

SUPPORTING INFORMATION

Bromo or Methoxy Group-Promoted Umpolung Electron Transfer Enabled Visible Light-Mediated Synthesis of 2-Substituted Indole-3-glyoxylates

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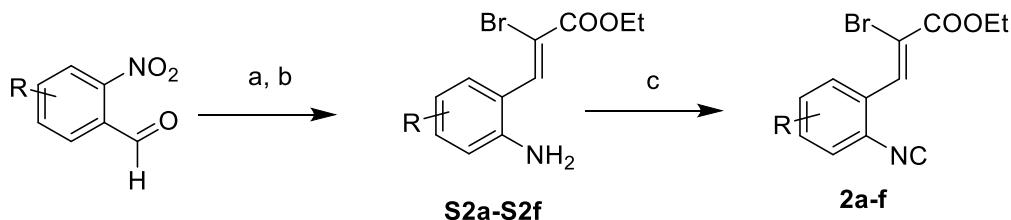
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Materials and Methods:

All commercial chemical materials were used as received without further purification and weight was calculated based on purity mentioned in the container. All the reactions were monitored by TLC and visualized by a dual short (254 nm) / long (366 nm) wavelength UV lamp. Analytical thin layer chromatography was performed on Merck TLC aluminum sheets silica gel 60 F 254. Purifications by column chromatography were performed on silica gel (0.063-0.200 mm). Melting points were recorded on Stanford Research Systems OptiMelt MPA 100 Automated melting point system. All products were characterized by appropriate techniques such as $^1\text{H-NMR}$, $^{19}\text{F-NMR}$, $^{13}\text{C-NMR}$, FT-IR and HRMS analysis. FT-IR (Cary 630) spectroscopy was carried out on a spectrometer, equipped with a Diamond Single Reflection ATR-System. NMR spectra were recorded on Bruker Avance 300 MHz, 400 MHz and 600 MHz spectrometers. Chemical shifts for $^1\text{H-NMR}$ were reported as δ , ppm, relative to the signal of CHCl_3 at 7.26 ppm and for DMSO at 2.50 ppm. Chemical shifts for $^{13}\text{C-NMR}$ were reported as δ , parts per million, relative to the signal of CHCl_3 at 77.2 ppm and for DMSO at 39.52 ppm. Coupling constants (J) are given in Hertz (Hz). The following notations indicate the multiplicity of the signals: s = singlet, br-s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet. Mass spectra were recorded at the Central Analytical Laboratory at the Department of Chemistry of the University of Regensburg on Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS.

General scheme for preparation of *o*-isocyano- α -bromocinnamates:



Scheme S1: a) TiCl_4 , Ethyl bromoacetate, Et_3N , DCM ; b) Fe powder/ HCl , $\text{EtOH}/\text{H}_2\text{O}$; (3 mmol scale); c) i) $\text{HCOOH}/\text{Ac}_2\text{O}$, THF ; ii) POCl_3 , Et_3N , THF 0°C to rt . (1.5 mmol scale).

The starting materials were prepared by following known procedures in the literature^{1,2}

Ethyl (Z)-3-(2-aminophenyl)-2-bromoacrylate (S2a)³:

Following the general procedure the title compound was synthesized and purified by a column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Yellow solid, (0.518 g, 64 % for two steps); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.18 (s, 1H), 7.69-7.57 (m, 1H), 7.24-7.18 (m, 1H), 6.84 (ddd, J = 8.0, 7.4, 0.8 Hz, 1H), 6.77 (dd, J = 8.1, 0.9 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 4.07 (bs, 2H), 1.38 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 163.33, 144.51, 137.49, 131.08, 129.58, 120.34, 118.71, 116.46, 115.98, 62.96, 14.40.

Ethyl (Z)-3-(2-amino-4,5-dimethoxyphenyl)-2-bromoacrylate (S2b):

Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 2) as eluent. Yellow solid, (0.673 g, 68% for two steps); **M.p.** 79-81 $^\circ\text{C}$; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.18 (s, 1H), 7.48 (s, 1H), 6.29 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 163.77, 152.16, 141.91, 140.99, 136.11, 112.24, 112.05, 111.28,

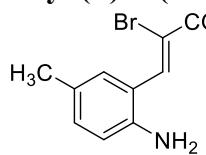
100.49, 62.79, 56.58, 55.98, 14.45; **IR (neat)** 1409, 1463, 1510, 16161, 1640, 1717, 2589, 2938, 2970, 3335 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{13}\text{H}_{16}\text{BrNO}_4$ ($\text{M}+\text{H}$) $^+$: 330.0335; Found: 330.0338.

Ethyl (*Z*)-3-(2-amino-5-chlorophenyl)-2-bromoacrylate (S2c):



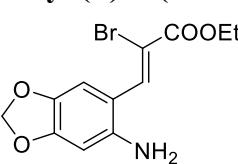
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Yellow Solid (0.538 g, 59% for two steps); **M.p.** 84-85 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 8.05 (s, 1H), 7.58 (d, J = 2.4 Hz, 1H), 7.13 (dd, J = 8.6, 2.4 Hz, 1H), 6.64 (t, J = 9.2 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 4.06-3.67 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H); **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 163.04, 143.56, 136.23, 130.73, 128.83, 122.99, 121.11, 117.38, 116.96, 63.09, 14.34. **IR (neat)** 1415, 1481, 1607, 1706, 2903, 2936, 2982, 3246, 3374, 3463 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{11}\text{H}_{11}\text{BrClNO}_2$ ($\text{M}+\text{H}$) $^+$: 304.9734 ; Found: 304.9737.

Ethyl (*Z*)-3-(2-amino-5-methylphenyl)-2-bromoacrylate (S2d):



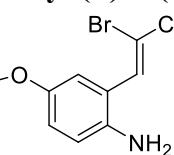
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Brownish sticky mass (0.468 g, 55% for two steps); **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 8.17 (s, 1H), 7.44 (s, 1H), 7.02 (dd, J = 8.1, 1.4 Hz, 1H), 6.69 (d, J = 8.1 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.88-3.06 (bs, 2H), 2.27 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 163.37, 142.07, 137.71, 131.85, 129.57, 128.07, 120.46, 116.71, 115.66, 62.90, 20.69, 14.39. **IR (neat)** 1498, 1602, 1627, 1708, 2862, 2923, 2981, 3235, 3371, 3490 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{12}\text{H}_{14}\text{BrNO}_2$ ($\text{M}+\text{H}$) $^+$: 284.0281; Found: 284.0284.

Ethyl (*Z*)-3-(6-aminobenzo[d][1,3]dioxol-5-yl)-2-bromoacrylate (S2e):



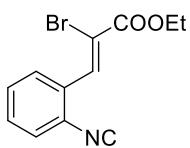
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 2) as eluent. Yellow solid (0.631 g, 67% for two steps); **M.p.** 86-89 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 8.12 (s, 1H), 7.38 (s, 1H), 6.28 (s, 1H), 5.91 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.93-3.54 (m, 2H), 1.36 (t, J = 7.1 Hz, 3H). **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 163.70, 150.43, 142.32, 140.49, 136.30, 112.56, 111.92, 108.19, 101.40, 97.95, 62.78, 14.43. **IR (neat)** 1477, 1501, 1587, 1699, 2774, 2899, 3368, 3238, 3368, 3445 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{12}\text{H}_{12}\text{BrNO}_4$ ($\text{M}+\text{H}$) $^+$: 314.0022; Found: 314.0025.

Ethyl (*Z*)-3-(2-amino-5-methoxyphenyl)-2-bromoacrylate (S2f):



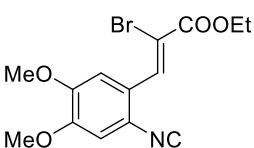
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. (E:Z = 16.5: 83.5) **Data for Z-S2f:** Yellow solid (0.639 g, 71% for two steps); **M.p.** (mixture) 79-83 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 8.17 (s, 1H), 7.29-7.24 (m, 1H), 6.83 (dt, J = 7.9, 2.9 Hz, 1H), 6.70 (d, J = 8.7 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H) 1.38 (t, J = 7.1 Hz, 3H); **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 163.31, 152.29, 139.00, 137.31, 120.99, 118.19, 117.85, 115.70, 113.63, 62.97, 55.97, 14.40; **IR (neat)** 1462, 1477, 1573, 1613, 1656, 1712, 2837, 2904, 2936, 2980, 3372, 3464 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{12}\text{H}_{14}\text{BrNO}_3$ ($\text{M}+\text{H}$) $^+$: 300.0230; Found: 300.0234.

Ethyl (Z)-2-bromo-3-(2-isocyanophenyl)acrylate (2a)



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 19) as eluent. Brown solid (0.310 g, 74%); **M.p.** 39-40 °C; **¹H NMR (300 MHz, CDCl₃)** δ 8.36 (s, 1H), 8.12-7.93 (m, 1H), 7.53-7.37 (m, 4H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** δ 168.78, 162.57, 135.51, 131.15, 130.57, 129.85, 129.22, 127.33, 118.66, 63.39, 14.32; **IR (neat)** 1363, 1389, 1446, 1475, 1616, 1717, 2113, 2872, 2906, 2939, 2980 cm⁻¹; **HRMS (EI-MS)**: m/z calculated for C₁₂H₁₂BrNO₃ (M)⁺: 278.9889; Found: 278.989.

Ethyl (Z)-2-bromo-3-(2-isocyno-4,5-dimethoxyphenyl)acrylate (2b)



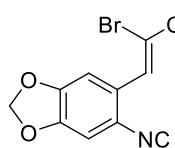
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 9) as eluent. Pink fluffy Solid (0.341 g, 67%); **M.p.** 130-134 °C; **¹H NMR (300 MHz, CDCl₃)** δ 8.39 (s, 1H), 7.77 (s, 1H), 6.92 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** δ 167.84, 162.88, 150.62, 149.22, 134.78, 123.52, 116.02, 111.21, 109.84, 63.32, 56.52, 56.46, 14.37; **IR (neat)** 1443, 1464, 1508, 1595, 1714, 2117, 2836, 2856, 2939, 2991 cm⁻¹; **HRMS (EI-MS)**: m/z calculated for C₁₄H₁₄BrNO₄ (M)⁺: 339.0101 ; Found: 339.0106.

Ethyl (Z)-2-bromo-3-(5-chloro-2-isocyanophenyl)acrylate (2c)



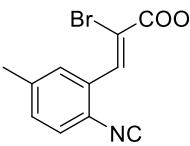
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 19) as eluent. White solid (0.363 g, 77%); **M.p.** 91-92 °C; **¹H NMR (400 MHz, CDCl₃)** δ 8.27 (s, 1H), 8.00 (d, *J* = 1.7 Hz, 1H), 7.43-7.38 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 170.19, 162.23, 135.36, 134.18, 132.72, 130.61, 129.80, 128.45, 119.92, 63.56, 14.30; **IR (neat)** 1407, 1466, 1516, 1579, 1620, 1710, 2121, 2933, 2983, 3083 cm⁻¹; **HRMS (EI-MS)**: m/z calculated for C₁₂H₉NO₂ClBr (M)⁺: 312.9499 ; Found: 312.9496.

Ethyl (Z)-2-bromo-3-(6-isocyanobenzo[d][1,3]dioxol-5-yl)acrylate (2d)



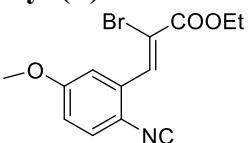
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 9) as eluent. White solid (0.374 g, 77%); **M.p.** 88-90 °C; **¹H NMR (400 MHz, CDCl₃)** δ 8.33 (s, 1H), 7.64 (s, 1H), 6.90 (s, 1H), 6.10 (s, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 168.25, 162.75, 149.26, 148.29, 134.97, 125.57, 116.85, 108.69, 107.71, 103.00, 63.33, 14.35. **IR (neat)** 1480, 1503, 1591, 1620, 1719, 2113, 2844, 2920, 2980 cm⁻¹; **HRMS (EI-MS)**: m/z calculated for C₁₃H₁₀NO₄Br (M)⁺: 322.9787. Found: 322.9784.

Ethyl (Z)-2-bromo-3-(2-isocyno-5-methylphenyl)acrylate (2e)



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 19) as eluent. Red solid (0.313 g, 71%); **M.p.** 63-65 °C; **¹H NMR (400 MHz, CDCl₃)** δ 8.33 (s, 1H), 7.81 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 168.18, 162.64, 139.71, 135.73, 131.23, 130.91, 130.17, 127.13, 118.37, 63.34, 21.67, 14.33; **IR (neat)** 1446, 1483, 1511, 1617, 1720, 2117, 2868, 2927, 2983 cm⁻¹; **HRMS (EI-MS)**: m/z calculated for C₁₃H₁₂BrNO₂ (M)⁺: 293.0046; Found: 293.0038.

Ethyl (Z)-2-bromo-3-(2-isocyano-5-methoxyphenyl)acrylate (2f)

 Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 9) as eluent. White solid (0.325 g, 70%); **M.p.** 100-101 °C; **¹H NMR (400 MHz, CDCl₃)** δ 8.33 (s, 1H), 7.55 (d, *J* = 2.7 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 167.46, 162.57, 159.52, 135.46, 132.36, 128.61, 118.64, 116.33, 114.64, 63.41, 55.96, 14.33; **IR (neat)** 1443, 1479, 1579, 1620, 1726, 2119, 2852, 2925, 2990 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₃H₁₂BrNO₃ (M+H)⁺: 310.0073 ; Found: 310.0076.

Reduction potentials of selected starting materials:

The redox potentials of the *o*-isocyano- α -bromocinnamates were measured in DMF containing 0.01 M tetra-*n*-butylammonium tetrafluoroborate as an electrolyte using ferrocene/ferrocenium (Fe/Fe⁺) as an internal reference. A glassy carbon electrode (working electrode), platinum wire counter electrode, and Ag quasi-reference electrode were employed. All values are given vs. Saturated Calomel Electrode (SCE). Prior to the measurement the solvent is degassed with argon.

Table S1: Reduction potentials of selected *o*-isocyano- α -bromocinnamates.

| <i>o</i> -isocyano- α -bromocinnamates | Reduction potential (V) |
|---|-------------------------|
| 2a | -1.33 |
| 2b | -1.41 |
| 2c | -1.23 |
| 2e | -1.34 |

General procedure visible light mediated reaction 2-substituted Indole-3-glyoxylates:

A Schlenk flask (5 mL size) equipped with a stirring bar was charged with *o*-isocyano α -bromo cinnamate derivative (0.25 mmol, 1.00 equiv), [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (2.8 mg, 0.01 equiv, 1.00 mol%) and aryl diazonium salt or aryl disulfide (0.50 mmol, 2.00 equiv). 2 mL of dry DMF was added followed by H₂O (0.009 mL, 0.50 mmol 2.00 equiv). The reaction mixture was degassed 3 times by Freeze-Pump-Thaw degassing method and the reaction mixture was closed under N₂ atmosphere. The flask was irradiated internally (12 h for aryl diazonium salts, 48 h for disulfides; See Figure S1) with a blue LED ($\lambda_{\text{max}} = 455$ nm) with continuous stirring at room temperature. Upon completion of the reaction, the mixture was diluted with ethyl acetate (30 mL), washed with water (2 x 15 mL), then brine. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography to yield pure product.

For an experiment on a 2 mmol scale, see page S16: **2-(2-(4-fluorophenyl)-1*H*-indol-3-yl)-N,N-dihexyl-2-oxoacetamide (12)**.

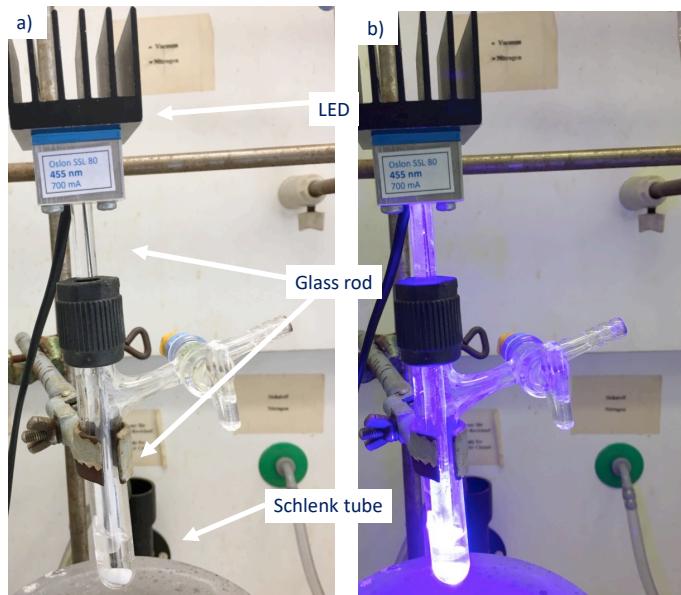
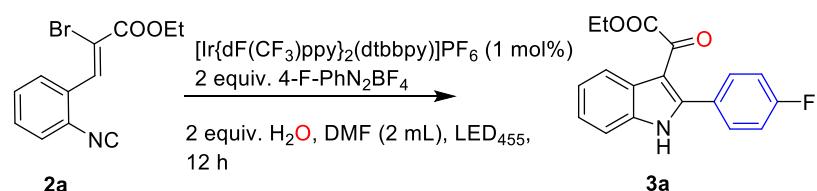


Figure S1: a) Photochemical reaction set up used for synthesis of indole derivatives; b) with the LED switched on

Table S2: further Optimizations:

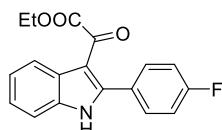


| S No | Deviation from standard conditions | Yield(%) ^a |
|------|---|-----------------------|
| 1 | DMSO used instead of DMF | 41 |
| 2 | CH ₃ CN used instead of DMF | 33 |
| 3 | DCM used instead of DMF | 21 |
| 4 | 3 equivalents of 4-F-PhN ₂ BF ₄ used instead of 2 equivalents | 62 |
| 5 | 3 equivalents of H ₂ O used instead of 2 equivalents | 44 |
| 6 | 2 equivalents of MeOH used instead of 2 equivalents H ₂ O | 18 |

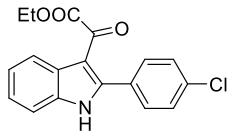
^a **2a** (0.25 mmol); NMR yields with diphenyl methane as internal standard.

Ethyl 2-(2-(4-fluorophenyl)-1*H*-indol-3-yl)-2-oxoacetate (3a):

Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellowish white solid (0.051 g, 66%); **M.p.** 179-182 °C; **¹H NMR** (300 MHz, CDCl₃) δ 9.08 (s, 1H), 8.43-8.17 (m, 1H), 7.54-7.45 (m, 2H), 7.45-7.37 (m, 1H), 7.36-7.29 (m, 2H), 7.18-7.08 (m, 2H), 3.75 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **¹⁹F NMR** (282 MHz, CDCl₃) δ -110.03; **¹³C NMR** (75 MHz, CDCl₃) δ 182.97, 164.85, 164.14 (d, *J* = 250.6 Hz), 146.59, 135.36, 131.53 (d, *J* = 8.5 Hz), 127.33, 127.08, 115.88 (d, *J* = 21.9 Hz), 111.34, 110.91, 61.72, 13.64; **IR (neat)** 1447, 1497, 1545, 1607, 1733, 2873, 2938, 2986, 3071, 3279 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₈H₁₄FNO₃ (M+H)⁺: 312.1030; Found: 312.1032.

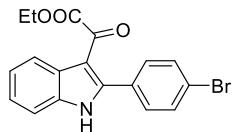


Ethyl 2-(2-(4-chlorophenyl)-1*H*-indol-3-yl)-2-oxoacetate (3b):



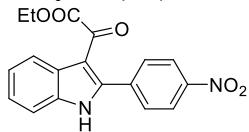
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.051 g, 63%); **M.p.** 171-174 °C; **1H NMR (400 MHz, CDCl₃)** δ 9.04 (s, 1H), 8.30 (dd, *J* = 6.6, 2.6 Hz, 1H), 7.47-7.39 (m, 5H), 7.37-7.31 (m, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); **13C NMR (101 MHz, CDCl₃)** δ 183.02, 164.93, 146.34, 136.64, 135.59, 130.95, 129.58, 129.12, 127.53, 124.88, 123.83, 122.40, 111.52, 111.18, 61.94, 13.80; **IR (neat)** 1440, 1478, 1600, 1727, 2854, 2925, 2981, 3061, 3249 cm⁻¹; **HRMS (EI-MS)**: m/z calculated for C₁₈H₁₄ClNO₃ (M)⁺: 327.0651; Found: 327.0652.

Ethyl 2-(2-(4-bromophenyl)-1*H*-indol-3-yl)-2-oxoacetate (3c):



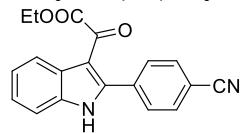
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.060 g, 65%); **M.p.** 170-172 °C; **1H NMR (300 MHz, CDCl₃)** δ 9.29 (s, 1H), 8.28 (dd, *J* = 6.4, 2.7 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.42 (dt, *J* = 7.3, 3.2 Hz, 1H), 7.36-7.31 (m, 4H), 3.75 (d, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **13C NMR (75 MHz, CDCl₃)** δ 183.04, 164.98, 146.53, 135.64, 132.03, 131.12, 129.98, 127.49, 124.87, 124.82, 123.83, 122.30, 111.65, 111.04, 62.00, 13.78; **IR (neat)** 1446, 1478, 1611, 1733, 2855, 2926, 2981, 3060, 3277 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₈H₁₄BrNO₃ (M)⁺: 371.0151 ; Found: 371.0.0142.

Ethyl 2-(2-(4-nitrophenyl)-1*H*-indol-3-yl)-2-oxoacetate (3d):



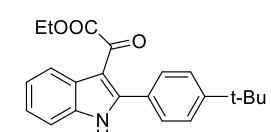
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Yellow solid (0.060 g, 71%); **M.p.** 227-229 °C; **1H NMR (300 MHz, DMSO)** δ 12.92 (s, 1H), 8.40 (d, *J* = 8.7 Hz, 2H), 8.12 (d, *J* = 6.9 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.46-7.16 (m, 2H), 3.71 (q, *J* = 7.1 Hz, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); **13C NMR (75 MHz, DMSO)** δ 182.04, 164.44, 148.15, 145.61, 137.09, 136.13, 131.24, 126.81, 124.45, 123.44, 123.30, 120.93, 112.63, 109.81, 61.52, 13.39; **IR (neat)** 1344, 1403, 1443, 1479, 1581, 1601, 1638, 1703, 2930, 2982, 3066, 3105, 3189, 3218 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₈H₁₄N₂O₅ (M+H)⁺: 339.0975 ; Found: 339.0977.

Ethyl 2-(2-(4-cyanophenyl)-1*H*-indol-3-yl)-2-oxoacetate (3e):



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Yellow solid (0.052 g, 65%); **M.p.** 170-171 °C; **1H NMR (300 MHz, DMSO)** δ 12.85 (s, 1H), 8.13 (dd, *J* = 6.6, 2.0 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.56 (dd, *J* = 6.5, 1.6 Hz, 1H), 7.41-7.28 (m, 2H), 3.69 (q, *J* = 7.1 Hz, 2H), 1.00 (t, *J* = 7.1 Hz, 3H); **13C NMR (75 MHz, DMSO)** δ 182.09, 164.44, 146.13, 135.98, 135.26, 132.30, 130.76, 126.78, 124.39, 123.26, 120.98, 118.41, 112.53, 112.43, 109.61, 61.42, 13.37; **IR (neat)** 1446, 1611, 1636, 1732, 2230, 2856, 2927, 2983, 3067, 3276 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₉H₁₄N₂O₃ (M+H)⁺: 319.1077; Found: 319.1081 .

Ethyl 2-(2-(4-(*tert*-butyl)phenyl)-1*H*-indol-3-yl)-2-oxoacetate (3f):



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellowish white solid (0.050 g, 58%); **M.p.** 197-199 °C; **1H NMR (400 MHz, CDCl₃)** δ 8.95 (s, 1H), 8.41-8.31 (m, 1H), 7.49-7.43 (m, 4H), 7.44-7.40 (m, 1H), 7.36-7.29 (m, 2H), 3.62 (q, *J* = 7.2 Hz, 2H), 1.33 (s, 9H), 0.94 (t, *J* = 7.2 Hz, 3H); **13C NMR (101 MHz, CDCl₃)** δ 183.31, 165.10, 153.70, 148.28, 135.51, 129.45, 128.26, 127.75, 125.87, 124.53, 123.58, 122.48, 111.36, 110.96, 61.67, 35.06, 31.32,

13.65; **IR (neat)** 1441, 1581, 1610, 1733, 2868, 2905, 2931, 2959, 3059, 3275 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{22}\text{H}_{23}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 350.1751 ; Found: 350.1752.

Ethyl 2-oxo-2-(*p*-tolyl)-1*H*-indol-3-yl)acetate (3g):

Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.052 g, 68%); **M.p.** 130-134 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 8.85 (s, 1H), 8.31 (dd, J = 8.5, 4.3 Hz, 2H), 7.38-7.33 (m, 3H), 7.28 (ddd, J = 5.3, 4.1, 2.9 Hz, 2H), 7.20 (m, 2H), 3.65 (q, J = 7.2 Hz, 2H), 2.35 (s, 3H), 0.98 (t, J = 7.2 Hz, 3H); **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 183.28, 165.04, 148.27, 140.55, 135.49, 129.56, 129.53, 128.27, 127.75, 124.51, 123.56, 122.45, 111.33, 110.83, 61.70, 21.58, 13.72; **IR (neat)** 1443, 1497, 1609, 1734, 2855, 2924, 2983, 3058, 3283 cm^{-1} ; **HRMS (EI-MS)**: m/z calculated for $\text{C}_{19}\text{H}_{17}\text{NO}_3$ (M) $^+$: 307.1202 ; Found: 307.1197.

Ethyl 2-oxo-2-(2-phenyl-1*H*-indol-3-yl)acetate (3h):

Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellowish white Solid (0.048 g, 66%); **M.p.** 159-162 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 8.96 (s, 1H), 8.44-8.31 (m, 1H), 7.56-7.41 (m, 6H), 7.38-7.29 (m, 2H), 3.65 (q, J = 7.2 Hz, 2H), 1.00 (t, J = 7.2 Hz, 3H); **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 183.25, 164.95, 147.97, 135.52, 131.20, 130.27, 129.68, 128.90, 127.67, 124.66, 123.66, 122.53, 111.40, 111.01, 61.73, 13.72; **IR (neat)** 1434, 1453, 1583, 1611, 1734, 2931, 2961, 2983, 2961, 3061, 3287 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{18}\text{H}_{15}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 294.1125 ; Found: 294.1128.

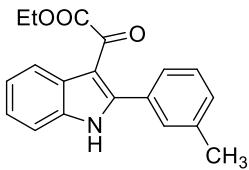
Ethyl 2-oxo-2-(*o*-tolyl)-1*H*-indol-3-yl)acetate (3i):

Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.043 g, 56%); **M.p.** 175-178 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 8.91 (s, 1H), 8.43-8.33 (m, 1H), 7.46-7.19 (m, 7H), 3.49 (q, J = 7.2 Hz, 2H), 2.25 (s, 3H), 1.04 (t, J = 7.2 Hz, 3H); **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 183.45, 165.14, 147.72, 138.49, 135.44, 131.31, 130.37, 130.31, 130.00, 126.90, 125.50, 124.55, 123.61, 122.64, 111.67, 111.35, 61.51, 20.14, 13.69; **IR (neat)** 1453, 1539, 1608, 1734, 2856, 2927, 2982, 3062, 3276 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{19}\text{H}_{17}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 308.1281 ; Found: 308.1281.

Ethyl 2-(2-(2-chlorophenyl)-1*H*-indol-3-yl)-2-oxoacetate (3j):

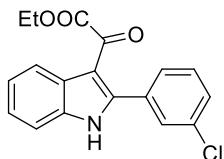
Following the general procedure the title compound was synthesized by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.047 g, 58%); **M.p.** 195-196 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl_3)** δ 8.99 (s, 1H), 8.39 (dd, J = 6.1, 3.2 Hz, 1H), 7.56-7.49 (m, 1H), 7.48-7.40 (m, 3H), 7.34 (m, 3H), 3.63 (q, J = 7.2 Hz, 2H), 1.09 (t, J = 7.2 Hz, 3H); **$^{13}\text{C NMR}$ (75 MHz, CDCl_3)** δ 182.88, 164.72, 143.97, 135.47, 134.30, 133.34, 131.54, 130.04, 129.89, 126.81, 126.73, 124.86, 123.68, 122.66, 112.16, 111.49, 61.74, 13.72; **IR (neat)** 1449, 1539, 1614, 1631, 1734, 2855, 2928, 2983, 3064, 3277 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{18}\text{H}_{14}\text{ClNO}_3$ ($\text{M}+\text{H}$) $^+$: 328.0735; Found: 328.0736.

Ethyl 2-oxo-2-(*m*-tolyl)-1*H*-indol-3-yl)acetate (3k):



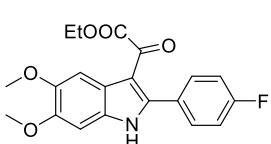
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.042 g, 55%); **M.p.** 141-144 °C; **1H NMR (400 MHz, CDCl₃)** δ 8.77 (s, 1H), 8.40-8.34 (m, 1H), 7.42 (dt, *J* = 6.4, 2.7 Hz, 1H), 7.39-7.28 (m, 6H), 3.68 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); **13C NMR (101 MHz, CDCl₃)** δ 183.29, 164.91, 148.06, 138.90, 135.43, 131.16, 131.02, 130.33, 128.90, 127.78, 126.71, 124.62, 123.63, 122.62, 111.22, 111.04, 61.66, 21.49, 13.73; **IR (neat)** 1453, 1537, 1584, 1610, 1735, 2856, 2925, 2982, 3060, 3277 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₉H₁₇NO₃ (M+H)⁺: 308.1281 ; Found: 308.1279.

Ethyl 2-(2-(3-chlorophenyl)-1H-indol-3-yl)-2-oxoacetate (3l):



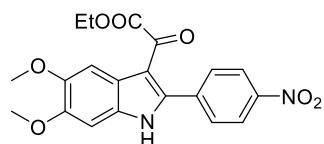
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.051 g, 62%); **M.p.** 161-163 °C; **1H NMR (400 MHz, CDCl₃)** δ 9.23 (s, 1H), 8.33-8.28 (m, 1H), 7.51 (s, 1H), 7.45-7.31 (m, 6H), 3.78 (q, *J* = 7.2 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H); **13C NMR (101 MHz, CDCl₃)** δ 183.05, 164.91, 145.97, 135.63, 134.86, 132.89, 130.22, 130.18, 129.58, 127.94, 127.49, 124.93, 123.84, 122.45, 111.61, 111.19, 62.05, 13.76; **IR (neat)** 1449, 1537, 1613, 1733, 2855, 2927, 2982, 3064, 3276 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₈H₁₄ClNO₃ (M+H)⁺: 328.0735; Found: 328.0737.

Ethyl 2-(2-(4-fluorophenyl)-5,6-dimethoxy-1H-indol-3-yl)-2-oxoacetate (3m):



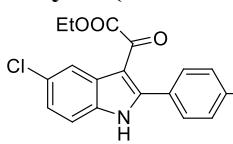
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 2) as eluent. Yellow solid (0.048 g, 52%); **M.p.** 170-172 °C; **1H NMR (300 MHz, CDCl₃)** δ 9.02 (s, 1H), 7.83 (s, 1H), 7.54-7.34 (m, 2H), 7.11 (t, *J* = 8.6 Hz, 3H), 6.89 (s, 1H), 3.95 (s, 3H), 3.87 (s, 3H), 3.72 (q, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 4H); **19F NMR (282 MHz, CDCl₃)** δ -110.57; **13C NMR (75 MHz, CDCl₃)** δ 183.02, 164.95, 164.02 (t, *J* = 250 Hz), 148.36, 147.55, 144.83, 131.41 (d, *J* = 8.4 Hz), 129.63, 127.34, 120.55, 115.78 (d, *J* = 21.9 Hz), 110.96, 103.44, 94.30, 61.62, 56.29, 56.15, 13.62; **IR (neat)** 1450, 1542, 1621, 1732, 2836, 2939, 2986, 3071, 3289 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₂₀H₁₈FNO₅ (M+H)⁺: 372.1242; Found: 372.1245.

Ethyl 2-(5,6-dimethoxy-2-(4-nitrophenyl)-1H-indol-3-yl)-2-oxoacetate (3n):



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 2) as eluent. Yellow solid (0.054 g, 55%); **M.p.** 196-198 °C; **1H NMR (300 MHz, CDCl₃)** δ 8.84 (s, 1H), 8.30 (d, *J* = 8.6 Hz, 2H), 7.78 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 6.93 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.82 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H); **13C NMR (75 MHz, CDCl₃)** δ 182.74, 164.68, 149.14, 148.19, 148.09, 142.29, 137.69, 130.40, 130.31, 123.82, 120.84, 111.80, 103.23, 94.38, 62.14, 56.44, 56.33, 13.85. **IR (neat)**: 1449, 1484, 1522, 1601, 1629, 1734, 2255, 2362, 2940, 2985, 3104, 3288 cm⁻¹; **HRMS (EI-MS)**: m/z calculated for C₂₀H₁₈N₂O₇ (M)⁺: 398.1108; Found: 398.1101.

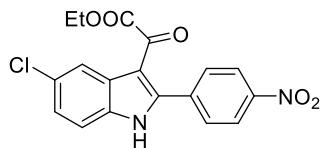
Ethyl 2-(5-chloro-2-(4-fluorophenyl)-1H-indol-3-yl)-2-oxoacetate (3o):



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.054 g, 63%); **M.p.** 199-202 °C; **1H NMR (400 MHz, DMSO)** δ 12.86 (s, 1H), 8.13 (s, 1H), 7.68-7.60 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 8.4 Hz, 3H), 7.36 (d, *J* = 7.9 Hz, 1H), 3.67 (dd, *J* = 13.4, 6.5 Hz, 2H), 1.00 (t, *J* = 6.9 Hz, 4H); **19F NMR (376 MHz, DMSO)** δ -109.97; **13C NMR (101 MHz, DMSO)**

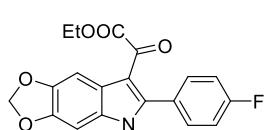
δ 182.28, 164.27, 163.37 (d, J = 249.5 Hz), 148.71, 134.31, 132.15 (d, J = 9 Hz), 127.99, 127.55, 126.50, 124.10, 120.05, 115.57 (d, J = 21.9 Hz), 113.98, 108.85, 61.34, 13.31; **IR (neat)** 1444, 1464, 1604, 1635, 1710, 2870, 2940, 2986, 3283, 3309 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{18}\text{H}_{13}\text{ClFNO}_3$ ($\text{M}+\text{H}$) $^+$: 346.0641; Found: 346.0649.

Ethyl 2-(5-chloro-2-(4-nitrophenyl)-1*H*-indol-3-yl)-2-oxoacetate (3p):



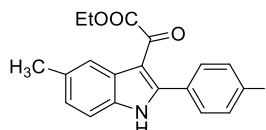
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Yellow Solid (0.057 g, 62%); **M.p.** 215-217 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, DMSO)** δ 13.12 (s, 1H), 8.41 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 1.9 Hz, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.59 (t, J = 6.8 Hz, 1H), 7.40 (dd, J = 8.7, 2.1 Hz, 1H), 3.69 (q, J = 7.1 Hz, 2H), 1.00 (t, J = 7.1 Hz, 3H). **IR (neat)** 1456, 1521, 1636, 1651 1747, 2268, 2340, 2942, 2980, 3111, 3285 cm^{-1} ; **$^{13}\text{C NMR}$ (75 MHz, DMSO)** δ 181.94, 164.02, 148.33, 146.76, 136.54, 134.59, 131.23, 127.93, 127.89, 124.59, 123.51, 120.12, 114.33, 109.47, 61.66, 13.35. **HRMS (EI-MS)**: m/z calculated for $\text{C}_{18}\text{H}_{13}\text{ClN}_2\text{O}_5$ (M) $^{+*}$: 372.0507; Found: 372.0501.

Ethyl 2-(6-(4-fluorophenyl)-5*H*-[1,3]dioxolo[4,5-f]indol-7-yl)-2-oxoacetate (3q):



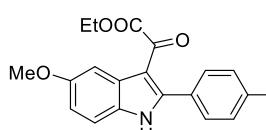
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Yellow solid (0.045 g, 51%); **M.p.** 196-198 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl₃)** δ 8.89 (s, 1H), 7.75 (s, 1H), 7.46 (dd, J = 8.7, 5.2 Hz, 2H), 7.13 (t, J = 8.6 Hz, 2H), 6.85 (s, 1H), 6.01 (s, 2H), 3.73 (q, J = 7.2 Hz, 2H), 1.06 (t, J = 7.2 Hz, 3H); **$^{19}\text{F NMR}$ (282 MHz, CDCl₃)** δ -110.51; **$^{13}\text{C NMR}$ (75 MHz, CDCl₃)** δ 183.05, 165.00, 163.6 (d, J = 250.5 Hz), 146.62, 145.84, 144.97, 131.54 (d, J = 8.5 Hz), 130.48, 127.37, 121.87, 116.00 (d, J = 21.9 Hz), 111.39, 101.43, 101.37, 92.25, 61.85, 13.79. **IR (neat)** 1463, 1506, 1606, 1732, 2902, 2921, 2984, 3086, 3290 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{19}\text{H}_{14}\text{FNO}_5$ ($\text{M}+\text{H}$) $^+$: 356.0929 ; Found: 356.0938.

Ethyl 2-(2-(4-fluorophenyl)-5-methyl-1*H*-indol-3-yl)-2-oxoacetate (3r):



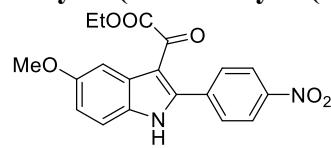
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.042 g, 52%); **M.p.** 136-139 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, CDCl₃)** δ 8.96 (s, 1H), 8.13 (d, J = 0.7 Hz, 1H), 7.56-7.41 (m, 2H), 7.30 (d, J = 8.3 Hz, 1H), 7.20-7.05 (m, 3H), 3.73 (q, J = 7.2 Hz, 2H), 2.49 (s, 3H), 1.06 (t, J = 7.2 Hz, 3H); **$^{19}\text{F NMR}$ (282 MHz, CDCl₃)** δ -110.22; **$^{13}\text{C NMR}$ (75 MHz, CDCl₃)** δ 183.13, 165.09, 163.70 (d, J = 250.0 Hz), 146.70, 133.79, 133.55, 131.65 (d, J = 8.5 Hz), 127.76, 127.34 (d, J = 3.4 Hz), 126.26, 122.08, 115.98 (d, J = 21.9 Hz), 111.09, 110.76, 61.81, 21.82, 13.79; **IR (neat)** 1443, 1492, 1543, 1604, 1729, 2858, 2922, 2982, 3066, 3259 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{19}\text{H}_{16}\text{FNO}_3$ ($\text{M}+\text{H}$) $^+$: 326.1187; Found: 326.1194.

Ethyl 2-(2-(4-fluorophenyl)-5-methoxy-1*H*-indol-3-yl)-2-oxoacetate (3s):



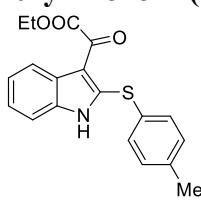
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. White solid (0.046 g, 54%); **M.p.** 185-187 $^{\circ}\text{C}$; **$^1\text{H NMR}$ (300 MHz, DMSO)** δ 12.56 (s, 1H), 7.61 (ddd, J = 12.1, 6.7, 2.3 Hz, 3H), 7.40 (dd, J = 11.7, 5.0 Hz, 3H), 6.95 (dd, J = 8.8, 2.5 Hz, 1H), 3.81 (s, 3H), 3.64 (q, J = 7.1 Hz, 2H), 0.99 (t, J = 7.1 Hz, 3H); **$^{19}\text{F NMR}$ (282 MHz, DMSO)** δ -110.46; **$^{13}\text{C NMR}$ (75 MHz, DMSO)** δ 182.28, 164.73, 162.09 (d J = 248.3 Hz), 156.21, 147.54, 132.08 (d, J = 8.7 Hz), 130.56, 127.80, 127.13, 115.47 (d, J = 21.9 Hz), 113.62, 113.14, 109.18, 102.84, 61.16, 55.37, 13.36; **IR (neat)**: 1451, 1489, 1543, 1622, 1733, 2854, 2927, 3073, 3277 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{19}\text{H}_{16}\text{FNO}_4$ ($\text{M}+\text{H}$) $^+$: 342.1136; Found: 342.1144.

Ethyl 2-(5-methoxy-2-(4-nitrophenyl)-1*H*-indol-3-yl)-2-oxoacetate (3t)



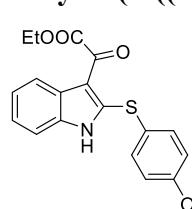
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Yellow solid (0.053 g, 58%); **M.p.** 189-191 °C; **1H NMR** (300 MHz, CDCl₃) δ 8.97 (s, 1H), 8.32-8.20 (m, 2H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.90 (s, 3H), 3.85-3.78 (m, 2H), 1.11 (t, *J* = 7.2 Hz, 3H). **13C NMR** (75 MHz, CDCl₃) δ 182.61, 164.62, 157.42, 148.51, 144.10, 137.55, 130.65, 130.48, 128.50, 123.90, 115.91, 112.58, 111.69, 103.56, 62.13, 55.98, 13.88; **IR (neat)**: 1455, 1487, 1521, 1604, 1625, 1733, 2334, 2357, 2971, 2997, 3101, 3285, 3316 cm⁻¹; **HRMS (EI-MS)**: m/z calculated for C₁₉H₁₆N₂O₆ (M)⁺: 368.1002; Found: 368.1003.

Ethyl 2-oxo-2-(2-(*p*-tolylthio)-1*H*-indol-3-yl)acetate (4a):



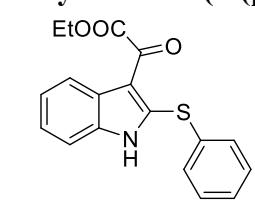
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellowish Sticky mass (0.038 g, 45%); **1H NMR** (300 MHz, CDCl₃) δ 8.10 (s, 1H), 7.90-7.83 (m, 1H), 7.54-7.50 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.25-7.15 (m, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H); **13C NMR** (75 MHz, CDCl₃) δ 180.60, 165.69, 146.77, 141.14, 136.15, 134.71, 131.46, 126.62, 125.12, 123.62, 123.14, 120.25, 111.38, 110.85, 62.25, 21.56, 14.23; **IR (neat)** 1431, 1470, 1598, 1732, 2855, 2923, 2980, 3056, 3275 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₉H₁₇NO₃S (M+H)⁺: 340.1002; Found: 340.1006.

Ethyl 2-(2-((4-methoxyphenyl)thio)-1*H*-indol-3-yl)-2-oxoacetate (4b):



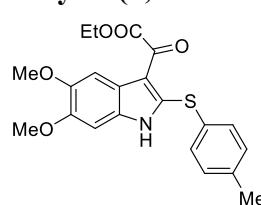
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellowish sticky mass (0.037 g, 42%); **1H NMR** (600 MHz, CDCl₃) 8.03 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.61-7.57 (m, 2H), 7.23-7.18 (m, 1H), 7.16 (d, *J* = 3.7 Hz, 2H), 7.06-7.01 (m, 2H), 4.48 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 4H), 1.43 (t, *J* = 7.2 Hz, 4H); **13C NMR** (150 MHz, CDCl₃) δ 180.17, 165.52, 161.56, 147.95, 136.78, 135.90, 126.49, 123.25, 122.89, 119.88, 118.33, 116.10, 110.62, 110.59, 62.04, 55.53, 44.06. **IR (neat)** 1429, 1468, 1491, 1590, 1731, 2838, 2959, 2925, 3259, 3274 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₉H₁₇NO₄S (M+H)⁺: 356.0951; Found: 356.0954.

Ethyl 2-oxo-2-(2-(phenylthio)-1*H*-indol-3-yl)acetate (4c):



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellowish sticky mass (0.034 g, 42%); **1H NMR** (300 MHz, CDCl₃) δ 8.42 (s, 1H), 7.98-7.90 (m, 1H), 7.62-7.55 (m, 2H), 7.50-7.43 (m, 3H), 7.25-7.17 (m, 3H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); **13C NMR** (75 MHz, CDCl₃) δ 181.01, 165.66, 144.80, 136.34, 133.87, 130.52, 130.14, 129.57, 126.54, 123.92, 123.24, 120.51, 112.29, 111.05, 62.27, 14.15; **IR (neat)** 1440, 1472, 1580, 1615, 1732, 2927, 2983, 3059, 3296 cm⁻¹; **HRMS (ESI)**: m/z calculated for C₁₈H₁₅NO₃S (M+H)⁺: 326.0845; Found: 326.0850.

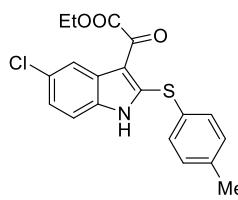
Ethyl 2-(5,6-dimethoxy-2-(*p*-tolylthio)-1*H*-indol-3-yl)-2-oxoacetate (4d):



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent. Yellow solid (0.044 g 44%); **M.p.** 138-139 °C; **1H NMR** (300 MHz, CDCl₃) δ 8.11 (s, 1H), 7.61 (s, 1H), 7.45-7.35 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 3.85 (s,

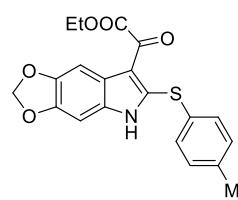
3H), 2.38 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); **^{13}C NMR (75 MHz, CDCl_3)** δ 181.63, 165.83, 148.18, 147.27, 140.15, 139.82, 132.76, 130.99, 130.79, 127.48, 119.93, 113.59, 102.86, 94.21, 62.21, 56.37, 56.23, 21.39, 14.13; **IR (neat)** 1440, 1462, 1487, 1626, 1733, 2855, 2926, 3286 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{21}\text{H}_{21}\text{NO}_5\text{S}$ ($\text{M}+\text{H}$) $^+$: 400.1213; Found: 400.1217.

Ethyl 2-(5-chloro-2-(*p*-tolylthio)-1*H*-indol-3-yl)-2-oxoacetate (4e):



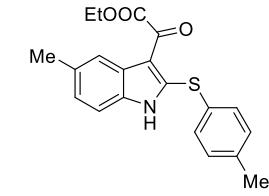
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.049 g, 53%); **M.p.** 86-88 $^{\circ}\text{C}$; **^1H NMR (300 MHz, CDCl_3)** δ 8.03 (s, 1H), 7.89 (s, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 4.48 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, CDCl_3)** δ 180.19, 165.29, 148.16, 141.28, 134.71, 134.59, 131.50, 129.00, 127.68, 124.74, 123.85, 120.11, 111.92, 110.92, 62.44, 21.54, 14.19; **IR (neat)**: 1436, 1489, 1533, 1598, 1733, 2860, 2922, 2979, 3052, 3260 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{19}\text{H}_{16}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 374.0612; Found: 374.0618.

Ethyl 2-oxo-2-(6-(*p*-tolylthio)-5*H*-[1,3]dioxolo[4,5-f]indol-7-yl)acetate (4f):



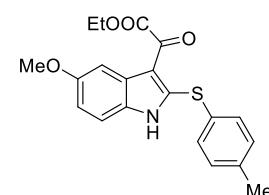
Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellow solid (0.048 g, 50%); **M.p.** 152-155 $^{\circ}\text{C}$; **^1H NMR (300 MHz, CDCl_3)** δ 8.29 (s, 1H), 7.50 (s, 1H), 7.42-7.33 (m, 2H), 7.21 (d, J = 7.9 Hz, 2H), 6.67 (s, 1H), 5.95 (s, 2H), 4.39 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); **^{13}C NMR (75 MHz, CDCl_3)** δ 181.46, 165.70, 146.20, 145.47, 140.47, 139.97, 132.95, 131.43, 131.07, 127.17, 121.08, 113.65, 101.35, 100.40, 92.09, 62.26, 21.42, 14.12; **IR (neat)** 1439, 1467, 1622, 1734, 2906, 2922, 2982, 3295, 3312 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{20}\text{H}_{17}\text{NO}_5\text{S}$ ($\text{M}+\text{H}$) $^+$: 384.0900; Found: 384.0906.

Ethyl 2-(5-methyl-2-(*p*-tolylthio)-1*H*-indol-3-yl)-2-oxoacetate (4g):



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. Yellowish white solid (0.053 g, 60%); **M.p.** 90-92 $^{\circ}\text{C}$; **^1H NMR (400 MHz, CDCl_3)** δ 8.06 (s, 1H), 7.71 (s, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 8.2 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 2.42 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, CDCl_3)** δ 180.81, 165.80, 145.86, 140.87, 134.49, 134.40, 132.80, 131.36, 126.92, 125.60, 125.12, 120.26, 111.43, 110.48, 62.18, 21.83, 21.52, 14.22; **IR (neat)** 1441, 1482, 1600, 1733, 2866, 2921, 2980, 3057, 3272 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{20}\text{H}_{19}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 354.1158 ; Found: 354.1158.

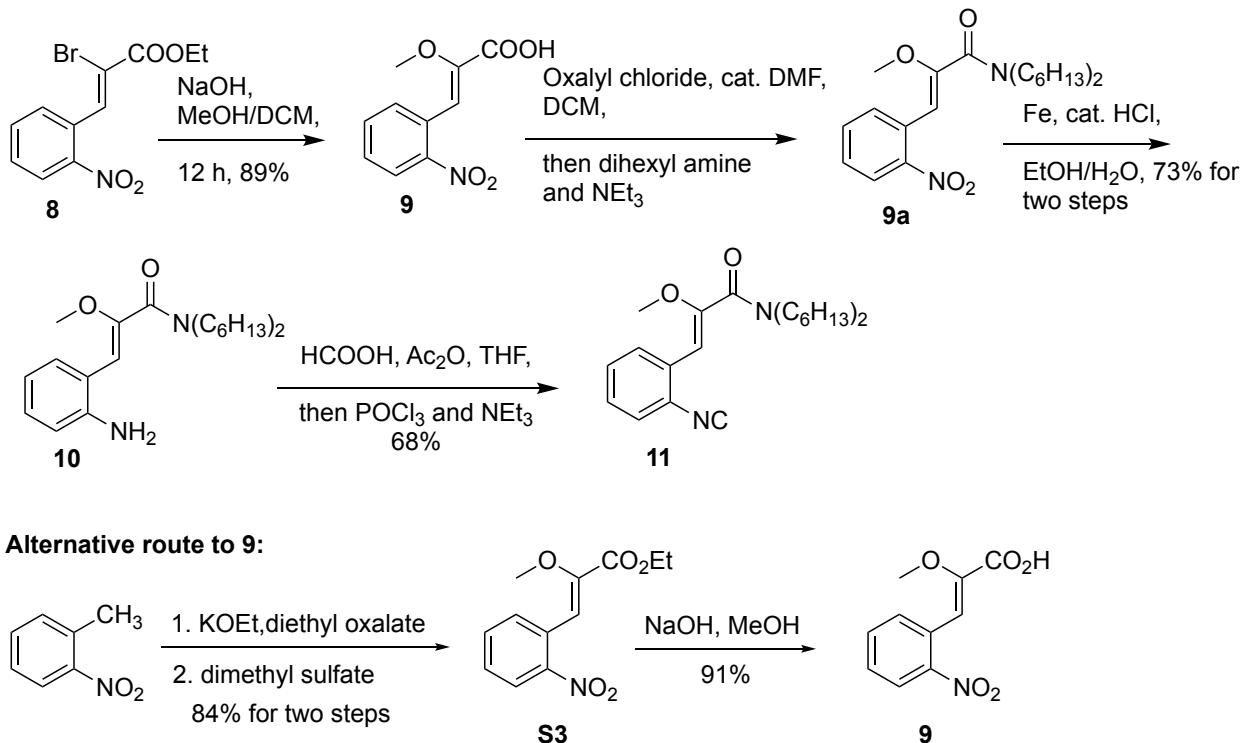
Ethyl 2-(5-methoxy-2-(*p*-tolylthio)-1*H*-indol-3-yl)-2-oxoacetate (4h):



Following the general procedure the title compound was synthesized and purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent. White solid (0.056 g, 61%); **M.p.** 141-143 $^{\circ}\text{C}$; **^1H NMR (400 MHz, CDCl_3)** δ 8.05 (s, 1H), 7.49 (dd, J = 4.7, 2.1 Hz, 2H), 7.47 (d, J = 1.8 Hz, 1H), 7.28 (d, J = 7.9 Hz, 2H), 7.06 (d, J = 8.8 Hz, 1H), 6.82 (dd, J = 8.8, 2.5 Hz, 1H), 4.45 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 2.41 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, CDCl_3)** δ 180.94, 165.76, 156.67, 145.16, 140.76, 134.14, 131.33, 131.08, 127.76, 125.88, 113.53, 112.08, 111.55, 103.06, 62.22, 55.93, 21.51, 14.23; **IR (neat)** 1449, 1479, 1612, 1733, 2855, 2925, 3291 cm^{-1} ; **HRMS (ESI)**: m/z calculated for $\text{C}_{20}\text{H}_{19}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$: 370.1108; Found: 370.1112.

Ethyl 2-(2-(4-fluorophenyl)-1*H*-indol-3-yl)acetate (5): The compound **3a** (0.0250 g, 0.080 mmol) was dissolved in 1,4-dioxane (3 mL), to this 6.5 mg Pd/C (10%) and a solution of NaH₂PO₂.H₂O (0.0420 g, 0.40 mmol) in H₂O (0.8 mL) added. The reaction mixture was stirred and heated to reflux (125–130 °C) for 4 hours. It was cooled to room temperature and a solution of NaH₂PO₂.H₂O (0.0420 g, 0.40 mmol) in H₂O (0.8 mL) was added and this was heated again to reflux for 4 hours. The reaction mixture was cooled to room temperature, filtered through celite, washed with several portions of DCM and the combined filtrate and washings were evaporated under reduced pressure. The residue was purified by chromatography using ethyl acetate and hexanes (1: 9) as eluent to give compound **5** (0.0155 g, 65% and 0.0040 g **3a** recovered). The spectral data is matching with reported data.⁴

2-(2-Phenyl-1*H*-indol-3-yl)ethan-1-ol (6): To a solution of **3h** (0.0250 g, 0.085 mmol) in dry THF (3 mL) at 0 °C, LiAlH₄ (0.0080 g, 0.20 mmol) was added. The resulting reaction mixture was refluxed for 4 hours. After completion of reaction, the reaction mixture was quenched by adding water (10 mL) and extracted with ethylacetate. The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate and hexanes (1: 4) as eluent to yield **6** (0.015 g, 69%). The spectral data is in correlation with reported one.⁵



Scheme S2: Synthesis of (Z)-*N,N*-dihexyl-3-(2-isocyanophenyl)-2-methoxyacrylamide

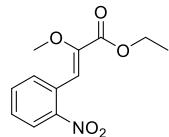
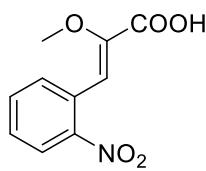
(Z)-2-Methoxy-3-(2-nitrophenyl)acrylic acid (9): The compound **8**³ (2.000 g, 6.66 mmol) was dissolved in DCM/MeOH (9:1) and NaOH (0.533 g 13.33 mmol) was added. The resulting reaction mixture was stirred for 12 hours at rt. After completion of the reaction the solvents were evaporated under reduced pressure, the residue was dissolved in water (100 mL) and washed with diethyl ether. The water layer was acidified by adding con. HCl and extracted twice with DCM (50 ml each). The combined organic layer was washed with water, brine, dried over Na₂SO₄ and concentrated to yield **9** as white solid (1.322 g, 89%). **M.p.** 160 °C; **¹H NMR (300 MHz, DMSO)** δ 13.36 (s, 1H), 8.00 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.74 (td, *J* = 7.6, 1.1 Hz, 1H), 7.62-7.50 (m, 1H), 7.07 (s, 1H), 3.64 (s, 3H); **¹³C NMR (75 MHz, DMSO)** δ 164.27, 148.25, 147.86, 133.16, 131.35, 129.31, 127.50, 124.39, 115.80, 59.03; **IR (neat):** 1446, 1472, 1513, 1630, 1687, 2113, 2798, 2818, 2920, 2958 cm⁻¹; **HRMS (ESI):** m/z calculated for C₁₀H₉NO₅ (M+NH₄)⁺: 241.0819; Found: 241.0825.

Alternative route to **9**:

Ethyl 2-nitro- α -methoxycinnamate⁸ (S3): Under N₂ atmosphere, 30.0 mL (0.50 mol) dry ethanol is added dropwise to a mixture of 3.91 g (100 mmol) potassium in 200 mL dry diethyl ether. After all metal was consumed the solution was cooled to ca. 10 °C and 17.5 g (120 mmol) diethyl oxalate in 100 mL dry diethyl ether was added and the mixture was stirred for 10 min. Then 17.8 g (130 mmol) 2-nitrotoluene in 20 mL diethyl ether was added and stirred for additional 30 min. After standing overnight at room temperature and cooling in an ice bath for 2 hours, the red crystals are collected by filtration under N₂, washed with diethyl ether/ethanol (10:1) (5 x 20 mL) and diethyl ether (5 x 20 mL) and dried under reduced pressure, yielding 16.5 g (60%) ethyl 2-nitrophenyl pyruvate potassium salt.

This potassium salt (16.5 g, 60.0 mmol) was dissolved 300 mL DMSO and 11.4 mL (120 mmol) dimethyl sulfate added dropwise to the mixture with stirring. After 10 min, the dark red color faded and sodium hydrogen carbonate in portions until the mixture stayed yellow. The mixture was poured into 500 mL water and extracted with diethyl ether (3 x 100 mL). The combined ether phase was washed with 100 mL water, dried over sodium sulfate and evaporated, yielding 12.7 g (84%) **S3** as yellow oil, which was used without further purification. **¹H NMR (300 MHz, CDCl₃)** δ 7.97 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.61 (ddd, *J* = 7.8, 6.8, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.26 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

(Z)-2-methoxy-3-(2-nitrophenyl) acrylic acid (9) from S3: A solution of 12.6 g (60.0 mmol) potassium hydroxide in 100 mL methanol is added to 10.4 g (40.0 mmol) of **S3** and stirred for 1 hour at room temperature. Then 50 mL water was added and the methanol was distilled off on a rotary evaporator. The remaining aqueous residue was washed with diethyl ether (2 x 20 mL), acidified with 2 M hydrochloric acid and cooled in an ice bath. The crude product was filtered off by suction and recrystallized from methanol to give white crystals. 10.2 g (91%), m.p. 160-161 °C.

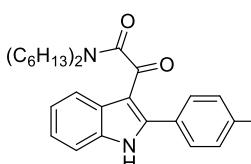
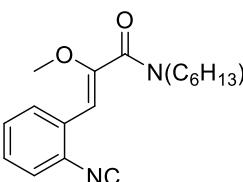
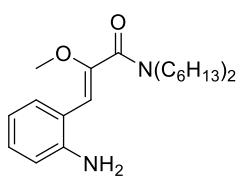


(Z)-3-(2-aminophenyl)-N,N-dihexyl-2-methoxyacrylamide (10): To a suspension of **9** (0.800 g, 3.58 mmol) in DCM, dropwise oxalylchloride (0.545 g, 4.30 mmol), followed by a drop of DMF was added. The resulting solution was gently warmed to 40 °C. Vigorous evolution of gases observed, when the gas evolution was completed the solvents were evaporated to obtain yellowish solid. The solid was dissolved in DCM and introduced in to solution of dihexyl amine (0.730 g, 3.94 mmol) and NEt₃ (0.537 g, 5.37 mmol) in DCM. The resulting solution was stirred at room temperature for 2h. After completion of the reaction the reaction mixture was diluted with 25 ml of DCM and washed with water, dried over Na₂SO₄ and concentrated to get **9a**. The crude **9a** was dissolved in EtOH/H₂O (9:1), Fe powder (0.998 g, 17.9 mmol) and con. HCl (0.5 mL) was added. The resulting reaction mixture was heated to 80 °C for 4 h. After completion of reaction the reaction mixture was passed through a celite bed solvents were evaporated. The residue was dissolved in DCM and washed with water, brine. The organic layer was dried over Na₂SO₄ and concentrated. The crude product was purified by column chromatography using ethyl acetate and hexanes (1: 3) as eluent to yield **10** as yellowish oil (0.941 g, 73% for 2 steps); **1H NMR** (300 MHz, CDCl₃) δ 7.46 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.06 (td, *J* = 7.7, 1.5 Hz, 1H), 6.76 (dt, *J* = 6.2, 3.1 Hz, 1H), 6.70 (td, *J* = 7.7, 1.0 Hz, 1H), 5.82 (s, 1H), 3.87 (bs, 2H), 3.64 (s, 3H), 3.41 (t, *J* = 7.5 Hz, 4H), 1.59 (m, 4H), 1.29 (m, 12H), 0.88 (m, 6H); **13C NMR** (75 MHz, CDCl₃) δ 166.47, 150.60, 144.40, 130.46, 128.54, 119.79, 118.44, 116.10, 107.64, 58.05, 48.66, 45.13, 31.70, 28.85, 27.51, 26.97, 26.73, 22.76, 14.18; **IR (neat):** 1425, 1454, 1490, 1616, 2360, 2856, 2927, 3237, 3351, 3443 cm⁻¹; **HRMS (ESI):** m/z calculated for C₂₂H₃₆N₂O₂ (M+H)⁺: 361.2850; Found: 361.2853.

(Z)-N,N-dihexyl-3-(2-isocyanophenyl)-2-methoxyacrylamide (11): To a solution of **10** (0.500 g, 1.39 mmol) in dry THF, Acetic formic anhydride (0.244 mL, 2.78 mmol; prepared by stirring 1 equiv of acetic anhydride and 1.1 equiv of formic acid for 2 h at 55 °C;) was added at 0 °C. The resulting reaction mixture was stirred at rt for 1 hour. After completion of reaction, the solvents were evaporated to dryness to obtain crude formanilide.

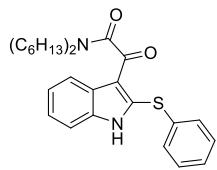
Dehydration: To a solution of crude formanilide in THF, NEt₃ (0.280 g, 2.78) was added and cooled to 0 °C, then POCl₃ (0.320 g, 2.08 mmol) was added dropwise and stirred for 6 hours at rt. After the reaction was completed, an aqueous saturated Na₂CO₃ solution was added at 0 °C to quench the reaction and the mixture was extracted with DCM. The crude product was purified through column chromatography using ethyl acetate and hexanes (1: 9) as eluent to yield **11** as yellowish sticky mass (0.350 g, 68%). **1H NMR** (300 MHz, CDCl₃) δ 8.09 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.34 (ddd, *J* = 7.2, 3.9, 1.9 Hz, 2H), 7.23-7.12 (m, 1H), 5.85 (s, 1H), 3.77 (s, 3H), 3.41 (m, 4H), 1.62 (m, 4H), 1.27 (m, 12H), 0.93-0.68 (m, 6H); **13C NMR** (75 MHz, CDCl₃) δ 166.77, 165.01, 152.58, 131.39, 129.65, 129.18, 127.15, 126.97, 101.73, 57.43, 48.73, 44.70, 31.69, 31.47, 28.60, 27.37, 26.94, 26.62, 22.74, 22.65, 14.17, 14.07; **IR (neat):** 1353, 1425, 1456, 1631, 2115, 2856, 2928 cm⁻¹; **HRMS (ESI):** m/z calculated for C₂₃H₃₄N₂O₂ (M+H)⁺: 371.2693; Found: 371.2701.

2-(2-(4-fluorophenyl)-1*H*-indol-3-yl)-N,N-dihexyl-2-oxoacetamide (12), 2 mmol scale: A 25 mL schlenk flask was charged with 741 mg (2.00 mmol) *N,N*-dihexyl-3-(2-isocyanophenyl)-2-methoxyacrylamide, 840 mg (4.00 mmol) 4-fluorophenyl diazonium tetrafluoroborate, 22.4 mg (20.0 μmol, 1 mol%) [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆. A mixture of 72.0 mg (4.00 mmol) water and 16 mL DMF was added. The mixture was degassed by three Freeze-Pump-Thaw cycles and closed under N₂ atmosphere. The flask was irradiated by one internal and four external blue LED with continuous stirring without external cooling. After 12 hours, the mixture was diluted with 120 mL ethyl acetate, washed with water (3 x 40 mL) and brine (40 mL). The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude

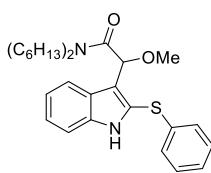


mixture was purified by column chromatography (eluent: hexanes and ethyl acetate gradient from 10% to 20% ethyl acetate) to yield 448 mg (50%) of **12**. **¹H NMR (300 MHz, CDCl₃)** δ 10.71 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.25-7.14 (m, 3H), 7.07 (dd, *J* = 8.7, 5.3 Hz, 2H), 6.63 (t, *J* = 8.7 Hz, 2H), 3.18-2.99 (m, 4H), 1.49 (s, 2H), 1.32-1.03 (m, 14H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.78 (t, *J* = 6.8 Hz, 3H); **¹⁹F NMR (282 MHz, CDCl₃)** δ -111.24; **¹³C NMR (75 MHz, CDCl₃)** δ 186.64, 168.48, 163.44 (d, *J* = 250 Hz), 146.44, 135.78, 131.59 (d, *J* = 8.4 Hz), 127.21, 126.77 (d, *J* = 3.4 Hz), 123.85, 123.20, 121.58, 115.25 (d, *J* = 22 Hz), 112.27, 110.37, 48.63, 45.14, 31.69, 31.42, 28.44, 27.25, 26.97, 26.50, 22.75, 22.59, 14.19, 14.09. **IR (neat):** 1400, 1427, 1498, 1543, 1608, 2858, 2927, 3073, 3185 cm⁻¹; **HRMS (ESI):** m/z calculated for C₂₈H₃₅FN₂O₂ (M+H)⁺: 451.2755; Found: 451.2764.

N,N-Dihexyl-2-oxo-2-(2-(phenylthio)-1H-indol-3-yl)acetamide (13a): Following general procedure, **11** (0.25 mmol) and diphenyl disulfide (0.50 mmol) was irradiated for 48 hours and purified by column chromatography (eluent : DCM and ethyl acetate gradient from 0% to 10% ethyl acetate) to give two products.



Main product **13a** (0.055 g, 47%), R_f 0.6 (DCM/ethyl acetate 10:1), yellowish viscous oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.29 (s, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.60 (m, 1H), 7.51-7.45 (m, 3H), 7.21-7.09 (m, 3H), 3.50 (pt, *J* = 7.8 Hz, 2H), 3.25 (pt, *J* = 7.8 Hz, 2H), 1.76-1.66 (m, 2H), 1.61-1.53 (m, 2H), 1.43-1.27 (m, 6H), 1.20-1.10 (m, 6H), 0.90 (t, *J* = 6.9 Hz, 3H), 0.79 (t, *J* = 6.7 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 185.43, 168.34, 144.33, 136.08, 134.33, 130.41, 130.12, 129.17, 126.57, 123.17, 122.73, 119.99, 111.97, 110.72, 47.97, 44.59, 31.67, 31.27, 28.49, 27.28, 26.88, 26.37, 22.65, 22.45, 14.09, 13.97. **IR (neat):** 1107, 1416, 1461, 1610, 2855, 2927, 3064, 3200 cm⁻¹; **HRMS (ESI):** m/z calculated for C₂₈H₃₇N₂O₂S (M+H)⁺: 465.2570; Found: 465.2570.



Minor product **N,N-Dihexyl-2-methoxy-2-(2-(phenylthio)-1H-indol-3-yl)-acetamide 13b** (0.019 g, 16%), R_f 0.6 (DCM/ethyl acetate 10:1), yellowish viscous oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.15 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.33-7.09 (m, 9H), 5.41 (s, 1H), 3.50-3.41 (m, 1H), 3.37-3.25 (m, 1H), 3.28 (s, 3H), 3.19-3.06 (m, 1H), 2.92-2.83 (m, 1H), 1.53-1.05 (m, 16H), 0.77 (t, *J* = 6.7 Hz, 3H), 0.69 (t, *J* = 6.8 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃)** δ 168.89, 137.20, 136.03, 136.02, 129.28, 127.18, 126.36, 124.37, 123.89, 122.01, 120.79, 118.29, 118.27, 110.64, 110.63, 74.60, 56.90, 47.21, 46.31, 31.58, 29.02, 27.59, 26.63, 26.41, 22.54, 14.00; some signals are doubled due to conformes. **IR (neat):** 910, 1095, 1345, 1439, 1636, 2855, 2926, 3056, 3228 cm⁻¹; **HRMS (ESI):** m/z calculated for C₂₉H₄₀N₂NaO₂ (M+Na)⁺: 503.2703; Found: 503.2703.

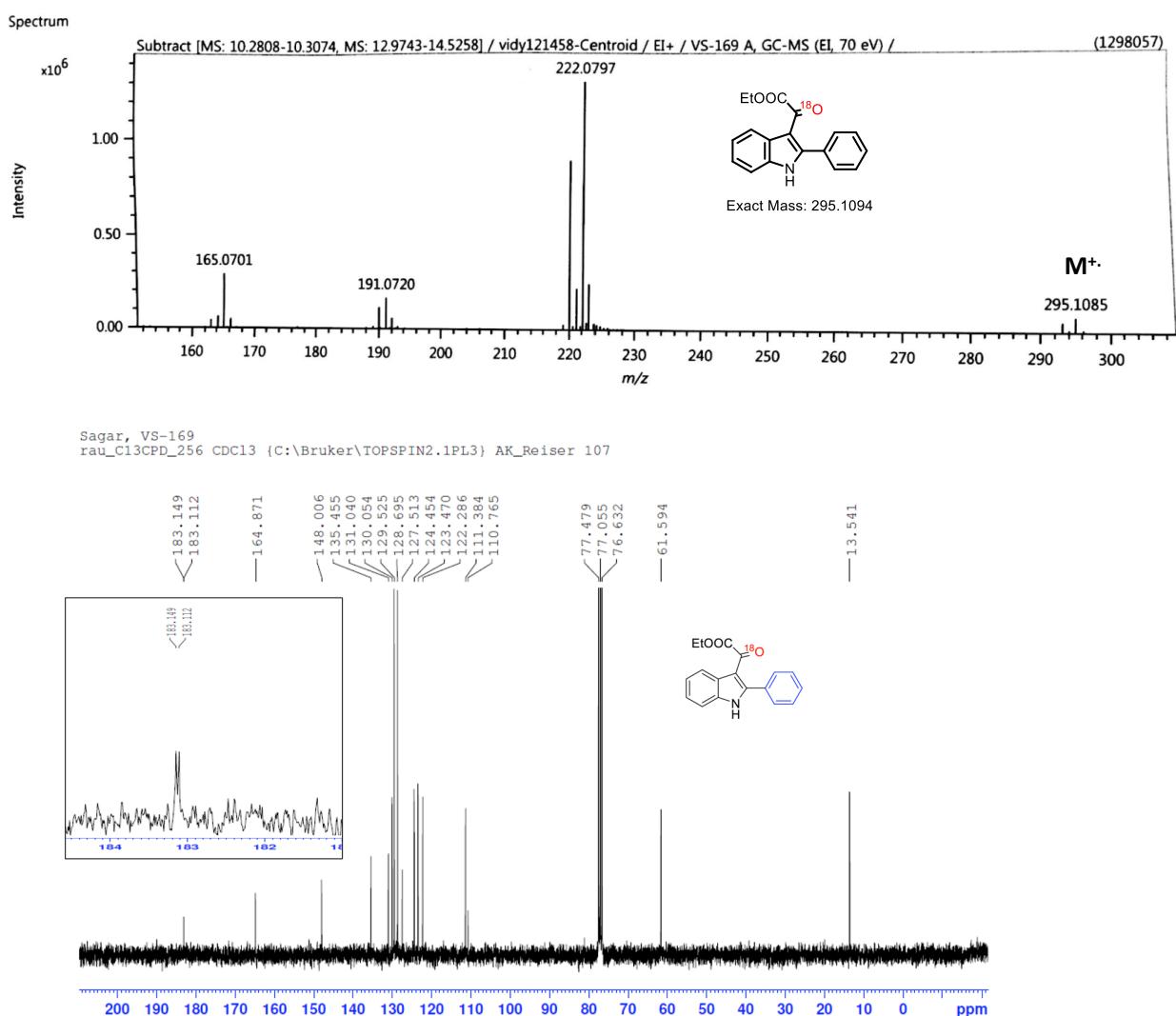


Figure S2: The HRMS and ¹³C of the ¹⁸O incorporated compound **3h** stemming from a labelling experiment in the presence of H₂¹⁸O.

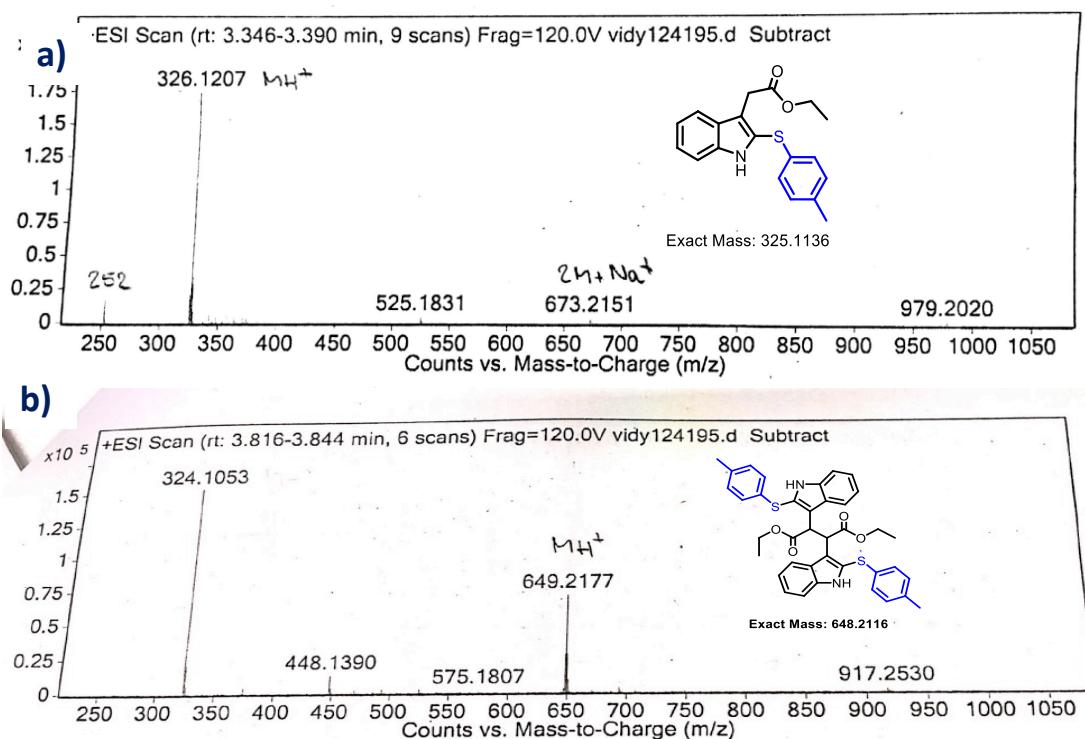
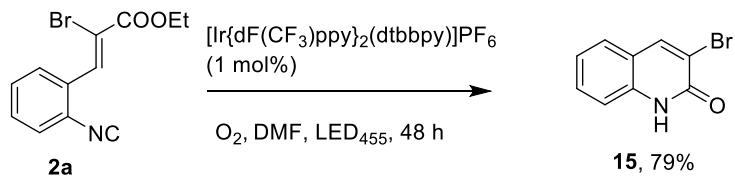


Figure S3: a) HRMS of compound **14a**; b) HRMS of compound **14b**

3-Bromoquinolin-2(1H)-one (15): A Schlenk flask (5 mL size) equipped with a stirring bar was charged with **2a** (0.070 g, 0.25 mmol), $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ (2.8 mg, 0.01 equiv, 1.00 mol%). Then 2 mL of dry DMF was added and the flask was equipped with oxygen balloon. Then the flask was irradiated internally (See Figure S1) with blue LED ($\lambda_{\text{max}} = 455$ nm) with continues stirring at room temperature under oxygen atmosphere. After 48 hours upon completion of the reaction, the mixture was diluted with ethyl acetate (15 mL), washed with water (2 x 15 mL), then brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography (eluent: hexanes and ethyl acetate gradient from 10% to 20% ethyl acetate) to yield pure **15** (0.044 g, 79%) as a white solid. The spectral data is in correlation with reported ones.⁶



Scheme S3: Formation of 3-bromoquinolin-2(1H)-one from **2a**

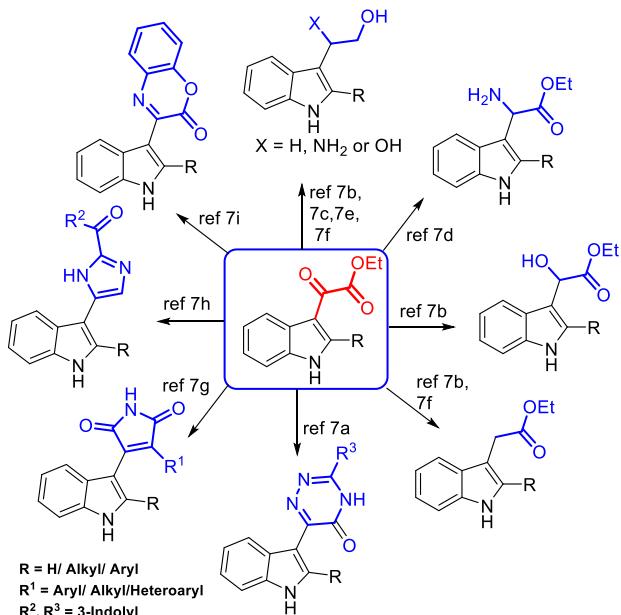
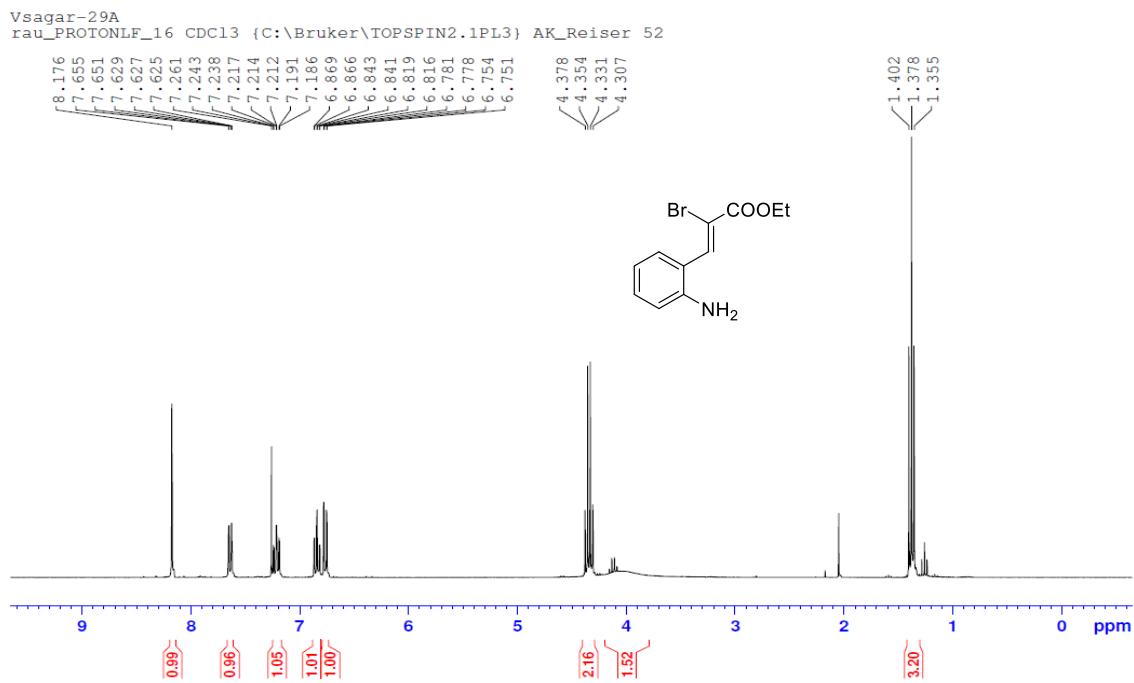


Figure S4: Application of glyoxylate functionality

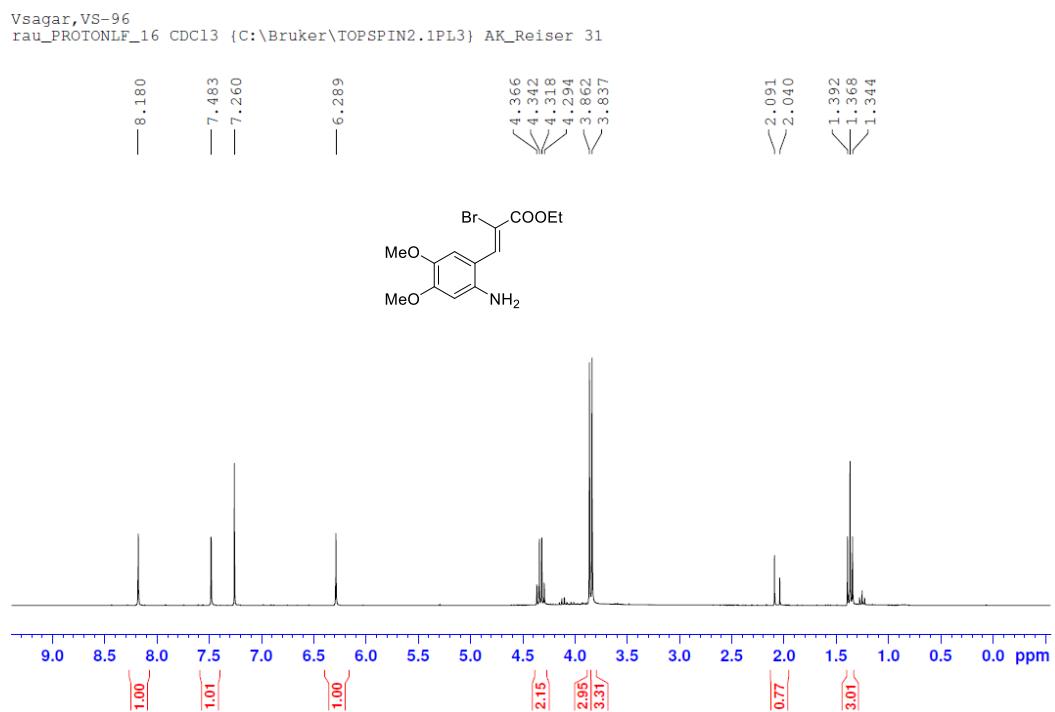
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¹H NMR of S2a

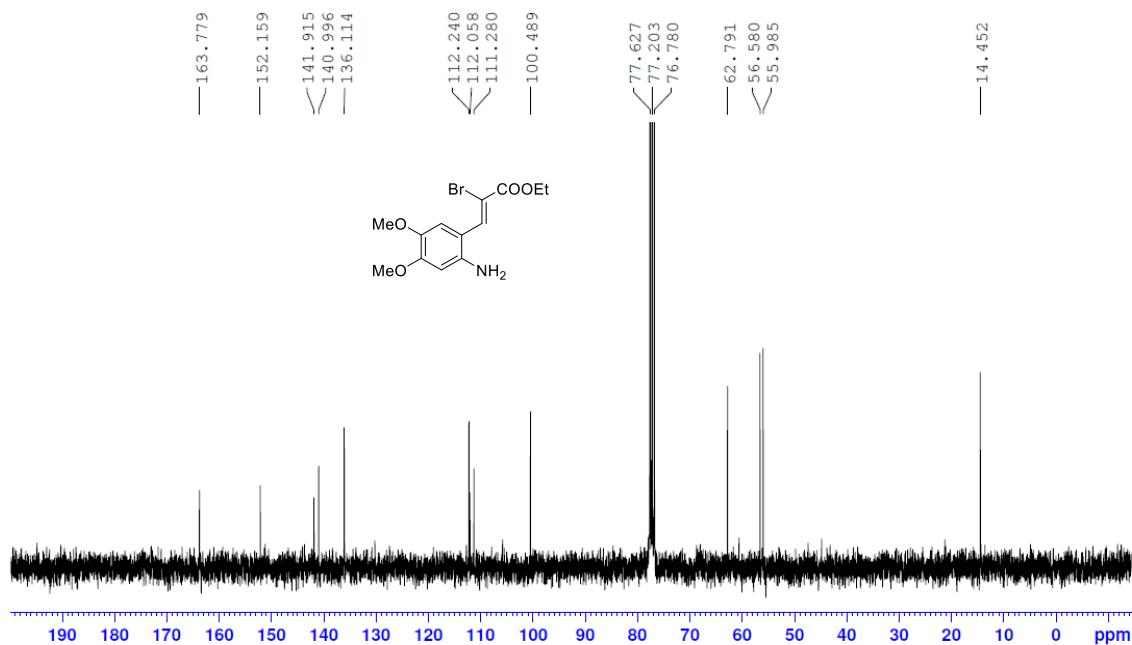


¹H NMR of S2b



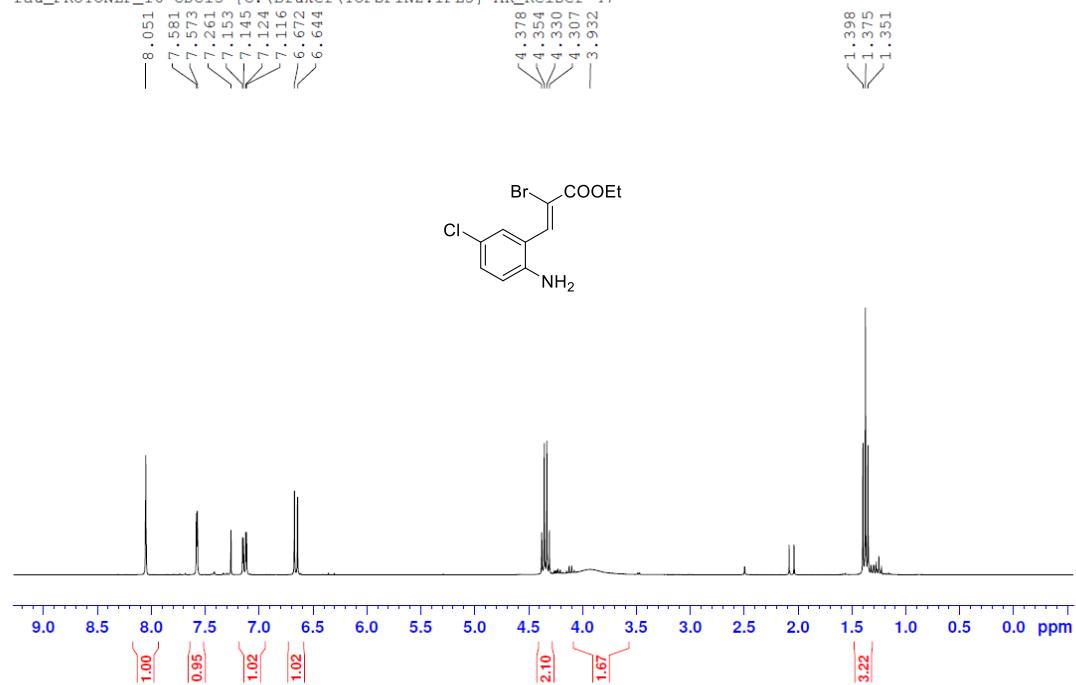
¹³C NMR of **S2b**

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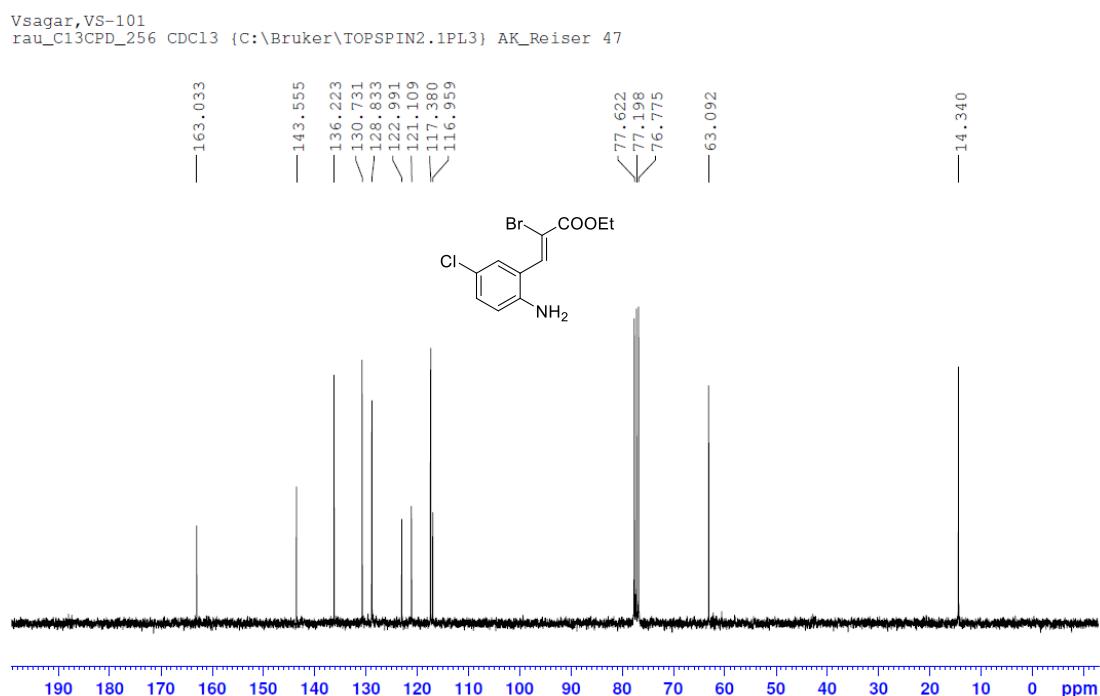


¹H NMR of **S2c**

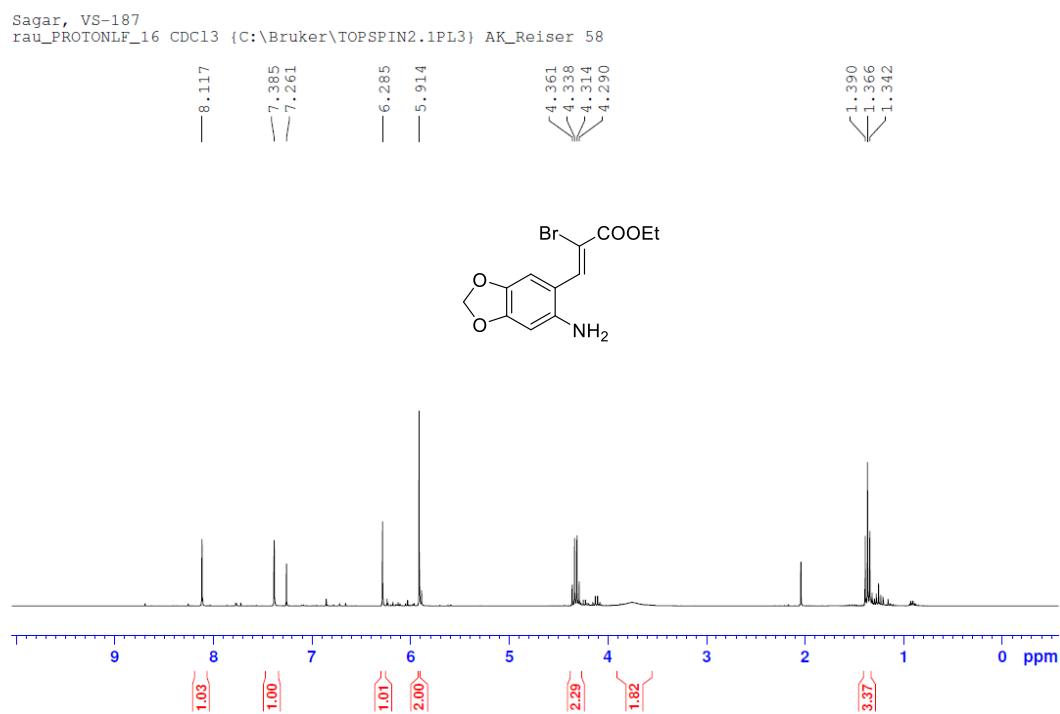
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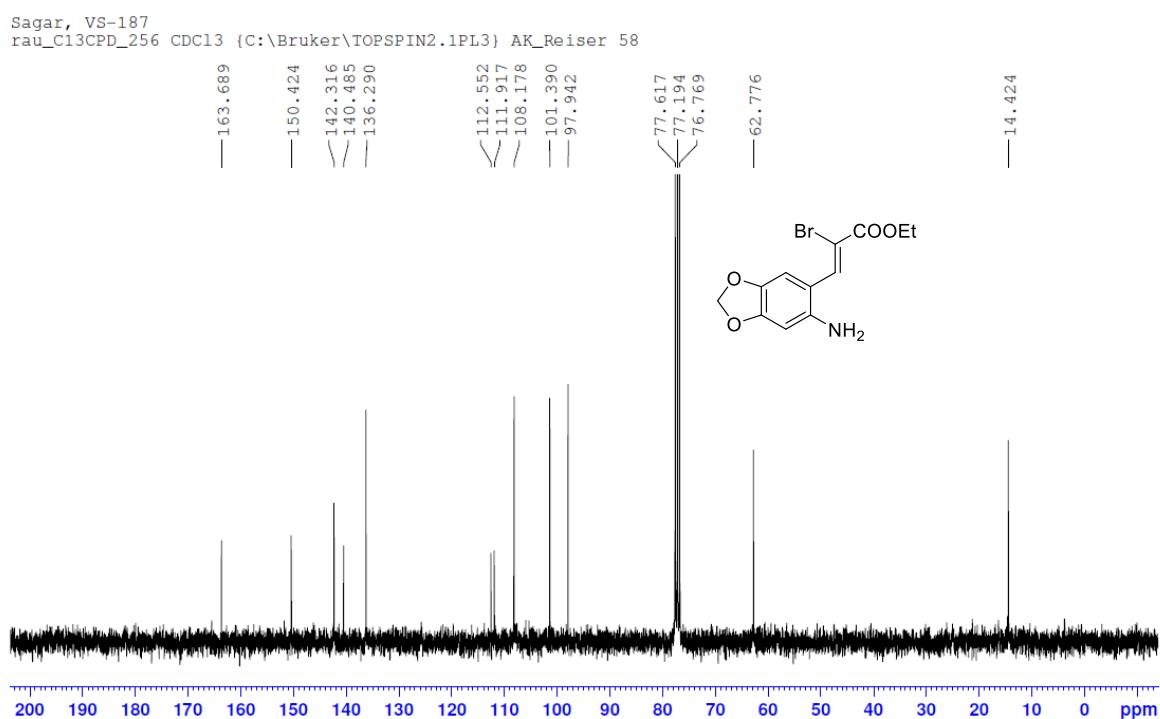
¹³C NMR of S2c



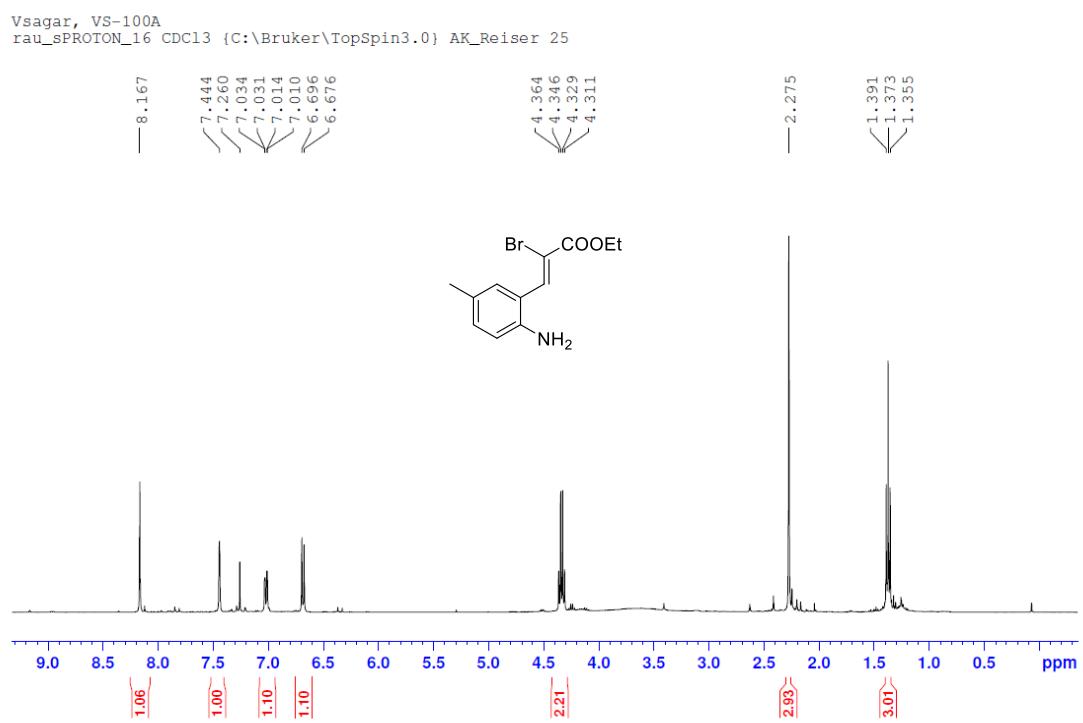
¹H NMR of S2d



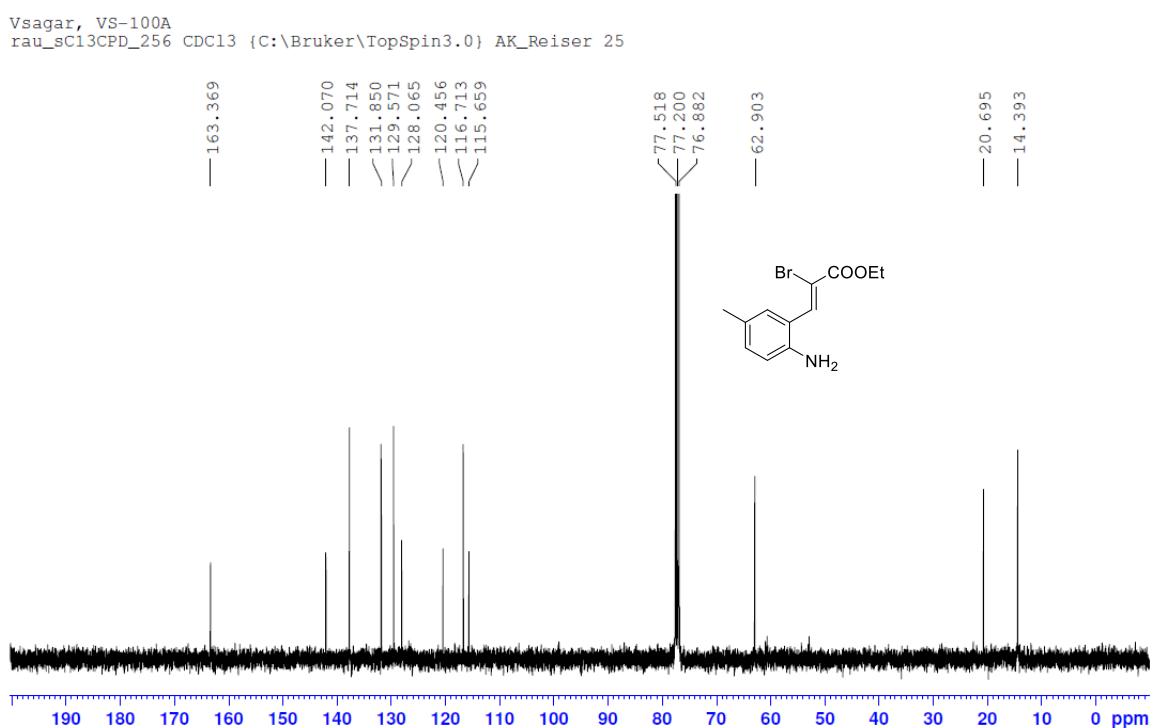
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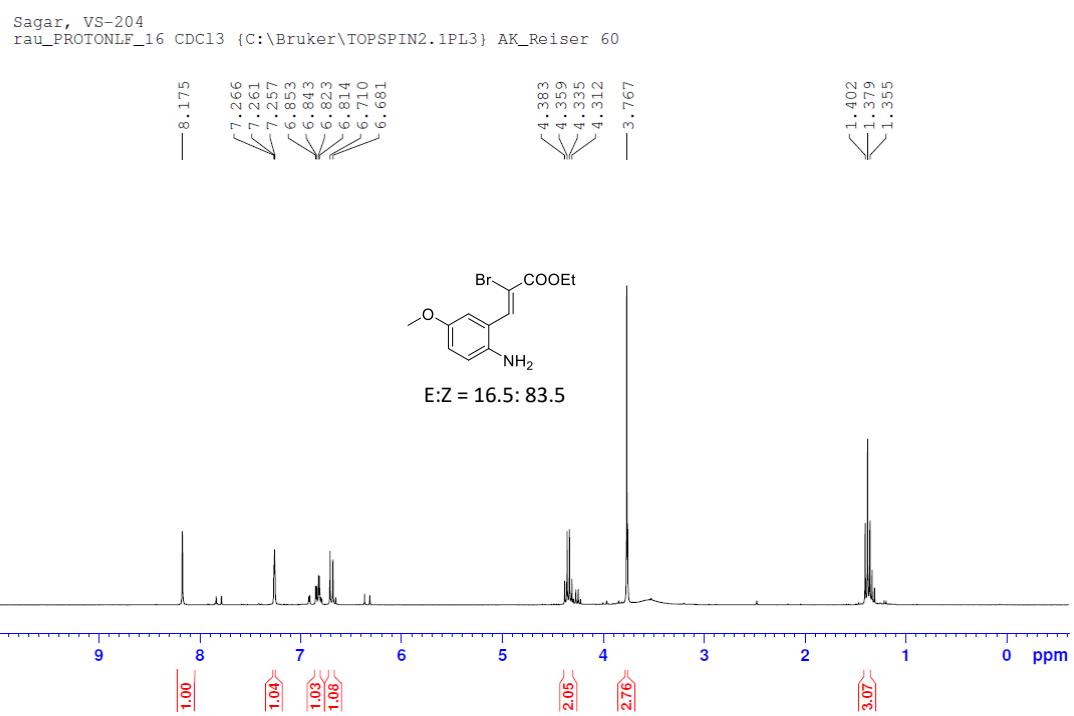
¹H NMR of S2e



¹³C NMR of S2e

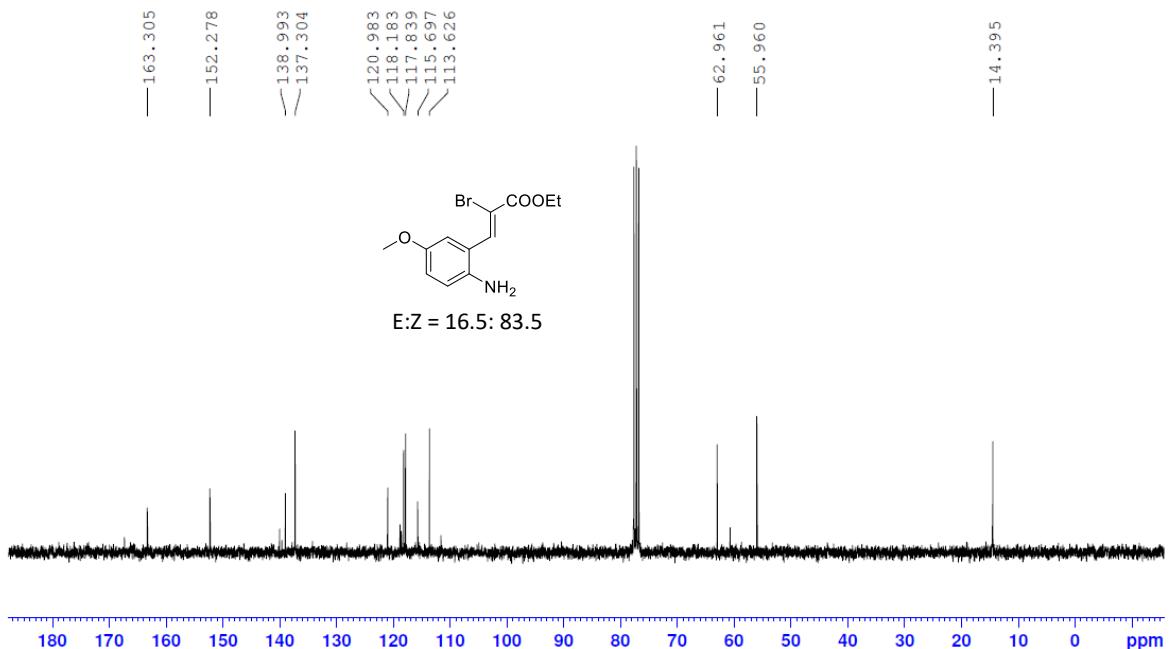


¹H NMR of S2f



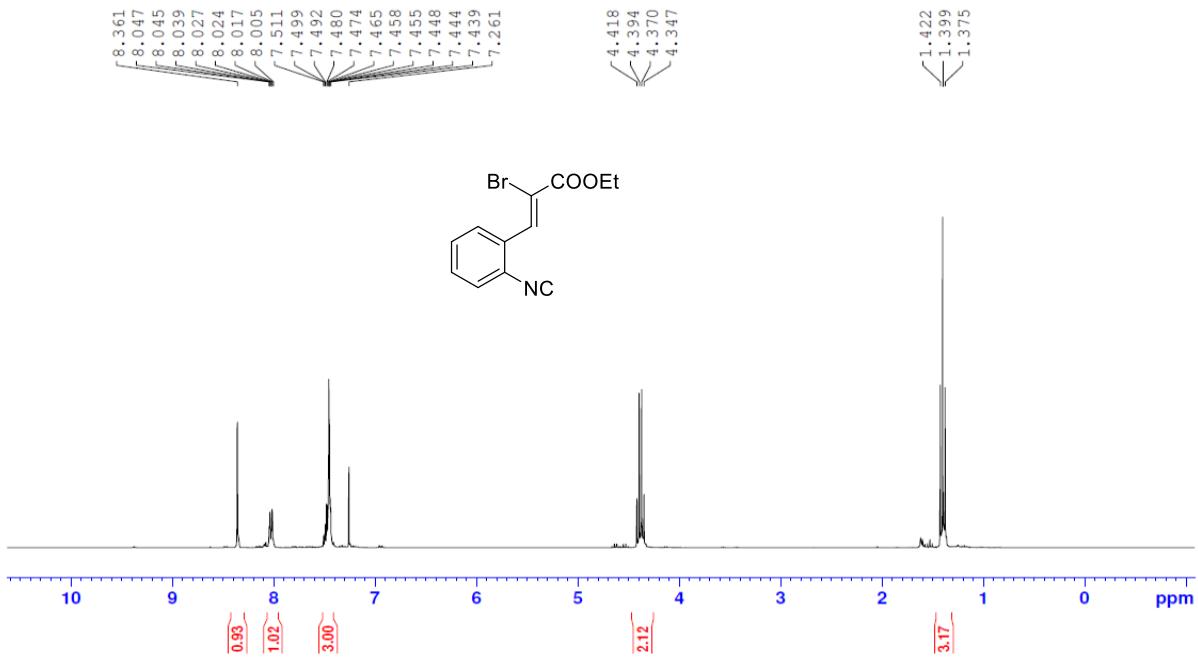
¹³C NMR of **S2f**

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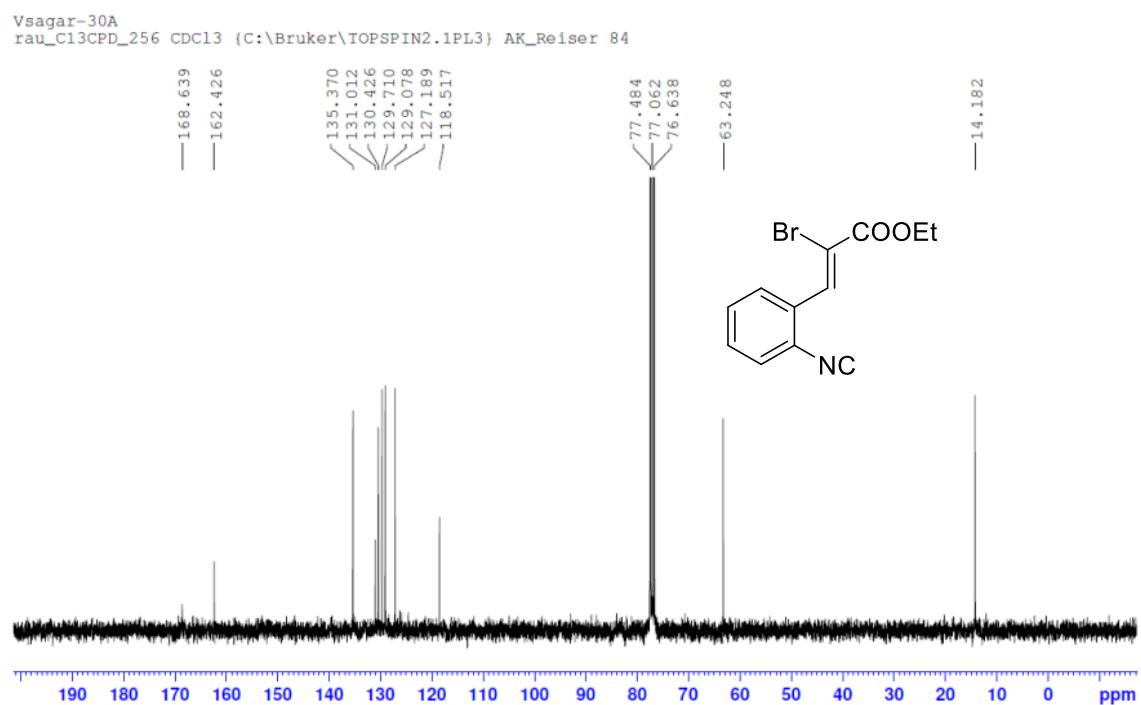


¹H NMR of **2a**

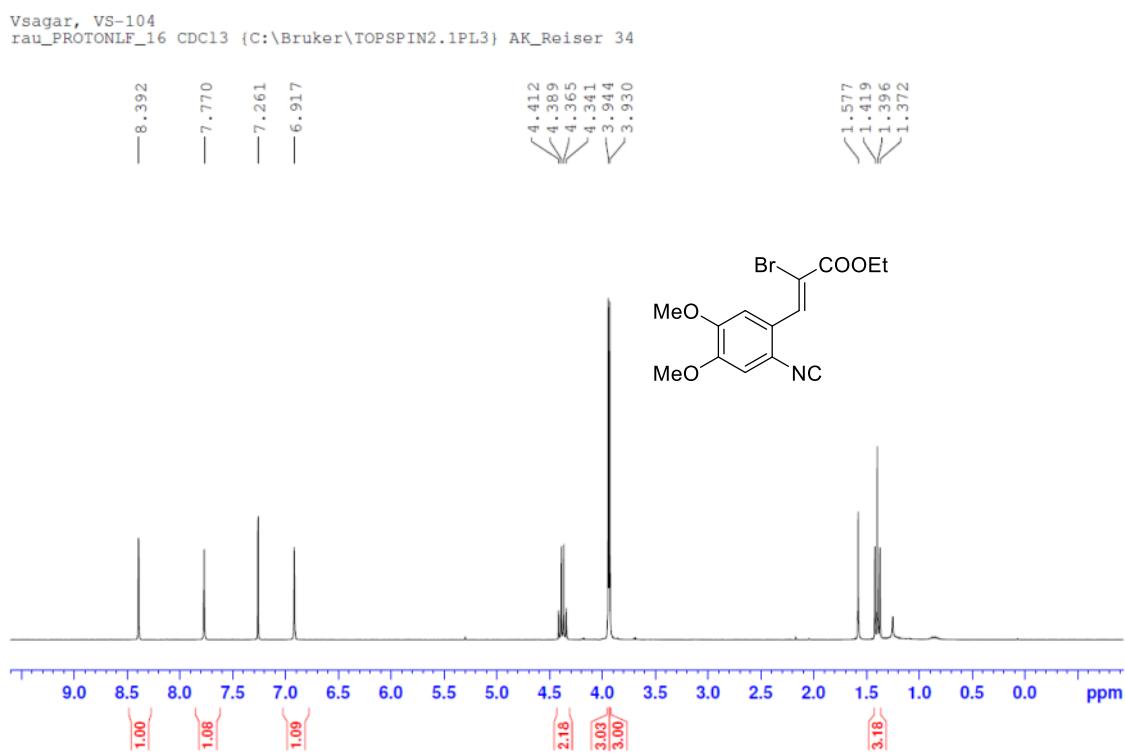
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¹³C NMR of **2a**

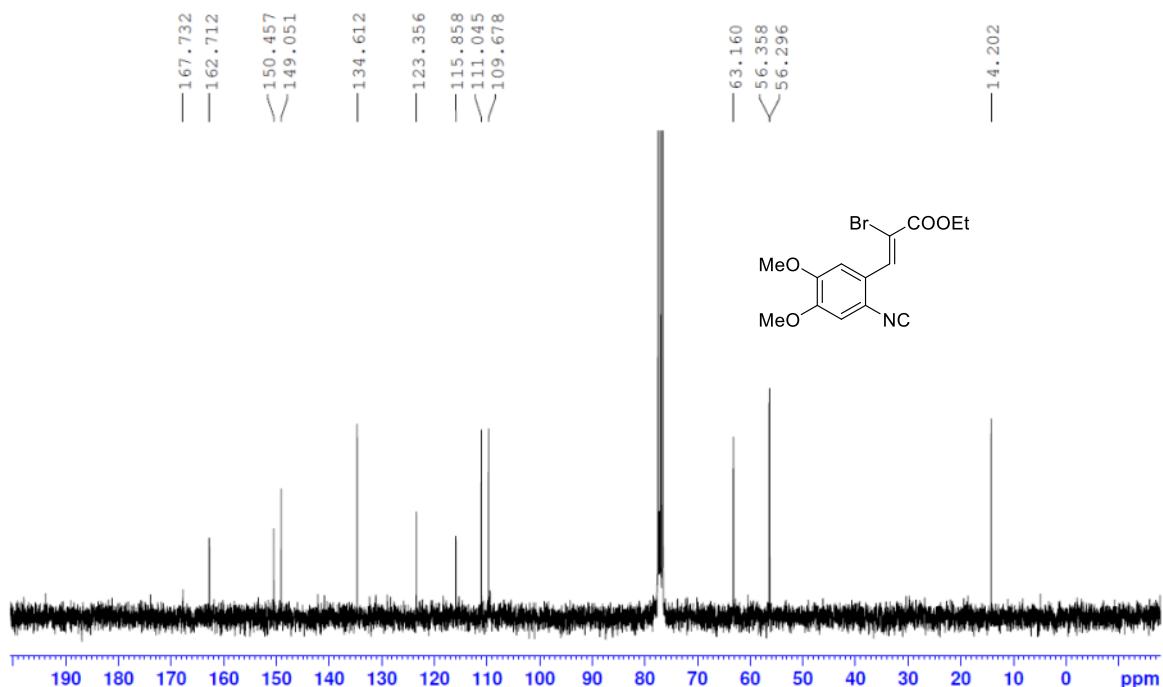


¹H NMR of **2b**



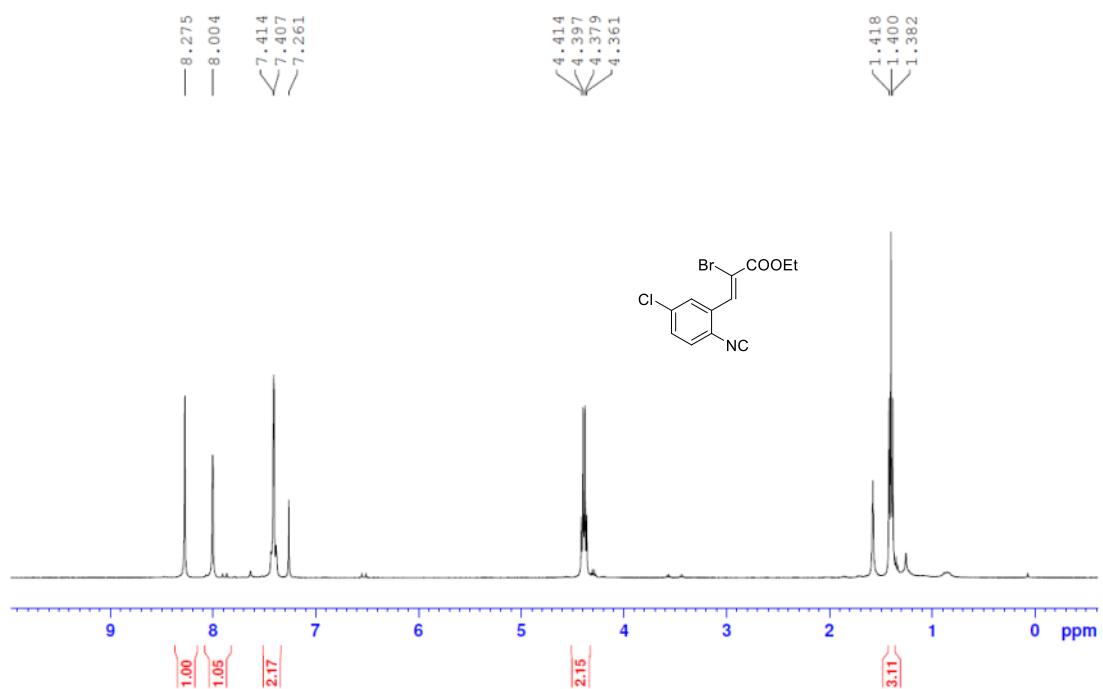
¹³C NMR of **2b**

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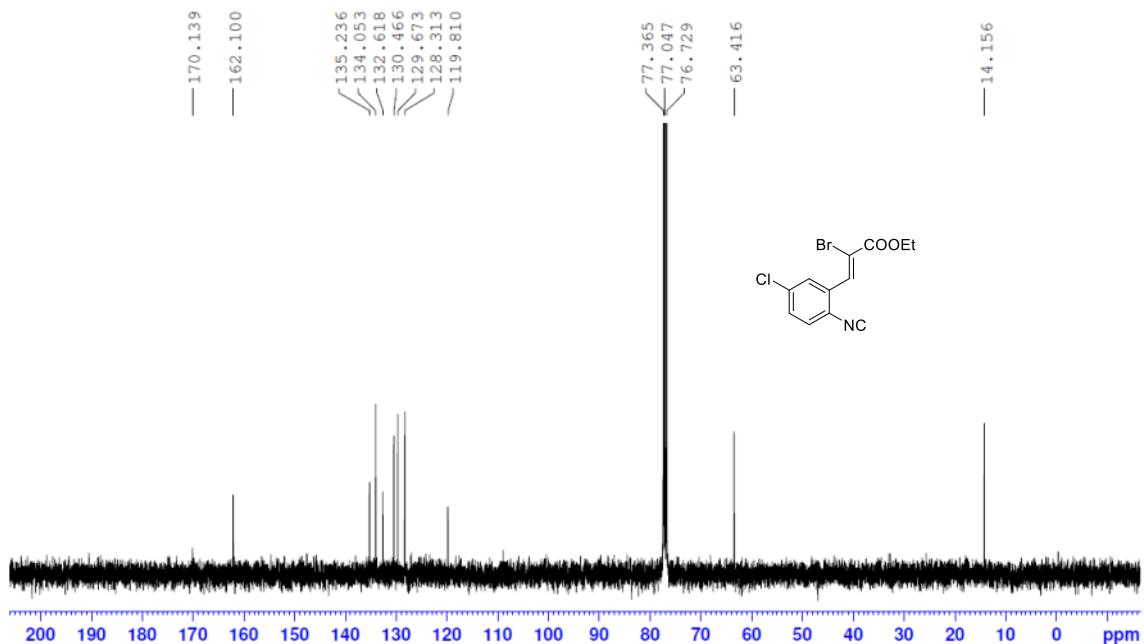
¹H NMR of **2c**

Vsagar, VS-105
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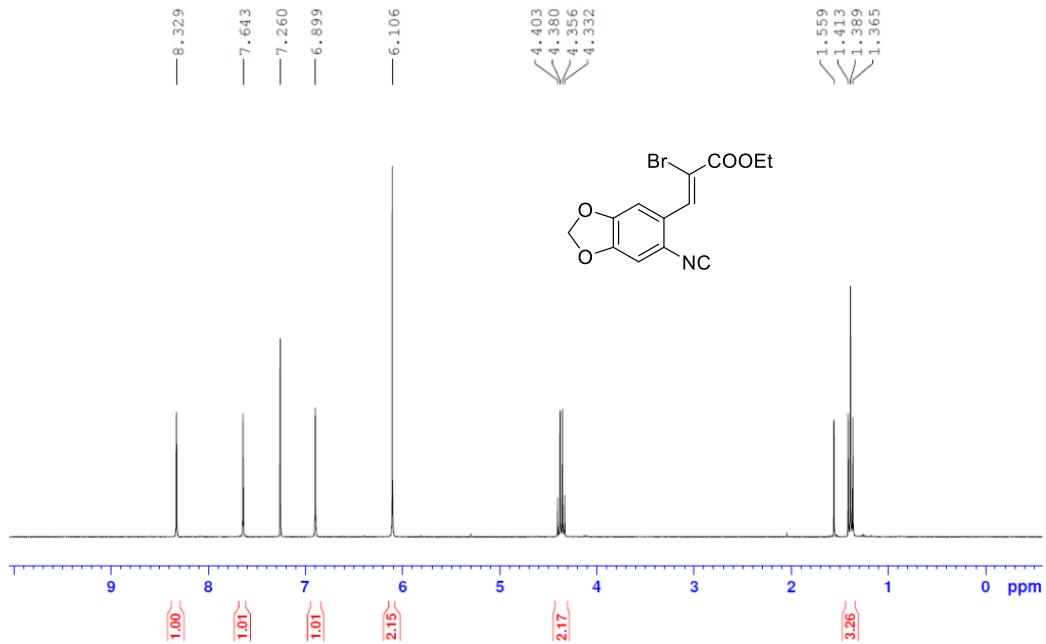
¹³C NMR of **2c**

Vsgaar, VS-105
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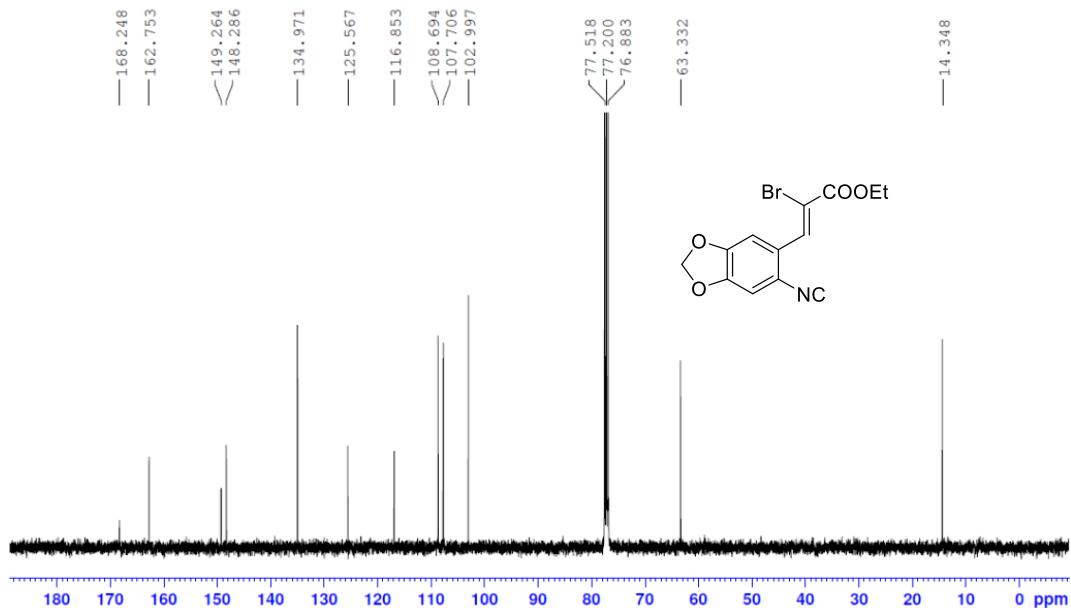
¹H NMR of **2d**

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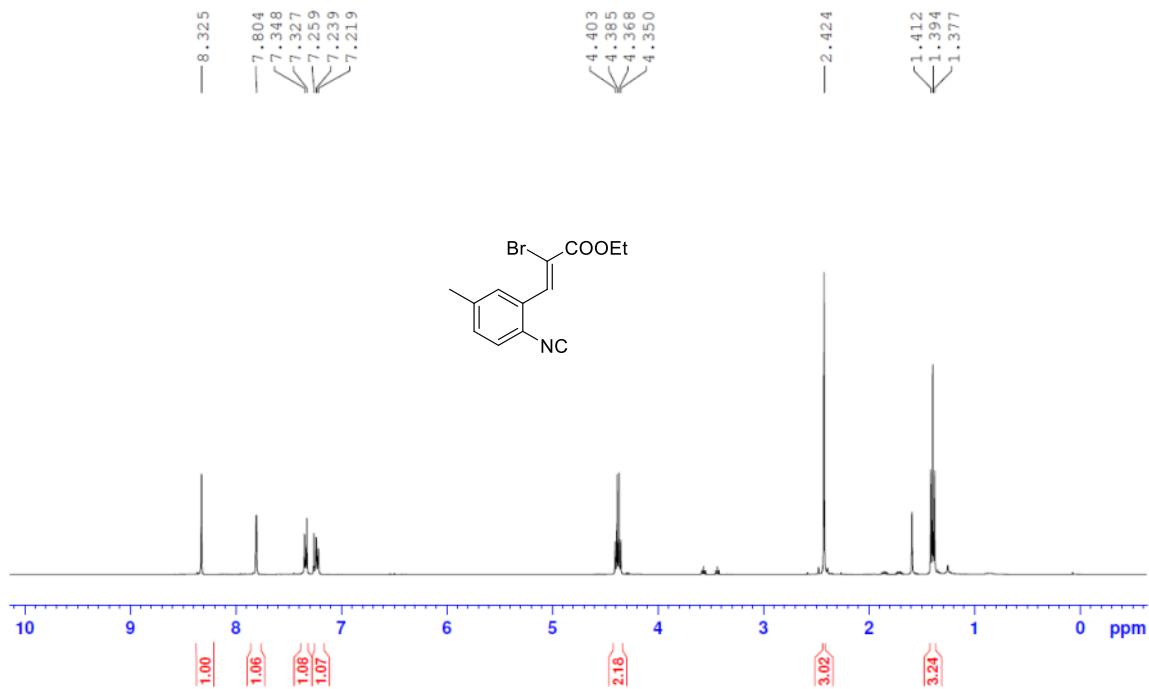
¹³C NMR of **2d**

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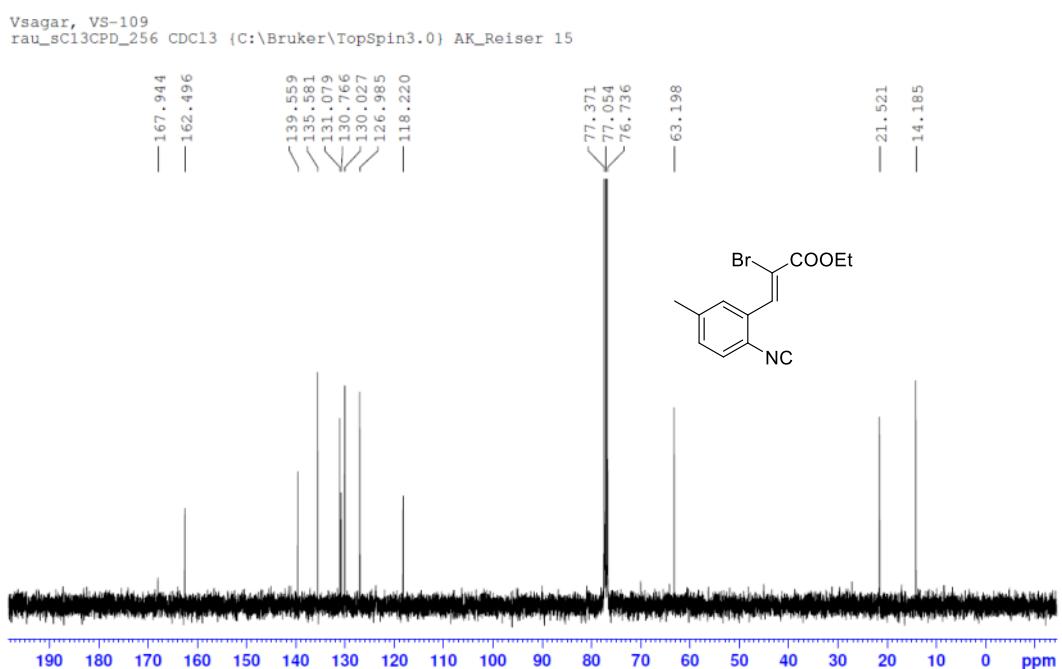


¹H NMR of **2e**

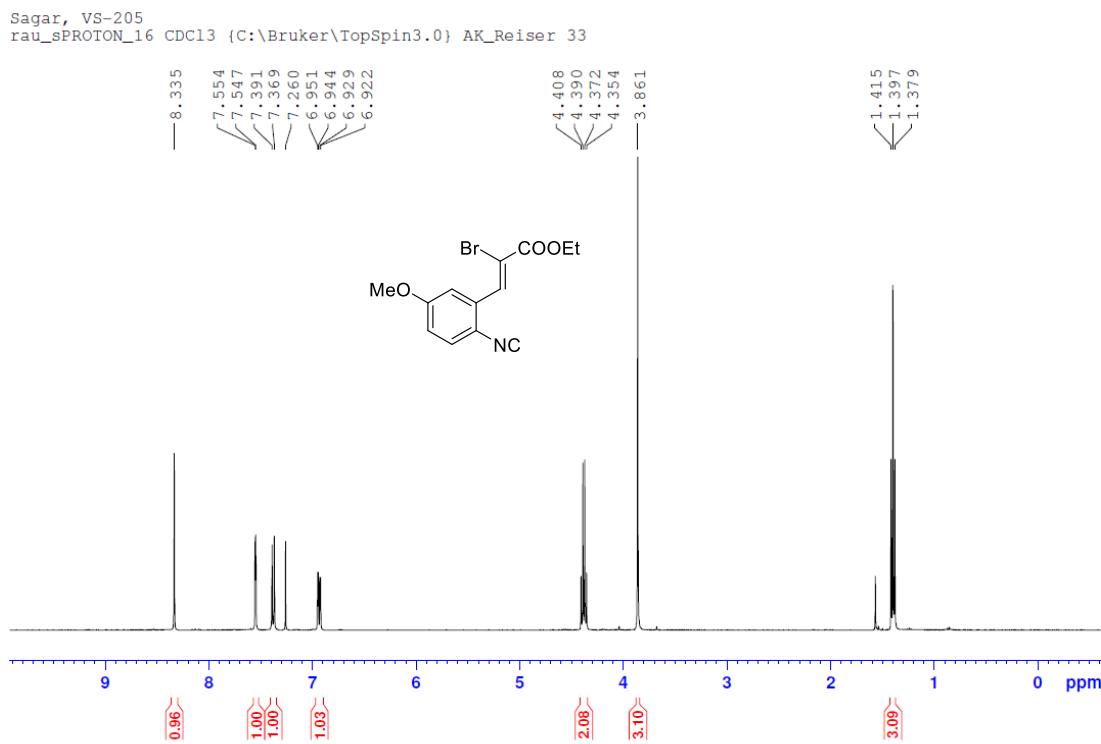
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¹³C NMR of **2e**

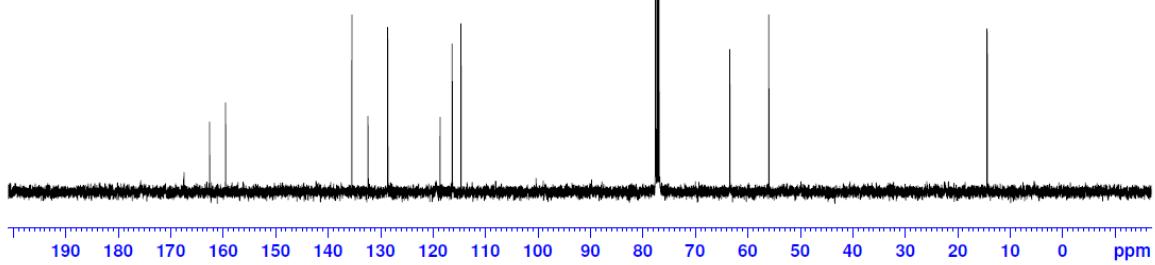
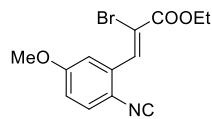
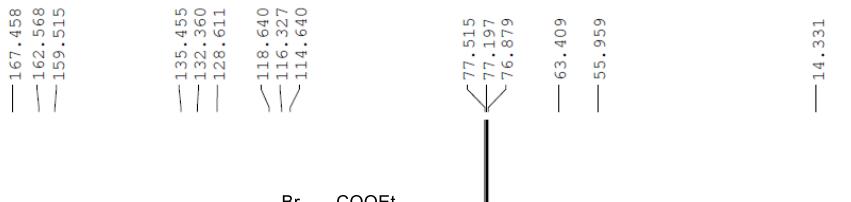


¹H NMR of **2f**



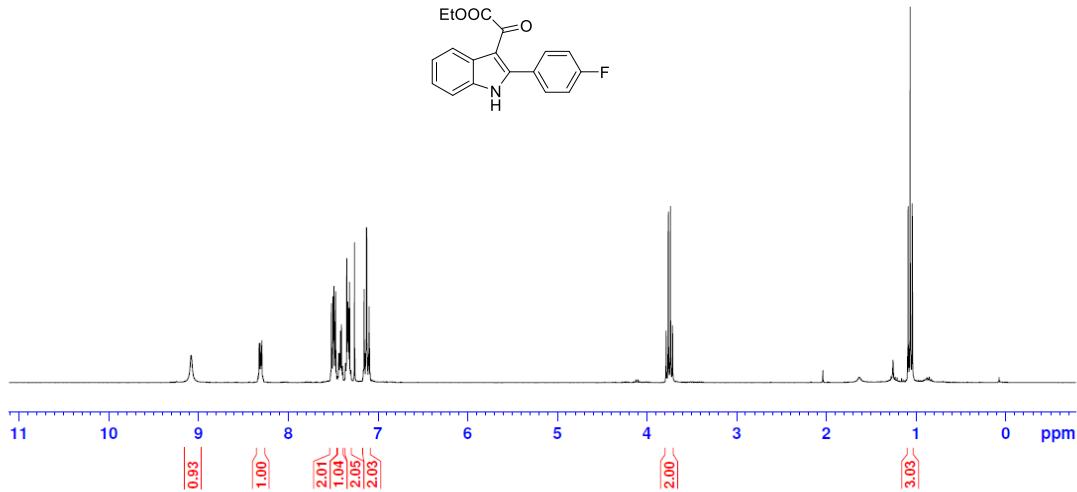
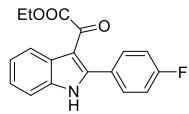
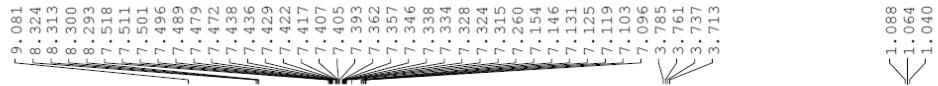
¹³C NMR of 2f

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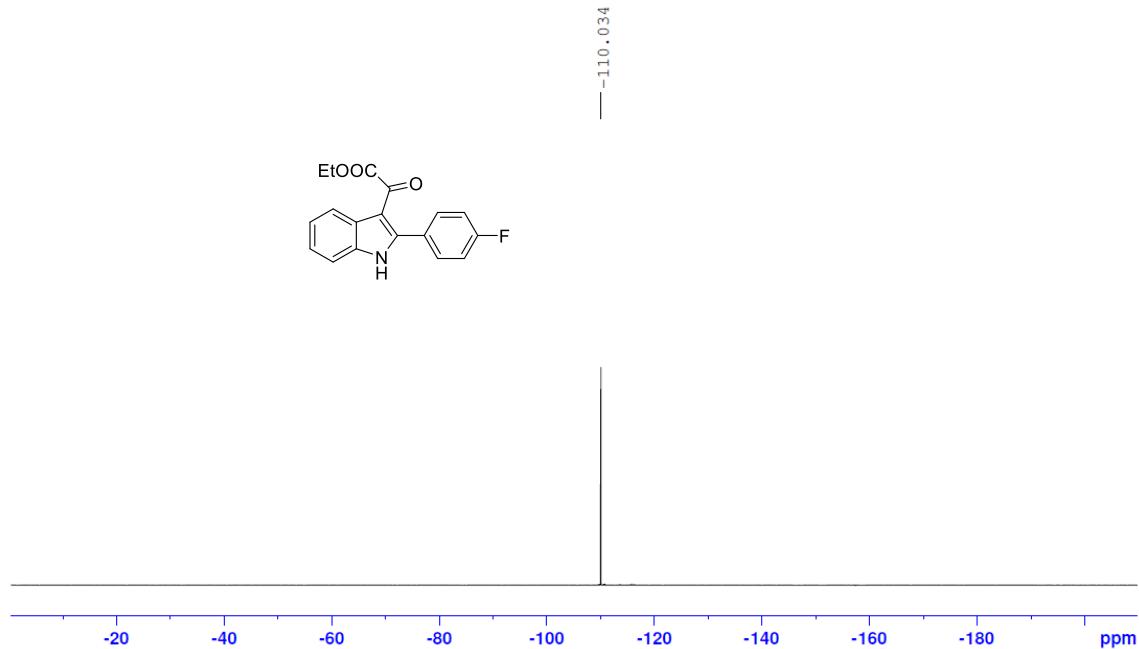
¹H NMR of 3a

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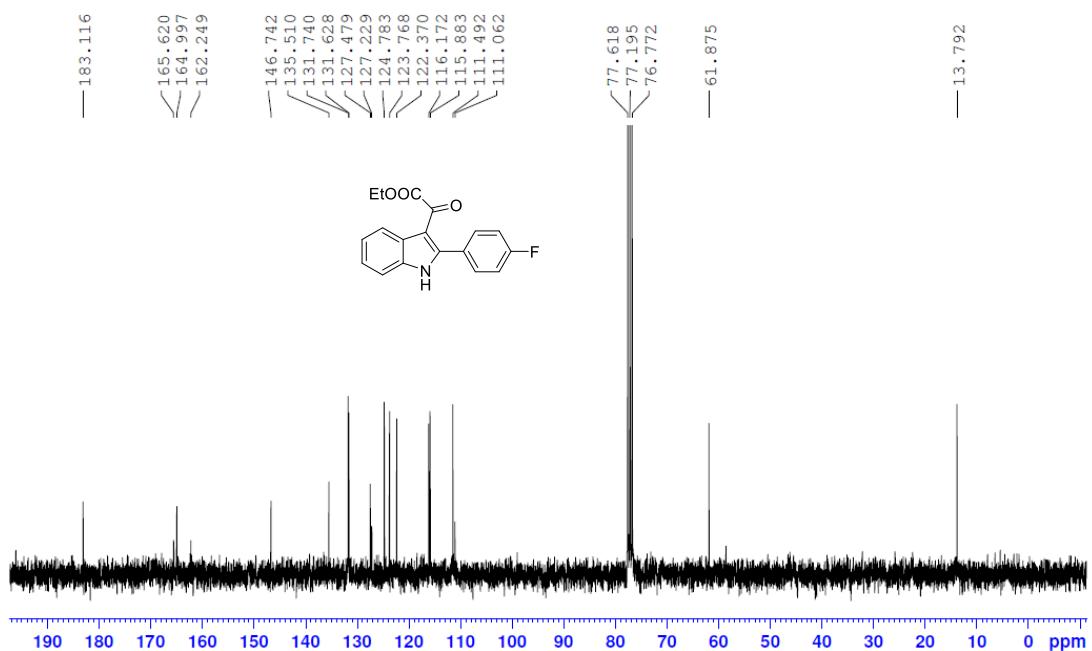
¹⁹F NMR of **3a**

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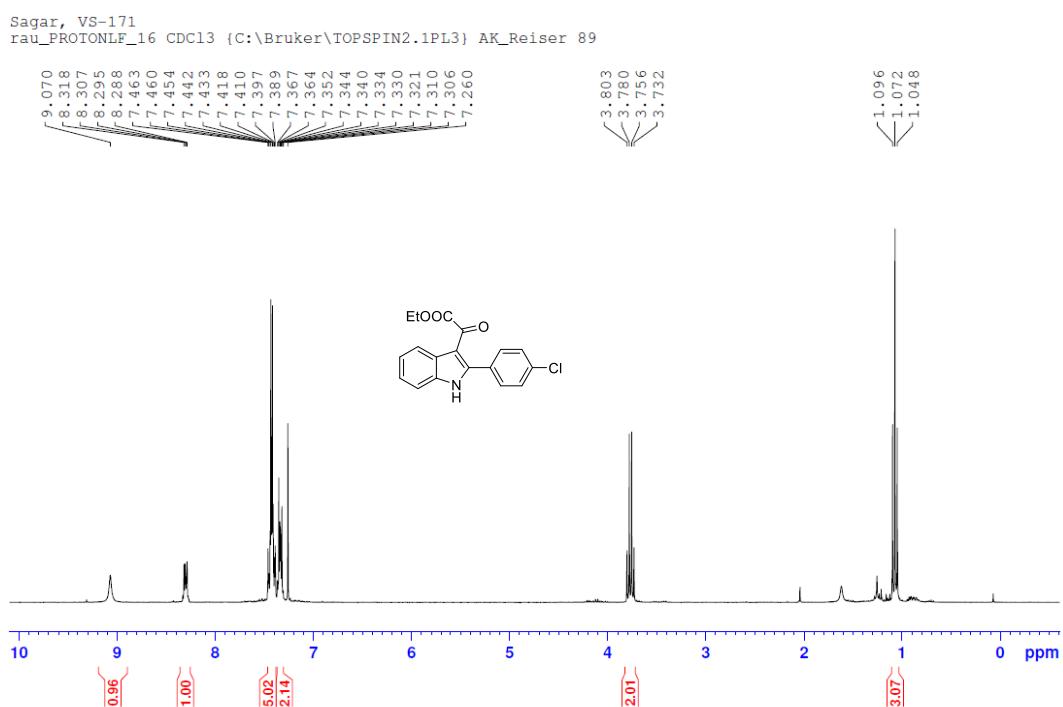


¹³C NMR of **3a**

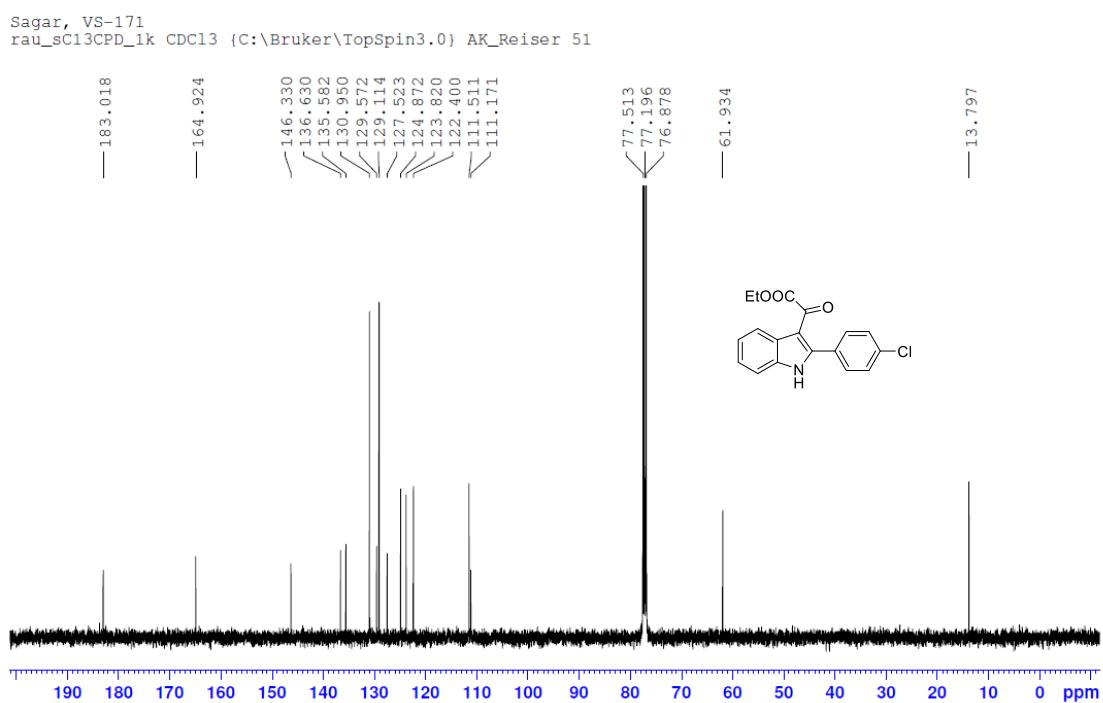
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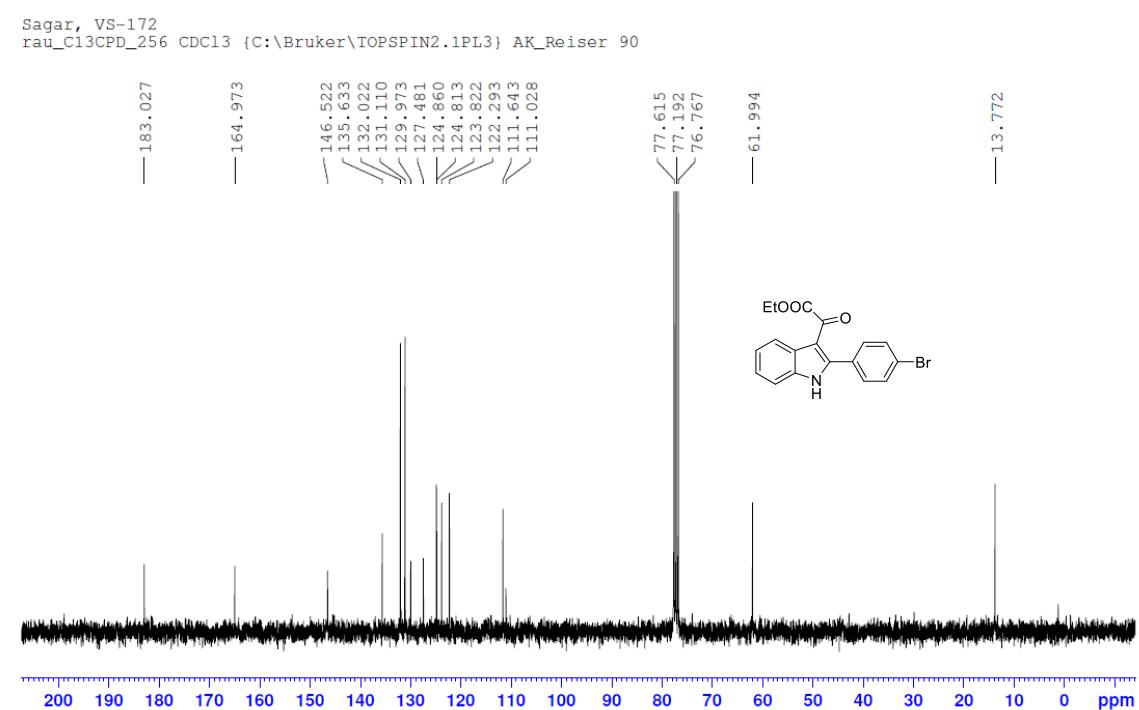
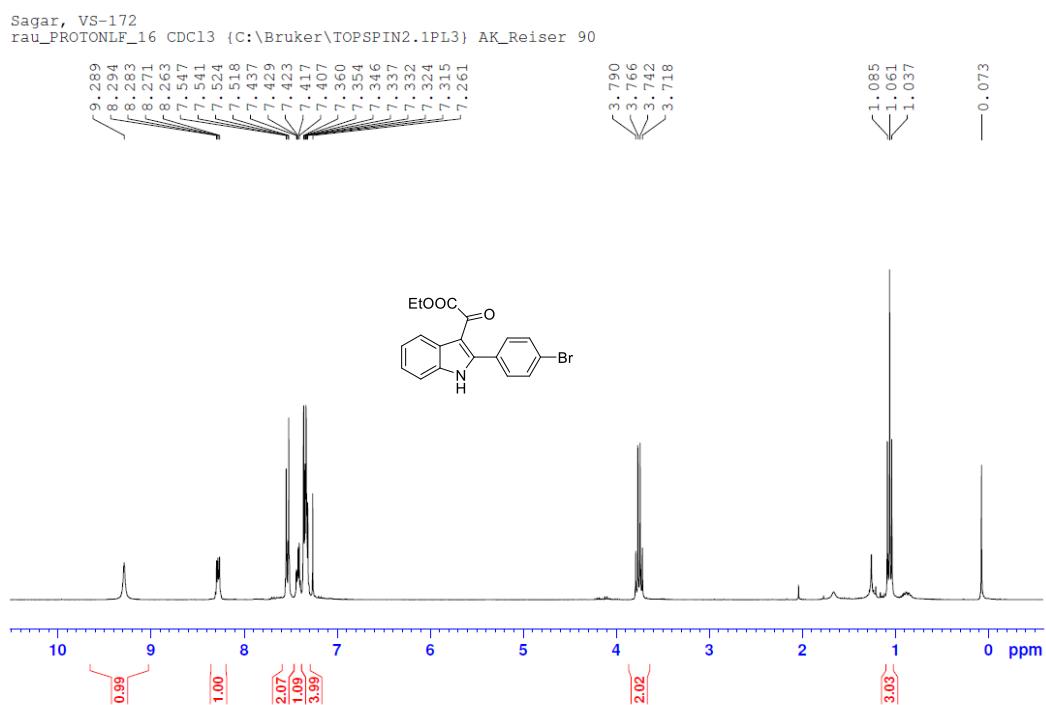
¹H NMR of **3b**



¹³C NMR of **3b**

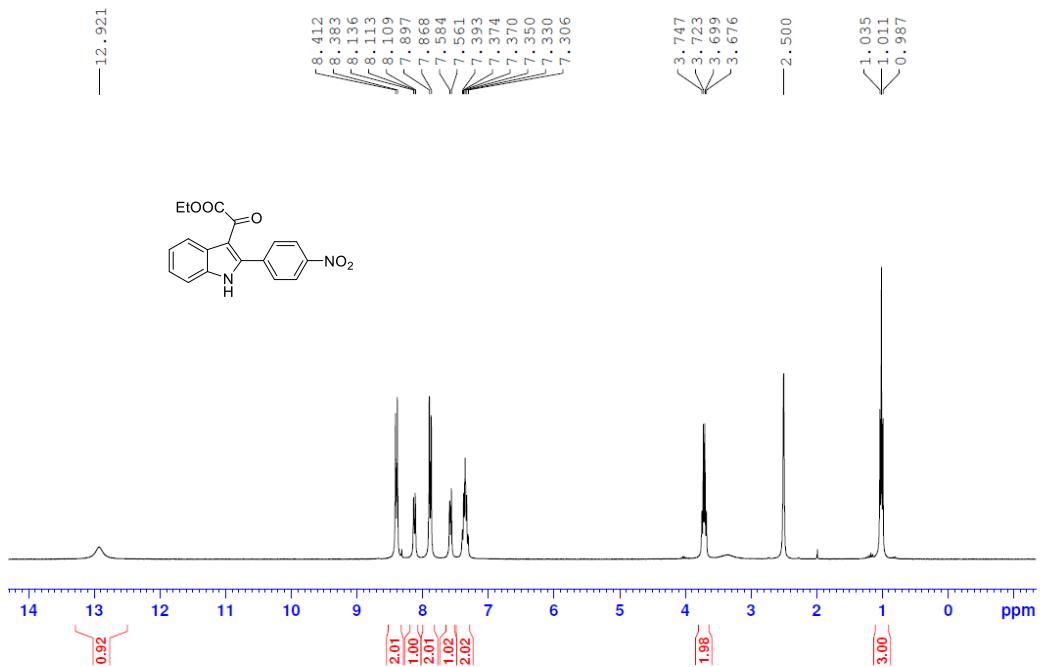


¹H NMR of **3c**



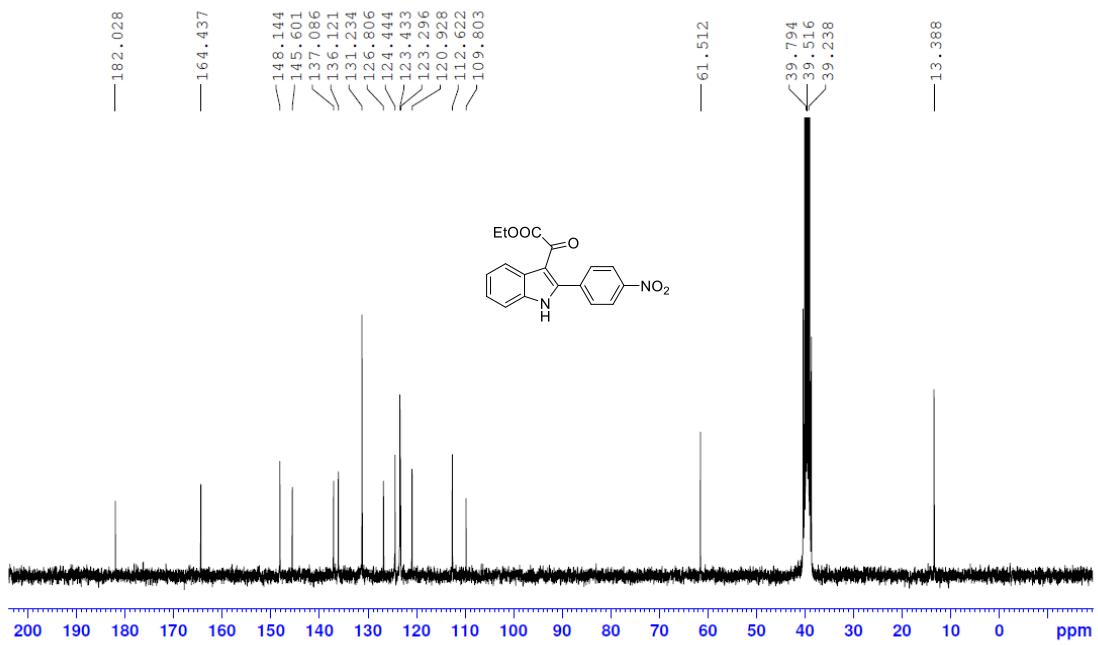
¹H NMR of 3d

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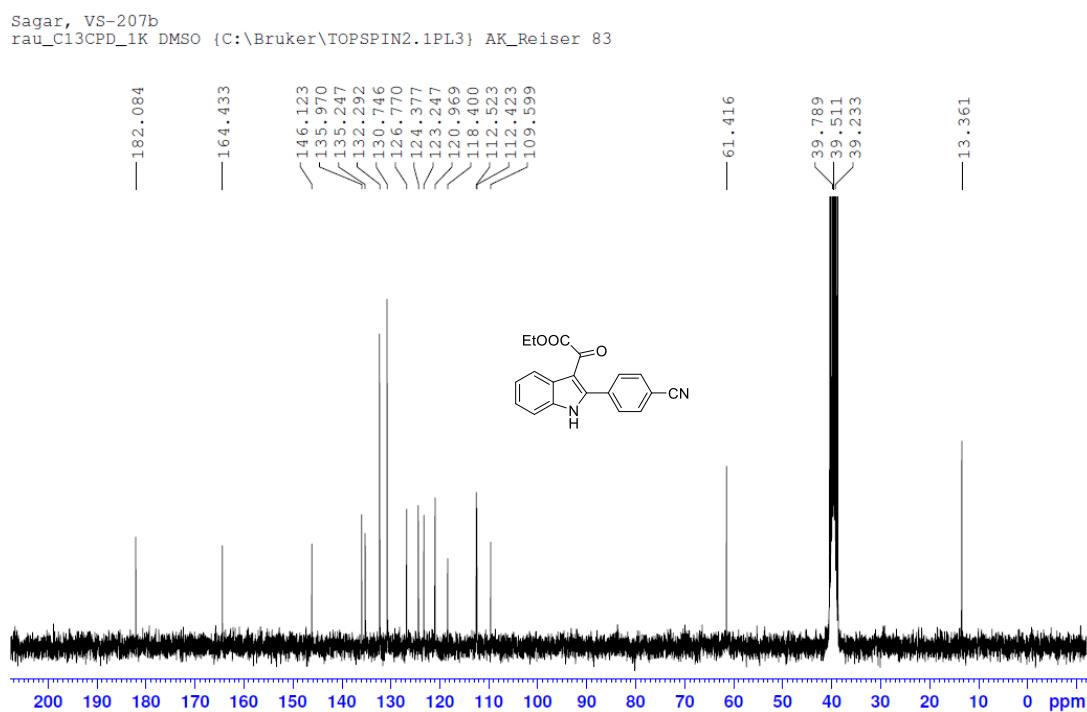
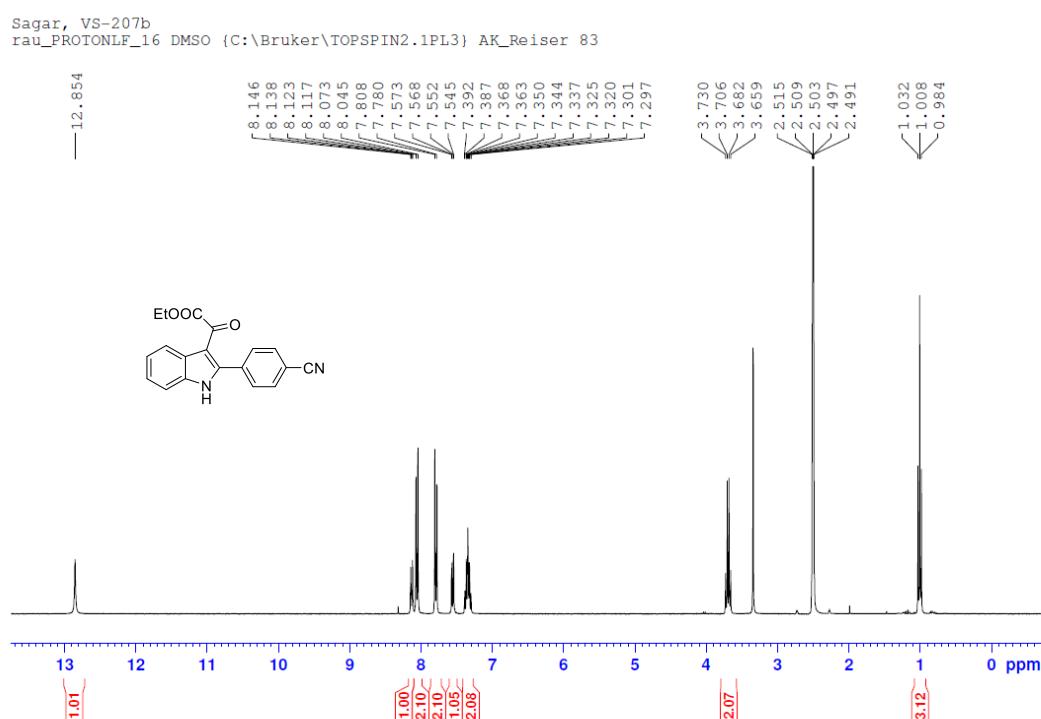


¹³C NMR of 3d

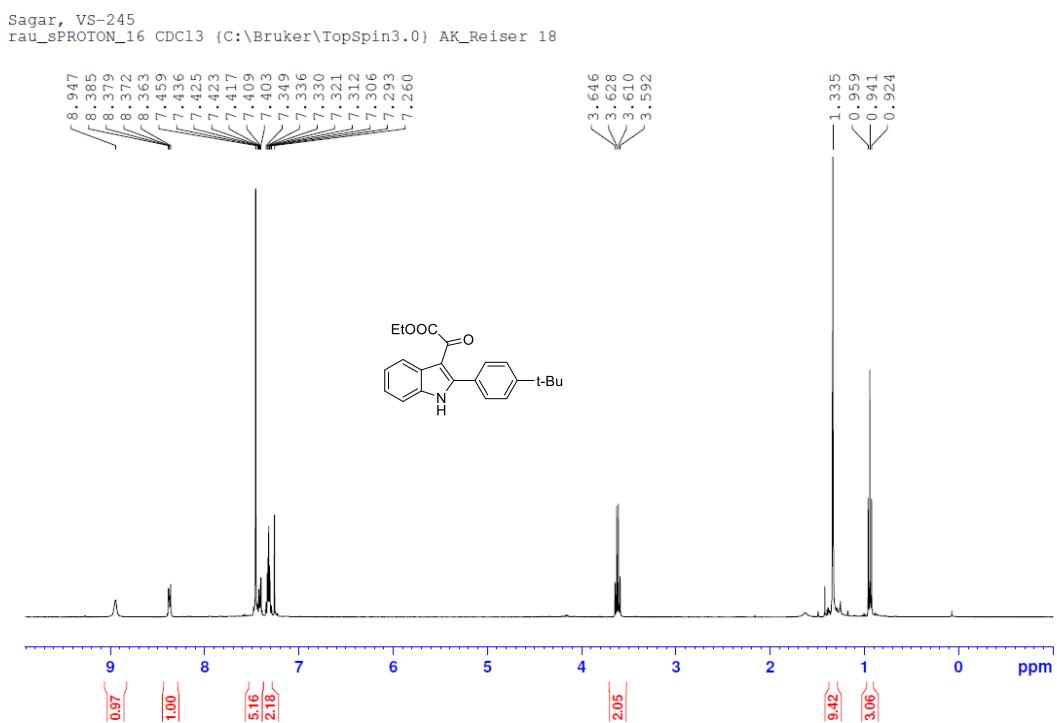
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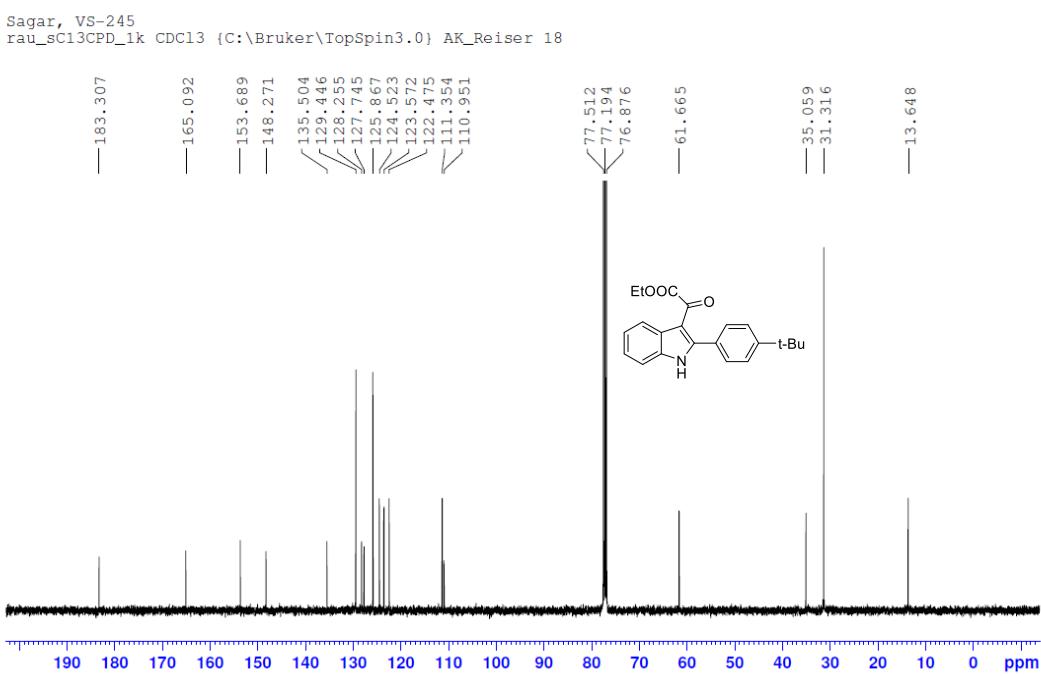
¹H NMR of **3e**



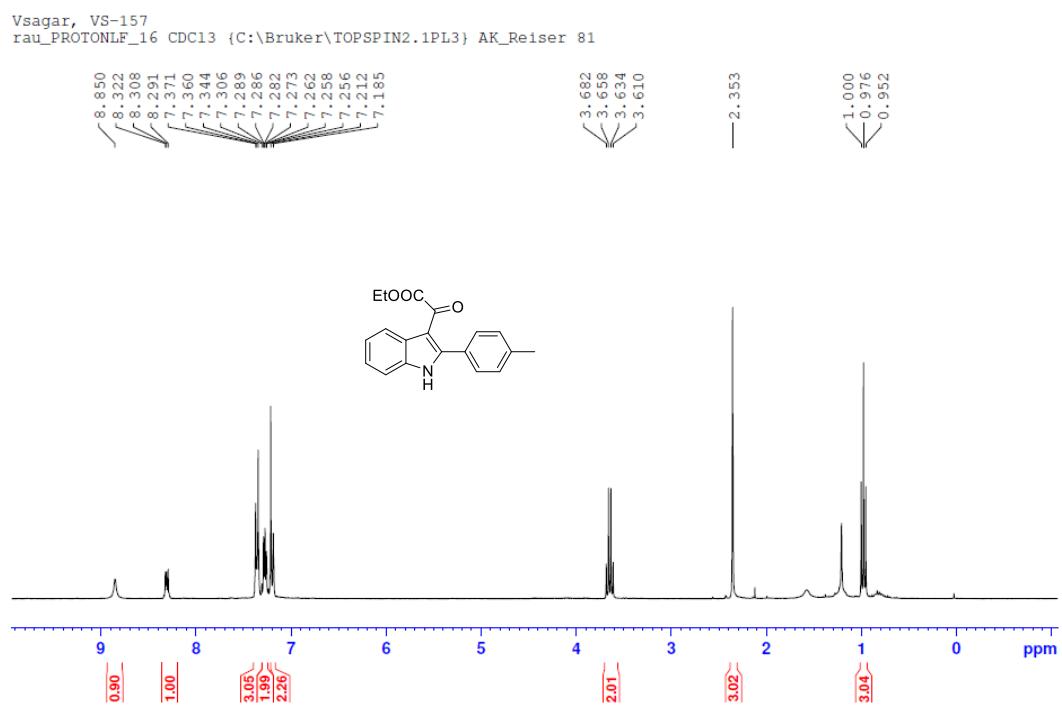
¹H NMR of 3f



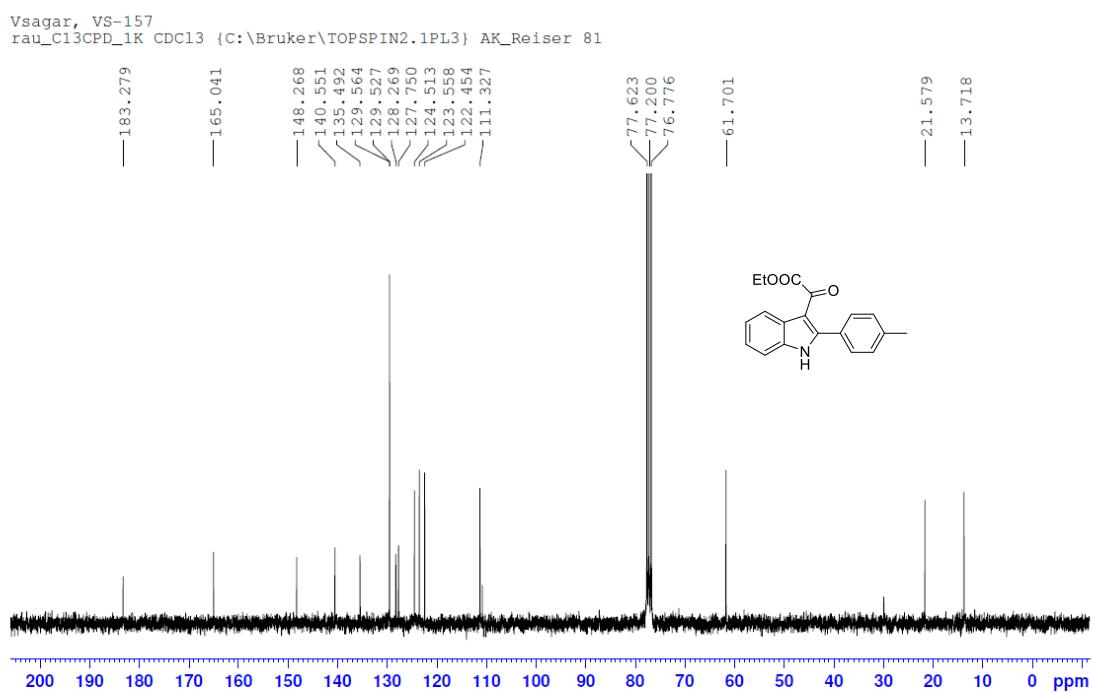
¹³C NMR of 3f



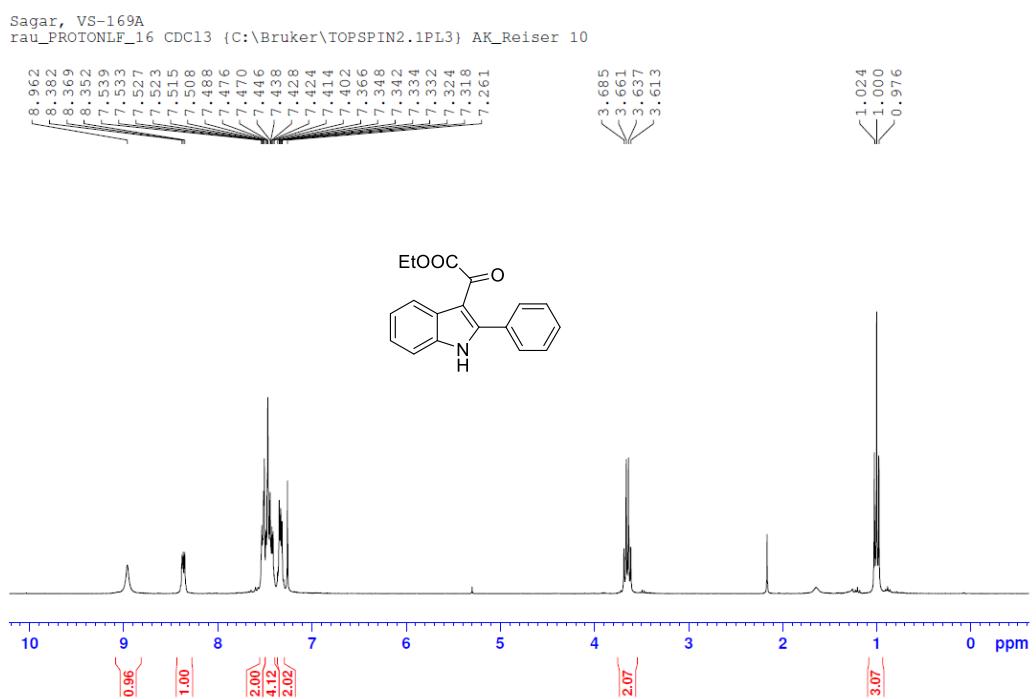
¹H NMR of **3g**



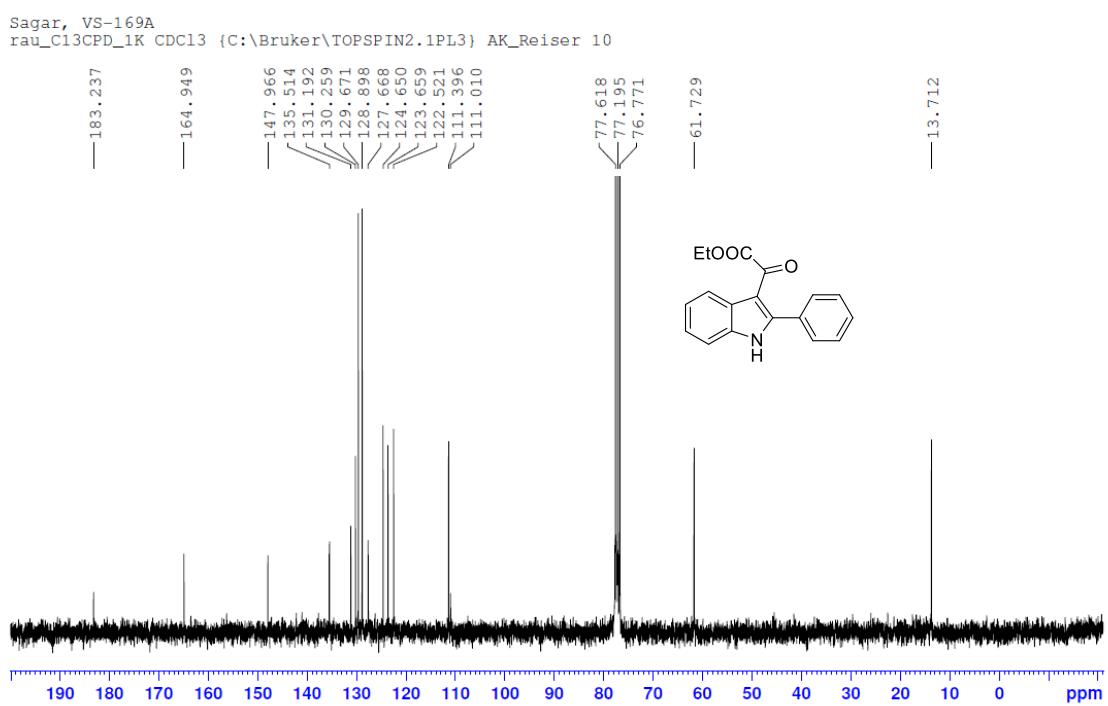
¹³C NMR of **3g**



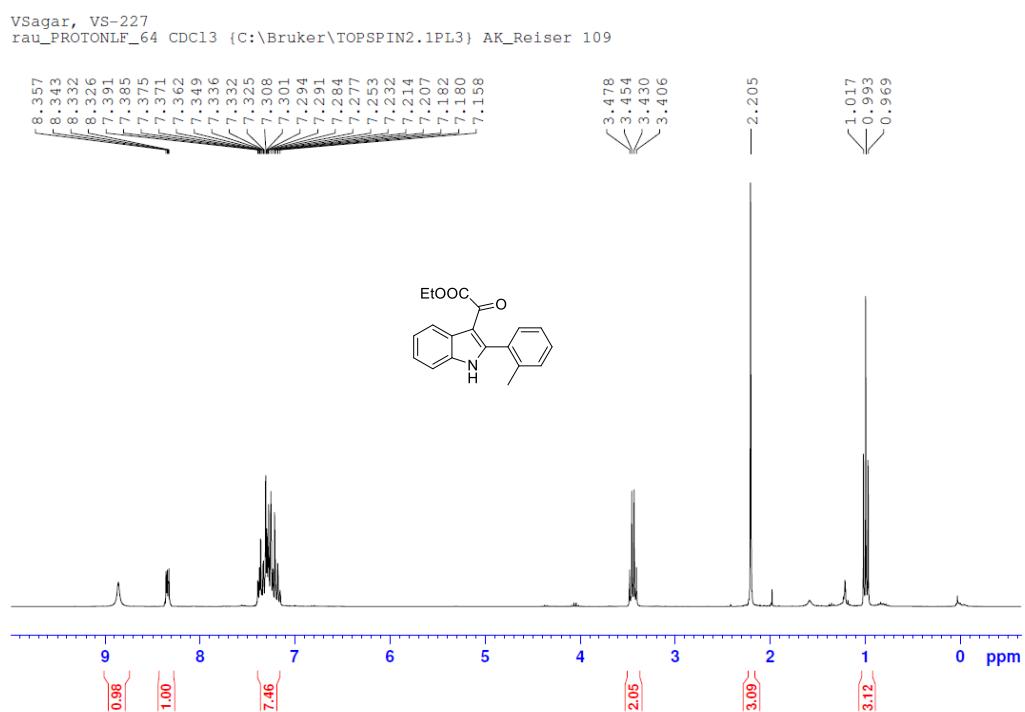
¹H NMR of **3h**



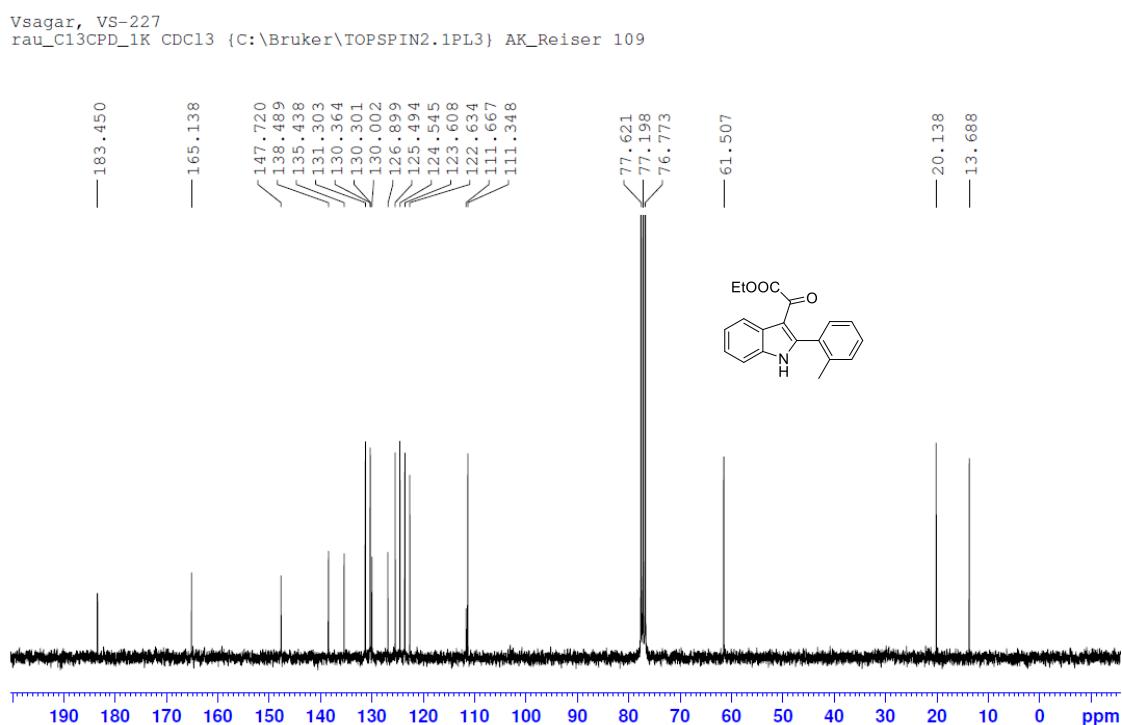
¹³C NMR of **3h**



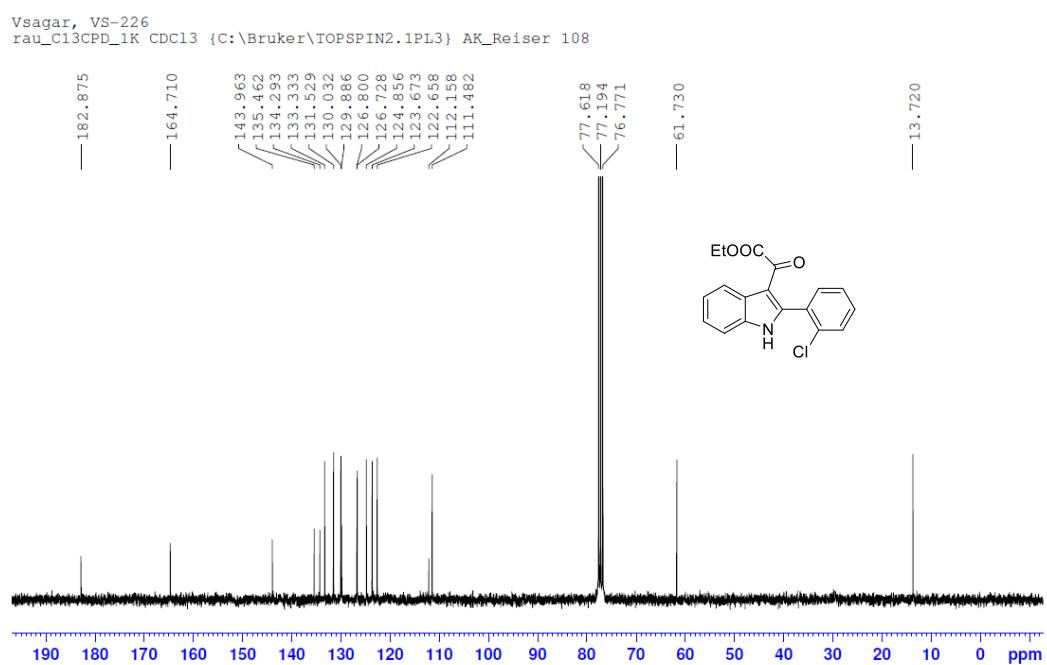
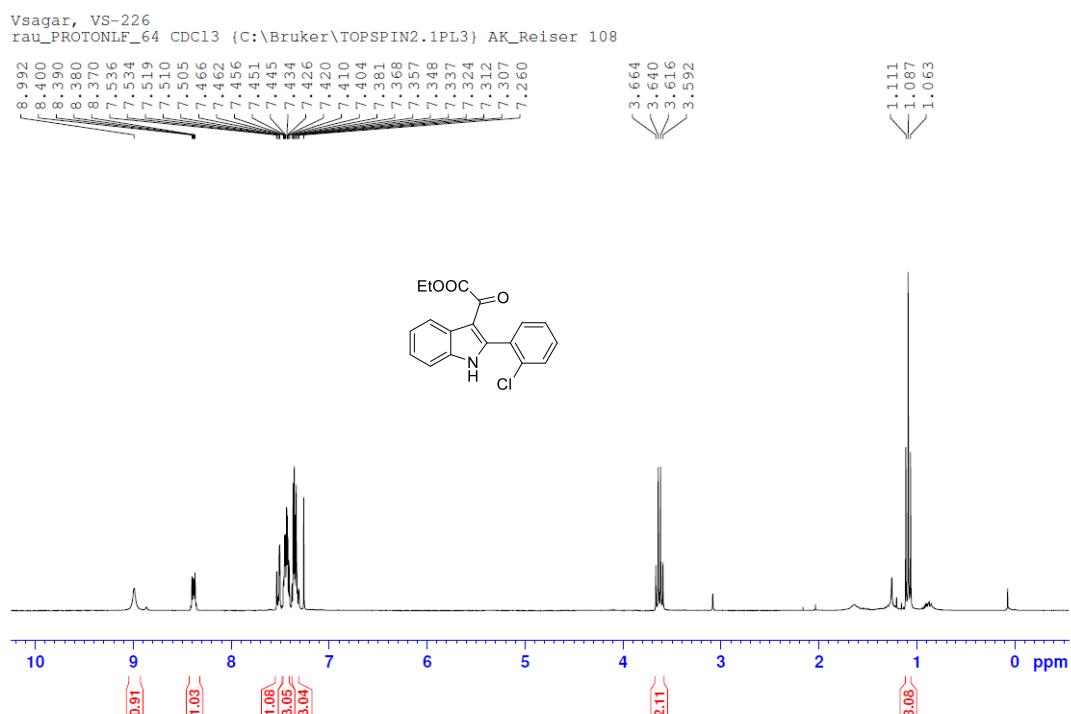
¹H NMR of 3i



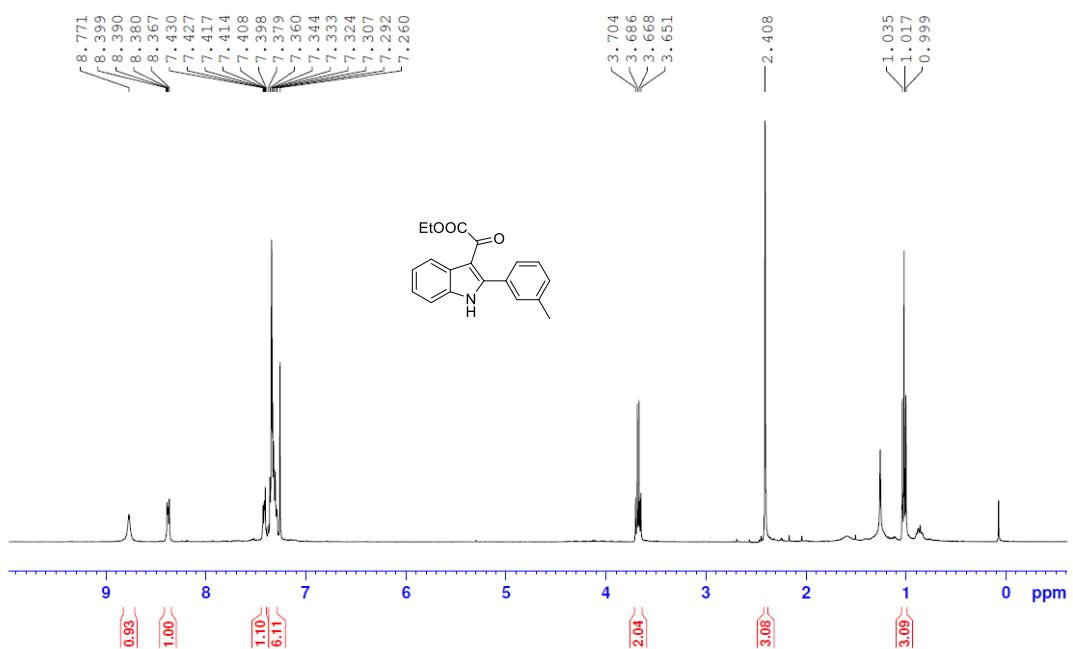
¹³C NMR of 3i



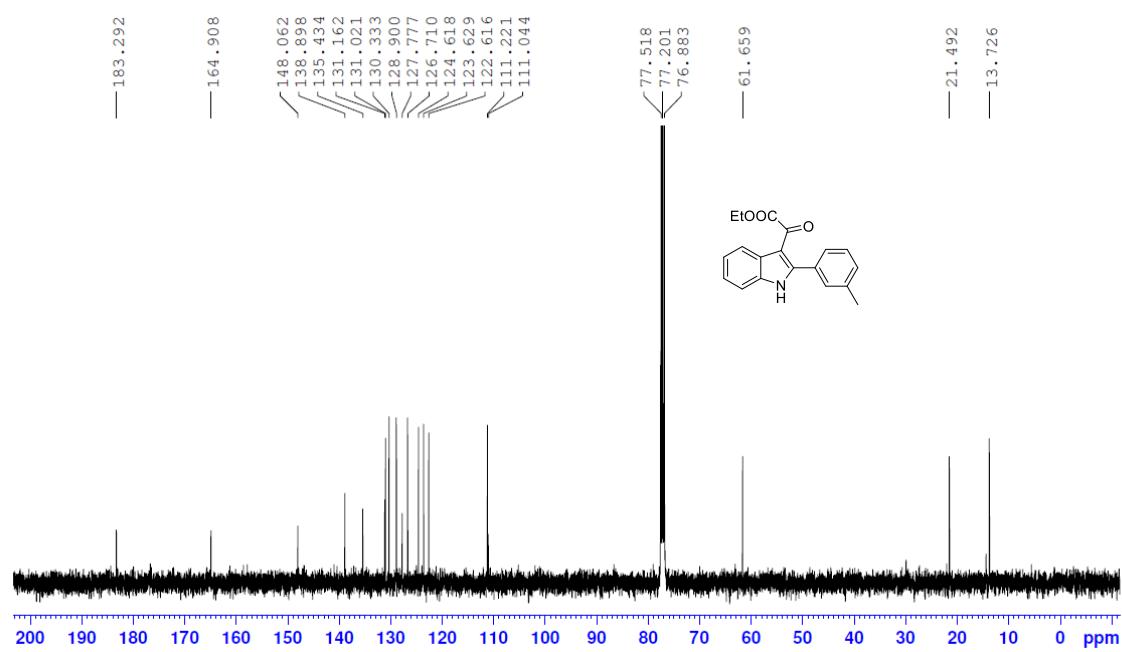
¹H NMR of **3j**



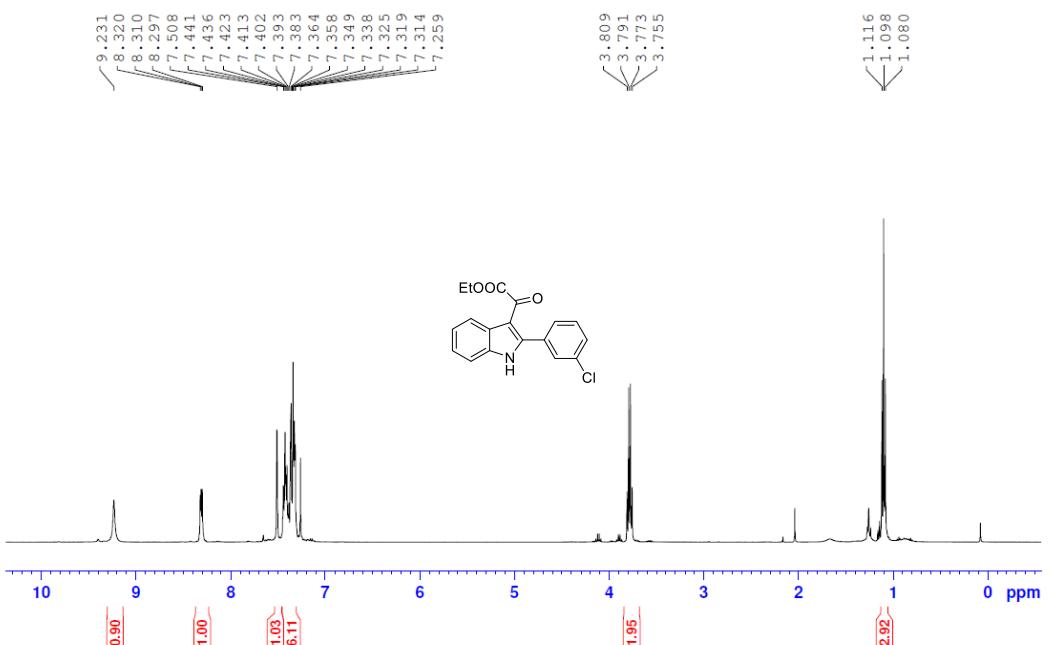
Sagar, VS-176
rau_sPROTON_16 CDCl₃ {C:\Bruker\TopSpin3.0} AK_Reiser 16



Sagar, VS-176
rau_sc13CPD_1k CDCl₃ {C:\Bruker\TopSpin3.0} AK_Reiser 4

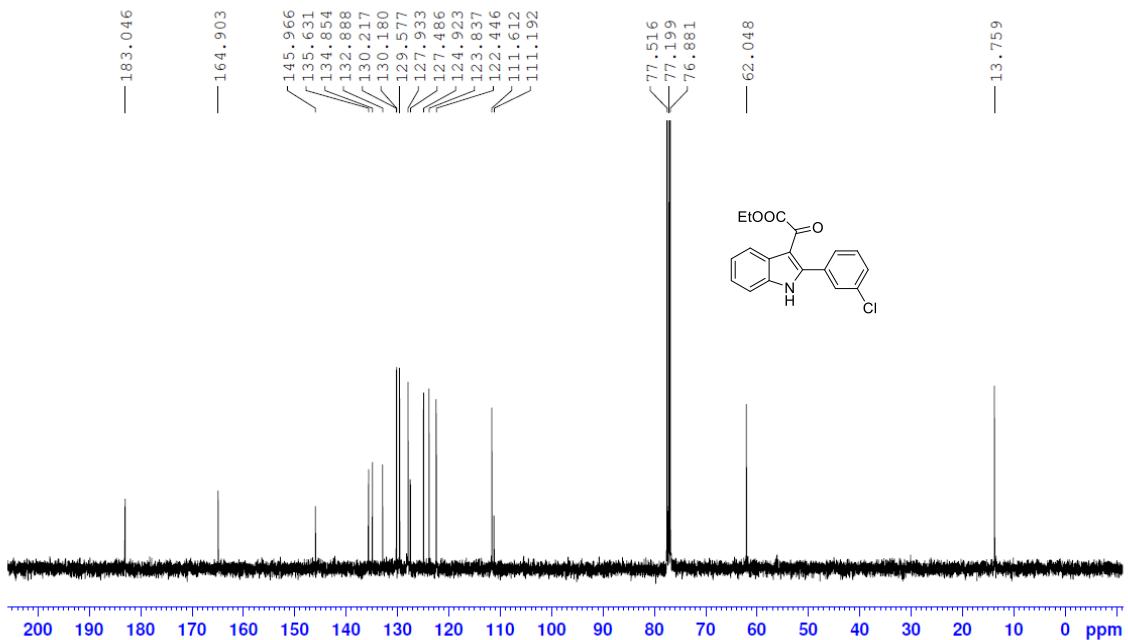


Sagar, VS-175
rau_sPROTON_16 CDCl₃ (C:\Bruker\TopSpin3.0) AK_Reiser 3



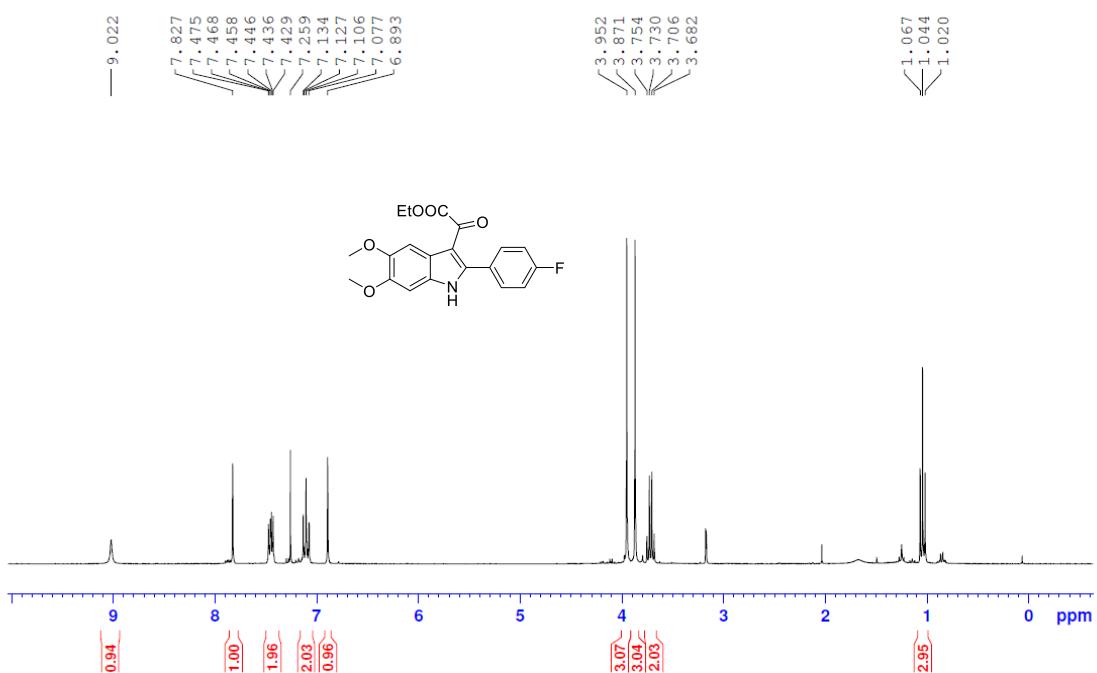
¹³C NMR of 3l

Sagar, VS-175
rau_sC13CPD_256 CDCl₃ (C:\Bruker\TopSpin3.0) AK_Reiser 3



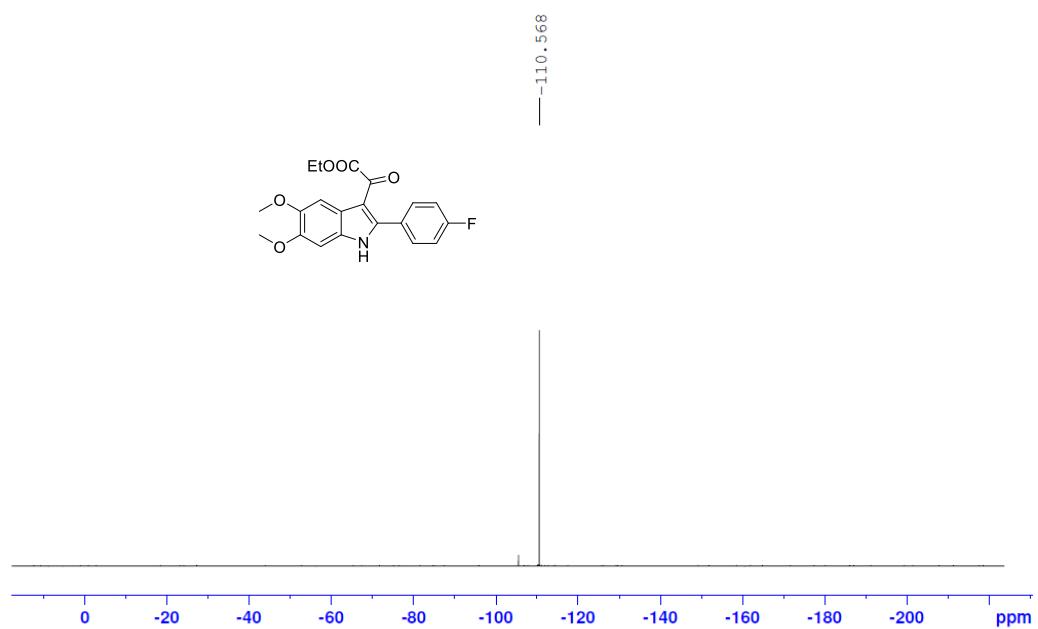
¹H NMR of 3m

Sagar, VS-198
rau_PROTONLF_16 CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 24



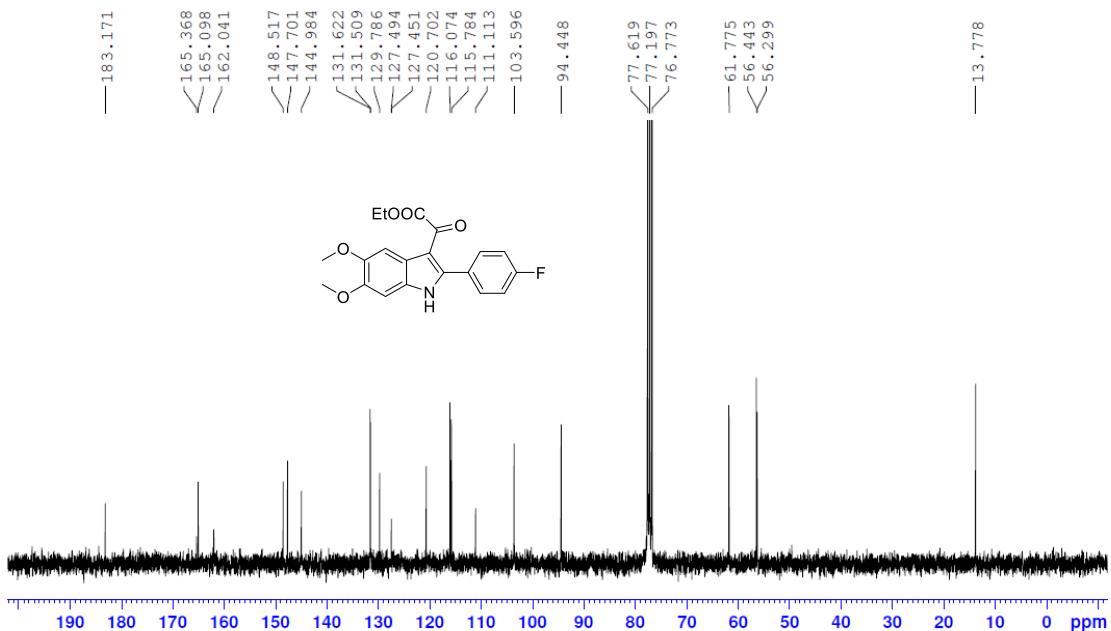
¹⁹F NMR of 3m

Sagar, VS-198
rau_F19CPD CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 24



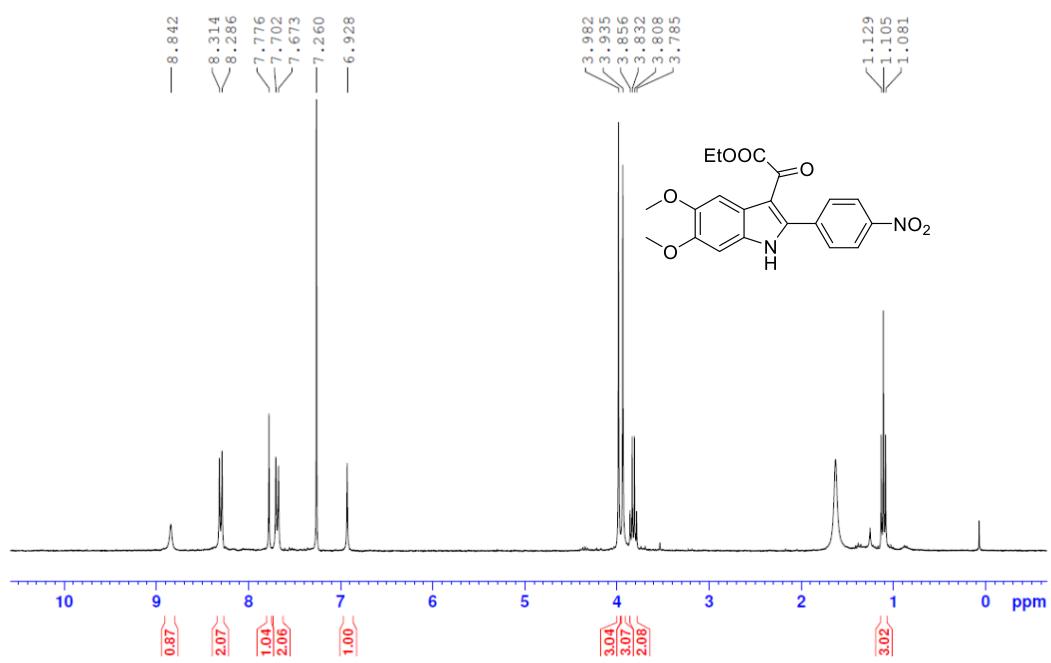
¹³C NMR of 3m

Sagar, VS-198
rau_C13CPD_1K CDCl₃ {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 24



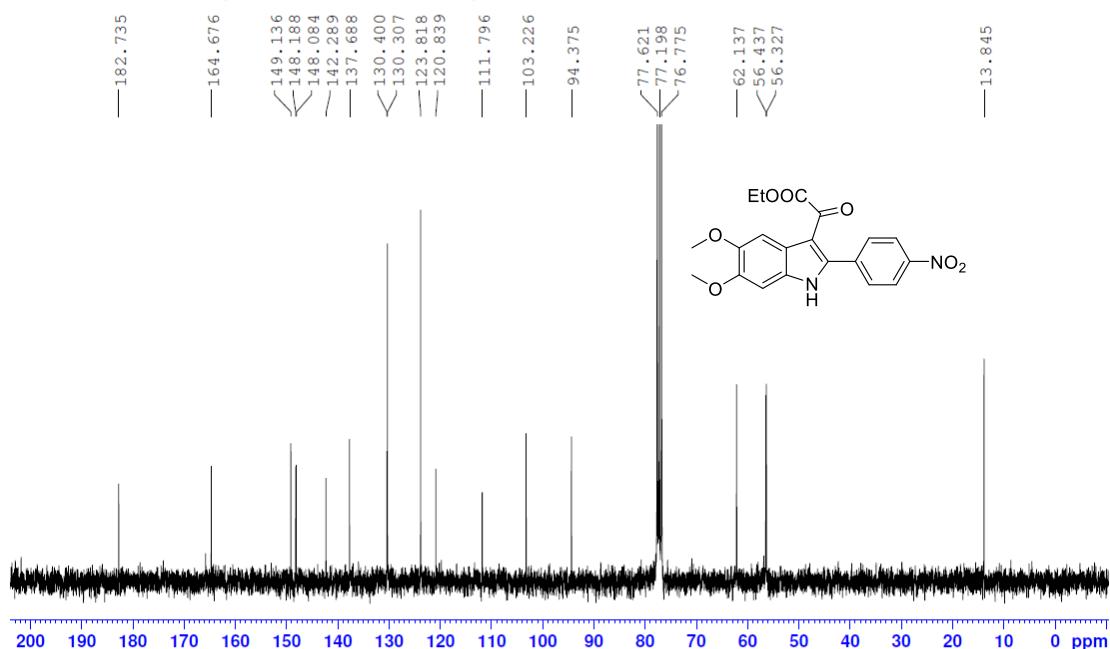
¹H NMR of 3n

Sagar, VS-251
rau_PROTONLF_16 CDCl₃ {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 6



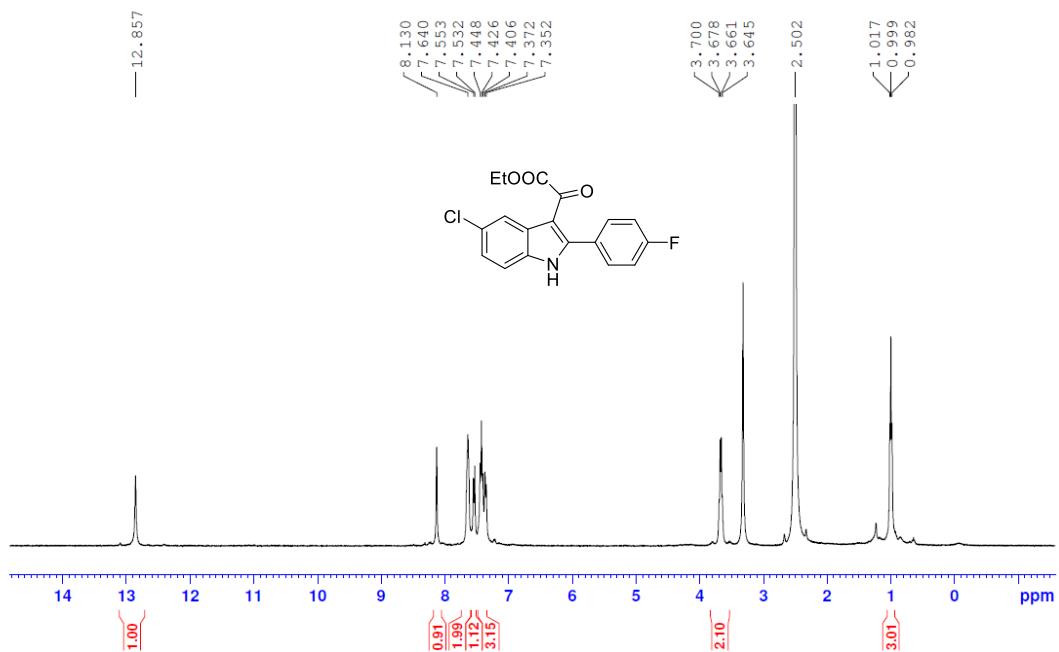
¹³C NMR of 3n

Sagar, VS-251
rau_C13CPD_1K CDCl₃ {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 59



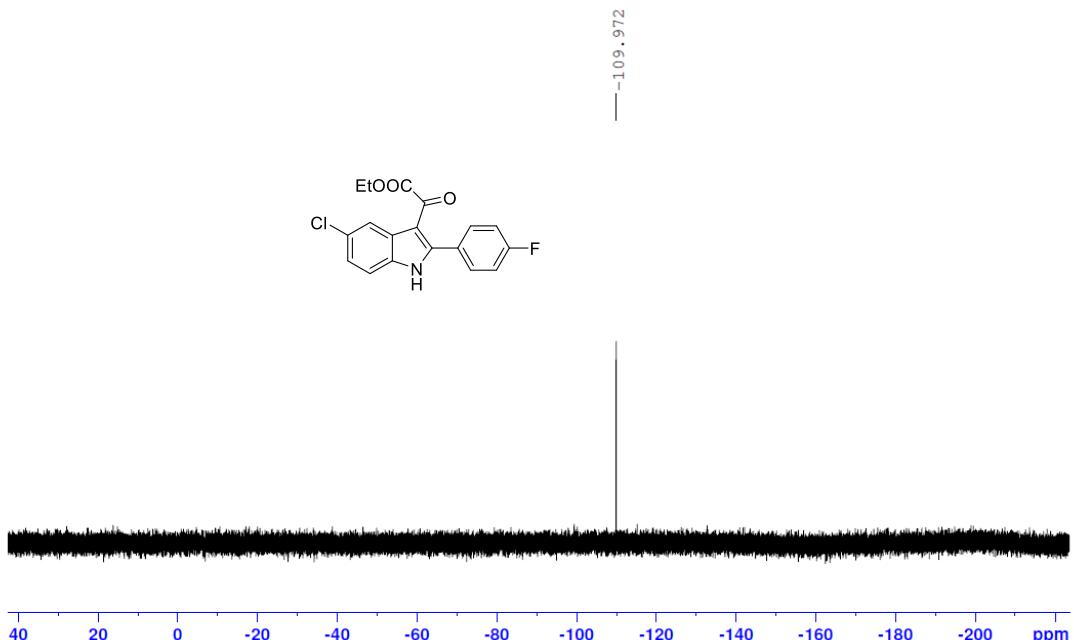
¹H NMR of 3o

Sagar, VS-196
rau_sPROTON_16 DMSO {C:\Bruker\TopSpin3.0} AK_Reiser 17



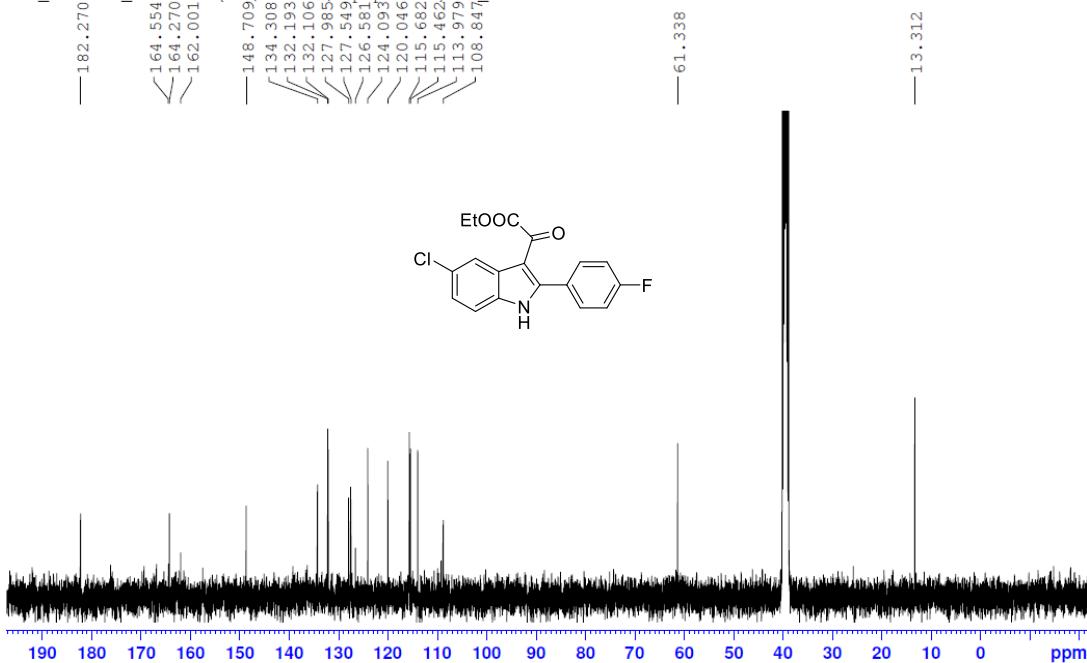
¹⁹F NMR of **3o**

Sagar, VS-196
rau_sF19CPD DMSO {C:\Bruker\TopSpin3.0} AK_Reiser 17

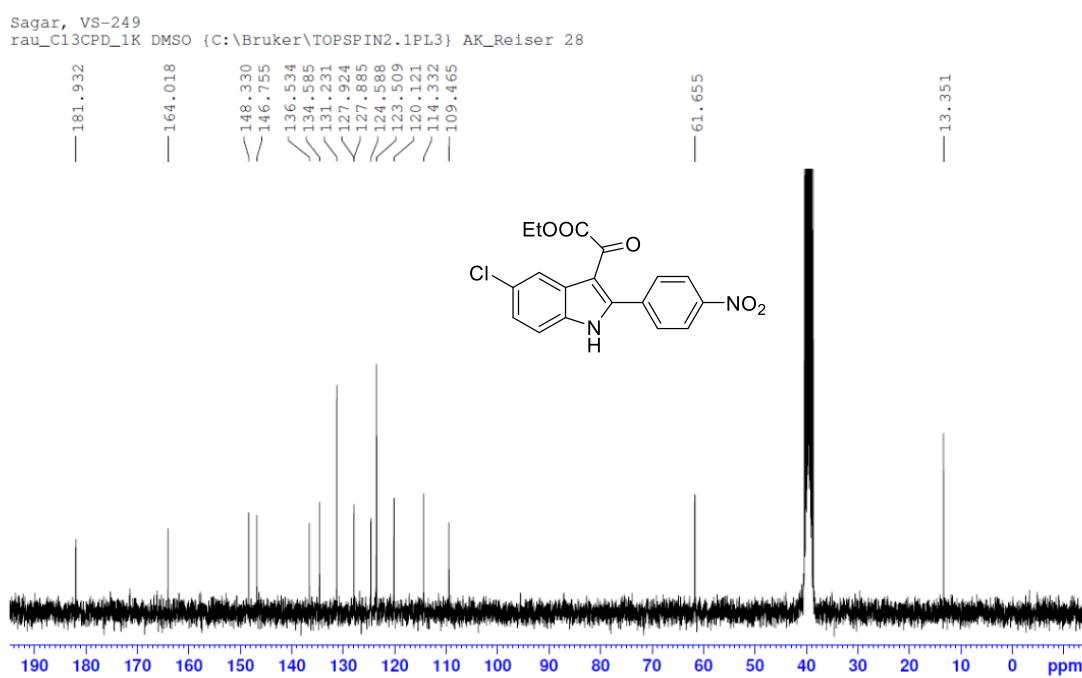
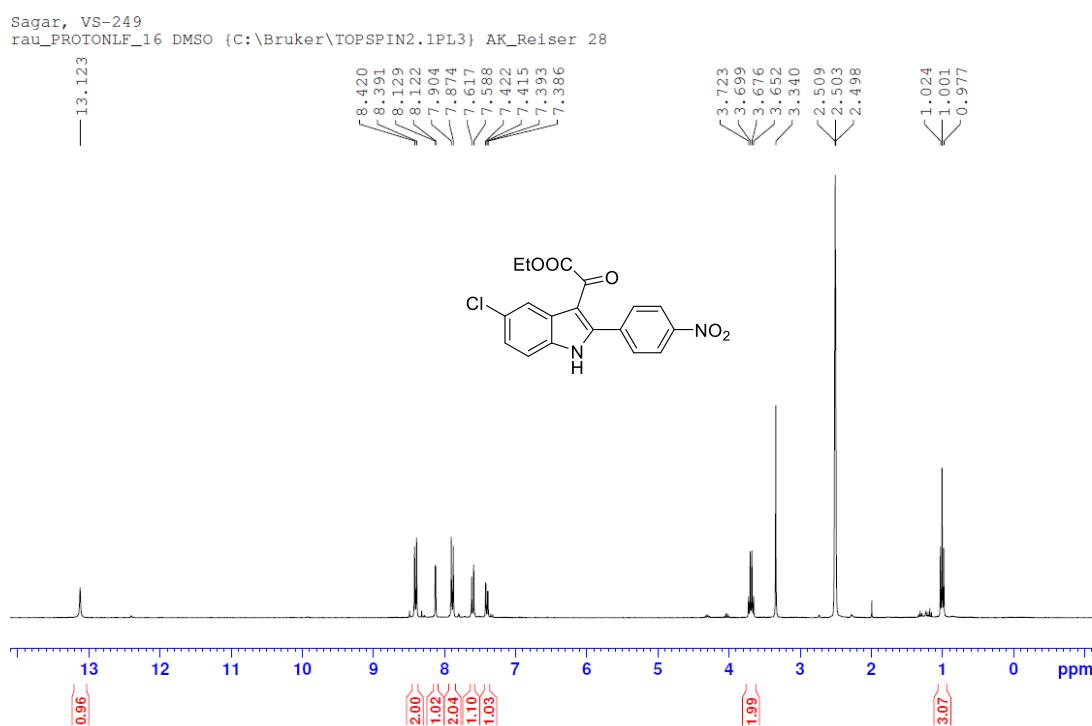


¹³C NMR of **3o**

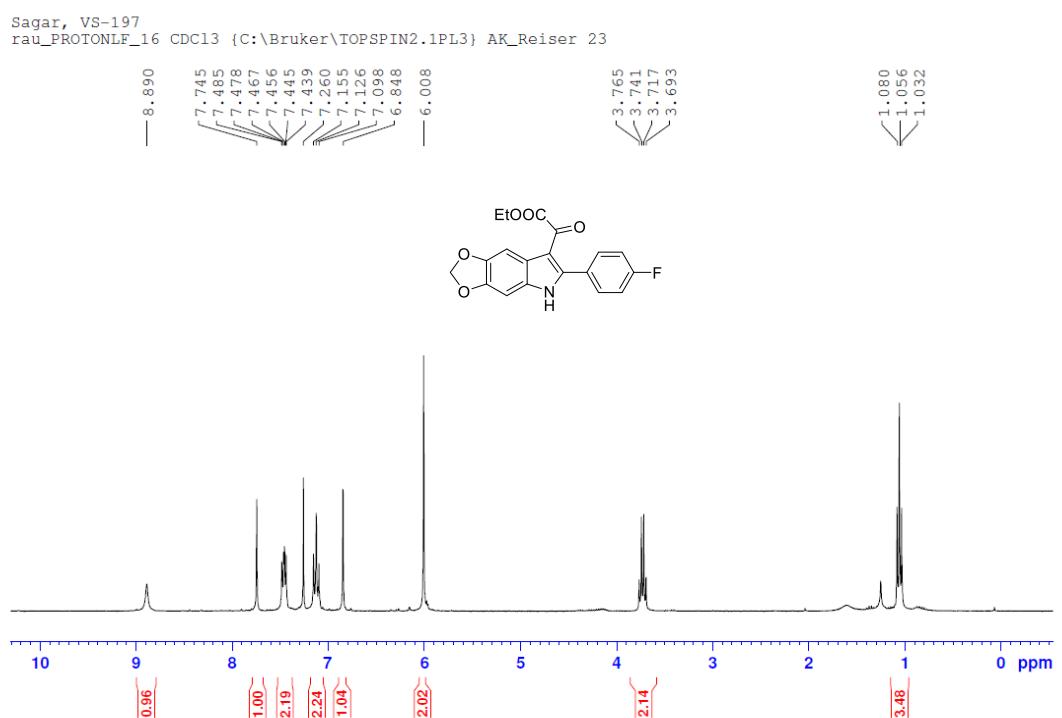
Sagar, VS-196
rau_sC13CPD_1k DMSO {C:\Bruker\TopSpin3.0} AK_Reiser 17



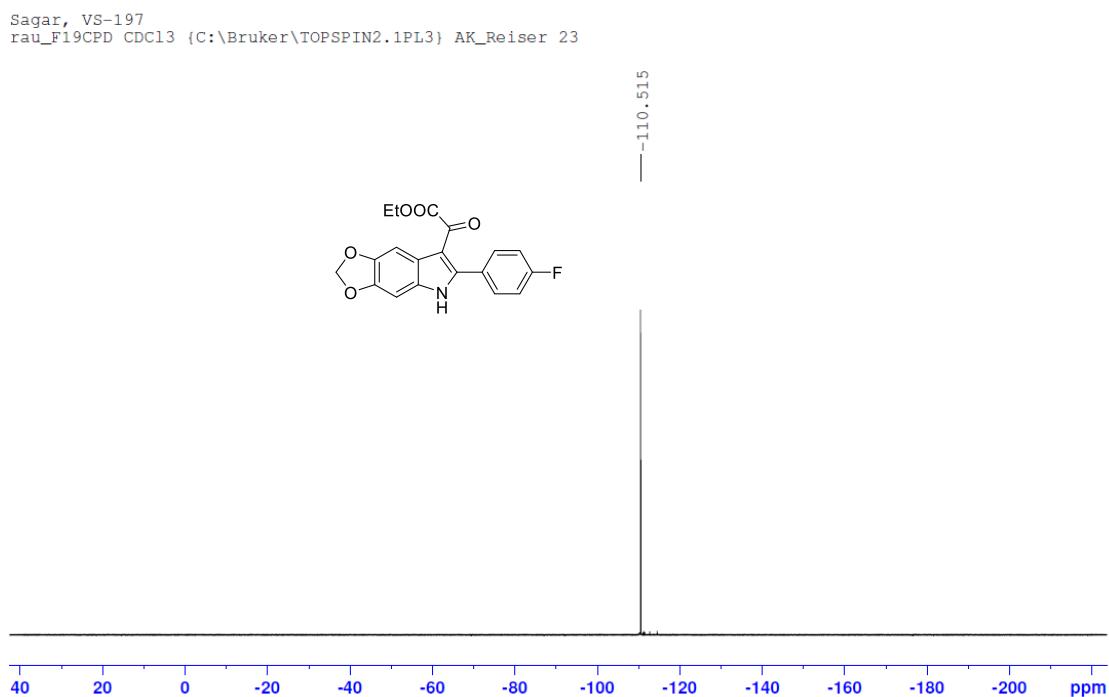
¹H NMR of **3p**



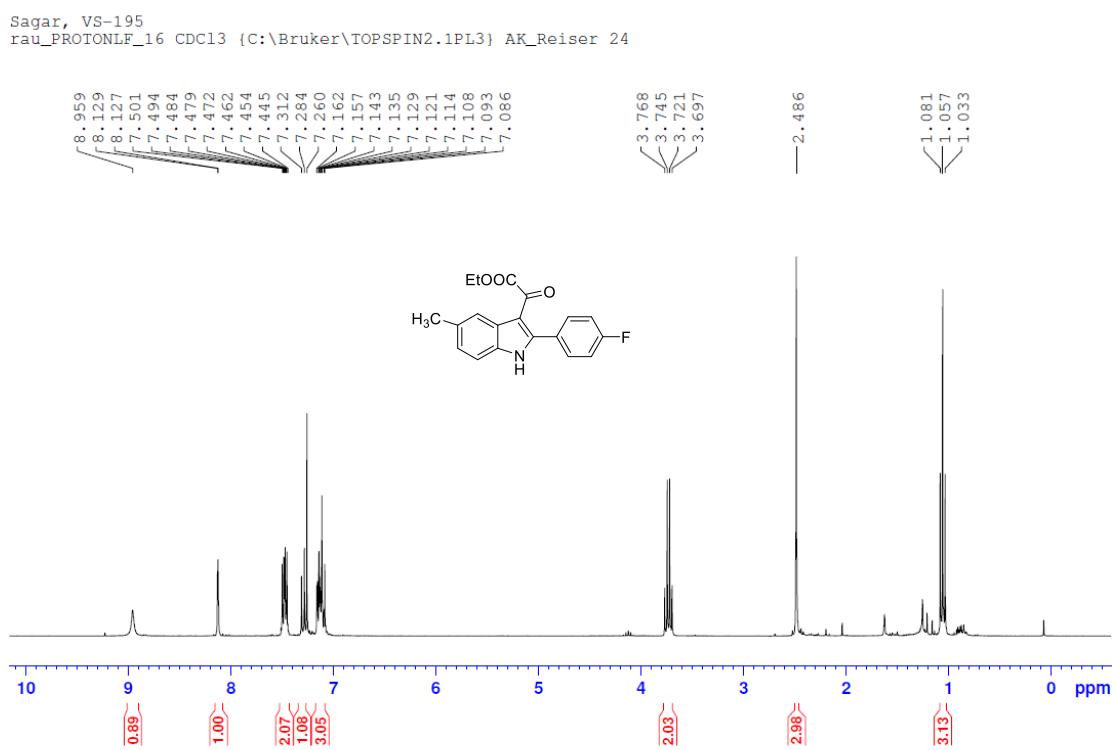
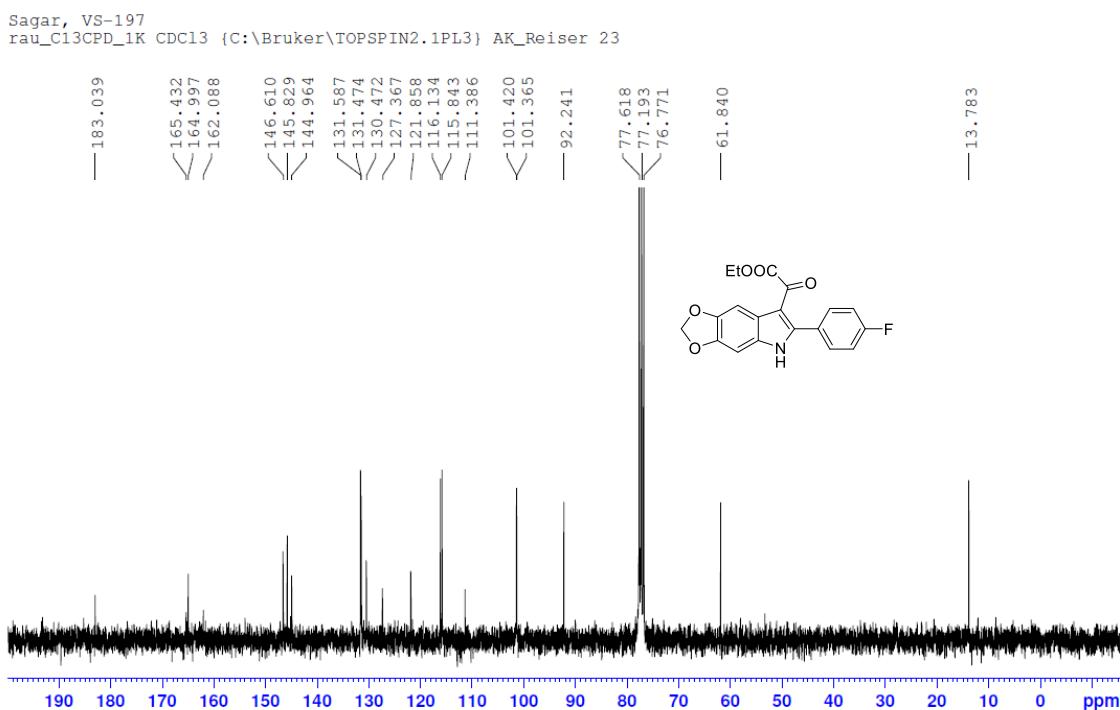
¹H NMR of **3q**



¹⁹F NMR of **3q**

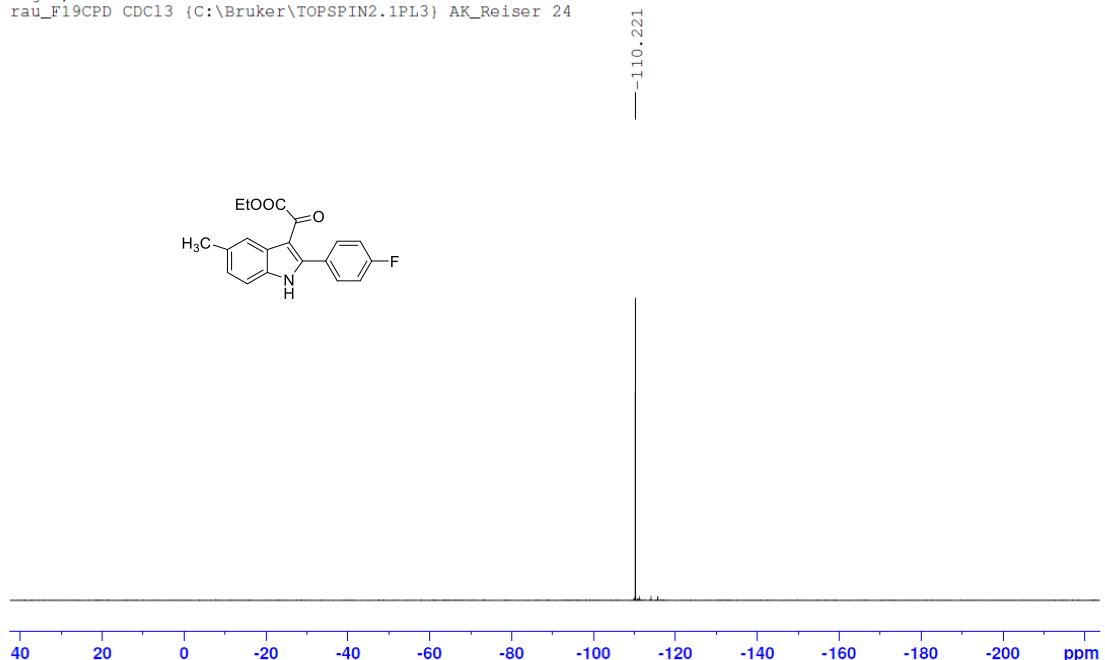


¹³C NMR of **3q**



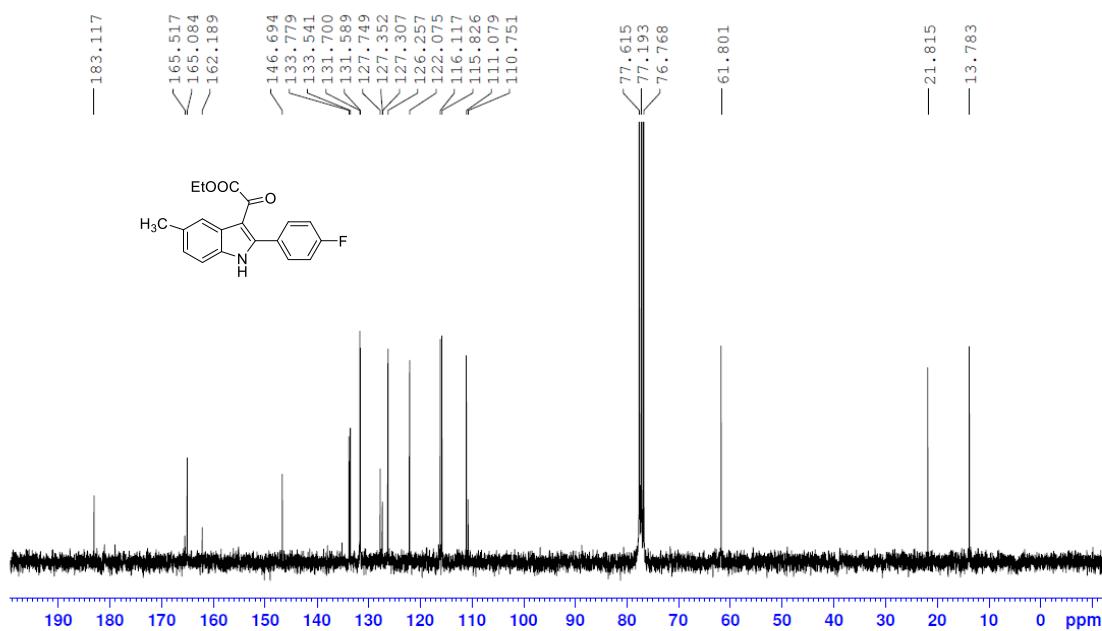
¹⁹F NMR of **3r**

Sagar, VS-195
rau_F19CPD CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 24

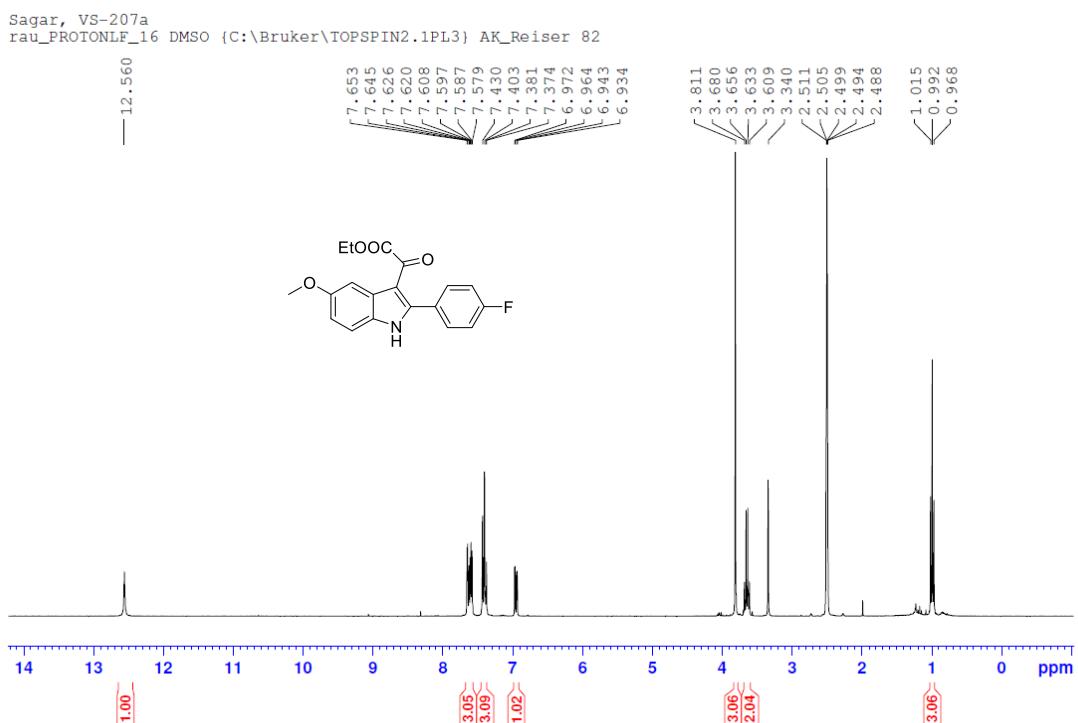


¹³C NMR of **3r**

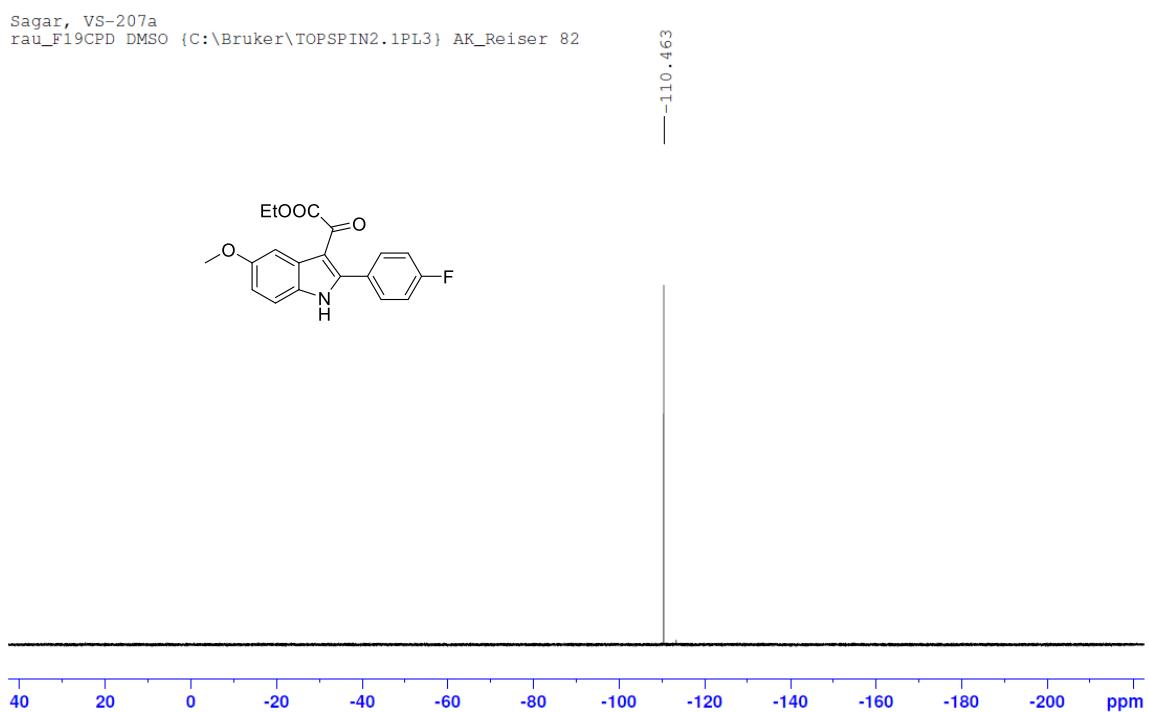
Sagar, VS-195
rau_C13CPD_1K CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 40



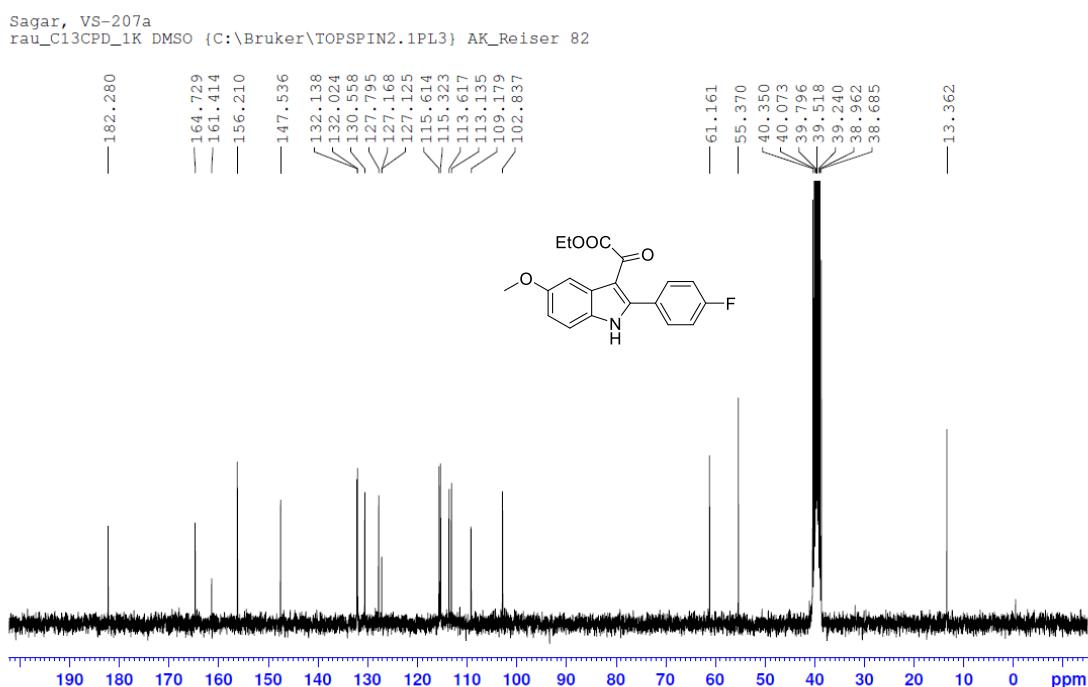
¹H NMR of **3s**



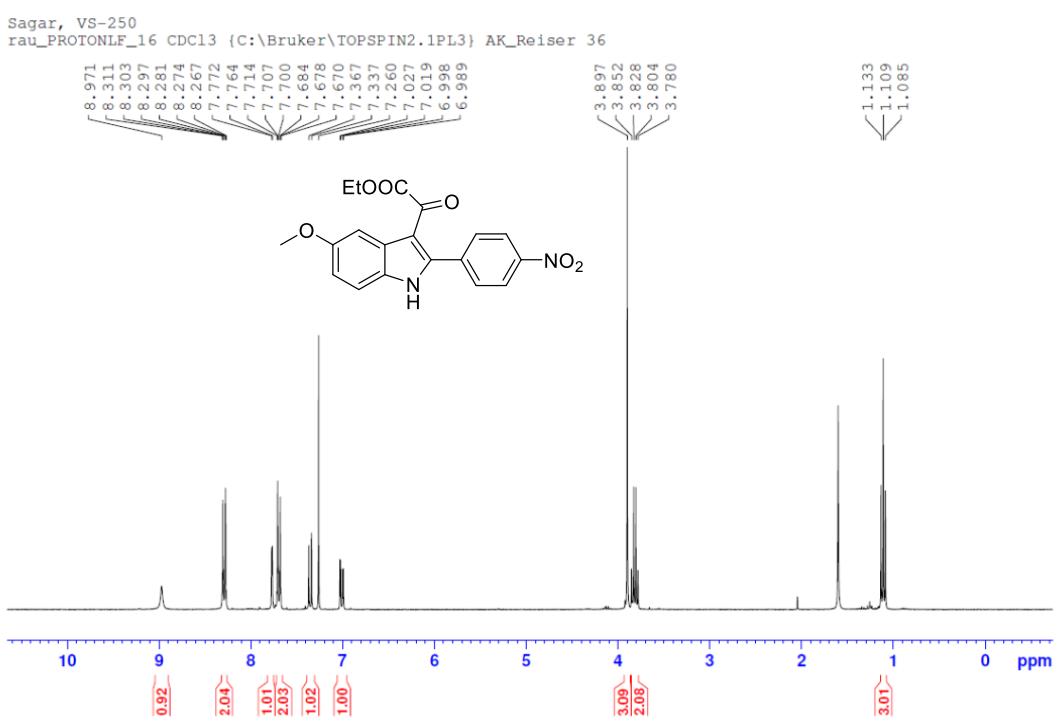
¹⁹F NMR of **3s**



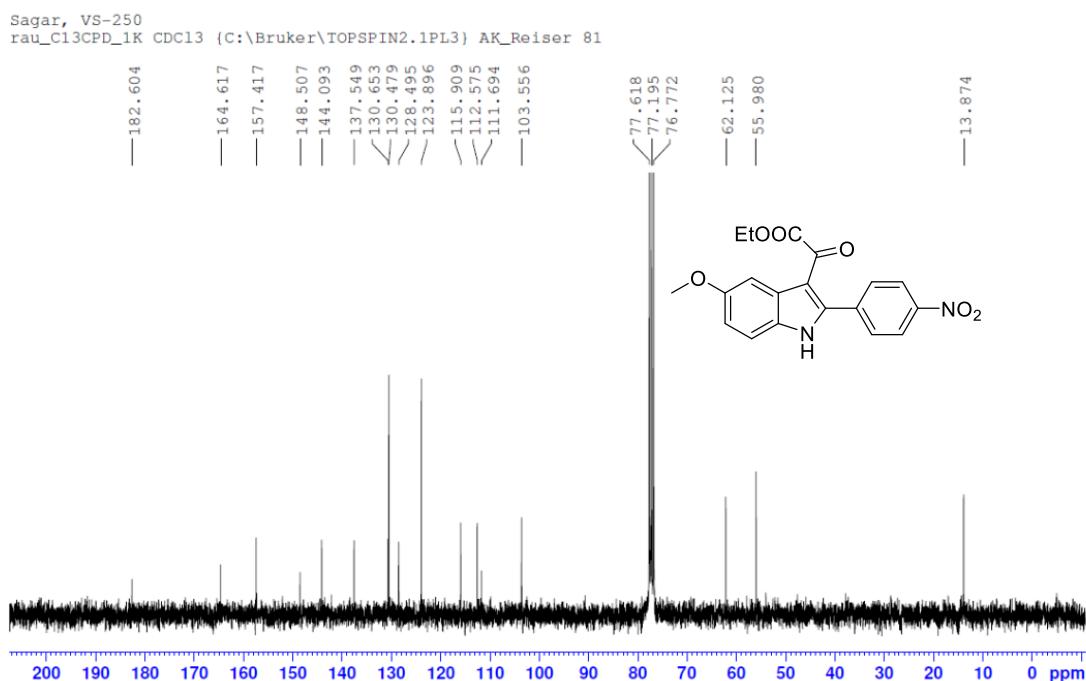
¹³C NMR of **3s**



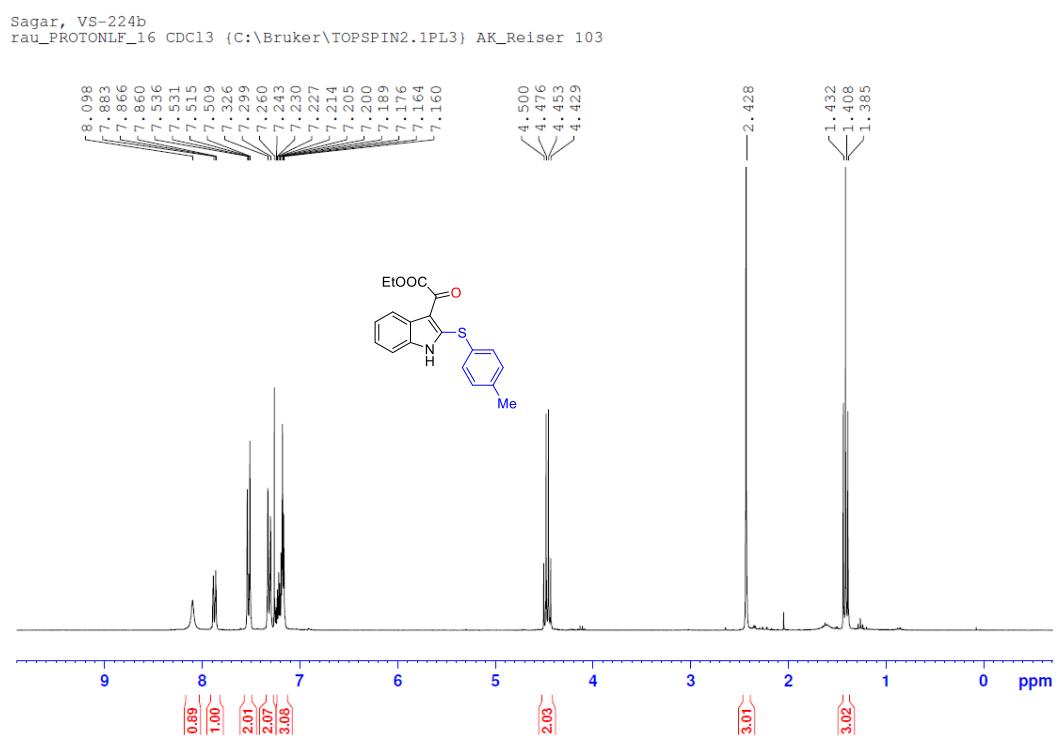
¹H NMR of **3t**



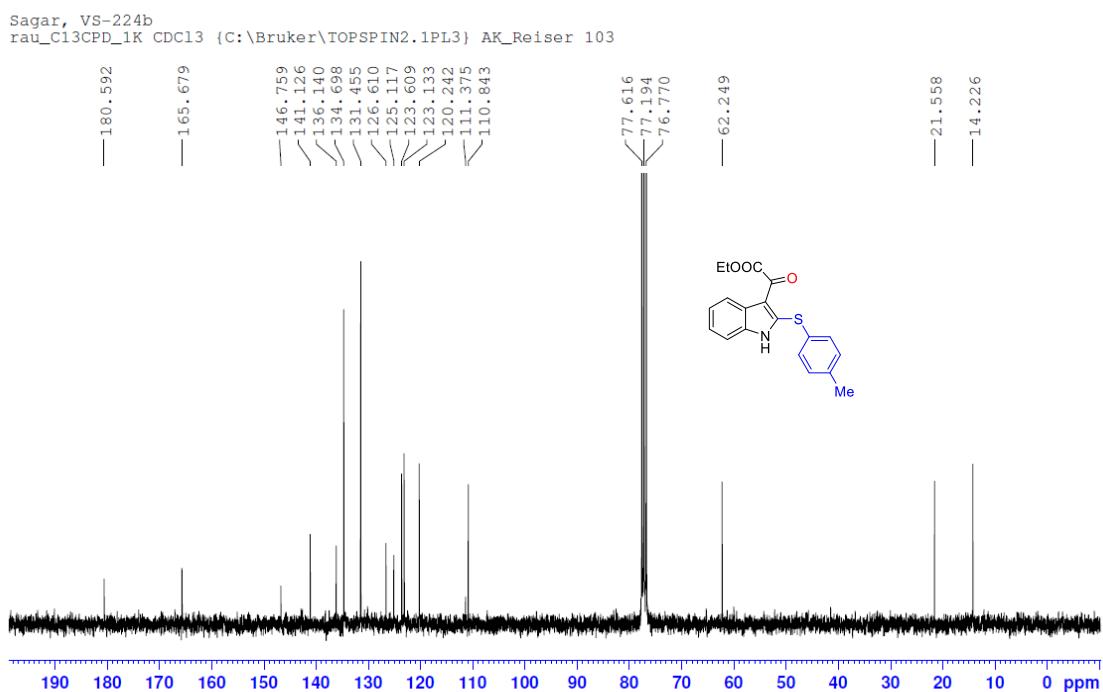
¹³C NMR of **3t**



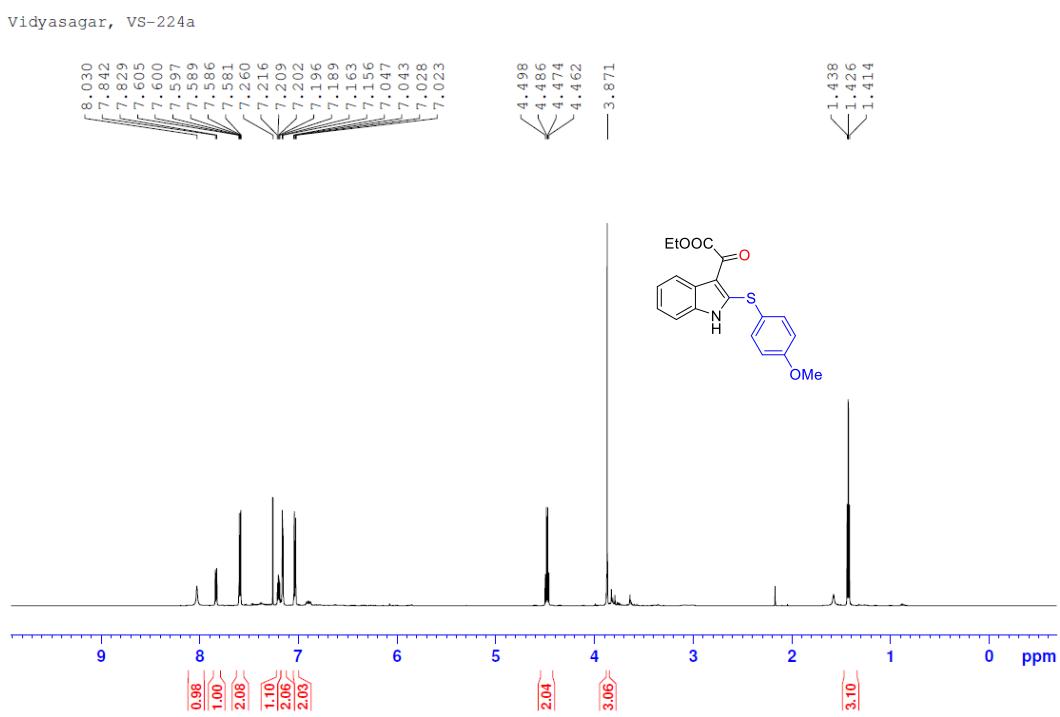
¹H NMR of **4a**



¹³C NMR of **4a**

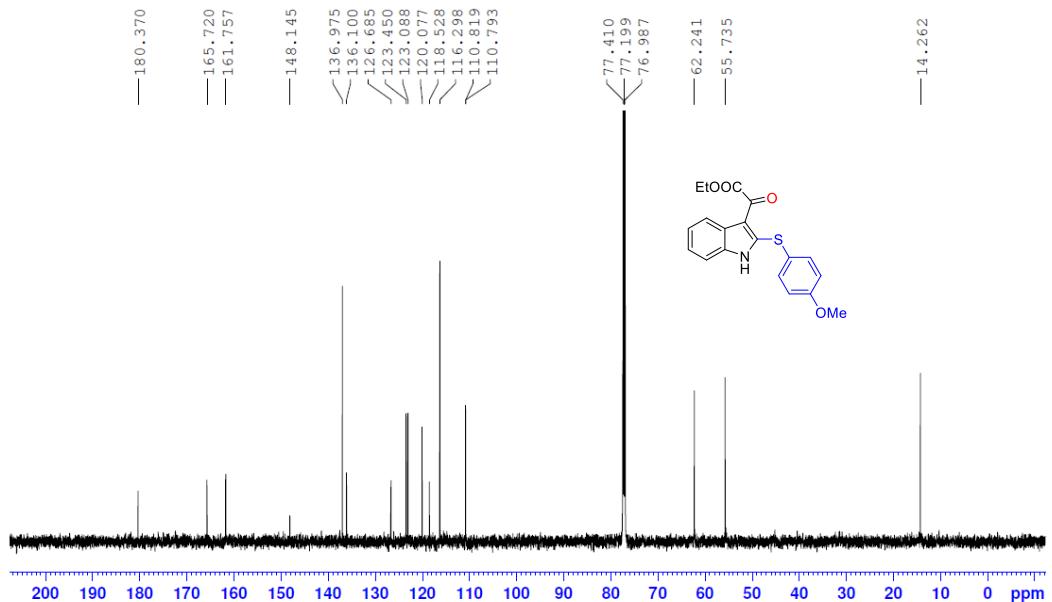


¹H NMR of **4b**



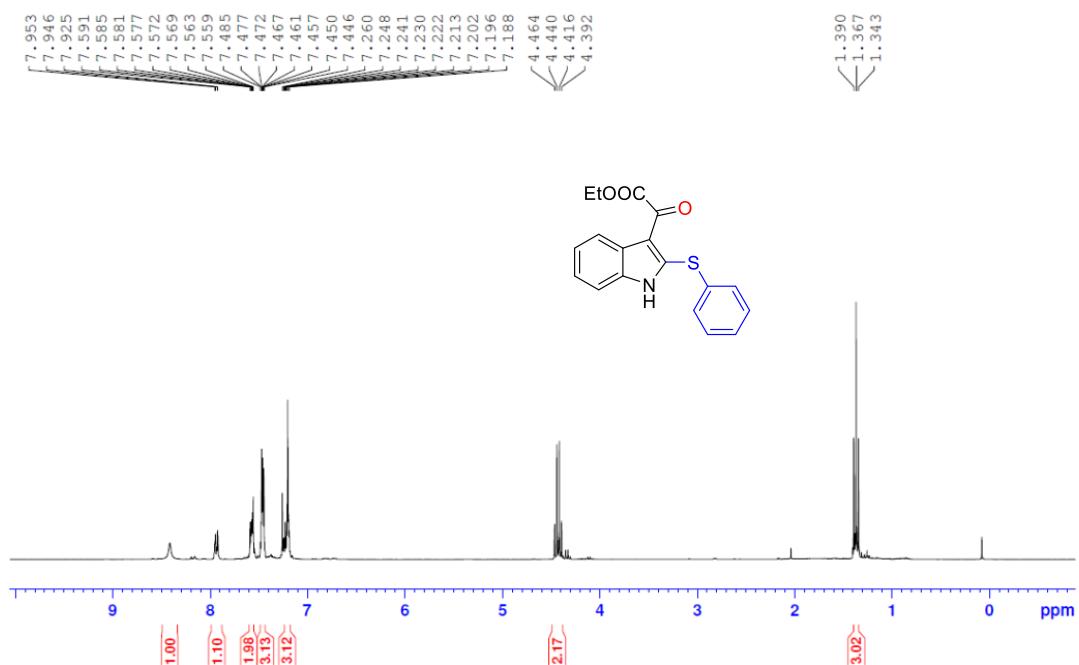
¹³C NMR of **4b**

Vidyasagar, VS-224a
C13{H1}



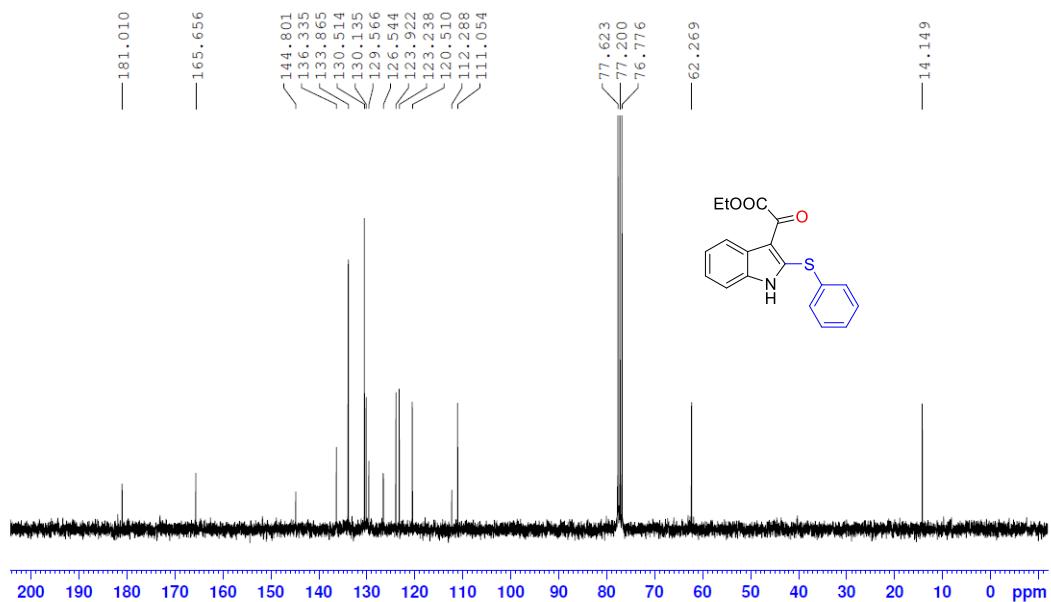
¹H NMR of **4c**

Sagar, VS-151a-i
rau_PROTONLF_16 CDCl₃ {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 59



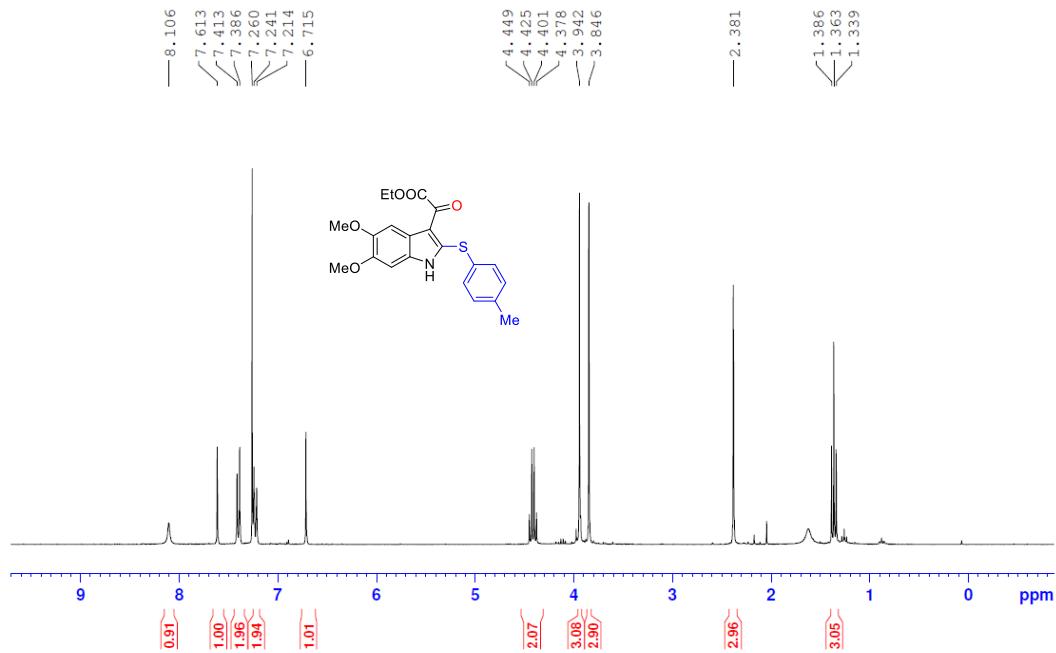
¹³C NMR of **4c**

Sagar, VS-151a-i
rau_C13CPD_256 CDCl₃ {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 59

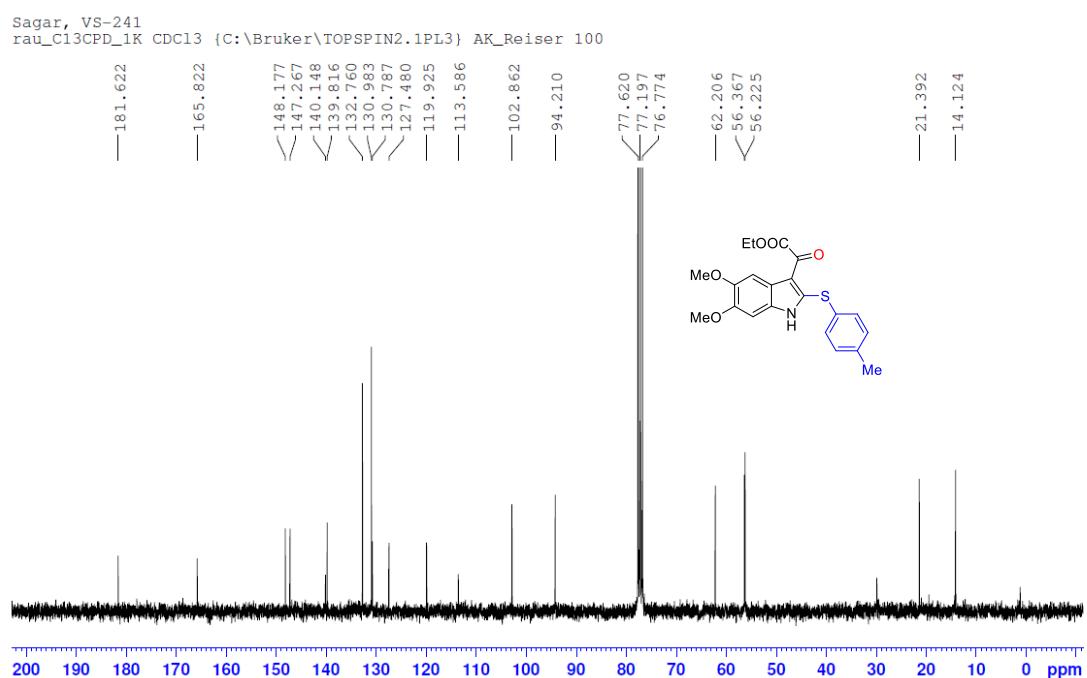


¹H NMR of **4d**

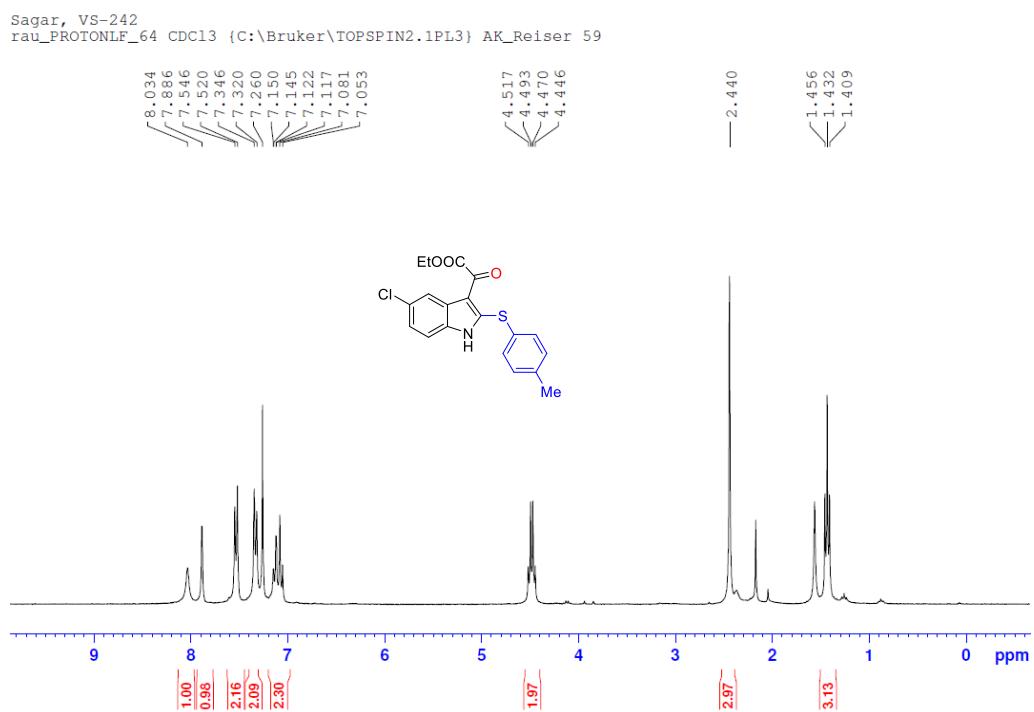
Sagar, VS-241
rau_PROTONLF_64 CDCl₃ {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 58



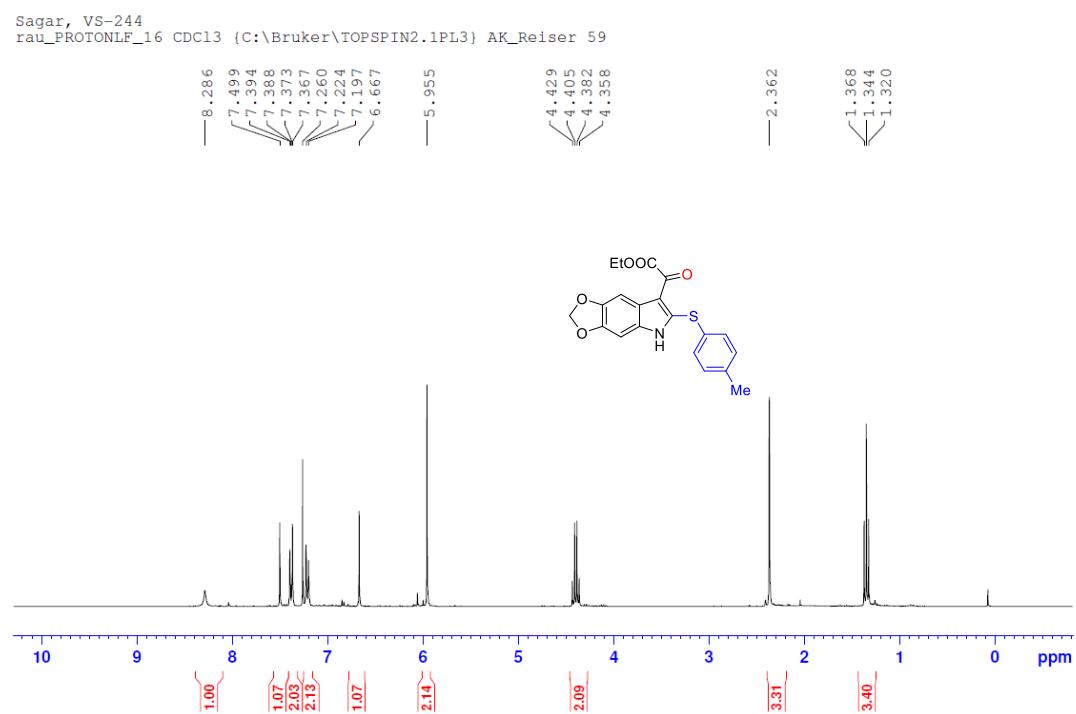
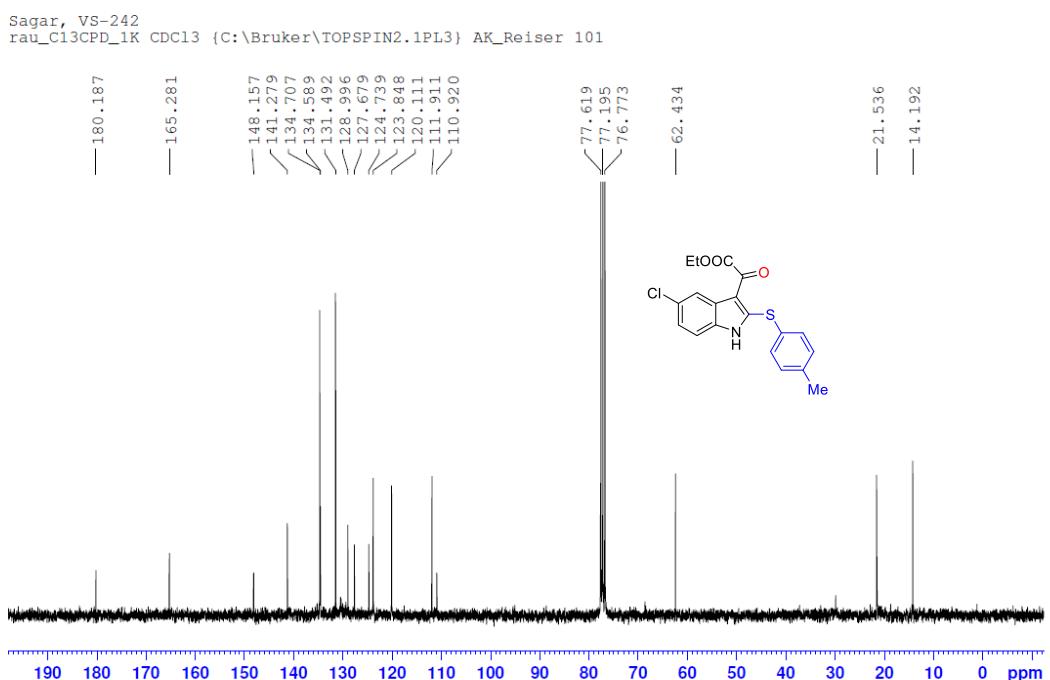
¹³C NMR of **4d**



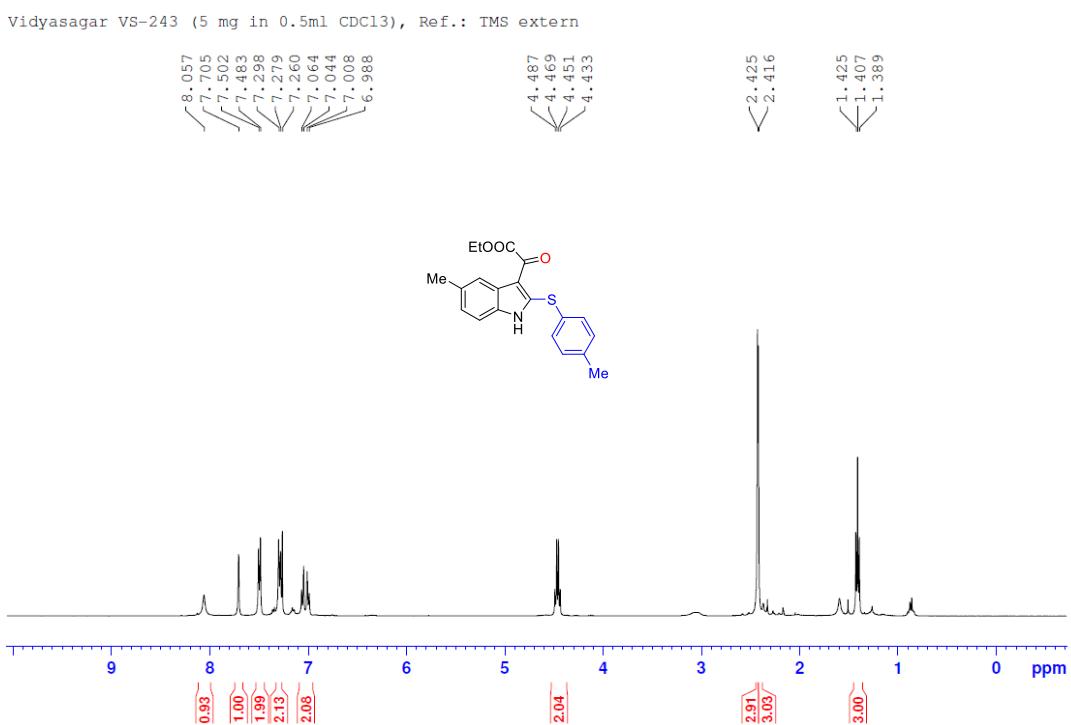
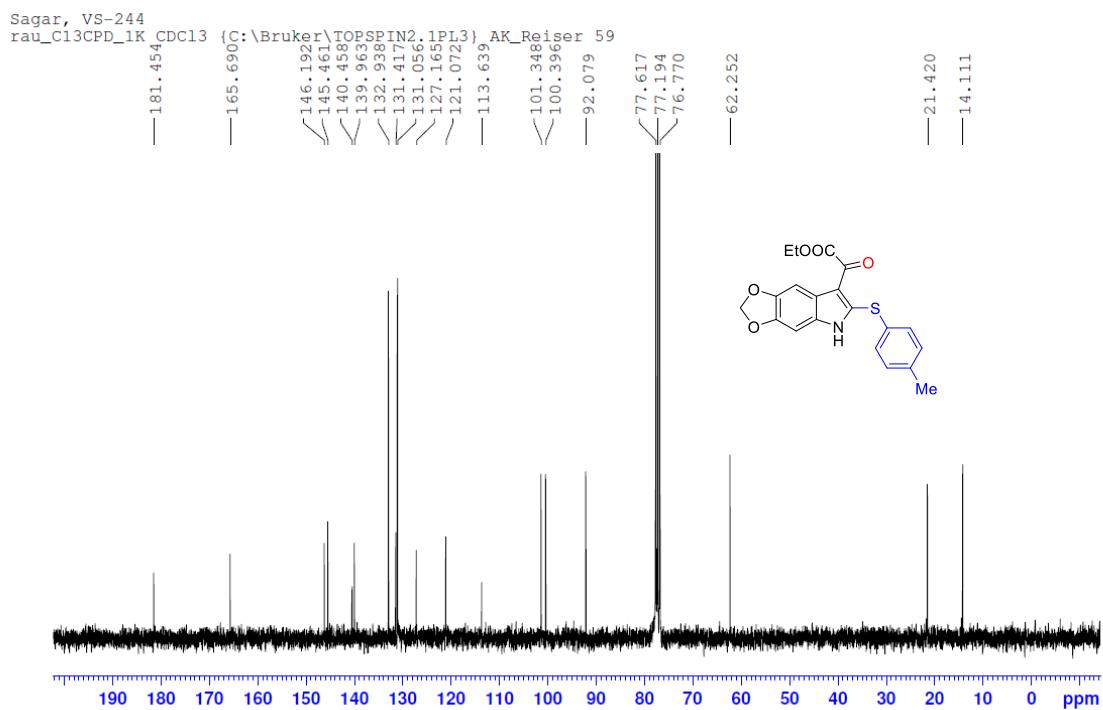
¹H NMR of **4e**



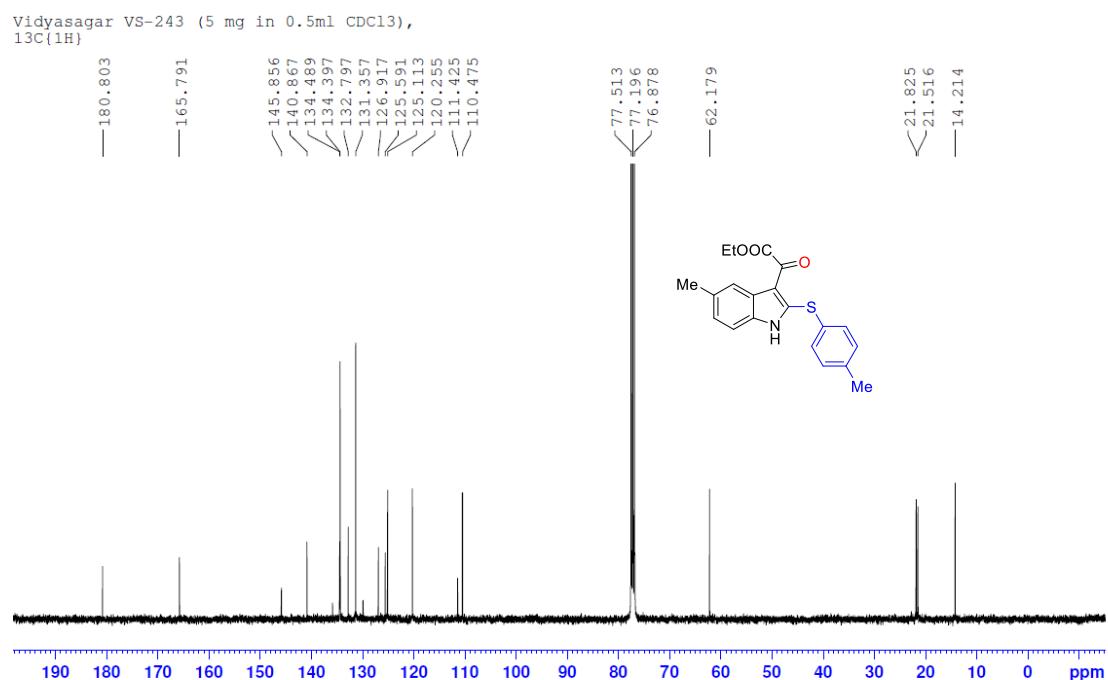
¹³C NMR of **4e**



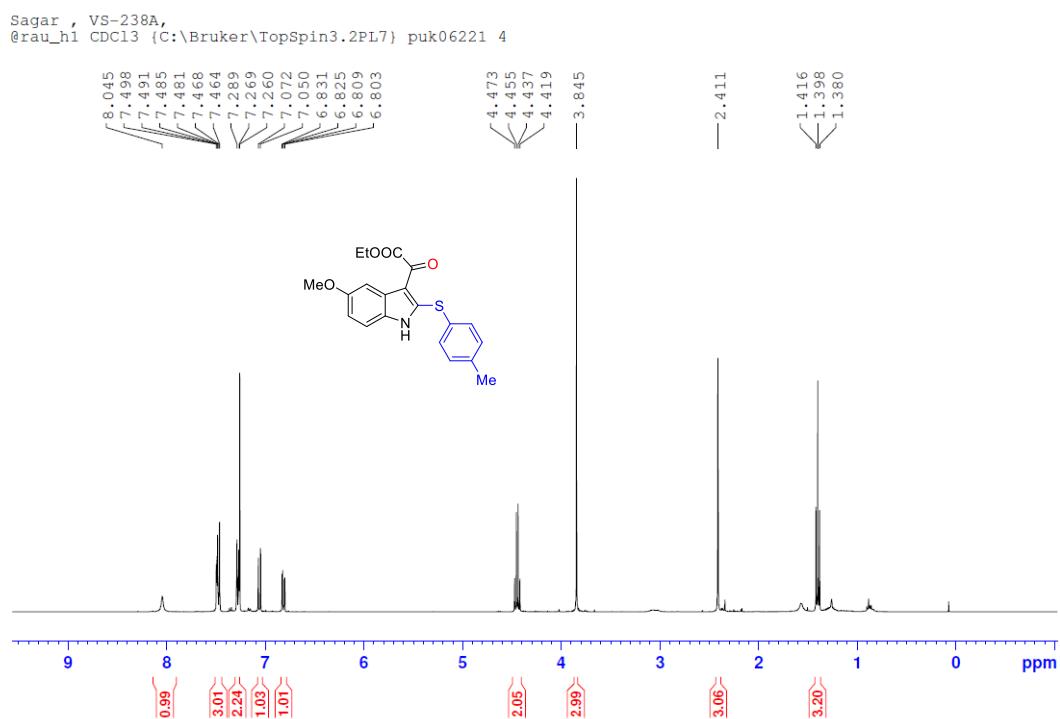
¹³C NMR of **4f**



¹³C NMR of **4g**

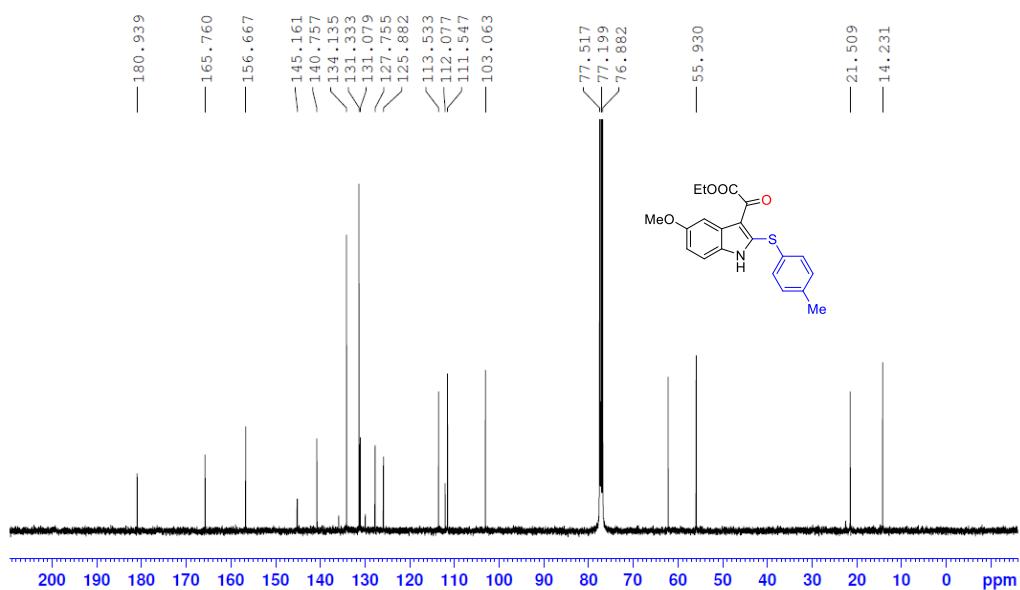


¹H NMR of **4h**



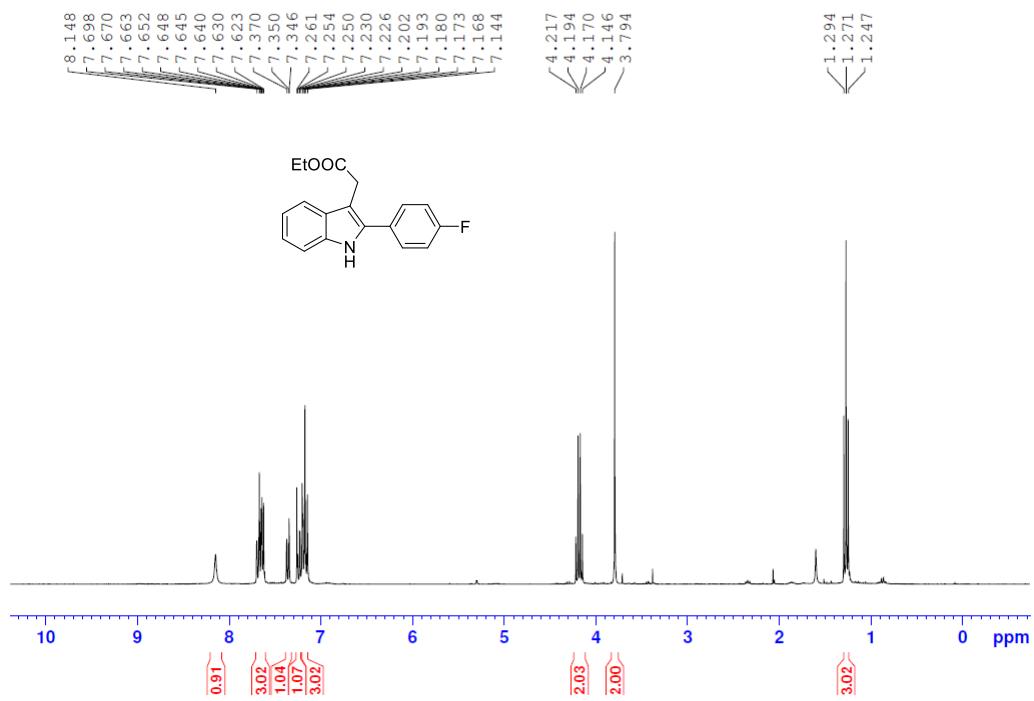
¹³C NMR of **4h**

Adiyala V. , VS-238A,
C13{H1}
rau_C13CPD CDC13 {C:\Bruker\TopSpin3.2PL7} puk06221 4



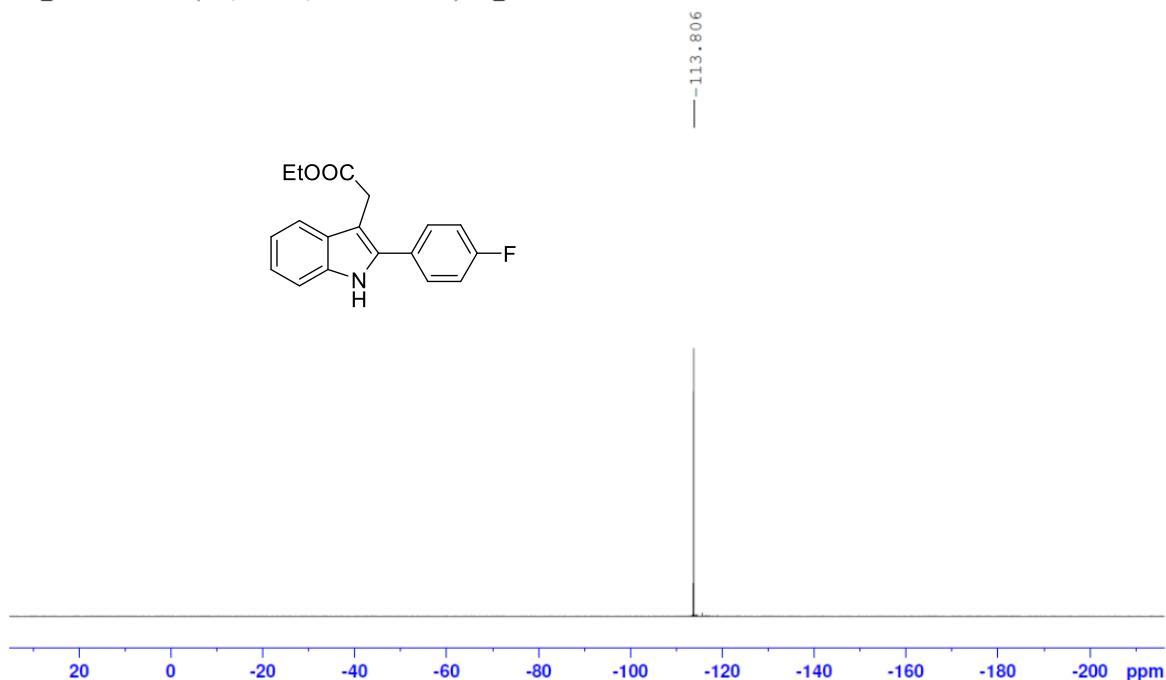
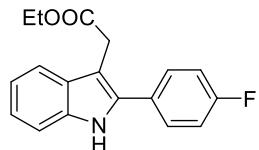
¹H NMR of 5

Sagar. VS-256
rau_PROTONLF_16 CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 71



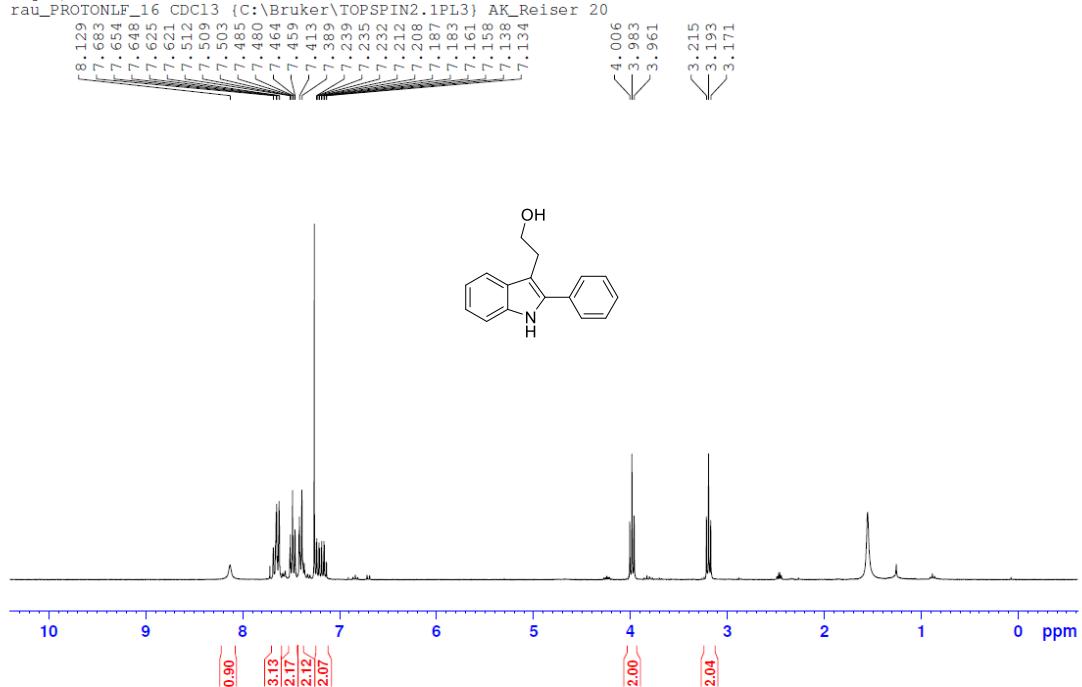
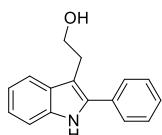
¹⁹F NMR of 5

Sagar. VS-256
rau_F19CPD CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 71



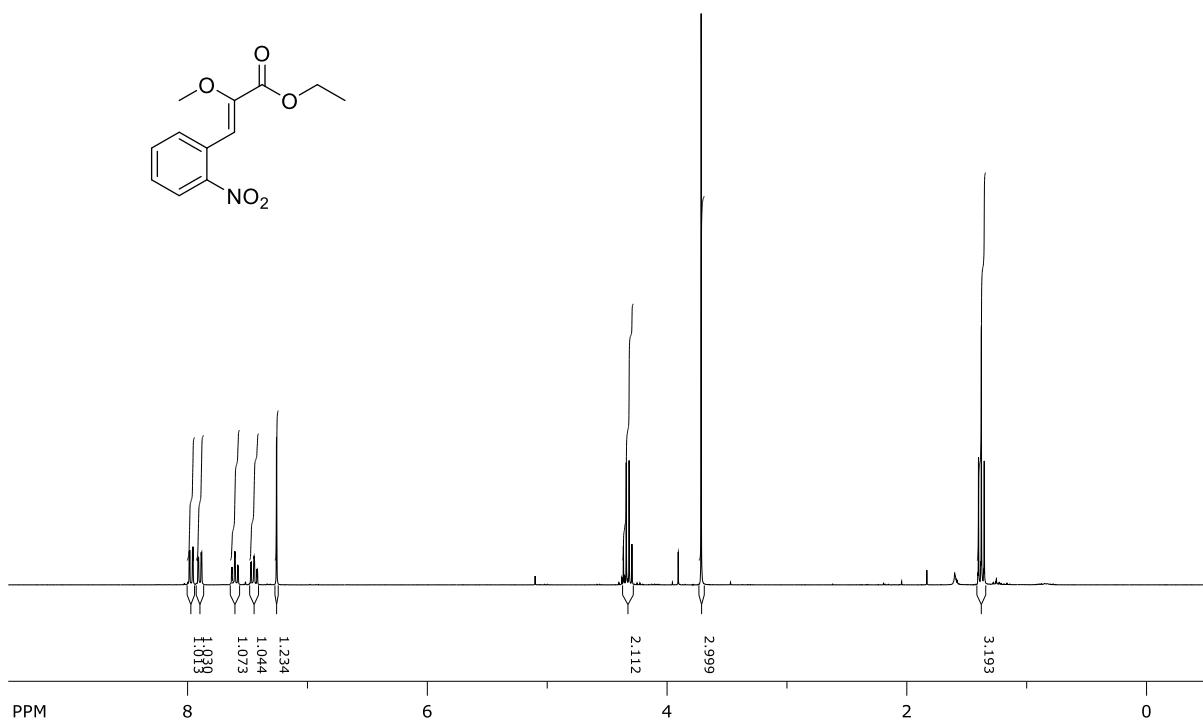
¹H NMR of **6**

Sagar, VS-257-1
rau PROTONLF 16 CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK Reiser 20



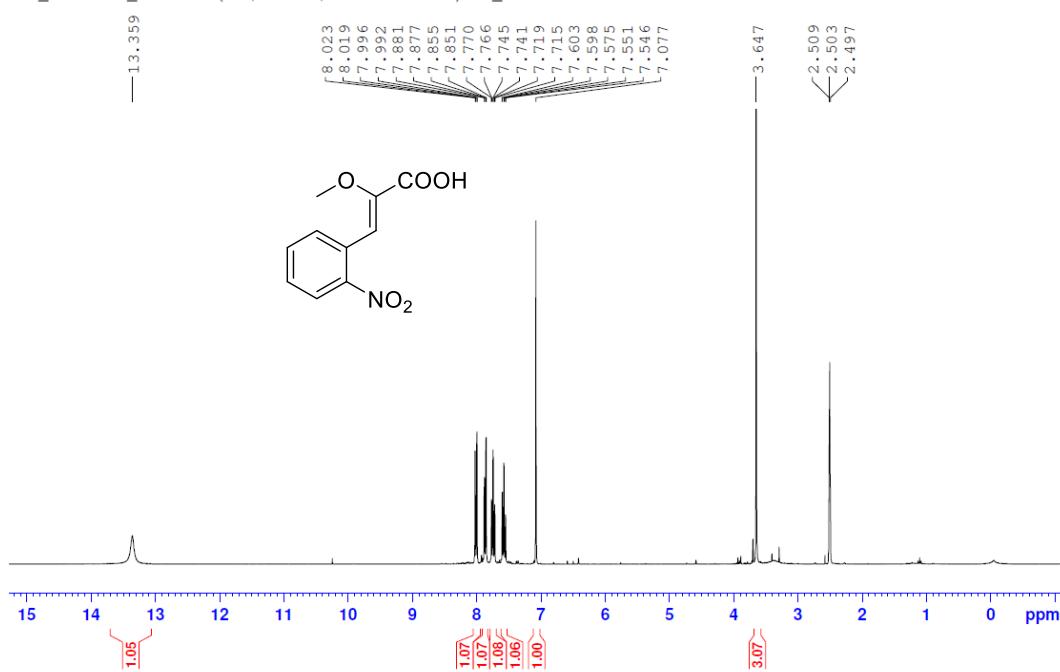
¹H NMR of S3

SpinWorks 4: Kreitmeier, Ethyl 2-nitro-alpha-methoxycinnamate,crude, CDCl3 rau_PROTONLF_16 CDCl3 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 12

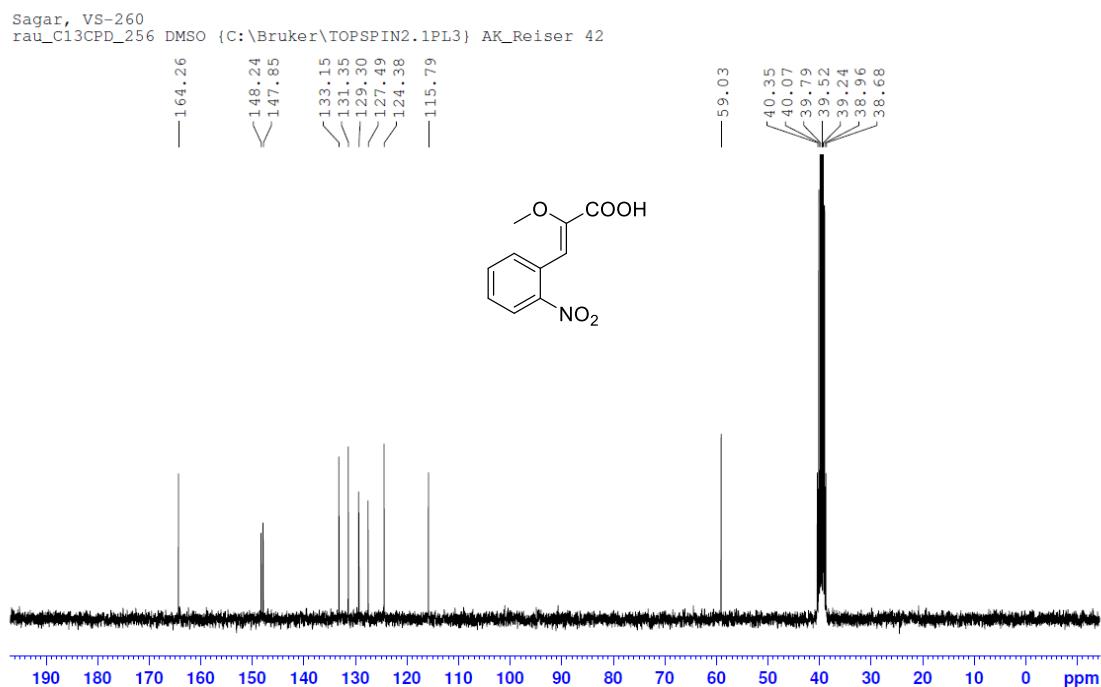


¹H NMR of **9**

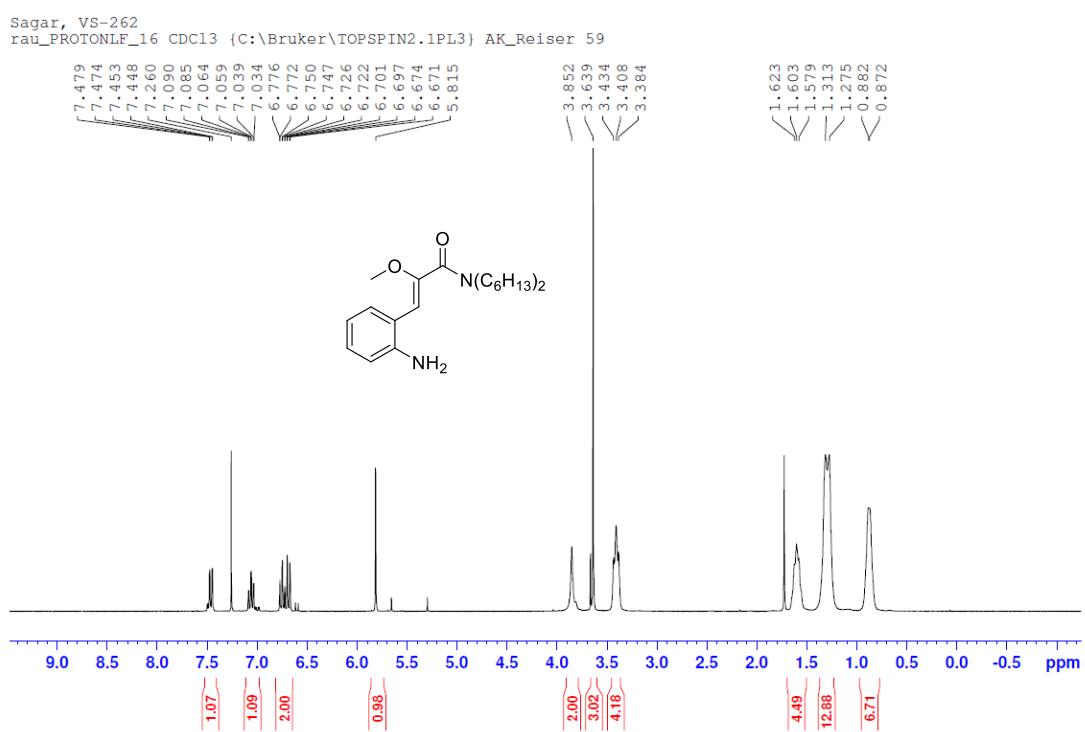
Sagar, VS-260
rau_PROTONLF_16 DMSO {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 42



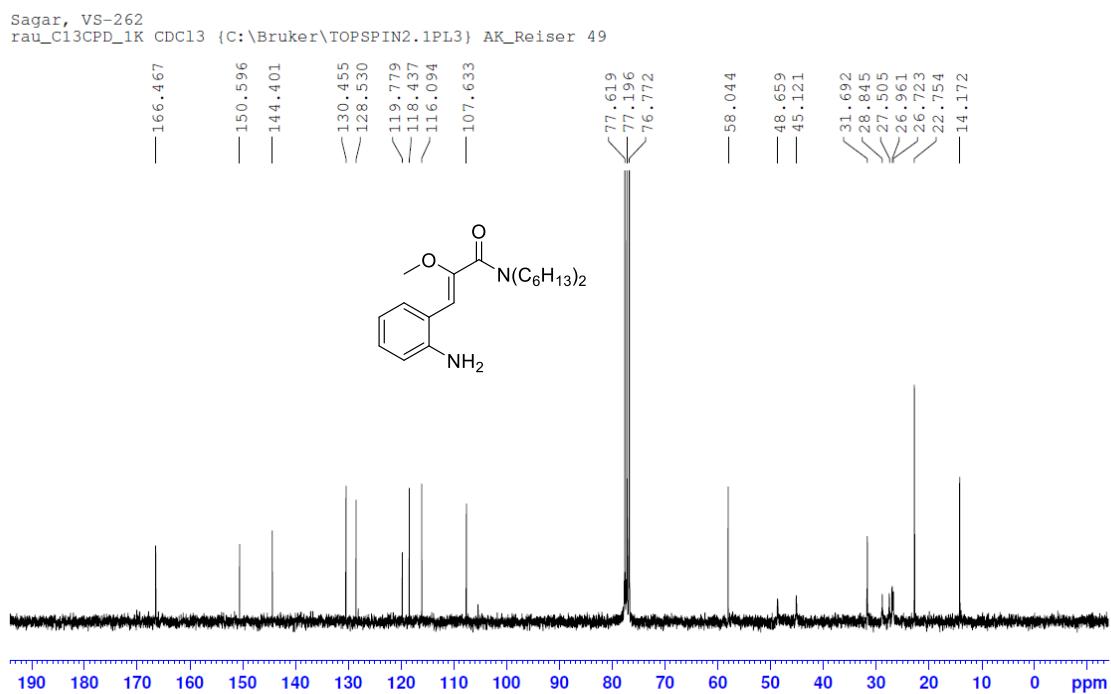
¹³C NMR of **9**



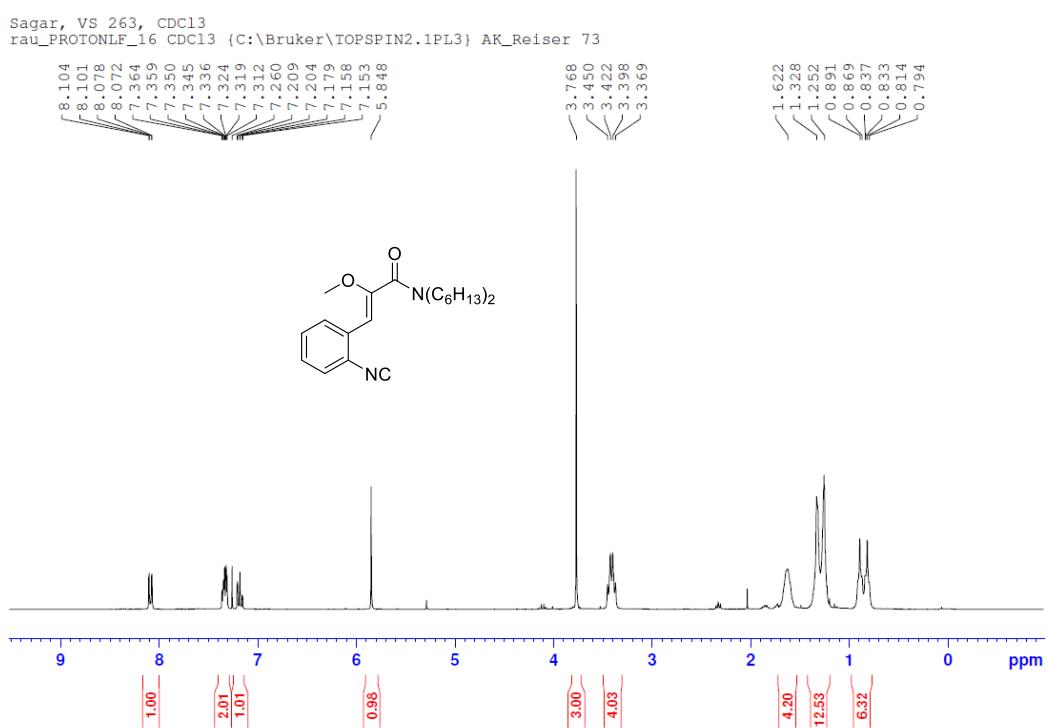
¹H NMR of **10**



¹³C NMR of **10**

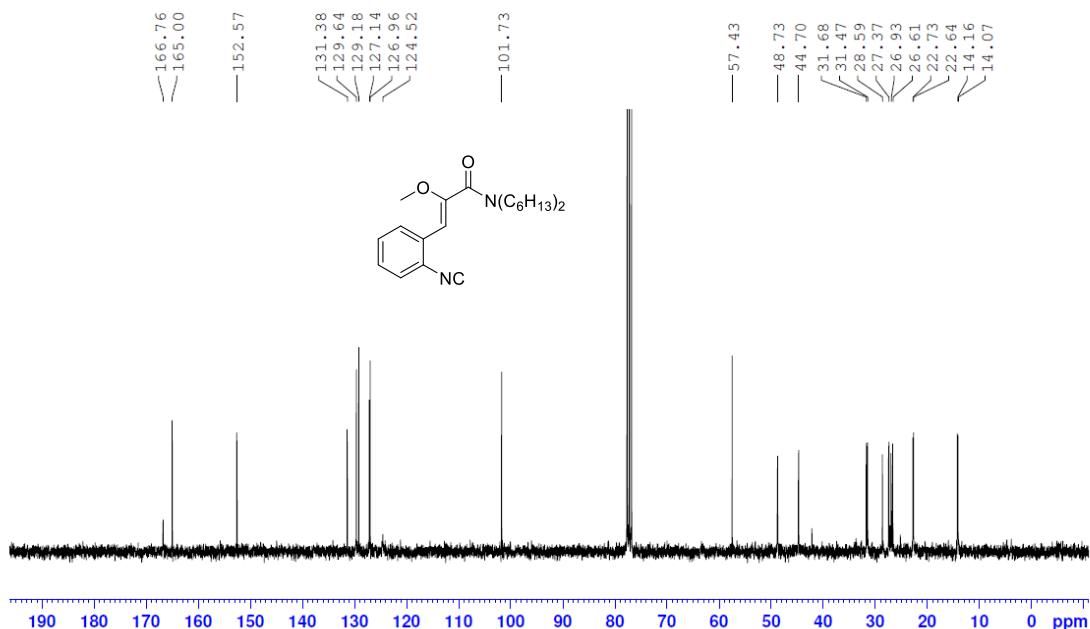


¹H NMR of **11**



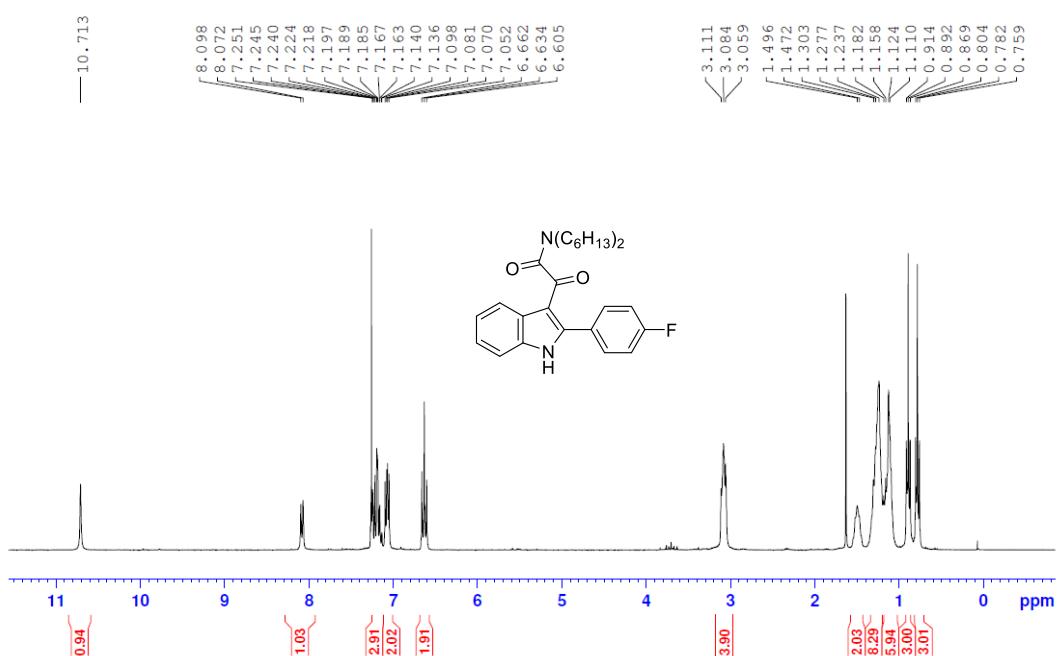
¹³C NMR of 11

Sagar, VS 263, CDC13
rau_C13CPD_256 CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 73



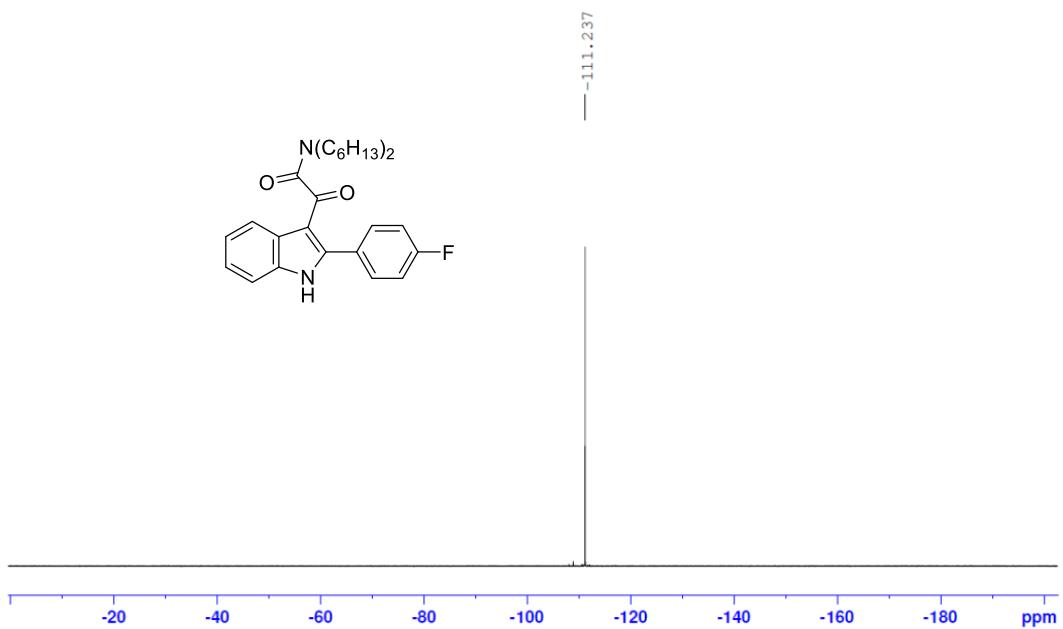
¹H NMR of 12

Sagar, VS-264
rau_PROTONLF_16 CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 70



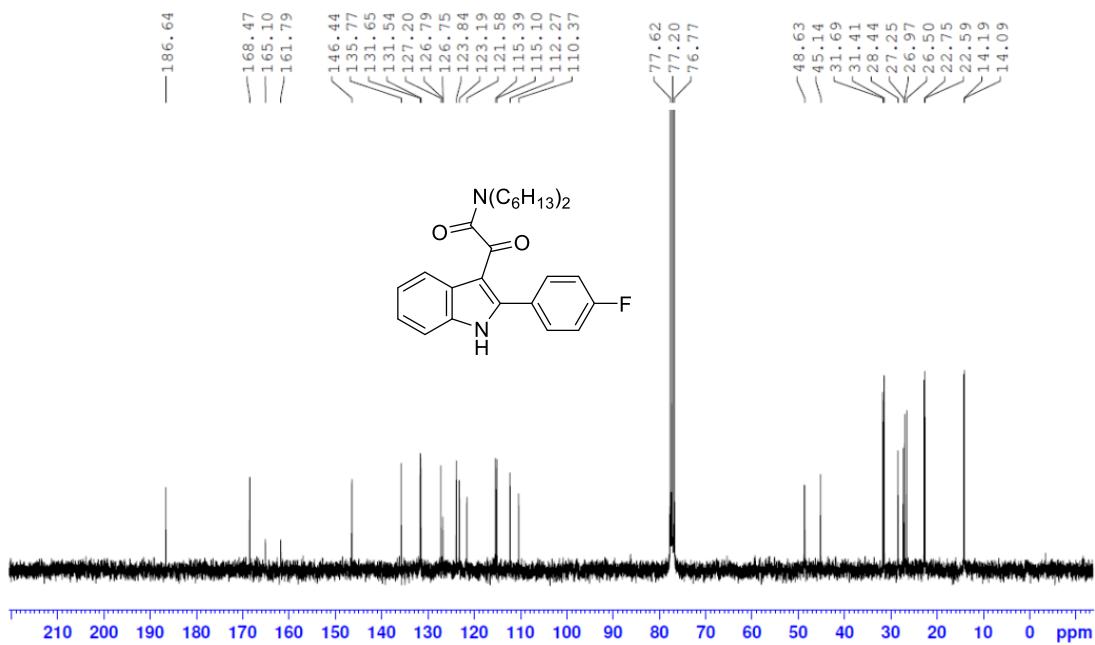
¹⁹F NMR of **12**

Sagar, VS-264
rau_F19CPD CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 70



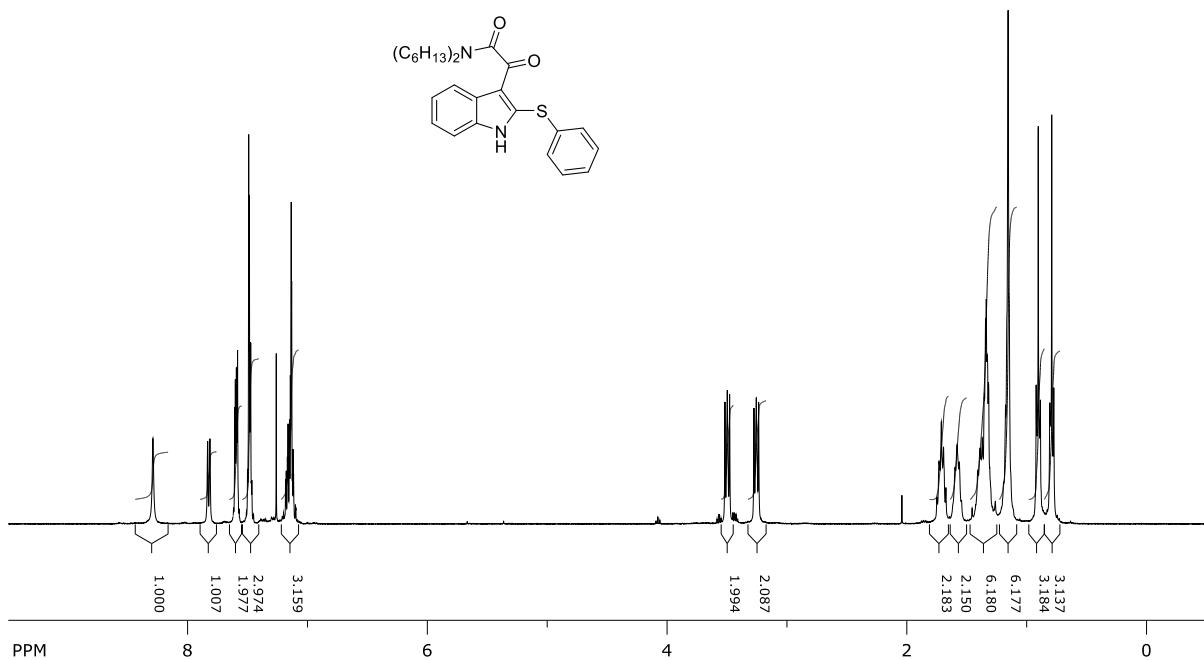
¹³C NMR of **12**

Sagar, VS-264
rau_C13CPD_1K CDC13 {C:\Bruker\TOPSPIN2.1PL3} AK_Reiser 70



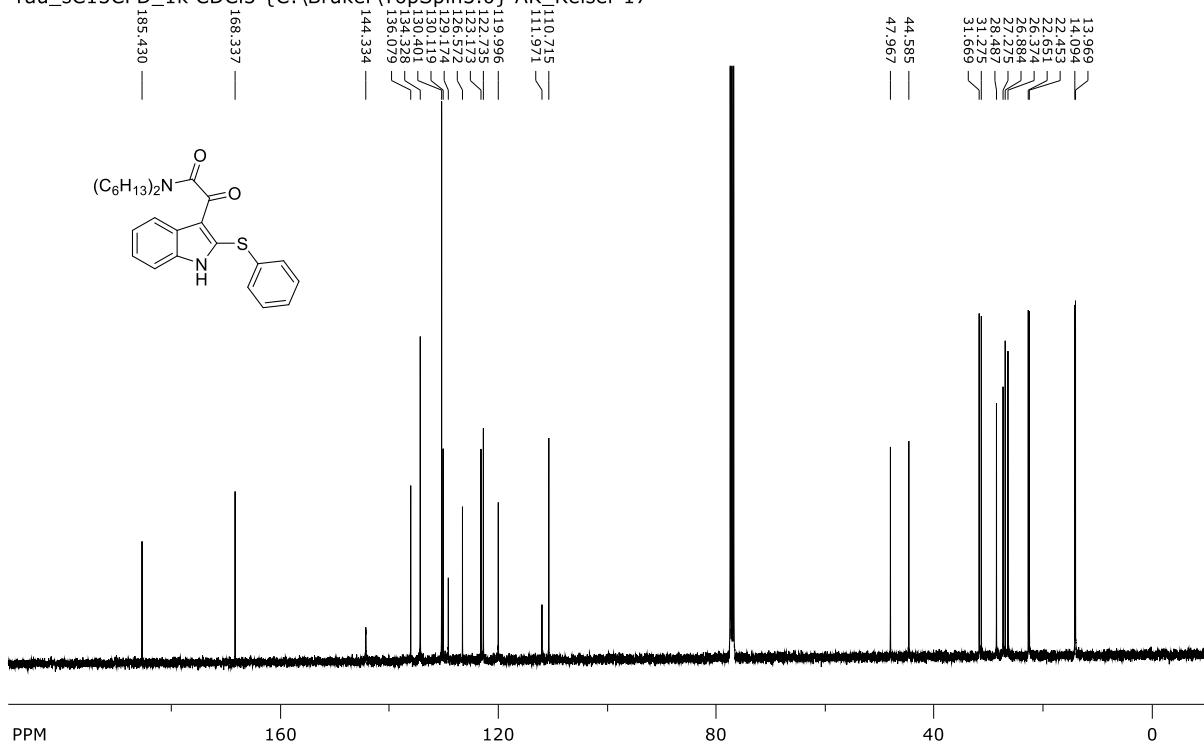
¹H NMR of **13a**

SpinWorks 4: Kreitmeier, N,N-Dihexyl-2-oxo-2-(2-(phenylthio)-1H-indol-3-yl)acetamide, CDCl₃
rau_sPROTON_16 CDCl₃ {C:\Bruker\TopSpin3.0} AK_Reiser 17



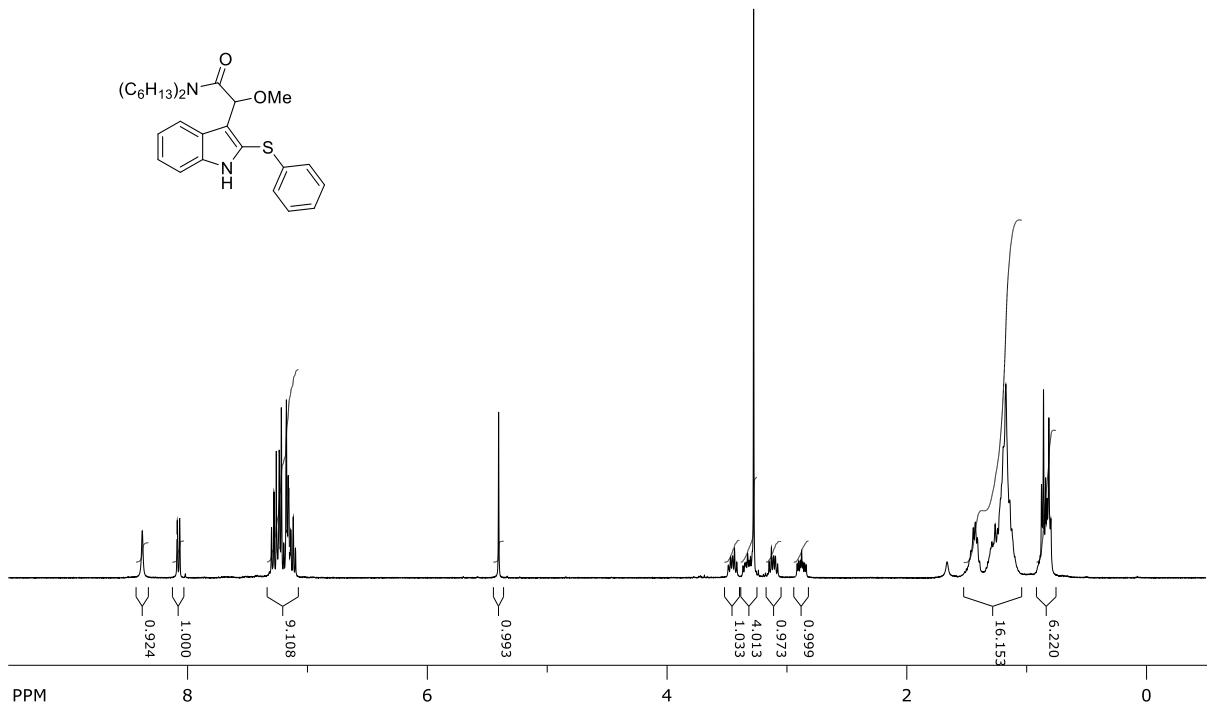
¹³C NMR of **13a**

SpinWorks 4: Kreitmeier, N,N-Dihexyl-2-oxo-2-(2-(phenylthio)-1H-indol-3-yl)acetamide, CDCl₃
rau_sC13CPD_1k CDCl₃ {C:\Bruker\TopSpin3.0} AK_Reiser 17



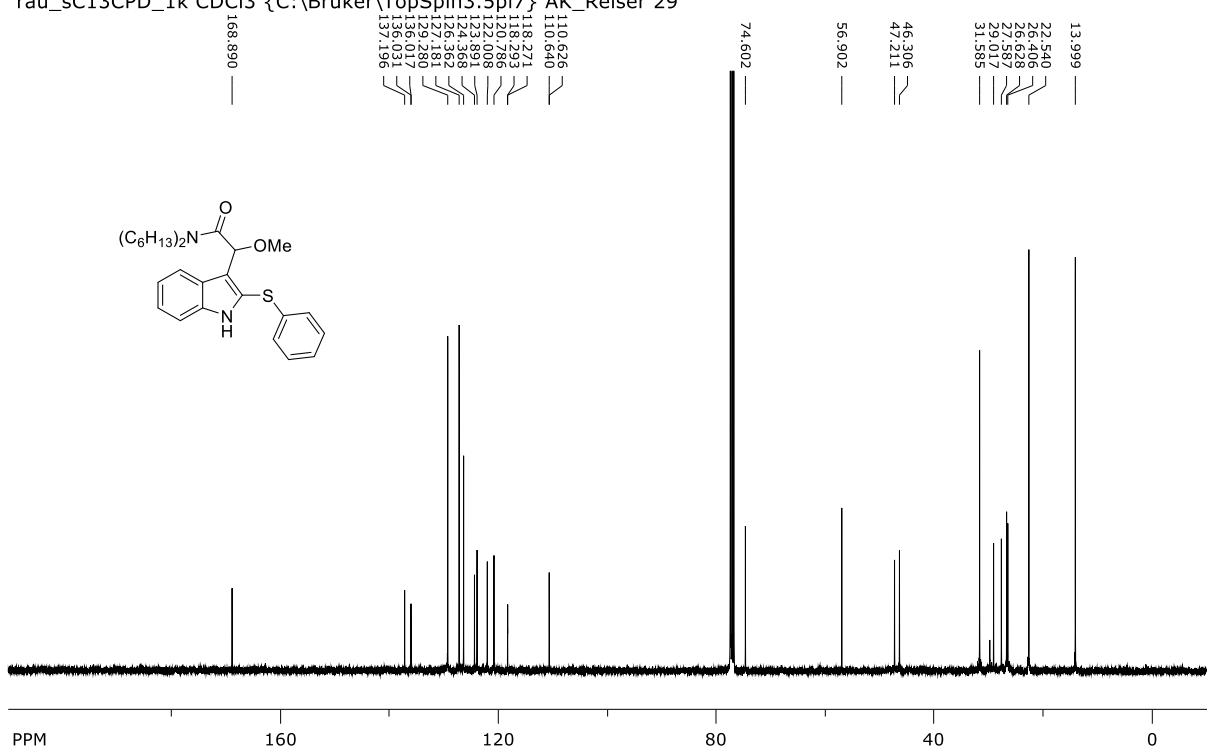
¹H NMR of **13b**

SpinWorks 4: Kreitmeier, N,N-Dihexyl-2-methoxy-2-(2-(phenylthio)-1H-indol-3-yl)acetamide, CDCl₃
rau_PROTONLF_16 CDCl₃ {C:\Bruker\TopSpin3.5pl7} AK_Reiser 29

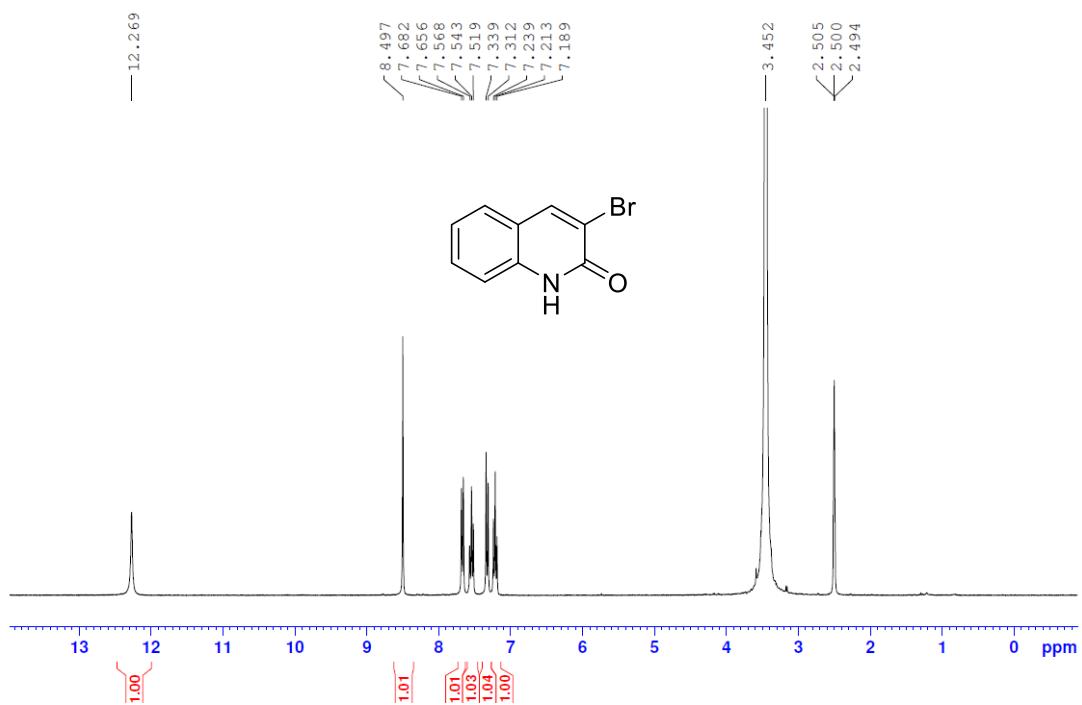


¹³C NMR of **13b**

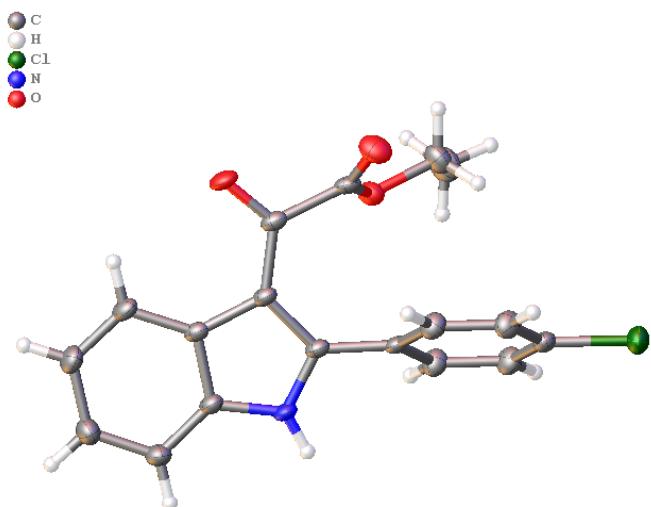
SpinWorks 4: Kreitmeier, N,N-Dihexyl-2-methoxy-2-(2-(phenylthio)-1H-indol-3-yl)acetamide, CDCl₃
rau_sC13CPD_1k CDCl₃ {C:\Bruker\TopSpin3.5pl7} AK_Reiser 29



¹H NMR of **15**



Crystal Data and Experimental of compound **3b**



Experimental. Single clear colourless block-shaped crystals of (**3b**) were obtained by recrystallisation from acetone. A suitable crystal ($0.20 \times 0.15 \times 0.11$ mm 3) was selected and mounted on a MITIGEN holder with inert oil on a SuperNova, Single source at offset, Atlas diffractometer. The crystal was kept at $T = 123.00(10)$ K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2016/6 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{18}H_{14}ClNO_3$, $M_r = 327.75$, orthorhombic, $Pbca$ (No. 61), $a = 14.3958(2)$ Å, $b = 10.23280(10)$ Å, $c = 21.1913(3)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 3121.68(7)$ Å 3 , $T = 123.00(10)$ K, $Z = 8$, $Z' = 1$, $\mu(\text{CuK}\alpha) = 2.294$, 43258 reflections measured, 3273 unique ($R_{int} = 0.0486$) which were used in all calculations. The final wR_2 was 0.0953 (all data) and R_1 was 0.0345 ($I > 2(I)$).

| Compound | 3b |
|-------------------------------------|--------------------------------|
| Formula | $C_{18}H_{14}ClNO_3$ |
| $D_{\text{calc.}}/\text{g cm}^{-3}$ | 1.395 |
| μ/mm^{-1} | 2.294 |
| Formula Weight | 327.75 |
| Colour | clear colourless |
| Shape | block |
| Size/mm 3 | $0.20 \times 0.15 \times 0.11$ |
| T/K | 123.00(10) |
| Crystal System | orthorhombic |
| Space Group | $Pbca$ |
| $a/\text{\AA}$ | 14.3958(2) |
| $b/\text{\AA}$ | 10.23280(10) |
| $c/\text{\AA}$ | 21.1913(3) |
| $\alpha/^\circ$ | 90 |
| $\beta/^\circ$ | 90 |
| $\gamma/^\circ$ | 90 |
| $V/\text{\AA}^3$ | 3121.68(7) |
| Z | 8 |
| Z' | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | $\text{CuK}\alpha$ |
| $\Theta_{\text{min}}/^\circ$ | 4.172 |
| $\Theta_{\text{max}}/^\circ$ | 76.494 |
| Measured Refl. | 43258 |
| Independent Refl. | 3273 |
| Reflections Used | 3016 |
| R_{int} | 0.0486 |
| Parameters | 209 |
| Restraints | 0 |
| Largest Peak | 0.245 |
| Deepest Hole | -0.245 |
| $GooF$ | 1.066 |
| wR_2 (all data) | 0.0953 |
| wR_2 | 0.0926 |
| R_1 (all data) | 0.0370 |
| R_1 | 0.0345 |

Structure Quality Indicators

| | | | | | | | | |
|--------------|-----------------------------|--------|------------|------|------------------|-------|---------------------------------|-------|
| Reflections: | $d_{\text{min}}(\text{Cu})$ | 0.79 | l/σ | 36.1 | R_{int} | 4.86% | complete at $2\theta=154^\circ$ | 100% |
| Refinement: | Shift | -0.001 | Max Peak | 0.2 | Min Peak | -0.2 | GooF | 1.066 |

A clear colourless block-shaped crystal with dimensions $0.20 \times 0.15 \times 0.11 \text{ mm}^3$ was mounted on a MITIGEN holder with inert oil. X-ray diffraction data were collected using a SuperNova, Single source at offset, Atlas diffractometer equipped with a Oxford Cryosystems CryoStream 700 low-temperature device, operating at $T = 123.00(10) \text{ K}$.

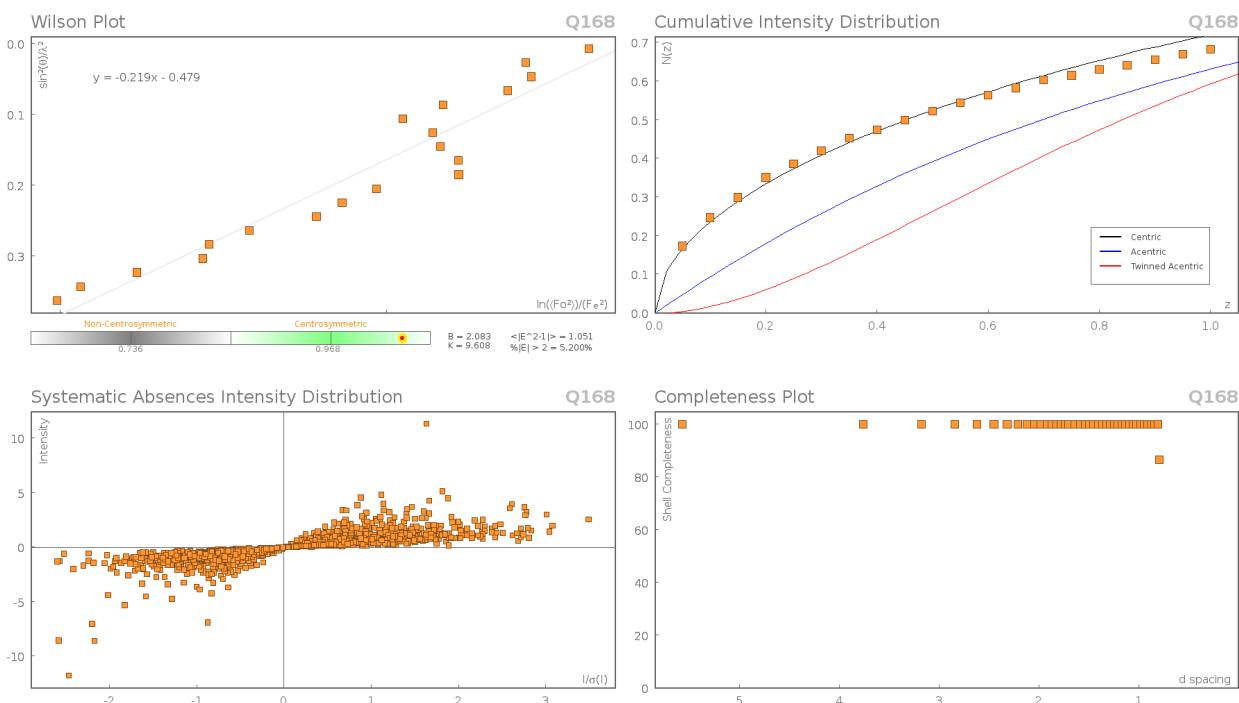
Data were measured using ω scans scans of 1.0° per frame for 5.5 s using $\text{CuK}\alpha$ radiation (micro-focus sealed X-ray tube, n/a kV, n/a mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent). The maximum resolution achieved was $\Theta = 76.494^\circ$.

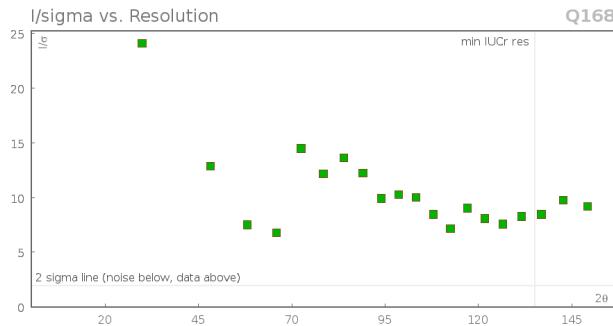
Cell parameters were retrieved using the CrysAlisPro (Agilent) software and refined using CrysAlisPro (Agilent) on 18757 reflections, 43 % of the observed reflections. Data reduction was performed using the CrysAlisPro (Agilent) software which corrects for Lorentz polarisation. The final completeness is 100.00 out to 76.494 in Θ . The absorption coefficient μ of this material is 2.294 at this wavelength ($\lambda = 1.54184$) and the minimum and maximum transmissions are 0.962 and 0.979.

The structure was solved in the space group Pbca (# 61) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2016/6 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

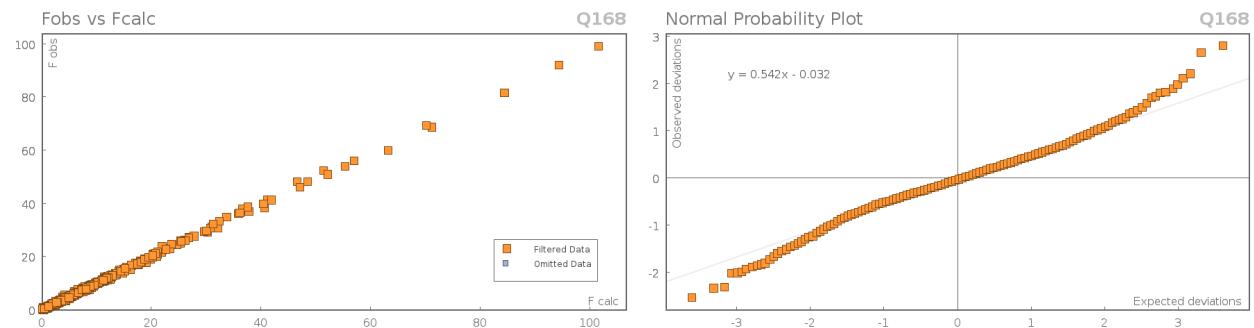
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

| | | | |
|-------------------------------------|--|--------------------------------|-----------------|
| Total reflections (after filtering) | 45963 | Unique reflections | 3273 |
| Completeness | 0.999 | Mean I/σ | 36.1 |
| hkl_{max} collected | (18, 12, 26) | hkl_{min} collected | (-18, -12, -26) |
| hkl_{max} used | (18, 12, 26) | hkl_{min} used | (0, 0, 0) |
| Lim d_{max} collected | 100.0 | Lim d_{min} collected | 0.77 |
| d_{max} used | 11.91 | d_{min} used | 0.79 |
| Friedel pairs | 6692 | Friedel pairs merged | 1 |
| Inconsistent equivalents | 1 | R_{int} | 0.0486 |
| R_{sigma} | 0.0184 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 0 |
| Multiplicity | (7426, 5238, 2823, 1515, 890, Maximum multiplicity 535, 301, 144, 113, 85, 43, 14, 7, 1) | Removed systematic absences | 2705 |
| Removed systematic absences | 2705 | Filtered off (Shel/OMIT) | 0 |

Images of the Crystal on the Diffractometer



Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

| Atom | x | y | z | U_{eq} |
|------|-----------|-----------|-----------|-----------|
| Cl1 | 4687.7(2) | 6157.5(3) | 7209.5(2) | 35.76(12) |

| Atom | x | y | z | U_{eq} |
|------|------------|------------|-----------|-----------|
| O1 | 7761.4(6) | 3122.1(9) | 6263.2(4) | 24.41(19) |
| O2 | 8746.9(6) | 2880.8(9) | 4911.9(4) | 27.2(2) |
| O3 | 8350.6(7) | 4952.1(10) | 5827.9(5) | 34.2(2) |
| N1 | 5646.3(6) | 1954.4(10) | 4860.0(5) | 21.2(2) |
| C4 | 5878.1(7) | 3587.3(12) | 5683.3(5) | 19.9(2) |
| C8 | 6120.3(8) | 1242.3(11) | 4406.9(5) | 21.2(2) |
| C5 | 6239.8(7) | 2733.4(11) | 5179.3(5) | 19.4(2) |
| C7 | 7066.2(7) | 1587.6(12) | 4445.1(5) | 20.2(2) |
| C6 | 7138.1(7) | 2550.8(11) | 4941.2(5) | 19.9(2) |
| C13 | 7990.7(8) | 3082.7(11) | 5170.3(5) | 20.6(2) |
| C14 | 8034.9(7) | 3870.7(12) | 5785.7(6) | 21.7(2) |
| C1 | 5149.1(8) | 5161.1(13) | 6620.6(6) | 24.9(2) |
| C3 | 5961.4(8) | 4936.3(13) | 5642.1(6) | 26.6(3) |
| C12 | 7702.9(8) | 945.4(13) | 4054.3(6) | 25.3(3) |
| C9 | 5781.2(8) | 330.1(13) | 3980.2(6) | 27.1(3) |
| C2 | 5590.9(9) | 5733.8(13) | 6112.7(7) | 29.2(3) |
| C11 | 7374.3(9) | 7.9(14) | 3638.4(6) | 30.2(3) |
| C16 | 5059.9(9) | 3823.0(13) | 6673.4(6) | 28.6(3) |
| C15 | 5422.4(9) | 3035.9(12) | 6199.7(6) | 26.4(3) |
| C10 | 6424.4(9) | -283.8(14) | 3596.2(6) | 31.2(3) |
| C17 | 7807.4(11) | 3688.2(14) | 6892.0(6) | 32.2(3) |
| C18 | 7646.2(12) | 2589.2(16) | 7342.5(7) | 39.7(3) |

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **3b.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

| Atom | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|------|-----------|----------|----------|------------|----------|----------|
| Cl1 | 28.04(19) | 43.5(2) | 35.7(2) | -16.81(13) | 3.65(12) | 2.62(12) |
| O1 | 24.0(4) | 29.3(4) | 20.0(4) | 0.6(3) | -2.0(3) | -3.3(3) |
| O2 | 11.7(4) | 39.7(5) | 30.0(5) | 0.2(4) | 1.5(3) | -1.8(3) |
| O3 | 37.0(5) | 30.8(5) | 34.6(5) | 1.1(4) | -2.9(4) | -11.0(4) |
| N1 | 10.5(4) | 29.3(5) | 24.0(5) | -2.9(4) | 0.5(3) | -0.7(3) |
| C4 | 11.1(4) | 27.1(6) | 21.5(5) | -0.8(4) | -1.2(4) | 0.2(4) |
| C8 | 14.1(5) | 28.4(6) | 21.0(5) | 0.2(4) | 0.5(4) | 0.8(4) |
| C5 | 12.5(5) | 25.0(5) | 20.7(5) | 2.6(4) | -0.5(4) | -0.7(4) |
| C7 | 13.9(5) | 28.0(6) | 18.8(5) | 2.8(4) | -0.3(4) | -0.2(4) |
| C6 | 12.7(5) | 27.0(5) | 19.9(5) | 1.9(4) | 0.5(4) | 0.2(4) |
| C13 | 13.7(5) | 26.3(5) | 21.9(5) | 5.2(4) | -0.3(4) | -0.3(4) |
| C14 | 12.4(5) | 27.6(6) | 25.0(6) | 3.2(4) | -2.9(4) | -1.3(4) |
| C1 | 15.6(5) | 33.3(6) | 25.8(6) | -6.8(5) | -1.4(4) | 1.8(4) |
| C3 | 24.2(6) | 28.3(6) | 27.2(6) | 1.7(5) | 4.7(5) | -1.2(5) |
| C12 | 15.7(5) | 37.2(6) | 22.9(6) | 0.2(5) | 3.5(4) | 0.9(5) |
| C9 | 18.3(5) | 35.1(6) | 28.1(6) | -4.8(5) | -0.7(4) | -2.8(4) |
| C2 | 28.3(6) | 24.1(6) | 35.1(7) | -2.1(5) | 2.7(5) | -0.6(5) |
| C11 | 25.1(6) | 39.9(7) | 25.7(6) | -5.6(5) | 6.9(5) | 2.6(5) |
| C16 | 26.2(6) | 34.7(7) | 24.9(6) | 0.3(5) | 6.7(5) | -1.2(5) |
| C15 | 26.2(6) | 24.9(6) | 28.2(6) | 0.7(5) | 5.5(5) | -1.4(4) |
| C10 | 29.0(6) | 37.9(7) | 26.6(6) | -9.7(5) | 0.9(5) | -2.9(5) |
| C17 | 38.7(7) | 35.9(7) | 22.1(6) | -3.9(5) | -4.0(5) | -1.7(5) |
| C18 | 49.7(9) | 47.0(8) | 22.4(6) | 2.2(6) | 2.0(6) | -2.3(7) |

Table 3: Bond Lengths in Å for **3b.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|------------|------|------|------------|
| Cl1 | C1 | 1.7431(12) | N1 | C8 | 1.3852(15) |
| O1 | C14 | 1.3289(15) | N1 | C5 | 1.3502(15) |
| O1 | C17 | 1.4544(15) | C4 | C5 | 1.4749(16) |
| O2 | C13 | 1.2359(15) | C4 | C3 | 1.3883(17) |
| O3 | C14 | 1.1997(16) | C4 | C15 | 1.3952(17) |

| Atom | Atom | Length/Å |
|------|------|------------|
| C8 | C7 | 1.4091(15) |
| C8 | C9 | 1.3882(17) |
| C5 | C6 | 1.4006(15) |
| C7 | C6 | 1.4450(16) |
| C7 | C12 | 1.3992(16) |
| C6 | C13 | 1.4277(15) |
| C13 | C14 | 1.5345(17) |
| C1 | C2 | 1.3806(19) |

| Atom | Atom | Length/Å |
|------|------|------------|
| C1 | C16 | 1.3798(19) |
| C3 | C2 | 1.3946(18) |
| C12 | C11 | 1.3859(18) |
| C9 | C10 | 1.3836(18) |
| C11 | C10 | 1.4025(19) |
| C16 | C15 | 1.3887(18) |
| C17 | C18 | 1.493(2) |

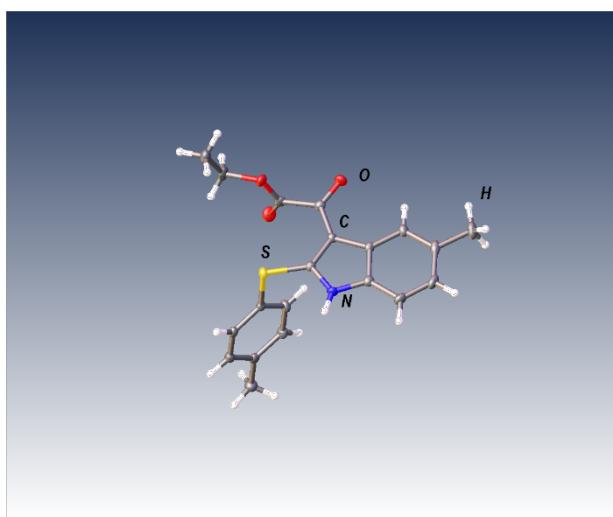
Table 4: Bond Angles in ° for **3b**.

| Atom | Atom | Atom | Angle/° |
|------|------|------|------------|
| C14 | O1 | C17 | 117.03(10) |
| C5 | N1 | C8 | 110.26(9) |
| C3 | C4 | C5 | 120.87(11) |
| C3 | C4 | C15 | 119.47(11) |
| C15 | C4 | C5 | 119.64(11) |
| N1 | C8 | C7 | 107.72(10) |
| N1 | C8 | C9 | 129.19(11) |
| C9 | C8 | C7 | 123.09(11) |
| N1 | C5 | C4 | 119.29(9) |
| N1 | C5 | C6 | 108.97(10) |
| C6 | C5 | C4 | 131.75(10) |
| C8 | C7 | C6 | 106.38(10) |
| C12 | C7 | C8 | 118.77(11) |
| C12 | C7 | C6 | 134.76(10) |
| C5 | C6 | C7 | 106.67(10) |
| C5 | C6 | C13 | 128.35(11) |
| C13 | C6 | C7 | 124.68(10) |
| O2 | C13 | C6 | 122.87(11) |
| O2 | C13 | C14 | 115.33(10) |
| C6 | C13 | C14 | 121.66(10) |
| O1 | C14 | C13 | 109.39(10) |
| O3 | C14 | O1 | 125.96(12) |
| O3 | C14 | C13 | 124.32(11) |
| C2 | C1 | Cl1 | 119.04(10) |
| C16 | C1 | Cl1 | 119.14(10) |
| C16 | C1 | C2 | 121.82(12) |
| C4 | C3 | C2 | 120.26(11) |
| C11 | C12 | C7 | 118.54(11) |
| C10 | C9 | C8 | 116.93(11) |
| C1 | C2 | C3 | 119.03(12) |
| C12 | C11 | C10 | 121.38(11) |
| C1 | C16 | C15 | 118.82(12) |
| C16 | C15 | C4 | 120.61(12) |
| C9 | C10 | C11 | 121.22(12) |
| O1 | C17 | C18 | 106.17(11) |

Table 5: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

| Atom | x | y | z | U_{eq} |
|------|---------|---------|---------|----------|
| H1 | 5058.4 | 1907.08 | 4928.25 | 25 |
| H3 | 6265.41 | 5309.59 | 5299.44 | 32 |
| H12 | 8332.83 | 1143.31 | 4073.22 | 30 |
| H9 | 5150.57 | 140.33 | 3953.74 | 33 |
| H2 | 5640.69 | 6638.06 | 6084.87 | 35 |
| H11 | 7792.44 | -437.15 | 3382.04 | 36 |
| H16 | 4762.33 | 3454.83 | 7019.95 | 34 |
| H15 | 5360.89 | 2132.99 | 6227.07 | 32 |
| H10 | 6223.19 | -901.26 | 3304.62 | 37 |
| H17A | 7334.68 | 4355.53 | 6942.8 | 39 |
| H17B | 8411.5 | 4080.51 | 6964.18 | 39 |
| H18A | 7063.94 | 2176.15 | 7247.58 | 60 |
| H18B | 7631.81 | 2922.38 | 7765.85 | 60 |
| H18C | 8139.12 | 1962.53 | 7303.61 | 60 |

Crystal Data and Experimental of compound **4g**



Crystal Data. $C_{20}H_{19}NO_3S$, $M_r = 353.42$, triclinic, $P-1$ (No. 2), $a = 7.3606(3) \text{\AA}$, $b = 9.5939(4) \text{\AA}$, $c = 13.4513(5) \text{\AA}$, $\alpha = 108.294(3)^\circ$, $\beta = 99.352(3)^\circ$, $\gamma = 102.148(3)^\circ$, $V = 854.54(6) \text{\AA}^3$, $T = 123.01(10) \text{ K}$, $Z = 2$, $Z' = 1$, $\mu(\text{CuK}_\alpha) = 1.841$, 9442 reflections measured, 3371 unique ($R_{int} = 0.0483$) which were used in all calculations. The final wR_2 was 0.1004 (all data) and R_1 was 0.0370 ($I > 2(I)$).

Experimental. Single clear colorless needle-shaped crystals of (**4g**) were obtained by recrystallization from ethylacetate and pentane. A suitable crystal ($0.32 \times 0.06 \times 0.04$ mm 3) was selected and mounted on a MITIGEN holder with inert oil on a SuperNova, Single source at offset/far, Atlas diffractometer. The crystal was kept at $T = 123.01(10)$ K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2016/6 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

| Compound | 4g |
|---|---|
| Formula | C ₂₀ H ₁₉ NO ₃ S |
| D _{calc.} / g cm ⁻³ | 1.374 |
| μ/mm ⁻¹ | 1.841 |
| Formula Weight | 353.42 |
| Colour | clear colourless |
| Shape | needle |
| Size/mm ³ | 0.32×0.06×0.04 |
| T/K | 123.01(10) |
| Crystal System | triclinic |
| Space Group | P-1 |
| a/Å | 7.3606(3) |
| b/Å | 9.5939(4) |
| c/Å | 13.4513(5) |
| α/° | 108.294(3) |
| β/° | 99.352(3) |
| γ/° | 102.148(3) |
| V/Å ³ | 854.54(6) |
| Z | 2 |
| Z' | 1 |
| Wavelength/Å | 1.54184 |
| Radiation type | CuK _α |
| Θ _{min} /° | 3.571 |
| Θ _{max} /° | 74.181 |
| Measured Refl. | 9442 |
| Independent Refl. | 3371 |
| Reflections Used | 2998 |
| R _{int} | 0.0483 |
| Parameters | 229 |
| Restraints | 0 |
| Largest Peak | 0.356 |
| Deepest Hole | -0.382 |
| GooF | 1.065 |
| wR ₂ (all data) | 0.1004 |
| wR ₂ | 0.0960 |
| R ₁ (all data) | 0.0419 |
| R ₁ | 0.0370 |

Structure Quality Indicators

| | | | | | | | | |
|--------------|-----------------------|-------|------------|------|------------------|-------|-------------------------|-------|
| Reflections: | $d_{\min}(\text{Cu})$ | 0.80 | I/σ | 23.4 | R_{int} | 4.83% | complete 100% (IUCr) | 97% |
| Refinement: | Shift | 0.001 | Max Peak | 0.4 | Min Peak | -0.4 | GooF | 1.065 |

A clear colourless needle-shaped crystal with dimensions $0.32 \times 0.06 \times 0.04$ mm³ was mounted on a MITIGEN holder with inert oil. X-ray diffraction data were collected using a SuperNova, Single source at offset/far, Atlas diffractometer equipped with an Oxford cryosystem 700 low-temperature device, operating at $T = 123.01(10)$ K.

Data were measured using ω scans scans of 1.0° per frame for $7.0/25.0$ s using CuK α radiation (micro-focus sealed X-ray tube, n/a kV, n/a mA). The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.37b, 2017). The maximum resolution achieved was $\Theta = 74.181^\circ$.

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.39.37b, 2017) software and refined using **CrysAlisPro** (Rigaku, V1.171.39.37b, 2017) on 5786 reflections, 61 % of the observed reflections. Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.39.37b, 2017) software which corrects for Lorentz polarisation. The final completeness is 99.60 % out to 74.181° in Θ .

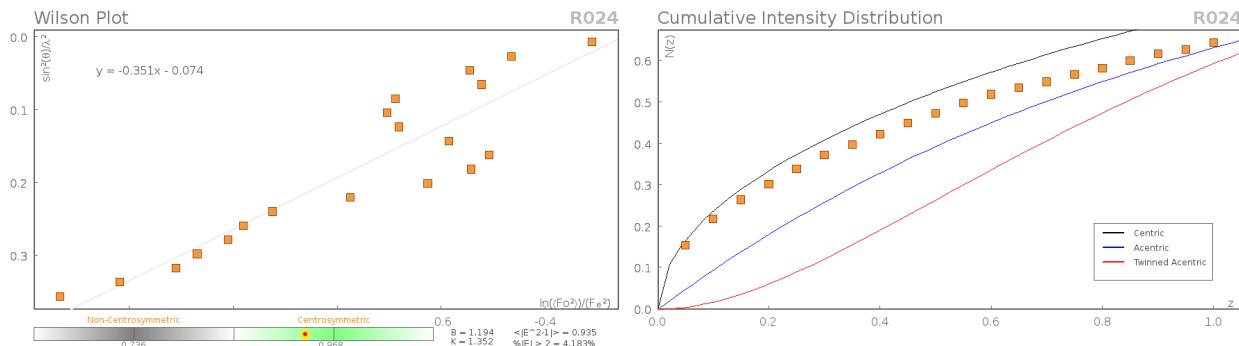
A Gaussian absorption correction was performed using CrysAlisPro 1.171.39.37b (Rigaku Oxford Diffraction, 2017) Numerical absorption correction based on Gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this material is 1.841 mm⁻¹ at this wavelength ($\lambda = 1.54184\text{\AA}$) and the minimum and maximum transmissions are 0.680 and 1.000..

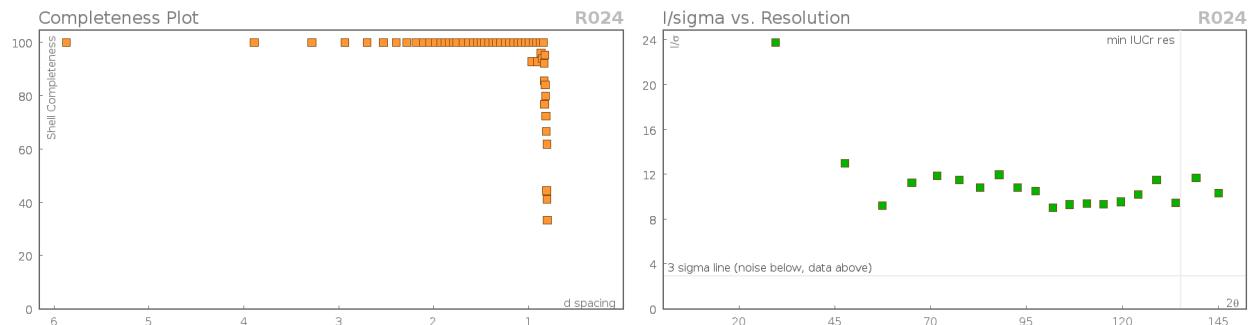
The structure was solved in the space group $P-1$ (# 2) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2016/6 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: CrysAlisPro 1.171.39.37b (Rigaku Oxford Diffraction, 2017) Numerical absorption correction based on Gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

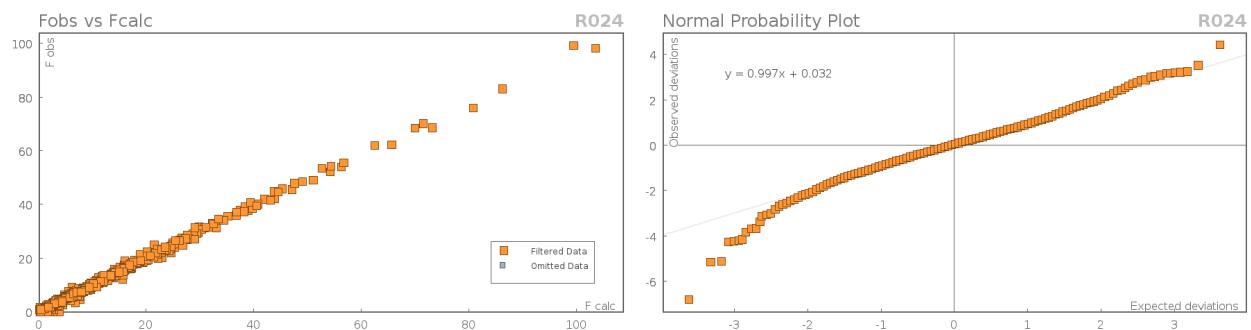
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

| | | | |
|-------------------------------------|-------------------------------|-------------------------------|----------------|
| Total reflections (after filtering) | 9442 | Unique reflections | 3371 |
| Completeness | 0.97 | Mean I/σ | 16.38 |
| hkl_{\max} collected | (9, 11, 16) | hkl_{\min} collected | (-7, -11, -16) |
| hkl_{\max} used | (8, 11, 16) | hkl_{\min} used | (-9, -11, 0) |
| Lim d_{\max} collected | 100.0 | Lim d_{\min} collected | 0.77 |
| d_{\max} used | 12.38 | d_{\min} used | 0.8 |
| Friedel pairs | 2073 | Friedel pairs merged | 1 |
| Inconsistent equivalents | 34 | R_{int} | 0.0483 |
| R_{sigma} | 0.0428 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 0 |
| Multiplicity | (2696, 1805, 682, 219, 38, 4) | Maximum multiplicity | 10 |
| Removed systematic absences | | Filtered off (Shel/OMIT) | 0 |

Images of the Crystal on the Diffractometer

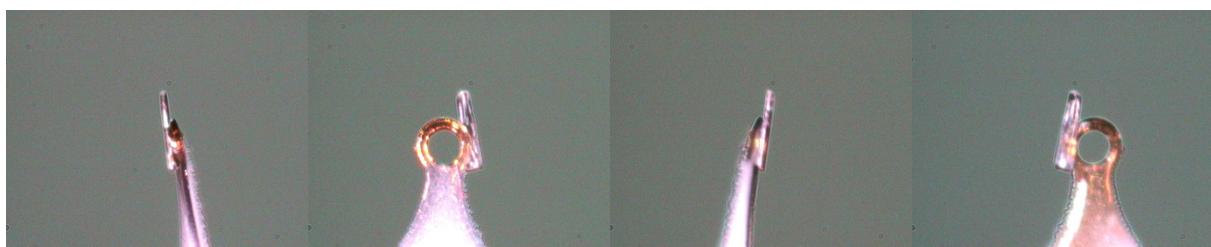


Table 6: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4g**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

| Atom | x | y | z | U_{eq} |
|------|------------|------------|-----------|-----------|
| S1 | 7620.1(5) | 7966.9(4) | 3005.6(3) | 15.59(12) |
| O1 | 3414.0(16) | 9010.1(12) | 2554.4(9) | 20.0(2) |
| O3 | 1087.4(15) | 5738.1(13) | 1473.7(9) | 21.1(2) |

| Atom | x | y | z | U_{eq} |
|------|------------|-------------|-------------|----------|
| O2 | 3481.2(17) | 7874.8(14) | 3796.9(9) | 25.8(3) |
| N1 | 7121.9(17) | 5171.3(14) | 1533.5(9) | 14.4(3) |
| C5 | 4258(2) | 5597.8(16) | 1635.2(11) | 13.3(3) |
| C6 | 6247(2) | 6205.4(16) | 2022.0(11) | 13.7(3) |
| C15 | 9992(2) | 8147.8(16) | 4855.0(12) | 15.8(3) |
| C7 | 3939(2) | 4080.6(16) | 860.2(11) | 13.7(3) |
| C4 | 2807(2) | 6319.0(16) | 1925.4(11) | 14.9(3) |
| C14 | 8232(2) | 7363.8(16) | 4115.7(11) | 14.2(3) |
| C8 | 5750(2) | 3846.5(17) | 824.4(11) | 15.5(3) |
| C18 | 7570(2) | 5747.0(17) | 5137.5(12) | 19.0(3) |
| C3 | 3320(2) | 7834.1(17) | 2883.4(12) | 17.4(3) |
| C16 | 10496(2) | 7745.4(17) | 5746.6(12) | 17.9(3) |
| C19 | 7012(2) | 6163.2(17) | 4263.8(12) | 18.4(3) |
| C17 | 9310(2) | 6540.7(17) | 5904.3(12) | 16.8(3) |
| C11 | 2494(2) | 1538.8(17) | -456.5(12) | 20.6(3) |
| C9 | 5990(2) | 2489.8(18) | 165.7(12) | 20.4(3) |
| C12 | 2289(2) | 2903.2(17) | 200.5(12) | 17.2(3) |
| C10 | 4339(3) | 1349.1(17) | -465.7(12) | 22.2(3) |
| C20 | 9851(2) | 6084.2(19) | 6859.2(13) | 23.5(3) |
| C1 | 4265(2) | 11687.5(19) | 2886.4(14) | 27.2(4) |
| C13 | 750(3) | 251.8(19) | -1170.8(13) | 28.1(4) |
| C2 | 3827(2) | 10513.4(18) | 3403.0(14) | 24.9(4) |

Table 7: Anisotropic Displacement Parameters ($\times 10^4$) **4g**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

| Atom | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|------|----------|-----------|-----------|----------|----------|----------|
| S1 | 17.0(2) | 13.67(18) | 13.41(19) | 4.45(13) | 2.61(13) | 0.29(13) |
| O1 | 23.7(6) | 15.9(5) | 18.5(5) | 1.4(4) | 6.5(4) | 8.2(4) |
| O3 | 12.8(5) | 25.1(6) | 23.6(6) | 6.0(4) | 5.2(4) | 5.5(4) |
| O2 | 31.1(6) | 29.1(6) | 18.0(6) | 5.8(5) | 12.8(4) | 9.2(5) |
| N1 | 11.2(6) | 17.9(6) | 15.6(6) | 5.8(5) | 5.5(4) | 5.7(4) |
| C5 | 14.4(7) | 13.9(6) | 11.3(6) | 4.1(5) | 3.9(5) | 3.1(5) |
| C6 | 15.6(7) | 15.4(7) | 11.6(6) | 5.9(5) | 5.0(5) | 4.2(5) |
| C15 | 14.4(7) | 13.6(6) | 18.2(7) | 3.7(5) | 5.8(5) | 3.3(5) |
| C7 | 17.2(7) | 14.8(7) | 10.8(6) | 5.4(5) | 5.8(5) | 4.9(5) |
| C4 | 16.4(7) | 17.0(7) | 13.9(7) | 7.1(5) | 6.9(5) | 5.4(5) |
| C14 | 16.4(7) | 13.8(6) | 12.8(7) | 3.5(5) | 6.3(5) | 5.0(5) |
| C8 | 19.1(7) | 17.2(7) | 12.0(7) | 6.2(5) | 5.7(5) | 5.7(5) |
| C18 | 19.1(7) | 17.7(7) | 19.5(7) | 7.0(6) | 7.2(6) | 1.5(6) |
| C3 | 14.1(7) | 20.9(7) | 18.2(7) | 4.5(6) | 7.9(5) | 7.6(5) |
| C16 | 15.9(7) | 17.4(7) | 17.2(7) | 2.8(5) | 2.1(5) | 4.4(6) |
| C19 | 16.7(7) | 18.4(7) | 16.4(7) | 4.7(6) | 3.4(5) | 0.2(5) |
| C17 | 19.5(7) | 16.5(7) | 15.9(7) | 4.3(5) | 6.7(5) | 8.8(5) |
| C11 | 32.2(9) | 15.1(7) | 11.6(7) | 4.9(5) | 4.8(6) | 0.6(6) |
| C9 | 27.0(8) | 20.9(7) | 18.8(7) | 7.4(6) | 11.2(6) | 13.2(6) |
| C12 | 19.3(7) | 17.2(7) | 13.5(7) | 5.4(5) | 3.8(5) | 1.9(5) |
| C10 | 38.8(9) | 14.9(7) | 15.2(7) | 4.3(6) | 11.0(6) | 10.7(6) |
| C20 | 26.8(8) | 23.9(8) | 20.4(8) | 8.8(6) | 4.1(6) | 8.2(6) |
| C1 | 25.5(9) | 17.4(7) | 32.0(9) | 1.1(6) | 6.1(6) | 4.8(6) |
| C13 | 38.3(10) | 19.1(8) | 16.5(8) | 1.6(6) | 4.0(6) | -4.1(7) |
| C2 | 28.7(9) | 17.4(8) | 24.4(8) | -1.8(6) | 12.6(6) | 7.6(6) |

Table 8: Bond Lengths in Å for **4g**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|------------|------|------|------------|
| S1 | C6 | 1.7523(14) | 01 | C2 | 1.4645(18) |
| S1 | C14 | 1.7891(14) | 03 | C4 | 1.2337(18) |
| O1 | C3 | 1.328(2) | 02 | C3 | 1.203(2) |

| Atom | Atom | Length/Å |
|------|------|------------|
| N1 | C6 | 1.3523(19) |
| N1 | C8 | 1.3895(18) |
| C5 | C6 | 1.3987(19) |
| C5 | C7 | 1.4439(19) |
| C5 | C4 | 1.432(2) |
| C15 | C14 | 1.391(2) |
| C15 | C16 | 1.390(2) |
| C7 | C8 | 1.403(2) |
| C7 | C12 | 1.4080(19) |
| C4 | C3 | 1.533(2) |
| C14 | C19 | 1.393(2) |

| Atom | Atom | Length/Å |
|------|------|----------|
| C8 | C9 | 1.391(2) |
| C18 | C19 | 1.384(2) |
| C18 | C17 | 1.397(2) |
| C16 | C17 | 1.390(2) |
| C17 | C20 | 1.504(2) |
| C11 | C12 | 1.385(2) |
| C11 | C10 | 1.409(3) |
| C11 | C13 | 1.511(2) |
| C9 | C10 | 1.385(2) |
| C1 | C2 | 1.506(2) |

Table 9: Bond Angles in ° for 4g.

| Atom | Atom | Atom | Angle/° |
|------|------|------|------------|
| C6 | S1 | C14 | 99.58(6) |
| C3 | O1 | C2 | 116.08(12) |
| C6 | N1 | C8 | 109.63(12) |
| C6 | C5 | C7 | 106.12(13) |
| C6 | C5 | C4 | 127.77(13) |
| C4 | C5 | C7 | 126.11(13) |
| N1 | C6 | S1 | 119.95(11) |
| N1 | C6 | C5 | 109.57(12) |
| C5 | C6 | S1 | 130.46(11) |
| C16 | C15 | C14 | 119.58(13) |
| C8 | C7 | C5 | 106.94(12) |
| C8 | C7 | C12 | 119.09(14) |
| C12 | C7 | C5 | 133.97(14) |
| O3 | C4 | C5 | 123.05(14) |
| O3 | C4 | C3 | 116.18(13) |
| C5 | C4 | C3 | 120.65(12) |
| C15 | C14 | S1 | 117.79(11) |
| C15 | C14 | C19 | 119.71(13) |
| C19 | C14 | S1 | 122.50(11) |
| N1 | C8 | C7 | 107.73(13) |
| N1 | C8 | C9 | 129.54(14) |
| C9 | C8 | C7 | 122.73(14) |
| C19 | C18 | C17 | 121.54(13) |
| O1 | C3 | C4 | 111.41(12) |
| O2 | C3 | O1 | 126.74(14) |
| O2 | C3 | C4 | 121.70(14) |
| C15 | C16 | C17 | 121.67(13) |
| C18 | C19 | C14 | 119.76(13) |
| C18 | C17 | C20 | 120.20(14) |
| C16 | C17 | C18 | 117.69(14) |
| C16 | C17 | C20 | 122.12(14) |
| C12 | C11 | C10 | 119.95(14) |
| C12 | C11 | C13 | 120.39(16) |
| C10 | C11 | C13 | 119.65(15) |
| C10 | C9 | C8 | 116.80(15) |
| C11 | C12 | C7 | 119.14(14) |
| C9 | C10 | C11 | 122.29(14) |
| O1 | C2 | C1 | 107.01(13) |

Table 10: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4g**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

| Atom | x | y | z | U_{eq} |
|------|----------|----------|----------|----------|
| H1 | 8341.89 | 5311.98 | 1644.64 | 17 |
| H15 | 10826.02 | 8936.42 | 4753.26 | 19 |
| H18 | 6768.15 | 4919.74 | 5215.73 | 23 |
| H16 | 11656.1 | 8295.98 | 6250.49 | 22 |
| H19 | 5825.89 | 5642.92 | 3777.4 | 22 |
| H9 | 7201.01 | 2355.28 | 150.09 | 24 |
| H12 | 1075.83 | 3039.94 | 205.96 | 21 |
| H10 | 4451.52 | 425.63 | -911.35 | 27 |
| H20A | 9106.68 | 6410.2 | 7365.66 | 35 |
| H20B | 11189.29 | 6557.83 | 7201.01 | 35 |
| H20C | 9602.05 | 4993.12 | 6620.66 | 35 |
| H1A | 3168.99 | 11536.72 | 2328.13 | 41 |
| H1B | 5340.54 | 11581.12 | 2579.15 | 41 |
| H1C | 4565.45 | 12693.28 | 3422.54 | 41 |
| H13A | 637.62 | -588.51 | -920.44 | 42 |
| H13B | 880.56 | -76.75 | -1900.66 | 42 |
| H13C | -376.32 | 602.99 | -1145.06 | 42 |
| H2A | 4916.15 | 10664.16 | 3977.61 | 30 |
| H2B | 2728.64 | 10597.62 | 3706.69 | 30 |