

Supplementary Information

Asymmetric Friedel-Crafts Addition of Indoles to *N*-Sulfonyl Aldimines Catalyzed by Cu(II) Chiral Amino Alcohols Based Schiff base Complexes

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A. General information

All reactions were performed in oven-dried (150 °C) glassware under an atmosphere of nitrogen and 4 Å MS was activated at 150 °C for overnight. Commercial reagents were used as received without further purification unless otherwise noticed. All the solvents used in the present study were dried following known purification technique¹. ¹H and ¹³C spectra were taken in CDCl₃ and in CD₃COCD₃ in special cases. For ¹H NMR (200 and 500 MHz), tetramethylsilane (TMS) served as internal standard (δ = 0 ppm) and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (in Hz), and integration. For ¹³C NMR (50 MHz and 125 MHz), CDCl₃, CD₃SOCD₃ were used as internal standard and spectra were obtained with complete proton decoupling. Enantiomeric excess (*ee*) were determined by HPLC using OD-H, OD, IA, IB and IC chiral columns with 2-propanol/hexane as eluent.

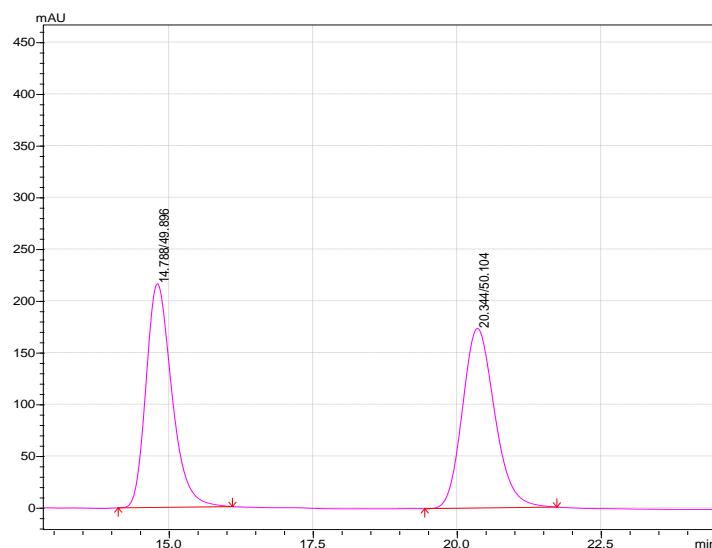
B. General procedure for asymmetric Friedel-Crafts reaction of addition of indoles to *N*-sulfonyl imine

Under an N₂ atmosphere, Cu(OTf)₂ (2.71 mg, 0.0075 mmol), and (*S*)-**L₂** (18.5 mg, 0.0041 mmol) were dissolved in DCM (2 mL). The solution was stirred at room temperature for 2 h, then 4 Å molecular sieves (100 mg) were added and stirred for another 10 min. Next, *N*-(3-nitrobenzylidene)-4-methylbenzenesulfonamide **2a** (91.2 mg, 0.30 mmol) and indole (70.29 mg, 0.6 mmol) were added, and the reaction mixture was stirred at 20 °C. After the reaction was complete, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel eluted with ethyl acetate/petroleum ether (1:3, v/v)] to afford the product *N*-[Indol-3-yl-(3-nitrophenyl)methyl]-4-methyl benzenesulfonamide as White powder.

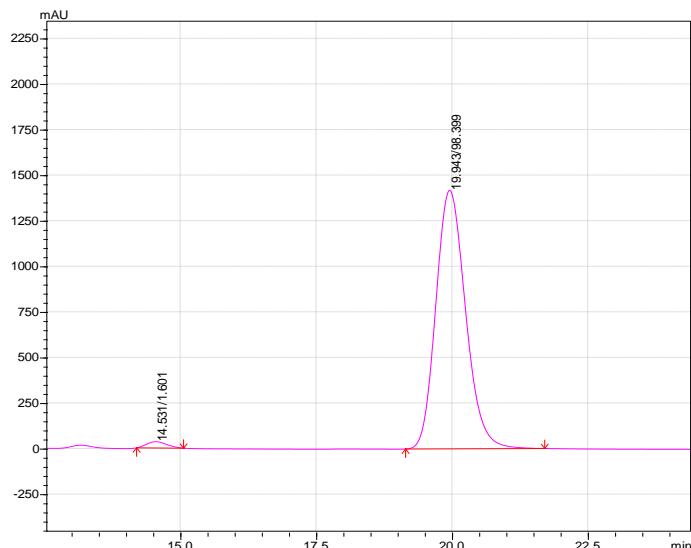
C. Characterization data and HPLC profiles of the products:

***N*-[Indol-3-yl-(3-nitrophenyl)methyl]-4-methylbenzenesulfonamide 3a^{2,3}:**

White powder, yield 96%, 97% ee [Daicel Chiralpak IA column, n-hexane/*i*-PrOH = 70:30, 0.7 mL/min ; t_r (minor) = 14.53 min, t_r (major) = 19.97 min]; ^1H NMR (500 MHz, DMSO-*d*₆): δ 2.24 (s, 3H), 5.91 (d, J = 8.5 Hz, 1H), 6.77 (s, 1H), 6.94 (t, J = 20.5 Hz, 1H), 7.06–7.09 (m, 3H), 7.32 (d, J = 8 Hz, 1H), 7.39 (d, J = 8 Hz, 1H), 7.45–7.47 (m, 3H), 7.72 (d, J = 8 Hz, 1H), 7.98 (d, J = 8 Hz, 1H), 8.06 (s, 1H), 8.67 (d, J = 8.5 Hz 2H), 10.989s, 1H). ^{13}C NMR (125 MHz, DMSO-*d*₆): δ 21.2, 54.2, 112.0, 115.1, 119.2, 121.9, 122.0, 122.1, 124.5, 125.7, 126.8, 129.4, 129.8, 134.4, 136.8, 138.7, 142.5, 143.9, 147.9.



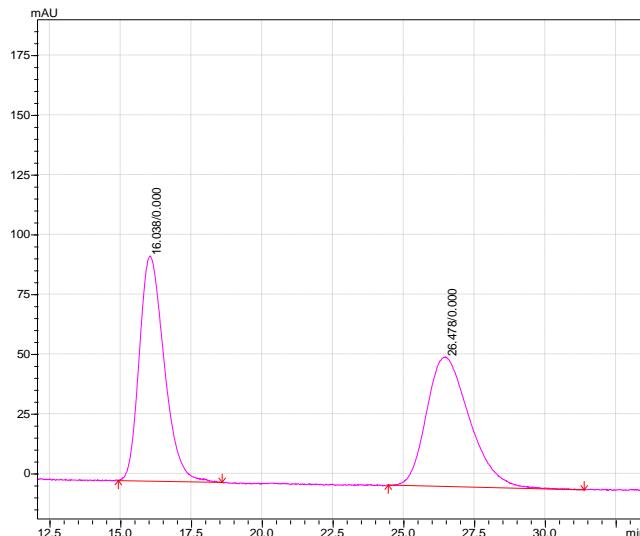
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 14.788 | 6730292 | 14.112 | 16.096 | 49.8962 |
| 2 | 20.344 | 6758290 | 19.435 | 21.728 | 50.1038 |



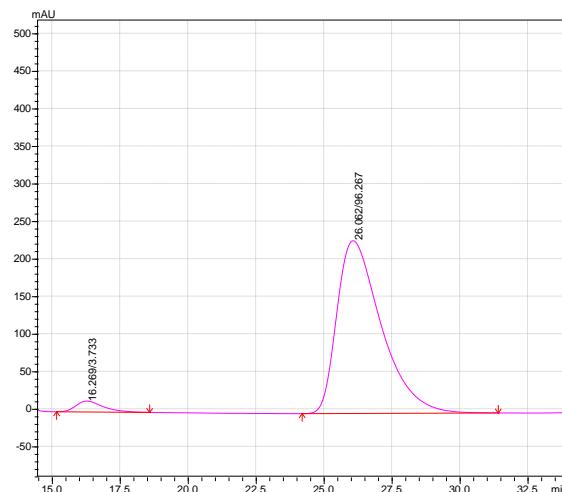
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|--------|
| 1 | 14.531 | 878200 | 14.187 | 15.051 | 1.601 |
| 2 | 19.943 | 53966216 | 19.136 | 21.696 | 98.399 |

N-[Indol-3-yl-(4-nitrophenyl)methyl]-4-methylbenzenesulfonamide 3b^{2,3}:

(S)-N-[indol-3-yl-(4-nitrophenyl)methyl]-4-methylbenzenesulfonamide **3b** White solid, yield 98%, 93% ee) [Daicel Chiralcel OD column, n-hexane/ *i*-PrOH = 80:20, 1.0 mL/min ; t_r (minor) = 16.25 min, t_r (major) = 26.06 min]; ^1H NMR (200 MHz, CD₃COCD₃): δ 2.34 (s, 3H), 6.02 (d, J = 6.2 Hz, 1H), 6.83 (d, J = 1.8 Hz, 1H), 6.93 (d, J = 14.8 Hz, 1H), 7.09 (t, J = 15, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.28 – 7.38 (m, 3H), 7.64 (t, J = 15.8 Hz, 4H), 8.09 (d, J = 8.8 Hz, 2H), 10.23 (s, 1H); ^{13}C NMR (50 MHz, DMSO-*d*₆): δ 20.9, 54.0, 111.7, 114.4, 118.8, 118.9, 121.6, 123.2, 124.2, 125.4, 126.7, 128.5, 129.2, 136.5, 138.5, 142.4, 146.3, 149.5.



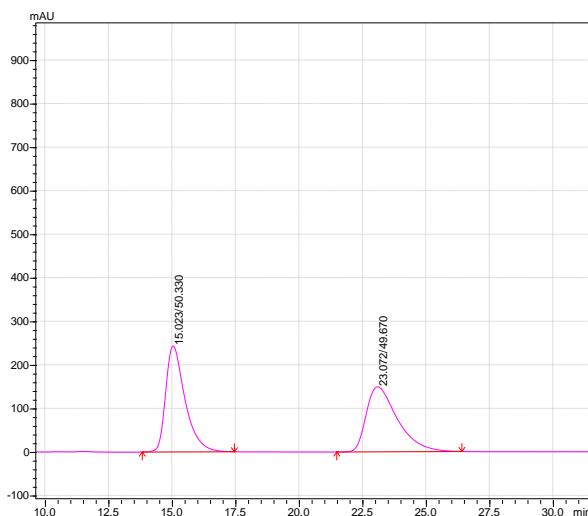
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 16.038 | 5754408 | 14.912 | 18.581 | 50.1661 |
| 2 | 26.478 | 5716307 | 24.448 | 31.371 | 49.8339 |



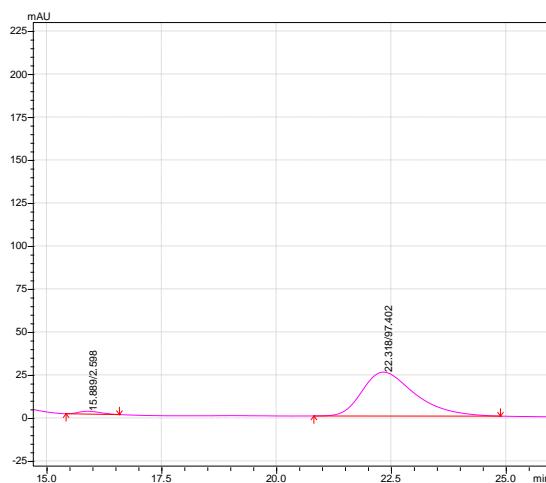
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 16.269 | 1011747 | 15.157 | 18.581 | 3.7328 |
| 2 | 26.062 | 26092841 | 24.192 | 31.403 | 96.2672 |

(S)-N-[Indol-3-yl-(4-bromophenyl)methyl]-4-methylbenzenesulfonamide 3c^{2,3}: White powder, yield 90%, 95% ee [Daicel Chiralcel OD column, n-hexane/i-PrOH = 76:24, 1.0 mL/min, t_r (minor) = 15.88 min, t_r (major) = 22.31 min]; ¹H NMR (200 MHz, CDCl₃): δ 2.40 (s, 3H), 4.99 (d, J = 6 Hz, 1H), 5.80 (d, J = 6.4 Hz, 1H), 6.63 (s, 1H), 7.01 (t, J = 14.8 Hz 1H), 7.13–7.22 (m, 6H), 7.31–7.35 (m, 3H), 7.56 (d, J = 8 Hz, 2H), 8.01 (s, 1H); ¹³C NMR

(50 MHz, DMSO-*d*₆): δ 21.3, 54.3, 111.9, 115.5, 119.1, 119.2, 121.8, 124.2, 125.7, 126.9, 129.7, 131.1, 136.8, 138.9, 141.3, 142.5.



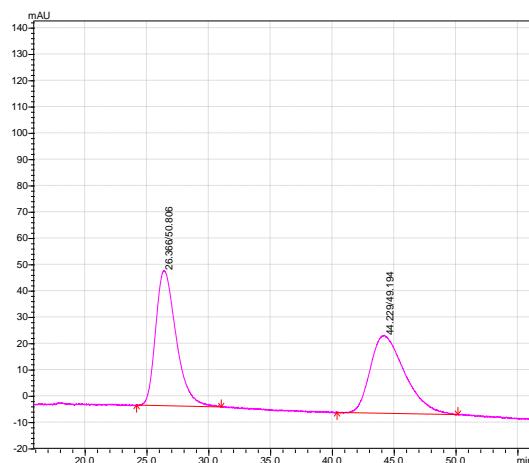
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|--------|
| 1 | 15.023 | 12901184 | 13.813 | 17.440 | 50.330 |
| 2 | 23.072 | 12732165 | 21.472 | 26.400 | 49.670 |



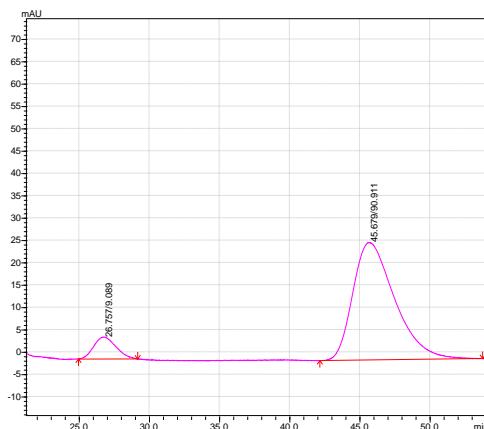
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 15.889 | 54441 | 15.413 | 16.576 | 2.5984 |
| 2 | 22.318 | 2040735 | 20.811 | 24.875 | 97.4016 |

***N*-[Indol-3-yl-(4-cyanphenyl)methyl]-4-methylbenzenesulfonamide 3d^{2,3}:** White powder, 82%ee [Daicel Chiralcel OD-H column, n-hexane/*i*-PrOH = 80:20, 1.0 mL / min, t_r (minor) = 25.75 min, t_r (major) = 45.6 min]; ¹H NMR (500 MHz, CDCl₃): δ 2.41 (s, 3H), 5.15 (d, *J* = 6

Hz, 1H), 5.86 (d, J = 6 Hz, 1H), 6.57 (d, J = 2.5 Hz, 1H), 7.01 (t, J = 15.5 Hz, 1H), 7.1 (d, J = 8, 1H) 7.17 – 7.21(m, 3H), 7.32 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 8 Hz, 2H), 7.52 (d, J = 8 Hz, 2H), 7.59 (d, J = 8 Hz, 2H), 8.01 (s, 1H); ^{13}C NMR (125 MHz, DMSO- d_6): δ 21.3, 54.5, 109.7, 112.0, 114.9, 119.2, 121.9, 124.3, 125.7, 126.9, 128.5, 129.5, 132.3, 136.7, 138.7, 142.6, 147.5.

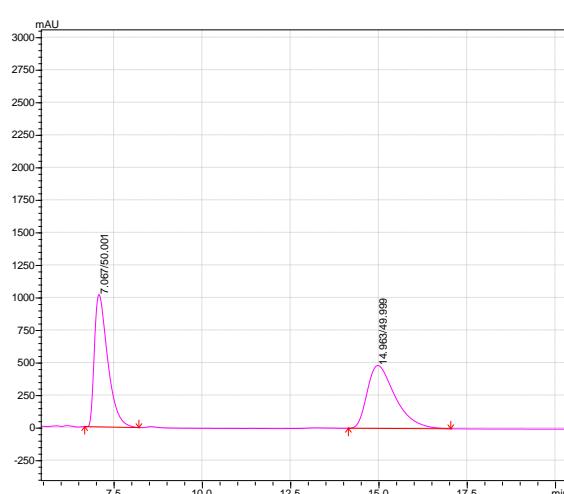


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 26.366 | 5904205 | 24.160 | 31.008 | 50.8058 |
| 2 | 44.229 | 5716912 | 40.373 | 50.155 | 49.1942 |

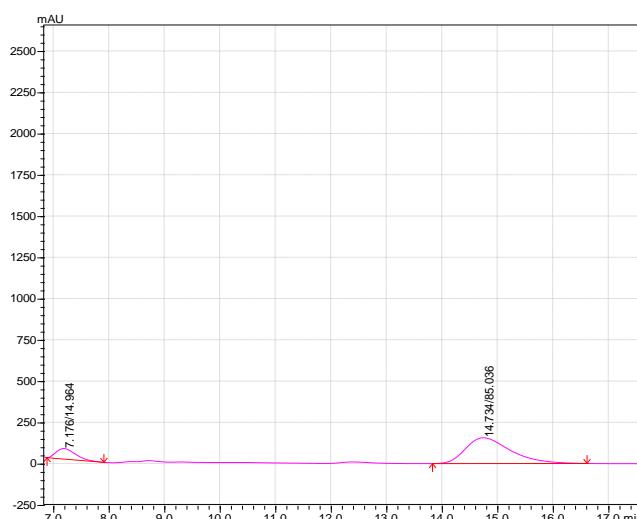


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 26.757 | 543804 | 24.939 | 29.163 | 9.0888 |
| 2 | 45.679 | 5439445 | 42.144 | 53.749 | 90.9112 |

N-[Indol-3-yl-(2-chlorophenyl)methyl]-4-methylbenzenesulfonamide 3e: White powder, yield 75%, 72% ee [Daicel Chiralcel OD column , *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, t_r (minor) = 7.17 min , t_r (major) = 14.73 min]; ^1H NMR (200 MHz, CDCl_3): δ 2.40 (s, 3H), 5.11 (d, J = 4.6 Hz, 1H), 6.21 (d, J = 5.2 Hz, 1H), 6.58 (s, 1H), 7.01(t, J = 13 Hz, 1H), 7.18 - 7.33(m, 8H), 7.50(d, J = 3.6 Hz, 1H), 7.67 (d, J = 7.4 Hz, 2H), 8.00 (s, 1H) ; ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): δ 21.3, 51.0, 112.0, 114.5, 118.9, 119.23, 121.9, 124.6, 126, 127.4, 128.7, 29.2, 129.5, 131.8, 136.1, 136.8, 138.7, 139.2, 142.6.

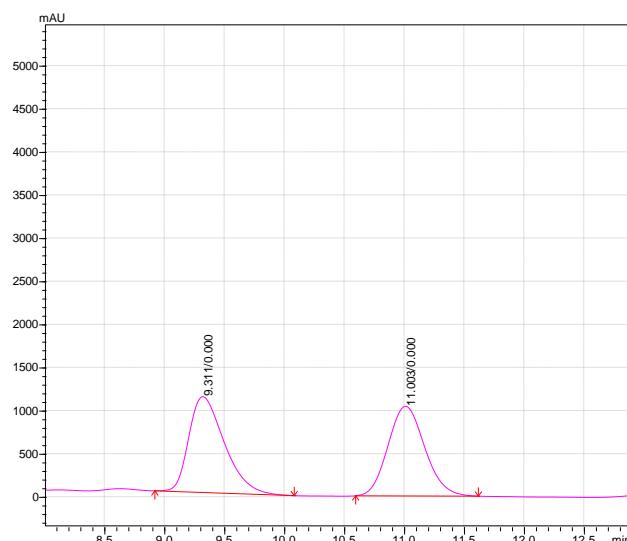


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 7.067 | 26637029 | 6.667 | 8.203 | 50.0005 |
| 2 | 14.963 | 26636485 | 14.133 | 17.035 | 49.9995 |

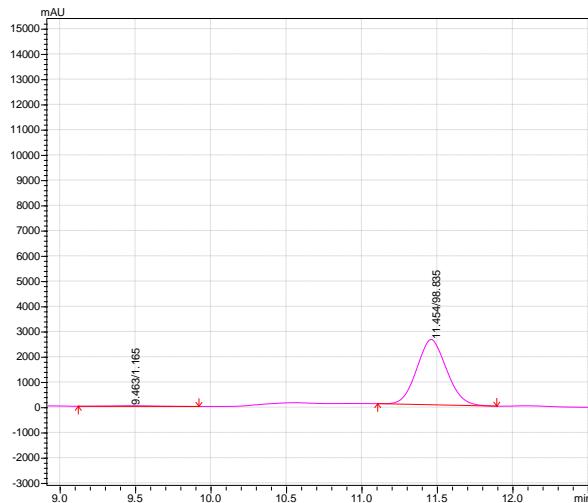


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 7.176 | 1544395 | 6.880 | 7.904 | 14.9644 |
| 2 | 14.734 | 8776041 | 13.824 | 16.608 | 85.0356 |

N-[Indol-3-yl-(3-chlorophenyl)methyl]-4-methylbenzenesulfonamide 3f^{2,3}: White powder, yield 85%, 97% ee [Daicel Chiralpak IA column, *n*-hexane/*i*-PrOH = 60:40, 0.5 mL/min, *t*_r (minor) = 9.46 min, *t*_r (major) = 11.45 (major) min]; ¹H NMR (200 MHz, CDCl₃): δ 2.39 (s, 3H), 5.12 (d, *J* = 5.8 Hz, 1H), 6.22 (d, *J* = 6 Hz, 1H), 6.57 (s, 1H), 7.00 (t, *J* = 13 Hz, 1H), 7.16-7.32 (m, 9H), 7.49 (d, *J* = 4.6 Hz, 1H), 7.66 (d, *J* = 7.8, 2H), 8.00 (s, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆): δ 20.9, 53.8, 111.5, 114.9, 118.6, 121.4, 123.4, 123.6, 125.3, 125.6, 126.2, 126.5, 126.8, 128.7, 129.7, 132.7, 136.2, 138.3, 142.2, 143.9.

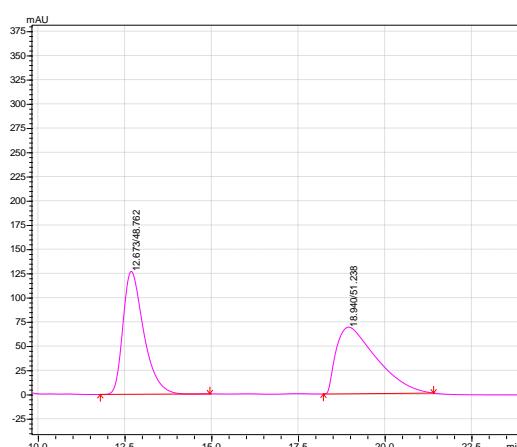


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 9.311 | 22885125 | 8.917 | 10.080 | 50.8253 |
| 2 | 11.003 | 22141928 | 10.592 | 11.616 | 49.1747 |

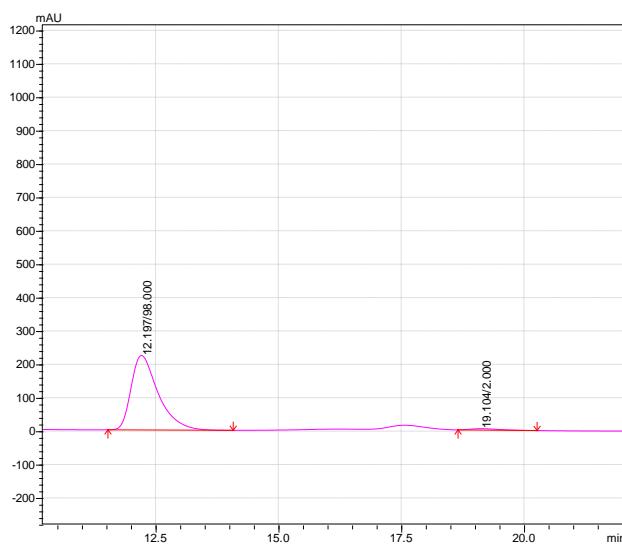


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 9.463 | 418680 | 9.120 | 9.920 | 1.1650 |
| 2 | 11.454 | 35518694 | 11.104 | 11.893 | 98.8350 |

N-[Indol-3-yl-(4-chlorophenyl)methyl]-4-methylbenzenesulfonamide 3g^{2,3}: White powder, yield 89%, 96% ee [Daicel Chiralcel OD column, n-hexane/i-PrOH = 80:20, 1.0 mL/min, t_r (major) = 12.30 min, t_r (minor) = 18.62 min]; ¹H NMR (500 MHz, CDCl₃): δ 2.38 (s, 3H), 5.18 (d, J = 5.5 Hz, 1H), 5.93 (d, J = 5.5 Hz, 1H), 6.61 (s, 1H), 7.03 (t, J = 15 Hz, 1H), 7.15–7.20 (m, 4H), 7.37 (d, J = 8 Hz, 1H), 7.43 (t, J = 15.5 Hz, 2H), 7.71 (d, J = 7.5 Hz, 1H), 8.05 (d, J = 9 Hz, 2H), 8.11 (s, 1H); ¹³C NMR (50 MHz, DMSO-d₆): δ 20.7, 53.9, 111.5, 115.3, 118.7, 118.9, 121.3, 123.6, 125.5, 126.6, 127.8, 128.9, 131.3, 136.5, 138.7, 140.6, 141.8.



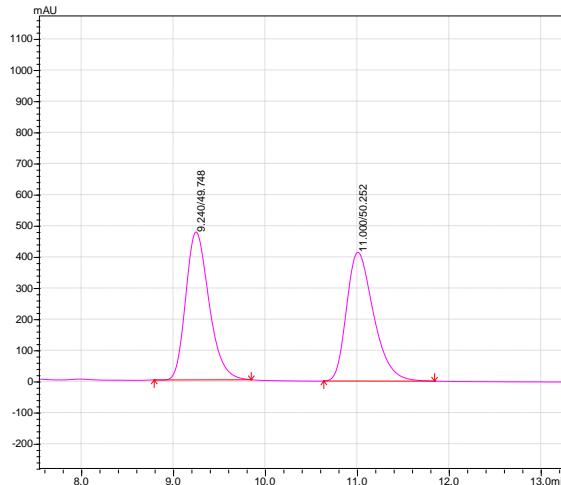
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 12.673 | 5276838 | 11.787 | 14.944 | 48.7617 |
| 2 | 18.940 | 5544851 | 18.219 | 21.397 | 51.2383 |



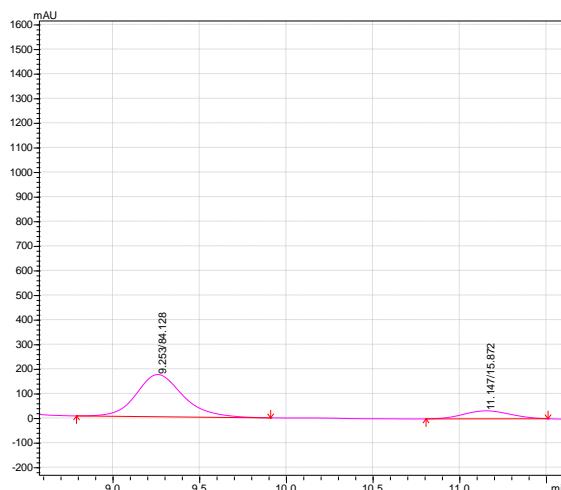
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|------|-----------|---------|------------|----------|---------|
| 1 | 12.197 | 8529052 | 11.520 | 14.069 | 98.0004 |
| 2 | 19.104 | 174026 | 18.645 | 20.256 | 1.9996 |

N-[Indol-3-yl-(2-trifluoromethylphenyl)methyl]-4-methylbenzenesulfonamide 3h^{2,3}:

White powder, yield 70%, 65% ee [Daicel Chiraldpak IA column, n-hexane/*i*-PrOH = 60:40, 0.7 mL/min, *t*_r (major) = 9.25 min, *t*_r (minor) = 11.14 min]; ¹H NMR (200 MHz, DMSO-*d*₆): δ 2.29 (s, 3H), 6.12 (d, *J* = 8.2 Hz, 1H), 6.33 (s, 1H), 6.95 (t, *J* = 14.6 Hz, 1H), 7.06 – 7.17 (m, 3H), 7.28 (d, *J* = 11 Hz, 2H), 7.36– 7.49 (m, 4H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 10.91 (s, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆): δ 26.0, 54.9, 116.7, 116.8, 120.1, 123.4, 123.5, 124.0, 126.7, 128.3, 129.8, 130.6, 130.8, 131.4, 131.5, 132.4, 132.4, 134.1, 134.2, 134.5, 137.4, 141.5, 143.4, 144.8, 147.4.



| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 9.240 | 8365082 | 8.789 | 9.845 | 49.7479 |
| 2 | 11.000 | 8449856 | 10.635 | 11.840 | 50.2521 |

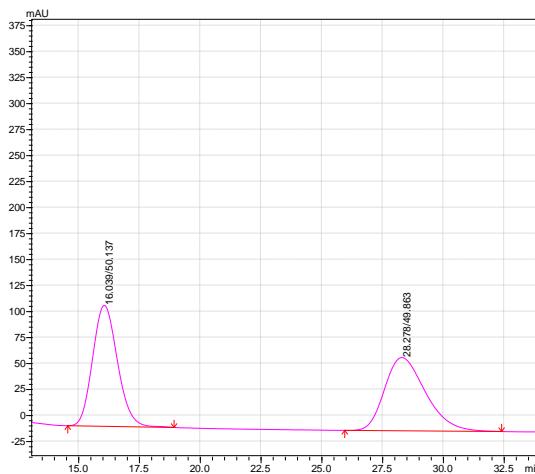


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 9.255 | 5893947 | 8.789 | 10.144 | 82.6014 |
| 2 | 11.146 | 1241462 | 10.837 | 11.584 | 17.3986 |

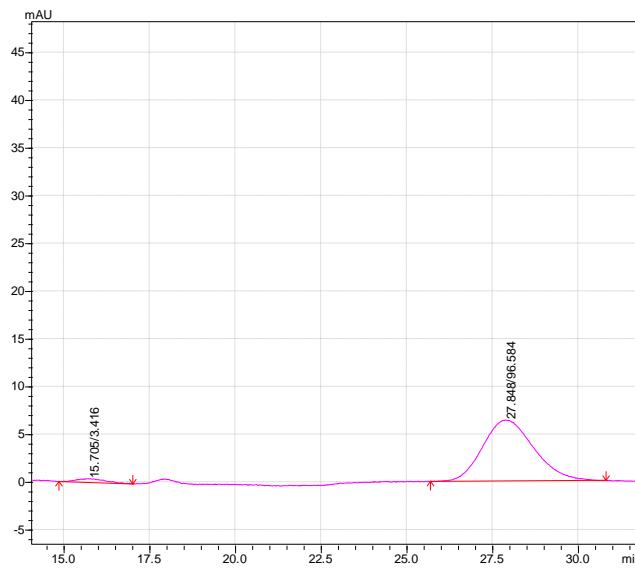
***N*-[Indol-3-yl-(4-trifluoromethylphenyl)methyl]-4-methylbenzenesulfonamide **3i**^{2,3} :**

White powder, yield 85%, 94% ee [Daicel Chiralcel OD-H column, n-hexane/ i-PrOH = 80:20, 1.0 mL/min, t_r (minor) = 15.69 min, t_r (major) = 27.86 min]; ^1H NMR (200 MHz, DMSO- d_6): δ 2.26 (s, 3H), 5.84 (d, J = 8.8 Hz, 1H), 6.79 (s, 1H), 6.93 (t, J = 14.6 Hz, 1H), 7.04–7.11 (m, 3H), 7.31–7.40 (m, 2H), 7.45–7.47 (m, 6H), 8.61 (d, J = 8.8 Hz, 1H), 10.97 (s,

1H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 21.1, 54.6, 112.0, 115.1, 119.2, 121.9, 124.3, 125.1, 125.3, 126.9, 128.3, 129.3, 136.8, 138.8, 142.4, 143.6, 146.4.



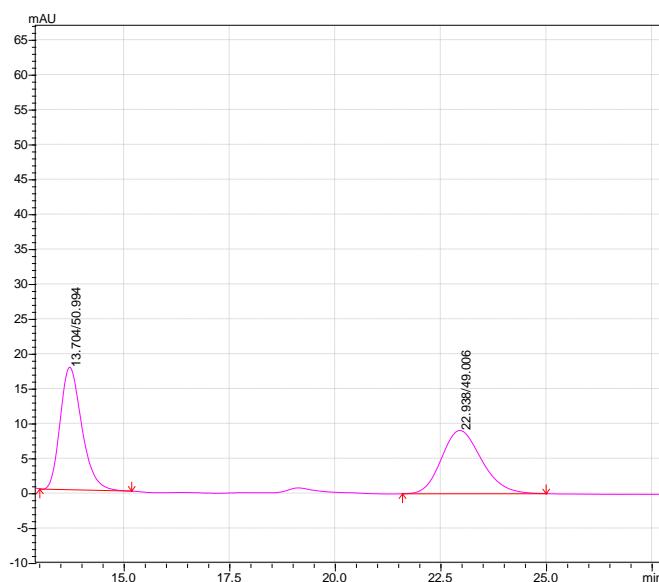
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 16.039 | 8275353 | 14.549 | 18.923 | 50.1369 |
| 2 | 28.278 | 8230170 | 25.941 | 32.395 | 49.8631 |



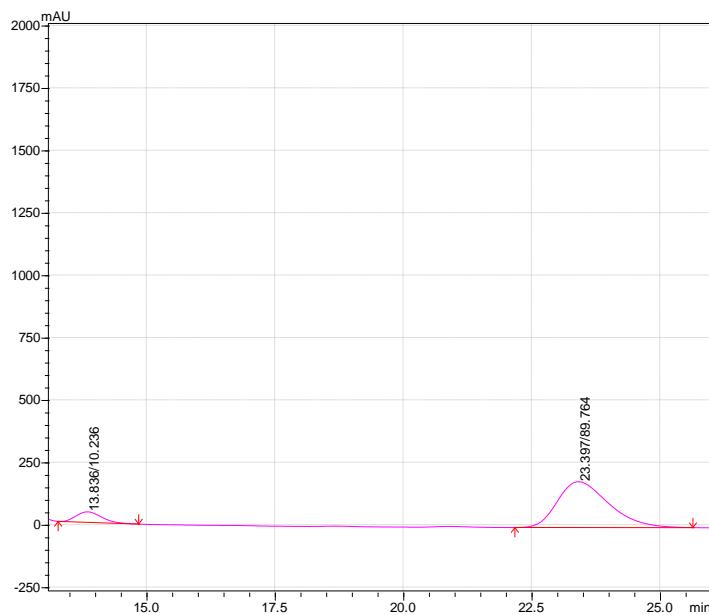
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|--------|------------|----------|---------|
| 1 | 15.697 | 24295 | 14.784 | 17.088 | 3.6665 |
| 2 | 27.866 | 638333 | 26.059 | 30.731 | 96.3335 |

N-(Indol-3-yl-phenylmethyl)-4-methylbenzenesulfonamide 3j^{2,3} : White powder, yield 84, 81% ee [Daicel Chiralcel OD-H column, n-hexane/*i*-PrOH = 70:30, 0.6 mL/min; t_r (minor) = 13.75 min, t_r (major) = 23.12 min]; ^1H NMR (200 MHz, Acetone- d_6): δ 2.33 (s, 3H), 5.89 (d,

$J = 8.2$ Hz, 1H), 6.81 (s, 1H), 6.90 (t, $J = 15.4$ Hz, 1H), 7.03–7.07 (m, 1H), 7.11–7.20 (m, 5H), 7.31–7.35 (m, 4H), 7.58 (d, $J = 8.2$ Hz, 2H), 8.47 (d, $J = 8.8$ Hz, 1H), 10.86 (s, 1H); ^{13}C NMR (125 MHz, DMSO- d_6): δ 21.1, 54.5, 111.5, 115.8, 118.5, 119.2, 121.3, 123.8, 125.6, 126.7, 126.8, 127.2, 128.0, 129.2, 136.7, 139.0, 141.9, 141.9.

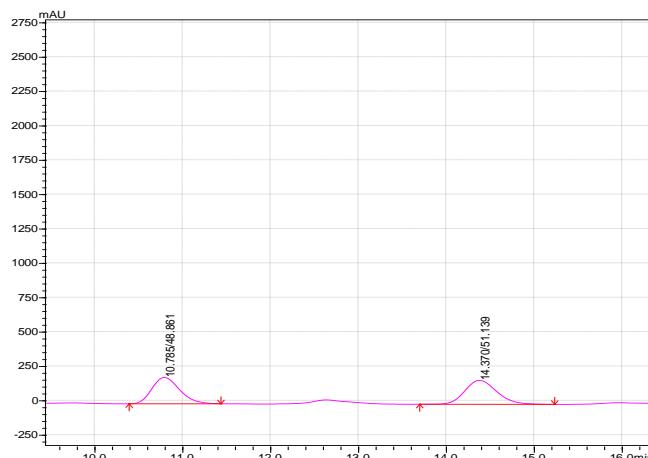


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|--------|------------|----------|---------|
| 1 | 13.704 | 626017 | 13.003 | 15.179 | 50.9937 |
| 2 | 22.938 | 601619 | 21.589 | 24.992 | 49.0063 |

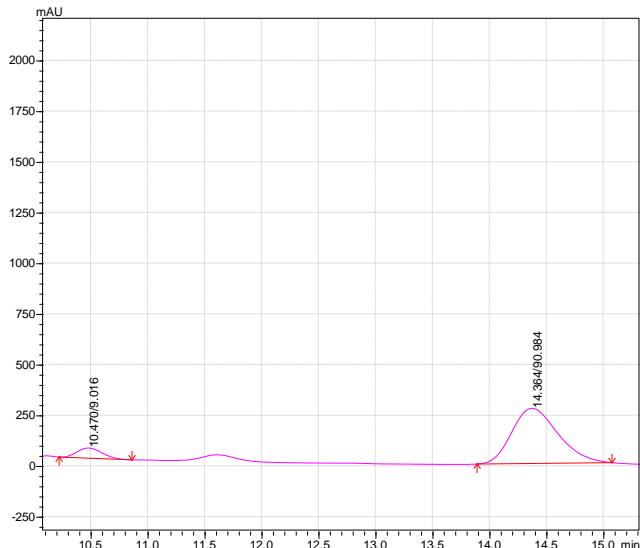


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 13.836 | 1437859 | 13.280 | 14.752 | 10.1549 |
| 2 | 23.397 | 12721338 | 22.112 | 25.888 | 89.8451 |

N-[Indol-3-yl-(4-methylphenyl)methyl]-4-methylbenzenesulfonamide 3k⁴: White powder with 70% yield after chromatography (silica gel: petroleum ether/ethyl acetate = 3/1) and 81% ee as determined by HPLC [Daicel Chiralpak IC, Hexanes/ IPA =70/30, 0.7ml/min, t_r (minor) = 10.46 min, t_r (minor) = 14.36min]. ¹H NMR (200M Hz, CDCl₃) δ 2.29 (s, 3H) 2.37 (s,3H), 5.11 (d, J = 6.78 Hz, 1H), 5.79 (d, J = 6.57 Hz, 1H), 6.71 (s, 1H), 6.98-7.29 (m, 10H), 7.55 (d, J = 7.68 Hz, 2H), 8.00 (s, 1H); ¹³C NMR (100M Hz, CDCl₃) δ 21.0, 21.5, 54.9, 111.2, 116.5, 119.3, 119.8, 122.4, 123.7, 125.4, 127.1, 128.9, 129.1, 136.6, 137.0, 137.3, 137.6, 142.9.

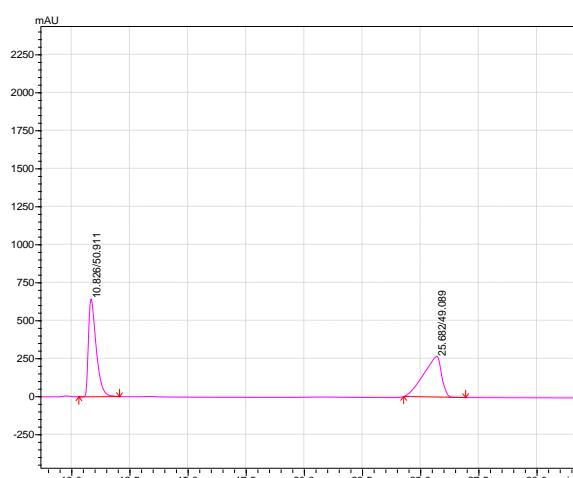


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 10.785 | 4207047 | 10.389 | 11.435 | 48.8613 |
| 2 | 14.370 | 4403142 | 13.696 | 15.232 | 51.1387 |

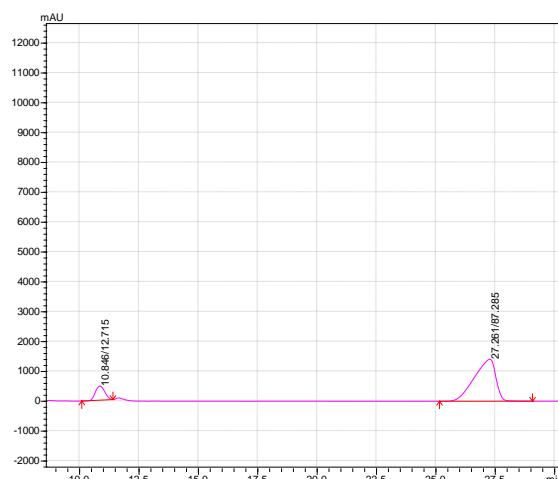


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 10.470 | 759314 | 10.219 | 10.859 | 9.0164 |
| 2 | 14.364 | 7662140 | 13.888 | 15.072 | 90.9836 |

N-[Indol-3-yl-(3-methylphenyl)methyl]-4-methylbenzenesulfonamide 3l⁴: White solid, 68% yield, m.p. 158–159 °C, 75% ee [Daicel Chiralpak IA column, n-hexane/*i*-PrOH = 70 : 30, 0.7 mL/min, *t*_r (minor) = 10.83 min, *t*_r (major) = 27.26 min]; ¹H NMR (500 MHz, CDCl₃) δ 7.98 (br, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.34 – 6.90 (m, 10H), 6.69 (d, *J* = 2.5 Hz, 1H), 5.81 (d, *J* = 6.9 Hz, 1H), 5.06 (d, *J* = 6.9 Hz, 1H), 2.37 (s, 3H), 2.20 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 142.8, 140.0, 137.8, 137.4, 136.5, 129.1, 128.2, 128.0, 127.8, 127.1, 125.4, 124.3, 123.8, 122.3, 119.8, 119.2, 116.3, 111.2, 55.0, 21.4, 21.2.

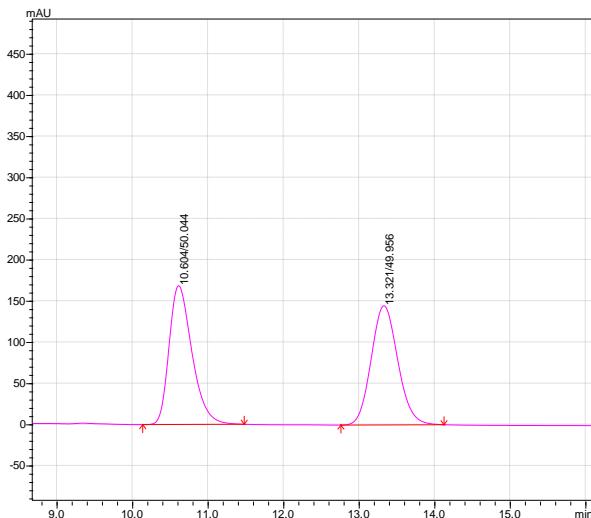


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 10.826 | 14903677 | 10.304 | 12.053 | 50.9108 |
| 2 | 25.682 | 14370409 | 24.267 | 26.933 | 49.0892 |

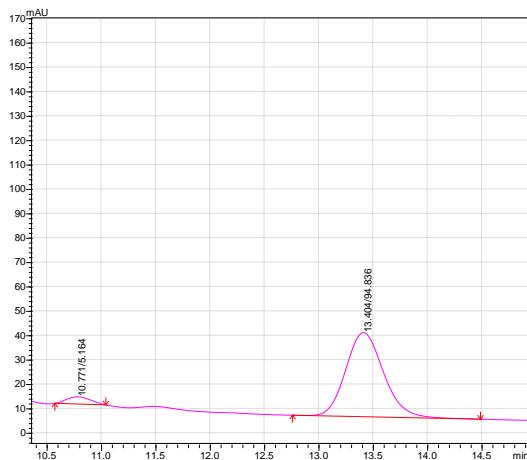


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 10.846 | 12865432 | 10.091 | 11.403 | 12.7147 |
| 2 | 27.261 | 88320130 | 25.152 | 29.067 | 87.2853 |

N-[Indol-3-yl-(3-bromophenyl)methyl]-benzenesulfonamide 3m: White powder, yield = 85%, 89% ee [Chiral pak IA column, n-hexane/*i*-PrOH = 70:30, 0.75 mL/min, t_r (minor) = 10.60 min, t_r (major) = 13.32 min]; ^1H NMR (200 MHz, CDCl_3): δ 5.21(d, J = 5.9 Hz, 1H), 5.83 (d, J = 5.9 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 7.02-7.10 (m 2H), 7.14-7.21(m, 2H), 7.24-7.37(m, 6H), 7.46 (d, 1H), 7.85(d, 2H), 8.05 (s, 1H). ^{13}C NMR: δ 54.2, 111.2, 112.1, 118.4, 119.3, 121.7, 122.9, 123.0, 125.8, 127.4, 129.0, 129.3, 129.6, 130.3, 130.3, 131.5, 131.9, 136.5, 144.5, 145.7.

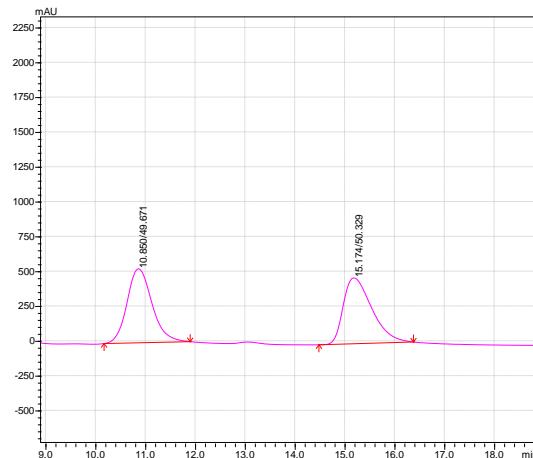


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 10.604 | 3551634 | 10.133 | 11.477 | 50.0440 |
| 2 | 13.321 | 3545382 | 12.757 | 14.123 | 49.9560 |

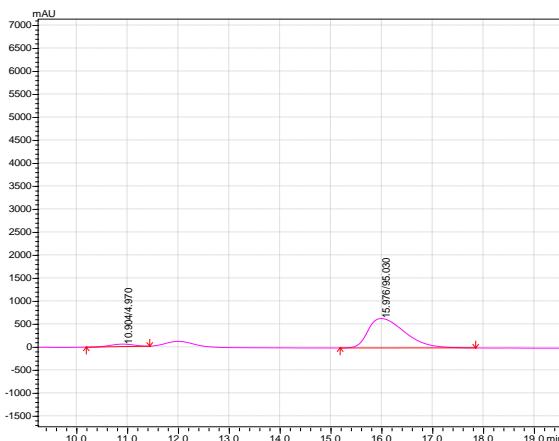


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|--------|------------|----------|---------|
| 1 | 10.771 | 45341 | 10.571 | 11.040 | 5.1642 |
| 2 | 13.404 | 832647 | 12.757 | 14.485 | 94.8358 |

N-[Indol-3-yl-(4-bromophenyl)methyl]-benzenesulfonamide 3n : White powder, 91% ee, [Chiral pak IB column, n-hexane/i-PrOH = 70:30, 0.7 mL/min, t_r (minor) = 10.60 min, t_r (major) = 13.32 min]; ^1H NMR (200 MHz, DMSO- d_6): δ 5.84 (d, J = 8.8 Hz, 1H), 6.7 (s, 1H), 6.93 (t, J = 15.8 Hz, 2H), 7.04-7.11 (m, 3H), 7.31-7.47 (m, 8H), 8.61 (d, J = 8.8 Hz, 1H), 10.9 (s, 1H). ^{13}C NMR: δ (125 MHz, DMSO- d_6): δ 54.3, 111.3, 112.4, 118.4, 119.6, 121.3, 121.7, 123.3, 127.6, 129.1, 129.3, 131.2, 131.8, 137.4, 141.2, 147.6.



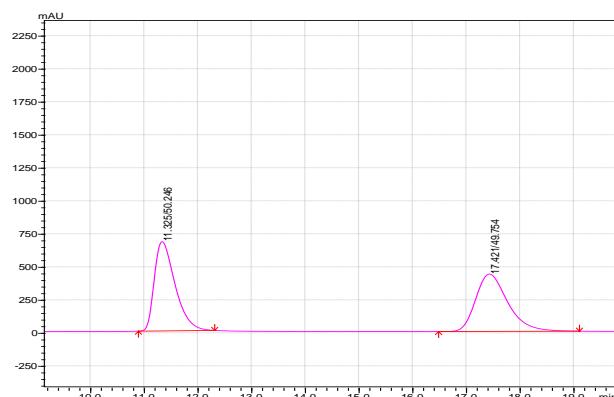
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 10.850 | 18521446 | 10.165 | 11.893 | 49.6711 |
| 2 | 15.174 | 18766693 | 14.475 | 16.373 | 50.3289 |



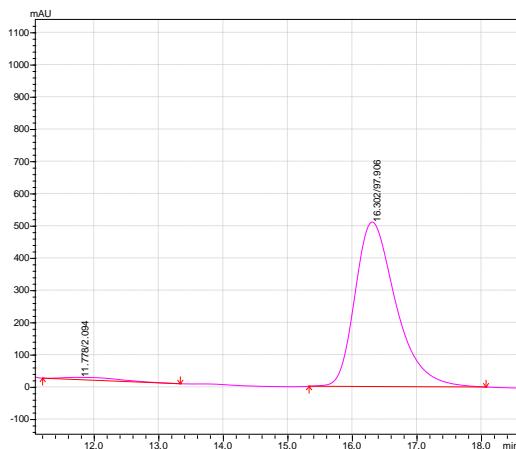
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 10.904 | 1679797 | 10.187 | 11.435 | 4.9702 |
| 2 | 15.976 | 32117811 | 15.179 | 17.845 | 95.0298 |

N-[Indol-3-yl-(4-bromophenyl)methyl]-4-nitrobenzenesulfonamide 3o : White powder, 94% [chiralpak IA column, n-hexane/i-PrOH = 80:20, 0.8 mL/min, t_r (minor = 11.77, t_r (major) = 16.30]; ^1H NMR, (500MHz, DMSO- d_6): δ 5.81 (d, J = 9 Hz, 1H), 6.83 (d, J = 2 Hz, 1H), 6.91 (t, J = 15 Hz, 1H), 7.03 (t, J = 15 Hz, 1H), 7.21 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8 Hz, 1H), 7.35 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8 Hz, 1H), 7.73 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5, 2H), 8.9 (d, J = 9 Hz, 1H), 10.9 (s, 1H). ^{13}C NMR (125MHz, DMSO- d_6):

δ 54.6, 111.9, 114.6, 119.2, 119.3, 120.5, 121.8, 124.0, 124.6, 125.5, 128.3, 129.9, 131.3, 136.8, 140.4, 147.1, 149.0.



| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 11.325 | 18151077 | 10.891 | 12.309 | 50.2460 |
| 2 | 17.421 | 17973323 | 16.480 | 19.104 | 49.7540 |



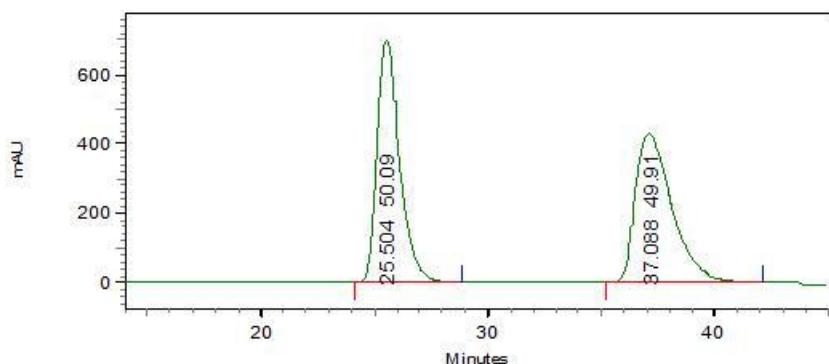
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 11.778 | 479871 | 11.200 | 13.333 | 2.0945 |
| 2 | 16.302 | 22431202 | 15.328 | 18.069 | 97.9055 |

N-[5-MeO-indol-3-yl-(3-nitrophenyl)methyl]-4-methylbenzenesulfonamide 3p :

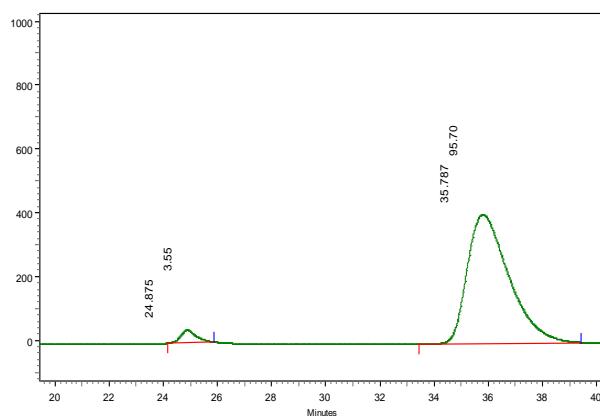
White powder, 93% ee [chiralpak IC column, n-hexane/i-PrOH = 70:30, 1.0 mL/min, t_r (minor) = 24.8 min, t_r (major) = 35.78 min]; ^1H NMR (200 MHz, CDCl_3): δ 2.33 (s, 3H), 3.75 (s, 3H), 5.20 (d, J = 5.9 Hz, 1H), 5.92 (d, J = 5.9 Hz, 1H), 6.54 (d, J = 2.4 Hz, 1H), 7.02–7.10 (m, 2H), 7.14–7.21 (m, 3H), 7.34 (d, J = 8.2 Hz, 1H), 7.39–7.47 (m, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 7.5 Hz, 1H), 7.81–7.93 (m, 2H), 8.06 (s, 1H); ^{13}C NMR (100

mHz, DMSO-*d*₆)

δ 21.2, 21, 54.2, 55.7, 101.2, 111.9, 112.7, 114.7, 122.0, 122.1, 125.1, 126.1, 126.8, 129.4, 129.8, 128.8, 131.9, 134.4, 138.8, 142.6, 144.2, 147.9, 153.6.



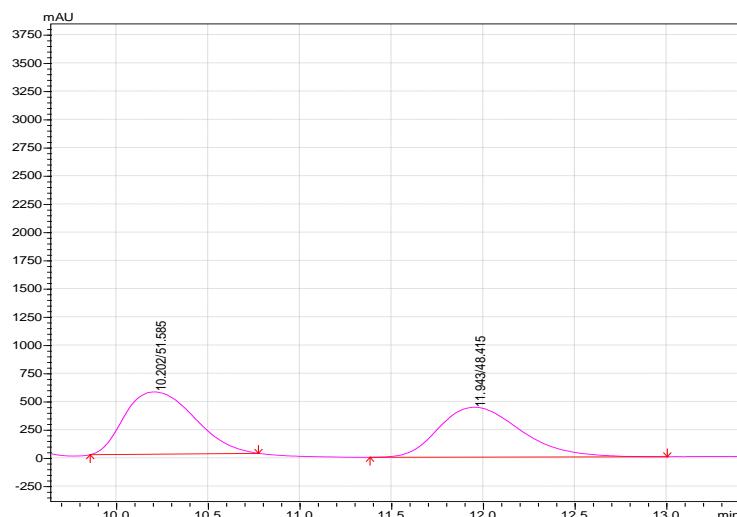
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|-------|
| 1 | 25.504 | 48532856 | 24.126 | 28.817 | 50.09 |
| 2 | 37.099 | 48367907 | 34.99 | 41.7433 | 49.91 |



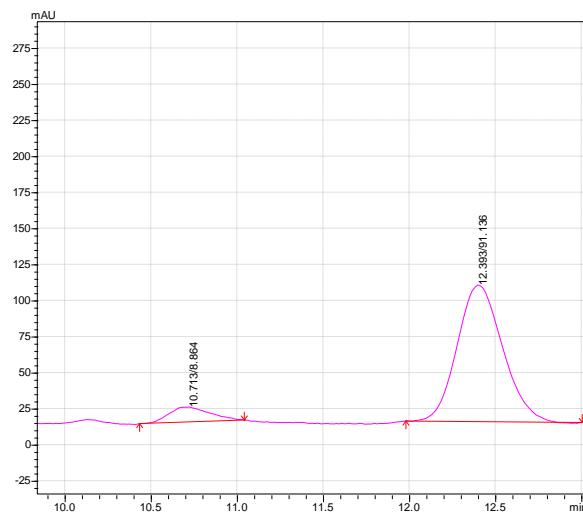
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|-------|
| 1 | 24.875 | 1514213 | 24.20 | 25.95 | 3.55 |
| 2 | 35.787 | 42932286 | 33.61 | 39.45 | 95.70 |

***N*-[2-Methyl-indol-3-yl-(3-nitrophenyl)methyl]-4-methylbenzenesulfonamide 3q** :White powder ,80% ee [Chiralkpak IC column, n-hexane/i-PrOH = 70:30, 0.7 mL/min, t_r (minor) = 21.66 min, t_r (major) = 23.68 min]; ¹H NMR (200 MHz, CDCl₃): δ 2.32 (s, 3H), 3.57 (s, 3H),

5.02 (d, $J = 5.8$ Hz, 1H), 5.84 (d, $J = 5.6$ Hz, 1H), 6.95 (t, $J = 13.6$ Hz, 1H), 7.09 (d, $J = 8.2$ Hz, 2H) 7.16-7.21(m, 3H), 7.37 (t, $J = 16.4$ Hz, 2H), 7.52 (d, $J = 8$ Hz, 1H), 7.66 (d, $J = 7.4$ Hz, 2H), 7.99 (d, $J = 5.8$ Hz 2H). ^{13}C NMR (50 MHz, DMSO- d_6): δ 13.3, 21.3, 55.3, 111.6, 113.0, 118.6, 119.6.2, 121.4 123.1, 126.8, 127.37, 129.1, 129.5, 130.9, 131.3, 133.5, 134.5, 136.2, 142.4, 147.5.



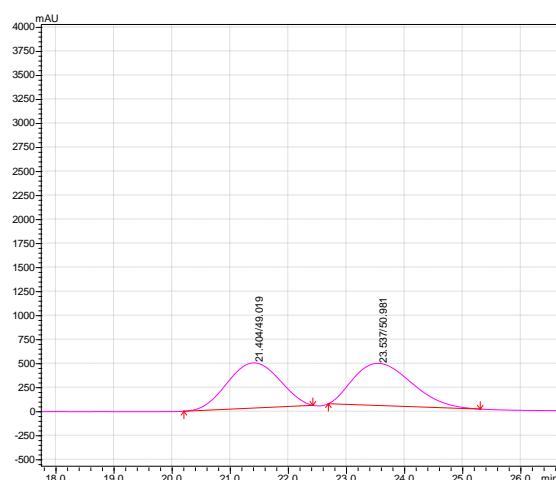
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 10.202 | 14645041 | 9.856 | 10.773 | 51.5848 |
| 2 | 11.943 | 13745183 | 11.381 | 13.003 | 48.4152 |



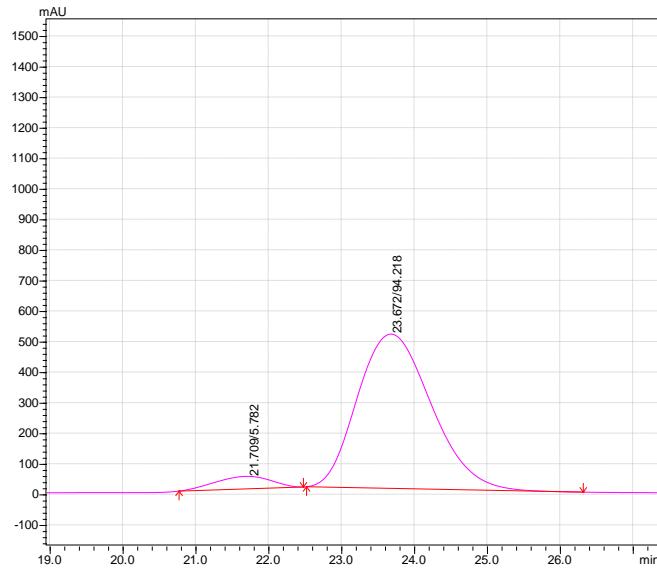
| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|---------|------------|----------|---------|
| 1 | 10.713 | 168728 | 10.432 | 11.040 | 8.8641 |
| 2 | 12.393 | 1734772 | 11.979 | 13.003 | 91.1359 |

N-[5-Fluoro-indol-3-yl-(3-nitrophenyl)methyl]-4-methylbenzenesulfonamide 3r :

White powder, 89% ee [Chiralpak IC column, n-hexane/i-PrOH = 80:20, 0.7 mL/min, t_r (minor) = 21.66 min, t_r (major) = 23.68 min]; ^1H NMR (500 MHz, DMSO-*d*₆): δ 2.24 (s, 3H), 5.88 (d, *J* = 9 Hz, 1H), 6.84 (s, 1H), 6.91 (t, *J* = 18 Hz, 1H), 7.03 (d, *J* = 9.5 Hz, 1H), 7.10 (d, *J* = 8, 2H), 7.30-7.37 (m, 2H), 7.48(d, *J* = 7.5 Hz, 1H), 7.69-7.75 (m, 2H), 8.0 (d, *J* = 8 Hz, 1H), 8.09 (s, 1H), 8.67(d, *J* = 9Hz, 1H), 11.0 (s, 1H); ^{13}C NMR (125 MHz, DMSO-*d*₆): δ 21.2, 53.9, 103.8, 104.0, 110.0, 113.0, 113.1, 115.33, 115.37, 122.1, 126.0, 126.9, 129.4, 129.9, 133.5, 134.4, 138.6, 142.7, 143.8, 147.9, 156.2, 158.



| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 21.404 | 29387620 | 20.203 | 22.421 | 49.0190 |
| 2 | 23.537 | 30563835 | 22.688 | 25.301 | 50.9810 |

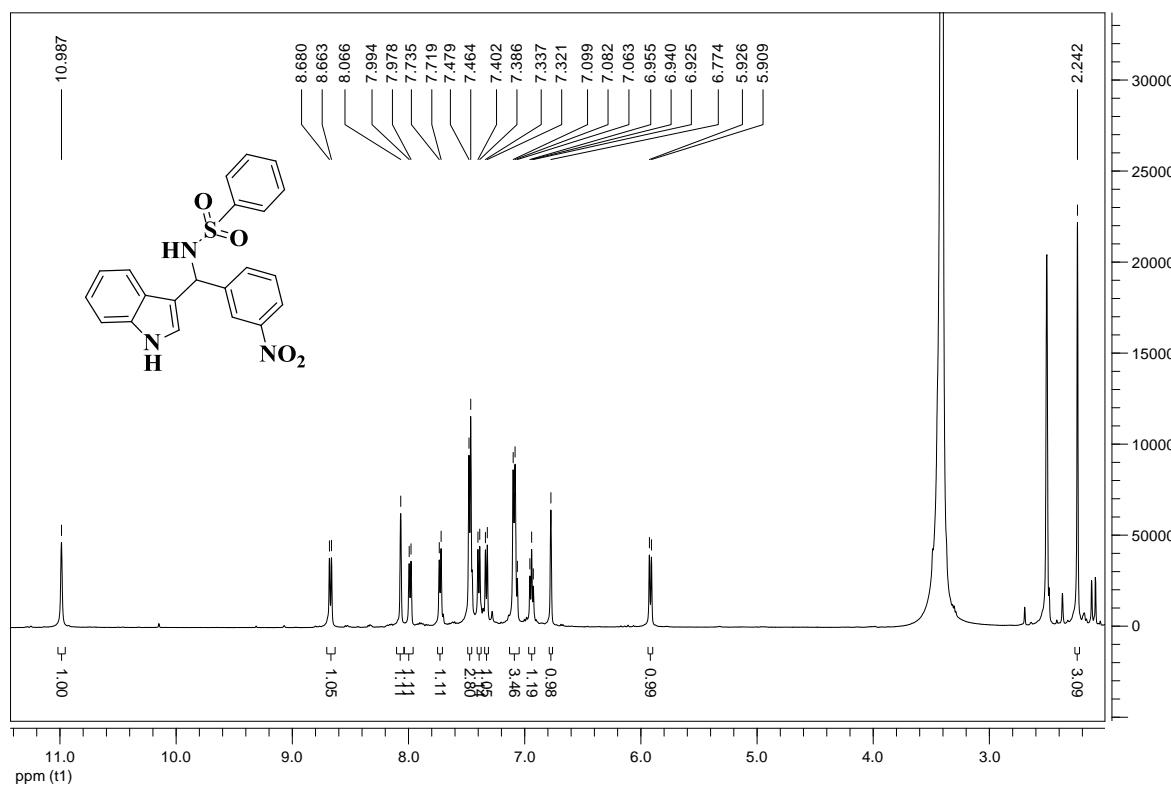


| Peak | Ret. Time | Area | Peak Start | Peak End | Area% |
|------|-----------|----------|------------|----------|---------|
| 1 | 21.709 | 2182754 | 20.768 | 22.475 | 5.7821 |
| 2 | 23.672 | 35567620 | 22.517 | 26.315 | 94.2179 |

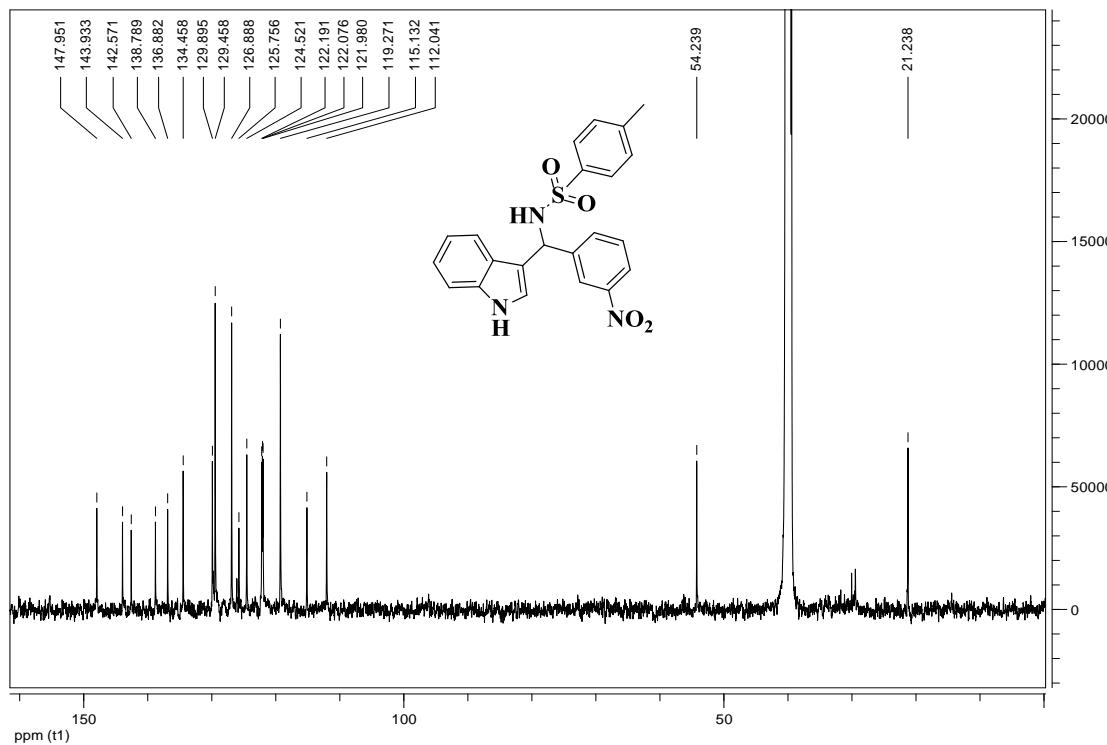
N-[N-Methyl-indol-3-yl-(3-nitrophenyl)methyl]-4-methylbenzenesulfonamide 3s⁴ : White powder , ¹H NMR (200 MHz, CDCl₃): δ 2.32 (s, 3H), 3.57 (s, 3H), 5.02 (d, *J* = 5.8 Hz, 1H), 5.84 (d, *J* = 5.6 Hz, 1H), 6.95 (*t*, *J* = 13.6 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 2H) 7.16-7.21(m, 3H), 7.37 (*t*, *J* = 16.4), 7.52 (d, *J* = 8 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 5.8 Hz, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 21.3, 34, 55, 109.6, 113.0, 118, 121.6.2, 123.4 126.1, 127.8, 128.37, 129.1, 133.0, 138.9, 141.3, 143.5, 147.5.

D. NMR Spectra of Products:

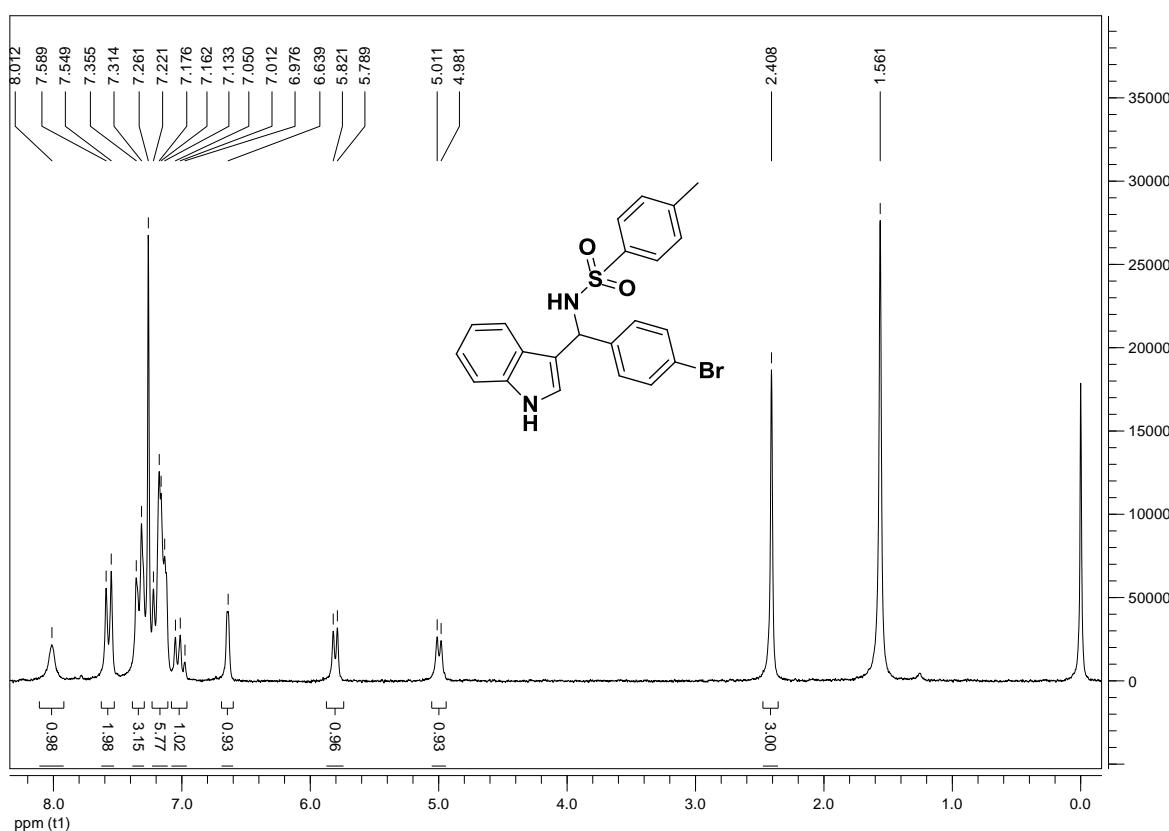
^1H spectrum of (-)-*N*-[Indol-3-yl-(3-nitrophenyl)methyl]-4-methylbenzenesulfonamide 3a.



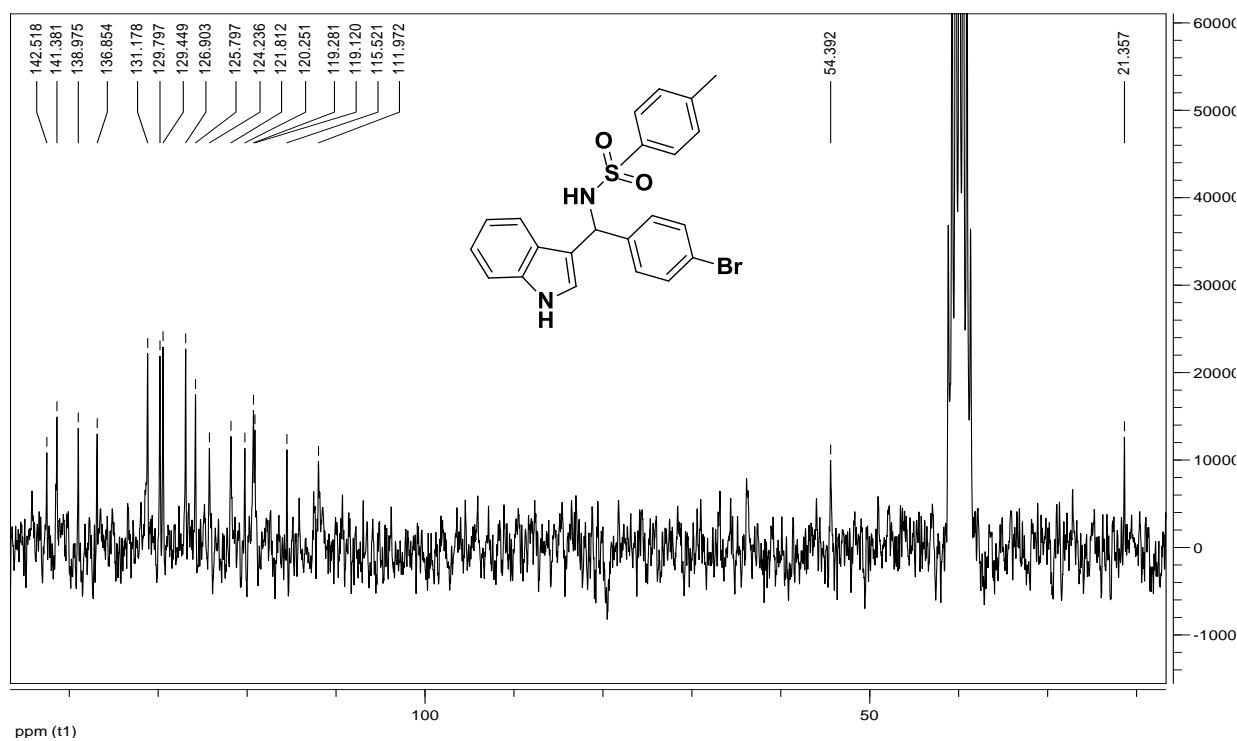
^{13}C spectrum of (-)-*N*-[Indol-3-yl-(3-nitrophenyl)methyl]-4-methylbenzenesulfonamide 3a.



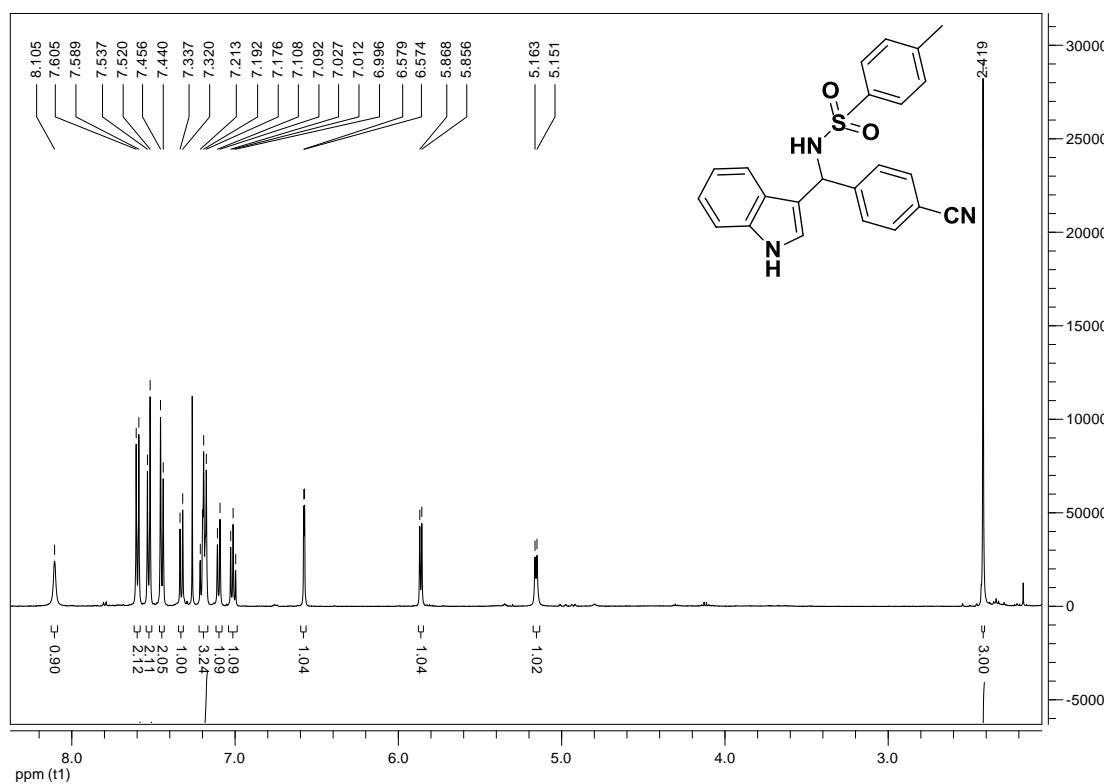
¹H spectrum of (*S*)-*N*-[Indol-3-yl-(4-bromophenyl)methyl]-4-methylbenzenesulfonamide 3c:



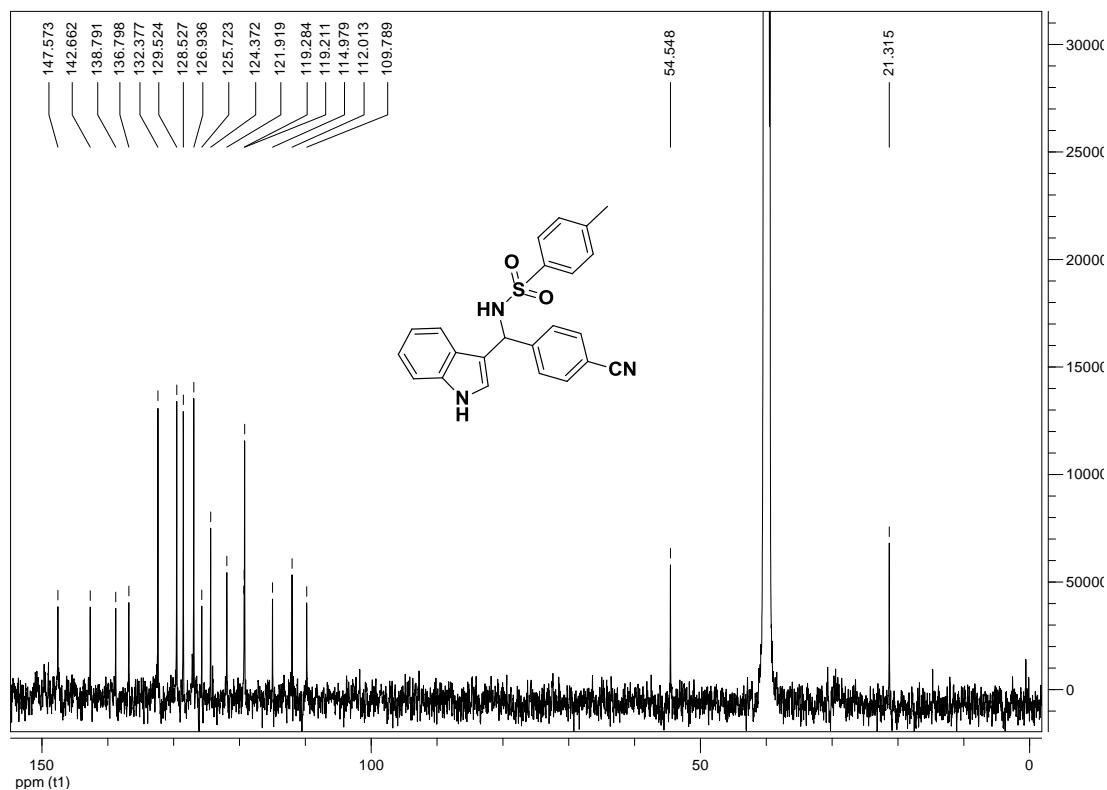
¹³C spectrum of (*S*)-*N*-[Indol-3-yl-(4-bromophenyl)methyl]-4-methylbenzenesulfonamide 3c:



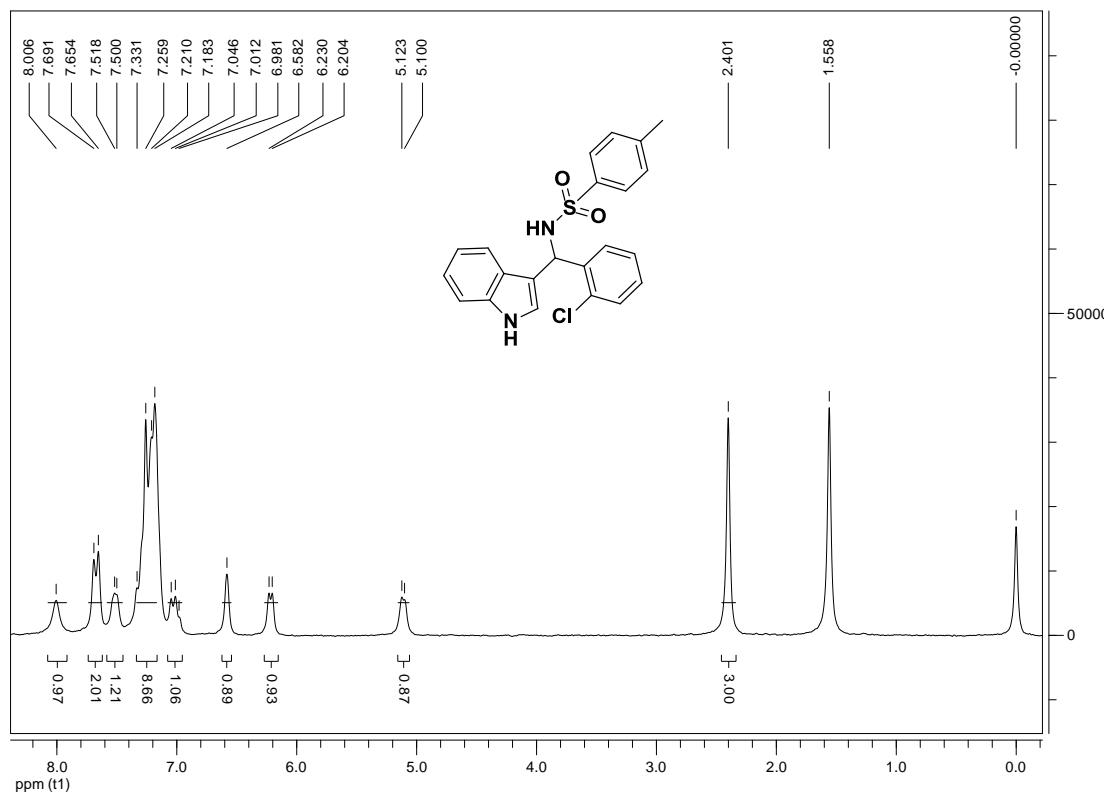
¹H spectrum of (-) *N*-[Indol-3-yl-(4-cyanophenyl)methyl]-4-methylbenzenesulfonamide 3d:



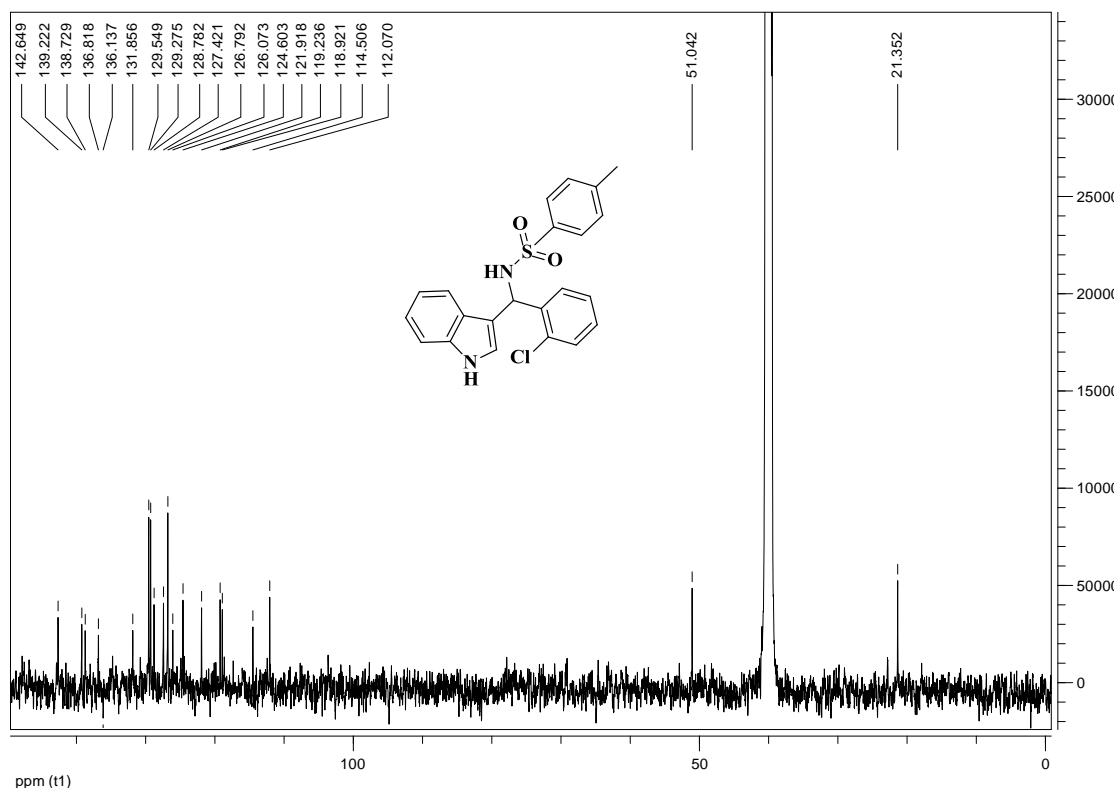
¹³C spectrum of (-) *N*-[Indol-3-yl-(4-cyanophenyl)methyl]-4-methylbenzenesulfonamide 3d:



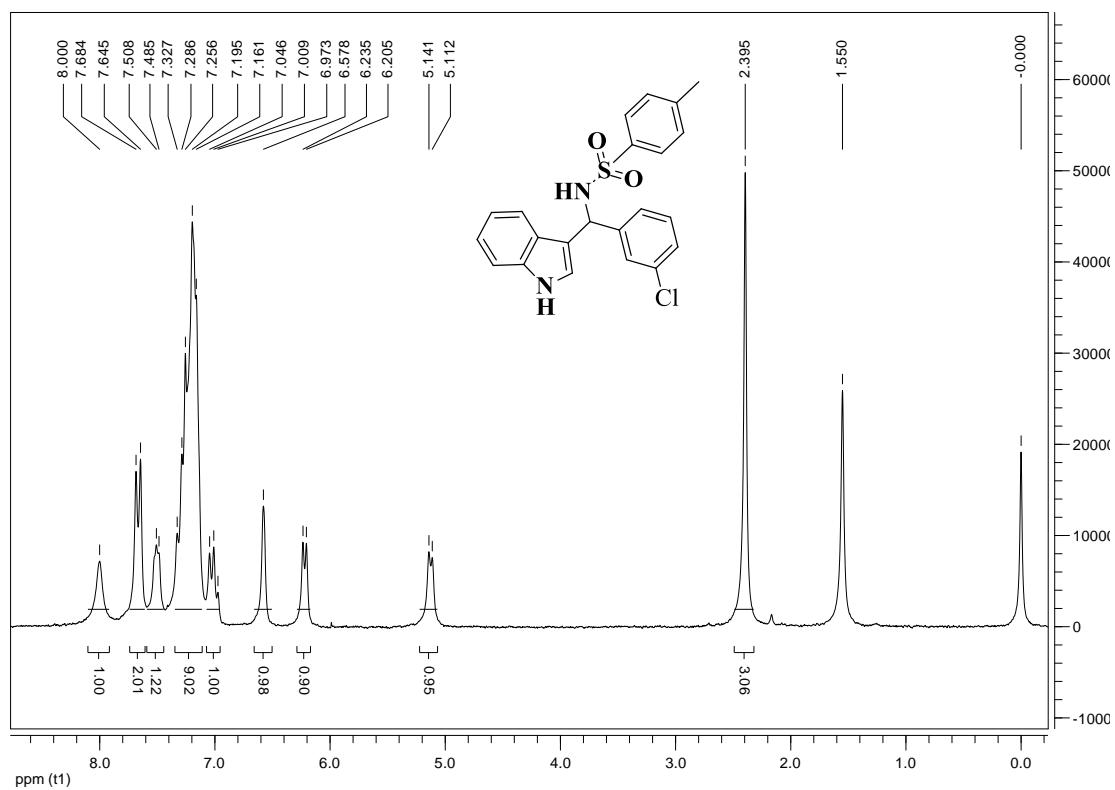
¹H spectrum of (-) *N*-[Indol-3-yl-(2-chlorophenyl)methyl]-4-methylbenzenesulfonamide (3e):



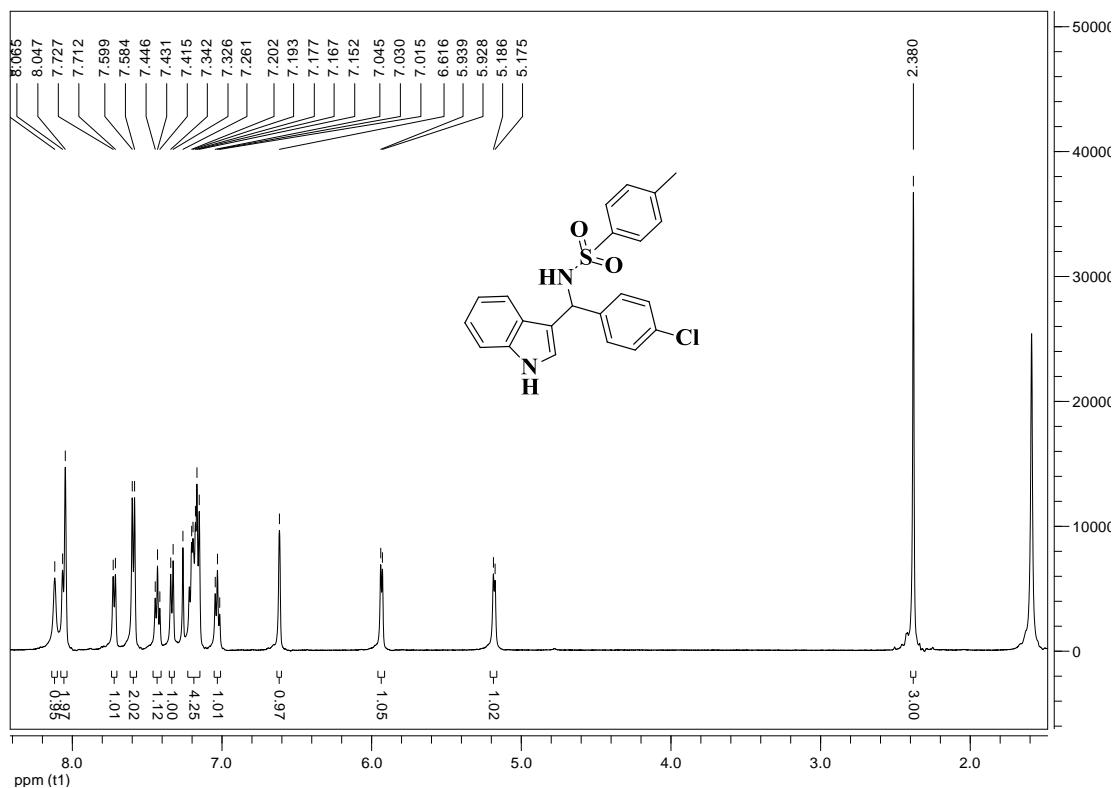
¹³C spectrum of (-) *N*-[Indol-3-yl-(2-chlorophenyl)methyl]-4-methylbenzenesulfonamide (3e):



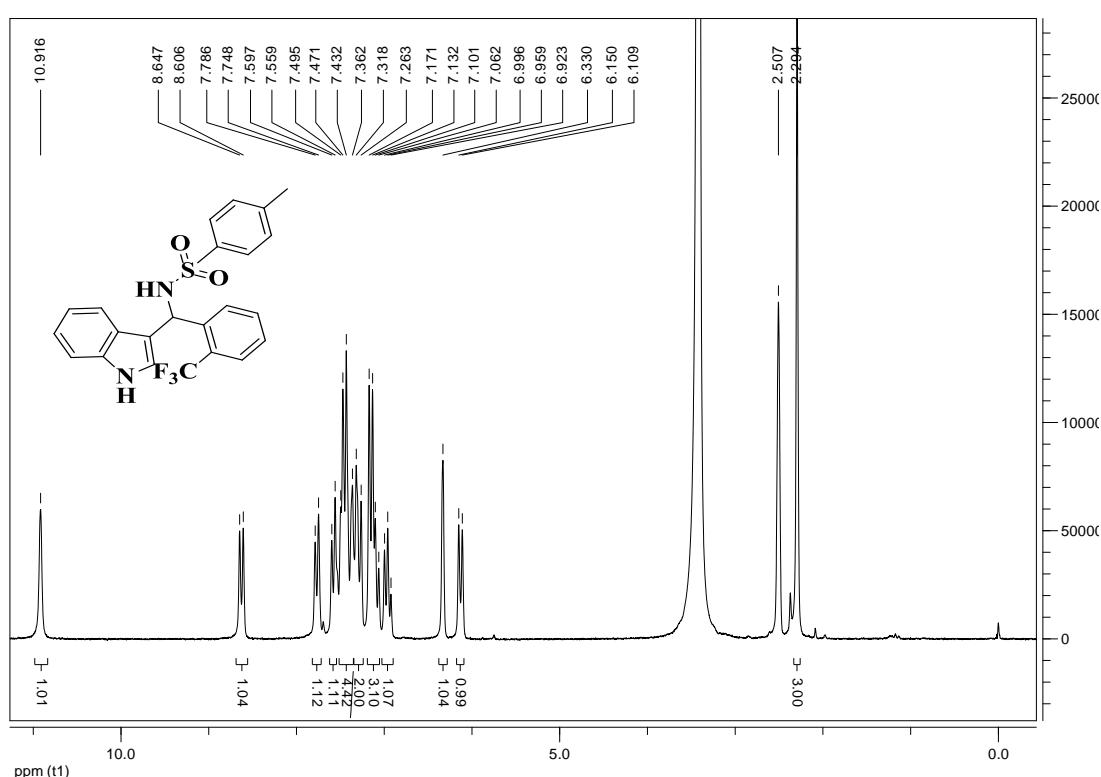
¹H spectrum of (-) *N*-[Indol-3-yl-(3-chlorophenyl)methyl]-4-methylbenzenesulfonamide 3f:



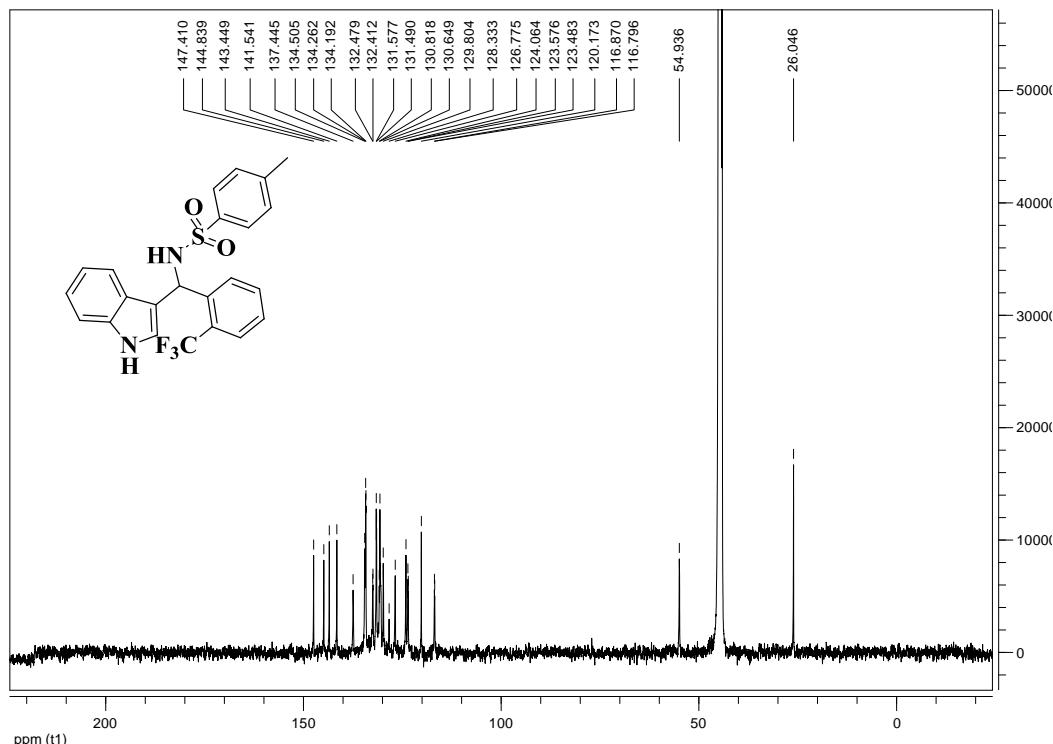
¹H spectrum of (-) *N*-[Indol-3-yl-(4-chlorophenyl)methyl]-4-methylbenzenesulfonamide 3g:



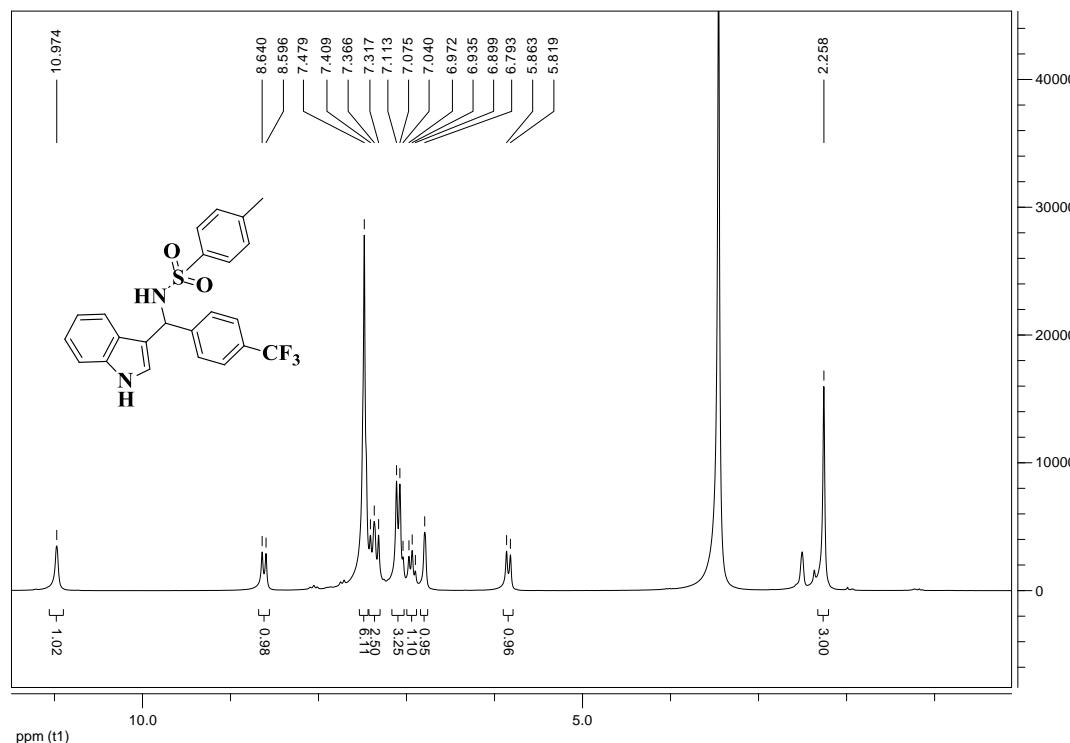
¹H spectrum of *N*-[Indol-3-yl-(2-trifluoromethylphenyl)methyl]-4-methyl benzenesulfonamide 3h:



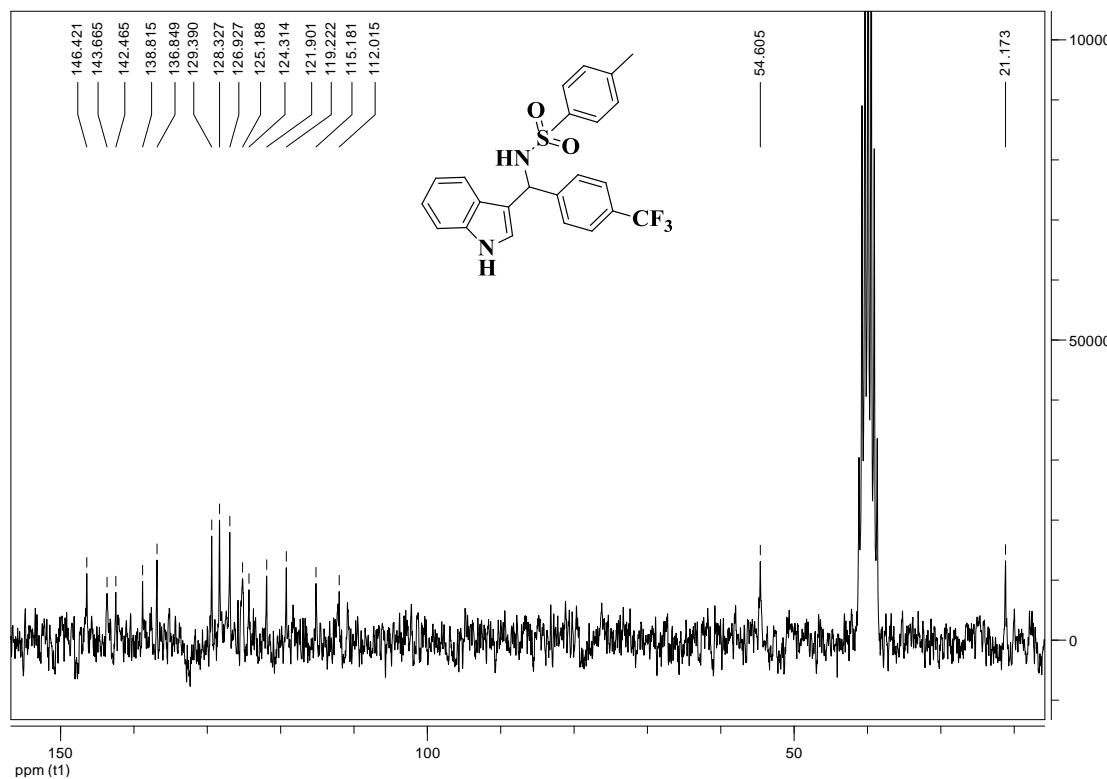
¹³C spectrum of *N*-[Indol-3-yl-(2-trifluoromethylphenyl)methyl]-4-methyl benzenesulfonamide 3h:



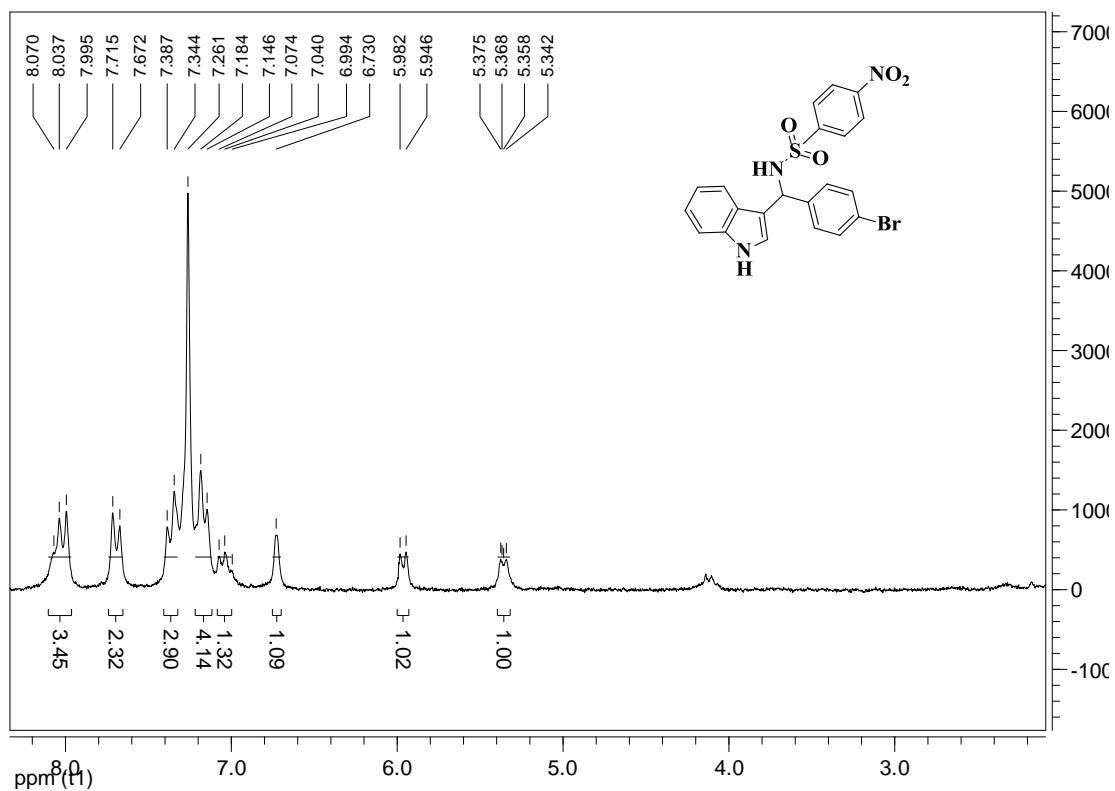
¹H spectrum of *N*-[Indol-3-yl-(4-trifluoromethylphenyl)methyl]-4-methyl benzenesulfonamide **3i**:



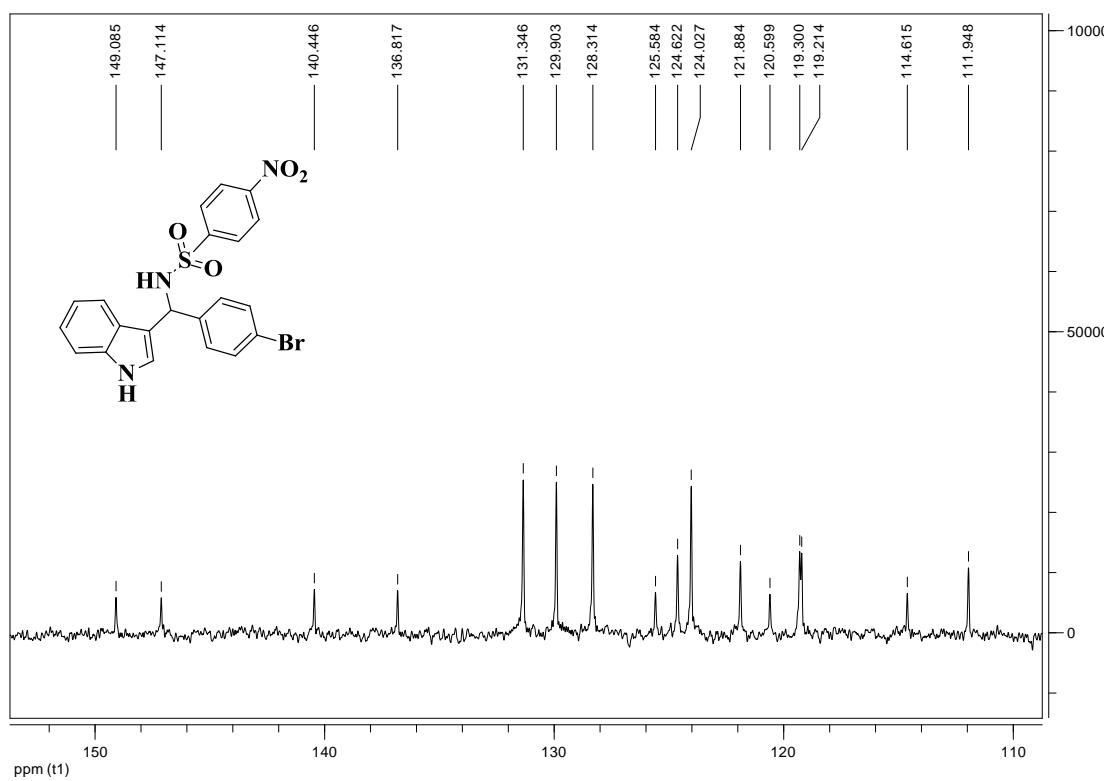
¹³C spectrum of *N*-[Indol-3-yl-(4-trifluoromethylphenyl)methyl]-4-methyl benzenesulfonamide **3i**:



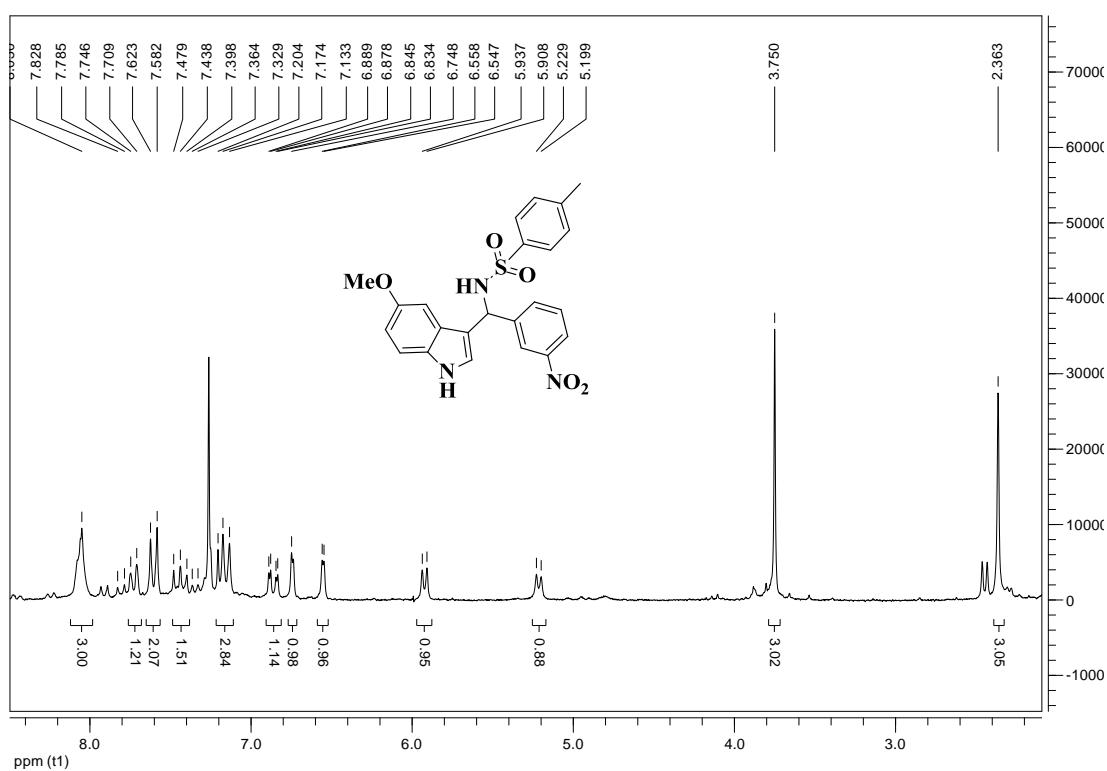
¹H spectrum of *N*-[Indol-3-yl-(4-bromophenyl)methyl]-4-nitrobenzenesulfonamide 3m:



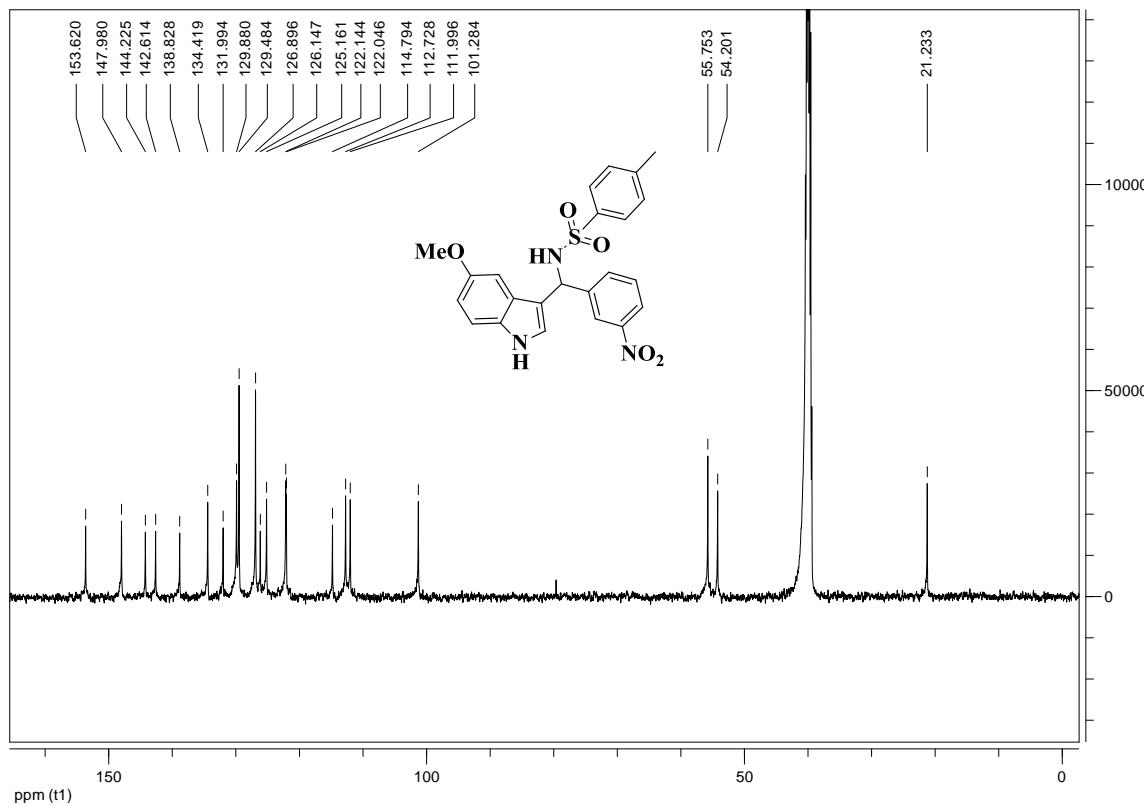
¹³C spectrum of (-) *N*-[Indol-3-yl-(4-bromophenyl)methyl]-4-nitrobenzenesulfonamide 3m:



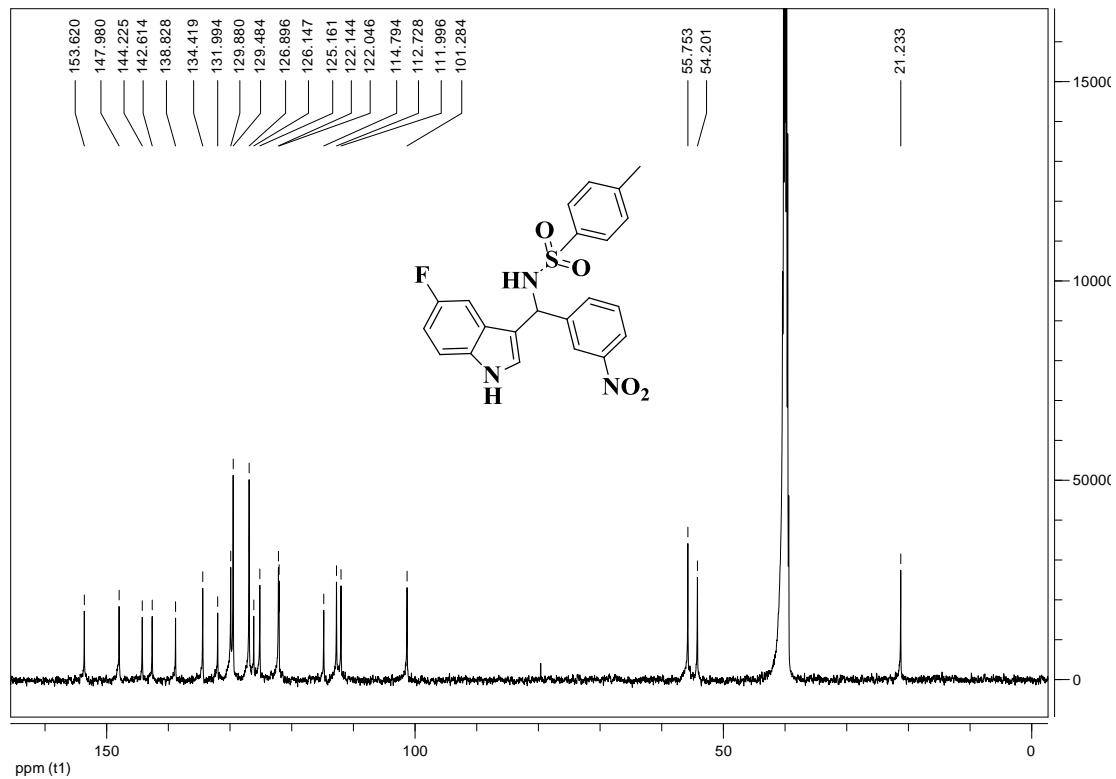
¹H spectrum of *N*-[5-MeO-indol-3-yl-(3-nitrophenyl)methyl]4-methylbenzenesulfonamide 3o:



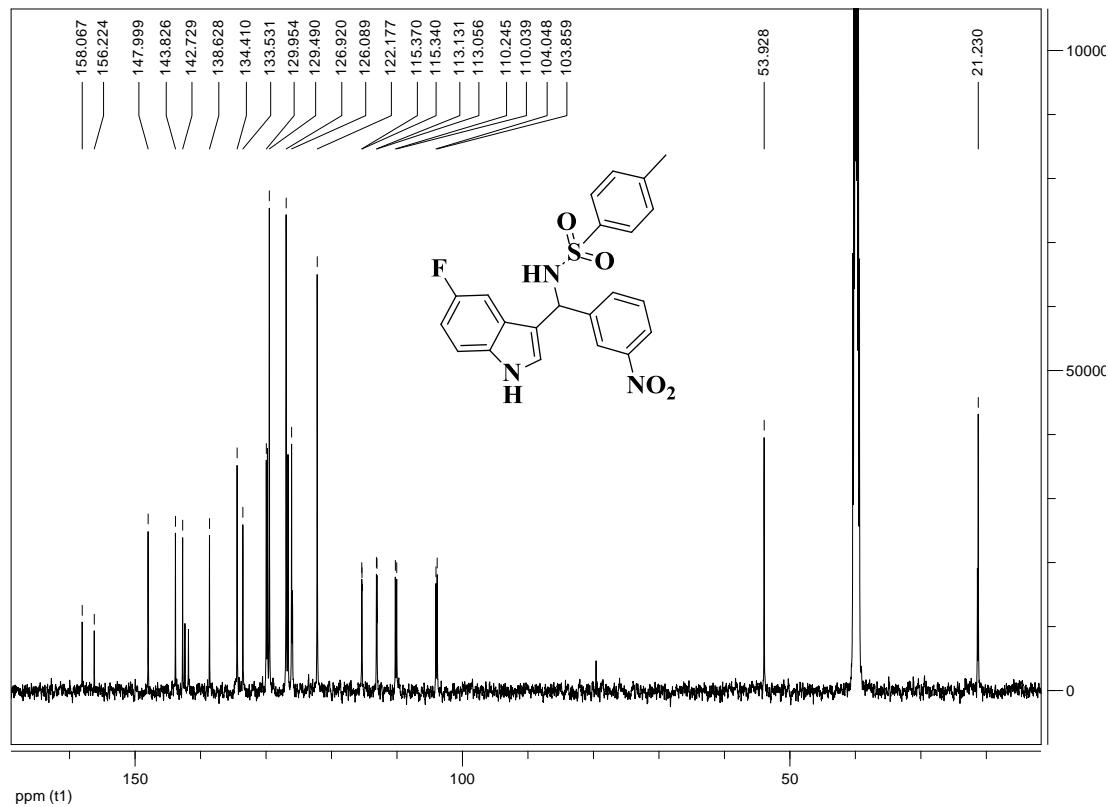
¹³C spectrum of *N*-[5-MeO-indol-3-yl-(3-nitrophenyl)methyl]4-methylbenzenesulfonamide 3o:



¹H spectrum of *N*-[5-F-indol-3-yl-(3-nitrophenyl)methyl]4-methylbenzenesulfonamide (3o):



¹³C spectrum of *N*-[5-F-indol-3-yl-(3-nitrophenyl)methyl]4methylbenzenesulfonamide (3o):



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