A Radical Cyclization Cascade of 2-Alkynylbenzonitriles with Sodium Arylsulfinates

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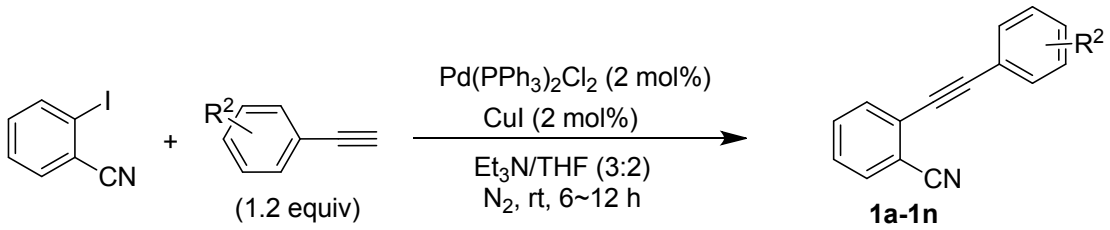
1) General Information

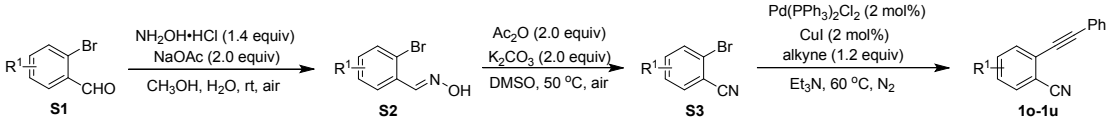
NMR spectra of the **3a-3w** were recorded using Bruker Avance-500 instruments, calibrated to TMS (^{1}H NMR spectra) and $CDCl_3$ (^{13}C NMR spectra) as the internal reference (0.00 ppm for ^{1}H NMR spectra and 77.00 ppm for ^{13}C NMR spectra). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected. Reactions were monitored by thin-layer chromatography. Column chromatography was performed on silica gel (200-300 mesh).

2) Synthesis of Starting Materials

(1) General Procedure for the Synthesis of 3-(2-iodophenyl)-1-phenylpropan-1-one derivatives.[1]



2-iodobenzonitrile (1.5 mmol) was dissolved in a 3:2 mixture of Et_3N/THF (10.0 mL) and degassed for 30 min at room temperature. After adding of Pd $(PPh_3)_2Cl_2$ (0.2 mol%), CuI (0.2 mol%) and alkyne (1.8 mmol) was added dropwise to the reaction suspension under nitrogen atmosphere. Subsequently the reaction mixture was stirred at room temperature until completion was indicated by TLC**.** After the completion of the reaction, the reaction mixture was filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to provide **1a-1n**.



S1 (3.0 mmol), hydroxylamine hydrochloride (4.2 mmol), sodium acetate (6.0 mmol), water (3.0 mL) and methanol (10.2 mL) were charged in 25 mL round-bottom

flask, and stirred for 4 h at room temperature. After the completion of the reaction (monitored by TLC), the reaction was then diluted with water and extracted three times with methylene chloride. The combined organic extracts were dried over Na_2SO_4, and the solvent was evaporated to give **S2**, which were used directly in the next step.

K_2CO_3 (3.0 mmol) was added to a stirred mixture of **S2** (1.5 mmol) and 6 mL DMSO, followed by Ac_2O (3.0 mmol). The resulting mixture was stirred at 50 ^oC for a specified period. After the reaction was completed (monitored by TLC), the reaction was then diluted with water and extracted three times with methylene chloride. The combined organic extracts were dried over Na_2SO_4, and the solvent was evaporated under vacuum to give **S3**, which were used directly in the next step.

S3 (1.5 mmol) was dissolved in Et_3N (5.0 mL) and degassed for 30 minutes at room temperature. Then $Pd(PPh_3)_2Cl_2$ (2.0 mol%), CuI (2.0 mol%) and the alkyne were added to **S3**/Et_3N solution under nitrogen atmosphere. The obtained dark brown suspension was stirred for 12 h at 60 °C. After cooling to room temperature the solvent of the reaction mixture was filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to provide **1o-1u**.

(2) General procedure for the preparation of 2-Naphthalenesulfonyl chloride.[2]

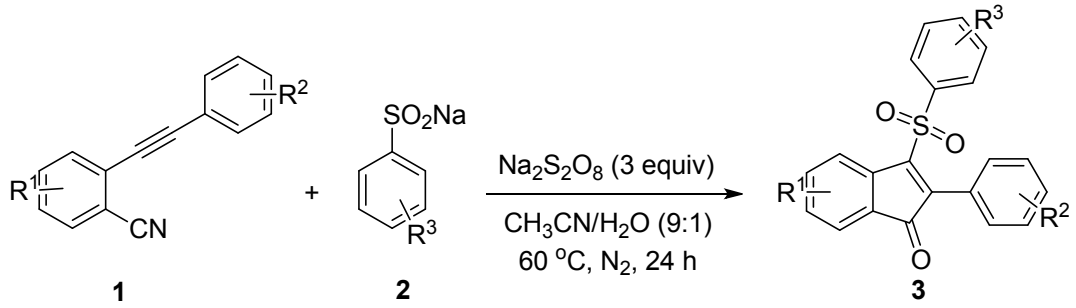
A mixture of 2-Naphthalenthiol (5.0 mmol), oxone (12.5 mmol) and KCl (5.0 mmol), water (20.0 mL) was taken into a round bottomed flask and stirred at 60 ^oC. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate (4x5 mL). The combined organic layers was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product obtained was purified by normal column chromatography (petroleum ether/ethyl acetate = 10:1) to obtain 2-Naphthalenesulfonyl chloride.

(3) General procedure for the preparation of sodium aryl sulfiantes.[3]

Sodium sulfite (2.5 g, 2 mmol, 2 equiv), sodium bicarbonate (1.68 g, 2 mmol, 2 equiv) and the corresponding aryl sulfonyl chloride (1 mmol, 1 equiv) were dissolved in distilled water (9.6 mL). The reaction mixture was stirred for 4 h at 80 °C. After cooling to rt, water was removed by lyophilization overnight. The white residue was extracted with ethanol (25 mL) to obtain the desired aryl sulfinate as white crystalline powder.

3) Typical Procedures

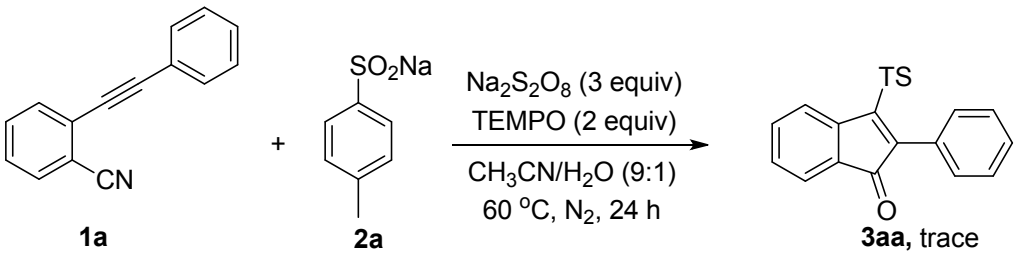
(1) Synthesis of Substituted Sulfonylated 1-indenones



Under nitrogen, the mixture of 2-alkynylbenzonitriles **1** (0.2 mmol), sodium sulfinates **2** (0.4 mmol, 2.0 equiv), $Na_2S_2O_8$ (0.6 mmol, 3.0 equiv), CH_3CN (1.8 mL) and H_2O (0.2 mL) were added to the Schlenk-tube. After stirring at 60 ^oC for 24 h, the reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent to afford the pure product **3**

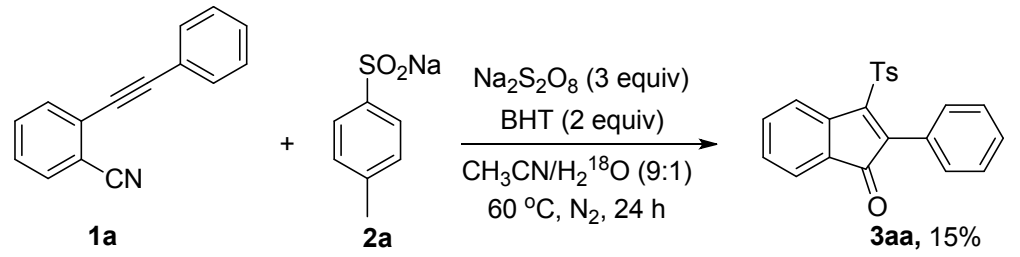
4) Mechanism Studies

(1) The reaction of **1a** and **2a** with TEMPO.



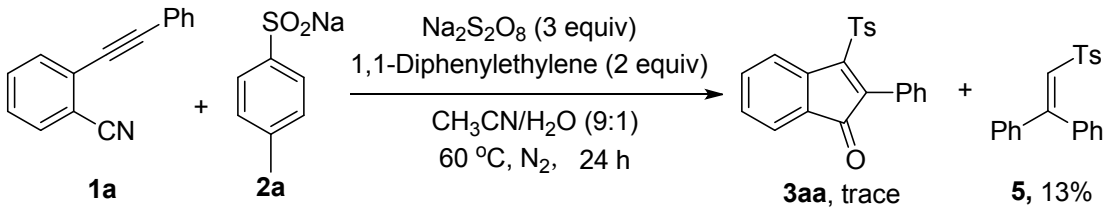
Under nitrogen, the mixture of 2-(phenylethynyl)benzonitrile **1a** (0.2 mmol), Sodium p-tolylsulfinate **2a** (0.4 mmol, 2.0 equiv), $Na_2S_2O_8$ (0.6 mmol, 3.0 equiv), TEMPO (0.4 mmol, 2 equiv)，CH_3CN (1.8 mL) and H_2O (0.2 mL) were added to the Schlenk-tube. After stirring at 60 °C for 24 h, the reaction mixture was concentrated in vacuum, no desired product **3aa** was detected.

(2) The reaction of **1a** and **2a** with BHT.



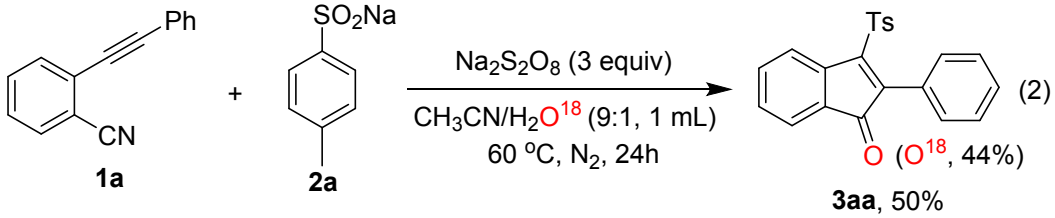
Under nitrogen, the mixture of 2-(phenylethynyl)benzonitrile **1a** (0.2 mmol), Sodium p-tolylsulfinate **2a** (0.4 mmol, 2 equiv), $Na_2S_2O_8$ (0.6 mmol, 3.0 equiv), BHT (0.4 mmol, 2 equiv)，CH_3CN (1.8 mL) and H_2O (0.2 mL) were added to the Schlenk-tube. After stirring at 60 °C for 24 h, the reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent to afford the pure product **3aa**.

(3) The reaction of **1a** and **2a** with 1,1-Diphenylethylene.

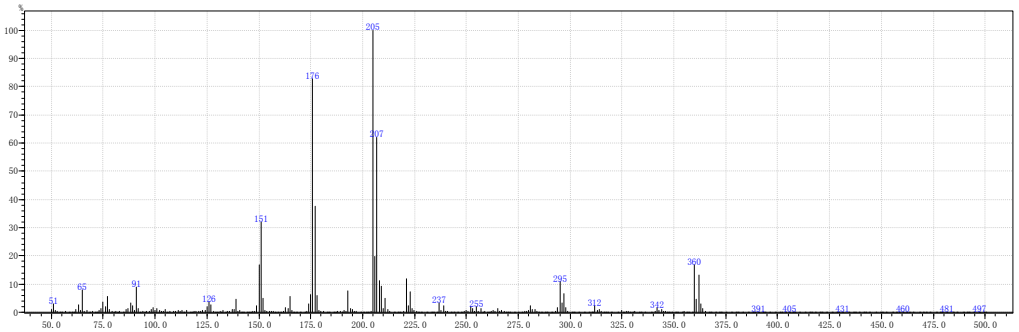


Under nitrogen, the mixture of 2-(phenylethynyl)benzonitrile **1a** (0.2 mmol), Sodium p-tolylsulfinate **2a** (0.4 mmol, 2.0 equiv), $Na_2S_2O_8$ (0.6 mmol, 3.0 equiv), 1,1-Diphenylethylene (0.4 mmol, 2 equiv)，CH_3CN (1.8 mL) and H_2O (0.2 mL) were added to the Schlenk-tube. After stirring at 60 °C for 24 h, the reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent to afford the pure product **5**.

(4) The O-18 labelling experiment using $H_2{}^{18}O$.



Under nitrogen, the mixture of 2-alkynylbenzonitriles **1** (0.1 mmol), sodium sulfinates **2** (0.2 mmol, 2.0 equiv), $Na_2S_2O_8$ (0.3 mmol, 3.0 equiv), CH_3CN (0.9 mL) and $H_2{}^{18}O$ (0.1 mL) were added to the Schlenk-tube. After stirring at 60 °C for 24 h, the reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent to afford the pure product **3aa'**.



[MS Spectrum]

# of Peaks 341

Raw Spectrum 22.665 (scan : 3334) Base Peak m/z 204.95 (Inten : 597,553)

Background No Background Spectrum

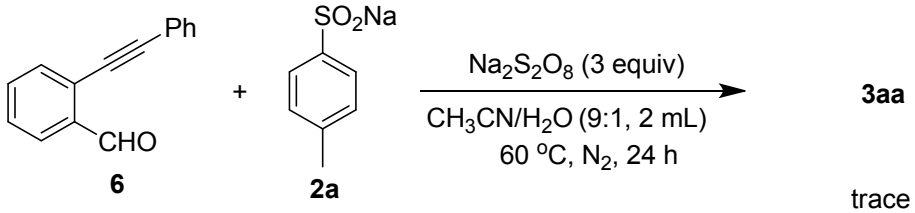
m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
50.05	5201	0.87	87.00	8383	1.40	121.90	2841	0.48
51.00	17935	3.00	88.05	20348	3.41	123.05	3996	0.67
52.05	3824	0.64	88.95	13574	2.27	124.00	3420	0.57
53.00	1129	0.19	89.95	3180	0.53	124.95	11612	1.94
54.00	570	0.10	91.00	53033	8.88	126.00	21060	3.52
55.00	601	0.10	92.05	6933	1.16	126.95	15390	2.58
57.05	1135	0.19	92.95	800	0.13	128.00	2900	0.49
58.80	906	0.15	94.15	1015	0.17	129.00	2	0.00
59.80	38	0.01	94.90	113	0.02	130.00	334	0.06
60.80	444	0.07	95.95	2512	0.42	131.35	2294	0.38
62.00	5098	0.85	97.05	1136	0.19	131.90	924	0.15
63.05	16433	2.75	97.95	6569	1.10	132.90	4106	0.69
64.00	4106	0.69	99.00	9369	1.57	133.95	833	0.14
65.00	46836	7.84	99.95	3700	0.62	134.90	1953	0.33
66.05	2444	0.41	100.95	6967	1.17	136.05	1083	0.18
67.00	3234	0.54	102.15	4601	0.77	137.00	5873	0.98
68.40	906	0.15	103.05	1876	0.31	137.95	4938	0.83
69.95	1061	0.18	103.80	2193	0.37	138.95	28028	4.69
71.25	886	0.15	105.00	5897	0.99	139.95	2918	0.49
72.00	71	0.01	106.00	500	0.08	140.90	3398	0.57
73.05	4910	0.82	107.00	1654	0.28	141.50	788	0.13
74.05	8556	1.43	108.80	1025	0.17	142.45	842	0.14
75.00	20807	3.48	109.95	2568	0.43	144.50	284	0.05
76.00	12166	2.04	110.95	4863	0.81	145.50	476	0.08
77.00	32570	5.45	111.95	2518	0.42	146.10	534	0.09
78.00	5586	0.93	113.05	4157	0.70	147.15	2385	0.40
79.10	1268	0.21	113.95	954	0.16	148.05	1256	0.21
80.10	108	0.02	115.00	4297	0.72	149.00	13646	2.28
81.20	1180	0.20	117.00	578	0.10	150.00	100562	16.83
81.80	338	0.06	117.80	95	0.02	151.00	190737	31.92
82.85	1230	0.21	118.75	1333	0.22	152.00	30337	5.08
84.85	970	0.16	119.85	1664	0.28	152.95	2957	0.49
86.00	4990	0.84	120.95	1131	0.19	153.90	1241	0.21

155.10	1849	0.31	199.10	946	0.16	247.60	820	0.14
156.05	1193	0.20	200.65	833	0.14	248.90	2534	0.42
157.00	1351	0.23	201.70	16	0.00	250.00	3911	0.65
158.00	8	0.00	202.70	126	0.02	250.95	2462	0.41
159.00	367	0.06	204.05	2951	0.49	252.00	12153	2.03
160.50	822	0.14	204.95	597553	100.00	252.90	8087	1.35
161.95	2419	0.40	205.95	117703	19.70	253.90	2228	0.37
163.00	10150	1.70	206.95	369592	61.85	254.95	11307	1.89
163.95	7285	1.22	207.95	66063	11.06	255.80	2038	0.34
165.00	33695	5.64	208.95	54994	9.20	256.95	7390	1.24
166.00	4617	0.77	210.00	8735	1.46	257.90	710	0.12
166.95	919	0.15	210.95	29927	5.01	258.80	1106	0.19
168.00	273	0.05	211.95	5181	0.87	260.40	782	0.13
170.00	758	0.13	213.10	1764	0.30	261.00	426	0.07
172.00	54	0.01	215.10	830	0.14	261.95	1197	0.20
173.05	1336	0.22	217.10	258	0.04	263.00	4330	0.72
174.00	16945	2.84	218.10	356	0.06	263.95	1947	0.33
175.00	37050	6.20	219.95	1923	0.32	264.95	8370	1.40
176.00	494474	82.75	220.95	71669	11.99	265.95	2228	0.37
177.00	224878	37.63	221.95	13600	2.28	266.90	4018	0.67
178.00	34545	5.78	223.00	43126	7.22	268.05	1761	0.29
179.00	4018	0.67	223.95	8275	1.38	269.10	415	0.07
179.95	1194	0.20	224.95	3566	0.60	270.10	852	0.14
181.10	1916	0.32	226.05	1653	0.28	271.10	127	0.02
183.10	782	0.13	227.10	369	0.06	273.10	698	0.12
184.10	322	0.05	228.10	809	0.14	275.10	458	0.08
186.10	825	0.14	231.10	561	0.09	276.65	933	0.16
186.80	327	0.05	233.10	529	0.09	278.00	1274	0.21
187.80	999	0.17	234.10	111	0.02	279.05	1614	0.27
189.10	1798	0.30	235.95	980	0.16	279.95	3249	0.54
190.00	62	0.01	236.95	19661	3.29	281.00	13812	2.31
190.95	4106	0.69	237.90	4502	0.75	281.95	4997	0.84
192.05	1257	0.21	238.95	14481	2.42	282.95	6806	1.14
193.00	46118	7.72	239.85	2351	0.39	284.10	1682	0.28
194.00	8433	1.41	240.95	1821	0.30	285.10	258	0.04
195.00	6879	1.15	242.90	303	0.05	286.10	783	0.13
195.90	1876	0.31	243.90	342	0.06	288.10	199	0.03
197.10	2314	0.39	245.90	689	0.12	289.10	377	0.06

291.10	591	0.10	343.95	6825	1.14	402.00	316	0.05
292.90	2177	0.36	344.90	1636	0.27	404.00	612	0.10
294.00	10511	1.76	345.90	1834	0.31	405.45	800	0.13
295.00	64834	10.85	346.90	137	0.02	407.40	382	0.06
296.00	20490	3.43	347.90	39	0.01	408.40	140	0.02
297.00	38908	6.51	348.90	580	0.10	410.40	622	0.10
297.95	10218	1.71	350.90	415	0.07	413.40	478	0.08
299.00	2417	0.40	351.90	84	0.01	415.40	498	0.08
301.00	265	0.04	353.90	646	0.11	416.40	29	0.00
302.00	362	0.06	355.10	1111	0.19	418.40	641	0.11
304.00	599	0.10	356.10	46	0.01	420.40	122	0.02
307.00	697	0.12	357.10	905	0.15	421.40	358	0.06
309.00	444	0.07	358.90	705	0.12	423.40	569	0.10
310.40	754	0.13	359.95	101323	16.96	426.40	610	0.10
311.00	410	0.07	360.95	28214	4.72	428.40	420	0.07
312.00	13322	2.23	361.95	78844	13.19	429.40	290	0.05
313.00	3071	0.51	362.95	18403	3.08	431.40	694	0.12
314.00	6634	1.11	363.95	8825	1.48	434.40	524	0.09
315.05	2526	0.42	365.00	2362	0.40	436.40	422	0.07
316.10	92	0.02	367.00	585	0.10	437.40	66	0.01
317.10	342	0.06	368.00	30	0.01	439.40	631	0.11
318.10	257	0.04	370.00	655	0.11	441.40	84	0.01
320.10	594	0.10	372.00	138	0.02	442.40	393	0.07
323.10	562	0.09	373.00	441	0.07	444.40	532	0.09
324.90	3138	0.53	375.00	630	0.11	447.40	609	0.10
325.80	174	0.03	378.00	628	0.11	449.40	210	0.04
326.85	2271	0.38	380.00	316	0.05	450.40	298	0.05
328.00	1394	0.23	381.00	241	0.04	452.40	599	0.10
329.00	22	0.00	383.00	634	0.11	455.40	538	0.09
330.00	452	0.08	386.00	489	0.08	457.40	377	0.06
331.15	1108	0.19	388.00	431	0.07	458.40	122	0.02
333.20	370	0.06	389.00	212	0.04	460.40	657	0.11
334.20	228	0.04	391.00	678	0.11	462.40	5	0.00
336.20	614	0.10	393.00	153	0.03	463.40	446	0.07
339.20	521	0.09	394.00	449	0.08	465.40	489	0.08
340.95	1253	0.21	396.00	540	0.09	468.40	628	0.11
341.95	9229	1.54	399.00	630	0.11	470.40	170	0.03
342.90	3769	0.63	401.00	351	0.06	471.40	300	0.05

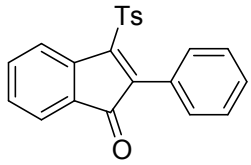
473.40	593	0.10	484.40	465	0.08	494.40	558	0.09
476.40	607	0.10	486.40	442	0.07	497.40	586	0.10
478.40	343	0.06	489.40	620	0.10	499.40	276	0.05
479.40	247	0.04	491.40	134	0.02	500.40	220	0.04
481.40	639	0.11	492.40	374	0.06			

(6) The reaction of **6** and **2a**.

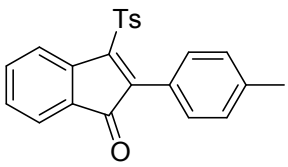


Under nitrogen, the mixture of 2-(phenylethynyl)benzaldehyde **6** (0.2 mmol), Sodium p-tolylsulfinate **2a** (0.4 mmol, 2.0 equiv), $Na_2S_2O_8$ (0.6 mmol, 3.0 equiv), CH_3CN (1.8 mL) and H_2O (0.2 mL) were added to the Schlenk-tube. After stirring at 60 °C for 24 h, the reaction mixture was concentrated in vacuum, no desired product **3aa** was detected.

5) Characterization Data

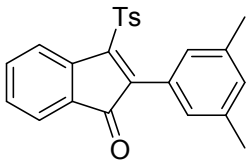


2-phenyl-3-tosyl-1H-inden-1-one (3aa): yellow solid, isolated yield 67% (48.3 mg), mp: 108.6-110.3 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.98 (d, *J* = 7.5Hz, 1H), 7.58-7.49 (m, 4H), 7.42-7.30 (m, 4H), 7.26-7.25 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H); 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.2, 151.3, 145.2, 141.1, 139.9, 136.8, 135.0, 130.4, 129.6, 129.5, 129.4, 128.8, 127.8, 127.6, 124.4, 123.9, 21.6. HRMS (ESI) m/z calcd for $C_{22}H_{17}O_3S^+$ $(M+H)^+$ 361.08929, found 361.08939.

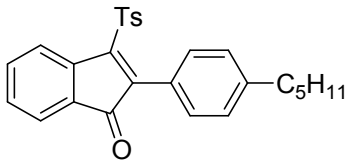


2-(p-tolyl)-3-tosyl-1H-inden-1-one (3ba): yellow solid, isolated yield 68% (50.9 mg), mp: 119.6-120.8 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.94 (d, *J* = 7.0 Hz, 1H), 7.59-7.55 (m, 3H), 7.49 (t, *J* =

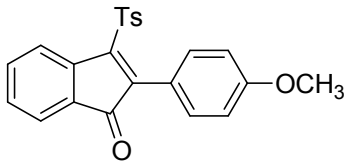
7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.19-7.15 (m, 6H), 2.40 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.4, 150.5, 145.1, 141.2, 140.1, 139.8, 137.0, 134.9, 130.4, 129.6, 129.3, 128.8, 128.3, 127.8, 124.8, 123.7, 21.6, 21.5. HRMS (ESI) m/z calcd for $C_{23}H_{19}O_3S^+$ $(M+H)^+$ 375.10494, found 375.10516.



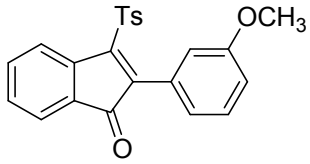
2-(3,5-dimethylphenyl)-3-tosyl-1H-inden-1-one (3ca): yellow solid, isolated yield 66% (51.2 mg); mp: 148.9-150.8 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.99 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 3H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 1H), 6.77 (s, 2H), 2.40 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.4, 151.1, 145.0, 141.2, 140.0, 137.0, 136.8, 134.9, 131.0, 129.3, 128.7, 127.8, 127.8, 127.6, 124.2, 123.8, 21.5, 21.1. HRMS (ESI) m/z calcd for $C_{24}H_{21}O_3S^+$ $(M+H)^+$ 389.12059, found 389.12076.



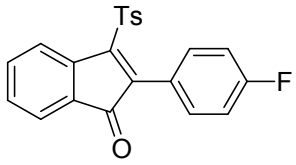
2-(4-pentylphenyl)-3-tosyl-1H-inden-1-one (3da): yellow solid, isolated yield 66% (56.8 mg), mp: 108.1-109.3 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.98 (d, *J* = 7.0 Hz, 1H), 7.55 (t, *J* = 4.0 Hz, 3H)), 7.49 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.21-7.16 (m, 4H), 7.11 (d, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.65 (s, 2H), 1.37 (s, 4H), 0.95 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.4, 150.6, 145.0, 144.8, 141.3, 140.0, 136.9, 134.9, 130.5, 129.4, 129.3, 128.7, 127.8, 127.6, 125.0, 124.3, 123.8, 35.8, 31.5, 30.9, 22.5, 21.5, 14.0. HRMS (ESI) m/z calcd for $C_{27}H_{27}O3S^+$ $(M+H)^+$ 431.16754, found 431.16760.



2-(4-methoxyphenyl)-3-tosyl-1H-inden-1-one (3ea): yellow soild, isolated yield 71% (55.4mg), mp: 86.5-87.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.93 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.48 (td, *J* = 8.0 Hz, 0.5 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.29-7.26 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.6, 160.9, 149.4, 145.1, 141.5, 139.8, 137.1, 135.0, 132.5, 129.6, 129.1, 128.7, 127.7, 124.3, 123.6, 119.9, 113.2, 55.2, 21.5. HRMS (ESI) m/z calcd for $C_{23}H_{19}O_4S^+$ $(M+H)^+$ 391.09986, found 391.09946.

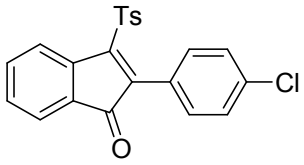


2-(3-methoxyphenyl)-3-tosyl-1H-inden-1-one (3fa): yellow solid, isolated yield 67% (52.2 mg); mp: 125.1-127.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.90 (d, *J* = 7.5 Hz, 1H), 7.47-7.46 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.17-7.14 (m, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 7.0 Hz, 1H), 6.64 (s, 1H), 3.69 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.0, 158.7, 151.6, 145.2, 141.1, 139.6, 136.7, 135.0, 129.5, 129.0, 128.7, 128.6, 127.9, 124.3, 123.9, 122.7, 115.5, 115.5, 55.2, 21.5. HRMS (ESI) m/z calcd for $C_{23}H_{19}O_4S^+$ $(M+H)^+$ 391.09986, found 391.09946.

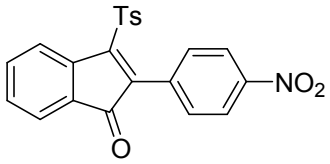


2-(4-fluorophenyl)-3-tosyl-1H-inden-1-one (3ga): yellow solid, isolated yield 64% (48.5 mg); mp: 89.6-90.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.96 (d, *J* = 7.0 Hz, 1H), 7.56 (d, *J* = 7.5 Hz,

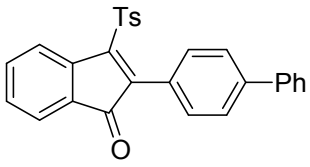
3H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.33-7.28 (m, 3H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.1, 163.5 (d, *J* = 249.0 Hz), 151.3, 145.4, 141.0, 138.8, 136.8, 135.1, 132.7 (d, *J* = 8.5 Hz), 129.7, 129.5, 128.6, 127.7, 124.4, 123.9, 123.7 (d, *J* = 3.0 Hz), 114.8 (d, *J* = 21.7 Hz), 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{16}FO_3S^+$ $(M+H)^+$ 379.07987, found 379.07977.



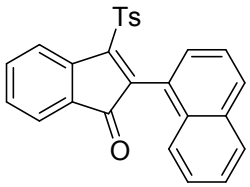
2-(4-chlorophenyl)-3-tosyl-1H-inden-1-one (3ha): yellow solid, isolated yield 68% (52.8 mg), mp: 97.5-98.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.95 (d, *J* = 7.5 Hz, 1H), 7.58-7.56 (m, 3H), 7.51 (td, *J* = 7.5 Hz, 1 Hz, 1H), 7.35-7.32 (m, 3H), 7.23-7.22 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.8, 151.6, 145.6, 140.9, 138.5, 136.7, 135.9, 135.1, 131.9, 129.7, 129.7, 128.7, 127.9, 127.8, 126.2, 124.5, 123.9, 21.6. HRMS (ESI) m/z calcd for $C_{22}H_{16}ClO_3S^+$ $(M+H)^+$ 395.05032, found 395.05032.



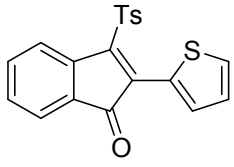
2-(4-nitrophenyl)-3-tosyl-1H-inden-1-one (3ia): yellow solid, isolated yield 40% (32.7 mg); mp: 181.0-182.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.22 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 3H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.0, 153.2, 148.1, 146.0, 140.4, 137.4, 136.4, 135.3, 134.7, 131.6, 130.2, 130.0, 128.7, 127.9, 124.8, 124.2, 122.6, 21.6.



2-([1,1'-biphenyl]-4-yl)-3-tosyl-1H-inden-1-one (3ja): yellow solid, isolated yield 62% (54.1 mg), mp: 161.4-162.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.00 (d, *J* = 7.0 Hz, 1H), 7.65-7.60 (m, 7H), 7.54-7.47 (m, 3H), 7.41-7.38 (m, 3H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.2, 151.1, 145.2, 142.3, 141.2, 140.3, 139.4, 136.8, 135.0, 131.0, 129.6, 129.4, 128.8, 128.7, 127.8, 127.7, 127.0, 126.7, 126.2, 124.4, 123.8, 21.5. HRMS (ESI) m/z calcd for $C_{28}H_{21}O_3S^+$ $(M+H)^+$ 437.12059, found 437.12030.

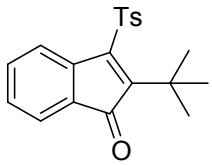


2-(naphthalen-1-yl)-3-tosyl-1H-inden-1-one (3ka): yellow solid, isolated yield 40% (32.8 mg); mp: 179.6-180.8 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.11 (d, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 6.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.43-7.36 (m, 3H), 7.27-7.23 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 2H), 2.08 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.2, 154.6, 144.7, 140.9, 138.8, 135.2, 135.0, 133.0, 131.4, 129.8, 129.4, 128.9, 128.8, 128.5, 128.1, 128.0, 126.0, 125.9, 125.4, 124.7, 124.5, 124.1, 21.3. HRMS (ESI) m/z calcd for $C_{26}H_{19}O_3S^+$ $(M+H)^+$ 411.10494, found 411.10474.

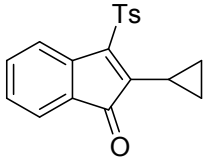


2-(thiophen-2-yl)-3-tosyl-1H-inden-1-one (3la): black solid, isolated yield 20% (14.6 mg), mp: 161.2-162.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.01-7.98 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 5 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.17 (t, *J* = 4.5 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.7,

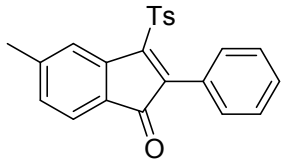
146.0, 145.3, 142.1, 137.1, 135.5, 135.3, 133.0, 132.6, 129.8, 129.1, 128.4, 128.0, 127.4, 127.3, 124.6, 124.0, 21.6.



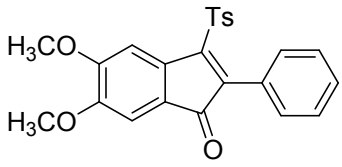
2-(tert-butyl)-3-tosyl-1H-inden-1-one (3ma): yellow solid, isolated yield 21% (14.2 mg), mp: 121.8-122.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.39 (d, *J* = 7.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.21-7.18 (m, 1H), 7.14-7.13 (m, 3H), 6.51 (d, *J* = 7.0 Hz, 1H), 2.41 (s, 3H), 1.16 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 198.6, 154.3, 147.8, 141.5, 137.7, 133.3, 132.3, 130.0, 128.9, 128.0, 127.8, 121.7, 120.4, 33.7, 30.7, 21.3.



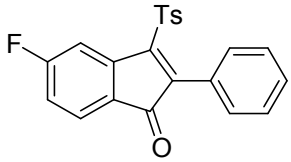
2-cyclopropyl-3-tosyl-1H-inden-1-one (3na): yellow solid, isolated yield 25% (16.2 mg), mp: 85.2-86.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.92 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.37-7.35 (m, 4H), 7.15 (t, *J* = 7.0 Hz, 1H), 2.93-2.88 (m, 1H), 2.43 (s, 3H), 1.55 (s, 2H), 2.37 (d, *J* = 5.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.6, 148.5, 145.4, 145.3, 140.9, 137.9, 135.0, 133.1, 129.0, 128.2, 127.3, 123.8, 121.6, 21.7, 11.6, 10.0.



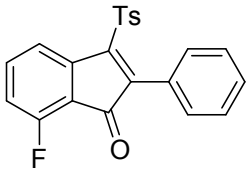
5-methyl-2-phenyl-3-tosyl-1H-inden-1-one (3oa): yellow solid, isolated yield 63% (47.1 mg), mp: 162.9-163.4 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.82 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.35-7.32 (m, 2H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 3H), 2.44 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.7, 151.0, 146.4, 145.1, 141.6, 140.4, 137.0, 130.4, 129.5, 129.5, 129.3, 128.0, 127.8, 127.5, 126.4, 125.1, 124.4, 22.3, 21.5. HRMS (ESI) m/z calcd for $C_{23}H_{19}O_3S^+$ $(M+H)^+$ 375.10494, found 375.10516.



5,6-dimethoxy-2-phenyl-3-tosyl-1H-inden-1-one (3pa): back solid, isolated yield 45% (37.8 mg), mp: 206.4-207.3 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.58 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.13-7.09 (m, 3H), 4.01 (s, 3H), 3.88 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.3, 153.9, 149.7, 149.4, 145.1, 139.2, 136.9, 136.1, 130.4, 129.4, 129.3, 128.0, 127.7, 127.5, 120.9, 108.2, 108.0, 56.5, 56.3, 21.5. HRMS (ESI) m/z calcd for $C_{24}H_{21}O_5S^+$ $(M+H)^+$ 421.11042, found 421.11057.

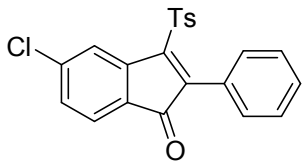


5-fluoro-2-phenyl-3-tosyl-1H-inden-1-one (3qa): yellow solid, isolated yield 65% (49.1 mg); mp: 159.9-161.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.75 (d, *J* = 8.5 Hz, 1H), 7.58-7.55 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.26 (d, *J* = 6.5 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.98-6.95 (m, 1H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 192.3, 167.0 (d, *J* = 255.1 Hz), 149.5, 145.4, 144.3 (d, *J* = 10.6 Hz), 141.4, 136.7, 130.4, 129.7, 129.6, 127.8, 127.6, 127.6, 126.2 (d, *J* = 10.0 Hz), 124.6, 115.4 (d, *J* = 23.4 Hz), 113.0 (d, *J* = 27.6 Hz), 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{16}FO_3S^+$ $(M+H)^+$ 379.07987, found 379.07977.

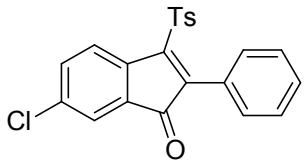


7-fluoro-2-phenyl-3-tosyl-1H-inden-1-one (3ra): yellow soild, isolated yield 70% (52.9 mg), mp: 160.3-161.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.84 (d, *J* = 6.0 Hz, 1H), 7.51 (d, *J* = 6.0 Hz, 3H), 7.40 (d, *J* = 5.5 Hz, 1H), 7.34 (s, 2H), 7.24 (d, *J* = 5.5 Hz, 2H), 7.12 (d, *J* = 6.5 Hz, 2H), 6.98

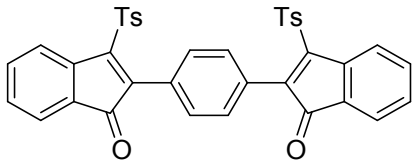
(s, 1H), 2.32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 190.0, 158.4 (d, *J* = 265.4 Hz), 150.5 (d, *J* = 3.9 Hz), 145.3, 142.6, 140.6, 137.5 (d, *J* = 8.6 Hz), 136.6, 130.4, 129.6, 129.6, 127.8, 127.5, 127.4, 120.3, 118.7 (d, *J* = 20.5 Hz), 114.4 (d, *J* = 13.1 Hz), 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{16}FO_3S^+$ $(M+H)^+$ 379.07987, found 379.07977.



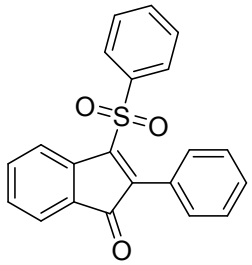
5-chloro-2-phenyl-3-tosyl-1H-inden-1-one (3sa): yellow solid, isolated yield 60% (47.2 mg), mp: 184.0-185.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.02 (s, 1H), 7.49 (t, *J* = 7.5 Hz 3H), 7.41 (t, *J* = 6.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.25-7.23 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 192.6, 150.2, 145.4, 142.9, 141.4, 141.0, 136.5, 130.4, 129.7, 129.6, 129.2, 127.8, 127.6, 127.4, 126.8, 125.1, 124.6, 21.6. HRMS (ESI) m/z calcd for $C_{22}H_{16}ClO_3S^+$ $(M+H)^+$ 395.05032, found 395.05032.



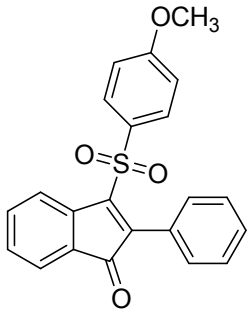
6-chloro-2-phenyl-3-tosyl-1H-inden-1-one (3ta): yellow solid, isolated yield 65% (51.4 mg); mp: 186.6-187.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.93 (d, *J* = 8.0 Hz, 1H), 7.51-7.49 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40-7.39 (m, 1H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.0, 151.2, 145.4, 139.8, 139.2, 136.5, 135.8, 134.1, 130.4, 130.3, 129.6, 127.8, 127.7, 127.6, 127.4, 124.8, 124.7, 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{16}ClO_3S^+$ $(M+H)^+$ 395.05032, found 395.05032.



2,2'-(1,4-phenylene)bis(3-tosyl-1H-inden-1-one) (3ua): yellow solid, isolated yield 53% (68.2 mg), mp: > 250 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.04 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.56-7.53 (m, 6H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.23 (s, 4H), 7.19 (d, *J* = 8.0 Hz, 4H), 2.34 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.8, 152.3, 145.6, 141.1, 139.2, 136.6, 135.1, 129.8, 129.7, 129.7, 129.2, 128.8, 127.9, 124.5, 124.1, 21.6.

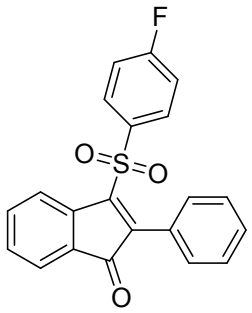


2-phenyl-3-(phenylsulfonyl)-1H-inden-1-one (3ab): yellow solid, isolated yield 56% (38.8 mg); mp: 98.5-99.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.00 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.53-7.48 (m, 2H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.35 (t, *J* = 6.5 Hz, 5H), 7.25 (d, *J* = 6.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.1, 151.0, 141.1, 140.3, 139.8, 135.1, 134.0, 130.4, 129.6, 129.5, 128.9, 128.7, 127.7, 127.6, 124.3, 123.9. HRMS (ESI) m/z calcd for $C_{21}H_{15}O_3S^+$ $(M+H)^+$ 347.07364, found 347.07385.

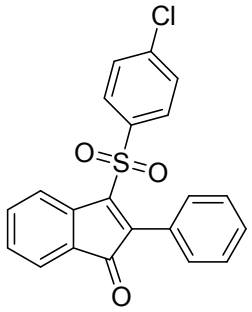


3-((4-methoxyphenyl)sulfonyl)-2-phenyl-1H-inden-1-one (3ac): yellow solid, isolated yield 55% (41.4 mg), mp: 90.8-91.4 °C;; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.99 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.40-7.30 (m, 4H), 7.25 (d, *J* = 7.5 Hz, 2H), 6.78 (d, *J* = 6.5 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ; 194.3, 164.0, 151.7, 141.2, 139.5, 135.0, 131.1, 130.4, 130.2, 129.5, 129.4, 128.8, 127.9, 127.6, 124.3, 123.9, 114.2, 55.6. HRMS

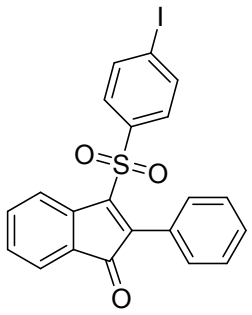
(ESI) m/z calcd for $C_{22}H_{17}O_4S^+$ $(M+H)^+$ 377.08421, found 377.08441.



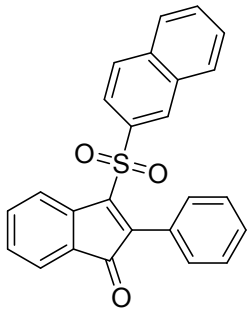
3-((4-fluorophenyl)sulfonyl)-2-phenyl-1H-inden-1-one (3ad): yellow solid, isolated yield 59% (43.0 mg); mp: 135.6-136.4 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.00 (d, *J* = 7.5 Hz, 1H), 7.64-7.62 (m, 2H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.36-7.32 (m, 3H), 7.22 (d, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 8.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.9, 165.8 (d, *J* = 256.1 Hz), 151.1, 140.9, 140.0, 135.7, 135.1, 130.7 (d, *J* = 9.6 Hz), 130.3, 129.6, 128.6, 127.7, 127.6, 124.5, 123.9, 116.2, 116.1. HRMS (ESI) m/z calcd for $C_{21}H_{14}FO_3S^+$ $(M+H)^+$ 365.06422, found 365.06461.



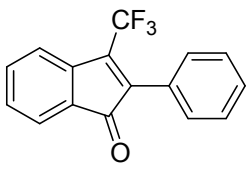
3-((4-chlorophenyl)sulfonyl)-2-phenyl-1H-inden-1-one (3ae): yellow solid, isolated yield 42% (31.9 mg), mp: 146.6-147.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.99 (d, *J* = 7.5 Hz, 1H), 7.64-7.62 (m, 2H), 7.60 (d, *J* = 7.0 Hz, 1H), 7.56-7.51 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38-7.34 (m, 3H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.9, 150.9, 140.9, 140.9, 140.3, 138.2, 135.2, 130.4, 129.7, 129.7, 129.2, 129.2, 128.6, 127.8, 127.6, 124.6, 123.9. HRMS (ESI) m/z calcd for $C_{21}H_{14}ClO_3S^+$ $(M+H)^+$ 381.03467, found 381.03470.



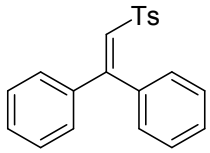
3-((4-iodophenyl)sulfonyl)-2-phenyl-1H-inden-1-one (3af): yellow solid, isolated yield 43% (40.6 mg); mp: 174.8-176.4 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.98 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.22(d, *J* = 7.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 193.8, 150.7, 140.9, 140.3, 139.3, 138.1, 135.1, 130.3, 129.7, 129.0, 128.6, 127.7, 127.6, 124.6, 123.9, 102.3. HRMS (ESI) m/z calcd for $C_{21}H_{14}IO_3S^+$ $(M+H)^+$ 472.97028, found 472.96951.



3-(naphthalen-2-ylsulfonyl)-2-phenyl-1H-inden-1-one (3ag): yellow solid, isolated yield 52% (41.2 mg), mp: 158.6-159.4 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 8.16 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.81-7.76 (m, 3H), 7.62-7.50 (m, 5H), 7.32-7.21 (m, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.1, 151.2, 141.2, 140.2, 136.2, 135.2, 135.1, 131.6, 130.3, 130.2, 129.5, 129.5, 129.4, 129.3, 128.7, 127.8, 127.7, 127.6, 127.5, 124.4, 124.0, 122.1. HRMS (ESI) m/z calcd for $C_{25}H_{17}O_3S^+$ $(M+H)^+$ 397.08929, found 397.08902.



3-(naphthalen-2-ylsulfonyl)-2-phenyl-1H-inden-1-one (4): yellow solid, isolated yield 35% (19.2 mg), mp: 87.6-88.4 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.63 (d, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.45-7.44 (m, 3H), 7.40-7.34 (m, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 194.7, 140.7 (d, *J* = 1.8 Hz), 140.4 (q, *J* = 35.6 Hz), 137.8 (q, *J* = 4.8 Hz), 134.8, 129.9 (d, *J* = 1.8 Hz), 129.6, 129.5, 128.8, 128.3, 128.1, 124.3, 122.5 (q, *J* = 271.6 Hz), 122.2 (d, *J* = 1.8 Hz).



(2-tosylethene-1,1-diyl)dibenzene (5)[4]: White solid, isolated yield 13% (17.3 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 7.48 (d, *J* = 7.0 Hz, 2H), 7.38-7.35 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 4H), 7.20 (d, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.0 Hz, 2H), 7.0 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ: 154.7, 143.7, 139.2, 138.6, 135.4, 130.2, 129.7, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 127.7, 21.5.

6) References

[1] (a) Letsinger, L. R.; Feare, E. T.; Savereide, T. J.; Nazy, J. R. *J. Org. Chem*. **1961**, *26*, 1271. (b) Zhang, H.-R.; Wang, K. K.; *J. Org. Chem*. **1990**, *64*, 7996. (c) Song, Y. P.; Shen, D. G.; Xu, G. Y. *Tetrahedron Letters*. **2014**, *55*, 639.

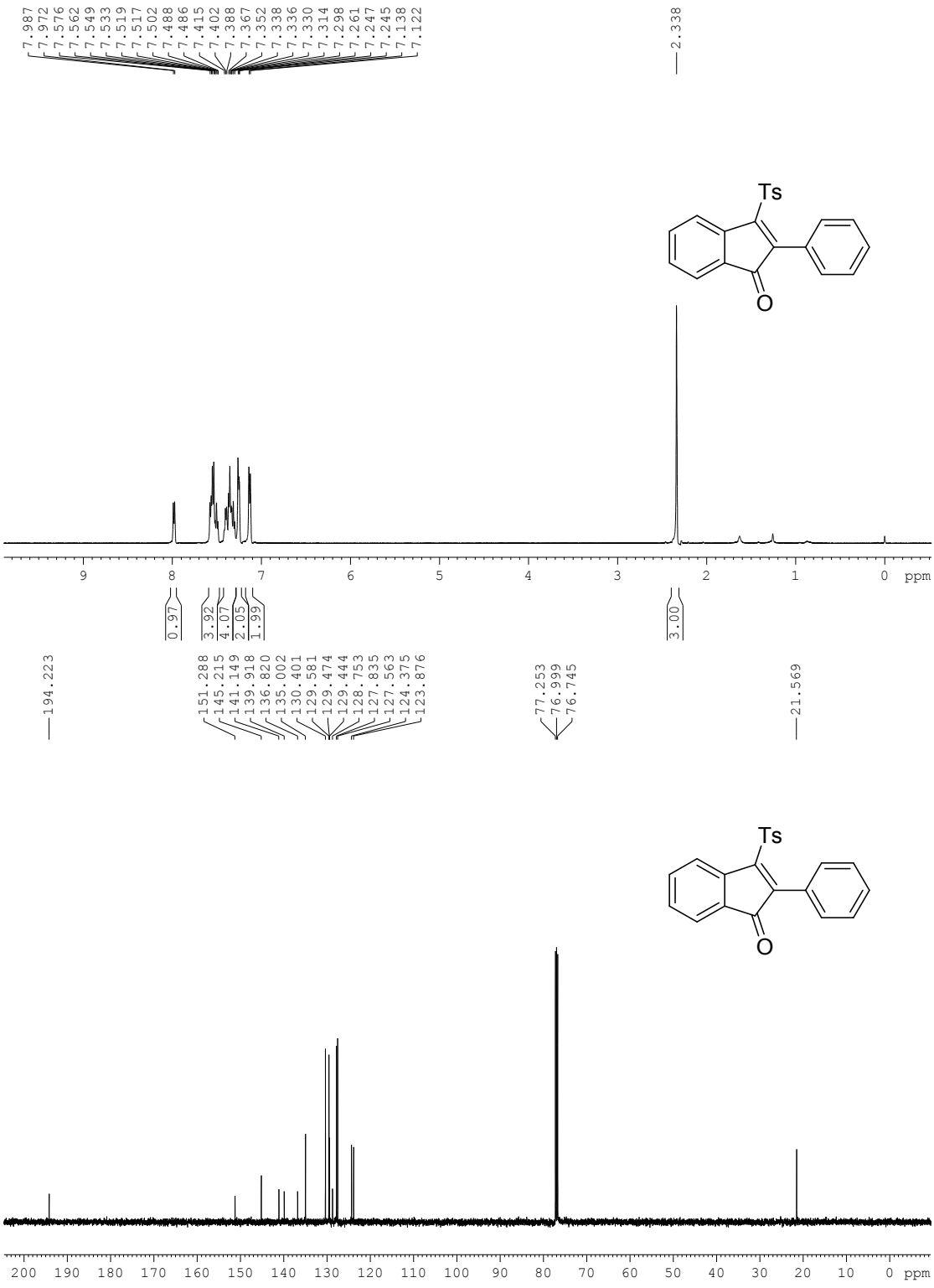
[2] Madabhushi, S.; Jillella, R.; Sriramojua, V.; Singh, R. *Green Chem.*, **2014,** *16,* 3125.

[3] (a) Liu, J.; Zhou, X.; Rao, H.; Xiao, F.; Li, C.-J.; Deng, G.-J. *Chem. Eur. J*. **2011**, *17*, 7996; (b) Liu, L. K.; Chi, Y.; Jen, K.-Y. *J. Org. Chem*. **1980**, *45*, 406.

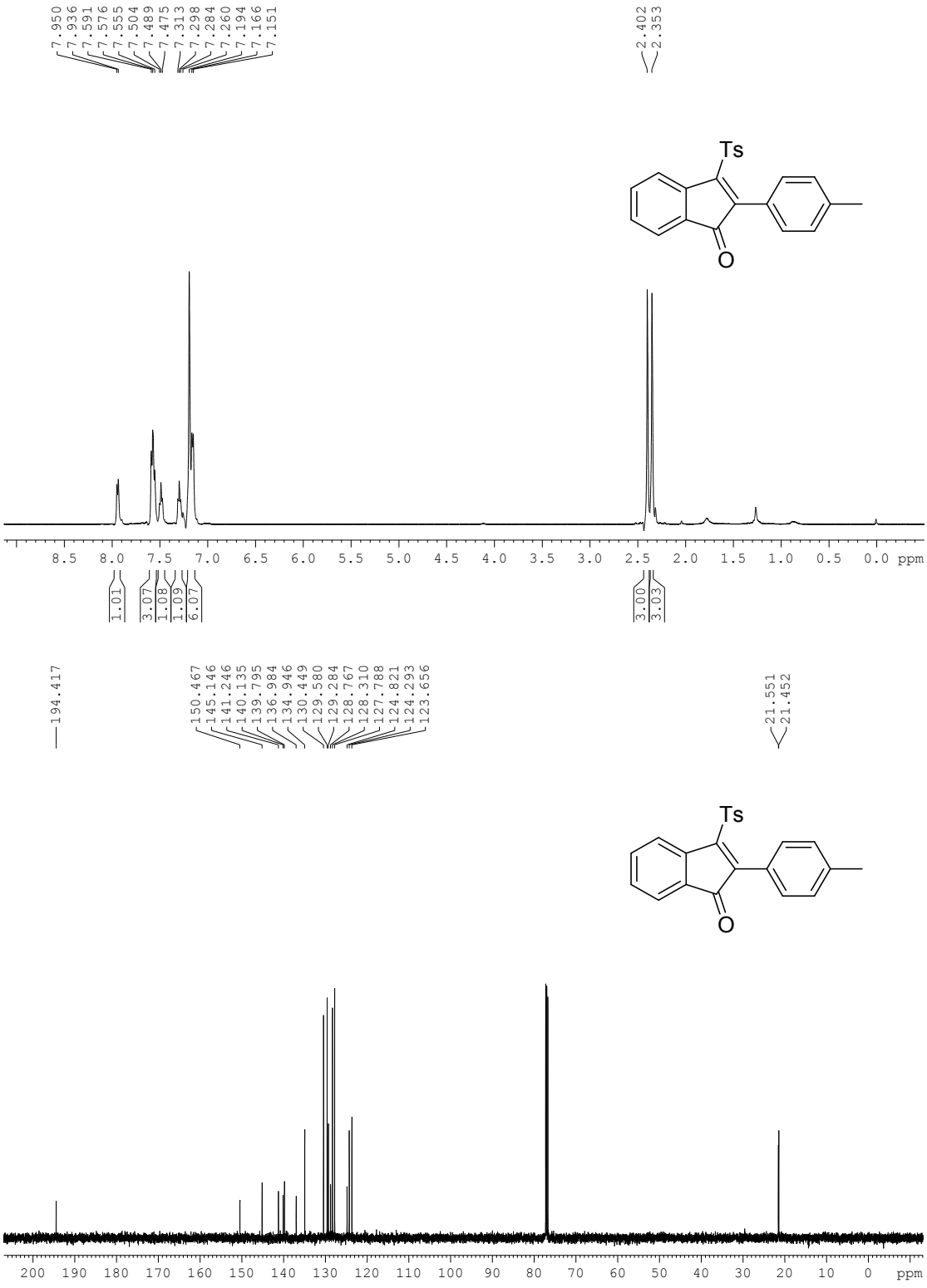
[4] Kadari, L.; Palakodety, R. K.; Yallapragada, L. P. *Org. Lett.* **2017**, *19*, 2580.

7) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

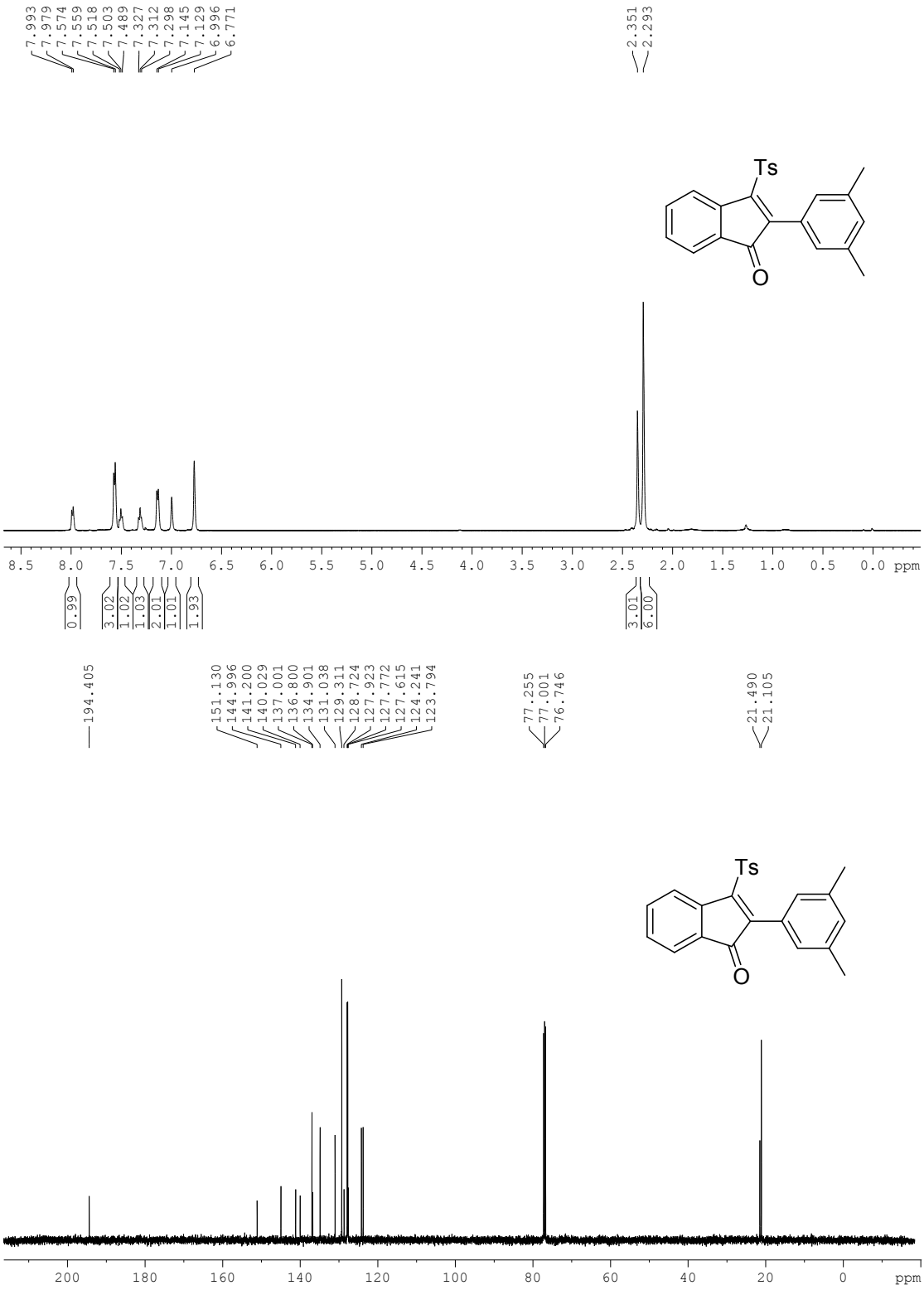
^{1}H and ^{13}C Spectrum of Compound **3aa**



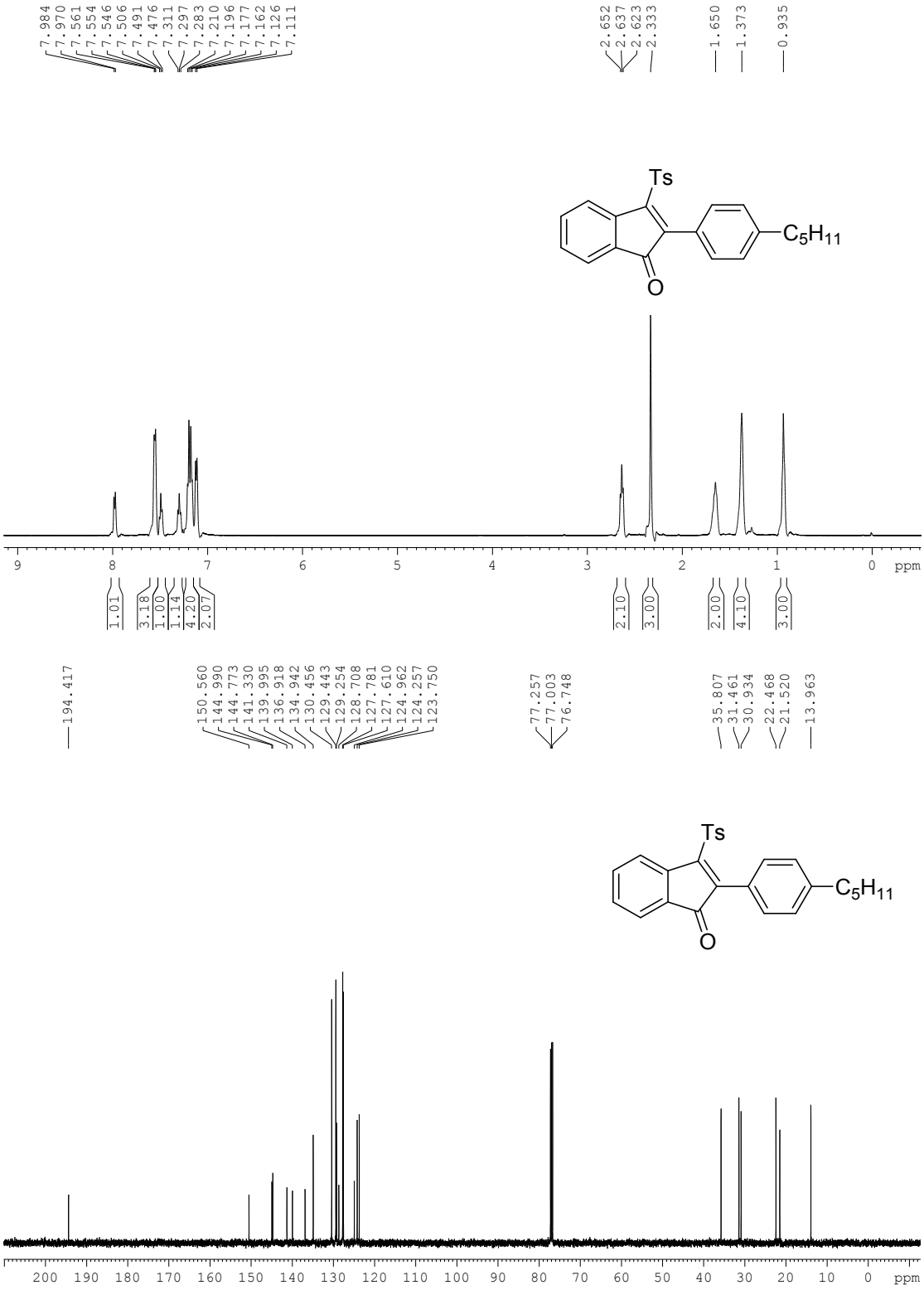
^{1}H and ^{13}C Spectrum of Compound **3ba**



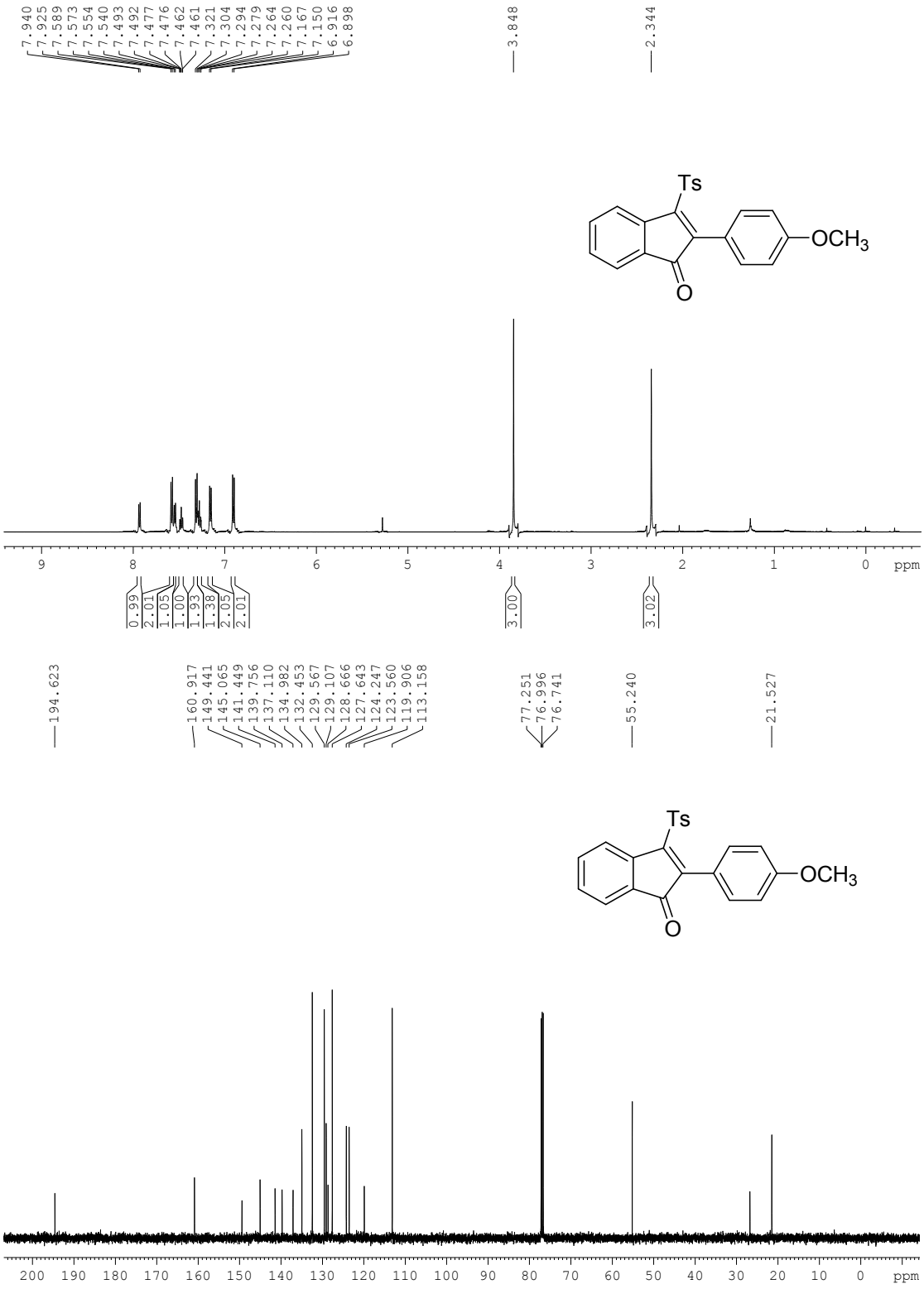
^{1}H and ^{13}C Spectrum of Compound **3ca**



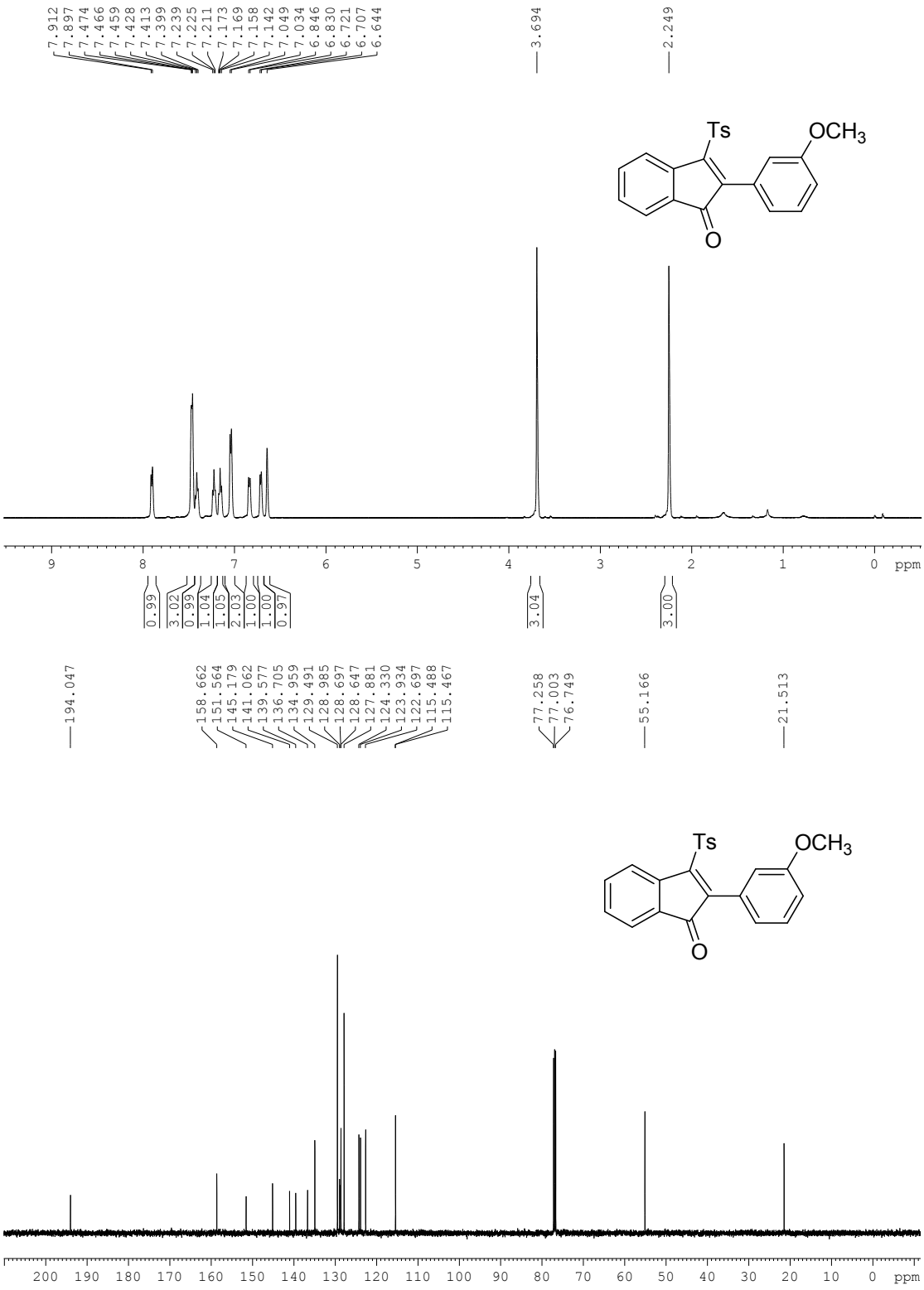
^{1}H and ^{13}C Spectrum of Compound **3da**



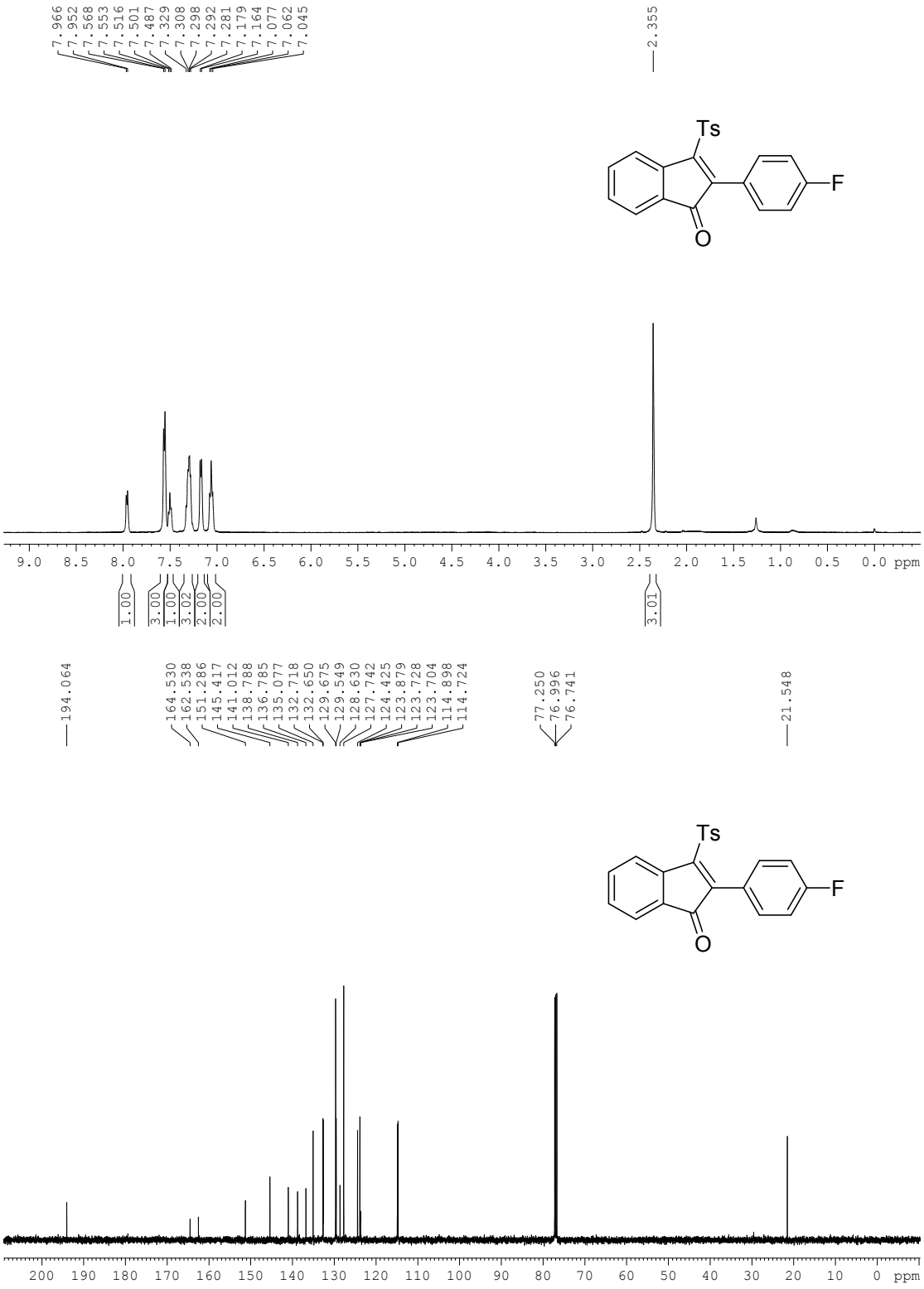
^{1}H and ^{13}C Spectrum of Compound **3ea**



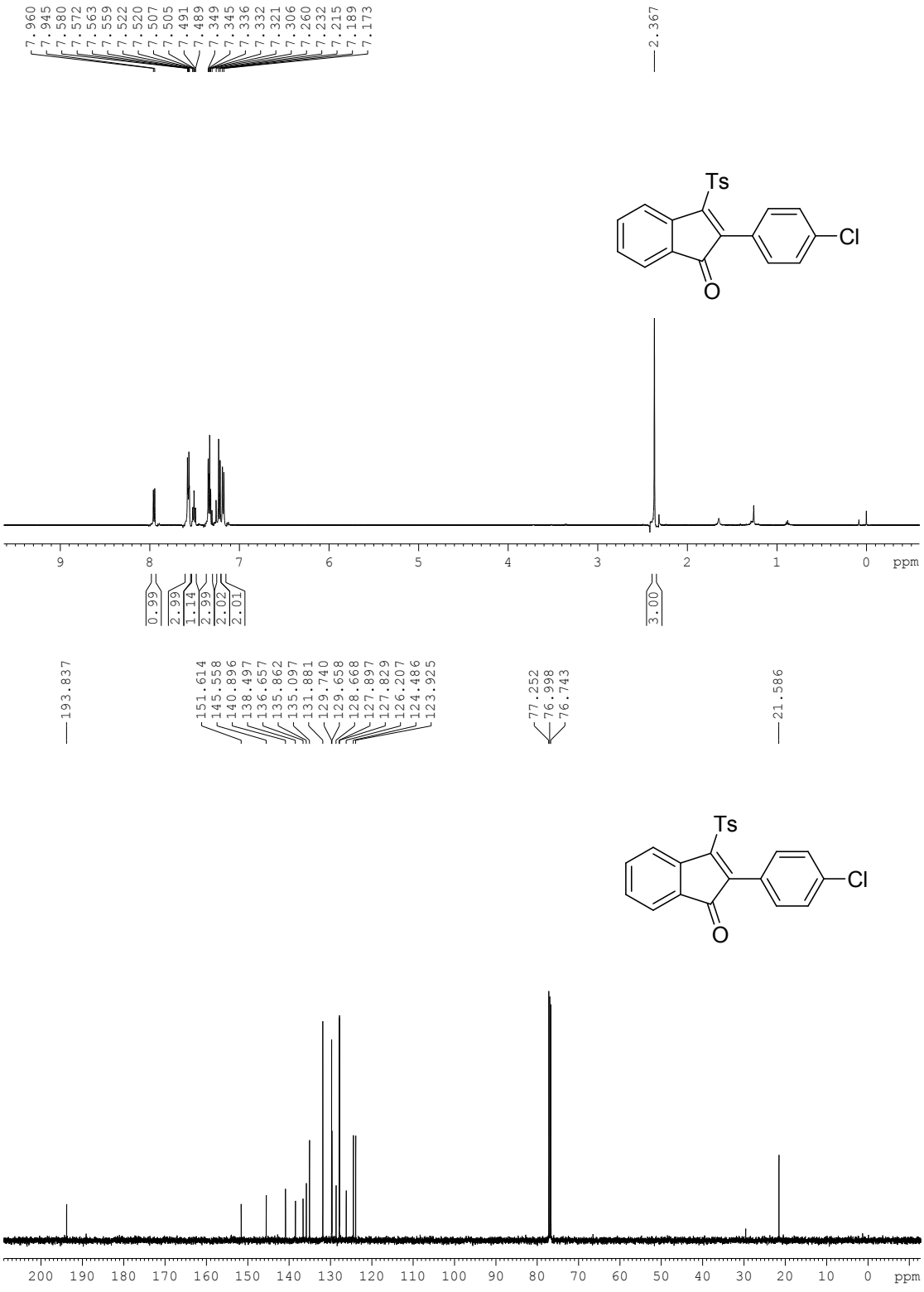
^{1}H and ^{13}C Spectrum of Compound **3fa**



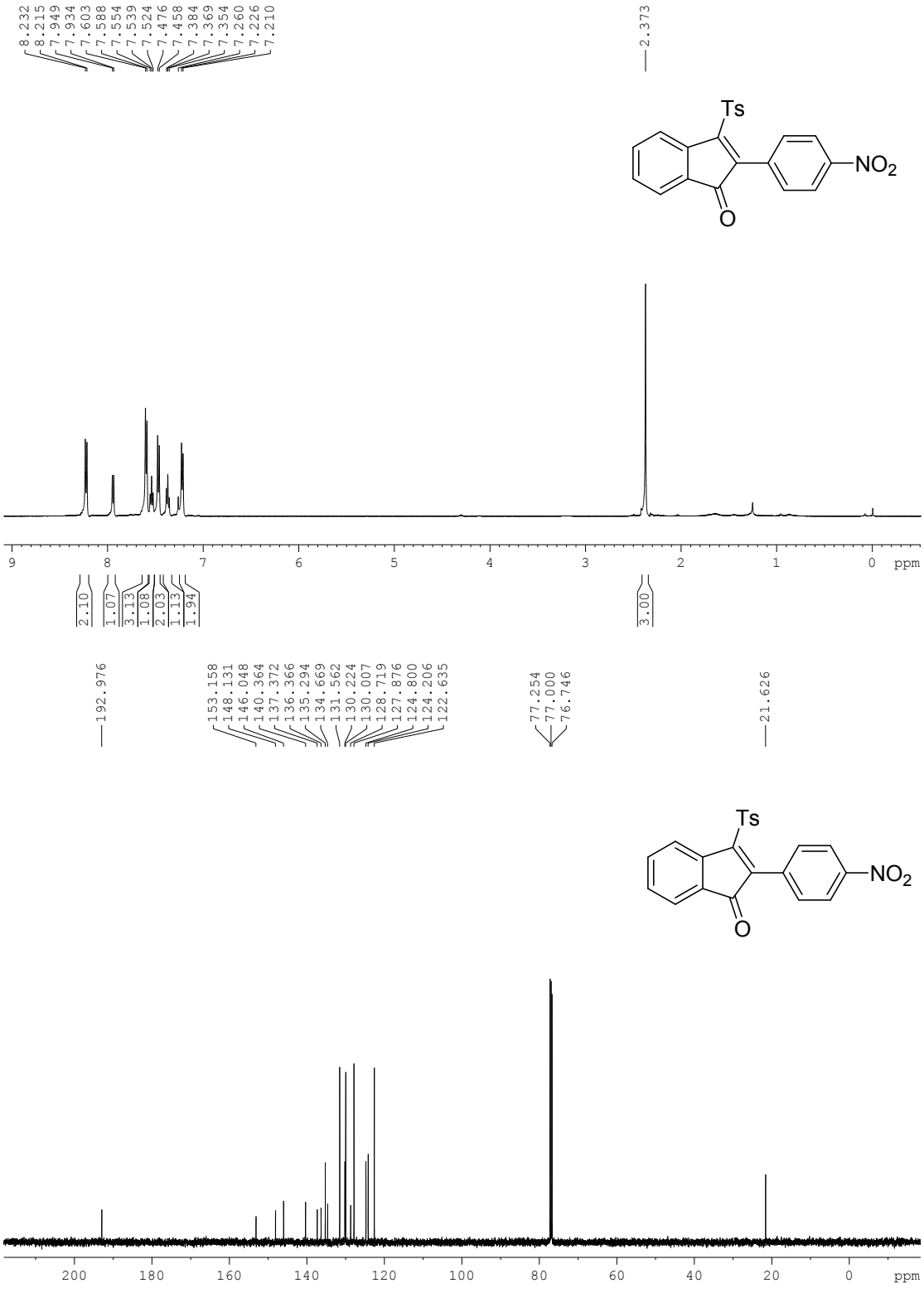
^{1}H and ^{13}C Spectrum of Compound **3ga**



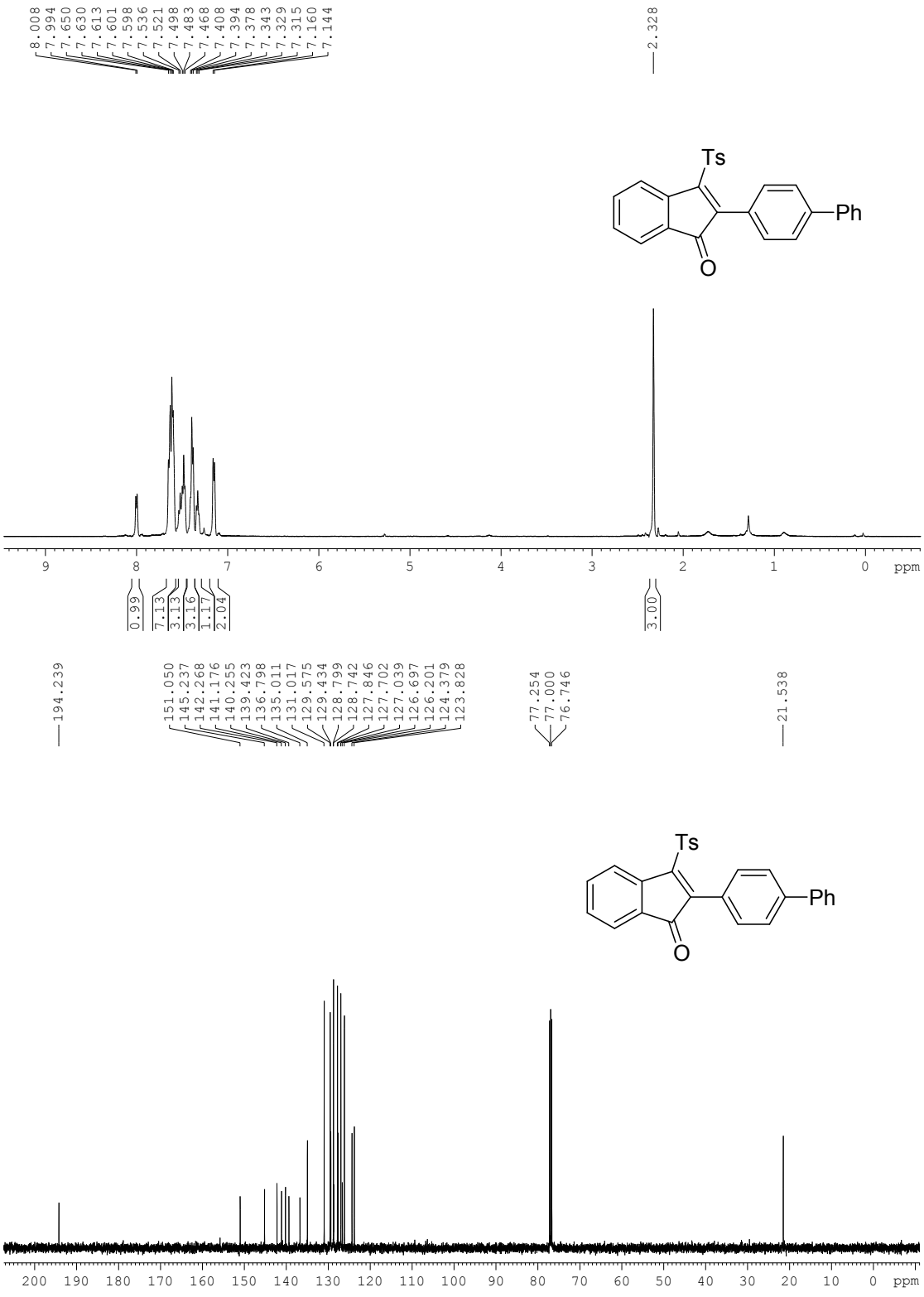
^{1}H and ^{13}C Spectrum of Compound **3ha**



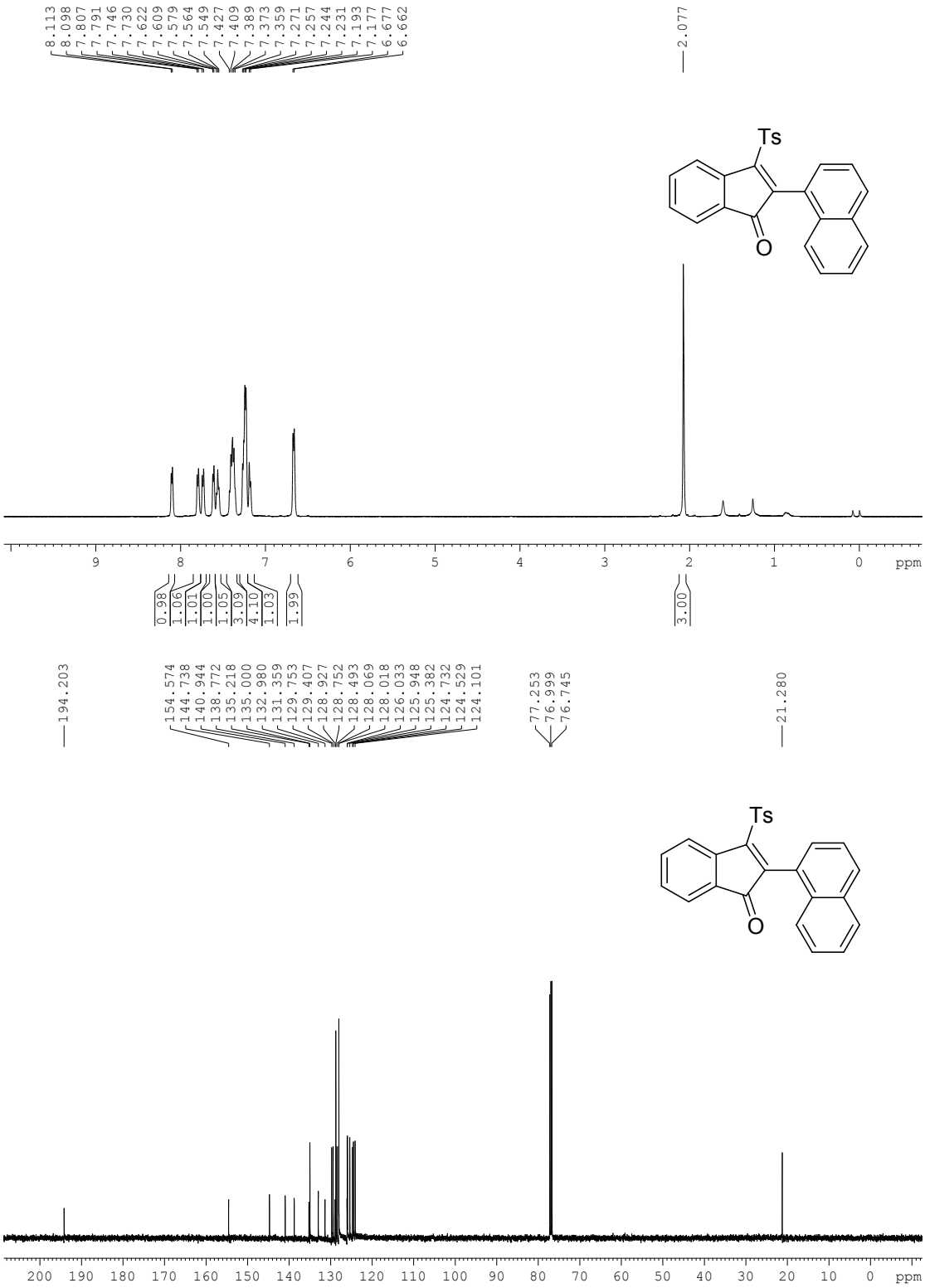
^{1}H and ^{13}C Spectrum of Compound **3ia**



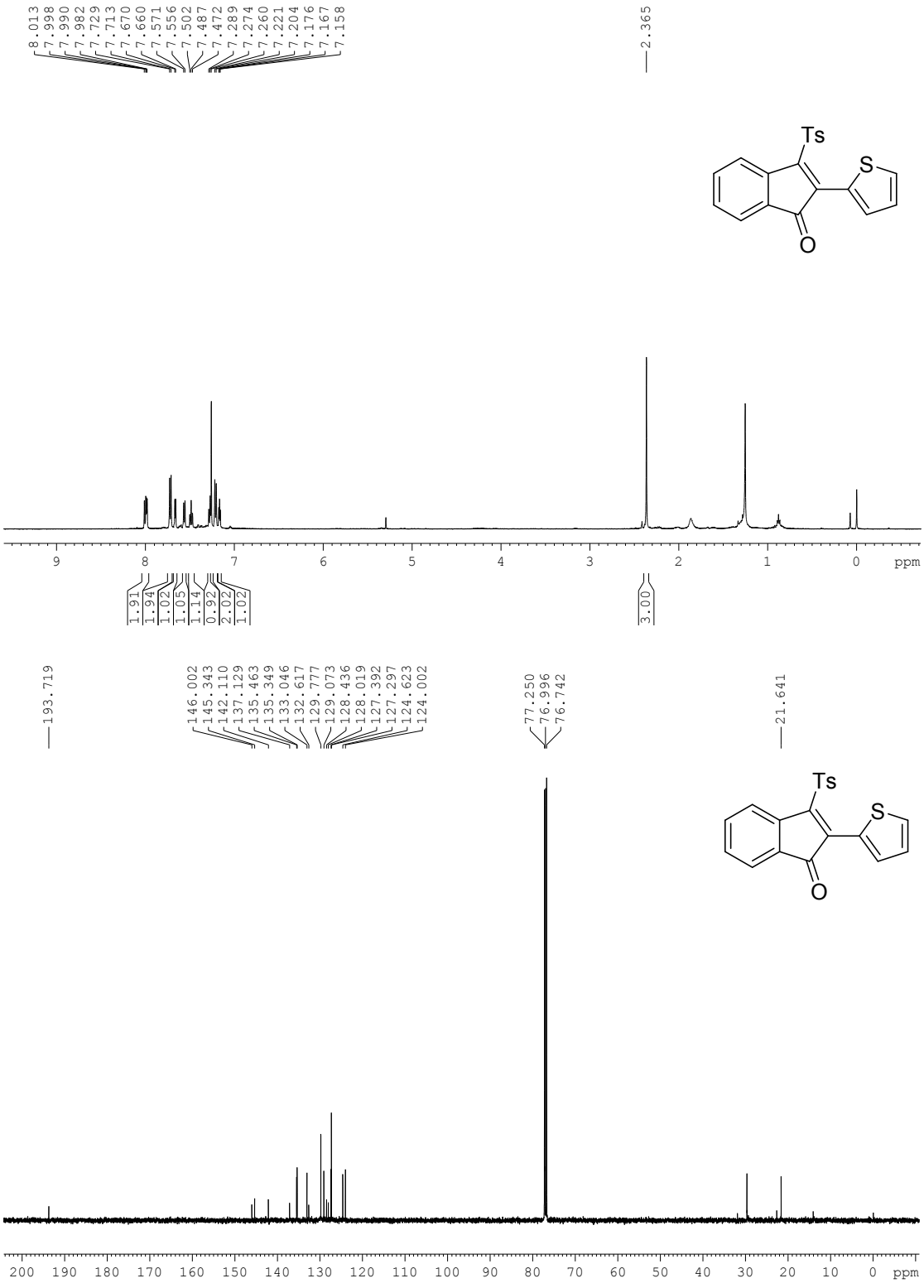
^{1}H and ^{13}C Spectrum of Compound **3ja**



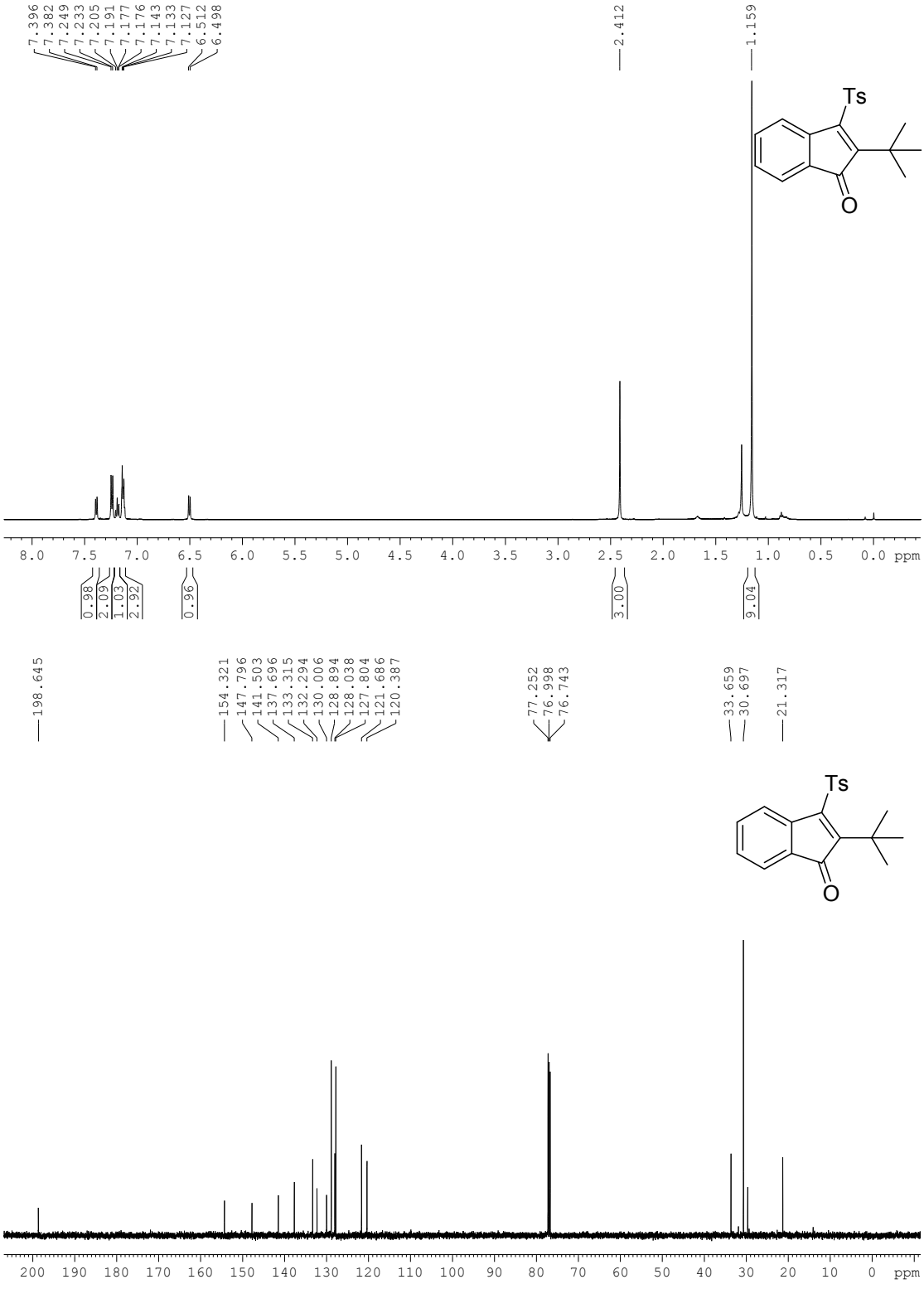
^{1}H and ^{13}C Spectrum of Compound **3ka**



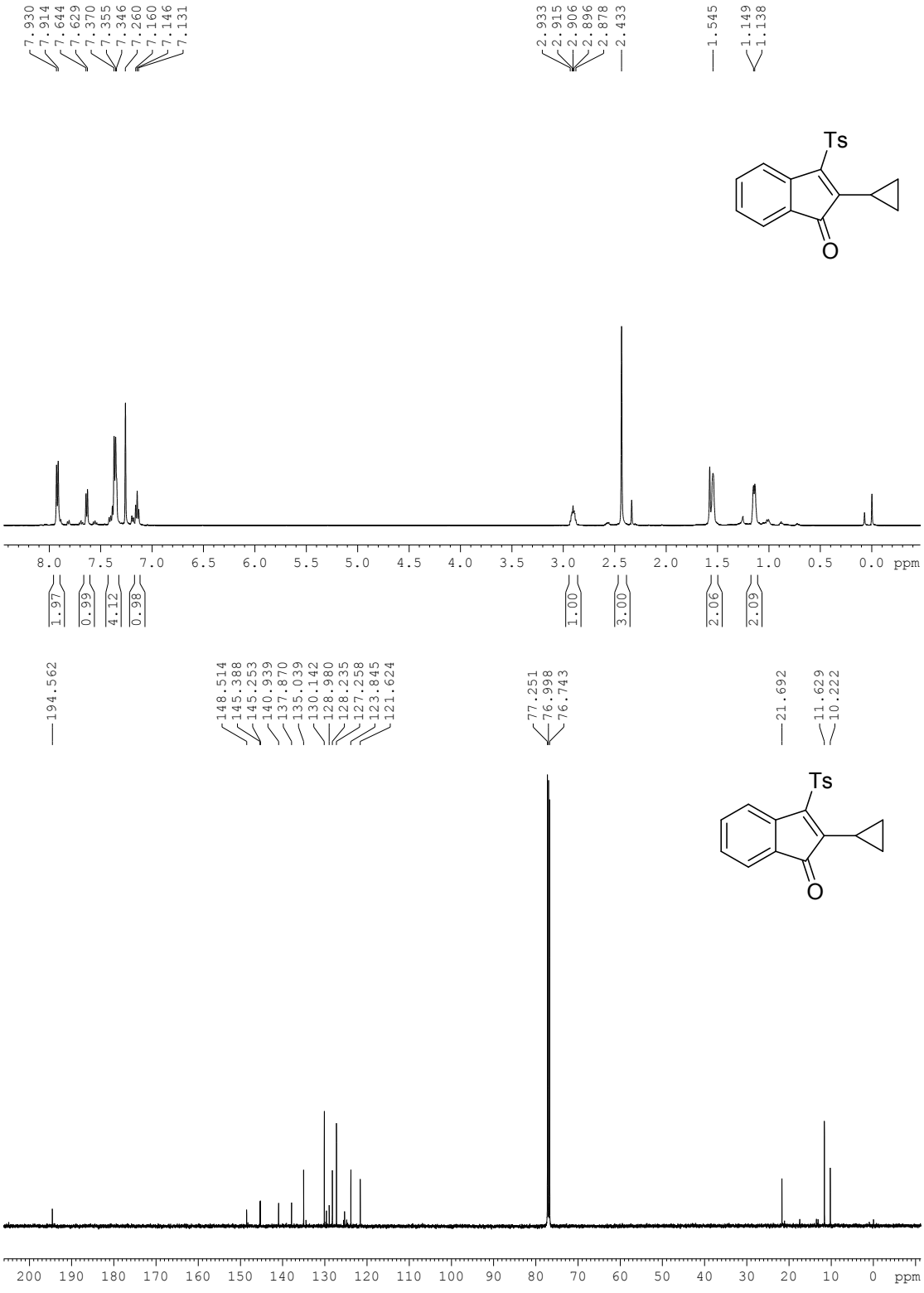
^{1}H and ^{13}C Spectrum of Compound **3la**



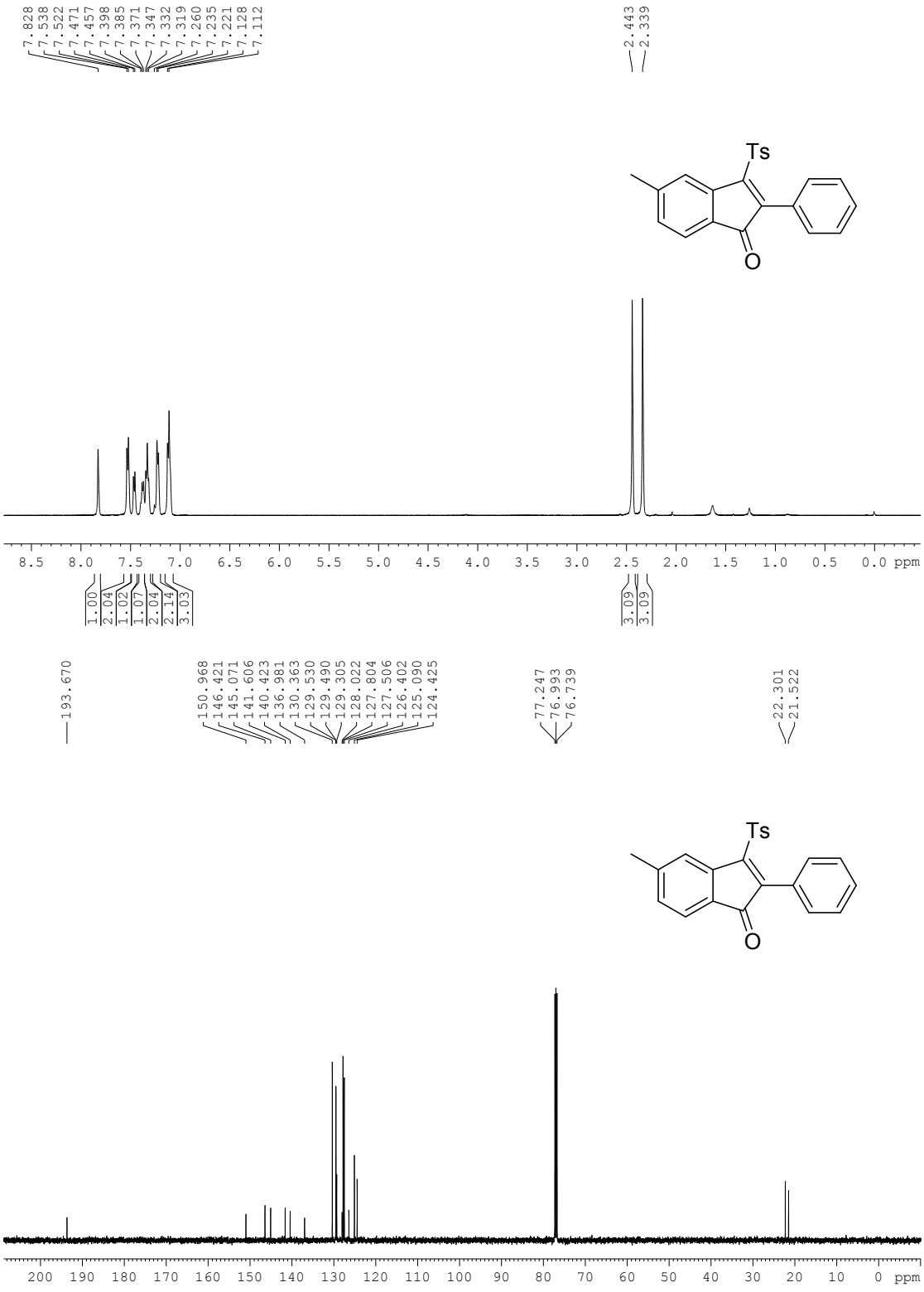
^{1}H and ^{13}C Spectrum of Compound **3ma**



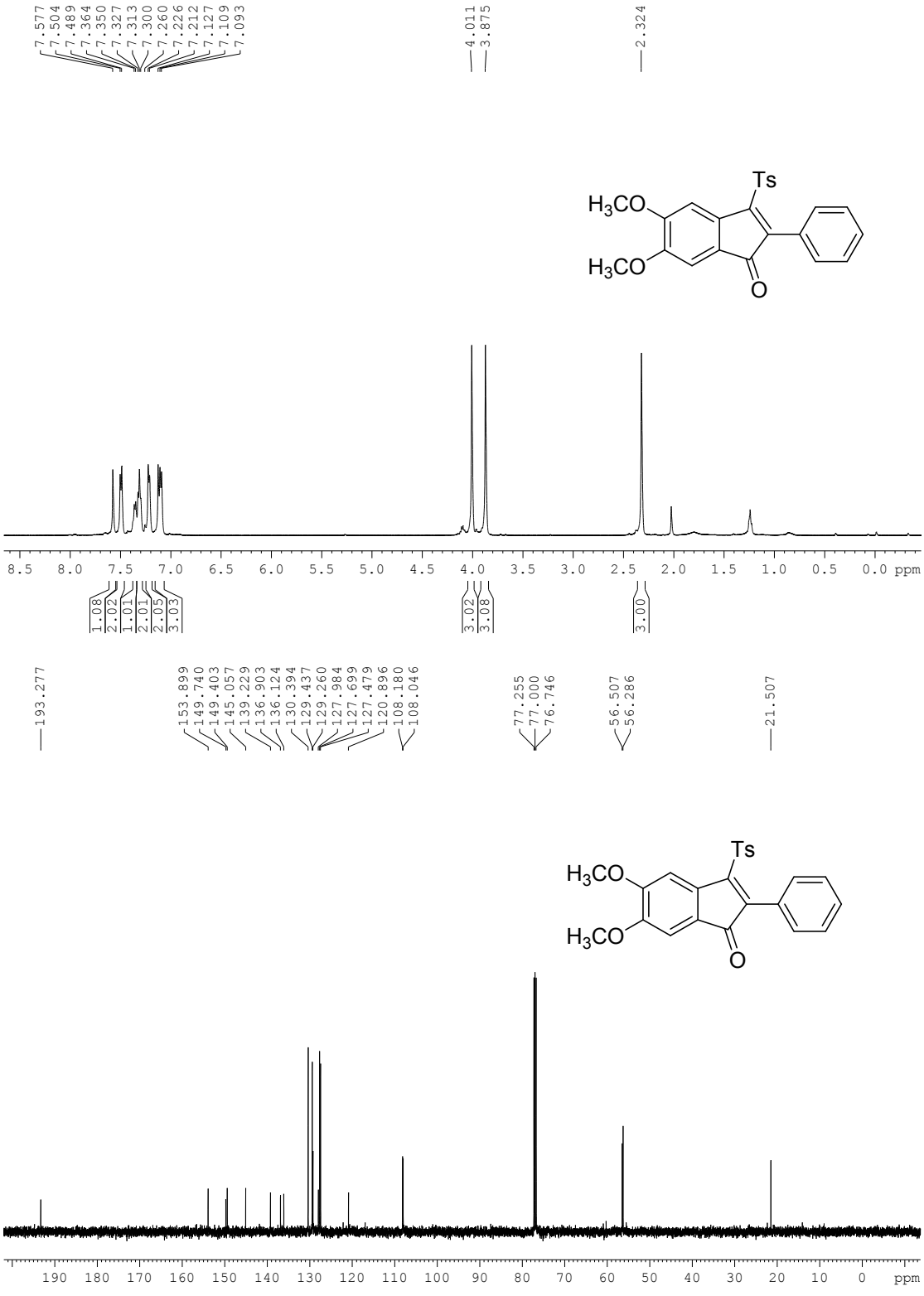
^{1}H and ^{13}C Spectrum of Compound **3na**



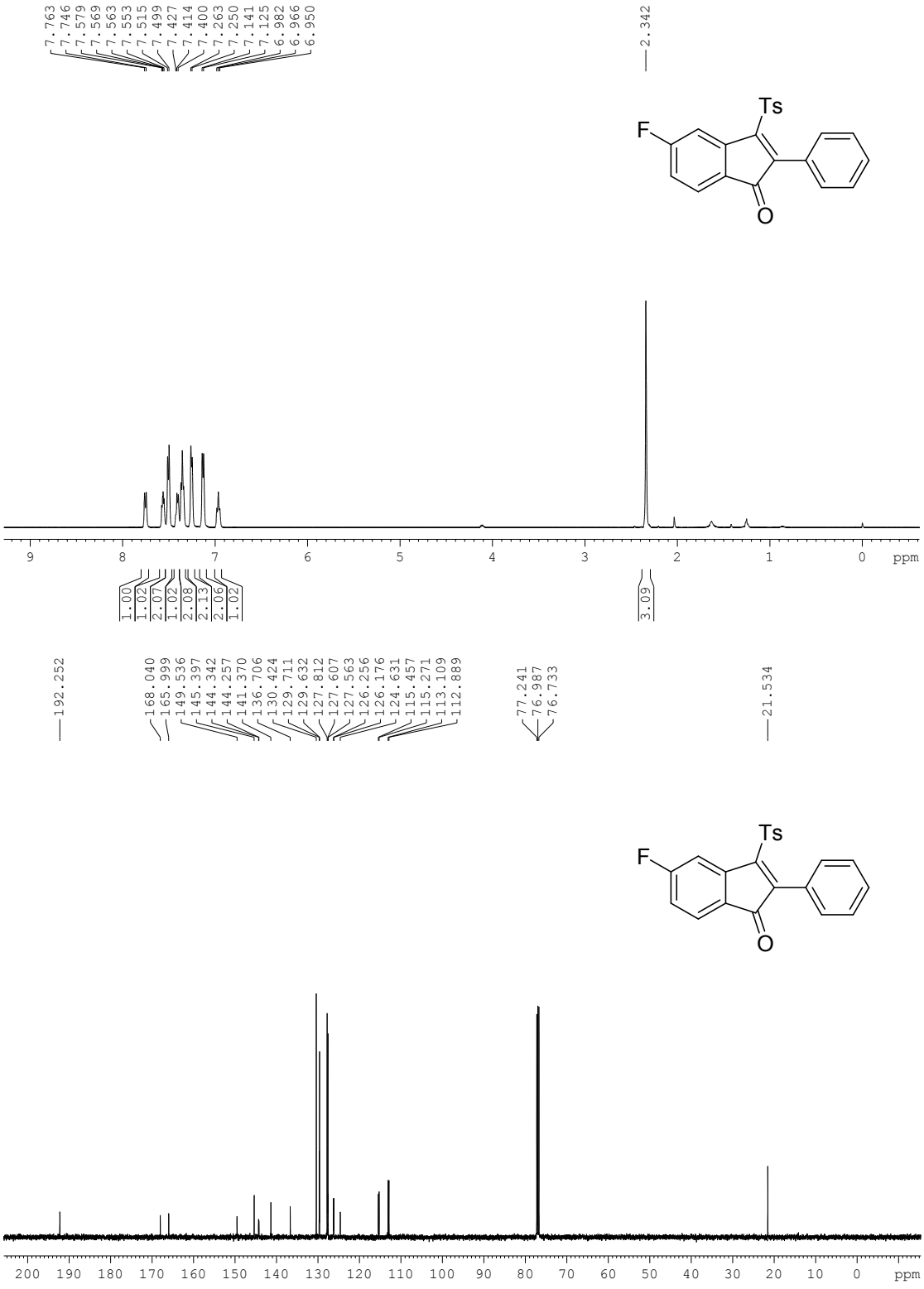
^{1}H and ^{13}C Spectrum of Compound **3oa**



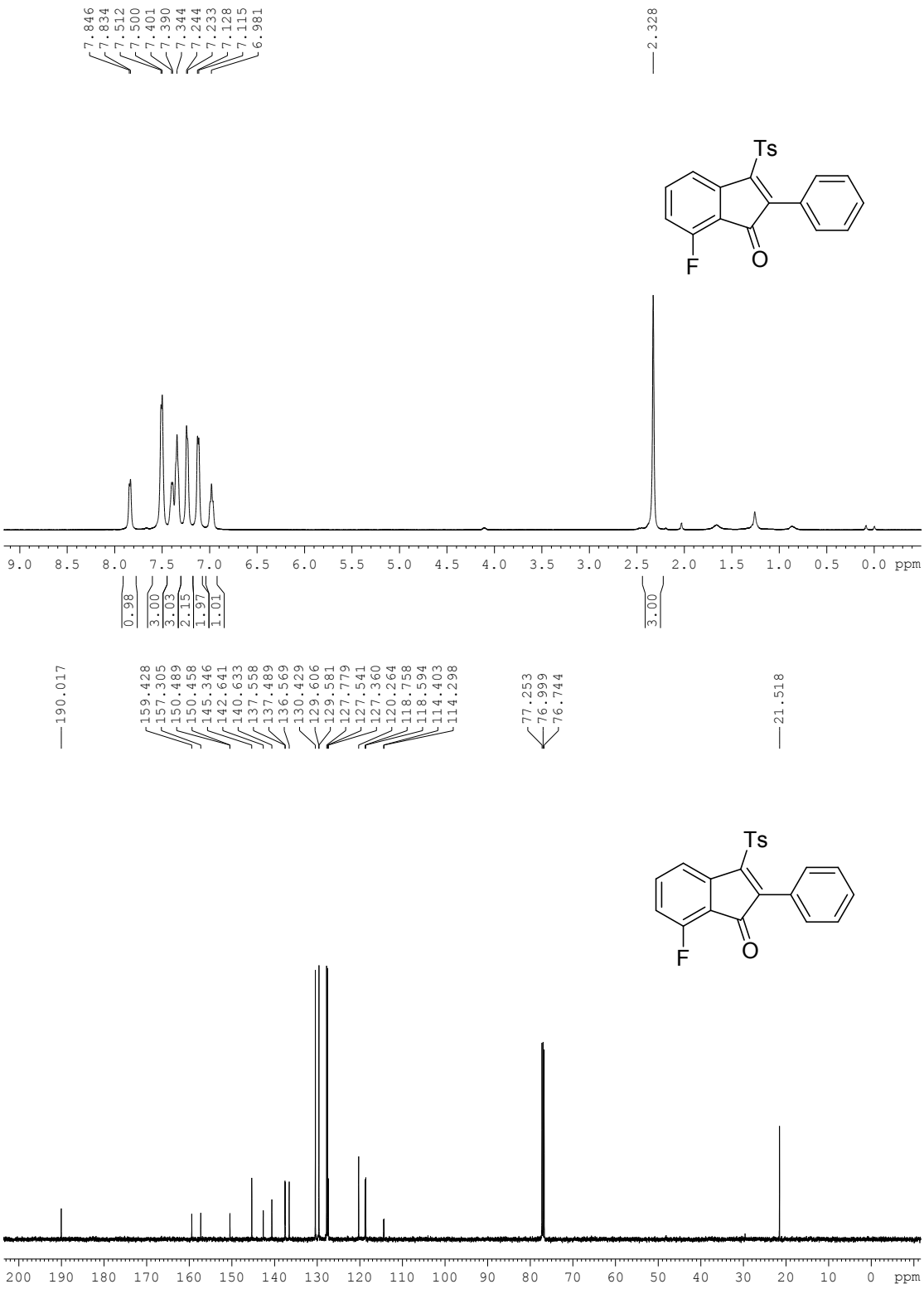
^{1}H and ^{13}C Spectrum of Compound **3pa**



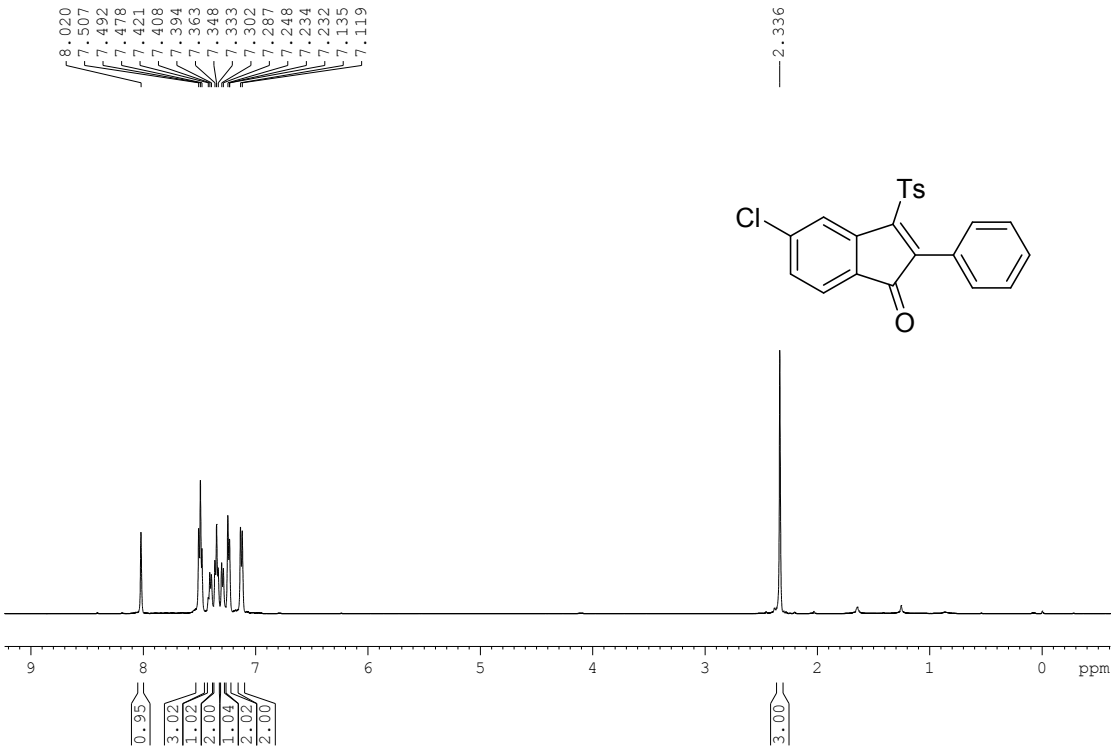
^{1}H and ^{13}C Spectrum of Compound **3qa**

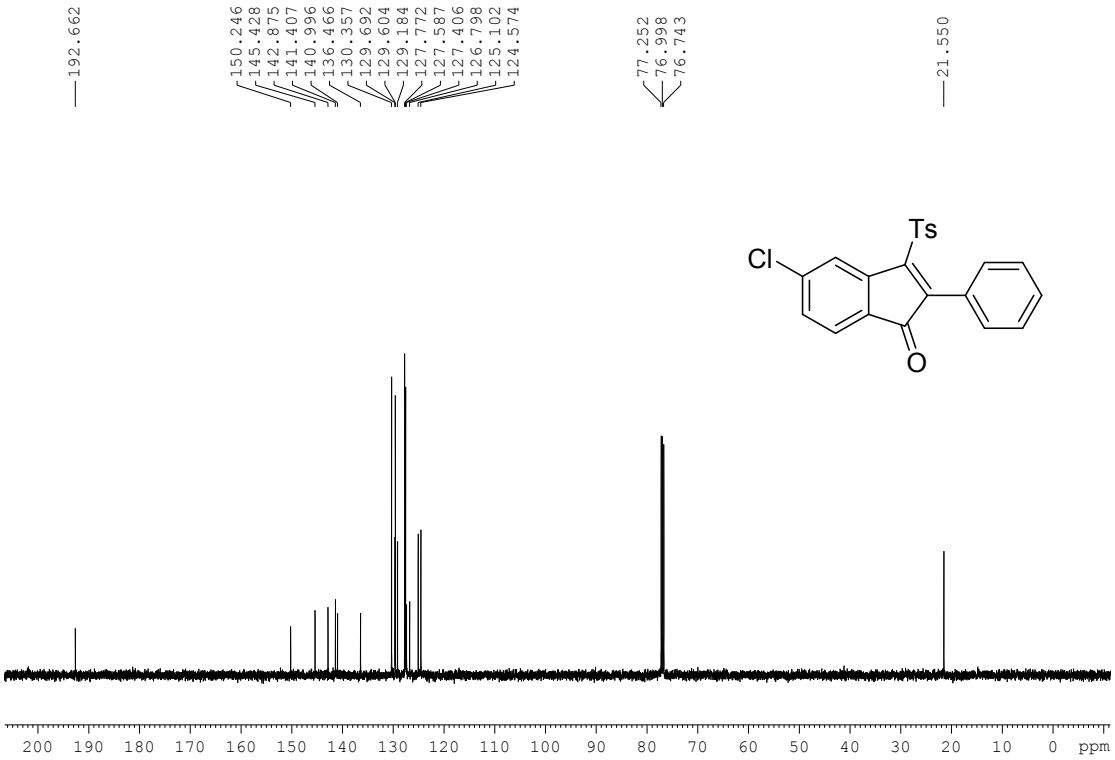


^{1}H and ^{13}C Spectrum of Compound **3ra**

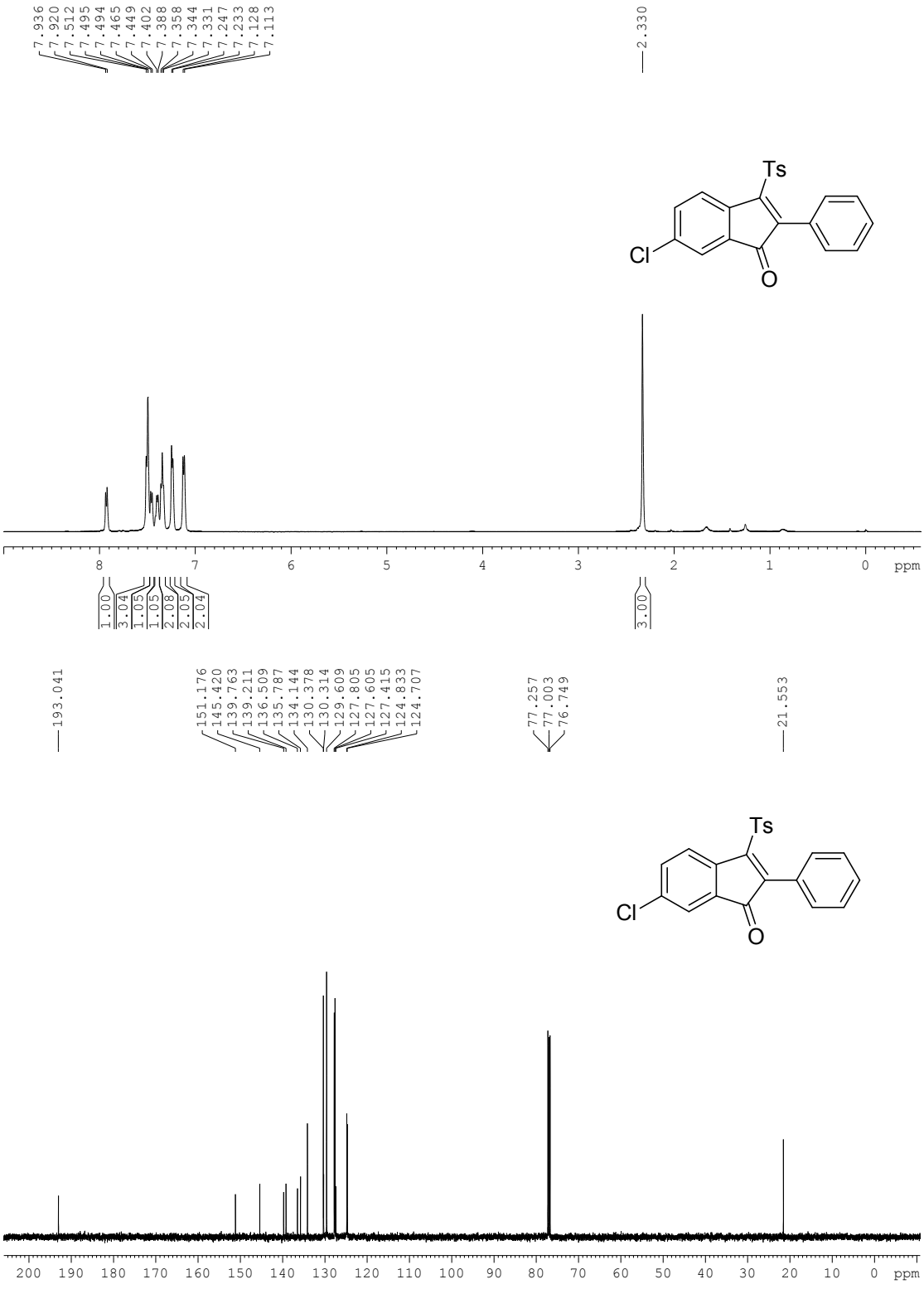


^{1}H and ^{13}C Spectrum of Compound **3sa**

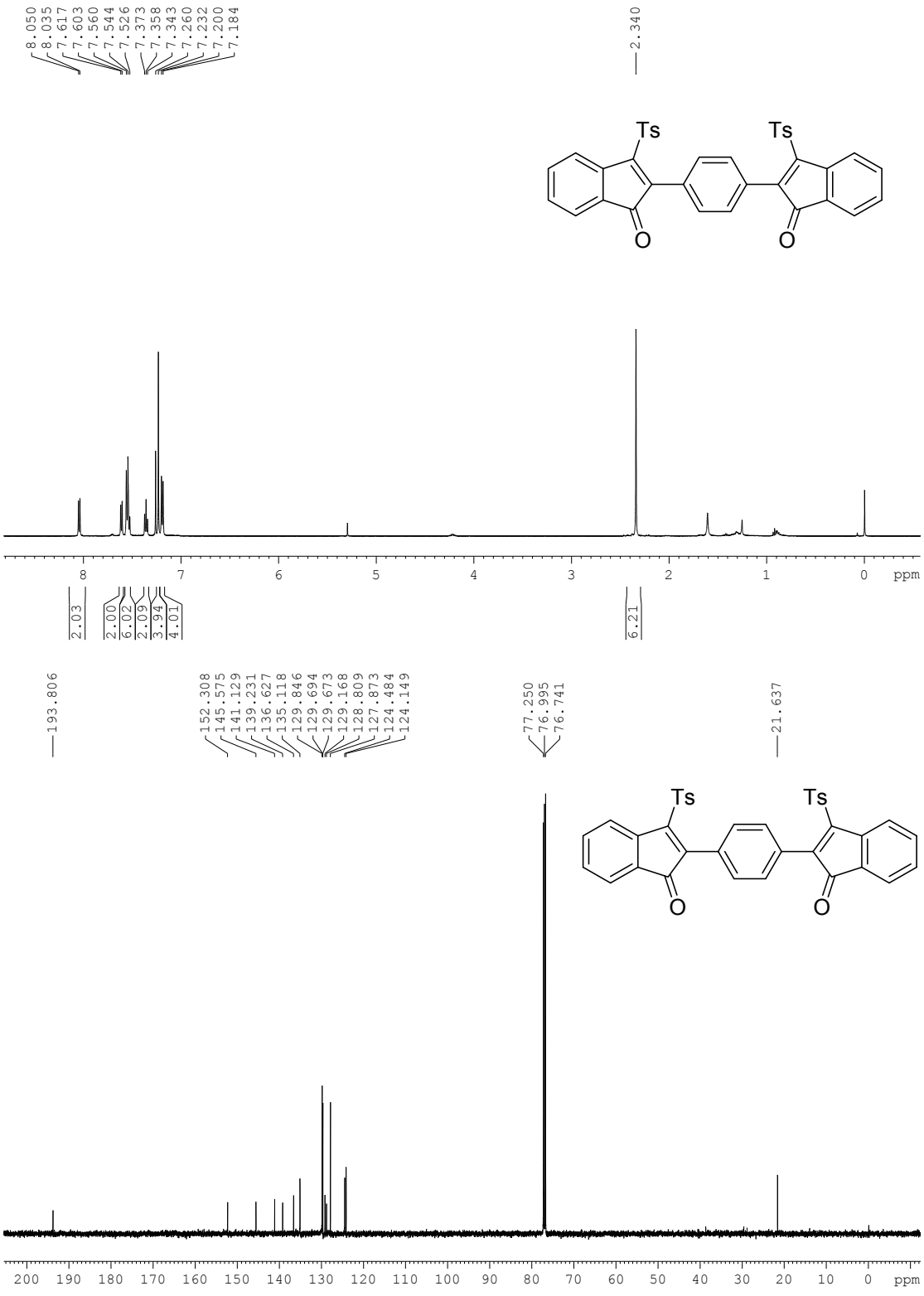




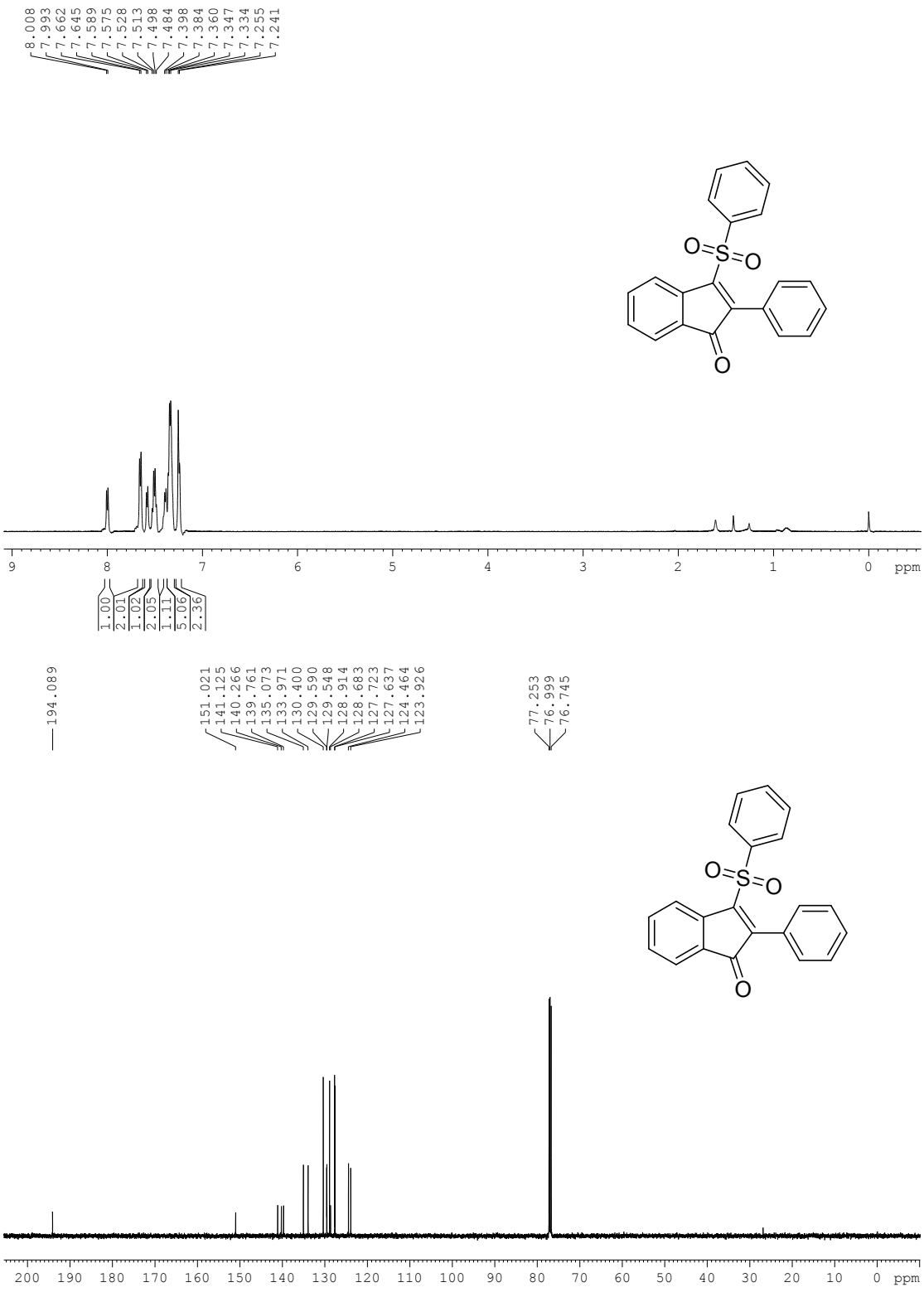
^{1}H and ^{13}C Spectrum of Compound **3ta**



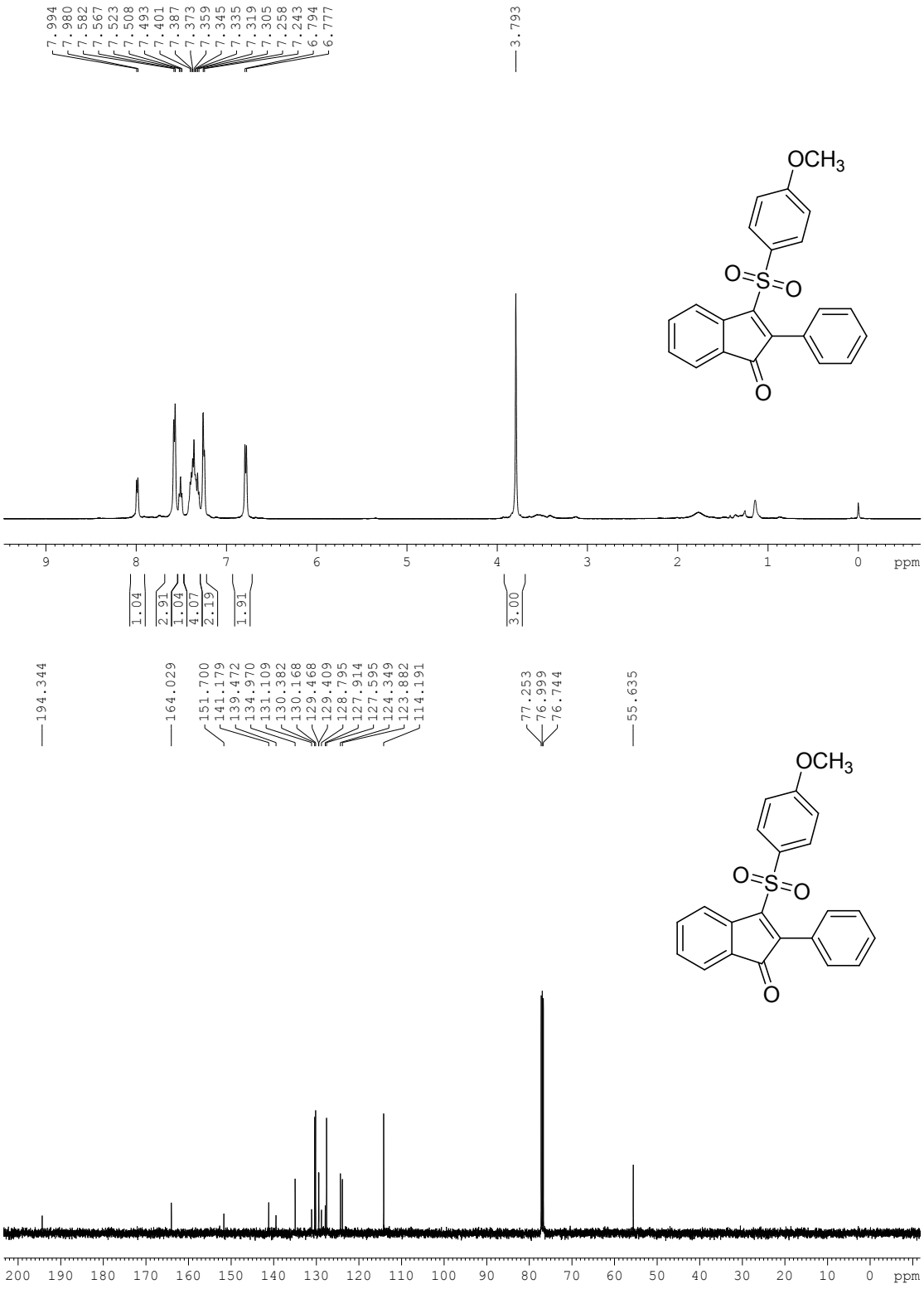
H and ^{13}C Spectrum of Compound **3ua**



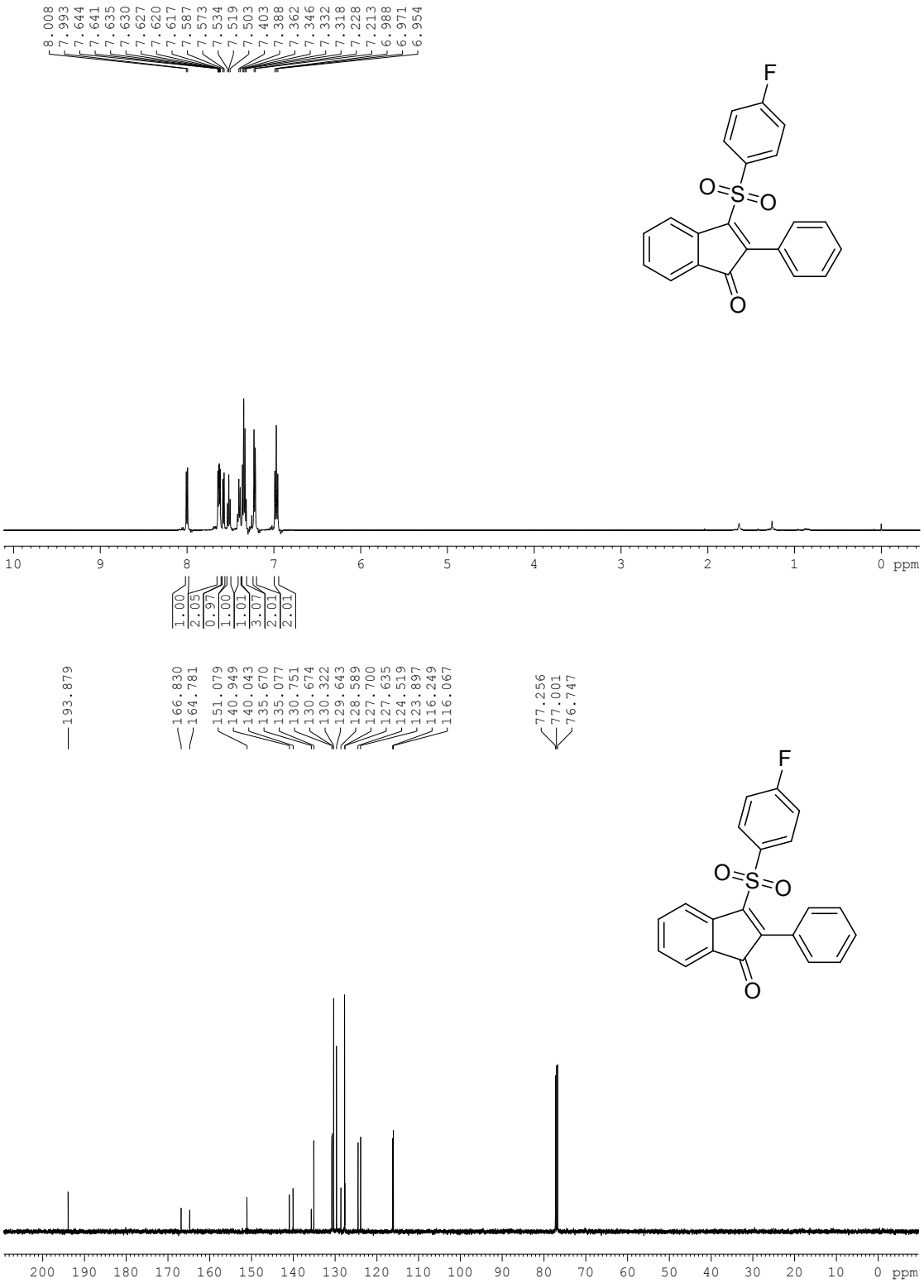
^{1}H and ^{13}C Spectrum of Compound **3ab**



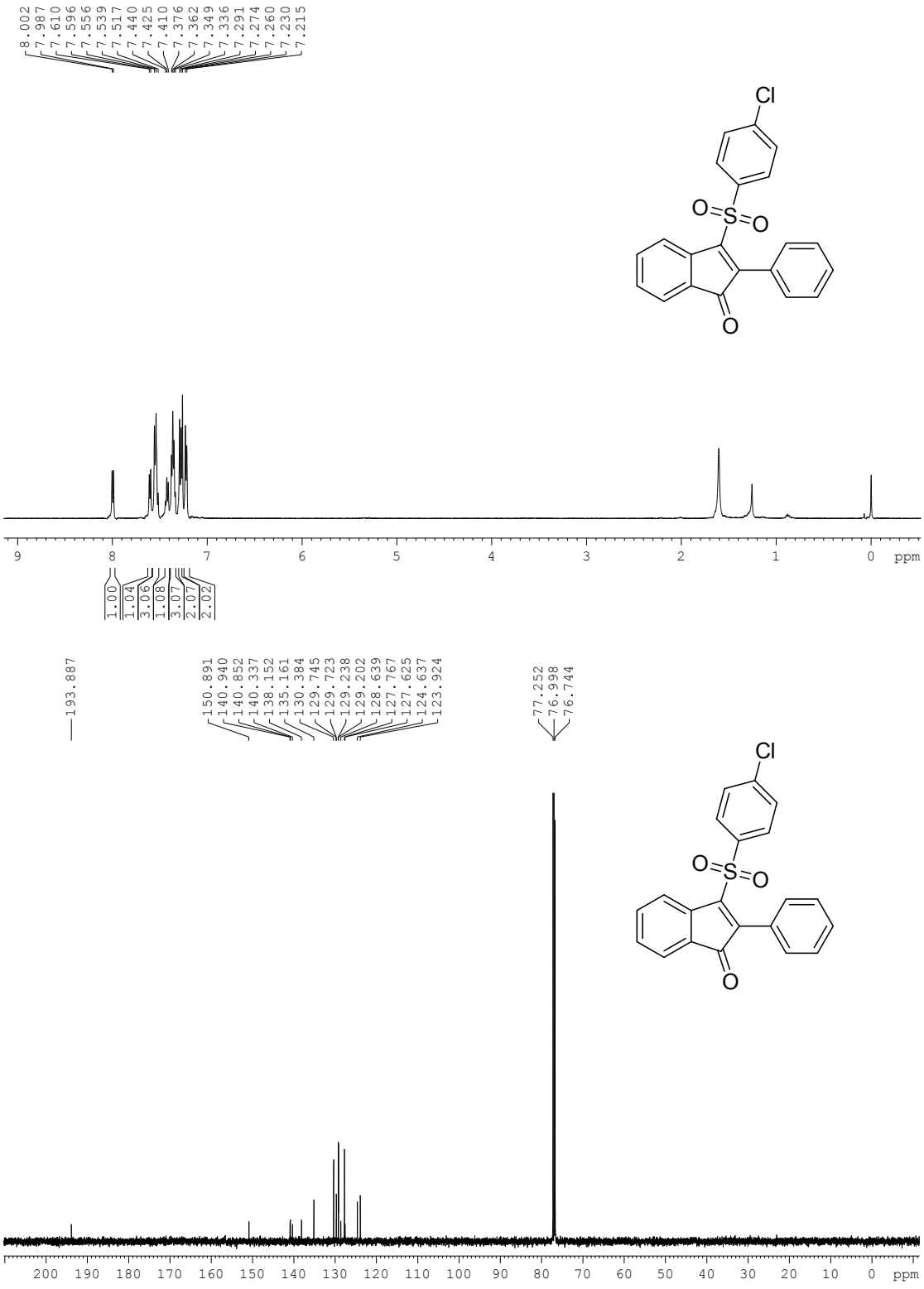
^{1}H and ^{13}C Spectrum of Compound **3ac**



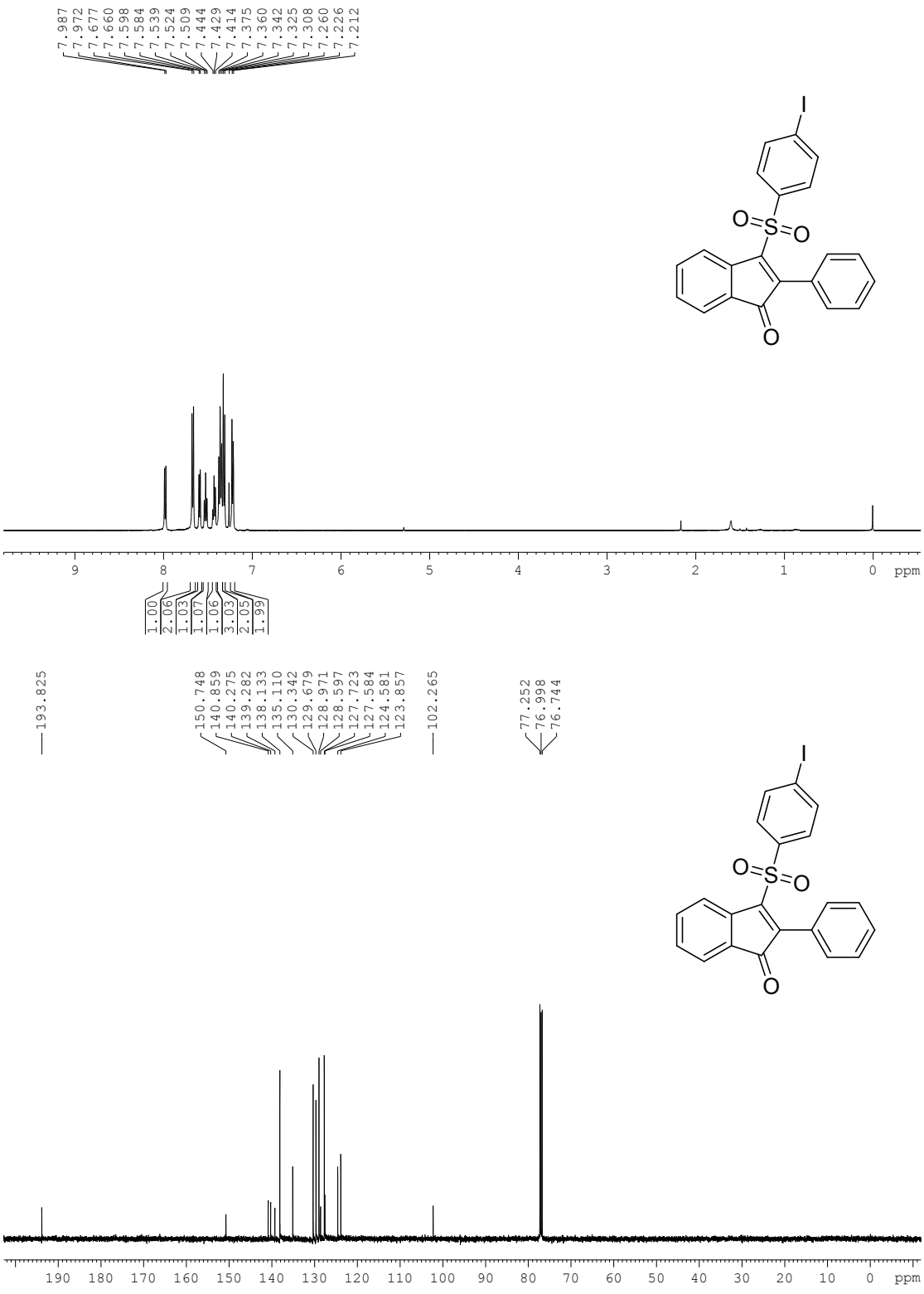
^{1}H and ^{13}C Spectrum of Compound **3ad**



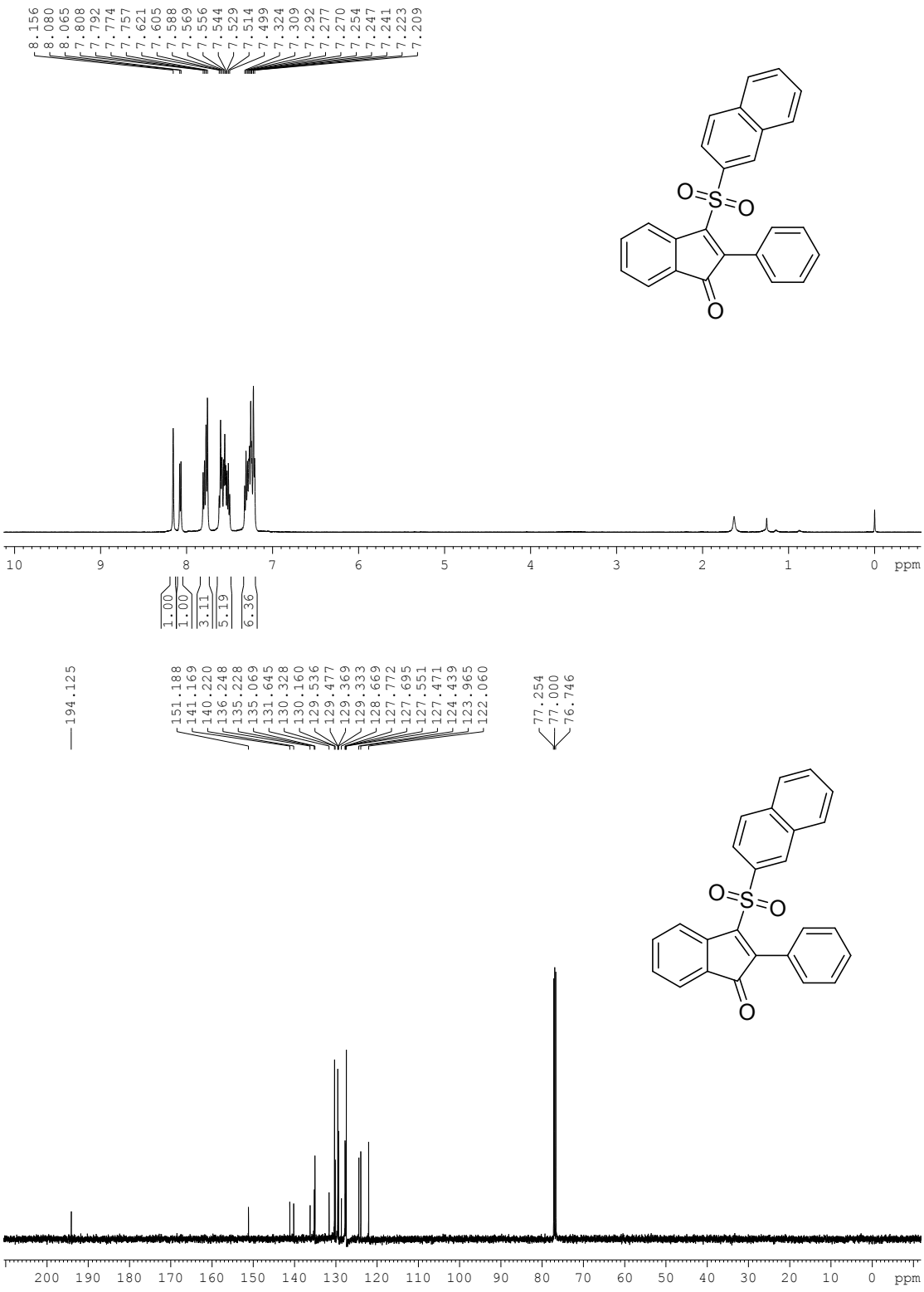
^{1}H and ^{13}C Spectrum of Compound **3ae**



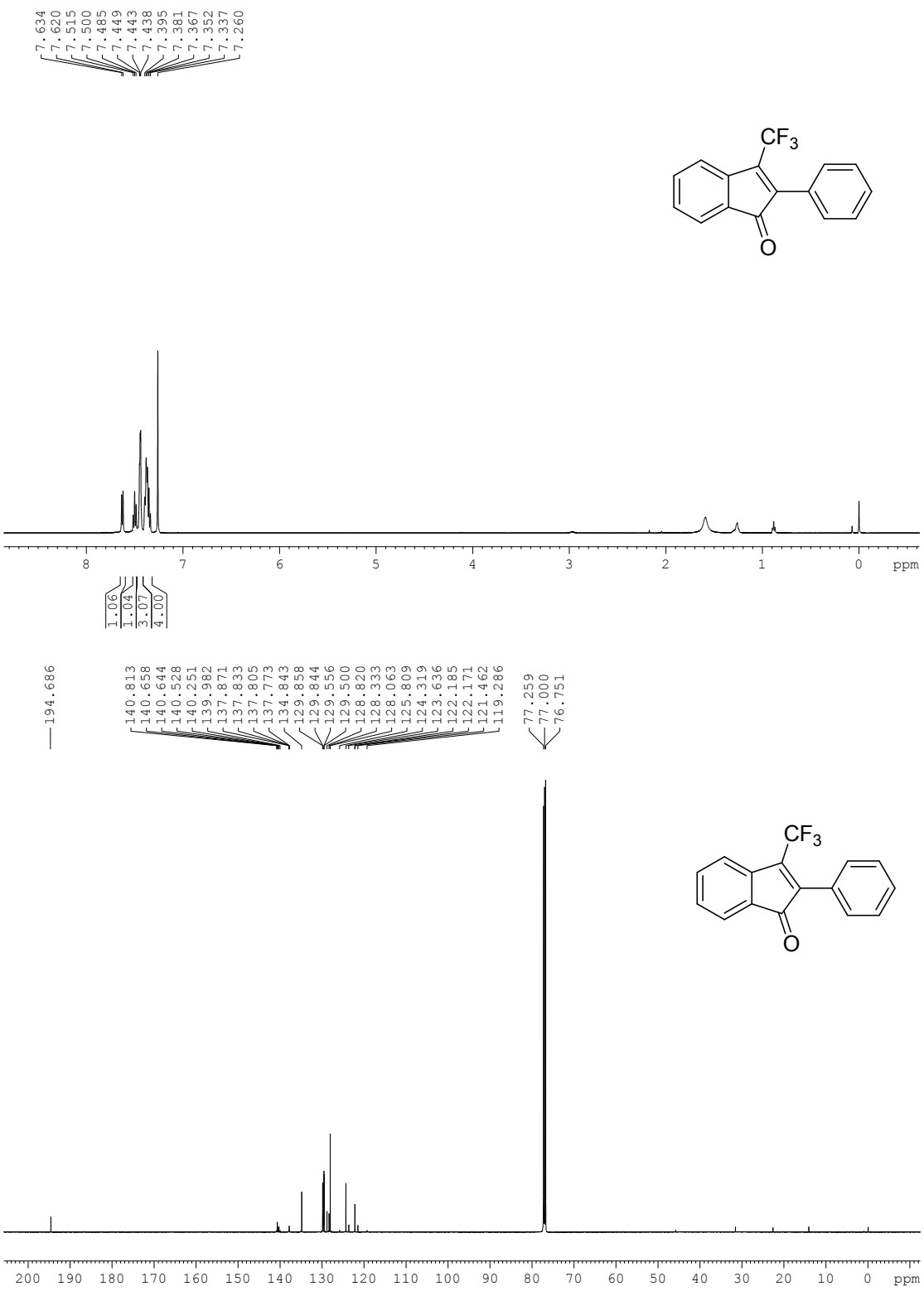
^{1}H and ^{13}C Spectrum of Compound **3af**



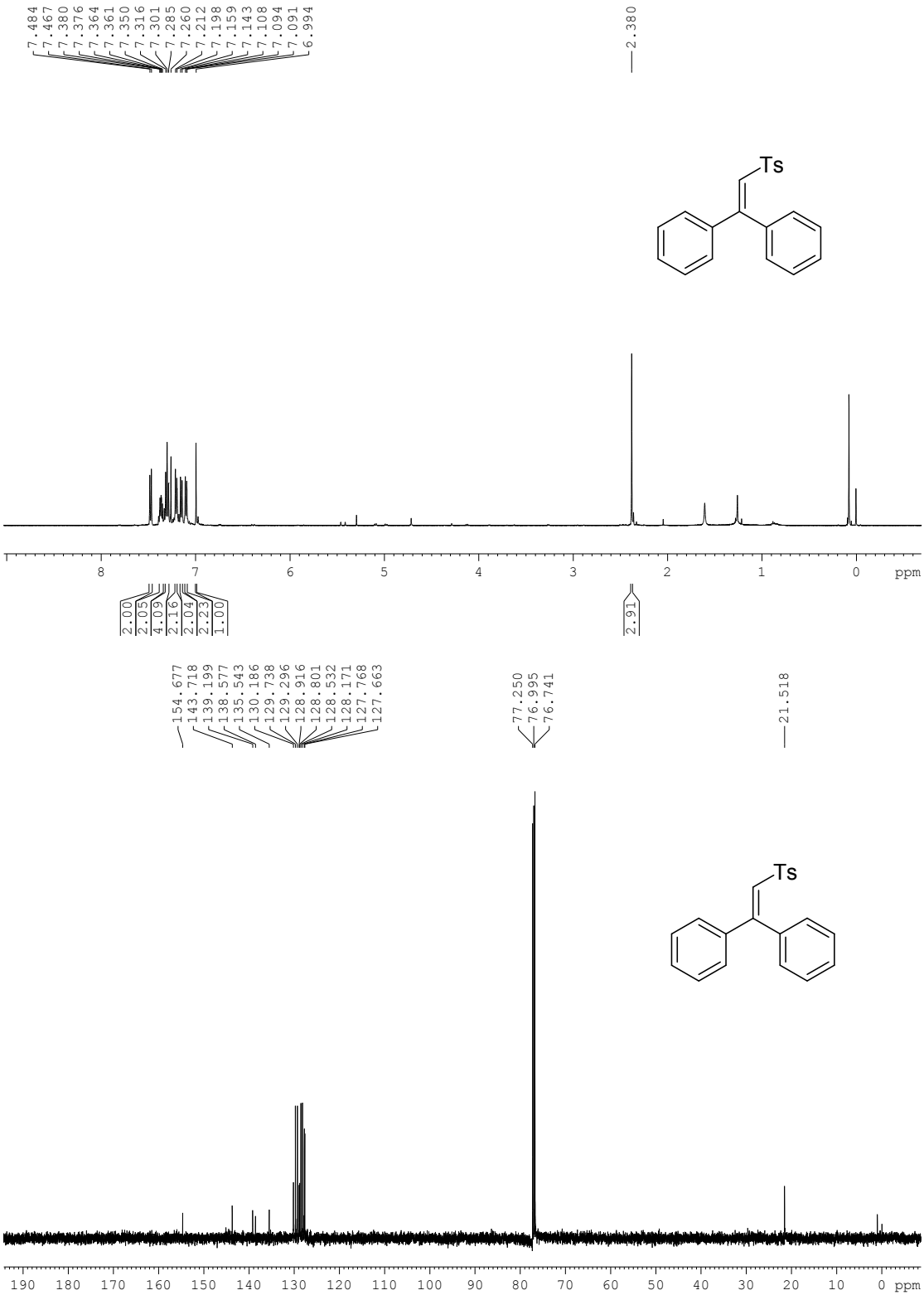
^{1}H and ^{13}C Spectrum of Compound **3ag**



^{1}H and ^{13}C Spectrum of Compound **4**



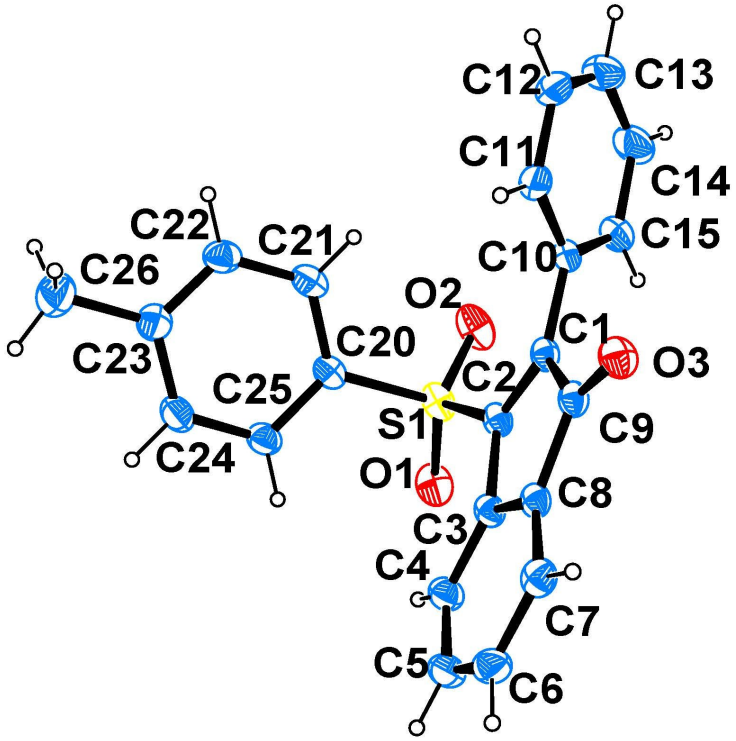
^{1}H and ^{13}C Spectrum of Compound **5**



8) Crystal Data

Table 1 Crystal data and structure refinement for 3a (CCDC: 1838957).

Identification code	exp_248
Empirical formula	$C_{22}H_{16}O_3S$
Formula weight	360.41
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	9.1358(3)
b/Å	18.8753(7)
c/Å	20.9542(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3613.4(2)
Z	8
ρ_{calc}g/cm^3	1.325
μ/mm^{-1}	0.198
F(000)	1504.0
Crystal size/mm^3	0.3 × 0.3 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.258 to 52.034
Index ranges	-11 ≤ h ≤ 11, -23 ≤ k ≤ 23, -25 ≤ l ≤ 25
Reflections collected	50439
Independent reflections	3548 [R_{int} = 0.0546, R_{sigma} = 0.0207]
Data/restraints/parameters	3548/0/236
Goodness-of-fit on F^2	1.211
Final R indexes [I>=2σ (I)]	R_1 = 0.0610, wR_2 = 0.1238
Final R indexes [all data]	R_1 = 0.0702, wR_2 = 0.1284
Largest diff. peak/hole / e Å^{-3}	0.22/-0.30


C12
C13
C11
C14
C22
C21
C10
C15
C26
O2
C1
C20
C23
C2
O3
C25
S1
C9
C24
O1
C8
C3
C4
C7
C5
C6