Supporting Information

Iridium(III)-Catalyzed Regioselective C7-Sulfonamidation of Indoles

Zengqiang Song[a,b] and Andrey P. Antonchick*[a,b]

[a] Max-Planck-Institut für molekulare Physiologie, Abteilung Chemische Biologie, Otto-Hahn-Straße 11, 44227 Dortmund, Germany

[b] Technische Universität Dortmund, Fakultät für Chemie und Chemische Biologie, Chemische Biologie, Otto-Hahn-Straße 4a, 44221 Dortmund, Germany

*Email: Andrey.Antonchick@mpi-dortmund.mpg.de

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General information and materials:

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade. Dry solvents were purified by the Solvent Purification System *M-BRAUN Glovebox Technology SPS-800*. Analytical thin layer chromatography (TLC) was performed on Merck silica gel *aluminium plates* with *F-254 indicator*, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume.

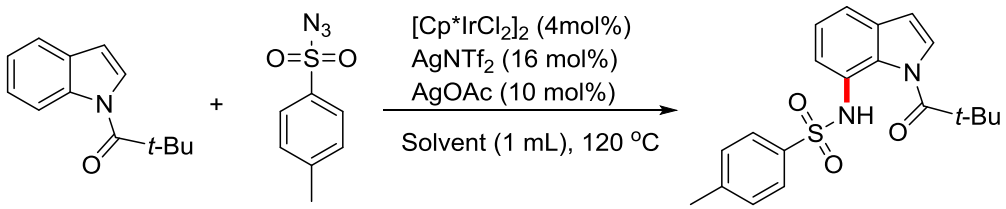
^{1}H-NMR and ^{13}C-NMR were recorded on a *Bruker DRX400 (400 MHz), DRX500 (500 MHz)* and *DRX600* (600 MHz) spectrometer in CD_2Cl_2 (δ = 5.320 ppm for ^{1}H, δ = 54.000 ppm for ^{13}C). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). High resolution mass spectra were recorded on a LTQ Orbitrap mass spectrometer coupled to an *Accela HPLC-System* (HPLC column: *Hypersyl GOLD*, 50 mm ×1 mm, 1.9 μm). Fourier transform infrared spectroscopy (FT- IR) spectra were obtained with a Bruker Tensor 27 spectrometer (ATR, neat) and are reported in terms of frequency of absorption (cm^{-1}). Chemical yields refer to isolated pure substances. Optical rotation was measured in a Schmidt + Haensch Polartronic HH8 polarimeter.

General procedure for C7-sulfonamidation of indoles

N-pivaloyl indoles (0.1 mmol) were dissolved in a 12 mL screw capped tube with 1 mL of DCE. Then sulfonyl azides (0.22 mmol) followed by [(IrCp*Cl_2)$_2$] (4 mol %), $AgNTf_2$ (16 mol %) and LiOAc (40 mol%) were added to the reaction mixture at room temperature. The reaction mixture was allowed to warm up to 120 °C and stirred for 1-12 h. After finishing the reaction, the reaction mixture was directly loaded on a silica gel column and purified with petroleum ether (40-60°C)/EtOAc mixture.

Optimization of reaction conditions

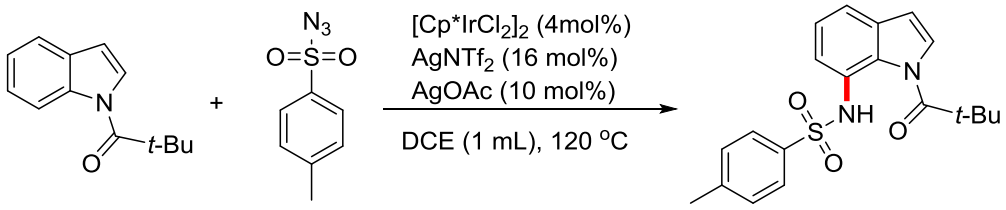
1. Optimization of solvent



Entry	Solvent	Reaction Time (h)	Yield (%)
1	**DCE**	**1**	**93**
2	Chloroform	1	69
3	1,4-Dioxane	24	12
4	Toluene	24	n.d.
5	Chlorobenzene	4	79
6	*tert*-Amyl alcohol	24	n.d.
7	DMF	24	n.r.
8	DMSO	24	n.r.

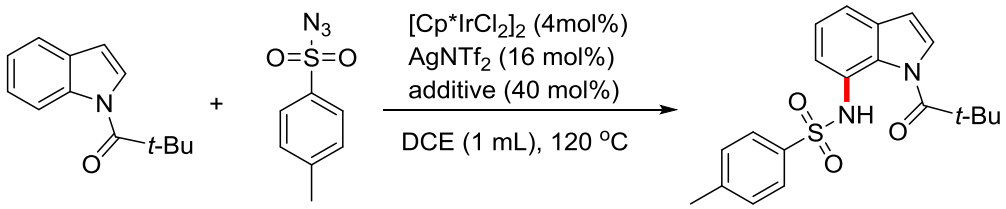
n.d. = the desired product was not detected. n.r. = reaction did not occur.

2. Optimization of loading of TsN_3



Entry	Amount of TsN_3 (equiv)	Reaction Time (h)	Yield (%)
1	**2.2**	**1**	**93**
2	1.6	1	86
3	1.1	1	58

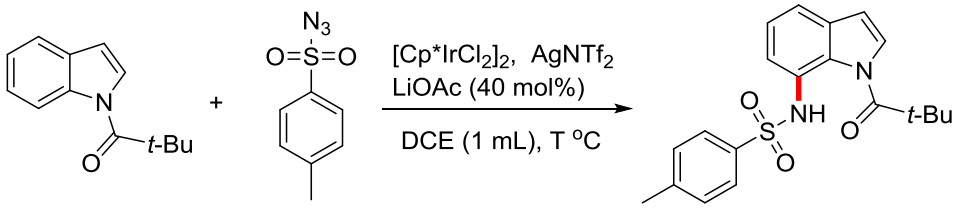
3. Optimization of additive



Entry	Additive	Reaction Time (h)	Yield (%)
1	-	24	18
2	$Cu(OAc)_2$	1	61
3	NaOAc	24	21
4	**LiOAc**	**1**	**98**
5	PivOH	24	34
6[a]	AgOAc	1	93

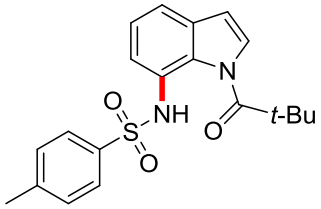
[a] 10 mol% AgOAc was used.

4. Optimization of catalyst, additive amount and reaction temperature



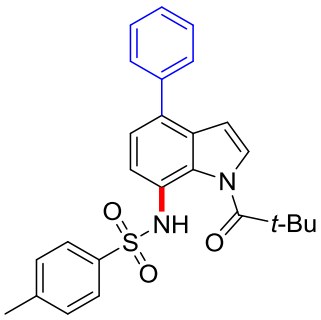
Entry	Catalyst and Additive Amount	T (°C)	Reaction Time (h)	Yield (%)
1	**$[Cp^*IrCl_2]_2$ (4mol%), $AgNTf_2$ (16 mol%)**	**120**	**1**	**98**
2	$[Cp^*IrCl_2]_2$ (2mol%), $AgNTf_2$ (8 mol%)	120	24	56
3	$[Cp^*IrCl_2]_2$ (4mol%), $AgNTf_2$ (16 mol%)	80	1	84

Characterization of products



4-Methyl-*N*-(1-pivaloyl-1*H*-indol-7-yl)benzenesulfonamide (3a):

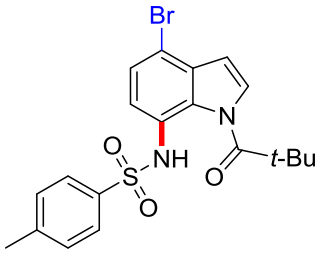
Brown amorphous solid; R_f = 0.25 (20% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.32 (brs, 1H), 7.56 (d, *J* = 3.9 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.40 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.36 – 7.35 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.11 – 7.09 (m, 2H), 6.61 (d, *J* = 3.9 Hz, 1H), 2.29 (s, 3H), 1.38 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.22, 144.11, 137.82, 133.01, 129.96, 129.80, 127.46, 127.21, 125.78, 125.63, 122.84, 119.29, 109.76, 42.21, 29.32, 21.66 ppm; FT-IR: $\tilde{\nu}$ = 3854, 3734, 3629, 3286, 3136, 2985, 2360, 2342, 1541, 1117 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{23}N_2O_3S$: 371.14239, found: 371.14304.



4-Methyl-*N*-(4-phenyl-1-pivaloyl-1*H*-indol-7-yl)benzenesulfonamide (3b):

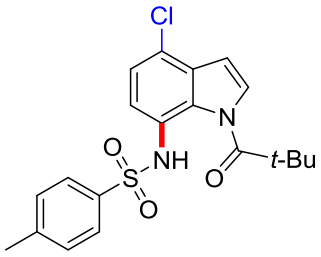
Brown oil; R_f = 0.25 (20% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.20 (brs, 1H), 7.59 – 7.54 (m, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.36 (m, 4H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.74 (d, *J* = 4.0 Hz, 1H), 2.31 (s, 3H), 1.38 (s, 9H) ppm ; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.35, 144.16, 139.86, 137.83, 133.29, 130.91, 130.10, 130.01, 129.44, 129.18, 127.98, 127.63, 127.17, 125.67, 124.77, 123.16, 108.81, 42.25, 29.25,

21.65 ppm; FT-IR: $\tilde{\nu}$ = 2975, 2360, 2342, 1672, 1481, 1377, 1361, 1233, 1218 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{26}H_{27}N_2O_3S$: 447.17369, found: 447.17411.



***N*-(4-Bromo-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3c):**

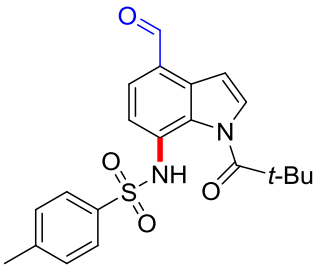
Brown amorphous solid; R_f = 0.25 (20% EtOAc in petroleum ether); ^1H NMR (500 MHz, CD_2Cl_2) δ 9.12 (brs, 1H), 7.62 (d, *J* = 4.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 4.0 Hz, 1H), 2.30 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.45, 144.34, 137.46, 133.01, 130.11, 130.07, 128.38, 128.04, 127.13, 125.07, 123.92, 112.52, 109.42, 42.30, 29.16, 21.65 ppm; FT-IR: $\tilde{\nu}$ = 3187, 2975, 2360, 2342, 1678, 1327, 1237 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{79}BrN_2O_3S$: 449.05290, found: 449.05352; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{81}BrN_2O_3S$: 451.05086, found: 451.05125.



***N*-(4-Chloro-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3d):**

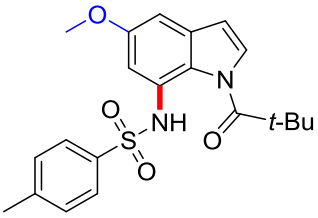
Brown amorphous solid; R_f = 0.15 (25% EtOAc in petroleum ether); ^1H NMR (500 MHz, CD_2Cl_2) δ 9.10 (brs, 1H), 7.60 (d, *J* = 4.0 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.73 (d, *J* = 4.0 Hz, 1H), 2.30 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.37, 144.32, 137.46, 131.17, 130.43, 130.05, 128.05, 127.13, 125.19, 124.44, 124.22,

123.79, 107.58, 42.27, 29.15, 21.64 ppm; FT-IR: $\tilde{\nu}$ = 2360, 2342, 1673, 1480, 1322, 1181, 1162, 1085 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{35}ClN_2O_3S$: 405.10342, found: 405.10461; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{37}ClN_2O_3S$: 407.10047, found: 407.10146.



***N*-(4-Formyl-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3e):**

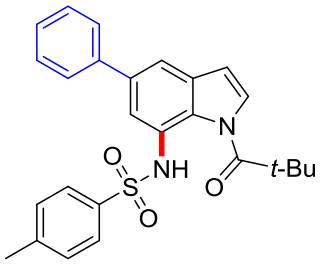
Yellow amorphous solid; R_f = 0.3 (20% EtOAc in petroleum ether); ^1H NMR (500 MHz, CD_2Cl_2) δ 10.33 (s, 1H), 9.81 (brs, 1H), 8.80 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.08 (m, 1H), 7.72 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.28 (s, 3H), 1.52 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 196.69, 177.56, 144.52, 136.57, 136.48, 134.68, 130.01, 128.83, 127.59, 125.67, 124.92, 122.11, 120.42, 118.00, 42.00, 28.76, 21.69 ppm; FT-IR: $\tilde{\nu}$ = 2360, 2342, 1706, 1668, 1561, 1217, 1154 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{21}H_{23}N_2O_4S$: 399.13730, found: 399.13721.



***N*-(5-Methoxy-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3f):**

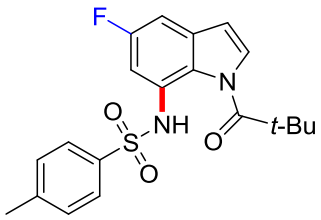
Brown amorphous solid; R_f = 0.15 (20% EtOAc in petroleum ether); ^1H NMR (500 MHz, CD_2Cl_2) δ 9.75 (brs, 1H), 7.54 (d, *J* = 3.9 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.13 (s, 1H), 7.11 – 7.10 (m, 2H), 6.84 (d, *J* = 2.5 Hz, 1H), 6.52 (d, *J* = 3.9 Hz, 1H), 3.84 (s, 3H), 2.30 (s, 3H), 1.37 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.68, 157.90, 144.15, 137.57, 133.82, 129.94, 128.21, 127.21, 126.57, 123.97, 109.89, 109.67,

101.86, 56.16, 42.02, 29.30, 21.65 ppm; FT-IR: $\tilde{\nu}$ = 2934, 2360, 2342, 1658, 1616, 1378, 1230, 1128, 1042 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{21}H_{25}N_2O_4S$: 401.15295, found: 401.15347.



4-Methyl-*N*-(5-phenyl-1-pivaloyl-1*H*-indol-7-yl)benzenesulfonamide (3g):

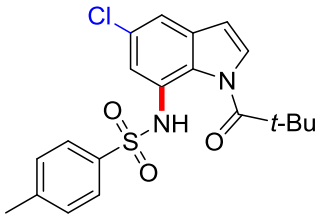
Brown oil; R_f = 0.25 (20% EtOAc in petroleum ether); ^1H NMR (500 MHz, CD_2Cl_2) δ 9.49 (brs, 1H), 7.79 (d, *J* = 1.7 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 1.7 Hz, 1H), 7.59 (d, *J* = 3.9 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 3.9 Hz, 1H), 2.30 (s, 3H), 1.38 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.02, 144.18, 140.47, 138.70, 137.63, 133.54, 129.97, 129.41, 128.98, 128.04, 128.00, 127.63, 127.22, 125.83, 121.85, 117.30, 110.02, 42.12, 29.22, 21.64 ppm; FT-IR: $\tilde{\nu}$ = 3151, 2974, 2930, 2360, 2342, 1670, 1332, 1220 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{26}H_{27}N_2O_3S$: 447.17369, found: 447.17420.



***N*-(5-Fluoro-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3h):**

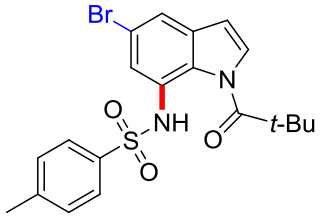
Brown amorphous solid; R_f = 0.15 (20% EtOAc in petroleum ether); ^1H NMR (500 MHz, CD_2Cl_2) δ 9.69 (brs, 1H), 7.62 (d, *J* = 3.9 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, *J* = 10.7, 2.5 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.04 (dd, *J* = 10.7, 2.5 Hz, 1H), 6.57 (d, *J* = 3.9 Hz, 1H), 2.30 (s, 3H), 1.38 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.18, 160.50 (d, *J* = 241.2 Hz), 144.43, 137.34, 133.73 (d, *J* = 11.2 Hz), 130.07,

129.08, 127.19, 127.00 (d, J = 12.0 Hz), 125.76 (d, J = 1.8 Hz), 109.71 (d, J = 4.1 Hz), 109.25 (d, J = 28.5 Hz), 104.25 (d, J = 23.6 Hz), 42.22, 29.27, 21.67 ppm; ^{19}F NMR (377 MHz, CD_2Cl_2) δ -117.81 ppm (dd, J = 10.6, 7.7 Hz); FT-IR: $\tilde{\nu}$ = 3198, 2975, 1661, 1600, 1473, 1334, 1184, 1160 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}FN_2O_3S$: 389.13297, found: 389.13290.



N-(5-Chloro-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3i):

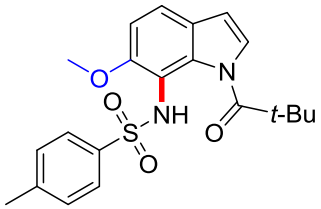
Brown amorphous solid; R_f = 0.15 (20% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.48 (brs, 1H), 7.59 (d, J = 3.9 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.40 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 2.0 Hz, 1H), 7.13 (d, J = 8.2 Hz, 2H), 6.55 (d, J = 3.9 Hz, 1H), 2.30 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.20, 144.42, 137.36, 133.91, 130.80, 130.07, 128.78, 128.11, 127.16, 126.63, 121.95, 118.48, 109.18, 42.22, 29.20, 21.66 ppm; FT-IR: $\tilde{\nu}$ = 2975, 2360, 2342, 1663, 1583, 1454, 1376, 1158, 1091 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{35}ClN_2O_3S$: 405.10342, found: 405.10339; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{37}ClN_2O_3S$: 407.10047, found: 407.10022.



***N*-(5-Bromo-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3j):**

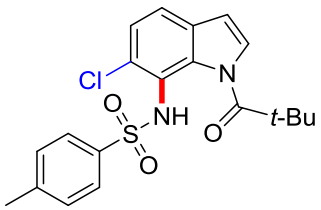
Brown amorphous solid; R_f = 0.15 (20% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.43 (brs, 1H), 7.64 (d, J = 1.9 Hz, 1H), 7.57 (d, J = 3.9 Hz, 1H), 7.52 (d, J = 1.9 Hz, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 6.55 (d, J = 3.9

Hz, 1H), 2.30 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.21, 144.42, 137.36, 134.31, 130.07, 128.64, 128.58, 127.15, 126.78, 124.75, 121.61, 118.27, 109.03, 42.22, 29.18, 21.66 ppm; FT-IR: $\tilde{\nu}$ = 2975, 2361, 2342, 1670, 1448, 1330, 1295, 1122, 1092 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{79}BrN_2O_3S$: 449.05290, found: 449.05215; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{81}BrN_2O_3S$: 451.05086; found: 451.05115.



***N*-(6-Methoxy-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3k):**

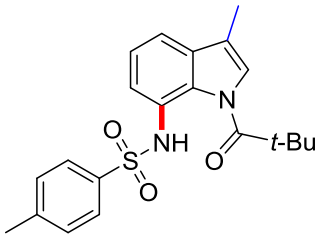
Brown amorphous solid; R_f = 0.2 (20% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.55 (d, *J* = 3.8 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.43 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 3.8 Hz, 1H), 3.50 (s, 3H), 2.38 (s, 3H), 1.47 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.64, 154.34, 143.73, 138.54, 133.99, 129.53, 127.57, 126.69, 126.38, 120.41, 114.00, 109.95, 108.05, 56.69, 42.13, 29.12, 21.70 ppm; FT-IR: $\tilde{\nu}$ = 2972, 2360, 2342, 1715, 1671, 1492, 1403, 1303, 1156 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{21}H_{25}N_2O_4S$: 401.15295, found: 401.15308.



***N*-(6-Chloro-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3l):**

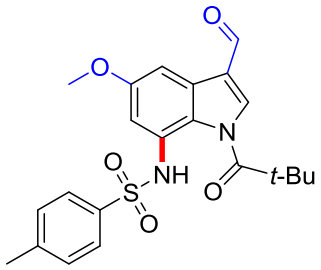
Brown amorphous solid; R_f = 0.2 (6% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.70 (brs, 1H), 7.65 (d, *J* = 3.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 3.8 Hz, 1H), 2.40 (s, 3H), 1.46 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.98,

144.57, 137.91, 134.53, 131.94, 131.80, 129.99, 128.23, 127.82, 126.64, 121.98, 121.38, 108.29, 42.22, 29.09, 21.80 ppm; FT-IR: $\tilde{\nu}$ = 3238, 2975, 2360, 2342, 1715, 1464, 1333, 1296, 1165 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{35}ClN_2O_3S$: 405.10342, found: 405.10345; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{37}ClN_2O_3S$: 407.10047, found: 407.10040.



4-Methyl-*N*-(3-methyl-1-pivaloyl-1*H*-indol-7-yl)benzenesulfonamide (3m):

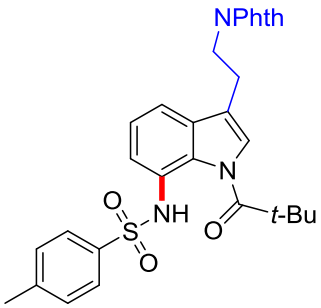
Brown amorphous solid; R_f = 0.25 (20% EtOAc in petroleum ether); ^1H NMR (600 MHz, CD_2Cl_2) δ 9.56 (brs, 1H), 7.52 – 7.50 (m, 1H), 7.36 – 7.31 (m, 5H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 2.21 (d, *J* = 1.2 Hz, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR (151 MHz, CD_2Cl_2) δ 179.70, 144.03, 137.79, 133.99, 129.97, 129.93, 127.17, 125.77, 125.36, 124.23, 122.66, 118.75, 117.04, 41.99, 29.23, 21.65, 9.93 ppm; FT-IR: $\tilde{\nu}$ = 2976, 2919, 2360, 2342, 1662, 1321, 1258, 1119 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{21}H_{25}N_2O_3S$: 385.15804, found: 385.15888.



***N*-(3-Formyl-5-methoxy-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3n):**

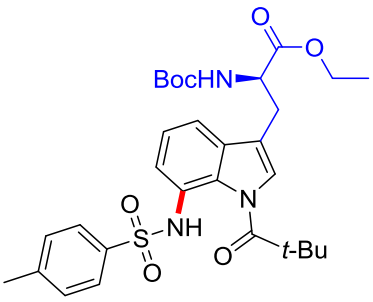
Brown amorphous solid; R_f = 0.2 (20% EtOAc in petroleum ether); ^1H NMR (500 MHz, CD_2Cl_2) δ 10.00 (s, 1H), 9.02 (brs, 1H), 8.38 (s, 1H), 8.25 (d, *J* = 9.2 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 9.2 Hz, 1H), 3.45 (s, 3H), 2.39 (s, 3H), 1.53 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 187.17, 177.46, 151.23,

143.70, 138.54, 138.15, 133.62, 129.36, 127.58, 122.79, 122.12, 119.67, 115.88, 112.43, 56.38, 42.19, 28.90, 21.75 ppm; FT-IR: $\tilde{\nu}$ = 3166, 2927, 2360, 2342, 1702, 1654, 1538, 1499, 1266 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{22}H_{25}N_2O_5S$: 429.14787, found: 429.14907.



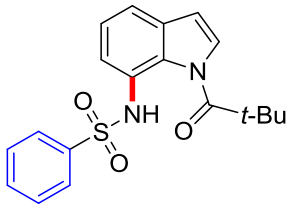
***N*-(3-(2-(1,3-Dioxoisoindolin-2-yl)ethyl)-1-pivaloyl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide (3o):**

Brown oil; R_f = 0.15 (25% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.40 (brs, 1H), 7.81 – 7.80 (m, 2H), 7.73 – 7.72 (m, 2H), 7.49 (td, *J* = 7.9, 0.9 Hz, 2H), 7.40 (s, 1H), 7.36 – 7.32 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.98 (t, *J* = 7.2 Hz, 2H), 3.06 (t, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 1.29 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.85, 168.62, 144.01, 137.72, 134.62, 132.87, 132.46, 130.03, 129.93, 127.09, 125.77, 125.49, 124.52, 123.60, 123.01, 119.33, 117.04, 41.96, 37.41, 29.06, 24.29, 21.63 ppm; FT-IR: $\tilde{\nu}$ = 3727, 2918, 2850, 2360, 2342, 1709, 1669, 1346, 1163 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{30}H_{30}N_3O_5S$: 544.19007, found: 544.19064.



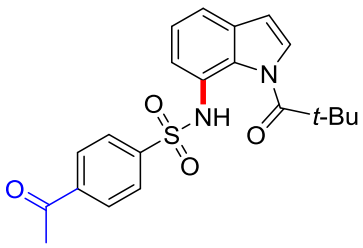
Ethyl(R)-2-((tert-butoxycarbonyl)amino)-3-(7-((4-methylphenyl)sulfonamido)-1-pivaloyl-1*H*-indol-3-yl)propanoate (3p):

Brown oil; R_f = 0.1 (25% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.39 (brs, 1H), 7.51 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.31 (m, 4H), 7.11 (d, *J* = 8.1 Hz, 2H), 5.11 – 5.09 (brs, 1H), 4.62 – 4.58 (m, 1H), 4.16 – 4.06 (m, 2H), 3.22 (dd, *J* = 13.0, 5.9 Hz, 1H), 3.08 (dd, *J* = 13.0, 5.9 Hz, 1H), 2.30 (s, 3H), 1.40 (s, 9H), 1.35 (s, 9H), 1.23 – 1.20 (m, 3H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 179.78, 172.05, 155.42, 144.11, 137.61, 133.16, 129.96, 129.83, 127.11, 125.81, 125.46, 125.35, 122.97, 117.68, 117.03, 80.37, 62.21, 42.06, 29.57, 29.22, 28.55, 27.88, 21.65, 14.43 ppm; FT-IR: ṽ = 2977, 2360, 2342, 1711, 1670, 1601, 1495, 1347, 1160 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{30}H_{40}N_3O_7S$: 586.25815, found: 586.25979; $[\alpha]_D^{RT}$ = 29.8 ($CHCl_3$, *c* = 1).



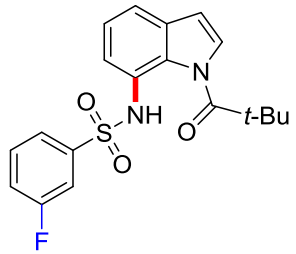
_N_-(1-pivaloyl-1_H_-indol-7-yl)benzenesulfonamide (3q):

Brown amorphous solid; R_f = 0.1 (20% EtOAc in petroleum ether); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.38 (brs, 1H), 7.55 (d, *J* = 4.0 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.43 – 7.40 (m, 1H), 7.34 – 7.28 (m, 3H), 6.60 (d, *J* = 4.0 Hz, 1H), 1.38 (s, 9H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 180.26, 140.72, 133.13, 133.04, 129.83, 129.38, 127.48, 127.17, 125.67, 125.62, 122.84, 119.41, 109.79, 42.23, 29.37 ppm; FT-IR: ṽ = 3118, 2360, 2342, 1663, 1580, 1363, 1326, 1174, 1163 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{19}H_{21}N_2O_3S$: 357.12674, found: 357.12782.



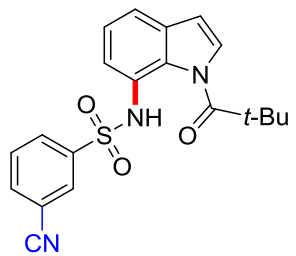
4-Acetyl-_N_-(1-pivaloyl-1_H_-indol-7-yl)benzenesulfonamide (3r):

Brown amorphous solid; R_f = 0.15 (25% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.58 (brs, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 3.7 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 6.61 (d, *J* = 3.7 Hz, 1H), 2.52 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 197.03, 180.24, 144.26, 140.43, 133.06, 129.61, 129.06, 127.52, 127.50, 125.76, 125.11, 122.54, 119.59, 109.91, 42.17, 29.27, 27.20 ppm; FT-IR: ṽ = 2925, 2360, 2342, 1686, 1667, 1321, 1230, 1180, 1164 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{21}H_{23}N_2O_4S$: 399.13730, found: 399.13777.



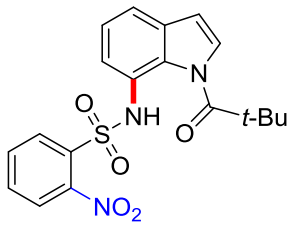
3-Fluoro-*N*-(1-pivaloyl-1*H*-indol-7-yl)benzenesulfonamide (3s):

Brown amorphous solid; R_f = 0.25 (20% EtOAc in petroleum ether); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.53 (brs, 1H), 7.58 (d, *J* = 4.0 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.43 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.35 – 7.22 (m, 4H), 7.17 – 7.13 (m, 1H), 6.62 (d, *J* = 4.0 Hz, 1H), 1.40 (s, 9H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 180.33, 162.69 (d, *J* = 250.7 Hz), 142.66 (d, *J* = 6.8 Hz), 133.13, 131.23 (d, *J* = 7.8 Hz), 129.83, 127.57, 125.80, 125.24, 123.15 (d, *J* = 3.3 Hz), 122.83, 120.28 (d, *J* = 21.2 Hz), 119.69, 114.53 (d, *J* = 24.4 Hz), 109.94, 42.26, 29.35 ppm; ^{19}F NMR (377 MHz, CD_2Cl_2) δ -110.71 ppm (td, *J* = 8.3, 5.0 Hz); FT-IR: ṽ = 2980, 2360, 2342, 1656, 1364, 1328, 1163, 1081 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{19}H_{20}FN_2O_3S$: 375.11732, found: 375.11799.



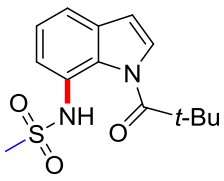
3-Cyano-*N*-(1-pivaloyl-1*H*-indol-7-yl)benzenesulfonamide (3t):

Brown amorphous solid; R_f = 0.1 (20% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.71 (brs, 1H), 7.78 (s, 1H), 7.73 – 7.70 (m, 2H), 7.59 (d, *J* = 3.9 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 3.9 Hz, 1H), 1.40 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.31, 141.95, 136.31, 133.17, 131.18, 130.83, 130.45, 129.61, 127.63, 125.94, 124.80, 122.45, 119.86, 117.44, 113.85, 110.09, 42.24, 29.34 ppm; FT-IR: $\tilde{\nu}$ = 2976, 2360, 2342, 2234, 1666, 1587, 1333, 1302, 1179, 1158 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{20}N_3O_3S$: 382.12199, found: 382.12259.



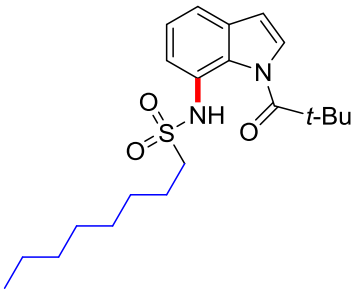
2-Nitro-*N*-(1-pivaloyl-1*H*-indol-7-yl)benzenesulfonamide (3u):

Yellow amorphous solid; R_f = 0.1 (20% EtOAc in petroleum ether); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.49 (brs, 1H), 7.77 – 7.75 (m, 1H), 7.68 (d, *J* = 3.9 Hz, 1H), 7.67 – 7.56 (m, 3H), 7.52 – 7.47 (m, 1H), 7.39 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 3.9 Hz, 1H), 1.50 (s, 9H) ppm; ^{13}C NMR (151 MHz, CD_2Cl_2) δ 180.39, 148.39, 134.37, 133.28, 133.26, 132.52, 131.86, 129.20, 127.91, 125.62, 125.08, 125.04, 120.15, 119.15, 109.65, 42.25, 29.27 ppm; FT-IR: $\tilde{\nu}$ = 3101, 2987, 2360, 2342, 1685, 1672, 1588, 1365, 1127 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{19}H_{20}N_3O_5S$: 402.11182, found: 402.11254.



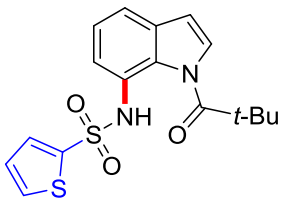
***N*-(1-Pivaloyl-1*H*-indol-7-yl)methanesulfonamide (3v):**

Brown oil; R_f = 0.2 (20% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.13 (brs, 1H), 7.79 (d, *J* = 3.9 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 3.9 Hz, 1H), 2.87 (s, 3H), 1.55 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.72, 133.37, 129.23, 127.77, 126.10, 125.77, 120.71, 119.00, 109.89, 42.53, 40.10, 29.46 ppm; FT-IR: $\tilde{\nu}$ = 3188, 2977, 2935, 2360, 2341, 1669, 1590, 1316, 1230, 1179, 1152 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{14}H_{19}N_2O_3S$: 295.11109, found: 295.11191.



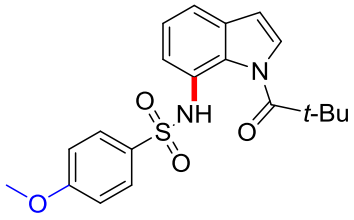
***N*-(1-Pivaloyl-1*H*-indol-7-yl)octane-1-sulfonamide (3w):**

Brown oil; R_f = 0.2 (12% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.05 (brs, 1H), 7.78 (d, *J* = 3.9 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 3.9 Hz, 1H), 2.97 – 2.94 (m, 2H), 1.73 – 1.67 (m, 2H), 1.56 (s, 9H), 1.33 – 1.17 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.79, 133.39, 129.06, 127.71, 126.43, 125.81, 119.92, 118.63, 109.95, 52.37, 42.57, 32.23, 29.54, 29.44, 29.41, 28.65, 23.95, 23.11, 14.37 ppm; FT-IR: $\tilde{\nu}$ = 3190, 2926, 2856, 2360, 2342, 1671, 1318, 1301, 1179, 1146 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{21}H_{33}N_2O_3S$: 393.22064, found: 393.22175.



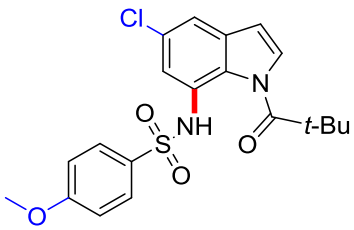
***N*-(1-Pivaloyl-1*H*-indol-7-yl)thiophene-2-sulfonamide (3x):**

Brown amorphous solid; R_f = 0.3 (33% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.56 (brs, 1H), 7.60 (d, *J* = 3.9 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.42 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.89 – 6.87 (m, 1H), 6.64 (d, *J* = 3.9 Hz, 1H), 1.41 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.24, 140.92, 133.02, 132.50, 132.21, 129.92, 127.72, 127.55, 125.67, 125.16, 123.27, 119.75, 109.84, 42.20, 29.33 ppm; FT-IR: ṽ = 3094, 2360, 2342, 1662, 1328, 1300, 1180, 1157, 1013 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{17}H_{19}N_2O_3S_2$: 363.08316, found: 363.08379.



4-Methoxy-*N*-(1-pivaloyl-1*H*-indol-7-yl)benzenesulfonamide (3y):

Brown amorphous solid; R_f = 0.1 (20% EtOAc in petroleum ether); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.31 (brs, 1H), 7.58 (d, *J* = 4.0 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 1H), 6.78 – 6.76 (m, 2H), 6.61 (d, *J* = 4.0 Hz, 1H), 3.75 (s, 3H), 1.41 (s, 9H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 180.23, 163.44, 133.03, 132.36, 129.80, 129.34, 127.49, 125.91, 125.62, 122.68, 119.21, 114.49, 109.79, 56.13, 42.25, 29.40 ppm; FT-IR: ṽ = 3141, 2969, 2360, 2342, 1672, 1597, 1331, 1305, 1261, 1162 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{23}N_2O_4S$: 387.13730, found: 387.13848.



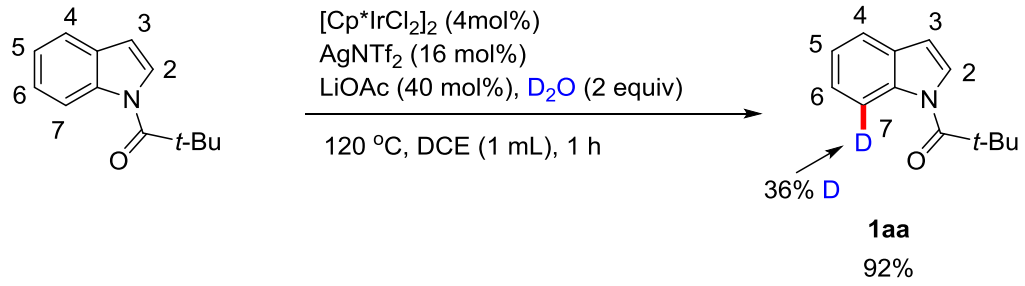
***N*-(5-Chloro-1-pivaloyl-1*H*-indol-7-yl)-4-methoxybenzenesulfonamide (3z):**

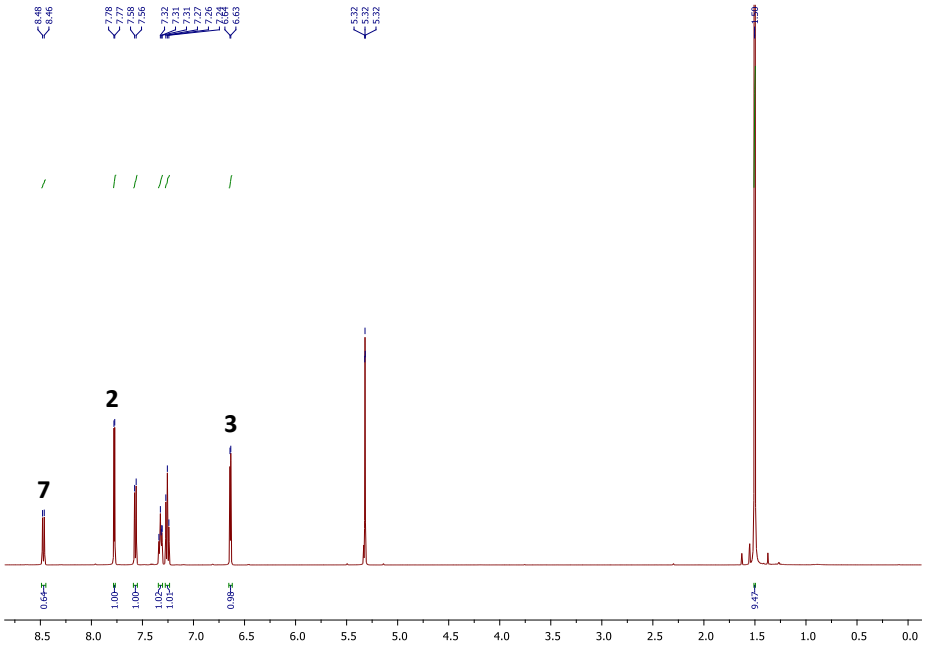
Brown amorphous solid; R_f = 0.15 (25% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.47 (brs, 1H), 7.62 (d, *J* = 3.9 Hz, 1H), 7.50 – 7.48 (m, 3H), 7.35 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.56 (d, *J* = 3.9 Hz, 1H), 3.76 (s, 3H), 1.40 (s, 9H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.27, 163.63, 133.99, 131.97, 130.87, 129.41, 128.83, 128.13, 126.89, 121.70, 118.37, 114.62, 109.24, 56.17, 42.33, 29.35 ppm; FT-IR: $\tilde{\nu}$ = 2932, 2360, 2342, 1667, 1582, 1501, 1328, 1303, 1266 1095 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{35}ClN_2O_4S$: 421.09833, found: 421.09866; HRMS: calc. for $[M+H]^+$ $C_{20}H_{22}{}^{37}ClN_2O_4S$: 423.09538, found:423.09548.

Study on reaction mechanism

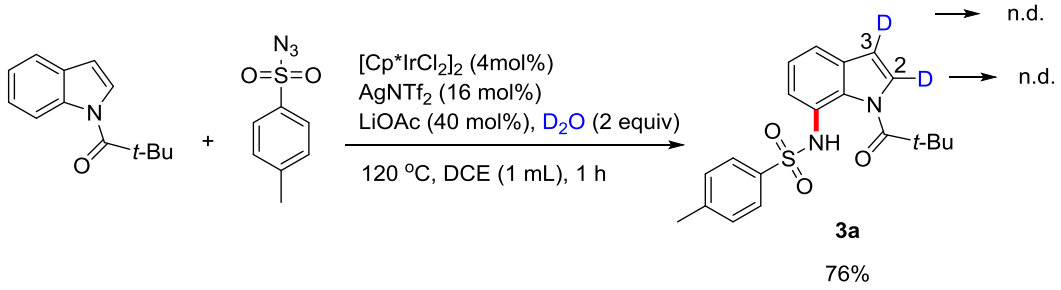
Deuterium labeling experiments

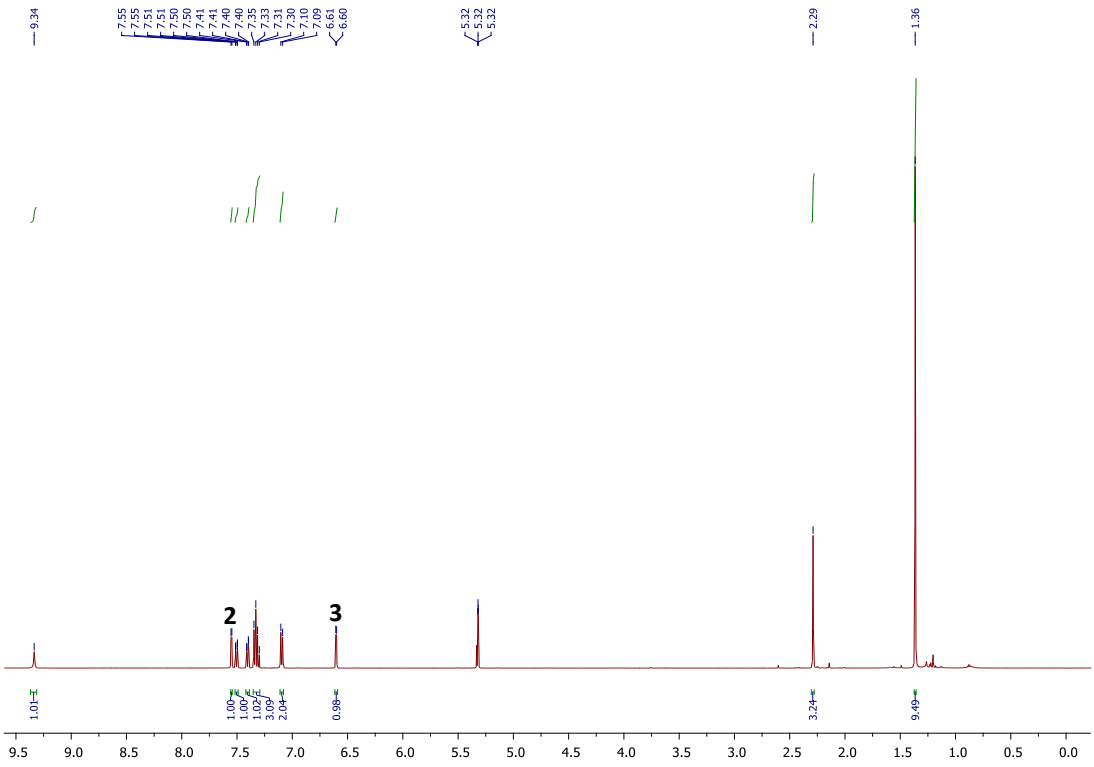
N-pivaloyl indole **1a** (0.1 mmol) was dissolved in a 12 mL screw capped tube with 1 mL of DCE, followed by [(IrCp*Cl_2)$_2$] (4 mol %). $AgNTf_2$ (16 mol %), LiOAc (40 mol%) and D_2O (2 equiv) were added to the reaction mixture at room temperature. The reaction mixture was allowed to warm up to 120 °C and stirred for 1h. After finishing the reaction, the reaction mixture was directly loaded on a silica gel column and purified with petroleum ether (40-60°C)/EtOAc mixture to afford the recovered starting material **1aa** in 92% yield. The analysis by ^{1}H NMR showed 36% deuterium incorporation at the C7-position of **1aa**.



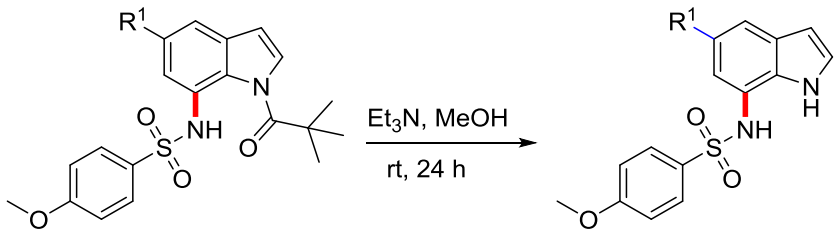


N-pivaloyl indole **1a** (0.1 mmol) and TsN_3 **2a** (0.22 mmol) were dissolved in a 12 mL screw capped tube with 1 mL of DCE, followed by $[(IrCp^*Cl_2)_2]$ (4 mol %). $AgNTf_2$ (16 mol %), LiOAc (40 mol%) and D_2O (2 equiv) were added to the reaction mixture at room temperature. The reaction mixture was allowed to warm up to 120 °C and stirred for 1h. After finishing the reaction, the reaction mixture was directly loaded on a silica gel column and purified with petroleum ether (40-60°C)/EtOAc mixture to afford the product **3a** in 76% yield. An analysis by ^1H NMR showed no deuterium incorporation on the ring of **1aa**.





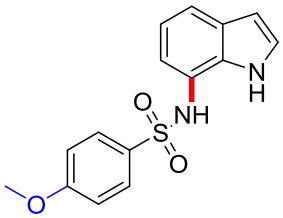
General procedure for removal of the directing group



3y, R^1 = H
3z, R^1 = Cl

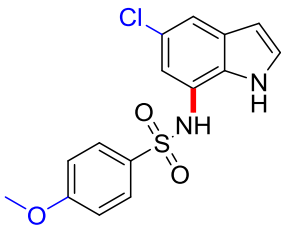
4a, R^1 = H, 90%
4b, R^1 = Cl, 92%

To a solution of **3y** or **3z** (0.1 mmol) in MeOH (1.0 mL) at room temperature was added Et_3N (0.2 mL) dropwise. Then the reaction was stirred for 24 h and quenched by addition of saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane. Combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was then purified by flash chromatography over silica gel with petroleum ether and ethyl acetate to give the corresponding product **4**.



***N*-(1*H*-indol-7-yl)-4-methoxybenzenesulfonamide (4a)[1]:**

Brown amorphous solid; R_f = 0.2 (25% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.32 (brs, 1H), 7.59 – 7.56 (m, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.29 (m, 1H), 6.88 – 6.84 (m, 3H), 6.55 – 6.54 (m, 1H), 6.44 (dd, *J* = 7.5, 0.5 Hz, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 163.93, 132.48, 130.68, 130.06, 130.00, 125.82, 120.80, 120.25, 120.14, 118.60, 114.66, 103.08, 56.20 ppm; FT-IR: $\tilde{\nu}$ = 3394, 3239, 2925, 2360, 2342, 1593, 1496, 1323, 1304, 1186 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{15}H_{15}N_2O_3S$: 303.07979, found: 303.08038.



***N*-(5-Chloro-1*H*-indol-7-yl)-4-methoxybenzenesulfonamide (4b)[2]:**

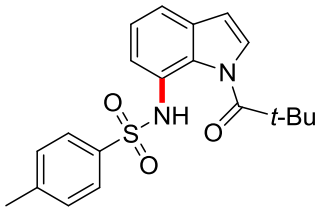
Brown amorphous solid; R_f = 0.2 (25% EtOAc in petroleum ether); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.47 (brs, 1H), 7.64 – 7.61 (m, 2H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 6.90 – 6.87 (m, 2H), 6.55 (d, *J* = 1.8 Hz, 1H), 6.49 (d, *J* = 2.3 Hz, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 164.13, 131.24, 130.56, 130.03, 129.73, 127.23, 125.02, 121.82, 119.21, 117.91, 114.85, 102.88, 56.25 ppm; FT-IR: $\tilde{\nu}$ = 3400, 3244, 3196, 2928, 2838, 2360, 2342, 1302, 1262, 1120 cm^{-1}; HRMS: calc. for $[M+H]^+$ $C_{15}H_{14}{}^{35}ClN_2O_3S$: 337.04082, found: 337.04158; HRMS: calc. for $[M+H]^+$ $C_{15}H_{14}{}^{37}ClN_2O_3S$: 339.03787, found: 339.03839.

References

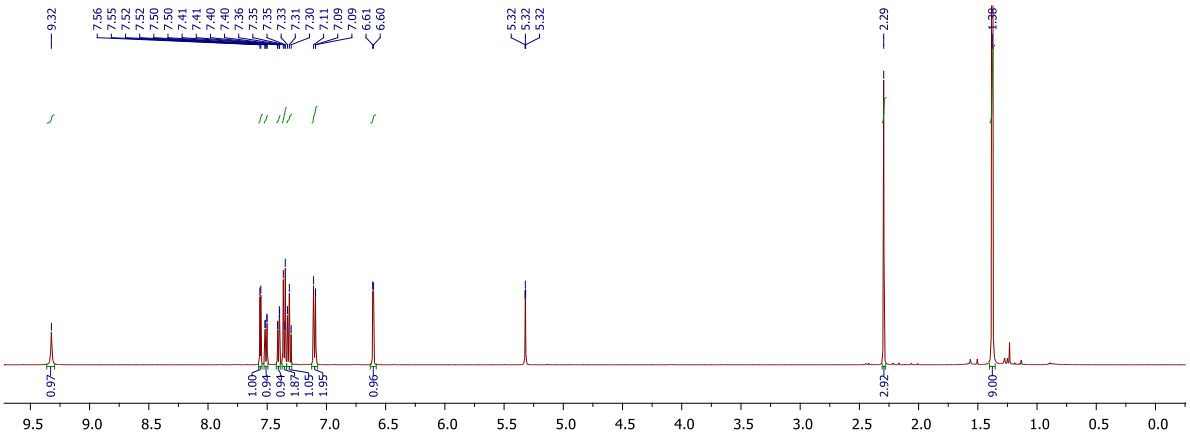
[1] T. Owa, H. Yoshino, T. Okauchi, K. Yoshimatsu, Y. Ozawa, N. H. Sugi, T. Nagasu, N. Koyanagi, K. Kitoh, *J. Med. Chem.* **1999**, *42*, 3789 – 3799.

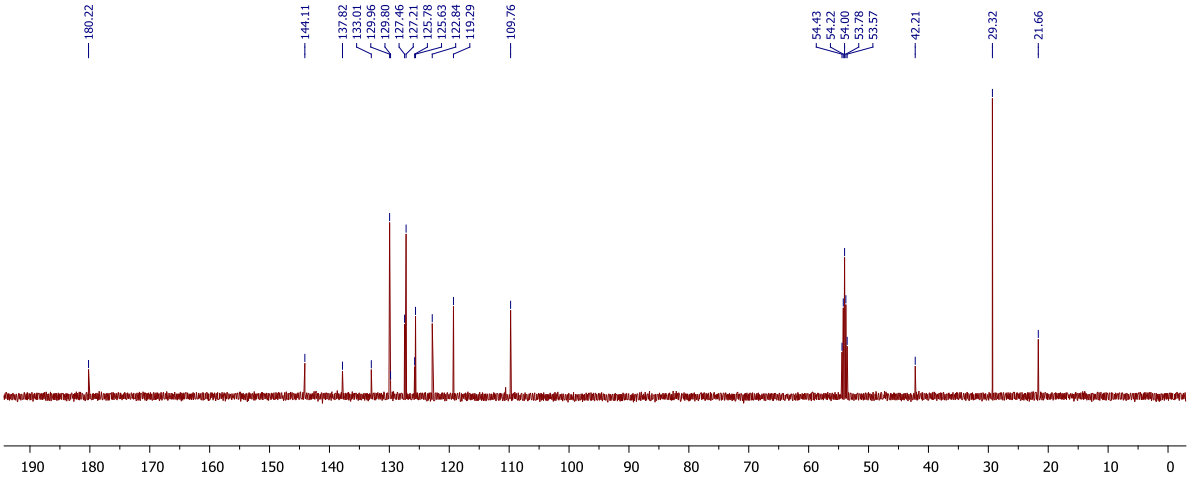
[2] M Banerjee, A. Poddar, G. Mitra, A. Surolia, T. Owa, B. Bhattacharyya, *J. Med. Chem.* **2005**, *48*, 547 – 555.

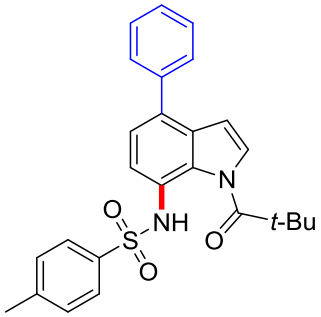
Copies of ^{1}H and ^{13}C NMR spectrum of products



3a



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O
N
O
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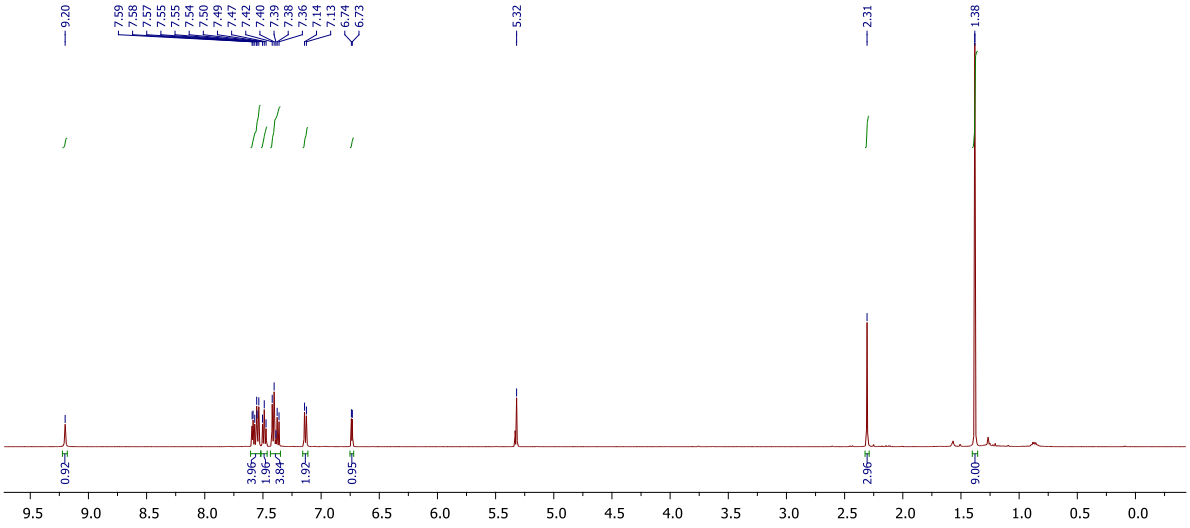
3b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7.39
7.38
7.36
7.14
7.13
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6.73
5.32
2.31
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3.96
1.96
3.84
1.92
0.95
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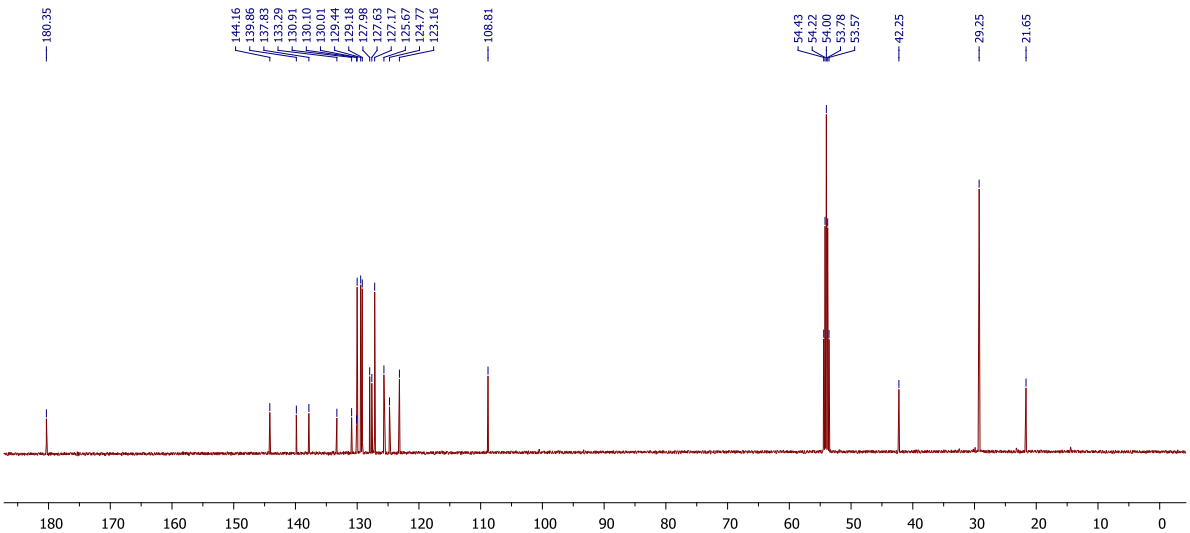
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54.22
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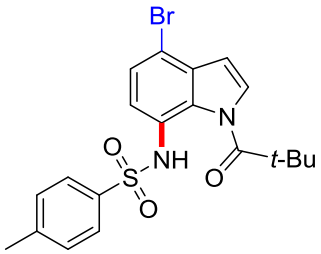
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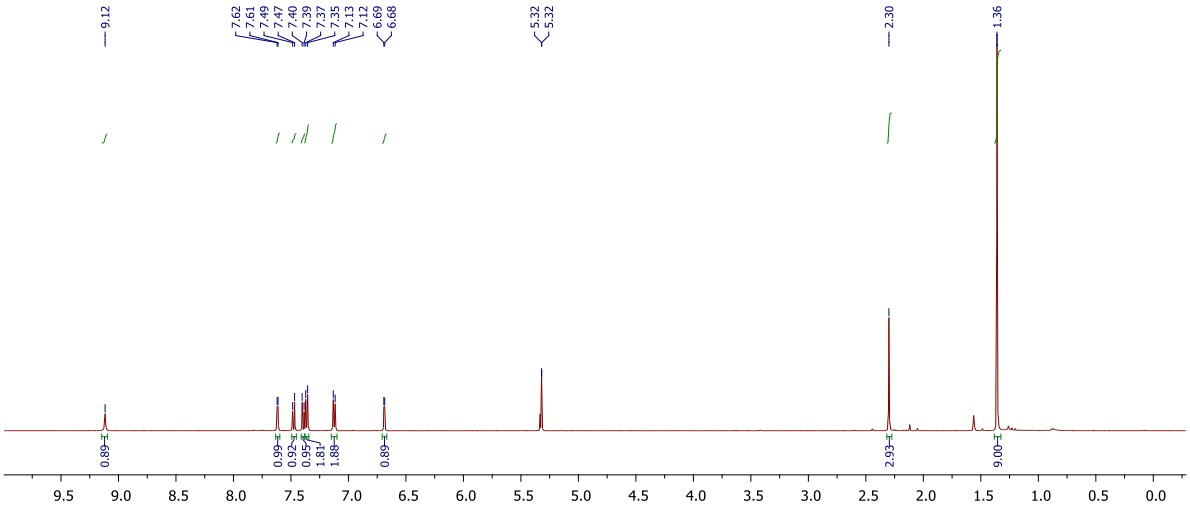
t-Bu

3c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0.92
0.95
1.81
1.88
0.89
2.93
9.00
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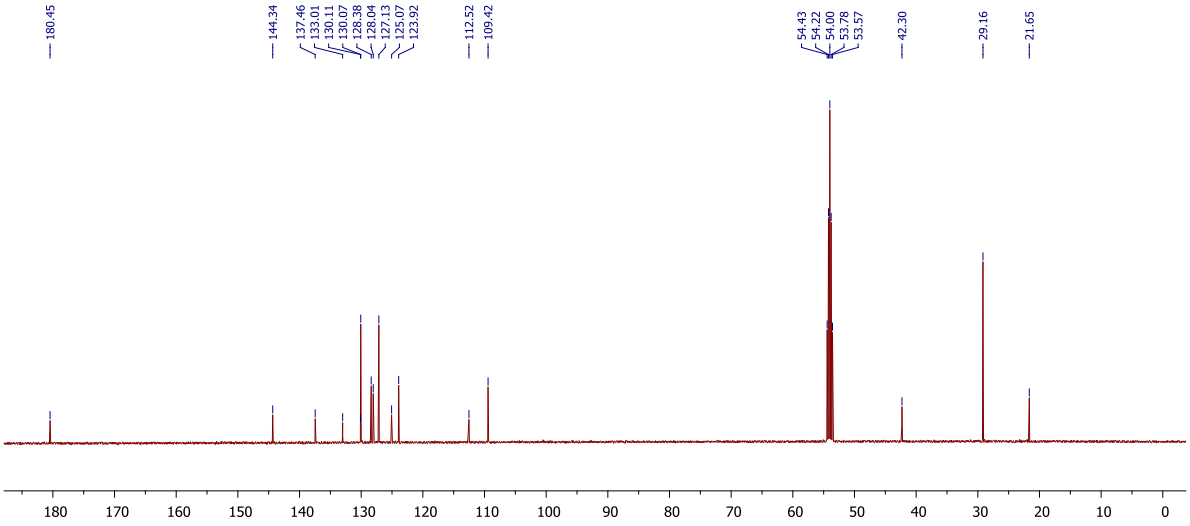
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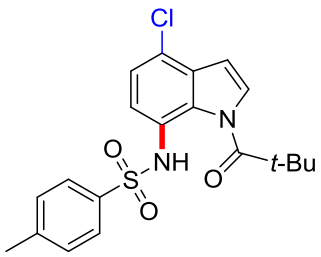
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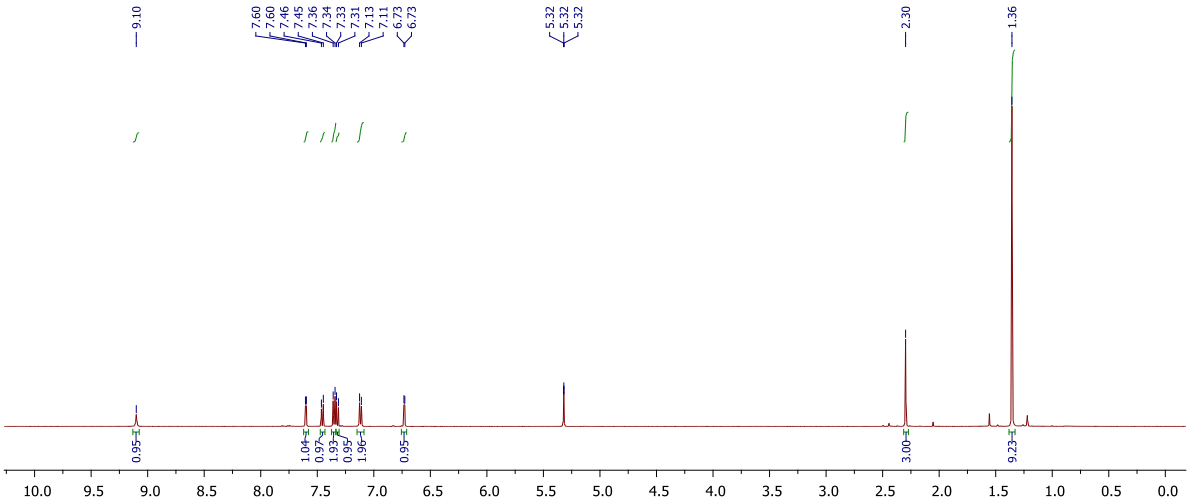
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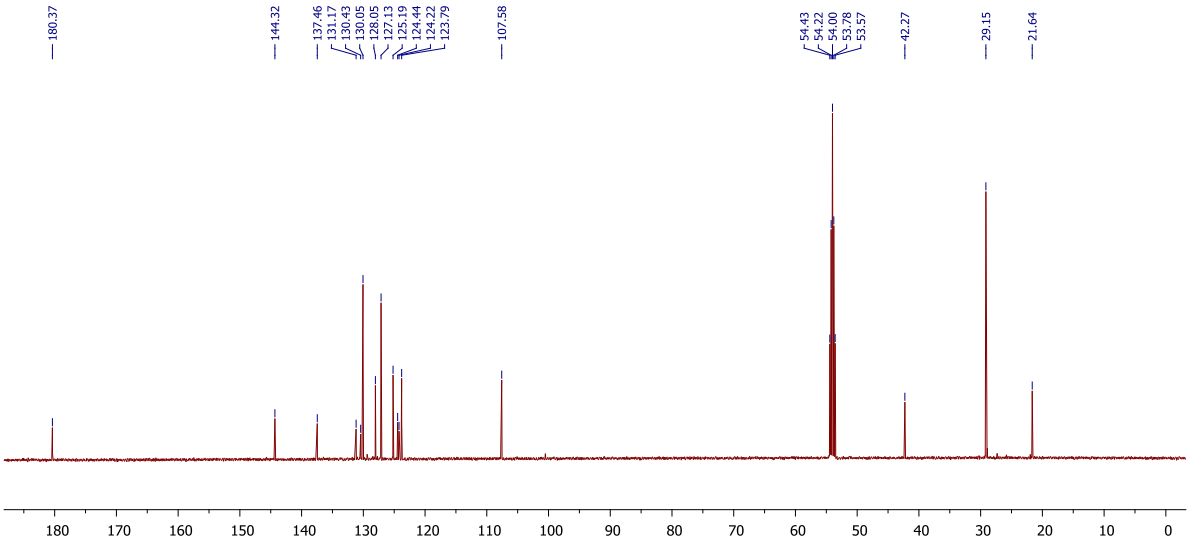
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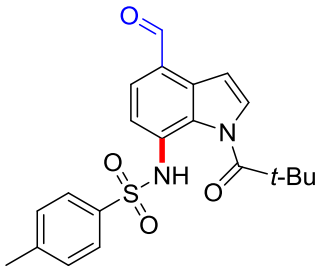
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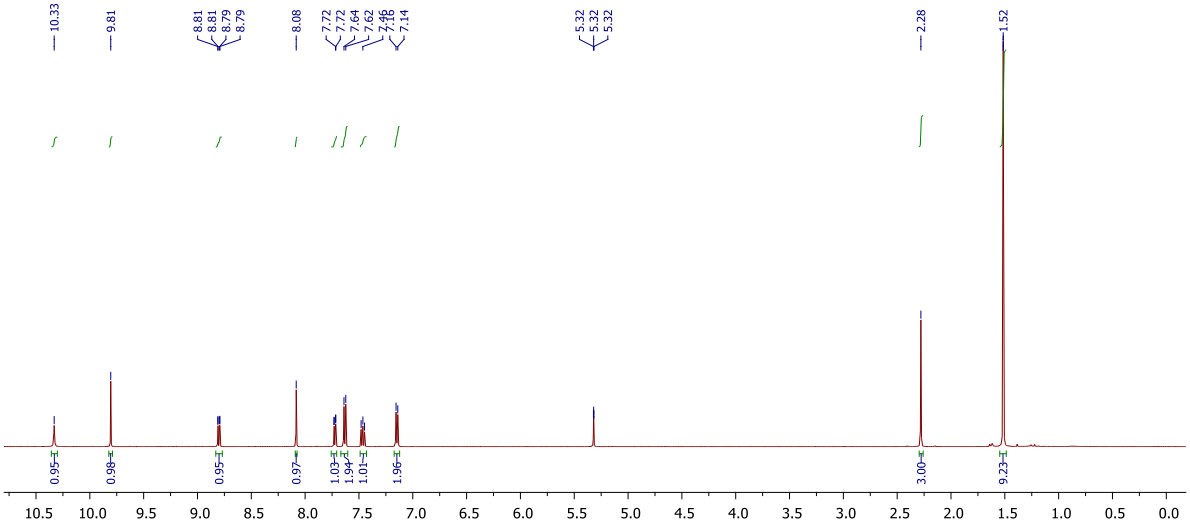
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1.96
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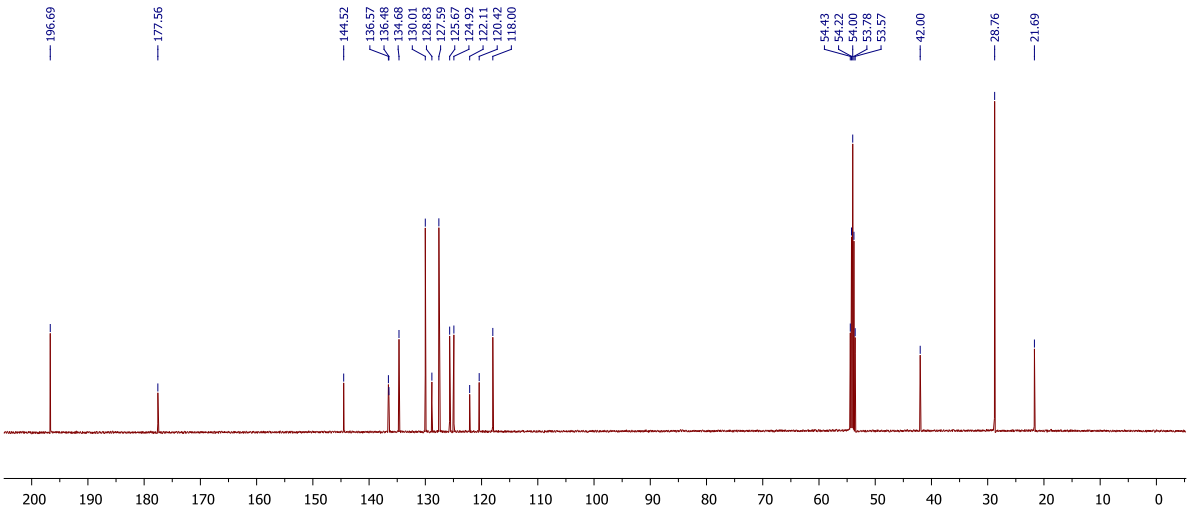
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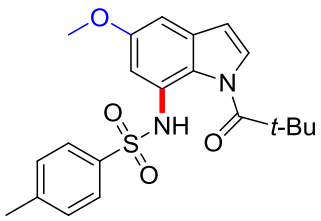
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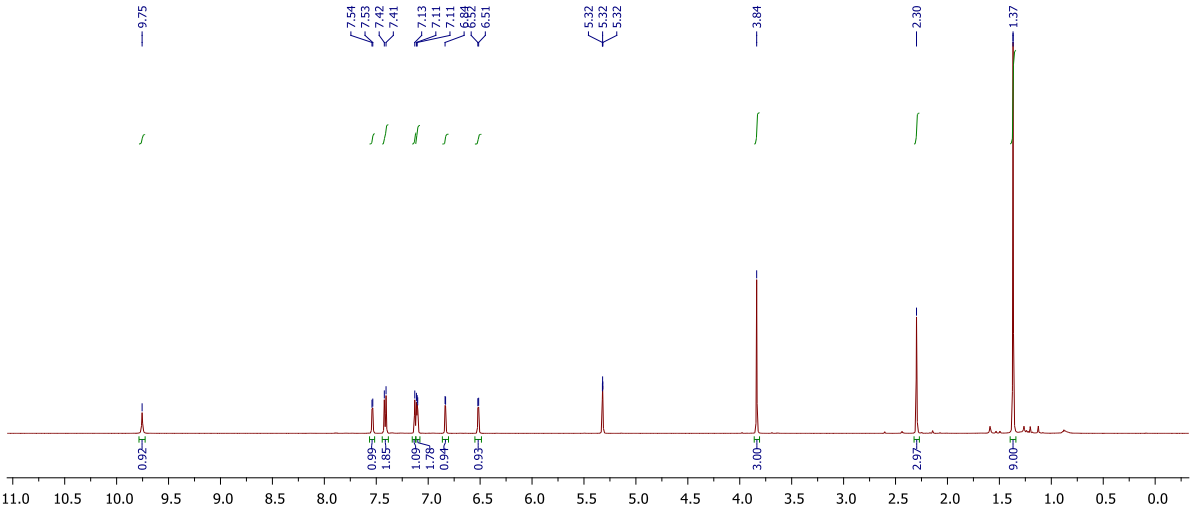
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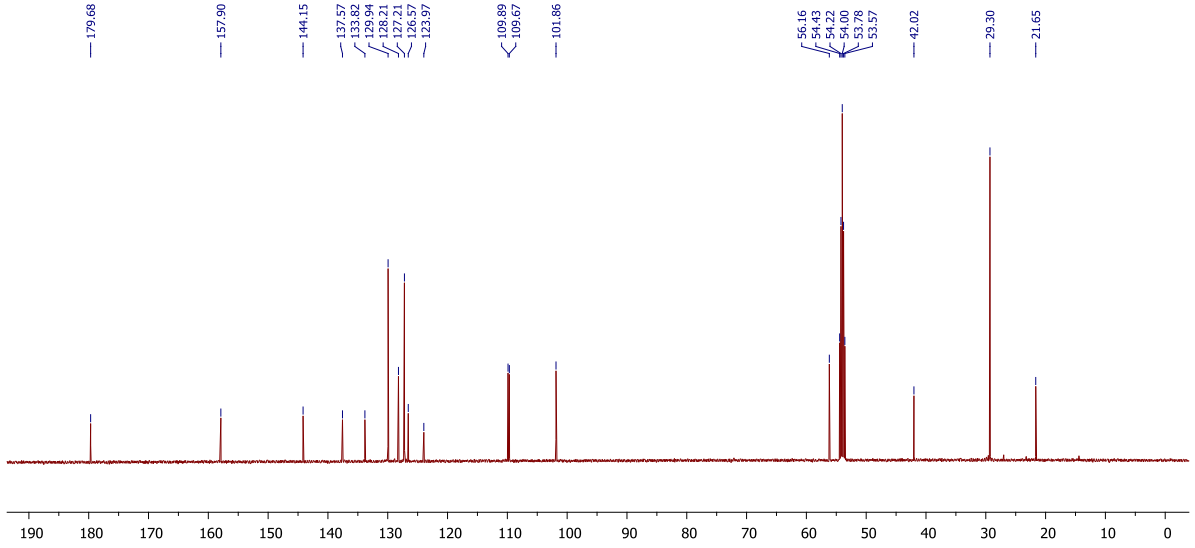
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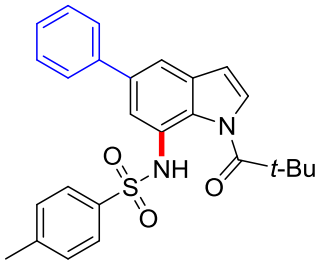
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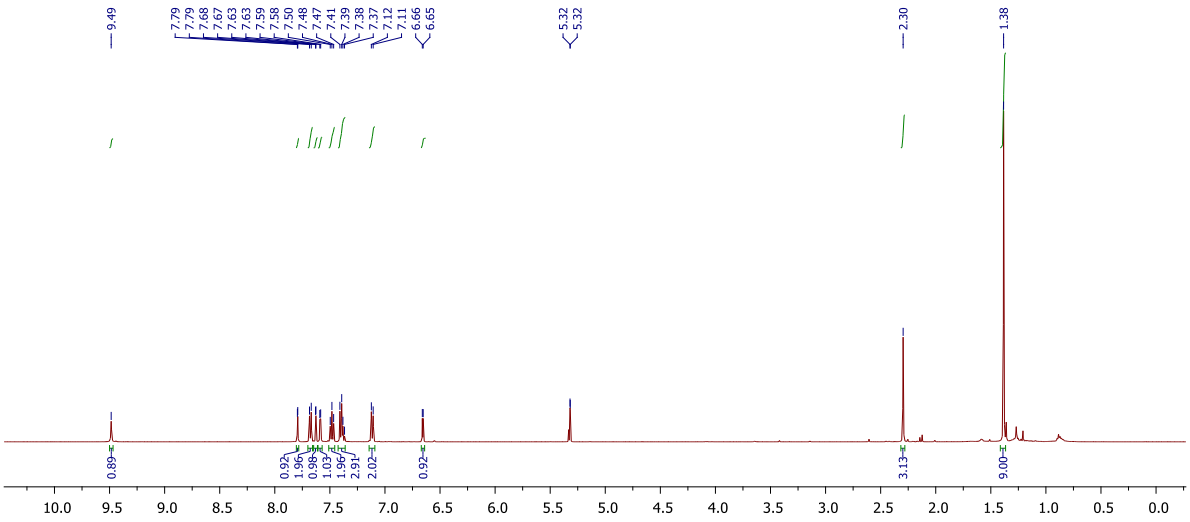
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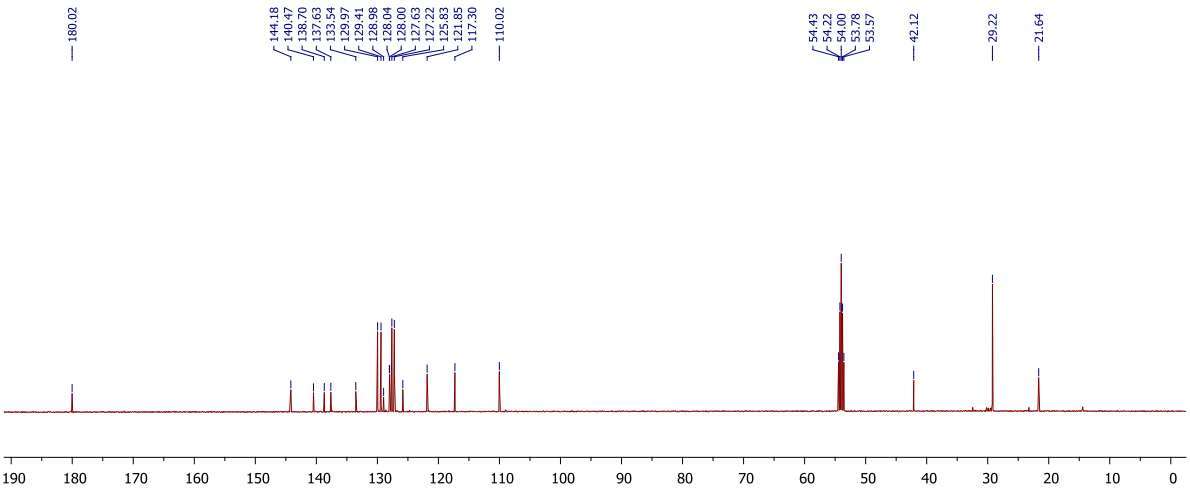
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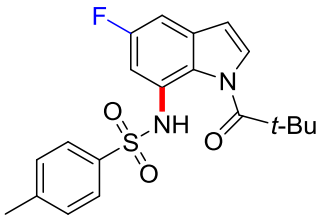
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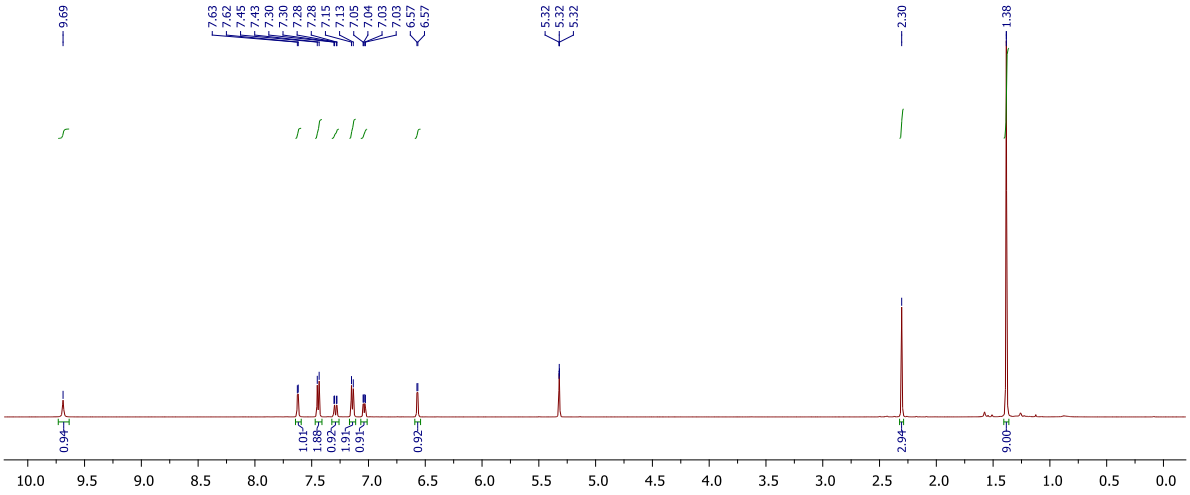
3h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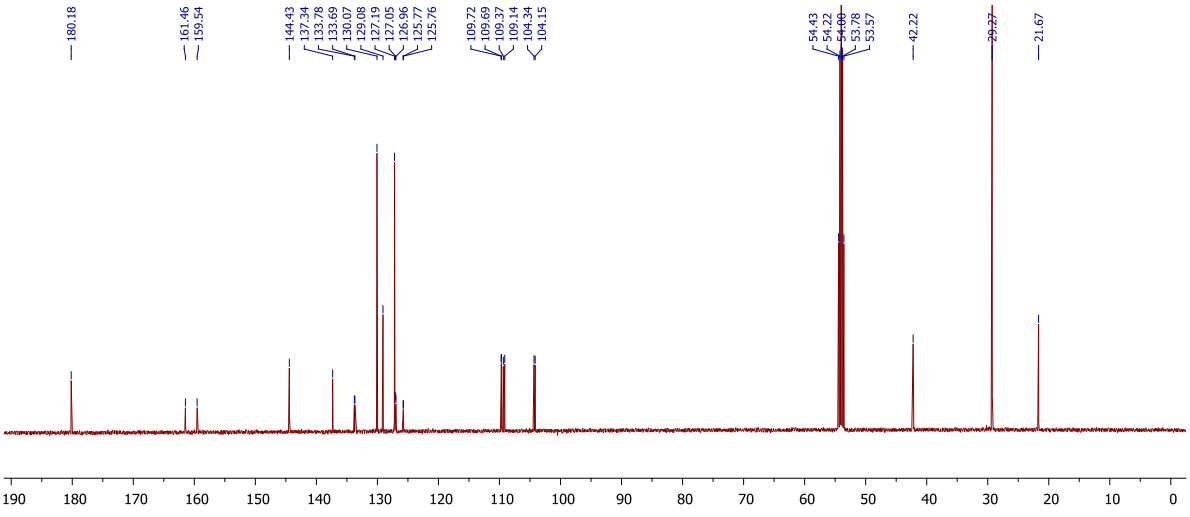
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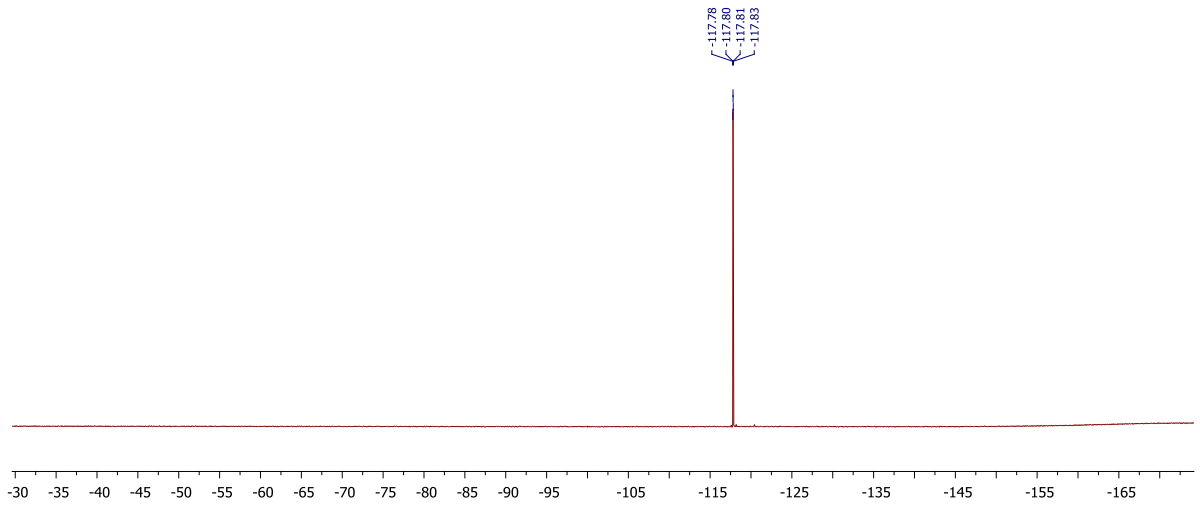
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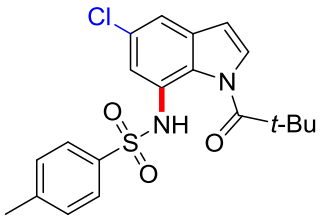
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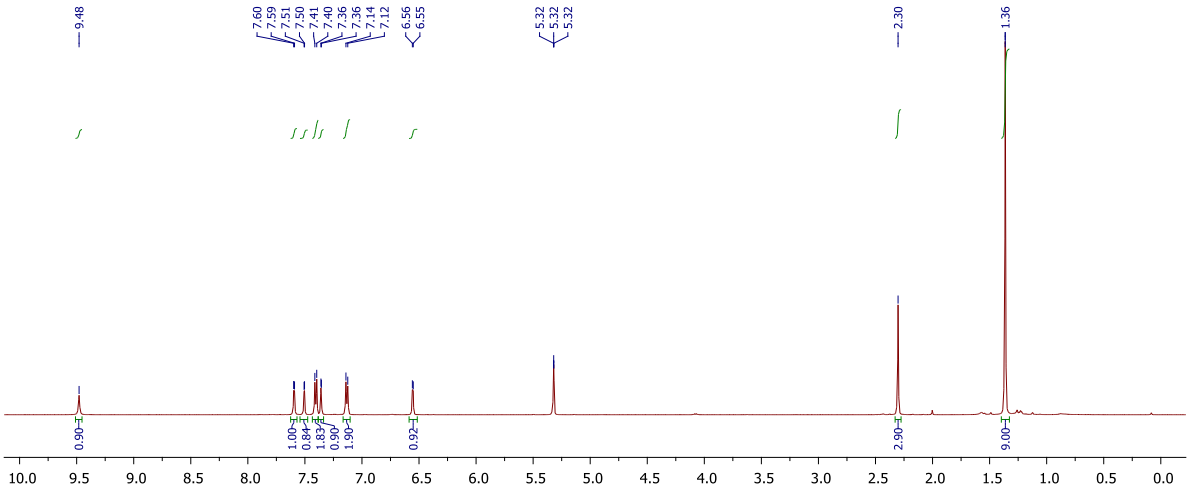
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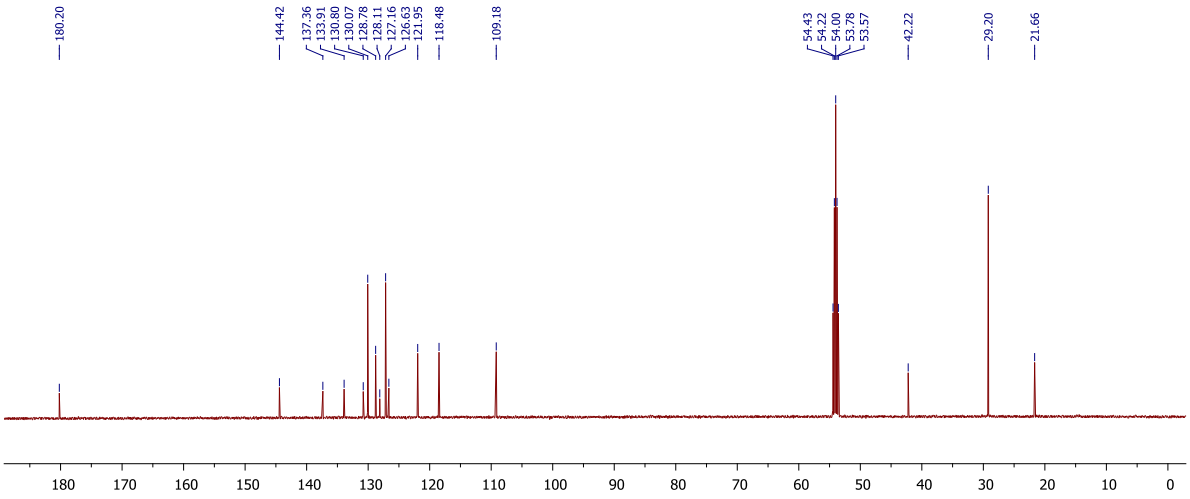
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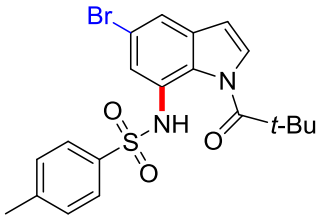
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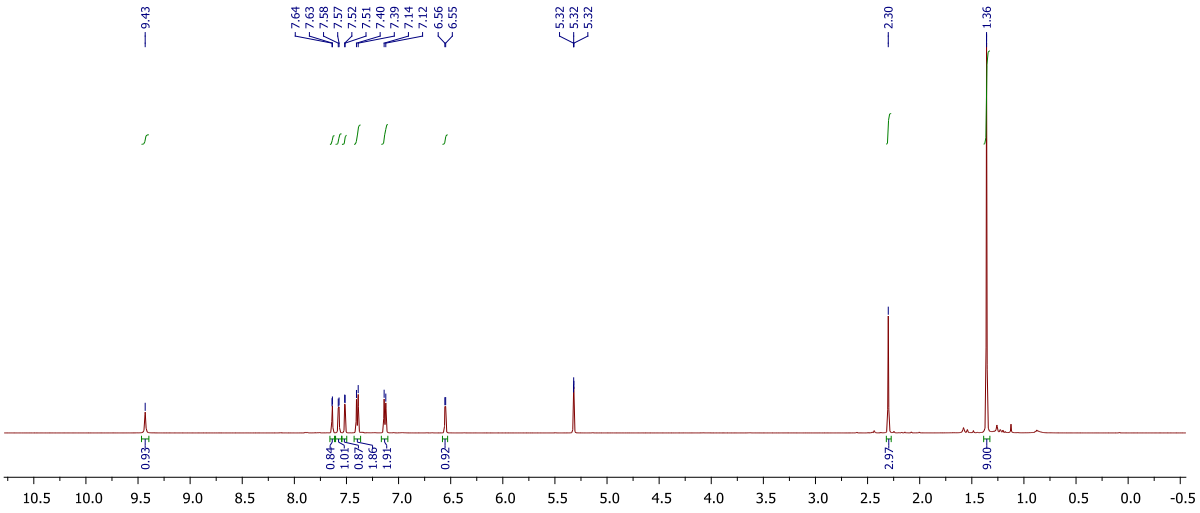
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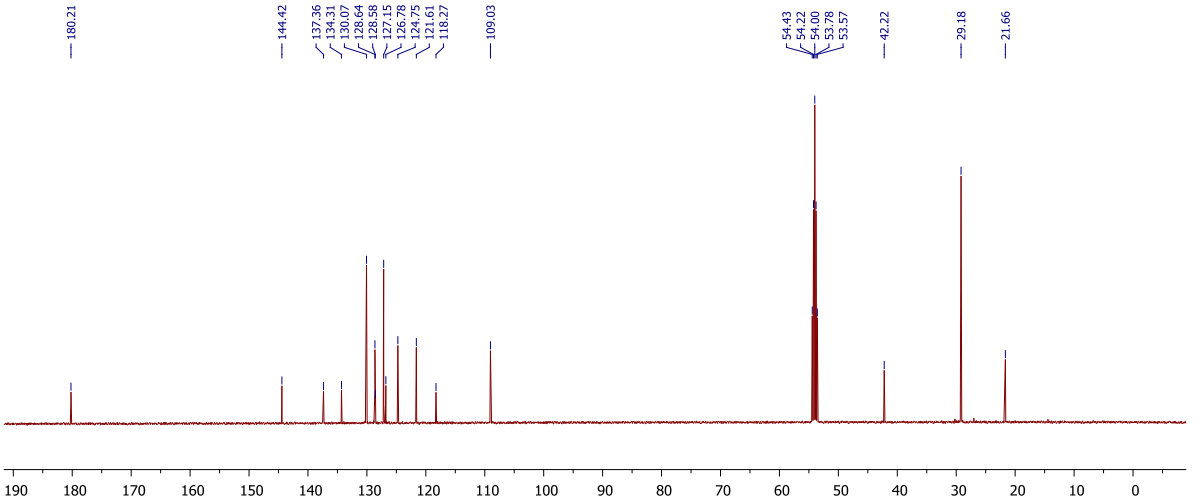
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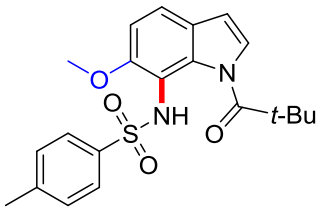
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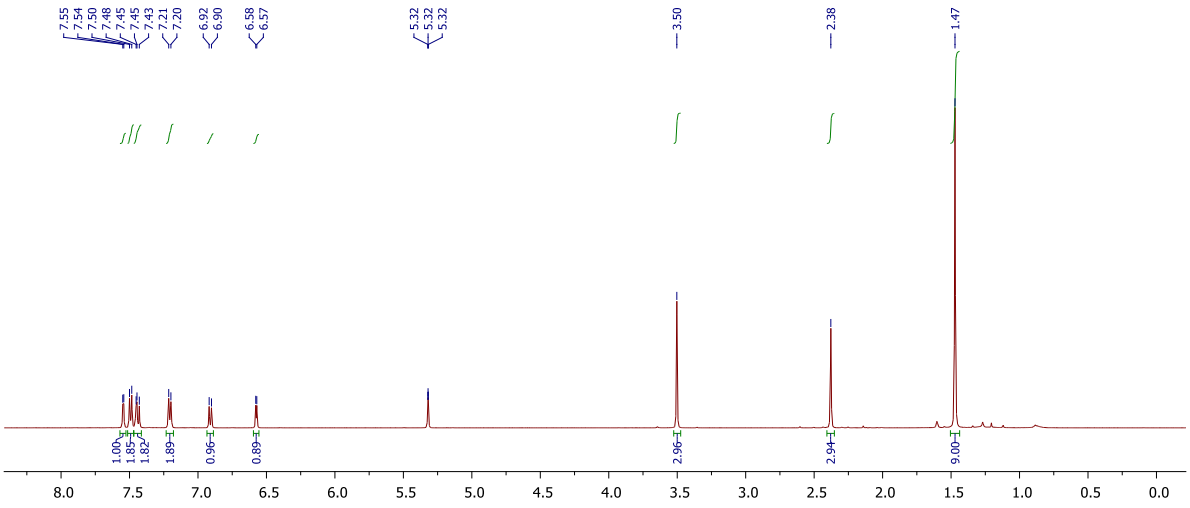
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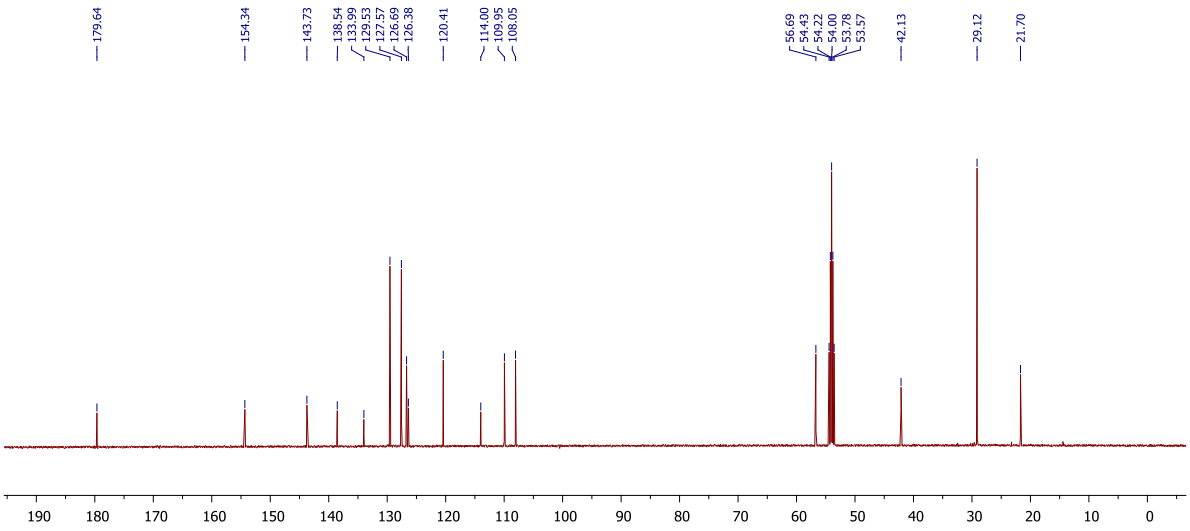
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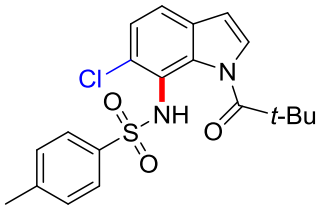
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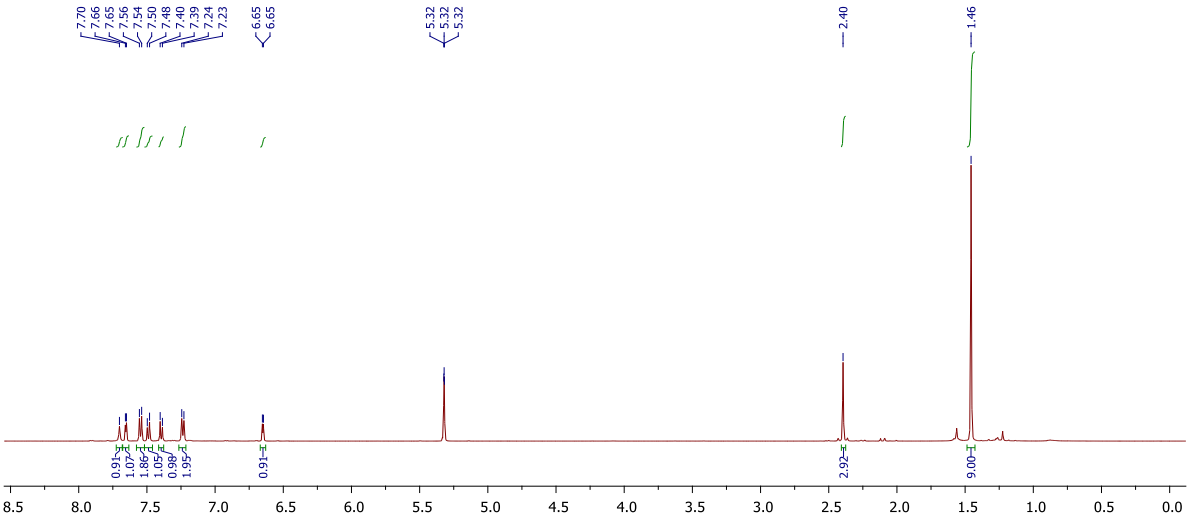
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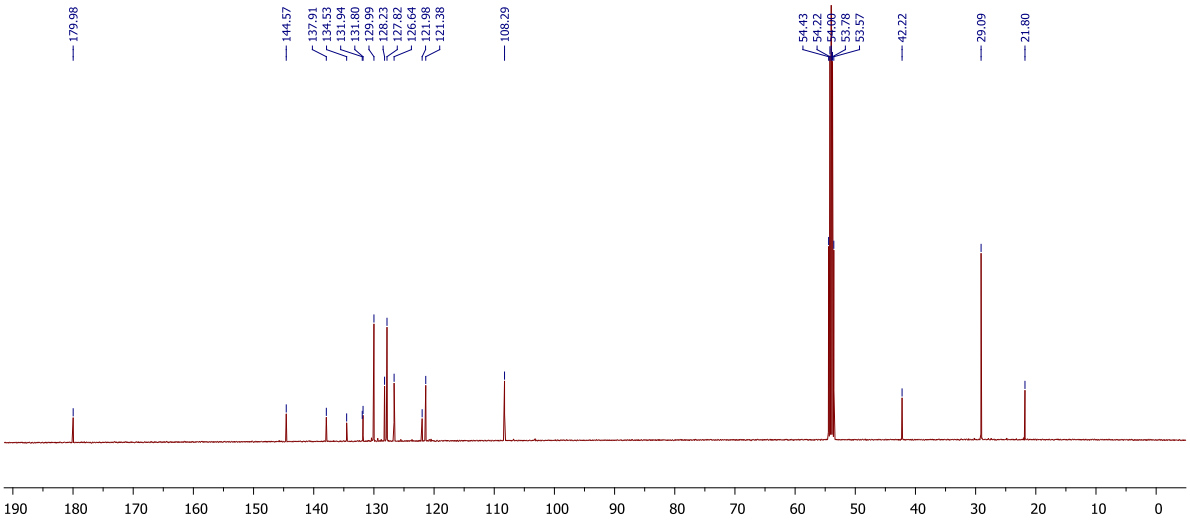
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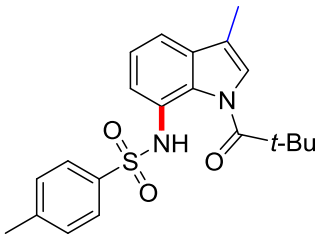
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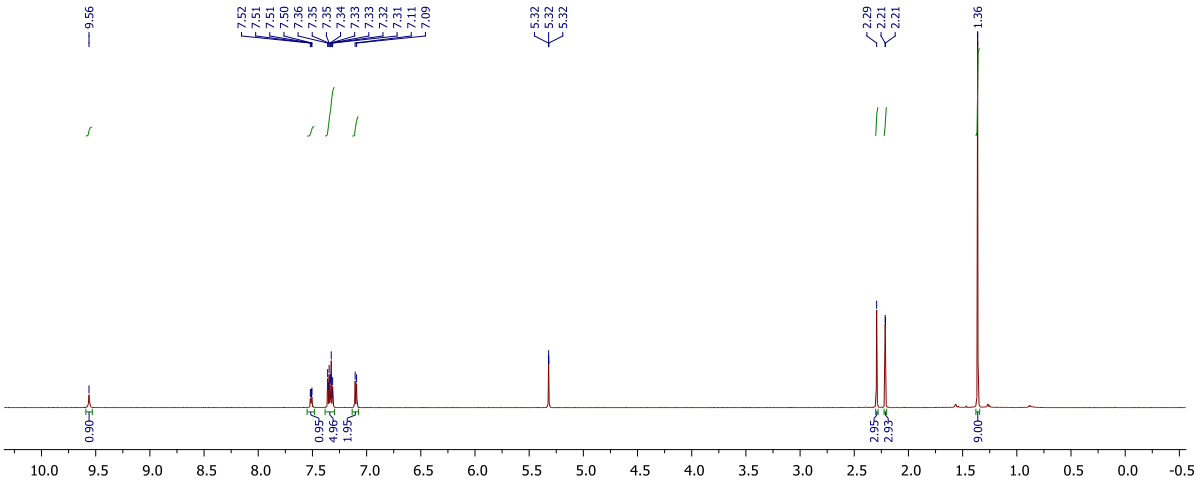
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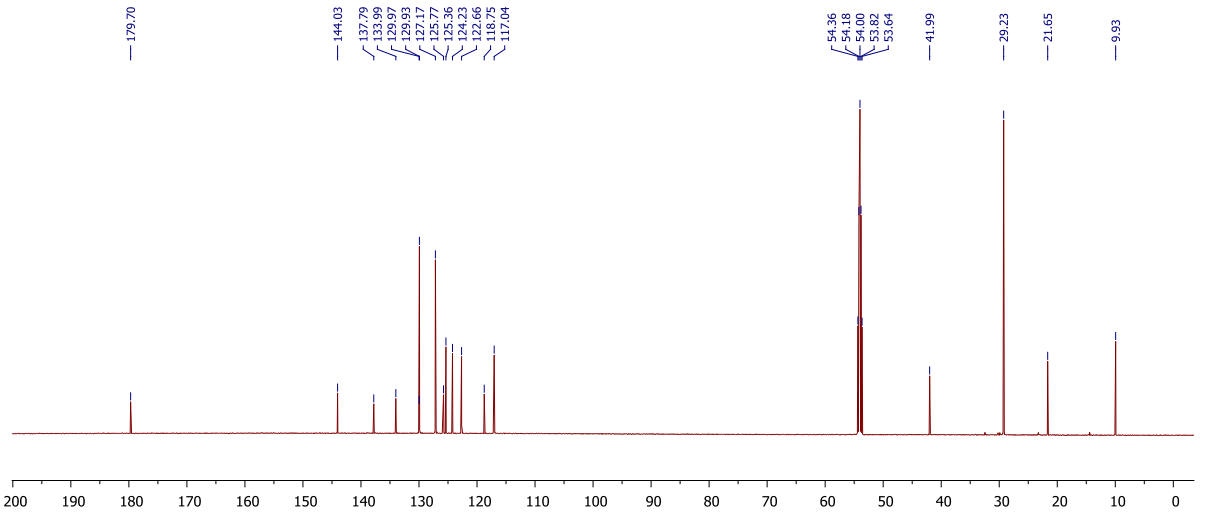
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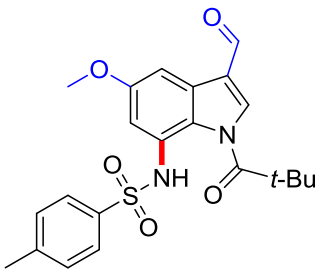
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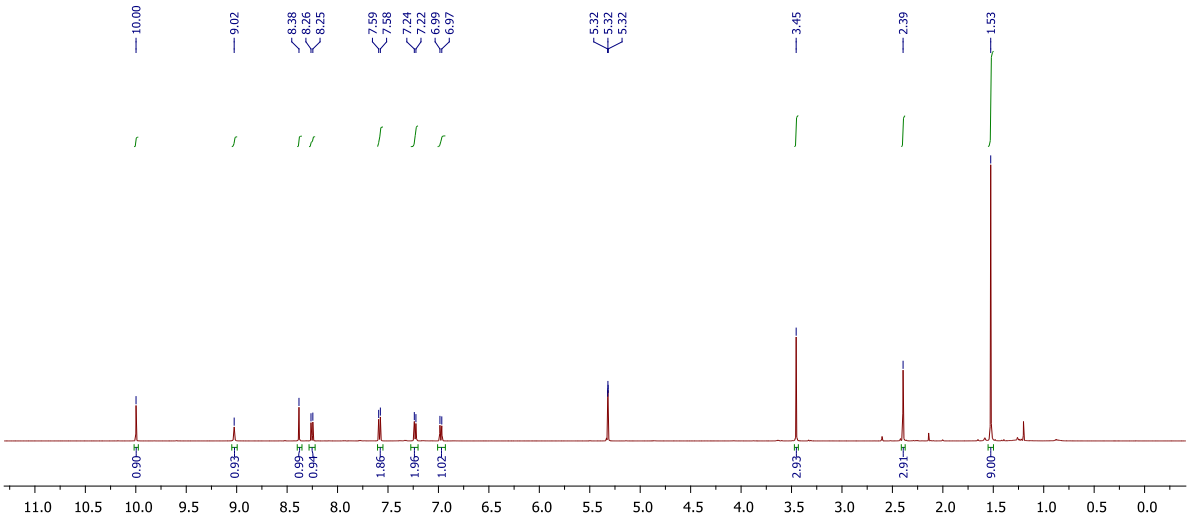
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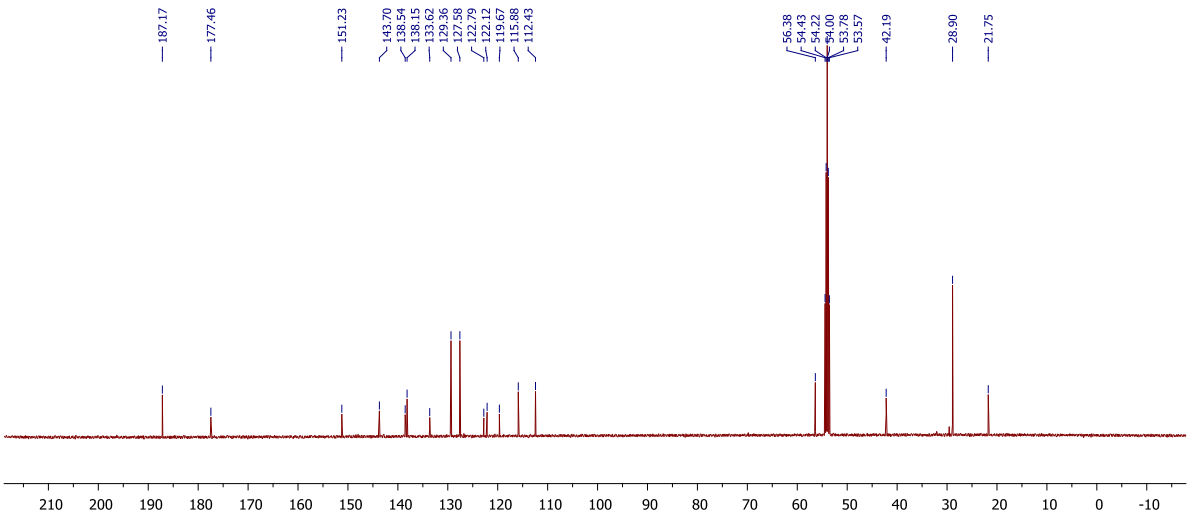
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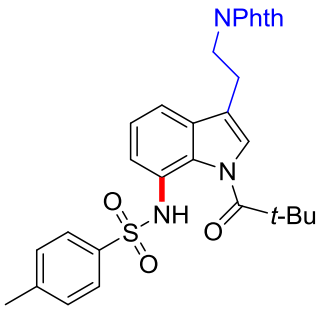
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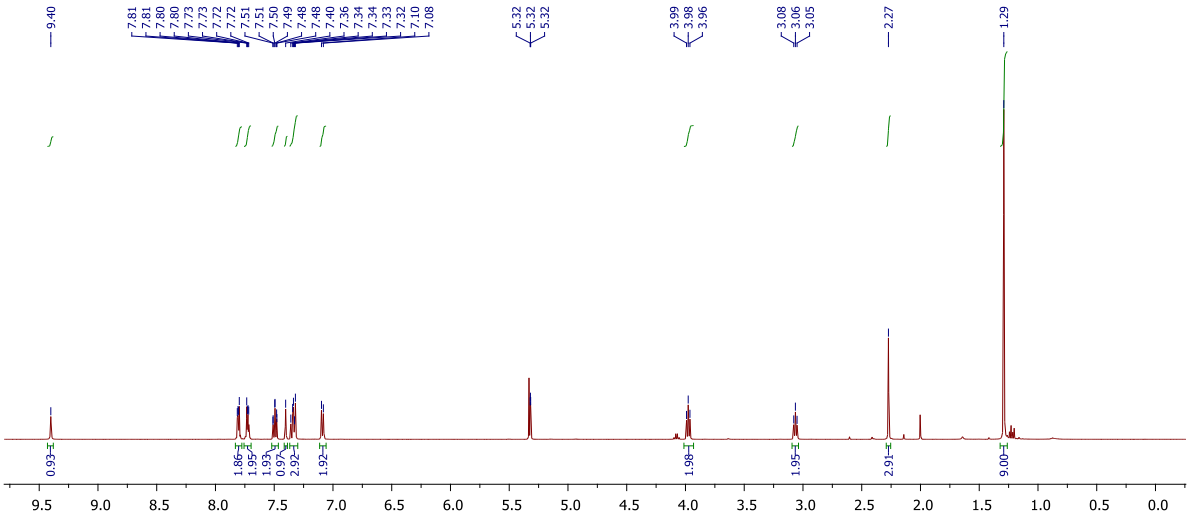
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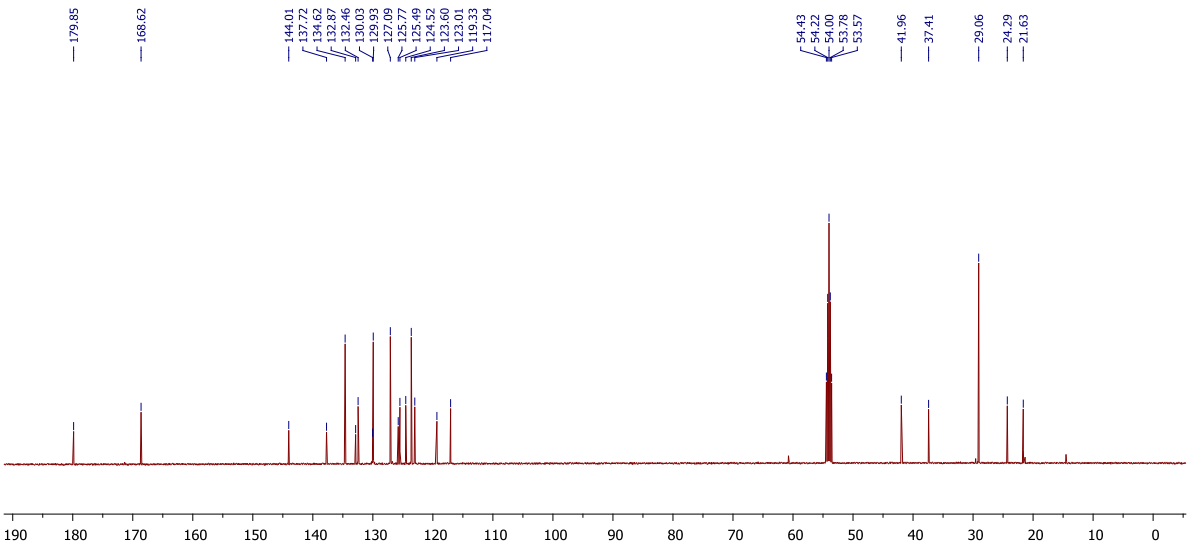
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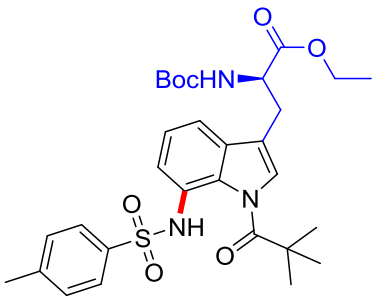
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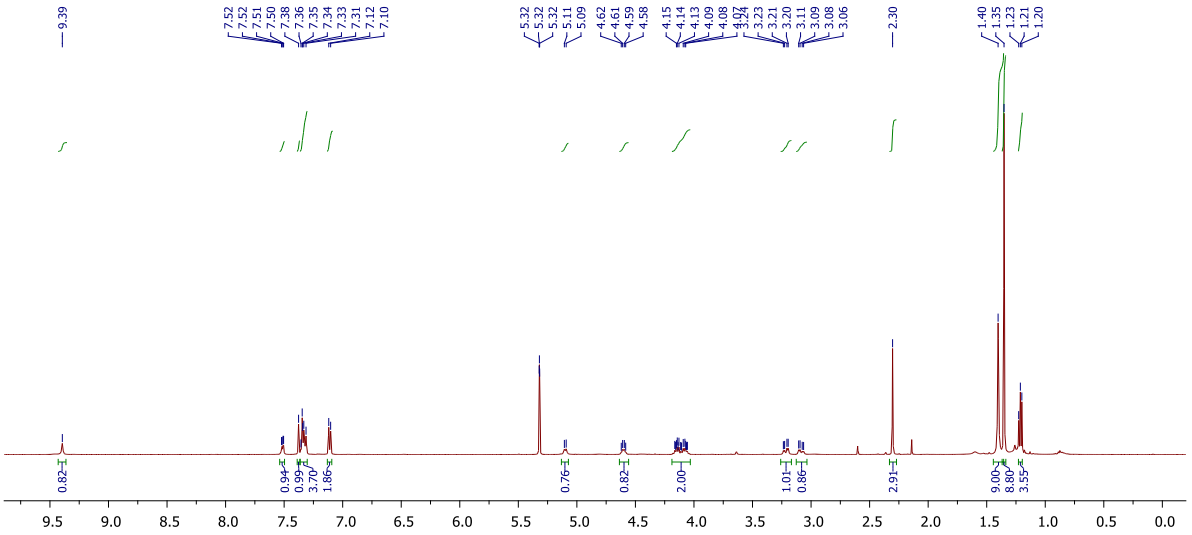
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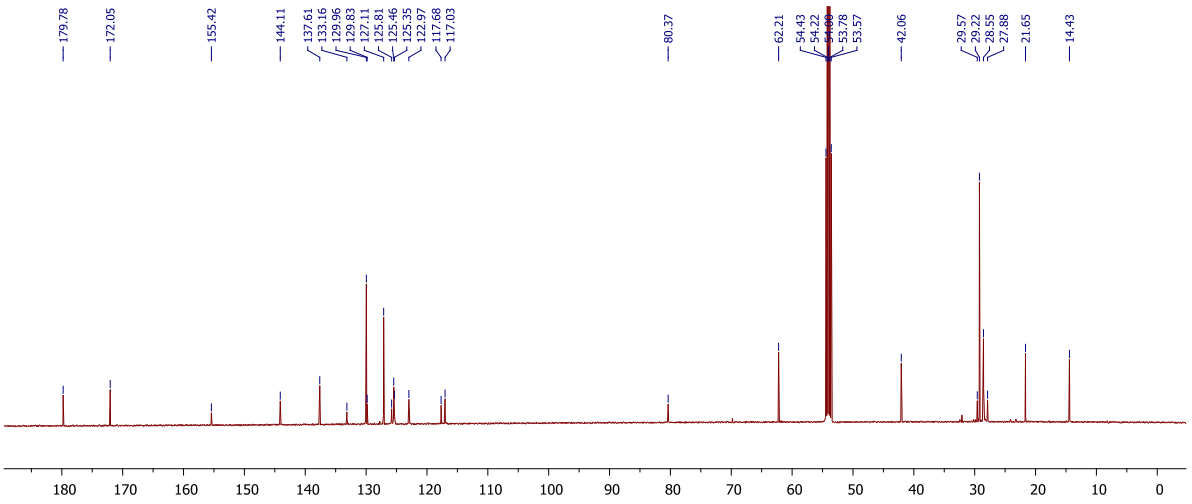
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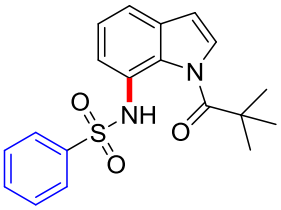
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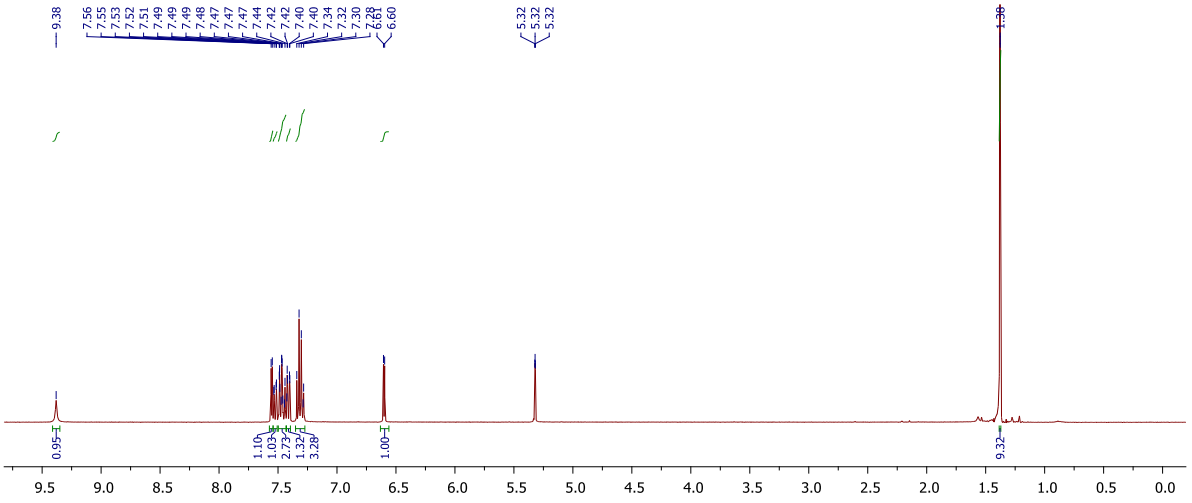
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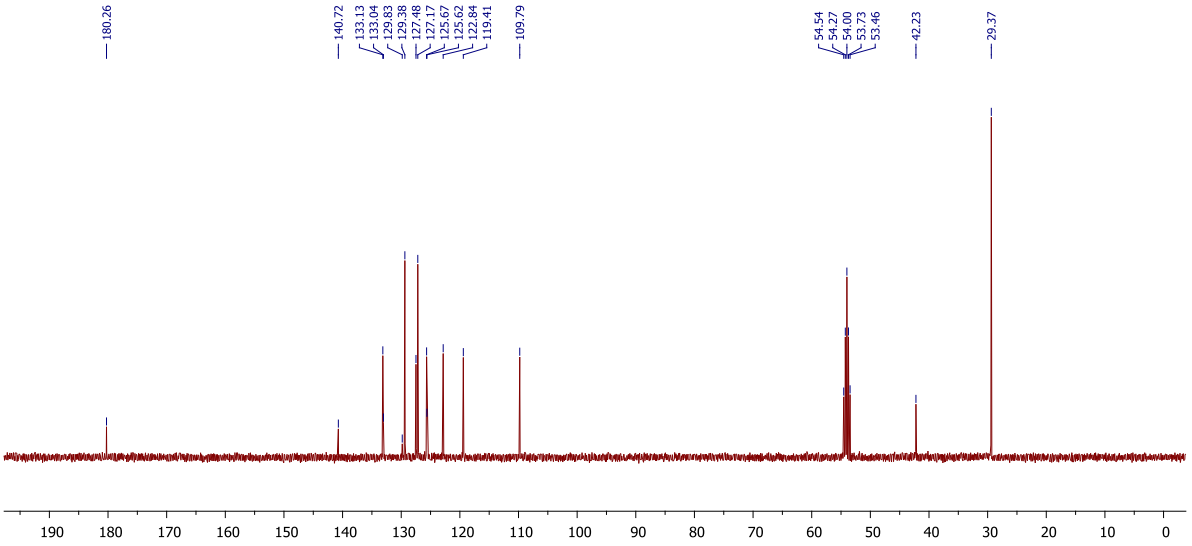
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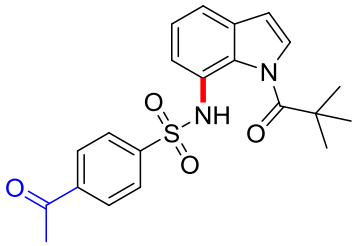

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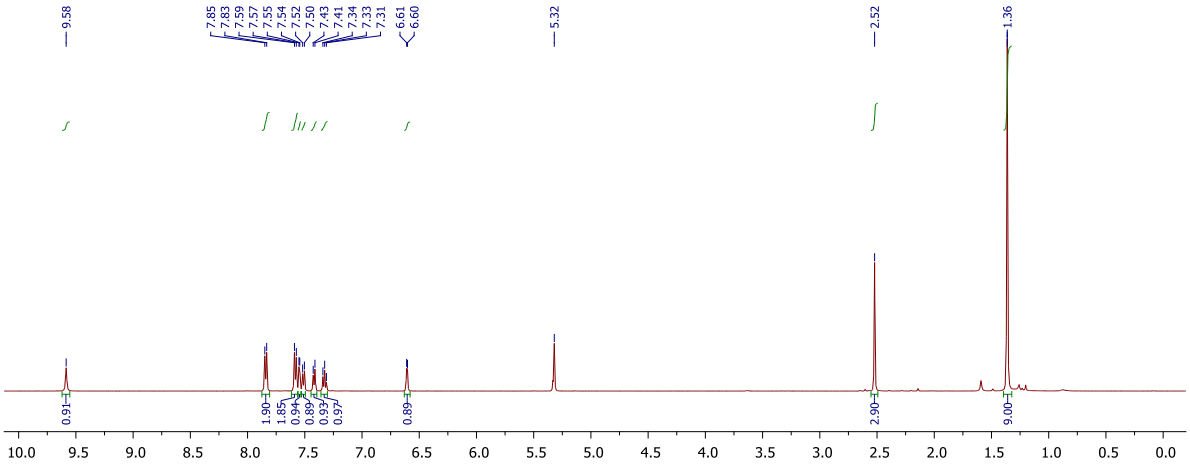
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2.90
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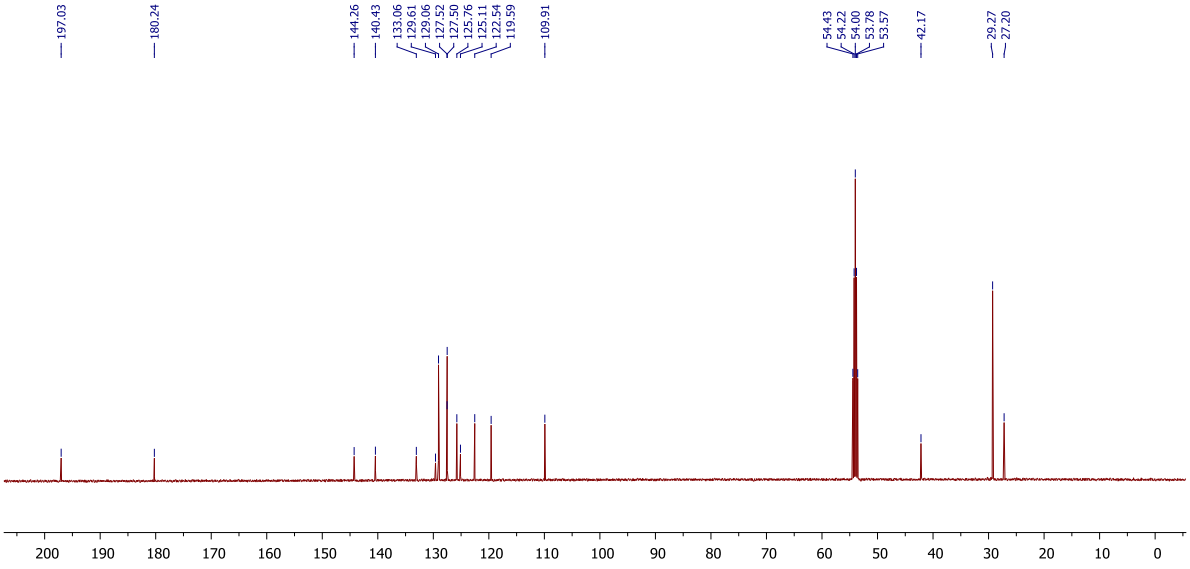
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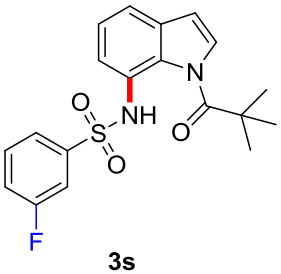
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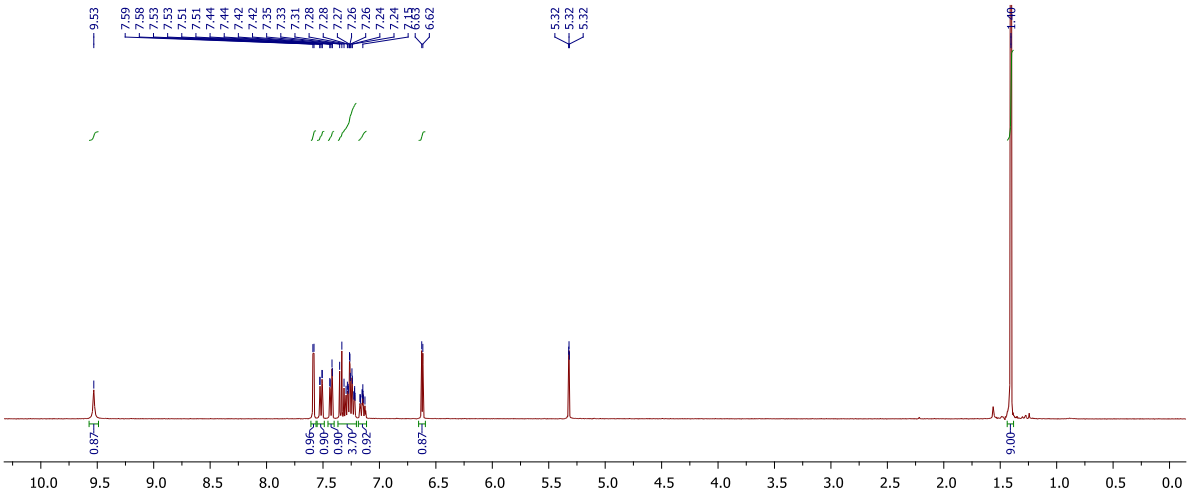
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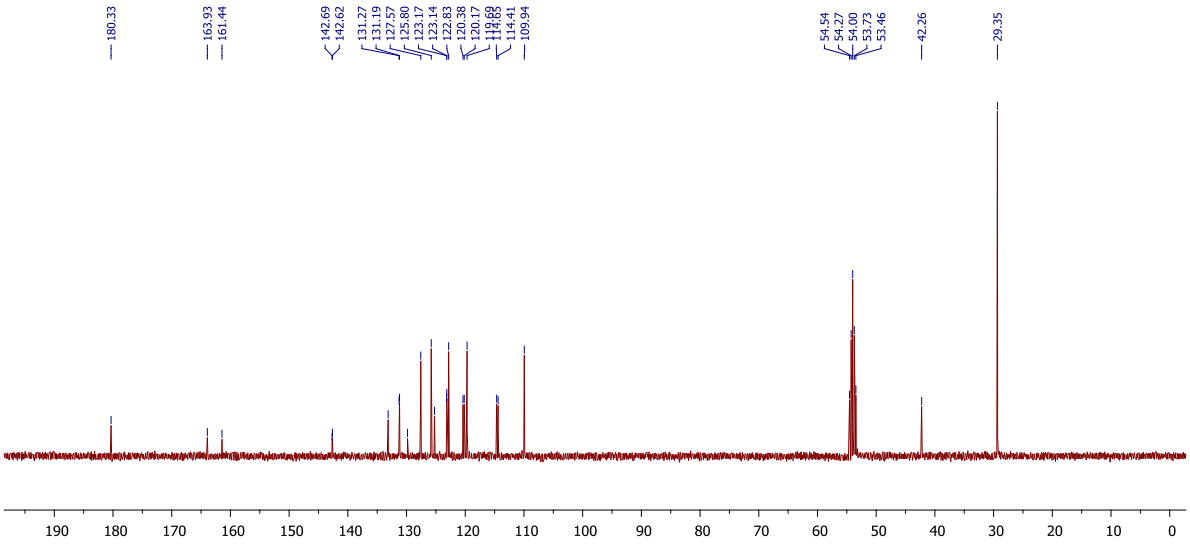
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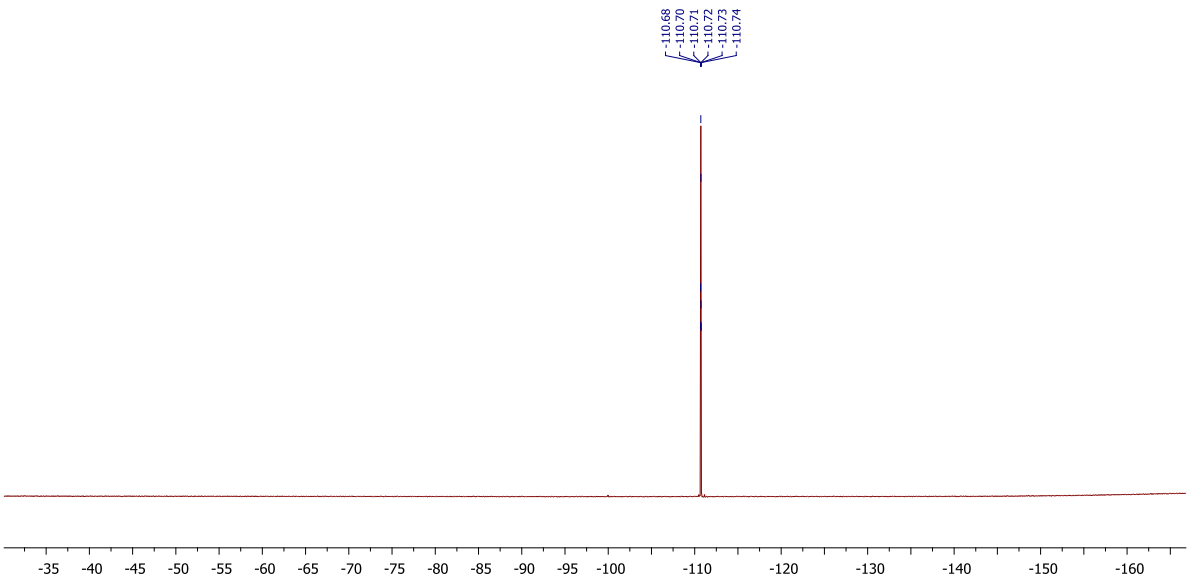
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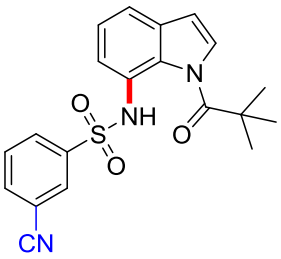
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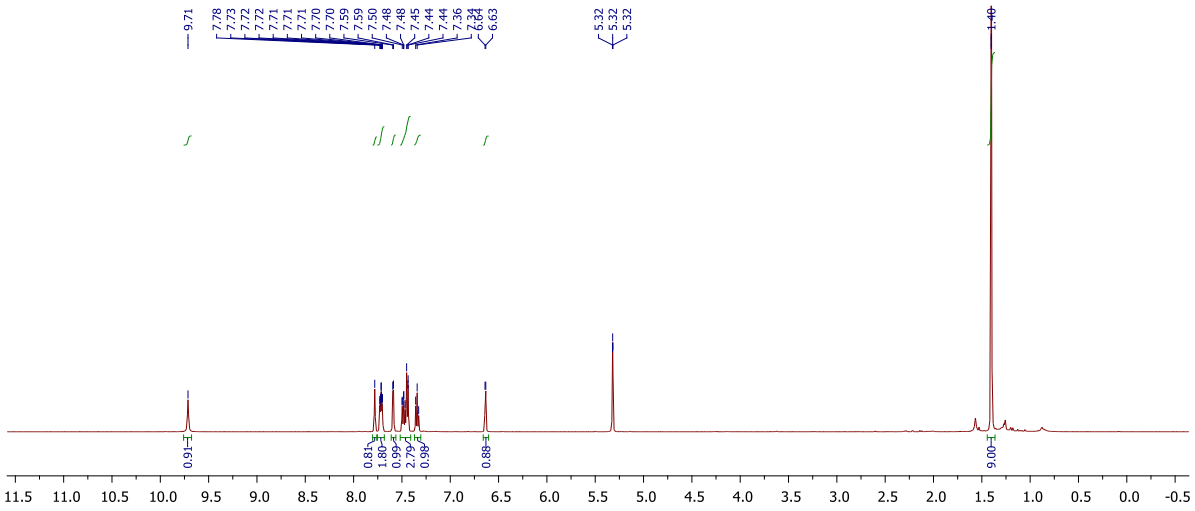
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7.48
7.45
7.44
7.44
7.36
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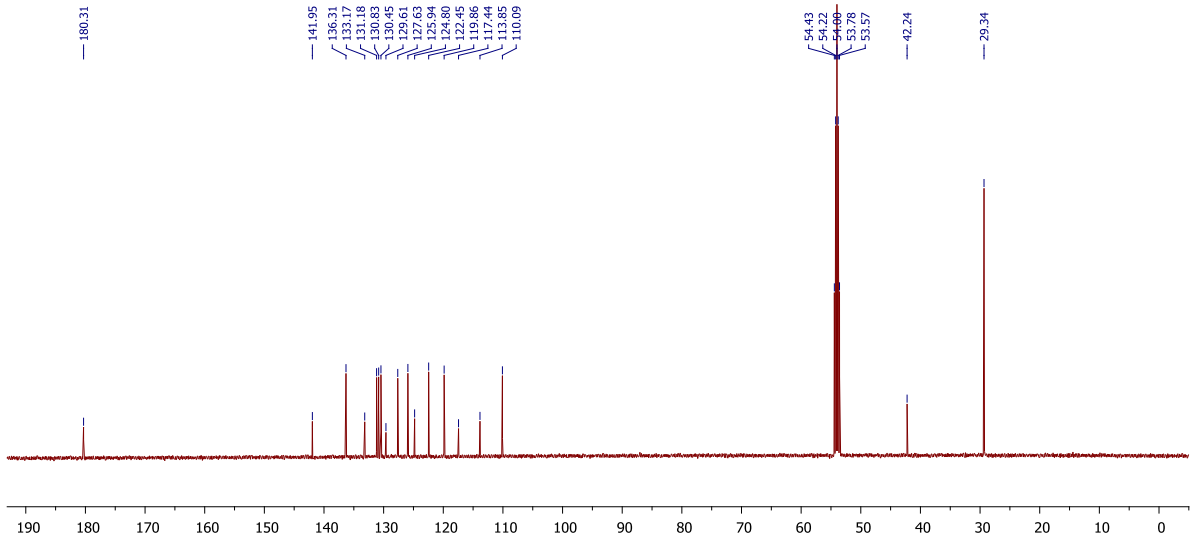
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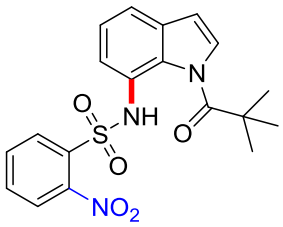

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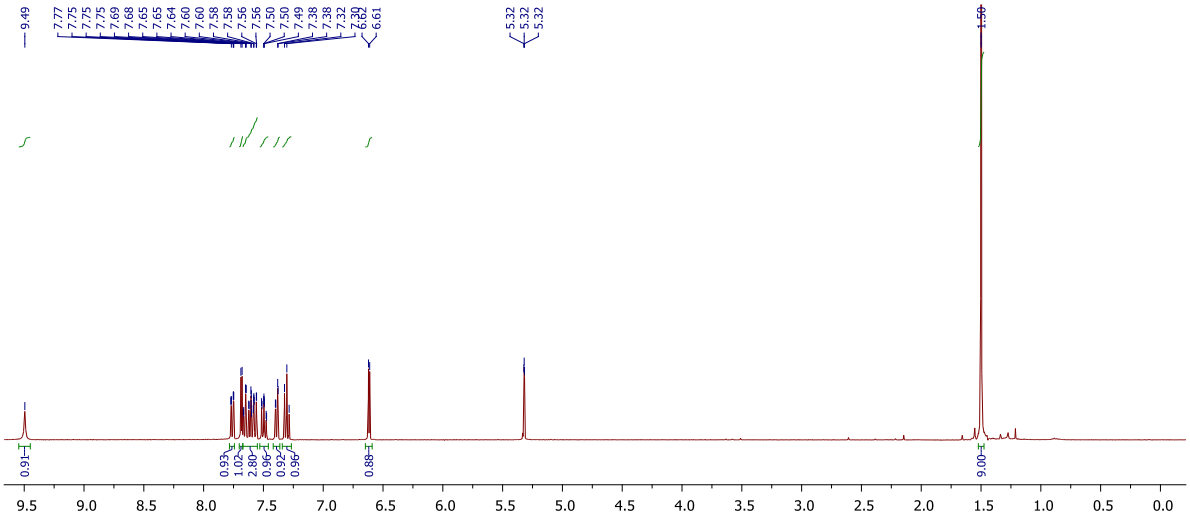

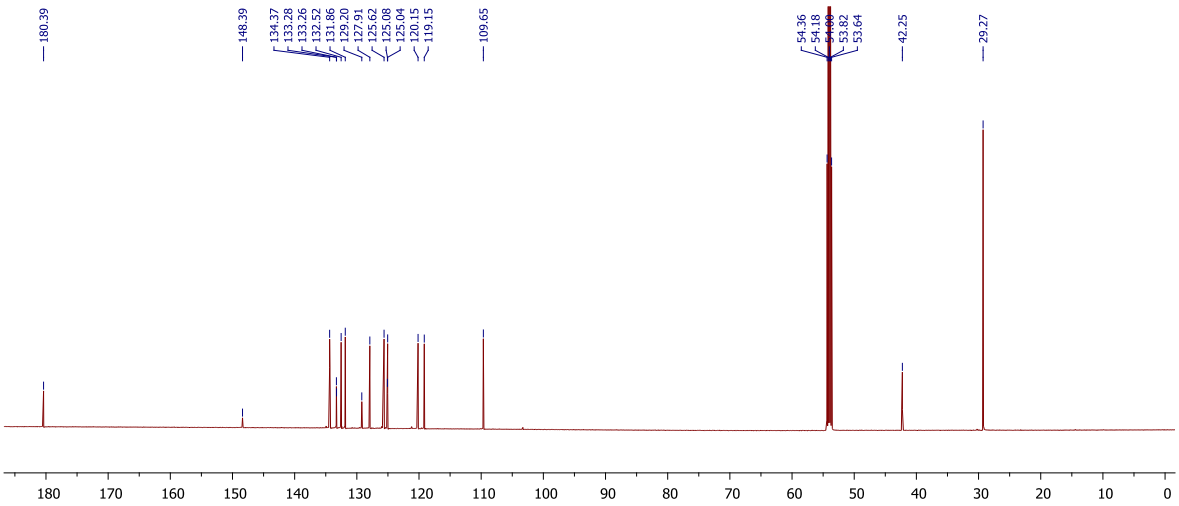

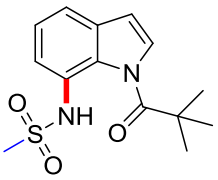
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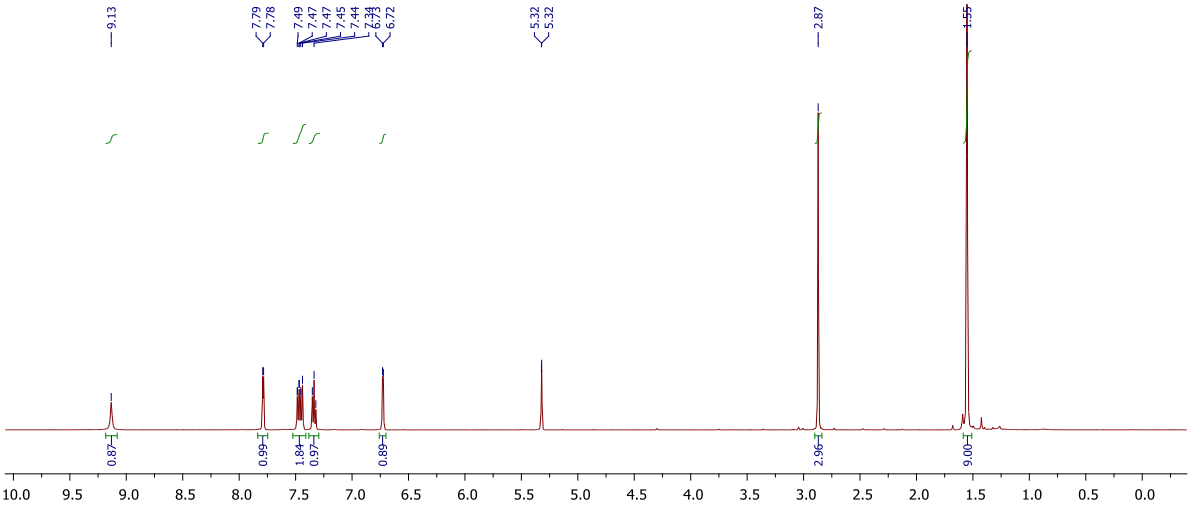
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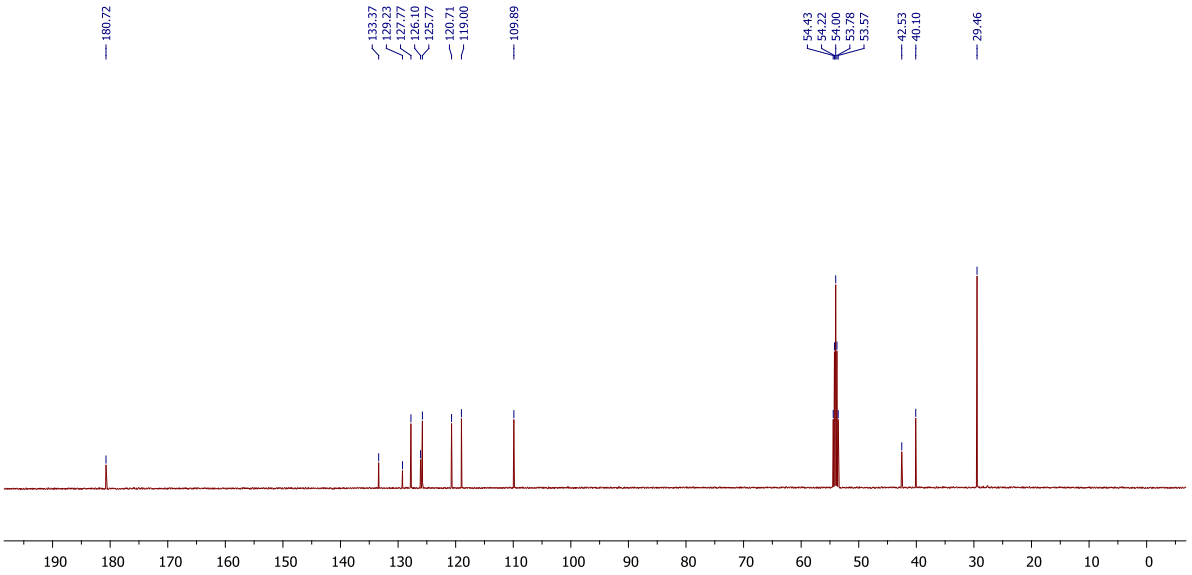
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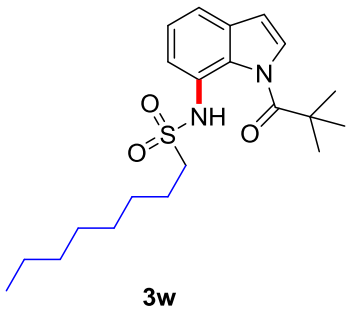

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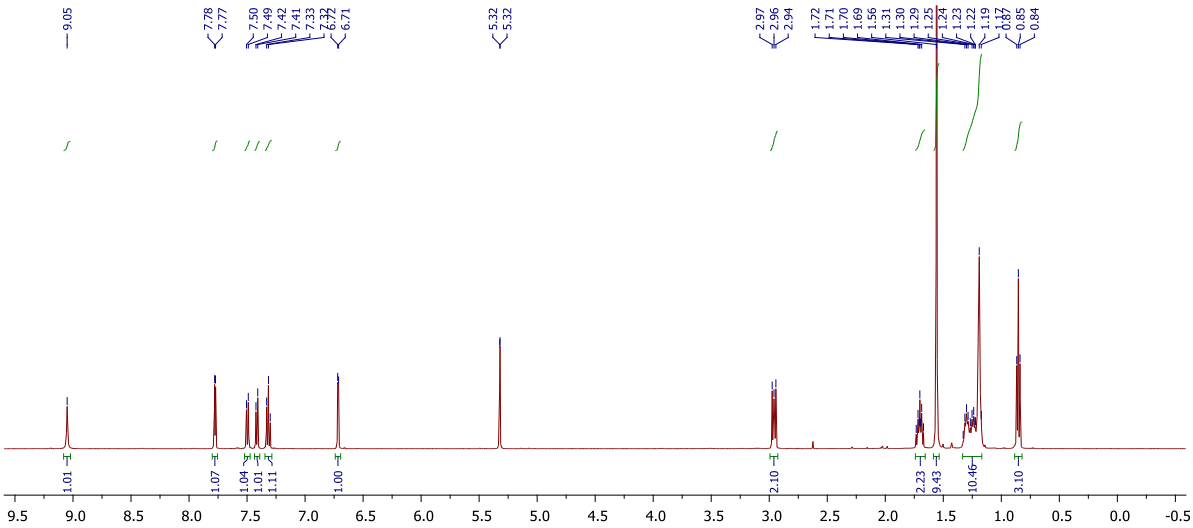
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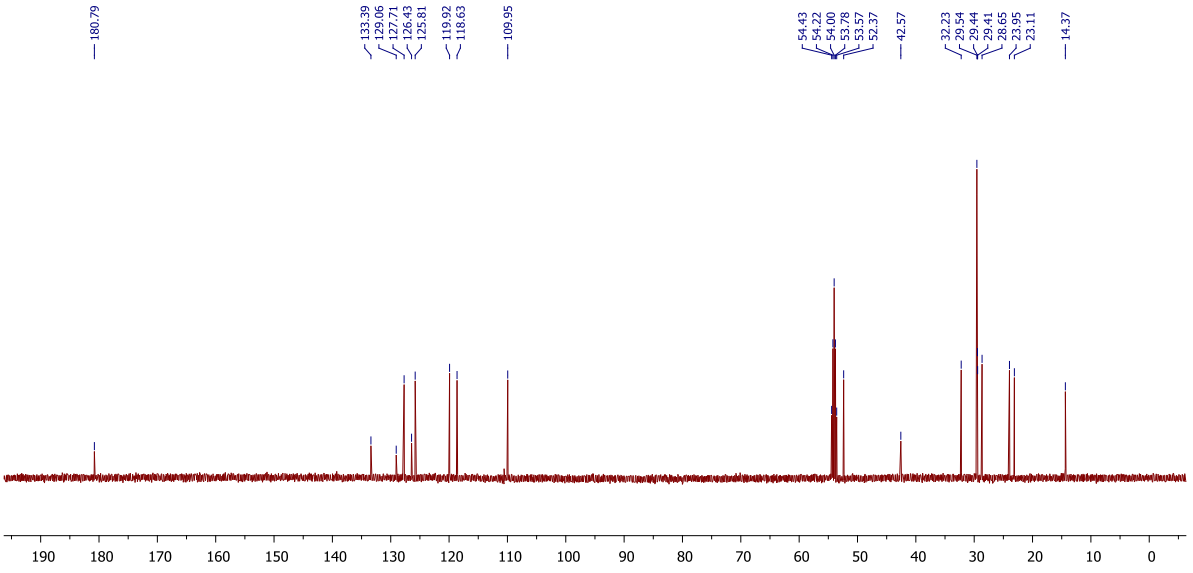
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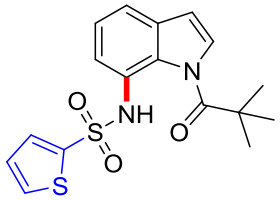

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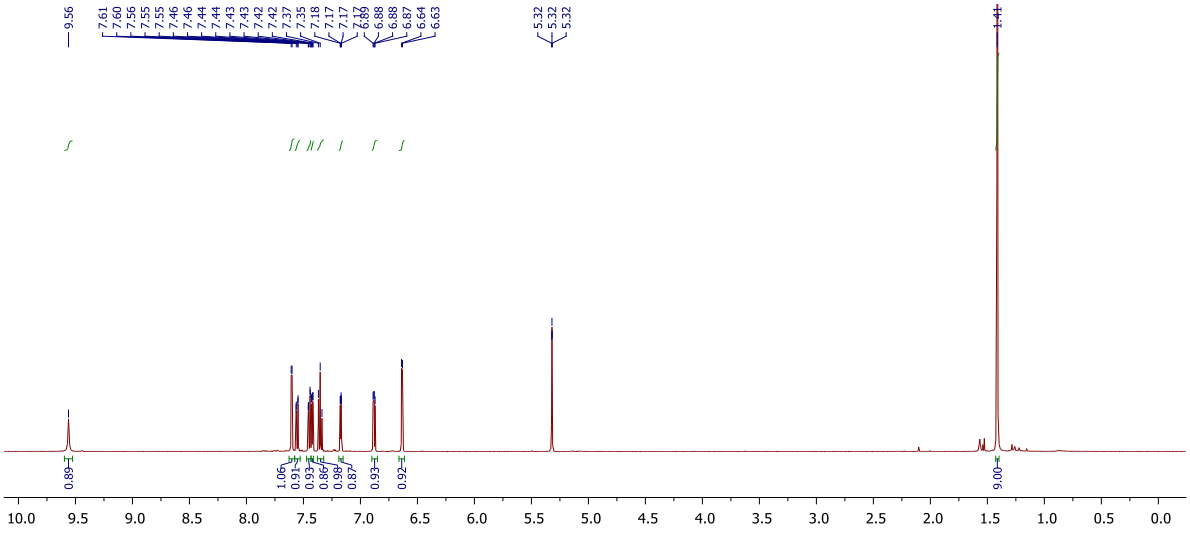
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0.92
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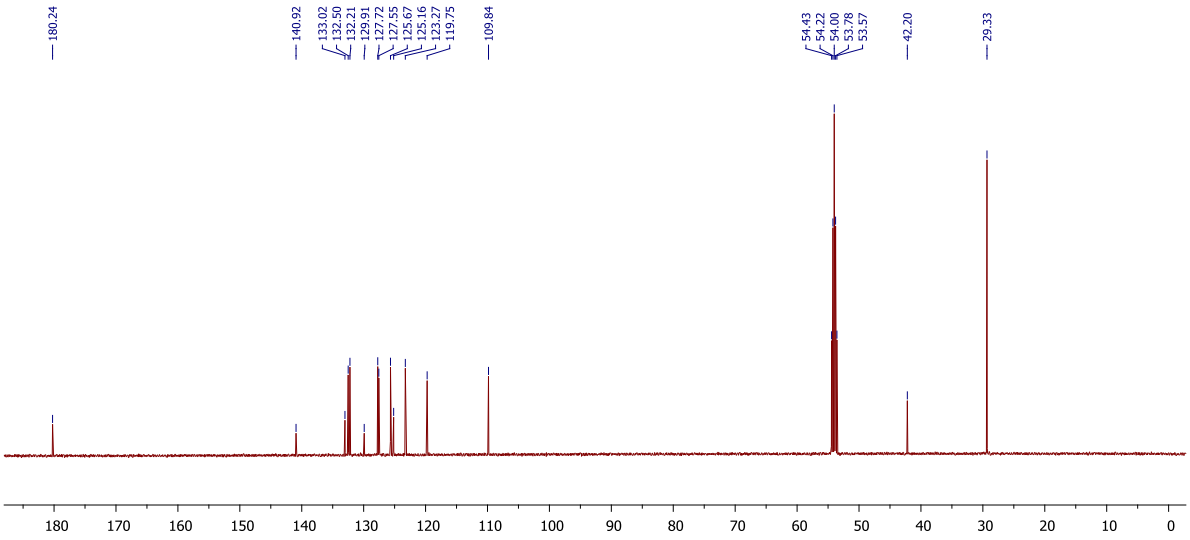
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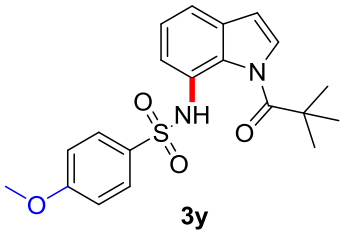
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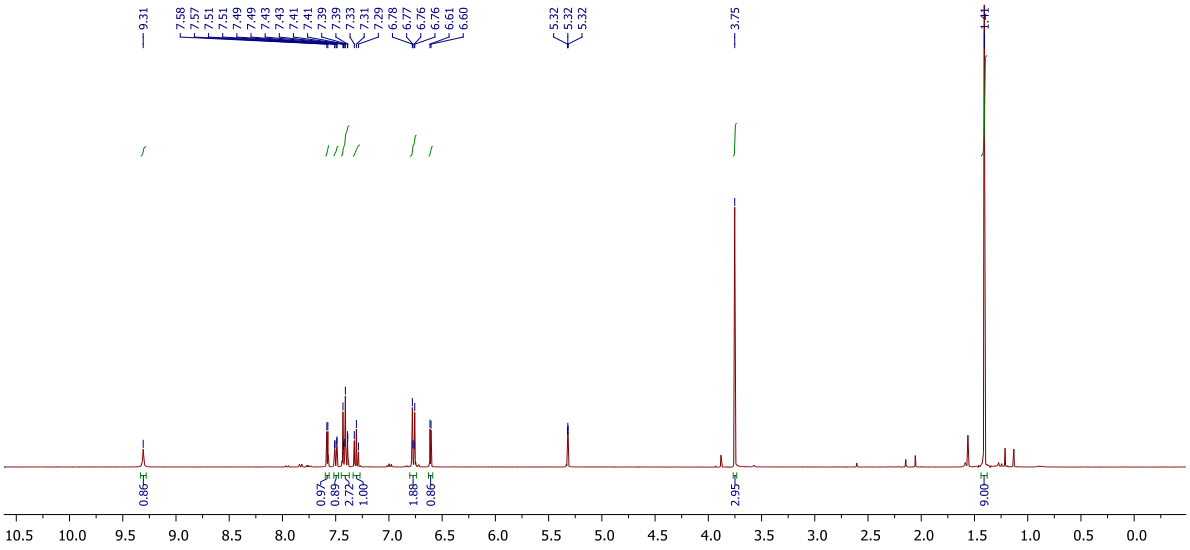
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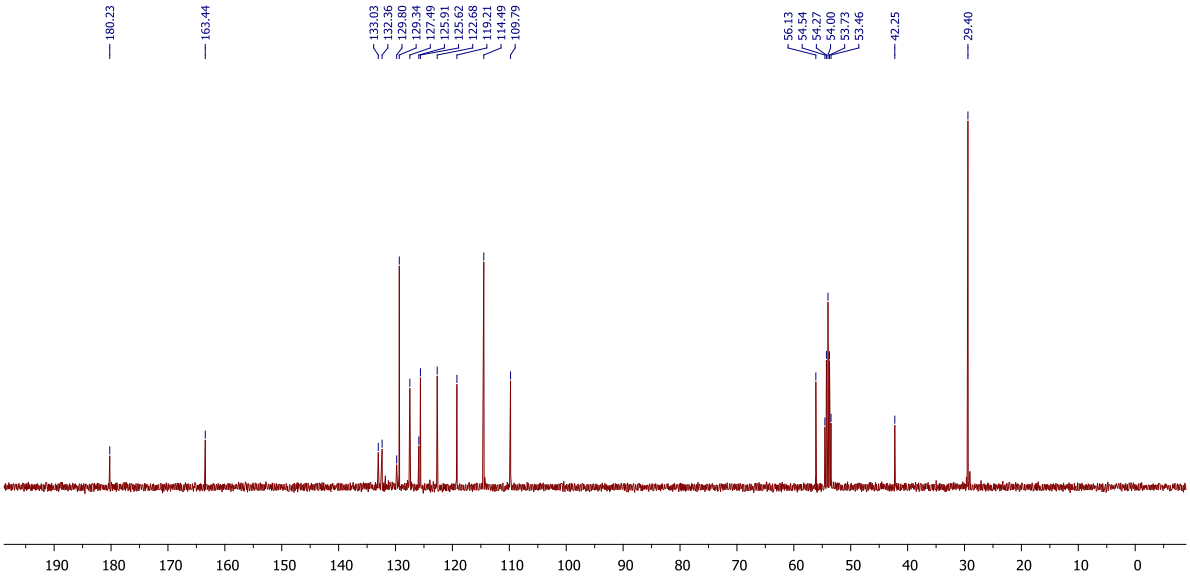
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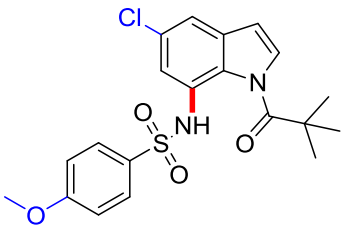
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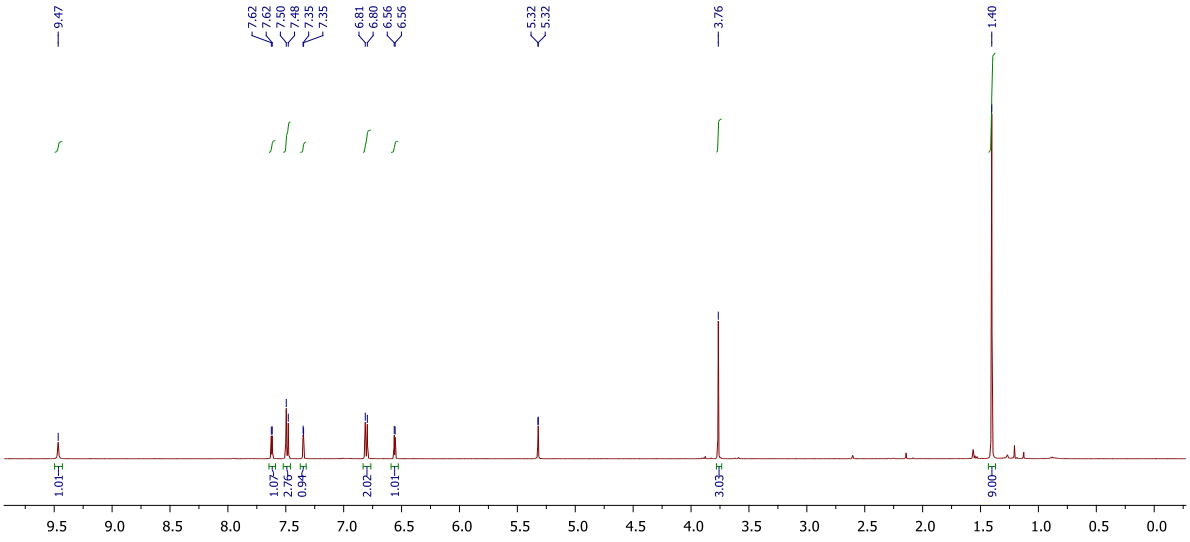
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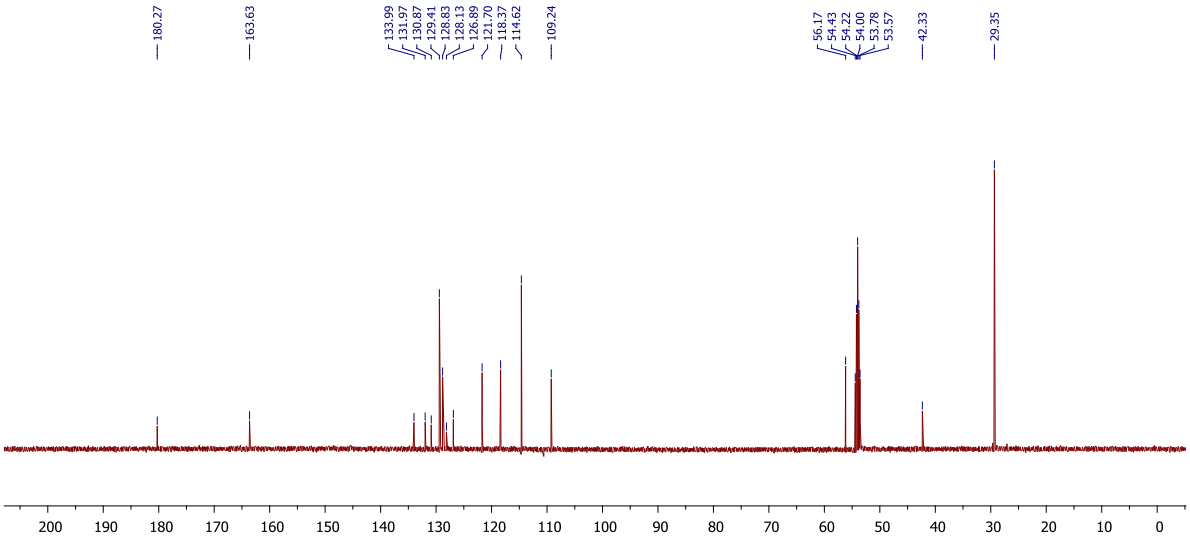
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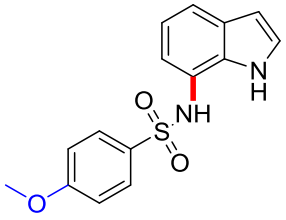
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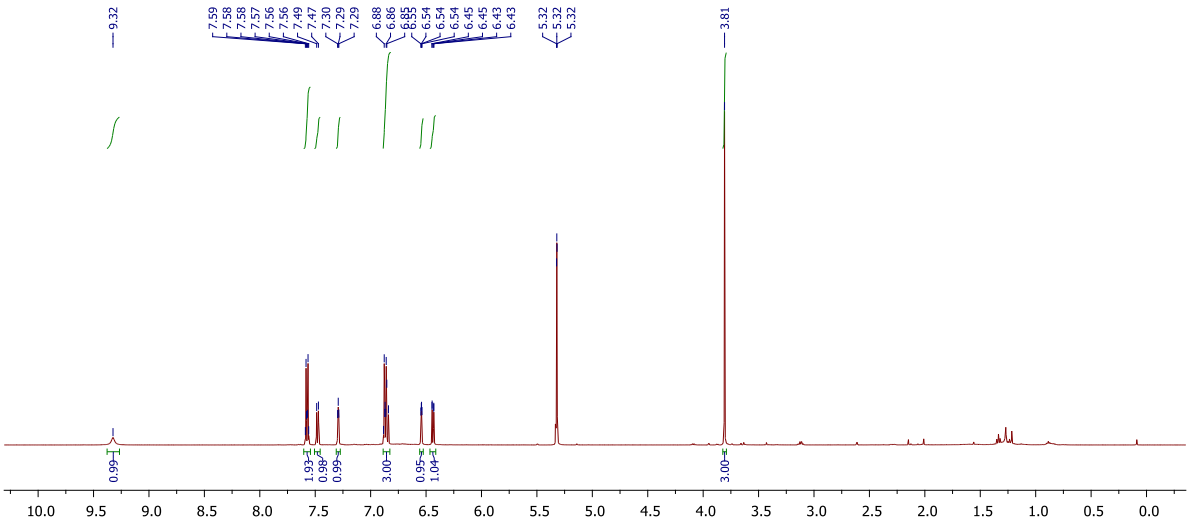
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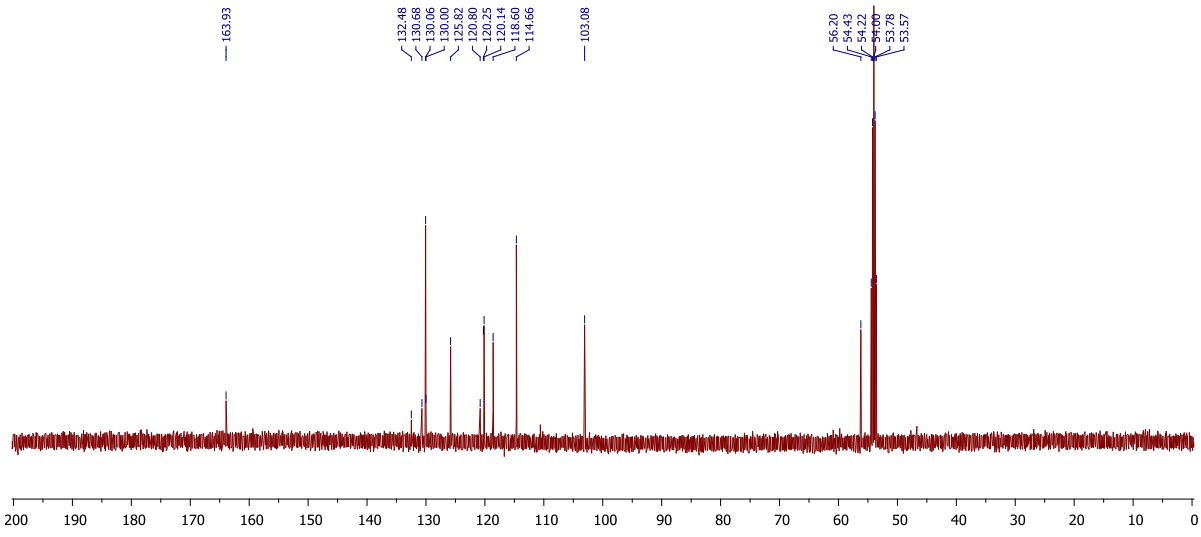
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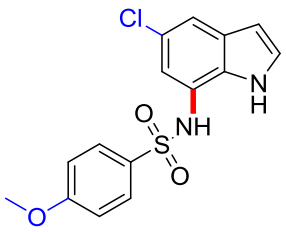
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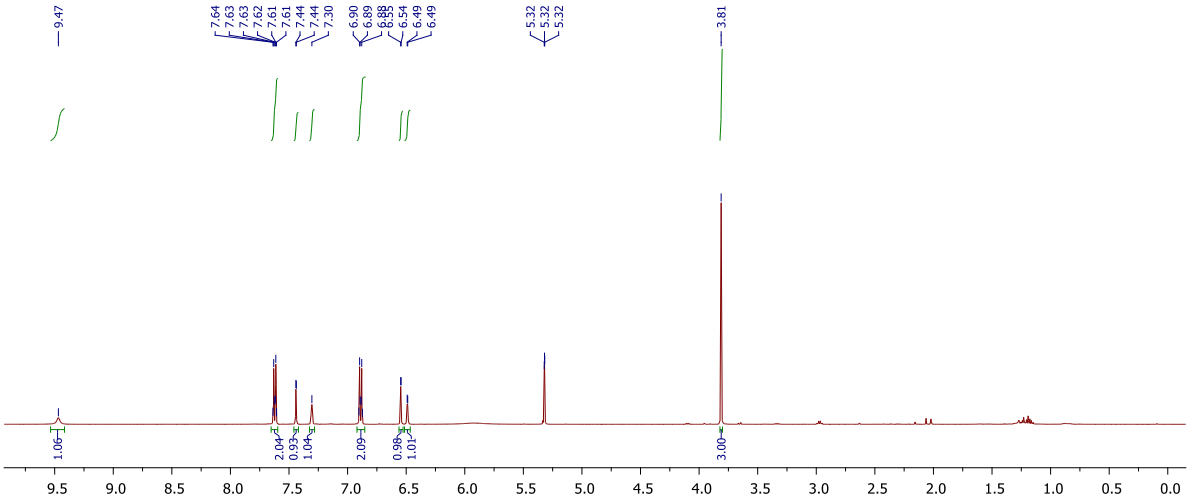
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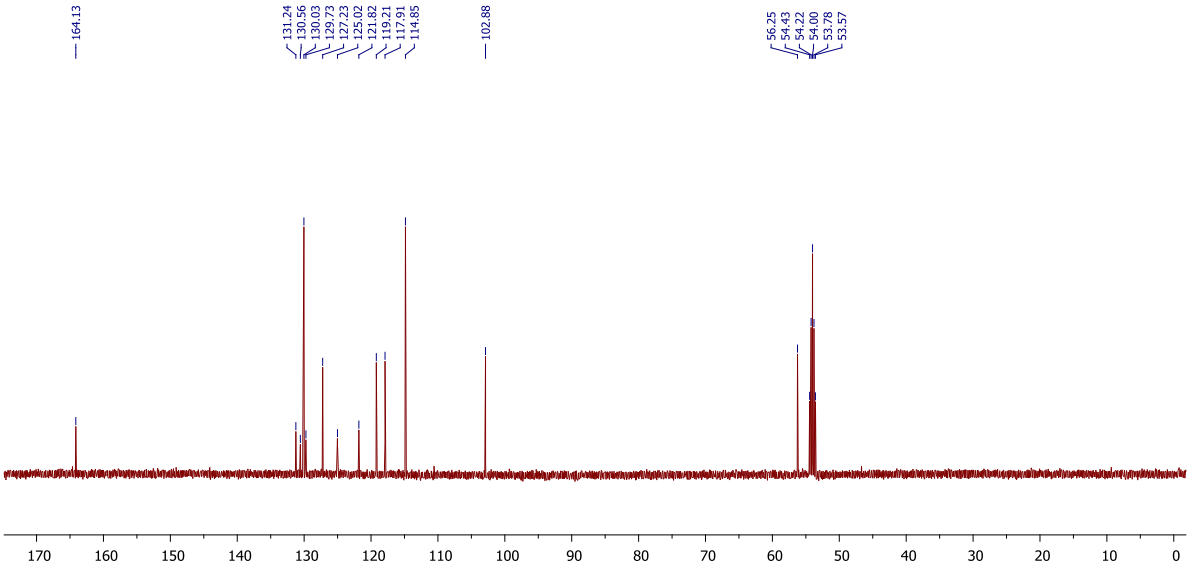
2.0
1.5
1.0
0.5
0.0


164.13
131.24
130.56
130.03
129.73
127.23
125.02
121.82
119.21
117.91
114.85
102.88
56.25
54.43
54.22
54.00
53.78
53.57
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0