Electronic Supporting Information

Nickel(II)-catalyzed asymmetric thio-Claisen rearrangement of α-diazo pyrazoleamides with thioindoles

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1 General information

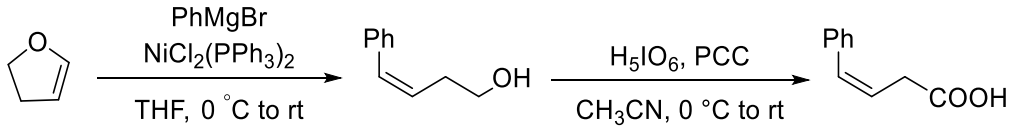
^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiple, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Melting points (Mp) were determined using OptiMelt automated melting point system. Enantiomeric excesses (ee) were determined by chiral HPLC analysis on Daicel chiralcel IA, chiralcel IC, chiralcel ID, chiralcel IE, chiralcel IF and chiralcel Phenomenex Lux 5u Cellulose-2 columns in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]^T_D$ (c: g/100 mL, in solvent). ESI-HRMS spectra were recorded on a commercial apparatus and methanol and water were used to dissolve the sample. THF was distilled from sodium benzophenone ketyl. CH_2Cl_2, $CHCl_3$, $ClCH_2CH_2Cl$, $Cl_2CHCHCl_2$, Cl_2CHCH_2Cl were distilled over CaH_2. Unless noted, other commercial reagents were used without further purification.

2 General procedure for the synthesis of substrates and ligands

2.1 General procedure for the synthesis of *α*-diazo pyrazoleamides

α-Diazo pyrazoleamides were synthesized according to our previous work[1]. Olefinic acid was synthesized according to the literature[2].

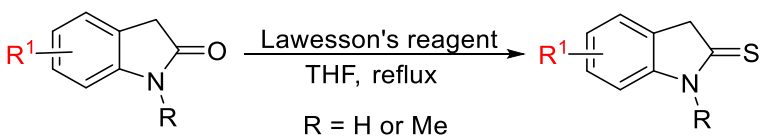
(*Z*)-4-phenylbut-3-enoic acid has been prepared according the following route:



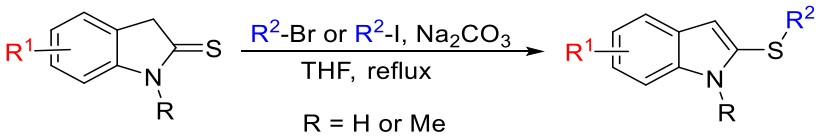
To a solution of $NiCl_2(PPh_3)_2$ (196 mg, 0.3 mmol, 0.02 equiv) in dry THF (15 mL) under nitrogen at 0 °C, 2,3-dihydrofuran (1.14 mL, 15 mmol, 1.0 equiv) was added. Then PhMgBr (24 mL, 24 mmol, 1 M in THF, 1.2 equiv) was added slowly into the mixture. The solution was stirred for 12 h at rt. The reaction was quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduce pressure. The crude residue was purified by flash chromatography on silica gel (EtOAc/PE = 1/5) to yield alcohol as colorless oil.

To a solution of the corresponding alcohol (1.0 equiv) in CH_3CN, periodic acid (2.0 equiv) was added at 0 °C. Finally the pyridinium chlorochromate (0.02 equiv). The reaction mixture was stirred at 35 °C. The reaction was quenched with saturated aqueous NaCl, and extracted with EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduce pressure. The crude residue was purified by flash chromatography on silica gel (EtOAc/PE = 1/1) to yield alcohol as pale yellow oil.

2.2 General procedure for the synthesis of 2-(alkylthio)-1*H*-indole



According to the literature report[3], to a solution of appropriate 2-oxindole (10 mmol, 1.0 equiv) in THF (15 mL), Lawesson's reagent (2.14g, 0.53 mmol, 0.53 equiv) was added. The reaction mixture was stirred under refluxing for 1 day. To the mixture was added saturated aq. $NaHCO_3$ (20 mL) and the aqueous layer was separated and extracted with ethyl acetate (20 mL × 2). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was used in the next step without further purification.

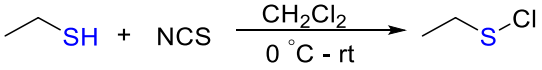


Alkyl bromide and alkyl iodide (15 mmol, 1.5 equiv) was added to a solution of corresponding indole-2-thione(10 mmol, 1.0 equiv) and sodium carbonate (1.59g, 15 mmol, 1.5 equiv) in THF (20 mL) and the mixture was stirred for 1 h under refluxing. The reaction mixture was diluted with water (20 mL), extracted with ethyl acetate (20 mL × 2) and the combined extracts were dried by anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified flash column chromatography (300-400 mesh silica gel) to afford the 2-(alkylthio)-1*H*-indole.

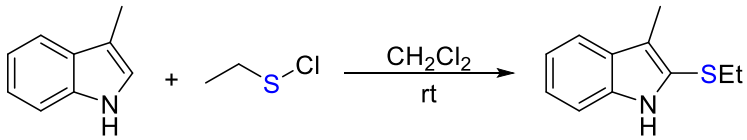
2.3 General procedure for the synthesis of 2-(phenylthio)-1*H*-indole

The 2-(phenylthio)-1*H*-indole (**2h**) was synthesized according to the literature[4].

2.4 General procedure for the synthesis of 2-(ethylthio)-3-methyl-1*H*-indole

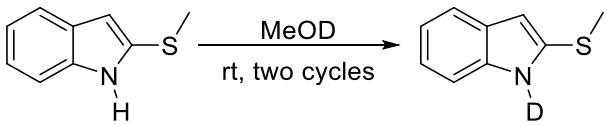


To a solution of NCS (2.40 g, 18 mmol, 1.2 equiv) in dry CH_2Cl_2 (15 mL) under nitrogen, the ethanethiol (1.08 mL, 15 mmol, 1.0 equiv) was added dropwise slowly into the mixture. The reaction was carried out for 30 minutes. The reation solution was filtered with a pad of celite and the filtrate was concentrated in vacuo. The crude product was used in the next step without further purification.



The 2-(ethylthio)-3-methyl-1*H*-indole (**2q**) was synthesized according to the literature report[5], to a solution of 3-methyl-1*H*-indole (1.31g, 10 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added ethyl hypochlorothioite (1.44g, 15 mmol, 1.5 equiv) dropwise slowly. After stirring for an additional 3h at room temperature, the reaction was quenched with saturated aq. $NaHCO_3$ (20 mL). After extraction of the aqueous phase with EtOAc (20 mL × 3), the combined organic extracts were washed with brine (70 mL × 1), dried over anhydrous Na_2SO_4, and concentrated. The crude material was purified by flash chromatography (300-400 mesh silica gel) to afford the 2-(ethylthio)-3-methyl-1*H*-indole.

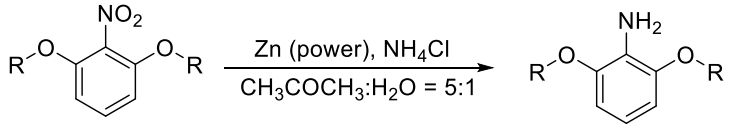
2.5 General procedure for the synthesis of deuterated substrate



The substrate **2a** (1.63g, 1.0 mmol) was dissolved in MeOD (1.00 mL) and the mixture was stirred at room temperature for 1 hour. The alcohol was removed under vacuum, and the residue was dissolved in another 1 mL MeOD. After another 1 hour at room temperature, the alcohol was evaporated and 1-deuteriothioindole was obtained, and characterized in $CHCl_3$-d_6 for ^{1}H NMR analysis (91% purity).

2.6 General procedure for the synthesis of ligands

The chiral *N,N'*-dioxides were synthesized from corresponding anilines according to the previous work[6]. 2,6-Dialkoxyanilines and 2,6-diphenoxyaniline were synthesized according to the procedure below.

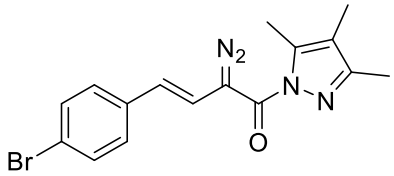


R = Me, Et, *i*Pr, *i*Bu, *i*pentyl, Bn, Ph

To a suspension of 1,3-dialkoxy-2-nitrobenzene[7] or ((2-nitro-1,3-phenylene)bis(oxy))dibenzene[8] (40.0 mmol, 1.0 equiv.) and NH_4Cl (27.5 g, 420.0 mmol, 10.5 equiv) in CH_3COCH_3 and H_2O (5:1, v/v, 600 mL) was added zinc power (32.1 g, 15.0 equiv) slowly at room temperature. After the substrate was consumed (detected by TLC), the reaction mixture was filtered through a pad of celite and CH_3COCH_3 was removed in vacuum. Subsequently, H_2O (150 mL) was added and the mixture was extracted with CH_2Cl_2 (80 mL × 3). The organic phase was dried over anhydrous Na_2SO_4, purified on silica gel to afford the crude product (Pet/EtOAc = 8/1), which was directly used in the next step.

3 Characterization of *α*-diazo pyrazoleamides

(*E*)-4-(4-bromophenyl)-2-diazo-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-3-en-1-one (1j)



Red solid; M.p. 117-120 °C.

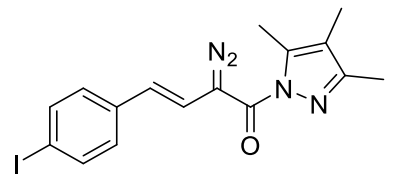
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 2H), 7.26 – 7.24 (m, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H), 2.17 (s, 3H), 1.92 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.6, 150.9, 139.5, 135.8, 131.7, 127.4, 120.8, 120.6, 116.9, 114.5, 65.9, 12.2, 12.2, 7.6.

ESI-HRMS: calcd for $C_{16}H_{16}N_4O^{79}Br^+$ ($[M + H]^+$) = 359.0502, found 359.0503. $C_{16}H_{16}N_4O^{81}Br^+$ ($[M + H]^+$) = 361.0482, found 361.0484.

IR (neat): 2923, 2008, 1664, 1489, 1431, 1384, 1358, 1121, 949, 742 cm^{-1}.

(*E*)-2-diazo-4-(4-iodophenyl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-3-en-1-one (1k)



Red solid; M.p. 130-133 °C.

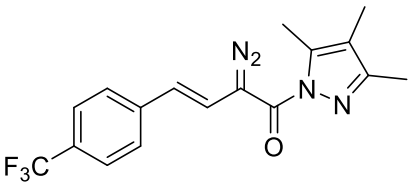
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 2H), 7.26 – 7.24 (m, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H), 2.17 (s, 3H), 1.92 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.6, 150.9, 139.5, 137.7, 136.4, 127.7, 120.9, 116.9, 114.7, 91.9, 66.0, 12.2, 12.2, 7.6.

ESI-HRMS: calcd for $C_{16}H_{16}N_4OI^+$ ($[M + H]^+$) = 407.0363, found 407.0362.

IR (neat): 2922, 2086, 1663, 1487, 1430, 1384, 1358, 1121, 1003, 739 cm^{-1}.

(*E*)-2-diazo-4-(4-(trifluoromethyl)phenyl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-3-en-1-one (1l)



Red solid; M.p. 109-111 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.55 (m, 2H), 7.48 – 7.46 (m, 2H), 7.08 (d, *J* = 16.0 Hz, 1H), 6.07 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H), 2.18 (s, 3H), 1.92 (s, 3H).

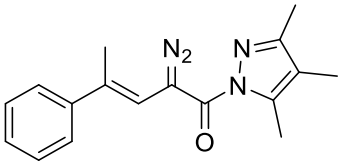
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.4, 151.1, 140.3 (d, *J* = 32.3 Hz), 139.5, 128.6 (d, *J* = 32.3 Hz), 126.0, 125.6 (q, *J* = 3.9 Hz), 120.3, 117.1, 116.8, 66.2, 12.2, 12.2, 7.6; the resonance resulting from diazo group makes the CF_3 carbon undetectable.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.43.

ESI-HRMS: calcd for $C_{17}H_{16}N_4OF_3^+$ ($[M + H]^+$) = 349.1271, found 349.1276.

IR (neat): 2088, 1664, 1611, 1423, 1385, 1322, 1163, 1116, 1066, 946, 852, 732cm^{-1}.

(*E*)-2-diazo-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)pent-3-en-1-one (1s)



Orange solid; M.p. 63-67 °C.

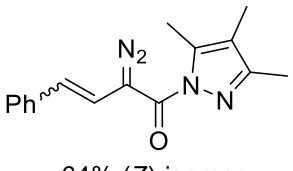
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.45 (m, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.25 (m, 1H), 6.34 (s, 1H), 2.46 (s, 3H), 2.18 (s, 3H), 2.12 (s, 3H), 1.91 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 162.7, 150.7, 142.5, 139.4, 135.7, 128.3, 127.3, 125.9, 116.5, 111.8, 64.5, 17.3, 12.2, 12.1, 7.6.

ESI-HRMS: calcd for $C_{17}H_{19}N_4O^+$ ($[M + H]^+$) = 295.1553, found 295.1552.

IR (neat): 1695, 1630, 1378, 1351, 1146, 735, 702, 529 cm^{-1}.

(*Z*/*E*)-2-diazo-4-phenyl-1-(3,4,5-trimethyl-1H-pyrazol-1-yl)but-3-en-1-one (1a)



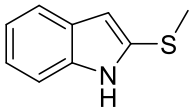
64% (*Z*)-isomer

Orange solid; M.p. 105-108 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.28 (m, 3H), 7.24 – 7.18 (m, 2H), 6.93 (d, *J* = 16.0, 0.36 H), 6.60 (d, *J* = 11.4, 0.64 H), 6.31 (d, *J* = 11.4, 0.64 H), 6.06 (d, *J* = 16.0, 0.36 H), 2.46 (s, 3H), 2.17 (s, 1.08 H), 2.13 (s, 1.92 H), 1.91 – 1.89 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 161.9, 160.8, 150.7, 139.4, 136.8, 135.1, 128.6, 128.5, 127.9, 126.95, 126.93, 125.9, 125.0, 122.2, 116.8, 116.6, 113.9, 113.4, 65.8, 65.3, 12.15, 12.14, 7.5.
IR (neat): 2081, 1659, 1381, 1351, 1263, 748 cm^{-1}.

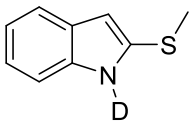
4 Characterization of 2-(alkylthio)-1*H*-indole

2-(methylthio)-1*H*-indole (2a)



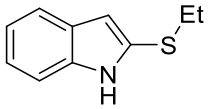
White solid; M.p. 54-56 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.54 – 7.52 (m, 1H), 7.28 – 7.23 (m, 1H), 7.18 – 7.14 (m, 1H), 7.11 – 7.07 (m, 1H), 6.54 (dd, *J* = 2.0, 0.8 Hz, 1H), 2.49 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.9, 131.3, 128.7, 122.2, 120.1, 119.8, 110.4, 105.8, 19.26.
ESI-HRMS: calcd for $C_9H_{10}NS^+$ ($[M+H]^+$) = 164.0528, found 164.0527.
IR (neat): 3368, 2361, 2335, 1481, 1441, 1314, 747, 633, 465, 432 cm^{-1}.

d-**2a**



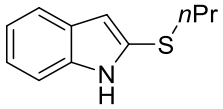
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 0.09H), δ 7.54 – 7.52 (m, 1H), 7.28 – 7.24 (m, 1H), 7.18 – 7.14 (m, 1H), 7.11 – 7.07 (m, 1H), 6.55 (s, 1H), 2.49 (s, 3H).

2-(ethylthio)-1*H*-indole (2b)



Pale yellow solid; M.p. 39-41 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.47 – 7.45 (m, 1H), 7.15 – 7.12 (m, 1H), 7.09 – 7.05 (m, 1H), 7.02 – 6.98 (m, 1H), 6.53 (dd, *J* = 2.4, 0.8 Hz, 1H), 2.69 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.9, 128.6, 128.5, 122.3, 120.0, 119.9, 110.4, 108.5, 30.5, 15.1.
ESI-HRMS: calcd for $C_{10}H_{12}NS^+$ ($[M+H]^+$) = 178.0685, found 178.0683.
IR (neat): 3381, 1437, 1337, 1313, 1282, 1257, 1230, 807, 746, 646, 511, 442 cm^{-1}.

2-(propylthio)-1*H*-indole (2c)



Pale yellow oil;

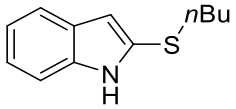
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.54 – 7.52 (m, 1H), 7.23 – 7.20 (m, 1H), 7.17 – 7.13 (m, 1H), 7.10 – 7.06 (m, 1H), 6.61 – 6.60 (m, 1H), 2.74(t, *J* = 7.2 Hz, 3H), 1.64 – 1.55 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.9, 129.0, 128.6, 122.3, 119.9, 110.5, 108.3, 108.3, 38.4, 23.1, 13.0.

ESI-HRMS: calcd for $C_{11}H_{13}NS^+$ ([M + H]$^+$) = 192.0841, found 192.0840.

IR (neat): 3400, 2962, 2927, 2870, 1444, 1397, 1339, 1316, 1287, 1233, 793, 743, 643 cm^{-1}.

2-(butylthio)-1*H*-indole (2d)



Pale green oil;

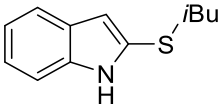
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.54 – 7.52 (m, 1H), 7.23 – 6.98 (m, 3H), 6.60 – 6.59 (m, 1H), 2.74(t, *J* = 7.6Hz, 2H), 1.58 – 1.53 (m, 2H), 1.41 – 1.31 (m, 2H), 0.85 (t, *J* = 7.4, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.8, 129.1, 128.6, 122.2, 119.9, 110.5, 108.1, 36.1, 31.7, 21.5, 13.5.

ESI-HRMS: calcd for $C_{12}H_{16}NS^+$ ([M + H]$^+$) = 206.0998, found 206.0996.

IR (neat): 3398, 2957, 2927, 2866, 1443, 1396, 1339, 1315, 1280, 1226, 792, 743, 642 cm^{-1}.

2-(isobutylthio)-1*H*-indole (2e)



Pale yellow oil;

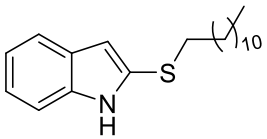
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.54 – 7.50 (m, 1H), 7.22 – 7.19 (m, 1H), 7.16 – 7.12 (m, 1H), 7.10 – 7.05 (m, 1H), 6.60 – 6.56 (m, 1H), 2.67 (d, *J* = 7.2 Hz, 2H), 1.83 – 1.73 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.8, 129.7, 128.6, 122.2, 119.9, 119.9, 110.4, 107.8, 45.4, 28.5, 21.6.

ESI-HRMS: calcd for $C_{12}H_{16}NS^+$ ([M + H]$^+$) = 206.0998, found 206.0996.

IR (neat): 3396, 2956, 2923, 2868, 1442, 1390, 1338, 1280, 1238, 791, 741, 641, 483, 443 cm^{-1}.

2-(dodecylthio)-1*H*-indole (2f)



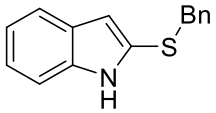
White solid; M.p. 44-46 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.57 – 7.55 (m, 1H), 7.33 – 7.31 (m, 1H), 7.21 – 7.17 (m, 1H), 7.13 – 7.09 (m, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 2.83 (t, *J* = 7.2 Hz 2H), 1.66 – 1.61 (m, 2H), 1.43 – 1.36 (m, 2H), 1.31 – 1.26 (m, 16H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.93, 129.2, 128.7, 122.4, 120.1, 120.0, 110.4, 108.4, 36.7, 31.9, 29.9, 29.6, 29.6, 29.5, 29.3, 29.1, 28.5, 22.7, 14.1.

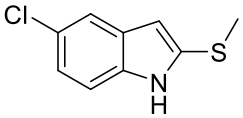
ESI-HRMS: calcd for $C_{20}H_{32}NS^+$ ([M + H]$^+$) = 318.2250, found 318.2245.
IR (neat): 3372, 2914, 2848, 1467, 1441, 1273, 750, 716, 637, 485 cm^{-1}.

2-(benzylthio)-1*H*-indole (2g)



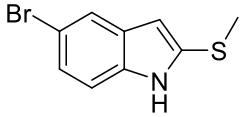
Pale yellow solid; M.p. 76-78 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.55 – 7.52 (m, 1H), 7.28 – 7.23 (m, 3H), 7.22 – 7.13 (m, 4H), 7.10 – 7.06 (m, 1H), 6.58 (dd, *J* = 2.0, 0.8 Hz, 1H), 3.98 (s, 2H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.3, 137.0, 128.8, 128.6, 128.4, 128.1, 127.3, 122.6, 120.3, 120.0, 110.5, 109.5, 41.9.
ESI-HRMS: calcd for $C_{15}H_{14}NS^+$ ([M + H]$^+$) = 240.0841, found 240.0839.
IR (neat): 3383, 1488, 1447, 1340, 1274, 923, 746, 706, 634, 470, 637 cm^{-1}.

5-chloro-2-(methylthio)-1*H*-indole (2i)



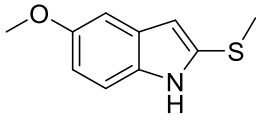
White solid; M.p. 89-91 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.50 – 7.49 (m, 1H), 7.20 – 7.17 (m, 1H), 7.13 – 7.10 (m, 1H), 6.46 – 6.45 (m, 1H), 2.51 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 135.1, 133.4, 129.8, 125.7, 122.3, 119.1, 111.2, 104.7, 18.8.
ESI-HRMS: calcd for $C_9H_9NS^{35}Cl^+$ ([M + H]$^+$) = 198.0139, found 198.0138. $C_9H_9NS^{37}Cl^+$ ([M + H]$^+$) = 200.0109, found 200.0106.
IR (neat): 3389, 1442, 1396, 1316, 1060, 914, 866, 800, 761, 687, 636, 587, 459, 432 cm^{-1}.

5-bromo-2-(methylthio)-1*H*-indole (2j)



Pale yellow solid; M.p. 93-95 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.64 (d, *J* = 1.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.15 – 7.13 (m, 1H), 6.44 – 6.43 (m, 1H), 2.50 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.4, 133.3, 130.5, 124.9, 122.2, 113.3, 111.7, 104.5, 18.8.
ESI-HRMS: calcd for $C_9H_9NS^{79}Br^+$ ([M + H]$^+$) = 241.9634, found 241.9630. $C_9H_9NS^{81}Br^+$ ([M + H]$^+$) = 243.9613, found 243.9609.
IR (neat): 3385, 1562, 1434, 1394, 1314, 1268, 1047, 866, 798, 759, 663, 635, 581, 466 cm^{-1}.

5-methoxy-2-(methylthio)-1*H*-indole (2k)



Pale yellow solid; M.p. 78-80 °C.

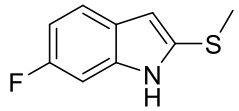
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.18 – 7.16 (m, 1H), 7.05 – 7.03 (m, 1H), 6.88 – 6.85 (m, 1H), 6.51 (dd, *J* = 2.0, 0.8 Hz, 1H), 3.87 (s, 3H), 2.49 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 154.2, 132.1, 131.9, 129.2, 112.4, 111.2, 105.6, 101.6, 55.8, 19.3.

ESI-HRMS: calcd for $C_{10}H_{12}NOS^+$ ([M + H]$^+$) = 194.0634, found 194.0633.

IR (neat): 3392, 2923, 1621, 1582, 1506, 1469, 1440, 1218, 1193, 1155, 1208, 973, 839, 795 cm^{-1}.

6-fluoro-2-(methylthio)-1*H*-indole (2l)



White solid; M.p. 76-78 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.44 (dd, *J* = 8.8, 5.4 Hz, 1H), 7.01 – 6.98 (m, 1H), 6.89 – 6.84 (m, 1H), 6.54 – 6.53 (m, 1H), 2.49 (s, 3H).

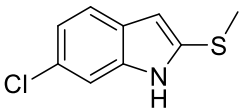
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.0 (d, *J* = 237.2 Hz), 136.7 (d, *J* = 12.4 Hz), 131.4 (d, *J* = 3.4 Hz), 125.2, 120.6 (d, *J* = 10.0 Hz), 108.9 (d, *J* = 24.3 Hz), 106.3, 96.9 (d, *J* = 26.1 Hz), 19.5.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -120.41.

ESI-HRMS: calcd for $C_9H_9NSF^+$ ([M + H]$^+$) = 182.0434, found 182.0431.

IR (neat): 3356, 1618, 1485, 1443, 1381, 1338, 1279, 1220, 1138, 960, 932, 843, 811, 758, 639, 612, 480, 441 cm^{-1}.

6-chloro-2-(methylthio)-1*H*-indole (2m)



White solid; M.p. 127-128 °C.

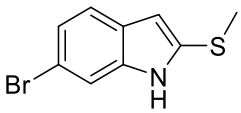
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.41 (d, 8.4 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.07 – 7.04 (m, 1H), 6.50 – 6.49 (m, 1H), 2.49 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 137.1, 132.4, 128.0, 127.3, 120.8, 120.6, 110.3, 105.5, 19.0.

ESI-HRMS: calcd for $C_9H_9NS^{35}Cl^+$ ([M + H]$^+$) = 198.0139, found 198.0138. $C_9H_9NS^{37}Cl^+$ ([M + H]$^+$) = 200.0109, found 200.0106.

IR (neat): 3352, 1436, 1369, 1333, 1290, 1059, 912, 854, 811, 761, 734, 638, 481, 434 cm^{-1}.

6-bromo-2-(methylthio)-1*H*-indole (2n)



White solid; M.p. 136-138 °C.

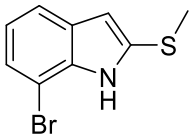
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.44 – 7.43 (m, 1H), 7.39 – 7.37 (m, 1H), 7.21 – 7.19 (m, 1H), 6.51 – 6.49 (m, 1H), 2.51 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.5, 132.5, 127.6, 123.4, 120.9, 115.6, 113.3, 105.5, 18.9.

ESI-HRMS: calcd for $C_9H_9NS^{79}Br^+$ ([M + H]$^+$) = 241.9634, found 241.9631. $C_9H_9NS^{81}Br^+$ ([M + H]$^+$) = 243.9613, found 243.9610

IR (neat): 3348, 2361, 2335, 1455, 1266, 1047, 900, 855, 811, 757, 638, 508, 483, 428 cm^{-1}.

7-bromo-2-(methylthio)-1*H*-indole (2o)



Pale green solid; M.p. 55-57 °C.

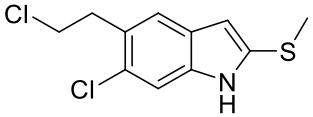
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.30 (m, 1H), 6.98 (t, *J* = 7.68 Hz, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 2.54 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 135.5, 132.7, 129.8, 124.4, 121.3, 118.9, 106.4, 103.7, 19.0.

ESI-HRMS: calcd for $C_9H_9NS^{79}Br^+$ ([M + H]$^+$) = 241.9634, found 241.9630. $C_9H_9NS^{81}Br^+$ ([M + H]$^+$) = 243.9613, found 243.9610

IR (neat): 3311, 2361, 2335, 1416, 1329, 1273, 965, 810, 757, 659, 527 cm^{-1}.

6-chloro-5-(2-chloroethyl)-2-(methylthio)-1*H*-indole (2p)



White solid; M.p. 96-97 °C.

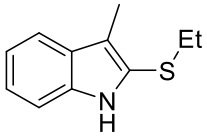
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.40 (s, 1H), 7.31 (s, 1H), 6.47 – 7.46 (m, 1H), 3.76 (t, *J* = 7.6 Hz, 2H), 3.26 (t, *J* = 7.6 Hz, 2H), 2.50 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 136.3, 133.1, 128.0, 127.8, 127.1, 121.7, 111.1, 105.1, 43.9, 37.3, 18.9.

ESI-HRMS: calcd for $C_{11}H_{12}NS^{35}Cl_2^+$ ([M + H]$^+$) = 260.0062, found 260.0060. $C_{11}H_{12}NS^{35}Cl^{37}Cl^+$ ([M + H]$^+$) = 262.0033, found 262.0029. $C_{11}H_{12}NS^{37}Cl_2^+$ ([M + H]$^+$) = 264.0003, found 263.9998.

IR (neat): 3356, 1453, 1320, 1267, 994, 913, 877, 758, 636, 484 cm^{-1}.

2-(ethylthio)-3-methyl-1*H*-indole (2q)



Pale yellow oil;

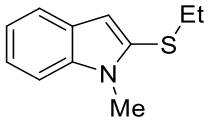
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.53 – 7.51 (m, 1H), 7.23 – 7.15 (m, 2H), 7.11 – 7.07 (m, 1H), 2.69 (q, *J* = 8.8 Hz, 2H), 2.37 (s, 3H), 1.18 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 136.2, 128.5, 124.5, 122.8, 119.3, 119.0, 117.9 , 110.5, 30.7, 15.3, 9.5.

ESI-HRMS: calcd for $C_{11}H_{14}NS^+$ ([M + H]$^+$) = 192.0841, found 192.0844.

IR (neat): 3401, 2920, 1446, 1374, 1331, 966, 740, 647 cm^{-1}.

2-(ethylthio)-1-methyl-1*H*-indole (2r)



Pale yellow oil;

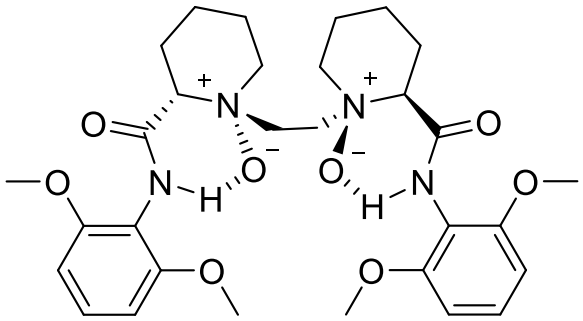
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.53 (m, 1H), 7.26 – 7.17 (m, 2H), 7.10 – 7.06 (m, 1H), 6.66 (s, 1H), 3.76 (s, 3H), 2.78 – 2.72 (m, 2H), 1.26 – 1.22 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 138.2, 131.3, 127.4, 121.9, 120.1, 119.6, 109.4, 108.2, 30.5, 29.8, 14.6.

ESI-HRMS: calcd for $C_{11}H_{14}NS^{+}$ ([M + H]$^{+}$) = 192.0841, found 192.0839.

IR (neat): 2923, 1454, 1317, 1258, 785, 739, 625 cm^{-1}.

5 Characterization of chiral *N,N'*-dioxides



L_2-Pi(OMe)$_2$

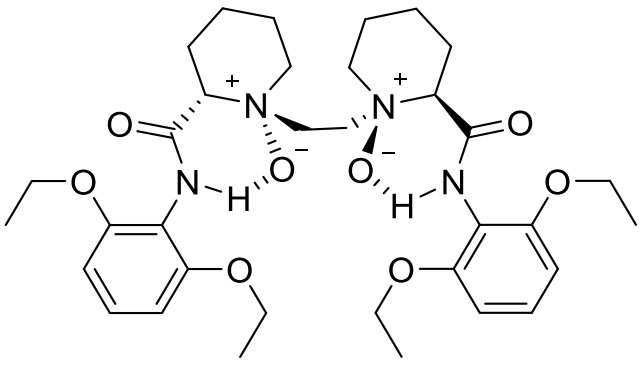
White power. M.p. 117-120 °C. $[\alpha]^{22}_{D}$ = +30.4 (*c* = 0.26, in MeOH).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.75 (s, 2H), 7.14 (t, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 8.4 Hz, 4H), 4.50 – 4.37 (m, 2H), 4.07 – 3.95 (m, 2H), 3.76 (s, 12H), 3.65 – 3.57 (m, 2H), 3.53 – 3.45 (m, 2H), 3.09 (td, *J* = 12.0, 2.8 Hz, 2H), 2.72 – 2.57 (m, 2H), 2.50 – 2.38 (m, 2H), 2.12 – 2.01 (m, 2H), 1.90 – 1.78 (m, 2H), 1.67 – 1.56 (m, 2H), 1.46 – 1.30 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.0, 155.7, 127.8, 113.4, 104.4, 75.1, 65.9, 62.1, 56.0, 25.9, 21.9, 20.4.

ESI-HRMS: calcd for $C_{30}H_{43}N_4O_8^{+}$ ([M + H]$^{+}$) = 587.3075, found 587.3080.

IR (neat): 1676, 1594, 1539, 1477, 1257, 1112 cm^{-1}.



L_2-Pi(OEt)$_2$

White foam. M.p. 87-90 °C. $[\alpha]^{22}_{D}$ = +24.4 (*c* = 0.36, in MeOH).

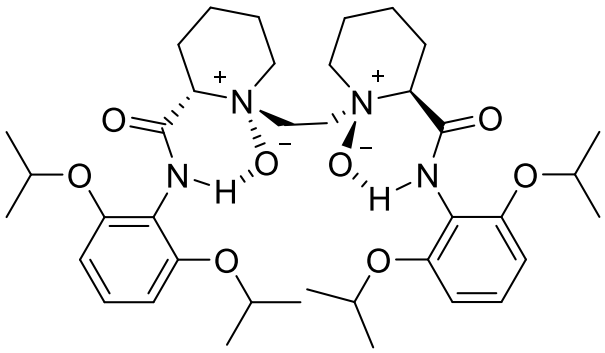
^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.76 (s, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 4H), 4.40 (td, *J* = 9.2, 8.7, 3.8 Hz, 2H), 4.04 – 3.92 (m, 10H), 3.64 – 3.55 (m, 2H), 3.52 – 4.42 (m,

2H), 3.08 (td, *J* = 12.0, 2.8 Hz, 2H), 2.69 – 2.59 (m, 2H), 2.48 – 2.38 (m, 2H), 2.07 – 2.01 (m, 2H), 1.87 – 1.78 (m, 2H), 1.63 – 1.54 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 14H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6, 154.9, 127.4, 114.2, 105.5, 75.1, 65.8, 64.4, 62.1, 25.9, 22.0, 20.3, 15.0.

ESI-HRMS: calcd for $C_{34}H_{51}N_4O_8^+$ ($[M+H]^+$) = 643.3701, found 643.3706.

IR (neat): 1680, 1591, 1538, 1465, 1254, 1118, 1093 cm^{-1}.



L$_2$-Pi(O*i*Pr)$_2$

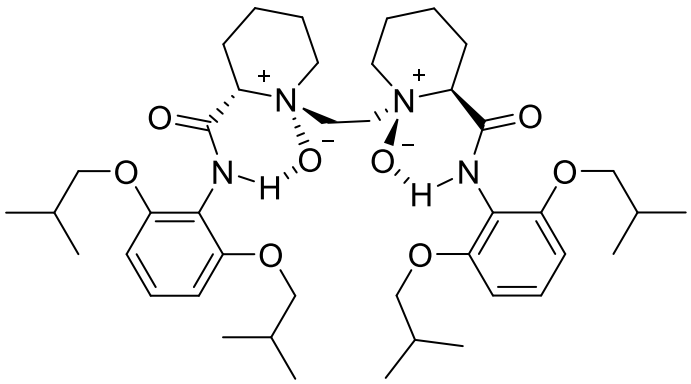
White foam. M.p. 88-91 °C. $[\alpha]^{22}_D$ = –19.6 (c = 0.28, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.65 (s, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 4H), 4.56 – 4.45 (m, 4H), 4.33 (s, 2H), 4.18 – 4.00 (m, 2H), 3.70 – 3.37 (m, 4H), 3.09 (q, *J* = 12.0 Hz, 2H), 2.72 – 2.58 (m, 2H), 2.50 – 2.36 (m, 2H), 2.06 – 2.00 (m, 2H), 1.86 – 1.75 (m, 2H), 1.62 – 1.48 (m, 2H), 1.33 (dd, *J* = 6.0, 3.2 Hz, 26H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 154.0, 127.1, 115.8, 106.5, 75.3, 71.2, 65.4, 62.2, 25.9, 22.4, 21.9, 20.2.

ESI-HRMS: calcd for $C_{38}H_{59}N_4O_8^+$ ($[M+H]^+$) = 699.4327, found 699.4326.

IR (neat): 1685, 1593, 1534, 1467, 1254, 1115, 1067 cm^{-1}.



L$_2$-Pi(O*i*Bu)$_2$

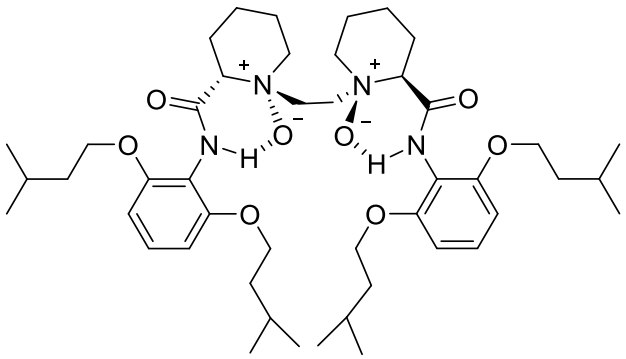
White foam. M.p. 88-91 °C. $[\alpha]^{22}_D$ = +43.6 (*c* = 0.58, in MeOH).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.69 (s, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.48 – 6.46 (m, 4H), 4.48 – 4.10 (m, 4H), 3.64 – 3.54 (m, 12H), 3.09 – 2.41 (m, 5H), 2.07 – 1.39 (m, 13H), 0.98 – 0.92 (m, 24H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 154.8, 127.2, 113.4, 104.6, 75.4, 74.7, 65.5, 61.6, 28.1, 25.9, 20.2, 19.2, 19.1.

ESI-HRMS: calcd for $C_{42}H_{67}N_4O_8^+$ ($[M+H]^+$) = 755.4953, found 755.4954.

IR (neat): 1687, 1596, 1537, 1463, 1257, 1101 cm^{-1}.



L_2-Pi(O*i*pentyl)$_2$

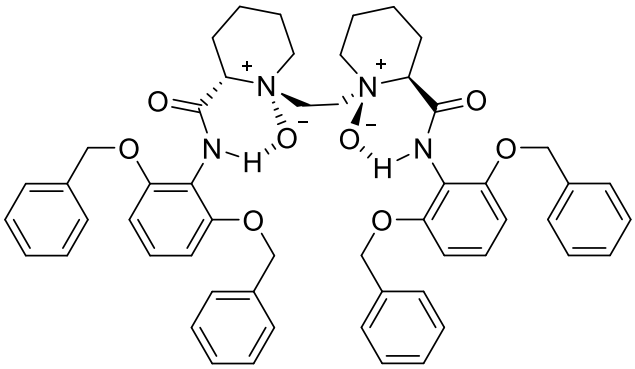
White foam. M.p. 88-92 °C. $[\alpha]^{21}_D$ = +53.0 (*c* = 0.26, in MeOH).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.63 (s, 2H), 7.11 (t, *J* = 8.3 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 4H), 4.43 (s, 2H), 4.08 – 3.92 (m, 8H), 3.58 (s, 4H), 3.11 – 1.40 (m, 28H), 0.92 – 0.91 (m, 24H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 154.9, 127.39, 113.6, 104.9, 75.1, 67.0, 65.3, 61.7, 37.8, 25.8, 24.8, 22.5, 21.8, 20.1.

ESI-HRMS: calcd for $C_{46}H_{75}N_4O_8^+$ ($[M+H]^+$) = 811.5579, found 811.5577.

IR (neat): 1679, 1593, 1537, 1462, 1253, 1096 cm^{-1}.



L_2-Pi(OBn)$_2$

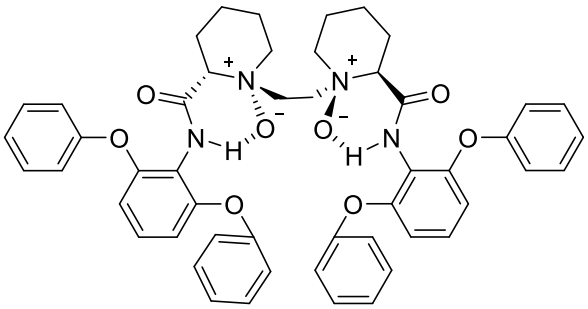
White foam. M.p. 88-91 °C. $[\alpha]^{21}_D$ = +46.7 (*c* = 0.42, in MeOH).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.04 (s, 2H), 7.50 – 7.43 (m, 8H), 7.38 (t, *J* = 7.2 Hz, 8H), 7.34 – 7.29 (m, 4H), 7.11 (t, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 4H), 5.08 (s, 8H), 4.00 (br, 2H), 3.70 (br, 2H), 3.3 – 2.7 (m, 4H), 2.60 (t, *J* = 12.0 Hz, 2H), 2.44 – 2.28 (m, 2H), 2.20 – 2.06 (m, 2H), 1.73 – 1.64 (m, 2H), 1.57 – 1.44 (m, 2H), 1.25 – 1.14 (m, 2H), 1.05 – 0.85 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 154.8, 136.9, 128.5, 128.0, 127.3, 114.5, 106.1, 74.5, 70.7, 64.8, 62.0, 25.9, 21.5, 20.0.

ESI-HRMS: calcd for $C_{54}H_{59}N_4O_8^+$ ($[M+H]^+$) = 891.4327, found 891.4316.

IR (neat): 1683, 1595, 1534, 1464, 1378, 1261, 1102, 744, 698 cm^{-1}.



L_2-Pi(OPh)$_2$

White foam. M.p. 98-101 °C. $[\alpha]^{21}_D$ = +39.6 (*c* = 0.26, in MeOH).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.12 (s, 2H), 7.36 – 7.28 (m, 8H), 7.13 – 7.00 (m, 14H), 6.57 (d, *J* = 8.4 Hz, 4H), 4.74 – 4.30 (m, 1H), 4.05 – 3.70 (m, 3H), 3.25 – 2.88 (m, 3H), 2.59 (t, *J* = 12.0 Hz, 2H), 2.16 – 1.98 (m, 4H), 1.60 – 1.38 (m, 4H), 1.29 – 1.18 (m, 1H), 1.09 – 0.62 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 156.5, 154.0, 129.9, 127.7, 123.9, 119.3, 118.8, 113.2, 100.0, 74.9, 65.3, 62.6, 25.4, 21.5, 20.0.

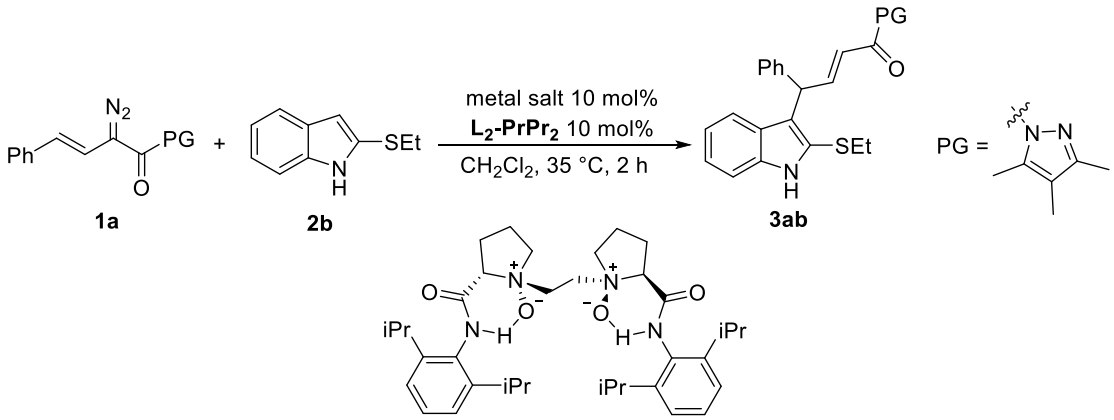
ESI-HRMS: calcd for $C_{50}H_{51}N_4O_8^+$ ([M + H]$^+$) = 835.3701, found 835.3701.

IR (neat): 1683, 1579, 1518, 1486, 1456, 1238, 1205, 1161, 1023, 752, 691 cm^{-1}.

6 Typical experimental procedure for the asymmetric [3,3]-rearrangement

6.1 Optimization of the reaction conditions

Table S1: Screen of metal salts

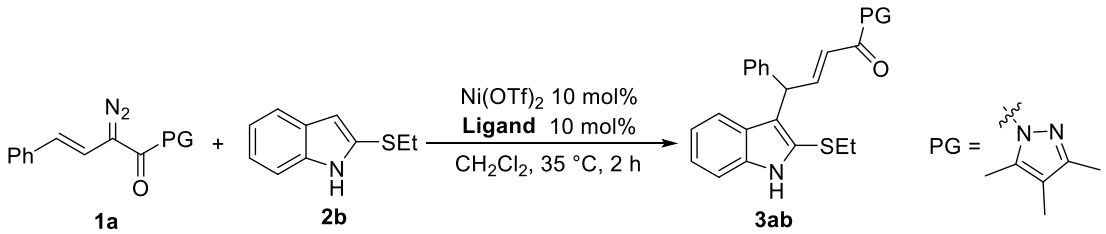


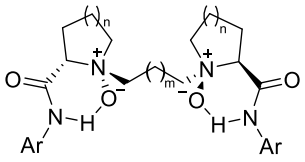
L_2-PrPr$_2$

entry[a]	metal salt	yield (%)[b]	ee (%)[c]
1	$Fe(OTf)_2$	34	7
2	$Fe(OTf)_3$	43	6
3	$Co(OTf)_2$	83	2
4	$Ni(OTf)_2$	80	13
5	$Cu(OTf)_2$	54	1

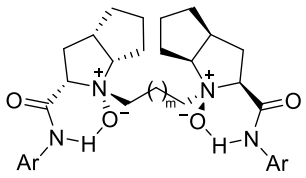
[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), metal salt (10 mol%), **L_2-PrPr$_2$** (10 mol%) and CH_2Cl_2 (0.1 M) at 35 °C. [b] Isolated yields of **3ab**. [c] Determined by HPLC on a chiral stationary phase.

Table S2: Screening of chiral *N,N'*-dioxide ligands

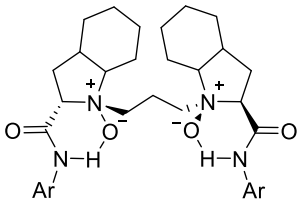




L_2-$PrPr_2$: Ar = 2,6-iPr$_2$C$_6$H$_3$, n = 1, m = 0
L_3-$PrPr_2$: Ar = 2,6-iPr$_2$C$_6$H$_3$, n = 1, m = 1
L_2-$PiPr_2$: Ar = 2,6-iPr$_2$C$_6$H$_3$, n = 2, m = 0
L_3-$PiPr_2$: Ar = 2,6-iPr$_2$C$_6$H$_3$, n = 2, m =1



L_2-$RaPr_2$: Ar = 2,6-iPr$_2$C$_6$H$_3$, m = 0
L_3-$RaPr_2$: Ar = 2,6-iPr$_2$C$_6$H$_3$, m = 1

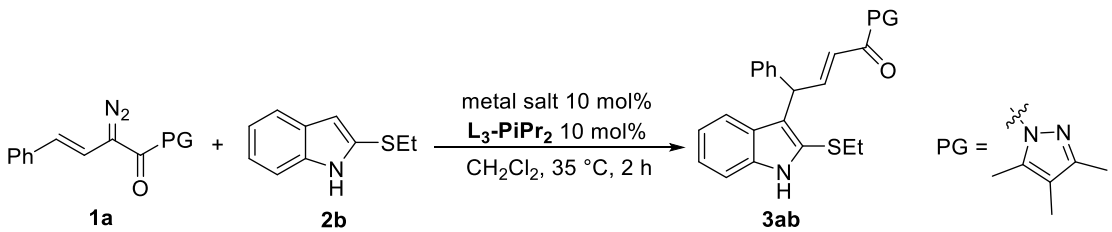


L_3-$PePr_2$: Ar = 2,6-iPr$_2$C$_6$H$_3$

entry[a]	**ligand**	yield (%)[b]	ee (%)[c]
1	**L_2-$PrPr_2$**	80	13
2	**L_3-$PrPr_2$**	75	18
3	**L_2-$PiPr_2$**	93	21
4	**L_3-$PiPr_2$**	96	31
5	**L_2-$RaPr_2$**	50	14
6	**L_3-$RaPr_2$**	74	29
7	**L_3-$PePr_2$**	40	25

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), Ni(OTf)$_2$ (10 mol%), **Ligand** (10 mol%) and CH_2Cl_2 (0.1 M) at 35 °C. [b] Isolated yields of **3ab**. [c] Determined by HPLC on a chiral stationary phase.

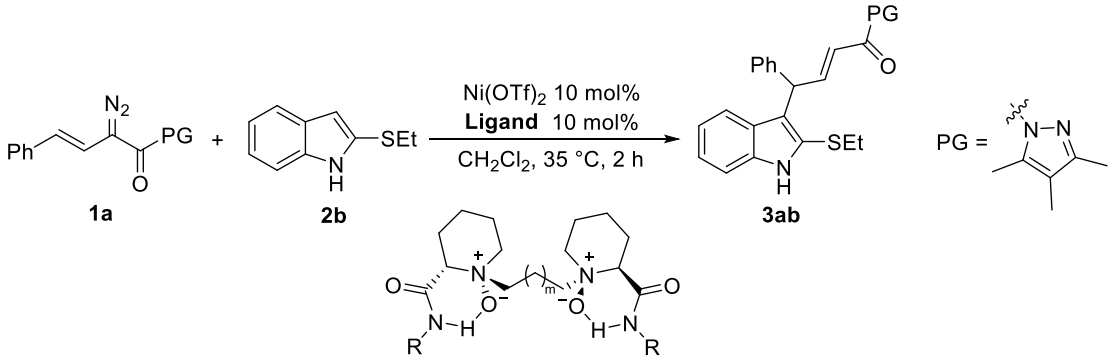
Table S3: Screen of metal salts



entry[a]	metal salt	yield (%)[b]	ee (%)[c]
1	$Ni(OTf)_2$	96	31
2	$Ni(NTf_2)_2$	88	4
3	$Ni(BF_4)_2.6H_2O$	85	13
4	$Ni(ClO_4)_2.6H_2O$	74	1
5	$Ni(AcAc)_2.2H_2O$	22	4
6	$Ni(C_2O_4).2H_2O$	29	9
7[d]	$Ni(DME)Br_2$	83	28

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), metal salt (10 mol%), **L_3-$PiPr_2$** (10 mol%) and CH_2Cl_2 (0.1 M) at 35 °C. [b] Isolated yields of **3ab**. [c] Determined by HPLC on a chiral stationary phase. [d] DME = 1,2-dimethoxyethane.

Table S4: Screening of chiral *N,N'*-dioxide ligands

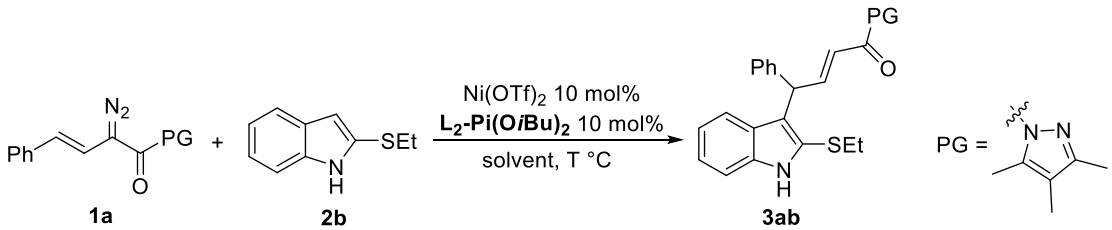


L2-Pi(OMe)2: R = 2,6-$(MeO)_2C_6H_3$, m = 0
L2-Pi(OEt)2: R = 2,6-$(EtO)_2C_6H_3$, m = 0
L2-Pi(O*i*Pr)2: R = 2,6-$(i\text{PrO})_2C_6H_3$, m = 0
L2-Pi(O*i*Bu)2: R = 2,6-$(i\text{BuO})_2C_6H_3$, m = 0
L2-Pi(OPh)2: R = 2,6-$(PhO)_2C_6H_3$, m = 0
L2-Pi(OBn)2: R = 2,6-$(BnO)_2C_6H_3$, m = 0
L4-PiMe2*t*Bu: R = 2,6-Me_2-4-*t*BuC_6H_2, m = 2
L3-PiMe2: R = 2,6-$Me_2C_6H_3$, m = 1
L3-PiEt2: R = 2,6-$Et_2C_6H_3$, m = 1
L3-PiMe3: R = 2,4,6-$Me_3C_6H_2$, m = 1
L3-PiPr3: R = 2,4,6-*i*$Pr_3C_6H_2$, m = 1
L3-Pi*t*Bu: R = *t*Bu, m = 1
L3-PiCHPh2: R = $CH(C_6H_5)_2$, m = 1
L4-PiPr3: R = 2,4,6-*i*$Pr_3C_6H_2$, m = 2

entry[a]	ligand	yield (%)[b]	ee (%)[c]
1	**L2-Pi(OMe)2**	94	33
2	**L2-Pi(OEt)2**	87	17
3	**L2-Pi(O*i*Pr)2**	93	31
4	**L2-Pi(O*i*Bu)2**	93	46
5	**L2-Pi(OPh)2**	84	29
6	**L2-Pi(OBn)2**	81	21
7	**L3-PiMe2**	77	13
8	**L3-PiEt2**	86	17
9	**L3-PiMe3**	83	24
10	**L3-PiEt2Me**	87	26
11	**L3-PiPr3**	89	23
12	**L3-Pi*t*Bu**	53	race
13	**L3-PiCHPh2**	52	race
14	**L4-PiMe2*t*Bu**	12	18
15	**L4-PiPr3**	19	4

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (10 mol%), **Ligand** (10 mol%) and CH_2Cl_2 (0.1 M) at 35 °C. [b] Isolated yields of **3ab**. [c] Determined by HPLC on a chiral stationary phase.

Table S5: Screening of solvents and temperature

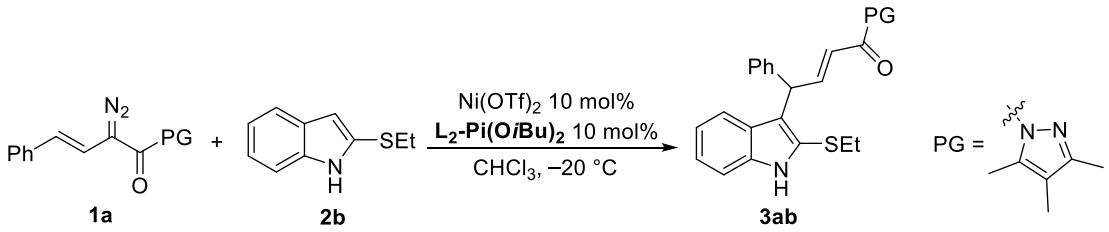


entry[a]	solvent	T (°C)	time	yield (%)[b]	ee (%)[c]
1[d]	THF	35	2 h	51	25

2[d]	$PhCH_3$	35	2 h	75	10
3[d]	Et_2O	35	2 h	85	2
4[d]	CH_3COOMe	35	2 h	81	16
5[d]	CH_3CN	35	2 h	65	17
6[d]	CH_2Cl_2	35	2 h	90	50
7[d]	$CHCl_3$	35	2 h	88	60
8[d]	CH_2ClCH_2Cl	35	2 h	72	42
9[d]	$CHCl_2CH_2Cl$	35	2 h	92	53
10[d]	$CHCl_2CHCl_2$	35	2 h	97	51
11[e]	CH_2Cl_2	0	1 d	85	63
12[e]	CH_2Cl_2	-10	1 d	91	77
13[e]	CH_2Cl_2	-20	2 d	85	80
14[e]	CH_2Cl_2	-30	4 d	10	50
15[e]	CH_2Cl_2	-40	4 d	6	22
16	$CHCl_3$	-20	2 d	84	90

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (10 mol%), **L_2-Pi(O*i*Bu)$_2$** (10 mol%) and $CHCl_3$ (0.1 M) at -20 °C. [b] Isolated yields of **3ab**. [c] Determined by HPLC on a chiral stationary phase. [d] The reactions were carried out at 35 °C. [e] The reactions were carried out in CH_2Cl_2 (0.1 M).

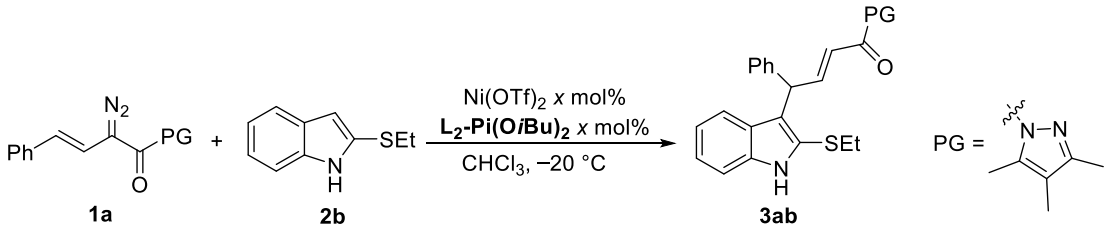
Table S6: Screening of the reaction concentration



entry[a]	concentration	time	yield (%)[b]	ee (%)[c]
1	0.2 M	31 h	87	92
2	0.1 M	2 d	84	90
3	0.05 M	3 d	81	87

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (10 mol%), **L_2-Pi(O*i*Bu)$_2$** (10 mol%) and $CHCl_3$ (0.2 M) at –20 °C. [b] Isolated yields of **3ab**. [c] Determined by HPLC on a chiral stationary phase.

Table S7: Screening of the catalyst loading

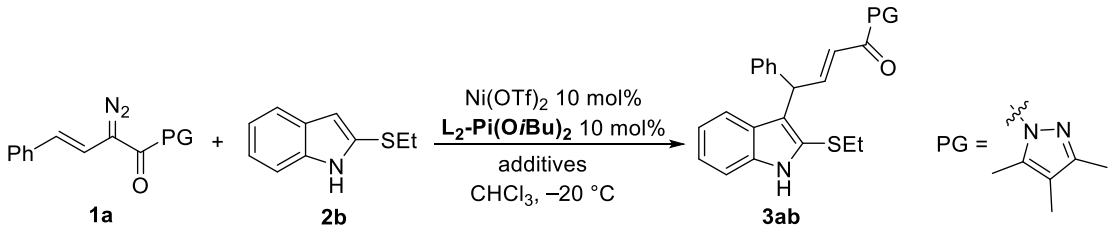


entry[a]	*x*	time	yield (%)[b]	ee (%)[c]
1	10	31 h	86	92
2	5.0	3 d	65	91

3	2.5	3 d	39	92

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (*x* mol%), **L_2-Pi(O*i*Bu)$_2$** (*x* mol%) and $CHCl_3$ (0.2 M) at –20 °C. [b] Isolated yields of **3ab**. [c] Determined by HPLC on a chiral stationary phase.

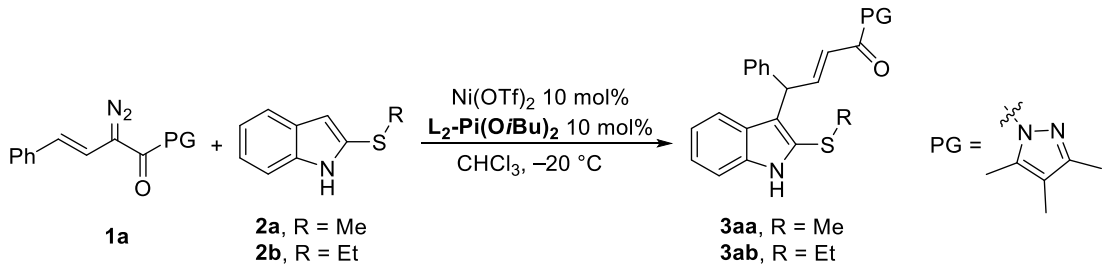
Table S8: Screening of additives



entry[a]	additive	time	yield (%)[b]	ee (%)[c]
1	3Å MS (10 mg)	30 h	68	90
2	4Å MS (10 mg)	30 h	68	88
3	5Å MS (10 mg)	30 h	70	91
4	$NaBAr^F_4$ (10 mol%)	36 h	59	80
5	*m*-CPBA (10 mol%)	27 h	79	90
6	3-Chlorobenzoic acid (10 mol%)	27 h	85	91
7	3-Nitrobenzoic acid (10 mol%)	27 h	77	86

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (10 mol%), **L_2-Pi(O*i*Bu)$_2$** (10 mol%), additives and $CHCl_3$ (0.2 M) at –20 °C. [b] Isolated yields of **3ab**. [c] Determined by HPLC on a chiral stationary phase.

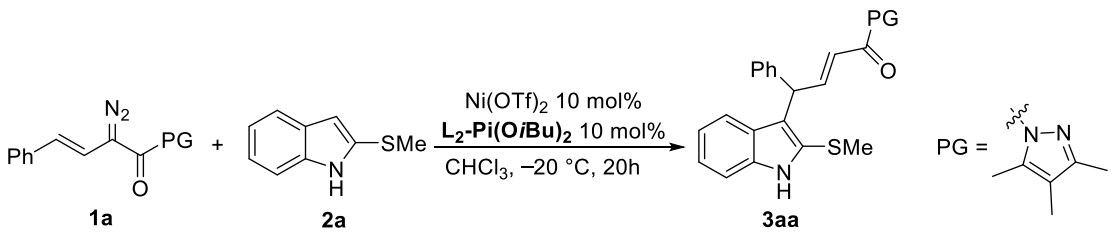
Table S9: Screening of the R group of 2-(alkylthio)-1*H*-indole **2**



entry[a]	R	time	yield (%)	ee (%)[b]
1[c]	Me	20 h	90	96
2[d]	Et	31 h	87	92

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-1*H*-indole **2b** (0.1 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (10 mol%), **L_2-Pi(O*i*Bu)$_2$** (10 mol%), and $CHCl_3$ (0.2 M) at –20 °C. [b] Determined by HPLC on a chiral stationary phase. [c] Isolated yields of **3aa**. [d] Isolated yields of **3ab**.

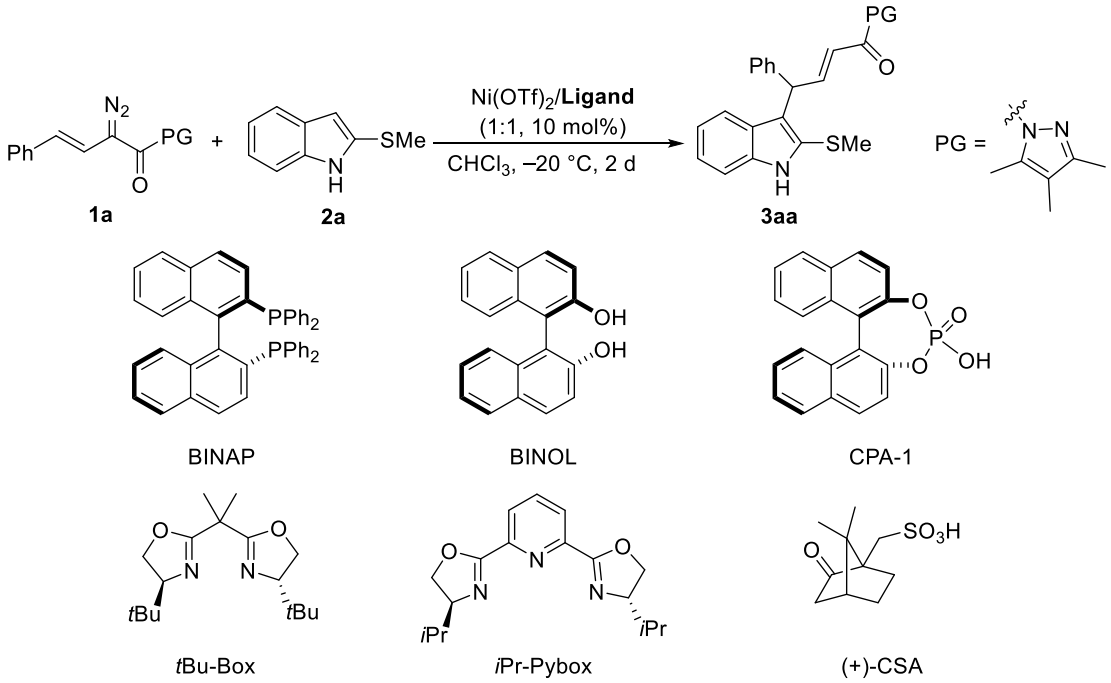
Table S10: Screen of the ratio of **1a** and **2a**



entry[a]	**1a:2a**	yield (%)[b]	ee (%)[c]
1	1.0:1.0	90	96
2[d]	1.0:1.2	94	96
3[e]	1.0:1.5	94	95
4[f]	1.0:2.0	91	95

[a] Unless otherwise noted, the reactions were carried out with 2-(methylthio)-1*H*-indole **2a** (0.1 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (10 mol%), **L_2-Pi(O*i*Bu)$_2$** (10 mol%), and $CHCl_3$ (0.2 M) at –20 °C. [b] Isolated yields of **3aa**. [c] Determined by HPLC on a chiral stationary phase. [d] **2a** (0.12 mmol) was used. [e] **2a** (0.15 mmol) was used. [f] **2a** (0.20 mmol) was used.

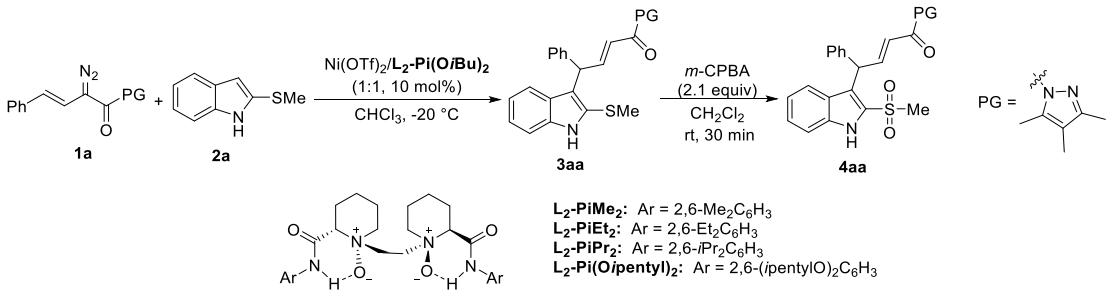
Table S11: Screen of other representative chiral ligand



entry[a]	**ligand**	yield (%)[b]	ee (%)
1	BINAP	N.R.	N.D.
2	BINOL	N.R.	N.D.
3[c]	CPA-1	trace	N.D.
4	*t*Bu-Box	N.R.	N.D.
5	*i*Pr-Pybox	N.R.	N.D.
6[c]	(+)-CSA	trace	N.D.

[a] Unless otherwise noted, the reactions were carried out with 2-(methylthio)-1*H*-indole **2a** (0.12 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (10 mol%), **Ligand** (10 mol%), and $CHCl_3$ (0.2 M) at –20 °C for 2 d. [b] Isolated yields of **3aa**. [c] Used as catalyst without $Ni(OTf)_2$.

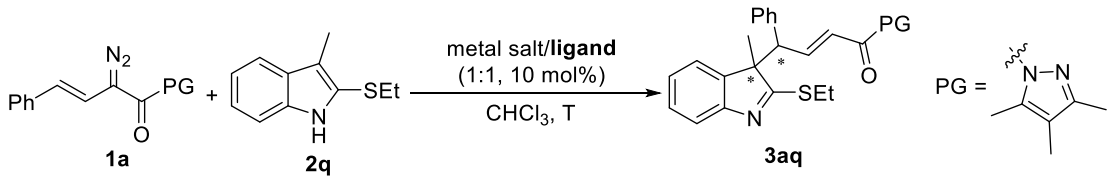
Table S12: Variations from standard conditions when **3aa** is derived to **4aa**



entry[a]	variations	yield of **3aa** (%)[b]	yield of **4aa** (%)[c]	ee of **4aa** (%)[d]
1[e]	without $Ni(OTf)_2$	N.R.	N.R.	N.D.
2[e]	without **L_2-Pi(O*i*Bu)$_2$**	N.R.	N.R.	N.D.
3	none	94	87	96
4[e]	$Fe(OTf)_2$ instead of $Ni(OTf)_2$	trace	trace	N.D.
5	$Cu(OTf)_2$ instead of $Ni(OTf)_2$	38	27	37
6	$Co(OTf)_2$ instead of $Ni(OTf)_2$	82	82	79
7	$Ni(NTf_2)_2$ instead of $Ni(OTf)_2$	92	85	95
8[f]	$Ni(DME)Br_2$ instead of $Ni(OTf)_2$	92	84	94
9	**L_2-PiMe$_2$** instead of **L_2-Pi(O*i*Bu)$_2$**	41	24	33
10	**L_2-PiEt$_2$** instead of **L_2-Pi(O*i*Bu)$_2$**	99	84	50
11	**L_2-PiPr$_2$** instead of **L_2-Pi(O*i*Bu)$_2$**	86	68	61
12	**L_2-Pi(OMe)$_2$** instead of **L_2-Pi(O*i*Bu)$_2$**	96	67	58
13	**L_2-Pi(OEt)$_2$** instead of **L_2-Pi(O*i*Bu)$_2$**	89	64	62
14	**L_2-Pi(O*i*Pr)$_2$** instead of **L_2-Pi(O*i*Bu)$_2$**	83	61	94
15	**L_2-Pi(O*i*pentyl)$_2$** instead of **L_2-Pi(O*i*Bu)$_2$**	86	74	77
16	CH_2Cl_2 instead of $CHCl_3$	76	54	90
17	THF instead of $CHCl_3$	13	10	14

[a] Unless otherwise noted, the reactions were carried out with 2-(methylthio)-1*H*-indole **2a** (0.12 mmol), diazo compound **1a** (0.1 mmol), $Ni(OTf)_2$ (10 mol%), **L_2-Pi(O*i*Bu)$_2$** (10 mol%), and $CHCl_3$ (0.2 M) at –20 °C. [b] Isolated yields of **3aa**. [c] Isolated yields of **4aa**. [d] Determined by HPLC on a chiral stationary phase. [e] NR = no reaction, ND = not detected. [f] DME = 1,2-dimethoxyethane.

Table S13: The detailed screening of conditions for substrate **2q**

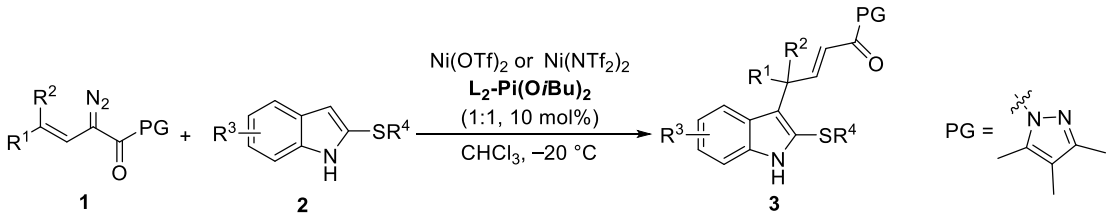


entry[a]	metal salt	**ligand**	T (°C)	yield (%)[b]	dr[c]	ee (%)[d]
1	$Ni(OTf)_2$	**L_2-Pi(O*i*Bu)$_2$**	35	83	70:30	6/12
2	$Ni(NTf_2)_2$	**L_2-Pi(O*i*Bu)$_2$**	35	87	60:40	14/race
3[e]	$Ni(DME)_2$	**L_2-Pi(O*i*Bu)$_2$**	35	56	40:60	13/6
4	$Co(OTf)_2$	**L_2-Pi(O*i*Bu)$_2$**	35	80	60:40	59/69

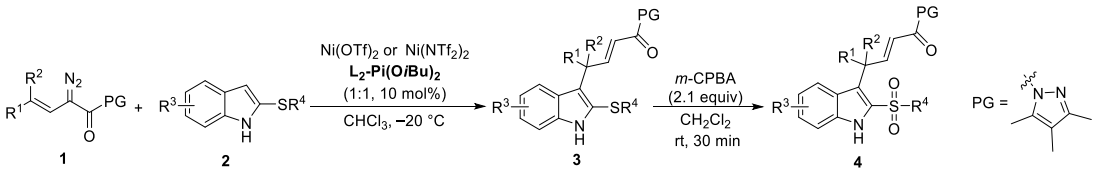
5	$Co(NTf_2)_2$	**L_2-Pi(O*i*Bu)$_2$**	35	79	50:50	53/61
6	$Co(ClO_4)_2·6H_2O$	**L_2-Pi(O*i*Bu)$_2$**	35	69	58:42	47/50
7	$Co(BF_4)_2·6H_2O$	**L_2-Pi(O*i*Bu)$_2$**	35	74	51:49	52/61
8	$Co(OTf)_2$	**L_2-Pi(O*i*Bu)$_2$**	20	69	42:58	62/80
9	$Co(OTf)_2$	**L_2-Pi(O*i*Bu)$_2$**	10	55	38:62	59/83
10	$Co(OTf)_2$	**L_2-Pi(O*i*Bu)$_2$**	0	27	36:64	50/86
11	$Co(OTf)_2$	**L_2-Pi(O*i*Bu)$_2$**	-10	24	34:66	52/89
12	$Co(OTf)_2$	**L_2-Pi(O*i*Pr)$_2$**	-10	53	25:75	60/80
13	$Co(OTf)_2$	**L_2-Pi(OPh)$_2$**	-10	53	33:67	56/73
14	$Co(OTf)_2$	**L_2-Pi(OBn)$_2$**	-10	52	20:80	71/89

[a] Unless otherwise noted, the reactions were carried out with 2-(ethylthio)-3-methyl-1*H*-indole **2q** (0.15 mmol), diazo compound **1a** (0.1 mmol), metal salt/**ligand** (1:1, 10 mol%) in $CHCl_3$ (0.2 M). [b] Isolated yields of **3aq**. [c] The dr value was determined by ^1H NMR analysis. [d] Determined by HPLC on a chiral stationary phase. [e] DME = 1,2-dimethoxyethane.

6.2 Typical procedure for the asymmetric [3,3]-rearrangement



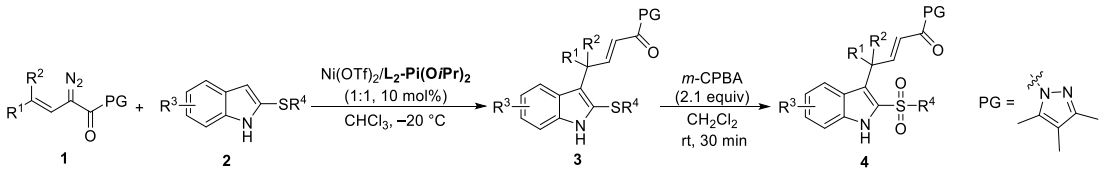
Procedure A: A dry reaction tube was charged with **L_2-Pi(O*i*Bu)$_2$** (7.6 mg, 10 mol%), $Ni(OTf)_2$ (3.6 mg, 10 mol%). Then $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, thioindole **2** (0.12 mmol) was added successively at 35 °C. Then transfer the reaction tube to –20 °C, diazo compound **1** (0.10 mmol) was added finally. The reaction was detected by TLC. After the diazo compound **1** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product (Pet/EtOAc = 15/1 to Pet/EtOAc = 7/1 as eluent). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IF in comparison with the authentic racemates.



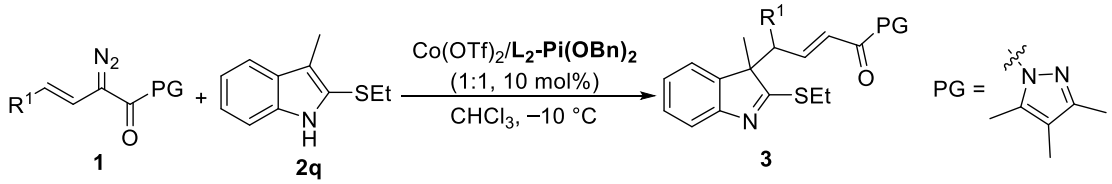
Procedure B: A dry reaction tube was charged with **L_2-Pi(O*i*Bu)$_2$** (7.6 mg, 10 mol%), $Ni(OTf)_2$ (3.6 mg, 10 mol%). Then $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, thioindole **2** (0.12 mmol) was added successively at 35 °C. Then transfer the reaction tube to –20 °C, diazo compound **1** (0.10 mmol) was added finally. The reaction was detected by TLC. After the diazo compound **1** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **3** (Pet/EtOAc = 15/1 to Pet/EtOAc = 7/1 as eluent). The product **3** was dissolved in 1.0 mL of CH_2Cl_2, *m*-CPBA (2.1 equiv) was added slowly. The reaction was stirred at room temperature for 30 min. To the mixture was added saturated aq. $NaHCO_3$ (3 mL) and the aqueous layer was separated and extracted with CH_2Cl_2 (3 mL × 2). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and

concentrated. The residue was purified by column chromatography on silica gel to afford the product **4** (Pet/EtOAc = 7/1 to Pet/EtOAc = 4/1 as eluent). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IA, Daicel chiralcel IE, Daicel chiralcel IF in comparison with the authentic racemates.

Procedure C: A dry reaction tube was charged with **L_2-Pi(O*i*Bu)$_2$** (7.6 mg, 10 mol%), $Ni(NTf_2)_2$ (6.2 mg, 10 mol%). Then $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, thioindole **2** (0.12 mmol) was added successively at 35 °C. Then transfer the reaction tube to –20 °C, diazo compound **1** (0.10 mmol) was added finally. The reaction was detected by TLC. After the diazo compound **1** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **3** (Pet/EtOAc = 15/1 to Pet/EtOAc = 7/1 as eluent). The product **3** was dissolved in 1.0 mL of CH_2Cl_2, *m*-CPBA (2.1 equiv) was added slowly. The reaction was stirred at room temperature for 30 min. To the mixture was added saturated aq. $NaHCO_3$ (3 mL) and the aqueous layer was separated and extracted with CH_2Cl_2 (3 mL × 2). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel to afford the product **4** (Pet/EtOAc = 7/1 to Pet/EtOAc = 4/1 as eluent). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IA, Daicel chiralcel IE, Daicel chiralcel IF in comparison with the authentic racemates.



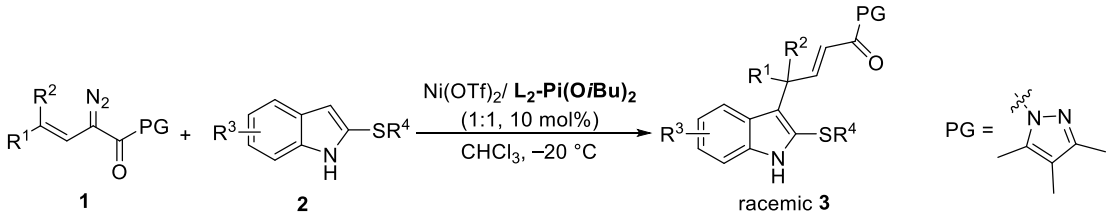
Procedure D: A dry reaction tube was charged with **L_2-Pi(O*i*Pr)$_2$** (7.0 mg, 10 mol%), $Ni(OTf)_2$ (3.6 mg, 10 mol%). Then $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, thioindole **2** (0.12 mmol) was added successively at 35 °C. Then transfer the reaction tube to –20 °C, diazo compound **1** (0.10 mmol) was added finally. The reaction was detected by TLC. After the diazo compound **1** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **3** (Pet/EtOAc = 15/1 to Pet/EtOAc = 7/1 as eluent). The product **3** was dissolved in 1.0 mL of CH_2Cl_2, *m*-CPBA (2.1 equiv) was added slowly. The reaction was stirred at room temperature for 30 min. To the mixture was added saturated aq. $NaHCO_3$ (3 mL) and the aqueous layer was separated and extracted with CH_2Cl_2 (3 mL × 2). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel to afford the product **4** (Pet/EtOAc = 7/1 to Pet/EtOAc = 4/1 as eluent). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IF in comparison with the authentic racemates.



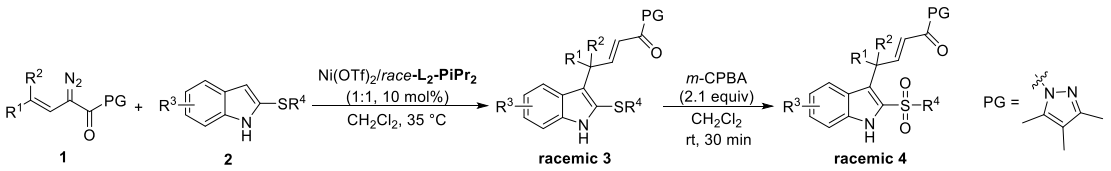
Procedure E: A dry reaction tube was charged with **L_2-Pi(OBn)$_2$** (8.9 mg, 10 mol%), $Co(OTf)_2$ (3.6 mg, 10 mol%). Then $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 35 °C for 30

minutes. Subsequently, thioindole **2q** (0.15 mmol) was added successively at 35 °C. Then transfer the reaction tube to –10 °C, diazo compound **1** (0.10 mmol) was added finally. The reaction was detected by TLC. After the diazo compound **1** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **3** (Pet/EtOAc = 20/1 to Pet/EtOAc = 15/1 as eluent). The dr value was determined by ^{1}H NMR analysis and the enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IA in comparison with the authentic racemates.

6.3 General procedure for the preparation of the racemic products

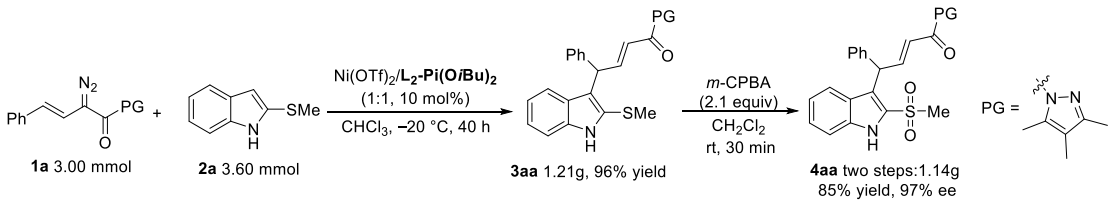


Procedure F: A dry reaction tube was charged with *race*- **L$_2$-PiPr$_2$** (6.3 mg, 10 mol%), Ni(OTf)$_2$ (3.6 mg, 10 mol%). Then CH_2Cl_2 (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, thioindole **2** (0.10 mmol) was added successively at 35 °C. Then transfer the reaction tube to 0 °C, diazo compound **1** (0.10 mmol) was added finally. The reaction was detected by TLC. After the diazo compound **1** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **3** (Pet/EtOAc = 15/1 to Pet/EtOAc = 7/1 as eluent). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IF.



Procedure G: A dry reaction tube was charged with *race*- **L$_2$-PiPr$_2$** (6.3 mg, 10 mol%), Ni(OTf)$_2$ (3.6 mg, 10 mol%). Then CH_2Cl_2 (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, thioindole **2** (0.10 mmol) was added successively at 35 °C. Then transfer the reaction tube to 0 °C, diazo compound **1** (0.10 mmol) was added finally. The reaction was detected by TLC. After the diazo compound **1** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **3** (Pet/EtOAc = 15/1 to Pet/EtOAc = 7/1 as eluent). The product **3** was dissolved in 1.0 mL of CH_2Cl_2, *m*-CPBA (2.1 equiv) was added slowly. The reaction was stirred at room temperature for 30 min. To the mixture was added saturated aq. $NaHCO_3$ (3 mL) and the aqueous layer was separated and extracted with CH_2Cl_2 (3 mL × 2). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel to afford the product **4** (Pet/EtOAc = 7/1 to Pet/EtOAc = 4/1 as eluent). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IA, Daicel chiralcel IE, Daicel chiralcel IF.

6.4 Procedure for the gram-scale of asymmetric [3,3]-rearrangement

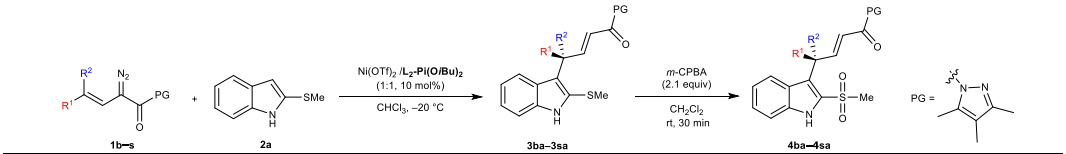


1a 3.00 mmol **2a** 3.60 mmol **3aa** 1.21g, 96% yield **4aa** two steps:1.14g 85% yield, 97% ee

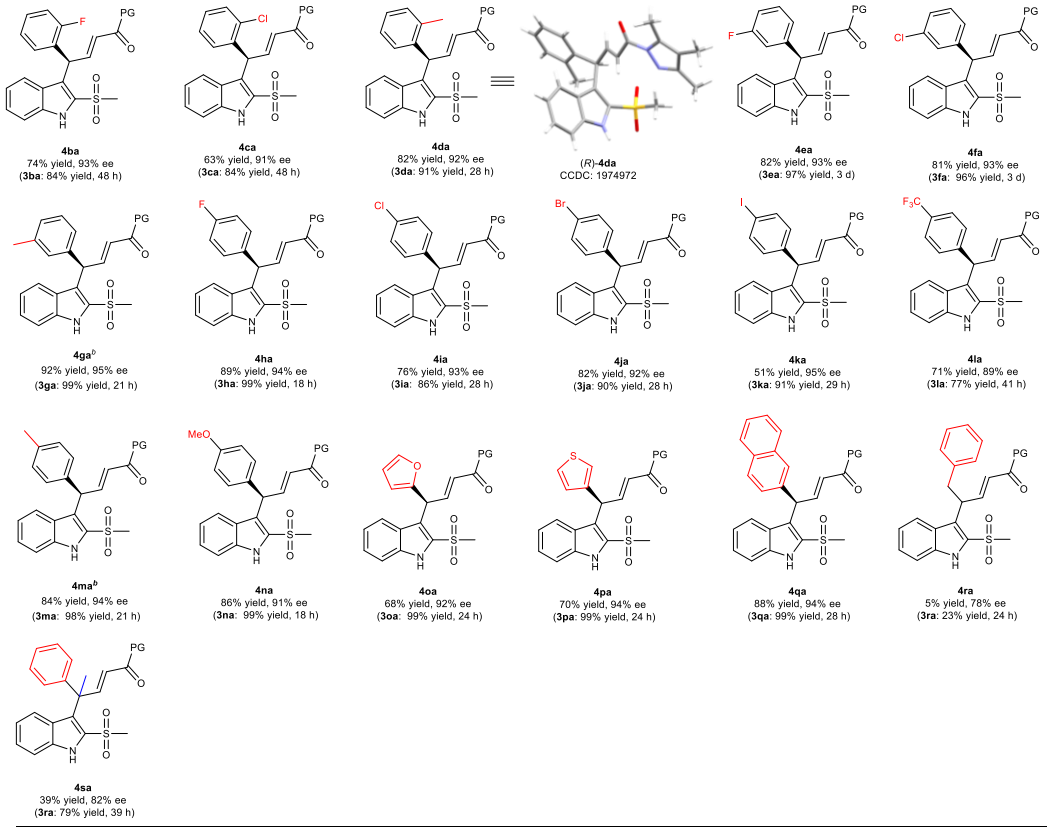
A 50 mL of dry round-bottom flask was charged with **L_2-Pi(O*i*Bu)$_2$** (226.5 mg, 10 mol%), $Ni(OTf)_2$ (106.8 mg, 10 mol%). Then $CHCl_3$ (15 mL) was added and the mixture was stirred at 35 °C for 10 hours. Subsequently, **2a** (586.8 mg, 3.60 mmol) was added successively at 35 °C. Then transfer the reaction flask to –20 °C, diazo compound **1a** (840.0 mg, 3.00 mmol) was added finally. After **1a** was fully consumed (40 hours), the residue was purified by column chromatography on silica gel to afford the product **3aa** as white solid (1.21 g, 96% yield). The product **3aa** was dissolved in 30 mL of CH_2Cl_2, *m*-CPBA (497.0 mg, 2.1 equiv) was added slowly. The reaction was stirred at room temperature for 30 min. To the mixture was added saturated aq. $NaHCO_3$ (30 mL) and the aqueous layer was separated and extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated.The residue was purified by column chromatography on silica gel to afford the product **4aa** as pale yellow solid (1.14 g, 85% yield, 97% ee).

7 The list of substrates scope

Table 7.1[a]



1b–s **2a** **3ba–3sa** **4ba–4sa**



4ba 74% yield, 93% ee (**3ba**: 84% yield, 48 h)

4ca 63% yield, 91% ee (**3ca**: 84% yield, 48 h)

4da 82% yield, 92% ee (**3da**: 91% yield, 28 h)

(*R*)-**4da** CCDC: 1974972

4ea 82% yield, 93% ee (**3ea**: 97% yield, 3 d)

4fa 81% yield, 93% ee (**3fa**: 96% yield, 3 d)

4ga[b] 92% yield, 95% ee (**3ga**: 99% yield, 21 h)

4ha 89% yield, 94% ee (**3ha**: 99% yield, 18 h)

4ia 76% yield, 93% ee (**3ia**: 86% yield, 28 h)

4ja 82% yield, 92% ee (**3ja**: 90% yield, 28 h)

4ka 51% yield, 95% ee (**3ka**: 91% yield, 29 h)

4la 71% yield, 89% ee (**3la**: 77% yield, 41 h)

4ma[b] 84% yield, 94% ee (**3ma**: 98% yield, 21 h)

4na 86% yield, 91% ee (**3na**: 99% yield, 18 h)

4oa 68% yield, 92% ee (**3oa**: 99% yield, 24 h)

4pa 70% yield, 94% ee (**3pa**: 99% yield, 24 h)

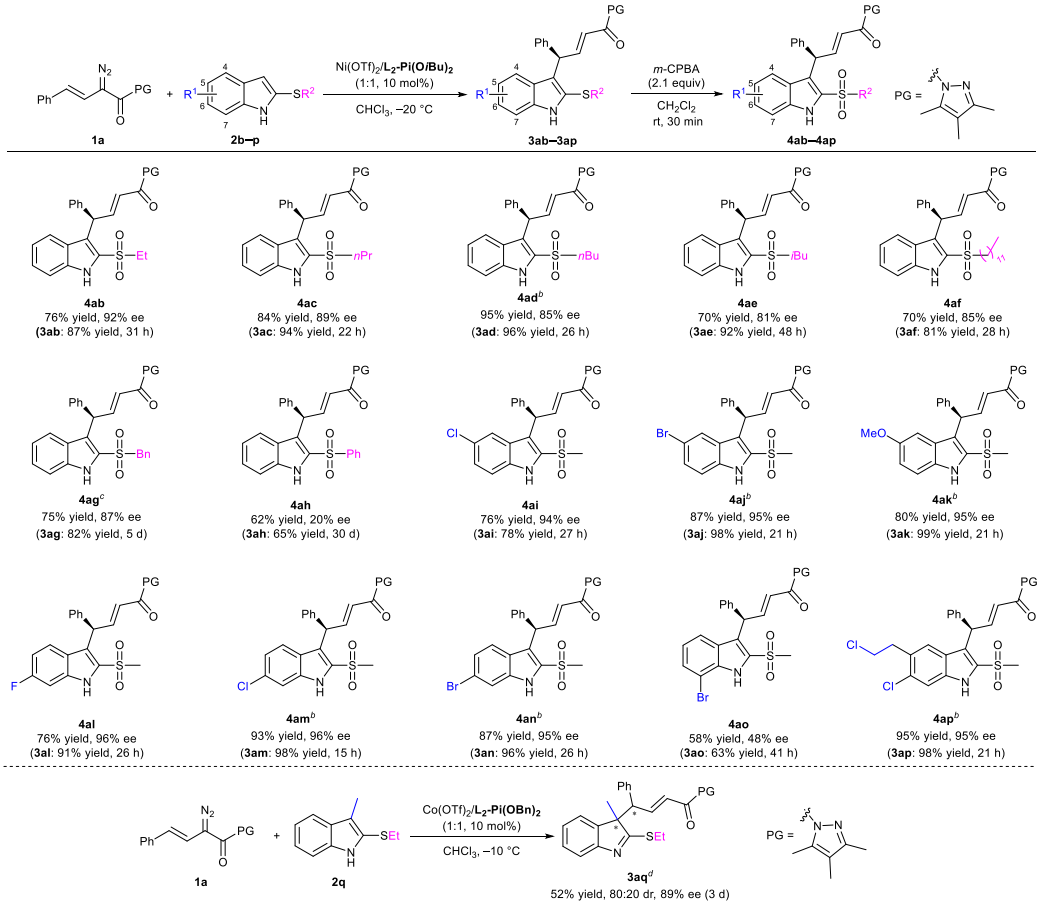
4qa 88% yield, 94% ee (**3qa**: 99% yield, 28 h)

4ra 5% yield, 78% ee (**3ra**: 23% yield, 24 h)

4sa 39% yield, 82% ee (**3ra**: 79% yield, 39 h)

[a] Unless otherwise noted, the initial reactions were carried out with **1** (0.10 mmol), **2a** (1.2 equiv), $Ni(OTf)_2$/**L_2-Pi(O*i*Bu)$_2$** (1:1, 10 mol%) in $CHCl_3$ (0.2 M) at –20 °C. Isolated yield of **3** and isolated yield of **4** after two steps. The ee value of **4** was determined by HPLC analysis on a chiral stationary phase. [b] $Ni(NTf_2)_2$ was used instead of $Ni(OTf)_2$.

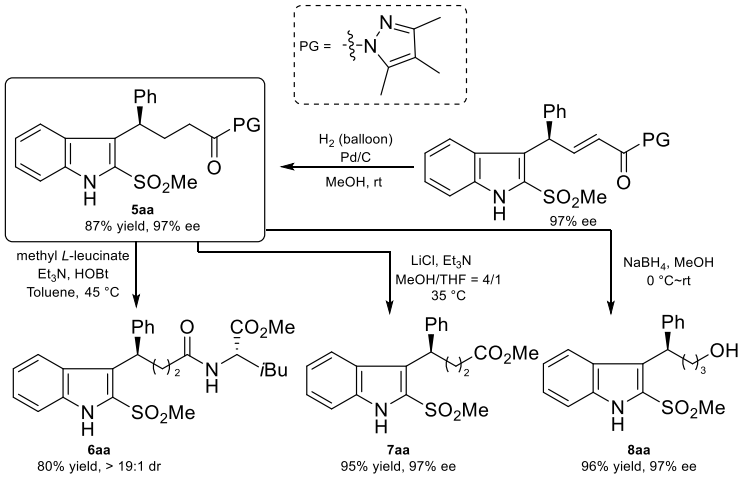
Table 7.2[a]



[a] Unless otherwise noted, the initial reactions were carried out with **1a** (0.10 mmol), **2** (1.2 equiv), $Ni(OTf)_2$/**L_2-Pi(O*i*Bu)$_2$** (1:1, 10 mol%) in $CHCl_3$ (0.2 M) at –20 °C. Isolated yield of **3** and isolated yield of **4** after two steps. The ee value of **4** was determined by HPLC analysis on a chiral stationary phase. [b] $Ni(NTf_2)_2$ was used instead of $Ni(OTf)_2$. [c] **L_2-Pi(O*i*Pr)$_2$** was used instead of **L_2-Pi(O*i*Bu)$_2$**. [d] The reaction was carried out with **1a** (0.10 mmol), **2q** (1.5 equiv), $Co(OTf)_2$/**L_2-Pi(OBn)$_2$** (1:1, 10 mol%) in $CHCl_3$ (0.2 M) at –10 °C. Isolated yield of **3aq**. The dr value was determined by ^1H NMR analysis and the ee value was for the major diastereoisomer.

8 Procedure for the transformation of product 3aa and 4aa

8.1 Transformation of product 4aa



8.1.1 Reduction of 4aa to 5aa

A dry tube was charged with 10% Pd/C (8.9 mg), **4aa** (0.20 mmol, 89.4 mg), then, MeOH (1.0 mL) was added. The mixture was stirred at room temperature for 24 h under an H_2 atmosphere. The reaction mixture was filtered with a pad of celite and the filtrate was concentrated in vacuo, the residue was purified by column chromatography on silica gel to afford the corresponding product **5aa** (Pet/EtOAc = 7/1 to Pet/EtOAc = 4/1 as eluent) as white solid (78.1 mg, 87% yield). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IC, in comparison with the authentic racemates.

8.1.2 Direct amidation with *L*-leucine methyl ester hydrochloride

According to literature report[9], *L*-leucin methyl ester hydrochlorid (18.2 mg, 2.0 equiv), toluene (0.5 mL), and Et_3N (13 μL, 2.0 equiv) was added into a reaction tube equipped with a stirring bar. After stirred at room temperature for 10 min, **5aa** (22.5 mg, 0.05 mmol), 1-hydroxybenzotriazole (14 mg, 2.0 equiv), and toluene (0.5 mL) was added continuously. Then the tube was sealed and heated at 45 °C for 5 days. The mixture was concentrated under reduced pressure and the crude residue was purified by silica gel column chromatography to give product **6aa** ((Pet/EtOAc = 4/1 to Pet/EtOAc = 2/1 as eluent) as white solid (19.4 mg, 80% yield). The diastereoselectivity was determined by ^1H NMR analysis.

8.1.3 Esterification

According to literature report[9], **5aa** (22.5 mg, 0.05 mmol), MeOH (0.4 mL) and THF (0.1 mL), LiCl (10.6 mg, 5.0 equiv), and Et_3N (34 μL, 5.0 equiv) was added in sequence to a dry tube equipped with a stirring bar. After stirred at 35 °C for 24 hours, the mixture was concentrated under reduced pressure and the crude residue was purified by silica gel column chromatography to give product **7aa** ((Pet/EtOAc = 7/1 to Pet/EtOAc = 4/1 as eluent) as white solid (17.6 mg, 95% yield). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IE, in comparison with the authentic racemates.

8.1.4 Reduction to alcohol

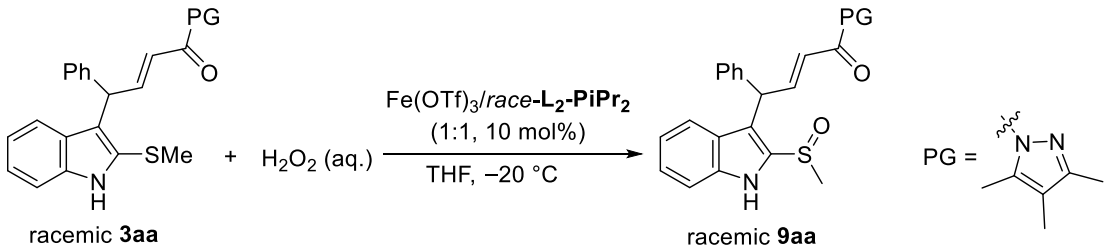
According to literature report[10], to a solution of **5aa** (64.2 mg, 0.14 mmol) in MeOH (1.0 mL) was added $NaBH_4$ (42.3 mg, 8.0 equiv) at 0 °C and the mixture was stirred overnight at room temperature. After quenching with 1.0 M HCl, the resultant mixture was extracted with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4. After evaporation of the organic solvent under reduced pressure, the crude mixture was purified by silica gel column chromatography to give

product **8aa** ((Pet/EtOAc = 4/1 to Pet/EtOAc = 1/1 as eluent) as white solid (47.1 mg, 96% yield). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IC, in comparison with the authentic racemates.

8.2 Transformation of product 3aa to chiral sulfoxide 9aa

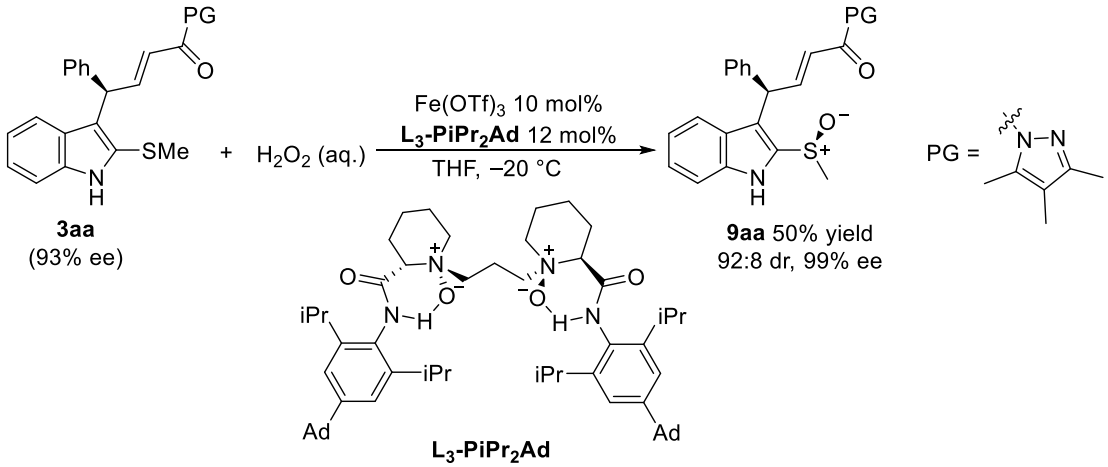
The sulfoxide were synthesized according to our previous work[9].

8.2.1 Procedure for the preparation of the racemic sulfoxide 9aa



A dry reaction tube was charged with racemic **L_2-PiPr$_2$** (3.2 mg, 10 mol%), $Fe(OTf)_3$ (2.5 mg, 10 mol%). Then THF (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, racemic sulfide **3aa** (20.7 mg, 0.05 mmol) was added successively at 35 °C. Transfer the reaction tube to -20 °C, then 10% H_2O_2 (25 μL, 5.0 equiv) was added finally. The reaction was detected by TLC. The reaction mixture was diluted by 2 ml H_2O, and extracted by EtOAc. The organic phase was passed through anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to afford the corresponding racemic sulfoxide 9**aa** (Pet/EtOAc = 4/1 to Pet/EtOAc = 1/2 as eluent) as white solid (8.6 mg, 40% yield).

8.2.2 Procedure for the preparation of the chiral sulfoxide 9aa

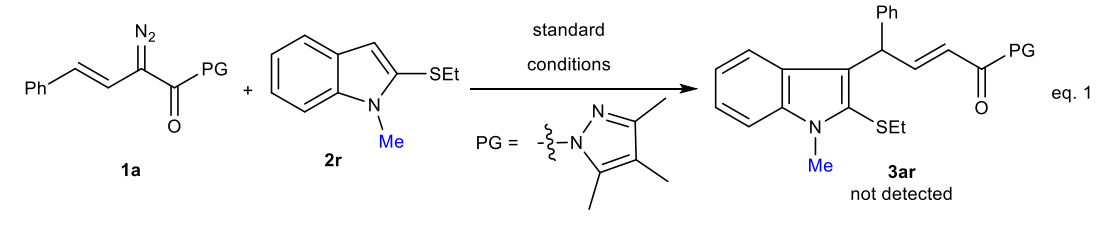


A dry reaction tube was charged with **L_3-PiPr$_2$Ad** (5.5 mg, 12 mol%), $Fe(OTf)_3$ (2.5 mg, 10 mol%). Then THF (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, sulfide **3aa** (20.7 mg, 0.05 mmol) was added successively at 35 °C. Then transfer the reaction tube to –20 °C, then 10% H_2O_2 (25 μL, 5.0 equiv) was added finally. The reaction was detected by TLC. The reaction mixture was diluted by 2 ml H_2O, and extracted by EtOAc. The organic phase was passed through anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to afford the corresponding sulfoxide **9aa** (Pet/EtOAc = 4/1 to Pet/EtOAc = 1/2 as eluent) as white solid (10.8 mg, 50% yield). The dr value

was determined by ^{1}H NMR analysis and the enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel ID in comparison with the authentic racemates.

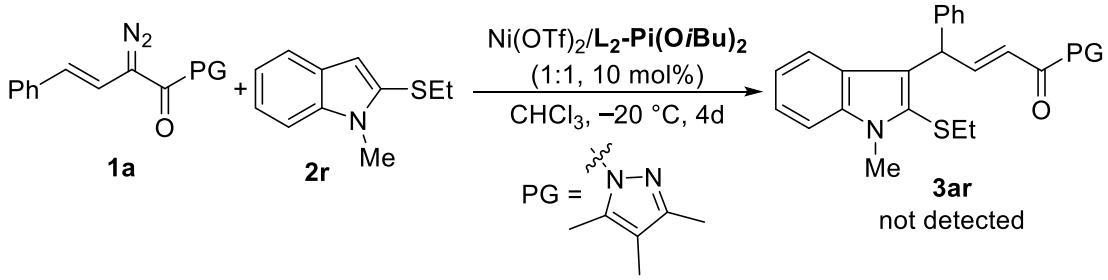
9 Control experiments and mechanistic studies

To verify the proton transfer process in this reaction, the 1-methyl-2-(methylthio)-1*H*-indole **2r** was subjected to the standard conditions, but the reaction resulted in a mixture with a large residue of the substrates, and **3ar** was not detected (eq. 1). It suggested the significant role of the N-H unit in forming the key sulfonium ylide intermediate through proton transfer. Furthermore, the *N*-deuterium-labeled indole **2a** was used to probe into the proton shift process (eq. 2). We carried out the experiments in dry solvent without additional water, and only minor deuterium labeled product was obtained. When trace amount of H_2O (around 1.5 equiv) was added, the product was found nearly non-deuterium. However, the *d*-**3aa** product was found to be the major one if D_2O was used instead. When non-deuterium **2a** with D_2O were used in the reaction, the *d*-**3aa** product was also detected. The results indicated the trace amount of water in the system might be in charge of proton-transfer.



		additives	Results
(a)	91% D	none	87% yield, 77% ee, 15% D
(b)	91% D	H_2O (3.0 μL)	87% yield, 69% ee, 0% D
(c)	91% D	D_2O (3.0 μL)	90% yield, 68% ee, 64% D
(d)	0% D	D_2O (3.0 μL)	86% yield, 69% ee, 50% D

9.1 The enantioselective thio-Claisen rearrangement reaction of α-diazo pyrazoleamides 1a and 2-(ethylthio)-1-methyl-1*H*-indole 2r



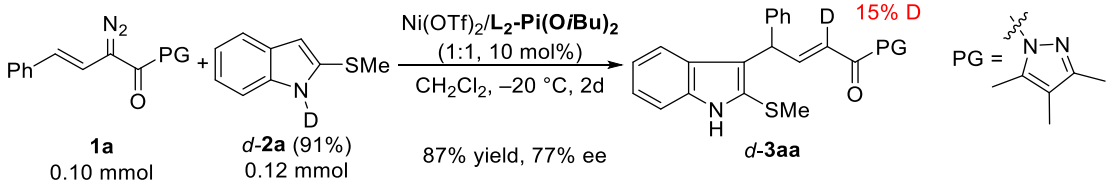
Procedure: A dry reaction tube was charged with **L_2-Pi(O*i*Bu)$_2$** (7.6 mg, 10 mol%), $Ni(OTf)_2$ (3.6 mg, 10 mol%), then $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, 2-(methylthio)-1*H*-indole **2r** (0.12 mmol, 1.2 equiv) was added successively at 35 °C.

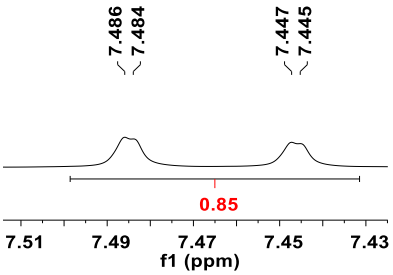
Then transfer the reaction tube to –20 °C, diazo compound **1a** (0.10 mmol) was added finally. The reaction was stirred at –20 °C and detected by TLC. The desired product **3ar** could not be detected.

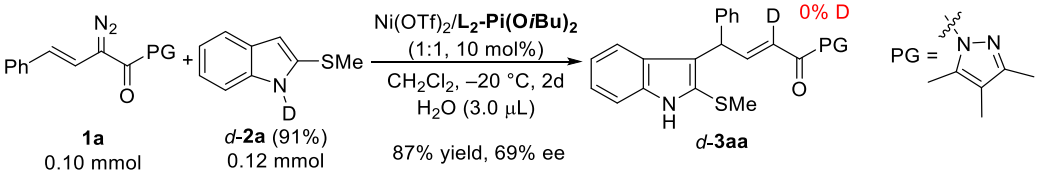
9.2 Deuterium labeled experiments

To gain insight into the mechanism of the asymmetric thio-Claisen rearrangement reaction, the deuterium-labeled experiments were performed according to the equations shown below. After distilled from CaH_2, the solvent CH_2Cl_2 was treated without water or oxygen and dried over 4 Å MS, which was activited at 600 °C for 1 hour before use. All the substrates and reaction solvent were added to the reaction tube in the glove box under an N_2 atmosphere at room temperature.

Procedure: A dry reaction tube was charged with **L_2-Pi(O*i*Bu)$_2$** (7.6 mg, 10 mol%) and $Ni(OTf)_2$ (3.6 mg, 10 mol%) in the glove box under an N_2 atmosphere. Then CH_2Cl_2 (0.5 mL) was added and the mixture was stirred at room temperature for 30 minutes. Subsequently, 2-(methylthio)-1*H*-indole **2a**-*d* (0.12 mmol, 1.2 equiv) and diazo compound **1a** (0.10 mmol) was added successively. Then transfer the reaction tube to –20 °C, the additive (around 1.5 equiv) was added finally. After the diazo compound **1a** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product. The deuterium-lablled ratios the products were detected by ^{1}H NMR.





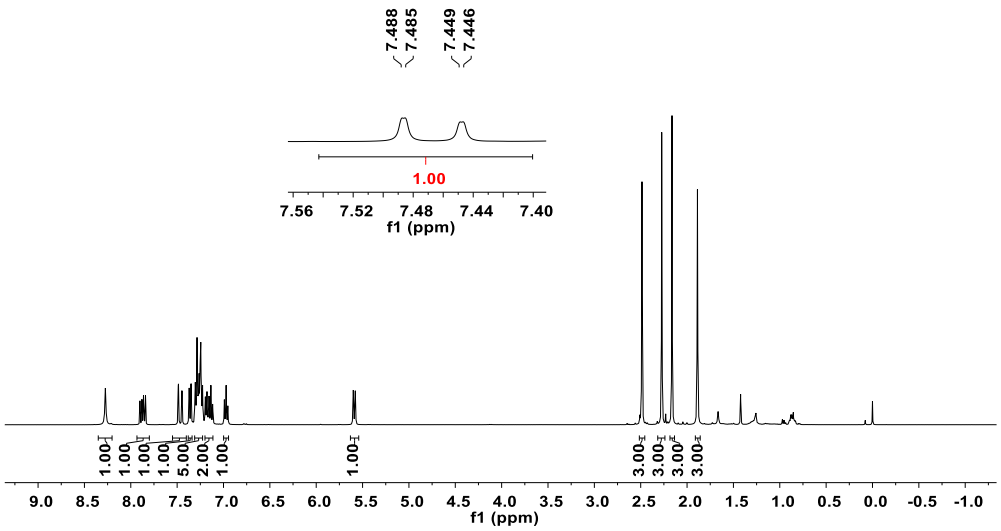


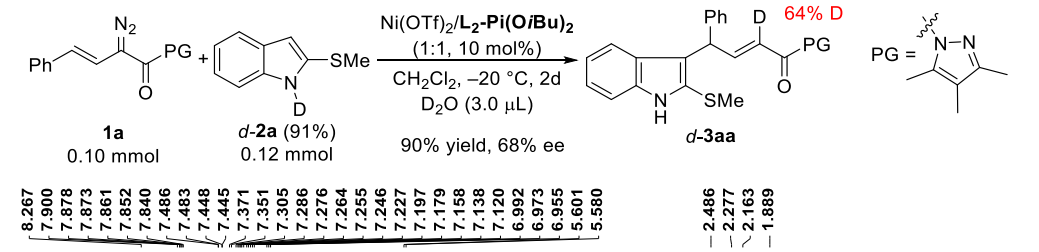
1a
0.10 mmol

d-**2a** (91%)
0.12 mmol

87% yield, 69% ee

d-**3aa**



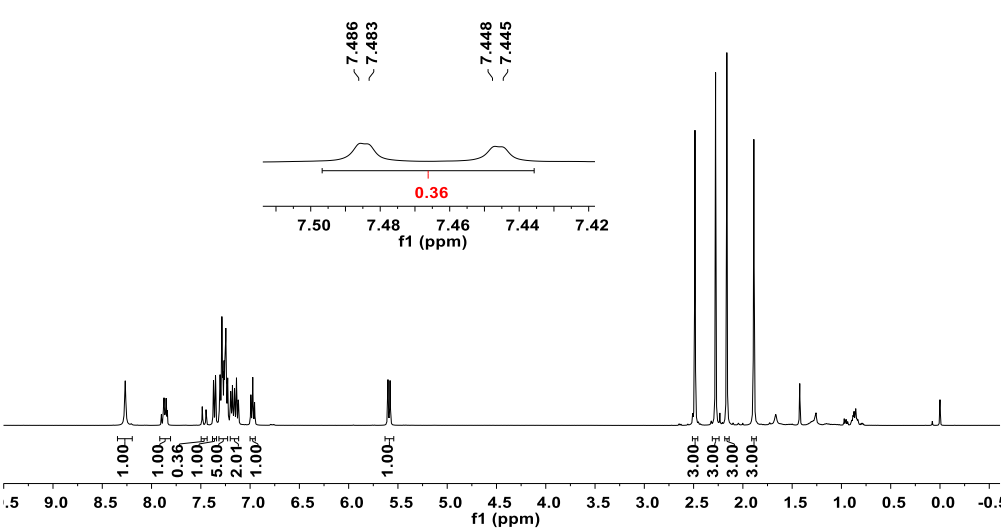


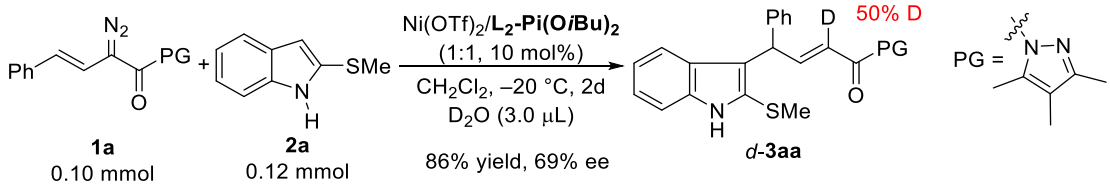
1a
0.10 mmol

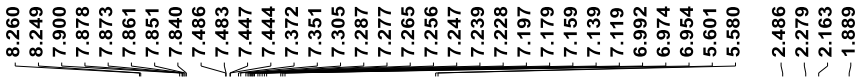
d-**2a** (91%)
0.12 mmol

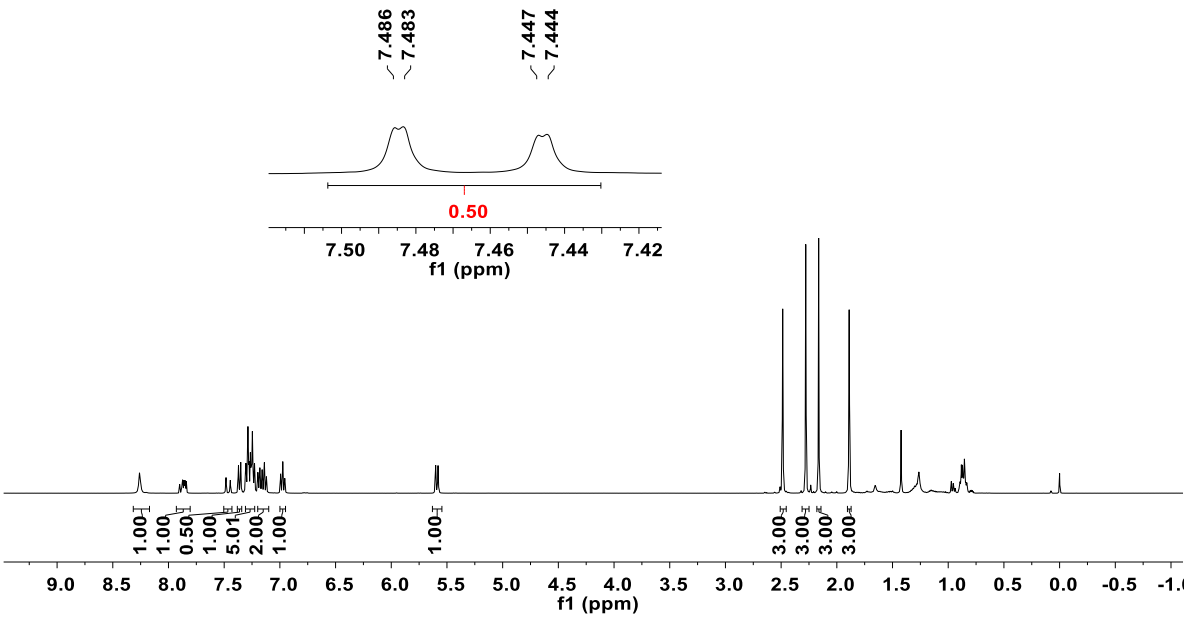
90% yield, 68% ee

d-**3aa**

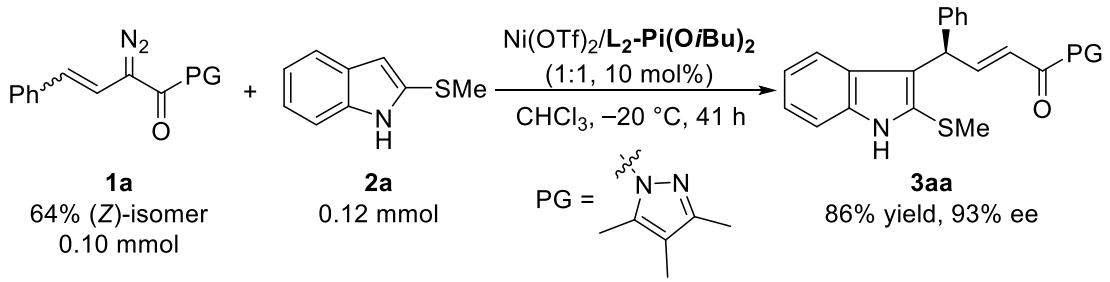






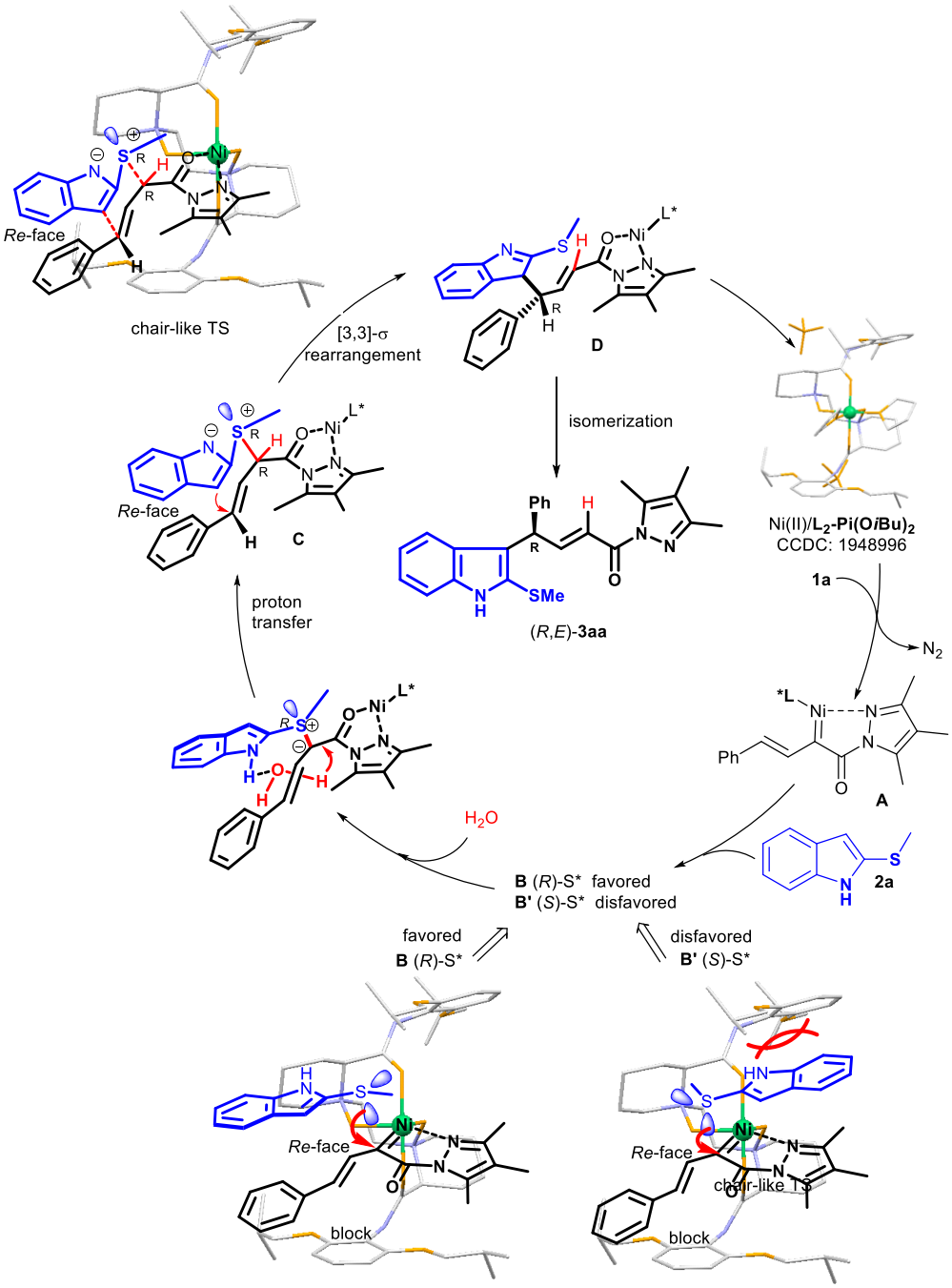


9.3 The enantioselective thio-Claisen rearrangement reaction of (*Z*/*E*)-2-diazo-4-phenyl-1-(3,4,5-trimethyl-1*H*pyrazol-1-yl)but-3-en-1-one and 2-(methylthio)-1*H*-indole 2a



Procedure: A dry reaction tube was charged with **L_2-Pi(O*i*Bu)$_2$** (7.6 mg, 10 mol%), $Ni(OTf)_2$ (3.6 mg, 10 mol%), then $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, 2-(methylthio)-1*H*-indole **2a** (0.12 mmol, 1.2 equiv) was added successively at 35 °C. Then transfer the reaction tube to –20 °C, diazo compound **1a** (0.10 mmol, *Z*/*E* = 1.77/1) was added finally. The reaction was stirred at –20 °C and detected by TLC. The desired product **3aa** was obtained in 86% yield with 93% ee. The enantioselectivity (ee) of product **3aa** was determined by high performance liquid chromatography (HPLC) with chiralcel IF in comparison with the authentic racemates.

9.4 Proposed catalytic model



10 X-ray crystal structure

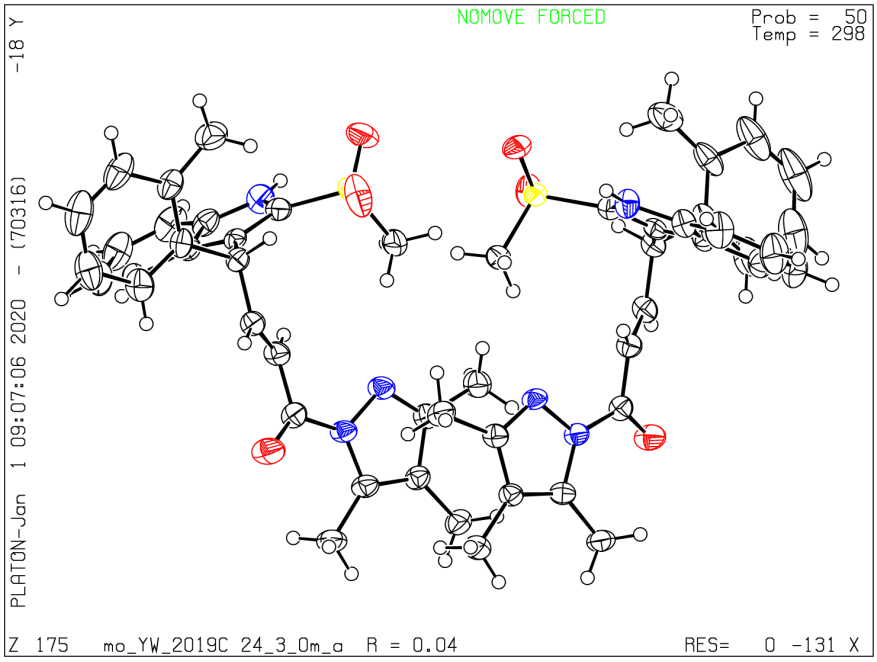


Figure S1. X-ray Crystal Structure of product **4da**

The crystal of product **4da** was obtained in the solvents of THF and n-hexane. CCDC 1974972 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/.

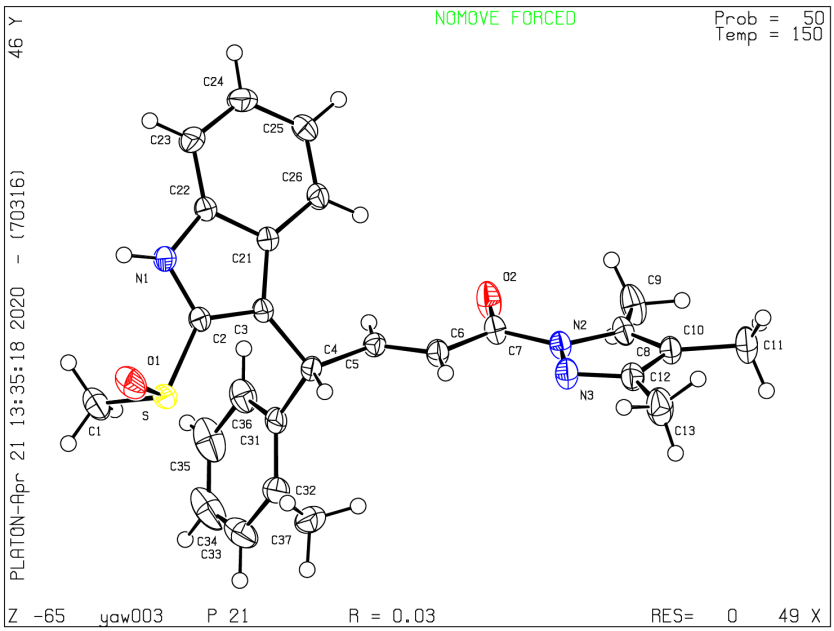
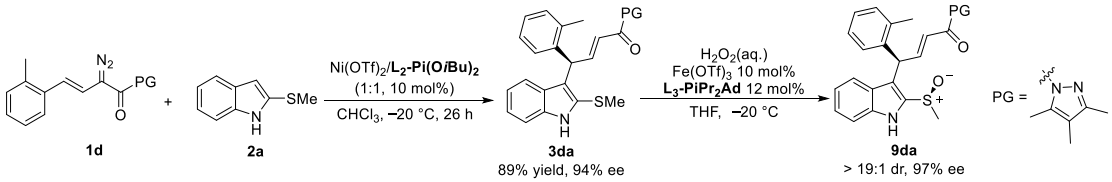


Figure S2. X-ray Crystal Structure of chiral sulfoxide **9da**

The crystal of product **4da** was obtained in the solvents of THF, Et_2O and n-hexane. CCDC 1998226 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/.

Note: The chiral sulfoxide **9da** could be obtained through the following procedure.



Step 1: A dry reaction tube was charged with **L_2-Pi(O*i*Bu)$_2$** (7.6 mg, 10 mol%), $Ni(OTf)_2$ (3.6 mg, 10 mol%). Then $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, sulfide **2a** (0.12 mmol) was added successively at 35 °C. Then transfer the reaction tube to –20 °C, diazo compound **1d** (0.10 mmol) was added finally. The reaction was detected by TLC. After the diazo compound **1d** was fully consumed (detected by TLC), the residue was purified by column chromatography on silica gel to afford the product **3da** as white solid (38.3 mg, 89% yield). The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IF in comparison with the authentic racemates.

Step 2: A dry reaction tube was charged with **L_3-PiPr$_2$Ad** (12 mol%), $Fe(OTf)_3$ (10 mol%). Then THF (0.5 mL) was added and the mixture was stirred at 35 °C for 30 minutes. Subsequently, sulfide **3da** (38 mg, 0.088 mmol) was added successively at 35 °C. Then transfer the reaction tube to –20 °C, then 10% H_2O_2 (5.0 equiv) was added finally. The reaction was detected by TLC. The reaction mixture was diluted by 2 ml H_2O, and extracted by EtOAc. The organic phase was passed through anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to afford the corresponding sulfoxide **9da** as white solid (33.1 mg, 84% yield). The dr value was determined by ^1H NMR analysis and the enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with Daicel chiralcel IB in comparison with the authentic racemates.

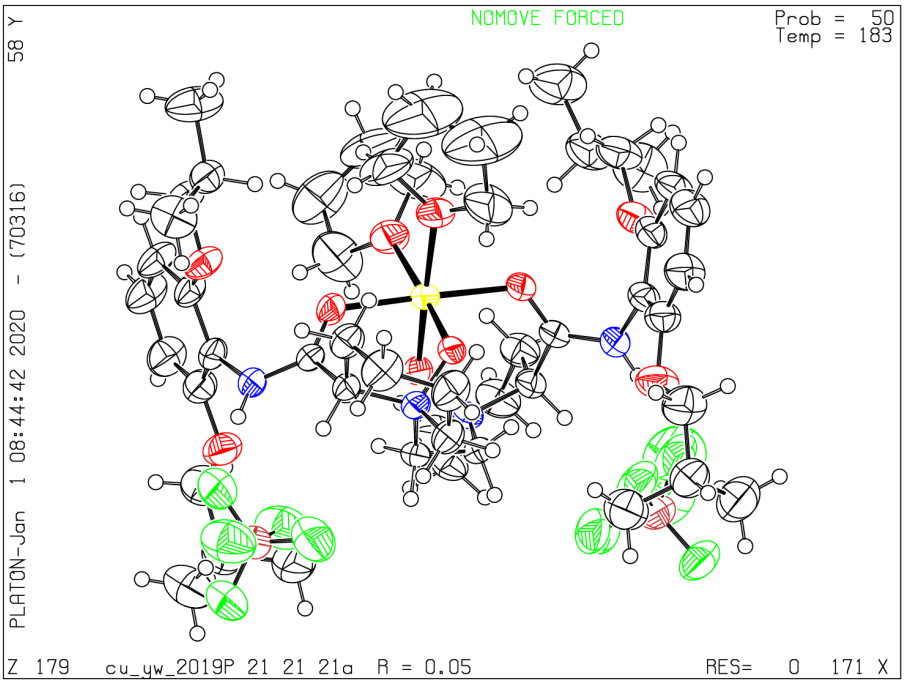
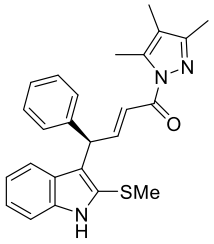


Figure S3. X-ray Crystal Structure of the chiral nickel(II) complex

The crystal of **L_2-Pi(O*i*Bu)$_2$**/$Ni(BF_4)_2 \cdot 6H_2O$ complex was obtained in the solvents of THF and *n*-hexane. CCDC 1948996 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/.

11 Spectral characterization data and HPLC conditions for the products

(*R*,*E*)-4-(2-(methylthio)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (3aa)



Following the typical procedure A.

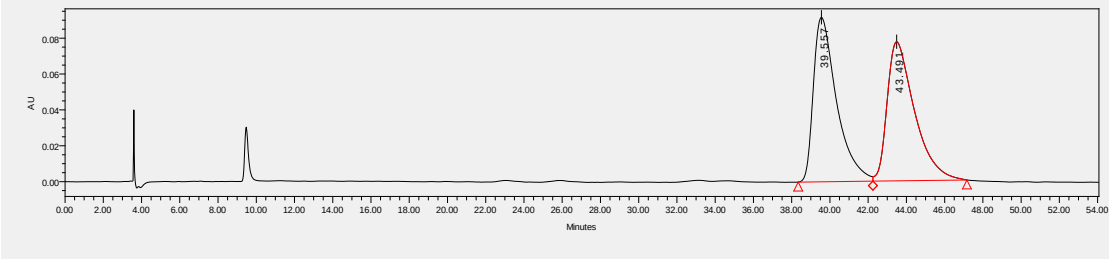
39.1 mg, 94% yield; white solid; M.p. 49-52 °C. R_f = 0.3 (Pet/EtOAc = 10/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (minor) = 39.490 min, t (major) = 42.727 min. ee = 96%. $[\alpha]^{22}_D$ = +24.2 (*c* = 0.48, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.87 (dd, *J* = 15.2, 8.4 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.23 (m, 5H), 7.20 – 7.11 (m, 2H), 7.00 – 6.96 (m, 1H), 5.59 (d, *J* = 8.8 Hz, 1H), 2.48 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H), 1.89 (s, 3H).

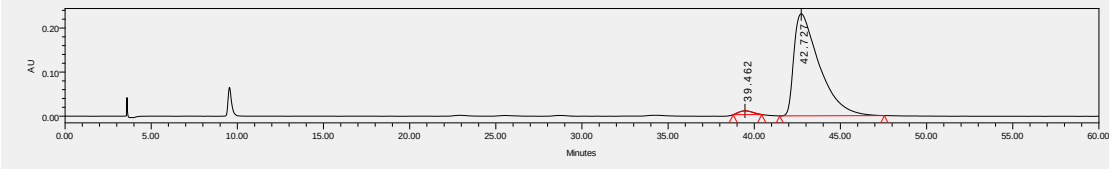
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 165.1, 152.1, 150.4, 141.7, 139.8, 136.7, 128.4, 128.0, 127.8, 126.5, 126.4, 122.9, 122.3, 120.5, 120.4, 119.9, 117.7, 110.8, 45.5, 20.2, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{26}N_3OS^+$ ([M + H]$^+$) = 416.1791, found 416.1786.

IR (neat): 1692, 1633, 1491, 1427, 1381, 1353, 1008, 742, 702 cm^{-1}.

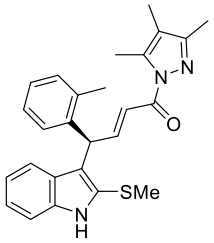


	Retention Time	Area	% Area
1	39.557	7723154	50.09
2	43.491	7693910	49.91



	Retention Time	Area	% Area
1	39.490	481744	2.02
2	42.727	23361773	97.98

(*R*,*E*)-4-(2-(methylthio)-1*H*-indol-3-yl)-4-(o-tolyl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (3da)



Following the typical procedure A.

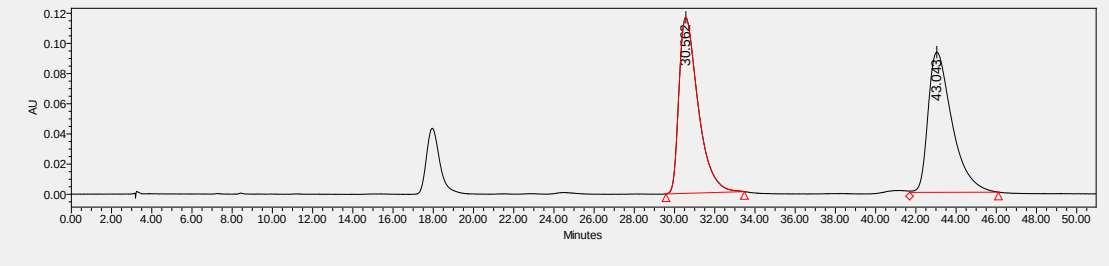
38.3 mg, 89% yield; white solid; M.p. 163-167 °C. R_f = 0.3 (Pet/EtOAc = 10/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (minor) = 30.931 min, t (major) = 42.863 min. ee = 94%. $[\alpha]^{21}_D$ = +34.9 (*c* = 0.76, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 7.83 (dd, *J* = 15.6, 7.6 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.31 – 7.24 (m, 2H), 7.16 – 7.08 (m, 4H), 6.98 – 6.94 (m, 1H), 5.64 – 5.62 (m, 1H), 2.49 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H), 2.12 (s, 3H), 1.88 (s, 3H).

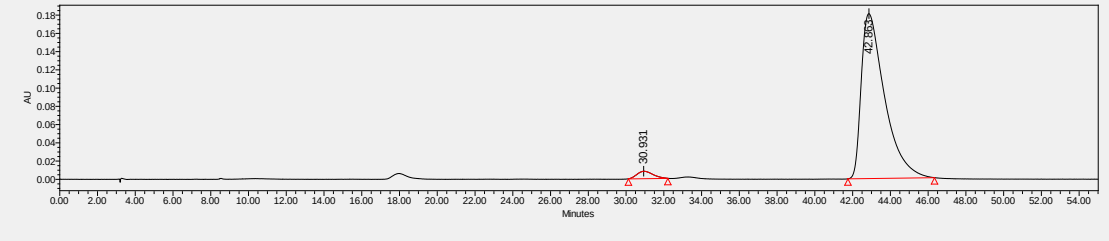
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 165.3, 152.1, 151.2, 140.0, 139.7, 136.54, 136.50, 130.5, 128.3, 127.7, 127.1, 126.7, 125.9, 122.7, 121.7, 120.1, 119.8, 119.7, 117.6, 110.7, 43.2, 19.8, 19.6, 12.8, 12.3, 7.7.

ESI-HRMS: calcd for $C_{26}H_{28}N_3OS^+$ ([M + H]$^+$) = 430.1948, found 430.1943.

IR (neat): 2923, 1683, 1631, 1426, 1008, 939, 740 cm^{-1}.

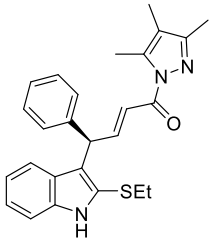


	Retention Time	Area	% Area
1	30.562	7704479	50.07
2	43.043	7683614	49.93



	Retention Time	Area	% Area
1	30.931	482922	3.02
2	42.863	15509772	96.98

(*R*,*E*)-4-(2-(ethylthio)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (3ab)



Following the typical procedure A.

37.3 mg, 87% yield; white solid; M.p. 50-55 °C. R_f = 0.3 (Pet/EtOAc = 10/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (minor) = 32.048 min, t (major) = 36.759 min. ee = 92%. $[\alpha]^{22}_D$ = +20.0 (*c* = 0.60, in CH_2Cl_2).

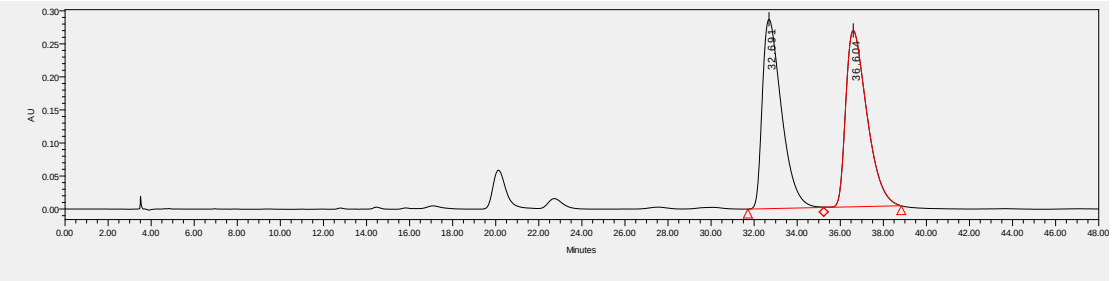
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.84 (dd, J = 15.6, 8.4 Hz, 1H), 7.47 – 7.43 (m,

1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.23 (m, 5H), 7.21 – 7.13 (m, 2H), 7.00 – 6.96 (m, 1H), 5.60 (d, *J* = 8.4 Hz, 1H), 2.71 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 2.16 (s, 3H), 1.89 (s, 3H), 1.18 (t, *J* = 7.3 Hz, 3H).

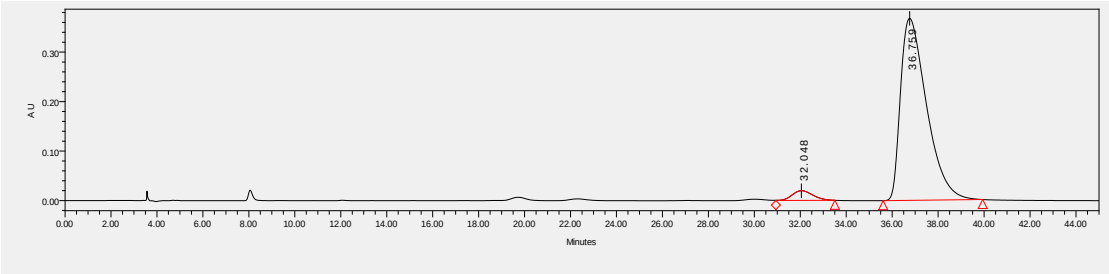
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 165.1, 152.1, 150.3, 141.7, 136.7, 128.3, 128.0, 126.4, 126.3, 122.9, 122.4, 121.3, 120.5, 119.7, 117.7, 110.7, 45.5, 31.1, 15.4, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{26}H_{28}N_3OS^+$ ([M + H]$^+$) = 430.1948, found 430.1946.

IR (neat): 1687, 1633, 1491, 1445, 1380, 1353, 1284, 1008, 939, 742, 701 cm^{-1}.

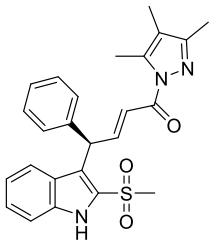


	Retention Time	Area	% Area
1	32.691	17808082	49.44
2	36.604	18208111	50.56



	Retention Time	Area	% Area
1	32.048	1180800	3.92
2	36.759	28942559	96.08

(*R*,*E*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4aa)



Following the typical procedure B.

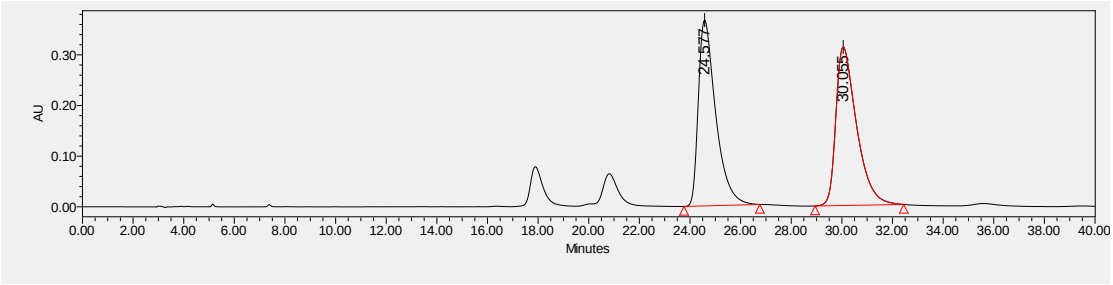
38.9 mg, 87% yield; white solid; M.p. 105-110 °C. R_f= 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel**IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 24.292 min, t (minor) = 29.860 min. ee = 96%. $[\alpha]^{17}_D$ = +81.4 (*c* = 0.69, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.78 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.32– 7.26 (m, 4H), 7.26 – 7.19 (m, 2H), 7.06 – 7.02 (m, 1H), 6.01 (d, *J* = 8.0 Hz, 1H), 3.04 (s, 3H), 2.47 (s, 3H), 2.13 (s, 3H), 1.88 (s, 3H).

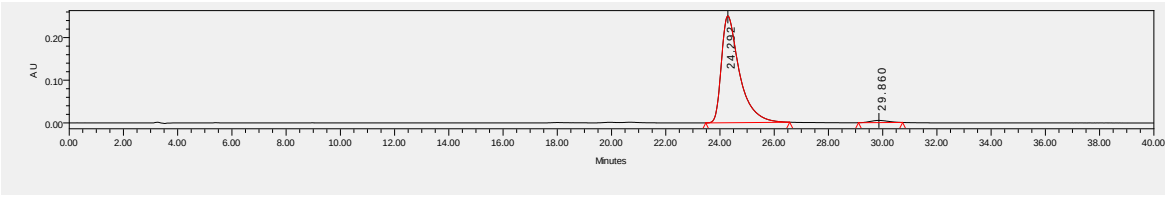
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.4 148.4, 140.4, 139.7, 136.0, 129.2, 128.6, 128.0, 126.9, 126.2, 126.0, 123.7, 122.8, 121.4, 121.3, 118.0, 112.5, 45.4, 43.6, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{26}N_3O_3S^+$ ([M + H]$^+$) = 448.1689, found 448.1693.

IR (neat): 1696, 1635, 1381, 1353, 1310, 1187, 1143, 1089, 1007, 958, 70, 701, 523, 432 cm^{-1}.

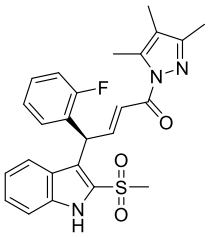


	Retention Time	Area	% Area
1	24.577	17498224	49.64
2	30.055	17750350	50.36



	Retention Time	Area	% Area
1	24.292	11578376	98.01
2	29.860	234710	1.99

(*R*,*E*)-4-(2-fluorophenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ba)



Following the typical procedure B.

34.2 mg, 74% yield; white solid; M.p. 102-106 °C. R_f = 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 27.239 min, t (minor) = 37.359 min. ee = 93%. $[\alpha]^{22}_D$ = +69.0 (*c* = 0.62, in CH_2Cl_2). 7

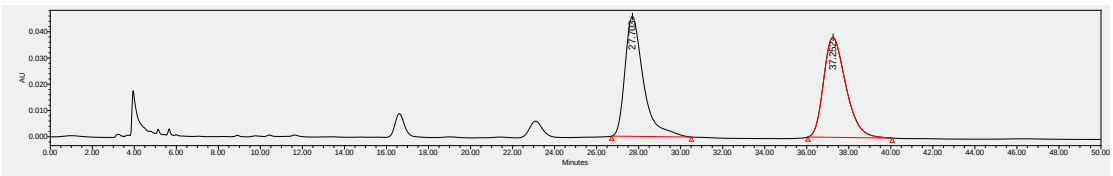
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.77 (dd, *J* = 15.6, 7.6 Hz, 1H), 7.54 – 7.52 (m, 1H), 7.47 – 7.38 (m, 3H), 7.33 – 7.29 (m, 1H), 7.26 – 7.21 (m, 1H), 7.14 – 6.97 (m, 3H), 6.19 (d, *J* = 7.6 Hz, 1H), 3.08 (s, 3H), 2.47 (s, 3H), 2.11 (s, 3H), 1.88 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 160.7 (d, *J* = 246.2 Hz), 152.4, 147.3, 139.7, 135.8, 129.7 (d, *J* = 3.7 Hz), 129.1 (d, *J* = 8.4 Hz), 128.8, 127.8 (d, *J* = 13.6 Hz), 126.3, 126.1, 124.2 (d, *J* = 3.5 Hz), 123.6, 122.3, 121.5, 120.2, 117.9, 115.8 (d, *J* = 21.6 Hz), 112.6, 45.2, 38.2, 12.7, 12.3, 7.7.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -114.53.

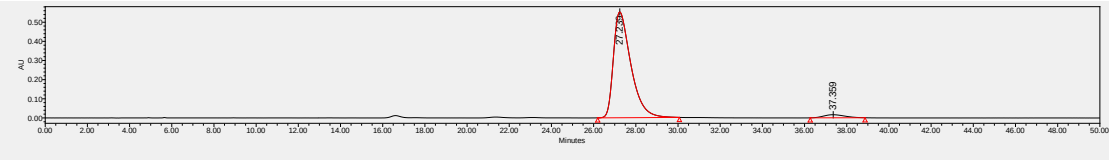
ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3FS^+$ ([M + H]$^+$) = 466.1595, found 466.1595.

IR (neat): 1705, 1695, 1380, 1353, 1339, 1139, 914, 752, 524 cm^{-1}.



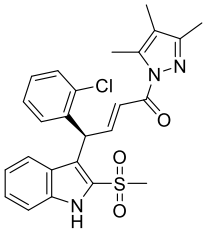
	Retention Time	Area	% Area

1	27.703	2778541	49.83
2	37.252	2797254	50.17



	Retention Time	Area	% Area
1	27.239	31694850	96.59
2	37.359	1117628	3.41

(*S*,*E*)-4-(2-chlorophenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ca)



Following the typical procedure B.

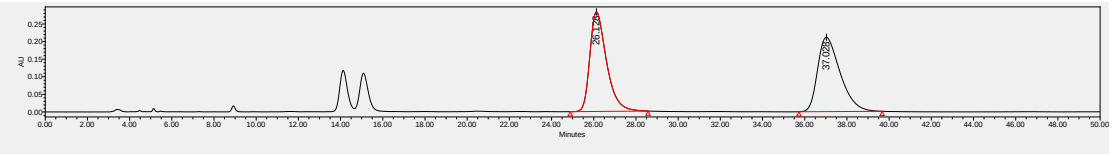
30.4 mg, 63% yield; white solid; M.p. 118-123 °C. R_f = 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 26.044 min, t (minor) = 37.556 min. ee = 91%. $[\alpha]^{22}_D$ = –16.0 (*c* = 0.52, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.36 (s, 1H), 7.70 (dd, *J* = 15.6, 7.2 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.45 – 7.39 (m, 2H), 7.38 – 7.28 (m, 3H), 7.24 – 7.18 (m, 2H), 7.08 – 7.04 (m, 1H), 6.26 (dd, *J* = 7.2, 1.6 Hz, 1H), 2.90 (s, 3H), 2.46 (s, 3H), 2.10 (s, 3H), 1.86 (s, 3H).

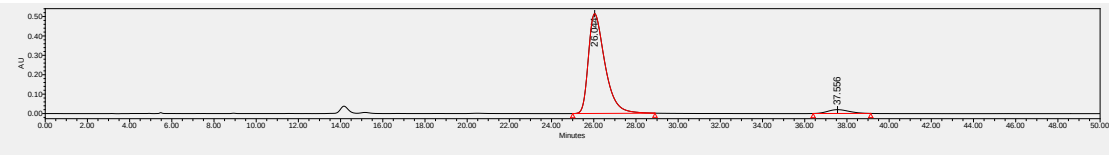
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.5, 147.9, 139.7, 138.1, 135.7, 134.4, 130.1, 130.1, 129.1, 128.7, 127.0, 126.9, 126.1, 123.6, 122.3, 121.6, 120.0, 117.9, 112.6, 44.8, 41.8, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{35}ClS^+$ ([M + H]$^+$) = 482.1300, found 482.1304. $C_{25}H_{25}N_3O_3{}^{37}ClS^+$ ([M + H]$^+$) = 484.1270, found 484.1277.

IR (neat): 1695, 1635, 1380, 1352, 1315, 1189, 1137, 1004, 958, 940, 745, 524, 503, 431 cm^{-1}.

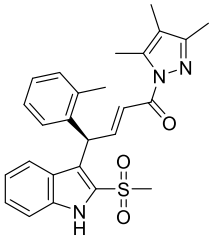


	Retention Time	Area	% Area
1	26.128	15525662	49.81
2	37.028	15642912	50.19



	Retention Time	Area	% Area
1	26.044	27945125	95.28
2	37.556	1383496	4.72

(*R*,*E*)-4-(2-(methylsulfonyl)-1H-indol-3-yl)-4-(o-tolyl)-1-(3,4,5-trimethyl-1H-pyrazol-1-yl)but-2-en-1-one (4da)



Following the typical procedure B.

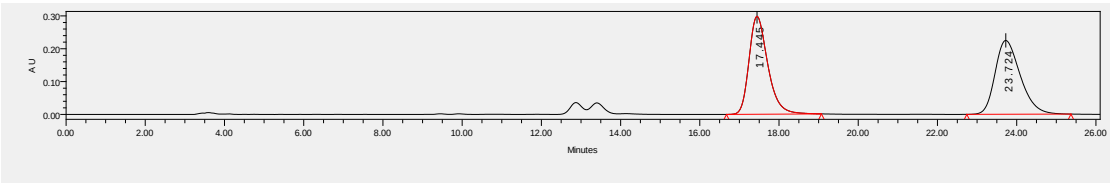
37.8 mg, 82% yield; white solid; M.p. 174-180 °C. R_f= 0.3 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 17.638 min, t (minor) = 24.729 min. ee = 92%. $[\alpha]^{19}_D$ = +11.5 (*c* = 0.75, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 7.76 (dd, *J* = 15.6, 6.8 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.19 – 7.12 (m, 3H), 7.08 – 7.04 (m, 1H), 6.13 (dd, *J* = 7.2, 1.6 Hz, 1H), 2.81 (s, 3H), 2.49 (s, 3H), 2.29 (s, 3H), 2.12 (s, 3H), 1.89 (s, 3H).

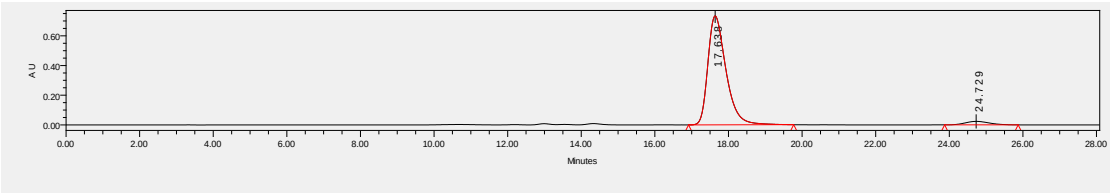
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.9, 152.39, 149.29, 139.7, 138.8, 137.3, 135.7, 130.9, 128.5, 128.3, 127.3, 127.0, 126.1, 123.1 , 122.7, 121.5, 121.2, 117.9, 112.4, 44.6, 41.5, 19.7, 19.7, 12.7, 12.3, 7.6.

ESI-HRMS: calcd for $C_{26}H_{28}N_3O_3S^+$ ($[M + H]^+$) = 462.1846, found 462.1850.

IR (neat): 2361, 2310, 1681, 1624, 1385, 1356, 1314, 1274, 1138, 758, 747 cm^{-1}.

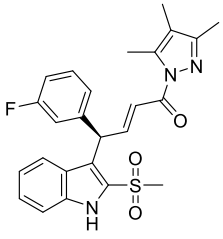


	Retention Time	Area	% Area
1	17.445	9799732	49.73
2	23.724	9907150	50.27



	Retention Time	Area	% Area
1	17.638	24956247	95.94
2	24.729	1056782	4.06

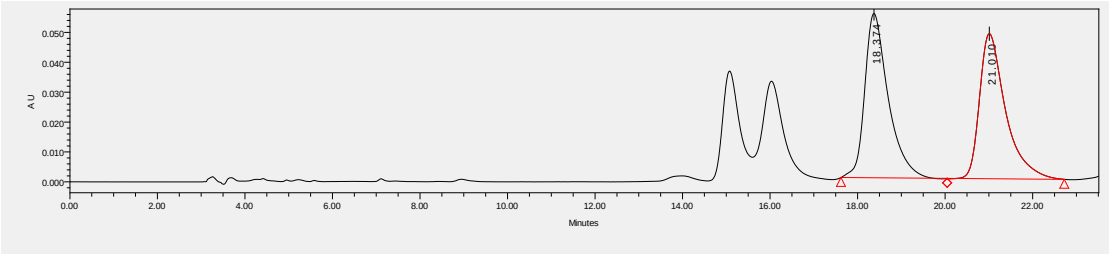
(*R*,*E*)-4-(3-fluorophenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ea)



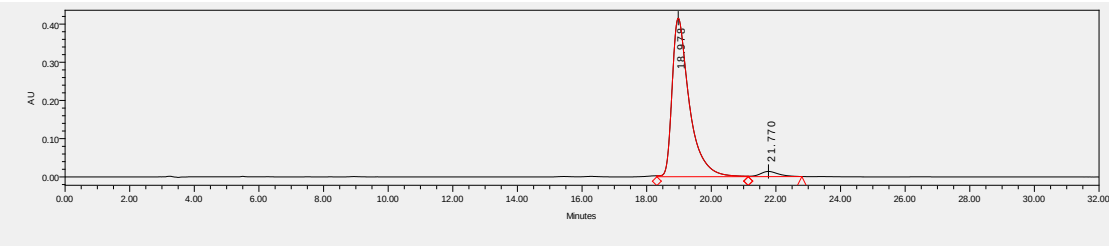
Following the typical procedure B.

38.2 mg, 82% yield; white solid; M.p. 104-107 °C. R_f = 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 18.978 min, t (minor) = 21.770 min. ee = 93%. $[\alpha]^{18}_D$ = +82.8 (*c* = 0.69, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.38 (s, 1H), 7.71 (dd, *J* = 15.2, 8.4 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.39 (m, 1H), 7.33 – 7.29 (m, 1H), 7.24 – 7.20 (m, 1H), 7.10 – 7.03 (m, 2H), 7.02 – 6.98 (m, 1H), 6.93 – 6.89 (m, 1H), 6.00 (d, *J* = 8.4 Hz, 1H), 3.09 (s, 3H), 2.47 (s, 3H), 2.13 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.6, 162.9 (d, *J* = 245.0 Hz), 152.6, 147.3, 142.9 (d, *J* = 6.8 Hz), 139.7, 136.0, 130.1 (d, *J* = 8.2 Hz), 129.3, 126.3, 125.7, 124.2, 123.7 (d, *J* = 2.9 Hz), 122.6, 121.6, 120.6, 118.1, 115.0 (d, *J* = 22.2 Hz), 113.9 (d, *J* = 20.9 Hz), 112.6, 45.6, 43.2 (d, *J* = 1.8 Hz), 12.7, 12.3, 7.7.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -112.39.
ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3FS^+$ ([M + H]$^+$) = 466.1595, found 466.1591.
IR (neat): 1696, 1381, 1353, 1312, 1136, 1007, 957, 937, 747, 523, 432 cm^{-1}.

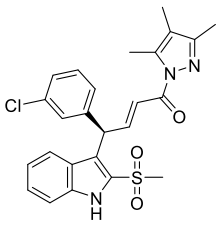


	Retention Time	Area	% Area
1	18.374	2050728	50.63
2	21.010	1999398	49.37



	Retention Time	Area	% Area
1	18.978	15326409	96.67
2	21.770	527544	3.33

(*R*,*E*)-4-(3-chlorophenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4fa)

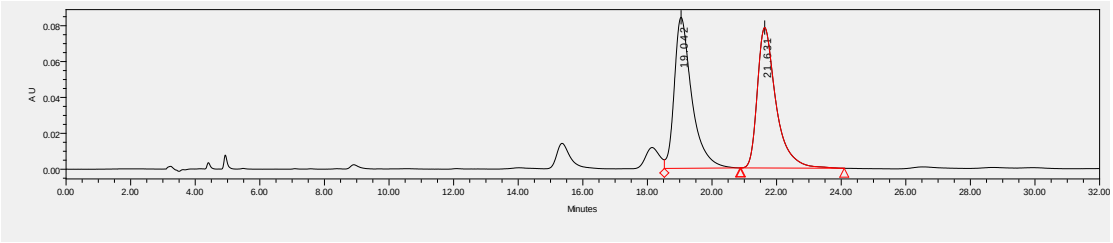


Following the typical procedure B.
39.0 mg, 81% yield; white solid; M.p. 111-115 °C. R_f = 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 18.162 min, t (minor) = 20.999 min. ee = 93%. $[\alpha]^{19}_D$ = +88.0 (*c* = 0.75, in CH_2Cl_2).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.41 (s, 1H), 7.72 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.42 – 7.40 (m, 1H), 7.35 – 7.30 (m, 2H), 7.22 – 7.18 (m, 3H), 7.10 – 7.05 (m, 1H), 6.01 (d, *J* = 8.4, 1H), 3.11 (s, 3H), 2.49 (s, 3H), 2.15 (s, 3H), 1.90 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.6, 152.6, 147.2, 142.5, 139.7, 136.0, 134.5, 129.8, 129.3, 128.0, 127.2, 126.3, 126.2, 125.7, 124.2, 122.5, 121.6, 120.5, 118.1 112.7, 45.6, 43.2, 12.7,

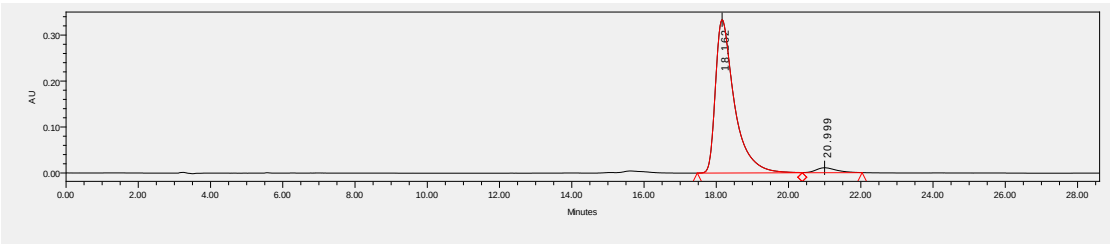
12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{35}ClS^+$ ([M + H]$^+$) = 482.1300, found 482.1304. $C_{25}H_{25}N_3O_3{}^{37}ClS^+$ ([M + H]$^+$) = 484.1270, found 484.1275.

IR (neat): 1696, 1636, 1426, 1381, 1353, 1312, 1187, 1144, 1087, 1006, 959, 831, 787, 744, 682, 523 cm^{-1}.

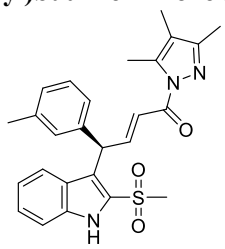


	Retention Time	Area	% Area
1	19.042	3165185	50.21
2	21.631	3138827	49.79



	Retention Time	Area	% Area
1	18.162	12103848	96.58
2	20.999	428117	3.42

(*R*,*E*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-(m-tolyl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ga)



Following the typical procedure C.

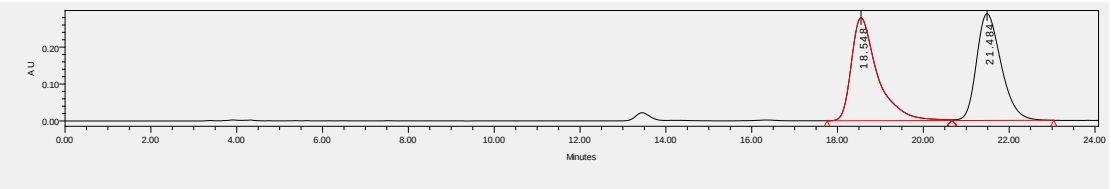
42.6 mg, 92% yield; white solid; M.p. 94-100 °C. R_f = 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 18.350 min, t (minor) = 21.557 min. ee = 95%. $[\alpha]^{18}_D$ = +80.9 (*c* = 0.47, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.16 (s, 1H), 7.78 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.34 – 7.30 (m, 1H), 7.18 – 7.13 (m, 2H), 7.11 – 7.02 (m, 3H), 5.98 (d, *J* = 8.4 Hz, 1H), 3.07 (s, 3H), 2.49 (s, 3H), 2.28 (s, 3H), 2.15 (s, 3H), 1.89 (s, 3H).

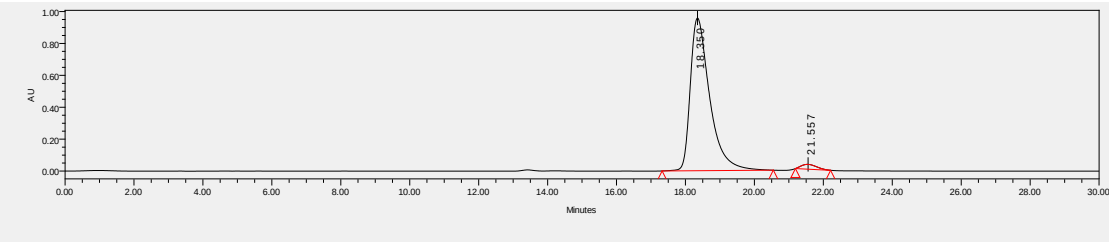
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.4, 148.5, 140.3, 139.7, 138.2, 136.0, 129.3, 128.7, 128.4, 127.7, 126.2 , 126.1, 125.0, 123.6, 122.9, 121.5, 121.4, 117.9, 112.5, 45.5, 43.6, 21.5, 12.7, 12.3, 7.6.

ESI-HRMS: calcd for $C_{26}H_{28}N_3O_3S^+$ ([M + H]$^+$) = 462.1846, found 462.1850.

IR (neat): 1696, 1636, 1380, 1352, 1311, 1128, 1142, 1089, 1007, 958, 750, 702, 523, 433 cm^{-1}.

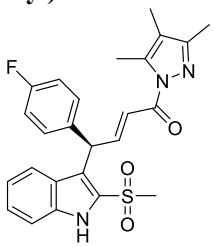


	Retention Time	Area	% Area
1	18.548	11782411	50.61
2	21.484	11497594	49.39



	Retention Time	Area	% Area
1	18.350	37298051	97.54
2	21.557	939831	2.46

(*R*,*E*)-4-(4-fluorophenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ha)



Following the typical procedure B.

41.5 mg, 89% yield; white solid; M.p. 100-105 °C. R_f = 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 16.412 min, t (minor) = 21.238 min. ee = 94%. $[\alpha]^{26}_D$ = +68.7 (*c* = 0.67, in CH_2Cl_2).

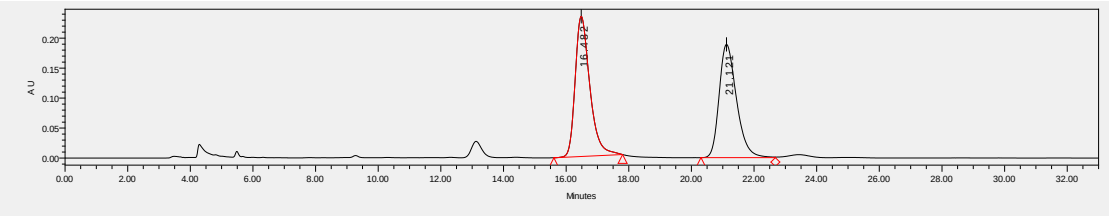
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.36 (s, 1H), 7.73 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.35 – 7.25 (m, 3H), 7.08 – 7.04 (m, 1H), 7.00 – 6.91 (m, 2H), 5.99 (d, *J* = 8.4 Hz, 1H), 3.09 (s, 3H), 2.48 (s, 3H), 2.15 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.7, 161.7 (d, *J* = 244.3 Hz), 152.5, 148.0, 139.7, 136.1 (d, *J* = 3.4 Hz), 136.0, 129.6 (d, *J* = 7.9 Hz), 129.3, 126.3, 125.8, 123.9, 122.7, 121.5, 121.1, 118.0, 115.4 (d, *J* = 21.2 Hz), 112.6, 45.5, 42.9, 12.6, 12.3, 7.6.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -115.68.

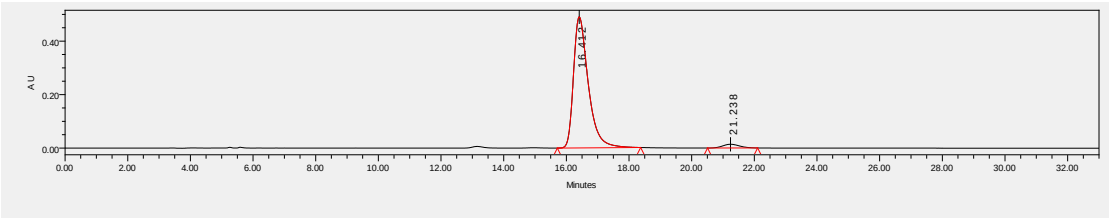
ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3FS^+$ ([M + H]$^+$) = 466.1595, found 466.1606.

IR (neat): 1697, 1636, 1505, 1381, 1353, 1312, 1224, 1144, 1090, 1008, 959, 824, 746, 523 cm^{-1}.



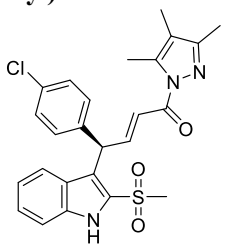
	Retention Time	Area	% Area

1	16.482	7595627	51.12
2	21.121	7262678	48.88



	Retention Time	Area	% Area
1	16.412	16041092	96.87
2	21.238	518703	3.13

(*R*,*E*)-4-(4-chlorophenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ia)



Following the typical procedure B.

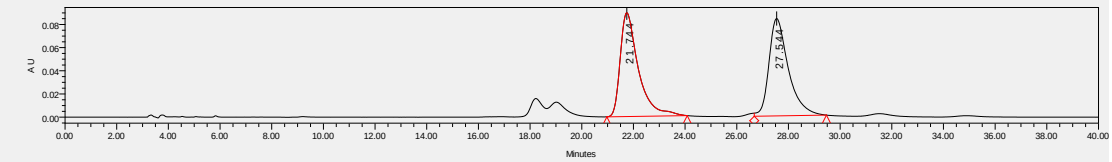
36.6 mg, 76% yield; white solid; M.p. 114-120 °C. R_f= 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 21.546 min, t (minor) = 27.640 min. ee = 93%. $[\alpha]^{19}_D$ = +67.5 (*c* = 0.73, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 7.72 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.41 – 7.39 (m, 1H), 7.35 – 7.31 (m, 1H), 7.26 – 7.24 (m, 4H), 7.09 – 7.04 (m, 1H), 5.98 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.10 (s, 3H), 2.48 (s, 3H), 2.15 (s, 3H), 1.90 (s, 3H).

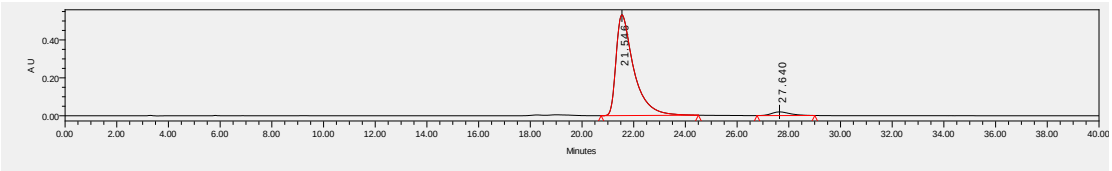
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.6, 152.6, 147.5, 139.7, 138.9, 136.0, 132.8, 129.3, 129.3, 128.7, 126.3, 125.7, 124.1, 122.6, 121.6, 120.7, 118.1, 112.6, 45.6, 42.9, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{35}ClS^+$ ([M + H]$^+$) = 482.1300, found 482.1305. $C_{25}H_{25}N_3O_3{}^{37}ClS^+$ ([M + H]$^+$) = 484.1270, found 482.1274.

IR (neat): 1696, 1636, 1489, 1380, 1353, 1311, 1279, 1186, 1144, 1090, 1008, 958, 940, 818, 750, 522 cm^{-1}.

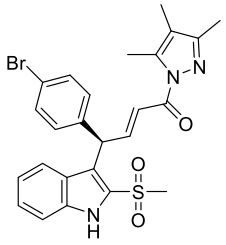


	Retention Time	Area	% Area
1	21.744	4368813	49.96
2	27.544	4375791	50.04



	Retention Time	Area	% Area
1	21.546	25231568	96.34
2	27.640	959913	3.66

(*R*,*E*)-4-(4-bromophenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ja)



Following the typical procedure B.

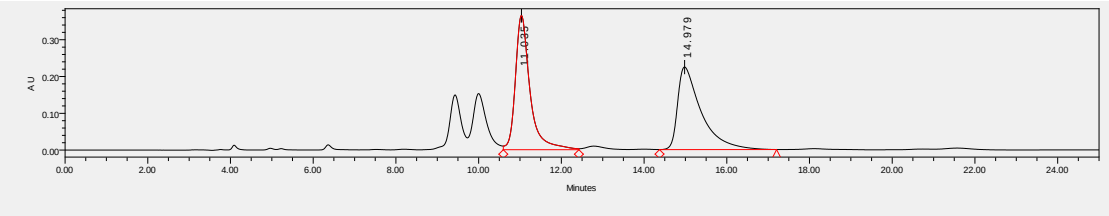
43.1 mg, 82% yield; white solid; M.p. 125-130 °C. R_f= 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 11.039 min, t (minor) = 14.767 min. ee = 92%. $[\alpha]^{24}_D$ = +55.8 (*c* = 0.76, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.36 (s, 1H), 7.71 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.51 – 7.38 (m, 5H), 7.35 – 7.30 (m, 1H), 7.20 – 7.18 (m, 2H), 7.10 – 7.03 (m, 1H), 5.97 (d, *J* = 8.4 Hz, 1H), 3.11 (s, 3H), 2.48 (s, 3H), 2.15 (s, 3H).

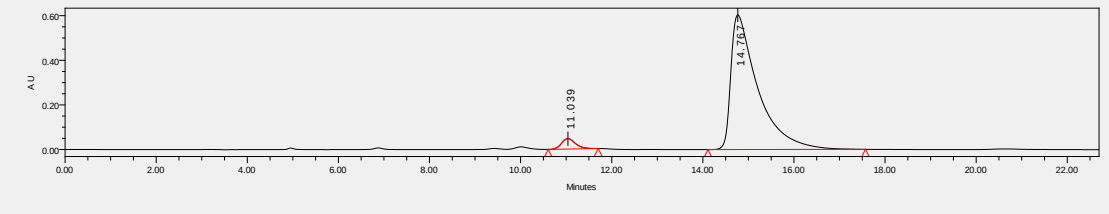
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.6, 152.6, 147.4, 139.7, 139.5, 136.1, 131.7, 129.7, 129.4, 126.4, 125.7, 124.2, 122.6, 121.6, 121.0 , 120.7, 118.1, 112.7, 45.6, 43.0, 12.6, 12.3, 7.6.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{79}BrS^+$ ([M + H]$^+$) = 526.0795, found 526.0801. $C_{25}H_{25}N_3O_3{}^{81}BrS^+$ ([M + H]$^+$) = 528.0774, found 528.0780.

IR (neat): 2361, 2354, 1696, 1636, 1380, 1353, 1310, 1144, 1007, 959 cm^{-1}.

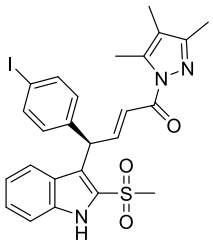


	Retention Time	Area	% Area
1	11.035	9003009	50.37
2	14.979	8869137	49.63



	Retention Time	Area	% Area
1	11.039	997561	3.86
2	14.767	24839138	96.14

(*R*,*E*)-4-(4-iodophenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ka)



Following the typical procedure B.

29.5 mg, 51% yield; pale yellow solid; M.p. 130-136 °C. R_f = 0.2 (Pet/EtOAc = 4/1).

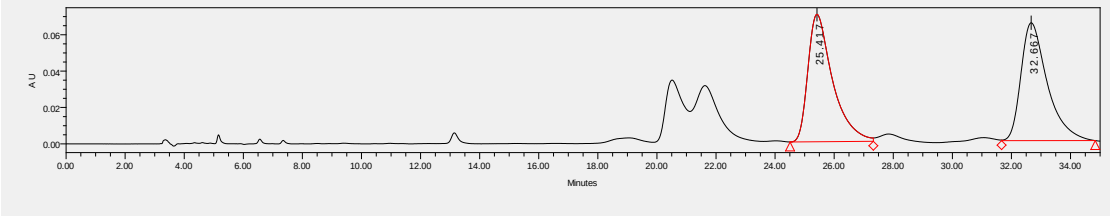
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 25.110 min, t (minor) = 32.542 min. ee = 95%. $[\alpha]^{23}_D$ = +47.3 (*c* = 0.64, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.70 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.50 – 7.40 (m, 3H), 7.35 – 7.31 (m, 1H), 7.10 – 7.05 (m, 3H), 5.96 (d, J = 8.4 Hz, 1H), 3.10 (s, 3H), 2.48 (s, 3H), 2.15 (s, 3H).

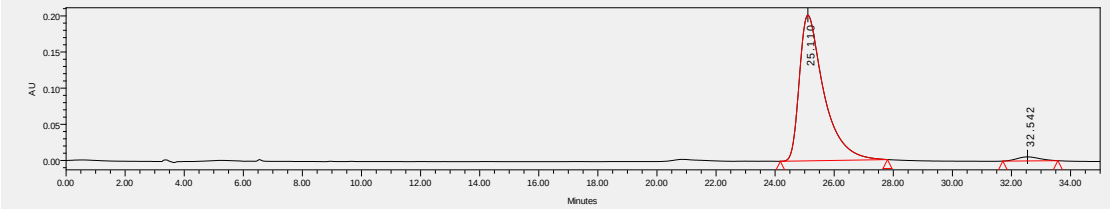
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.6, 152.6, 147.4, 140.2, 139.7, 137.7, 136.0, 130.0, 129.4, 126.4, 125.8, 124.2, 122.6, 121.6, 120.7, 118.1, 112.6, 92.5, 45.6, 43.1, 12.6, 12.3, 7.6.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3IS^+$ ([M + H]$^+$) = 574.0656, found 574.0672.

IR (neat): 2361, 2355, 1696, 1353, 1308, 1143, 750, 521 cm^{-1}.

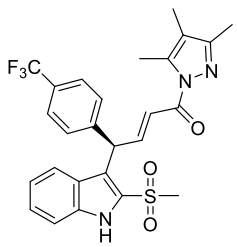


	Retention Time	Area	% Area
1	25.417	4068326	50.36
2	32.667	4010647	49.64



	Retention Time	Area	% Area
1	25.110	11551346	97.50
2	32.542	296345	2.50

(*R*,*E*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-(4-(trifluoromethyl)phenyl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4la)



Following the typical procedure B.

36.6 mg, 71% yield; white solid; M.p. 103-108 °C. R_f = 0.2 (Pet/EtOAc = 4/1).

Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 16.381 min, t (minor) = 20.901 min. ee = 89%. $[\alpha]^{24}_D$ = +56.9 (*c* = 0.58, in CH_2Cl_2).

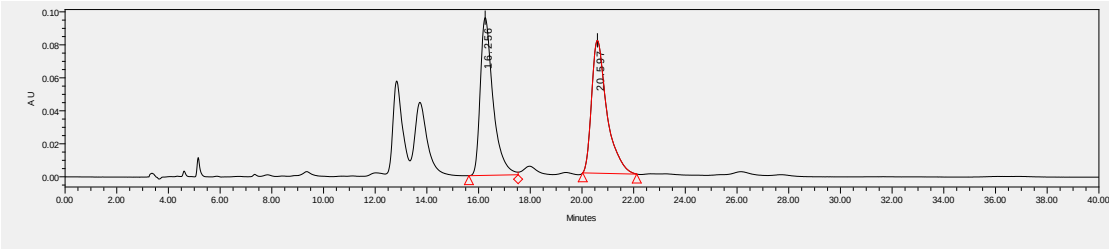
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.74 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.55 – 7.43 (m, 6H), 7.40 – 7.32 (m, 2H), 7.10 – 7.06 (m, 1H), 6.07 (d, *J* = 8.4 Hz, 1H), 3.13 (s, 3H), 2.48 (s, 3H), 2.15 (s, 3H), 1.90 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.6, 152.7, 146.9, 144.5, 139.8, 136.1, 129.5, 129.3 (d, *J* = 32.0 Hz), 128.3, 126.8 (q, J = 275.7 Hz), 126.5, 125.7, 125.6 (q, *J* = 3.6 Hz), 124.5, 122.5, 121.7, 120.4, 118.1, 112.7, 45.7, 43.4, 12.6, 12.3, 7.6.

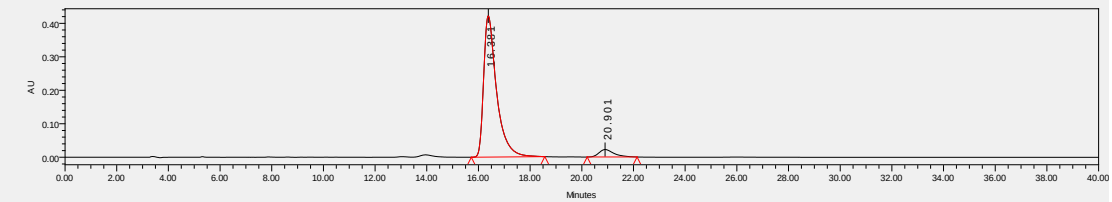
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.46.

ESI-HRMS: calcd for $C_{26}H_{25}N_3O_3F_3S^+$ ($[M+H]^+$) = 516.1563, found 516.1562.

IR (neat): 2360, 2351, 1697, 1354, 1320, 1121, 1067, 10111, 958, 824, 750, 522 cm^{-1}.

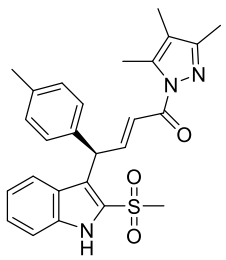


	Retention Time	Area	% Area
1	16.256	3286912	49.92
2	20.597	3297135	50.08



	Retention Time	Area	% Area
1	16.381	14627255	94.25
2	20.901	892518	5.75

(*R*,*E*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-(p-tolyl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ma)



Following the typical procedure C.

38.7 mg, 84% yield; white solid; M.p. 100-106 °C. R_f = 0.2 (Pet/EtOAc = 4/1).

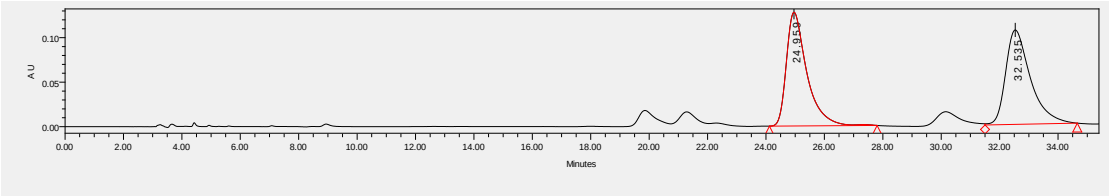
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 24.881 min, t (minor) = 32.764 min. ee = 94%. $[\alpha]^{18}_D$ = +65.3 (*c* = 0.53, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.78 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.35 – 7.29 (m, 1H), 7.21 – 7.19 (m, 2H), 7.11 – 7.02 (m, 3H), 5.98 (d, *J* = 8.4 Hz, 1H), 3.06 (s, 3H), 2.48 (s, 3H), 2.30 (s, 3H), 2.15 (s, 3H), 1.89 (s, 3H).

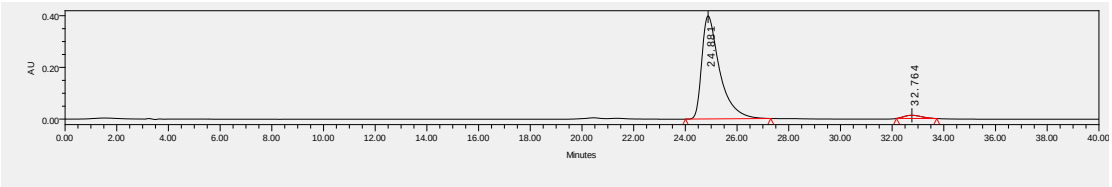
$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.4, 148.6, 139.7, 137.3, 136.5, 136.0, 129.3, 129.2, 127.9, 126.2, 126.1, 123.6, 122.9, 121.6, 121.4, 117.9, 112.5 , 45.6, 43.3, 21.0, 12.7, 12.3, 7.6.

ESI-HRMS: calcd for $C_{26}H_{28}N_3O_3S^+$ ([M + H]$^+$) = 462.1846, found 462.1850.

IR (neat): 1696, 1635, 1380, 1352, 1311, 1187, 1143, 1007, 958, 939, 811, 749, 522 cm^{-1}.

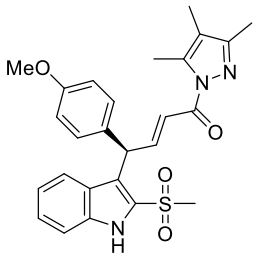


	Retention Time	Area	% Area
1	24.959	6199263	49.87
2	32.535	6230813	50.13



	Retention Time	Area	% Area
1	24.881	19135177	97.05
2	32.764	582078	2.95

(*R*,*E*)-4-(4-methoxyphenyl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4na)



Following the typical procedure B.

41.1 mg, 86% yield; white solid; M.p. 100-104 °C. R_f = 0.1 (Pet/EtOAc = 4/1).

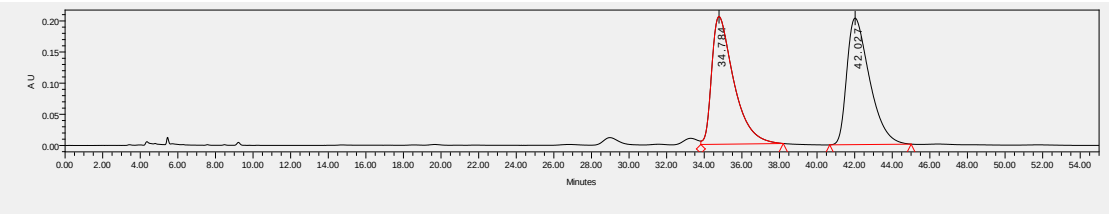
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 34.050 min, t (minor) = 42.393 min. ee = 91%. $[\alpha]^{23}_D$ = +47.2 (*c* = 0.69, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.76 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.33 – 7.29 (m, 1H), 7.23 – 7.19 (m, 2H), 7.08 – 7.04 (m, 1H), 6.83 – 6.77 (m, 2H), 5.96 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 3H), 3.05 (s, 3H), 2.48 (s, 3H), 2.14 (s, 3H), 1.89 (s, 3H).

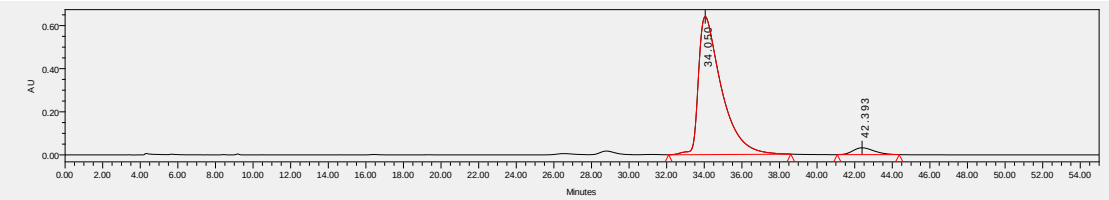
$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 164.9, 158.4, 152.4, 148.8, 139.7, 136.0, 132.5, 129.1, 129.1, 126.2, 126.1, 123.5, 122.9, 121.7, 121.4, 117.9, 114.0, 112.5, 77.2, 55.2, 45.4, 42.9, 12.7, 12.3, 7.6.

ESI-HRMS: calcd for $C_{26}H_{28}N_3O_4S^+$ ([M + H]$^+$) = 478.1795, found 478.1801.

IR (neat): 2362, 2250, 1696, 1634, 1509, 1353, 1303, 1247, 1180, 1143, 1007, 959, 823 cm^{-1}.

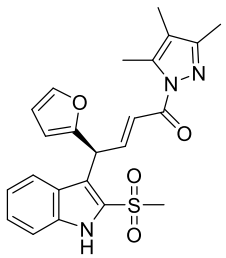


	Retention Time	Area	% Area
1	34.784	16722550	49.54
2	42.027	17034081	50.46



	Retention Time	Area	% Area
1	34.050	54177694	95.61
2	42.393	2487693	4.39

(*S*,*E*)-4-(furan-2-yl)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4oa)



Following the typical procedure B.

29.7 mg, 68% yield; pale yellow solid; M.p. 103-109 °C. R_f = 0.2 (Pet/EtOAc = 4/1).

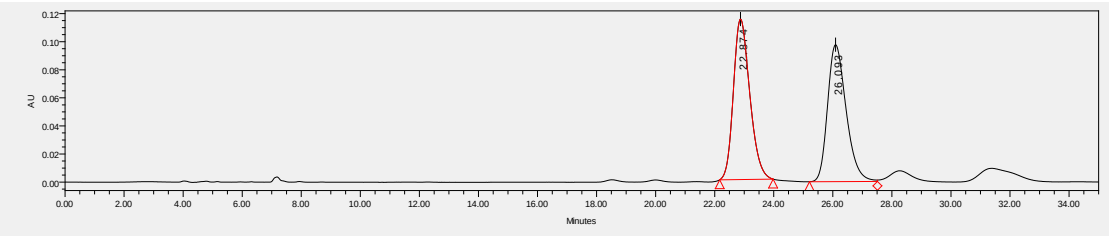
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 23.315 min, t (minor) = 26.133 min. ee = 92%. $[\alpha]^{25}_D$ = +36.7 (*c* = 0.48, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.22 (s, 1H), 7.66 (dd, *J* = 15.6, 7.2 Hz, 1H), 7.59 – 7.57 (m, 1H), 7.50 – 7.42 (m, 2H), 7.37 – 7.28 (m, 2H), 7.13 – 7.09 (m, 1H), 6.33 – 6.25 (m, 2H), 6.03 (d, *J* = 7.2 Hz, 1H), 3.20 (s, 3H), 2.47 (s, 3H), 2.13 (s, 3H), 1.88 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.7, 152.9, 152.4, 145.3, 142.1, 139.6, 135.9, 129.1, 126.3, 125.9, 124.1, 122.6, 121.5, 119.1, 118.0, 112.4, 110.4, 107.1, 45.8, 38.2, 12.7, 12.3, 7.6.

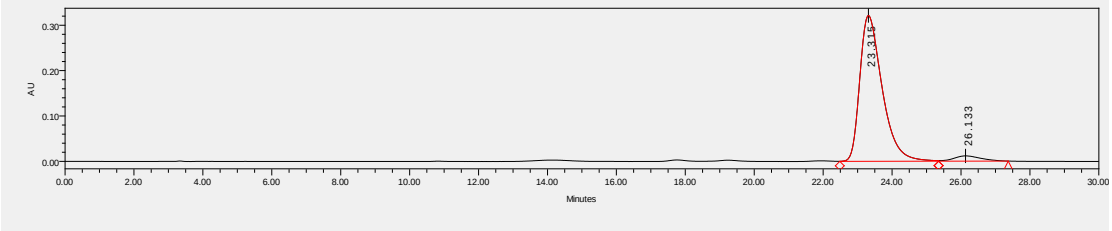
ESI-HRMS: calcd for $C_{23}H_{24}N_3O_4S^+$ ([M + H]$^+$) = 438.1482, found 438.1484.

IR (neat): 2361, 2356, 1697, 1639, 1353, 1313, 1142, 1009, 959,747, 522, 433 cm^{-1}.



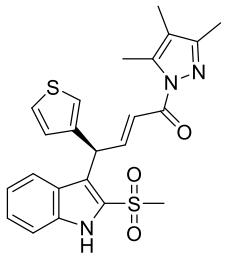
	Retention Time	Area	% Area

1	22.874	4402311	50.88
2	26.093	4250383	49.12



	Retention Time	Area	% Area
1	23.315	14417834	95.81
2	26.133	630185	4.19

(*R*,*E*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-(thiophen-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4pa)



Following the typical procedure B.

32.1 mg, 70% yield; pale yellow solid; M.p. 90-94 °C. R_f = 0.2 (Pet/EtOAc = 4/1).

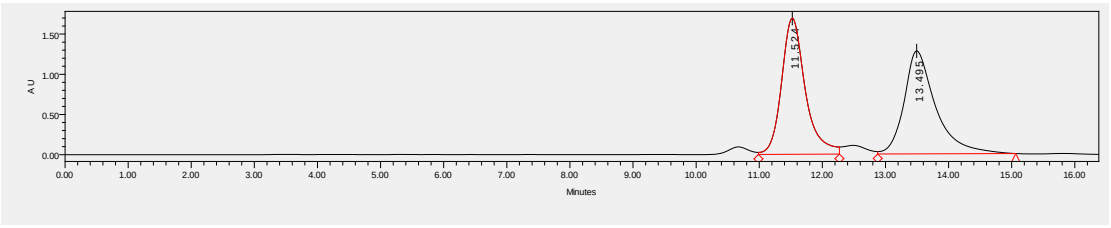
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (minor) = 11.522 min, t (major) = 13.465 min. ee = 94%. $[\alpha]^{24}_D$ = +50.0 (*c* = 0.49, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 7.73 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.35 – 7.31 (m, 1H), 7.26 – 7.23 (m, 1H), 7.13 – 7.02 (m, 2H), 6.94 – 6.92 (m, 1H), 5.98 (d, *J* = 8.0, Hz, 1H), 3.10 (s, 3H), 2.48 (s, 3H), 2.15 (s, 3H), 1.89 (s, 3H).

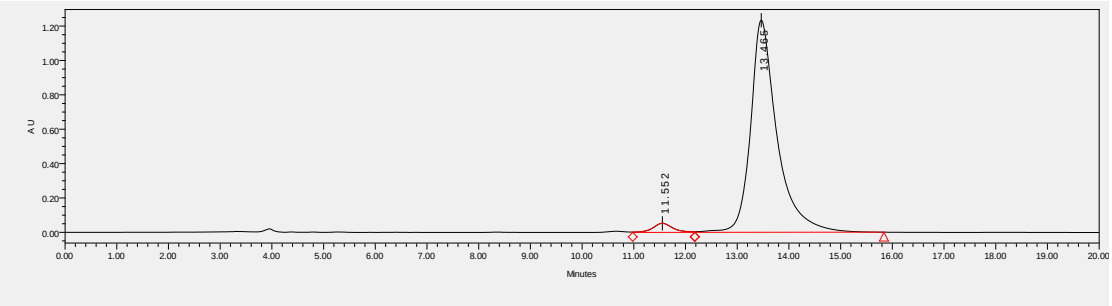
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.5, 147.9, 140.9, 139.7, 136.0 , 128.9, 127.8, 126.3, 126.1, 125.9, 123.3, 122.7, 121.8, 121.4, 121.0, 118.0, 112.5, 45.6, 39.9, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{23}H_{24}N_3O_3S_2^+$ ([M + H]$^+$) = 454.1254, found 454.1262.

IR (neat): 1696, 1636, 1381, 1352, 1311, 1141, 1008, 959, 832, 747, 523, 433 cm^{-1}.

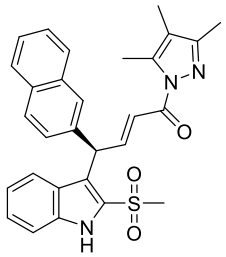


	Retention Time	Area	% Area
1	11.524	44209759	49.86
2	13.495	44452280	50.14



	Retention Time	Area	% Area
1	11.552	1402786	3.09
2	13.465	44036773	96.91

(*R*,*E*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-(naphthalen-2-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4qa)



Following the typical procedure B.

43.9 mg, 88% yield; pale yellow solid; M.p. 132-136 °C. R_f = 0.2 (Pet/EtOAc = 4/1).

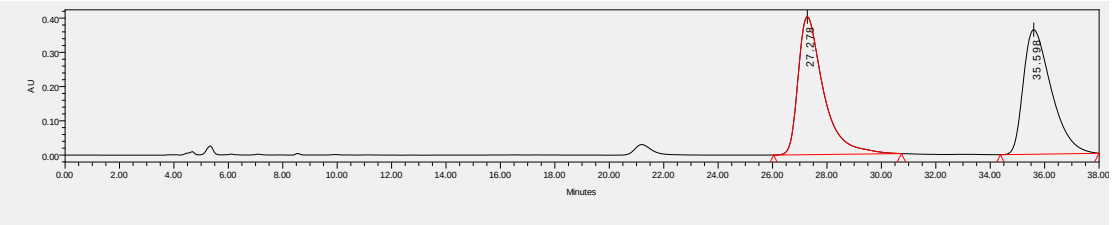
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 27.178 min, t (minor) = 36.345 min. ee = 94%. $[\alpha]^{23}_D$ = +104.1 (*c* = 0.59, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 7.90 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.83 – 7.76 (m, 3H), 7.74 – 7.72 (m, 1H), 7.57 – 7.53 (m, 1H), 7.47 – 7.44 (m, 4H), 7.41 – 7.39 (m, 1H), 7.33 – 7.28 (m, 1H), 7.04 – 6.98 (m, 1H), 6.20 (d, *J* = 8.4 Hz, 1H), 3.10 (s, 3H), 2.51 (s, 3H), 2.15 (s, 3H).

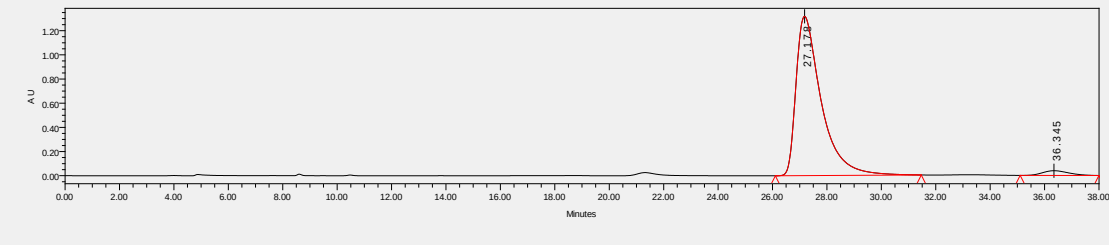
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.5, 148.2, 139.7, 138.0, 136.1, 133.3, 132.3, 129.4, 128.4, 127.9, 127.6, 126.5, 126.2, 126.2, 126.1, 125.9, 124.0, 122.8, 121.5, 121.2, 118.0, 112.5, 77.2, 45.5, 43.7, 12.7, 12.3, 7.6.

ESI-HRMS: calcd for $C_{29}H_{28}N_3O_3S^+$ ([M + H]$^+$) = 498.1846, found 498.1852.

IR (neat): 1696, 1634, 1381, 1352, 1312, 1142, 958, 820, 747, 523, 477, 432 cm^{-1}.

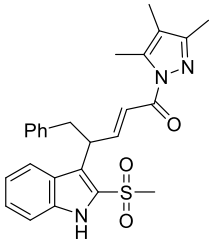


	Retention Time	Area	% Area
1	27.278	25985452	50.04
2	35.598	25941592	49.96



	Retention Time	Area	% Area
1	27.178	84552113	97.01
2	36.345	2604004	2.99

(*E*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-5-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)pent-2-en-1-one (4ra)



Following the typical procedure B.

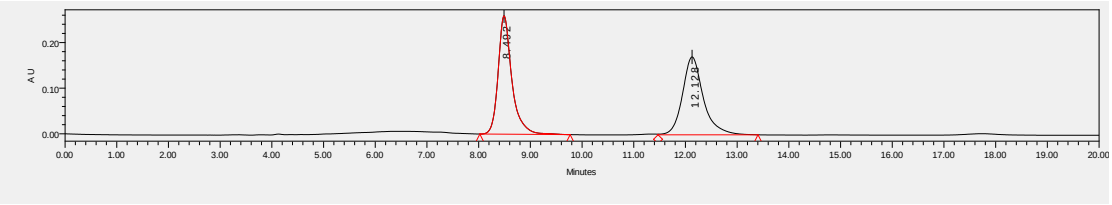
2.5 mg, 5% yield; white solid; M.p. 72-78 °C. R_f = 0.3 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (minor) = 8.594 min, t (major) = 12.229 min. ee = 78%. $[\alpha]^{21}_D$ = –50.0 (*c* = 0.08, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 7.60 – 7.58 (m, 1H), 7.46 – 7.38 (m, 3H), 7.26 – 7.22 (m, 2H), 7.15 – 7.08 (m, 3H), 6.94 – 6.92 (m, 2H), 4.82 – 4.76(m, 1H), 3.51 – 3.45 (m, 1H), 3.39 – 3.35 (m, 1H), 2.46 (s, 3H), 2.37 (s, 3H), 2.17 (s, 3H), 1.89 (s, 3H).

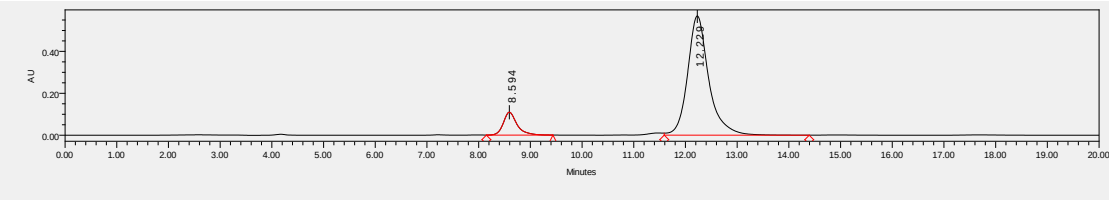
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 165.3, 155.8, 152.3, 145.5, 139.8, 134.9, 130.2, 128.6, 127.7, 126.9, 126.8, 126.5, 125.6, 123.8, 121.0, 118.5, 117.8, 112.2, 47.3, 44.9, 25.8, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{26}H_{28}N_3O_3S^+$ ([M + H]$^+$) = 462.1846, found 462.1848.

IR (neat): 1696, 1634, 1380, 1352, 1300, 1142, 1089, 1013, 962, 937, 821, 751, 700, 521 cm^{-1}.

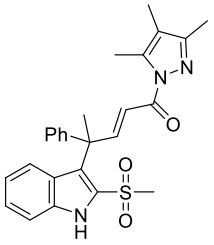


	Retention Time	Area	% Area
1	8.492	4789849	50.04
2	12.128	4781959	49.96



	Retention Time	Area	% Area
1	8.594	2016843	11.05
2	12.229	16239190	88.95

(*E*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)pent-2-en-1-one (4sa)



Following the typical procedure B.

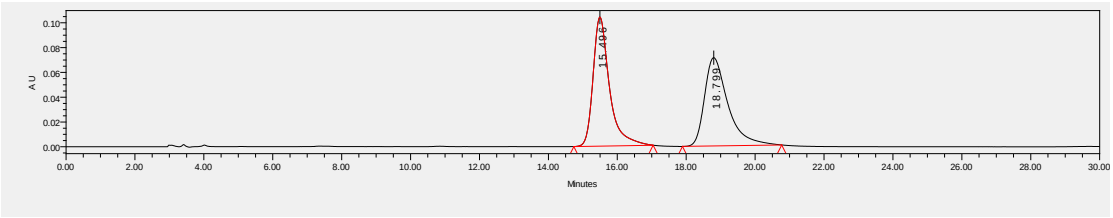
18.0 mg, 39% yield; white solid; M.p. 85-90 °C. R_f = 0.4 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (minor) = 15.541 min, t (major) = 18.840 min. ee = 82%. $[\alpha]^{28}_D$ = –191.5 (*c* = 0.26, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.25 (s, 1H), 8.04 (d, *J* = 16.0 Hz, 1H), 7.42 – 7.37 (m, 4H), 7.32 – 7.17 (m, 4H), 7.19 – 7.17 (m, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 2.84 (s, 3H), 2.50 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H), 1.90 (s, 3H).

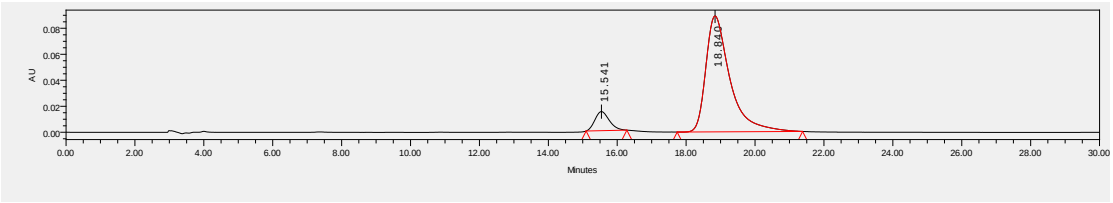
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.9, 152.3, 150.0, 139.5, 135.9, 133.7 , 130.2, 129.8, 129.3, 128.4, 126.5, 126.2 , 122.7, 121.9, 121.4, 121.0, 117.8, 112.7, 44.8, 42.0, 40.1, 12.8, 12.3, 7.7.

ESI-HRMS: calcd for $C_{26}H_{28}N_3O_3S^+$ ($[M + H]^+$) = 462.1846, found 462.1848.

IR (neat): 1695, 1630, 1378, 1351, 1321, 1264, 1146, 1027, 735, 702, 529, 434 cm^{-1}.

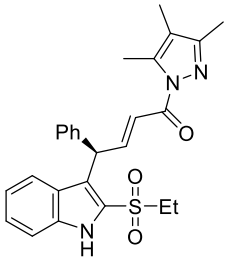


	Retention Time	Area	% Area
1	15.496	3436950	50.62
2	18.799	3353364	49.38



	Retention Time	Area	% Area
1	15.541	425156	8.96
2	18.840	4321626	91.04

(*R*,*E*)-4-(2-(ethylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ab)

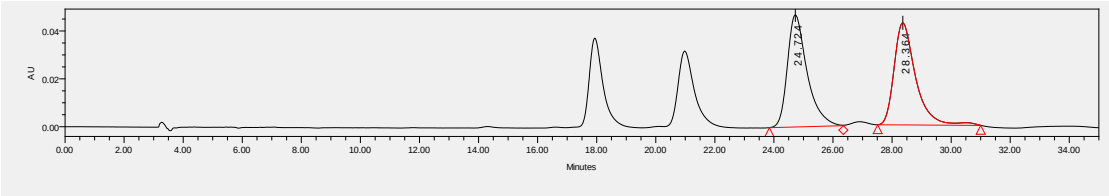


Following the typical procedure B.

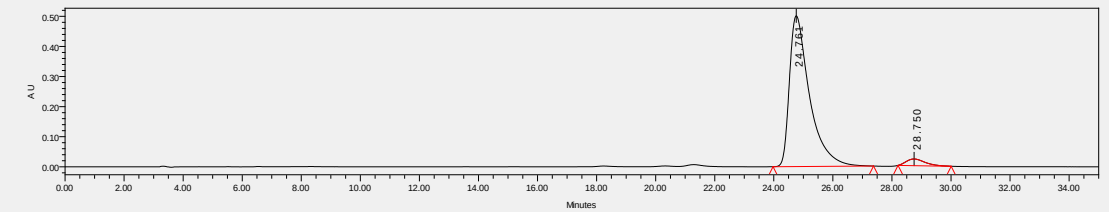
35.0 mg, 76% yield; white solid; M.p. 100-104 °C. R_f = 0.3 (Pet/EtOAc = 4/1).

Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 24.761 min, t (minor) = 28.750 min. ee = 92%. $[\alpha]^{18}_D$ = +83.4 (*c* = 0.70, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.71 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.26 – 7.13 (m, 6H), 7.00 – 6.96 (m, 1H), 5.91 (d, J = 8.0 Hz, 1H), 3.14 – 3.01 (m, 2H), 2.40 (s, 3H), 2.06 (s, 3H), 1.81 (s, 3H), 1.16 (t, *J* = 7.4 Hz, 3H).
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.3, 148.4, 140.5, 139.7, 136.2, 128.6, 128.0, 127.7, 126.9, 126.1, 126.1, 123.8, 122.9, 121.8, 121.3, 117.9, 112.5, 51.7, 43.6, 12.7, 12.3, 7.6, 7.3.
ESI-HRMS: calcd for $C_{26}H_{28}N_3O_3S^+$ ([M + H]$^+$) = 462.1846, found 462.1850.
IR (neat): 1696, 1635, 1380, 1352, 1311, 1276, 1185, 1129, 1090, 987, 938, 831, 754, 727, 701, 622, 526, 506 cm^{-1}.

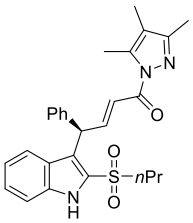


	Retention Time	Area	% Area
1	24.724	2170506	50.09
2	28.364	2162682	49.91



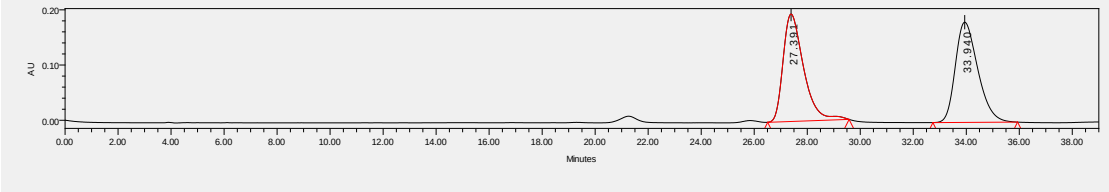
	Retention Time	Area	% Area
1	24.761	23646608	96.00
2	28.750	984210	4.00

(*R*,*E*)-4-phenyl-4-(2-(propylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ac)

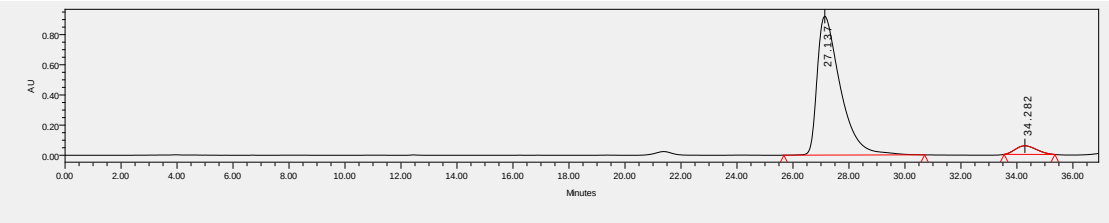


Following the typical procedure B.
40.5 mg, 84% yield; white solid; M.p. 111-115 °C. R_f = 0.4 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 27.137 min, t (minor) = 34.282 min. ee = 89%. $[\alpha]^{24}_D$ = +56.5 (*c* = 0.20, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 7.80 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.36 – 7.26 (m, 5H), 7.24 – 7.19 (m, 1H), 7.08 – 7.04 (m, 1H), 5.98 (d, *J* = 8.0 Hz, 1H), 3.13 – 3.00 (m, 2H), 2.48 (s, 3H), 2.14 (s, 3H), 1.89 (s, 3H), 1.73 – 1.64 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H).
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.3, 148.6, 140.5, 139.6, 136.0, 128.6, 128.2, 128.0, 126.9, 126.2, 126.0, 123.7, 122.9, 121.6, 121.4, 117.9, 112.5, 59.0, 43.7, 16.4, 12.7, 12.3, 12.3, 7.7.
ESI-HRMS: calcd for $C_{27}H_{30}N_3O_3S^+$ ([M + H]$^+$) = 476.2002, found 476.2008.
IR (neat): 1697, 1637, 1381, 1354, 1315, 1181, 1132, 1088, 1011, 959, 846, 803, 760, 728, 701, 531, 430 cm^{-1}.

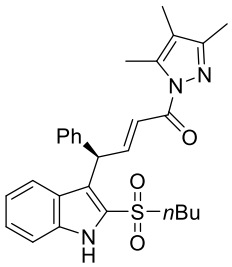


	Retention Time	Area	% Area
1	27.391	10422587	49.35
2	33.940	10698578	50.65



	Retention Time	Area	% Area
1	27.137	52712748	94.60
2	34.282	3010237	5.40

(*R*,*E*)-4-(2-(butylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ad)



Following the typical procedure C.

46.4 mg, 95% yield; white solid; M.p. 90-92 °C. R_f = 0.5 (Pet/EtOAc = 4/1).

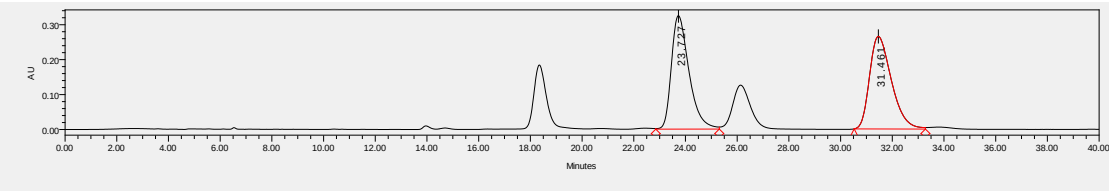
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 23.254 min, t (minor) = 31.040 min. ee = 85%. $[\alpha]^{23}_D$ = +48.7 (*c* = 0.45, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 7.80 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.35 – 7.26 (m, 5H), 7.24 – 7.19 (m, 1H), 7.10 – 7.05 (m, 1H), 5.98 (d, *J* = 8.4 Hz, 1H), 3.14 – 3.03 (m, 2H), 2.48 (s, 3H), 2.14 (s, 3H), 1.67 – 1.58 (m, 2H), 1.27 – 1.18 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.7, 152.3, 148.7, 140.5, 139.6, 136.1, 128.6, 128.3, 128.0, 126.9, 126.2, 126.0, 123.6, 122.9, 121.6, 121.4, 117.9, 112.5, 57.2, 43.7, 24.4, 21.3, 13.3, 12.7, 12.3, 7.7.

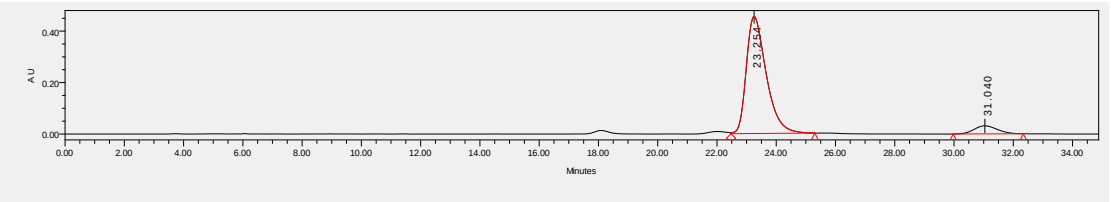
ESI-HRMS: calcd for $C_{28}H_{32}N_3O_3S^+$ ([M + H]$^+$) = 490.2159, found 490.2162.

IR (neat): 1696, 1635, 1380, 1352, 1294, 1127, 1089, 1005, 936, 745, 701, 625, 522 cm^{-1}.



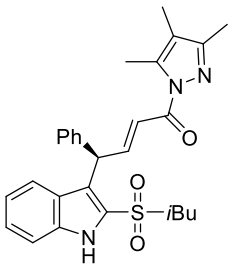
	Retention Time	Area	% Area

1	23.727	15389195	49.54
2	31.461	15673136	50.46



	Retention Time	Area	% Area
1	23.254	21171881	92.52
2	31.040	1711200	7.48

(*R*,*E*)-4-(2-(isobutylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ae)



Following the typical procedure C.

34.2 mg, 70% yield; white solid; M.p. 91-96 °C. R_f = 0.4 (Pet/EtOAc = 4/1).

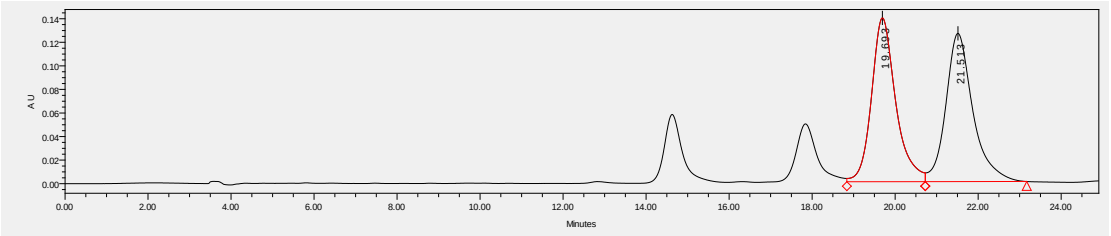
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (minor) = 19.974 min, t (major) = 21.6417777 min. ee = 81%. $[\alpha]^{22}_D$ = +45.6 (*c* = 0.50, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.20 (s, 1H), 7.80 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.37 – 7.26 (m, 5H), 7.24 – 7.20 (m, 1H), 7.10 – 7.05 (m, 1H), 5.98 (d, *J* = 8.0 Hz, 1H), 3.04 – 2.95 (m, 2H), 2.49 (s, 3H), 2.22 – 2.17 (m, 1H), 2.15 (s, 3H), 1.90 (s, 3H), 0.96 – 0.92 (m, 6H).

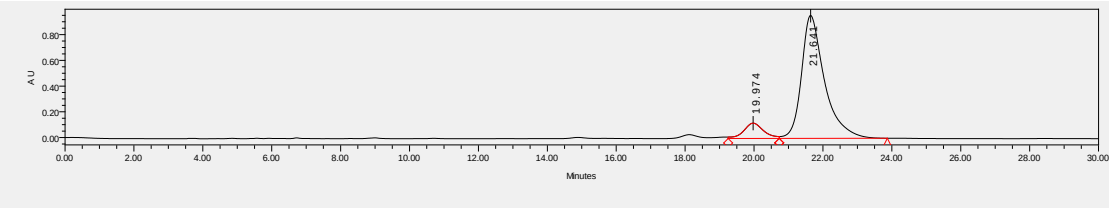
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.7, 152.3, 148.6, 140.5, 139.6, 136.0, 129.1, 128.6, 128.1 , 126.9, 126.2, 126.0, 123.6, 122.9, 121.4, 121.3, 117.9, 112.5, 65.0, 43.8, 24.0, 22.5, 22.5, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{28}H_{32}N_3O_3S^+$ ([M + H]$^+$) = 490.2159, found 490.2153.

IR (neat): 1696, 1635, 1380, 1352, 1230, 1130, 1086, 1006, 938, 832, 746, 700, 627, 518 cm^{-1}.

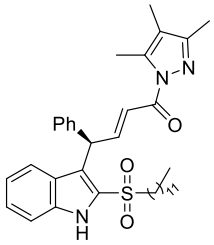


	Retention Time	Area	% Area
1	19.693	5631621	49.79
2	21.513	5679543	50.21



	Retention Time	Area	% Area
1	19.974	4731951	9.65
2	21.641	44278422	90.35

(*R*,*E*)-4-(2-(dodecylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4af)



Following the typical procedure B.

41.8 mg, 70% yield; colorless oil; R_f = 0.5 (Pet/EtOAc = 4/1).

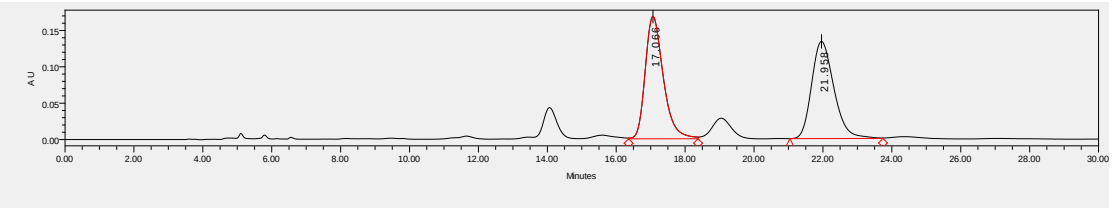
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 16.883 min, t (minor) = 22.012 min. ee = 85%. $[\alpha]^{23}_D$ = +53.8 (*c* = 0.71, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.80 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.55 – 7.42 (m, 3H), 7.34 – 7.19 (m, 6H), 7.08 – 7.04 (m, 1H), 5.99 (d, *J* = 8.4 Hz, 1H), 3.10 – 3.06 (m, 2H), 2.48 (s, 3H), 2.14 (s, 3H), 1.89 (s, 3H), 1.69 – 1.55 (m, 2H), 1.29 – 1.03 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H).

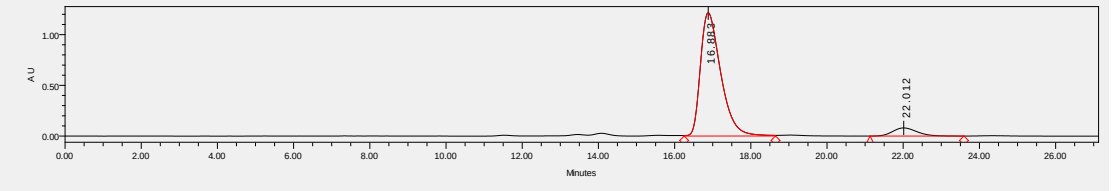
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.7, 152.3, 148.7, 140.6, 139.6, 136.1, 128.6, 128.2, 128.0, 126.9, 126.2, 126.0, 123.6, 122.9, 121.6, 121.3, 117.9, 112.5, 57.4, 43.7, 31.9, 29.5, 29.5, 29.3, 29.3, 29.2, 28.8, 28.0, 22.6, 22.6, 14.1, 12.7, 12.3, 7.6.

ESI-HRMS: calcd for $C_{36}H_{48}N_3O_3S^+$ ([M + H]$^+$) = 602.3411, found 602.3421.

IR (neat): 2852, 1699, 1635, 1380, 1352, 1296, 1129, 1006, 745, 523 cm^{-1}.



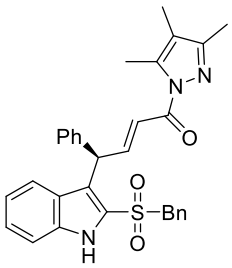
	Retention Time	Area	% Area
1	17.066	6138805	50.56
2	21.958	6002792	49.44



	Retention Time	Area	% Area

1	16.883	44878308	92.68
2	22.012	3545345	7.32

(*R*,*E*)-4-(2-(benzylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ag)



Following the typical procedure D.

39.1 mg, 75% yield; pale yellow solid; M.p. 96-100 °C. R_f = 0.3 (Pet/EtOAc = 4/1).

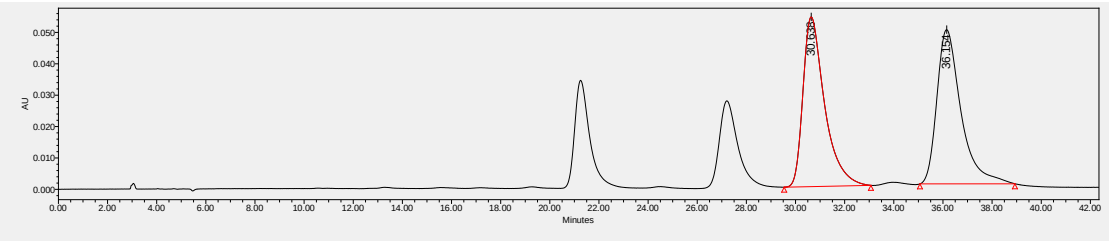
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 30.322 min, t (minor) = 36.249 min. ee = 87%. $[\alpha]^{20}_D$ = +50.2 (*c* = 0.76, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 7.78 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.36 – 7.25 (m, 6H), 7.24 – 7.19 (m, 2H), 7.17 – 7.12 (m, 2H), 7.07 – 6.99 (m, 3H), 6.02 (d, *J* = 8.0, 1H), 4.35 – 4.25 (m, 2H), 2.48 (s, 3H), 2.10 (s, 3H), 1.87 (s, 3H).

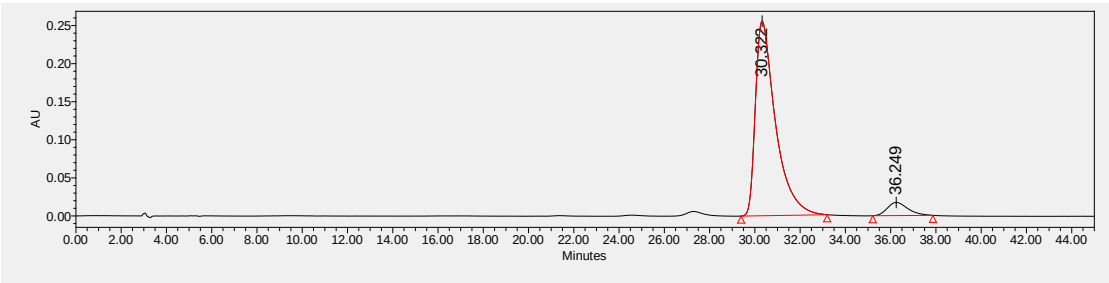
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.4, 148.8, 140.6, 139.6, 136.0, 130.7, 129.0, 128.6, 128.6, 128.2, 127.3, 127.2, 126.9, 126.1, 125.8, 123.6, 122.8, 122.5, 121.3, 117.9, 112.4, 63.4, 43.6, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{31}H_{30}N_3O_3S^+$ ([M + H]$^+$) = 524.2002, found 524.2008.

IR (neat): 1693, 1634, 1380, 1351, 1312, 1190, 1147, 1117, 1089, 1005, 936, 914, 871, 830, 726, 696, 640, 601, 516, 430 cm^{-1}.

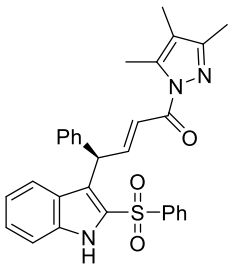


	Retention Time	Area	% Area
1	30.638	3300653	49.74
2	36.154	3335086	50.26



	Retention Time	Area	% Area
1	30.322	15736056	93.51
2	36.249	1092402	6.49

(*R*,*E*)-4-phenyl-4-(2-(phenylsulfonyl)-1*H*-indol-3-yl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ah)



Following the typical procedure B.

31.6 mg, 62% yield; white solid; M.p. 87-91 °C. R_f = 0.3 (Pet/EtOAc = 4/1).

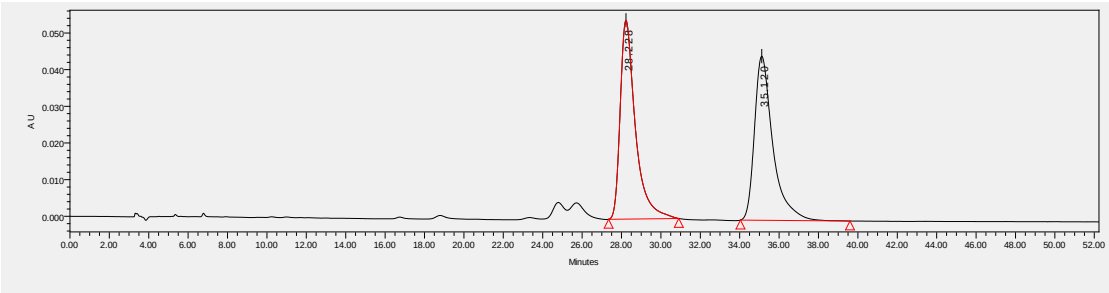
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 28.159 min, t (minor) = 35.053 min. ee = 20%. $[\alpha]^{22}_D$ = +17.2 (*c* = 0.60, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 7.93 – 7.91 (m, 2H), 7.65 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.43 – 7.32 (m, 6H), 7.31 – 7.28 (m, 1H), 7.20 – 7.12 (m, 5H), 7.02 – 6.98 (m, 1H), 6.00 (d, *J* = 8.4 Hz, 1H), 2.46 (s, 3H), 2.19 (s, 3H), 1.91 (s, 3H).

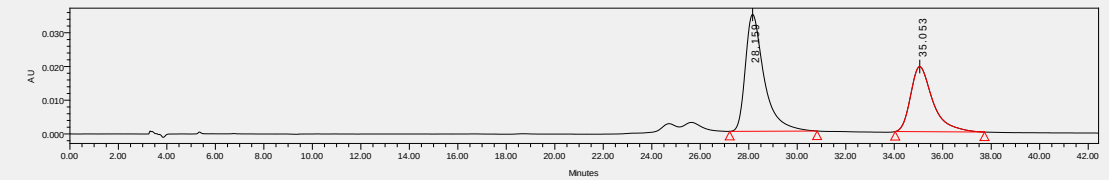
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.7, 152.1, 147.8, 141.4, 140.3, 139.6, 136.2, 133.3, 130.2, 129.3, 128.4, 127.9, 127.1, 126.7, 126.2, 126.1, 123.7, 122.9, 121.4, 121.3, 117.8, 112.4, 43.5, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{30}H_{28}N_3O_3S^+$ ([M + H]$^+$) = 510.1846, found 510.1848.

IR (neat): 1694, 1634, 1353, 1304, 1184, 1147, 1086, 1005, 936, 831, 749, 723, 618, 549, 431cm^{-1}.

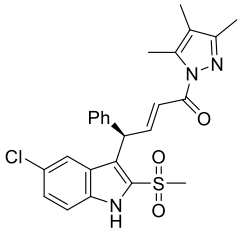


	Retention Time	Area	% Area
1	28.228	2903889	50.06
2	35.120	2897487	49.94



	Retention Time	Area	% Area
1	28.159	1859627	60.21
2	35.053	1228756	39.79

(*R*,*E*)-4-(5-chloro-2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ai)



Following the typical procedure B.

36.4 mg, 76% yield; white solid; M.p. 110-114 °C. R_f = 0.2 (Pet/EtOAc = 4/1).

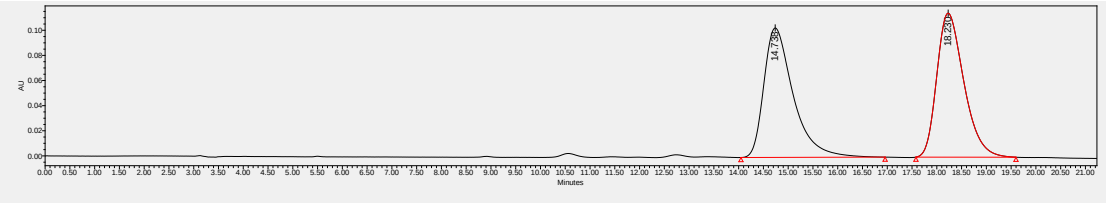
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 14.679 min, t (minor) = 18.418 min. ee = 94%. $[\alpha]^{22}_D$ = +103.2 (*c* = 0.72, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.57 (s, 1H), 7.71 (dd, *J* = 15.6, 8.4, 1.2 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.38 – 7.34 (m, 2H), 7.29 – 7.23 (m, 6H), 5.97 (d, *J* = 8.4 Hz, 1H), 3.07 (s, 3H), 2.49 (s, 3H), 2.14 (s, 3H), 1.90 (s, 3H).

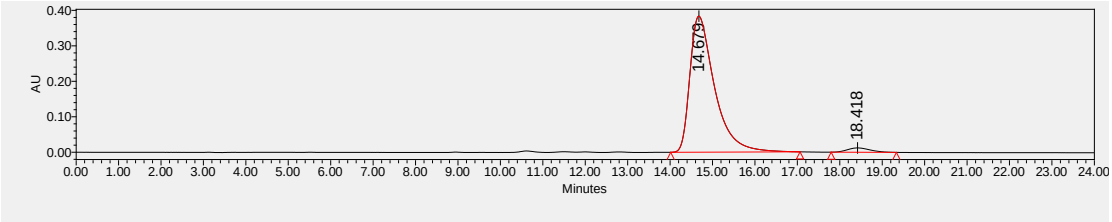
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.6, 147.7, 139.9, 139.8, 134.3, 130.6, 128.7, 127.9, 127.2, 127.1, 126.9, 126.8, 124.2, 121.8, 120.7, 118.0, 113.8, 45.4, 43.4, 12.7, 12.3, 7.6.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{35}ClS^+$ ([M + H]$^+$) = 482.1300, found 482.1299. $C_{25}H_{25}N_3O_3{}^{37}ClS^+$ ([M + H]$^+$) = 484.1270, found 484.1271.

IR (neat): 1696, 1635, 1354, 1307, 1137, 960, 758, 701, 535, 431cm^{-1}.

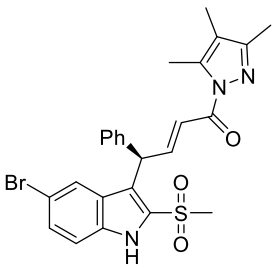


	Retention Time	Area	% Area
1	14.738	4244328	49.42
2	18.230	4344377	50.58



	Retention Time	Area	% Area
1	14.679	15454206	97.13
2	18.418	456355	2.87

(*R*,*E*)-4-(5-bromo-2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4aj)



Following the typical procedure C.

45.5 mg, 87% yield; white solid; M.p. 107-111 °C. R_f = 0.2 (Pet/EtOAc = 4/1).

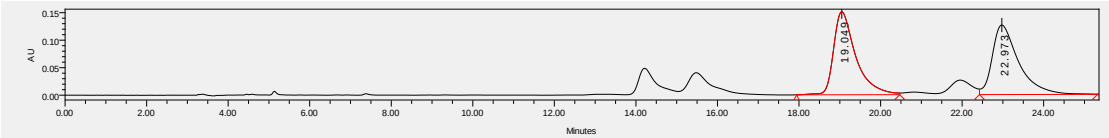
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 18.909 min, t (minor) = 23.142 min. ee = 95%. $[\alpha]^{17}_D$ = +126.5 (*c* = 0.43, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 7.69 (dd, *J* = 15.4, 8.4, 1H), 7.52 – 7.41 (m, 2H), 7.38 – 7.35 (m, 1H), 7.31 – 7.22 (m, 6H), 5.94 (d, *J* = 8.4 Hz, 1H), 3.05 (s, 3H), 2.47 (s, 3H), 2.13 (s, 3H), 1.88 (s, 3H).

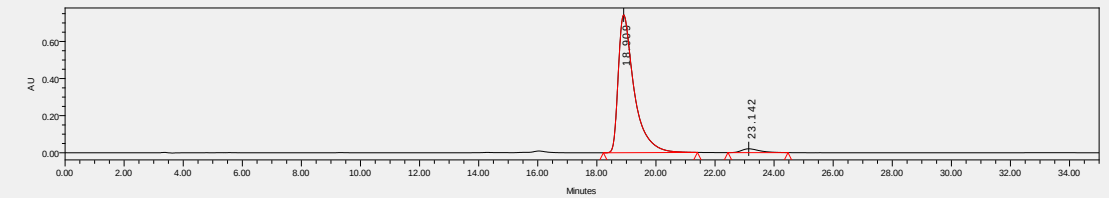
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.7, 152.6, 147.6, 139.8, 139.8, 134.4, 130.4, 129.4, 128.7, 127.9, 127.4, 127.2, 124.9, 124.1, 120.6, 118.1, 114.6, 114.1, 45.4, 43.3, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{79}BrS^+$ ([M + H]$^+$) = 526.0795, found 526.0798. $C_{25}H_{25}N_3O_3{}^{81}BrS^+$ ([M + H]$^+$) = 528.0774, found 528.0779.

IR (neat): 1697, 1636, 1381, 1354, 1308, 1137, 1005, 959, 937, 802, 759, 700, 533, 429 cm^{-1}.

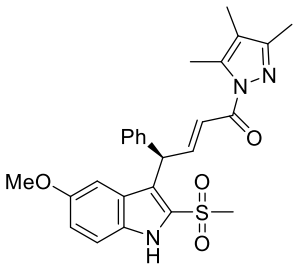


	Retention Time	Area	% Area
1	19.049	5699916	50.00
2	22.973	5699393	50.00



	Retention Time	Area	% Area
1	18.909	34632145	97.51
2	23.142	884361	2.49

(*R*,*E*)-4-(5-methoxy-2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ak)



Following the typical procedure C.

38.0 mg, 80% yield; white solid; M.p. 111-116 °C. R_f = 0.2 (Pet/EtOAc = 3/1).

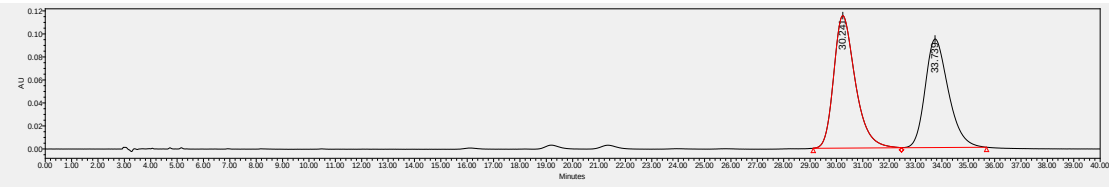
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IF** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 30.334 min, t (minor) = 34.237 min. ee = 95%. $[\alpha]^{18}_D$ = +123.0 (*c* = 0.30, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.05 (s, 1H), 7.73 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.34 – 7.27 (m, 5H), 7.25 – 7.21 (m, 1H), 7.00 – 6.97 (m, 1H), 6.73 – 6.72 (m, 1H), 6.00 (d, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.04 (s, 3H), 2.46 (s, 3H), 2.12 (s, 3H), 1.88 (s, 3H).

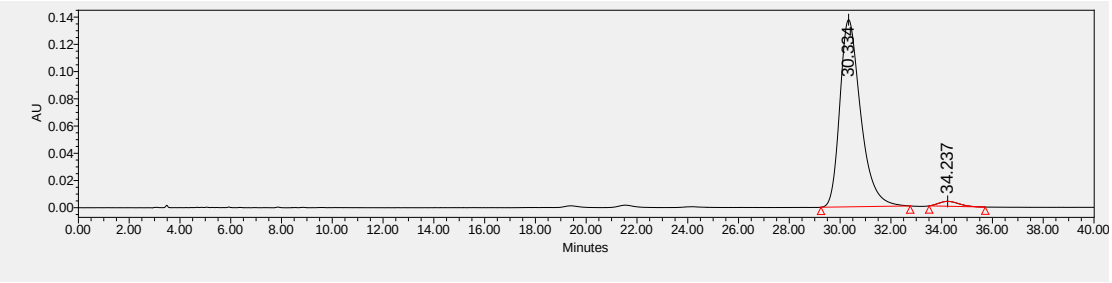
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.9, 154.6, 152.4, 148.1, 140.3, 139.6, 131.2, 129.5, 128.6, 128.1, 126.9, 126.5, 123.8, 120.6, 118.0, 117.9, 113.4, 102.6, 55.4, 45.4, 43.5, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{26}H_{28}N_3O_4S^+$ ($[M + H]^+$) = 478.1795, found 478.1800.

IR (neat): 1696, 1634, 1456, 1380, 1354, 1308, 1218, 1178, 1133, 1081, 1024, 1005, 968, 941, 836, 807, 759, 703, 622, 517, 434 cm^{-1}.

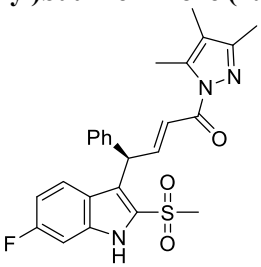


	Retention Time	Area	% Area
1	30.241	5902159	50.86
2	33.739	5703648	49.14



	Retention Time	Area	% Area
1	30.334	7807778	97.56
2	34.237	195516	2.44

(*R*,*E*)-4-(6-fluoro-2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4al)



Following the typical procedure B.

35.2 mg, 76% yield; pale yellow solid; M.p. 91-96 °C. R_f = 0.3 (Pet/EtOAc = 4/1).

Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 15.172 min, t (minor) = 19.361 min. ee = 96%. $[\alpha]^{21}_D$ = +76.4 (*c* = 0.42, in CH_2Cl_2).

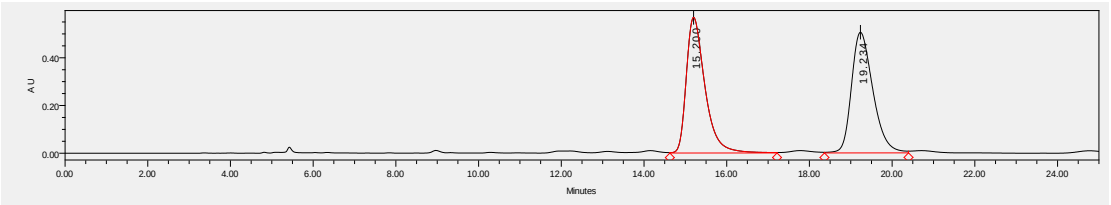
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 7.73 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.39 – 7.35 (m, 1H), 7.30 – 7.26 (m, 4H), 7.26 – 7.22 (m, 1H), 7.12 – 7.09 (m, 1H), 6.85 – 6.80 (m, 1H), 6.00 (d, *J* = 8.0, 1H), 3.06 (s, 3H), 2.49 (s, 3H), 2.15 (s, 3H), 1.90 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 161.9 (d, *J* = 243.3 Hz), 152.6, 148.0 , 140.2, 139.8, 136.2 (d, *J* = 12.6 Hz), 130.0 (d, J = 38.6 Hz), 129.7 (d, *J* = 3.8 Hz), 128.7, 128.0, 127.1, 124.3 (d, *J* = 10.2 Hz), 124.0, 122.2 (d, *J* = 87.4 Hz), 118.05 , 111.3 (d, *J* = 25.0 Hz), 98.4 (d, *J* = 25.9 Hz), 45.5, 43.5 , 12.7, 12.3, 7.7.

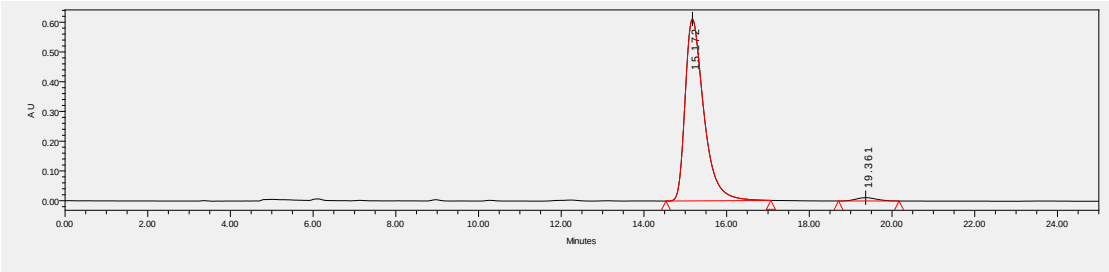
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -113.86.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3FS^+$ ([M + H]$^+$) = 466.1595, found 466.1599.

IR (neat): 1696, 1629, 1354, 1303, 1191, 1133, 957, 756, 702, 557, 488 cm^{-1}.

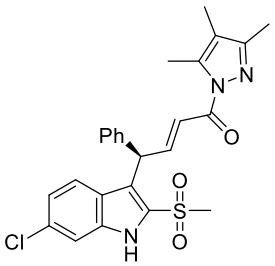


	Retention Time	Area	% Area
1	15.200	10477926	49.89
2	19.234	10525882	50.11



	Retention Time	Area	% Area
1	15.172	19182322	98.02
2	19.361	388009	1.98

(*R*,*E*)-4-(6-chloro-2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4am)



Following the typical procedure C.

44.9 mg, 93% yield; white solid; M.p. 120-125 °C. R_f = 0.3 (Pet/EtOAc = 4/1).

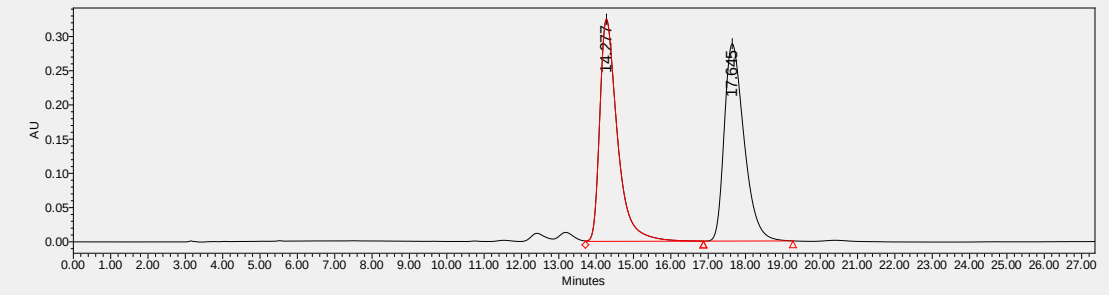
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 14.252 min, t (minor) = 17.824 min. ee = 96%. $[\alpha]^{21}_D$ = +84.9 (*c* = 0.59, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 7.70 (dd, *J* = 15.6, 8.4 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.32 – 7.21 (m, 6H), 7.00 – 6.98 (m, 1H), 5.98 (d, *J* = 8.4, 1H), 3.05 (s, 3H), 2.47 (s, 3H), 2.13 (s, 3H), 1.88 (s, 3H).

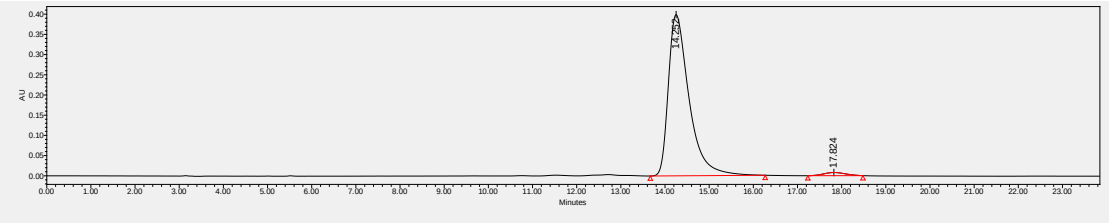
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.6, 147.9, 140.1, 139.7, 136.2, 132.3, 129.9, 128.7, 127.9, 127.1, 124.5, 124.1, 123.8, 122.5, 121.6, 118.1, 112.3, 45.4, 43.4, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{35}ClS^+$ ([M + H]$^+$) = 482.1300, found 482.1299. $C_{25}H_{25}N_3O_3{}^{37}ClS^+$ ([M + H]$^+$) = 484.1270, found 484.1271.

IR (neat): 1696, 1354, 1314, 1274, 1132, 959, 847, 757, 701, 534 cm^{-1}.

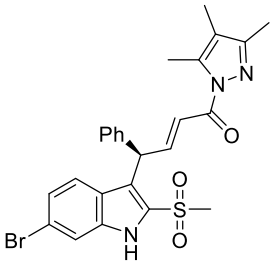


	Retention Time	Area	% Area
1	14.277	10644440	50.07
2	17.645	10615350	49.93



	Retention Time	Area	% Area
1	14.252	12964558	97.96
2	17.824	269612	2.04

(*R*,*E*)-4-(6-bromo-2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4an)



Following the typical procedure C.

45.6 mg, 87% yield; white solid; M.p. 105-109 °C. R_f = 0.3 (Pet/EtOAc = 4/1).

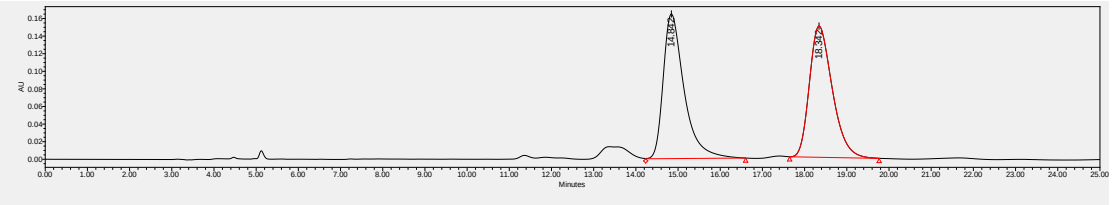
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 14.776 min, t (minor) = 18.503 min. ee = 95%. $[\alpha]^{22}_D$ = +74.1 (*c* = 0.46, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.40 (s, 1H), 7.69 (dd, *J* = 15.6, 8.0, 1H), 7.59 – 7.57 (m, 1H), 7.45 – 7.40 (m, 1H), 7.28 – 7.26 (m, 4H), 7.25 – 7.21 (m, 2H), 7.14 – 7.11 (m, 1H), 5.97 (d, *J* = 8.0, 1H), 3.04 (s, 3H), 2.47 (s, 3H), 2.13 (s, 3H), 1.88 (s, 3H).

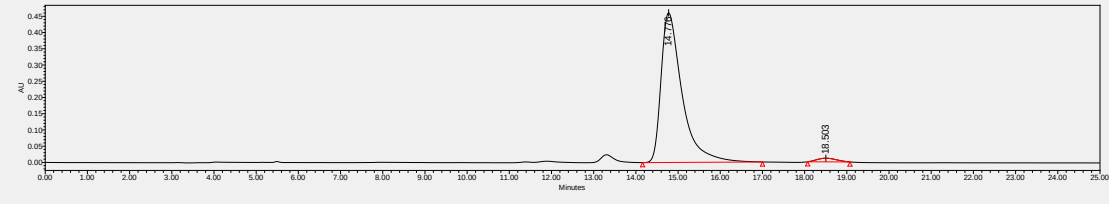
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.6, 147.9, 140.1, 139.8, 136.6, 130.2, 129.8, 128.7, 127.9, 127.1, 125.1, 124.8, 124.0, 121.6, 120.1, 118.1, 115.4, 45.4, 43.4, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{79}BrS^+$ ([M + H]$^+$) = 526.0795, found 526.0796. $C_{25}H_{25}N_3O_3{}^{81}BrS^+$ ([M + H]$^+$) = 528.0774, found 528.0779.

IR (neat): 1696, 1637, 1381, 1354, 1314, 1276, 1182, 1132, 1088, 1007, 959, 845, 803, 757, 701, 530 cm^{-1}.



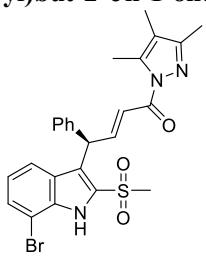
	Retention Time	Area	% Area
1	14.842	5636851	50.13
2	18.342	5607945	49.87



	Retention Time	Area	% Area

1	14.776	15892912	97.51
2	18.503	359045	2.49

(*R*,*E*)-4-(7-bromo-2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ao)



Following the typical procedure B.

30.4 mg, 58% yield; white solid; M.p. 102-105 °C. R_f = 0.3 (Pet/EtOAc = 4/1).

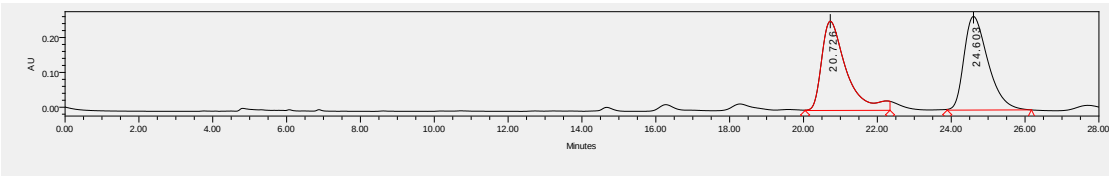
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 20.808 min, t (minor) = 24.880 min. ee = 48%. $[\alpha]^{21}_D$ = +33.3 (*c* = 0.21, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (s, 1H), 7.73 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.31 – 7.28 (m, 4H), 7.26 – 7.22 (m, 1H), 6.98 – 6.94 (m, 1H), 6.01 (d, *J* = 8.0, 1H), 3.09 (s, 3H), 2.48 (s, 3H), 2.15 (s, 3H), 1.90 (s, 3H).

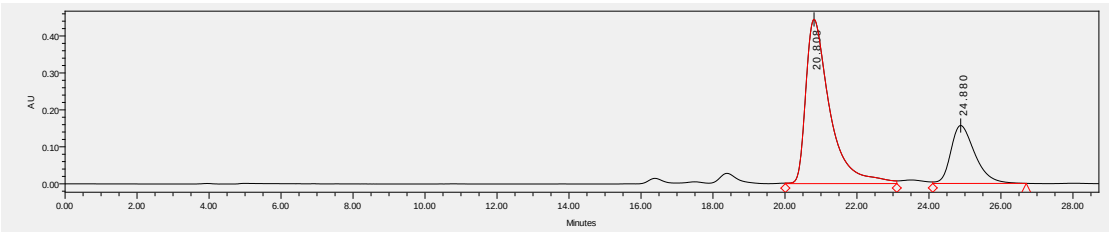
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.6, 152.5, 147.7, 140.0, 139.7, 134.7, 130.2, 128.7, 128.5, 128.0, 127.1, 127.1, 124.1, 122.6, 122.5, 122.2, 118.0, 105.7, 45.4, 43.6, 26.9, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{25}N_3O_3{}^{79}BrS^+$ ([M + H]$^+$) = 526.0795, found 526.0796. $C_{25}H_{25}N_3O_3{}^{81}BrS^+$ ([M + H]$^+$) = 528.0774, found 528.0771.

IR (neat): 2361, 2310, 1695, 1636, 1425, 1381, 1354, 1316, 1187, 1141, 1092, 961 cm^{-1}.

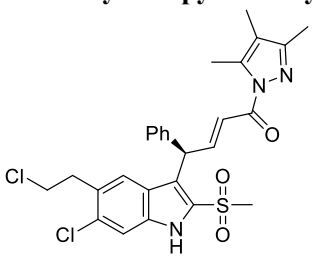


	Retention Time	Area	% Area
1	20.726	11970687	49.65
2	24.603	12141059	50.35



	Retention Time	Area	% Area
1	20.808	20585135	73.90
2	24.880	7270801	26.10

(*R*,*E*)-4-(6-chloro-5-(2-chloroethyl)-2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (4ap)



Following the typical procedure C.

51.5 mg, 95% yield; white solid; M.p. 95-101 °C. R_f = 0.3 (Pet/EtOAc = 4/1).

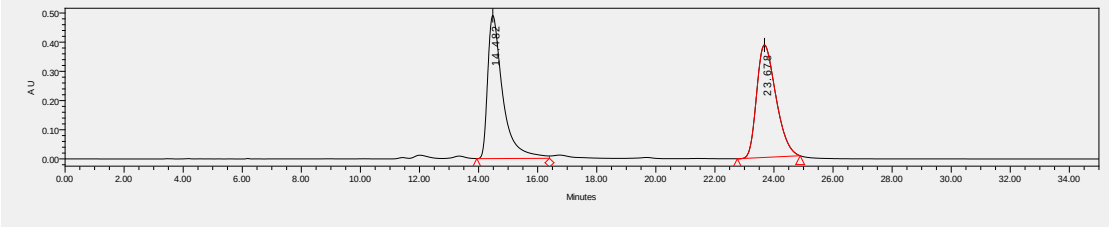
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 14.514 min, t (minor) = 23.941 min. ee = 95%. $[\alpha]^{21}_D$ = +86.8 (*c* = 0.59, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.39 (s, 1H), 7.71 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.47 – 7.42 (m, 1H), 7.31 – 7.28 (m, 5H), 7.25 – 7.21 (m, 1H), 5.99 (d, *J* = 8.0, 1H), 3.65 – 3.56 (m, 2H), 3.18 – 3.08 (m, 2H), 3.07 (s, 3H), 2.49 (s, 3H), 2.14 (s, 3H), 1.90 (s, 3H).

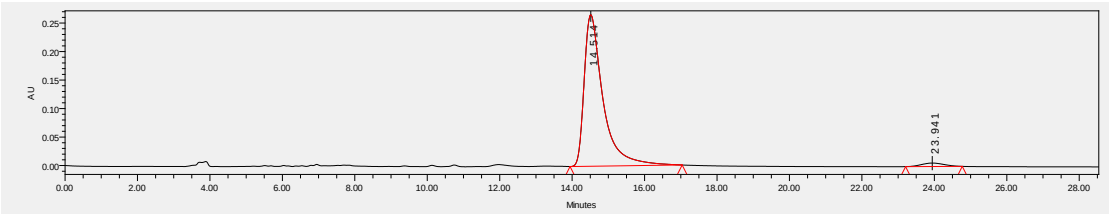
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.6, 147.9, 139.9, 139.8, 135.4, 132.5, 130.3, 128.8, 128.7, 128.0, 127.2, 125.0, 124.8, 124.1, 121.3, 118.1, 113.2, 45.4, 43.5, 43.4, 37.0, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{27}H_{28}N_3O_3{}^{35}Cl_2S^+$ ([M + H]$^+$) = 544.1223, found 544.1226. $C_{27}H_{28}N_3O_3{}^{35}Cl^{37}ClS^+$ ([M + H]$^+$) = 546.1193, found 546.1197. $C_{27}H_{28}N_3O_3{}^{37}Cl_2S^+$ ([M + H]$^+$) = 548.1164, found 548.1168.

IR (neat): 1696, 1633, 1354, 1311, 1175, 1132, 956, 853, 756, 702, 558 cm^{-1}.

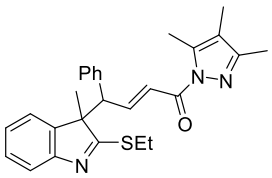


	Retention Time	Area	% Area
1	14.482	17417640	50.01
2	23.678	17410576	49.99



	Retention Time	Area	% Area
1	14.514	9597395	97.34
2	23.941	261762	2.66

(*E*)-4-(2-(ethylthio)-3-methyl-3*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (3aq)



Following the typical procedure E.

22.9 mg, 52% yield; pale yellow oil. R_f = 0.2 (Pet/EtOAc = 10/1).

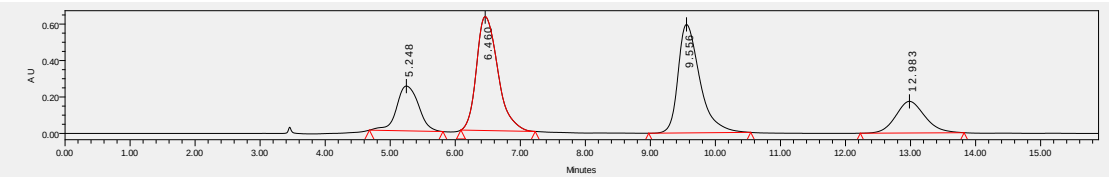
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/i-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm, retention time: $t_{minor\ isomer}$ (minor) = 5.405 min, $t_{major\ isomer}$ (major) = 6.609 min. $t_{major\ isomer}$ (minor) = 9.698 min, $t_{minor\ isomer}$ (major) = 13.217 min. 80:20 dr (determined by ^{1}H NMR analysis), 89% ee (major), 77% ee (minor). $[\alpha]^{22}_D$ = +82.4 (*c* = 0.45, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.28 (m, 3H), 7.26 – 7.18 (m, 3H), 7.15 – 6.94 (m, 4H), 6.91 – 6.89 (m, 0.8H), 6.68 – 6.66 (m, 0.2H), 4.00 (d, *J* = 10.0 Hz, 0.8H), 3.95 (d, *J* = 10.0 Hz, 0.2H), 3.86 – 3.30 (m, 0.8H), 3.25 – 3.19 (m, 0.8H), 3.15 – 3.10 (m, 0.2H), 3.08 – 3.01 (m, 0.2H), 2.52 (s, 0.6 H), 2.44 (s, 2.4 H), 2.22 (s, 0.6 H), 2.17 (s, 2.4 H), 1.92 (s, 0.6 H), 1.88 (s, 2.4 H), 1.48 (s, 0.6 H), 1.41 (t, *J* = 7.2 Hz, 2.4H), 1.33 (s, 0.6 H), 1.26 – 1.23 (m, 0.6H).

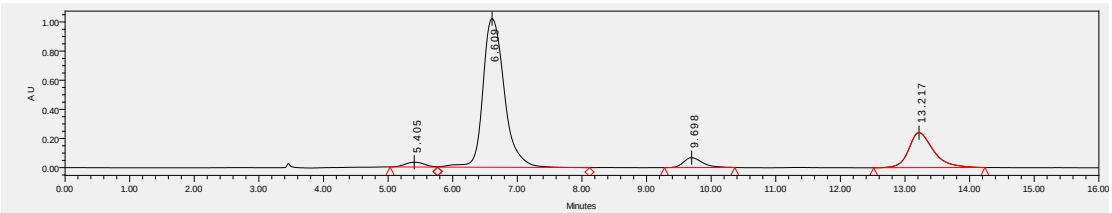
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.3, 155.0, 152.1, 146.8, 140.9, 137.8, 129.6, 128.3, 127.9, 127.3, 123.9, 123.42, 123.40, 118.7, 117.7, 61.9, 55.7, 25.3, 22.9, 14.1, 12.7, 12.3, 7.6.

ESI-HRMS: calcd for $C_{27}H_{30}N_3OS^+$ ([M + H]$^+$) = 444.2104, found 444.2102.

IR (neat): 2926, 1701, 1638, 1507, 1452, 1353, 1007, 770, 708 cm^{-1}.

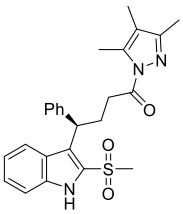


	Retention Time	Area	% Area
1	5.248	5525888	14.17
2	6.460	14038671	35.99
3	9.556	14034772	35.98
4	12.983	5408318	13.86



	Retention Time	Area	% Area
1	5.405	684669	2.14
2	6.609	23460238	73.49
3	9.698	1401843	4.39
4	13.217	6377267	19.98

(*R*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)butan-1-one (5aa)



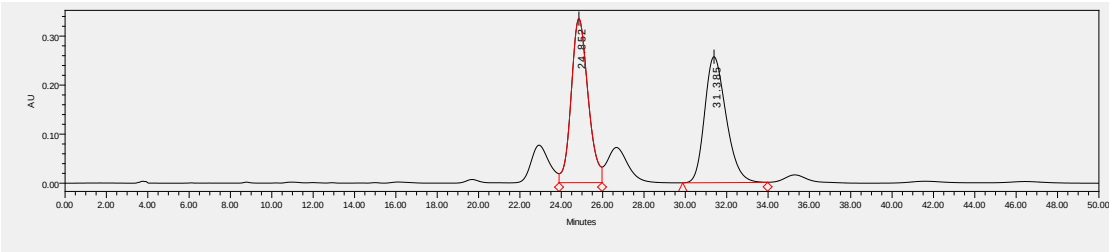
78.1 mg, 87% yield; white solid; M.p. 85-88 °C. R_f = 0.4 (Pet/EtOAc = 3/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IC** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 24.882 min, t (minor) = 31.536 min. ee = 97%. $[\alpha]^{21}_D$ = +42.3 (*c* = 0.44, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.03 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.26 – 7.16 (m, 3H), 7.10 – 7.03 (m, 2H), 4.99 (d, *J* = 8.0, 1H), 3.18 – 2.95 (m, 2H), 2.95 (s, 3H), 2.81 – 2.63 (m, 2H), 2.33 (s, 3H), 2.01 (s, 3H), 1.77 (s, 3H).

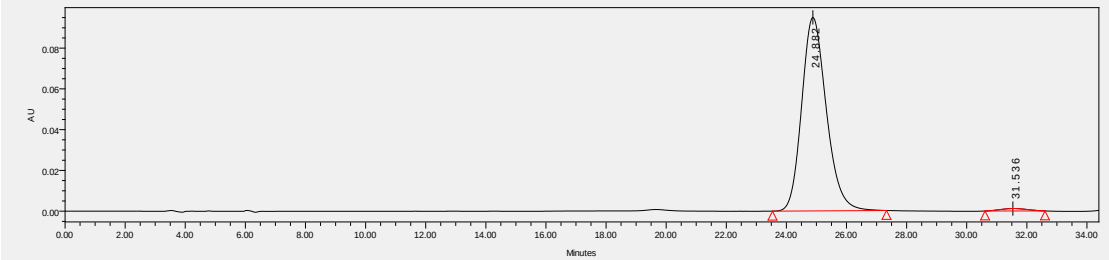
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 173.3, 152.0, 142.7, 139.3, 136.0, 129.3, 128.4, 127.9, 126.4, 126.3, 125.9, 124.0, 123.0, 121.1, 117.1, 112.5, 45.4, 40.3, 34.0, 29.1, 12.6, 12.2, 7.5.

ESI-HRMS: calcd for $C_{25}H_{28}N_3O_3S^+$ ([M + H]$^+$) = 450.1846, found 450.1846.

IR (neat): 3316, 1714, 1492, 1303, 1189, 1141, 957, 931, 835, 746, 702, 588, 523, 431 cm^{-1}.

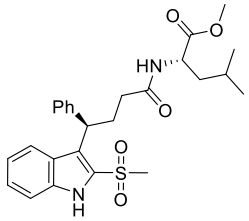


	Retention Time	Area	% Area
1	24.852	18911670	50.50
2	31.385	18539925	49.50



	Retention Time	Area	% Area
1	24.882	5406861	98.62
2	31.536	75511	1.38

methyl ((*R*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenylbutanoyl)-*L*-leucinate (6aa)



19.4 mg, 80% yield; white solid; M.p. 90-94 °C. R_f = 0.2 (Pet/EtOAc = 2/1). >19:1 dr (determined by ^{1}H NMR analysis). $[\alpha]^{19}_D$ = +21.8 (*c* = 0.22, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.00 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.39 – 7.34 (m, 3H), 7.28 – 7.24 (m, 2H), 7.19 – 7.13 (m, 2H), 5.91 (d, *J* = 8.0 Hz, 1H), 4.93 – 4.89 (m, 1H), 4.64 – 4.58 (m, 1H),

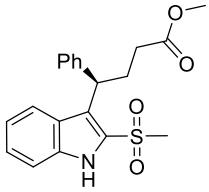
3.70 (s, 3H), 2.98 (s, 3H), 2.77 – 2.61 (m, 2H), 2.36 – 2.30 (m, 1H), 2.24 – 2.16 (m, 1H), 1.66 (s, 1H), 1.61 – 1.47 (m, 2H), 0.92 (t, *J* = 6.0 Hz, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 173.6, 172.3, 142.5, 135.8, 129.6, 128.5, 127.9, 126.5, 126.1, 123.4, 123.0, 121.3, 112.6, 52.2, 50.7, 45.3, 41.6, 40.4, 34.7, 30.3, 24.8, 22.8, 22.0.

ESI-HRMS: calcd for $C_{26}H_{33}N_2O_5S^+$ ($[M+H]^+$) = 485.2105, found 485.2104.

IR (neat): 3353, 2957, 2361, 1740, 1654, 1527, 1445, 1310, 1204, 1144, 959, 751, 701, 525 cm^{-1}.

methyl (*R*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenylbutanoate (7aa)



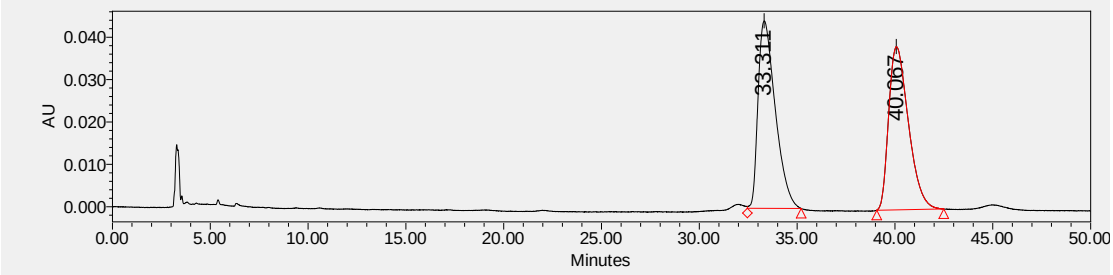
17.6 mg, 95% yield; white solid; M.p. 49-53 °C. R_f = 0.2 (Pet/EtOAc = 4/1). Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (major) = 33.061 min, t (minor) = 40.515 min. ee = 97%. $[\alpha]^{19}_D$ = +35.8 (*c* = 0.26, in CH_2Cl_2).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.34 (m, 4H), 7.29 – 7.25 (m, 2H), 7.20 – 7.13 (m, 2H), 4.97 – 4.93 (m, 1H), 3.60 (s, 3H), 2.94 (s, 3H), 2.76 – 2.60 (m, 2H), 2.47 – 2.27 (m, 2H).

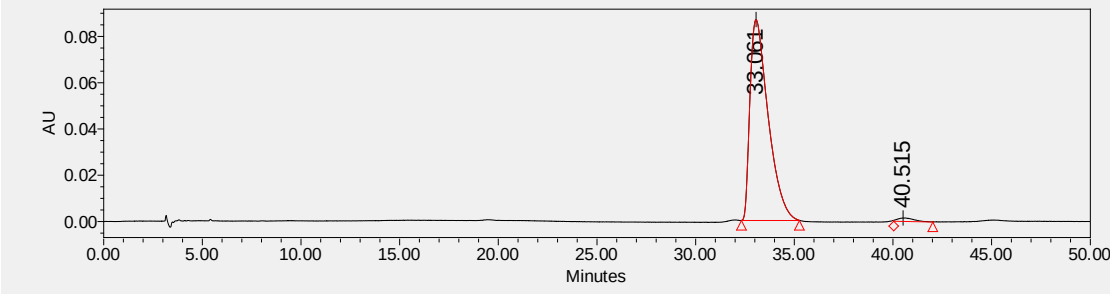
$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 173.7, 142.5, 135.9, 129.5, 128.5, 127.9, 126.5, 126.4, 126.1, 123.5, 122.8, 121.3, 112.6, 51.5, 45.3, 40.2, 32.5, 29.5.

ESI-HRMS: calcd for $C_{20}H_{22}NO_4S^+$ ($[M+H]^+$) = 372.1264, found 372.1269.

IR (neat): 2361, 1729, 1445, 1307, 1143, 957, 752, 700, 525 cm^{-1}.

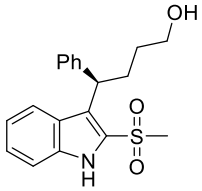


	Retention Time	Area	% Area
1	33.311	2709119	50.11
2	40.067	2696782	49.89



	Retention Time	Area	% Area
1	33.061	5561369	98.47
2	40.515	86614	1.53

(*R*)-4-(2-(methylsulfonyl)-1*H*-indol-3-yl)-4-phenylbutan-1-ol (8aa)



47.1 mg, 96% yield; white solid; M.p. 58-61 °C. R_f = 0.2 (Pet/EtOAc = 2/1).

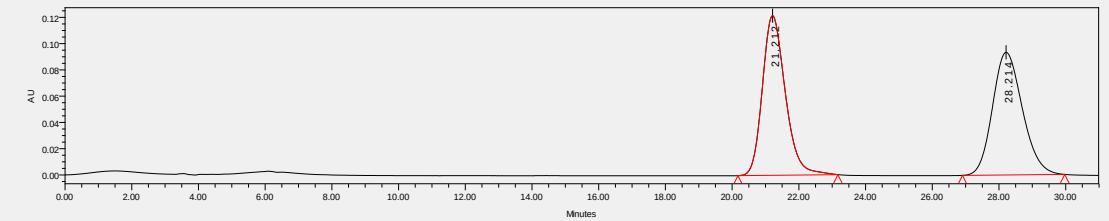
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IC** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: t (minor) = 21.326 min, t (major) = 28.040 min. ee = 97%. $[\alpha]^{21}_D$ = +35.4 (*c* = 0.84, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.25 – 7.21 (m, 1H), 7.18 – 7.14 (m, 2H), 7.10 – 7.01 (m, 2H), 4.87 (t, *J* = 8.0 Hz, 1H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.82 (s, 3H), 2.34 (q, *J* = 8.0 Hz, 2H), 1.83 – 1.80 (m, 1H), 1.62 – 1.53 (m, 1H), 1.46 – 1.37 (m, 1H).

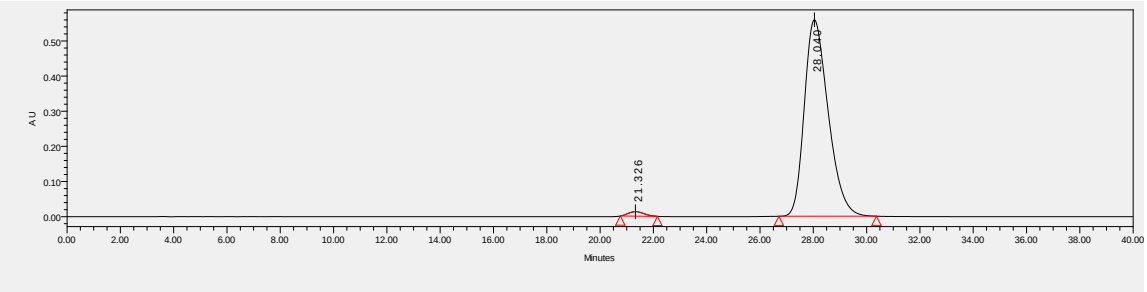
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 143.3, 136.0, 129.1, 128.4, 127.8, 126.4, 126.3, 125.9, 124.3, 122.8, 121.1, 112.6, 62.5, 45.3, 40.7, 31.2, 30.9.

ESI-HRMS: calcd for $C_{19}H_{22}NO_3S^+$ ([M + H]$^+$) = 344.1315, found 344.1316.

IR (neat): 3316, 1520, 1447, 1299, 1189, 1132, 1053, 957, 744, 700, 578, 522, 431 cm^{-1}.

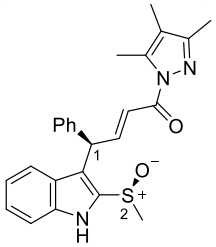


	Retention Time	Area	% Area
1	21.212	5798999	49.95
2	28.214	5811609	50.05



	Retention Time	Area	% Area
1	21.326	523615	1.48
2	28.040	34809613	98.52

(1*R*,2*S*,*E*)-4-(2-(methylsulfinyl)-1*H*-indol-3-yl)-4-phenyl-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (9aa)



10.8 mg, 50% yield; white solid; M.p. 113-117 °C. R_f = 0.2 (Pet/EtOAc = 1/1).

Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **ID** column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm, retention time: $t_{major\ isomer}$ (major) = 35.759 min, $t_{major\ isomer}$ (minor) = 58.670 min. $t_{minor\ isomer}$ (minor) = 28.885 min, $t_{minor\ isomer}$ (major) = 49.096 min. 92:8 dr (determined

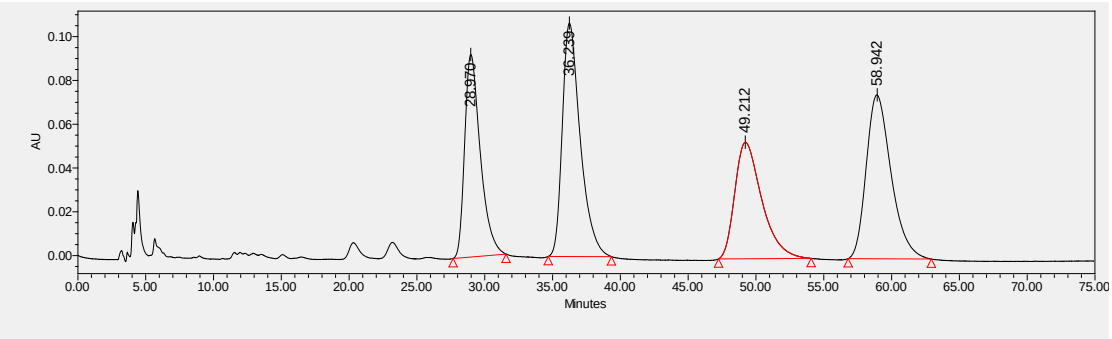
by ^{1}H NMR analysis), 99% ee (major). $[\alpha]^{19}_D = -219.1$ (c = 0.11, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.22 (s, 1H), 7.67 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.30 – 7.28 (m, 3H), 7.26 – 7.22 (m, 3H), 7.08 – 7.04 (m, 1H), 5.43 (d, *J* = 8.0 Hz, 1H), 2.84 (s, 3H), 2.49 (s, 3H), 2.16 (s, 3H), 1.90 (s, 3H).

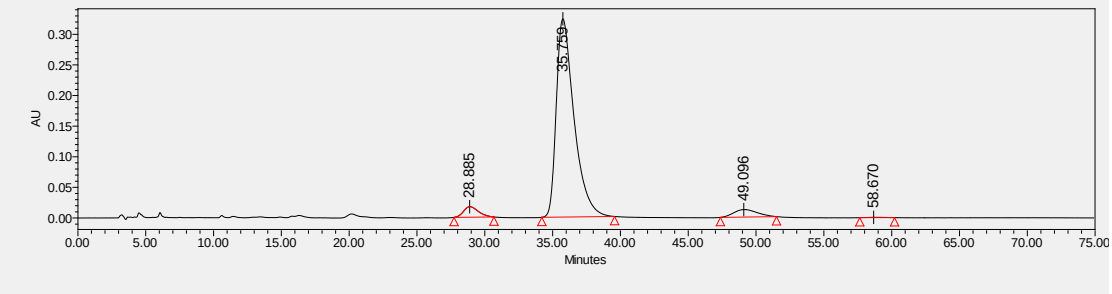
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.7, 152.4, 149.3, 140.7, 139.7, 137.3, 133.1, 128.8, 128.0, 127.2, 126.6, 124.6, 123.1, 120.8, 120.7, 117.9, 117.9, 112.3, 45.1, 42.3, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{25}H_{26}N_3O_2S^+$ ([M + H]$^+$) = 432.1740, found 432.1745.

IR (neat): 2361, 1699, 1636, 1380, 1353, 1284, 1025, 748, 701 cm^{-1}.

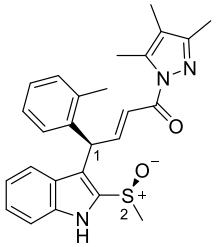


	Retention Time	Area	% Area
1	28.970	7551734	21.93
2	36.239	9787482	28.42
3	49.212	7441539	21.61
4	58.942	9661530	28.05



	Retention Time	Area	% Area
1	28.885	1314145	4.07
2	35.759	29421903	91.18
3	49.096	1484824	4.60
4	58.670	46388	0.14

(1*R*,2*S*,*E*)-4-(2-(methylsulfinyl)-1*H*-indol-3-yl)-4-(o-tolyl)-1-(3,4,5-trimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one (9da)



33.1 mg, 84% yield; white solid; M.p. 170-175 °C. R_f = 0.2 (Pet/EtOAc = 1/1).

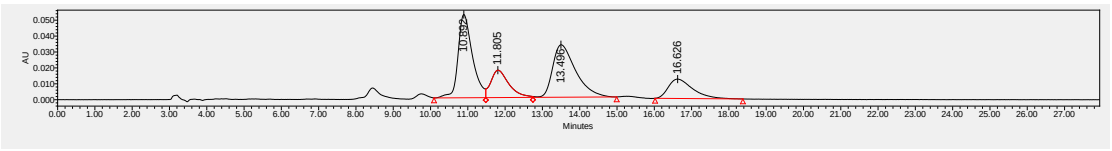
Dissolved in isopropanol for HPLC; **HPLC** (Chiralcel **IB** column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: $t_{minor\ isomer}$ (minor) = 10.502 min, $t_{major\ isomer}$ (minor) = 10.983 min. $t_{minor\ isomer}$ (major) = 13.591 min, $t_{major\ isomer}$ (minor) = 15.928 min. > 19:1 dr (determined by ^{1}H NMR analysis), 97% ee (major). $[\alpha]^{19}_D$ = –214.0 (*c* = 0.20, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.53 (s, 1H), 7.60 (dd, *J* = 15.6, 7.2 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.35 – 7.33 (m, 1H), 7.24 – 7.10 (m, 6H), 7.08 – 7.04 (m, 1H), 5.53 (d, *J* = 7.2 Hz, 1H), 2.77 (s, 3H), 2.47 (s, 3H), 2.23 (s, 3H), 2.10 (s, 3H), 1.87 (s, 3H).

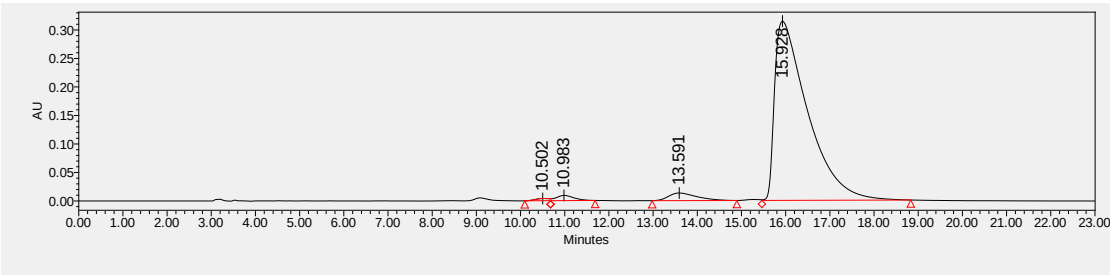
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.8, 152.3, 149.4, 139.7, 138.7, 137.1, 136.5, 133.1, 130.9, 128.2, 127.5, 127.0, 126.3, 124.5, 123.2, 120.6, 120.4, 117.9, 112.3, 110.0, 42.13, 42.06, 19.8, 12.7, 12.3, 7.7.

ESI-HRMS: calcd for $C_{26}H_{28}N_3O_2S^+$ ([M + H]$^+$) = 446.1897, found 446.1893.

IR (neat): 2922, 1698, 1634, 1377, 1352, 1089, 1023, 742 cm^{-1}.



	Retention Time	Area	% Area
1	10.892	1395443	35.43
2	11.805	575872	14.62
3	13.496	1410469	35.81
4	16.626	556962	14.14



	Retention Time	Area	% Area
1	10.502	85390	0.49
2	10.983	257150	1.49
3	13.591	588102	3.40
4	15.928	16349968	94.61

12 References

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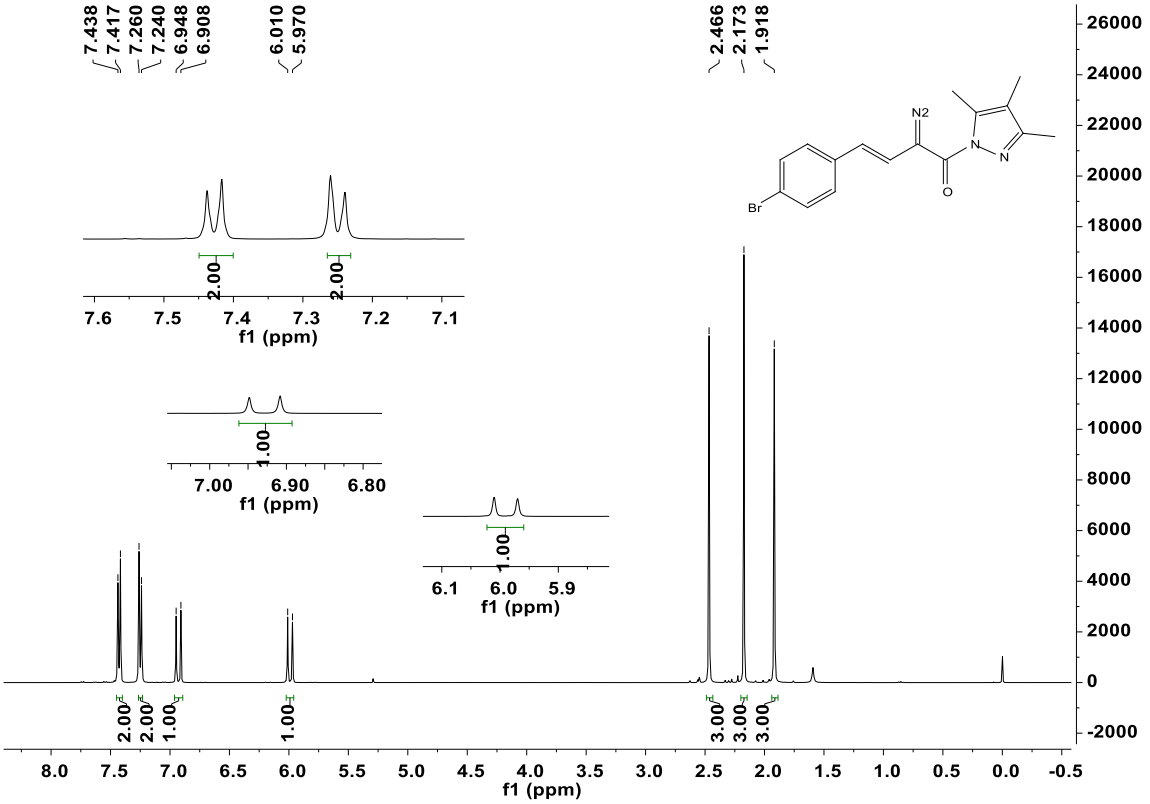
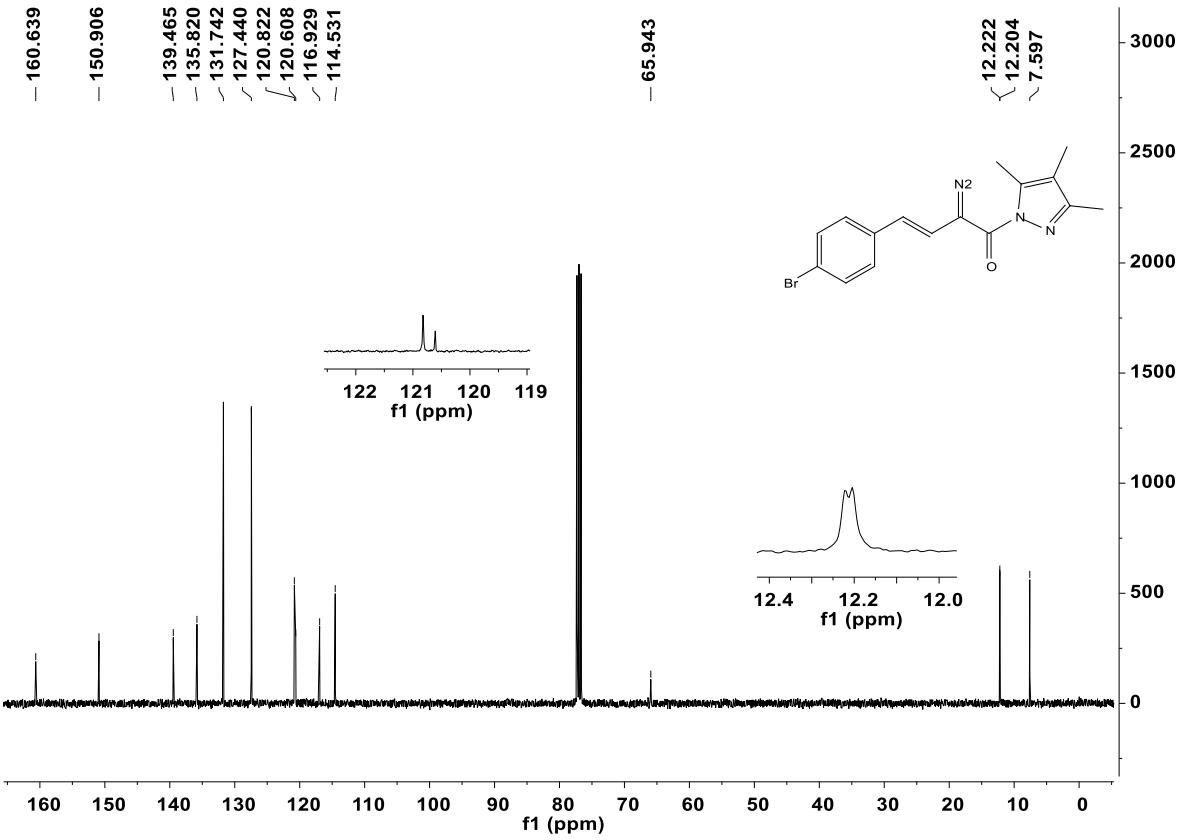
13 ^{1}H, ^{13}C NMR spectra of the substrates and products

1J





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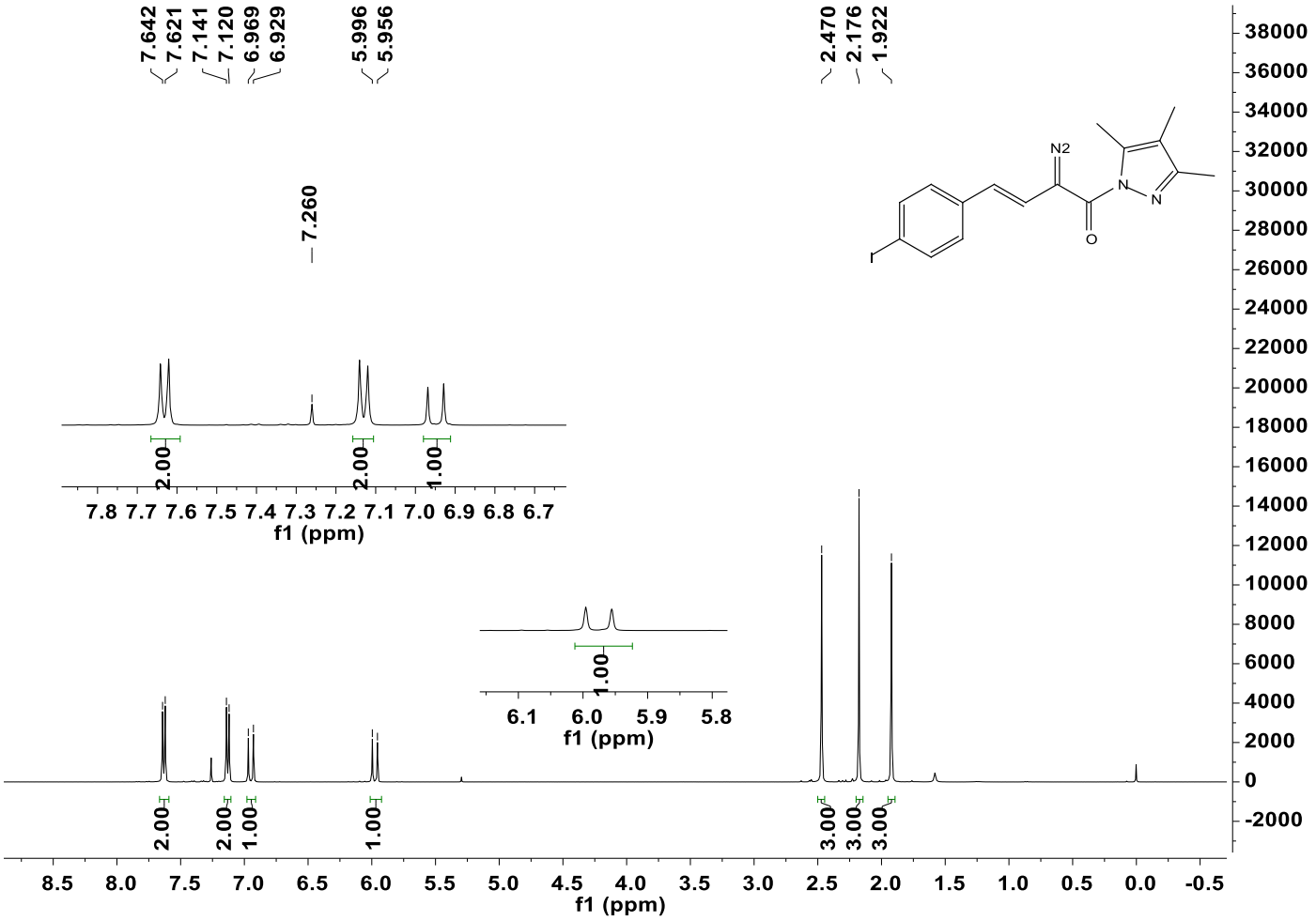
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7.260
N2
N
N
O
I
2.00
2.00
1.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
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6.1 6.0 5.9 5.8
f1 (ppm)
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2.00
1.00
1.00
3.00
3.00
3.00
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 -0.5
f1 (ppm)
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36000
34000
32000
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24000
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18000
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12000
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4000
2000
0
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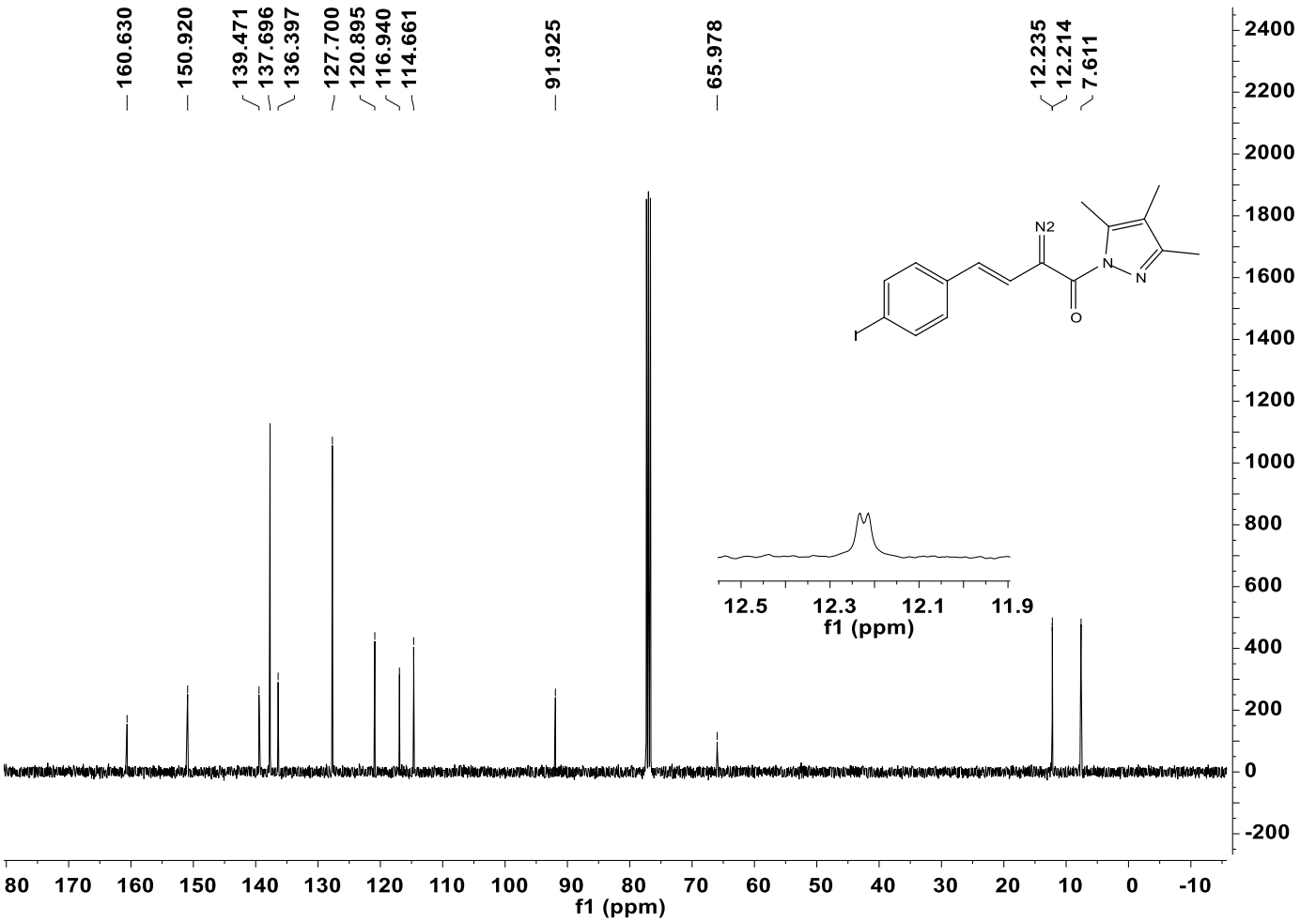
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120.895
116.940
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65.978
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12.214
7.611
N2
N
N
O
I
12.5 12.3 12.1 11.9
f1 (ppm)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2400
2200
2000
1800
1600
1400
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1000
800
600
400
200
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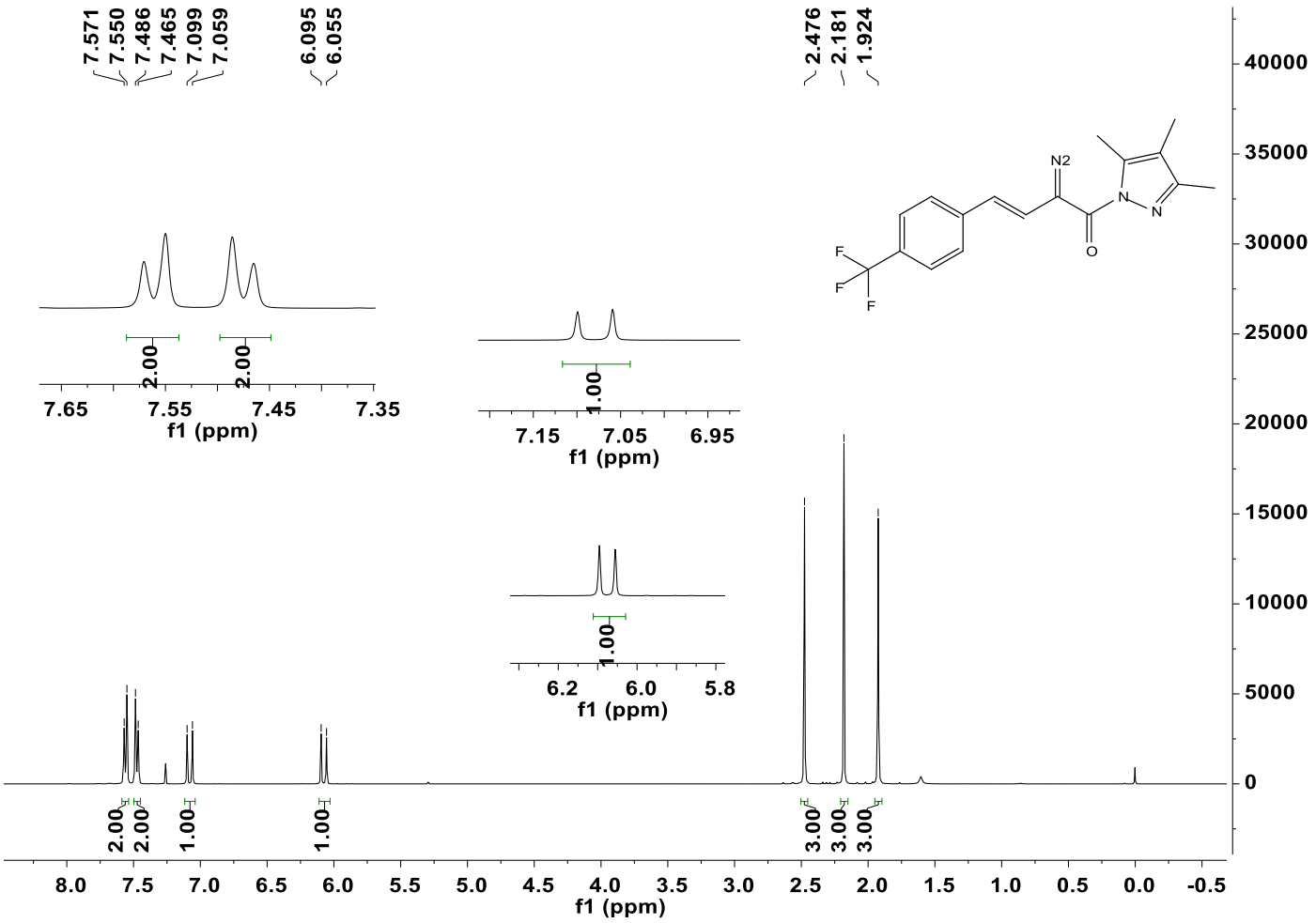
1l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F
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1.00
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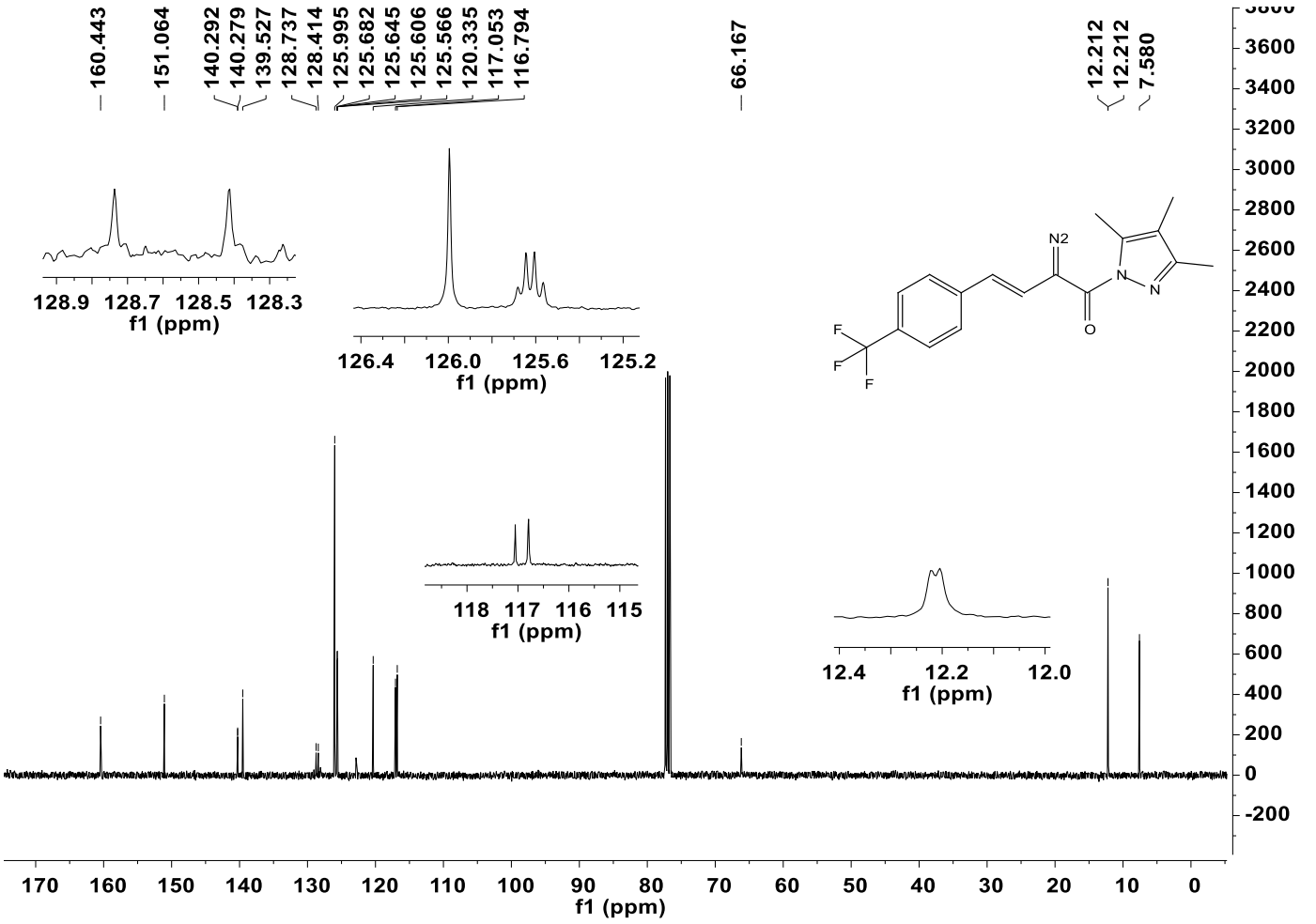
1.00
3.00
3.00
3.00
f1 (ppm)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125.566
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12.212
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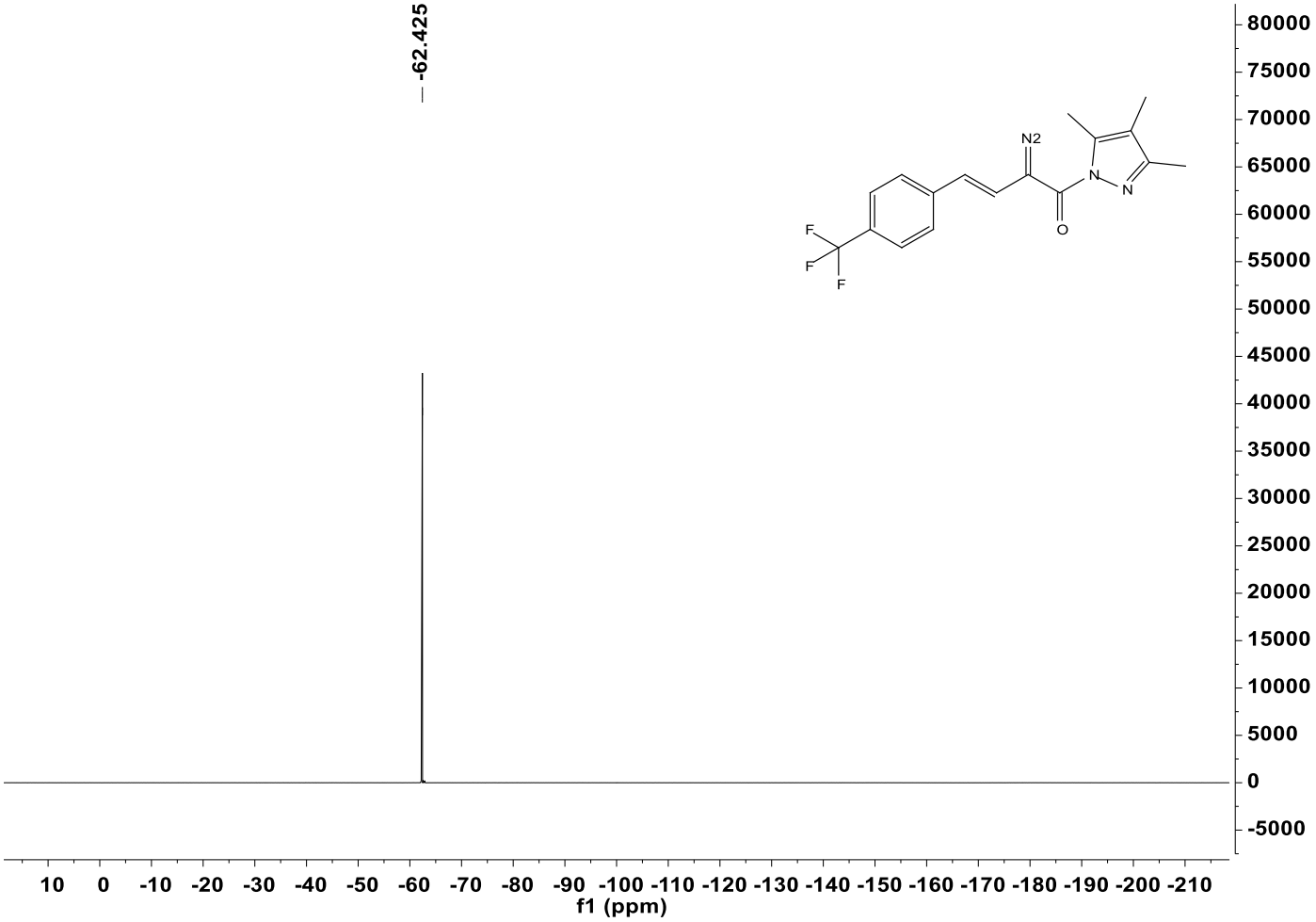
7.580
N2
O
F
F
F
f1 (ppm)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35000
30000
25000
20000
15000
10000
5000
0
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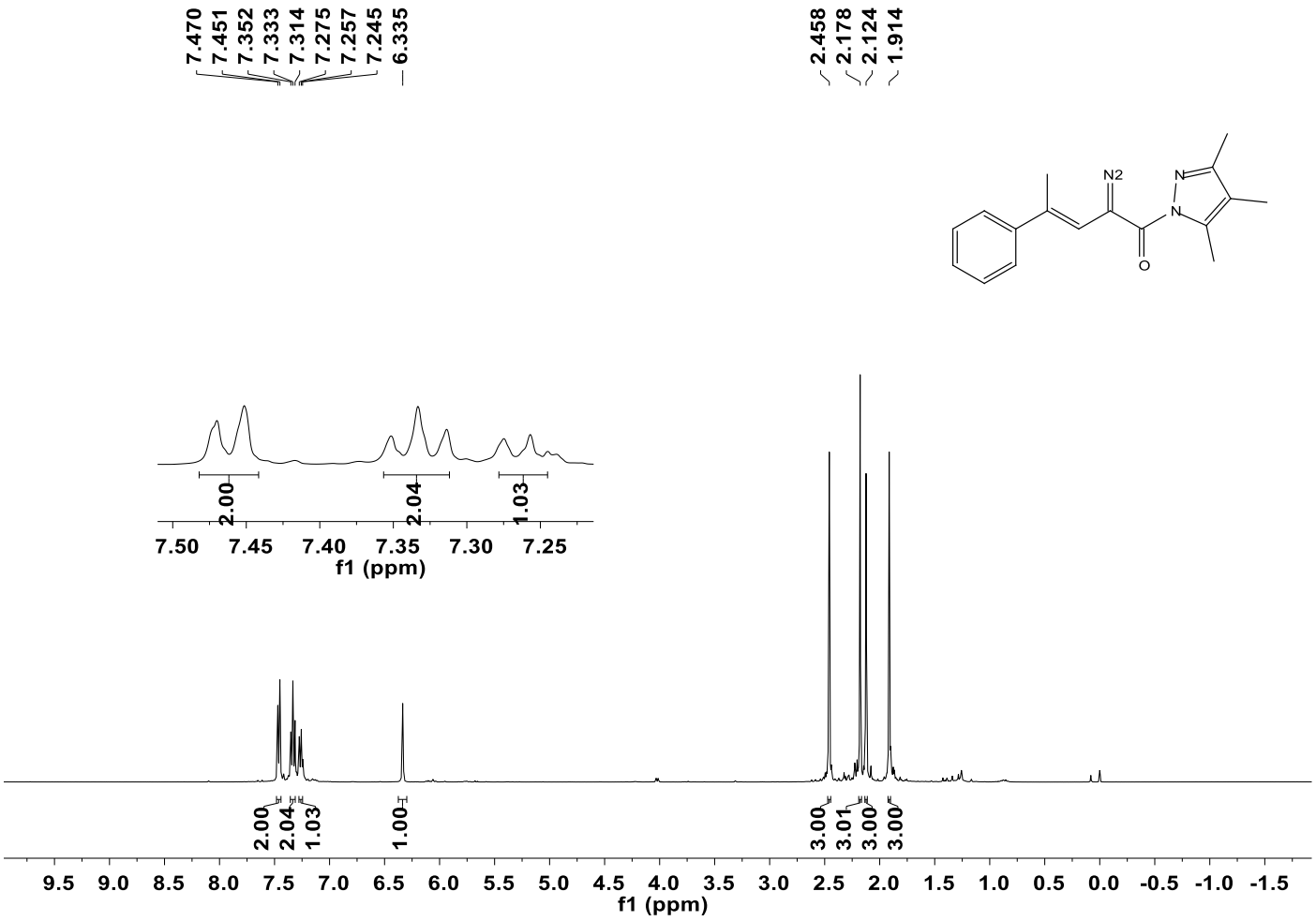
f1 (ppm)

1s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7.245
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N2
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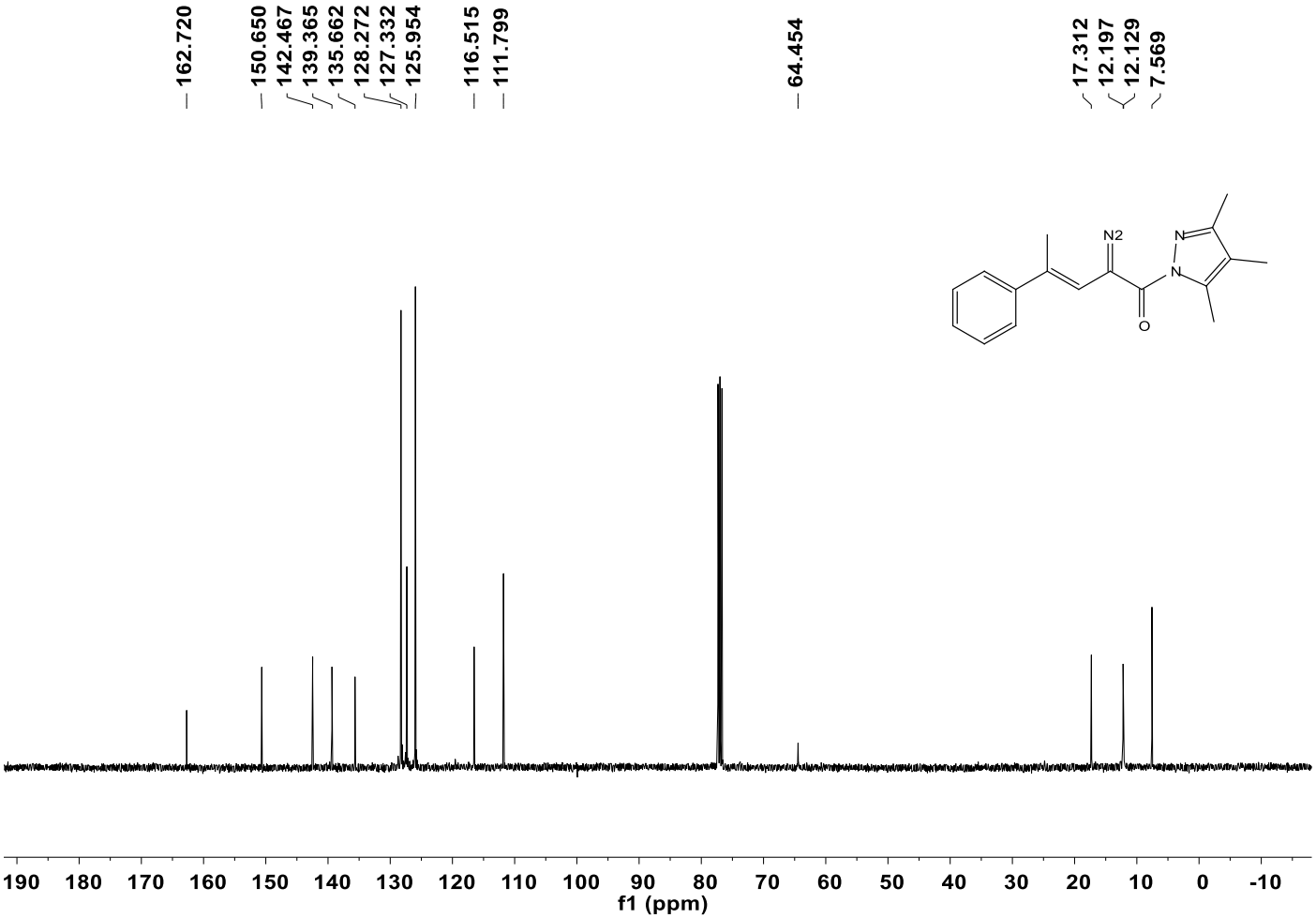
N
O
2.00
2.04
1.03
7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
2.00
2.04
1.03
1.00
3.00
3.01
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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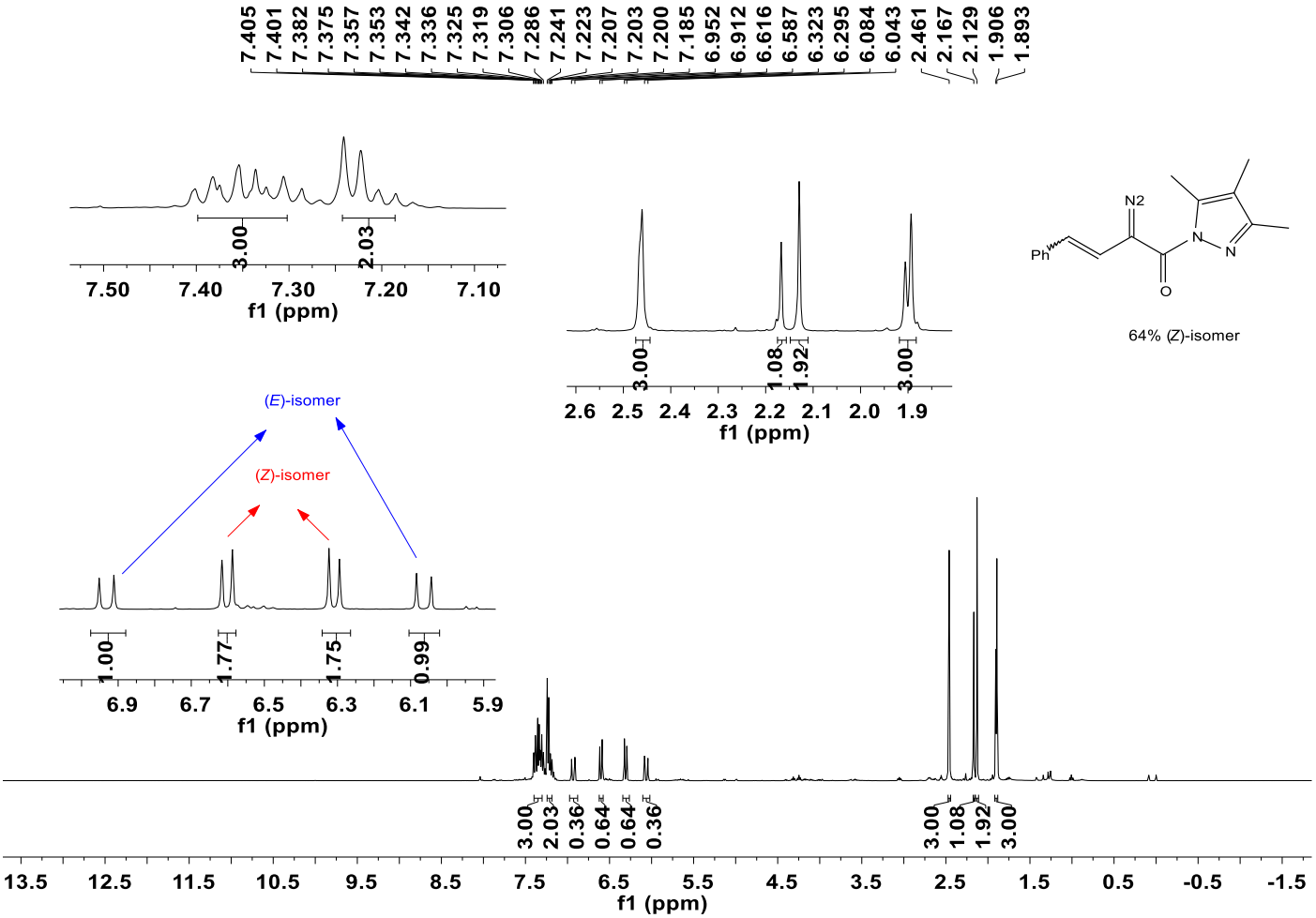
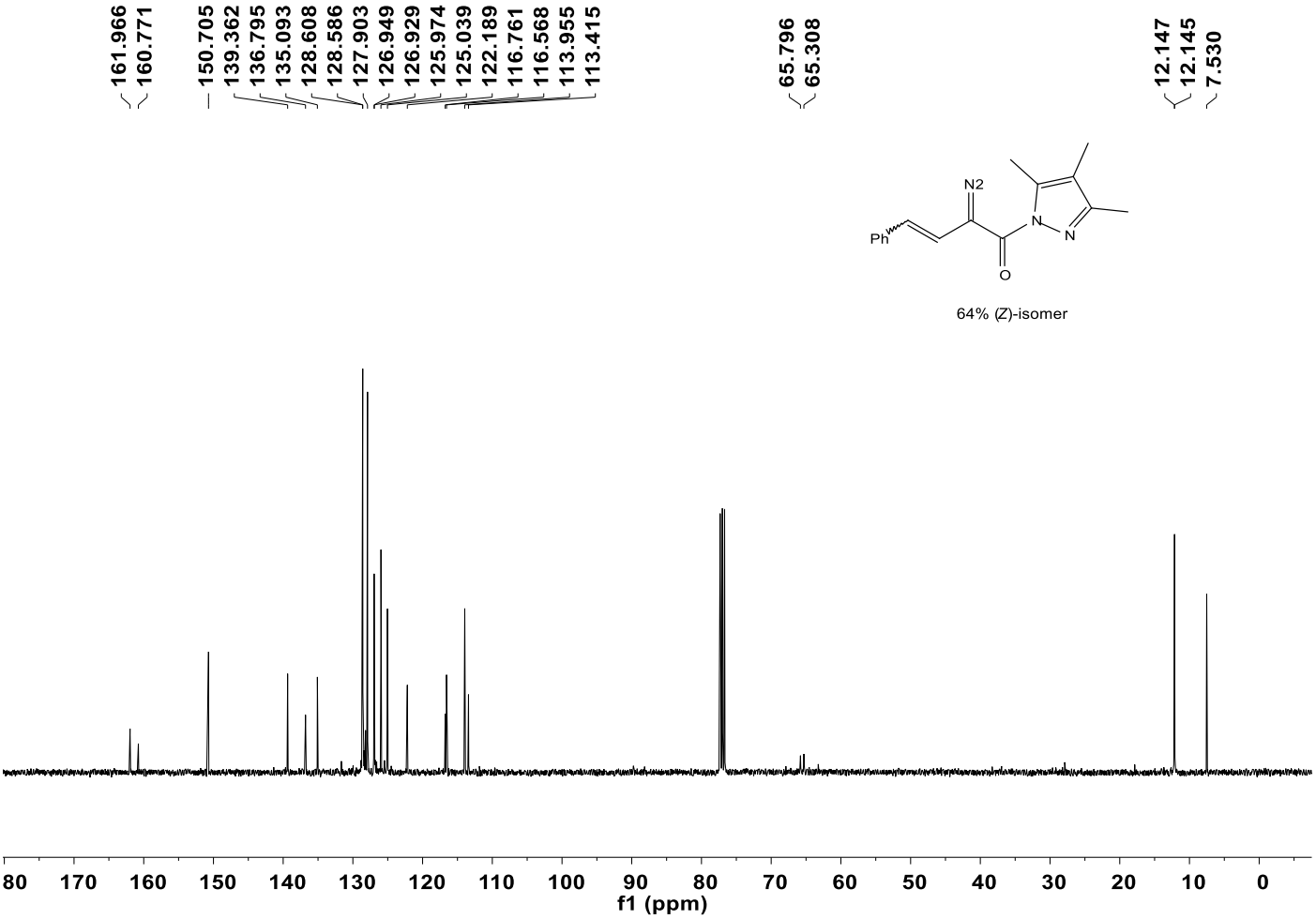
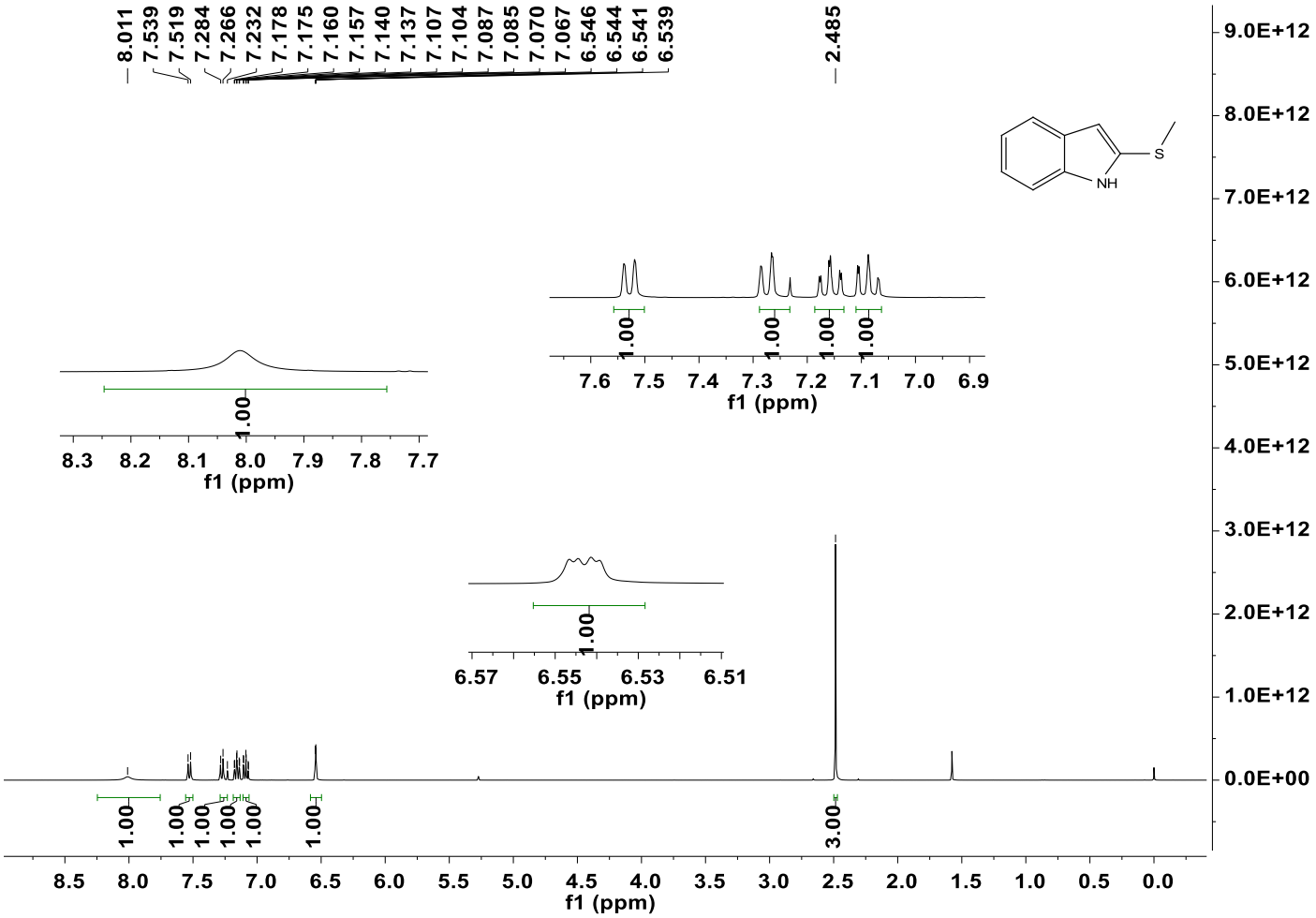
12.197
12.129
7.569
N2
N
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

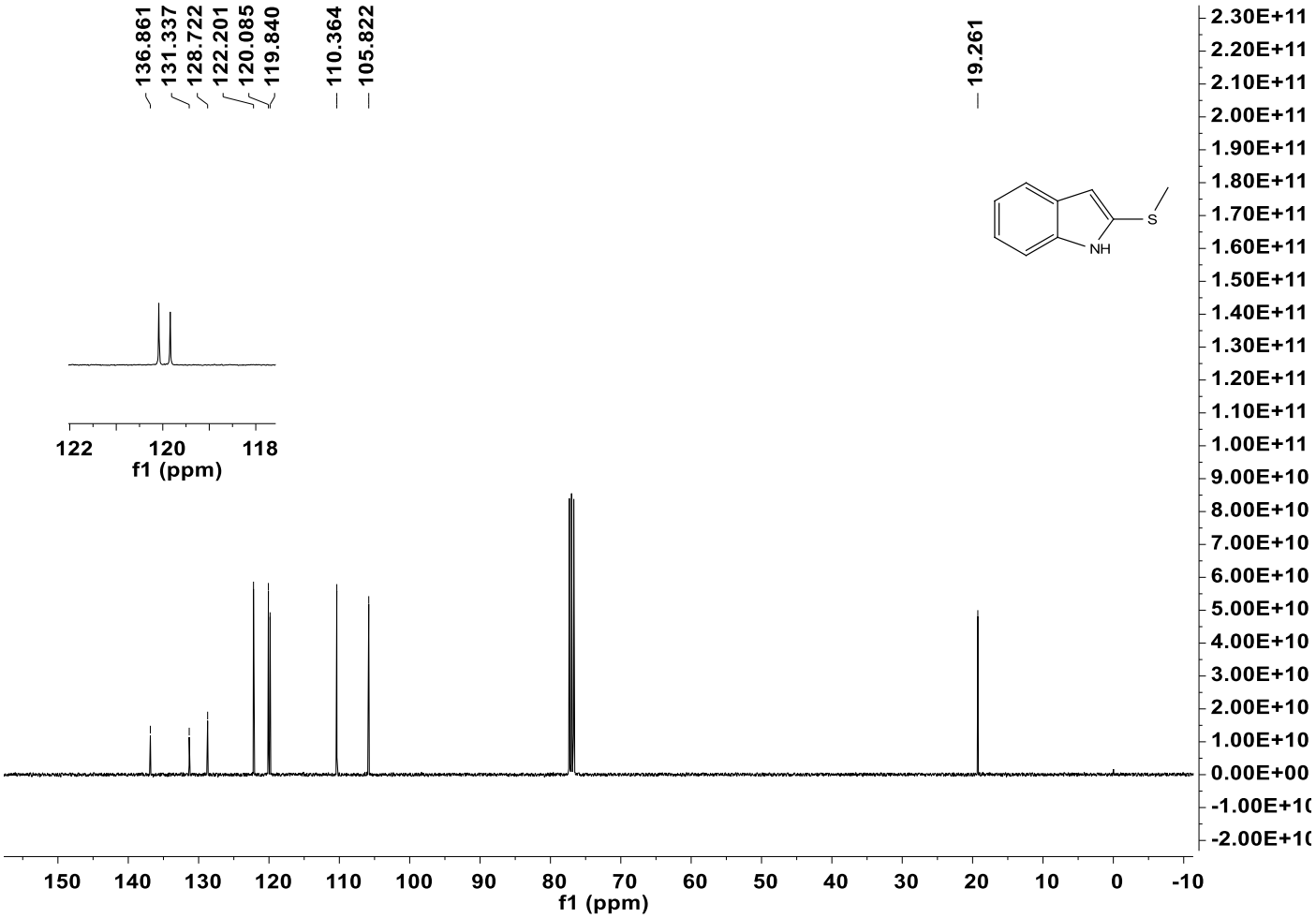
(*Z*/*E*)-2-diazo-4-phenyl-1-(3,4,5-trimethyl-1H-pyrazol-1-yl)but-3-en-1-one



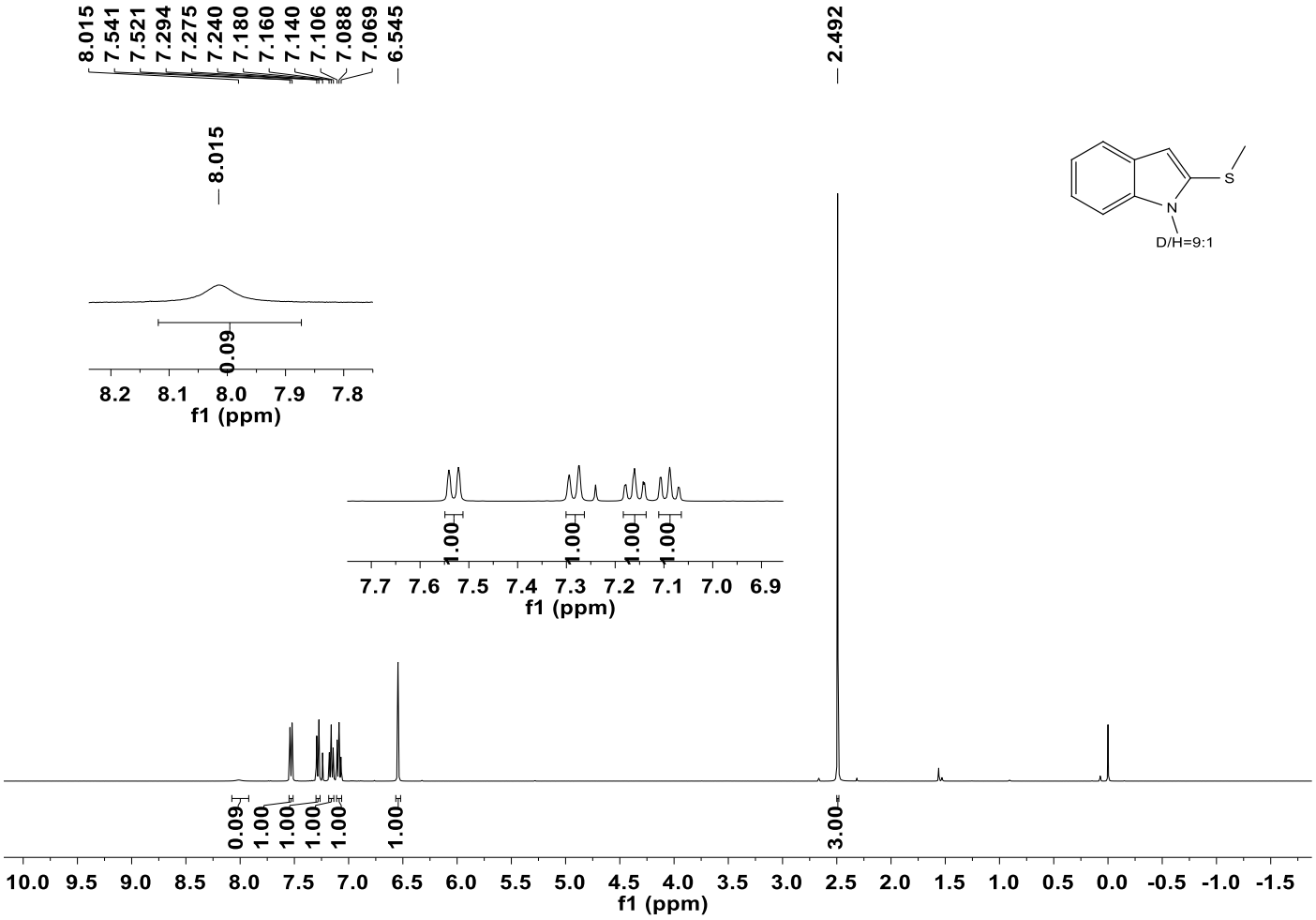


2a

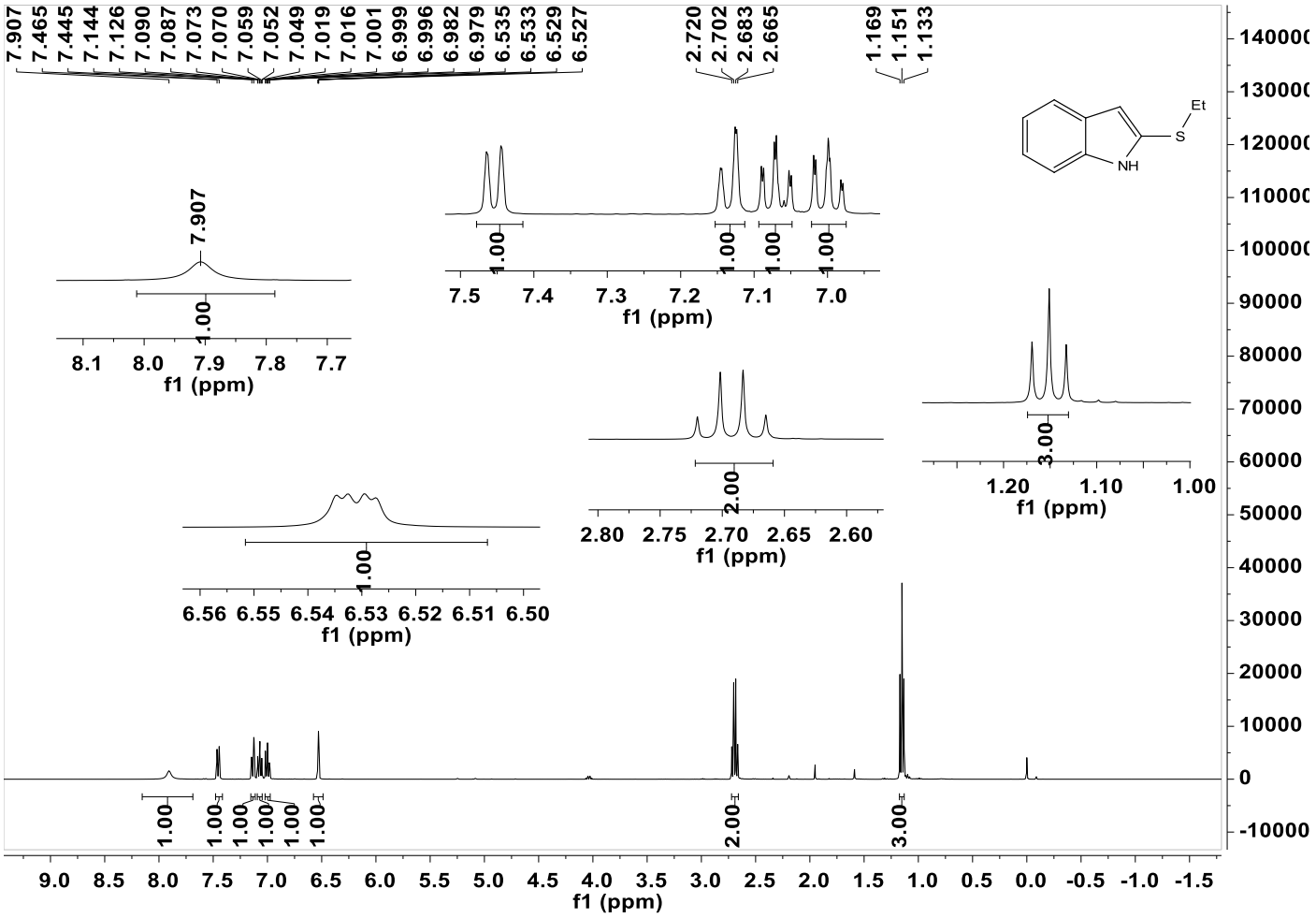

8.011
7.539
7.519
7.284
7.266
7.232
7.178
7.175
7.160
7.157
7.140
7.137
7.107
7.104
7.087
7.085
7.070
7.067
6.546
6.544
6.541
6.539
2.485
S
NH
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

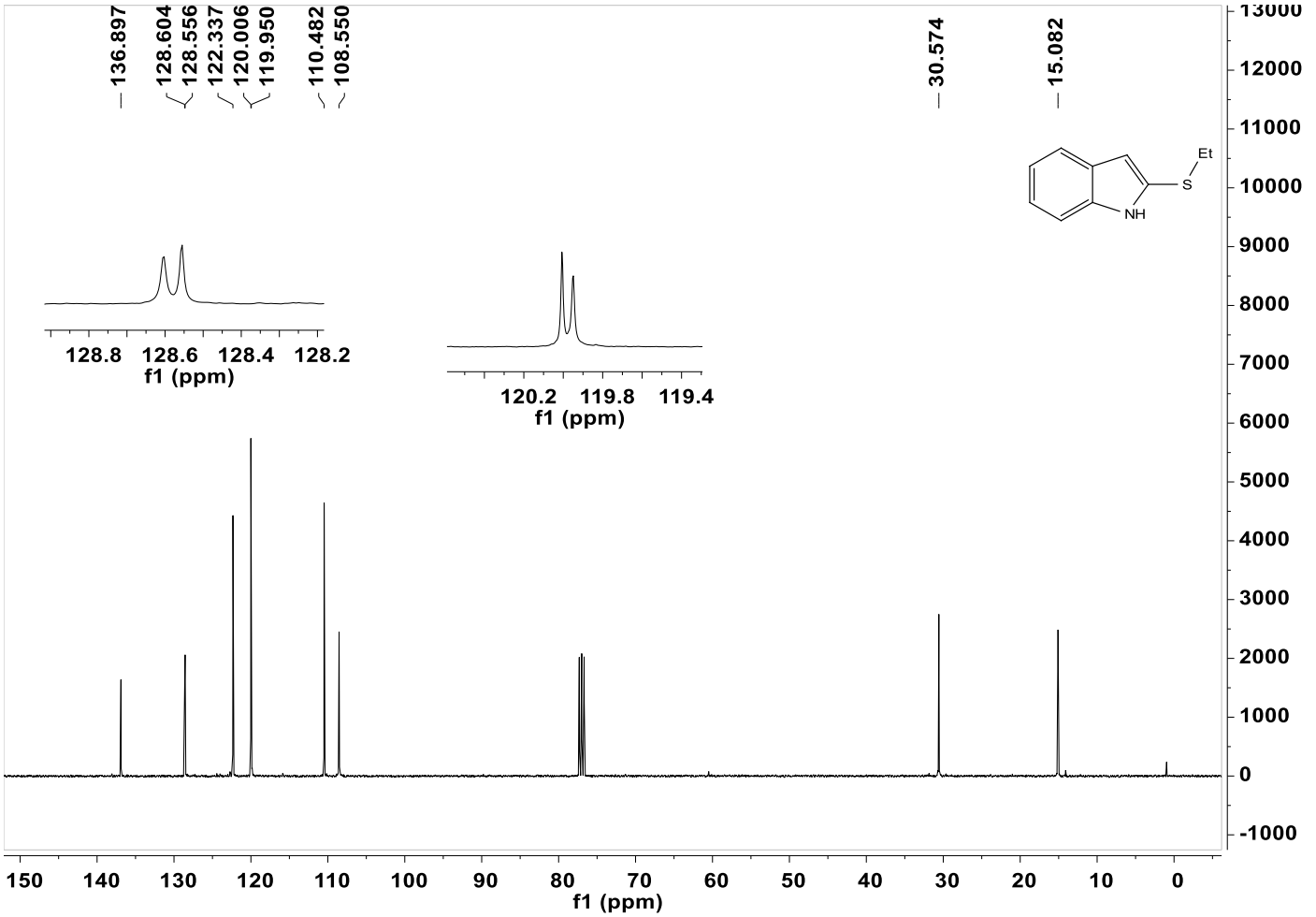

136.861
131.337
128.722
122.201
120.085
119.840
110.364
105.822
19.261
S
NH
f1 (ppm)

d-**2a**

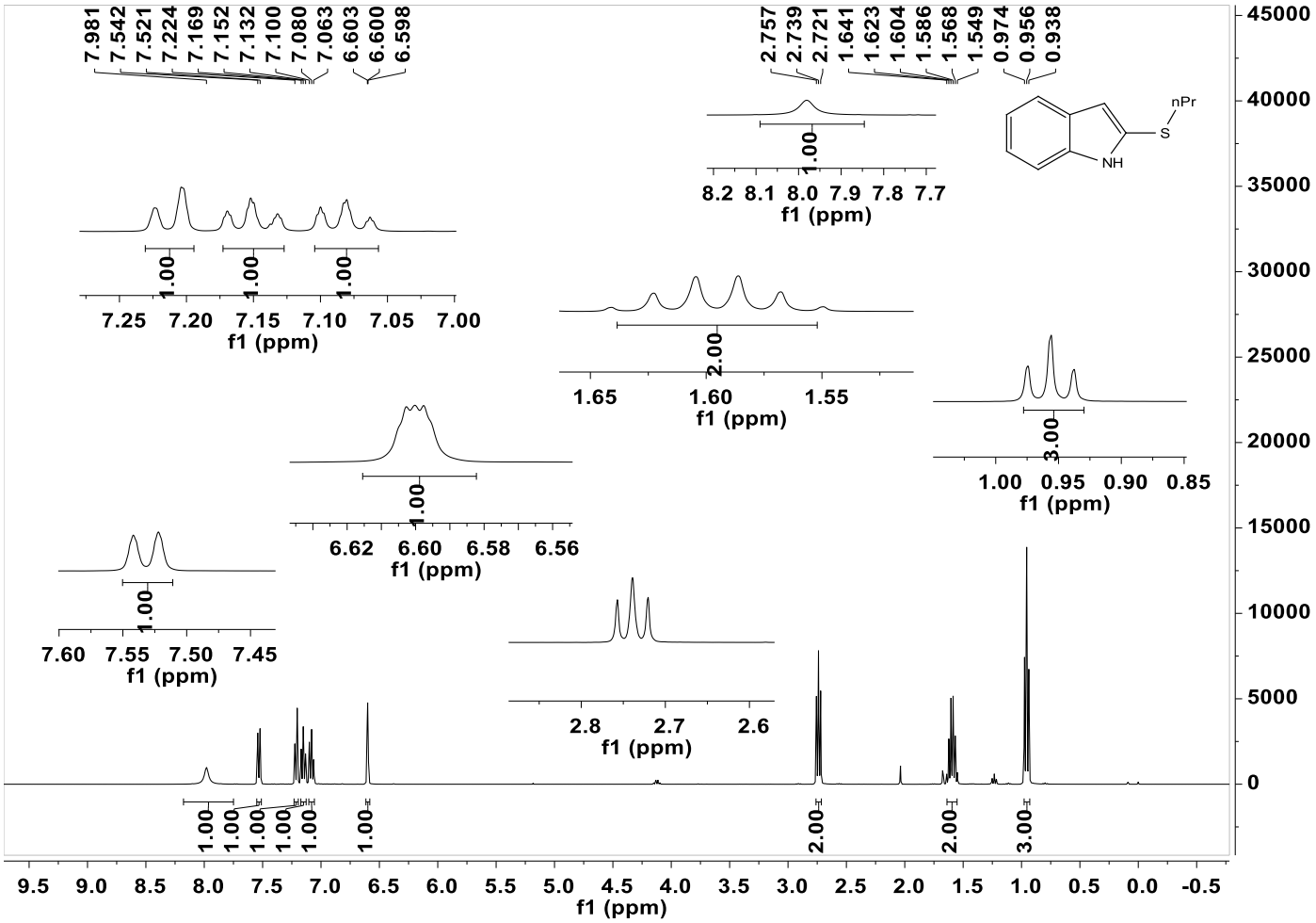

8.015
7.541
7.521
7.294
7.275
7.240
7.180
7.160
7.140
7.106
7.088
7.069
6.545
2.492
8.015
0.09
8.2 8.1 8.0 7.9 7.8
f1 (ppm)
1.00
1.00
1.00
1.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
S
N
D/H=9:1
0.09
1.00
1.00
1.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

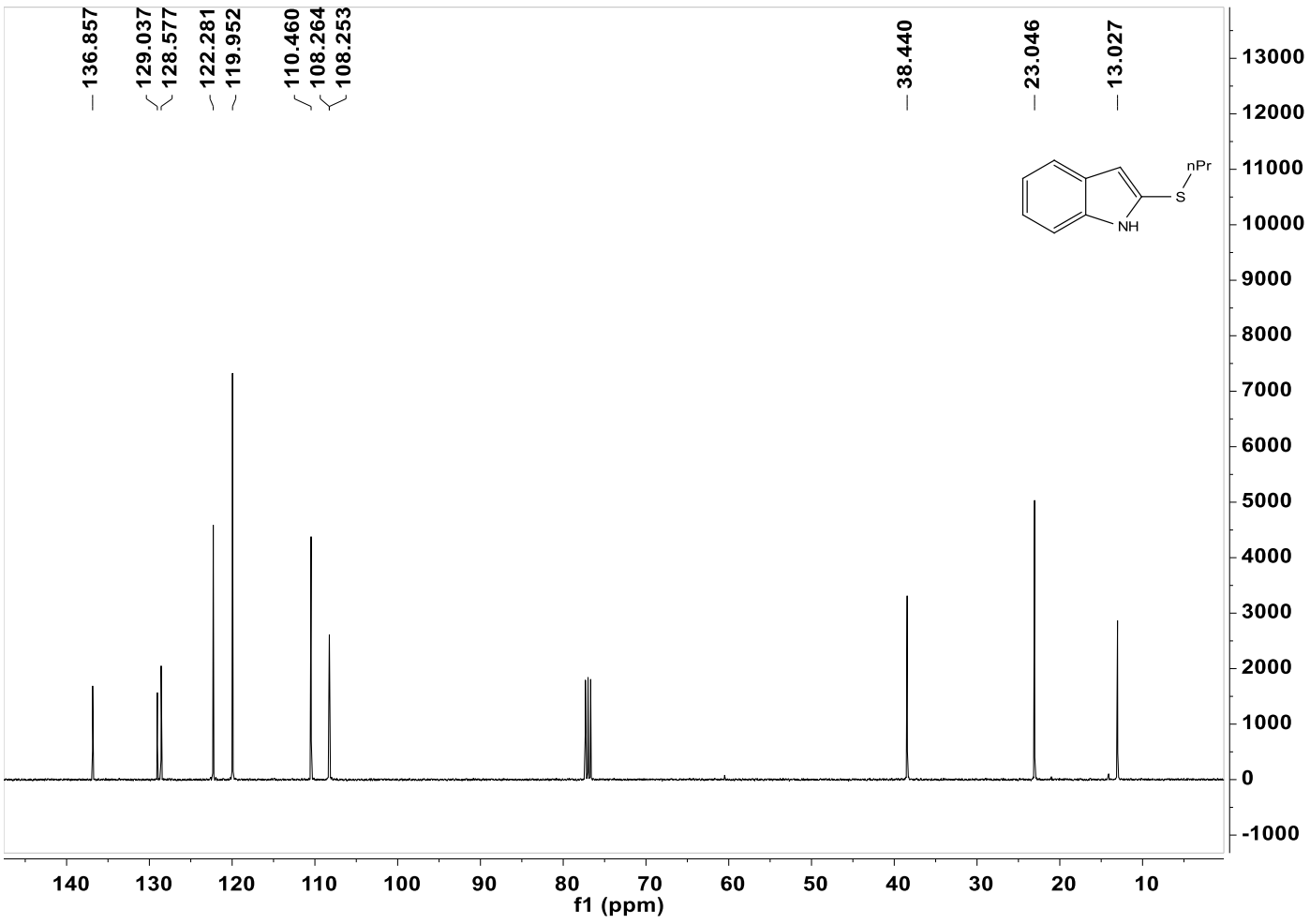
2b


7.907
7.465
7.445
7.144
7.126
7.090
7.087
7.073
7.070
7.059
7.052
7.049
7.019
7.016
7.001
6.999
6.996
6.982
6.979
6.535
6.533
6.529
6.527
2.720
2.702
2.683
2.665
1.169
1.151
1.133
Et
S
NH
f1 (ppm)

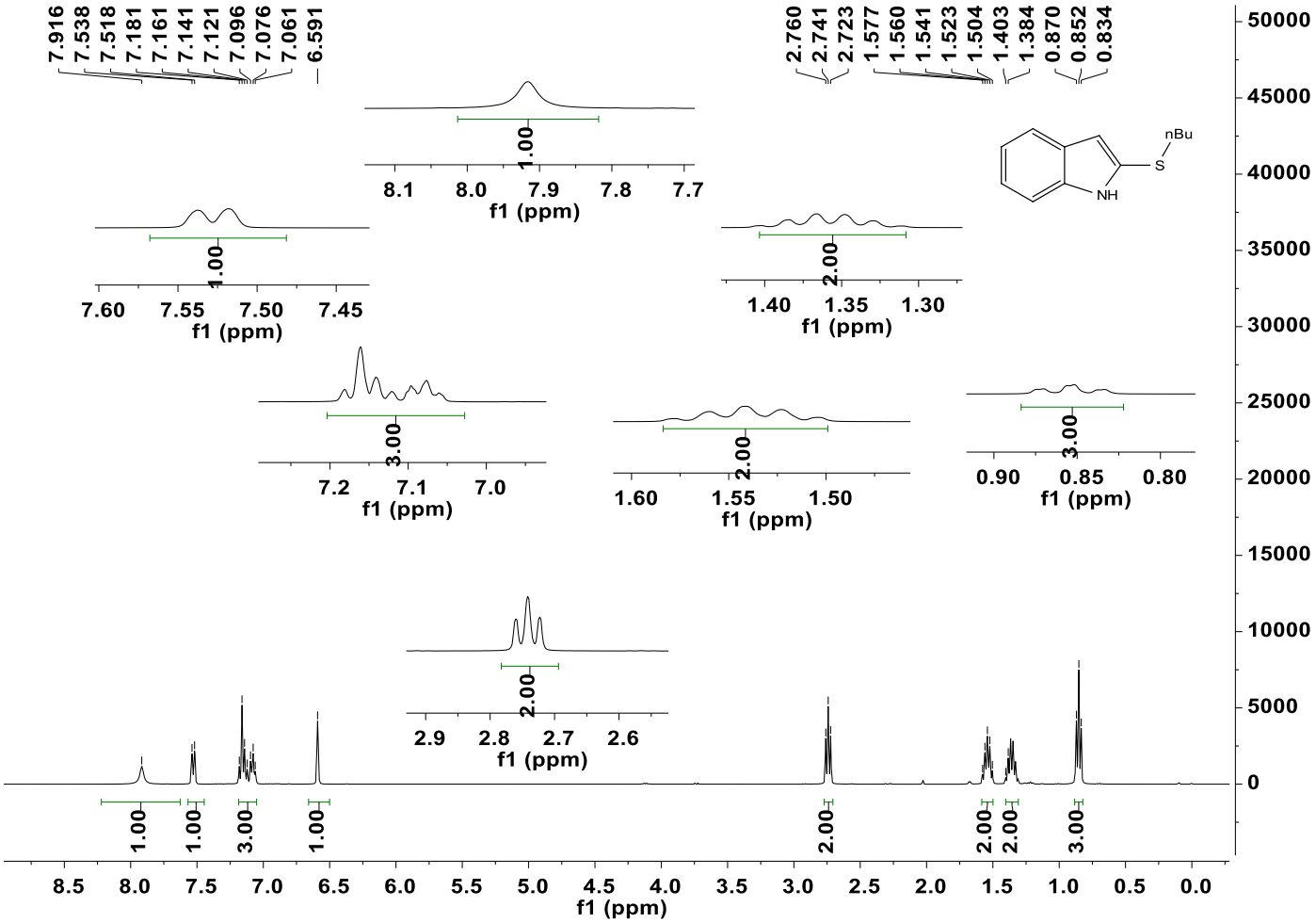

136.897
128.604
128.556
122.337
120.006
119.950
110.482
108.550
30.574
15.082
Et
S
NH
f1 (ppm)

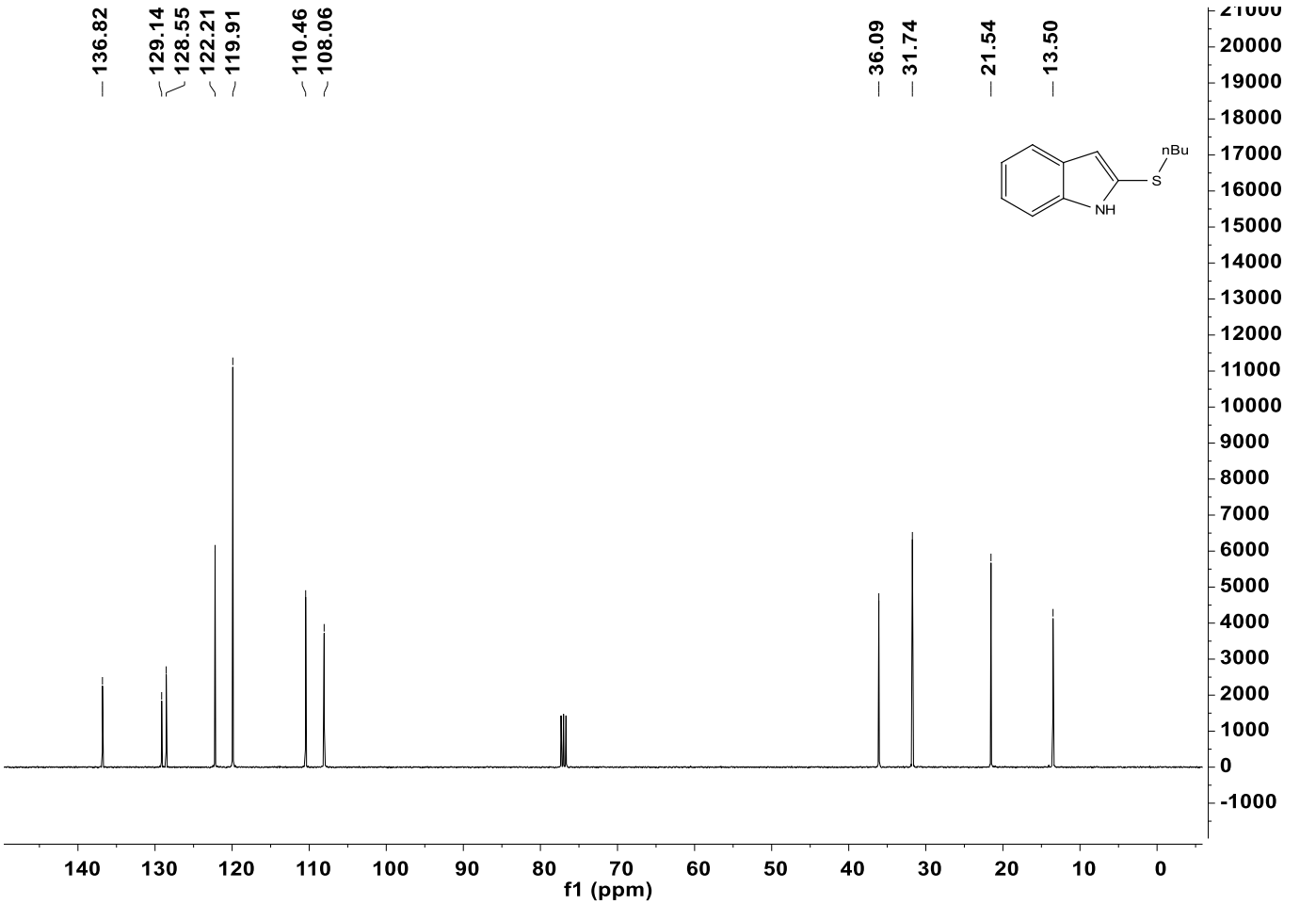
2c


7.981
7.542
7.521
7.224
7.169
7.152
7.132
7.100
7.080
7.063
6.603
6.600
6.598
2.757
2.739
2.721
1.641
1.623
1.604
1.586
1.568
1.549
0.974
0.956
0.938
nPr
S
NH
f1 (ppm)

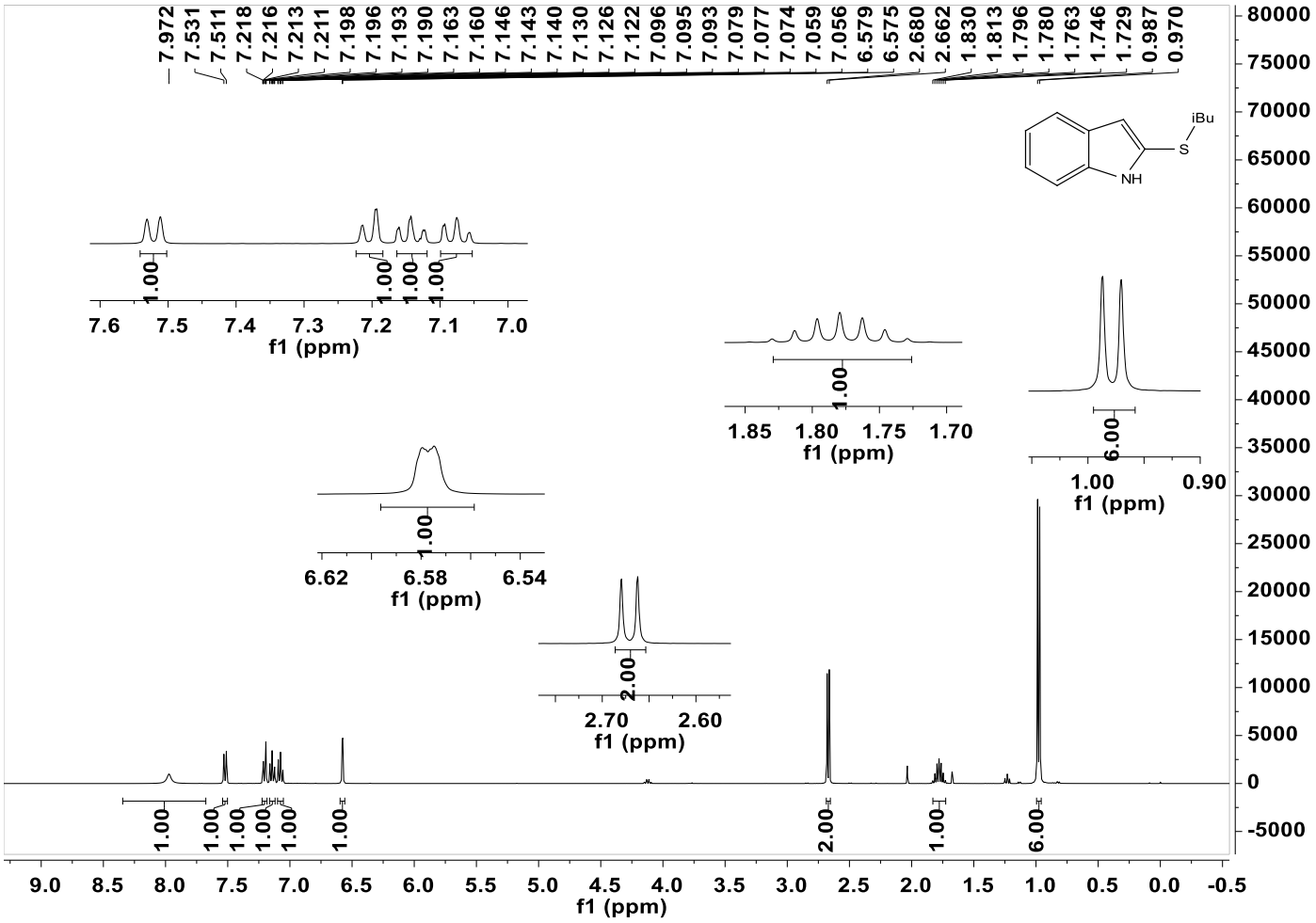

136.857
129.037
128.577
122.281
119.952
110.460
108.264
108.253
38.440
23.046
13.027
nPr
S
NH
f1 (ppm)

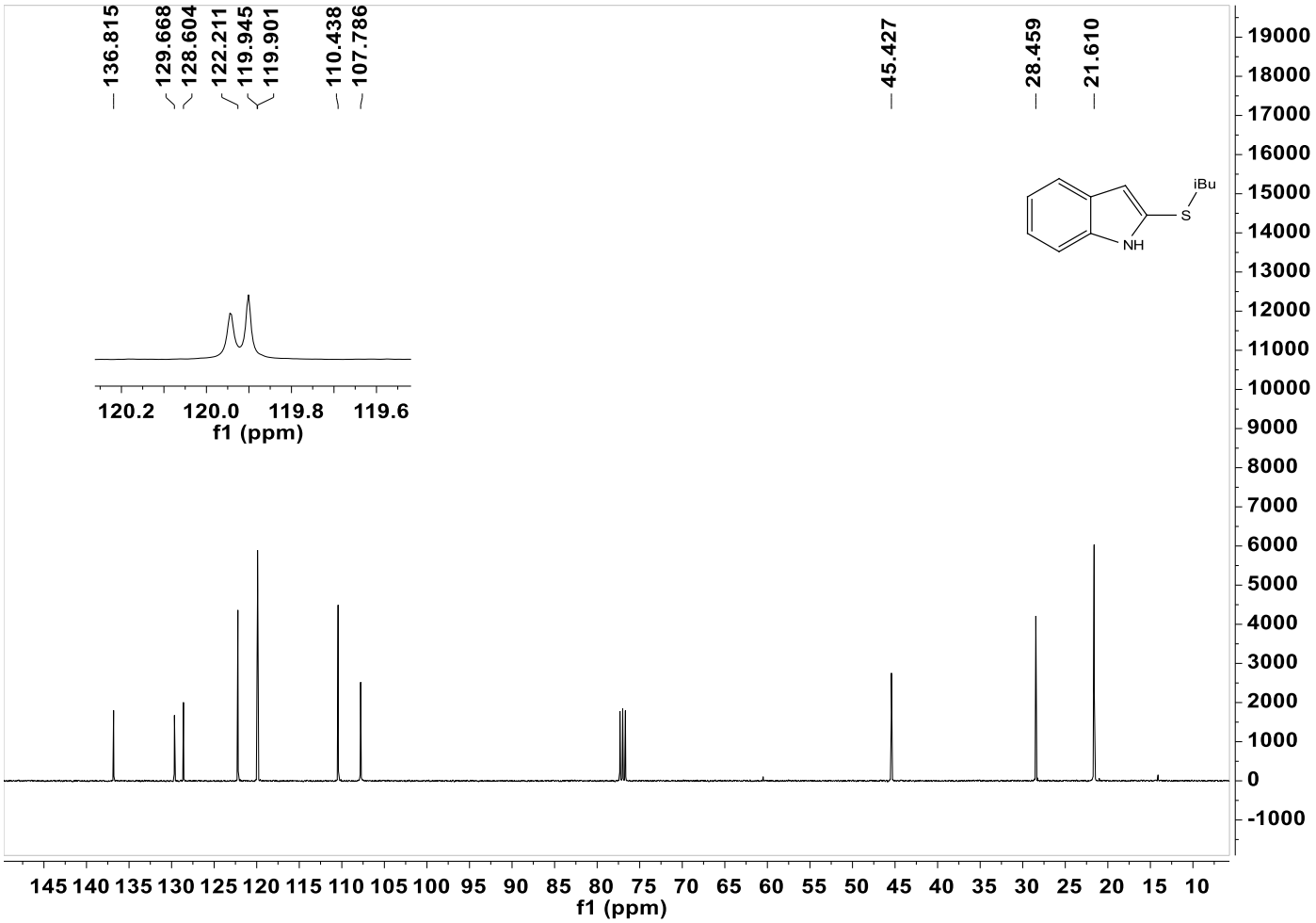
2d


7.916
7.538
7.518
7.181
7.161
7.141
7.121
7.096
7.076
7.061
6.591
2.760
2.741
2.723
1.577
1.560
1.541
1.523
1.504
1.403
1.384
0.870
0.852
0.834
nBu
S
NH
f1 (ppm)

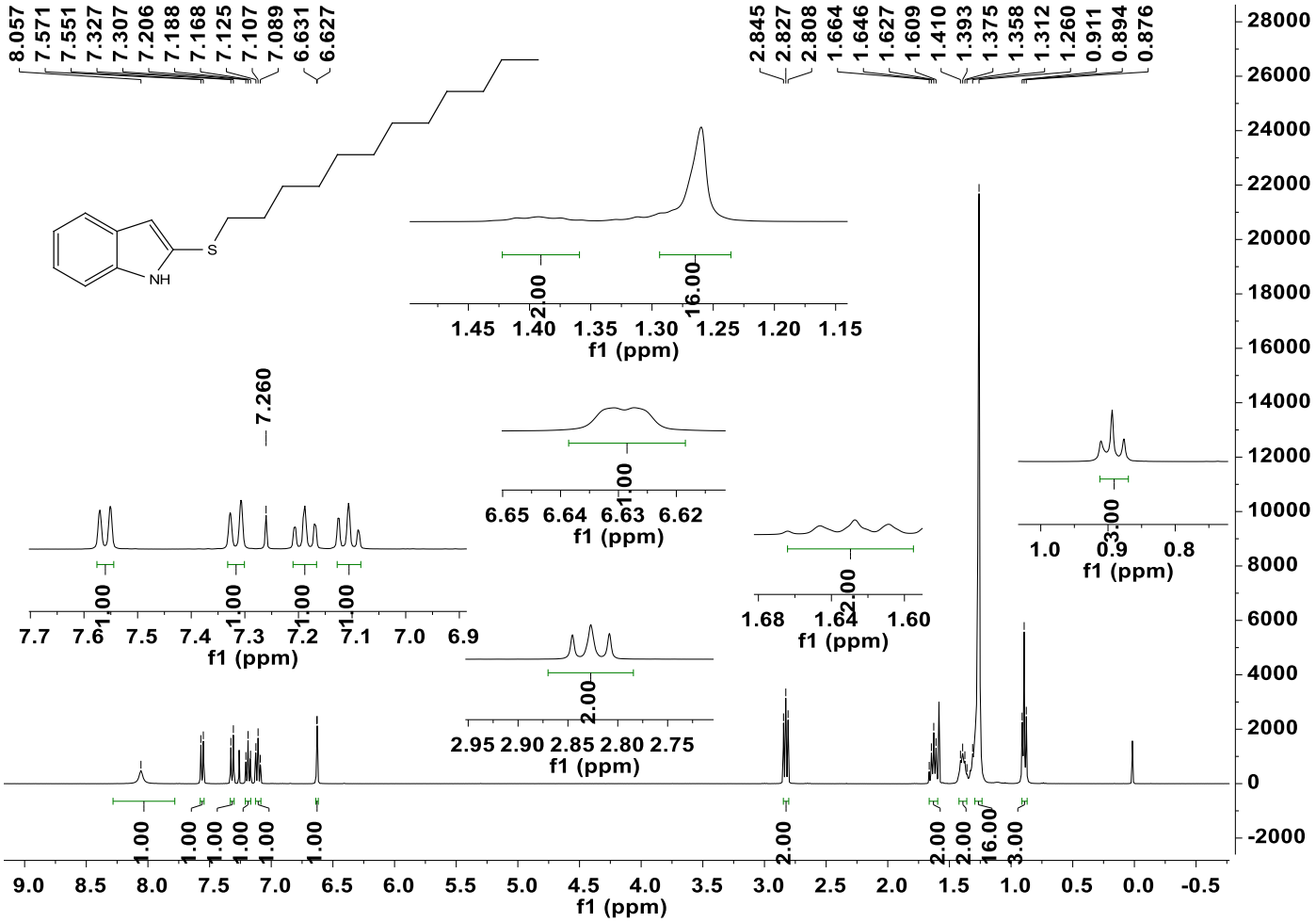

136.82
129.14
128.55
122.21
119.91
110.46
108.06
36.09
31.74
21.54
13.50
nBu
S
NH
f1 (ppm)

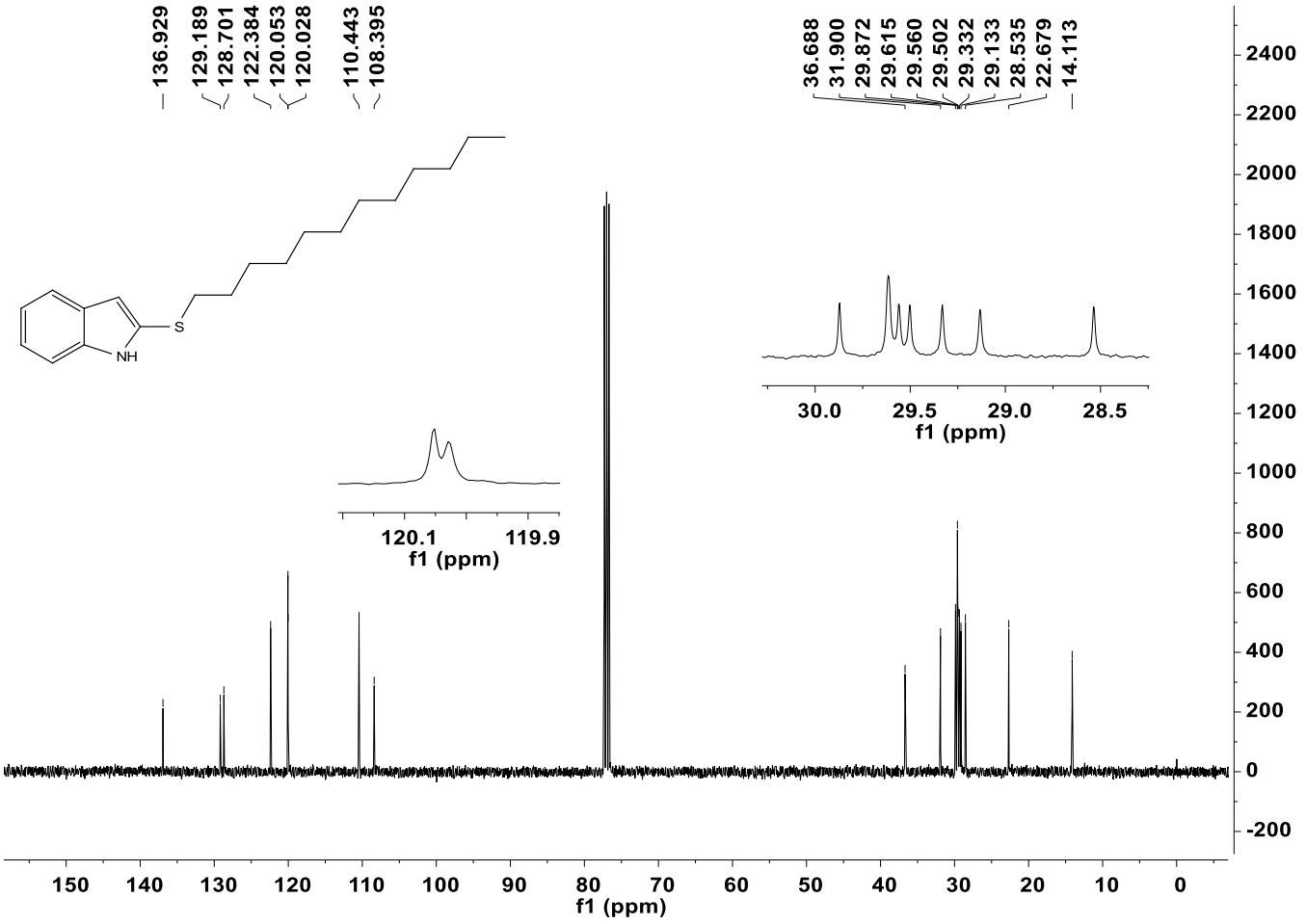
2e


7.972
7.531
7.511
7.218
7.216
7.213
7.211
7.198
7.196
7.193
7.190
7.163
7.160
7.146
7.143
7.140
7.130
7.126
7.122
7.096
7.095
7.093
7.079
7.077
7.074
7.059
7.056
6.579
6.575
2.680
2.662
1.830
1.813
1.796
1.780
1.763
1.746
1.729
0.987
0.970
iBu
S
NH
f1 (ppm)

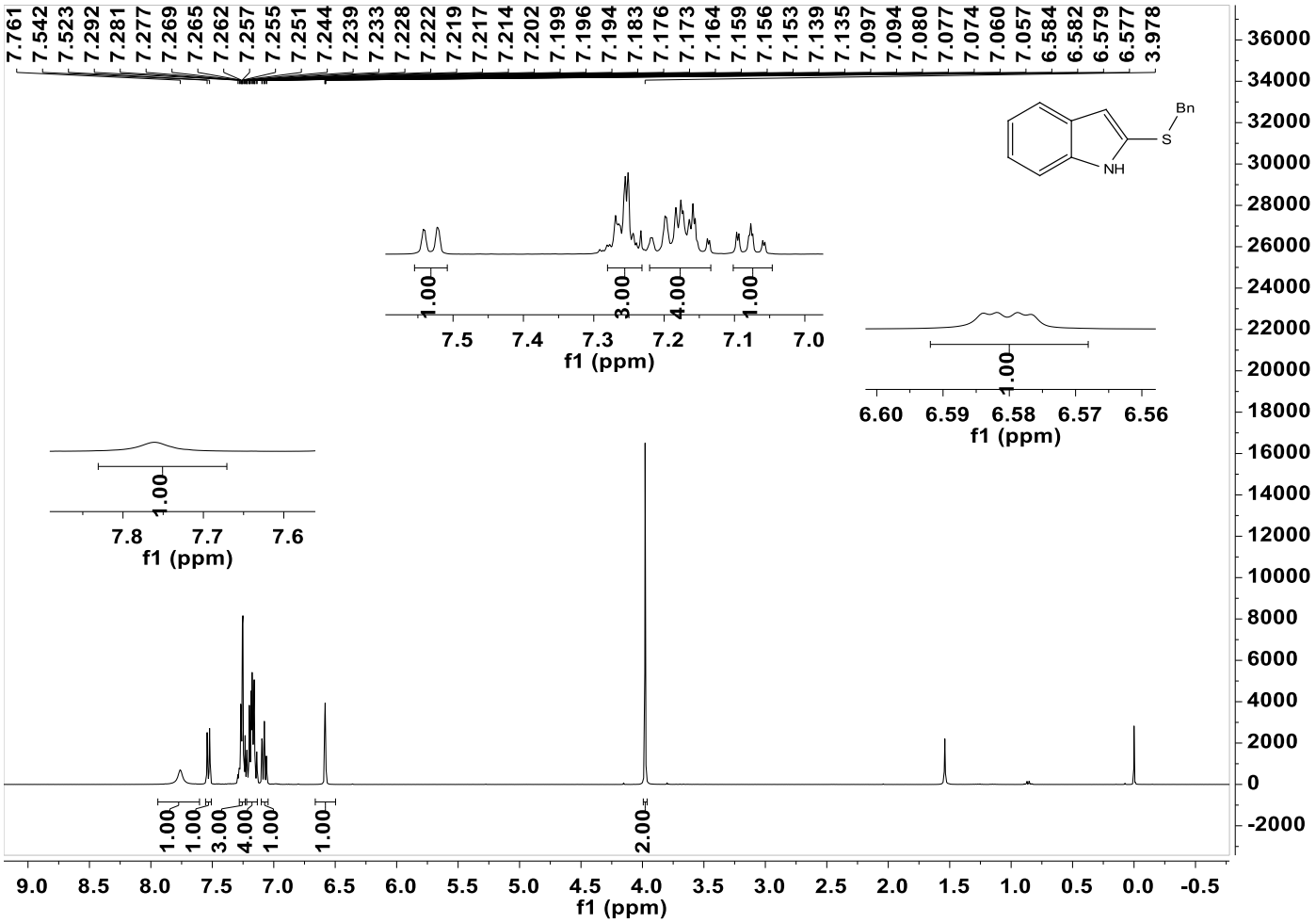

136.815
129.668
128.604
122.211
119.945
119.901
110.438
107.786
45.427
28.459
21.610
iBu
S
NH
f1 (ppm)

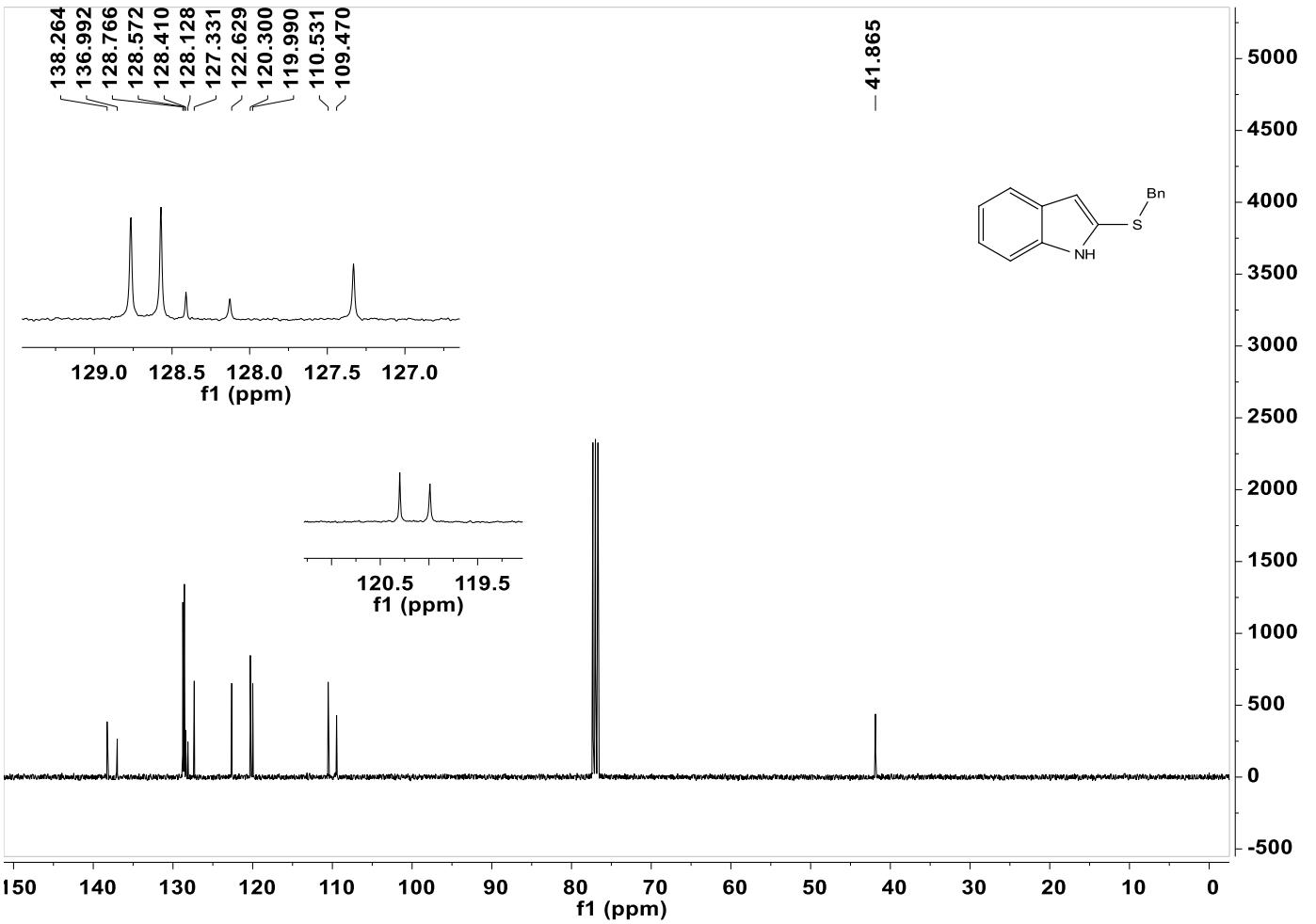
2f


8.057
7.571
7.551
7.327
7.307
7.206
7.188
7.168
7.125
7.107
7.089
6.631
6.627
2.845
2.827
2.808
1.664
1.646
1.627
1.609
1.410
1.393
1.375
1.358
1.312
1.260
0.911
0.894
0.876
7.260
S
NH
f1 (ppm)

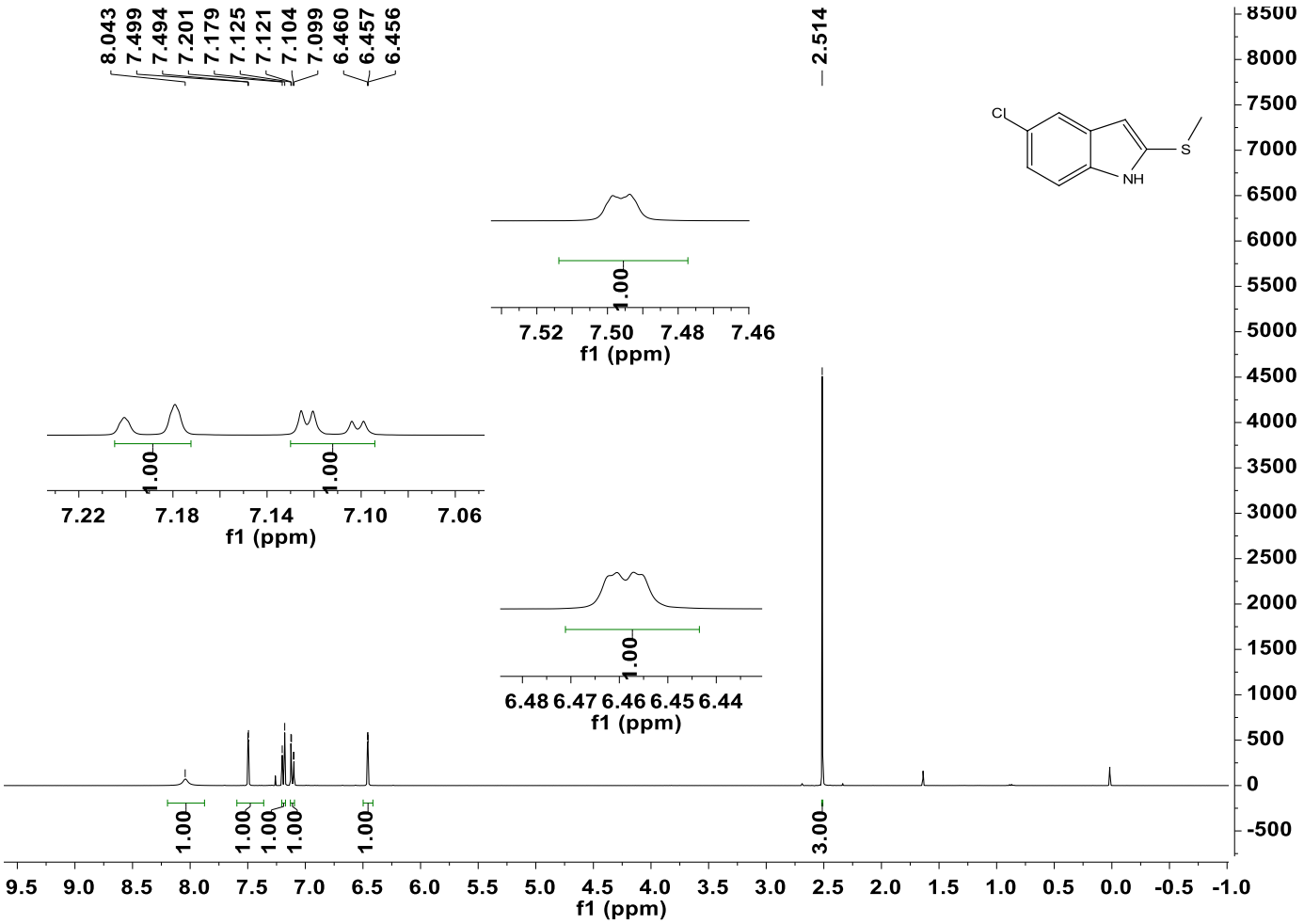

136.929
129.189
128.701
122.384
120.053
120.028
110.443
108.395
36.688
31.900
29.872
29.615
29.560
29.502
29.332
29.133
28.535
22.679
14.113
S
NH
f1 (ppm)

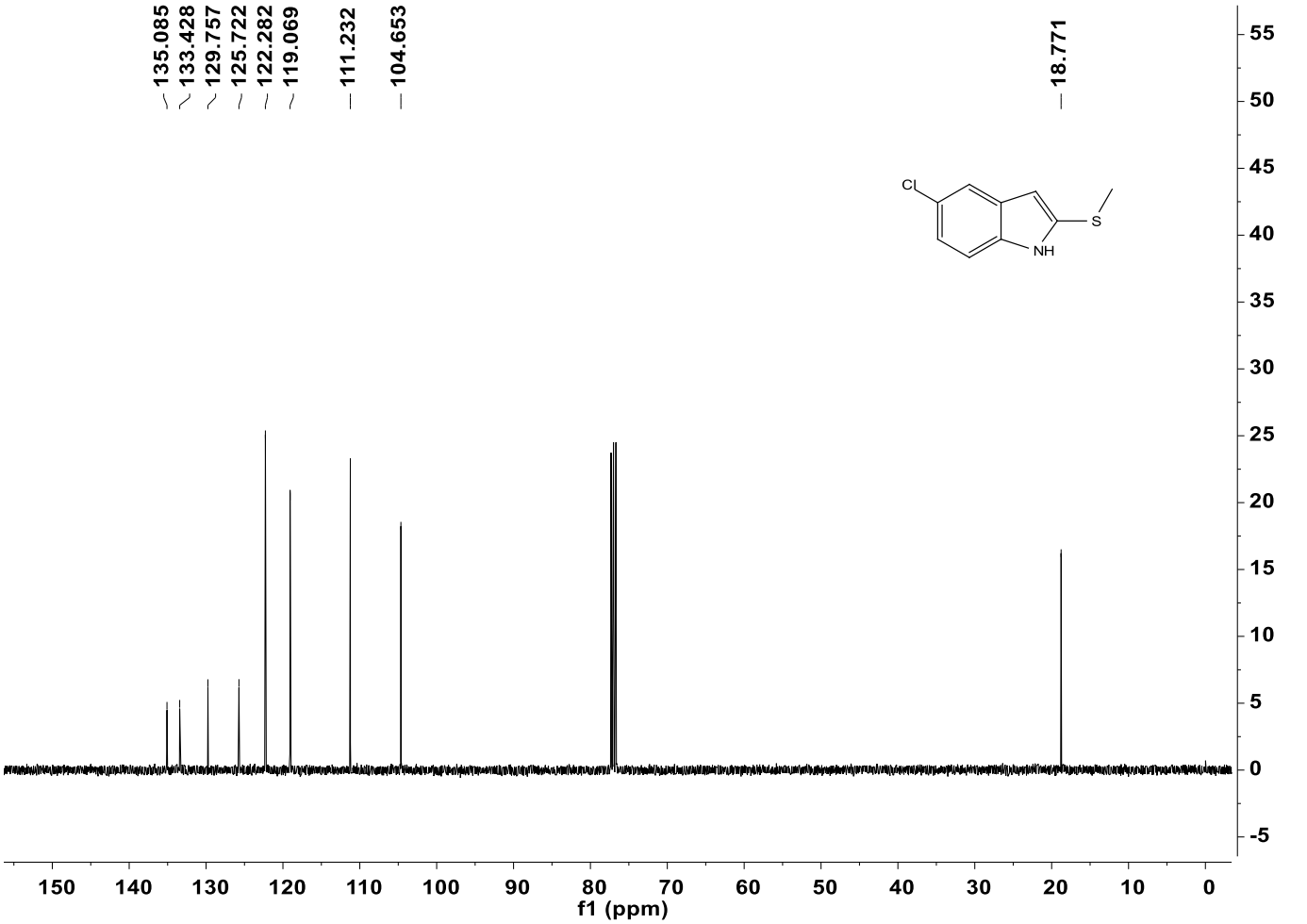
2g


7.761 7.542 7.523 7.292 7.281 7.277 7.269 7.265 7.262 7.257 7.255 7.251 7.244 7.239 7.233 7.228 7.222 7.219 7.217 7.214 7.202 7.199 7.196 7.194 7.183 7.176 7.173 7.164 7.159 7.156 7.153 7.139 7.135 7.097 7.094 7.080 7.077 7.074 7.060 7.057 6.584 6.582 6.579 6.577 3.978
Bn
S
NH
1.00 3.00 4.00 1.00
f1 (ppm)
1.00
f1 (ppm)
1.00
f1 (ppm)
1.00 1.00 3.00 4.00 1.00 1.00 2.00
f1 (ppm)

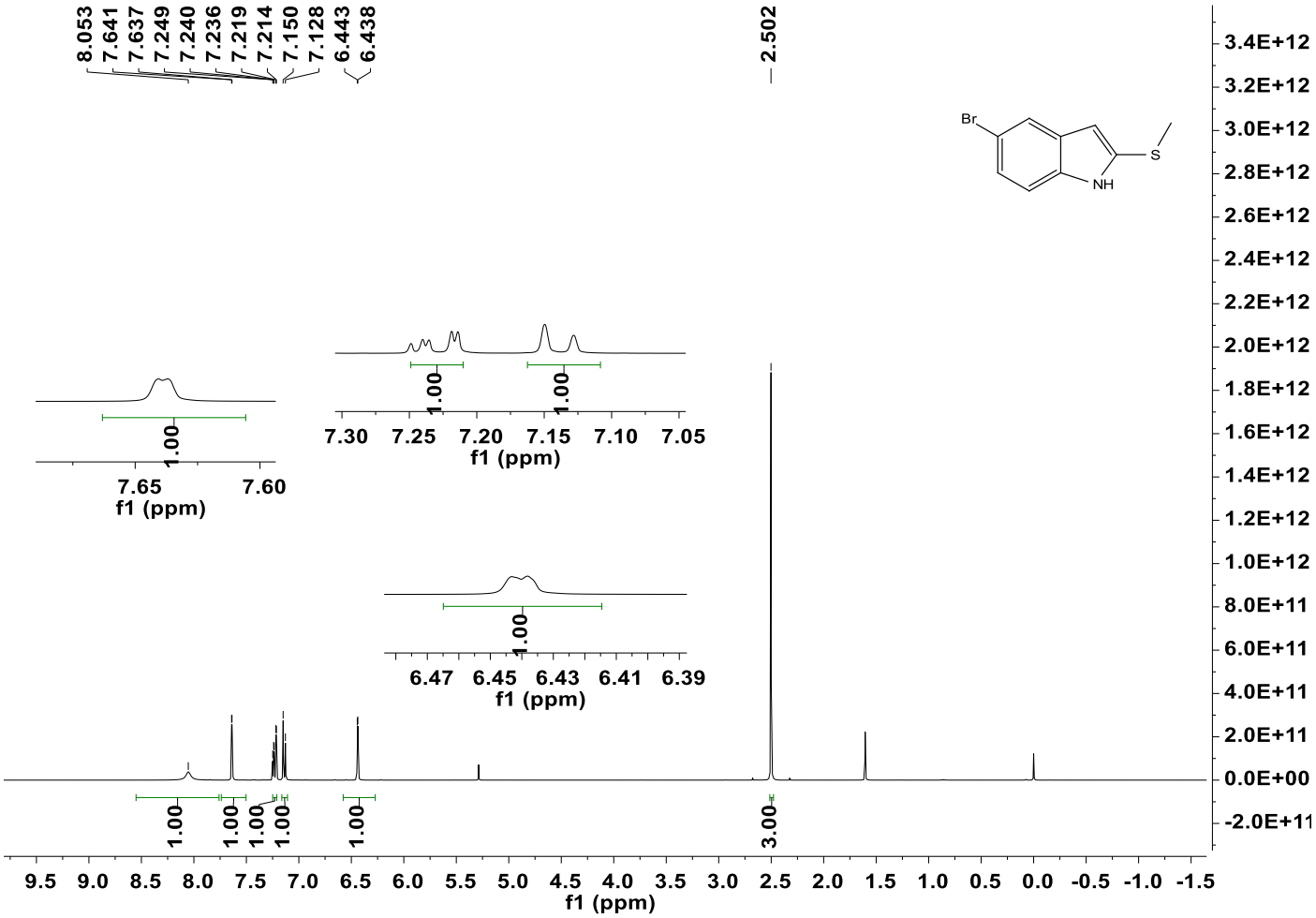

138.264 136.992 128.766 128.572 128.410 128.128 127.331 122.629 120.300 119.990 110.531 109.470
41.865
Bn
S
NH
f1 (ppm)
f1 (ppm)
f1 (ppm)

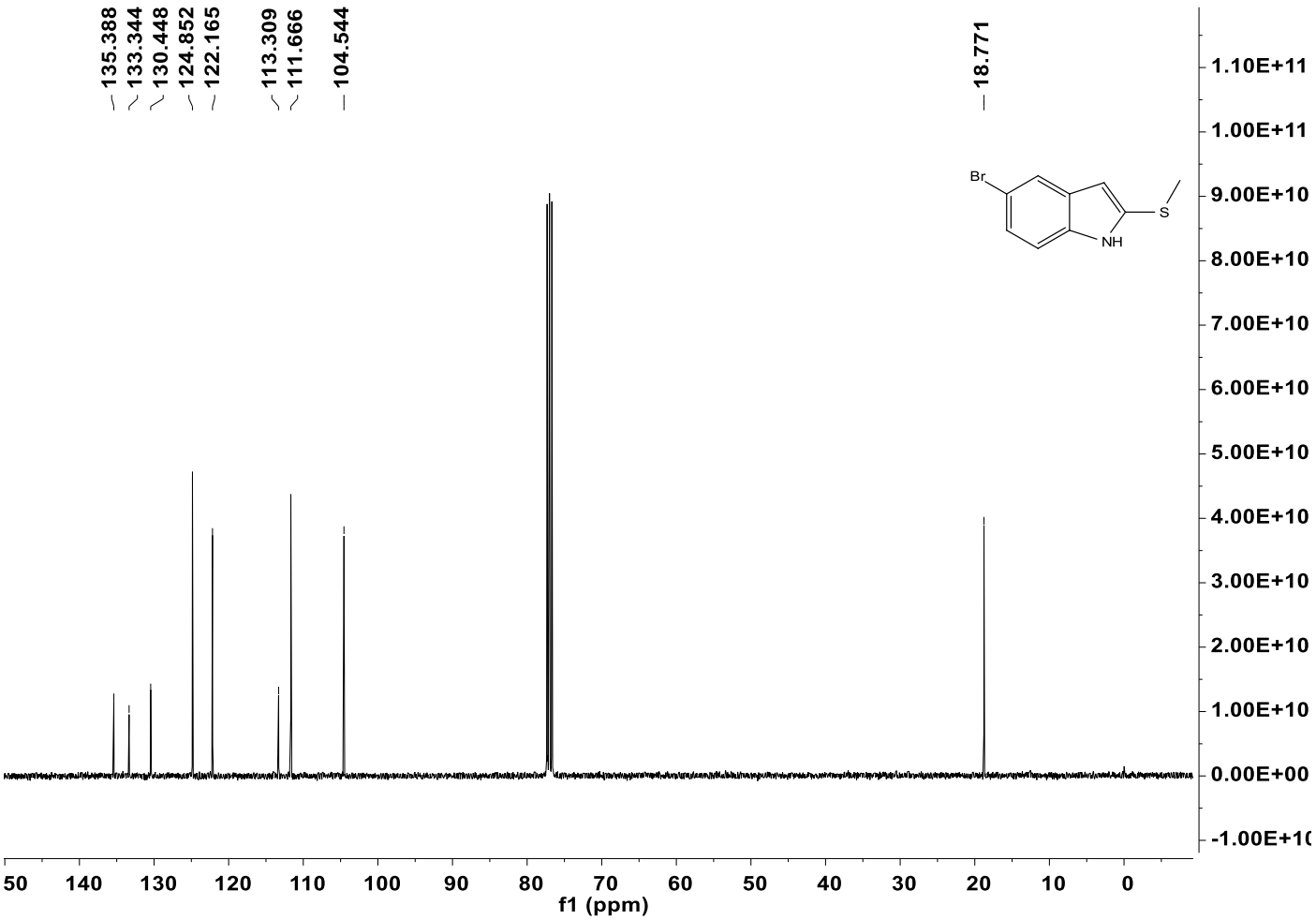
2i


8.043
7.499
7.494
7.201
7.179
7.125
7.121
7.104
7.099
6.460
6.457
6.456
2.514
Cl
S
NH
1.00
7.52 7.50 7.48 7.46
f1 (ppm)
1.00
1.00
7.22 7.18 7.14 7.10 7.06
f1 (ppm)
1.00
6.48 6.47 6.46 6.45 6.44
f1 (ppm)
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

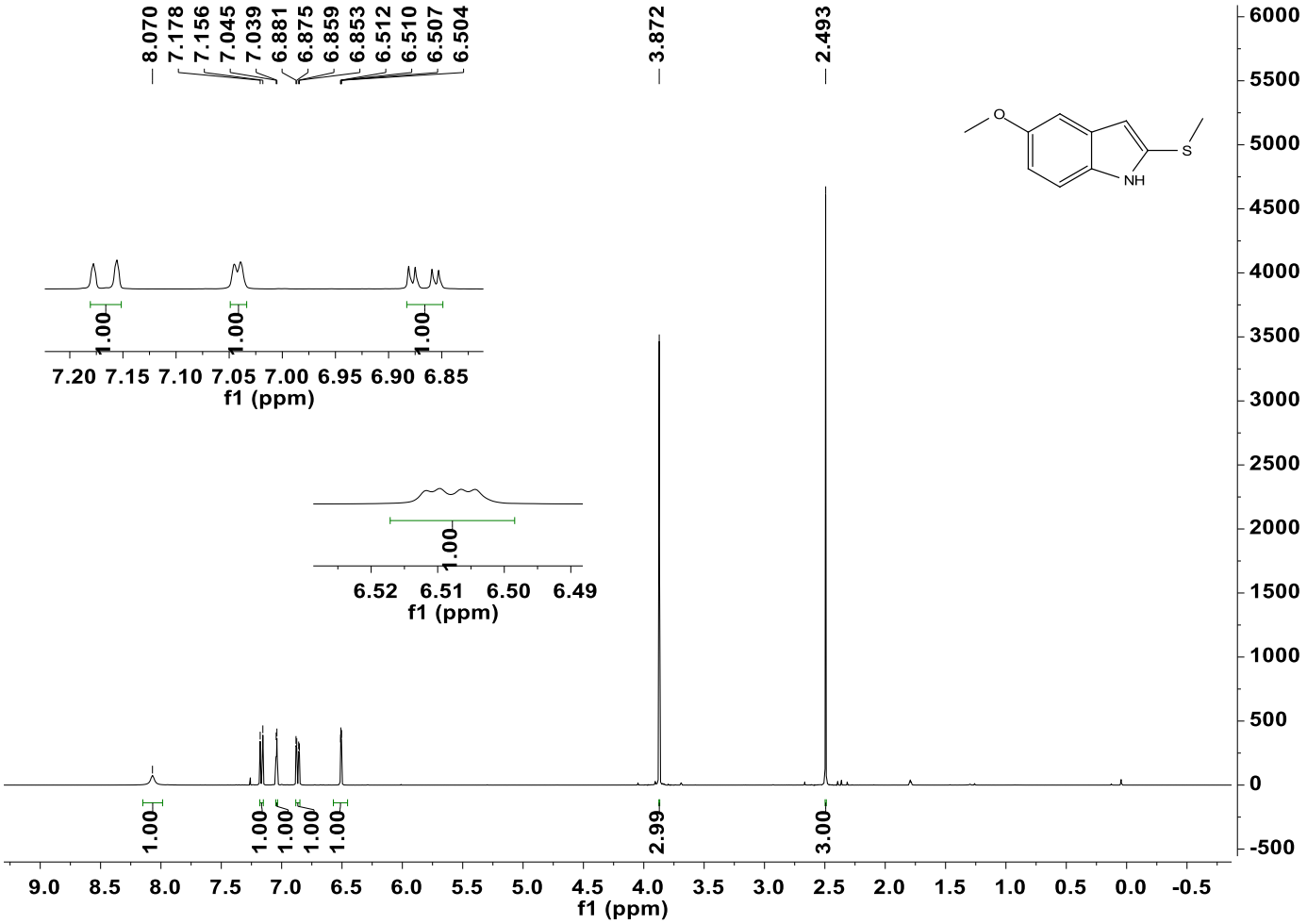

135.085
133.428
129.757
125.722
122.282
119.069
111.232
104.653
18.771
Cl
S
NH
f1 (ppm)

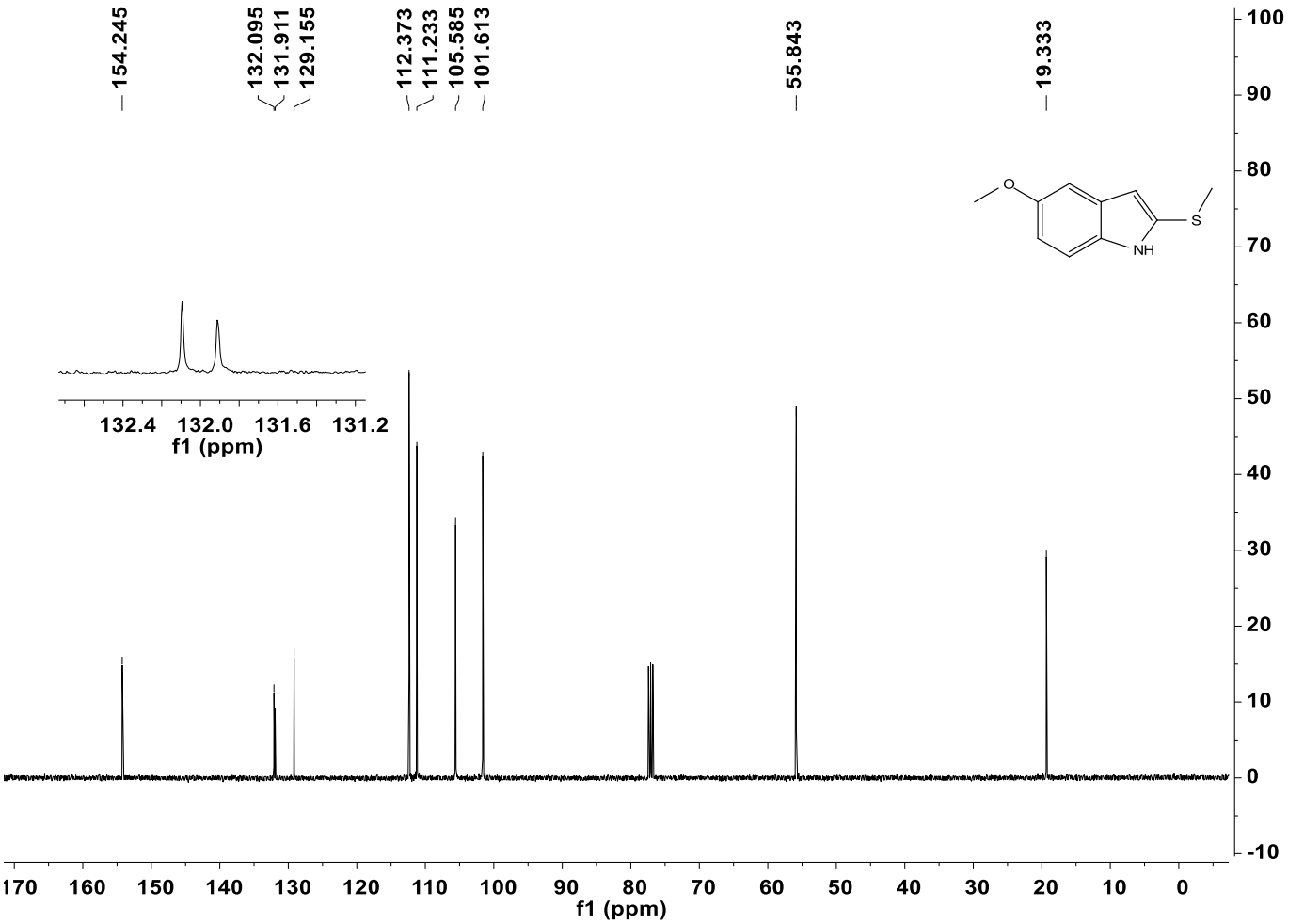
2j


8.053
7.641
7.637
7.249
7.240
7.236
7.219
7.214
7.150
7.128
6.443
6.438
2.502
Br
S
NH
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

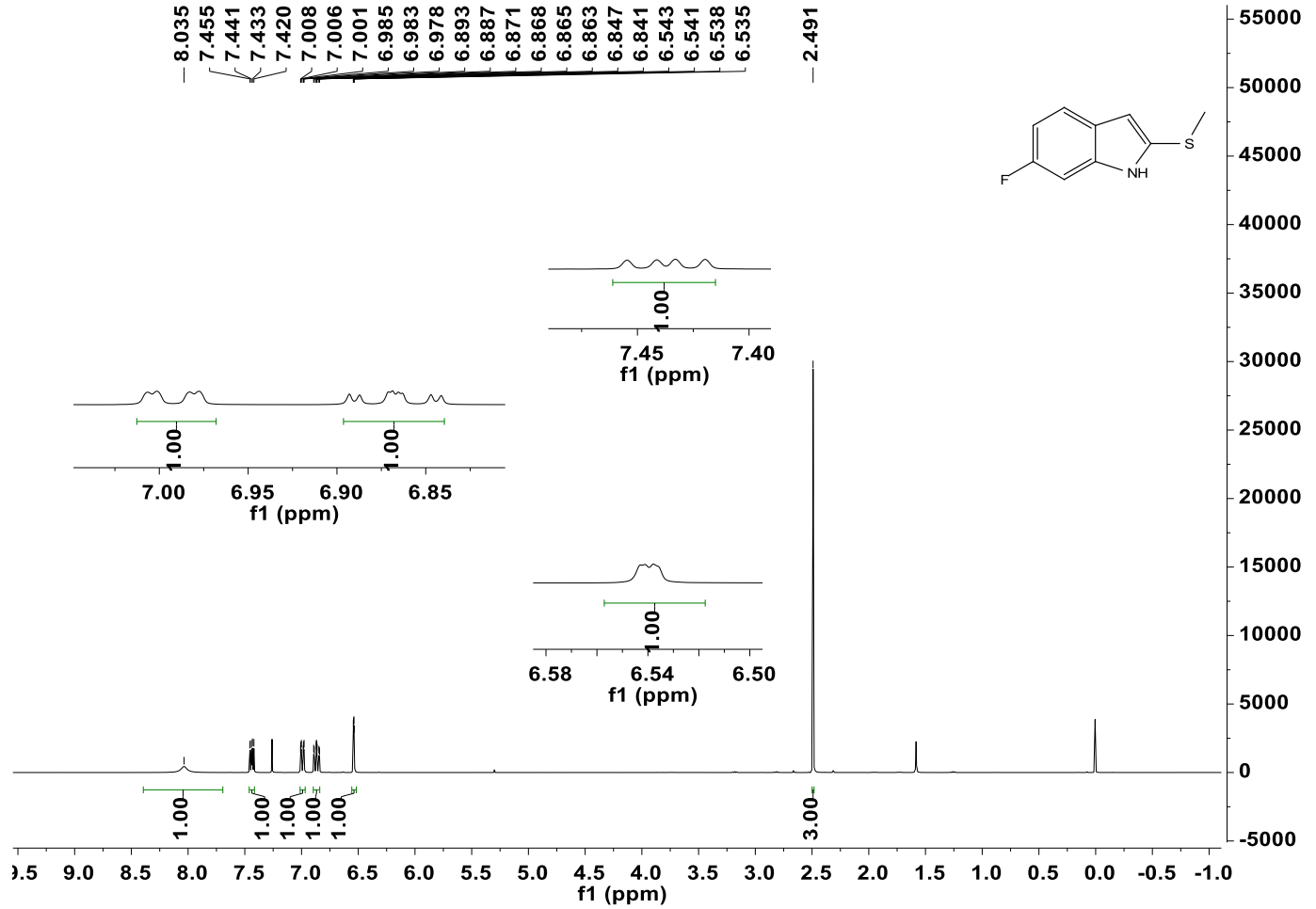

135.388
133.344
130.448
124.852
122.165
113.309
111.666
104.544
18.771
Br
S
NH
f1 (ppm)

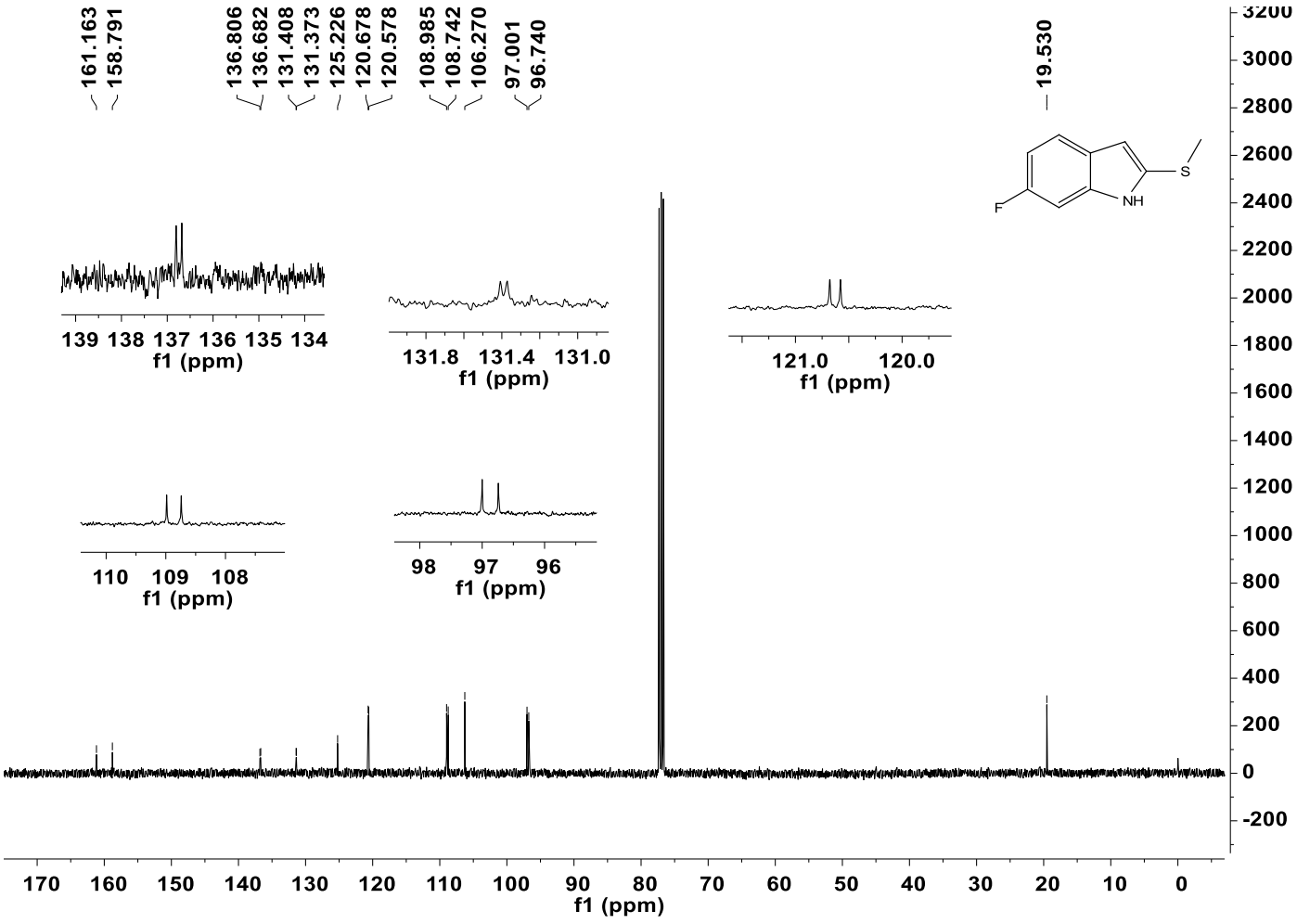
2k

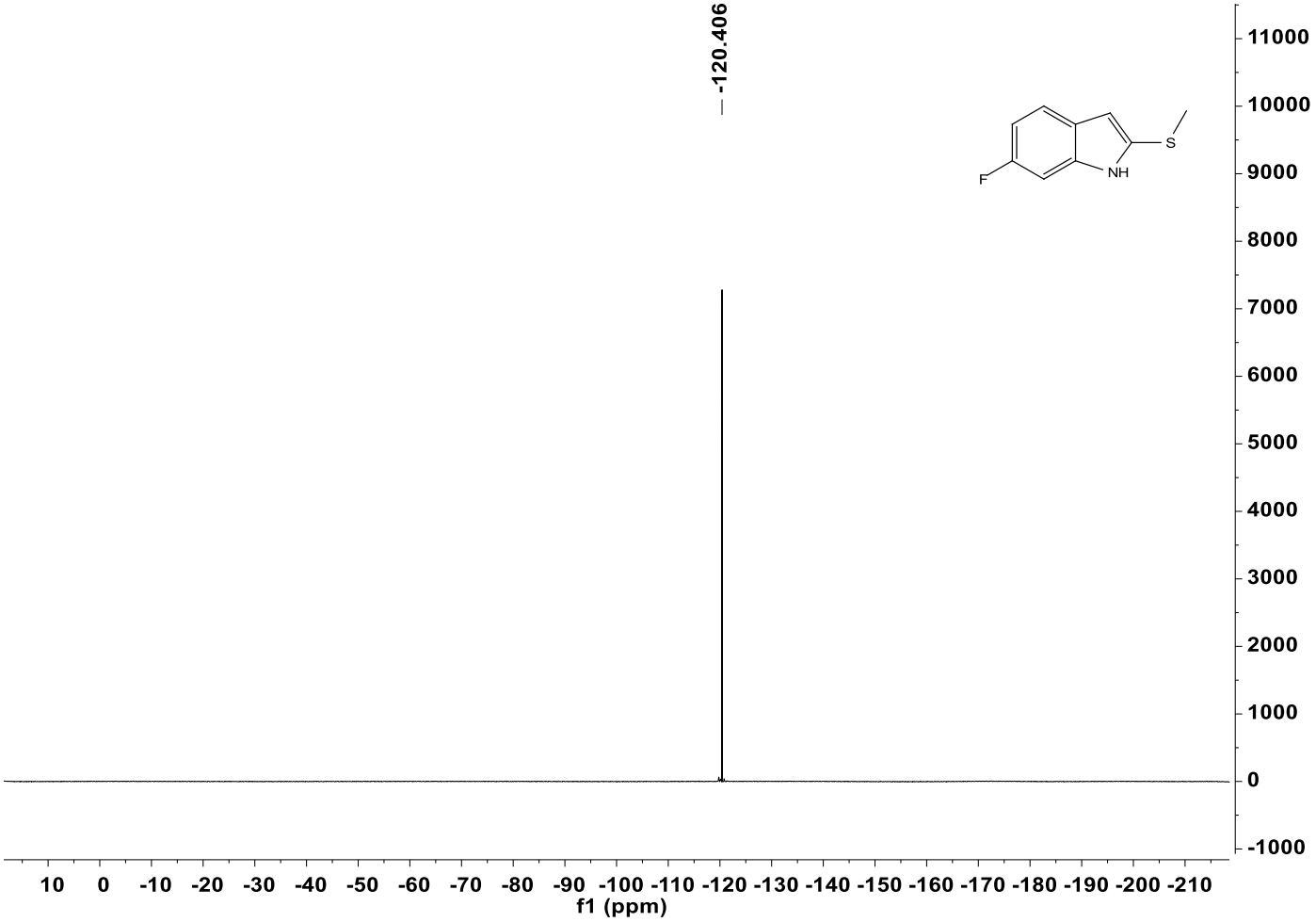

8.070
7.178
7.156
7.045
7.039
6.881
6.875
6.859
6.853
6.512
6.510
6.507
6.504
3.872
2.493
1.00
1.00
1.00
7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85
f1 (ppm)
1.00
6.52 6.51 6.50 6.49
f1 (ppm)
1.00
1.00
1.00
1.00
1.00
2.99
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500
O
S
NH


154.245
132.095
131.911
129.155
112.373
111.233
105.585
101.613
55.843
19.333
132.4 132.0 131.6 131.2
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 90 80 70 60 50 40 30 20 10 0 -10
O
S
NH

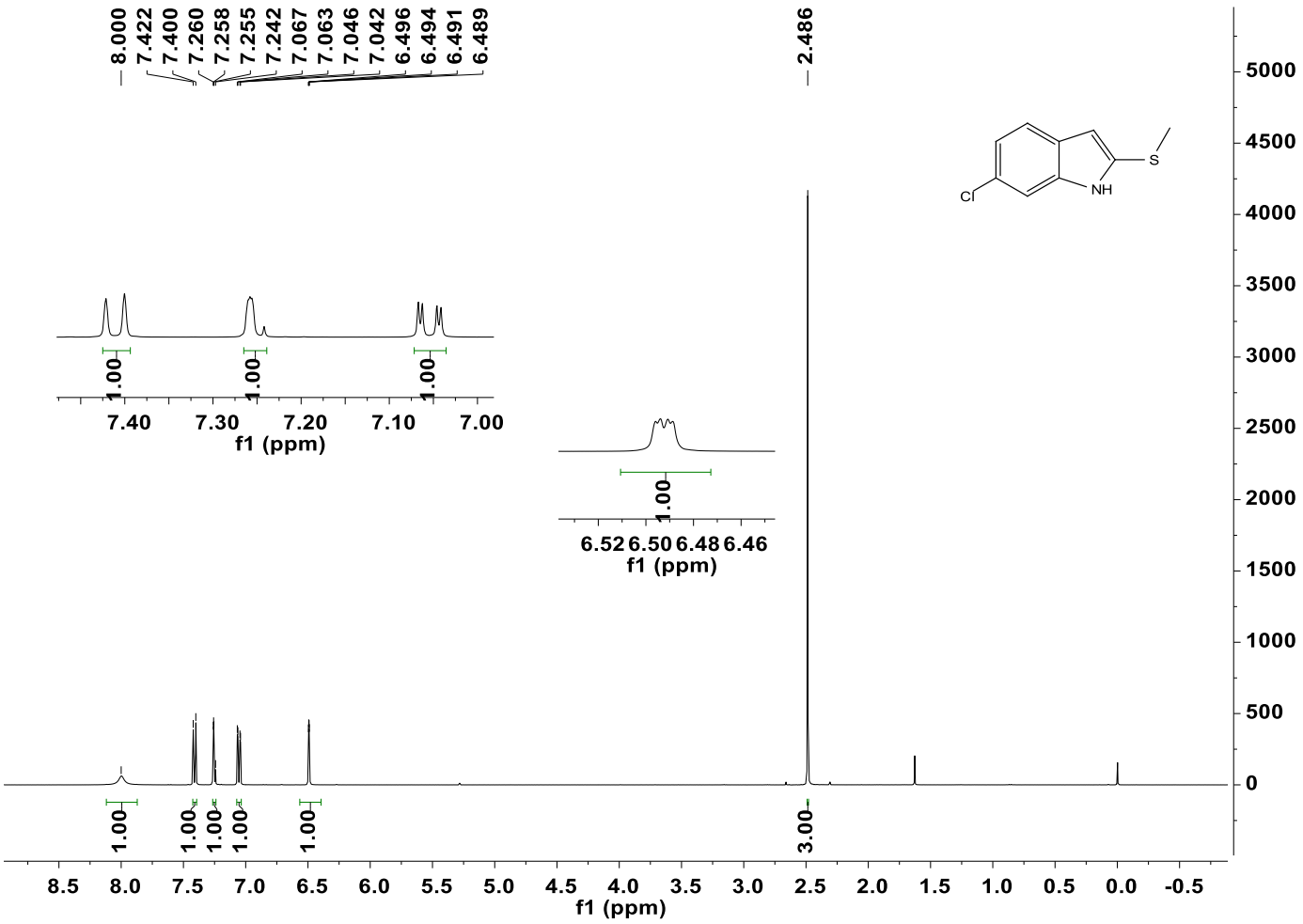
2l

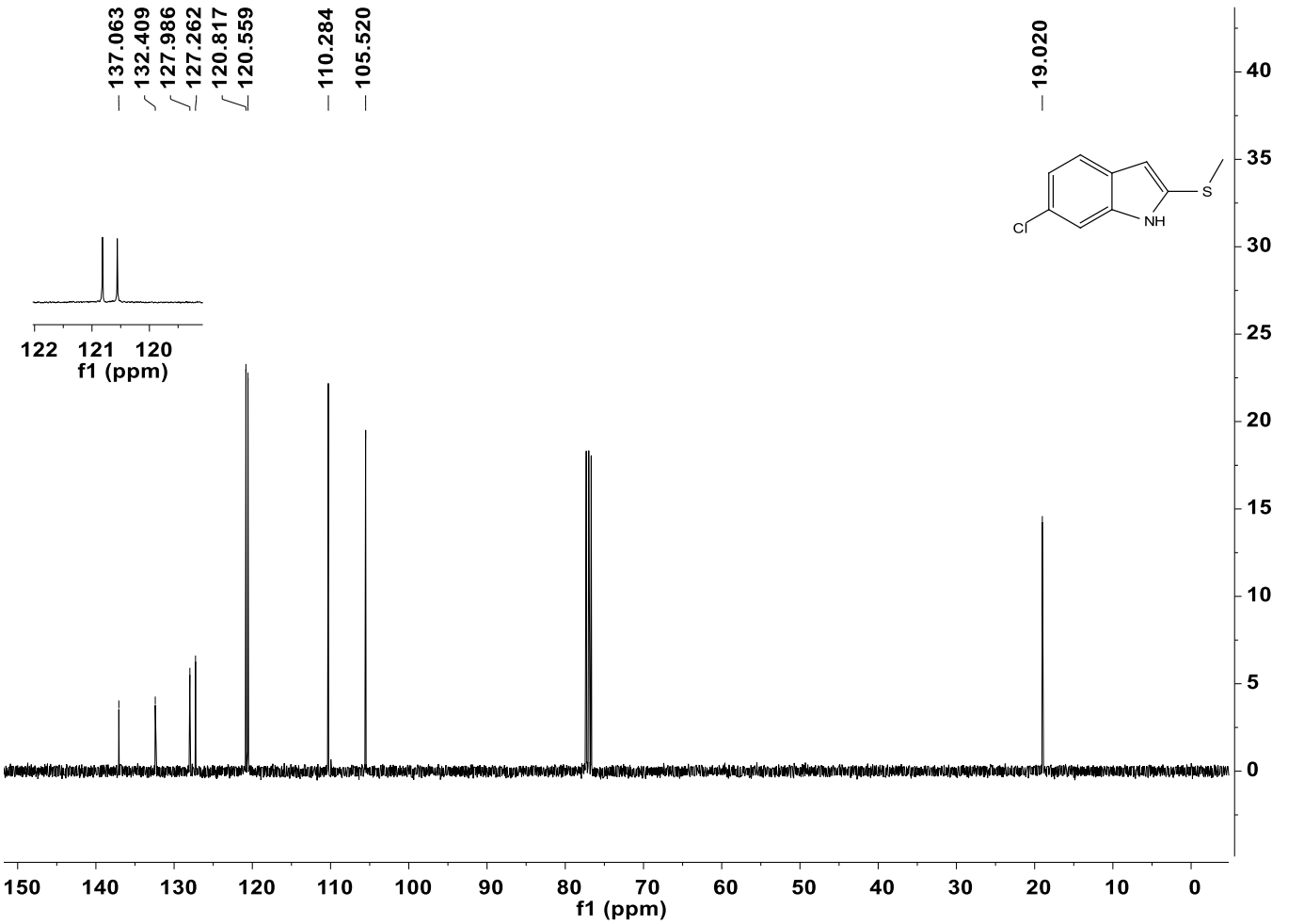

8.035
7.455
7.441
7.433
7.420
7.008
7.006
7.001
6.985
6.983
6.978
6.893
6.887
6.871
6.868
6.865
6.863
6.847
6.841
6.543
6.541
6.538
6.535
2.491
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)


161.163
158.791
136.806
136.682
131.408
131.373
125.226
120.678
120.578
108.985
108.742
106.270
97.001
96.740
19.530
f1 (ppm)

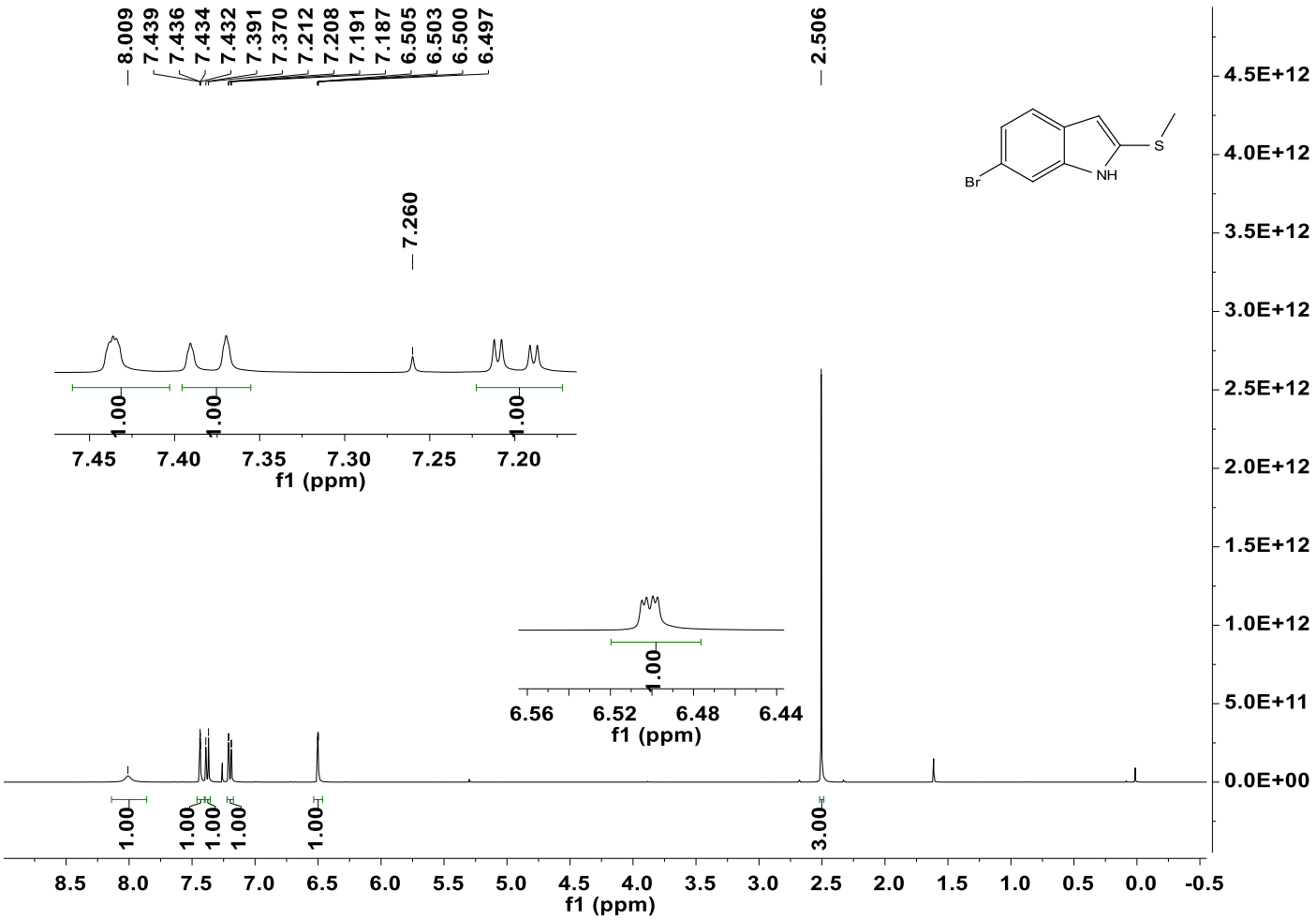

-120.406
F
NH
S
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

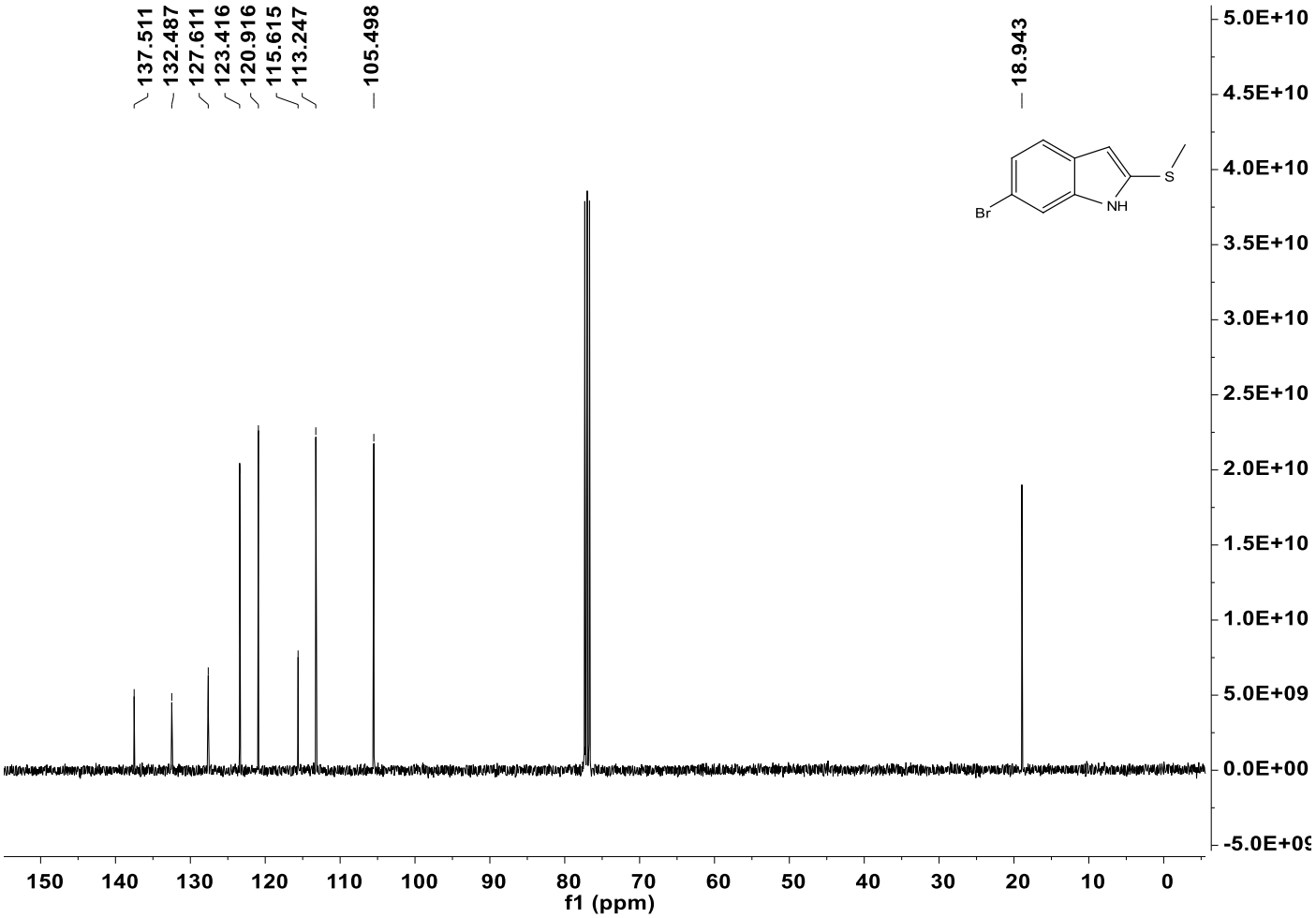
2m


8.000
7.422
7.400
7.260
7.258
7.255
7.242
7.067
7.063
7.046
7.042
6.496
6.494
6.491
6.489
2.486
Cl
NH
S
1.00
1.00
1.00
7.40
7.30
7.20
7.10
7.00
f1 (ppm)
1.00
6.52
6.50
6.48
6.46
f1 (ppm)
1.00
1.00
1.00
1.00
1.00
3.00
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
-0.5
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0

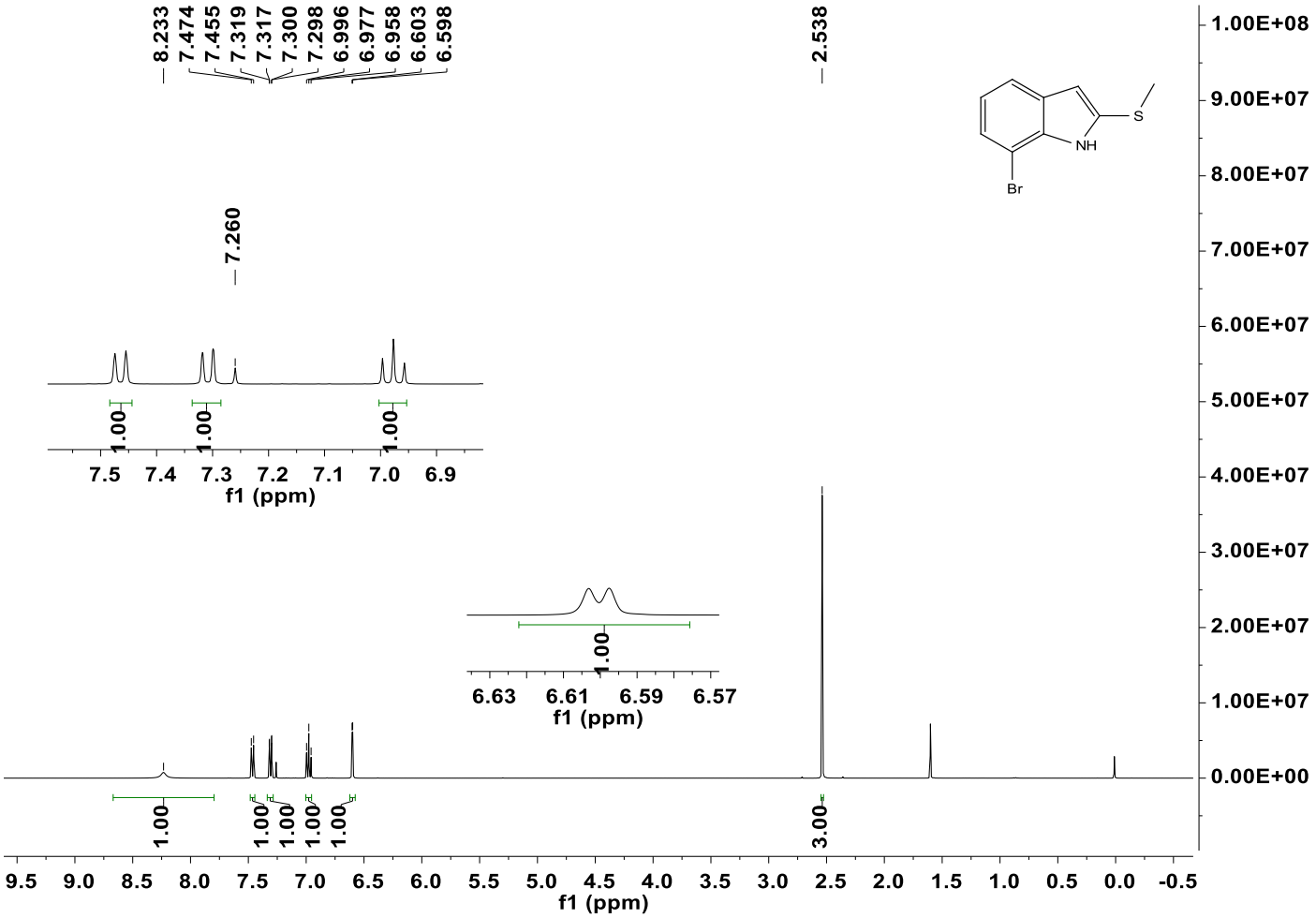

137.063
132.409
127.986
127.262
120.817
120.559
110.284
105.520
19.020
Cl
NH
S
122
121
120
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
40
35
30
25
20
15
10
5
0

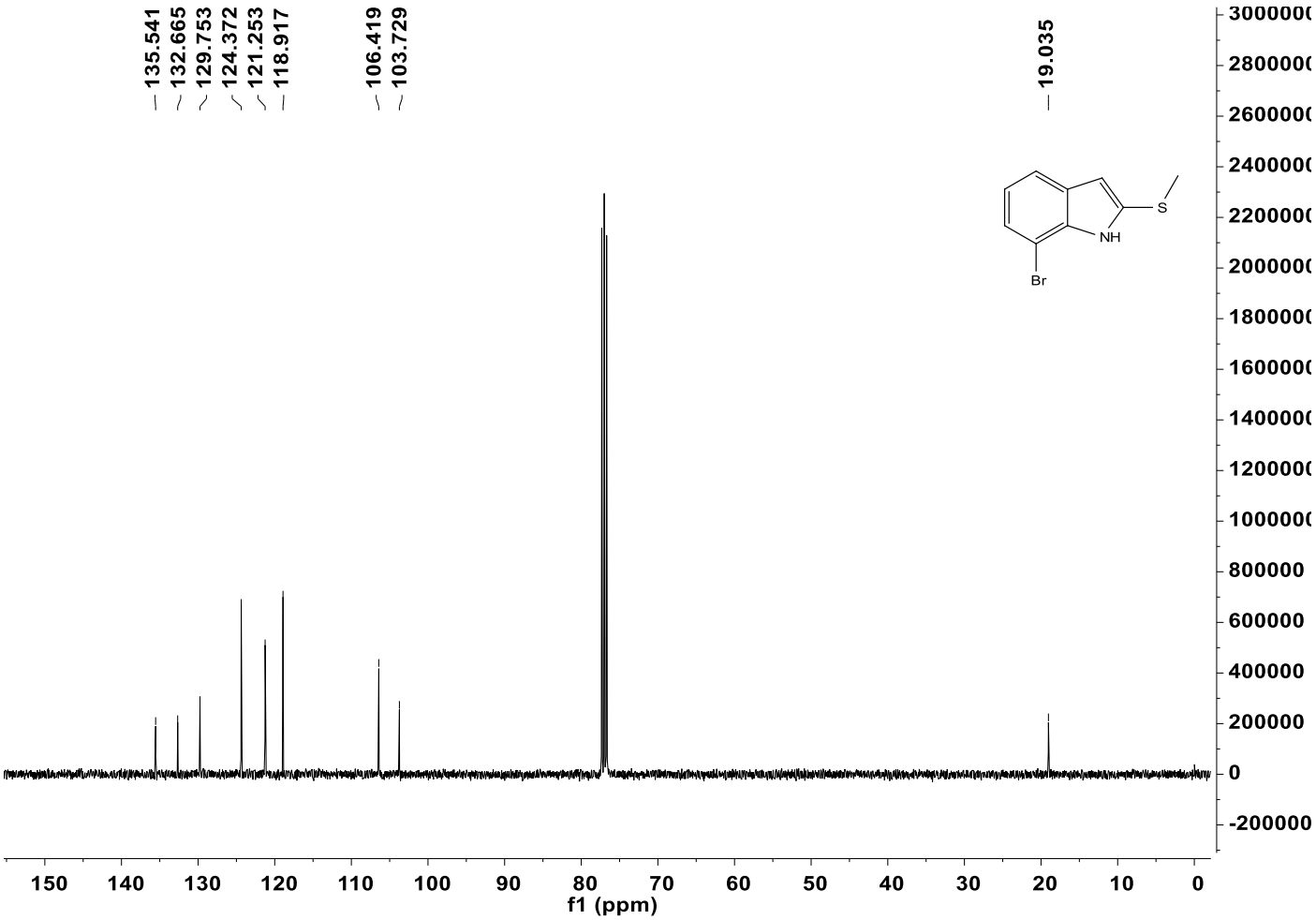
2n


8.009
7.439
7.436
7.434
7.432
7.391
7.370
7.212
7.208
7.191
7.187
6.505
6.503
6.500
6.497
2.506
7.260
Br
NH
S
1.00
1.00
1.00
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
1.00
6.56
6.52
6.48
6.44
f1 (ppm)
1.00
1.00
1.00
1.00
1.00
3.00
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
-0.5
f1 (ppm)
4.5E+12
4.0E+12
3.5E+12
3.0E+12
2.5E+12
2.0E+12
1.5E+12
1.0E+12
5.0E+11
0.0E+00

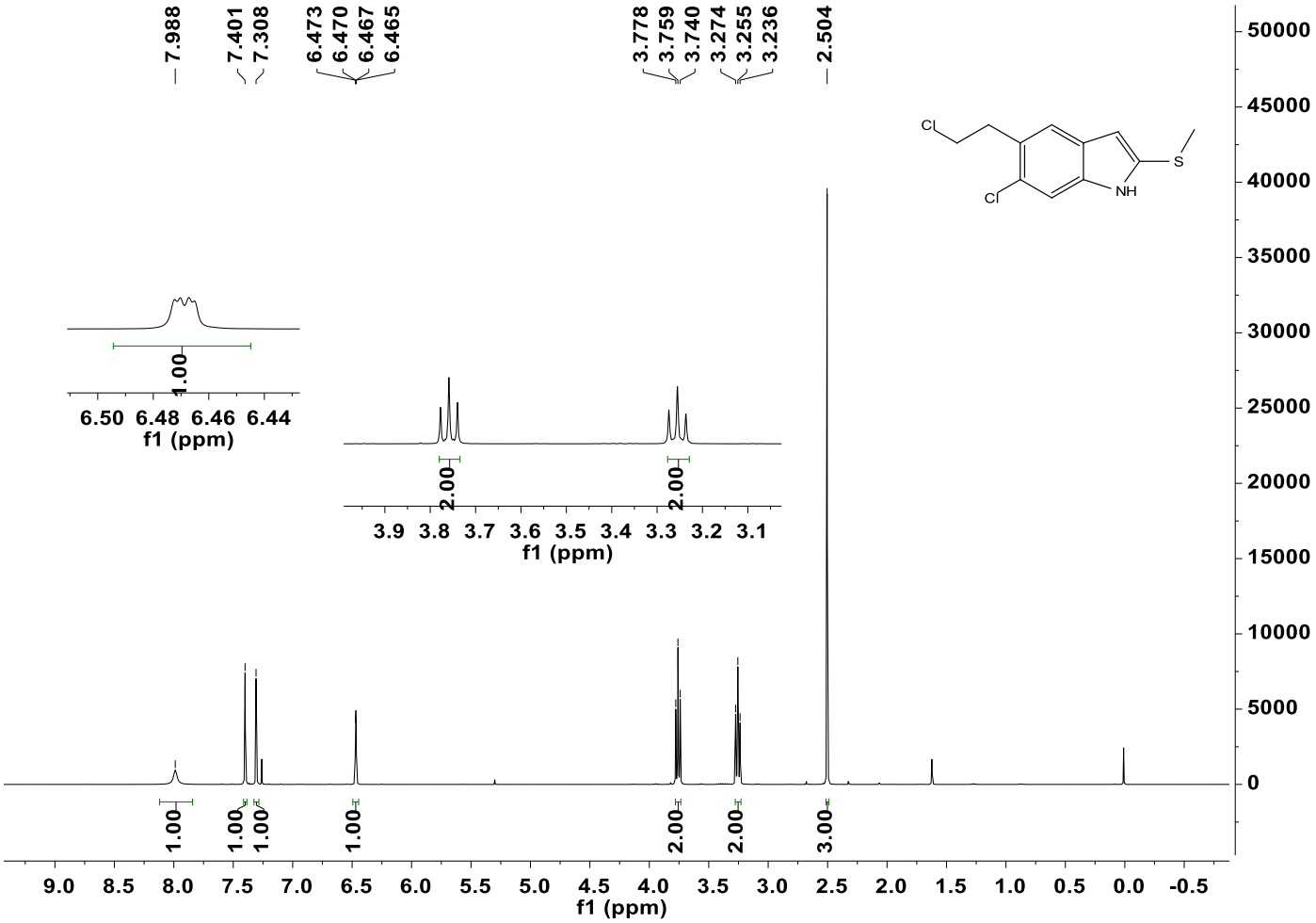

137.511
132.487
127.611
123.416
120.916
115.615
113.247
105.498
18.943
Br
NH
S
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
5.0E+10
4.5E+10
4.0E+10
3.5E+10
3.0E+10
2.5E+10
2.0E+10
1.5E+10
1.0E+10
5.0E+09
0.0E+00
-5.0E+09

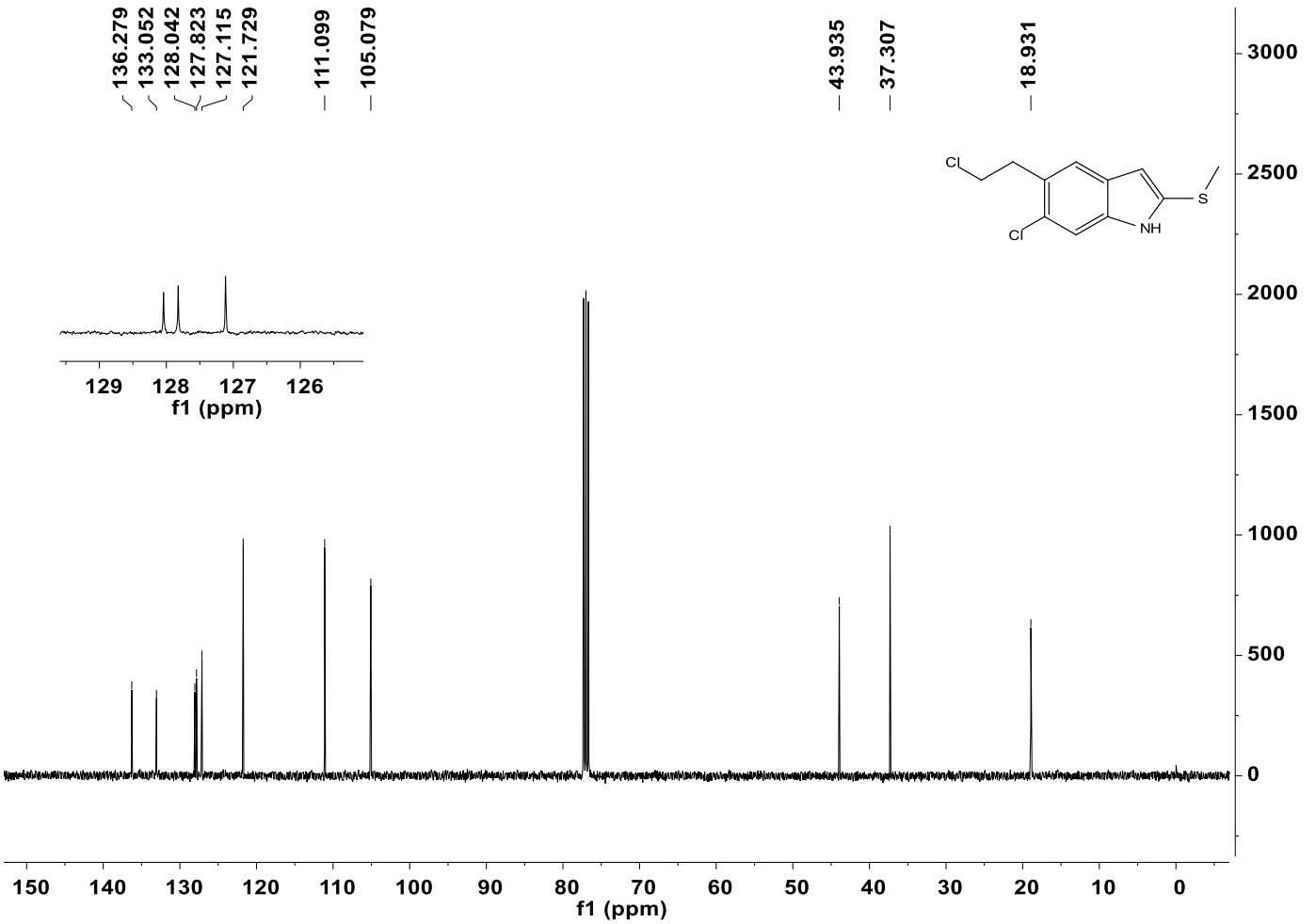
2o


8.233
7.474
7.455
7.319
7.317
7.300
7.298
6.996
6.977
6.958
6.603
6.598
2.538
7.260
S
NH
Br
1.00
1.00
1.00
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.00
6.63 6.61 6.59 6.57
f1 (ppm)
1.00
1.00
1.00
1.00
3.00
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 -0.5
f1 (ppm)
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00

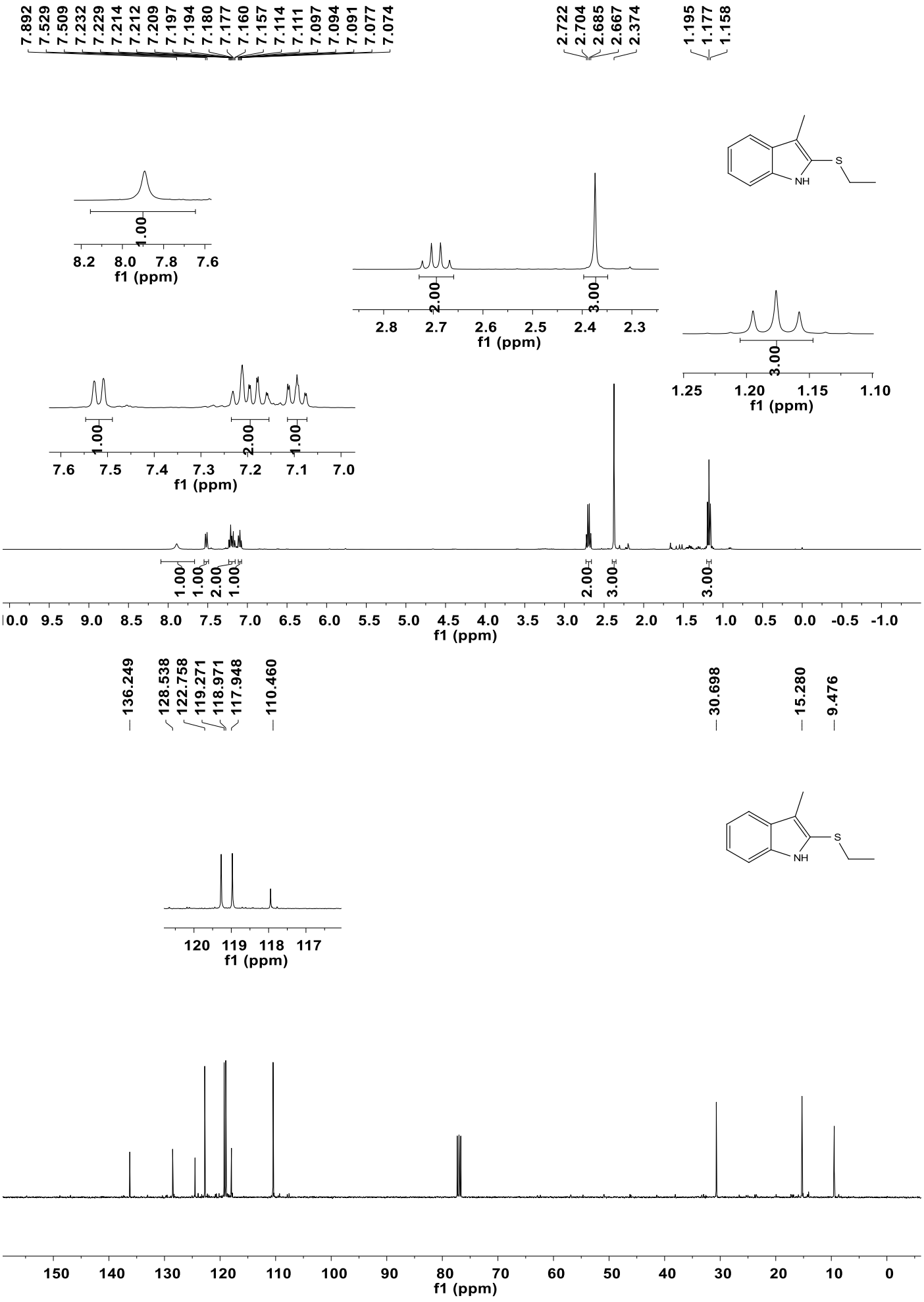

135.541
132.665
129.753
124.372
121.253
118.917
106.419
103.729
19.035
S
NH
Br
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000

2p

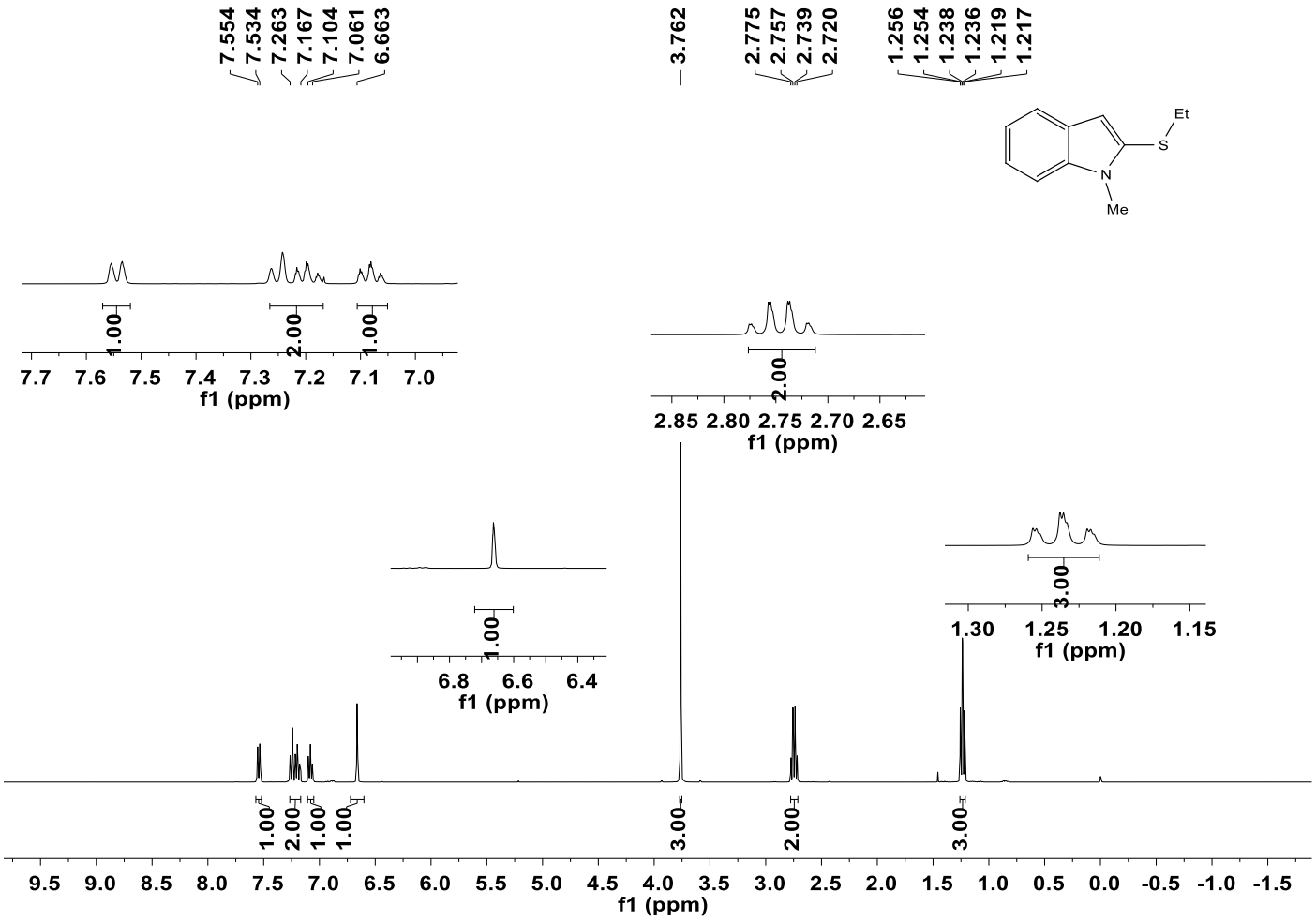

7.988
7.401
7.308
6.473
6.470
6.467
6.465
3.778
3.759
3.740
3.274
3.255
3.236
2.504
Cl
Cl
S
NH
1.00
6.50 6.48 6.46 6.44
f1 (ppm)
2.00
2.00
3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
f1 (ppm)
1.00
1.00
1.00
1.00
2.00
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0

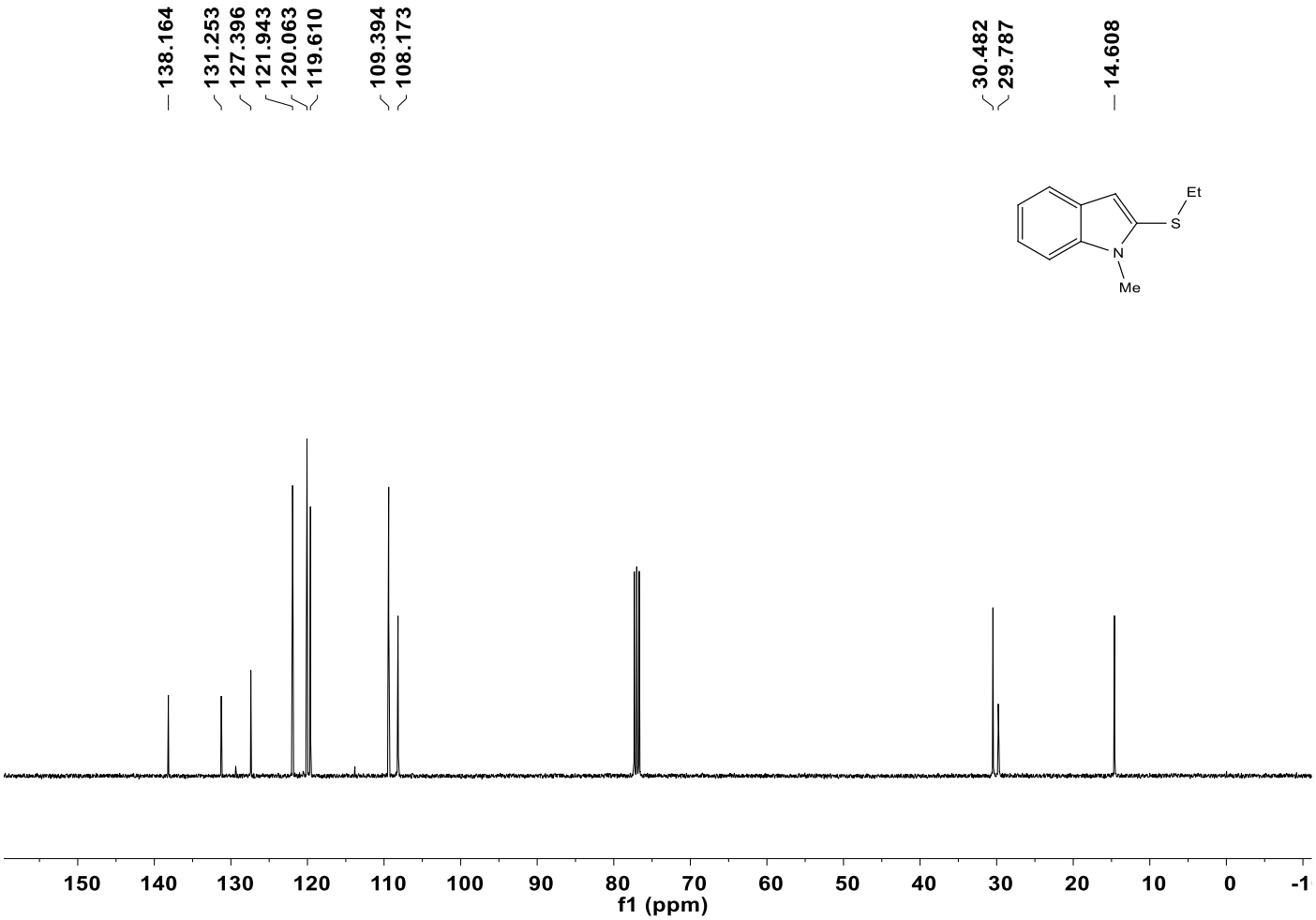

136.279
133.052
128.042
127.823
127.115
121.729
111.099
105.079
43.935
37.307
18.931
Cl
Cl
S
NH
129 128 127 126
f1 (ppm)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3000
2500
2000
1500
1000
500
0

2q

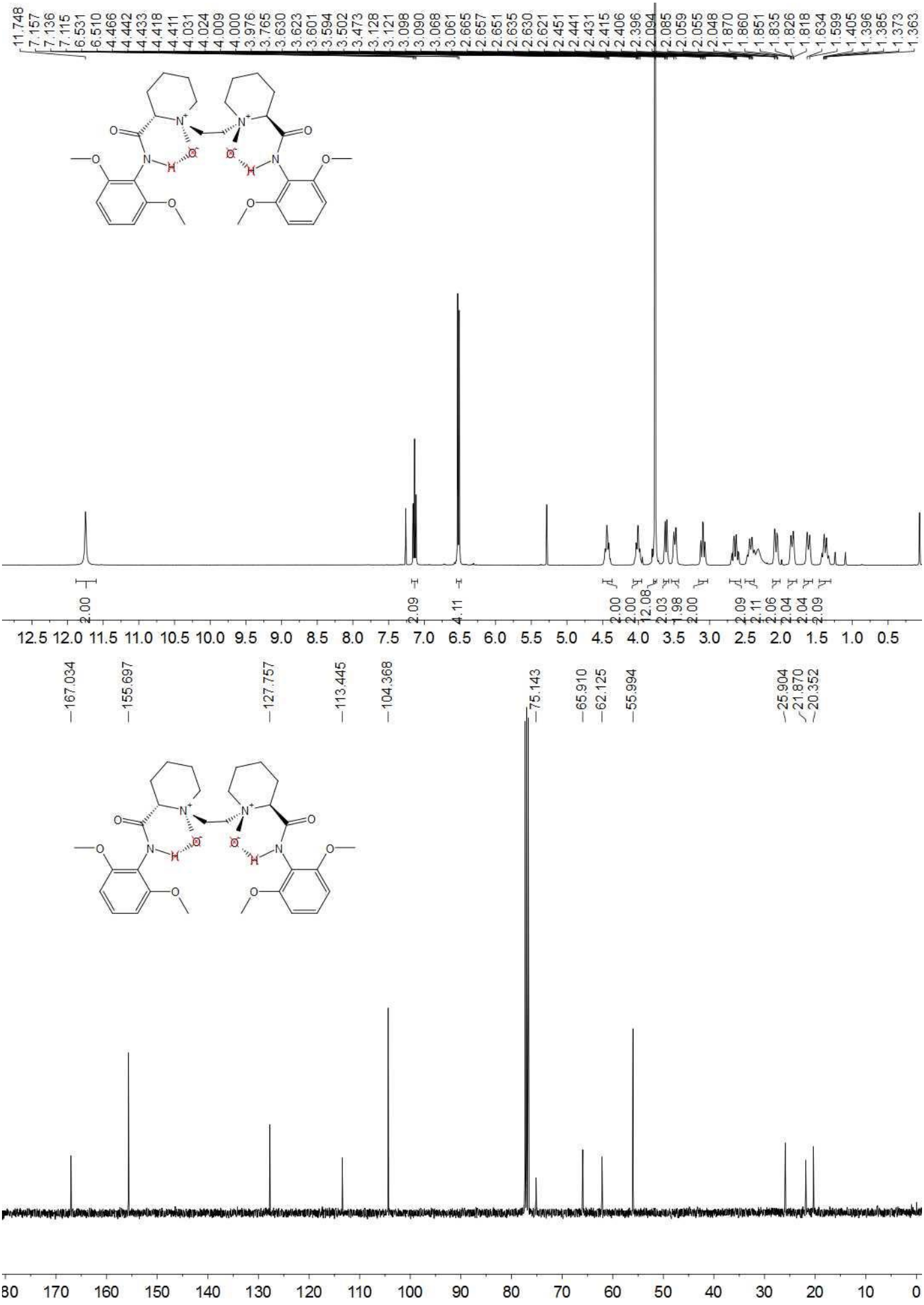

7.892
7.529
7.509
7.232
7.229
7.214
7.212
7.209
7.197
7.194
7.180
7.177
7.160
7.157
7.114
7.111
7.097
7.094
7.091
7.077
7.074
2.722
2.704
2.685
2.667
2.374
1.195
1.177
1.158
S
NH
f1 (ppm)
136.249
128.538
122.758
119.271
118.971
117.948
110.460
30.698
15.280
9.476

2r

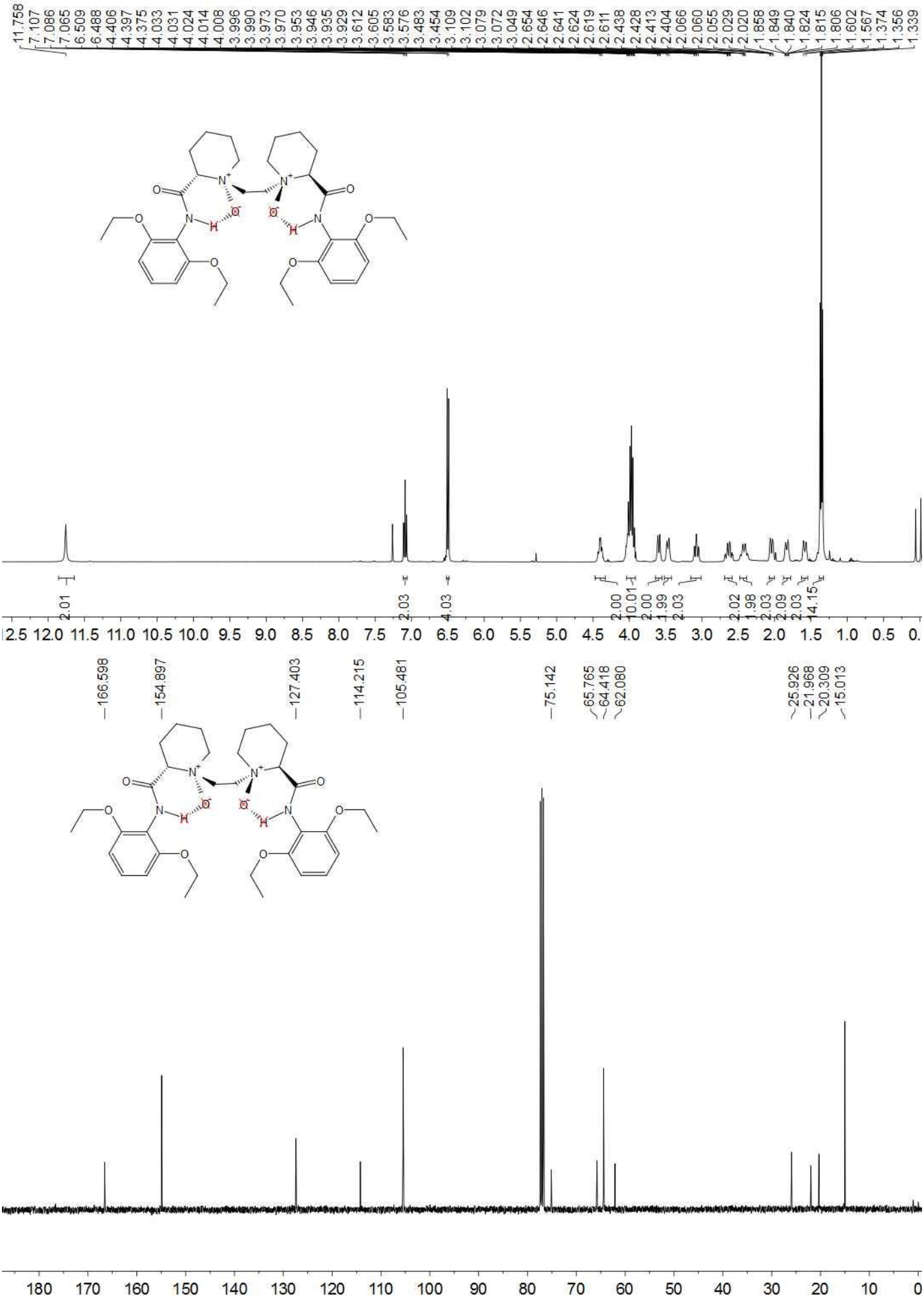

7.554
7.534
7.263
7.167
7.104
7.061
6.663
3.762
2.775
2.757
2.739
2.720
1.256
1.254
1.238
1.236
1.219
1.217
Et
S
N
Me
1.00
2.00
1.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.00
2.85 2.80 2.75 2.70 2.65
f1 (ppm)
1.00
6.8 6.6 6.4
f1 (ppm)
3.00
1.30 1.25 1.20 1.15
f1 (ppm)
1.00
2.00
1.00
1.00
3.00
2.00
3.00
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 -0.5 -1.0 -1.5
f1 (ppm)


138.164
131.253
127.396
121.943
120.063
119.610
109.394
108.173
30.482
29.787
14.608
Et
S
N
Me
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

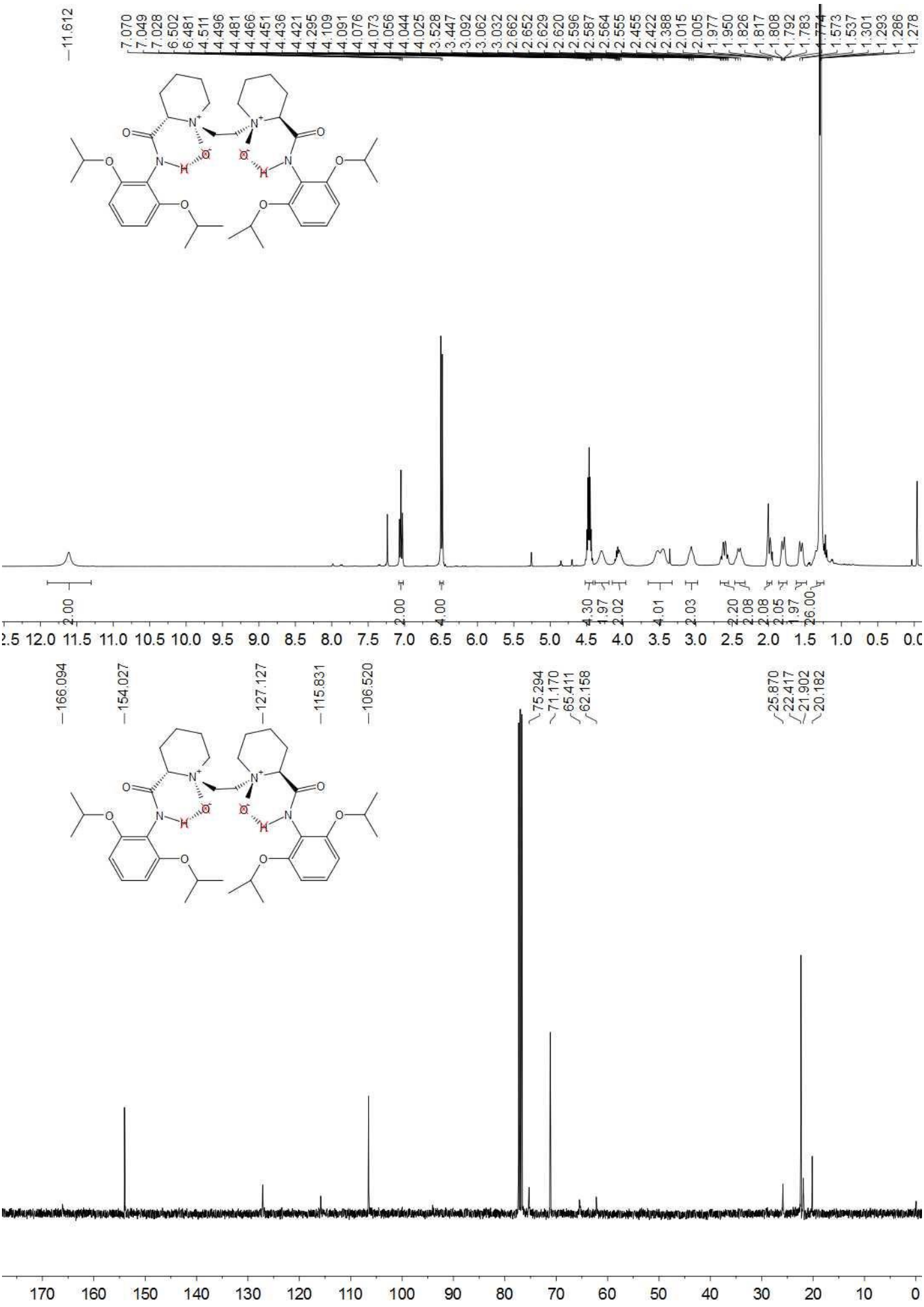
L_2-Pi(OMe)$_2$


11.748
7.157
7.136
7.115
6.531
6.510
4.466
4.442
4.433
4.418
4.411
4.031
4.024
4.009
4.000
3.976
3.765
3.630
3.623
3.601
3.594
3.502
3.473
3.128
3.121
3.098
3.090
3.068
3.061
2.665
2.657
2.651
2.635
2.630
2.621
2.451
2.441
2.431
2.415
2.406
2.396
2.094
2.085
2.059
2.055
2.048
1.870
1.860
1.851
1.835
1.826
1.818
1.634
1.599
1.405
1.396
1.385
1.373
1.363
2.00
2.09
4.11
2.00
2.00
12.08
2.03
1.98
2.00
2.09
2.11
2.06
2.04
2.04
2.09
12.5 12.0 11.5 11.0 10.5 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
167.034
155.697
127.757
113.445
104.368
75.143
65.910
62.125
55.994
25.904
21.870
20.352
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

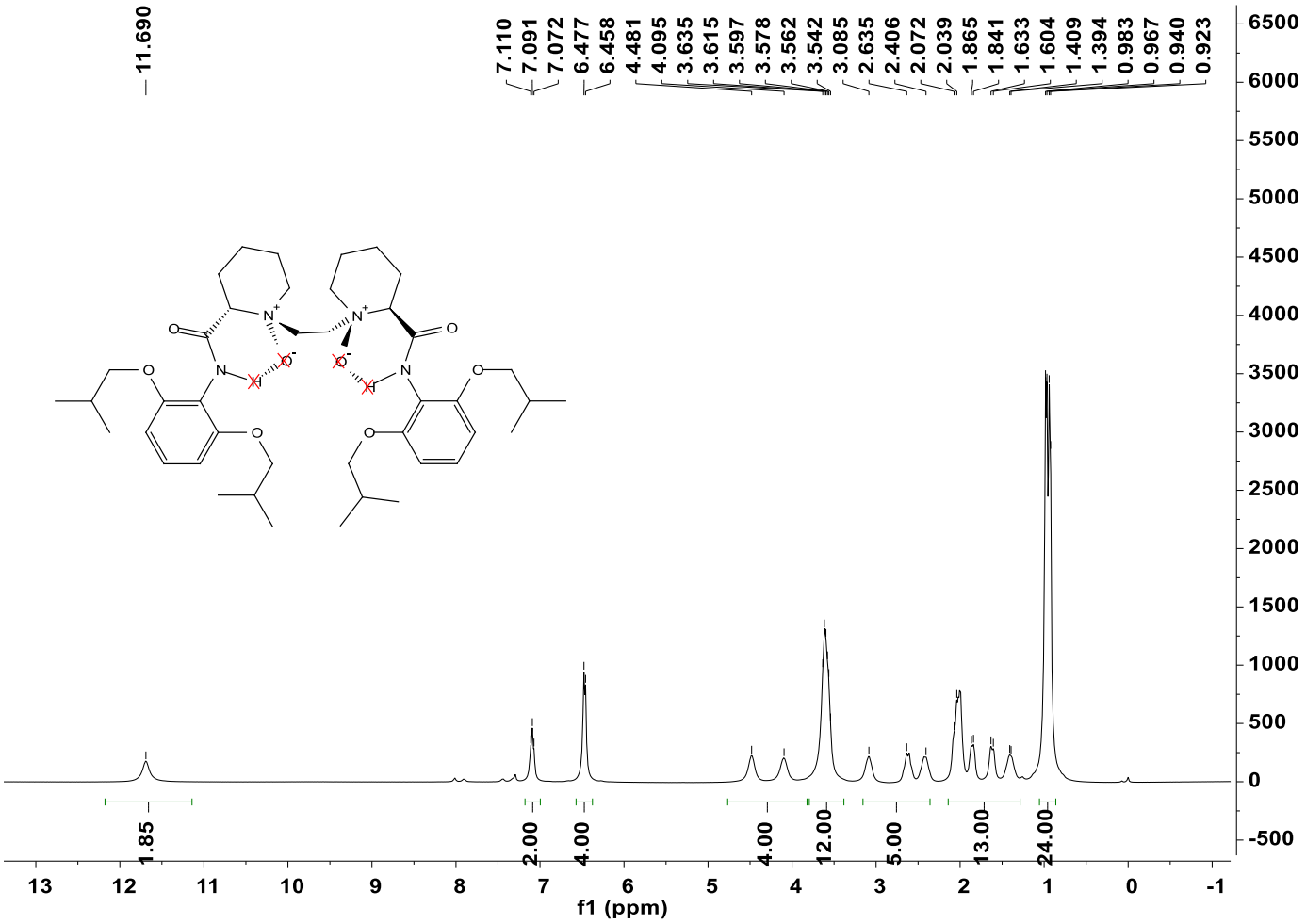
L_2-Pi$(OEt)_2$

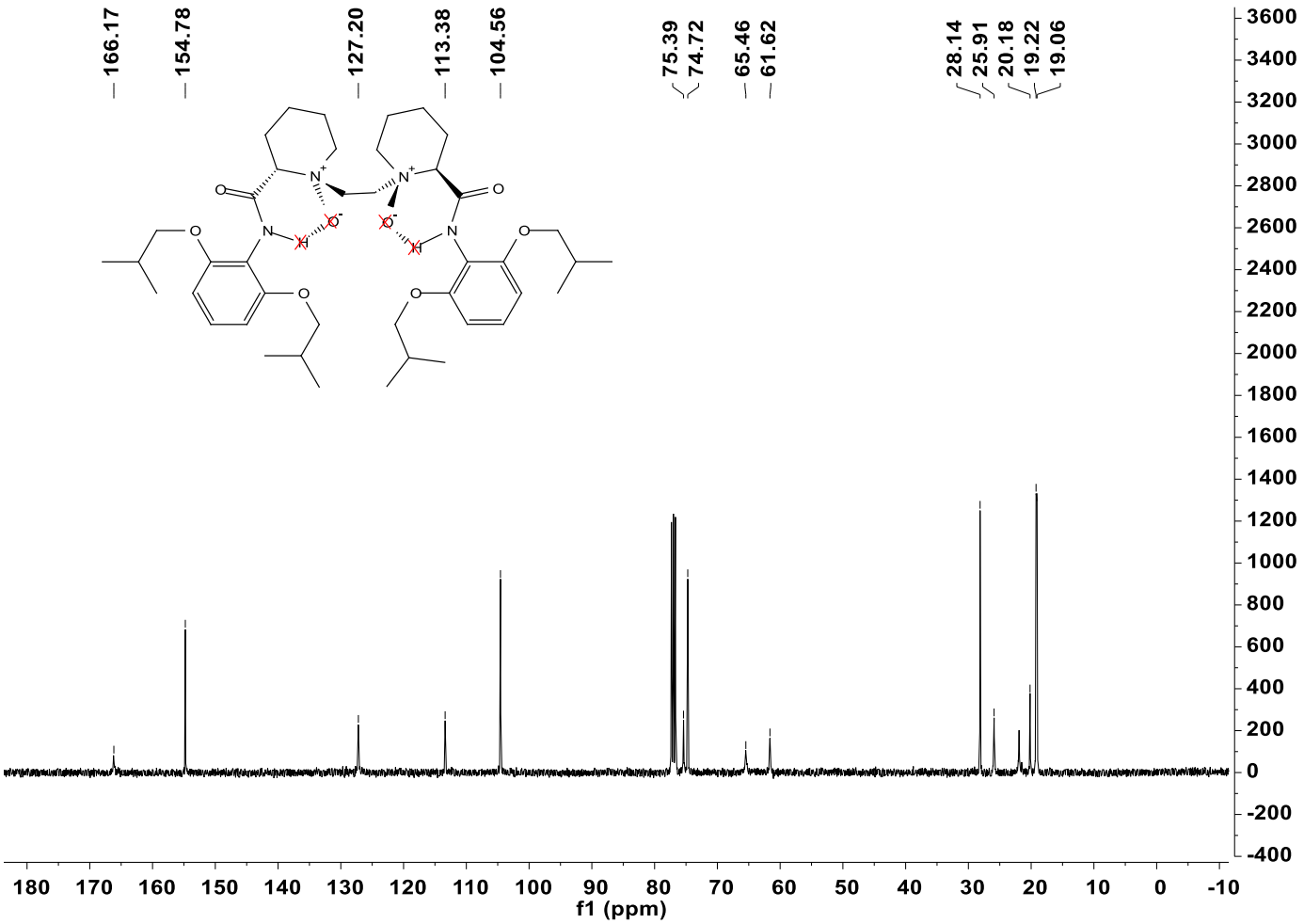

11.758
7.107
7.086
7.065
6.509
6.488
4.406
4.397
4.375
4.033
4.031
4.024
4.014
4.008
3.996
3.990
3.973
3.970
3.953
3.946
3.935
3.929
3.612
3.605
3.583
3.576
3.483
3.454
3.109
3.102
3.079
3.072
3.049
2.654
2.646
2.641
2.624
2.619
2.611
2.438
2.428
2.413
2.404
2.066
2.060
2.055
2.029
2.020
1.858
1.849
1.840
1.824
1.815
1.806
1.602
1.567
1.374
1.356
1.339
2.01
2.03
4.03
2.00
10.01
2.00
1.99
2.03
2.02
1.98
2.03
2.09
2.03
14.15
2.5 12.0 11.5 11.0 10.5 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.
166.598
154.897
127.403
114.215
105.481
75.142
65.765
64.418
62.080
25.926
21.968
20.309
15.013
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

L_2-Pi(O*i*Pr)$_2$

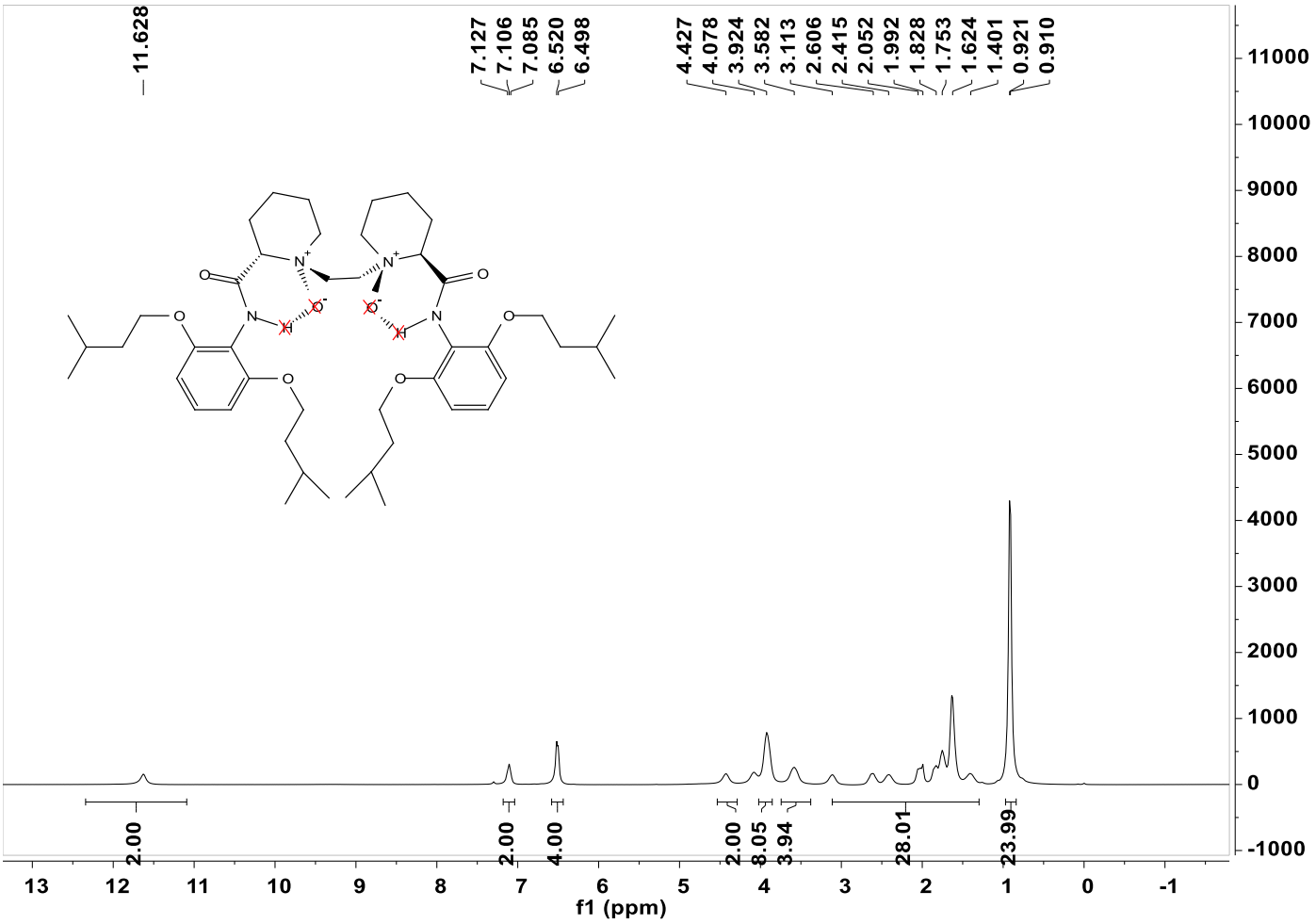

11.612
7.070
7.049
7.028
6.502
6.481
4.511
4.496
4.481
4.466
4.451
4.436
4.421
4.295
4.109
4.091
4.076
4.073
4.056
4.044
4.025
3.528
3.447
3.092
3.062
3.032
2.662
2.652
2.629
2.620
2.596
2.587
2.564
2.555
2.455
2.422
2.388
2.015
2.005
1.977
1.950
1.826
1.817
1.808
1.792
1.783
1.774
1.573
1.537
1.301
1.293
1.286
1.278
2.00
2.00
4.00
4.30
1.97
2.02
4.01
2.03
2.20
2.08
2.08
2.05
1.97
26.00
166.094
154.027
127.127
115.831
106.520
75.294
71.170
65.411
62.158
25.870
22.417
21.902
20.182

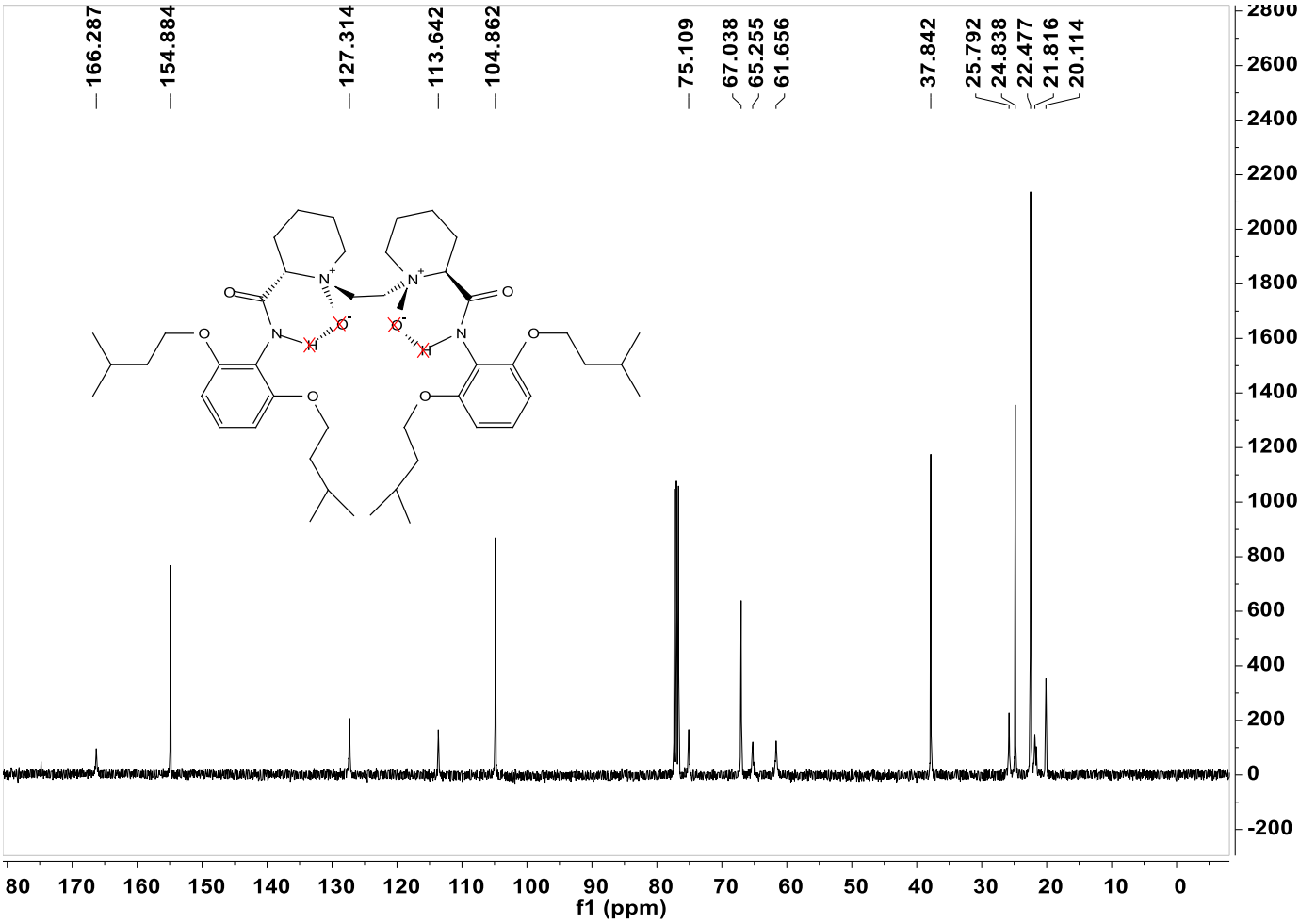
L_2-Pi(O*i*Bu)$_2$


11.690
7.110
7.091
7.072
6.477
6.458
4.481
4.095
3.635
3.615
3.597
3.578
3.562
3.542
3.085
2.635
2.406
2.072
2.039
1.865
1.841
1.633
1.604
1.409
1.394
0.983
0.967
0.940
0.923
1.85
2.00
4.00
4.00
12.00
5.00
13.00
24.00
f1 (ppm)

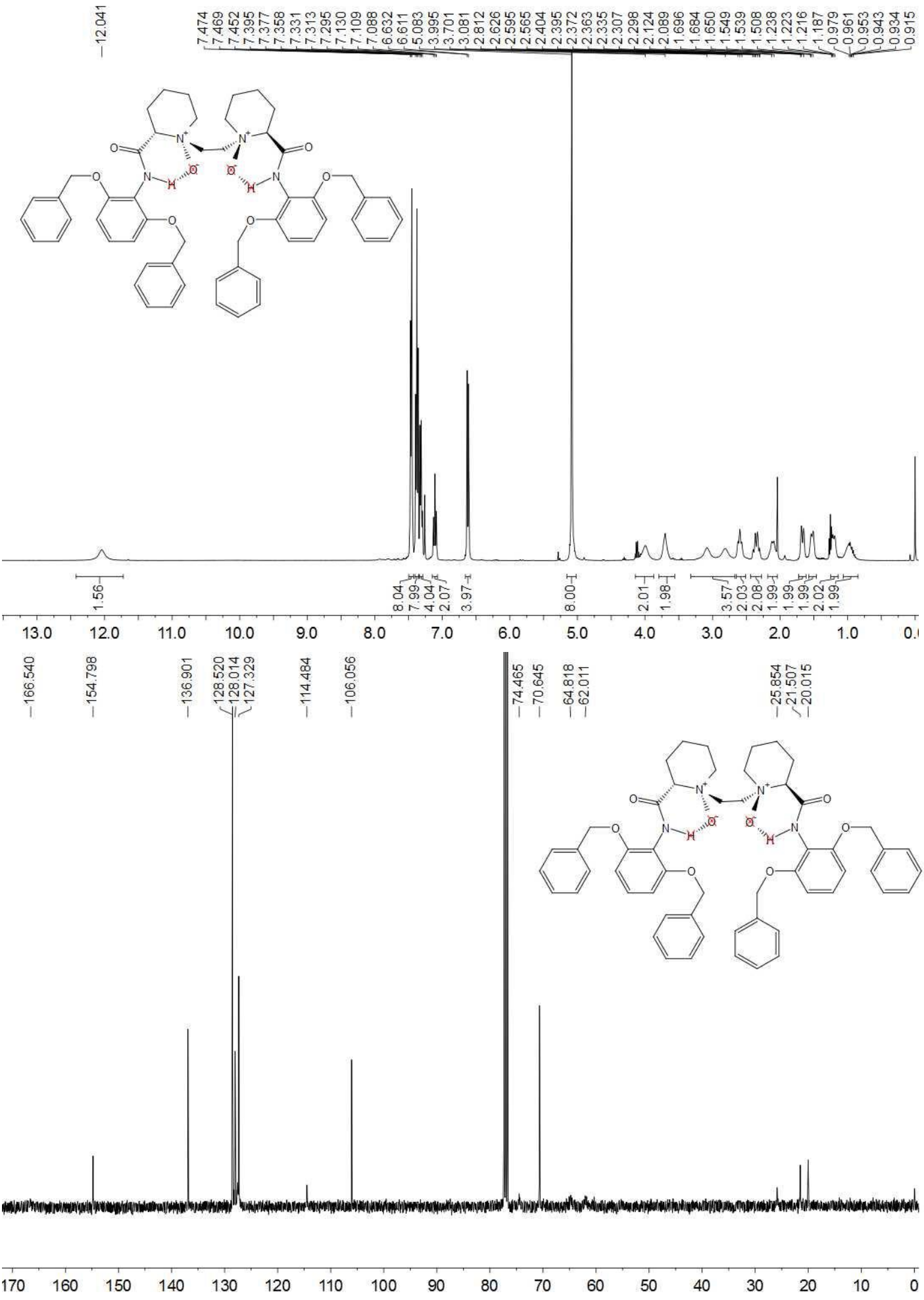

166.17
154.78
127.20
113.38
104.56
75.39
74.72
65.46
61.62
28.14
25.91
20.18
19.22
19.06
f1 (ppm)

L_2-Pi(O*i*pentyl)$_2$





L_2-Pi(OBn)$_2$


12.041
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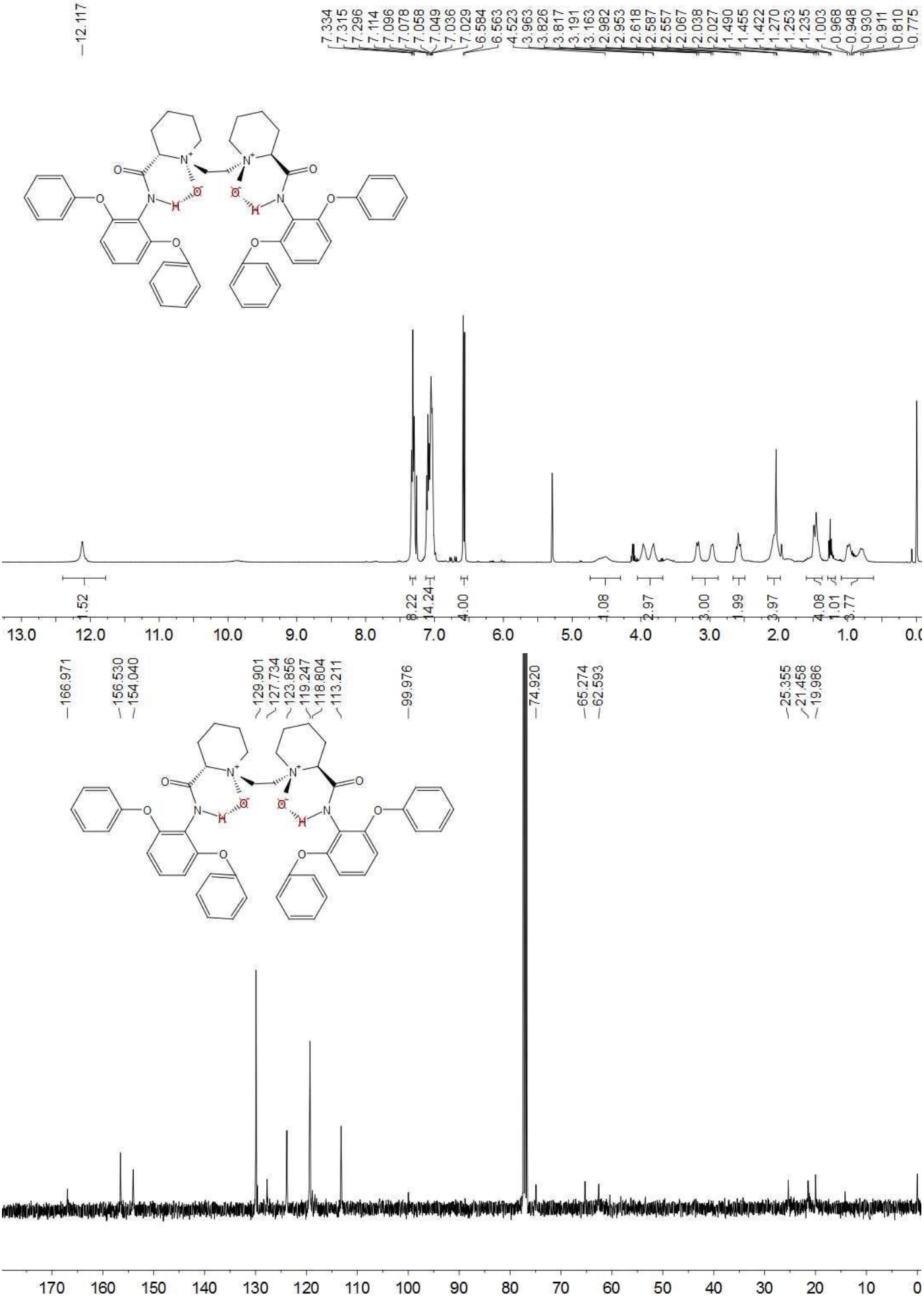
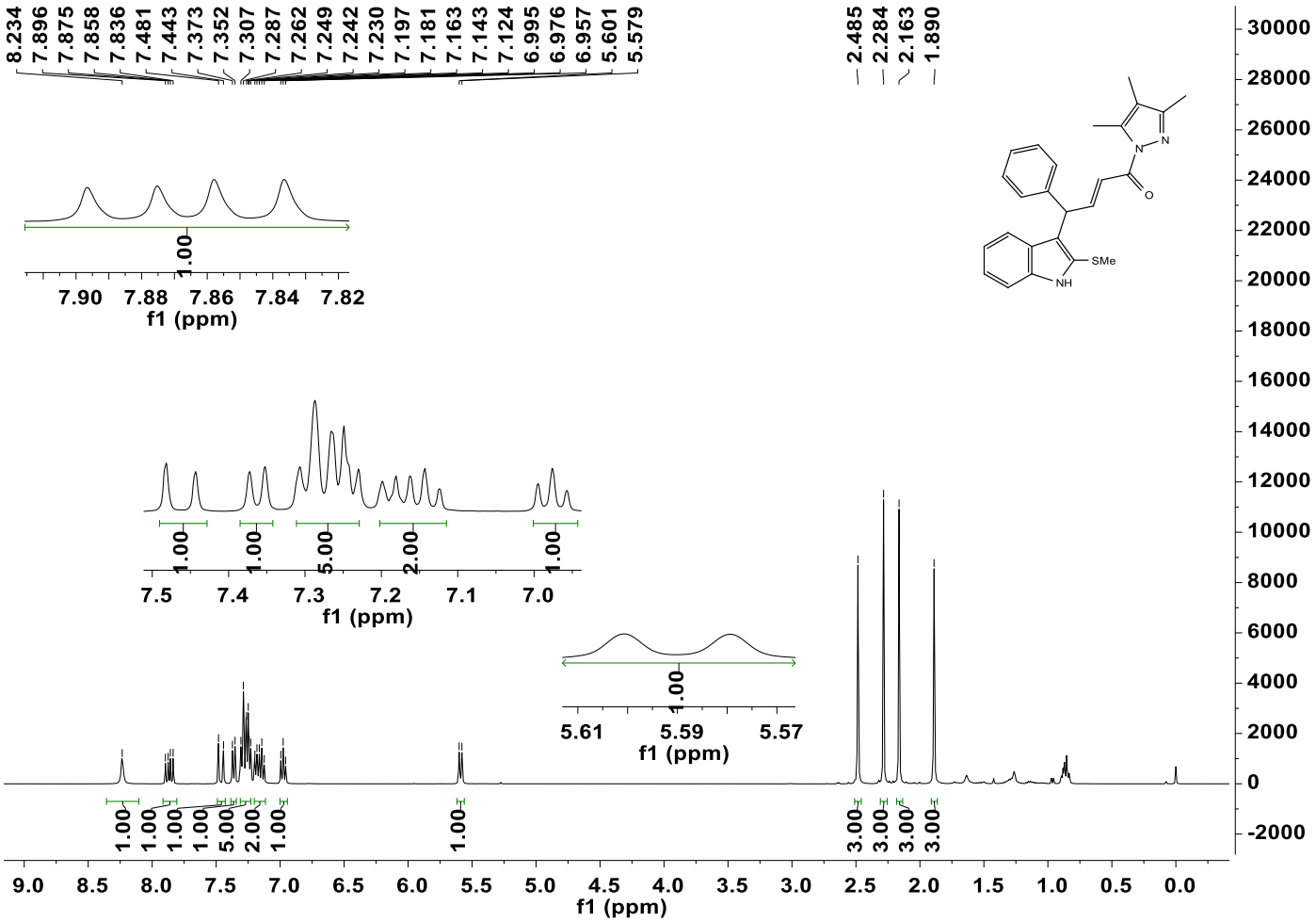
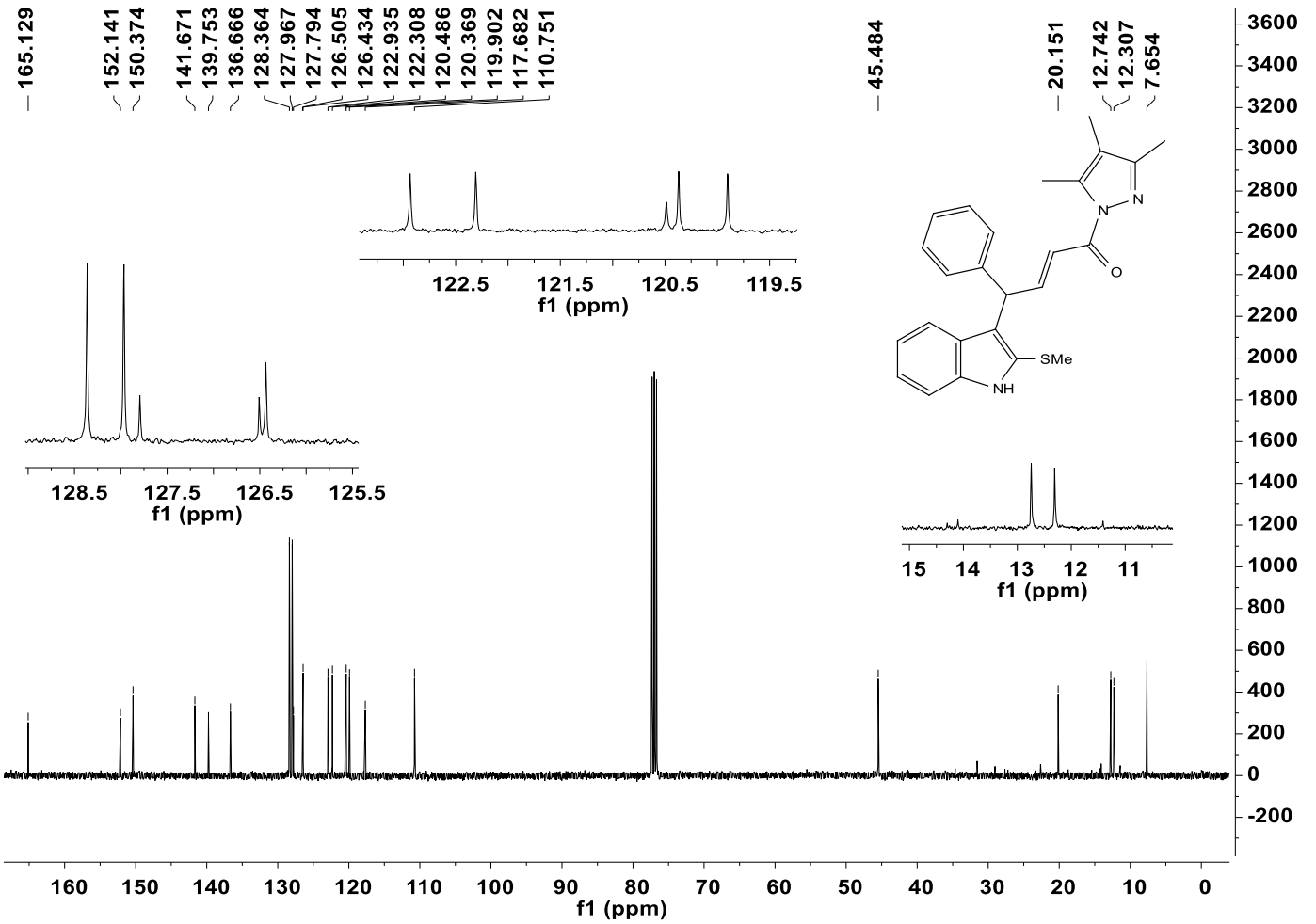
7.469
7.452
7.395
7.377
7.358
7.331
7.313
7.295
7.130
7.109
7.088
6.632
6.611
5.083
3.995
3.701
3.081
2.812
2.626
2.595
2.565
2.404
2.395
2.372
2.363
2.335
2.307
2.298
2.124
2.089
1.696
1.684
1.650
1.549
1.539
1.508
1.238
1.223
1.216
1.187
0.979
0.961
0.953
0.943
0.934
0.915
1.56
8.04
7.99
4.04
2.07
3.97
8.00
2.01
1.98
3.57
2.03
2.08
1.99
1.99
1.99
2.02
1.99
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
166.540
154.798
136.901
128.520
128.014
127.329
114.484
106.056
74.465
70.645
64.818
62.011
25.854
21.507
20.015
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

L_2-Pi$(OPh)_2$

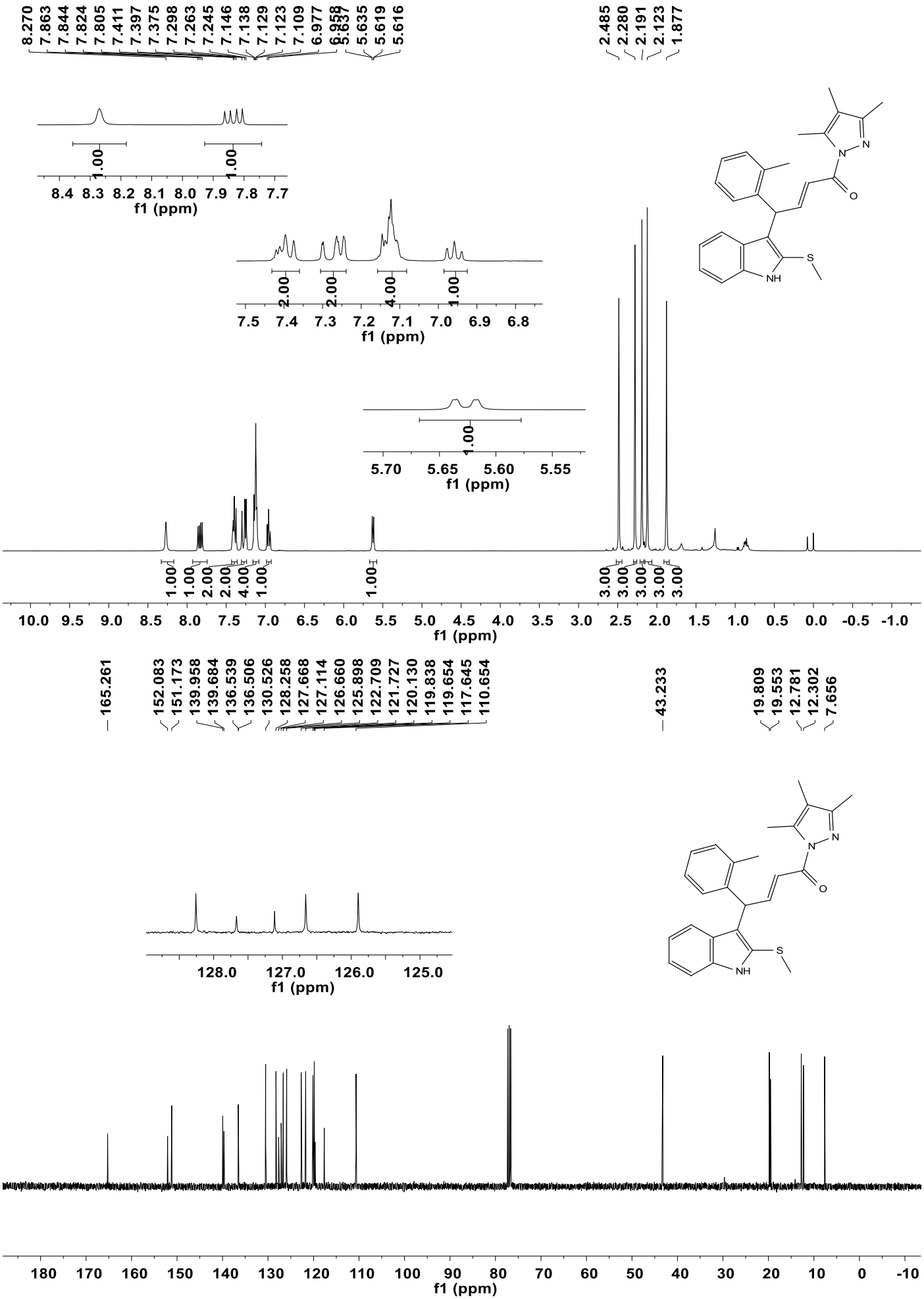

12.117
7.334
7.315
7.296
7.114
7.096
7.078
7.058
7.049
7.036
7.029
6.584
6.563
4.523
3.963
3.826
3.817
3.191
3.163
2.982
2.953
2.618
2.587
2.557
2.067
2.038
2.027
1.490
1.455
1.422
1.270
1.253
1.235
1.003
0.968
0.948
0.930
0.911
0.810
0.775
1.52
8.22
14.24
4.00
1.08
2.97
3.00
1.99
3.97
4.08
1.01
3.77
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
166.971
156.530
154.040
129.901
127.734
123.856
119.247
118.804
113.211
99.976
74.920
65.274
62.593
25.355
21.458
19.986
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3aa

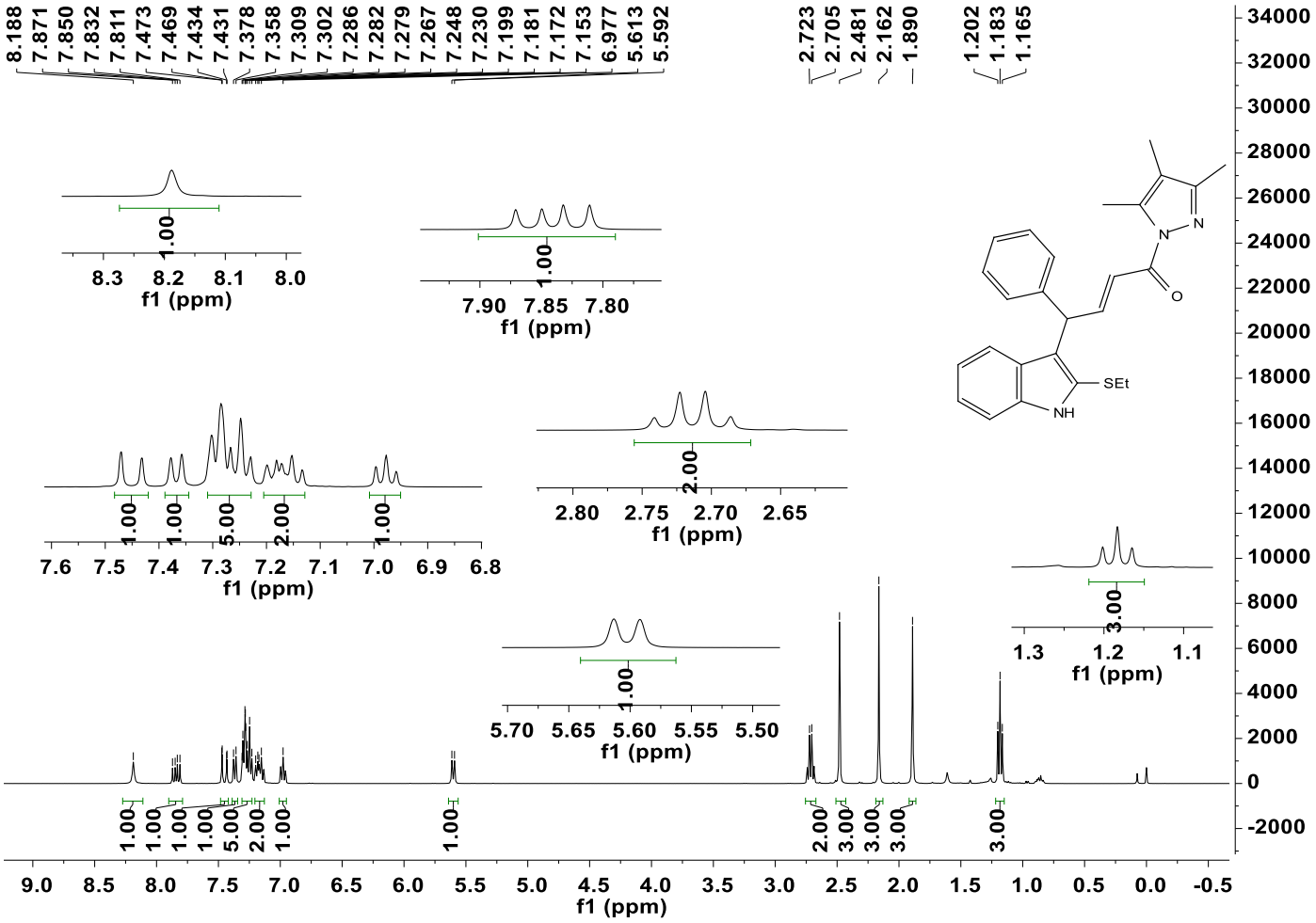

8.234
7.896
7.875
7.858
7.836
7.481
7.443
7.373
7.352
7.307
7.287
7.262
7.249
7.242
7.230
7.197
7.181
7.163
7.143
7.124
6.995
6.976
6.957
5.601
5.579
2.485
2.284
2.163
1.890
SMe
NH
f1 (ppm)

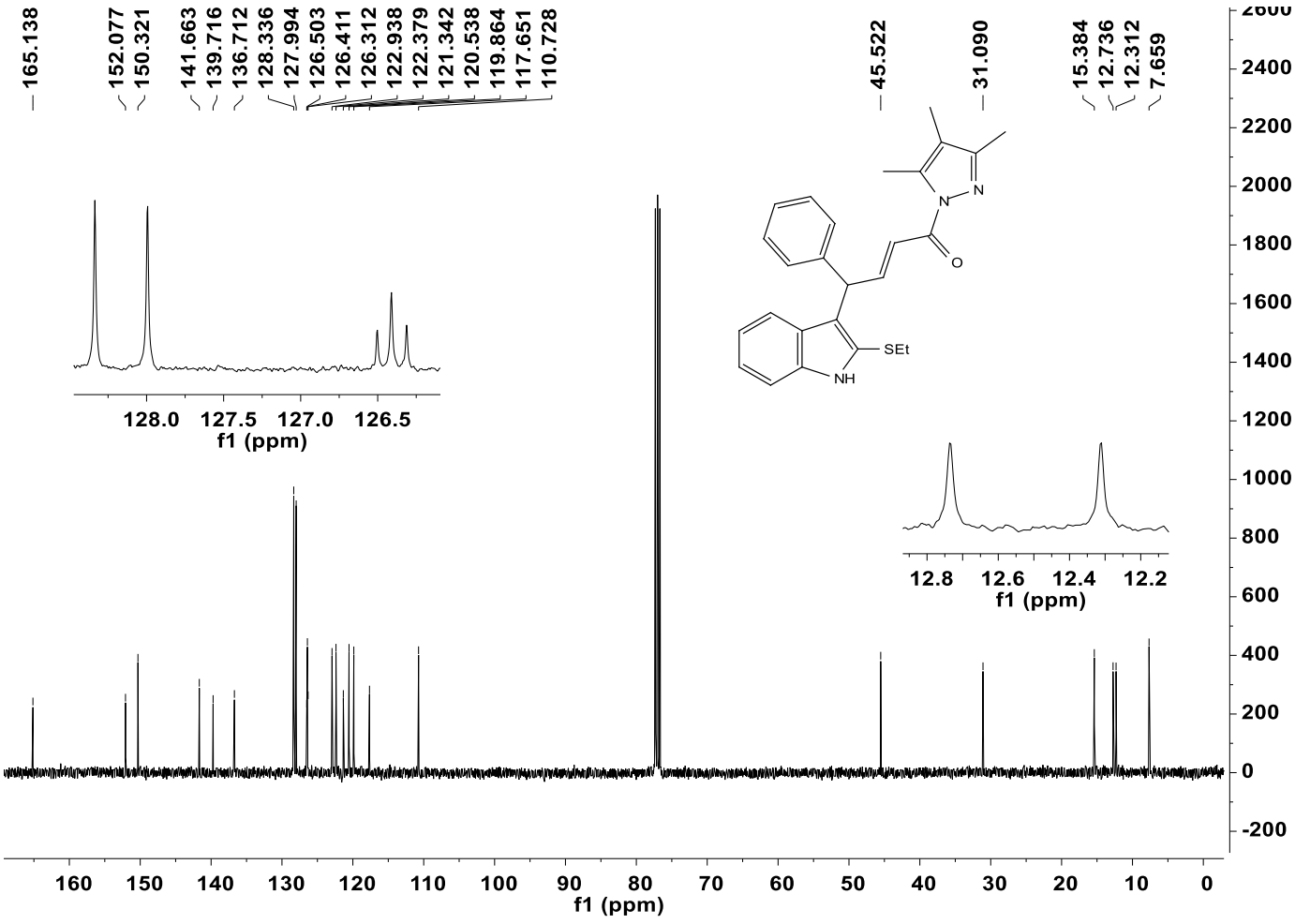

165.129
152.141
150.374
141.671
139.753
136.666
128.364
127.967
127.794
126.505
126.434
122.935
122.308
120.486
120.369
119.902
117.682
110.751
45.484
20.151
12.742
12.307
7.654
SMe
NH
f1 (ppm)

3da

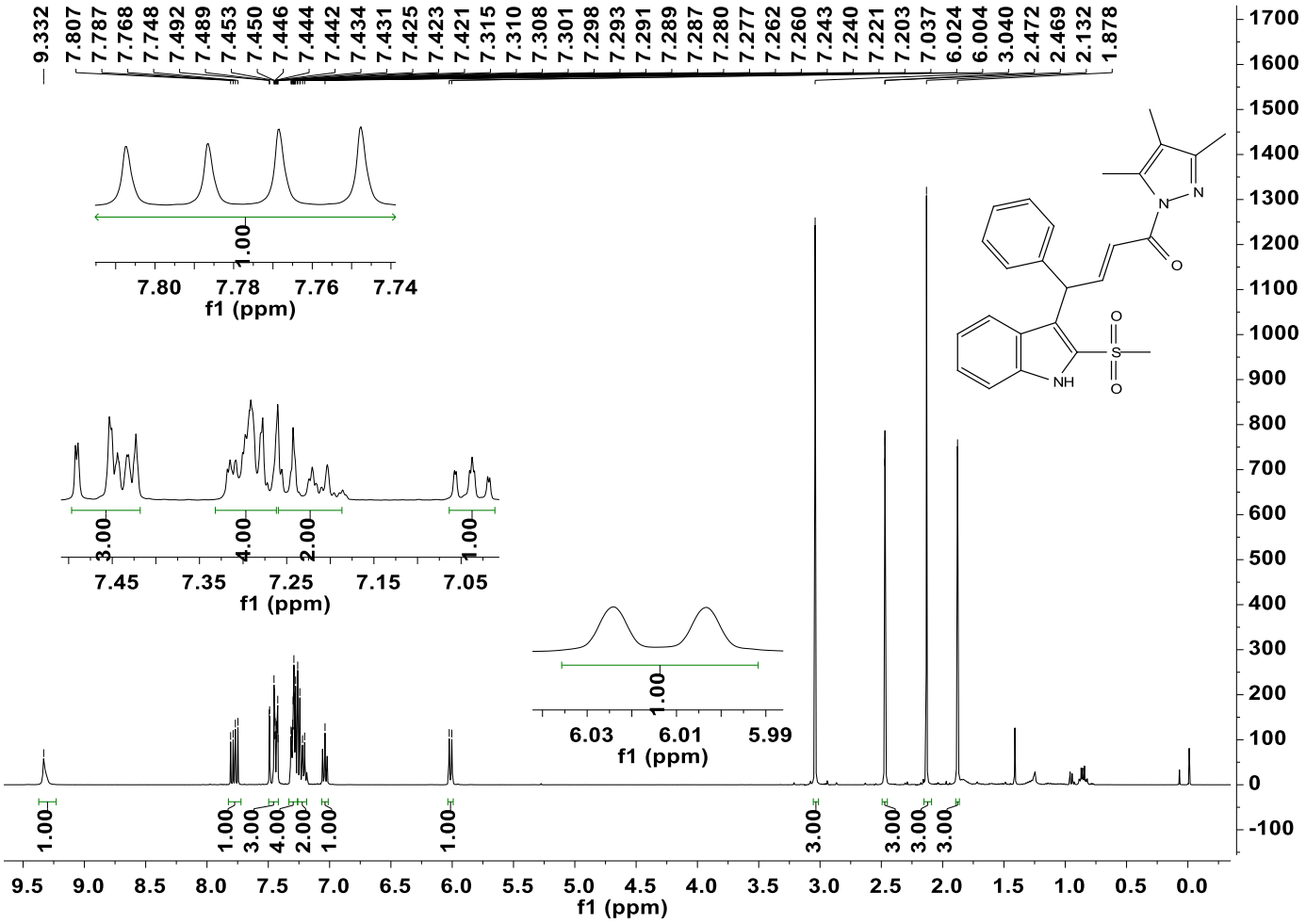

8.270
7.863
7.844
7.824
7.805
7.411
7.397
7.375
7.298
7.263
7.245
7.146
7.138
7.129
7.123
7.109
6.977
6.958
6.837
5.635
5.619
5.616
2.485
2.280
2.191
2.123
1.877
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)
165.261
152.083
151.173
139.958
139.684
136.539
136.506
130.526
128.258
127.668
127.114
126.660
125.898
122.709
121.727
120.130
119.838
119.654
117.645
110.654
43.233
19.809
19.553
12.781
12.302
7.656
f1 (ppm)
f1 (ppm)
f1 (ppm)
N
O
S
NH

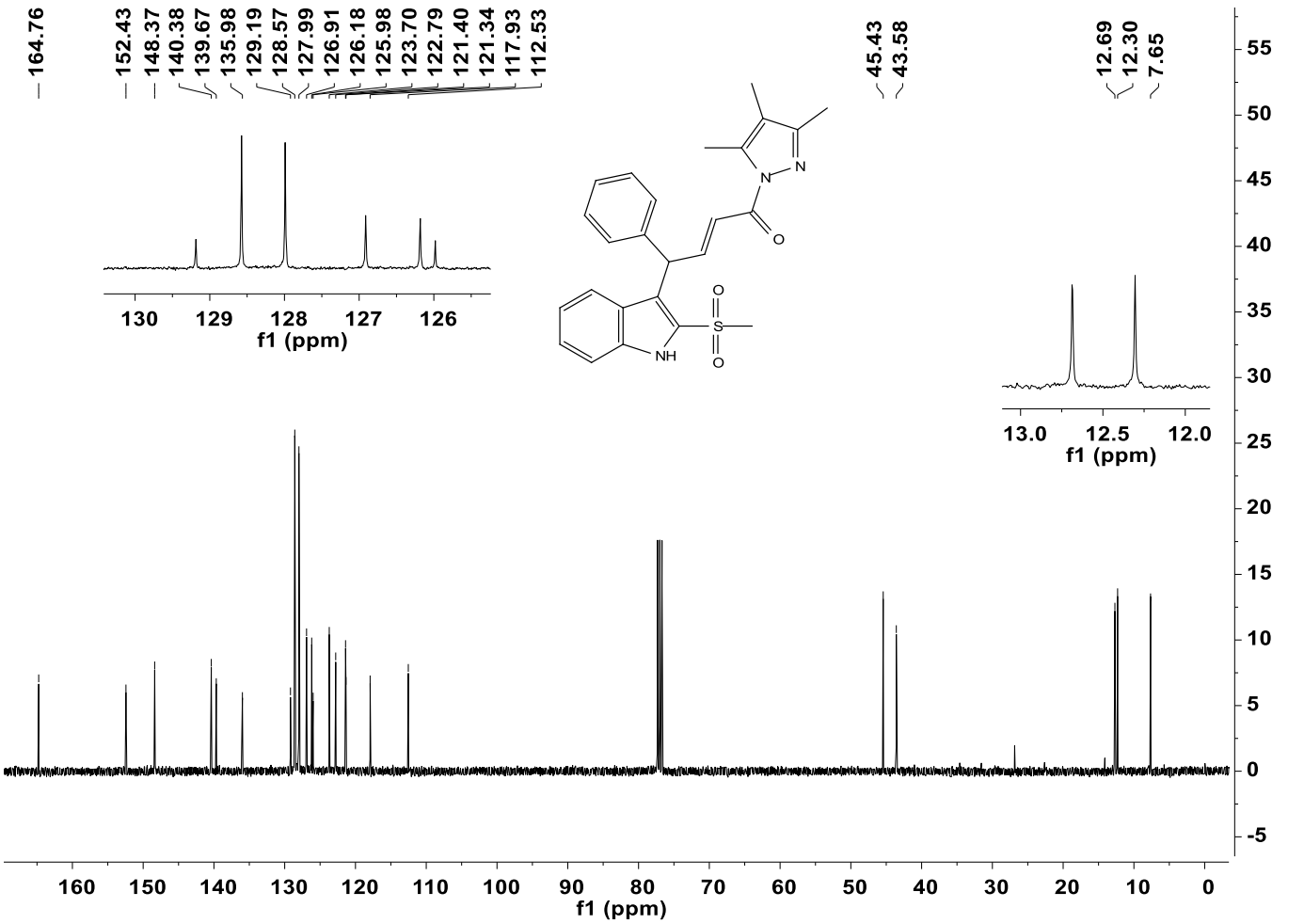
3ab


8.188
7.871
7.850
7.832
7.811
7.473
7.469
7.434
7.431
7.378
7.358
7.309
7.302
7.286
7.282
7.279
7.267
7.248
7.230
7.199
7.181
7.172
7.153
6.977
5.613
5.592
2.723
2.705
2.481
2.162
1.890
1.202
1.183
1.165
SEt
NH
f1 (ppm)

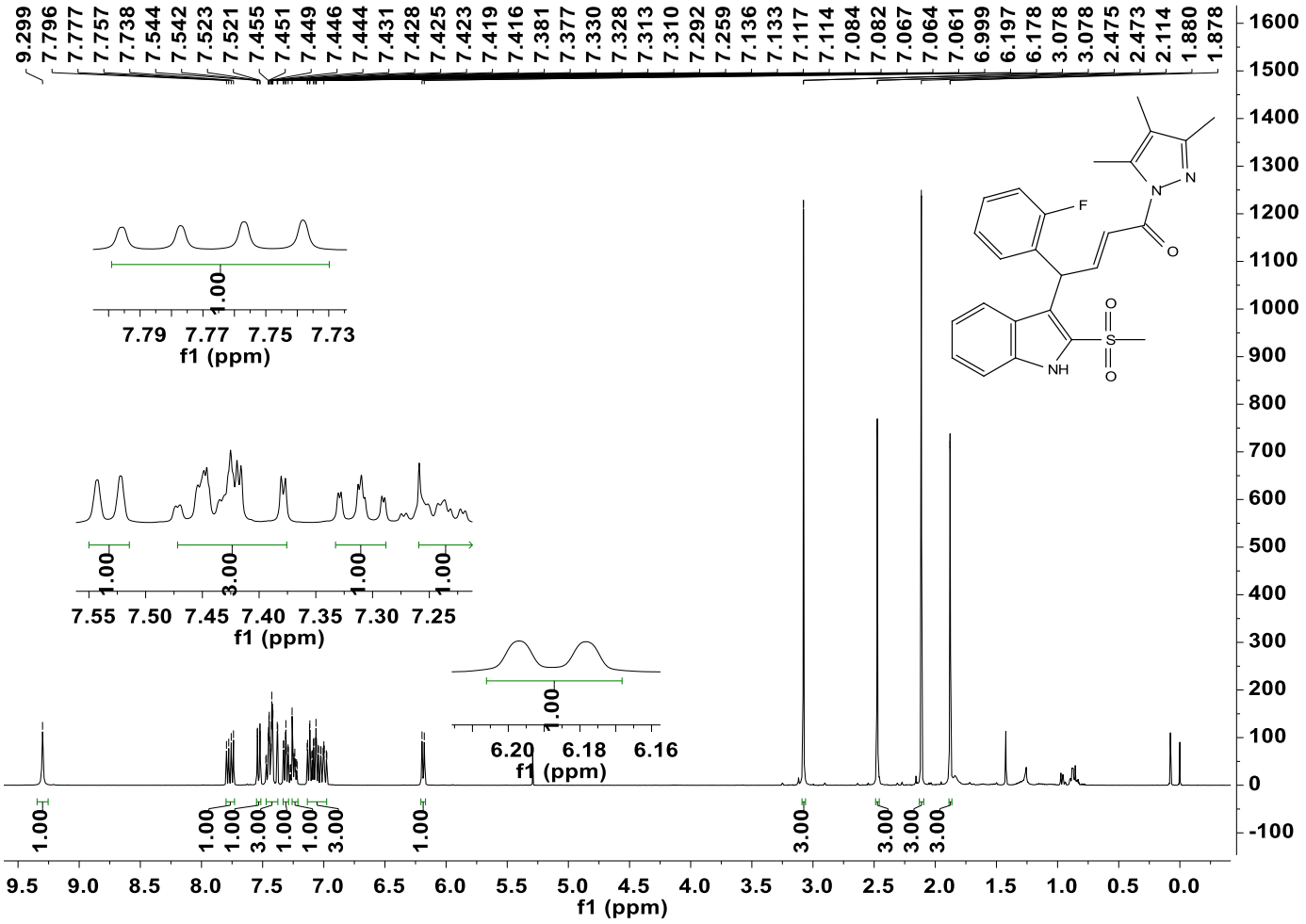

165.138
152.077
150.321
141.663
139.716
136.712
128.336
127.994
126.503
126.411
126.312
122.938
122.379
121.342
120.538
119.864
117.651
110.728
45.522
31.090
15.384
12.736
12.312
7.659
SEt
NH
f1 (ppm)

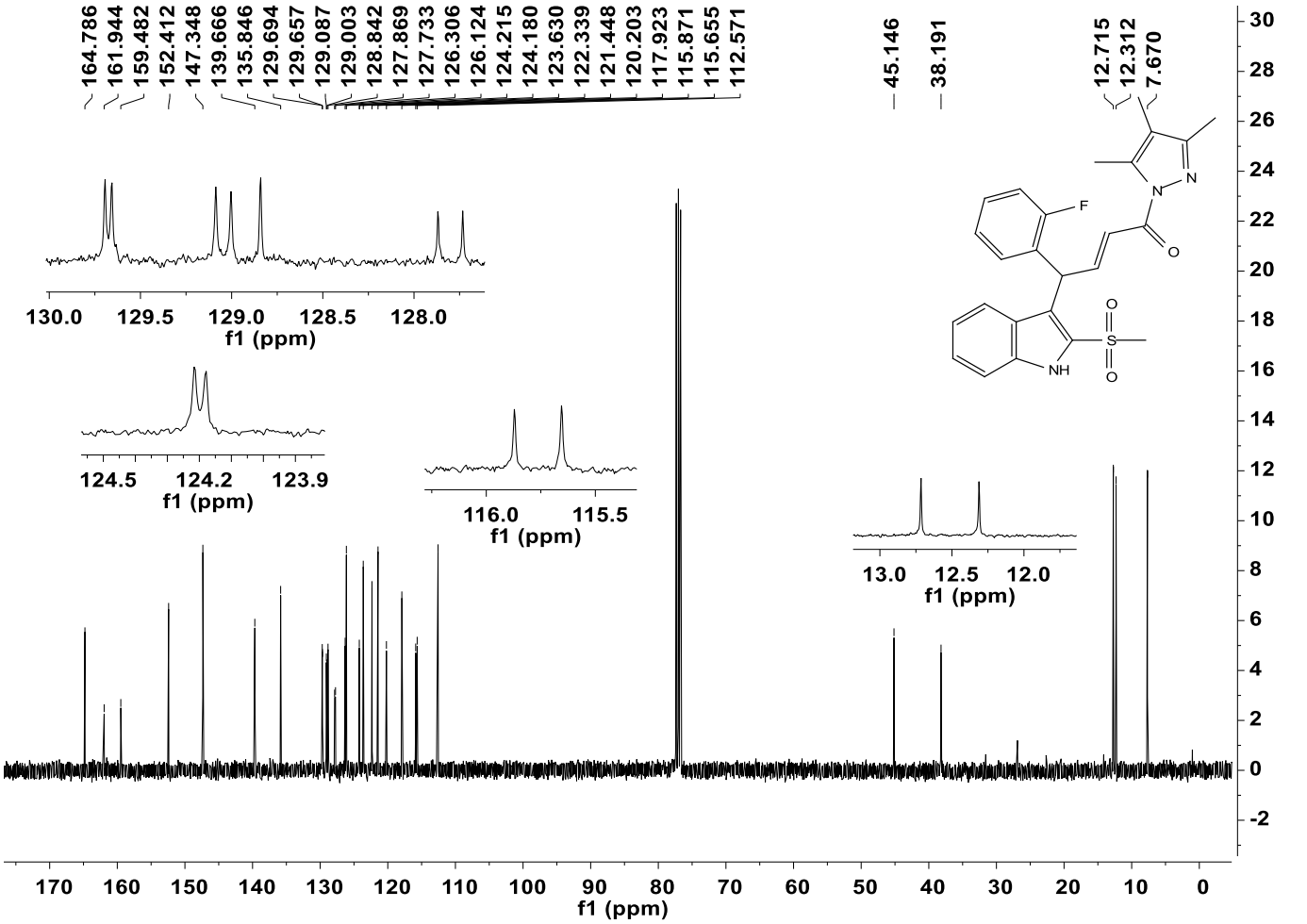
4aa

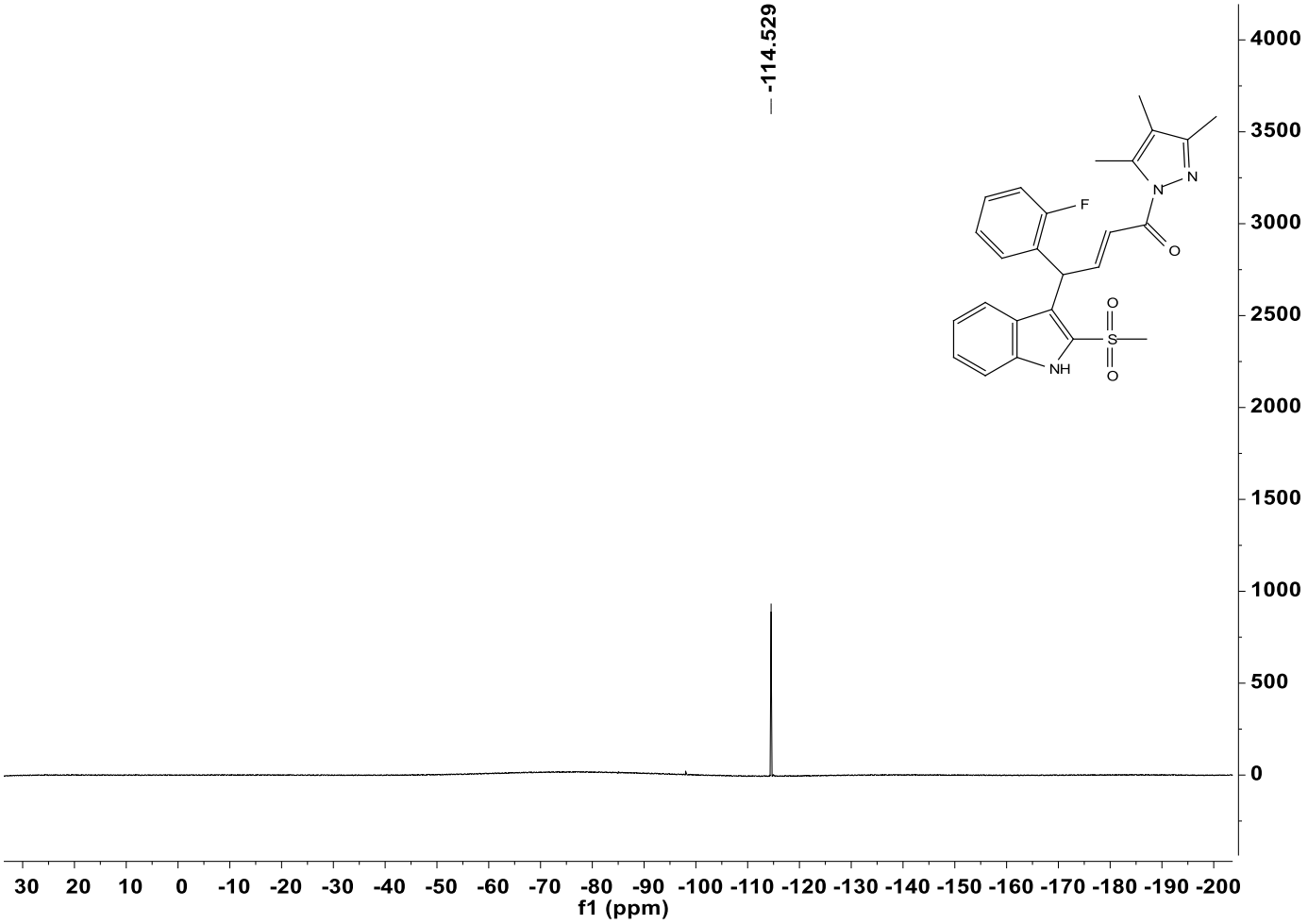

9.332
7.807
7.787
7.768
7.748
7.492
7.489
7.453
7.450
7.446
7.444
7.442
7.434
7.431
7.425
7.423
7.421
7.315
7.310
7.308
7.301
7.298
7.293
7.291
7.289
7.287
7.280
7.277
7.262
7.260
7.243
7.240
7.221
7.203
7.037
6.024
6.004
3.040
2.472
2.469
2.132
1.878
1.00
7.80
7.78
7.76
7.74
f1 (ppm)
3.00
4.00
2.00
1.00
7.45
7.35
7.25
7.15
7.05
f1 (ppm)
1.00
6.03
6.01
5.99
f1 (ppm)
1.00
1.00
3.00
4.00
2.00
1.00
1.00
3.00
3.00
3.00
3.00
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
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
N
N
O
O
S
O
NH


164.76
152.43
148.37
140.38
139.67
135.98
129.19
128.57
127.99
126.91
126.18
125.98
123.70
122.79
121.40
121.34
117.93
112.53
45.43
43.58
12.69
12.30
7.65
130
129
128
127
126
f1 (ppm)
13.0
12.5
12.0
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
55
50
45
40
35
30
25
20
15
10
5
0
-5
N
N
O
O
S
O
NH

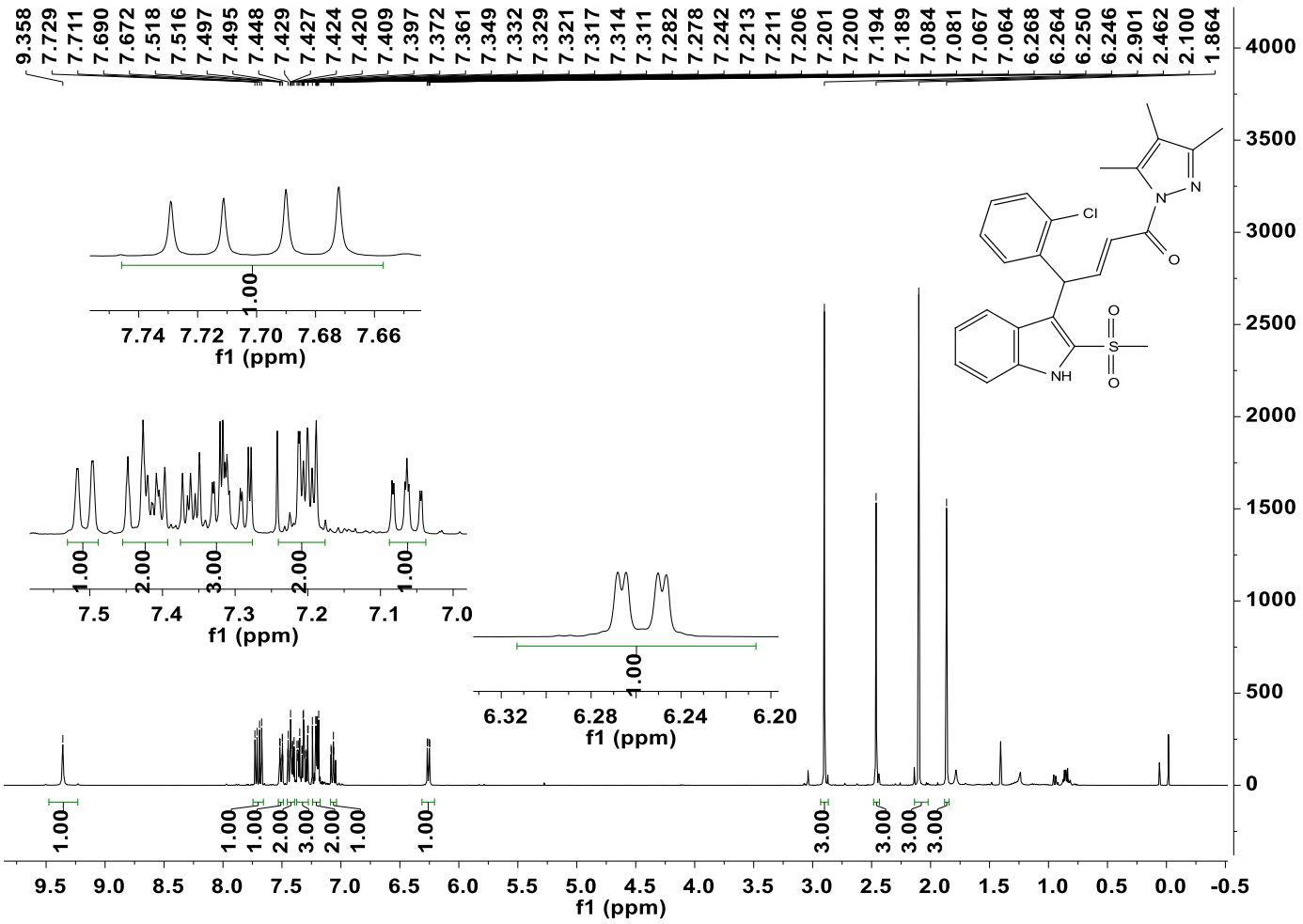
4ba

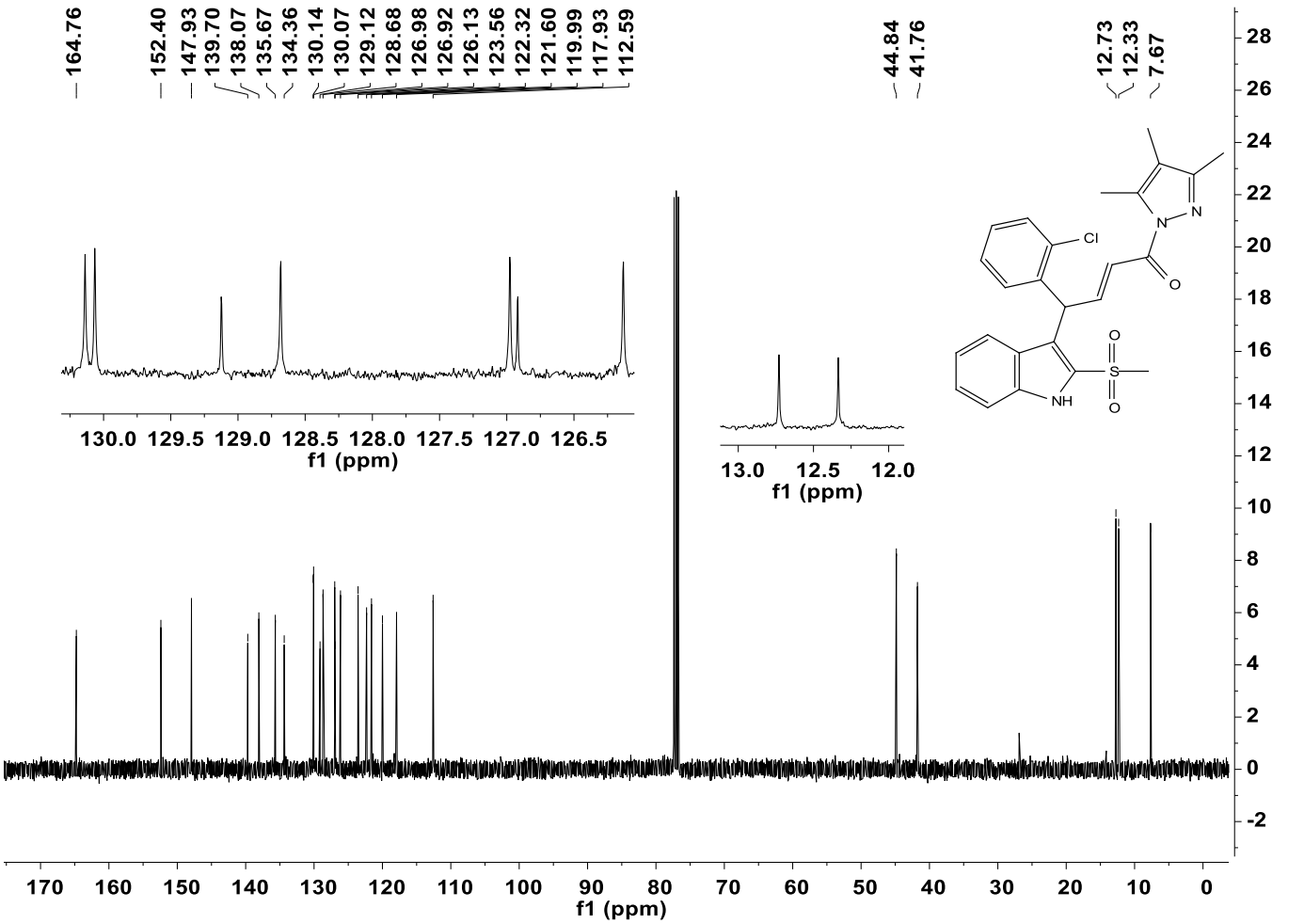

9.299 7.796 7.777 7.757 7.738 7.544 7.542 7.523 7.521 7.455 7.451 7.449 7.446 7.444 7.431 7.428 7.425 7.423 7.419 7.416 7.381 7.377 7.330 7.328 7.313 7.310 7.292 7.259 7.136 7.133 7.117 7.114 7.084 7.082 7.067 7.064 7.061 6.999 6.197 6.178 3.078 3.078 2.475 2.473 2.114 1.880 1.878
1.00
7.79 7.77 7.75 7.73
f1 (ppm)
1.00 3.00 1.00 1.00
7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
1.00
6.20 6.18 6.16
f1 (ppm)
1.00 1.00 3.00 1.00 1.00 3.00 1.00 3.00 3.00 3.00 3.00
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
f1 (ppm)
1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100
F
N
N
O
NH
S
O
O


164.786 161.944 159.482 152.412 147.348 139.666 135.846 129.694 129.657 129.087 129.003 128.842 127.869 127.733 126.306 126.124 124.215 124.180 123.630 122.339 121.448 120.203 117.923 115.871 115.655 112.571
45.146
38.191
12.715 12.312 7.670
130.0 129.5 129.0 128.5 128.0
f1 (ppm)
124.5 124.2 123.9
f1 (ppm)
116.0 115.5
f1 (ppm)
13.0 12.5 12.0
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2
F
N
N
O
NH
S
O
O

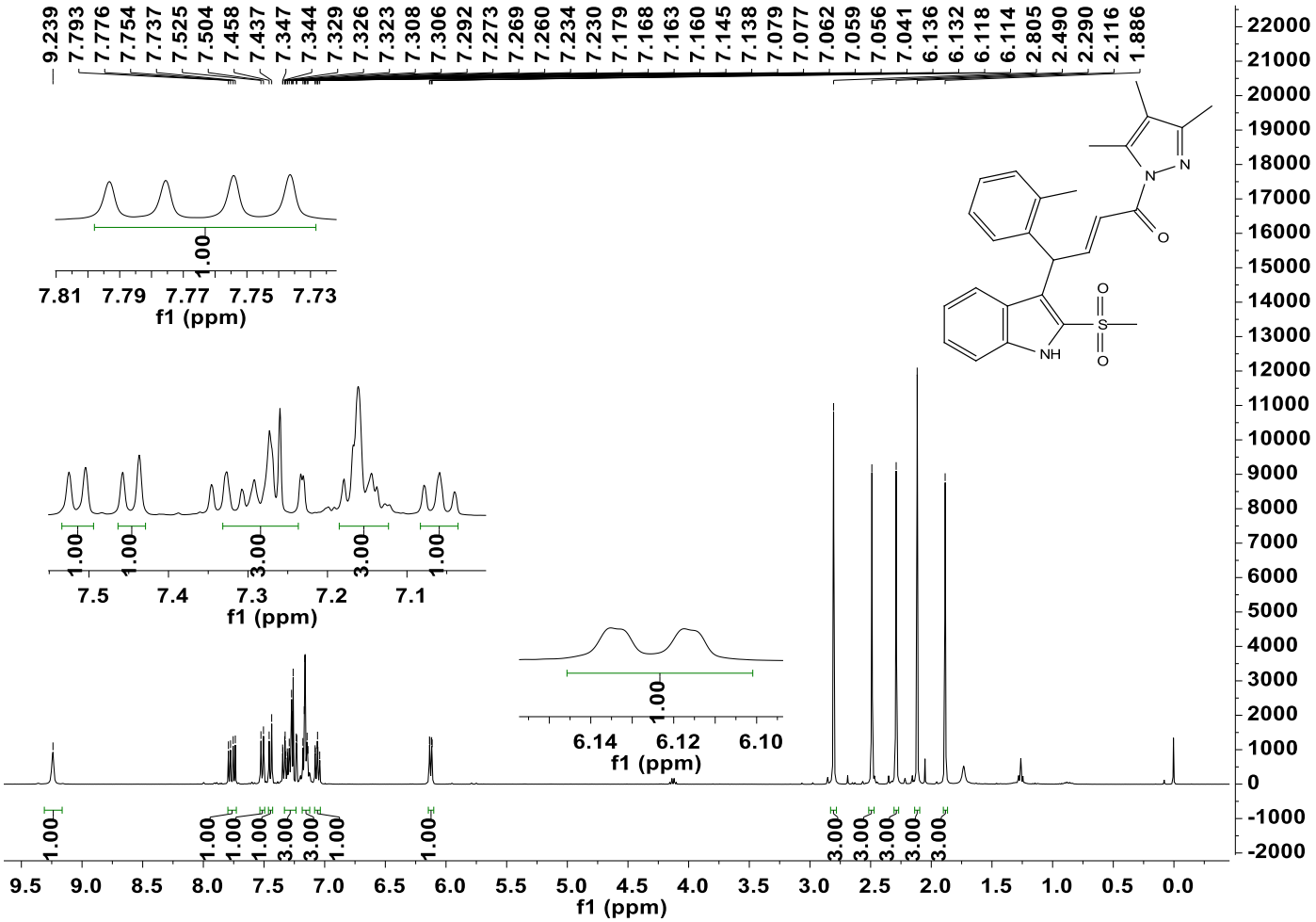

-114.529
4000
3500
3000
2500
2000
1500
1000
500
0
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)
F
N
N
O
O
S
O
NH

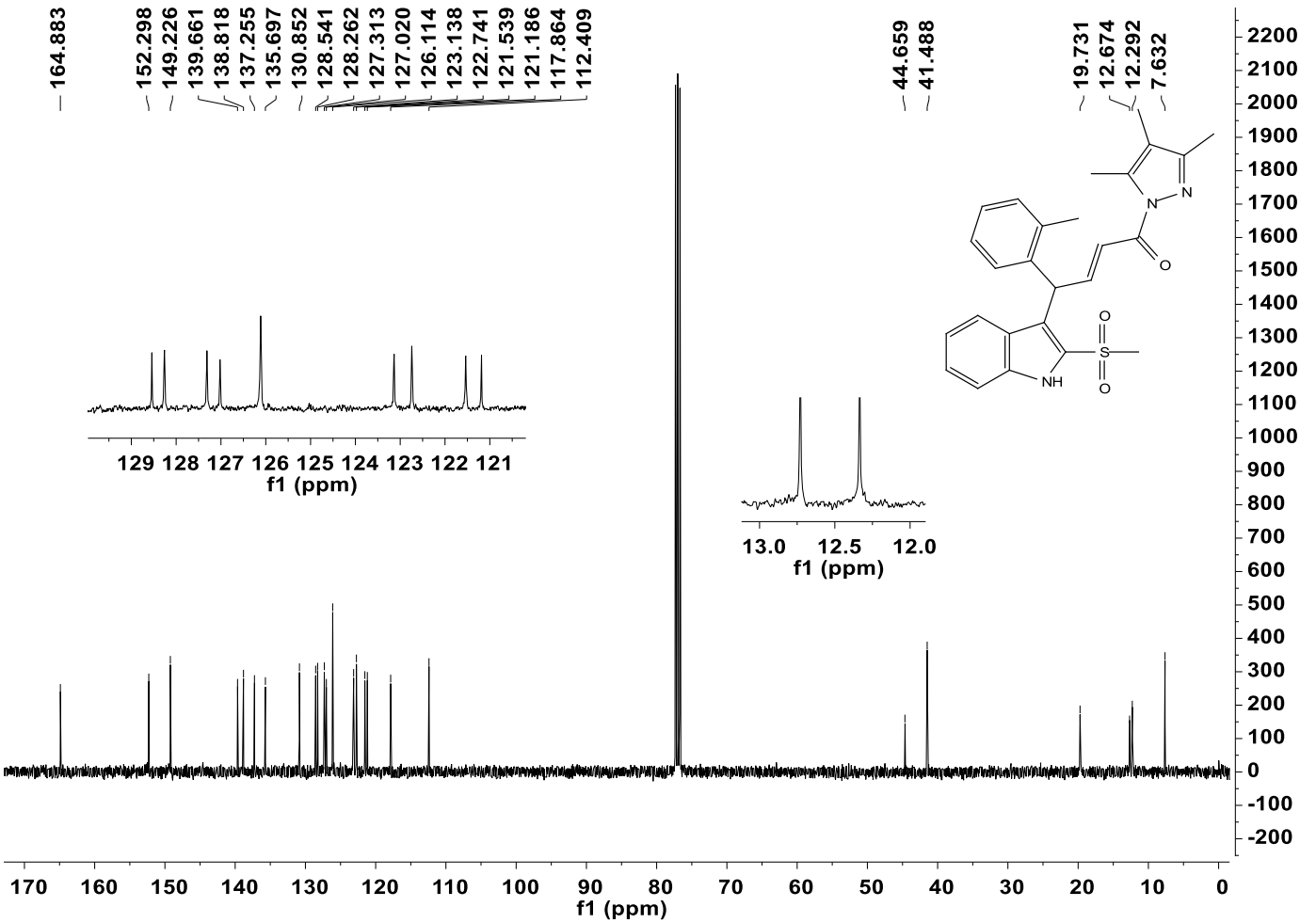
4ca


9.358 7.729 7.711 7.690 7.672 7.518 7.516 7.497 7.495 7.448 7.429 7.427 7.424 7.420 7.409 7.397 7.372 7.361 7.349 7.332 7.329 7.321 7.317 7.314 7.311 7.282 7.278 7.242 7.213 7.211 7.206 7.201 7.200 7.194 7.189 7.084 7.081 7.067 7.064 6.268 6.264 6.250 6.246 2.901 2.462 2.100 1.864
Cl
O
N
N
O
S
O
O
NH
1.00
7.74 7.72 7.70 7.68 7.66
f1 (ppm)
1.00 2.00 3.00 2.00 1.00
7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.00
6.32 6.28 6.24 6.20
f1 (ppm)
1.00 1.00 1.00 2.00 3.00 2.00 1.00 1.00 3.00 3.00 3.00 3.00
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 -0.5
f1 (ppm)
4000 3500 3000 2500 2000 1500 1000 500 0

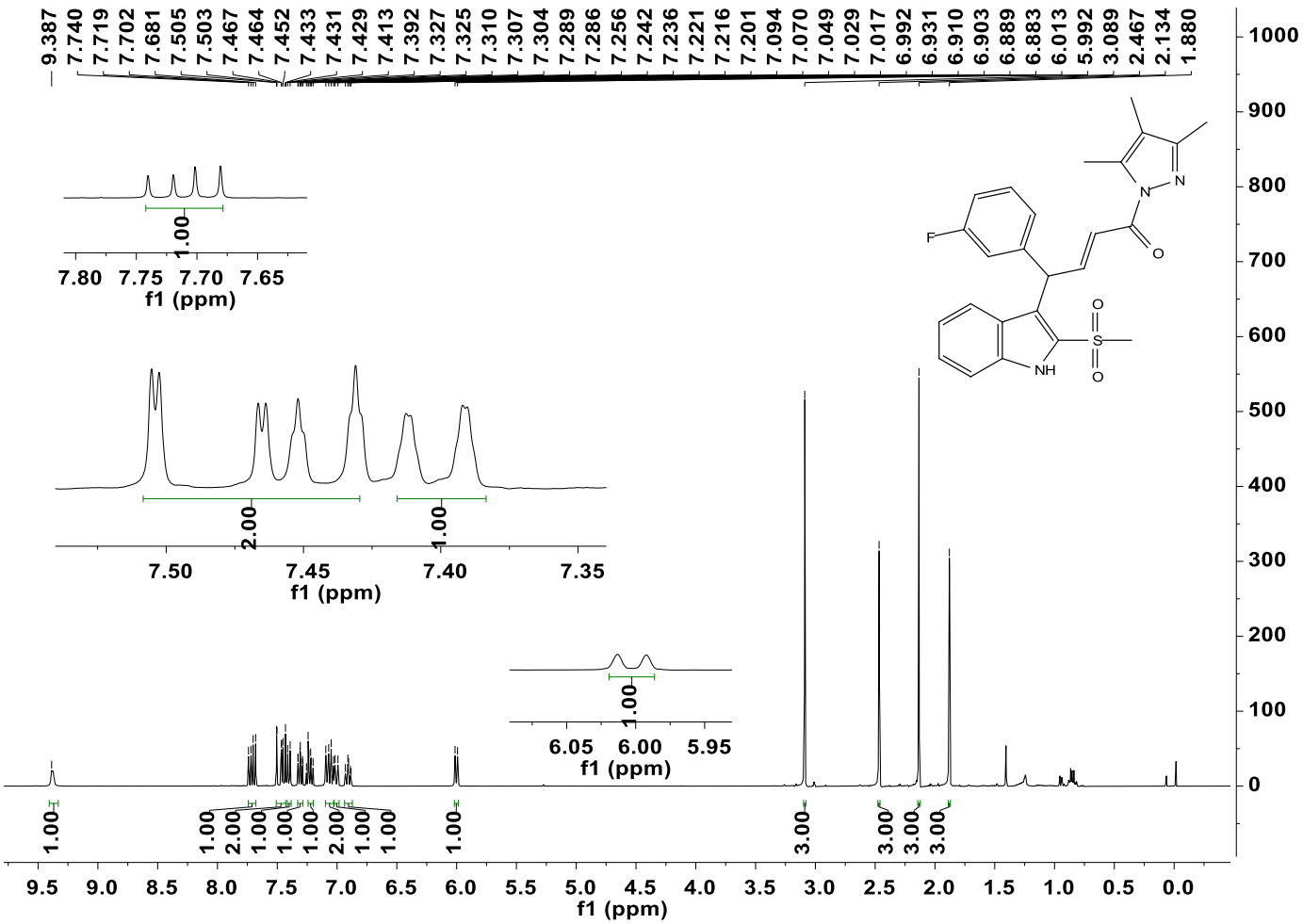

164.76 152.40 147.93 139.70 138.07 135.67 134.36 130.14 130.07 129.12 128.68 126.98 126.92 126.13 123.56 122.32 121.60 119.99 117.93 112.59
44.84 41.76
12.73 12.33 7.67
Cl
O
N
N
O
S
O
O
NH
130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
13.0 12.5 12.0
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2

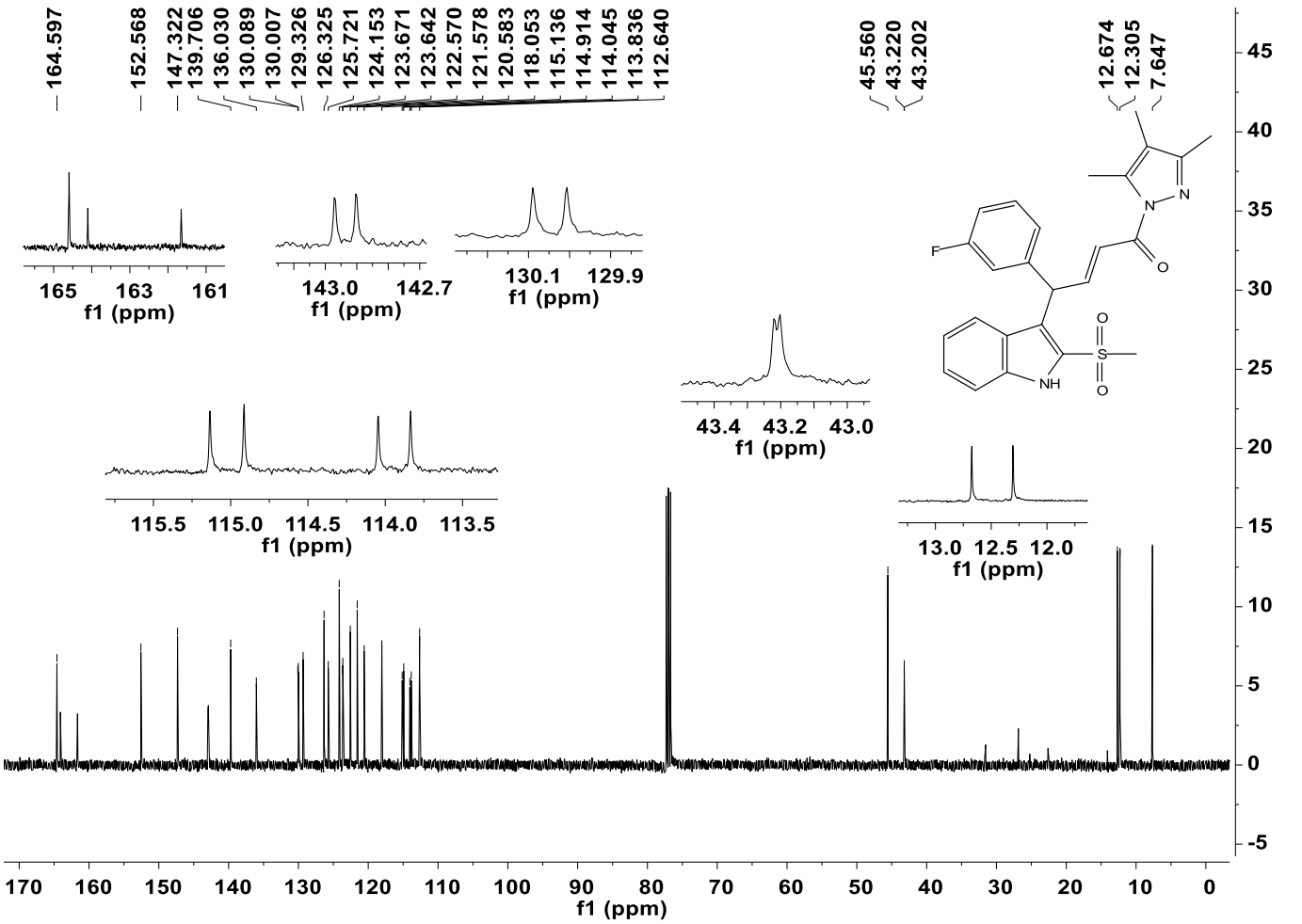
4da


9.239
7.793
7.776
7.754
7.737
7.525
7.504
7.458
7.437
7.347
7.344
7.329
7.326
7.323
7.308
7.306
7.292
7.273
7.269
7.260
7.234
7.230
7.179
7.168
7.163
7.160
7.145
7.138
7.079
7.077
7.062
7.059
7.056
7.041
6.136
6.132
6.118
6.114
2.805
2.490
2.290
2.116
1.886
f1 (ppm)


164.883
152.298
149.226
139.661
138.818
137.255
135.697
130.852
128.541
128.262
127.313
127.020
126.114
123.138
122.741
121.539
121.186
117.864
112.409
44.659
41.488
19.731
12.674
12.292
7.632
f1 (ppm)

4ea


9.387
7.740
7.719
7.702
7.681
7.505
7.503
7.467
7.464
7.452
7.433
7.431
7.429
7.413
7.392
7.327
7.325
7.310
7.307
7.304
7.289
7.286
7.256
7.242
7.236
7.221
7.216
7.201
7.094
7.070
7.049
7.029
7.017
6.992
6.931
6.910
6.903
6.889
6.883
6.013
5.992
3.089
2.467
2.134
1.880
1.00
7.80 7.75 7.70 7.65
f1 (ppm)
2.00
1.00
7.50 7.45 7.40 7.35
f1 (ppm)
1.00
6.05 6.00 5.95
f1 (ppm)
1.00 1.00 2.00 1.00 1.00 2.00 1.00 1.00 1.00 3.00 3.00 3.00 3.00
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
f1 (ppm)
F
N
N
O
O
S
O
O
NH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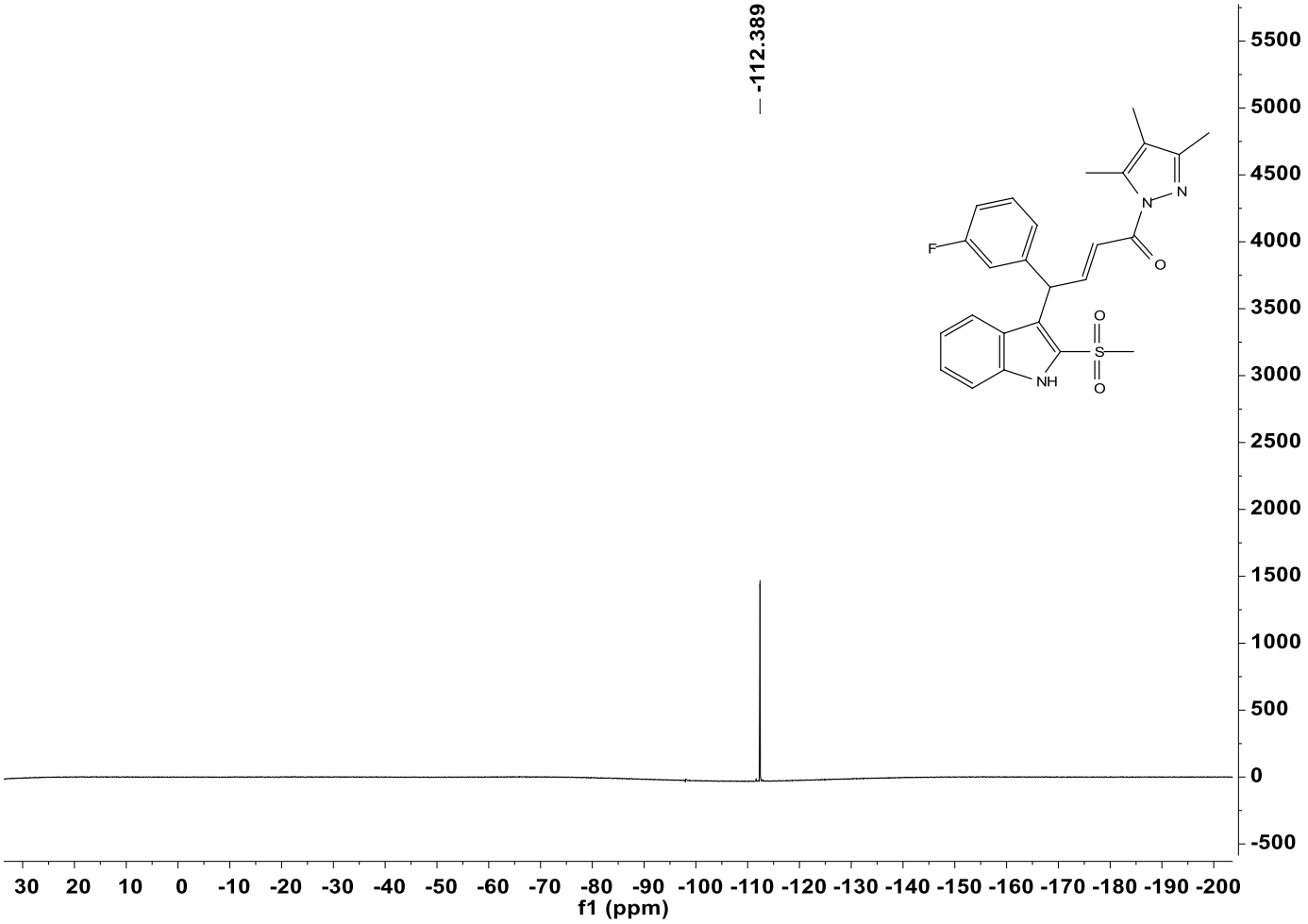
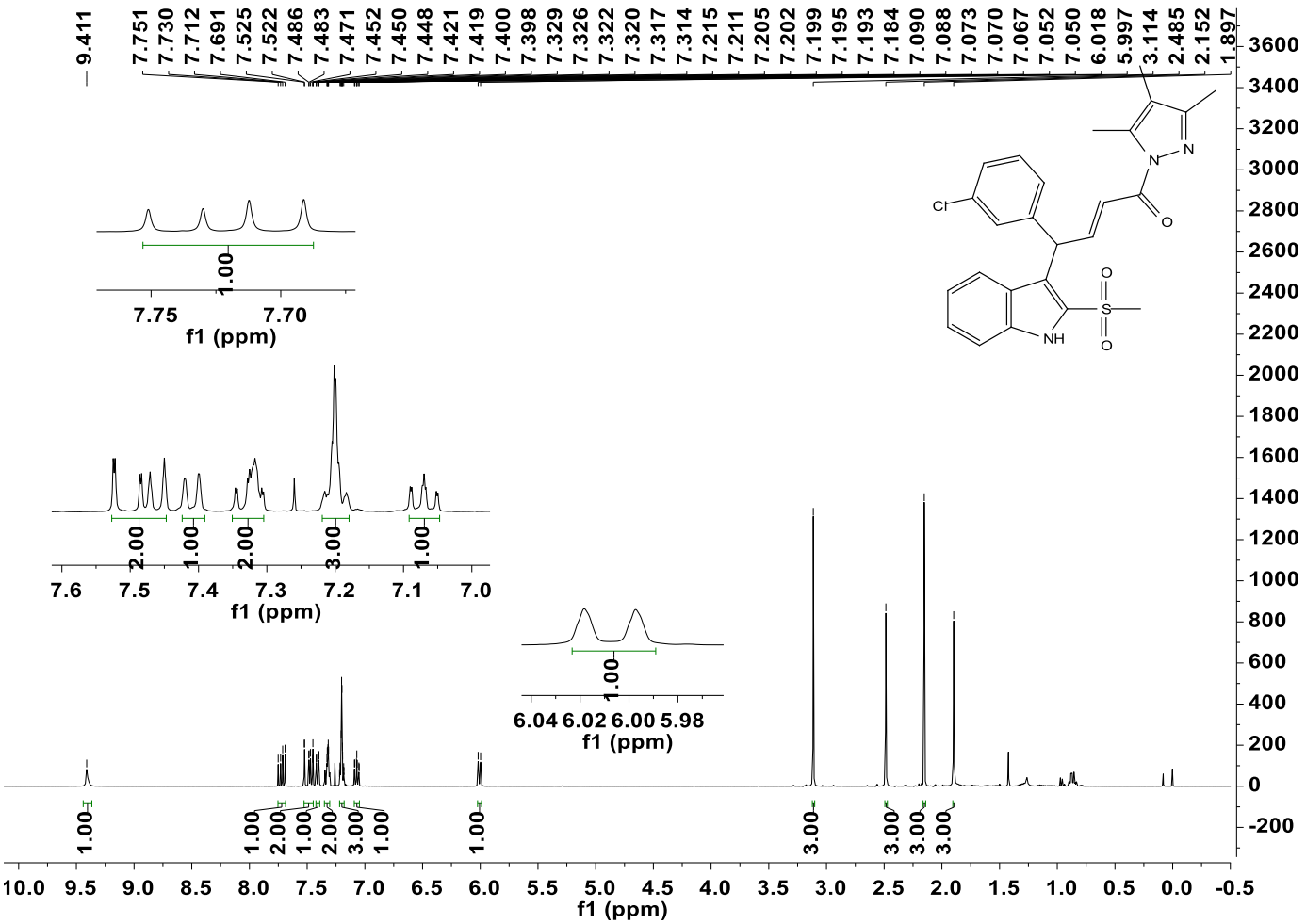
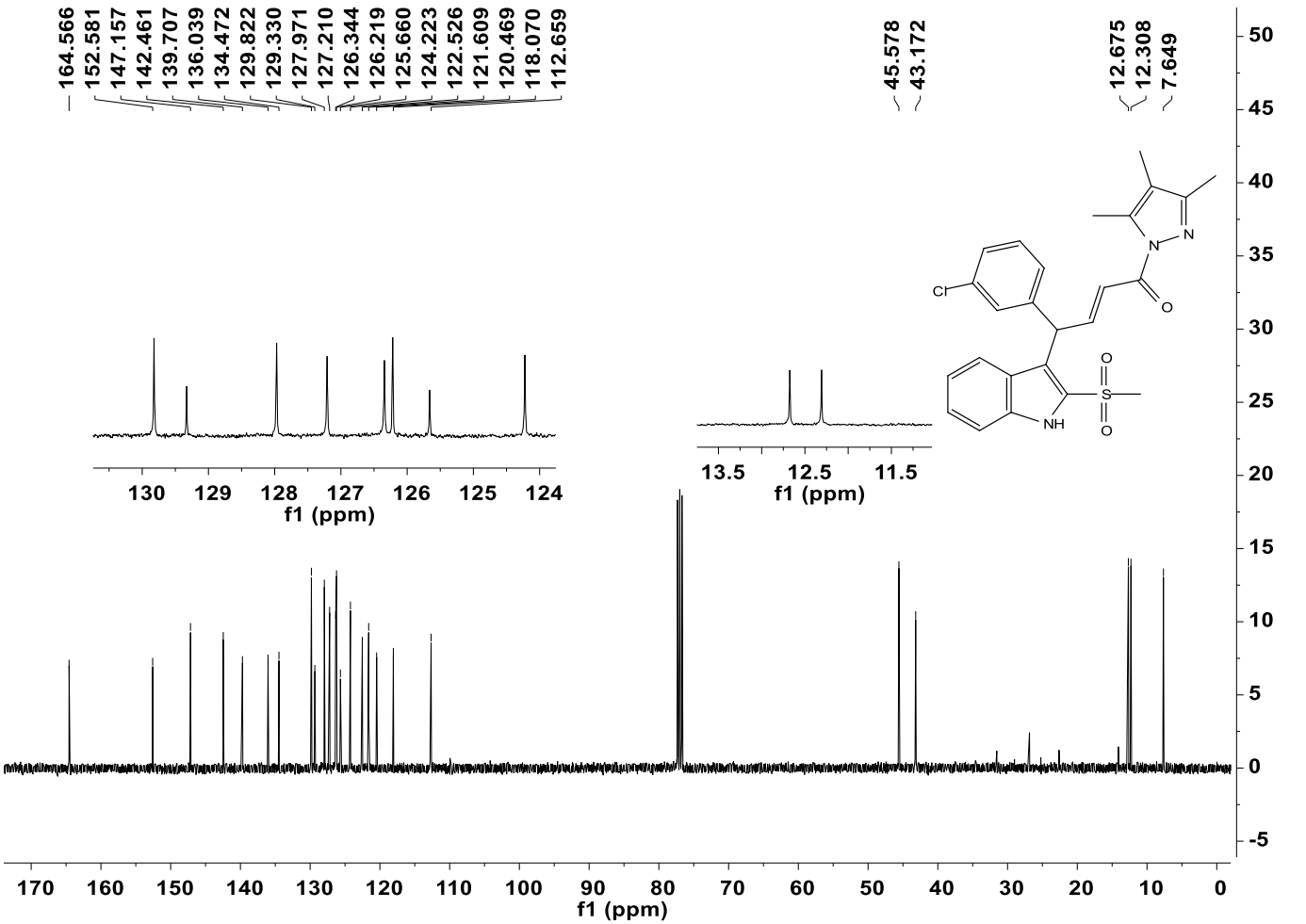
152.568
147.322
139.706
136.030
130.089
130.007
129.326
126.325
125.721
124.153
123.671
123.642
122.570
121.578
120.583
118.053
115.136
114.914
114.045
113.836
112.640
45.560
43.220
43.202
12.674
12.305
7.647
165 163 161
f1 (ppm)
143.0 142.7
f1 (ppm)
130.1 129.9
f1 (ppm)
43.4 43.2 43.0
f1 (ppm)
115.5 115.0 114.5 114.0 113.5
f1 (ppm)
13.0 12.5 12.0
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
F
N
N
O
O
S
O
O
NH

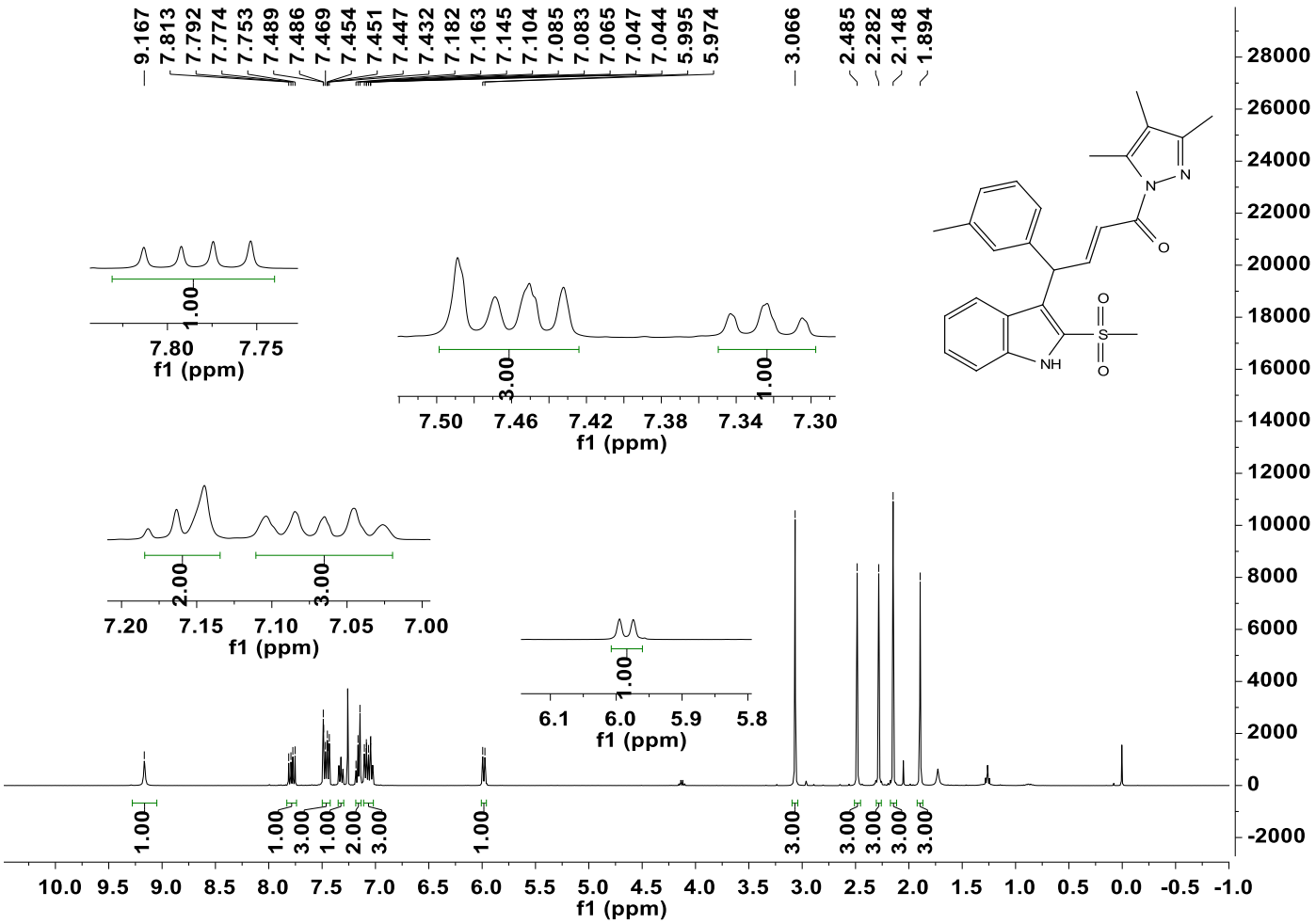

-112.389
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)
F
N
N
O
O
S
O
NH

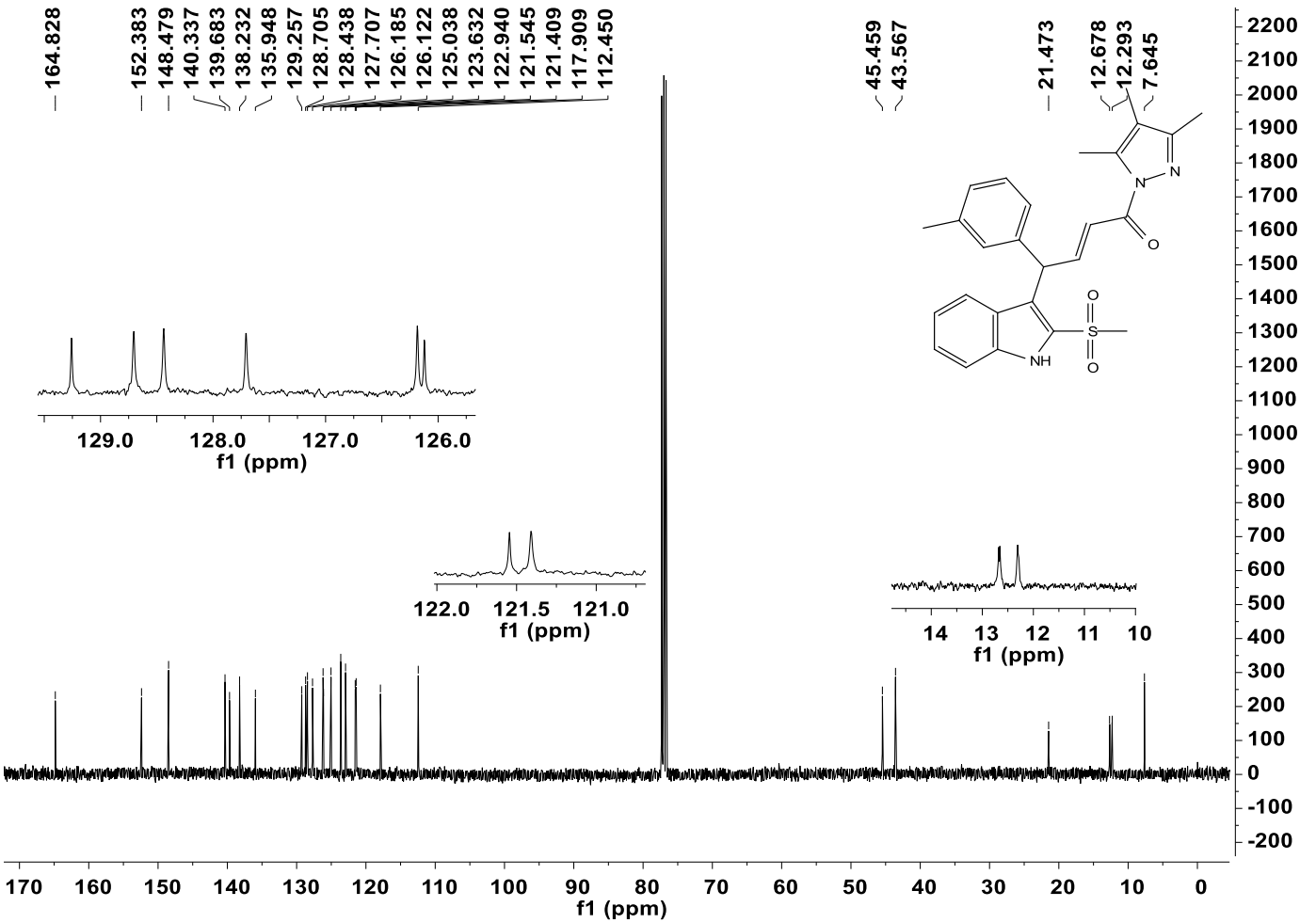
4fa


9.411
7.751
7.730
7.712
7.691
7.525
7.522
7.486
7.483
7.471
7.452
7.450
7.448
7.421
7.419
7.400
7.398
7.329
7.326
7.322
7.320
7.317
7.314
7.215
7.211
7.205
7.202
7.199
7.195
7.193
7.184
7.090
7.088
7.073
7.070
7.067
7.052
7.050
6.018
5.997
3.114
2.485
2.152
1.897
1.00
7.75
7.70
f1 (ppm)
2.00
1.00
2.00
3.00
1.00
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
1.00
6.04 6.02 6.00 5.98
f1 (ppm)
1.00
1.00
2.00
1.00
2.00
3.00
1.00
1.00
3.00
3.00
3.00
3.00
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 -0.5
f1 (ppm)
Cl
N
N
O
NH
S
O
O

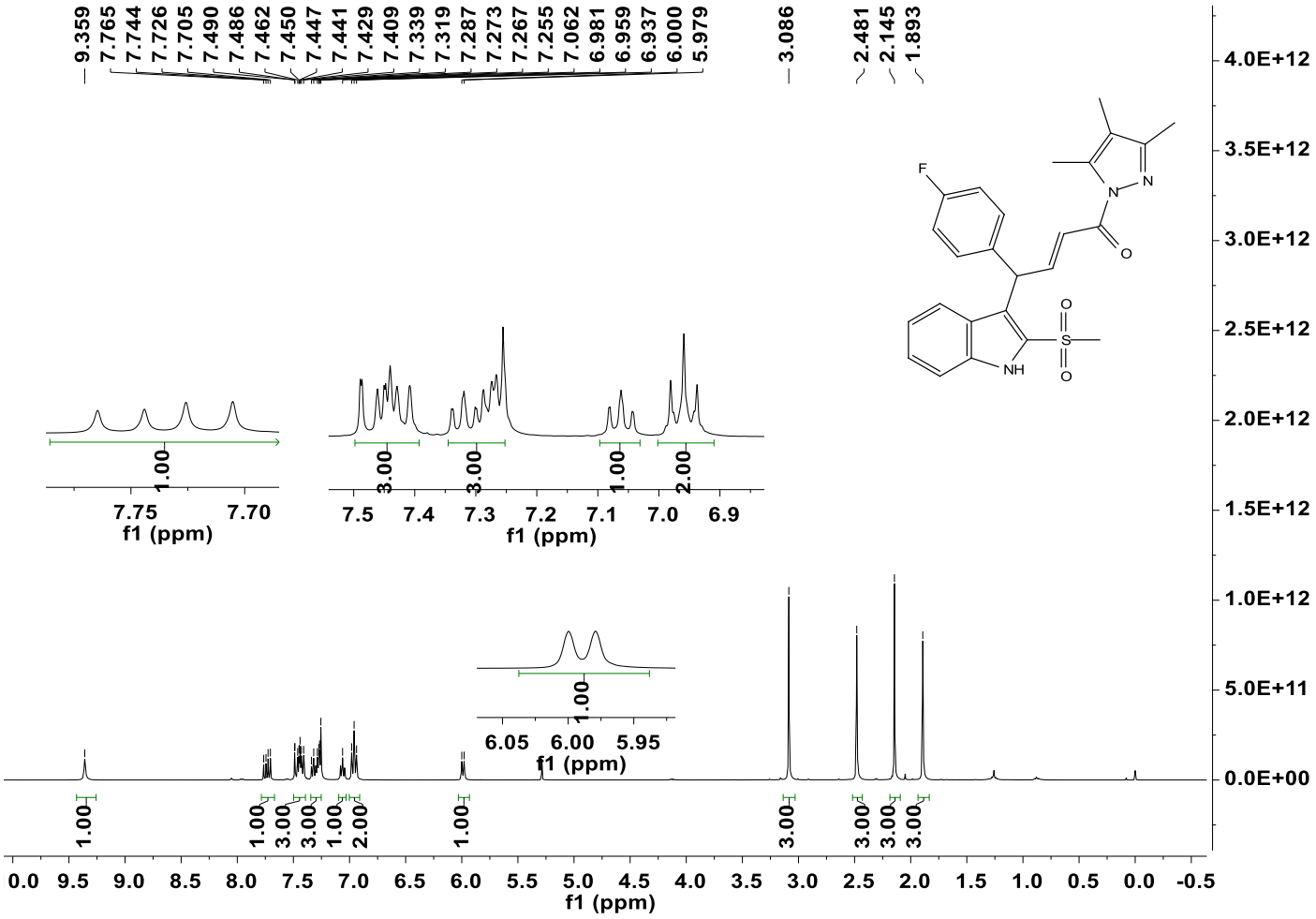

164.566
152.581
147.157
142.461
139.707
136.039
134.472
129.822
129.330
127.971
127.210
126.344
126.219
125.660
124.223
122.526
121.609
120.469
118.070
112.659
45.578
43.172
12.675
12.308
7.649
130
129
128
127
126
125
124
f1 (ppm)
13.5
12.5
11.5
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Cl
N
N
O
NH
S
O
O

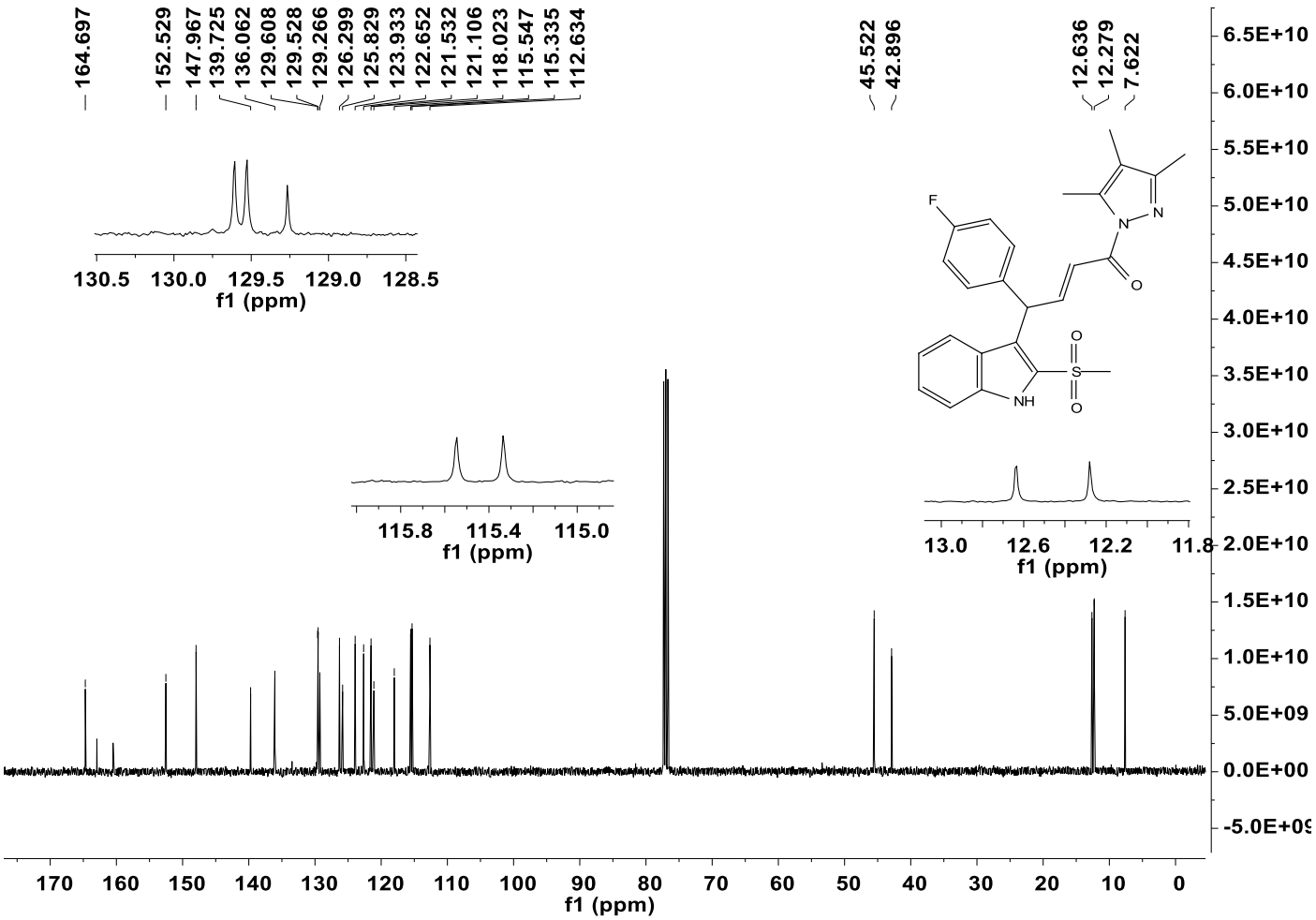
4ga

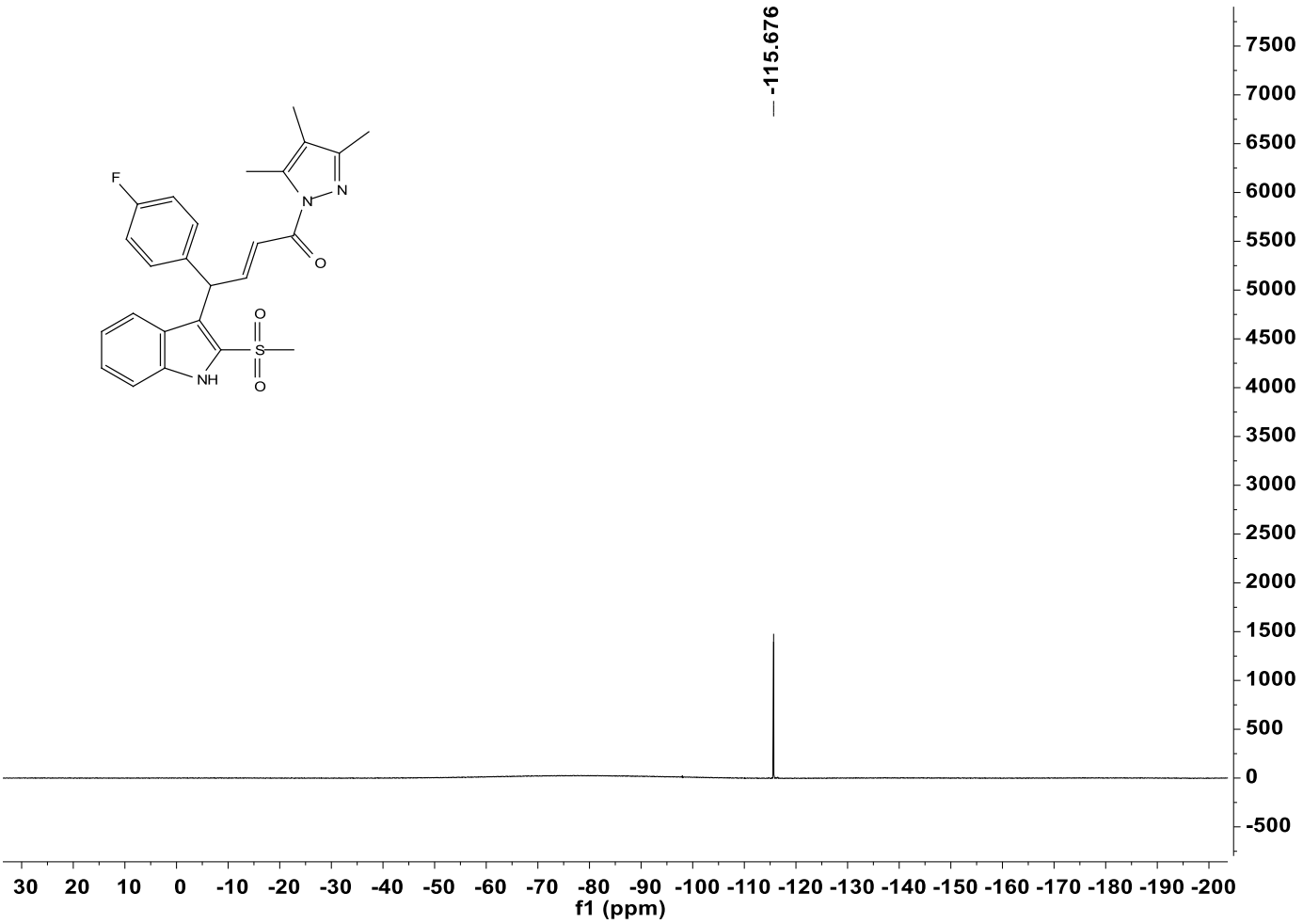

9.167
7.813
7.792
7.774
7.753
7.489
7.486
7.469
7.454
7.451
7.447
7.432
7.182
7.163
7.145
7.104
7.085
7.083
7.065
7.047
7.044
5.995
5.974
3.066
2.485
2.282
2.148
1.894
f1 (ppm)


164.828
152.383
148.479
140.337
139.683
138.232
135.948
129.257
128.705
128.438
127.707
126.185
126.122
125.038
123.632
122.940
121.545
121.409
117.909
112.450
45.459
43.567
21.473
12.678
12.293
7.645
f1 (ppm)

4ha


9.359
7.765
7.744
7.726
7.705
7.490
7.486
7.462
7.450
7.447
7.441
7.429
7.409
7.339
7.319
7.287
7.273
7.267
7.255
7.062
6.981
6.959
6.937
6.000
5.979
3.086
2.481
2.145
1.893
F
N
N
O
O
S
O
O
NH
1.00
7.75
7.70
f1 (ppm)
3.00
3.00
1.00
2.00
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
1.00
6.05
6.00
5.95
f1 (ppm)
1.00
1.00
3.00
3.00
1.00
2.00
1.00
3.00
3.00
3.00
3.00
0.0
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
-0.5
f1 (ppm)
4.0E+12
3.5E+12
3.0E+12
2.5E+12
2.0E+12
1.5E+12
1.0E+12
5.0E+11
0.0E+00


164.697
152.529
147.967
139.725
136.062
129.608
129.528
129.266
126.299
125.829
123.933
122.652
121.532
121.106
118.023
115.547
115.335
112.634
45.522
42.896
12.636
12.279
7.622
F
N
N
O
O
S
O
O
NH
130.5
130.0
129.5
129.0
128.5
f1 (ppm)
115.8
115.4
115.0
f1 (ppm)
13.0
12.6
12.2
11.8
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
6.5E+10
6.0E+10
5.5E+10
5.0E+10
4.5E+10
4.0E+10
3.5E+10
3.0E+10
2.5E+10
2.0E+10
1.5E+10
1.0E+10
5.0E+09
0.0E+00
-5.0E+09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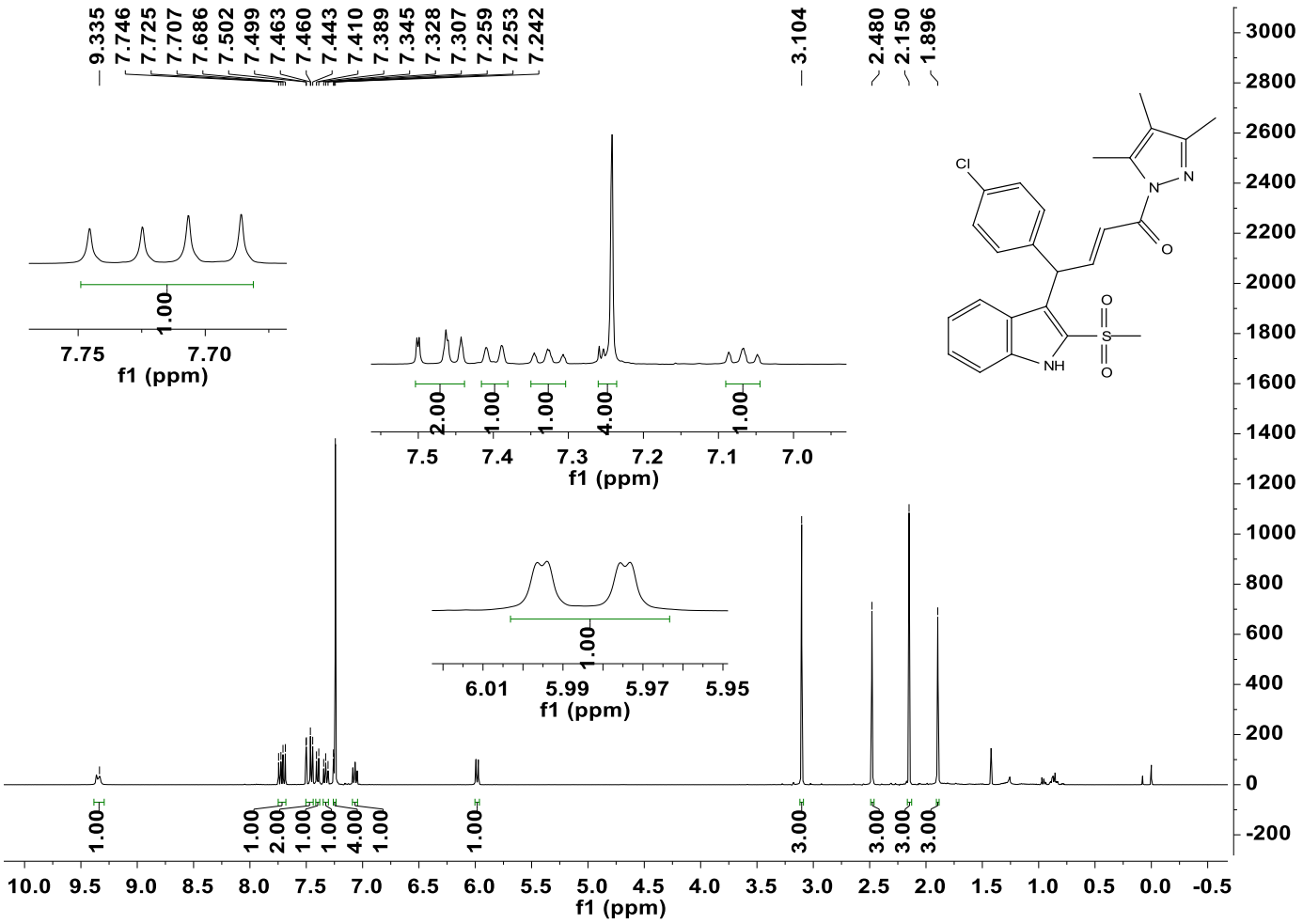
F
N
N
O
O
S
O
O
NH
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

4ia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7.499
7.463
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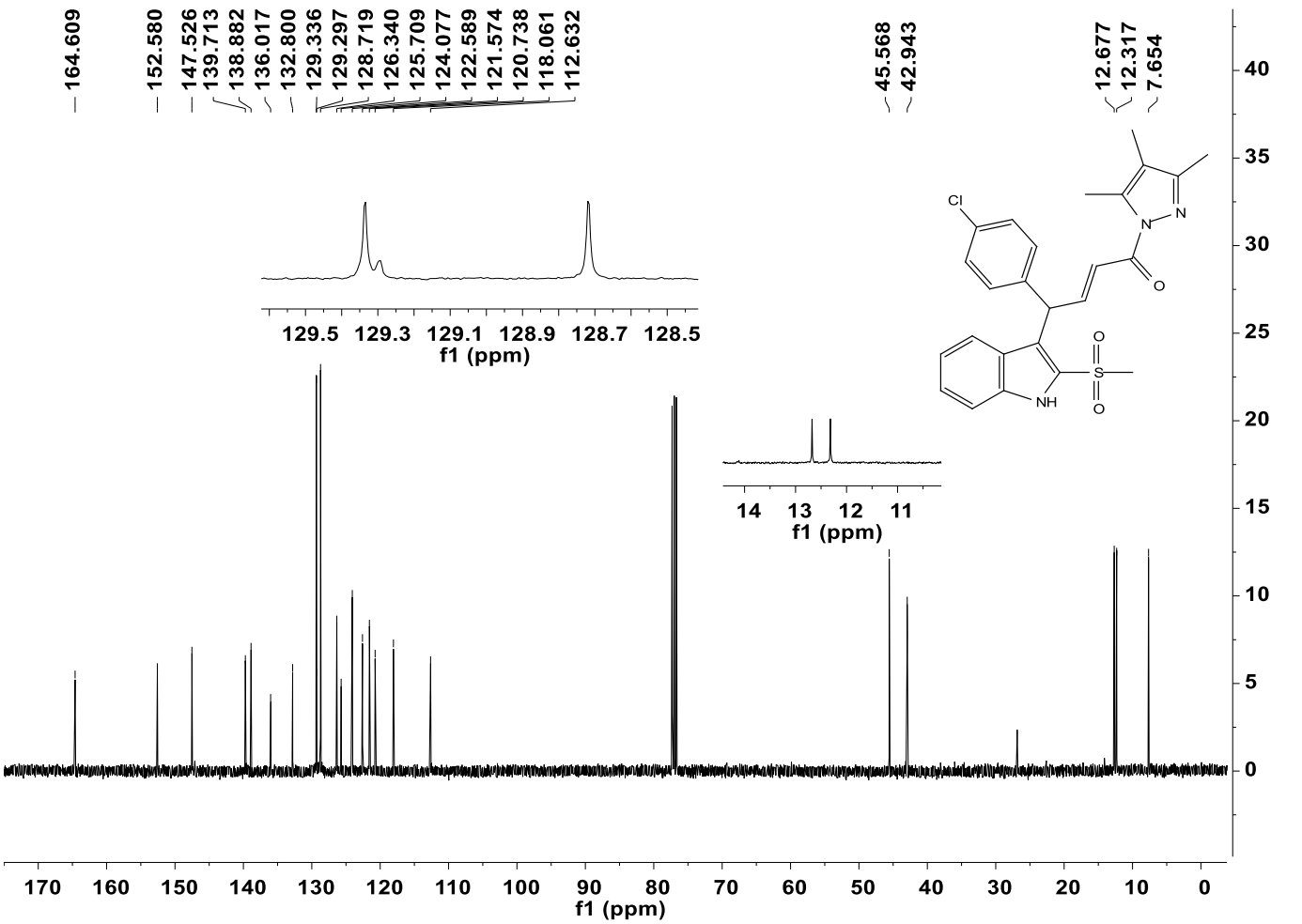
7.443
7.410
7.389
7.345
7.328
7.307
7.259
7.253
7.242
3.104
2.480
2.150
1.896
Cl
N
O
NH
S
f1 (ppm)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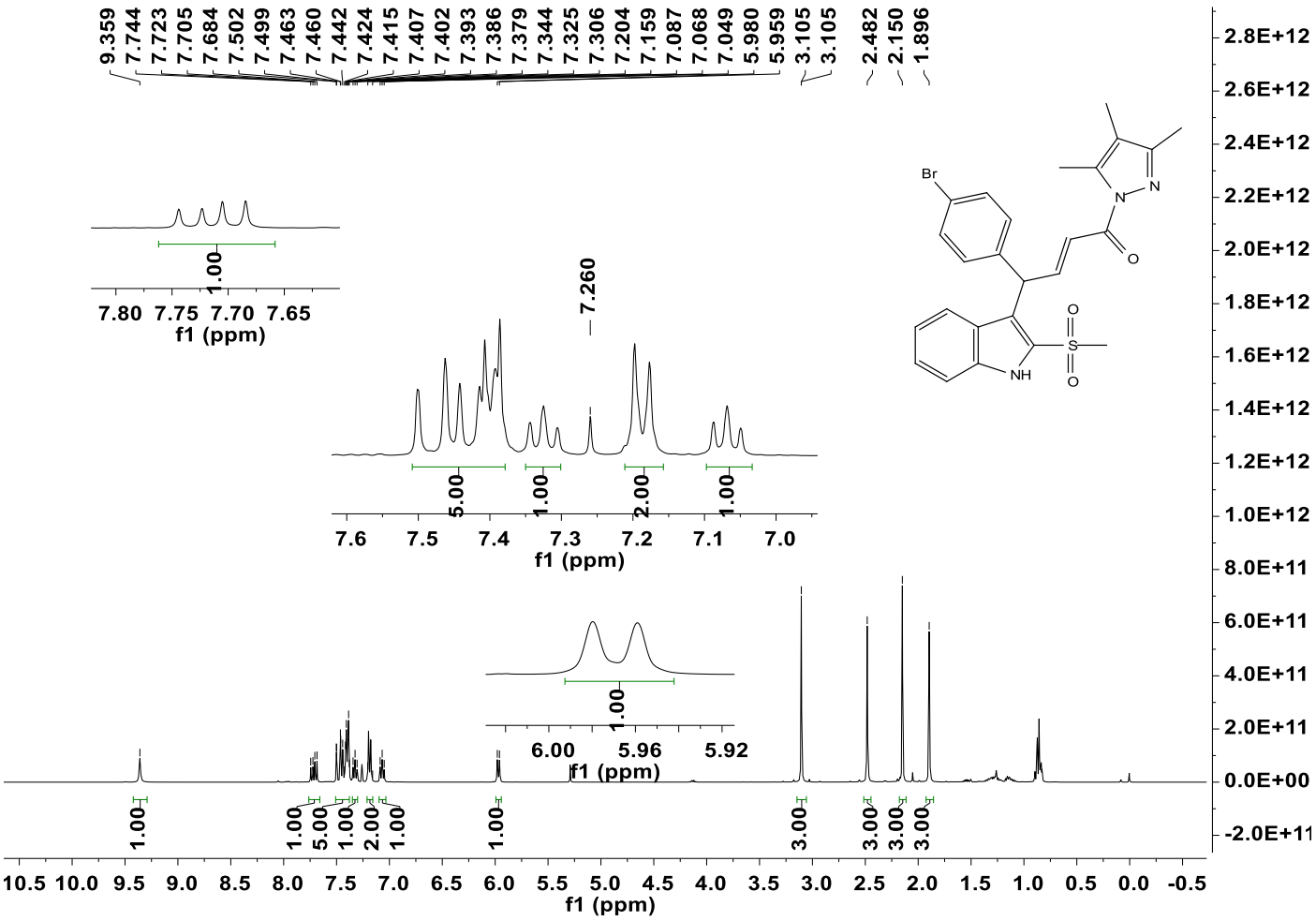
152.580
147.526
139.713
138.882
136.017
132.800
129.336
129.297
128.719
126.340
125.709
124.077
122.589
121.574
120.738
118.061
112.632
45.568
42.943
12.677
12.317
7.654
Cl
N
O
NH
S
f1 (ppm)

4ja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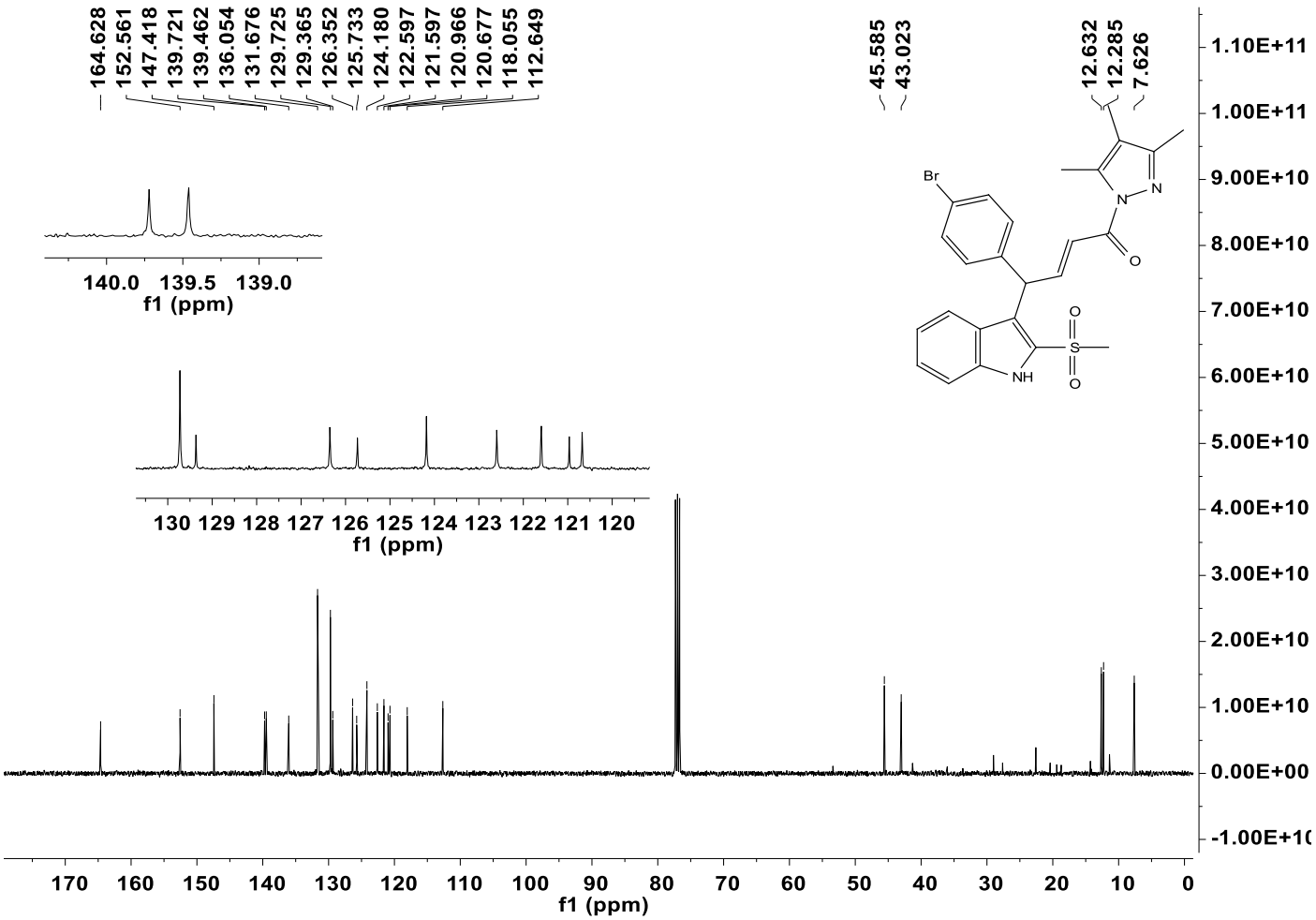
7.684
7.502
7.499
7.463
7.460
7.442
7.424
7.415
7.407
7.402
7.393
7.386
7.379
7.344
7.325
7.306
7.204
7.159
7.087
7.068
7.049
5.980
5.959
3.105
3.105
2.482
2.150
1.896
7.260
Br
N
N
O
O
S
O
NH
f1 (ppm)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147.418
139.721
139.462
136.054
131.676
129.725
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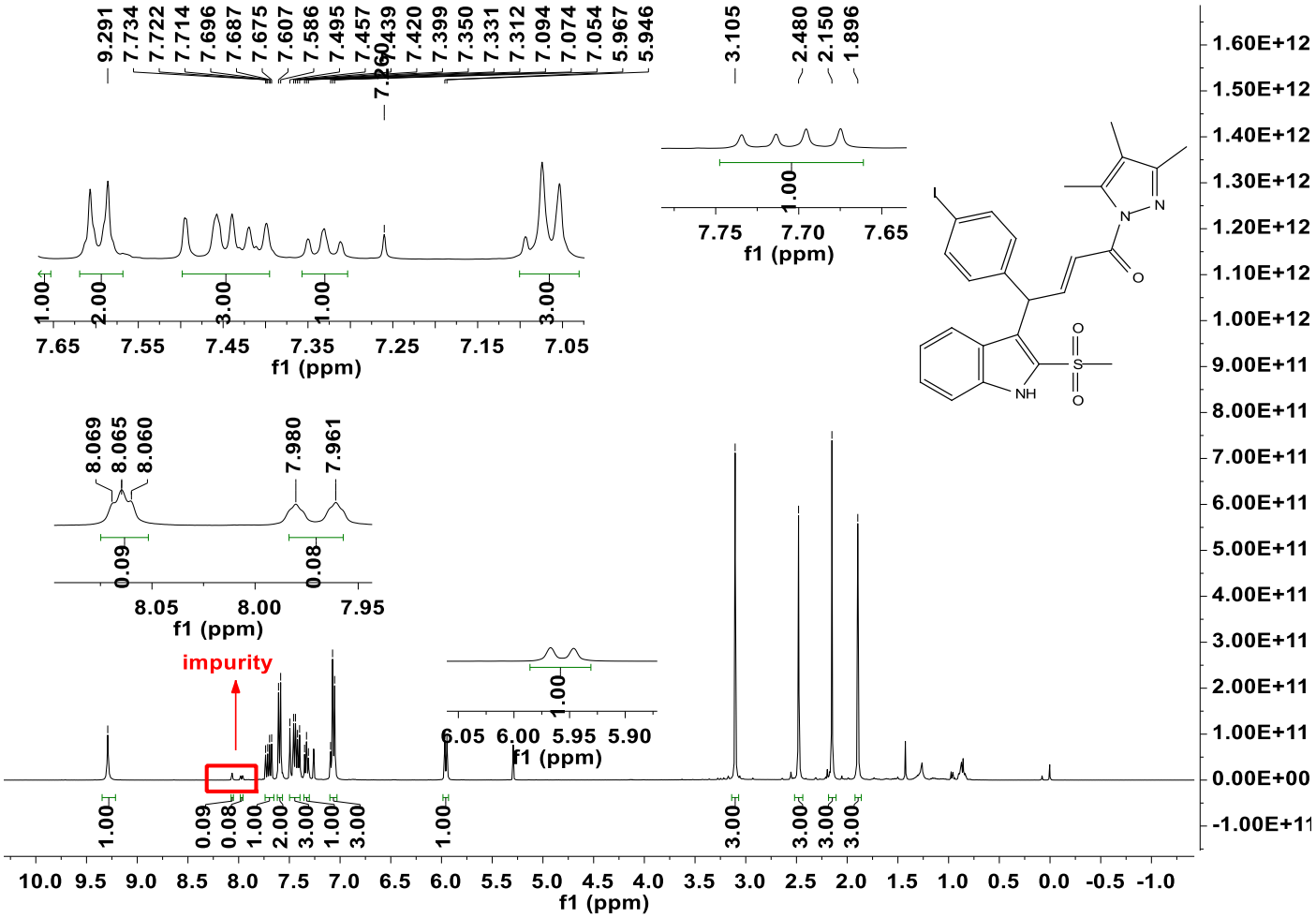
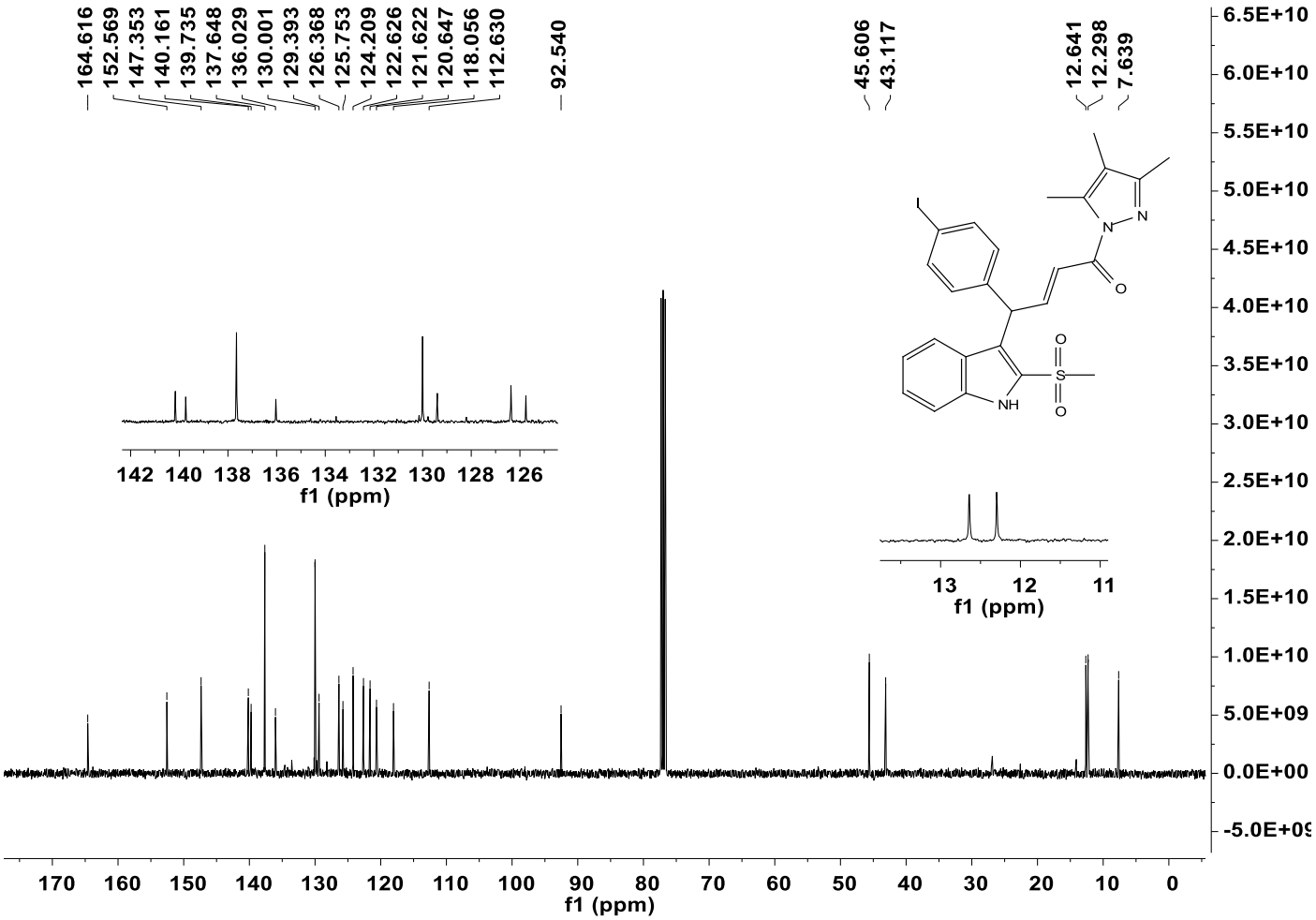
126.352
125.733
124.180
122.597
121.597
120.966
120.677
118.055
112.649
45.585
43.023
12.632
12.285
7.626
Br
N
N
O
O
S
O
NH
f1 (ppm)

4ka


9.291
7.734
7.722
7.714
7.696
7.687
7.675
7.607
7.586
7.495
7.457
7.439
7.420
7.399
7.350
7.331
7.312
7.094
7.074
7.054
5.967
5.946
7.260
3.105
2.480
2.150
1.896
f1 (ppm)
8.069
8.065
8.060
7.980
7.961
impurity
NH
O
S
N
I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147.353
140.161
139.735
137.648
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130.001
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126.368
125.753
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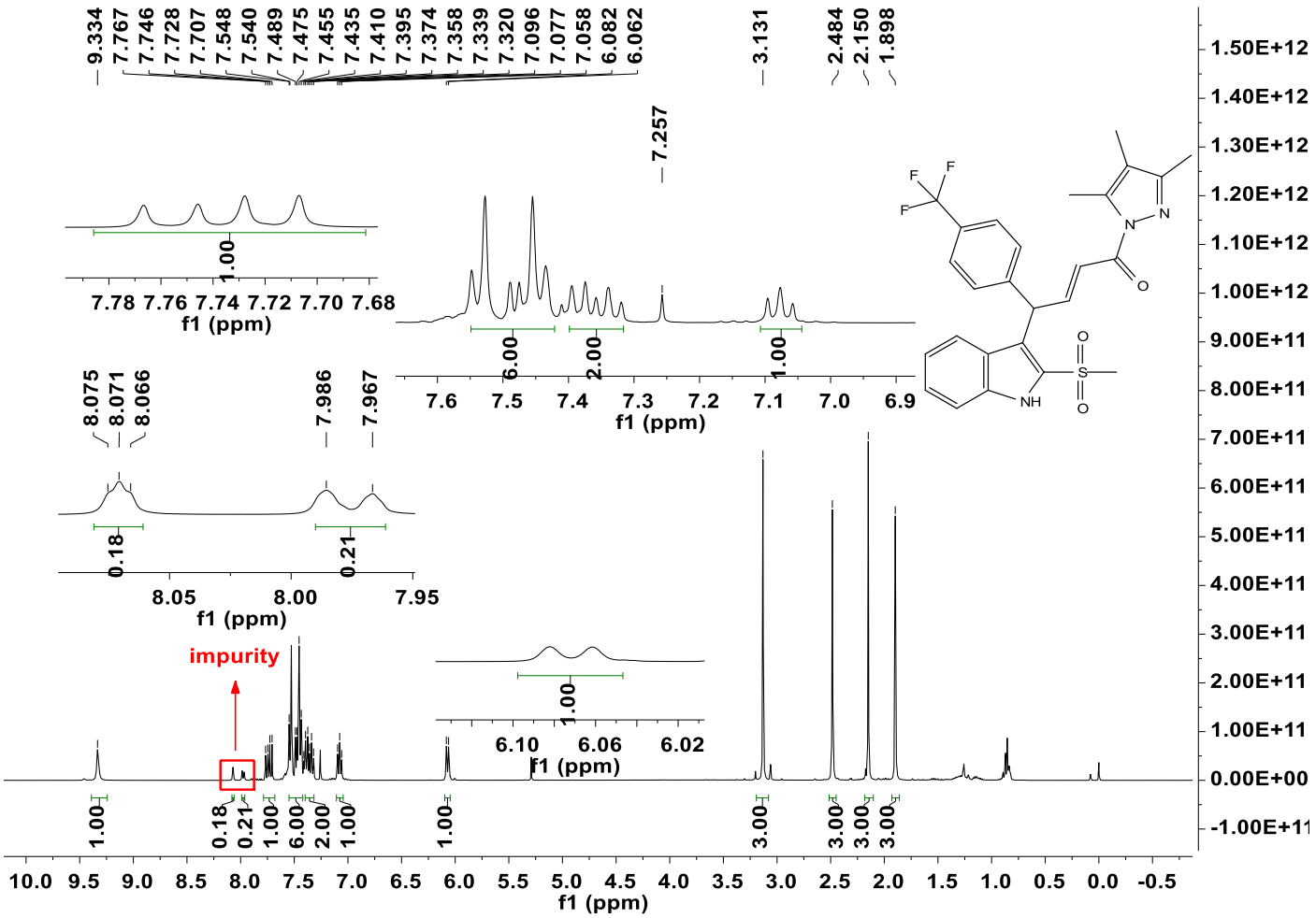
122.626
121.622
120.647
118.056
112.630
92.540
45.606
43.117
12.641
12.298
7.639
f1 (ppm)
NH
O
S
N
I

4la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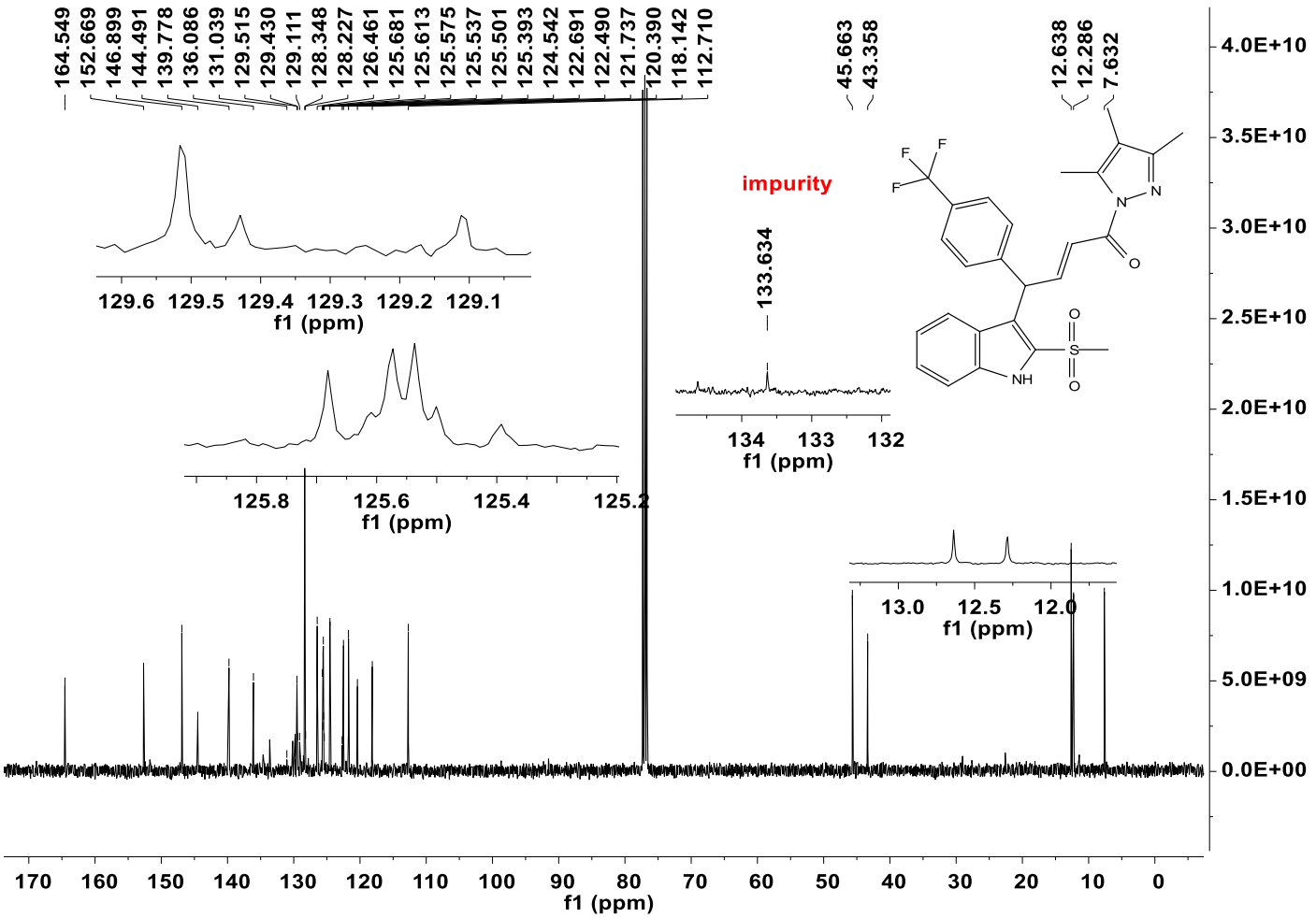
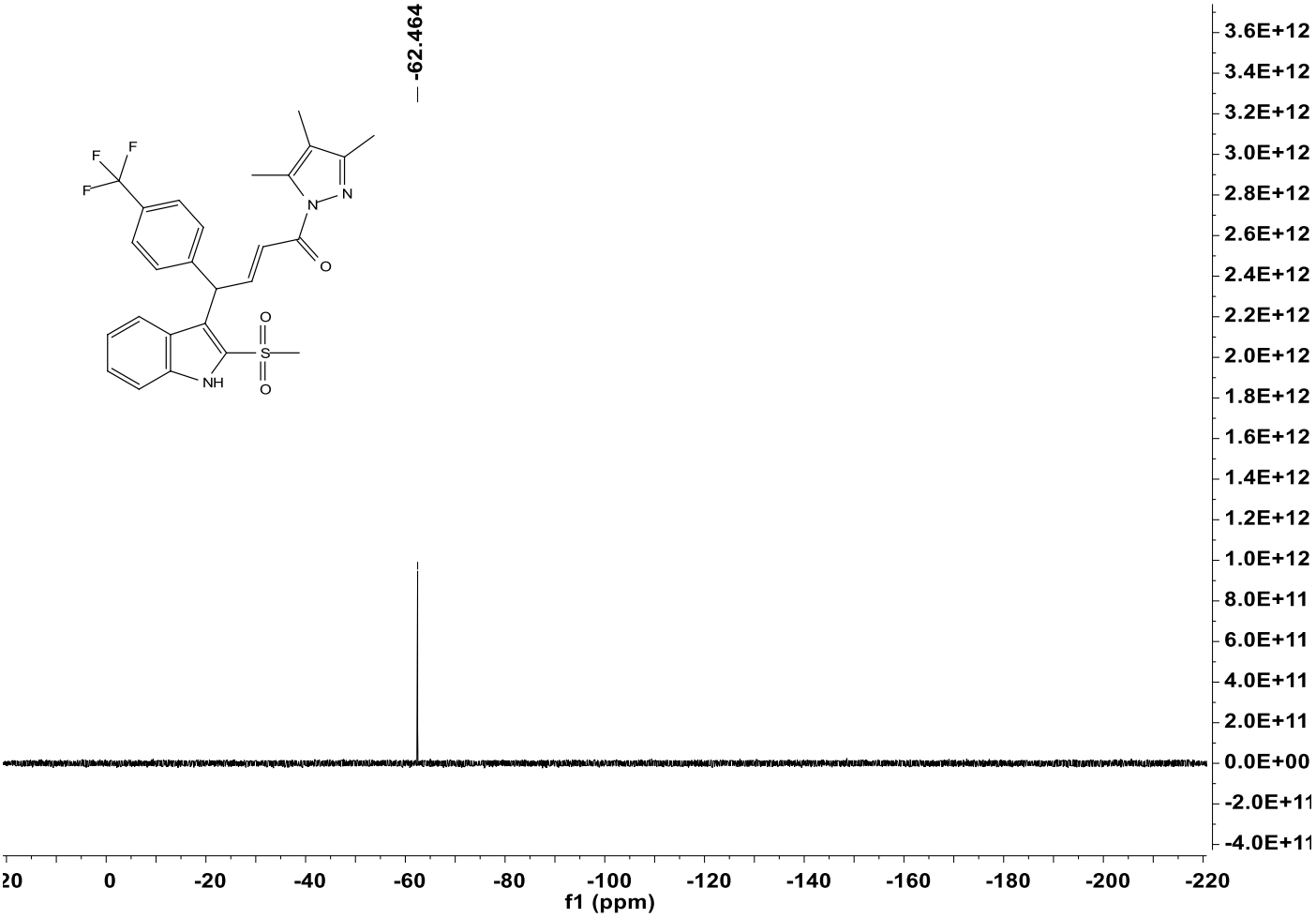
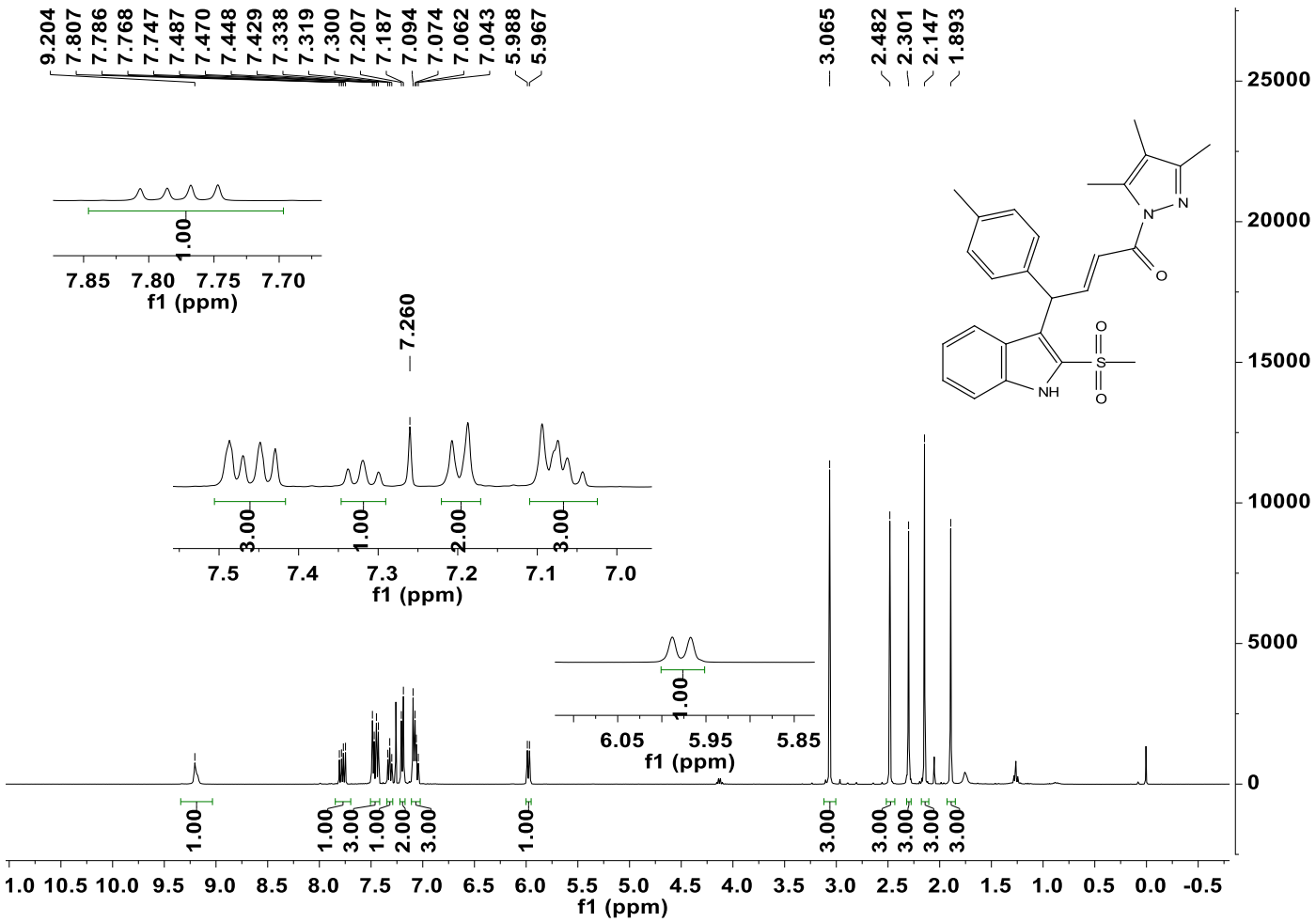
7.767
7.746
7.728
7.707
7.548
7.540
7.489
7.475
7.455
7.435
7.410
7.395
7.374
7.358
7.339
7.320
7.096
7.077
7.058
6.082
6.062
3.131
2.484
2.150
1.898
7.257
impurity
f1 (ppm)


164.549
152.669
146.899
144.491
139.778
136.086
131.039
129.515
129.430
129.111
128.348
128.227
126.461
125.681
125.613
125.575
125.537
125.501
125.393
124.542
122.691
122.490
121.737
120.390
118.142
112.710
45.663
43.358
12.638
12.286
7.632
impurity
133.634
f1 (ppm)


-62.464
F
F
F
N
N
O
O
S
O
NH
3.6E+12
3.4E+12
3.2E+12
3.0E+12
2.8E+12
2.6E+12
2.4E+12
2.2E+12
2.0E+12
1.8E+12
1.6E+12
1.4E+12
1.2E+12
1.0E+12
8.0E+11
6.0E+11
4.0E+11
2.0E+11
0.0E+00
-2.0E+11
-4.0E+11
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

4ma


9.204
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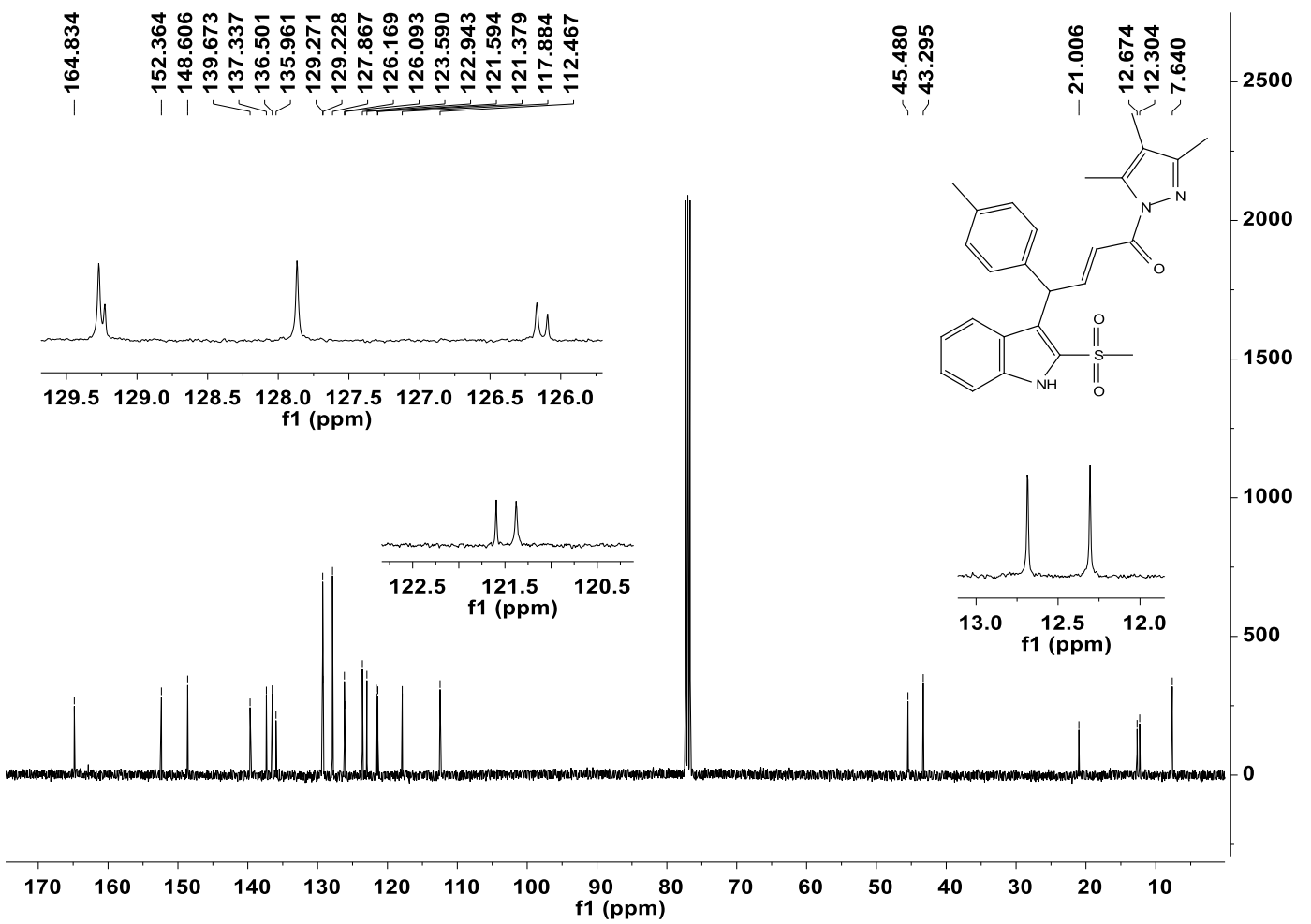
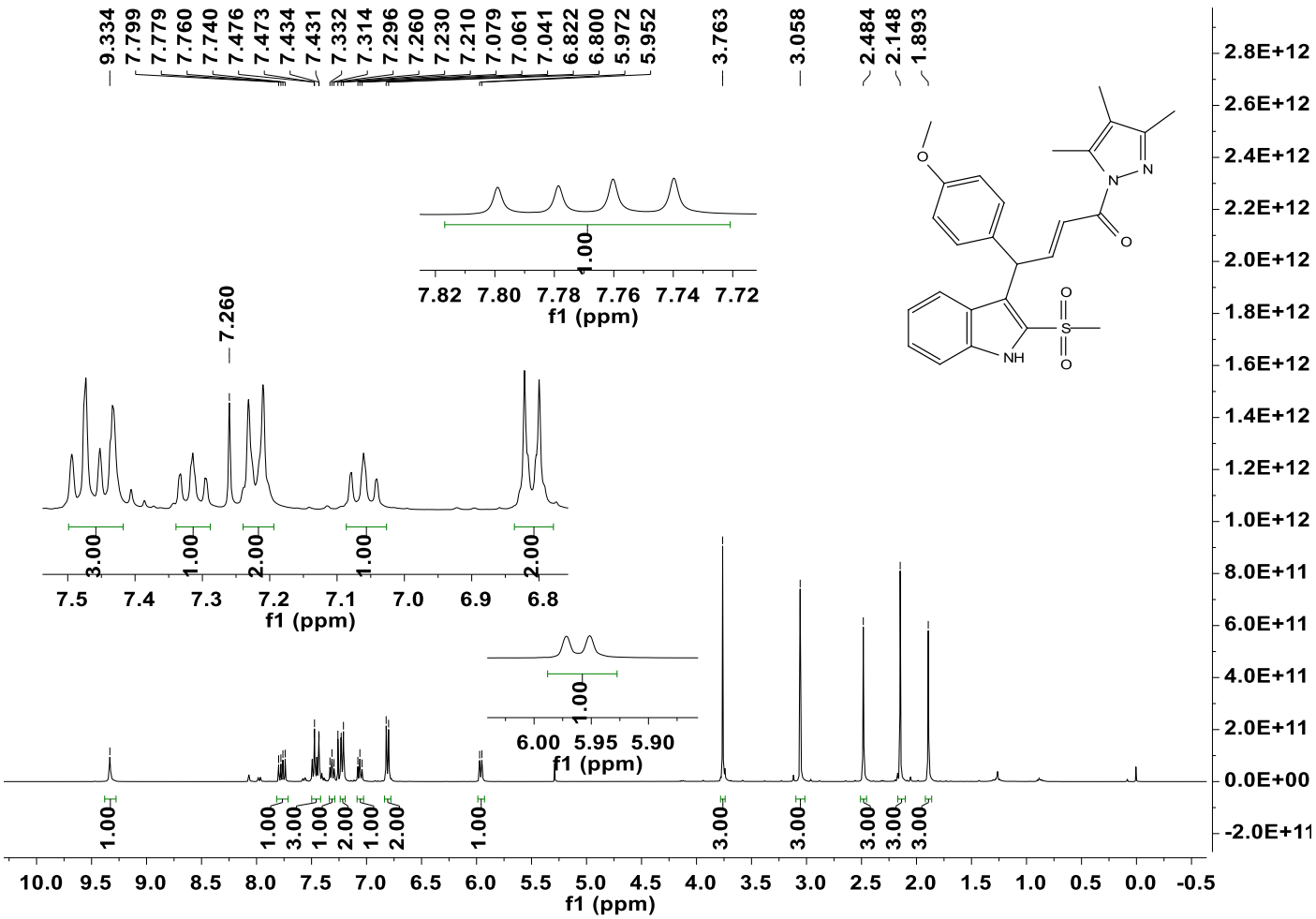
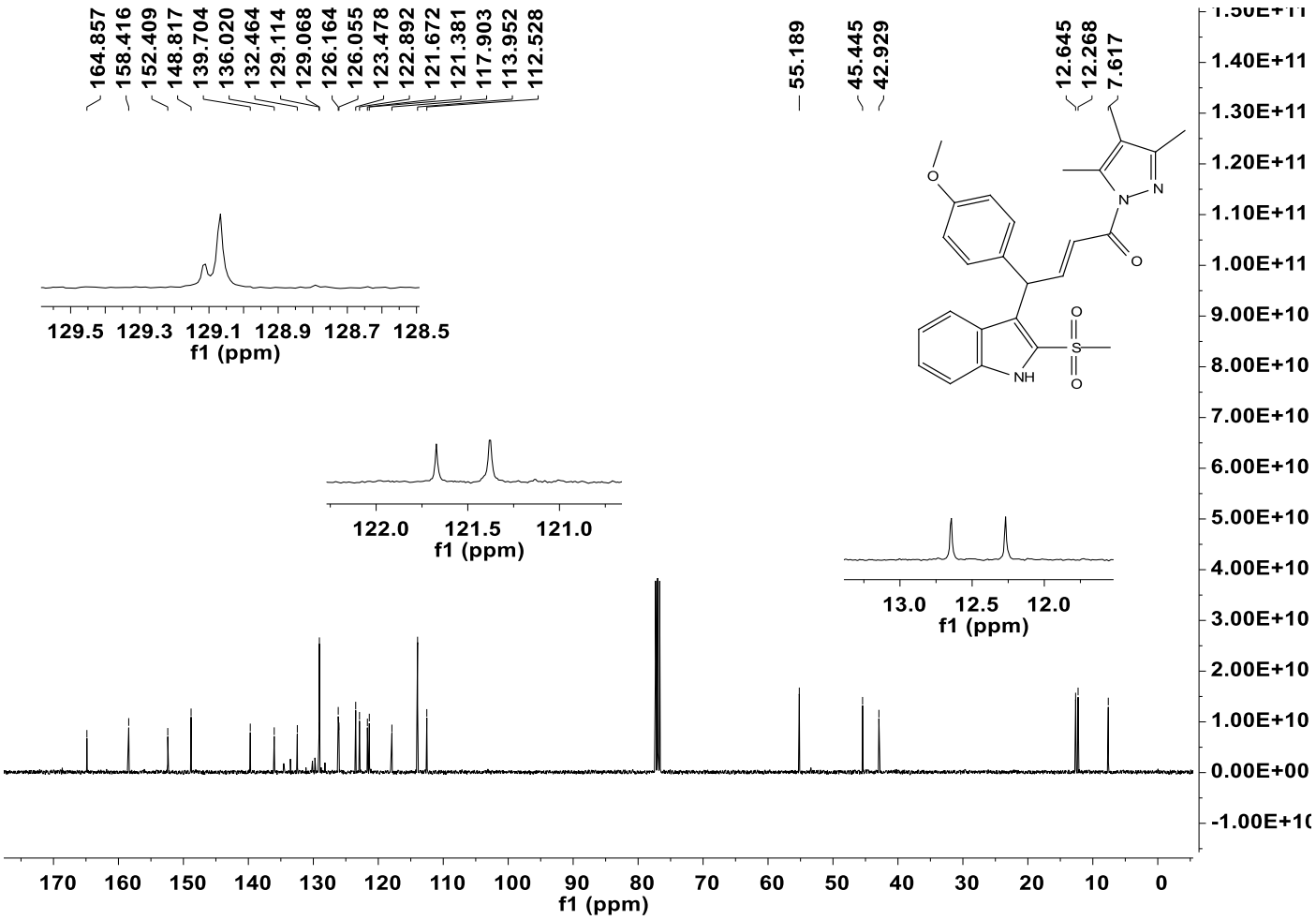
7.786
7.768
7.747
7.487
7.470
7.448
7.429
7.338
7.319
7.300
7.207
7.187
7.094
7.074
7.062
7.043
5.988
5.967
3.065
2.482
2.301
2.147
1.893
7.260
f1 (ppm)

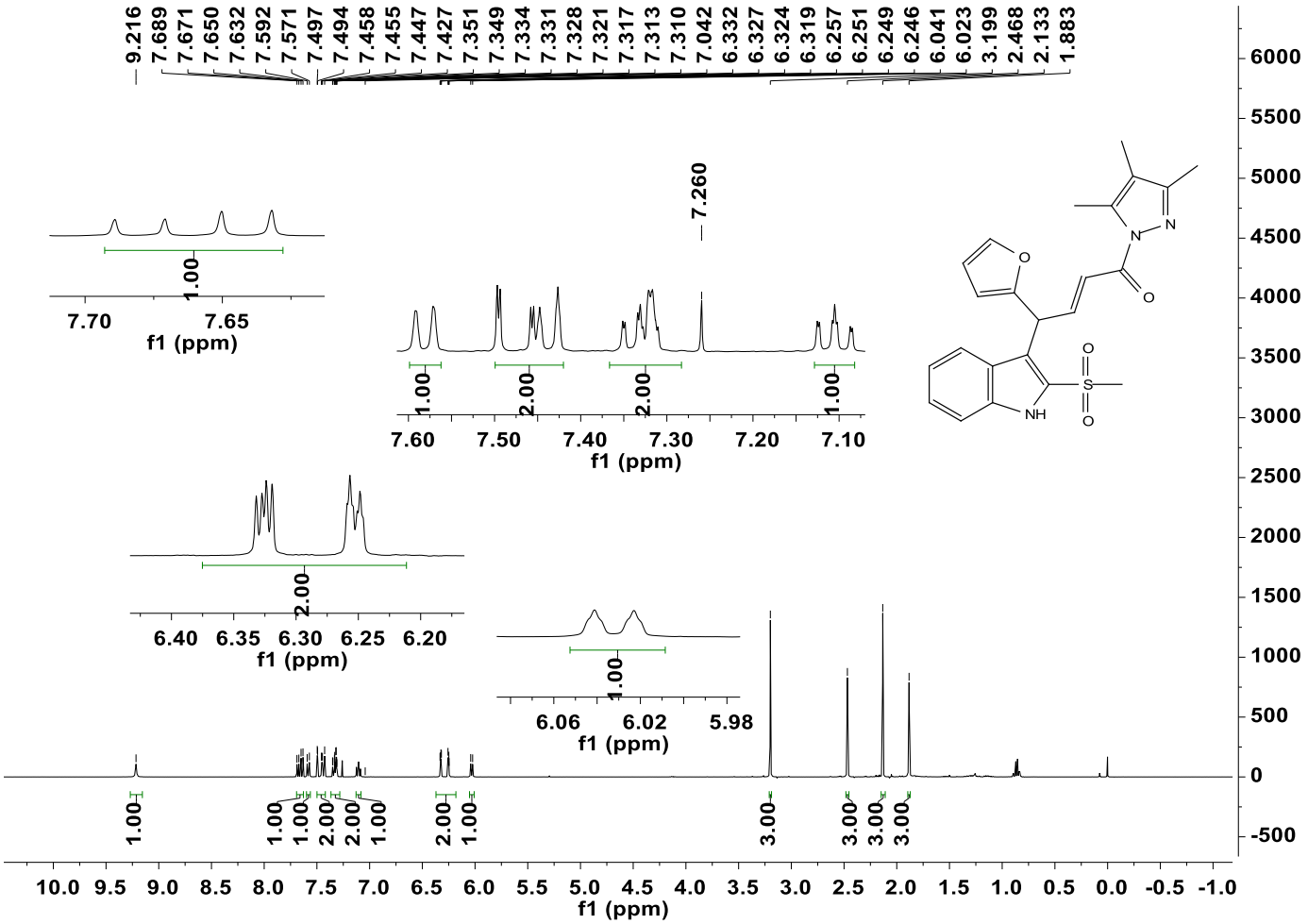

164.834
152.364
148.606
139.673
137.337
136.501
135.961
129.271
129.228
127.867
126.169
126.093
123.590
122.943
121.594
121.379
117.884
112.467
45.480
43.295
21.006
12.674
12.304
7.640
f1 (ppm)

4na


9.334
7.799
7.779
7.760
7.740
7.476
7.473
7.434
7.431
7.332
7.314
7.296
7.260
7.230
7.210
7.079
7.061
7.041
6.822
6.800
5.972
5.952
3.763
3.058
2.484
2.148
1.893
f1 (ppm)


164.857
158.416
152.409
148.817
139.704
136.020
132.464
129.114
129.068
126.164
126.055
123.478
122.892
121.672
121.381
117.903
113.952
112.528
55.189
45.445
42.929
12.645
12.268
7.617
f1 (ppm)

4oa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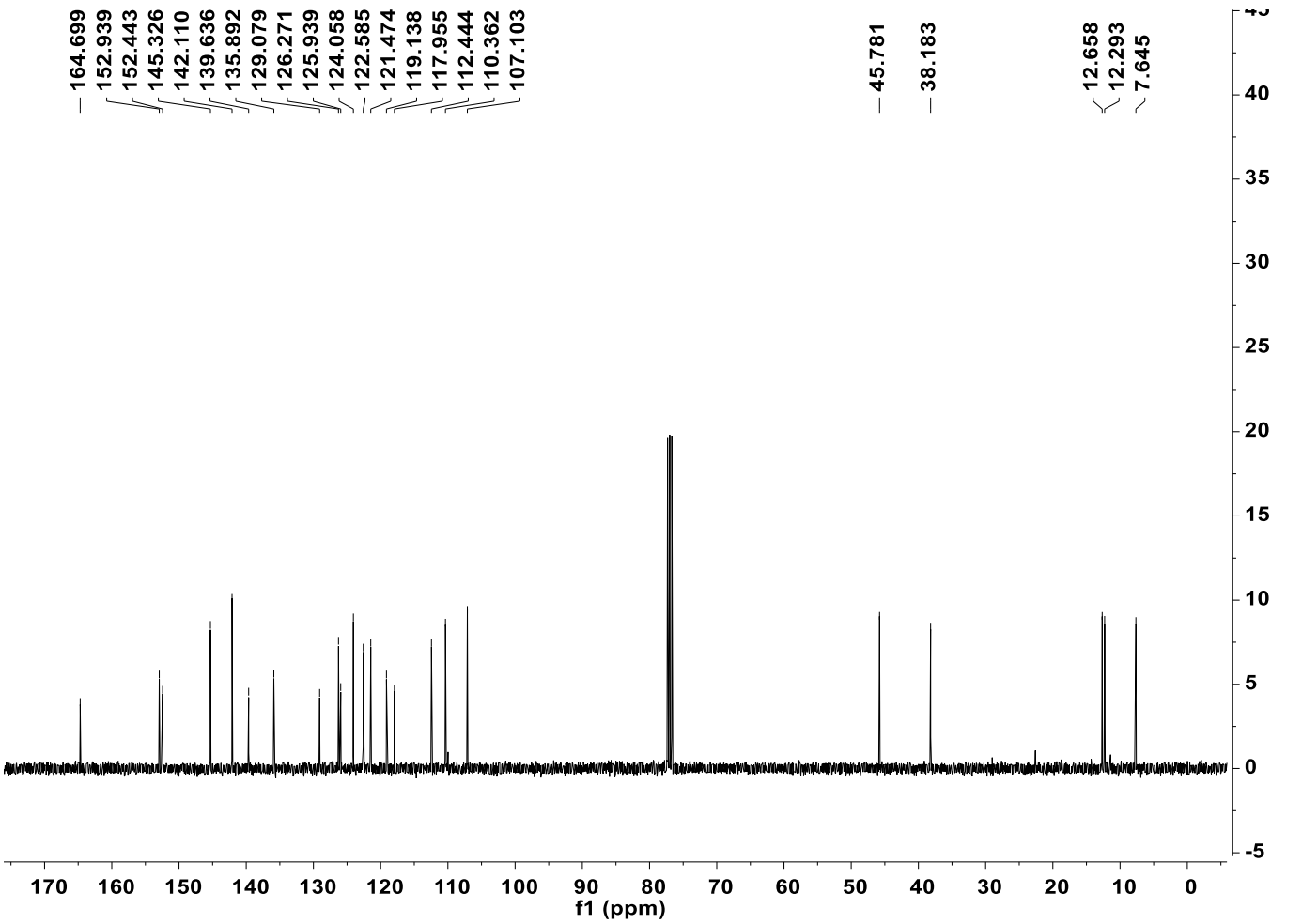
7.689
7.671
7.650
7.632
7.592
7.571
7.497
7.494
7.458
7.455
7.447
7.427
7.351
7.349
7.334
7.331
7.328
7.321
7.317
7.313
7.310
7.042
6.332
6.327
6.324
6.319
6.257
6.251
6.249
6.246
6.041
6.023
3.199
2.468
2.133
1.883
7.260
f1 (ppm)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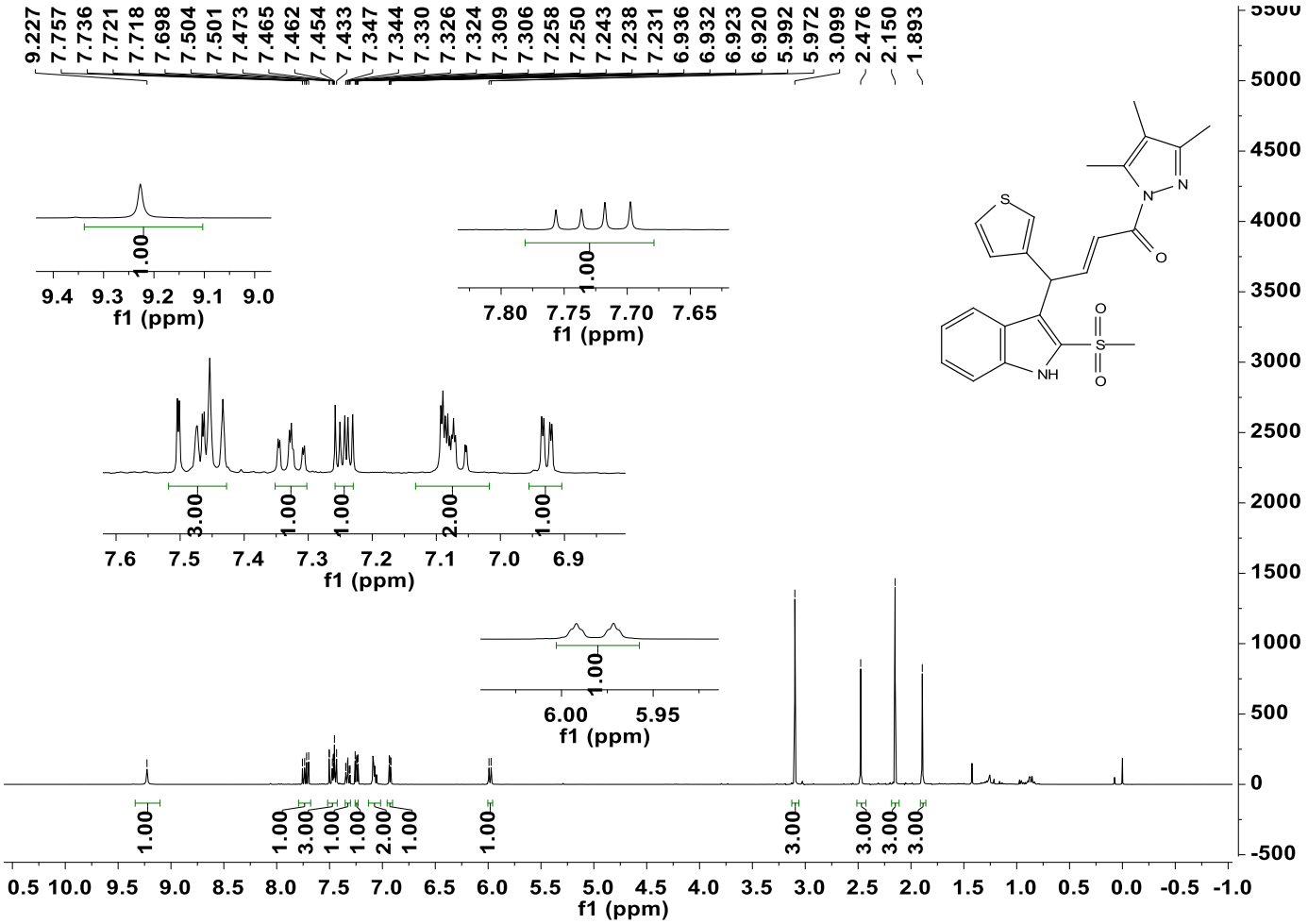
152.939
152.443
145.326
142.110
139.636
135.892
129.079
126.271
125.939
124.058
122.585
121.474
119.138
117.955
112.444
110.362
107.103
45.781
38.183
12.658
12.293
7.645
f1 (ppm)

4pa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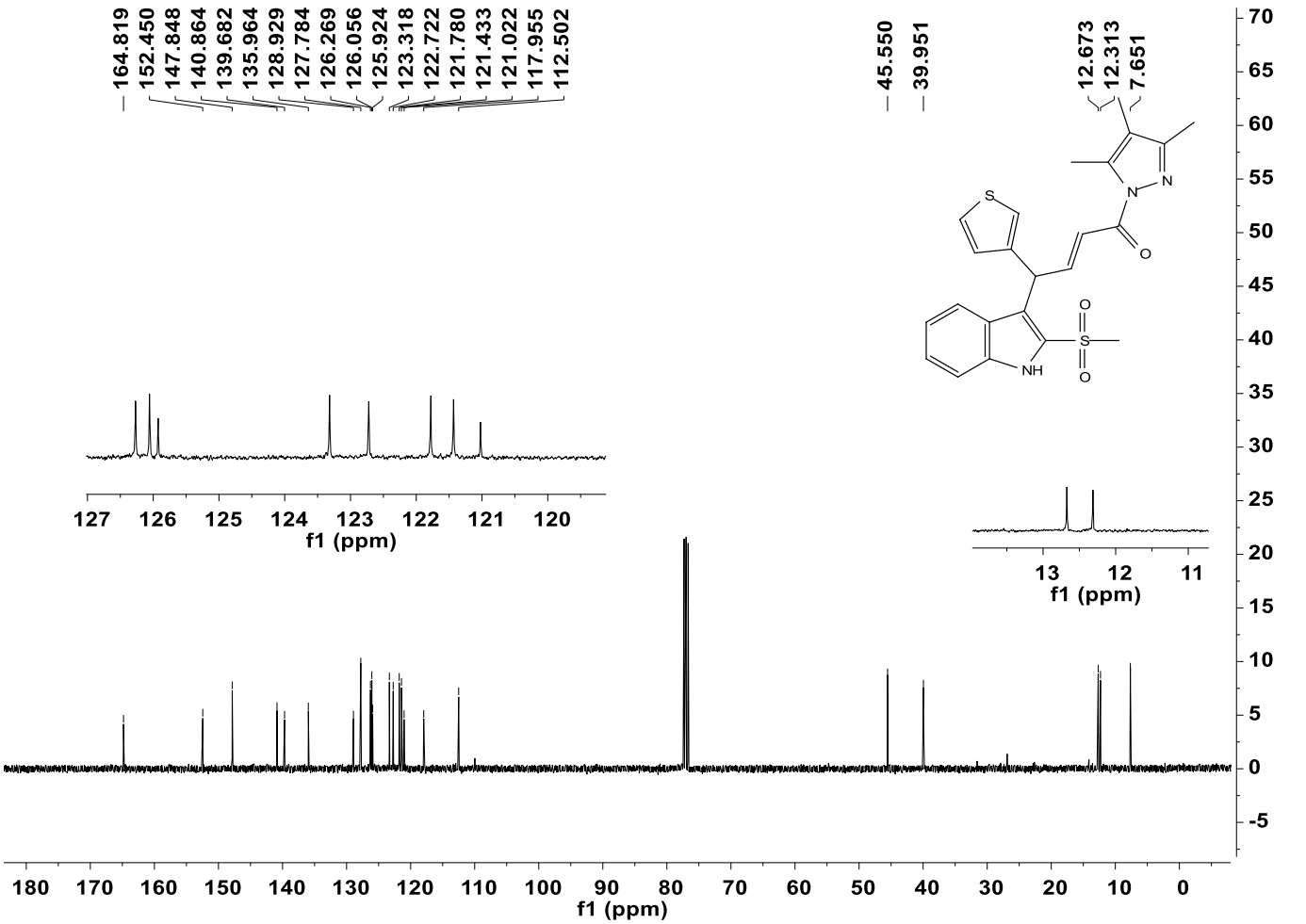
7.757
7.736
7.721
7.718
7.698
7.504
7.501
7.473
7.465
7.462
7.454
7.433
7.347
7.344
7.330
7.326
7.324
7.309
7.306
7.258
7.250
7.243
7.238
7.231
6.936
6.932
6.923
6.920
5.992
5.972
3.099
2.476
2.150
1.893
f1 (ppm)


164.819
152.450
147.848
140.864
139.682
135.964
128.929
127.784
126.269
126.056
125.924
123.318
122.722
121.780
121.433
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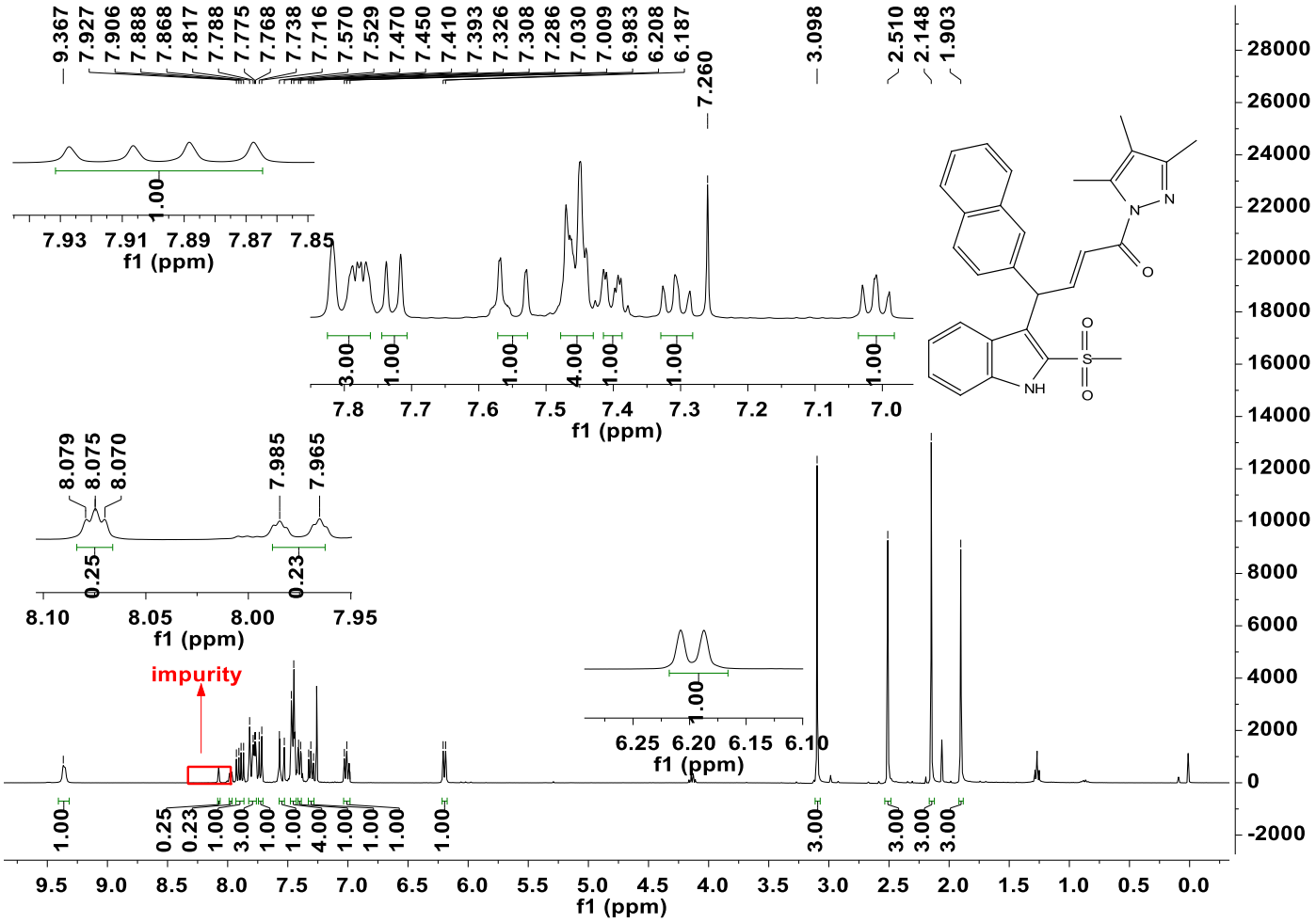
117.955
112.502
45.550
39.951
12.673
12.313
7.651
f1 (ppm)

4qa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7.927
7.906
7.888
7.868
7.817
7.788
7.775
7.768
7.738
7.716
7.570
7.529
7.470
7.450
7.410
7.393
7.326
7.308
7.286
7.030
7.009
6.983
6.208
6.187
7.260
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2.148
1.903
8.079
8.075
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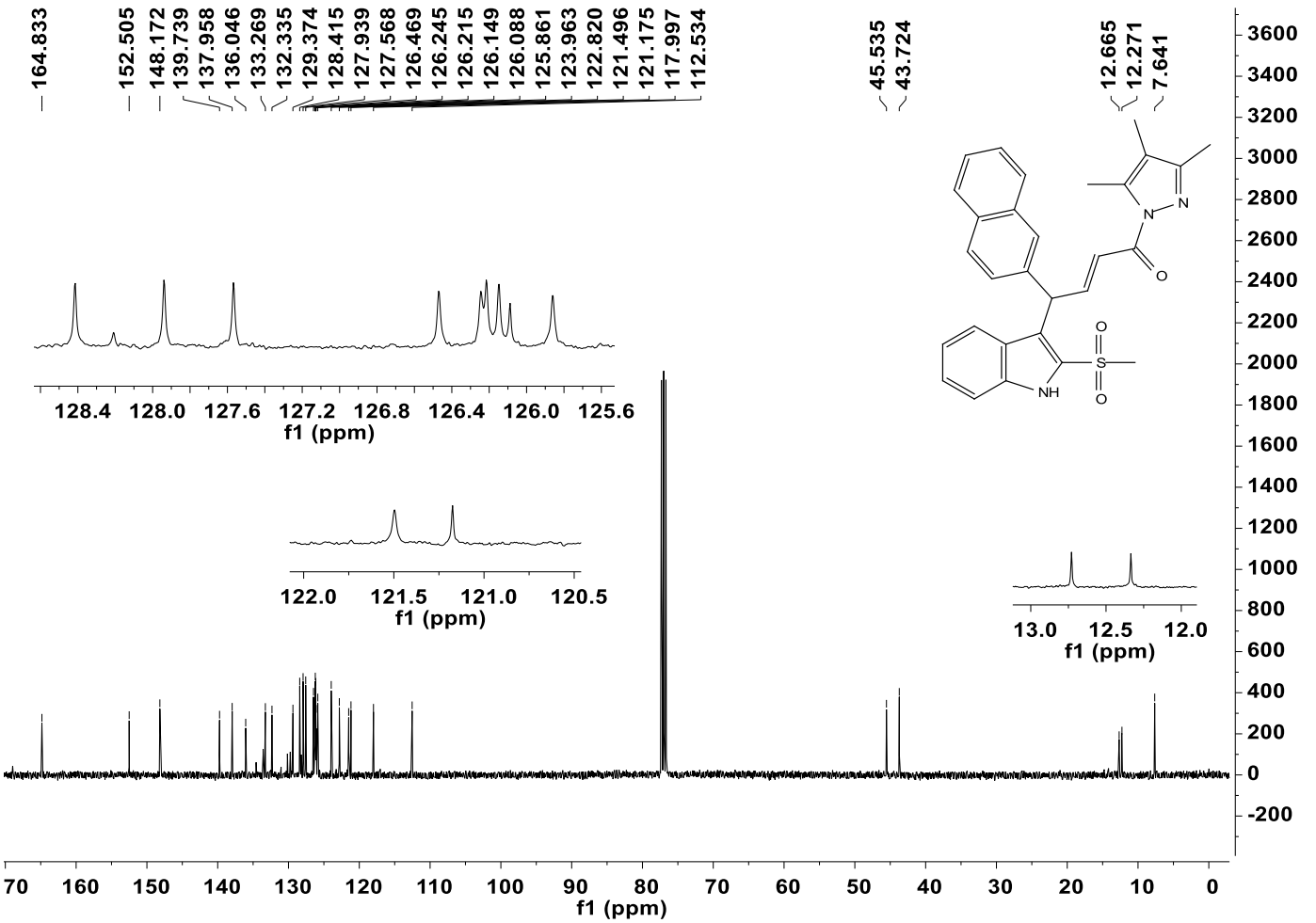
7.985
7.965
impurity
f1 (ppm)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148.172
139.739
137.958
136.046
133.269
132.335
129.374
128.415
127.939
127.568
126.469
126.245
126.215
126.149
126.088
125.861
123.963
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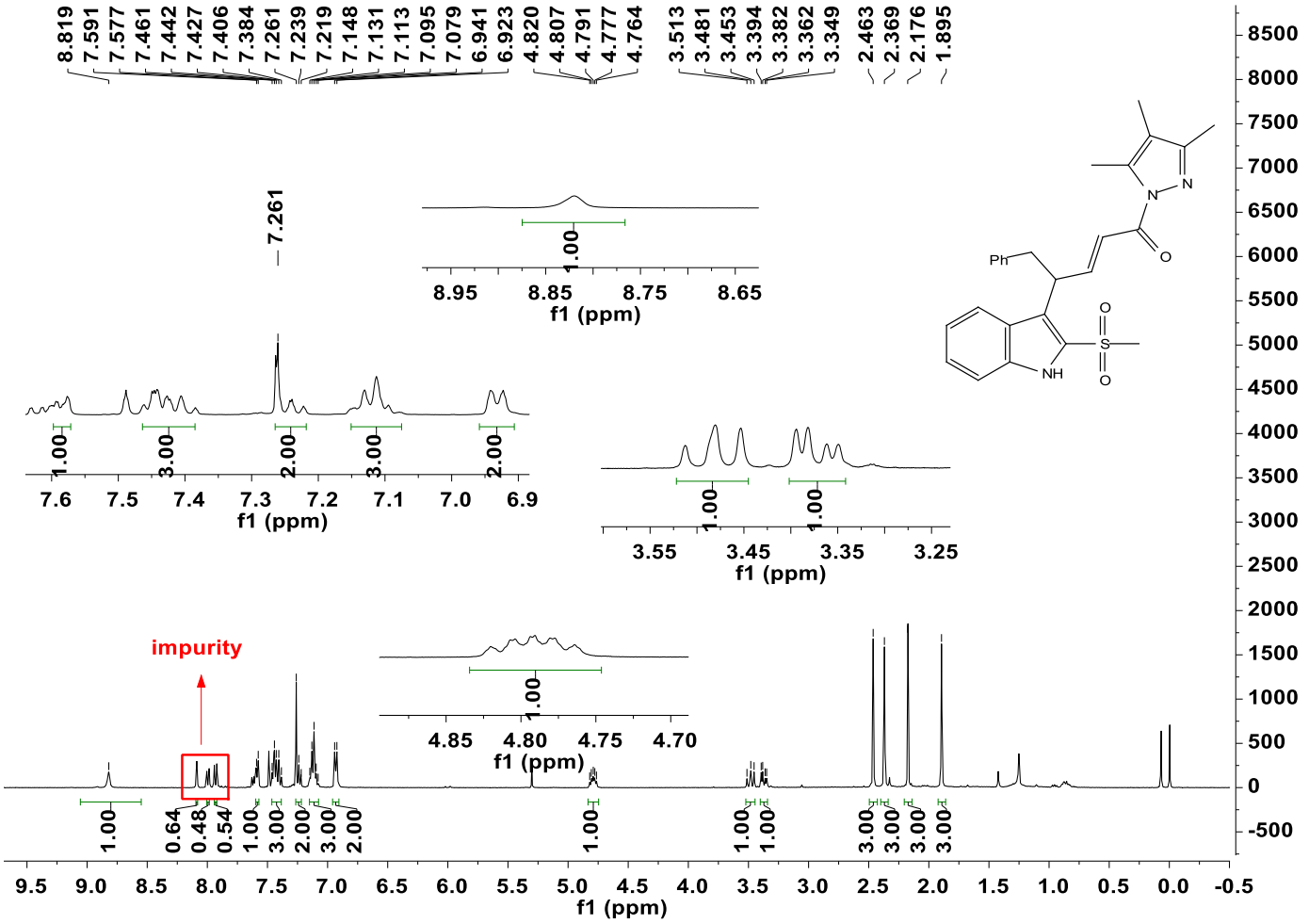
117.997
112.534
45.535
43.724
12.665
12.271
7.641
f1 (ppm)

4ra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7.591
7.577
7.461
7.442
7.427
7.406
7.384
7.261
7.239
7.219
7.148
7.131
7.113
7.095
7.079
6.941
6.923
4.820
4.807
4.791
4.777
4.764
3.513
3.481
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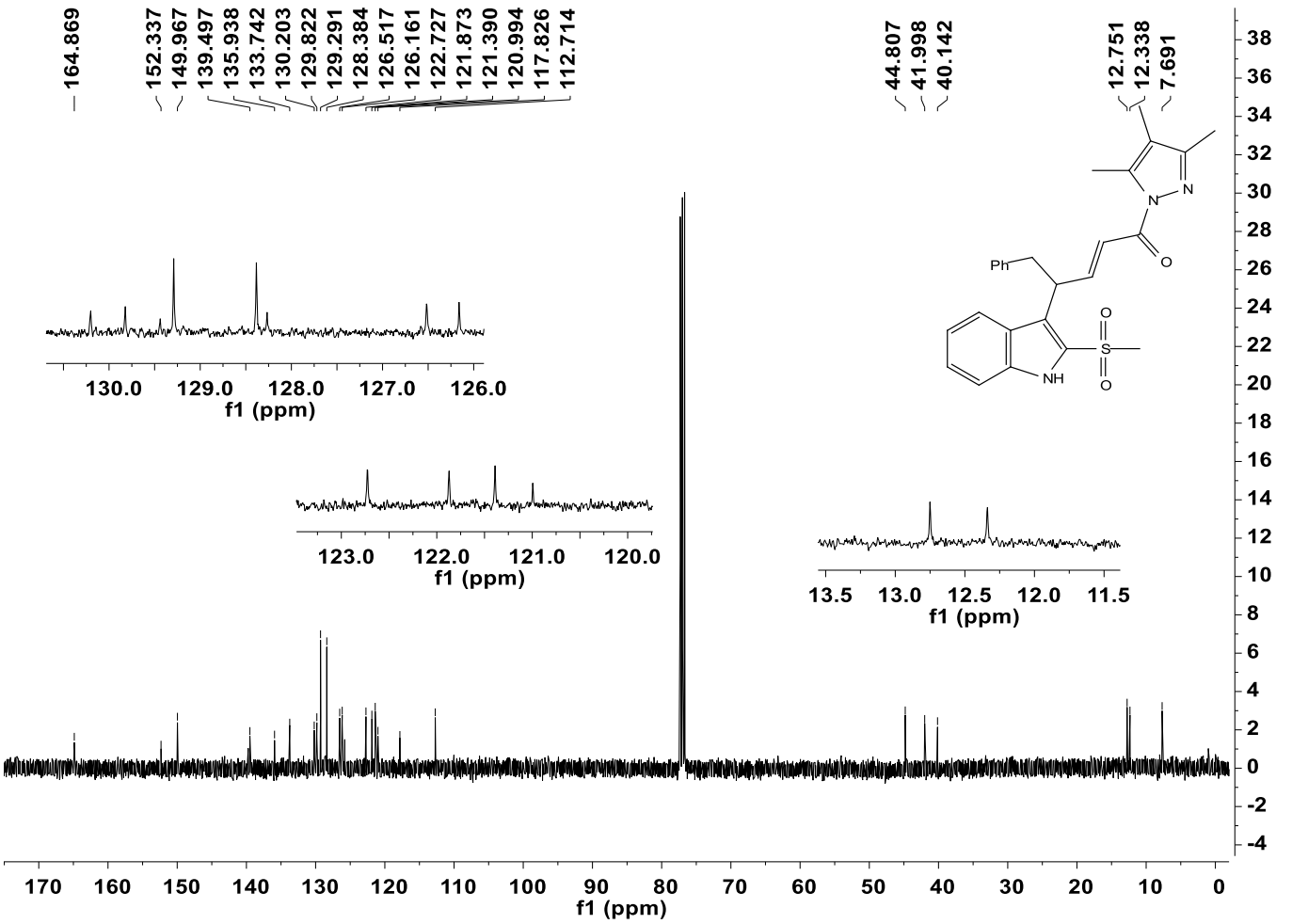
3.362
3.349
2.463
2.369
2.176
1.895
7.261
impurity
f1 (ppm)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139.497
135.938
133.742
130.203
129.822
129.291
128.384
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126.161
122.727
121.873
121.390
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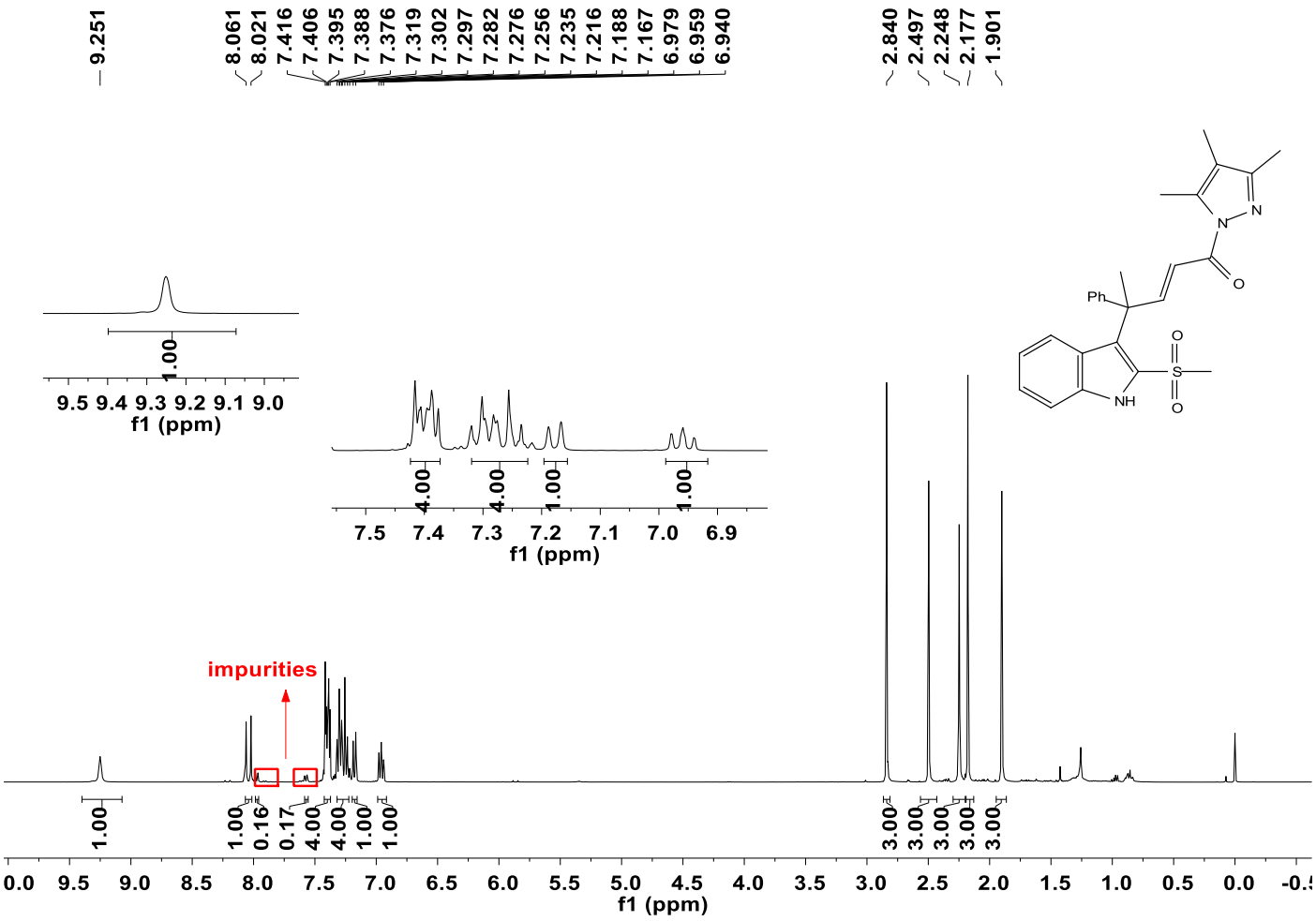
112.714
44.807
41.998
40.142
12.751
12.338
7.691
f1 (ppm)

4sa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7.406
7.395
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7.319
7.302
7.297
7.282
7.276
7.256
7.235
7.216
7.188
7.167
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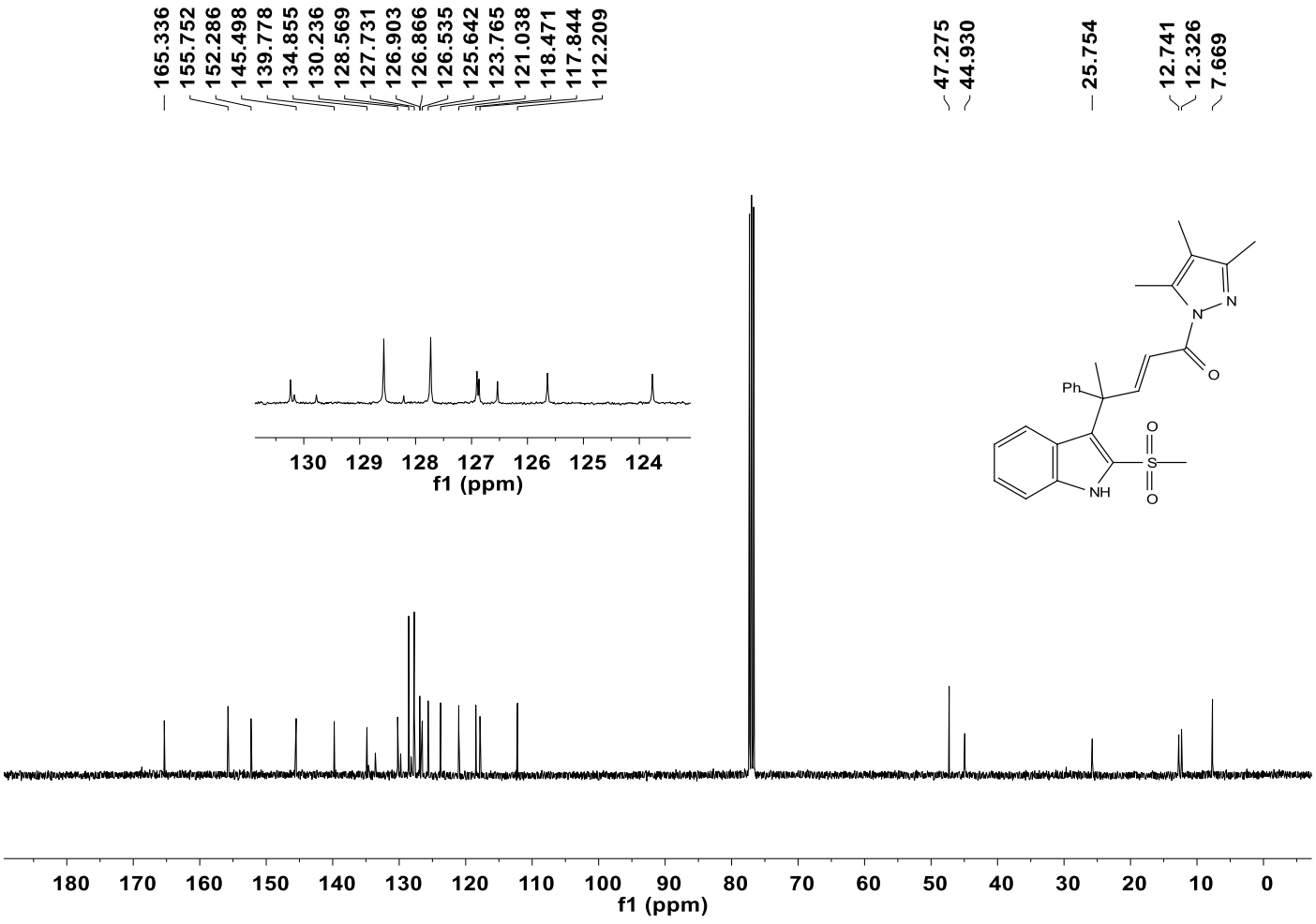
6.959
6.940
2.840
2.497
2.248
2.177
1.901
impurities
f1 (ppm)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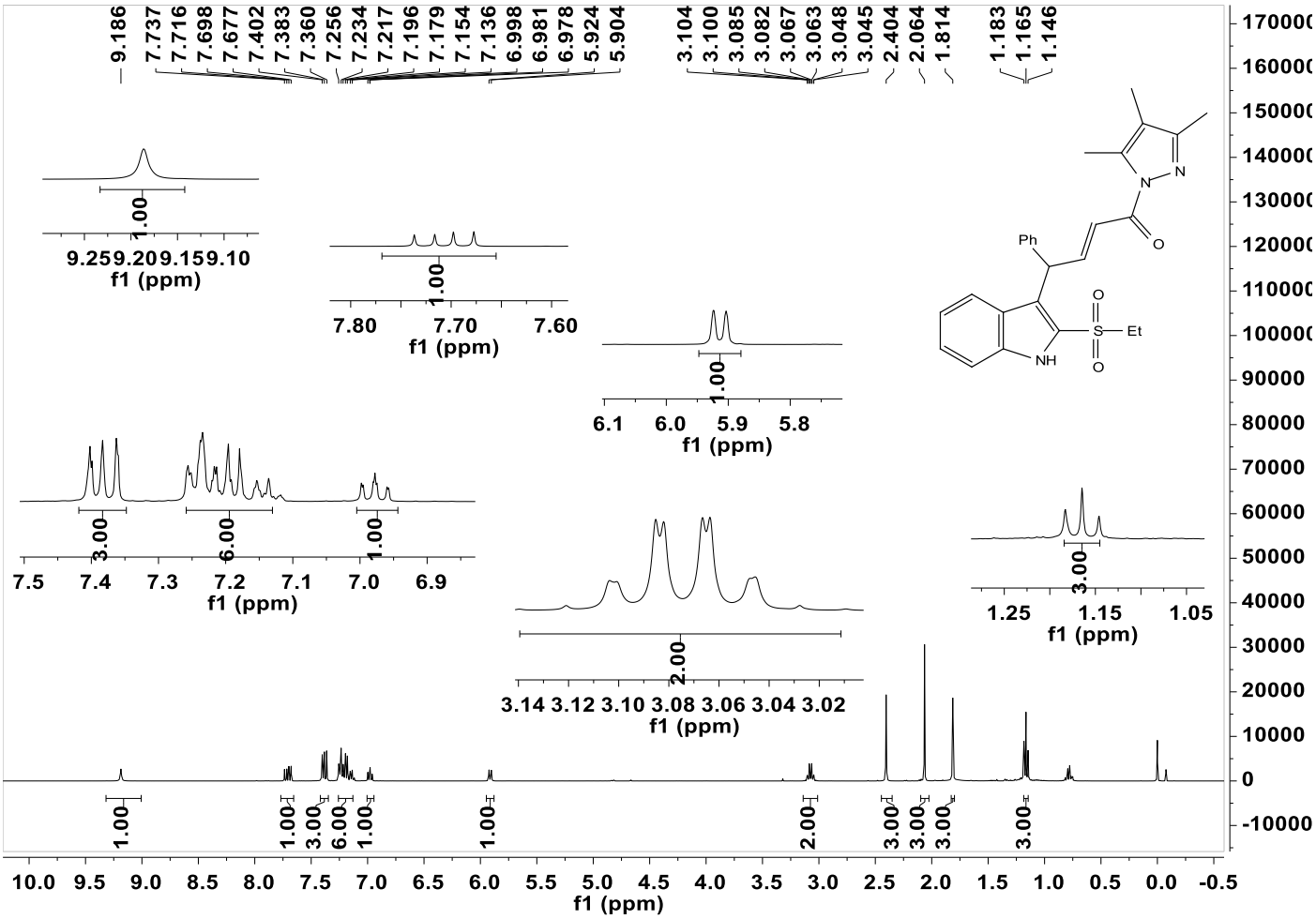
145.498
139.778
134.855
130.236
128.569
127.731
126.903
126.866
126.535
125.642
123.765
121.038
118.471
117.844
112.209
47.275
44.930
25.754
12.741
12.326
7.669
f1 (ppm)

4ab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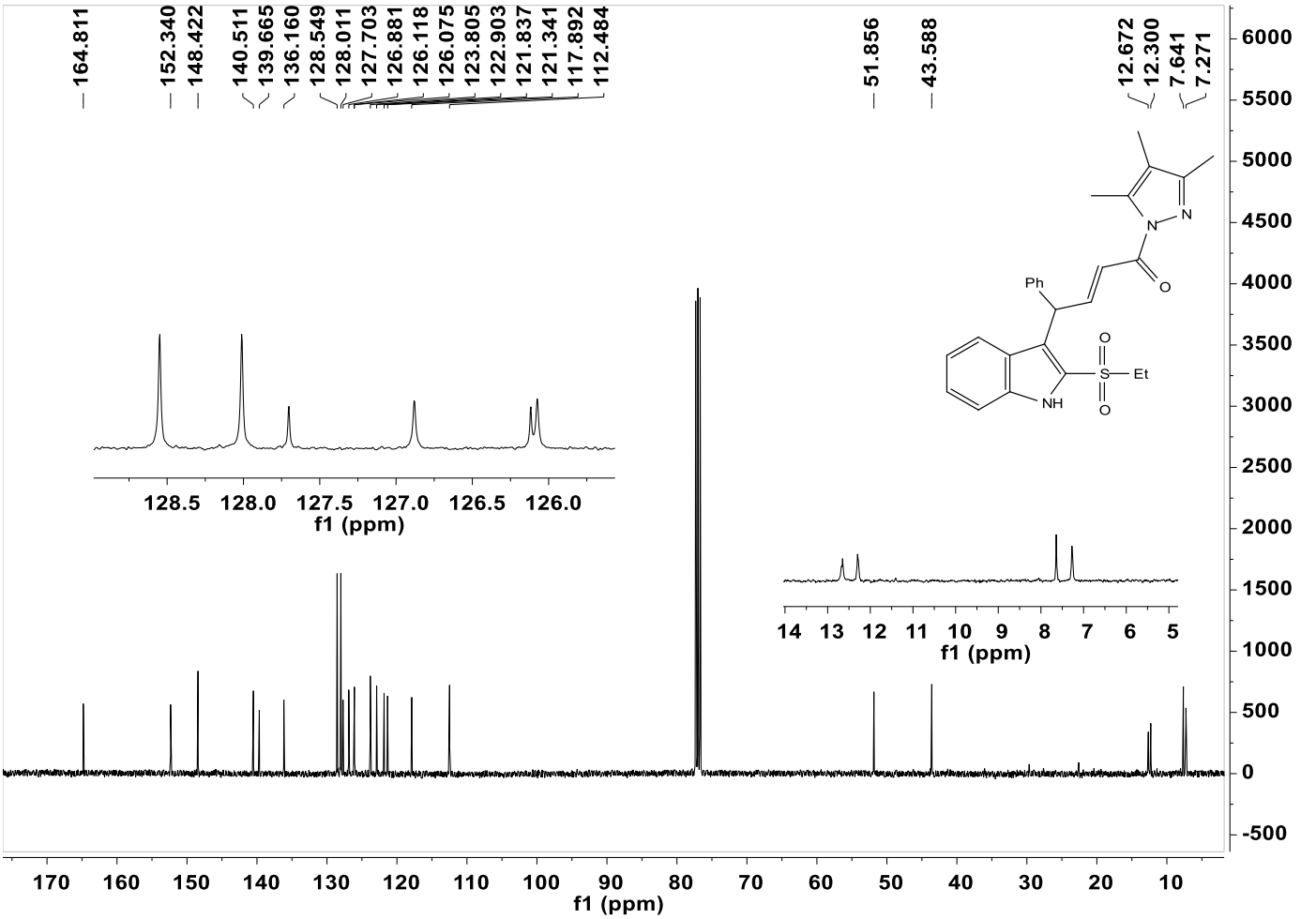
7.716
7.698
7.677
7.402
7.383
7.360
7.256
7.234
7.217
7.196
7.179
7.154
7.136
6.998
6.981
6.978
5.924
5.904
3.104
3.100
3.085
3.082
3.067
3.063
3.048
3.045
2.404
2.064
1.814
1.183
1.165
1.146
Ph
O
N
N
O
S
Et
O
O
NH
f1 (ppm)


164.811
152.340
148.422
140.511
139.665
136.160
128.549
128.011
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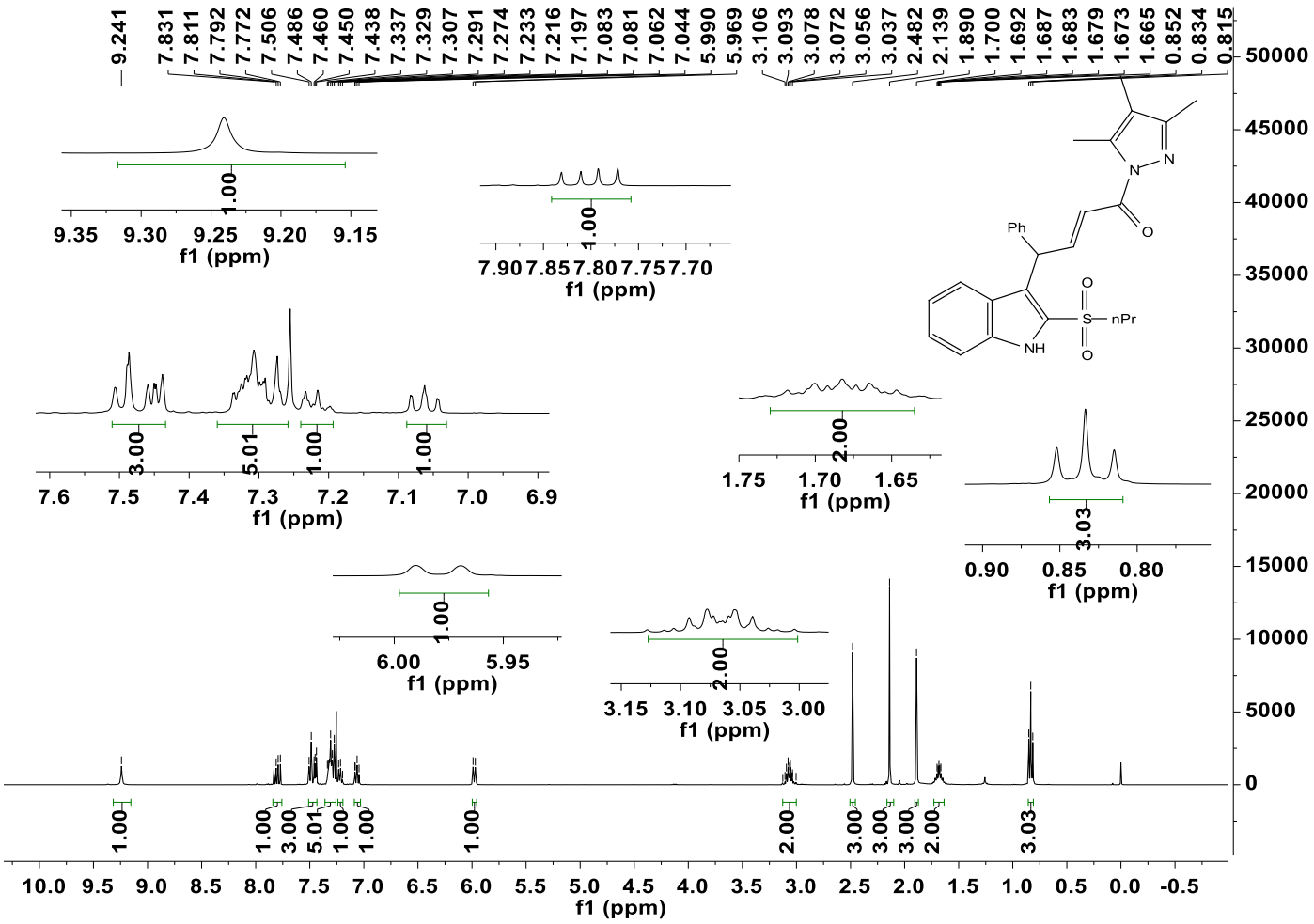
126.881
126.118
126.075
123.805
122.903
121.837
121.341
117.892
112.484
51.856
43.588
12.672
12.300
7.641
7.271
Ph
O
N
N
O
S
Et
O
O
NH
f1 (ppm)

4ac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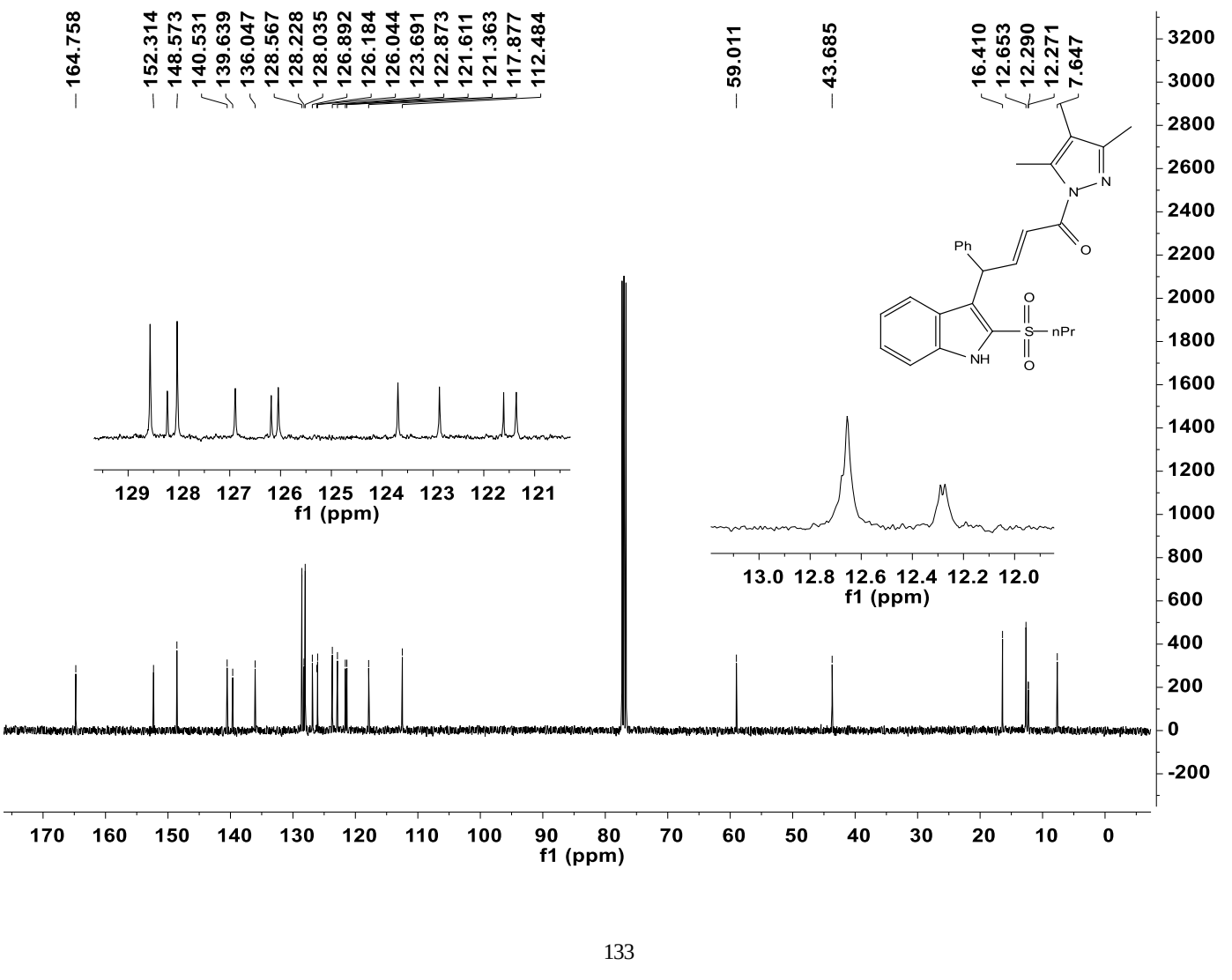
7.460
7.450
7.438
7.337
7.329
7.307
7.291
7.274
7.233
7.216
7.197
7.083
7.081
7.062
7.044
5.990
5.969
3.106
3.093
3.078
3.072
3.056
3.037
2.482
2.139
1.890
1.700
1.692
1.687
1.683
1.679
1.673
1.665
0.852
0.834
0.815
Ph
O
N
NH
S
nPr
f1 (ppm)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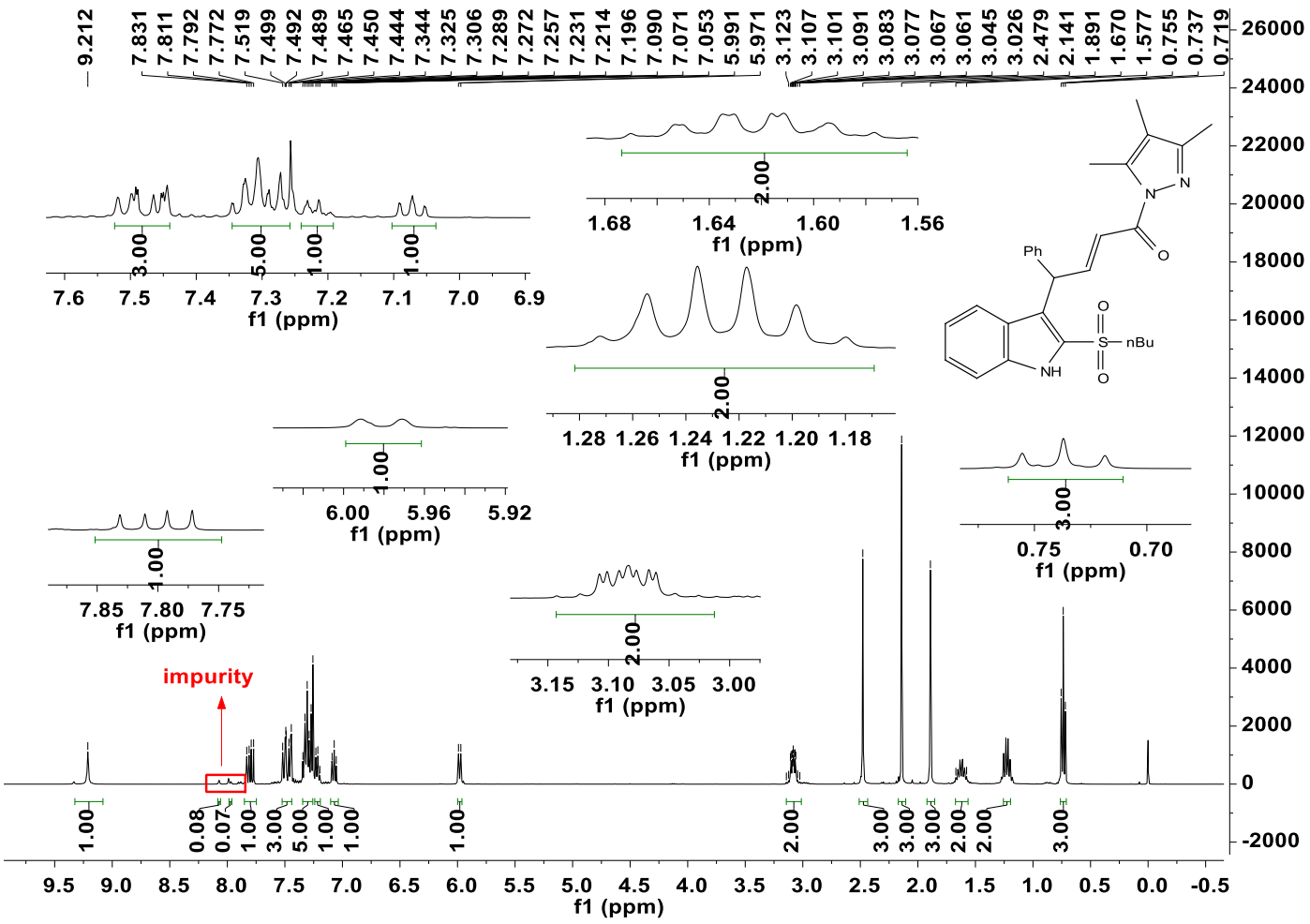
140.531
139.639
136.047
128.567
128.228
128.035
126.892
126.184
126.044
123.691
122.873
121.611
121.363
117.877
112.484
59.011
43.685
16.410
12.653
12.290
12.271
7.647
Ph
O
N
NH
S
nPr
f1 (ppm)

4ad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7.811
7.792
7.772
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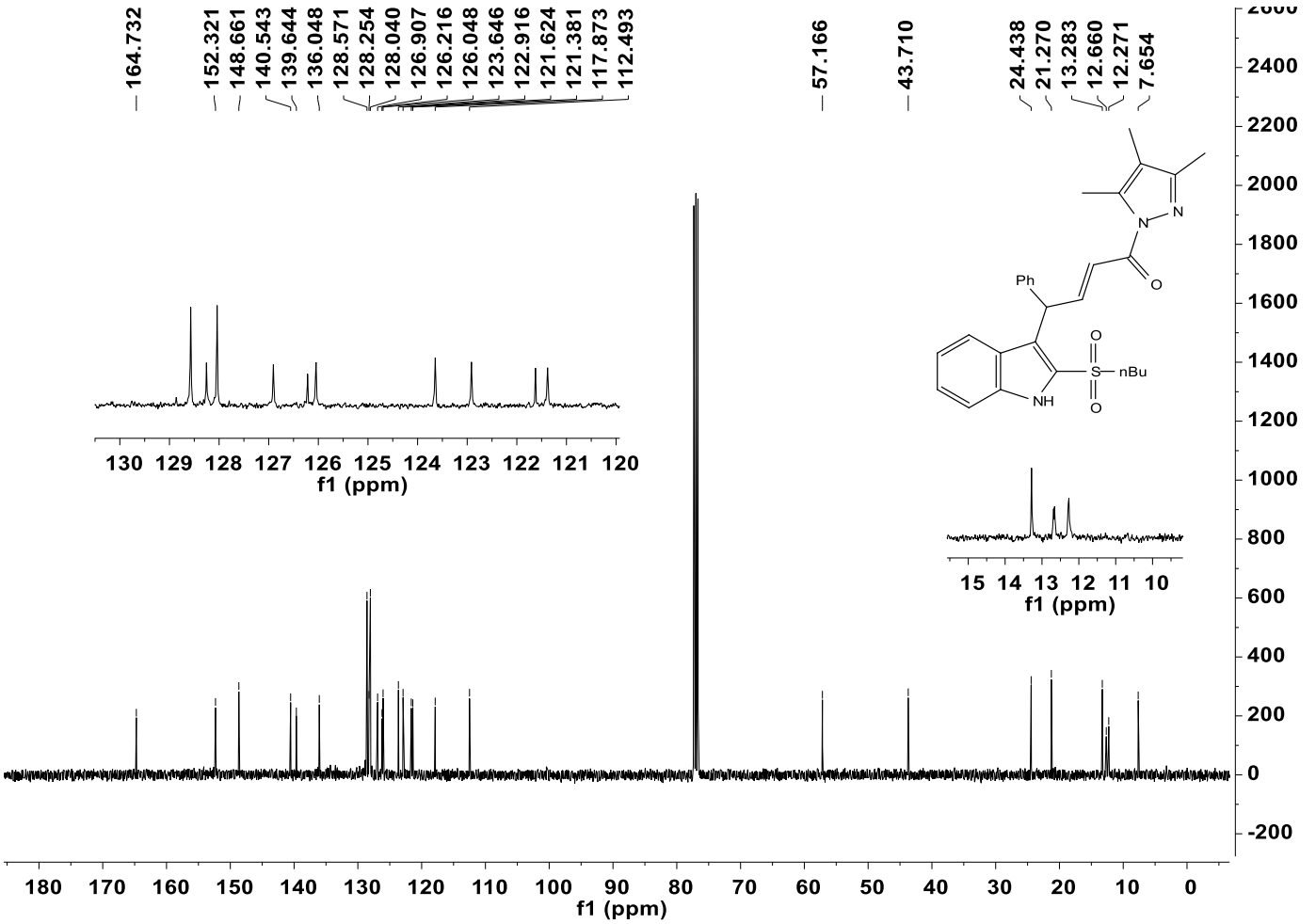
7.499
7.492
7.489
7.465
7.450
7.444
7.344
7.325
7.306
7.289
7.272
7.257
7.231
7.214
7.196
7.090
7.071
7.053
5.991
5.971
3.123
3.107
3.101
3.091
3.083
3.077
3.067
3.061
3.045
3.026
2.479
2.141
1.891
1.670
1.577
0.755
0.737
0.719
impurity
f1 (ppm)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128.571
128.254
128.040
126.907
126.216
126.048
123.646
122.916
121.624
121.381
117.873
112.493
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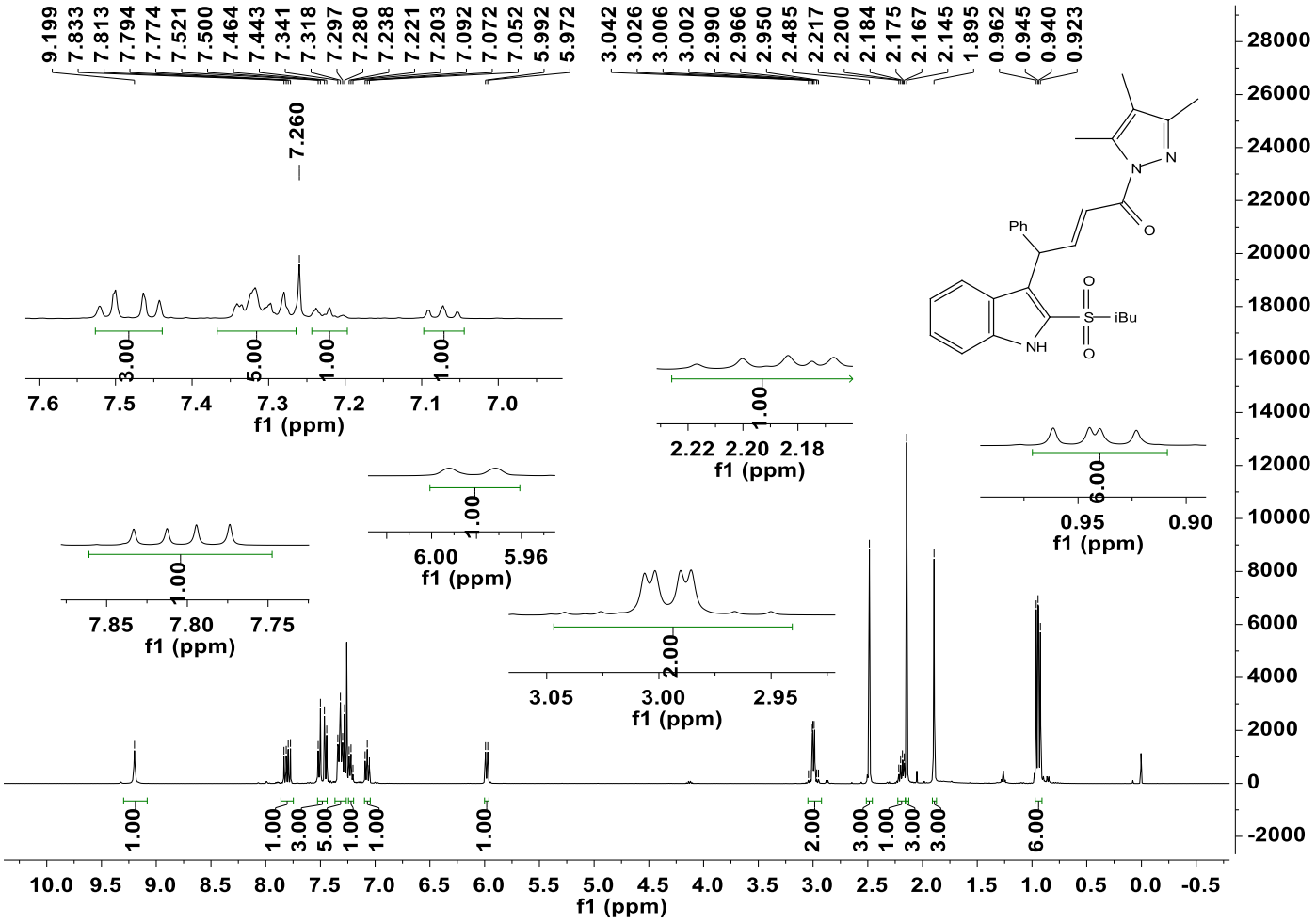
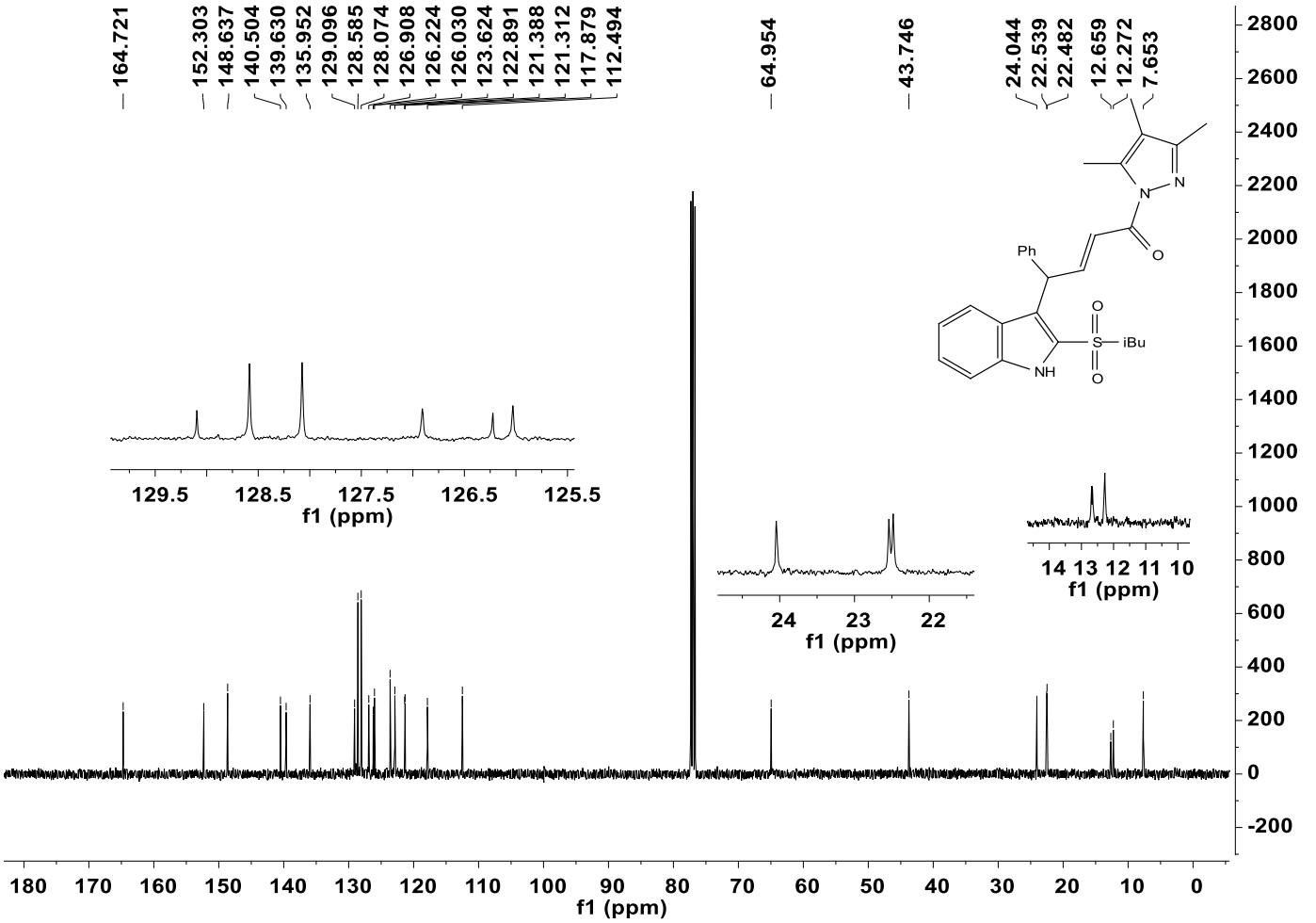
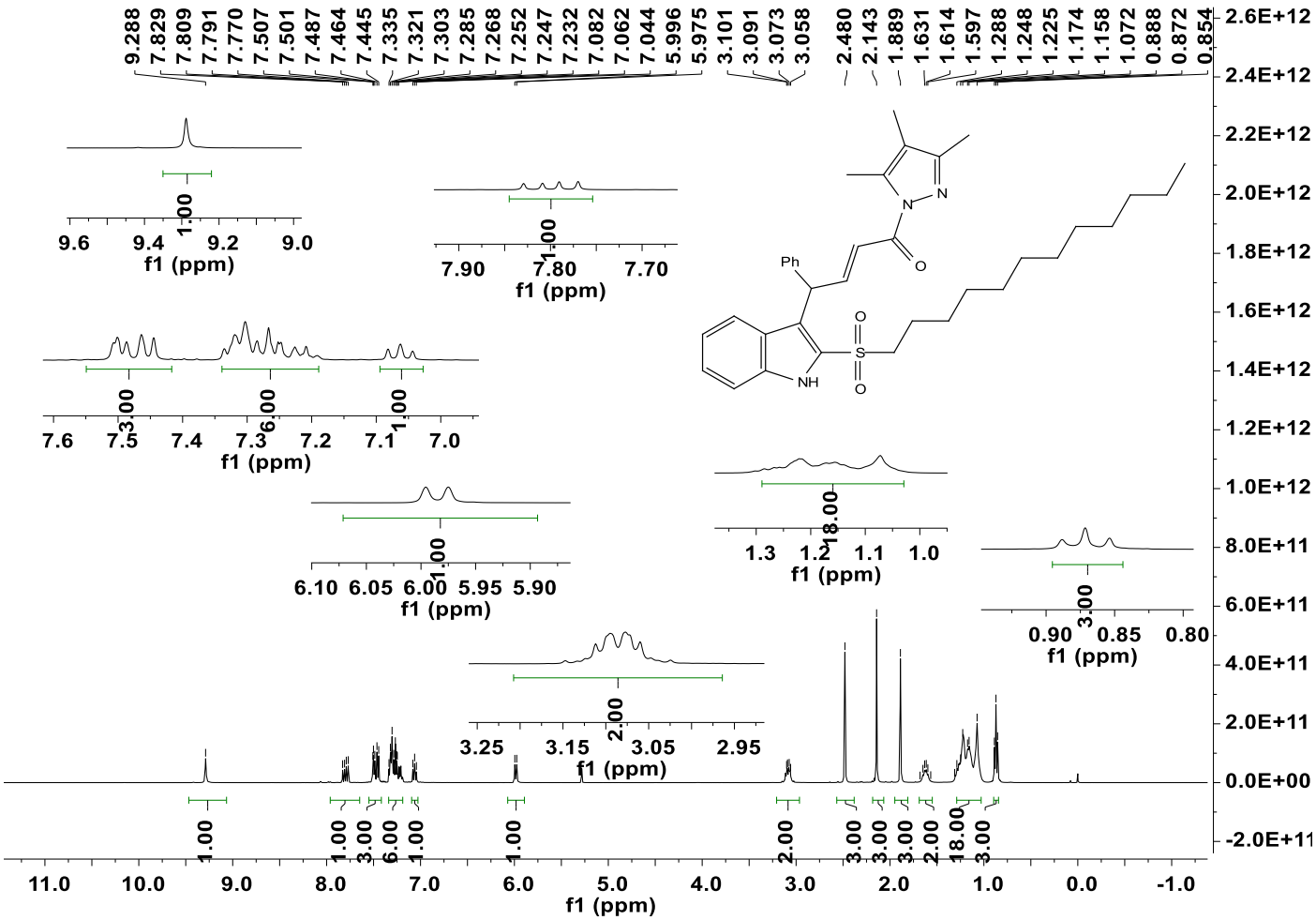
43.710
24.438
21.270
13.283
12.660
12.271
7.654
f1 (ppm)

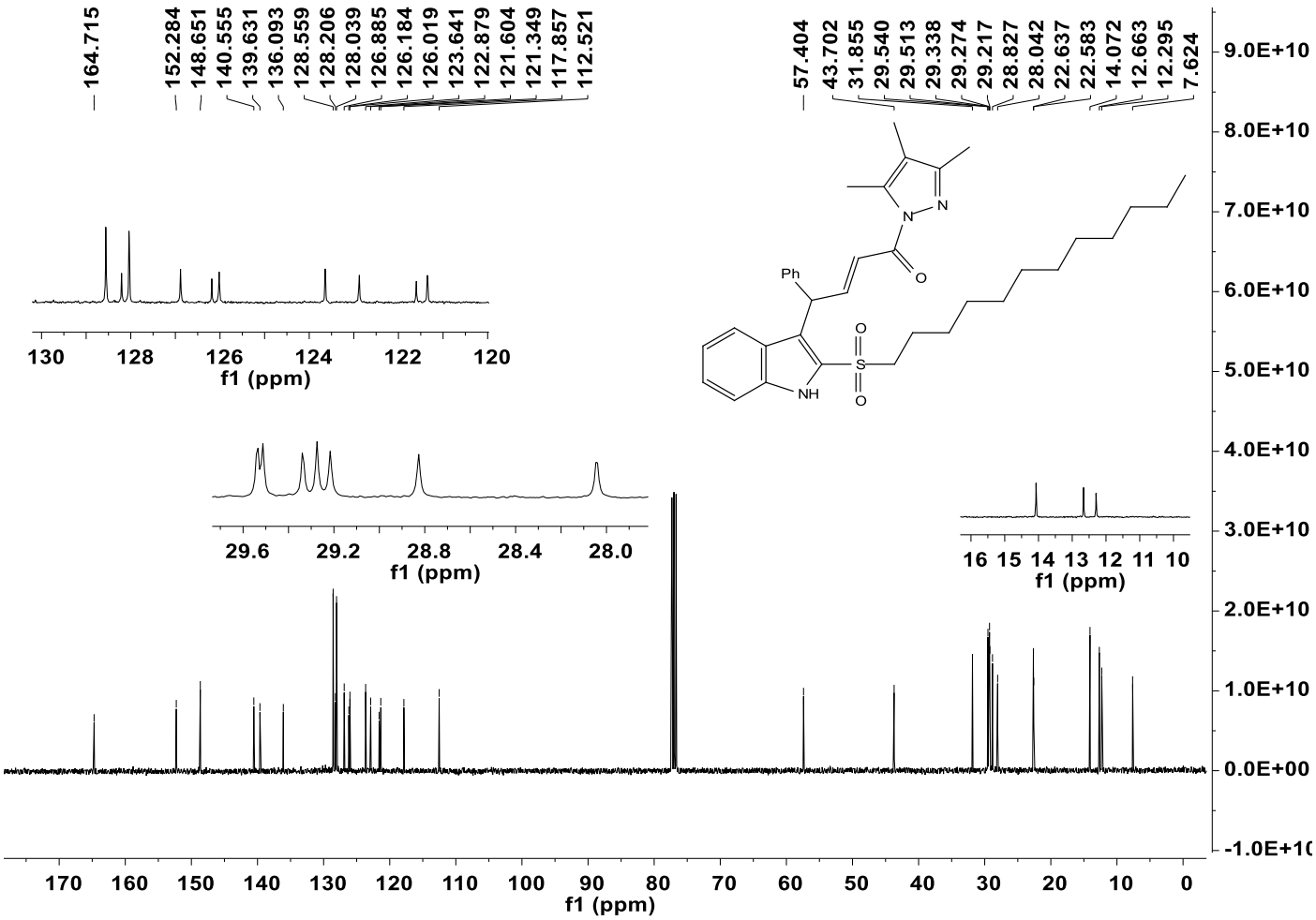
4ae


9.199 7.833 7.813 7.794 7.774 7.521 7.500 7.464 7.443 7.341 7.318 7.297 7.280 7.238 7.221 7.203 7.092 7.072 7.052 5.992 5.972
3.042 3.026 3.006 3.002 2.990 2.966 2.950 2.485 2.217 2.200 2.184 2.175 2.167 2.145 1.895 0.962 0.945 0.940 0.923
7.260
Ph
iBu
NH
f1 (ppm)

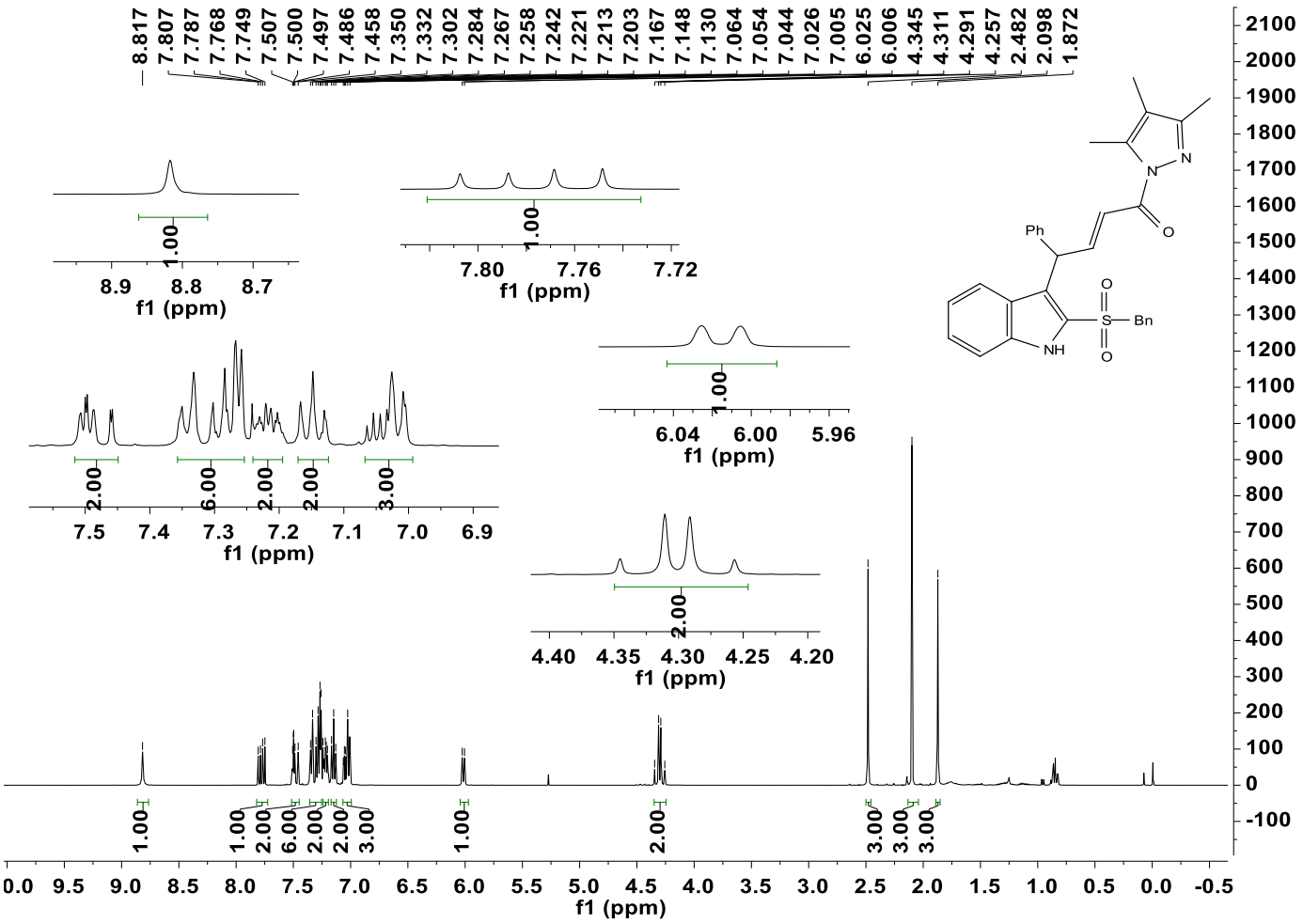

164.721 152.303 148.637 140.504 139.630 135.952 129.096 128.585 128.074 126.908 126.224 126.030 123.624 122.891 121.388 121.312 117.879 112.494
64.954 43.746 24.044 22.539 22.482 12.659 12.272 7.653
Ph
iBu
NH
f1 (ppm)

4af


9.288 7.829 7.809 7.791 7.770 7.507 7.501 7.487 7.464 7.445 7.335 7.321 7.303 7.285 7.268 7.252 7.247 7.232 7.082 7.062 7.044 5.996 5.975 3.101 3.091 3.073 3.058 2.480 2.143 1.889 1.631 1.614 1.597 1.288 1.248 1.225 1.174 1.158 1.072 0.888 0.872 0.854
f1 (ppm)


164.715 152.284 148.651 140.555 139.631 136.093 128.559 128.206 128.039 126.885 126.184 126.019 123.641 122.879 121.604 121.349 117.857 112.521 57.404 43.702 31.855 29.540 29.513 29.338 29.274 29.217 28.827 28.042 22.637 22.583 14.072 12.663 12.295 7.624
f1 (ppm)

4ag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7.787
7.768
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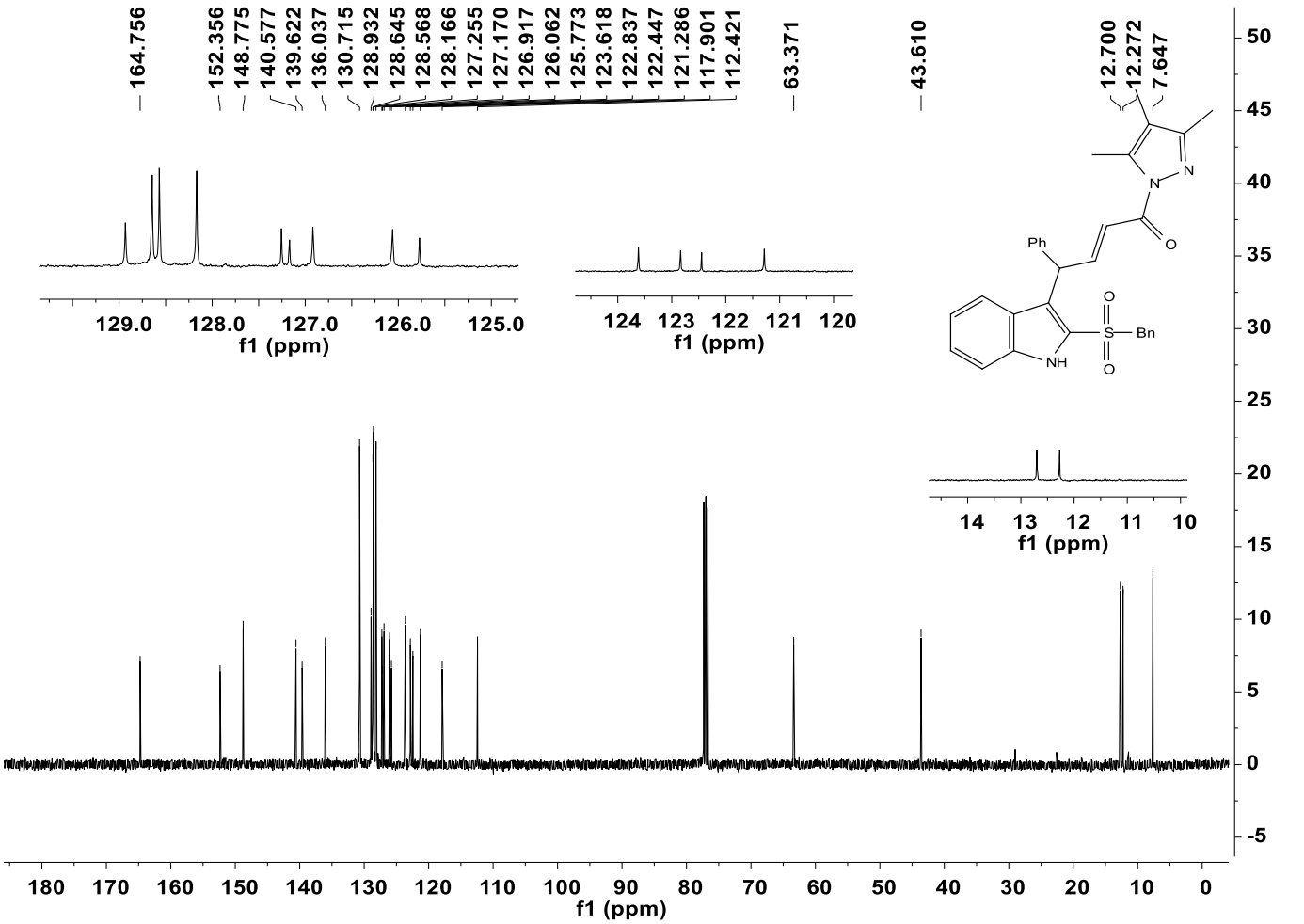
7.500
7.497
7.486
7.458
7.350
7.332
7.302
7.284
7.267
7.258
7.242
7.221
7.213
7.203
7.167
7.148
7.130
7.064
7.054
7.044
7.026
7.005
6.025
6.006
4.345
4.311
4.291
4.257
2.482
2.098
1.872
f1 (ppm)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128.932
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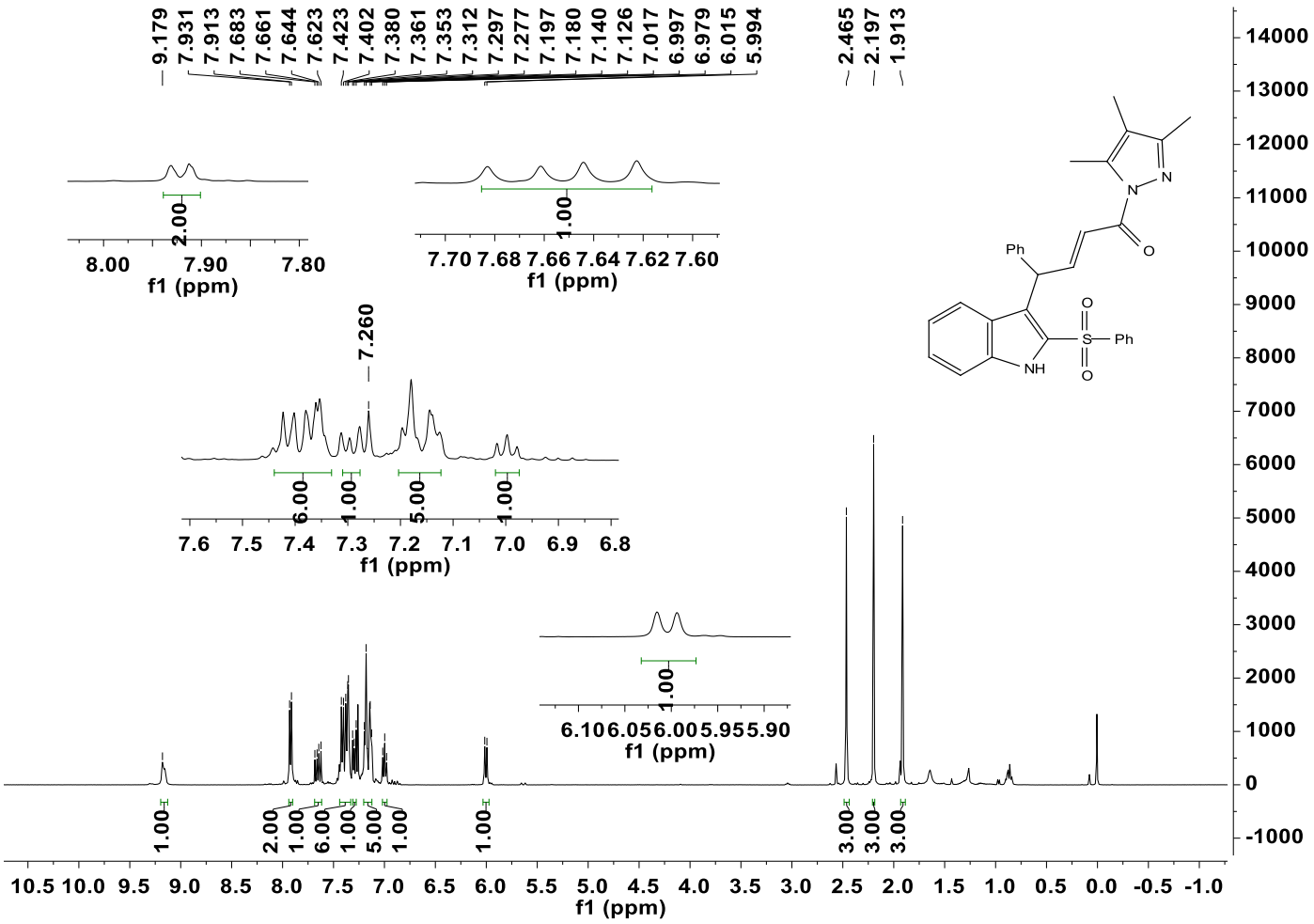
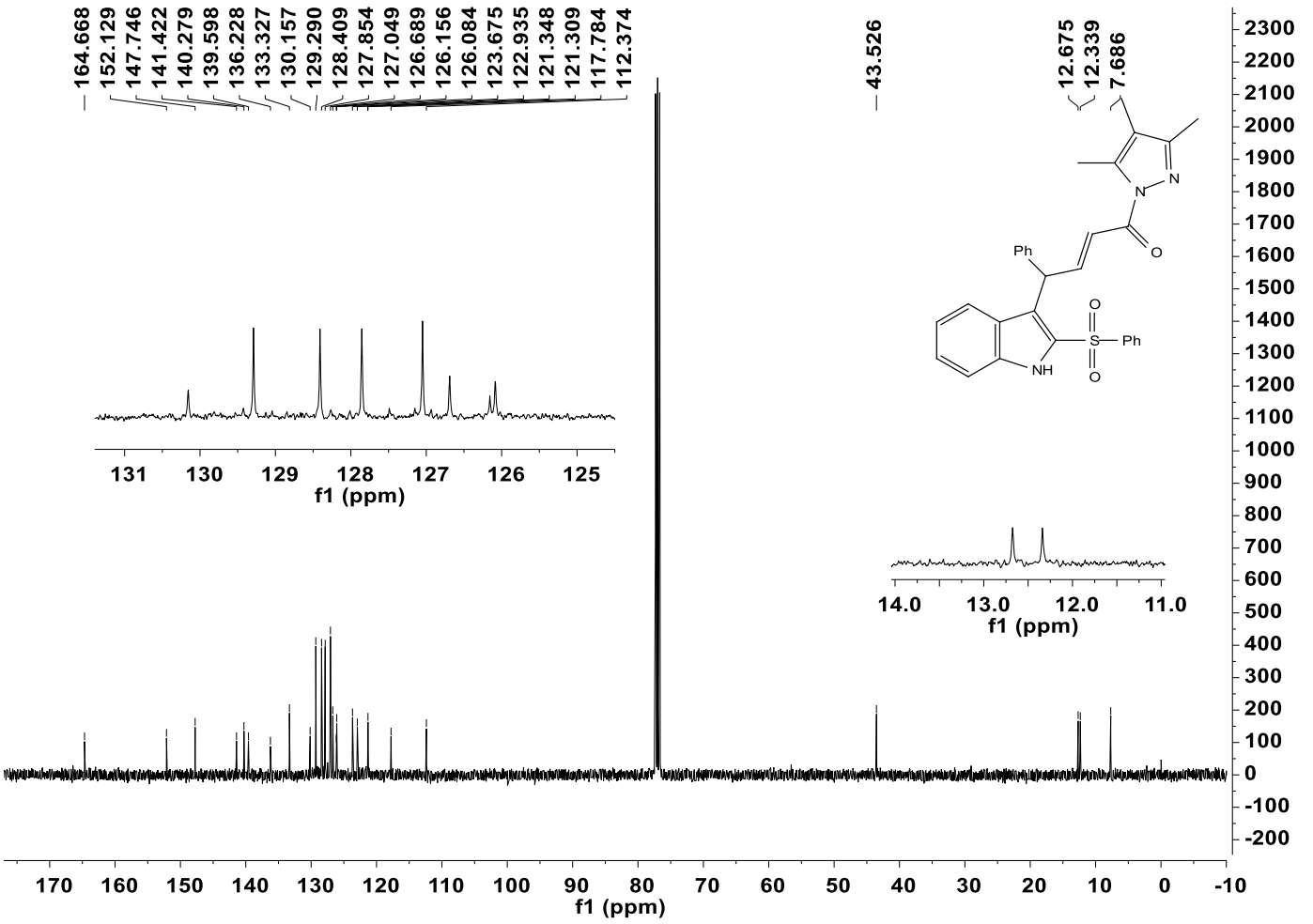
128.568
128.166
127.255
127.170
126.917
126.062
125.773
123.618
122.837
122.447
121.286
117.901
112.421
63.371
43.610
12.700
12.272
7.647
f1 (ppm)

4ah


9.179
7.931
7.913
7.683
7.661
7.644
7.623
7.423
7.402
7.380
7.361
7.353
7.312
7.297
7.277
7.197
7.180
7.140
7.126
7.017
6.997
6.979
6.015
5.994
2.465
2.197
1.913
7.260
f1 (ppm)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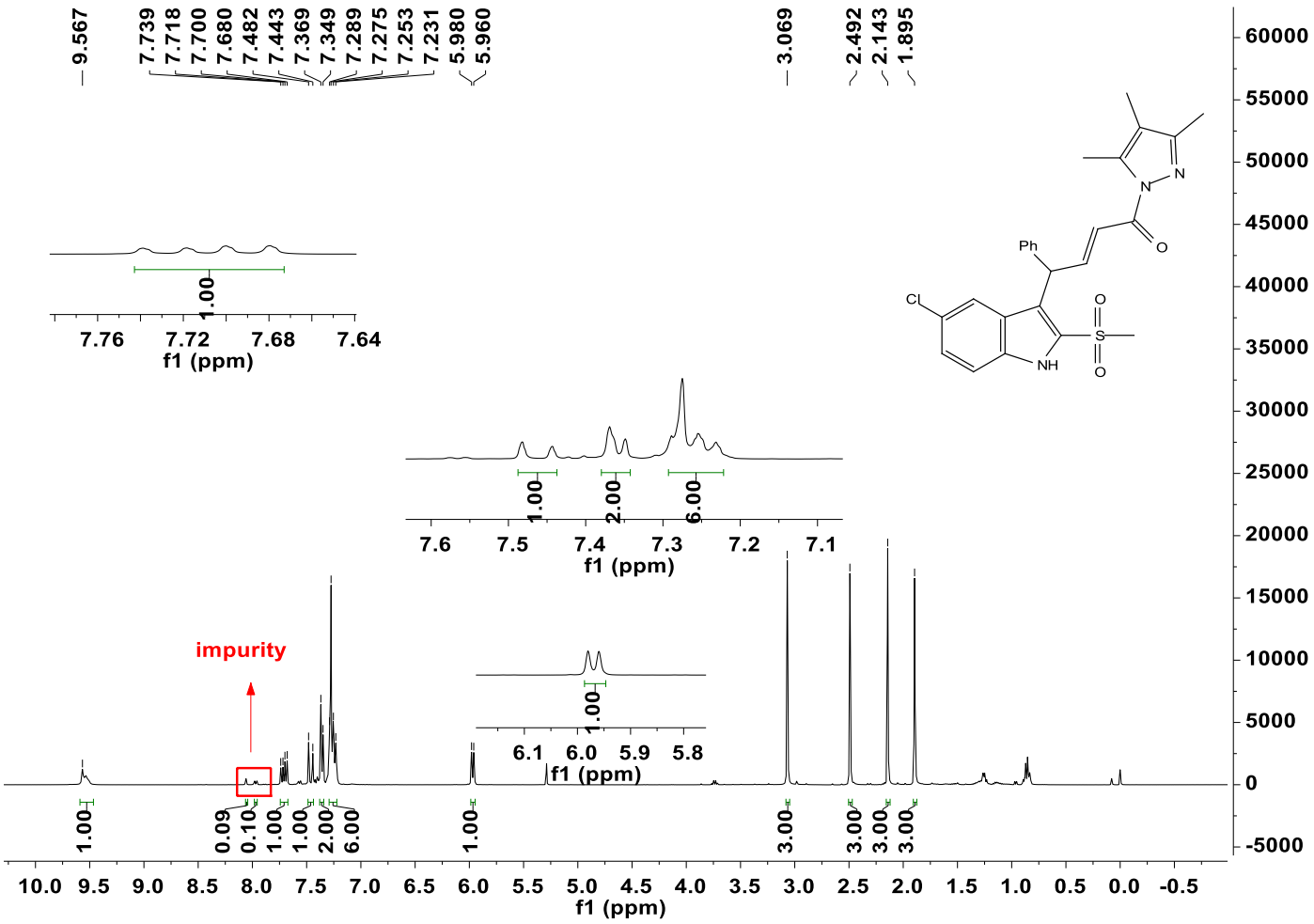
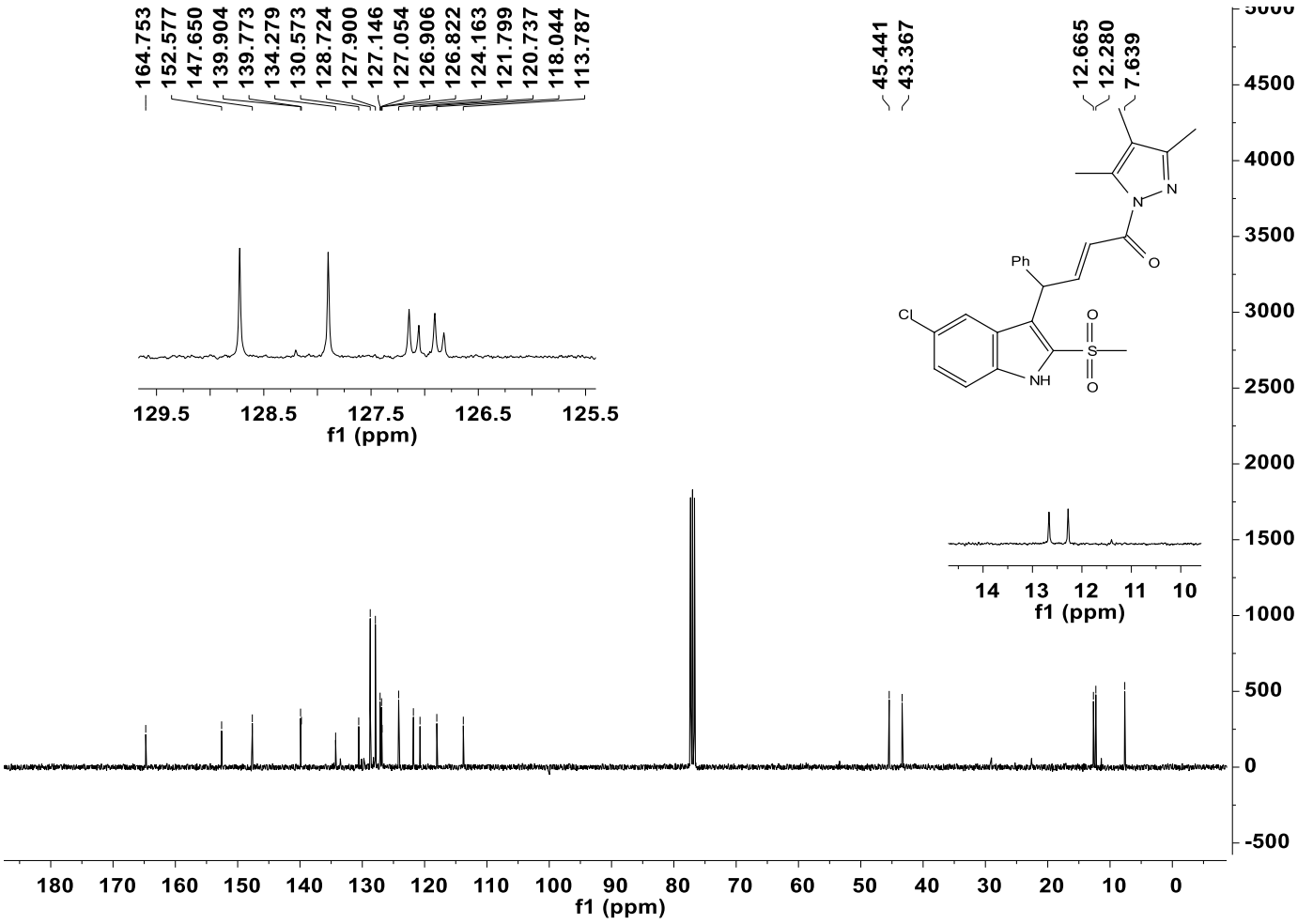
152.129
147.746
141.422
140.279
139.598
136.228
133.327
130.157
129.290
128.409
127.854
127.049
126.689
126.156
126.084
123.675
122.935
121.348
121.309
117.784
112.374
43.526
12.675
12.339
7.686
f1 (ppm)

4ai


9.567
7.739
7.718
7.700
7.680
7.482
7.443
7.369
7.349
7.289
7.275
7.253
7.231
5.980
5.960
3.069
2.492
2.143
1.895
impurity
1.00
0.09
0.10
1.00
1.00
2.00
6.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)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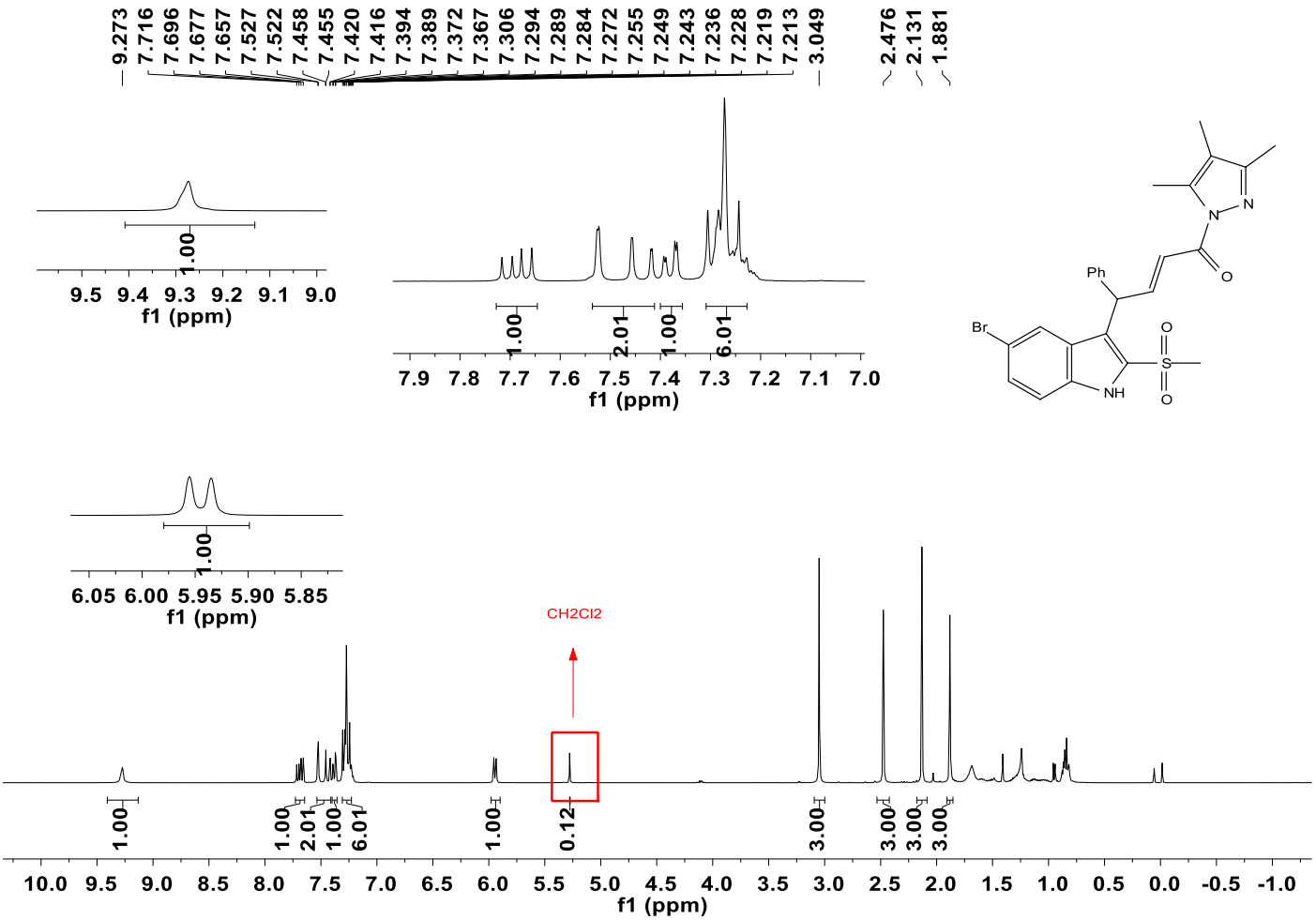
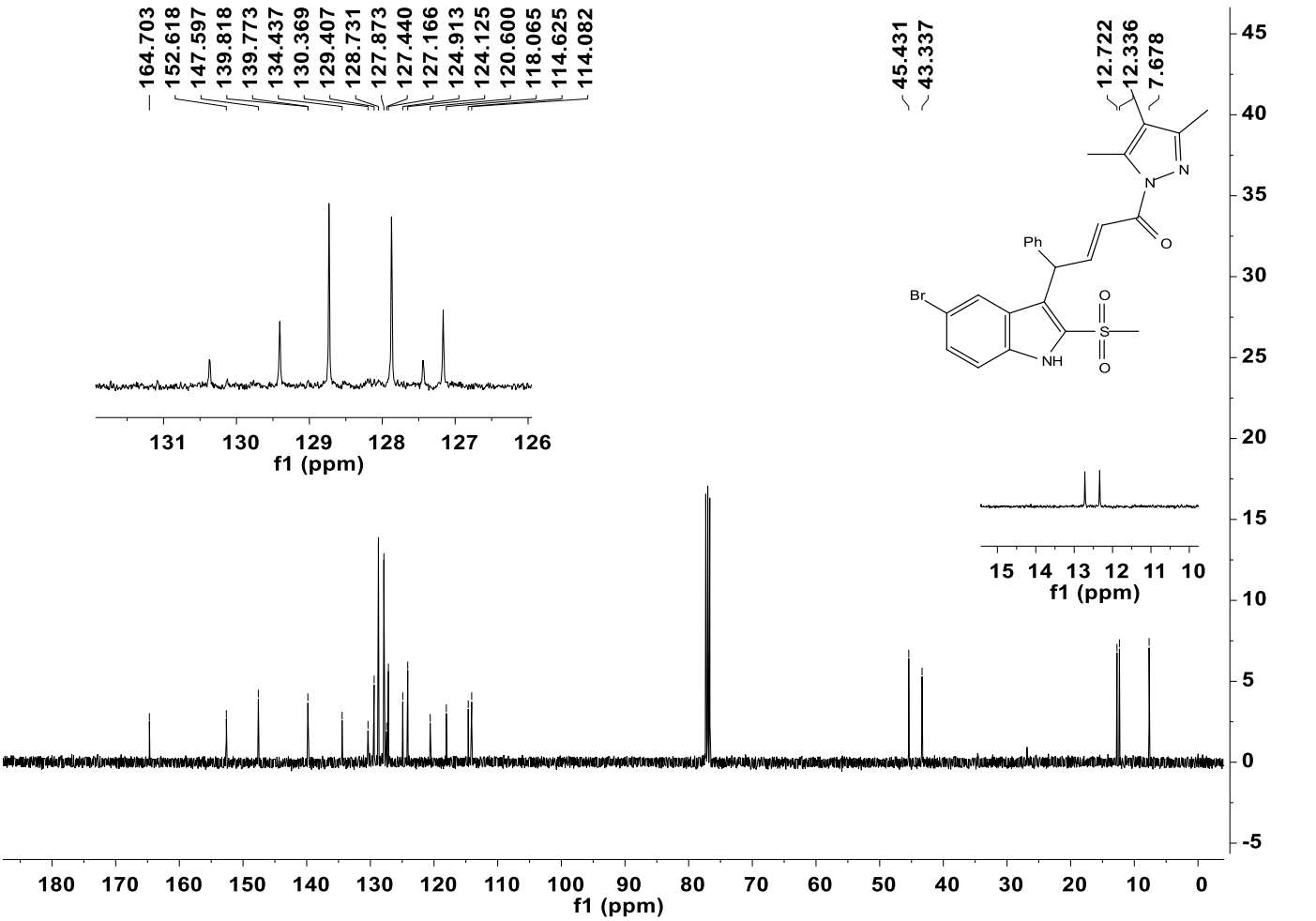
147.650
139.904
139.773
134.279
130.573
128.724
127.900
127.146
127.054
126.906
126.822
124.163
121.799
120.737
118.044
113.787
45.441
43.367
12.665
12.280
7.639
f1 (ppm)

4aj


9.273 7.716 7.696 7.677 7.657 7.527 7.522 7.458 7.455 7.420 7.416 7.394 7.389 7.372 7.367 7.306 7.294 7.289 7.284 7.272 7.255 7.249 7.243 7.236 7.228 7.219 7.213 3.049 2.476 2.131 1.881
1.00
9.5 9.4 9.3 9.2 9.1 9.0
f1 (ppm)
1.00 2.01 1.00 6.01
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
Ph
Br
NH
O
S
N
1.00
6.05 6.00 5.95 5.90 5.85
f1 (ppm)
CH2Cl2
1.00 1.00 2.01 1.00 6.01 1.00 0.12 3.00 3.00 3.00 3.00
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 -0.5 -1.0
f1 (ppm)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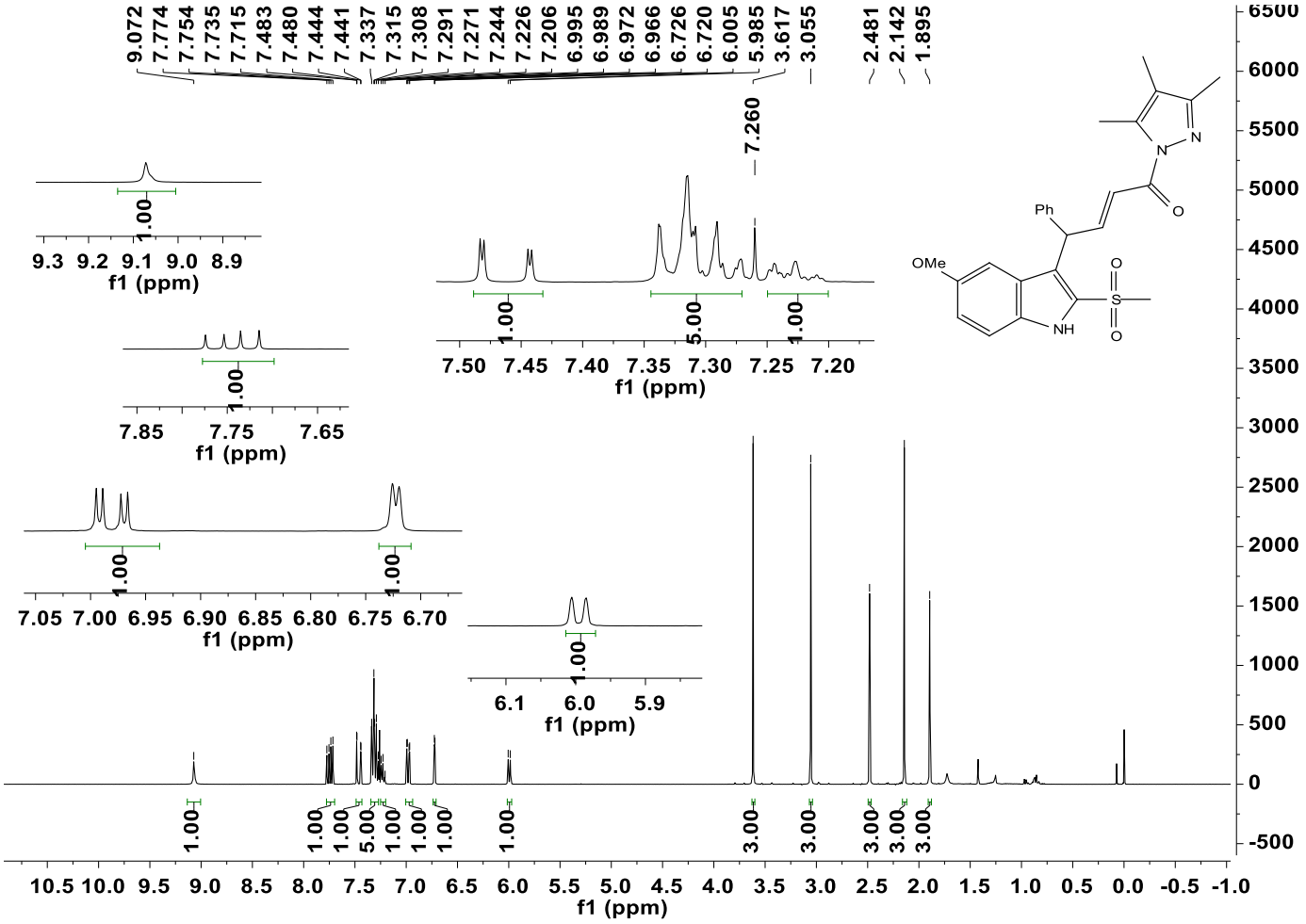
45.431 43.337
12.722 12.336 7.678
Ph
Br
NH
O
S
N
131 130 129 128 127 126
f1 (ppm)
15 14 13 12 11 10
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
45 40 35 30 25 20 15 10 5 0 -5

4ak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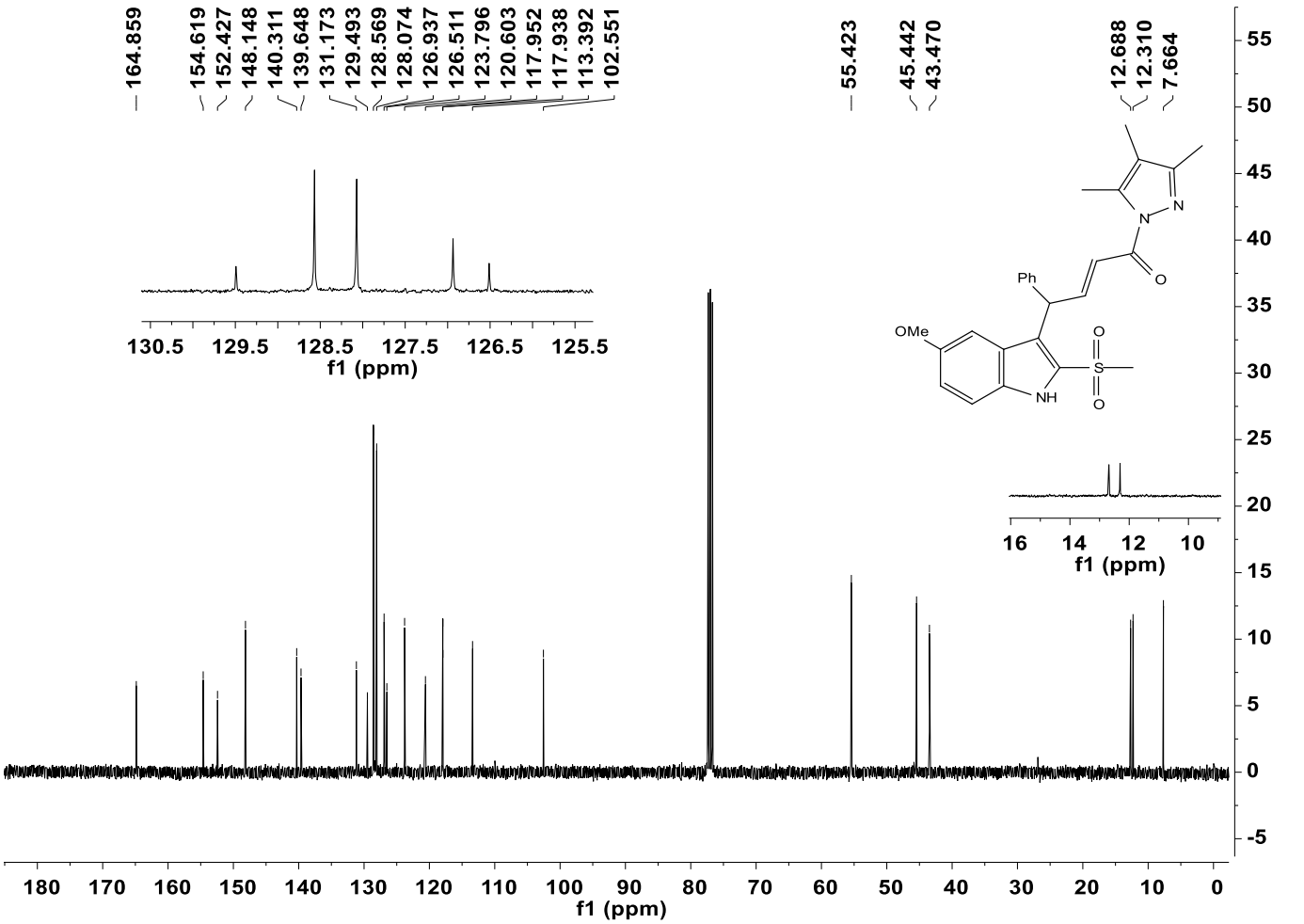
7.774
7.754
7.735
7.715
7.483
7.480
7.444
7.441
7.337
7.315
7.308
7.291
7.271
7.244
7.226
7.206
6.995
6.989
6.972
6.966
6.726
6.720
6.005
5.985
3.617
3.055
2.481
2.142
1.895
7.260
Ph
OMe
NH
f1 (ppm)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152.427
148.148
140.311
139.648
131.173
129.493
128.569
128.074
126.937
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123.796
120.603
117.952
117.938
113.392
102.551
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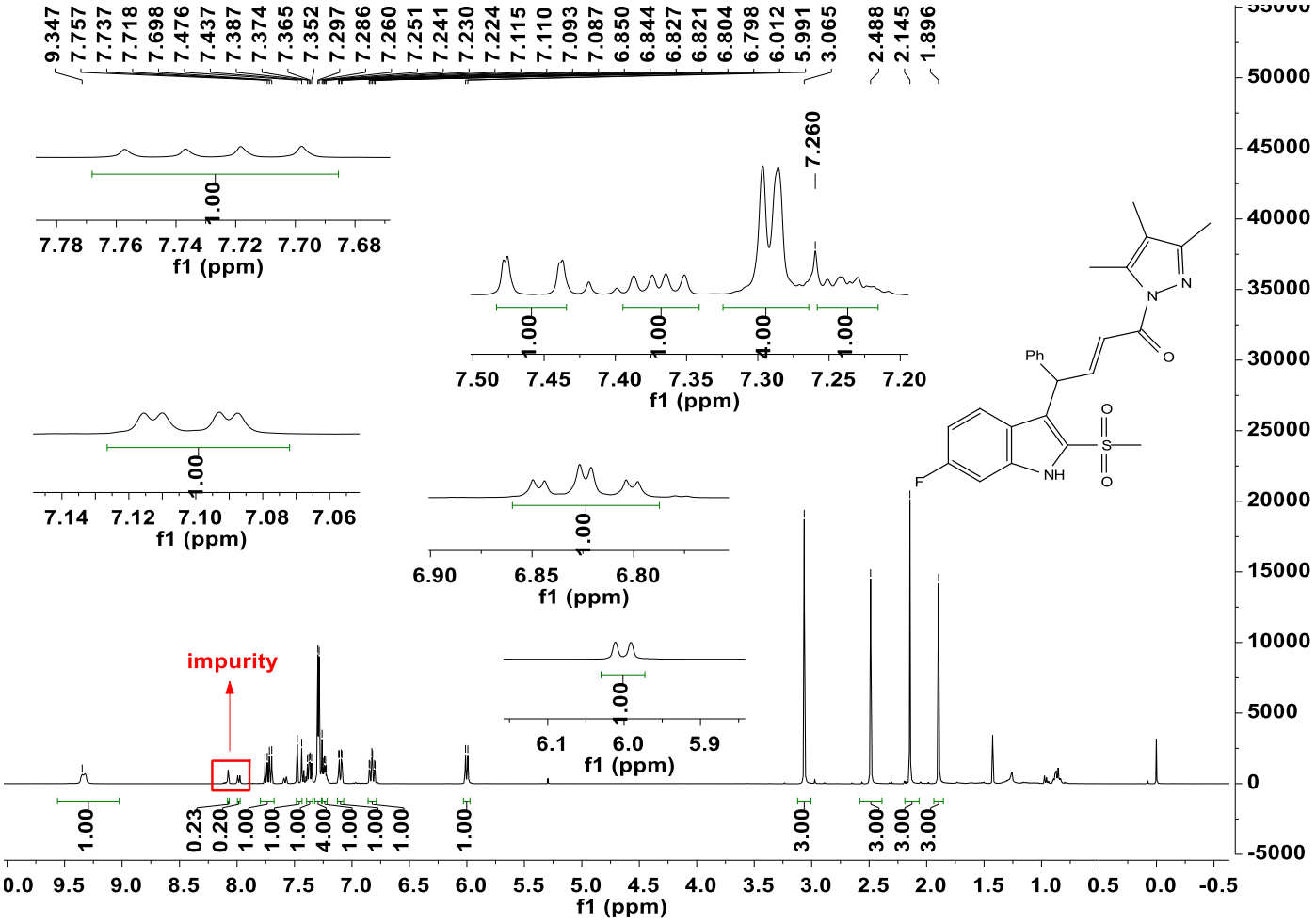
45.442
43.470
12.688
12.310
7.664
Ph
OMe
NH
f1 (ppm)

4al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7.737
7.718
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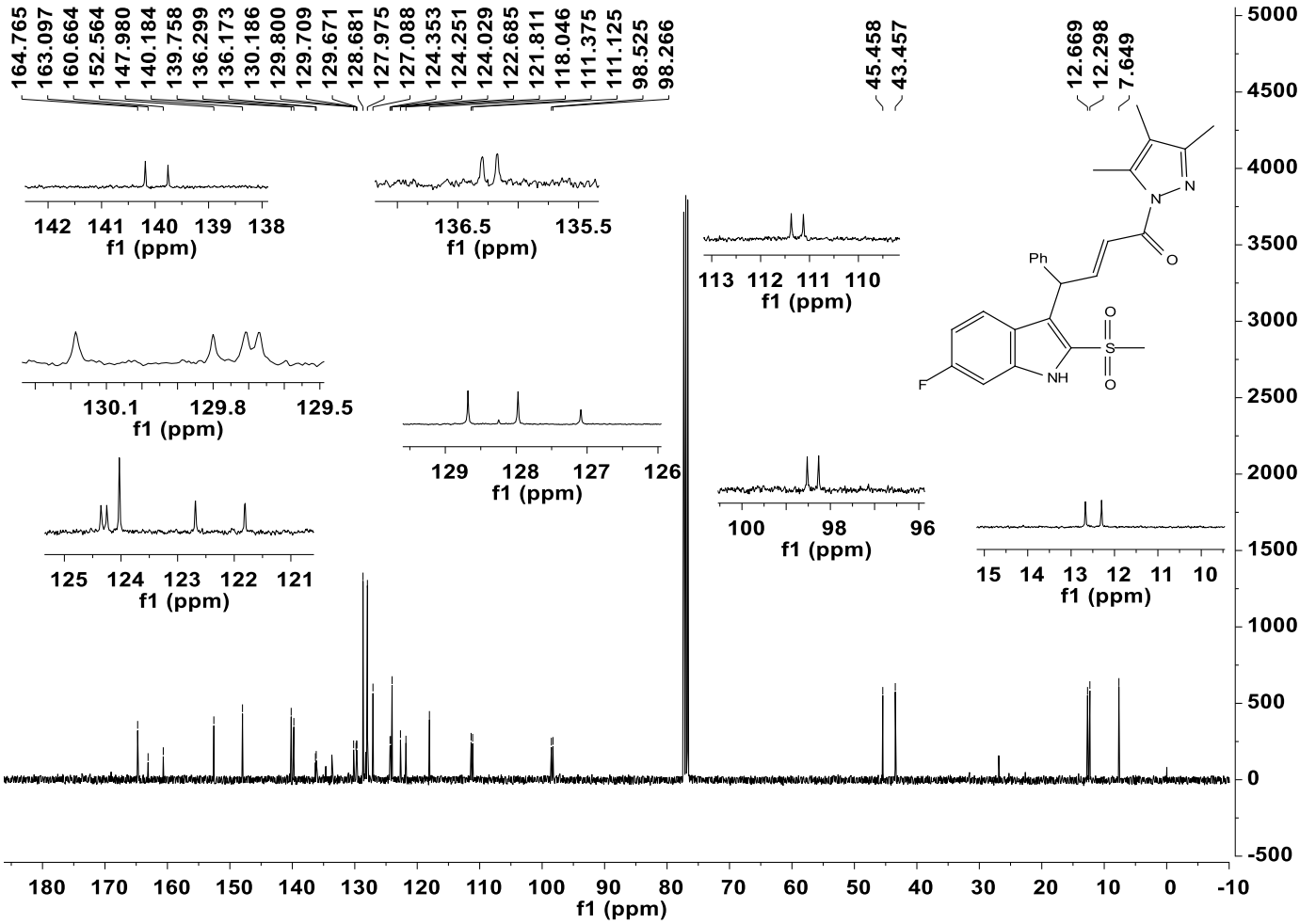
7.476
7.437
7.387
7.374
7.365
7.352
7.297
7.286
7.260
7.251
7.241
7.230
7.224
7.115
7.110
7.093
7.087
6.850
6.844
6.827
6.821
6.804
6.798
6.012
5.991
3.065
2.488
2.145
1.896
7.260
impurity
f1 (ppm)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163.097
160.664
152.564
147.980
140.184
139.758
136.299
136.173
130.186
129.800
129.709
129.671
128.681
127.975
127.088
124.353
124.251
124.029
122.685
121.811
118.046
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111.125
98.525
98.266
45.458
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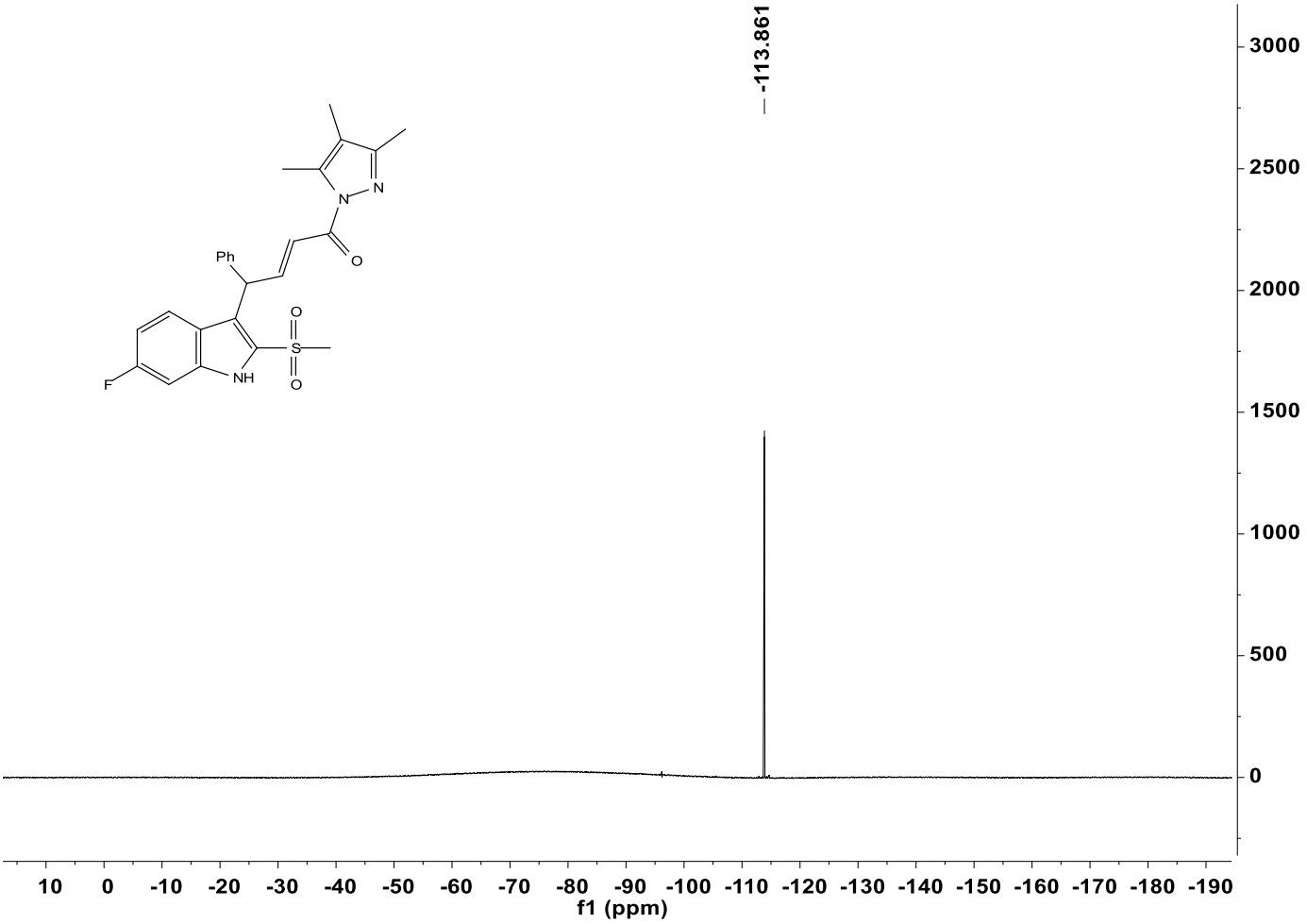
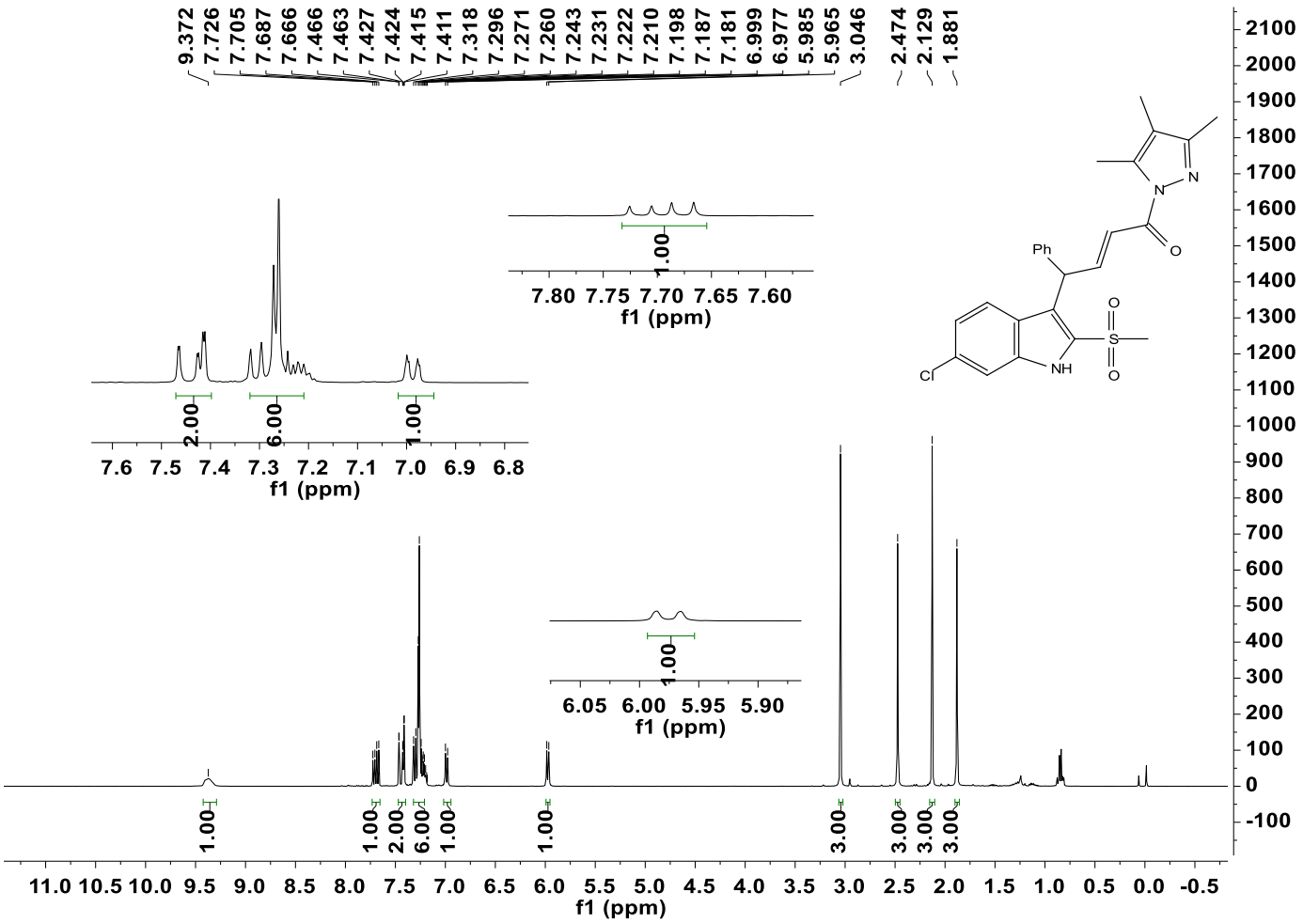
12.669
12.298
7.649
f1 (ppm)


-113.861
3000
2500
2000
1500
1000
500
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)
Ph
O
N
N
O
S
O
NH
F

4am


9.372
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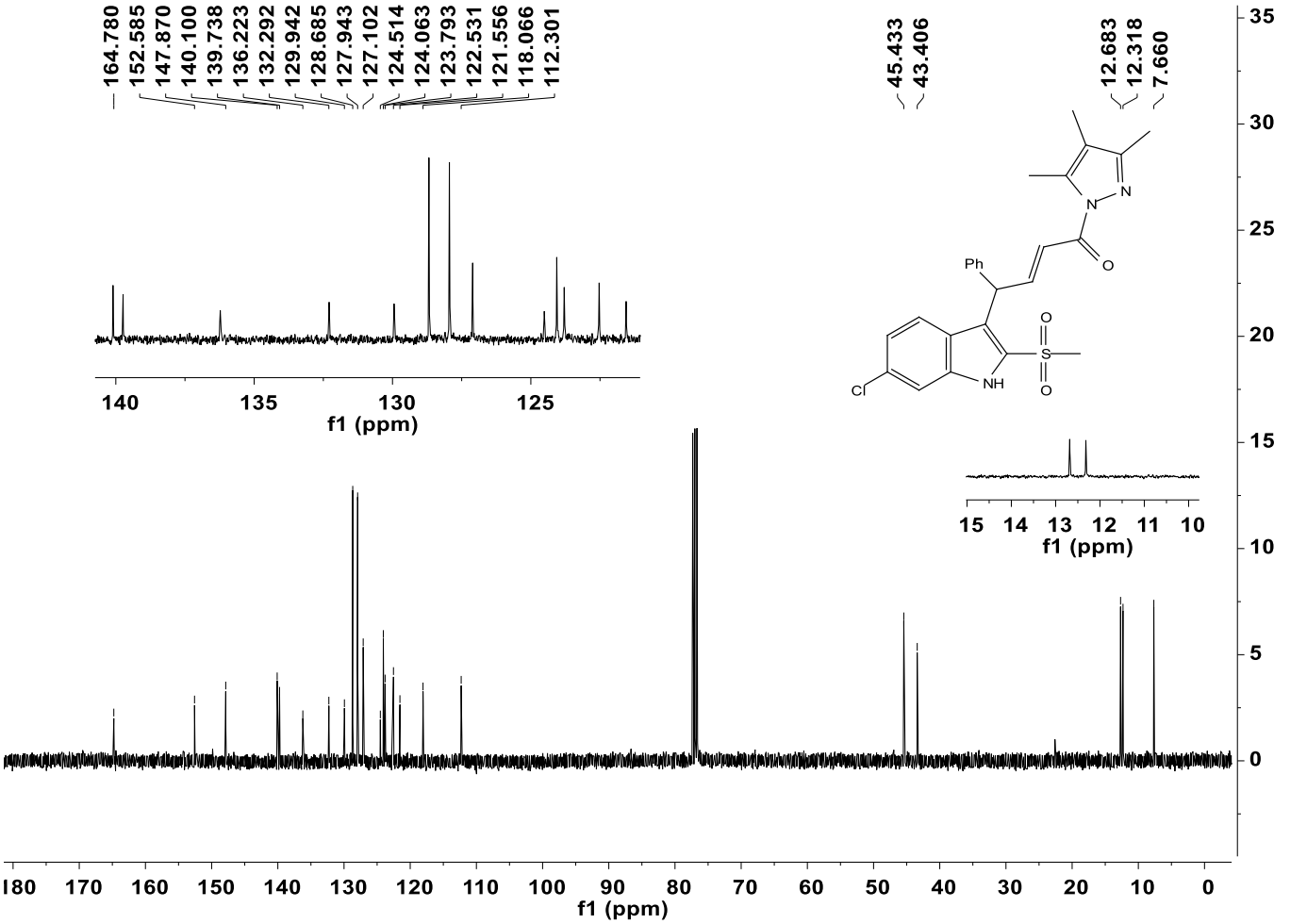
7.687
7.666
7.466
7.463
7.427
7.424
7.415
7.411
7.318
7.296
7.271
7.260
7.243
7.231
7.222
7.210
7.198
7.187
7.181
6.999
6.977
5.985
5.965
3.046
2.474
2.129
1.881
1.00
7.80 7.75 7.70 7.65 7.60
f1 (ppm)
2.00
6.00
1.00
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00
6.05 6.00 5.95 5.90
f1 (ppm)
Ph
O
N
N
O
S
O
O
Cl
NH
1.00
1.00
2.00
6.00
1.00
1.00
3.00
3.00
3.00
3.00
11.0 10.5 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 -0.5
f1 (ppm)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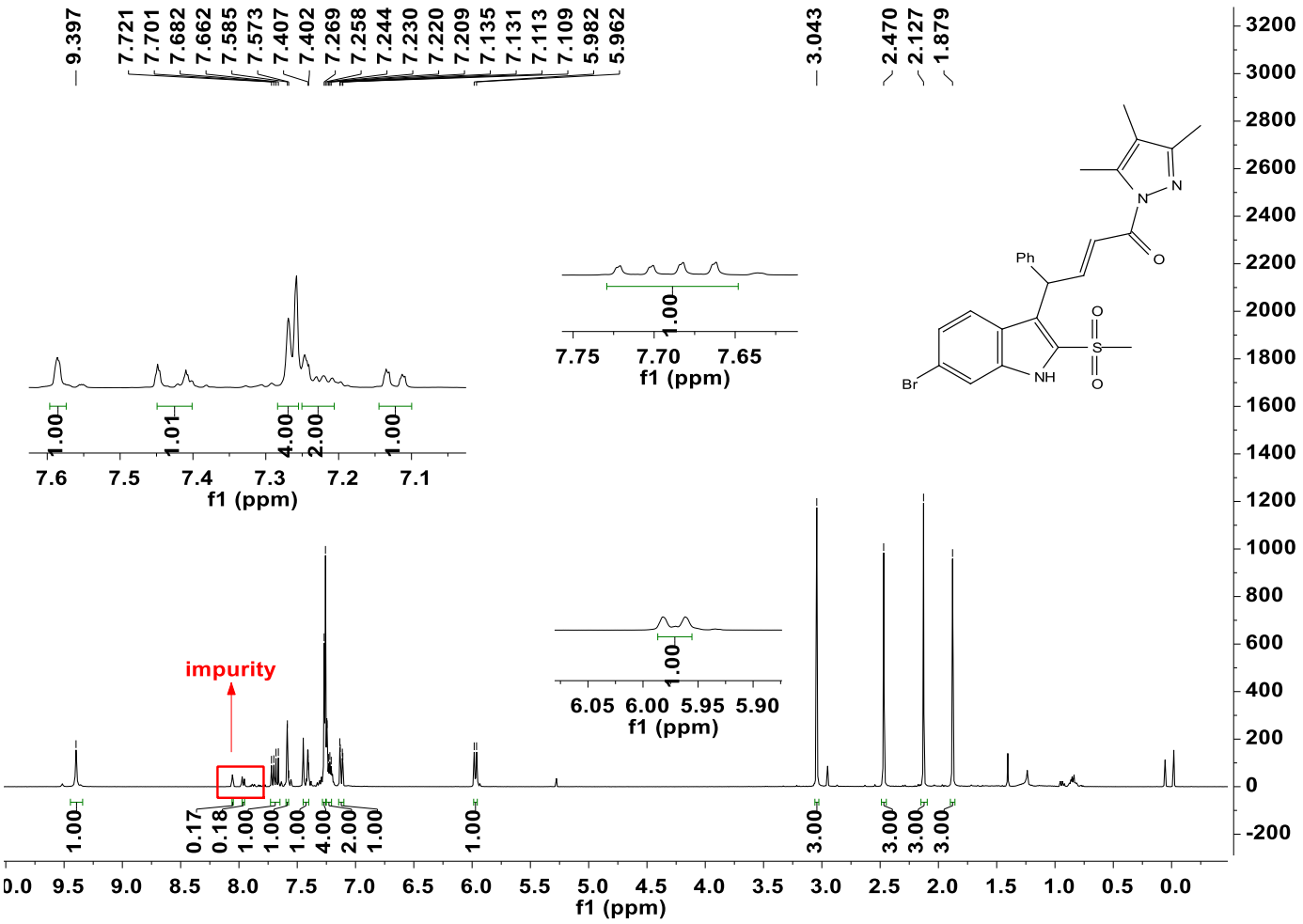
139.738
136.223
132.292
129.942
128.685
127.943
127.102
124.514
124.063
123.793
122.531
121.556
118.066
112.301
140
135
130
125
f1 (ppm)
45.433
43.406
12.683
12.318
7.660
Ph
O
N
N
O
S
O
O
Cl
NH
15 14 13 12 11 10
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4an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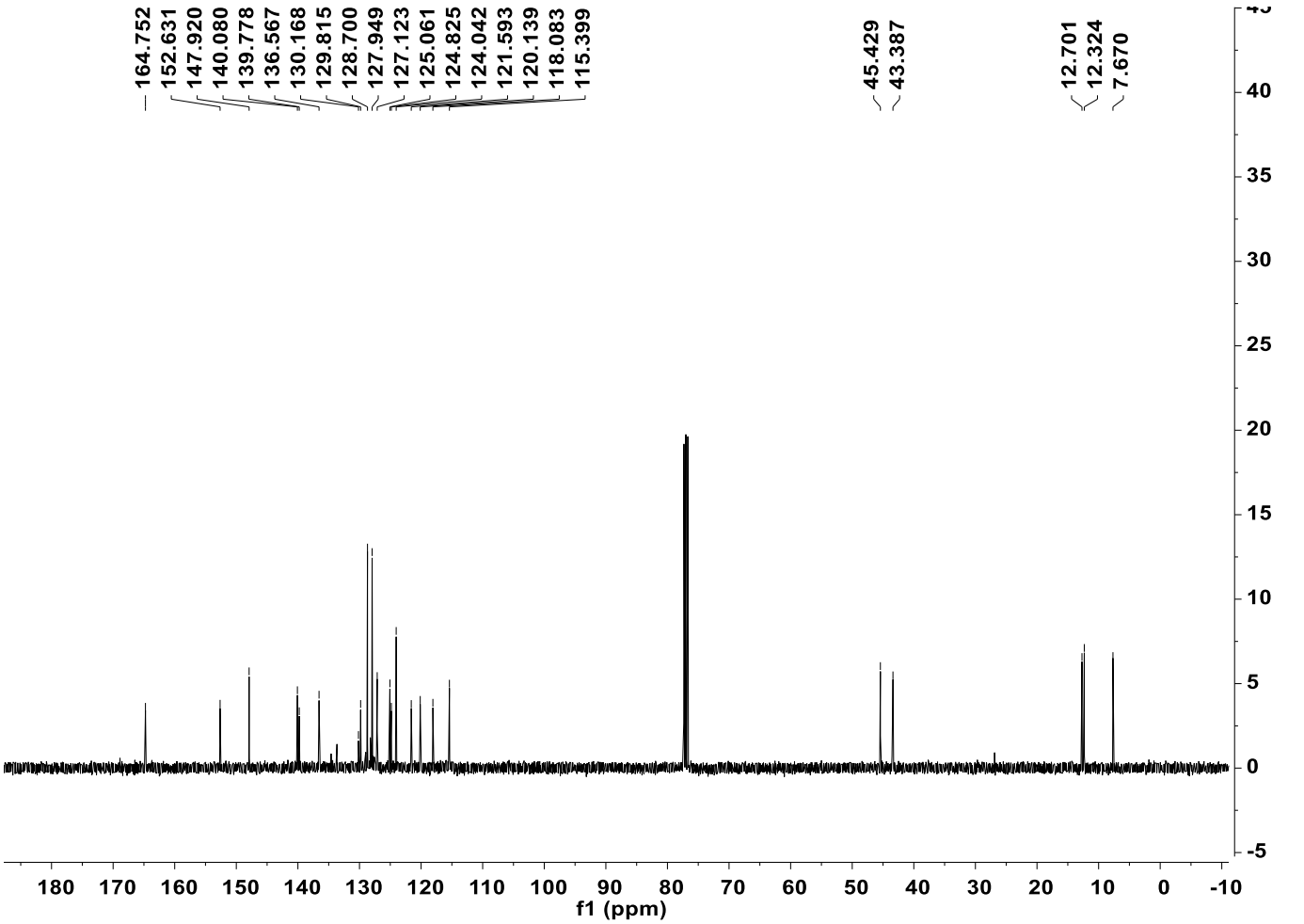
7.701
7.682
7.662
7.585
7.573
7.407
7.402
7.269
7.258
7.244
7.230
7.220
7.209
7.135
7.131
7.113
7.109
5.982
5.962
3.043
2.470
2.127
1.879
impurity
f1 (ppm)


164.752
152.631
147.920
140.080
139.778
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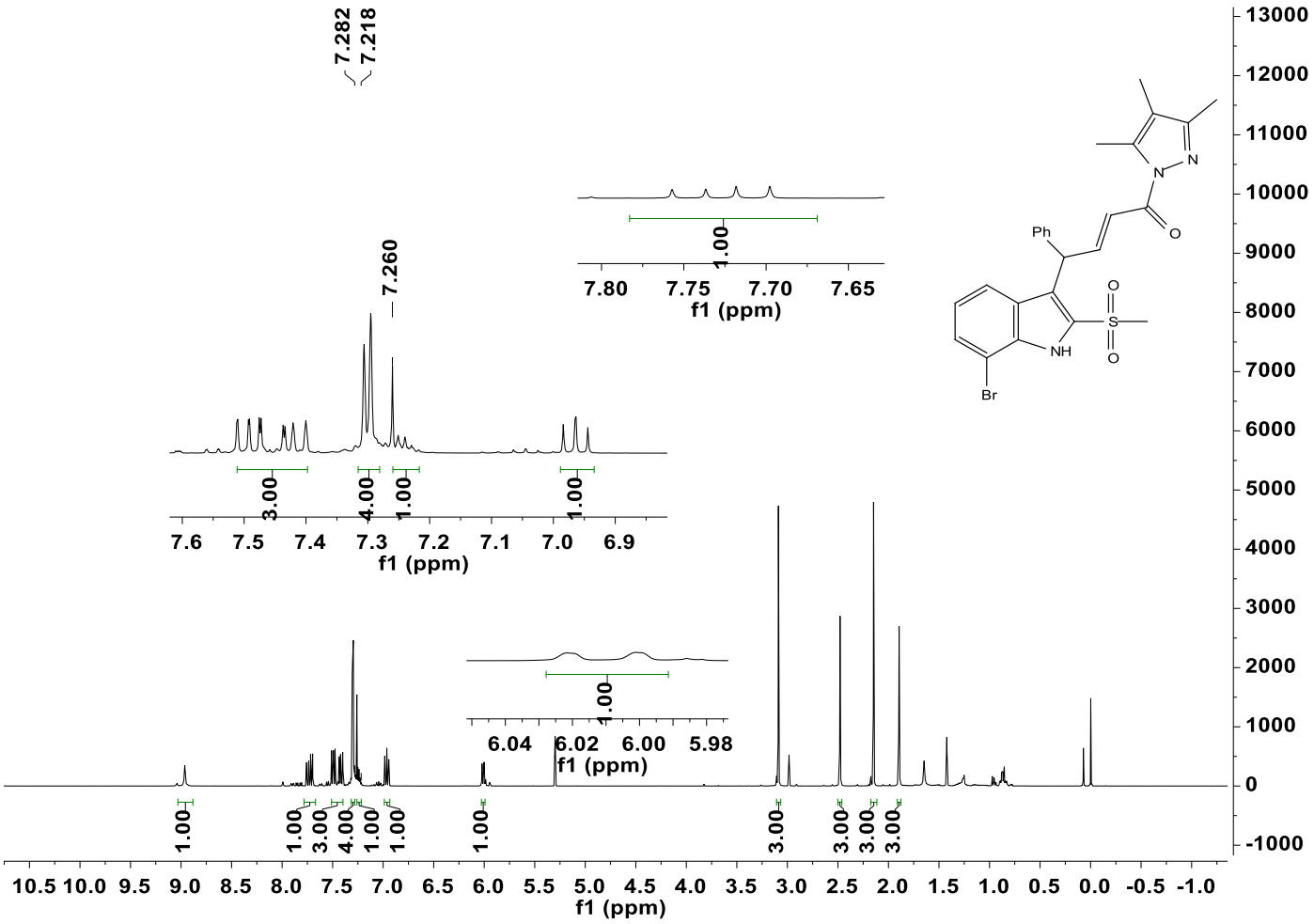
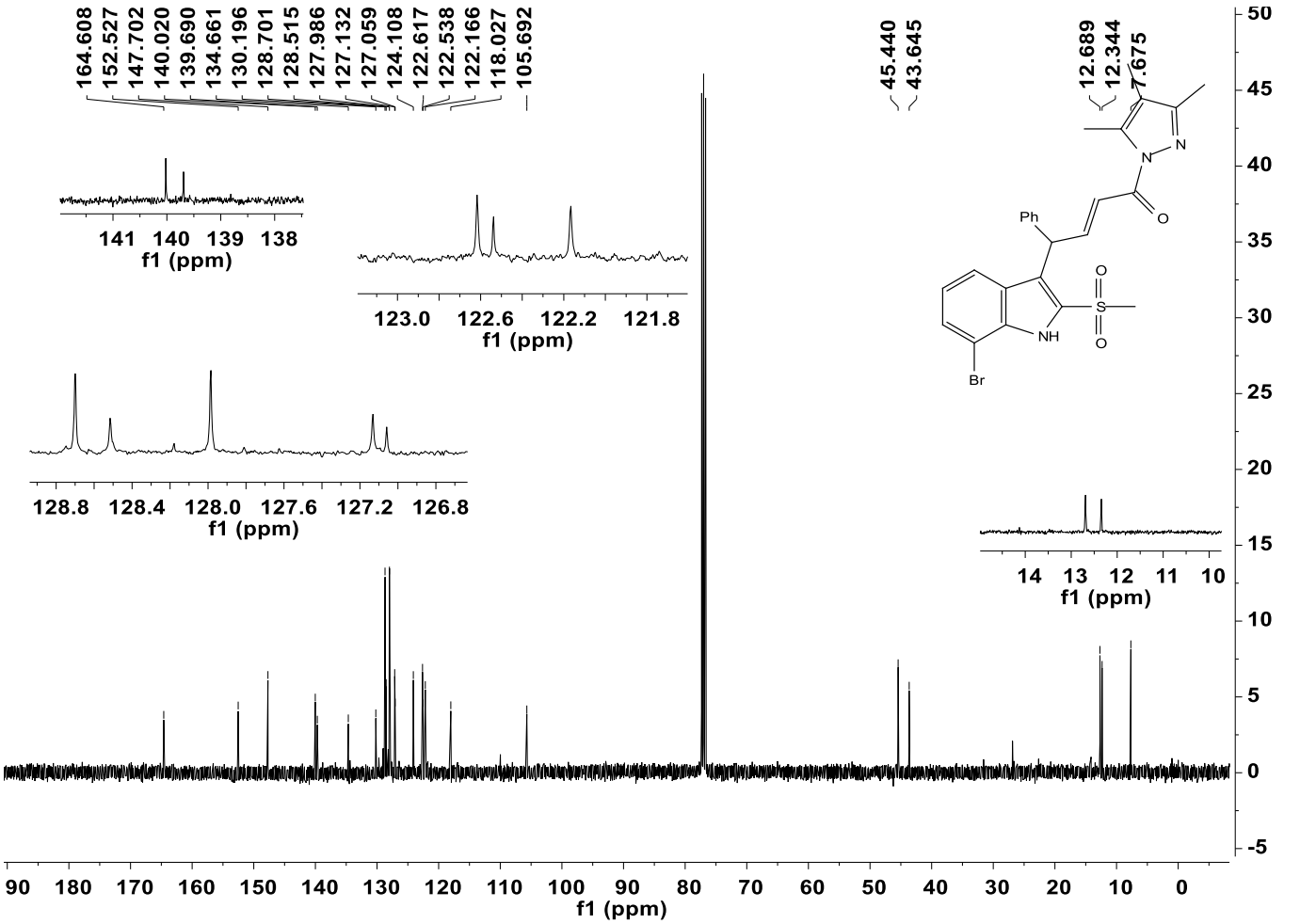
130.168
129.815
128.700
127.949
127.123
125.061
124.825
124.042
121.593
120.139
118.083
115.399
45.429
43.387
12.701
12.324
7.670
f1 (ppm)

4ao


7.282
7.218
7.260
1.00
7.80 7.75 7.70 7.65
f1 (ppm)
3.00
4.00
1.00
1.00
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.00
6.04 6.02 6.00 5.98
f1 (ppm)
1.00
1.00
3.00
4.00
1.00
1.00
1.00
3.00
3.00
3.00
3.00
10.5 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 -0.5 -1.0
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Ph
O
N
N
O
S
O
NH
Br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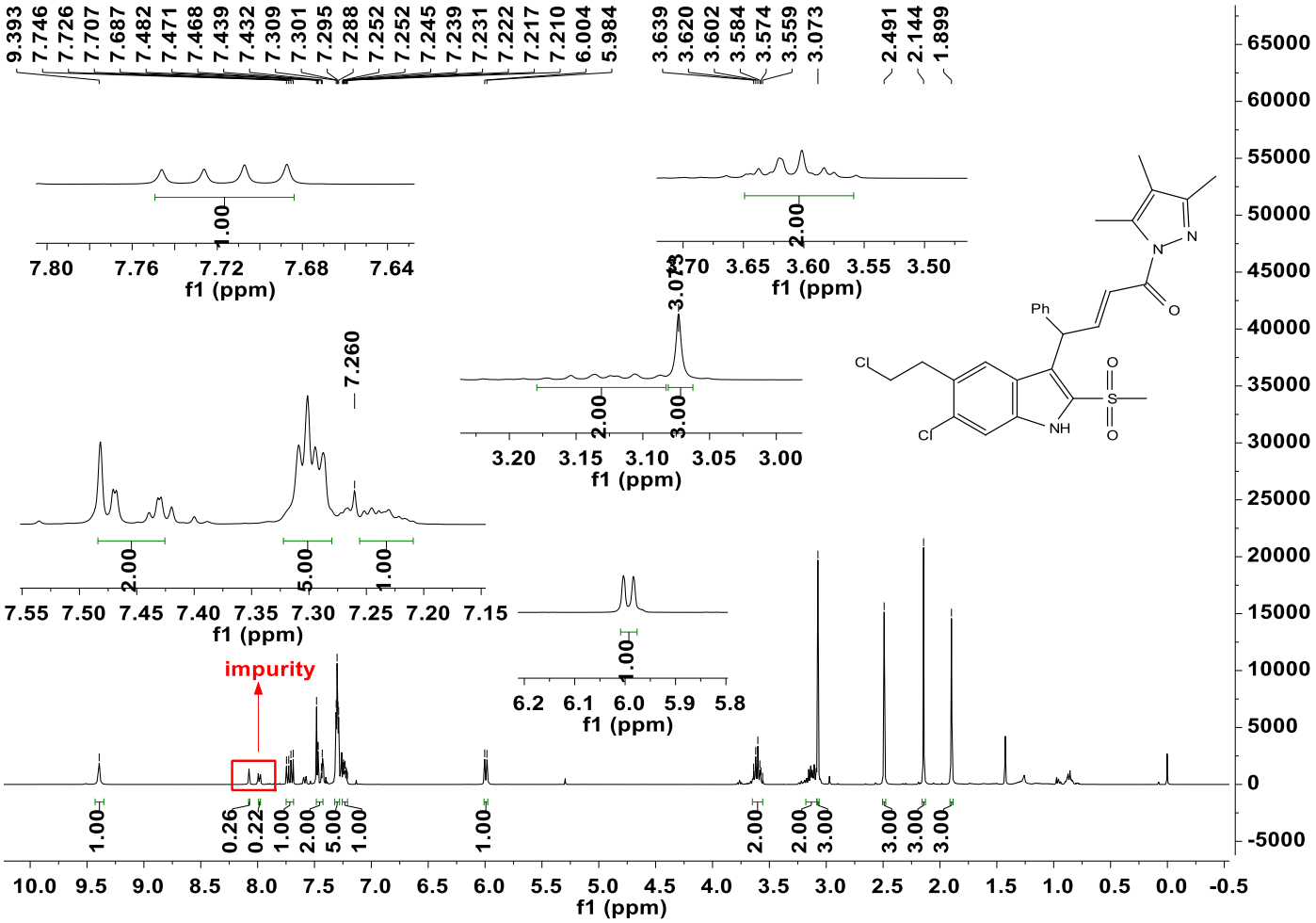
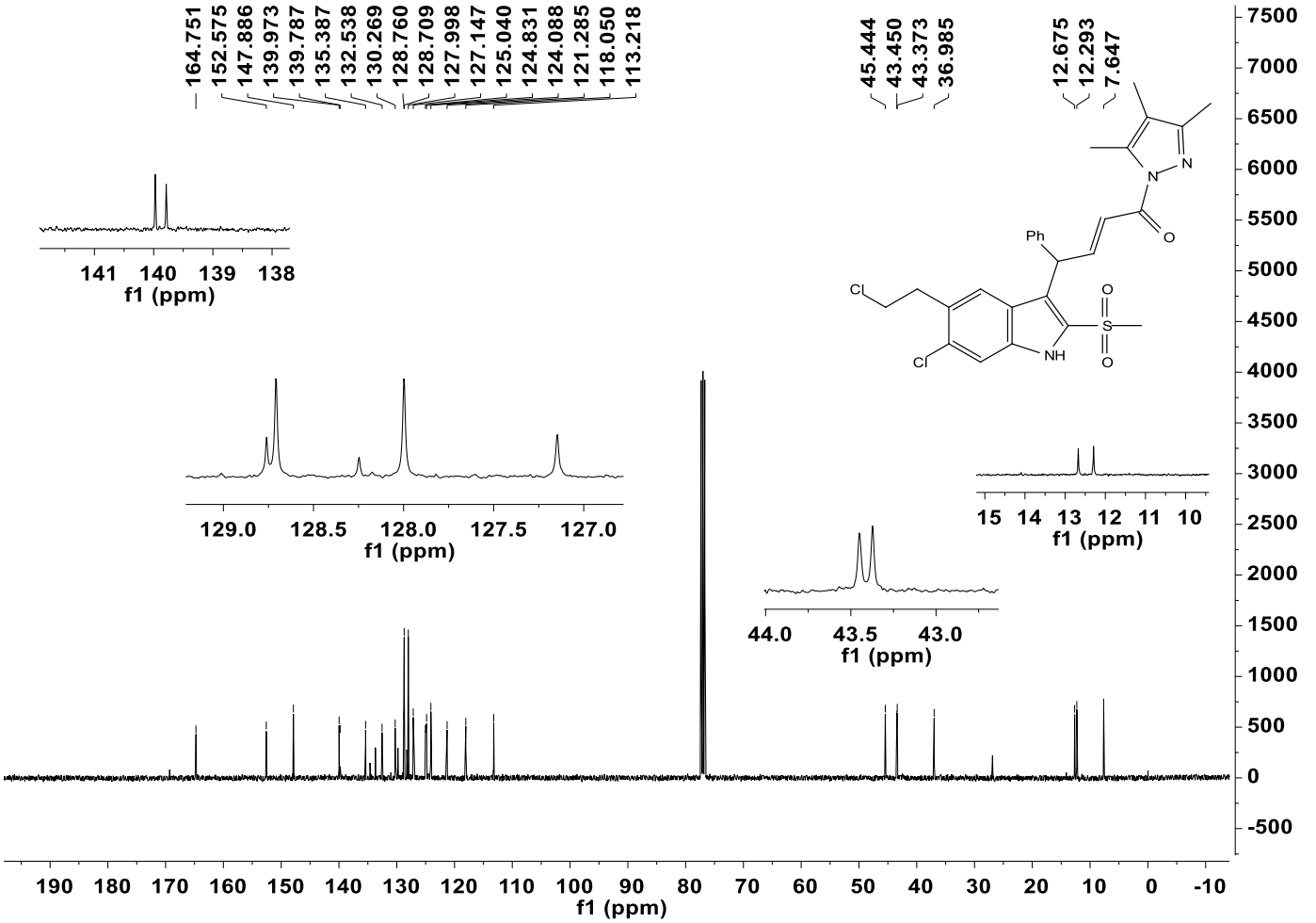
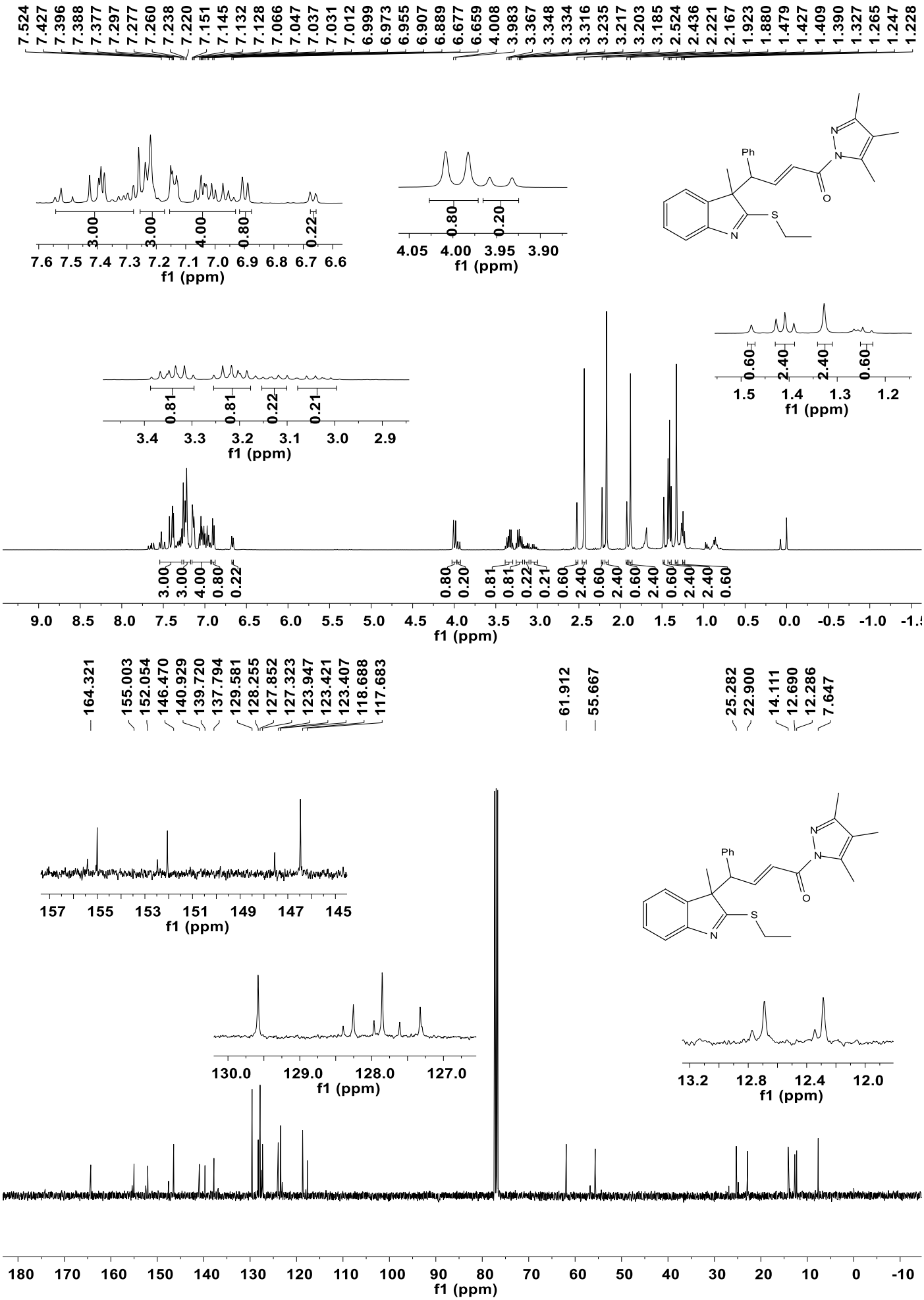
152.527
147.702
140.020
139.690
134.661
130.196
128.701
128.515
127.986
127.132
127.059
124.108
122.617
122.538
122.166
118.027
105.692
141 140 139 138
f1 (ppm)
123.0 122.6 122.2 121.8
f1 (ppm)
128.8 128.4 128.0 127.6 127.2 126.8
f1 (ppm)
45.440
43.645
12.689
12.344
7.675
14 13 12 11 10
f1 (ppm)
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
50
45
40
35
30
25
20
15
10
5
0
-5
Ph
O
N
N
O
S
O
NH
Br

4ap

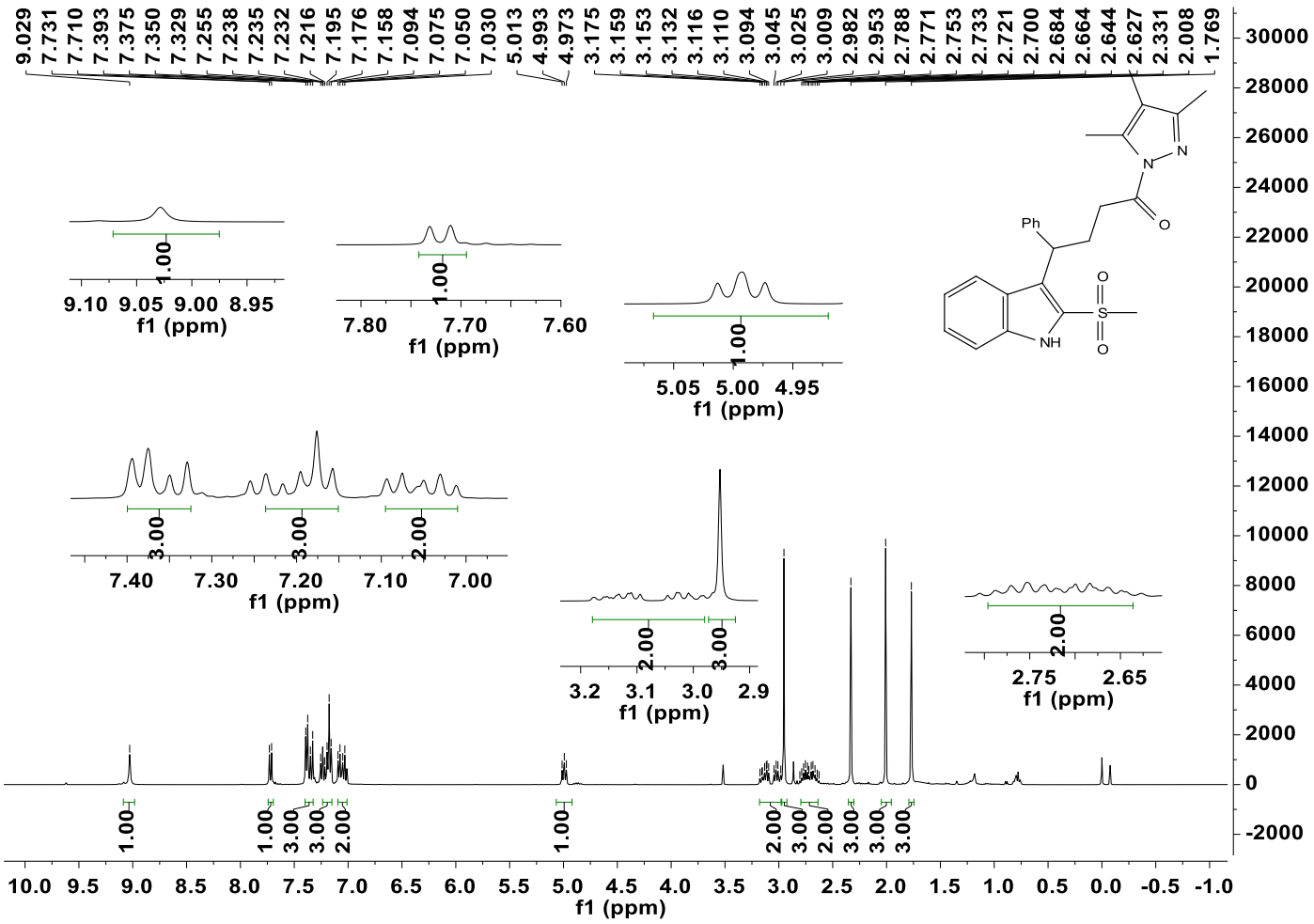

9.393 7.746 7.726 7.707 7.687 7.482 7.471 7.468 7.439 7.432 7.309 7.301 7.295 7.288 7.252 7.252 7.245 7.239 7.231 7.222 7.217 7.210 6.004 5.984
3.639 3.620 3.602 3.584 3.574 3.559 3.073
2.491 2.144 1.899
7.260
impurity
f1 (ppm)

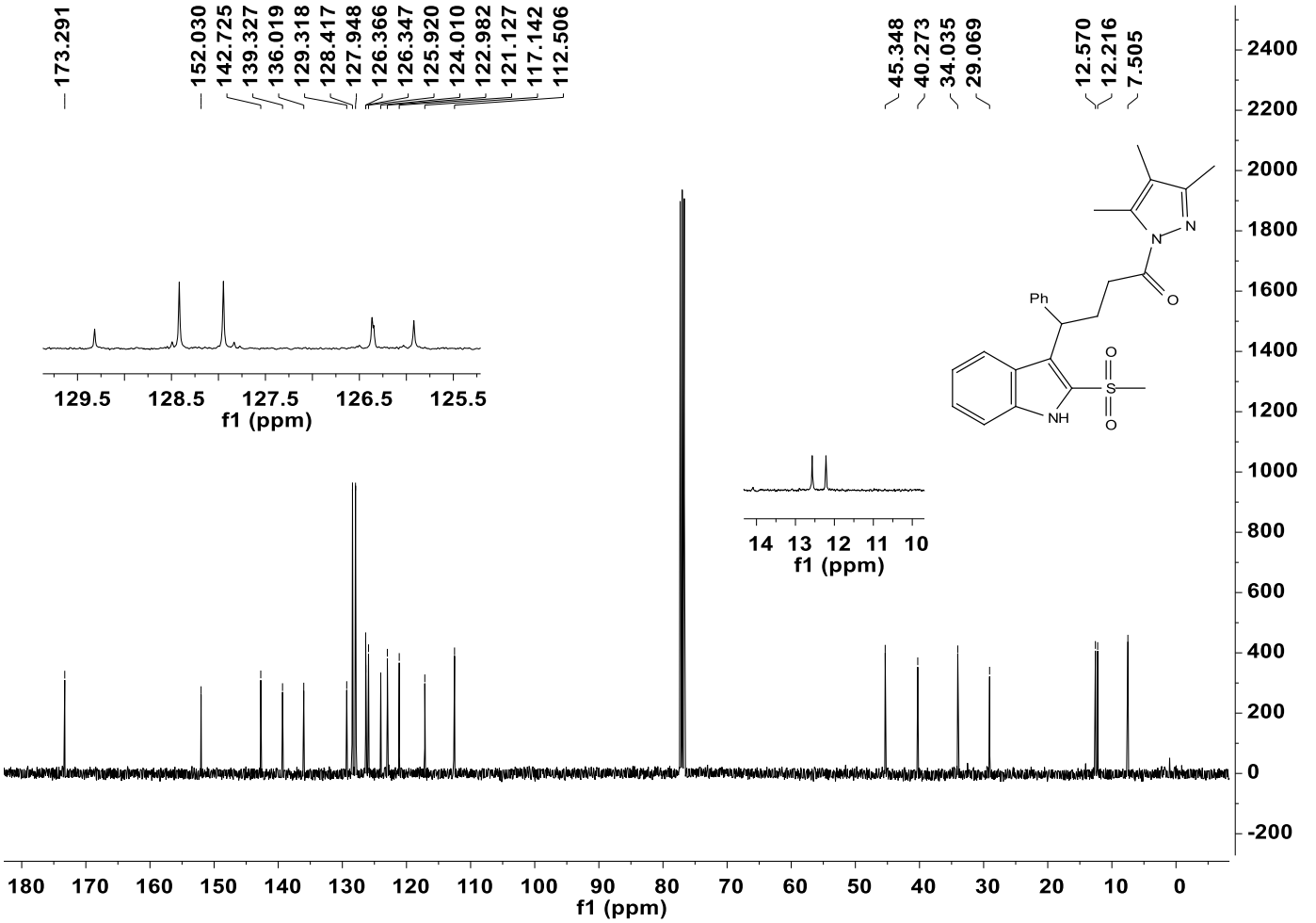

164.751 152.575 147.886 139.973 139.787 135.387 132.538 130.269 128.760 128.709 127.998 127.147 125.040 124.831 124.088 121.285 118.050 113.218
45.444 43.450 43.373 36.985
12.675 12.293 7.647
f1 (ppm)

3aq

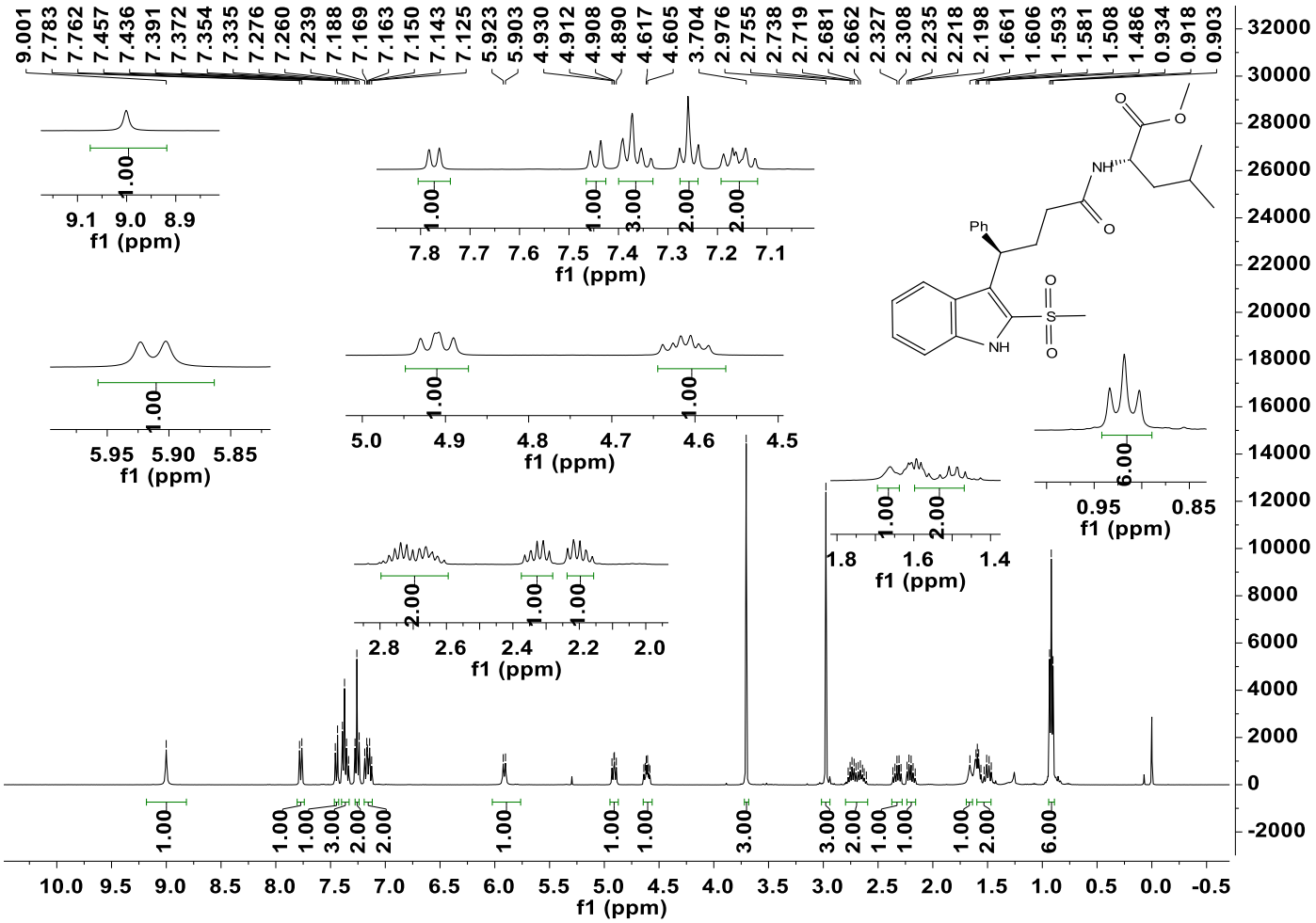

7.524 7.427 7.396 7.388 7.377 7.297 7.277 7.260 7.238 7.220 7.151 7.145 7.132 7.128 7.066 7.047 7.037 7.031 7.012 6.999 6.973 6.955 6.907 6.889 6.677 6.659 4.008 3.983 3.367 3.348 3.334 3.316 3.235 3.217 3.203 3.185 2.524 2.436 2.221 2.167 1.923 1.880 1.479 1.427 1.409 1.390 1.327 1.265 1.247 1.228
3.00 3.00 4.00 0.80 0.22
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
0.80 0.20
4.05 4.00 3.95 3.90
f1 (ppm)
Ph
N
N
O
S
N
0.81 0.81 0.22 0.21
3.4 3.3 3.2 3.1 3.0 2.9
f1 (ppm)
0.60 2.40 2.40 0.60
1.5 1.4 1.3 1.2
f1 (ppm)
3.00 3.00 4.00 0.80 0.22 0.80 0.20 0.81 0.81 0.22 0.21 0.60 2.40 0.60 2.40 0.60 2.40 0.60 2.40 2.40 0.60
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 -0.5 -1.0
f1 (ppm)
164.321 155.003 152.054 146.470 140.929 139.720 137.794 129.581 128.255 127.852 127.323 123.947 123.421 123.407 118.688 117.683
61.912 55.667
25.282 22.900 14.111 12.690 12.286 7.647
157 155 153 151 149 147 145
f1 (ppm)
Ph
N
N
O
S
N
130.0 129.0 128.0 127.0
f1 (ppm)
13.2 12.8 12.4 12.0
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

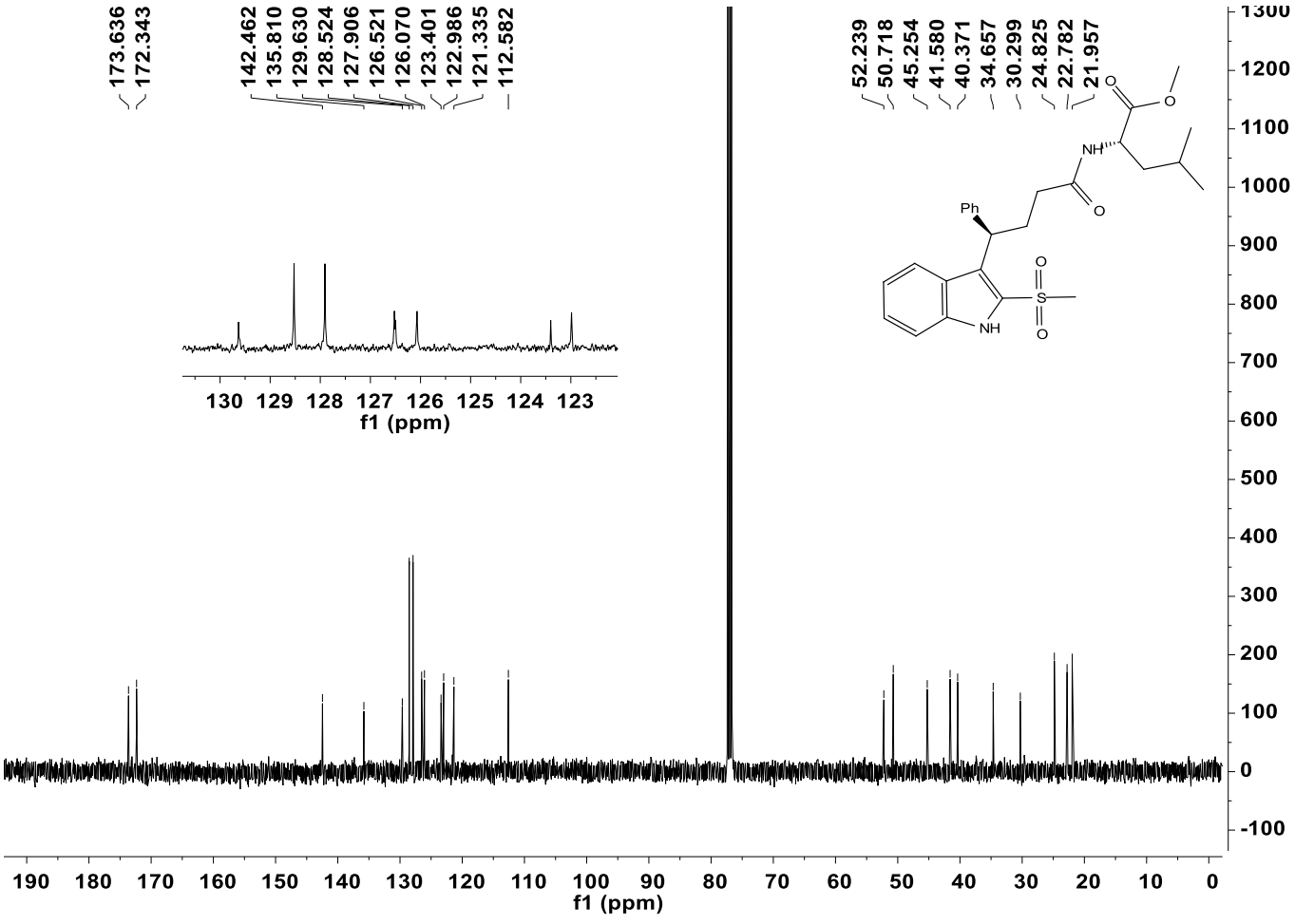
5aa


9.029 7.731 7.710 7.393 7.375 7.350 7.329 7.255 7.238 7.235 7.232 7.216 7.195 7.176 7.158 7.094 7.075 7.050 7.030 5.013 4.993 4.973 3.175 3.159 3.153 3.132 3.116 3.110 3.094 3.045 3.025 3.009 2.982 2.953 2.788 2.771 2.753 2.733 2.721 2.700 2.684 2.664 2.644 2.627 2.331 2.008 1.769
f1 (ppm)

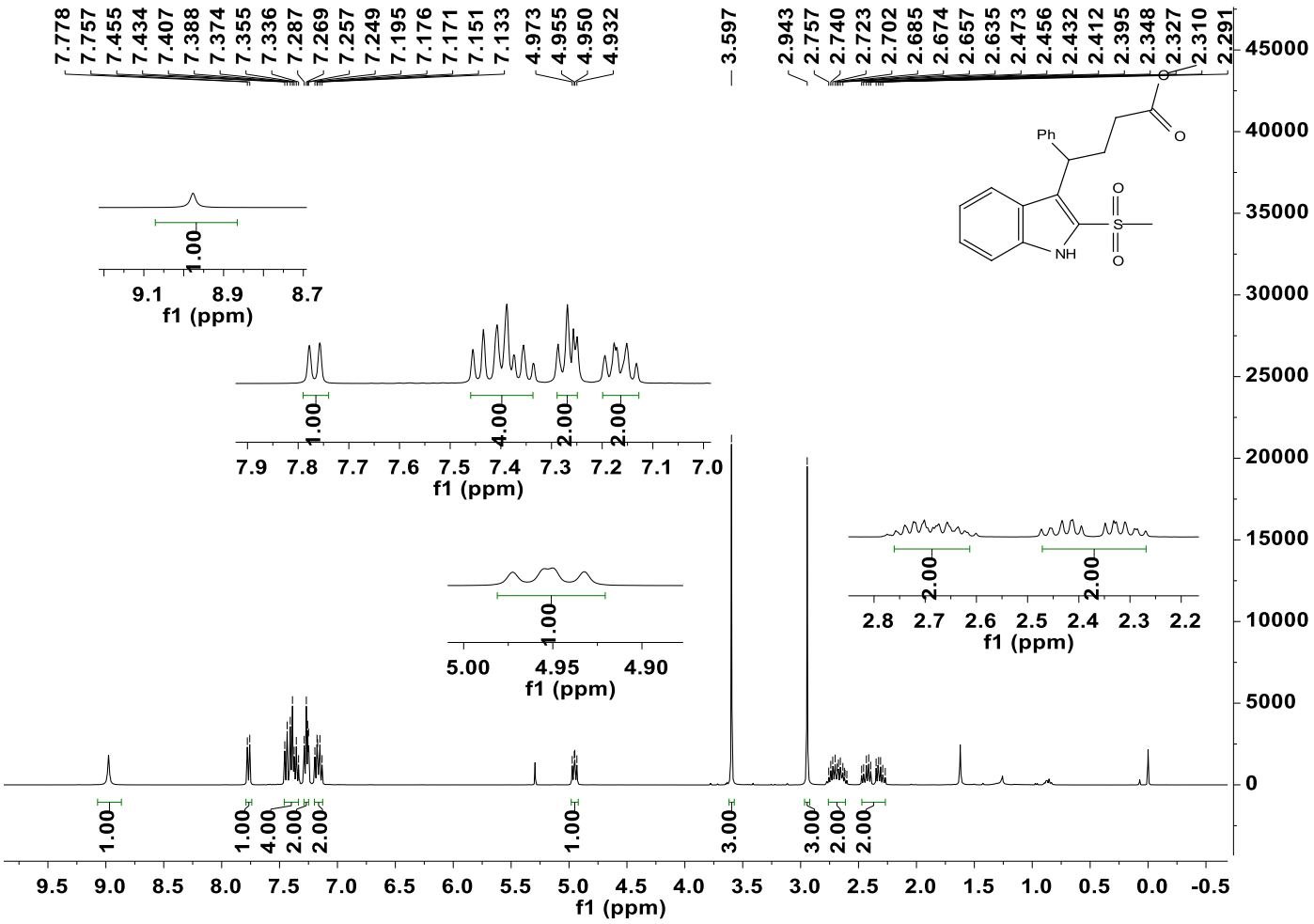

173.291 152.030 142.725 139.327 136.019 129.318 128.417 127.948 126.366 126.347 125.920 124.010 122.982 121.127 117.142 112.506 45.348 40.273 34.035 29.069 12.570 12.216 7.505
f1 (ppm)

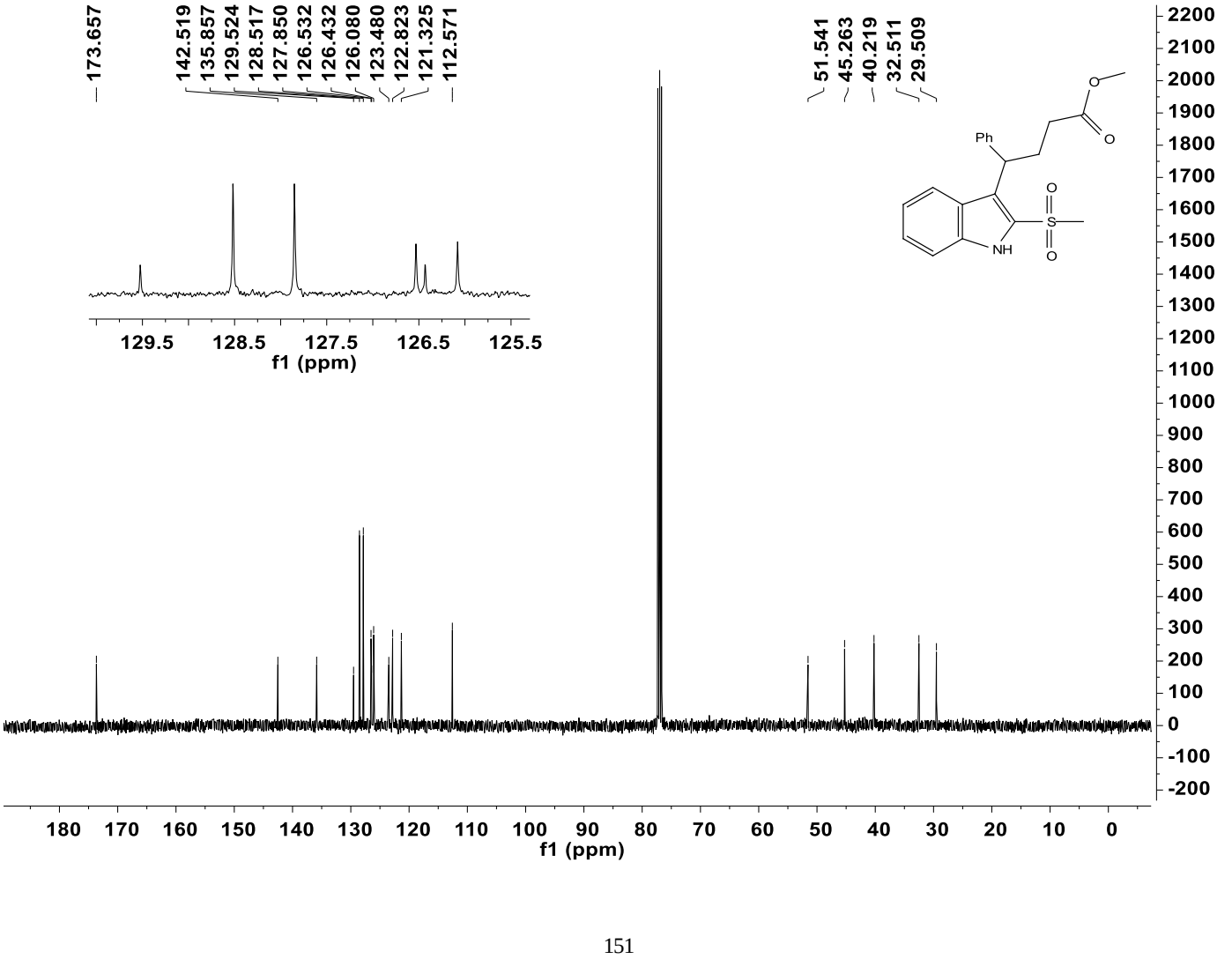
6aa


9.001 7.783 7.762 7.457 7.436 7.391 7.372 7.354 7.335 7.276 7.260 7.239 7.188 7.169 7.163 7.150 7.143 7.125 5.923 5.903 4.930 4.912 4.908 4.890 4.617 4.605 3.704 2.976 2.755 2.738 2.719 2.681 2.662 2.327 2.308 2.235 2.218 2.198 1.661 1.606 1.593 1.581 1.508 1.486 0.934 0.918 0.903
f1 (ppm)

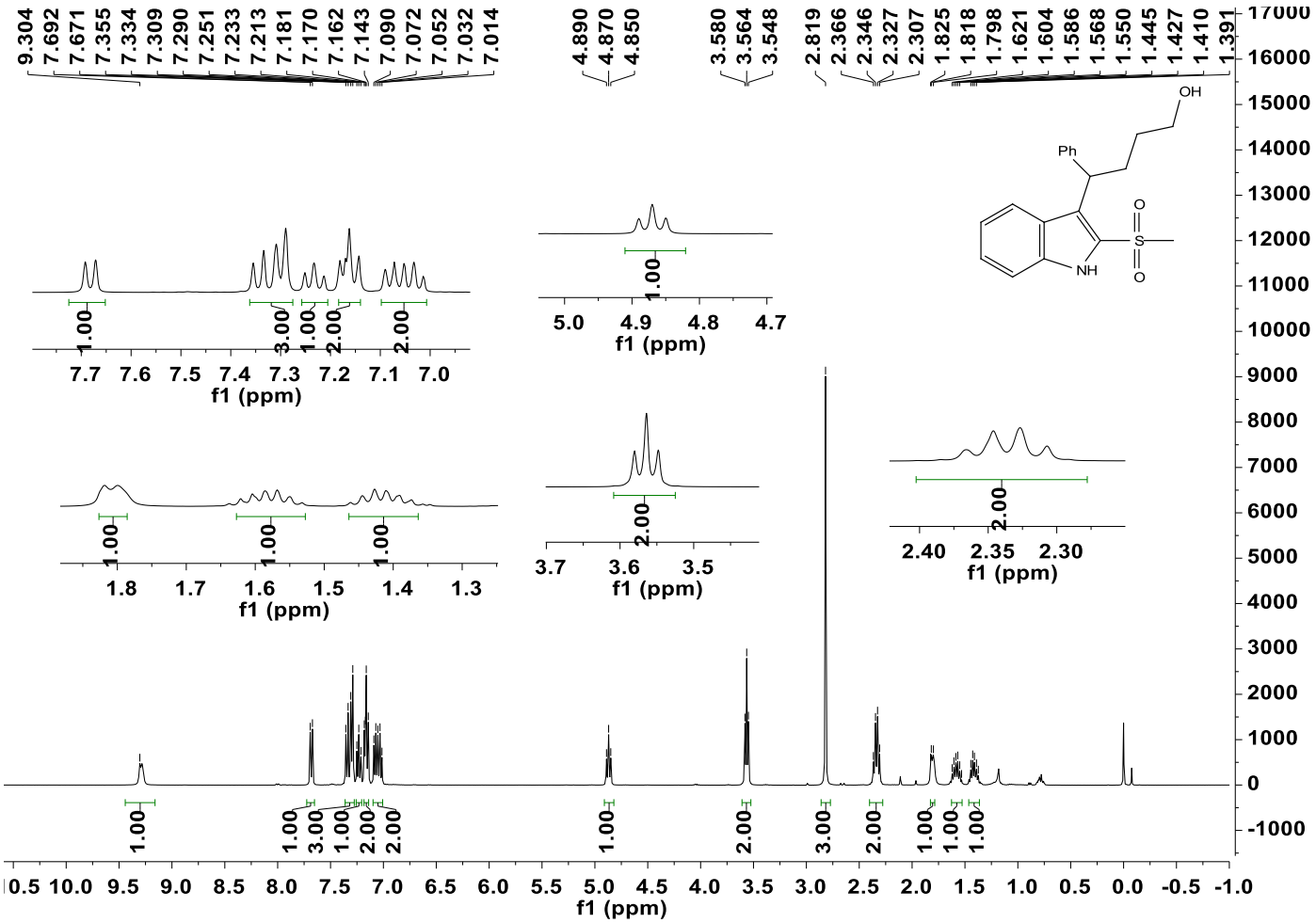

173.636 172.343 142.462 135.810 129.630 128.524 127.906 126.521 126.070 123.401 122.986 121.335 112.582 52.239 50.718 45.254 41.580 40.371 34.657 30.299 24.825 22.782 21.957
f1 (ppm)

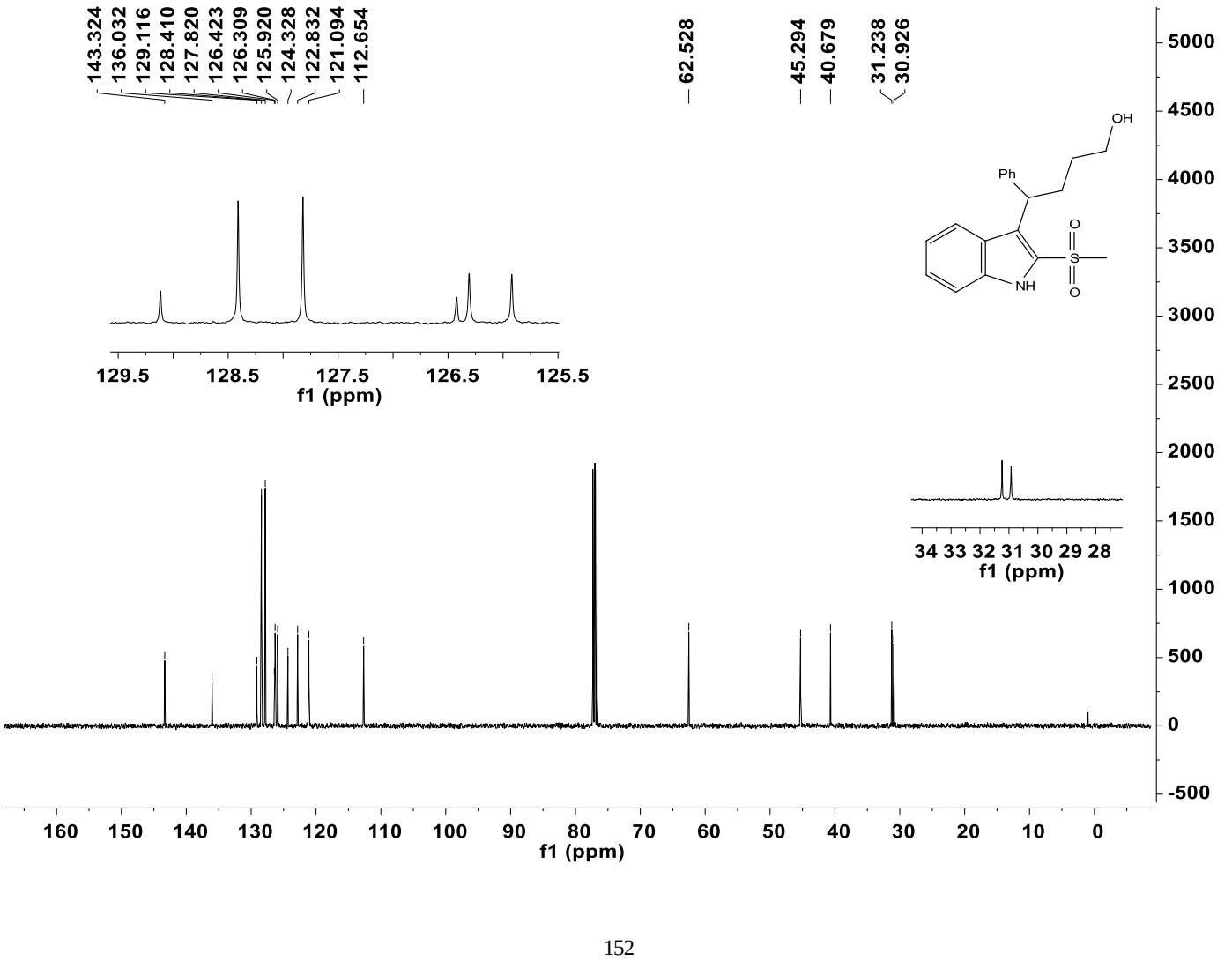
7aa


7.778 7.757 7.455 7.434 7.407 7.388 7.374 7.355 7.336 7.287 7.269 7.257 7.249 7.195 7.176 7.171 7.151 7.133 4.973 4.955 4.950 4.932 3.597 2.943 2.757 2.740 2.723 2.702 2.685 2.674 2.657 2.635 2.473 2.456 2.432 2.412 2.395 2.348 2.327 2.310 2.291
Ph
O
O
S
O
O
NH
f1 (ppm)

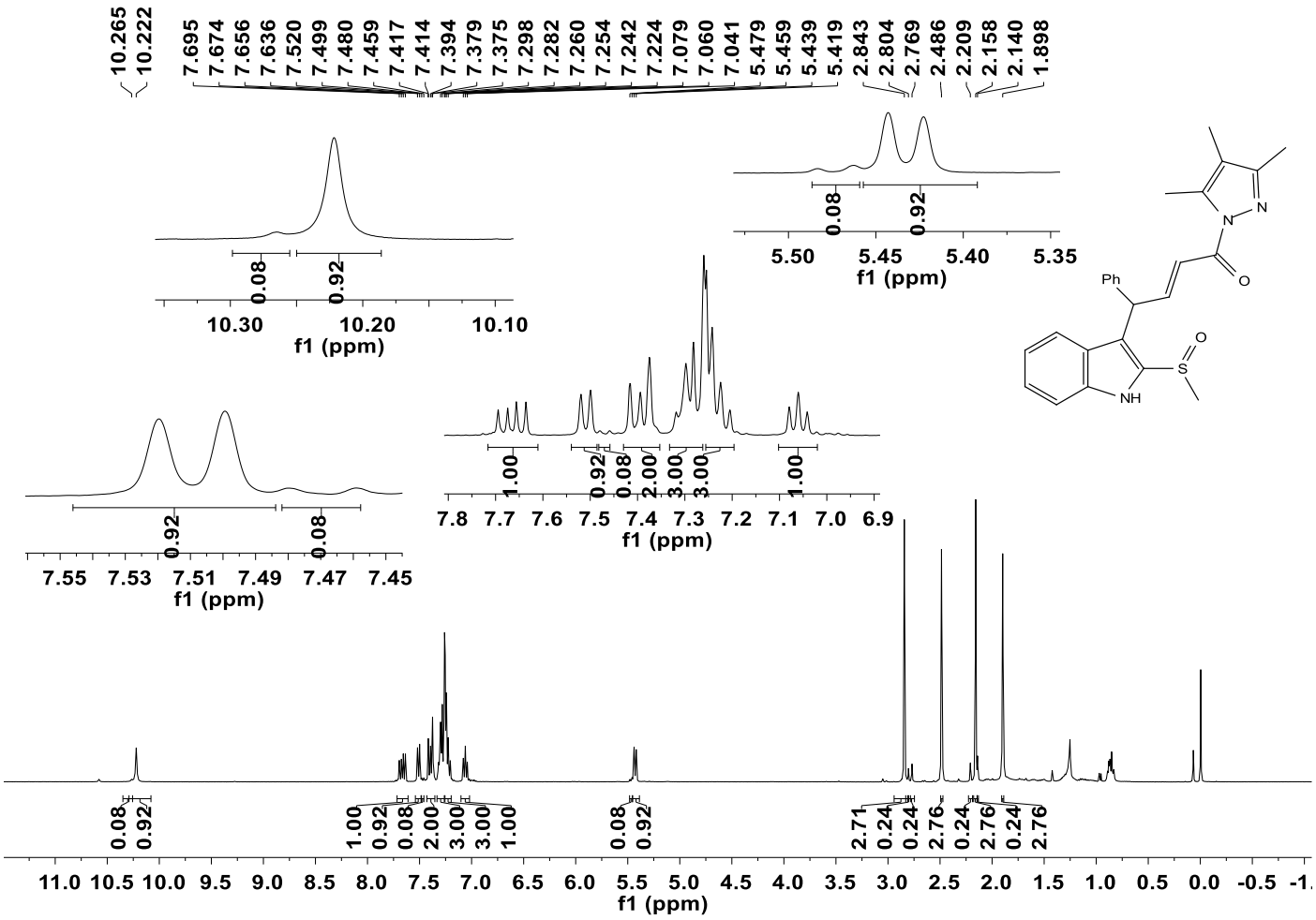

173.657 142.519 135.857 129.524 128.517 127.850 126.532 126.432 126.080 123.480 122.823 121.325 112.571 51.541 45.263 40.219 32.511 29.509
Ph
O
O
S
O
O
NH
f1 (ppm)

8aa


9.304 7.692 7.671 7.355 7.334 7.309 7.290 7.251 7.233 7.213 7.181 7.170 7.162 7.143 7.090 7.072 7.052 7.032 7.014
4.890 4.870 4.850
3.580 3.564 3.548
2.819 2.366 2.346 2.327 2.307
1.825 1.818 1.798 1.621 1.604 1.586 1.568 1.550 1.445 1.427 1.410 1.391
OH
Ph
NH
S
O
f1 (ppm)


143.324 136.032 129.116 128.410 127.820 126.423 126.309 125.920 124.328 122.832 121.094 112.654
62.528
45.294 40.679
31.238 30.926
OH
Ph
NH
S
O
f1 (ppm)

9aa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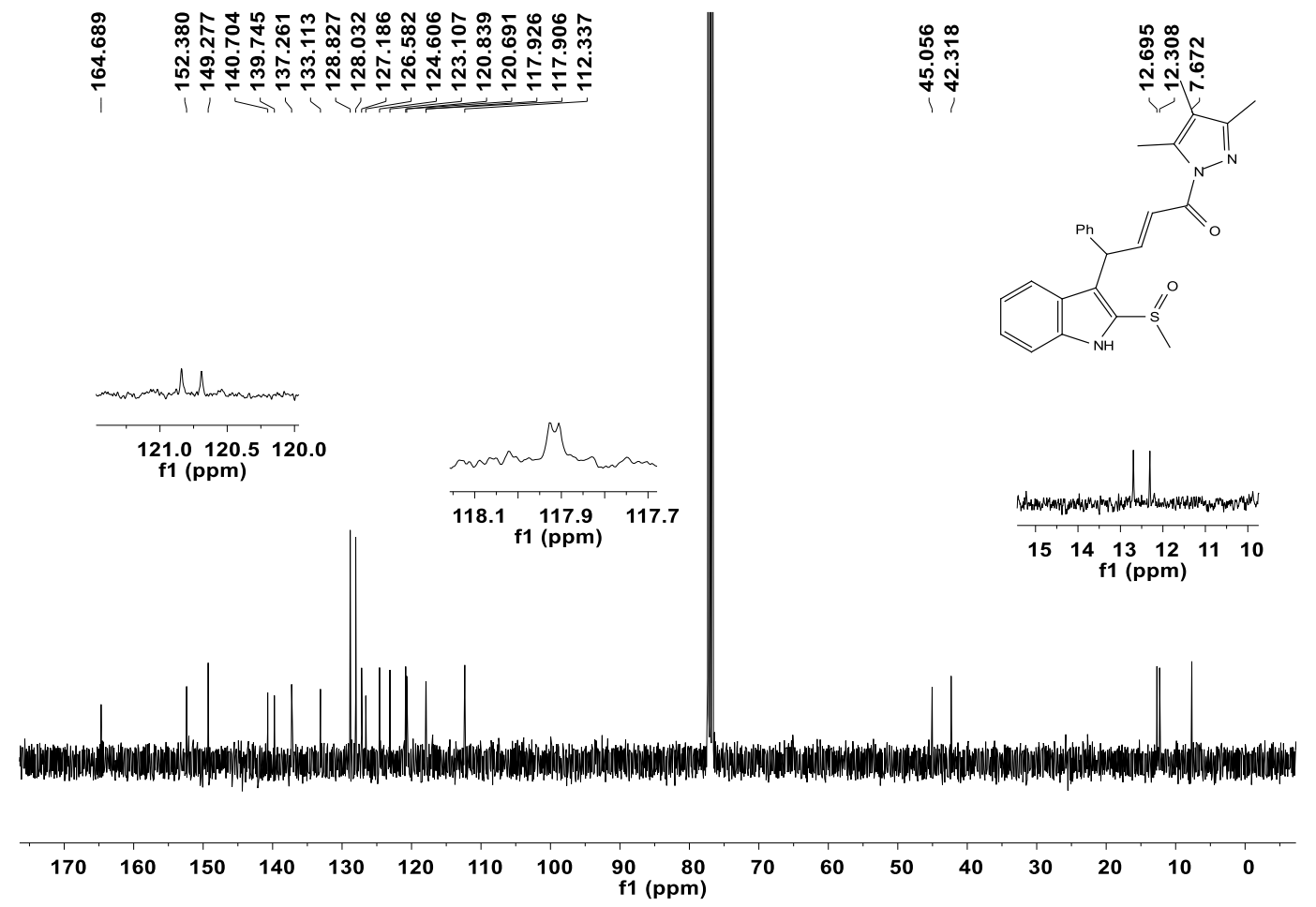
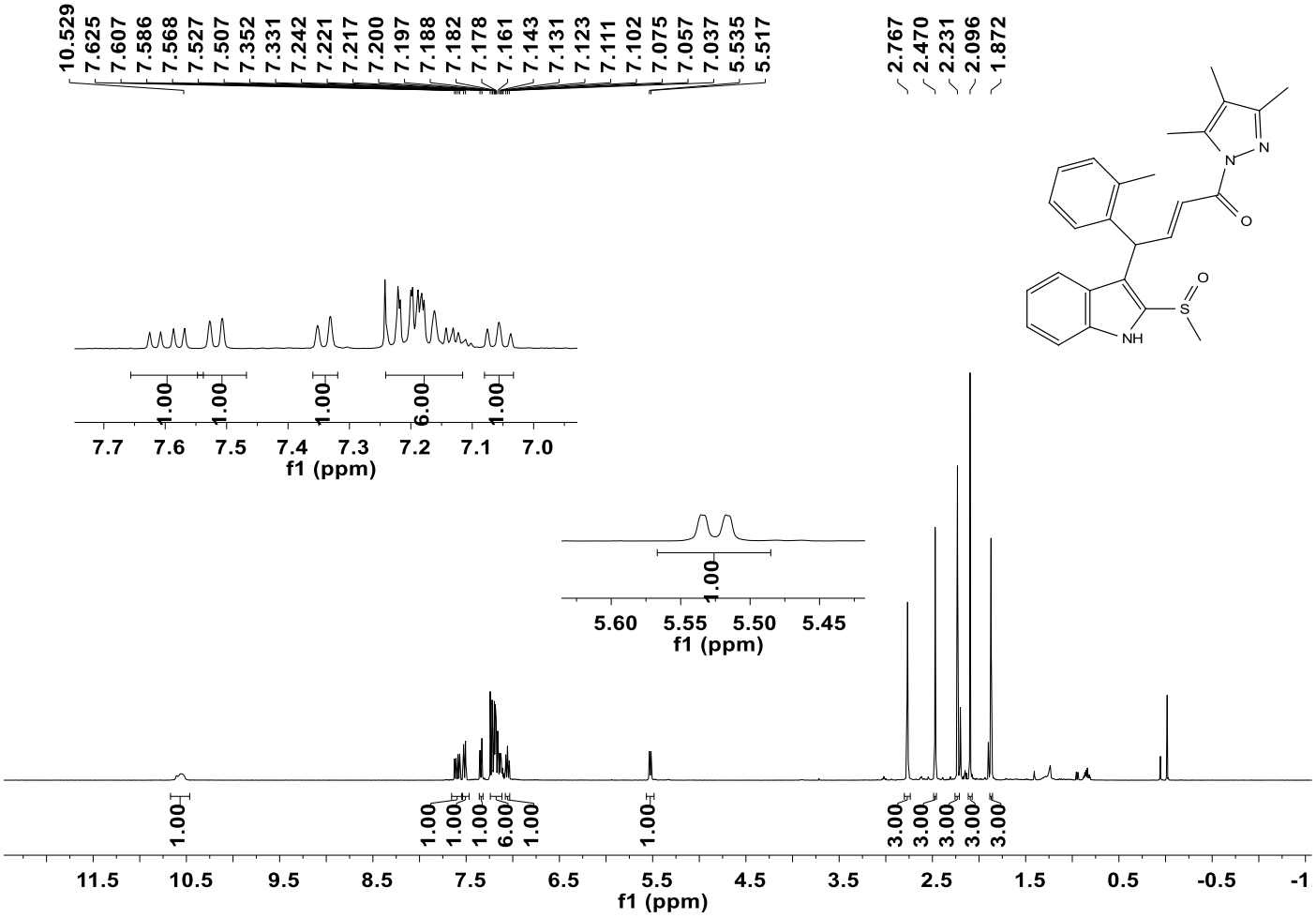
10.222
7.695
7.674
7.656
7.636
7.520
7.499
7.480
7.459
7.417
7.414
7.394
7.379
7.375
7.298
7.282
7.260
7.254
7.242
7.224
7.079
7.060
7.041
5.479
5.459
5.439
5.419
2.843
2.804
2.769
2.486
2.209
2.158
2.140
1.898
f1 (ppm)


164.689
152.380
149.277
140.704
139.745
137.261
133.113
128.827
128.032
127.186
126.582
124.606
123.107
120.839
120.691
117.926
117.906
112.337
45.056
42.318
12.695
12.308
7.672
f1 (ppm)

9da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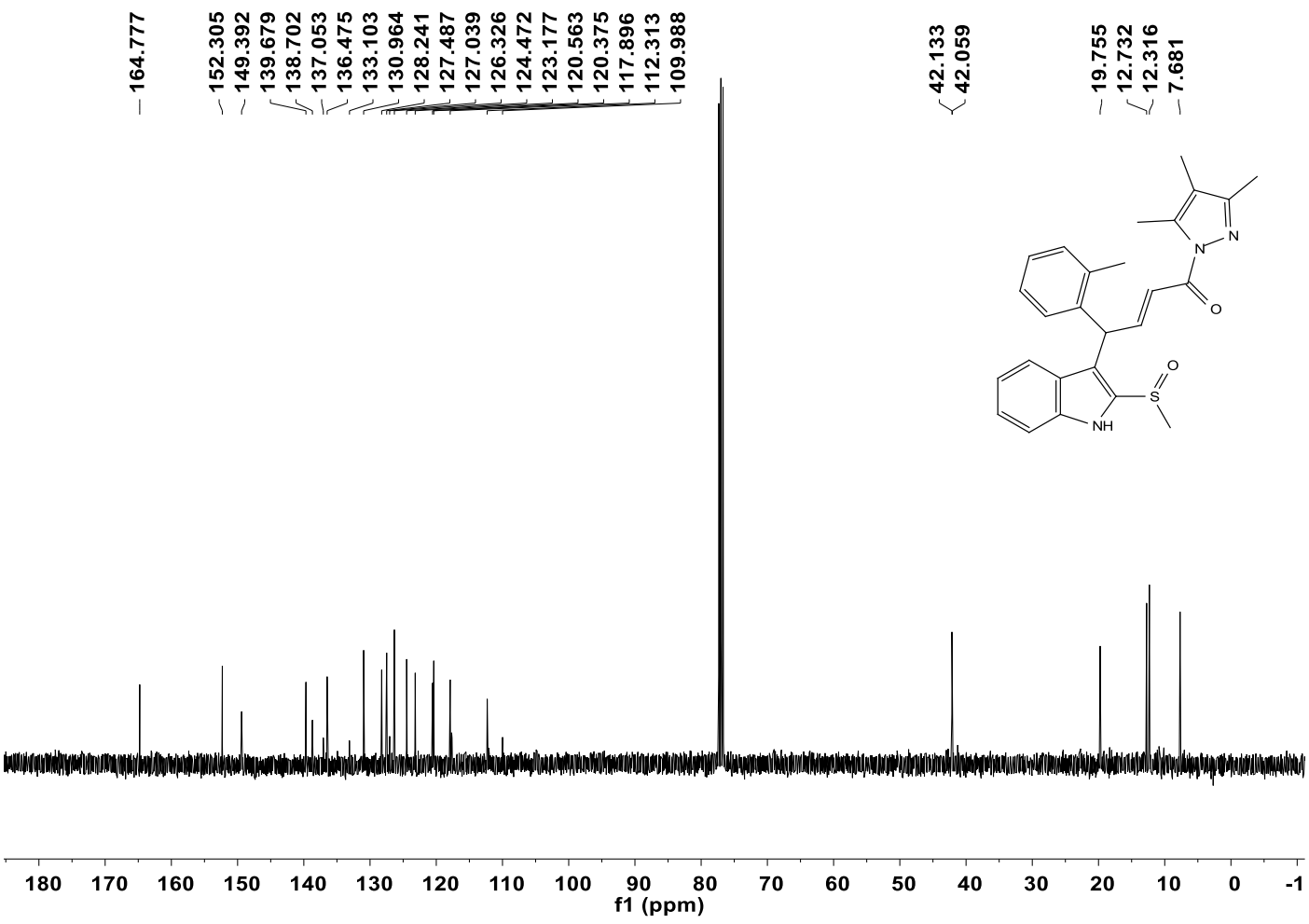
7.607
7.586
7.568
7.527
7.507
7.352
7.331
7.242
7.221
7.217
7.200
7.197
7.188
7.182
7.178
7.161
7.143
7.131
7.123
7.111
7.102
7.075
7.057
7.037
5.535
5.517
2.767
2.470
2.231
2.096
1.872
1.00
1.00
1.00
6.00
1.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.00
5.60 5.55 5.50 5.45
f1 (ppm)
1.00
1.00
1.00
6.00
1.00
1.00
3.00
3.00
3.00
3.00
3.00
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1
f1 (ppm)


164.777
152.305
149.392
139.679
138.702
137.053
136.475
133.103
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128.241
127.487
127.039
126.326
124.472
123.177
120.563
120.375
117.896
112.313
109.988
42.133
42.059
19.755
12.732
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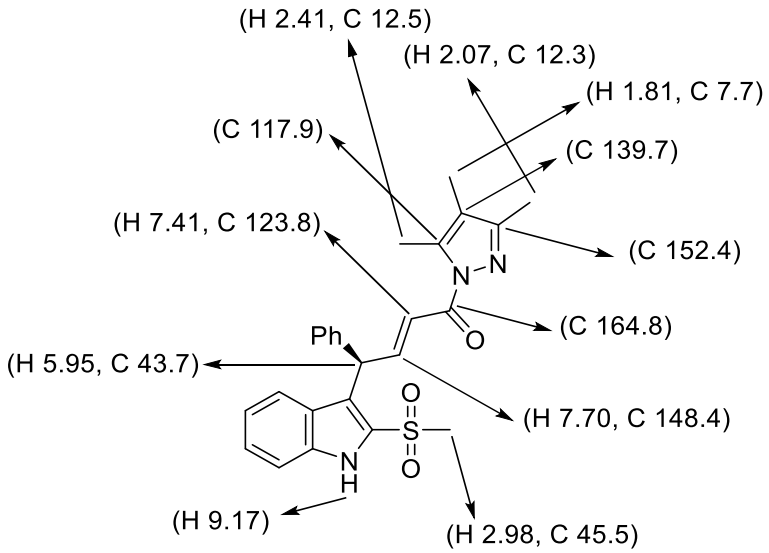
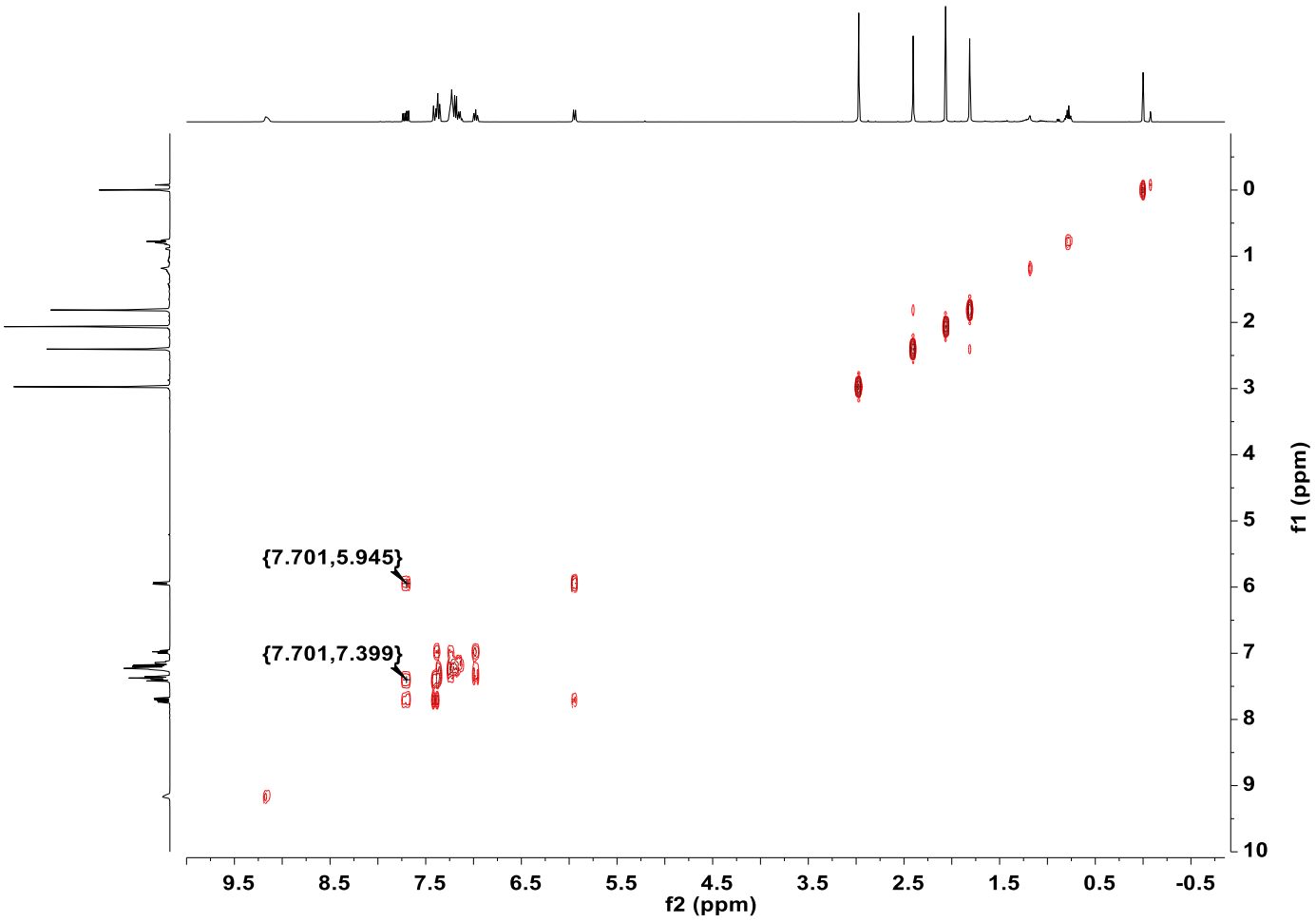
7.681
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

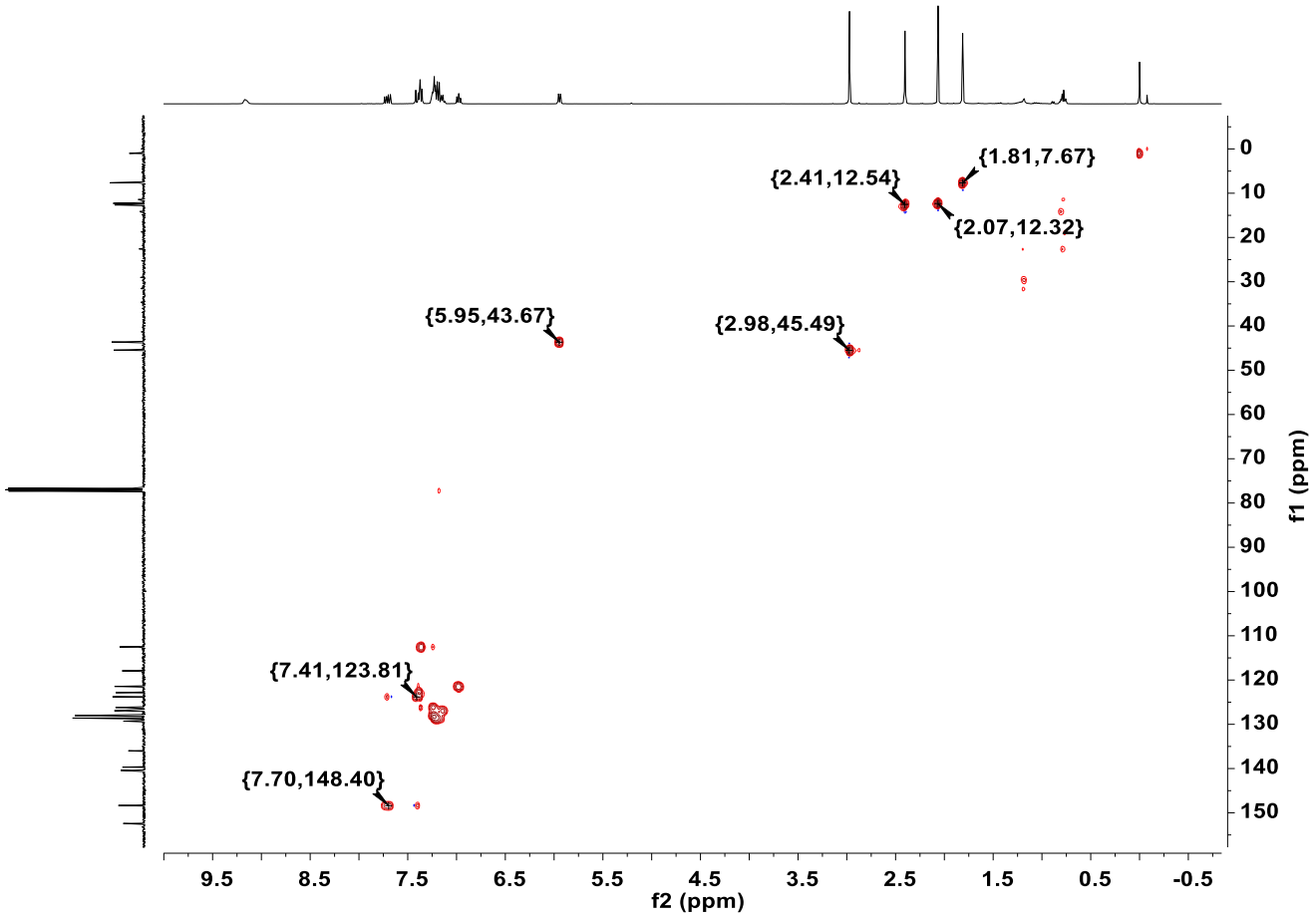
2D NMR Spectra of **4aa**



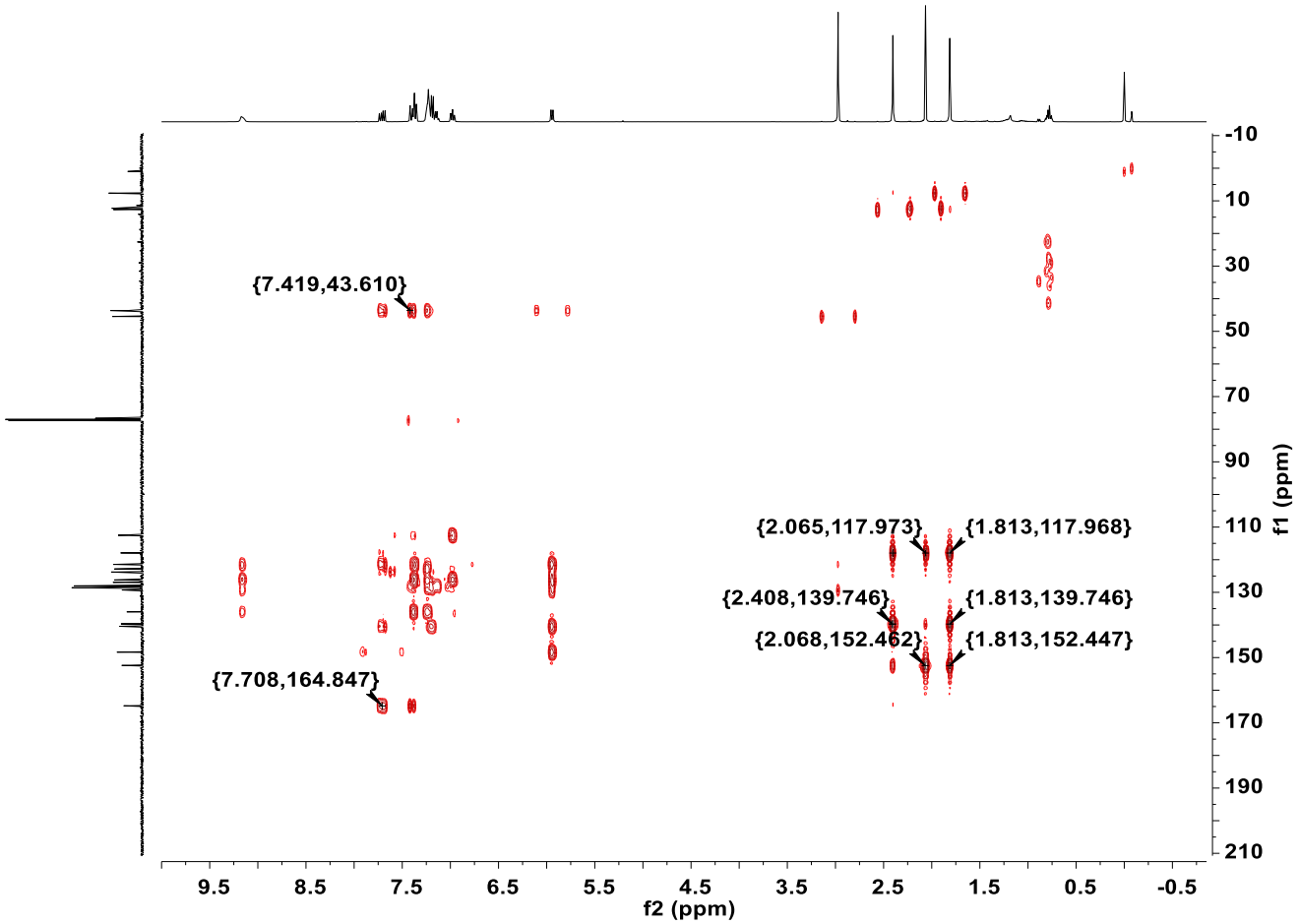
COSY spectra of **4aa**



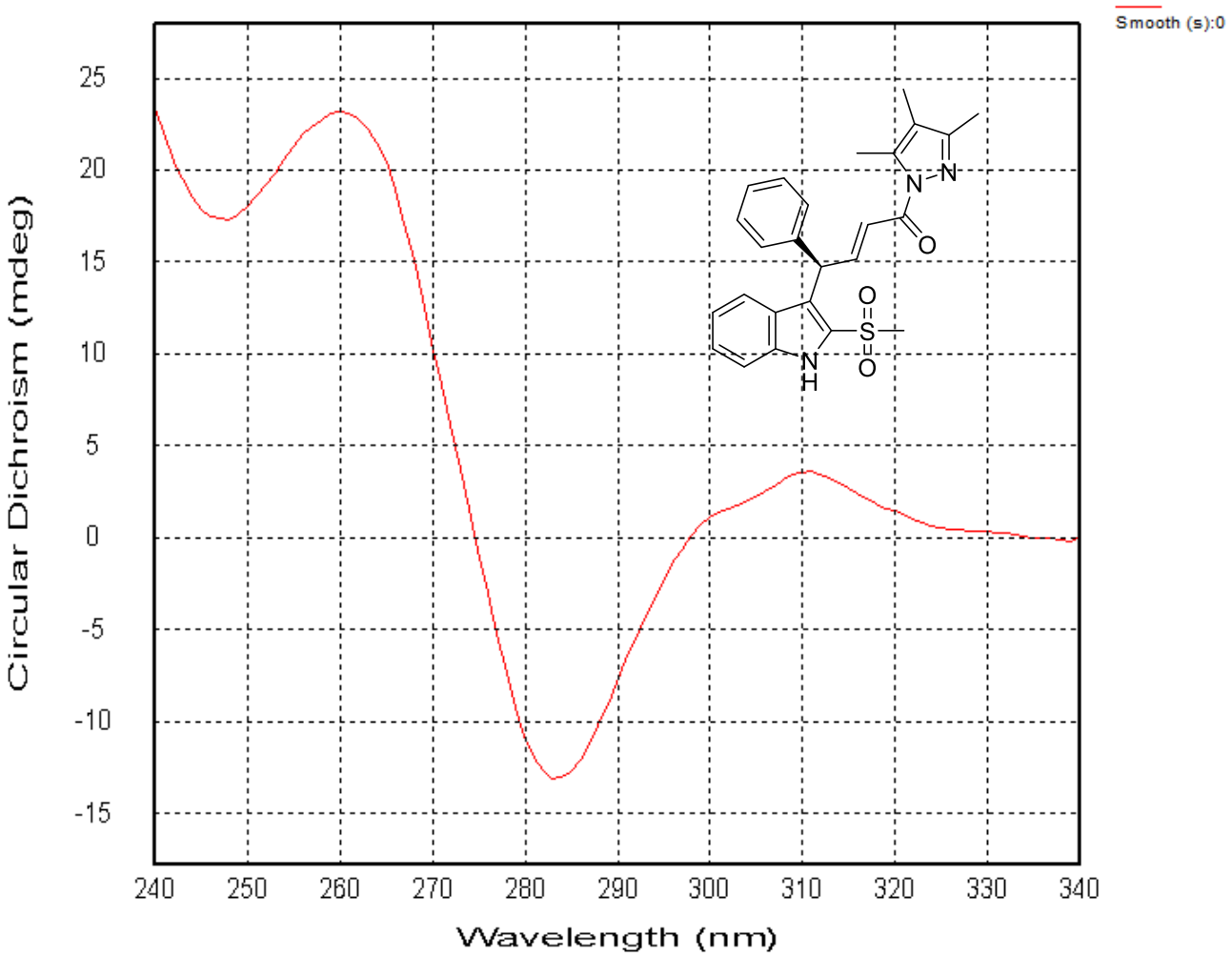
HSQC spectra of **4aa**

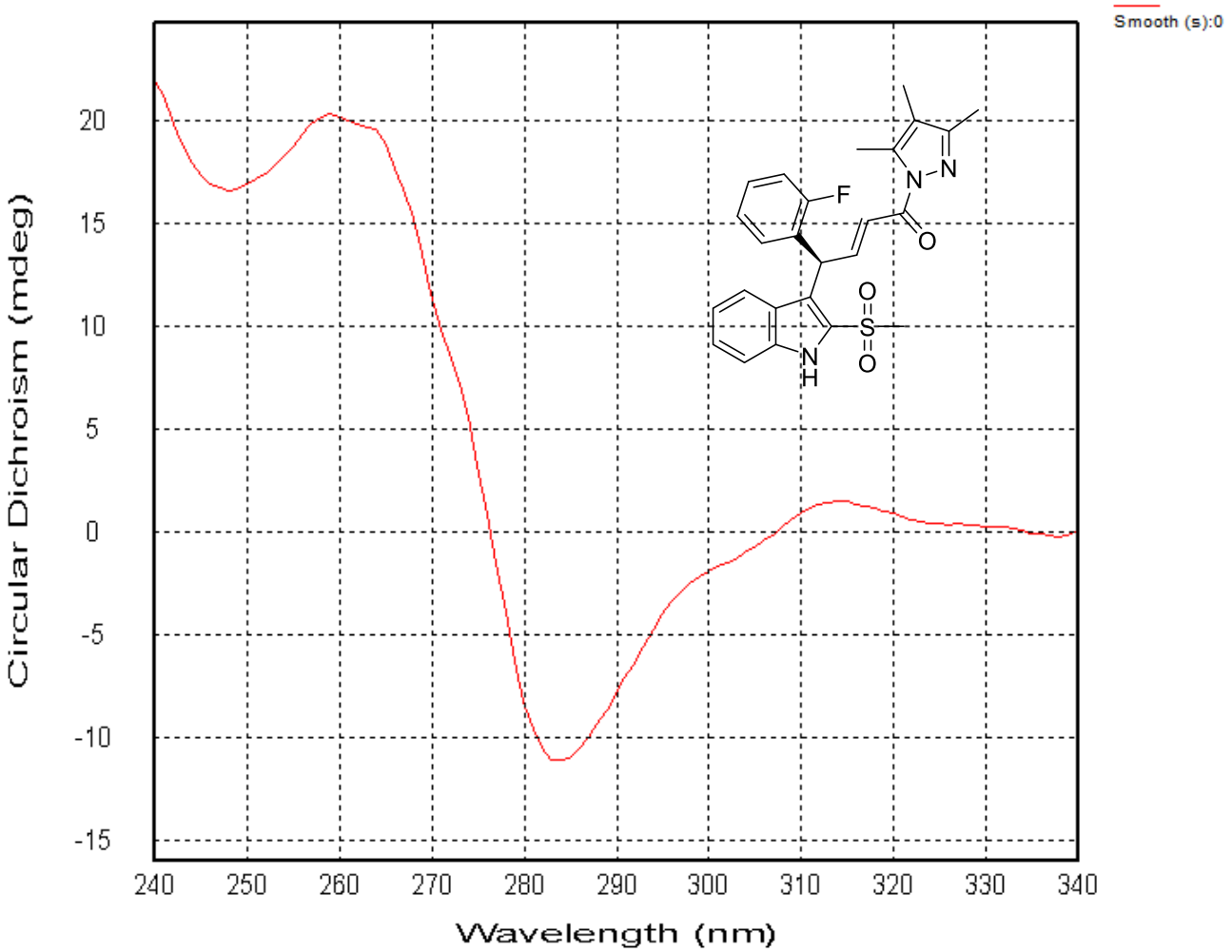


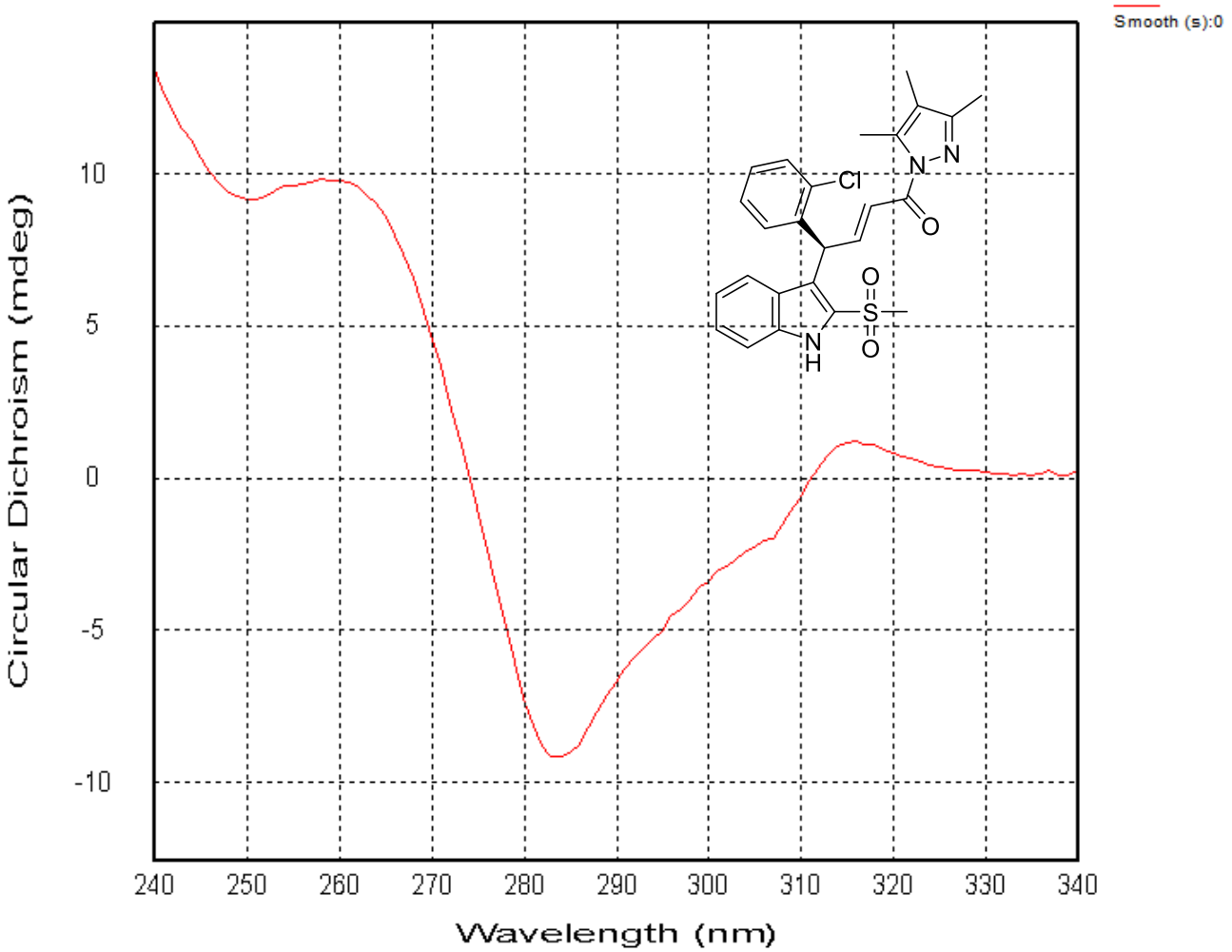
HMBC spectra of **4aa**



14 Copies of CD spectra in CH_2Cl_2




Smooth (s):0
Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
F
N
N
O
O
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
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-5
-10
240
250
260
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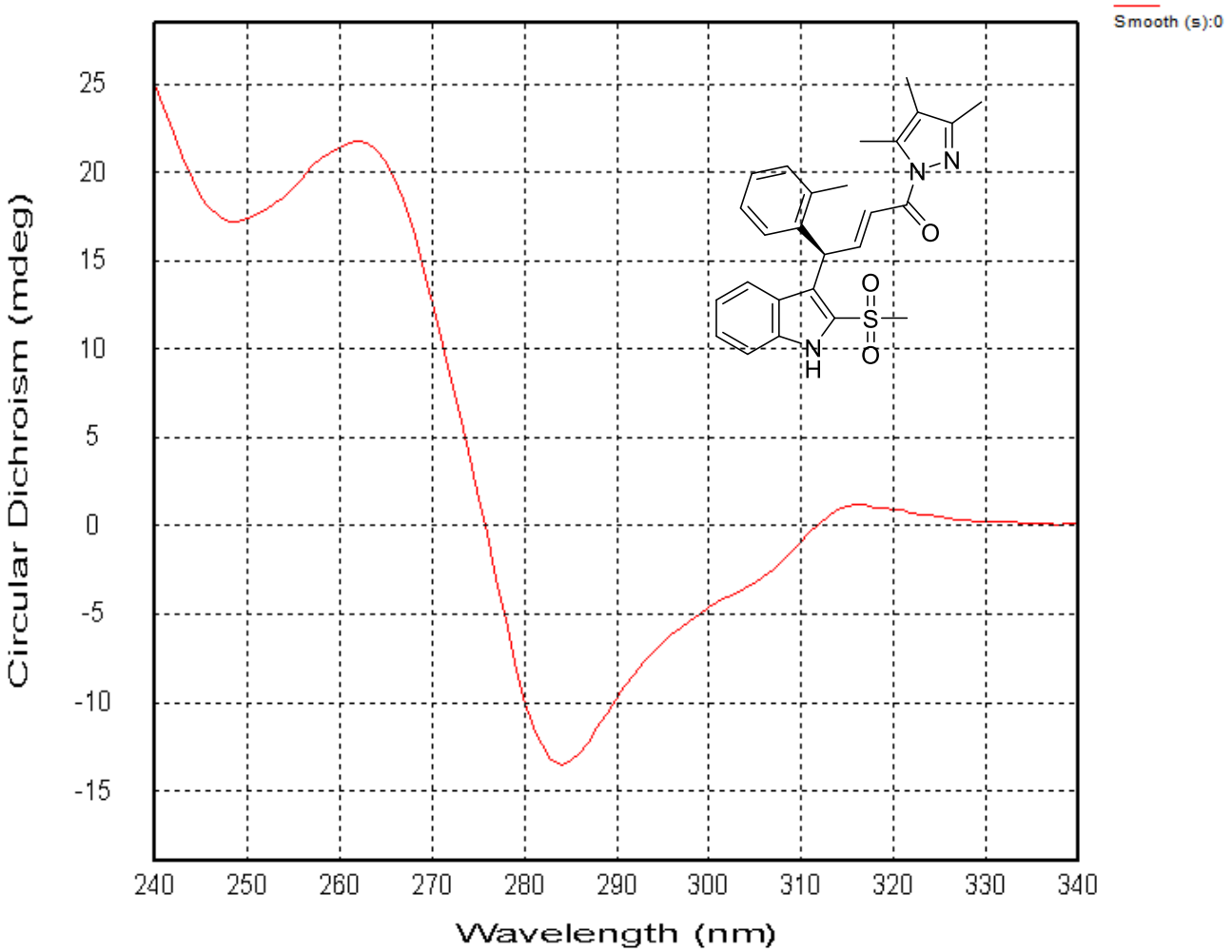
280
290
300
310
320
330
340
Wavelength (nm)
Cl
N
N
O
O
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
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20
15
10
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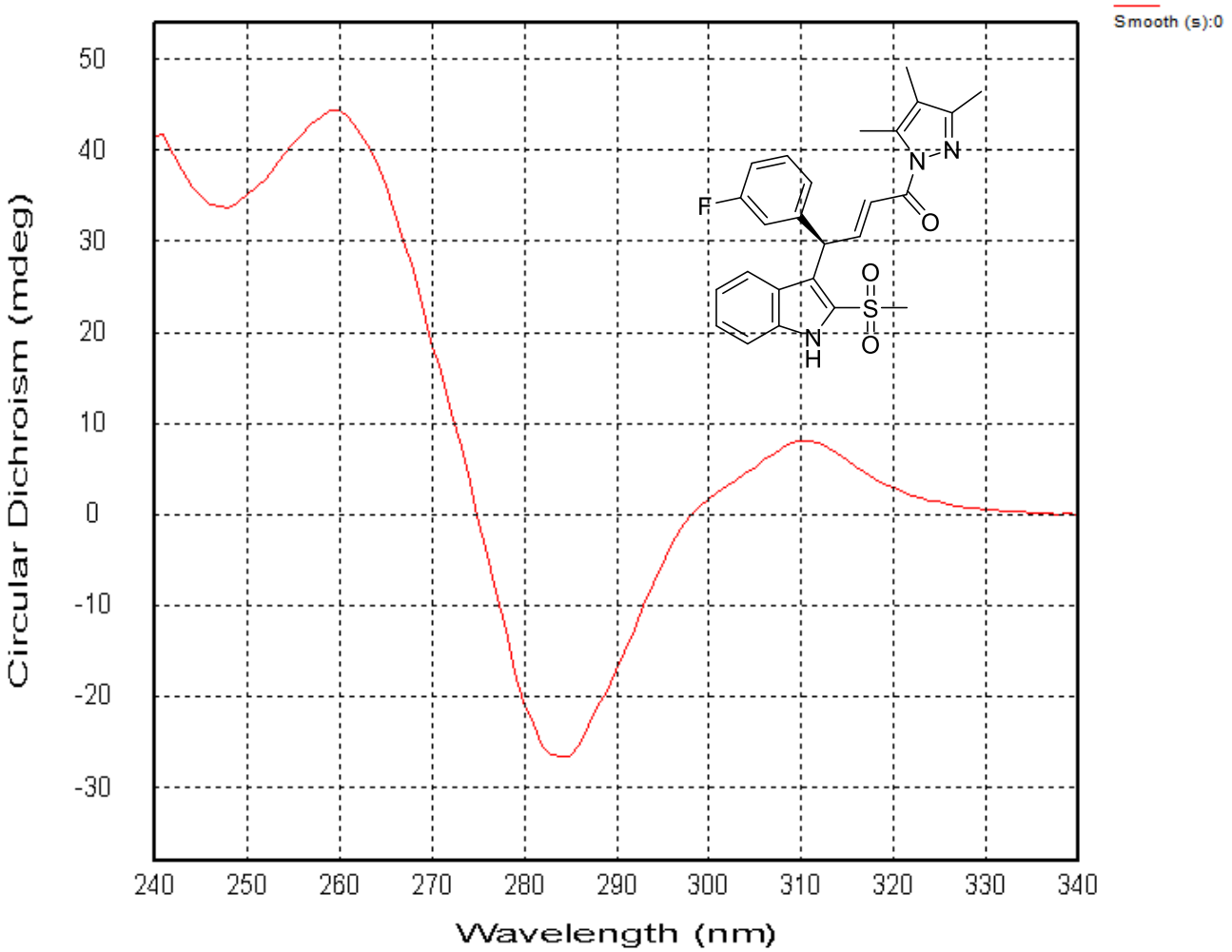
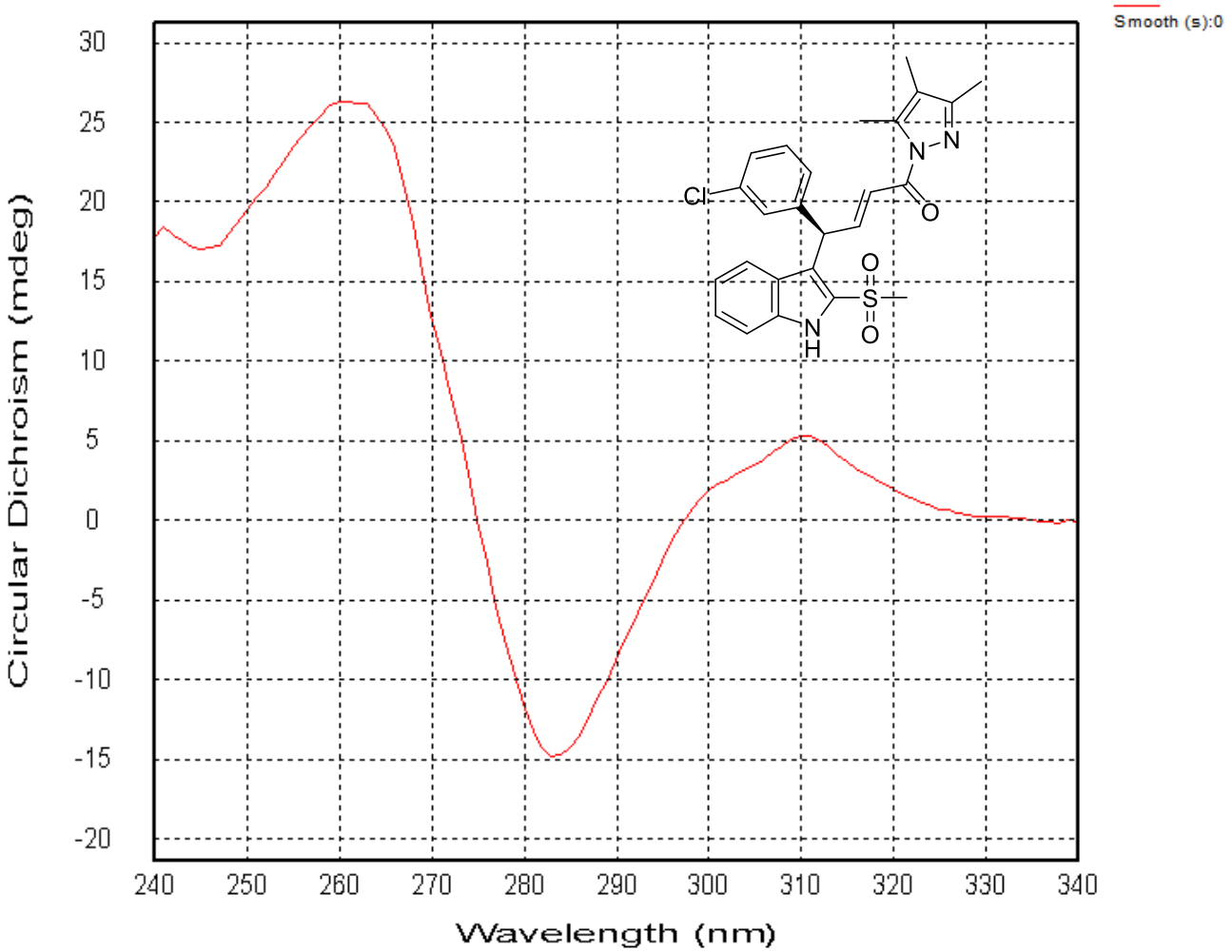
-5
-10
-15
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
N
N
O
O
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
-20
-30
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
F
N
N
O
O
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
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-15
-20
240
250
260
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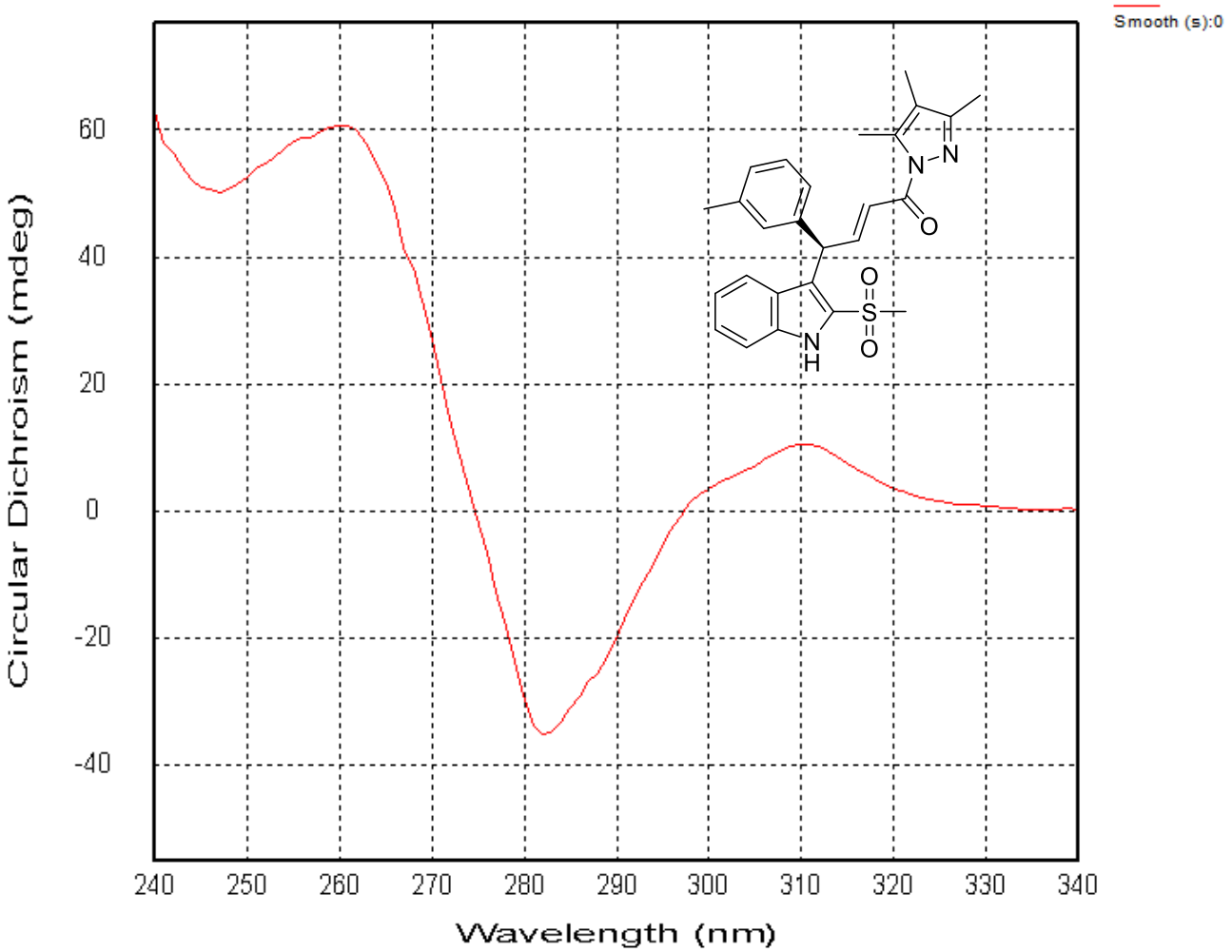
310
320
330
340
Wavelength (nm)
Cl
N
N
O
O
S
O
N
H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-20
-40
240
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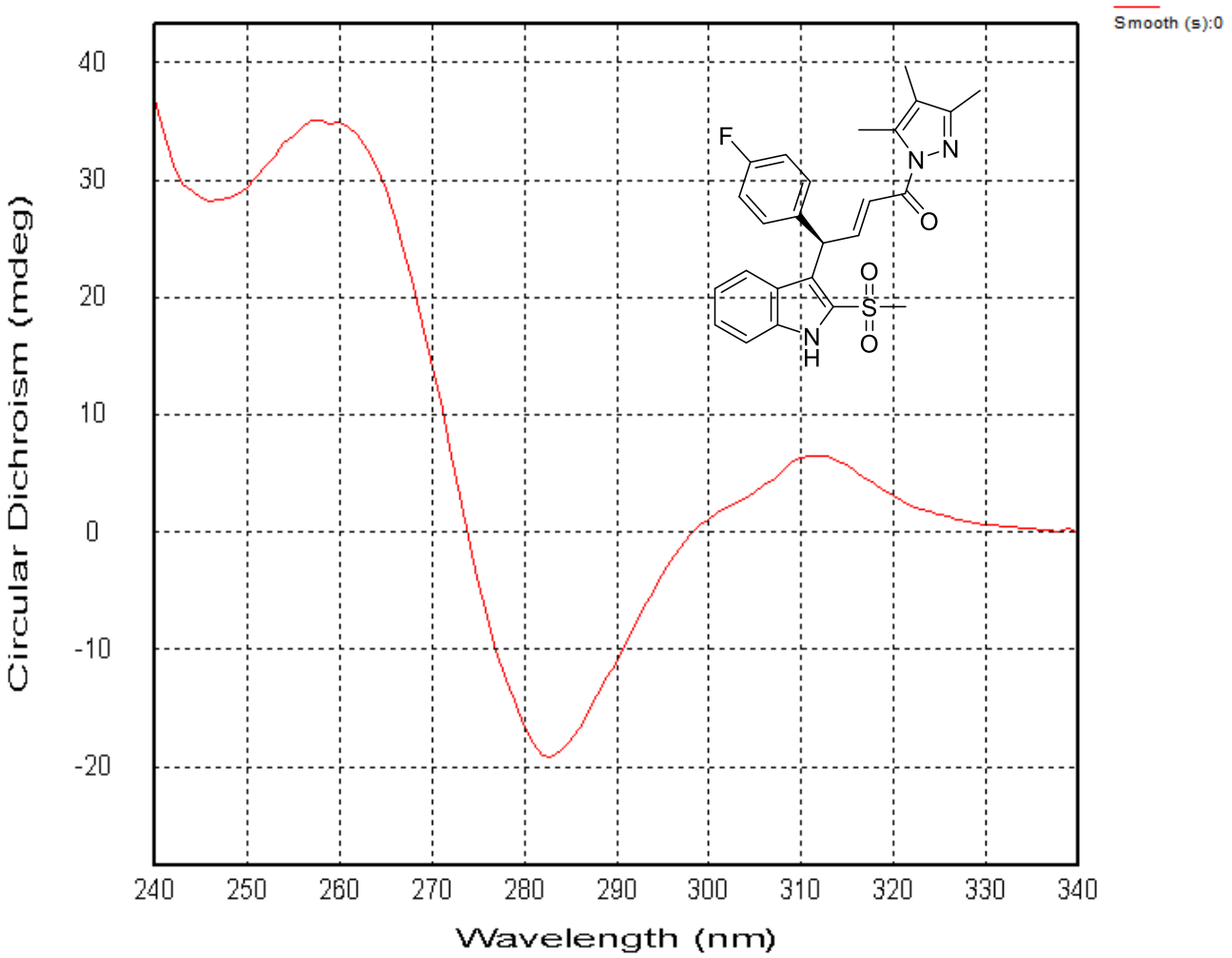
320
330
340
Wavelength (nm)
N
N
O
O
S
O
N
H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Circular Dichroism (mdeg)
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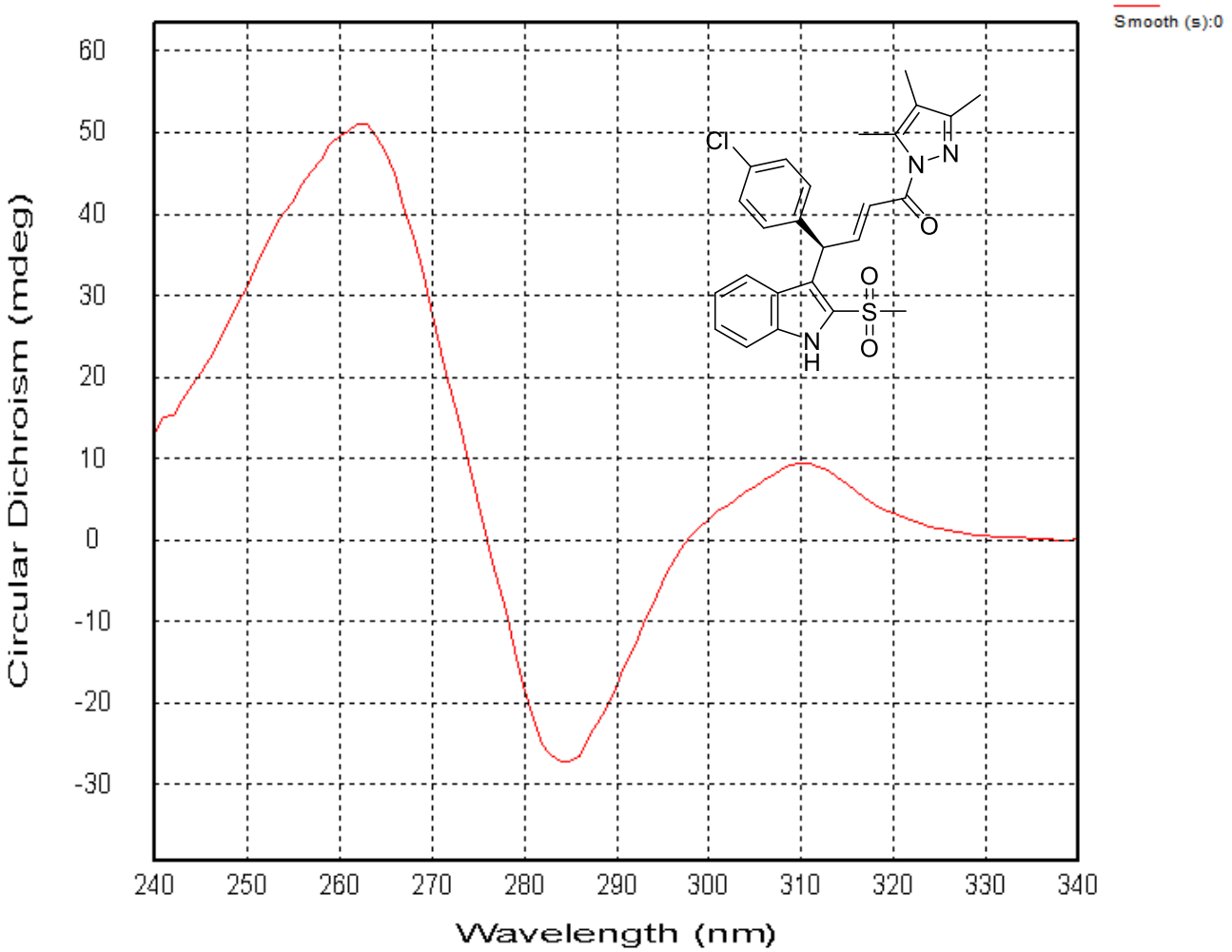
310
320
330
340
Wavelength (nm)
F
N
N
O
O
S
O
N
H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Circular Dichroism (mdeg)
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30
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-30
240
250
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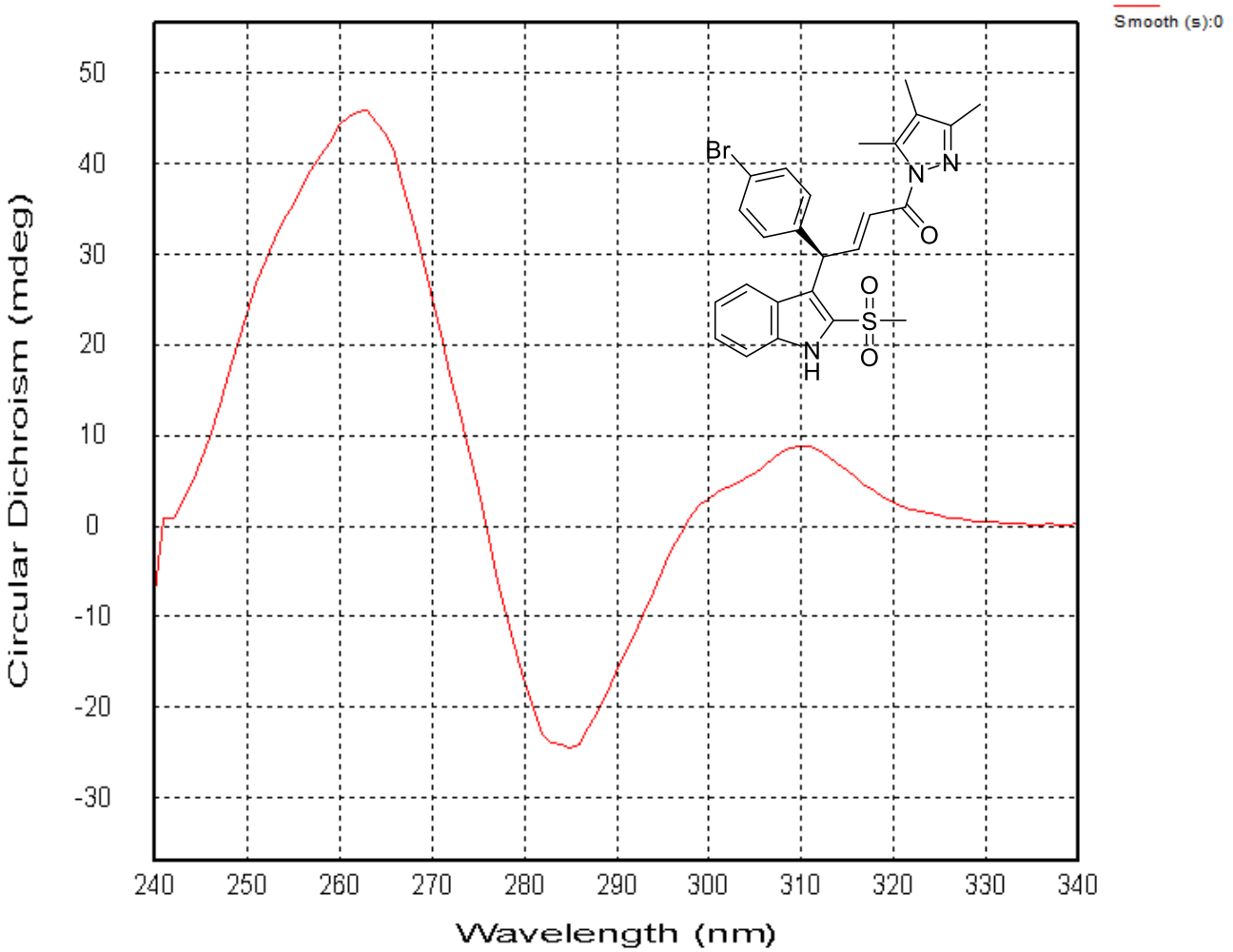
270
280
290
300
310
320
330
340
Wavelength (nm)
Cl
N
N
O
O
S
O
N
H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Circular Dichroism (mdeg)
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10
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240
250
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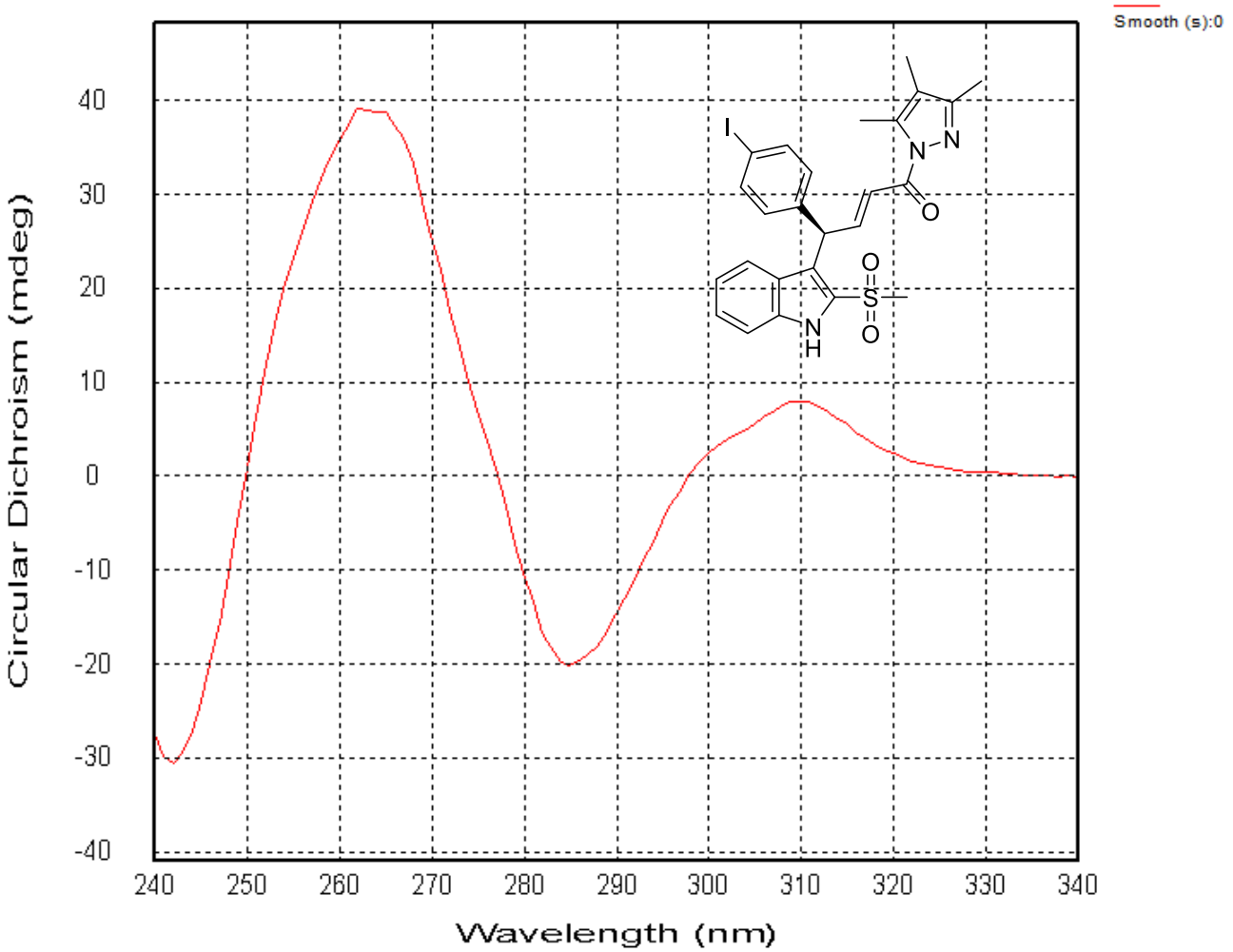
280
290
300
310
320
330
340
Wavelength (nm)
Br
N
N
O
O
S
O
N
H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Circular Dichroism (mdeg)
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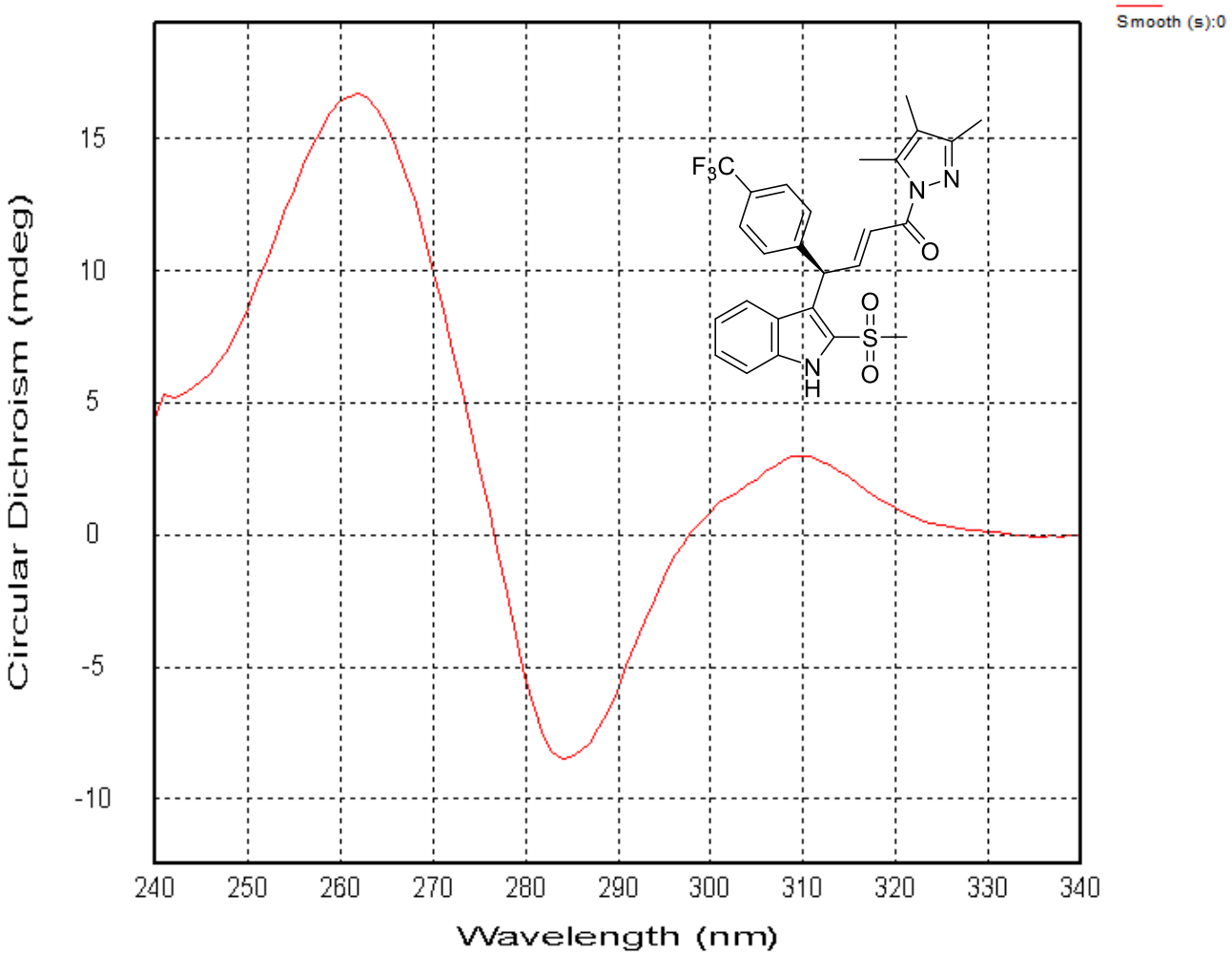
30
20
10
0
-10
-20
-30
-40
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
I
N
N
O
O
S
O
N
H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Circular Dichroism (mdeg)
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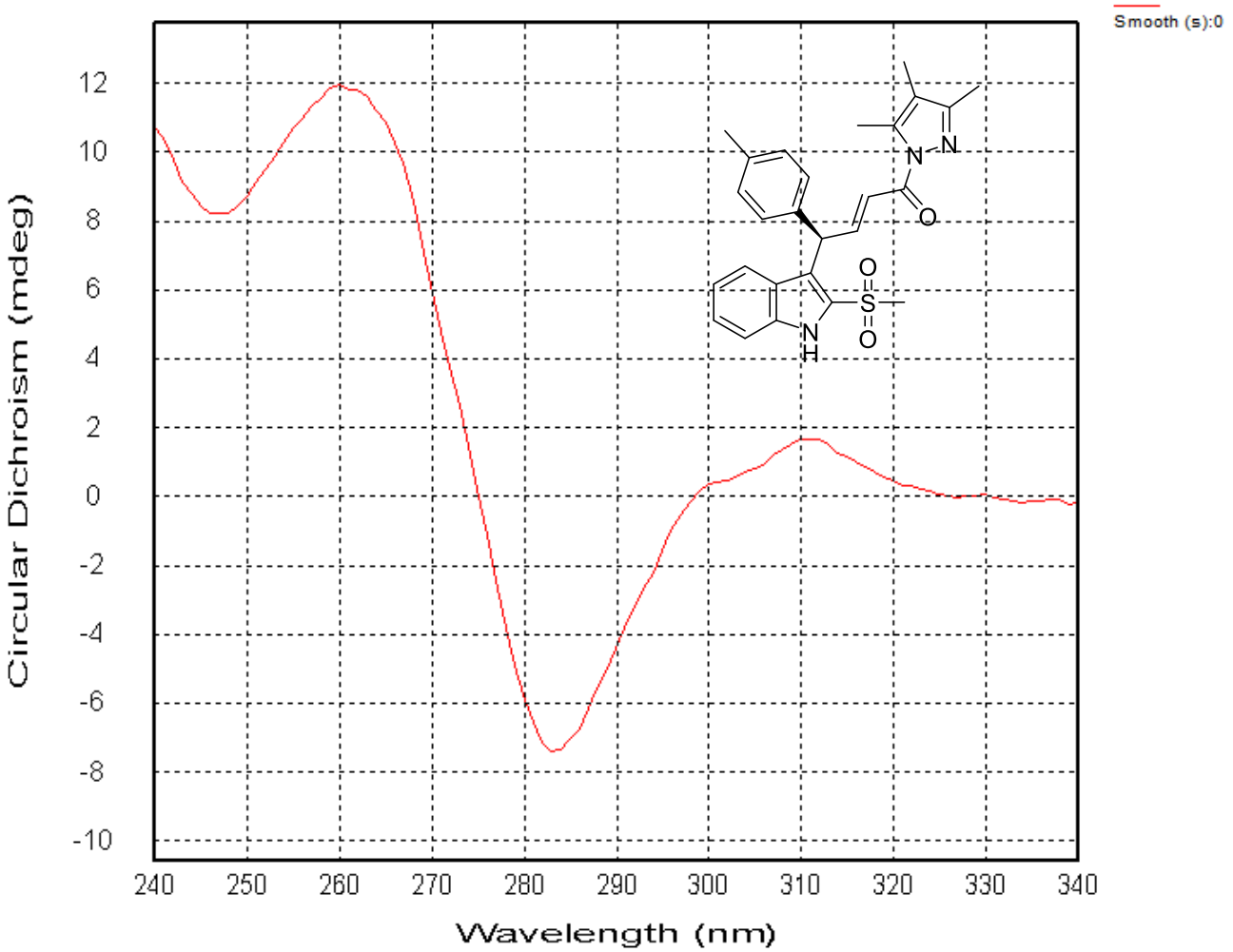
0
-5
-10
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
F3C
N
N
O
O
S
O
N
H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Circular Dichroism (mdeg)
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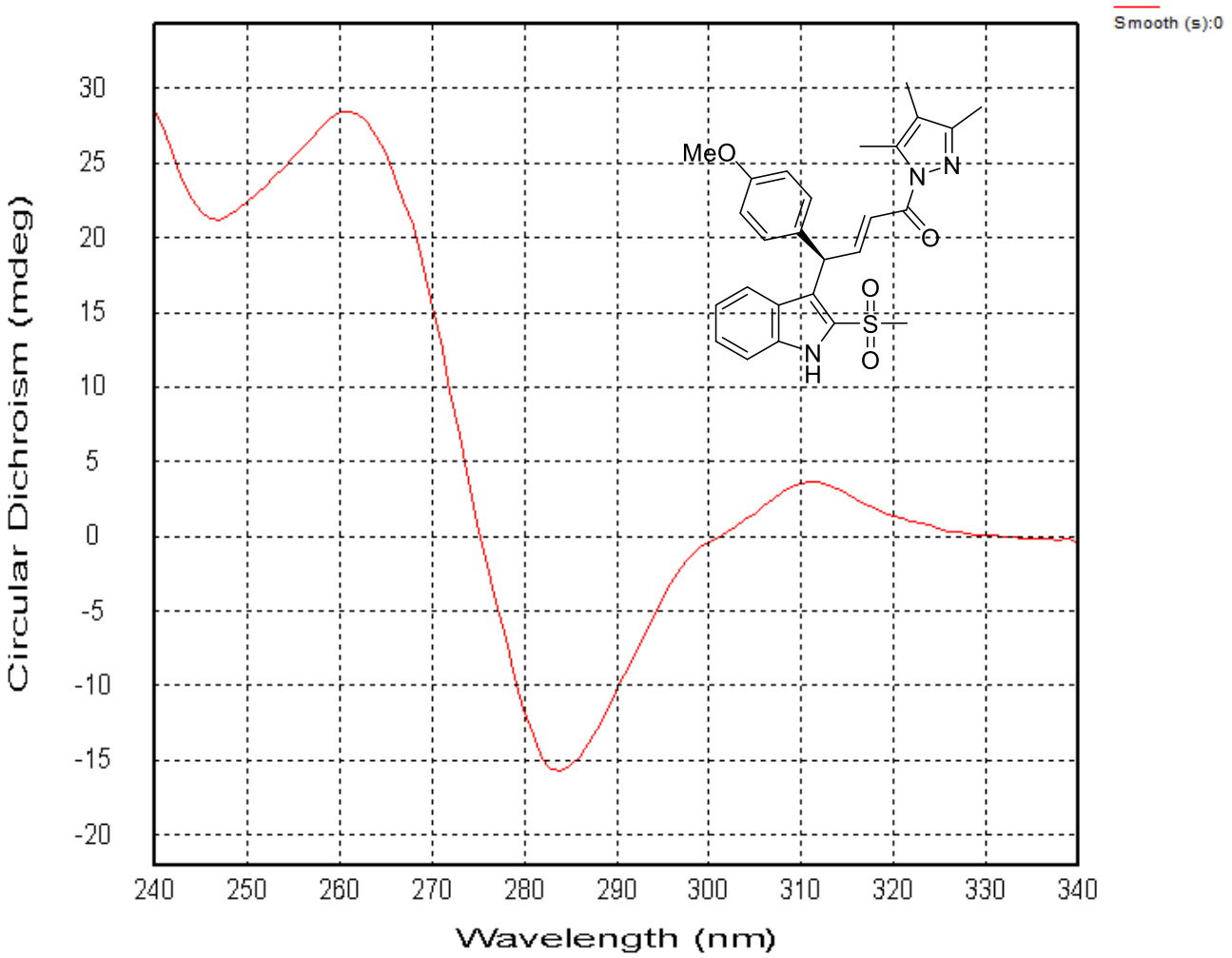
10
8
6
4
2
0
-2
-4
-6
-8
-10
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
N
N
O
O
S
O
N
H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Circular Dichroism (mdeg)
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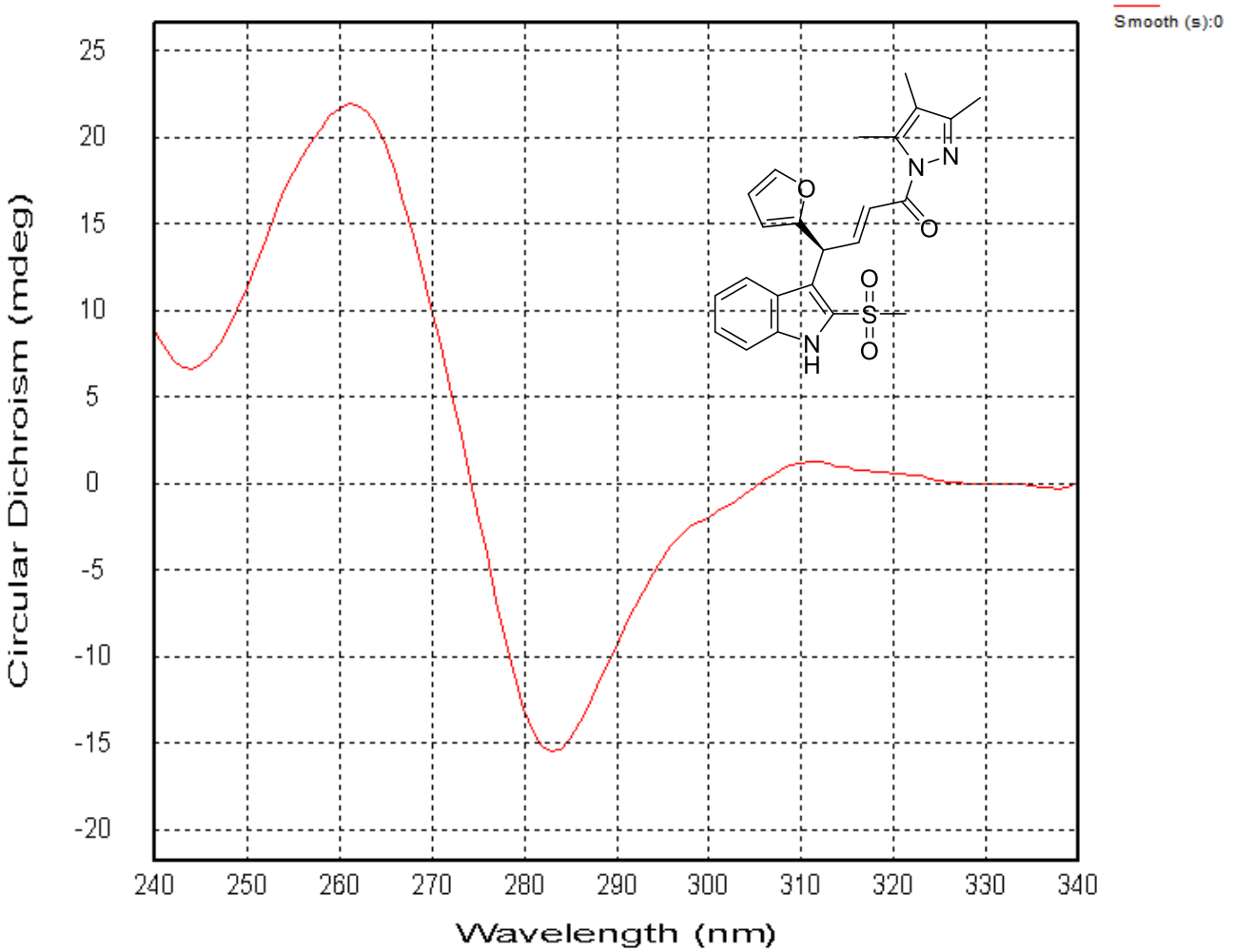
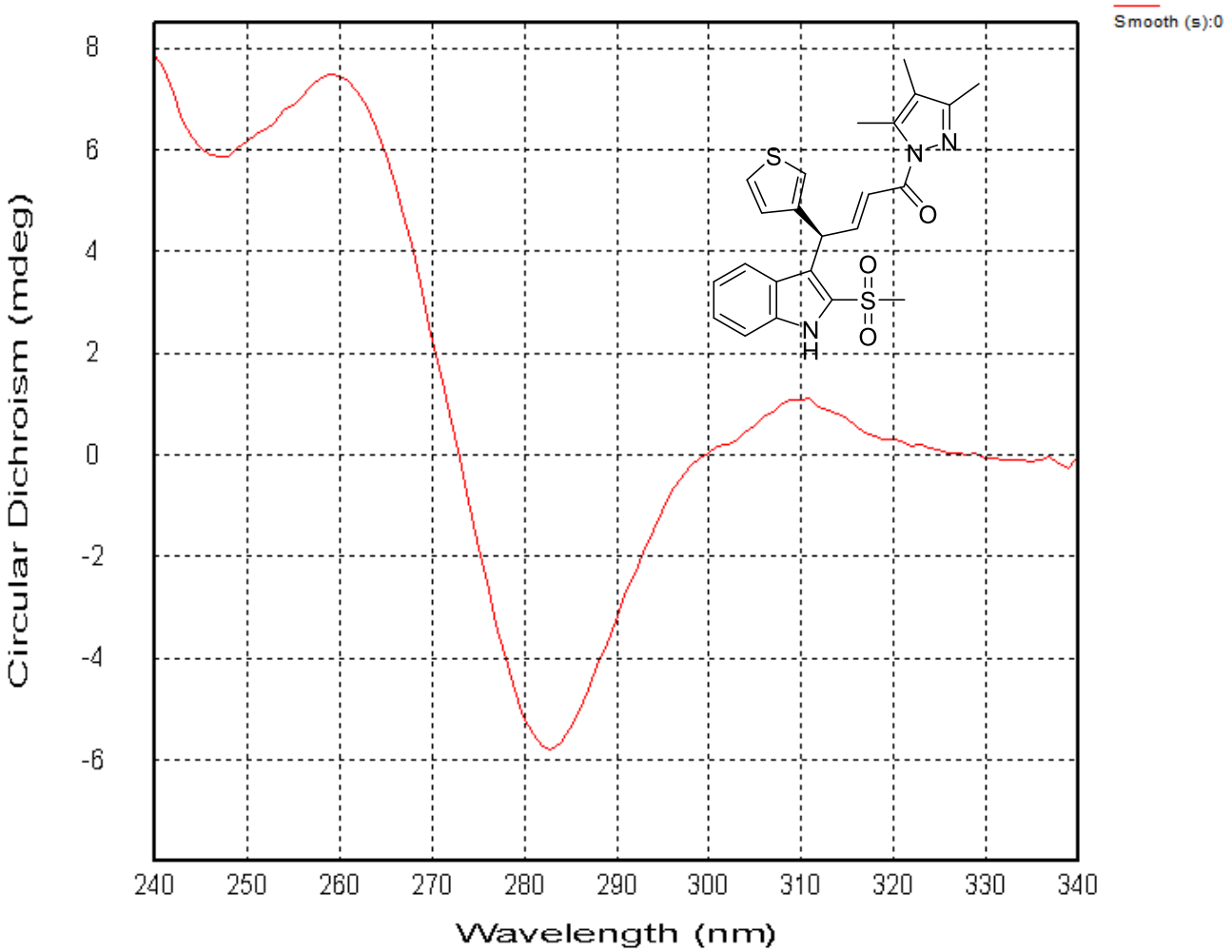
25
20
15
10
5
0
-5
-10
-15
-20
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
MeO
N
N
O
O
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
25
20
15
10
5
0
-5
-10
-15
-20
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
O
N
N
O
O
S
O
N
H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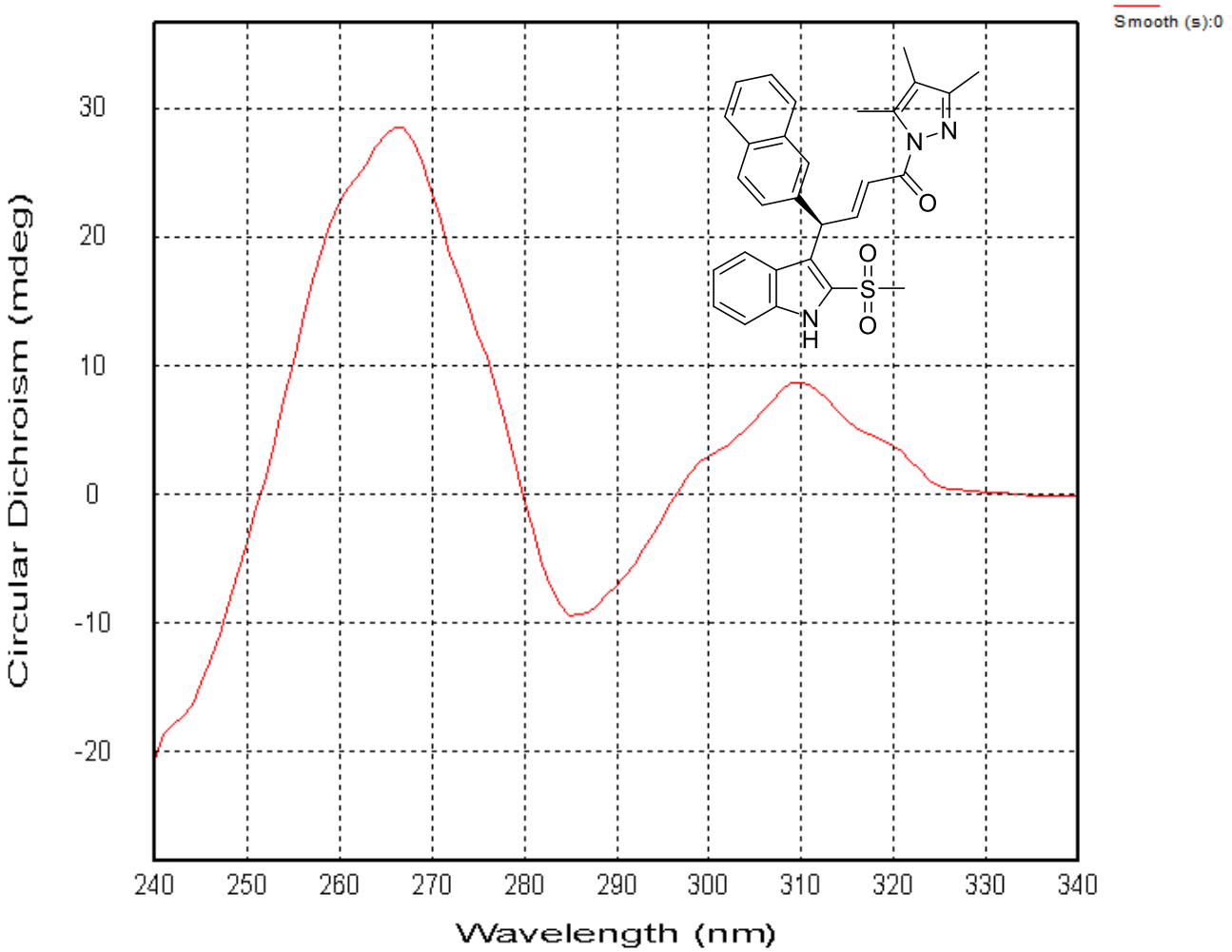
Circular Dichroism (mdeg)
8
6
4
2
0
-2
-4
-6
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
S
N
N
O
O
S
O
N
H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Circular Dichroism (mdeg)
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20
10
0
-10
-20
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
N
N
O
O
S
O
N
H

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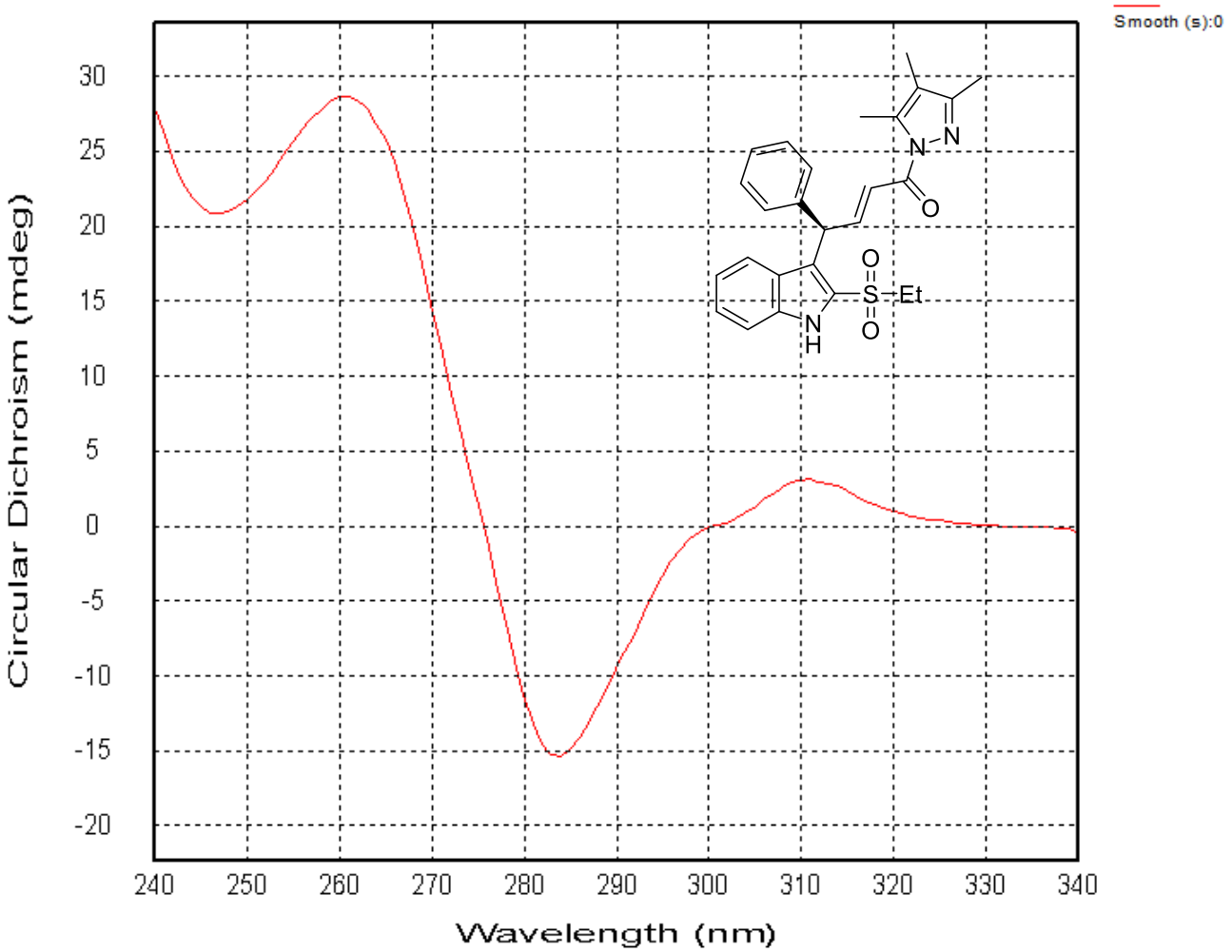
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Circular Dichroism (mdeg)
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25
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15
10
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0
-5
-10
-15
-20
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
N
N
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Et
O
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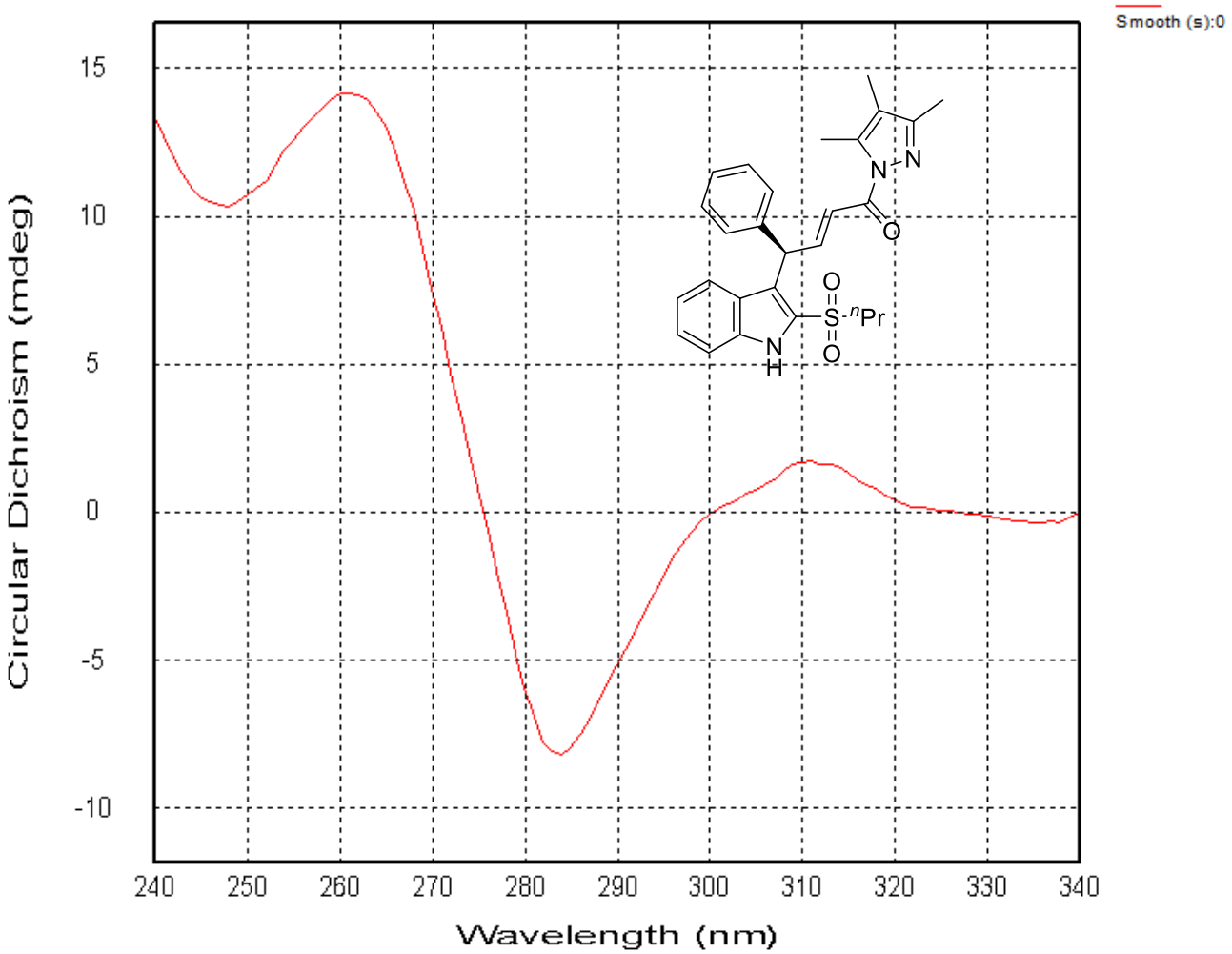
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Circular Dichroism (mdeg)
15
10
5
0
-5
-10
240
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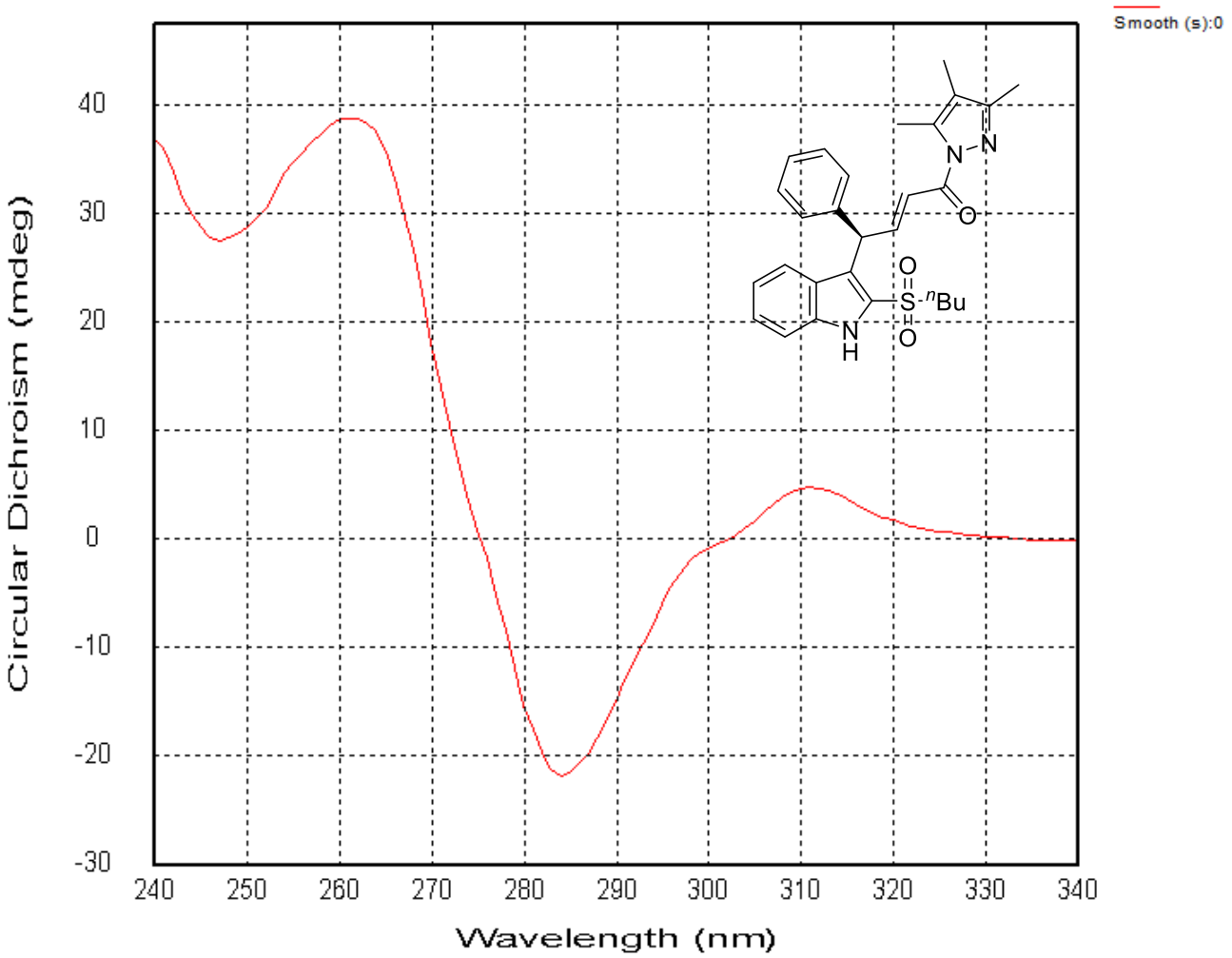
290
300
310
320
330
340
Wavelength (nm)
N
N
O
O
S
nPr
N
H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Circular Dichroism (mdeg)
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30
20
10
0
-10
-20
-30
240
250
260
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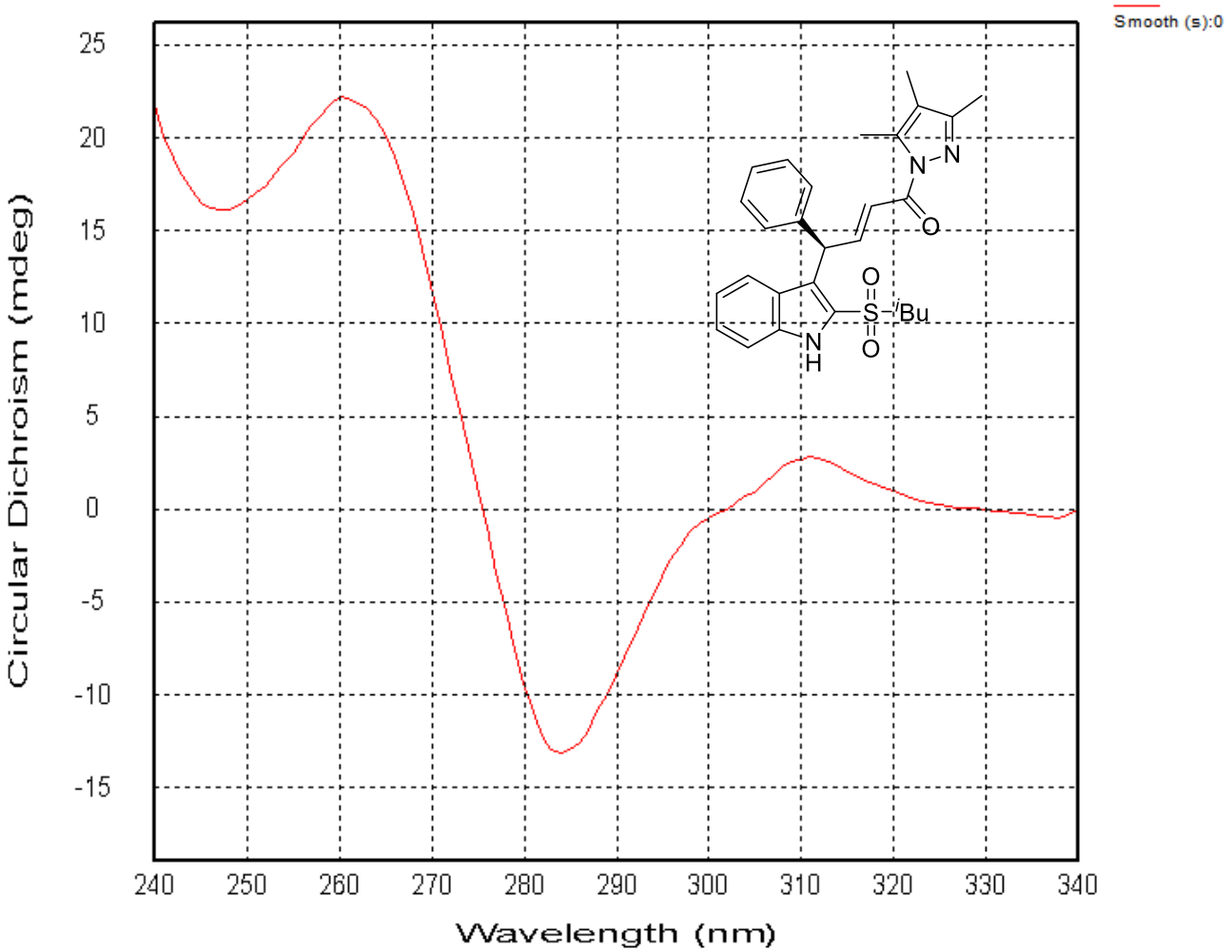
280
290
300
310
320
330
340
Wavelength (nm)
N
N
O
O
S
nBu
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
25
20
15
10
5
0
-5
-10
-15
240
250
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280
290
300
310
320
330
340
Wavelength (nm)
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O
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tBu
O
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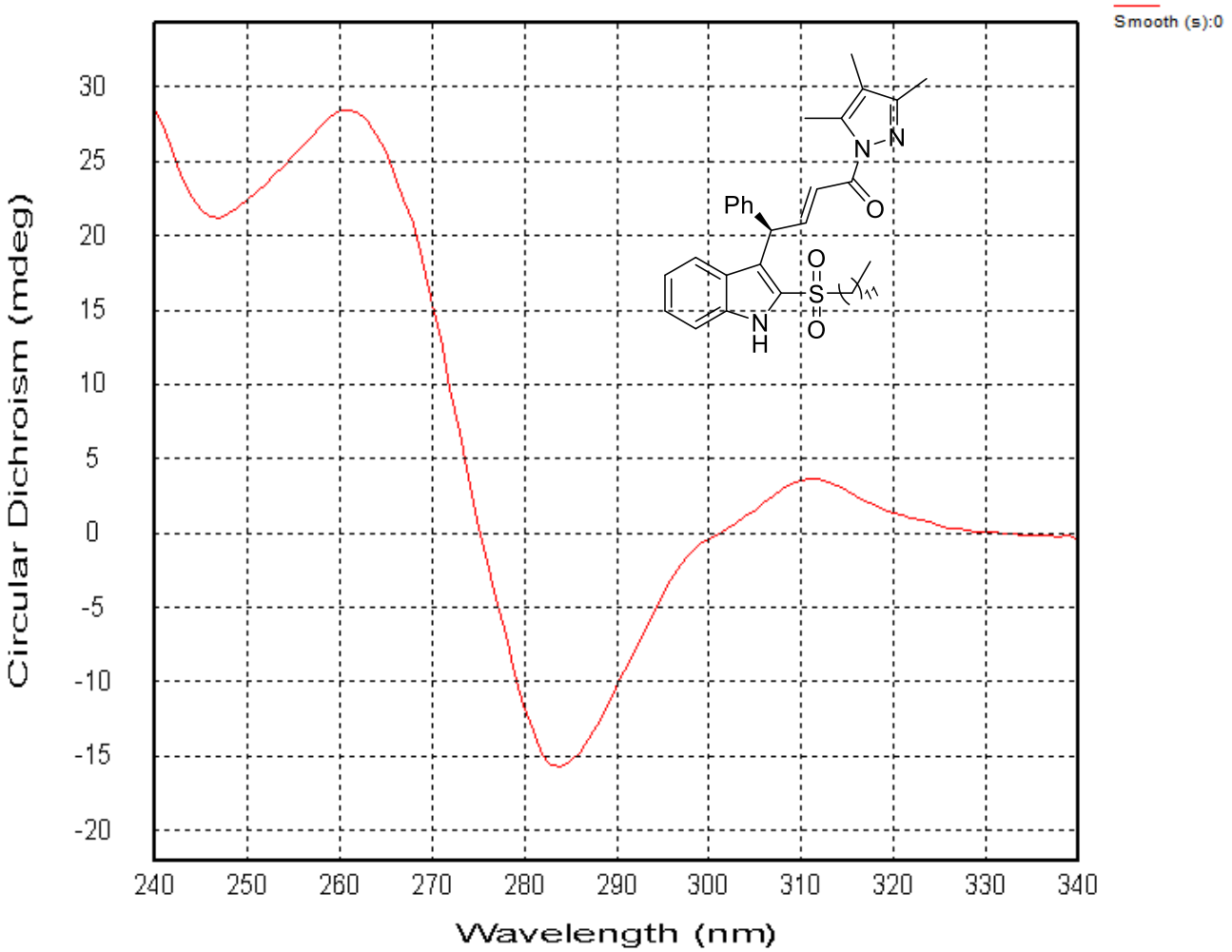
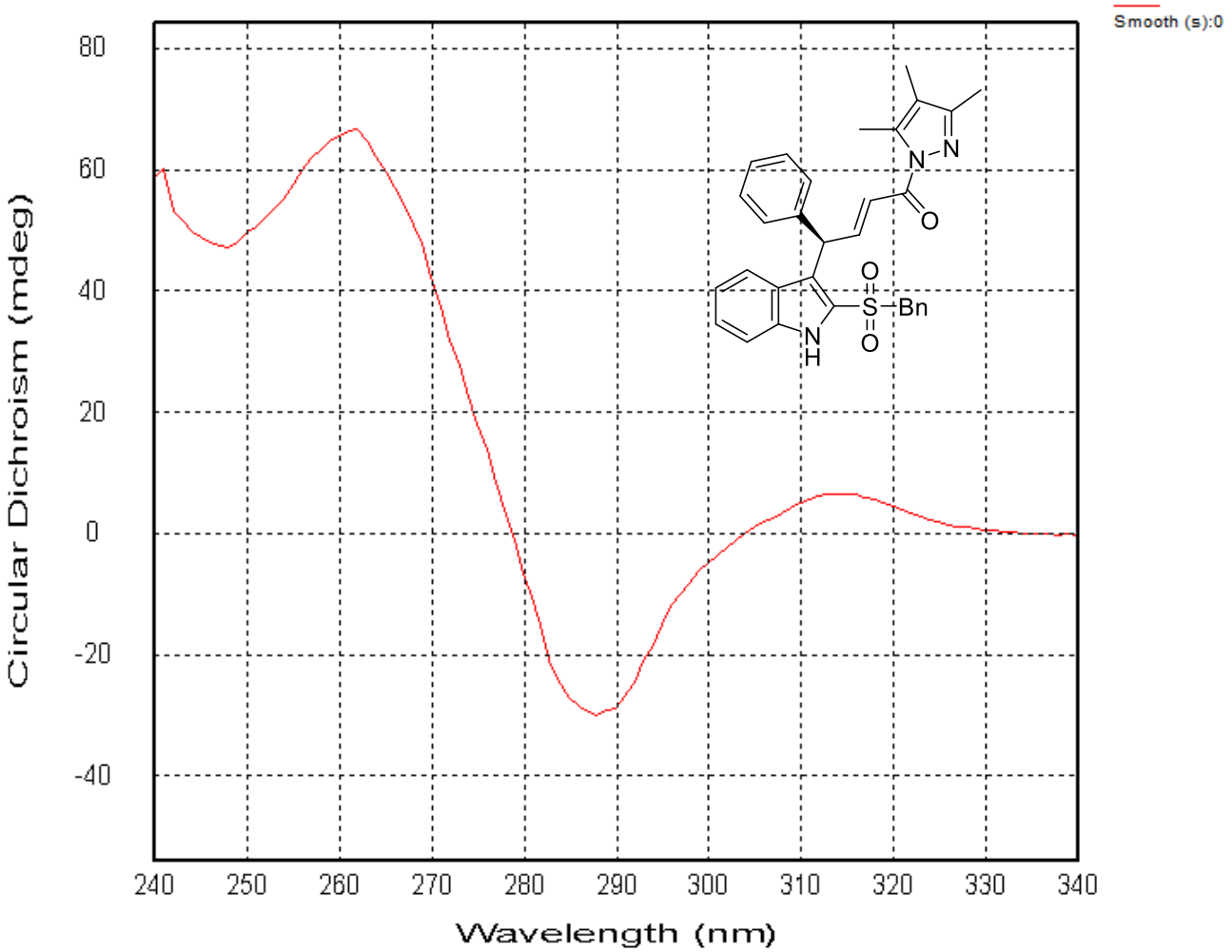
H


Smooth (s):0
Circular Dichroism (mdeg)
30
25
20
15
10
5
0
-5
-10
-15
-20
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
N
N
Ph
O
O
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
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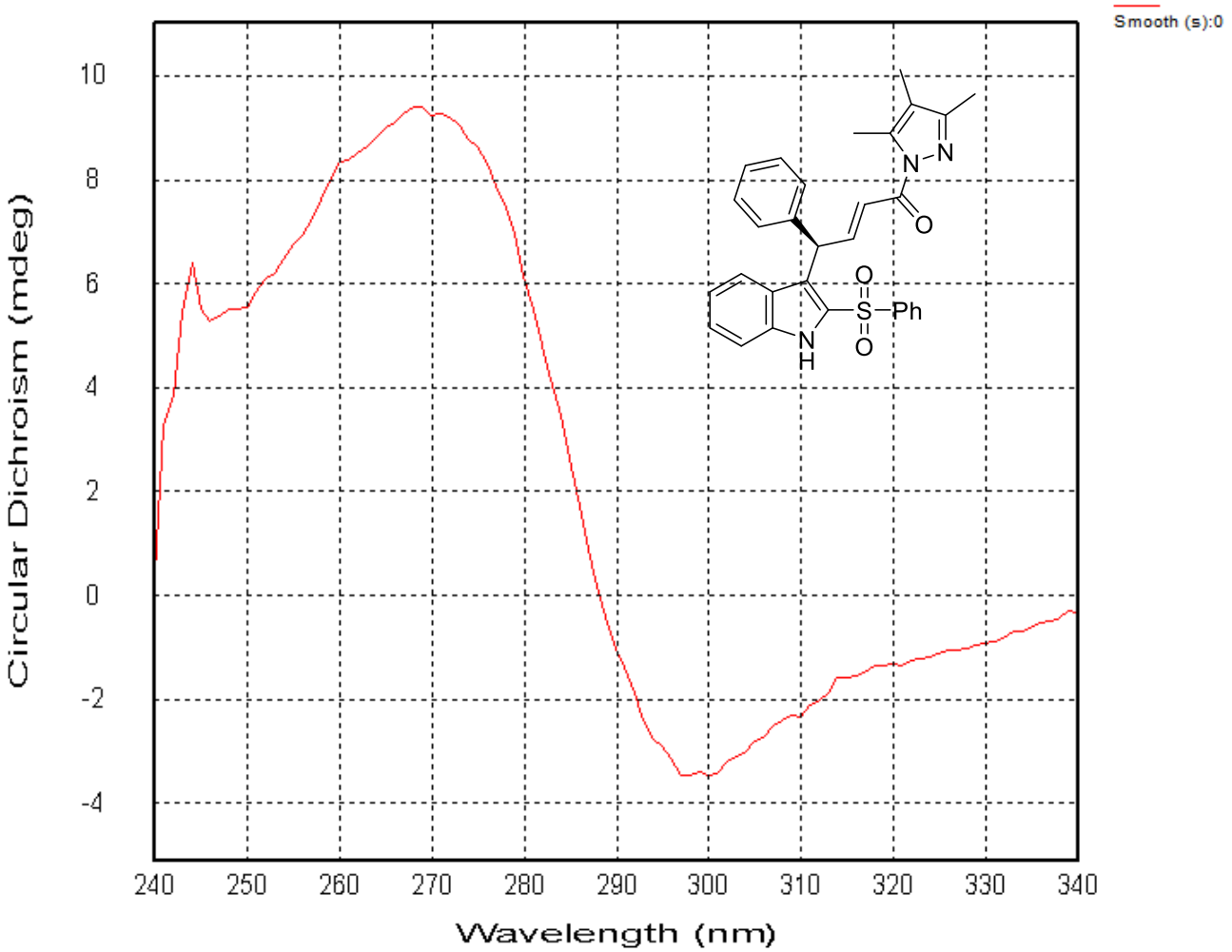
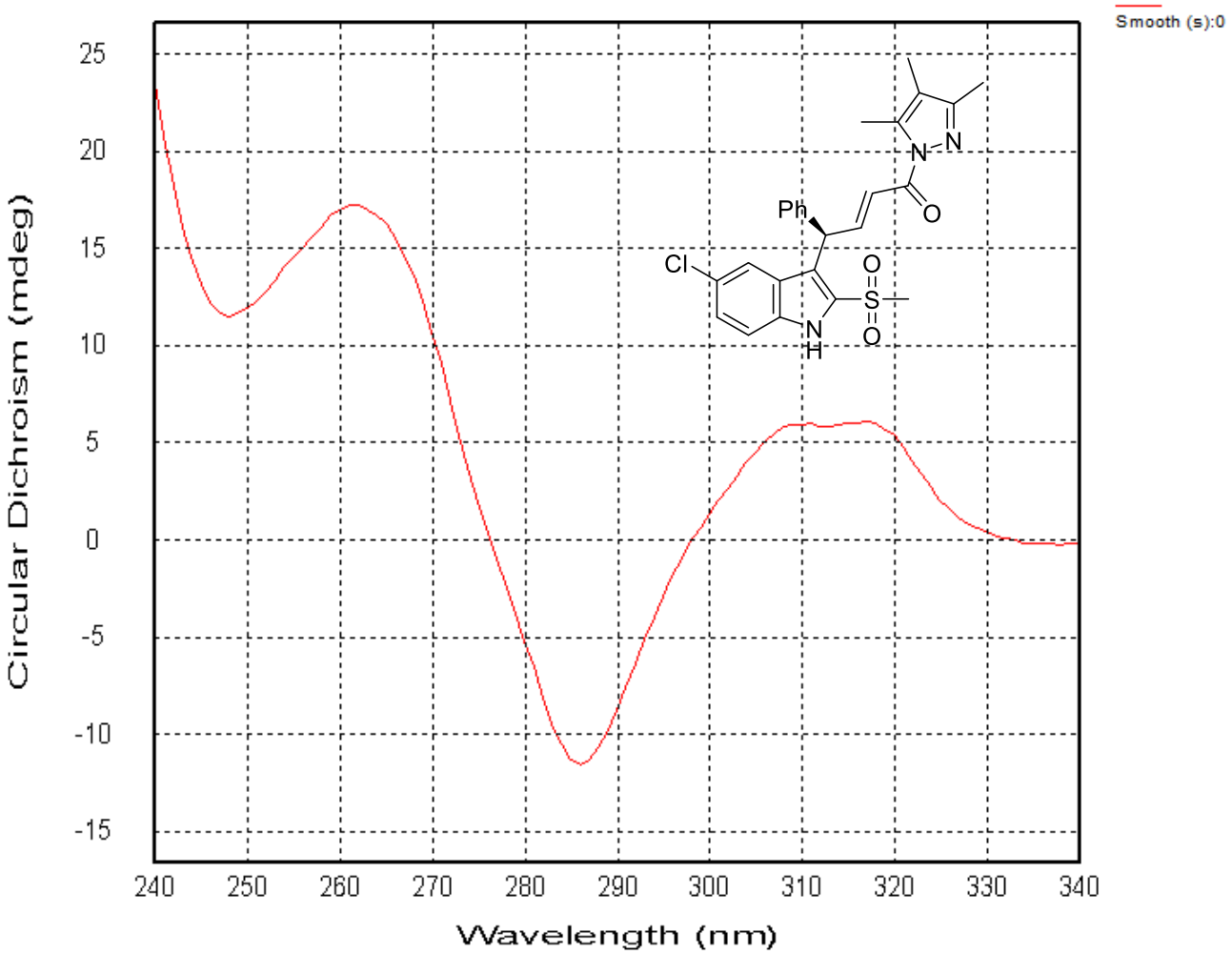
60
40
20
0
-20
-40
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
N
N
O
O
S
Bn
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
10
8
6
4
2
0
-2
-4
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
N
N
O
O
S
Ph
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
25
20
15
10
5
0
-5
-10
-15
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
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N
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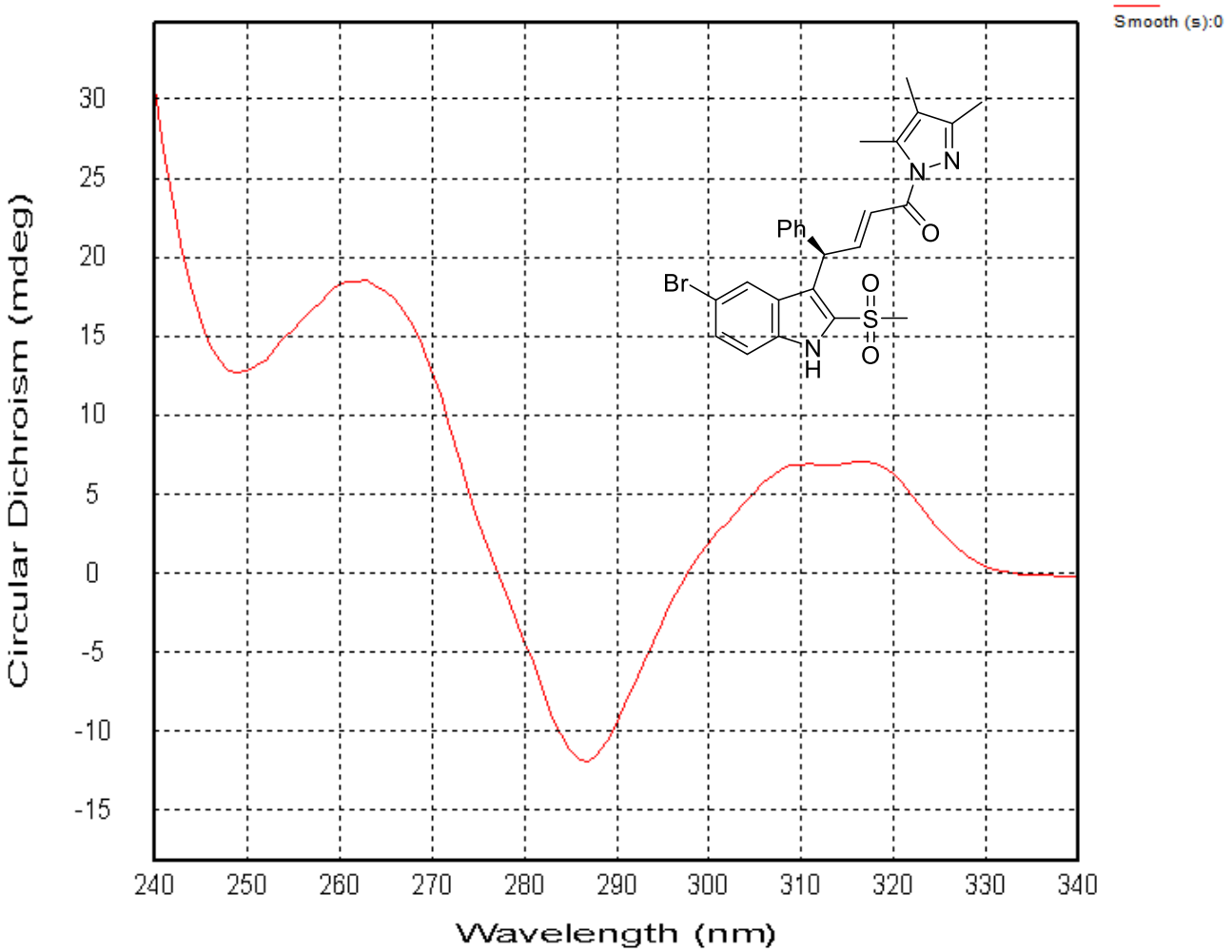
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
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25
20
15
10
5
0
-5
-10
-15
240
250
260
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290
300
310
320
330
340
Wavelength (nm)
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Ph
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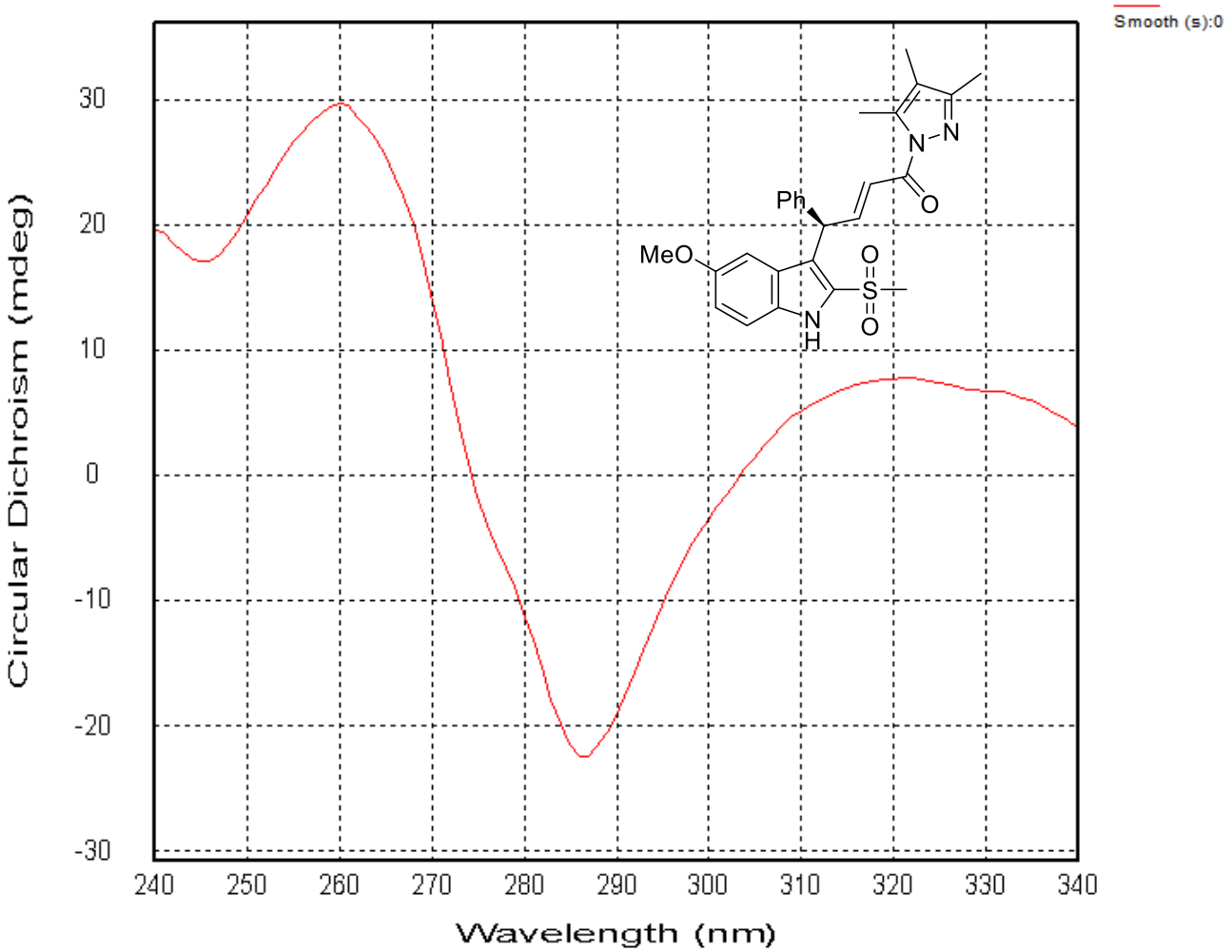
N
N
O
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
240
250
260
270
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290
300
310
320
330
340
Wavelength (nm)
Ph
MeO
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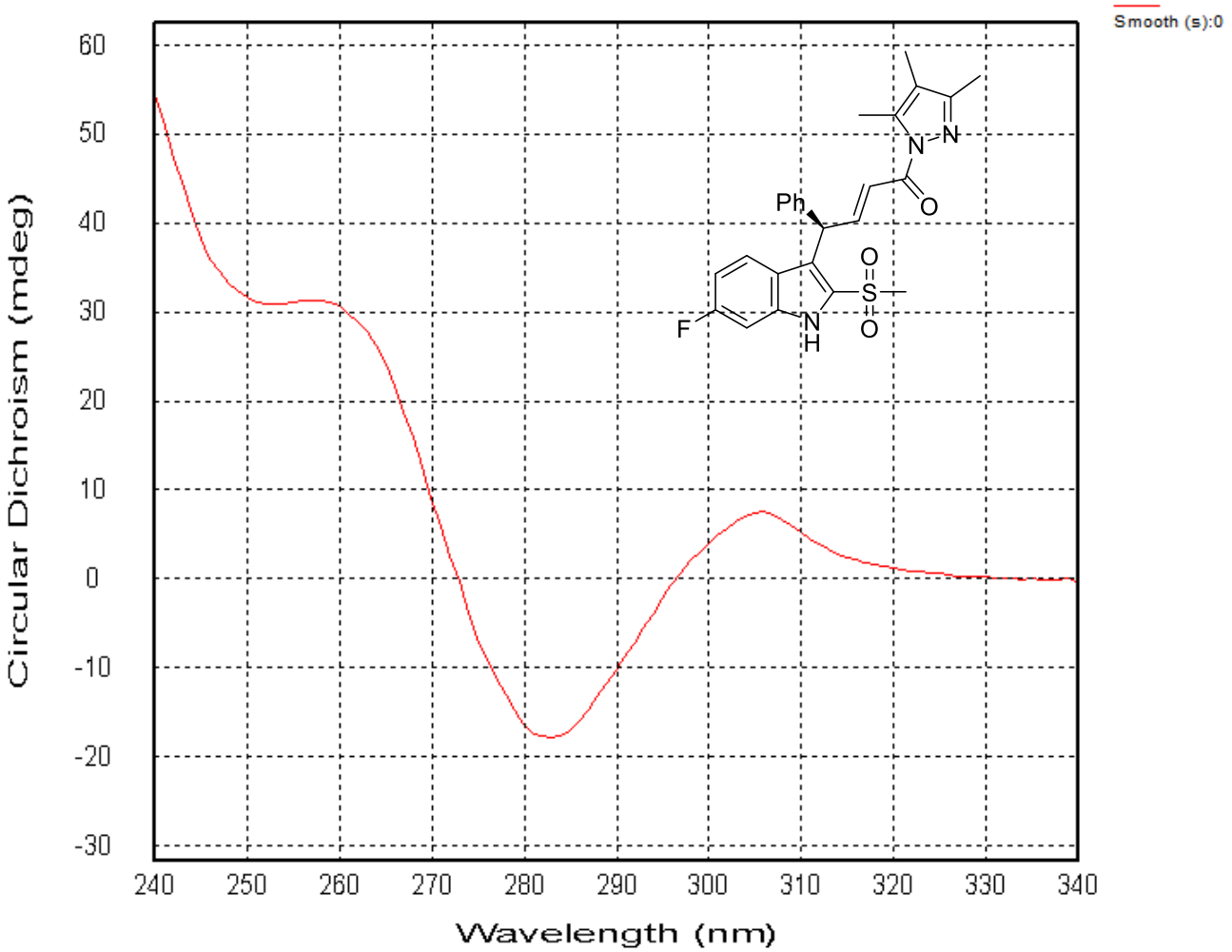
N
O
O
S
O
N
H


Smooth (s):0
Circular Dichroism (mdeg)
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50
40
30
20
10
0
-10
-20
-30
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
Ph
O
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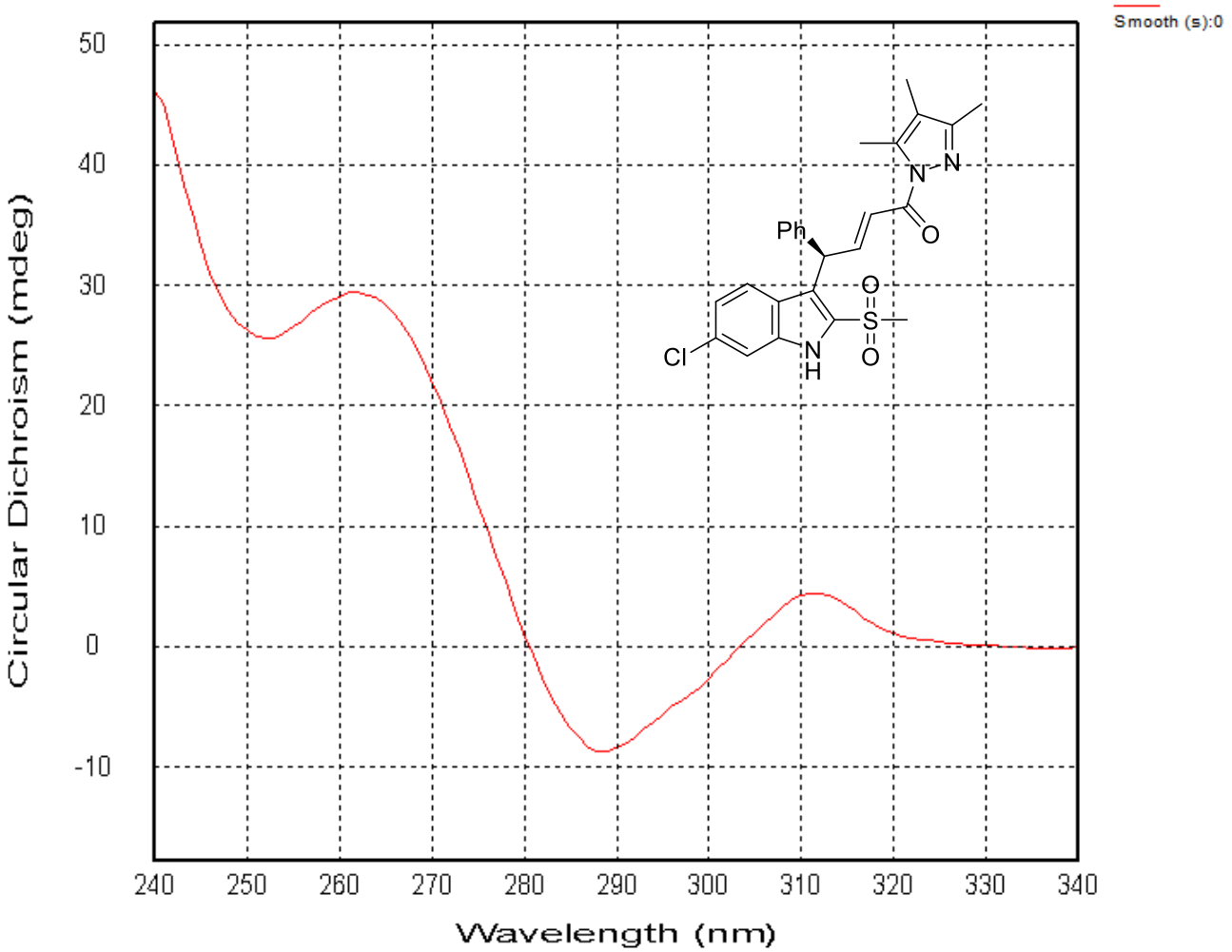
N
O
S
O
F
N
H


Smooth (s):0
Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
Ph
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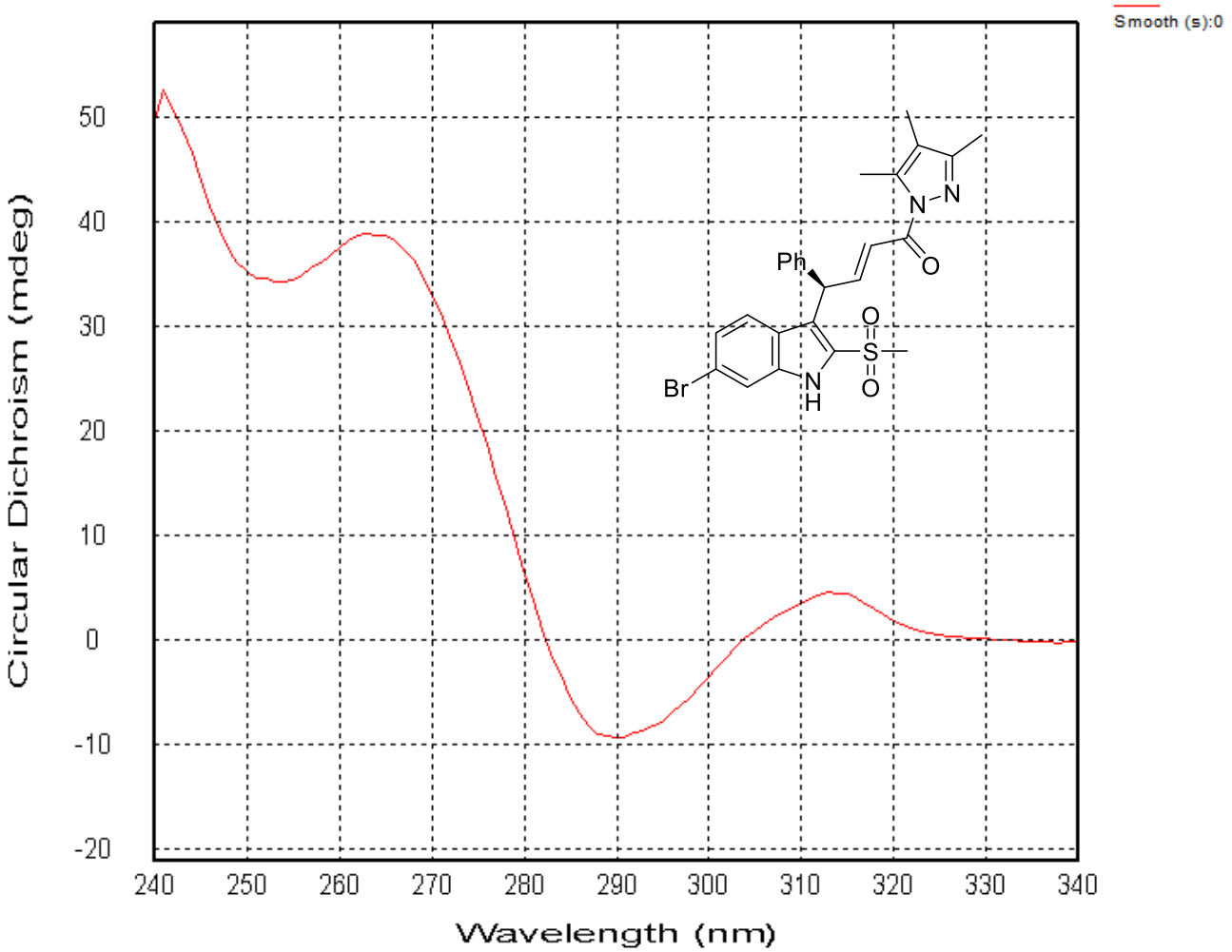
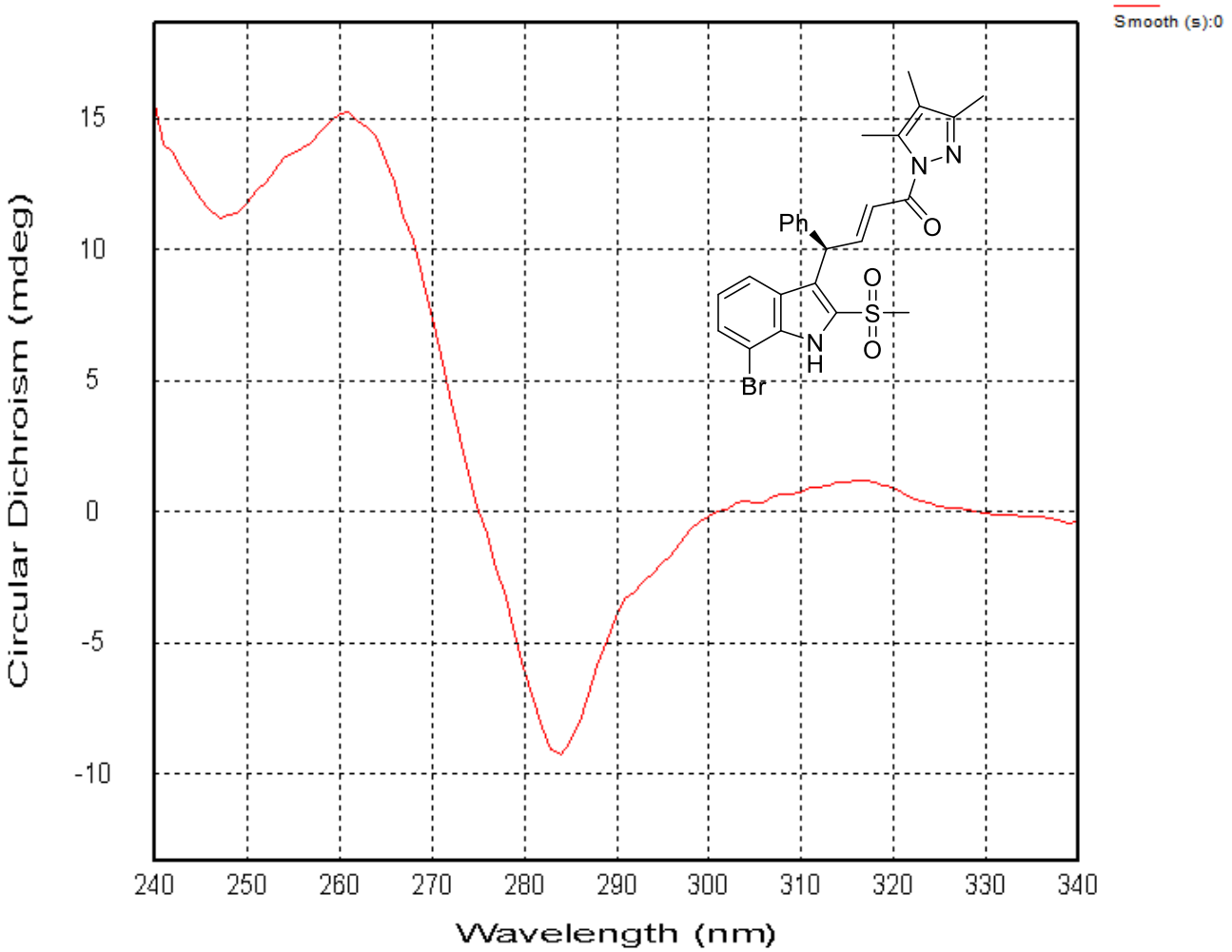
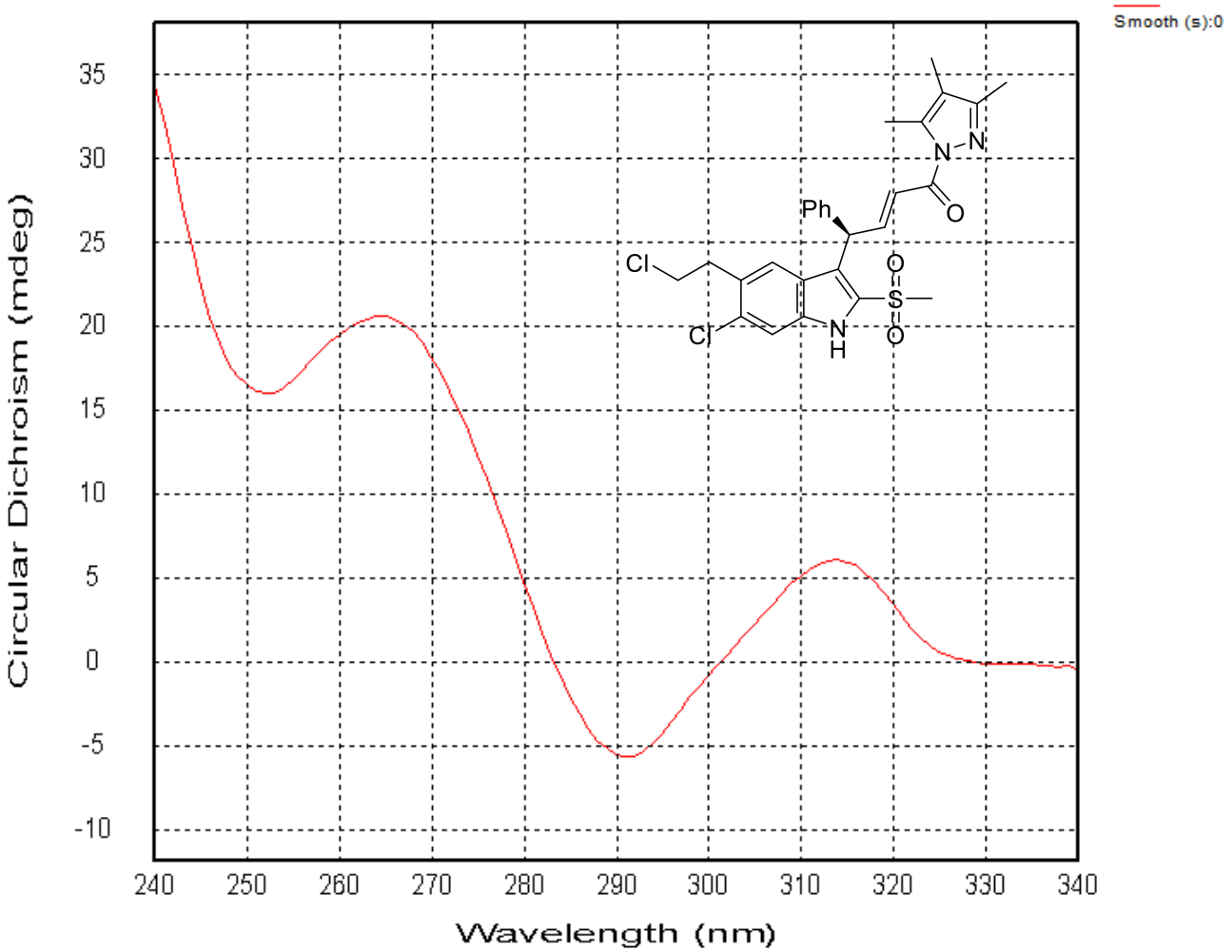
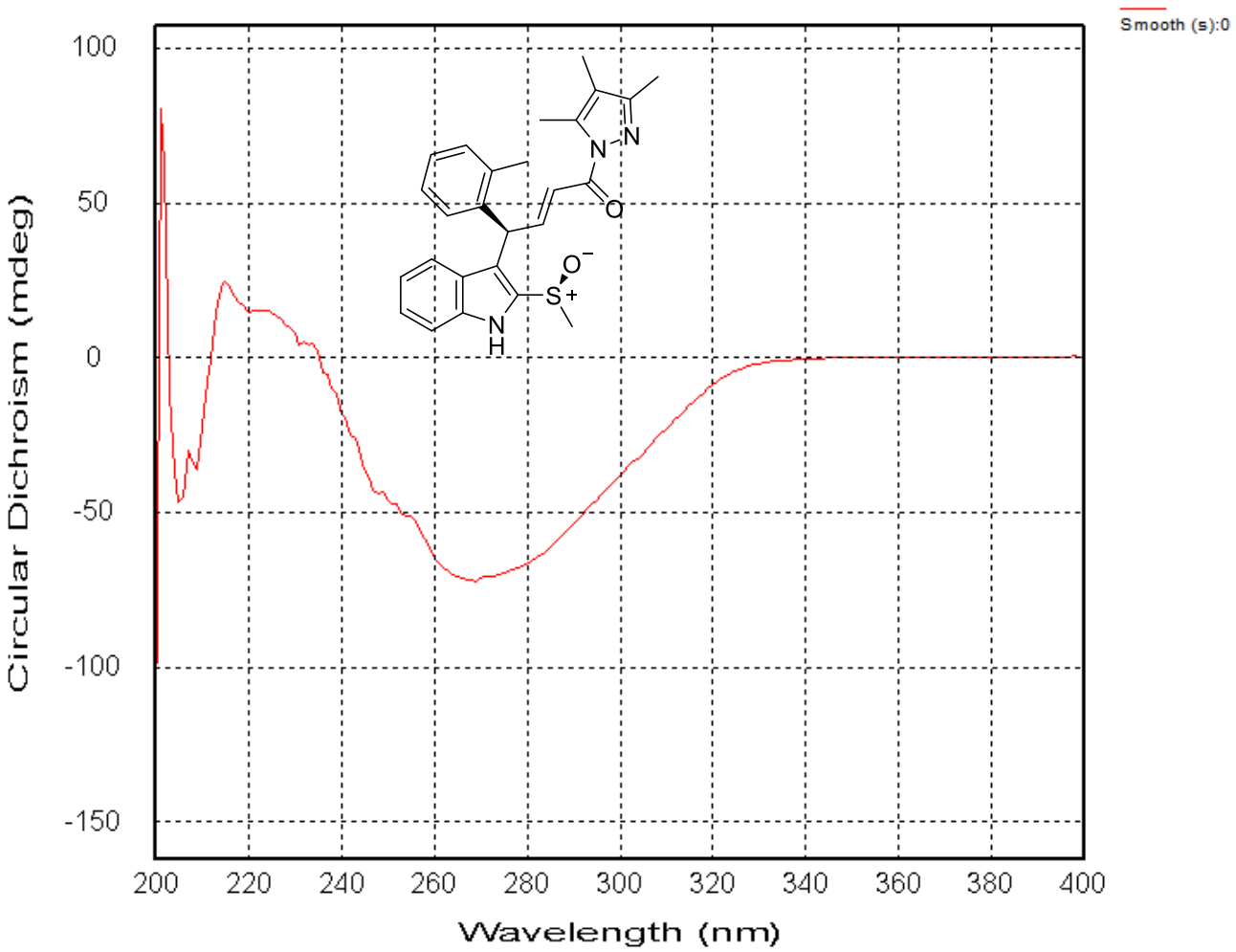
O
Cl
N
H


Smooth (s):0
Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
-20
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
N
N
O
Ph
O
S
O
Br
N
H


Smooth (s):0
Circular Dichroism (mdeg)
15
10
5
0
-5
-10
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
Ph
O
N
N
O
S
O
N
H
Br


Smooth (s):0
Circular Dichroism (mdeg)
35
30
25
20
15
10
5
0
-5
-10
240
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
Ph
Cl
Cl
N
H
O
S
O
O
N
N


Smooth (s):0
Circular Dichroism (mdeg)
100
50
0
-50
-100
-150
200
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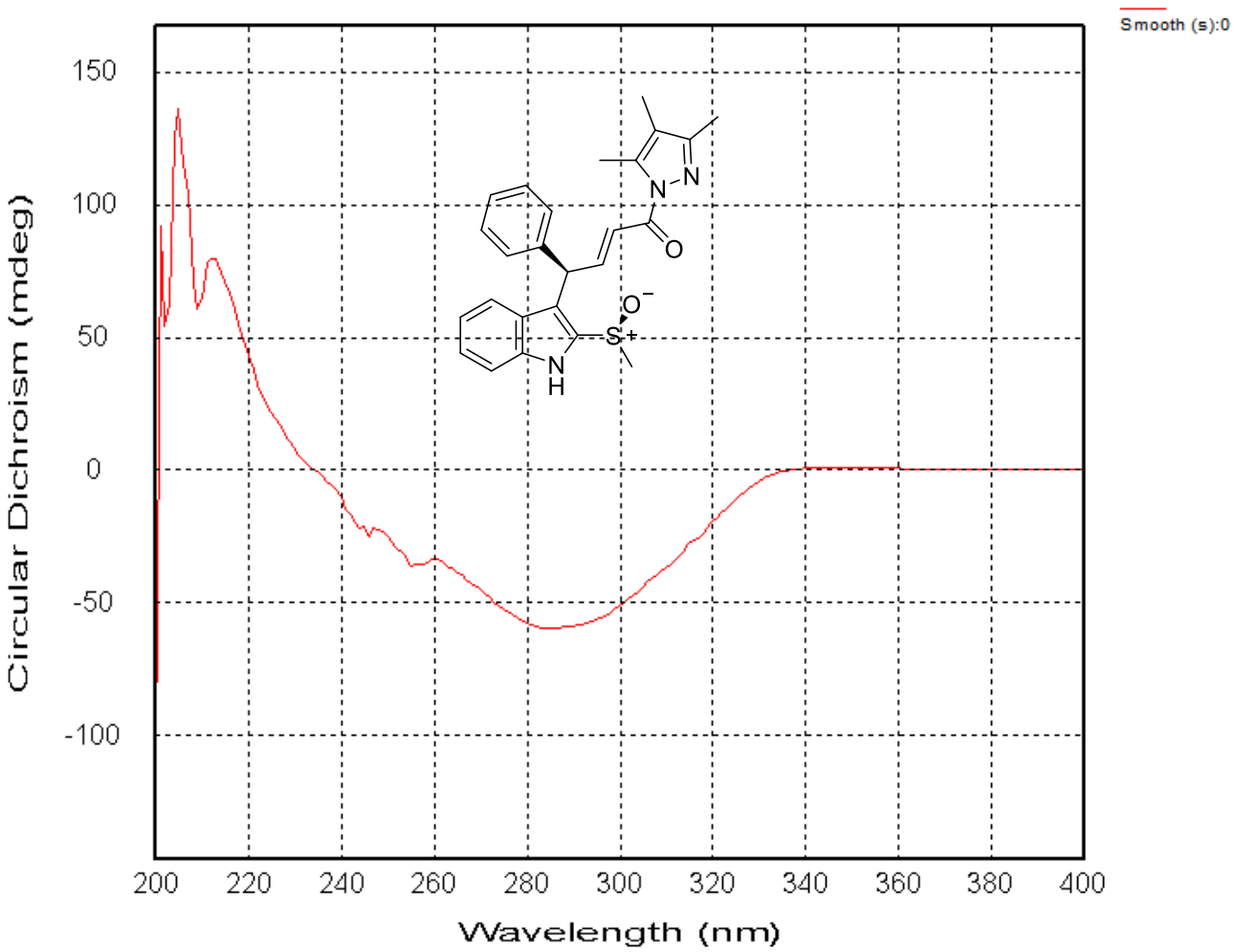
280
300
320
340
360
380
400
Wavelength (nm)
N
N
O
O⁻
S+
N
H


Smooth (s):0
Circular Dichroism (mdeg)
150
100
50
0
-50
-100
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
N
N
O
O⁻
S⁺
N
H