

Supporting Information

Transition metal- and base-free electrochemical aza-Michael addition of aromatic aza-heterocycles or Ts-protected amines to α,β -unsaturated alkenes mediated by NaI

Cao-Cao Sun, Kun Xu and Cheng-Chu Zeng *

Beijing Key Laboratory of Environmental and Viral Oncology, College of Life Science & Bioengineering, Beijing University of Technology, Pingleyuan 100, Chaoyang District, Beijing 100124, China.

Total number of pages : 71

Total number of figures : 88

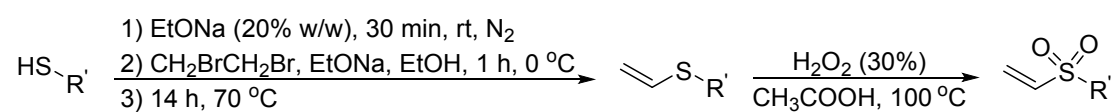
Contents

Contents	S1
Instruments and reagents.....	S2
Typical procedure for the synthesis of vinyl sulfones	S2
Typical procedure for the synthesis of imidazoles	S3
Analytical data of the prepared compounds.....	S4
References.....	S14
Spectra of prepared compounds.....	S15

Instruments and reagents

All melting points were measured with an electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded using a 600 MHz (600 MHz ^1H frequency, 150 MHz ^{13}C frequency) or 400 MHz (400 MHz ^1H frequency, 100 MHz ^{13}C frequency) or 300 MHz (300 MHz ^1H frequency, 75 MHz ^{13}C frequency). Chemical shifts are given as δ values (internal standard: TMS). Coupling constants are reported in Hz. The chemical shifts were referenced to signals at 7.28 ppm or 2.50 ppm. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). All starting materials and solvents were obtained from commercial sources and used without further purification. Products were purified by chromatography on silica gel (petroleum ether/EtOAc or $\text{CH}_2\text{Cl}_2/\text{MeOH}$).

Typical procedure for the synthesis of vinyl sulfones^{1,2}

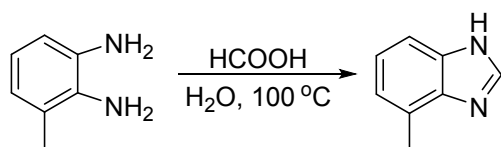


To a stirred solution of EtONa (17.6 mmol, 20% w/w) was added thiol (17.6 mmol) under an N_2 atmosphere, and the resultant reaction mixture was stirred at room temperature for 30 min. After that time, the solution of the corresponding thiolate was slowly added to a pre-cooled (0 $^\circ\text{C}$) stirring solution of 1,2-dibromoethane (26.4 mmol) in ethanol (2.0 mL) within 1 h under N_2 atmosphere and stirred for 1 h at room temperature. Then a solution of sodium ethoxide (44.3 mmol, 20% w/w) was added under the same reaction conditions. The reaction mixture was stirred at 70 $^\circ\text{C}$ for 14 h under N_2 atmosphere. After that, the solvent was removed in vacuo and treated with water and CH_2Cl_2 . The organic phase was separated, washed with water and brine, then dried over anhydrous Na_2SO_4 . After filtration, purification by silica gel column chromatography (using pure petroleum ether) afford the corresponding vinyl sulfide.

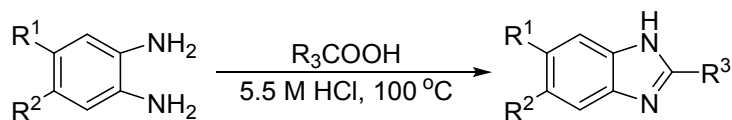
Hydrogen peroxide (12 mmol, 30%) was added slowly to a magnetically stirred solution of vinyl sulfide (3 mmol) in glacial acetic acid (3 mL) at such a rate as to

maintain a reaction temperature of 70 °C. The reaction mixture was refluxed for 20 min, cooled to room temperature and treated with CH₂Cl₂ and water. The organic phase was separated, washed with water and brine, then dried over anhydrous Na₂SO₄. After filtration, purification by silica gel column chromatography (using a solvent mixture of petroleum ether:EtOAc) yielded the desired pure vinyl sulfone.

Typical procedure for the synthesis of imidazoles^{3, 4}

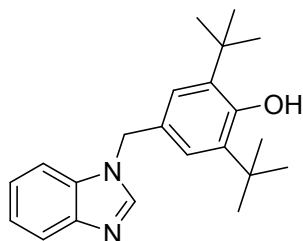


A mixture of 2,3-diaminotoluene (1.22 g, 10 mmol), formic acid (1.84 g, 40 mmol) and water (10 mL) was stirred at 100 °C for 16 h in a sealed tube. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ and the organic phase was washed with sat. aq. NaHCO₃, dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified via flash chromatography (CH₂Cl₂/MeOH = 10:1) to afford the 4-methyl-1*H*-benzo[*d*]imidazole as a light brown solid.

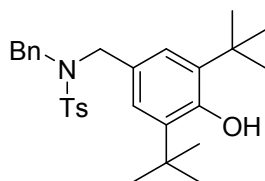


The others benzoimidazole derivatives was prepared using the Phillips procedure⁴ using benzene-1,2-diamine derivatives (10 mmol) and R₃COOH (15 mmol) dissolved in hydrochloric acid (20 mL, 5.5 M). The reaction was heated under reflux for 3-24 h and then cooled to room temperature. Then the mixture was added sat. aq. NaHCO₃ until the pH $\approx$ 7, and the water phase was extracted with CH₂Cl₂, the organic phase was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified via flash chromatography (using a solvent mixture of CH₂Cl₂:MeOH) to afford the benzoimidazole derivatives.

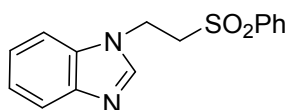
Analytical Data of the prepared compounds



4-((1H-benzo[d]imidazol-1-yl)methyl)-2,6-di-tert-butylphenol (4) White solid; 139 mg; Yield 69%; m.p.: 147-150 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.38 (s, 18H), 5.22 (s, 1H), 5.42 (s, 1H), 7.05 (s, 2H), 7.24-7.30 (m, 2H), 7.38-7.41 (m, 1H), 7.80-7.82 (m, 1H), 7.87 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 30.2, 34.4, 49.2, 110.0, 120.4, 122.1, 122.9, 124.5, 125.8, 134.1, 136.8, 143.0, 144.0, 153.9. HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 337.2274, Found 337.2288.

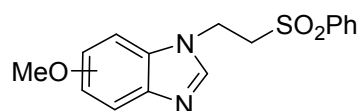


N-benzyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl)-4-methylbenzenesulfonamide (5) Yellow solid; 198 mg; Yield 69%; m.p.: 113-115 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.31 (s, 18H), 2.42 (s, 3H), 4.22 (s, 2H), 4.28 (s, 2H), 5.12 (s, 1H), 6.74 (s, 2H), 7.09-7.12 (m, 2H), 7.18-7.24 (m, 3H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.5, 30.2, 34.2, 50.5, 51.3, 125.8, 125.9, 127.2, 127.4, 128.3, 128.5, 129.7, 135.8, 136.4, 137.9, 143.1, 153.3. HRMS (ESI) m/z calculated for $\text{C}_{29}\text{H}_{37}\text{NO}_3\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 502.2386, Found 502.2393.

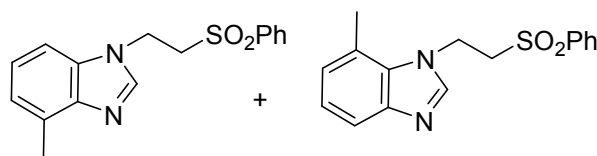


1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (3aa) White solid; 85 mg; Yield 99%; m.p.: 162-164 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.62 (t, $J = 7.2$ Hz, 2H), 4.64 (t, $J = 7.2$ Hz, 2H), 7.22-7.29 (m, 3H), 7.46-7.50 (m, 2H), 7.60 (tt, $J = 7.6, 1.2$ Hz, 1H), 7.72-7.74 (m, 1H), 7.79-7.82 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.5, 54.9, 109.0, 120.8, 122.6, 123.4, 127.6, 129.5, 132.9, 134.2, 138.5, 142.8, 143.8. HRMS (ESI) m/z

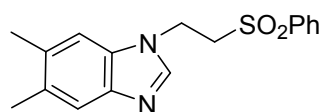
calculated for C₁₅H₁₅ N₂O₂S (M+H)⁺ 287.0849, found 287.0836.



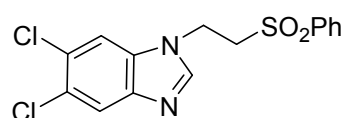
6-methoxy-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (3ba) and **5-methoxy-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (3ba')** Yellow foam; 94 mg; Yield 99%; ¹H NMR (600 MHz, CDCl₃) of the mixture of isomers **3ba** and **3ba'** δ 3.59-3.62 (m, 4H), 3.80 (s, 3H), 3.81 (s, 3H), 4.54-4.58 (m, 4H), 6.68-6.68 (m, 1H), 6.85-6.90 (m, 2H), 7.09-7.10 (m, 1H), 7.17-7.18 (m, 1H), 7.45-7.48 (m, 4H), 7.56-7.59 (m, 3H), 7.71-7.80 (m, 6H); ¹³C NMR of the mixture of isomers **3ba** and **3ba'** (150 MHz, CDCl₃) δ 36.3, 36.6, 52.6, 52.8, 53.7, 53.9, 90.7, 100.6, 107.4, 109.7, 111.4, 119.0, 125.4, 125.5, 125.5, 127.4, 131.5, 132.1, 132.2, 136.0, 136.4, 136.4, 139.9, 141.0, 142.5, 154.3, 155.0. HRMS (ESI) m/z calculated for C₁₆H₁₇N₂O₃S (M+H)⁺ 317.0954, found 317.0955.



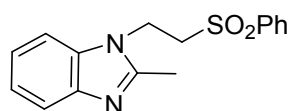
4-methyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (3ca) and **7-methyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (3ca')** White solid; 89 mg; Yield 99%; m.p.: 115-118 °C; ¹H NMR for **3ca** (400 MHz, CDCl₃) δ 2.61 (s, 3H), 3.60 (t, *J* = 6.8 Hz, 2H), 4.61 (t, *J* = 6.8 Hz, 2H), 7.04-7.06 (m, 2H), 7.10-7.17 (m, 1H), 7.45-7.49 (m, 2H), 7.53-7.61 (m, 1H), 7.77-7.80 (m, 3H); ¹H NMR for **3ca'** (400 MHz, CDCl₃) δ 2.53 (s, 3H), 3.53-3.55 (m, 2H), 4.76-4.80 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 7.10-7.17 (m, 1H), 7.53-7.61 (m, 3H), 7.66 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.75 (s, 1H), 7.87-7.89 (m, 2H); ¹³C NMR of **3ba** and **3ba'** (100 MHz, CDCl₃) δ 16.6, 18.3, 38.6, 39.9, 54.8, 57.2, 106.5, 118.8, 120.4, 122.7, 123.0, 123.3, 126.0, 127.6, 127.8, 129.4, 129.7, 130.7, 131.7, 132.5, 134.1, 134.4, 138.4, 138.6, 141.9, 143.1, 143.8, 144.6. HRMS (ESI) m/z calculated for C₁₆H₁₇N₂O₂S (M+H)⁺ 301.1005, found 301.1008.



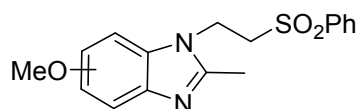
5,6-dimethyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3da) White solid; 93 mg; Yield 99%; m.p.: 120-123 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H), 2.35 (s, 3H), 3.59 (t, *J* = 6.8 Hz, 2H), 4.58 (t, *J* = 7.2 Hz, 2H), 6.97 (s, 1H), 7.49-7.55 (m, 3H), 7.65 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.69 (s, 1H), 7.84-7.86 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 20.2, 20.5, 38.4, 54.9, 109.11, 120.6, 127.7, 129.5, 131.4, 131.5, 132.6, 134.2, 138.5, 141.9, 142.4. HRMS (ESI) *m/z* calculated for C₁₇H₁₉N₂O₂S (M+H)⁺ 315.1162, found 315.1167.



5,6-dichloro-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ea) White solid; 101 mg; Yield 99%; m.p.: 169-170 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 4.06 (t, *J* = 6.4 Hz, 2H), 4.65 (t, *J* = 6.4 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.80-7.82 (m, 2H), 7.86 (d, *J* = 9.6 Hz, 2H), 8.26 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 39.0, 53.8, 112.9, 120.9, 124.8, 125.4, 127.7, 129.7, 133.3, 134.3, 139.3, 143.2, 147.1. HRMS (ESI) *m/z* calculated for C₁₅H₁₃N₂O₂S (M+H)⁺ 355.0069, Found 355.0076.

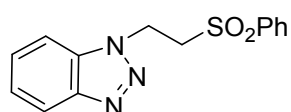


2-Methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3fa)⁵ White solid; 87 mg; Yield 97%; m.p.: 178-181 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.52 (s, 3H), δ 3.49 (t, *J* = 7.2 Hz, 2H), 4.50 (t, *J* = 7.2 Hz, 2H), 7.04-7.07 (m, 1H), 7.12-7.17 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.56-7.63 (m, 2H), 7.80 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.6, 37.2, 54.2, 108.5, 119.4, 122.3, 122.5, 127.5, 129.5, 134.1, 134.2, 138.4, 142.6, 151.1.

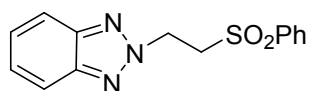


6-methoxy-2-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ga) and 5-methoxy-2-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ga') yellow solid; 53 mg; Yield 59%; m.p.: 153-154 °C; ¹H NMR of the mixture of isomers

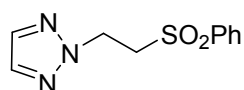
3ga and 3ga' (300 MHz, CDCl₃) δ 2.48 (s, 3H), 2.49 (s, 3H), 3.48 (t, J = 7.2 Hz, 4H), 3.78 (s, 3H), 3.79 (s, 3H), 4.43-4.50 (m, 4H), 6.55 (d, J = 2.1 Hz, 1H), 6.79 (dd, J = 8.7, 2.1 Hz, 2H), 6.93 (d, J = 8.7 Hz, 1H), 7.08 (d, J = 2.1 Hz, 1H), 7.43-7.53 (m, 5H), 7.59-7.62 (m, 2H), 7.79-7.84 (m, 4H); ¹³C NMR of **3ga and 3ga'** (75 MHz, CDCl₃) δ 13.6, 13.7, 37.1, 37.2, 54.1, 54.3, 55.8, 55.9, 92.9, 102.2, 108.8, 110.8, 111.9, 119.8, 127.5, 127.6, 128.6, 129.5, 129.5, 134.2, 134.3, 134.7, 137.0, 138.4, 143.4, 150.1, 151.3, 156.3, 156.4. HRMS (ESI) m/z calculated for C₁₇H₁₉N₂O₃S (M+H)⁺ 331.1111, Found 331.1115.



1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d][1,2,3]triazole (3ha)⁶ White solid; 44 mg; Yield 38%; m.p.: 100-102 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.90 (t, J = 6.9 Hz, 2H), 5.03 (t, J = 6.9 Hz, 2H), 7.33-7.43 (m, 3H), 7.48-7.55 (m, 3H), 7.72-7.75 (m, 2H), 7.96 (d, J = 8.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 41.5, 54.9, 109.1, 120.1, 124.2, 127.5, 127.9, 129.3, 132.8, 134.1, 138.3, 145.7.

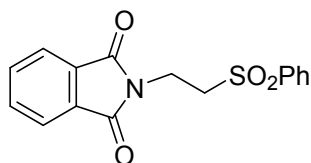


2-(2-(phenylsulfonyl)ethyl)-2H-benzo[d][1,2,3]triazole (3ha') White solid; 71 mg; Yield 61%; m.p.: 108-110 °C; ¹H NMR (300 MHz, CDCl₃) δ 4.00 (t, J = 6.9 Hz, 2H), 5.11 (t, J = 6.9 Hz, 2H), 7.31-7.38 (m, 4H), 7.41-7.46 (m, 1H), 7.69-7.73 (m, 2H), 7.78-7.80 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 50.1, 55.0, 117.9, 126.7, 127.9, 129.0, 133.8, 138.2, 144.3. HRMS (ESI) m/z calculated for C₁₄H₁₄N₃O₂S (M+H)⁺ 288.0801, found 288.0809.

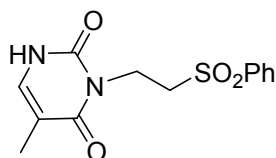


2-(2-(phenylsulfonyl)ethyl)-2H-1,2,3-triazole (3ia) White solid; 42 mg; Yield 59%; m.p.: 78-80 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.83 (t, J = 6.8 Hz, 2H), 4.83 (t, J = 6.8 Hz, 2H), 7.49 (s, 2H), 7.53 (t, J = 8.0 Hz, 2H), 7.66 (t, J = 7.2, 1H), 7.86-7.88 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 48.3, 54.8, 128.0, 129.4, 134.1, 134.7, 138.5. HRMS

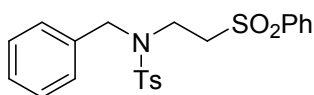
(ESI) m/z calculated for $C_{10}H_{12}N_3O_2S$ ($M+H$)⁺ 238.0645, found 238.0649.



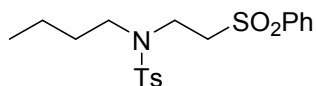
2-(2-(phenylsulfonyl)ethyl)isoindoline-1,3-dione (3ja) White solid; 54 mg; Yield 57%; m.p.: 191-193 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.75 (t, *J* = 6.4 Hz, 2H), 3.88 (t, *J* = 6.4 Hz, 2H), 7.56-7.65 (m, 3H), 7.81 (s, 4H), 7.86-7.89 (m, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 32.3, 52.1, 123.5, 128.1, 129.9, 131.8, 134.4, 134.9, 139.0, 167.7. HRMS (ESI) m/z calculated for $C_{16}H_{14}NO_4S$ ($M+H$)⁺ 316.0638, Found 316.0645.



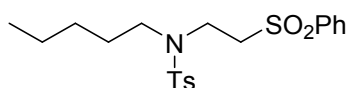
5-methyl-3-(2-(phenylsulfonyl)ethyl)pyrimidine-2,4(1H,3H)-dione (3ka) White solid; 10 mg; Yield 11%; m.p.: 191-193 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 1.73 (d, *J* = 0.8 Hz, 3H), 3.58 (t, *J* = 7.2 Hz, 2H), 4.06 (t, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 0.8 Hz, 1H), 7.66-7.69 (m, 2H), 7.76-7.79 (m, 1H), 7.91-7.93 (m, 2H), 10.9 (br, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 12.8, 34.3, 52.1, 107.6, 128.1, 129.9, 134.5, 137.0, 139.2, 151.3, 163.9. HRMS (ESI) m/z calculated for $C_{13}H_{15}N_2O_4S$ ($M+H$)⁺ 295.0747, found 295.0747.



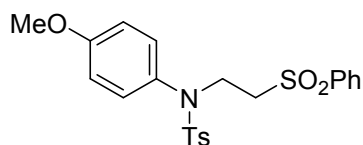
***N*-benzyl-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (3la)** White solid; 113 mg; Yield 88%; m.p.: 105-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.44 (s, 3H), 3.10-3.14 (m, 2H), 3.29-3.33 (m, 2H), 4.22 (s, 2H), 7.15-7.17 (m, 2H), 7.24-7.31 (m, 5H), 7.51-7.59 (m, 4H), 7.66 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.71-7.73 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 41.9, 53.4, 54.8, 127.2, 127.9, 128.4, 128.5, 129.0, 129.4, 130.0, 133.9, 135.3, 135.4, 138.6, 144.0. HRMS (ESI) m/z calculated for $C_{22}H_{24}NO_4S_2$ ($M+H$)⁺ 430.1141, found 430.1141.



***N*-butyl-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (3ma)** White solid; 106 mg; Yield 90%; m.p.: 86-87 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.21-1.30 (m, 2H), 1.37-1.45 (m, 2H), 2.42 (s, 3H), 3.07 (t, *J* = 7.2 Hz, 2H), 3.36-3.40 (m, 2H), 3.42-3.46 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.50-7.52 (m, 2H), 7.60-7.63 (m, 2H), 7.72 (tt, *J* = 7.6, 2.0 Hz, 1H), 7.90-7.92 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 19.7, 21.5, 30.4, 41.8, 49.2, 55.4, 127.1, 128.0, 129.5, 129.8, 134.1, 135.4, 138.8, 143.8. HRMS (ESI) *m/z* calculated for C₁₉H₂₆NO₄S₂ (M+H)⁺ 396.1298, found 396.1298.

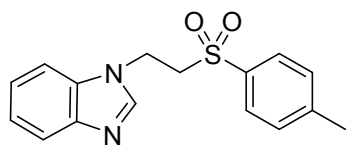


4-methyl-*N*-pentyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (3na) White solid; 111 mg; Yield 91%; m.p.: 65-67 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.15-1.31 (m, 4H), 1.39-1.46 (m, 2H), 2.42 (s, 3H), 3.06 (t, *J* = 7.2 Hz, 2H), 3.36-3.40 (m, 2H), 3.42-3.46 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.60-7.64 (m, 2H), 7.72 (tt, *J* = 7.6, 2.0 Hz, 1H), 7.90-7.92 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 21.5, 22.2, 28.0, 28.6, 41.8, 49.4, 55.4, 127.2, 128.0, 129.5, 129.8, 134.1, 135.5, 138.8, 143.8. HRMS (ESI) *m/z* calculated for C₂₀H₂₈NO₄S₂ (M+H)⁺ 410.1454, found 410.1450.

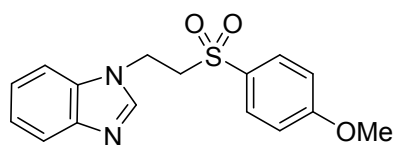


***N*-(4-methoxyphenyl)-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (3oa)** White solid; 82 mg; Yield 62%; m.p.: 132-135 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.42 (s, 3H), 3.31-3.35 (m, 2H), 3.79 (s, 3H), 3.86-3.90 (m, 2H), 6.76 (s, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.37-7.39 (m, 2H), 7.57-7.61 (m, 2H), 7.70 (tt, *J* = 7.6, 2.0 Hz, 1H), 7.88-7.90 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 45.0, 54.7, 55.5, 114.5, 127.8, 128.1, 129.5, 129.6, 129.7, 131.0, 134.1, 134.2, 139.0, 144.0, 159.4. HRMS (ESI) *m/z*

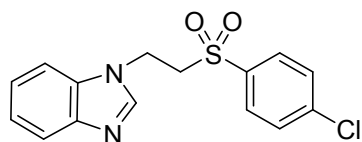
calculated for $C_{22}H_{24}NO_5S_2$ (M+H)⁺ 446.1090, found 446.1088.



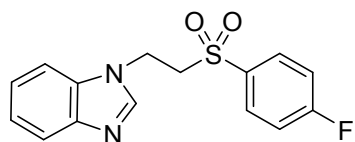
1-(2-tosylethyl)-1H-benzo[d]imidazole (3ab) White solid; 76 mg; Yield 84%; m.p.: 173-175 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.38 (s, 3H), 3.59 (t, *J* = 6.8 Hz, 2H), 4.60 (t, *J* = 6.8 Hz, 2H), 7.23-7.24 (m, 5H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.70-7.72 (m, 1H), 7.81 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 38.6, 54.8, 109.1, 120.6, 122.5, 123.3, 127.6, 130.1, 132.9, 135.5, 142.9, 143.8, 145.4. HRMS (ESI) *m/z* calculated for $C_{16}H_{17}N_2O_2S$ (M+H)⁺ 301.1005, found 301.1009.



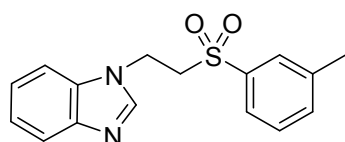
1-(2-((4-methoxyphenyl)sulfonyl)ethyl)-1H-benzo[d]imidazole (3ac) White solid; 69 mg; Yield 73%; m.p.: 150-152 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.58 (t, *J* = 6.8 Hz, 2H), 3.83 (s, 3H), 4.60 (t, *J* = 7.2 Hz, 2H), 6.88-6.91 (m, 2H), 7.23-7.26 (m, 3H), 7.67-7.74 (m, 3H), 7.84 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 38.7, 55.0, 55.8, 109.1, 114.7, 120.6, 122.5, 123.4, 129.8, 129.9, 132.9, 142.9, 143.8, 164.1. HRMS (ESI) *m/z* calculated for $C_{16}H_{17}N_2O_2S$ (M+H)⁺ 317.0954, found 317.0958.



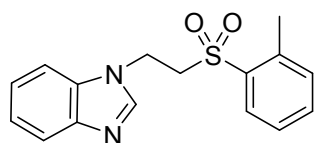
1-(2-((4-chlorophenyl)sulfonyl)ethyl)-1H-benzo[d]imidazole (3ad) White solid; 95 mg; Yield 99%; m.p.: 173-175 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 4.05 (t, *J* = 6.6 Hz, 2H), 4.60 (t, *J* = 6.6 Hz, 2H), 7.13-7.23 (m, 2H), 7.45-7.57 (m, 4H), 7.74-7.77 (m, 2H), 8.12 (s, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 43.5, 58.7, 115.5, 124.6, 126.8, 127.5, 134.3, 134.4, 138.4, 142.6, 144.1, 148.5, 149.2. HRMS (ESI) *m/z* calculated for $C_{15}H_{14}ClN_2O_2S$ (M+H)⁺ 321.0459, found 3021.0463.



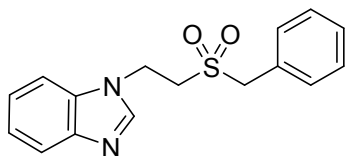
1-(2-((4-fluorophenyl)sulfonyl)ethyl)-1H-benzo[d]imidazole (3ae) White solid; 89 mg; Yield 98%; m.p.: 131-132 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.64 (t, J = 6.8 Hz, 2H), 4.66 (t, J = 6.8 Hz, 2H), 7.10 (t, J = 8.0 Hz, 2H), 7.26-7.27 (m, 3H), 7.72-7.77 (m, 3H), 7.85 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.6, 54.9, 108.9, 116.8 (d, J_{CF} = 23.0 Hz), 120.8, 122.7, 123.5, 130.4 (d, J_{CF} = 10.0 Hz), 132.8, 134.5 (d, J_{CF} = 3.0 Hz), 142.8, 143.8, 165.9 (d, J_{CF} = 256.0 Hz). HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 305.0755, found 305.0759.



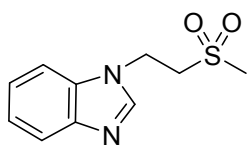
1-(2-(m-tolylsulfonyl)ethyl)-1H-benzo[d]imidazole (3af) White solid; 80 mg; Yield 89%; m.p.: 140-142 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.35 (s, 3H), 3.62 (t, J = 6.9 Hz, 2H), 4.64 (t, J = 6.9 Hz, 2H), 7.22-7.27 (m, 3H), 7.33-7.37 (m, 2H), 7.54 (s, 1H), 7.57-7.62 (m, 1H), 7.72-7.75 (m, 1H), 7.81 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.2, 38.6, 54.8, 109.0, 120.7, 122.6, 123.4, 124.6, 127.8, 129.3, 132.9, 135.0, 138.3, 139.9, 142.8, 143.8. HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 301.1005, found 301.1013.



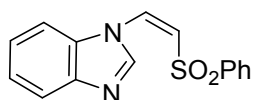
1-(2-(o-tolylsulfonyl)ethyl)-1H-benzo[d]imidazole (3ag) White solid; 89 mg; Yield 99%; m.p.: 116-118 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.58 (s, 3H), 3.64 (t, J = 6.8 Hz, 2H), 4.64 (t, J = 6.8 Hz, 2H), 7.23-7.29 (m, 4H), 7.32 (t, J = 7.2 Hz, 1H), 7.47 (td, J = 7.6, 1.6 Hz, 1H), 7.12-7.74 (m, 1H), 7.80 (s, 1H), 7.92 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.1, 38.4, 53.9, 108.9, 120.7, 122.6, 123.4, 126.8, 129.7, 132.9, 134.2, 136.5, 137.6, 142.8, 143.8. HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 301.1005, found 301.1009.



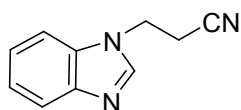
1-(2-(benzylsulfonyl)ethyl)-1H-benzo[d]imidazole (3ah) White solid; 77 mg; Yield 86%; m.p.: 172-173 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.30 (t, J = 6.8 Hz, 2H), 3.93 (s, 3H), 4.59 (t, J = 6.8 Hz, 2H), 7.06 (d, J = 7.2 Hz, 2H), 7.28-7.37 (m, 6H), 7.83-7.85 (m, 1H), 7.95 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.3, 50.1, 61.2, 109.2, 121.0, 122.9, 123.7, 126.9, 129.2, 129.4, 130.5, 133.0, 143.2, 143.9. HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 301.1005, found 301.1009.



1-(2-(methylsulfonyl)ethyl)-1H-benzo[d]imidazole (3ai) Colorless oil; 55 mg; Yield 82%; ^1H NMR (400 MHz, CDCl_3) δ 2.61 (s, 3H), 3.47 (t, J = 6.4 Hz, 2H), 4.63 (t, J = 6.4 Hz, 2H), 7.26-7.33 (m, 2H), 7.39-7.41 (m, 1H), 7.77-7.79 (m, 1H), 7.95 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.2, 41.9, 53.2, 109.4, 120.7, 122.8, 123.6, 132.9, 143.4, 143.7. HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 225.0692, Found 225.0695.

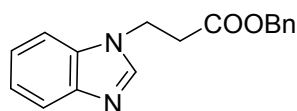


(Z)-1-(2-(phenylsulfonyl)vinyl)-1H-benzo[d]imidazole (3aj) Yellow solid; 45 mg; Yield 53% m.p.: 118-119 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.29 (d, J = 10.0 Hz, 1H), 7.20 (d, J = 9.6 Hz, 1H), 7.31-7.36 (m, 3H), 7.47-7.51 (m, 2H), 7.58 (tt, J = 7.6, 1.2 Hz, 1H), 7.79-7.81 (m, 1H), 7.89-7.92 (m, 2H), 8.92 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 109.4, 119.1, 121.0, 124.3, 124.7, 127.3, 127.8, 129.5, 133.2, 134.1, 140.3, 143.0, 144.1. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 285.0692, Found 285.0681.

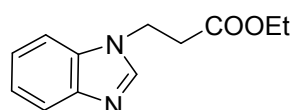


3-(1H-benzo[d]imidazol-1-yl)propanenitrile (3ak)⁷ White solid; 51 mg; Yield 99%;

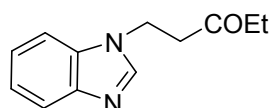
m.p.: 106-107 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.82 (t, $J = 6.4$ Hz, 2H), 4.63 (t, $J = 6.4$ Hz, 2H), 7.32-7.37 (m, 3H), 7.80-7.82 (m, 1H), 7.93 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.1, 40.5, 109.1, 116.8, 120.7, 122.8, 123.6, 133.0, 142.7, 143.9.



benzyl 3-(1H-benzo[d]imidazol-1-yl)propanoate (3al)⁸ Colorless oil; 61 mg; Yield 72%; ^1H NMR (400 MHz, CDCl_3) δ 2.86 (t, $J = 6.4$ Hz, 2H), 4.44 (t, $J = 6.4$ Hz, 2H), 7.23-7.36 (m, 8H), 7.78-7.81 (m, 1H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 34.4, 40.3, 67.0, 109.4, 120.5, 122.3, 123.1, 128.4, 128.6, 128.7, 133.4, 135.2, 143.4, 143.8, 170.5.



ethyl 3-(1H-benzo[d]imidazol-1-yl)propanoate (3am)⁸ Colorless oil; 47 mg; Yield 72%; ^1H NMR (400 MHz, CDCl_3) δ 1.19 (t, $J = 6.8$ Hz, 3H), 2.85 (t, $J = 7.2$ Hz, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 4.48 (t, $J = 6.8$ Hz, 2H), 7.26-7.33 (m, 2H), 7.39-7.41 (m, 1H), 7.79-7.81 (m, 1H), 7.96 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 34.4, 40.3, 61.2, 109.3, 120.5, 122.2, 123.0, 133.4, 143.4, 143.8, 170.6.



1-(1H-benzo[d]imidazol-1-yl)pentan-3-one (3an) Yellow oil; 30 mg; Yield 50%; ^1H NMR (400 MHz, CDCl_3) δ 1.02 (t, $J = 7.2$ Hz, 3H), 2.37 (q, $J = 7.2$ Hz, 2H), 2.96 (q, $J = 6.4$ Hz, 2H), 4.48 (t, $J = 6.4$ Hz, 2H), 7.27-7.33 (m, 2H), 7.38-7.40 (m, 1H), 7.81 (d, $J = 7.2$ Hz, 1H), 7.97 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 7.5, 36.4, 39.1, 41.5, 109.3, 120.5, 122.2, 123.0, 133.4, 143.6, 143.8, 208.2. HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}$ ($\text{M}+\text{H}$)⁺ 203.1179, Found 203.1176.

References

- 1 Lao, J. R.; Fernández-Pérez, H.; Vidal-Ferran, A. *Org. Lett.* **2015**, *17*, 4114.
- 2 Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976.
- 3 Ueda, S.; Su, M.-J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2012**, *134*, 700.
- 4 Phillips, M. A. *J. Chem. Soc.* **1928**, *CCCXVII*, 2393.
- 5 Kim, S.; Kang, S.; Kim, G.; Lee, Y. *J. Org. Chem.* **2016**, *81*, 4048.
- 6 Medina, F.; Duhal, N.; Michon, C.; Agbossou-Niedercorn, F. *C. R. Chim.* **2013**, *16*, 311.
- 7 Zbancioc, G.; Mangalagiu, I. I.; Moldoveanu C. *Ultrason. Sonochem.* **2015**, *23*, 376.
- 8 Wen, J.; Luo, Y.-L.; Zhou, C.-H.; Cai, G.-X. *Chinese Chem. Lett.*, **2016**, *27*, 391.

Spectra of prepared compounds

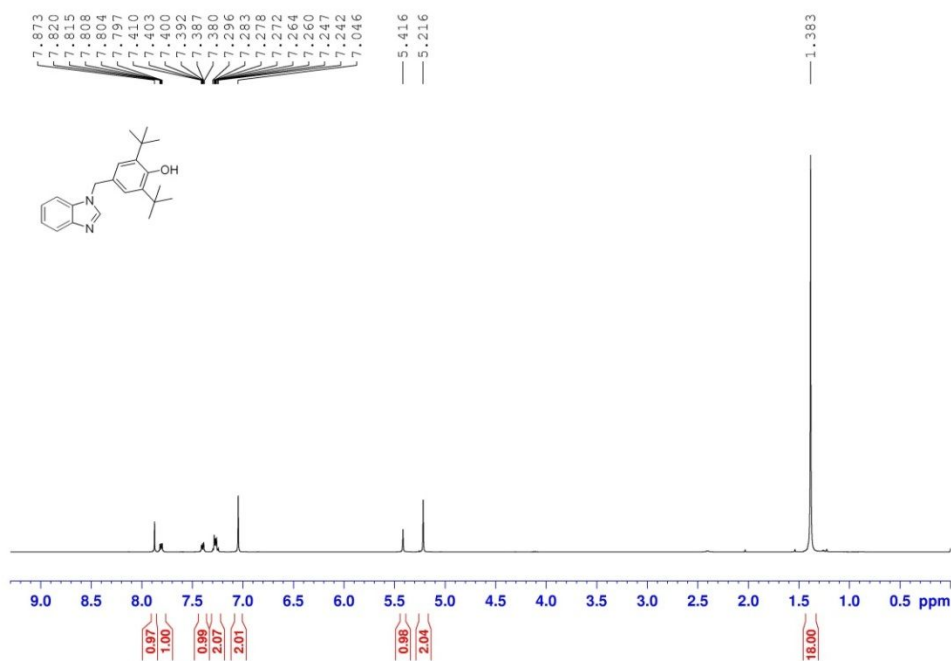


Figure S1 ¹H NMR spectra of 4-((1H-benzo[d]imidazol-1-yl)methyl)-2,6-di-tert-butylphenol (**4**)

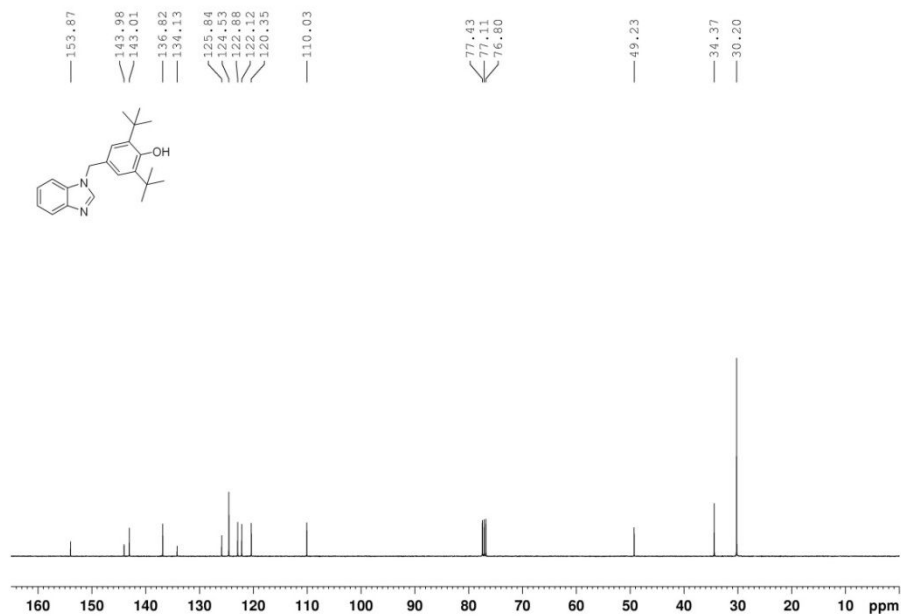


Figure S2 ¹³C NMR spectra of 4-((1H-benzo[d]imidazol-1-yl)methyl)-2,6-di-tert-butylphenol (**4**)

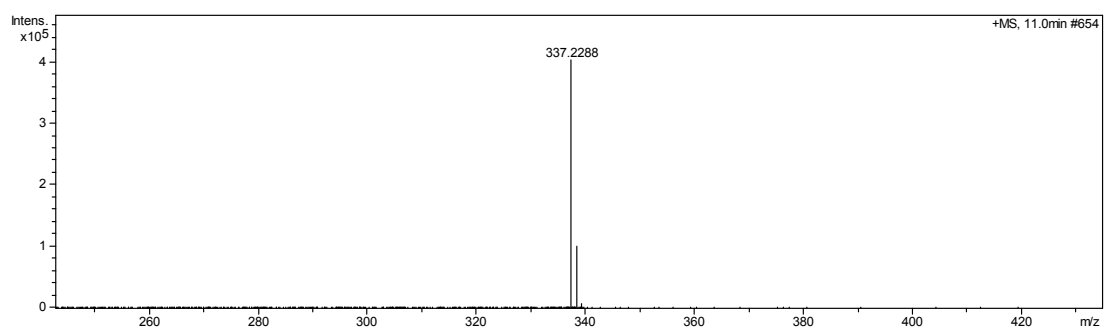


Figure S3 HRMS spectra of 4-((1*H*-benzo[*d*]imidazol-1-yl)methyl)-2,6-di-tert-butylphenol (**4**)

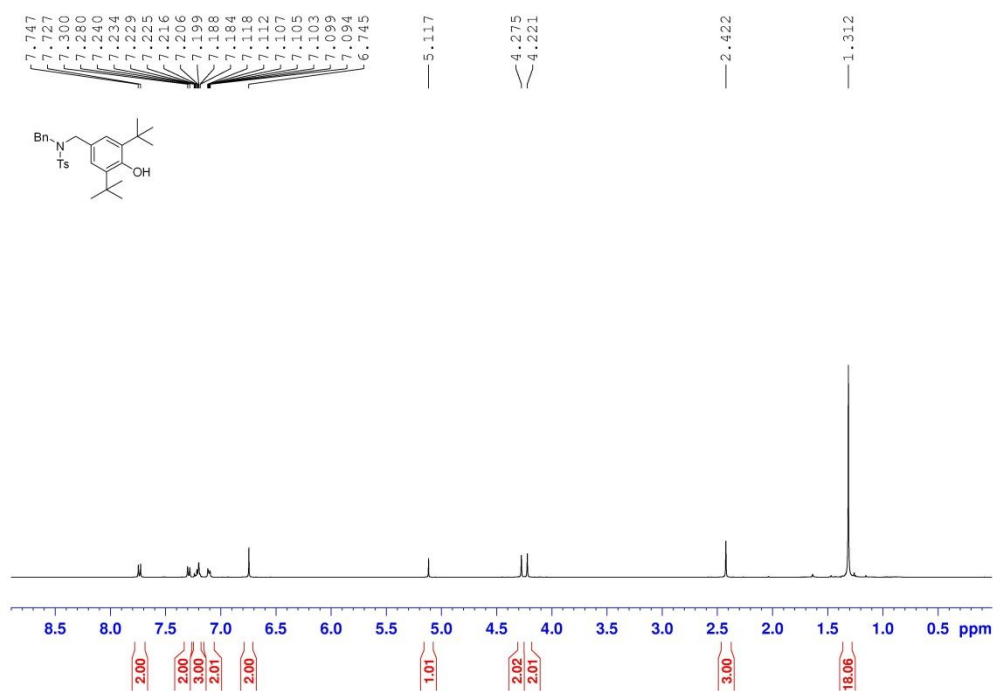


Figure S4 ¹H NMR spectra of *N*-benzyl-*N*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-4-methylbenzenesulfonamide (**5**)

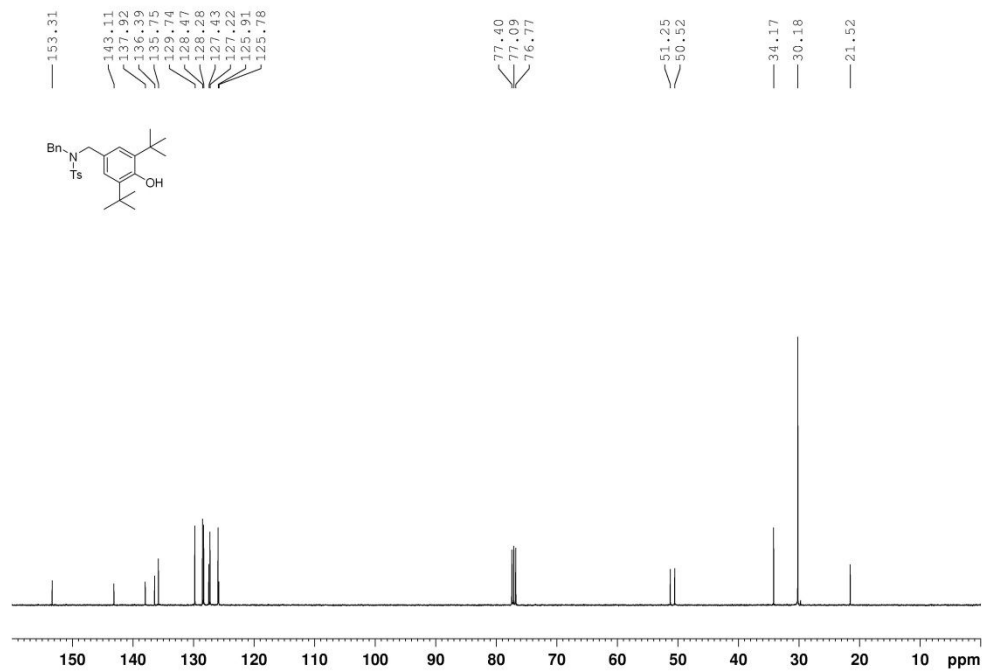


Figure S5 ¹³C NMR spectra of *N*-benzyl-*N*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-4-methylbenzenesulfonamide (**5**)

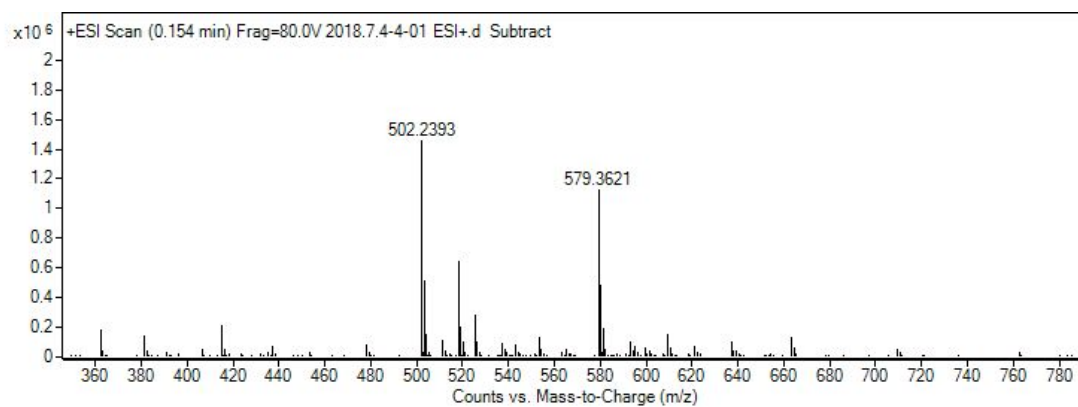


Figure S6 HRMS NMR spectra of *N*-benzyl-*N*-(3,5-di-tert-butyl-4-hydroxybenzyl)-4-methylbenzenesulfonamide (**5**)

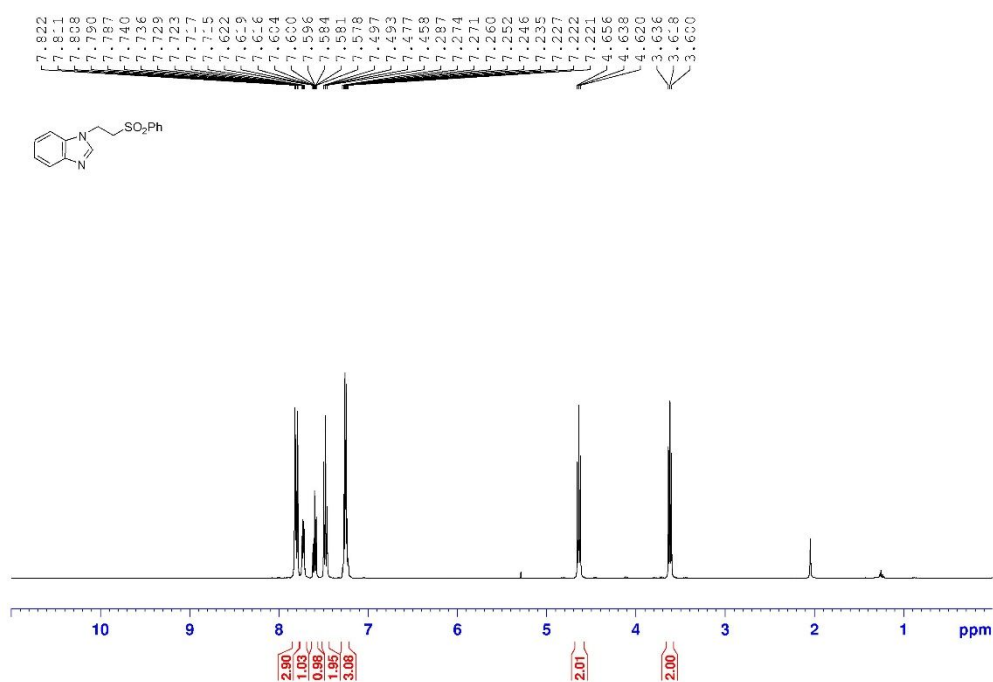


Figure S7 ¹H NMR spectra of 1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3aa**)

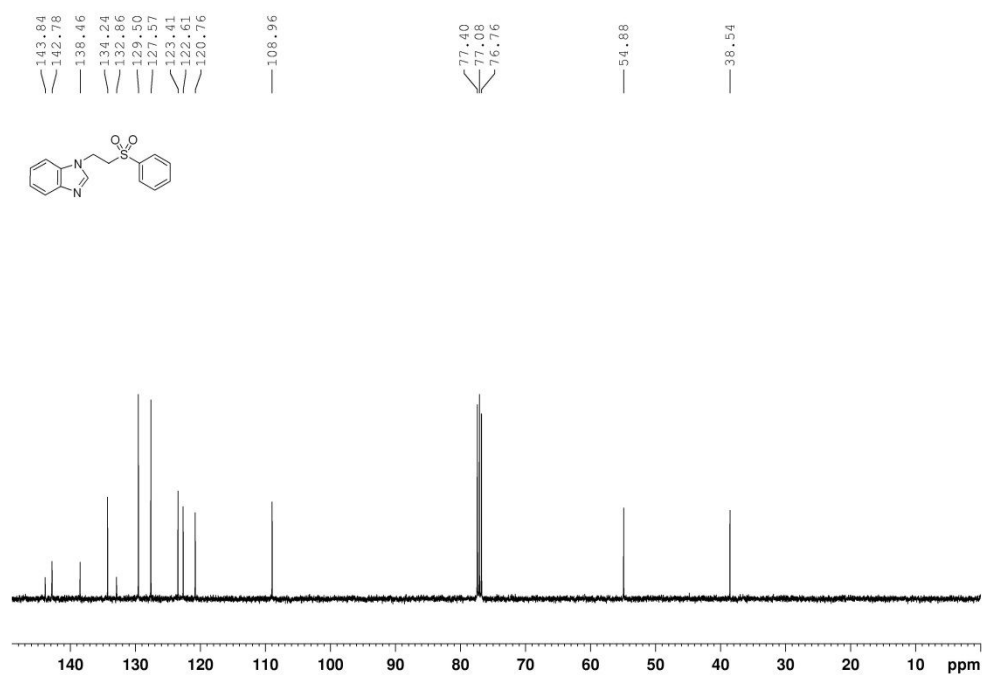


Figure S8 ¹³C NMR spectra of 1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3aa**)

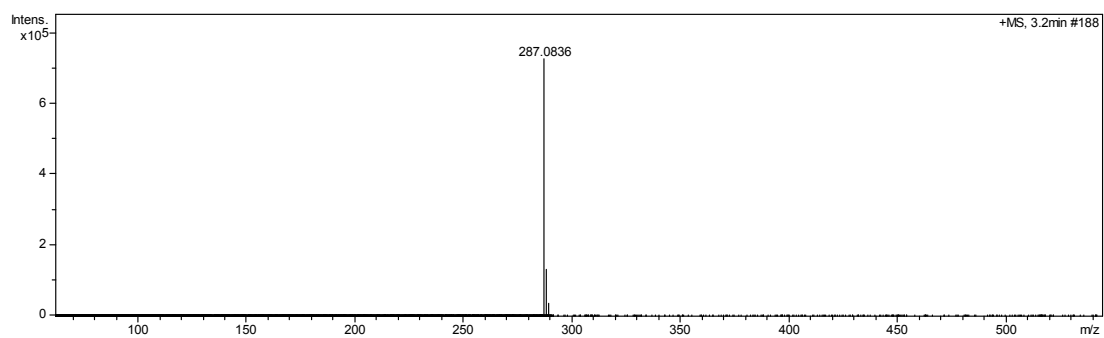


Figure S9 HRMS spectra of 1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3aa**)

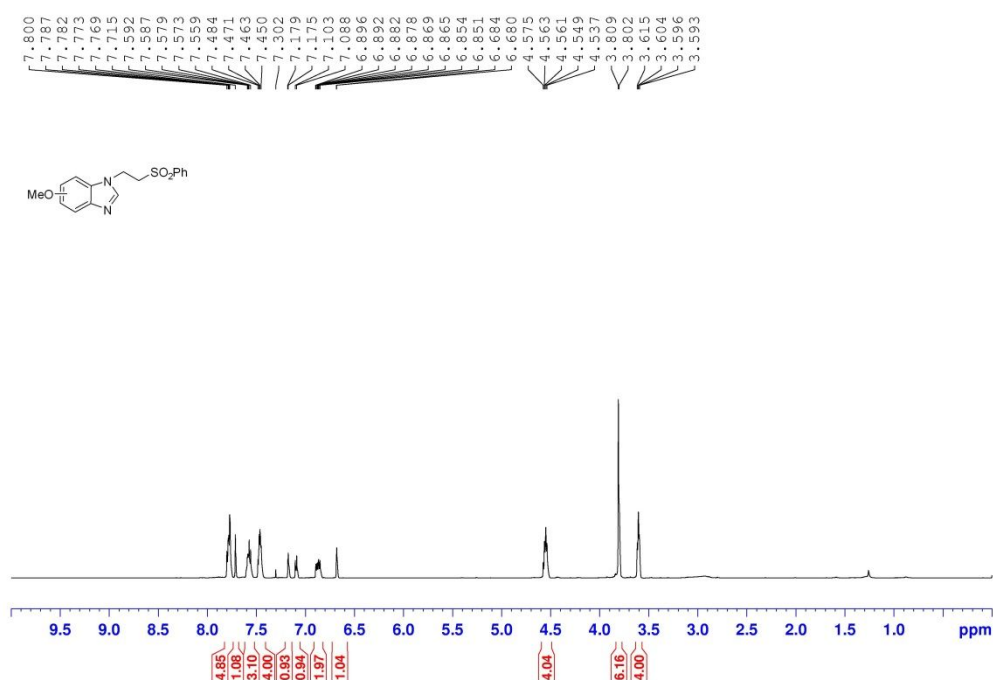


Figure S10 ¹H NMR spectra of 6-methoxy-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ba**) and 5-methoxy-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ba'**)

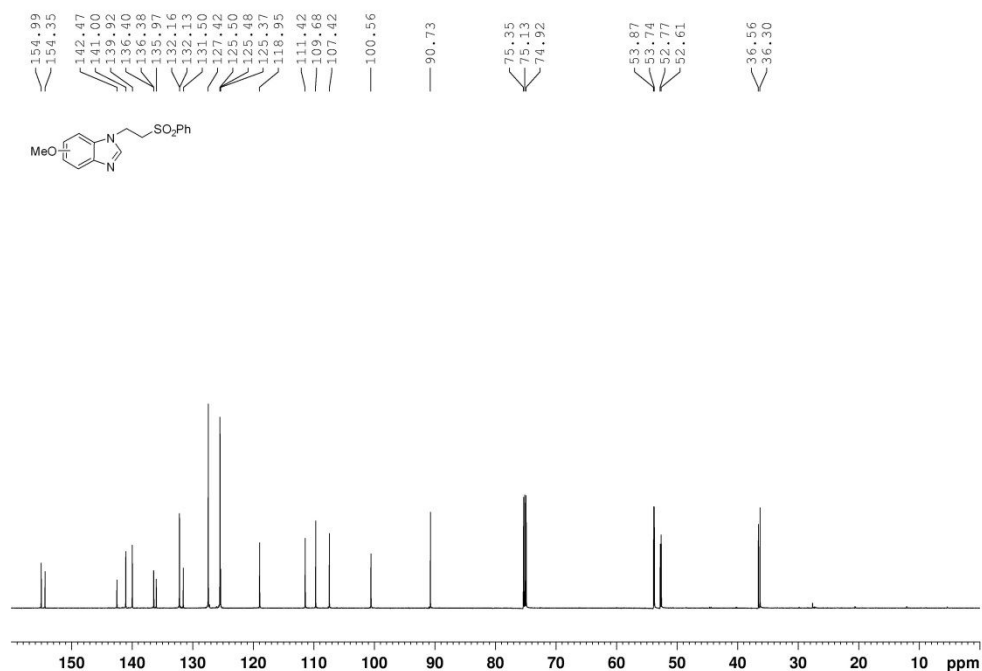


Figure S11 ¹³C NMR spectra of 6-methoxy-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ba**) and 5-methoxy-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ba'**)

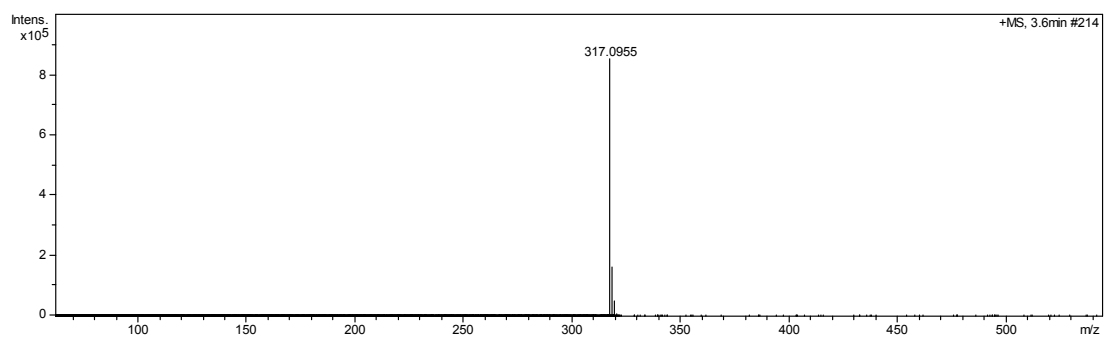


Figure S12 HRMS NMR spectra of 6-methoxy-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ba**) and 5-methoxy-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ba'**)

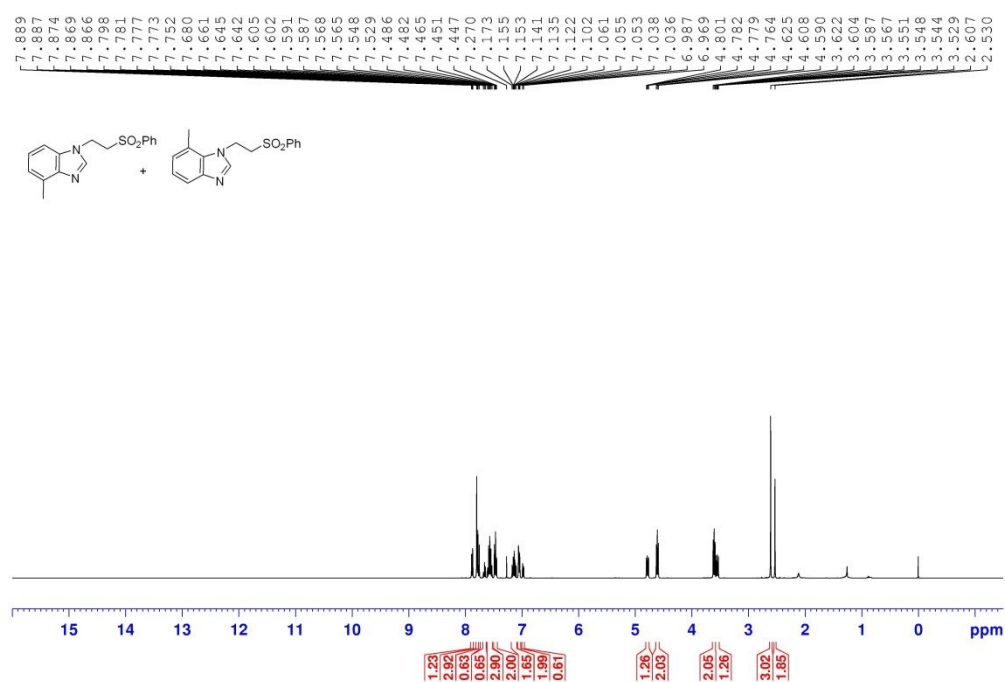


Figure S13 ¹H NMR spectra of 4-methyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**3ca**) and 7-methyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**3ca'**)

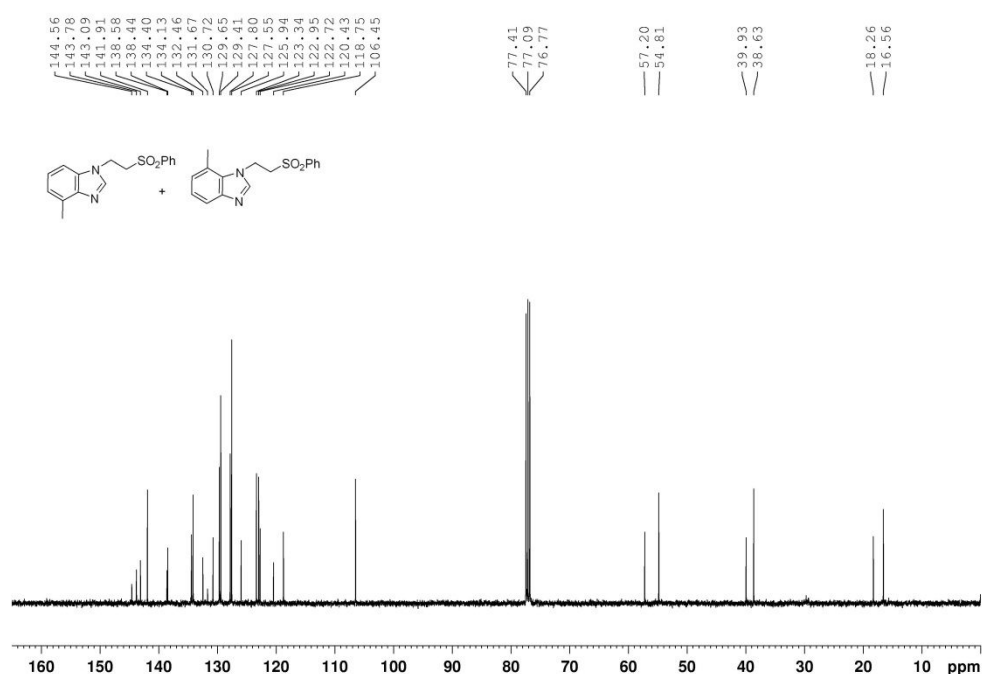


Figure S14 ¹³C NMR spectra of 4-methyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**3ca**) and 7-methyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**3ca'**)

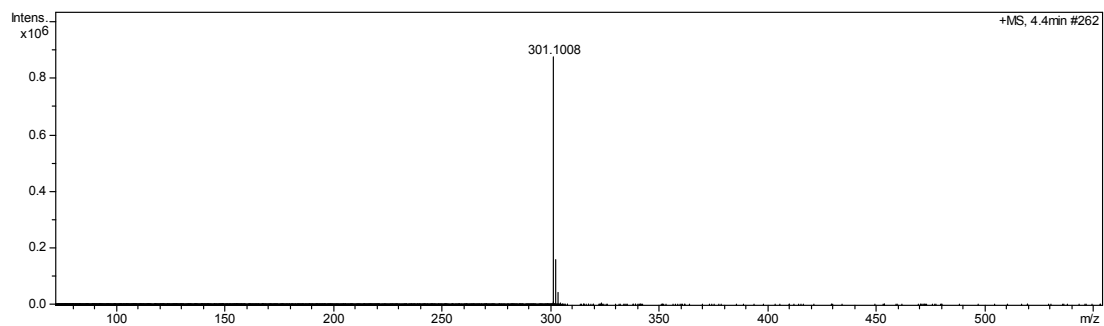


Figure S15 HRMS spectra of 4-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ca**) and 7-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ca'**)

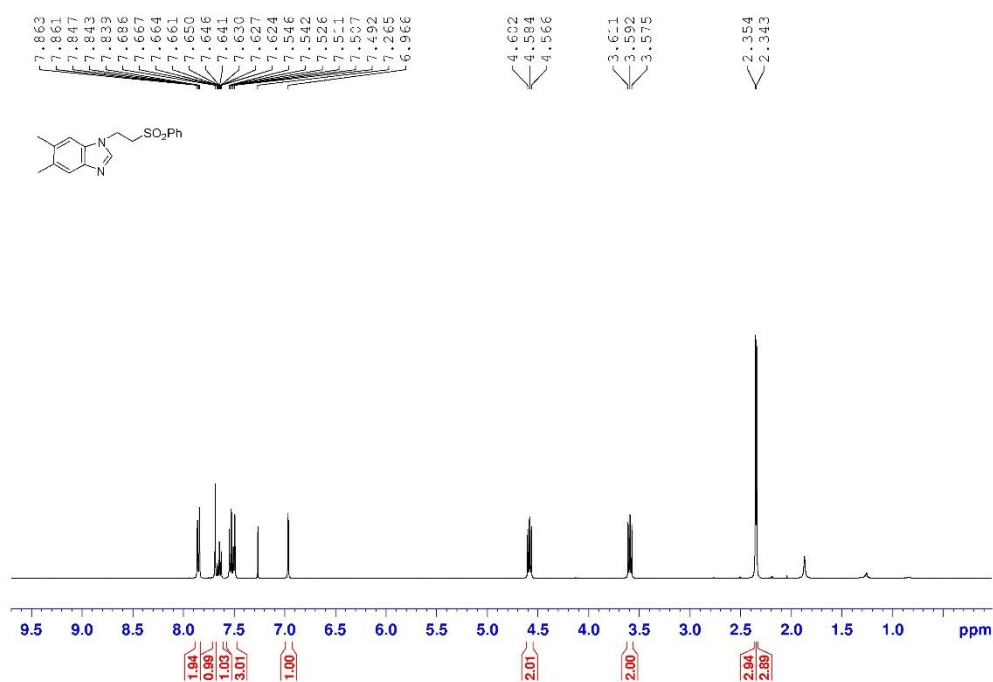


Figure S16 ¹H NMR spectra of 5,6-dimethyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**3da**)

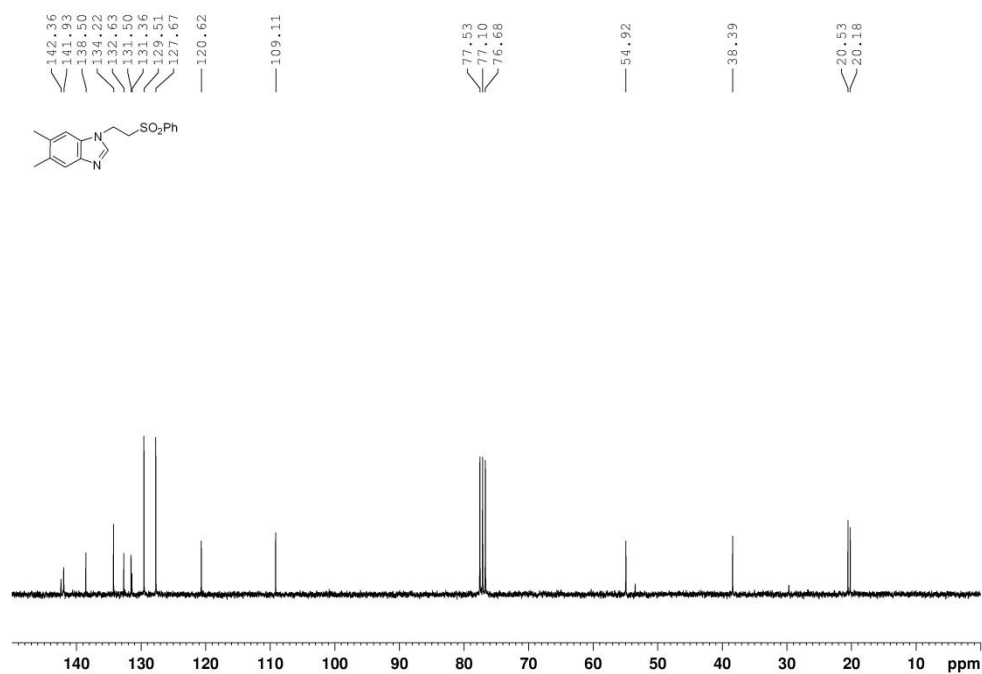


Figure S17 ¹³C NMR spectra of 5,6-dimethyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**3da**)

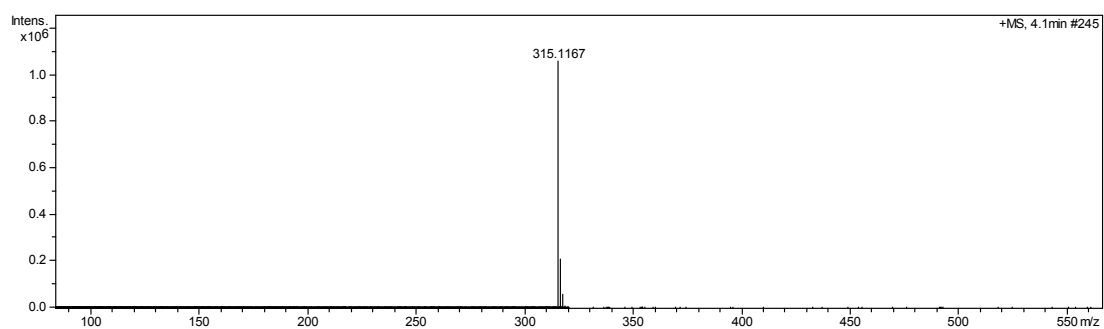


Figure S18 HRMS spectra of 5,6-dimethyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3da**)

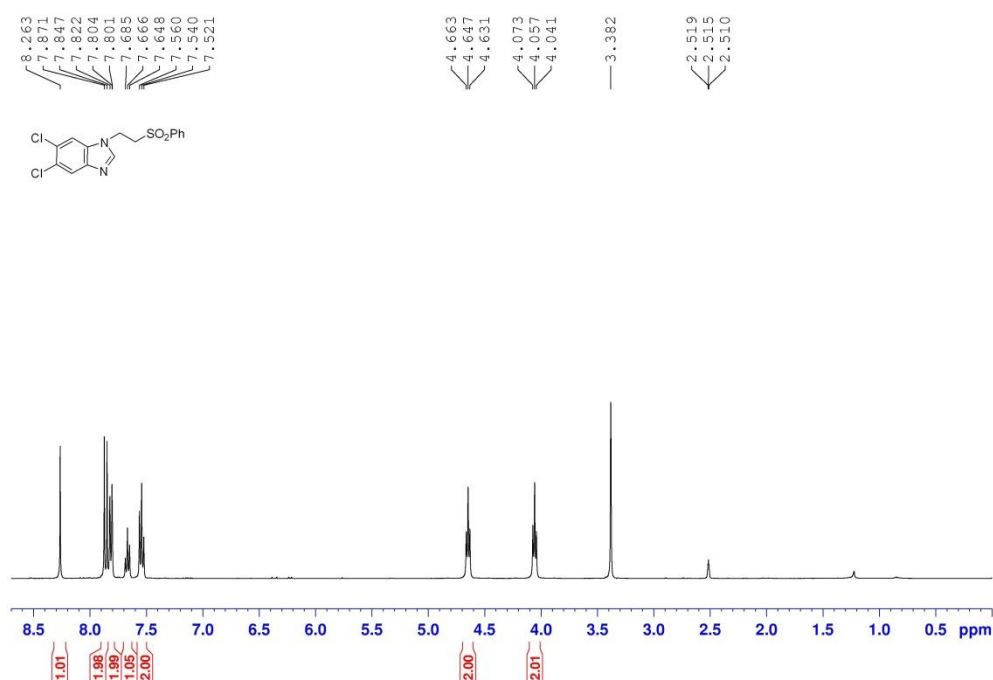


Figure S19 ¹H NMR spectra of 5,6-dichloro-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**3ea**)

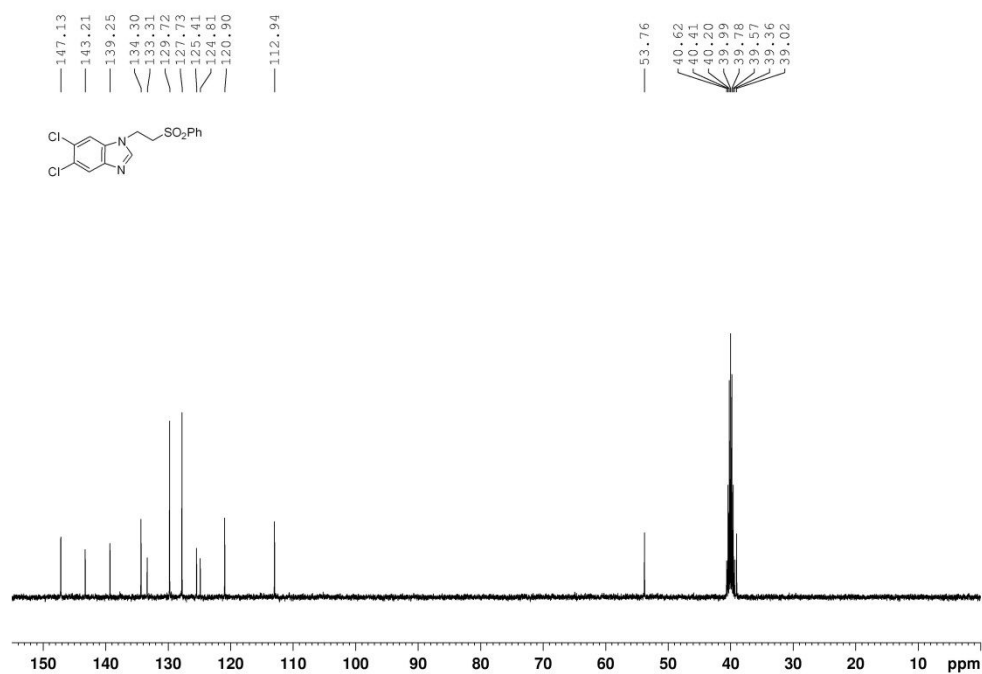


Figure S20 ¹³C NMR spectra of 5,6-dichloro-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**3ea**)

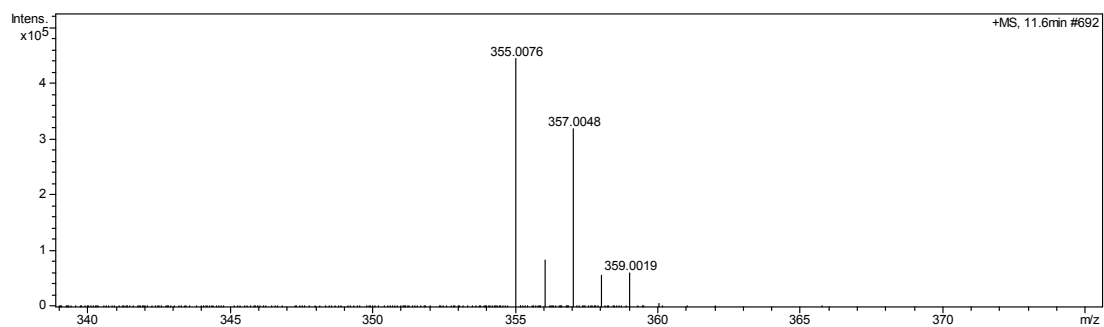


Figure S21 HRMS spectra of 5,6-dichloro-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ea**)

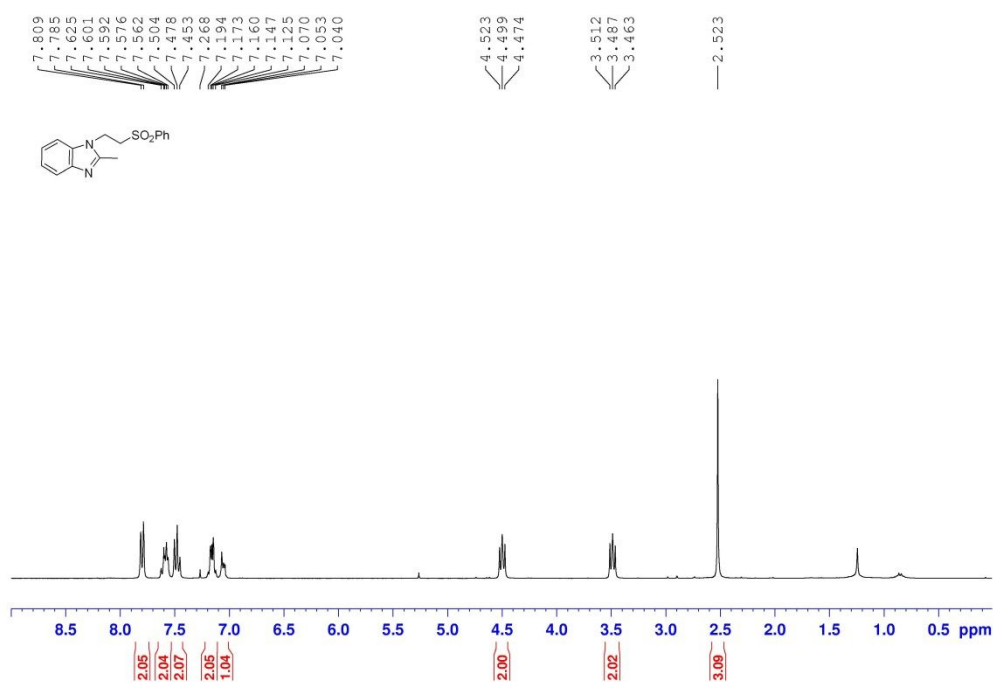


Figure S22 ¹H NMR spectra of 2-Methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3fa**)⁵

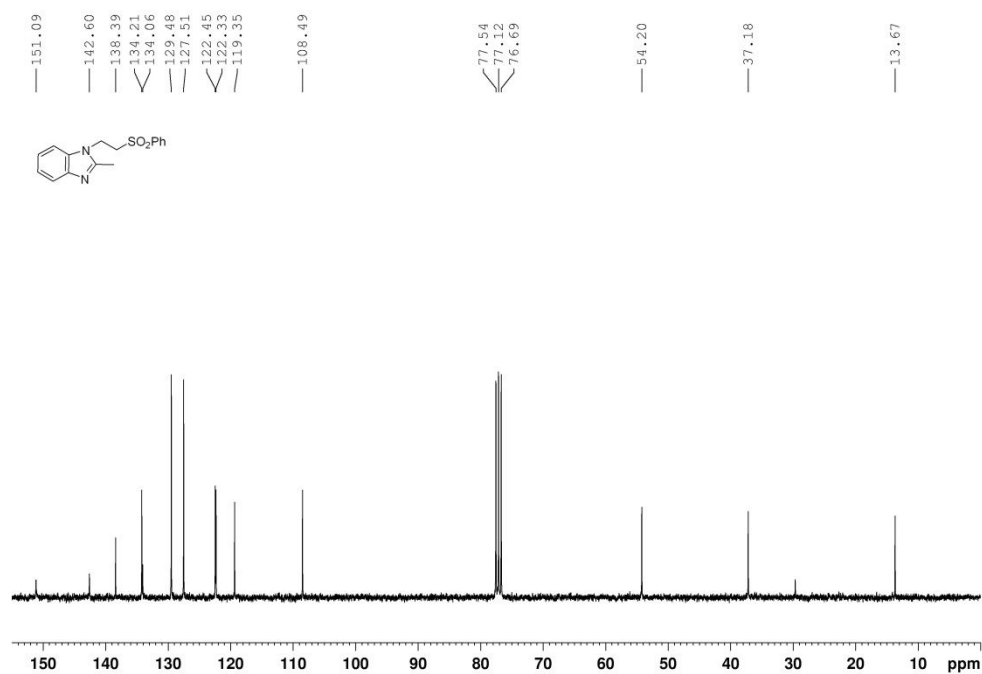


Figure S23 ¹³C NMR spectra of 2-Methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3fa**)⁵

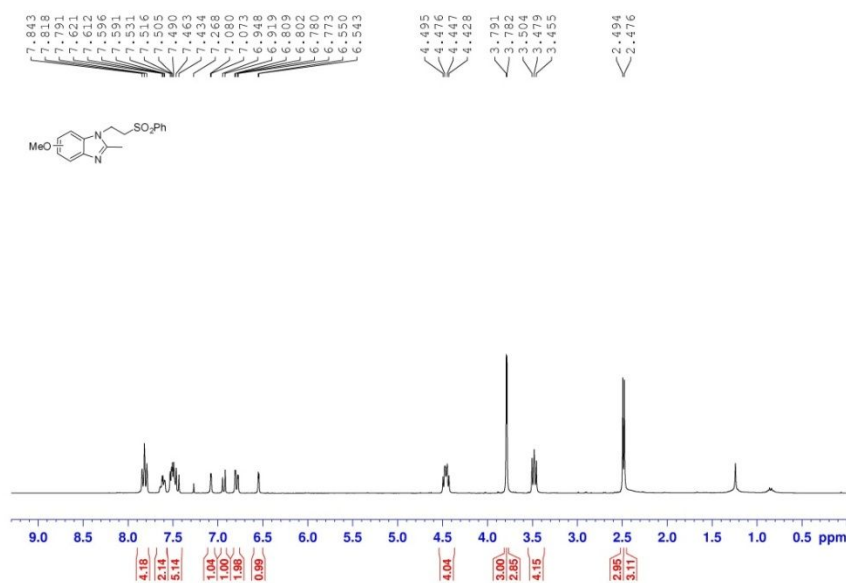


Figure S24 ¹H NMR spectra of 6-methoxy-2-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ga**) and 5-methoxy-2-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ga'**)

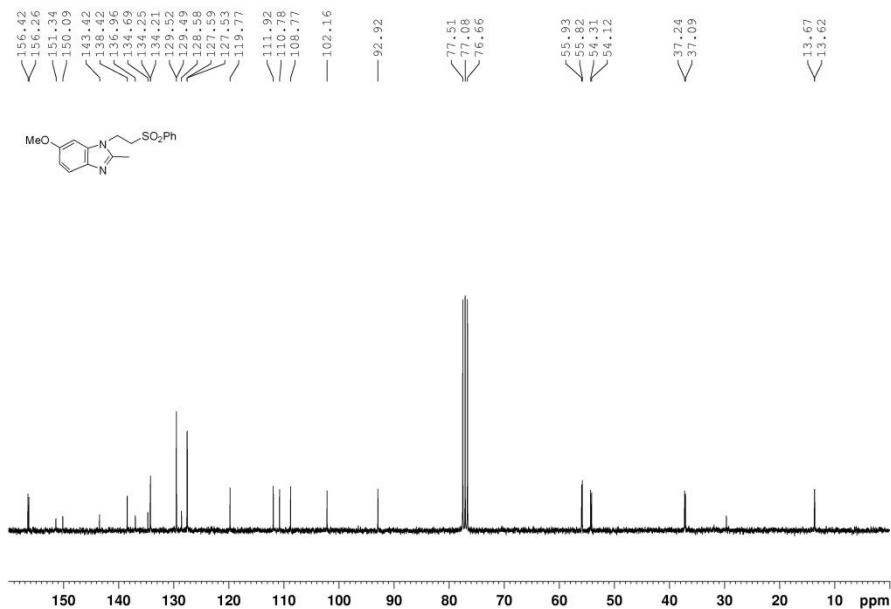


Figure S25 ¹³C NMR spectra of 6-methoxy-2-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ga**) and 5-methoxy-2-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ga'**)

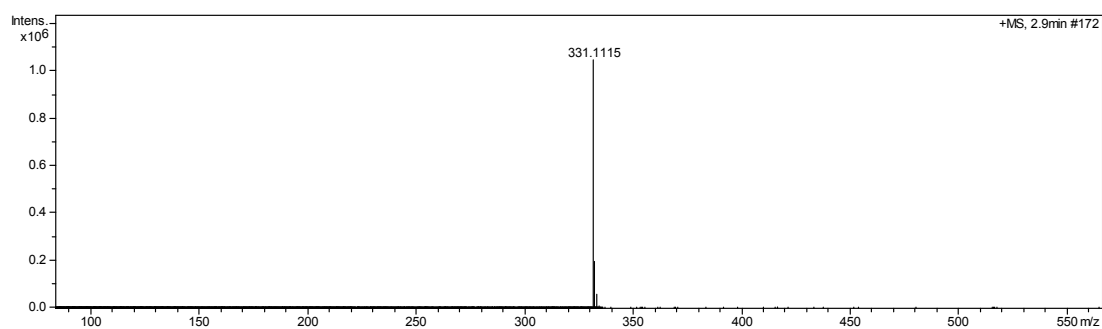


Figure S26 HMRS spectra of 6-methoxy-2-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ga**) and 5-methoxy-2-methyl-1-(2-(phenylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ga'**)

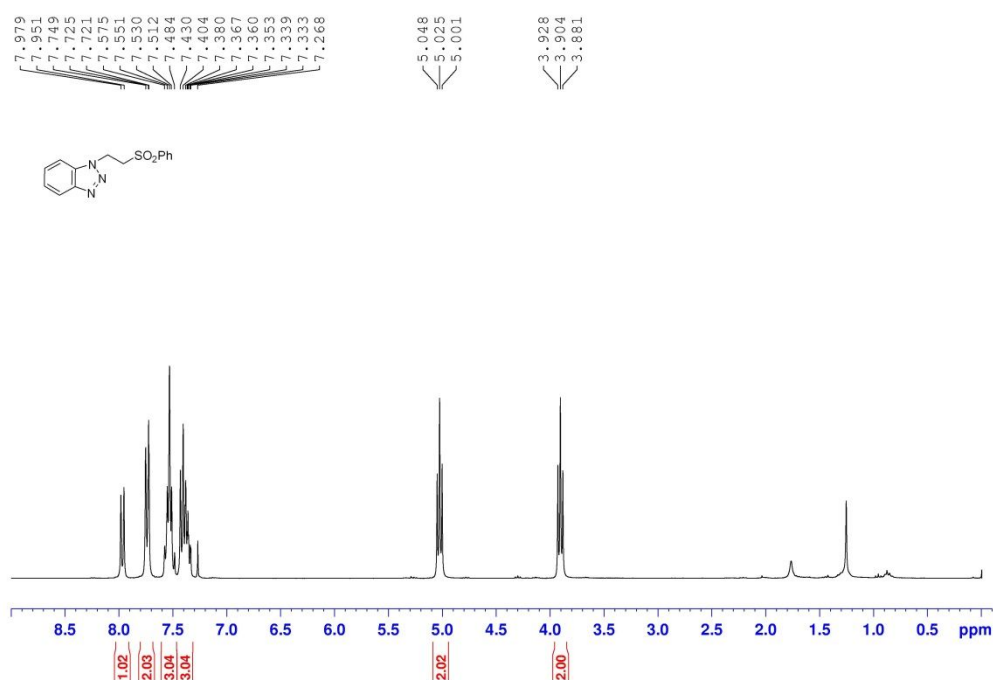


Figure S27 ¹H NMR spectra of 1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d][1,2,3]triazole (**3ha**)⁶

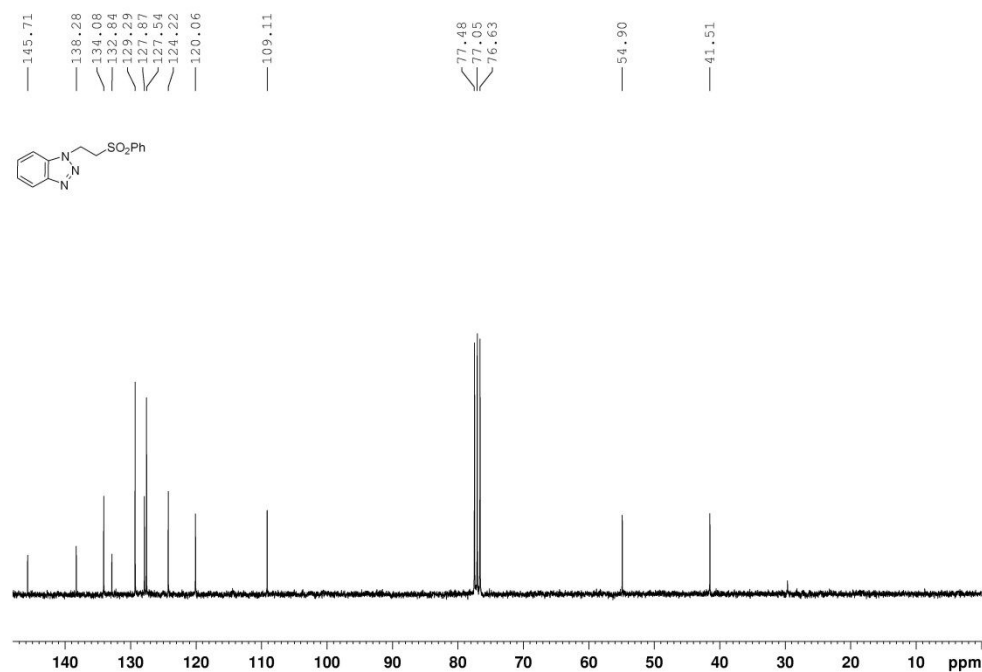


Figure S28 ¹³C NMR spectra of 1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d][1,2,3]triazole (**3ha**)⁶

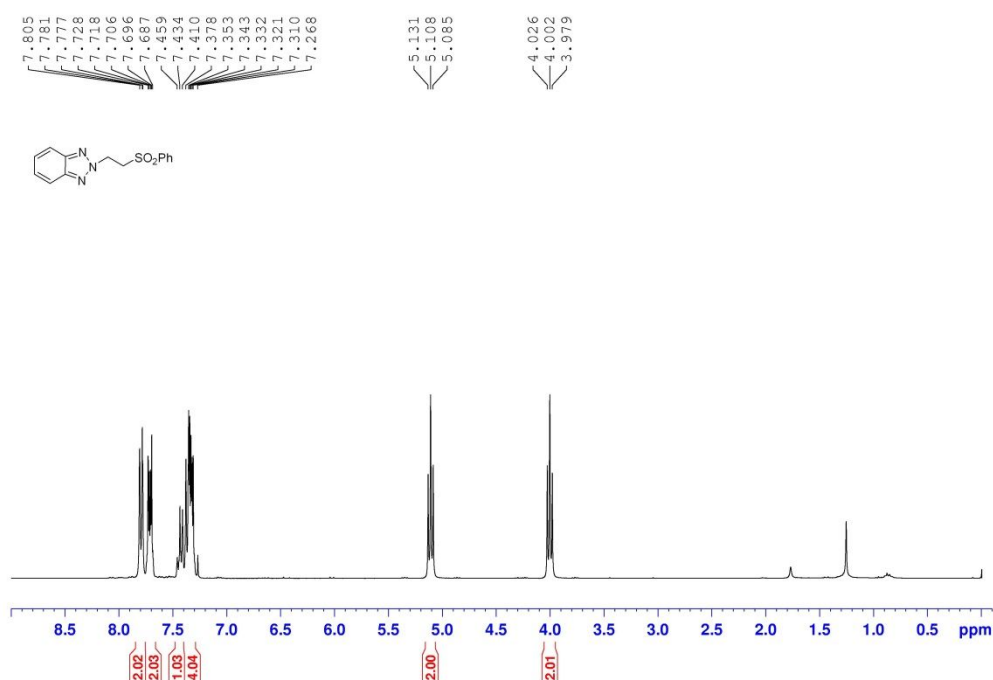


Figure S29 ¹H NMR spectra of 2-(2-(phenylsulfonyl)ethyl)-2*H*-benzo[*d*][1,2,3]triazole (**3ha'**)

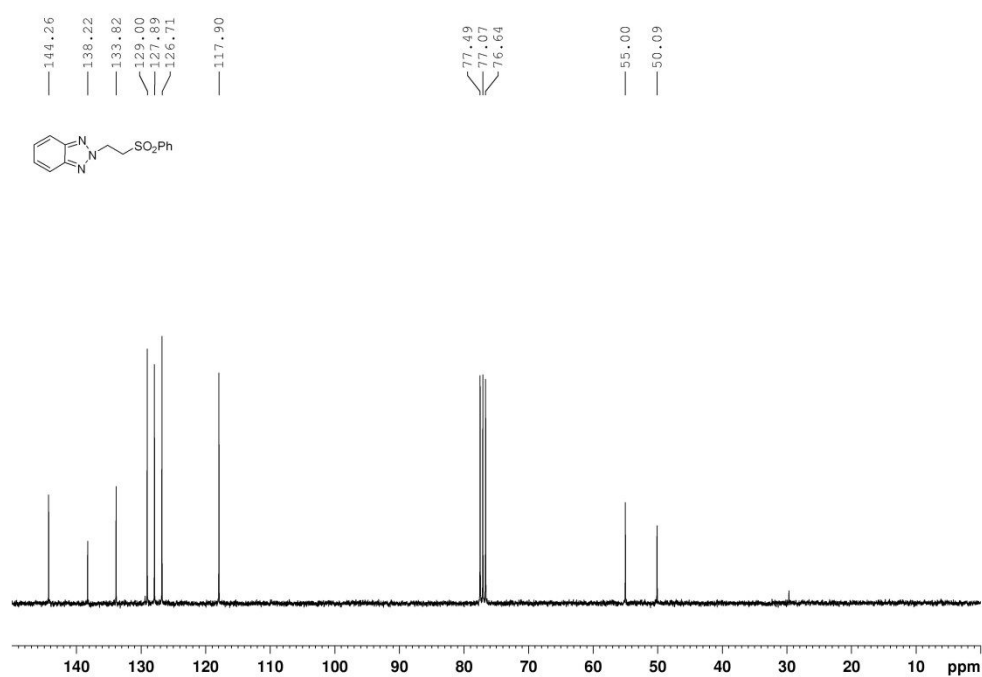


Figure S30 ¹³C NMR spectra of 2-(2-(phenylsulfonyl)ethyl)-2*H*-benzo[*d*][1,2,3]triazole (**3ha'**)

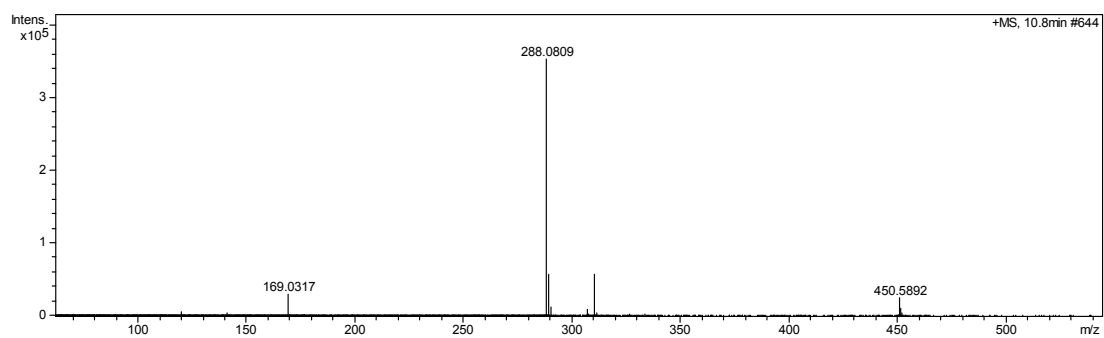


Figure S31 HRMS spectra of 2-(2-(phenylsulfonyl)ethyl)-2*H*-benzo[*d*][1,2,3]triazole (3ha')

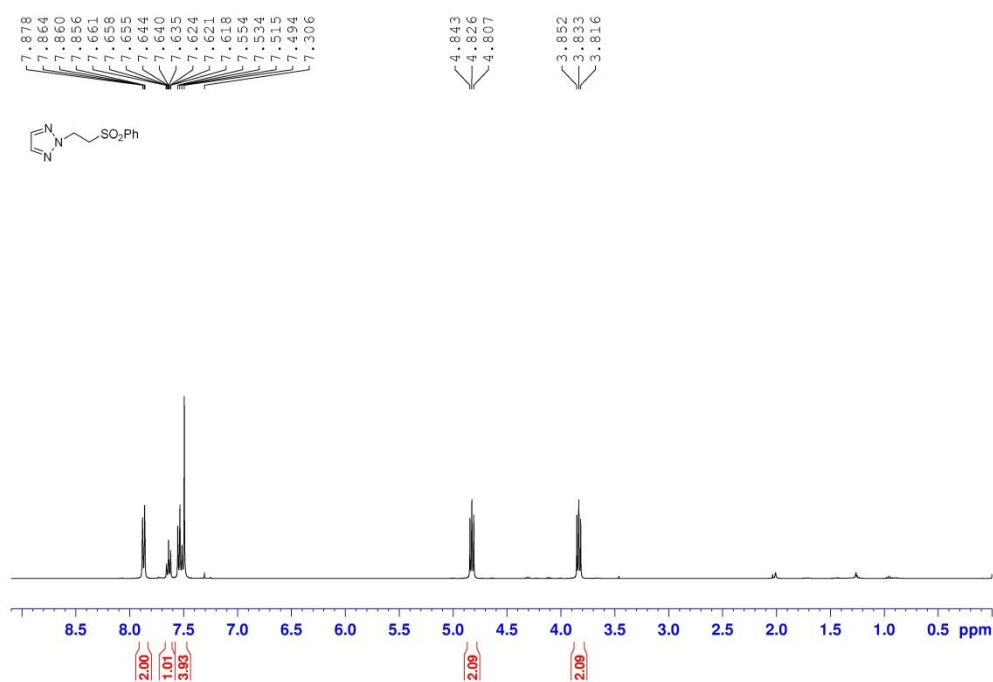


Figure S32 ¹H NMR spectra of 2-(2-(phenylsulfonyl)ethyl)-2*H*-1,2,3-triazole (**3ia**)

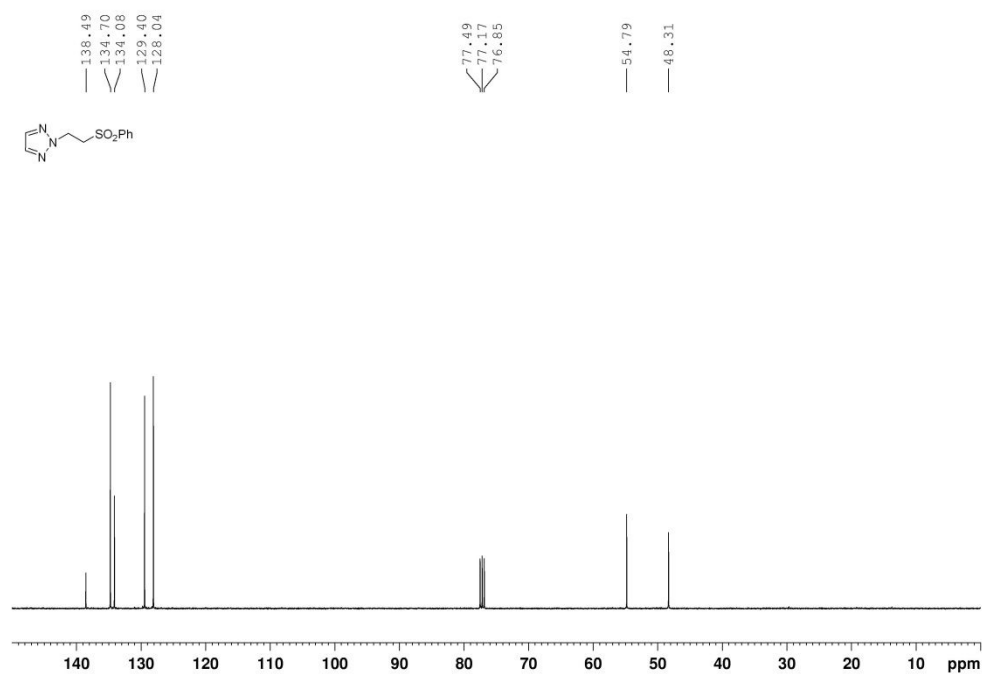


Figure S33 ¹³C NMR spectra of 2-(2-(phenylsulfonyl)ethyl)-2*H*-1,2,3-triazole (**3ia**)

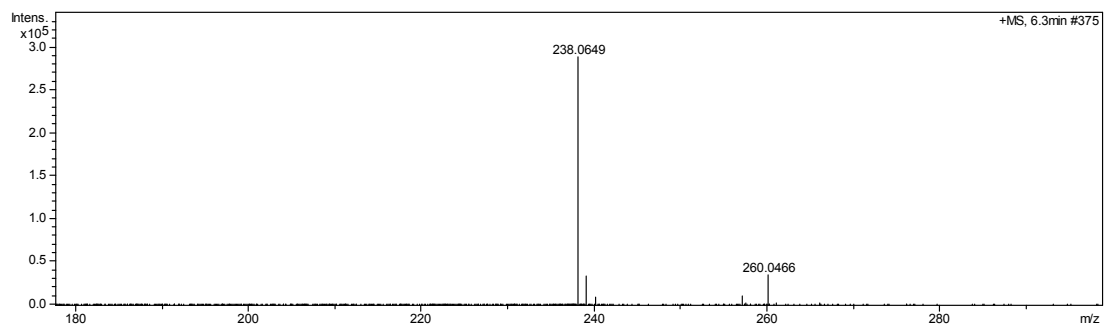


Figure S34 HRMS spectra of 2-(2-(phenylsulfonyl)ethyl)-2H-1,2,3-triazole (**3ia**)

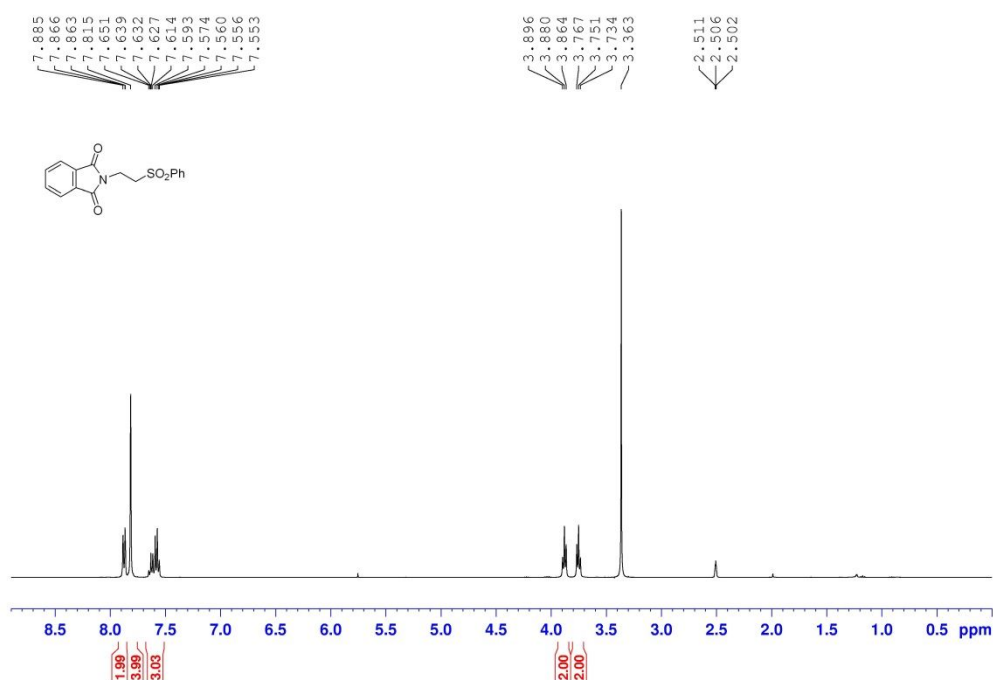


Figure S35 ¹H NMR spectra of 2-(2-(phenylsulfonyl)ethyl)isoindoline-1,3-dione (**3ja**)

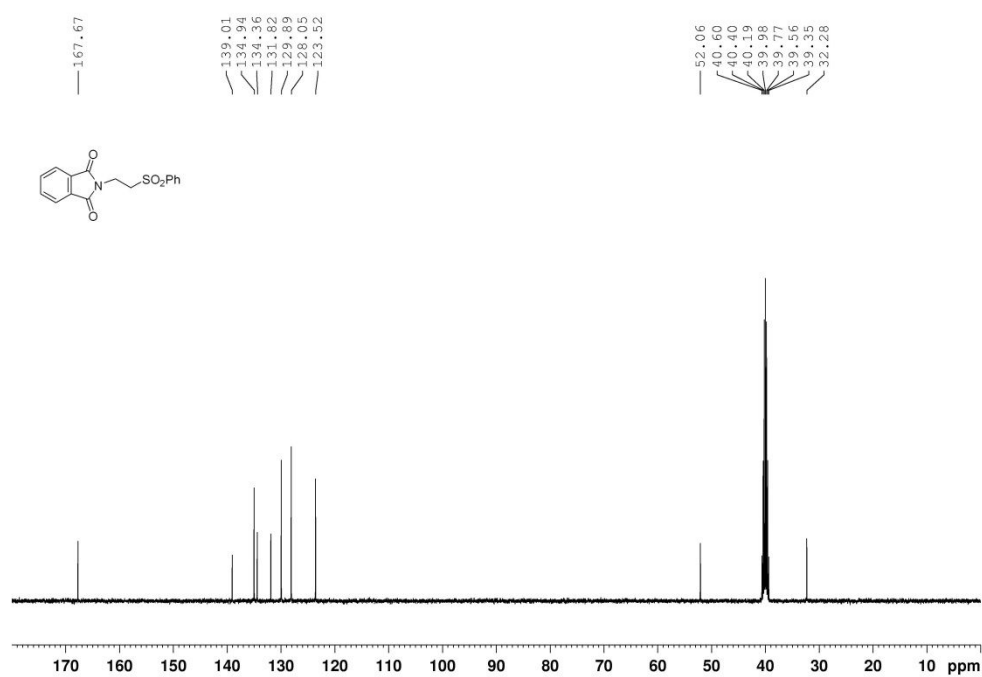


Figure S36 ¹³C NMR spectra of 2-(2-(phenylsulfonyl)ethyl)isoindoline-1,3-dione (**3ja**)

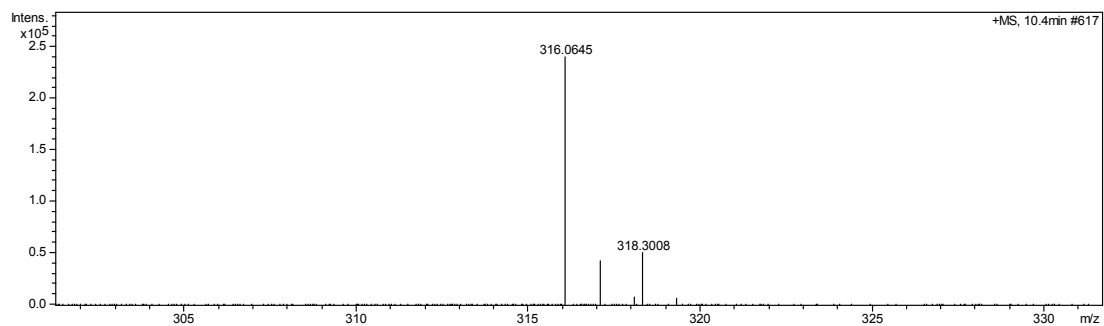


Figure S37 HRMS spectra of 2-(2-(phenylsulfonyl)ethyl)isoindoline-1,3-dione (**3ja**)

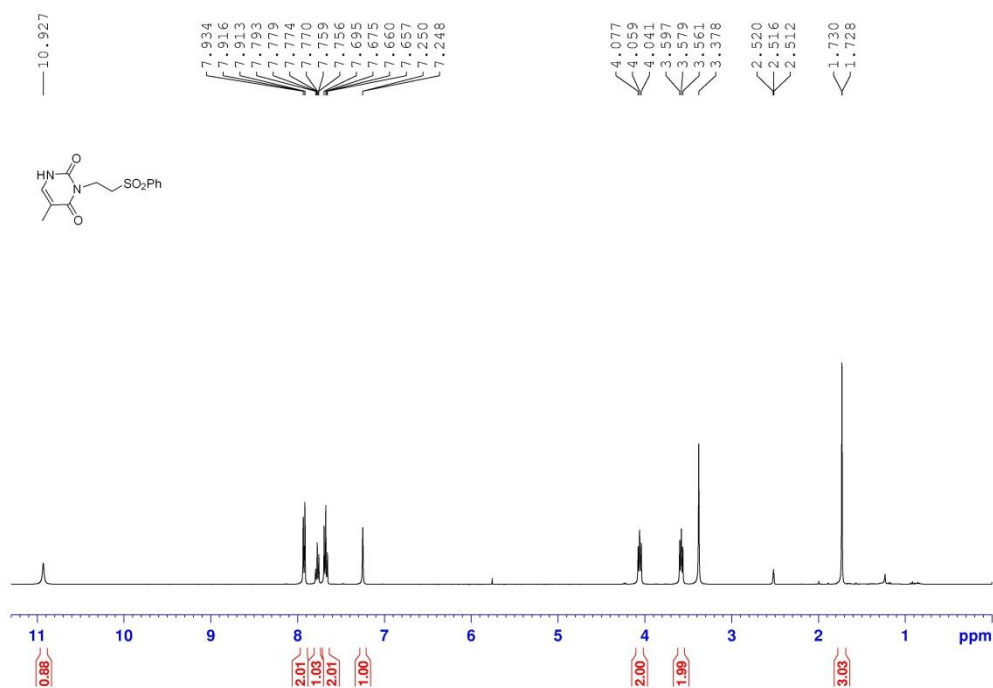


Figure S38 ¹H NMR spectra of 5-methyl-3-(2-(phenylsulfonyl)ethyl)pyrimidine-2,4(1H,3H)-dione (**3ka**)

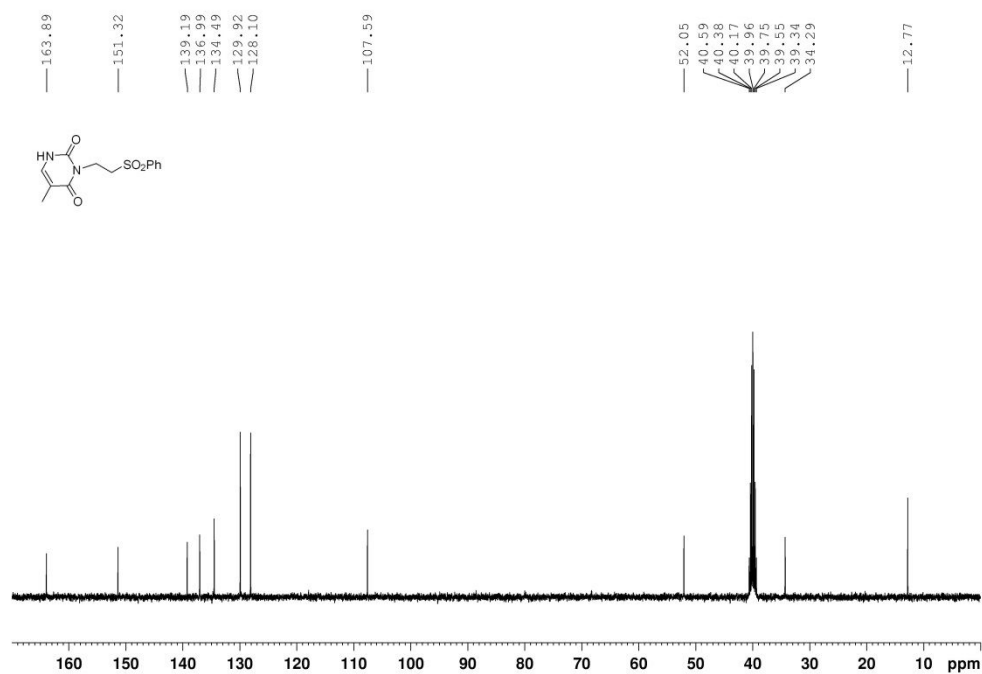


Figure S39 ¹³C NMR spectra of 5-methyl-3-(2-(phenylsulfonyl)ethyl)pyrimidine-2,4(1H,3H)-dione (**3ka**)

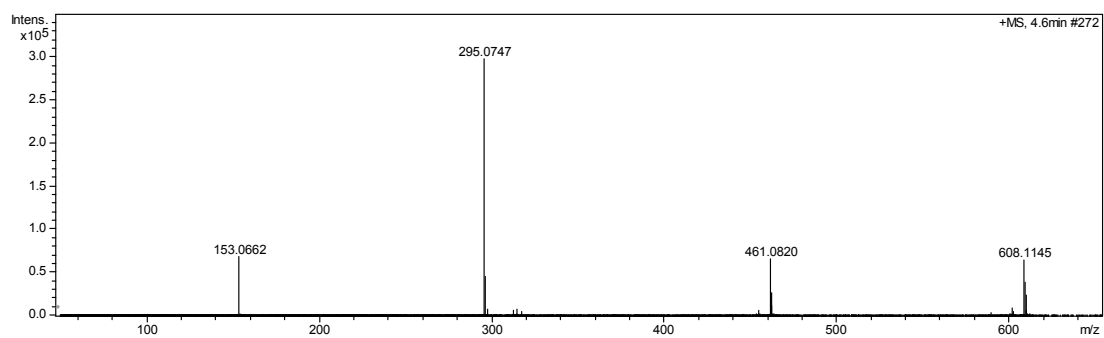


Figure S40 HRMS spectra of 5-methyl-3-(2-(phenylsulfonyl)ethyl)pyrimidine-2,4(1*H*,3*H*)-dione (**3ka**)

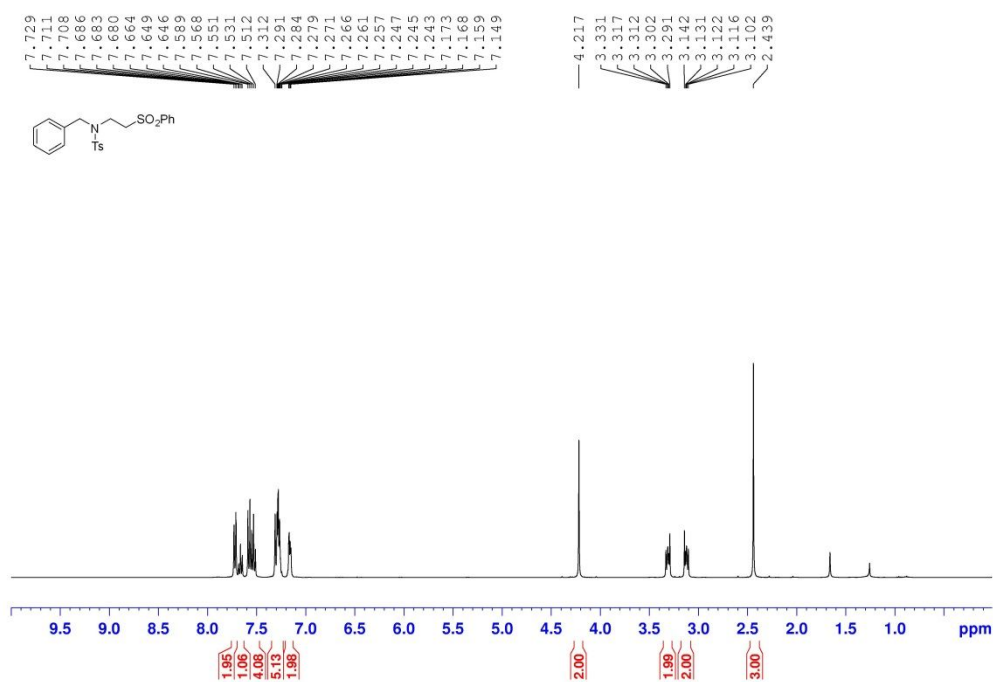


Figure S41 ¹H NMR spectra of *N*-benzyl-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**3la**)

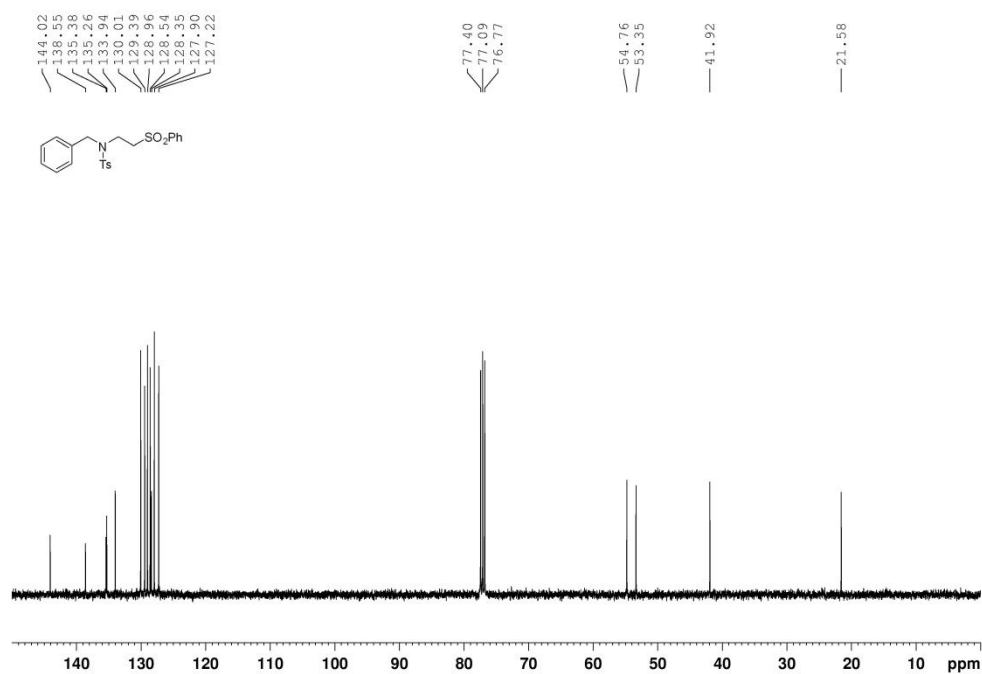


Figure S42 ¹³C NMR spectra of *N*-benzyl-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**3la**)

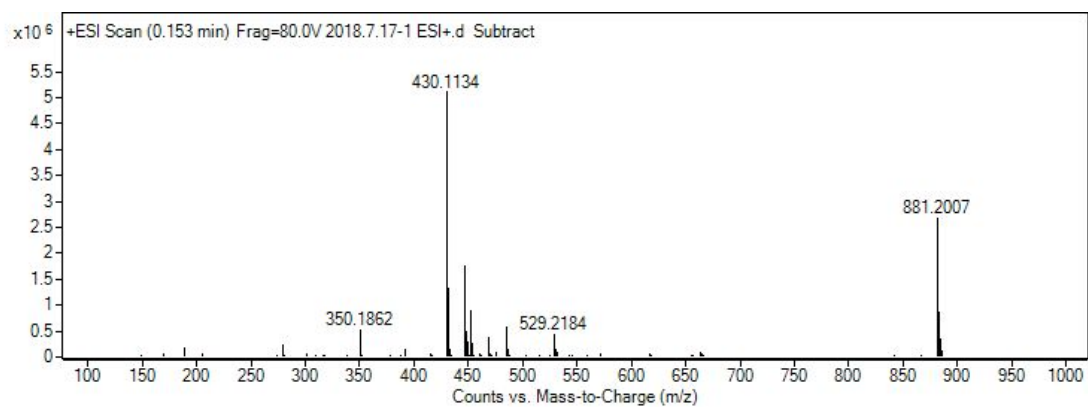


Figure S43 HRMS NMR spectra of *N*-benzyl-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**31a**)

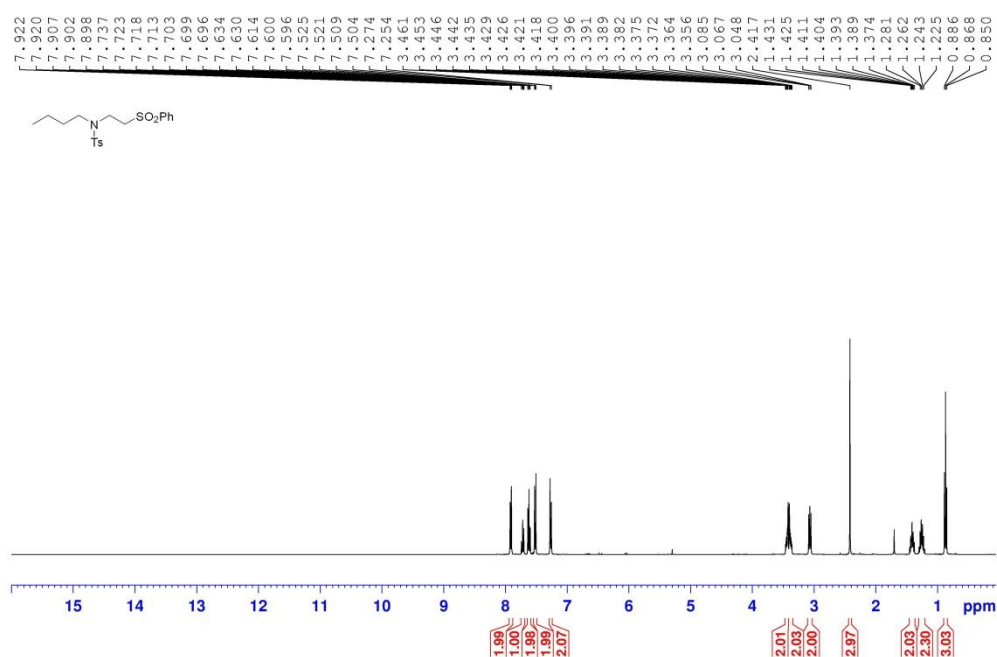


Figure S44 ¹H NMR spectra of *N*-butyl-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**3ma**)

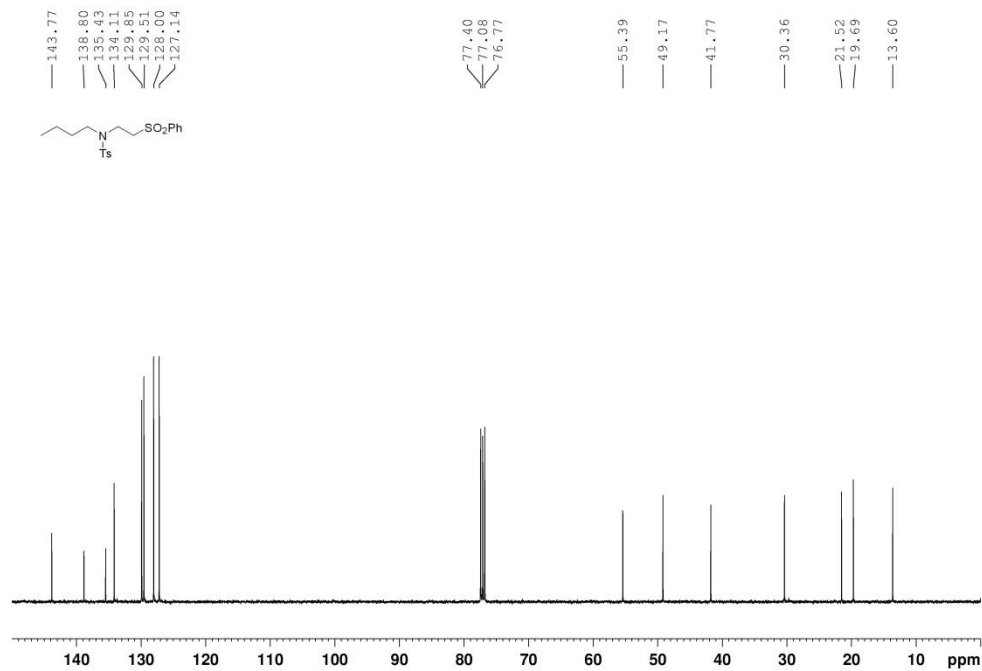


Figure S45 ¹³C NMR spectra of *N*-butyl-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**3ma**)

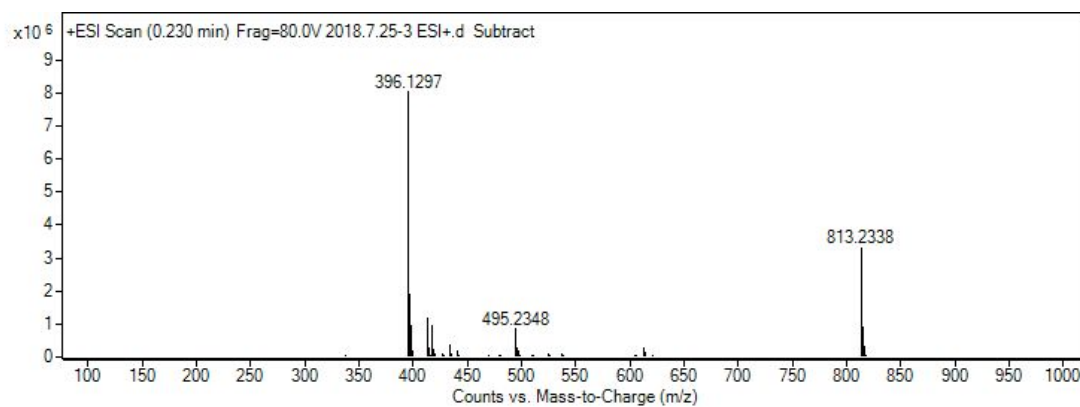


Figure S46 HRMS NMR spectra of *N*-butyl-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**3ma**)

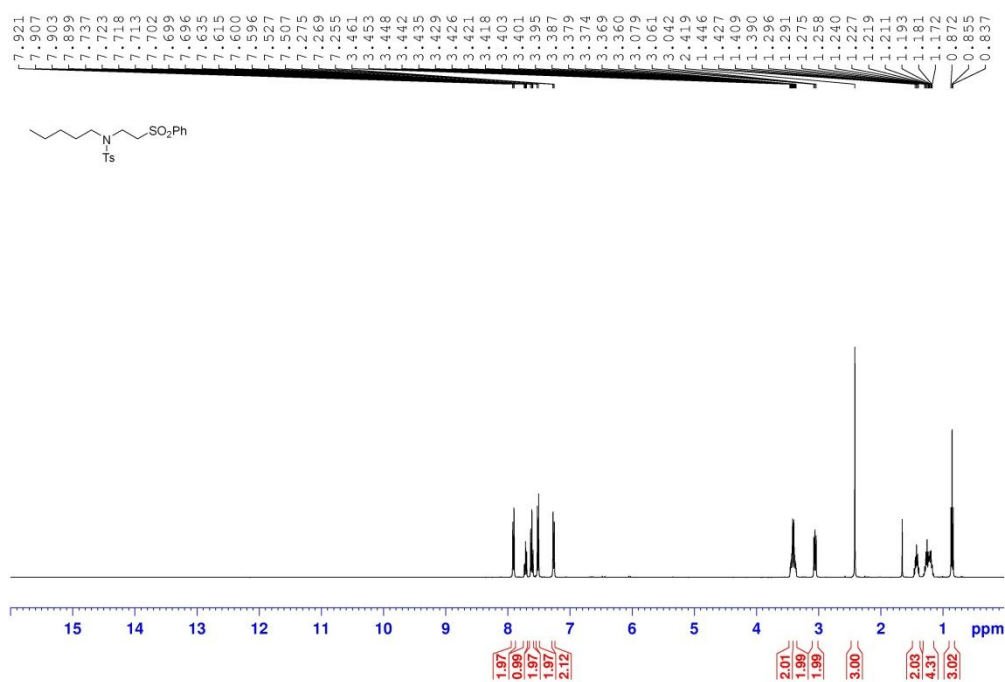


Figure S47 ¹H NMR spectra of 4-methyl-N-pentyl-N-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**3na**)

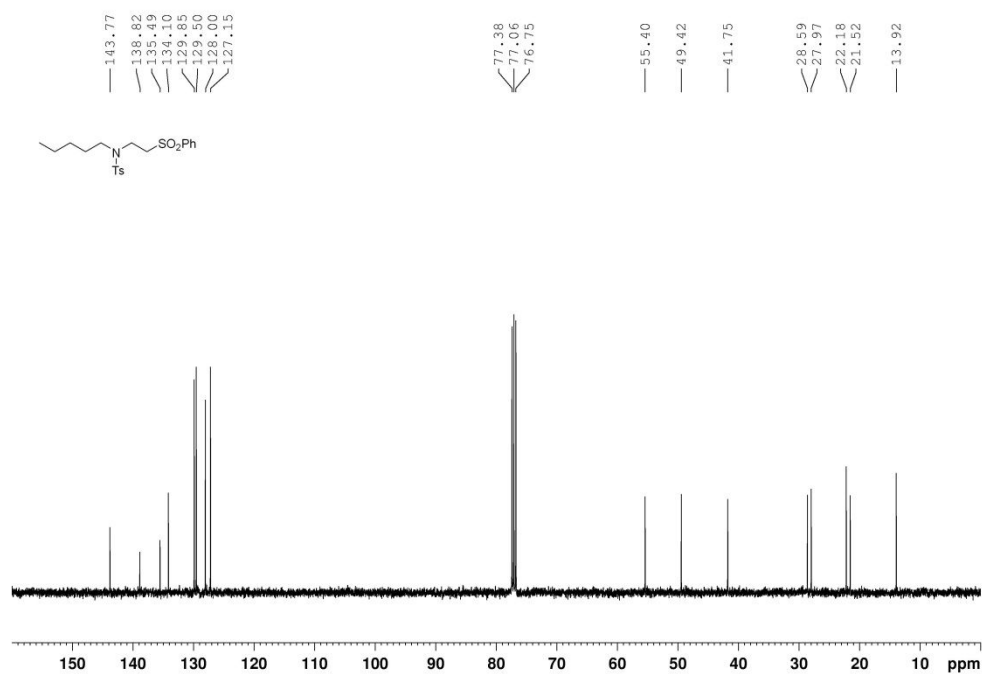


Figure S48 ¹³C NMR spectra of 4-methyl-N-pentyl-N-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**3na**)

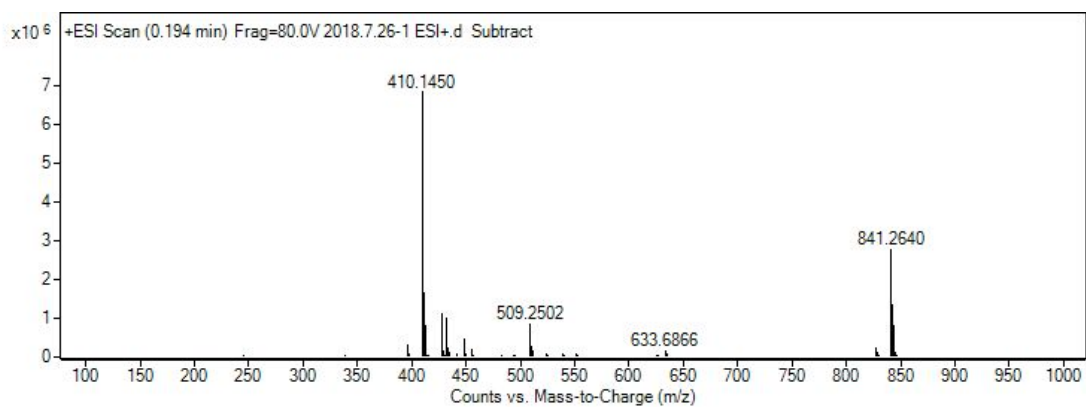


Figure S49 HRMS NMR spectra of 4-methyl-N-pentyl-N-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**3na**)

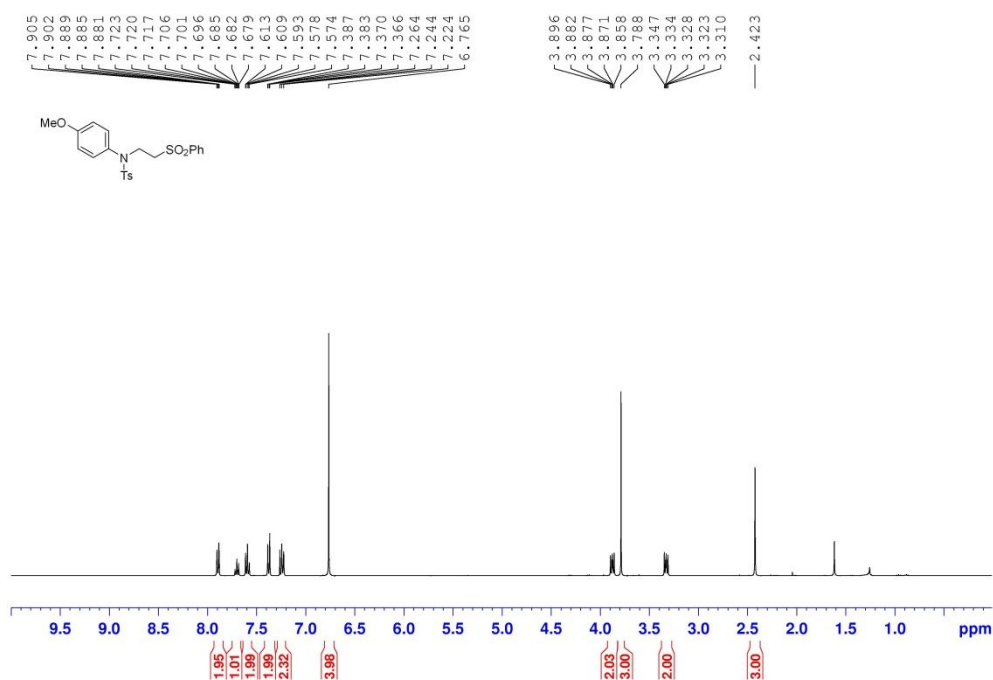


Figure S50 ¹H NMR spectra of *N*-(4-methoxyphenyl)-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**30a**)

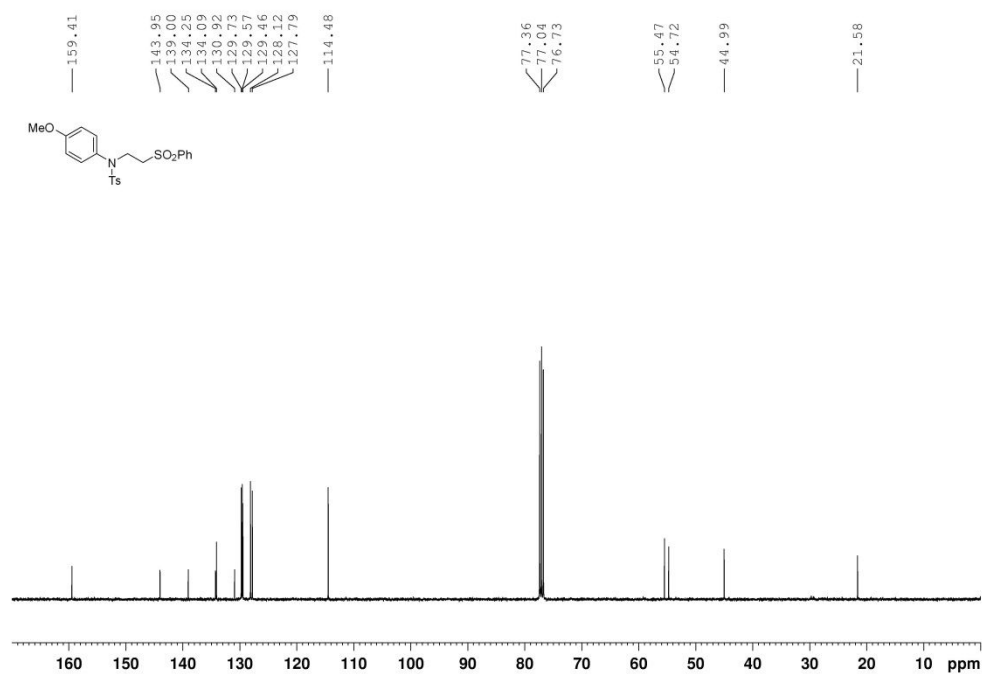


Figure S51 ¹³C NMR spectra of *N*-(4-methoxyphenyl)-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**30a**)

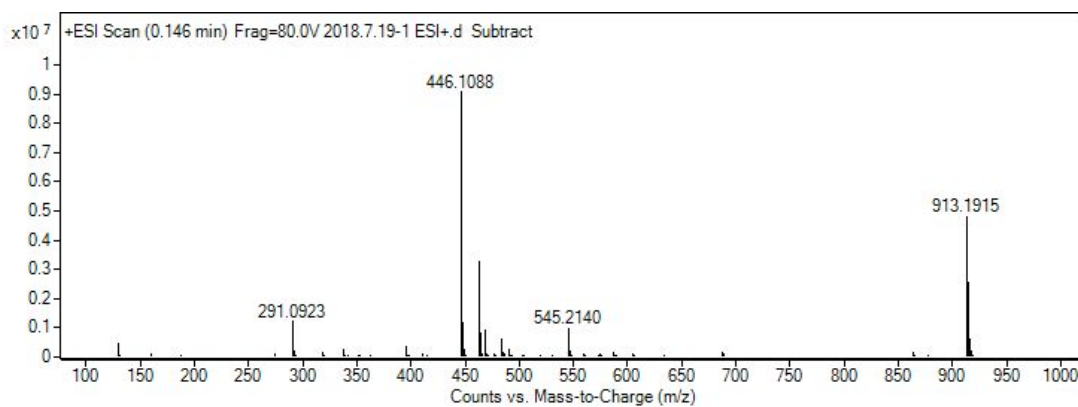


Figure S52 HRMS NMR spectra of *N*-(4-methoxyphenyl)-4-methyl-*N*-(2-(phenylsulfonyl)ethyl)benzenesulfonamide (**30a**)

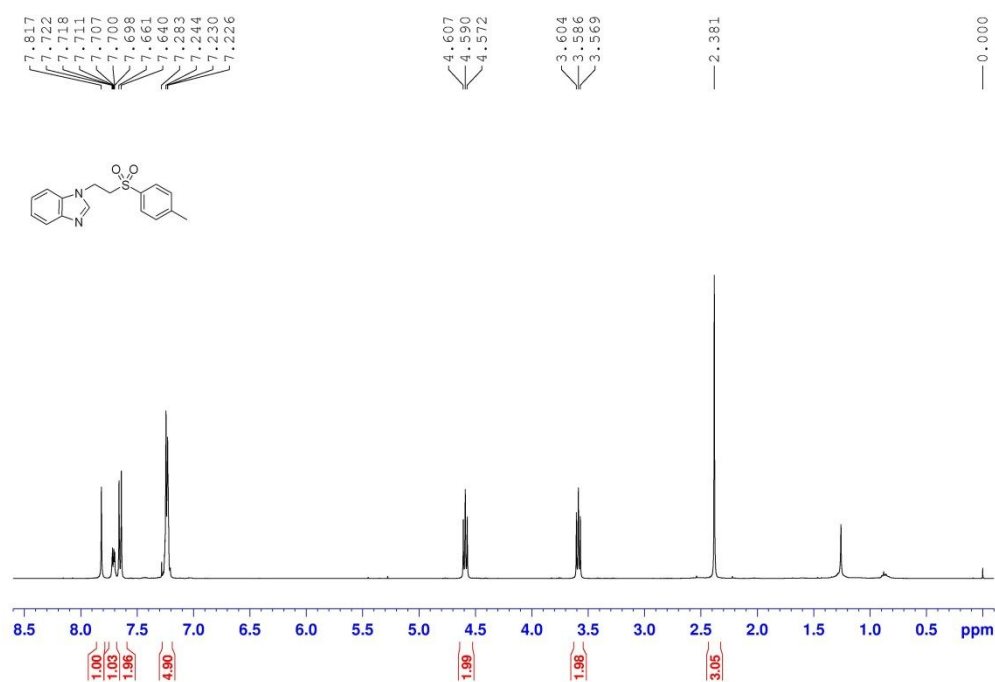


Figure S53 ¹H NMR spectra of 1-(2-tosylethyl)-1*H*-benzo[*d*]imidazole (**3ab**)

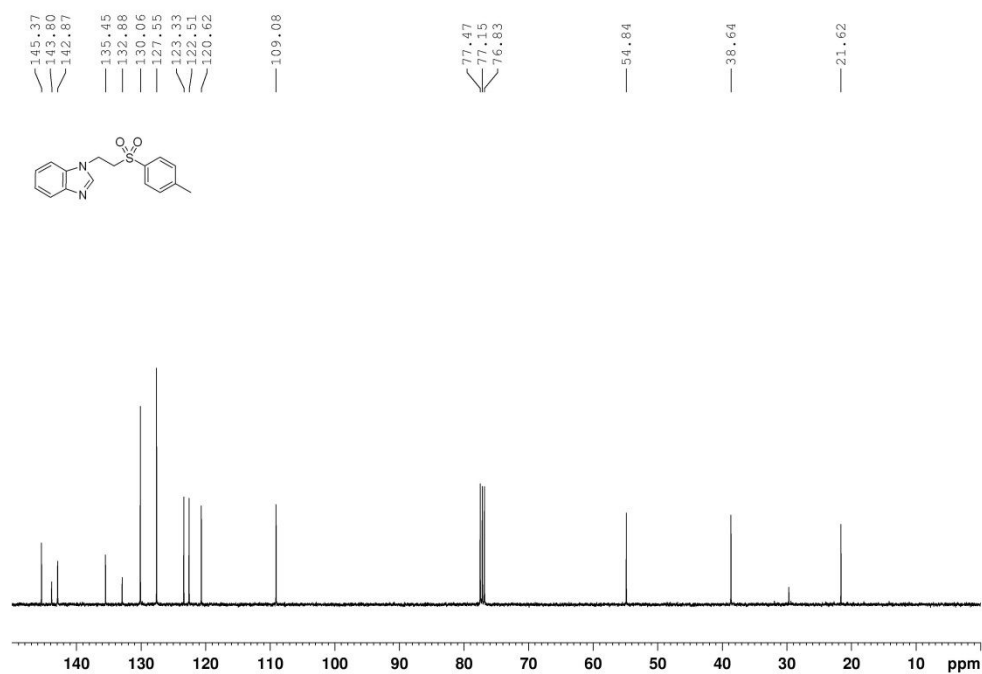


Figure S54 ¹³C NMR spectra of 1-(2-tosylethyl)-1*H*-benzo[*d*]imidazole (**3ab**)

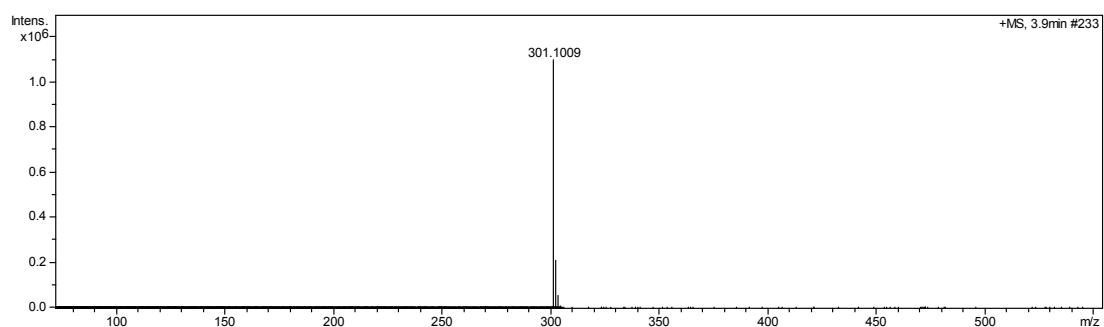


Figure S55 HRMS spectra of 1-(2-tosylethyl)-1*H*-benzo[*d*]imidazole (**3ab**)

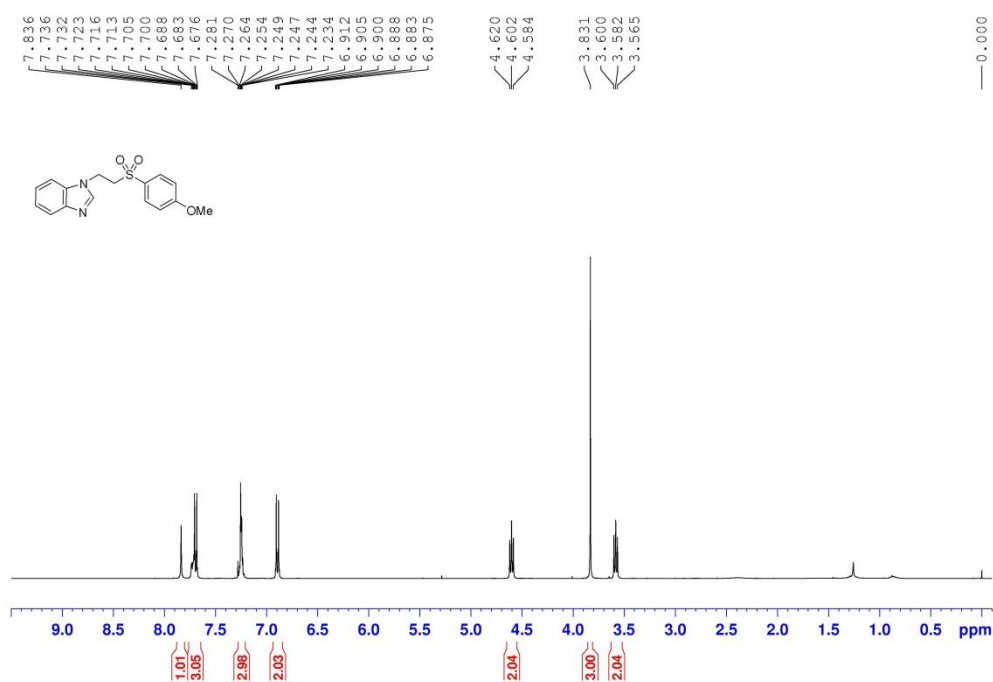


Figure S56 ¹H NMR spectra of 1-(2-((4-methoxyphenyl)sulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ac**)

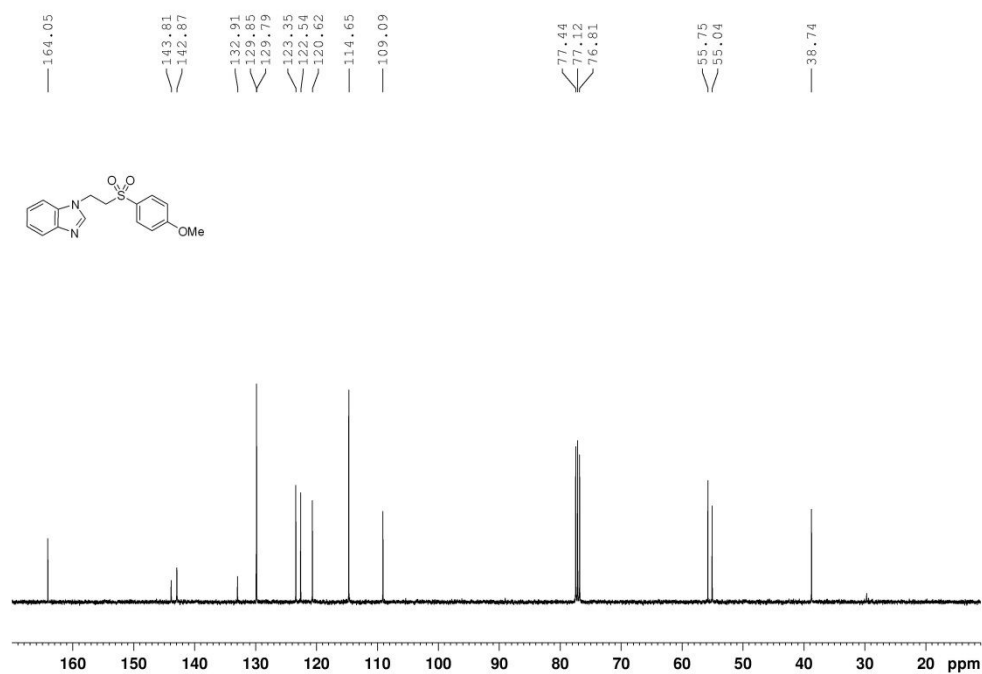


Figure S57 ¹³C NMR spectra of 1-(2-((4-methoxyphenyl)sulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ac**)

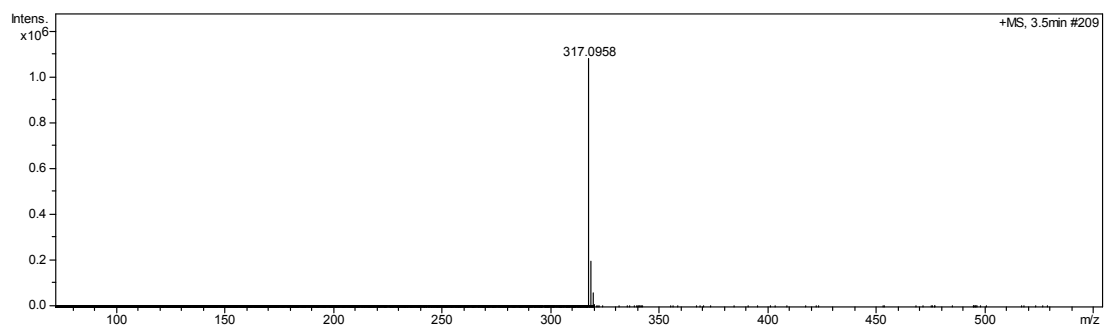


Figure S58 HRMS spectra of 1-(2-((4-methoxyphenyl)sulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ac**)

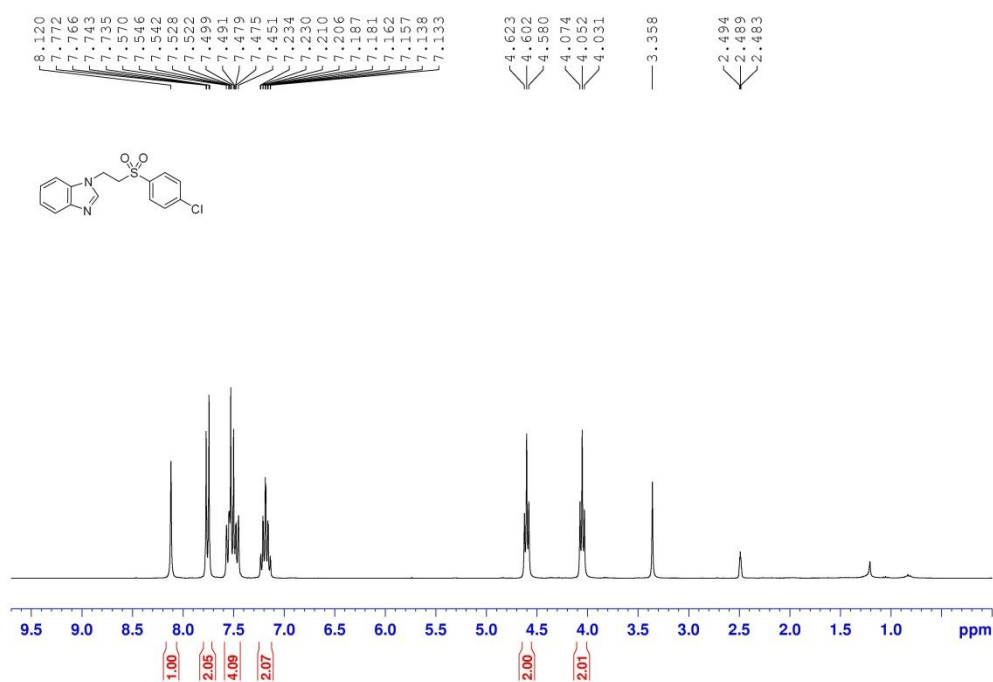


Figure S59 ¹H NMR spectra of 1-(2-((4-chlorophenyl)sulfonyl)ethyl)-1H-benzo[d]imidazole (**3ad**)

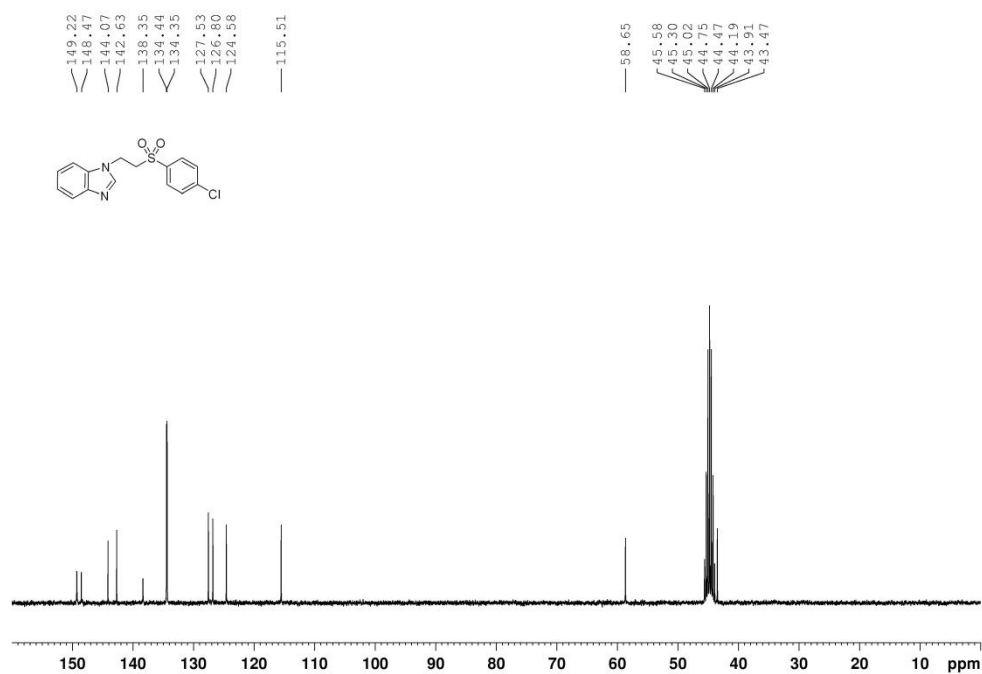


Figure S60 ¹³C NMR spectra of 1-(2-((4-chlorophenyl)sulfonyl)ethyl)-1H-benzo[d]imidazole (**3ad**)

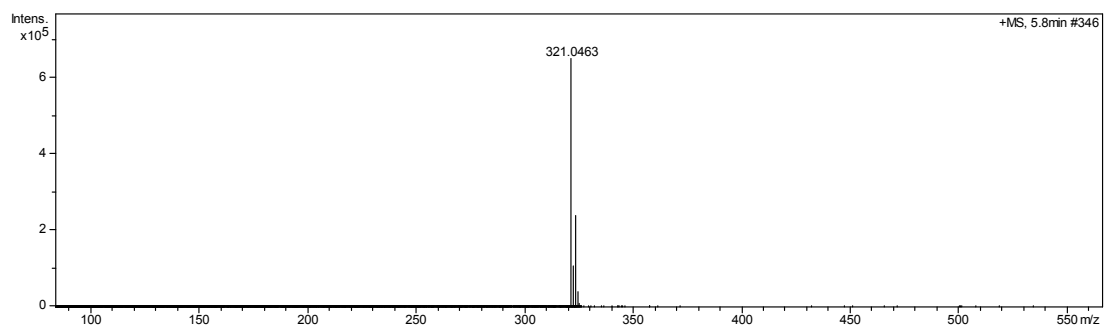


Figure S61 HRMS spectra of spectra of 1-(2-((4-chlorophenyl)sulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ad**)

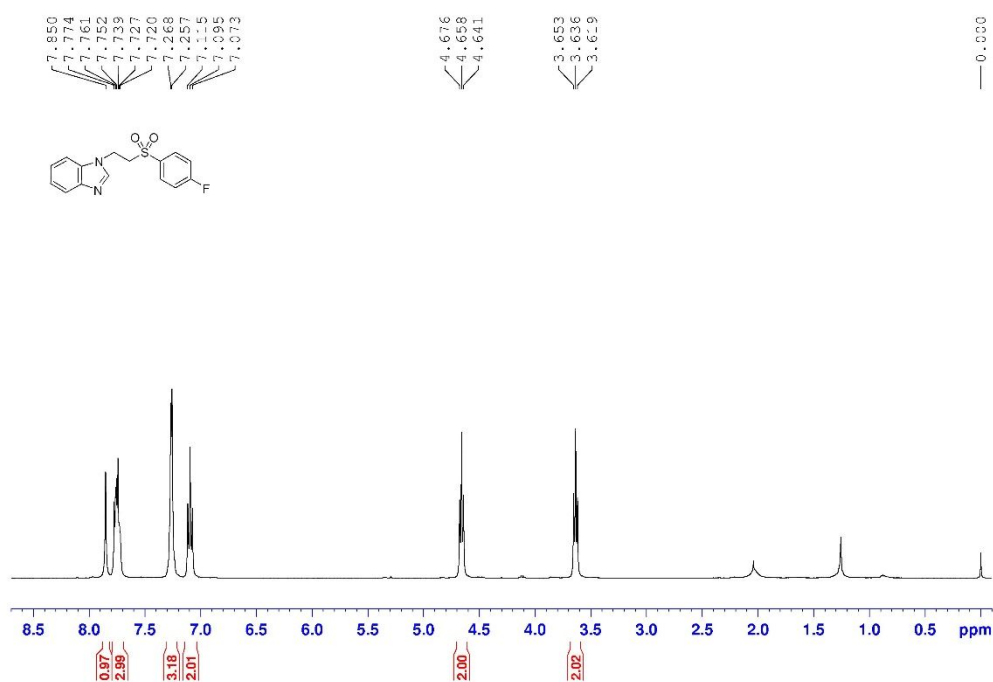


Figure S62 ¹H NMR spectra of 1-(2-((4-fluorophenyl)sulfonyl)ethyl)-1H-benzo[d]imidazole (**3ae**)

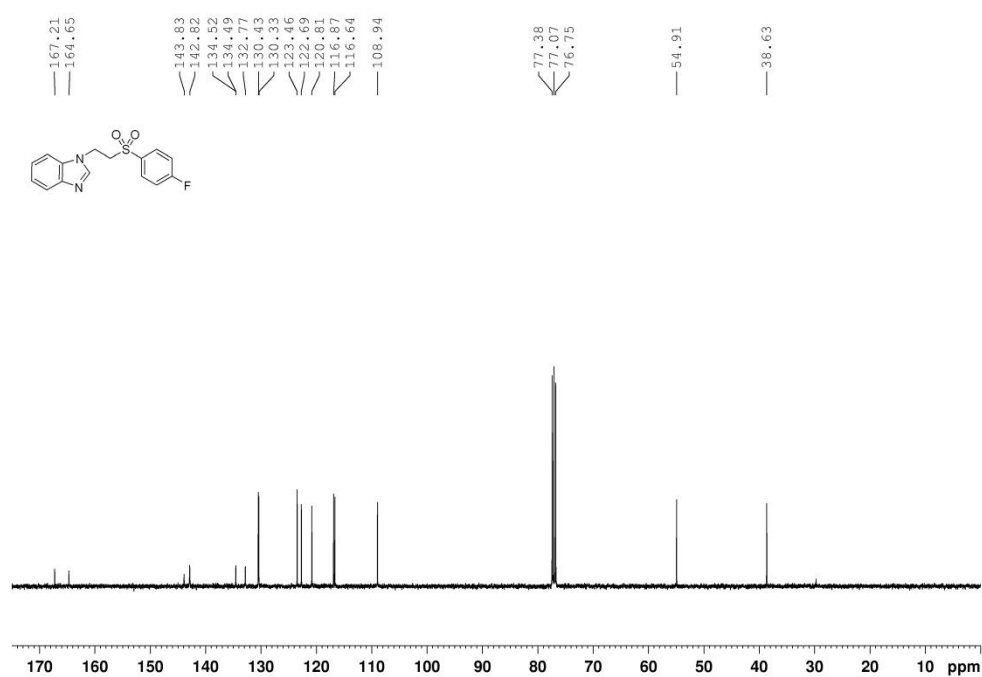


Figure S63 ¹³C NMR spectra of 1-(2-((4-fluorophenyl)sulfonyl)ethyl)-1H-benzo[d]imidazole (**3ae**)

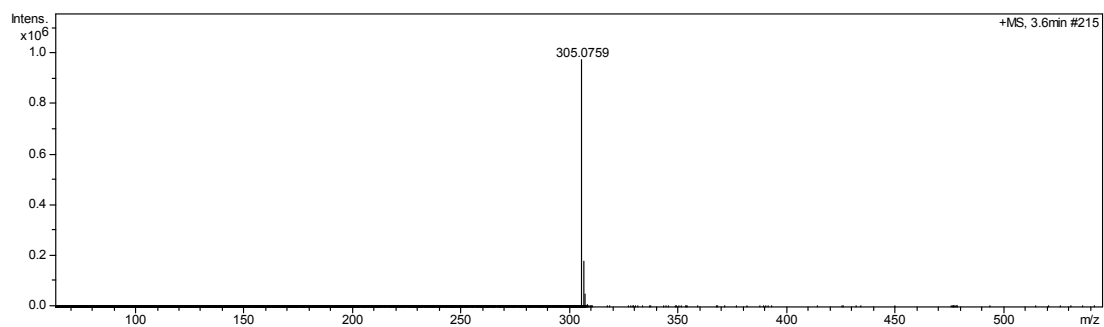


Figure S64 HRMS spectra of 1-(2-((4-fluorophenyl)sulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ae**)

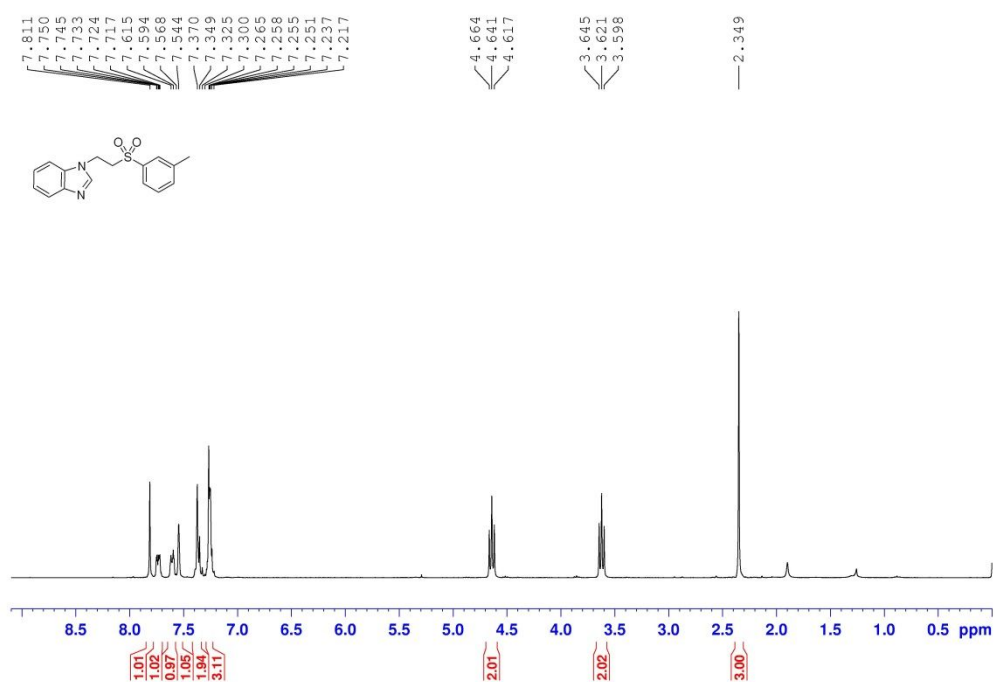


Figure S65 ¹H NMR spectra of 1-(2-(m-tolylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3af)

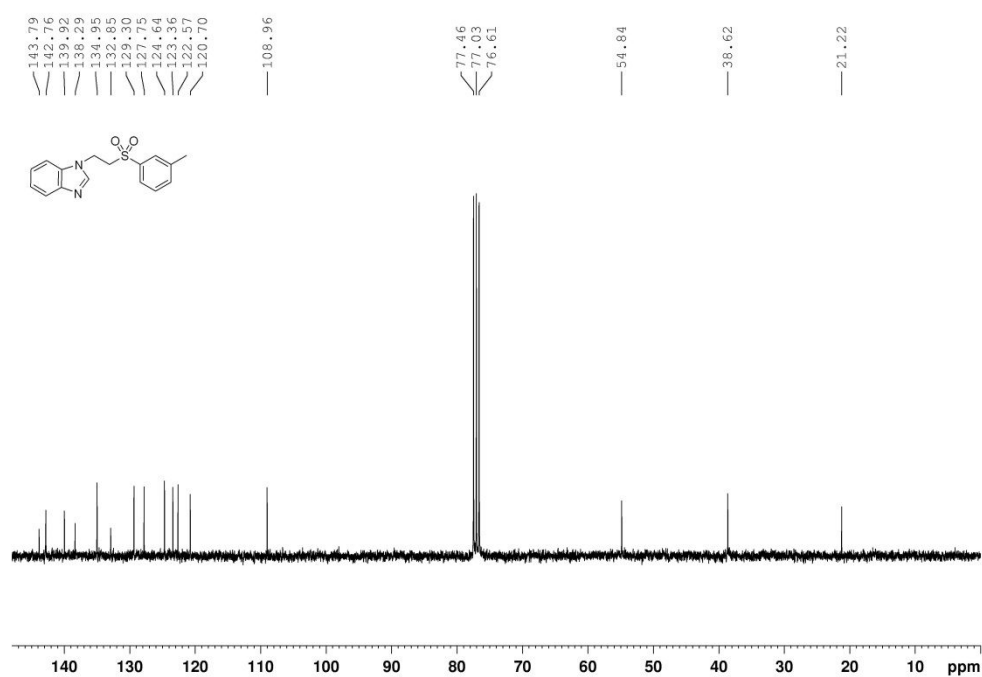


Figure S66 ¹³C NMR spectra of 1-(2-(m-tolylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3af)

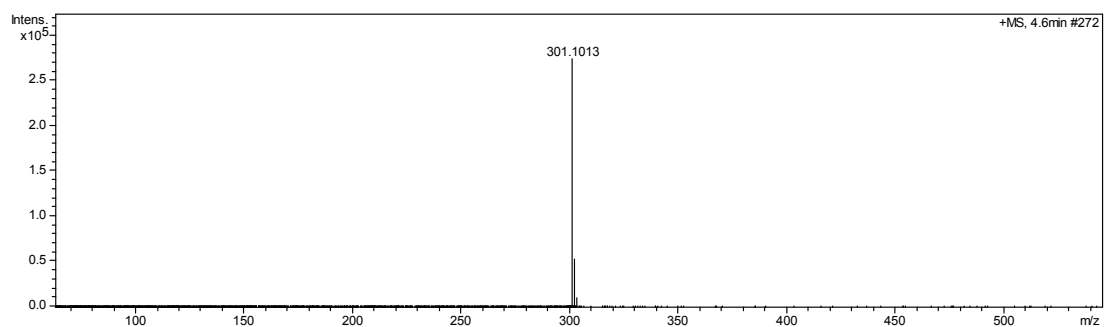


Figure S67 HRMS spectra of 1-(2-(m-tolylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3af**)

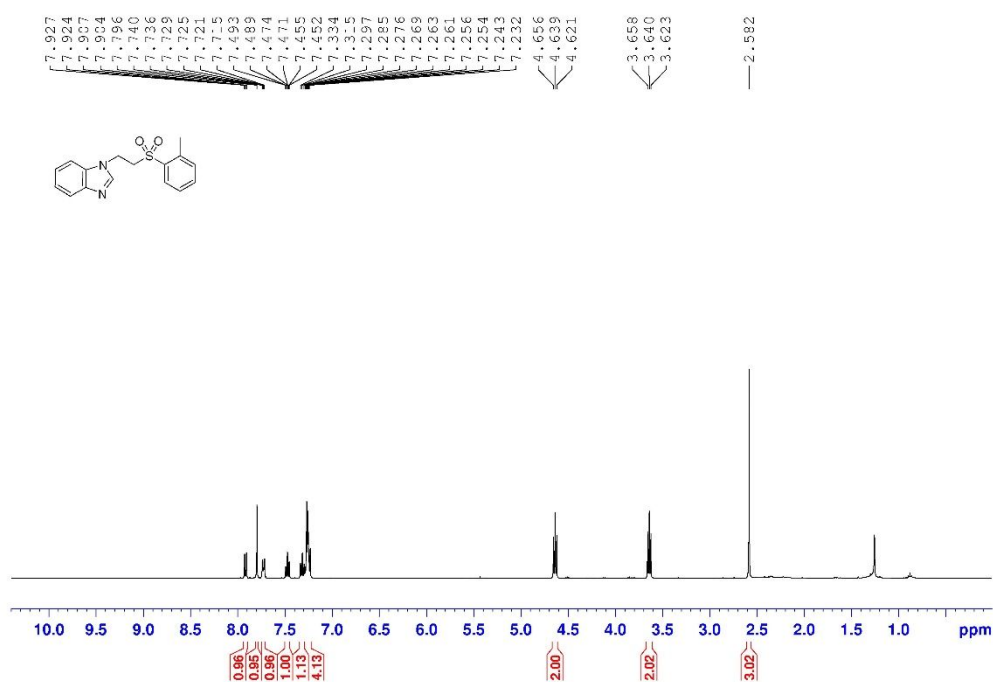


Figure S68 ¹H NMR spectra of 1-(2-(o-tolylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ag)

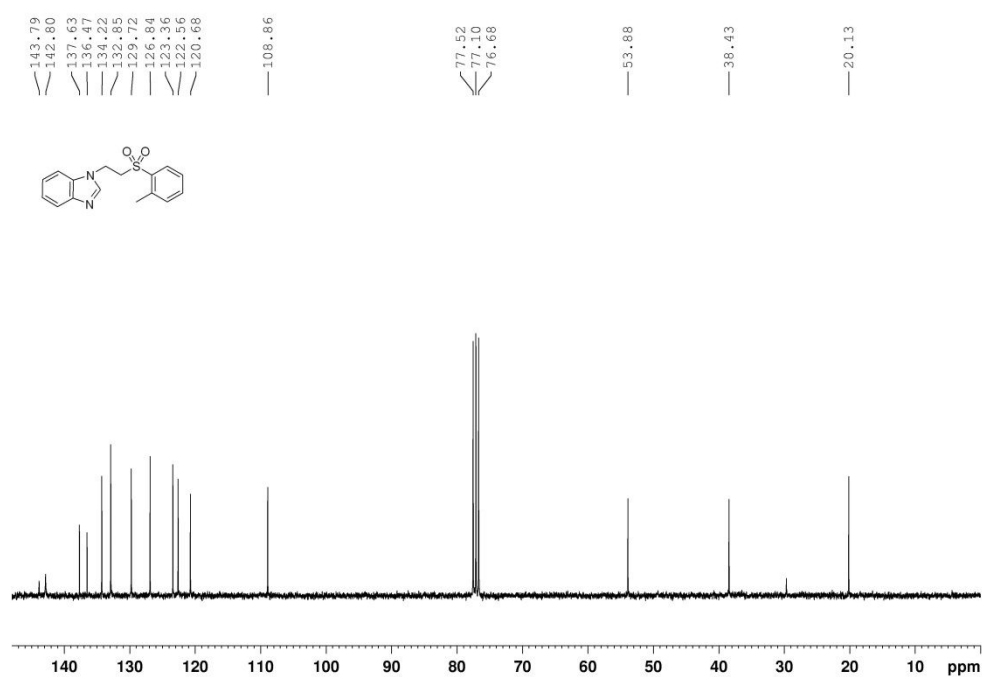


Figure S69 ¹³C NMR spectra of 1-(2-(o-tolylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ag)

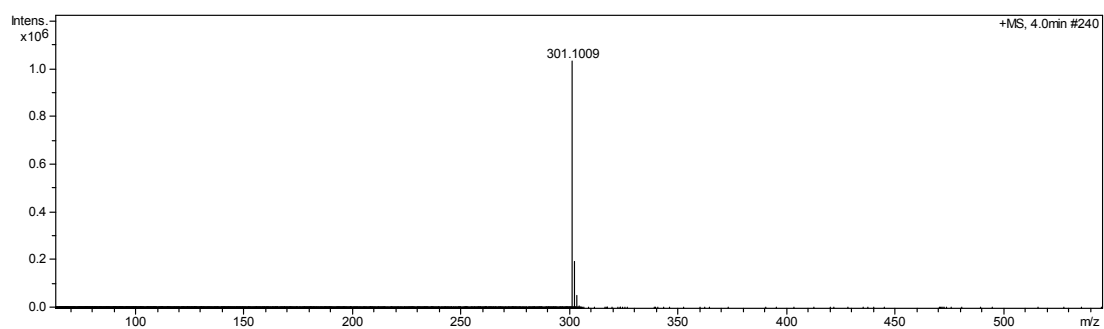


Figure S70 HRMS spectra of 1-(2-(o-tolylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ag**)

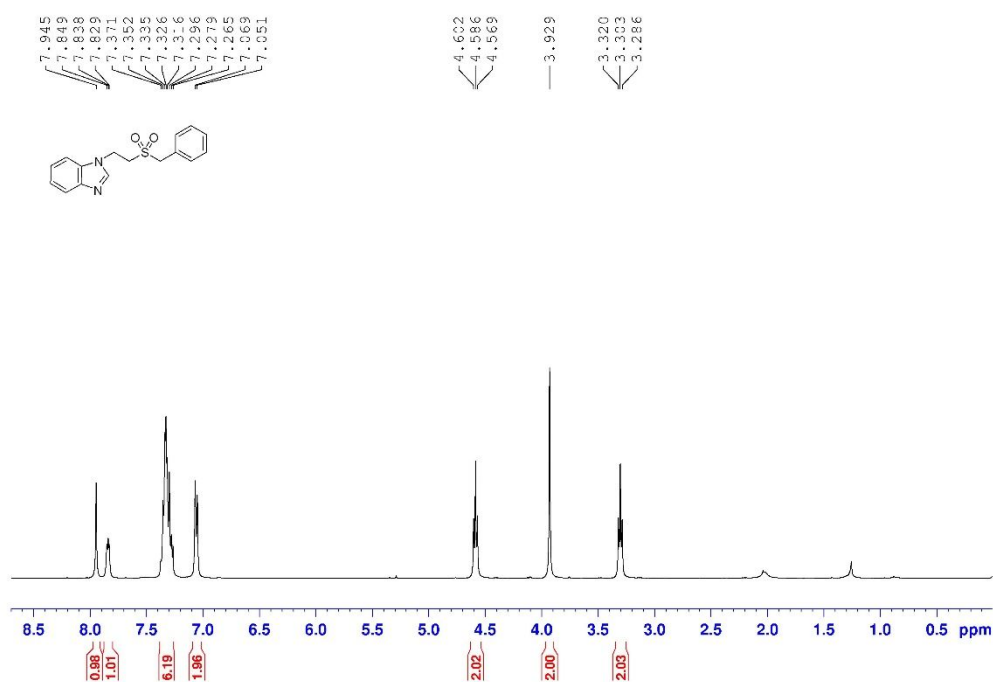


Figure S71 ¹H NMR spectra of 1-(2-(benzylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ah)

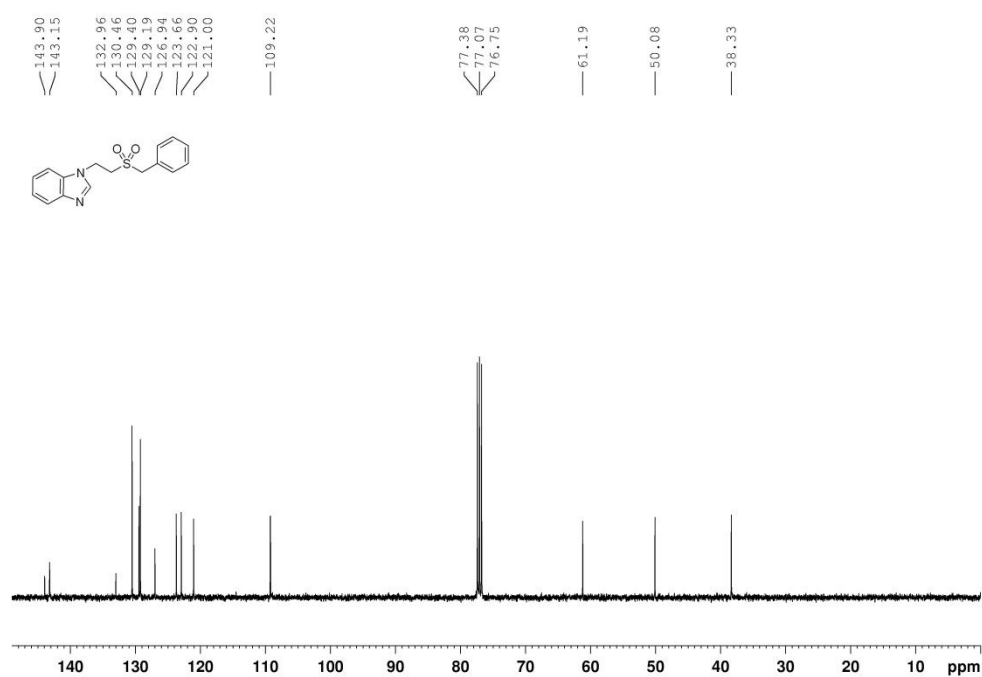


Figure S72 ¹³C NMR spectra of 1-(2-(benzylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ah)

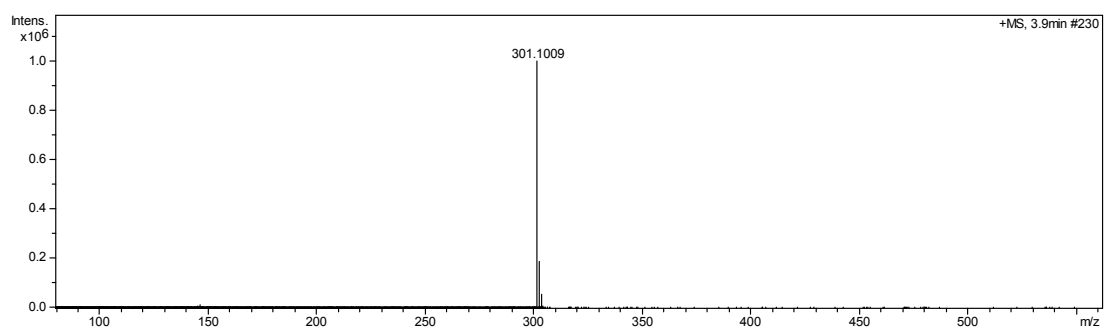


Figure S73 HRMS spectra of 1-(2-(benzylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ah**)

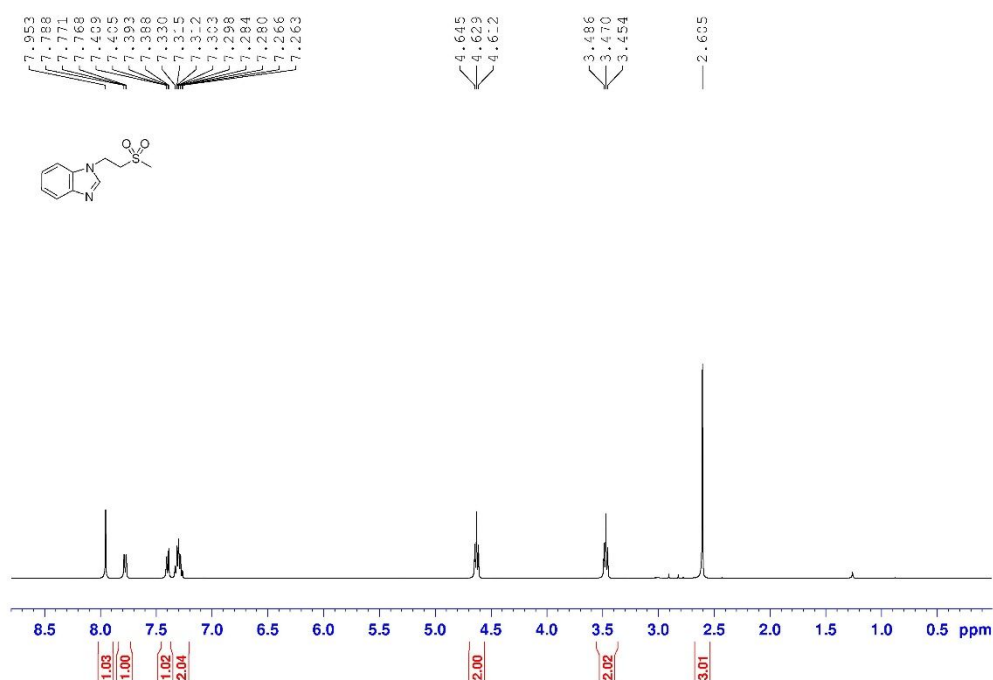


Figure S74 ¹H NMR spectra of 1-(2-(methylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ai)

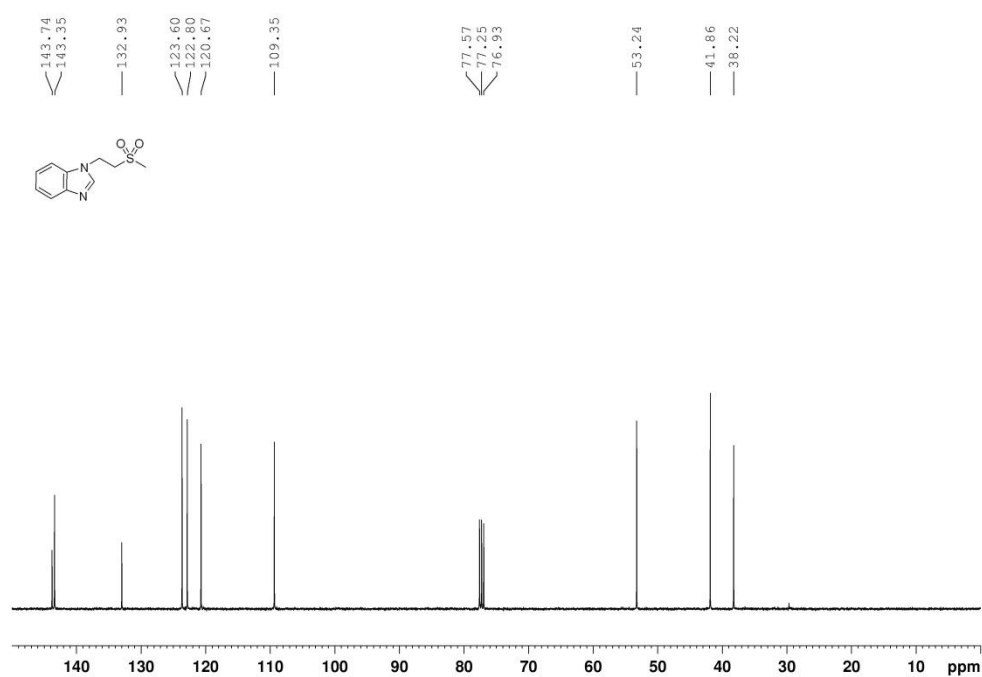


Figure S75 ¹³C NMR spectra of 1-(2-(methylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (3ai)

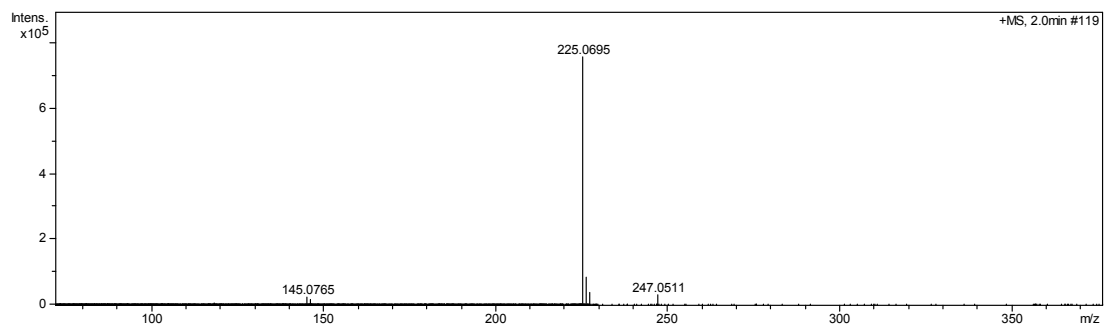


Figure S76 HRMS spectra of 1-(2-(methylsulfonyl)ethyl)-1*H*-benzo[*d*]imidazole (**3ai**)

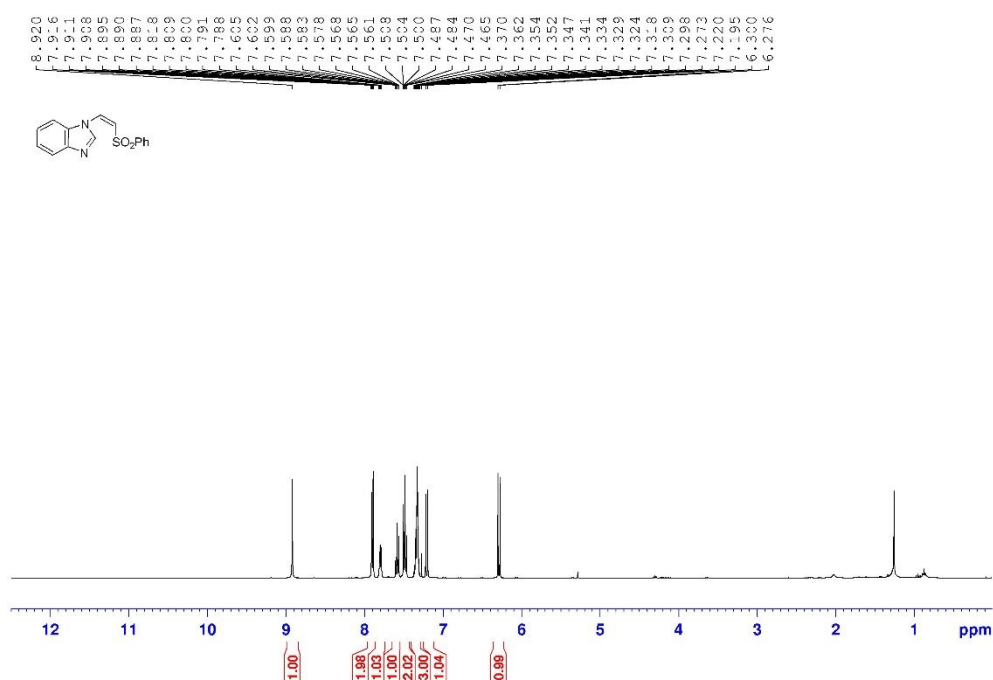


Figure S77 ¹H NMR spectra of (Z)-1-(2-(phenylsulfonyl)vinyl)-1H-benzo[d]imidazole (3aj)

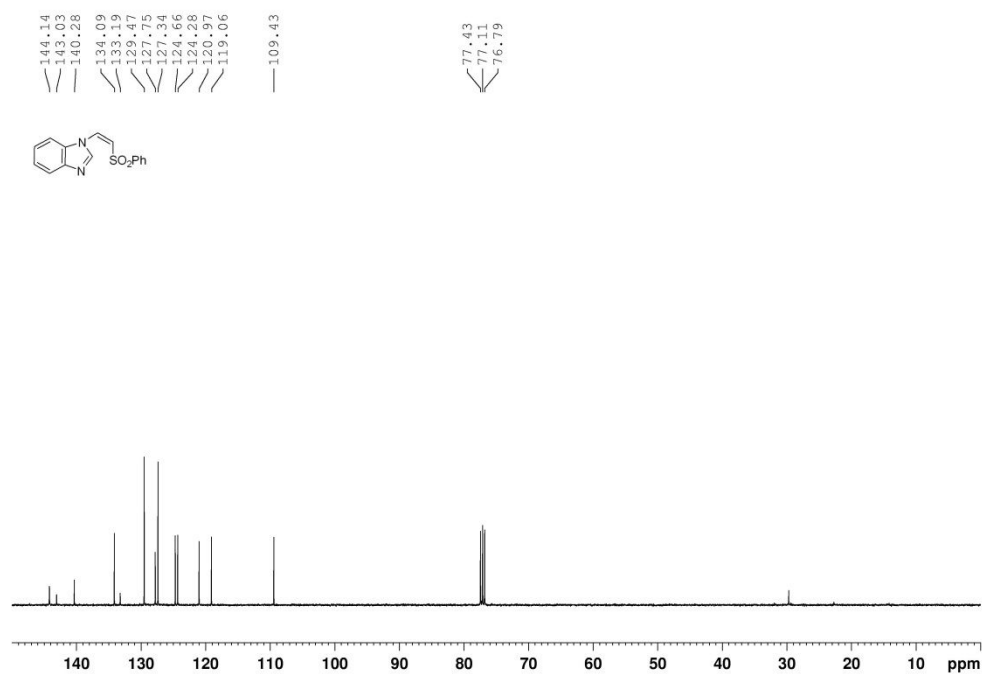


Figure S78 ¹³C NMR spectra of (Z)-1-(2-(phenylsulfonyl)vinyl)-1H-benzo[d]imidazole (3aj)

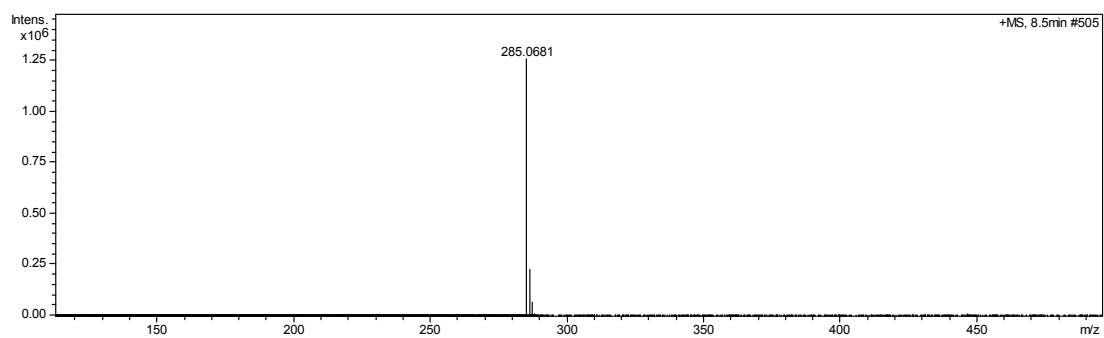


Figure S79 HRMS spectra of (Z)-1-(2-(phenylsulfonyl)vinyl)-1*H*-benzo[*d*]imidazole (3aj)

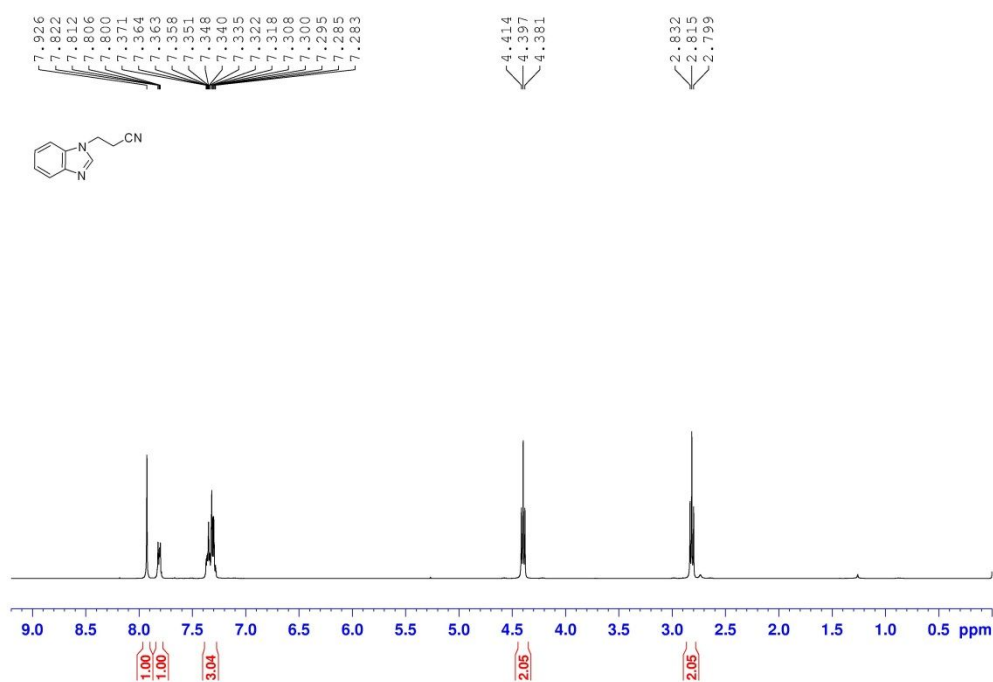


Figure S80 ¹H NMR spectra of 3-(1*H*-benzo[*d*]imidazol-1-yl)propanenitrile (**3ak**)⁷

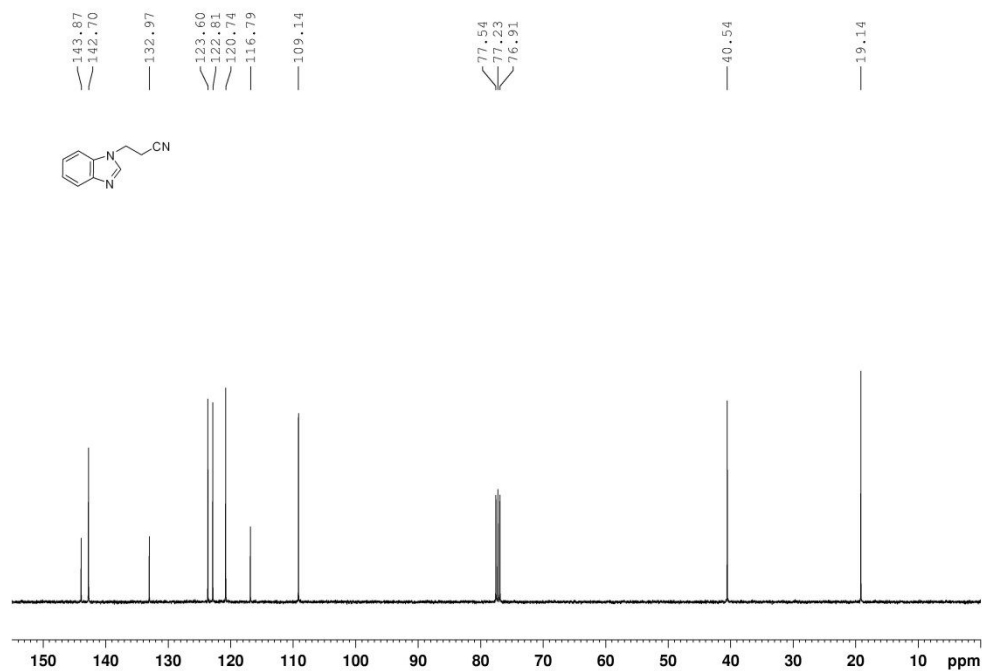


Figure S81 ¹³C NMR spectra of 3-(1*H*-benzo[*d*]imidazol-1-yl)propanenitrile (**3ak**)⁷

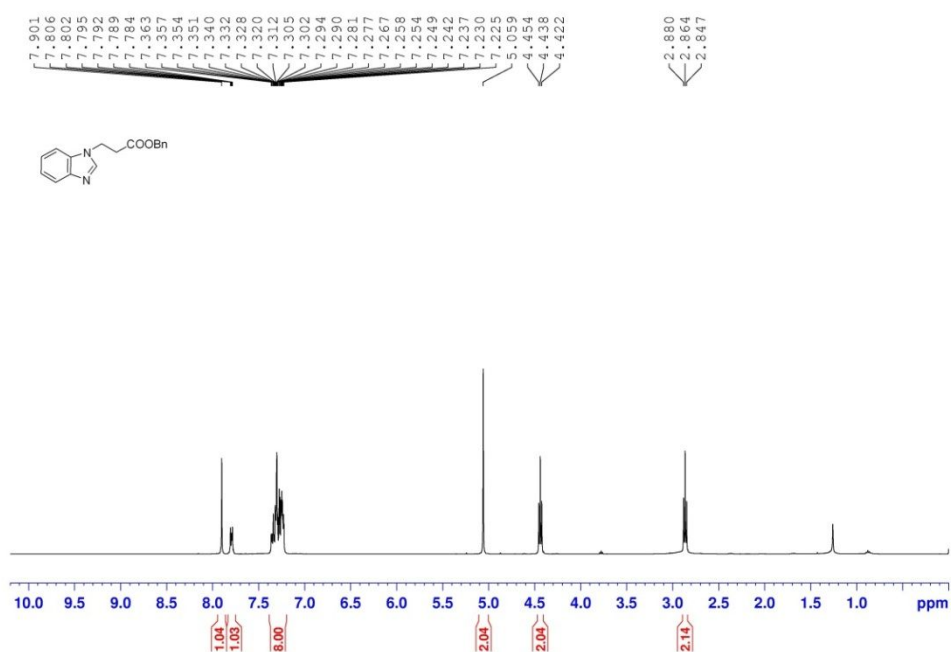


Figure S82 ¹H NMR spectra of benzyl 3-(1H-benzo[d]imidazol-1-yl)propanoate (**3al**)⁸

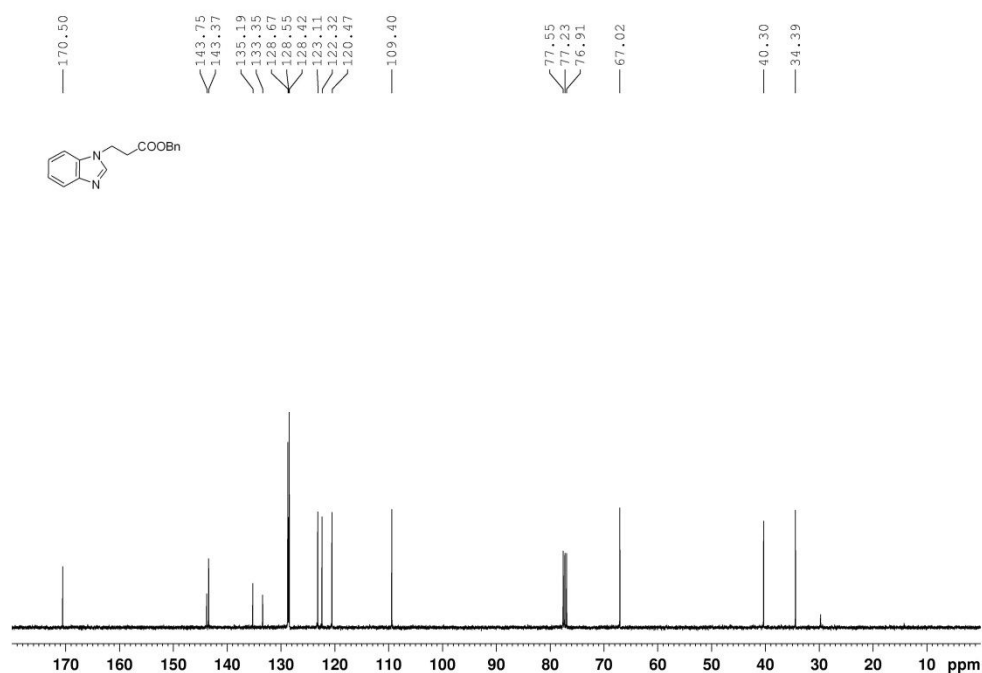


Figure S83 ¹³C NMR spectra of benzyl 3-(1H-benzo[d]imidazol-1-yl)propanoate (**3al**)

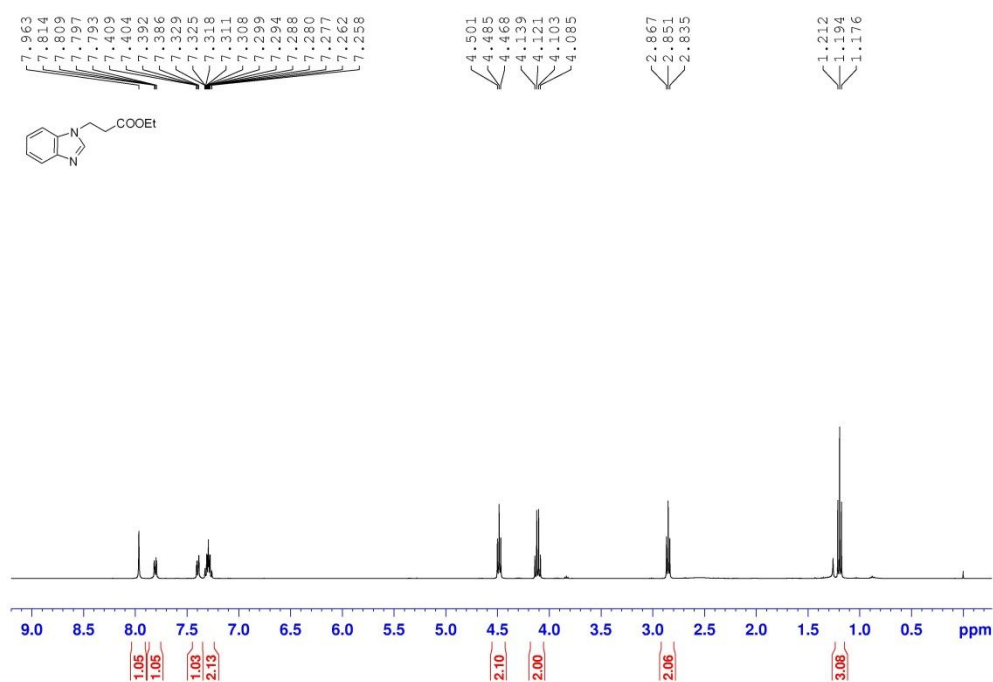


Figure S84 ¹H NMR spectra of ethyl 3-(1*H*-benzo[*d*]imidazol-1-yl)propanoate (**3am**)⁸

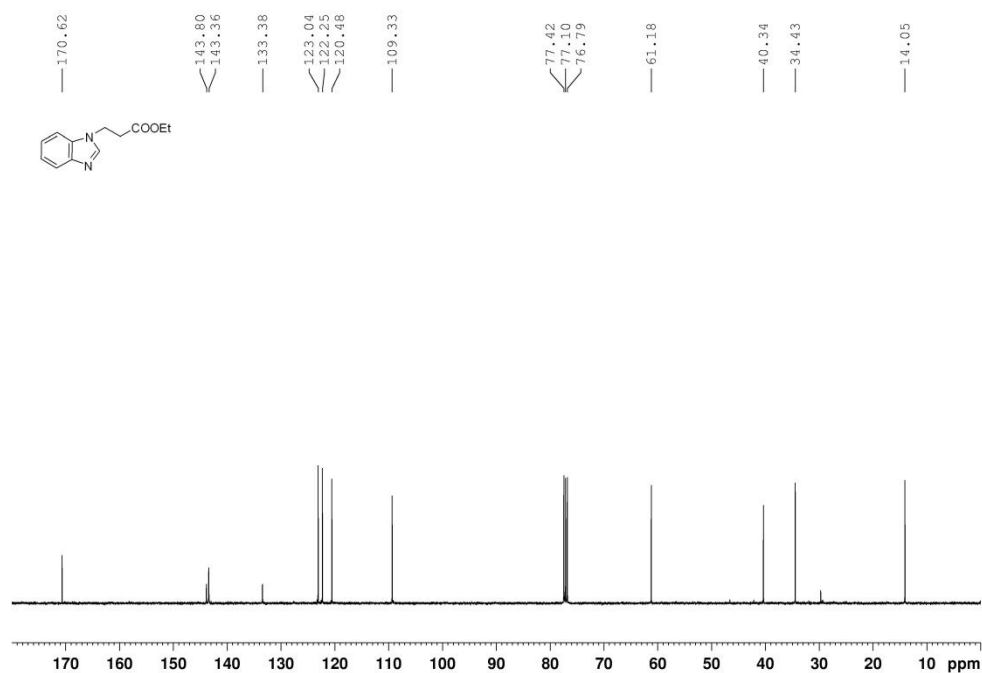


Figure S85 ¹³C NMR spectra of ethyl 3-(1*H*-benzo[*d*]imidazol-1-yl)propanoate (**3am**)⁸

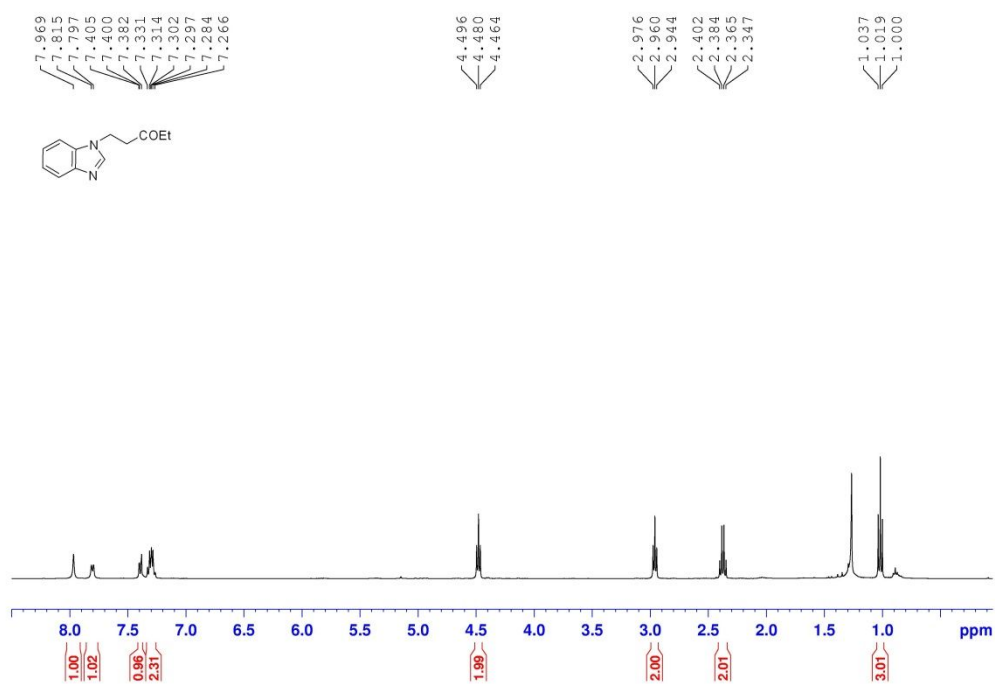


Figure S86 ¹H NMR spectra of 1-(1H-benzo[d]imidazol-1-yl)pentan-3-one (**3an**)

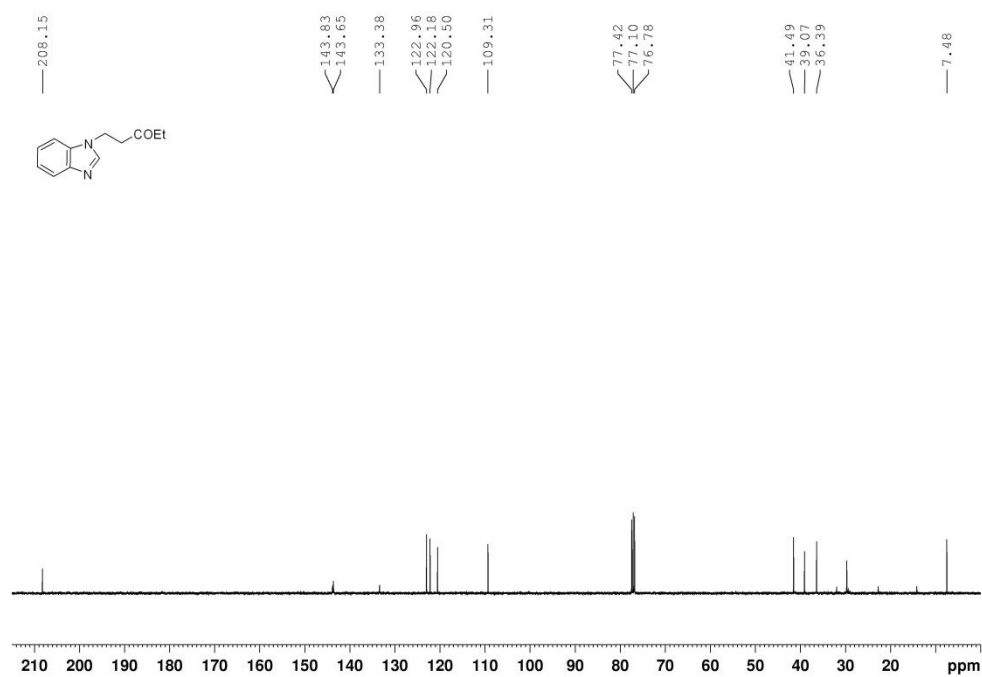


Figure S87 ¹³C NMR spectra of 1-(1H-benzo[d]imidazol-1-yl)pentan-3-one (**3an**)

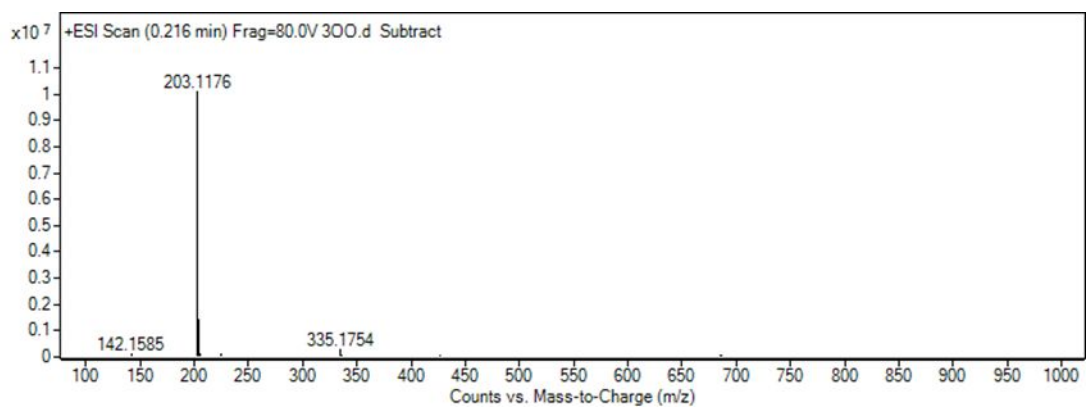


Figure S88 HRMS spectra of 1-(1*H*-benzo[*d*]imidazol-1-yl)pentan-3-one (**3an**)