Electronic Supplementary Material (ESI) for CrystEngComm.

Crystal Engineering for Intramolecular π—π Stacking: Effect of Substitution of Electron Donating and Withdrawing Group on Molecular Geometry in Conformationally Flexible Sulfoesters and Sulfonamides

Samir R. Shaikh,[a,b] *Rupesh L. Gawade,*[a] *Niteen B. Dabke,*[a] *Soumya R. Dash,*[a,b] *Kumar Vanka,*[a,b] *Rajesh G. Gonnade**[,a,b]

[a]Physical and Materials Chemistry Division, CSIR–National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India.

[b]Academy of Scientific and Innovative Research (AcSIR), Sector 19, Kamla Nehru Nagar, Ghaziabad, Uttar Pradesh- 201 002., India.

Correspondence email: rg.gonnade@ncl.res.in

Contents:

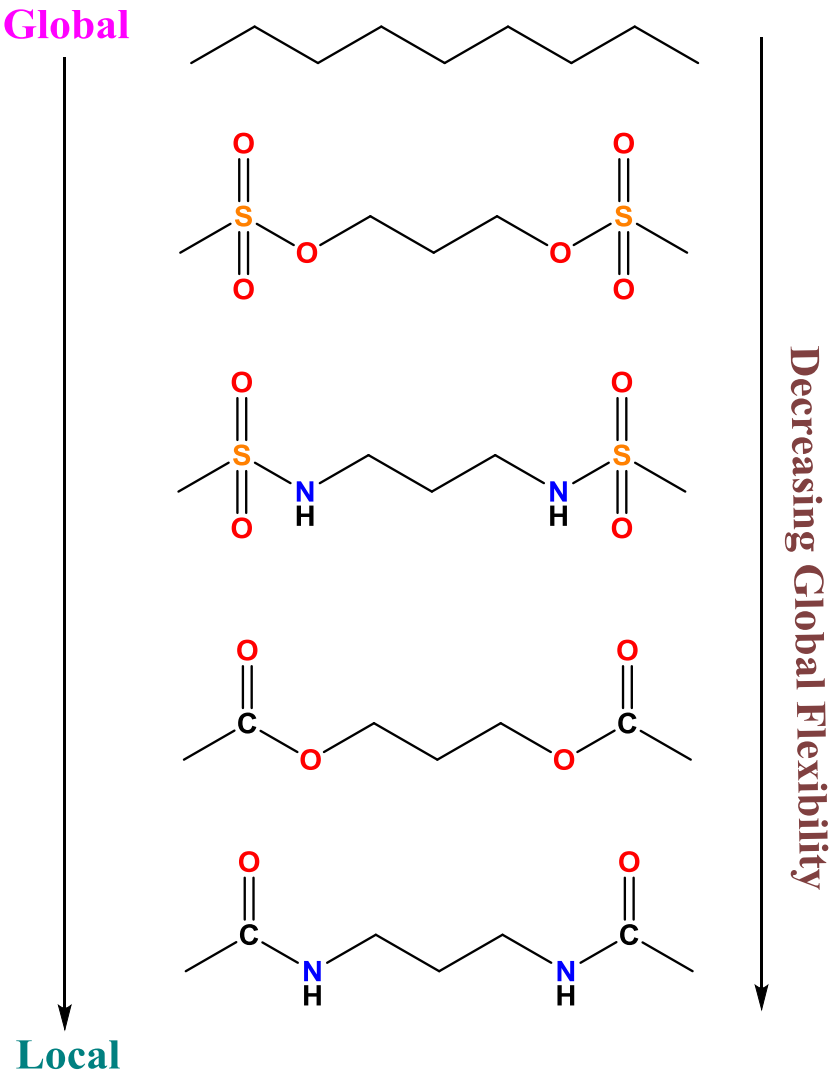


Figure S1. Decrease in the global conformational flexibility in the descending order.

1. Experimental Methods:

1.1 General Synthetic Procedure for the Preparation of Sulfoesters: To the cooled solution of 1.0 eq. of 2-phenylethan-1-ol in dry DCM, 1.2 eq. of dry Et_3N was added in dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) followed by slow addition of 1.2 eq. of *p*-substituted benzene sulfonyl chloride in dry DCM at 0 ˚C to yield corresponding dimeric sulfonamides. The reaction mixture was allowed to reach room temperature and was further stirred. After the reaction (monitored by TLC), the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: ethyl acetate/pet ether), yielded pure product. The purified sulfoester derivatives (**1a** to **7a**) were crystallized from organic solvents or a mixture of organic solvents by slow evaporation.

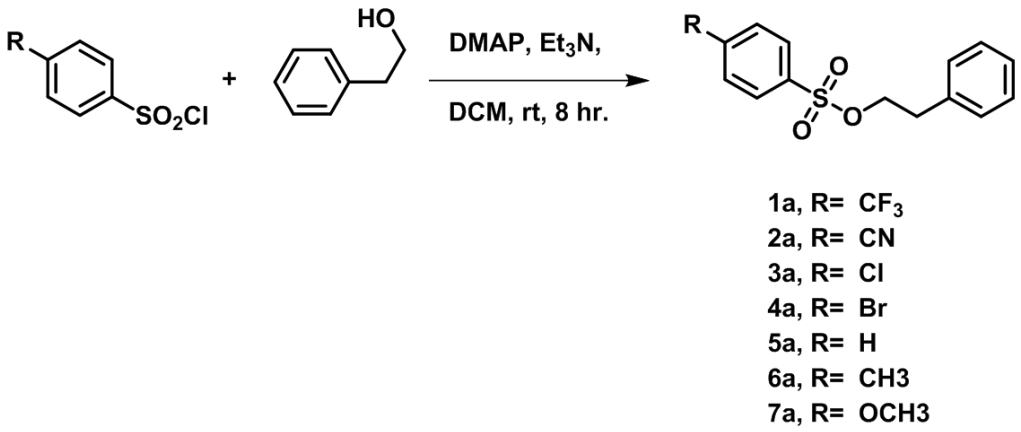


Figure S2. Scheme-Synthetic procedure for the preparation of Sulfoesters (**1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **7a**).

1.2 Synthesis of phenethyl 4-(trifluoromethyl)benzenesulfonate (1a): To a solution of 2-phenylethan-1-ol (150 mg, 1.23 mmol, 1.0eq) in dry DCM (10 mL), dry Et_3N (0.21 mL, 1.48 mmol, 1.2 eq) was added in dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (15 mg, 0.123 mmol, 0.1eq) followed by slow addition of 4-trifluoromethyl benzenesulfonyl chloride (362 mg, 1.48 mmol, 1.2 eq) in dry DCM at 0 ˚C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded **(1a)**. Solid; yield = 210 mg, 52%; R_f = 0.54 (ethyl acetate/petroleum ether = 30/70); mp = 65-67 °C, **^{1}H NMR** (**200MHz, $CDCl_3$**) δ = 7.84 - 7.73 (m, *J* = 8.3 Hz, 2 H), 7.69 - 7.57 (m, *J* = 8.5 Hz, 2 H), 7.23 - 7.10 (m, 4 H), 7.07 - 6.95 (m, 2 H), 4.22 (t, *J* = 6.8 Hz, 2 H), 2.90 (t, *J* = 6.8 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 139.4, 135.9, 128.8, 128.6, 128.2, 127.0, 126.3, 126.3, 126.2, 126.1, 77.6, 76.4, 71.5, 35.3 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{13}O_3F_3S_1Na$ $[M+ Na]^+$ 353.31, found 353.0385.

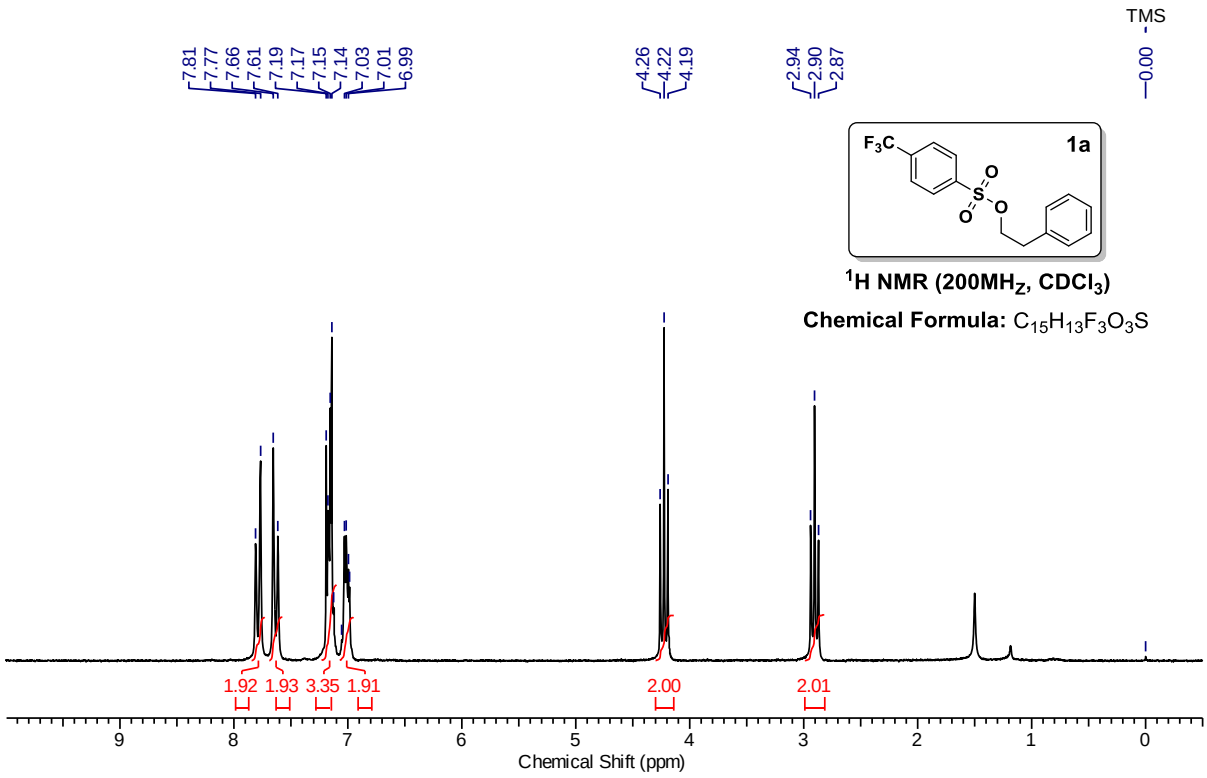


Figure S3. ^{1}H NMR spectrum of **1a** in $CDCl_3$.

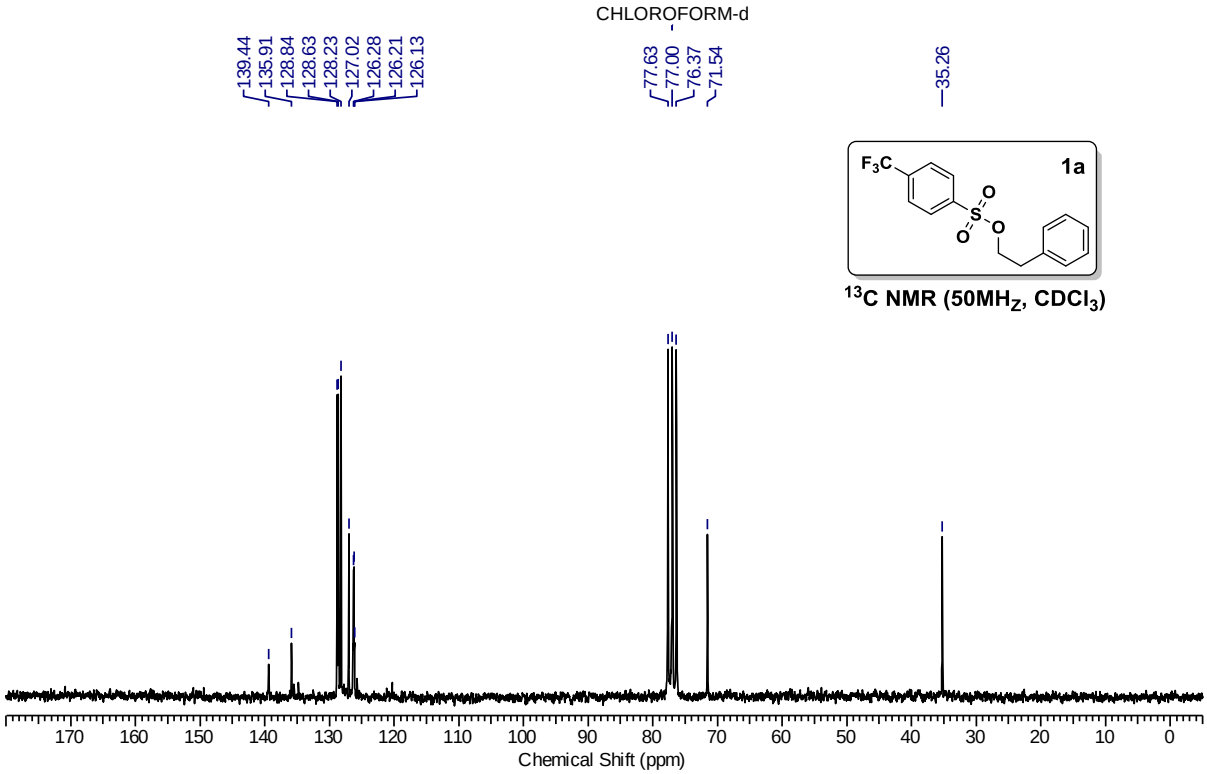


Figure S4. ^{13}C NMR spectrum of **1a** in $CDCl_3$.

1.3 Synthesis of phenethyl 4-cyanobenzenesulfonate (2a): To a solution of 2-phenylethan-1-ol (100 mg, 0.82 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14 mL, 0.98 mmol, 1.2 eq) was added in dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.082 mmol, 0.1 eq) followed by slow addition of 4-cyanobenzenesulfonyl chloride (198 mg, 0.98 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which yielded on purification by flash column chromatography (eluent: pet ether/ethyl acetate) (**2a**), liquid; yield = 160 mg, 68%; R_f = 0.56 (ethyl acetate/petroleum ether = 30/70); **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.82 - 7.59 (m, 4 H), 7.25 - 7.11 (m, 3 H), 7.08 - 6.94 (m, 2 H), 4.23 (t, *J* = 6.7 Hz, 2 H), 2.91 (t, *J* = 6.7 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 140.1, 135.9, 132.8, 128.9, 128.7, 128.3, 127.1, 117.3, 117.0, 71.8, 35.3 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{13}N_1O_3S_1Na$ $[M+ Na]^+$ 310.0508, found 310.0509.

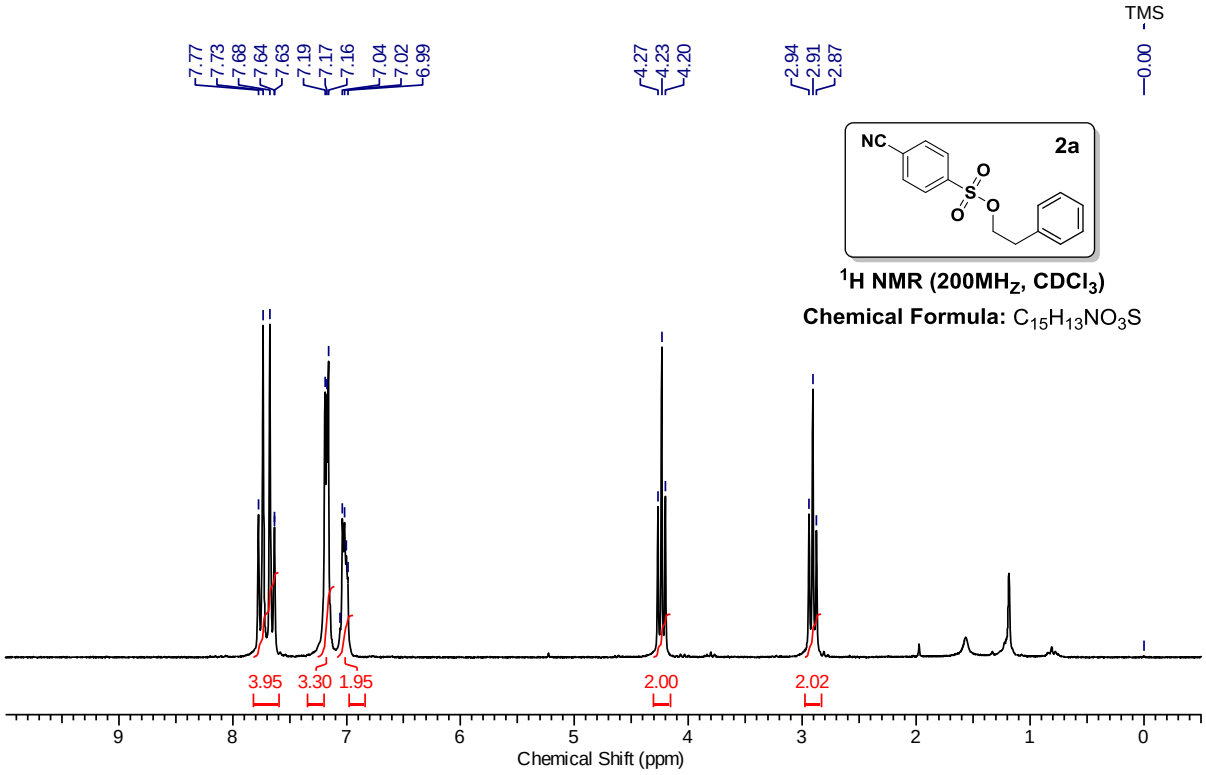


Figure S5. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

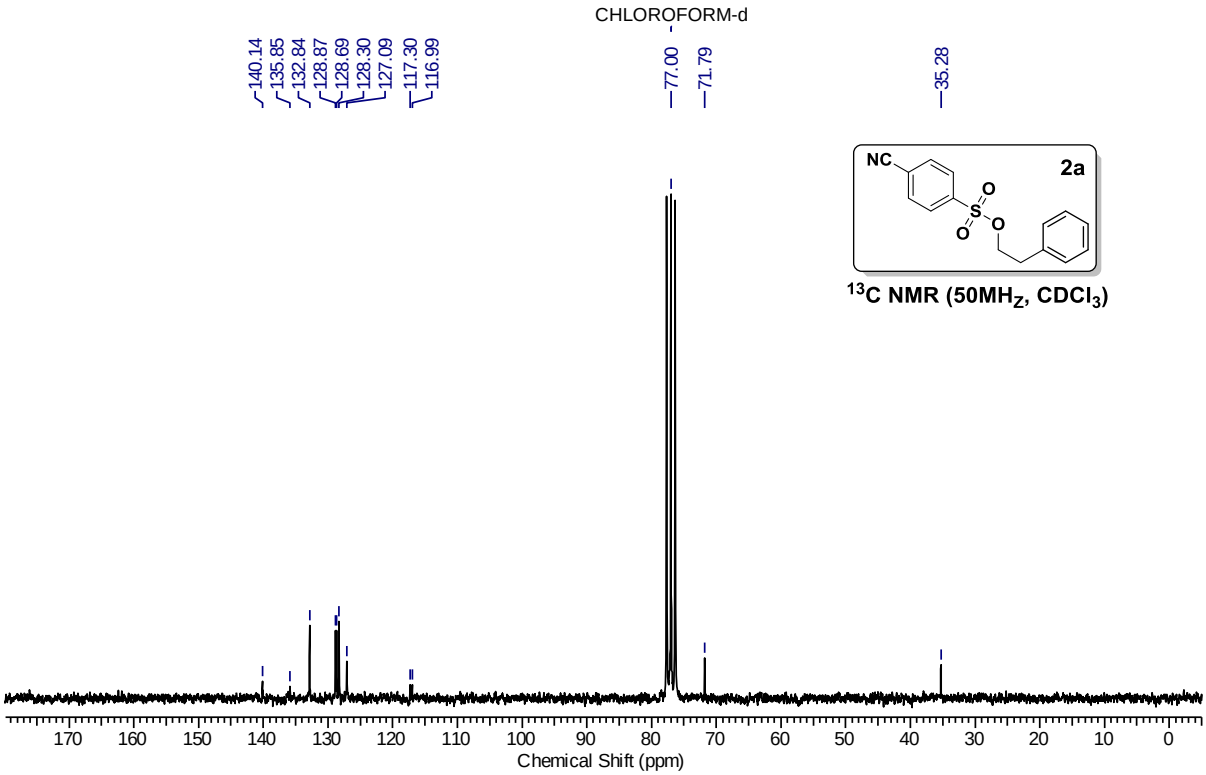


Figure S6. ^{13}C NMR spectrum of **2a** in $CDCl_3$.

1.4 Synthesis of phenethyl 4-Chlorobenzenesulfonate (3a): To a solution of 2-phenylethan-1-ol (200 mg, 1.64 mmol, 1.0 eq) in dry DCM (10 ml), dry Et_3N (0.27 mL, 1.97 mmol, 1.2 eq) was added in dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (20 mg, 0.164mmol, 0.1 eq) followed by slow addition of 4-Chlorobenzenesulfonyl chloride (416 mg, 1.97 mmol, 1.2 eq) in dry DCM at 0 ˚C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded **(3a).** Solid; yield = 390 mg, 80%; R_f = 0.59 (ethyl acetate/petroleum ether = 30/70); mp = 50-52 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.68 - 7.54 (m, 2 H), 7.42 - 7.29 (m, 2 H), 7.25 - 7.10 (m, 3 H), 7.08 - 6.95 (m, 2 H), 4.17 (t, *J* = 6.9 Hz, 2 H), 2.89 (t, *J* = 6.8 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 140.3, 136.0, 134.4, 129.5, 129.2, 128.9, 128.6, 127.0, 77.6, 76.4, 71.1, 35.3 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{13}ClO_3S_1Na$ $[M+ Na]^+$ 319.0166, found 319.0170.

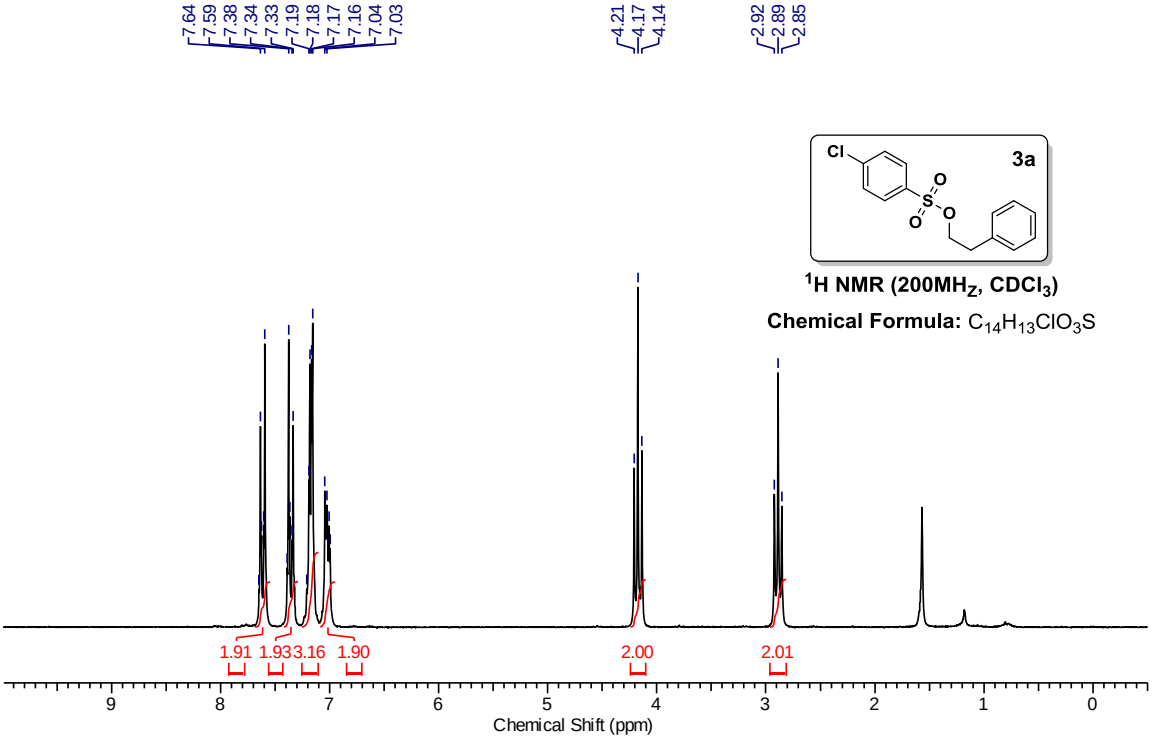


Figure S7. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

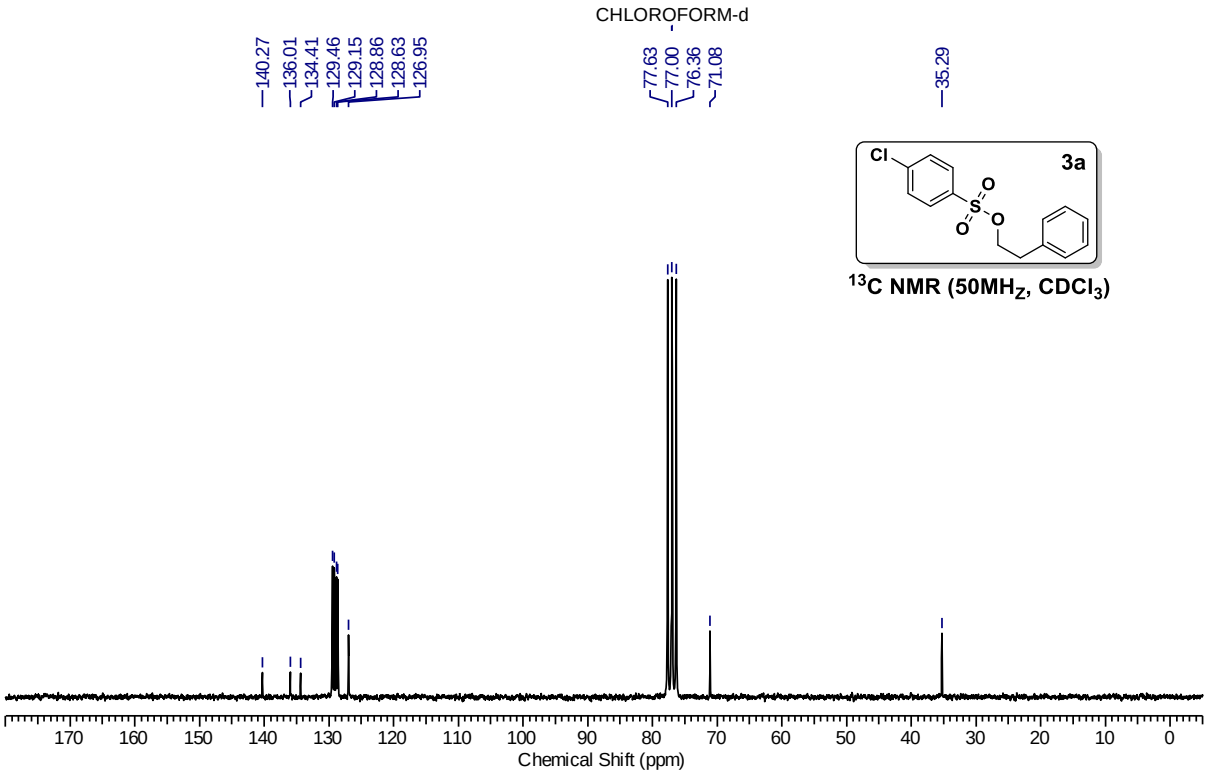


Figure S8. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

1.5 Synthesis of phenethyl 4-Bromobenzenesulfonate (4a): To a solution of 2-phenylethan-1-ol (150 mg, 1.23 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.21 mL, 1.48 mmol, 1.2 eq) was added in dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (15 mg, 0.123 mmol, 0.1 eq) followed by slow addition of 4-bromobenzene sulfonyl chloride (378 mg, 1.48 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**4a**)**.** Solid; yield = 270 mg, 64%; R_f = 0.55 (ethyl acetate/petroleum ether = 30/70); mp = 60-62 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.64 (s, 4 H), 7.36 - 7.21 (m, 3 H), 7.20 - 7.06 (m, 2 H), 4.29 (t, *J* = 6.8 Hz, 2 H), 3.00 (t, *J* = 6.8 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 136.0, 135.0, 132.5, 129.2, 128.9, 128.6, 127.0, 77.6, 76.4, 71.1, 35.3 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{13}Br_1O_3S_1Na$ $[M+Na]^+$ 364.9641, found 364.9636.

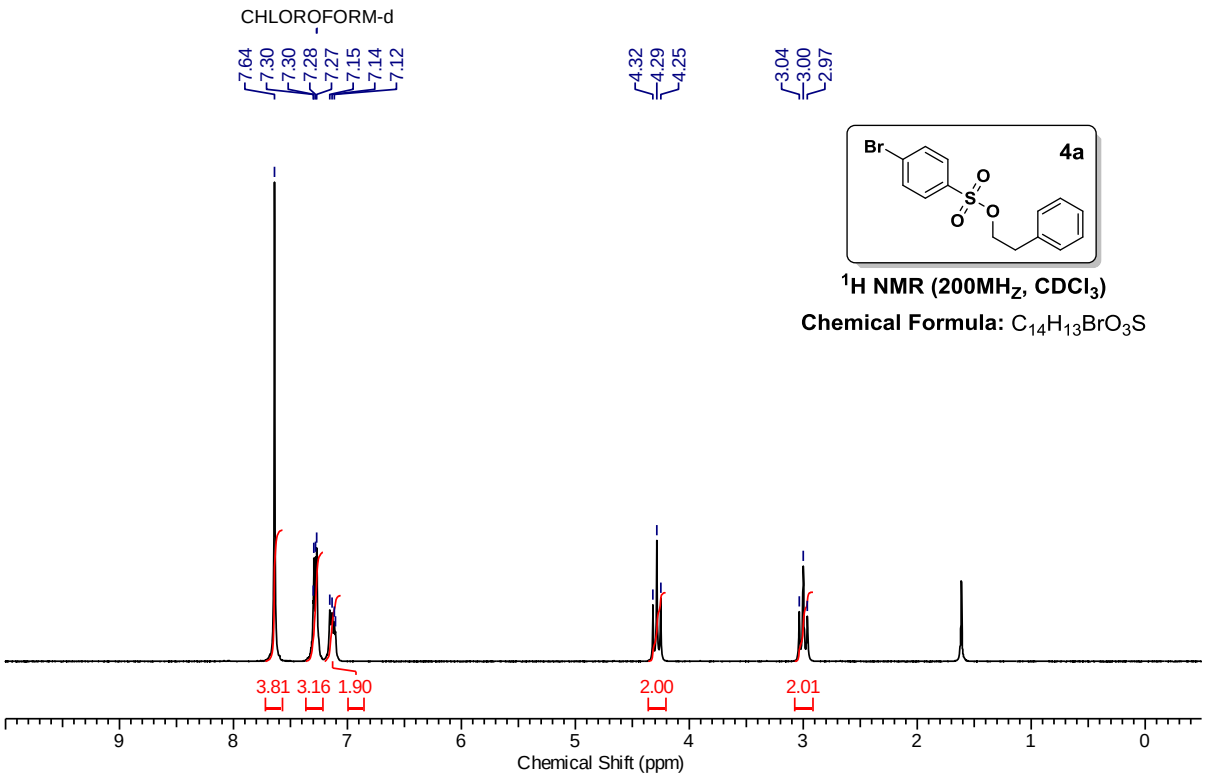


Figure S9. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

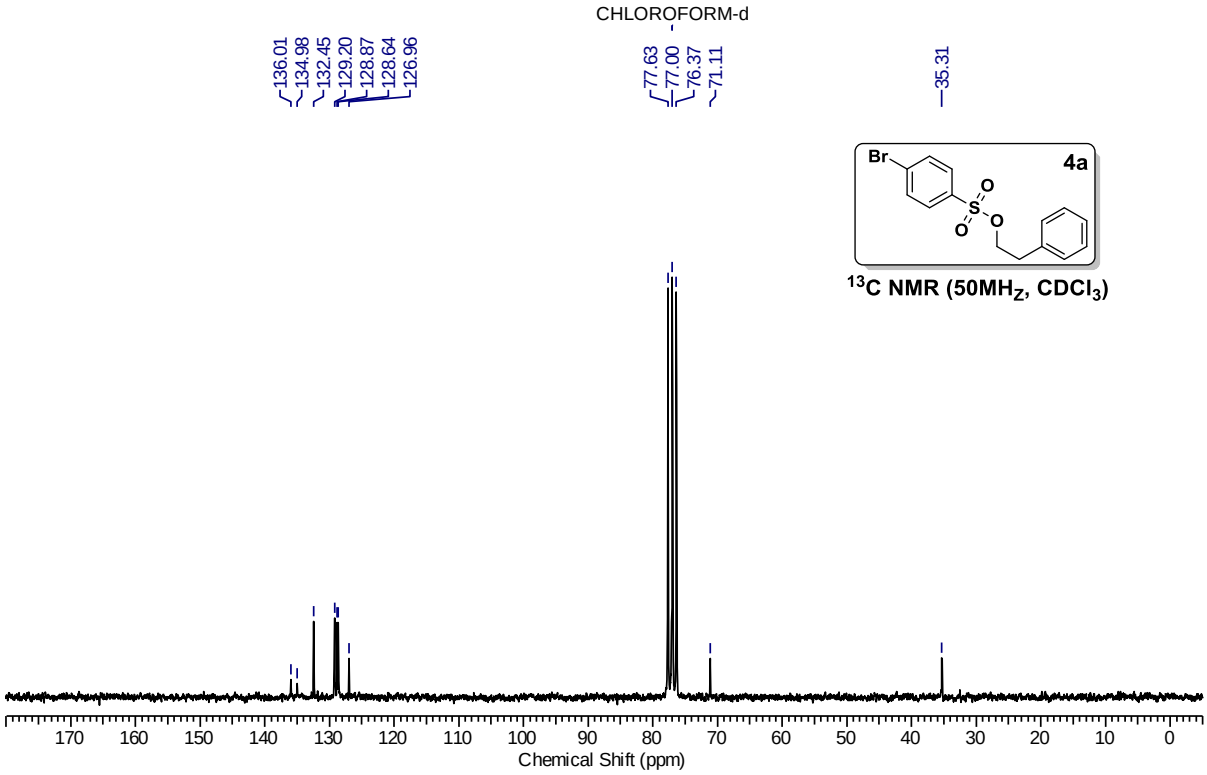


Figure S10. ^{13}C NMR spectrum of **4a** in $CDCl_3$.

1.6 Synthesis of Phenethyl benzenesulfonate (5a): To a solution of 2-phenylethan-1-ol (150 mg, 1.23 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.21 mL, 1.48 mmol, 1.2 eq) was added in a dropwise manner in the presence of the catalytic amount of DMAP (dimethylaminopyridine) (15 mg, 0.123 mmol, 0.1 eq) followed by slow addition of benzenesulfonyl chloride (0.19 mL, 1.48 mmol, 1.2 eq) in dry DCM at 0 ˚C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate) yielded **(5a)**, liquid; yield = 230 mg, 71%; R_f = 0.63(ethyl acetate/petroleum ether = 30/70); **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.95 - 7.78 (m, 2 H), 7.73 - 7.46 (m, 3 H), 7.38 - 7.07 (m, 5 H), 4.27 (t, *J* = 7.0 Hz, 2 H), 3.00 (t, *J* = 7.0 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 136.1, 135.9, 133.6, 129.1, 128.8, 128.6, 127.7, 126.9, 77.6, 76.4, 70.8, 35.3 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{14}O_3S_1Na$ $[M+Na]^+$ 285.0556, found 285.0556.

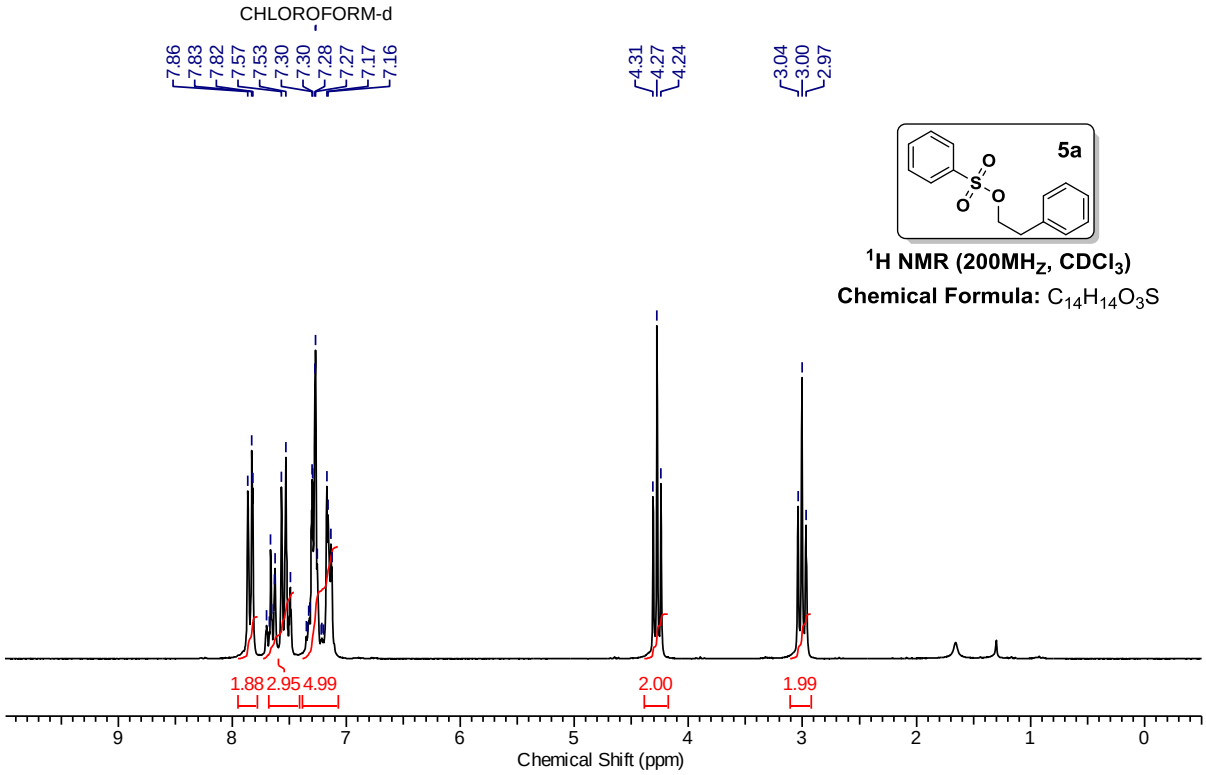


Figure S11. ^{1}H NMR spectrum of **5a** in $CDCl_3$.

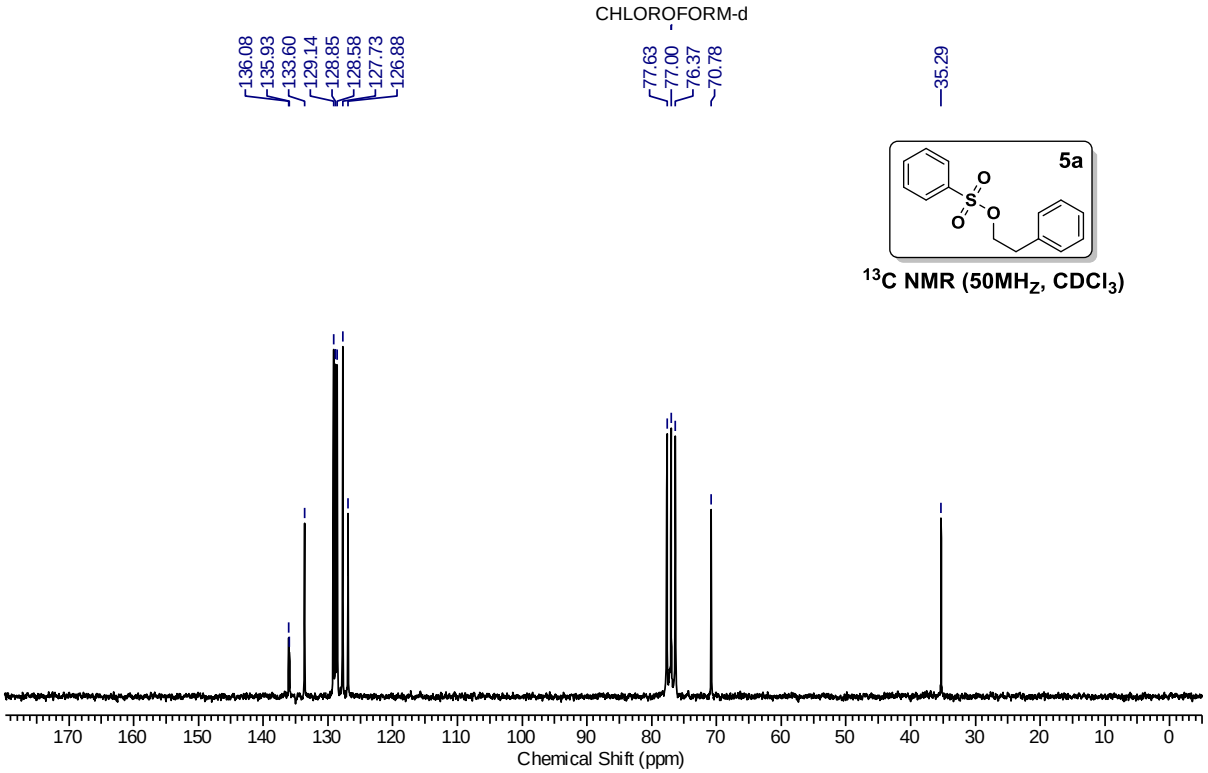


Figure S12. ^{13}C NMR spectrum of **5a** in $CDCl_3$.

1.7 Synthesis of Phenethyl 4-Methylbenzenesulfonate (6a): To a solution of 2-phenylethan-1-ol (100 mg, 0.82 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14 mL, 0.98 mmol, 1.2 eq) was added in dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (10mg, 0.082 mmol, 0.1 eq) followed by slow addition of p-toulenesulfonyl chloride (188 mg, 0.98 mmol, 1.2 eq) in dry DCM at 0 ˚C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**6a**). Solid; yield = 205 mg, 90%; R_f = 0.61 (ethyl acetate/petroleum ether = 30/70); mp = 39-41 °C, **^{1}H NMR (400MHz, $CDCl_3$)** δ = 7.72 (d, *J* = 7.9 Hz, 2 H), 7.39 - 7.22 (m, 5 H), 7.14 (d, *J* = 6.7 Hz, 2 H), 4.24 (t, *J* = 7.3 Hz, 2 H), 2.99 (t, *J* = 7.0 Hz, 2 H), 2.46 (s, 3 H), **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 144.6, 136.2, 132.9, 129.8, 128.9, 128.6, 127.8, 126.8, 77.3, 76.7, 70.6, 35.3, 21.6 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{16}O_3S_1Na$ $[M+Na]^+$ 299.0712, found 299.0712.

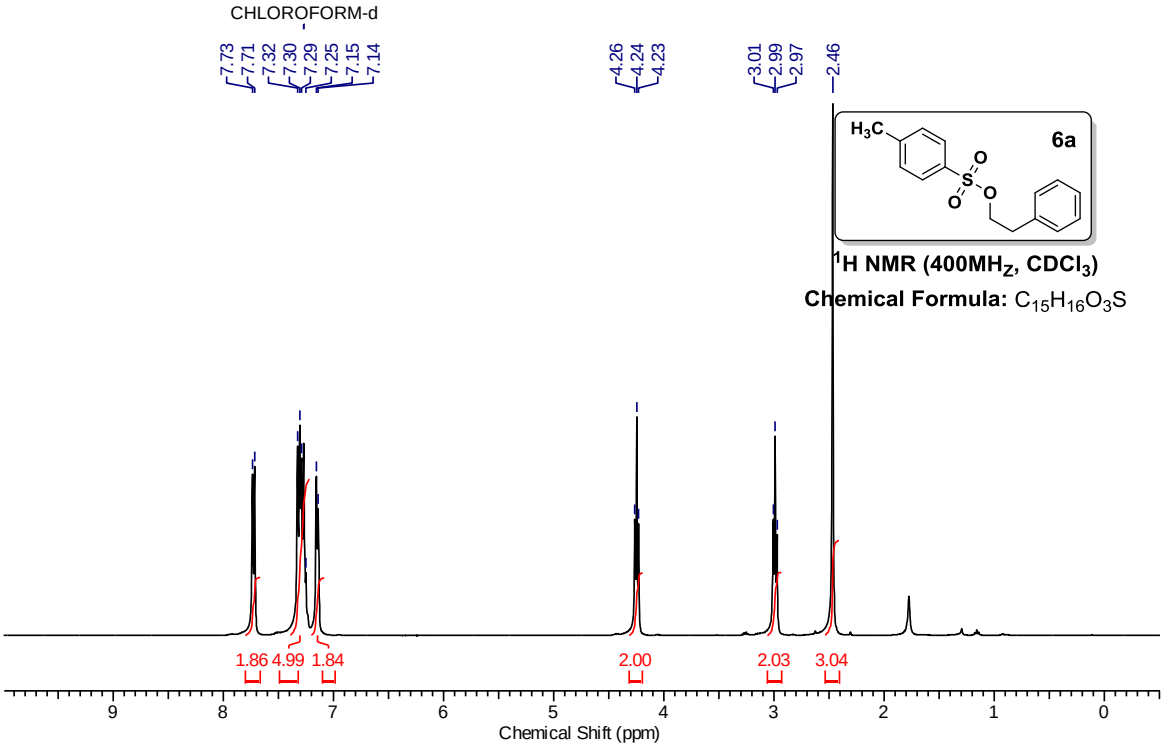


Figure S13. ^{1}H NMR spectrum of **6a** in $CDCl_3$.

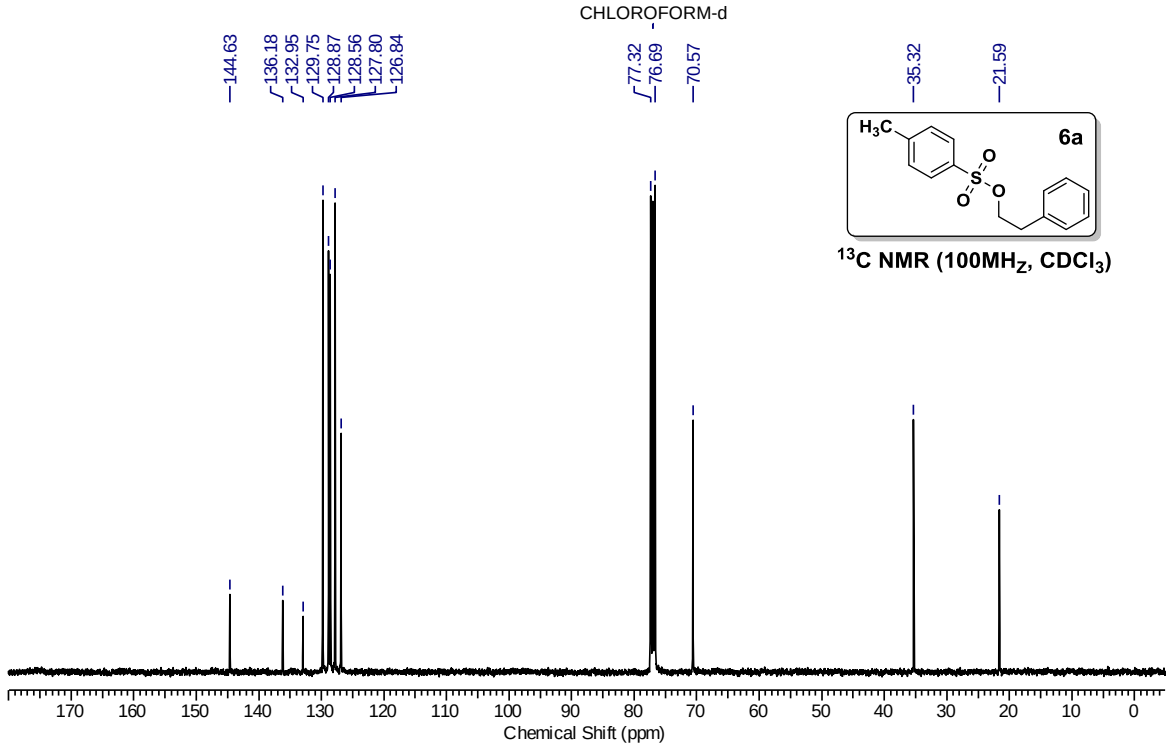


Figure S14. ^{13}C NMR spectrum of **6a** in $CDCl_3$.

1.8 Synthesis of phenethyl 4-Methoxybenzenesulfonate (7a): To a solution of 2-phenylethan-1-ol (100 mg, 0.82 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14 mL, 0.98 mmol, 1.2 eq) was added in dropwise manner in the presence of the catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.082 mmol, 0.1 eq) followed by slow addition of 4-methoxybenzenesulfonyl chloride (203 mg, 0.98 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**7a**), liquid; yield = 210 mg, 87%; R_f = 0.55(ethyl acetate/petroleum ether = 30/70); **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.83 - 7.72 (m, 2 H), 7.32 - 7.23 (m, 3 H), 7.20 - 7.10 (m, 2 H), 7.04 - 6.92 (m, 2 H), 4.23 (t, *J* = 7.1 Hz, 2 H), 3.91 (s, 3 H), 2.99 (t, *J* = 7.1 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 163.6, 136.2, 129.9, 128.8, 128.5, 127.3, 126.8, 114.3, 77.6, 76.4, 70.4, 55.6, 35.3 ppm.

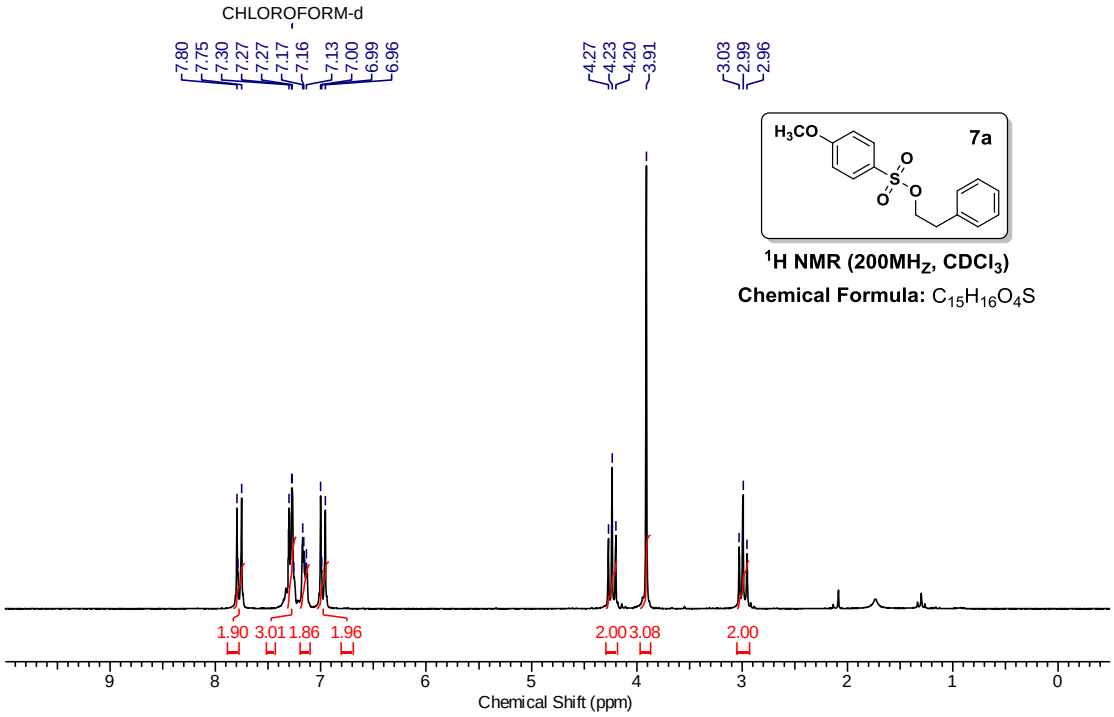


Figure S15. ^{1}H NMR spectrum of **7a** in $CDCl_3$.

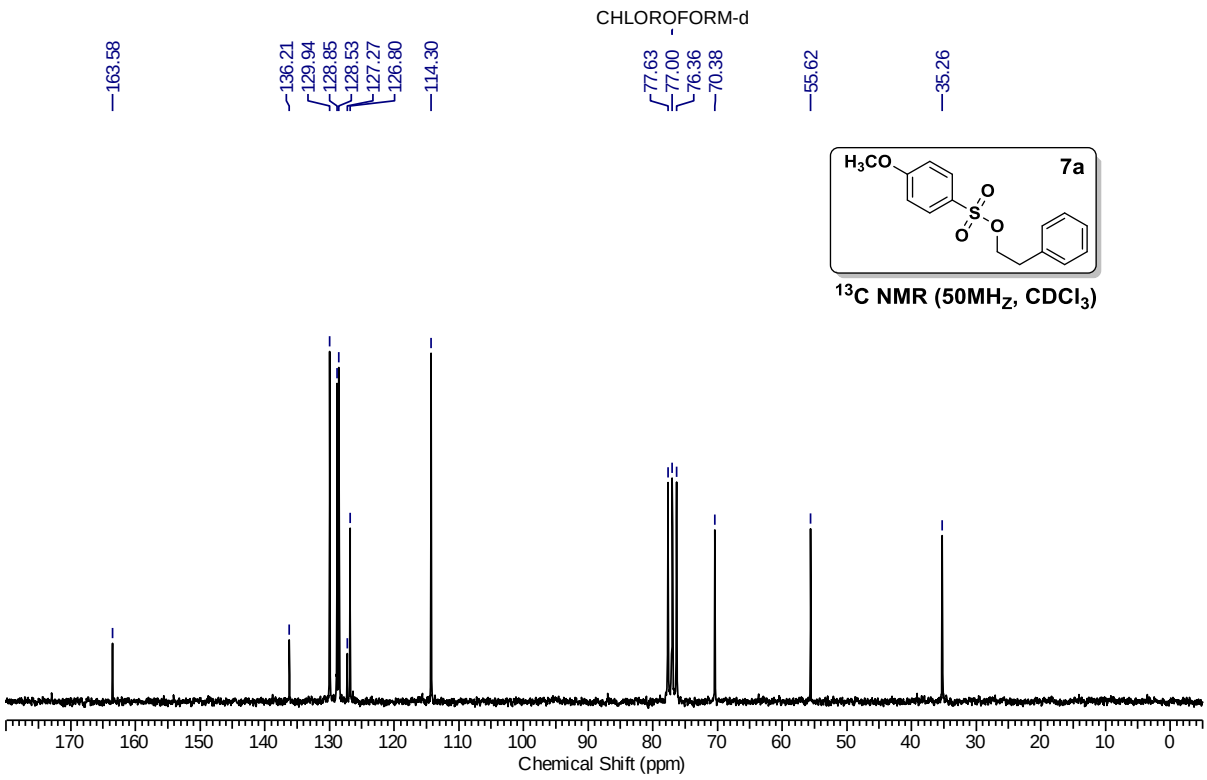
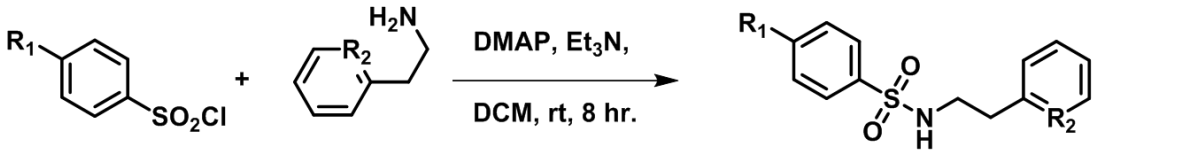


Figure S16. ^{13}C NMR spectrum of **7a** in $CDCl_3$.

1.9 General Synthetic Procedure for the Preparation of Sulfonamides: To the cooled solution of 1.0 eq. of 2- phenylethanamine/2-(pyridin-2-yl)ethan-1-amine in dry DCM, 1.2 eq. of dry Et_3N was added in dropwise manner in the presence of the catalytic amount of DMAP (dimethylaminopyridine) followed by slow addition of 1.2 eq. of *p*-substituted benzene sulfonyl chloride in dry DCM at 0 ˚C to yield corresponding dimeric sulfonamides. The reaction mixture was allowed to reach room temperature and was further stirred. After the reaction (monitored by TLC), the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: ethyl acetate/pet ether), yielded pure product. The purified products were crystallized from organic solvents or a mixture of organic solvents by slow evaporation.

A similar reaction procedure has been followed for the synthesis of sulfonamide-like sulfoesters. The crude organic product has been purified by flash column chromatography (eluent: ethyl acetate/pet ether). The Purified products were crystallized from organic solvents or a mixture of organic solvents by slow evaporation. Here in sulfonamide synthesis **2-phenylethanamine** used as a limiting reactant in synthesis of (**1b**, **2b**, **3b**, **4b**, **5b**, **6b**, **7b**) and **2-(pyridin-2-yl)ethan-1-amine** for (**1c**, **2c**, **3c**, **4c**, **5c**, **6c**, **7c**) instead of **2-phenylethan-1-ol** which is used as a limiting reactant in sulfoester synthesis.



1b, R_1= CF_3,	**R_2=CH**	**1c, R_1= CF_3,**	**R_2=N**
2b, R_1= CN,	**R_2=CH**	**2c, R_1= CN,**	**R_2=N**
3b, R_1= Cl,	**R_2=CH**	**3c, R_1= Cl,**	**R_2=N**
4b, R_1= Br,	**R_2=CH**	**4c, R_1= Br,**	**R_2=N**
5b, R_1= H,	**R_2=CH**	**5c, R_1= H,**	**R_2=N**
6b, R_1= CH_3,	**R_2=CH**	**6c, R_1= CH_3,**	**R_2=N**
7b, R_1= OCH_3,	**R_2=CH**	**7c, R_1= OCH_3,**	**R_2=N**

Figure S17. Scheme-Synthetic procedure for the preparation of Sulfonamides (**1b**, **2b**, **3b**, **4b**, **5b**, **6b**, **7b**) and (**1c**, **2c**, **3c**, **4c**, **5c**, **6c**, **7c**).

1.10 Synthesis of N-phenethyl-4-(trifluoromethyl) benzenesulfonamide (1b): To a solution of 2- phenylethanamine (100 mg, 0.83 mmol, 1.0eq) in dry DCM (10 mL), dry Et_3N (0.14 mL, 0.99 mmol, 1.2 eq) was added in dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.083 mmol, 0.1eq) followed by slow addition of 4-trifluoromethylbenzenesulfonyl chloride (240 mg, 0.99 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**1b**). Solid; yield = 140 mg, 53%; R_f = 0.56 (ethyl acetate/petroleum ether = 30/70); mp = 112-114 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.96 - 7.85 (m, *J* = 8.2 Hz, 2 H), 7.80 - 7.69 (m, *J* = 8.3 Hz, 2 H), 7.34 - 7.21 (m, 4 H), 7.13 - 7.02 (m, 2 H), 4.55 (t, *J* = 5.9 Hz, 1 H), 3.29 (q, *J* = 6.6 Hz, 2 H), 2.80 (t, *J* = 6.8 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 143.4, 137.3, 128.8, 128.7, 127.5, 126.9, 126.3, 126.3, 126.2, 126.1, 77.6, 76.4, 44.2, 35.8 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{14}NO_2F_3SNa$ $[M+Na]^+$ 352.0590, found 352.0580.

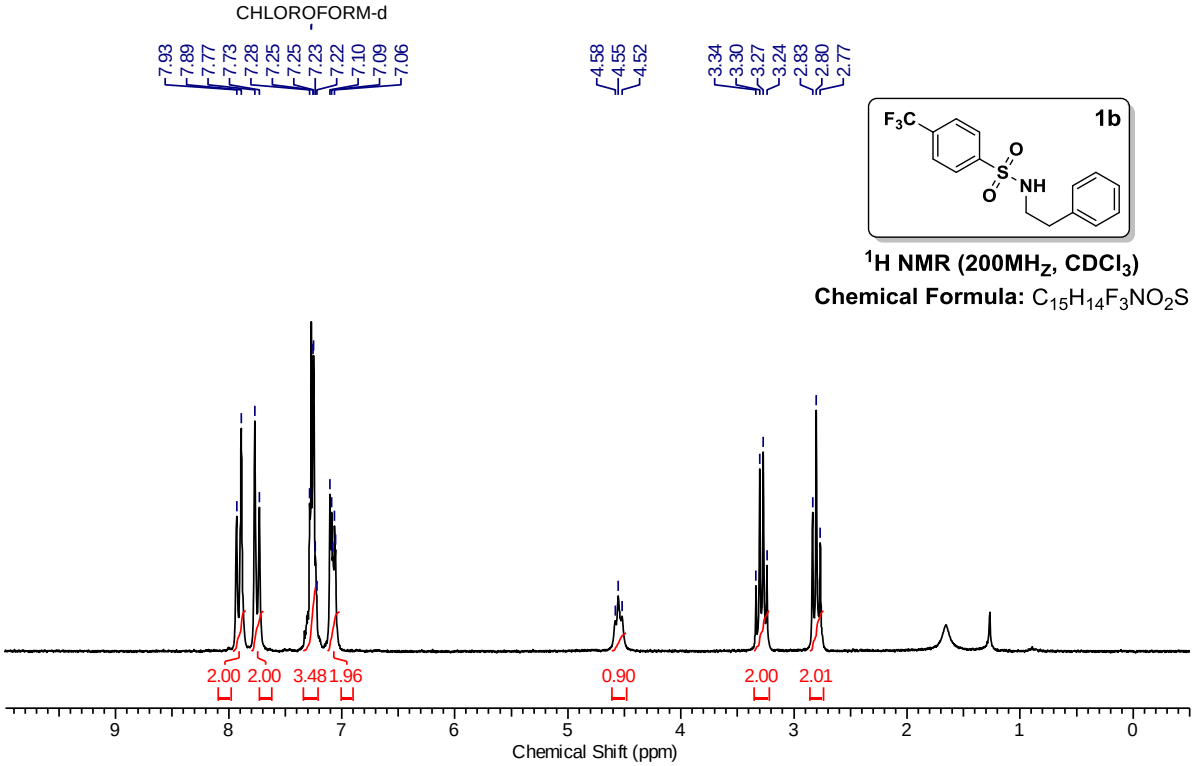


Figure S18. ^{1}H NMR spectrum of **1b** in $CDCl_3$.

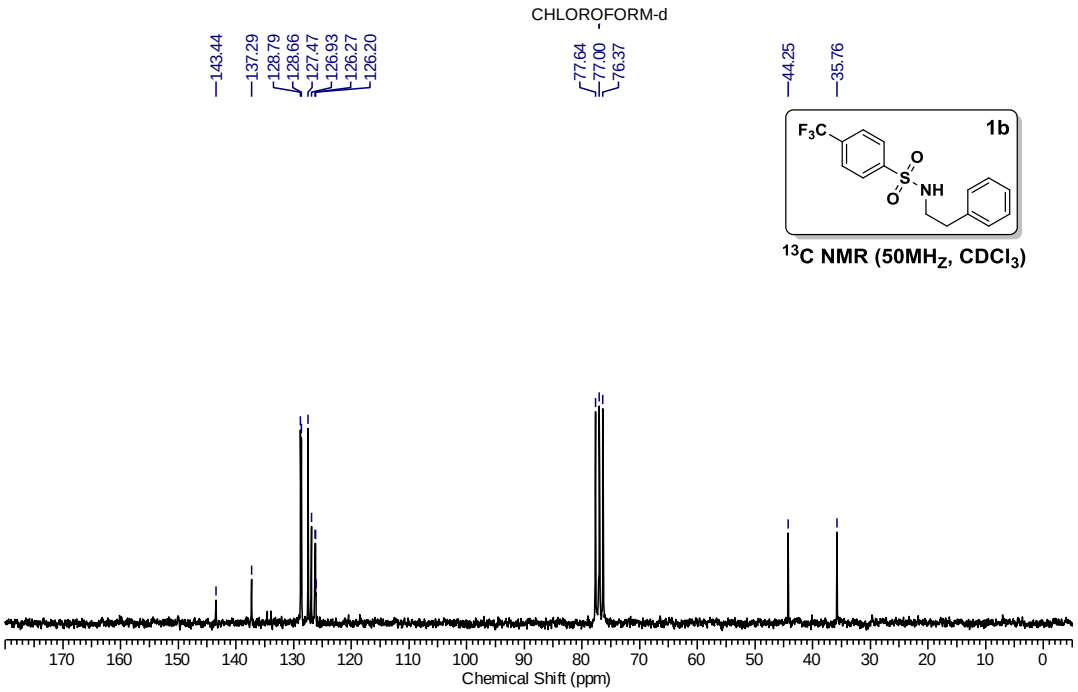


Figure S19. ^{13}C NMR spectrum of **1b** in $CDCl_3$.

1.11 Synthesis of 4-cyano-N-phenethylbenzenesulfonamide (2b): To a solution of 2-phenylethanamine (100 mg, 0.83 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14 mL, 0.99 mmol, 1.2 eq) was added in a dropwise manner in presence of the catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.083 mmol, 0.1 eq) followed by slow addition of 4-cyanobenzenesulfonyl chloride (198 mg, 0.99 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**2b**). Solid; yield = 145 mg, 62%; R_f = 0.35 (ethyl acetate/petroleum ether = 30/70); mp = 118-119 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.94 - 7.83 (m, 2 H), 7.82 - 7.71 (m, 2 H), 7.34 - 7.19 (m, 4 H), 7.13 - 7.02 (m, 2 H), 4.61 (t, *J* = 5.9 Hz, 1 H), 3.29 (q, *J* = 6.6 Hz, 2 H), 2.80 (t, *J* = 6.8 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 144.2, 137.2, 132.9, 128.8, 128.6, 127.6, 127.0, 117.3, 116.3, 77.6, 76.4, 44.3, 35.8 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{15}N_2O_2S$ $[M+H]^+$ 287.0849, found 287.0849.

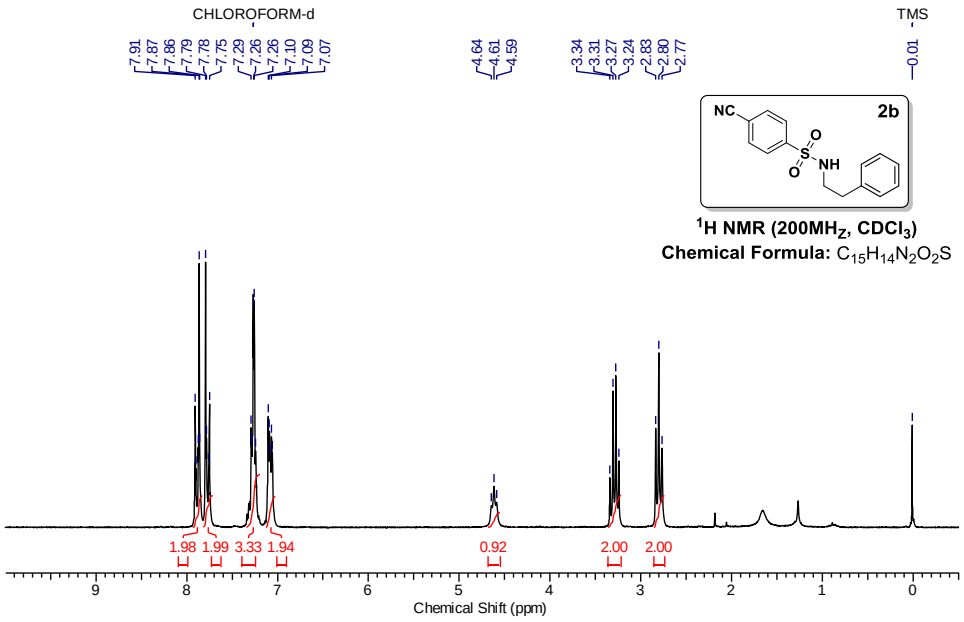


Figure S20. ^{1}H NMR spectrum of **2b** in $CDCl_3$.

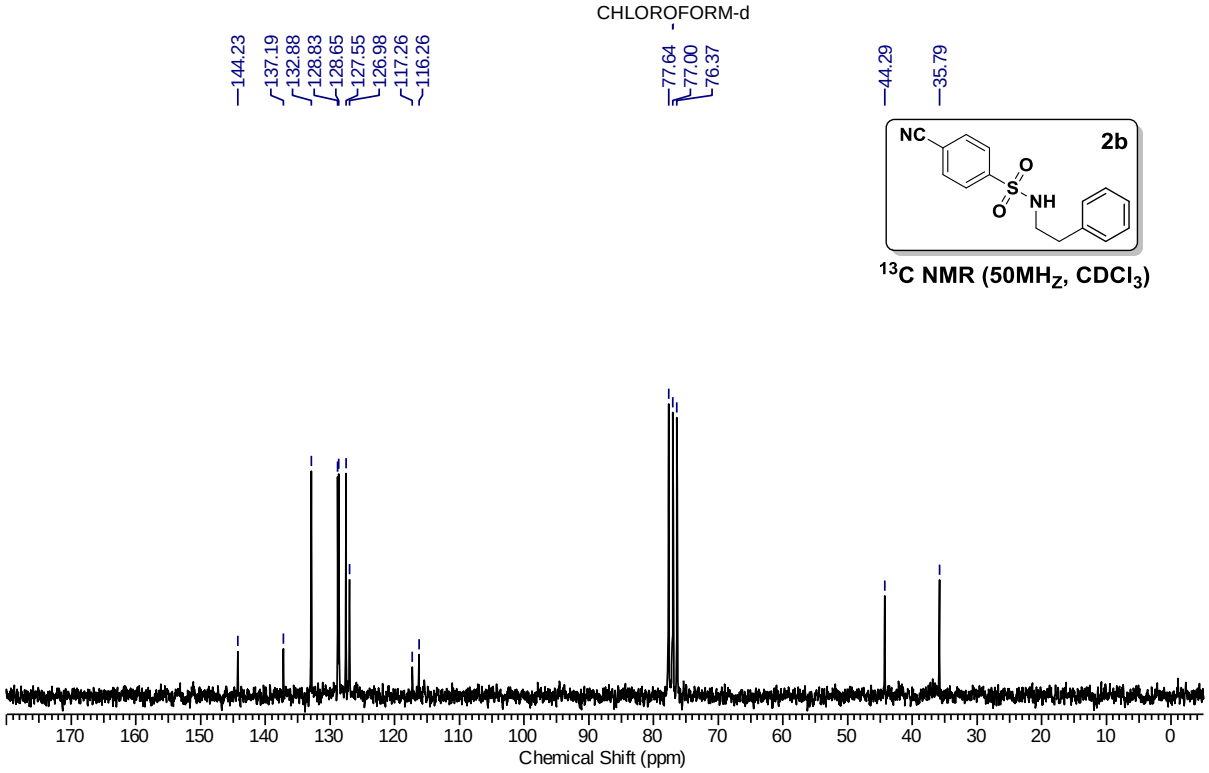


Figure S21. ^{13}C NMR spectrum of **2b** in $CDCl_3$.

1.12 Synthesis of 4-chloro-N-phenethylbenzenesulfonamide (3b): To a solution of 2-phenylethanamine (150 mg, 1.24 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.21 mL, 1.49 mmol, 1.2 eq) was added in dropwise manner in the presence of the catalytic amount of DMAP (dimethylaminopyridine) (15 mg, 0.124mmol, 0.1 eq) followed by slow addition of 4-chlorobenzenesulfonyl chloride (314 mg, 1.49 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded(**3b**)**.** Solid; yield = 318mg, 88%; R_f = 0.50 (ethyl acetate/petroleum ether = 30/70); mp = 89-91 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.72 - 7.59 (m, 4 H), 7.36 - 7.20 (m, 3 H), 7.17 - 7.03 (m, 2 H), 4.68 (br. s., 1 H), 3.34 - 3.17 (m, 2 H), 2.87 - 2.72 (m, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 138.8, 137.4, 132.3, 128.8, 128.7, 128.5, 127.5, 126.8, 77.6, 76.4, 44.2, 35.7 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{14}ClNO_2SNa$ $[M+Na]^+$ 318.0326, found 318.0323.

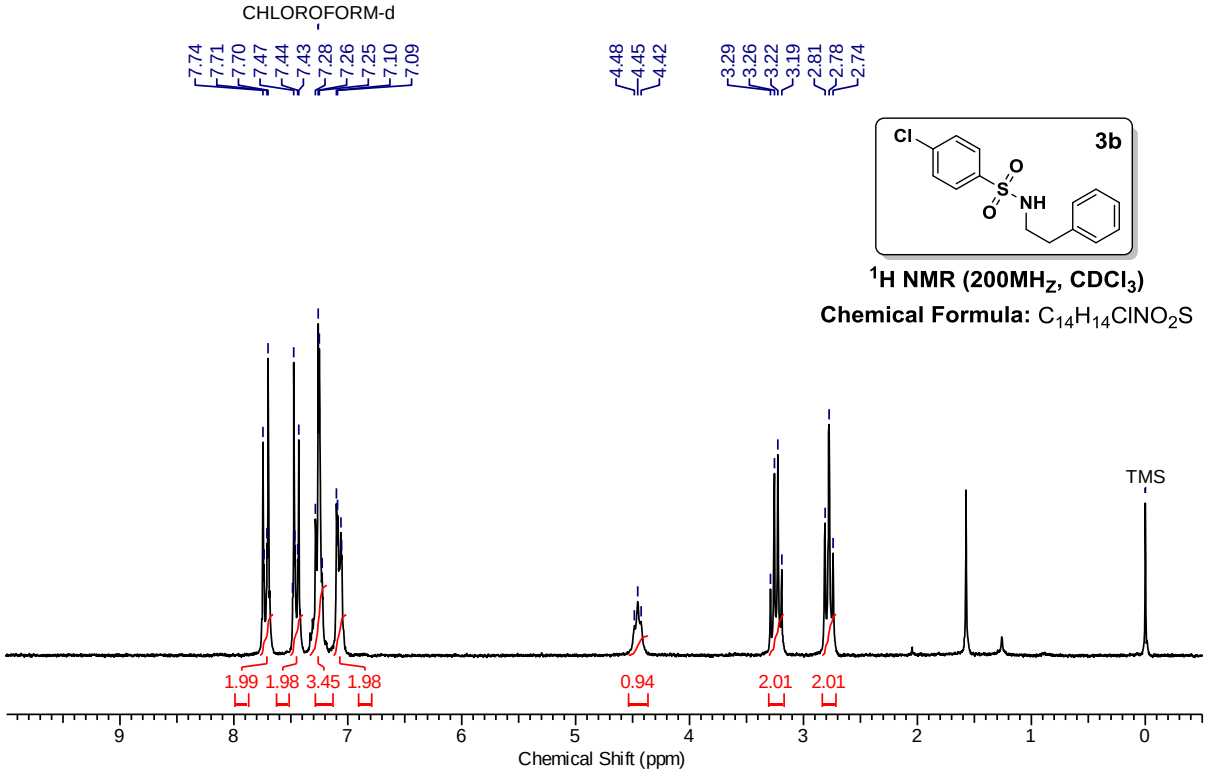


Figure S22. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

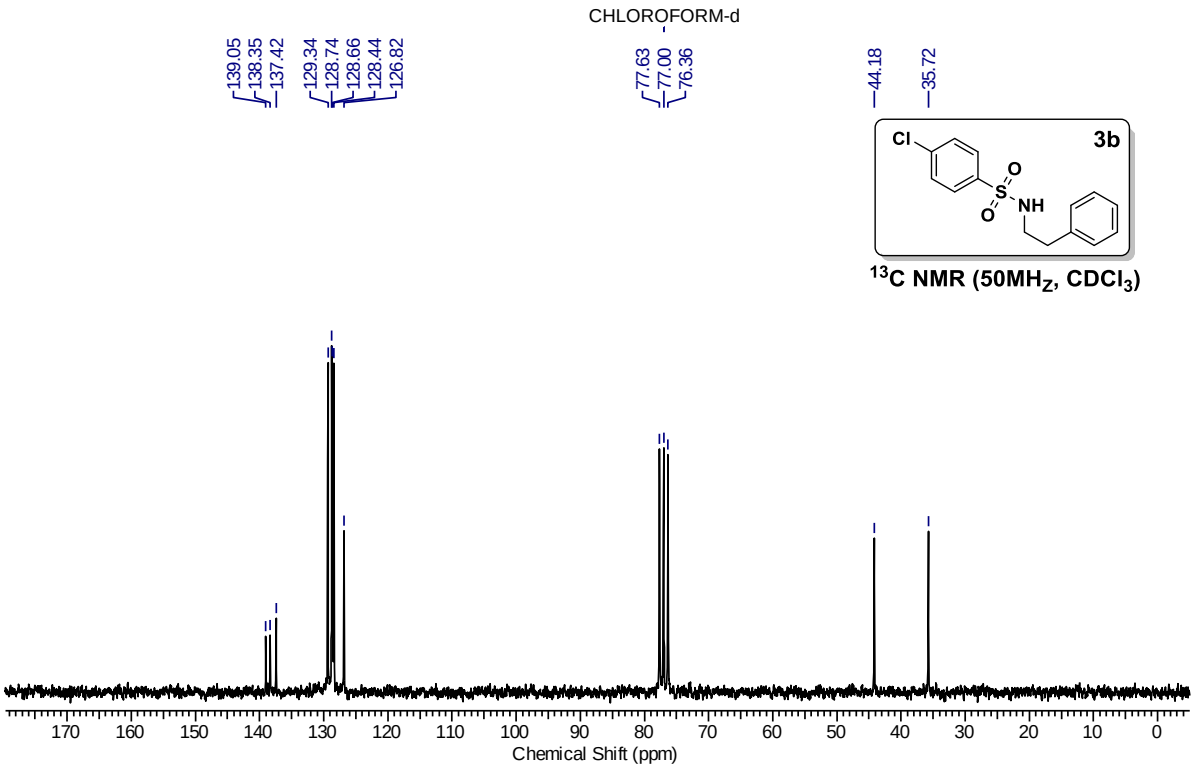


Figure S23. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

1.13 Synthesis of 4-Bromo-N-phenethylbenzenesulfonamide (4b): To a solution of 2-phenylethanamine (100 mg, 0.83 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14 ml, 0.99 mmol, 1.2 eq) was added in a dropwise manner in the presence of the catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.083mmol, 0.1 eq) followed by slow addition of 4-bromobenzenesulfonyl chloride (250 mg, 0.99 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**4b**)**.** Solid; yield = 210 mg, 76%; R_f = 0.50 (ethyl acetate/petroleum ether = 30/70); mp = 88-90 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.77 - 7.65 (m, 2 H), 7.51 - 7.39 (m, 2 H), 7.34 - 7.18 (m, 4 H), 7.07 (dd, *J* = 2.0, 7.3 Hz, 2 H), 4.45 (t, *J* = 5.9 Hz, 1 H), 3.24 (q, *J* = 6.6 Hz, 2 H), 2.78 (t, *J* = 6.8 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 139.1, 138.3, 137.4, 129.3, 128.7, 128.7, 128.4, 126.8, 44.2, 35.7 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{15}BrNO_2S$ $[M+H]^+$ 340.0001, found 340.0002.

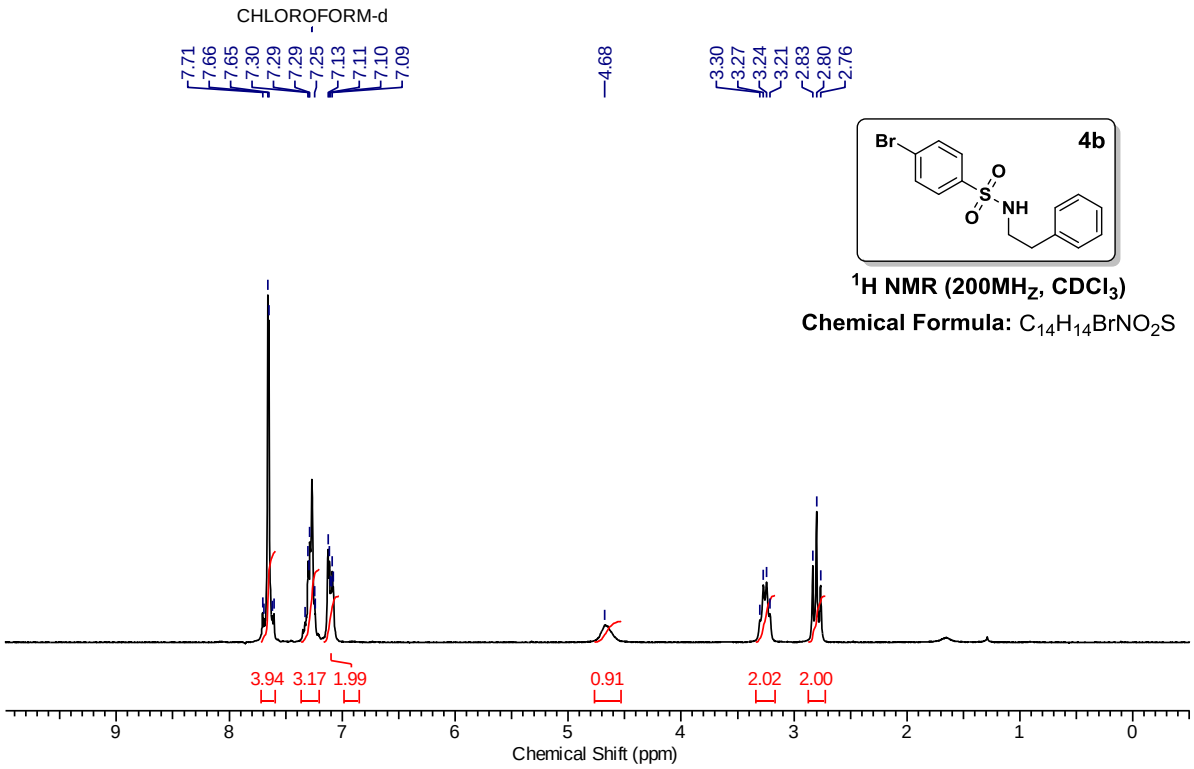


Figure S24. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

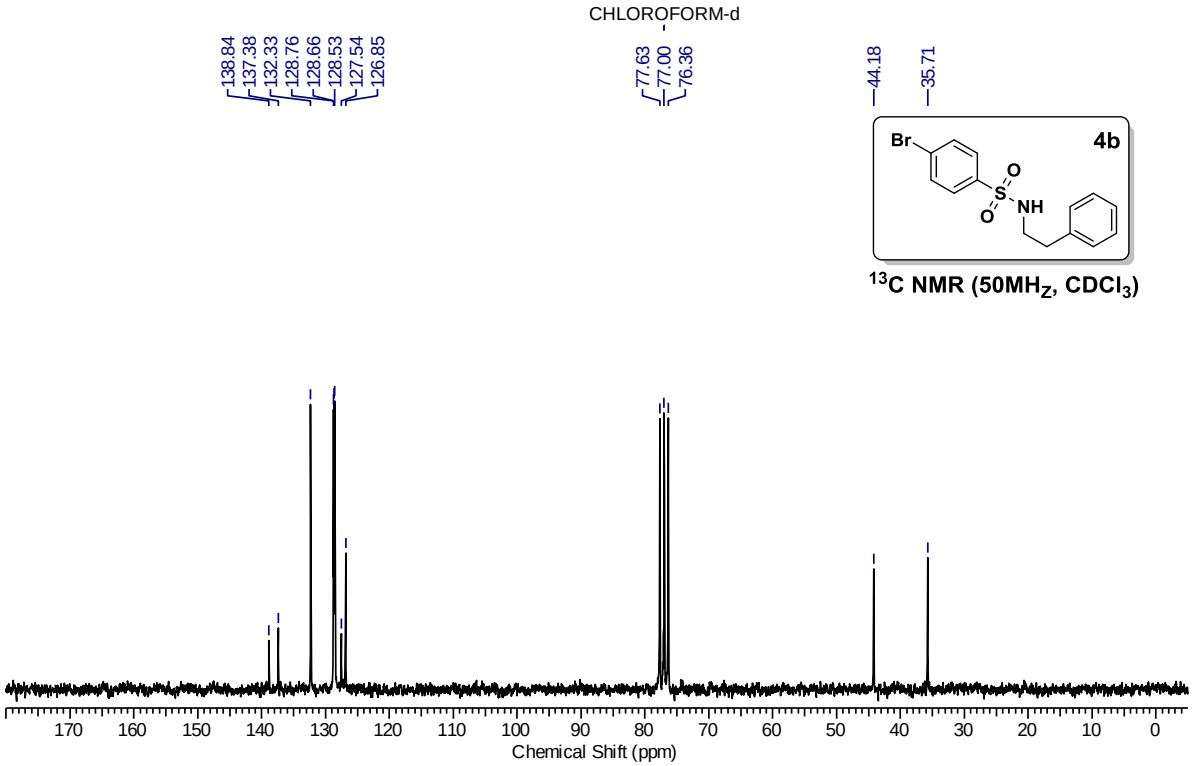


Figure S25. ^{13}C NMR spectrum of **4b** in $CDCl_3$.

1.14 Synthesis of N-phenethylbenzenesulfonamide (5b): To a solution of 2-phenylethanamine (50 mg, 0.41 mmol, 1.0 eq) in dry DCM (5 mL), dry Et_3N (0.07 mL, 0.49 mmol, 1.2 eq) was added in dropwise manner in presence of catalytic amount of DMAP (dimethylamino pyridine) (5 mg, 0.041mmol, 0.1 eq) followed by slow addition of benzenesulfonyl chloride (0.06 mL, 0.99 mmol, 1.2 eq) in dry DCM at 0 ˚C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**5b**)**.** Solid; yield = 90mg, 84%; R_f = 0.46 (ethyl acetate/petroleum ether = 30/70); mp = 65-67 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.89 - 7.79 (m, 2 H), 7.66 - 7.46 (m, 3 H), 7.36 - 7.20 (m, 4 H), 7.10 (dd, *J* = 1.9, 7.5 Hz, 2 H), 4.49 (br. s., 1 H), 3.27 (t, *J* = 6.8 Hz, 2 H), 2.79 (t, *J* = 6.9 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 139.8, 137.6, 132.6, 129.1, 128.7, 128.7, 127.0, 126.8, 77.6, 76.4, 44.2, 35.7 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{16}NO_2S$ $[M+H]^+$ 262.0896, found 262.0894.

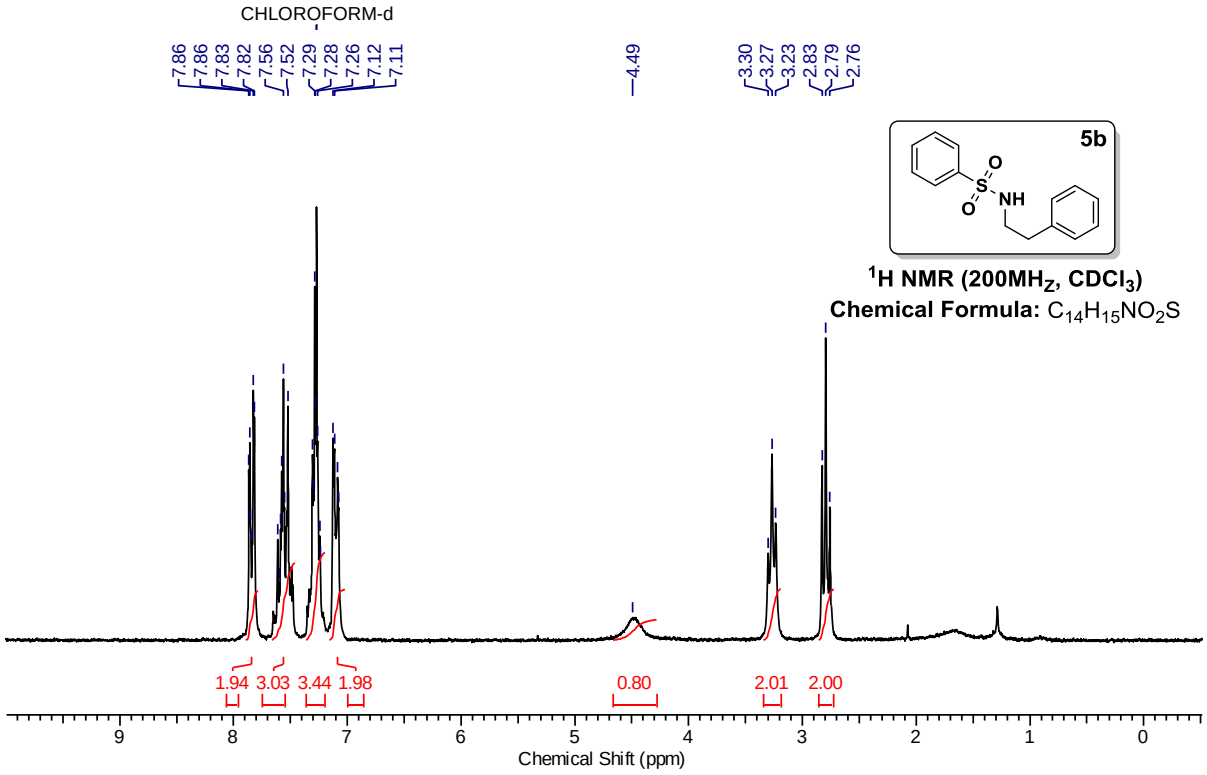


Figure S26. ^{1}H NMR spectrum of **5b** in $CDCl_3$.

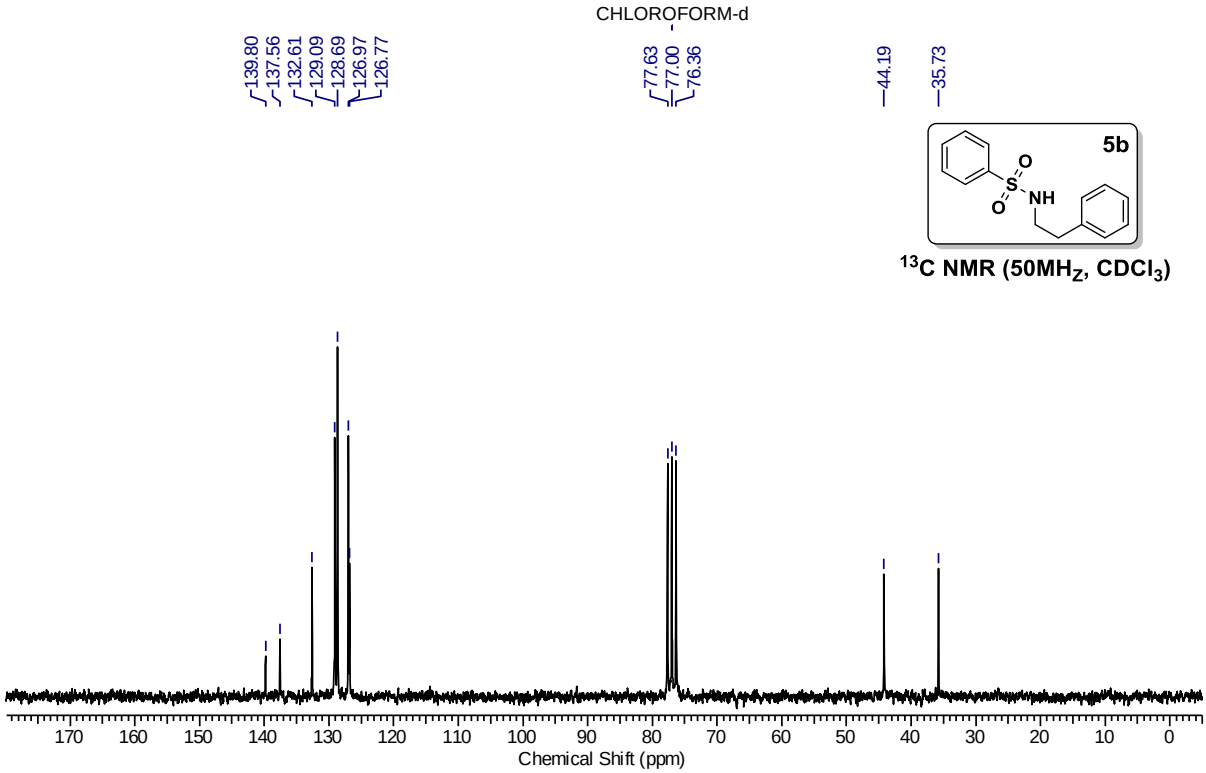


Figure S27. ^{13}C NMR spectrum of **5b** in $CDCl_3$.

1.15 Synthesis of 4-Methyl-N-phenethylbenzenesulfonamide (6b): To a solution of 2-phenylethanamine (150 mg, 1.24 mmol, 1.0 eq) in dry DCM (10 mL), dry Et3N (0.21 mL, 1.49 mmol, 1.2 eq) was added in dropwise manner in the presence of the catalytic amount of DMAP(dimethylaminopyridine) (15 mg, 0.124mmol, 0.1 eq) followed by slow addition of *p*-Toulenesulfonyl chloride (284 mg, 1.49 mmol, 1.2 eq) in dry DCM at 0 ˚C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous $Na2SO_4$ and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**6b**)**.** Solid; yield = 270 mg, 80%; R_f = 0.46 (ethyl acetate/petroleum ether = 30/70); mp = 64-66 °C, **^{1}H NMR (200MHz, CDCl3)** δ = 7.78 - 7.66 (m, 2 H), 7.38 - 7.22 (m, 5 H), 7.11 (dd, *J* = 1.9, 7.5 Hz, 2 H), 4.54 (br. s., 1 H), 3.24 (t, *J* = 6.9 Hz, 2 H), 2.79 (t, *J* = 6.9 Hz, 2 H), 2.46 (s, 3 H), **^{13}C NMR (50MHz, CDCl3)** δ = 143.4, 137.7, 136.8, 129.7, 128.7, 127.0, 126.7, 77.6, 76.4, 44.2, 35.7, 21.5 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{18}NO_2S$ $[M+H]^+$ 276.1053, found 276.1048.

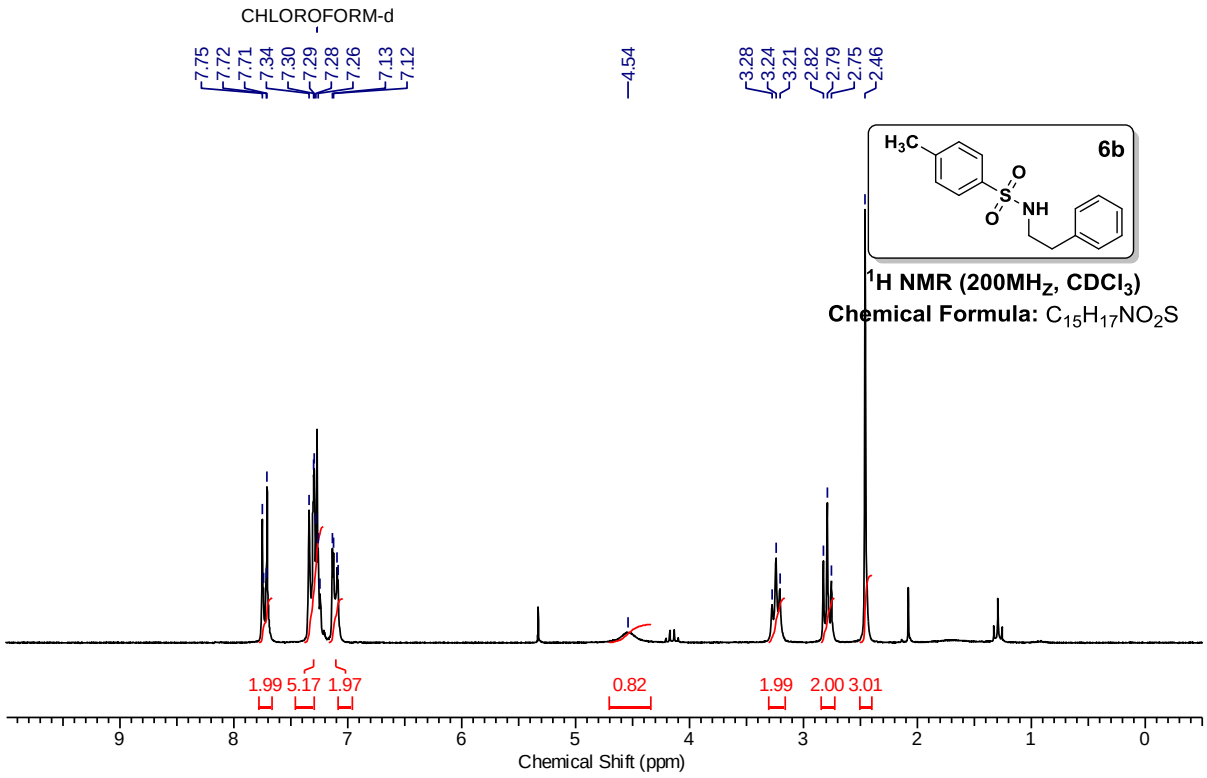


Figure S28. ^{1}H NMR spectrum of **6b** in $CDCl_3$.

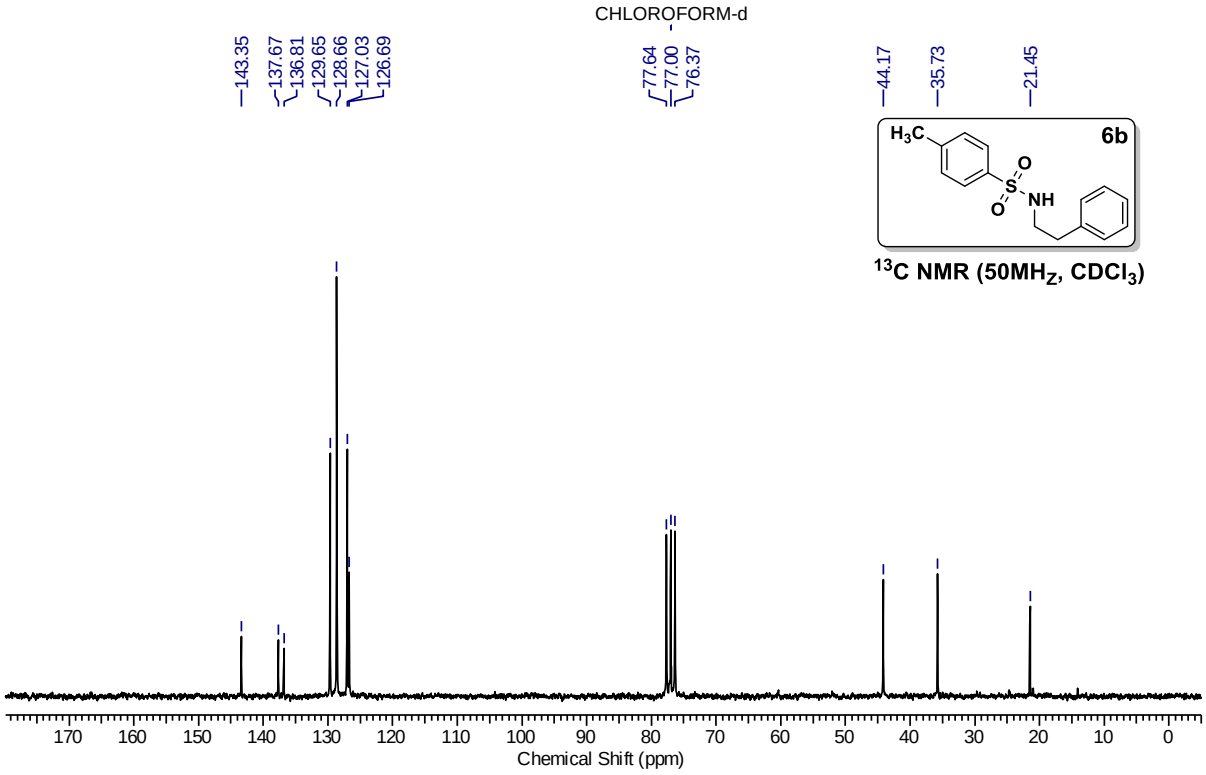


Figure S29. ^{13}C NMR spectrum of **6b** in $CDCl_3$.

1.16 Synthesis of 4-Methoxy-N-phenethylbenzenesulfonamide (7b): To a solution of 2-phenylethanamine (100 mg, 0.83 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14 mL, 0.99 mmol, 1.2 eq) was added in a dropwise manner in the presence of the catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.083 mmol, 0.1 eq) followed by slow addition of 4-methoxybenzenesulfonyl chloride (202 mg, 0.99 mmol, 1.2 eq) in dry DCM at 0 ˚C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**7b**)**.** Solid; yield = 200 mg, 84%; R_f = 0.32 (ethyl acetate/petroleum ether = 30/70); mp = 41-43 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 7.83 - 7.71 (m, 2 H), 7.36 - 7.19 (m, 3 H), 7.11 (dd, *J* = 1.8, 7.5 Hz, 2 H), 7.04 - 6.93 (m, 2 H), 3.90 (s, 3 H), 3.23 (t, *J* = 7.0 Hz, 2 H), 2.79 (t, *J* = 7.0 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 162.8, 137.7, 131.4, 129.2, 128.7, 126.7, 114.2, 77.6, 76.4, 55.6, 44.1, 35.7 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{17}NO_3SNa$ $[M+Na]^+$ 314.0821, found 314.0818.

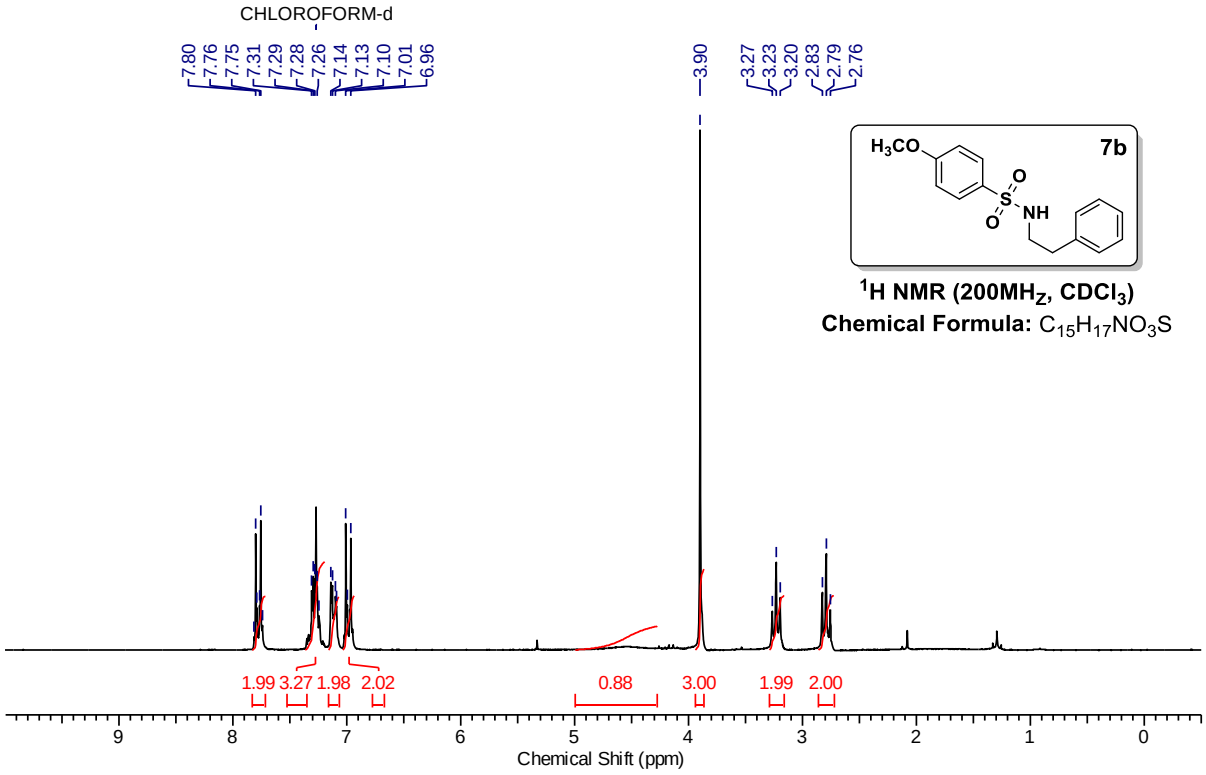


Figure S30. ^{1}H NMR spectrum of **7b** in $CDCl_3$.

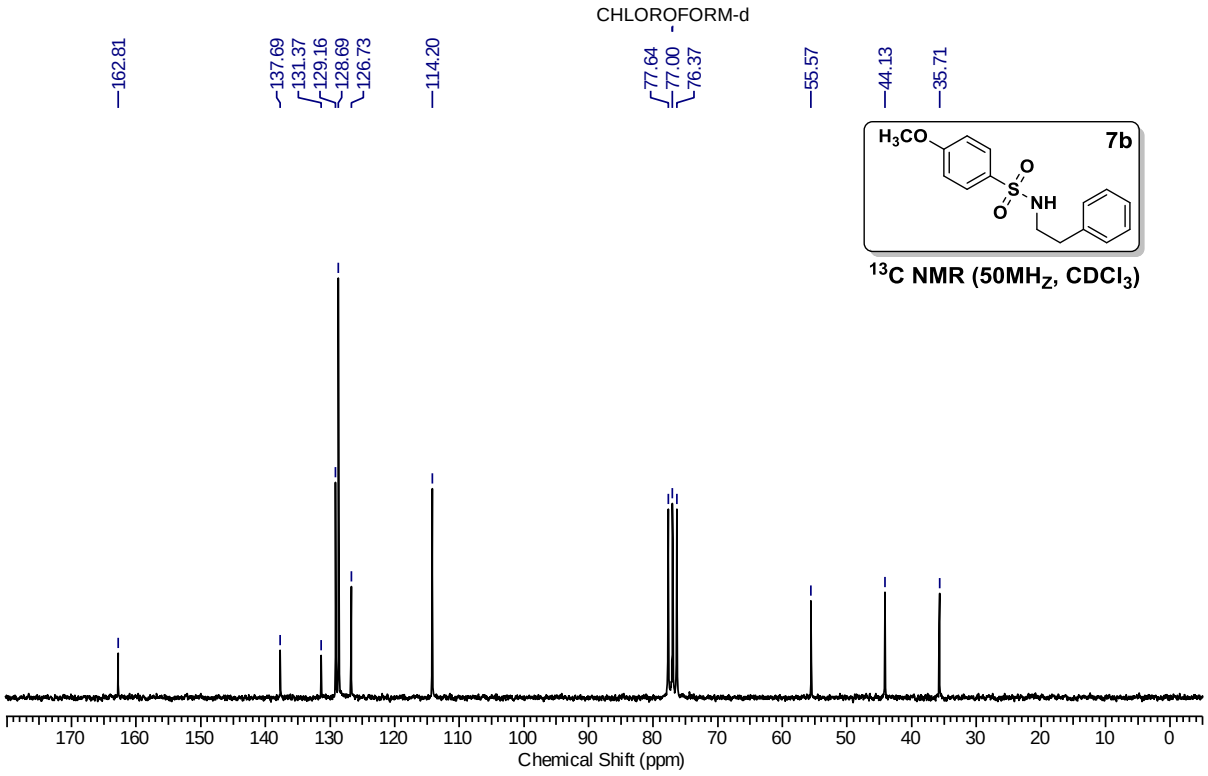


Figure S31. ^{13}C NMR spectrum of **7b** in $CDCl_3$.

1.17 Synthesis of N-(2-(pyridin-2-yl)ethyl)-4-(trifluoromethyl)benzenesulfonamide (1c): To a solution of 2-(2-Pyridyl)ethylamine (75 mg, 0.61 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.10 mL, 0.73mmol, 1.2 eq) was added in a dropwise manner in the presence of the catalytic amount of DMAP (dimethylaminopyridine) (8 mg, 0.061 mmol, 0.1eq) followed by slow addition of 4-trifluoromethylbenzenesulfonyl chloride (179 mg, 0.73 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded(**1c**). Solid; yield = 155 mg, 77%; R_f = 0.24 (ethyl acetate/petroleum ether = 40/60); mp = 102-104 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 8.55 - 8.33 (m, 1 H), 7.98 (d, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 7.59 (dt, *J* = 1.8, 7.7 Hz, 1 H), 7.22 - 6.97 (m, 2 H), 6.55 (br. s., 1 H), 3.53 - 3.27 (m, 2 H), 2.96 (t, *J* = 5.9 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 158.7, 148.9, 143.8, 136.8, 127.4, 126.2, 126.2, 126.1, 126.0, 125.9, 123.5, 121.9, 77.6, 76.4, 42.2, 35.9 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{14}N_2O_2F_3S$ $[M+H]^+$ 287.0849, found 287.0849.

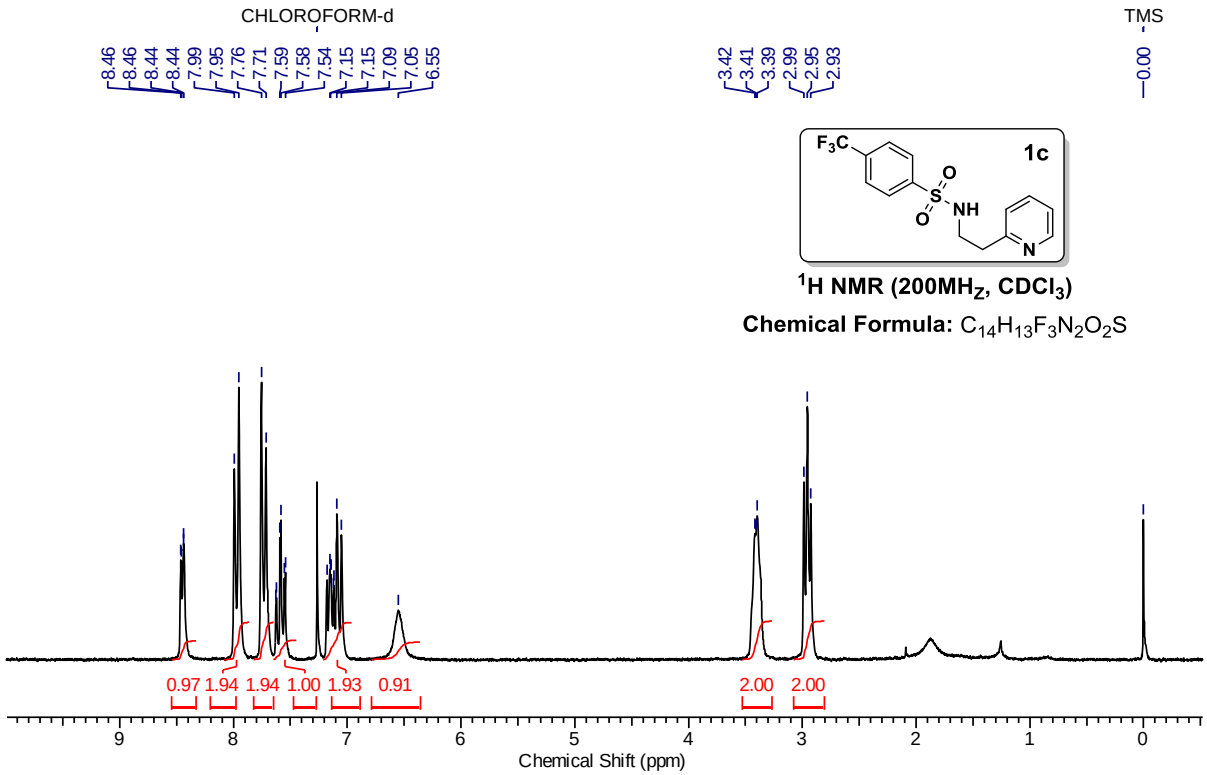


Figure S32. ^{1}H NMR spectrum of **1c** in $CDCl_3$.

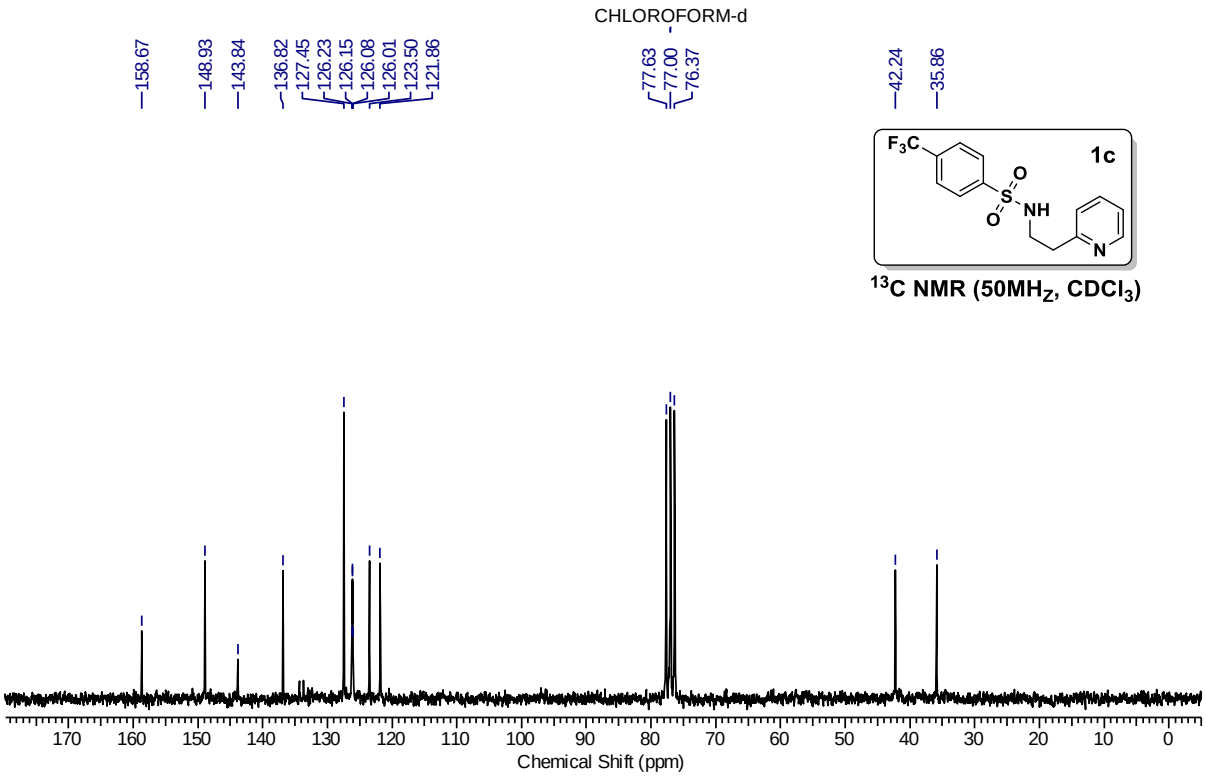


Figure S33. ^{13}C NMR spectrum of **1c** in $CDCl_3$.

1.18 Synthesis of 4-cyano-N-(2-(pyridin-2-yl)ethyl)benzenesulfonamide (2c): To a solution of 2-(2-Pyridyl)ethylamine (150 mg, 1.23 mmol, 1.0 eq)in dry DCM (10 mL), dry Et_3N (0.21 mL, 1.48 mmol, 1.2 eq) was added in a dropwise manner in presence of catalytic amount of DMAP(dimethylaminopyridine) (15 mg, 0.12 mmol, 0.1 eq) followed by slow addition of 4-cyanobenzenesulfonyl chloride (298 mg, 1.48 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**2c**). Solid; yield = 195mg, 56%; R_f = 0.17 (ethyl acetate/petroleum ether = 40/60); mp = 147-149 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 8.51 - 8.39 (m, 1 H), 8.03 - 7.90 (m, 2 H), 7.84 - 7.71 (m, 2 H), 7.60 (dt, *J* = 1.9, 7.7 Hz, 1 H), 7.22 - 7.02 (m, 2 H), 6.72 (br. s., 1 H), 3.40 (br. s., 2 H), 2.95 (t, *J* = 5.9 Hz, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 158.6, 148.8, 144.6, 137.0, 132.8, 127.6, 123.6, 121.9, 117.3, 116.0, 77.6, 76.4, 42.2, 35.7 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{14}N_3O_2S$ $[M+H]^+$ 288.0801, found 288.0799.

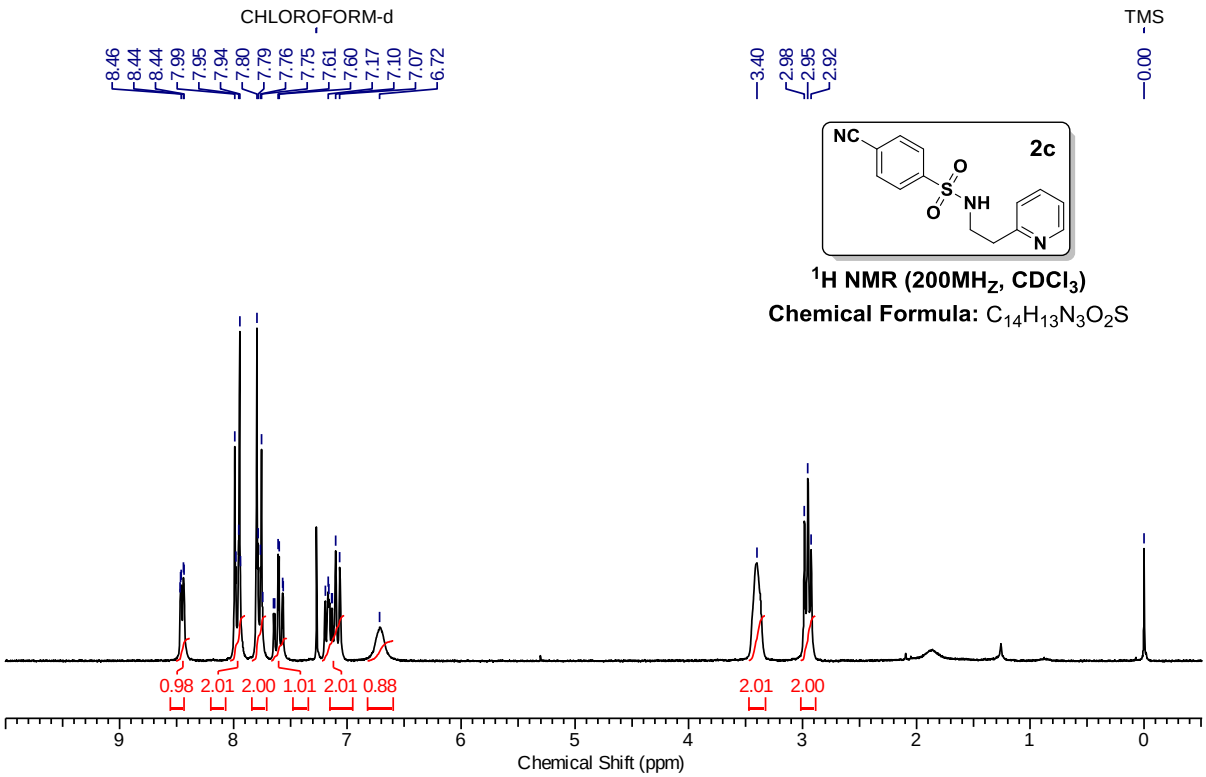


Figure S34. ^{1}H NMR spectrum of **2c** in $CDCl_3$.

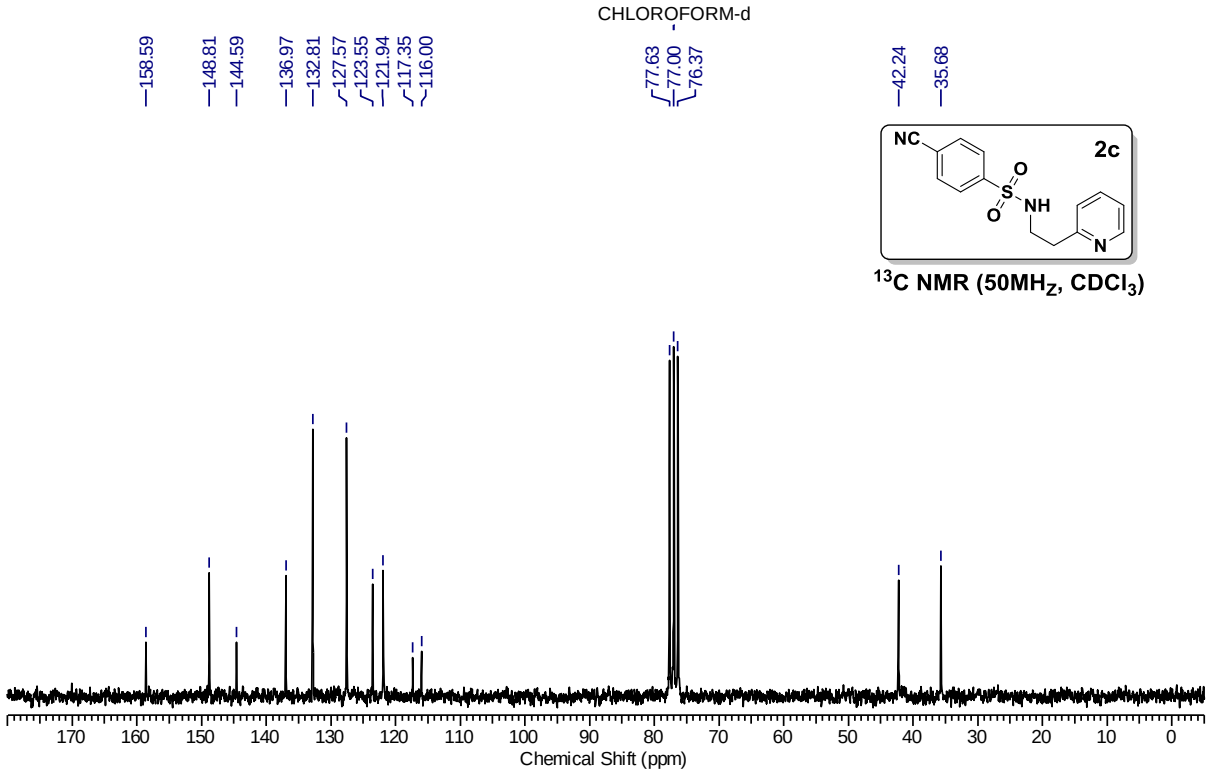


Figure S35. ^{13}C NMR spectrum of **2c** in $CDCl_3$.

1.19 Synthesis of 4-chloro-N-(2-(pyridin-2-yl)ethyl)benzenesulfonamide (3c): To a solution of 2-(2-Pyridyl)ethylamine (100 mg, 0.83 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14 mL, 0.99 mmol, 1.2 eq) was added in a dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.083 mmol, 0.1 eq) followed by slow addition of 4-chlorobenzenesulfonyl chloride (206 mg, 0.99mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**3c**). Solid; yield = 190 mg, 78%; R_f = 0.29 (ethyl acetate/petroleum ether = 40/60); mp = 110-112 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 8.48 (d, *J* = 4.2 Hz, 1 H), 7.83 - 7.75 (m, 2 H), 7.67 (dt, *J* = 1.8, 7.7 Hz, 1 H), 7.49 - 7.39 (m, 2 H), 7.26 - 7.10 (m, 2 H), 6.47 (t, *J* = 5.6 Hz, 1 H), 3.39 (q, *J* = 5.9 Hz, 2 H), 3.06 - 2.95 (m, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 158.5, 148.3, 138.8, 138.7, 137.4, 129.3, 128.5, 123.8, 122.0, 42.2, 35.7 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{14}N_2O_2ClS$ $[M+H]^+$ 297.0459, found 297.0467.

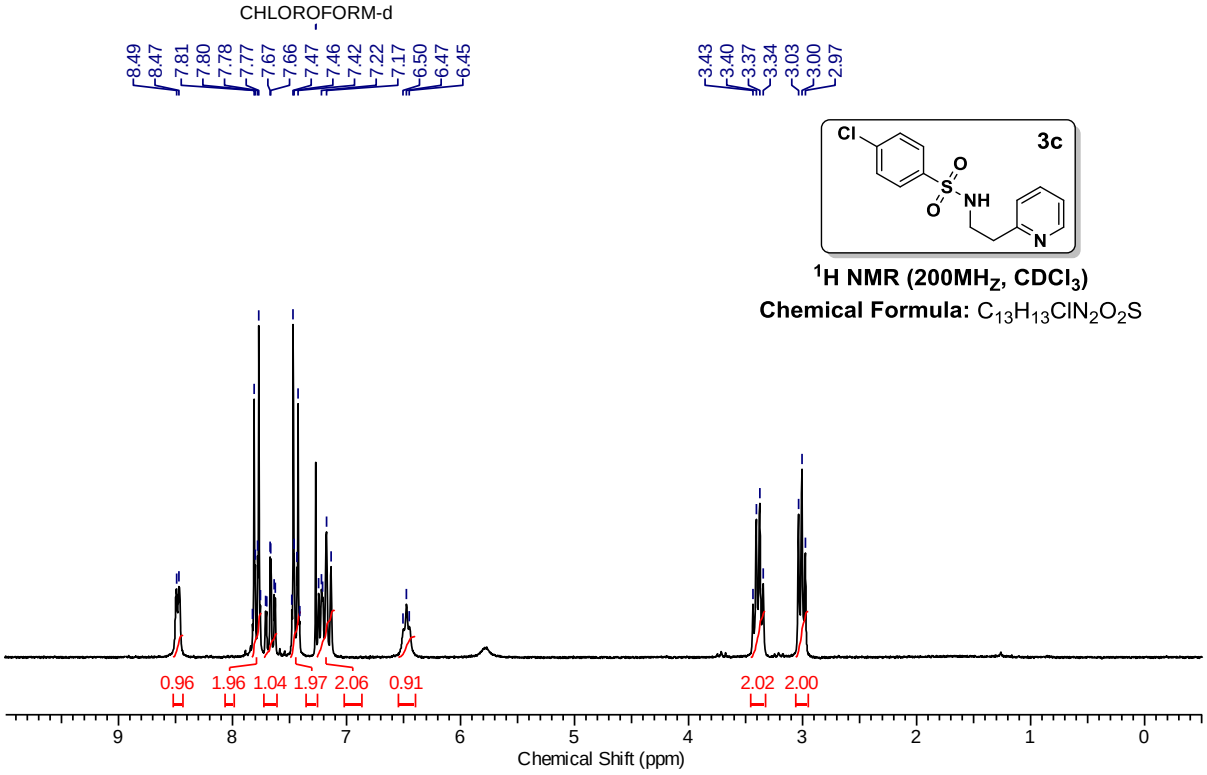


Figure S36. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

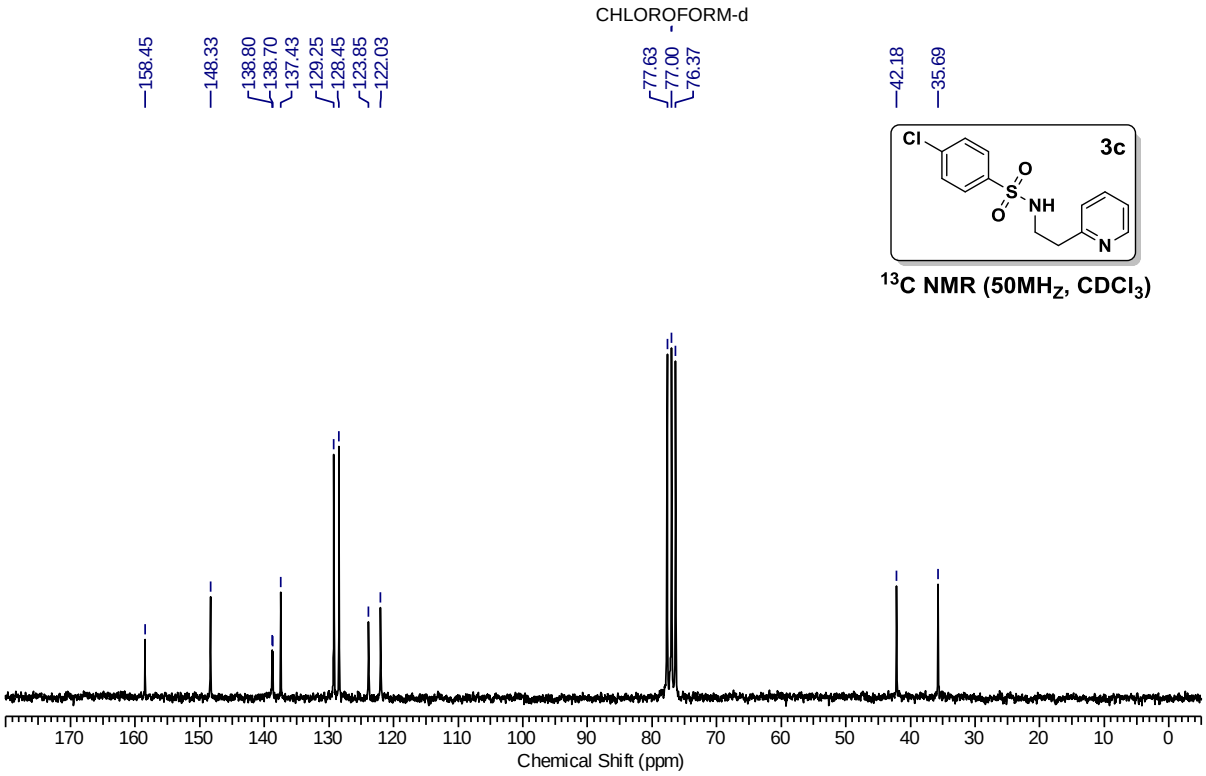


Figure S37. ^{13}C NMR spectrum of **3c** in $CDCl_3$.

1.20 Synthesis of 4-Bromo-N-(2-(pyridin-2-yl)ethyl)benzenesulfonamide (4c): To a solution of 2-(2-Pyridyl)ethylamine (75 mg, 0.61 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.10 mL, 0.73 mmol, 1.2 eq) was added in a dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (8 mg, 0.061 mmol, 0.1 eq) followed by slow addition of 4-bromobenzenesulfonyl chloride (187 mg, 0.73 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**4c**). Solid; yield = 110mg, 53%; R_f = 0.24 (ethyl acetate/petroleum ether = 40/60); mp = 100-102 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 8.45 (d, *J* = 4.2 Hz, 1 H), 7.75 - 7.55 (m, 5 H), 7.23 - 7.06 (m,2 H), 6.52 (t, *J* = 5.2 Hz, 1 H), 3.37 (q, *J* = 5.8 Hz, 2 H), 3.03 - 2.90 (m, 2 H) **^{13}C NMR (50MHz, $CDCl_3$)** δ = 158.4, 148.4, 139.2, 137.4, 132.2, 128.5, 127.2, 123.8, 122.0, 77.6, 76.4, 42.2, 35.7 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{14}N_2O_2BrS$ $[M+H]^+$ 342.9933, found 342.9930.

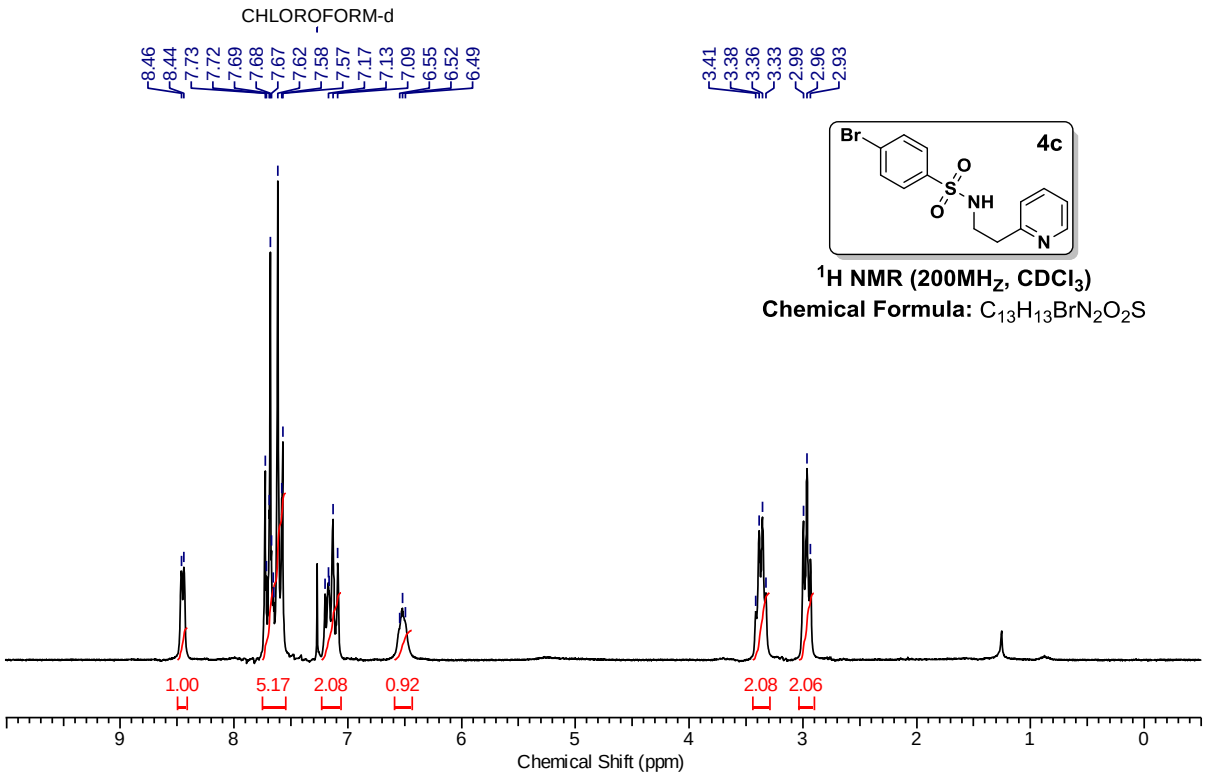


Figure S38. ^{1}H NMR spectrum of **4c** in $CDCl_3$.

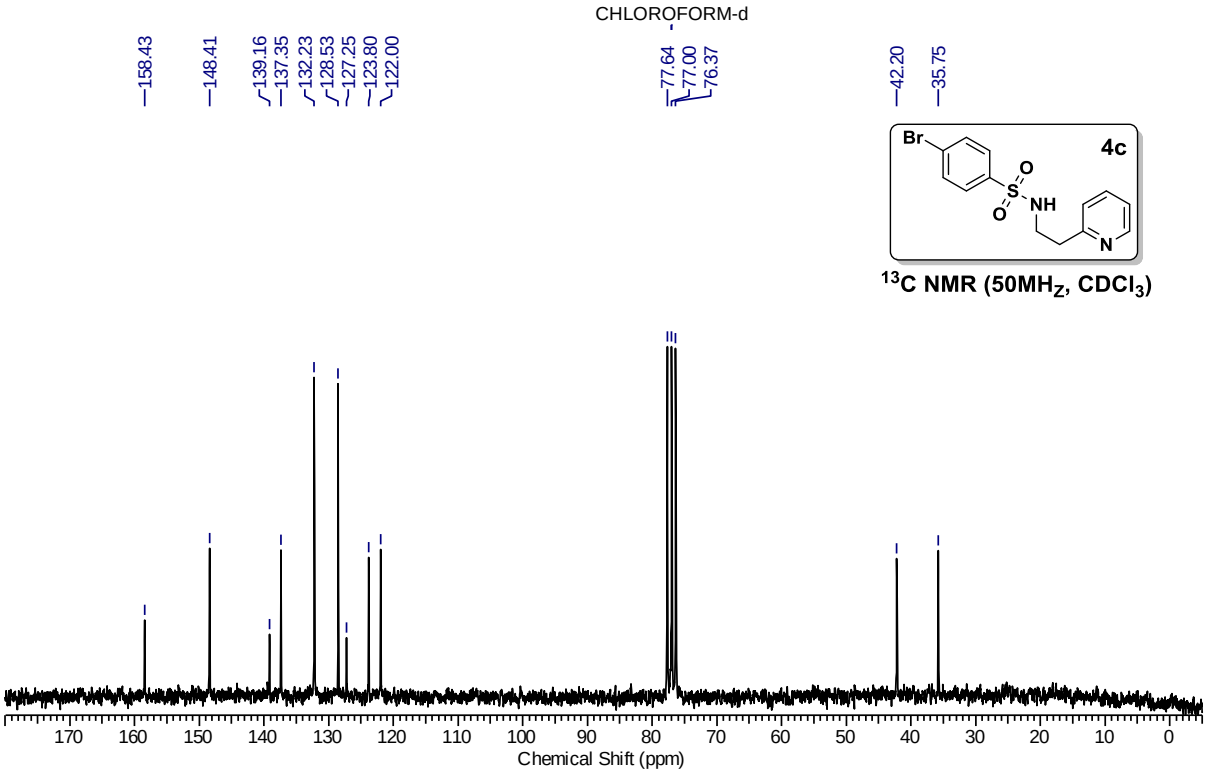


Figure S39. ^{13}C NMR spectrum of **4c** in $CDCl_3$.

1.21 Synthesis of N-(2-(pyridin-2-yl)ethyl)benzenesulfonamide (5c): To a solution of 2-(2-Pyridyl)ethylamine (100 mg, 0.83 mmol, 1.0 eq) in dry DCM (10 mL), dry Et3N (0.14 mL, 0.99 mmol, 1.2 eq) was added in a dropwise manner in presence of catalytic amount of DMAP (dimethylaminopyridine) (10mg, 0.083mmol, 0.1 eq) followed by slow addition of Benzenesulfonyl chloride (125 mg, 0.99 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**5c**). Solid; yield = 140 mg, 65%; R_f = 0.20 (ethyl acetate/petroleum ether = 40/60); mp = 97-99 °C, **^{1}H NMR (200MHz, CDCl3)** δ = 8.51 - 8.40 (m, 1 H), 7.91 - 7.78 (m, 2 H), 7.64 - 7.42 (m, 4 H), 7.19 - 7.01 (m, 2 H), 6.20 (br. s., 1 H), 3.45 - 3.30 (m, 2 H), 2.94 (t, *J* = 6.1 Hz, 2 H), **^{13}C NMR(50MHz, CDCl3)**δ = 158.5, 148.3, 140.1, 137.4, 132.4, 129.0, 126.9, 123.8, 122.0, 77.6, 76.4, 42.2, 35.8 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{15}N_2O_2S$ $[M+H]^+$ 263.0849, found 263.0847.

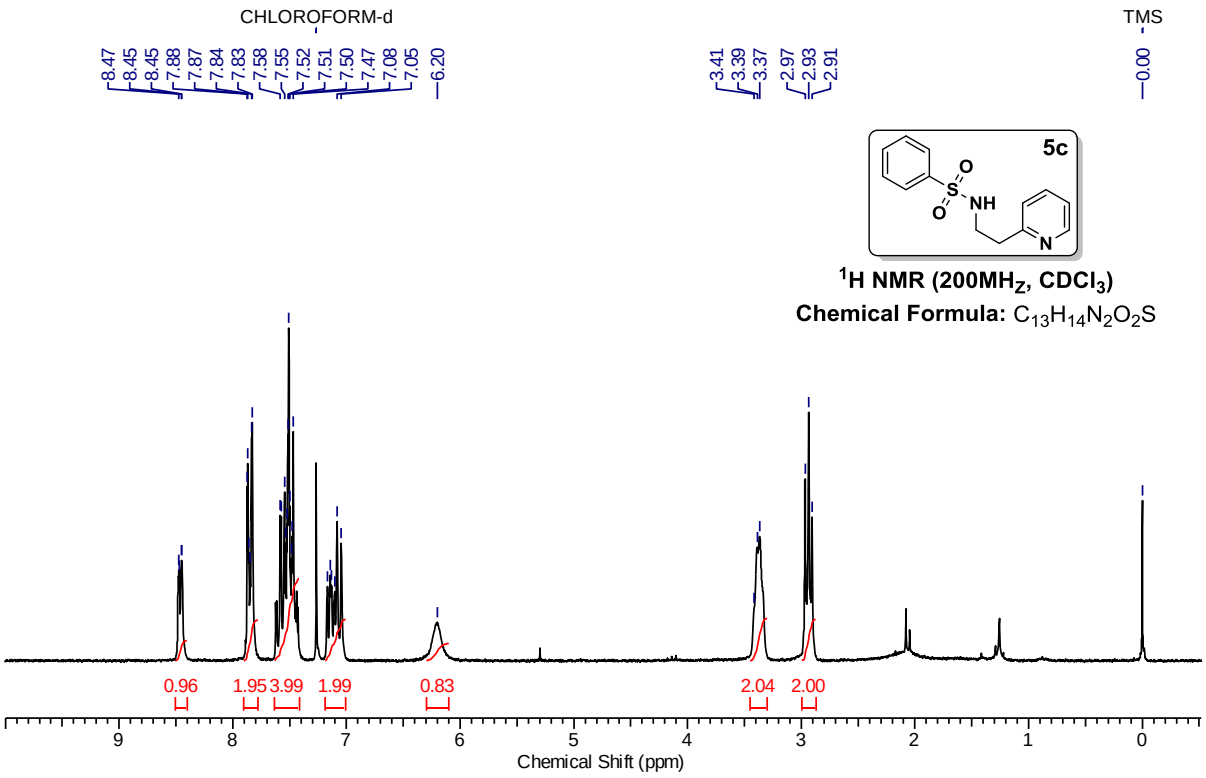


Figure S40. ^{1}H NMR spectrum of **5c** in $CDCl_3$.

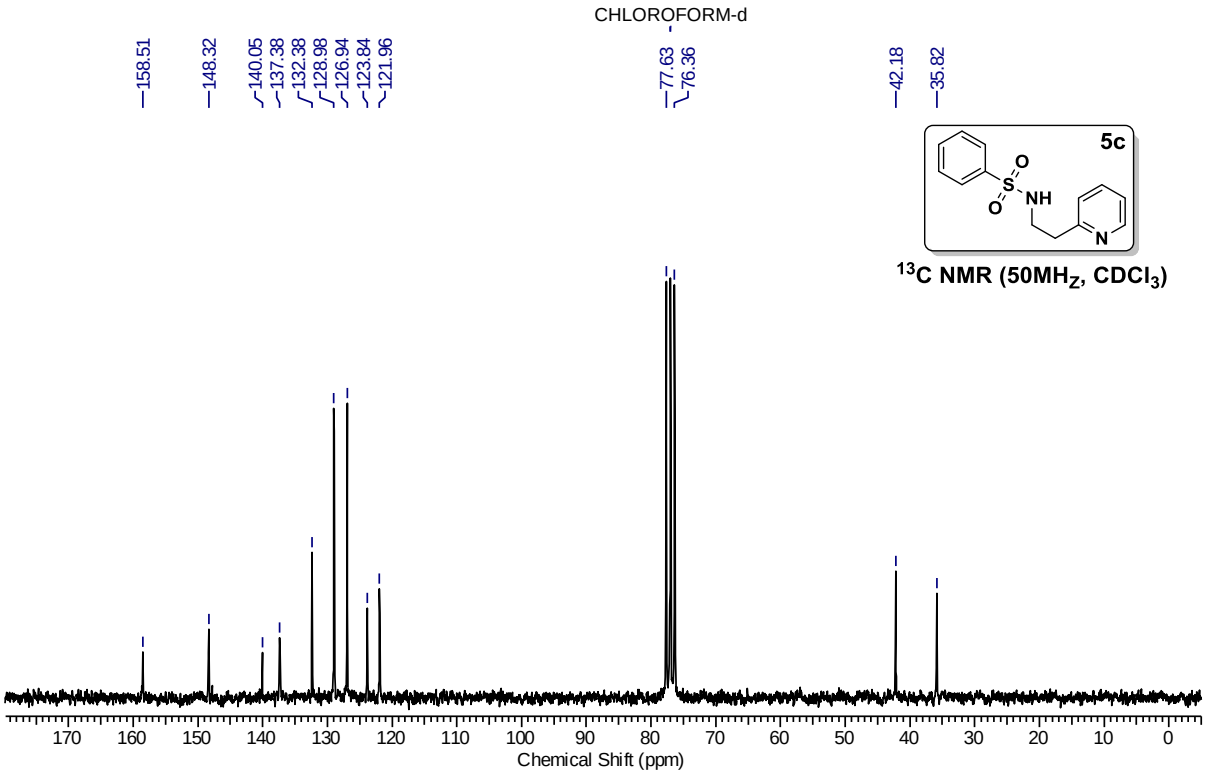


Figure S41. ^{13}C NMR spectrum of **5c** in $CDCl_3$.

1.22 Synthesis of 4-Methyl-N-(2-(pyridin-2-yl)ethyl)benzenesulfonamide (6c): To a solution of 2-(2-Pyridyl)ethylamine (100 mg, 0.83 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14 mL, 0.99 mmol, 1.2 eq) was added in a dropwise in the manner in the presence of catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.0.83mmol, 0.1 eq) followed by slow addition of p-toulenesulfonyl chloride (187 mg, 0.99 mmol, 1.2 eq) in dry DCM at 0 $^{\circ}$C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded (**6c**). Solid; yield = 160 mg, 71%; R_f = 0.18 (ethyl acetate/petroleum ether = 40/60); mp = 120-122 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 8.49 (d, *J* = 4.3 Hz, 1 H), 7.78 - 7.59 (m, 3 H), 7.29 (s, 1 H), 7.26 - 7.10 (m, 3 H), 6.16 (br. s., 1 H), 3.37 (q, *J* = 6.0 Hz, 2 H), 3.00 (t, *J* = 6.1 Hz, 2 H), 2.41 (s, 3 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 158.6, 148.5, 143.1, 137.2, 137.0, 129.6, 127.0, 123.7, 121.9, 77.6, 76.4, 42.2, 36.0, 21.4 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{17}N_2O_2S$ $[M+H]^+$ 277.1005, found 277.1001.

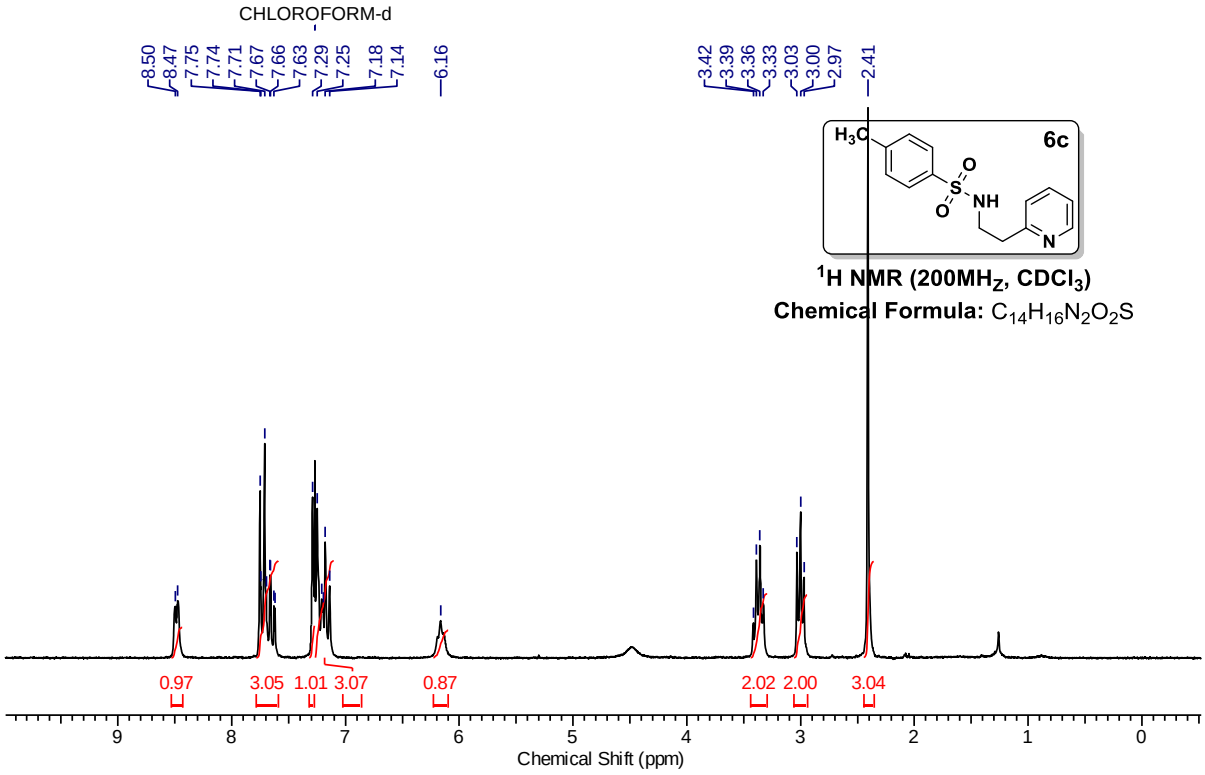


Figure S42. ^{1}H NMR spectrum of **6c** in $CDCl_3$.

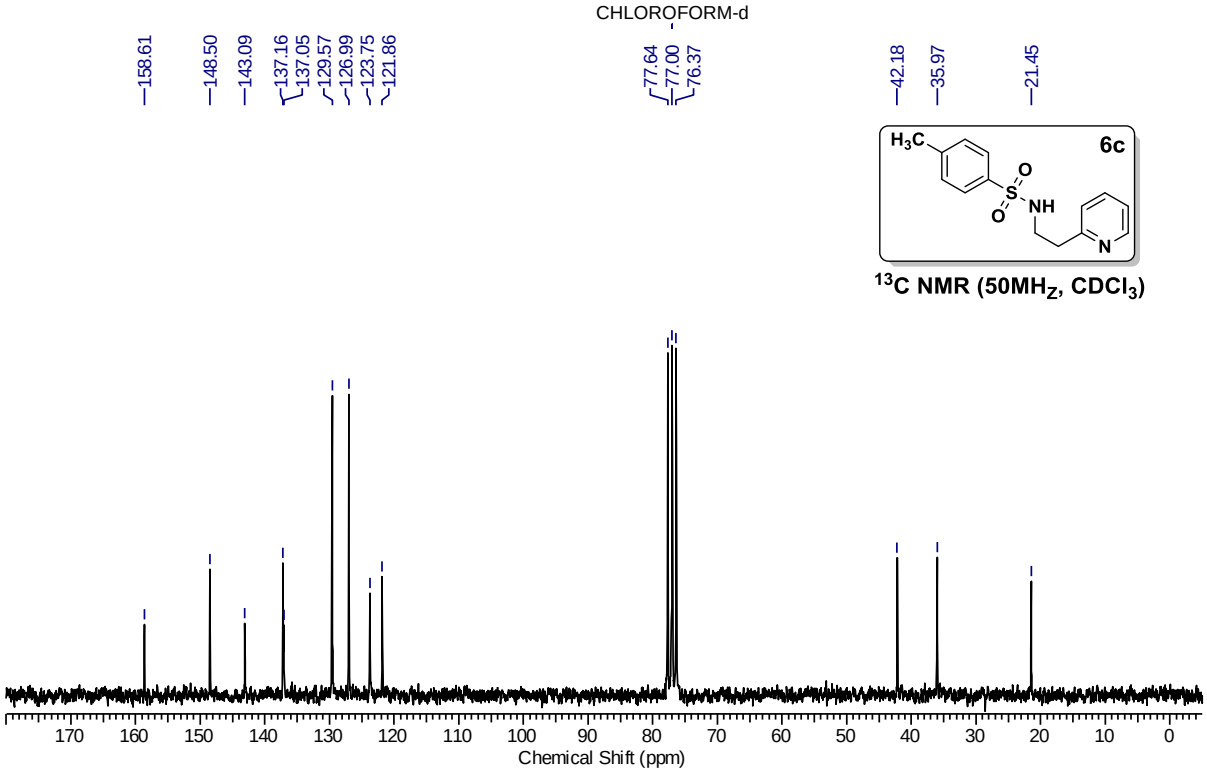


Figure S43. ^{13}C NMR spectrum of **6c** in $CDCl_3$.

1.23 Synthesis of 4-Methoxy-N-(2-(pyridin-2-yl)ethyl)benzenesulfonamide (7c): To a solution of 2-(2-Pyridyl)ethylamine (100 mg, 0.83 mmol, 1.0 eq) in dry DCM (10 mL), dry Et_3N (0.14mL, 0.99 mmol, 1.2 eq) was added in a dropwise manner in the presence of catalytic amount of DMAP (dimethylaminopyridine) (10 mg, 0.083 mmol, 0.1 eq) followed by slow addition of 4-methoxybenzenesulfonyl chloride (203mg, 0.99 mmol, 1.2 eq) in dry DCM at 0 °C. The reaction mixture was allowed to reach room temperature and was further stirred for 8 h. After the reaction (monitored by TLC) was completed, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with dichloromethane (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to get the crude product, which, on purification by flash column chromatography (eluent: pet ether/ethyl acetate), yielded(**7c**). Solid; yield = 184 mg, 77%; R_f = 0.12 (ethyl acetate/petroleum ether = 40/60); mp = 106-108 °C, **^{1}H NMR (200MHz, $CDCl_3$)** δ = 8.51 - 8.42 (m, 1 H), 7.84 - 7.71 (m, 2 H), 7.65 - 7.51 (m, 1 H), 7.19 - 7.02 (m, 2 H), 7.00 - 6.88 (m, 2 H), 6.05 (br. s., 1 H), 3.86 (s, 3 H), 3.35 (q, *J* = 5.9 Hz, 2 H), 2.99 - 2.88 (m, 2 H), **^{13}C NMR (50MHz, $CDCl_3$)** δ = 162.6, 158.8, 149.0, 136.6, 131.7, 129.1, 123.5, 121.7, 114.1, 77.6, 76.4, 55.5, 42.2, 36.2 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{17}N_2O_3S$ $[M+H]^+$293.0954, found 293.0950.

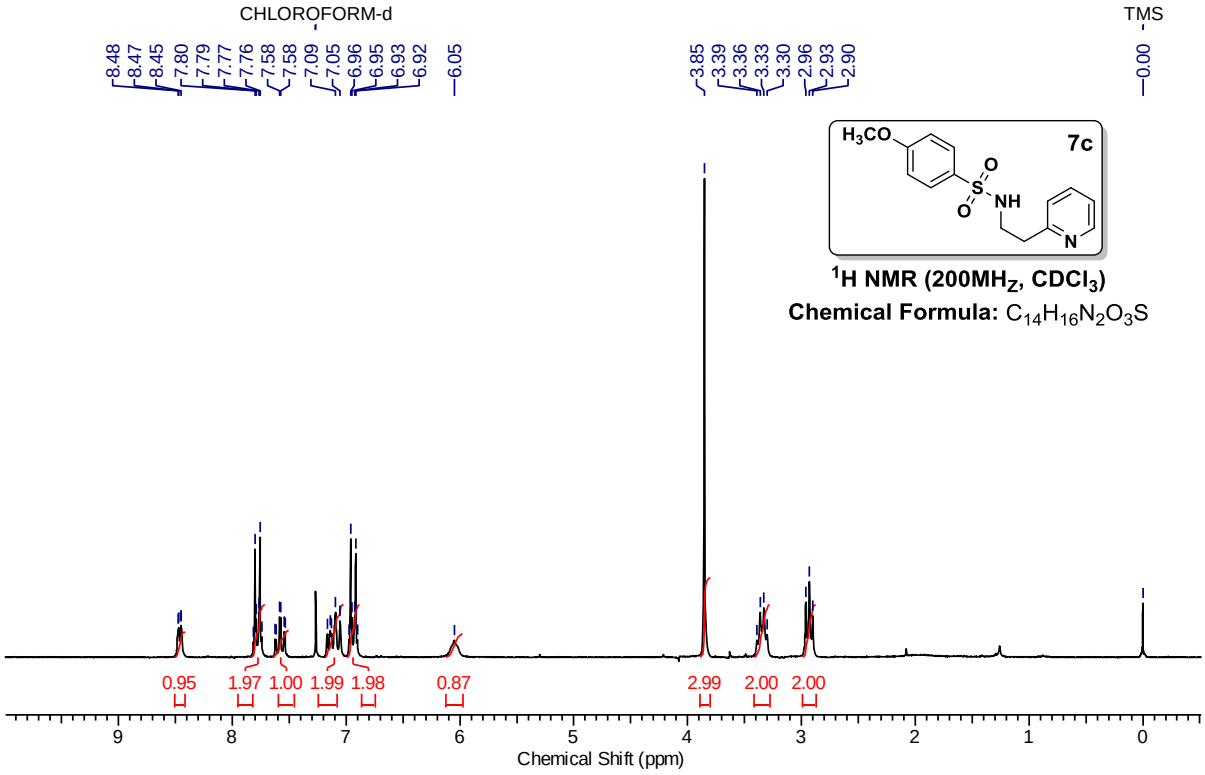


Figure S44. ^{1}H NMR spectrum of **7c** in $CDCl_3$.

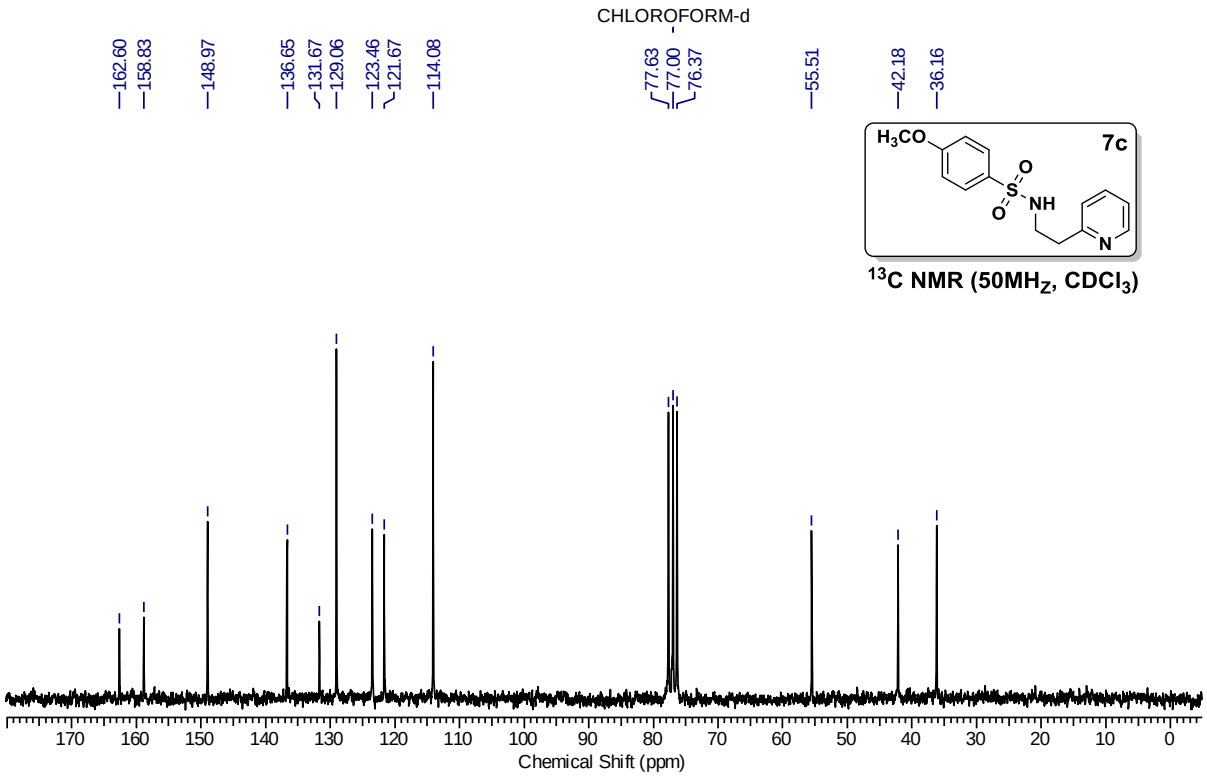


Figure S45. ^{13}C NMR spectrum of **7c** in $CDCl_3$.

Table S1. Summary of the crystallographic data for phenethyl benzenesulfonate (**1a**, **3a**, **4a**, **6a**).

Crystal Data	**1a**	**3a**	**4a**	**6a**
Formula	$C_{15}H_{13}F_3O_3S$	$C_{14}H_{13}ClO_3S$	$C_{14}H_{13}BrO_3S$	$C_{15}H_{16}O_3S$
M_r	330.31	296.75	341.21	276.34
Crystal Size, mm	0.20×0.13×0.08	0.24×0.14×0.09	0.21×0.13×0.07	0.24×0.15×0.09
Temperature (K)	296(2)	293(2)	296(2)	296(2)
Crystal Syst.	Monoclinic	monoclinic	monoclinic	triclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1$	P-1
a/Å	16.719(6)	15.5325(8)	7.5635(5)	7.3793(6)
b/Å	7.935(3)	7.7124(3)	24.1053(16)	8.1389(7)
c/Å	11.680(4)	11.711(16)	8.0213(5)	24.315(2)
$\alpha/^0$	90	90	90	85.636(5)
$\beta/^0$	101.248(6)	100.106(4)	104.6860(10)	89.814(5)
$\gamma/^0$	90	90	90	74.498(4)
V/Å^3	1519.8(9)	1381.10(11)	1414.67(16)	1402.9(2)
Z	4	4	4	4
D_{calc}/g cm^{-3}	1.444	1.427	1.602	1.308
m/mm^{-1}	0.254	0.428	3.053	0.232
F(000)	680	616	688	584
Ab. Correct.	*multi-scan*	*multi-scan*	*multi-scan*	*multi-scan*
T_{min}/T_{max}	0.951/0.980	0.904/0.963	0.566/0.815	0.947/0.979
$2\theta_{max}$	51	56	56	52
Total reflns.	9953	12254	10556	9648
Unique reflns.	2991	3292	6162	4877
Obs. reflns.	2356	3000	4339	3911
h, k, l (min, max)	(-20, 18), (-8, 9), (-14, 13)	(-18, 20), (-10, 10), (-15, 15)	(-9, 9), (-29, 31), (-10, 9)	(-9, 9), (-10, 8), (-29, 24)
R_{int}/R_{sig}	0.0872/0.0746	0.0234/0.0238	0.0793/0.1720	0.0546/0.0734
No. of Para/Restraints	208/1	172/0	344/1	345/0
R1 [$I> 2\sigma(I)$]	0.0815	0.0320	0.0497	0.1224
wR2[$I> 2\sigma(I)$]	0.1986	0.0852	0.1328	0.3000
R1 [all data]	0.1001	0.0354	0.0931	0.1373
wR2 [all data]	0.2126	0.0882	0.1596	0.3076
goodness-of-fit	1.068	1.025	0.940	1.103
$\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	+0.372, -0.309	+0.362, -0.377	+0.510, -0.415	+0.970, -0.520
CCDC No.	2337437	2337438	2337439	2337440

Table S2. Summary of the crystallographic data for phenethyl benzenesulfonate (**1b** to **7b**).

Crystal Data	**1b**	**2b**	**3b**	**4b**	**5b**
Formula	$C_{15}H_{14}NO_2SF3$	$C_{15}H_{14}N_2O_2S$	$C_{14}H_{14}ClNO_2S$	$C_{14}H_{14}BrNO_2S$	$C_{14}H_{15}NO_2S$
M_r	329.33	286.34	295.77	340.23	261.33
Crystal Size, mm	0.24×0.13×0.09	0.16×0.14×0.03	0.28×0.07×0.04	0.18×0.10×0.07	0.28×0.16×0.03
Temperature (K)	100(2)	100(2)	100(2)	110(2)	100(2)
Crystal Syst.	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space Group	$P2_1$	$Pca2_1$	Pc	Pc	$Pca2_1$
a/Å	10.1905(6)	9.1812(6)	26.5795(11)	26.8683(14)	9.1017(4)
b/Å	26.3756(19)	5.7029(5)	5.7691(2)	5.8303(3)	5.7077(2)
c/Å	11.0620(8)	53.043(5)	9.0833(4)	9.0640(5)	25.1568(11)
α/^{0}	90	90	90	90	90
β/^{0}	94.342(2)	90	98.9910(10)	98.976(2)	90
γ/^{0}	90	90	90	90	90
V/Å^3	2964.7(3)	2770.7(4)	1375.72(10)	1402.49(13)	1306.89(9)
Z	8	8	4	4	4
D_{calc}/g cm^{-3}	1.476	1.373	1.428	1.611	1.328
m/mm^{-1}	0.257	0.236	0.426	3.076	0.241
F(000)	1360	1200	616	688	552
Ab. Correct.	multi-scan	multi-scan	Multi-scan	multi-scan	multi-scan
T_{min}/ T_{max}	0.941/0.977	0.962/0.993	0.890/0.983	0.607/0.813	0.936/0.993
$2\theta_{max}$	56	56	56	56	54
Total reflns.	42830	14214	15835	27785	15214
Unique reflns.	13377	5863	8669	6645	2829
Obs. reflns.	11918	5488	7973	6299	2802
h, k, l (min, max)	(-13, 12), (-34, 34), (-14, 14)	(-11, 11), (-7, 7), (-68, 69)	(-37, 39), (-8, 7), (-13, 13)	(-35, 35), (-7, 7), (-11, 11)	(-11, 11), (-7, 7), (-32, 32)
R_{int}/R_{sig}	0.0332/0.0388	0.0445	0.0241/0.0400	0.0323/0.0416	0.0202/0.0153
No. of Para/Restraints	810	370	352/2	352/4	167/1
R1 [$I> 2\sigma(I)$]	0.0559	0.0886	0.0335	0.0312	0.0241
wR2[$I> 2\sigma(I)$]	0.1515	0.2034	0.0759	0.0746	0.0624
R1 [all data]	0.0642	0.0903	0.0385	0.0341	0.0244
wR2 [all data]	0.1585	0.2042	0.0783	0.0759	0.0626
goodness-of-fit	1.048	1.166	1.029	1.101	1.083
$\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	+0.662, -0.758	+1.108, -2.184	+0.456, -0.345	+0.974, -0.562	+0.313, -0.271
CCDC No.	2337441	2337442	2337443	2337444	2337445

Table S2 continued…

Crystal Data	**6b**	**7b**
Formula	$C_{15}H_{17}NO_2S$	$C_{15}H_{17}NO_3S$
M_r	275.35	291.35
Crystal Size, mm	0.21×0.16×0.11	0.18×0.12×0.08
Temp. (K)	100(2)	100(2)
Crystal Syst.	Monoclinic	Triclinic
Space Group	$P2_1/n$	P-1
a/Å	15.270(4)	7.6373(3)
b/Å	5.4721(15)	11.5197(4)
c/Å	17.456(5)	16.1227(6)
α/^{0}	90	89.7740(10)
β/^{0}	109.587(8)	80.1100(10)
γ/^{0}	90	85.6640(10)
V/Å^3	1374.2(7)	1393.33(9)
Z	4	4
D_{calc}/g cm^{-3}	1.331	1.389
m/mm^{-1}	0.233	0.239
F(000)	584	616
Ab. Correct.	multi-scan	multi-scan
T_{min}/ T_{max}	0.953/0.975	0.958/0.981
$2\theta_{max}$	50	60
Total reflns.	9936	64204
Unique reflns.	2360	8038
Obs. reflns.	2052	7689
h, k, l (min, max)	(-18, 17), (-6, 6), (-20, 20)	(-10, 10), (-16, 16), (-22, 22)
R_{int}/R_{sig}	0.0455/0.0462	0.0218/0.0117
No. of Para/Restraints	254/169	371/0
R1 [I> 2σ(I)]	0.1141	0.0299
wR2[I> 2σ(I)]	0.3133	0.0826
R1 [all data]	0.1268	0.0311
wR2 [all data]	0.3314	0.0838
goodness-of-fit	1.071	1.040
$\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	+1.599, -0.479	+0.463, -0.370
CCDC No.	2337446	2337447

Table S3. Summary of the crystallographic data for N-(pyridin-2 yl)ethyl) benzenesulfonamide (**1c** to **7c**).

Crystal Data	**1c**	**2c**	**3c**	**4c**	**5c**
Formula	$C_{14}H_{13}F_3N_2O_2S$	$C_{14}H_{13}N_3O_2S$	$C_{13}H_{13}ClN_2O_2S$	$C_{13}H_{13}BrN_2O_2S$	$C_{13}H_{14}N_2O_2S$
M_r	330.32	287.33	296.76	341.22	262.32
Crystal Size, mm	0.33×0.13×0.08	0.16×0.14×0.03	0.40×0.34×0.23	0.21×0.10×0.04	0.30×0.19×0.12
Temp. (K)	100(2)	100 (2)	100(2)	100(2)	100(2)
Crystal Syst.	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space Group	*C2/c*	$P2_1/c$	$P2_1/c$	*P*-1	$P2_1/c$
a/Å	25.3896(8)	14.7745(4)	14.225(3)	5.5952(2)	5.4885(3)
b/Å	5.0011(2)	6.9327(2)	7.0381(14)	12.3194(4)	9.4202(5)
c/Å	22.3676(8)	14.9312(4)	14.882(3)	20.3022(7)	24.6029(14)
$\alpha/^0$	90	90	90	88.8110(10)	90
$\beta/^0$	94.337(2)	118.4840(10)	116.423(7)	85.7720(10)	95.597(2)
$\gamma/^0$	90	90	90	76.8740(10)	90
V/Å^3	2832.01(18)	1344.23(7)	1334.3(5)	1359.14(8)	1265.97(12)
Z	8	4	4	4	4
D_{calc}/g cm^{-3}	1.549	1.420	1.477	1.668	1.376
m/mm^{-1}	0.271	0.245	0.441	3.177	0.251
F(000)	1360	600	616	688	552
Ab. Correct.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
T_{min}/ T_{max}	0.916/0.979	0.962/0.993	0.843/0.905	0.555/0.883	0.928/0.971
$2\theta_{max}$	56	56	61	73	69
Total reflns.	21863	17833	41523	67292	11985
Unique reflns.	3414	3230	4025	12244	4127
Obs. reflns.	3197	3036	3842	11050	3702
h, k, l (min, max)	(-33, 33), (-6, 6), (-29, 29)	(-19, 19), (-8, 9), (-19, 19)	(-20, 20), (-10, 10), (-21, 21)	(-9, 9), (-18, 20), (-33, 33)	(-8, 8), (-14, 10), (-37, 35)
R_{int}/R_{sig}	0.0427/0.0290	0.0174/0.0128	0.0186/0.0097	0.0216/0.0169	0.0186/0.0234
No. of Para/Restraints	203/0	185/0	176/0	351/0	167/0
R1 [$I> 2\sigma(I)$]	0.0453	0.0320	0.0265	0.0230	0.0384
wR2[$I> 2\sigma(I)$]	0.1049	0.0803	0.0728	0.0580	0.0947
R1 [all data]	0.0478	0.0340	0.0276	0.0277	0.0443
wR2 [all data]	0.1066	0.0816	0.0737	0.0597	0.0981
goodness-of-fit	1.074	1.081	1.065	1.025	1.065
$\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	+0.861, -0.541	+0.406, -0.441	+0.461, -0.337	+0.631, -0.490	+0.504, -0.370
CCDC No.	2337448	2337449	2337450	2337451	2337452

Table S3 Continued…

Crystal Data	**6c**	**7c**
Formula	$C_{14}H_{16}N_2O_2S$	$C_{14}H_{16}N_2O_3S$
M_r	276.35	292.35
Crystal Size, mm	0.38×0.19×0.13	0.28×0.18×0.14
Temp. (K)	100(2)	90(2)
Crystal Syst.	Orthorhombic	Monoclinic
Space Group	*P*bca	$P2_1/c$
a/Å	7.7896(10)	7.5399(5)
b/Å	15.722(2)	7.6427(5)
c/Å	22.587(3)	24.2467(16)
$\alpha/^0$	90	90
$\beta/^0$	90	93.270(4)
$\gamma/^0$	90	90
V/Å^3	2766.2(6)	1394.95(16)
Z	8	4
D_{calc}/g cm^{-3}	1.327	1.392
m/mm^{-1}	0.233	0.241
F(000)	1168	616
Ab. Correct.	multi-scan	multi-scan
T_{min}/ T_{max}	0.917/0.970	0.936/0.967
$2\theta_{max}$	67	61
Total reflns.	36770	19381
Unique reflns.	5428	4298
Obs. reflns.	4697	3772
h, k, l (min, max)	(-11, 11), (-23, 23), (-35, 25)	(-10, 10), (-10, 10), (-33, 33)
R_{int}	0.0368/0.0253	0.0504/0.0405
No. of para	177/0	186/0
R1 [$I > 2\sigma(I)$]	0.0597	0.0452
wR2[$I > 2\sigma(I)$]	0.1328	0.1059
R1 [all data]	0.0707	0.0528
wR2 [all data]	0.1382	0.1097
goodness-of-fit	1.166	1.117
$\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	+0.502, -0.570	+0.502, -0.442
CCDC No.	2337453	2337454

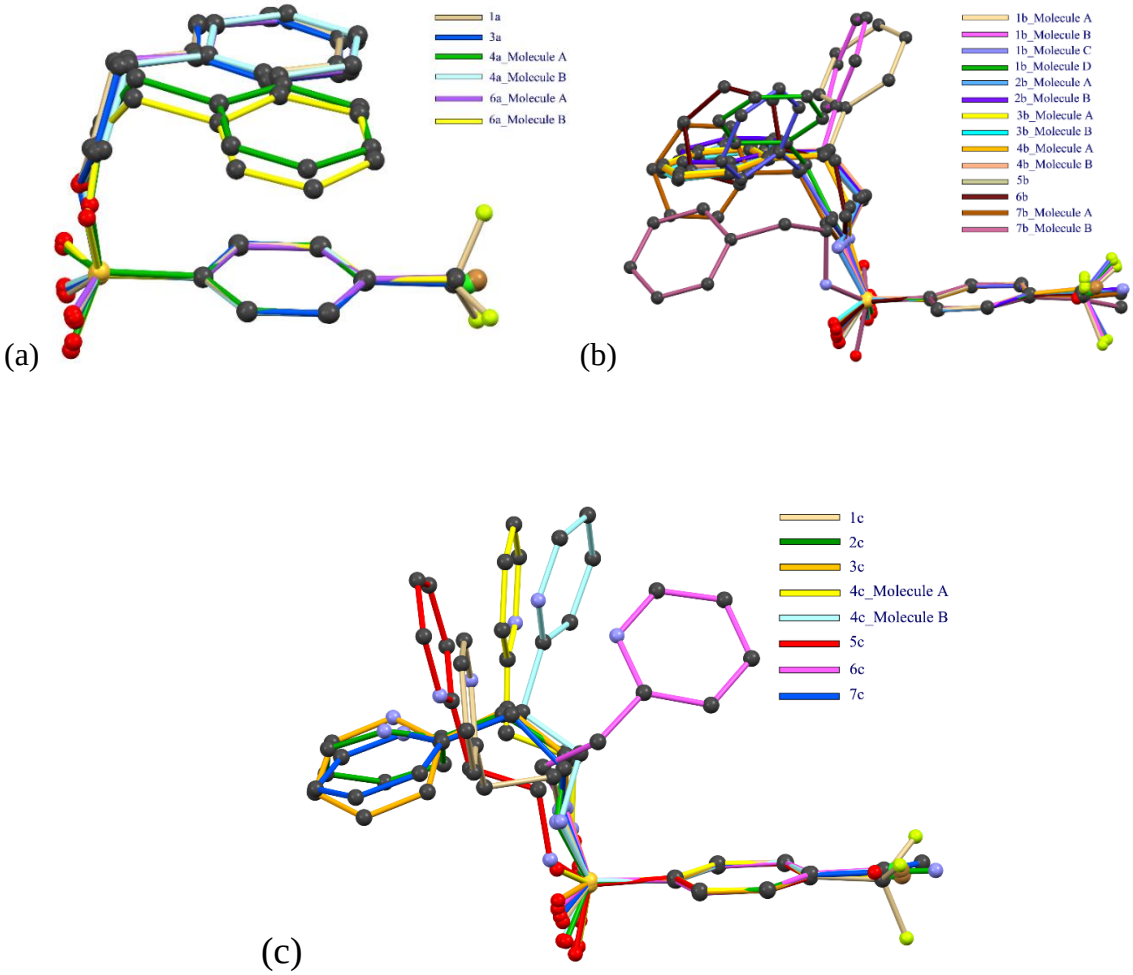


Figure S46. Structure overlay for molecules in (a) **1a** series, (b) **1b** series and (c) **1c** series.

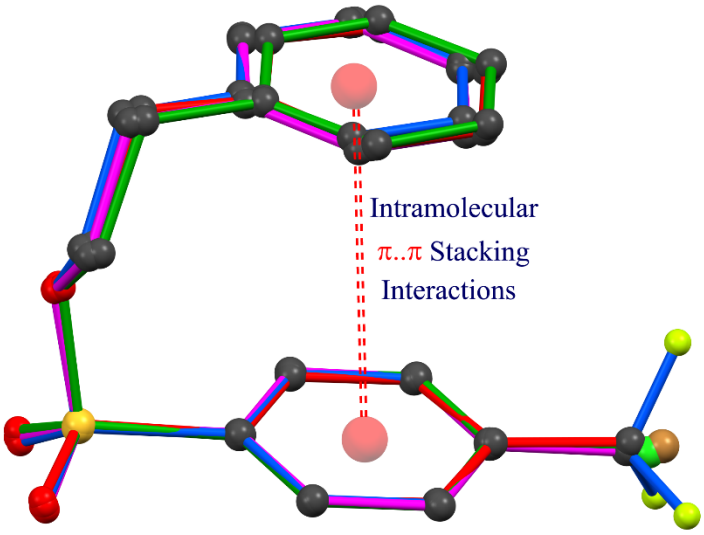


Figure S47. Intramolecular π···π stacking interactions in **1a** series of molecules.

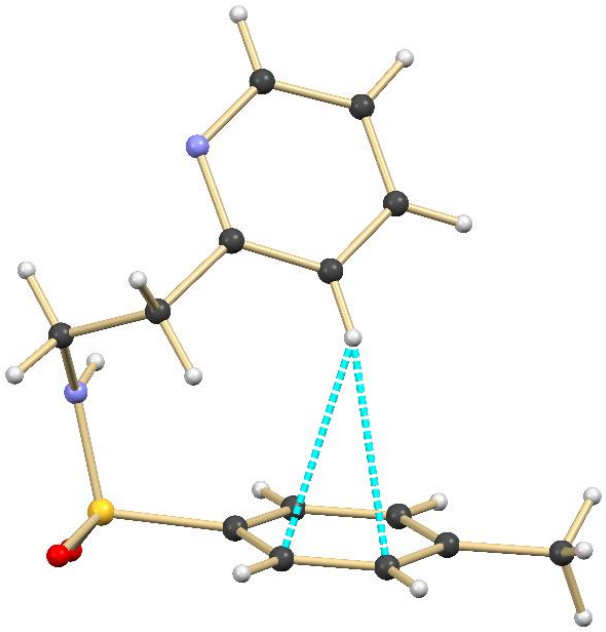
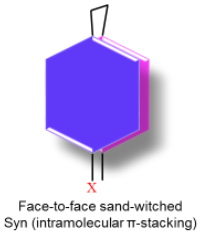
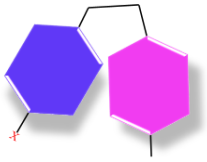
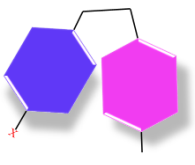
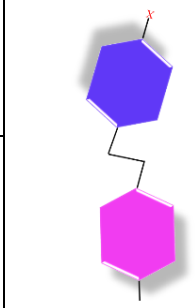
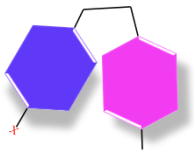
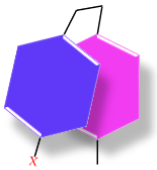
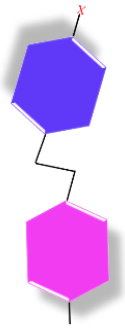


Figure S48. Syn geometry in **6c** facilitated by C-H···π interactions.

Table S4. Intramolecular π-stacking in sulphoester (**1a**, **3a**, **4a**, **6a**), sulfonamide benzene (**1b** to **7b**) and sulfonamide pyridine (**1c** to **7c**) derivatives.

Compound	Substitution (X)	Cg···Cg	α (°)	Slippage (Å)	Representation
1a	CF_3	3.937 (3)	7.0(2)	1.739	 Face-to-face sand-witched Syn (intramolecular π-stacking)
3a	Cl	3.848(5)	5.5(7)	1.510	
4a	Br	3.892(5) 3.970(5)	3.8(4) 1.0(4)	1.433 1.636	
6a	CH_3	3.882(5) 3.925(5)	6.2(4) 7.8(4)	1.634 1.271	
1b	CF_3	-	-	-	 Midway (no π-stacking)
2b	CN	-	-	-	 Anti (no π-stacking)
3b	Cl				
4b	Br				
5b	H				
6b	CH_3				
7b	OCH_3				
1c	CF_3	-	-	-	 Midway (no π-stacking)

2c	CN	-	-	-	 Anti (no π-stacking)
3c	Cl	-	-	-	
4c	Br	-	-	-	 Midway (no π-stacking)
5c	H				
6c	CH_3	-	-	-	 Parallel off-set Syn (no π-stacking)
7c	OCH_3	-	-	-	 Anti (no π-stacking)
Cg···Cg = Distance between ring centroids (Å), α = dihedral angle between planes I and J (°), slippage = distance between Cg (I) and perpendicular projection of Cg (J) on ring I (Å).					

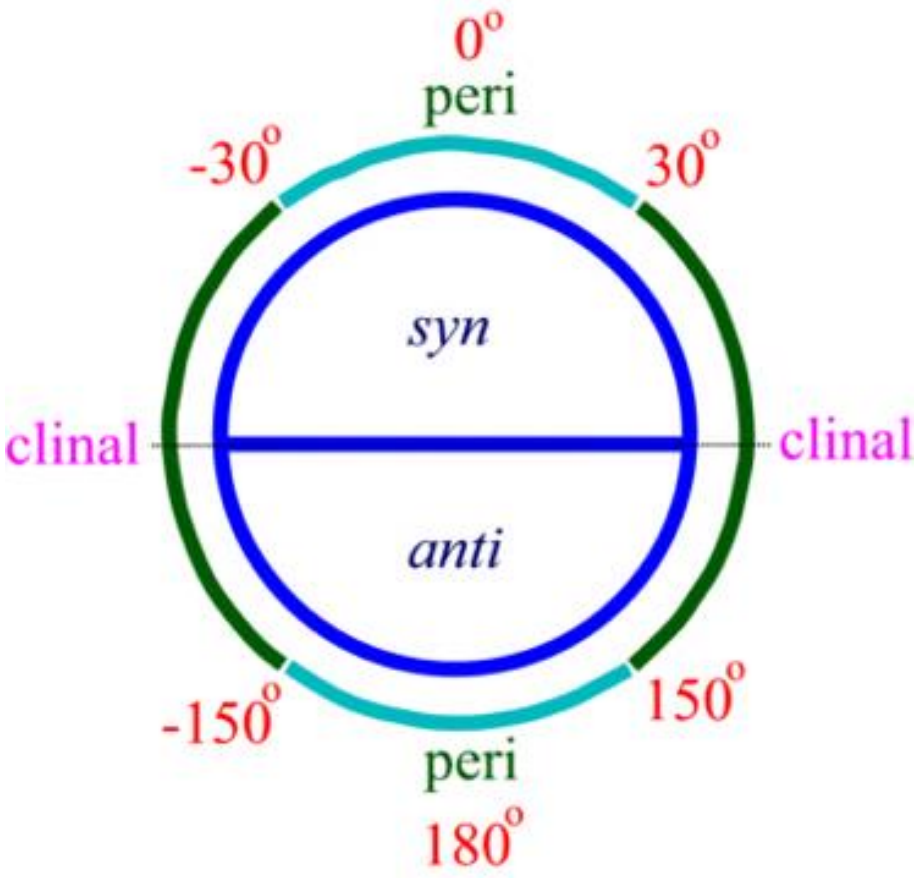


Figure S49. Description of conformations about a single bond.

Table S5. Torsion angles (°) for sulfoester derivatives (**1a**, **3a**, **4a**, **6a**).

Sr. No.	Compounds	C4−S1−O3−C7 (τ_1)	S1−O3−C7−C8 (τ_2)	O3−C7−C8−C9 (τ_3)
1	**1a**	-77.8(3)	149.0(3)	-64.8(5)
2	**3a**	-75.28(15)	147.76(11)	-64.80(19)
3	**4a**	74.2(5) (A) -73.6(6) (B)	-148.0(6) (A) 148.3(7) (B)	67.4(9) (A) -69.4(11) (B)
4	**6a**	-74.6(6) (A), 74.0(6)(B)	145.9(6) (A), -146.7(6) (B)	-68.3(9) (A), 71.8(10) (B)
Note: A and B are the labels given to the symmetry-independent molecules present in the asymmetric unit of the respective crystal structure.				

Table S6. Torsion angles (°) for sulfonamide benzene derivatives (**1b** to **7b**).

Sr. No.	Compounds	C4−S1−N1−C7 (τ_1)	S1−N1−C7−C8 (τ_2)	N1−C7−C8−C9 (τ_3)
1	**1b**	70.0(5) (A) 71.0(5) (B) -71.5(6) (C) -70.2(6) (D)	168.3(4) (A) 163.2(4) (B) -167.5(5) (C) -173.5(5) (D)	-177.5(5) (A) -174.0(5) (B) 172.7(6) (C) 174.8(6) (D)
	2b	58.9(9) (A) 59.1(9) (B)	169.2(7) (A) 170.2(7) (B)	-61.1(13) (A) -65.5(13) (B)
2	**3b**	-57.94(18) (A) -58.40(19) (B)	-171.89(15) (A) -170.81(16) (B)	64.7(3) (A) 62.7(3) (B)
	4b	-57.9(3) (A) 58.9(4) (B)	-171.2(3) (A) 169.9(3) (B)	64.3(5) (A) -63.5(5) (B)
3	**5b**	61.41(17)	170.12(13)	-62.7(2)
	6b	-59.6(16)	169.22(6)	66(2)
4	**7b**	-70.66(8) (A) 64.81(8) (B)	-175.31(6) (A) -178.86(6) (B)	62.01(11)(A) -55.68(10) (B)
Note: A and B are the labels given to the symmetry-independent molecules present in the asymmetric unit of the respective crystal structure.				

Table S7. Torsion angles (°) for sulfonamide pyridine derivatives (**1c** to **7c**).

Sr. No.	Compounds	C5−S1−N1−C8 (τ_1)	S1−N1−C8−C9 (τ_2)	N1−C8−C9−C10 (τ_3)
1	**1c**	-72.74(15)	-93.46(16)	-172.74(14)
2	**2c**	71.47(10)	146.33(8)	-62.64(13)
2	**3c**	-69.18(9)	-145.41(7)	62.32(11)
	4c	-69.09(12) (A) 62.02(13) (B)	-93.81(13) (A) 115.08(13) (B)	-173.97(12) (A) 177.51(13) (B)
3	**5c**	81.46(11)	95.97(12)	169.30(11)
	6c	-88.87(14)	75.03(17)	64.75(19)
4	**7c**	-65.44(12)	-155.96(10)	67.90(15)

Note: A and B are the labels given to the symmetry-independent molecules present in the asymmetric unit of the respective crystal structure.

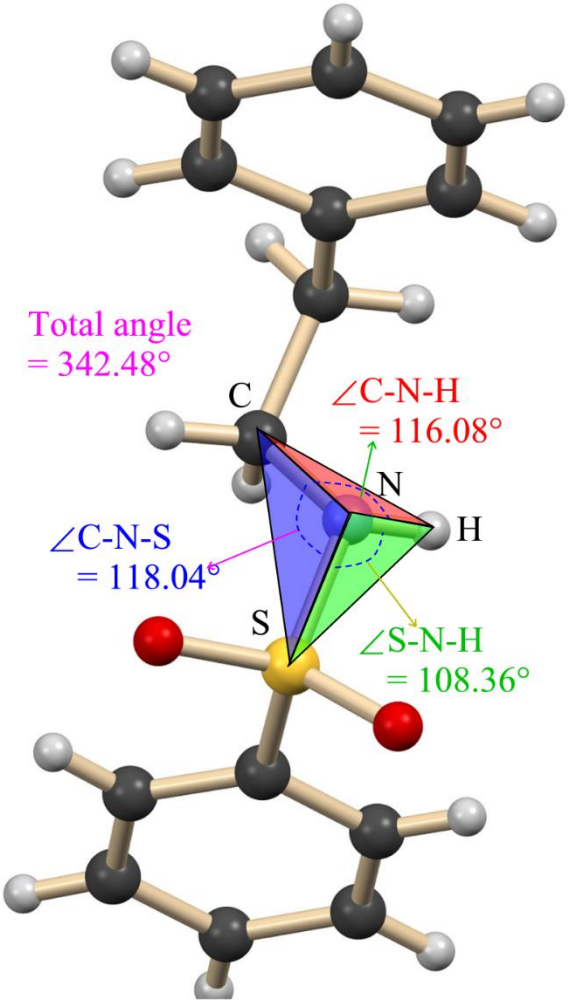


Figure S50. A diagram showing the distortion of the N-H bond for **5b**.

Table S8. The angles around N atoms and total sum.

Compounds	∠SNC (°)	∠SNH (°)	∠CNH (°)	Angles sum (°)
1b	119.56 (A) 120.14 (B) 118.69 (C) 118.41 (D)	106.98 (A) 115.57 (B) 106.47 (C) 109.80 (D)	110.62 (A) 100.72 (B) 122.65 (C) 116.16 (D)	337.16 336.43 347.81 344.37
2b	118.23 (A) 117.74 (B)	120.90 (A) 121.14 (B)	120.87(A) 121.12 (B)	360.0 (A) 360.0 (B)
3b	118.04 (A) 118.27 (B)	108.59 (A) 105.98 (B)	116.97(A) 117.22 (B)	343.6 (A) 341.47 (B)
4b	118.32 (A) 117.95 (B)	112.01 (A) 105.52 (B)	111.37 (A) 120.79 (B)	341.7 (A) 344.26 (B)
5b	118.04	108.36	116.08	342.48
6b	114.63	115.38	112.90	342.91
7b	118.34 (A) 119.76 (B)	111.54 (A) 113.03 (B)	115.72 (A) 116.71 (B)	345.6 (A) 349.5 (B)
1c	121.17	113.38	119.78	354.33
2c	121.27	113.51	115.31	350.09
3c	121.08	113.22	114.71	349.01
4c	121.12 (A) 119.94 (B)	115.31 (A) 113.87 (B)	119.57 (A) 117.67 (B)	356.0(A) 351.48 (B)
5c	122.77	117.84	117.66	358.27
6c	122.12	114.76	118.39	355.27
7c	119.26	109.97	116.51	345.74

Table S9. Geometrical parameters of intermolecular interactions in Phenethyl benzenesulfonate (**1a, 3a**, **4a**, **6a**).

Comp.	S. No.	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A /α(°)	Symmetry Codes
1a	1.	C7-H7B···O2	0.97	2.65	3.444(5)	140	1-*x*,1/2+*y*,3/2-*z*
	2.	C3-H3···O2	0.93	2.49	3.244(5)	139	*x*,-1/2-*y*,1/2+*z*
	3.	F3…F2		2.889(13)		167.6(6	2-*x*, 1/2+*y*, 5/2-
	4.	Cg1···Cg2			4.001(3)	7.1(2)	*x*,-1+*y*,*z*
	5.	Cg1···Cg2			3.937(3)	7.1(2)	*x*,*y*,*z*
	Cg1= C1-C2-C3-C4-C5-C6; Cg2= C9-C10-C11-C12-C13-C14						
3a	6.	C7-H7B···O2	0.97	2.59	3.411(5)	143	-*x*,1/2+*y*,1/2-*z*
	7.	C3-H3···O2	0.93	2.45	3.142(5)	131	*x*,1/2-*y*,1/2+*z*
	8.	Cg1···Cg2			3.848(5)	5.52(7)	*x*,-1+*y*,*z*
	9.	Cg1···Cg2			3.875(5)	5.52 (7)	*x*,*y*,*z*
	Cg1= C1-C2-C3-C4-C5-C6; Cg2= C9-C10-C11-C12-C13-C14						
4a	10.	C8A-H8AB···O2A	0.97	2.58	3.430(11)	147	-1+*x*,*y*,*z*
	11.	C6A-H6A···O1A	0.93	2.68	3.464(12)	142	*x*,*y*,1+*z*
	12.	C12A-H12A···O2A	0.93	2.61	3.454(11)	152	1+*x*,*y*,1+*z*
	13.	C12B-H12B···O2B	0.93	2.61	3.428(14)	151	-1+*x*,*y*,-1+*z*
	14.	C14B-H14B··· Cg2	0.93	2.77	3.558(9)	143	1-*x*,-1/2+*y*,1-*z*
	15.	Cg1···Cg2			3.892(5)	3.8(4)	*x*,*y*,*z*
	16.	Cg1···Cg3			3.970(5)	1.0(4)	*x*,*y*,*1*+z
	17.	Cg3···Cg4			3.945(5)	4.8(4)	*x*,*y*,*z*
	Cg1=C1A-C2A-C3A-C4A-C5A-C6A; Cg2= C9A-C10A-C11A-C12A-C13A-C14A; Cg3= C1B-C2B-C3B-C4B-C5B-C6B; Cg4= C9B-C10B-C11B-C12B-C13B-C14B						
6a	18.	C8A-H8AB···O1A	0.97	2.64	3.435(12)	140	1+*x*,*y*,*z*
	19.	C12A-H12A···O1A	0.93	2.57	3.425(11)	153	1+*x*,-1+*y*,*z*
	20.	C3B-H3B···O1B	0.93	2.67	3.484(12)	146	1-*x*,2-*y*,1-*z*
	21.	C12B-H12B···O2B	0.93	2.59	3.448(11)	154	1+*x*,-1+*y*,*z*
	22.	C14B-H14B···O2B	0.93	2.70	3.463(12)	140	1+*x*,*y*,*z*
	23.	C10B-H10B···Cg2	0.93	2.72	3.516(9)	145	*x*,*y*,*z*
	24.	Cg1···Cg1			3.859(5)	0.0(4)	-*x*,1-*y*,2-*z*
	25.	Cg1···Cg2			3.882(5)	6.2(4)	*x*,*y*,*z*
	30.	Cg3···Cg3			3.852(5)	0.0(4)	1-*x*,1-*y*,1-*z*
	31.	Cg3···Cg4			3.925(5)	7.8(4)	*x*,*y*,*z*

	Cg1= C1A-C2A-C3A-C4A-C5A-C6A; Cg2= C9A-C10A-C11A-C12A-C13A-C14A; Cg3= C1B-C2B-C3B-C4B-C5B-C6B; Cg4= C9B-C10B-C11B-C12B-C13B-C14B; α - the dihedral angle between two rings, Cg – Centroid of the ring, Cg···Cg – Distance between two ring centroids.

Table S10. Geometrical parameters of intermolecular interactions in N-Phenethyl benzenesulfonamide (**1b** to **7b**).

Compound	**S. No.**	**D-H···A**	**D-H (Å)**	**H···A (Å)**	**D···A (Å)**	**D-H···A /α (°)**	***Symmetry Codes***
1b	1.	N1A-H1NA···O1B	0.88(3)	2.06(3)	2.942(7)	179.(9)	*x, y, z*
	2.	N1B-H1NB···O1A	0.89(3)	2.13(4)	2.969(7)	158.(7)	1+*x, y, z*
	3.	N1C-H1NC···O2D	0.88(3)	2.11(3)	2.977(7)	168.(6)	-1+*x, y, z*
	4.	N1D-H1ND···O2C	0.88(3)	2.09(3)	2.956(7)	168.(5)	*x, y, z*
	5.	C3A-H3A···O1C	0.95	2.48	3.257(7)	139	-*x*, -1/2+*y*, 2-*z*
	6.	C3B-H18···O1D	0.95	2.5	3.354(8)	149	1-*x*, -1/2+*y*, 2-*z*
	7.	C3C-H3C···O2B	0.95	2.46	3.278(8)	144	1-*x*, ½+*y*, 1-*z*
	8.	C3D-H3D···O2A	0.95	2.51	3.342(8)	149	1-*x*, ½+*y*, 1-*z*
	9.	C7B-H8D···O1C	0.99	2.68	3.642(7)	163	1-*x*,-1/2+*y*,2-*z*
	10.	C7C-H8E···O2A	0.99	2.64	3.531(8)	150	-*x*, ½+*y*, 1-*z*
	11.	C11A-H11A···Cg7	0.95	2.84	3.647(7)	143	1-*x*,-1/2+*y*,2-*z*
	12.	C13D-H13D···Cg3	0.95	2.83	3.655(7)	145	1-*x*,1/2+*y*,1-*z*
	13.	C12A-H12A···F2A	0.95	2.67	3.518(6)	149	-*x*,-1/2+*y*,2-*z*
	14.	C12B-H12B···F2B	0.95	2.62	3.440(8)	145	1-*x*,-1/2+*y*,2-*z*
	15.	C12C-H12C···F2D	0.95	2.59	3.403(8)	144	1-*x*,1/2+*y*,1-*z*
	16.	F2A···F2C		2.732(8)		133.7(4)	*x, y, z*
	17.	F2B···F2D		2.732(8)		145.9(5)	*x, y, z*
2b	18.	N1A-H1A···O1A	0.88	2.49	2.992(13)	116	½+*x*, -*y*, *z*
	19.	N1B-H1B···O2B	0.88	2.51	2.991(12)	115	-1/2+*x*, 1-*y*, *z*
	20.	C5A-H5A···O2A	0.95	2.52	3.107(15)	120	*x*, 1+*y*, *z*
	21.	C7A-H7AB···O1A	0.99	2.59	3.304(14)	129	½+*x*, *1-y*, *z*
	22.	C8A-H8A···O2A	0.97	2.59	3.277(13)	128	1/2+*x*,*1-y*,*z*
	23.	C3B-H3B···O1B	0.95	2.47	3.099(15)	124	*x*, 1+*y*, *z*
	24.	C7B-H7BB···O2B	0.99	2.59	3.295(14)	128	-1/2+*x*, 2-*y*, *z*
	25.	C8B-H8D···O2B	0.97	2.60	3.293(12)	129	-1/2+*x*,2-*y*,*z*
	26.	C6B-H6B···N2A	0.95	2.51	3.375(15)	151	*x, y, z*
	27.	C2A-H2A···N2B	0.95	2.53	3.403(15)	152	*x*,-1+*y*,*z*
3b	28.	N1A-H1NA···O1A	0.86(4)	2.16(4)	2.992(3)	166(4)	*x*, 1-*y*, ½+*z*
	29.	N1B-H1NB...O1B	0.81(3)	2.17(3)	2.978(3)	171(3)	*x*, -*y*, ½+*z*
	30.	N1A-H1NA···S1A	0.86(4)	3.02(4)	3.7475(19)	145(3)	*x*, 1-*y*, ½+*z*
	31.	N1B-H1NB···S1B	0.81(3)	3.03(4)	3.736(2)	146(3)	*x*, -*y*, ½+*z*
	32.	C3A-H3A···O2A	0.95	2.49	3.121(3)	124	*x*, -1+*y*, *z*

	33.	C7A-H7A1···O1A	0.99	2.60	3.297(3)	127	*x*, -*y*, ½+*z*
	34.	C3B-H3B···O2B	0.95	2.46	3.087(3)	123	*x*, 1+*y*, *z*
	35.	C6B-H6B···Cl1A	0.95	2.96	3.853(2)	156	*x*, -*y*, ½+*z*
	36.	C7B-H7B1···O1B	0.99	2.60	3.313(3)	129	*x*, 1-*y*, ½+*z*
4b	37.	N1A-H1NA···O2A	0.88(3)	2.12(3)	2.981(5)	166(7)	*x*, 1-*y*, -½+*z*
	38.	N1B-H1NB···O1B	0.86(3)	2.12(3)	2.955(5)	165(6)	*x*, 2-*y*, -½+*z*
	39.	N1A-H1NA···S1A	0.88(3)	2.93(4)	3.734(4)	152.(6)	*x*, 1-*y*, -½+*z*
	40.	N1B-H1NB···S1B	0.86(3)	3.01(5)	3.719(4)	141.(6)	*x*, 2-*y*, -½+*z*
	41.	C3A-H3A···O1A	0.95	2.49	3.135(6)	125	*x*, -1+*y*, *z*
	42.	C7A-H7A1···O2A	0.99	2.64	3.330(5)	127	*x*, -*y*, -½+*z*
	43.	C3B-H3B···O2B	0.95	2.47	3.091(6)	123	*x*, -1+*y*, *z*
	44.	C7B-H7B2···O1B	0.99	2.64	3.346(6)	129	*x*, 1-*y*, -½+*z*
5b	45.	N1-H1N···O2	0.86(3)	2.14(3)	2.980(2)	167(3)	1/2+*x*,1-*y*,*z*
	46.	N1-H1N···S1	0.86(3)	2.98(3)	3.707(17)	145(2)	1/2+*x*,1-*y*,*z*
	47.	C3-H3···O2	0.95	2.70	3.374(2)	128	1/2+*x*,1-*y*,*z*
	48.	C5-H5···O1	0.95	2.59	3.293(3)	131	*x*,-1+*y*,*z*
	49.	C7-H7B···O1	0.99	2.71	3.280(2)	117	1/2+*x*,1-*y*,*z*
	50.	C7-H7B···O2	0.99	2.61	3.300(2)	127	1/2+*x*,-*y*,*z*
	51.	C7-H7A···O1	0.99	2.68	3.403(2)	130	*x*,-1+*y*,*z*
6b	52.	N1A-H1N···O2	0.88(6)	2.07(6)	2.928(8)	166(8)	3/2-*x*,-1/2+*y*,3/2-*z*
	53.	C3'-H3'···O2	0.95	2.59	3.455(13)	152	3/2-*x*,-1/2+*y*,3/2-*z*
	54.	C7-H7A···O1	0.99	2.53	3.33(2)	137	*x*,-1+*y*,*z*
	55.	C7-H7B···O1	0.99	2.57	3.54(2)	168	1-*x*,2-*y*,1-*z*
	56.	C14'-H14'···O1	0.99	2.43	3.375(10)	175	1-*x*,2-*y*,1-*z*
7b	57.	N1A-H1NA···O1A	0.842(16)	2.123(16)	2.9588(11)	171.6(15)	-*x*,2-*y*,1-*z*
	58.	N1B-H1NB···O2B	0.852(15)	2.101(16)	2.9458(10)	171.3(14)	2-*x*,1-*y*,-*z*
	59.	C12A-H12A···O1B	0.95	2.68	3.586(12)	160	-1+*x*,*y*,1+*z*
	60.	C12B-H12B···O2A	0.95	2.50	3.4371(12)	170	1+*x*,*y*,-1+*z*
	61.	C15A-H15A···O1B	0.98	2.56	3.3946(12)	153	-1+*x*,*y*,*z*
	62.	C15B-H15D···O2A	0.98	2.59	3.3552(12)	135	1+*x*,*y*,*z*
	63.	C15B-H15E...O3B	0.98	2.65	3.5035(12)	146	1-*x*,1-*y*,1-*z*
	64.	C2A-H2A···Cg3	0.95	2.85	3.5747(10)	134	*x*,*y*,*z*
	65.	C5B-H5B···Cg1	0.95	2.93	3.5861(9)	128	1+*x*,*y*,*z*
	66.	C14A-H14A···Cg1	0.95	2.98	3.7638(10)	141	1-*x*,2-*y*,1-*z*
	67.	C14B-H14C···Cg2	0.95	2.93	3.4698(10)	117	*x*,*y*,-1+*z*
	Cg1= C1A-C2A-C3A-C4A-C5A-C6A; Cg2= C9A-C10A-C11A-C12A-C13A-C14A; Cg3= C1B-C2B-C3B-C4B-C5B-C6B; α- Dihedral angle, Cg-Centroid of ring.						

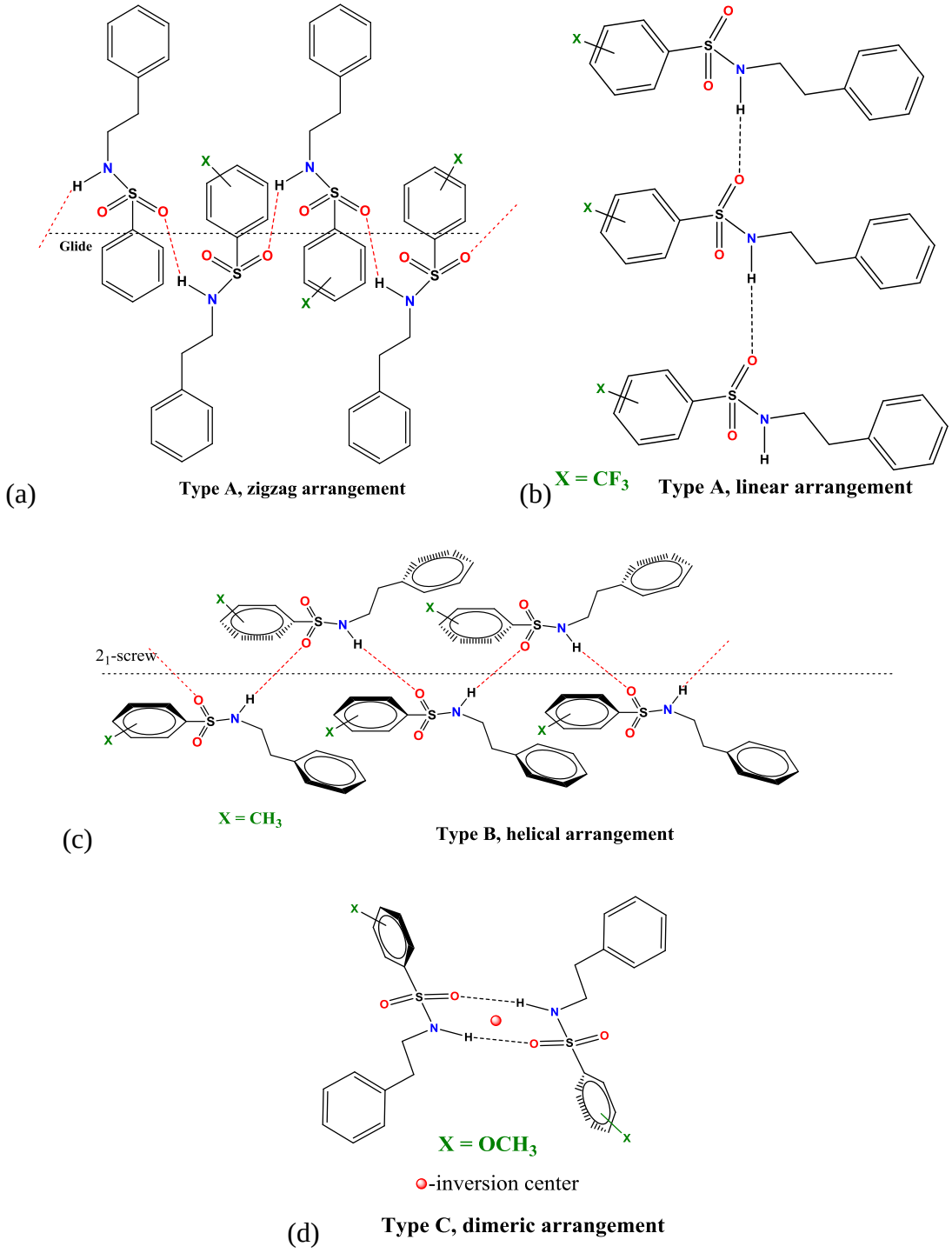
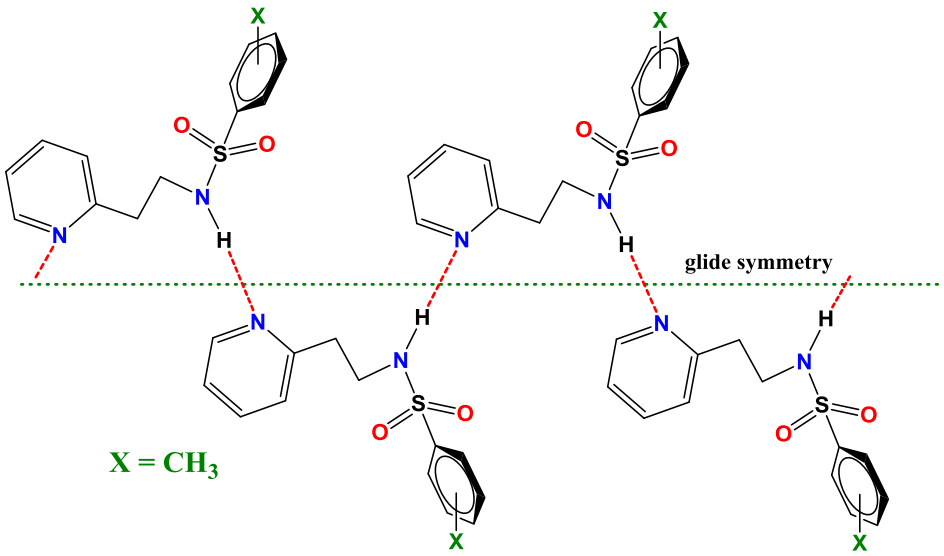


Figure S51. Different hydrogen bonding motifs observed in sulphonamides (**1b** to **7b**).

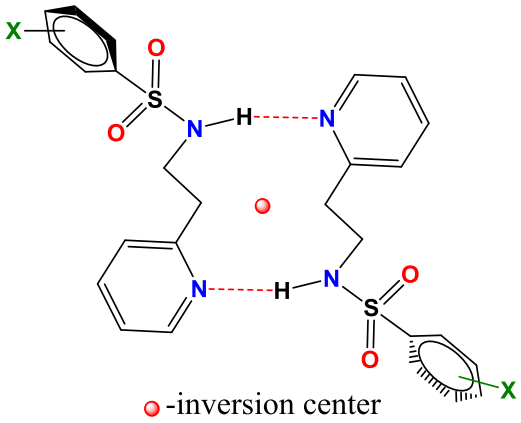
Table S11. Geometrical parameters of intermolecular interactions inN-(pyridin-2 yl)ethyl) benzenesulfonamide (**1c** to **7c**).

Comp.	S. No.	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A /α (°)	Symmetry Codes
1c	1.	N1-H1N···N2	0.85(2)	2.06(3)	2.899(2)	171(2)	1/2-*x*,3/2-*y*,1-*z*
	2.	C2-H2···O1	0.95	2.66	3.561(2)	159	1-*x*,1-*y*,1-*z*
	3.	C13-H13···O2	0.95	2.54	3.300(2)	137	1/2-*x*,3/2-*y*,1-*z*
	4.	F1···F1		2.929(2)		130.52(12)	1-*x*,*y*,1/2-*z*
2c	5.	N1-H1N···N2	0.874(19)	2.013(19)	2.8730(14)	167.6(18)	-*x*,1-*y*,1-*z*
	6.	C2-H2···O1	0.95	2.41	3.2883(14)	153	*x*,3/2-*y*,-1/2+*z*
	7.	C6-H6···O2	0.95	2.40	3.3464(17)	174	1-*x*,-1/2+*y*,3/2-*z*
	8.	C7-H7B···N3	0.99	2.59	3.5254(17)	157	1-*x*,1-*y*,1-*z*
	9.	C8-H8B···O2	0.99	2.61	3.3176(16)	128	*x*,-1+*y*,*z*
	10.	C12-H12···O2	0.95	2.61	3.4421(16)	146	-*x*,-1/2+*y*,3/2-*z*
	11.	C5-H5···Cg2	0.95	2.82	3.6495(13)	146	1-*x*,-1/2+*y*,3/2-*z*
	12.	Cg1···Cg1			3.7323(7)	11.24(6)	-*x*,1/2+*y*,3/2-*z*
	Cg1 = N2-C9-C10-C11-C12-C13; Cg2 = C1-C2-C3-C4-C5-C6						
3c	13.	N1-H1N···N2	0.846(15)	2.053(15)	2.8807(13)	166.0(14)	-*x*,1-*y*,1-*z*
	14.	C2-H2···O2	0.95	2.42	3.2804(13)	150	*x*,1/2-*y*,-1/2+*z*
	15.	C6-H6···O1	0.95	2.44	3.3522(15)	161	1-*x*,1/2+*y*,3/2-*z*
	16.	C8-H8A···O1	0.99	2.54	3.2941(14)	133	*x*,1+*y*,*z*
	17.	C12-H12···O1	0.95	2.59	3.4211(17)	146	-*x*,1/2+*y*,3/2-*z*
	18.	C7-H7A···Cl1	0.99	2.80	3.7152(14)	154	1-*x*,1-*y*,1-*z*
	19.	Cg1···Cg1			3.7505(10)	12.15(4)	-*x*,1/2+*y*,3/2-*z*
	Cg1 = N2-C9-C10-C11-C12-C13						
4c	20.	N1A-H1NA···N2A	0.865(17)	2.061(17)	2.9246(12)	175.5(17)	2-*x*,1-*y*,1-*z*
	21.	N1B-H1NB···N2B	0.837(18)	2.060(18)	2.8918(12)	172.7(18)	2-*x*,1-*y*,-*z*
	22.	C5-H5A···O1A	0.95	2.55	3.1945(12)	126	1+*x*,*y*,*z*
	23.	C11B-H11B···O1A	0.95	2.51	3.3882(13)	153	1-*x*,1-*y*,1-*z*
	24.	C12A-H12A···O1B	0.95	2.64	3.2482(12)	122	1+*x*,*y*,*z*
	25.	C11A-H11A···O1B	0.95	2.63	3.247(1)	123	1+*x*,*y*,*z*
	26.	C13A-H13A···O1A	0.95	2.61	3.3664(12)	137	2-*x*,1-*y*,1-*z*
	27.	C7B-H7B2···O1B	0.99	2.62	3.3967(12)	135	1+*x*,*y*,*z*
	28.	C6A-H6A···Br1B	0.95	3.11	3.8102(10)	131	2-*x*,2-*y*,1-*z*

	29.	C13B-H13B···Br1B	0.95	3.06	3.7789(10)	134	1+*x*,-1+*y*,*z*
	30.	C1A-Br1A···Cg1	1.8943(10)	3.5654(5)	5.4189(11)	165.27(3)	2-*x*,2-*y*,1-*z*
	31.	C1B-Br1B···Cg3	1.8907(10)	3.4432(5)	5.1172(11)	145.70(4)	*x*,1+*y*,*z*
	32.	Cg1···Cg3			4.1721(6)	15.93(5)	*x*,*y*,*z*
	Cg1 = N2A-C9A-C10A-C11A-C12A-C13A; Cg3 = N2B-C9B-C10B-C11B-C12B-C13B						
5c	33.	N1-H1N···N2	0.879(19)	2.048(19)	2.9249(14)	175.4(19)	1-*x*,-*y*,1-*z*
	34.	C3-H3···O2	0.95	2.53	3.2251(14)	131	1+*x*,*y*,*z*
	35.	C6-H6···O2	0.95	2.61	3.3209(16)	132	-*x*,1/2+*y*,1/2-*z*
	36.	C8-H8B···O2	0.99	2.55	3.3665(16)	137	-*x*,-*y*,1-*z*
	37.	C11-H11···O1	0.95	2.63	3.3144(15)	129	-*x*,1-*y*,1-*z*
	38.	C13-H13···O2	0.95	2.53	3.3412(15)	143	1-*x*,-*y*,1-*z*
	39.	C1-H1···Cg1	0.95	2.96	3.7772(13)	144	*x*,1/2-*y*,-1/2+*z*
	Cg1 = N2-C9-C10-C11-C12-C13						
6c	40.	N1-H1N···N2	0.84(2)	2.13(2)	2.9679(18)	177(2)	-1/2+*x*,*y*,3/2-*z*
	41.	C6-H6···O2	0.95	2.58	3.2262(19)	126	1/2-*x*,1/2+*y*,*z*
	42.	C7-H7B···O1	0.99	2.49	3.416(2)	156	1/2+*x*,*y*,3/2-*z*
	43.	C8-H8A···O1	0.99	2.32	3.2913(19)	168	1+*x*,*y*,*z*
	44.	C11-H11···O1	0.95	2.61	3.366(2)	137	1/2-*x*,1/2+*y*,*z*
	45.	C14-H144B···O2	0.98	2.55	3.423(2)	148	1/2-*x*,1/2+*y*,*z*
	46.	C10-H10···Cg2	0.95	2.85	3.6089(17)	137	*x*,*y*,*z*
	Cg2= C1-C2-C3-C4-C5-C6						
7c	47.	N1-H1N···N2	0.83(2)	2.08(2)	2.9060(17)	176(2)	1-*x*,1-*y*,1-*z*
	48.	C2-H2···O1	0.95	2.54	3.4881(18)	173	1-*x*,-1/2+*y*,1/2-*z*
	49.	C8-H8A···O1	0.99	2.46	3.3439(18)	149	*x*,-1+*y*,*z*
	50.	C10-H10···O3	0.95	2.58	3.3816(18)	142	1-*x*,-1/2+*y*,1/2-*z*
	51.	C12-H12···O1	0.95	2.65	3.4891(18)	147	-*x*,1-*y*,1-*z*
	52.	C3-H3···Cg2	0.95	2.78	3.5489(15)	138	1-*x*,-1/2+*y*,1/2-*z*
	53.	Cg1···Cg1			4.1845(9)	0.02(7)	-*x*,-*y*,1-*z*
	54.	Cg1···Cg1			4.0447(9)	0.02(7)	-*x*,1-*y*,1-*z*
	Cg1= N2-C9-C10-C11-C12-C13; Cg2= C1-C2-C3-C4-C5-C6; *α - dihedral angle between two rings, Cg – Centroid of the ring, Cg···Cg – Distance between two ring centroids*						



Type D, zigzag arrangement



Type E, dimeric arrangement

Figure S52. Different hydrogen bonding motifs observed in sulphonamides pyridine derivatives (**1c** to **7c**).

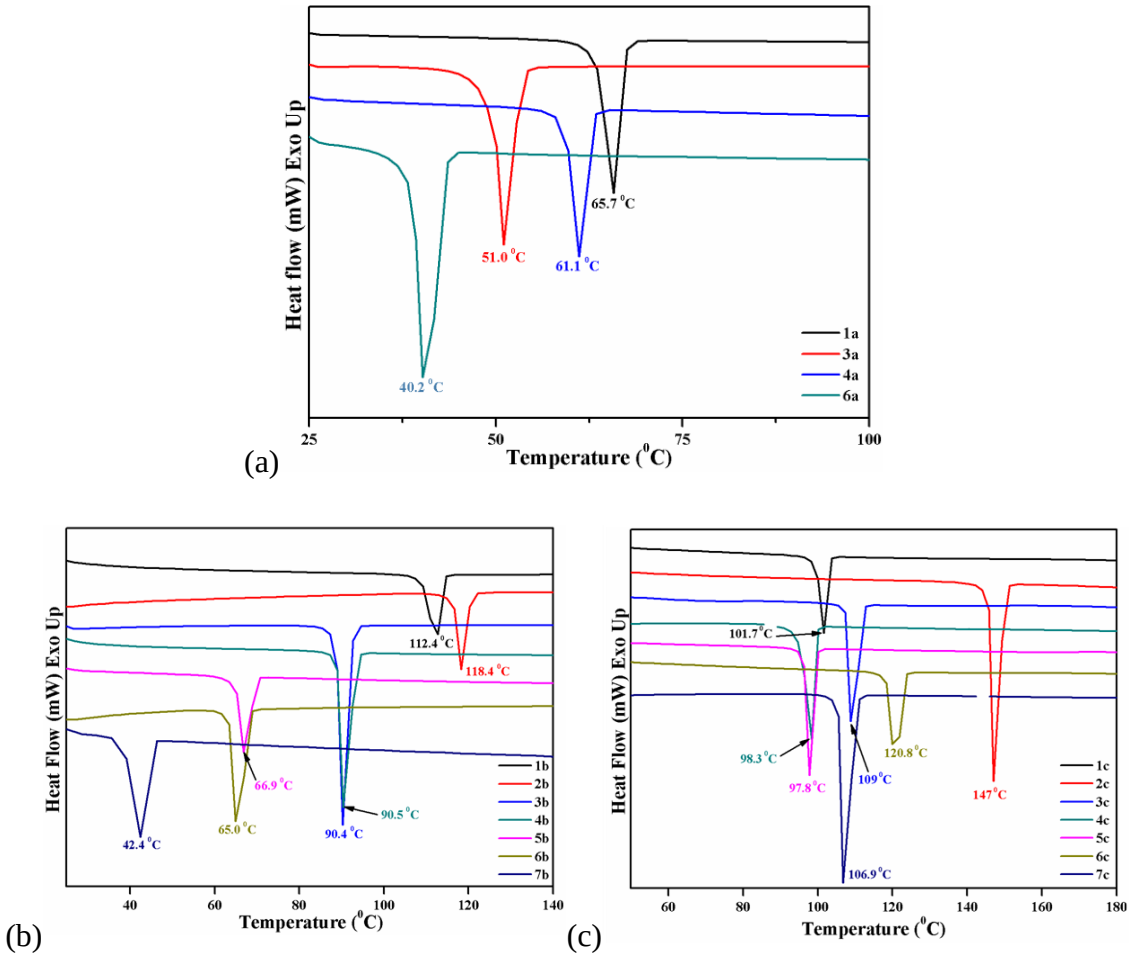


Figure S53. Overlay of DSC profiles of (a) phenethyl benzenesulfonate, (b) N-Phenethyl benzenesulfonamides and (c) N-(pyridin-2-yl)ethyl)benzenesulfonamides.

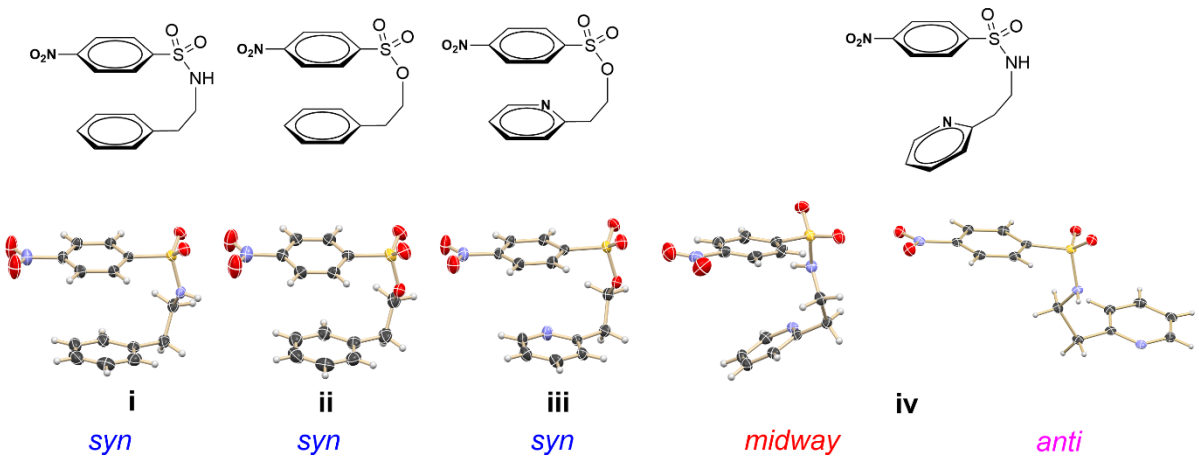


Figure S54. The geometry of sulphonamide and sulfoester derivatives with –NO2 substitution. The data has been taken from Cryst. Growth Des.2016, 16, 2416−2428.

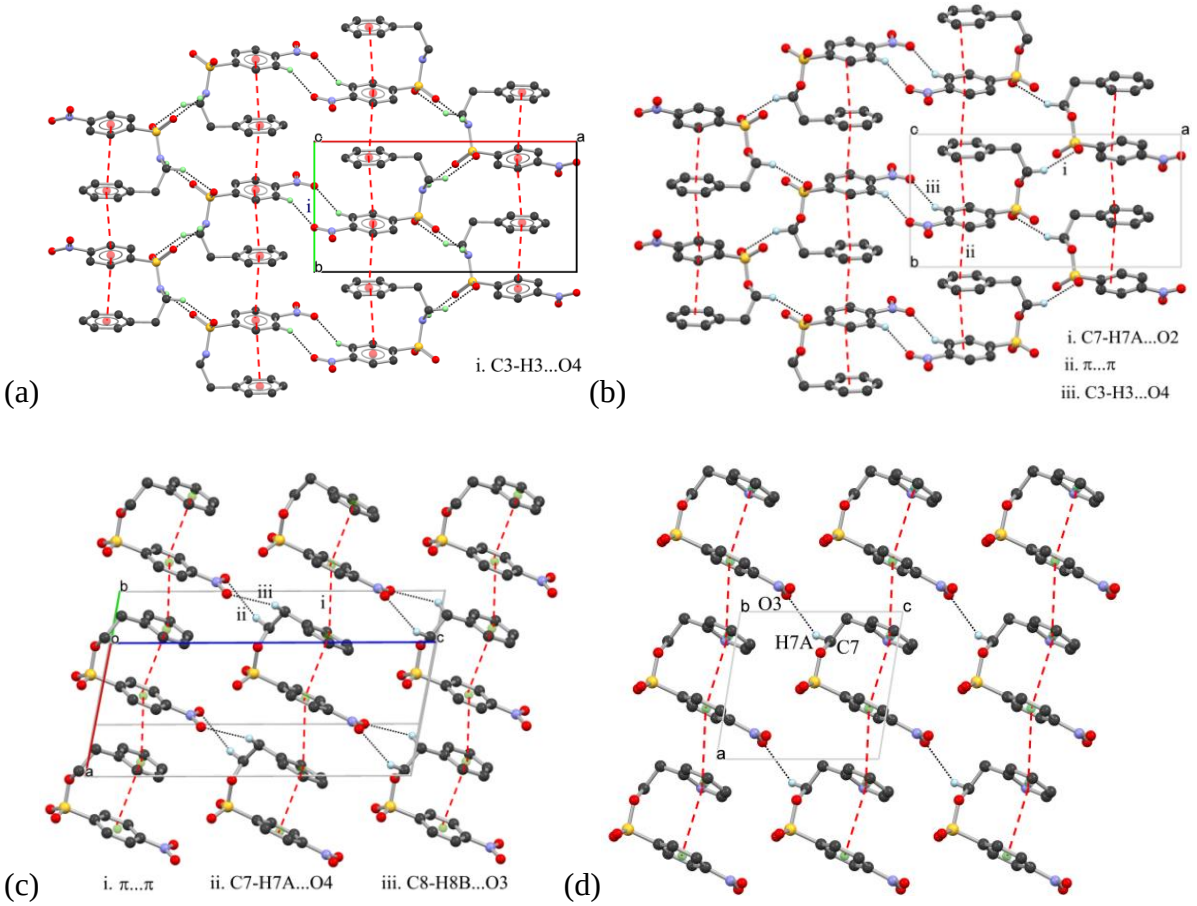


Figure S55. Molecules in compounds **i**, **ii** and **iii** linked via extended chains of parallel displaced π—π stacking interactions.

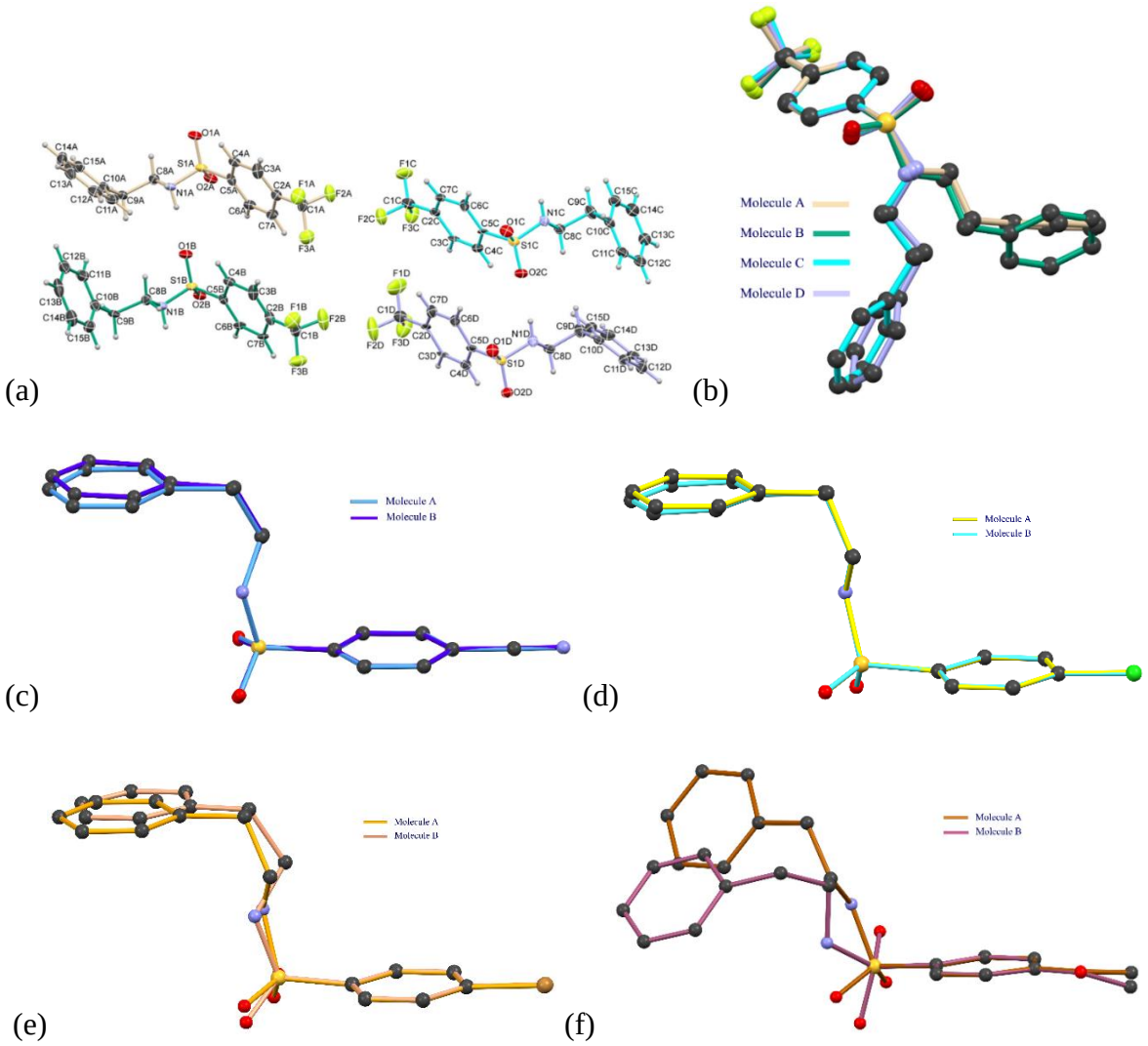


Figure S56. (a) The ORTEP presentation illustrates the molecules of sulfonamide **1b** in an *anti*-conformation, featuring an atom numbering scheme. The displacement ellipsoids are represented at the 40% probability level, and H atoms are depicted as small spheres with arbitrary radii. The structure overlay of symmetry-independent molecules in the crystal structure of compounds (b) **1b**, (c) **2b**, (d) **3b**, (e) **4b** and (f) **7b**.

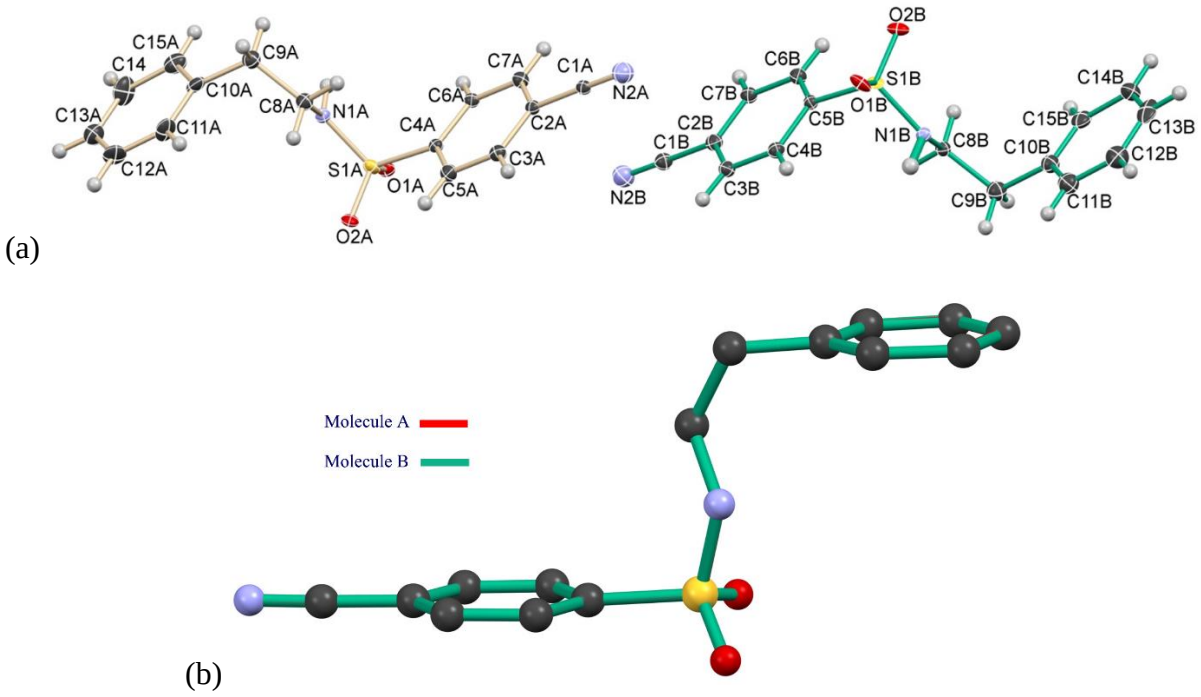


Figure S57. (a) The ORTEP presentation illustrates the molecules of sulfonamide **2b** in an *anti*-conformation, featuring an atom numbering scheme. The displacement ellipsoids are represented at the 40% probability level, and H atoms are depicted as small spheres with arbitrary radii. (b) The structure overlay compares symmetry-independent molecules of 2b, revealing that molecules A and B share a similar conformation.

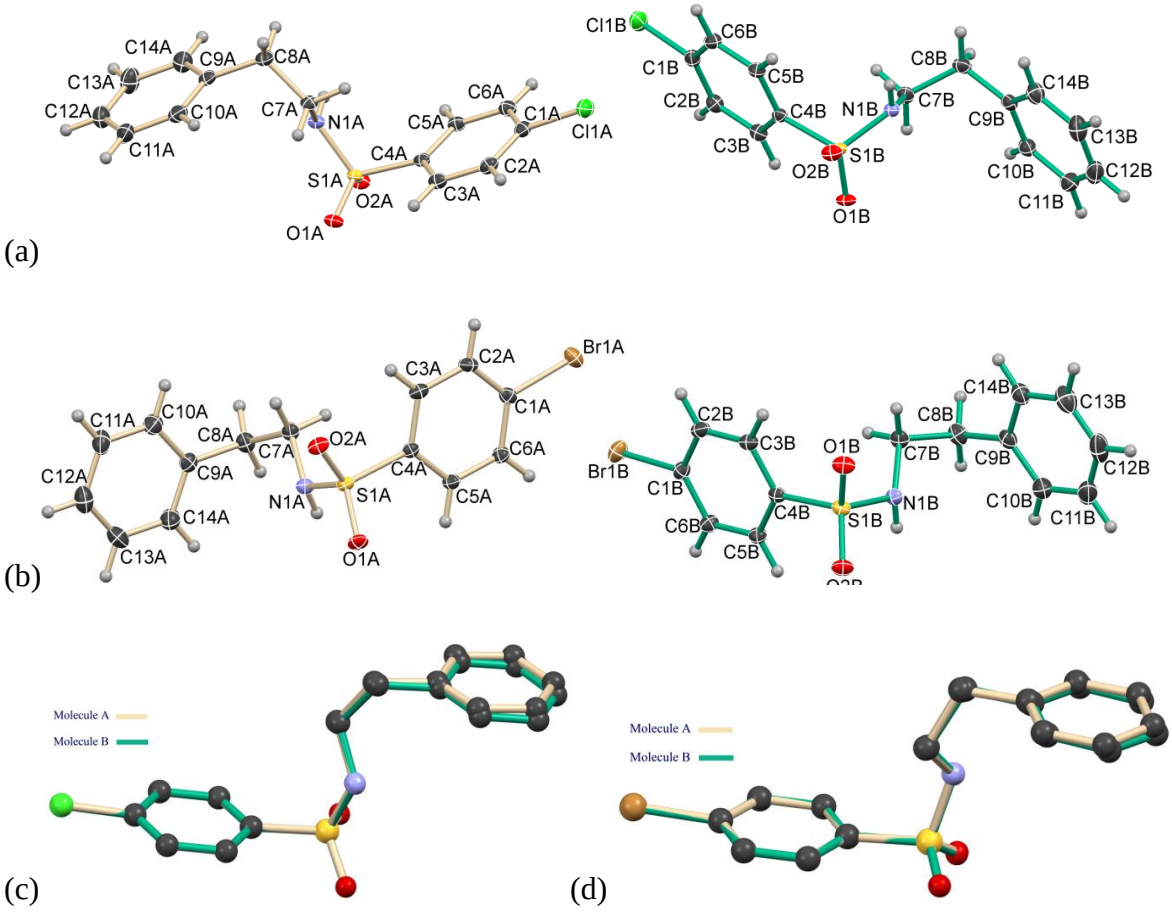


Figure S58. (a) and (b) ORTEPs display molecules of sulfonamide **3b** and **4b**, respectively, in an anti-conformation, accompanied by the atom numbering scheme. The displacement ellipsoids are depicted at the 40% probability level, and H atoms are represented as small spheres with arbitrary radii. (c) and (d) illustrate the structural overlay of both symmetry-independent molecules of **3b** and **4b**, respectively.

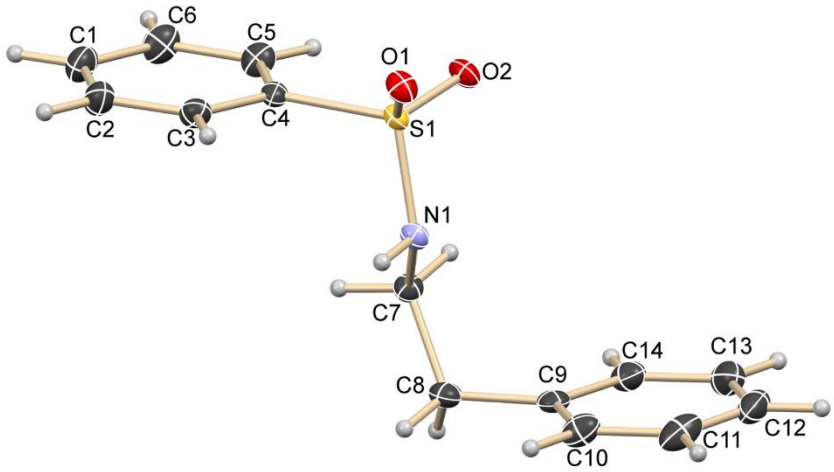


Figure S59. ORTEP of a molecule of compound **5b** with the atom numbering scheme. The displacement ellipsoids are drawn at 50% probability, and H atoms are shown as small spheres with arbitrary radii.

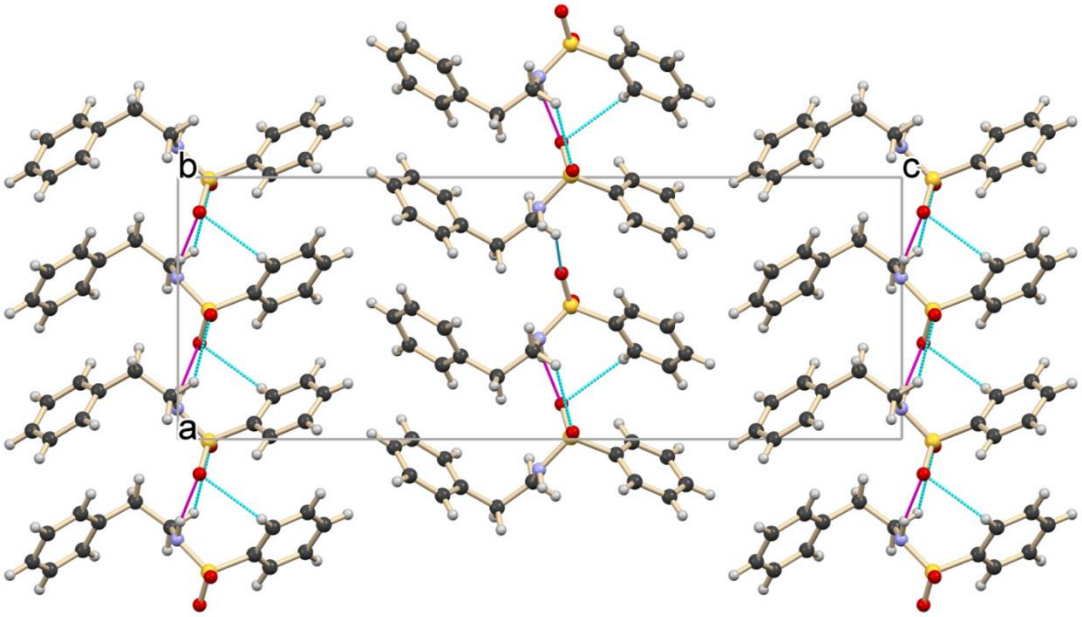


Figure S60. View of molecular packing along the c-axis in **5b** showing a loose association between the adjacent zigzag chain through van der Waals forces.

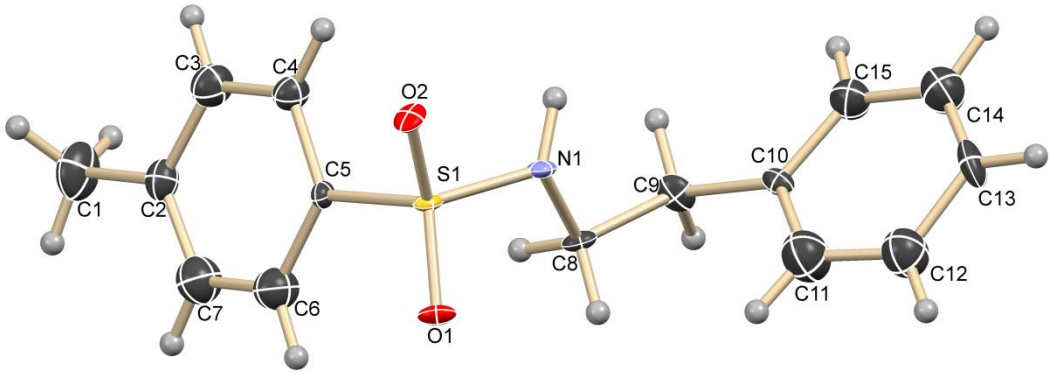


Figure S61. ORTEP of a molecule of compound **6b** with the atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii.

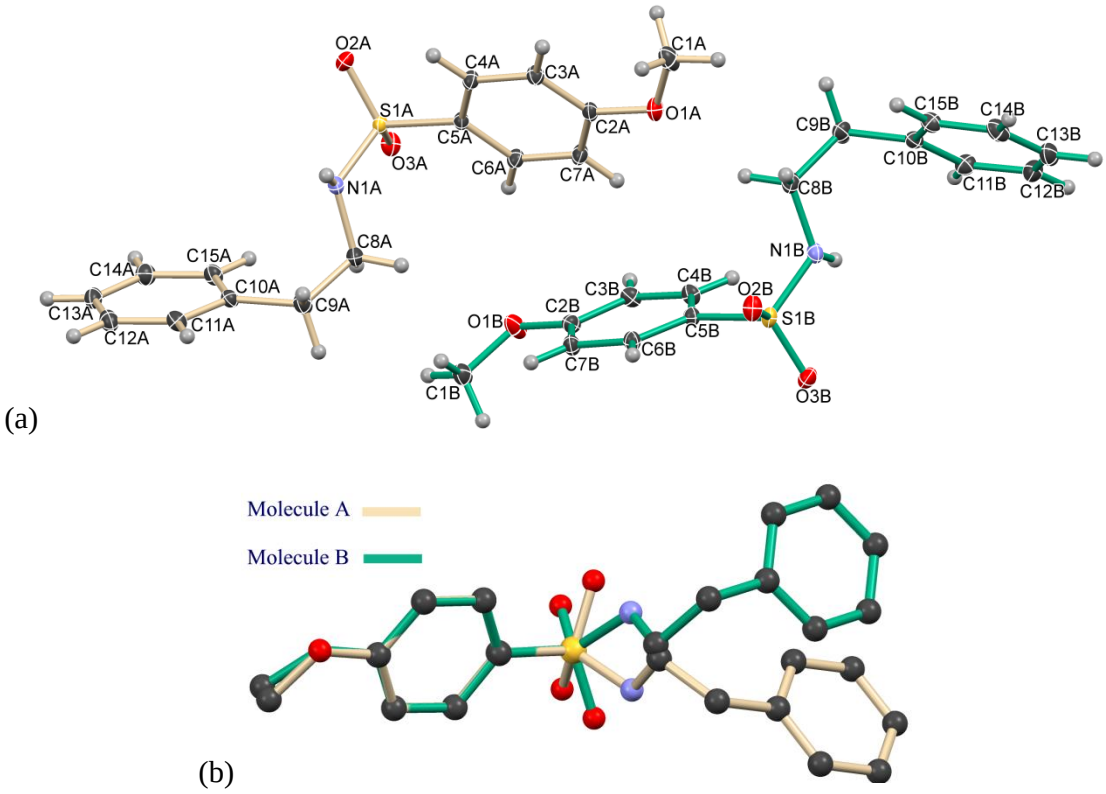


Figure S62. (a) ORTEP of a molecule of compound **7b** with the atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii, (b) the structural overlay of symmetry-independent molecules of 7b.

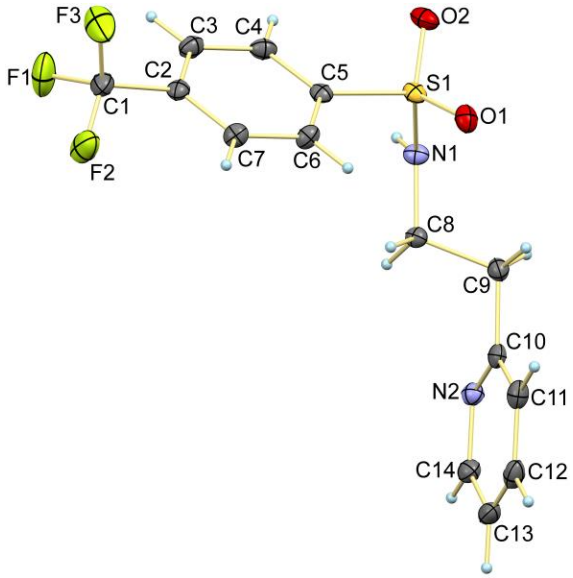


Figure S63. ORTEP of a molecule of compound **1c** with the atom numbering scheme. The displacement ellipsoids are drawn at 40% probability, and H atoms are shown as small spheres with arbitrary radii.

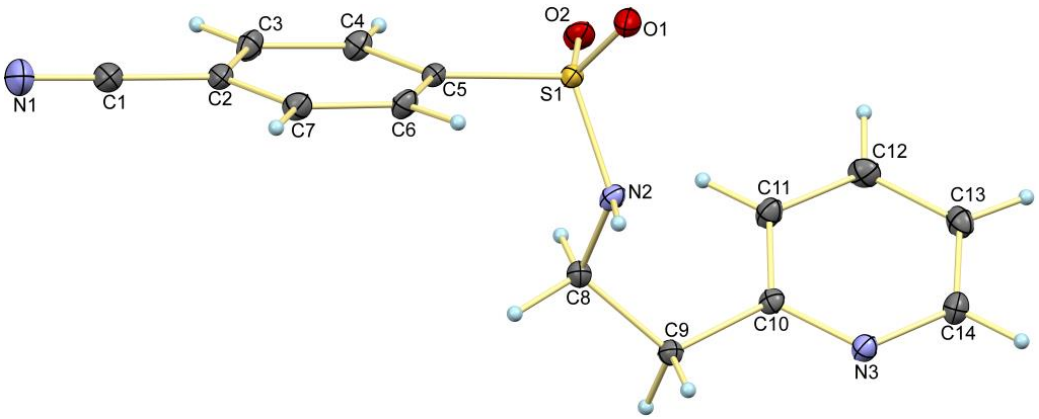


Figure S64. ORTEP of a molecule of compound **2c** with the atom numbering scheme. The displacement ellipsoids are drawn at 40% probability, and H atoms are shown as small spheres with arbitrary radii.

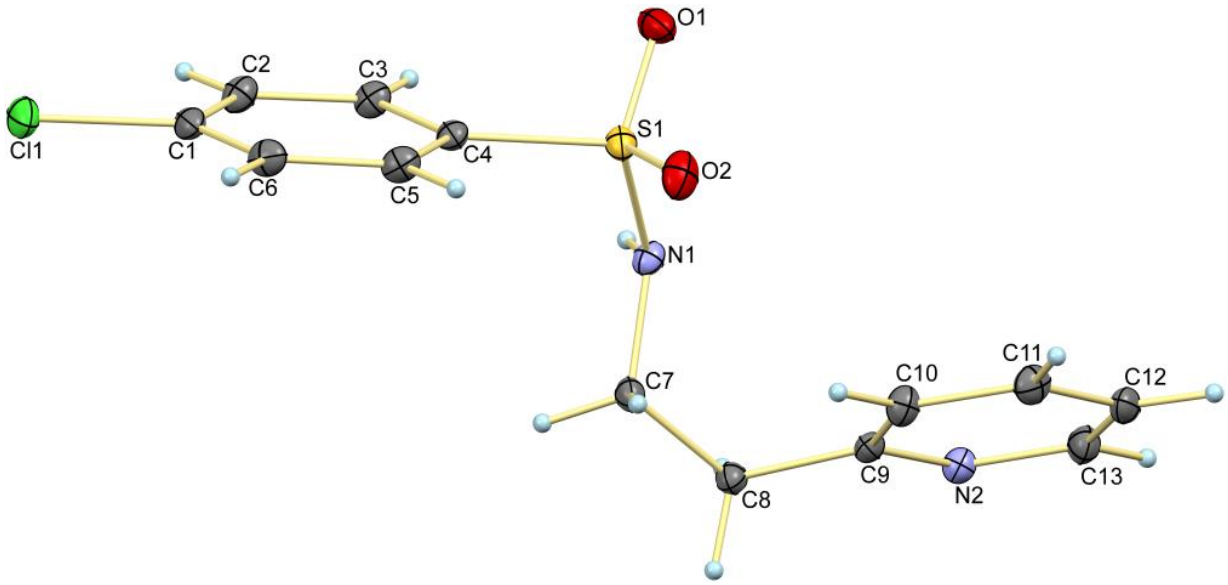


Figure S65. ORTEP of a molecule of compound **3c** with the atom numbering scheme. The displacement ellipsoids are drawn at 40% probability, and H atoms are shown as small spheres with arbitrary radii.

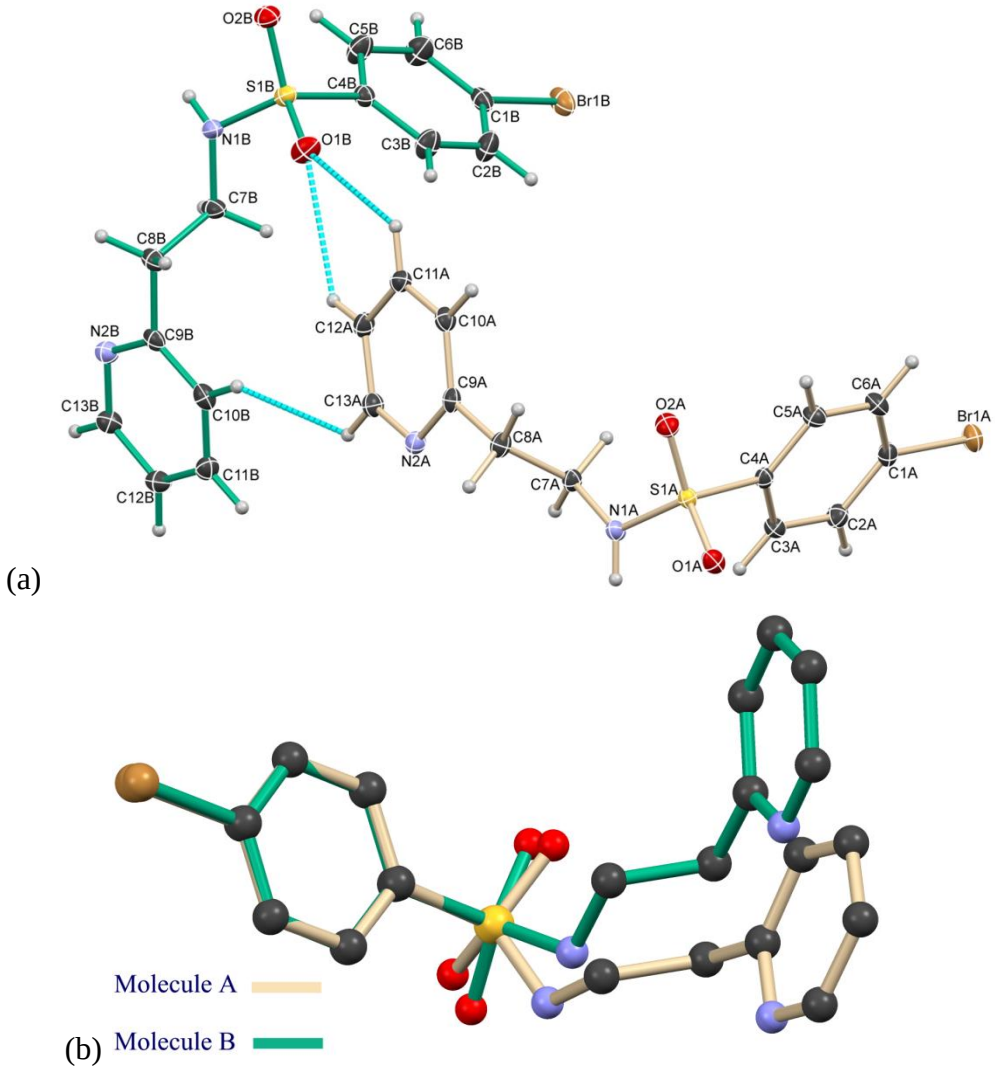


Figure S66. (a) ORTEP of a molecule of compound **4c** with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres with arbitrary radii and (b) the structural overlay of symmetry-independent molecules.

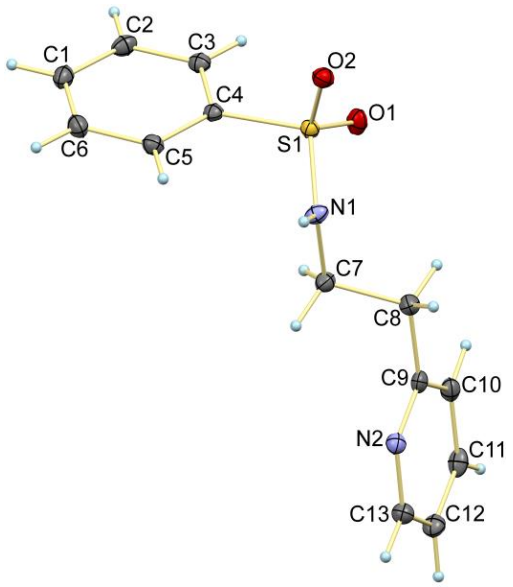


Figure S67. ORTEP of a molecule of compound **5c** with the atom numbering scheme. The displacement ellipsoids are drawn at 40% probability, and H atoms are shown as small spheres with arbitrary radii.

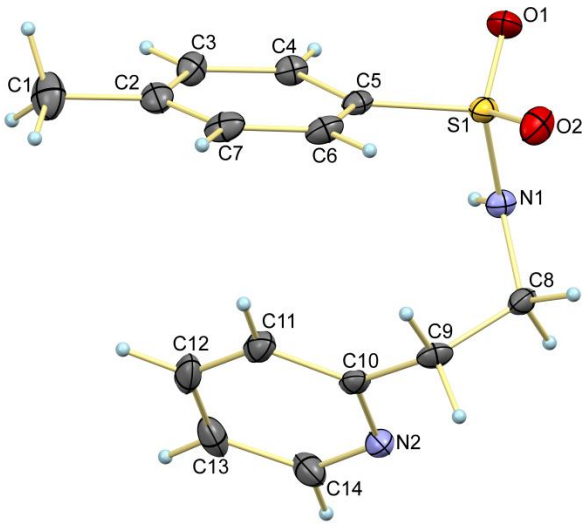


Figure S68. ORTEP of a molecule of compound **6c** with the atom numbering scheme. The displacement ellipsoids are drawn at 40% probability, and H atoms are shown as small spheres with arbitrary radii.

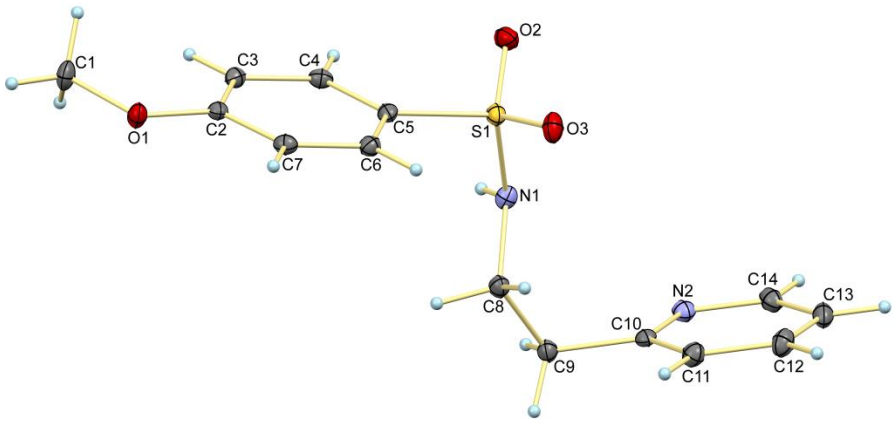


Figure S69. ORTEP of a molecule of compound **7c** with the atom numbering scheme. The displacement ellipsoids are drawn at 40% probability, and H atoms are shown as small spheres with arbitrary radii.

Table S12. Comparative analysis of Packing energy and density parameters.

Compounds	Packing Energy (kJ/mol)	Density (g/cm^3)
1a	-127.3	1.444
3a	-134.5	1.427
4a	-138.9	1.602
6a	-134.4	1.308
1b	-161.4	1.476
2b	-163.4	1.383
3b	-160.9	1.428
4b	-161.5	1.611
5b	-152.1	1.328
6b	-147.3	1.331
7b	-176.7	1.389
1c	-181.9	1.549
2c	-187.1	1.420
3c	-176.3	1.477
4c	-178.9	1.668
5c	-171.4	1.376
6c	-159.2	1.327
7c	-185.7	1.392

Table S13. Intermolecular interactions and potentials values.

Compounds	Intermolecular Interactions	Intermolecular potentials (IMP) (kJ/mol)
1a	An extended π…π assembly	-29.3
	C-H…O	-30.4 & -20.0
3a	An extended π…π assembly	-30.7
	C-H…O	-31.4 & -20.45
4a	An extended π…π assembly	-39.1
	C-H…O and C-H…π	-32.8 & -27.0
6a	An extended π…π assembly	-36.9
	C-H…O and C-H…π	-31.8 & -24.8
1b	Catemer N-H…O	-54.4, -53.0, -52.1 & -50.8
	C-H…O	-46.5, -45.5, -44.4 & -42.7
2b	Catemer N-H…O	-49.6 & -48.5
	C-H…O	-37.6, -36.2, -33.2 & -33.1
3b	Catemer N-H…O	-55.4 & -54.7
	C-H…O	-36.5, -35.4, -32.0 & -31.4
4b	Catemer N-H…O	-56.6 & -55.6
	C-H…O	-36.9, -36.0, -31.6 & -31.0
5b	Catemer N-H…O	-56.3
	C-H…O	-31.4 & -30.0
6b	Catemer N-H…O	-47.1 & -41.0
	C-H…O	-38.1, -34.9, -31.9, -30.7 & -29.5
7b	Dimer N-H…O	-86.9 & -78.1
	C-H…O and C-H…π	-41.0, -35.4, -34.6, -32.3 & -29.3
1c	Dimer N-H…N	-76.6
	C=O…π	-58.5
	C-H…F and C-F…π	-30.1
2c	Dimer N-H…N	-83.7
	C-H…O and C-H…N	-35.4, -30.6 & -30.3
3c	Dimer N-H…N	-79.6

4c	C-H…O, C-H…π & C-H…Cl	-31.8, -31.1 & -25.9
	Dimer N-H…N	-77.1, -74.2
	C-H…O and van der Walls interactions	-45.3, -43.6, -41.6 & -30.0
5c	Dimer N-H…N	-78.8
	C-H…O & C-H…π	-38.7 & -34.5
6c	Catemer N-H…N	-53.8
	C-H…O & C-H…π	-33.5 & -20.4
7c	Dimer N-H…N	-82.9
	C-H…O, C-H…π & π…π	-40.4, -39.4 & -22.0

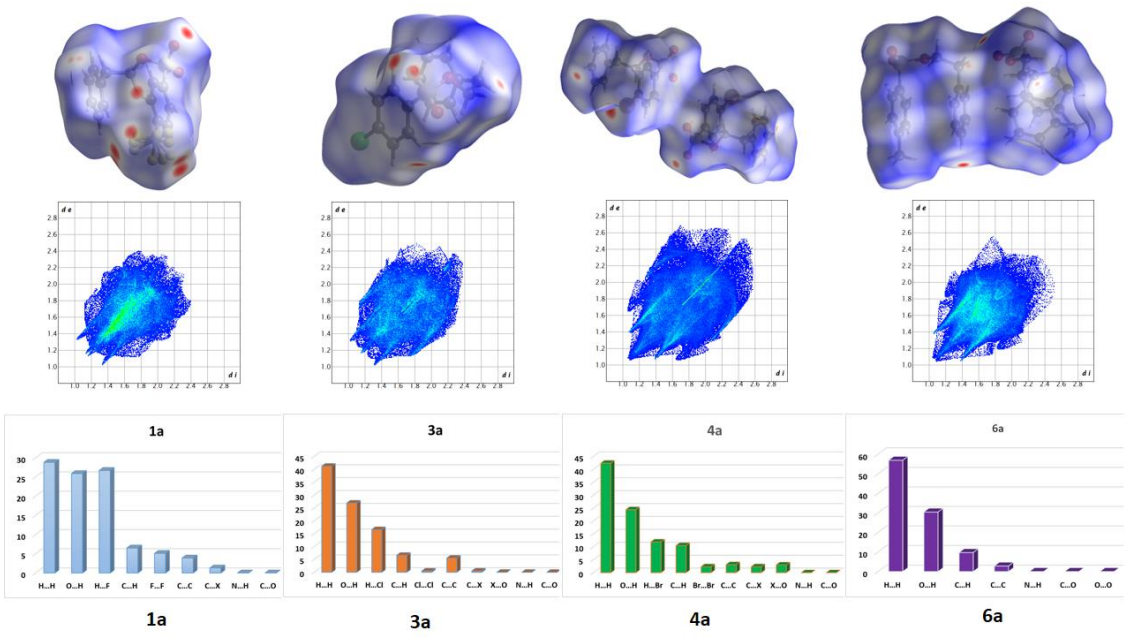


Figure S70. Hirshfeld surfaces, fingerprint plots and the contributions of various intermolecular interactions to Hirshfield surface areas for sulfoester derivatives **1a** to **6a**.

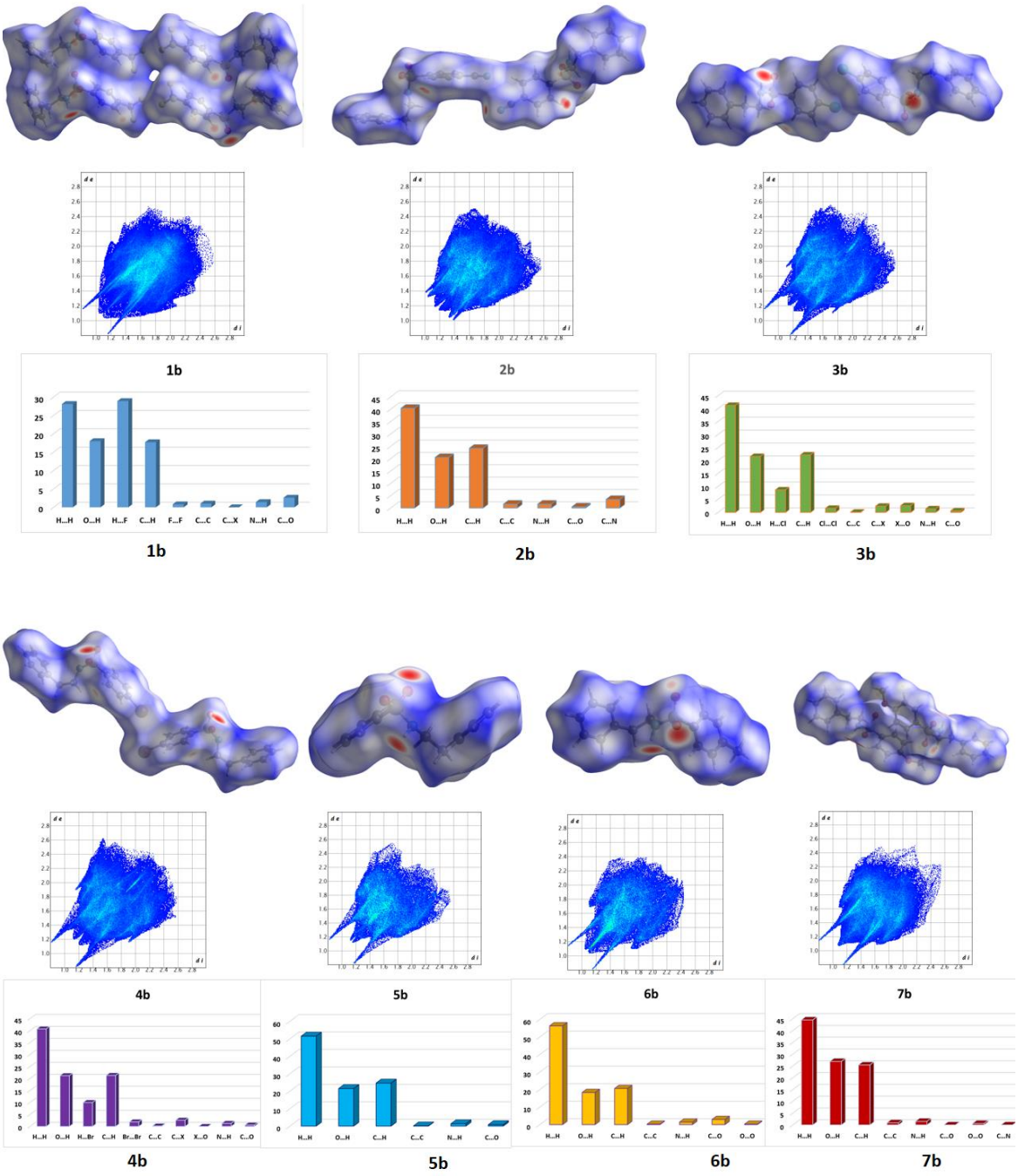


Figure S71. Hirshfeld surfaces, fingerprint plots and the contributions of various intermolecular interactions to Hirshfield surface areas for sulphonamide derivatives **1b** to **7b**.

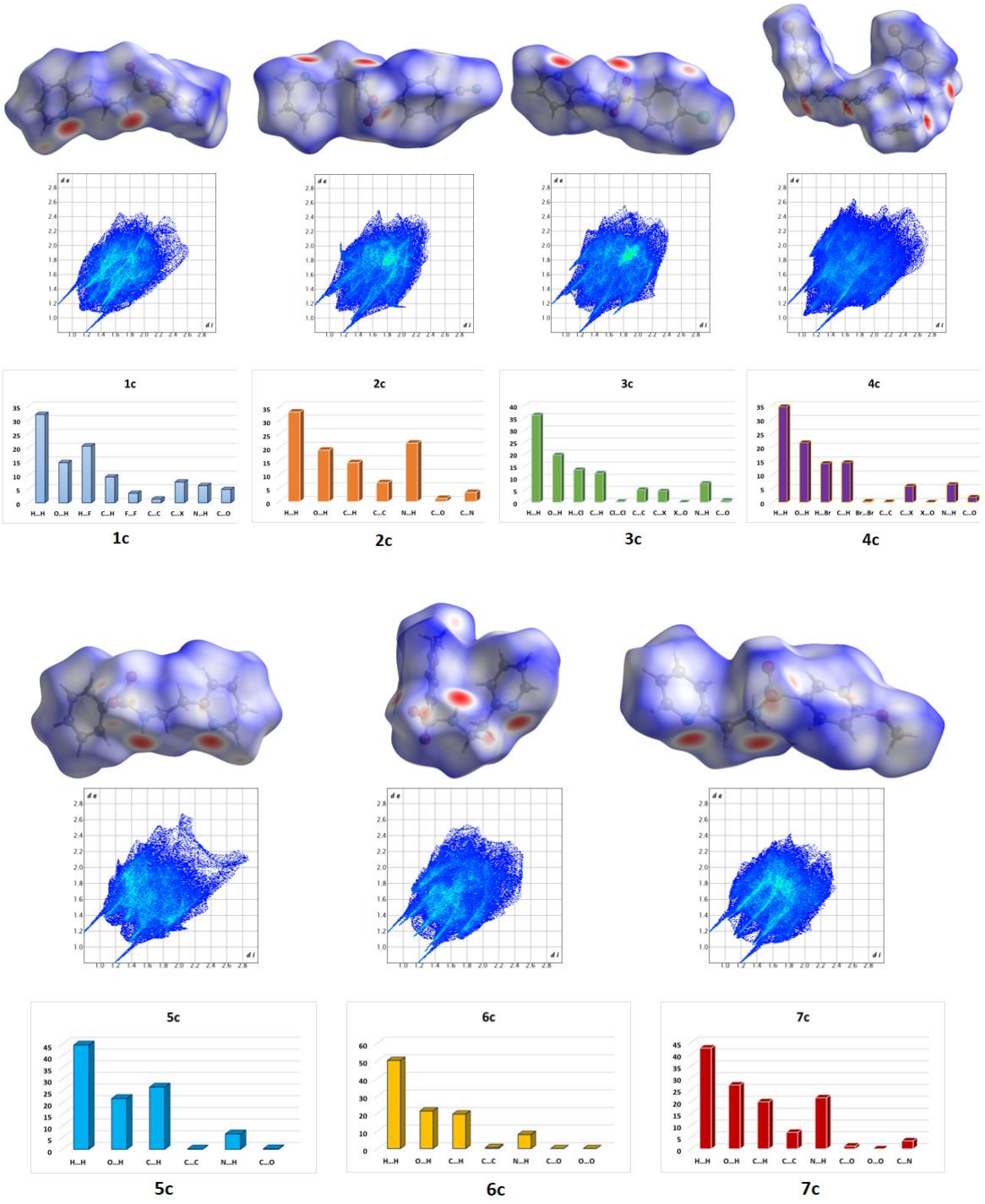
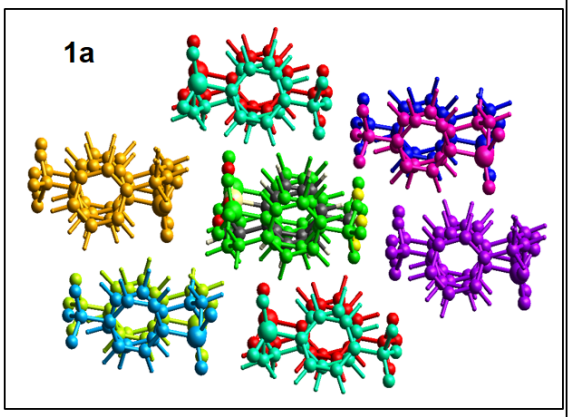


Figure S72. Hirshfeld surfaces, fingerprint plots and the contributions of various intermolecular interactions to Hirshfield surface areas for sulphonamide derivatives **1c** to **7c**.



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

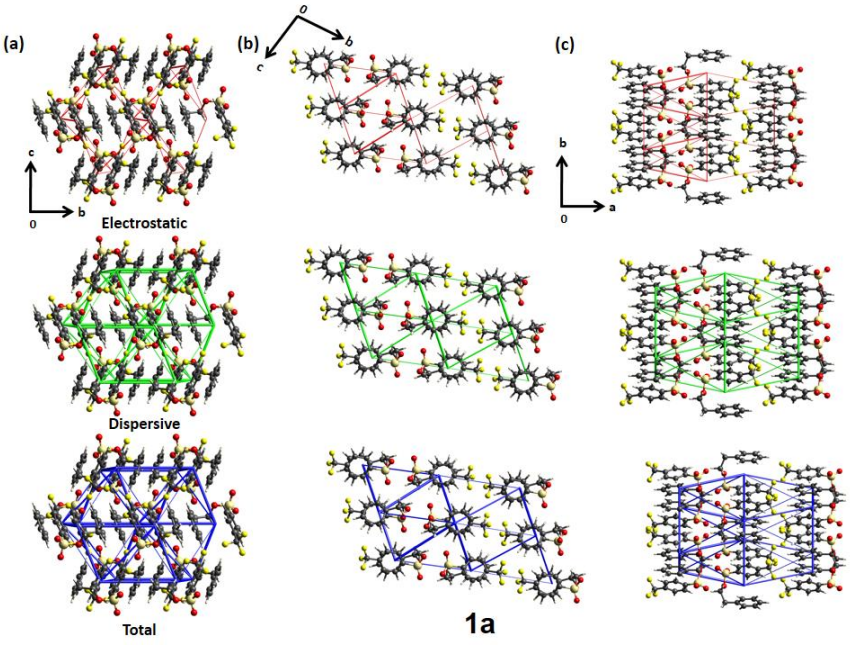
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, -y+1/2, z+1/2	7.35	B3LYP/6-31G(d,p)	-8.5	-3.3	-17.3	12.5	-18.7
	2	-x, y+1/2, -z+1/2	9.91	B3LYP/6-31G(d,p)	-4.8	-3.0	-12.2	6.9	-13.7
	1	-x, -y, -z	8.50	B3LYP/6-31G(d,p)	-15.7	-4.5	-18.2	9.6	-29.8
	2	x, y, z	7.94	B3LYP/6-31G(d,p)	-4.7	-1.2	-29.4	10.5	-25.0
	2	x, -y+1/2, z+1/2	6.79	B3LYP/6-31G(d,p)	-6.3	-3.3	-30.8	13.1	-27.8
	1	-x, -y, -z	11.28	B3LYP/6-31G(d,p)	2.9	-0.7	-5.1	1.1	-1.2
	1	-x, -y, -z	8.27	B3LYP/6-31G(d,p)	-4.8	-0.7	-17.8	5.7	-17.5
	2	-x, y+1/2, -z+1/2	10.17	B3LYP/6-31G(d,p)	-0.1	-0.1	-8.5	1.3	-6.8
	1	-x, -y, -z	11.11	B3LYP/6-31G(d,p)	0.6	-0.1	-2.3	0.0	-1.4

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

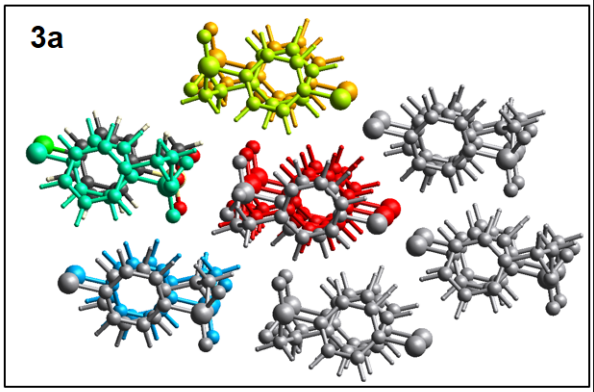
(a)



(b)

Figure S73. The interaction energy is based on energy frameworks for compound **1a** (a) and (b) that show electrostatic and dispersion energy contributions to the total energy.

(a)



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	-x, y+1/2, -z+1/2	9.10	B3LYP/6-31G(d,p)	-4.5	-2.9	-12.4	8.1	-12.7
	1	-x, -y, -z	7.73	B3LYP/6-31G(d,p)	-16.5	-2.3	-19.8	12.3	-28.8
	1	-x, -y, -z	10.22	B3LYP/6-31G(d,p)	2.9	-4.2	-6.3	1.7	-4.5
	0	x, -y+1/2, z+1/2	7.58	B3LYP/6-31G(d,p)	-9.9	nan	-16.1	15.6	nan
	1	x, y, z	7.71	B3LYP/6-31G(d,p)	-4.3	-1.4	-31.2	14.1	-24.0
	1	x, -y+1/2, z+1/2	6.53	B3LYP/6-31G(d,p)	-9.6	-4.0	-32.3	18.5	-29.8
	0	-x, -y, -z	8.01	B3LYP/6-31G(d,p)	-6.0	-0.9	-22.0	15.8	-16.4
	0	-x, y+1/2, -z+1/2	10.28	B3LYP/6-31G(d,p)	-0.3	-0.1	-8.0	5.1	-4.2
	0	-x, -y, -z	10.43	B3LYP/6-31G(d,p)	0.1	-0.3	-7.2	2.6	-4.8

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(b)

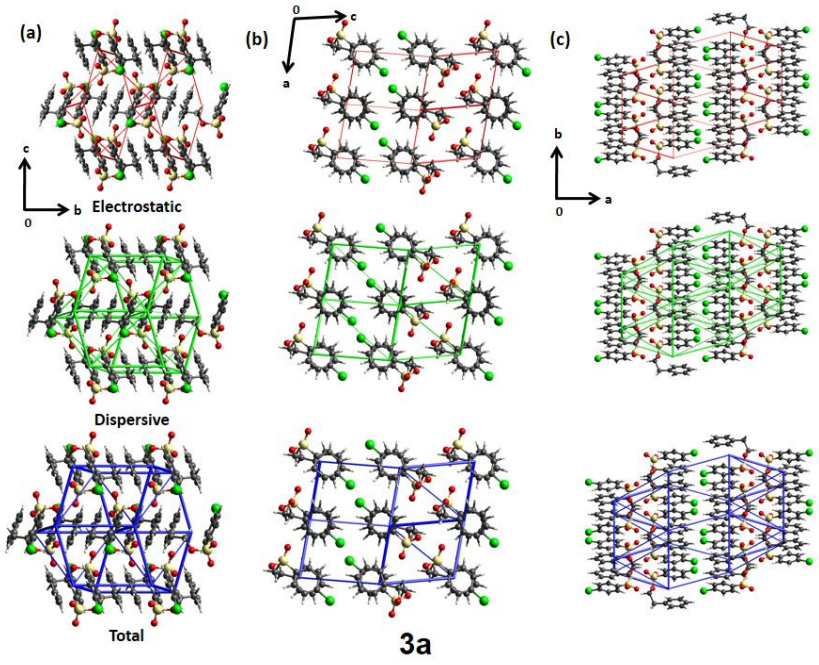
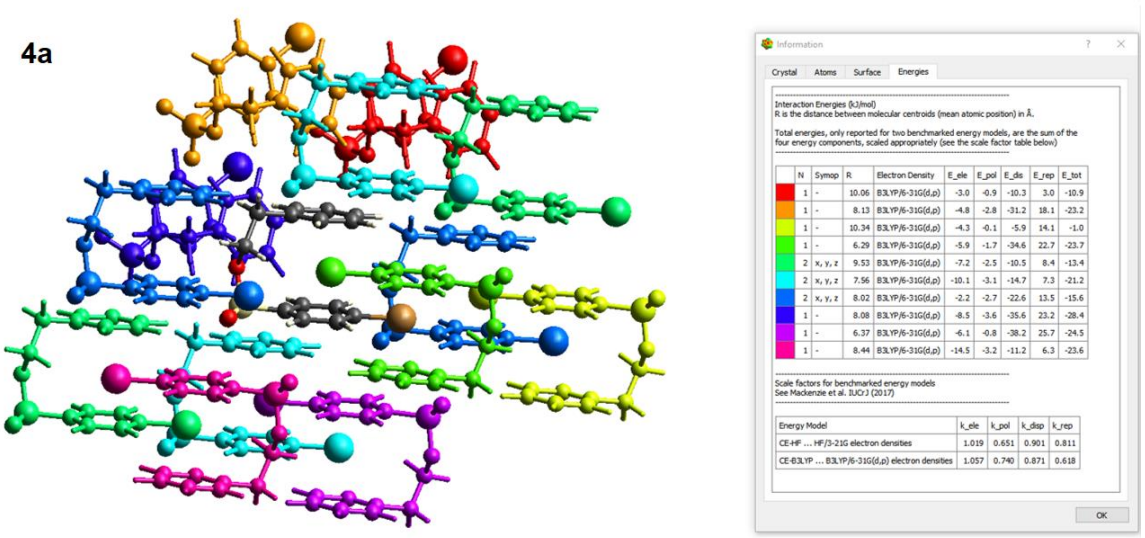
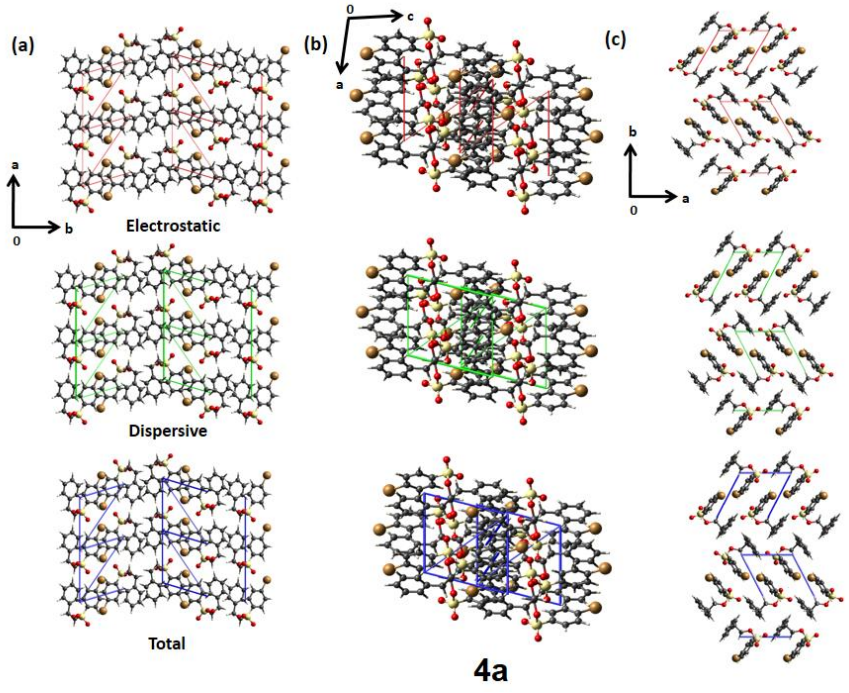


Figure S74. The interaction energy is based on energy frameworks for compound **3a** (a), and (b) that show electrostatic and dispersion energy contributions to the total energy.



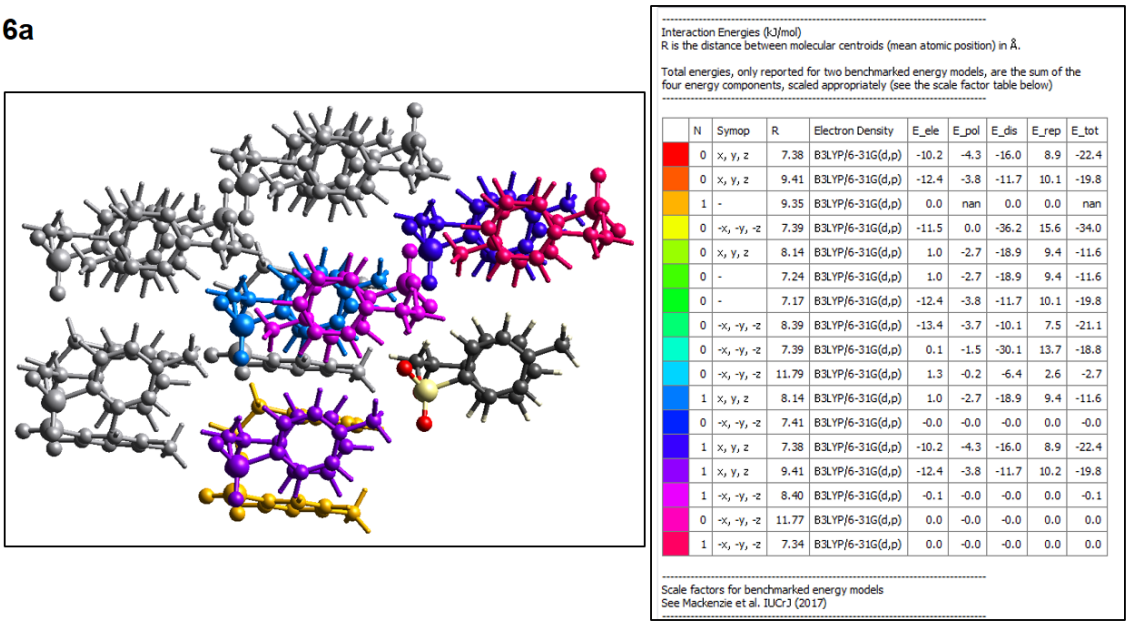
(a)



(b)

Figure S75. The interaction energy is based on energy frameworks for compound **4a** (a), and (b) that show and dispersion energy contributions to the total energy.

(a)



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	0	x, y, z	7.38	B3LYP/6-31G(d,p)	-10.2	-4.3	-16.0	8.9	-22.4
	0	x, y, z	9.41	B3LYP/6-31G(d,p)	-12.4	-3.8	-11.7	10.1	-19.8
	1	-	9.35	B3LYP/6-31G(d,p)	0.0	nan	0.0	0.0	nan
	0	-x, -y, -z	7.39	B3LYP/6-31G(d,p)	-11.5	0.0	-36.2	15.6	-34.0
	0	x, y, z	8.14	B3LYP/6-31G(d,p)	1.0	-2.7	-18.9	9.4	-11.6
	0	-	7.24	B3LYP/6-31G(d,p)	1.0	-2.7	-18.9	9.4	-11.6
	0	-	7.17	B3LYP/6-31G(d,p)	-12.4	-3.8	-11.7	10.1	-19.8
	0	-x, -y, -z	8.39	B3LYP/6-31G(d,p)	-13.4	-3.7	-10.1	7.5	-21.1
	0	-x, -y, -z	7.39	B3LYP/6-31G(d,p)	0.1	-1.5	-30.1	13.7	-18.8
	0	-x, -y, -z	11.79	B3LYP/6-31G(d,p)	1.3	-0.2	-6.4	2.6	-2.7
	1	x, y, z	8.14	B3LYP/6-31G(d,p)	1.0	-2.7	-18.9	9.4	-11.6
	0	-x, -y, -z	7.41	B3LYP/6-31G(d,p)	-0.0	-0.0	-0.0	0.0	-0.0
	1	x, y, z	7.38	B3LYP/6-31G(d,p)	-10.2	-4.3	-16.0	8.9	-22.4
	1	x, y, z	9.41	B3LYP/6-31G(d,p)	-12.4	-3.8	-11.7	10.2	-19.8
	1	-x, -y, -z	8.40	B3LYP/6-31G(d,p)	-0.1	-0.0	-0.0	0.0	-0.1
	0	-x, -y, -z	11.77	B3LYP/6-31G(d,p)	0.0	-0.0	-0.0	0.0	0.0
	1	-x, -y, -z	7.34	B3LYP/6-31G(d,p)	0.0	-0.0	-0.0	0.0	0.0

(b)

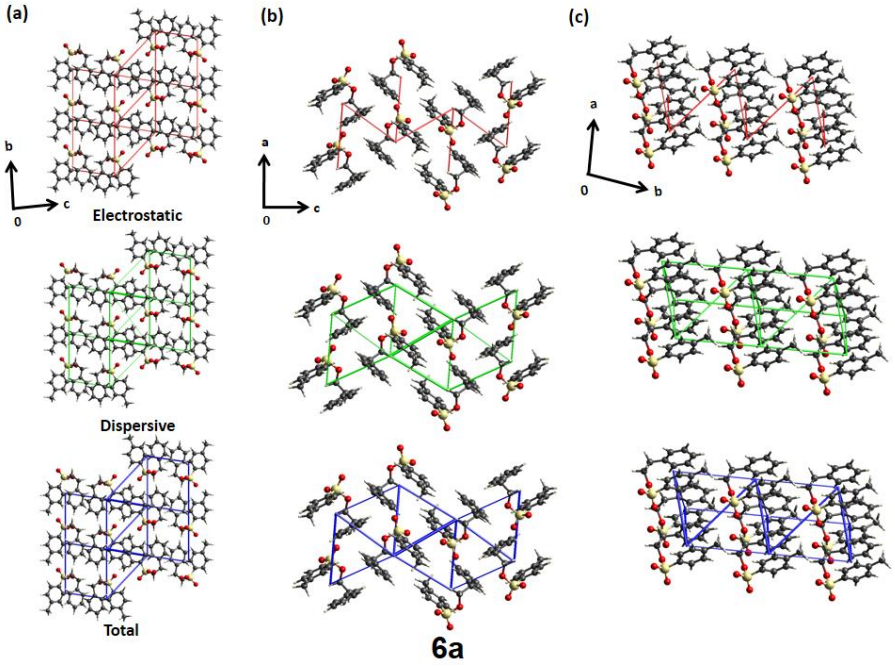
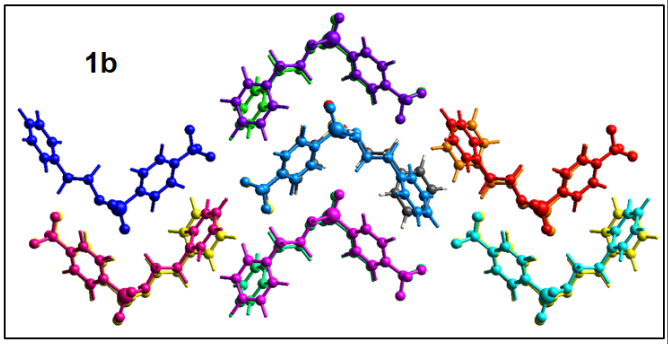


Figure S76. The interaction energy is based on energy frameworks for compound **6a** (a) and (b) that show electrostatic and dispersion energy contributions to the total energy.



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

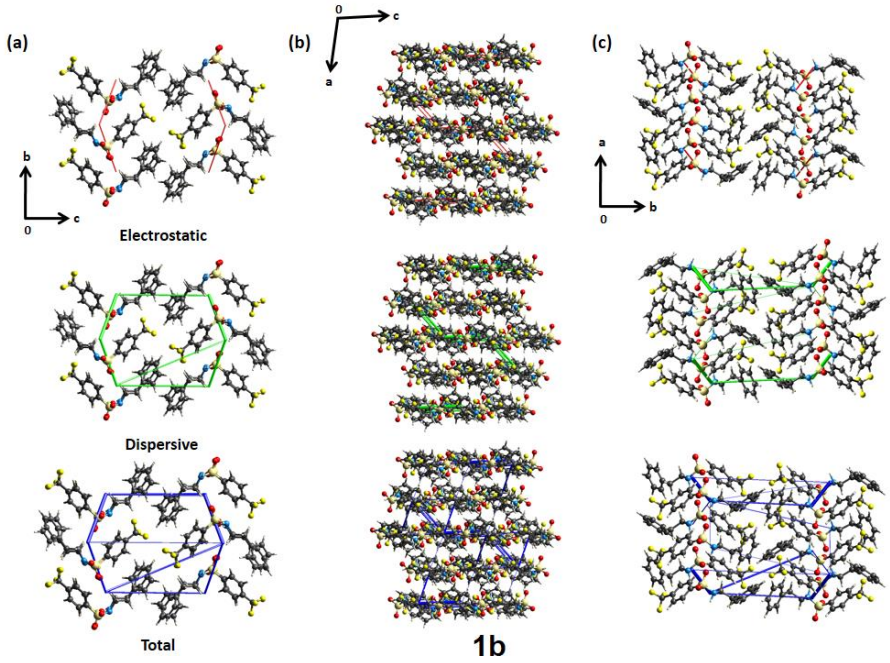
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-	13.13	B3LYP/6-31G(d,p)	-2.9	-2.4	-22.6	13.1	-16.4
	1	-	13.94	B3LYP/6-31G(d,p)	0.0	-29.7	0.0	0.0	-22.0
	2	-x, y+1/2, -z	14.65	B3LYP/6-31G(d,p)	-1.8	-0.6	-6.1	3.3	-5.5
	1	-	5.03	B3LYP/6-31G(d,p)	0.0	-5.5	0.0	0.0	-4.1
	1	-	5.82	B3LYP/6-31G(d,p)	-15.9	-0.0	-43.6	23.7	-40.1
	1	-	6.38	B3LYP/6-31G(d,p)	-12.1	-0.0	-32.2	27.9	-23.5
	1	-	14.65	B3LYP/6-31G(d,p)	-1.8	-7.0	-6.1	3.3	-10.3
	1	-	5.16	B3LYP/6-31G(d,p)	-0.6	-5.6	-0.7	0.0	-5.5
	1	-	13.29	B3LYP/6-31G(d,p)	-0.1	-5.5	-4.4	0.8	-7.6
	1	-	6.30	B3LYP/6-31G(d,p)	0.0	-5.6	0.0	0.0	-4.2
	1	-	5.93	B3LYP/6-31G(d,p)	-1.8	-7.0	-6.1	3.3	-10.3
	1	-	14.69	B3LYP/6-31G(d,p)	-1.8	-0.2	-6.1	3.3	-5.2

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

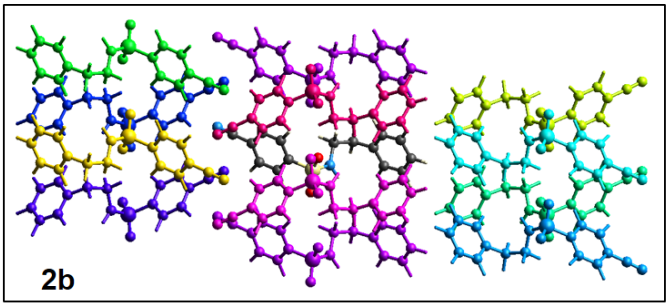
(a)



(b)

Figure S77. The interaction energy is based on energy frameworks for compound **1b** (a) and (b) that show electrostatic and dispersion energy contributions to the total energy.

(a)



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
0	x+1/2, -y, z	5.27	B3LYP/6-31G(d,p)	-18.6	-0.6	-44.7	33.4	-38.4
0	x, y, z	5.72	B3LYP/6-31G(d,p)	-4.4	-5.4	-35.2	24.8	-24.0
1	-	12.53	B3LYP/6-31G(d,p)	0.0	-0.2	0.0	0.0	-0.1
1	-	14.49	B3LYP/6-31G(d,p)	-0.1	-2.8	-0.0	0.0	-2.2
0	x+1/2, -y, z	5.56	B3LYP/6-31G(d,p)	-6.1	-5.6	-39.9	22.2	-31.7
1	-	13.86	B3LYP/6-31G(d,p)	-4.4	-5.7	-35.2	24.8	-24.2
1	-	14.52	B3LYP/6-31G(d,p)	-0.1	-0.0	-0.0	0.0	-0.1
1	-	14.32	B3LYP/6-31G(d,p)	-0.1	-5.2	-0.0	0.0	-4.0
1	-	15.34	B3LYP/6-31G(d,p)	-0.1	-0.2	-0.0	0.0	-0.2
1	-	13.83	B3LYP/6-31G(d,p)	-18.6	-0.1	-44.7	33.4	-38.0
1	-	13.86	B3LYP/6-31G(d,p)	-6.1	-0.1	-39.9	22.2	-27.5
2	x, y, z	5.72	B3LYP/6-31G(d,p)	-4.4	-0.0	-35.2	24.8	-20.1
2	x+1/2, -y, z	5.32	B3LYP/6-31G(d,p)	-6.1	-0.2	-39.9	22.2	-27.6
2	x+1/2, -y, z	5.50	B3LYP/6-31G(d,p)	-18.6	-0.2	-44.7	33.4	-38.0

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811

(b)

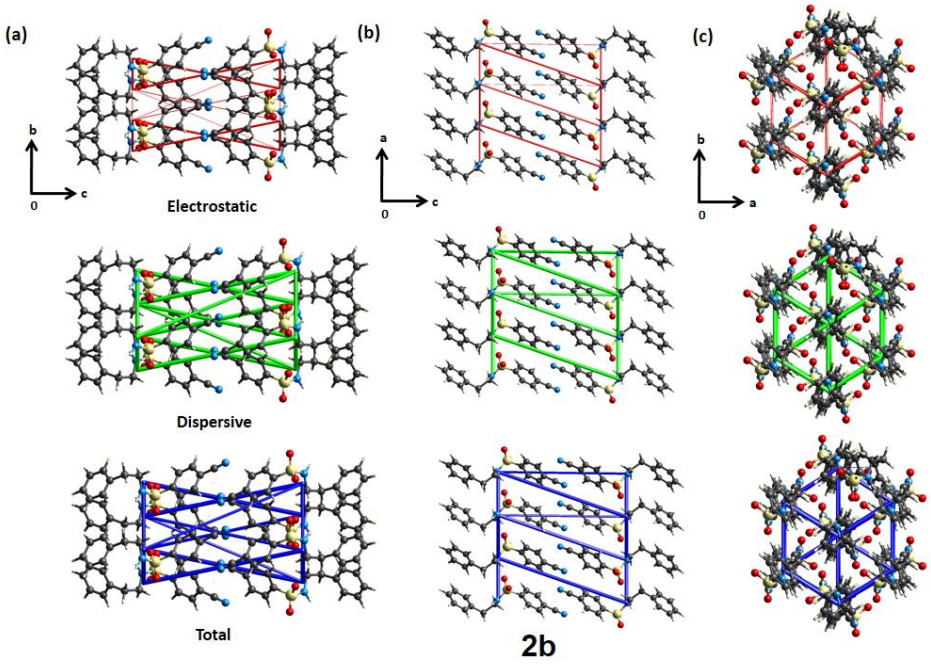
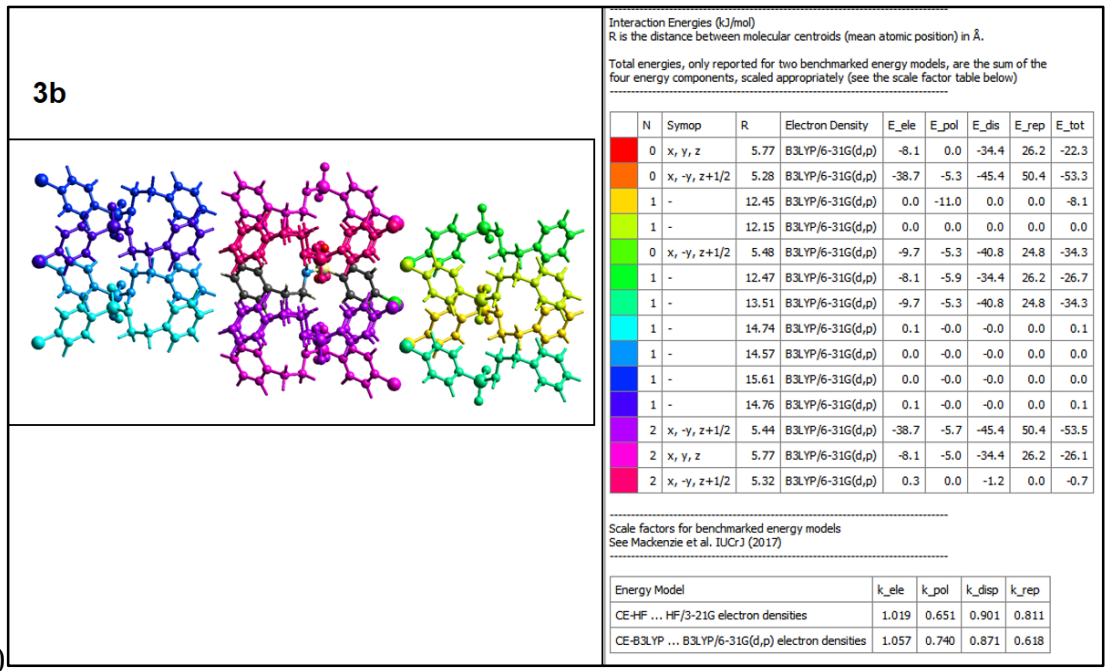


Figure S78. The interaction energy is based on energy frameworks for compound **2b** (a) and (b) that show electrostatic and dispersion energy contributions to the total energy.

(a)



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	0	x, y, z	5.77	B3LYP/6-31G(d,p)	-8.1	0.0	-34.4	26.2	-22.3
	0	x, -y, z+1/2	5.28	B3LYP/6-31G(d,p)	-38.7	-5.3	-45.4	50.4	-53.3
	1	-	12.45	B3LYP/6-31G(d,p)	0.0	-11.0	0.0	0.0	-8.1
	1	-	12.15	B3LYP/6-31G(d,p)	0.0	0.0	0.0	0.0	0.0
	0	x, -y, z+1/2	5.48	B3LYP/6-31G(d,p)	-9.7	-5.3	-40.8	24.8	-34.3
	1	-	12.47	B3LYP/6-31G(d,p)	-8.1	-5.9	-34.4	26.2	-26.7
	1	-	13.51	B3LYP/6-31G(d,p)	-9.7	-5.3	-40.8	24.8	-34.3
	1	-	14.74	B3LYP/6-31G(d,p)	0.1	-0.0	-0.0	0.0	0.1
	1	-	14.57	B3LYP/6-31G(d,p)	0.0	-0.0	-0.0	0.0	0.0
	1	-	15.61	B3LYP/6-31G(d,p)	0.0	-0.0	-0.0	0.0	0.0
	1	-	14.76	B3LYP/6-31G(d,p)	0.1	-0.0	-0.0	0.0	0.1
	2	x, -y, z+1/2	5.44	B3LYP/6-31G(d,p)	-38.7	-5.7	-45.4	50.4	-53.5
	2	x, y, z	5.77	B3LYP/6-31G(d,p)	-8.1	-5.0	-34.4	26.2	-26.1
	2	x, -y, z+1/2	5.32	B3LYP/6-31G(d,p)	0.3	0.0	-1.2	0.0	-0.7

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(b)

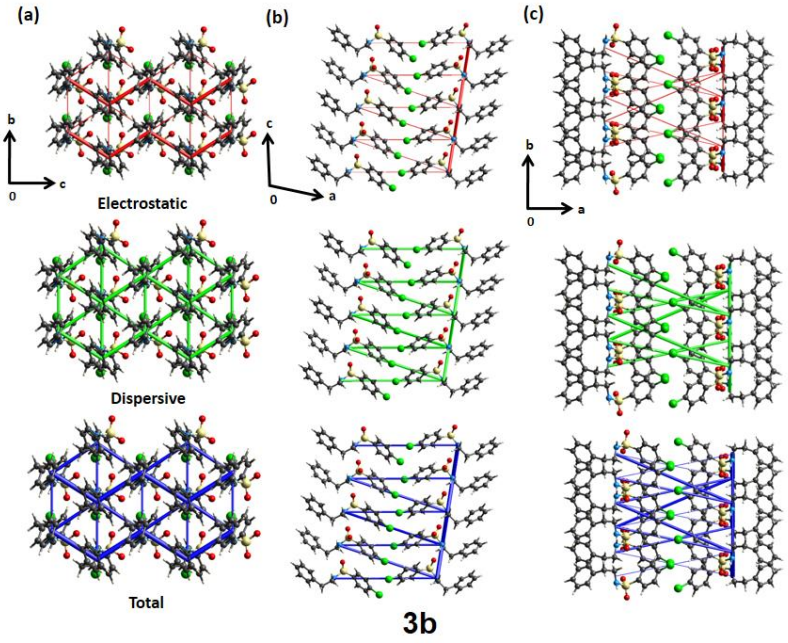
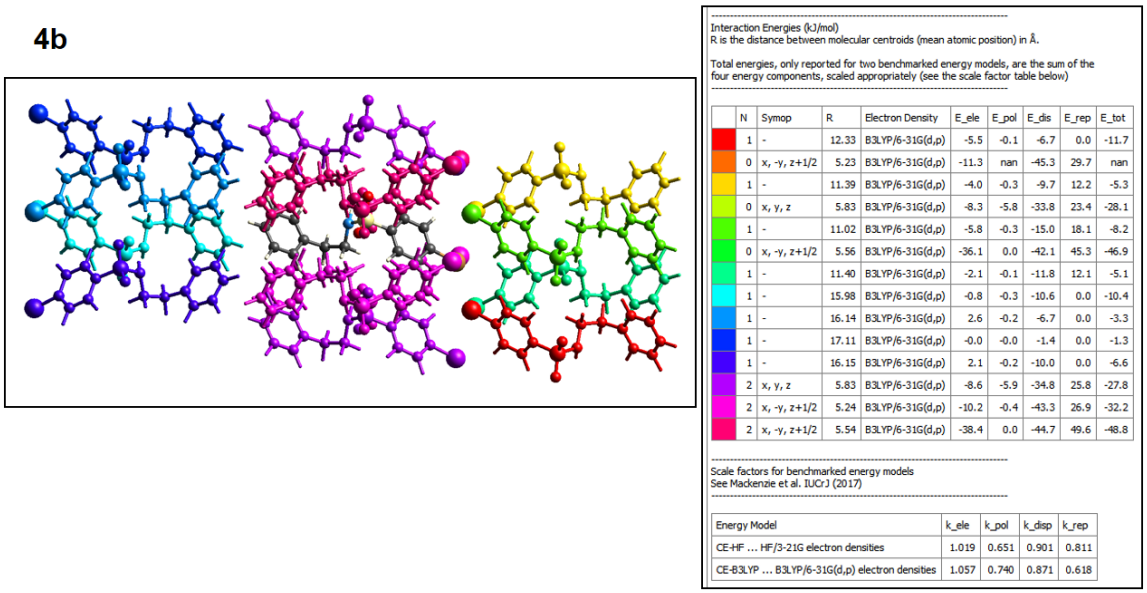


Figure S79. The interaction energy is based on energy frameworks for compound **3b** (a) nd (b) that show electrostatic and dispersion energy contributions to the total energy.

(a)



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	-	12.33	B3LYP/6-31G(d,p)	-5.5	-0.1	-6.7	0.0	-11.7
0	x, -y, z+1/2	5.23	B3LYP/6-31G(d,p)	-11.3	nan	-45.3	29.7	nan
1	-	11.39	B3LYP/6-31G(d,p)	-4.0	-0.3	-9.7	12.2	-5.3
0	x, y, z	5.83	B3LYP/6-31G(d,p)	-8.3	-5.8	-33.8	23.4	-28.1
1	-	11.02	B3LYP/6-31G(d,p)	-5.8	-0.3	-15.0	18.1	-8.2
0	x, -y, z+1/2	5.56	B3LYP/6-31G(d,p)	-36.1	0.0	-42.1	45.3	-46.9
1	-	11.40	B3LYP/6-31G(d,p)	-2.1	-0.1	-11.8	12.1	-5.1
1	-	15.98	B3LYP/6-31G(d,p)	-0.8	-0.3	-10.6	0.0	-10.4
1	-	16.14	B3LYP/6-31G(d,p)	2.6	-0.2	-6.7	0.0	-3.3
1	-	17.11	B3LYP/6-31G(d,p)	-0.0	-0.0	-1.4	0.0	-1.3
1	-	16.15	B3LYP/6-31G(d,p)	2.1	-0.2	-10.0	0.0	-6.6
2	x, y, z	5.83	B3LYP/6-31G(d,p)	-8.6	-5.9	-34.8	25.8	-27.8
2	x, -y, z+1/2	5.24	B3LYP/6-31G(d,p)	-10.2	-0.4	-43.3	26.9	-32.2
2	x, -y, z+1/2	5.54	B3LYP/6-31G(d,p)	-38.4	0.0	-44.7	49.6	-48.8

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(b)

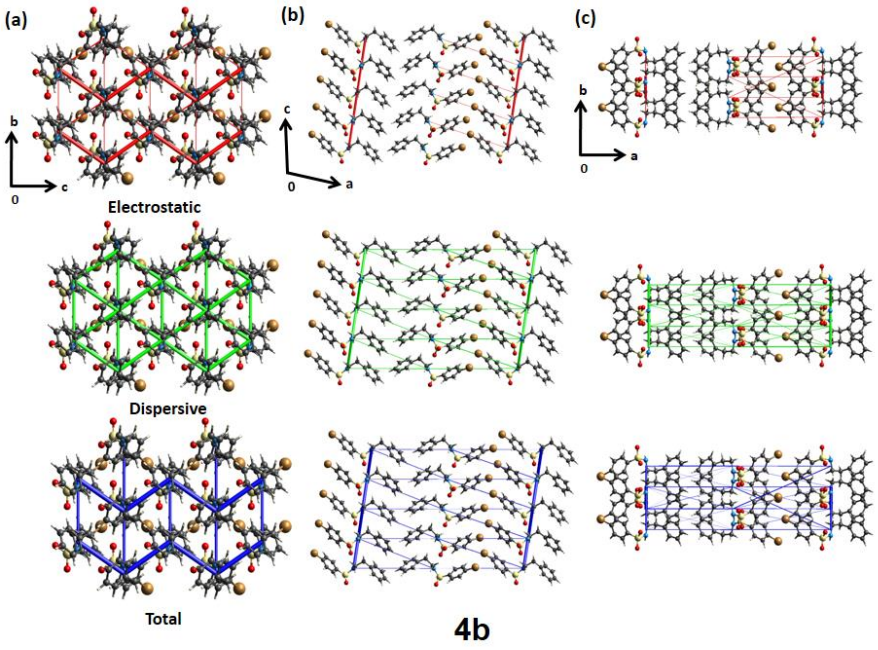
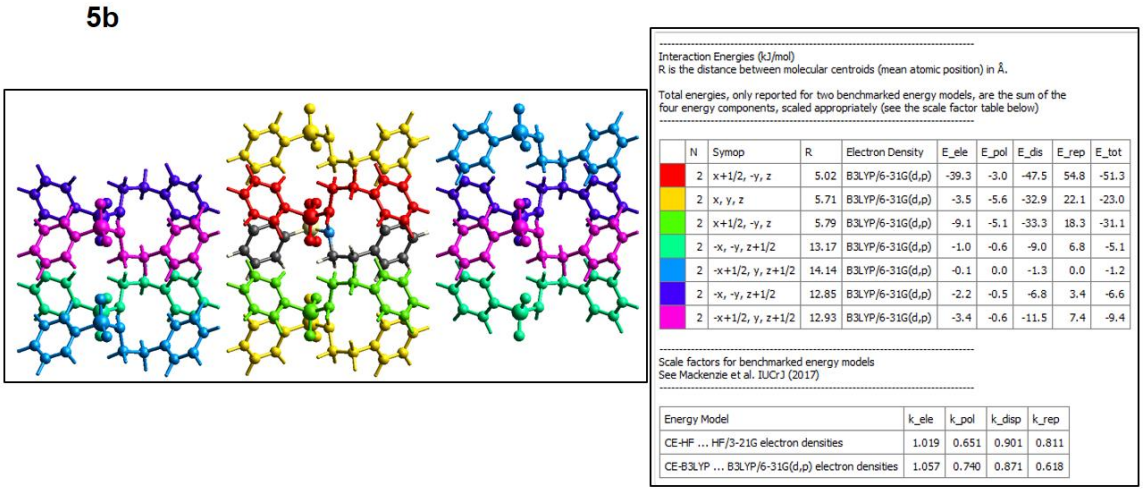


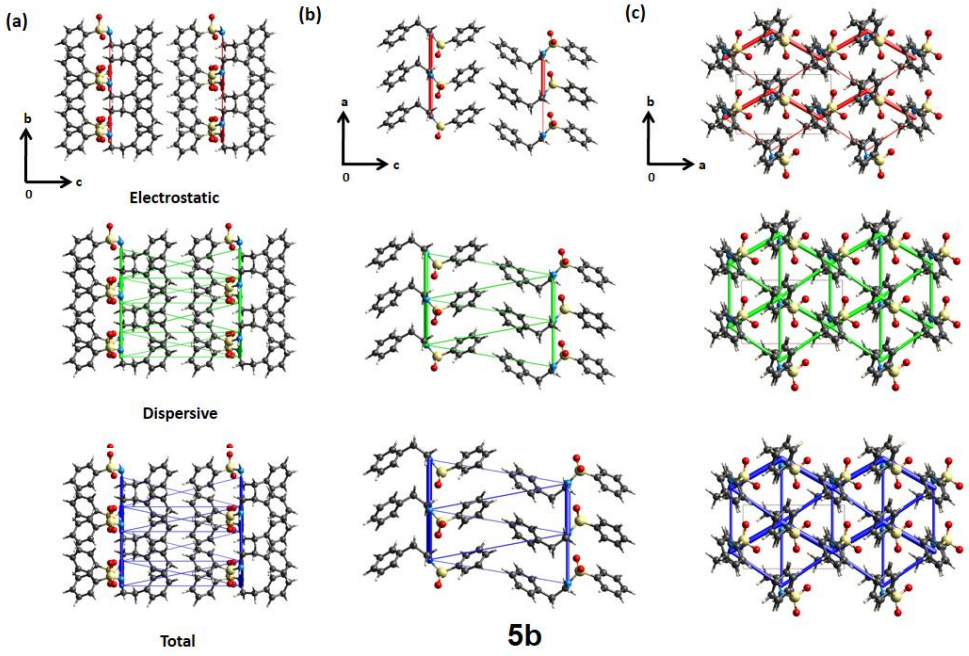
Figure S80. The interaction energy is based on energy frameworks for compound **4b** (a) and (b) that show electrostatic and dispersion energy contributions to the total energy.



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x+1/2, -y, z	5.02	B3LYP/6-31G(d,p)	-39.3	-3.0	-47.5	54.8	-51.3
	2	x, y, z	5.71	B3LYP/6-31G(d,p)	-3.5	-5.6	-32.9	22.1	-23.0
	2	x+1/2, -y, z	5.79	B3LYP/6-31G(d,p)	-9.1	-5.1	-33.3	18.3	-31.1
	2	-x, -y, z+1/2	13.17	B3LYP/6-31G(d,p)	-1.0	-0.6	-9.0	6.8	-5.1
	2	-x+1/2, y, z+1/2	14.14	B3LYP/6-31G(d,p)	-0.1	0.0	-1.3	0.0	-1.2
	2	-x, -y, z+1/2	12.85	B3LYP/6-31G(d,p)	-2.2	-0.5	-6.8	3.4	-6.6
	2	-x+1/2, y, z+1/2	12.93	B3LYP/6-31G(d,p)	-3.4	-0.6	-11.5	7.4	-9.4

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

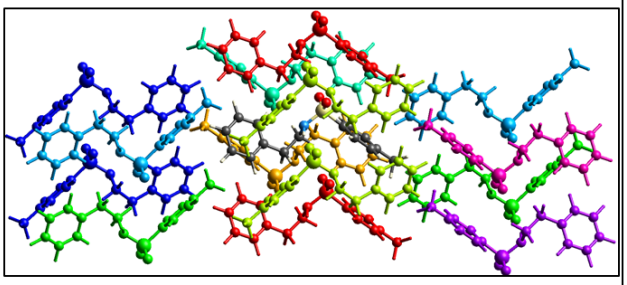
(a)



(b)

Figure S81. The interaction energy is based on energy frameworks for compound **5b** (a) and (b) that show electrostatic and dispersion energy contributions to the total energy.

6b



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

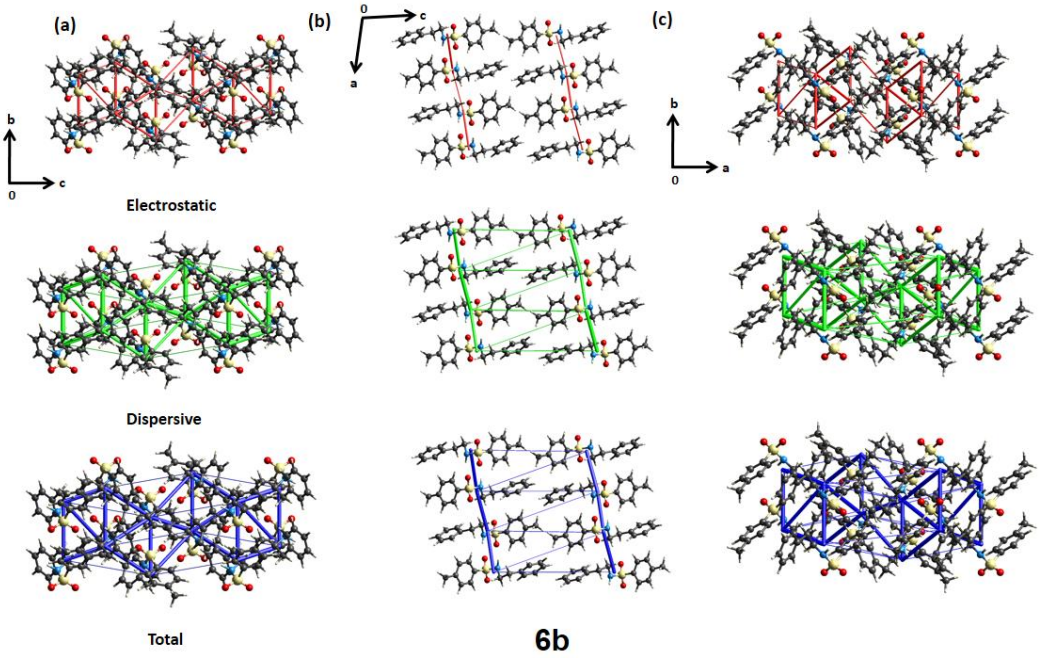
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	x, y, z	5.47	B3LYP/6-31G(d,p)	-25.5	-7.7	-48.7	61.6	-37.1
1	-x, -y, -z	5.39	B3LYP/6-31G(d,p)	-9.7	-2.8	-50.7	24.6	-41.3
2	-x+1/2, y+1/2, -z+1/2	5.35	B3LYP/6-31G(d,p)	-21.8	-10.0	-36.8	40.4	-37.5
2	x+1/2, -y+1/2, z+1/2	14.28	B3LYP/6-31G(d,p)	-2.5	-0.4	-6.8	13.4	-0.6
1	-x, -y, -z	5.86	B3LYP/6-31G(d,p)	-14.3	-6.0	-30.6	20.3	-33.6
2	x+1/2, -y+1/2, z+1/2	13.39	B3LYP/6-31G(d,p)	-1.4	-0.4	-6.7	3.2	-5.6
2	-x+1/2, y+1/2, -z+1/2	14.13	B3LYP/6-31G(d,p)	-2.1	-0.2	-9.9	7.1	-6.6
1	-x, -y, -z	15.33	B3LYP/6-31G(d,p)	1.4	-0.2	-3.7	1.3	-1.1
1	-x, -y, -z	13.43	B3LYP/6-31G(d,p)	-4.4	-1.1	-14.2	17.6	-7.0

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

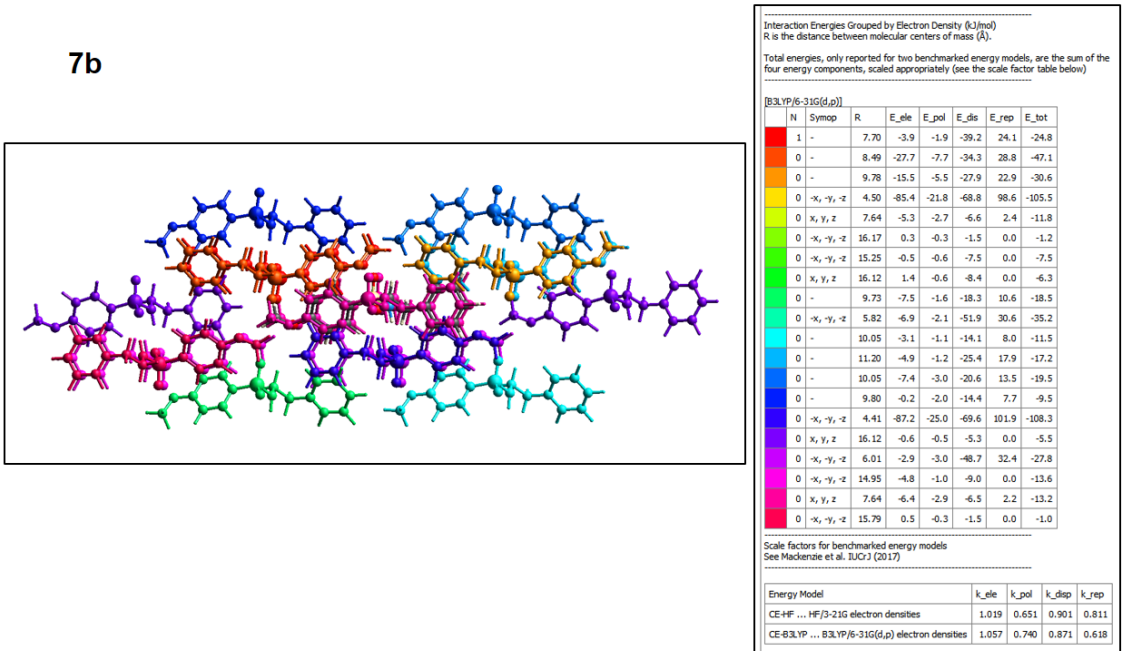
(a)



(b)

Figure S82. The interaction energy is based on energy frameworks for compound **6b** (a) and (b) thgat show electrostatic and dispersion energy contributions to the total energy.

(a)



(b)

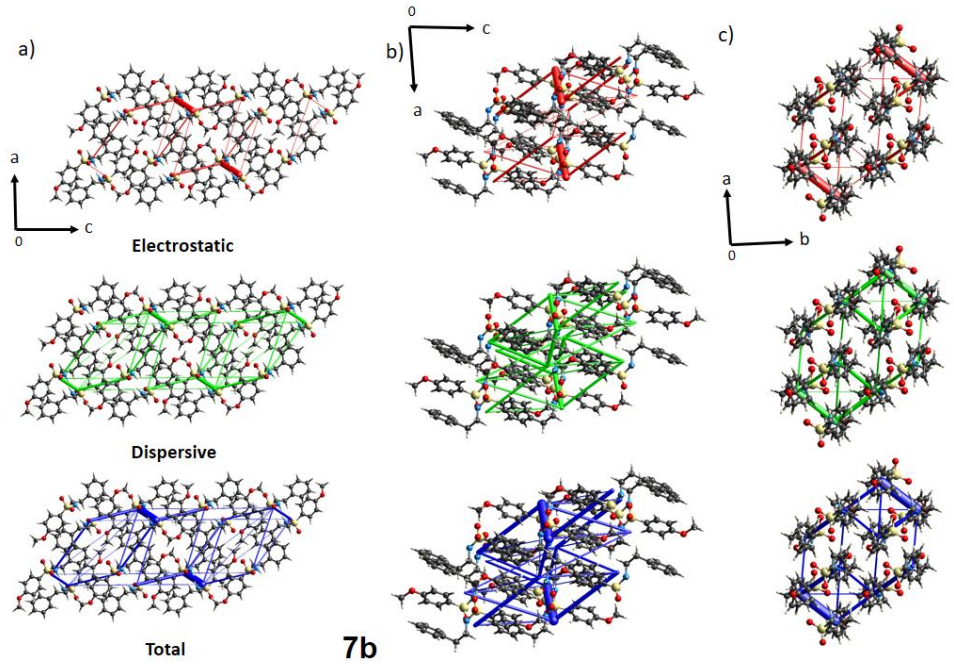
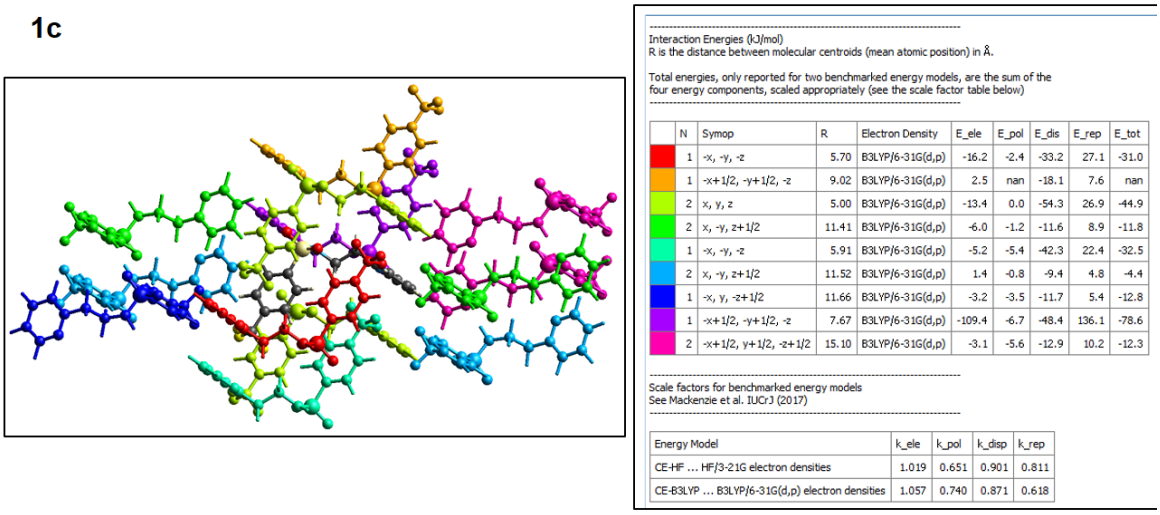


Figure S83. The interaction energy is based on energy frameworks for compound **7b** (a) and (b) that show electrostatic and dispersion energy contributions to the total energy.

(a)



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	5.70	B3LYP/6-31G(d,p)	-16.2	-2.4	-33.2	27.1	-31.0
	1	-x+1/2, -y+1/2, -z	9.02	B3LYP/6-31G(d,p)	2.5	nan	-18.1	7.6	nan
	2	x, y, z	5.00	B3LYP/6-31G(d,p)	-13.4	0.0	-54.3	26.9	-44.9
	2	x, -y, z+1/2	11.41	B3LYP/6-31G(d,p)	-6.0	-1.2	-11.6	8.9	-11.8
	1	-x, -y, -z	5.91	B3LYP/6-31G(d,p)	-5.2	-5.4	-42.3	22.4	-32.5
	2	x, -y, z+1/2	11.52	B3LYP/6-31G(d,p)	1.4	-0.8	-9.4	4.8	-4.4
	1	-x, y, -z+1/2	11.66	B3LYP/6-31G(d,p)	-3.2	-3.5	-11.7	5.4	-12.8
	1	-x+1/2, -y+1/2, -z	7.67	B3LYP/6-31G(d,p)	-109.4	-6.7	-48.4	136.1	-78.6
	2	-x+1/2, y+1/2, -z+1/2	15.10	B3LYP/6-31G(d,p)	-3.1	-5.6	-12.9	10.2	-12.3

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(b)

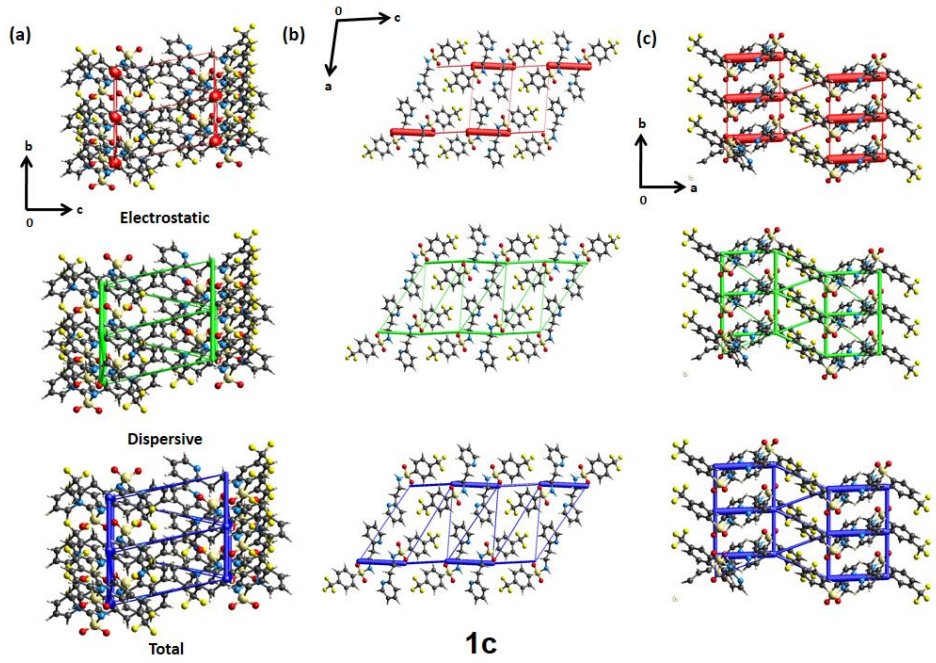
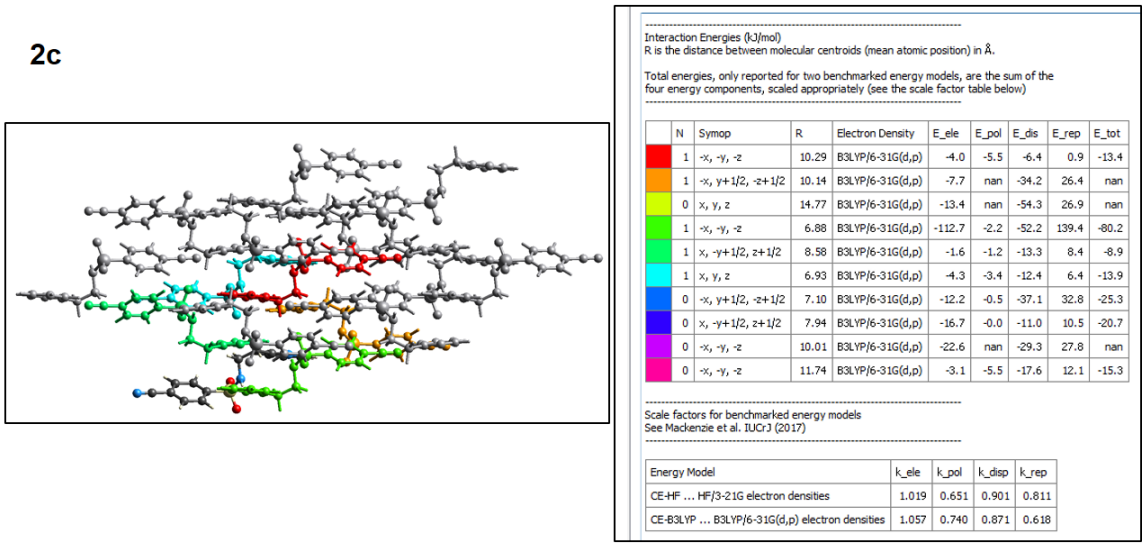


Figure S84. The interaction energy is based on energy frameworks for compound **1c** (a) and (b), which show electrostatic and dispersion energy contributions to the total energy.

(a)



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	10.29	B3LYP/6-31G(d,p)	-4.0	-5.5	-6.4	0.9	-13.4
	1	-x, y+1/2, -z+1/2	10.14	B3LYP/6-31G(d,p)	-7.7	nan	-34.2	26.4	nan
	0	x, y, z	14.77	B3LYP/6-31G(d,p)	-13.4	nan	-54.3	26.9	nan
	1	-x, -y, -z	6.88	B3LYP/6-31G(d,p)	-112.7	-2.2	-52.2	139.4	-80.2
	1	x, -y+1/2, z+1/2	8.58	B3LYP/6-31G(d,p)	-1.6	-1.2	-13.3	8.4	-8.9
	1	x, y, z	6.93	B3LYP/6-31G(d,p)	-4.3	-3.4	-12.4	6.4	-13.9
	0	-x, y+1/2, -z+1/2	7.10	B3LYP/6-31G(d,p)	-12.2	-0.5	-37.1	32.8	-25.3
	0	x, -y+1/2, z+1/2	7.94	B3LYP/6-31G(d,p)	-16.7	-0.0	-11.0	10.5	-20.7
	0	-x, -y, -z	10.01	B3LYP/6-31G(d,p)	-22.6	nan	-29.3	27.8	nan
	0	-x, -y, -z	11.74	B3LYP/6-31G(d,p)	-3.1	-5.5	-17.6	12.1	-15.3

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(b)

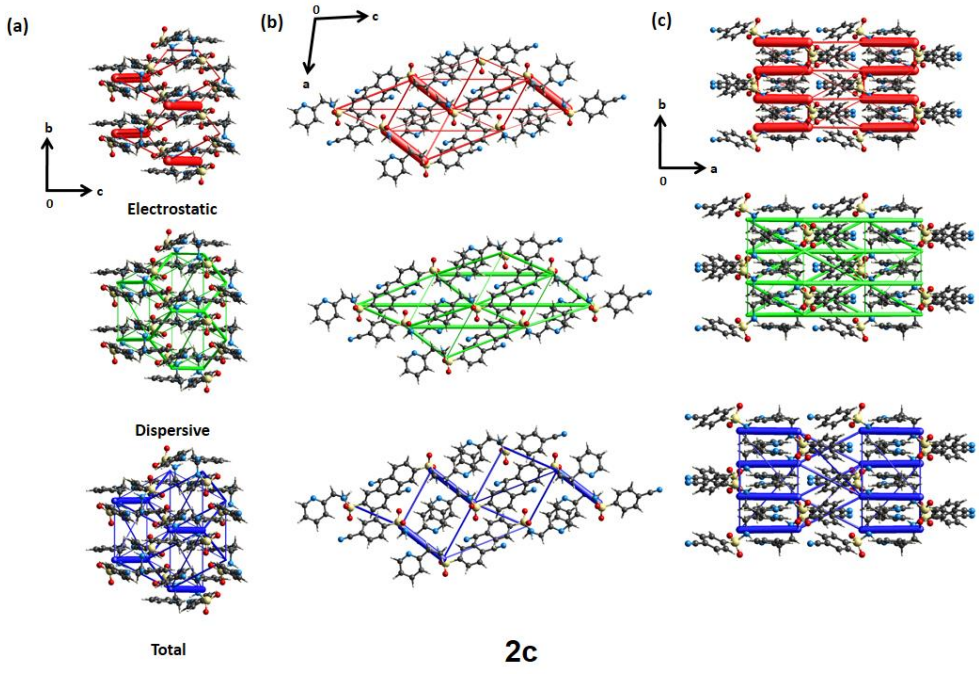
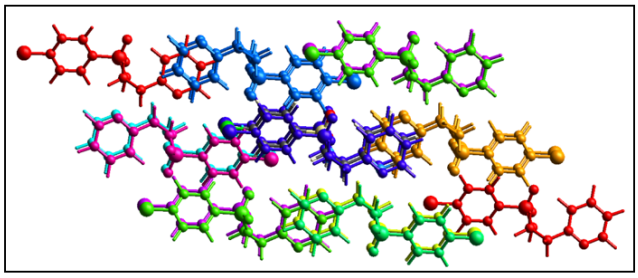


Figure S85. The interaction energy is based on energy frameworks for compound **2c** (a) and (b), which show electrostatic and dispersion energy contributions to the total energy.

(a)



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	14.23	B3LYP/6-31G(d,p)	0.6	-0.1	-2.6	0.0	-1.7
	2	-x, y+1/2, -z+1/2	10.41	B3LYP/6-31G(d,p)	-7.5	-2.8	-33.6	25.0	-23.8
	1	-x, -y, -z	7.18	B3LYP/6-31G(d,p)	-109.6	-30.1	-51.3	134.6	-99.6
	2	x, -y+1/2, z+1/2	8.69	B3LYP/6-31G(d,p)	-1.5	-0.8	-12.4	7.0	-8.7
	1	-x, -y, -z	10.70	B3LYP/6-31G(d,p)	-3.7	-0.5	-4.9	0.4	-8.3
	1	-x, -y, -z	10.85	B3LYP/6-31G(d,p)	-5.4	-1.0	-18.9	16.1	-12.9
	2	-x, y+1/2, -z+1/2	6.68	B3LYP/6-31G(d,p)	-10.9	-3.4	-32.0	26.5	-25.5
	2	x, y, z	7.04	B3LYP/6-31G(d,p)	-6.0	-3.6	-11.5	7.2	-14.6
	2	x, -y+1/2, z+1/2	7.87	B3LYP/6-31G(d,p)	-14.2	-3.2	-11.3	10.2	-20.8
	1	-x, -y, -z	9.05	B3LYP/6-31G(d,p)	-6.1	0.0	-33.9	32.4	-15.9

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(b)

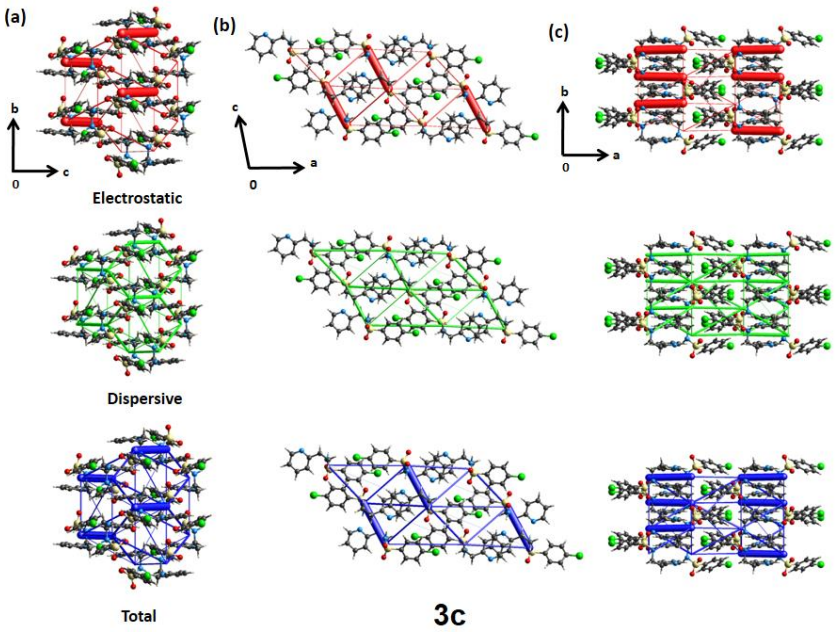
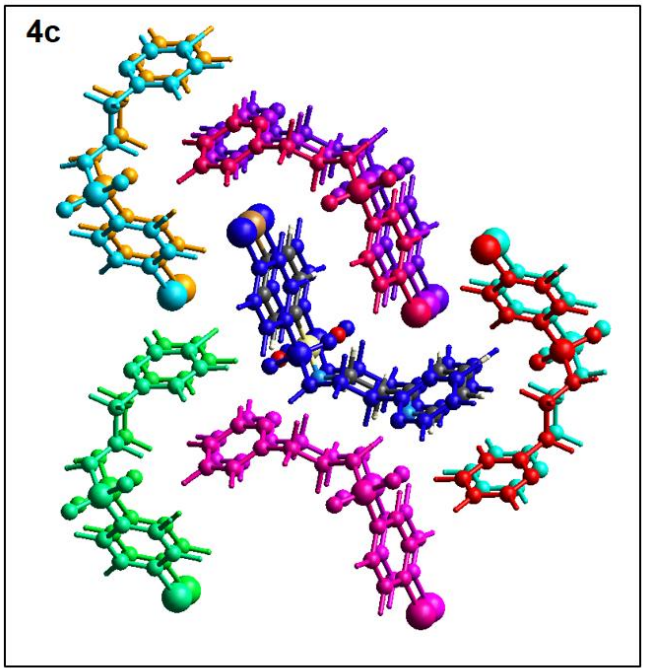


Figure S86. The interaction energy is based on energy frameworks for compound **3c** (a) and (b), which show electrostatic and dispersion energy contributions to the total energy.

(a)



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	-	9.47	B3LYP/6-31G(d,p)	-7.9	-0.4	-22.4	20.3	-15.7
0	x, y, z	5.60	B3LYP/6-31G(d,p)	-17.0	-1.1	-40.3	24.6	-38.7
1	-	8.81	B3LYP/6-31G(d,p)	-3.2	-2.2	-14.1	7.7	-12.6
0	-x, -y, -z	9.11	B3LYP/6-31G(d,p)	-0.9	-0.2	-24.7	15.4	-13.0
0	-x, -y, -z	7.88	B3LYP/6-31G(d,p)	-109.4	-29.6	-45.6	131.3	-96.1
0	-x, -y, -z	8.22	B3LYP/6-31G(d,p)	-9.6	-3.9	-18.1	9.8	-22.7
0	x, y, z	12.32	B3LYP/6-31G(d,p)	-1.1	-0.2	-14.5	0.0	-14.0
1	-	10.52	B3LYP/6-31G(d,p)	-9.7	-2.2	-5.4	6.6	-12.5
1	-	9.92	B3LYP/6-31G(d,p)	-0.5	-1.7	-14.9	12.1	-7.2
1	-	8.16	B3LYP/6-31G(d,p)	-1.0	-0.9	-30.3	14.3	-19.4
1	-	9.82	B3LYP/6-31G(d,p)	-3.0	-0.3	-10.4	9.3	-6.7
0	x, y, z	12.32	B3LYP/6-31G(d,p)	10.5	-0.4	-12.2	0.0	0.1
0	-x, -y, -z	8.83	B3LYP/6-31G(d,p)	2.1	-1.2	-9.1	3.7	-4.3
2	x, y, z	5.60	B3LYP/6-31G(d,p)	-21.9	-5.8	-45.2	34.9	-45.3
1	-x, -y, -z	8.62	B3LYP/6-31G(d,p)	-4.9	-0.5	-2.9	0.0	-8.1
1	-x, -y, -z	4.71	B3LYP/6-31G(d,p)	-6.6	-3.3	-51.6	42.1	-28.3
1	-x, -y, -z	9.14	B3LYP/6-31G(d,p)	-2.9	-3.5	-19.0	11.3	-15.2
1	-x, -y, -z	7.92	B3LYP/6-31G(d,p)	-105.0	-29.2	-46.3	120.3	-98.6
1	-x, -y, -z	5.73	B3LYP/6-31G(d,p)	-10.0	-0.4	-31.3	27.6	-21.1

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(b)

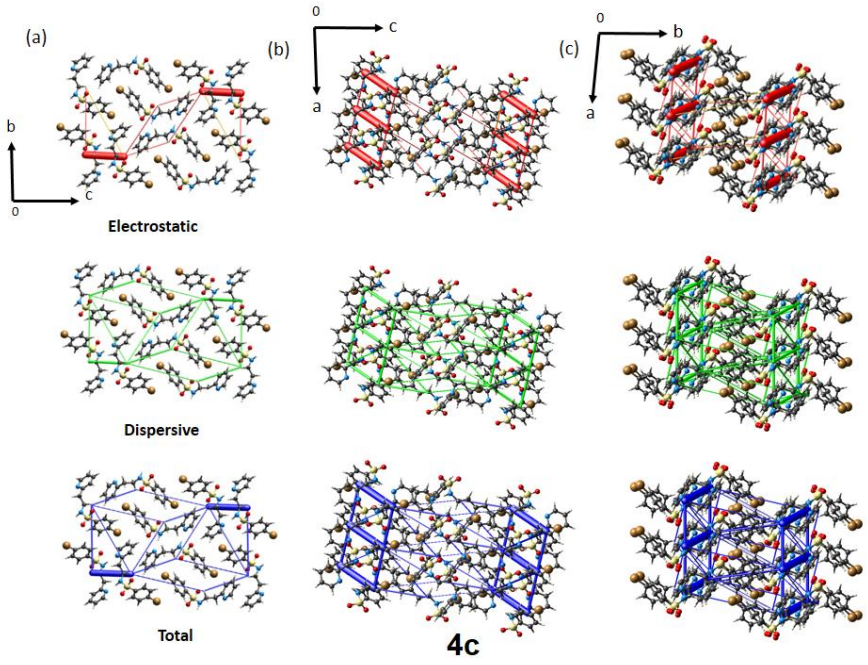
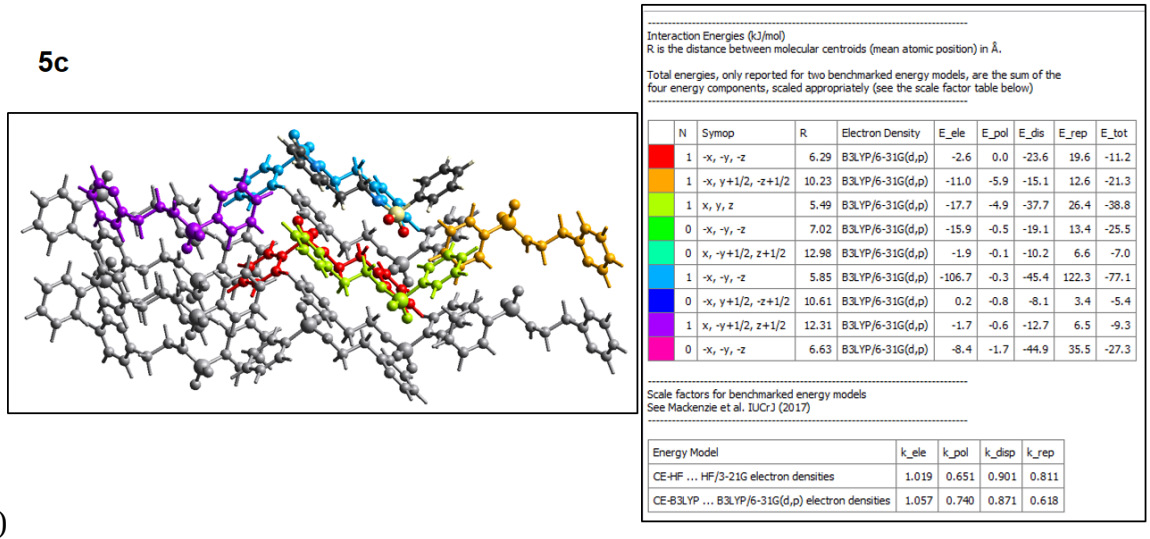


Figure S87. The interaction energy is based on energy frameworks for compound **4c** (a) and (b), which show electrostatic and dispersion energy contributions to the total energy.



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

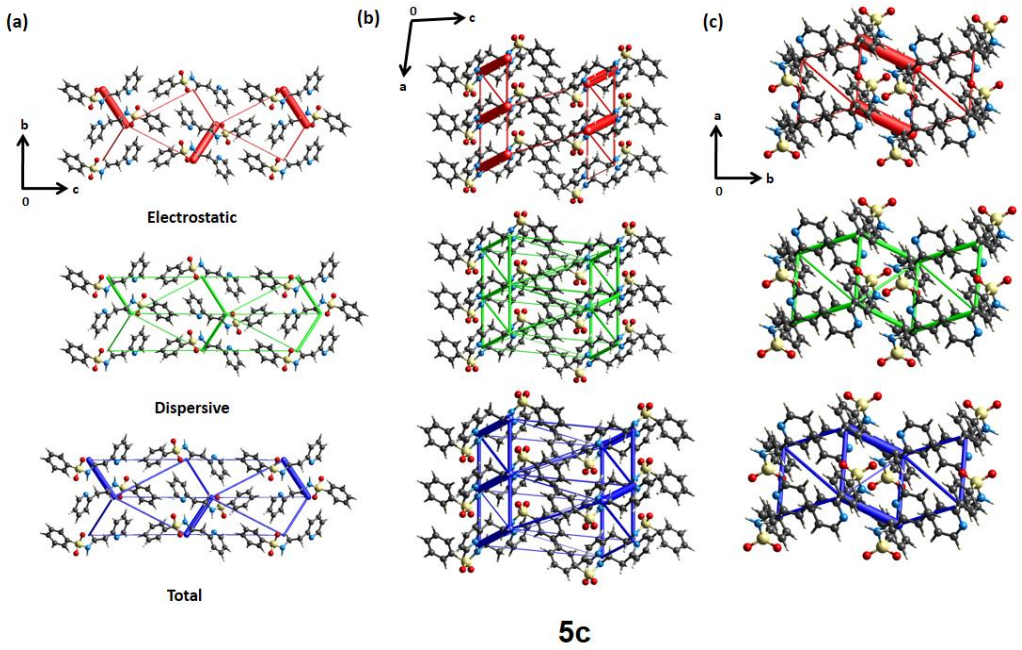
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	6.29	B3LYP/6-31G(d,p)	-2.6	0.0	-23.6	19.6	-11.2
	1	-x, y+1/2, -z+1/2	10.23	B3LYP/6-31G(d,p)	-11.0	-5.9	-15.1	12.6	-21.3
	1	x, y, z	5.49	B3LYP/6-31G(d,p)	-17.7	-4.9	-37.7	26.4	-38.8
	0	-x, -y, -z	7.02	B3LYP/6-31G(d,p)	-15.9	-0.5	-19.1	13.4	-25.5
	0	x, -y+1/2, z+1/2	12.98	B3LYP/6-31G(d,p)	-1.9	-0.1	-10.2	6.6	-7.0
	1	-x, -y, -z	5.85	B3LYP/6-31G(d,p)	-106.7	-0.3	-45.4	122.3	-77.1
	0	-x, y+1/2, -z+1/2	10.61	B3LYP/6-31G(d,p)	0.2	-0.8	-8.1	3.4	-5.4
	1	x, -y+1/2, z+1/2	12.31	B3LYP/6-31G(d,p)	-1.7	-0.6	-12.7	6.5	-9.3
	0	-x, -y, -z	6.63	B3LYP/6-31G(d,p)	-8.4	-1.7	-44.9	35.5	-27.3

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

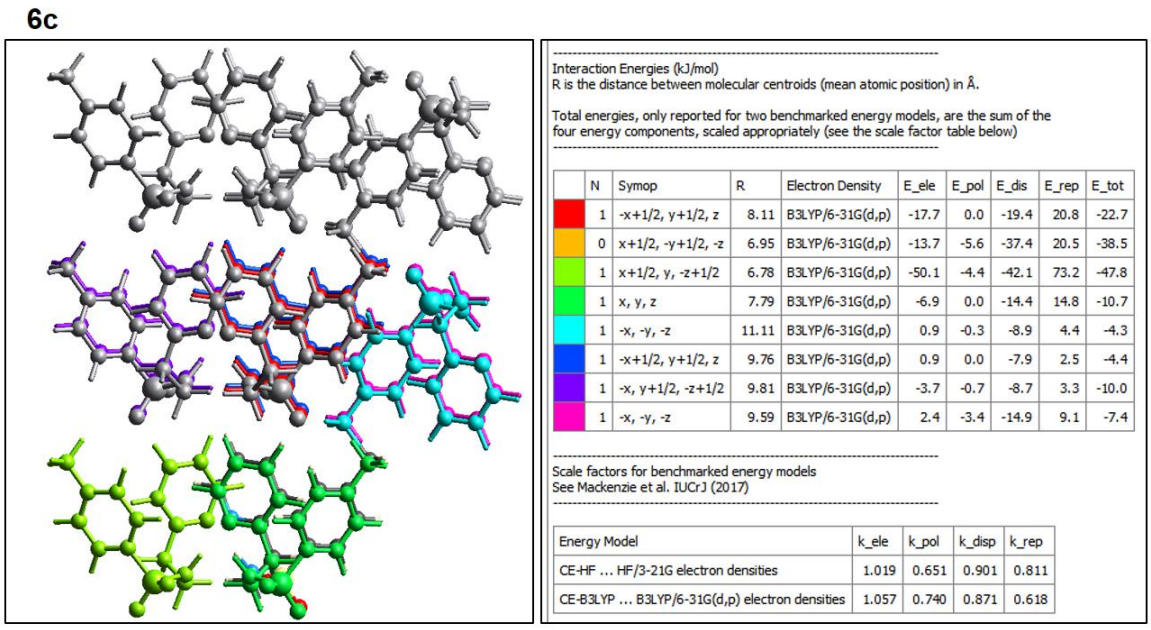
(a)



(b)

Figure S88. The interaction energy is based on energy frameworks for compound **5c** (a) and (b), which show electrostatic and dispersion energy contributions to the total energy.

(a)



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x+1/2, y+1/2, z	8.11	B3LYP/6-31G(d,p)	-17.7	0.0	-19.4	20.8	-22.7
	0	x+1/2, -y+1/2, -z	6.95	B3LYP/6-31G(d,p)	-13.7	-5.6	-37.4	20.5	-38.5
	1	x+1/2, y, -z+1/2	6.78	B3LYP/6-31G(d,p)	-50.1	-4.4	-42.1	73.2	-47.8
	1	x, y, z	7.79	B3LYP/6-31G(d,p)	-6.9	0.0	-14.4	14.8	-10.7
	1	-x, -y, -z	11.11	B3LYP/6-31G(d,p)	0.9	-0.3	-8.9	4.4	-4.3
	1	-x+1/2, y+1/2, z	9.76	B3LYP/6-31G(d,p)	0.9	0.0	-7.9	2.5	-4.4
	1	-x, y+1/2, -z+1/2	9.81	B3LYP/6-31G(d,p)	-3.7	-0.7	-8.7	3.3	-10.0
	1	-x, -y, -z	9.59	B3LYP/6-31G(d,p)	2.4	-3.4	-14.9	9.1	-7.4

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(b)

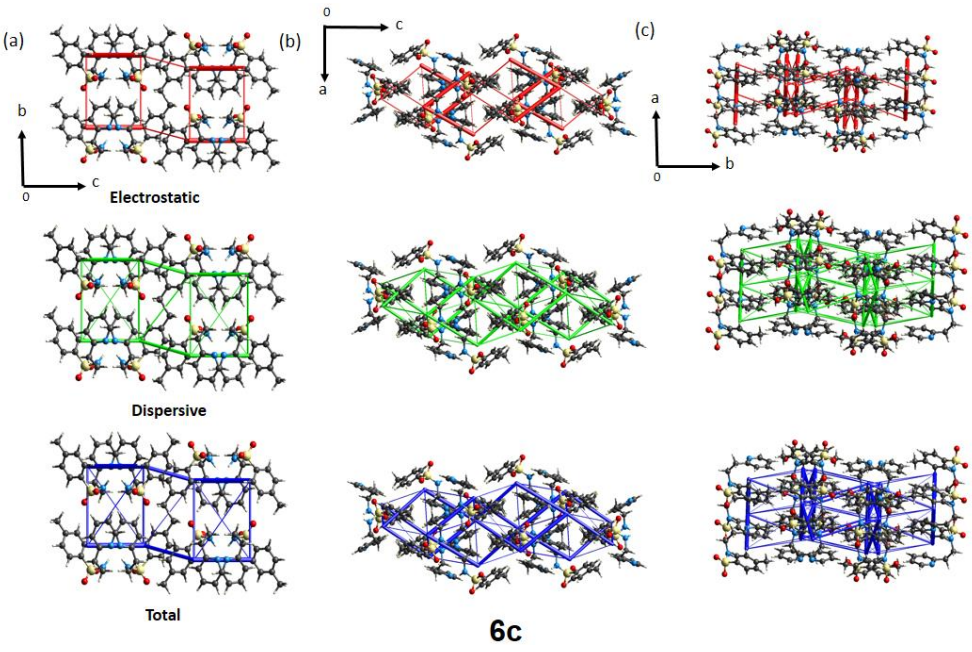
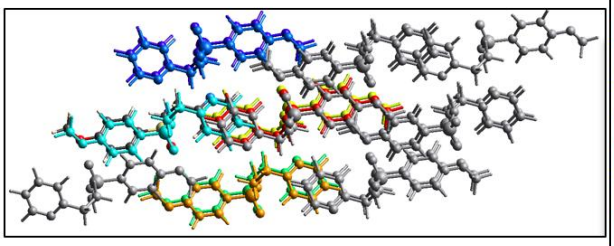


Figure S89. The interaction energy is based on energy frameworks for compound **6c** (a) and (b), which show electrostatic and dispersion energy contributions to the total energy.



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

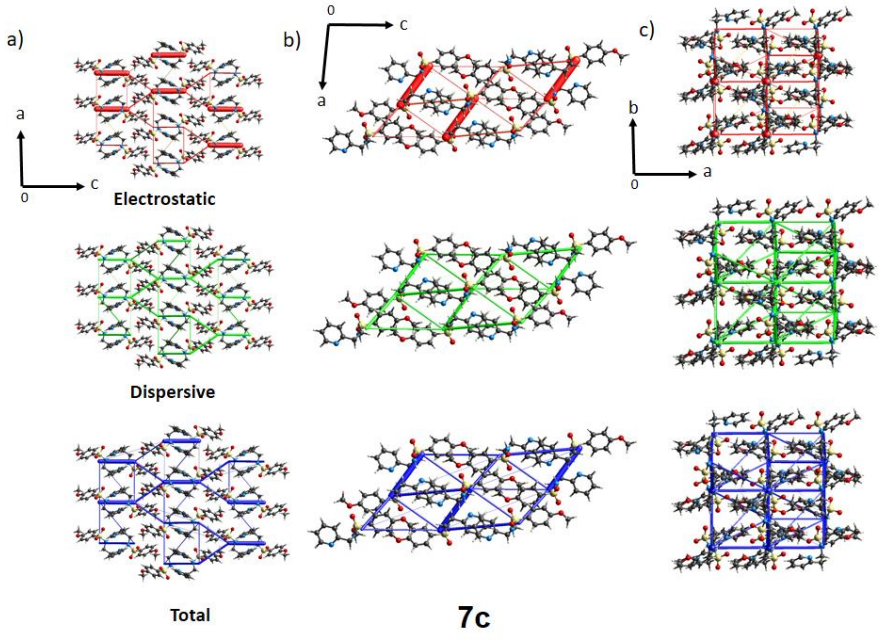
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	12.63	B3LYP/6-31G(d,p)	5.5	-0.5	-19.8	0.0	-11.7
	1	x, y, z	10.74	B3LYP/6-31G(d,p)	1.8	0.0	-3.9	0.3	-1.3
	1	-x, -y, -z	9.64	B3LYP/6-31G(d,p)	-19.3	-3.3	-40.6	36.8	-35.5
	0	-x, y+1/2, -z+1/2	6.93	B3LYP/6-31G(d,p)	-21.5	0.0	-46.3	41.1	-37.6
	1	x, y, z	7.54	B3LYP/6-31G(d,p)	-8.9	0.0	-23.5	14.2	-21.2
	1	x, y, z	7.64	B3LYP/6-31G(d,p)	-8.3	-3.8	-10.7	9.7	-15.0
	1	-x, -y, -z	10.40	B3LYP/6-31G(d,p)	-2.3	-4.9	-5.7	0.3	-10.9
	1	-x, -y, -z	6.45	B3LYP/6-31G(d,p)	-108.3	-0.9	-51.9	133.8	-77.7
	0	-x, y+1/2, -z+1/2	11.00	B3LYP/6-31G(d,p)	-6.6	-3.4	-23.8	17.9	-19.1
	0	x, -y+1/2, z+1/2	15.00	B3LYP/6-31G(d,p)	-1.8	-0.2	-1.7	0.0	-3.5

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

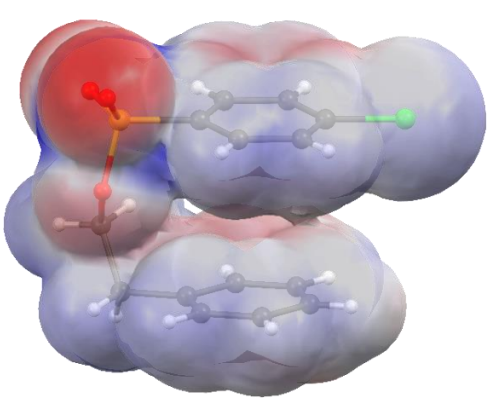
Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

(a)

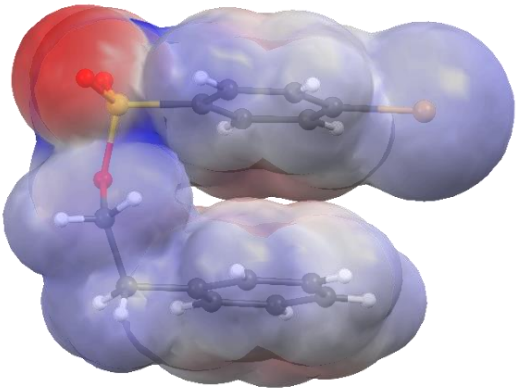


(b)

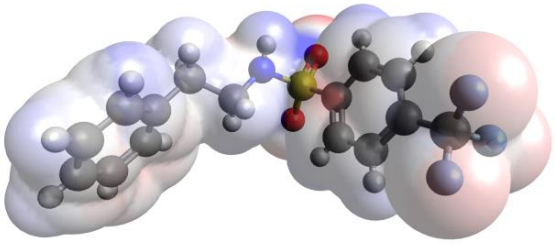
Figure S90. The interaction energy is based on energy frameworks for compound **7c** (a) and (b), which show electrostatic and dispersion energy contributions to the total energy.



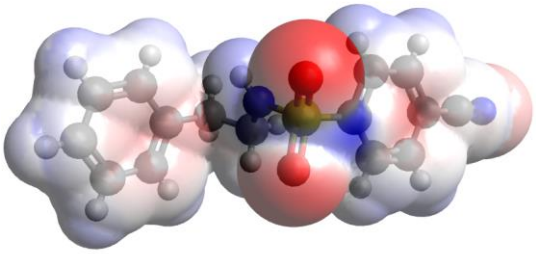
(a)



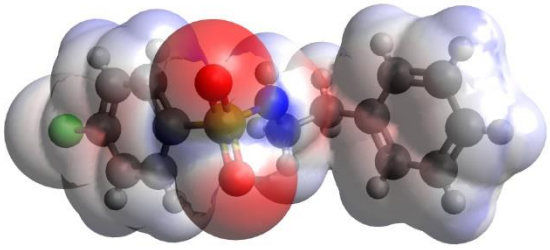
(b)



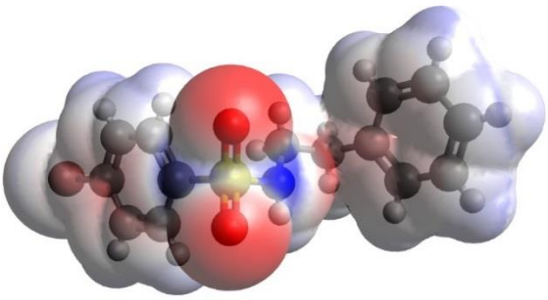
(c)



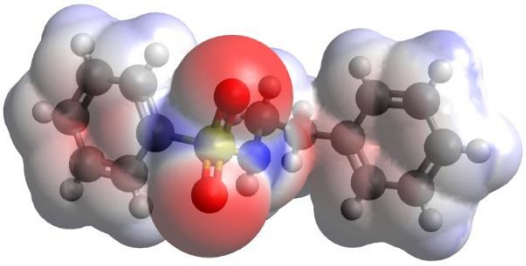
(d)



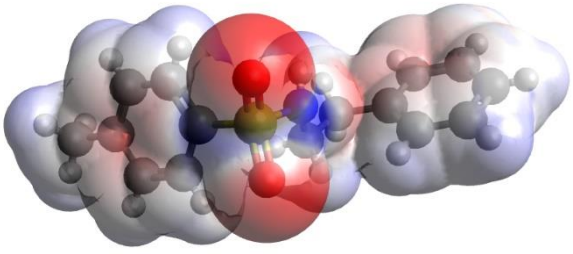
(e)



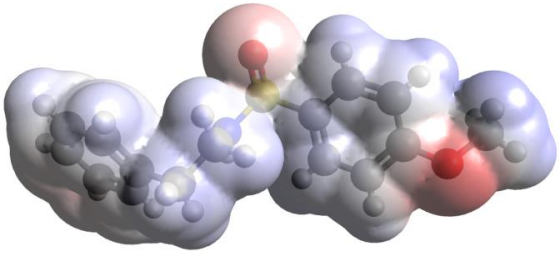
(f)



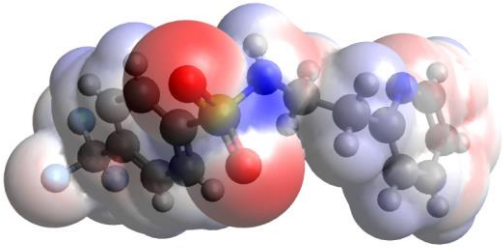
(g)



(h)



(i)



(j)

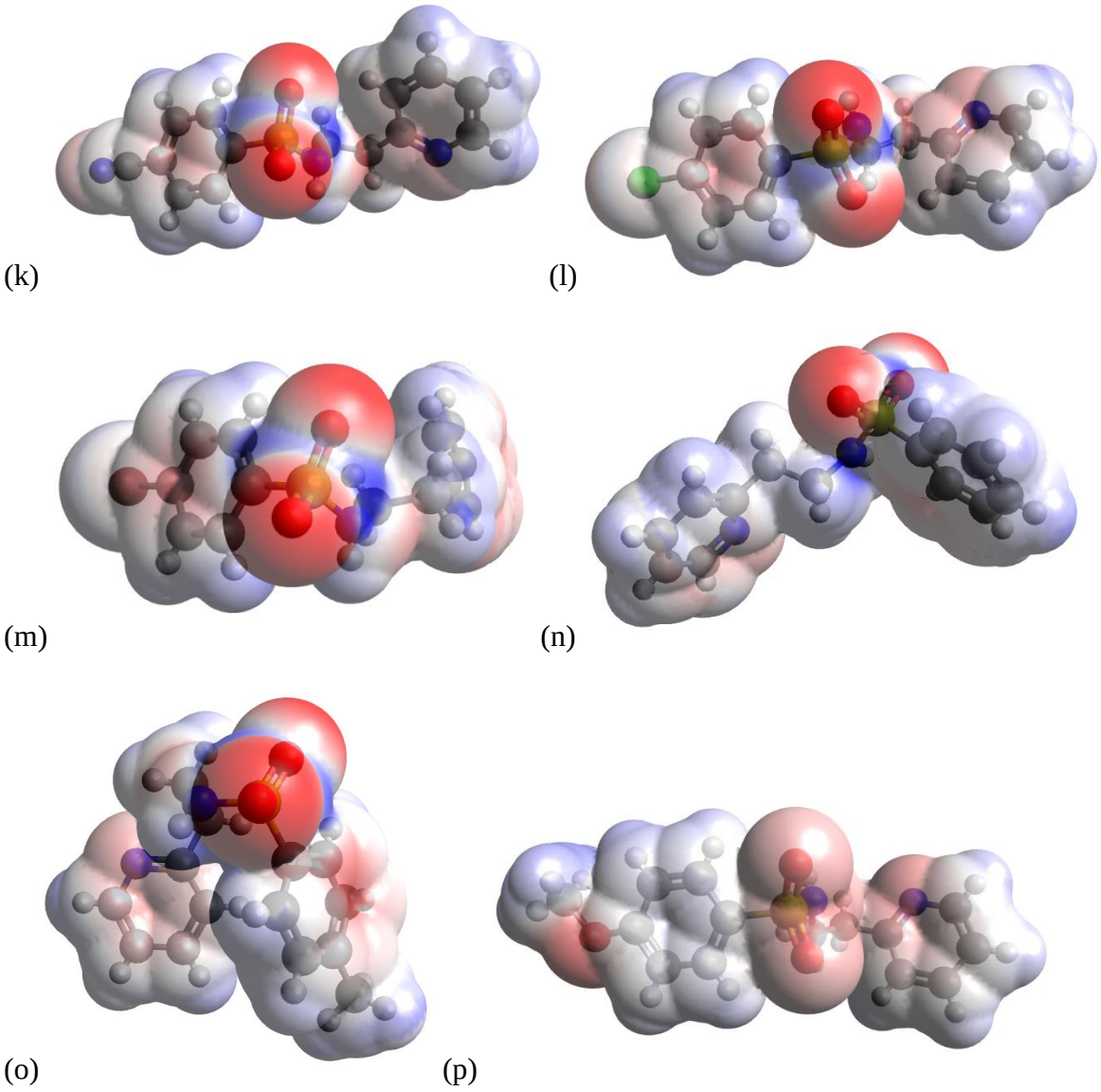


Figure S91. The molecular electrostatic potential (MEP) mapped onto the molecular van der Waals surface, using a colour code, blue (electropositive regions), white (neutral) and red (electronegative regions), (a) **3a**, (b) **4a**,(c) **1b**, (d) **2b**,(e) **3b**, (f) **4b**, (g) **5b**, (h) **6b**, (i) **7b**, (j) **1c**, (k) **2c**, (l) **3c**, (m) **4c**, (n) **5c**, (o) **6c** and (p) **7c**.

DFT Studies

Table S14. Energy difference between different conformations (ΔE, in kcal/mol).

Model	*Syn*	*Midway*	*Anti*	Mid-H (with H Bonding)
Sulfonyl compounds				
1a	0.0	+4.2	+4.7	-
3a	0.0	+4.0	+4.5	-
4a	0.0	+6.2	+6.8	-
6a	0.0	+3.1	+3.7	-
Benzene sulfonamide compounds				
1b	0.0	+3.0	+4.4	-
2b	0.0	+3.8	+4.6	-
3b	0.0	+3.6	+4.3	-
4b	0.0	+5.8	+6.4	-
5b	0.0	+2.1	+3.0	-
6b	0.0	+2.5	+3.4	-
7b	0.0	+3.2	+3.8	-
Pyridine sulfonamide compounds				
1c	0.0	+4.2	+4.7	+1.3
2c	0.0	+2.6	+3.2	+1.4
3c	0.0	+2.5	+3.2	+1.8
4c	0.0	+5.1	+5.5	+4.1
5c	0.0	+1.3	+1.7	+0.6
6c	0.0	+4.3	+4.9	+1.6
7c	0.0	+3.5	+4.0	+1.2

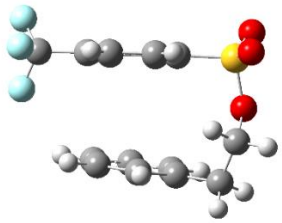
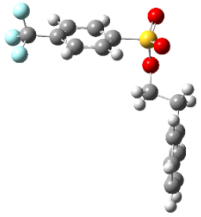
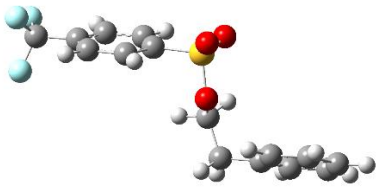
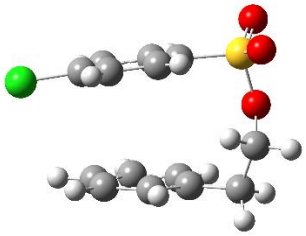
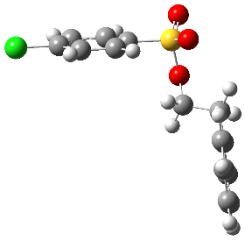
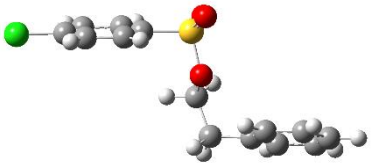
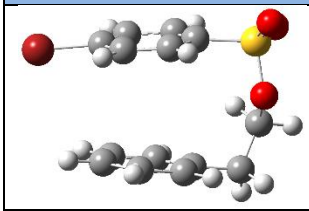
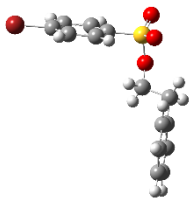
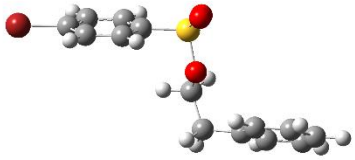
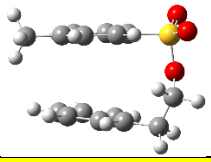
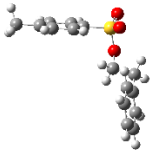
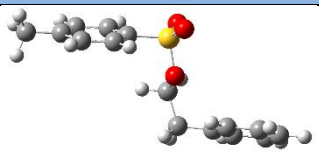
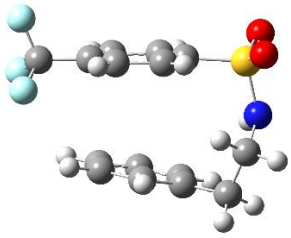
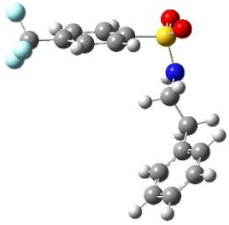
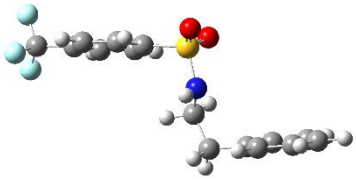
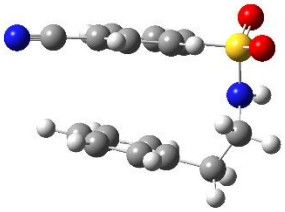
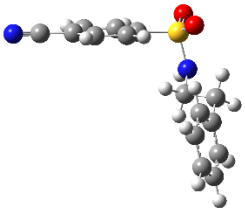
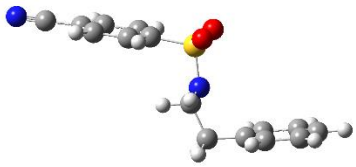
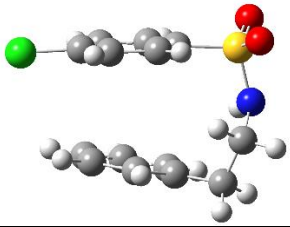
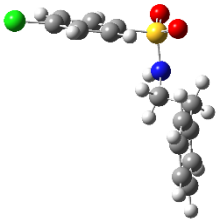
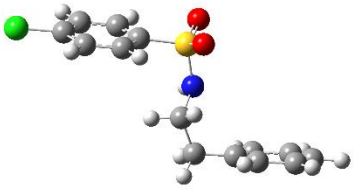
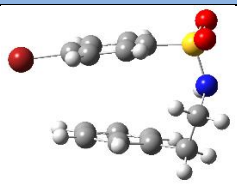
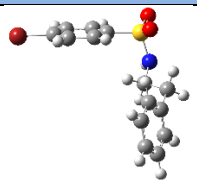
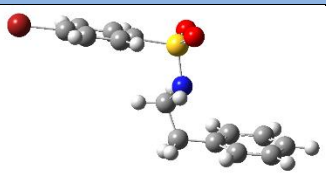
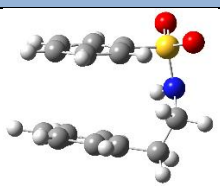
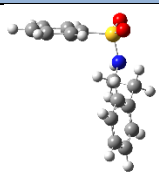
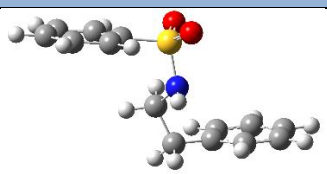
1a (*Syn*)	**1a** (*Midway*)	**1a** (*Anti*)
		
0.0	+4.2	+4.7
3a (*Syn*)	**3a** (*Midway*)	**3a** (*Anti*)
		
0.0	+4.0	+4.5
4a (*Syn*)	**4a** (*Midway*)	**4a** (*Anti*)
		
0.0	+6.2	+6.8
6a (*Syn*)	**6a** (*Midway*)	**6a** (*Anti*)
		
0.0	+3.1	+3.7

Figure S92. DFT optimized (M06-2X/6-31+g*) conformers in *syn*, *midway* and *anti* geometries for sulfonyl compounds (**1a** to **6a**); all energy values are in kcal/mol.

1b (*Syn*)	**1b** (*Midway*)	**1b** (*Anti*)
		
0.0	+3.0	+4.4
2b(*Syn*)	**2b** (*Midway*)	**2b** (*Anti*)
		
0.0	+3.8	+4.6
3b(*Syn*)	**3b** (*Midway*)	**3b** (*Anti*)
		
0.0	+3.6	+4.3
4b (*Syn*)	**4b** (*Midway*)	**4b** (*Anti*)
		
0.0	+5.8	+6.4
5b (*Syn*)	**5b** (*Midway*)	**5b** (*Anti*)
		

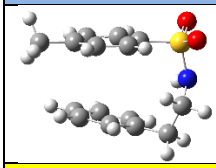
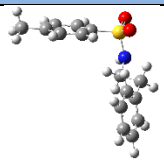
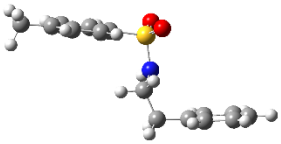
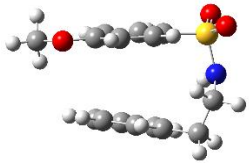
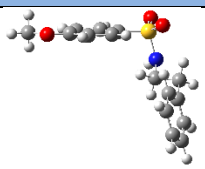
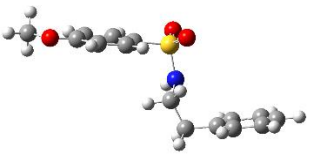
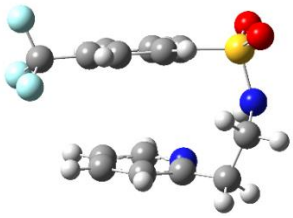
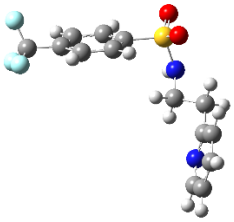
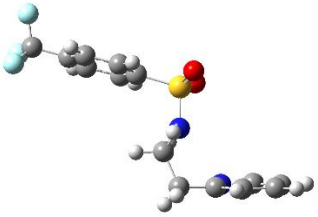
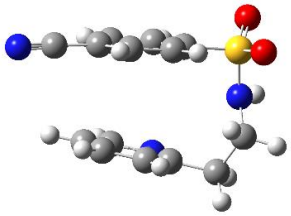
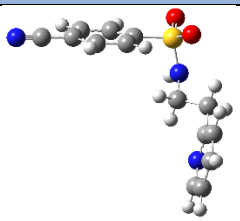
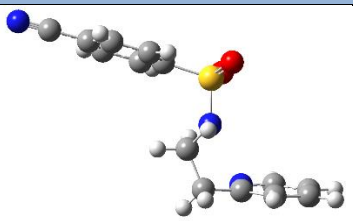
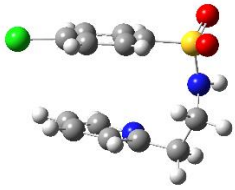
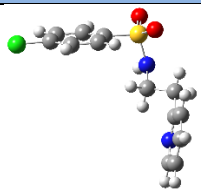
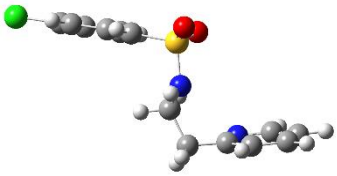
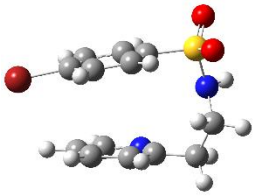
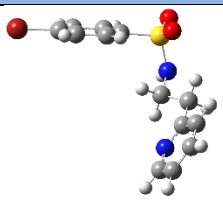
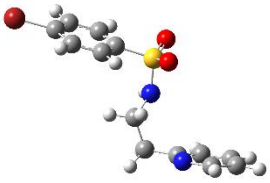
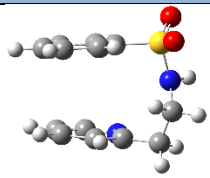
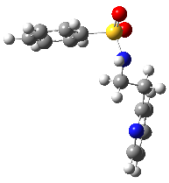
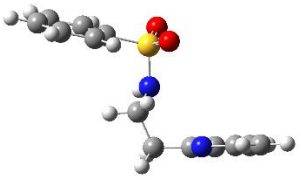
0.0	+2.1	+3.0
6b (*Syn*)	**6b** (*Midway*)	**6b** (*Anti*)
		
0.0	+2.5	+3.4
7b (*Syn*)	**7b** (*Midway*)	**7b** (*Anti*)
		
0.0	+3.2	+3.8

Figure S93. DFT optimized (M06-2X/6-31+g*) conformers in *syn*, *midway* and *anti* geometries for benzene sulfonamide compounds (**1b** to **7b**); all energy values are in kcal/mol.

1c (*Syn*)	**1c** (*Midway*)	**1c** (*Anti*)
		
0.0	+4.2	+4.7
2c (*Syn*)	**2c** (*Midway*)	**2c** (*Anti*)
		
0.0	+2.6	+3.2
3c (*Syn*)	**3c** (*Midway*)	**3c** (*Anti*)
		
0.0	+2.5	+3.2
4c (*Syn*)	**4c** (*Midway*)	**4c** (*Anti*)
		
0.0	+5.1	+5.5
5c (*Syn*)	**5c** (*Midway*)	**5c** (*Anti*)
		
0.0	+1.3	+1.7

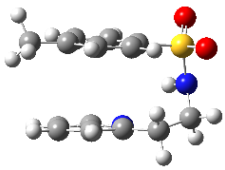
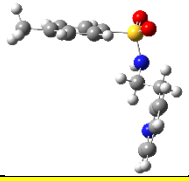
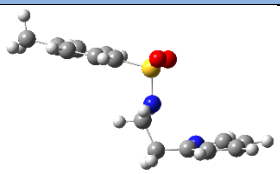
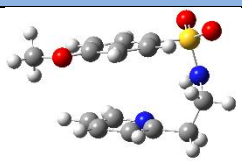
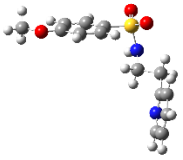
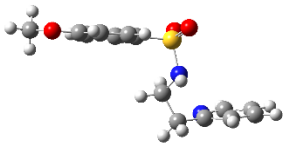
6c (*Syn*)	**6c** (*Midway*)	**6c** (*Anti*)
		
0.0	+4.3	+4.9
7c (*Syn*)	**7c** (*Midway*)	**7c** (*Anti*)
		
0.0	+3.5	+4.0

Figure S94. DFT optimized (M06-2X/6-31+g*) conformers in *syn*, *midway* and *anti* geometries for pyridine sulfonamide compounds (**1c** to **7c**); all energy values are in kcal/mol.

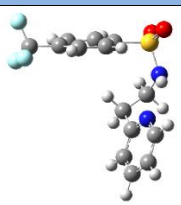
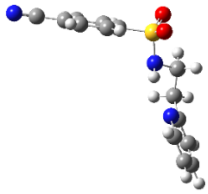
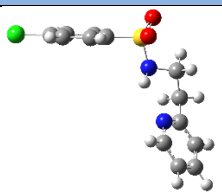
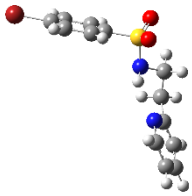
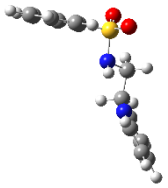
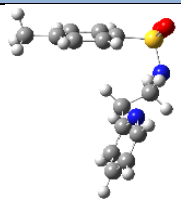
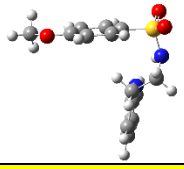
1c (*Midway*)	**2c** (*Midway*)	**3c** (*Midway*)
		
+1.3	+1.4	+1.8
4c (*Midway*)	**5c** (*Midway*)	**6c** (*Midway*)
		
+4.1	+0.6	+1.6
7c (*Midway*)		
		
+1.2		

Figure S95. DFT optimized (M06-2X/6-31+g*) conformers in midway geometries for pyridine sulfonamide compounds (**1c** to **7c**) with intramolecular N-H···N H-bonding interactions; all energy values are in kcal/mol.