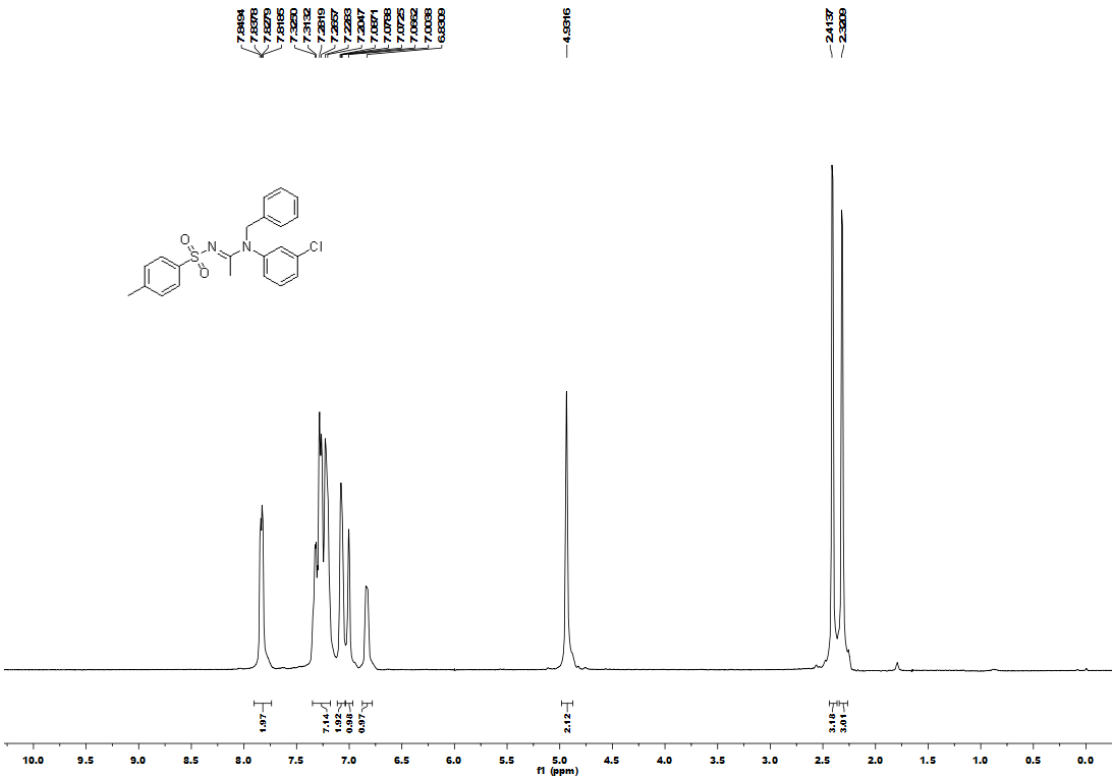


Fig. S66 ^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-*N*-benzyl-*N*-(3-chlorophenyl)-*N*'-tosylacetimidamide (6)

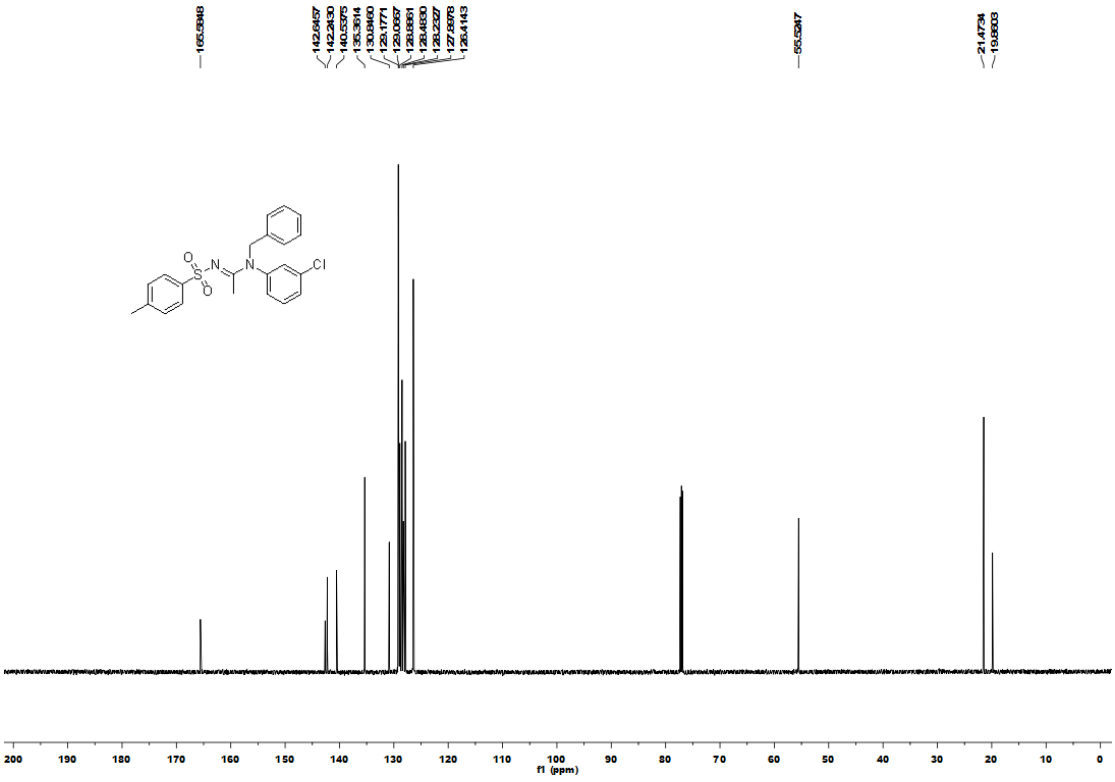


Fig. S67 ^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-*N*-benzyl-*N*-(3-chlorophenyl)-*N*'-tosylacetimidamide (6)

6. X-Ray Single-Crystal Diffraction Data for 3a

Table 1 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{15}H_{24}N_2O_2S$
Formula weight	296.42
Temperature/K	149.98(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.8198(2)
b/Å	25.8453(4)
c/Å	8.26570(10)
α/°	90
β/°	101.258(2)
γ/°	90
Volume/Å^3	1638.40(5)
Z	4
ρ_{calc}g/cm^3	1.202
μ/mm^{-1}	1.779
F(000)	640.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.84 to 153.832
Index ranges	$-8 \le h \le 9$, $-31 \le k \le 31$, $-10 \le l \le 10$
Reflections collected	9787
Independent reflections	3224 [R_{int} = 0.0487, R_{sigma} = 0.0323]
Data/restraints/parameters	3224/0/187
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0513, wR_2 = 0.1429
Final R indexes [all data]	R_1 = 0.0528, wR_2 = 0.1444

Largest diff. peak/hole / e $Å^{-3}$	0.33/-0.66

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	5327.6(5)	6344.3(2)	5729.1(4)	28.12(17)
O1	3777.0(17)	6143.6(6)	6206.0(16)	39.3(3)
O2	6042.6(19)	6810.8(5)	6568.4(15)	38.8(3)
N1	3880.4(18)	6742.3(5)	1273.0(16)	27.7(3)
N2	5125.6(19)	6398.1(6)	3756.1(17)	30.4(3)
C1	3960(2)	6713.7(6)	2898.9(19)	28.9(4)
C2	6487(3)	5362.7(7)	6497(3)	41.9(4)
C3	9953(3)	5617.6(9)	6684(3)	50.5(5)
C4	6942(2)	5861.4(6)	6161.8(19)	29.0(4)
C5	9526(3)	5118.0(9)	7058(3)	47.8(5)
C6	4985(2)	6415.7(7)	402(2)	28.3(4)
C7	10950(4)	4724.6(12)	7620(4)	75.8(9)
C8	6923(2)	6541.5(7)	887(2)	34.1(4)
C9	3651(3)	7488.2(8)	-630(2)	44.6(5)
C10	2654(2)	7097.7(7)	203(2)	34.9(4)
C11	1331(3)	6794.2(10)	-1031(3)	50.6(5)
C12	4609(3)	5840.7(7)	514(2)	36.8(4)
C13	7783(3)	4993.7(8)	6934(3)	52.6(6)
C14	8676(2)	5987.7(8)	6242(3)	42.0(4)
C15	2715(3)	7040.6(8)	3651(2)	41.7(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	32.4(3)	34.1(3)	17.7(2)	-0.13(13)	4.42(17)	0.61(14)
O1	35.9(7)	55.0(8)	28.8(7)	4.5(6)	10.8(5)	0.9(6)
O2	54.4(8)	34.5(6)	25.7(6)	-5.0(5)	3.8(5)	-0.3(6)
N1	29.2(7)	34.1(7)	19.4(6)	1.6(5)	3.6(5)	5.5(5)
N2	33.3(7)	38.5(7)	19.2(7)	1.2(5)	4.6(6)	5.3(6)
C1	29.5(8)	34.6(8)	22.7(8)	-0.3(6)	5.4(6)	1.6(6)
C2	41.8(10)	36.1(9)	49.8(11)	5.9(8)	14.1(8)	-3.8(8)
C3	32.2(10)	54.9(12)	59.9(14)	-0.2(10)	-2.3(9)	2.3(8)
C4	32.1(8)	33.2(8)	19.9(7)	-0.2(6)	0.7(6)	-2.6(6)
C5	54.4(12)	49.9(12)	36.2(10)	5.3(8)	2.0(9)	16.6(9)
C6	30.1(8)	35.2(9)	19.4(7)	-0.6(6)	4.5(6)	4.8(6)
C7	82.5(19)	76.8(18)	63.6(17)	13.2(14)	3.3(14)	42.2(16)
C8	31.1(9)	44.7(10)	27.2(8)	1.2(7)	7.4(7)	4.2(7)
C9	60.1(12)	39.9(10)	34.9(10)	9.3(8)	12.0(9)	10.7(9)
C10	34.5(9)	43.8(10)	25.4(8)	5.1(7)	3.2(7)	13.8(7)
C11	31.2(9)	77.5(15)	38.4(11)	0.4(10)	-4.6(8)	7.9(9)
C12	43.2(10)	35.7(9)	30.9(9)	-4.0(7)	5.2(7)	1.6(7)
C13	66.0(14)	36.5(10)	58.9(14)	16.0(10)	21.4(11)	7.5(10)
C14	34.0(9)	37.8(9)	51.4(12)	1.9(8)	1.2(8)	-5.5(8)
C15	47.2(11)	53.8(11)	26.1(9)	3.6(8)	11.9(8)	18.3(9)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.4427(13)	C2	C13	1.387(3)
S1	O2	1.4479(13)	C3	C5	1.383(3)
S1	N2	1.6134(14)	C3	C14	1.380(3)
S1	C4	1.7616(17)	C4	C14	1.384(3)
N1	C1	1.335(2)	C5	C7	1.512(3)
N1	C6	1.490(2)	C5	C13	1.385(3)
N1	C10	1.488(2)	C6	C8	1.525(2)
N2	C1	1.321(2)	C6	C12	1.521(3)
C1	C15	1.512(2)	C9	C10	1.520(3)
C2	C4	1.380(2)	C10	C11	1.521(3)

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	115.78(8)	C2	C4	S1	119.99(14)
O1	S1	N2	112.68(8)	C2	C4	C14	119.99(17)
O1	S1	C4	107.29(8)	C14	C4	S1	119.95(14)
O2	S1	N2	111.41(8)	C3	C5	C7	120.0(2)
O2	S1	C4	107.36(8)	C3	C5	C13	118.50(19)
N2	S1	C4	101.02(7)	C13	C5	C7	121.5(2)
C1	N1	C6	122.50(13)	N1	C6	C8	113.12(14)
C1	N1	C10	122.03(14)	N1	C6	C12	112.76(14)
C10	N1	C6	115.46(13)	C12	C6	C8	112.72(15)
C1	N2	S1	121.09(12)	N1	C10	C9	110.54(15)
N1	C1	C15	118.41(15)	N1	C10	C11	110.80(16)
N2	C1	N1	117.76(14)	C9	C10	C11	112.35(16)
N2	C1	C15	123.83(15)	C5	C13	C2	121.22(19)
C4	C2	C13	119.37(18)	C3	C14	C4	120.05(18)
C14	C3	C5	120.84(19)				

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N2	C1	N1	179.28(12)	C4	S1	N2	C1	177.14(14)
S1	N2	C1	C15	-1.0(3)	C4	C2	C13	C5	0.7(3)
S1	C4	C14	C3	175.84(17)	C5	C3	C14	C4	-0.2(3)
O1	S1	N2	C1	62.97(16)	C6	N1	C1	N2	3.0(2)
O1	S1	C4	C2	13.87(17)	C6	N1	C1	C15	-176.70(16)
O1	S1	C4	C14	-163.09(15)	C6	N1	C10	C9	-62.5(2)
O2	S1	N2	C1	-69.11(16)	C6	N1	C10	C11	62.8(2)
O2	S1	C4	C2	138.94(15)	C7	C5	C13	C2	176.8(2)
O2	S1	C4	C14	-38.03(17)	C10	N1	C1	N2	-178.05(16)
N2	S1	C4	C2	-104.29(16)	C10	N1	C1	C15	2.2(2)
N2	S1	C4	C14	78.75(16)	C10	N1	C6	C8	114.77(17)
C1	N1	C6	C8	-66.3(2)	C10	N1	C6	C12	-115.86(17)
C1	N1	C6	C12	63.1(2)	C13	C2	C4	S1	-176.09(16)
C1	N1	C10	C9	118.55(18)	C13	C2	C4	C14	0.9(3)
C1	N1	C10	C11	-116.22(18)	C14	C3	C5	C7	-177.0(2)
C2	C4	C14	C3	-1.1(3)	C14	C3	C5	C13	1.7(3)
C3	C5	C13	C2	-2.0(3)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H2	5296.87	5272.87	6429.06	50
H3	11140.36	5706.84	6733.03	61
H6	4639.15	6507.08	-792.66	34
H7A	11911.78	4784.19	7039.21	114
H7B	10483.33	4375.36	7373.49	114
H7C	11377.77	4759.4	8810.62	114
H8A	7091.56	6915.96	817.85	51
H8B	7556.15	6364.7	134.51	51
H8C	7366.54	6424.52	2018.49	51
H9A	4507.37	7667.13	207.51	67
H9B	2834.58	7741.07	-1235.49	67
H9C	4254.32	7308.24	-1399.4	67
H10	1998.64	7294.11	928.98	42
H11A	1929.13	6615.39	-1806.59	76
H11B	460.59	7032.2	-1638.07	76
H11C	752.25	6539.58	-442.83	76
H12A	5053	5719.55	1641.64	55
H12B	5184.9	5649.94	-253.94	55
H12C	3348.28	5782.18	227.56	55
H13	7469.03	4649.3	7153.06	63
H14	8987.4	6329.63	5991.34	50
H15A	2863.56	7405.64	3389.17	63
H15B	2960.01	6994.15	4850.95	63
H15C	1513.57	6933.89	3201.1	63

Experimental

Single crystals of $C_{15}H_{24}N_2O_2S$ [**3a**] were selected on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 149.98(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [3a]

Crystal Data for $C_{15}H_{24}N_2O_2S$ (M =296.42 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 7.8198(2) Å, b = 25.8453(4) Å, c = 8.26570(10) Å, β = 101.258(2)°, V = 1638.40(5) Å^3, Z = 4, T = 149.98(10) K, μ(Cu Kα) = 1.779 mm^{-1}, *Dcalc* = 1.202 g/cm^3, 9787 reflections measured (6.84° ≤ 2Θ ≤ 153.832°), 3224 unique (R_{int} = 0.0487, R_{sigma} = 0.0323) which were used in all calculations. The final R_1 was 0.0513 (I > 2σ(I)) and wR_2 was 0.1444 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

 At 1.2 times of:

  All C(H) groups

 At 1.5 times of:

  All C(H,H,H) groups

2.a Ternary CH refined with riding coordinates:

 C6(H6), C10(H10)

2.b Aromatic/amide H refined with riding coordinates:

 C2(H2), C3(H3), C13(H13), C14(H14)

2.c Idealised Me refined as rotating group:

 C7(H7A,H7B,H7C), C8(H8A,H8B,H8C), C9(H9A,H9B,H9C), C11(H11A,H11B,H11C), C12(H12A,H12B,H12C), C15(H15A,H15B,H15C)