

Supporting Information - Synthesis

Ethyl 2-(diethoxyphosphoryl)-2-ethoxyacetate 9. ν_{\max} (film)/ cm^{-1} 1746, 1265, 1145, 1039; ^{13}C NMR (CDCl_3): δ 167.33^P (C, J 2.0 Hz), 76.55^P (CH, J 157.0Hz), 68.29^P (CH₂, J 12.0Hz), 63.43^P (CH₂, J 7.0Hz), 63.34 (CH₂, J 7.0Hz), 61.45 (CH₂), 16.12^P (CH₃, J 6.0Hz), 14.70 (CH₃), 13.88 (CH₃).

(Z)-Ethyl 2-ethoxy-3-(1H-indol-5-yl)acrylate 11 and (E)-ethyl 2-ethoxy-3-(1H-indol-5-yl)acrylate 12. *Z* isomer **11**: ν_{\max} (nujol)/ cm^{-1} 3267, 2923-2850, 1731, 1687, 1550, 1378; ^{13}C NMR (CDCl_3): δ 165.30 (C), 142.56, 136.03, 127.98 (C), 126.19 (CH), 125.60 (C), 124.90 (CH), 124.56 (CH), 123.46 (CH), 111.00 (CH), 103.36 (CH), 67.46 (CH₂), 60.92 (CH₂), 15.55, 14.35 (CH₃); *E* isomer **12**: ν_{\max} (nujol)/ cm^{-1} 3330, 2923-2850, 1702, 1621, 1379, 1227, 1176; ^{13}C NMR (CDCl_3): δ 165.24 (C), 146.23, 134.93, 127.82, 126.17 (C), 124.54 (CH), 122.99 (CH), 120.54 (CH), 111.47 (CH), 110.58 (CH), 102.57 (CH), 64.62 (CH₂), 61.07 (CH₂), 14.53 (CH₃), 13.68 (CH₃).

Methyl 2-ethoxy-3-(1H-indol-5-yl)propanoate 15. ν_{\max} (film)/ cm^{-1} 3408, 2977-2850, 1741, 1444, 1209, 1110; ^{13}C NMR (CDCl_3): δ 173.30 (C), 134.80 (C), 128.19 (C), 127.98 (C), 124.38 (CH), 123.54 (CH), 121.04 (CH), 110.74 (CH), 102.23 (CH), 80.98 (CH), 66.21 (CH₂), 51.73 (CH₃), 39.51 (CH₂), 15.02 (CH₃).

2-Ethoxy-3-(1H-indol-5-yl)propanoic acid 2. ν_{\max} (DCM film)/ cm^{-1} 3411, 2978-2929, 1724, 1265, 1105; ^{13}C NMR (CDCl_3): δ 177.33 (C), 134.76 (C), 127.84 (C), 127.49 (C), 124.63 (CH), 123.25 (CH), 120.95 (CH), 110.93 (CH), 101.80 (CH), 80.27 (CH), 66.52 (CH₂), 38.91 (CH₂), 14.82 (CH₃).

Ethyl 2-diazo-2-(diethoxyphosphoryl)acetate 18. ν_{\max} (film)/ cm^{-1} 2987, 2131, 1707, 1284, 1026; ^{13}C NMR (CDCl_3): δ 163.34^P (C, d, J 12.0 Hz), 127.90^P (C, d, J 316.0 Hz), 63.56^P (CH₂, d, J 6.0 Hz), 61.61 (CH₂), 16.06 (CH₃, d, J 7.0 Hz), 14.25 (CH₃).

Ethyl 2-(diethoxyphosphoryl)-2-(2,2,2-trifluoroethoxy)acetate 10. ν_{\max} (film)/ cm^{-1} 1743, 1265, 1041; ^{13}C NMR (CDCl_3): δ 166.09 (C), 123.35 (C, q, J 277.5 Hz), 77.11^P (CH, d, J 156.0 Hz), 68.52^P (CH₂, dq, J 35.0, 11.5 Hz), 63.99^P (CH₂, t, J 6.0 Hz), 62.21 (CH₂), 16.23^P (CH₃, d, J 6.0 Hz), 13.99 (CH₃).

(Z)-Ethyl 3-(1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)acrylate 13 and (E)-ethyl 3-(1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)acrylate 14. *Z* isomer **13**: ν_{\max} (nujol)/ cm^{-1} 3343, 2977-2850, 1691, 1459, 1371, 1261, 1056; ^{13}C NMR (CDCl_3): δ 164.05 (C), 140.54 (C), 136.37 (C), 128.08 (C), 123.43 (C, q, J 277.0 Hz), 127.34 (CH), 125.06 (CH), 124.84 (CH), 124.84 (C), 124.19 (CH), 111.16 (CH), 103.62 (CH), 67.86 (CH₂, q, J 34.5 Hz), 61.34 (CH₂), 14.29 (CH₃); *E* isomer **14**: ν_{\max} (nujol)/ cm^{-1} 3372, 2950-2850, 1711, 1461, 1378, 1269, 1157; ^{13}C NMR (CDCl_3): δ 163.51 (C), 143.55 (C), 135.52 (C), 127.76 (C), 124.77 (CH), 124.54 (C), 123.42 (CH), 123.24 (C, q, J 277.0 Hz), 121.67 (CH), 121.56 (CH), 110.62 (CH), 103.00 (CH), 68.16 (CH₂, q, J 35.0 Hz), 61.29 (CH₂), 13.75 (CH₃).

Methyl 3-(1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)propanoate 16. ν_{\max} (DCM film)/ cm^{-1} 3377, 2933, 1741, 1513, 1278, 1164; ^{13}C NMR (CDCl_3): δ 171.50 (C), 134.91 (C), 128.05 (C), 123.56 (C, q, J 277.0 Hz), 127.42 (C), 124.43 (CH), 123.62 (CH), 121.25 (CH), 110.84 (CH), 102.47 (CH), 82.02 (CH), 67.89 (CH₂, q, J 34.0 Hz), 52.11 (CH₂), 39.17 (CH₂).

3-(1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)propanoic acid 3. ν_{\max} (DCM film)/ cm^{-1} 3415, 2933, 1726, 1279, 1167; ; ^{13}C NMR ($\text{CDCl}_3/\text{MeOD}$ 2:1): δ 173.97 (C), 135.68 (C), 128.53 (C),

124.18 (C, q, J 277.0 Hz), 127.67 (CH), 125.20 (CH), 123.52 (CH), 121.31 (CH), 111.40 (CH), 101.73 (CH), 82.44 (CH), 68.18 (CH₂, q, J 34.5 Hz), 39.63 (CH₂).

1-Benzenesulfonyl-1H-indole-5-carbonitrile 21. ν_{\max} (nujol)/cm⁻¹ 2222, 1458, 1375, 1080, 721; ¹³C NMR (CDCl₃): δ 137.73 (C), 136.43 (C), 134.42 (CH), 130.65 (C), 129.54 (CH), 128.37 (CH), 127.59 (CH), 126.77 (CH), 126.36 (CH), 119.18 (C), 114.27 (CH), 108.65 (CH), 107.03 (C).

2-Benzyl-1-(phenylsulfonyl)-1H-indole-5-carbonitrile 22. ν_{\max} (nujol)/cm⁻¹ 2220, 1460, 1371, 1053; ¹³C NMR (CDCl₃): δ 143.63 (C), 138.98 (C), 138.59 (C), 136.99 (C), 134.19 (CH), 129.46 (CH), 129.38 (C), 129.33 (CH), 128.69 (CH), 127.18 (CH), 127.03 (CH), 126.39 (CH), 125.04 (CH), 119.32 (C), 115.35 (CH), 110.07 (CH), 107.10 (C), 35.12 (CH₂).

2-Benzyl-1H-indole-5-carbonitrile 24. ν_{\max} (nujol)/cm⁻¹ 3300, 3056-2850, 2229, 1373, 1056, 740; ¹³C NMR (CDCl₃): δ 140.38 (C), 137.94 (C), 137.53 (C), 128.94 (CH), 128.82 (CH), 128.49 (C), 127.10 (CH), 125.40 (CH), 124.49 (CH), 120.82 (C), 111.26 (CH), 102.84 (C), 101.66 (CH), 34.59 (CH₂).

2-Benzyl-1H-indole-5-carbaldehyde 26. ν_{\max} (nujol)/cm⁻¹ 3324, 3056-2850, 1671, 1373, 1056, 739; ¹³C NMR (CDCl₃): δ 192.47 (CH), 139.95 (C), 139.88 (C), 137.76 (C), 129.67 (CH), 128.87 (CH), 128.81 (CH), 128.54 (C), 127.00 (CH), 125.05 (CH), 122.10 (CH), 111.04 (CH), 102.58 (CH), 34.65 (CH₂).

(Z)-Ethyl 3-(2-benzyl-1H-indol-5-yl)-2-ethoxyacrylate 28 and (E)-ethyl 3-(2-benzyl-1H-indol-5-yl)-2-ethoxyacrylate 29. *Z* isomer **28**: ν_{\max} (DCM film)/cm⁻¹ 3441, 3055, 1743, 1646, 1051, 740; ¹³C NMR (CDCl₃): δ 165.31 (C), 142.43 (C), 138.67 (C), 138.21 (C), 136.56 (C), 128.81 (CH), 128.77 (CH), 126.82 (CH), 126.30 (CH), 125.53 (C), 124.08 (CH), 122.71 (CH), 110.43 (CH), 101.73 (CH), 67.41 (CH₂), 60.87 (CH₂), 34.69 (CH₂), 15.56 (CH₃), 14.36 (CH₃). *E*

isomer **29**: ν_{\max} (DCM film)/ cm^{-1} 3441, 3055-2850, 1725, 1644, 1548, 1266, 1043, 738; ^{13}C NMR (CDCl_3): δ 165.20 (C), 146.16 (C), 138.41 (C), 138.16 (C), 135.44 (C), 128.81 (CH), 128.74 (CH), 126.76 (CH), 126.26 (C), 122.40 (CH), 119.96 (CH), 111.60 (CH), 110.00 (CH), 101.20 (CH), 64.63 (CH_2), 61.05 (CH_2), 34.73 (CH_2), 14.58 (CH_3), 13.77 (CH_3).

Methyl 3-(2-benzyl-1H-indol-5-yl)-2-ethoxypropanoate 36. ν_{\max} (DCM film)/ cm^{-1} 3392, 3027-2900, 1741, 1644, 1446, 1115, 705; ^{13}C NMR (CDCl_3): δ 173.28 (C), 138.51 (C), 138.03 (C), 135.28 (C), 128.83 (C), 128.80 (CH), 128.68 (CH), 128.24 (C), 126.69 (CH), 122.91 (CH), 120.44 (CH), 110.16 (CH), 100.86 (CH), 81.04 (CH), 66.19 (CH_2), 51.73 (CH_2), 39.55 (CH_2), 34.72 (CH_2), 15.06 (CH_3).

3-(2-Benzyl-1H-indol-5-yl)-2-ethoxy-propanoic acid 4. ν_{\max} (DCM film)/ cm^{-1} 3620, 3398, 1710, 1646, 1461, 1108; ^{13}C NMR (CDCl_3): δ 175.40 (C), 138.45 (C), 138.15 (C), 135.35 (C), 128.86 (C), 128.81 and 128.70 (CH each), 127.69 (C), 126.71 (CH), 122.95 (CH), 120.63 (CH), 110.27 (CH), 100.89 (CH), 80.36 (CH), 66.82 (CH_2), 38.85 (CH_2), 34.71 (CH_2), 15.05 (CH_2).

(Z)-Ethyl 3-(2-benzyl-1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)acrylate 30 and (E)-ethyl 3-(2-benzyl-1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)acrylate 31. *Z* isomer **30**: ν_{\max} (DCM film)/ cm^{-1} 3441, 1743, 1548, 1371, 1265, 1055; ^{13}C NMR (CDCl_3): δ 164.08 (C), 140.33 (C), 138.91 (C), 138.10 (C), 136.91 (C), 128.88 (C), 128.81 (CH), 128.80 (CH), 123.42 (C, *q*, *J* 277.0 Hz), 127.52 (CH), 126.87 (CH), 124.33 (CH), 124.24 (C), 123.36 (CH), 110.61 (CH), 101.85 (CH), 67.80 (CH_2 , *q*, *J* 35.0 Hz), 61.30 (CH_2), 34.66 (CH_2), 14.28 (CH_3); *E* isomer **31**: ν_{\max} (DCM film)/ cm^{-1} 3441, 1743, 1548, 1265, 1053; ^{13}C NMR (CDCl_3): δ 163.53 (C), 143.28 (C), 138.55 (C), 138.26 (C), 136.03 (C), 128.79 (CH), 128.74 (CH), 128.54 (C), 123.23 (C, *q*, *J* 277.0 Hz), 126.79 (CH), 124.31 (C), 122.75 (CH), 121.76 (CH), 120.95 (CH), 110.08 (CH), 101.32 (CH), 67.64 (CH_2 , *q*, *J* 35.0 Hz), 61.26 (CH_2), 34.65 (CH_2), 13.78 (CH_3).

Methyl 3-(2-benzyl-1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)propanoate 37. ν_{\max} (DCM film)/ cm^{-1} 3361, 2920-2846, 1741, 1448, 1275, 1157, 790; ^{13}C NMR (CDCl_3): δ 171.50 (C), 138.43 (C), 138.16 (C), 135.37 (C), 128.86 (C), 128.81 (CH), 128.70 (CH), 123.74 (C, q, J 278.0 Hz), 127.28 (C), 126.72 (CH), 122.85 (CH), 120.54 (CH), 110.29 (CH), 100.88 (CH), 82.02 (CH), 67.85 (CH_2 , q, J 34.5 Hz), 52.08 (CH_3), 39.17 (CH_2), 34.69 (CH_2).

3-(2-Benzyl-1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)propanoic acid 5. ν_{\max} (DCM film)/ cm^{-1} 3289, 2950-2850, 1702, 1651, 1425, 1053; ^{13}C NMR (CDCl_3): δ 174.74 (C), 138.37 (C), 138.31 (C), 135.46 (C), 128.93 (C), 128.83 (CH), 128.74 (CH), 123.42 (C, q, J 277.0 Hz), 126.92 (C), 126.77 (CH), 122.86 (CH), 120.67 (CH), 110.43 (CH), 100.93 (CH), 81.63 (CH), 68.13 (CH_2 , q, J 34.5 Hz), 38.98 (CH_2), 34.72 (CH_2).

2-(Naphthalen-2-ylmethyl)-1-(phenylsulfonyl)-1H-indole-5-carbonitrile 23. ν_{\max} (nujol)/ cm^{-1} 2950-2850, 2222, 1651, 1548, 1379, 1055; ^{13}C NMR (CDCl_3): δ 143.41 (C), 139.07 (C), 138.57 (C), 134.41 (C), 134.09 (CH), 133.47 (C), 132.44 (C), 129.34 (CH), 128.36 and 127.95 (CH), 127.65, 127.61, 127.45, 127.25, 126.29, 126.25, 125.92, 125.08 (CH), 119.32 (C), 115.38 (CH), 110.30 (CH), 107.14 (C), 35.24 (CH_2).

2-(Naphthalen-2-ylmethyl)-1H-indole-5-carbonitrile 25. ν_{\max} (nujol)/ cm^{-1} 3206, 2980-2850, 2215, 1461, 1371, 1053; ^{13}C NMR (CDCl_3): δ 140.25 (C), 137.95 (C), 134.96 (C), 133.54 (C), 132.47 (C), 128.76 (CH), 128.51 (C), 127.74, 127.54, 127.30, 127.23, 126.99, 126.47, 125.99, 125.44, 124.53 (CH), 120.81 (C), 111.28 (CH), 102.88 (C), 101.77 (CH), 34.79 (CH_2).

2-(Naphthalen-2-ylmethyl)-1H-indole-5-carbaldehyde 27. ν_{\max} (nujol)/ cm^{-1} 3221, 2980-2850, 1660, 1306, 796; ^{13}C NMR ($\text{CDCl}_3/\text{MeOD}$ 1:2): δ 194.21 (CH), 141.47 (C), 141.20 (C), 136.49 (C), 134.11 (C), 132.84 (C), 129.29 (C), 129.08 (C), 128.65, 128.03, 127.96, 127.63,

127.51, 126.54, 126.02 (CH), 125.93 (CH), 121.94 (CH), 111.83 (CH), 102.50 (CH), 35.13 (CH₂).

(Z)-Ethyl 2-ethoxy-3-(2-(naphthalen-2-ylmethyl)-1H-indol-5-yl)acrylate 32 and (E)-ethyl 2-ethoxy-3-(2-(naphthalen-2-ylmethyl)-1H-indol-5-yl)acrylate 33. *Z* isomer **32**: ν_{\max} (DCM film)/cm⁻¹ 3352, 3053-2900, 1701, 1620, 1252, 1095, 740; ¹³C NMR (CDCl₃): δ 165.32 (C), 142.39, 138.60, 136.60, 135.70, 133.52, 132.36, 128.81 (C), 128.45, 127.67, 127.53, 127.16, 127.12, 126.34, 126.26, 125.74 (CH), 125.48 (C), 124.07 (CH), 122.70 (CH), 110.50 (CH), 101.81 (CH), 67.40 (CH₂), 60.87 (CH₂), 34.83 (CH₂), 15.54 (CH₃), 14.32 (CH₃); *E* isomer **33**: ν_{\max} (DCM film)/cm⁻¹ 3392, 3050-2900, 1712, 1635, 1228, 1153, 740; ¹³C NMR (CDCl₃): δ 165.19 (C), 146.09, 138.06, 135.90, 135.46, 133.52, 132.33, 128.67 (C), 128.39, 127.66, 127.52, 127.19, 127.07, 126.23 (CH), 126.20 (C), 125.69 (CH), 122.37 (CH), 119.92 (CH), 111.61 (CH), 110.05 (CH), 101.25 (CH), 64.60 (CH₂), 61.04 (CH₂), 34.70 (CH₂), 14.53 (CH₃), 13.73 (CH₃).

Methyl 2-ethoxy-3-(2-(naphthalen-2-ylmethyl)-1H-indol-5-yl)propanoate 38. ν_{\max} (DCM film)/cm⁻¹ 3392, 3050-2900, 1741, 1643, 1273, 1114, 740; ¹³C NMR (CDCl₃): δ 173.30 (C), 137.89, 135.97, 135.30, 133.53, 133.18, 132.33, 128.90 (C), 128.41 (CH), 128.26 (C), 127.72, 127.52, 127.24, 127.09, 126.35, 125.69 (CH), 122.95 (CH), 120.47 (CH), 110.19 (CH), 101.02 (CH), 81.02 (CH), 66.20 (CH₂), 51.77 (CH₃), 39.53 (CH₂), 34.92 (CH₂), 15.07 (CH₃).

2-Ethoxy-3-(2-(naphthalen-2-ylmethyl)-1H-indol-5-yl)propanoic acid 6. ν_{\max} (DCM film)/cm⁻¹ 3403, 3053-2900, 1720, 1644, 1267, 1110, 739; ¹³C NMR (CDCl₃): δ 174.59 (C), 138.03, 135.90, 135.39, 133.53, 132.35, 128.87 (C), 128.44 (CH), 127.68 (CH), 127.65 (C), 127.53, 127.24, 127.12, 126.25, 125.72 (CH), 123.01 (CH), 120.69 (CH), 110.32 (CH), 101.04 (CH), 80.31 (CH), 66.89 (CH₂), 38.75 (CH₂), 34.93 (CH₂), 15.07 (CH₃).

(Z)-Ethyl 3-(2-(naphthalen-2-ylmethyl)-1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)acrylate 34 and (E)-ethyl 3-(2-(naphthalen-2-ylmethyl)-1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)acrylate 35. *Z* isomer **34**: ν_{\max} (DCM film)/ cm^{-1} 3408, 2975, 1702, 1620, 1263, 1167, 742; ^{13}C NMR (CDCl_3): δ 164.08 (C), 140.38, 138.80, 136.95, 135.56, 133.56, 132.42, 128.93 (C), 128.58 (CH), 127.71 (CH), 123.43 (C, *q*, *J* 277.0 Hz), 127.55, 127.48, 127.18, 127.15 126.34, 125.82 (CH), 124.38 (CH), 124.30 (C), 123.39 (CH), 110.64 (CH), 102.00 (CH), 67.82 (CH₂, *q*, *J* 35.0 Hz), 61.30 (CH₂), 34.88 (CH₂), 14.28 (CH₃). *E* isomer **35**: ν_{\max} (DCM film)/ cm^{-1} 3441, 2970-2850, 1709, 1645, 1267, 1132, 740; ^{13}C NMR (CDCl_3): δ 163.51 (C), 143.33, 138.42, 136.08, 135.73, 133.54, 132.38, 128.58 (C), 128.49, 127.70, 127.53 (CH), 123.25 (CH₂, *q*, *J* 277.0 Hz), 127.16, 127.13, 126.31, 125.78 (CH), 124.37 (C), 122.82 (CH), 121.82 (CH), 121.00 (CH), 110.11 (CH), 101.49 (CH), 67.68 (CH₂, *q*, *J* 35.0 Hz), 61.26 (CH₂), 34.87 (CH₂), 13.79 (CH₃).

Methyl 3-(2-(naphthalen-2-ylmethyl)-1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)propanoate 39. ν_{\max} (DCM film)/ cm^{-1} 3403, 3054-2850, 1743, 1645, 1279, 1165, 739; ^{13}C NMR (CDCl_3): δ 171.49 (C), 138.05, 135.90, 135.44, 133.56, 132.38, 128.92 (C), 128.46 (CH), 123.58 (C, *q*, *J* 277.0 Hz), 127.69 (CH), 127.55 (CH), 127.36 (C), 127.24, 127.13, 126.26, 125.73 (CH), 122.93 (CH), 120.60 (CH), 110.33 (CH), 101.07 (CH), 82.04 (CH), 67.89 (CH₂, *q*, *J* 34.5 Hz), 52.09 (CH₃), 39.18 (CH₂), 34.94 (CH₂).

3-(2-(Naphthalen-2-ylmethyl)-1H-indol-5-yl)-2-(2,2,2-trifluoroethoxy)propanoic acid 7. ν_{\max} (DCM film)/ cm^{-1} 3441, 3000-2700, 1706, 1646, 1267, 1049, 740; δ_{C} (CDCl_3) 174.21 (C), 138.19, 135.85, 135.50, 133.55, 132.38, 128.96 (C), 128.48, 127.69 (CH), 123.43 (C, *q*, *J* 277.0 Hz), 127.54, 127.23, 127.14 (3xCH), 126.98 (C), 126.27, 125.74 (CH), 122.91 (CH), 120.70

(CH), 110.46 (CH), 101.07 (CH), 81.65 (CH), 68.13 (CH₂, q, *J* 34.5 Hz), 38.98 (CH₂), 34.93 (CH₂).

Supporting Information — X-Ray Crystallography

The phenyl ring of the tosyl moiety in the structure of **22** was found to be disordered. Two orientations were identified of *ca.* 70 and 30% occupancy (see Fig. S2), and the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

- Fig. S1** The molecular structure of the 2-benzyl indole species **22** (50% probability ellipsoids).
- Fig. S2** The molecular structure of the 2-benzyl indole species **22** showing the disorder in the phenyl ring of the tosyl moiety. The major occupancy orientation (*ca.* 70%) has been drawn with dark bonds, and the minor occupancy orientation (*ca.* 30%) with open bonds.
- Fig. S3** The molecular structure of the 2-naphthylmethyl indole species **23** (50% probability ellipsoids).

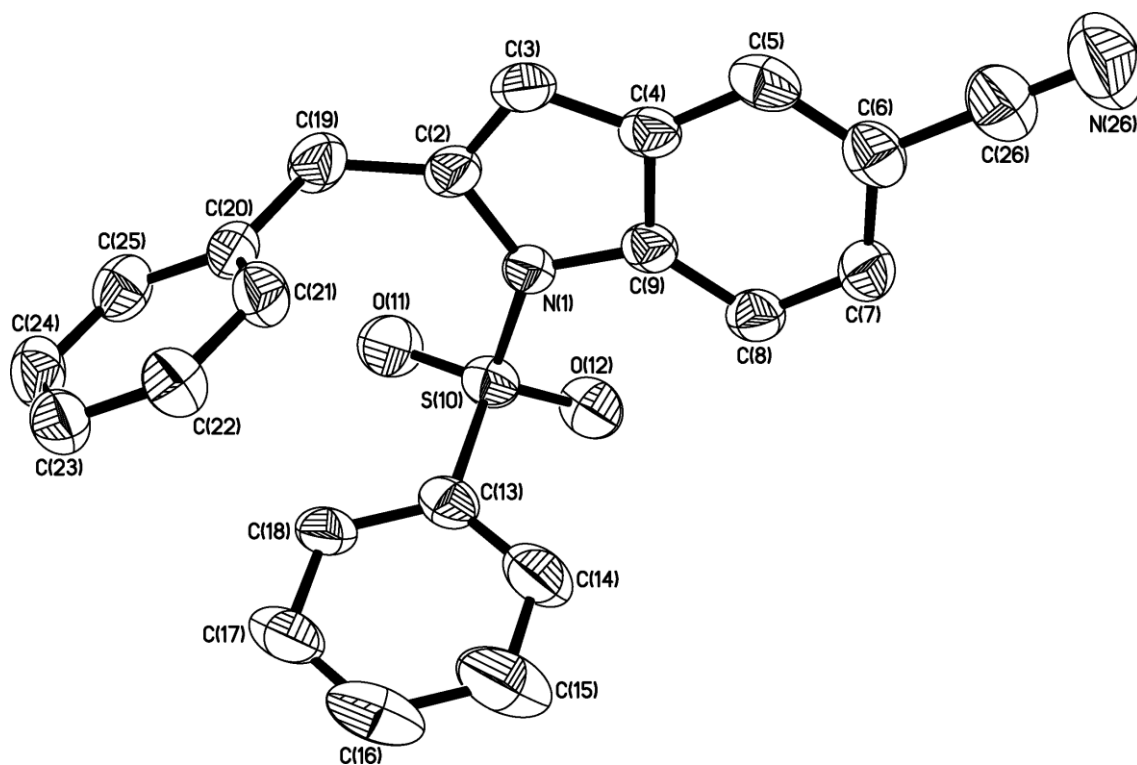


Fig. S1

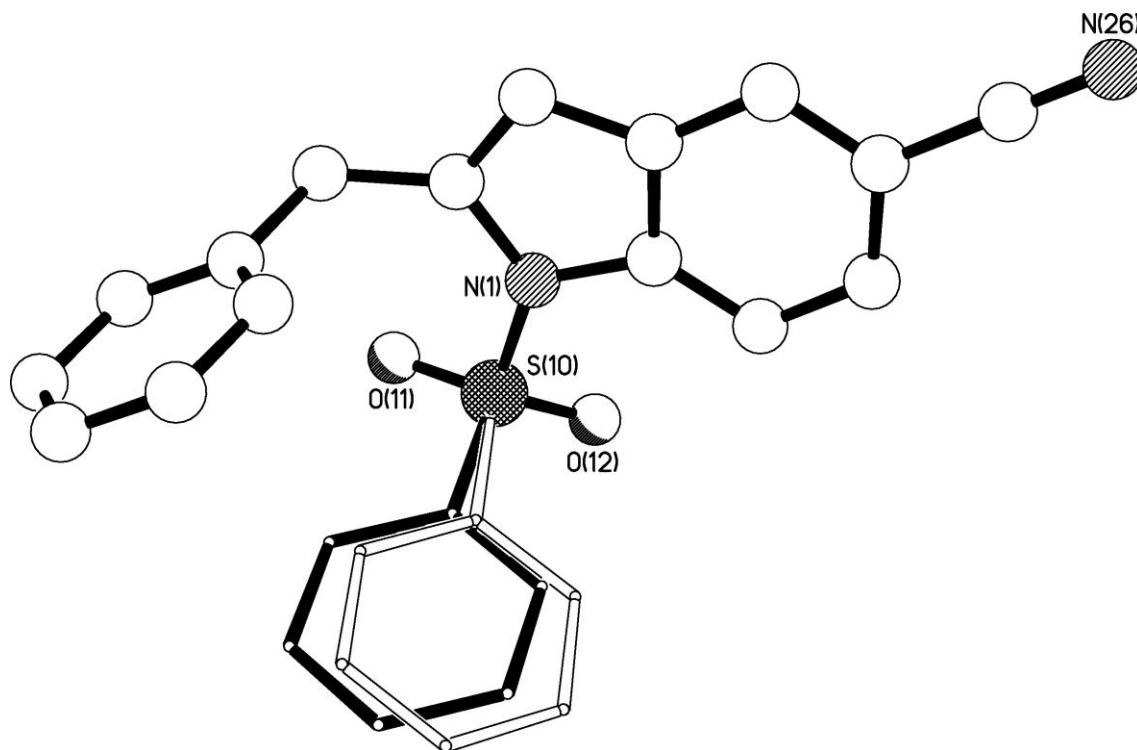


Fig. S2

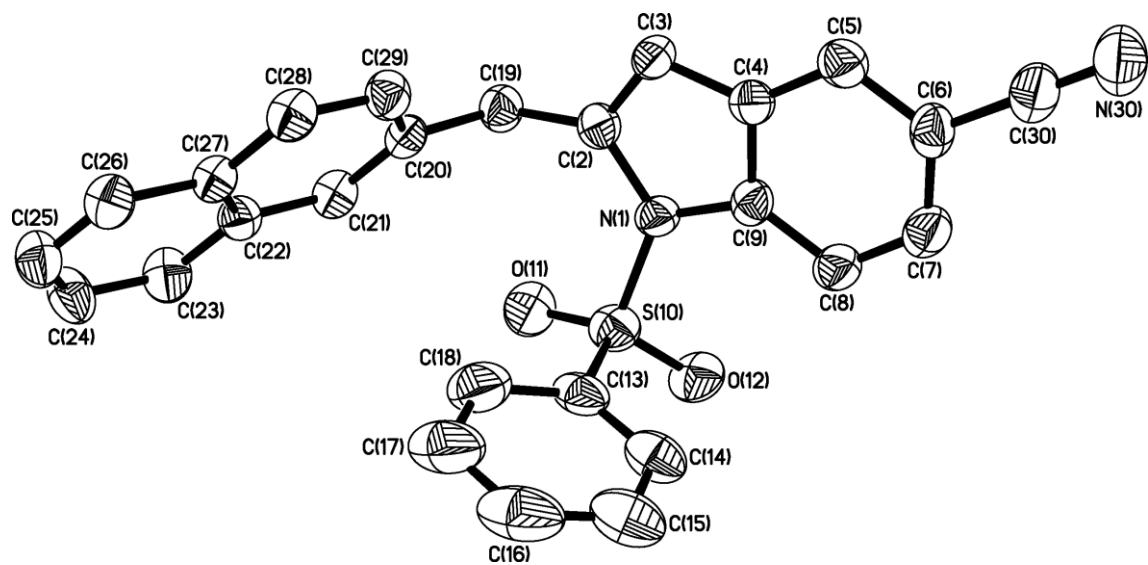


Fig. S3