Electronic Supplementary Information

Visible light-induced 3-sulfenylation of *N*-methylindoles with arylsulfonyl chlorides

Min Chen, Zhi-Tang Huang and Qi-Yu Zheng

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Chinese Academy of Sciences, Beijing 100190, China

Fax: +86 10 62554449; Tel: +86 10 62652811; E-mail: zhengqy@iccas.ac.cn

Content

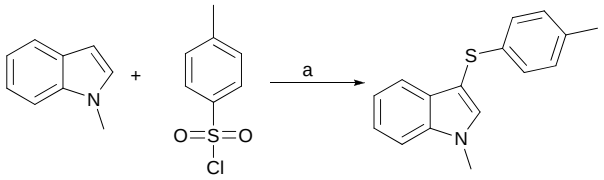
1. General methods

Unless specified noted, all reagents were purchased from commercial suppliers without further purification. All the solvents were treated according to general methods. Column chromatography was performed using 200-300 mesh silica gel (YanTai, China). ^{1}H NMR spectra were recorded on BRUKER 400 (400 MHz) spectrophotometer. Chemical shifts (δ) are reported in ppm from TMS as the internal standard (TMS 0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on BRUKER 400 (100 MHz) with complete proton decoupling spectrophotometer. Mass spectra were measured on a Micromass UK MS spectrometer (EI) or Bruker Apex IV FTMS (ESI).

2. Optimization of the reaction of *N*-methylindole with *p*-toluene sulfonyl chloride

A 25 ml Schlenk tube equipped with stir-bar was charged with *p*-tolylsulfonyl chloride (**2a,** 1 mmol), photocatalyst (2% mol), additives (2 mmol, if it existed as solid). The system was evacuated 3 times and backfilled with Ar before *N*-methylindoles (**1a**), solvent and other liquid additives were added by syringe. Then the vial was evacuated 3 times and backfilled with Ar again at -78 ^{o}C and slowly warmed to 40 ^{o}C. After given time 12 hours under 23 w fluorescent light, the reaction mixture was diluted with CH_2Cl_2 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.

Table S1 Evaluation of various parameters in the photoredox reaction



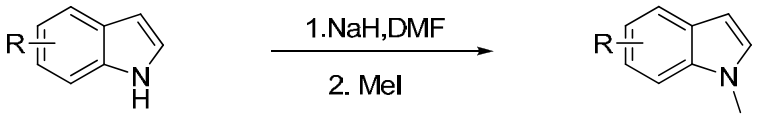
1a **2a** **3a**

Entry[a]	Photocatalyst	Solvent	Ratio of **1a**/**2a**	Additive	Yield[b]
1	$Ru(bpy)_3Cl_2$	CH_3CN	1	_	23%
2	$Ru(bpy)_3Cl_2$	CH_3CN	1	K_2HPO_4	_
3	$Ru(bpy)_3Cl_2$	CH_3CN	1	$NaHCO_3$	_
4	$Ru(bpy)_3Cl_2$	CH_3CN	1	2,6-lutidine	_
5	$Ru(bpy)_3Cl_2$	CH_3CN	1	TMEDA	Trace
6	$Ru(bpy)_3Cl_2$	CH_3CN	1	*i*-Pr_2NEt	_[c]
7	$Ru(bpy)_3Cl_2$	CH_3CN	3	_	57%
8	$Ru(bpy)_3Cl_2$	CH_3CN	2	_	26%
9	$Ru(bpy)_3Cl_2$	CH_3CN	5	_	58%
10[d]	$Ru(bpy)_3Cl_2$	CH_3CN	3	_	[e]
11[f]	$Ru(bpy)_3Cl_2$	CH_3CN	3	_	55%
12	$Ru(bpy)_3(PF_6)_2$	CH_3CN	3	_	59%
13	$Ru(bpy)_3(PF_6)_2$	DMF	3	_	Trace
14	$Ru(bpy)_3(PF_6)_2$	DMSO	3	_	_
15	$Ru(bpy)_3(PF_6)_2$	NMP	3	_	_
16	$Ru(bpy)_3(PF_6)_2$	CH_3CN/DMF[g]	3	_	Trace
17	$Ru(bpy)_3(PF_6)_2$	CH_3CN	3	4Å MS	_
18[h]	$Ru(bpy)_3(PF_6)_2$	CH_3CN	3	_	_

[a] Unless otherwise specified, all reactions were carried out with **1a**, **2a** (1 mmol), photocatalyst (2% mol), under 23 w fluorescent light at 40 °C with atmosphere of Ar for 12 h. [b] Isolated yield. [c] Indoles were not involved in reactions. [d] At temperature of 20 °C. [e] similar conversion as entry 7 indicated by TLC, but not isolated. [f] At temperature of 30 °C. [g] 10 mmol CH_3CN with 2.5 mmol DMF. [h] No light.

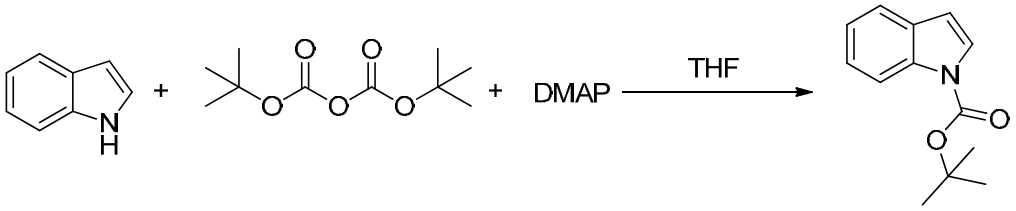
3. The procedure for the synthesis of reactants

General procedure for the synthesis of substitued *N*-alkylindoles.



To a stirred solution of substituted 1*H*-indole (10 mmol) in dry DMF (25 mL), NaH (640 mg, 60% suspension in mineral oil, 16 mmol) was added portionwise under Ar atmosphere at 0 ^{o}C. The reaction mixture was then warmed to room temperature and stirred for 30 min. After cooling to 0 ^{o}C, alkyl agents MeI (12 mmol) or benzyl bromide (12 mmol) was added dropwise to the solution, warming to room temperature. Water was added to quench the system when TLC indicated it was over (**Caution!**). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give desired compound.

Procedure for the synthesis of *tert*-butyl 1*H*-indole-1-cabxylate.



To the THF solution of 1*H*-indole (585 mg, 5 mmol), *N*,*N*-dimethylpyridin-4-amine (DMAP) (915 mg, 7.5 mmol) and Boc anhydride (2.18 g, 10 mmol) was added and the solution was stirred under room temperature. The reaction mixture was quenched by saturated sodium bicarbonate solution (20 mL) extracted by ethyl acetate (3 x 20 mL). Combined organic phase were washed by water, brine and dried over anhydrous Na_2SO_4, concentrated under vacuum. The residue was then purified by flash chromatography on silica gel.

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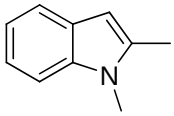
4. General procedure for the 3-sulfenlylation of *N*-methylindoles with arylsulfonyl chlorides

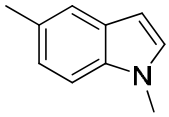
A 25 ml Schlenk tube equipped with stir-bar was charged with arylsulfonyl chloride (if it was solid, 1 mmol), photocatalyst $Ru(bpy)_3(PF_6)_2$ (2% mol) and indole derivatives (if it was solid, 3 mmol). The system was evacuated 3 times and backfilled with Ar before solvent 2.5 ml CH_3CN and liquid reactants were added by syringe. Then the vial was evacuated 3 times and backfilled with Ar again at -78 ^oC and warmed to 40 ^oC. After given time under 23 w fluorescent light, the reaction mixture was diluted with CH_2Cl_2 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.

5. Experimental data for the described substances



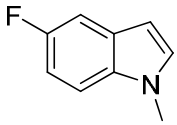
1,2-Dimethyl-1*H*-indole

Yielding the title compound as yellow solid in 80% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.26-7.30 (m, 1H), 7.19-7.22 (m, 1H), 6.38 (s, 1H), 3.74 (s, 3H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.5, 136.9, 128.2, 120.6, 119.8, 119.4, 108.9, 99.7, 29.5, 12.9. The spectroscopic data are in accordance with those reproted.[1]



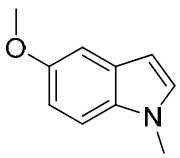
1,5-Dimethyl-1*H*-indole

Yielding the title compound as yellow oil in 75% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (s, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.91 (d, J =3.2 Hz, 1H), 6.36 (d, J = 3.2 Hz, 1H), 3.63 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.3, 129.0, 128.9, 128.5, 123.3, 120.6, 109.0, 100.4, 32.8, 21.6. The spectroscopic data are in accordance with those reproted.[2]



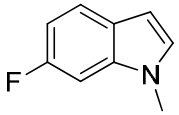
5-Fluoro-1-methyl-1*H*-indole

Yielding the title compound as white solid in 73% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 (dd, J = 2.4, 10 Hz, 1H), 7.16 (dd, J = 4.2, 8.9 Hz, 1H), 7.02 (d, J =3.0 Hz, 1H), 6.93 (dt, J = 2.4, 9.1 Hz, 1H), 6.40 (d, J =3.0 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 156.9, 133.6, 130.6, 128.9, 128.8, 110.1, 110.0, 109.91, 109.85, 105.8, 105.5, 101.02, 100.97, 33.1. The spectroscopic data are in accordance with those reproted.[3]



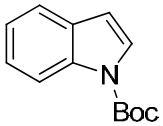
5-Methoxy-1-methyl-1*H*-indole

Yielding the title compound as a white solid in 92% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 2.2 Hz, 1H), 7.01 (d, J = 2.6 Hz, 1H), 6.89 (dd, J =2.3, 8.8 Hz, 1H), 6.40 (d, J = 2.6 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.2, 132.3, 129.5, 129.0, 112.0, 110.0, 102.7, 100.5, 56.0, 33.0. The spectroscopic data are in accordance with those reproted.[1]



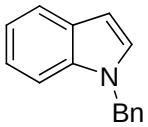
6-Fluoro-1-methyl-1*H*-indole

Yielding the title compound as yellow oil in 75% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (dd, J = 5.4, 8.6 Hz, 1H), 6.82-6.86 (m, 2H), 6.73-6.78 (m, 1H), 6.33 (d, J = 3.1 Hz, 1H), 3.53 (s, 3H), ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.2, 158.8, 137.0, 136.9, 129.40, 129.36, 125.1, 121.7, 121.6, 108.3, 108.2, 101.3, 95.9, 95.6, 32.9. The spectroscopic data are in accordance with those reproted.[2]



***tert*-Butyl 1*H*-indole-1-carboxylate**

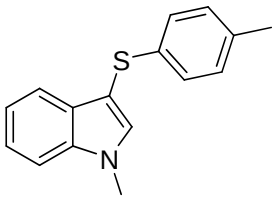
Yielding the title compound as a white solid in 100% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16 (d, J = 5.4 Hz, 1H), 7.57 (d, J = 1.8 Hz, 1H), 7.52 (d, J = 4 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 6.52 (d, J = 1.8 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.9, 135.3, 130.7, 125.9, 124.3, 122.7, 121.0, 115.3, 107.4, 83.6, 28.3. The spectroscopic data are in accordance with those reproted.[4]



1-Benzyl-1*H*-indole

Yielding the title compound as white solid in 94% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, J = 7.7 Hz, 1H), 7.22-7.30 (m, 4H), 7.14-7.18 (m, 1H), 7.09-7.12 (m, 4H), 6.54 (d, J = 3.1 Hz, 1H), 5.31 (s, 2H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.6, 136.4, 128.8, 128.7, 128.3, 127.6, 126.8, 121.7, 121.0, 119.6, 109.7, 101.7, 50.1. The spectroscopic data are in

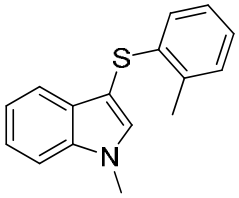
accordance with those reproted.[2]



3a

1-Methyl-3-(*p*-tolylthio)-1*H*-indole

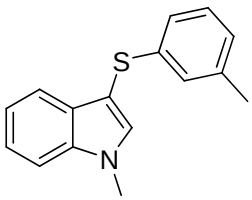
Prepared according to the general procedure from **1a** (3 mmol), **2a** (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (64% yield). M.p.: 122-123 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.21–7.28 (m, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 3.79 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 136.2, 135.0, 134.7, 130.1, 129.6, 126.4, 122.7, 120.6, 120.0, 109.9, 101.5, 33.2, 21.0. IR (film, cm^{-1}): v 1631, 1488, 1458, 740. HRMS (EI): Calcd for $C_{16}H_{15}NS$ $[M]^+$: m/z 253.0925; found: 253.0928.



3b

1-Methyl-3-(*o*-tolylthio)-1*H*-indole

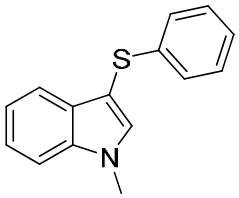
Prepared according to the general procedure from **1a** (3 mmol), 2-methylbenzene-1-sulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 24 hours to provide the title compound as a white solid in 44% yield. M.p.: 130-131 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.26-7.29 (m, 2H), 7.10-7.16 (m, 2H), 6.95 (t, J = 7.2 Hz, 1H), 6.87 (t, J = 7.2 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): δ 138.7, 137.7, 135.1, 134.3, 130.0, 129.8, 126.2, 125.3, 124.4, 122.6, 120.5, 119.8, 109.7, 100.3, 33.1, 19.9. IR (film, cm^{-1}): v 1631, 1466. HRMS (EI): Calcd for $C_{16}H_{15}NS$ $[M]^+$: m/z 253.0925; found: 253.0929.



3c

1-Methyl-3-(*m*-tolylthio)-1*H*-indole

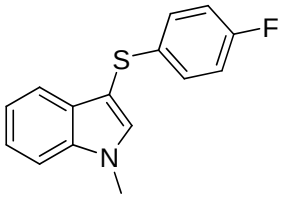
Prepared according to the general procedure from **1a** (3 mmol), 3-methylbenzene-1-sulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (60% yield). M.p.: 87-88 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.28 (t, J = 8.2 Hz, 2H), 7.15 (t, J = 8.2 Hz, 1H), 6.97-7.04 (m, 2H), 6.85 (t, J = 7.1 Hz, 2H), 3.82 (s, 3H), 2.21 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 138.4, 137.6, 135.0, 130.0, 128.6, 126.5, 125.7, 123.0, 122.5, 120.5, 119.8, 109.7, 100.9, 33.1, 21.4. IR (film, cm^{-1}): ν 1590, 1573, 1458. HRMS (EI): Calcd for $C_{16}H_{15}NS$ $[M]^+$: m/z 253.0925; found: 253.0930



3d

1-Methyl-3-(phenylthio)-1*H*-indole

Prepared according to the general procedure from **1a** (3 mmol), benzenesulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (66% yield). ^1H NMR (400 MHz, $CDCl_3$) : δ 7.60 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.08-7.17 (m, 5H), 7.00-7.04 (m, 1H), 3.80 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 137.8, 135.2, 130.0, 128.8, 126.0, 124.9, 122.8, 120.7, 119.9, 109.9, 100.8, 33.3. The spectroscopic data are in accordance with those reproted.[5]

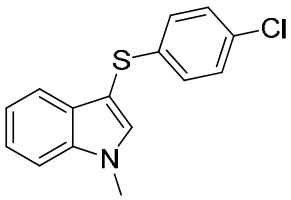


3e

3-((4-Fluorophenyl)thio)-1-methyl-1*H*-indole

Prepared according to the general procedure from **1a** (3 mmol), 4-fluorobenzene-1-sulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (68% yield). M.p.: 56-58 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.27 (t, J = 6.5 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 7.05-7.08 (m, 2H), 6.84 (t, J = 8.7 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 159.9, 137.8, 135.1, 134.8, 134.7, 129.8, 128.03,

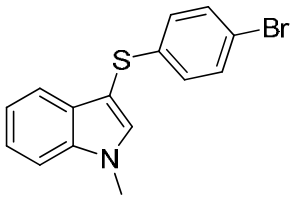
127.96, 122.9, 120.8, 119.8, 116.0, 115.8, 110.0, 101.3, 33.3. IR (film, cm^{-1}): *v* 1631, 1510, 1487, 1457. HRMS (EI): Calcd for $C_{15}H_{12}FNS$ $[M]^+$: *m/z* 257.0674; found:257.0677.



3f

3-((4-Chlorophenyl)thio)-1-methyl-1*H*-indole

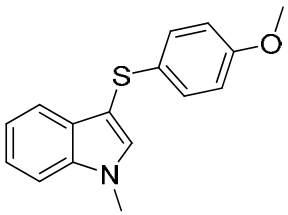
Prepared according to the general procedure from **1a** (3 mmol), 4-chlorobenzene-1-sulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (68% yield). M.p.: 137-138 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 137.8, 135.3, 130.6, 129.8, 128.9, 127.2, 122.9, 120.9, 119.8, 110.0, 100.4, 33.3. IR (film, cm^{-1}): *v* 1656, 1628, 1508, 1470. HRMS (EI): Calcd for $C_{15}H_{12}ClNS$ $[M]^+$: *m/z* 273.0379; found: 273.0382



3g

3-((4-bromophenyl)thio)-1-methyl-1H-indole

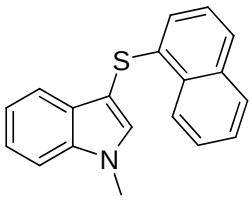
Prepared according to the general procedure from **1a** (3 mmol), 4-bromobenzene-1-sulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (63% yield). M.p.: 170-171 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.28-7.32 (m, 2H), 7.23-7.25 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 8.6Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 137.8, 135.3, 131.8, 129.7, 127.5, 122.9, 120.9, 119.8, 118.4, 110.0, 100.1, 33.3. IR (film, cm^{-1}): *v* 1504, 1472. HRMS (EI): Calcd for $C_{15}H_{12}{}^{79}BrNS$ $[M]^+$: *m/z* 316.9874; found: 316.9877; $C_{15}H_{12}{}^{81}BrNS$ $[M]^+$: *m/z* 318.9853; found: 318.9856



3h

3-((4-Methoxyphenyl)thio)-1-methyl-1*H*-indole

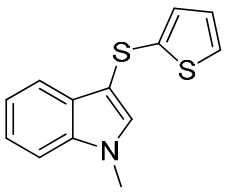
Prepared according to the general procedure from **1a** (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J =7.9 Hz, 1H), 7.23-7.34 (m, 3H), 7.10-7.16 (m, 3H), 6.72 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 137.5, 134.5, 130.1, 129.8, 128.5, 122.5, 120.4, 119.8, 114.5, 109.7, 102.5, 55.4, 33.1. The spectroscopic data are in accordance with those reproted.[5]



3i

1-Methyl-3-(naphthalen-1-ylthio)-1*H*-indole

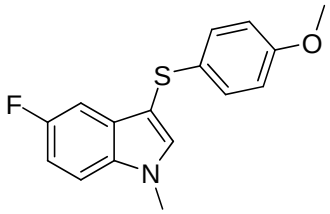
Prepared according to the general procedure from **1a** (3 mmol), naphthalene-1-sulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (45% yield). M.p.: 150-151 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.48-7.59 (m, 4H), 7.36 (t, J = 9.4 Hz, 2H), 7.28 (t, J = 8.1Hz, 1H), 7.13 (t, J = 7.7 Hz, 2H), 6.94 (t, J = 7.3 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 136.9, 135.5, 133.9, 130.9, 130.0, 128.7, 126.2, 126.1, 125.9, 125.3, 124.2, 123.4, 122.8, 120.7, 120.0, 110.0, 100.0, 33.3. IR (film, cm^{-1}): ν 1655, 1560, 1508. HRMS (ESI): Calcd for $C_{19}H_{15}NS$ $[M+H]^+$: m/z 290.0998; found: 290.0997



3j

1-Methyl-3-(thiophen-2-ylthio)-1*H*-indole

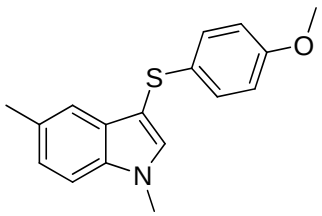
Prepared according to the general procedure from **1a** (3 mmol), thiophene-2-sulfonyl chloride (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (45% yield). M.p.: 70-71 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 7.8 Hz, 1H), 7.17-7.29 (m, 4H), 7.10-7.12 (m, 1H), 7.07 (d, J = 3.4 Hz, 1H), 6.82-6.84 (m, 1H), 3.72(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 137.4, 133.9, 129.8, 129.4, 127.4, 127.3, 122.7, 120.6, 119.7, 109.9, 104.7, 33.2. IR (film, cm^{-1}): v 1508, 1454, 741. HRMS (EI): Calcd for $C_{13}H_{11}NS_2$ $[M]^+$: m/z 245.0333; found: 245.0336.



4a

5-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole

Prepared according to the general procedure from 5-fluoro-1-methyl-1*H*-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (**2h**, 1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (65% yield). M.p.: 91-92 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 1H), 7.23-7.28 (m, 2H), 7.11 (d, J = 8.8 Hz, 2H), 7.00 (dt, J = 2.4, 9 Hz, 2H), 6.73 (d, J = 8.8 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 158.1, 157.6, 136.1, 134.3, 130.7, 130.6, 129.7, 128.8, 114.7, 111.3, 111.1, 110.7, 110.6, 105.0, 104.8, 102.8, 55.5, 33.5. IR (film, cm^{-1}): v 1631, 1592, 1490. HRMS (ESI): Calcd for $C_{16}H_{14}FNSO$ $[M+H]^+$: m/z 288.0858; found: 288.0854

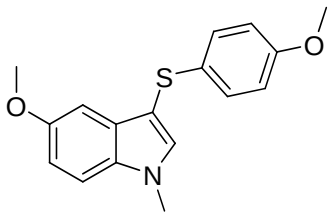


4b

3-((4-Methoxyphenyl)thio)-1,5-dimethyl-1*H*-indole

Prepared according to the general procedure from 1,5-dimethyl-1*H*-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (**2h**, 1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a yellow oil (61% yield). M.p.: 91-92 ^oC.^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 1H), 7.20-7.22

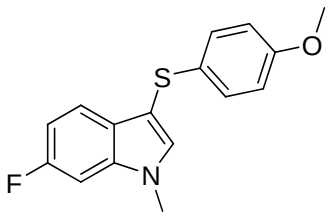
(m, 2H), 7.06-7.10 (m, 3H), 6.70 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 136.0, 134.7, 130.4, 130.1, 129.9, 128.2, 124.2, 119.3, 114.6, 109.4, 101.5, 55.4, 33.1, 21.5. HRMS (ESI): Calcd for $C_{17}H_{17}NSO$ $[M+H]^+$: *m*/*z* 284.1109; found: 284.1104.



4c

5-Methoxy-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole

Prepared according to the general procedure from 5-methoxy-1-methyl-1*H*-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (**2h**, 1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (47% yield). M.p.: 97-98 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 7.22 (d, *J* = 9.2 Hz, 1H), 7.09 (d, *J* = 1.9 Hz, 2H), 7.05 (d, *J* = 2.4 Hz , 1H), 6.90 (d, *J* = 2.4, 1.0 Hz, 1H), 6.73 (d, *J* = 1.9 Hz, 1H), 6.71 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 155.2, 135.2, 132.8, 130.7, 130.4, 128.3, 114.7, 113.2, 110.7, 101.7, 101.2, 56.0, 55.5, 33.4. IR (film, cm^{-1}): *v* 1610, 1490. HRMS (ESI): Calcd for $C_{17}H_{17}NO_2S$ $[M+H]^+$: *m*/*z* 300.1058; found: 300.1056.

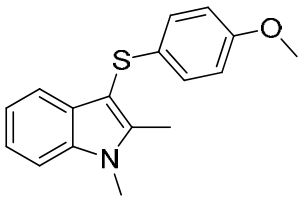


4d

6-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole

Prepared according to the general procedure from 6-fluoro-1-methyl-1*H*-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (**2h**, 1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (46% yield). M.p.: 96-97 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 5.4, 8.6 Hz, 1H), 7.26 (s, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 7.00 (dd, *J* = 1.9, 9.5 Hz , 1H), 6.86-6.91 (m, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 3.74 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 159.2, 157.9, 137.6, 137.5, 134.64, 134.62, 129.6, 128.7, 126.1, 120.8, 120.7, 114.5,

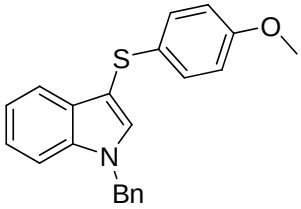
109.3, 109.0, 103.2, 96.3, 96.0, 55.3, 33.2. IR (film, cm^{-1}): *v* 1622, 1511, 1491, 1463. HRMS (ESI): Calcd for $C_{16}H_{14}FNSO$ $[M+H]^+$: *m*/*z* 288.0858; found: 288.0853.



4e

3-((4-Methoxyphenyl)thio)-1,2-dimethyl-1*H*-indole

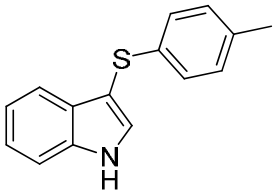
Prepared according to the general procedure from 1,2-dimethyl-1*H*-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (**2h**, 1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 48 hours to provide the title compound as a white solid (46% yield). M.p.: 96-97 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz , 1H), 7.19-7.24 (m, 1H), 7.10-7.14 (m, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 142.6, 137.3, 130.6, 130.0, 128.0, 121.9, 120.6, 119.2, 114.7, 109.2, 100.0, 55.6, 30.5, 11.1. IR (film, cm^{-1}): *v* 1650, 1630, 1491, 1466. HRMS (ESI): Calcd for $C_{17}H_{17}NSO$ $[M+H]^+$: *m*/*z* 284.1109; found: 284.1105.



4f

1-Benzyl-3-((4-methoxyphenyl)thio)-1*H*-indole

Prepared according to the general procedure from 1-benzyl-1*H*-indole (3 mmol), 4-methoxybenzene-1-sulfonyl chloride (**2h**, 1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 24 hours to provide the title compound as a white solid (44% yield). M.p.: 99-100 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.36 (s, 1H), 7.27-7.31 (m, 4H), 7.18-7.21 (m, 1H), 7.11-7.15 (m, 5H), 6.73 (d, *J* = 8.8 Hz, 2H), 5.31 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 137.2, 136.7, 133.9, 130.0, 129.8, 128.9, 128.5, 127.9, 127.0, 122.7, 120.6, 119.9, 114.5, 110.2, 103.3, 55.4, 50.4. IR (film, cm^{-1}): *v* 1589, 1488, 1450. HRMS (ESI): Calcd for $C_{22}H_{19}NSO$ $[M+H]^+$: *m*/*z* 346.1266; found: 346.1258.



4g

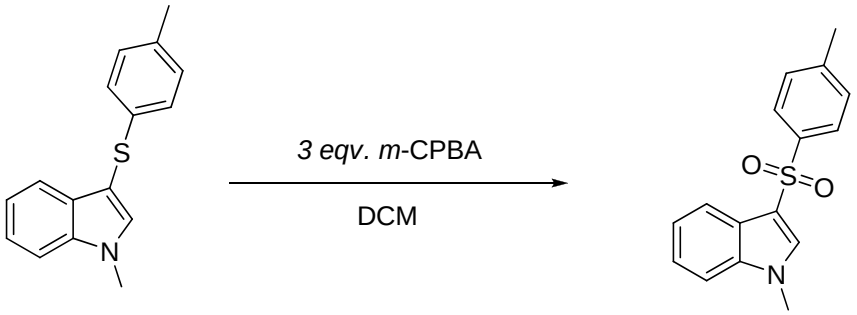
3-(*p*-Tolylthio)-1*H*-indole

Prepared according to the general procedure from 1*H*-indole (4 mmol), 4-methylbenzene-1-sulfonyl chloride (**2a**, 1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 mmol) and CH_3CN (2.5 mL) under visible light irradiation 12 hours to provide the title compound as a white solid (33% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 2.3 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 135.7, 134.8, 130.6, 130.1, 129.7, 129.3, 126.5, 123.1, 121.0, 119.9, 111.7, 21.0. The spectroscopic data are in accordance with those reproted.[6]

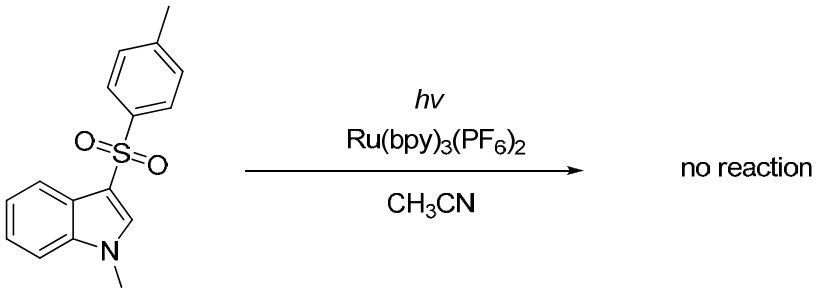
6. Controlled experiments for the mechanistic investigation

A. Synthesis of 1-methyl-3-tosyl-1*H*-indole and its reaction under reaction photocatalysis condition

To a solution of 1-methyl-3-(*p*-tolylthio)-1*H*-indole (**3a**, 1 mmol) in dry CH_2Cl_2 (25 ml) at 0 ^oC, 10 ml CH_2Cl_2 solution of *m*-CPBA (3 mmol) was added dropwise. After 10 mins, the solution warmed to r.t. and its color got darker with time. When **3a** was consumed indicated by TLC, the reaction mixture was washed by Na_2SO_3, $NaHCO_3$ and brine successively, and dried over anhydrous $MgSO_4$. The residue was available by concentrated under vacuum, which was purified by Column chromatography on silica gel giving desired compound in 80 % yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88-7.93 (m, 3H), 7.72 (s, 1H), 7.20-7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 140.9, 137.5, 133.7, 129.8, 126.9, 124.4, 123.7, 122.5, 120.0, 115.6, 110.5, 33.7, 21.6. MS $[M]^+$: *m*/*z* 285. The spectroscopic data are in accordance with those reproted.[7]

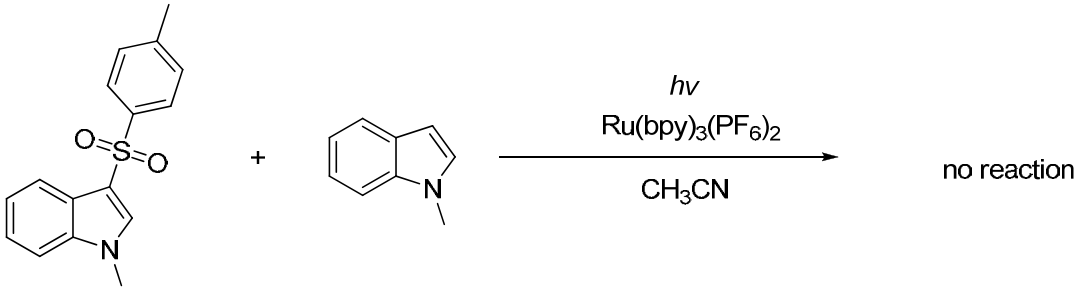


A 25 ml Schlenk tube equipped with stir-bar was charged with 1-methyl-3-tosyl-1*H*-indole (0.3 mmol), photocatalyst $Ru(bpy)_3(PF_6)_2$ (2% mol). The system was evacuated 3 times and backfilled with Ar before solvent 2.5 ml CH_3CN were added by springe. Then the vial was evacuated 3 times and backfilled with Ar again at -78 ^oC and warmed to 40 ^oC. After 24 hours under 23 w fluorescent light, TLC indicated no new product generated.



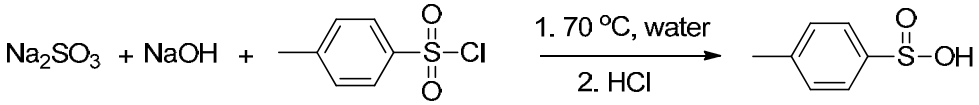
At the same time, a 25 ml Schlenk tube equipped with stir-bar was charged with 1-methyl-3-tosyl-1*H*-indole (0.3 mmol), photocatalyst $Ru(bpy)_3(PF_6)_2$ (2% mol). The system

was evacuated 3 times and backfilled with Ar before solvent 2.5 ml CH_3CN **and *N*-methylindole** were added by springe. Then the vial was evacuated 3 times and backfilled with Ar again at -78 ^oC and slowly warmed to 40 ^oC. After 24 hours under 23 w fluorescent light, TLC indicated no new product generated.



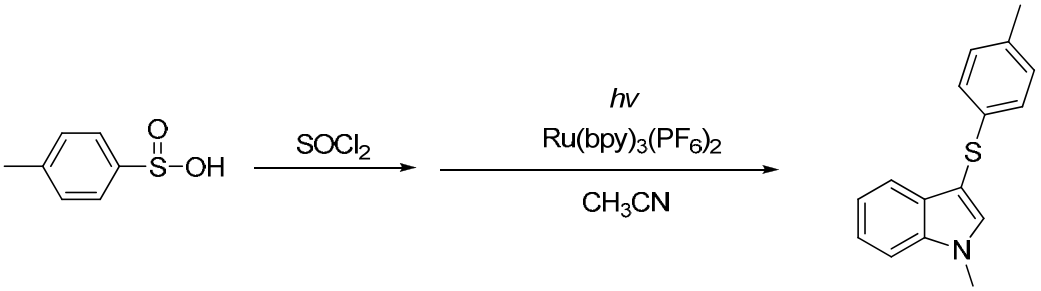
B. The reaction of 4-methylbenzene-1-sulfinic chloride with *N*-methylindole

According to literature, to the 9 ml aqueous solution of NaOH (3.6 g), 35 ml aqueous solution of Na_2SO_3 (6.8 g) was added. The *p*-toluene sulfonyl chloride (7.65 g) was added to the above mixed solution portionwise. Then the reaction system was stirred for 3 hours at 70 ^oC. The precipitated sodium salt of 4-methyl-bensenefulfinic acid after placed in the fridge was filtered cold, dissolved in water, and hydrolyzed with concentrated hydrochloric acid. The precipitation was filtered and washed by cold water. ^1H NMR ($CDCl_3$): δ 2.40 (s, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 9.35-9.45 (m, 1H). The spectroscopic data are in accordance with those reproted.[8]

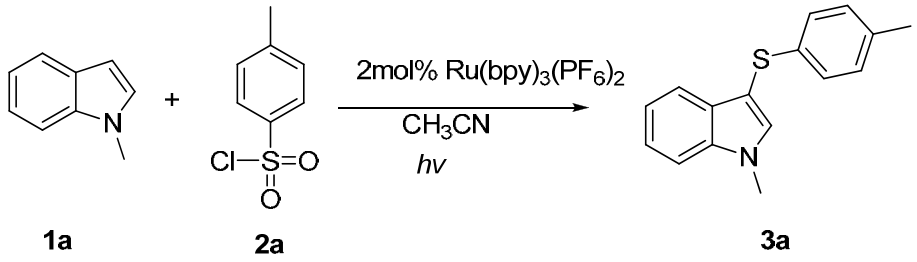


To the solution of 0.8 ml thionyl chloride in 50 ml dry ether, 1 g 4-methyl-benzensuylfinic acid was added portionwise under Ar atmosphere. The reaction mixture was stirred for 3 hours at room, and then excess of thionyl chloride was removed by rotavapor. The obtained residue was dissolved in 50 ml x 3 hexane and concentrated on rotavapor. No further purification was done and the obtained product was used under standard photocatalysist reaction condition. A 25 ml Schlenk tube equipped with stir-bar was charged with photocatalyst $Ru(bpy)_3(PF_6)_2$ (18 mg, 0.02 mmol). The system was evacuated 3 times and backfilled with Ar before 2.5 ml CH_3CN, *p*-toluene sulfonyl chloride (1mmol) and *N*-methylindole were added by springe. Then the vial was evacuated 3 times and backfilled with Ar again at -78 ^oC and warmed to 40 ^oC. After 12 hours under 23 w fluorescent light, the

reaction mixture was diluted with CH_2Cl_2 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product in 63% yield.

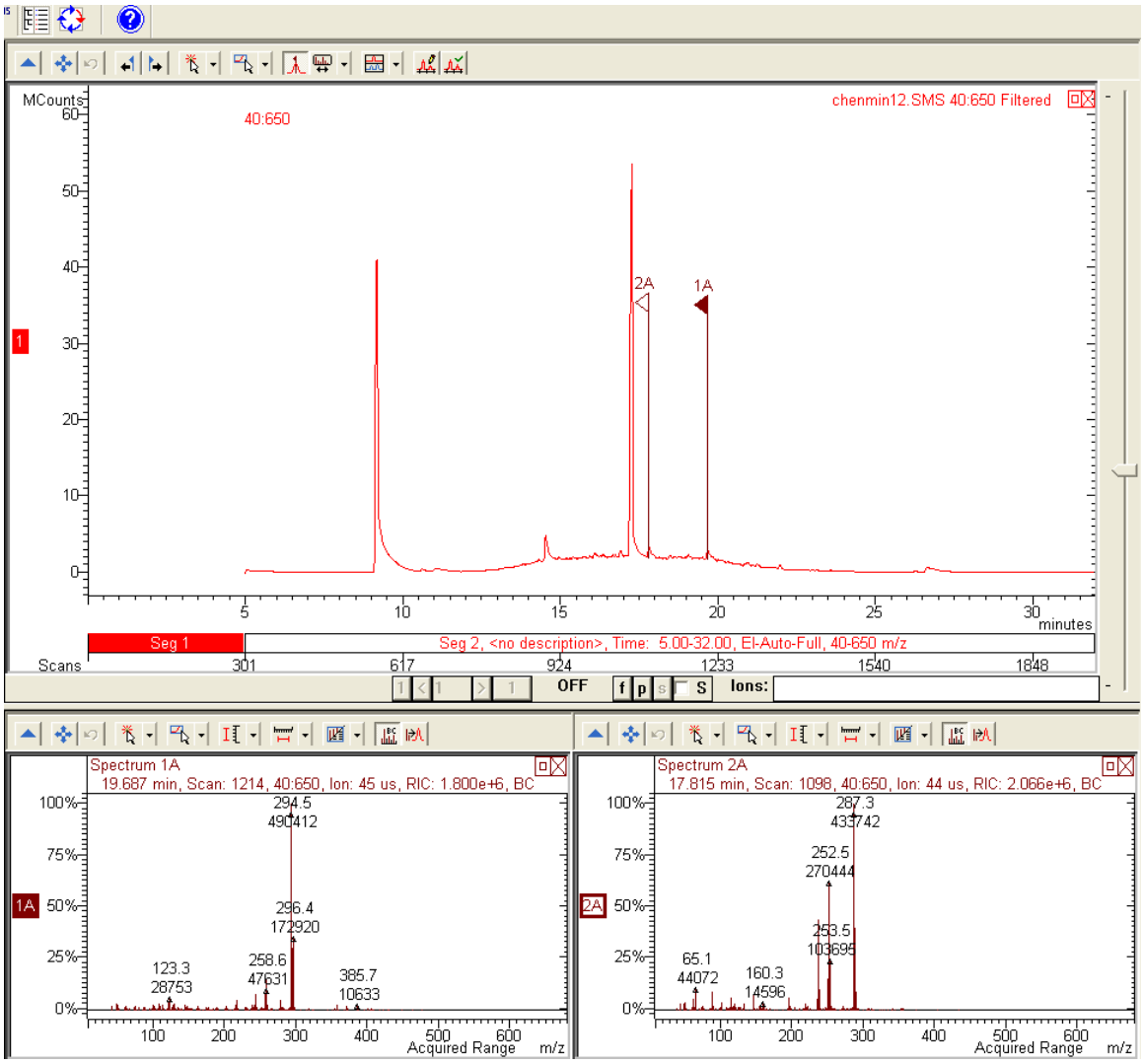


C. GC-MS

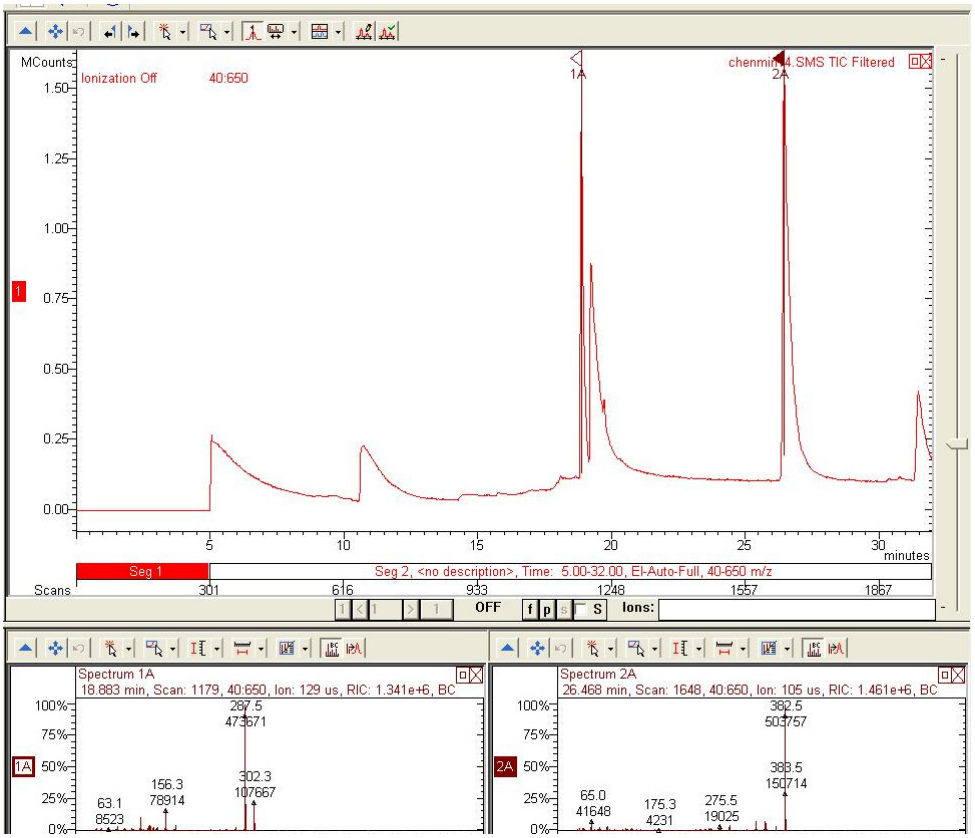


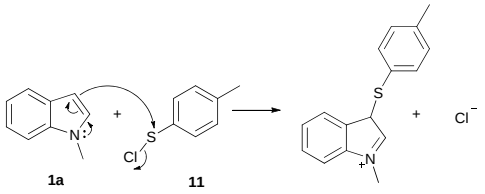
The reaction of **1a** with **2a** under standard condition was carried out, and the residue of reaction mixture under vacuum was analyzed by GC-MS. (S-1) After the desired product obtained by column chromatography, the remained fraction eluted by ethyl acetate was also analyzed by GC-MS. (S-2) We found that besides of the desired product, byproduct *m*/*z* 287, *m*/*z* 294, and *m*/*z* 382 were detected. With the ^{1}H NMR of byproduct *m*/*z* 294, we deduced it may be addition product of *N*-methylindole. Moreover, it was hard to purify the product of byproduct *m*/*z* 382, for it became symmetrical trimers when recrystallized. In S-3, we tried to explain the reaction routines.

S-1

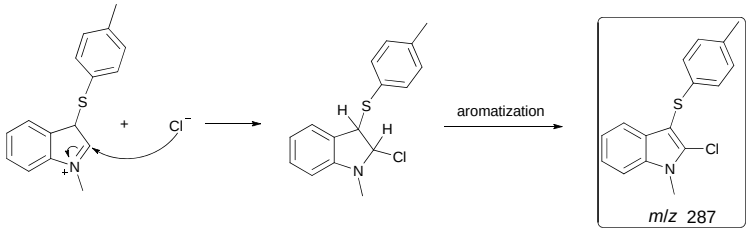

chenmin12.SMS 40:650 Filtered
MCounts
40:650
2A
1A
minutes
Seg 1
Seg 2, <no description>, Time: 5.00-32.00, EI-Auto-Full, 40-650 m/z
Scans
OFF
Ions:
Spectrum 1A
19.687 min, Scan: 1214, 40:650, Ion: 45 us, RIC: 1.800e+6, BC
294.5
490412
296.4
172920
123.3
28753
258.6
47631
385.7
10633
Acquired Range
m/z
Spectrum 2A
17.815 min, Scan: 1098, 40:650, Ion: 44 us, RIC: 2.066e+6, BC
287.3
433742
252.5
270444
253.5
103695
65.1
44072
160.3
14596
Acquired Range
m/z

S-2

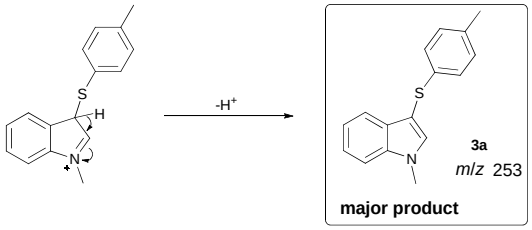

MCounts
Ionization Off
40:650
1A
2A
chenmin4.SMS TIC Filtered
1.50
1.25
1.00
0.75
0.50
0.25
0.00
5
10
15
20
25
30
minutes
Seg 1
Seg 2, <no description>, Time: 5.00-32.00, EI-Auto-Full, 40-650 m/z
Scans
301
616
933
1248
1557
1867
OFF
Ions:
Spectrum 1A
18.883 min, Scan: 1179, 40:650, Ion: 129 us, RIC: 1.341e+6, BC
287.5
473671
302.3
107667
156.3
78914
63.1
8523
Spectrum 2A
26.468 min, Scan: 1648, 40:650, Ion: 105 us, RIC: 1.461e+6, BC
382.5
503757
383.5
150714
65.0
41648
175.3
4231
275.5
19025
100%
75%
50%
25%
0%



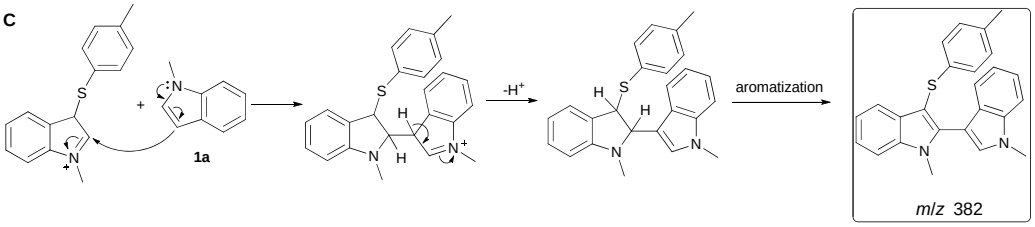
Routine A



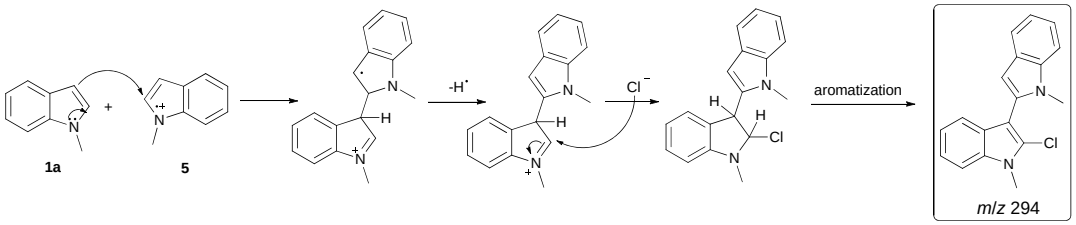
Routine B



Routine C



Routine D



The routine D was referred to the similar example: A. Berlin et al. *Tetrahedron*, 1996, 52, 7947-7960.

7. References

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4. Q. Liu, Q. Y. Zhao, J. Liu, P. Wu, H. Yi and A. Lei, *Chem. Commun.*, 2012, **48**, 3239.
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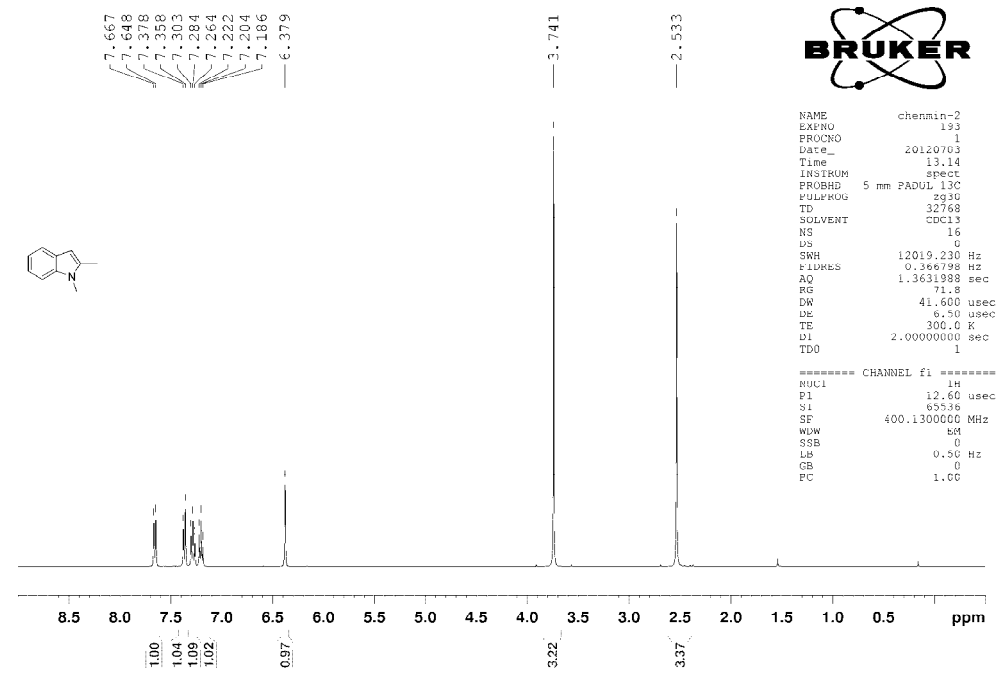
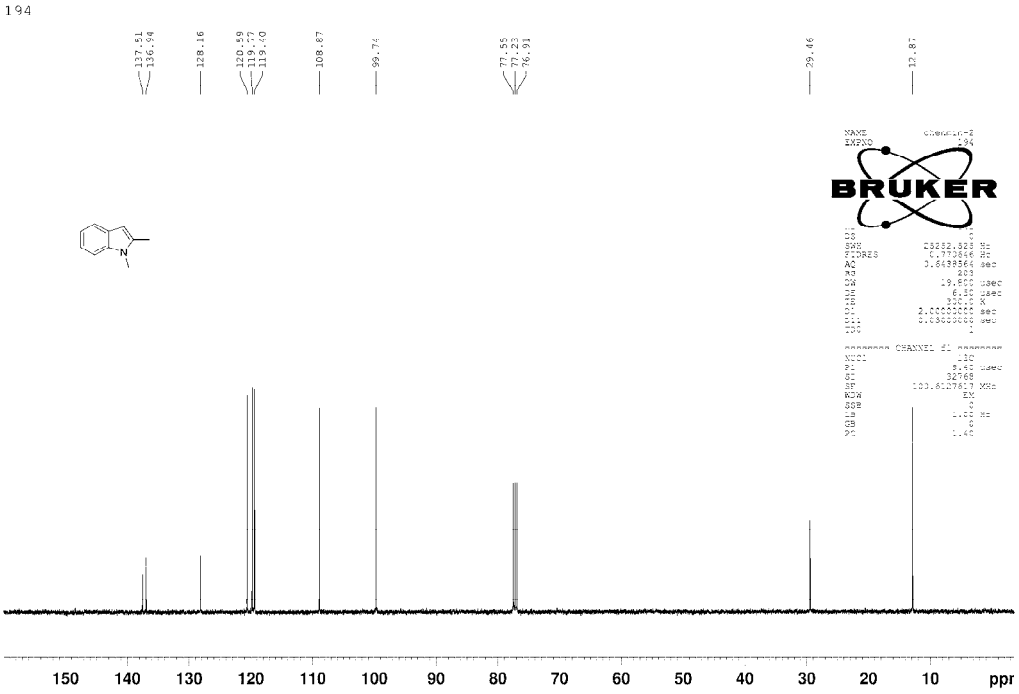
7. D. U. Singh, P. R. Singh and S. D. Samant, *Tetrahedron Lett.* , 2004, **45**, 9079.
8. L. B. Krasnova and A. K. Yudin, *J. Org. Chem.*, 2004, **69**, 2584.

8. Copies of ^{1}H, ^{13}C NMR spectra and HRMS spectra

1,2-Dimethyl-1*H*-indole





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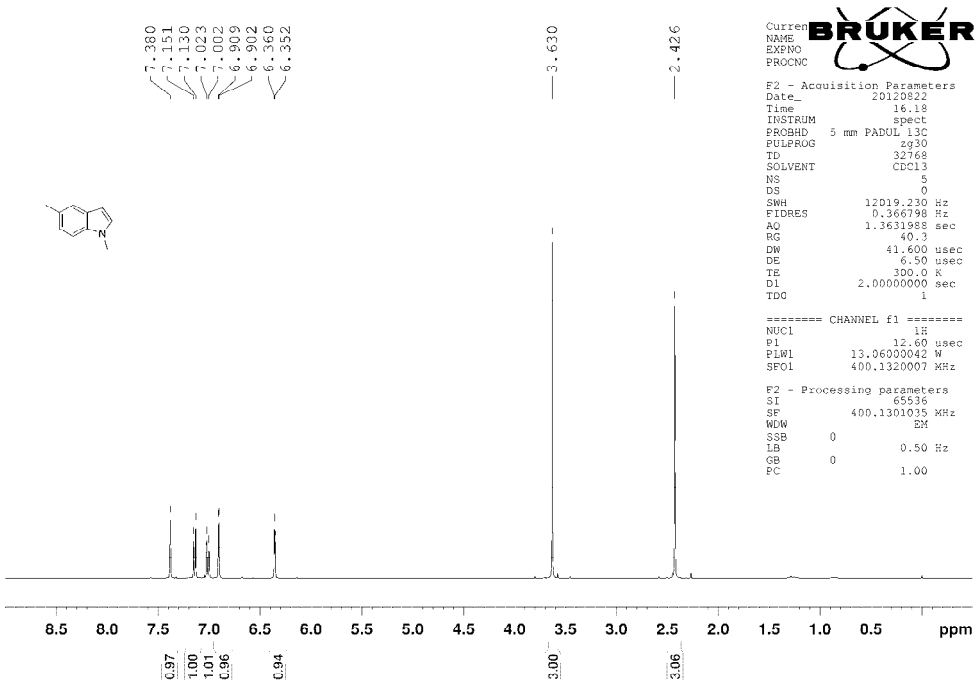
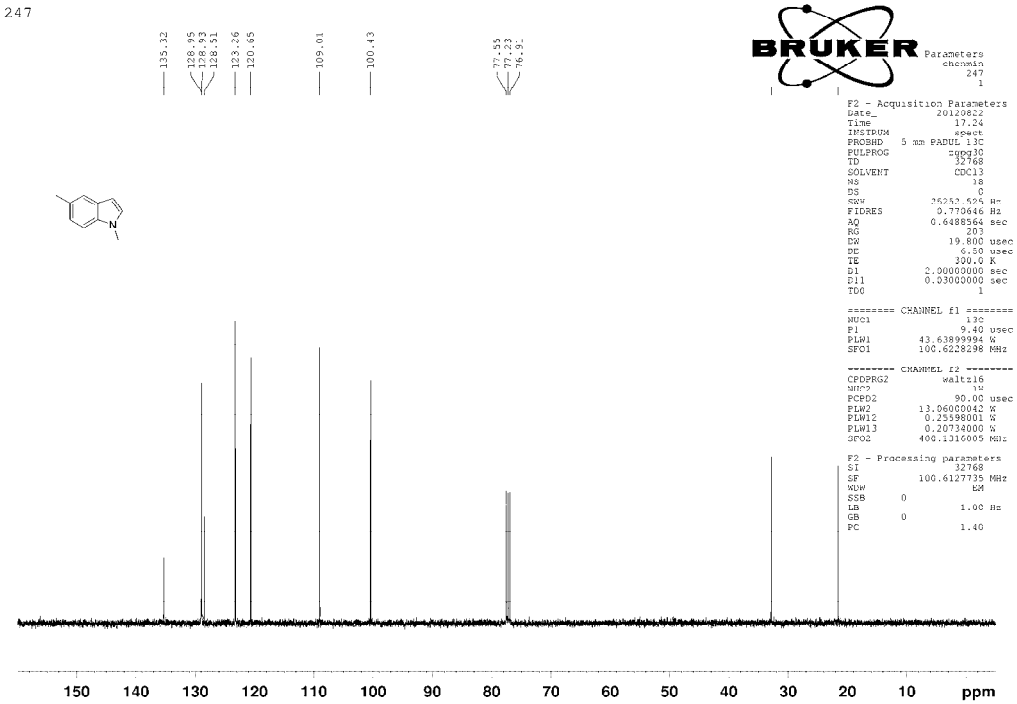
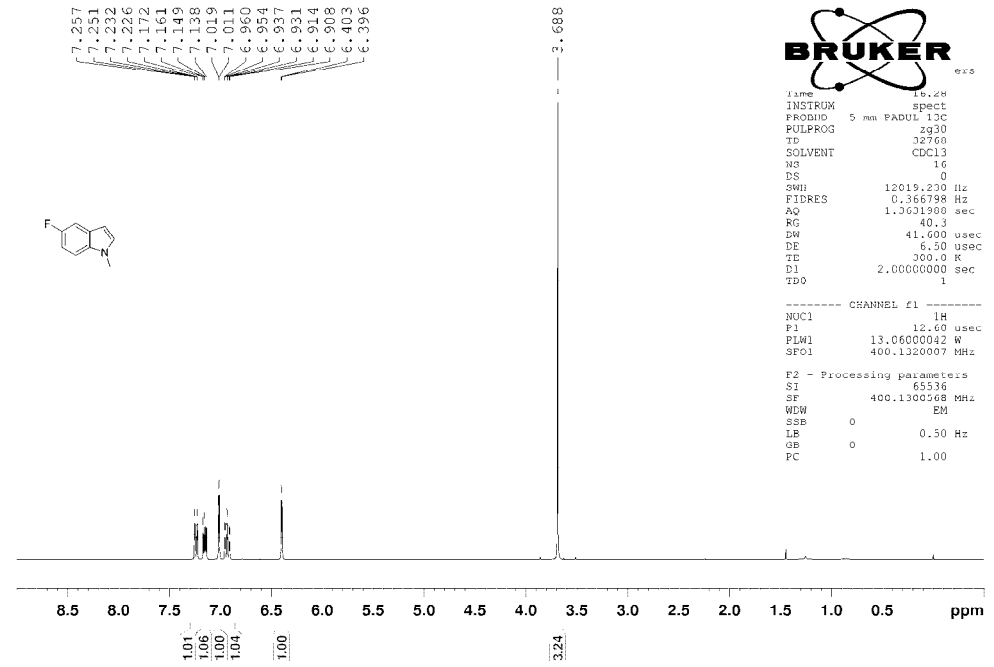
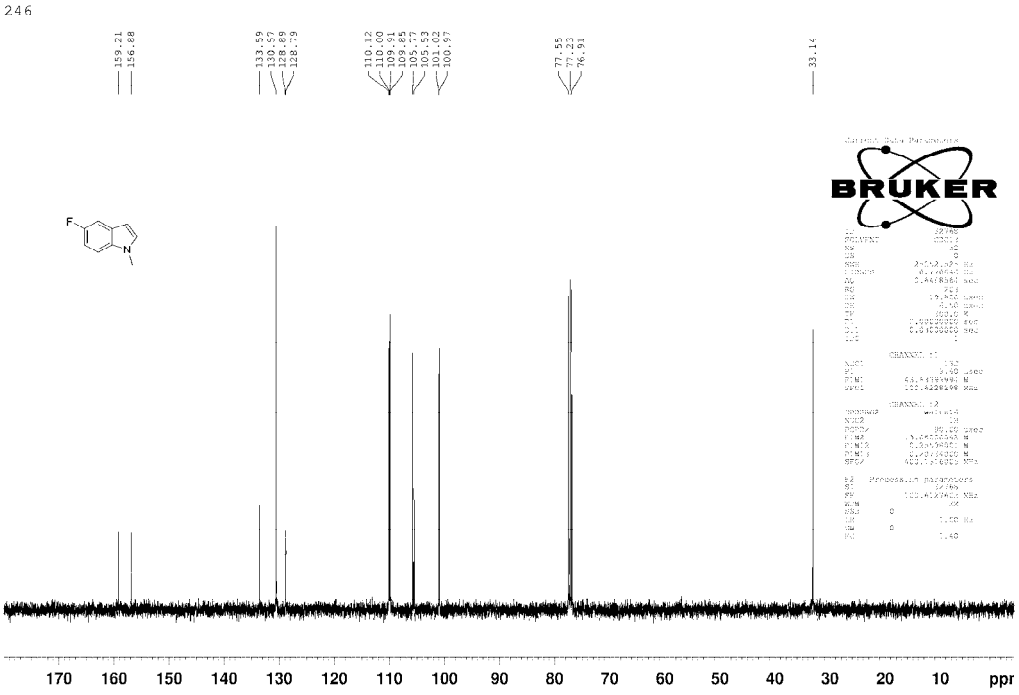




5-Fluoro-1-methyl-1*H*-indole





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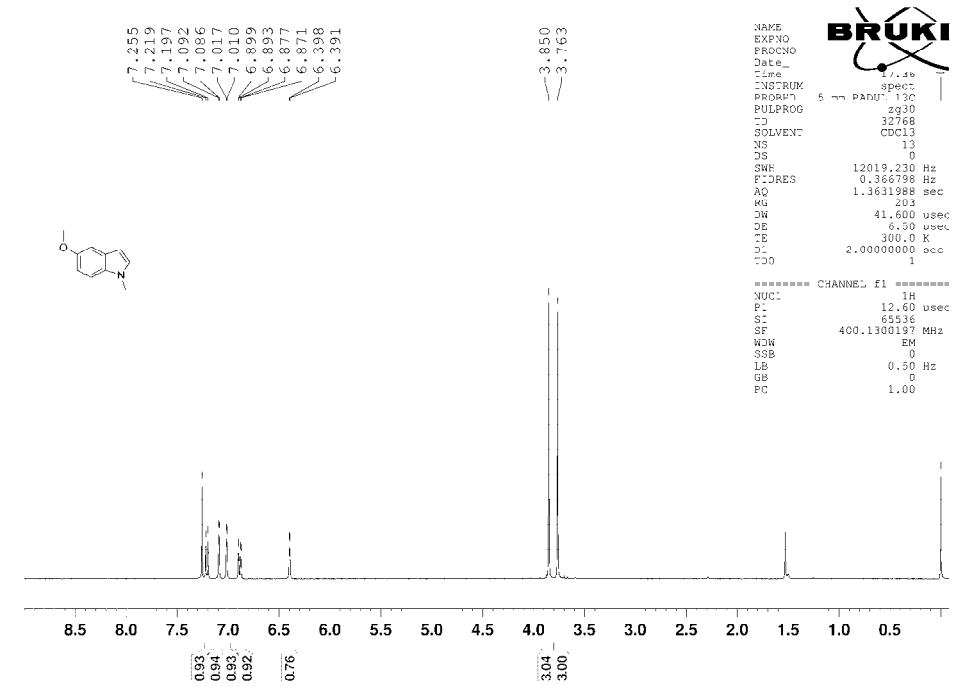

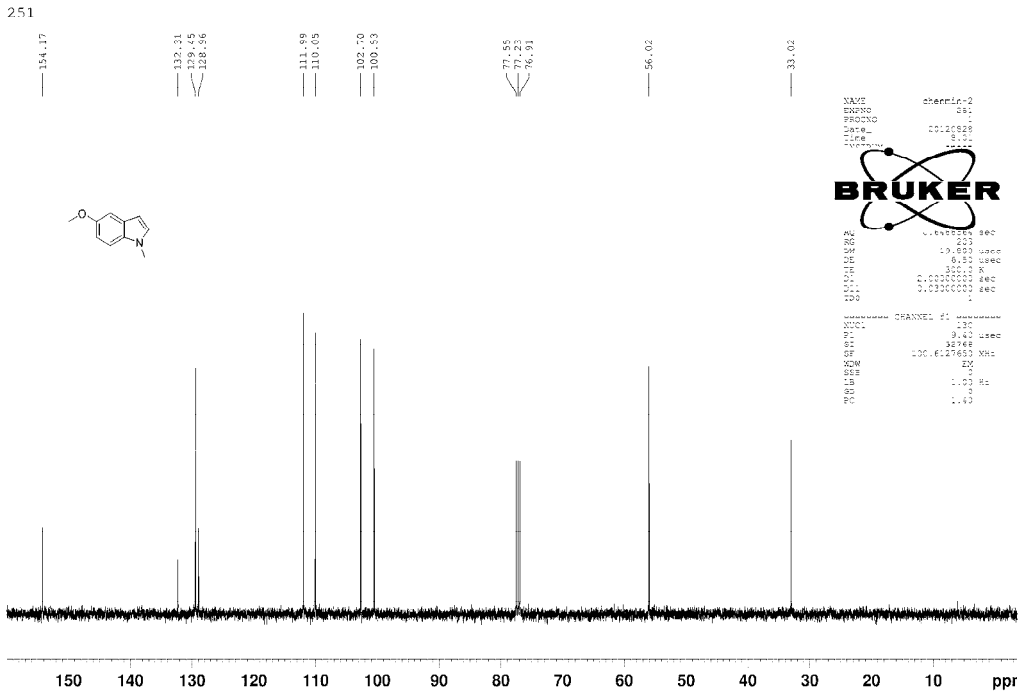

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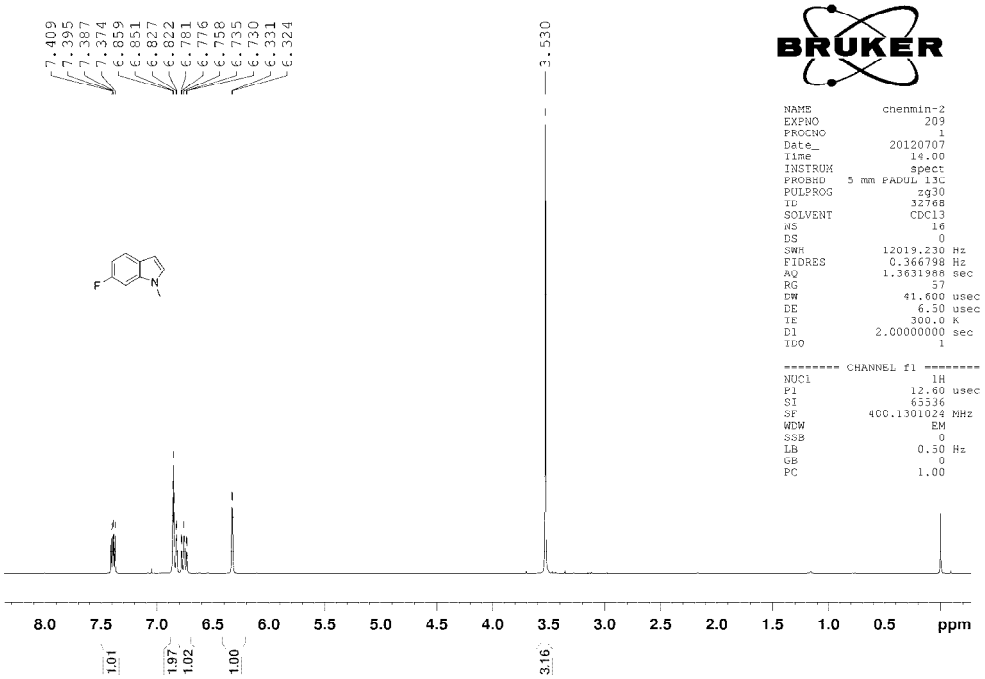
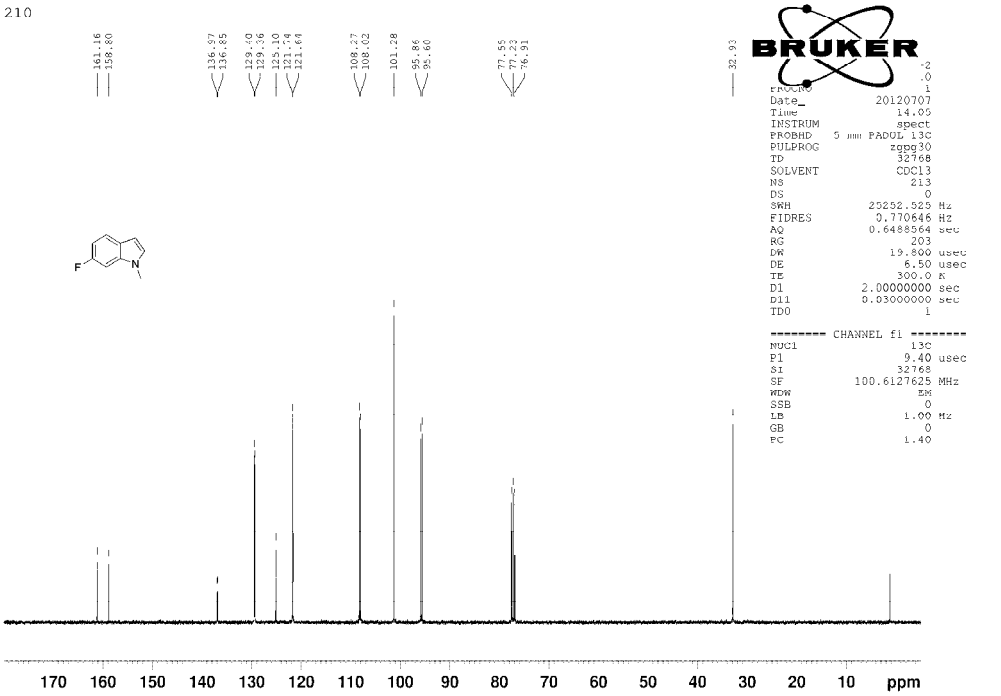
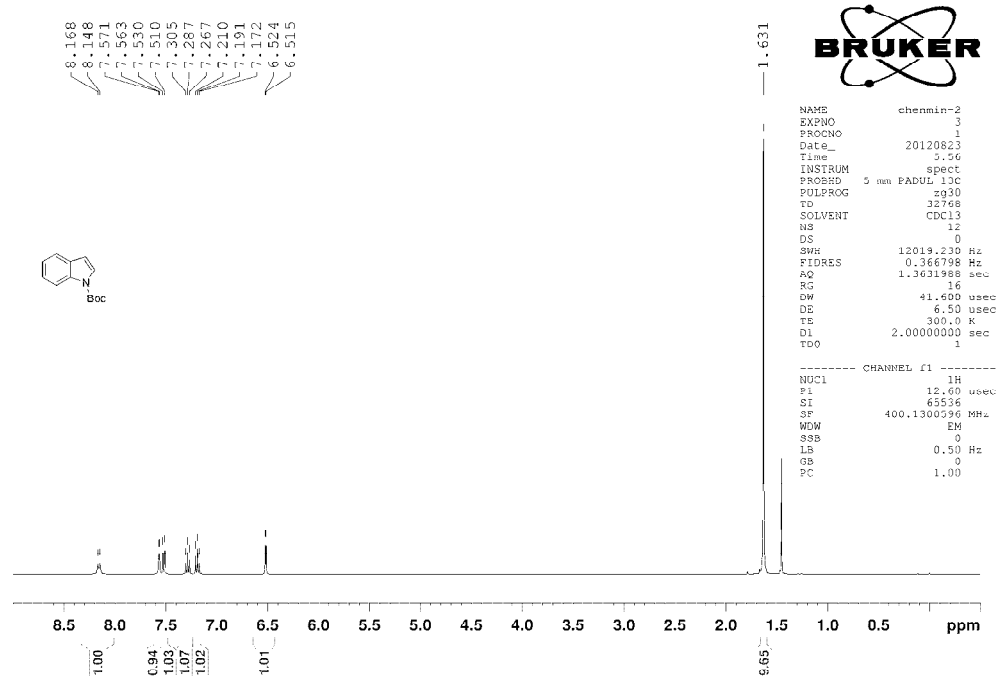
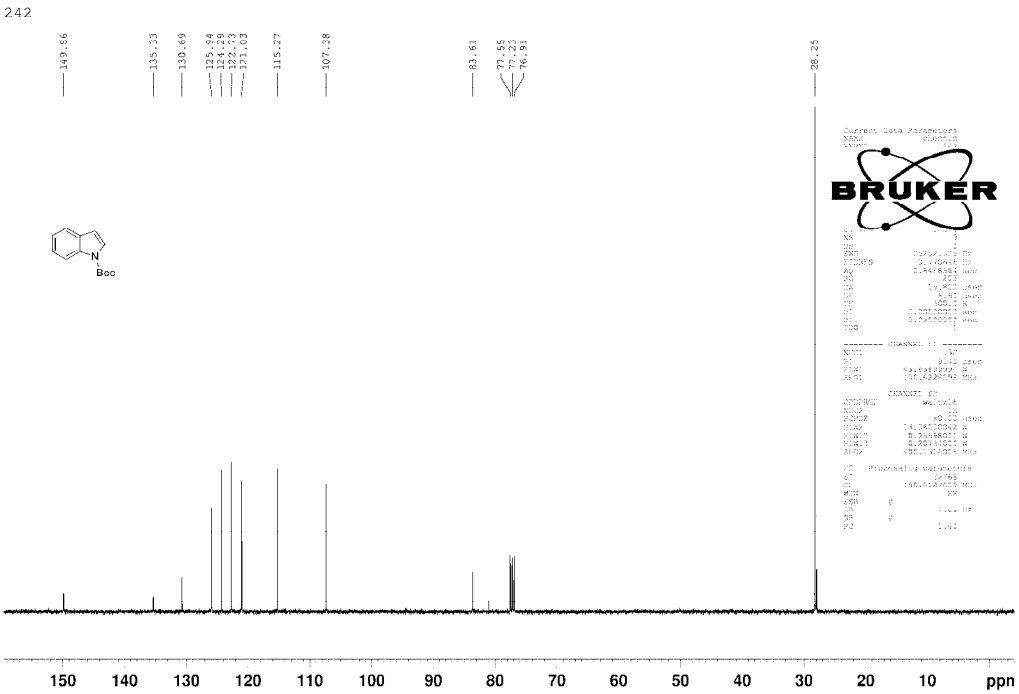


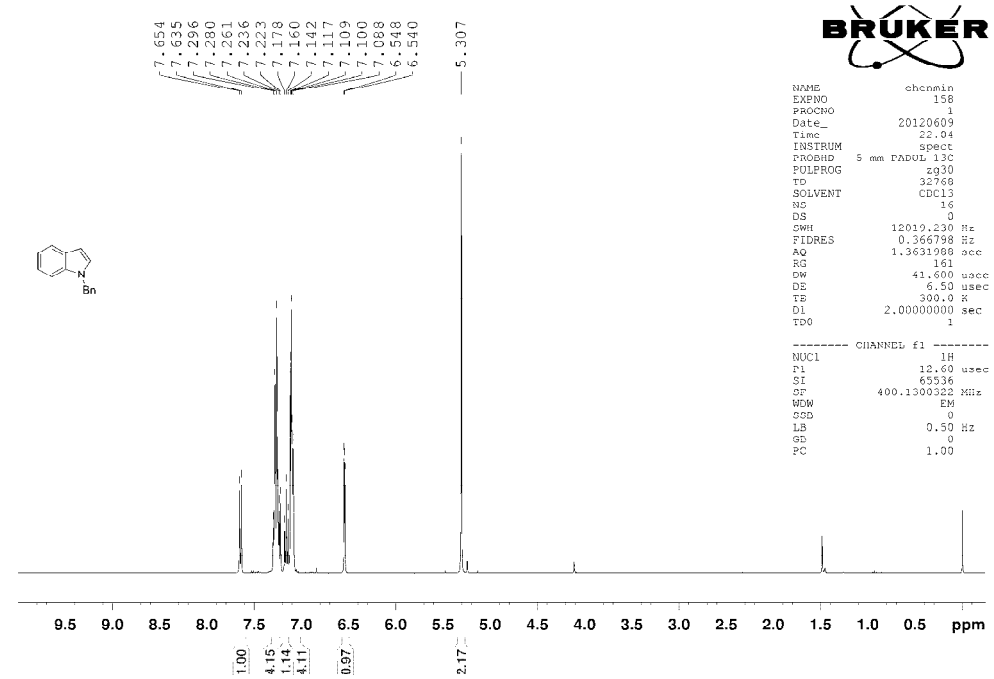


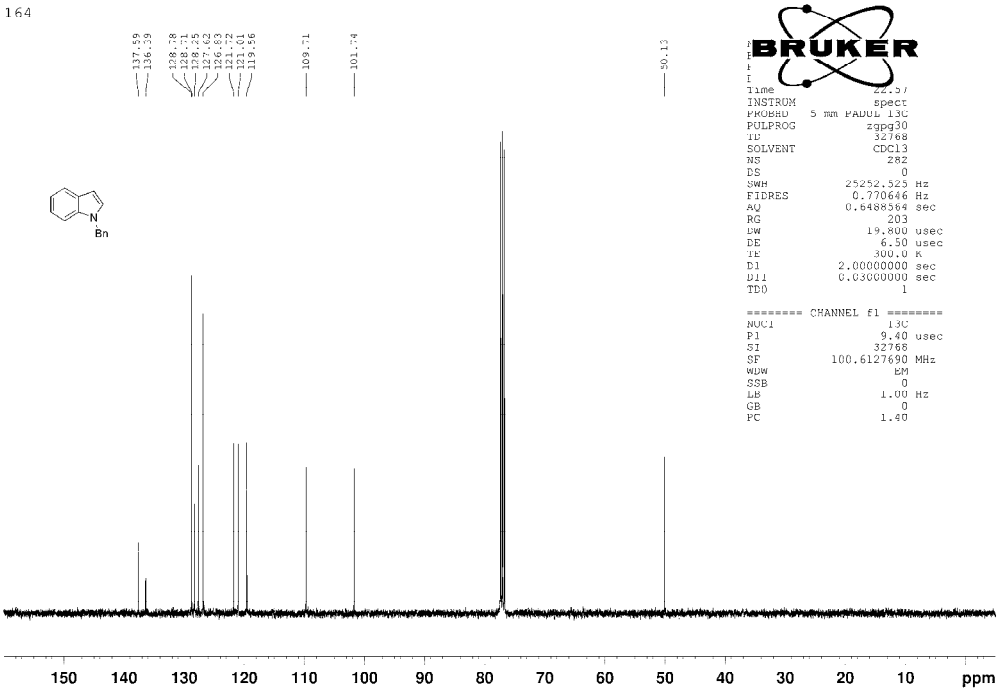
tert-Butyl 1_H_-indole-1-carboxylate



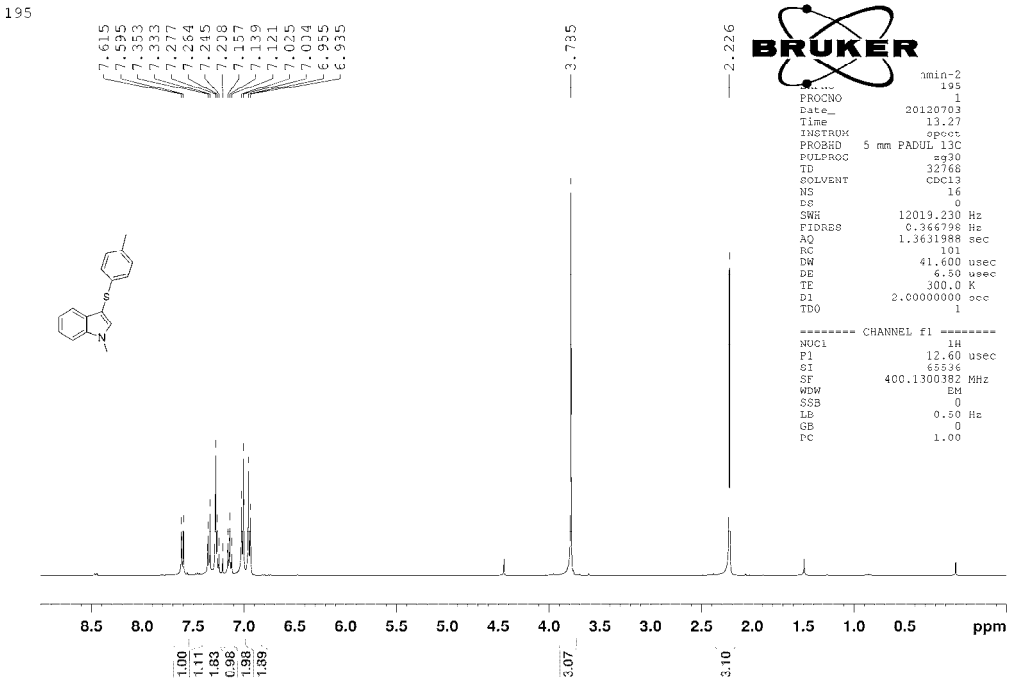


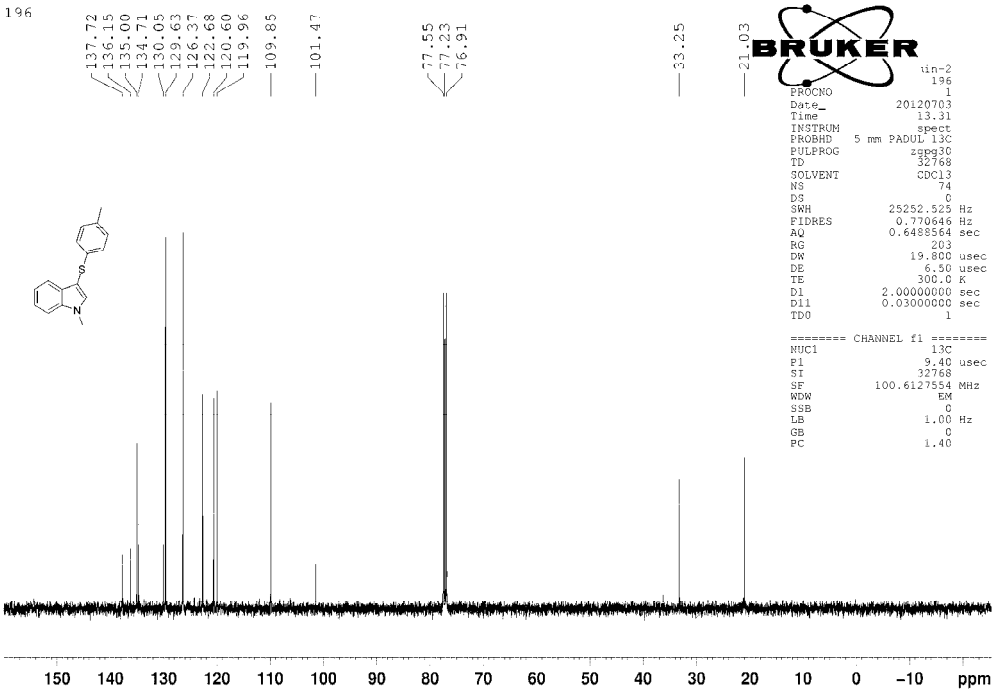
1-Benzyl-1*H*-indole



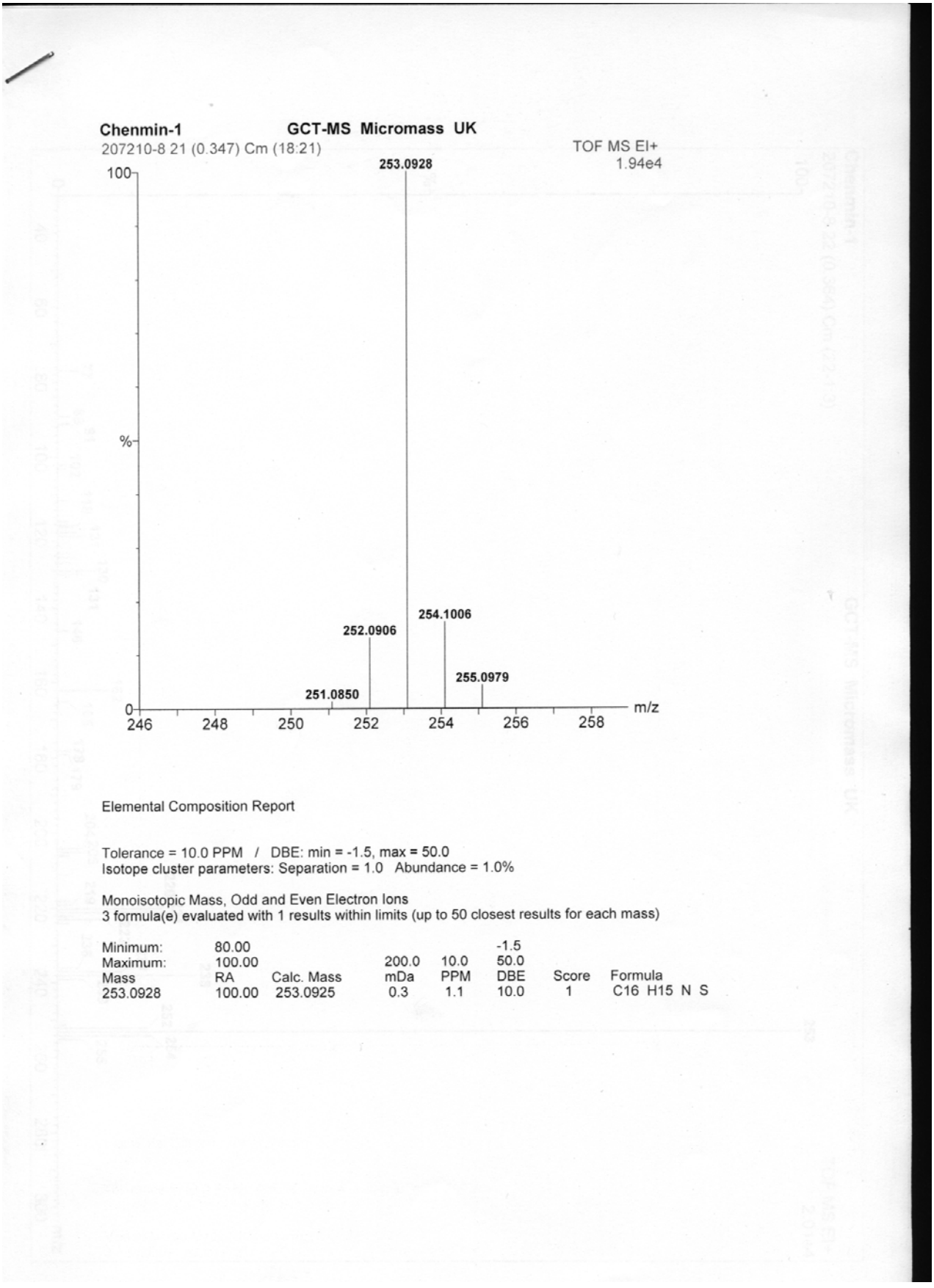


1-Methyl-3-(*p*-tolylthio)-1*H*-indole (3a)





1-Methyl-3-(*p*-tolylthio)-1*H*-indole (3a)



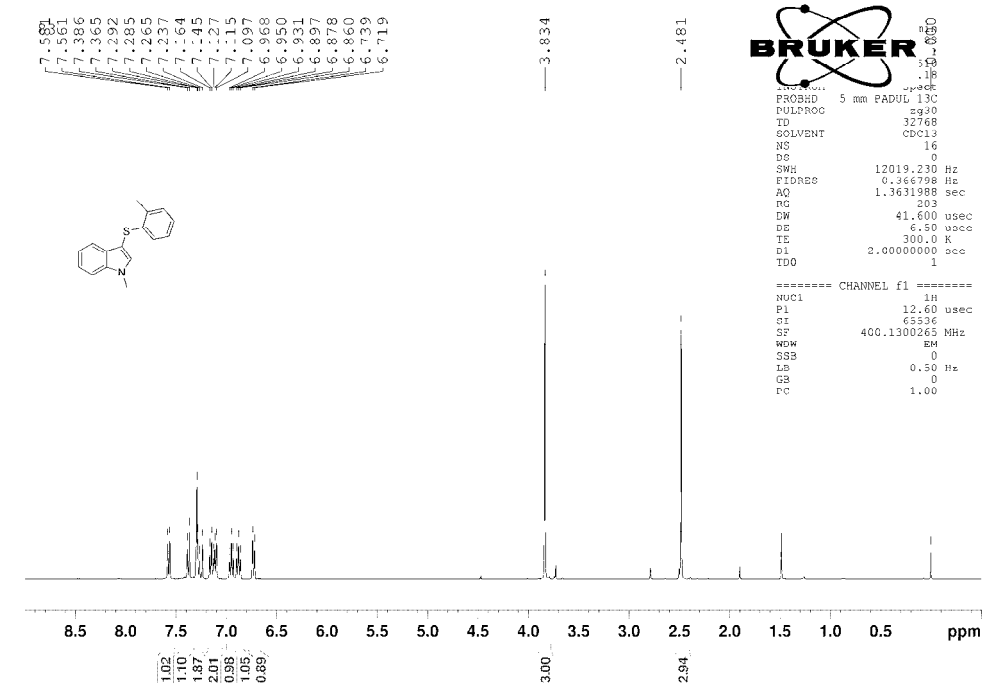
Elemental Composition Report

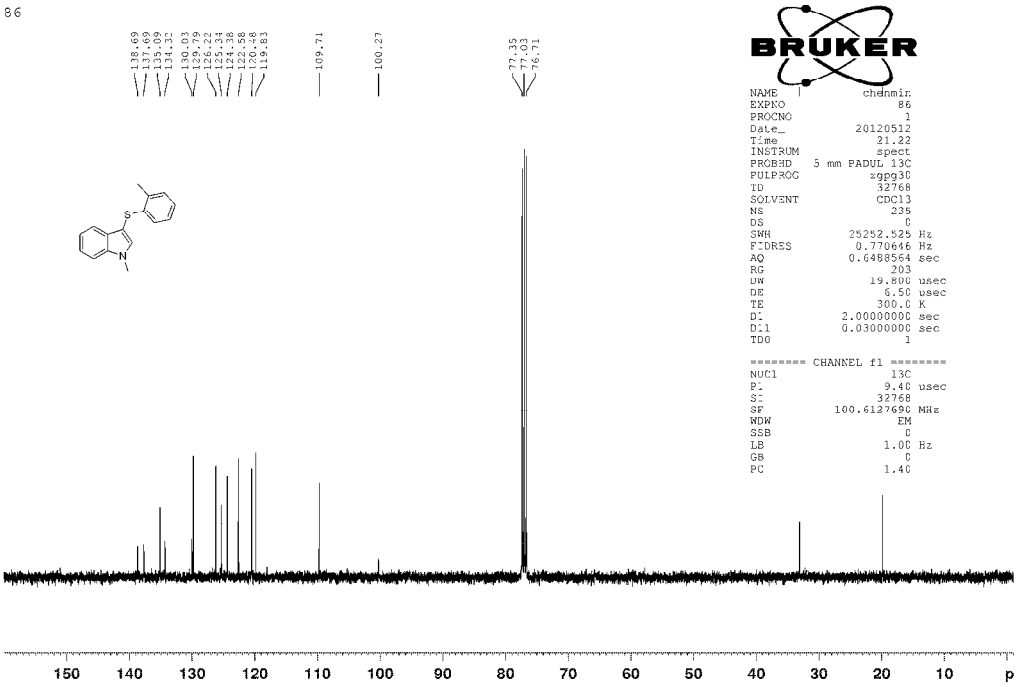
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

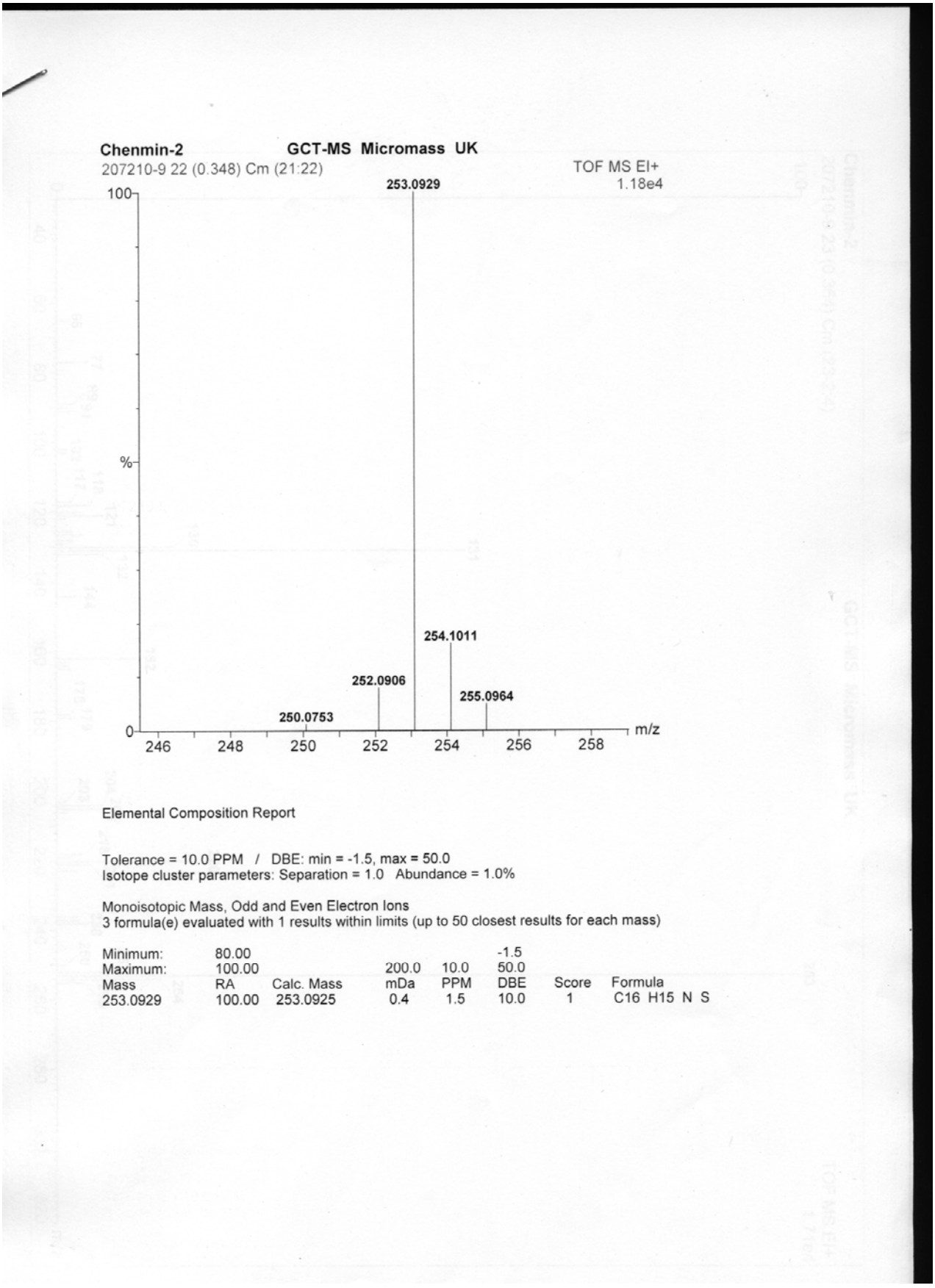
Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
253.0928	100.00	253.0925	0.3	1.1	10.0	1	C16 H15 N S

1-Methyl-3-(*o*-tolylthio)-1*H*-indole (3b)





1-Methyl-3-(*o*-tolylthio)-1*H*-indole (3b)



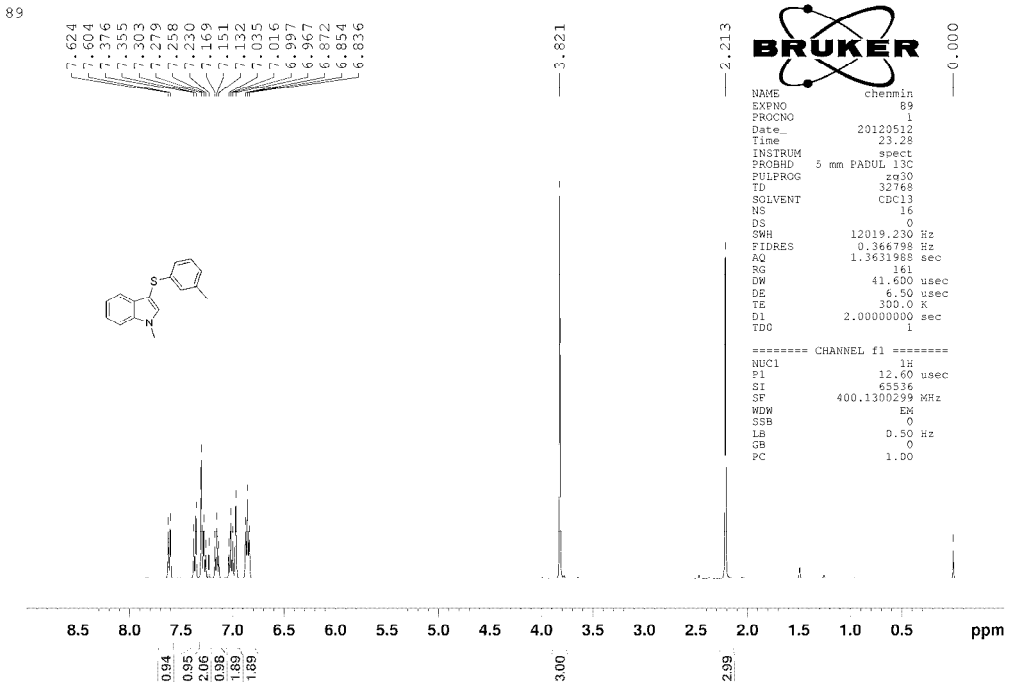
Elemental Composition Report

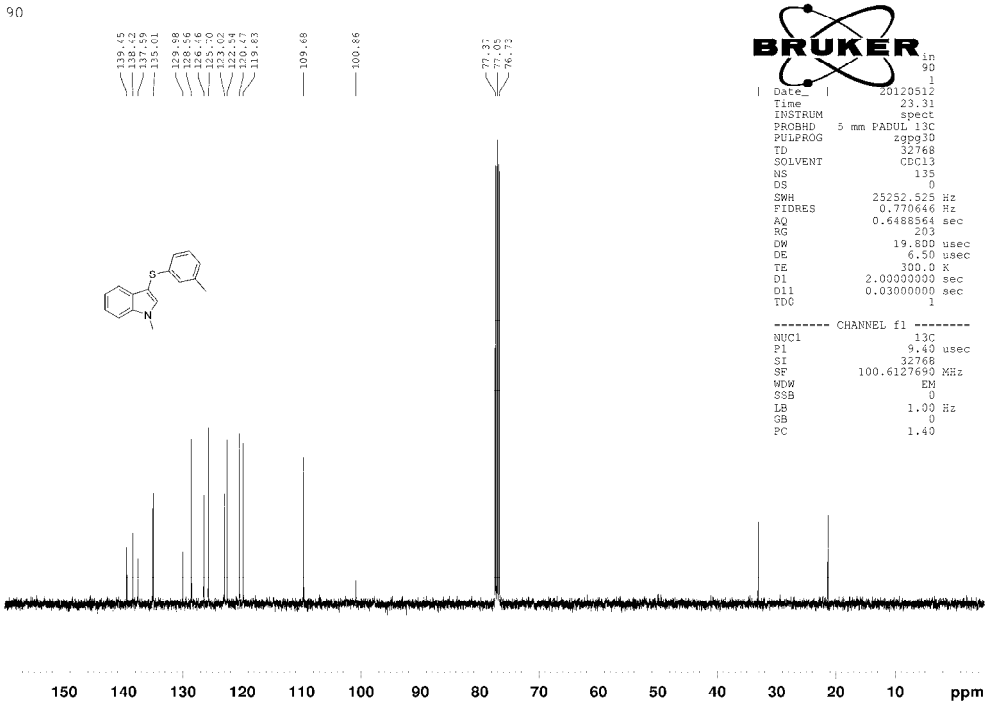
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

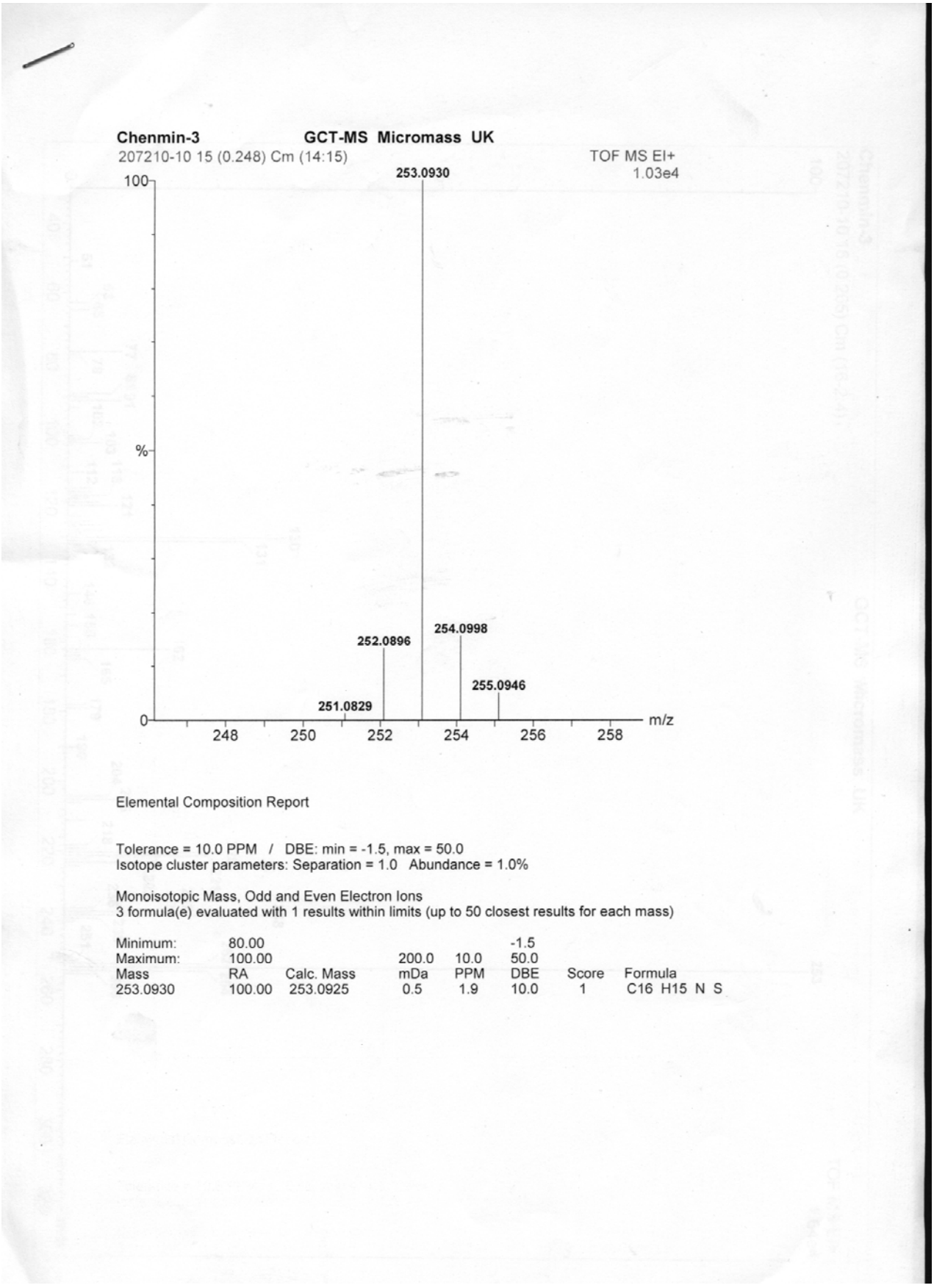
Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
253.0929	100.00	253.0925	0.4	1.5	10.0	1	C16 H15 N S

1-Methyl-3-(*m*-tolylthio)-1*H*-indole (3c)





1-Methyl-3-(*m*-tolylthio)-1*H*-indole (3c)



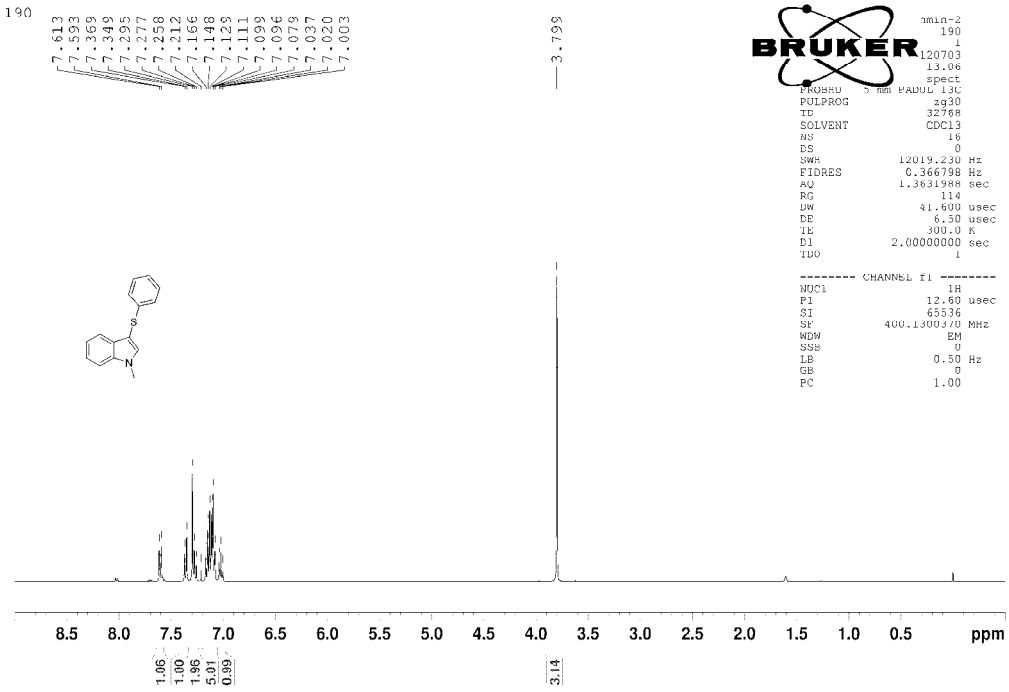
Elemental Composition Report

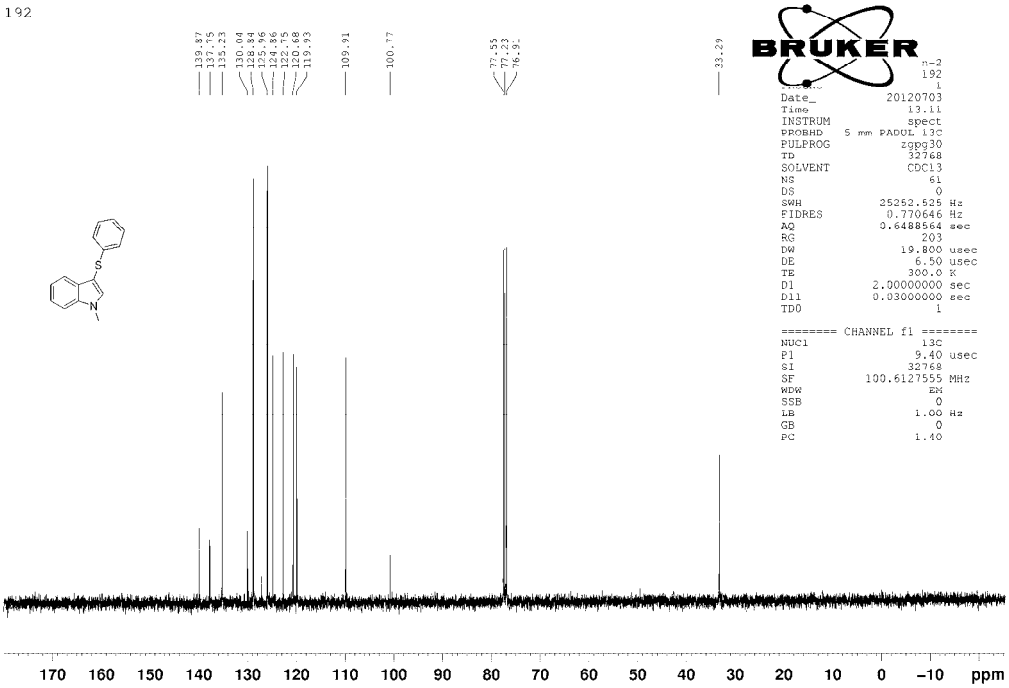
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

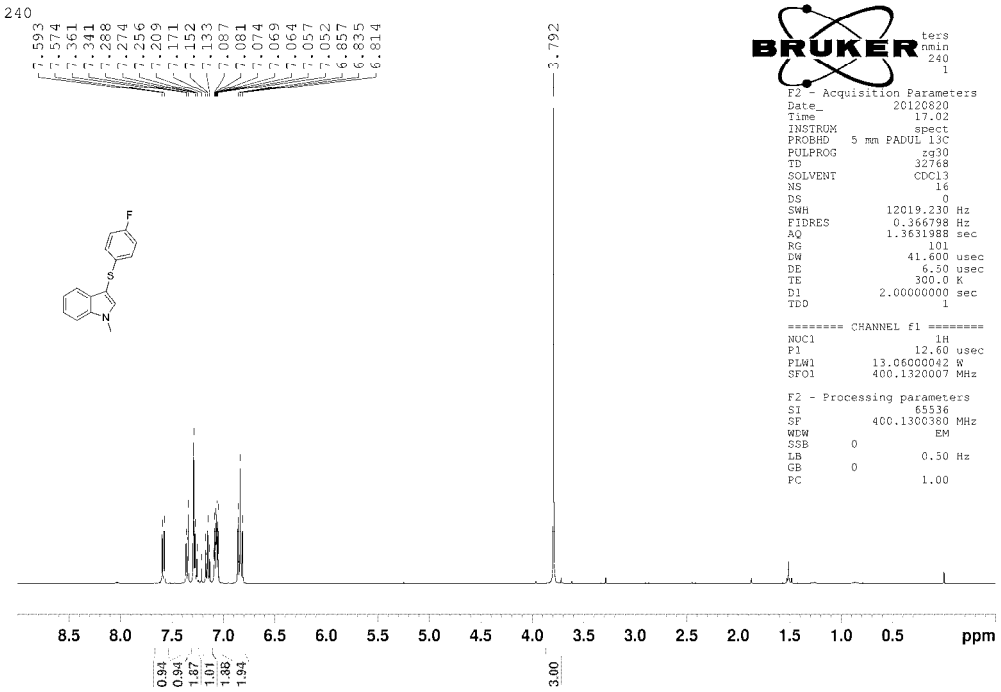
Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
253.0930	100.00	253.0925	0.5	1.9	10.0	1	C16 H15 N S

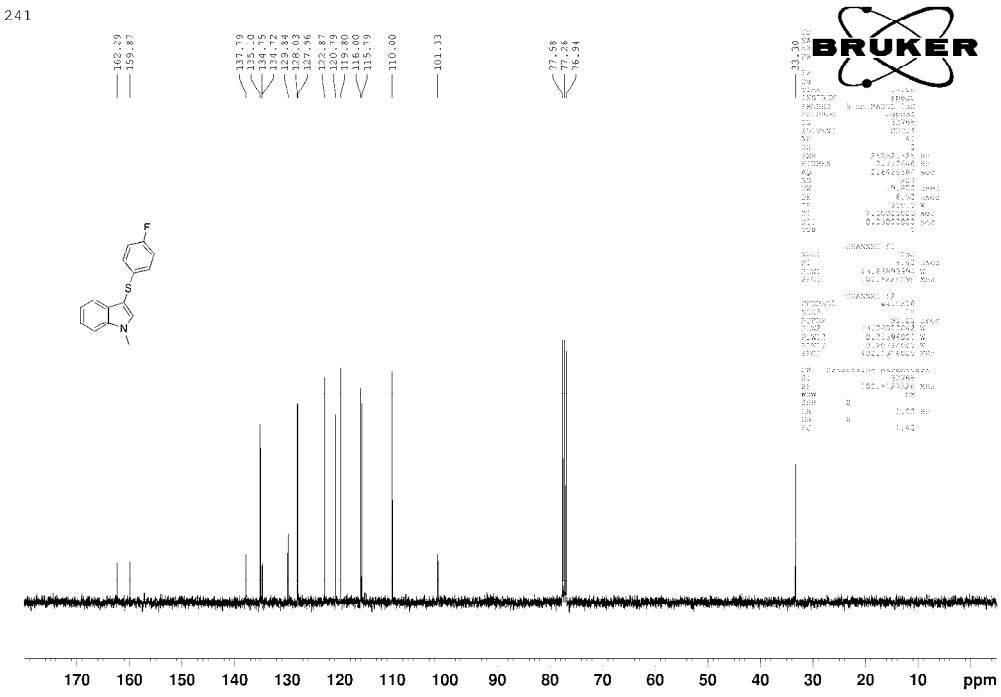
1-Methyl-3-(phenylthio)-1*H*-indole (3d)



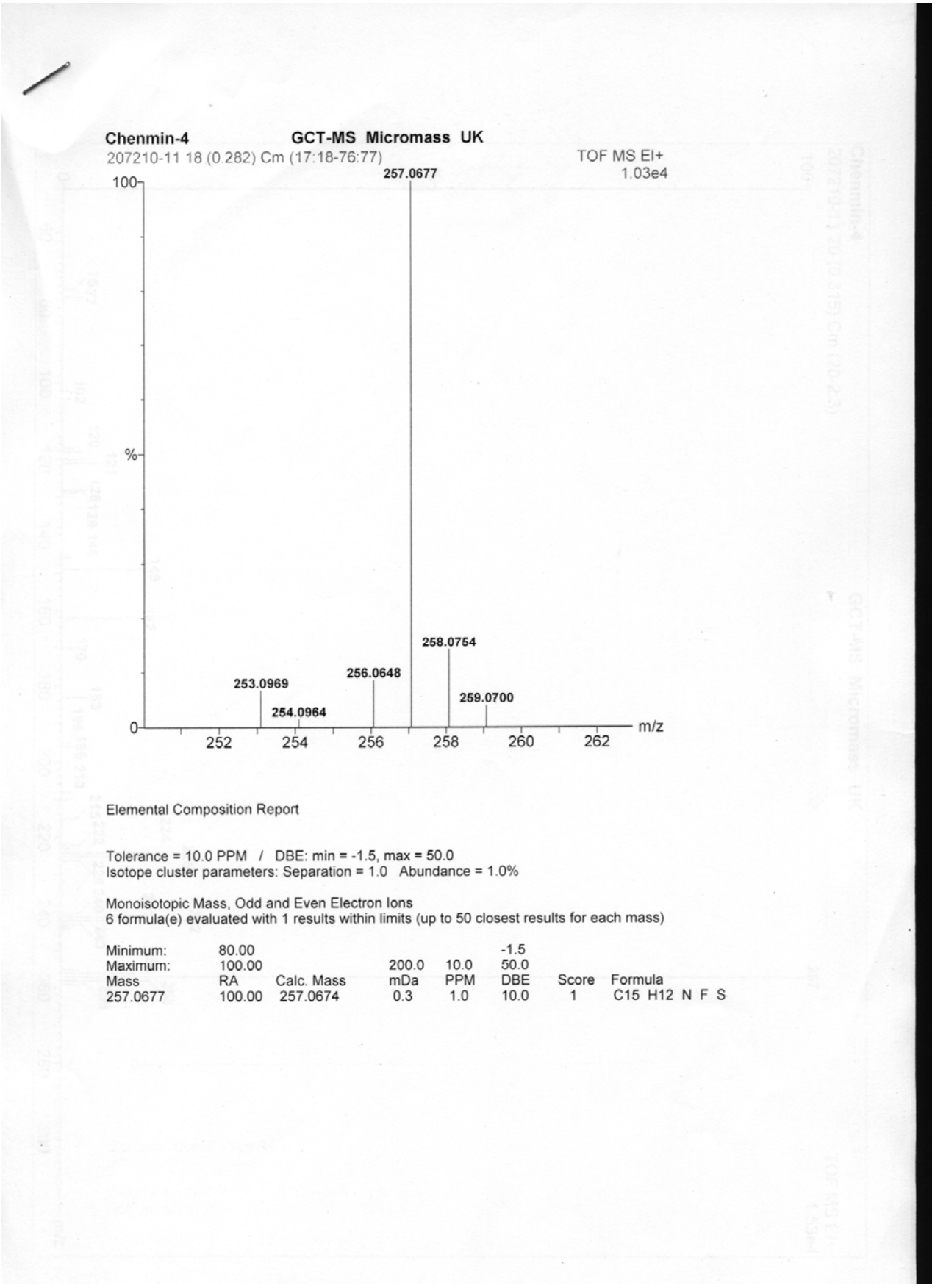


3-((4-Fluorophenyl)thio)-1-methyl-1*H*-indole (3e)





3-((4-Fluorophenyl)thio)-1-methyl-1*H*-indole (3e)



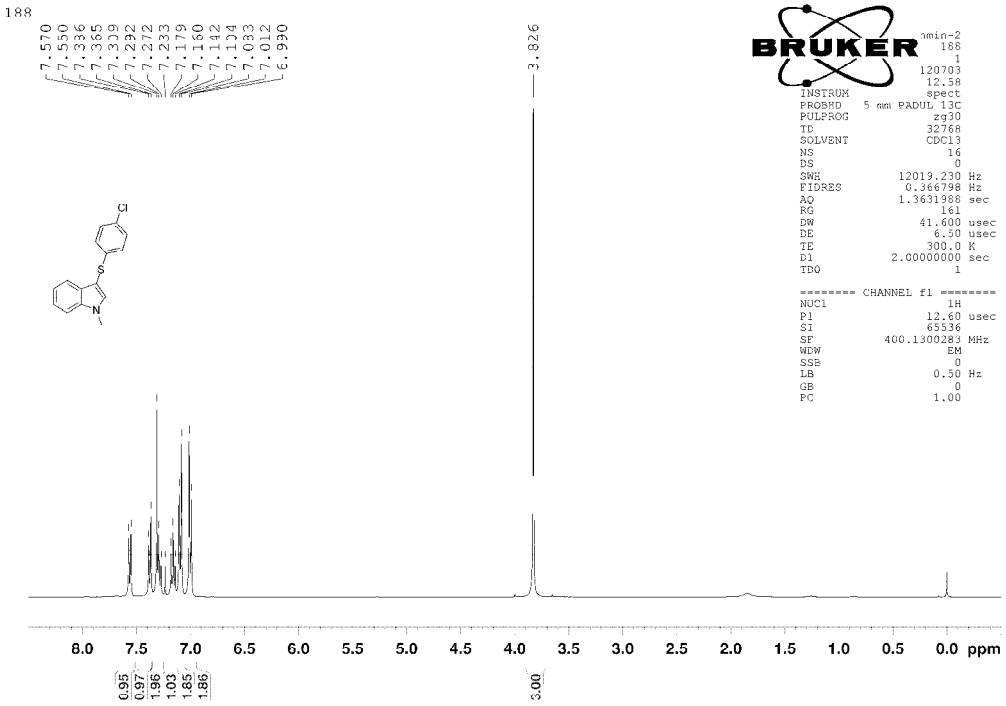
Elemental Composition Report

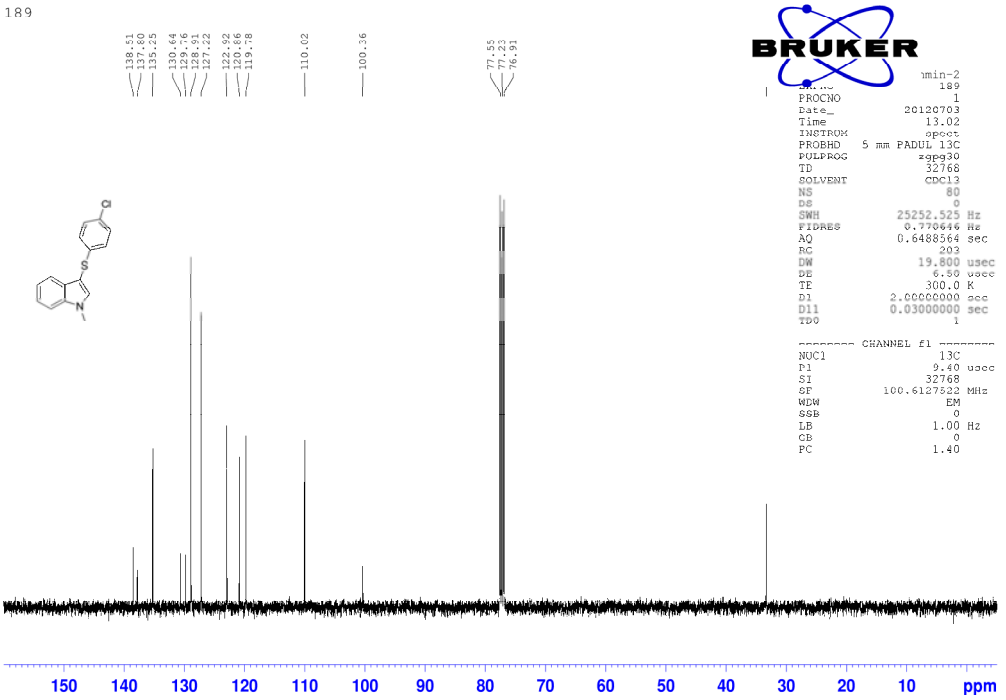
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

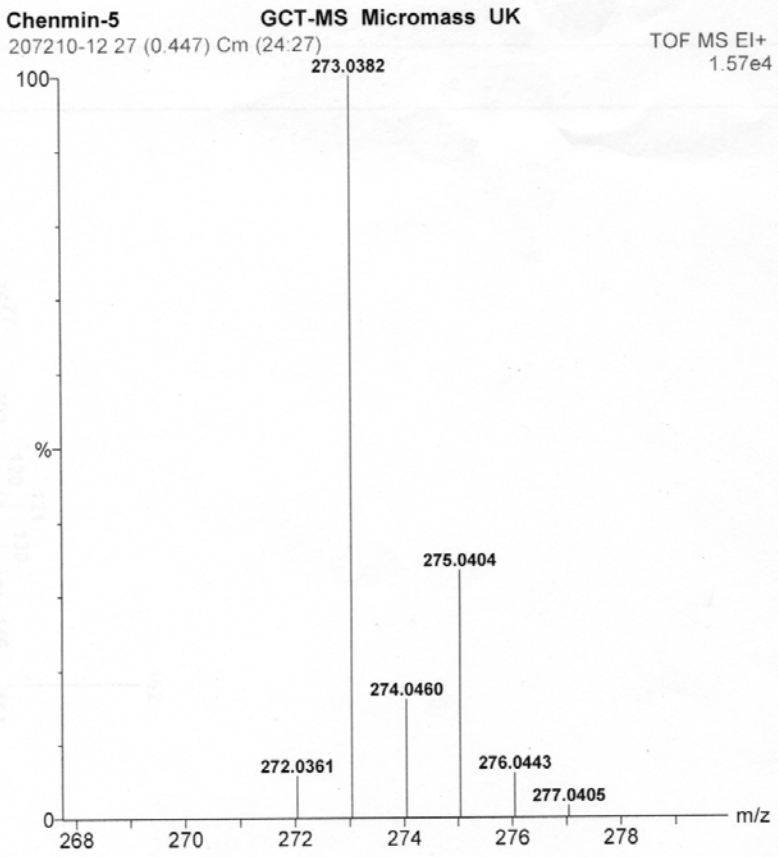
Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
257.0677	100.00	257.0674	0.3	1.0	10.0	1	C15 H12 N F S

3-((4-Chlorophenyl)thio)-1-methyl-1*H*-indole (3f)





3-((4-Chlorophenyl)thio)-1-methyl-1*H*-indole (3f)



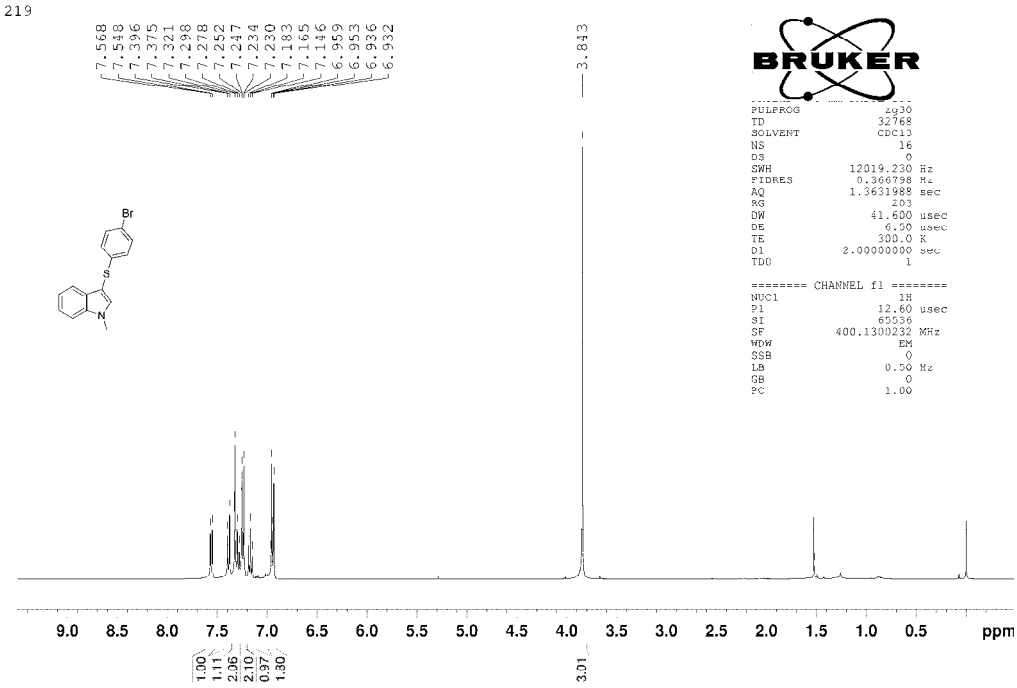
Elemental Composition Report

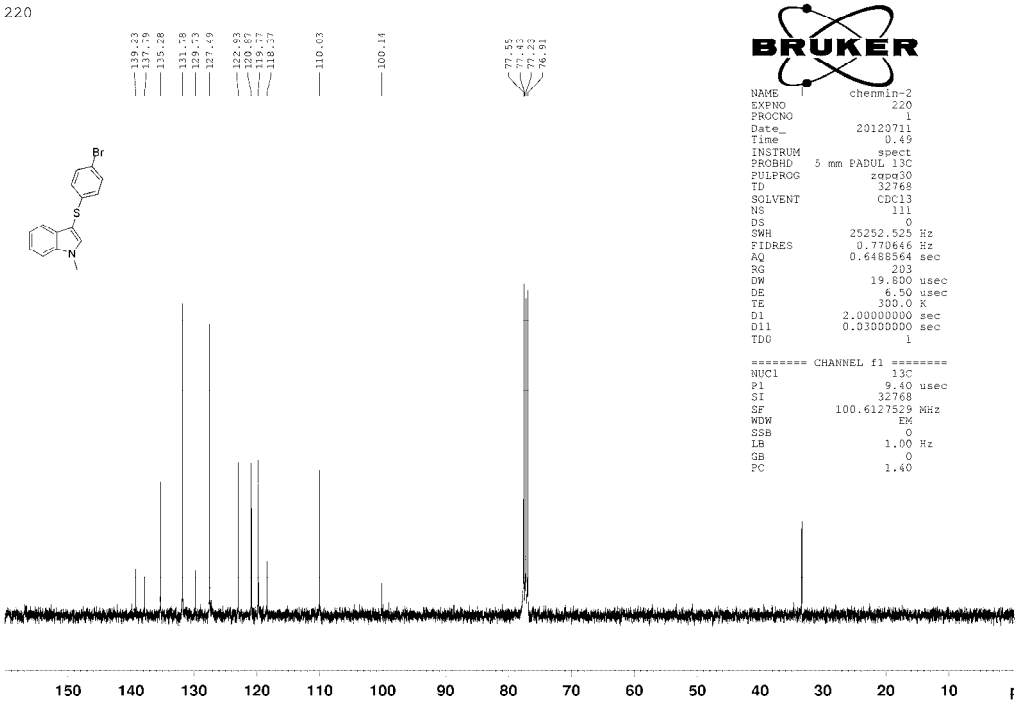
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

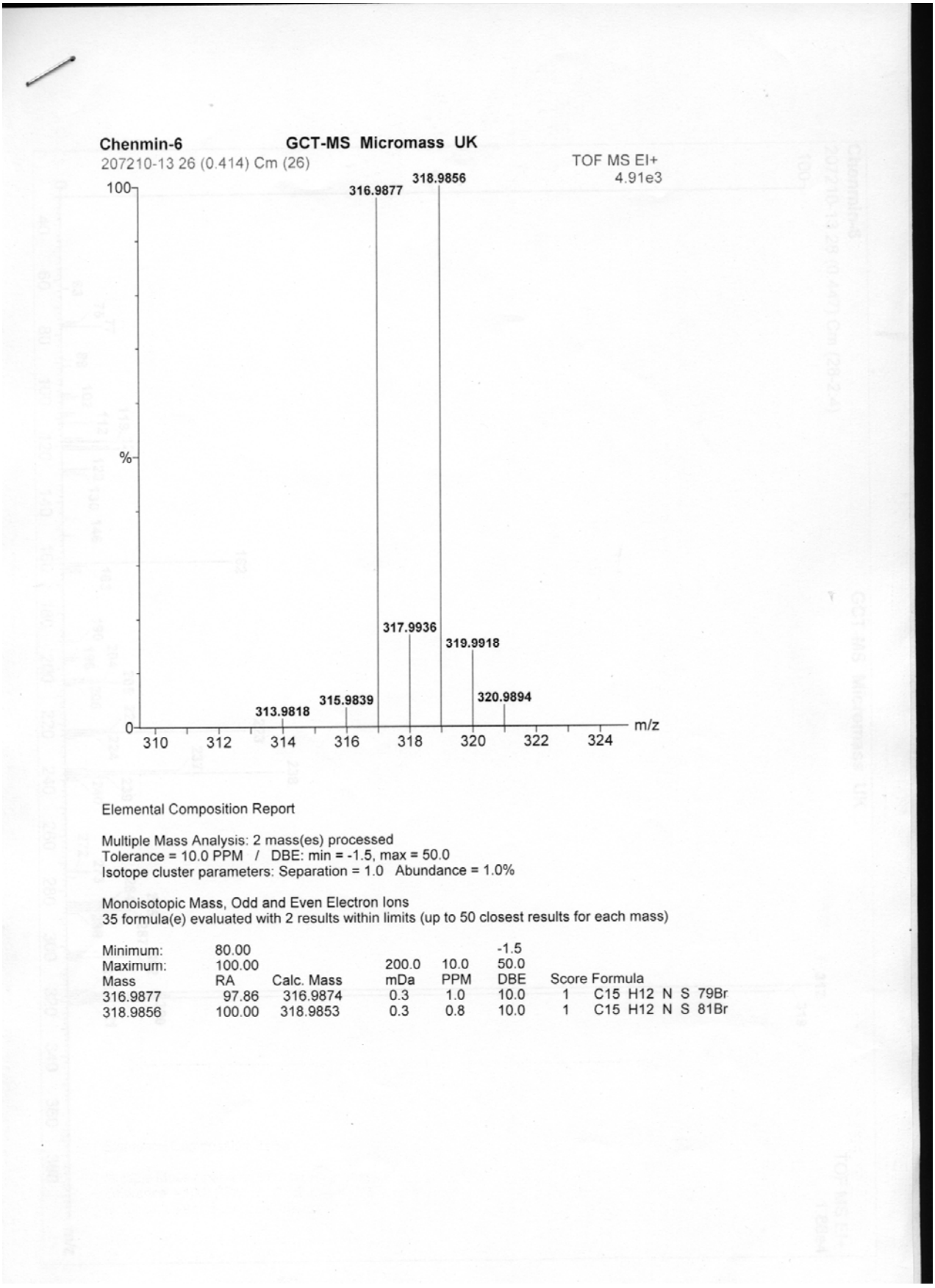
Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
273.0382	100.00	273.0379	0.3	1.1	10.0	1	C15 H12 N S Cl

3-((4-bromophenyl)thio)-1-methyl-1H-indole (3g)





3-((4-bromophenyl)thio)-1-methyl-1H-indole (3g)



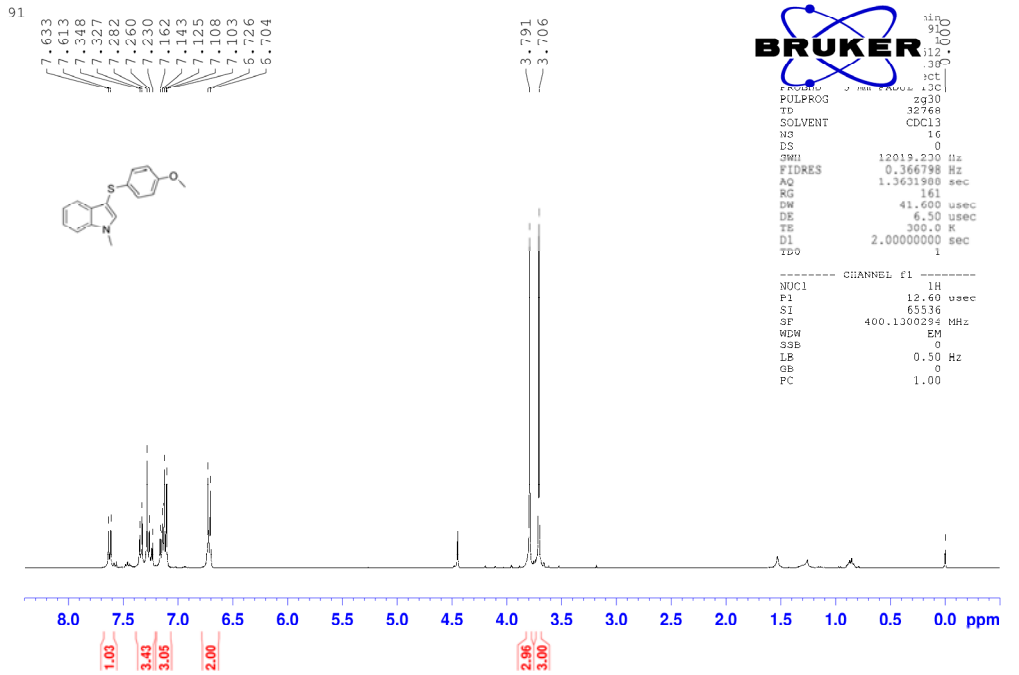
Elemental Composition Report

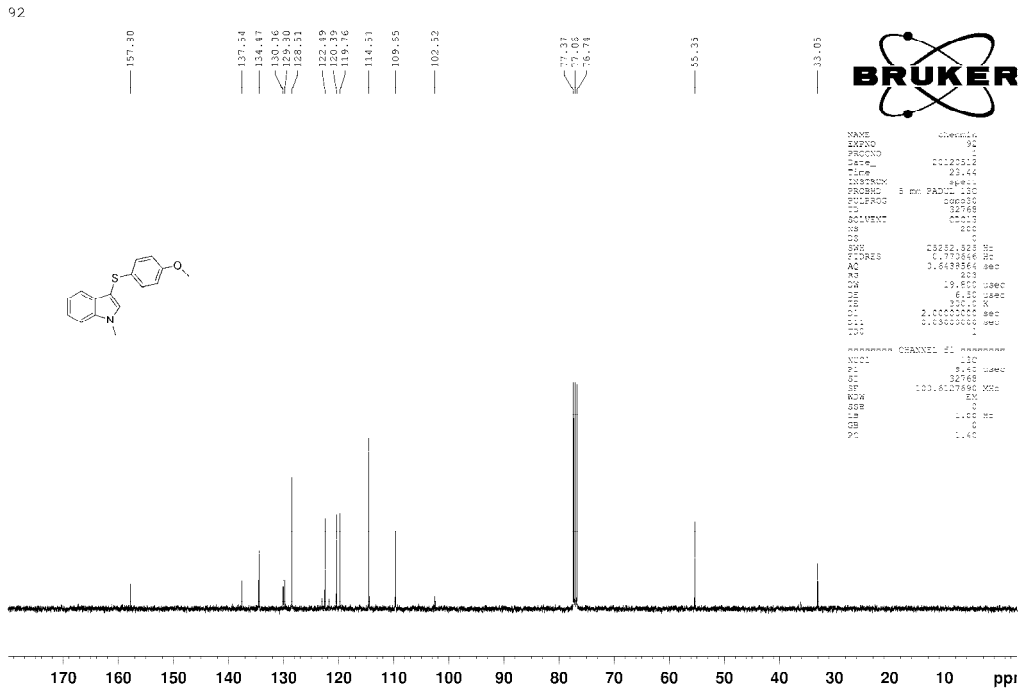
Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
35 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

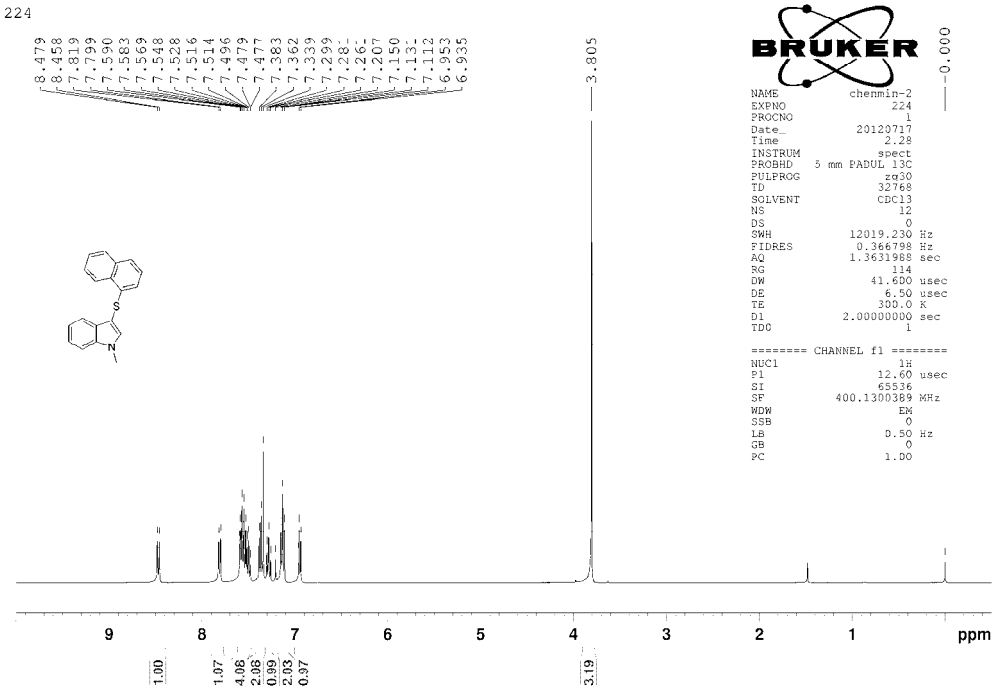
Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
316.9877	97.86	316.9874	0.3	1.0	10.0	1	C15 H12 N S 79Br
318.9856	100.00	318.9853	0.3	0.8	10.0	1	C15 H12 N S 81Br

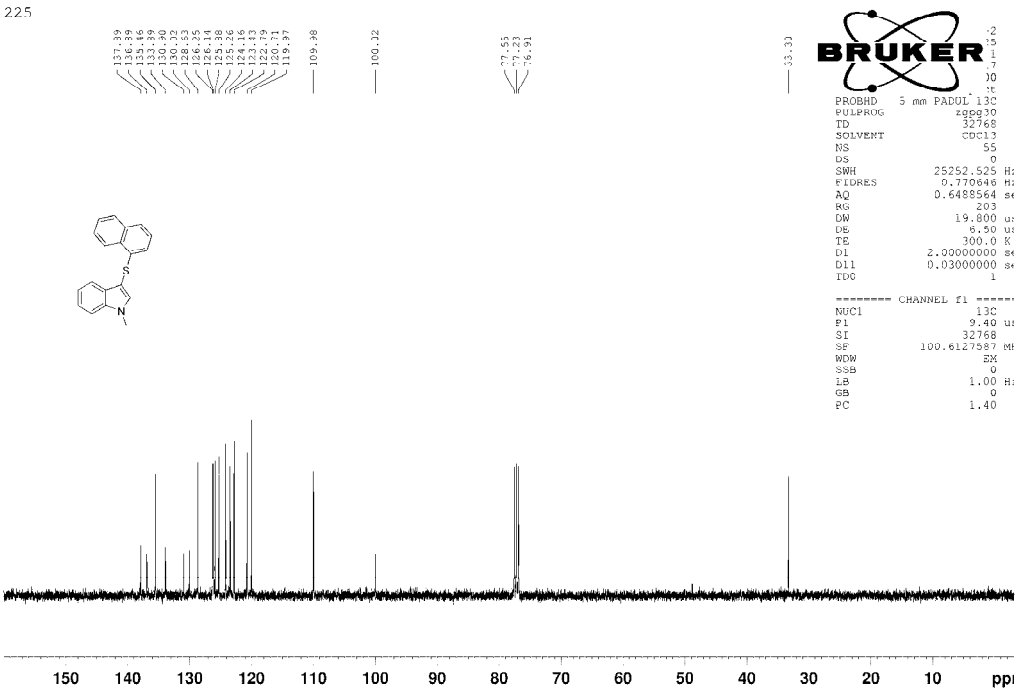
3-((4-Methoxyphenyl)thio)-1-methyl-1*H*-indole (3h)





1-Methyl-3-(naphthalen-1-ylthio)-1*H*-indole (3i)

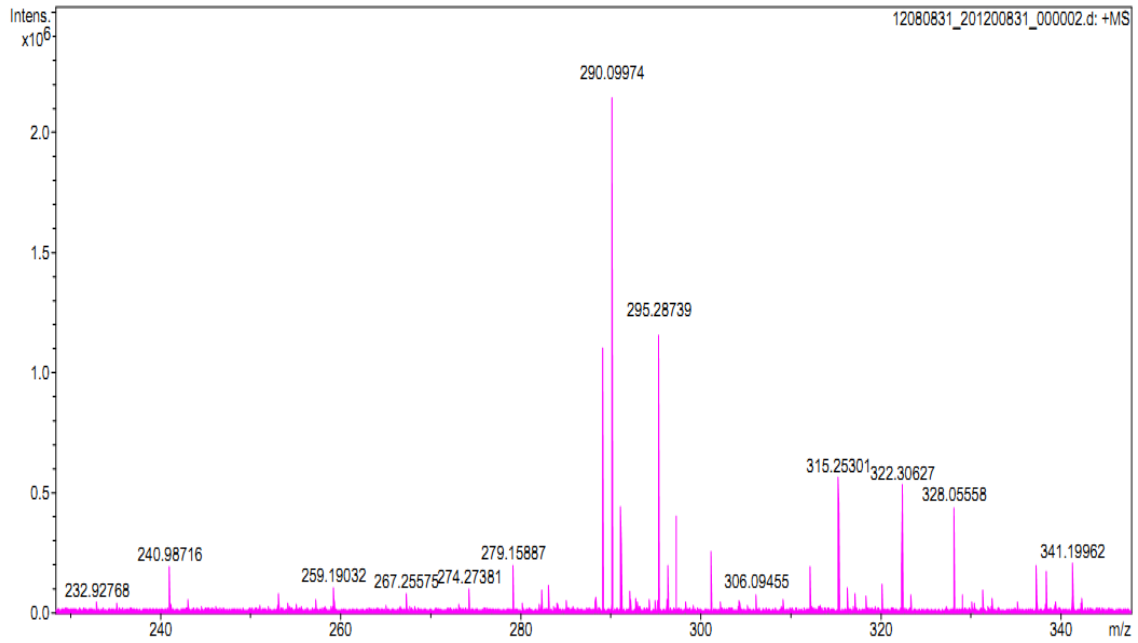




1-Methyl-3-(naphthalen-1-ylthio)-1*H*-indole (3i)

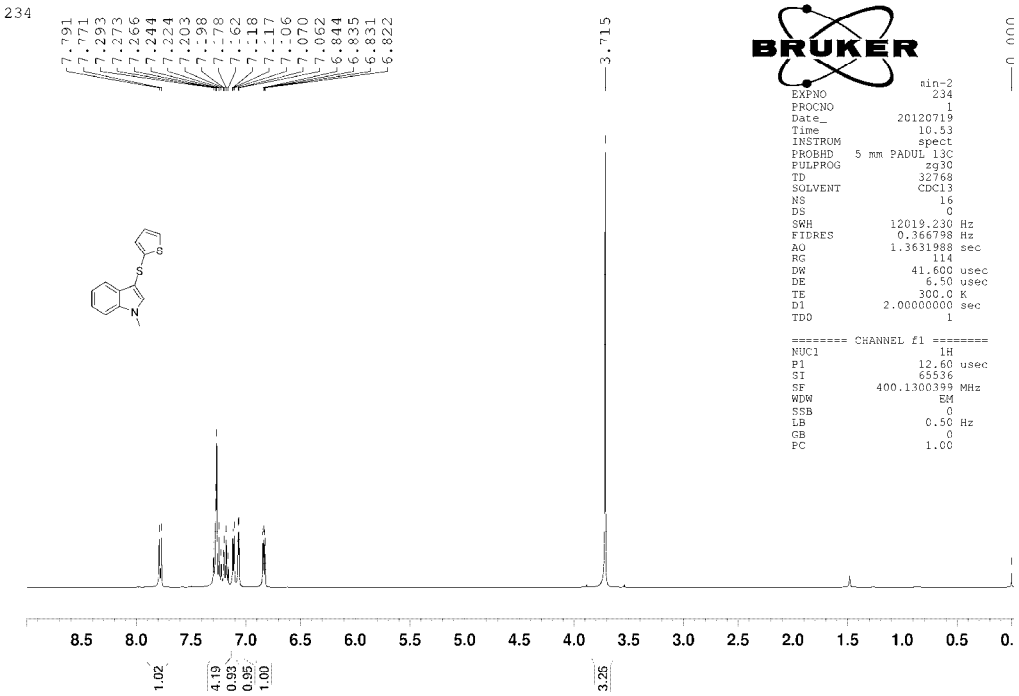
Analysis Info

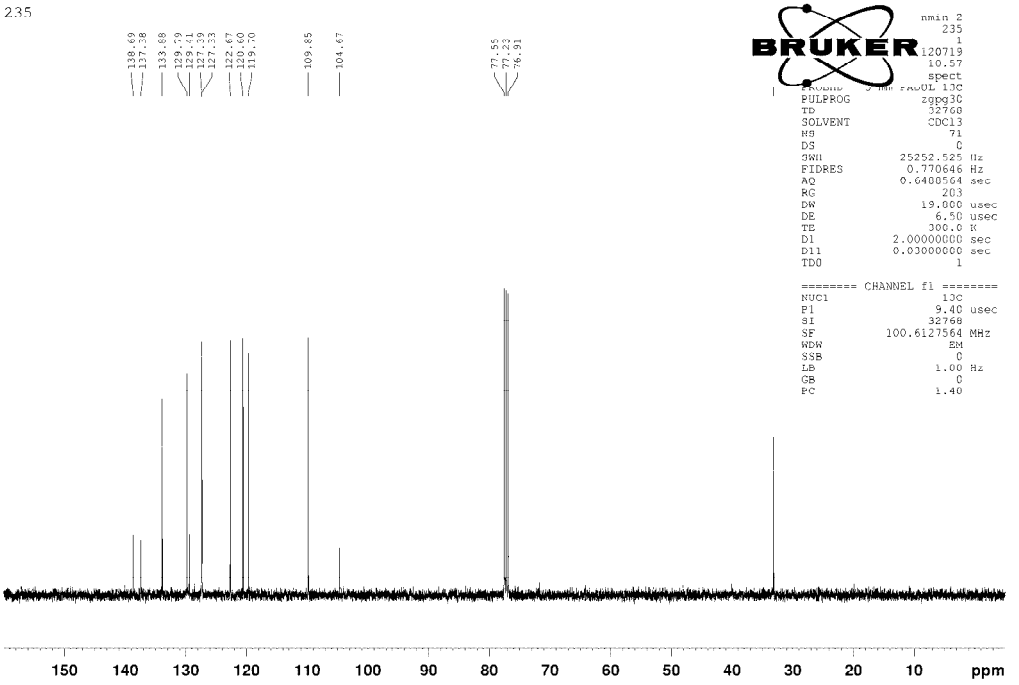
Analysis Name	12080831_201200831_000002.d	Acquisition Date	8/31/2012 10:40:19 AM
Sample	chenmin-14	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



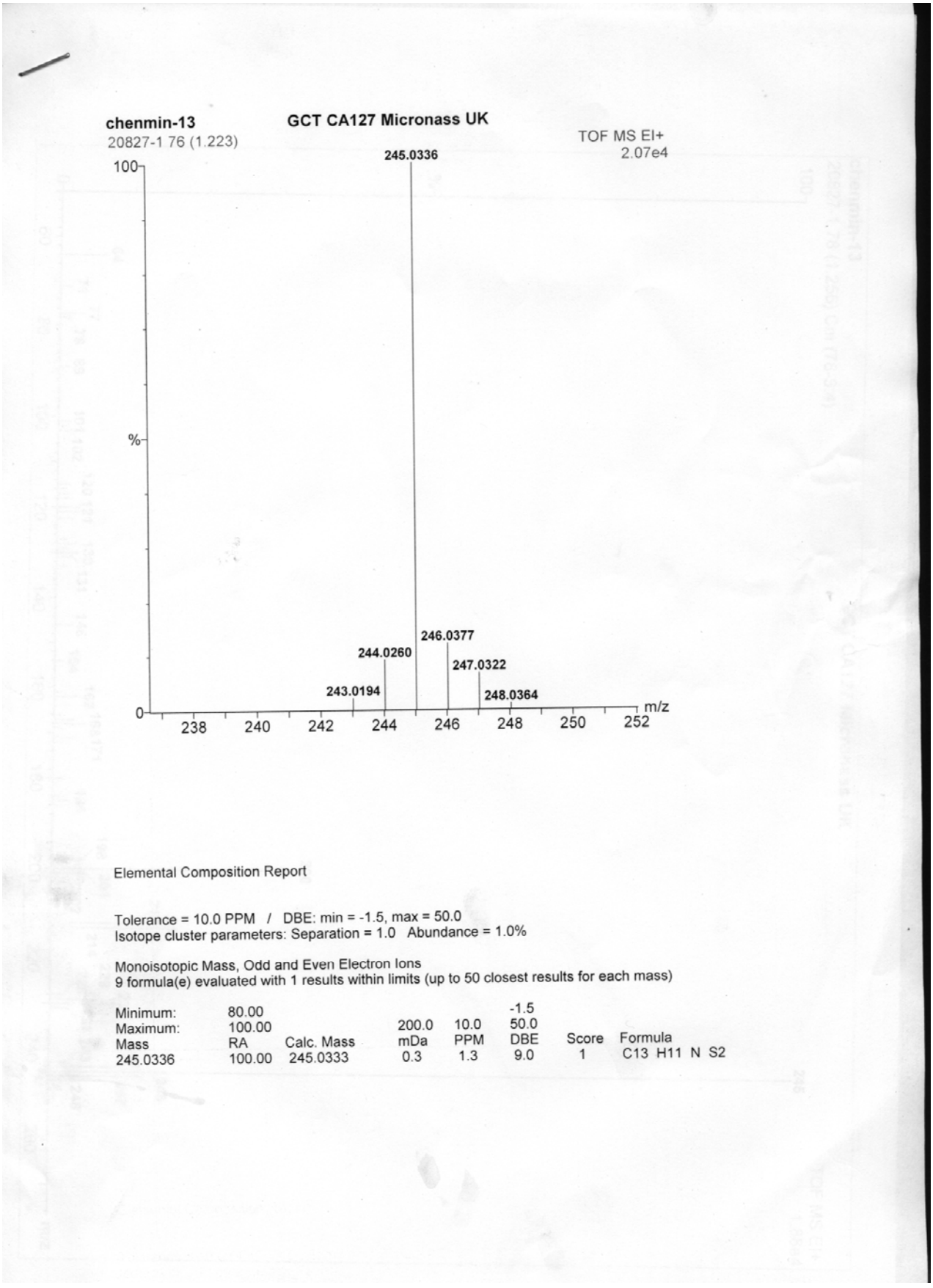
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
290.09974	1	C 19 H 16 N S	100.00	290.09980	0.1	0.2	14.8	12.5	even	ok

1-Methyl-3-(thiophen-2-ylthio)-1*H*-indole (3j)





1-Methyl-3-(thiophen-2-ylthio)-1*H*-indole (3j)



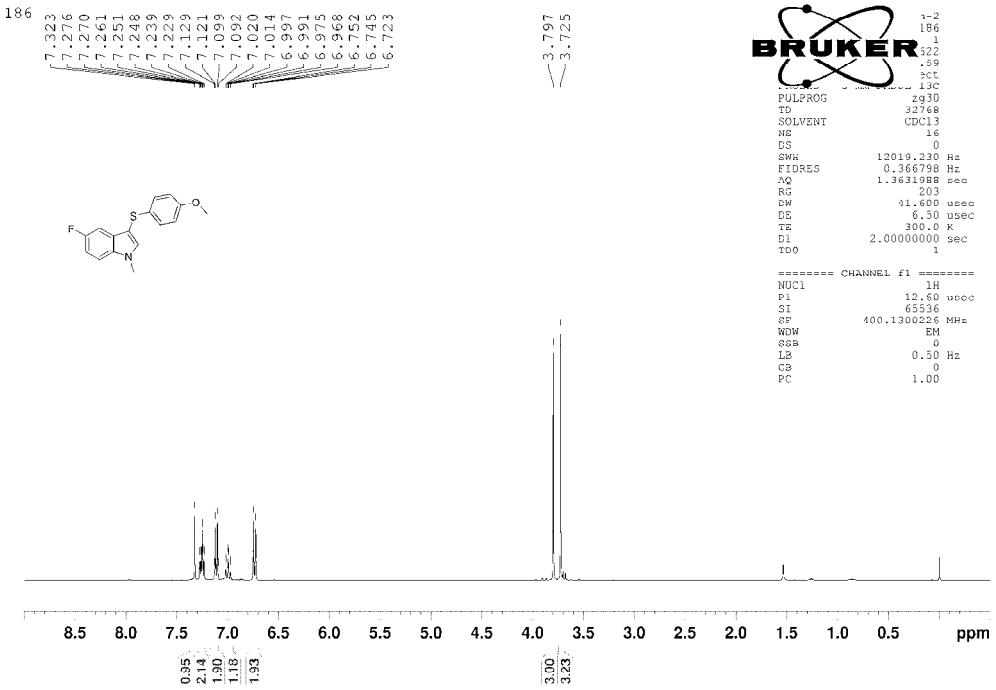
Elemental Composition Report

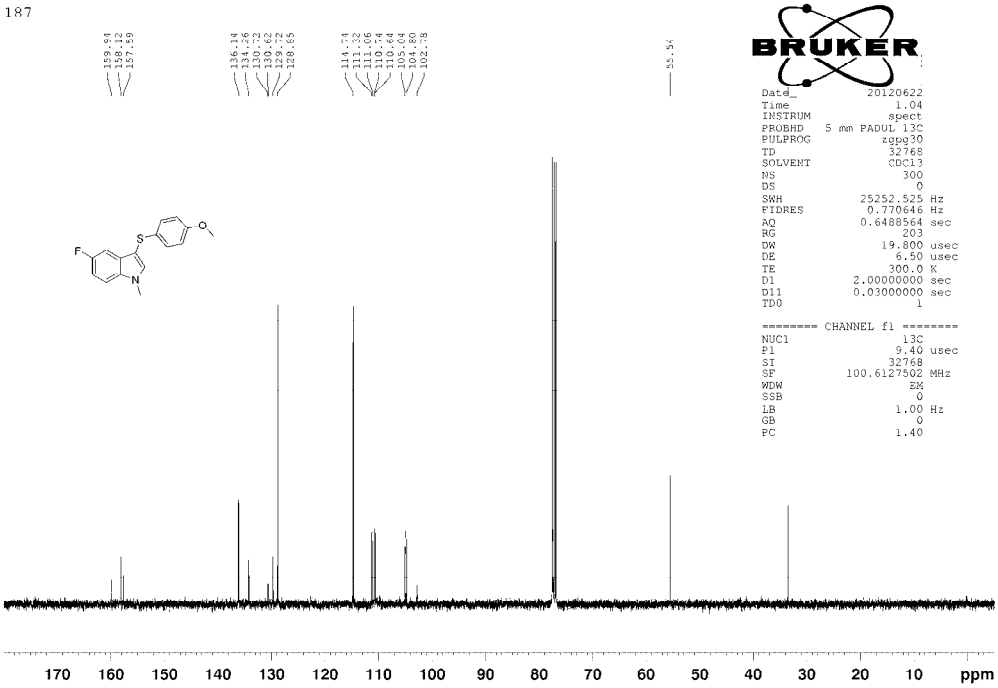
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
245.0336	100.00	245.0333	0.3	1.3	9.0	1	C13 H11 N S2

5-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (4a)



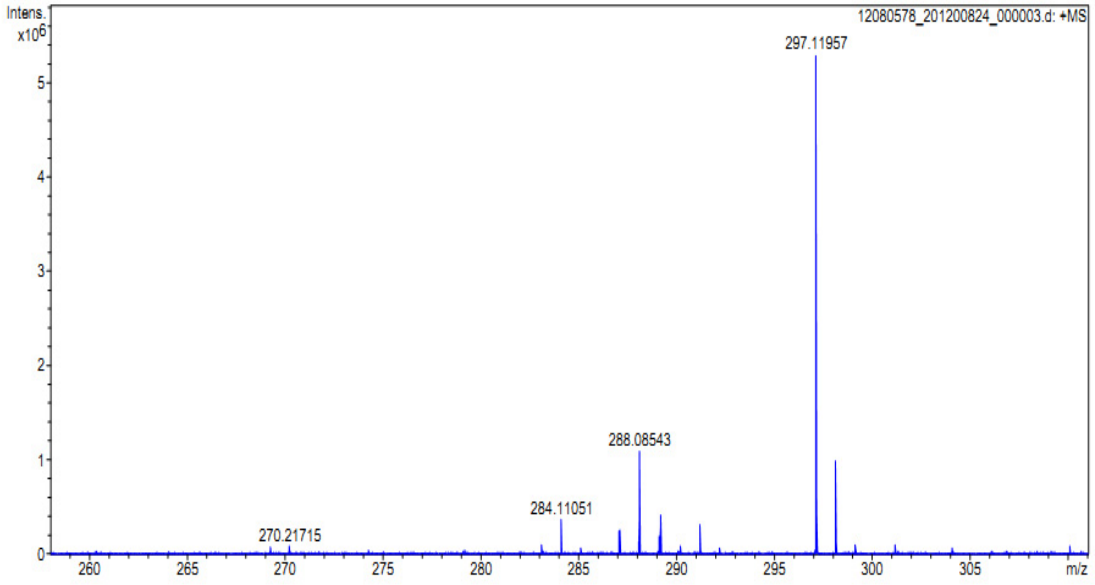


5-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (4a)

Peking University Mass Spectrometry Sample Analysis Report

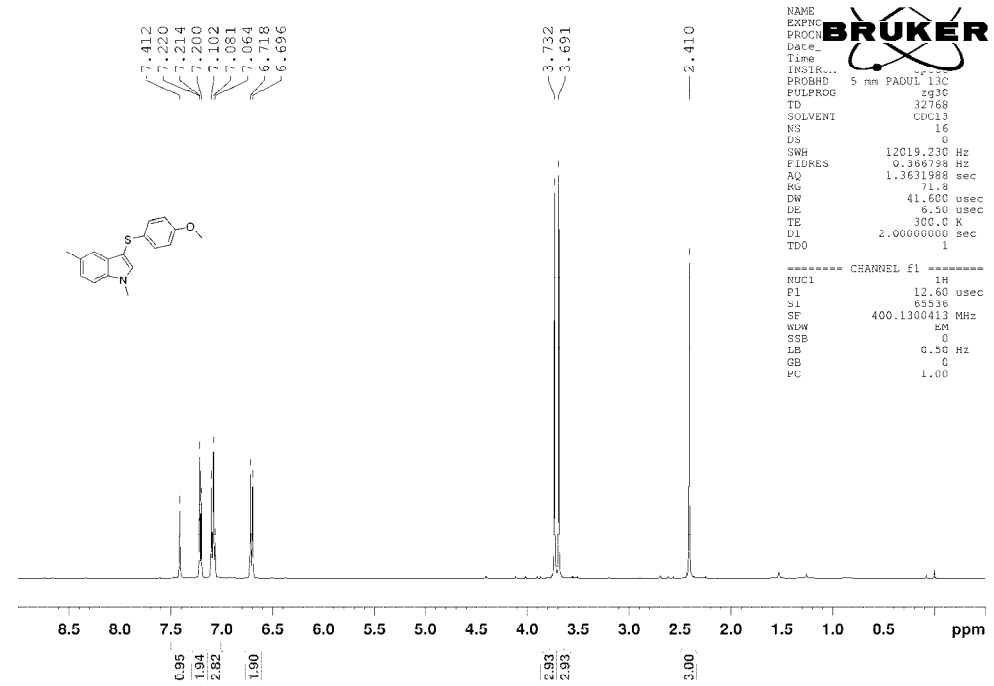
Analysis Info

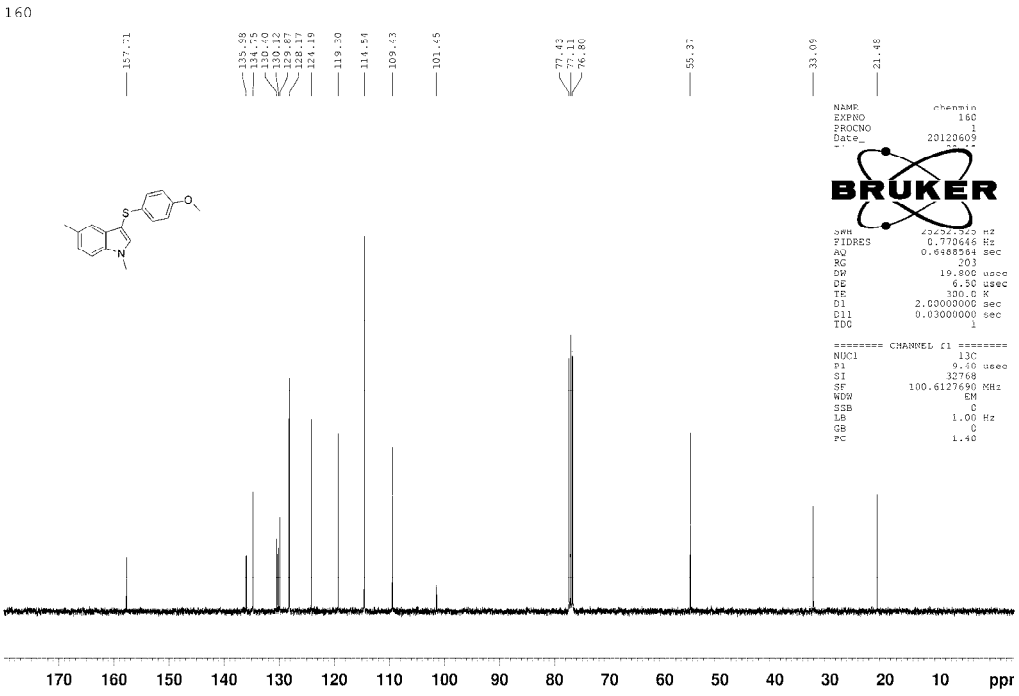
Analysis Name	12080578_201200824_000003.d	Acquisition Date	8/24/2012 4:49:27 PM
Sample	8	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
288.08543	1	C 16 H 15 F N O S	100.00	288.08529	-0.1	-0.5	30.9	9.5	even	ok

3-((4-Methoxyphenyl)thio)-1,5-dimethyl-1*H*-indole (4b)



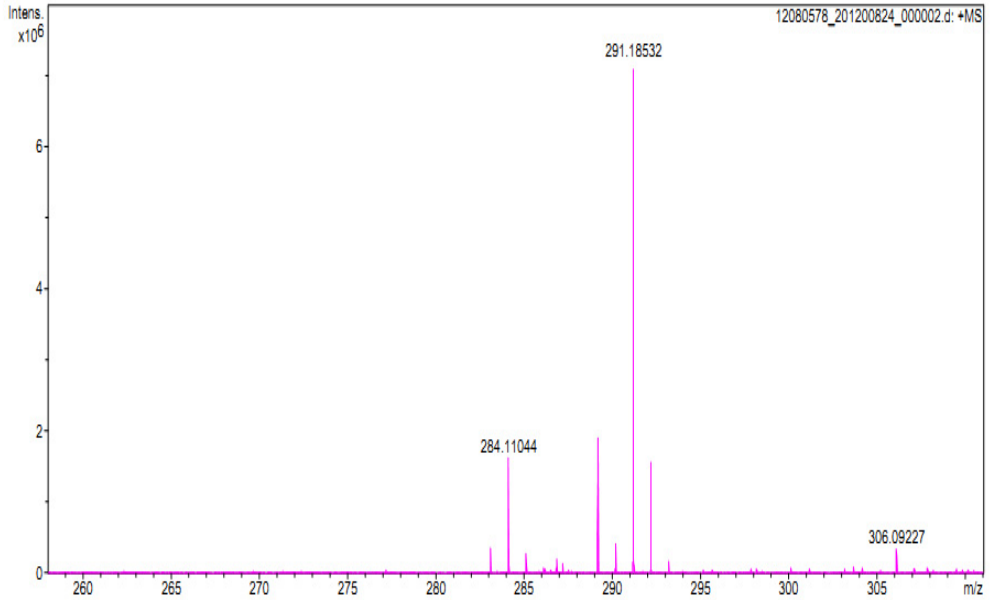


3-((4-Methoxyphenyl)thio)-1,5-dimethyl-1*H*-indole (4b)

Peking University Mass Spectrometry Sample Analysis Report

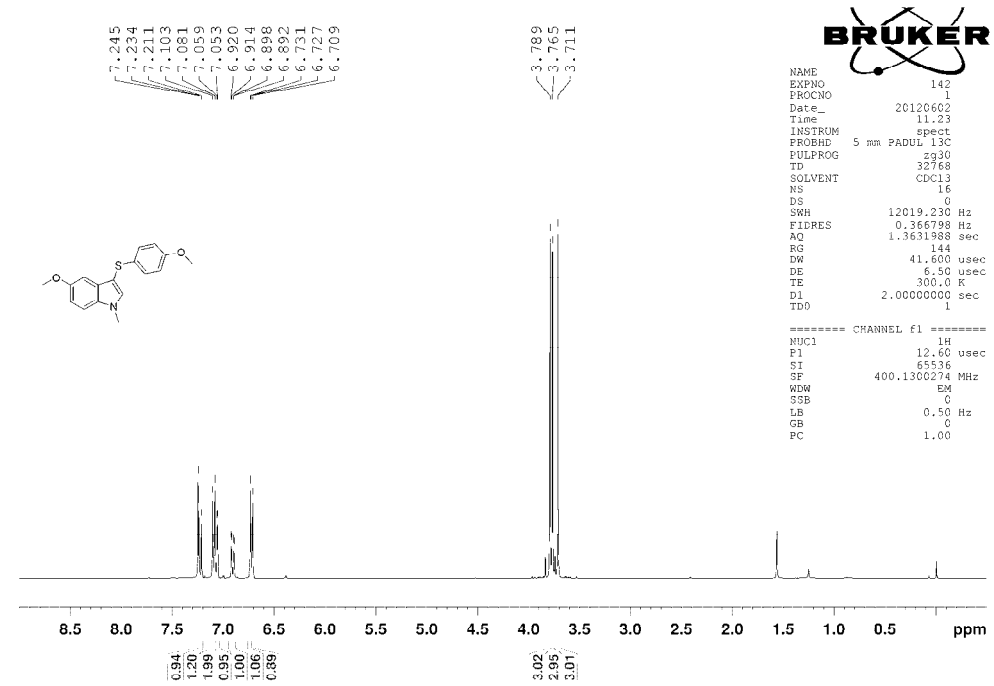
Analysis Info

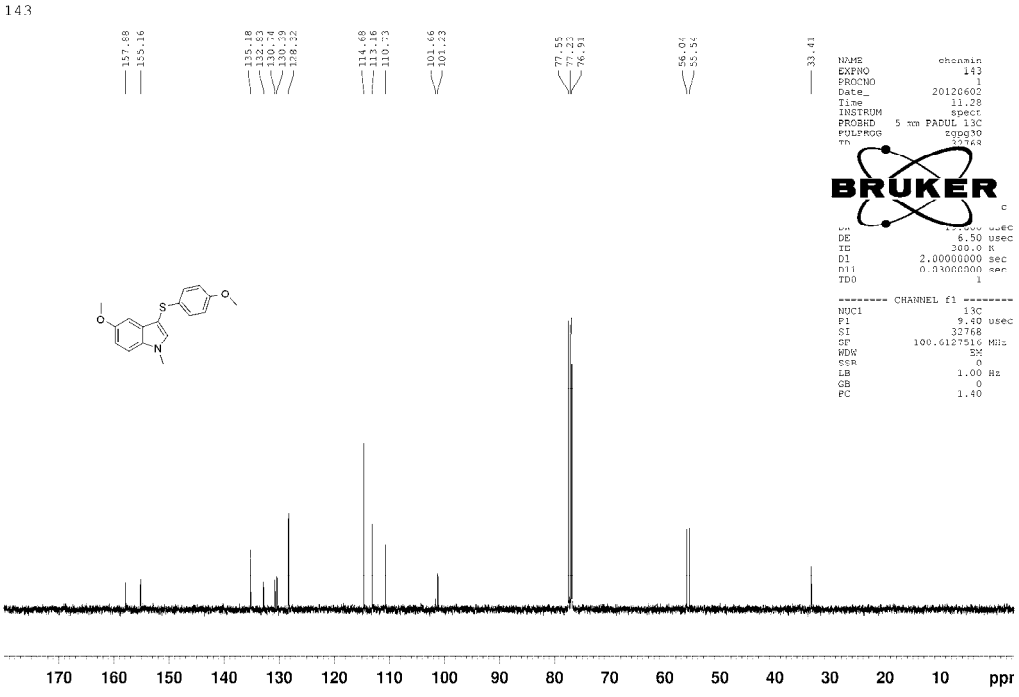
Analysis Name	12080578_201200824_000002.d	Acquisition Date	8/24/2012 4:48:25 PM
Sample	7	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



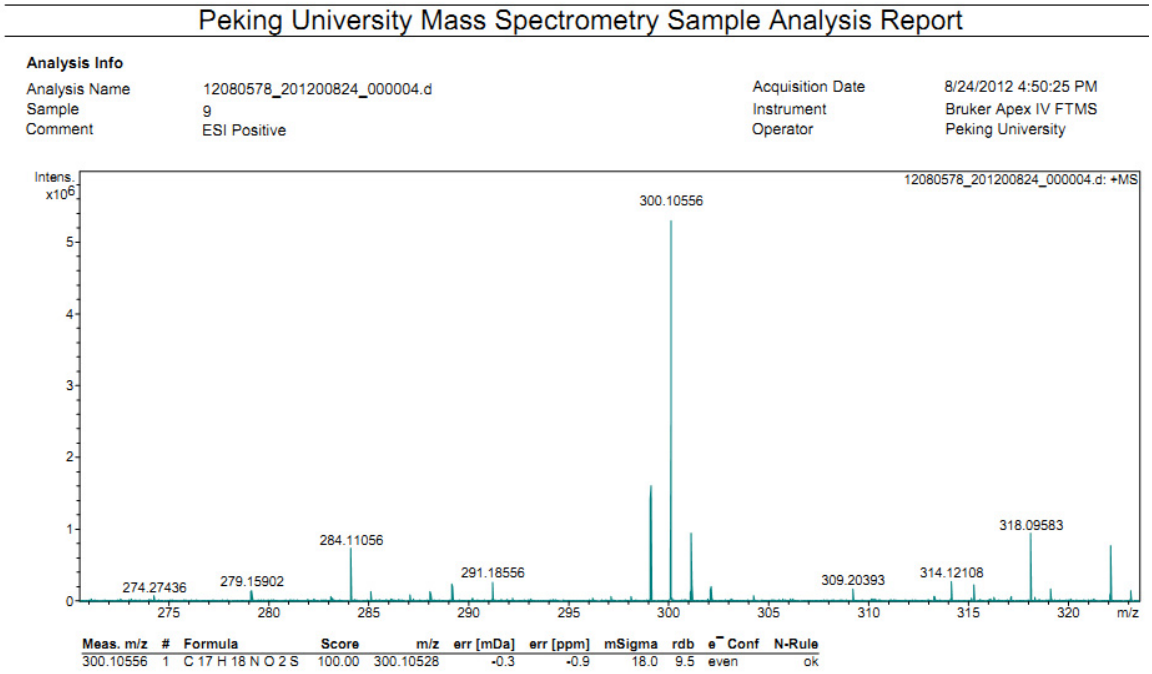
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
284.11044	1	C 17 H 18 N O S	100.00	284.11036	-0.1	-0.3	12.2	9.5	even	ok

5-Methoxy-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (4c)

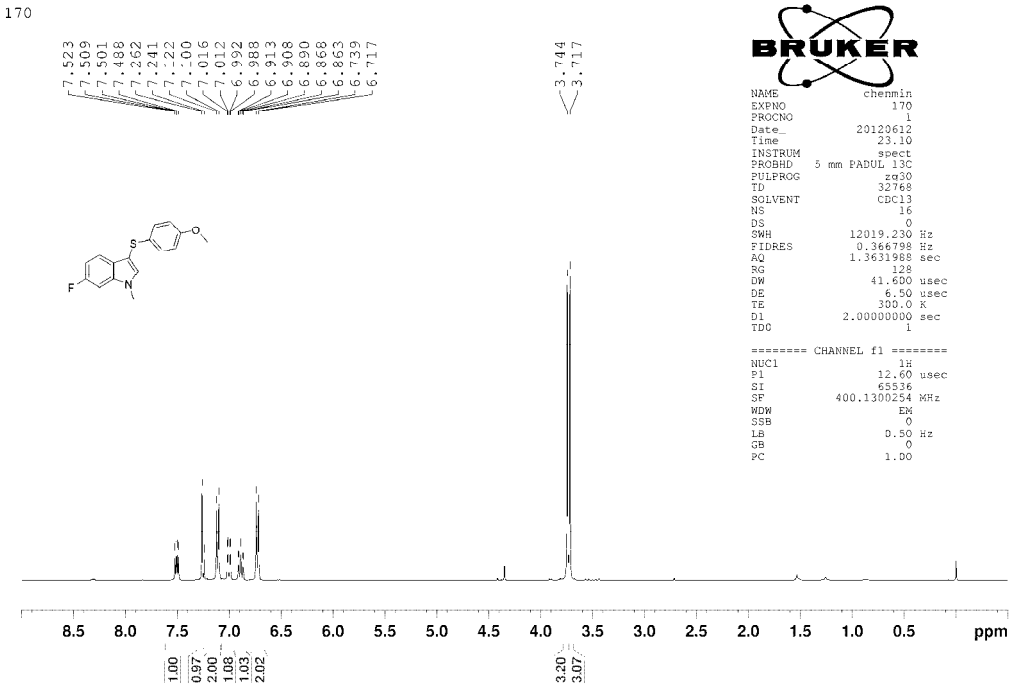


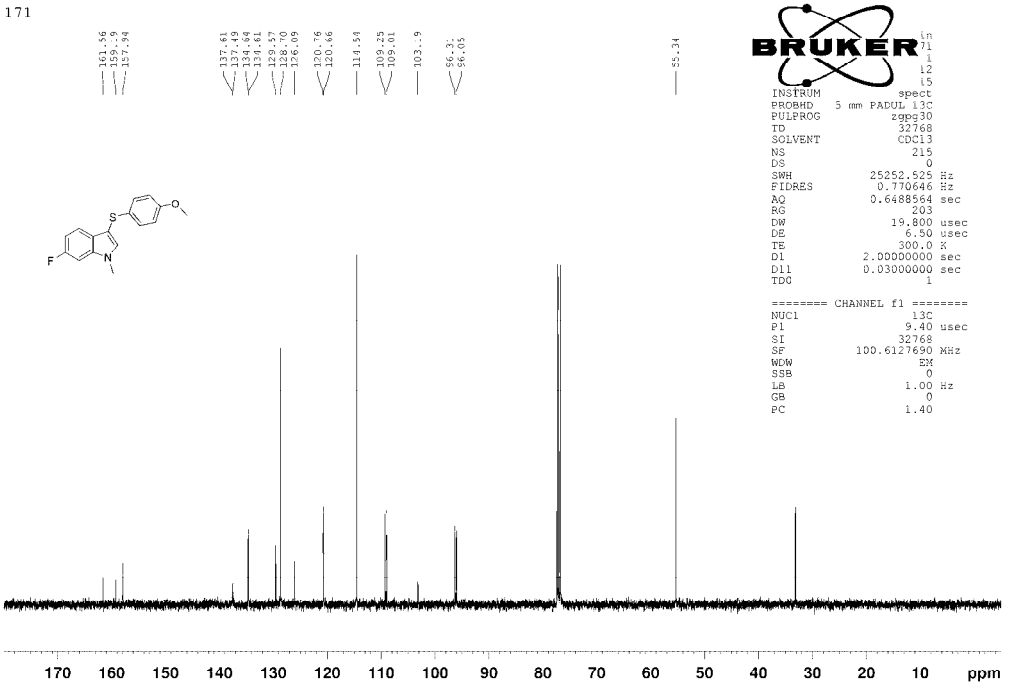


5-Methoxy-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (4c)



6-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (4d)



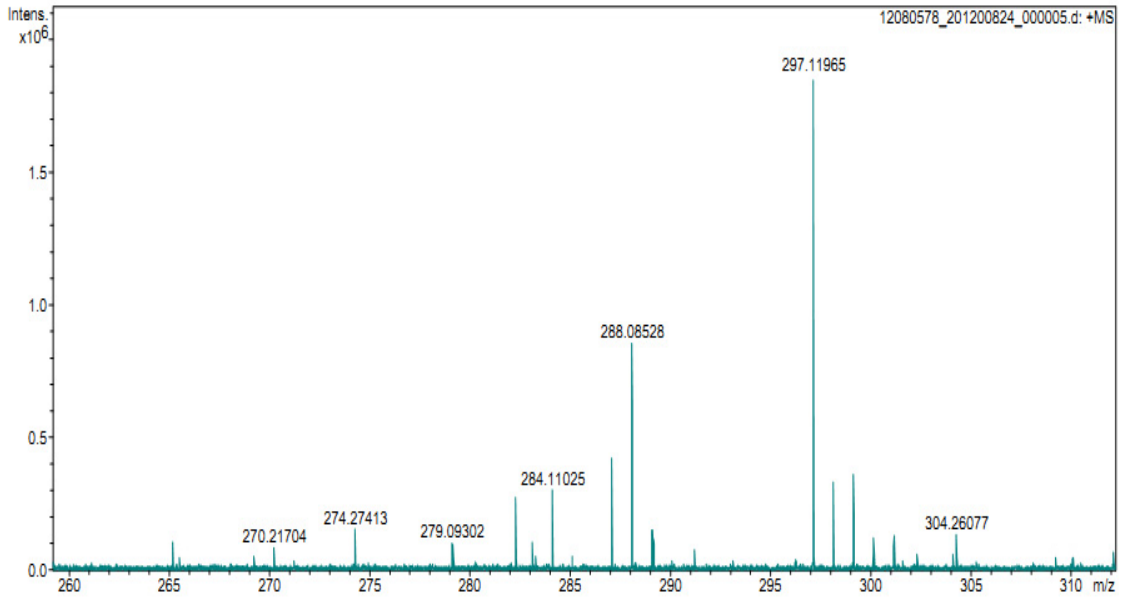


6-Fluoro-3-((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (4d)

Peking University Mass Spectrometry Sample Analysis Report

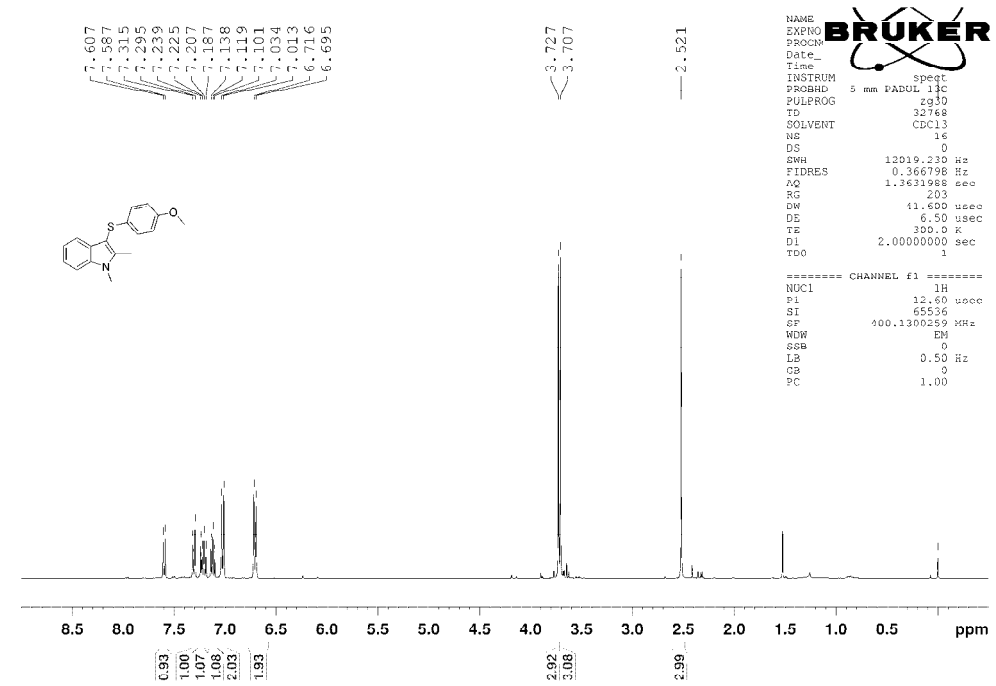
Analysis Info

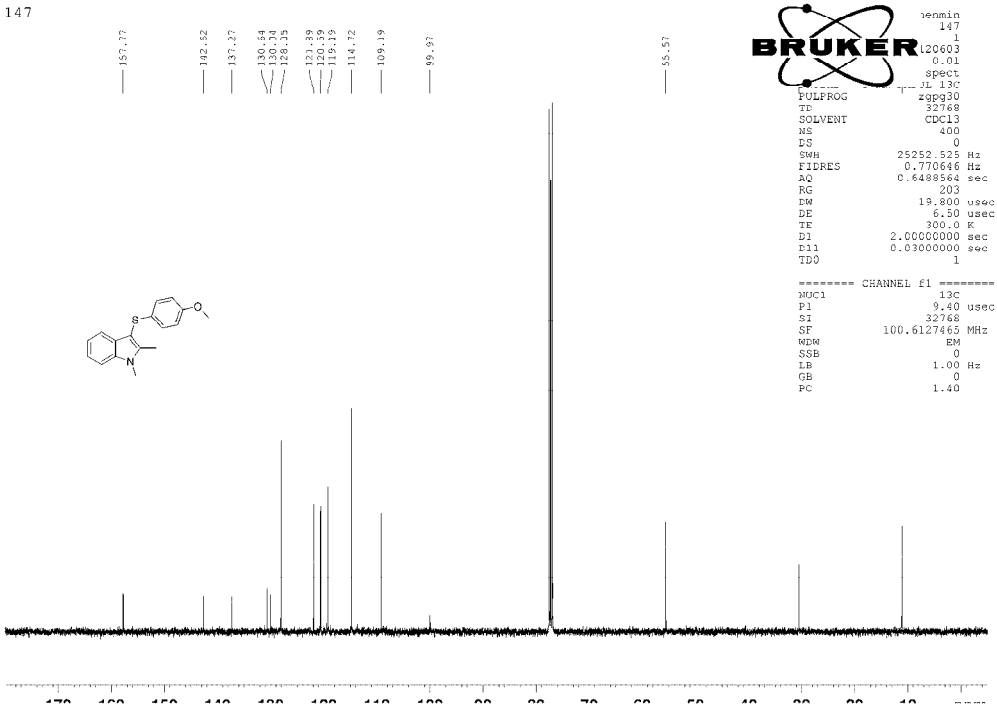
Analysis Name	12080578_201200824_000005.d	Acquisition Date	8/24/2012 4:51:27 PM
Sample	10	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
288.08528	1	C 16 H 15 F N O S	100.00	288.08529	0.0	0.0	30.9	9.5	even	ok

3-((4-Methoxyphenyl)thio)-1,2-dimethyl-1*H*-indole (4e)



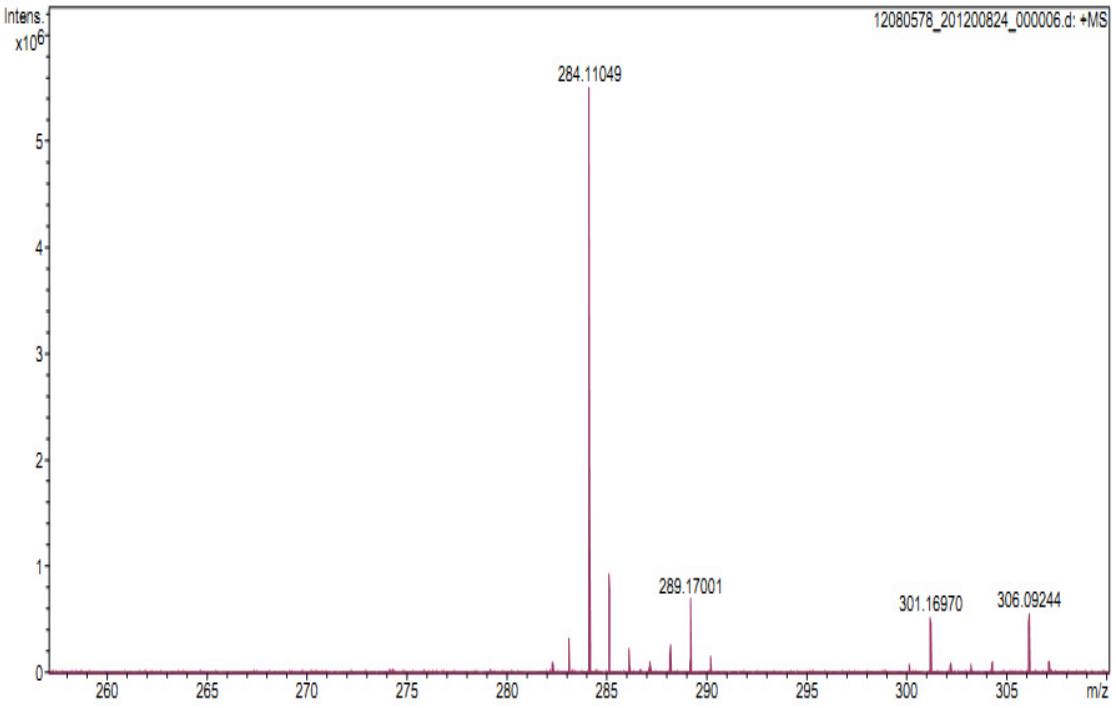


3-((4-Methoxyphenyl)thio)-1,2-dimethyl-1*H*-indole (4e)

Peking University Mass Spectrometry Sample Analysis Report

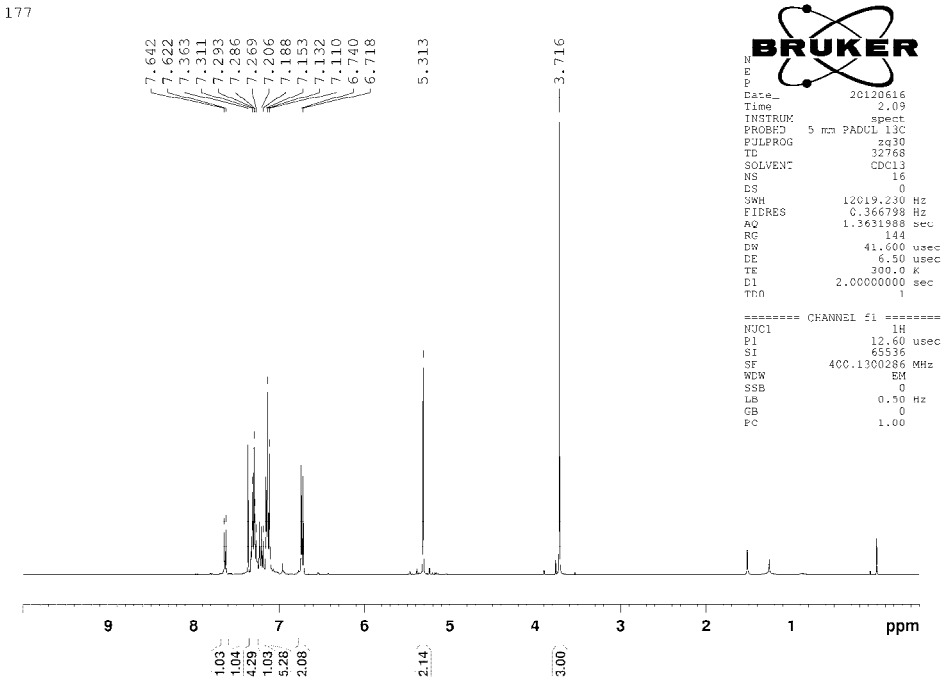
Analysis Info

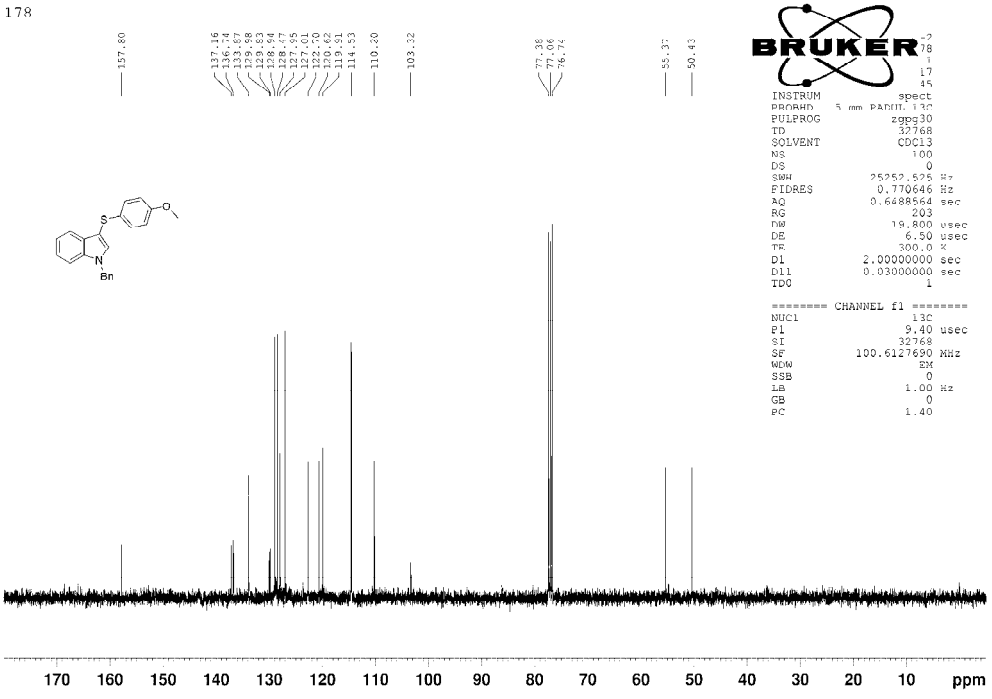
Analysis Name	12080578_201200824_000006.d	Acquisition Date	8/24/2012 4:52:22 PM
Sample	11	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
284.11049	1	C 17 H 18 N O S	100.00	284.11036	-0.1	-0.4	16.3	9.5	even	ok

1-Benzyl-3-((4-methoxyphenyl)thio)-1*H*-indole (4f)



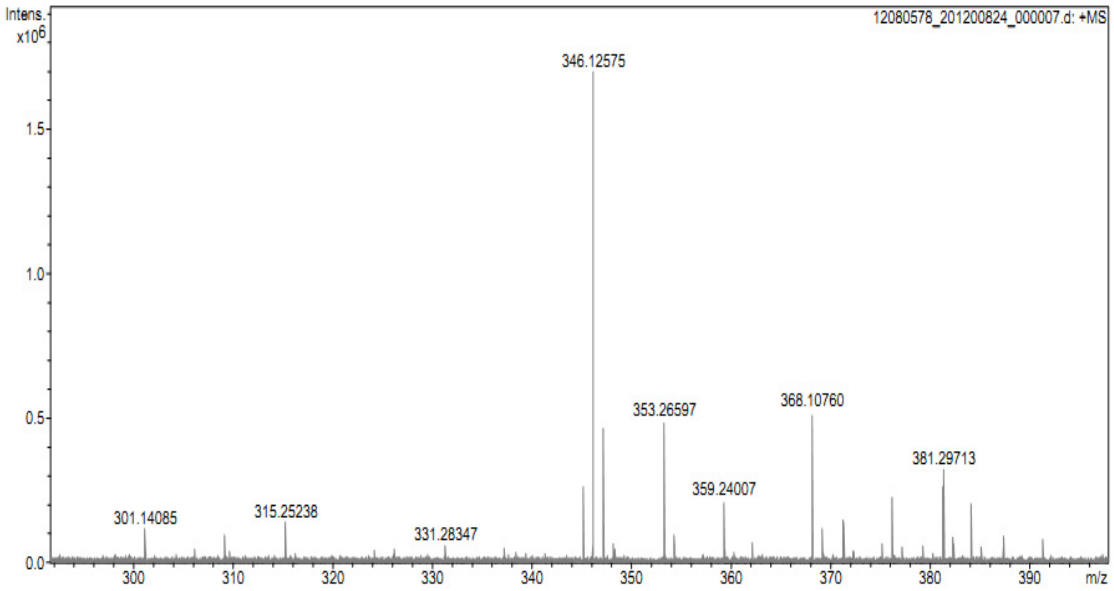


1-Benzyl-3-((4-methoxyphenyl)thio)-1*H*-indole (4f)

Peking University Mass Spectrometry Sample Analysis Report

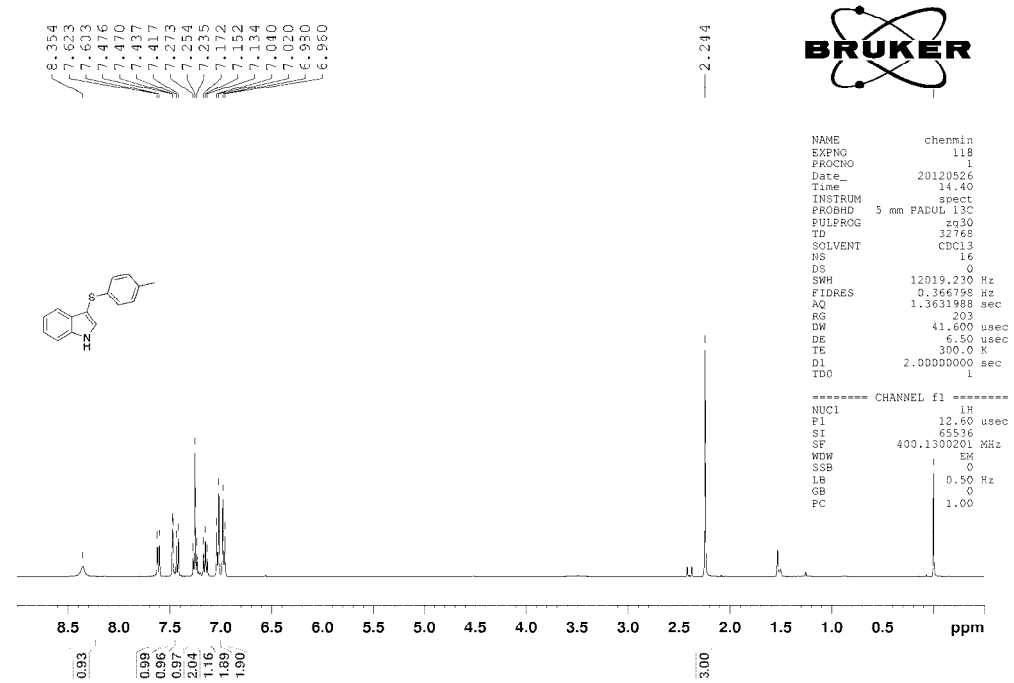
Analysis Info

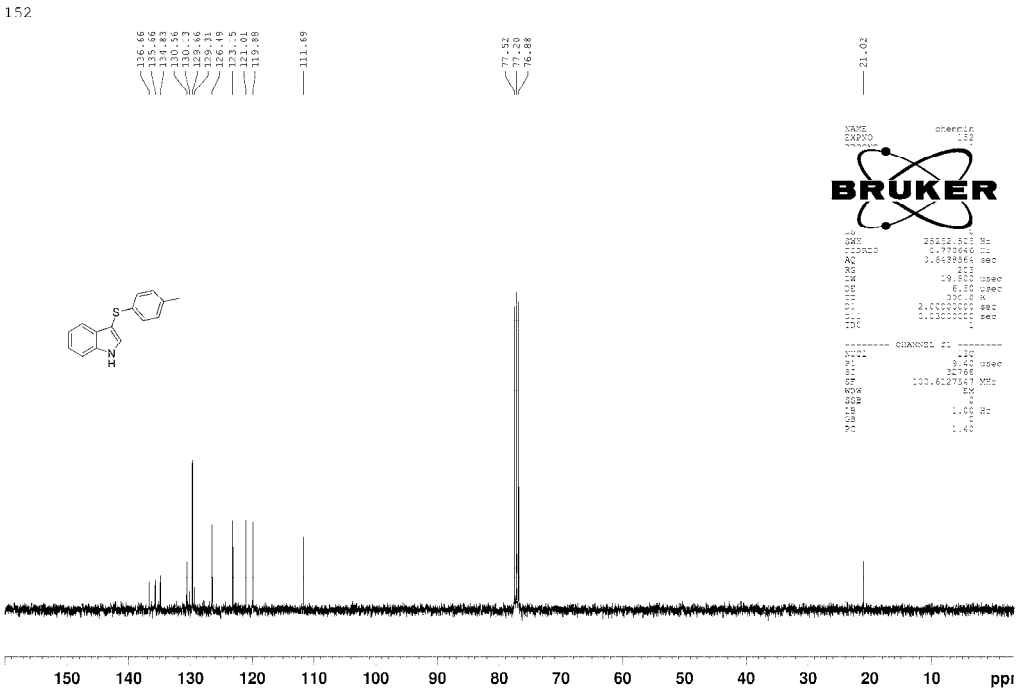
Analysis Name	12080578_201200824_000007.d	Acquisition Date	8/24/2012 4:53:23 PM
Sample	12	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



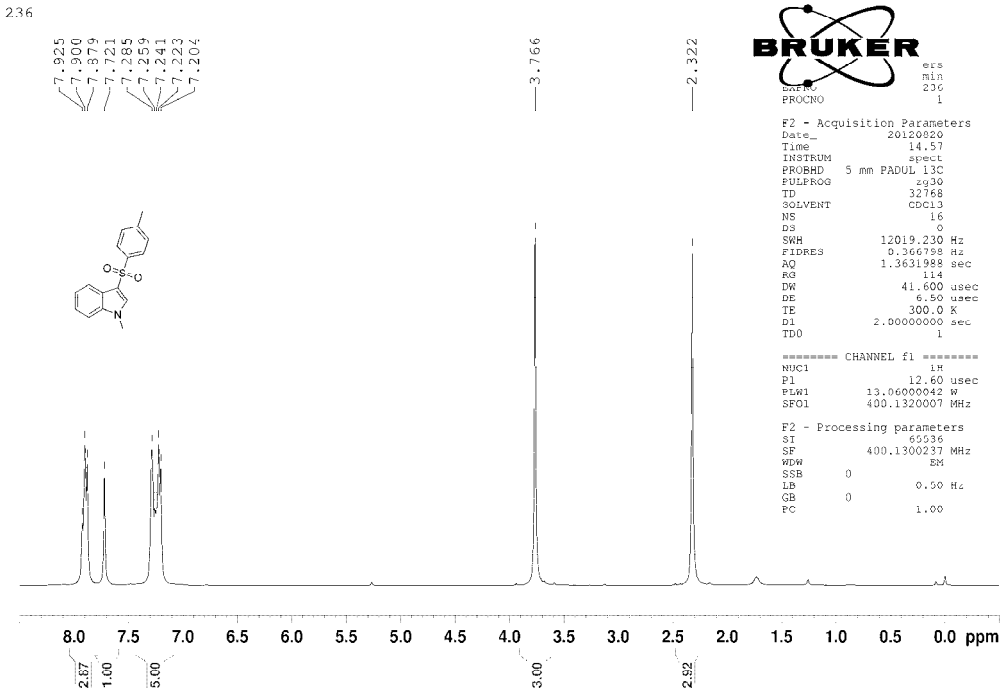
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
346.12575	1	C 22 H 20 N O S	100.00	346.12601	0.3	0.7	22.8	13.5	even	ok

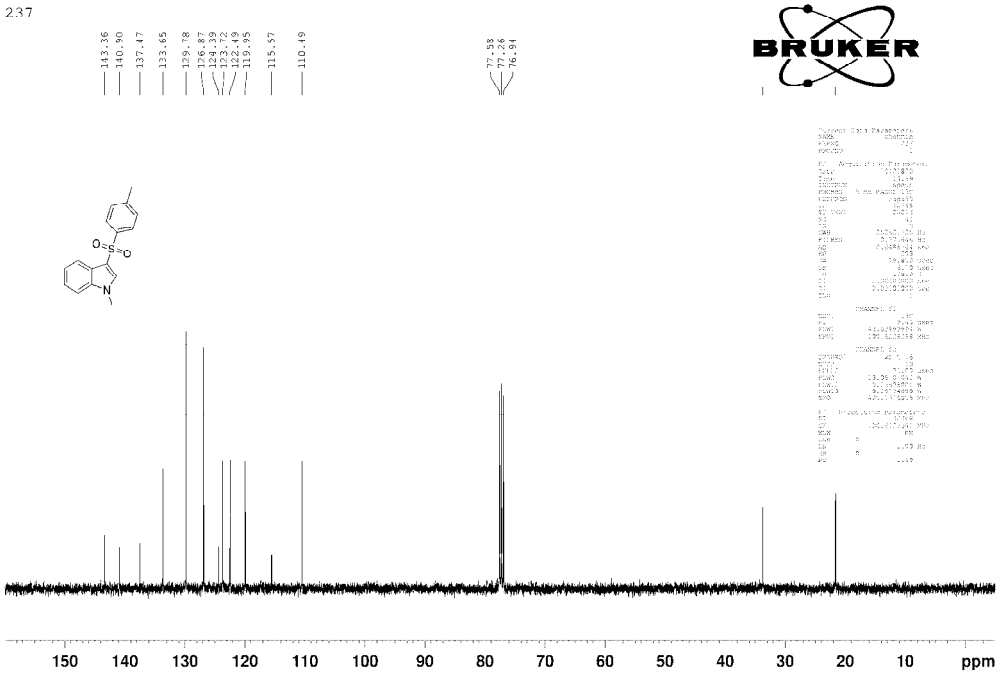
3-(*p*-Tolylthio)-1*H*-indole (4g)



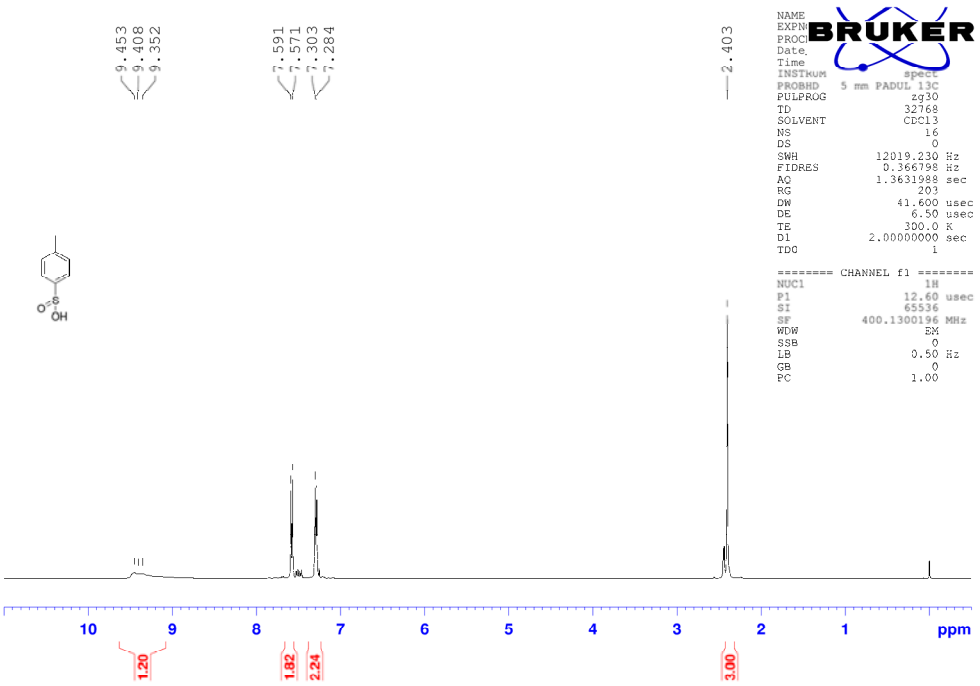


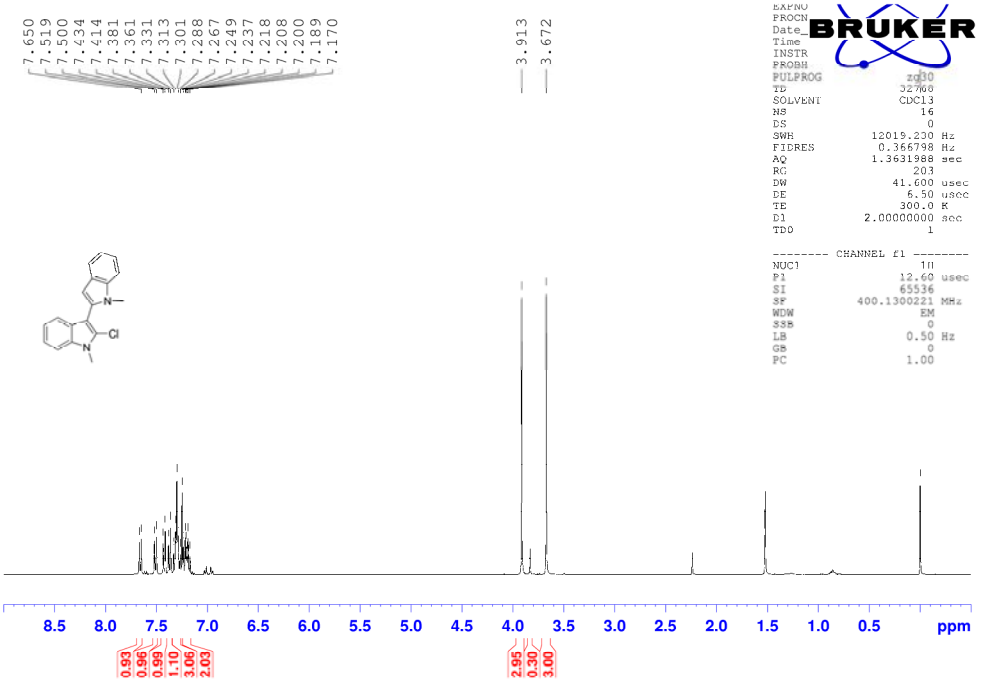
1-Methyl-3-tosyl-1*H*-indole

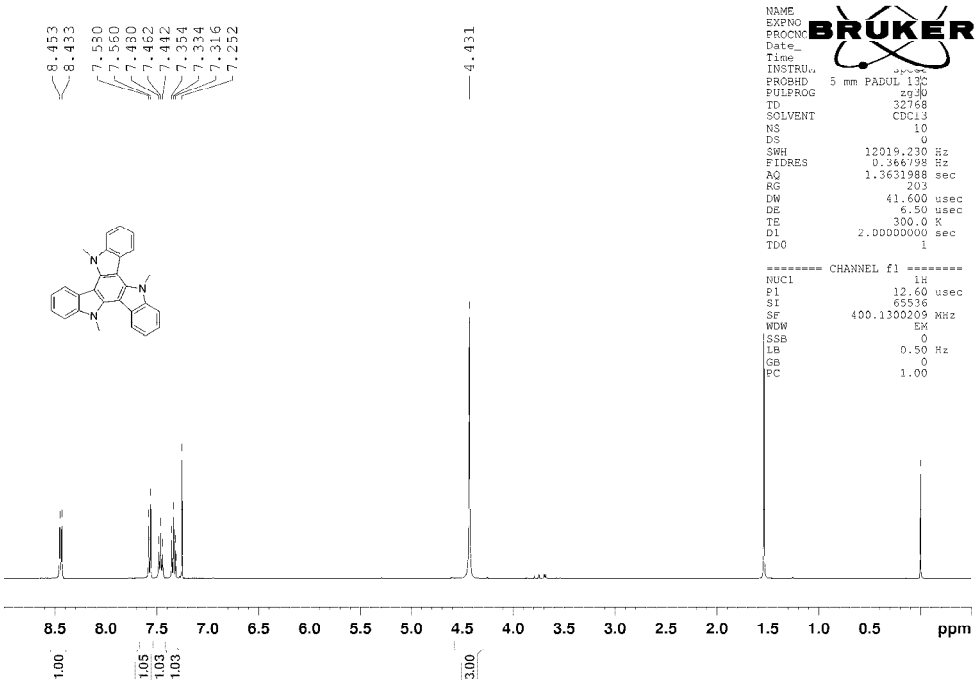


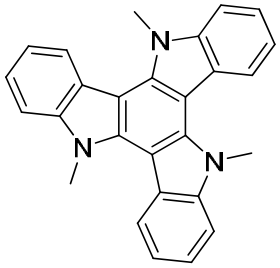


4-Methylbenzene-1-sulfinic chloride






8.453
8.433
7.580
7.560
7.480
7.462
7.442
7.354
7.334
7.316
7.252
4.431
BRUKER
NAME
EXPNO
PROCNO
Date_
Time
INSTRU
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10
DS 0
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 41.600 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.60 usec
SI 65536
SF 400.1300209 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.00
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 ppm
1.00
1.05
1.03
1.03
3.00



MS spectrum of