Supporting Information

Synthesis of di(hetero)aryl sulfides by directly using arylsulfonyl chlorides as sulfur source

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I. General remarks

NMR spectra were obtained on a Bruker AMX-400 or a Bruker AMX-600. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to tetramethylsilane or $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz or 150 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). Low-resolution mass spectra (MS) were obtained by ESI or AP-MS. High resolution mass spectra (HR-MS) were obtained with a Waters-Q-TOF-Premier (ESI). X-Ray single-crystal diffraction data were collected on a Bruker SMART 1000 CCD areadetector diffractometer. Melting points were determined with XRC-1 and are uncorrected. ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) analysis was conducted on VG PQ-ExCell. AAS (Atomic Absorption Spectrometry) analysis was conducted on SpectrAA-200FS using germanium and indium as internal standard elements.

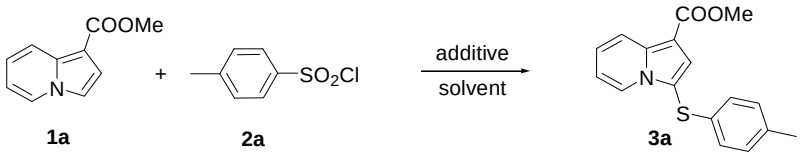
Unless otherwise noted, all reagents were obtained from commercial supplier and used without further purification. Indolizine derivatives,[1] indole derivatives,[2] diphenyl disulfide,[3] and benzenesulfenyl chloride[4] were prepared according to the literature procedure. Solvents were dried by refluxing for at least 24 h over CaH_2 (DMF or DMSO) or sodium (1, 4-dioxane or toluene), and distilled freshly prior to use. Toluene was washed with conc. H_2SO_4 and water before drying. All synthesis and manipulations were carried out under N_2 atmosphere.

II. Optimization of the cross-coupling of methyl indolizine-1-carboxylate with *p*-tolylsulfonyl chloride

A sealed tube with a magnetic stirring bar was charged with methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), *p*-tolylsulfonyl chloride **2a** (0.75 mmol), additive (0.75 mmol) and solvent (1.5 mL). The system was evacuated twice and backfilled with N_2. The mixture was stirred for 10 min at room temperature, and then heated at indicated temperature for 24 h. After being cooled to ambient

temperature, the reaction mixture was diluted with 15-20 mL of CH_2Cl_2, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.

Table S1 Optimization of the coupling of indolizine **1a** with *p*-tolylsulfonyl chloride **2a**[a]



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

Entry	Additive (equiv)	Temp. (°C)	Solvent	Yield (%)[b]
1	NMM (3.0)	120	toluene	50
2	*i*-Pr_2NEt (3.0)	120	toluene	64
3	Ph_3N (3.0)	120	toluene	29
4	*n*-Pr_3N (3.0)	120	toluene	61
5	DBU (3.0)	120	toluene	58
6	NMI (3.0)	120	toluene	65
7	Me_3SiCl (3.0)	120	toluene	58
8	$HP(OPh)_2$ (3.0)	120	toluene	n.r
9	$P(OEt)_3$ (3.0)	120	toluene	24
10	PPh_3 (3.0)	120	toluene	60
11	PPh_3 (3.0)	120	DMF	48
12	PPh_3 (3.0)	120	DMSO	n.r
13	PPh_3 (3.0)	120	1,4-dioxane	26
14	PPh_3 (3.0)	100	toluene	53
15	PPh_3 (3.0)	130	toluene	88
16	PPh_3 (3.0)	140	toluene	88
17	PPh_3 (3.0)	150	toluene	76
18	PPh_3 (1.0)	130	toluene	46
19[c]	PPh_3 (3.0)	130	toluene	54
20[d]	PPh_3 (3.0)	130	toluene	54

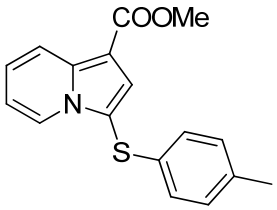
[a] Reactions were carried out using **1a** (0.25 mmol), **2a** (0.75 mmol), and additive (0.75 mmol) in 1.5 mL of solvent at indicated temperature for 24 h. [b] Isolated yield based

on **1a**. [c] 12 h. [d] *p*-tolylsulfonyl chloride **2a** (0.5 mmol). NMM = *N*-methylmorpholine, *i*-Pr_2NEt = ethyldiisopropylamine, Ph_3N = triphenylamine, *n*-Pr_3N = tri-*n*-propyl amine, DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene, NMI = *N*-methylimidazole, Me_3SiCl = chlorotrimethylsilane, $HP(OPh)_2$ = diphenyl phosphonite, $P(OEt)_3$ = triethylphosphite, DMF = *N*, *N*-dimethylformamide, DMSO = dimethylsulfoxide, n.r = no reaction.

III. General procedure for the sulfenylation of (hetero)arenes with arylsulfonyl chlorides

A sealed tube with a magnetic stirring bar was charged with (hetero)arene (0.25 mmol), arylsulfonyl chloride (0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL). The system was evacuated twice and backfilled with N_2. The mixture was stirred for 10 min at room temperature, and then heated at indicated temperature for 24 h. After being cooled to ambient temperature, the reaction mixture was diluted with 15-20 mL of CH_2Cl_2, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the desired product.

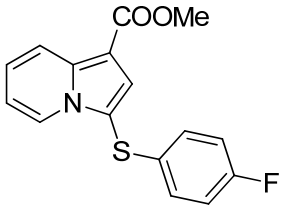
IV. Experimental data for the described substances



Methyl 3-(*p*-tolylthio)indolizine-1-carboxylate (3a)

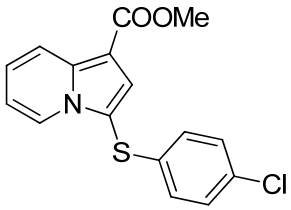
Methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (142.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column (CH_2Cl_2/petroleum ether = 1.5/1, v/v) afforded **3a** as a white solid (88% yield). M.p.: 97-100 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.92 (s, 3H), 6.77 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.66 (s, 1H), 8.26 (s, 1H), 8.27 (d, J = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 21.0, 51.2, 104.4, 111.4, 113.3, 119.9, 124.1, 124.7, 126.4, 126.6, 130.1, 132.0, 136.2, 138.5, 164.9 ppm. HRMS (ESI^+): calcd for $C_{17}H_{16}NO_2S$ $[M+H]^+$ 298.0902, found 298.0899.



Methyl 3-(4-fluorophenylthio)indolizine-1-carboxylate (3b)

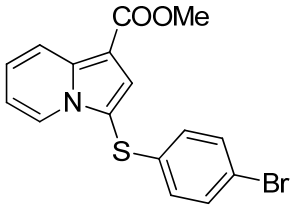
Methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), 4-fluorobenzenesulfonyl chloride (146.0 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1.5/1, v/v) afforded **3b** as a white solid (86% yield). M.p.: 138-140 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 6.80 (t, J = 6.8 Hz, 1H), 6.88 (t, J = 8.4 Hz, 2H), 6.96-6.99 (m, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.67 (s, 1H), 8.25-8.30 (m, J = 8.8 Hz, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 51.2, 104.6, 111.0, 113.5, 116.4, 116.6, 120.0, 124.3, 124.5, 126.6, 128.27, 138.32, 130.58, 130.60, 138.5, 160.8, 162.5, 164.8 ppm. HRMS (ESI^+): calcd for $C_{16}H_{13}FNO_2S$ $[M+H]^+$ 302.0651, found 302.0654.



Methyl 3-(4-chlorophenyl)thioindolizine-1-carboxylate (3c)

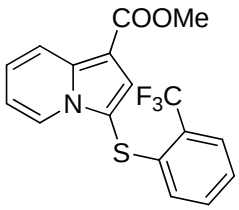
Methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), 4-chlorobenzenesulfonyl chloride (158.3 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1.5/1, v/v) afforded **3c** as a white solid (81% yield). M.p.: 84-86 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 6.80

(t, J = 6.8 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.68 (s, 1H), 8.21 (d, J = 6.8 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.1, 104.6, 109.9, 113.5, 119.9, 124.2, 124.4, 126.7, 127.2, 129.4, 132.0, 134.2, 138.5, 164.7 ppm. MS (ESI$^+$) m/z: 318 $[M+H]^+$.



Methyl 3-(4-bromophenylthio)indolizine-1-carboxylate (3d)

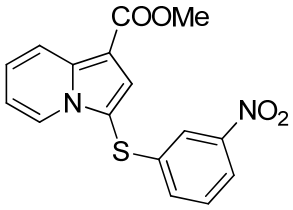
Methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), 4-bromobenzenesulfonyl chloride (191.6 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1.5/1, v/v) afforded **3d** as a pale yellow solid (76% yield). M.p.: 117-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 6.80-6.82 (m, 3H), 7.19 (t, J = 8.4 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.67 (s, 1H), 8.20 (d, J = 7.6 Hz, 1H) 8.28 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.2, 104.7, 109.8, 113.6, 119.9, 120.0, 124.4, 124.5, 126.9, 127.6, 132.4, 135.1, 138.7, 164.7 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{13}BrNO_2S$ $[M+H]^+$ 361.9850, found 361.9845.



Methyl 3-(2-(trifluoromethyl)phenylthio)indolizine-1-carboxylate (3e)

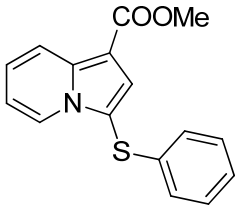
Methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), 2-trifluoromethylbenzenesulfonyl chloride (115.7 μL, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (petroleum ether/diethyl ether = 4/1, v/v) afforded **3e** as a pale yellow solid (85% yield). M.p.:

109-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3H), 6.59 (t, J = 4.0 Hz, 1H), 6.81 (t, J = 6.8 Hz, 1H), 7.19-7.23 (m, 3H), 7.65 (t, J = 4.0 Hz, 1H), 7.74 (s, 1H), 8.20 (d, J = 7.2 Hz, 1H), 8.30 (d, J = 9.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.2, 105.0, 113.8, 120.0, 124.5, 124.6, 125.9, 127.05, 127.09, 127.17, 127.2, 127.3, 127.8, 132.4, 135.7, 138.9, 164.7 ppm. MS (ESI) m/z: 374 $[M+Na]^+$.



Methyl 3-(3-nitrophenylthio)indolizine-1-carboxylate (3f)

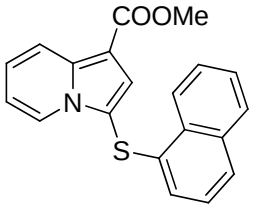
Methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), 3-nitrobenzenesulfonyl chloride (166.2 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **3f** as a yellow solid (43% yield). M.p.: 142-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 6.83 (t, J = 6.8 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.86 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 6.8 Hz, 1H), 8.31 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 51.3, 105.2, 108.2, 113.9, 120.2, 120.6, 121.0, 124.2, 124.7, 127.5, 130.1, 131.3, 138.9, 139.2, 148.9, 164.6 ppm. HRMS (ESI^+): calcd for $C_{16}H_{13}N_2O_4S$ $[M+H]^+$ 329.0596, found 329.0594.



Methyl 3-(phenylthio)indolizine-1-carboxylate (3g)

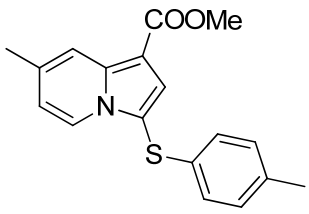
Methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), benzenesulfonyl chloride (96 μL, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL)

at 140 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **3g** as yellow oil (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 6.78 (t, J = 6.8 Hz, 1H), 6.95 (d, J = 7.6 Hz, 2H), 7.10 (t, J = 7.2 Hz, 1H), 7.18-7.19 (m, 3H), 7.69 (s, 1H), 8.26-8.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.2, 104.6, 110.7, 113.4, 119.9, 124.1, 124.7, 126.2, 126.7, 129.4, 135.8, 138.6, 164.8 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{14}NO_2S$ $[M+H]^+$ 284.0745, found 284.0748.



Methyl 3-(naphthalen-1-ylthio)indolizine-1-carboxylate (3h)

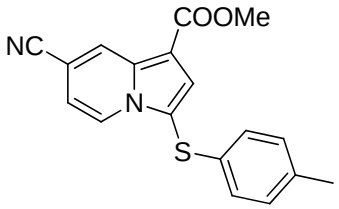
Methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), naphthalenesulfonyl chloride (170 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (petroleum ether/Et_2O = 10/1, v/v) afforded **3h** as an off-white solid (73% yield). M.p.: 72-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 3H), 6.61 (d, J = 7.2 Hz, 1H), 6.73 (t, J = 6.4 Hz, 1H), 7.15-7.20 (m, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.62-7.63 (m, 2H), 7.78 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 6.8 Hz, 1H), 8.31 (d, J = 9.2 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 51.2, 104.7, 109.6, 113.4, 119.9, 123.2, 123.7, 124.2, 124.8, 125.9, 126.55, 126.58, 126.59, 127.1, 128.8, 130.9, 132.5, 134.1, 138.8, 164.9 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{16}NO_2S$ $[M+H]^+$ 334.0902, found 334.0892.



Methyl 7-methyl-3-(*p*-tolylthio)indolizine-1-carboxylate (4a)

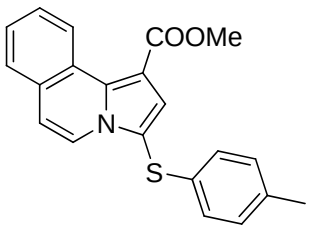
Methyl 7-methylindolizine-1-carboxylate (47.2 mg, 0.25 mmol), *p*-tosylsulfonyl

chloride (142.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 140 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 3/1, v/v) afforded **4a** as a yellow solid (63% yield). M.p.: 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.40 (s, 3H), 3.91 (s, 3H), 6.61 (dd, J = 7.2 Hz, J = 2.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 7.60 (s, 1H), 8.06 (s, 1H), 8.13 (d, J = 6.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 21.3, 51.0, 102.9, 110.3, 115.8, 118.3, 124.0, 126.3, 130.0, 132.2, 135.3, 135.9, 138.9, 164.9 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{18}NO_2S$ $[M+H]^+$ 312.1058, found 312.1066.



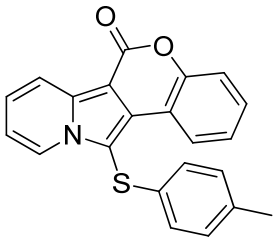
Methly 7-cyano-3-(*p*-tolylthio)indolizine-1-carboxylate (4b)

Methyl 7-cyanolindolizine-1-carboxylate (50.0 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (142.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 4/1, v/v) afforded **4b** as a yellow solid (62% yield). M.p.: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 3.95 (s, 3H), 6.86 (d, J = 6.8 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 7.76 (s, 1H), 8.29 (d, J = 7.2 Hz, 1H), 8.66 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 51.7, 106.3, 108.7, 112.9, 116.0, 118.0, 125.1, 126.4, 127.4, 127.5, 130.2, 130.4, 135.3, 137.1, 163.9 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{15}N_2O_2S$ $[M+H]^+$ 323.0854, found 323.0847.



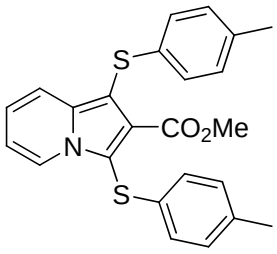
Methyl 3-(*p*-tolylthio)pyrrolo[2, 1-*a*]isoquinoline-1-carboxylate (4c)

Methyl 3-(*p*-tolylthio)pyrrolo[2, 1-*a*]isoquinoline-1-carboxylate (56.3 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (142.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 140 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3/2, v/v) afforded **4c** as an off-white solid (77% yield). M.p.: 68-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.96 (s, 3H), 6.91 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 3H), 7.54 (t, J = 6.8 Hz, 1H), 7.62 (t, J = 7.6 Hz, 2H), 7.72 (s, 1H), 8.18 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 51.7, 109.1, 113.3, 114.3, 122.2, 125.6, 126.5, 126.9, 127.0, 127.5, 127.8, 128.4, 129.5, 130.1, 132.5, 135.3, 136.2, 165.4 ppm. MS (ESI$^+$) m/z: 348 $[M+H]^+$.



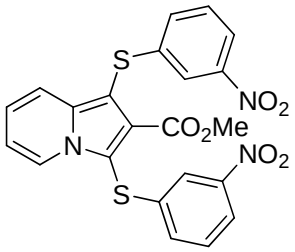
12-(*p*-Tolylthio)-6*H*-chromeno[3, 4-*a*]indolizin-6-one (4d)

6*H*-Chromeno[3, 4-*a*]indolizin-6-one (58.8 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (142.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 140 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (petroleum ether/acetone = 6/1, v/v) afforded **4d** as an off-white solid (73% yield). M.p.: 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 6.93 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 6.8 Hz, 1H), 7.25 (t, J = 6.8 Hz, 1H), 7.40-7.48 (m, 3H), 8.45 (d, J = 8.8 Hz, 1H), 8.60 (d, J = 6.8 Hz, 1H), 8.89 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 98.2, 104.6, 115.5, 116.2, 117.7, 119.6, 124.0, 124.5, 124.6, 125.8, 126.2, 129.8, 130.3, 130.8, 131.2, 136.5, 137.0, 152.9, 158.4 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{16}NO_2S$ $[M+H]^+$ 358.0902, found 358.0901.



Methyl 1, 3-bis(*p*-tolylthio)indolizine-2-carboxylate (4e)

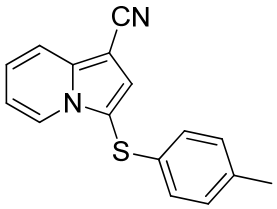
Methyl indolizine-2-carboxylate (43.8 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (142.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **4e** as a yellow solid (44% yield). M.p.: 123-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 2.27 (s, 3H), 3.84 (s, 3H), 6.74 (t, J = 6.8 Hz, 1H), 6.96-7.00 (m, 9H), 7.70 (d, J = 9.2 Hz, 1H), 8.33 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.03, 21.07, 52.2, 100.8, 113.1, 114.0, 118.9, 122.4, 124.5, 126.8, 127.2, 129.6, 130.2, 130.3, 131.7, 135.0, 135.7, 136.3, 138.6, 164.7 ppm. MS (ESI$^+$) m/z: 420 $[M+H]^+$.



Methyl 1, 3-bis((3-nitrophenyl)thio)indolizine-2-carboxylate (4f)

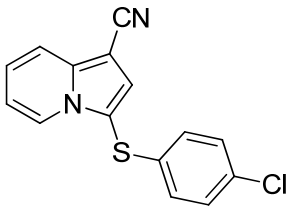
Methyl indolizine-2-carboxylate (43.8 mg, 0.25 mmol), 3-nitrobenzenesulfonyl chloride (166.2 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **4f** as a yellow solid (42% yield). M.p.: 148-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 6.90 (t, J = 6.8 Hz, 1H), 7.14 (t, J = 8.0 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.39-7.40 (m, 3H), 7.75 (d. J = 8.8 Hz, 1H), 7.84 (s, 1H), 7.92-7.94 (m, 2H), 7.99 (d, J =7.6 Hz, 1H), 8.42 (d, J = 6.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.3, 98.6,

111.3, 115.0, 118.6, 120.0, 120.3, 121.0, 121.2, 124.0, 124.4, 129.5, 130.3, 131.0, 131.4, 131.8, 138.3, 139.4, 142.3, 148.6, 148.8, 163.7 ppm. HRMS (ESI^+): calcd for $C_{22}H_{16}N_3O_6S_2$ $[M+H]^+$ 482.0481, found 482.0477.



1-Cyano-3-(*p*-tolylthio)indolizine (4g)

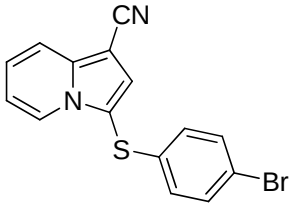
1-Cyano-indolizine (33.5 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (124.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 140 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **4g** as an off-white solid (83% yield). M.p.: 82-85 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 6.82 (t, J = 6.8 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.44 (s, 1H), 7.70 (d, J = 9.2 Hz, 1H), 8.28 (d, J = 6.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 82.8, 112.5, 113.8, 116.2, 118.0, 124.2, 125.1, 126.5, 126.9, 130.3, 131.1, 136.7, 140.3 ppm. HRMS (ESI^+): calcd for $C_{16}H_{13}N_2S$ $[M+H]^+$ 265.0799, found 265.0801.



1-Cyano-3-(*p*-chlorophenylthio)indolizine (4h)

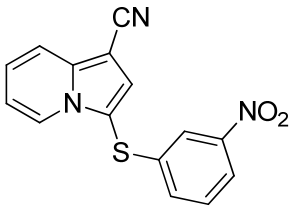
1-Cyano-indolizine (33.5 mg, 0.25 mmol), 4-chlorobenzenesulfonyl chloride (158.3 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **4h** as an off-white solid (87% yield). M.p.: 140 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.86-6.90 (m, 3H), 7.17

(d, J = 5.6 Hz, 2H), 7.22 (t, J = 5.2 Hz, 1H), 7.46 (s, 1H), 7.73 (d, J = 5.6 Hz, 1H), 8.23 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 83.2, 111.1, 114.1, 115.9, 118.2, 124.5, 124.9, 127.0, 127.6, 129.6, 132.6, 133.4, 140.4 ppm. HRMS (ESI^+): Calcd for $C_{15}H_{10}ClN_2S$ $[M+H]^+$ 285.0253, found 285.0258.



1-Cyano-3-(*p*-bromophenylthio)indolizine (4i)

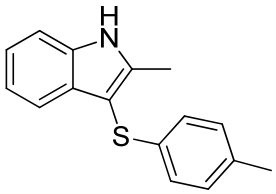
1-Cyano-indolizine (33.5 mg, 0.25 mmol), 4-bromobenzenesulfonyl chloride (191.6 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **4i** as an off-white solid (96% yield). M.p.: 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81 (d, J = 8.0 Hz, 2H), 6.86 (t, J = 6.8 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.46 (s, 1H), 7.73 (d, J = 8.8 Hz, 1H), 8.22 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.2, 111.0, 114.1, 115.9, 118.2, 120.4, 124.5, 124.9, 127.1, 127.9, 132.6, 134.1, 140.5 ppm. HRMS (ESI^+): calcd for $C_{15}H_{10}BrN_2S$ $[M+H]^+$ 328.9748, found 328.9749.



1-Cyano-3-(*m*-nitrophenylthio)indolizine (4j)

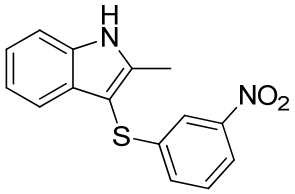
1-Cyano-indolizine (33.5 mg, 0.25 mmol), 3-nitrobenzenesulfonyl chloride (166.2 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 3/1, v/v) afforded **4j** as a yellow solid (91% yield). M.p.:

128-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (t, J = 6.8 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 8.4 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.53 (s, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.87 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.7, 109.3, 114.4, 115.6, 118.3, 120.8, 121.3, 124.6, 124.8, 127.6, 130.3, 131.4, 138.1, 140.6, 148.9 ppm. HRMS (ESI^+): calcd for $C_{15}H_{10}N_3O_2S$ $[M+H]^+$ 296.0494, found 296.0492.



2-Methyl-3-(*p*-tolylthio)-1*H*-indole (4k)

2-Methylindole (32.8 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (124.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1.5, v/v) afforded **4k** as a yellow solid (69% yield). M.p.: 78-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 2.52 (s, 3H), 6.98-7.00 (m, 4H), 7.12 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 8.19 (s, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 12.3, 21.0, 99.9, 110.7, 119.1, 120.8, 122.2, 125.9, 129.6, 130.4, 134.4, 135.5, 135.8, 141.1 ppm. MS (ESI^-) m/z: 252 $[M-H]^+$.



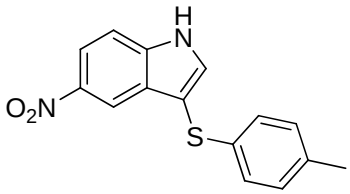
2-Methyl-3-(*m*-nitrophenylthio)-1*H*-indole (4l)

Method A: *N*-pivaloyl-2-methylindole (53.8 mg, 0.25 mmol), 3-nitrobenzenesulfonyl chloride (166.2 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **4l** as a yellow

solid (71% yield).

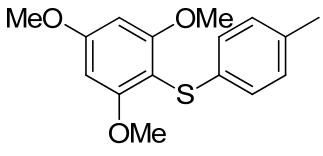
Method B: 2-Methylindole (32.8 mg, 0.25 mmol), 3-nitrobenzenesulfonyl chloride (166.2 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (CH_2Cl_2/petroleum ether = 1/1, v/v) afforded **4l** as a yellow solid (46% yield).

M.p.: 134-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (s, 3H), 7.13 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.29-7.30 (m, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.86-7.89 (m, 2H), 8.41 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.3, 97.6, 111.1, 118.7, 119.6, 120.0, 121.2, 122.8, 129.5, 129.8, 131.1, 135.7, 141.8, 142.8, 148.8 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{13}N_2O_2S$ $[M+H]^+$ 285.0698, found 285.0705.



5-Nitro-3-(*p*-tolylthio)-1*H*-indole (4m)

5-Nitroindole (40.5 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (124.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (diethyl ether/petroleum ether = 1.5/1, v/v) afforded **4m** as a yellow solid (51% yield). M.p.:189-193 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.19 (s, 3H), 6.98 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 9.2 Hz, 1H), 8.06-8.07 (m, 2H), 8.24 (s, 1H), 12.38 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.4, 103.4, 113.1, 114.1, 114.8, 117.5, 126.2, 128.1, 129.7, 134.8, 136.2, 140.0, 141.5 ppm. HRMS (ESI): calcd for $C_{15}H_{13}N_2O_2S$ $[M+H]^+$ 285.0698, found 285.0701.



***p*-Tolyl 2, 4, 6-trimethoxyphenyl thioether (4n)**[5]

Method A: 1, 3, 5-Trimethoxybenzene (42.0 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (142.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol) and toluene (1.5 mL) at 130 °C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (petroleum ether/EtOAc = 4/1, v/v) afforded **4n** as an off-white solid (51% yield).

Method B: 1, 3, 5-Trimethoxybenzene (42.0 mg, 0.25 mmol), *p*-tosylsulfonyl chloride (142.9 mg, 0.75 mmol), triphenylphosphine (196.7 mg, 0.75 mmol), $FeCl_3$ (8.1 mg, 0.05 mmol) and toluene (1.5 mL) at 130°C for 24 h under N_2 atmosphere. Purification via silica gel column chromatography (petroleum ether/EtOAc = 4/1, v/v) afforded **4n** as an off-white solid (67% yield).

M.p.: 90-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.81 (s, 6H), 3.87 (s, 3H), 6.21 (s, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H) ppm. HRMS (ESI): calcd for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1055, found 291.1049.

V. ICP-MS and AAS analysis for the contents of transition metals in the samples

Preparation of samples: Methyl indolizine-1-carboxylate (0.0938 g), *p*-tosylsulfonyl chloride (0.2003 g), and triphenylphosphine (0.2009 g) were respectively dissolved in 4 mL of concentrated nitric acid, and heated until the nitric acid was gone. Then 10 mL of pure water was added to the digested samples, followed by filtration. The filtrate (2.50 mL) was transferred to 25 mL of volumetric flask, and then diluted with pure water.

Analysis A: ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) of samples: analysis was conducted on VG PQ-ExCell. The contents of elements (Pd and Cu) were found to be less than detection limit (1.0 ppb).

Analysis B: AAS (Atomic Absorption Spectrometry) of samples: analysis was conducted on SpectrAA-200FS using germanium and indium as internal standard elements. The contents of Fe were found to be less than 30 ppb.

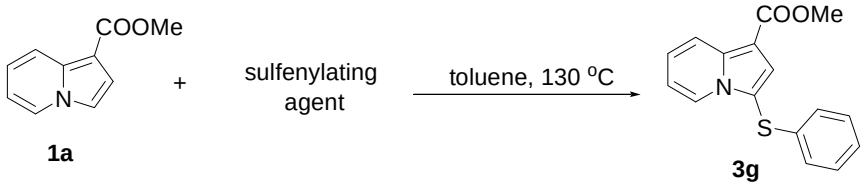
Table S2 ICP-MS and AAS Analysis on the contents of metal elements in samples

Content of metal	Methyl indolizine-1-carboxylate	*p*-Tosylsulfonyl chloride	Triphenylphosphine

Pd (ppb)	< 1.0	< 1.0	< 1.0
Cu (ppb)	< 1.0	< 1.0	< 1.0
Fe (ppb)	22	20	30

VI. Controlled experiments for the mechanistic investigation

Part A: Sulfenylation of methyl indolizine-1-carboxylate **1a** with various sulfenylating agents



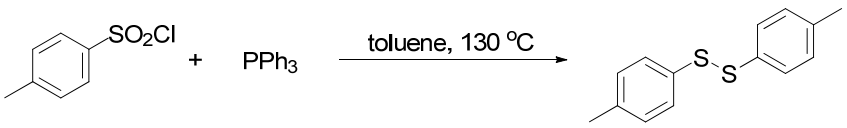
1a **3g**

A sealed tube with a magnetic stirring bar was charged with methyl indolizine-1-carboxylate **1a** (43.8 mg, 0.25 mmol), sulfenylting agent (0.75 mmol), and toluene (1.5 mL). The system was evacuated twice and backfilled with N_2. The mixture was stirred for 10 min at room temperature, and then heated at 130 °C for 24 h. Purification was via silica gel column chromatography.

Table S3 Sulfenylation of methyl indolizine-1-carboxylate **1a** with various sulfenylating agents

Entry	Sulfenylating agent	Additive	Yield (%)
1	PhSCl	-	82
2	PhS-SPh	-	n.r
3	PhSH	-	n.r

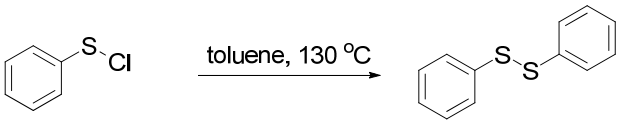
Part B: Reduction of *p*-tosylsulfonyl chloride to 1, 2-di-*p*-tolyl disulfide[6]



A sealed tube with a magnetic stirring bar was charged with *p*-tolylsulfonyl chloride (57.2 mg, 0.3 mmol), PPh_3 (78.7 mg, 0.3 mmol) and toluene (1.5 mL). The system was evacuated twice and backfilled with N_2, stirred for 10 min at room temperature, and then heated at 130 °C for 24 h. Purification via silica gel column chromatography (petroleum ether) afforded 1, 2-di-*p*-tolyl disulfide as a white solid (89% yield). ^{1}H

NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 6H), 7.09 (d, J = 7.6 Hz, 4H), 7.37 (d, J = 7.6 Hz, 4H) ppm. MS (AP) m/z: 245 $[M-H]^+$.

Part C: Homocoupling of benzenesulfenyl chloride[7]



A sealed tube with a magnetic stirring bar was charged with benzenesulfenyl chloride (28.2 μL, 0.3 mmol) and toluene (1.5 mL). The system was evacuated twice and backfilled with N_2, stirred for 10 min at room temperature, and then heated at 130 °C for 24 h. Purification via silica gel column chromatography (petroleum ether) afforded diphenyl disulfie as a white solid (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21-7.26 (m, 2H), 7.28 (t, J = 7.6 Hz, 4H), 7.49 (d, J = 7.6 Hz, 4H) ppm.

VII. References

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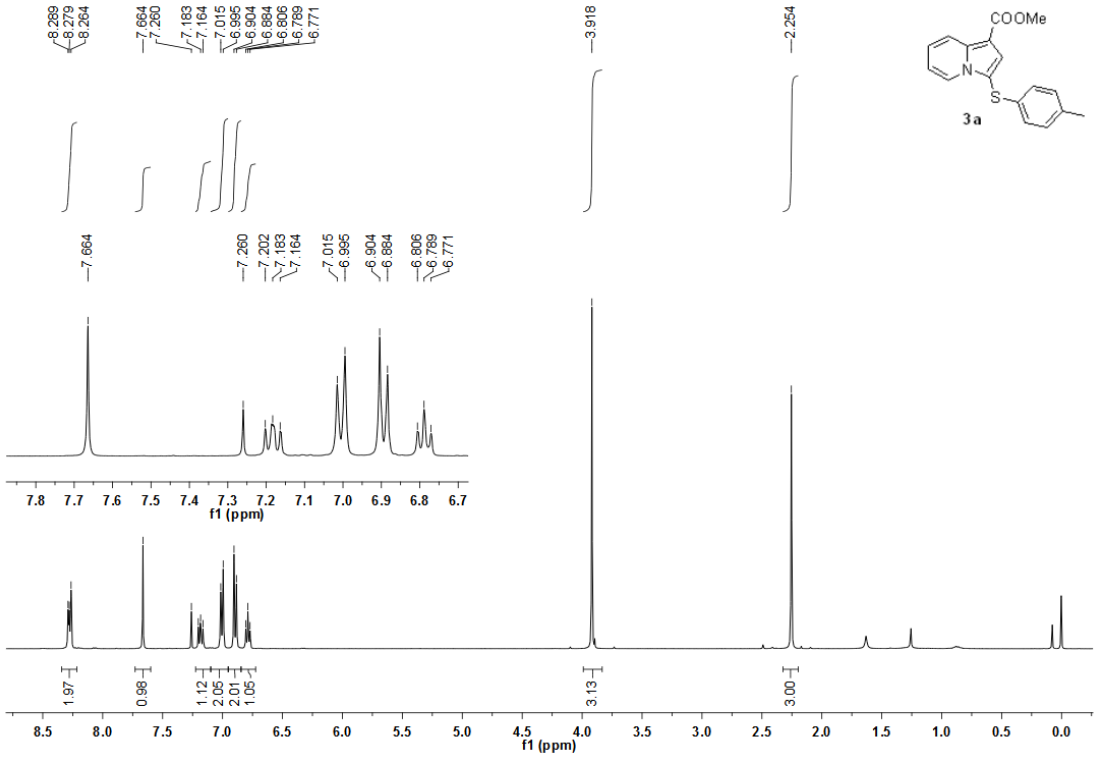
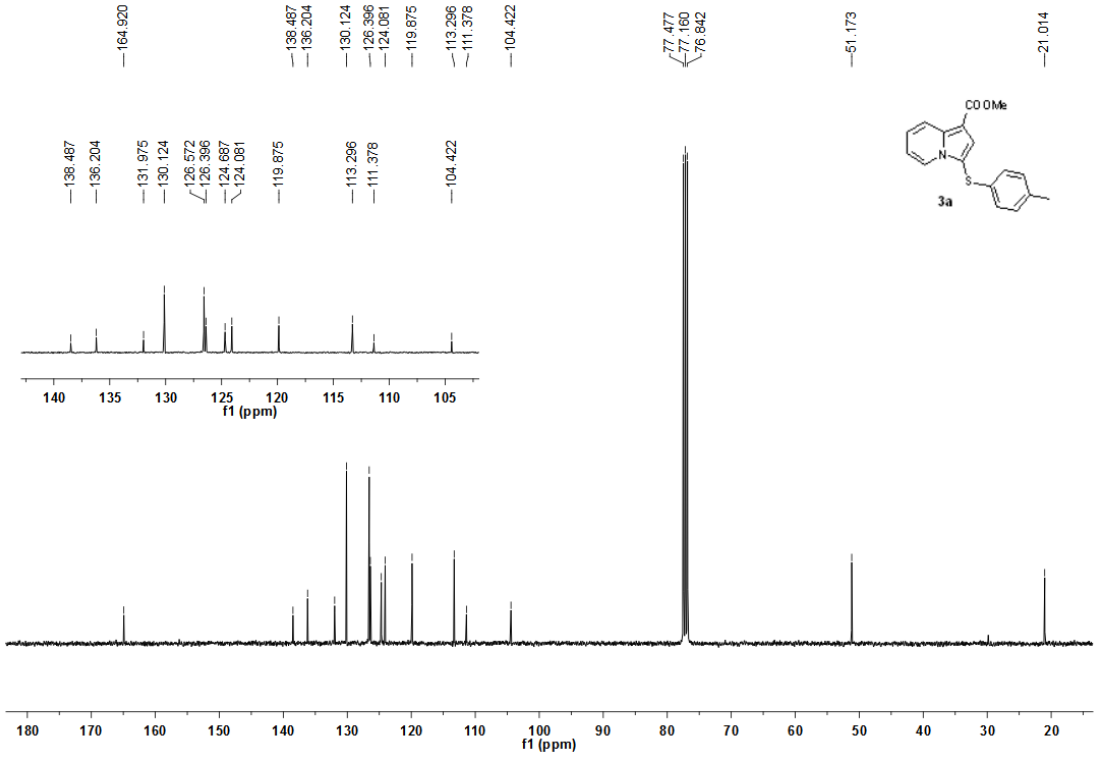
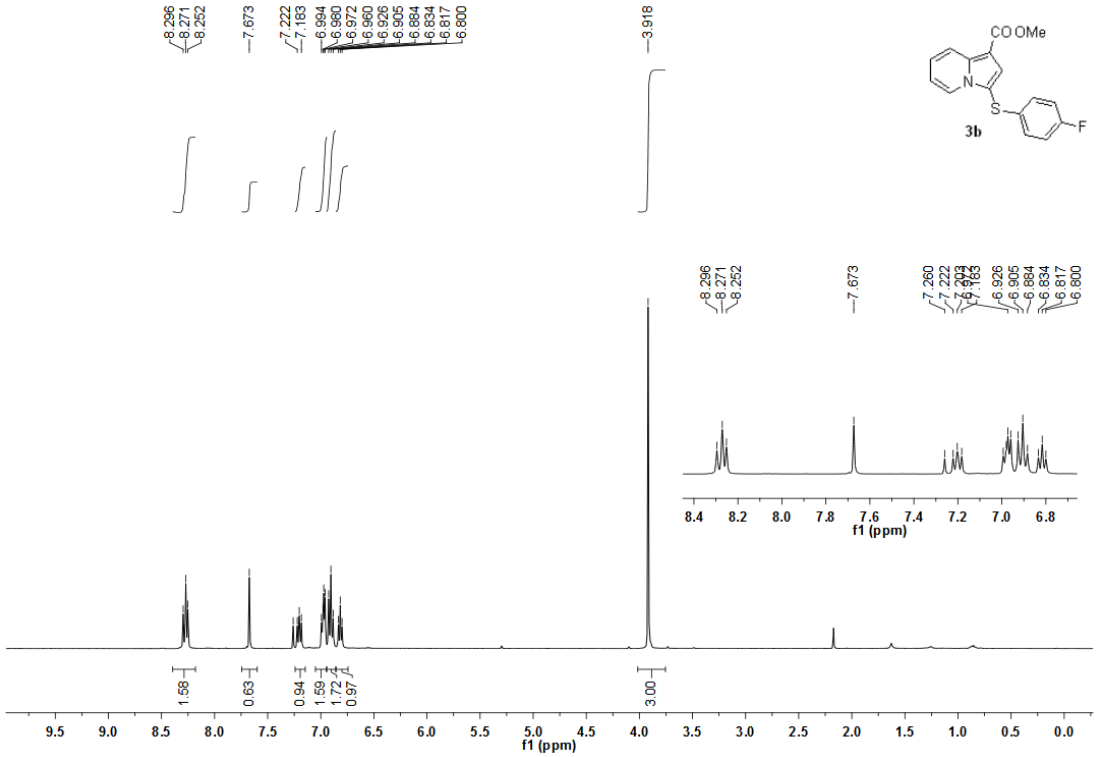
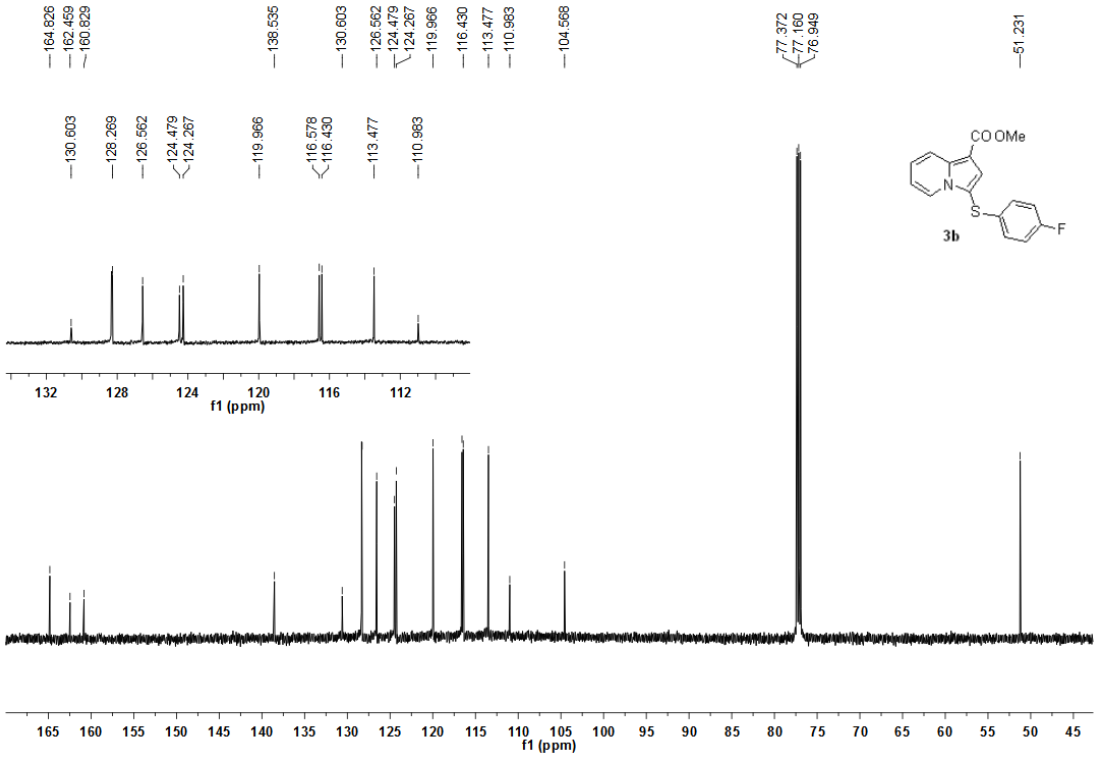
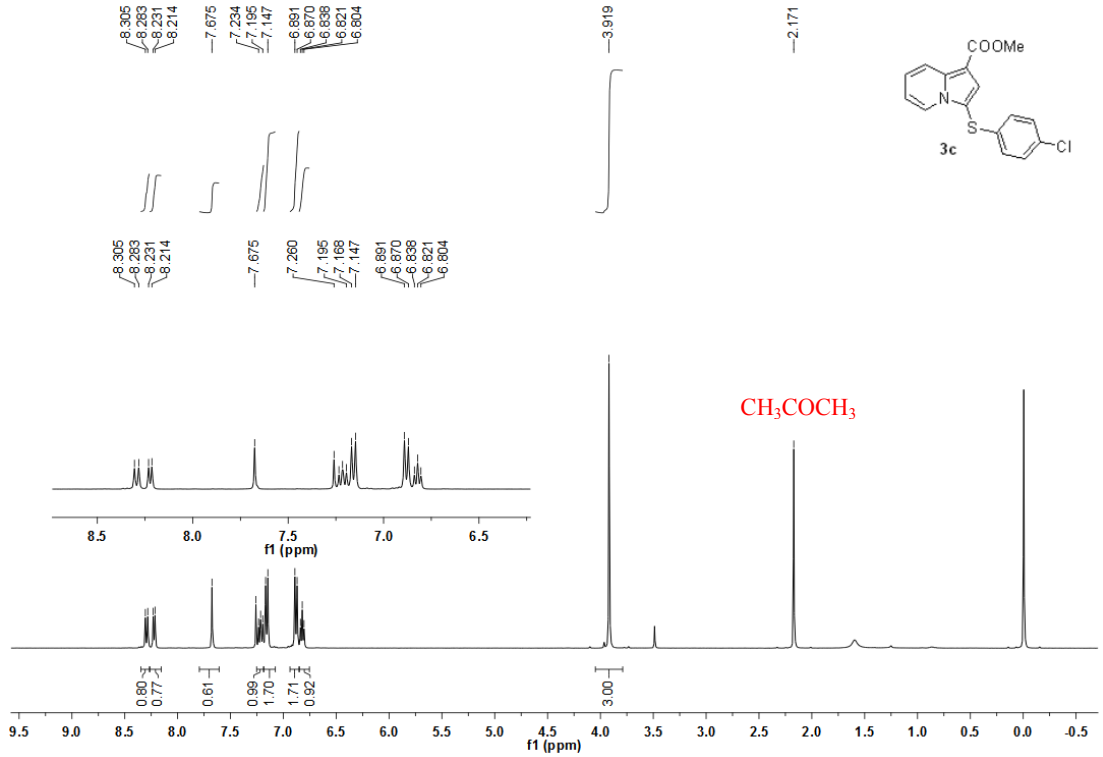
VIII. Copies of ^{1}H and ^{13}C NMR spectra

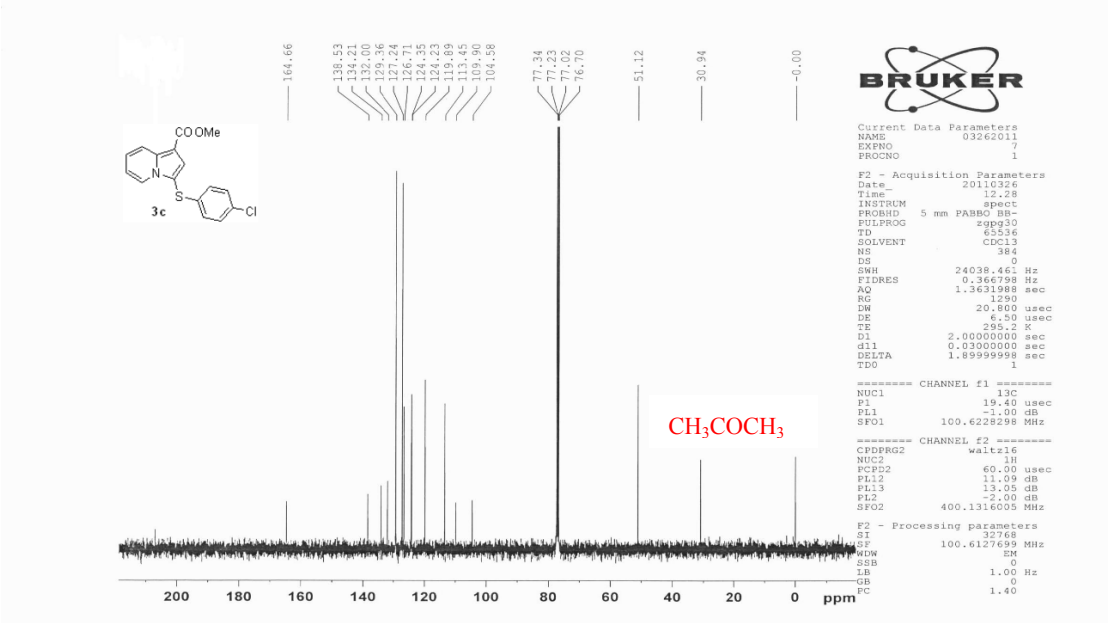


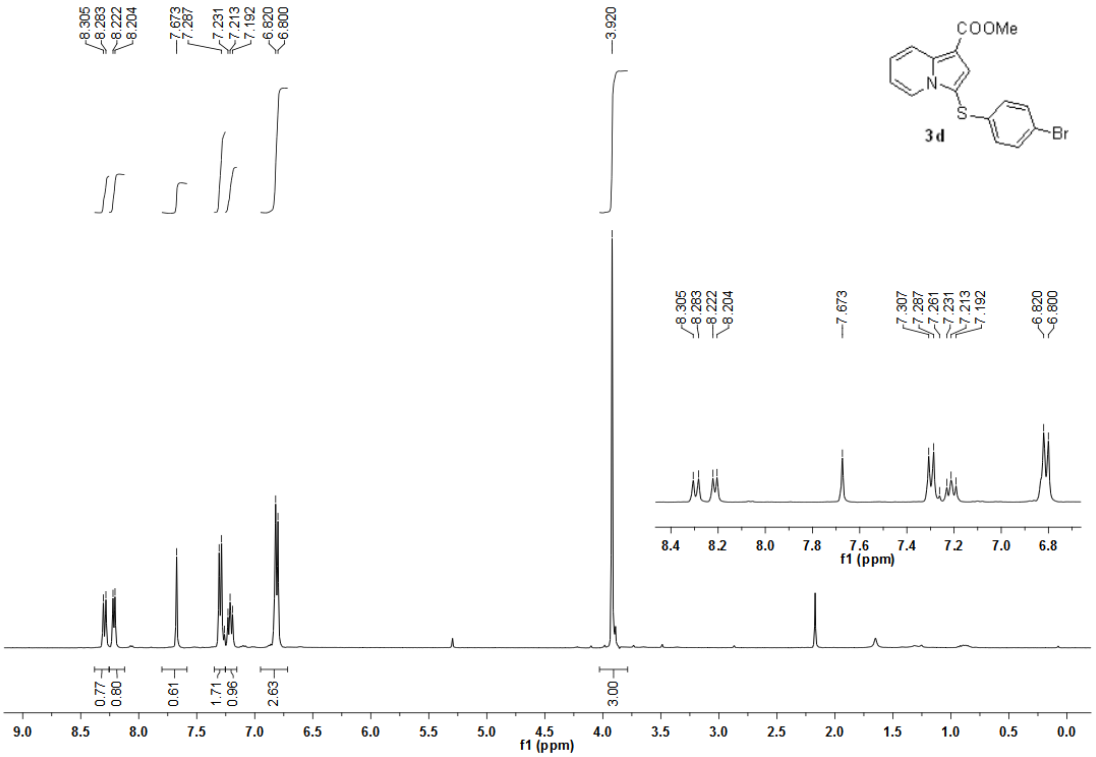


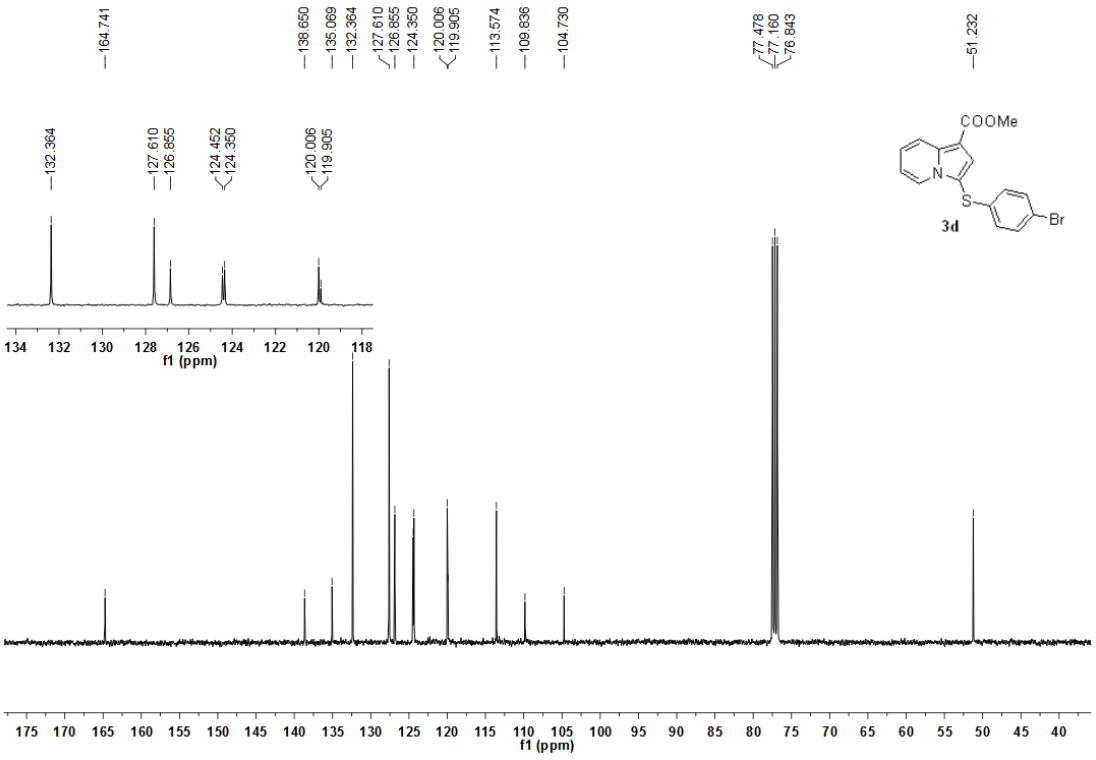

8.296
8.271
8.252
7.673
7.222
7.183
6.994
6.980
6.972
6.960
6.926
6.905
6.884
6.834
6.817
6.800
3.918
CO OMe
S
F
3b
1.58
0.63
0.94
1.59
1.72
0.97
3.00
f1 (ppm)

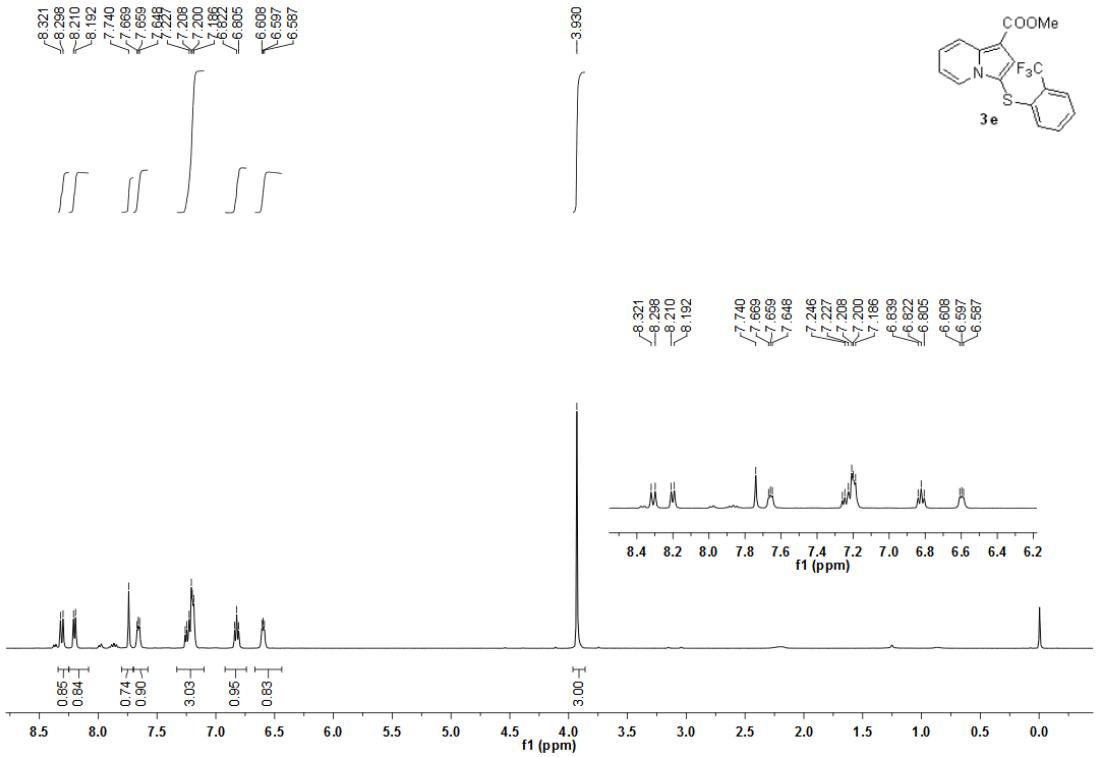

164.826
162.459
160.829
138.535
130.603
126.562
124.479
124.267
119.966
116.430
113.477
110.983
104.568
77.372
77.160
76.949
51.231
CO OMe
S
F
3b
f1 (ppm)

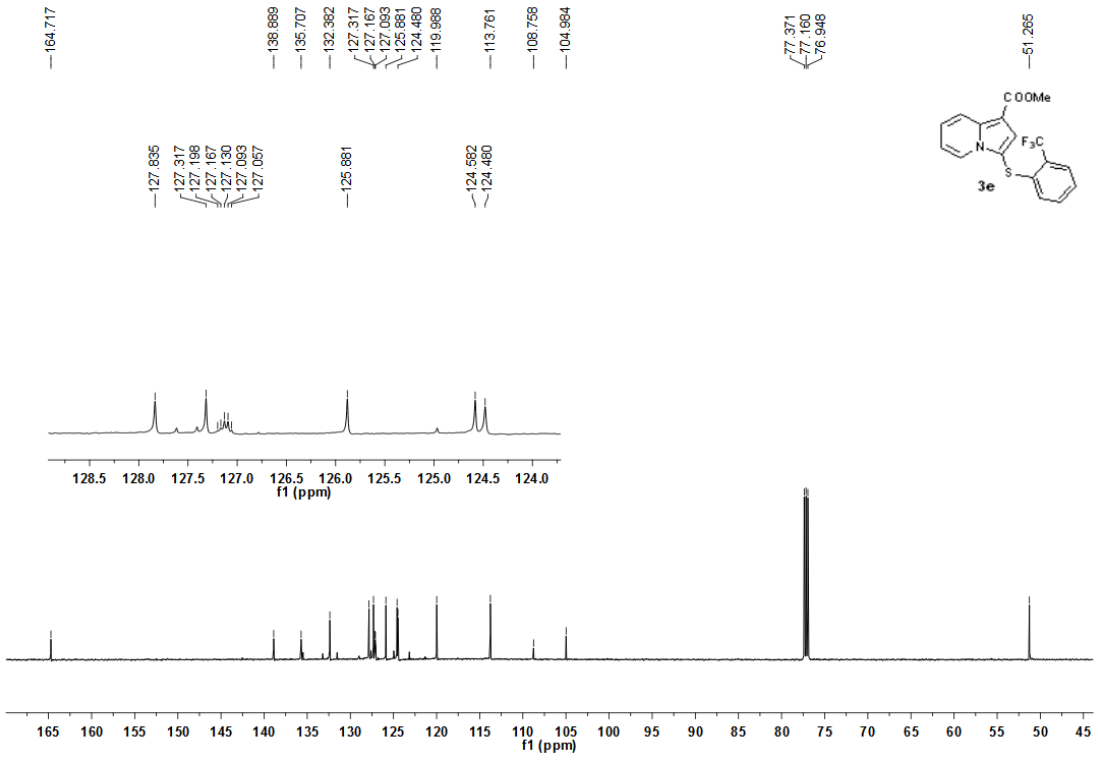

8.305
8.283
8.231
8.214
7.675
7.234
7.195
7.147
6.891
6.870
6.838
6.821
6.804
3.919
2.171
COOMe
N
S
Cl
3c
7.260
7.168
CH3COCH3
f1 (ppm)
0.80
0.77
0.61
0.99
1.70
1.71
0.92
3.00

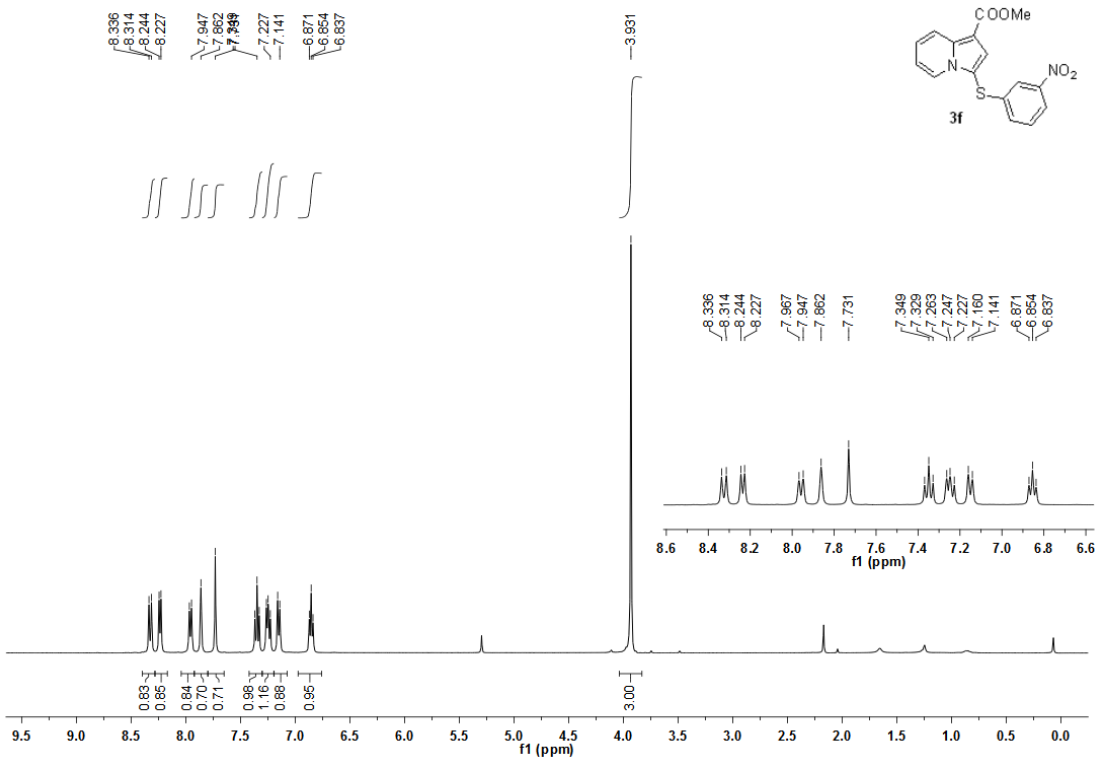

164.66
138.53
134.21
132.00
129.36
127.24
126.71
124.35
124.23
119.69
113.45
109.90
104.58
77.34
77.23
77.02
76.70
51.12
30.94
-0.00
BRUKER
COOMe
3c
CH3COCH3
ppm

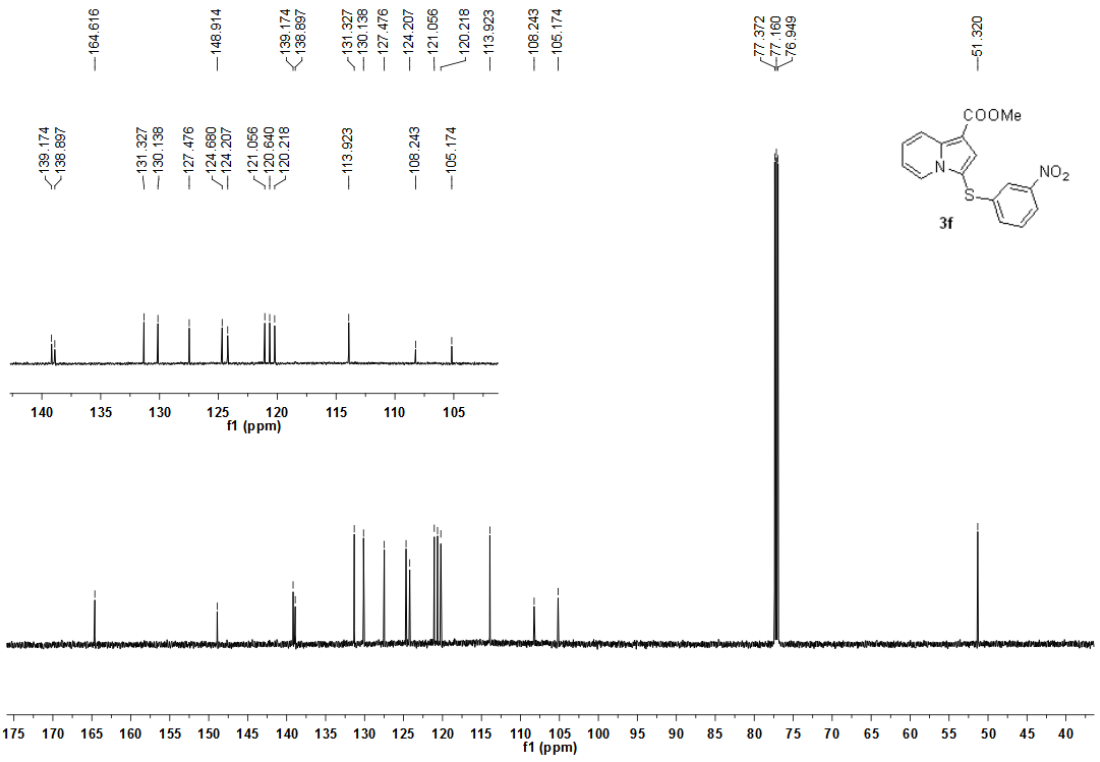

8.305
8.283
8.222
8.204
7.673
7.287
7.231
7.213
7.192
6.820
6.800
3.920
COOMe
N
S
Br
3d
0.77
0.80
0.61
1.71
0.96
2.63
3.00
f1 (ppm)

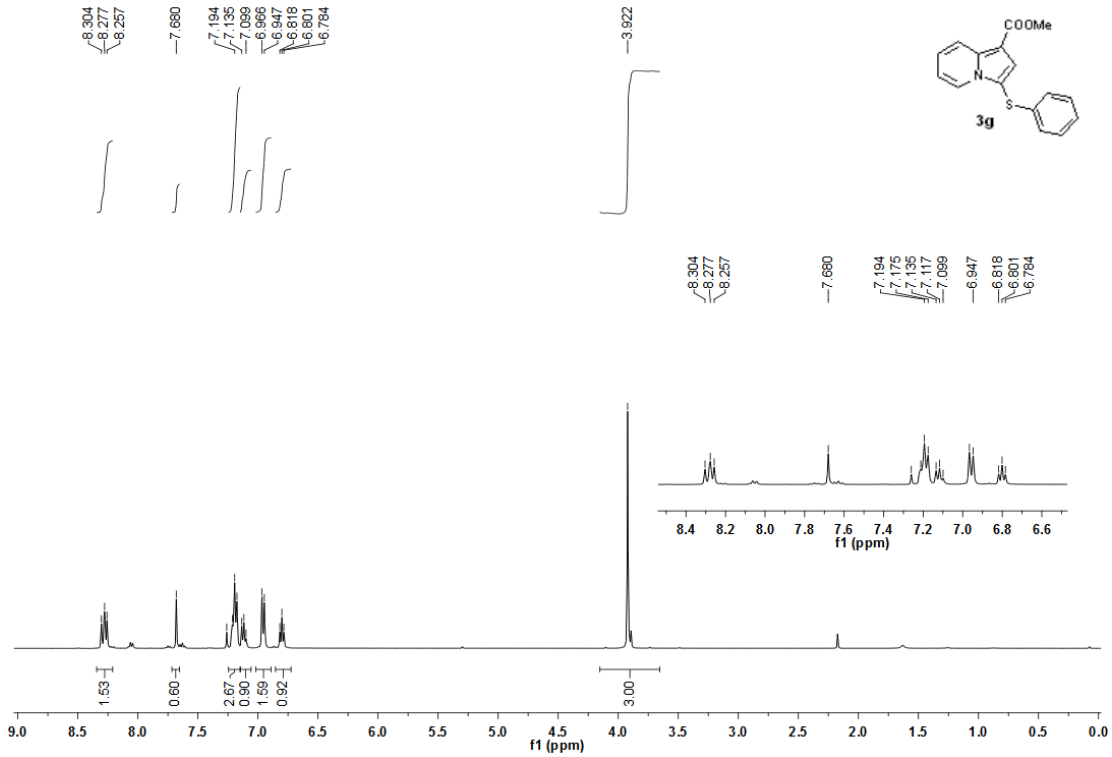

164.741
138.650
135.069
132.364
127.610
126.855
124.350
120.006
119.905
113.574
109.836
104.730
77.478
77.160
76.843
51.232
COOMe
N
S
Br
3d
f1 (ppm)

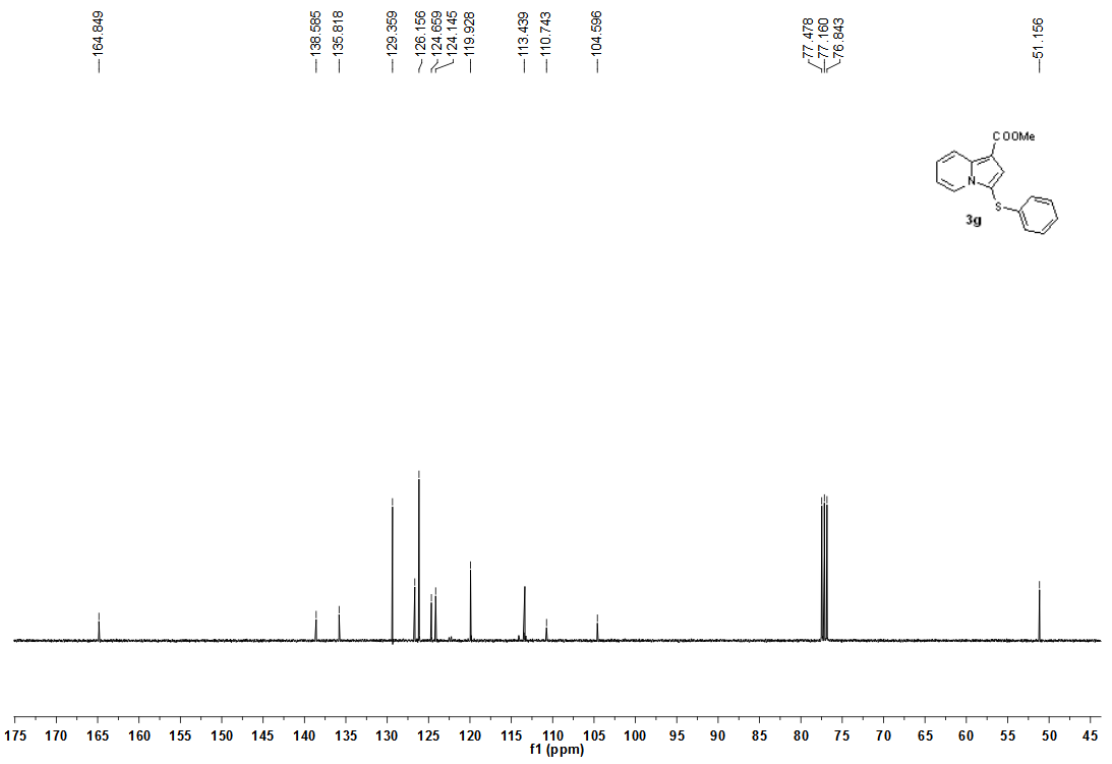

8.321
8.298
8.210
8.192
7.740
7.669
7.659
7.648
7.227
7.208
7.200
7.186
6.822
6.805
6.608
6.597
6.587
3.930
COOMe
F3C
N
S
3e
f1 (ppm)
0.85
0.84
0.74
0.90
3.03
0.95
0.83
3.00

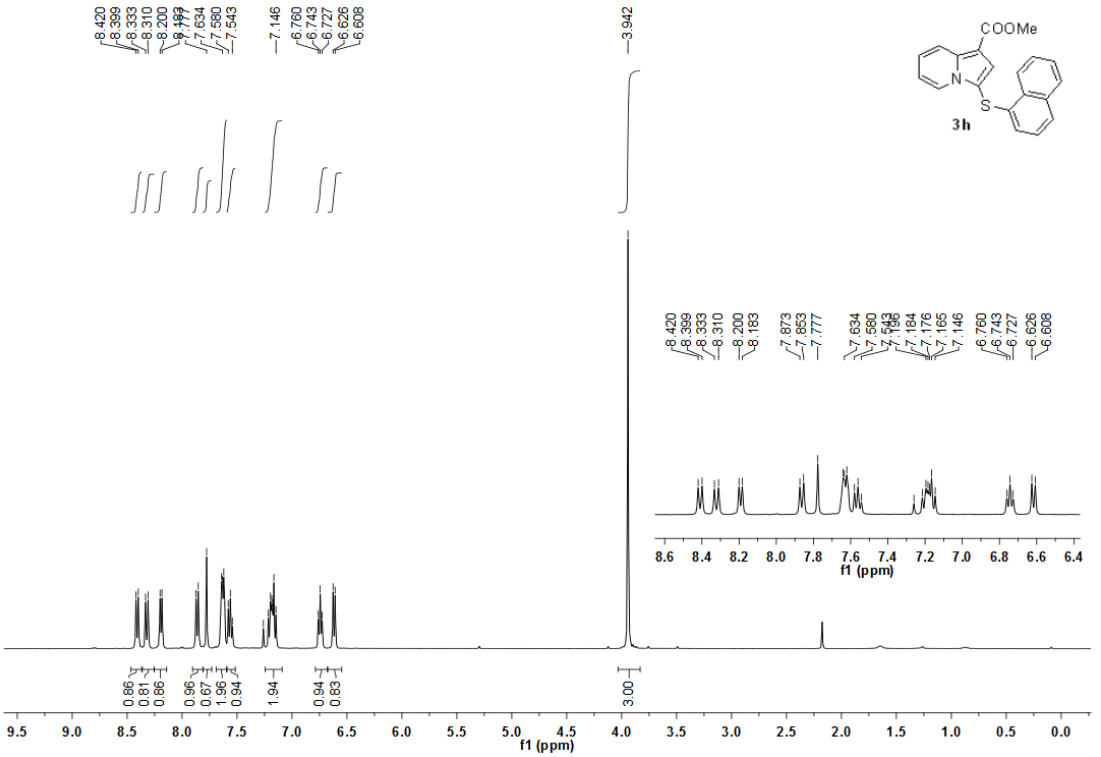

164.717
138.889
135.707
132.382
127.317
127.167
127.093
125.881
124.480
119.988
113.761
108.758
104.984
77.371
77.160
76.948
51.265
127.835
127.317
127.198
127.167
127.130
127.093
127.057
125.881
124.562
124.480
COOMe
F3C
N
S
3e
f1 (ppm)

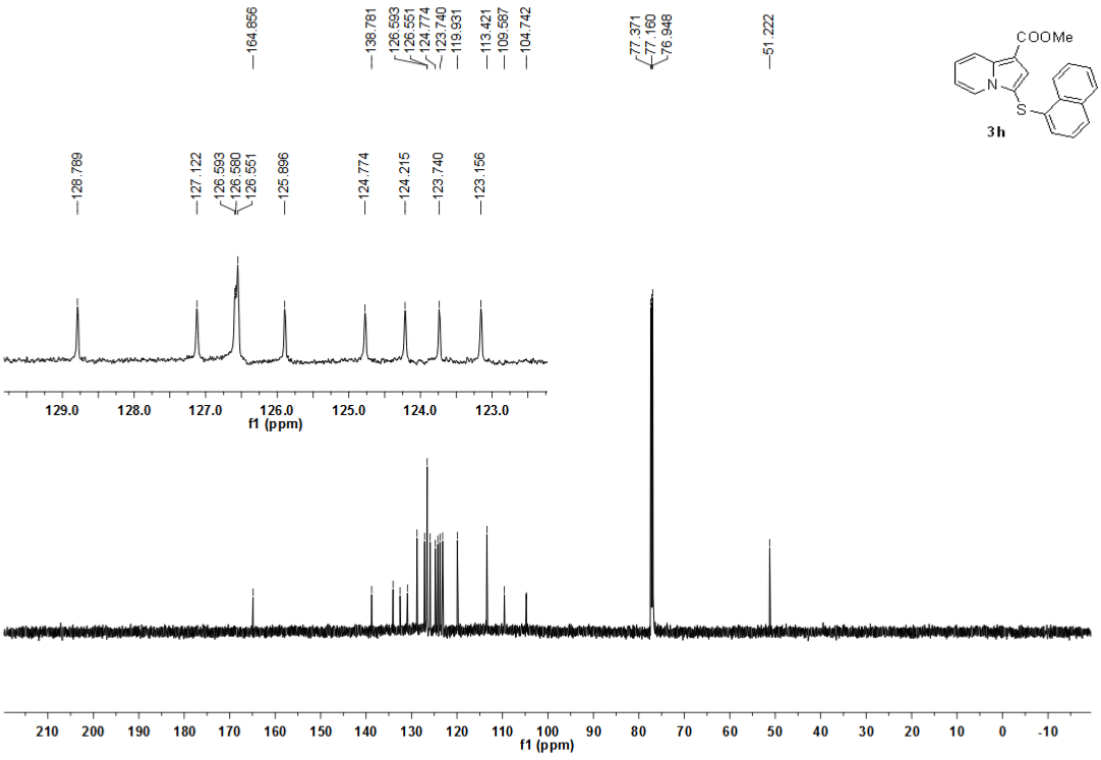

8.336
8.314
8.244
8.227
7.947
7.862
7.227
7.141
6.871
6.854
6.837
3.931
COOMe
N
S
NO2
3f
0.83
0.85
0.84
0.70
0.71
0.98
1.16
0.88
0.95
3.00
f1 (ppm)

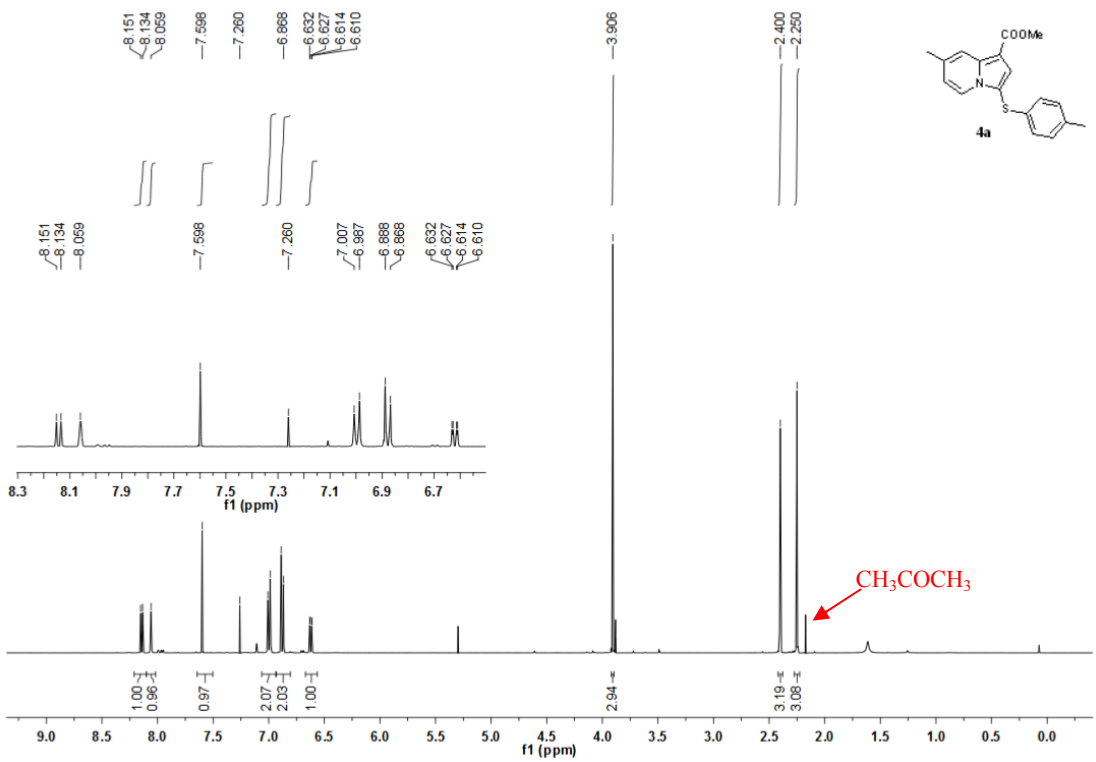

164.616
148.914
139.174
138.897
131.327
130.138
127.476
124.207
121.056
120.218
113.923
108.243
105.174
77.372
77.160
76.949
51.320
124.680
120.640
COOMe
N
S
NO2
3f
f1 (ppm)

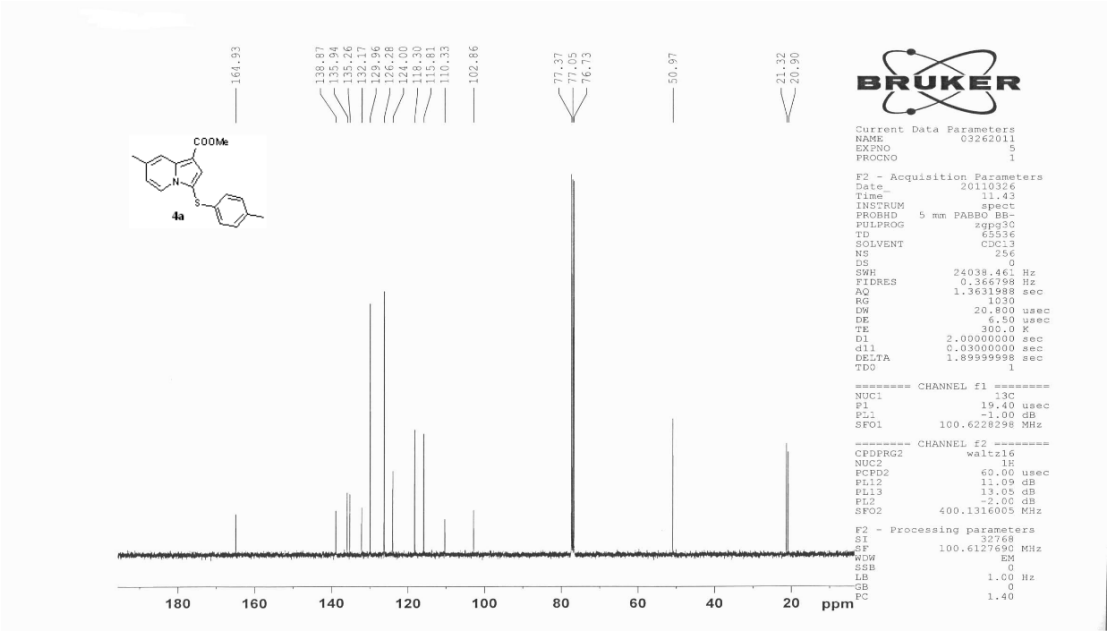

8.304
8.277
8.257
7.680
7.194
7.135
7.099
6.966
6.947
6.818
6.801
6.784
3.922
COOMe
N
S
3g
1.53
0.60
2.67
0.90
1.59
0.92
3.00
f1 (ppm)

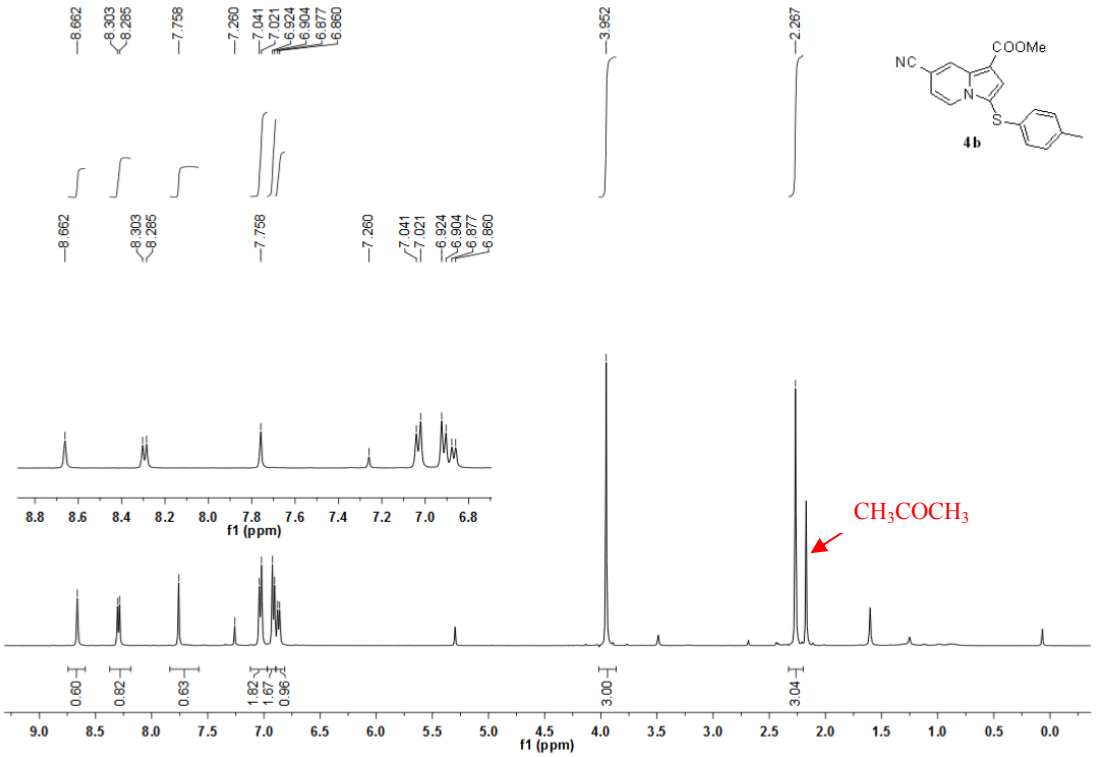

164.849
138.585
135.818
129.359
126.156
124.659
124.145
119.928
113.439
110.743
104.596
77.478
77.160
76.843
51.156
COOMe
N
S
3g
f1 (ppm)

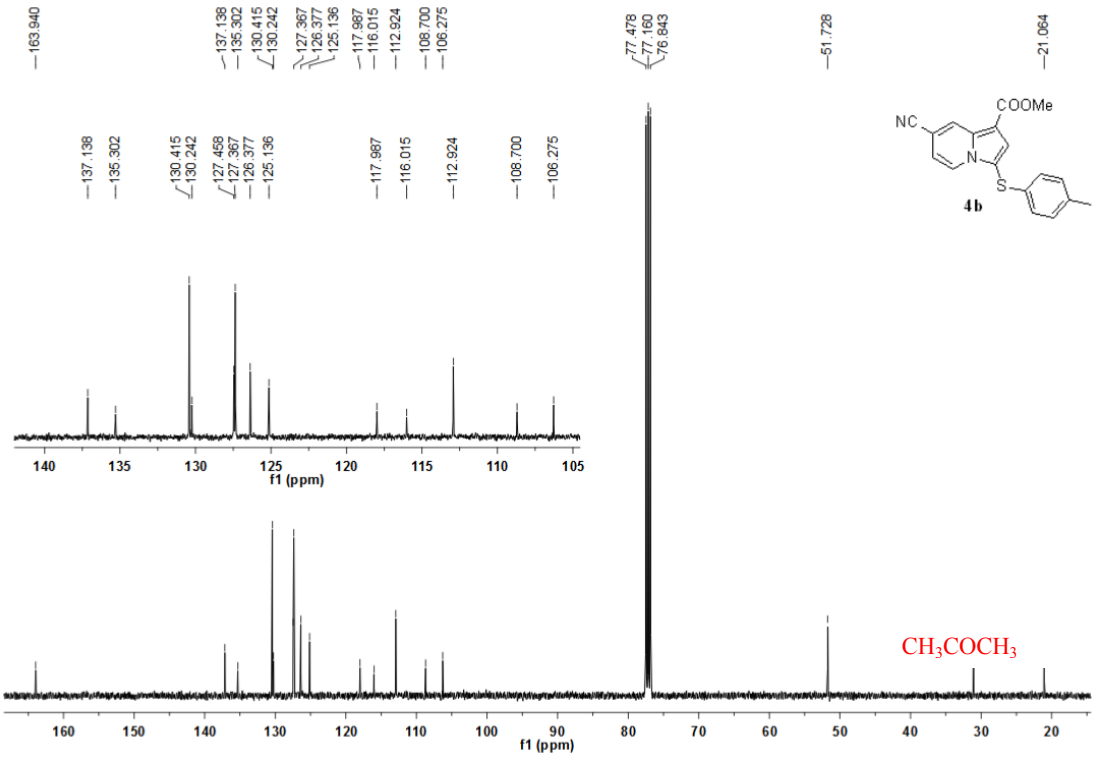

8.420
8.399
8.333
8.310
8.200
8.183
7.873
7.853
7.777
7.634
7.580
7.543
7.198
7.184
7.176
7.165
7.146
6.760
6.743
6.727
6.626
6.608
3.942
COOMe
N
S
3h
0.86
0.81
0.86
0.96
0.67
1.96
0.94
1.94
0.94
0.83
3.00
f1 (ppm)

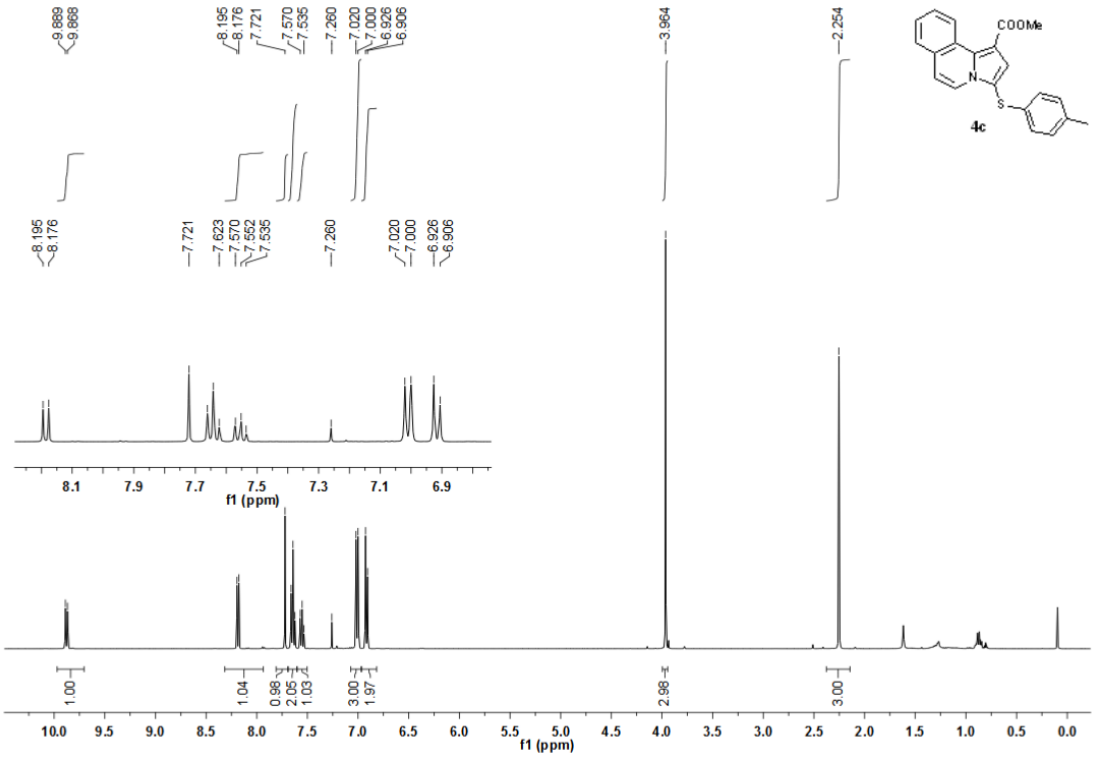

164.856
138.781
126.593
126.551
124.774
123.740
119.931
113.421
109.587
104.742
77.371
77.160
76.948
51.222
COOMe
N
S
3h
128.789
127.122
126.593
126.580
126.551
125.896
124.774
124.215
123.740
123.156
f1 (ppm)

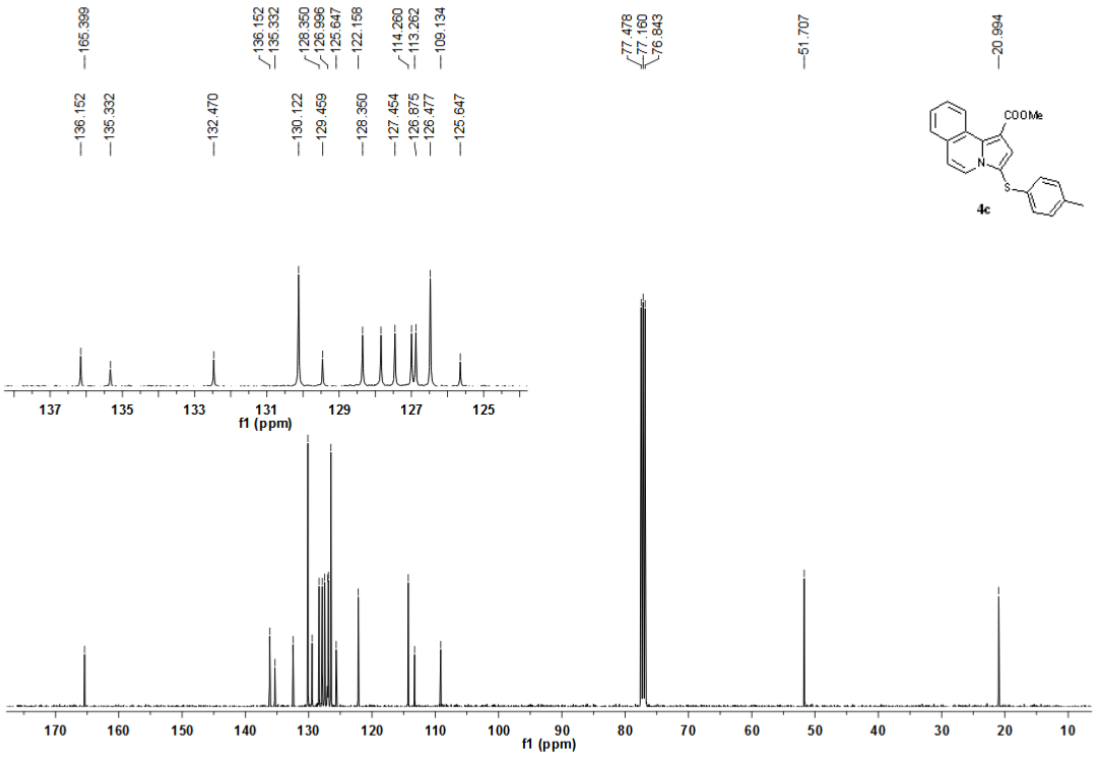

8.151
8.134
8.059
7.598
7.260
6.868
6.632
6.627
6.614
6.610
3.906
2.400
2.250
COOMe
4a
7.007
6.987
6.888
6.868
f1 (ppm)
CH3COCH3
1.00
0.98
0.97
2.07
2.03
1.00
2.94
3.19
3.08

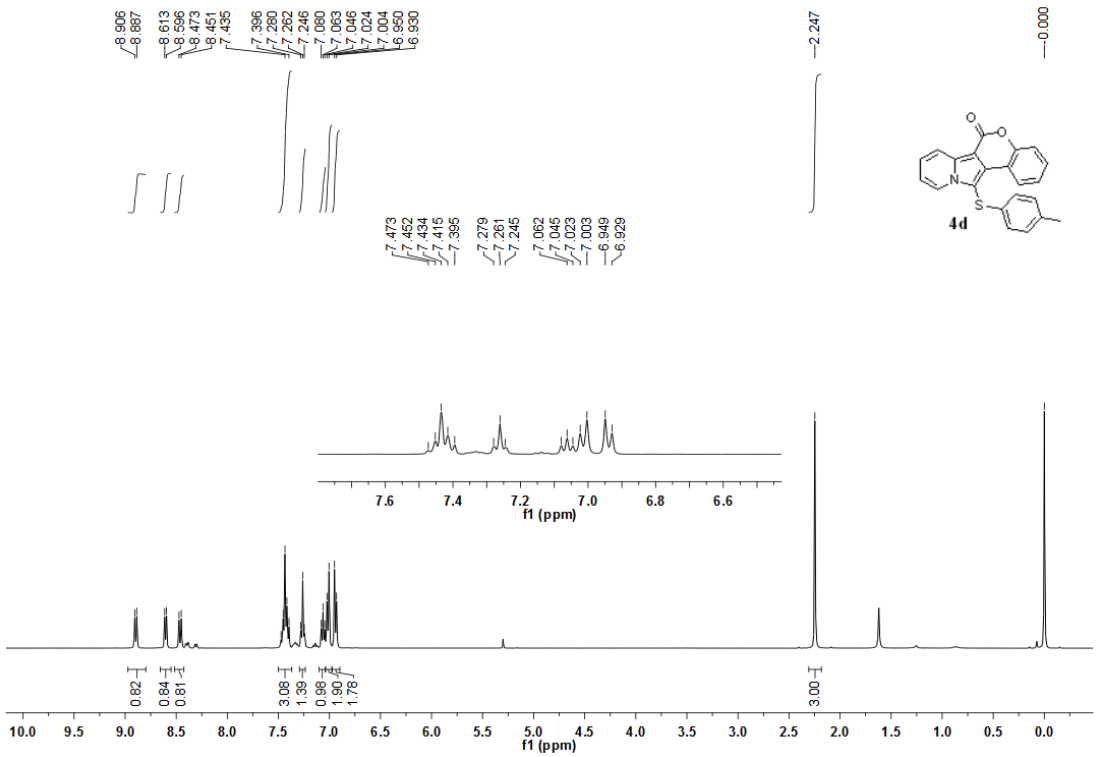

164.93
138.87
135.94
135.26
132.17
129.96
126.28
124.00
118.30
115.81
110.33
102.86
77.37
77.05
76.73
50.97
21.32
20.90
COOMe
4a
BRUKER
Current Data Parameters
NAME 03262011
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110326
Time 11.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 19.40 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 11.09 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm

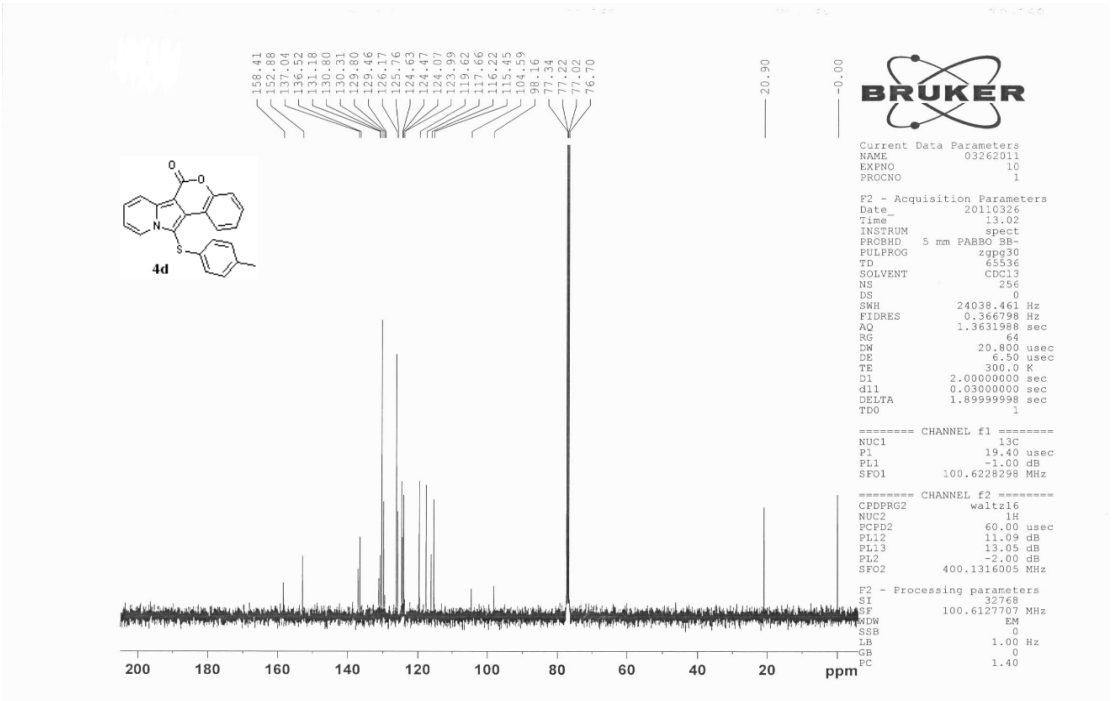

8.662
8.303
8.285
7.758
7.260
7.041
7.021
6.924
6.904
6.877
6.860
3.952
2.267
COOMe
NC
N
S
4b
f1 (ppm)
CH3COCH3
0.60
0.62
0.63
1.82
1.67
0.96
3.00
3.04

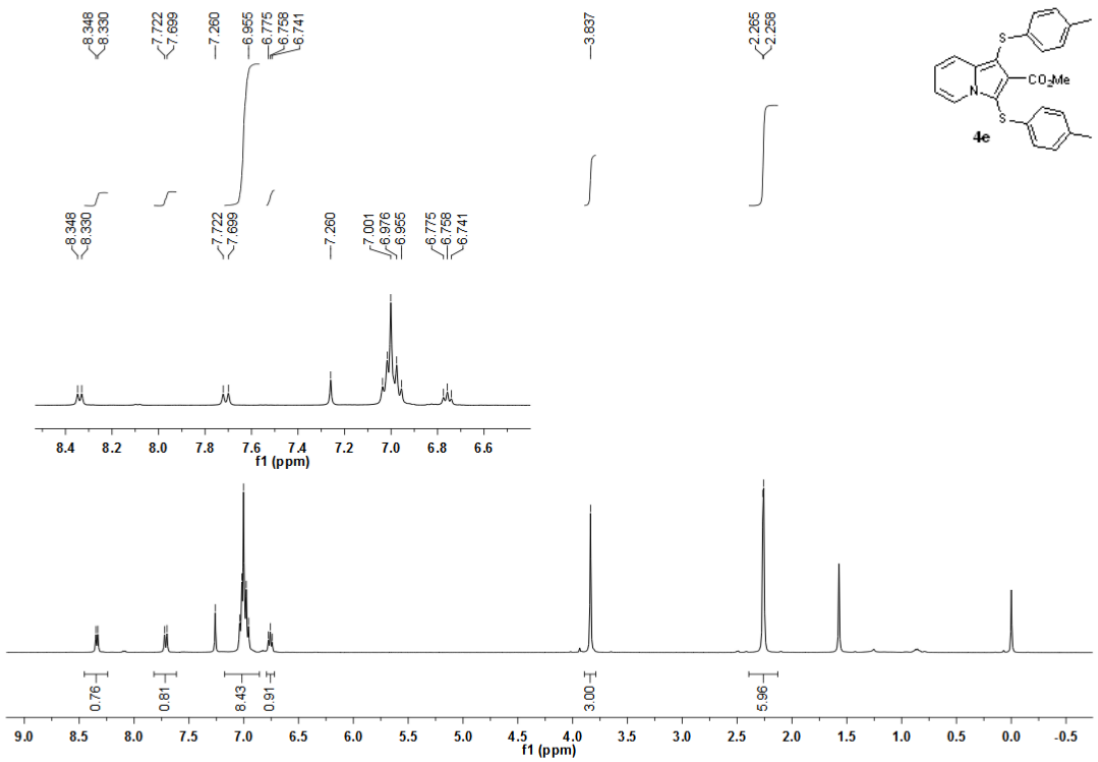

163.940
137.138
135.302
130.415
130.242
127.367
126.377
125.136
117.987
116.015
112.924
108.700
106.275
77.478
77.160
76.843
51.728
21.064
COOMe
NC
N
S
4b
f1 (ppm)
CH3COCH3

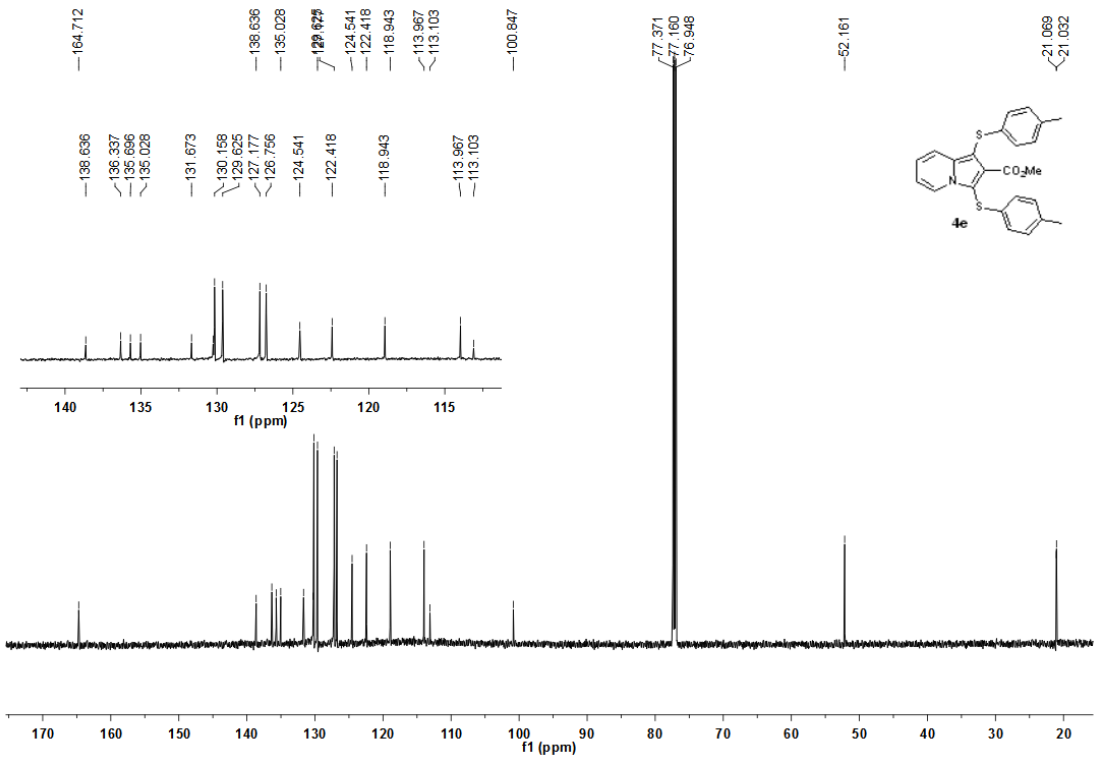

9.889
9.868
8.195
8.176
7.721
7.570
7.535
7.260
7.020
7.000
6.926
6.906
3.964
2.254
COOMe
4c
f1 (ppm)
1.00
1.04
0.98
2.05
1.03
3.00
1.97
2.98
3.00

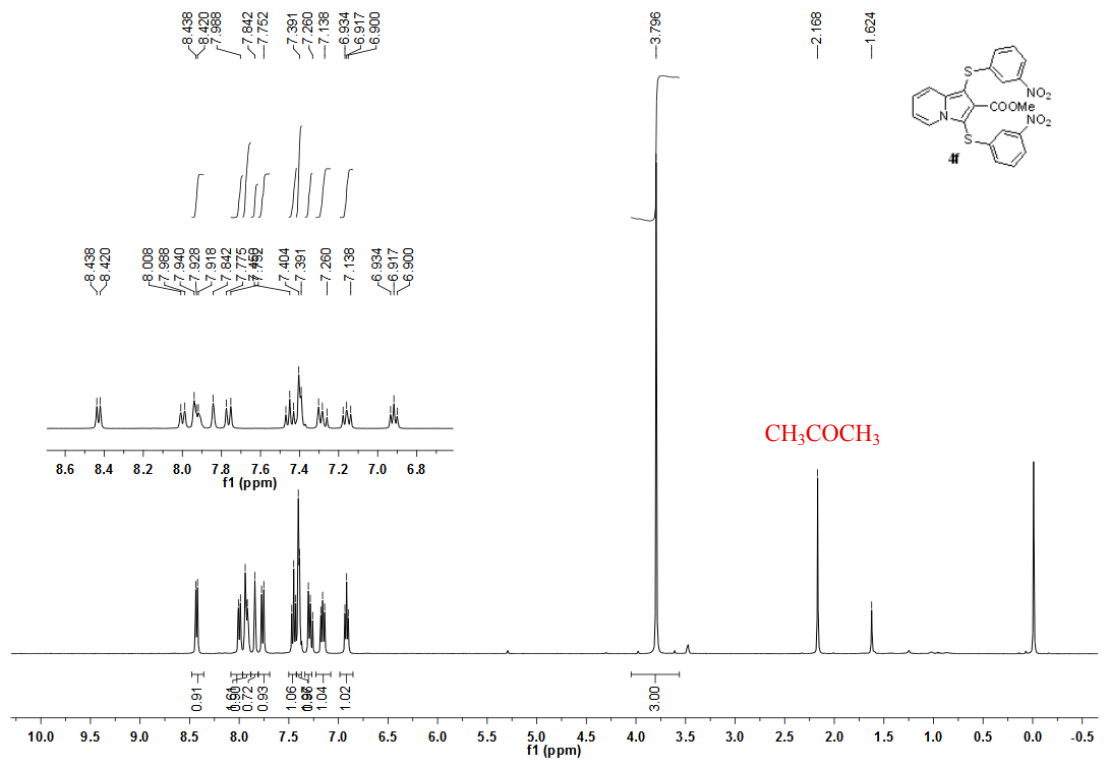

165.399
136.152
135.332
132.470
130.122
129.459
128.350
127.454
126.875
126.477
125.647
122.158
114.260
113.262
109.134
77.478
77.160
76.843
51.707
20.994
COOMe
4c
f1 (ppm)

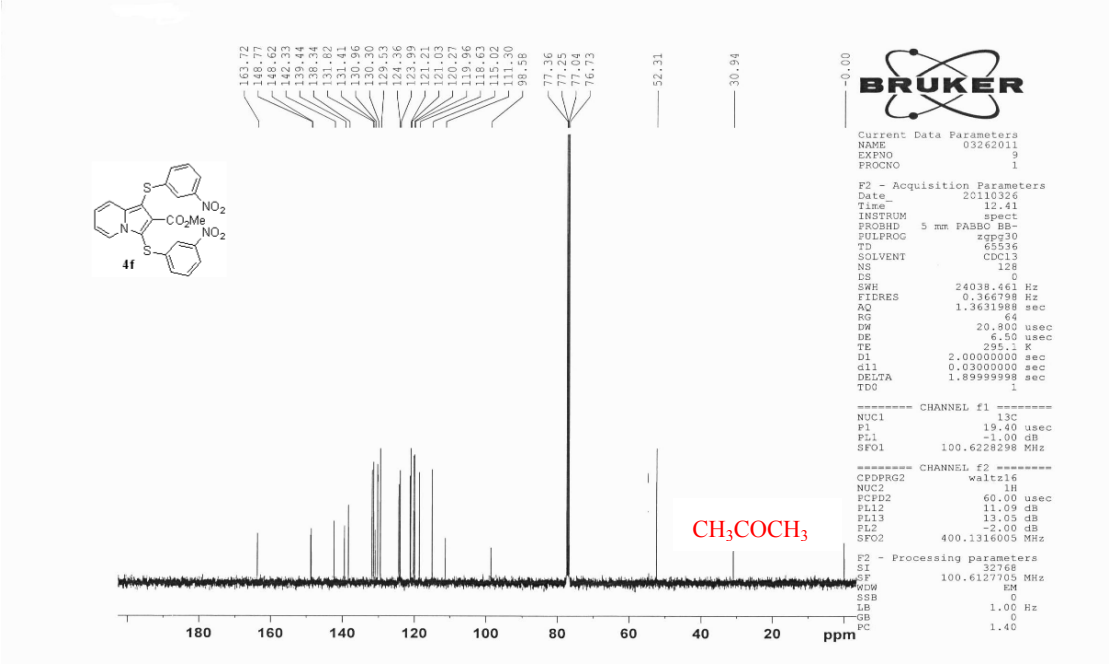

8.906
8.887
8.613
8.596
8.473
8.451
8.435
7.396
7.280
7.262
7.246
7.080
7.063
7.046
7.024
7.004
6.950
6.930
2.247
0.000
7.473
7.452
7.434
7.415
7.395
7.279
7.261
7.245
7.062
7.045
7.023
7.003
6.949
6.929
4d
f1 (ppm)
0.82
0.84
0.81
3.08
1.39
0.98
1.90
1.78
3.00

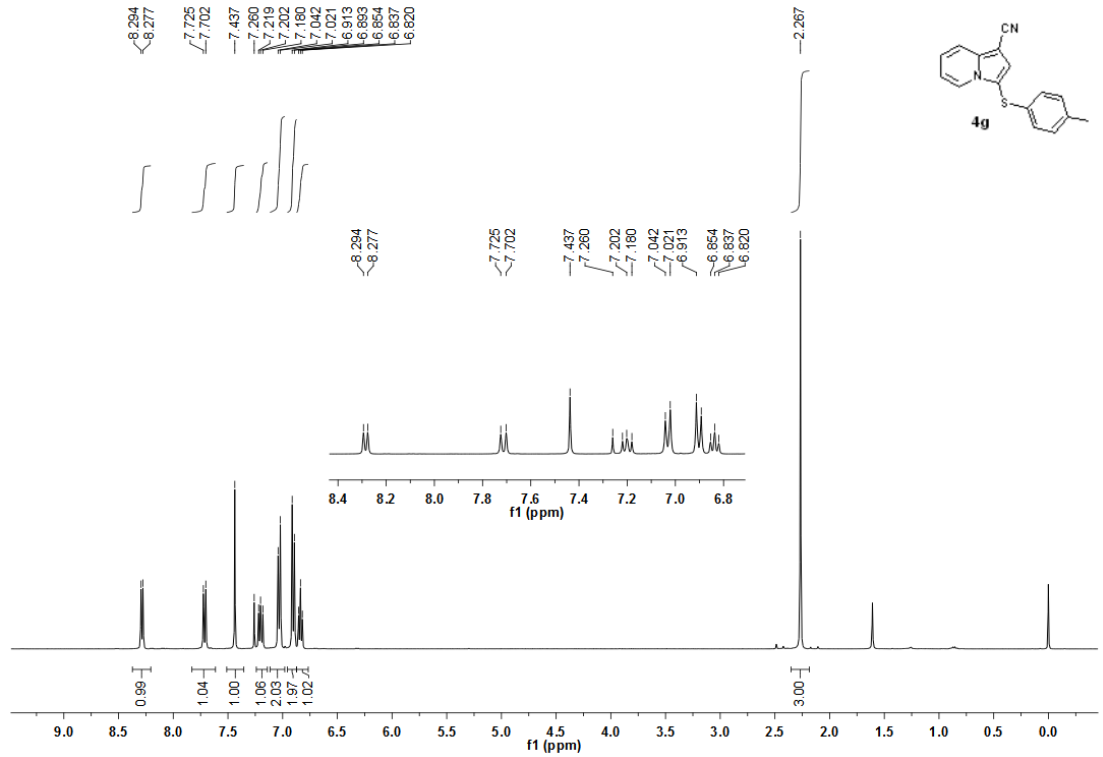

158.41
152.88
137.04
136.52
131.18
130.80
130.31
129.80
129.46
126.17
125.76
124.63
124.47
124.07
123.99
119.62
117.66
116.22
115.45
104.59
98.16
77.34
77.22
77.02
76.70
20.90
-0.00
4d
BRUKER
Current Data Parameters
NAME 03262011
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110326
Time 13.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 64
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 19.40 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 11.09 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
ppm

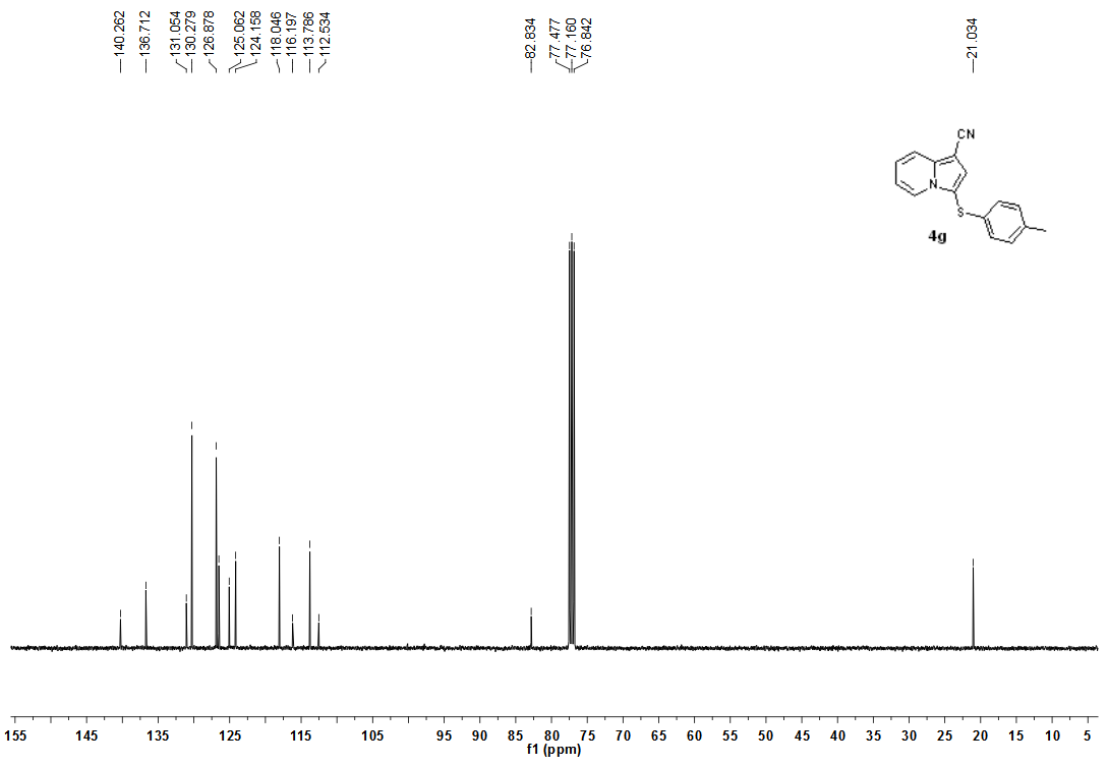

8.348
8.330
7.722
7.699
7.260
6.955
6.775
6.758
6.741
3.837
2.265
2.258
CO2Me
4e
f1 (ppm)
0.76
0.81
8.43
0.91
3.00
5.96

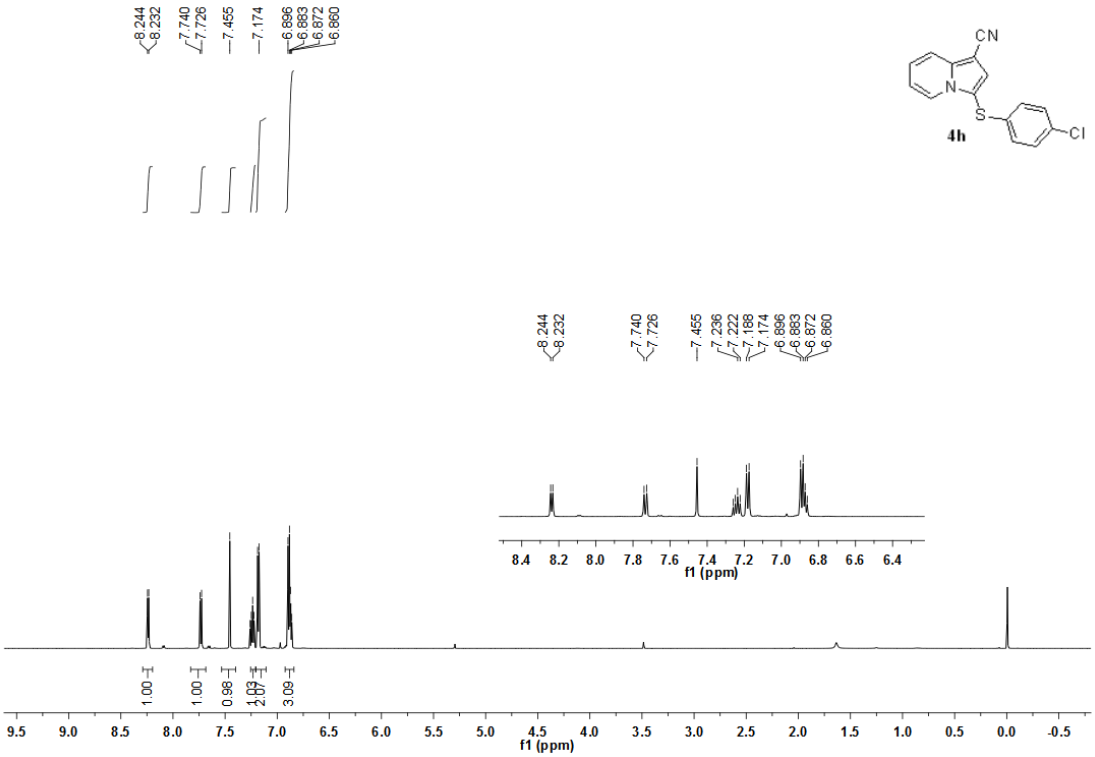

164.712
138.636
135.028
124.541
122.418
118.943
113.967
113.103
100.847
77.371
77.160
76.948
52.161
21.069
21.032
136.337
135.696
131.673
130.158
129.625
127.177
126.756
CO2Me
4e
f1 (ppm)

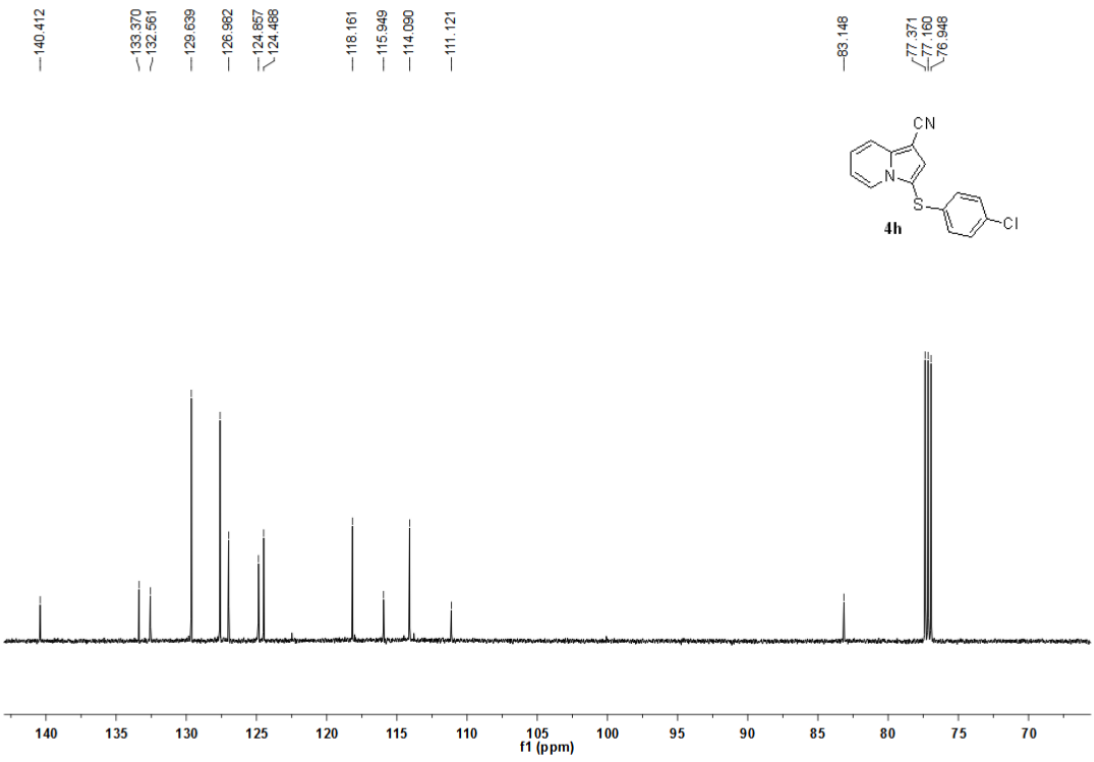

8.438
8.420
7.988
7.842
7.752
7.391
7.260
7.138
6.934
6.917
6.900
3.796
2.168
1.624
NO2
COOMe
NO2
4f
CH3COCH3
f1 (ppm)

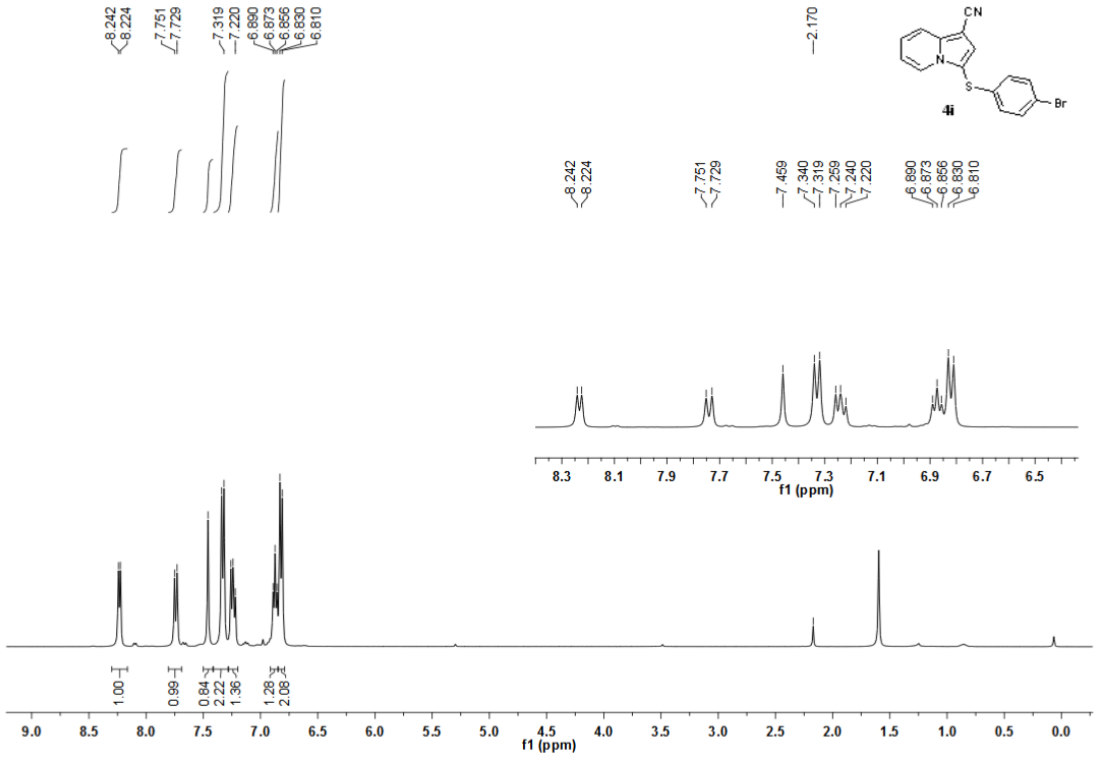

163.72
148.77
148.62
142.33
139.44
138.34
131.82
131.41
130.96
130.30
129.53
124.36
123.99
121.21
121.03
120.27
119.96
118.63
115.02
111.30
98.58
77.36
77.25
77.04
76.73
52.31
30.94
0.00
BRUKER
Current Data Parameters
NAME 03262011
EXPNO 9
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110326
Time 12.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 64
DW 20.800 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 19.40 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 11.09 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127705 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NO2
CO2Me
NO2
4f
CH3COCH3
ppm

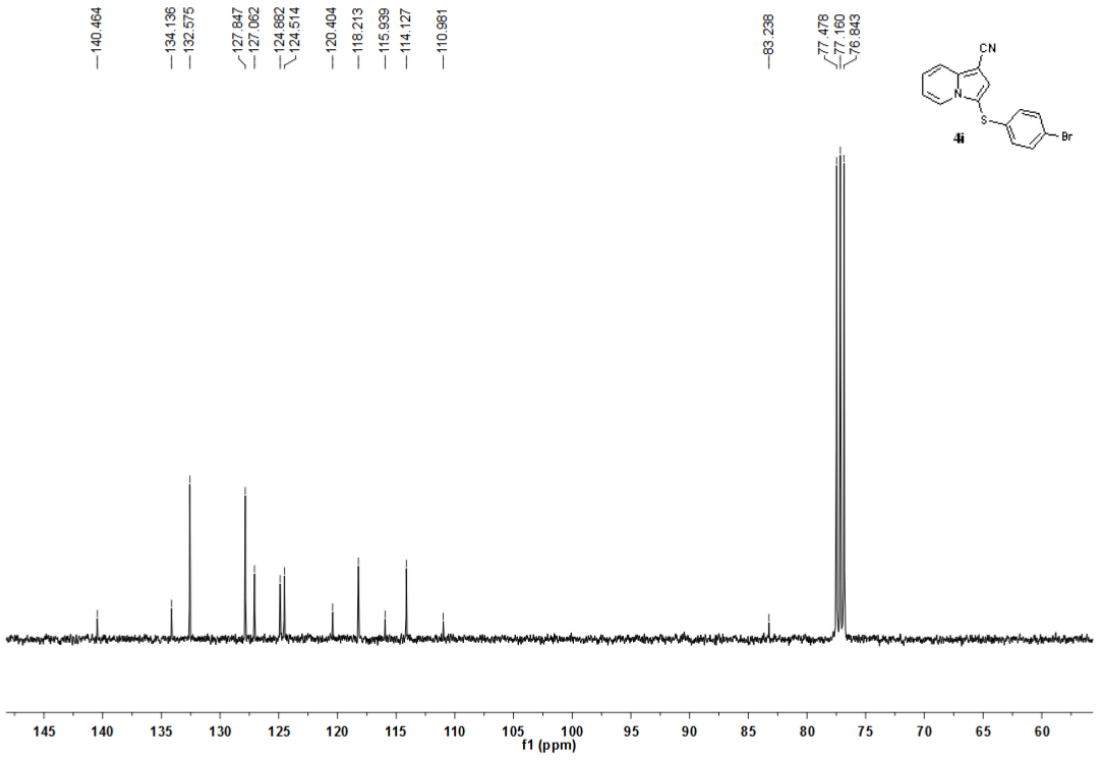

8.294
8.277
7.725
7.702
7.437
7.260
7.219
7.202
7.180
7.042
7.021
6.913
6.893
6.854
6.837
6.820
2.267
CN
S
4g
f1 (ppm)
0.99
1.04
1.00
1.06
2.03
1.97
1.02
3.00

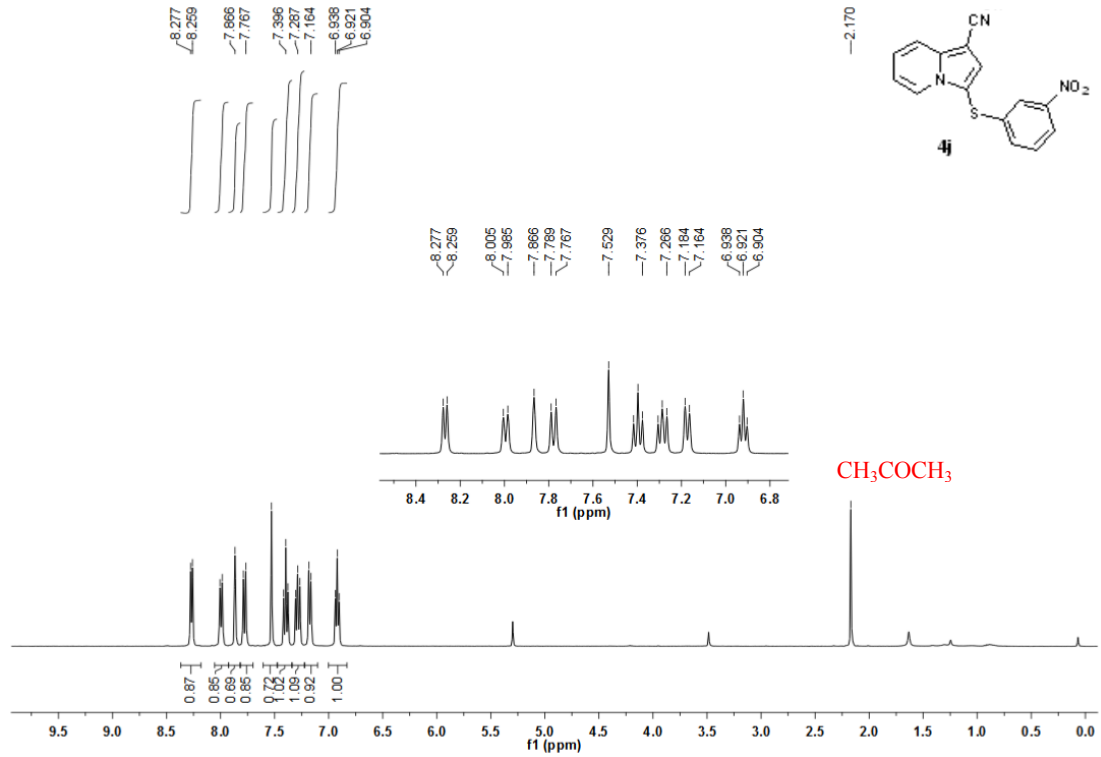

140.262
136.712
131.054
130.279
126.878
125.062
124.158
118.046
116.197
113.786
112.534
82.834
77.477
77.160
76.842
21.034
CN
S
4g
f1 (ppm)

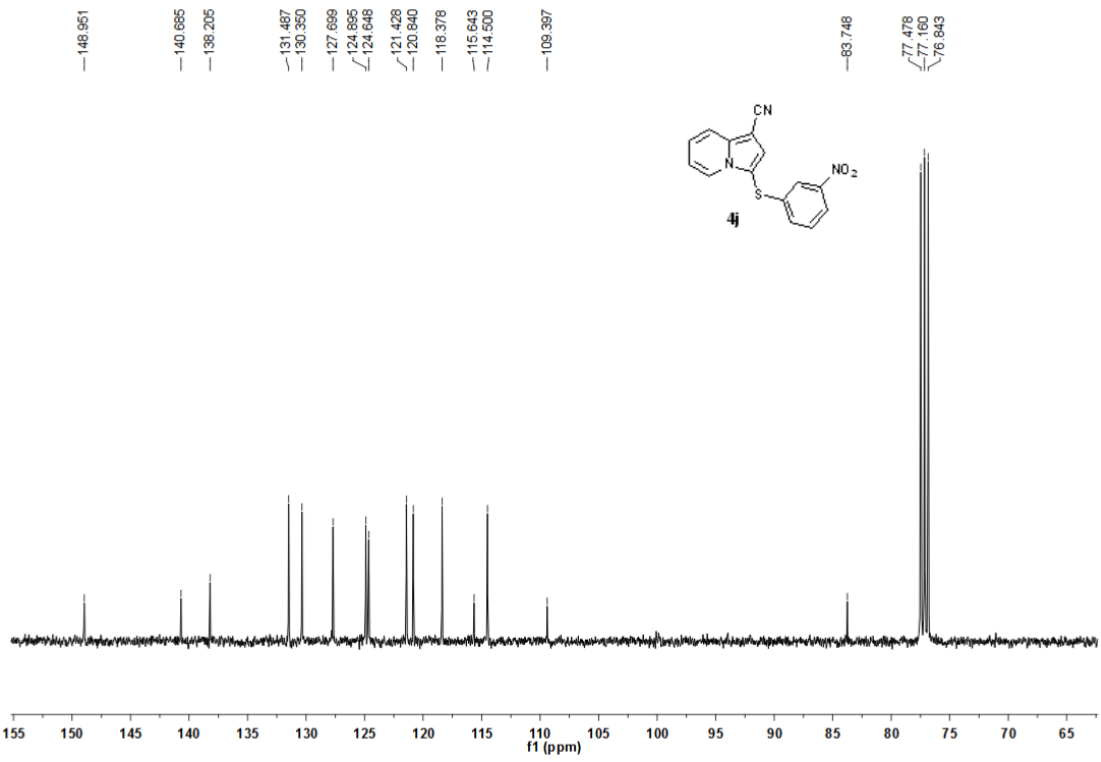

8.244
8.232
7.740
7.726
7.455
7.236
7.222
7.188
7.174
6.896
6.883
6.872
6.860
CN
N
S
Cl
4h
1.00
1.00
0.98
2.07
3.09
f1 (ppm)

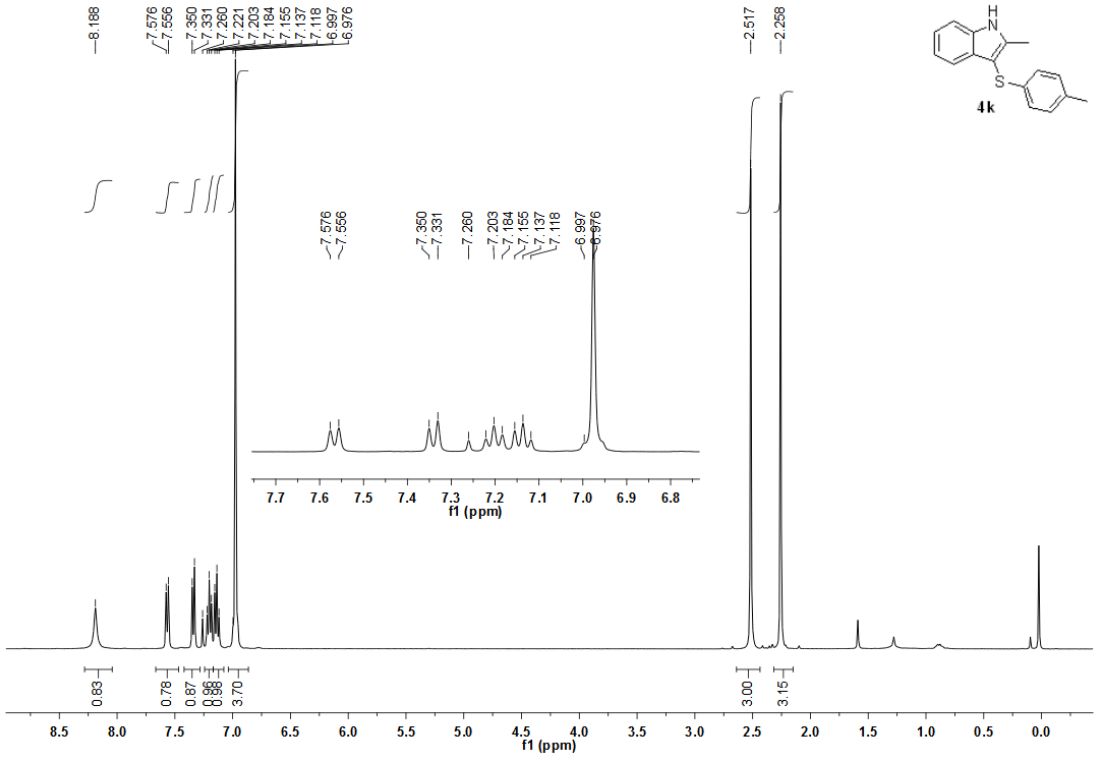

140.412
133.370
132.561
129.639
126.982
124.857
124.488
118.161
115.949
114.090
111.121
83.148
77.371
77.160
76.948
CN
N
S
Cl
4h
f1 (ppm)

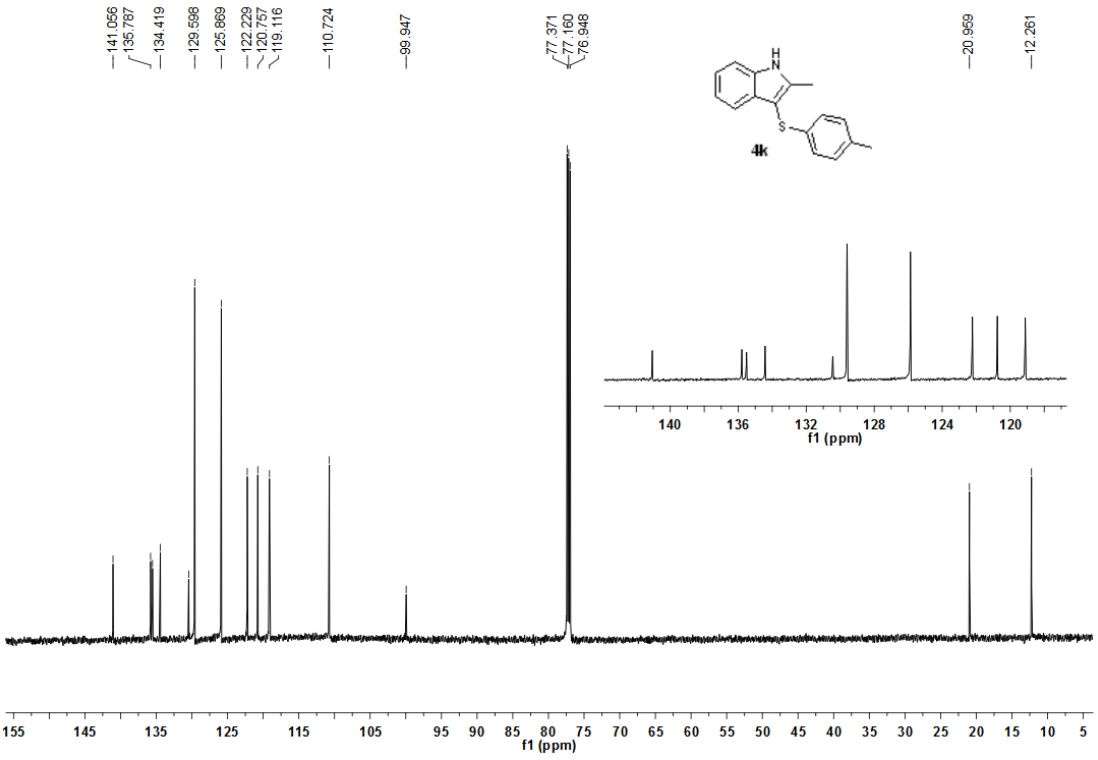

8.242
8.224
7.751
7.729
7.319
7.220
6.890
6.873
6.856
6.830
6.810
2.170
CN
N
S
Br
4i
7.459
7.340
7.259
7.240
8.3
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
f1 (ppm)
1.00
0.99
0.84
2.22
1.36
1.28
2.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

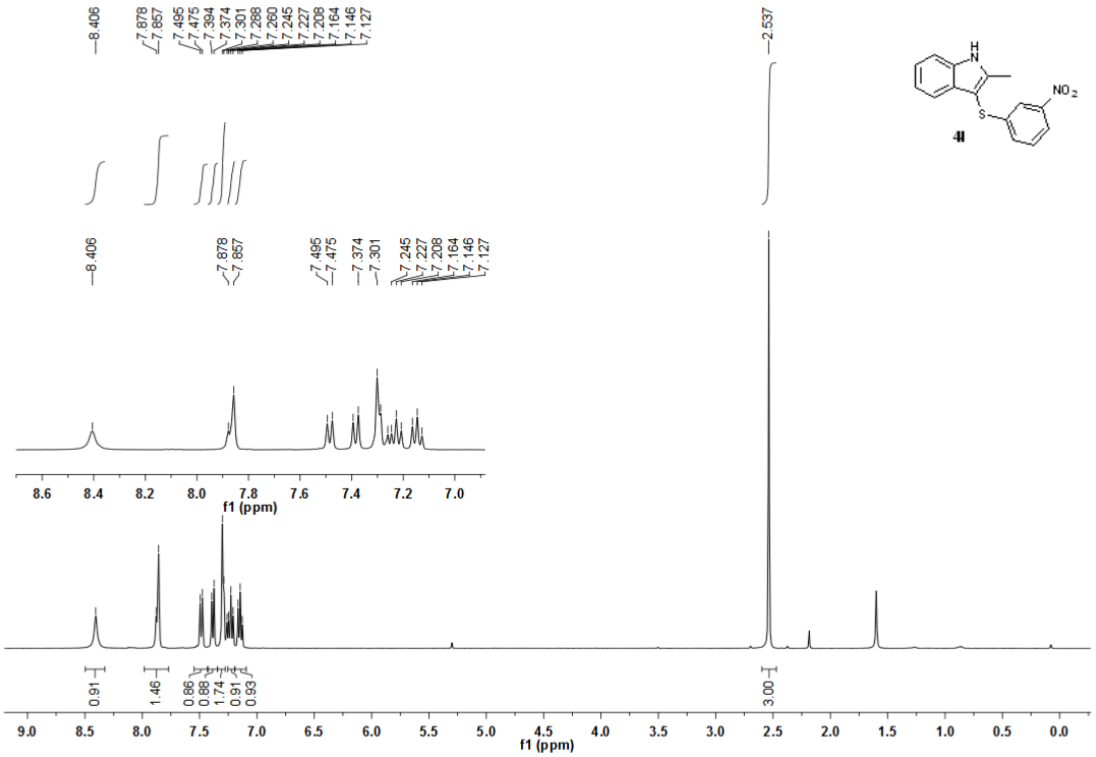

140.464
134.136
132.575
127.847
127.062
124.882
124.514
120.404
118.213
115.939
114.127
110.981
83.238
77.478
77.160
76.843
CN
S
Br
4i
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)

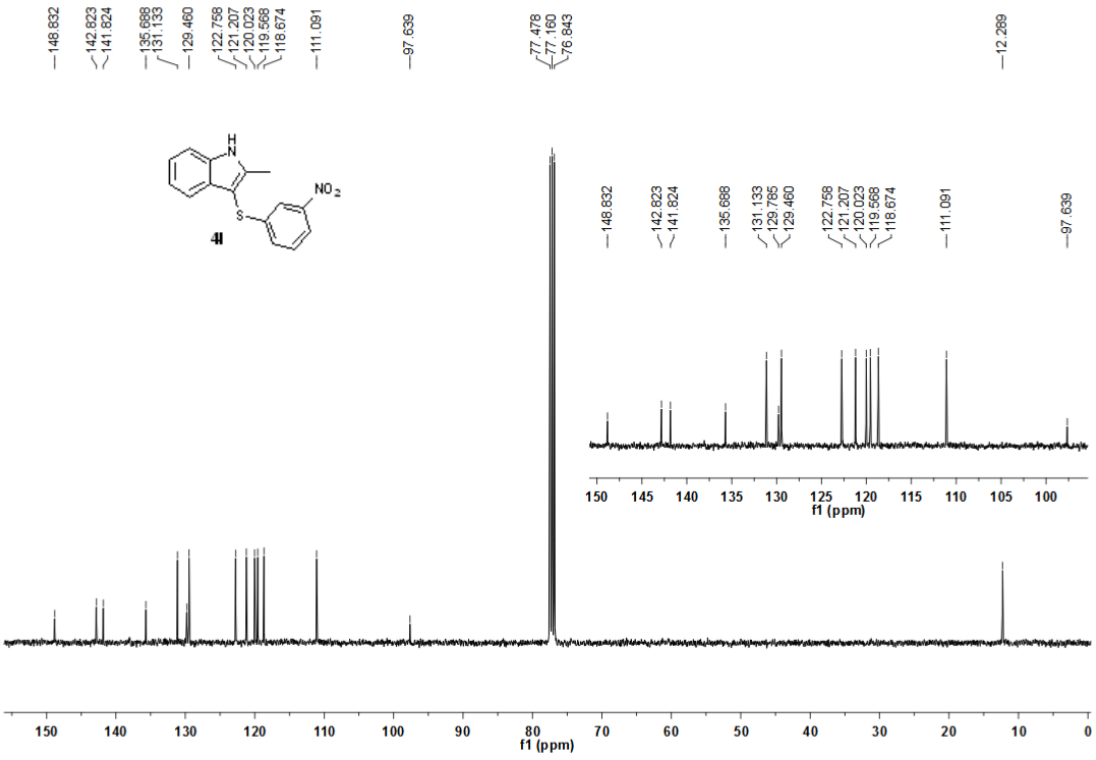

8.277
8.259
7.866
7.767
7.396
7.287
7.164
6.938
6.921
6.904
2.170
CN
NO2
S
4j
8.277
8.259
8.005
7.985
7.866
7.789
7.767
7.529
7.376
7.266
7.184
7.164
6.938
6.921
6.904
CH3COCH3
f1 (ppm)
0.87
0.85
0.69
0.85
1.02
1.09
0.92
1.00
f1 (ppm)

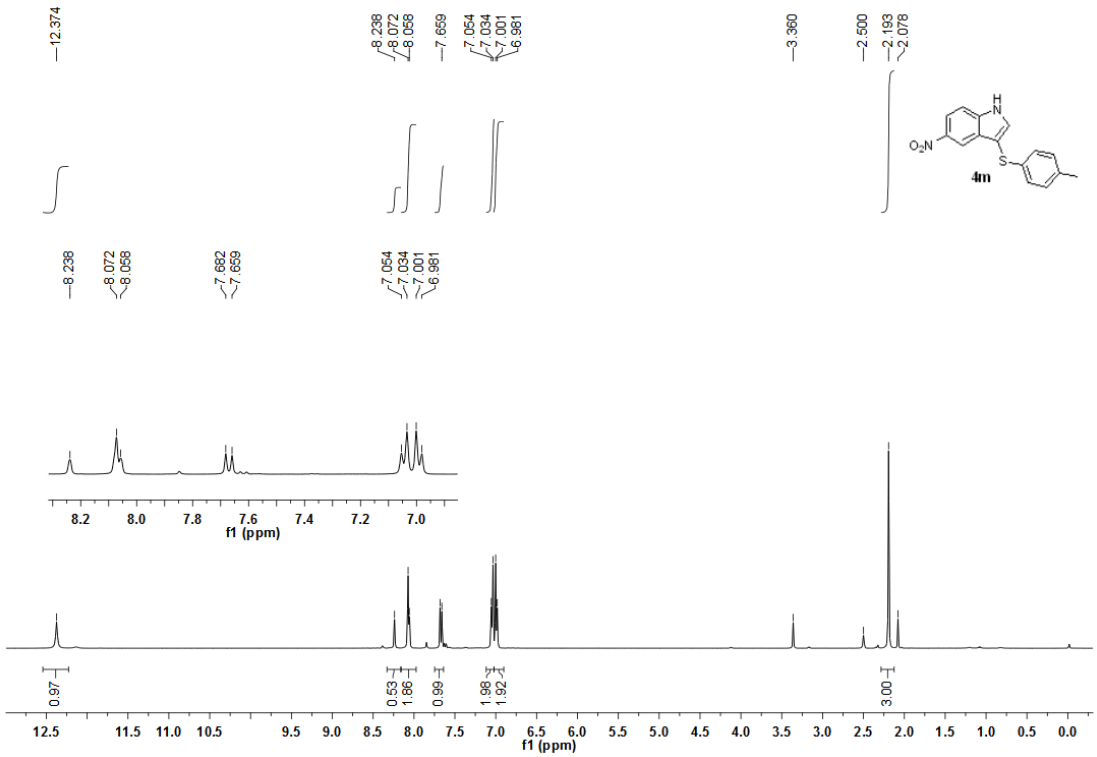

148.951
140.685
138.205
131.487
130.350
127.699
124.895
124.648
121.428
120.840
118.378
115.643
114.500
109.397
83.748
77.478
77.160
76.843
CN
NO2
S
4j
f1 (ppm)

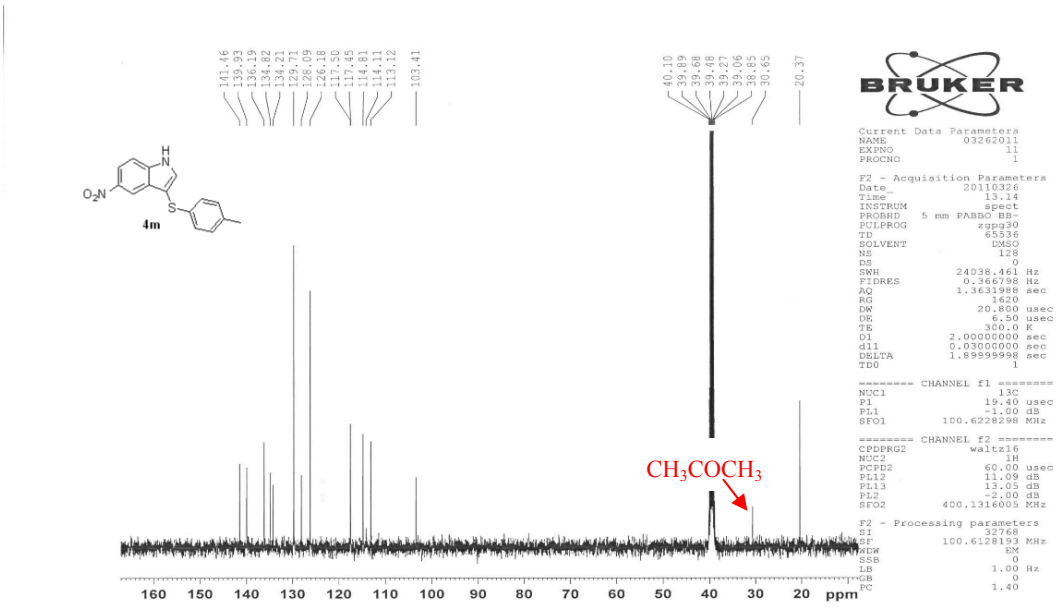

8.188
7.576
7.556
7.350
7.331
7.260
7.221
7.203
7.184
7.155
7.137
7.118
6.997
6.976
2.517
2.258
4k
f1 (ppm)
0.83
0.78
0.87
3.70
3.00
3.15

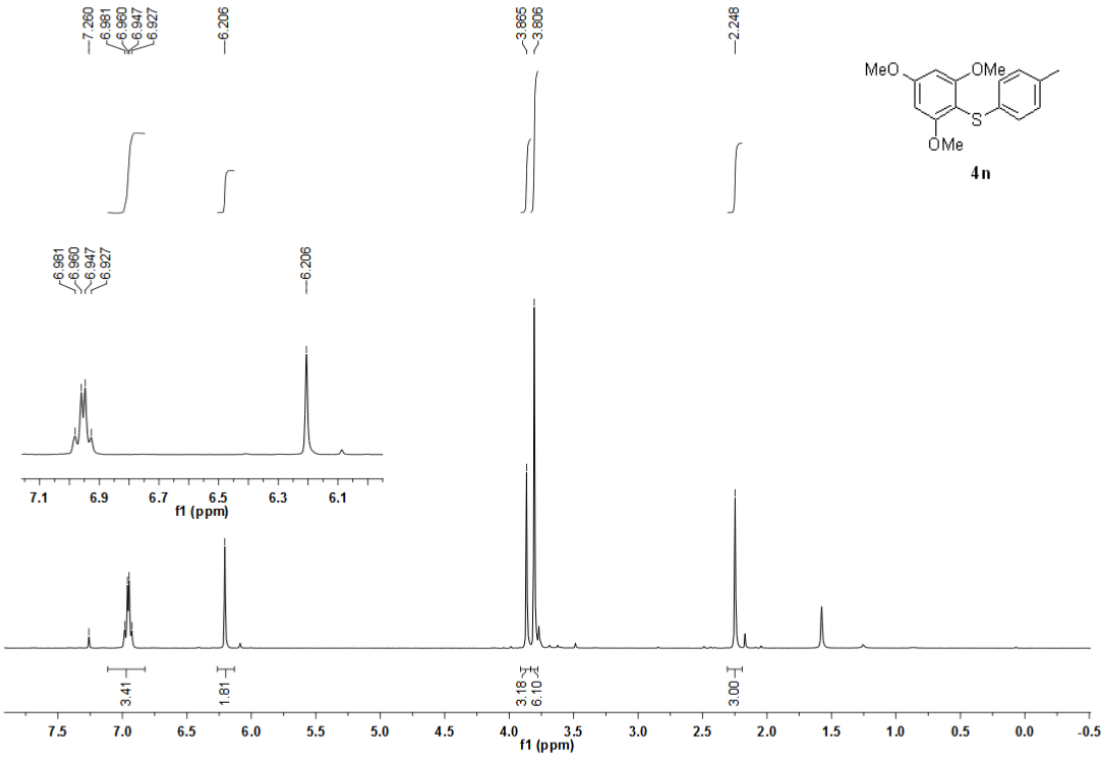

141.056
135.787
134.419
129.598
125.869
122.229
120.757
119.116
110.724
99.947
77.371
77.160
76.948
20.959
12.261
4k
f1 (ppm)

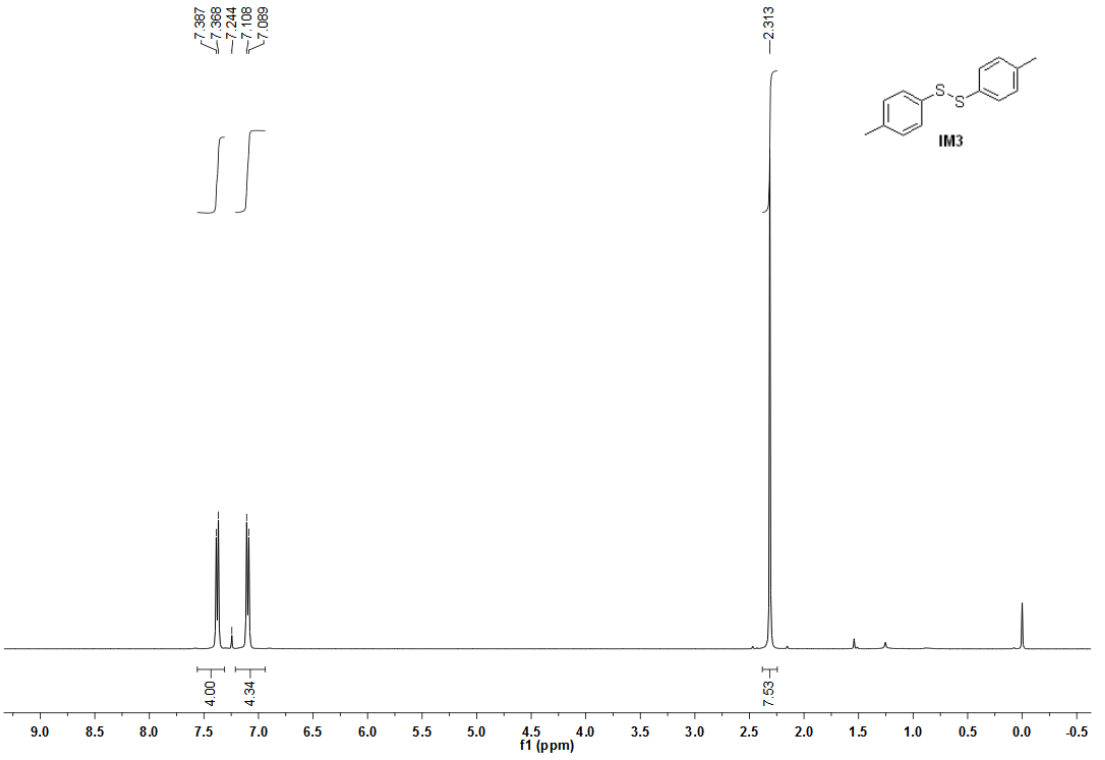

8.406
7.878
7.857
7.495
7.475
7.394
7.374
7.301
7.288
7.260
7.245
7.227
7.208
7.164
7.146
7.127
2.537
4ll
f1 (ppm)
0.91
1.46
0.86
0.88
1.74
0.91
0.93
3.00

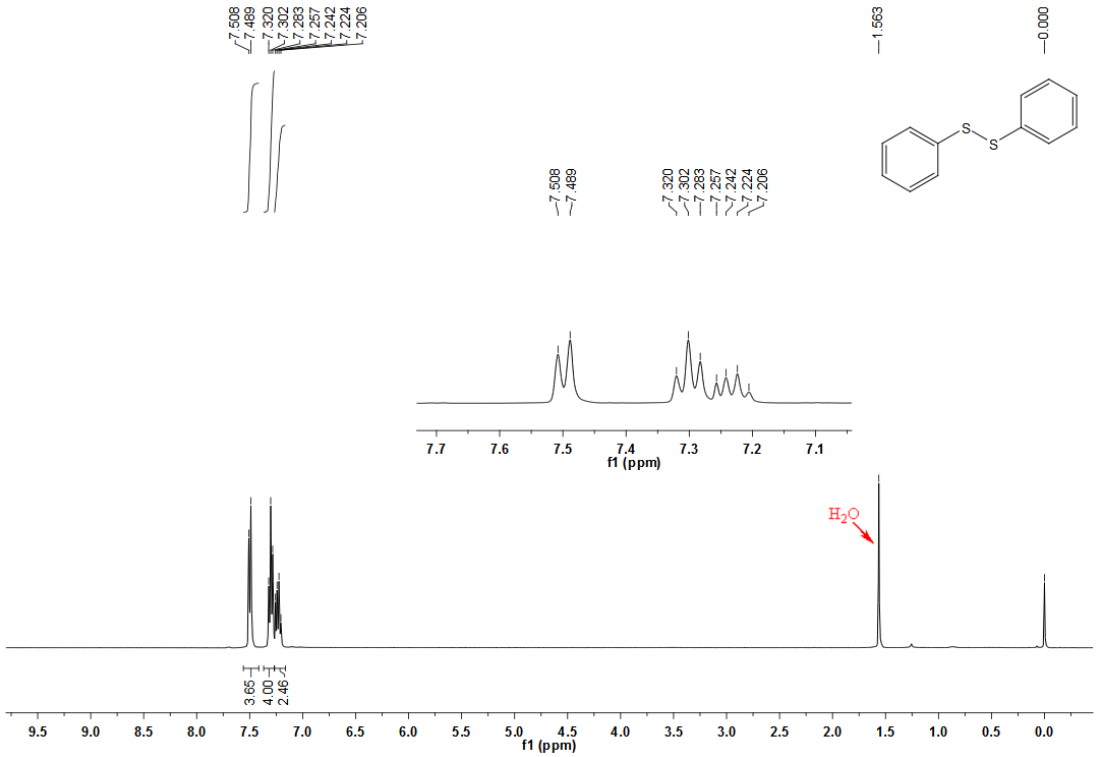

148.832
142.823
141.824
135.688
131.133
129.460
122.758
121.207
120.023
119.568
118.674
111.091
97.639
77.478
77.160
76.843
12.289
4ll
f1 (ppm)


12.374
8.238
8.072
8.058
7.659
7.054
7.034
7.001
6.981
3.360
2.500
2.193
2.078
4m
f1 (ppm)
0.97
0.53
1.86
0.99
1.98
1.92
3.00


4m
CH3COCH3
ppm
BRUKER
Current Data Parameters
NAME 03262011
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110326
Time 13.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 128
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1620
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 19.40 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 11.09 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6128193 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.260
6.981
6.960
6.947
6.927
6.206
3.865
3.606
2.248
MeO
OMe
OMe
S
4n
6.981
6.960
6.947
6.927
6.206
7.1
6.9
6.7
6.5
6.3
6.1
f1 (ppm)
3.41
1.81
3.18
6.10
3.00
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)


7.387
7.368
7.244
7.108
7.089
2.313
S
S
IM3
4.00
4.34
7.53
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)


7.508
7.489
7.320
7.302
7.283
7.257
7.242
7.224
7.206
1.563
0.000
S
S
f1 (ppm)
H2O
3.65
4.00
2.46
f1 (ppm)