SUPPORTING INFORMATION

Expedient Organocatalytic Aza-Morita-Baylis-Hillman Reaction Through Ball-Milling

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Number of pages: 106

Number of tables: 2

Number of figures: 131

Table of Contents

1. General Information

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. β-Isocupreidine[1] and α-isocupreine[2] were synthesised according to the literature.

Room temperature (rt) refers to 20-25 °C. Ice/water baths were used to obtain temperatures of 0 °C. All reactions involving heating were carried out using DrySyn blocks and a contact thermometer.

Analytical thin layer chromatography was carried out using aluminium plates coated with silica (Kieselgel 60 F_{254} silica) and visualization was achieved using ultraviolet light (254 nm), followed by staining with a 1% aqueous $KMnO_4$ solution. Flash chromatography used Kieselgel 60 silica in the solvent system stated. The petroleum ether (PE) utilised was in the 40 – 60 °C boiling range.

Melting points (mp) were recorded on a Gallenkamp melting point apparatus and are reported corrected by linear calibration to benzophenone (47 – 49 °C) and benzoic acid (121 – 123 °C).

Infrared spectra were recorded on a Shimadzu IRAffinity-1 Fourier Transform ATIR spectrometer as thin films using a Pike MIRacle ATR accessory, with absorbance peaks quoted (ν_{max}/cm^{-1}).

^{1}H, ^{13}C, ^{19}F NMR spectra were obtained on a Bruker Avance 300 (300 MHz ^{1}H, 75 MHz ^{13}C, 282 MHz ^{19}F), a Bruker Avance 400 (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F) or a Bruker Avance 500 (500 MHz ^{1}H, 126 MHz ^{13}C, 471 MHz ^{19}F) spectrometer at rt in the solvent stated. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent signal. All coupling constants, *J*, are quoted in Hertz (Hz). Multiplicities are reported based on their apparent appearance, with the following symbols: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and multiples thereof.

High resolution mass spectral (HRMS) data were obtained on a Waters MALDI-TOF mx in Cardiff University.

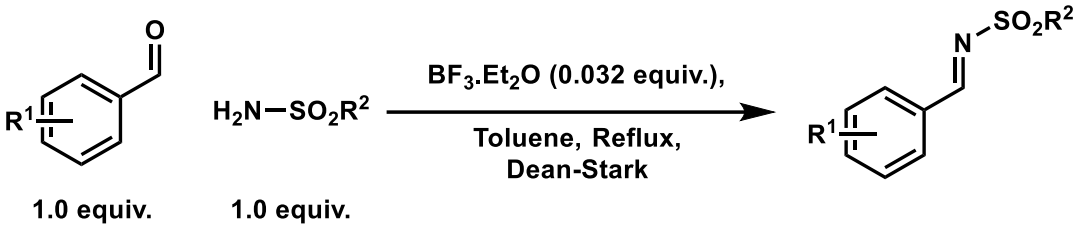
The ball mill used was an In Solido Technologies (IST) 400 Mixer Mill. Unless otherwise stated, mechanochemical reactions were carried out in 14 mL stainless steel jars from IST, with a 9 mm diameter 3 g stainless steel ball. Reactions longer than 99 minutes were carried out by setting the machine's timer to '0' and stopping the operation once the desired time had elapsed. No rest period was necessary.

HPLC analyses were obtained on a Gilson HPLC consisting of a Gilson 305 pump, Gilson 306 pump, Gilson 811C dynamic mixer, Gilson 805 manometric module, Gilson 401C dilutor, Gilson 213XL sample injector and sample detection was performed with a Gilson 118 UV/vis detector, at 211 nm. Separation was achieved using a Chiralpak IA column.

2. Experimental and Characterization Data

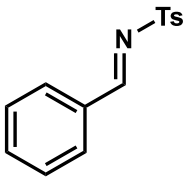
2.1. Synthesis of Starting Materials

2.1.1. General Procedure A



A solution of the corresponding aldehyde (1.0 equiv.), sulfonamide (1.0 equiv.) and $BF_3.Et_2O$ (0.032 equiv.) in toluene (0.4 M) was equipped with a Dean-Stark apparatus, condenser and heated to reflux for the time stated. Upon cooling to room temperature, a precipitate formed which was collected by filtration. If no precipitate was formed upon cooling to room temperature, hexane was added, and the mixture was cooled to -20 ˚C to form the precipitate. The solid was then recrystallised from the stated solvent/solvent mixture.

***N*-benzylidene-4-methylbenzenesulfonamide (1)**



Prepared according to general procedure A from benzaldehyde (25 mmol) and *p*-toluenesulfonamide (25 mmol) for 2 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as a white solid (3.84 g, 59%), with physical properties and spectroscopic data in accordance with the literature;[3] R_F = 0.49 (1.5:8.5 EtOAc/PE); mp 120 - 122 ˚C (lit. 110 - 111 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.03 (s, 1H), 7.97 – 7.87 (m, 4H), 7.63 – 7.59 (m, 1H), 7.51 – 7.46 (m, 2H), 7.36 – 7.33 (m, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ_C: 170.3, 144.8, 135.3, 135.1, 132.5, 131.5, 130.0, 129.3, 128.2, 21.8.

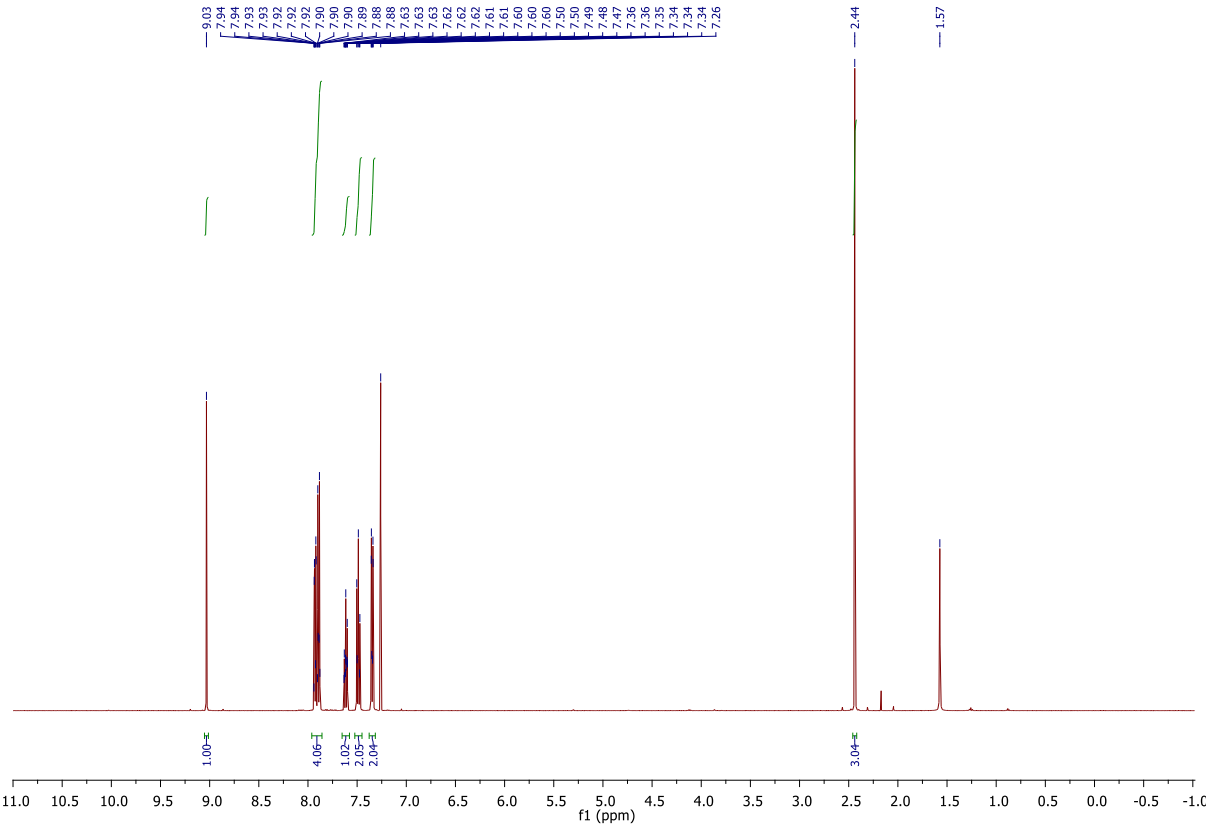


Figure S1. ^{1}H NMR of **1**.

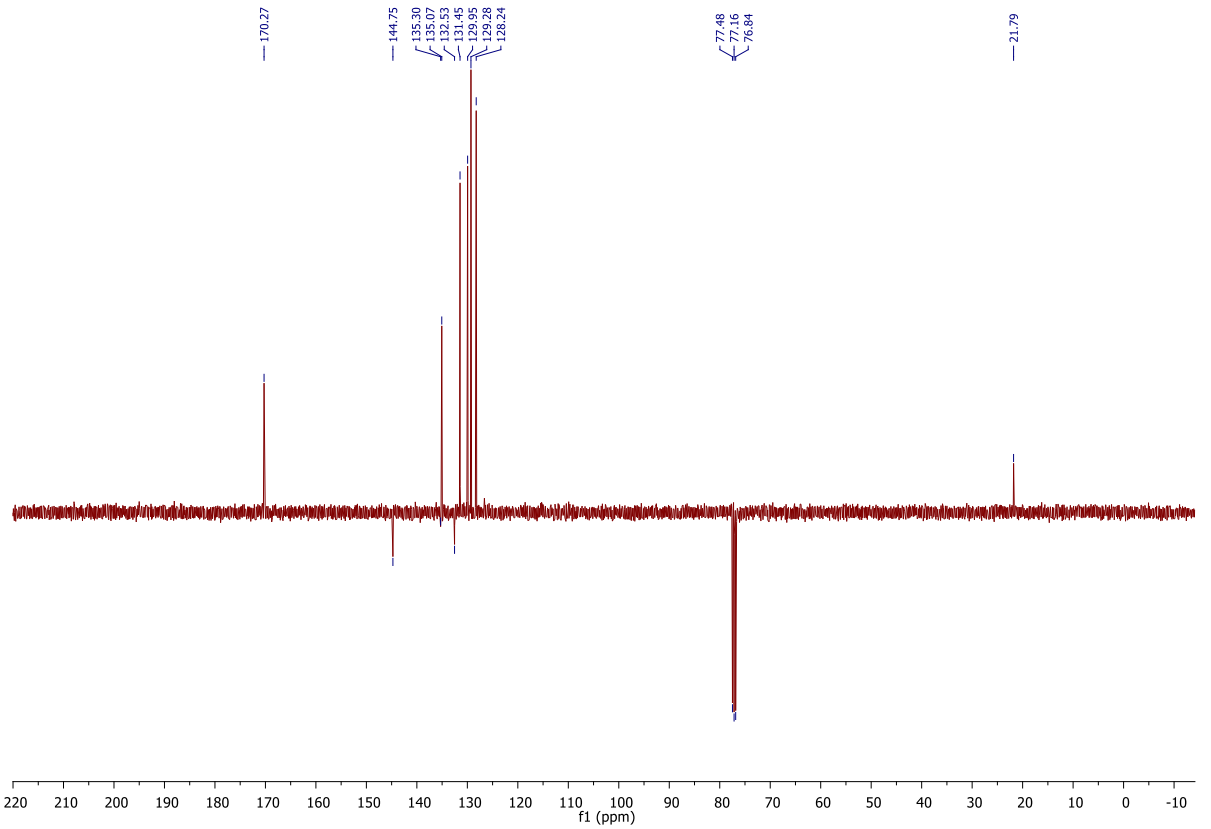
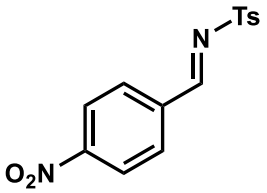


Figure S2. ^{13}C {^{1}H} NMR of **1**.

4-methyl-*N*-(4-nitrobenzylidene)benzenesulfonamide (SM1)



Prepared according to general procedure A from *p*-nitrobenzaldehyde (25 mmol) and *p*-toluenesulfonamide (25 mmol) for 2 h, followed by recrystallisation from toluene to give the title compound as a beige solid (2.45 g, 32%), with physical properties and spectroscopic data in accordance with the literature;[3] R_F = 0.56 (1.5:8.5 EtOAc/PE); mp 215 - 217 ˚C (lit. 208 - 209 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.10 (s, 1H), 8.37 – 8.28 (m, 2H), 8.14 – 8.07 (m, 2H), 7.93 – 7.87 (m, 2H), 7.41 – 7.34 (m, 2H), 2.46 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ_C: 167.4, 151.3, 145.5, 137.6, 134.3, 132.0, 130.2, 128.6, 124.3, 21.9.

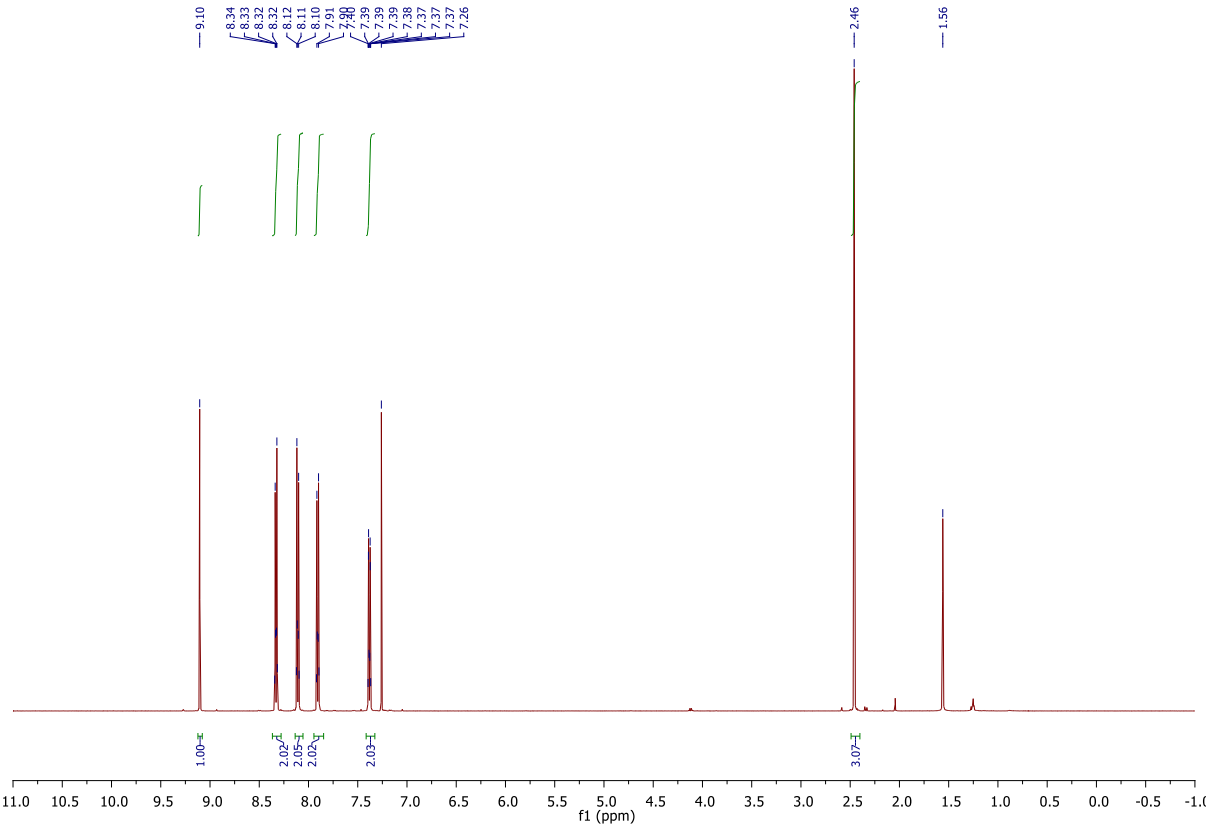


Figure S3. ^{1}H NMR of **SM1**.

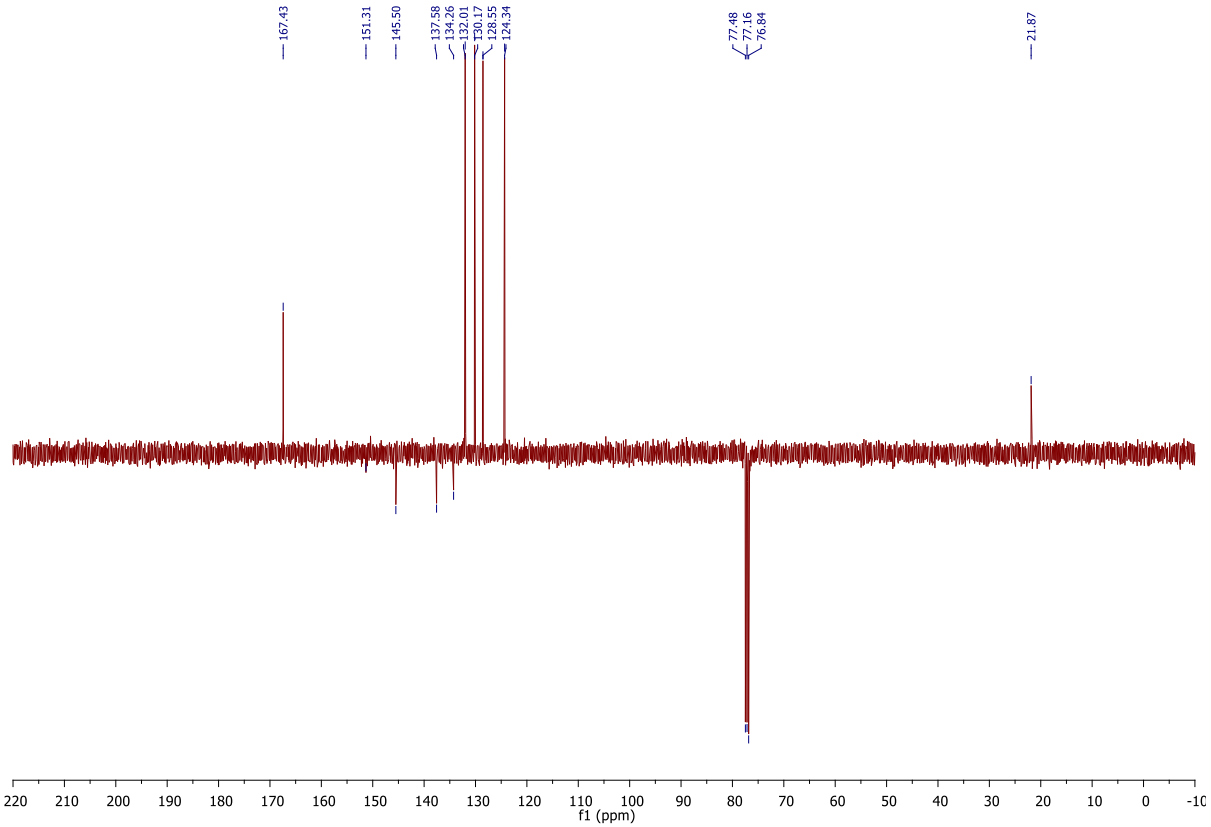
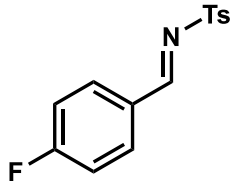


Figure S4. ^{13}C {^{1}H} NMR of **SM1**.

***N*-(4-fluorobenzylidene)-4-methylbenzenesulfonamide (SM2)**



Prepared according to general procedure A from *p*-fluorobenzaldehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a white solid (1.36 g, 49%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.45 (1.5:8.5 EtOAc/PE); mp 126 – 118 ˚C (lit. 117 – 118 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.99 (s, 1H), 7.99 – 7.93 (m, 2H), 7.91 – 7.86 (m, 2H), 7.38 – 7.33 (m, 2H), 7.21 – 7.13 (m, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ_C: 168.7, 167.0 (d, *J* = 259.6), 144.8, 135.2, 133.9 (d, *J* = 9.1), 130.0, 128.9 (d, *J* = 3.0), 128.3, 116.8 (d, *J* = 23.2), 21.80; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -101.1.

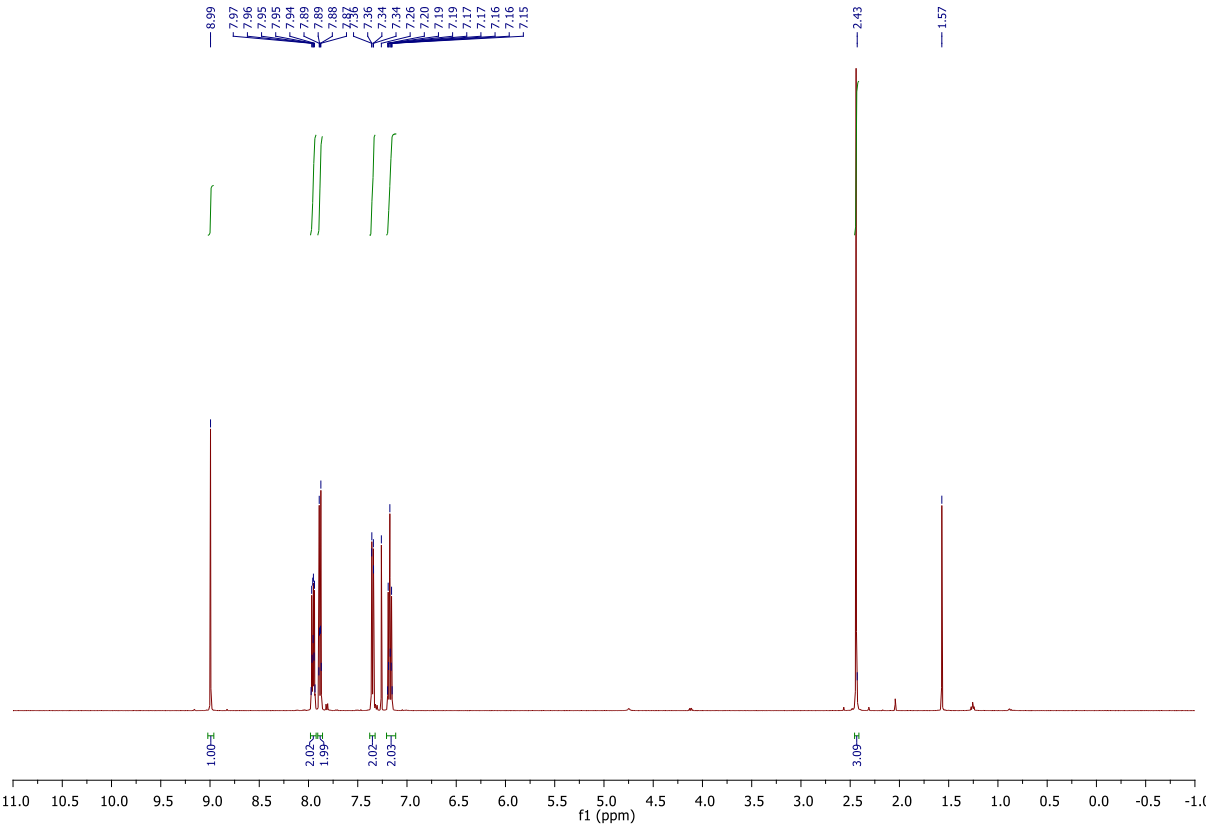


Figure S5. ^{1}H NMR of **SM2**.

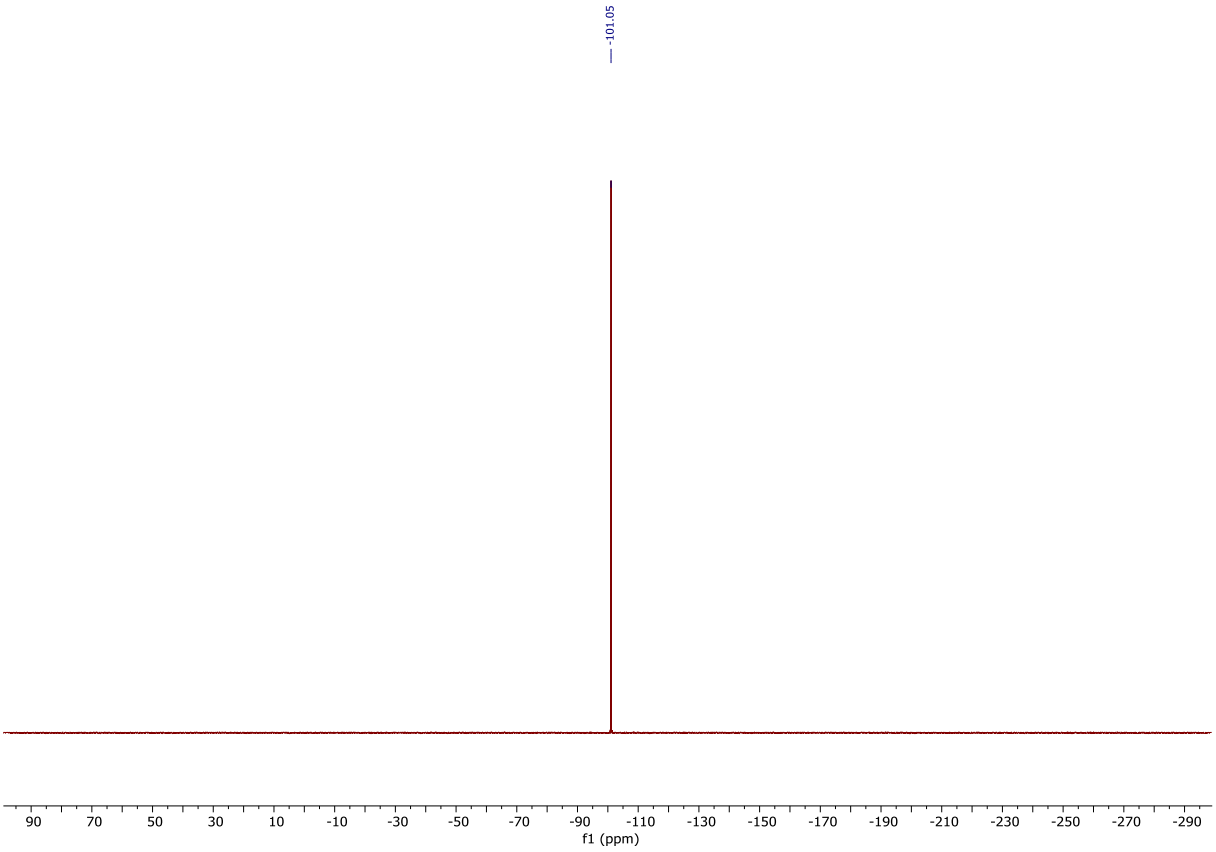


Figure S6. ^{19}F {^{1}H} NMR of **SM2**.

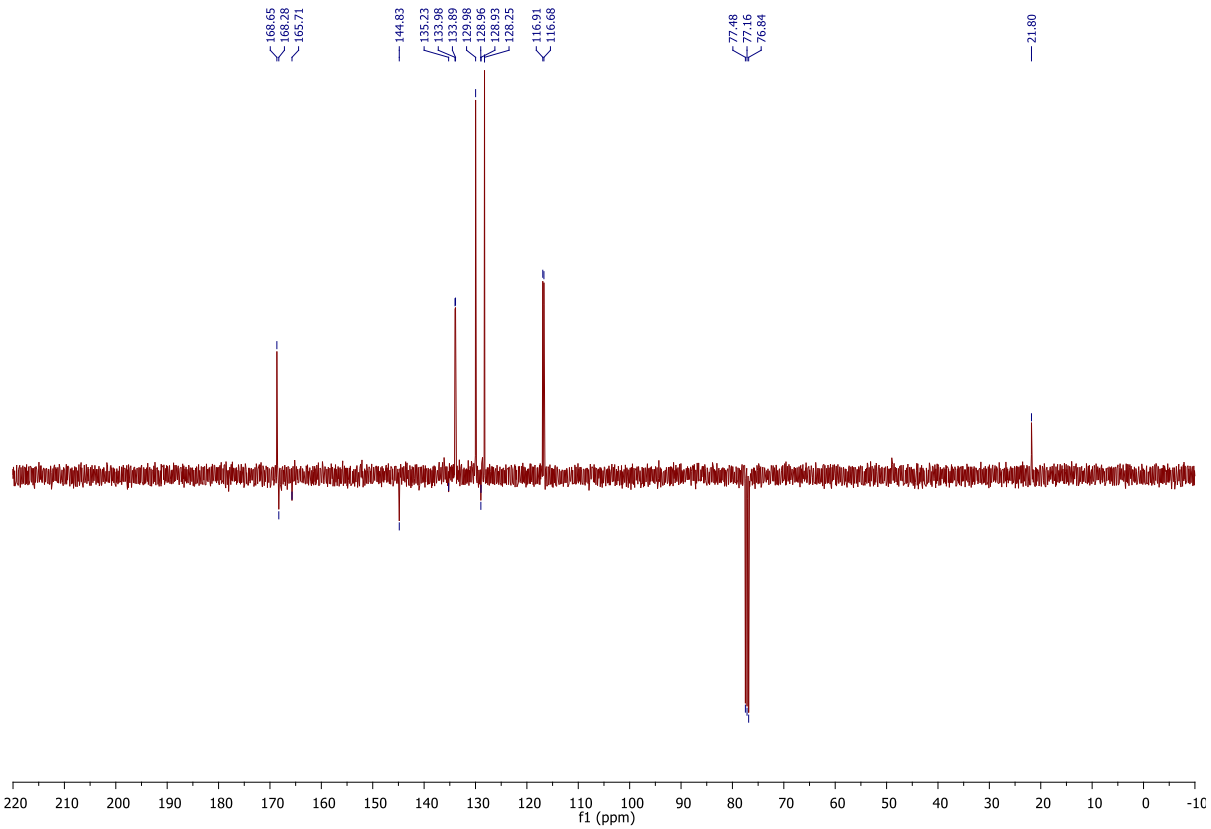
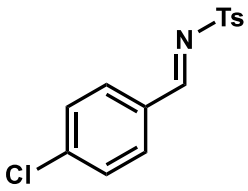


Figure S7. ^{13}C {^{1}H} NMR of **SM2**.

***N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (SM3)**



Prepared according to general procedure A from *p*-chlorobenzaldehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a white solid (1.44 g, 49%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.50 (1.5:8.5 EtOAc/PE); mp 185 – 187 ˚C (lit. 176 – 177 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.99 (s, 1H), 7.91 – 7.84 (m, 4H), 7.49 – 7.44 (m, 2H), 7.38 – 7.33 (m, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 168.8, 144.9, 141.6, 135.1, 132.5, 131.0, 130.0, 129.8, 128.3, 21.8.

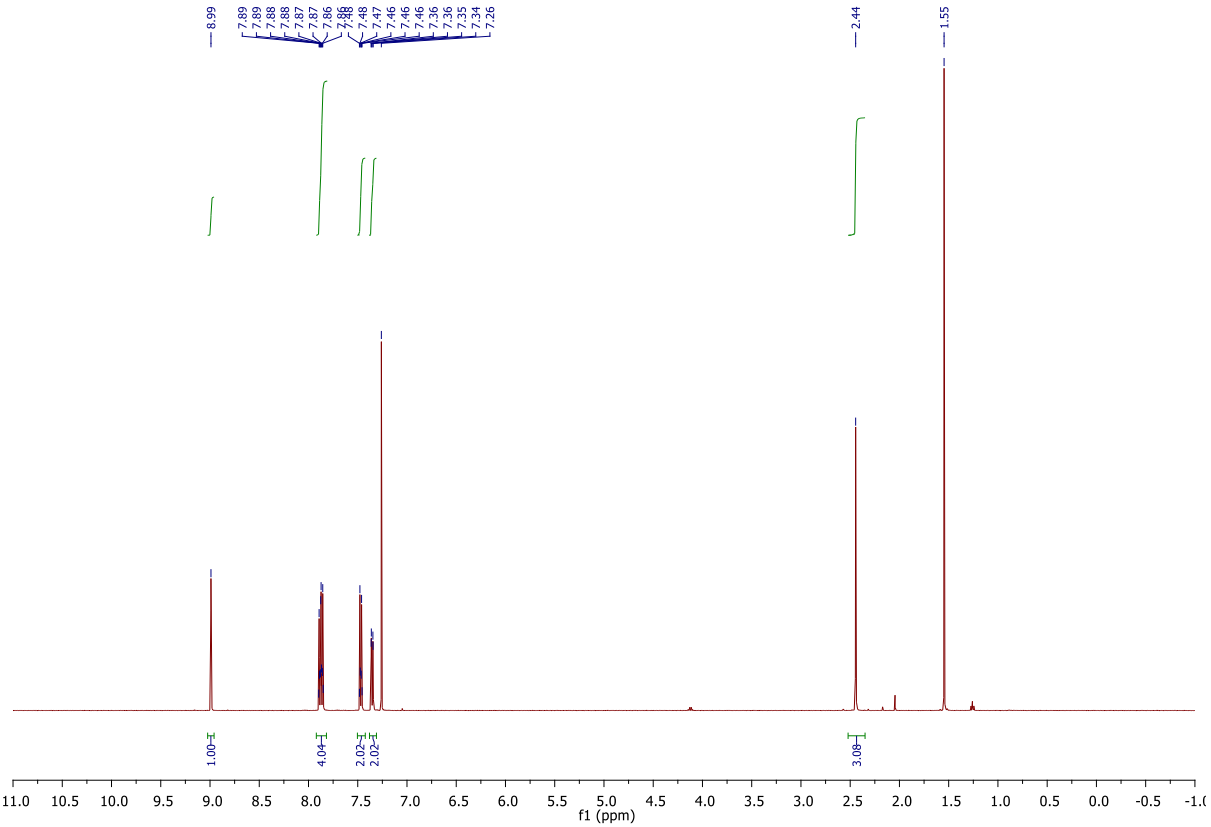


Figure S8. ^{1}H NMR of **SM3**.

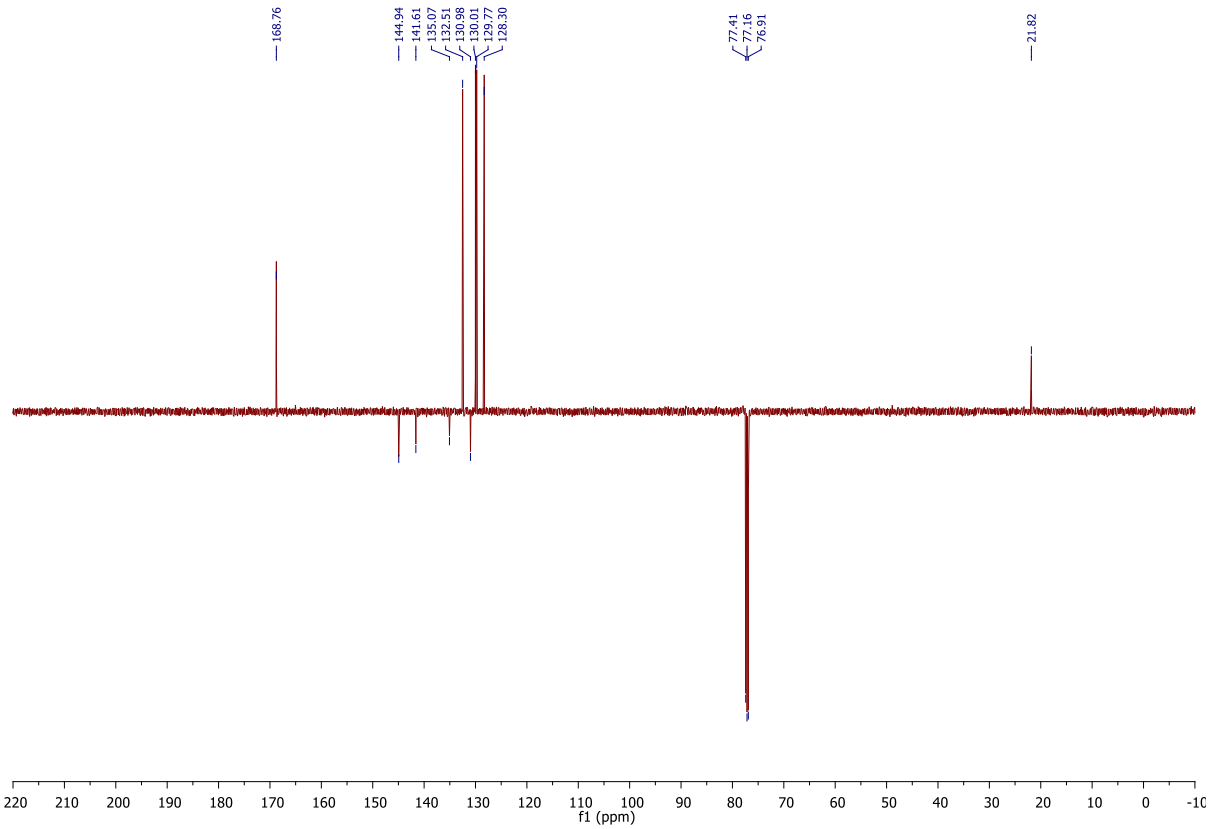
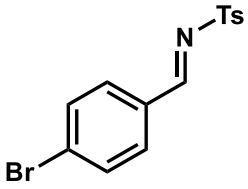


Figure S9. ^{13}C {^{1}H} NMR of **SM3**.

***N*-(4-bromobenzylidene)-4-methylbenzenesulfonamide (SM4)**



Prepared according to general procedure A from *p*-bromobenzaldehyde (5 mmol) and *p*-toluenesulfonamide (5 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a white solid (925 mg, 55%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.50 (1.5:8.5 EtOAc/PE); mp 201 – 203 ˚C (lit. 180 – 181 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.98 (s, 1H), 7.92 – 7.84 (m, 2H), 7.82 – 7.74 (m, 2H), 7.68 – 7.60 (m, 2H), 7.39 – 7.31 (m, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 168.9, 145.0, 135.0, 132.8, 132.5, 131.4, 130.4, 130.0, 128.3, 21.8.

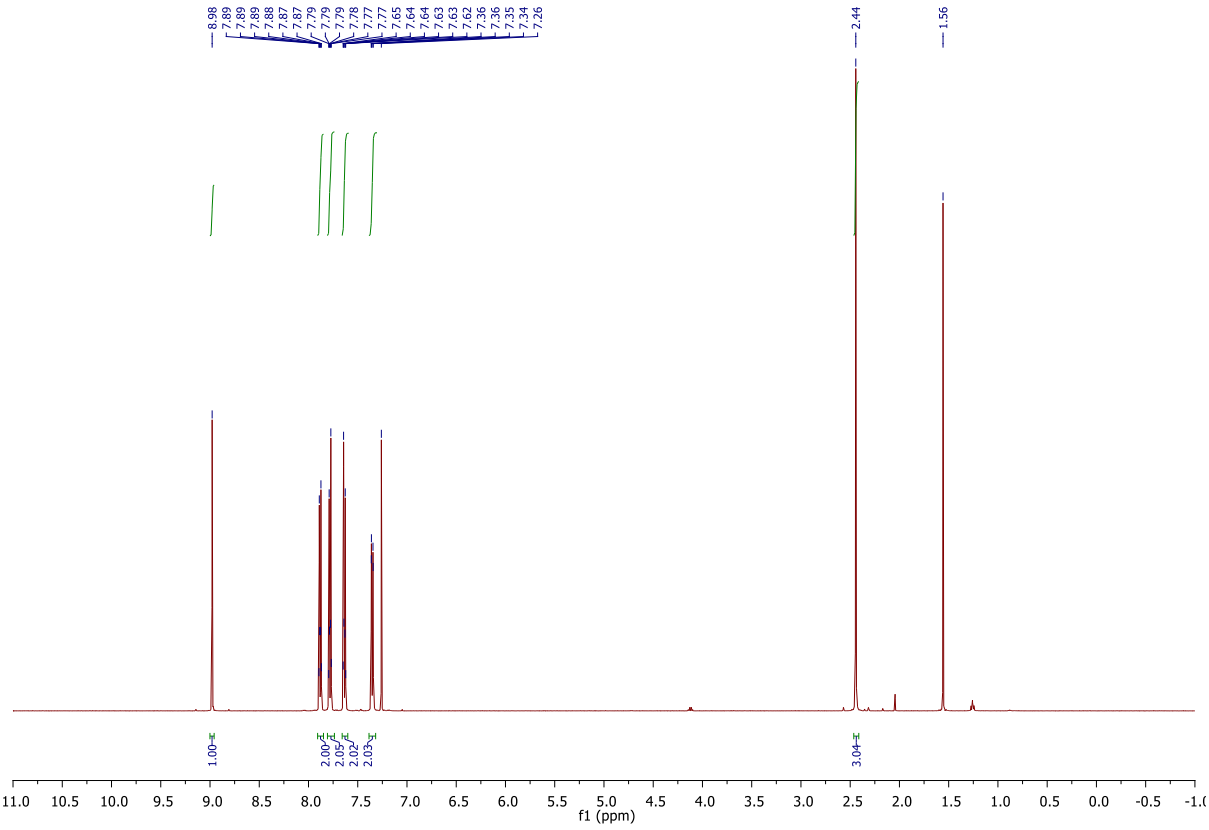


Figure S10. ^{1}H NMR of **SM4**.

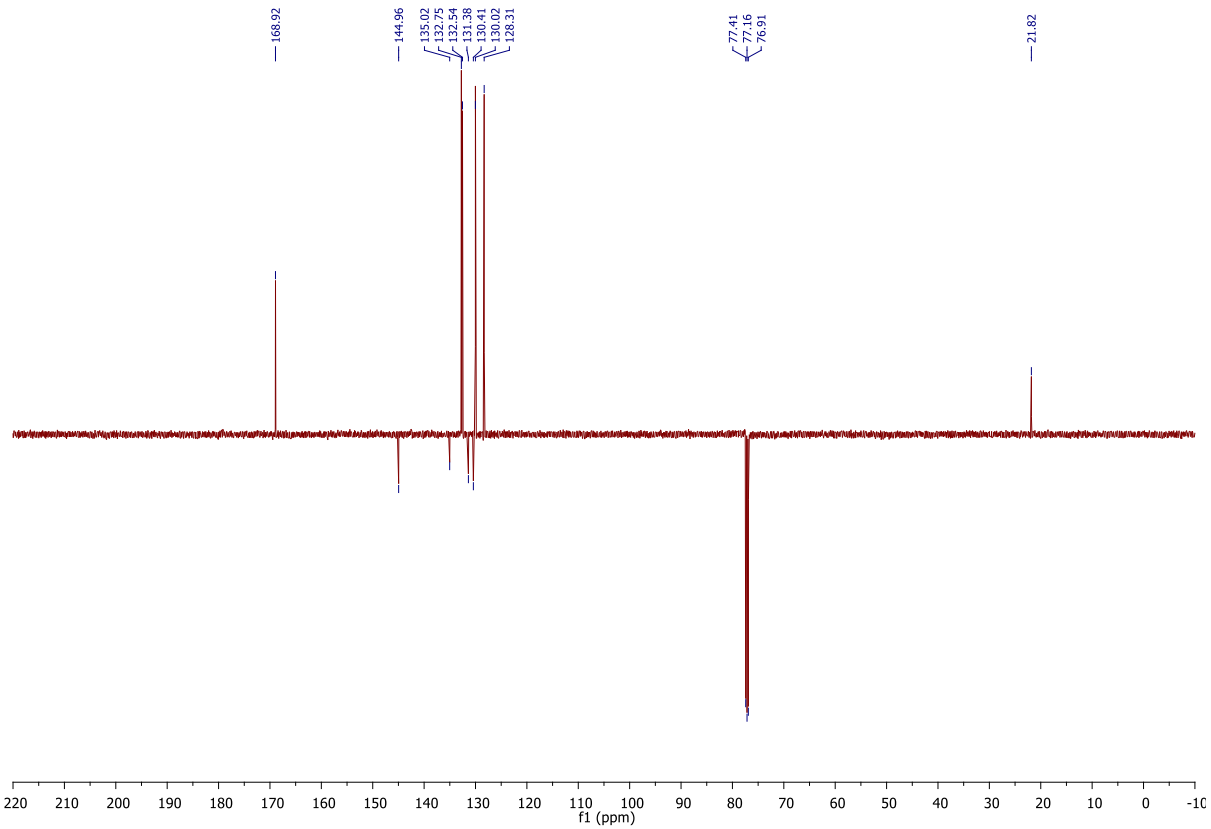
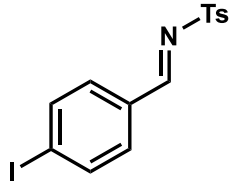


Figure S11. ^{13}C {^{1}H} NMR of **SM4**.

***N*-(4-iodobenzylidene)-4-methylbenzenesulfonamide (SM5)**



Prepared according to general procedure A from *p*-iodobenzaldehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a white solid (2.73 g, 71%); R_F = 0.48 (1.5:8.5 EtOAc/PE); mp 208 – 210 ˚C; ν_{max}/cm^{-1} (film): 1602, 1583, 1552, 1315, 1290, 1278, 1159, 1088, 1051, 1007, 1000, 867, 811, 797, 780, 704, 676, 639; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.96 (s, 1H), 7.91 – 7.83 (m, 4H), 7.67 – 7.58 (m, 2H), 7.39 – 7.32 (m, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 169.2, 145.0, 138.7, 135.0, 132.3, 131.9, 130.0, 128.3, 103.4, 21.8; HRMS (ES^+) calculated for $[C_{14}H_{13}NO_2SI]^+$ $(M+H)^+$: m/z 385.9713 found 385.9712 (-0.3 ppm).

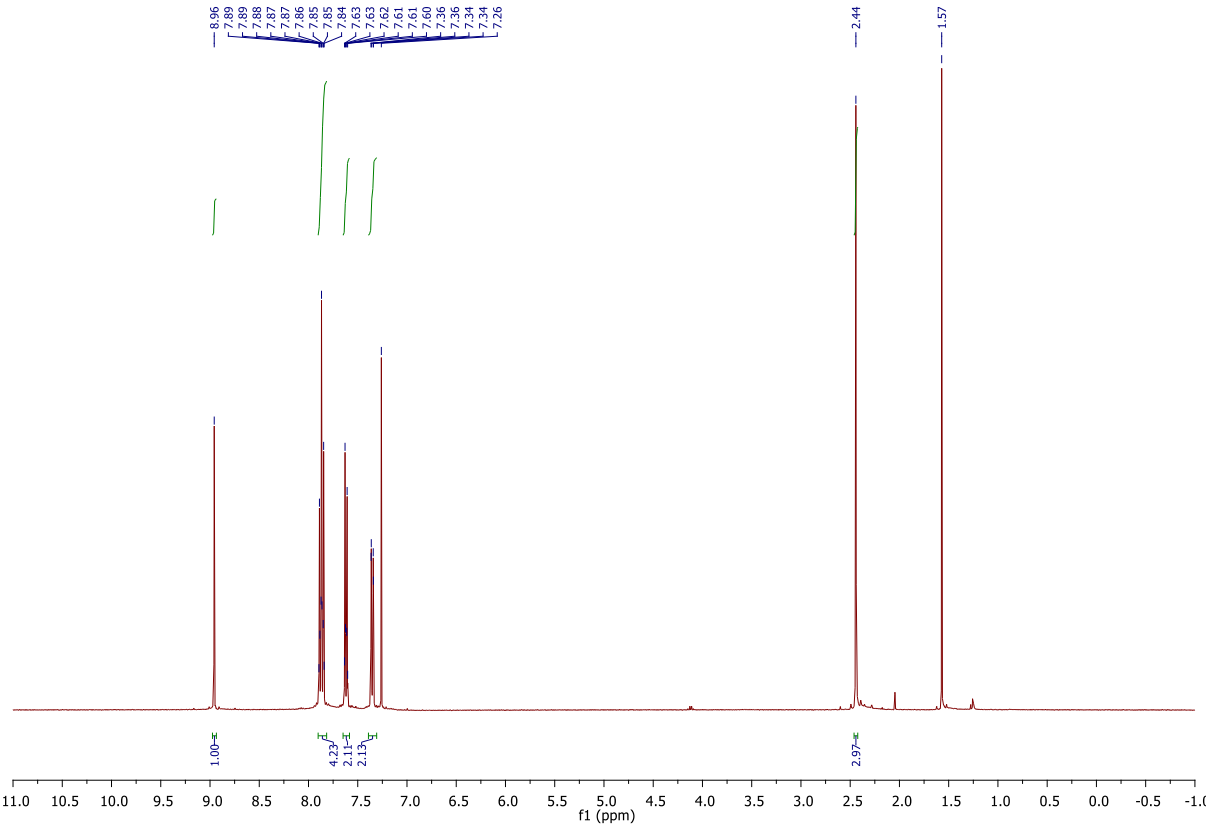


Figure S12. ^{1}H NMR of **SM5**.

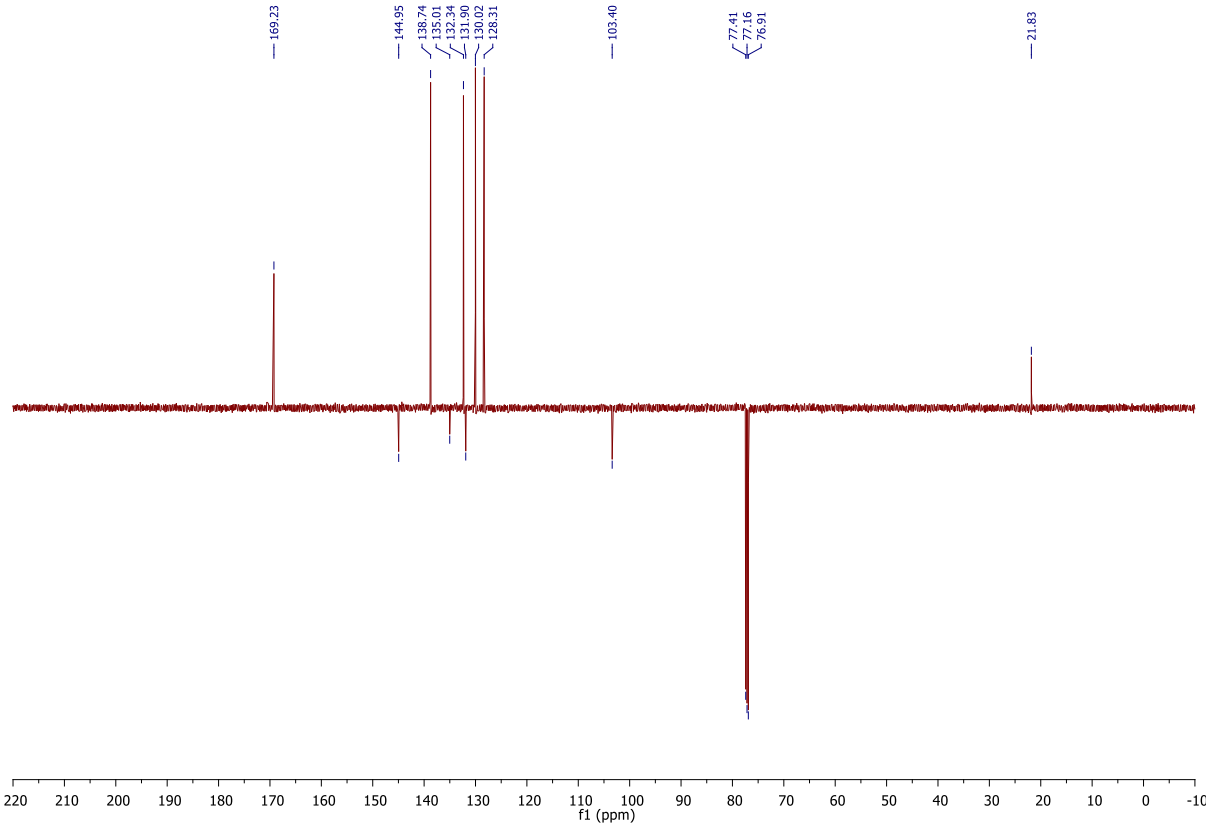
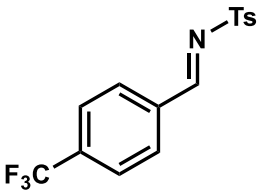


Figure S13. ^{13}C {^{1}H} NMR of **SM5**.

4-methyl-*N*-(4-(trifluoromethyl)benzylidene)benzenesulfonamide (SM6)



Prepared according to general procedure A from *p*-(trifluoromethyl)benzaldehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from EtOAc to give the title compound as a white solid (240 mg, 7%) with physical and spectroscopic data in accordance with the literature;[4] R_F = 0.50 (1:4 EtOAc/PE); mp 168 – 170 ˚C (lit. 154 – 156 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.07 (s, 1H), 8.05 (d, *J* = 8.0, 2H), 7.92 – 7.88 (m, 2H), 7.75 (d, *J* = 8.0, 2H), 7.39 – 7.35 (m, 2H), 2.45 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 168.5, 145.2, 136.0 (q, *J* = 40.3), 135.5, 134.7, 131.5, 130.1, 128.4, 126.3 (q, *J* = 3.8), 123.5 (q, *J* = 274.7), 21.9; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -63.3.

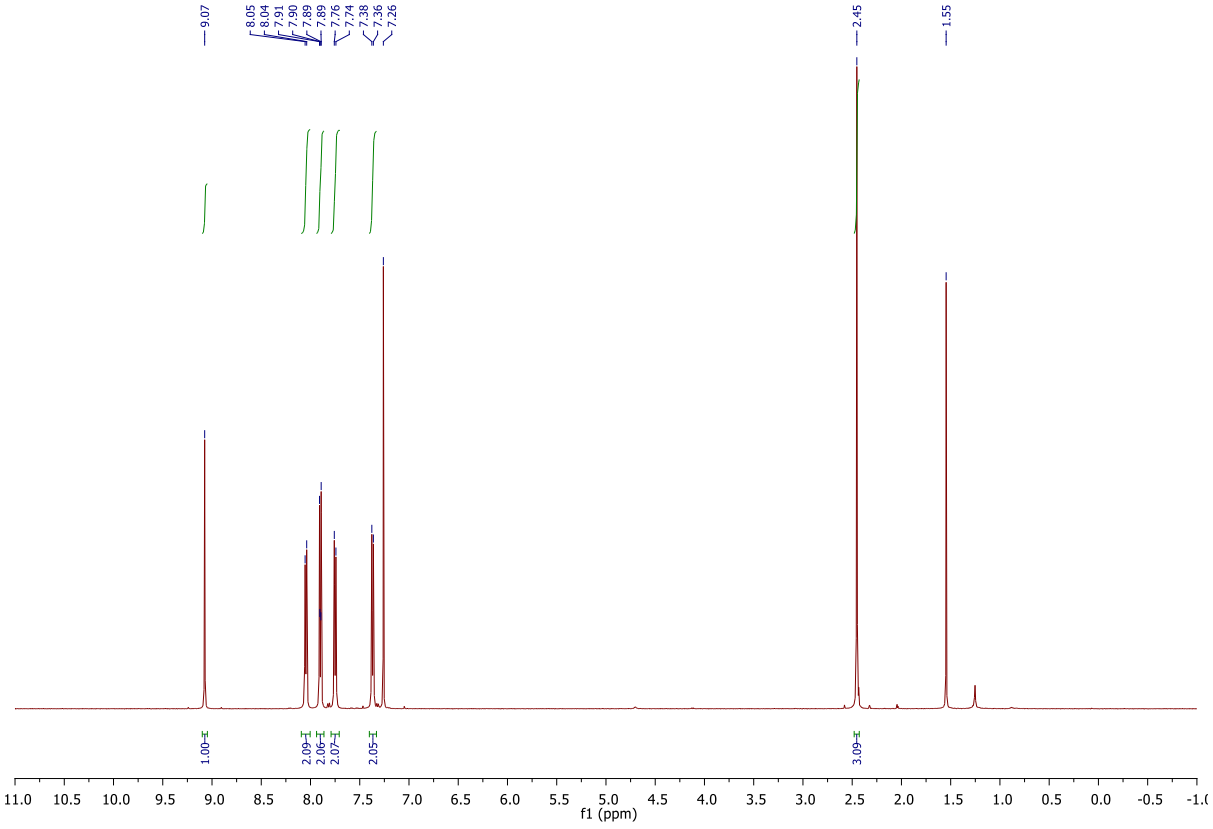


Figure S14. ^{1}H NMR of **SM6**.

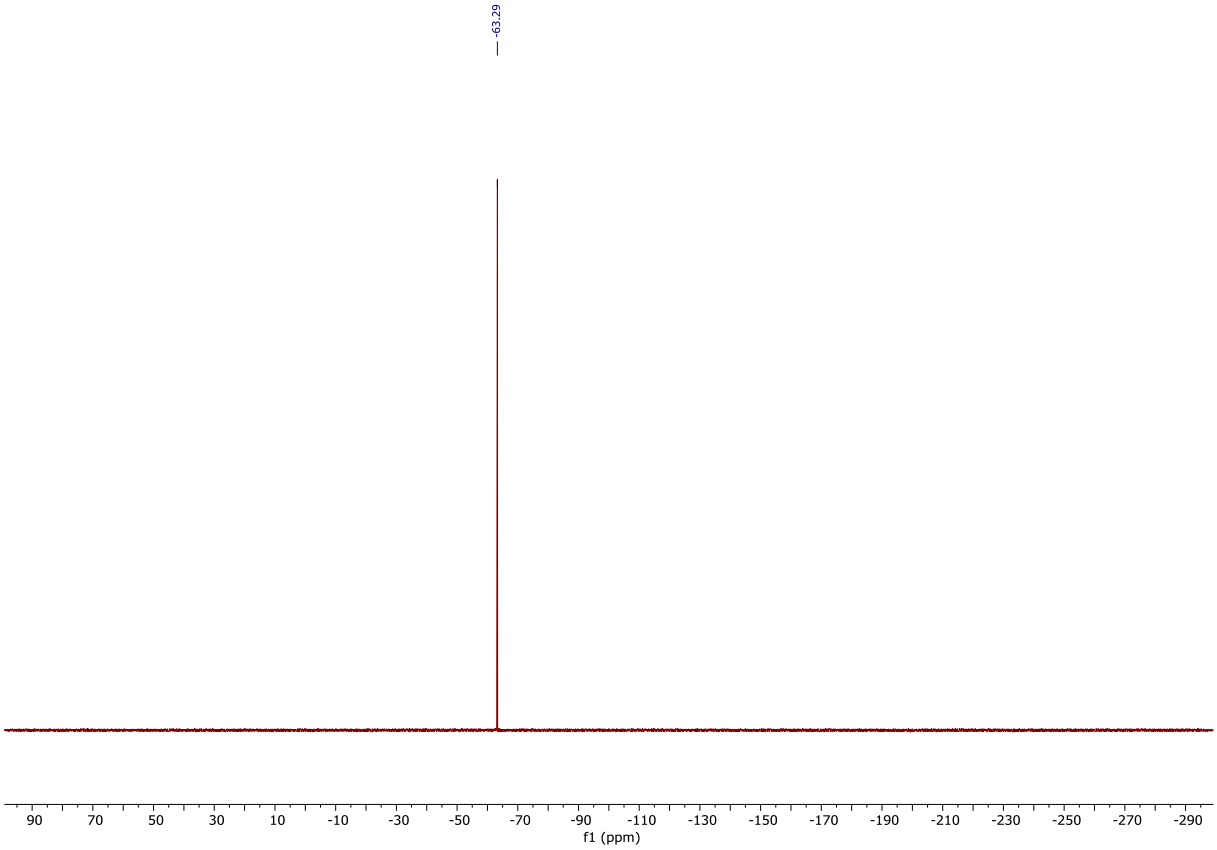


Figure S15. ^{19}F {^{1}H} NMR of **SM6**.

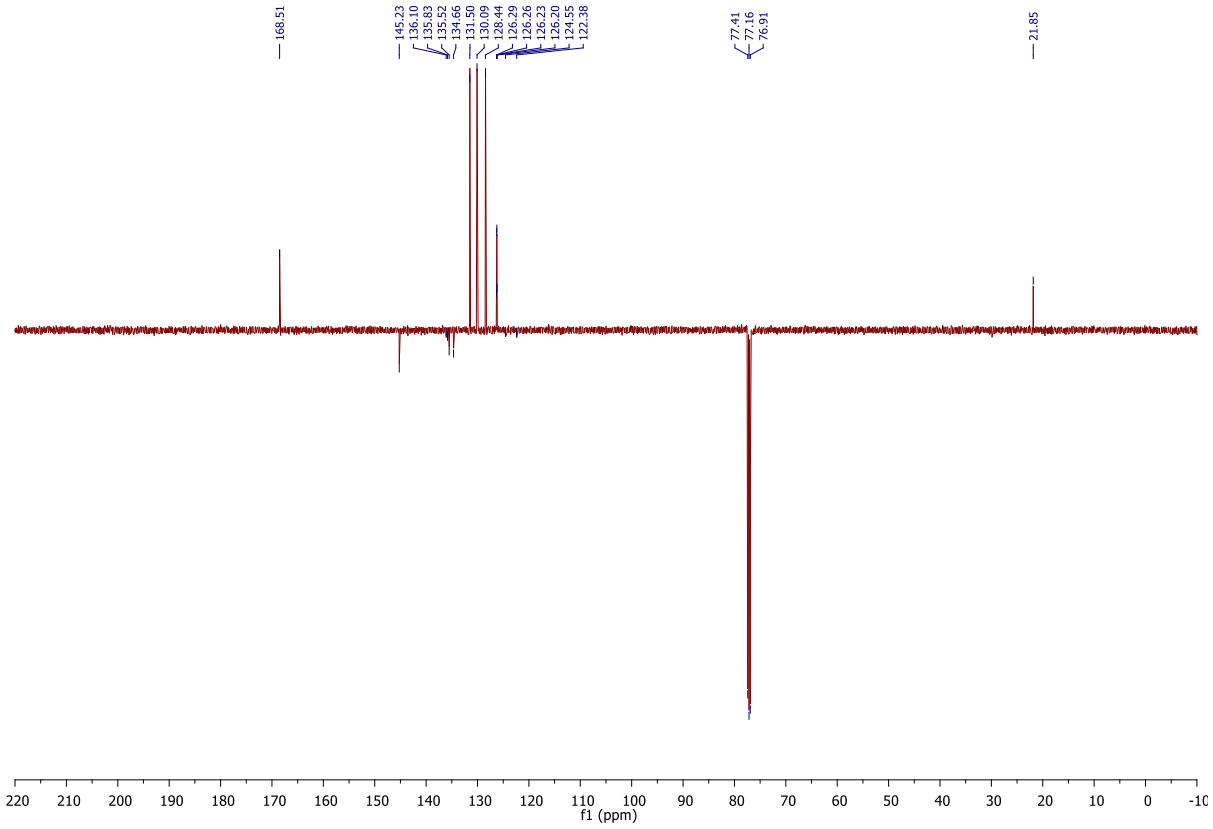
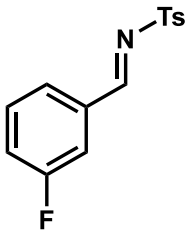


Figure S16. ^{13}C {^{1}H} NMR of **SM6**.

***N*-(3-fluorobenzylidene)-4-methylbenzenesulfonamide (SM7)**



Prepared according to general procedure A from *m*-fluorobenzaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, to give the title compound as a white solid (1.00 g, 36%) with no further purification required and physical and spectroscopic data in accordance with the literature;[4] R_F = 0.45 (1:4 EtOAc/PE); mp 103 – 105 ˚C (lit. 82 – 84 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.00 (d, *J* = 1.3, 1H), 7.92 – 7.87 (m, 2H), 7.70 – 7.63 (m, 2H), 7.51 – 7.45 (m, 1H), 7.38 – 7.34 (m, 2H), 7.31 (tdd, *J* = 8.3, 2.7, 1.0, 1H), 2.45 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 168.8 (d, *J* = 2.5), 163.0 (*J* = 249.5), 145.0, 134.9, 134.7 (d, *J* = 7.6), 131.0 (d, *J* = 7.6), 130.0, 128.3, 128.0 (d, *J* = 3.8), 122.1 (d, *J* = 21.4), 116.8 (d, *J* = 21.4), 21.8; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -110.9.

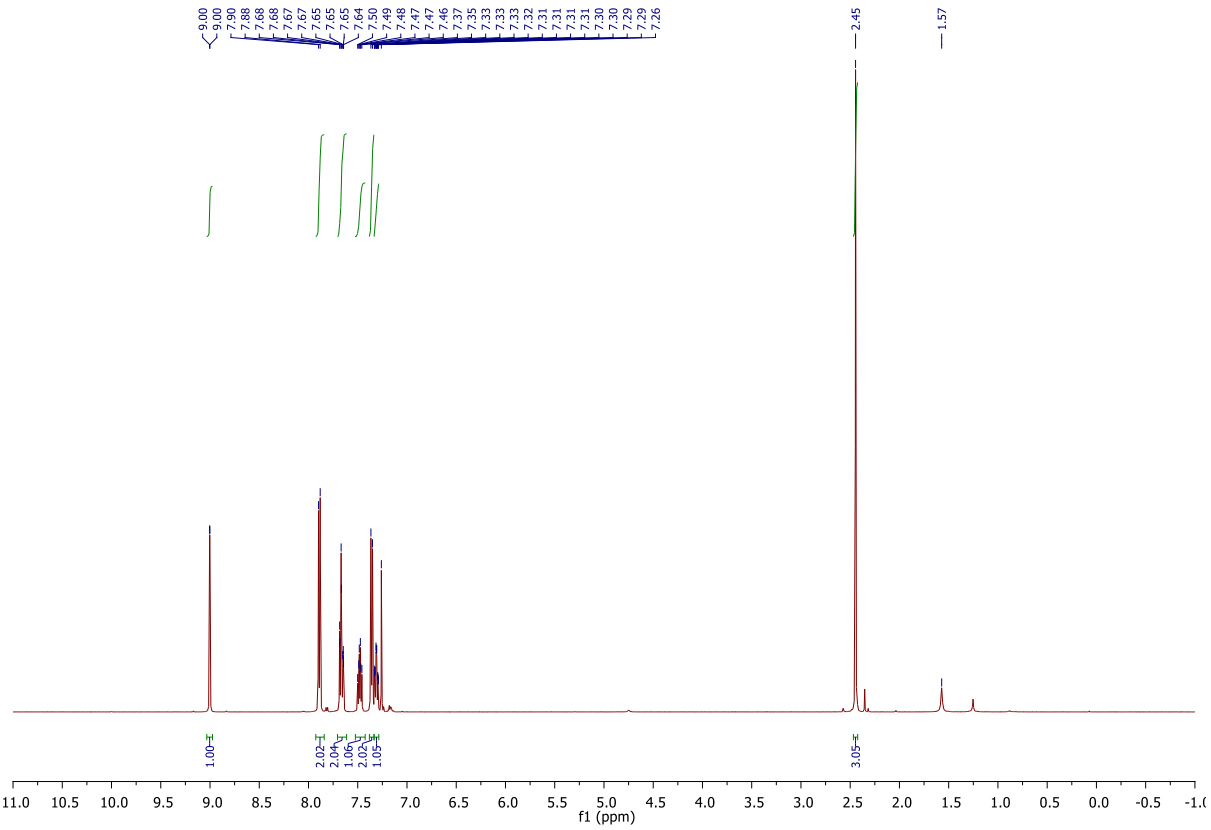


Figure S17. ^{1}H NMR of **SM7**.

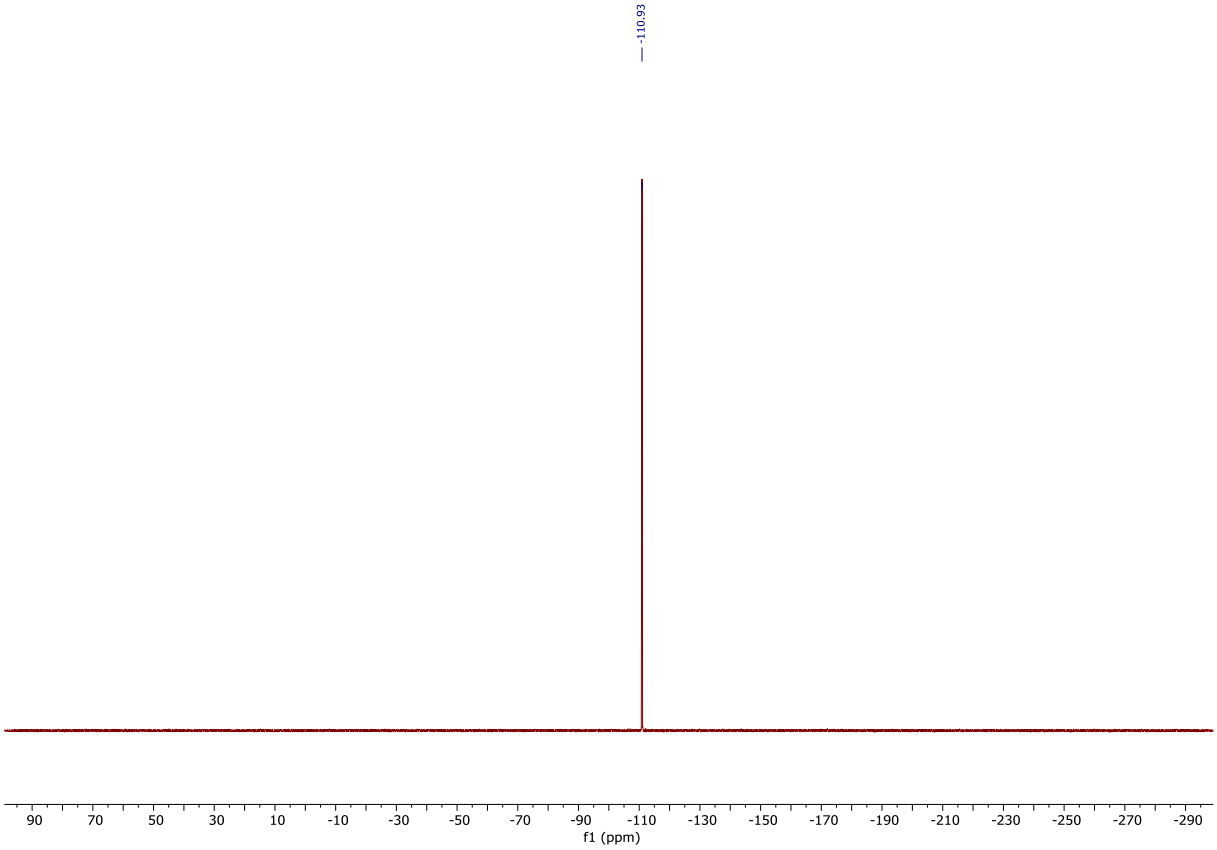


Figure S18. ^{19}F {^{1}H} NMR of **SM7**.

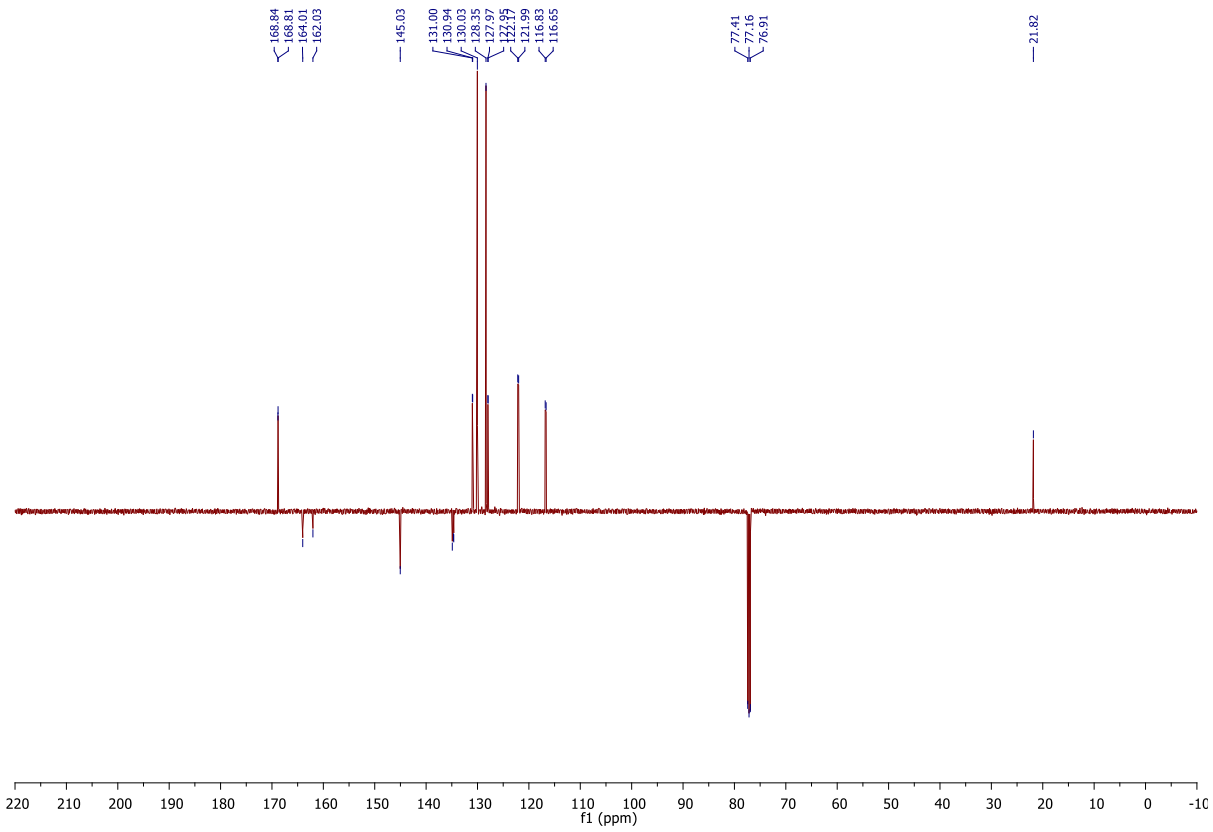
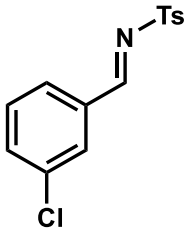


Figure S19. ^{1}H NMR of **SM7**.

***N*-(3-chlorobenzylidene)-4-methylbenzenesulfonamide (SM8)**



Prepared according to general procedure A from *m*-chlorobenzaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as a white solid (0.57 g, 19%) with physical and spectroscopic data in accordance with the literature;[5] R_F = 0.32 (1:4 EtOAc/PE); mp 96 – 98 ˚C (lit. 98 ˚C); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.98 (s, 1H), 7.96 – 7.93 (m, 1H), 7.89 (d, *J* = 8.3, 2H), 7.82 – 7.73 (m, 1H), 7.62 – 7.52 (m, 1H), 7.44 (t, *J* = 7.8, 1H), 7.36 (d, *J* = 8.0, 2H), 2.45 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 168.7, 145.1, 135.6, 134.9, 134.8, 134.2, 130.6, 130.4, 130.0, 129.9, 128.4, 21.8.

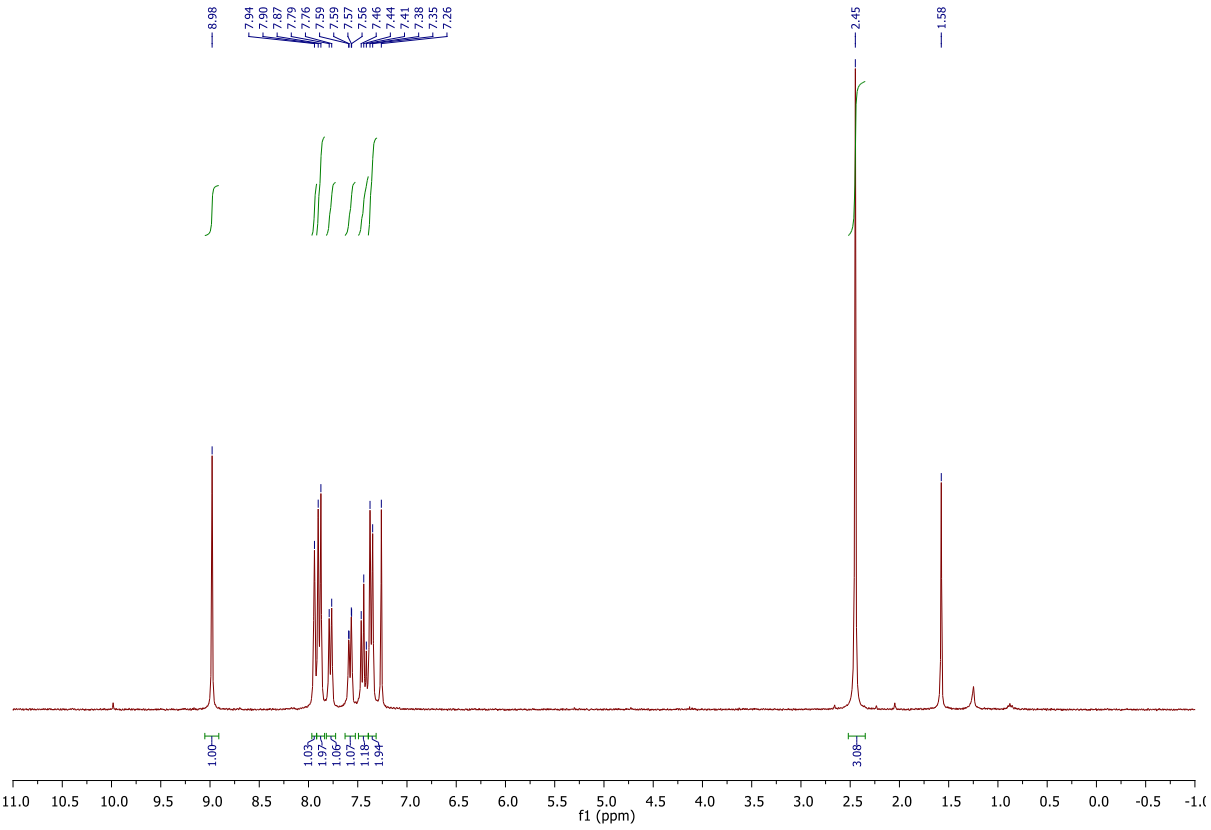


Figure S20. ^{1}H NMR of **SM8**.

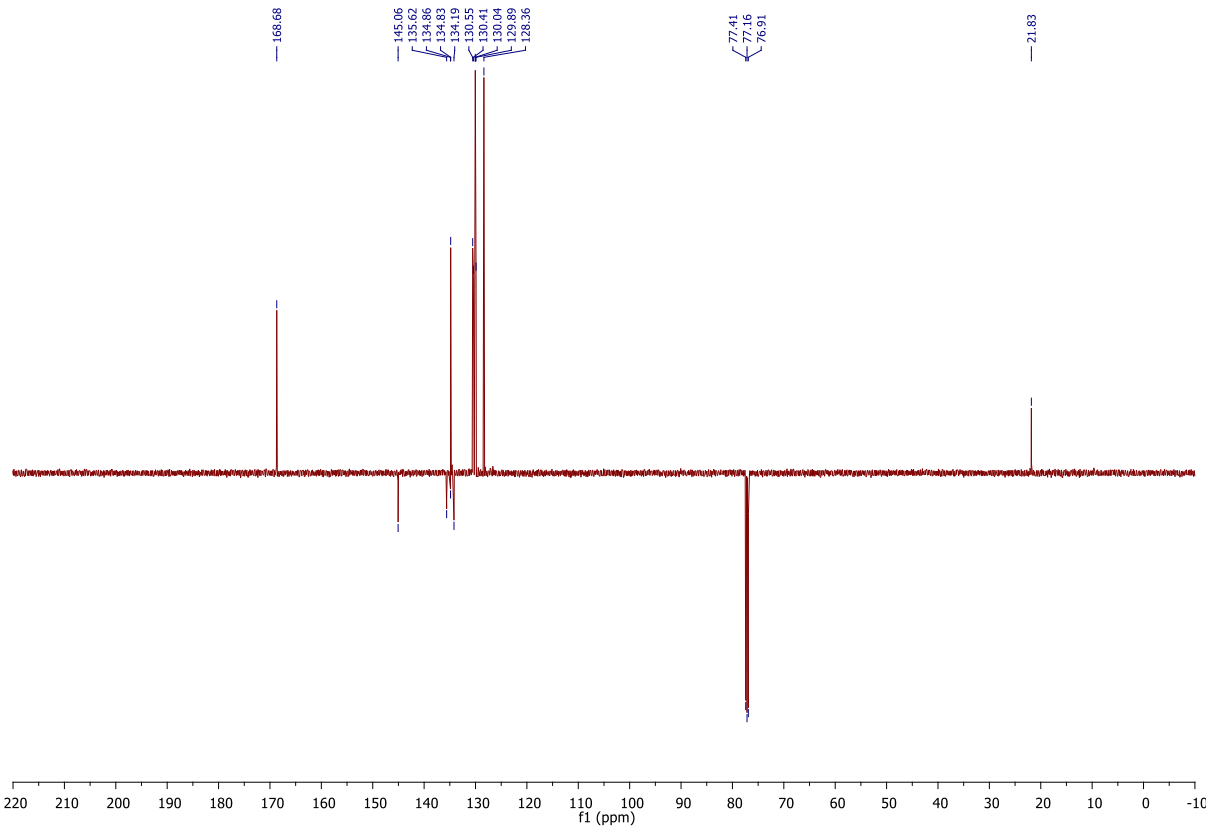
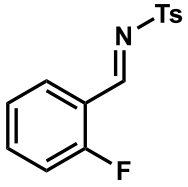


Figure S21. ^{13}C {^{1}H} NMR of **SM8**.

***N*-(2-fluorobenzylidene)-4-methylbenzenesulfonamide (SM9)**



Prepared according to general procedure A from *o*-fluorobenzaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a white solid (1.93 g, 70%) with physical and spectroscopic data in accordance with the literature;[4] R_F = 0.30 (1:4 EtOAc/PE); mp 147 – 149 ˚C (lit. 135 – 137 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.36 (s, 1H), 8.09 – 8.06 (m, 1H), 7.91 – 7.87 (m, 2H), 7.63 – 7.58 (m, 1H), 7.39 – 7.33 (m, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.15 (m, 1H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 164.5 (d, *J* = 260.8), 163.8 (d, *J* = 6.3), 144.9, 137.1 (d, *J* = 10.1), 135.0, 130.0, 129.5 (d, *J* = 1.3), 128.4, 125.0 (d, *J* = 3.8), 120.7 (d, *J* = 8.8), 116.5 (d, *J* = 21.4), 21.8; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -116.1.

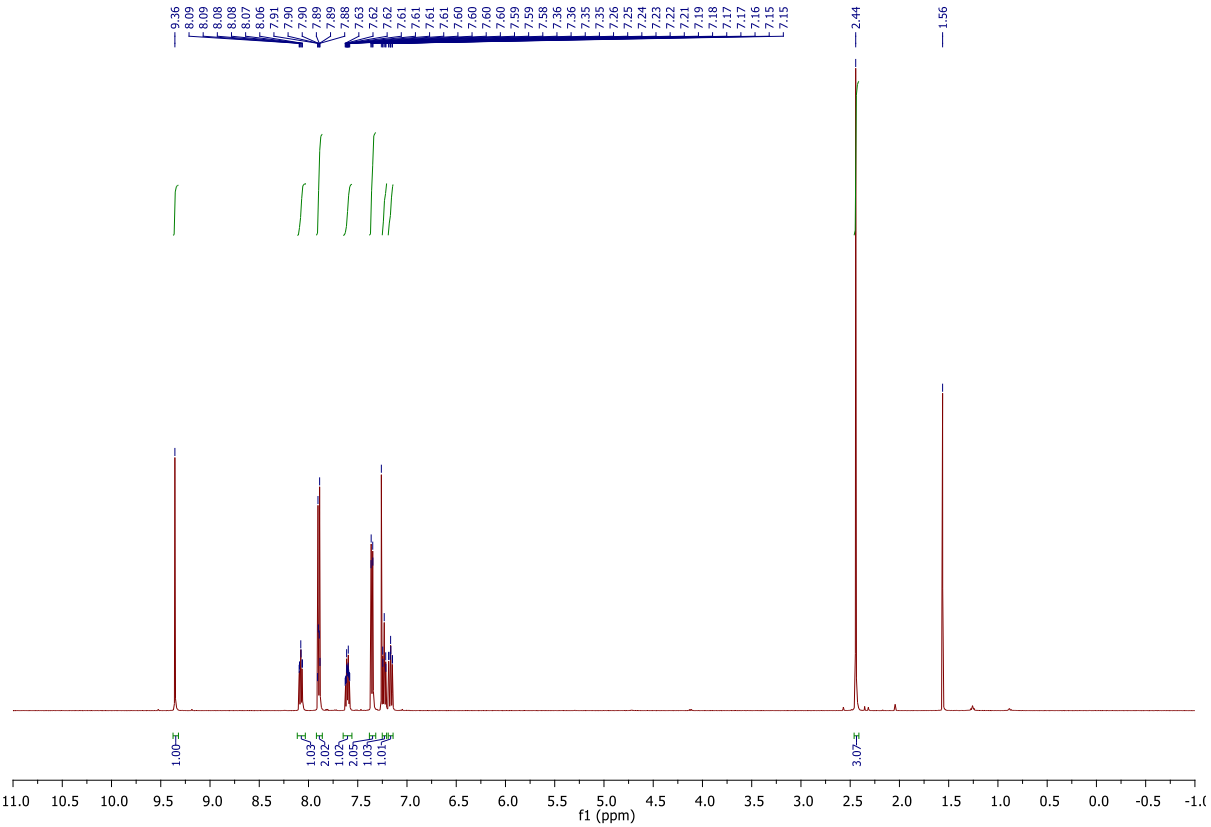


Figure S22. ^{1}H NMR of **SM9**.

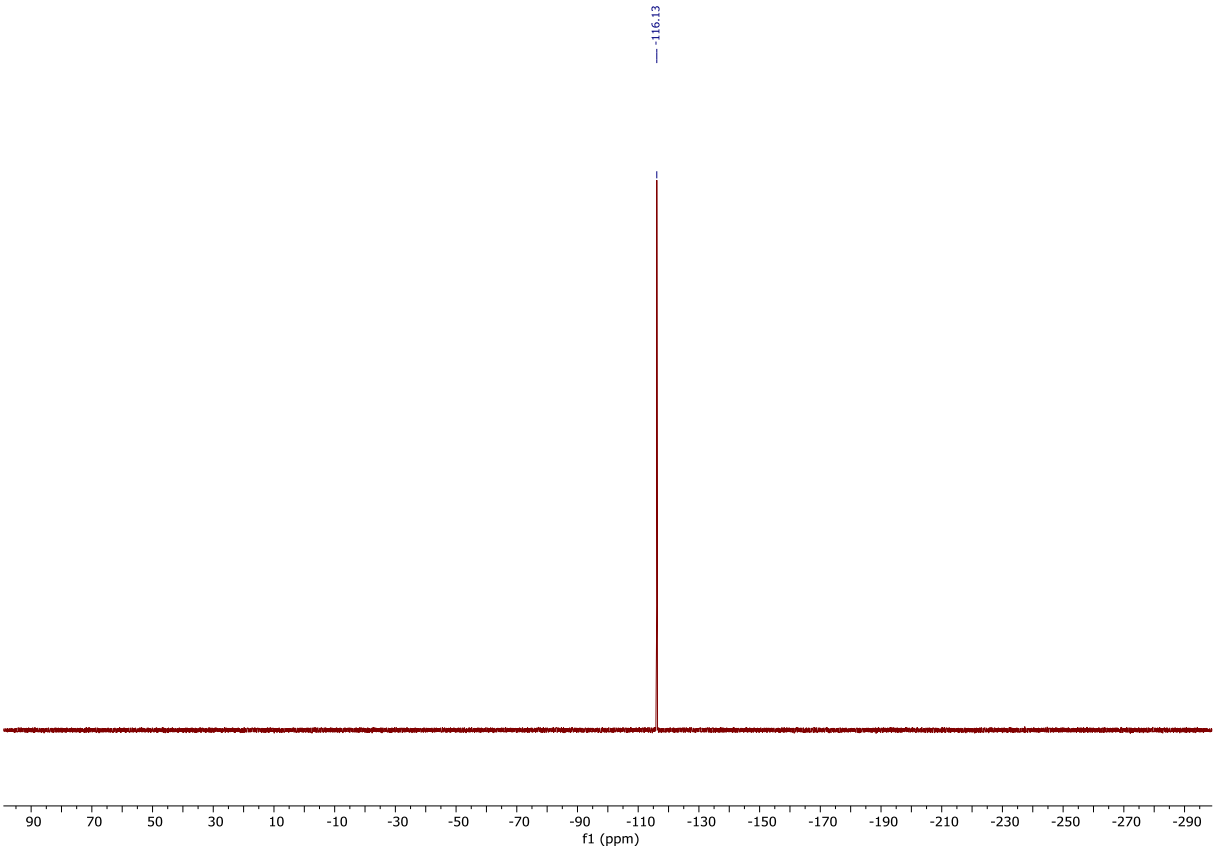


Figure S23. ^{19}F {^{1}H} NMR of **SM9**.

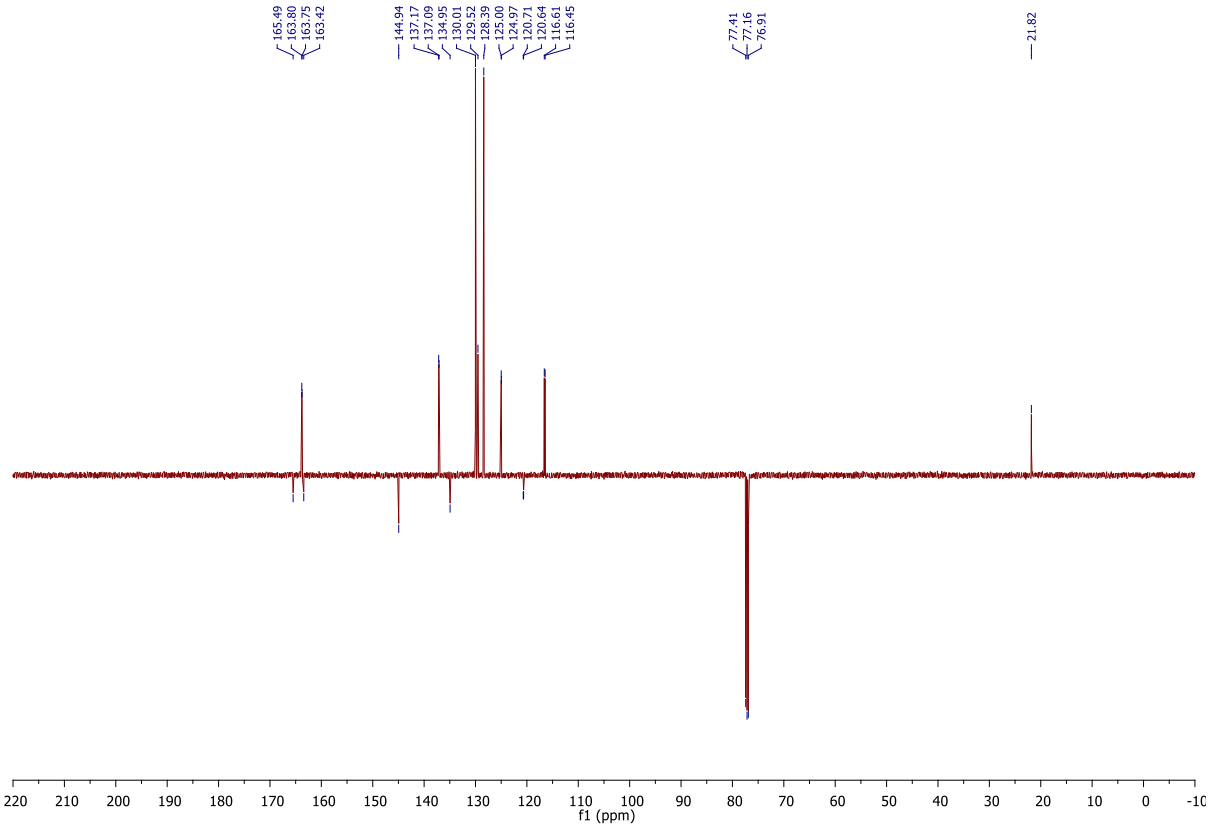
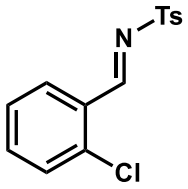


Figure S24. ^{13}C {^{1}H} NMR of **SM9**.

***N*-(2-chlorobenzylidene)-4-methylbenzenesulfonamide (SM10)**



Prepared according to general procedure A from *o*-chlorobenzaldehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as a white solid (1.03 g, 35%) with physical and spectroscopic data in accordance with the literature;[6] R_F = 0.32 (1:4 EtOAc/PE); mp 145 – 147 ˚C (lit. 131 – 132 ˚C); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 9.50 (s, 1H), 8.16 (d, *J* = 9.0, 1H), 7.95 – 7.86 (m, 2H), 7.56 – 7.45 (m, 2H), 7.38 – 7.31 (m, 3H), 2.45 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 166.9, 145.0, 139.1, 135.8, 134.9, 130.6, 130.4, 130.0 (2C), 128.4, 127.5, 21.8.

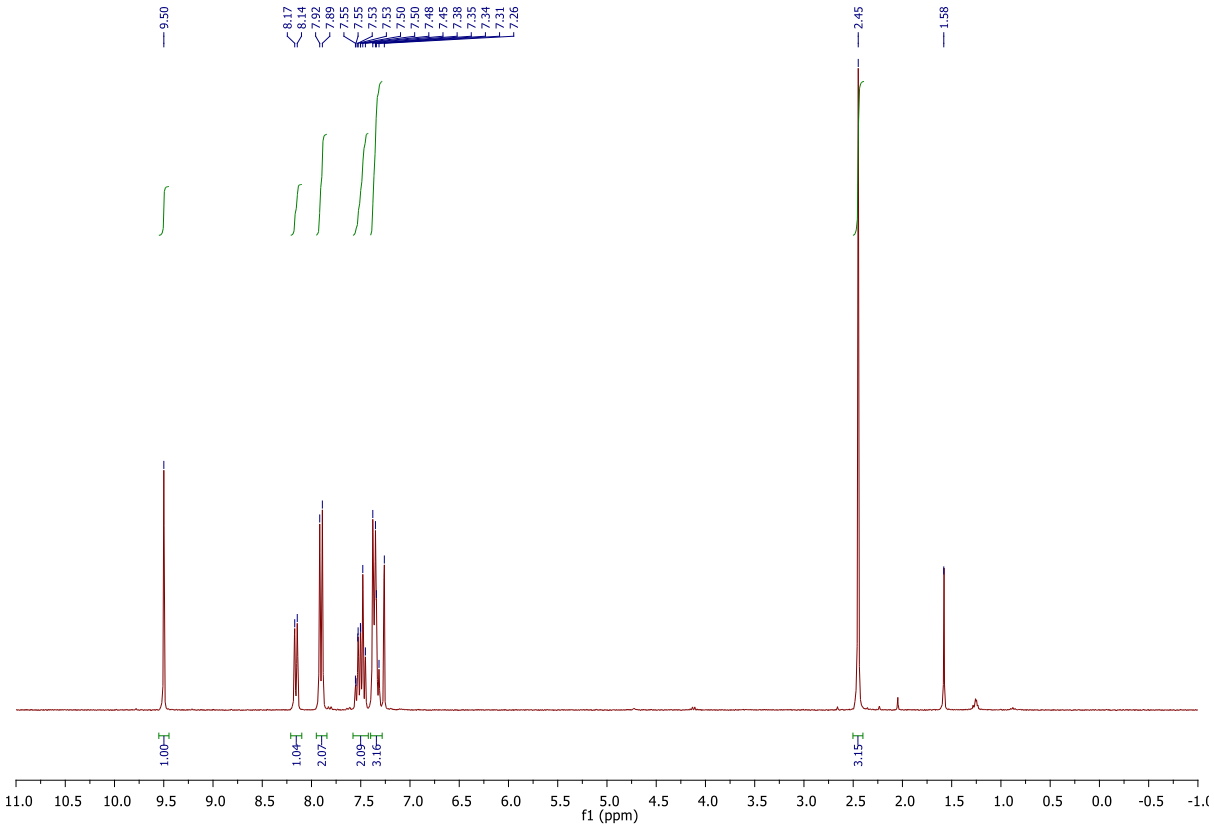


Figure S25. ^{1}H NMR of **SM10**.

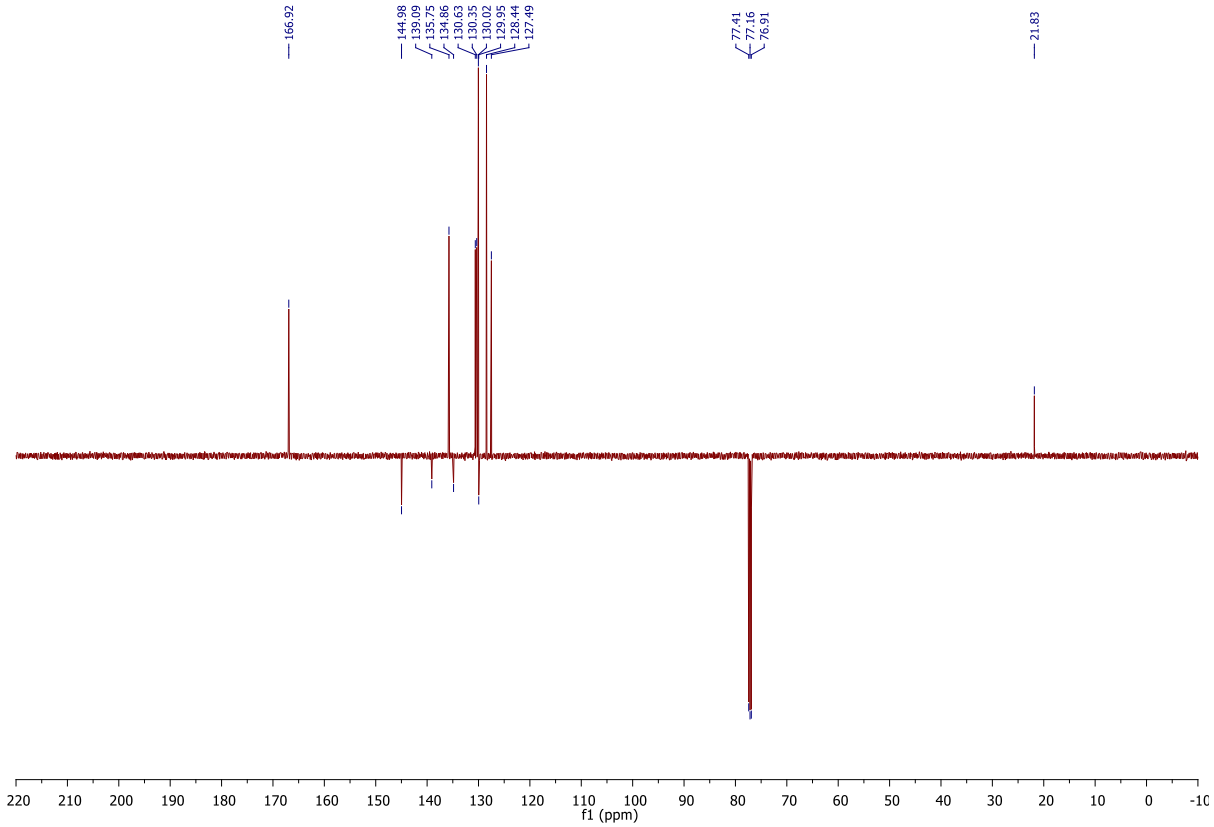
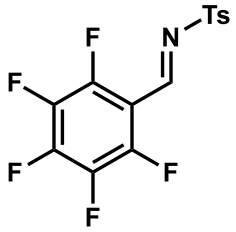


Figure S26. ^{13}C {^{1}H} NMR of **SM10**.

4-methyl-*N*-((perfluorophenyl)methylene)benzenesulfonamide (SM11)



Prepared according to general procedure A from pentafluorobenzaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a white solid (2.20 g, 63%) with physical and spectroscopic data in accordance with the literature;[7] R_F = 0.45 (1:4 EtOAc/PE); mp 139 – 141 ˚C (lit. 118 – 122 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.21 (s, 1H), 7.89 (d, *J* = 8.0, 2H), 7.37 (d, *J* = 8.0, 2H), 2.46 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ_C: 158.7, 145.6, 134.0, 130.2, 128.6, 21.9 (unidentifiable signals between 135 – 150 ppm, due to broadening from multiple ^{13}C-^{19}F couplings); ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -135.9, -142.3, -159.7.

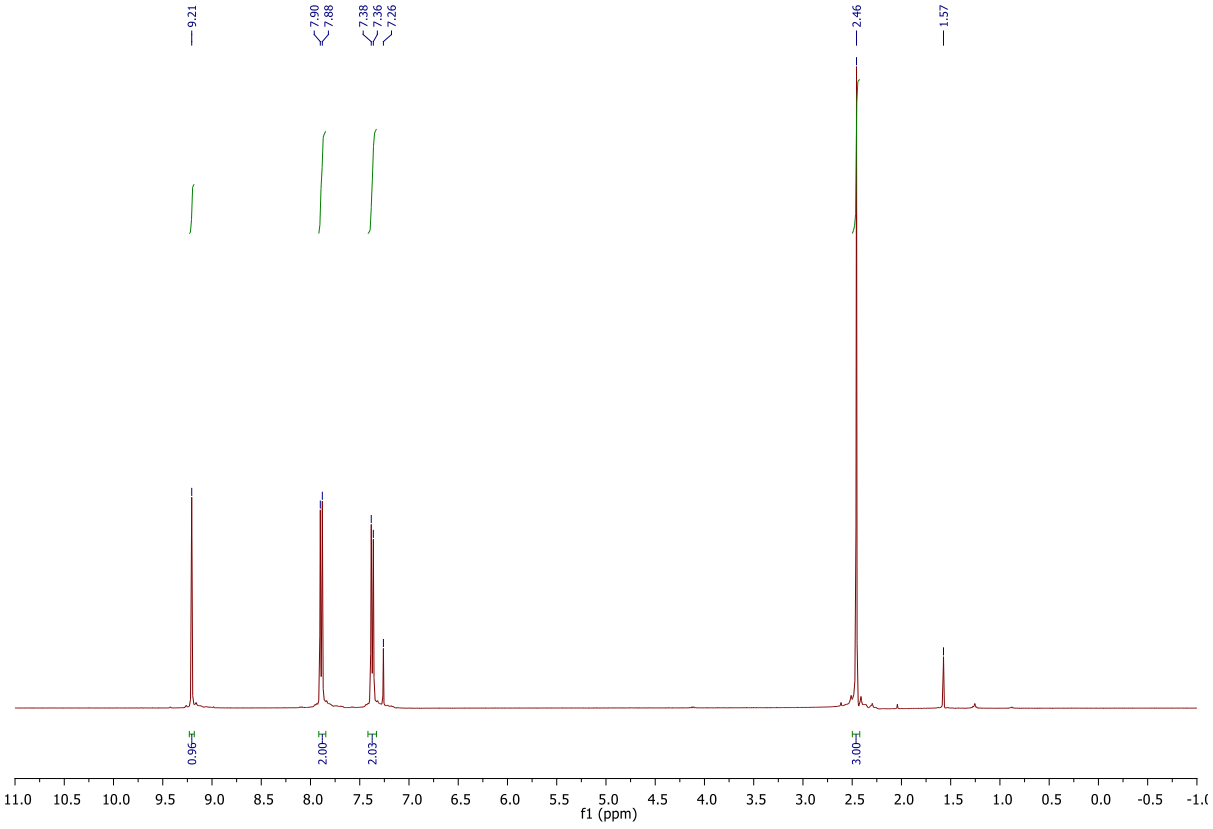


Figure S27. ^{1}H NMR of **SM11**.

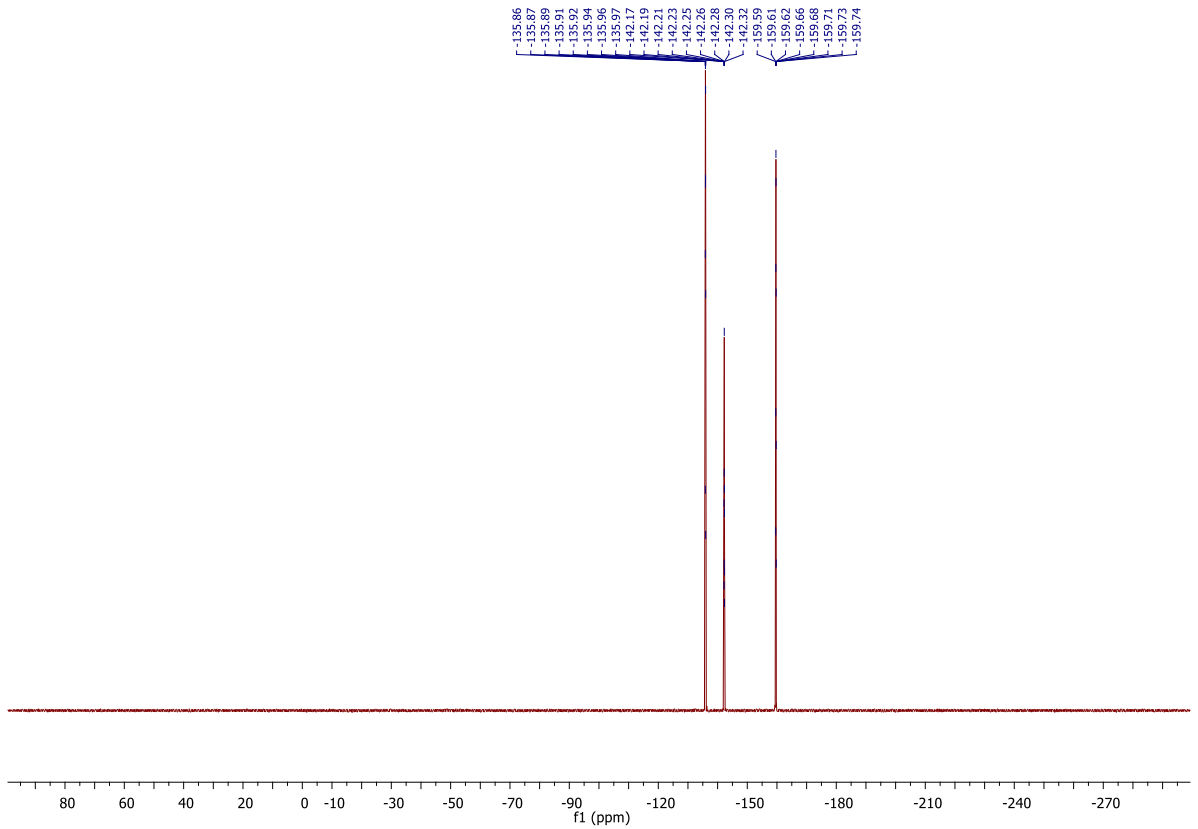


Figure S28. ^{19}F $\{^{1}H\}$ NMR of **SM11**.

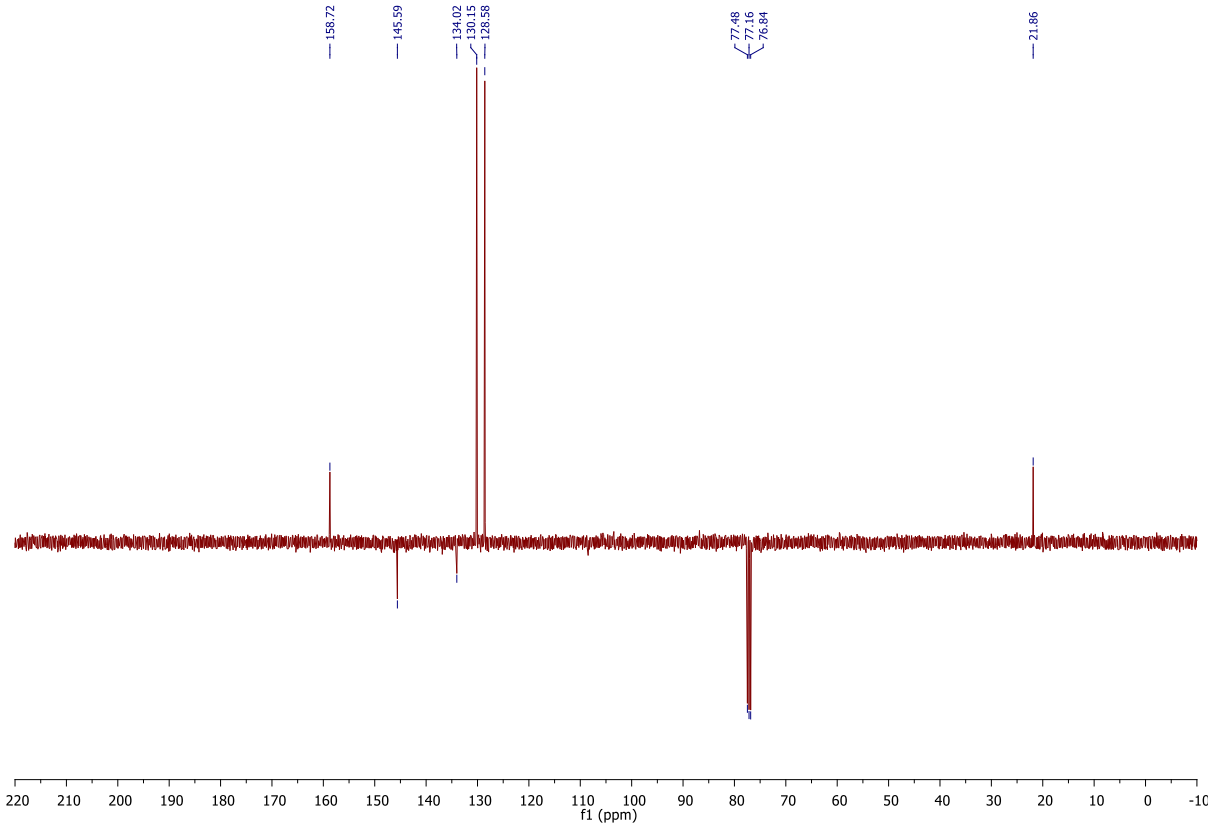
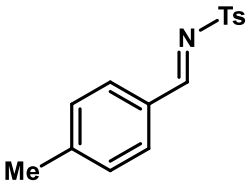


Figure S29. ^{13}C $\{^{1}H\}$ NMR of **SM11**.

4-methyl-*N*-(4-methylbenzylidene)benzenesulfonamide (SM12)



Prepared according to general procedure A from *p*-tolualdehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as a white solid (1.12 g, 41%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.38 (1:4 EtOAc/PE); mp 124 – 126 ˚C (lit. 114 – 115 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.99 (s, 1H), 7.91 – 7.86 (m, 2H), 7.85 – 7.79 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 2.44 – 2.42 (m , 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 170.1, 146.5, 144.6, 135.6, 131.6, 130.1, 130.0, 129.9, 128.2, 22.1, 21.8.

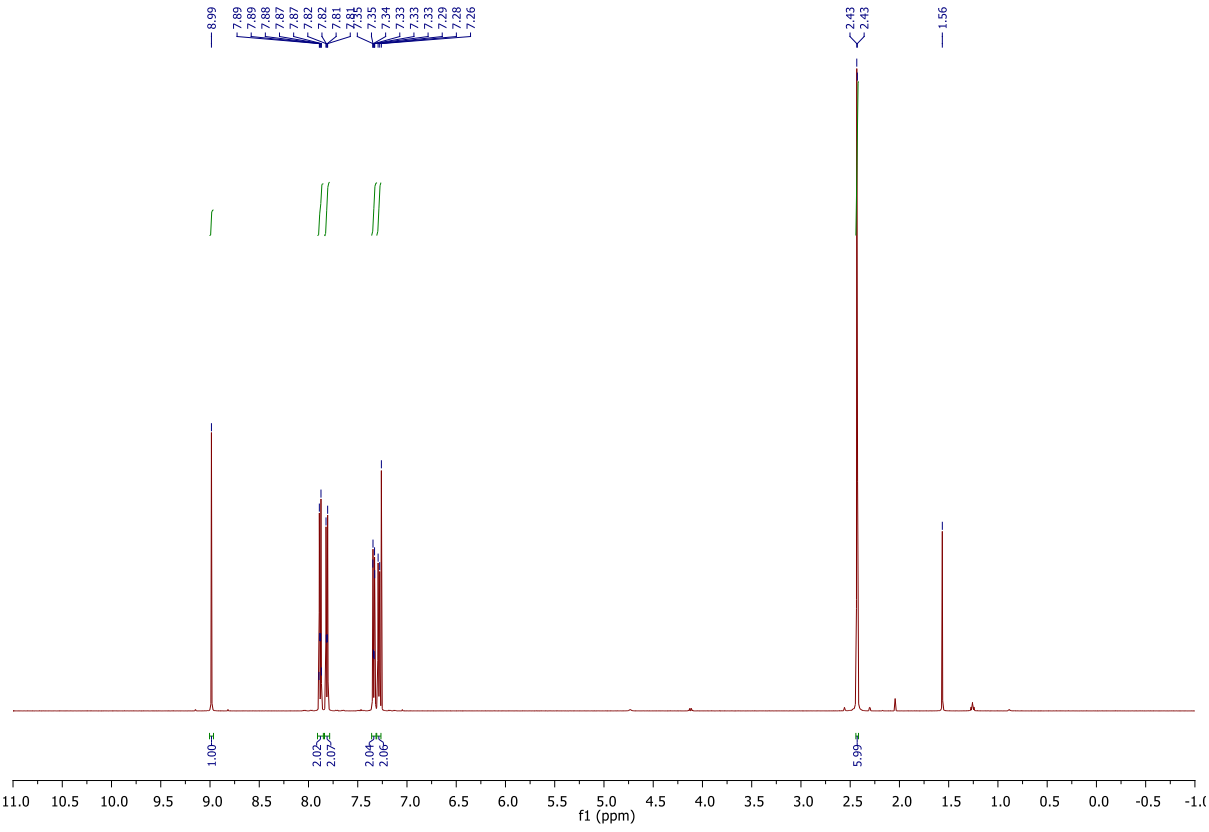


Figure S30. ^{1}H NMR of **SM12**.

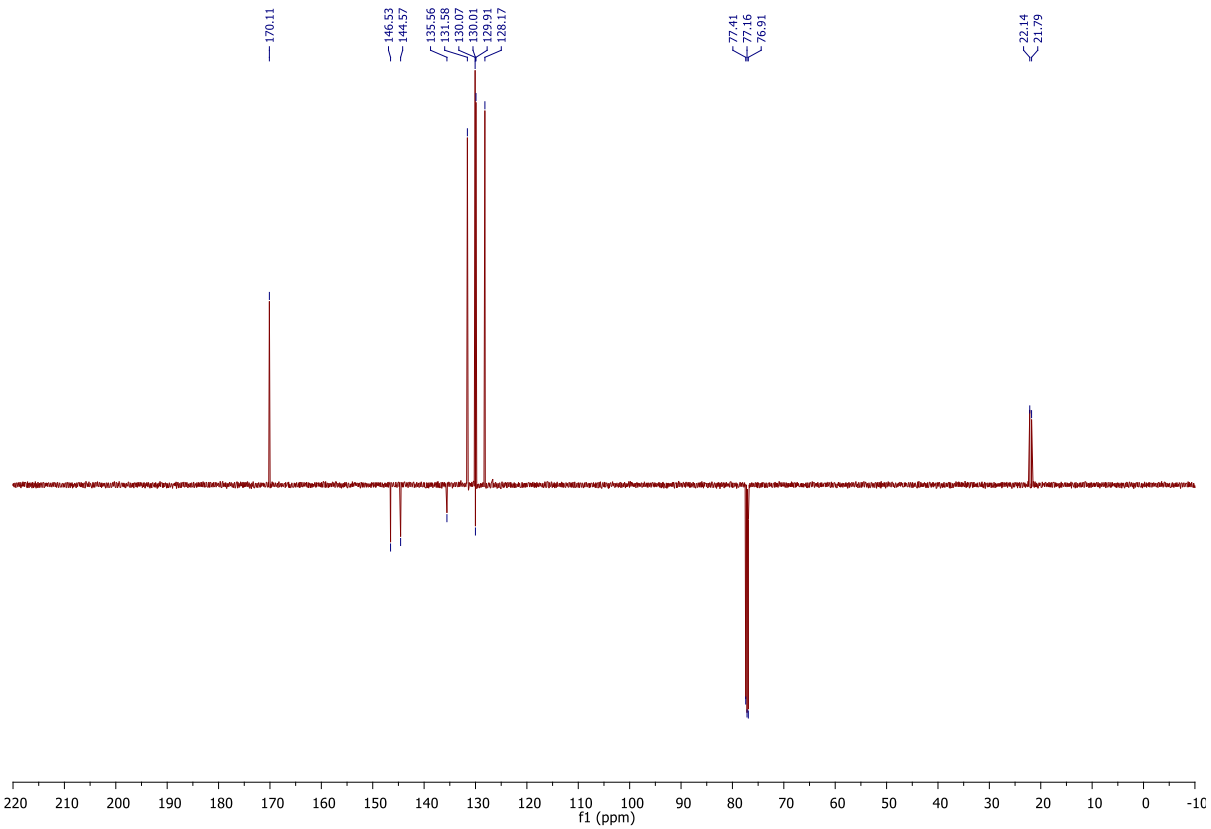
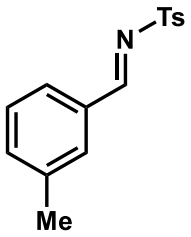


Figure S31. ^{13}C {^{1}H} NMR of **SM12**.

4-methyl-*N*-(3-methylbenzylidene)benzenesulfonamide (SM13)



Prepared according to general procedure A from *m*-tolualdehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as a white solid (0.98 g, 36%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.50 (1.5:8.5 EtOAc/PE); mp 98 – 100 ˚C (lit. 90 – 91 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.00 (s, 1H), 7.90 – 7.87 (m, 2H), 7.76 (s, 1H), 7.73 – 7.68 (m, 1H), 7.44 – 7.41 (m, 1H), 7.39 – 7.33 (m, 3H), 2.44 (s, 3H), 2.39 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 170.5, 144.7, 139.3, 136.0, 135.4, 132.5, 131.5, 129.9, 129.2 (2C), 128.2, 21.8, 21.3.

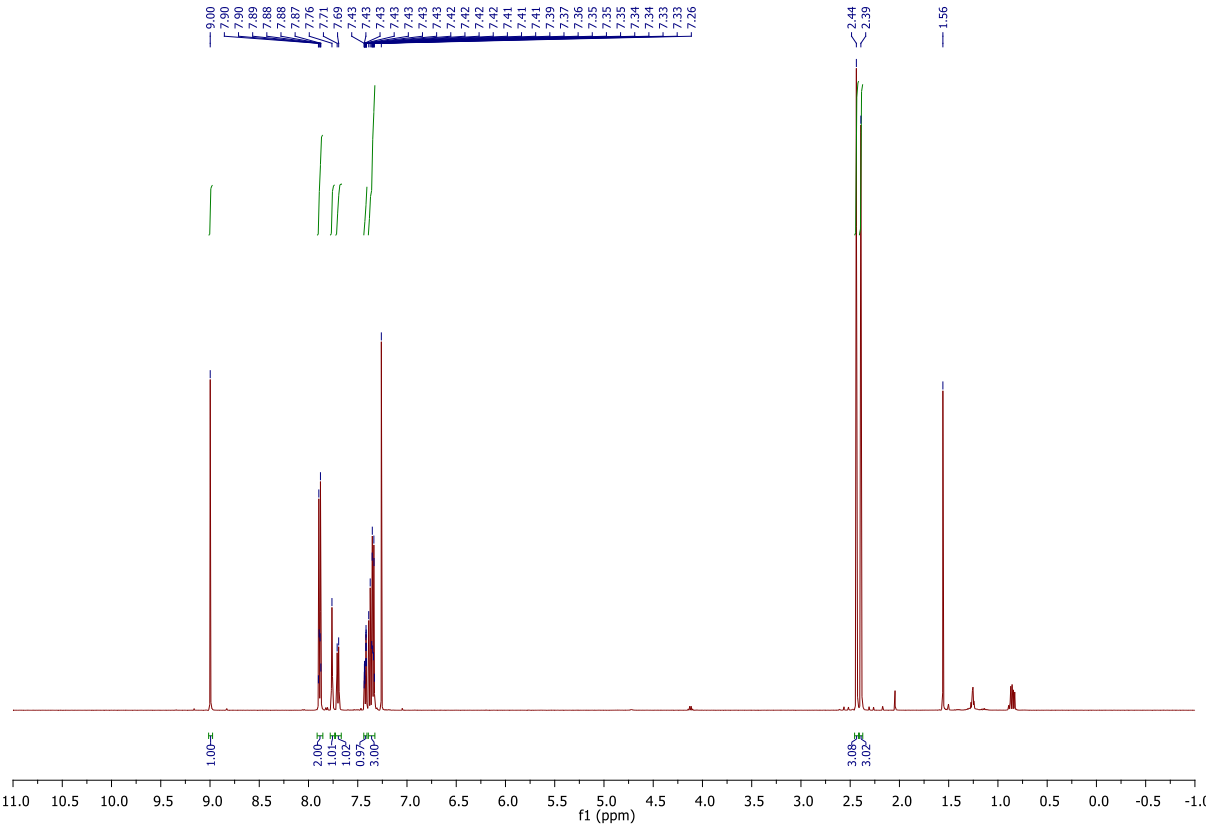


Figure S32. ^{1}H NMR of **SM13**.

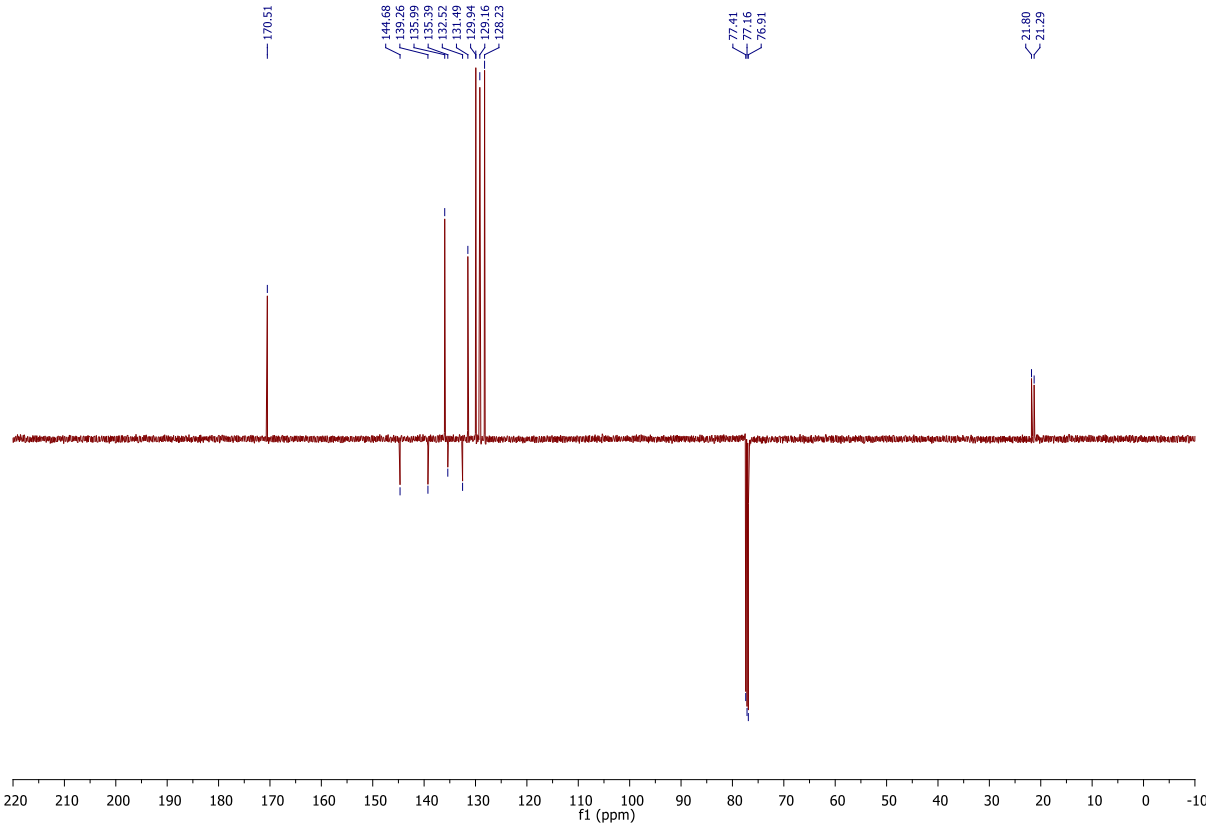
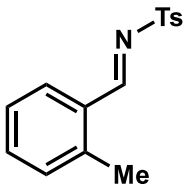


Figure S33. ^{13}C {^{1}H} NMR of **SM13**.

4-methyl-*N*-(2-methylbenzylidene)benzenesulfonamide (SM14)



Prepared according to general procedure A from *o*-tolualdehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as a white solid (0.38 g, 14%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.55 (1:4 EtOAc/PE); mp 104 – 106 ˚C (lit. 94 – 95 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.34 (s, 1H), 8.01 (dd, *J* = 7.8, 1.5, 1H), 7.93 – 7.87 (m, 2H), 7.47 (td, *J* = 7.5, 1.5, 1H), 7.38 – 7.32 (m, 2H), 7.30 – 7.25 (m, 2H), 2.61 (s, 3H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 168.8, 144.6, 142.4, 135.6, 134.7, 131.7, 130.8, 130.6, 129.9, 128.2, 126.8, 21.8, 19.8.

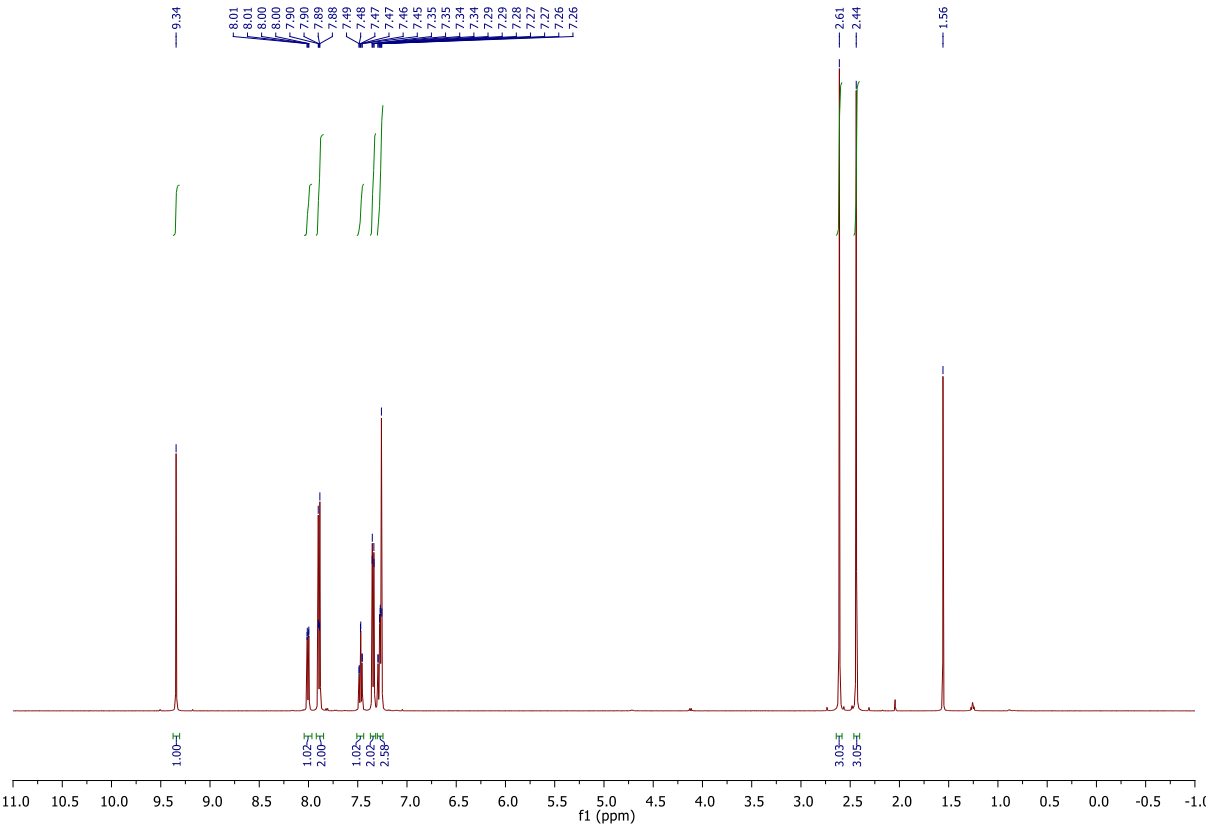


Figure S34. ^{1}H NMR of **SM14**.

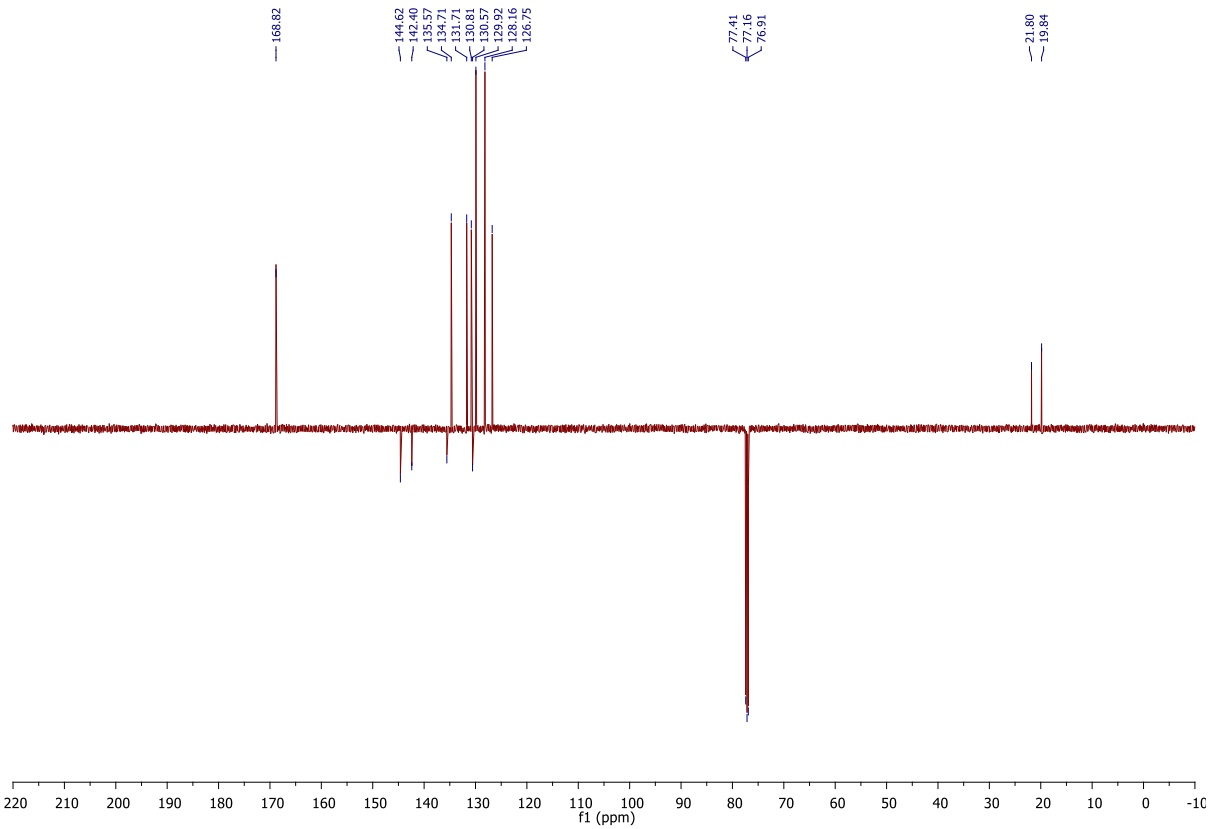
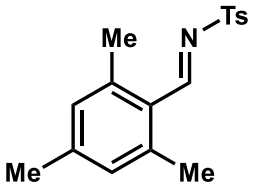


Figure S35. ^{13}C {^{1}H} NMR of **SM14**.

4-methyl-*N*-(2,4,6-trimethylbenzylidene)benzenesulfonamide (32)



Prepared according to general procedure A from mesitaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a white solid (1.78 g, 59%) with physical and spectroscopic data in accordance with the literature;[8] R_F = 0.48 (1.5:8.5 EtOAc/PE); mp 112 – 114 ˚C (lit. 80 – 82 ˚C); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 9.46 (s, 1H), 7.92 – 7.85 (m, 2H), 7.37 – 7.29 (m, 2H), 6.92 (s, 2H), 2.53 (s, 6H), 2.43 (s, 3H), 2.31 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 169.2, 144.8, 144.3, 143.1, 136.2, 130.8, 129.9, 128.0, 126.3, 21.9, 21.8, 21.7.

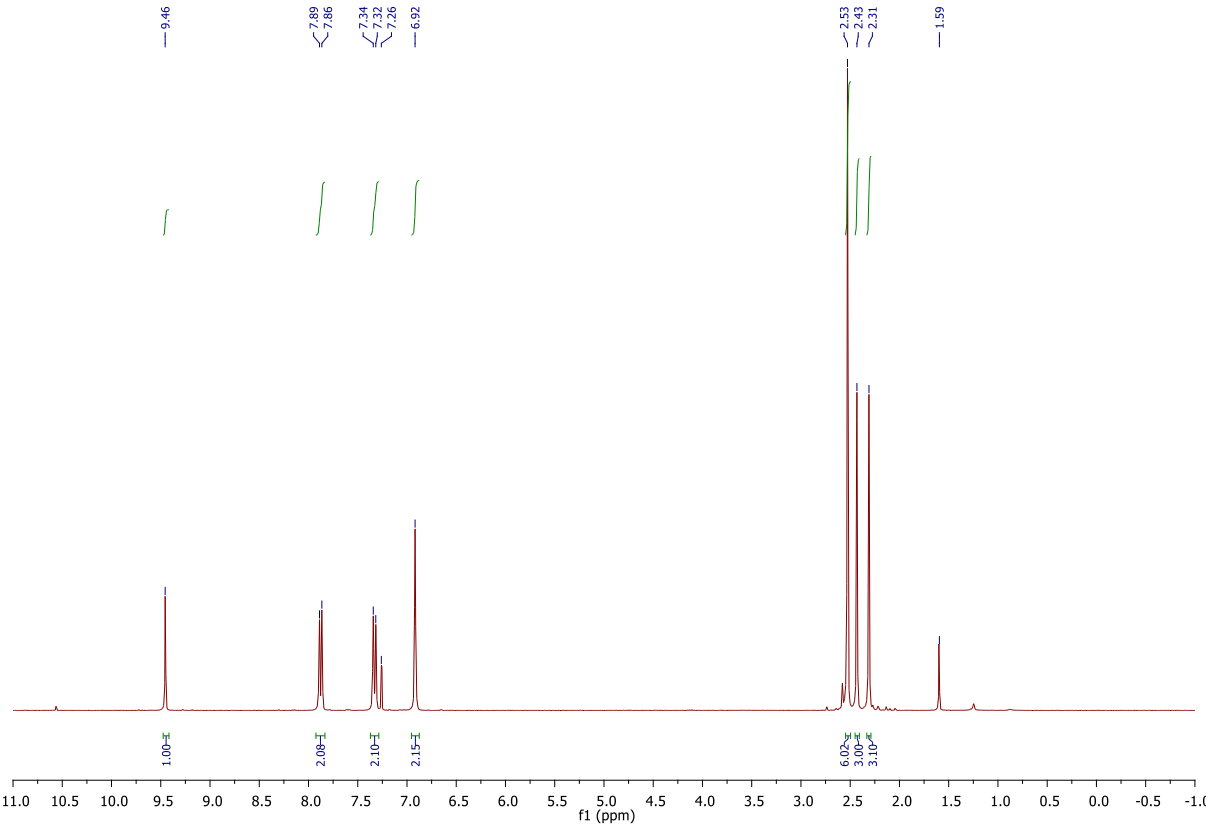


Figure S36. ^{1}H NMR of **32**.

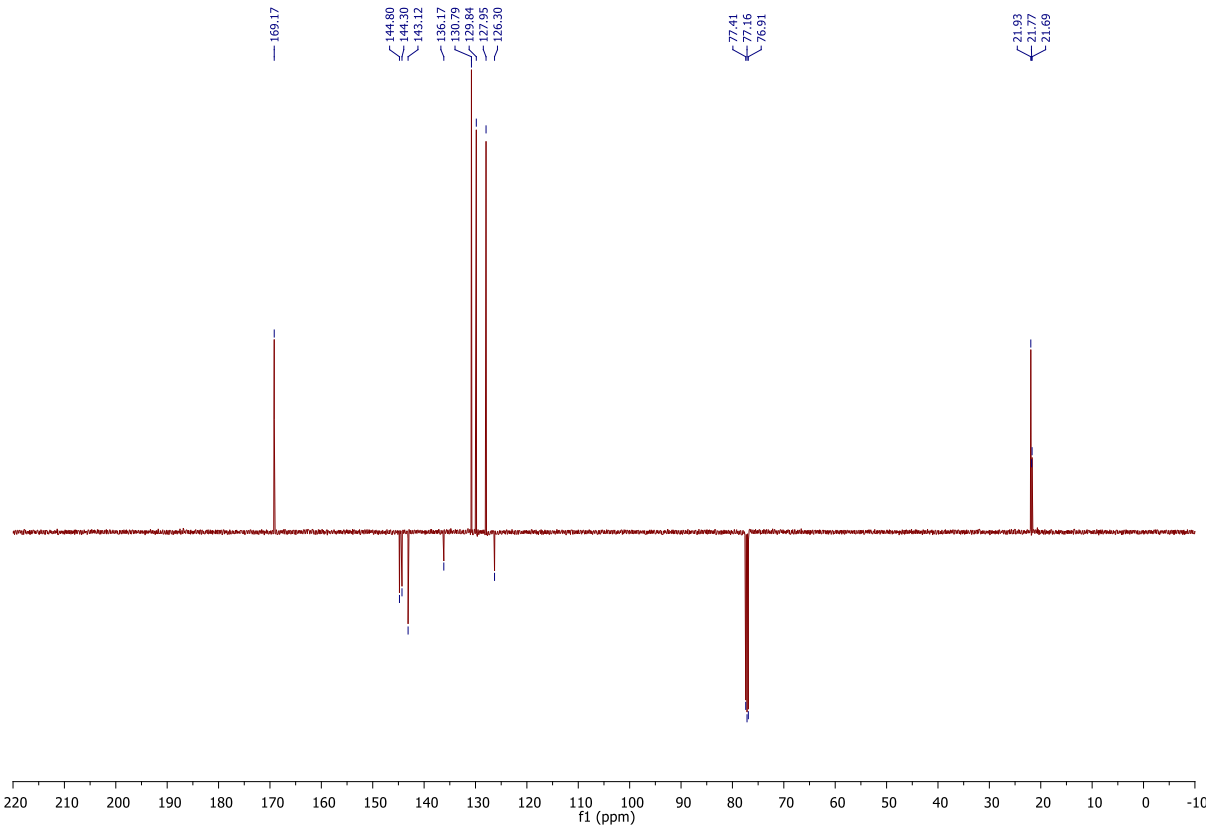
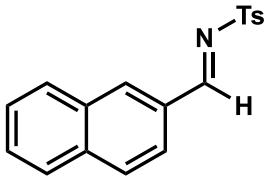


Figure S37. ^{13}C {^{1}H} NMR of **32**.

4-methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide (SM15)



Prepared according to general procedure A from 2-naphthaldehyde (10 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as an off-white solid (1.35 g, 44%) with physical and spectroscopic data in accordance with the literature;[4] R_F = 0.50 (1.5:8.5 EtOAc/PE); mp 123 – 125 ˚C (lit. 112 – 113 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.17 (s, 1H), 8.36 – 8.32 (m, 1H), 8.03 (dd, *J* = 8.6, 1.7, 1H), 7.98 – 7.92 (m, 3H), 7.91 – 7.86 (m, 2H), 7.64 (ddd, *J* = 8.2, 6.9, 1.3, 1H), 7.58 (ddd, *J* = 8.1, 6.9, 1.3, 1H), 7.39 – 7.34 (m, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 170.2, 144.7, 136.7, 136.3, 135.4, 132.8, 130.3, 130.0, 129.7, 129.6, 129.3, 128.3, 128.2, 127.4, 124.3, 21.8.

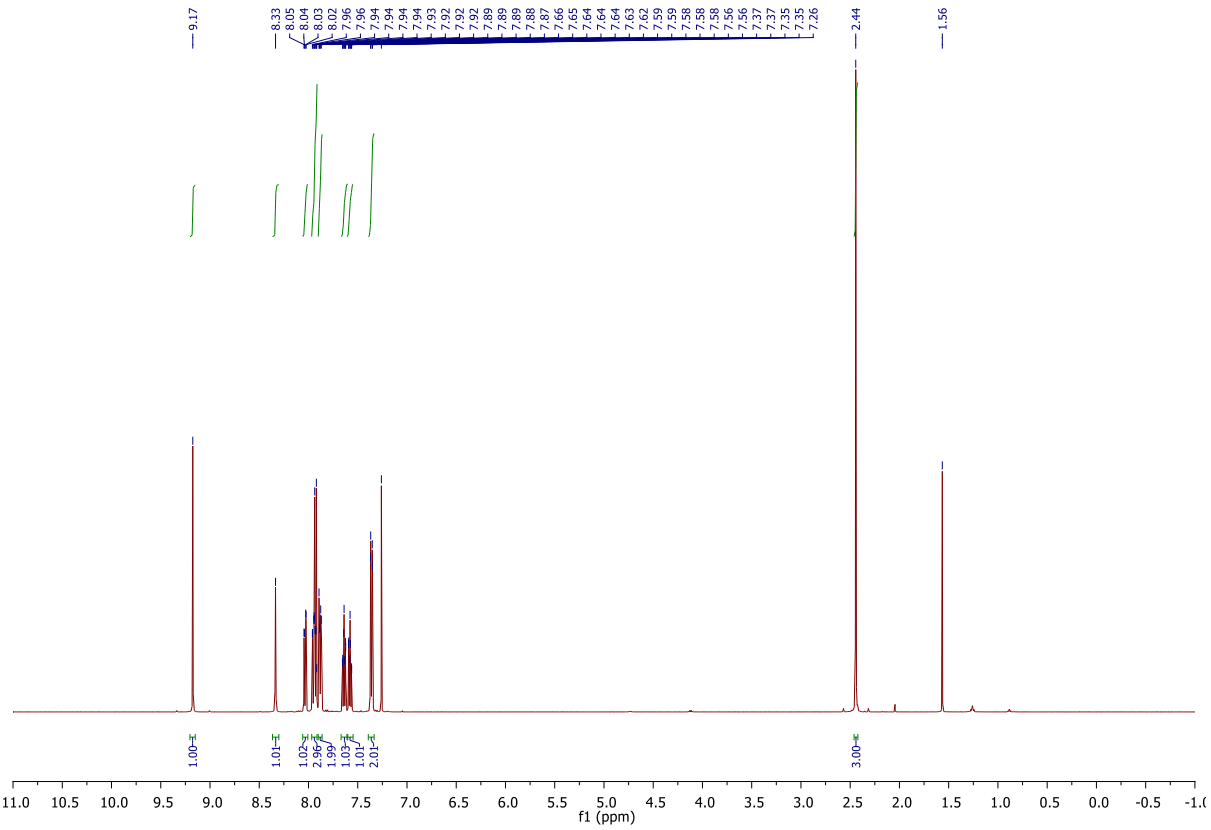


Figure S38. ^{1}H NMR of **SM15**.

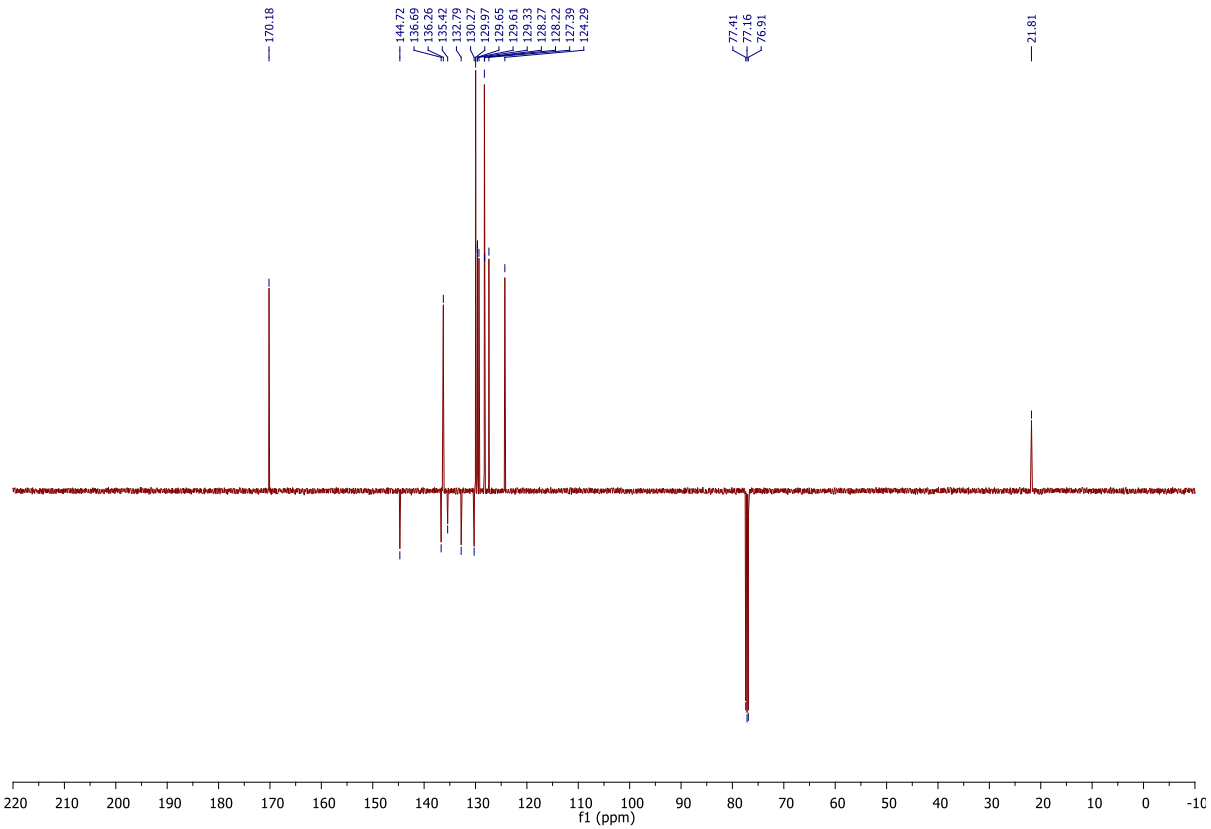
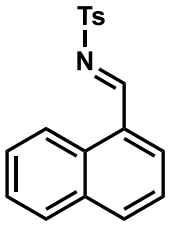


Figure S39. ^{13}C {^{1}H} NMR of **SM15**.

4-methyl-*N*-(naphthalen-1-ylmethylene)benzenesulfonamide (SM16)



Prepared according to general procedure A from 1-naphthaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/toluene to give the title compound as a pale yellow solid (2.22 g, 72%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.33 (1:4 EtOAc/PE); mp 143 – 145 ˚C (lit. 133 – 134 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.61 (s, 1H), 8.99 (d, *J* = 8.5, 1H), 8.16 (dd, *J* = 7.3, 1.3, 1H), 8.10 (d, *J* 8.2, 1H), 7.97 – 7.94 (m, 2H), 7.93 – 7.91 (m, 1H), 7.68 (ddd, *J* = 8.5, 6.9, 1.4, 1H), 7.61 – 7.56 (m, 2H), 7.37 – 7.34 (m, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 169.9, 144.7, 136.3, 135.6, 135.3, 133.9, 132.0, 130.0, 129.2, 129.1, 128.2, 127.8, 127.1, 125.3, 124.4, 21.8.

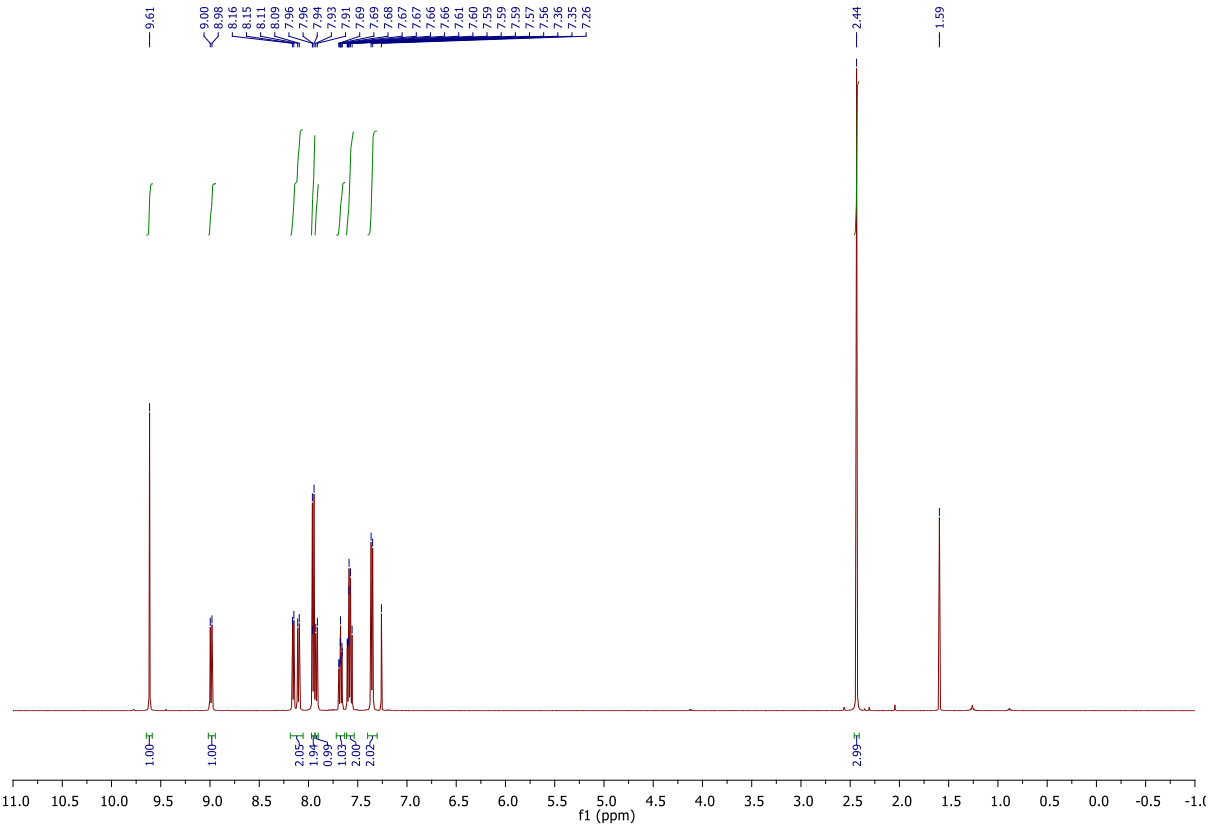


Figure S40. ^{1}H NMR of **SM16**.

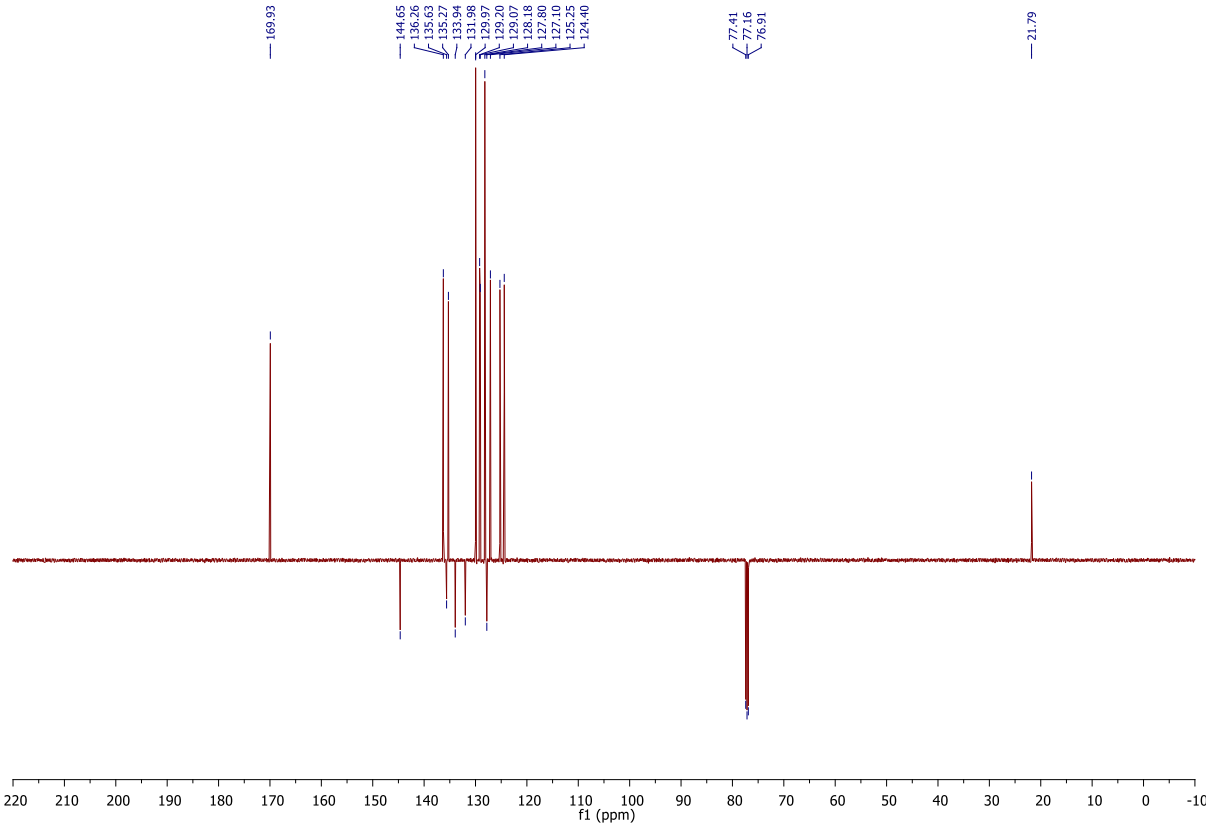
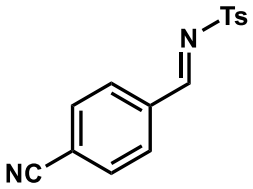


Figure S41. ^{13}C {^{1}H} NMR of **SM16**.

***N*-(4-cyanobenzylidene)-4-methylbenzenesulfonamide (SM17)**



Prepared according to general procedure A from *p*-cyanobenzaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as a white solid (2.02 g, 71%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.48 (1:4 EtOAc/PE); mp 189 – 191 ˚C (lit. 179 – 180 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.05 (s, 1H), 8.06 – 8.00 (m, 2H), 7.92 – 7.86 (m, 2H), 7.81 – 7.75 (m, 2H), 7.40 – 7.34 (m, 2H), 2.45 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 167.9, 145.4, 136.1, 134.4, 132.9, 131.4, 130.1, 128.5, 117.8 (2C), 21.9.

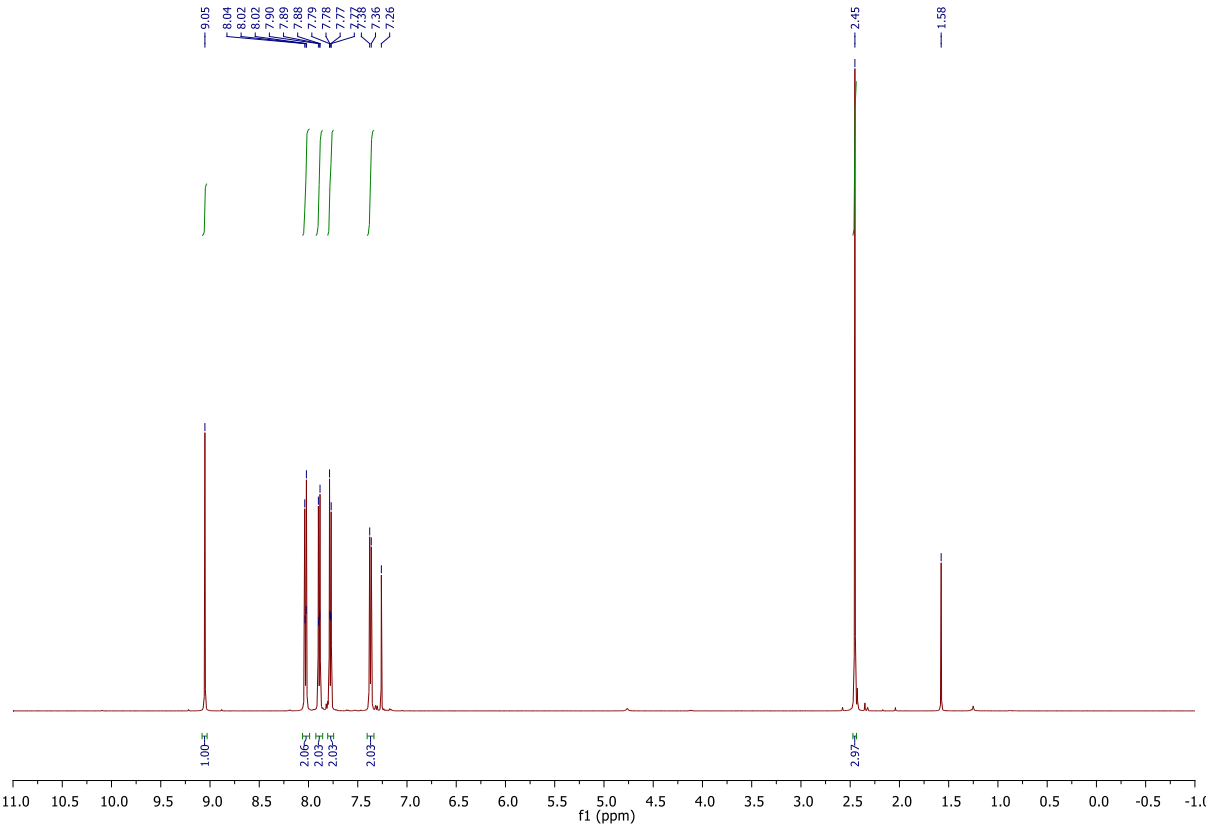


Figure S42. ^{1}H NMR of **SM17**.

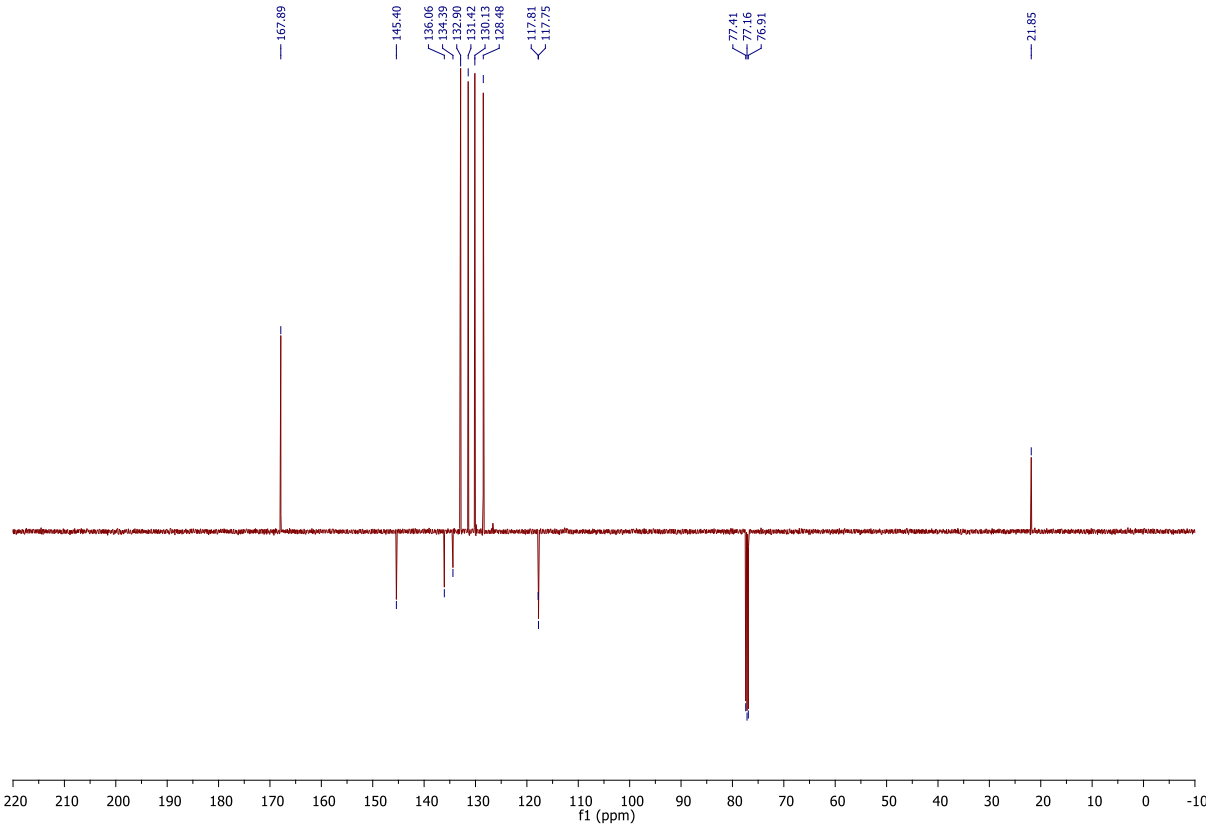
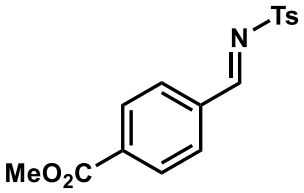


Figure S43. ^{13}C {^{1}H} NMR of **SM17**.

Methyl-4-((tosylimino)methyl)benzoate (SM18)



Prepared according to general procedure A from methyl-4-formylbenzoate (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from toluene to give the title compound as a white solid (2.27 g, 72%) with physical and spectroscopic data in accordance with the literature;[9] R_F = 0.23 (1:4 EtOAc/PE); mp 191 – 192 ˚C (lit. 183 – 185 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.06 (s, 1H), 8.18 – 8.07 (m, 2H), 8.01 – 7.96 (m, 2H), 7.92 – 7.87 (m, 2H), 7.38 – 7.33 (m, 2H), 3.95 (s, 3H), 2.45 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 169.0, 166.0, 145.1, 136.0, 135.5, 134.8, 131.2, 130.3, 130.1, 128.4, 52.6, 21.8.

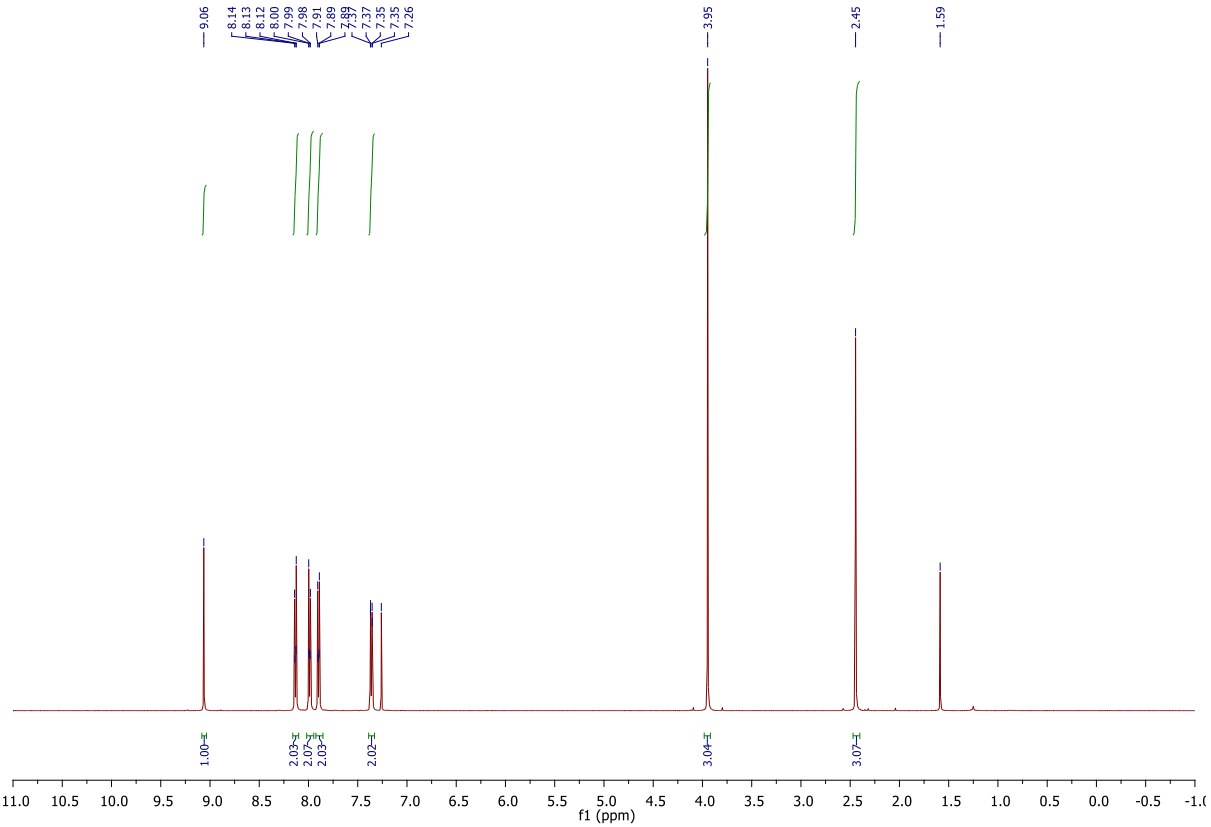


Figure S44. ^{1}H NMR of **SM18**.

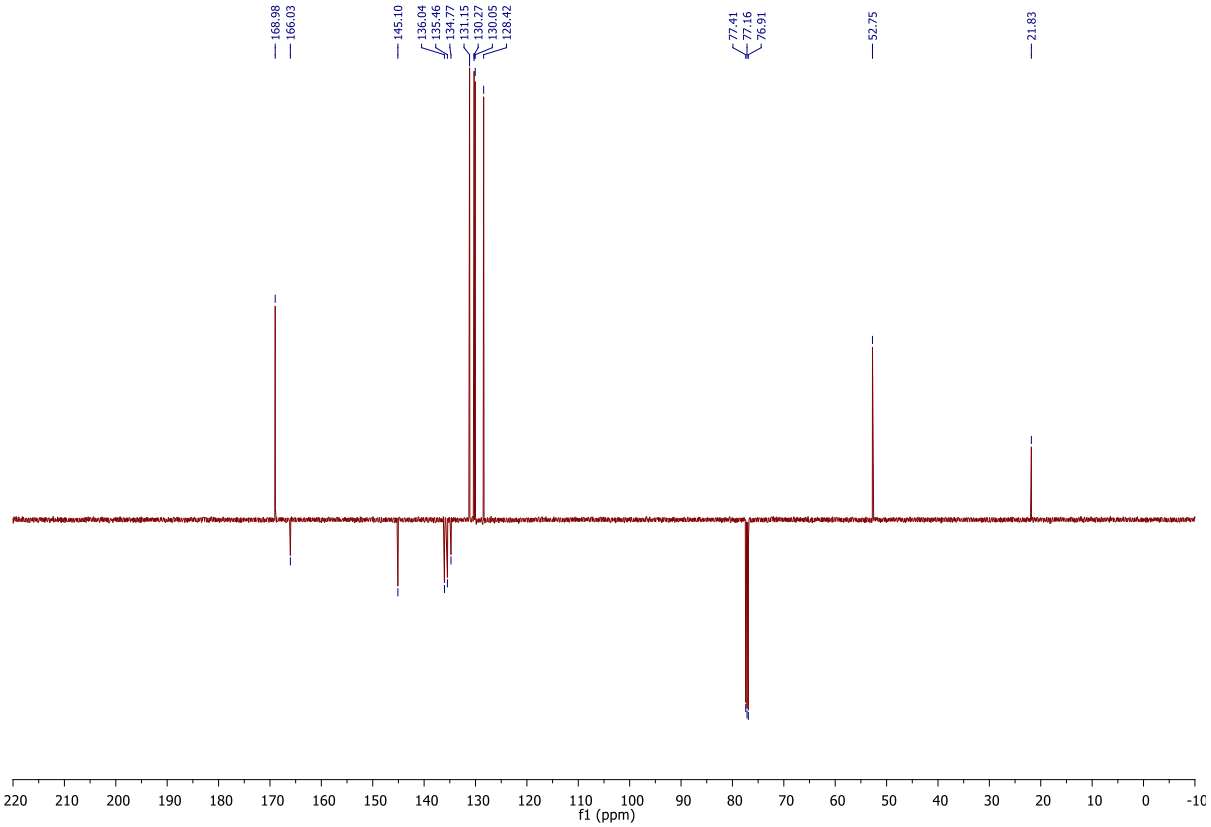
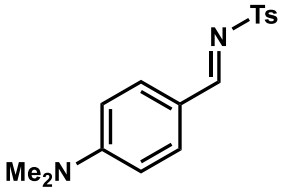


Figure S45. ^{13}C {^{1}H} NMR of **SM18**.

***N*-(4-(dimethylamino)benzylidene)-4-methylbenzenesulfonamide (30)**



Prepared according to general procedure A from *p*-(dimethylamino)benzaldehyde (5.5 mmol) and *p*-toluenesulfonamide (5 mmol) for 16 h, to give the title compound as a yellow solid (1.32 g, 87%), with no further purification required and physical and spectroscopic data in accordance with the literature;[3] R_F = 0.38 (1:4 EtOAc:PE); mp 183 – 185 ˚C (lit. 171 – 172 ˚C); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.82 (s, 1H), 7.89 – 7.82 (m, 2H), 7.80 – 7.74 (m, 2H), 7.34 – 7.27 (m, 2H), 6.70 – 6.61 (m, 2H), 3.10 (s, 6H), 2.41 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 169.2, 155.0, 143.7, 137.0, 134.1, 129.7, 127.7, 120.1, 111.5, 40.3, 21.7.

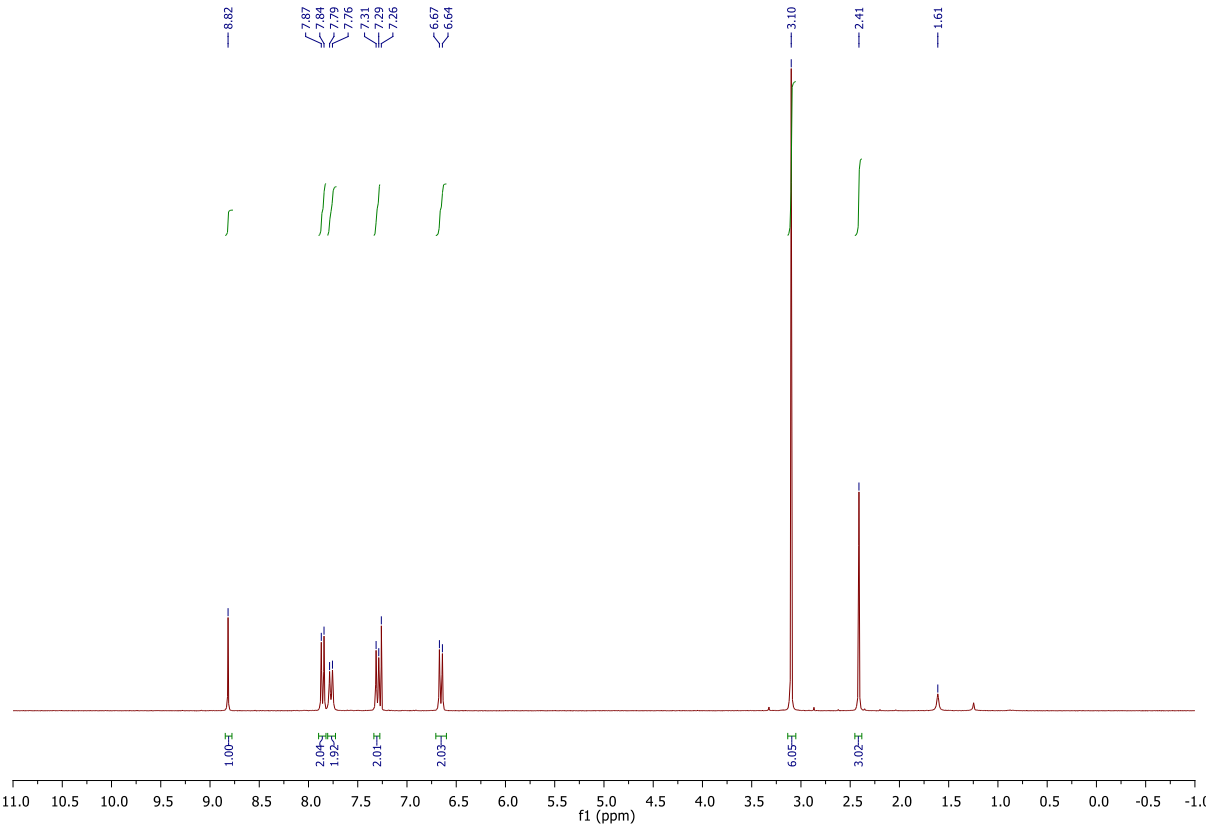


Figure S46. ^{1}H NMR of **30**.

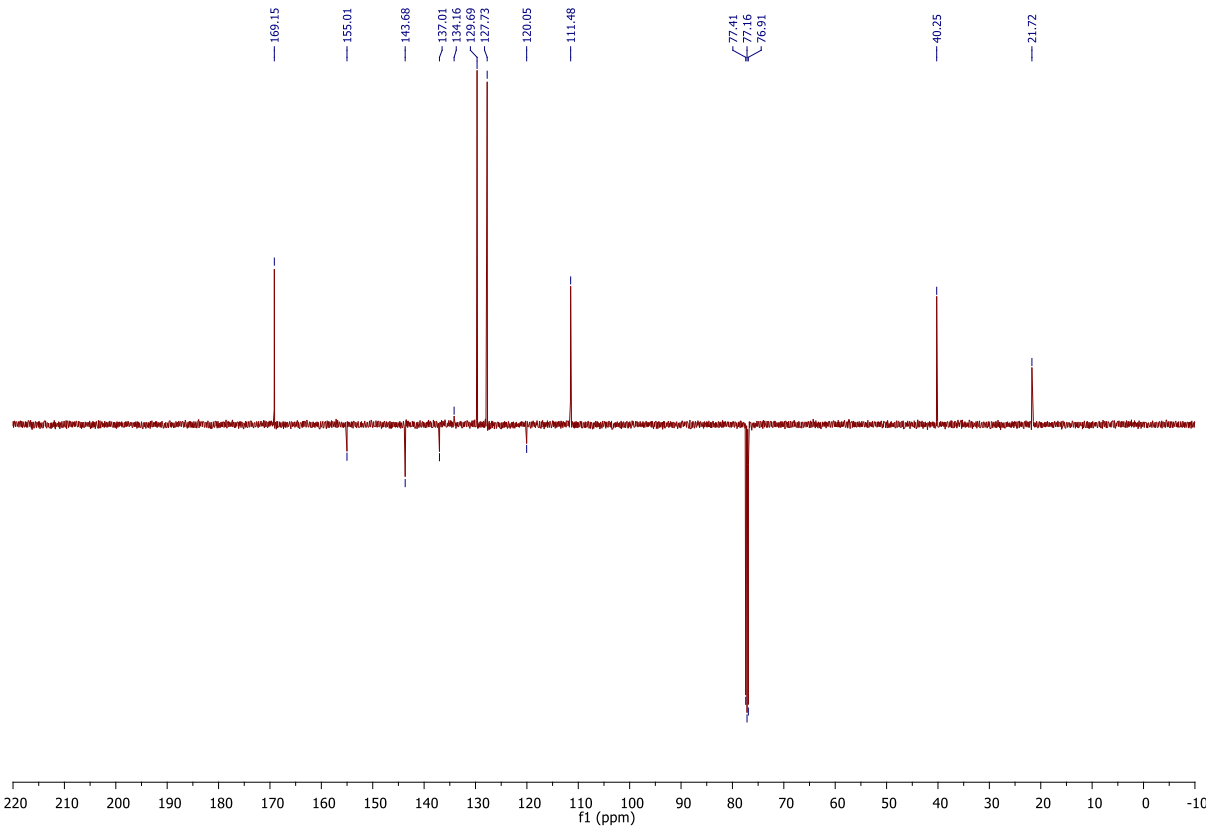
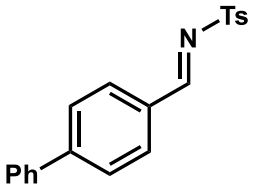


Figure S47. ^{13}C {^{1}H} NMR of **30**.

***N*-([1,1'-biphenyl]-4-ylmethylene)-4-methylbenzenesulfonamide (SM19)**



Prepared according to general procedure A from biphenyl-4-carboxaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a white solid (2.35 g, 70%) with physical and spectroscopic data in accordance with the literature;[10] R_F = 0.48 (1:4 EtOAc/PE); mp 130 – 132 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 9.07 (s, 1H), 8.00 (d, *J* = 8.2, 2H), 7.95 – 7.86 (m, 2H), 7.71 (d, *J* = 8.2, 2H), 7.66 – 7.59 (m, 2H), 7.52 – 7.40 (m, 3H), 7.36 (d, *J* = 8.1, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 169.8, 147.8, 144.7, 139.6, 135.4, 132.0, 131.4, 130.0, 129.2, 128.8, 128.2, 127.9, 127.4, 21.8.

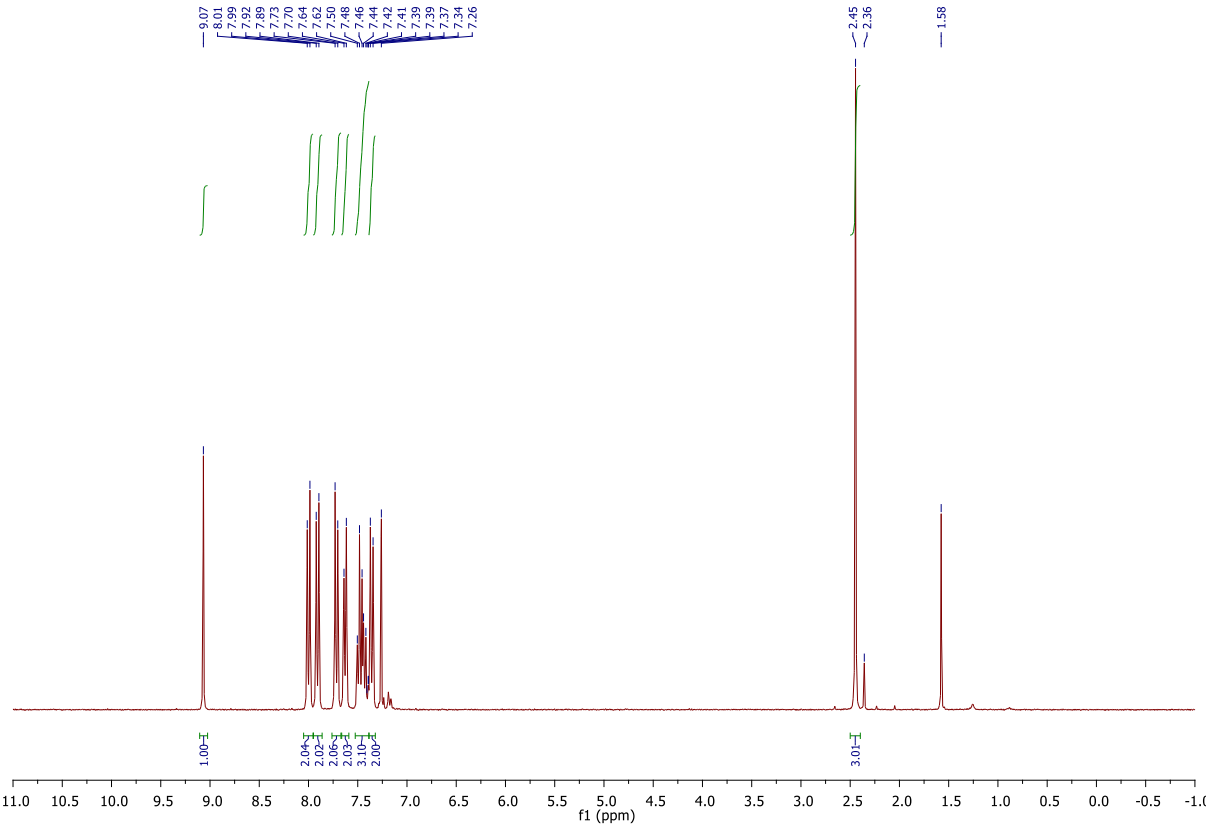


Figure S48. ^{1}H NMR of **SM19**.

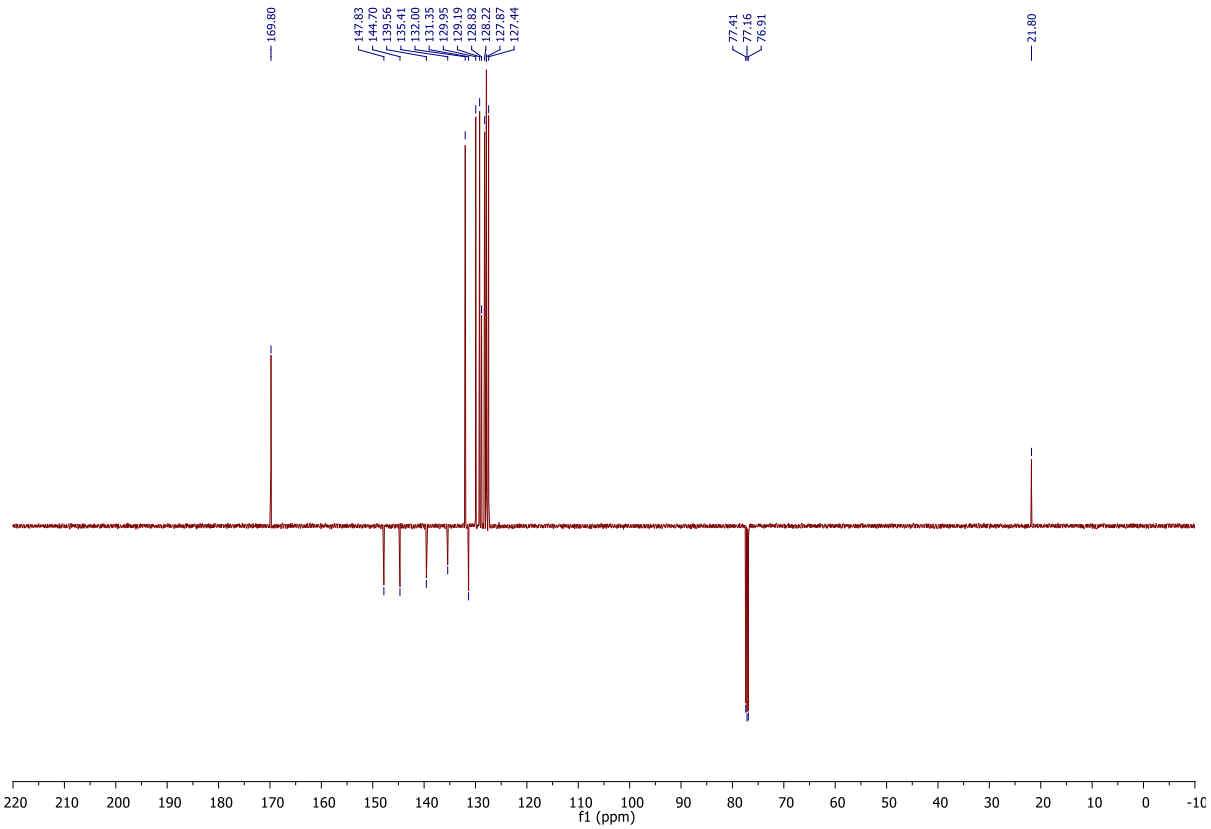
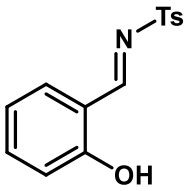


Figure S49. ^{13}C {^{1}H} NMR of **SM19**.

***N*-(2-hydroxybenzylidene)-4-methylbenzenesulfonamide (31)**



Prepared according to general procedure A from salicylaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, to give the title compound as a pink solid (2.39 g, 87%), with no further purification required and NMR data in accordance with the literature;[11] R_F = 0.48 (1:4 EtOAc:PE); mp 120 – 122 ˚C (lit. 120 ˚C);[5] ν_{max}/cm^{-1} (film): 3052, 1623, 1594, 1556, 1489, 1457, 1362, 1318, 1303, 1273, 1153, 1084, 903, 845, 816, 701, 624, 569; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 10.82 (s, 1H), 9.09 (s, 1H), 7.91 – 7.82 (m, 2H), 7.54 – 7.48 (m, 2H), 7.37 – 7.34 (m, 2H), 7.03 – 6.99 (m, 2H), 2.44 (s, 3H); ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ_C: 171.6, 162.3, 145.2, 137.5, 135.6, 135.2, 130.2, 128.1, 120.4, 118.1, 116.8, 21.8; HRMS (ES^+) calculated for $[C_{14}H_{14}NO_3S]^+$ $(M+H)^+$: m/z 276.0683 found 276.0694 (-4.0 ppm).

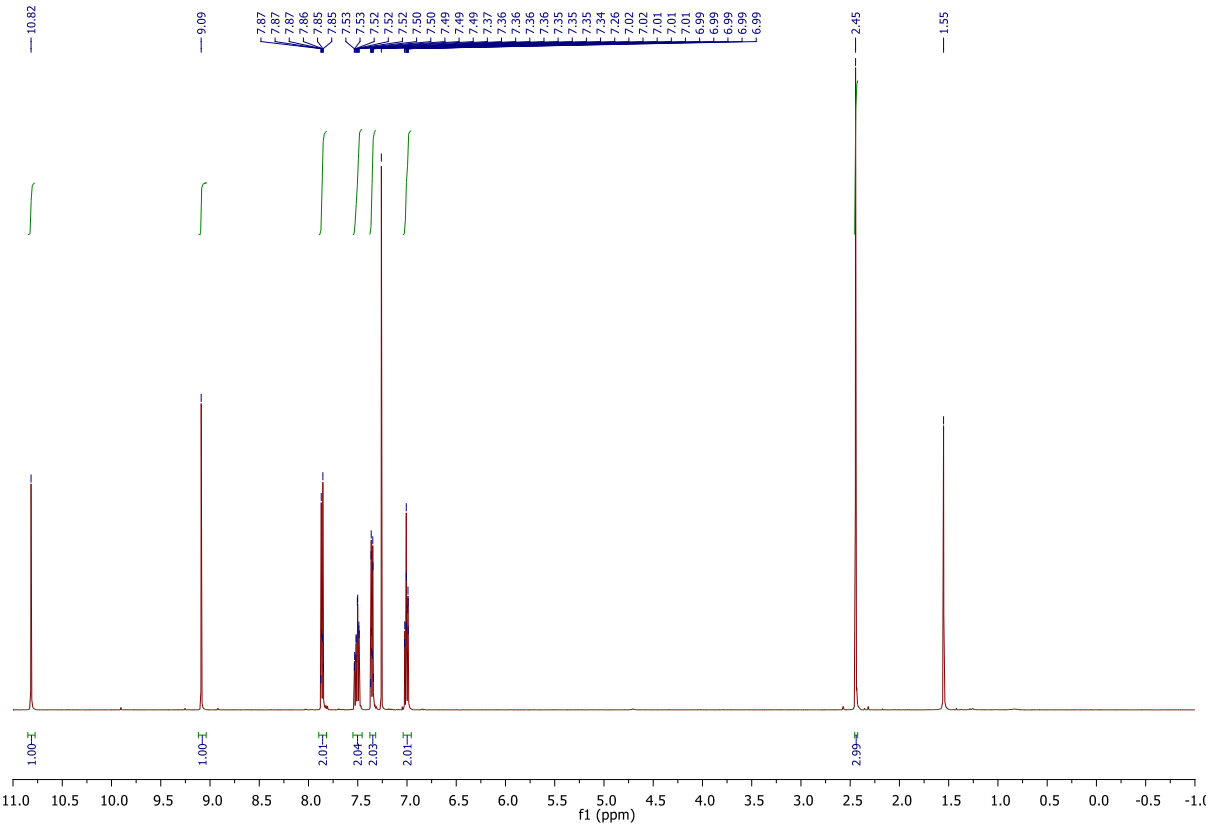


Figure S50. ^1H NMR of **31**.

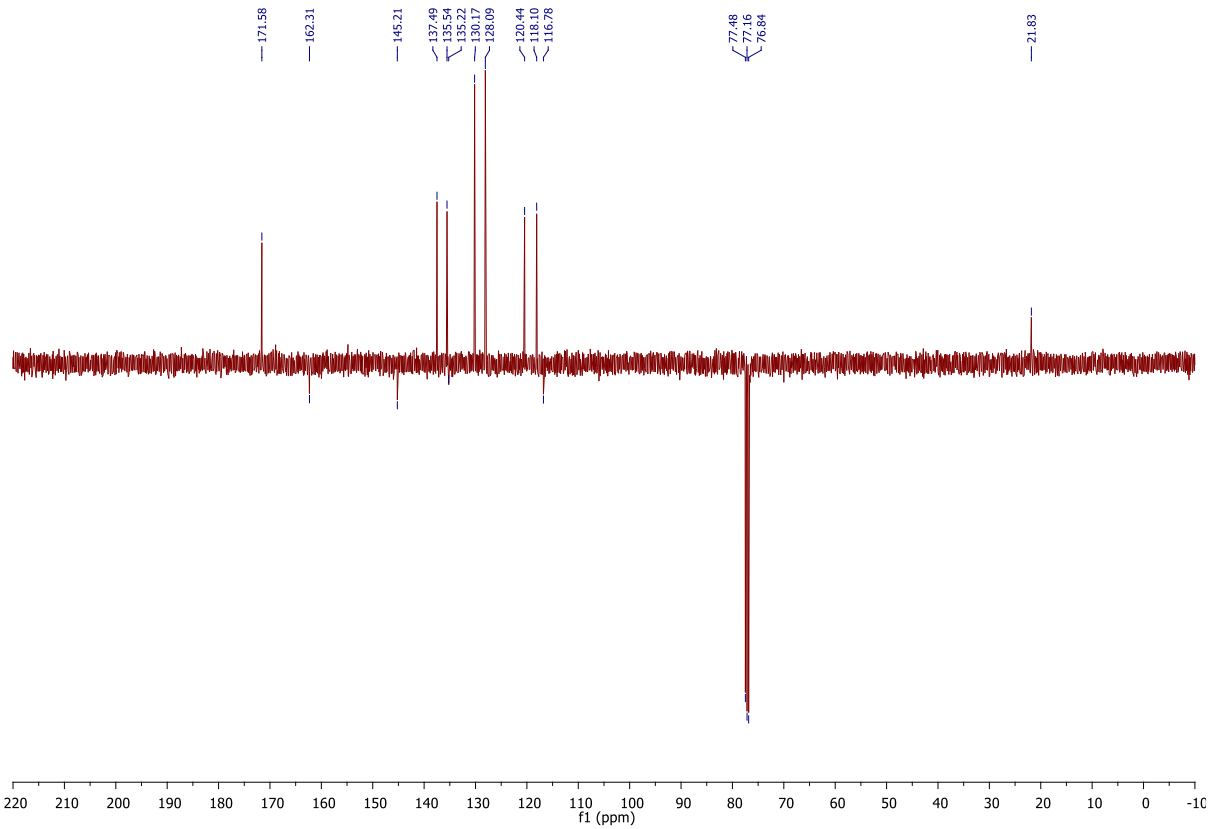
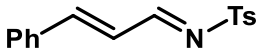


Figure S51. ^{13}C {^{1}H} NMR of **31**.

4-methyl-*N*-((1*E*,2*E*)-3-phenylallylidene)benzenesulfonamide (SM20)



Prepared according to general procedure A from *trans*-cinnamaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a brown solid (0.56 g, 20%) with physical and spectroscopic data in accordance with the literature;[3] R_F = 0.30 (1:4 EtOAc/PE); mp 126 – 128 ˚C (lit. 117 – 118 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.78 (d, *J* = 9.4, 1H), 7.86 (d, *J* = 8.4, 2H), 7.57 – 7.53 (m, 2H), 7.49 (d, *J* = 15.8, 1H), 7.46 – 7.39 (m, 3H), 7.37 – 7.32 (m, 2H), 6.99 (dd, *J* = 15.8, 9.4, 1H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 171.0, 153.9, 144.7, 135.5, 134.3, 131.8, 130.0, 129.4, 128.8, 128.1, 124.9, 21.8.

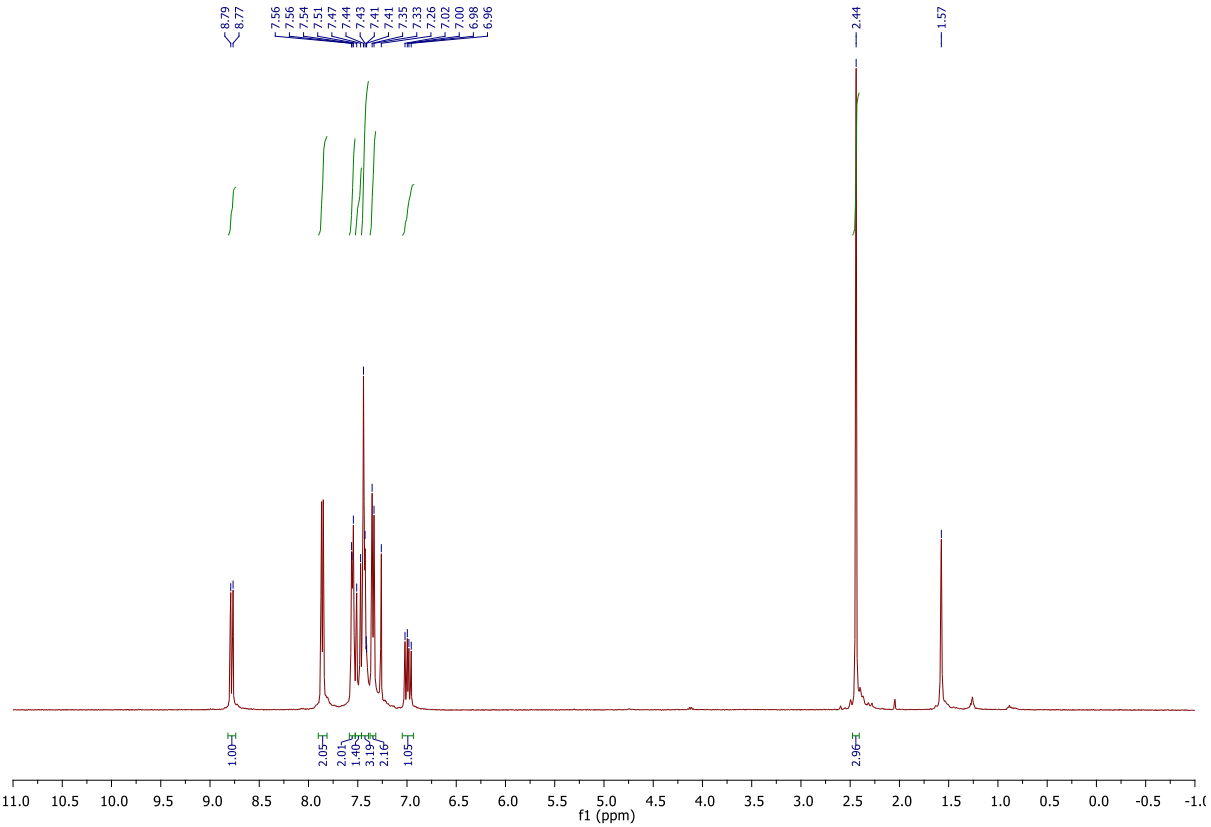


Figure S52. ^{1}H NMR of **SM20**.

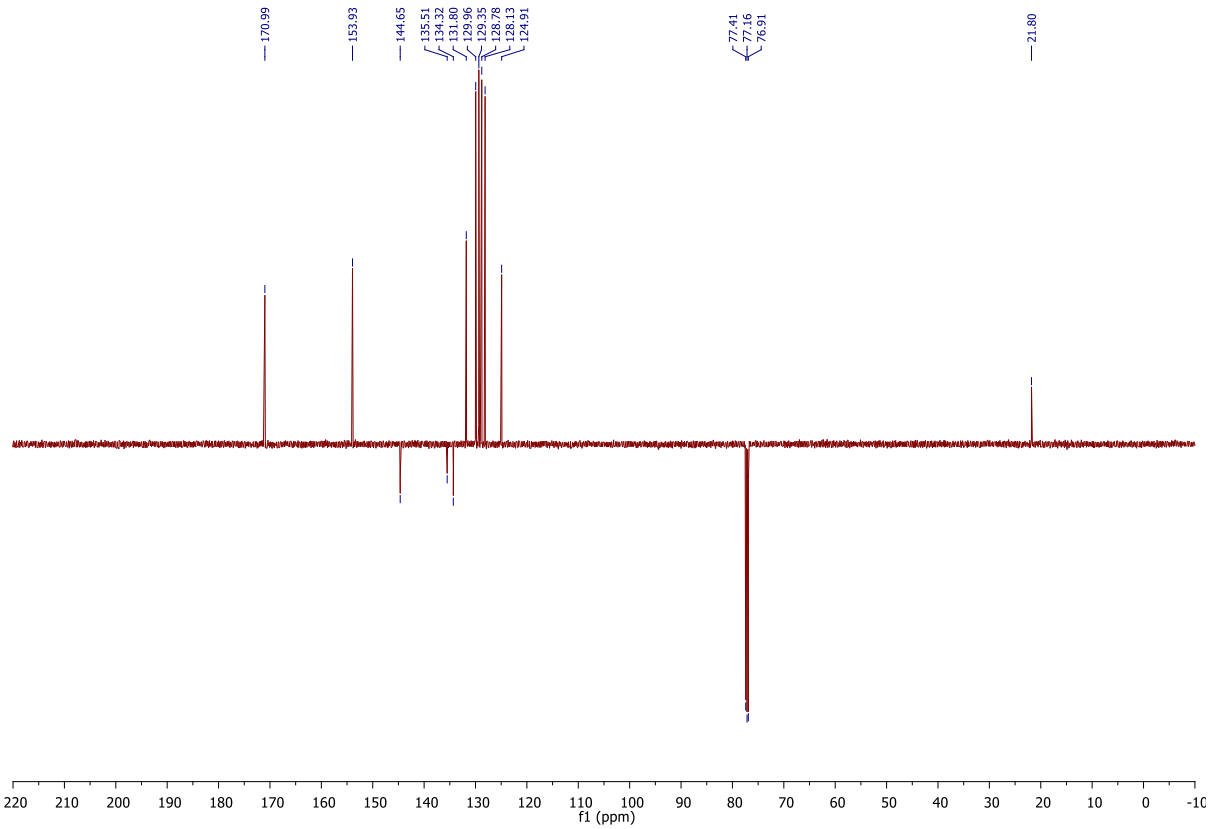
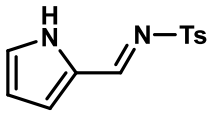


Figure S53. ^{13}C {^{1}H} NMR of **SM20**.

***N*-((1H-pyrrol-2-yl)methylene)-4-methylbenzenesulfonamide (33)**



Prepared according to general procedure A from pyrrole-2-carboxaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a dark red solid (167 mg, 7%) with physical and spectroscopic data in accordance with the literature;[12] R_F = 0.40 (1:4 EtOAc/PE); mp 128 – 130 ˚C (lit. 93 – 95 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.67 (s, 1H), 8.72 (s, 1H), 7.84 – 7.78 (m, 2H), 7.30 – 7.27 (m, 2H), 7.21 – 7.17 (m, 1H), 7.03 (ddd, *J* = 3.9, 2.5, 1.4, 1H), 6.39 (dt, *J* = 4.0, 2.4, 1H), 2.42 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 157.4, 144.1, 136.5, 129.8, 128.9, 127.7, 126.6, 125.0, 113.0, 21.7.

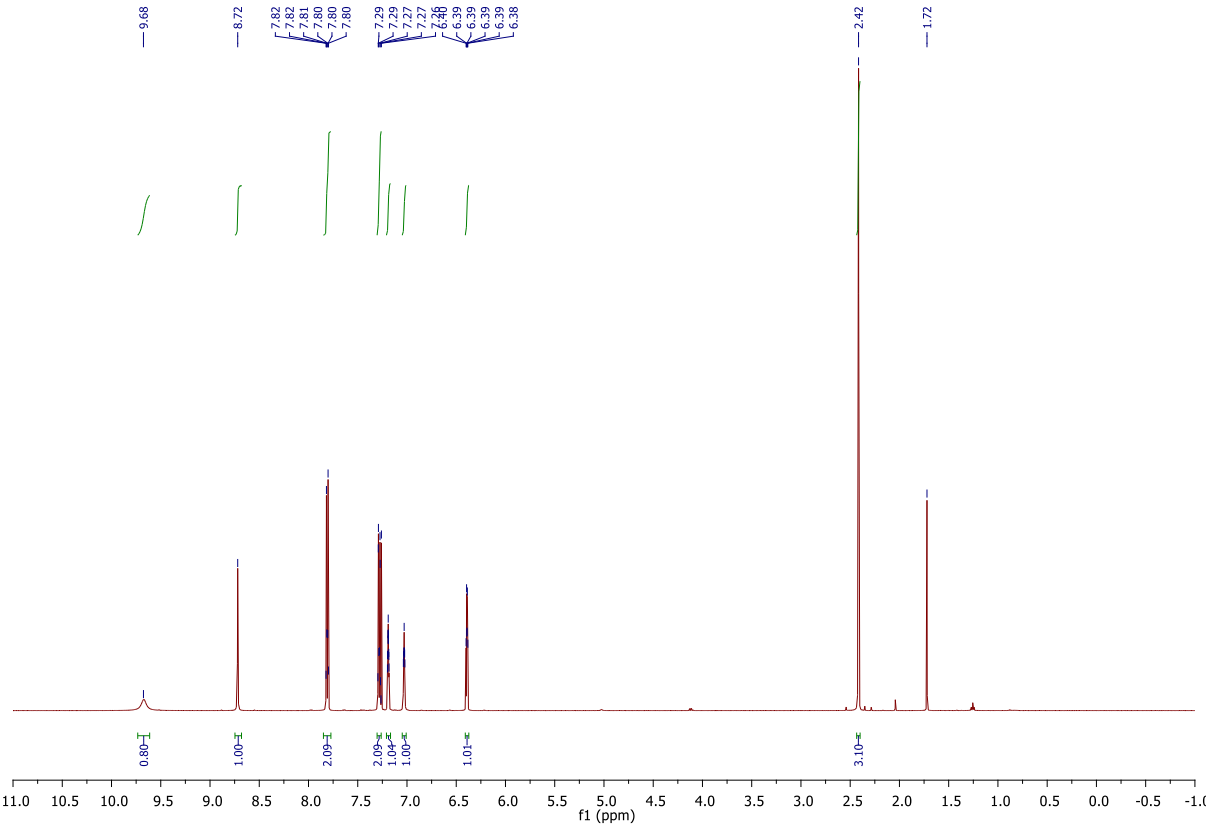


Figure S54. ^{1}H NMR of **33**.

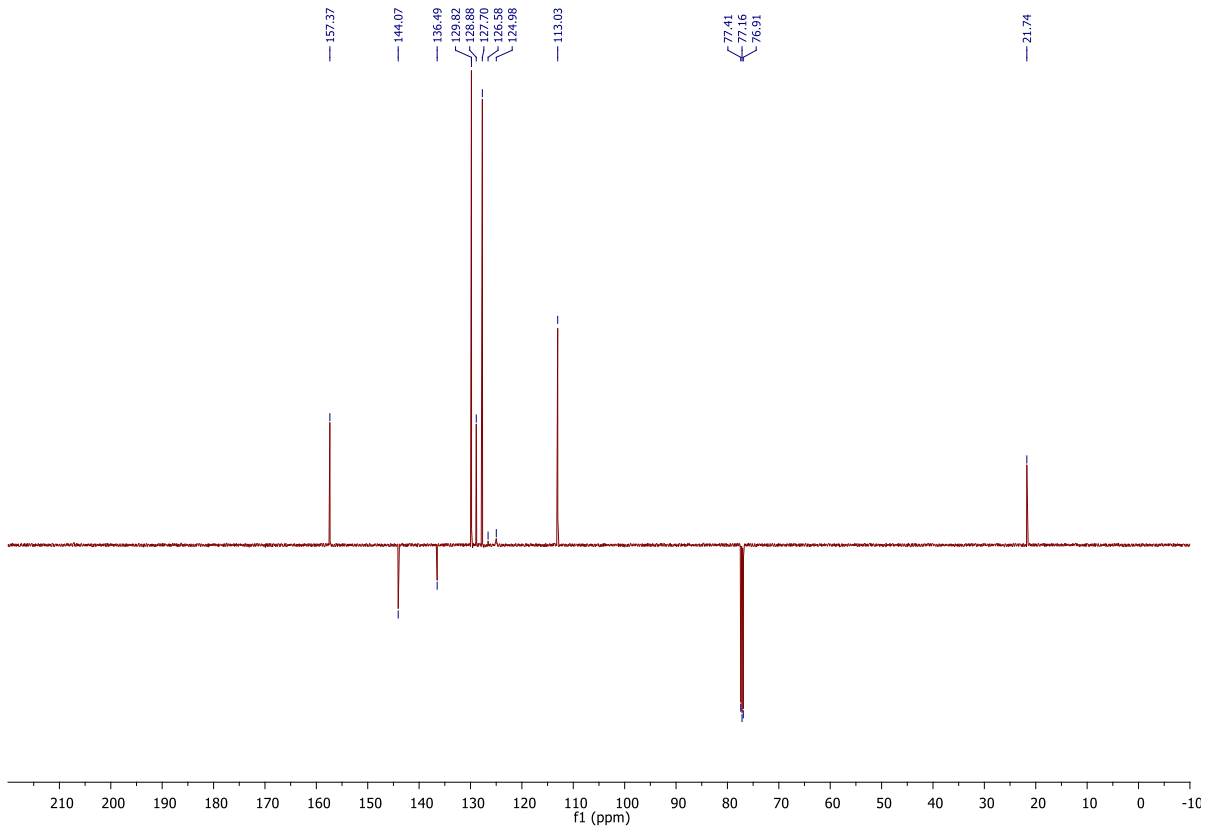
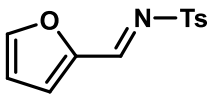


Figure S55. ^{13}C {^{1}H} NMR of **33**.

***N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (SM21)**



Prepared according to general procedure A from furfural (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 2:2:1 EtOAc/hexane/toluene to give the title compound as a dark brown solid (1.29 g, 52%) with physical and spectroscopic data in accordance with the literature;[13] R_F = 0.12 (1:4 EtOAc/PE); mp 111 – 113 ˚C (lit. 100 – 101 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.81 (s, 1H), 7.89 – 7.84 (m, 2H), 7.74 (dt, *J* = 1.5, 0.7, 1H), 7.36 – 7.30 (m, 3H), 6.64 (dd, *J* = 3.6, 1.7, 1H), 2.42 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 155.8, 149.9, 149.2, 144.7, 135.3, 129.9, 128.2, 124.7, 113.8, 21.8.

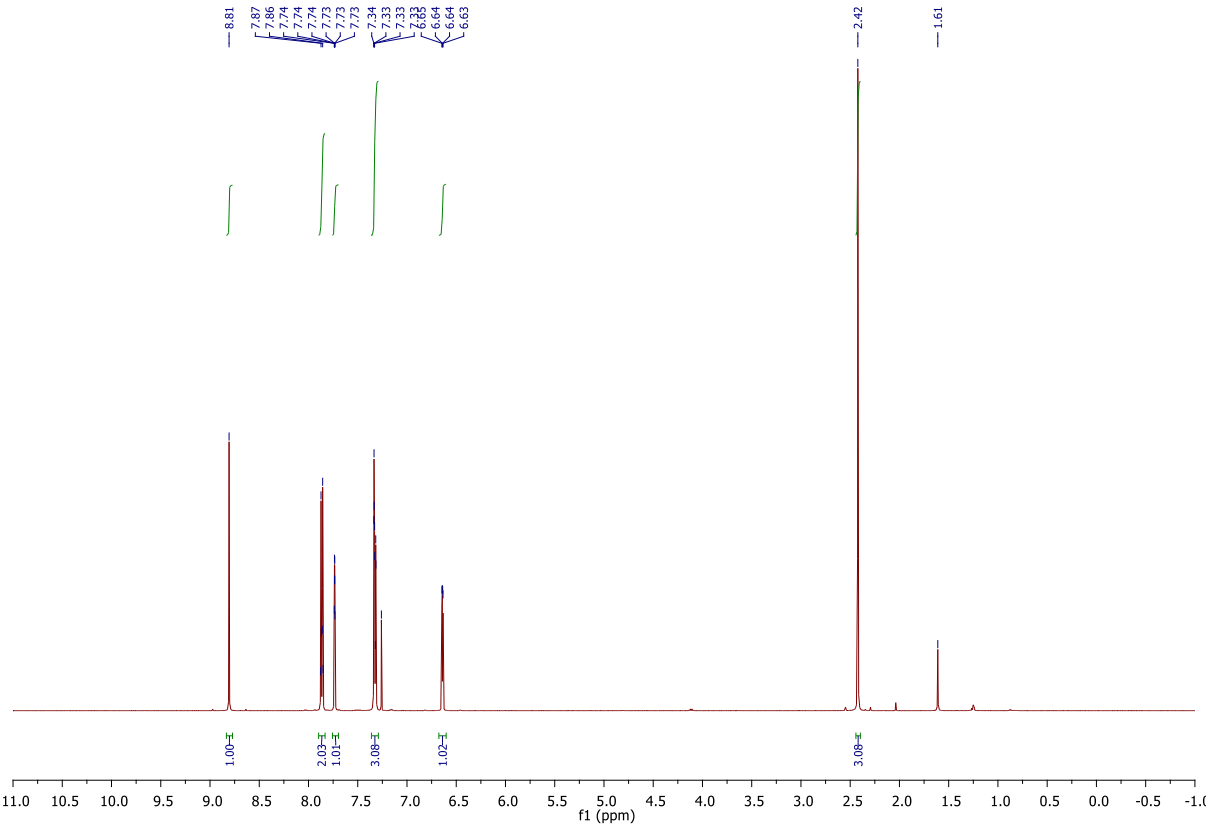


Figure S56. ^{1}H NMR of **SM21**.

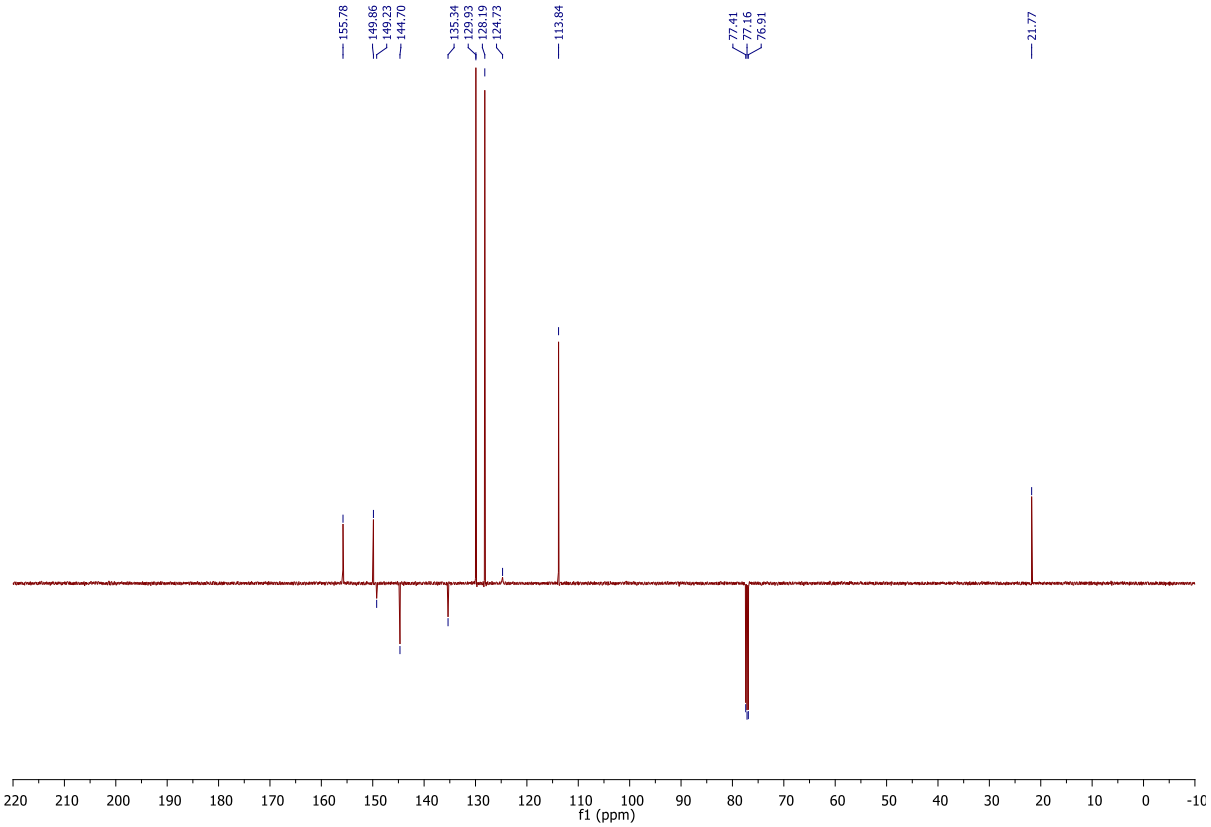
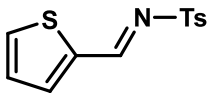


Figure S57. ^{13}C {^{1}H} NMR of **SM21**.

4-methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide (SM22)



Prepared according to general procedure A from thiophene-2-carboxaldehyde (11 mmol) and *p*-toluenesulfonamide (10 mmol) for 16 h, to give the title compound as a grey solid (2.33 g, 88%), with no further purification required and physical and spectroscopic data in accordance with the literature;[3] R_F = 0.21 (1:4 EtOAc/PE); mp 129 – 131 ˚C (lit. 95 – 96 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.11 (q, *J* = 0.9, 1H), 7.90 – 7.84 (m, 2H), 7.79 – 7.74 (m, 2H), 7.35 – 7.31 (m, 2H), 7.22 – 7.19 (m, 1H), 2.43 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 162.3, 144.6, 139.1, 138.3, 136.8, 135.6, 129.9, 129.0, 128.1, 21.8.

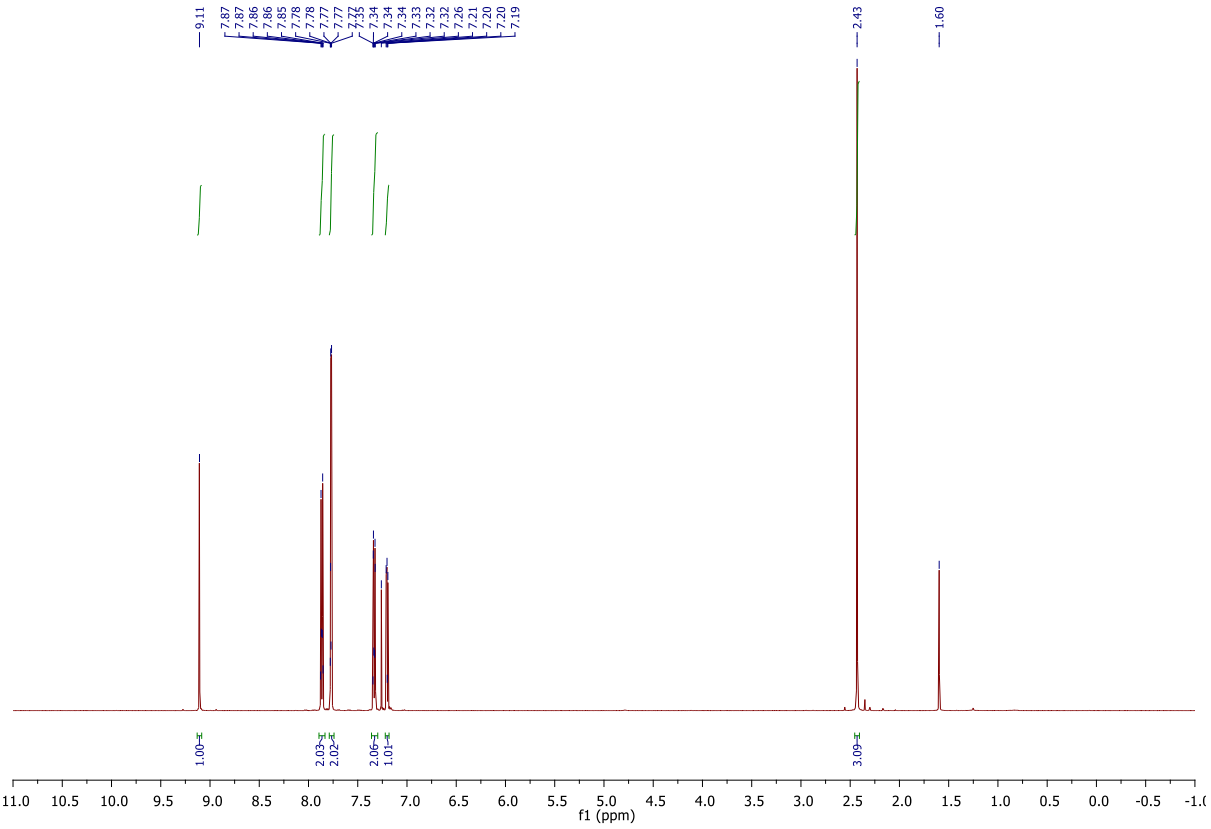


Figure S58. ^{1}H NMR of **SM22**.

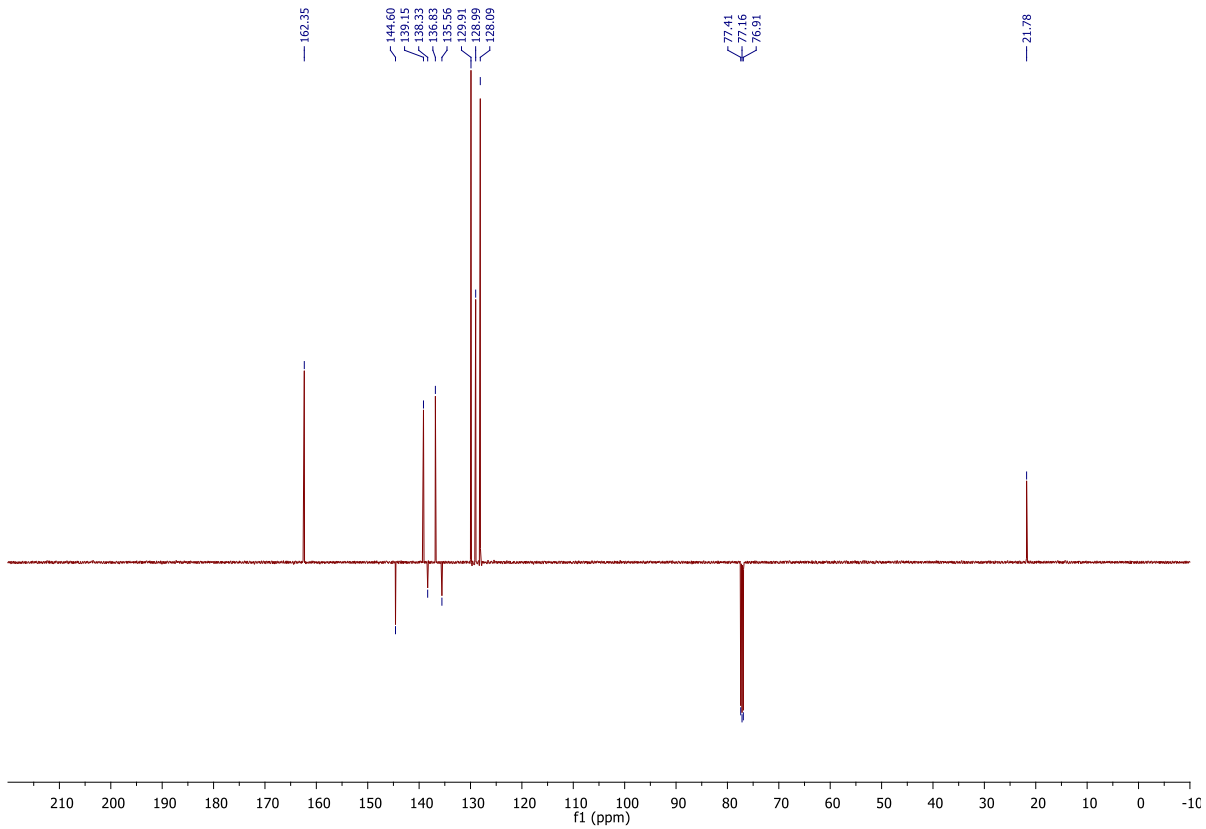
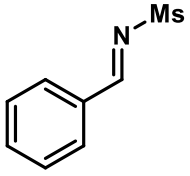


Figure S59. ^{13}C {^{1}H} NMR of **SM22**.

***N*-benzylidenemethanesulfonamide (SM23)**



Prepared according to general procedure A from benzaldehyde (11 mmol) and methanesulfonamide (10 mmol) for 16 h, followed by recrystallisation from 1:1 EtOAc/hexane to give the title compound as a white solid (0.69 g, 38%) with physical and spectroscopic data in accordance with the literature;[14] R_F = 0.43 (3:7 EtOAc/PE); mp 70 – 72 ˚C (lit. 90 – 93 ˚C); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 9.04 (s, 1H), 7.96 (d, *J* = 7.4, 2H), 7.67 (t, *J* = 7.7, 1H), 7.54 (t, *J* = 7.7, 2H), 3.15 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 171.8, 135.3, 132.2, 131.5, 129.4, 40.4.

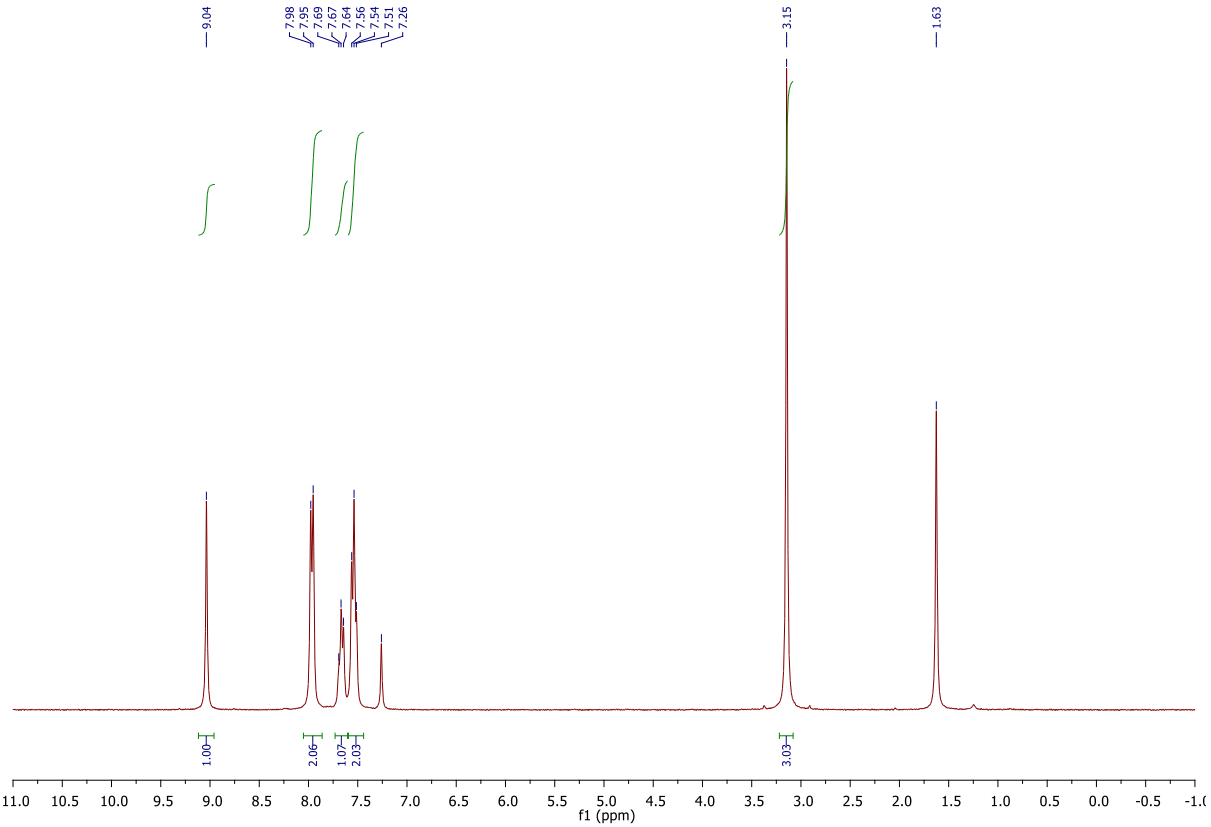


Figure S60. ^{1}H NMR of **SM23**.

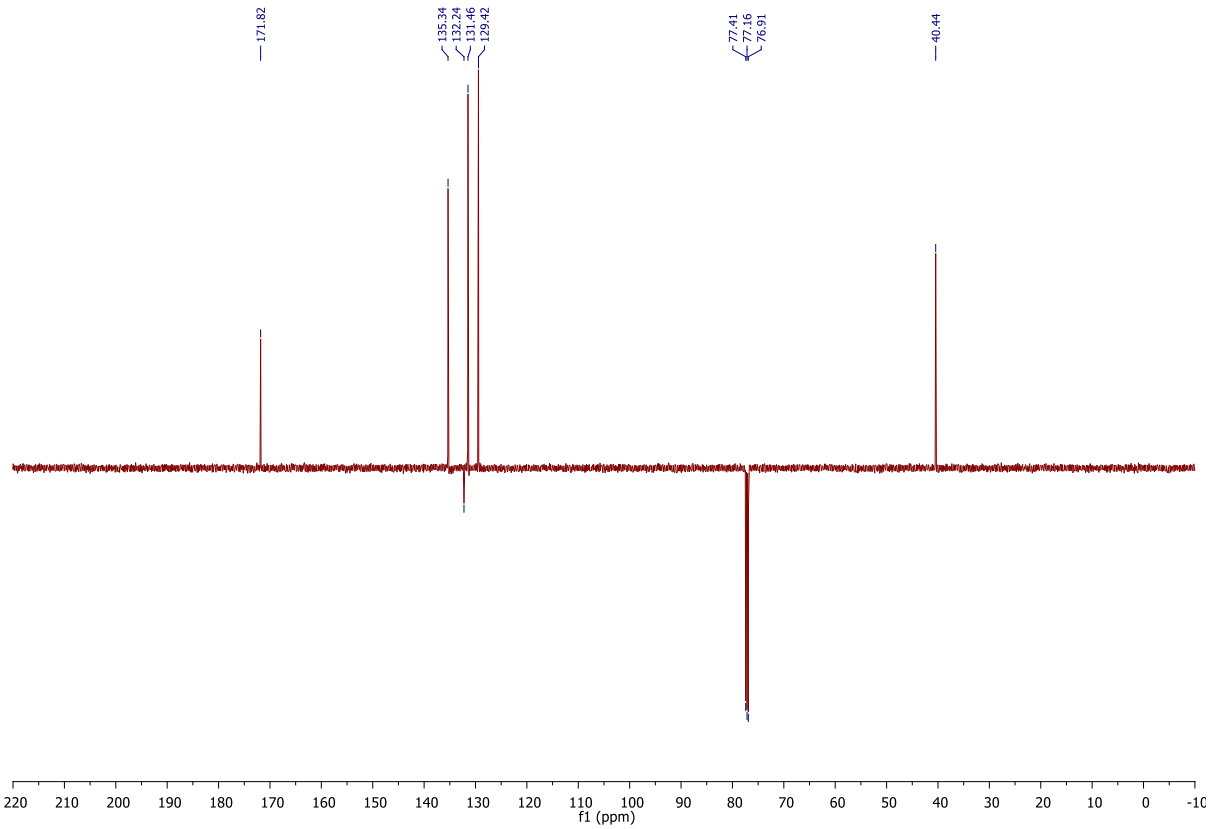
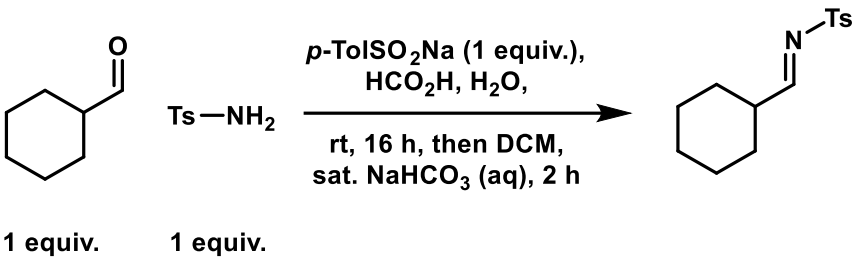


Figure S61. ^{13}C {^{1}H} NMR of **SM23**.

***N*-(cyclohexylmethylene)-4-methylbenzenesulfonamide (34)**



A mixture of cyclohexanecarboxaldehyde (1.21 mL, 10 mmol, 1 equiv.), *p*-toluenesulfonamide (1.71 g, 10 mmol, 1 equiv.), sodium *p*-toluenesulfinate (1.78 g, 10 mmol, 1 equiv.), formic acid (15 mL) and water (15 mL) was stirred at room temperature for 16 h. After this period, the formed precipitate was filtered, washed with water (25 mL) and pentane (25 mL), and dissolved in dichloromethane (100 mL). Saturated aqueous sodium bicarbonate (70 mL) was added, and the mixture was stirred at room temperature for 2 h. The organic phase was collected, the aqueous phase extracted with dichloromethane (50 mL) and the combined organic phases were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to yield the crude product. The crude solid was recrystallised from a 1:1 mixture of ethyl acetate and hexane to give the title compound as a white solid (1.52 g, 57%), with physical and spectroscopic data in accordance with the literature;[4] R_F = 0.45 (1:4 EtOAc/PE); mp 114 – 116 ˚C (lit. 106 – 108 ˚C); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.47 (d, *J* = 4.4, 1H), 7.84 – 7.76 (m, 2H), 7.33 (d, *J* = 8.1, 2H), 2.45 – 2.39 (m, 4H), 1.94 – 1.61 (m, 5H), 1.40 – 1.14 (m, 5H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 181.2, 144.7, 135.0, 129.9, 128.2, 43.8, 28.5, 25.8, 25.2, 21.8.

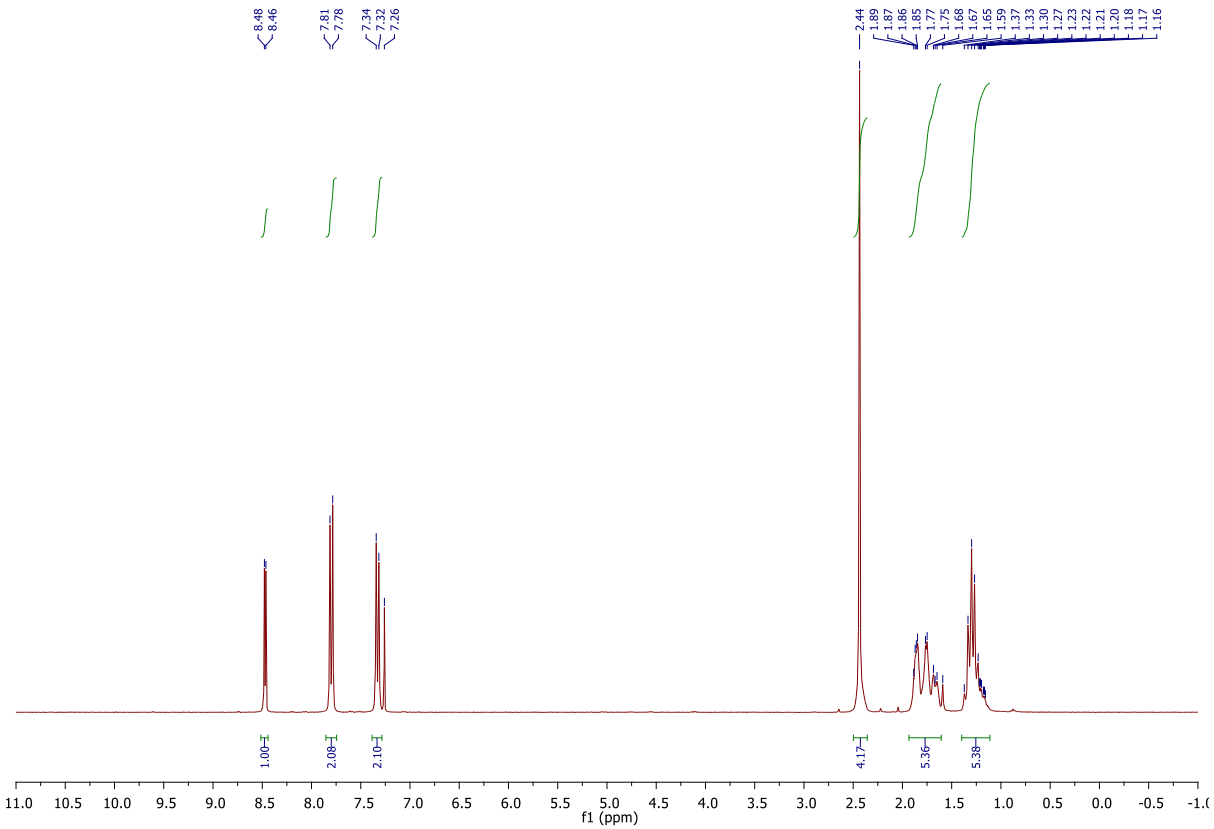


Figure S62. ^{1}H NMR of **34**.

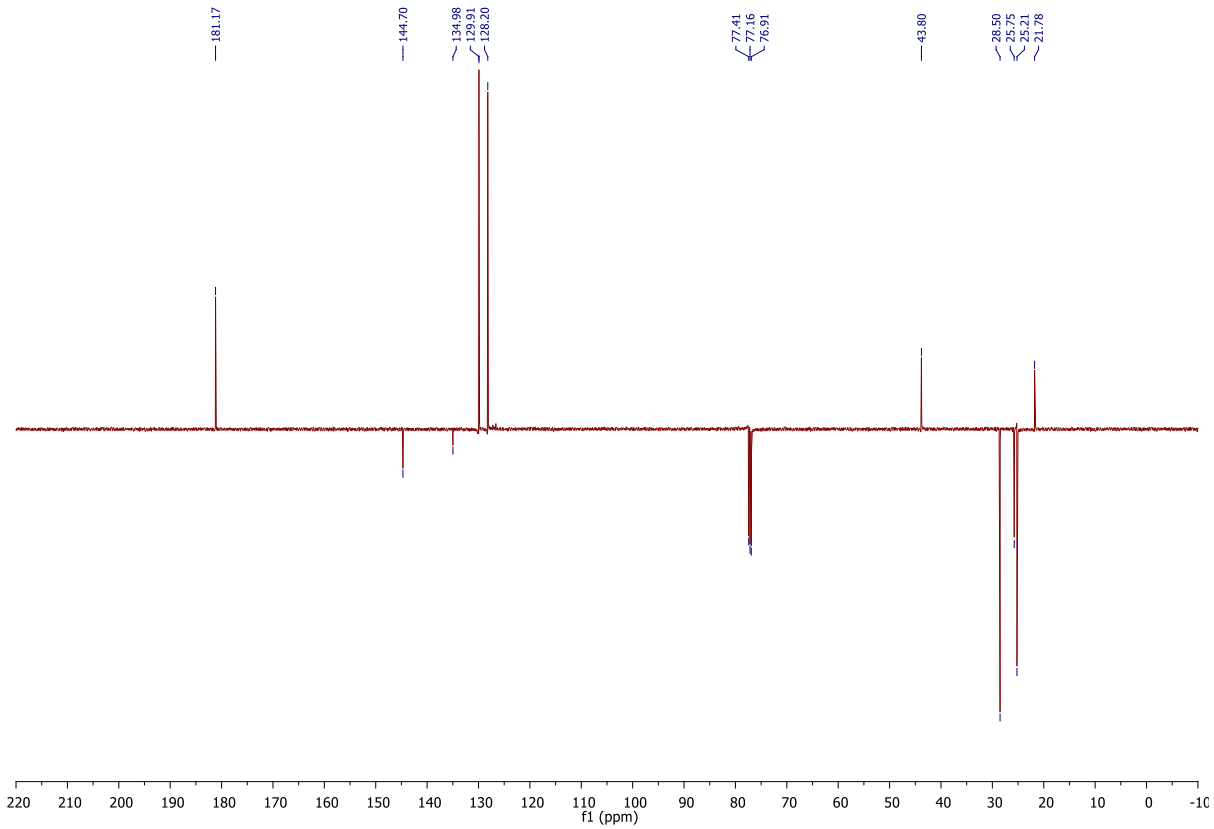
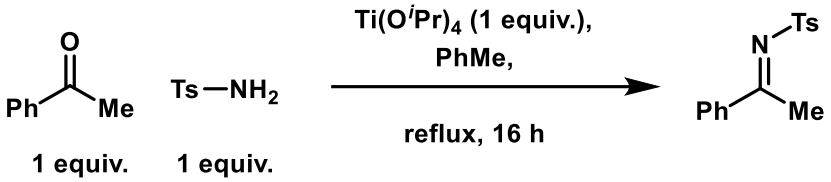


Figure S63. ^{13}C {^{1}H} NMR of **34**.

4-methyl-*N*-(1-phenylethylidene)benzenesulfonamide (35)



A mixture of acetophenone (2.4 mL, 20 mmol, 1 equiv.), *p*-toluenesulfonamide (3.42 g, 20 mmol, 1 equiv.), titanium (IV) isopropoxide (5.92 mL, 20 mmol, 1 equiv.) and toluene (0.5 M) was heated to reflux for 16 h. After this period, the toluene was removed *in vacuo* and the resultant residue was purified *via* Flash Column Chromatography (FCC) on silica (1:9 EtOAc/PE) to give the title compound as a white solid (0.55 g, 10%), with physical and spectroscopic data in accordance with the literature;[15] R_F = 0.32 (1:4 EtOAc/PE); mp 82 – 84 ˚C (lit. 89 – 90 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.95 – 7.86 (m, 4H), 7.56 – 7.51 (m, 1H), 7.45 – 7.39 (m, 2H), 7.37 – 7.33 (m, 2H), 2.99 (s, 3H), 2.45 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 180.0, 143.7, 138.9, 137.7, 133.3, 129.6, 128.8, 128.4, 127.3, 21.7, 21.3.

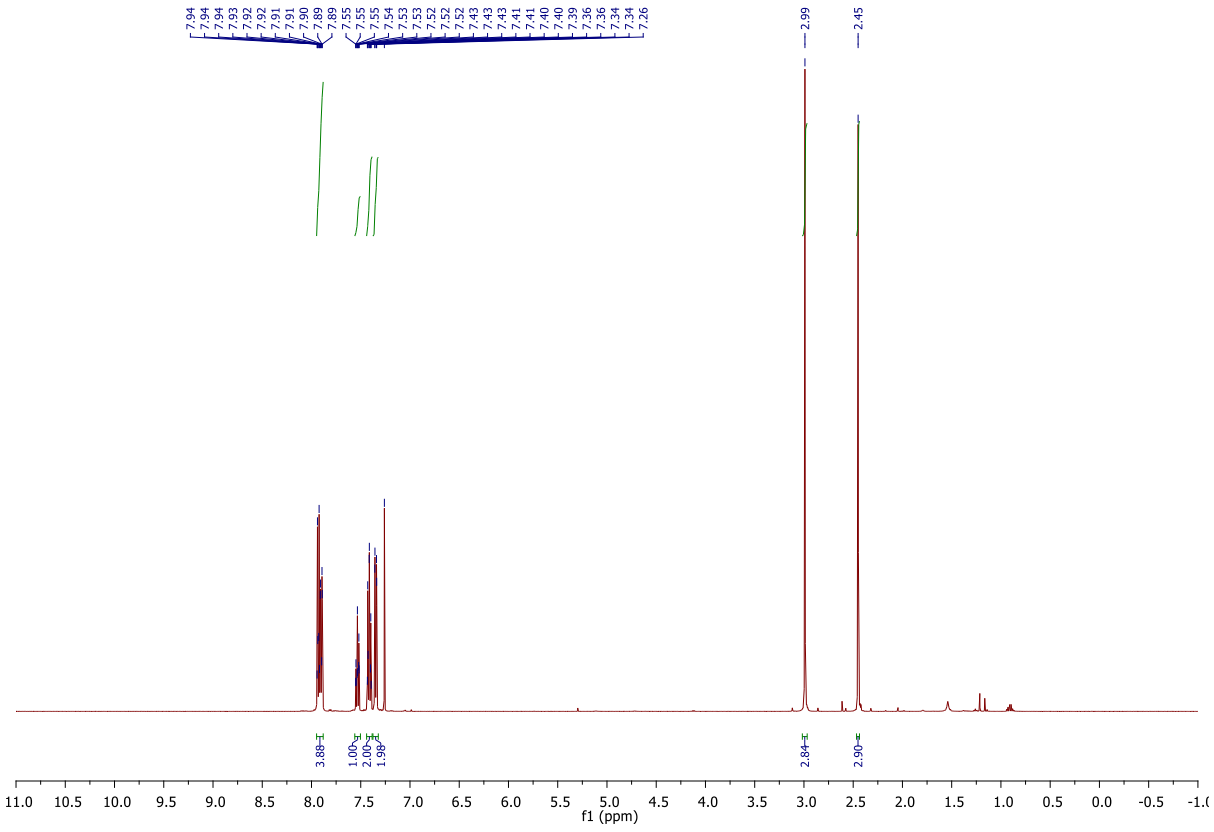


Figure S64. ^{1}H NMR of **35**.

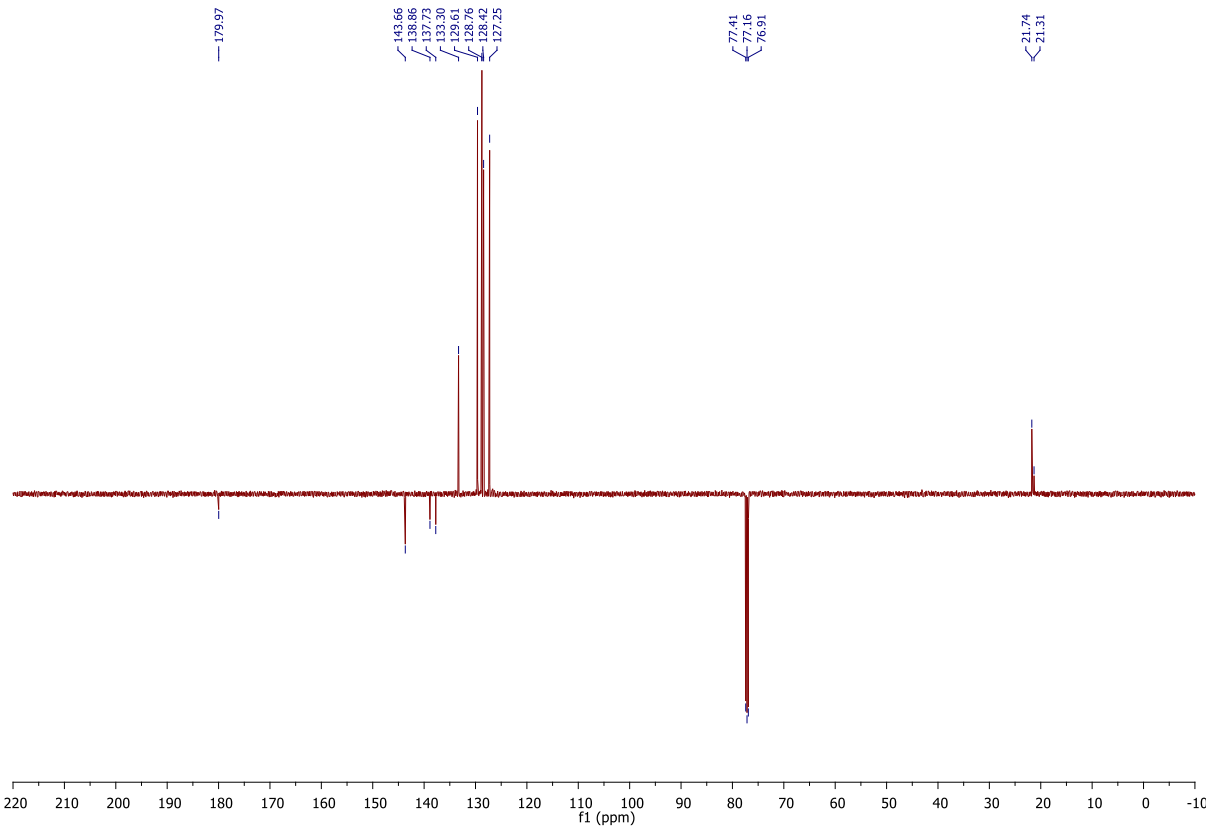
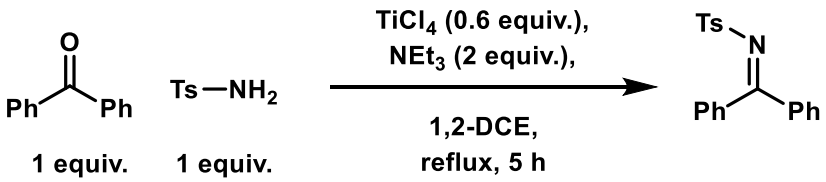


Figure S65. ^{13}C {^{1}H} NMR of **35**.

***N*-(diphenylmethylene)-4-methylbenzenesulfonamide (36)**



Titanium (IV) tetrachloride (0.66 mL, 6 mmol, 0.6 equiv.) was added slowly to a stirred mixture of benzophenone (1.82 g, 10 mmol, 1 equiv.), *p*-toluenesulfonamide (1.71 g, 10 mmol, 1 equiv.) and triethylamine (2.79 mL, 20 mmol, 2 equiv.) in 1,2-dichloroethane (0.5 M). The mixture was heated at reflux for 5 h, after which the mixture was quenched with saturated aqueous sodium bicarbonate (25 mL). The organic phase was collected, the aqueous phase extracted two more times with dichloromethane (2 x 25 mL) and the combined organic phases dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude solid was recrystallised from a 1:1 mixture of EtOAc/hexane to give the title compound as a beige solid (1.25 g, 37%), with physical and spectroscopic data in accordance with the literature;[16] R_F = 0.48 (1.5:8.5 EtOAc/PE); mp 110 – 112 ˚C (lit. 102 – 104 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.83 (d, *J* = 7.9, 2H), 7.66 – 7.34 (m, 10H), 7.29 (d, *J* = 8.0, 2H), 2.43 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 178.9, 143.5, 138.6, 129.5, 128.3 (broadened, due to multiple C-H_{Aryl} contributions), 127.5, 21.7.

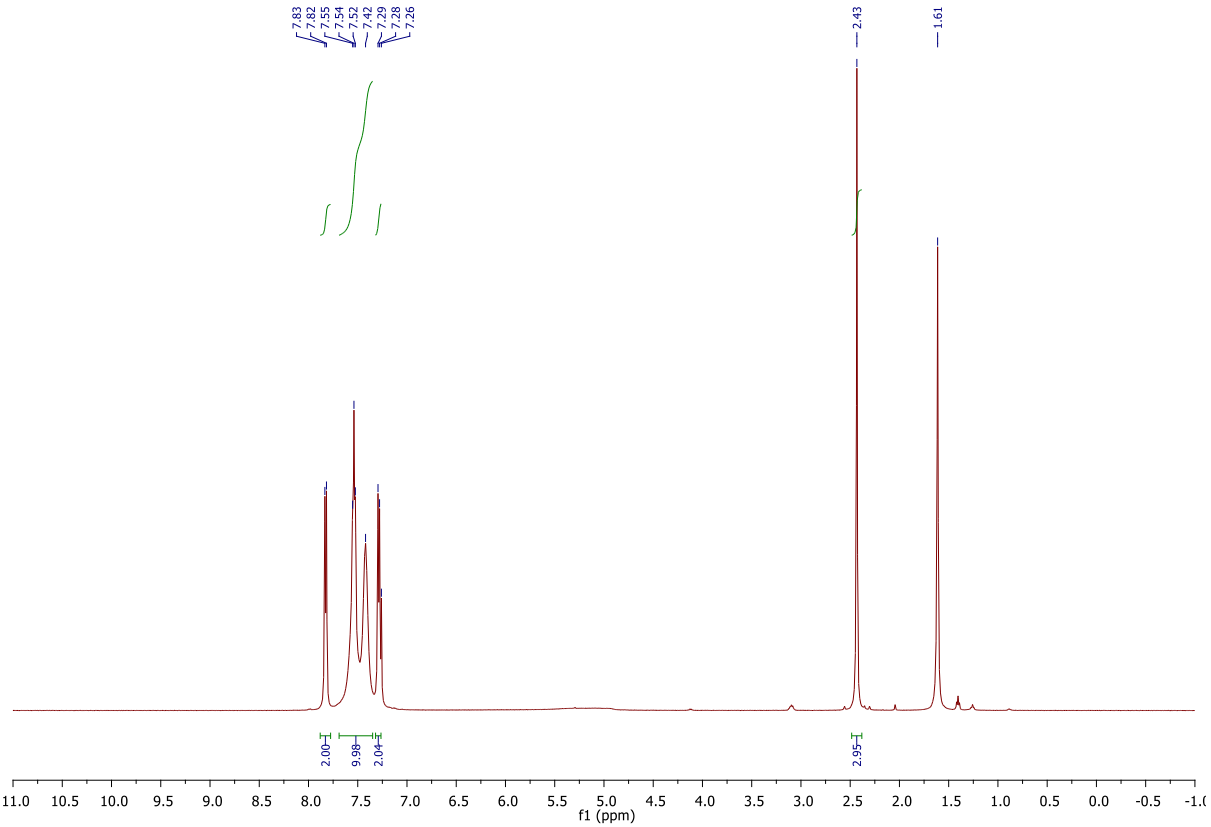


Figure S66. ^{1}H NMR of **36**.

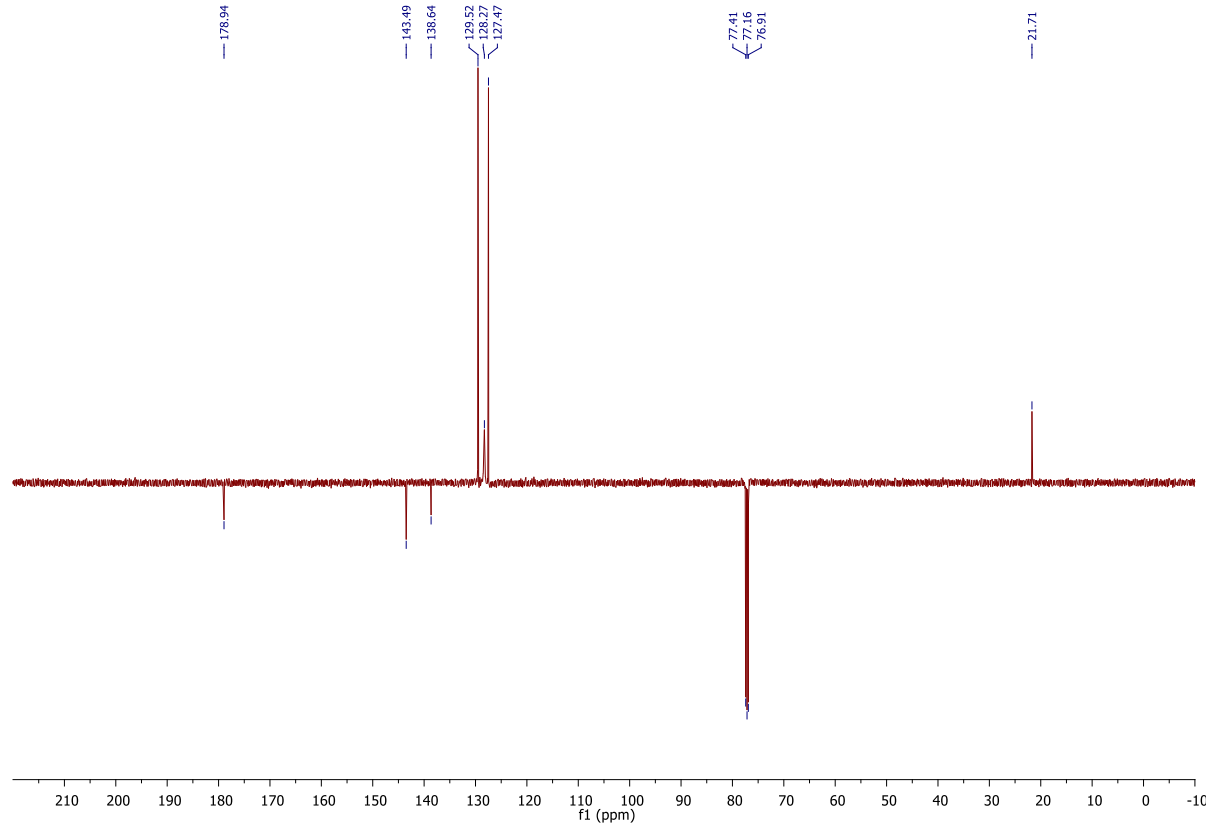
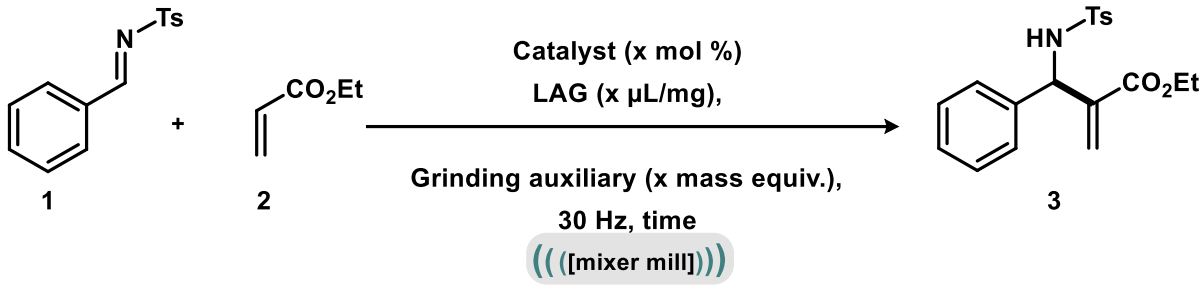


Figure S67. ^{13}C {^{1}H} NMR of **36**.

3. Optimisation of Model aza-MBH Reaction in the Ball-Mill



To a 14 mL stainless steel jar was charged imine **1** (x mmol, 1.0 equiv.), ethyl acrylate **2** (x mmol, x equiv.), catalyst (x mol %), LAG (x µL/mg, with respect to reactants mass), grinding auxiliary (x mass equiv., with respect to reactants mass) and a stainless steel ball (9 mm, 3 g). The mixture was milled at 30 Hz for the specified time, unless stated otherwise. After completion, the reaction mixture was transferred to a separatory funnel by washing with EtOAc (25 mL) and distilled water (25 mL). The organic layer was quenched with 1 M HCl (15 mL) and the aqueous phase was extracted two more times with EtOAc (2 x 25 mL). The combined organic phases were washed with brine (15 mL), dried over $MgSO_4$ and concentrated *in vacuo*.

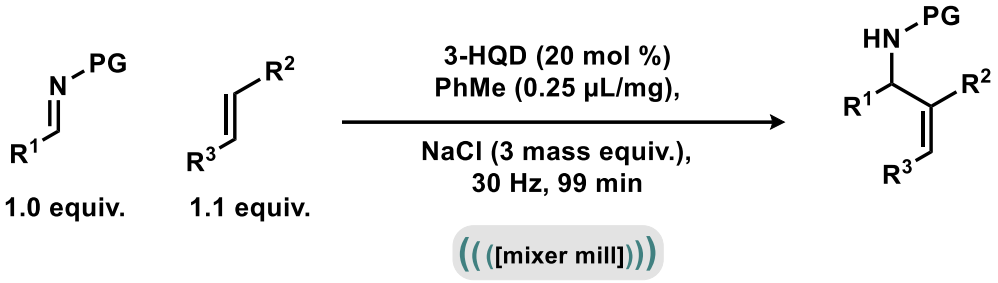
Table S1. Optimisation table for model aza-MBH reaction.

Entry	1 (mmol)	2 (mmol)	Catalyst + loading (mol %)	LAG (µL)	Grinding auxiliary (mass equiv.)	Time	3 (%)[a]
1	0.25	0.28	DABCO (20)	-	Sand (6)	99 min	23 (21)
2	0.25	0.28	DABCO (20)	MeCN (25)	Sand (6)	99 min	52
3	0.25	0.28	DABCO (20)	MeCN (25)	NaCl (6)	99 min	60
4	**0.25**	**0.28**	**DABCO (20)**	**MeCN (25)**	**NaCl (3)**	**99 min**	**61 (57)**
5	0.25	0.28	DABCO (20)	MeCN (25)	$MgSO_4$ (3)	99 min	32
6	0.25	0.28	DABCO (20)	MeCN (25)	Na_2SO_4 (3)	99 min	29
7	0.25	0.28	DABCO (20)	MeCN (25)	Molecular sieves (3)	99 min	12
8	**0.25**	**0.28**	**Quinuclidine (20)**	**MeCN (25)**	**NaCl (3)**	**99 min**	**78 (71)**
9	0.25	0.28	Quinuclidine (10)	MeCN (25)	NaCl (3)	99 min	45
10	**0.25**	**0.28**	**3-HQD (20)**	**MeCN (25)**	**NaCl (3)**	**99 min**	**81**
11	0.25	0.28	3-HQD (20)	-	NaCl (3)	99 min	67
12	0.25	0.28	3-HQD (20)	MeCN (25)	-	99 min	57
13	0.25	0.28	3-HQD (20)	-	-	99 min	61
14	0.25	0.28	-	MeCN (25)	NaCl (3)	99 min	0
15	0.25	0.28	3-HQD (20)	MeCN (25)	NaCl (3)	30 min	71
16	0.25	0.28	3-HQD (20)	MeCN (50)	NaCl (3)	99 min	64
17	1	1.1	3-HQD (20)	MeCN (100)	NaCl (3)	99 min	75
18	0.25	0.28	3-HQD (20)	Hexane (25)	NaCl (3)	99 min	82
19	**0.25**	**0.28**	**3-HQD (20)**	**Toluene (25)**	**NaCl (3)**	**99 min**	**89 (85)**
20	0.25	0.28	3-HQD (20)	EtOAc (25)	NaCl (3)	99 min	86
21	0.25	0.28	3-HQD (20)	CH_2Cl_2 (25)	NaCl (3)	99 min	85
22	0.25	0.28	3-HQD (20)	^{i}PrOH (25)	NaCl (3)	99 min	71
23	0.25	0.28	3-HQD (20)	MeOH (25)	NaCl (3)	99 min	65
24	0.25	0.28	3-HQD (20)	DMSO (25)	NaCl (3)	99 min	63
25	0.25	0.28	3-HQD (20)	H_2O (25)	NaCl (3)	99 min	19

[a] Yield determined *via* ^{1}H NMR analysis of the crude reaction mixture, using mesitylene as an internal standard. Isolated yields in parentheses.

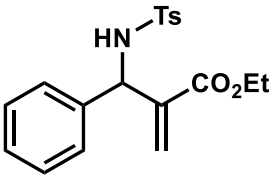
4. Substrate Scope

4.1. General Procedure B



To a 14 mL stainless steel jar was charged the corresponding imine (1.0 equiv.), Michael acceptor (1.1 equiv.), 3-HQD (20 mol %), toluene (0.25 µL/mg, with respect to reactants), sodium chloride (3.0 mass equiv., with respect to reactants) and a stainless steel ball (9 mm, 3 g). The mixture was milled at 30 Hz for 99 min, unless stated otherwise. After completion, the reaction mixture was transferred to a separatory funnel by washing with EtOAc (25 mL) and distilled water (25 mL). The organic layer was quenched with 1 M HCl (15 mL) and the aqueous phase was extracted two more times (three total) with EtOAc (2 x 25 mL). The combined organic phases were washed with brine (15 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography (FCC) on silica gel, to yield the corresponding aza-MBH product.

Ethyl 2-(((4-methylphenyl)sulfonamido)(phenyl)methyl)acrylate (3)



Prepared according to general procedure B from *N*-benzylidene-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol); purified by FCC (1.5:8.5 EtOAc/PE) to give the title compound as a white solid (76 mg, 85%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.40 (1:4 EtOAc/PE); mp 108 – 110 ˚C (lit. 100 - 101 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.71 – 7.65 (m, 2H), 7.26 – 7.18 (m, 5H), 7.15 (m, 2H), 6.21 (d, *J* = 0.9, 1H), 5.80 (t, *J* = 0.9, 1H), 5.65 (d, *J* = 8.9, 1H), 5.30 (d, *J* = 8.9, 1H), 4.05 (q, *J* = 7.1, 2H), 2.41 (s, 3H), 1.14 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.4, 143.5, 138.8 (2C), 137.8, 129.6, 128.7, 127.9, 127.8, 127.4, 126.6, 61.2, 59.3, 21.7, 14.1.

3 mmol scale reaction

To a 25 mL stainless steel jar was charged *N*-benzylidene-4-methylbenzenesulfonamide (778 mg, 3 mmol, 1.0 equiv.), ethyl acrylate (360 µL, 3.3 mmol, 1.1 equiv.), 3-HQD (76 mg, 0.6 mmol, 20 mol %), toluene (300 µL), sodium chloride (3 g, 3.0 mass equiv.) and a stainless steel ball (14 mm, 12 g). The mixture was milled at 30 Hz for 3 h on a Retsch MM 400 mixer mill. After completion, the reaction mixture was transferred to a separatory funnel by washing with EtOAc (30 mL) and distilled water (30 mL). The organic layer was quenched with 1 M HCl (20 mL) and the aqueous phase was extracted two more times with EtOAc (2 x 30 mL). The combined organic phases were washed with brine (15 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by FCC on silica (1:4 EtOAc/PE) to yield **3** (859 mg, 80%) as a white solid.

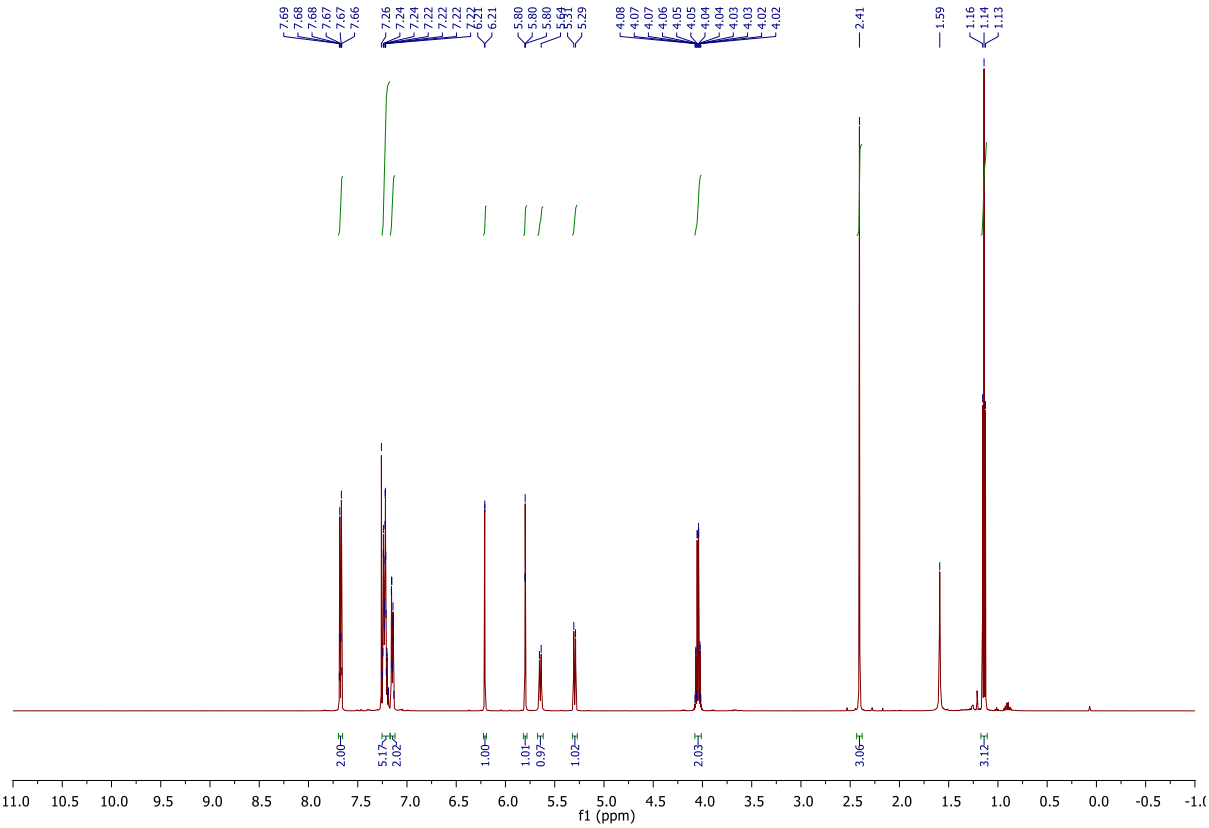


Figure S68. ^{1}H NMR of **3**.

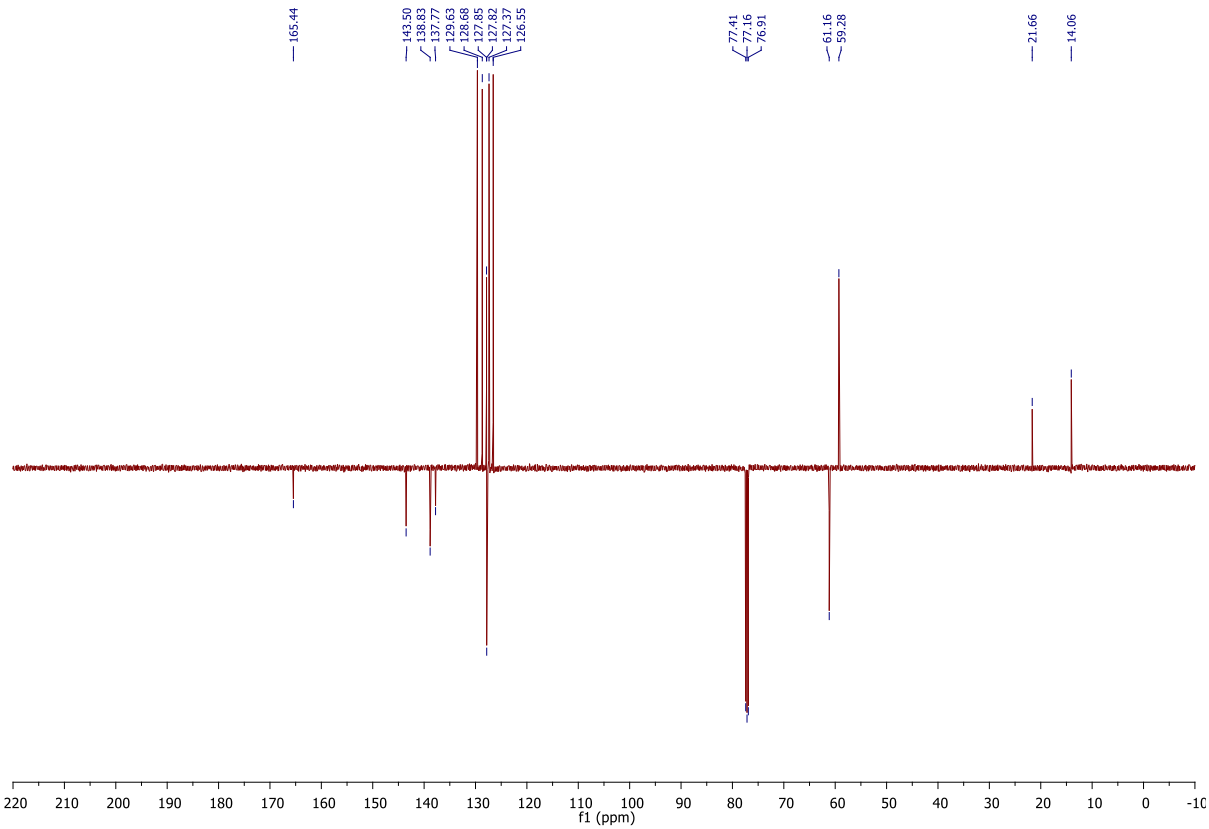
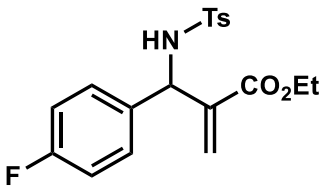


Figure S69. ^{13}C {^{1}H} NMR of **3**.

Ethyl 2-((4-fluorophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (4)



Prepared according to general procedure B from *N*-(4-fluorobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1.5:8.5 EtOAc/PE) to give the title compound as a white solid (64 mg, 68%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.33 (1.5:8.5 EtOAc/PE); mp 65 - 67 ˚C (lit. 66 – 68 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.68 – 7.65 (m, 2H), 7.25 – 7.21 (m, 2H), 7.16 – 7.10 (m, 2H), 6.95 – 6.89 (m, 2H), 6.19 (s, 1H), 5.77 (s, 1H), 5.65 (d, *J* = 9.0, 1H), 5.27 (d, *J* = 9.0, 1H), 4.06 (q, *J* = 7.1, 2H), 2.41 (s, 3H), 1.16 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.3, 162.4 (d, *J* = 248.2), 143.6, 138.7, 137.8, 134.7 (d, *J* = 3.8), 129.7, 128.3 (d, *J* = 8.8), 127.9, 127.4, 115.5 (d, *J* = 21.4), 61.23, 58.8, 21.7, 14.1; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -114.7.

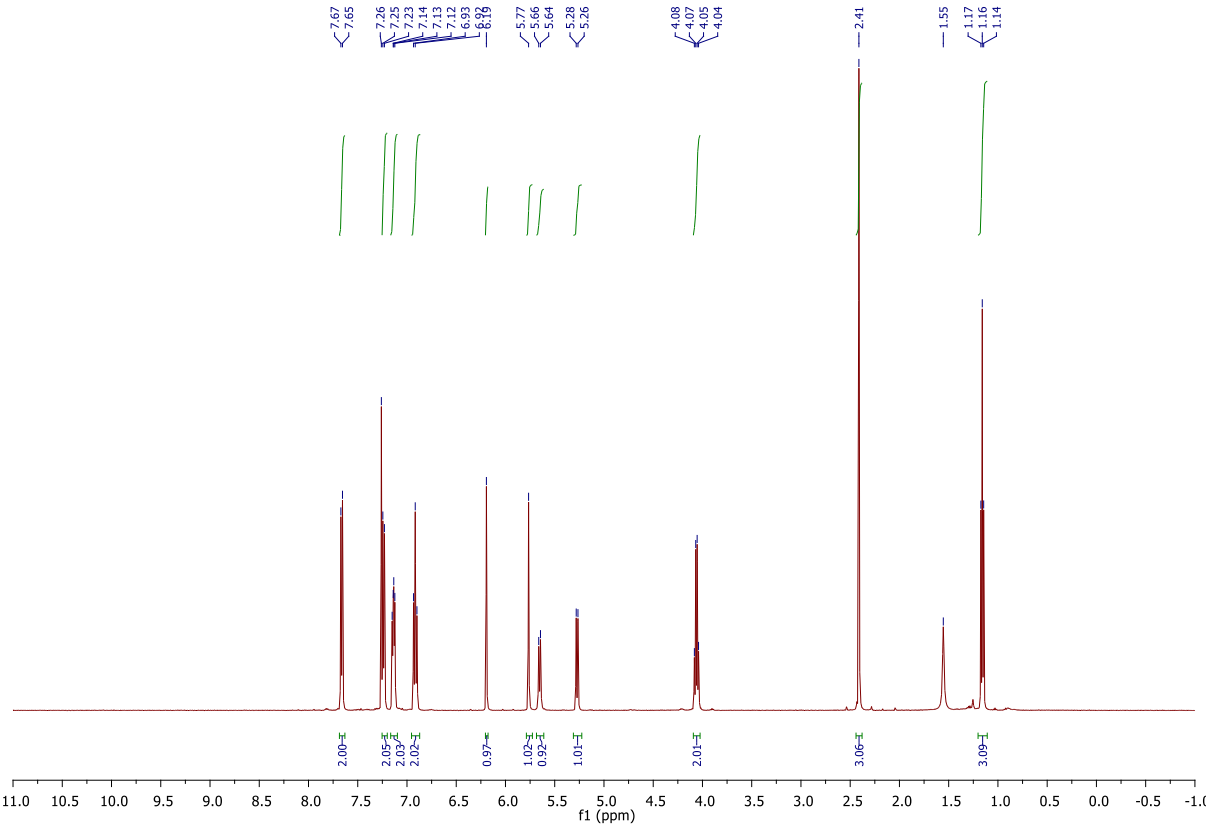


Figure S70. ^{1}H NMR of **4**.

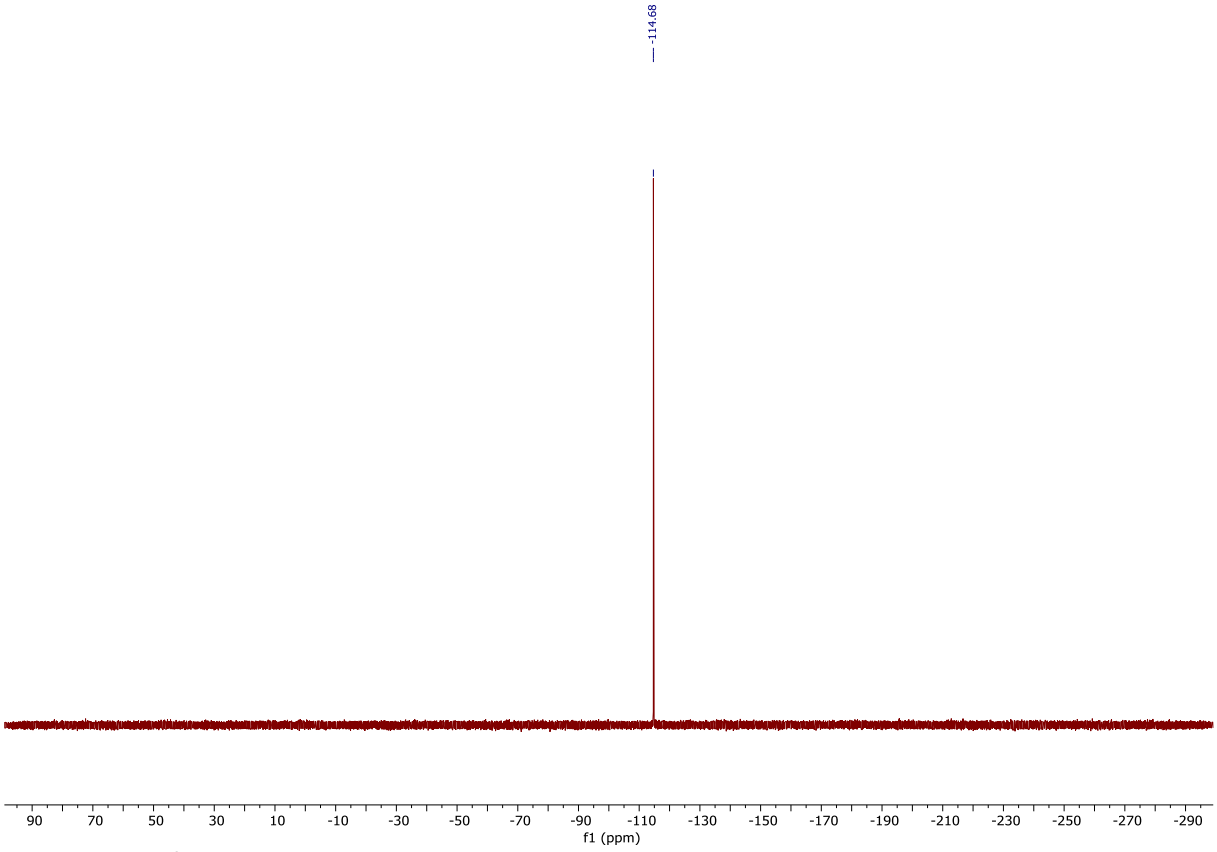


Figure S71. ^{19}F {^{1}H} NMR of **4**.

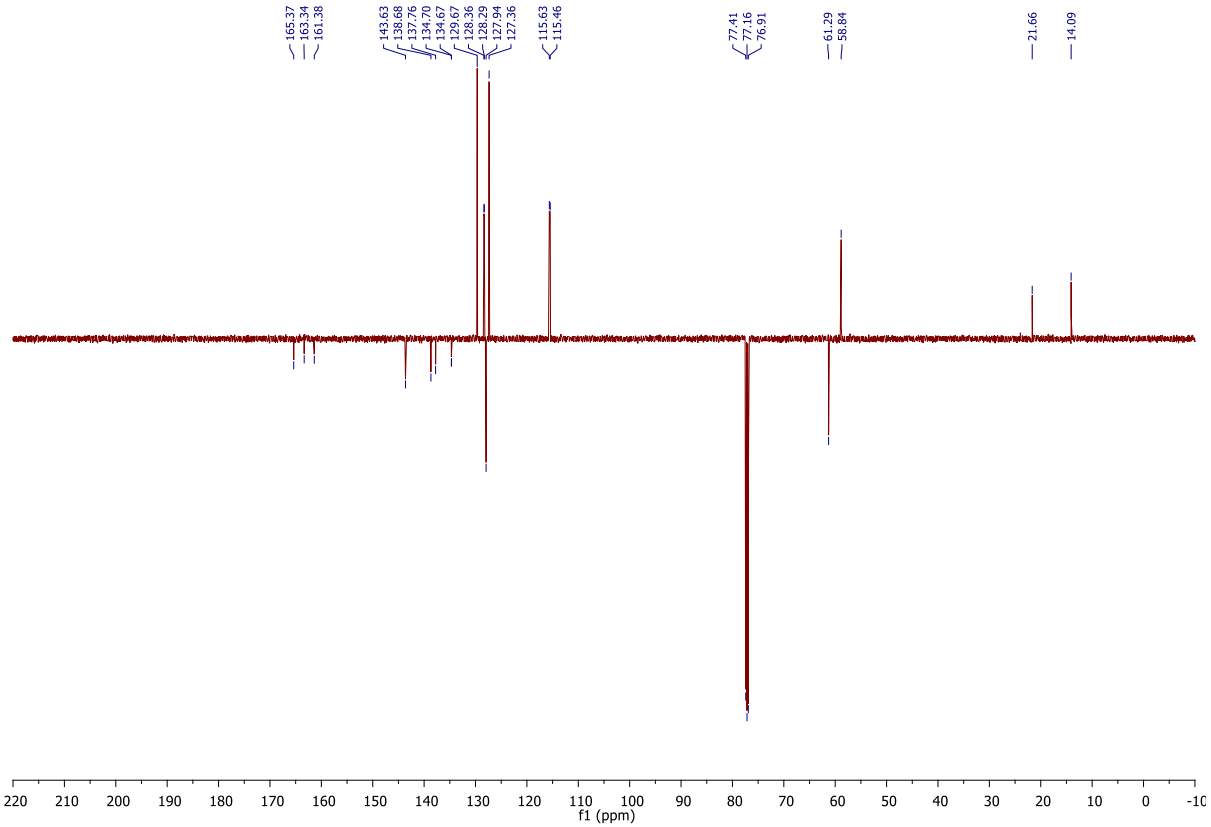
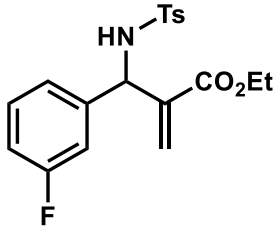


Figure S72. ^{13}C {^{1}H} NMR of **4**.

Ethyl 2-((3-fluorophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (5)



Prepared according to general procedure B from *N*-(3-fluorobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (73 mg, 78%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.19 (1:4 EtOAc/PE); mp 101 – 103 ˚C (lit. 86 – 88 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.70 – 7.63 (m, 2H), 7.24 (d, *J* = 7.9, 2H), 7.22 – 7.18 (m, 1H), 6.99 – 6.95 (m, 1H), 6.93 – 6.84 (m, 2H), 6.21 (d, *J* = 0.7, 1H), 5.77 (t, *J* = 0.8, 1H), 5.74 (d, *J* = 8.7, 1H), 5.27 (d, *J* = 9.3, 1H), 4.10 – 4.02 (m, 2H), 2.41 (s, 3H), 1.16 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.1, 162.8 (d, *J* = 246.8), 143.6, 141.4 (d, *J* = 7.0), 138.2, 137.6, 130.1 (d, *J* = 8.2), 129.6, 128.3, 127.2, 122.0 (d, *J* = 2.9), 114.7 (d, *J* = 21.1), 113.6 (d, *J* = 22.9), 61.2, 58.9 (d, *J* = 2.1), 21.5, 13.9; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -112.5.

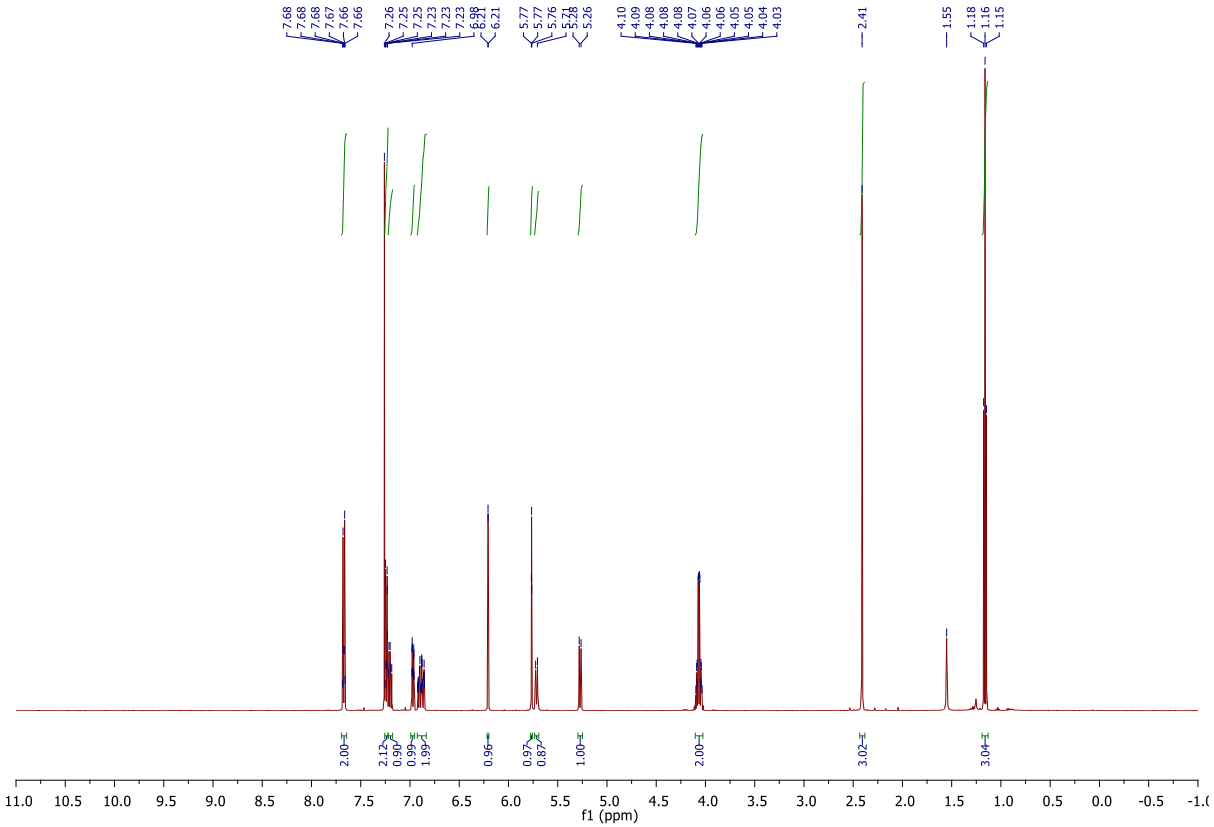


Figure S73. ^{1}H NMR of **5**.

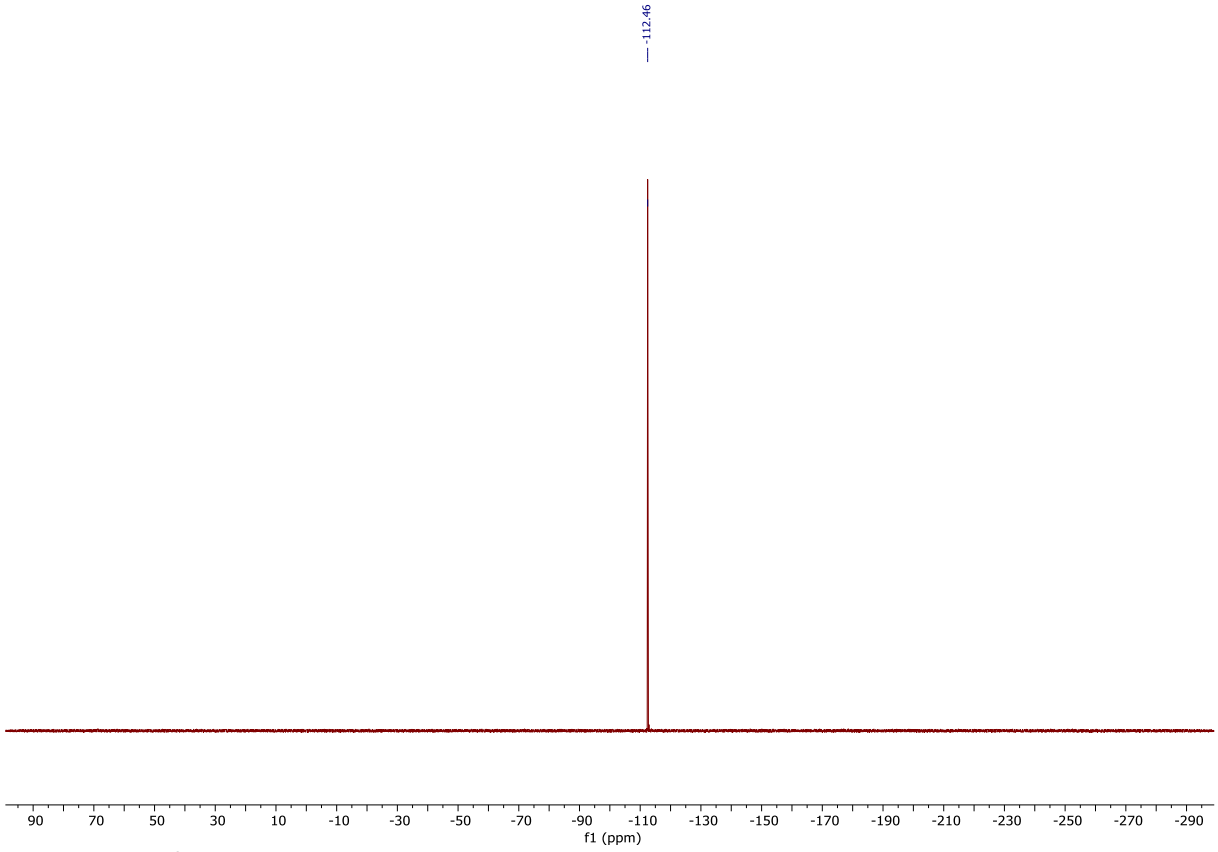


Figure S74. ^{19}F {^{1}H} NMR of **5**.

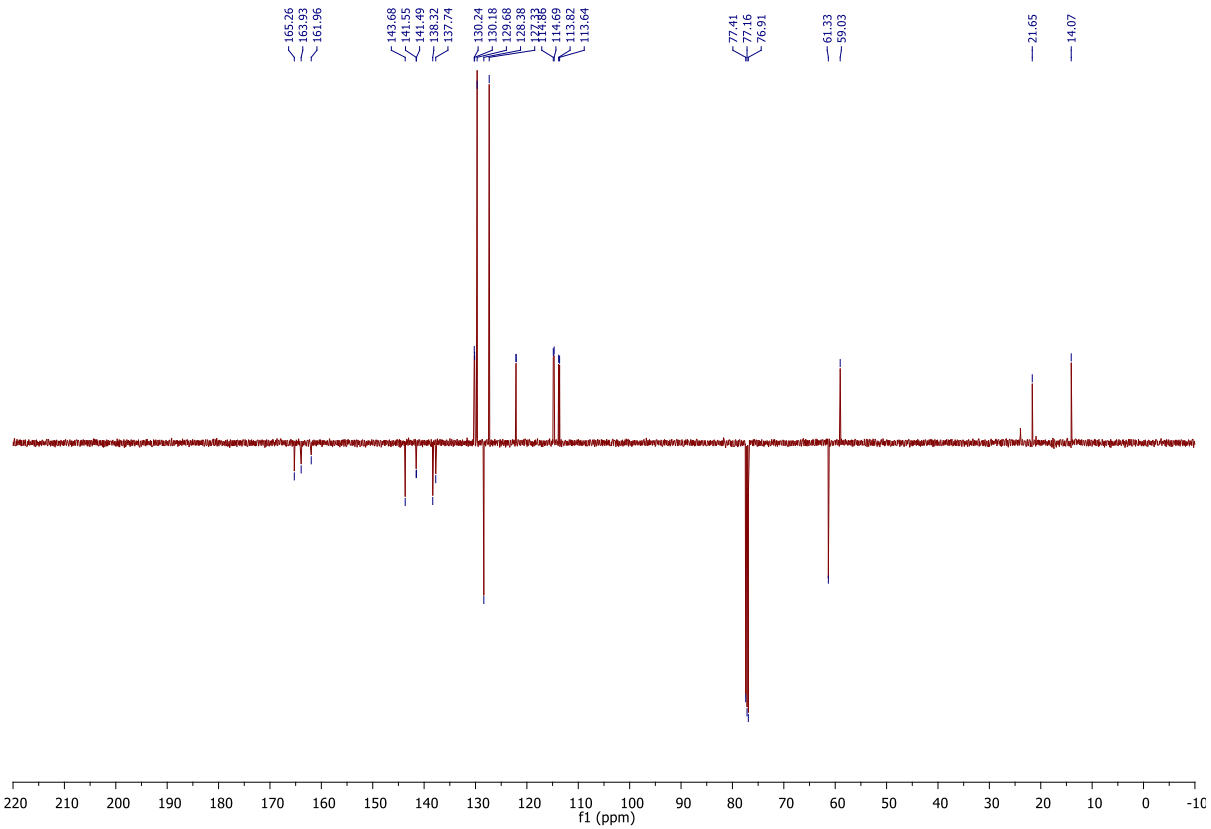
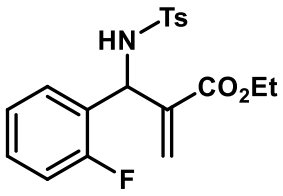


Figure S75. ^{13}C {^{1}H} NMR of **5**.

Ethyl 2-((2-fluorophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (6)



Prepared according to general procedure B from *N*-(2-fluorobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (46 mg, 49%), with physical and spectroscopic data in accordance with the literature;[17] R_F = 0.12 (1:4 EtOAc/PE); mp 92 – 94 ˚C (lit. 75 – 77 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.66 – 7.61 (m, 2H), 7.25 – 7.13 (m, 4H), 6.98 (td, *J* = 7.6, 1.2, 1H), 6.89 (ddd, *J* = 10.6, 8.2, 1.2, 1H), 6.22 (d, *J* = 0.8, 1H), 5.87 – 5.86 (m, 1H), 5.76 (d, *J* = 9.4, 1H), 5.58 (d, *J* = 9.4, 1H), 4.08 (q, *J* = 7.1, 2H), 2.37 (s, 3H), 1.18 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ_C: 165.4, 159.9 (d, *J* = 247.8), 143.4, 137.9 (d, *J* = 86.3), 129.6, 129.5 (2C), 128.8 (d, *J* = 3.3), 127.5, 127.2, 126.1 (d, *J* = 13.0), 124.2 (d, *J* = 3.5), 115.6 (d, *J* = 21.7), 61.2, 53.4 (d, *J* = 2.7), 21.6, 14.0; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -116.8.

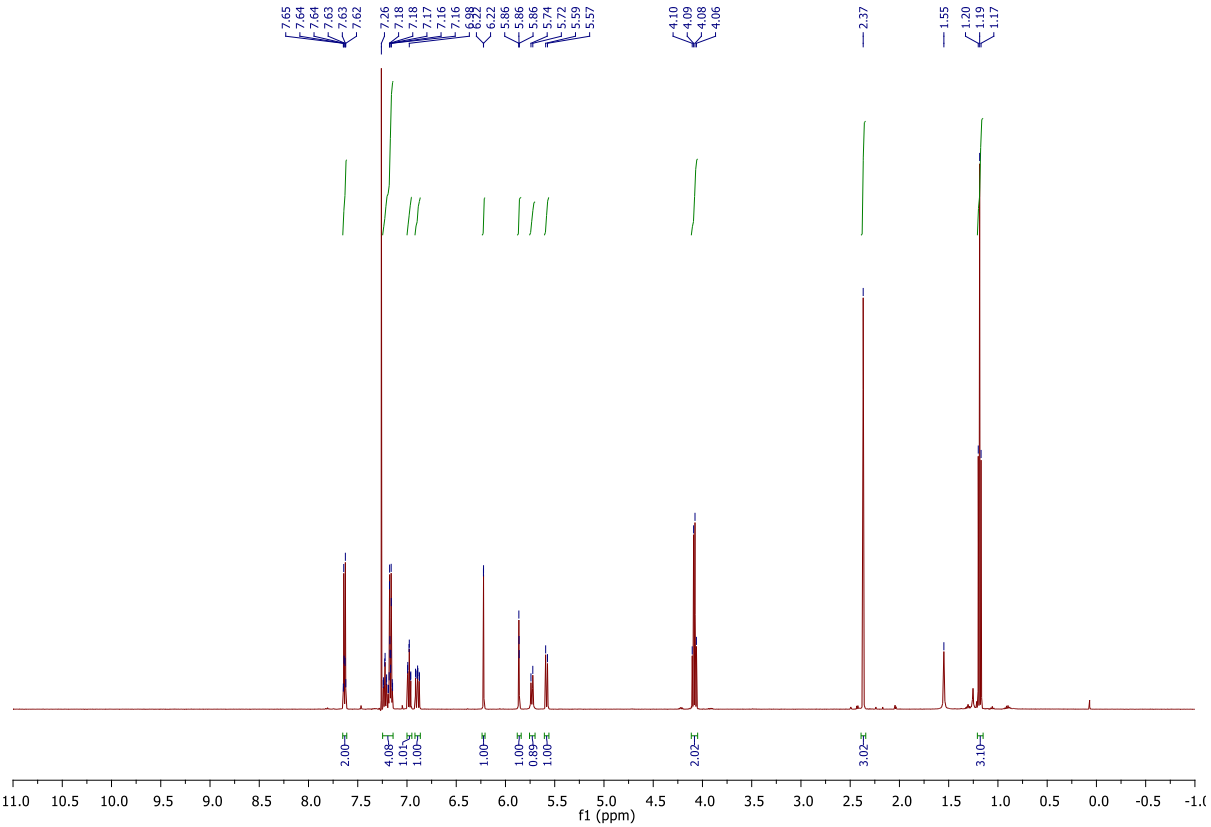


Figure S76. ^{1}H NMR of **6**.

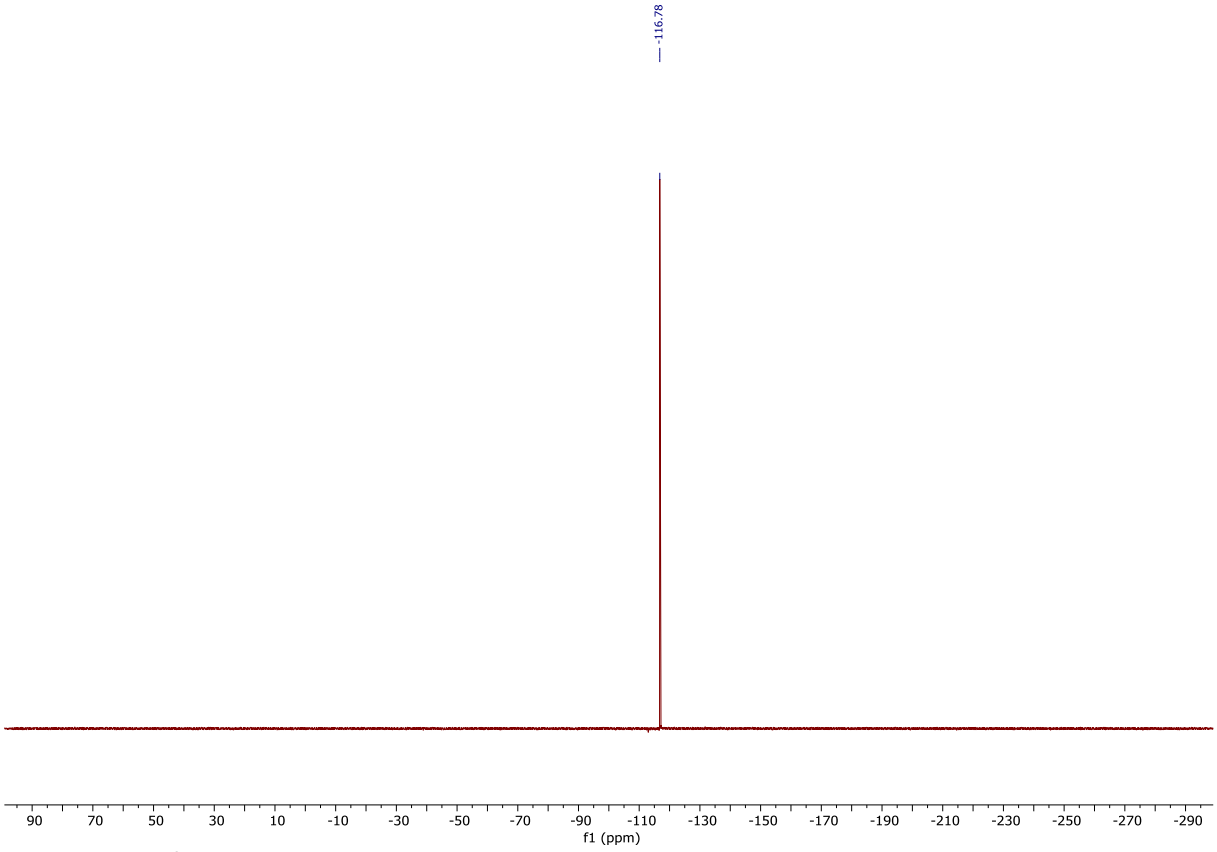


Figure S77. ^{19}F {^{1}H} NMR of **6**.

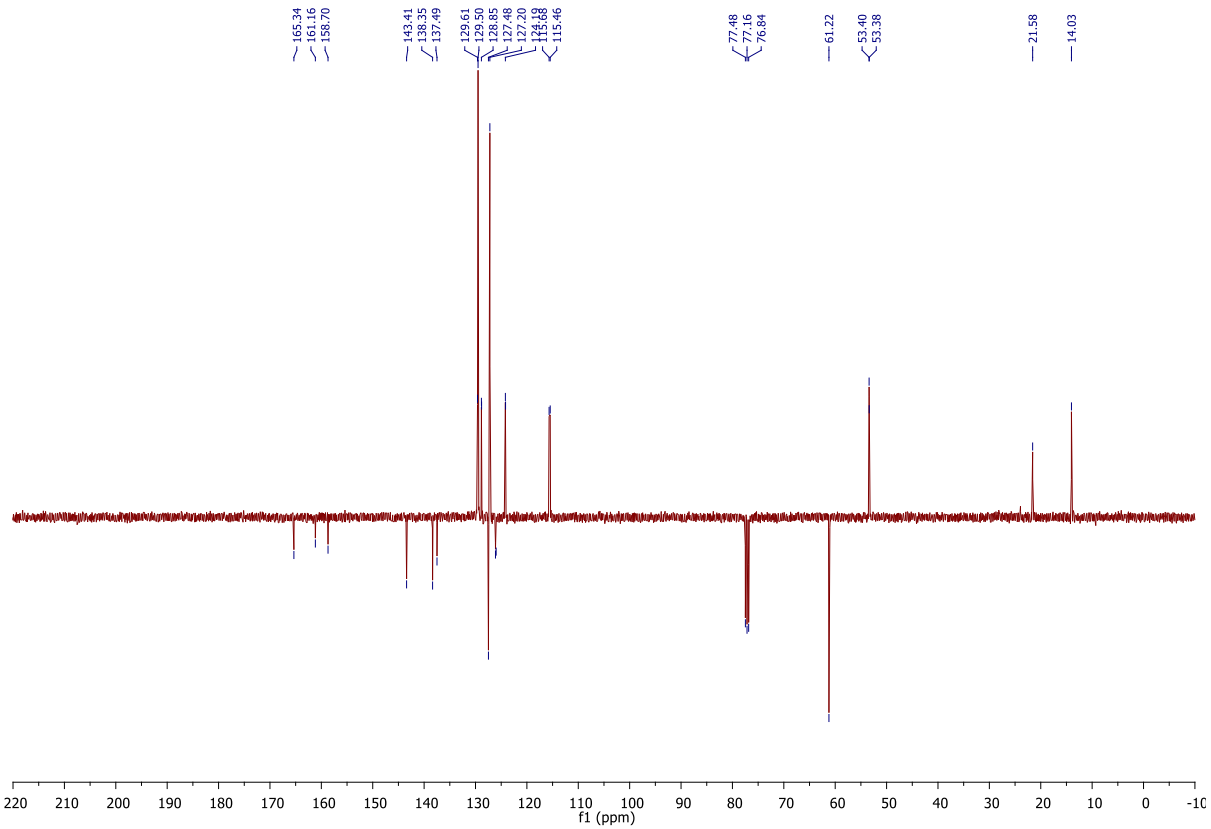
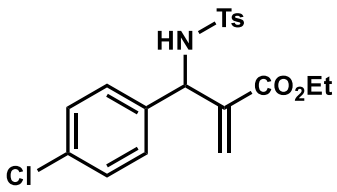


Figure S78. ^{13}C {^{1}H} NMR of **6**.

Ethyl 2-((4-chlorophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (7)



Prepared according to general procedure B from *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time and 40 mol % catalyst; purified by FCC (1.5:8.5 EtOAc/PE) to give the title compound as a white solid (60 mg, 61%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.35 (1.5:8.5 EtOAc/PE); mp 93 – 95 ˚C (lit. 65 – 67 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.68 – 7.61 (m, 2H), 7.24 – 7.16 (m, 4H), 7.13 – 7.07 (m, 2H), 6.19 (d, *J* = 0.7, 1H), 5.75 (t, *J* = 0.8, 1H), 5.69 (d, *J* = 9.2, 1H), 5.26 (d, *J* = 9.2, 1H), 4.09 – 4.03 (m, 2H), 2.41 (s, 3H), 1.16 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.3, 143.7, 138.5, 137.7, 137.4, 133.7, 129.7, 128.8, 128.1, 128.0, 127.3, 61.3, 58.8, 21.7, 14.1.

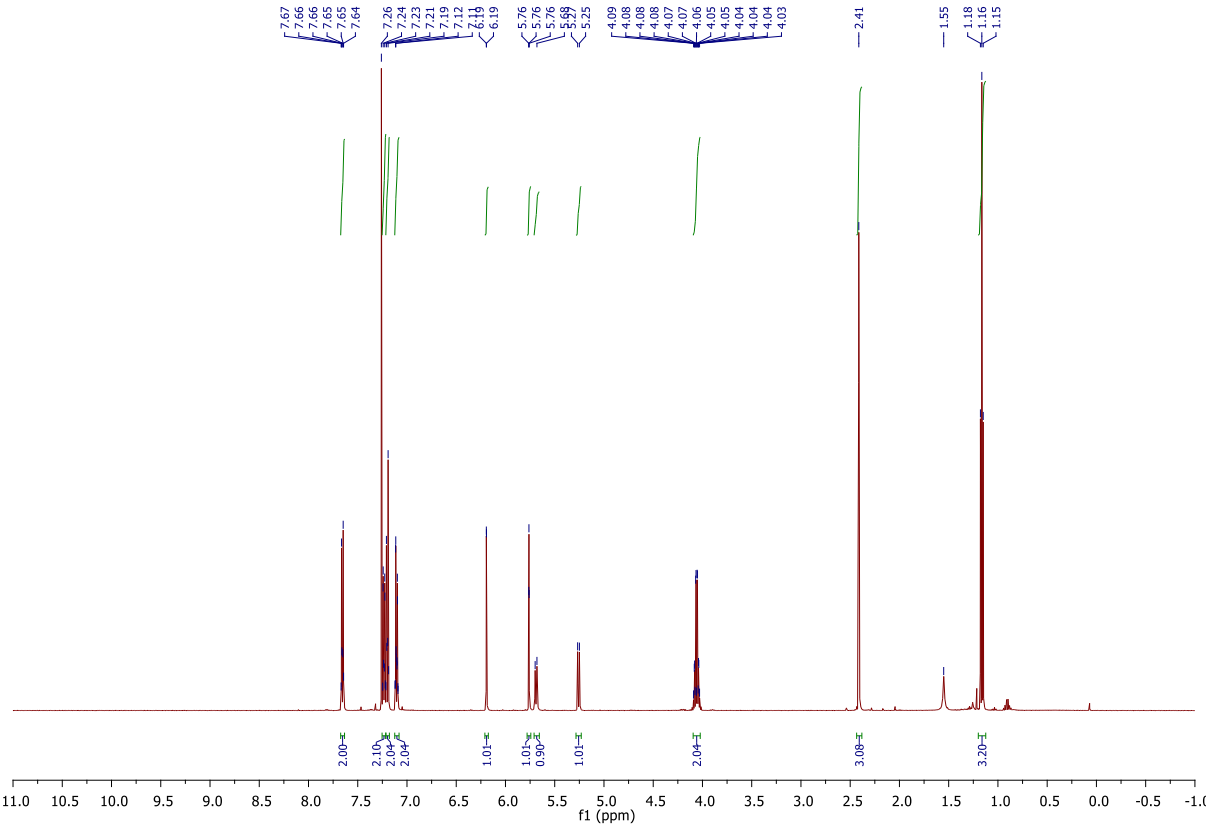


Figure S79. ^{1}H NMR of **7**.

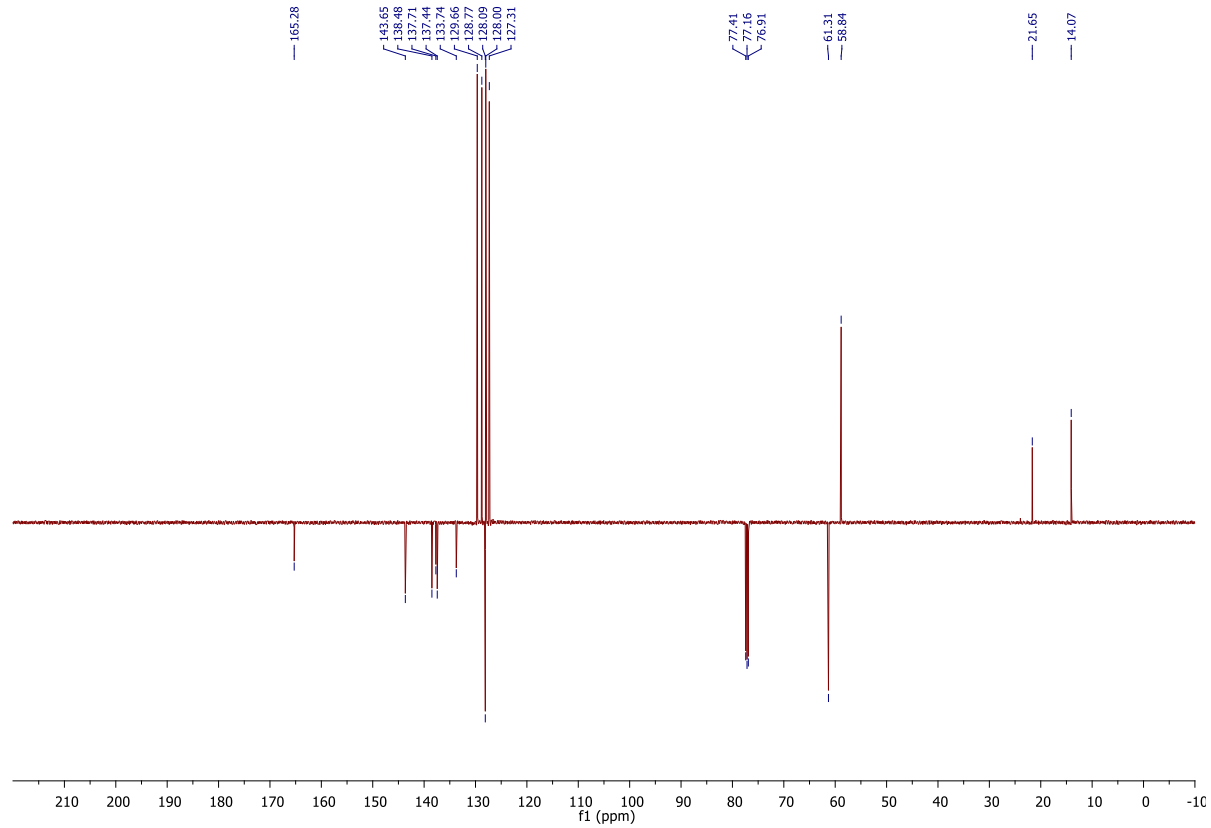
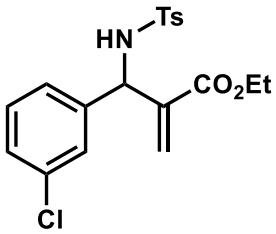


Figure S80. ^{13}C {^{1}H} NMR of **7**.

Ethyl 2-((3-chlorophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (8)



Prepared according to general procedure B from *N*-(3-chlorobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time and 40 mol % catalyst; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (69 mg, 70%); R_F = 0.19 (1:4 EtOAc/PE); mp 103 – 105 ˚C; ν_{max}/cm^{-1} (film): 3296, 2364, 1714, 1597, 1433, 1329, 1160, 1094, 814, 668; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.68 – 7.63 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.15 (m, 2H), 7.09 – 7.05 (m, 2H), 6.22 (d, *J* = 0.7, 1H), 5.78 (t, *J* = 0.8, 1H), 5.69 (d, *J* = 9.2, 1H), 5.26 (dd, *J* = 9.2, 0.6, 1H), 4.12 – 4.03 (m, 2H), 2.41 (s, 3H), 1.17 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.2, 143.7, 140.9, 138.3, 137.7, 134.6, 129.9, 129.7, 128.4, 128.0, 127.3, 126.9, 124.7, 61.4, 59.0, 21.7, 14.1; HRMS (ES$^+$) calculated for $[C_{19}H_{20}NO_4SClNa]^+$ $(M+Na)^+$: m/z 416.0698 found 416.0699 (-0.2 ppm).

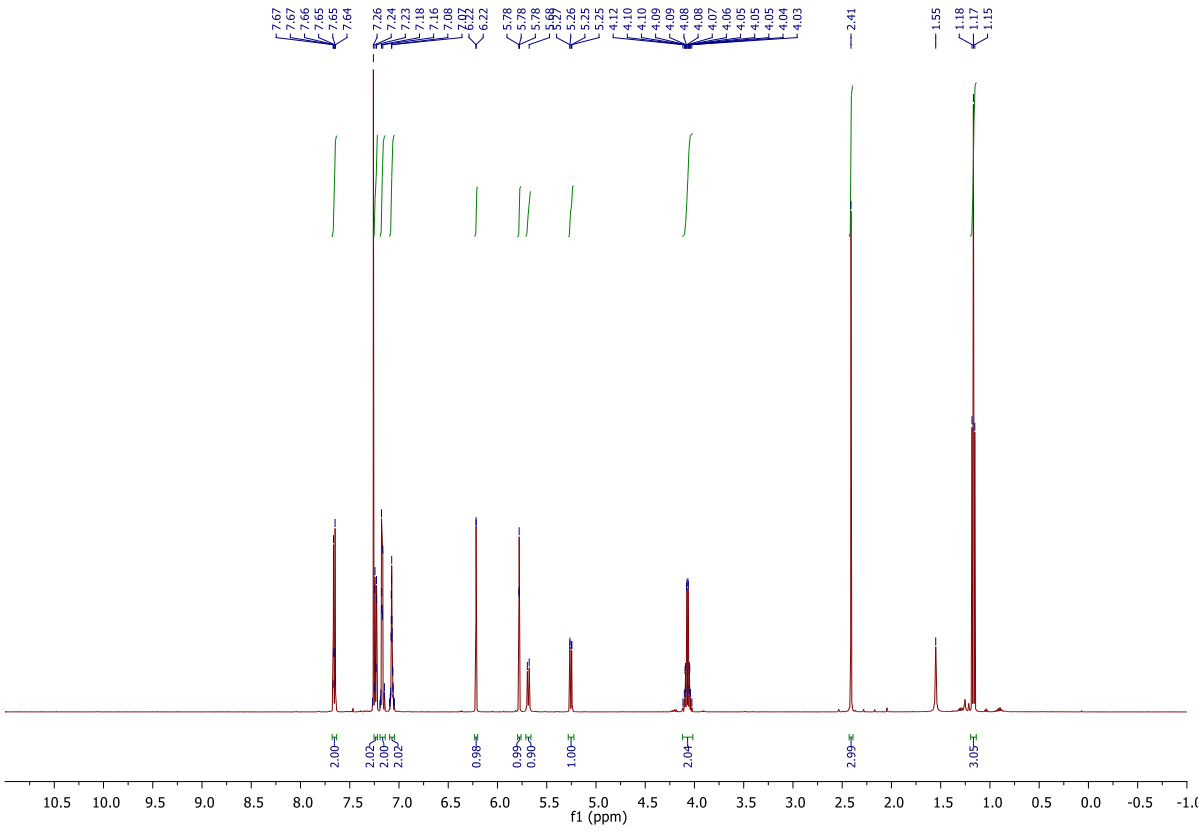


Figure S81. ^{1}H NMR of **8**.

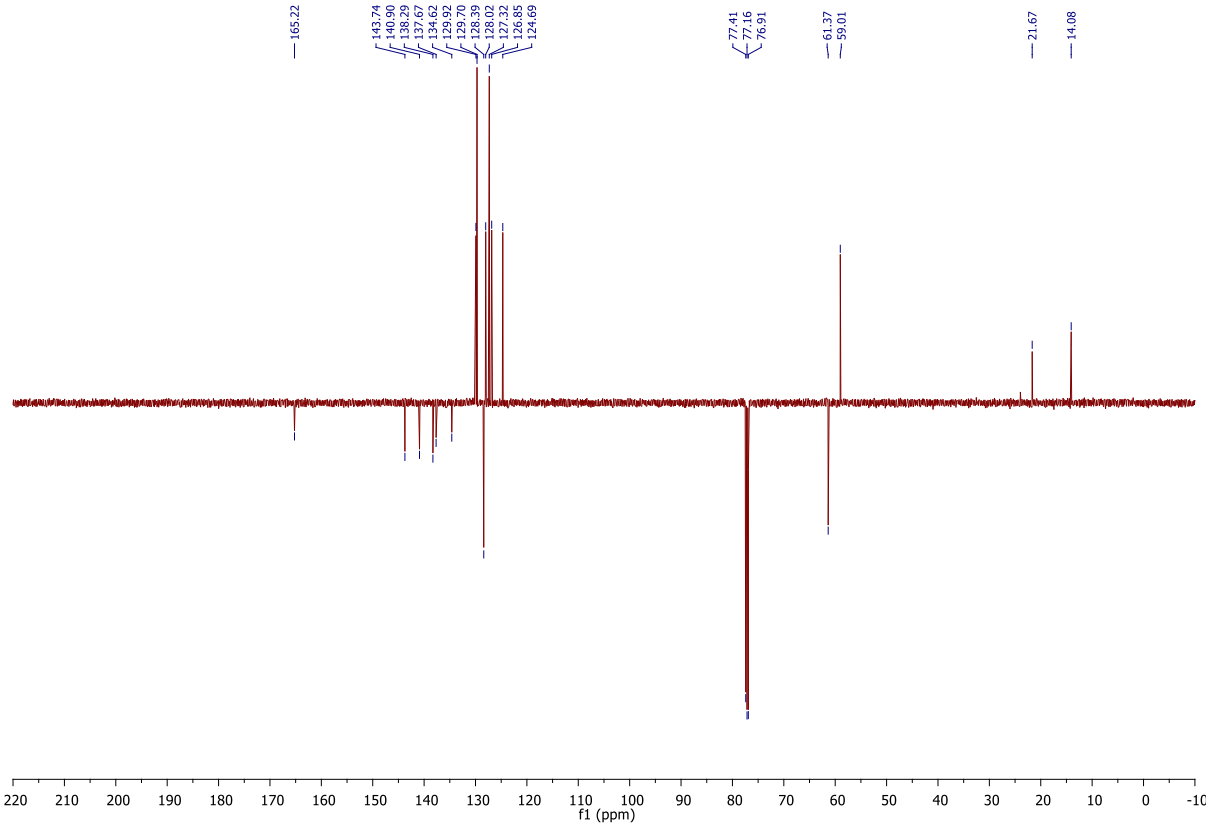
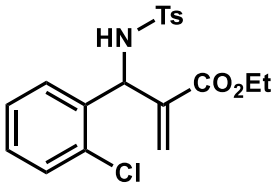


Figure S82. ^{13}C {^{1}H} NMR of **8**.

Ethyl 2-((2-chlorophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (9)



Prepared according to general procedure B from *N*-(2-chlorobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time and 40 mol % catalyst; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (69 mg, 70%); R_F = 0.16 (1:4 EtOAc/PE); mp 104 – 106 ˚C; ν_{max}/cm^{-1} (film): 3360, 2364, 2334, 1718, 1161, 913, 680; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.66 – 7.62 (m, 2H), 7.32 – 7.29 (m, 1H), 7.26 – 7.22 (m, 1H), 7.19 – 7.15 (m, 2H), 7.15 – 7.08 (m, 2H), 6.29 (s, 1H), 5.90 (s, 1H), 5.75 (d, *J* = 8.5, 1H), 5.67 (d, *J* = 8.6, 1H), 4.08 (q, *J* = 7.1, 2H), 2.37 (s, 3H), 1.18 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.5, 143.5, 138.0, 137.5, 136.0, 133.1, 129.9, 129.5, 129.1 (2C), 128.6, 127.4, 127.0, 61.3, 56.0, 21.6, 14.1; HRMS (ES^+) calculated for $[C_{19}H_{20}NO_4SClNa]^+$ $(M+Na)^+$: m/z 416.0701 found 416.0699 (+0.2 ppm).

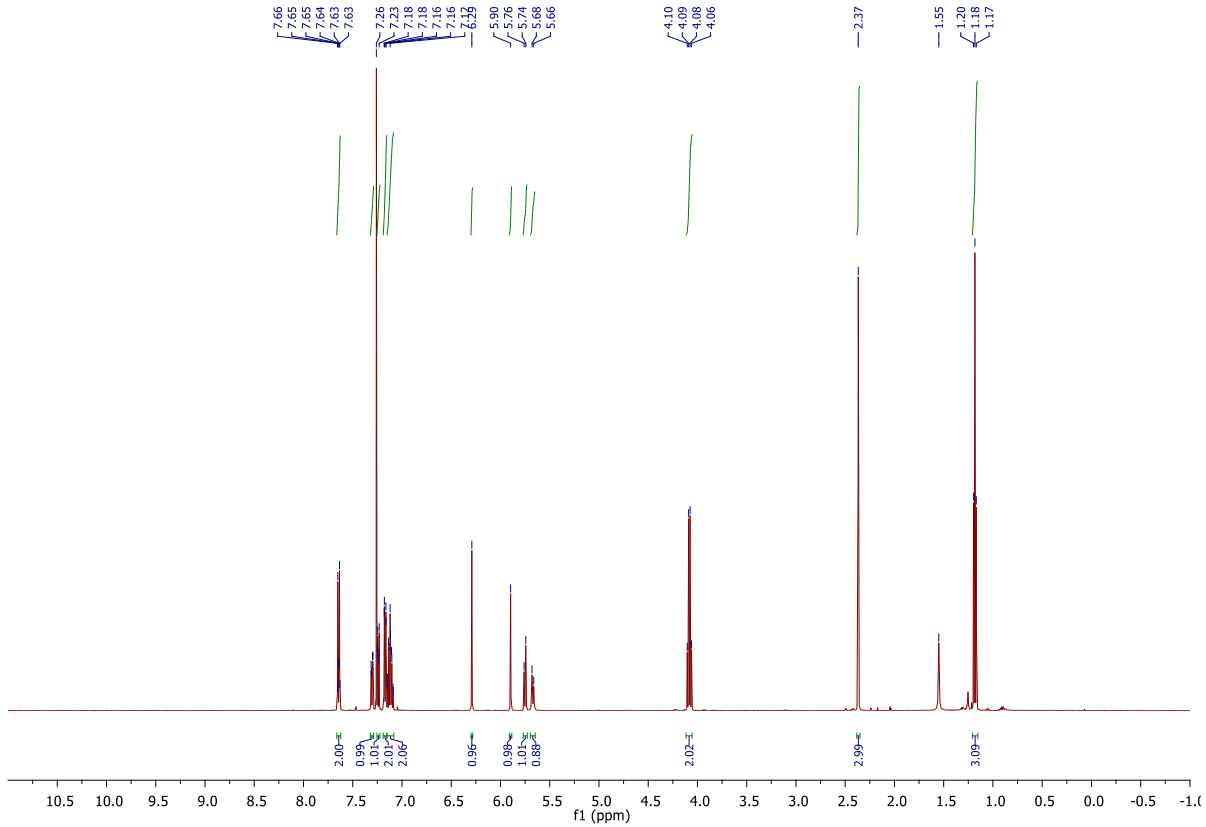


Figure S83. ^{1}H NMR of **9**.

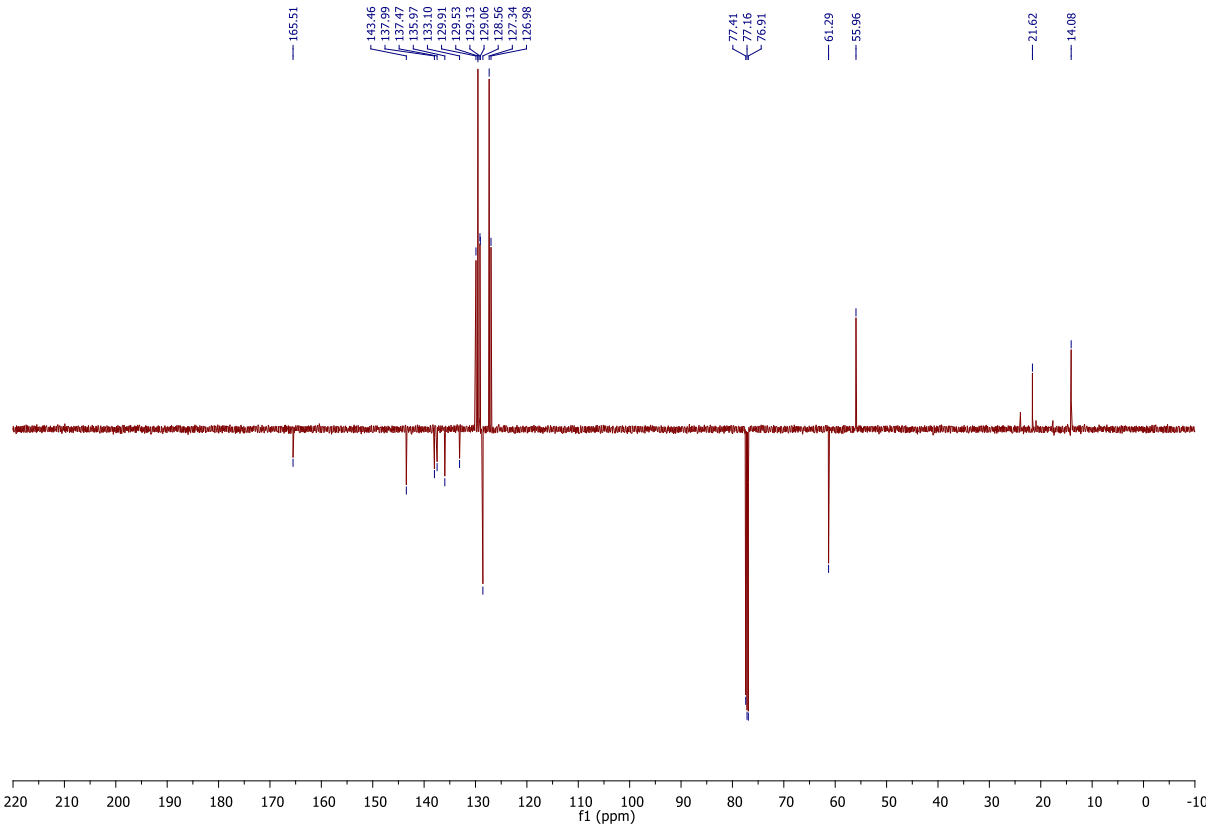
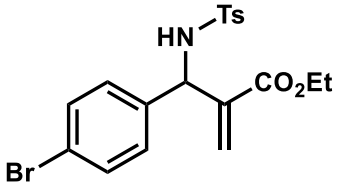


Figure S84. ^{13}C {^{1}H} NMR of **9**.

Ethyl 2-((4-bromophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (10)



Prepared according to general procedure B from *N*-(4-bromobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time and 40 mol % catalyst; purified by FCC (1.5:8.5 EtOAc/PE) to give the title compound as a white solid (56 mg, 51%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.34 (1.5:8.5 EtOAc/PE); mp 96 – 98 ˚C (lit. 77 – 79 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.67 – 7.63 (m, 2H), 7.37 – 7.33 (m, 2H), 7.25 – 7.22 (m, 2H), 7.06 – 7.02 (m, 2H), 6.19 (s, 1H), 5.76 (s, 1H), 5.70 (d, *J* = 9.2, 1H), 5.24 (d, *J* = 9.1, 1H), 4.11 – 4.02 (m, 2H), 2.41 (s, 3H), 1.17 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.3, 143.7, 138.4, 138.0, 137.7, 131.7, 129.7, 128.3, 128.2, 127.3, 121.9, 61.3, 59.0, 21.67, 14.1.

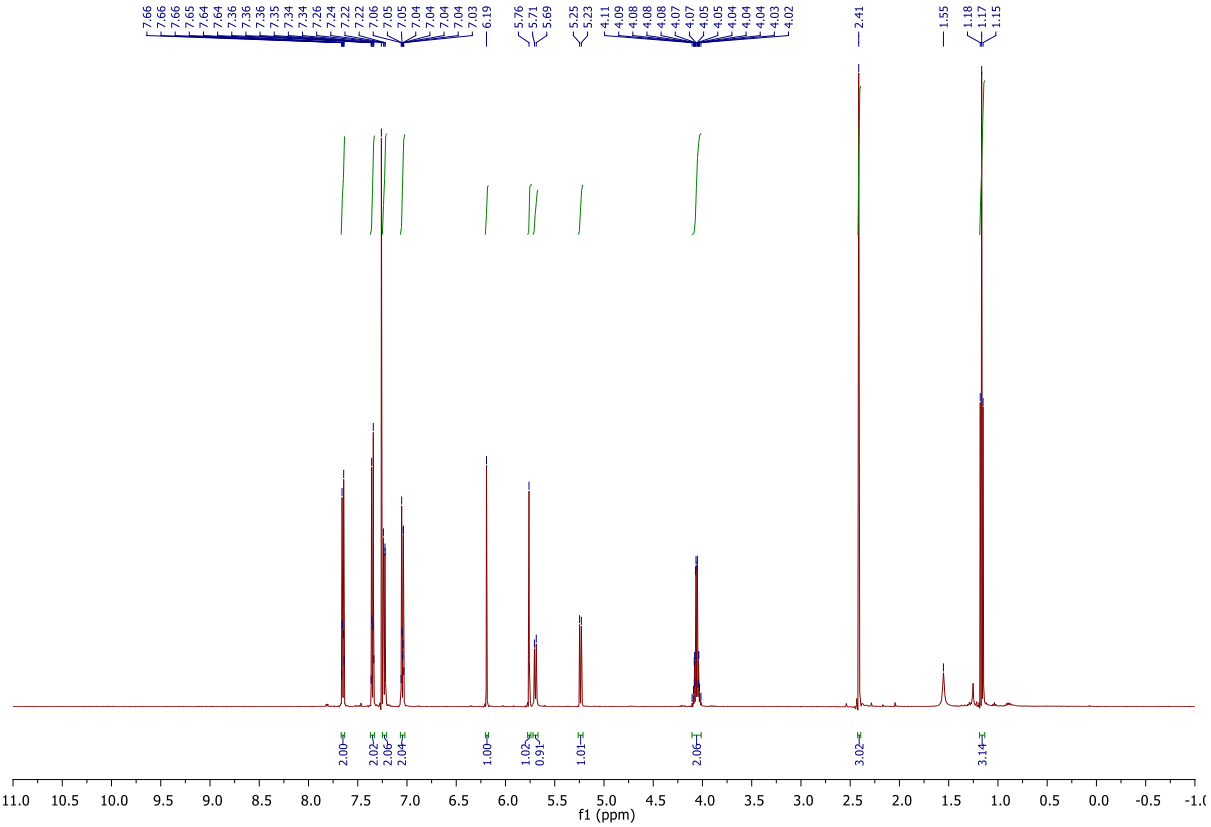


Figure S85. ^{1}H NMR of **10**.

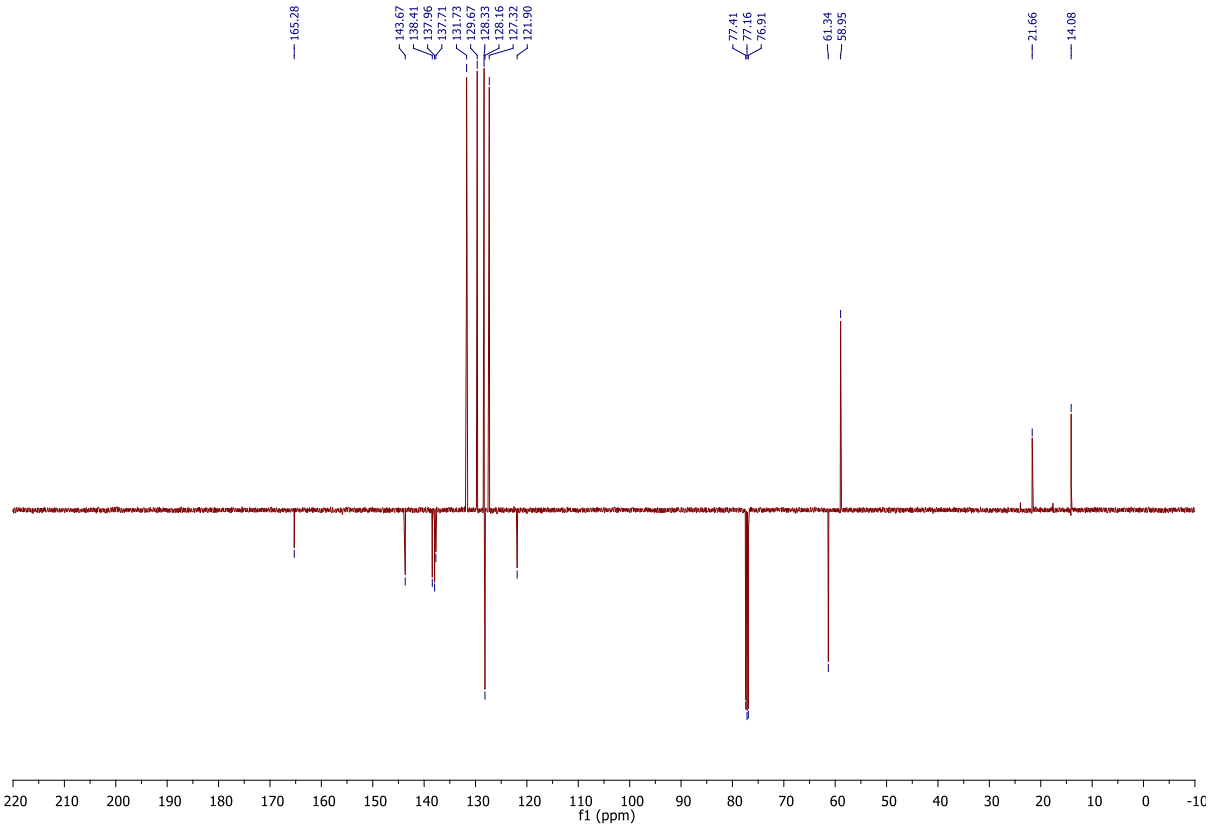
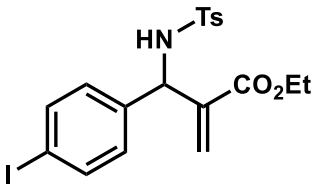


Figure S86. ^{13}C {^{1}H} NMR of **10**.

Ethyl 2-((4-iodophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (11)



Prepared according to general procedure B from *N*-(4-iodobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time and 40 mol % catalyst; purified by FCC (1.5:8.5 EtOAc/PE) to give the title compound as a viscous, colourless oil (46 mg, 38%); R_F = 0.31 (1.5:8.5 EtOAc/PE); ν_{max}/cm^{-1} (film): 2364, 1719, 1329, 1160, 1007, 668; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.66 – 7.62 (m, 2H), 7.57 – 7.52 (m, 2H), 7.25 – 7.21 (m, 2H), 6.93 – 6.89 (m, 2H), 6.19 (d, *J* = 0.7, 1H), 5.76 (t, *J* = 0.8, 1H), 5.67 (d, *J* = 9.2, 1H), 5.22 (d, *J* = 8.8, 1H), 4.09 – 4.03 (m, 2H), 2.42 (s, 3H), 1.17 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.3, 143.7, 138.7, 138.4, 137.7, 137.6, 129.7, 128.6, 128.2, 127.3, 93.5, 61.4, 59.1, 21.7, 14.1; HRMS (ES^+) calculated for $[C_{19}H_{20}NO_4SINa]^+$ $(M+Na)^+$: m/z 508.0061 found 508.0055 (+1.2 ppm).

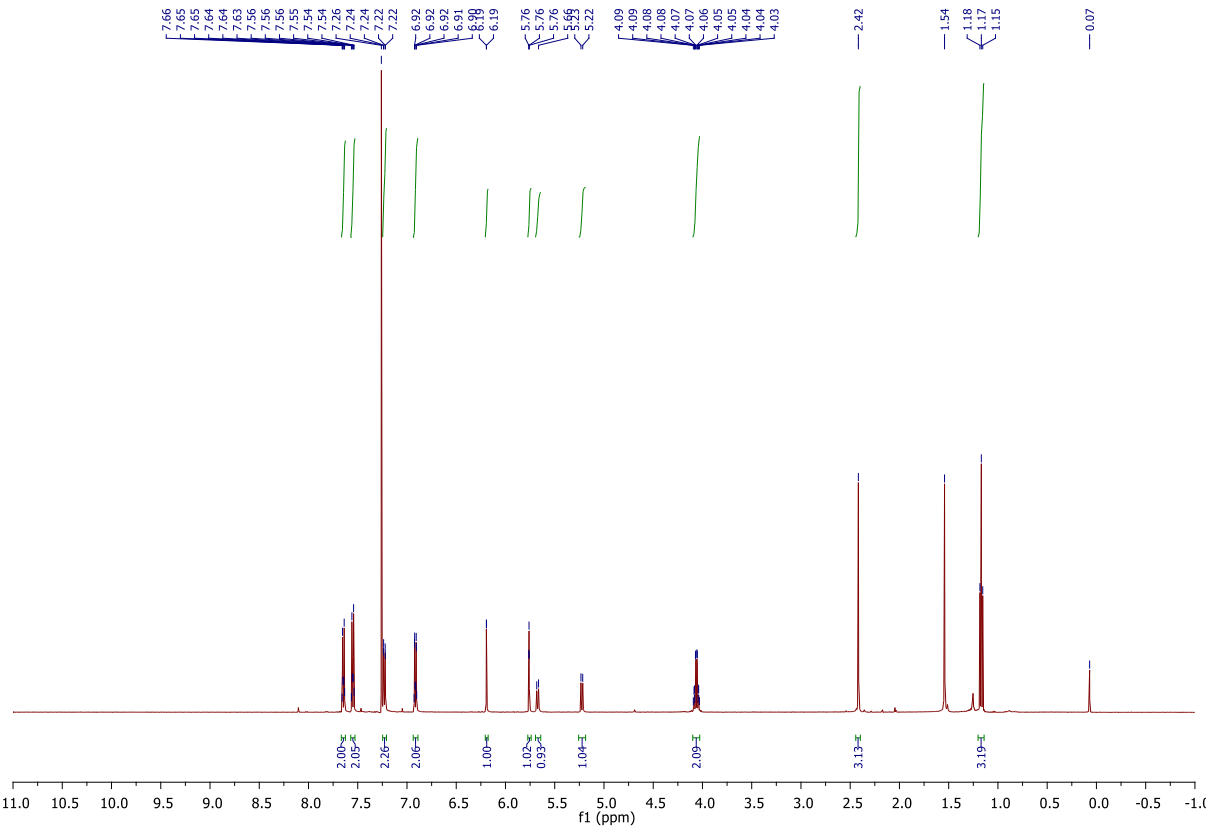


Figure S87. ^{1}H NMR of **11**.

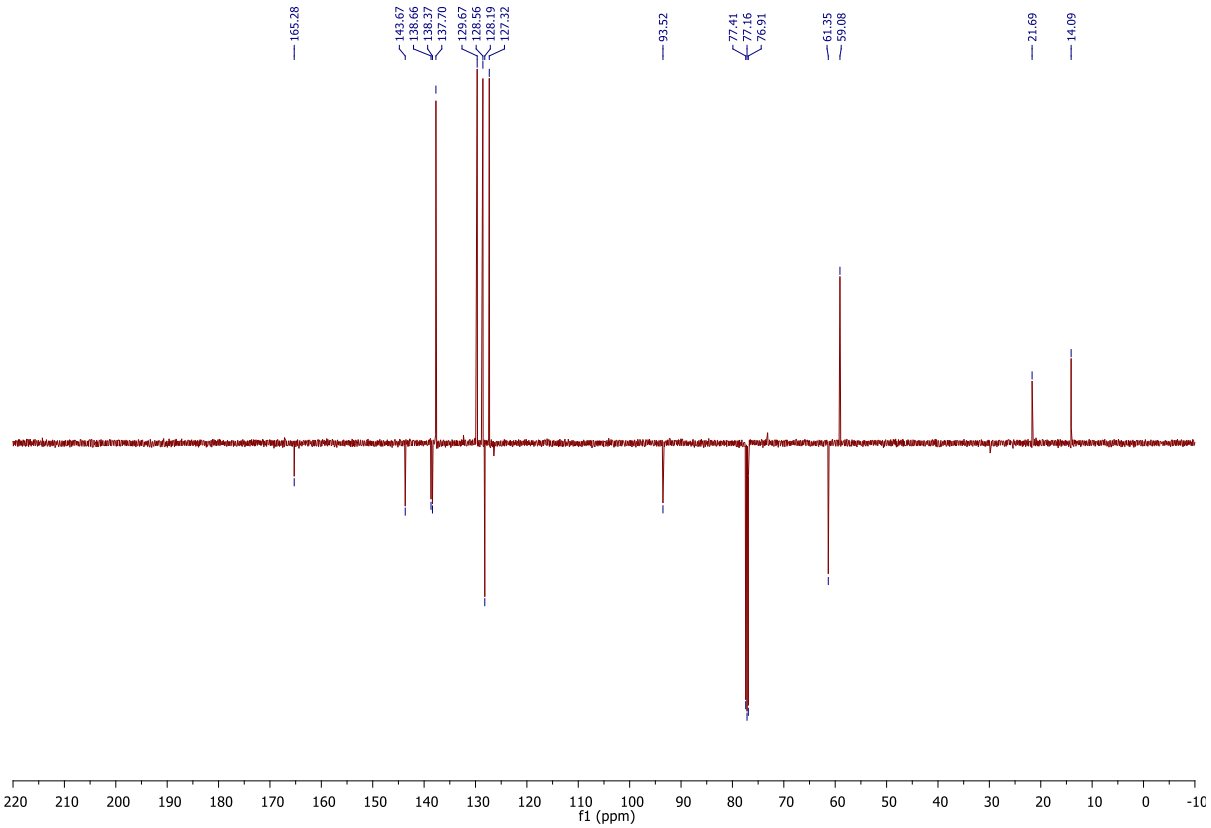
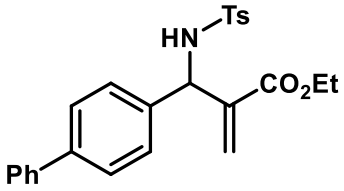


Figure S88. ^{13}C {^{1}H} NMR of **11**.

Ethyl 2-([1,1'-biphenyl]-4-yl((4-methylphenyl)sulfonamido)methyl)acrylate (12)



Prepared according to general procedure B from *N*-([1,1'-biphenyl]-4-ylmethylene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1.5:8.5 EtOAc/PE) to give the title compound as a white solid (72 mg, 66%); R_F = 0.31 (1:4 EtOAc/PE); mp 170 – 172 ˚C; ν_{max}/cm^{-1} (film): 3265, 1709, 1320, 1280, 1180, 1072, 1027, 920, 823, 811, 767, 705, 690, 665, 563; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.72 – 7.66 (m, 2H), 7.55 – 7.50 (m, 2H), 7.48 – 7.39 (m, 4H), 7.36 – 7.32 (m, 1H), 7.25 – 7.21 (m, 4H), 6.24 (s, 1H), 5.84 (s, 1H), 5.71 (d, *J* = 9.0, 1H), 5.35 (d, *J* = 8.9, 1H), 4.08 (q, *J* = 7.1, 2H), 2.40 (s, 3H), 1.17 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.5, 143.5, 140.8, 140.6, 138.8, 137.9, 137.8, 129.6, 128.9, 127.9, 127.6, 127.4 (2C), 127.2, 127.0, 61.2, 59.2, 21.7, 14.1; HRMS (ES$^+$) calculated for $[C_{25}H_{25}NO_4SNa]^+$ (M+Na)$^+$: m/z 458.1402 found 458.1402 (0.0 ppm).

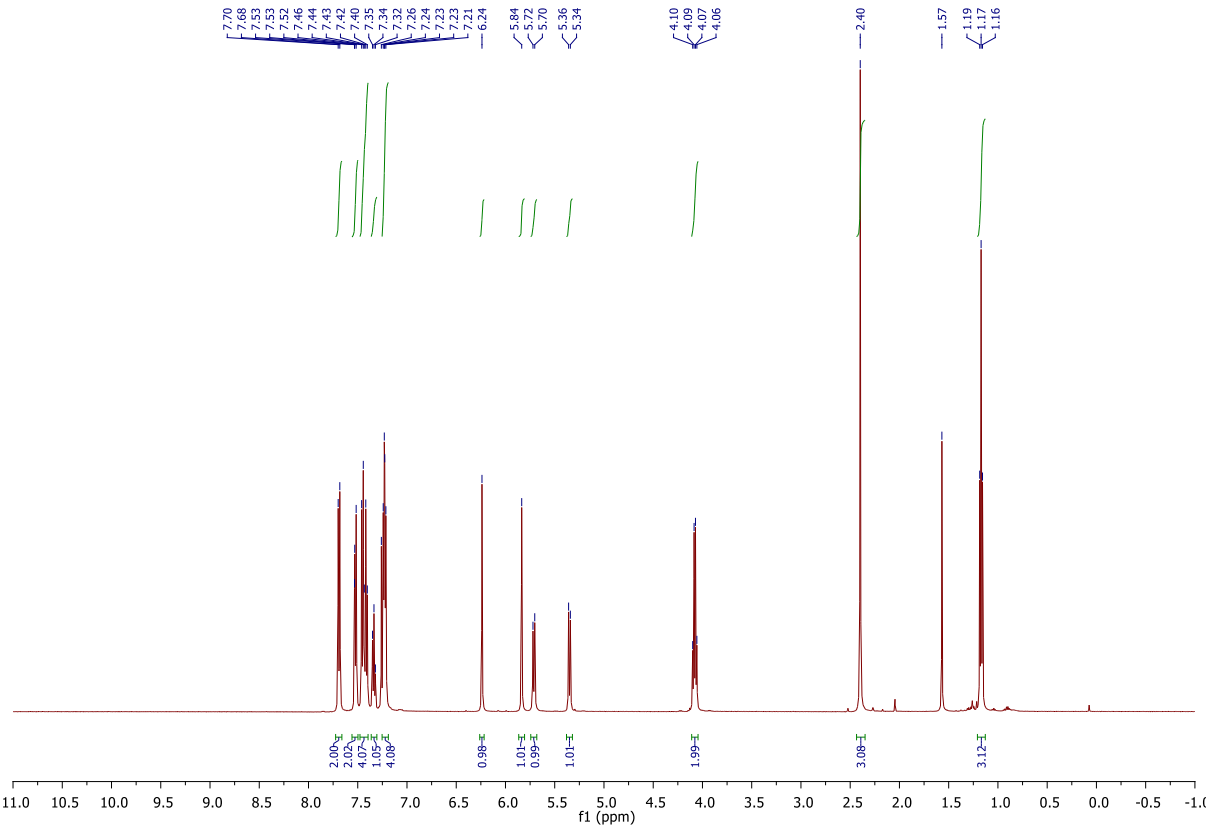


Figure S89. ^{1}H NMR of **12**.

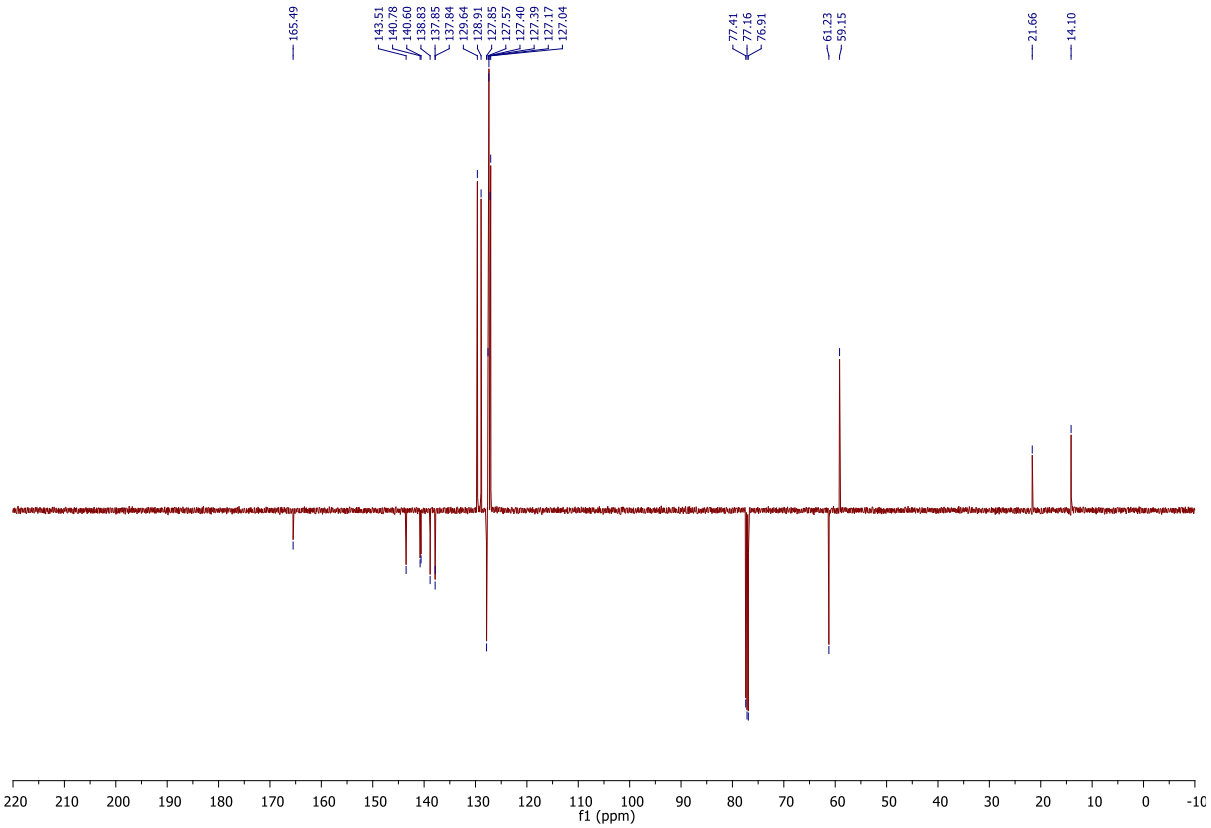
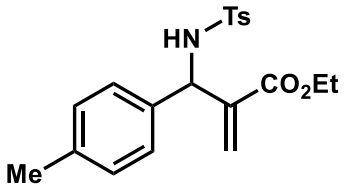


Figure S90. ^{13}C {^{1}H} NMR of **12**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(*p*-tolyl)methyl)acrylate (13)



Prepared according to general procedure B from 4-methyl-*N*-(4-methylbenzylidene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a colourless, viscous oil (27 mg, 29%); R_F = 0.25 (1:4 EtOAc/PE); ν_{max}/cm^{-1} (film): 3289, 1712, 1433, 1326, 1158, 1094, 813, 668; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.71 – 7.65 (m, 2H), 7.26 – 7.21 (m, 2H), 7.05 – 6.99 (m, 4H), 6.20 (s, 1H), 5.80 (s, 1H), 5.56 (d, *J* = 8.7 , 1H), 5.26 (d, *J* = 8.8, 1H), 4.05 (q, *J* = 7.1, 2H), 2.41 (s, 3H), 2.28 (s, 3H), 1.15 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.5, 143.5, 139.0, 137.8, 137.6, 135.9, 129.6, 129.4, 127.5, 127.4, 126.5, 61.1, 59.1, 21.7, 21.1, 14.1; HRMS (ES^+) calculated for $[C_{20}H_{23}NO_4SNa]^+$ $(M+Na)^+$: m/z 396.1248 found 396.1245 (+0.8 ppm).

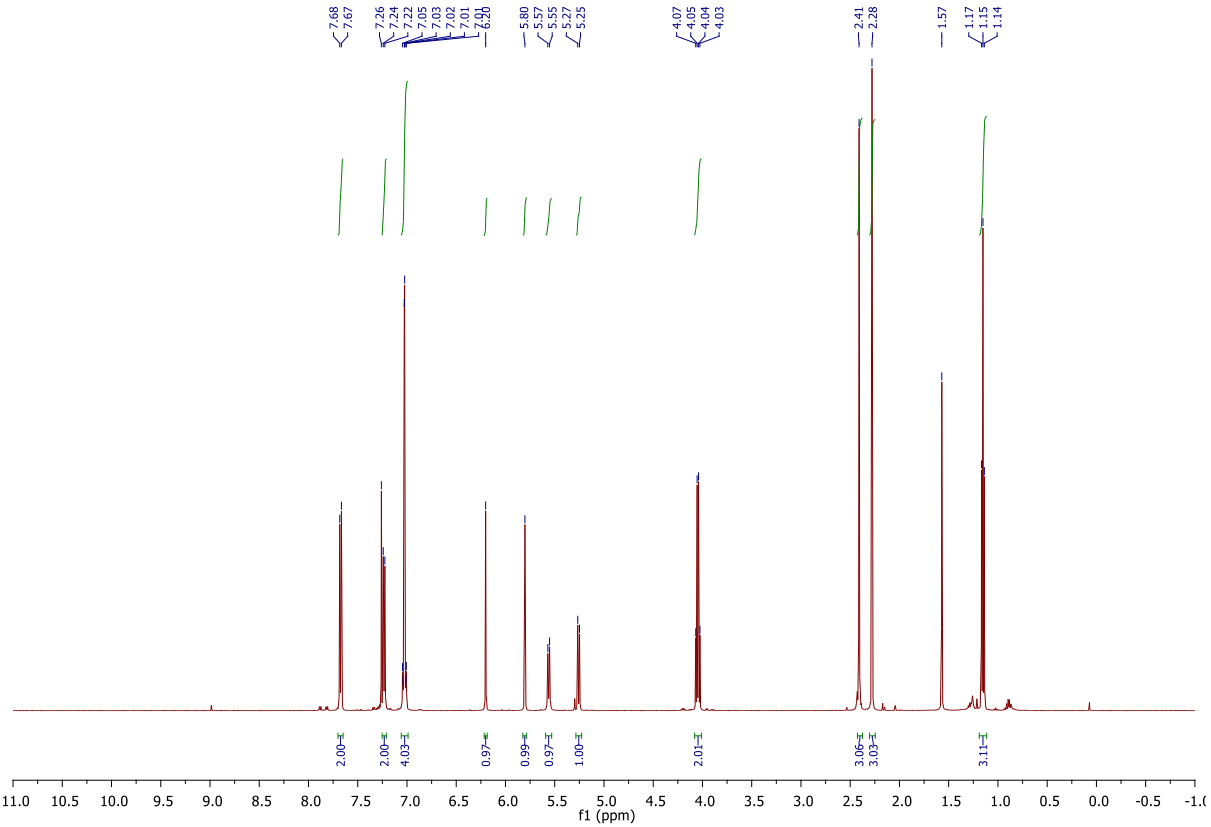


Figure S91. ^{1}H NMR of **13**.

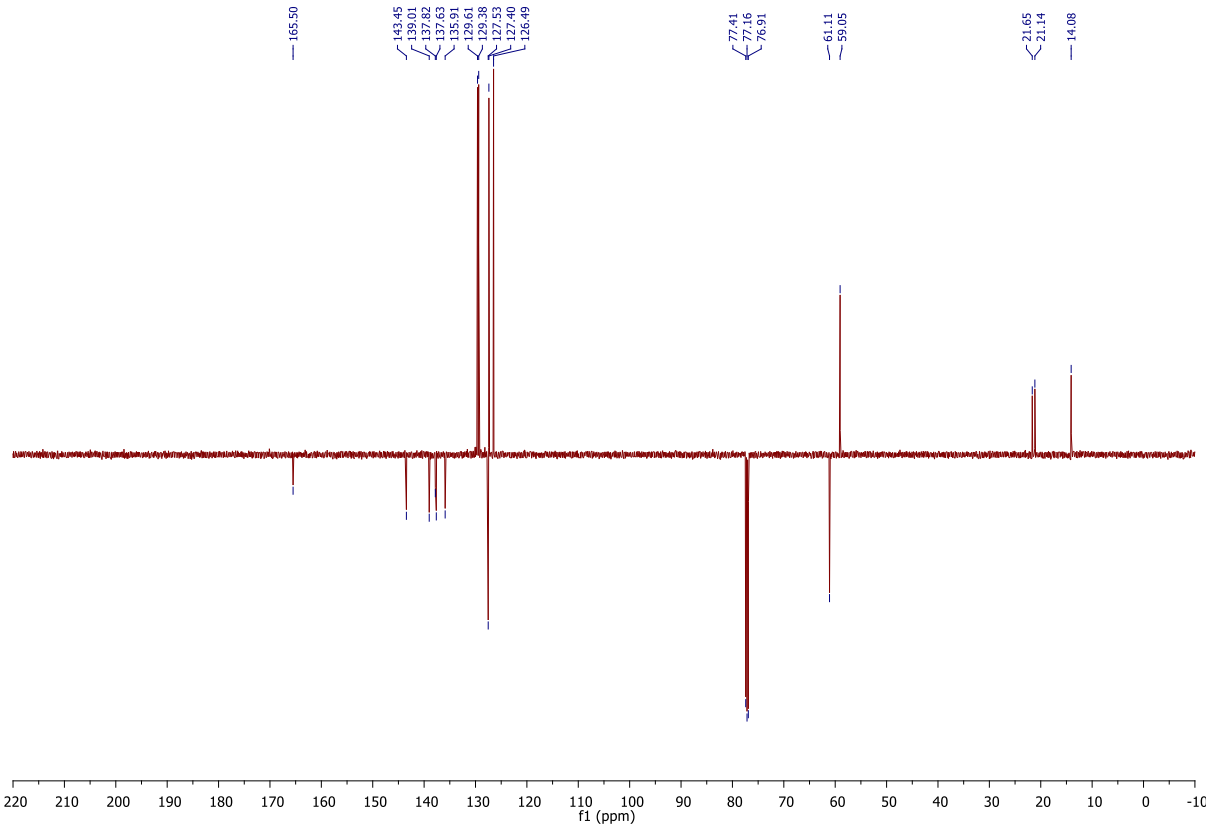
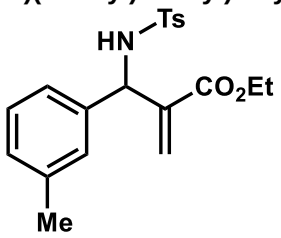


Figure S92. ^{13}C {^{1}H} NMR of **13**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(*m*-tolyl)methyl)acrylate (14)



Prepared according to general procedure B from 4-methyl-*N*-(3-methylbenzylidene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (66 mg, 70%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.36 (1.5:8.5 EtOAc/PE); mp 72 – 74 ˚C (lit. 62 – 64 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.69 – 7.64 (m, 2H), 7.25 – 7.21 (m, 2H), 7.11 (t, *J* = 7.6, 1H), 7.03 – 6.99 (m, 1H), 6.93 – 6.87 (m, 2H), 6.21 (d, *J* = 0.5, 1H), 5.81 (t, *J* = 0.9, 1H), 5.55 (d, *J* = 8.8, 1H), 5.26 (d, *J* = 8.7, 1H), 4.06 (q, *J* = 7.1, 2H), 2.41 (s, 3H), 2.24 (s, 3H), 1.15 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.5, 143.4, 139.0, 138.7, 138.3, 137.8, 129.6, 128.6, 128.5, 127.6, 127.4, 127.3, 123.6, 61.1, 59.2, 21.6, 21.5, 14.1.

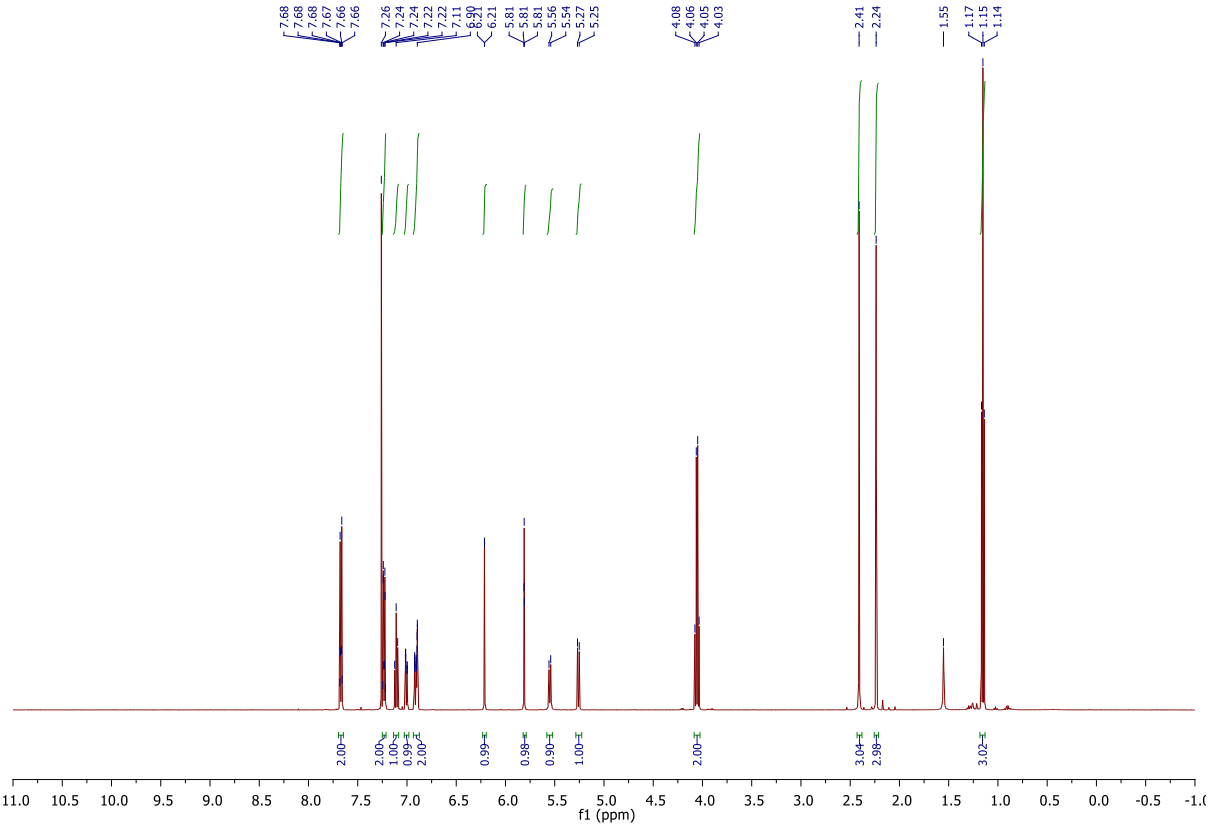


Figure S93. ^{1}H NMR of **14**.

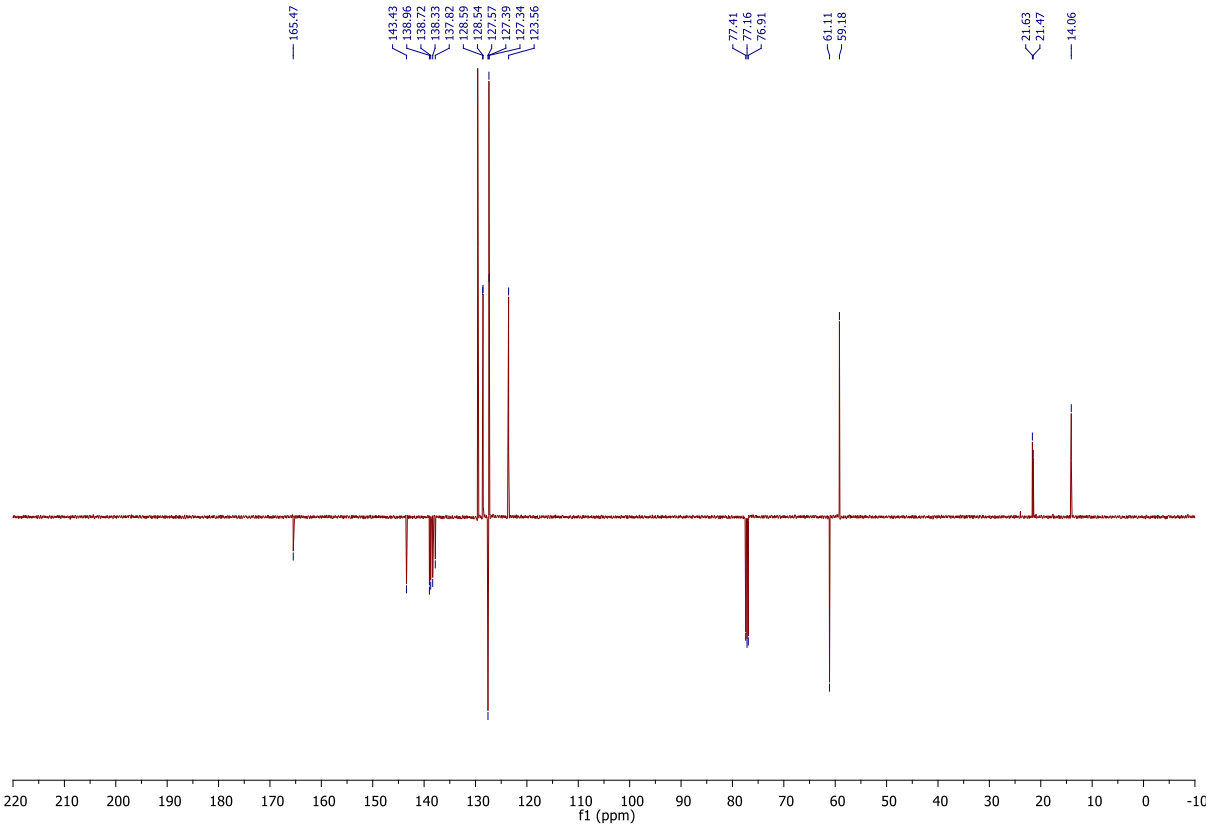
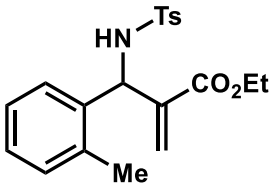


Figure S94. ^{13}C {^{1}H} NMR of **14**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(*o*-tolyl)methyl)acrylate (15)



Prepared according to general procedure B from 4-methyl-*N*-(2-methylbenzylidene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time and 40 mol % catalyst; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (44 mg, 47%); R_F = 0.33 (1:4 EtOAc/PE); mp 101 – 103 ˚C; ν_{max}/cm^{-1} (film): 3284, 2971, 1715, 1329, 1268, 1159, 1095, 1064, 815; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.68 – 7.63 (m, 2H), 7.24 – 7.20 (m, 2H), 7.14 – 7.09 (m, 1H), 7.09 – 7.03 (m, 3H), 6.30 (t, *J* = 0.9, 1H), 5.85 (dd, *J* = 1.5, 0.8, 1H), 5.60 (dt, *J* = 7.3, 0.9, 1H), 5.14 – 5.08 (m, 1H), 4.12 – 3.98 (m, 2H), 2.40 (s, 3H), 2.16 (s, 3H), 1.15 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.7, 143.5, 139.7, 137.6, 136.9, 136.2, 130.9, 129.6, 128.1, 127.4, 126.7, 126.6, 126.4, 61.1, 54.7, 21.6, 19.2, 14.1; HRMS (ES^+) calculated for $[C_{20}H_{23}NO_4SNa]^+$ $(M+Na)^+$: m/z 396.1246 found 396.1245 (+0.3 ppm).

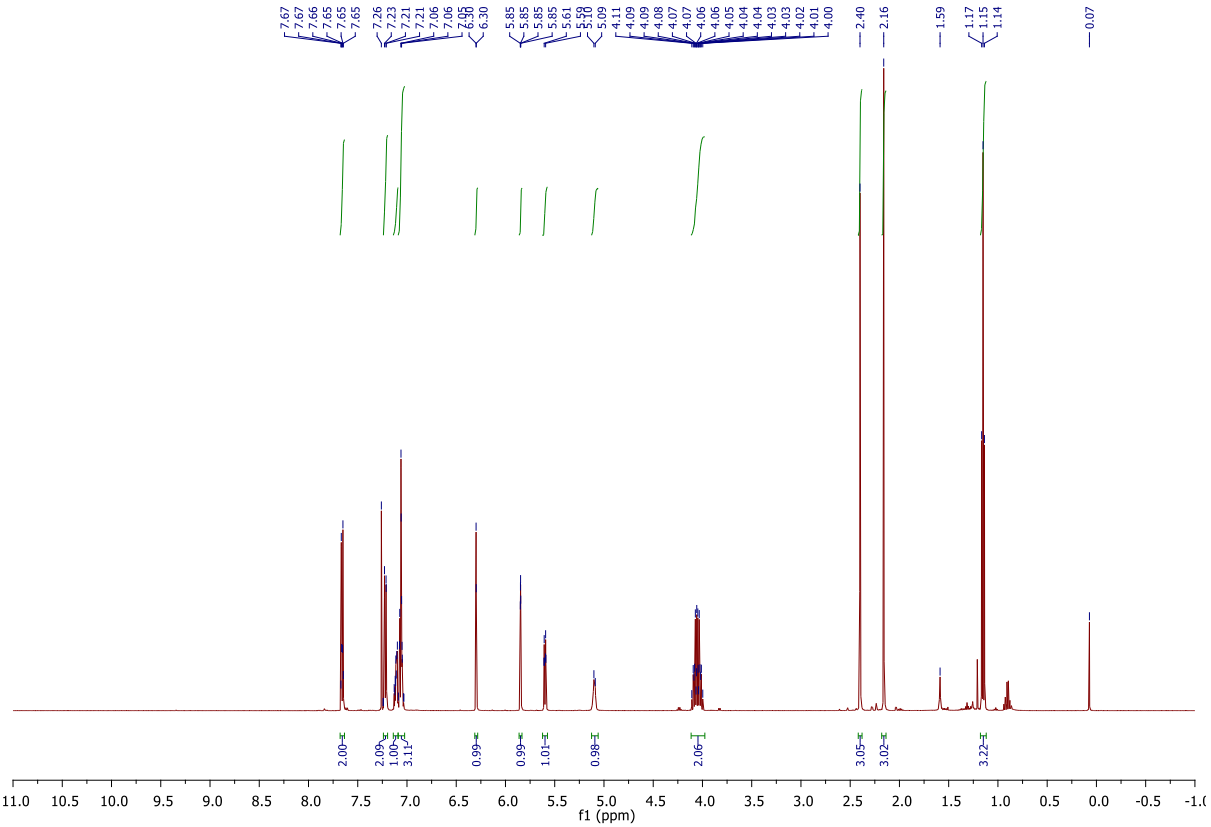


Figure S95. ^{1}H NMR of **15**.

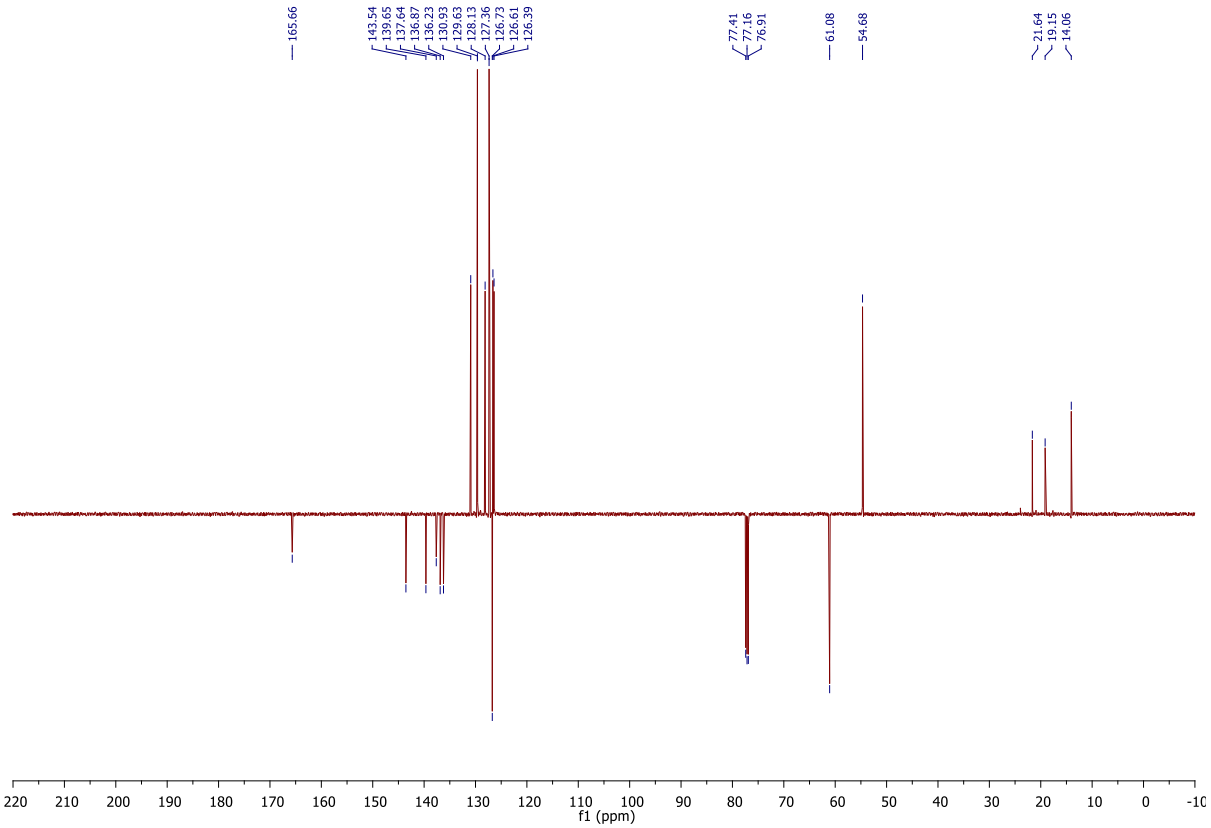
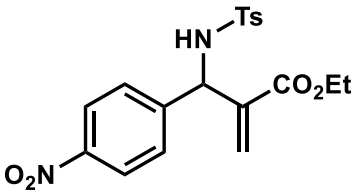


Figure S96. ^{13}C {^{1}H} NMR of **15**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(4-nitrophenyl)methyl)acrylate (16)



Prepared according to general procedure B from 4-methyl-*N*-(4-nitrobenzylidene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol, with a 3 h reaction time; purified by FCC (1.5:8.5 to 1:4 EtOAc/PE) to give the title compound as a viscous, colourless oil (48 mg, 47%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.24 (1.5:8.5 EtOAc/PE); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.12 – 8.07 (m, 2H), 7.69 – 7.64 (m, 2H), 7.43 – 7.38 (m, 2H), 7.26 – 7.23 (m, 2H), 6.23 (d, *J* = 0.5, 1H), 5.92 (d, *J* = 9.5, 1H), 5.79 (s, 1H), 5.36 (d, *J* = 9.1, 1H), 4.13 – 4.01 (m, 2H), 2.41 (s, 3H), 1.17 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.0, 147.4, 146.2, 143.9, 137.8, 137.6, 129.7, 129.0, 127.5, 127.2, 123.8, 61.6, 59.0, 21.6, 14.0.

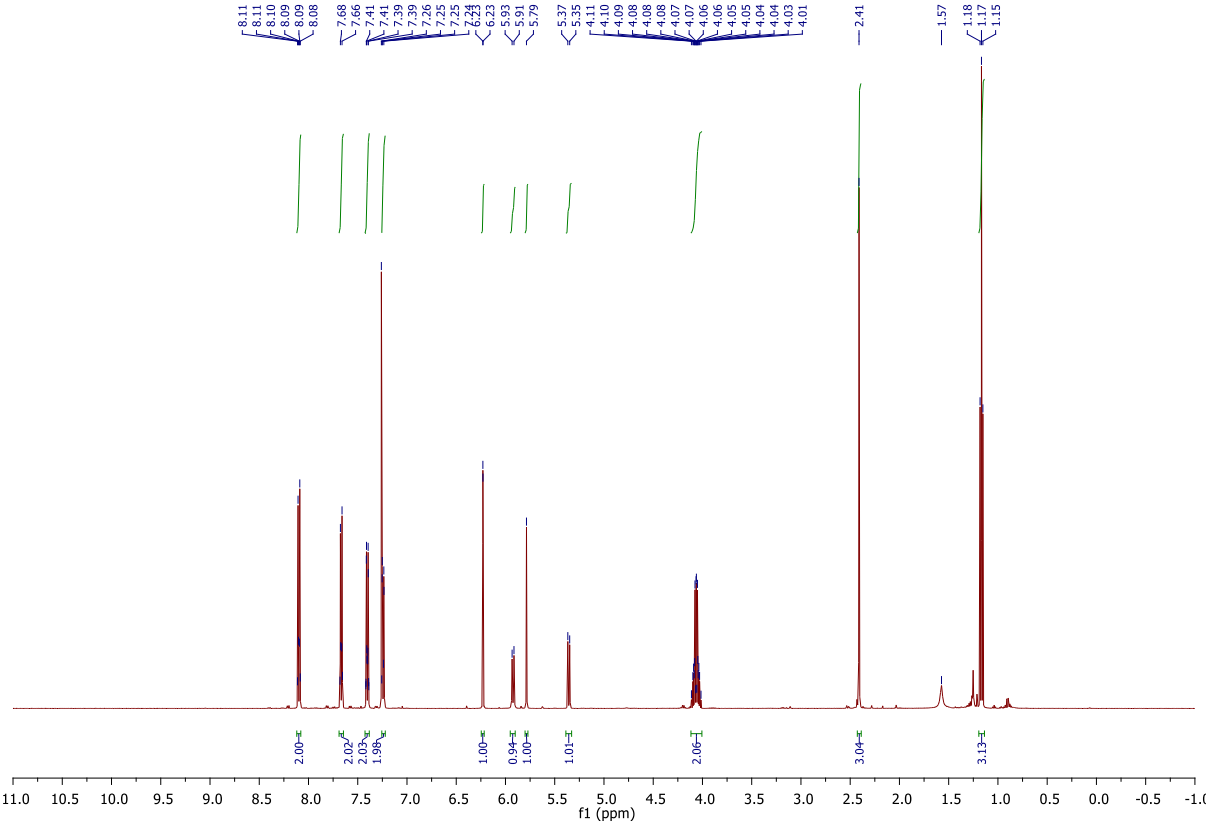


Figure S97. ^{1}H NMR of **16**.

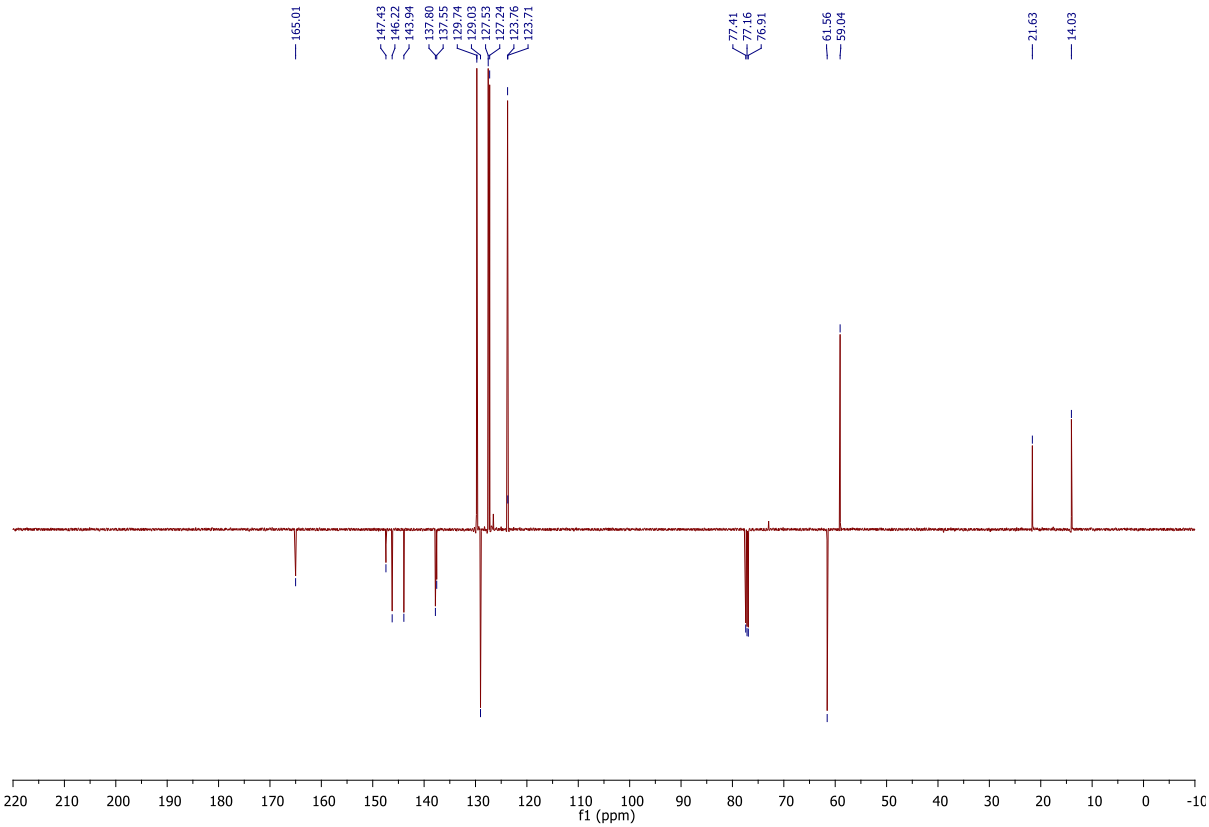
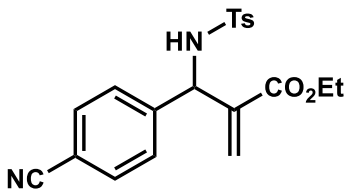


Figure S98. ^{13}C {^{1}H} NMR of **16**.

Ethyl 2-((4-cyanophenyl)((4-methylphenyl)sulfonamido)methyl)acrylate (17)



Prepared according to general procedure B from *N*-(4-cyanobenzylidene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a colourless, viscous oil (42 mg, 44%); R_F = 0.18 (1:4 EtOAc/PE); ν_{max}/cm^{-1} (film): 3278, 2240, 1711, 1430, 1329, 1161, 1071, 815; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.68 – 7.64 (m, 2H), 7.56 – 7.52 (m, 2H), 7.37 – 7.32 (m, 2H), 7.26 – 7.22 (m, 2H), 6.21 (d, *J* = 0.6, 1H), 5.88 (d, *J* = 9.5, 1H), 5.76 (t, *J* = 0.6, 1H), 5.31 (d, *J* = 9.5, 1H), 4.12 – 4.01 (m, 2H), 2.42 (s, 3H), 1.16 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.1, 144.3, 143.9, 137.8, 137.6, 132.4, 129.7, 129.0, 127.3, 127.3, 118.6, 111.7, 61.5, 59.2, 21.7, 14.0; HRMS (ES^+) calculated for $[C_{20}H_{20}N_2O_4SNa]^+$ $(M+Na)^+$: m/z 407.1049 found 407.1041 (+2.0 ppm).

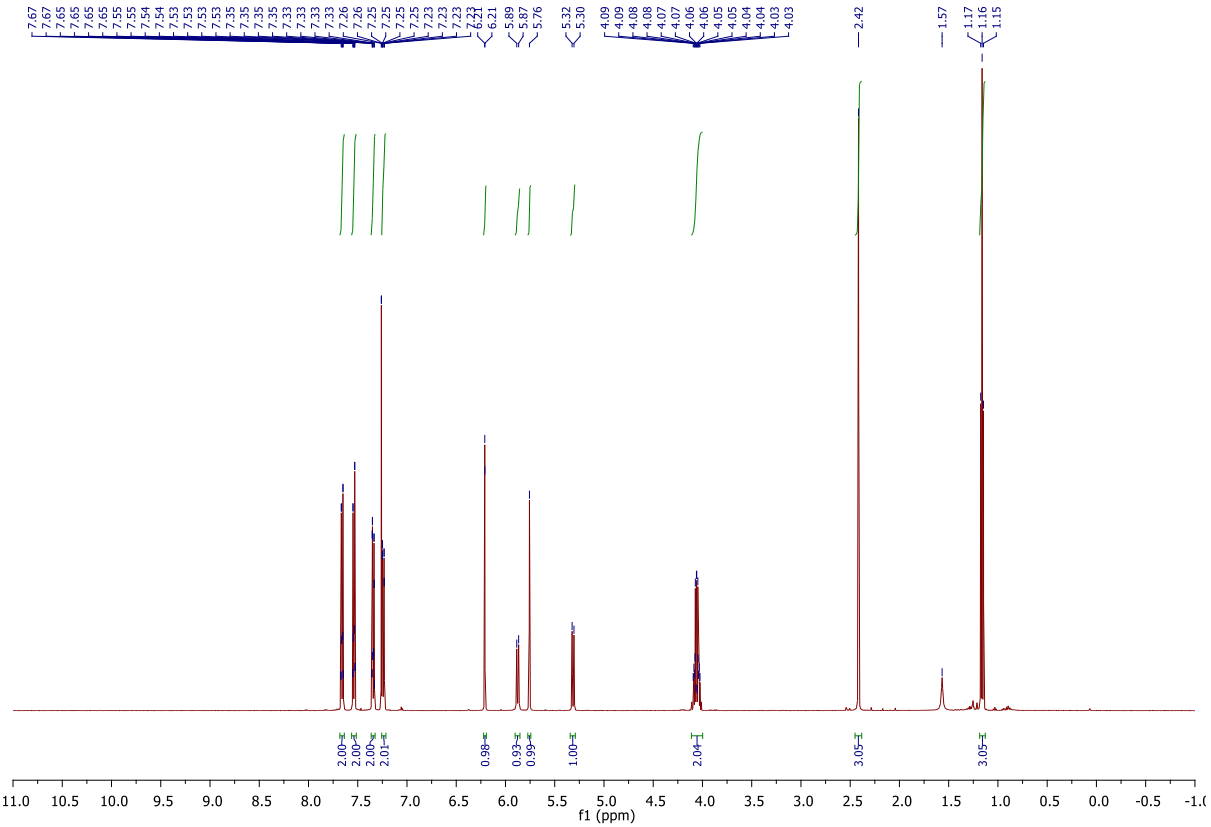


Figure S99. ^{1}H NMR of **17**.

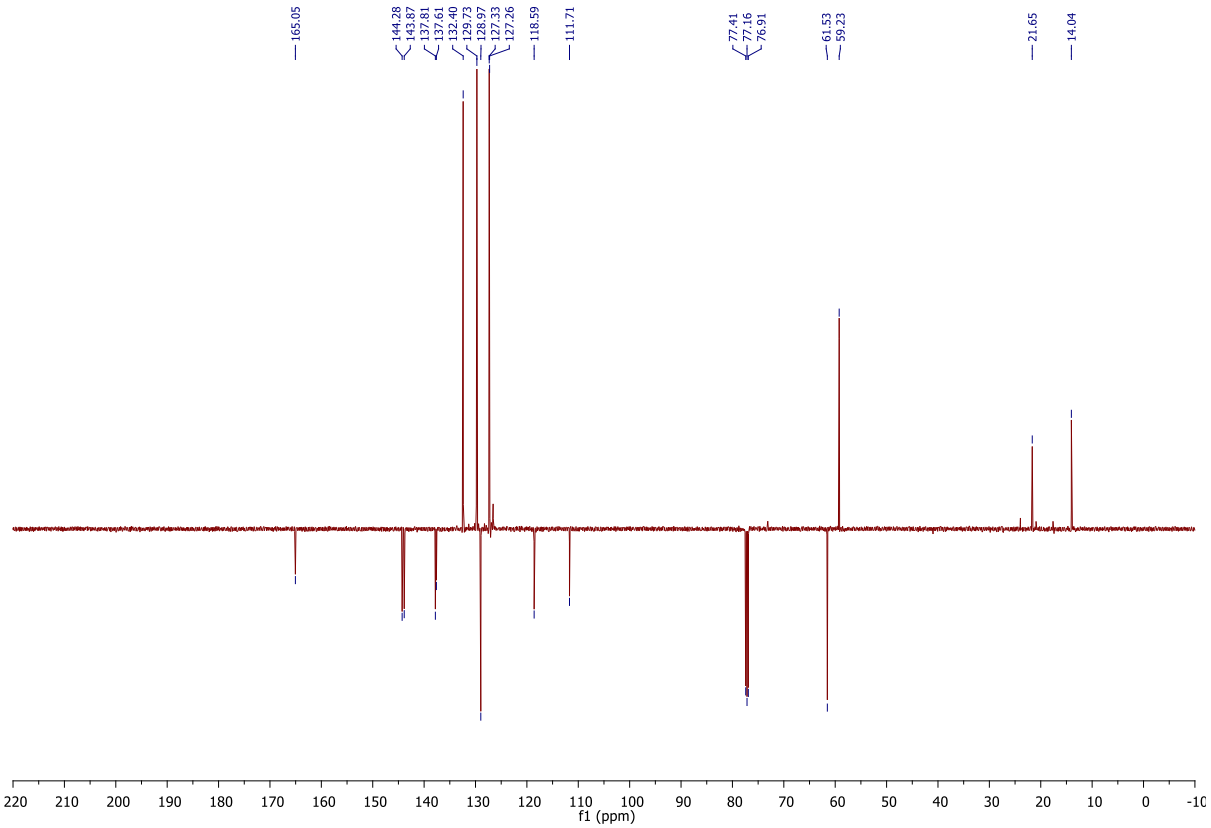
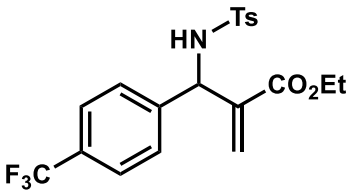


Figure S100. ^{13}C {^{1}H} NMR of **17**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(4-(trifluoromethyl)phenyl)methyl)acrylate (18)



Prepared according to general procedure B from 4-methyl-*N*-(4-(trifluoromethyl)benzylidene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:9 to 1:4 EtOAc/PE) to give the title compound as a white solid (61 mg, 57%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.35 (1:4 EtOAc/PE); mp 79 – 81 ˚C (lit. 74 – 76 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.64 (d, *J* = 8.1, 2H), 7.48 (d, *J* = 8.2, 2H), 7.31 (d, *J* = 8.1, 2H), 7.22 (d, *J* = 8.0, 2H), 6.22 (s, 1H), 5.82 (d, *J* = 9.3, 1H), 5.79 (s, 1H), 5.34 (d, *J* = 9.2, 1H), 4.10 – 4.04 (m, 2H), 2.40 (s, 3H), 1.17 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.2, 143.7, 142.8, 138.2, 137.7, 130.1 (q, *J* = 32.8), 129.7, 128.6, 127.3, 127.0, 125.6 (q, *J* = 3.8), 124.1 (q, *J* = 268.4), 61.5, 59.3, 21.6, 14.1; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -62.6.

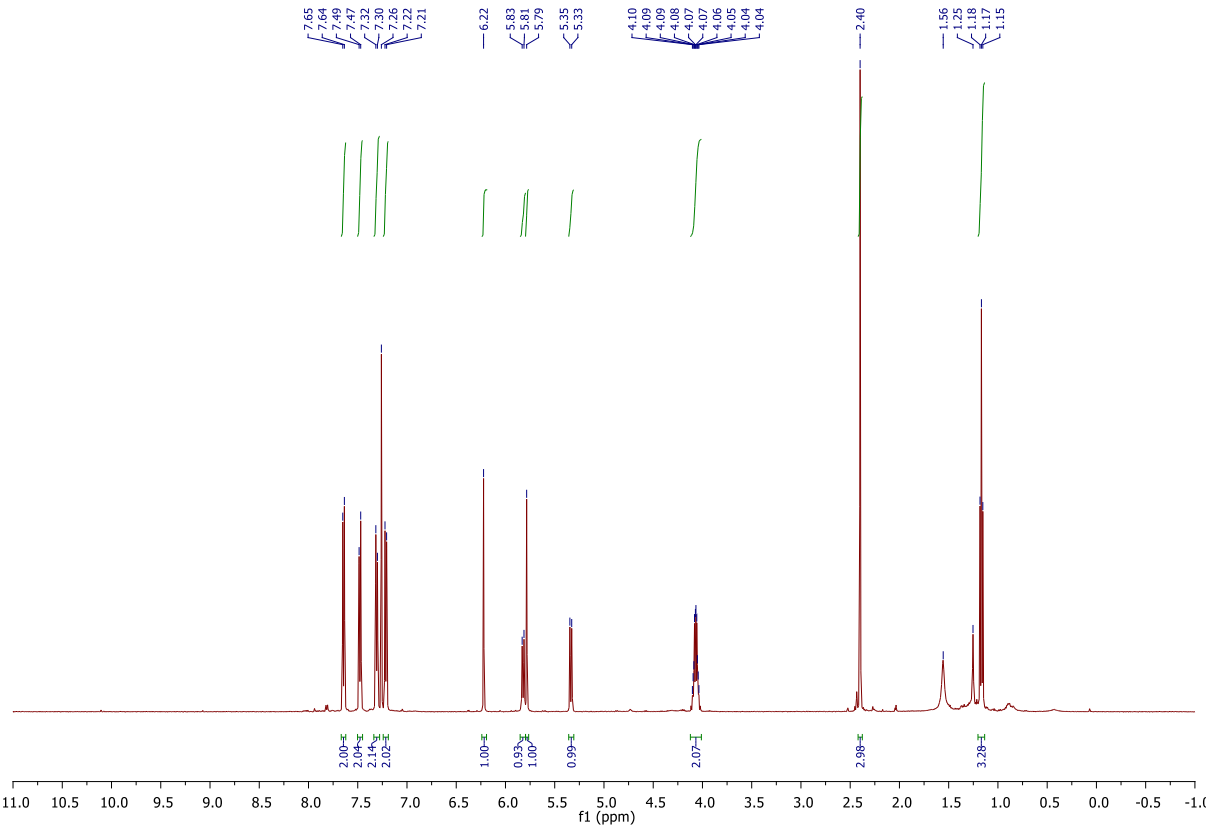


Figure S101. ^{1}H NMR of **18**.

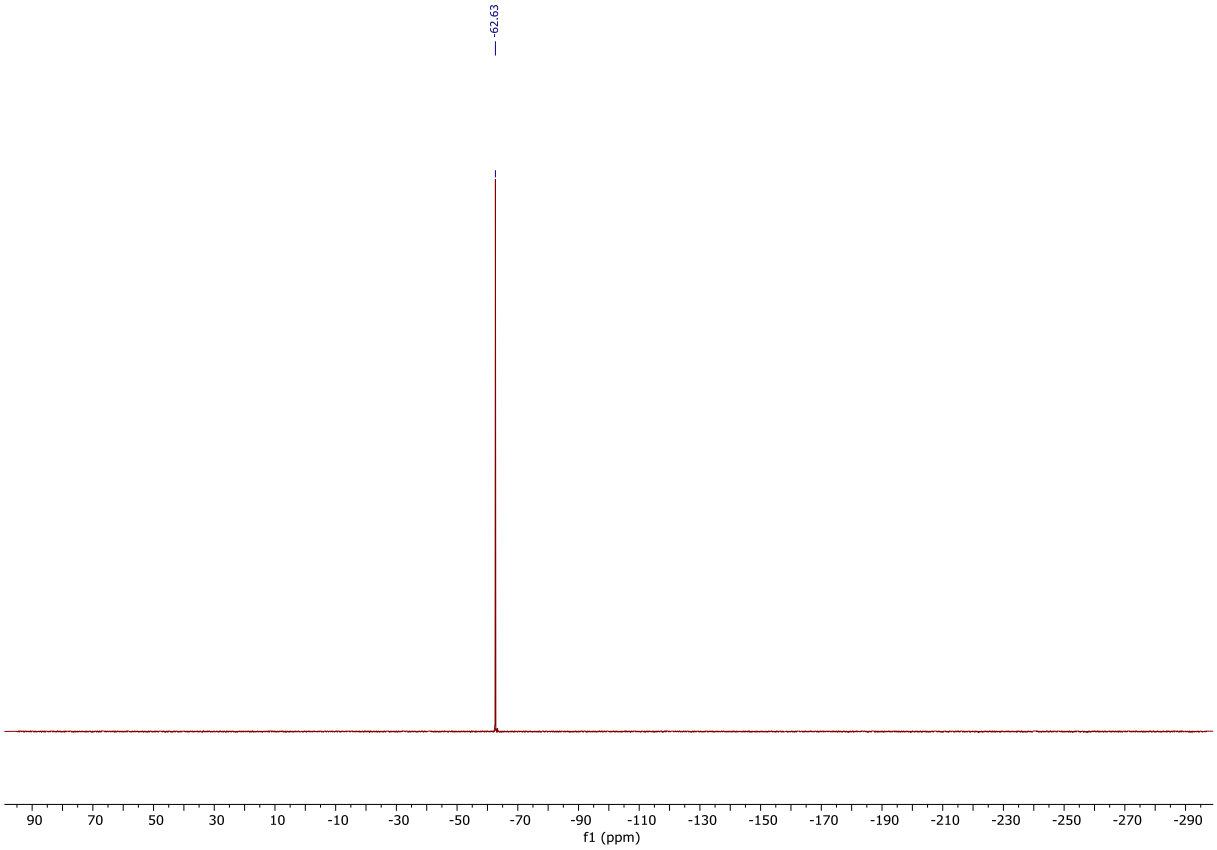


Figure S102. ^{19}F {^{1}H} NMR of **18**.

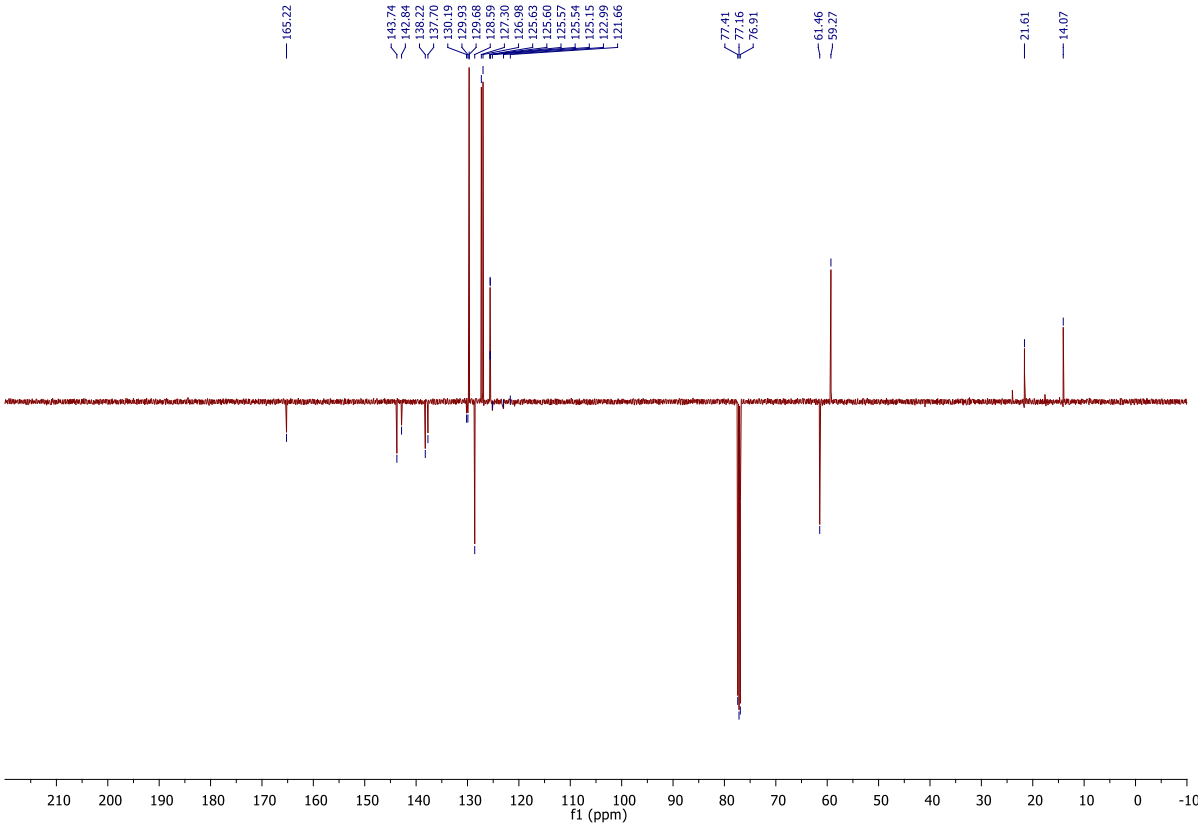
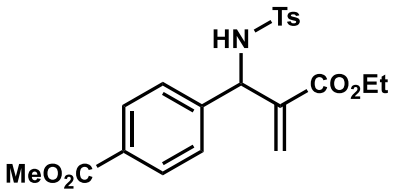


Figure S103. ^{13}C {^{1}H} NMR of **18**.

Methyl 4-(2-(ethoxycarbonyl)-1-((4-methylphenyl)sulfonamido)allyl)benzoate (19)



Prepared according to general procedure B from methyl-4-((tosylimino)methyl)benzoate (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time and 40 mol % catalyst; purified by FCC (3:7 EtOAc/PE) to give the title compound as a white solid (53 mg, 51%); R_F = 0.13 (1:4 EtOAc/PE); mp 102 – 104 ˚C; ν_{max}/cm^{-1} (film): 3286, 1719, 1436, 1329, 1282, 1161, 1112, 565; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.92 – 7.88 (m, 2H), 7.69 – 7.64 (m, 2H), 7.28 – 7.21 (m, 4H), 6.21 (s, 1H), 5.81 – 5.74 (m, 2H), 5.33 (d, *J* = 9.0, 1H), 4.05 (qd, *J* = 7.1, 3.1, 2H), 3.89 (s, 3H), 2.40 (s, 3H), 1.14 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 166.8, 165.2, 143.9, 143.7, 138.3, 137.7, 129.9, 129.7, 129.6, 128.5, 127.3, 126.6, 61.3, 59.3, 52.3, 21.6, 14.1; HRMS (ES$^+$) calculated for $[C_{21}H_{23}NO_6SNa]^+$ $(M+Na)^+$: m/z 440.1150 found 440.1144 (+1.4 ppm).

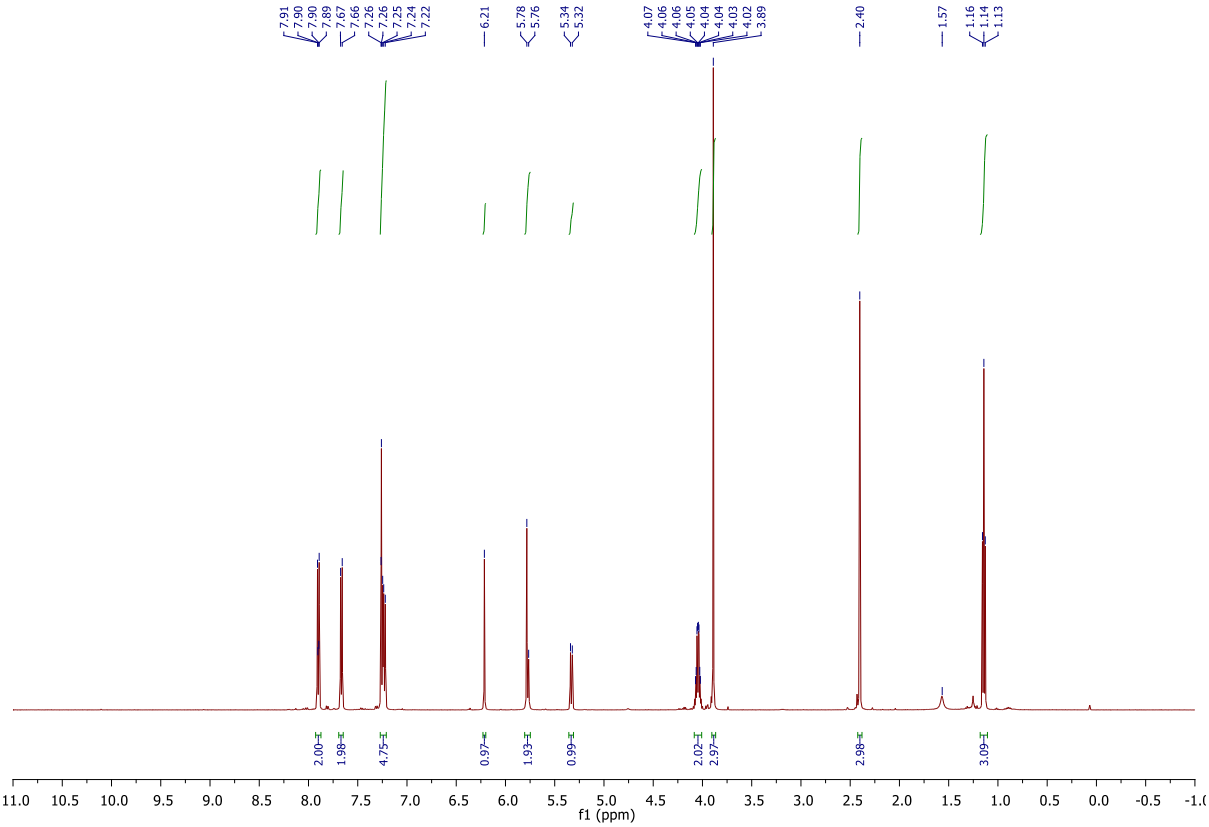


Figure S104. ^{1}H NMR of **19**.

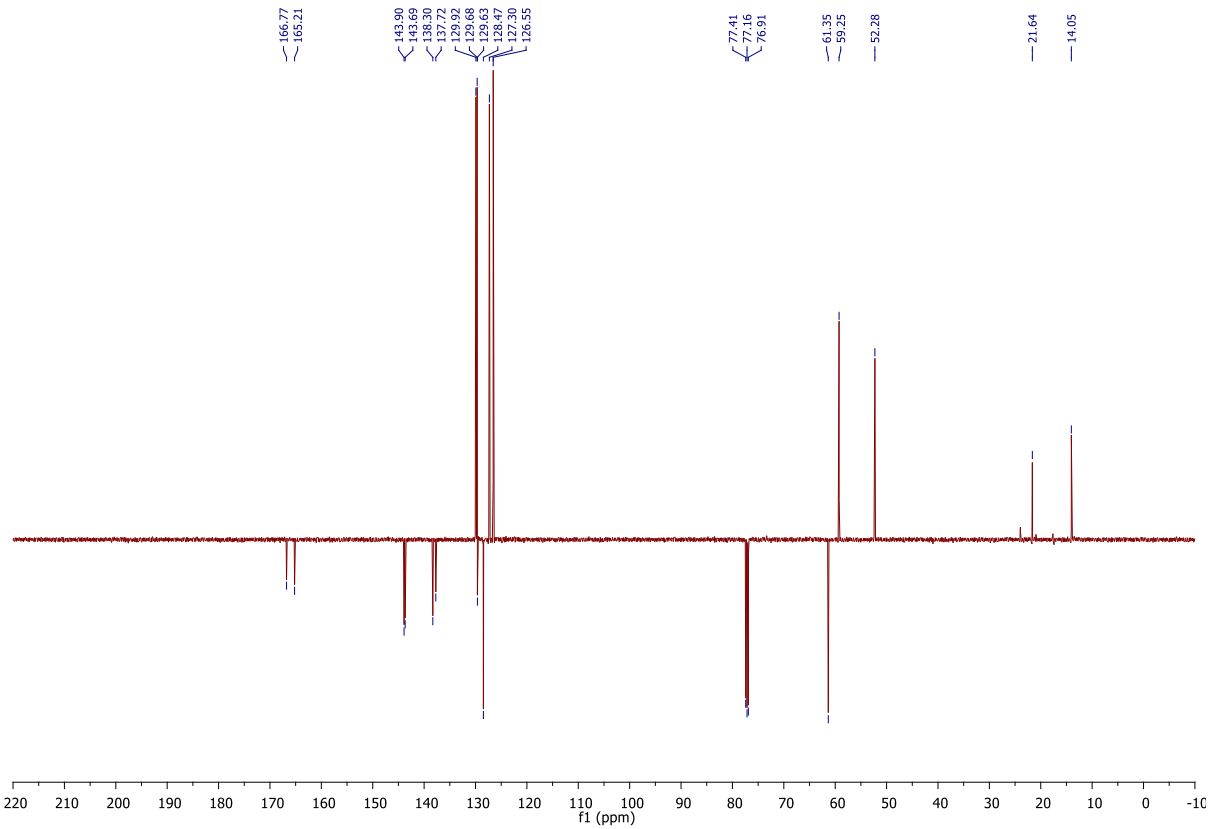
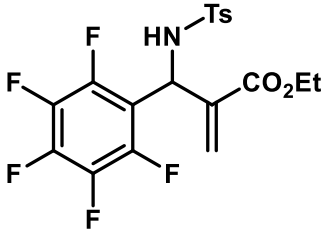


Figure S105. ^{13}C {^{1}H} NMR of **19**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(perfluorophenyl)methyl)acrylate (20)



Prepared according to general procedure B from 4-methyl-*N*-((perfluorophenyl)methylene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (35 mg, 31%); R_F = 0.29 (1:4 EtOAc/PE); mp 164 – 166 ˚C; ν_{max}/cm^{-1} (film): 3266, 1716, 1518, 1506, 1342, 1330, 1275, 1166, 1119, 1078, 994, 817, 764, 749, 714, 669, 554, 536; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.67 – 7.61 (m, 2H), 7.23 – 7.18 (m, 2H), 6.43 (s, 1H), 5.97 (s, 1H), 5.72 (d, *J* = 10.3, 1H), 5.55 (d, *J* = 10.4, 1H), 4.19 – 4.07 (m, 2H), 2.38 (s, 3H), 1.23 (t, *J* = 7.1, 3H);); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ_C: 164.6, 144.2, 136.9, 136.8, 129.6, 127.5, 127.2, 61.7, 48.8, 21.5, 14.0 (unidentifiable signals between 135 – 150 ppm, due to broadening from multiple ^{13}C-^{19}F couplings); ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ_F: -141.2, -154.1, -161.5; HRMS (ES^+) calculated for $[C_{19}H_{16}NO_4F_5SNa]^+$ $(M+Na)^+$: m/z 472.0618 found 472.0618 (0.0 ppm).

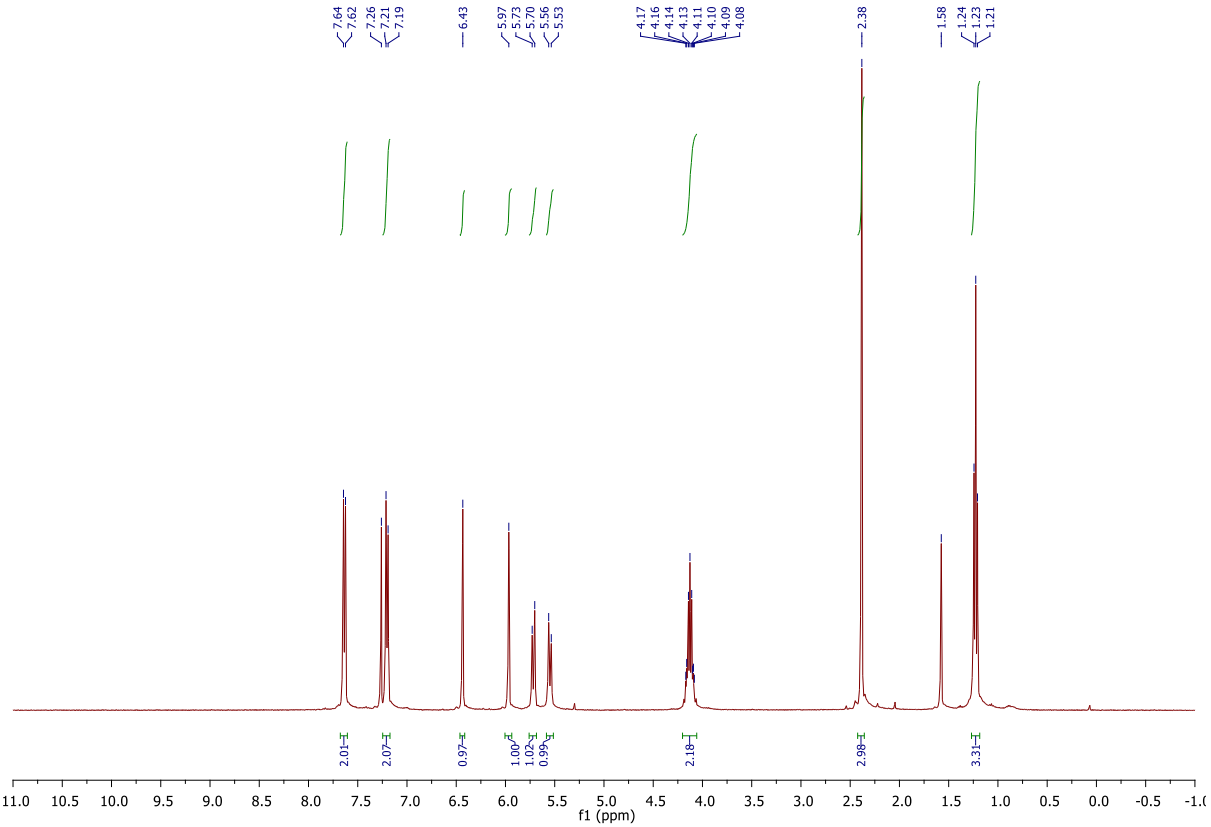


Figure S106. ^{1}H NMR of **20**.

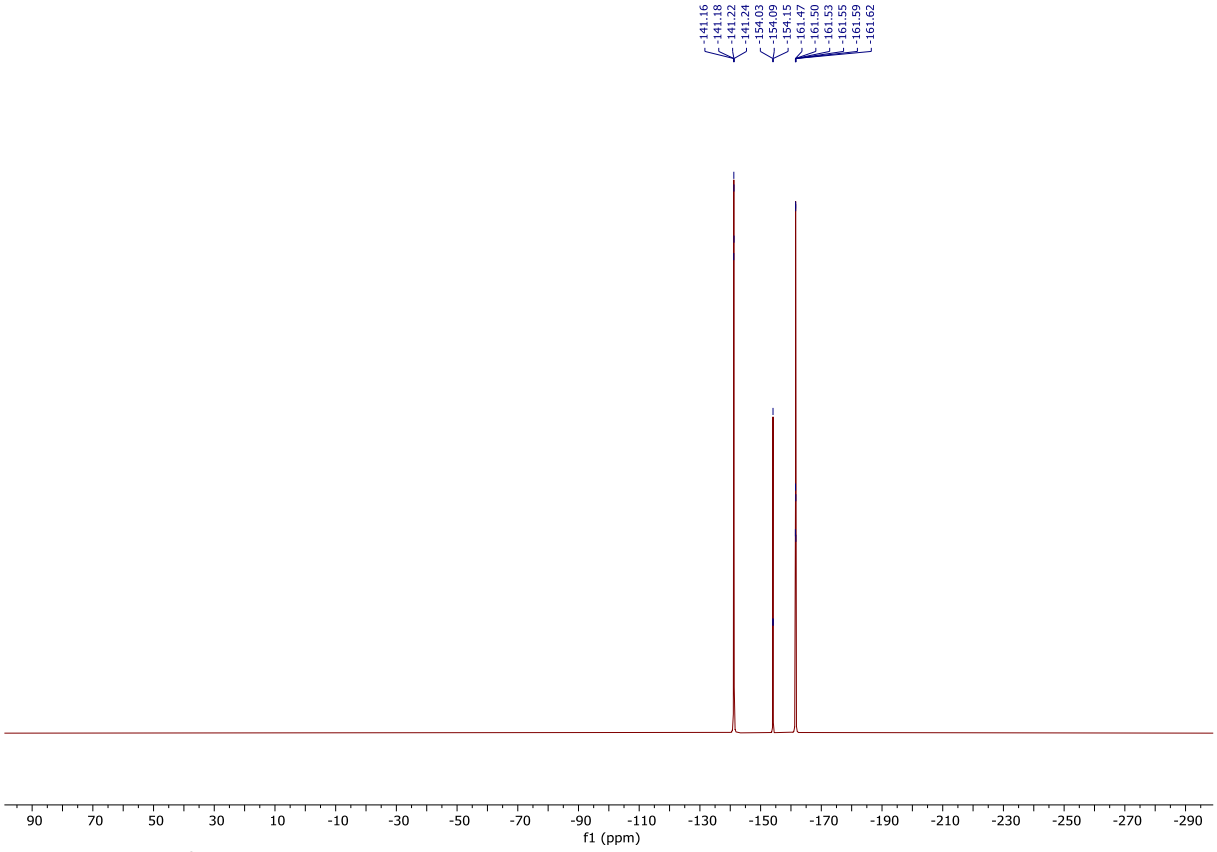


Figure S107. ^{19}F $\{^{1}H\}$ NMR of **20**.

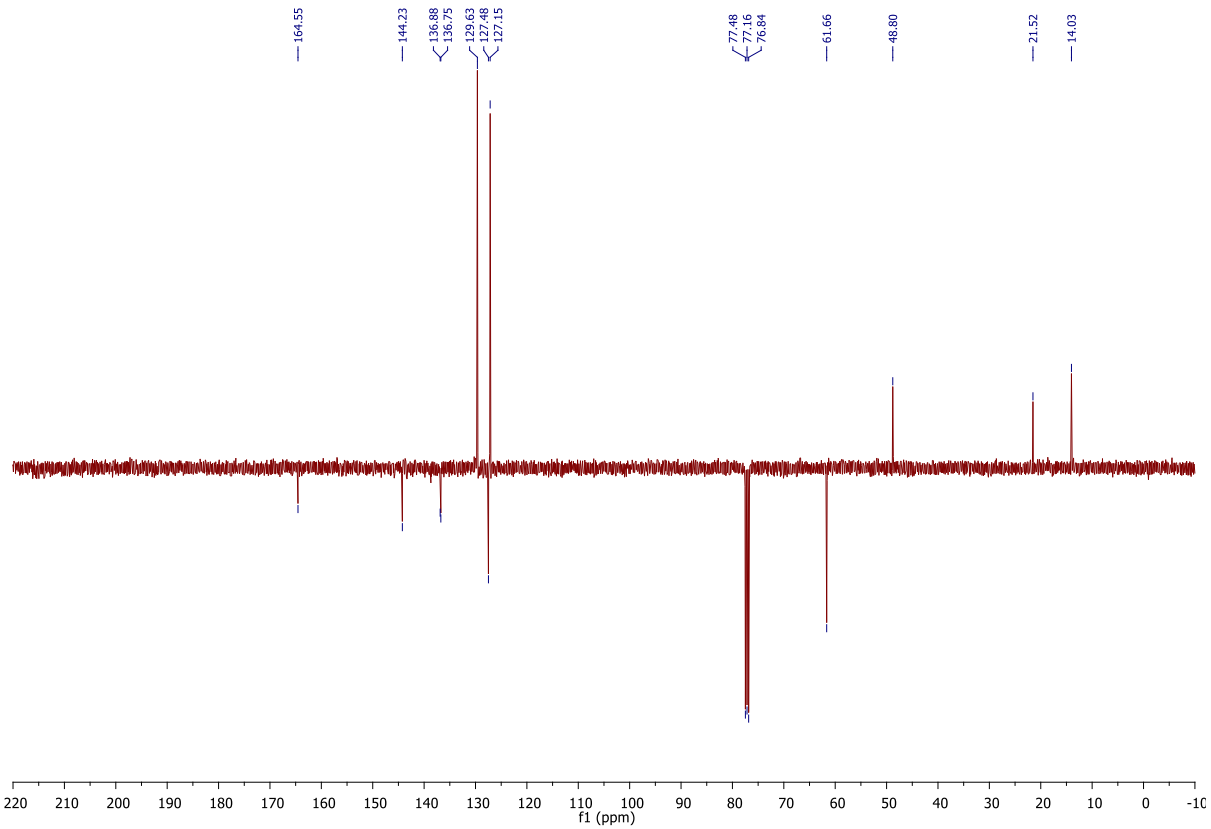
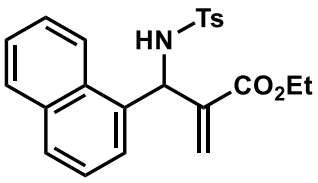


Figure S108. ^{13}C {^{1}H} NMR of **20**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(naphthalen-1-yl)methyl)acrylate (21)



Prepared according to general procedure B from methyl-*N*-(naphthalen-1-ylmethylene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (25 mg, 25%); R_F = 0.20 (1:4 EtOAc/PE); mp 167 – 169 ˚C; ν_{max}/cm^{-1} (film): 3284, 2984, 1715, 1325, 1275, 1158, 1093, 1069, 765, 671; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.85 – 7.78 (m, 2H), 7.74 (d, *J* = 7.8, 1H), 7.66 – 7.63 (m, 2H), 7.48 – 7.43 (m, 1H), 7.39 – 7.35 (m, 1H), 7.33 – 7.27 (m, 2H), 7.19 – 7.16 (m, 2H), 6.39 (s, 1H), 6.20 (d, *J* = 7.4, 1H), 5.94 (s, 1H), 5.12 (d, *J* = 7.4, 1H), 4.07 – 3.96 (m, 2H), 2.40 (s, 3H), 1.06 (t, *J* = 7.1, 3H);^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.7, 143.6, 139.8, 137.4, 134.6, 134.1, 130.6, 129.6, 129.1, 128.9, 127.5, 127.3, 126.7, 126.0, 125.2, 125.1, 123.1, 61.1, 54.2, 21.7, 14.0; HRMS (ES^+) calculated for $[C_{23}H_{23}NO_4SNa]^+$ $(M+Na)^+$: m/z 432.1249 found 432.1245 (+0.9 ppm).

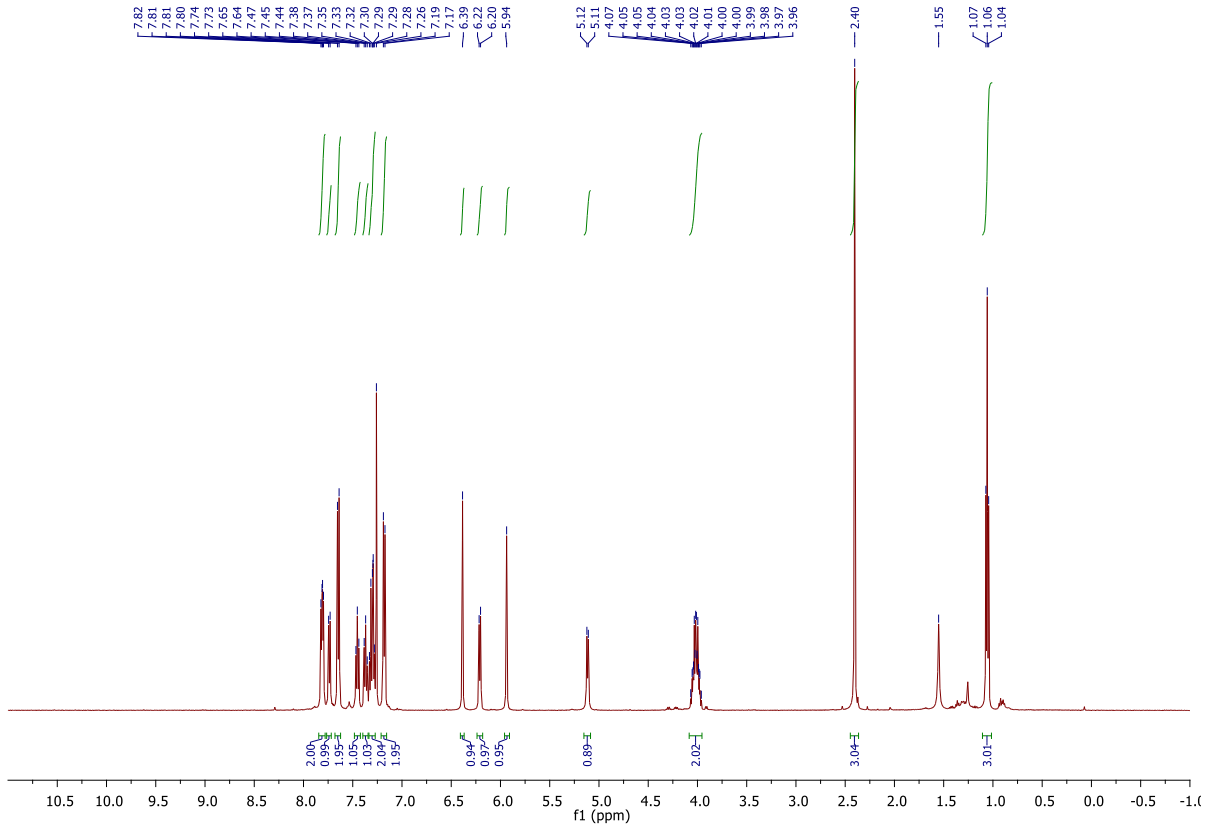


Figure S109. ^{1}H NMR of **21**.

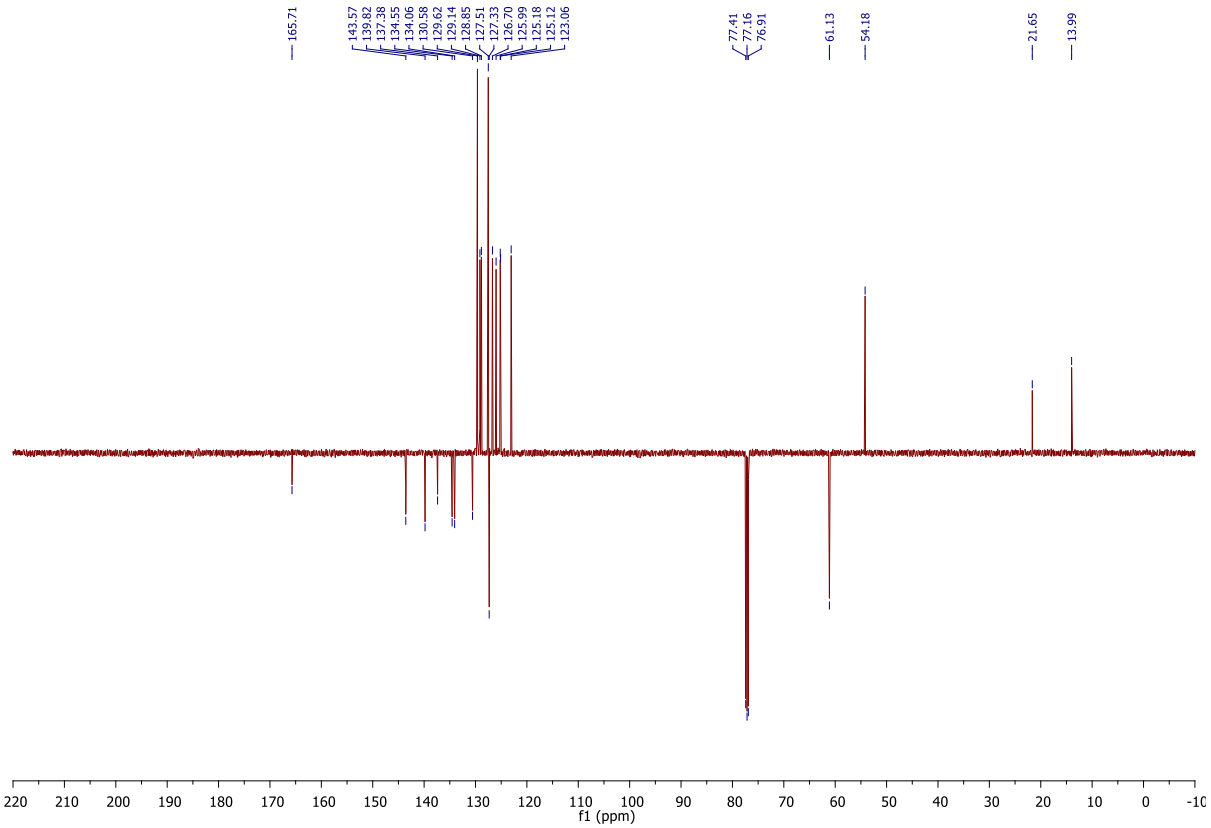
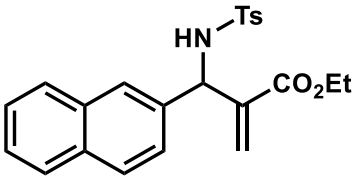


Figure S109. ^{13}C {^{1}H} NMR of **21**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(naphthalen-2-yl)methyl)acrylate (22)



Prepared according to general procedure B from 4-methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1.5:8.5 EtOAc/PE) to give the title compound as a white solid (68 mg, 66%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.35 (1.5:8.5 EtOAc/PE); mp 111 – 113 ˚C (lit. 102 – 104 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.79 – 7.74 (m, 1H), 7.72 – 7.65 (m, 4H), 7.57 – 7.54 (m, 1H), 7.47 – 7.42 (m, 2H), 7.25 (dd, *J* = 8.5, 1.9, 1H), 7.20 – 7.16 (m, 2H), 6.27 (d, *J* = 0.8, 1H), 5.88 (t, *J* = 0.9, 1H), 5.73 (d, *J* = 8.9, 1H), 5.47 (d, *J* = 8.8, 1H), 4.07 – 4.01 (m, 2H), 2.36 (s, 3H), 1.14 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.5, 143.5, 138.9, 137.8, 136.1, 133.2, 132.9, 129.6, 128.5, 128.2, 127.8, 127.7, 127.4, 126.4, 126.3, 125.7, 124.6, 61.2, 59.4, 21.6, 14.1.

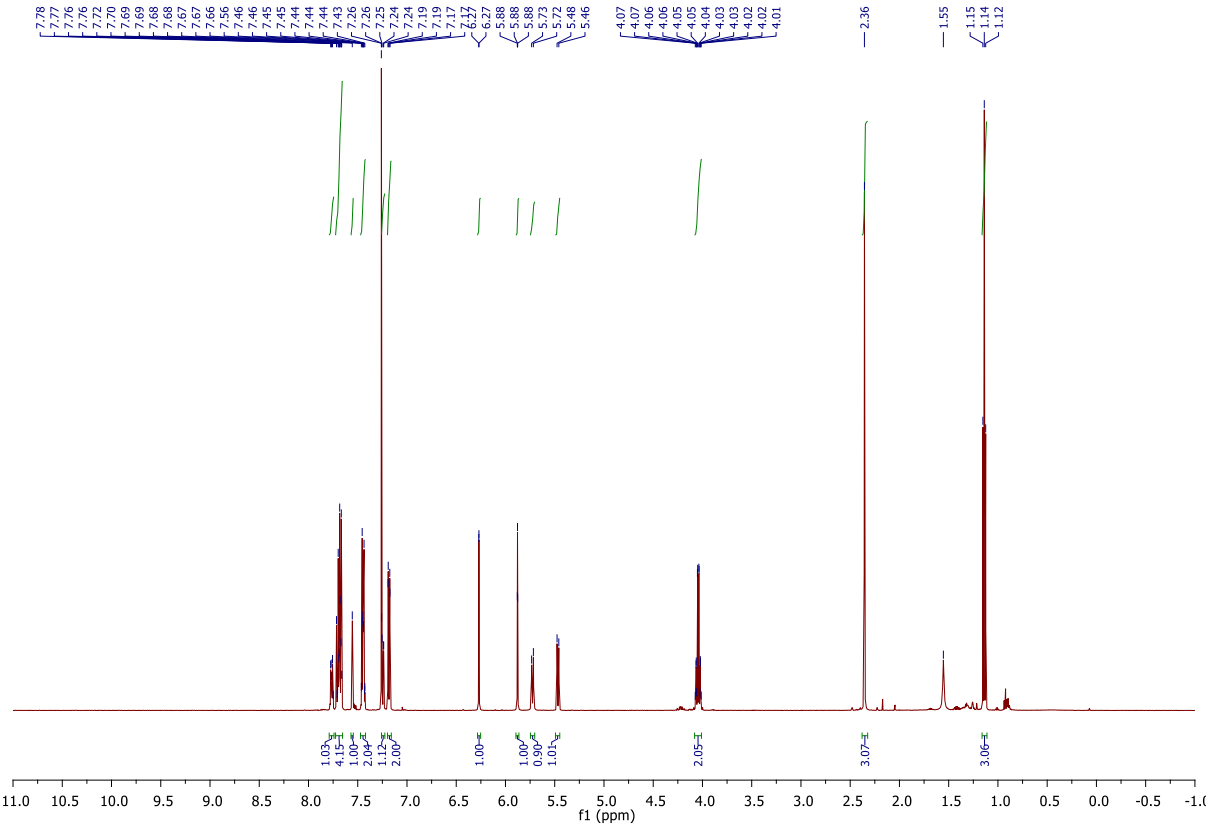


Figure S110. ^{1}H NMR of **22**.

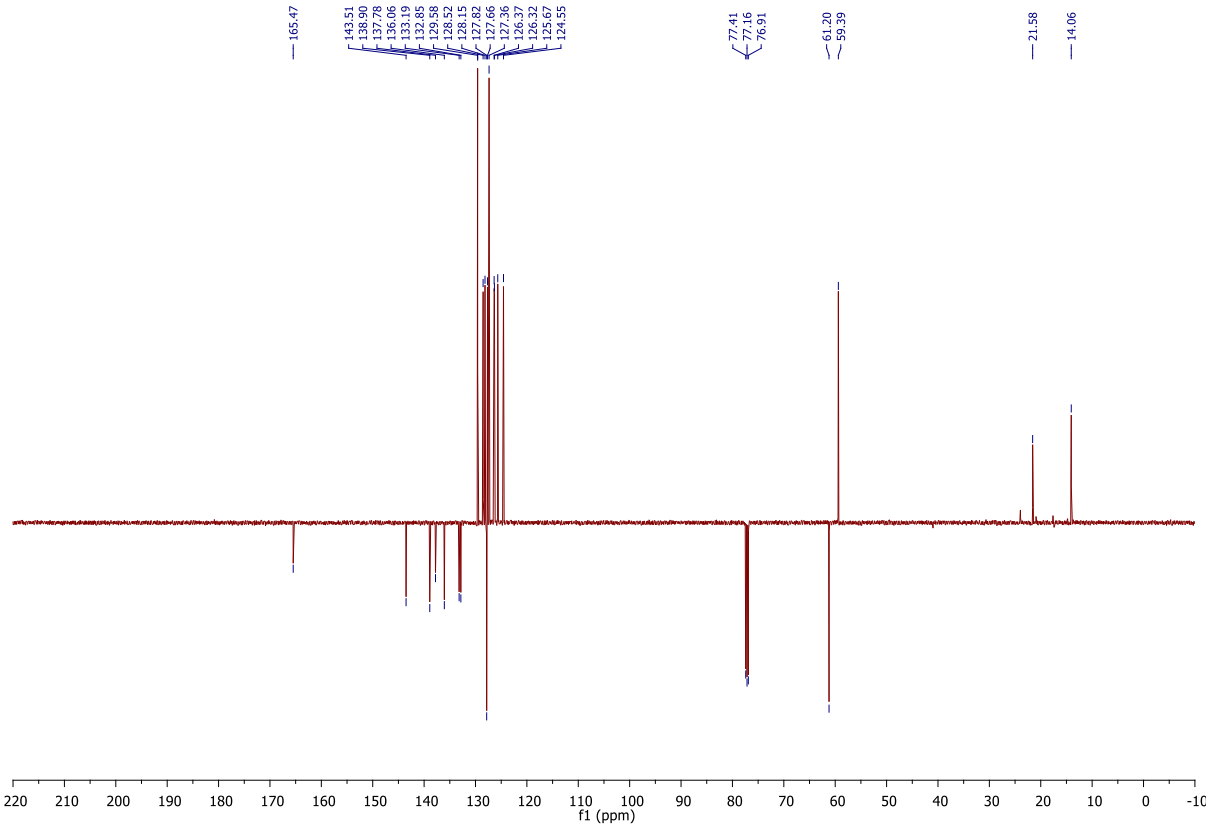
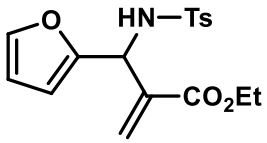


Figure S111. ^{13}C {^{1}H} NMR of **22**.

Ethyl 2-(furan-2-yl((4-methylphenyl)sulfonamido)methyl)acrylate (23)



Prepared according to general procedure B from *N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a white solid (52 mg, 60%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.18 (1:4 EtOAc/PE); mp 103 – 105 ˚C (lit. 88 – 90 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.71 – 7.65 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 (dd, *J* = 1.8, 0.9, 1H), 6.22 (s, 1H), 6.21 (dd, *J* = 3.3, 1.8, 1H), 6.05 (dt, *J* = 3.3, 0.9, 1H), 5.81 (t, *J* = 0.8, 1H), 5.70 (d, *J* = 9.3, 1H), 5.38 (dt, *J* = 9.3, 1.0, 1H), 4.12 (q, *J* = 7.1, 2H), 2.40 (s, 3H), 1.21 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.2, 151.4, 143.5, 142.3, 137.7, 137.2, 129.6, 128.2, 127.3, 110.7, 107.5, 61.3, 53.8, 21.7, 14.1.

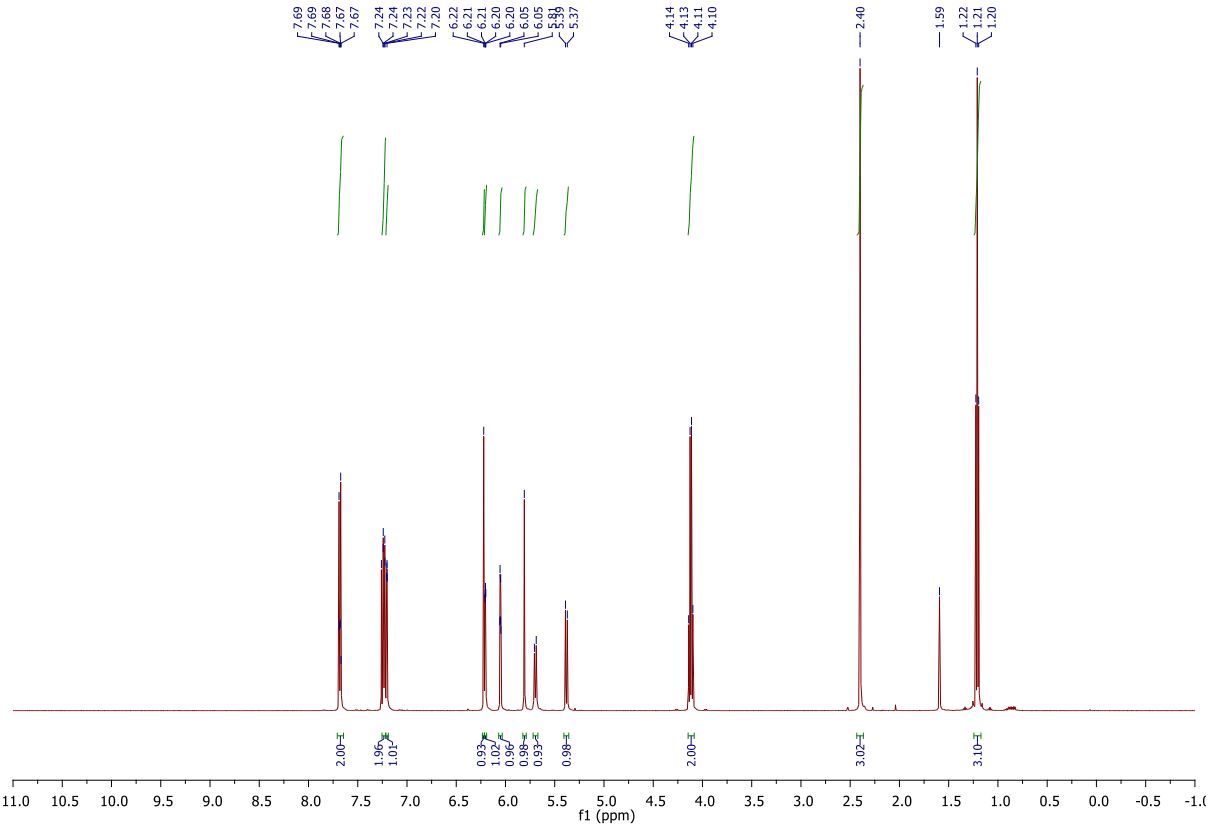


Figure S112. ^{1}H NMR of **23**.

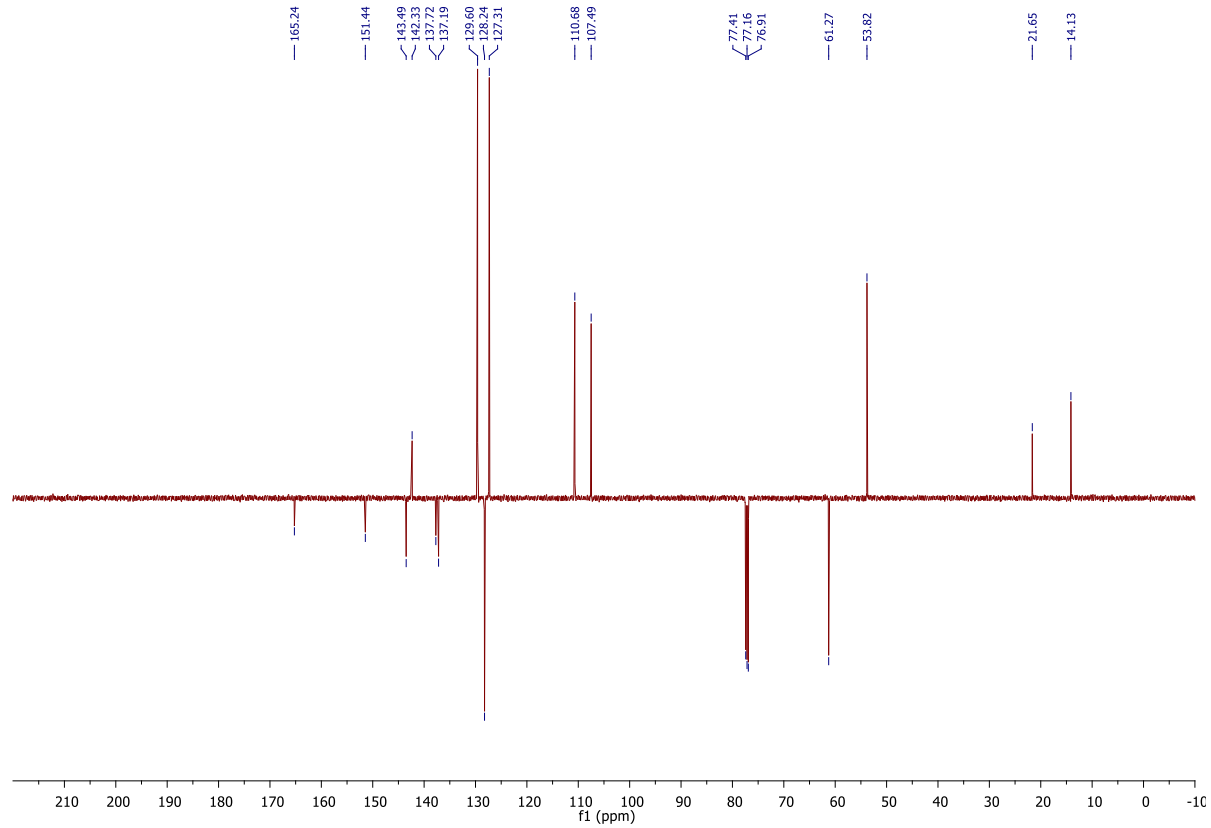
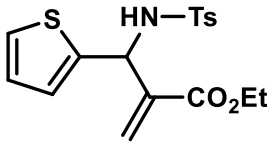


Figure S113. ^{13}C {^{1}H} NMR of **23**.

Ethyl 2-(((4-methylphenyl)sulfonamido)(thiophen-2-yl)methyl)acrylate (24)



Prepared according to general procedure B from 4-methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time and 40 mol % catalyst; purified by FCC (0.5:9.5 Acetone/PhMe) to give the title compound as a white solid (32 mg, 35%), with physical properties and spectroscopic data in accordance with the literature;[17] R_F = 0.24 (1:4 EtOAc/PE); mp 117 – 119 ˚C (lit. 104 – 106 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.72 – 7.69 (m, 2H), 7.26 – 7.24 (m, 2H), 7.15 (dd, *J* = 5.1, 1.3, 1H), 6.85 (dd, *J* = 5.1, 3.6, 1H), 6.75 (dt, *J* = 3.6, 1.2, 1H), 6.20 (s, 1H), 5.86 (d, *J* = 9.4, 1H), 5.81 (s, 1H), 5.47 (d, *J* = 9.3, 1H), 4.10 (q, *J* = 7.1, 2H), 2.41 (s, 3H), 1.19 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.3, 143.6, 143.3, 138.4, 137.7, 129.7, 128.0, 127.4, 127.2, 125.6, 125.1, 61.3, 56.1, 21.7, 14.1.

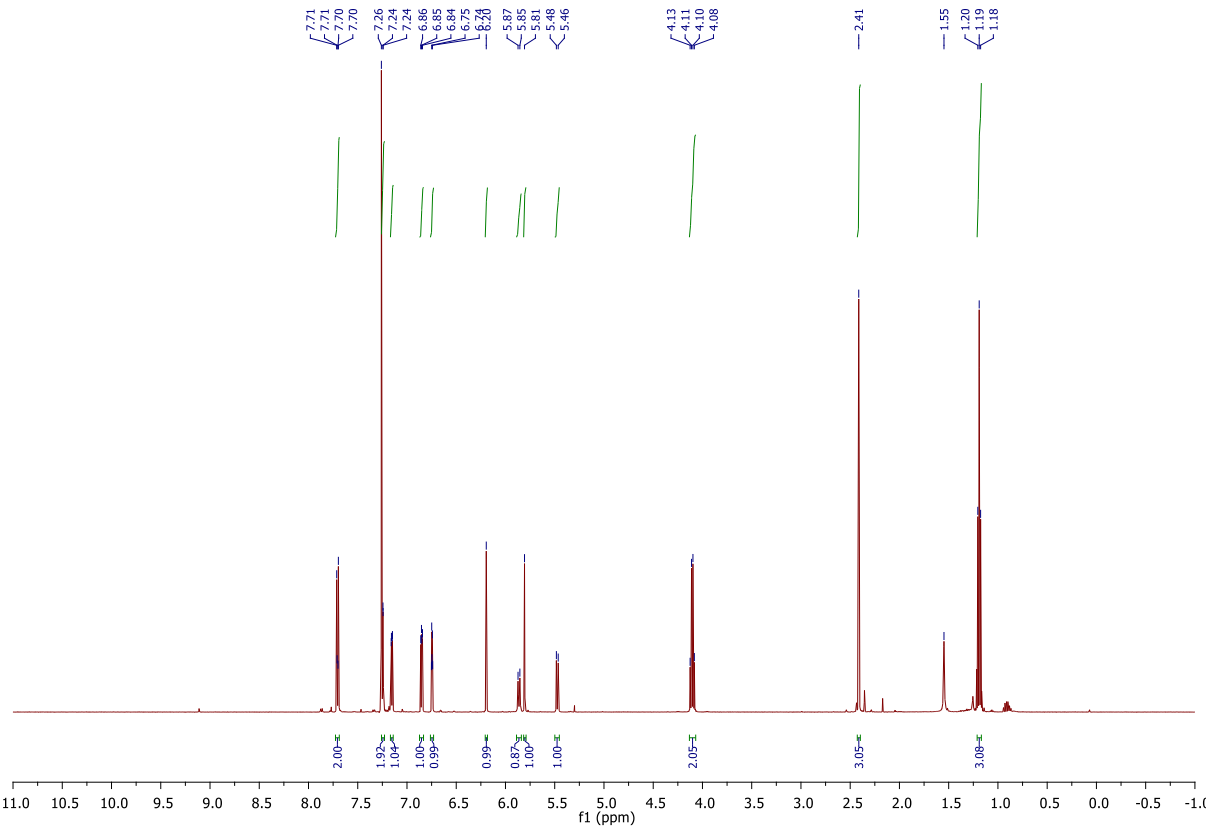


Figure S114. ^{1}H NMR of **24**.

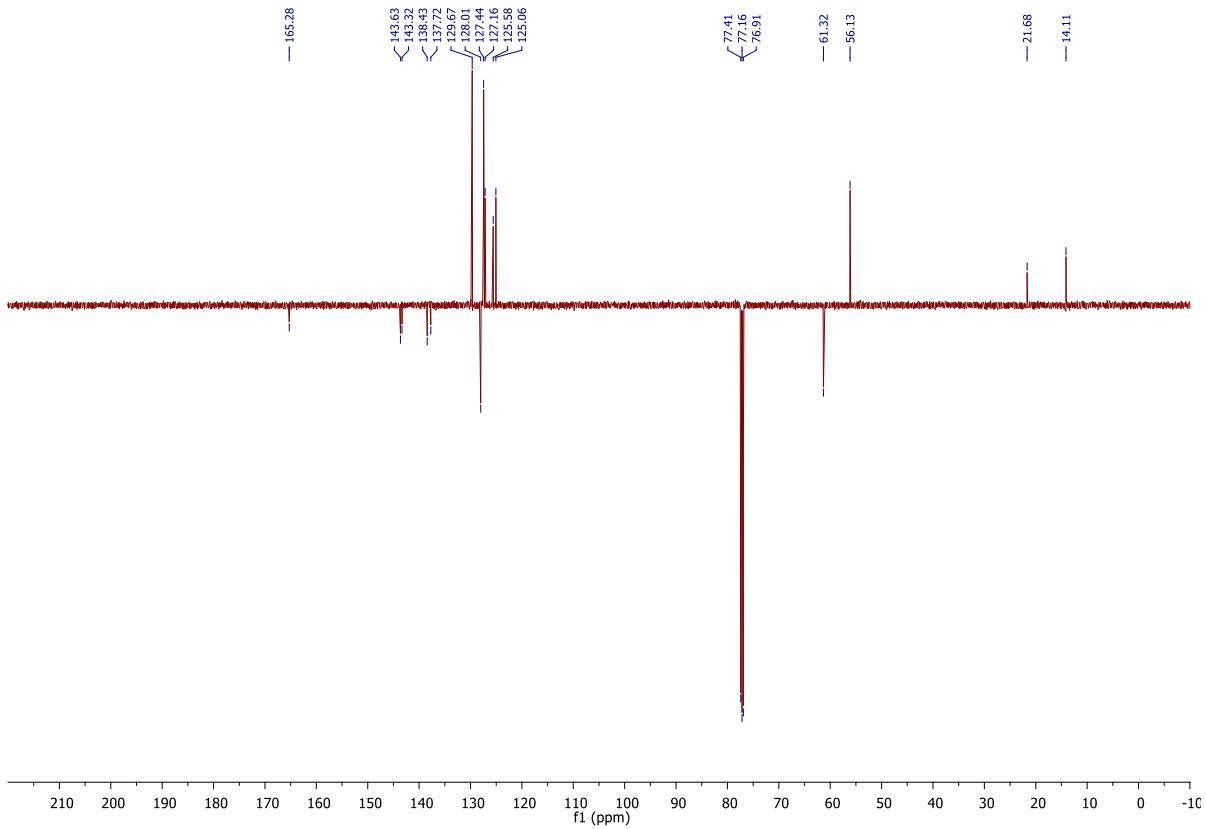
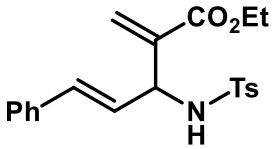


Figure S115. ^{13}C {^{1}H} NMR of **24**.

Ethyl (*E*)-2-methylene-3-((4-methylphenyl)sulfonamido)-5-phenylpent-4-enoate (25)



Prepared according to general procedure B from 4-methyl-N-((1*E*,2*E*)-3-phenylallylidene)benzenesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 EtOAc/PE) to give the title compound as a pale yellow solid (39 mg, 40%),; R_F = 0.21 (1:4 EtOAc/PE); mp 126 – 128 ˚C; v_{max}/cm^{-1} (film): 3292, 1709, 1323, 1286, 1161, 1138, 1091, 1041, 974, 956, 816, 755, 697, 669, 563, 543; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.73 – 7.69 (m, 2H), 7.28 – 7.16 (m, 7H), 6.33 (dd, *J* = 16.0, 1.4, 1H), 6.12 (d, *J* = 0.7, 1H), 6.03 (dd, *J* = 15.9, 6.5, 1H), 5.72 (t, *J* = 0.8, 1H), 5.62 (d, *J* = 9.5, 1H), 4.83 (dddd, *J* = 9.5, 6.6, 1.5, 0.7, 1H), 4.19 – 4.10 (m, 2H), 2.34 (s, 3H), 1.25 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 165.5, 143.5, 138.6, 138.2, 136.1, 132.3, 129.6, 128.6, 128.1, 127.6, 127.4, 127.1, 126.7, 61.3, 58.7, 21.6, 14.2; HRMS (ES$^+$) calculated for $[C_{21}H_{23}NO_4SNa]^+$ (M+Na)$^+$: m/z 408.1245 found 408.1245 (0.0 ppm).

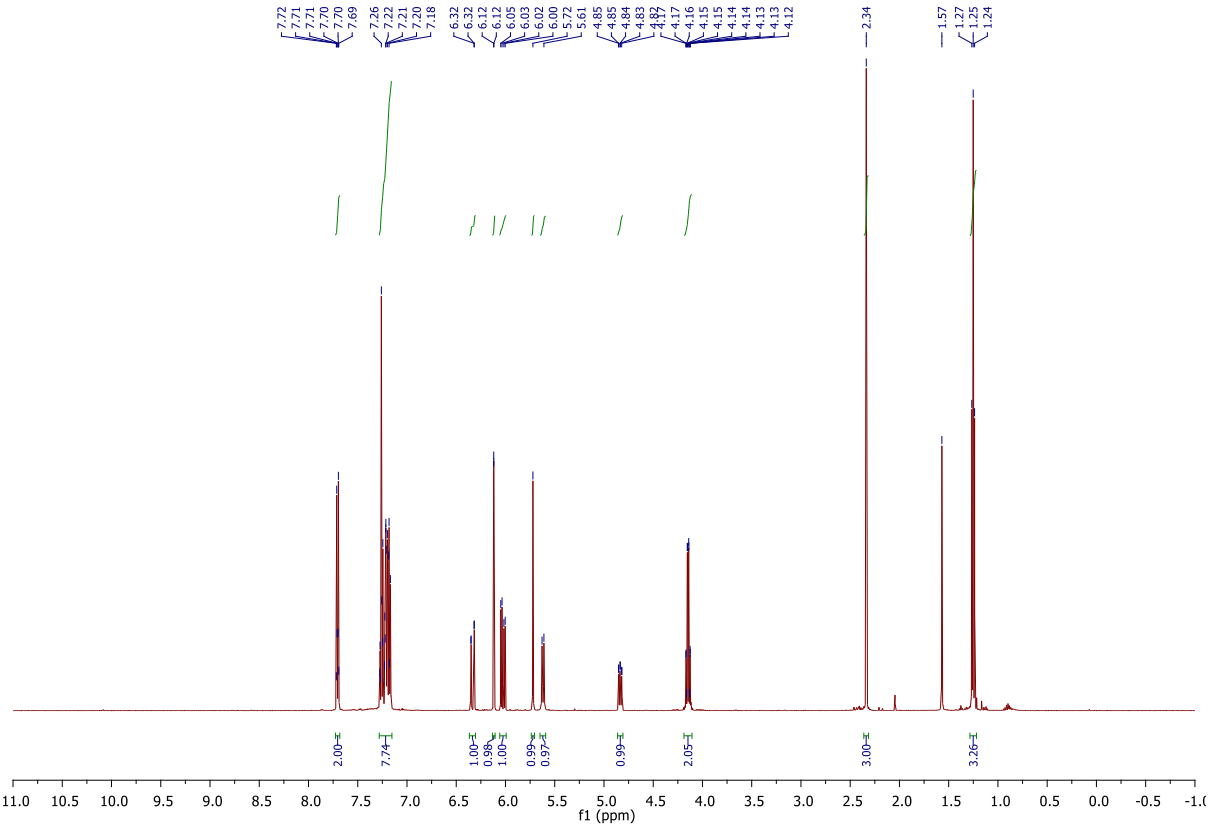


Figure S116. ^{1}H NMR of **25**.

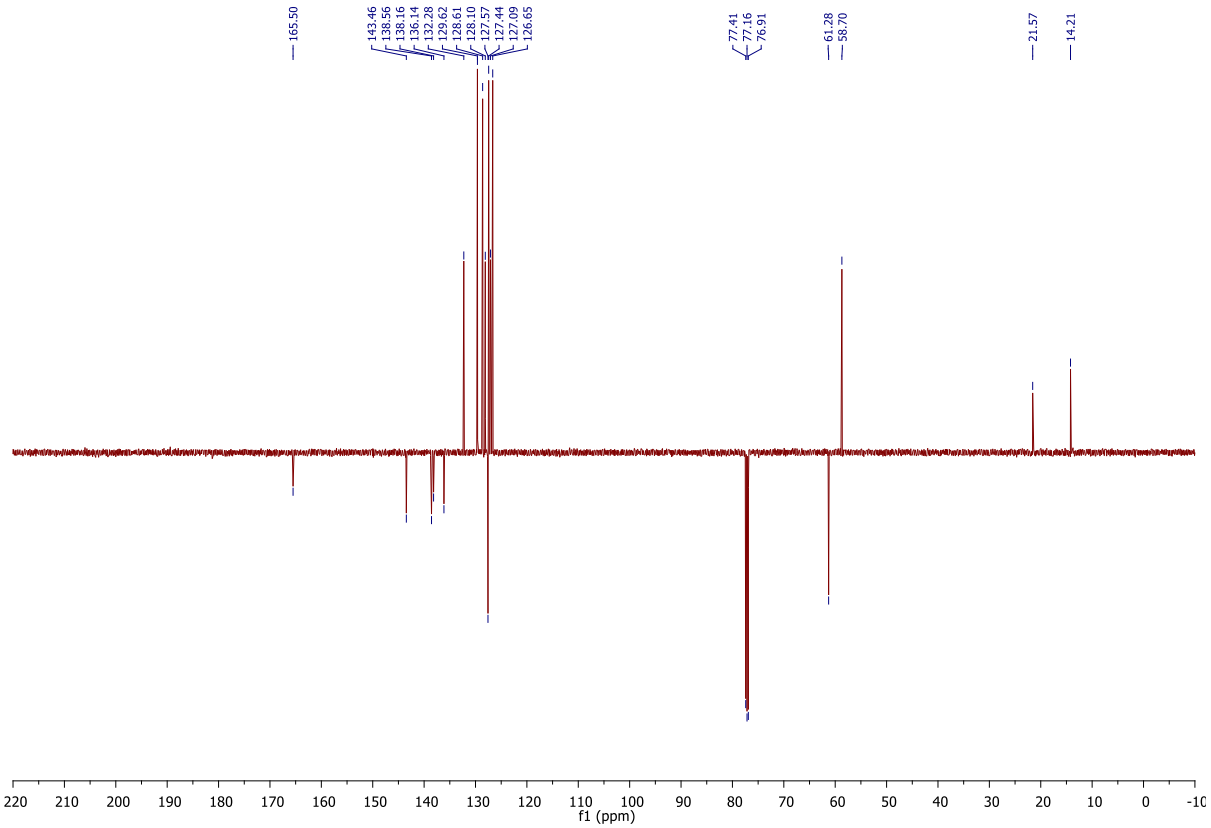
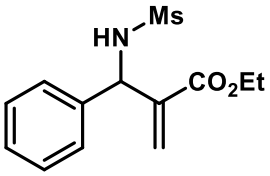


Figure S117. ^{13}C {^{1}H} NMR of **25**.

Ethyl 2-(methylsulfonamido(phenyl)methyl)acrylate (26)



Prepared according to general procedure B from *N*-benzylidenemethanesulfonamide (0.25 mmol) and ethyl acrylate (0.28 mmol), with a 3 h reaction time; purified by FCC (3:7 EtOAc/PE) to give the title compound as a viscous, colourless oil (45 mg, 64%); R_F = 0.31 (3:7 EtOAc/PE); ν_{max}/cm^{-1} (film): 3281, 1710, 1315, 1159, 1083, 1062, 978, 757, 698, 517; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 7.38 – 7.27 (m, 5H), 6.42 (s, 1H), 5.96 (s, 1H), 5.56 (d, *J* = 9.1, 1H), 5.47 (d, *J* = 9.0, 1H), 4.21 – 4.10 (m, 2H), 2.88 (s, 3H), 1.22 (t, *J* = 7.1, 3H); ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ_C: 165.6, 139.9, 139.0, 128.9, 128.1, 127.7, 126.7, 61.4, 59.3, 42.0, 14.1; HRMS (ES^+) calculated for $[C_{13}H_{18}NO_4S]^+$ $(M+H)^+$: m/z 284.0956 found 284.0957 (-0.4 ppm).

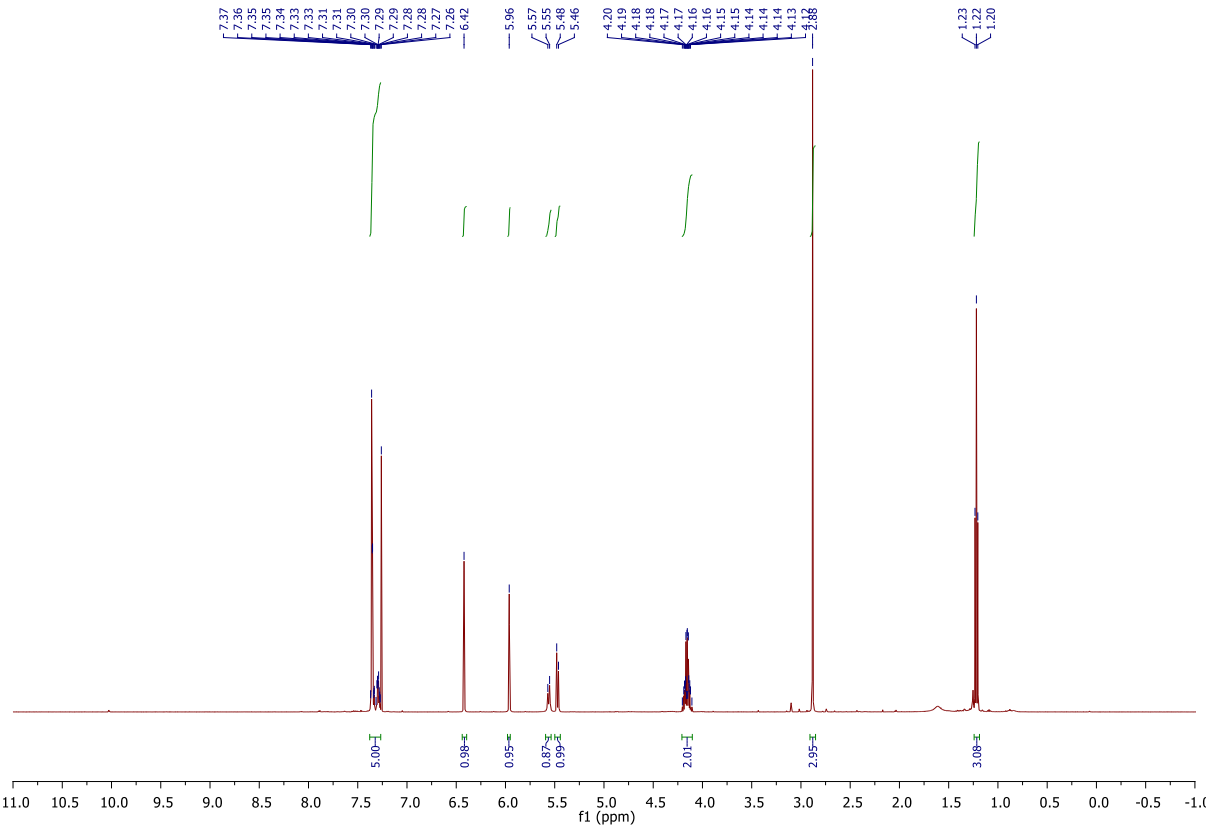


Figure S118. ^1H NMR of **26**.

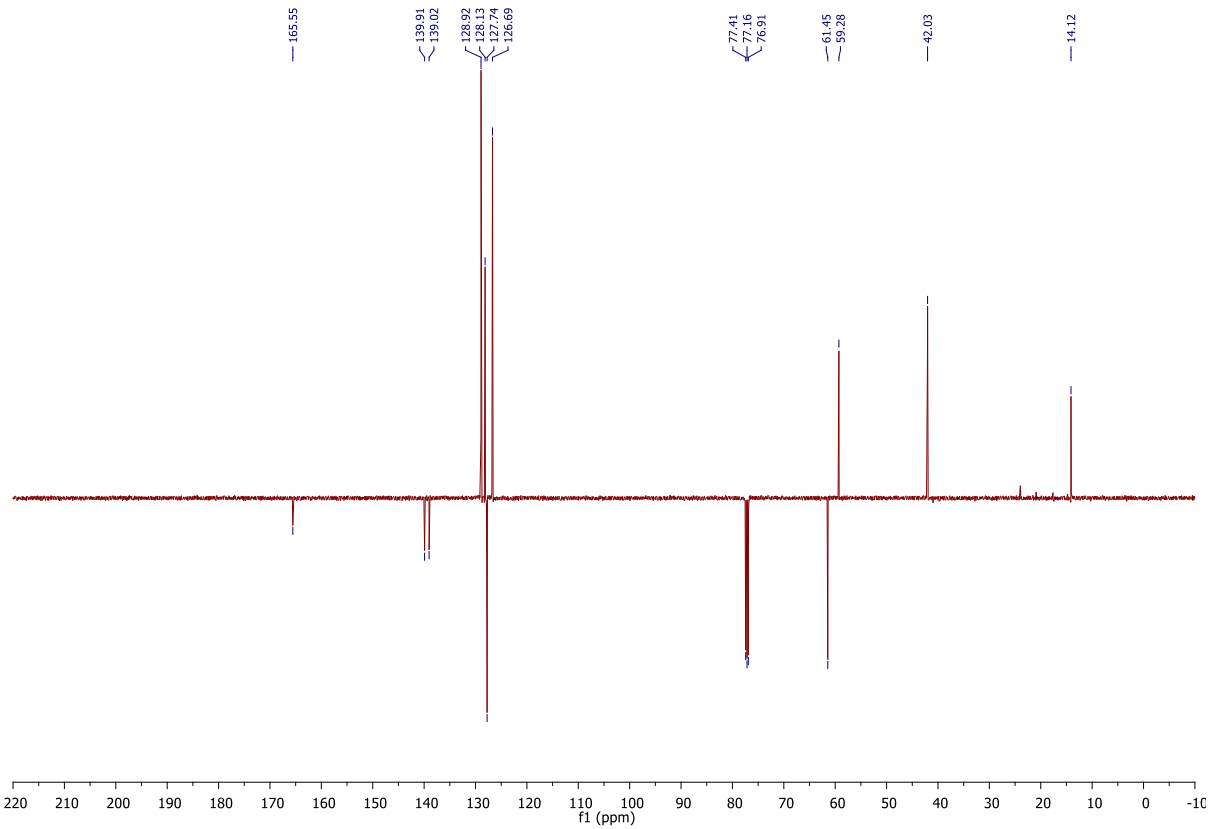
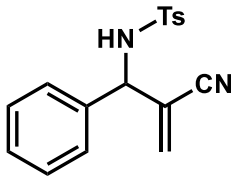


Figure S119. ^{13}C {^{1}H} NMR of **26**.

***N*-(2-cyano-1-phenylallyl)-4-methylbenzenesulfonamide (27)**



Prepared according to general procedure B from *N*-benzylidene-4-methylbenzenesulfonamide (0.25 mmol) and acrylonitrile (0.28 mmol); purified by FCC (1.5:8.5 to 3:7 EtOAc/PE) to give the title compound as a white solid (47 mg, 60%), with physical properties and spectroscopic data in accordance with the literature;[18] R_F = 0.26 (1.5:8.5 EtOAc/PE); mp 119 – 121 ˚C (lit. 126 – 127 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.73 – 7.69 (m, 2H), 7.34 – 7.27 (m, 5H), 7.14 – 7.08 (m, 2H), 6.08 (d, *J* = 1.4, 1H), 6.01 (d, *J* = 1.1, 1H), 5.05 (d, *J* = 7.0, 1H), 4.96 (d, *J* = 7.0, 1H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 144.3, 136.9, 136.3, 132.0, 129.9, 129.5, 129.3, 127.5, 127.0, 123.5, 116.6, 60.0, 21.7.

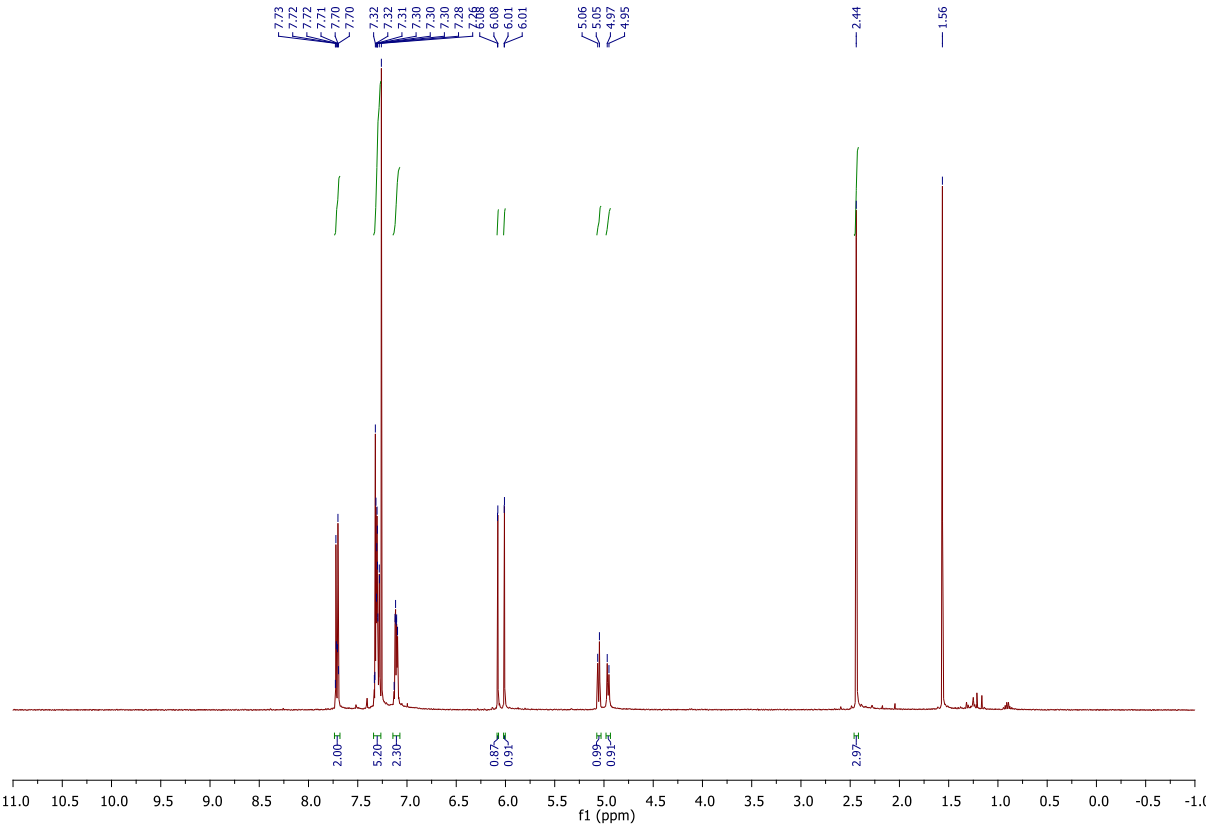


Figure S120. ^{1}H NMR of **27**.

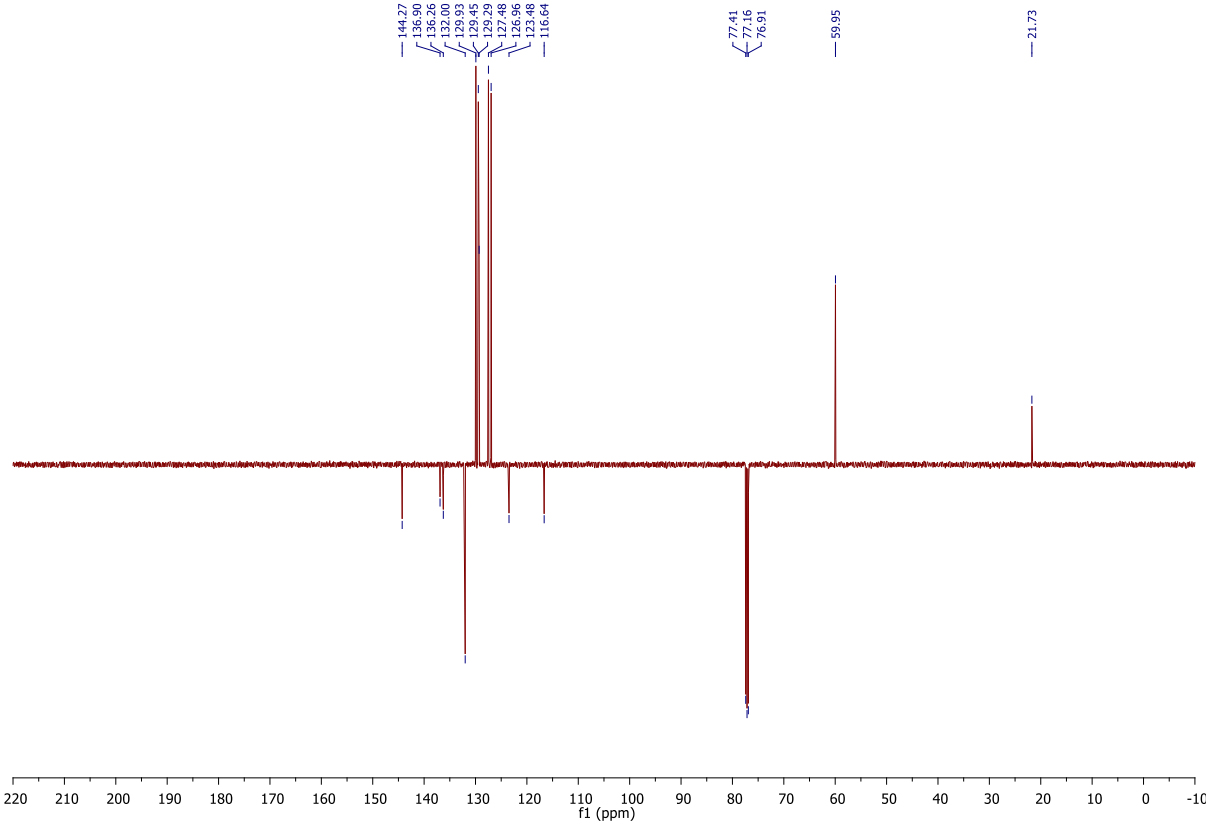
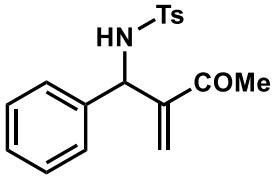


Figure S121. ^{13}C {^{1}H} NMR of **27**.

4-methyl-*N*-(2-methylene-3-oxo-1-phenylbutyl)benzenesulfonamide (28)



Prepared according to general procedure B from *N*-benzylidene-4-methylbenzenesulfonamide (0.25 mmol) and methyl vinyl ketone (0.28 mmol); purified by FCC (1.5:8.5 to 2.5:7.5 EtOAc/PE) to give the title compound as a white solid (26 mg, 31%), with physical properties and spectroscopic data in accordance with the literature;[19] R_F = 0.33 (2.5:7.5 EtOAc/PE); mp 109 – 111 ˚C (lit. 113 -114 ˚C); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.67 – 7.64 (m, 2H), 7.26 – 7.16 (m, 5H), 7.13 – 7.08 (m, 2H), 6.11 (s, 1H), 6.09 (d, *J* = 0.9, 1H), 5.61 (d, *J* = 8.6, 1H), 5.27 (d, *J* = 8.5, 1H), 2.41 (s, 3H), 2.16 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 199.0, 146.6, 143.5, 139.0, 137.7, 129.7, 128.7, 128.4, 127.8, 127.4, 126.5, 59.1, 26.5, 21.7.

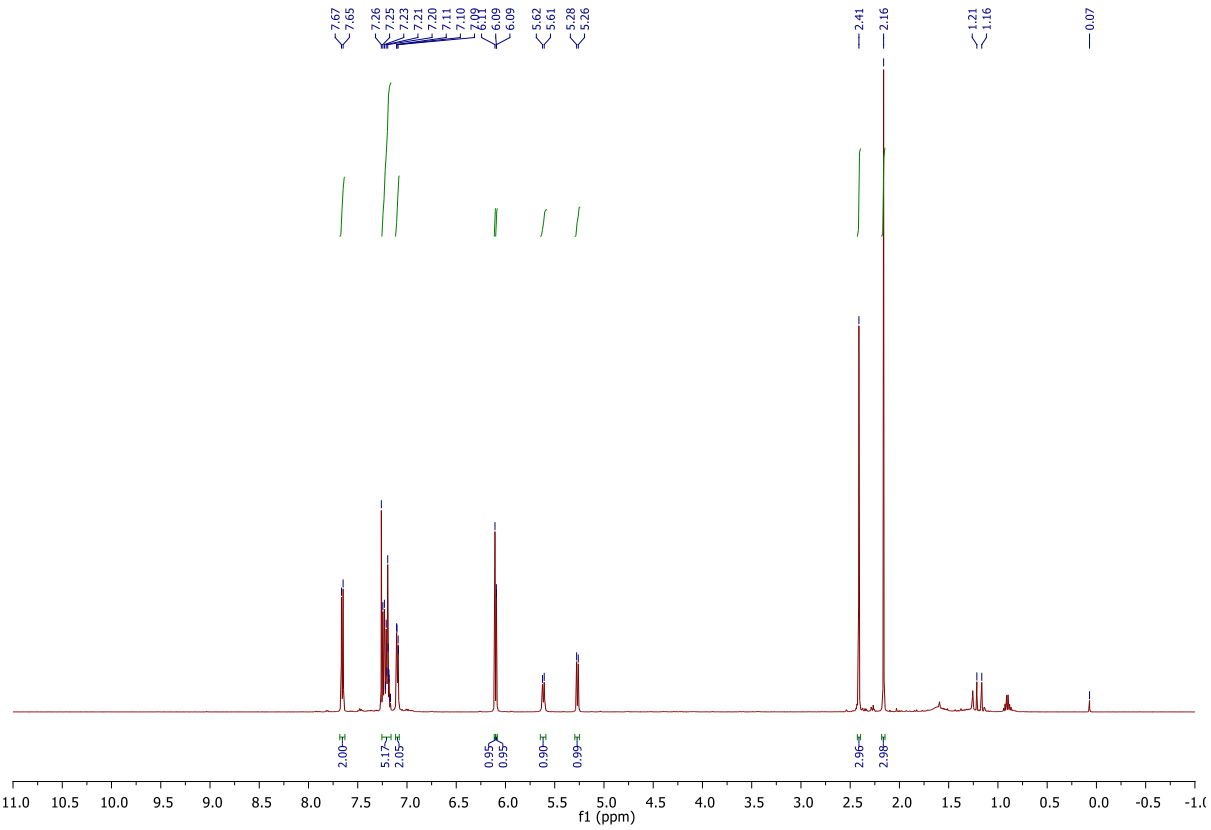


Figure S122. ^{1}H NMR of **28**.

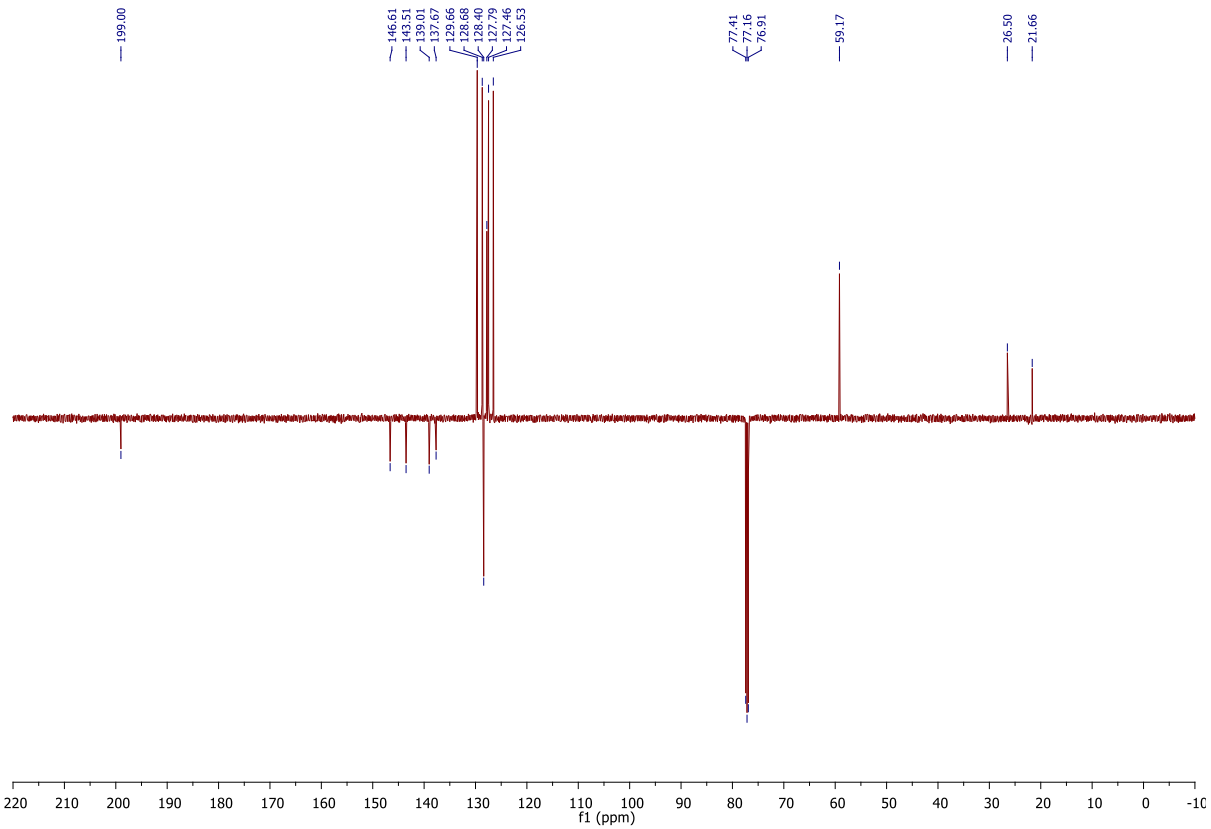
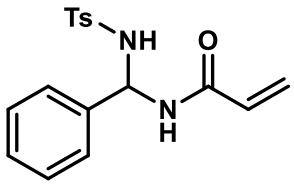


Figure S123. ^{13}C {^{1}H} NMR of **27**.

***N*-(((4-methylphenyl)sulfonamido)(phenyl)methyl)acrylamide (29)**



Prepared according to general procedure B from *N*-benzylidene-4-methylbenzenesulfonamide (0.25 mmol) and acrylamide (0.28 mmol), with a 3 h reaction time; purified by FCC (1:4 to 2:3 EtOAc/PE) to give the title compound as a white solid (19 mg, 23%); R_F = 0.43 (1:1 EtOAc/PE); mp 160 – 162 ˚C; v-$_{max}$/cm^{-1} (film): 3351, 3274, 1662, 1625, 1529, 1495, 1451, 1439, 1407, 1158, 1078, 1057, 981, 895, 817, 802, 694, 677, 577, 540; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ_H: 8.70 (d, *J* = 8.8, 1H), 8.57 (d, *J* = 8.4, 1H), 7.65 (d, *J* = 8.1, 2H), 7.35 – 7.23 (m, 7H), 6.32 (t, *J* = 8.5, 1H), 6.11 (dd, *J* = 17.1, 10.0, 1H), 6.00 (dd, *J* = 17.1, 2.3, 1H), 5.54 (dd, *J* = 10.0, 2.4, 1H), 2.35 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz,$(CD_3)_2SO$) δ_C: 163.4, 142.4, 139.3, 138.6, 131.0, 129.3, 128.3, 127.9, 126.6, 126.3, 126.0, 60.9, 21.0; HRMS (ES^+) calculated for $[C_{17}H_{18}N_2O_3SNa]^+$ $(M+Na)^+$: m/z 353.0936 found 353.0936 (0.0 ppm).

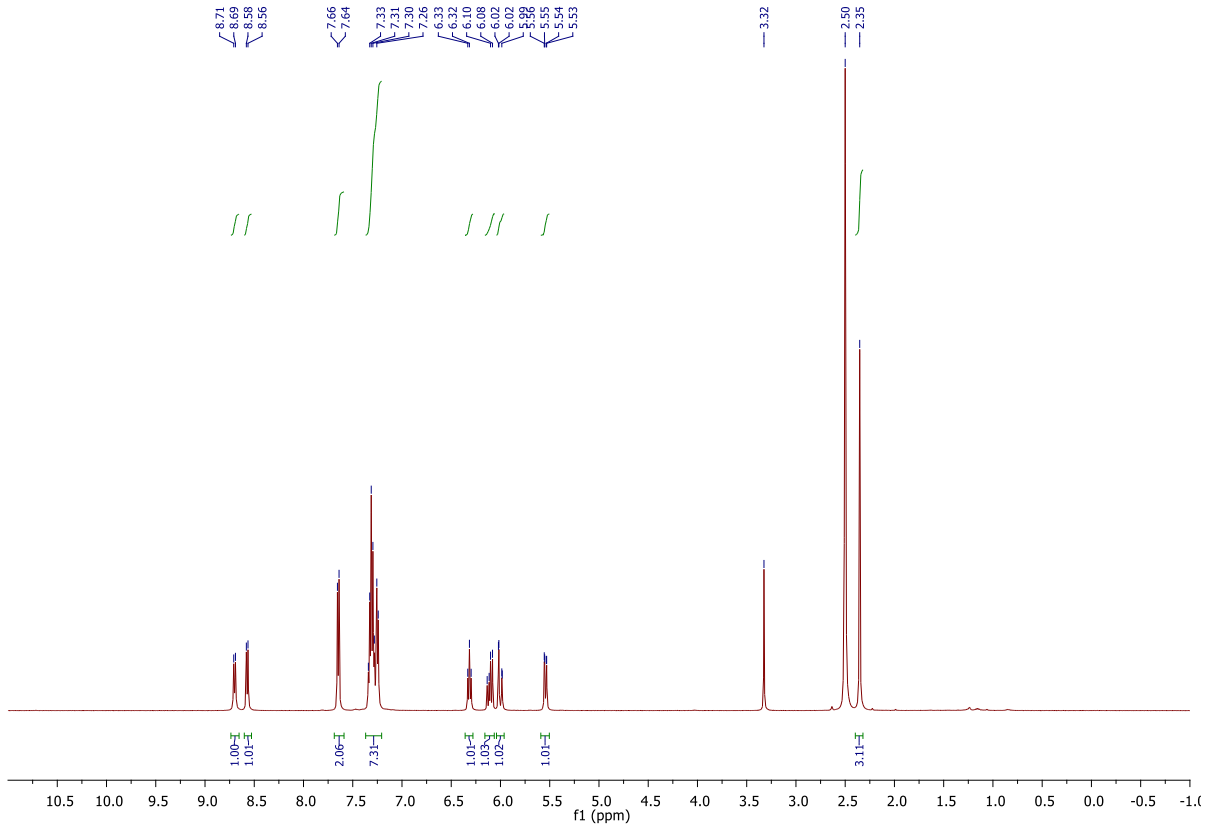


Figure S124. ^{1}H NMR of **29**.

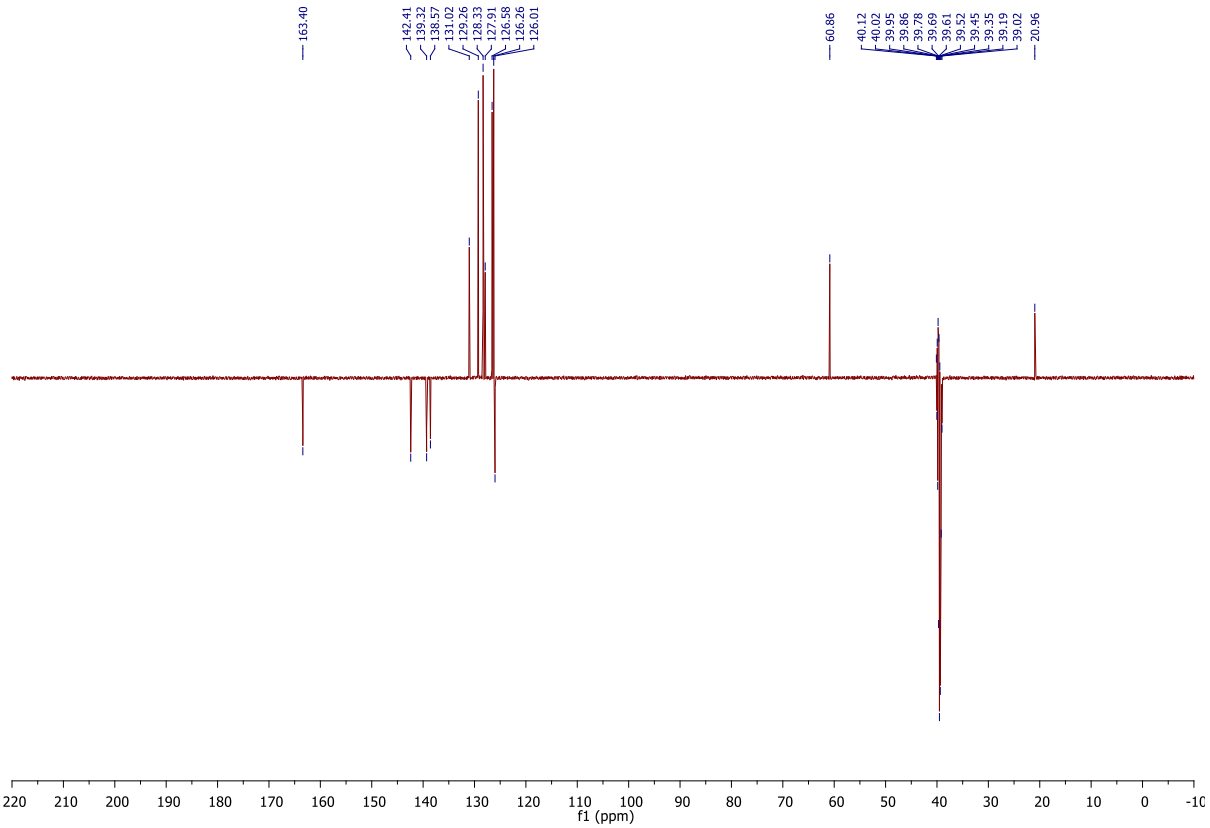
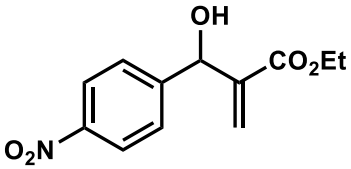


Figure S125. ^{13}C {^{1}H} NMR of **29**.

Ethyl 2-(hydroxy(4-nitrophenyl)methyl)acrylate (40)



Prepared according to general procedure B from *p*-nitrobenzaldehyde (0.25 mmol) and ethyl acrylate (0.28 mmol); purified by FCC (1:4 EtOAc/PE) to give the title compound as a pale yellow oil (36 mg, 57%), with physical properties and spectroscopic data in accordance with the literature;[20] R_F = 0.25 (2.5:7.5 EtOAc/PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.24 – 8.17 (m, 2H), 7.64 – 7.53 (m, 2H), 6.40 – 6.39 (m, 1H), 5.84 (t, *J* = 1.0, 1H), 5.62 (d, *J* = 5.2, 1H), 4.19 (q, *J* = 7.1, 2H), 3.34 (d, *J* = 6.3, 1H), 1.27 (t, *J* = 7.1, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 166.1, 148.8, 147.6, 141.3, 127.5, 127.3, 123.8, 73.1, 61.5, 14.2.

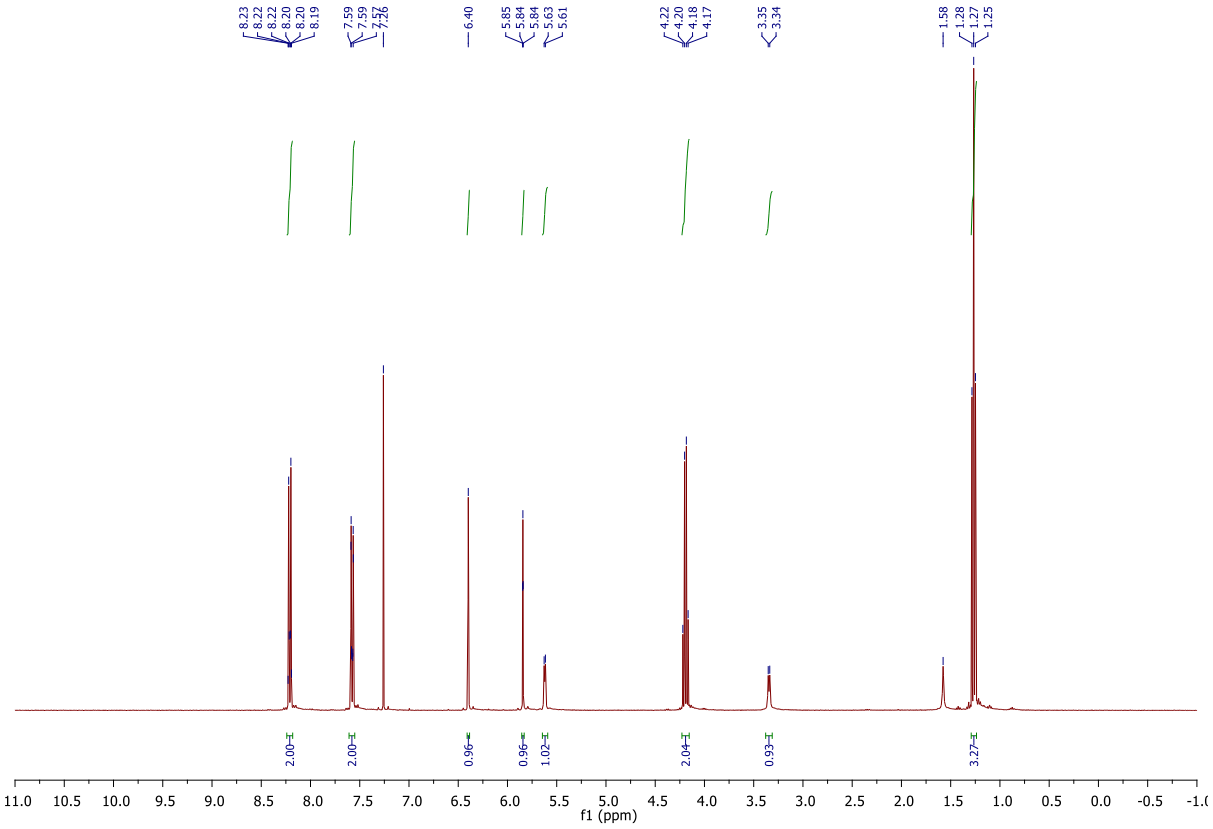


Figure S126. ^{1}H NMR of **40**.

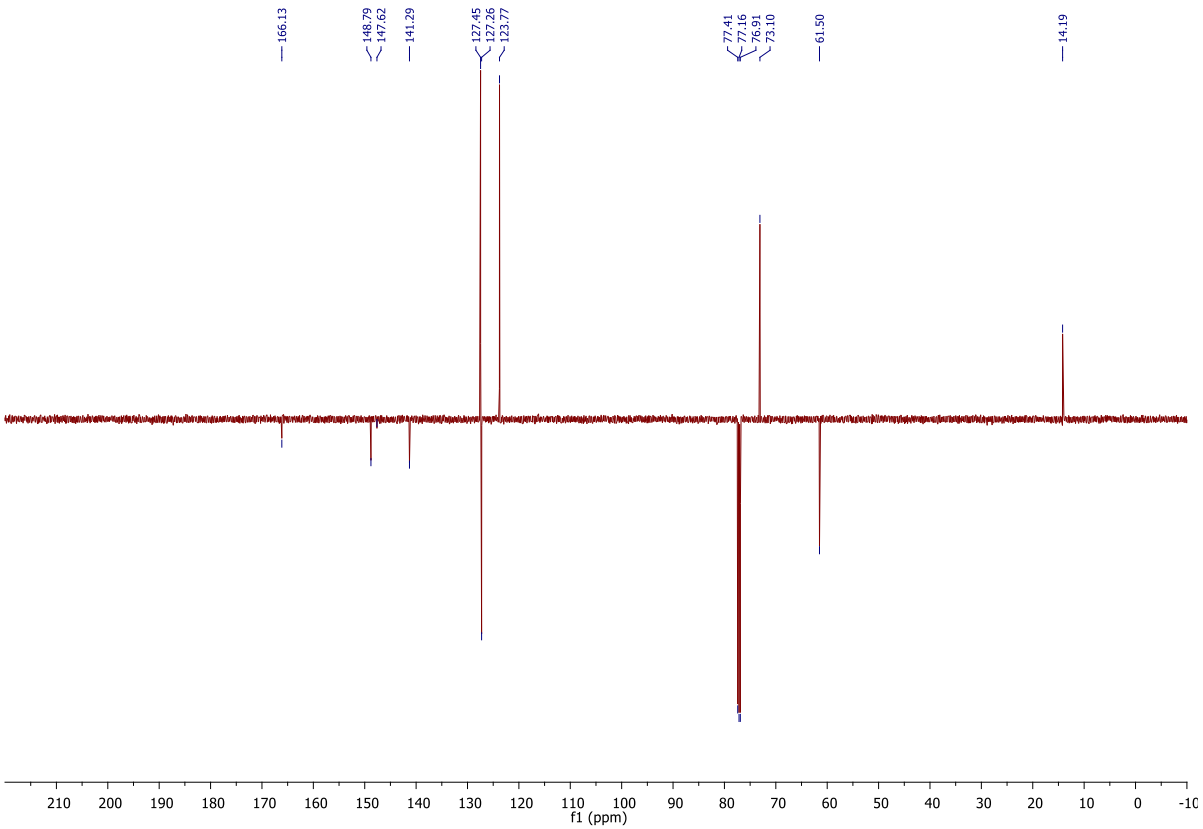


Figure S127. ^{13}C {^{1}H} NMR of **40**.

5. Solution-stirred and neat-stirred comparison studies

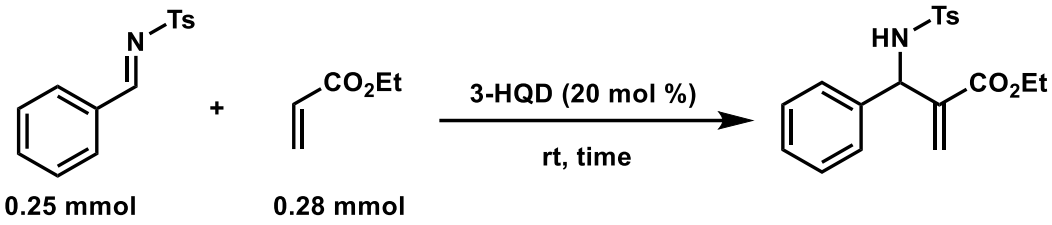


Table S2. Comparison of mixer mill method to solution stirring and neat stirring techniques.

	NMR yield of product (%)[c]				
Method	**t = 5 min**	**t = 30 min**	**t = 1 h**	**t = 2 h**	**t = 3 h**
Mixer mill[a]	25	47	76	80	88
Solution-stirred in 1 mL toluene[b]	<2	5	10	17	25
Neat-stirred[b]	29	45	52	66	70
Dry stirred with 3 mass equiv. NaCl[b]	13	35	52	53	58
Dry stirred with 3 mass equiv. NaCl and 25 µL toluene[b]	9	44	52	56	64

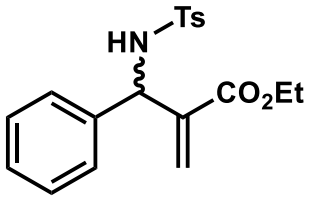
[a] Carried out in a 14 mL stainless steel jar, with a 9 mm 3 g stainless steel ball, 3 mass equiv. sodium chloride and 25 µL toluene at 30 Hz.

[b] Carried out in a 10 mL vial.

[c] Determined by ^{1}H NMR analysis, using mesitylene as an internal standard.

6. HPLC traces for asymmetric studies

Ethyl 2-(((4-methylphenyl)sulfonamido)(phenyl)methyl)acrylate (3)



HPLC Chiralpak IA, 90:10 Hexane/IPA, 1 mL/min, 60 min; $t_{r\ maj}$ = 22 min $t_{r\ min}$ = 24 min

	Inj. Number	Peak Name	R. Time	Area	Area %	Sample Descrip.
1	1.00	*1	22.06	11176699.00	48.13	MV2-008-rac
2	1.00	*2	23.83	12042916.00	51.87	MV2-008-rac
3						

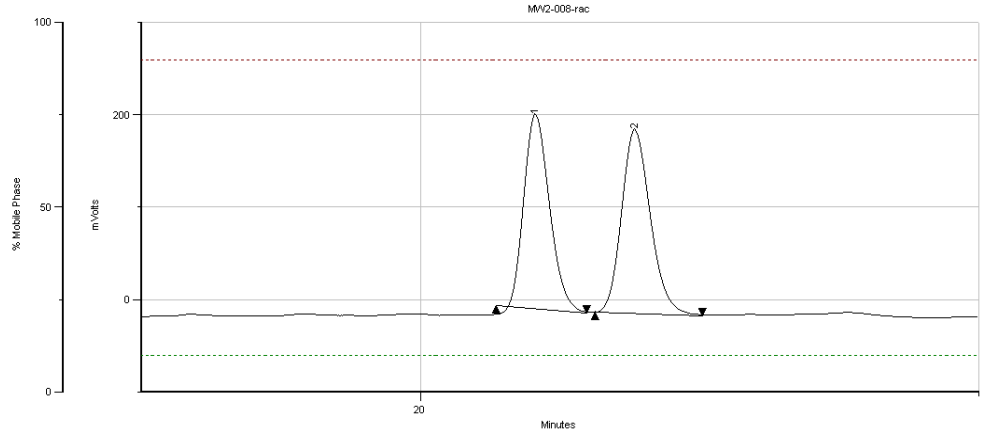


Figure S128. HPLC trace for racemic **3**.

	Inj. Number	Peak Name	R. Time	Area	Area %	Sample Descrip.
1	1.00	*1	22.63	20031926.00	49.33	2-008-(R)3H
2	1.00	*2	24.52	20573238.00	50.67	2-008-(R)3H
3						

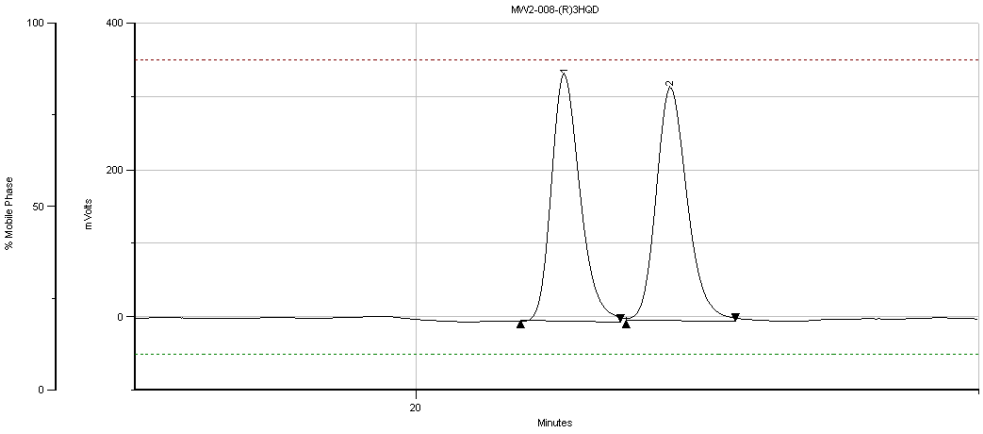


Figure S129. HPLC trace for **3** using (*R*)-3-HQD as catalyst.

	Inj. Number	Peak Name	R. Time	Area	Area %	Sample Descrip.
1	1.00	*1	23.16	25699936.00	18.17	MV2-008-b_IC
2	1.00	*2	25.16	15737000.00	81.83	MV2-008-b_IC
3						

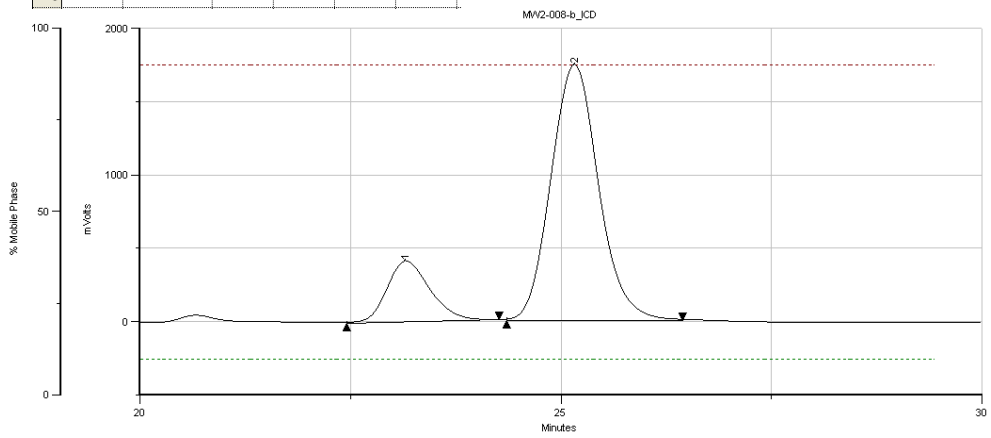


Figure S130. HPLC trace for **3** using β-Isocupreidine as catalyst.

	Inj. Number	Peak Name	R. Time	Area	Area %	Sample Descrip.
1	1.00	*1	23.13	75591448.00	62.60	MV2-008-a_IC
2	1.00	*2	25.20	45166832.00	37.40	MV2-008-a_IC
3						

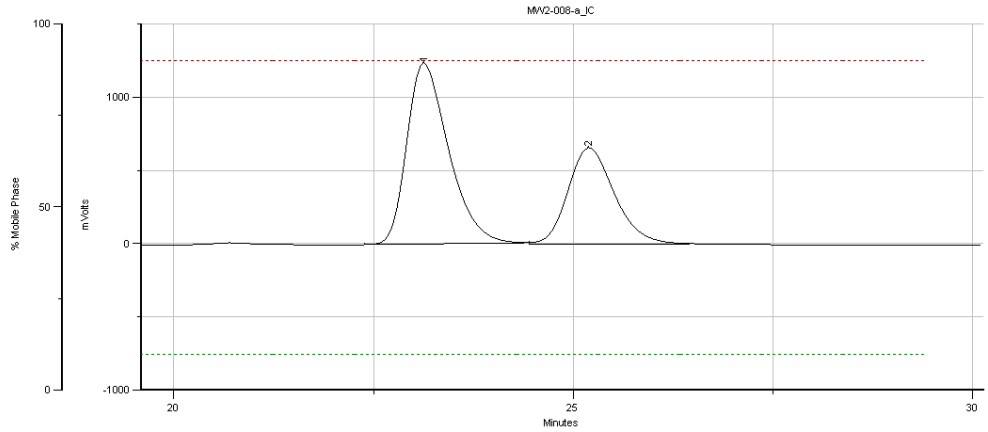
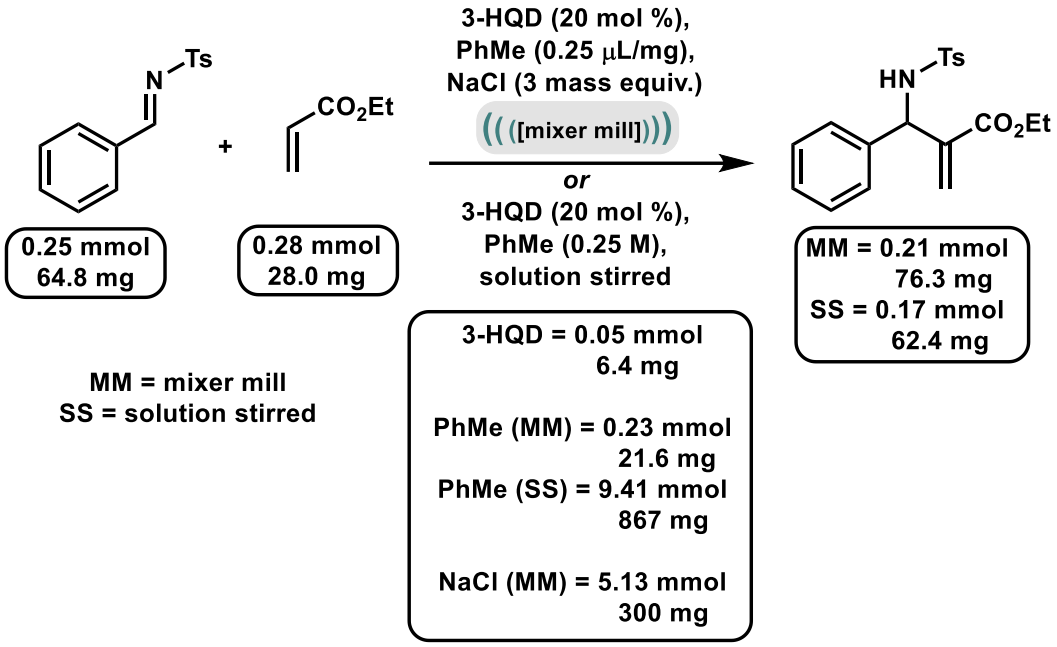


Figure S131. HPLC trace for **3** using α-Isocupreine as catalyst.

7. Calculation of green metrics



$$\text{E factor} = \frac{\text{mass of waste}}{\text{mass of product}} \text{ or } \frac{(\text{mass of reactants and reagents}) - (\text{mass of product})}{\text{mass of product}} \quad (Eq.S1)$$

$$\text{E factor (mixer mill)} = \frac{(64.8 + 28.0 + 6.4 + 21.6 + 300) - (76.3)}{76.3} = 4.5 \quad (Eq.S1a)$$

$$\text{E factor (solution stirred)} = \frac{(64.8 + 28.0 + 6.4 + 867) - (62.4)}{62.4} = 14.5 \quad (Eq.S1b)$$

$$\text{Mass Intensity (MI)} = \frac{\text{total mass in process}}{\text{mass of product}} \quad (Eq.S2)$$

$$\text{Mass Intensity (mixer mill)} = \frac{64.8 + 28.0 + 6.4 + 21.6 + 300}{76.3} = 5.5 \text{ mg/mg} \quad (Eq.S2a)$$

$$\text{Mass Intensity (solution stirred)} = \frac{64.8 + 28.0 + 6.4 + 867}{62.4} = 15.5 \text{ mg/mg} \quad (Eq.S2b)$$

$$\text{Reaction mass efficiency (\%)} = \frac{\text{mass of product}}{\text{mass of (stoichiometric) reactants}} \times 100 \quad (Eq.S3)$$

$$\text{Reaction mass efficiency (mixer mill)} = \frac{76.3}{64.8 + 28.0} \times 100 = 82\% \quad (Eq.S3a)$$

$$\text{Reaction mass efficiency (solution stirred)} = \frac{62.4}{64.8 + 28.0} \times 100 = 67\% \quad (Eq.S3b)$$

$$\text{Molar efficiency (\%)} = \frac{\text{moles product}}{(\text{moles reactants} + \text{moles cat.} + \text{moles solvent} + \text{moles additives})} \times 100 \quad (Eq.S4)$$

$$\text{Molar efficiency (mixer mill)} = \frac{0.21}{(0.25 + 0.28 + 0.05 + 0.23 + 5.13)} \times 100 = 4\% \quad (Eq.S4a)$$

$$\text{Molar efficiency (solution stirred)} = \frac{0.17}{(0.25 + 0.28 + 0.05 + 9.41)} \times 100 = 2\% \quad (Eq.S4b)$$

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