

Interrupted Intramolecular Hydroaminomethylation of *N*-Protected-2-vinyl anilines: Novel access to 3-substitued indoles or indoline-2-ols.

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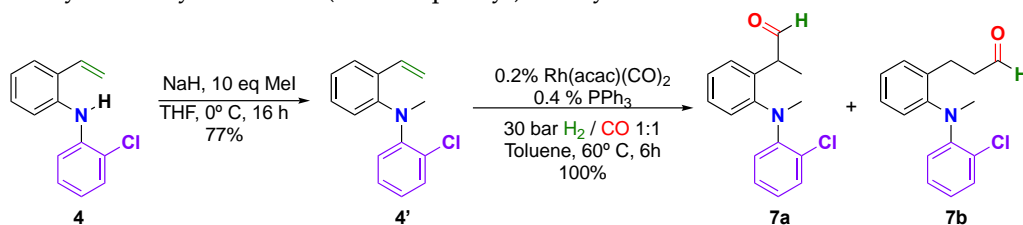
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S1. Hydroformylation of N (2-chlorophenyl)-2-vinyl aniline

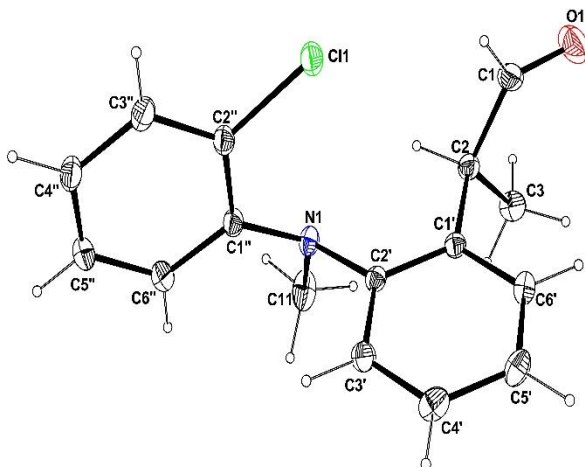


To a solution of *N*-protected-2-vinyl-aniline (0.6mmole) in toluene (20 mL) was added Rh(acac)(CO)₂ (0.001 mmol, 0.2%) and PPh₃ (0.002 mmol, 0.4%). The mixture was transferred into the autoclave 90 mL inox (TOP INDUSTRIE), which was flushed several times with H₂/CO gas, and the mixture was stirred at 200 rpm. The autoclave was pressurized to an initial 20 bar pressure of syngas (H₂/CO 1:1), heated to the 60°C. Once the temperature is reached, the pressure is increased to 30 bar and the stirring was setting at 1000 rpm. The reaction was monitored by GC and stopped until no detected starting material. After the catalytic reaction, the autoclave was then cooled and carefully depressurized. The conversion and selectivity of the reaction was determined by GC. The mixture was evaporated and analyzed by NMR. The two aldehydes were separated by chromatography (silica gel, n-hexane/ethyl acetate 95/5)

2-[2-N-(2-chlorophenyl)(methylamino)phenyl]propanal (7a): yellow solid, ¹H (300 MHz, CDCl₃) δ (ppm) 1.12 (d, J=4.5 Hz, 3H), 3.11 (s, 3H), 4.01 (quat, 1H, J=6 Hz), 6.86-7.00 (m, 3H), 7.06-7.11 (m, 3H), 7.18-7.29 (m, 3H), 9.37 (s, 1H). ¹³C (75 MHz, CDCl₃) 14.5 (C-CH₃), 42.3 (N-CH₃), 46.9 (-CH-CO), 123.5 (CH_{ar}), 124.3 (CH_{ar}), 124.5 (CH_{ar}), 125.1 (CH_{ar}), 127.7 (CH_{ar}), 128.3 (CH_{ar}), 128.9 (C_{ar}), 129.5 (CH_{ar}), 131.2 (CH_{ar}), 134.2 (C_{ar}), 148.5 (C_{ar}), 149.6 (C_{ar}), 201.5 (COH).

3-[2-N-(2-chlorophenyl)(methylamino)phenyl]propanal (7b): brown oil, ¹H (300 MHz, CDCl₃) 2.52-2.56 (m, 2H), 2.60-2.65 (m, 2H), 3.12 (s, 3H), 6.76-6.79 (m, 1H), 6.88-6.93 (m, 1H), 6.99-7.16 (m, 5H), 7.27-7.30 (m, 1H), 9.61 (T, 1H, J=3 Hz). ¹³C (75 MHz, CDCl₃) 23.1 (Ar-CH₂-), 28.7 (-CH₂-CO), 40.4 (N-CH₃), 42.5 (CH_{ar}), 121.3 (CH_{ar}), 123.2 (CH_{ar}), 123.3 (CH_{ar}), 123.5 (CH_{ar}), 126.2 (CH_{ar}), 126.6 (CH_{ar}), 128.1 (C_{ar}), 129.3 (CH_{ar}), 130.0 (CH_{ar}), 135.0 (C_{ar}), 147.4 (C_{ar}), 147.6 (C_{ar}), 201.2 (COH).

S2 Figure S1: Molecular view of compound **7a** with the atom labelling scheme. Ellipsoids are drawn at the 30% probability level. H atoms are represented as small circle of arbitrary radii.



S3 Tables of X-ray structural analysis of compound **7a** and 3-methyl-N-tosyl-indolyl-2-ol (**6f**)

Single crystal of each compound was mounted under inert perfluoropolyether at the tip of glass fiber and cooled in the cryostream of a Nonius APEXII CCD diffractometer.

The structures were solved by direct methods SHELX¹ and refined by least-squares procedures on F^2 using SHELXL-2018². All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models, only the methine H attached to C2 in 3-methyl-N-tosyl-indoline-2-ol (**5R**) has been refined. The hydroxyl H in **5R** has been also treated as riding on the parent O atom. In compound **5R**, within the N1 C2 C3 C3A C7A ring the C3 atom bearing the methyl group is disordered over two position in the ratio 70/30, resulting in the inversion of configuration on C3 (C3b). The disordered model has been refined using the tools available in SHELXL-2018. The drawing of the molecules was realised with the help of ORTEP3^{3,4}. Crystal data and refinement parameters are shown in Table 1.

Table S1. Crystal data and structure refinement

| Identification code | 7a | 6f |
|-----------------------------------|--|--|
| Empirical formula | C ₁₆ H ₁₆ Cl N O | C ₁₆ H ₁₇ N O ₃ S |
| Formula weight | 273.75 | 303.36 |
| Temperature, K | 180(2) | 180(2) |
| Wavelength, Å | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | P2 ₁ /n | Pb a |
| a, Å | 10.7681(6) | 13.542(2) |
| b, Å | 11.5110(5) | 13.242(3) |
| c, Å | 11.6060(7) | 16.590(4) |
| α ° | 90.0 | 90.0 |
| β ° | 105.238(2) | 90.0 |
| γ ° | 90.0 | 90.0 |
| Volume, Å ³ | 1388.01(13) | 2975.1(11) |
| Z | 4 | 8 |
| Density (calc), Mg/m ³ | 1.315 | 1.355 |

¹ Sheldrick, G.M., Crystal structure refinement with SHELXL. *Acta Cryst.* 2015, *C71*, 3-8. DOI 10.1107/S2053229614024218

² Sheldrick, G.M., SHELXT – Integrated space-group and crystal-structure determination. *Acta Cryst.* 2015, *A71*, 3-8. DOI 10.1107/S2053273314026370

³ Farrugia, L. J., ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface *J. Appl. Cryst.* 1997, 30, 565, DOI 10.1107/S0021889897003117

⁴ Burnett, M. N., Johnson, C. K., ORTEP-III. Report ORNL-6895, Oak Ridge National Laboratory, Tennessee, USA, 1996.

| | | |
|---------------------------------------|-----------------------|--------------------|
| Abs. coefficient, mm ⁻¹ | 0.266 | 0.227 |
| F(000) | 576 | 1280 |
| Crystal size, mm ³ | 0.500 x 0.500 x 0.350 | 0.25 x 0.10 x 0.02 |
| Theta range, ° | 2.297 to 28.276°. | 2.880 to 24.107°. |
| Reflections collected | 20972 | 9604 |
| Indpt reflections (R _{int}) | 3434 (0.0333) | 2364 (0.0778) |
| Absorption correction | Multi-scan | Multi-scan |
| Max. / min. transmission | 0.7470 / 0.7024 | 0.7454 / 0.5482 |
| Refinement method | F ² | F ² |
| Data /restraints/parameters | 3435 / 0 / 175 | 2622 / 8 / 203 |
| Goodness-of-fit on F ² | 1.089 | 1.038 |
| R1, wR2 [I>2σ(I)] | 0.0413, 0.1150 | 0.0589, 0.1434 |
| R1, wR2 (all data) | 0.0484, 0.1268 | 0.1081, 0.1747 |
| Residual density, e.Å ⁻³ | 0.636 / -0.504 | 0.485 / -0.364 |

Table S2. Bond lengths [Å] and angles [°].

| 7a | | | |
|---------------|------------|---------------|------------|
| Cl(1)-C(2'') | 1.7384(14) | O(1)-C(1) | 1.200(2) |
| N(1)-C(1'') | 1.4163(17) | N(1)-C(2') | 1.4405(16) |
| N(1)-C(11) | 1.4637(19) | C(2')-C(3') | 1.3943(18) |
| C(2')-C(1') | 1.4015(17) | C(1'')-C(6'') | 1.3991(19) |
| C(3')-C(4') | 1.388(2) | C(2'')-C(3'') | 1.3906(19) |
| C(4')-C(5') | 1.385(2) | C(3'')-C(4'') | 1.385(2) |
| C(5')-C(6') | 1.386(2) | C(4'')-C(5'') | 1.374(2) |
| C(6')-C(1') | 1.3943(18) | C(5'')-C(6'') | 1.390(2) |
| C(1')-C(2) | 1.5175(18) | C(2)-C(1) | 1.507(2) |
| C(1'')-C(2'') | 1.398(2) | C(2)-C(3) | 1.5275(19) |

| | | | |
|-------------------|------------|----------------------|------------|
| C(1'')-N(1)-C(2') | 116.57(10) | C(3')-C(2')-C(1') | 119.53(12) |
| C(1'')-N(1)-C(11) | 116.03(11) | C(3')-C(2')-N(1) | 120.58(11) |
| C(2')-N(1)-C(11) | 112.67(11) | C(1')-C(2')-N(1) | 119.82(11) |
| C(4')-C(3')-C(2') | 120.97(13) | C(3'')-C(2'')-Cl(1) | 118.01(11) |
| C(5')-C(4')-C(3') | 119.84(13) | C(1'')-C(2'')-Cl(1) | 120.10(10) |
| C(6')-C(5')-C(4') | 119.33(13) | C(4'')-C(3'')-C(2'') | 120.07(14) |

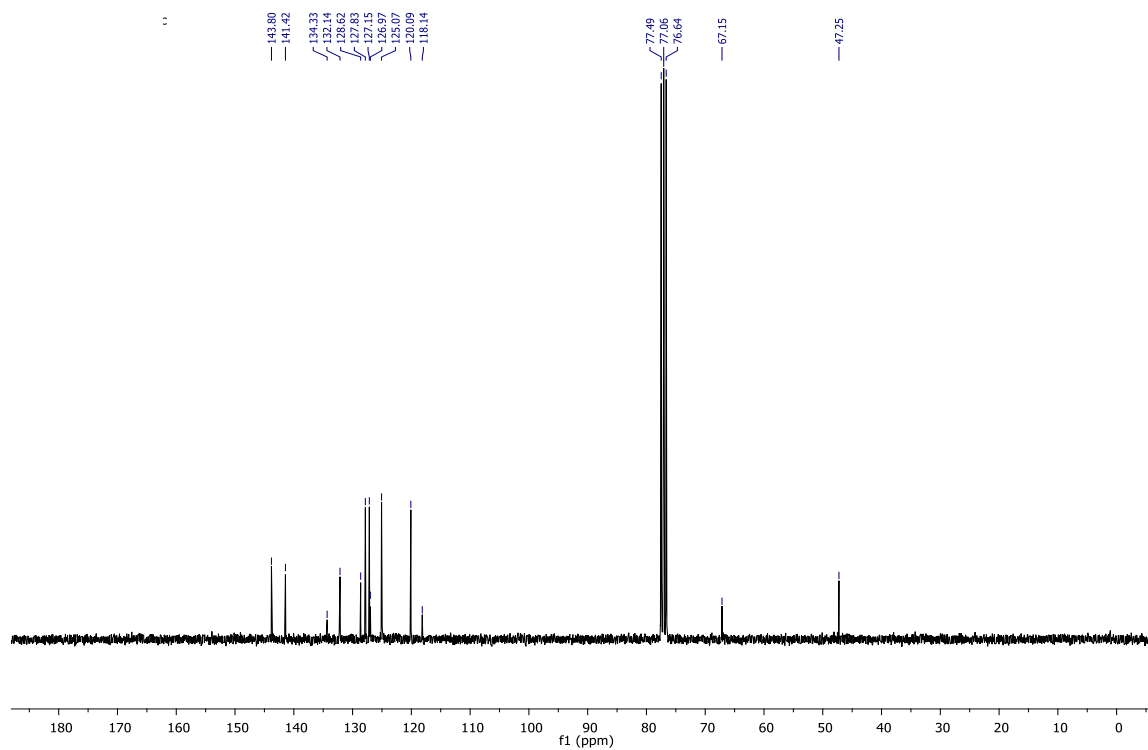
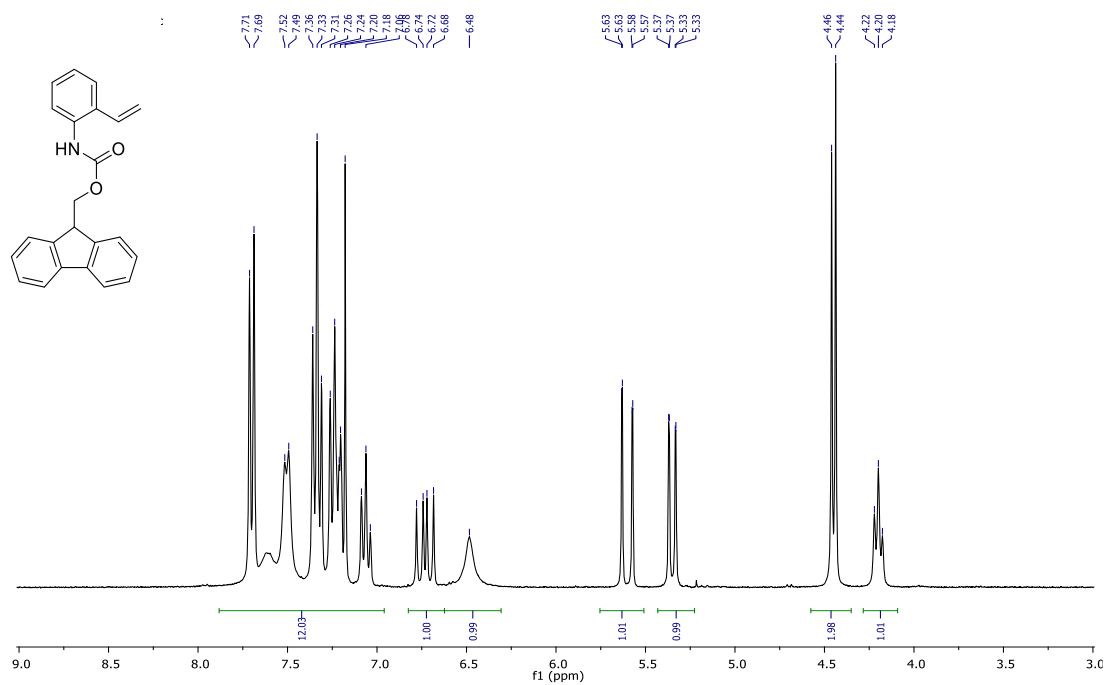
| | | | |
|----------------------|------------|----------------------|------------|
| C(5')-C(6')-C(1') | 121.80(13) | C(5'')-C(4'')-C(3'') | 119.26(14) |
| C(6')-C(1')-C(2') | 118.53(12) | C(4'')-C(5'')-C(6'') | 120.64(14) |
| C(6')-C(1')-C(2) | 119.07(12) | C(5'')-C(6'')-C(1'') | 121.55(15) |
| C(2')-C(1')-C(2) | 122.38(11) | C(1)-C(2)-C(1') | 108.20(11) |
| C(2'')-C(1'')-C(6'') | 116.61(13) | C(1)-C(2)-C(3) | 111.93(12) |
| C(2'')-C(1'')-N(1) | 120.34(12) | C(1')-C(2)-C(3) | 113.17(11) |
| C(6'')-C(1'')-N(1) | 122.98(13) | O(1)-C(1)-C(2) | 125.57(15) |
| C(3'')-C(2'')-C(1'') | 121.85(13) | | |

| 6f | | | |
|-------------|----------|--------------|-----------|
| S(1)-O(11) | 1.434(3) | S(1)-O(12) | 1.422(3) |
| S(1)-N(1) | 1.637(3) | S(1)-C(11) | 1.758(3) |
| O(2)-C(2) | 1.381(5) | N(1)-C(7A) | 1.442(4) |
| N(1)-C(2) | 1.499(5) | C(2)-C(3B) | 1.543(11) |
| C(2)-C(3) | 1.606(6) | C(3A)-C(3B) | 1.610(12) |
| C(3)-C(3A) | 1.503(6) | C(3B)-C(31B) | 1.499(16) |
| C(3)-C(31) | 1.529(7) | C(11)-C(12) | 1.386(5) |
| C(3A)-C(7A) | 1.374(5) | C(11)-C(16) | 1.387(4) |
| C(3A)-C(4) | 1.383(5) | C(12)-C(13) | 1.386(5) |
| C(7A)-C(7) | 1.381(5) | C(13)-C(14) | 1.383(4) |
| C(4)-C(5) | 1.361(6) | C(14)-C(15) | 1.392(5) |
| C(5)-C(6) | 1.363(6) | C(14)-C(17) | 1.507(4) |
| C(6)-C(7) | 1.401(6) | C(15)-C(16) | 1.378(5) |

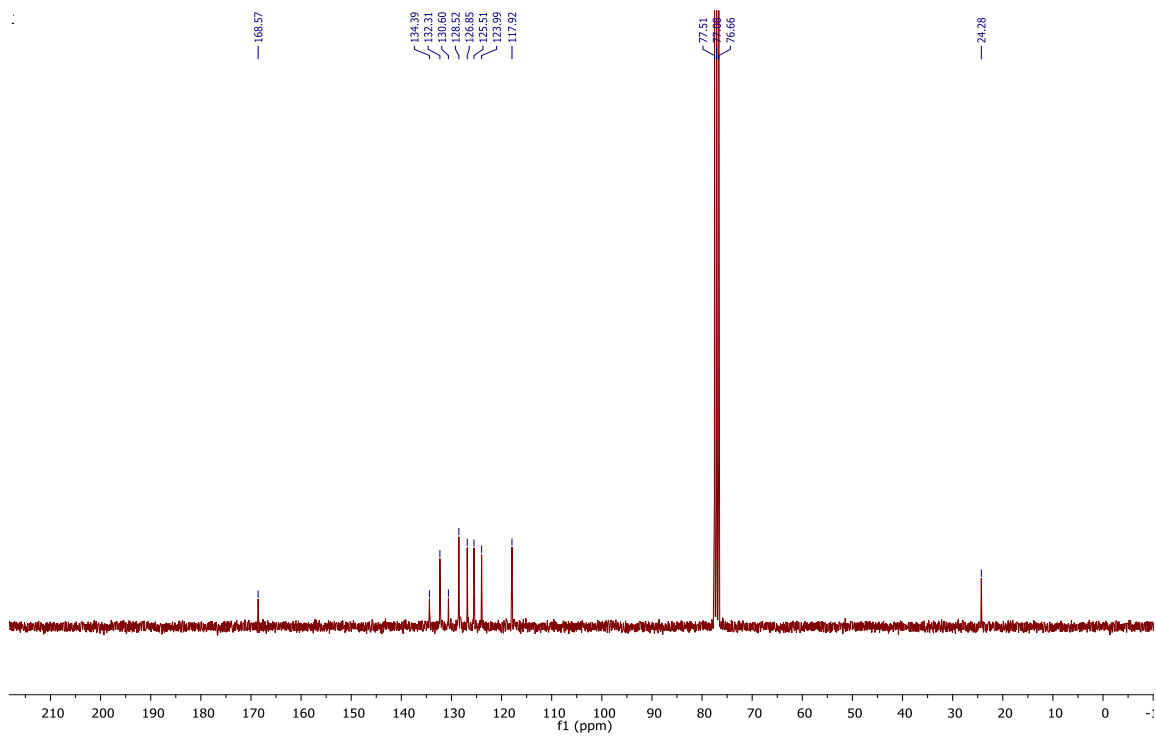
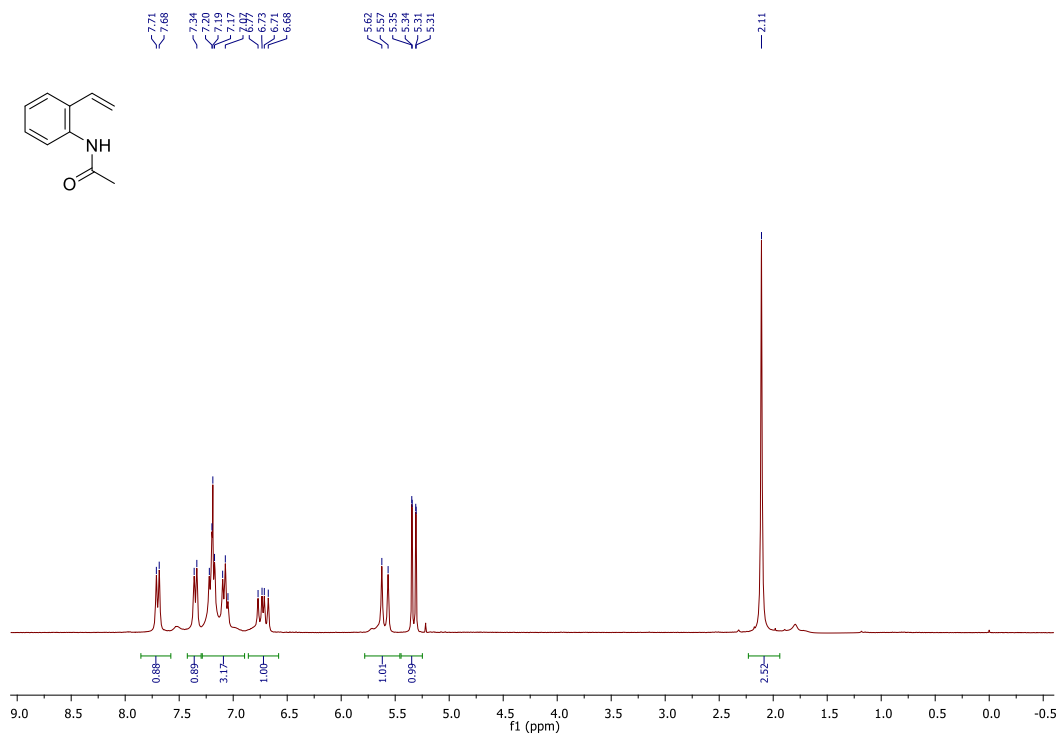
| | | | |
|------------------|------------|--------------------|------------|
| O(12)-S(1)-O(11) | 119.85(16) | O(12)-S(1)-C(11) | 108.84(18) |
| O(12)-S(1)-N(1) | 107.60(15) | O(11)-S(1)-C(11) | 107.76(16) |
| O(11)-S(1)-N(1) | 104.89(17) | N(1)-S(1)-C(11) | 107.23(15) |
| C(2)-N(1)-S(1) | 118.9(2) | C(7A)-N(1)-S(1) | 121.8(2) |
| C(7A)-N(1)-C(2) | 108.2(3) | C(31B)-C(3B)-C(2) | 106.9(10) |
| O(2)-C(2)-N(1) | 111.2(3) | C(31B)-C(3B)-C(3A) | 112.0(10) |
| O(2)-C(2)-C(3B) | 127.0(6) | C(2)-C(3B)-C(3A) | 99.2(6) |
| N(1)-C(2)-C(3B) | 99.8(5) | C(5)-C(4)-C(3A) | 120.2(4) |
| O(2)-C(2)-C(3) | 101.2(4) | C(4)-C(5)-C(6) | 120.5(4) |
| N(1)-C(2)-C(3) | 106.3(3) | C(5)-C(6)-C(7) | 121.1(4) |

| | | | |
|-------------------|----------|-------------------|----------|
| C(3A)-C(3)-C(31) | 110.0(5) | C(7A)-C(7)-C(6) | 117.3(4) |
| C(3A)-C(3)-C(2) | 101.1(4) | C(12)-C(11)-C(16) | 120.2(3) |
| C(31)-C(3)-C(2) | 109.2(5) | C(12)-C(11)-S(1) | 119.6(3) |
| C(7A)-C(3A)-C(4) | 119.2(4) | C(16)-C(11)-S(1) | 120.1(3) |
| C(7A)-C(3A)-C(3) | 113.5(3) | C(11)-C(12)-C(13) | 119.5(3) |
| C(4)-C(3A)-C(3) | 126.7(4) | C(14)-C(13)-C(12) | 121.2(3) |
| C(7A)-C(3A)-C(3B) | 103.6(5) | C(13)-C(14)-C(15) | 118.0(3) |
| C(4)-C(3A)-C(3B) | 133.6(5) | C(13)-C(14)-C(17) | 121.3(3) |
| C(3A)-C(7A)-C(7) | 121.7(3) | C(15)-C(14)-C(17) | 120.6(3) |
| C(3A)-C(7A)-N(1) | 110.5(3) | C(16)-C(15)-C(14) | 121.7(3) |
| C(7)-C(7A)-N(1) | 127.6(3) | C(15)-C(16)-C(11) | 119.2(3) |

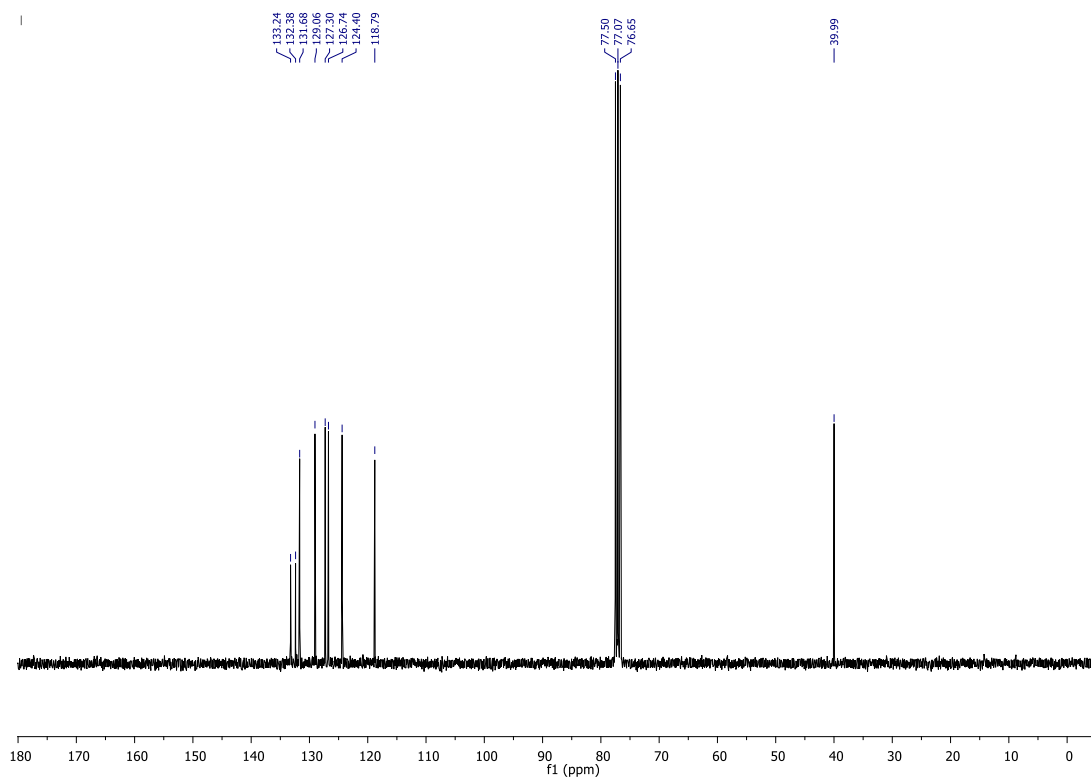
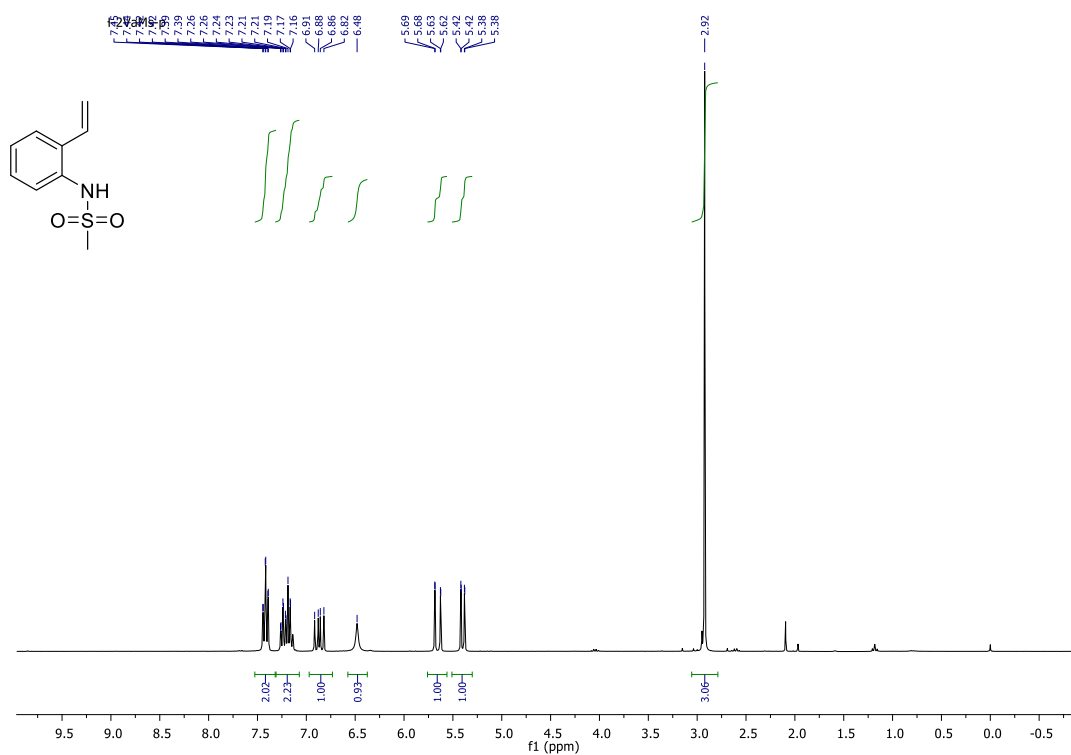
S4 ^1H and ^{13}C NMR Spectra of **3c**



S5 ^1H and ^{13}C NMR Spectra of **3d**



S6 ^1H and ^{13}C NMR Spectra of 3e



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Chemical structure: C=Cc1ccccc1Nc2ccccc2Cl

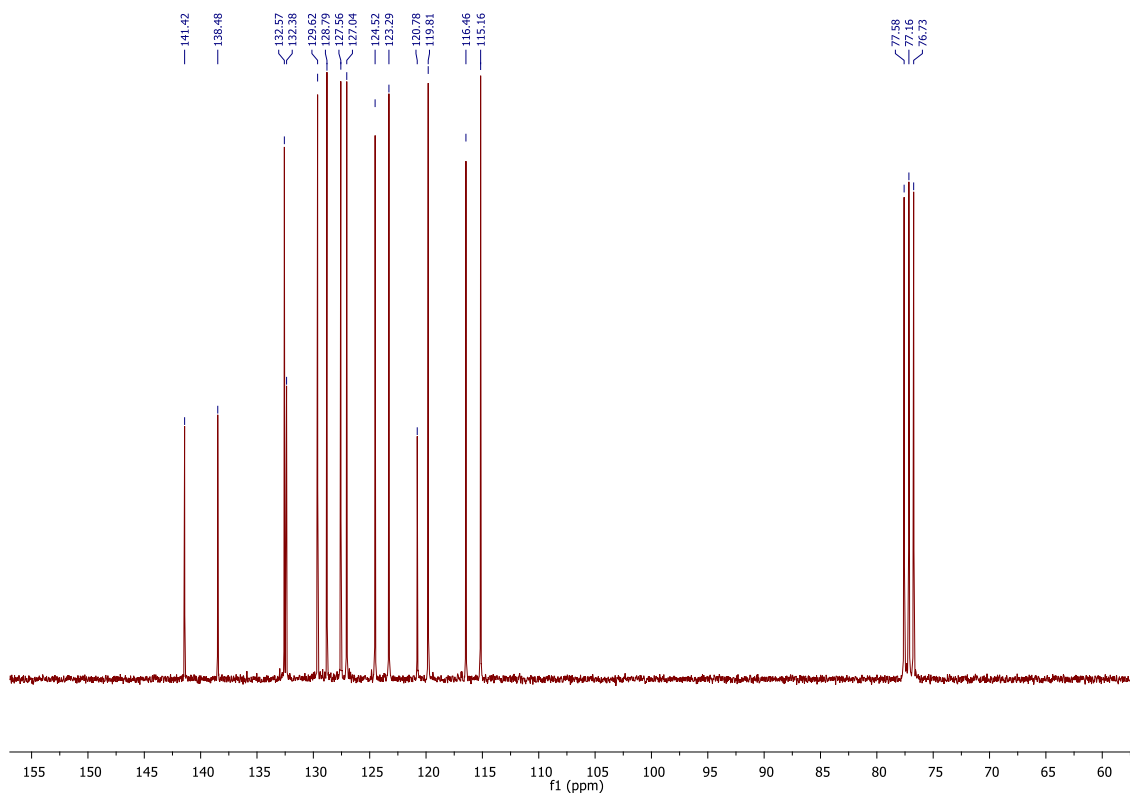
¹H NMR spectrum (ppm):

- 7.15, 7.11, 7.06, 7.05, 7.03, 7.02, 6.98, 6.96, 6.97, 6.94, 6.94, 6.83, 6.80, 6.80, 6.77, 6.77, 6.74, 6.68, 6.66, 6.65, 6.65, 6.63, 6.68, 5.66, 5.66, 5.65, 5.60, 5.24, 5.23, 5.20, 5.20

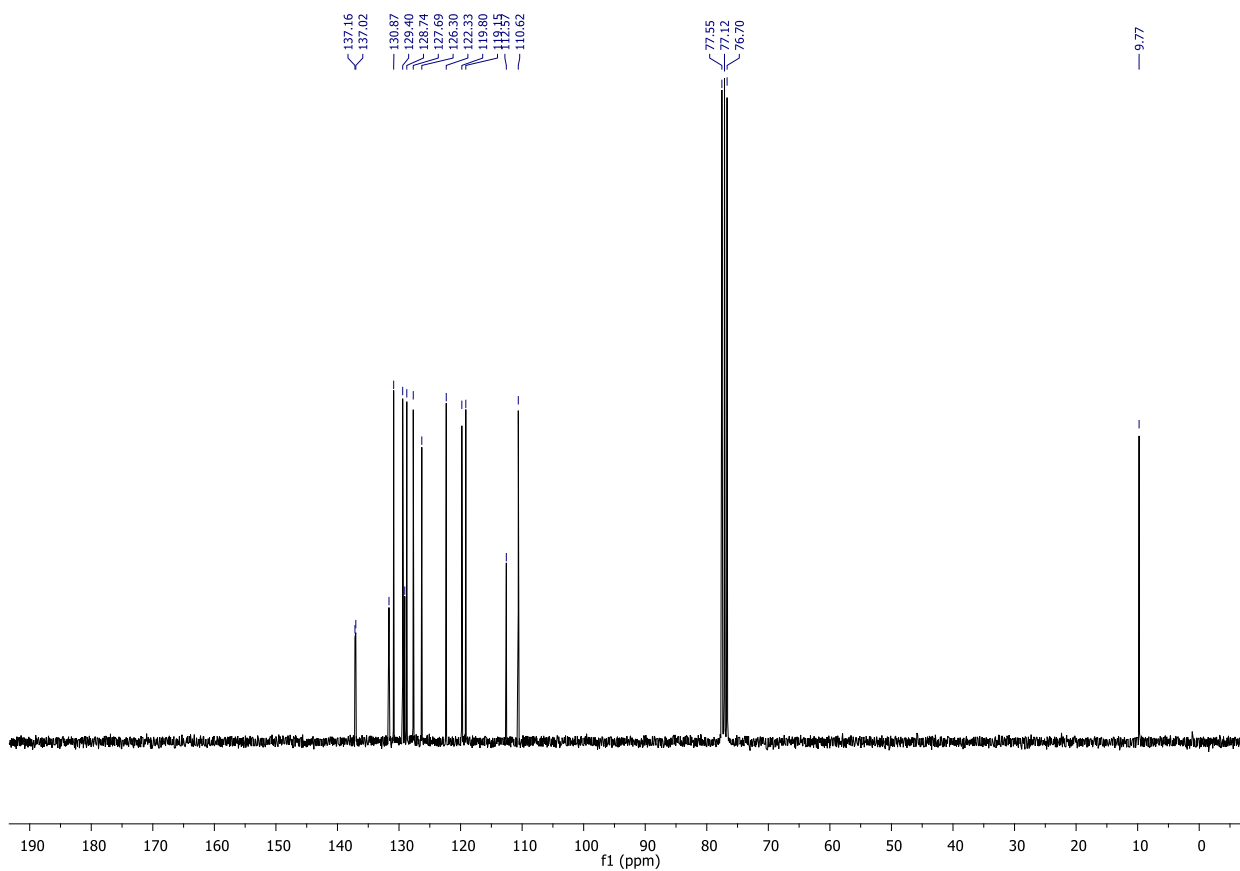
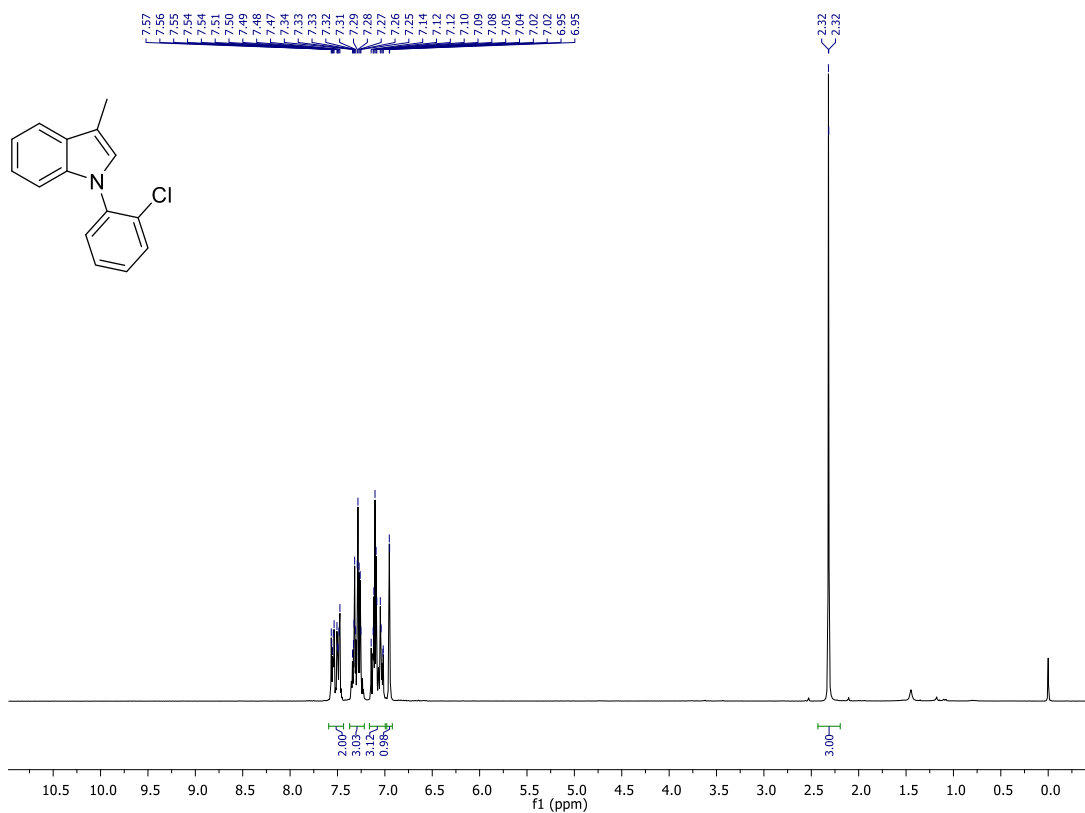
Integration values:

- 1.00, 0.98, 1.92, 1.95, 1.83, 0.93, 0.88, 0.97, 0.96

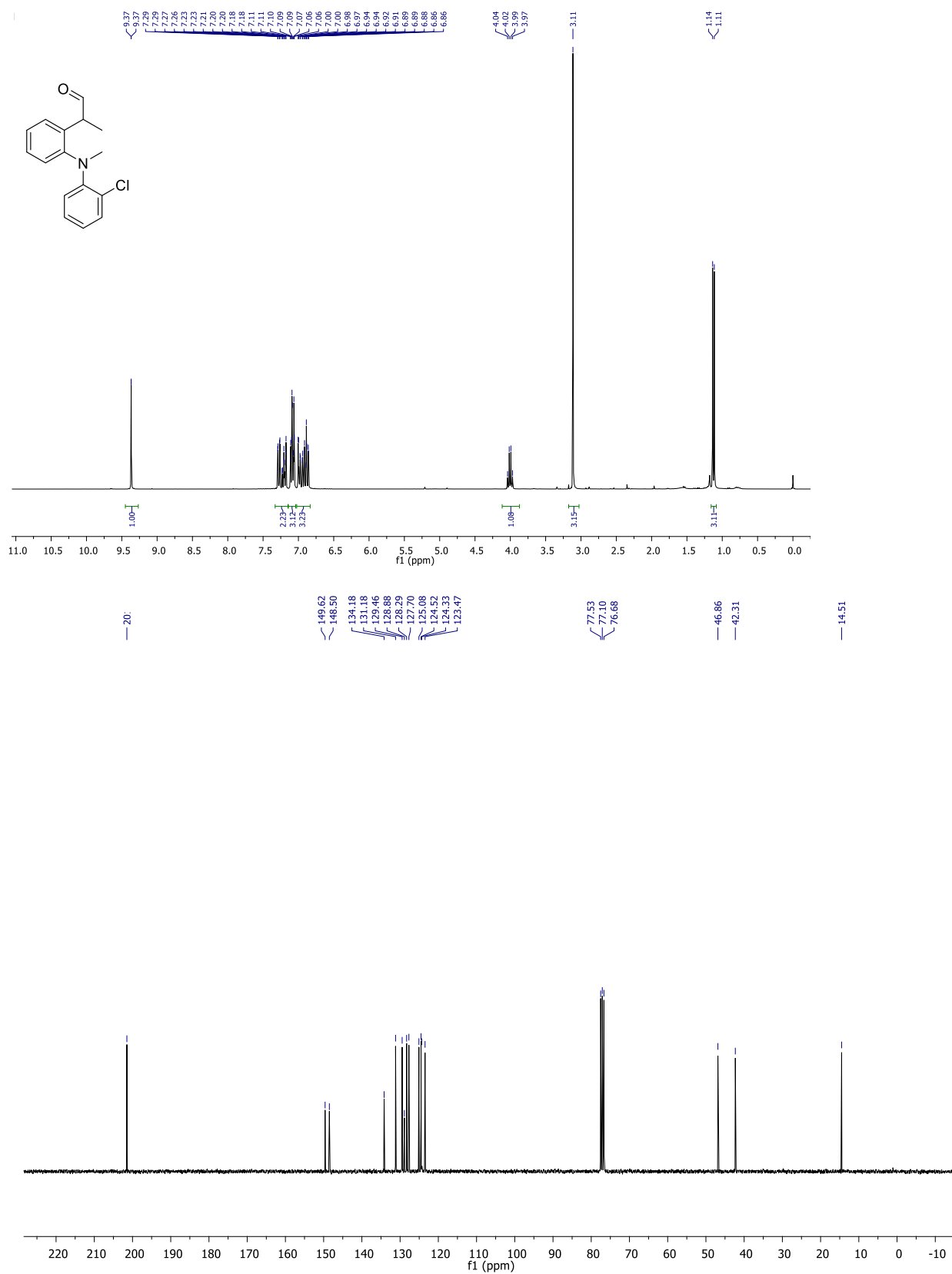
Chemical structure: C=Cc1ccccc1Nc2ccccc2Cl



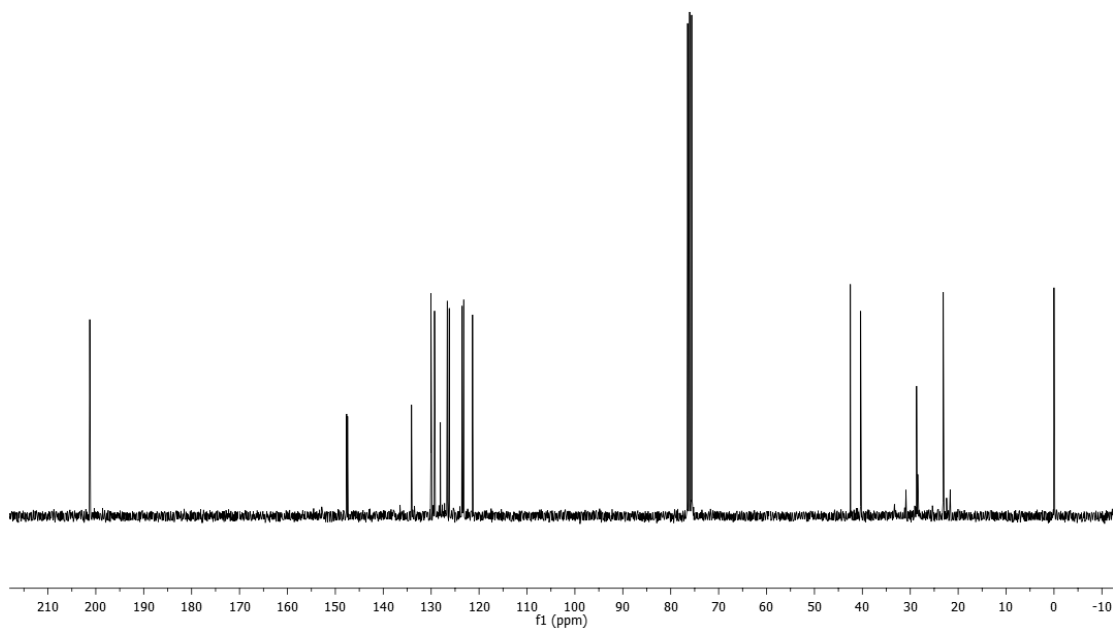
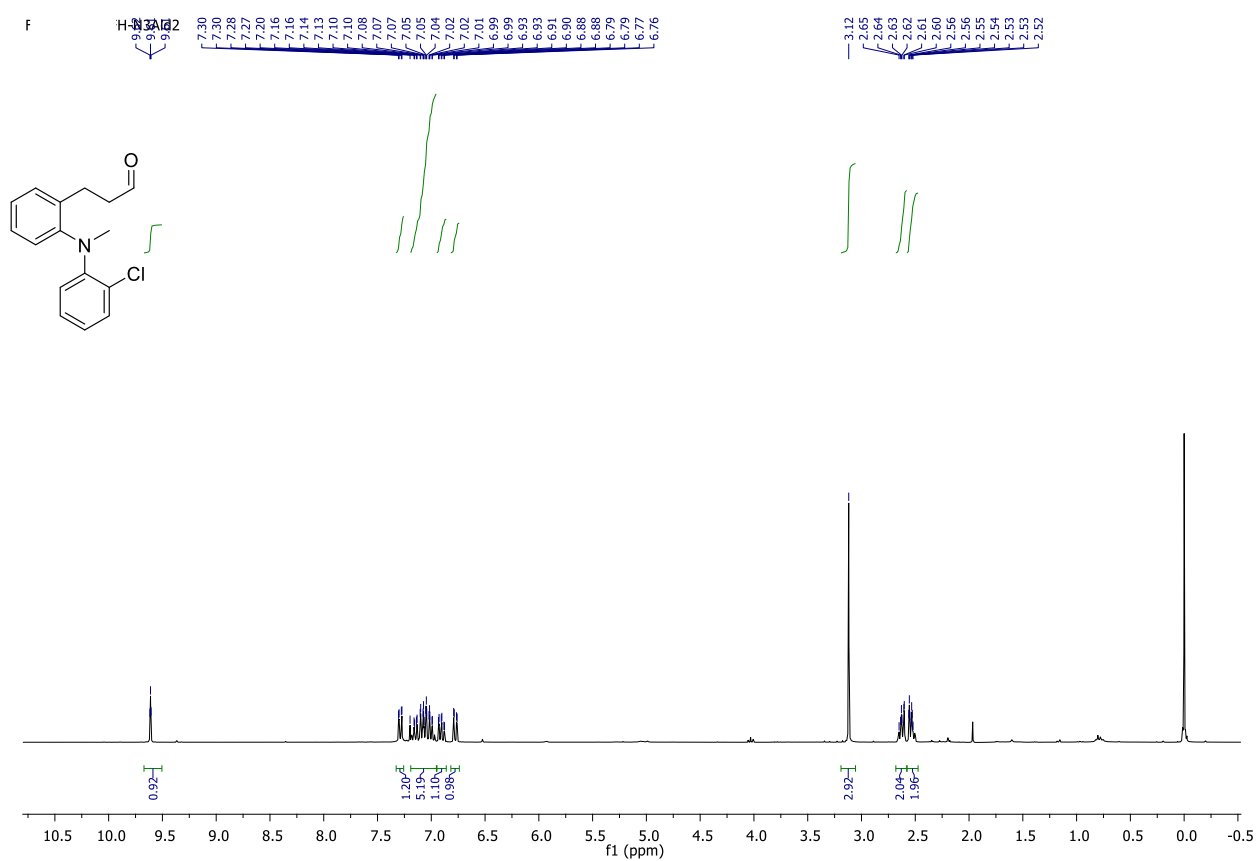
S8 ^1H and ^{13}C NMR Spectra of **7g**



S9 ^1H and ^{13}C NMR Spectra of 9a



S10 ^1H and ^{13}C NMR Spectra of **9b**

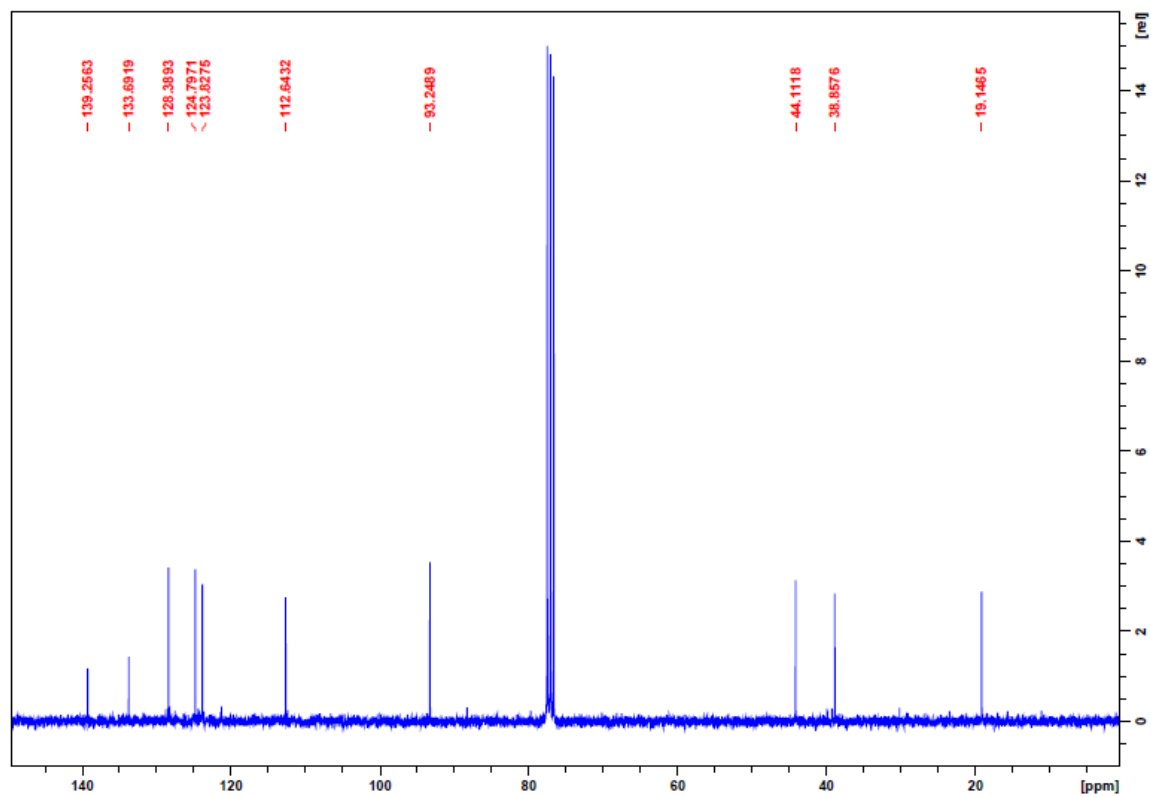


Chemical structure of compound **1** is shown as an inset. The structure is a benzimidazole derivative with a sulfonamide group and a methyl group.

¹H NMR spectrum (CDCl₃) of compound **1** is displayed. The spectrum shows peaks corresponding to the structure, with integration values provided for several regions.

Chemical shift (ppm): 10.0, 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.0.

Integration values: 0.17, 0.45, 0.99, 0.17, 0.45, 0.99, 1.02, 1.04, 1.04, 2.98, 1.25, 3.00, 1.22, 2.98, 2.94, 2.91.



Chemical structure of compound 10 is shown in the top left. The ^1H NMR spectrum (400 MHz, CDCl_3) is displayed below, with two insets providing expanded views of the aromatic and aliphatic regions.

Chemical Shifts (ppm):

- 8.00, 7.95, 7.90, 7.85, 7.80, 7.75, 7.70, 7.65, 7.60, 7.55, 7.50, 7.45, 7.40, 7.35, 7.30, 7.25, 7.20, 7.15, 7.10, 7.05, 7.00, 6.95, 6.90, 6.85, 6.80, 6.75, 6.70, 6.65, 6.60, 6.55, 6.50, 6.45, 6.40, 6.35, 6.30, 6.25, 6.20, 6.15, 6.10, 6.05, 6.00, 5.95, 5.90, 5.85, 5.80, 5.75, 5.70, 5.65, 5.60, 5.55, 5.50, 5.45, 5.40, 5.35, 5.30, 5.25, 5.20, 5.15, 5.10, 5.05, 5.00, 4.95, 4.90, 4.85, 4.80, 4.75, 4.70, 4.65, 4.60, 4.55, 4.50, 4.45, 4.40, 4.35, 4.30, 4.25, 4.20, 4.15, 4.10, 4.05, 4.00, 3.95, 3.90, 3.85, 3.80, 3.75, 3.70, 3.65, 3.60, 3.55, 3.50, 3.45, 3.40, 3.35, 3.30, 3.25, 3.20, 3.15, 3.10, 3.05, 3.00, 2.95, 2.90, 2.85, 2.80, 2.75, 2.70, 2.65, 2.60, 2.55, 2.50, 2.45, 2.40, 2.35, 2.30, 2.25, 2.20, 2.15, 2.10, 2.05, 2.00, 1.95, 1.90, 1.85, 1.80, 1.75, 1.70, 1.65, 1.60, 1.55, 1.50, 1.45, 1.40, 1.35, 1.30, 1.25, 1.20, 1.15, 1.10, 1.05, 1.00, 0.95, 0.90, 0.85, 0.80, 0.75, 0.70, 0.65, 0.60, 0.55, 0.50, 0.45, 0.40, 0.35, 0.30, 0.25, 0.20, 0.15, 0.10, 0.05, 0.00, -0.05, -0.10, -0.15, -0.20, -0.25, -0.30, -0.35, -0.40, -0.45, -0.50.

Integration Values:

- 2.56, 1.63, 2.80, 0.42, 0.95, 0.97, 0.22, 0.45, 0.96, 4.14, 0.53, 0.68, 3.00.

Chemical Shifts (ppm) in Insets:

- Aromatic Region (5.3-5.8 ppm):** 5.75, 5.74, 5.72, 5.32, 5.31, 5.30, 5.29.
- Aliphatic Region (2.9-3.4 ppm):** 3.42, 3.41, 3.33, 3.32, 3.19, 3.17, 3.14, 3.13, 3.05, 3.03, 3.02, 3.01, 3.00, 2.98, 2.97, 2.96, 2.87.

