Synthesis

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Supporting Information

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Supporting Information

Custom-made pyrene photocatalyst-promoted desulfonylation of arylethenyl sulfones using green light-emitting diodes

Hikaru Watanabe,[a] Kazuki Nakajima,[a] Kento Ekuni,[a] Ryota Edagawa,[a] Yuta Akagi,[a] Yasuhiro Okuda,[a] Kan Wakamatsu,[b] Akihiro Orita*[a]

[a]Department of Applied Chemistry and Biotechnology, Okayama University of Science, 1-1, Ridai-cho, Kita-ku, Okayama 700-0005 Japan

[b]Department of Chemistry, Okayama University of Science,

1-1, Ridai-cho, Kita-ku, Okayama 700-0005 Japan

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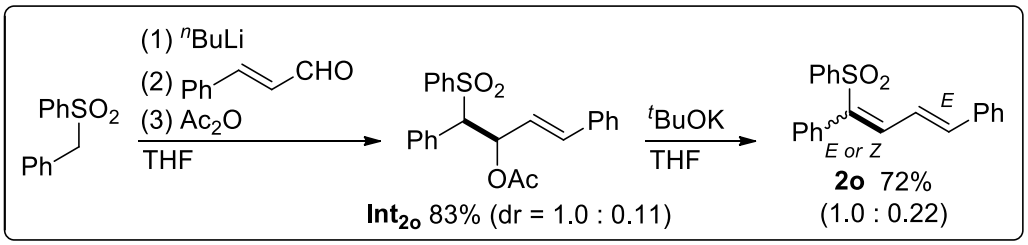
1. Synthesis of **2o**



To a round-bottomed flask were added benzyl sulfone (465 mg, 2.0 mmol) and THF (20 mL). Butyllithium (1.59 M in hexane, 1.4 mL, 2.2 mmol) was dropwisely added at –78 °C, and the mixture was stirred for 1 h. To the solution was added *trans*-cinnamaldehyde (529 mg, 4.0 mmol), and the mixture was stirred for 1 h. Acetic anhydride (265 mg, 2.6 mmol) was added, and the mixture was stirred at –78 °C for 1 h and then 0 °C for 1 h. To the reaction mixture was added saturated aqueous NH_4Cl (5 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc, and combined organic layer was washed with water and brine. The combined organic layer was dried over $MgSO_4$ and evaporated. The residue was subjected to filtration through a thin pad of silica gel (hexane/EtOAc, 7:3) to afford a crude acetate **Int2o** in an 83% yield (675 mg, dr = 1.0:0.11, a white solid).

To a round-bottomed flask were added the crude acetate **Int2o** (102 mg, 0.25 mmol) and THF (5 mL). Potassium *tert*-butoxide (34 mg, 0.3 mmol) was added at –78 °C, and the mixture was stirred at –78 °C for 2 h and then 0 °C for 2 h. To the mixture was added saturated aqueous NH_4Cl (5 mL), and the organic layer and aqueous layers were separated. The aqueous layer was extracted with EtOAc, and combined organic layer was washed with water and brine and dried over $MgSO_4$. The solvents were evaporated, and the crude product was subjected to flash chromatography (hexane/EtOAc, 8:2) and then recrystallization from MeOH to afford the desired ethenyl sulfone **2o**. Yield: 72% 62 mg) ((1*E*,3*E*)/(1*Z*,3*E*) 1.0/0.22); white solid; mp 115–116 °C.

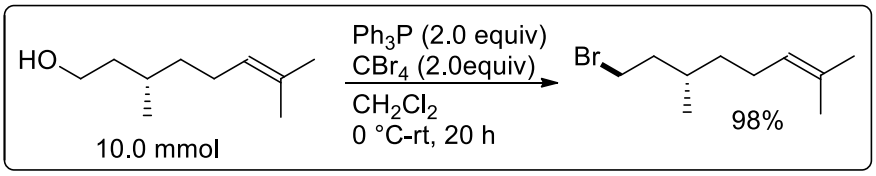
^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.54 8.34 (dd, 1H, *J* = 15.6 15.5, 10.8 11.5Hz), 7.06 6.85 (d, 1H, *J* = 15.6 15.5 Hz), 7.13 7.58 (d, 2H, *J* = 6.8 7.4 Hz), 7.27–7.42 (m, 10H), 7.49–7.54 (m, 1H), 7.62 7.70 (d, 2H, *J* = 7.6 7.4 Hz), 7.74 6.77 (d, 1H, *J* = 10.8 11.5 Hz).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 122.8, 123.2, 127.5, 127.7, 127.9, 128.2, 128.4, 128.5, 128.78, 128.85, 128.87, 128.92, 129.0, 129.2, 129.48, 129.55, 130.2, 130.8, 131.1, 133.2, 135.76, 135.82, 136.2, 138.6, 139.5, 141.0, 141.1, 142.1, 142.9, 143.4.

HRMS (MALDI-TOF): *m/z* $[M+Na]^+$ Calcd for $C_{22}H_{18}NaO_2S$ 369.0925; Found 369.0918.

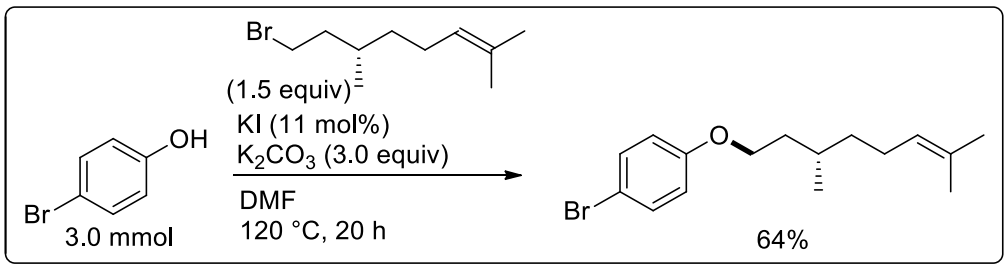
2. Synthesis of **1**

(i) Synthesis of (*S*)-(+)-citronellyl bromide:[S1]



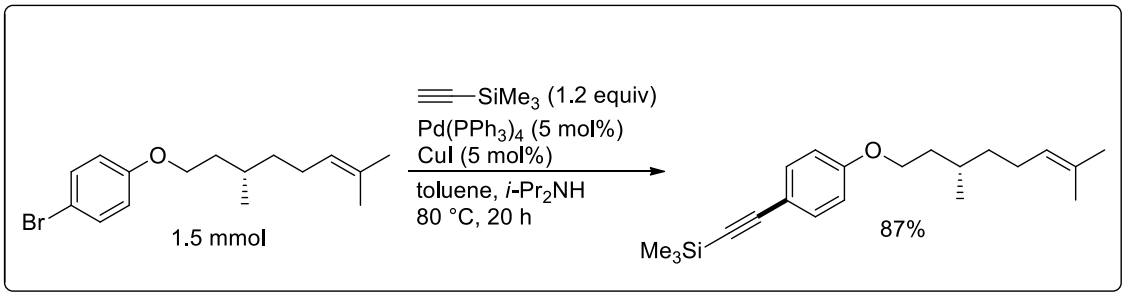
To a round-bottomed flask were added Ph_3P (5.2 g, 20.0 mmol), CBr_4 (6.6 g, 20.0 mmol), (*S*)-(-)-citronellol (1.6 g, 10.0 mmol), and CH_2Cl_2 (50 mL) at 0 °C, and the mixture was stirred at rt for 20 h. The mixture was filtered by a thin pad of silica gel with hexane. The filtrate was evaporated, and the crude citronellyl bromide was used in subsequent etherification without further purification. Yield: 98% (1.07 g, colorless liquid). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.90–0.91 (m, 3H), 1.14–1.26 (m, 1H), 1.30–1.39 (m, 1H), 1.61–1.72 (m, 8H), 1.84–2.06 (m, 3H), 3.37–3.50 (m, 2H), 5.07–5.12 (m, 1H).

(ii) Synthesis of 4-((*S*)-citronellyloxy)phenyl bromide:[S2]



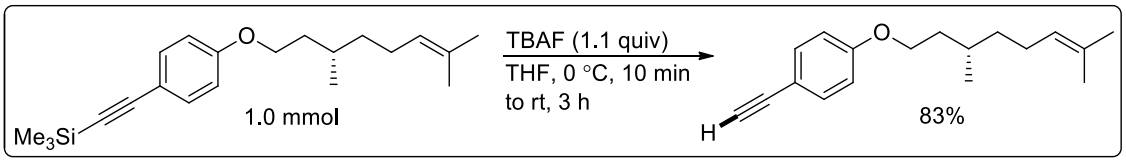
To a round-bottomed flask were added (*S*)-(+)-citronellyl bromide (986 mg, 4.5 mmol), 4-bromophenol (519 mg, 3.0 mmol), KI (55 mg, 0.33 mmol), K_2CO_3 (331 mg, 2.4 mmol), and DMF (10 mL), and the mixture was stirred at 120 °C for 20 h. To the mixture was added water (10 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc, and combined organic layer was washed with water and brine. The organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to flash chromatography (hexane) to afford the desired ether in a 64% yield (399 mg, colorless liquid). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.94–0.95 (m, 3H), 1.17–1.26 (m, 1H), 1.34–1.45 (m, 1H), 1.55–1.71 (m, 8H), 1.76–1.86 (m, 1H), 1.92–2.08 (m, 2H), 3.91–4.00 (m, 2H), 5.08–5.12(m, 1H), 6.77 (d, 2H, J = 9.0 Hz), 7.36 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 17.8, 19.7, 25.6, 25.9, 29.6, 36.1, 37.2, 66.6, 112.7, 116.4, 124.7, 131.4, 132.3, 158.3.

(iii) Synthesis of 1-((*S*)-citronellyloxy)-4-((trimethylsilyl)ethynyl)benzene:



To a round-bottomed flask were added 4-((*S*)-citronellyloxy)phenyl bromide (467 mg, 1.5 mmol), $Pd(PPh_3)_4$ (87 mg, 0.08 mmol), CuI (14 mg, 0.08 mmol), trimethylsilylethyne (177 mg, 1.8 mmol), *i*-Pr_2NH (1.0 mL, 7.0 mmol), and toluene (10.0 mL), and the mixture was stirred at 80 °C for 20 h. To the mixture was added saturated aqueous NH_4Cl (10 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc, and combined organic layer was washed with water and brine. The organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to flash chromatography (hexane/CH_2Cl_2, 95:5) to afford the desired silylethynyl-coupling product in an 87% yield (429 mg, colorless liquid). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.24 (s, 9H), 0.94–0.96 (m, 3H), 1.17–1.26 (m, 1H), 1.34–1.43 (m, 1H), 1.57–1.71 (m, 8H), 1.76–1.87 (m, 1H), 1.92–2.08 (m, 2H), 3.94–4.03 (m, 2H), 5.08–5.12 (m, 1H), 6.80 (d, 2H, J = 8.8 Hz), 7.39 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 0.2, 17.8, 19.7, 25.6, 25.9, 29.6, 36.2, 37.2, 66.4, 92.4, 105.5, 114.5, 115.1, 124.7, 131.5, 133.6, 159.4. HRMS (MALDI-TOF): *m/z* $[M+Na]^+$ Calcd for $C_{21}H_{32}NaOSi$ 351.2121; Found: 351.2124.

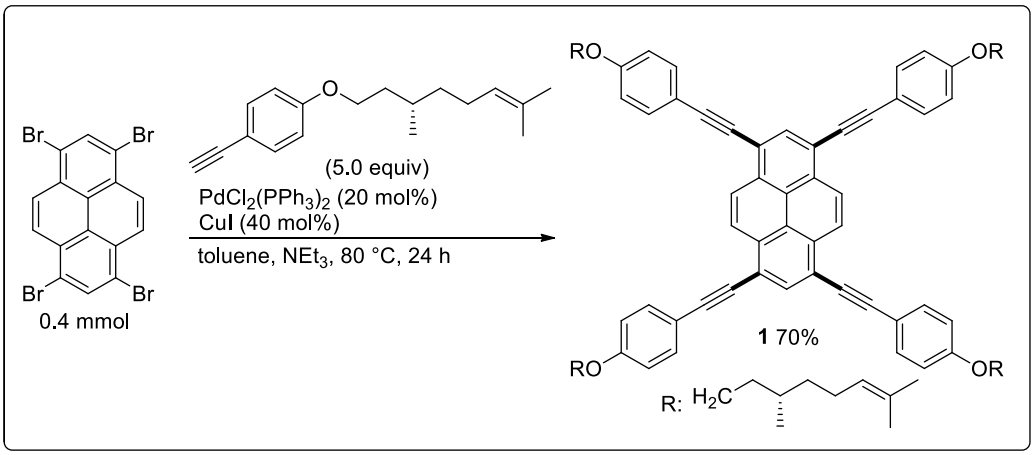
(iv) Synthesis of 1-((*S*)-citronellyloxy)-4-ethynylbenzene:



To a round-bottomed flask were added 1-((*S*)-citronellyloxy)-4-((trimethylsilyl)ethynyl)benzene (329 mg, 1.0 mmol) and THF (5 mL). To the mixture was dropwisely added a THF solution of TBAF (1.0 M, 1.1 mL, 1.1 mmol of TBAF) at 0 °C, and the mixture was stirred at 0 °C for 10 min and then at rt 3 h. To the mixture was added water (5 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with CH_2Cl_2, and combined organic layer was washed with water and brine. The organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to flash chromatography (hexane/CH_2Cl_2, 9:1) to afford the desired terminal ethyne in an 83% yield (213 mg, colorless liquid). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.94–0.96 (m, 3H), 1.17–1.27 (m, 1H), 1.34–1.43 (m, 1H), 1.56–1.76 (m, 8H), 1.79–1.87 (m, 1H), 1.92–2.09 (m, 2H), 2.99 (s, 1H), 3.94–4.04

(m, 2H), 5.08–5.12 (m, 1H), 6.83 (d, 2H, J = 9.0 Hz), 7.41 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 17.8, 19.7, 25.6, 25.9, 29.6, 36.1, 37.2, 66.4, 75.8, 83.9, 114.0, 114.6, 124.7, 131.4, 133.7, 159.6. HRMS (MALDI-TOF): *m/z* Calcd for $C_{18}H_{24}NaO$ 279.1725; Found: 279.1690.

(v) 1,3,6,8-Tetra(4-((*S*)-citronellyloxy)phenylethynyl)pyrene (1):



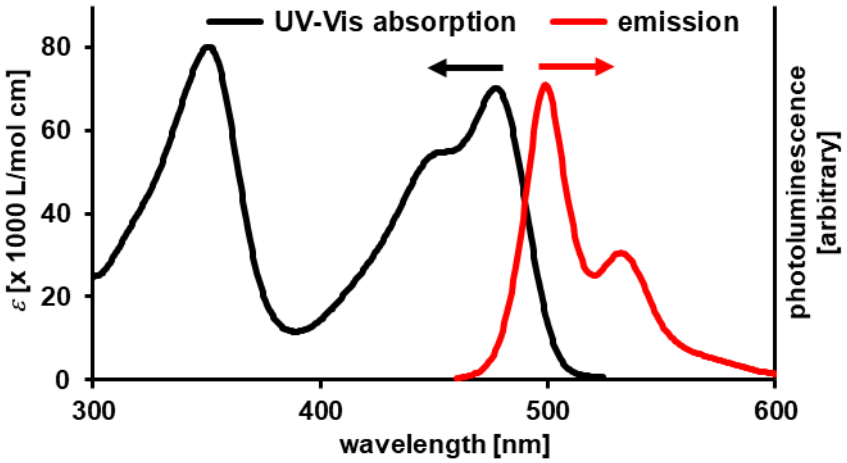
To a round-bottomed flask were added 1,3,6,8-tetrabromopyrene (231 mg, 0.4 mmol), $PdCl_2(PPh_3)_2$ (58 mg, 0.08 mmol), CuI (30 mg, 0.16 mmol), Ph_3P (15 mg, 0.16 mmol), 1-((*S*)-citronellyloxy)-4-ethynylbenzene (513 mg, 2.0 mmol), and triethylamine (8 mL, 57 mmol), and toluene (4 mL), and the mixture was stirred at 80 °C for 24 h. To the mixture was added saturated aqueous NH_4Cl (5 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with EtOAc, and combined organic layer was washed with water and brine. The organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to flash chromatography (hexane/CH_2Cl_2, 7:3) to afford the desired substituted pyrene **1** in a 70% yield (342 mg, an orange solid). Mp: 106–107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.98–1.00 (m, 12H), 1.21–1.30 (m, 4H), 1.39–1.47 (m, 4H), 1.59–1.79 (m, 32H), 1.84–1.93 (m, 4H), 1.98–2.10 (m, 8H), 4.02– 4.09 (m, 8H), 5.11–5.15 (m, 4H), 6.96 (d, 8H, J = 8.6 Hz), 7.65 (d, 8H, J = 8.6 Hz), 8.40 (s, 2H), 8.73 (s, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 17.8, 19.7, 25.6, 25.9, 29.7, 36.2, 37.3, 66.5, 86.9, 96.2, 114.8, 115.4, 119.0, 123.9, 124.8, 126.5, 131.3, 131.5, 133.2, 133.4, 159.5. HRMS (MALDI-TOF): *m/z* Calcd for $C_{88}H_{98}O_4$ 1218.7465; Found: 1218.7421.

3. Solubility of **1** in common organic solvents (Table S1)

solvent	At rt (20 °C)	At heating (~reflux)
CH_2Cl_2	soluble	soluble
AcOEt	soluble	soluble
$CHCl_3$	soluble	soluble
Toluene	soluble	soluble
Benzene	soluble	soluble
Hexane	insoluble	partially soluble
MeCN	insoluble	insoluble
Acetone	soluble	soluble
THF	soluble	soluble
Dioxane	soluble	soluble
MeOH	insoluble	insoluble
EtOH	insoluble	partially soluble

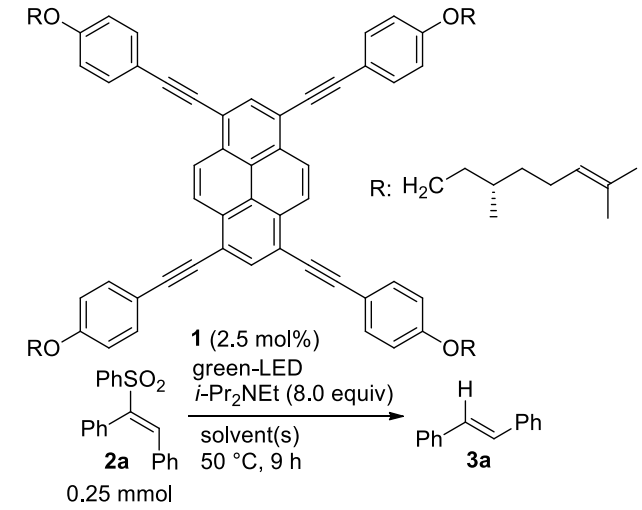
4. UV-vis absorption and photoluminescence spectra of **1** in $CHCl_3$ (Figure S1)

Figure S1. UV-vis absorption (1.0×10^{-5} M) and photoluminescence spectra (1.0×10^{-7} M) of **1**



5. Solvent effect in **1**/green-LED-promoted reductive desulfonylation (Scheme S1)

Scheme S1



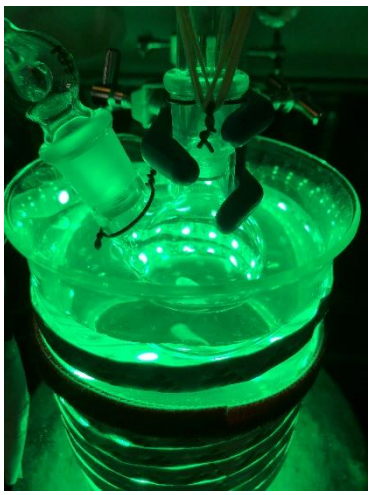
solvent(s)	yield %
MeCN (2.5 mL), THF (0.5 mL)	**3a** 88%
DMF (2.5 mL)	**3a** 5% (**2a** 95% recovered)[a]
DMSO (2.5 mL)	nr[b] (**2a** quantitatively recovered)[a]
THF (2.5 mL)	nr[b] (**2a** quantitatively recovered)[a]
toluene (2.5 mL), THF (0.5 mL)	nr[b] (**2a** insoluble in this solvents system)

[a]Obtained by using 1,4-dioxane as an internal standard.

[b]No reaction occured.

6. Reaction apparatus: photoreactor for the reductive desulfonylation.

Green-light irradiation was conducted in a glass water-bath which was surrounded by ca. 2 meters of LED strip lightning (30 W, λ =514 nm ± 70 nm).



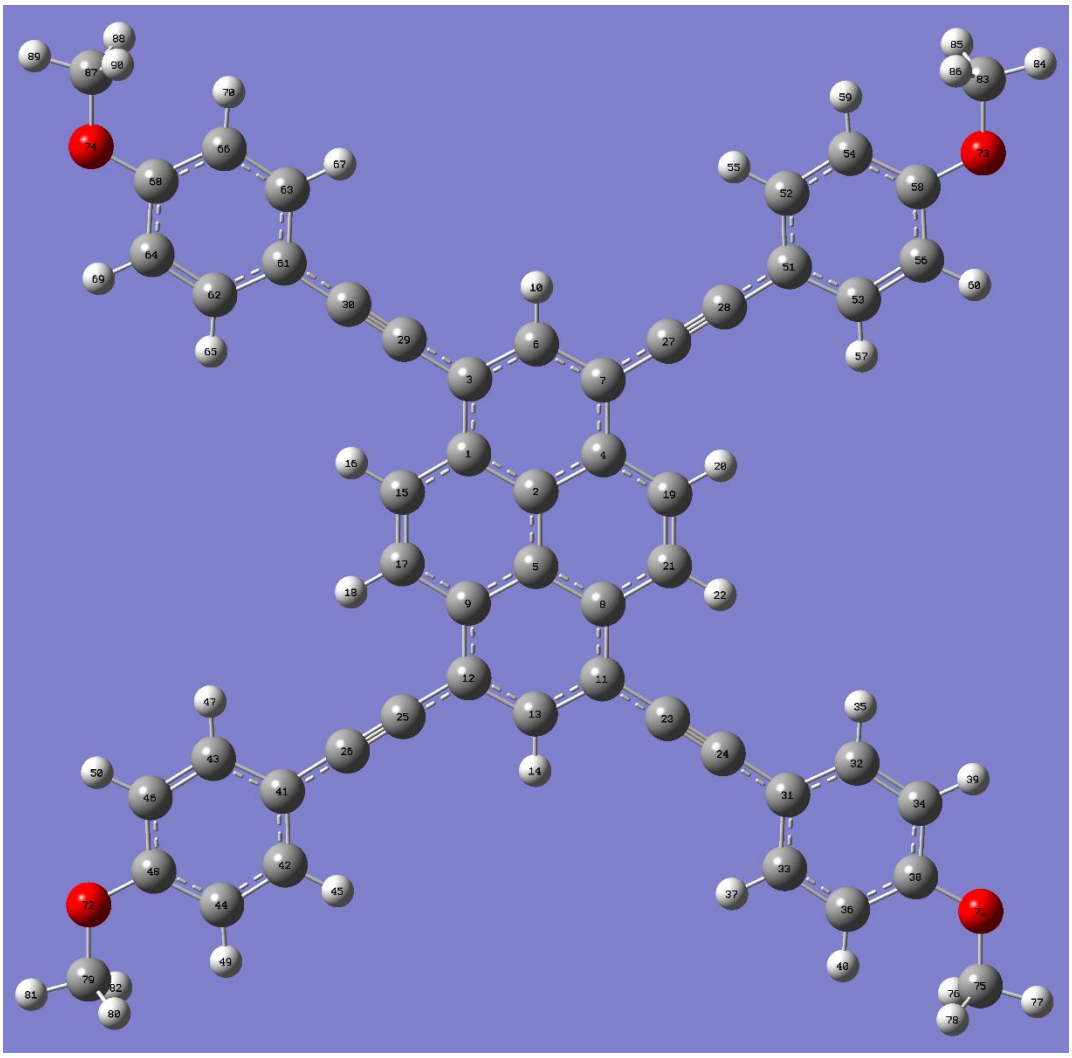
7. DFT calculations for **1**, **1 radical anion**, **2a**, **2d**, and **2e** (Tables S2 and S3)

DFT calculations of **1**, **1 radical anion**, **2a**, **2d**, and **2e** were performed at the B3LYP/6-31G(d) level by using Gaussian09 program package.[S3]

Table S2. Potential energies of the frontier orbitals of **1**, **1 radical anion**, and (*E*)-**2a**.

	1 [eV]	**1 radical anion**[a] [eV]	(*E*)-**2a** [eV]
LUMO	-2.13	-1.35	-1.64
SOMO		-0.44	
HOMO	-4.60		-6.31
[a]α spin			

Cartesian coordinates for optimized structure of **1** (ground state).



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.426821	1.238030	-0.001242
2	6	0	0.717064	-0.000882	-0.001397
3	6	0	2.853274	1.222422	-0.001107
4	6	0	1.424003	-1.241402	-0.001497
5	6	0	-0.717241	0.000742	-0.001334
6	6	0	3.530501	-0.004074	-0.001108
7	6	0	2.850498	-1.229021	-0.001348

8	6	0	-1.426996	-1.238173	-0.001353
9	6	0	-1.424183	1.241260	-0.001143
10	1	0	4.614946	-0.005300	-0.001017
11	6	0	-2.853448	-1.222565	-0.001119
12	6	0	-2.850687	1.228875	-0.000906
13	6	0	-3.530680	0.003929	-0.000895
14	1	0	-4.615126	0.005147	-0.000695
15	6	0	0.685226	2.457431	-0.001143
16	1	0	1.235342	3.392761	-0.001052
17	6	0	-0.679827	2.458975	-0.001093
18	1	0	-1.227827	3.395544	-0.000960
19	6	0	0.679652	-2.459119	-0.001567
20	1	0	1.227656	-3.395687	-0.001584
21	6	0	-0.685401	-2.457577	-0.001507
22	1	0	-1.235518	-3.392906	-0.001509
23	6	0	-3.604641	-2.428921	-0.001024
24	6	0	-4.268969	-3.450116	-0.000867
25	6	0	-3.599059	2.436984	-0.000568
26	6	0	-4.260801	3.459857	-0.000159
27	6	0	3.598908	-2.437108	-0.001352
28	6	0	4.260722	-3.459935	-0.001249
29	6	0	3.604471	2.428775	-0.001010
30	6	0	4.268800	3.449969	-0.000975
31	6	0	-5.048021	-4.639973	-0.000626
32	6	0	-4.433813	-5.912864	-0.001168
33	6	0	-6.453408	-4.584757	0.000201
34	6	0	-5.193817	-7.070162	-0.000885
35	1	0	-3.350153	-5.978070	-0.001807
36	6	0	-7.224597	-5.745141	0.000498
37	1	0	-6.944092	-3.616301	0.000630
38	6	0	-6.596471	-6.997612	-0.000039
39	1	0	-4.726303	-8.049763	-0.001293
40	1	0	-8.305368	-5.662391	0.001149
41	6	0	-5.036487	4.651908	0.000420
42	6	0	-6.442014	4.600862	0.003497
43	6	0	-4.418504	5.922988	-0.001991

44	6	0	-7.209758	5.763538	0.004208
45	1	0	-6.935590	3.633877	0.005395
46	6	0	-5.175061	7.082530	-0.001326
47	1	0	-3.334658	5.984969	-0.004399
48	6	0	-6.577925	7.014135	0.001808
49	1	0	-8.290769	5.684017	0.006632
50	1	0	-4.704640	8.060737	-0.003173
51	6	0	5.036581	-4.651880	-0.000934
52	6	0	6.442066	-4.600580	0.009784
53	6	0	4.418873	-5.923044	-0.011175
54	6	0	7.210034	-5.763104	0.010446
55	1	0	6.935406	-3.633506	0.017823
56	6	0	5.175658	-7.082444	-0.010666
57	1	0	3.335067	-5.985198	-0.019579
58	6	0	6.578469	-7.013803	0.000213
59	1	0	8.290997	-5.683394	0.018944
60	1	0	4.705455	-8.060724	-0.018563
61	6	0	5.047829	4.639842	-0.000943
62	6	0	4.433598	5.912722	-0.002279
63	6	0	6.453216	4.584651	0.000414
64	6	0	5.193581	7.070033	-0.002253
65	1	0	3.349936	5.977907	-0.003348
66	6	0	7.224384	5.745049	0.000458
67	1	0	6.943916	3.616204	0.001455
68	6	0	6.596236	6.997509	-0.000878
69	1	0	4.726050	8.049625	-0.003286
70	1	0	8.305156	5.662319	0.001527
71	8	0	-7.249082	-8.193562	0.000201
72	8	0	-7.226968	8.212017	0.002270
73	8	0	7.227723	-8.211584	-0.000078
74	8	0	7.248825	8.193470	-0.000968
75	6	0	-8.668729	-8.188177	0.001101
76	1	0	-9.070609	-7.694779	-0.893541
77	1	0	-8.971023	-9.236849	0.001168
78	1	0	-9.069468	-7.694990	0.896371
79	6	0	-8.646625	8.210862	0.005608

80	1	0	-9.047292	7.719414	0.901868
81	1	0	-8.945791	9.260431	0.005546
82	1	0	-9.051520	7.718114	-0.888036
83	6	0	8.647357	-8.210272	0.011259
84	1	0	8.946652	-9.259801	0.009399
85	1	0	9.057216	-7.714506	-0.878439
86	1	0	9.042874	-7.721770	0.911402
87	6	0	8.668472	8.188111	0.000422
88	1	0	9.070667	7.694328	-0.893867
89	1	0	8.970748	9.236788	0.000135
90	1	0	9.068913	7.695321	0.896045

Cartesian coordinates for optimized structure of **1 radical anion**
Numbered similar to **1** (ground state).

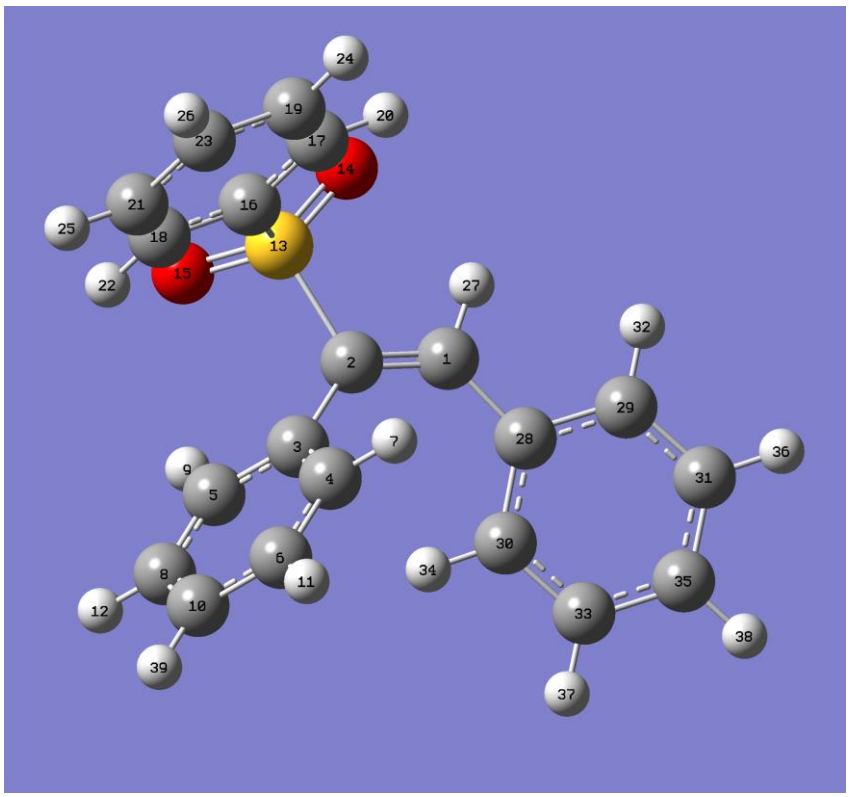
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.428066	-1.245210	-0.000119
2	6	0	-0.718556	-0.000003	-0.000150
3	6	0	-2.875093	-1.228036	-0.000003
4	6	0	-1.428031	1.245223	-0.000080
5	6	0	0.718528	-0.000022	-0.000243
6	6	0	-3.546421	0.000036	0.000085
7	6	0	-2.875059	1.228089	0.000044
8	6	0	1.428038	1.245184	-0.000266
9	6	0	1.428003	-1.245249	-0.000300
10	1	0	-4.632304	0.000051	0.000178
11	6	0	2.875064	1.228011	-0.000338
12	6	0	2.875031	-1.228115	-0.000366
13	6	0	3.546392	-0.000062	-0.000382
14	1	0	4.632276	-0.000076	-0.000429
15	6	0	-0.690946	-2.446462	-0.000192
16	1	0	-1.233774	-3.387120	-0.000171
17	6	0	0.690850	-2.446480	-0.000278

18	1	0	1.233653	-3.387153	-0.000324
19	6	0	-0.690878	2.446455	-0.000113
20	1	0	-1.233681	3.387127	-0.000056
21	6	0	0.690918	2.446436	-0.000206
22	1	0	1.233746	3.387094	-0.000224
23	6	0	3.625833	2.425078	-0.000351
24	6	0	4.287388	3.453574	-0.000352
25	6	0	3.625761	-2.425207	-0.000397
26	6	0	4.287283	-3.453724	-0.000407
27	6	0	-3.625790	2.425181	0.000138
28	6	0	-4.287305	3.453703	0.000236
29	6	0	-3.625861	-2.425104	0.000023
30	6	0	-4.287417	-3.453599	0.000043
31	6	0	5.065101	4.638783	-0.000344
32	6	0	4.458053	5.918789	-0.000329
33	6	0	6.474303	4.591927	-0.000347
34	6	0	5.219880	7.076369	-0.000313
35	1	0	3.374341	5.985602	-0.000327
36	6	0	7.245643	5.753826	-0.000332
37	1	0	6.966565	3.624019	-0.000359
38	6	0	6.620853	7.005931	-0.000313
39	1	0	4.749957	8.055607	-0.000299
40	1	0	8.327006	5.668385	-0.000334
41	6	0	5.064984	-4.638940	-0.000396
42	6	0	6.474187	-4.592108	-0.000186
43	6	0	4.457915	-5.918936	-0.000583
44	6	0	7.245508	-5.754019	-0.000156
45	1	0	6.966466	-3.624208	-0.000039
46	6	0	5.219722	-7.076528	-0.000552
47	1	0	3.374201	-5.985731	-0.000749
48	6	0	6.620696	-7.006113	-0.000334
49	1	0	8.326873	-5.668599	0.000007
50	1	0	4.749783	-8.055758	-0.000691
51	6	0	-5.064968	4.638944	0.000394
52	6	0	-6.474172	4.592156	0.001266
53	6	0	-4.457859	5.918921	-0.000297

54	6	0	-7.245457	5.754092	0.001460
55	1	0	-6.966481	3.624272	0.001812
56	6	0	-5.219629	7.076537	-0.000102
57	1	0	-3.374143	5.985681	-0.000981
58	6	0	-6.620605	7.006166	0.000786
59	1	0	-8.326823	5.668706	0.002138
60	1	0	-4.749659	8.055752	-0.000625
61	6	0	-5.065134	-4.638805	0.000066
62	6	0	-4.458091	-5.918813	-0.000110
63	6	0	-6.474336	-4.591945	0.000266
64	6	0	-5.219921	-7.076391	-0.000086
65	1	0	-3.374379	-5.985630	-0.000266
66	6	0	-7.245680	-5.753841	0.000291
67	1	0	-6.966595	-3.624035	0.000404
68	6	0	-6.620894	-7.005948	0.000116
69	1	0	-4.750002	-8.055630	-0.000221
70	1	0	-8.327043	-5.668396	0.000448
71	8	0	7.280603	8.211375	-0.000296
72	8	0	7.280424	-8.211568	-0.000321
73	8	0	-7.280294	8.211643	0.000908
74	8	0	-7.280648	-8.211390	0.000123
75	6	0	8.693932	8.189962	-0.000242
76	1	0	9.095157	7.690847	-0.893748
77	1	0	9.012949	9.234961	-0.000202
78	1	0	9.095085	7.690798	0.893269
79	6	0	8.693754	-8.190179	0.000050
80	1	0	9.094714	-7.691074	0.893679
81	1	0	9.012753	-9.235183	0.000099
82	1	0	9.095190	-7.691020	-0.893337
83	6	0	-8.693625	8.190303	0.002169
84	1	0	-9.012588	9.235318	0.002306
85	1	0	-9.095644	7.691065	-0.890912
86	1	0	-9.094035	7.691303	0.896104
87	6	0	-8.693978	-8.189972	0.000350
88	1	0	-9.095308	-7.690776	-0.893063
89	1	0	-9.012998	-9.234969	0.000336

90	1	0	-9.095021	-7.690886	0.893954

Cartesian coordinates for optimized structure of (*E*)-**2a**



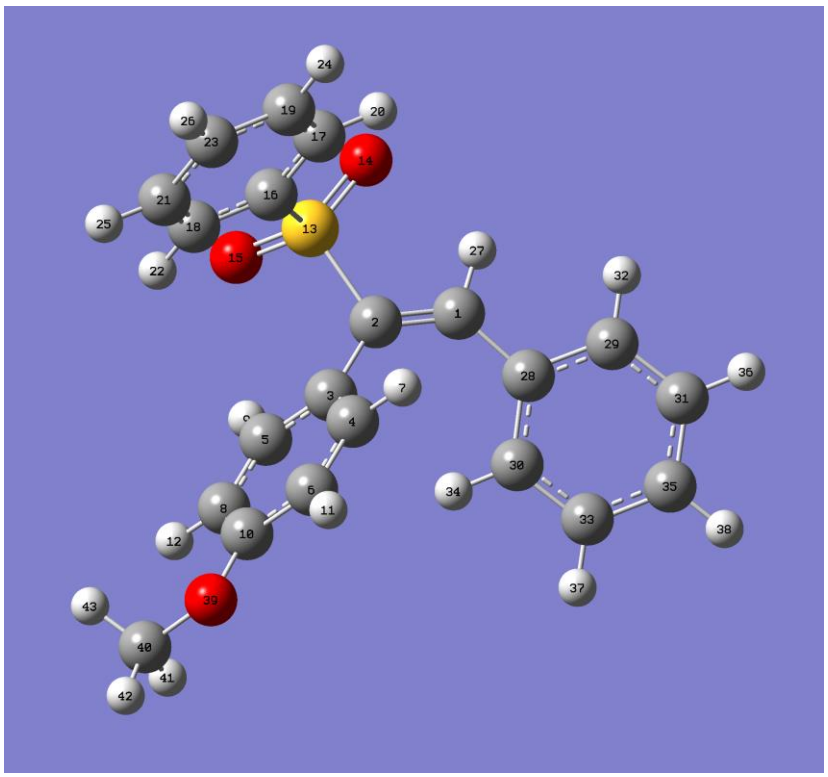
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.320815	-1.130637	0.436747
2	6	0	0.285998	-0.286085	0.614677
3	6	0	0.192389	1.162604	0.306928
4	6	0	0.242929	1.592772	-1.030075
5	6	0	0.035506	2.119491	1.323915
6	6	0	0.156188	2.948408	-1.342250
7	1	0	0.353904	0.856526	-1.820790
8	6	0	-0.050338	3.475453	1.006157
9	1	0	-0.023809	1.792496	2.356055
10	6	0	0.010968	3.893706	-0.324541

11	1	0	0.198525	3.265646	-2.380751
12	1	0	-0.165310	4.205936	1.802409
13	16	0	-1.213773	-1.048894	1.314508
14	8	0	-0.972786	-2.496355	1.459269
15	8	0	-1.622948	-0.238048	2.476126
16	6	0	-2.467334	-0.839066	0.037877
17	6	0	-2.613838	-1.828250	-0.937220
18	6	0	-3.275798	0.298740	0.051523
19	6	0	-3.586286	-1.665775	-1.923356
20	1	0	-1.987880	-2.713821	-0.904283
21	6	0	-4.245422	0.449527	-0.940513
22	1	0	-3.152409	1.037822	0.835373
23	6	0	-4.397700	-0.527964	-1.926295
24	1	0	-3.716081	-2.430465	-2.684031
25	1	0	-4.884224	1.328154	-0.939707
26	1	0	-5.155524	-0.406752	-2.695604
27	1	0	1.114219	-2.175238	0.663802
28	6	0	2.696909	-0.869373	-0.006515
29	6	0	3.462661	-1.978127	-0.415820
30	6	0	3.307469	0.399625	-0.014025
31	6	0	4.778393	-1.826936	-0.846466
32	1	0	3.011594	-2.967304	-0.396389
33	6	0	4.626580	0.547205	-0.434040
34	1	0	2.754568	1.267271	0.324554
35	6	0	5.365271	-0.560671	-0.858520
36	1	0	5.346526	-2.696957	-1.164105
37	1	0	5.082932	1.533398	-0.425957
38	1	0	6.393725	-0.437773	-1.187139
39	1	0	-0.056669	4.950709	-0.567850

Table S3. Potential energies of the frontier orbitals of (*E*)-**2d** and (*E*)-**2e**.

	(*E*)-**2d** [eV]	(*E*)-**2e** [eV]
LUMO	-1.57	-1.87
HOMO	-5.93	-6.53

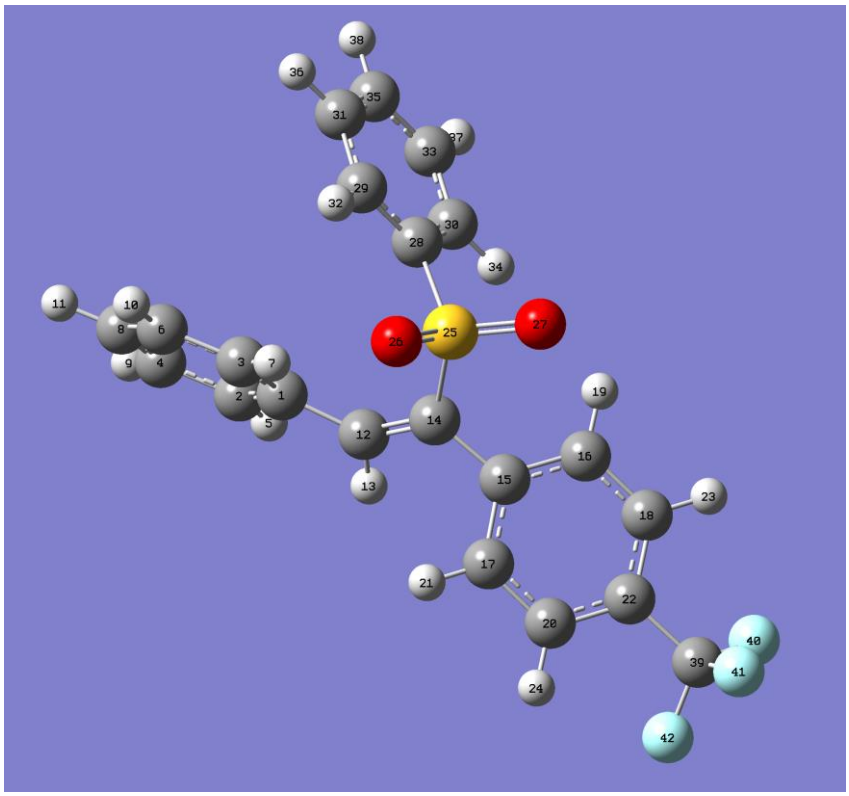
Cartesian coordinates for optimized structure of (*E*)-**2d**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.434477	-1.558299	0.426724
2	6	0	0.351959	-0.778528	0.620067
3	6	0	0.167414	0.662330	0.329821
4	6	0	0.240070	1.126082	-0.998675
5	6	0	-0.100585	1.594627	1.341726
6	6	0	0.069137	2.468716	-1.299449
7	1	0	0.436404	0.418383	-1.798725
8	6	0	-0.273817	2.949447	1.050366
9	1	0	-0.180438	1.255285	2.368410
10	6	0	-0.188176	3.393425	-0.274763
11	1	0	0.124574	2.828361	-2.322089
12	1	0	-0.472897	3.641671	1.860324
13	16	0	-1.097103	-1.646025	1.306173

14	8	0	-0.768070	-3.078156	1.432202
15	8	0	-1.558766	-0.880672	2.479879
16	6	0	-2.362226	-1.497709	0.031298
17	6	0	-2.449254	-2.483280	-0.954555
18	6	0	-3.237917	-0.411042	0.056152
19	6	0	-3.429693	-2.369218	-1.939659
20	1	0	-1.770670	-3.329487	-0.930956
21	6	0	-4.214532	-0.308010	-0.935090
22	1	0	-3.159804	0.325826	0.847818
23	6	0	-4.307949	-1.282296	-1.931317
24	1	0	-3.512878	-3.132138	-2.708612
25	1	0	-4.904734	0.530831	-0.925916
26	1	0	-5.071323	-1.198393	-2.700116
27	1	0	1.290044	-2.617878	0.630832
28	6	0	2.793801	-1.206935	-0.006383
29	6	0	3.624310	-2.258739	-0.439085
30	6	0	3.329960	0.095149	0.019967
31	6	0	4.930271	-2.020797	-0.860185
32	1	0	3.231601	-3.272674	-0.445545
33	6	0	4.639478	0.329425	-0.390366
34	1	0	2.725448	0.920249	0.376313
35	6	0	5.442676	-0.722732	-0.838955
36	1	0	5.548940	-2.848342	-1.196484
37	1	0	5.037556	1.340049	-0.356436
38	1	0	6.463064	-0.532202	-1.160441
39	8	0	-0.340034	4.688011	-0.671678
40	6	0	-0.605008	5.670340	0.318881
41	1	0	0.211540	5.736233	1.049683
42	1	0	-0.688203	6.618169	-0.215699
43	1	0	-1.545987	5.467261	0.846541

Cartesian coordinates for optimized structure of (*E*)-**2e**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.114754	1.852303	0.161878
2	6	0	-2.585594	2.585277	1.269799
3	6	0	-2.958698	1.709916	-0.954741
4	6	0	-3.871342	3.116359	1.285336
5	1	0	-1.932913	2.727541	2.128007
6	6	0	-4.239685	2.260415	-0.942235
7	1	0	-2.598831	1.192829	-1.836393
8	6	0	-4.704938	2.954370	0.175768
9	1	0	-4.218768	3.666525	2.155474
10	1	0	-4.874472	2.151990	-1.817558
11	1	0	-5.704949	3.379576	0.178173
12	6	0	-0.726700	1.369284	0.218410
13	1	0	-0.077221	2.029844	0.794704

14	6	0	-0.083297	0.277382	-0.258045
15	6	0	1.397685	0.180745	-0.140178
16	6	0	2.054498	-0.912755	0.450986
17	6	0	2.173647	1.264074	-0.588502
18	6	0	3.437061	-0.910878	0.601711
19	1	0	1.483122	-1.767317	0.790304
20	6	0	3.557828	1.268090	-0.437486
21	1	0	1.682609	2.103619	-1.070789
22	6	0	4.193032	0.179189	0.160935
23	1	0	3.930475	-1.754191	1.073437
24	1	0	4.141199	2.114123	-0.785180
25	16	0	-0.907646	-1.104866	-1.125983
26	8	0	-1.423359	-0.629658	-2.423726
27	8	0	0.028966	-2.239315	-1.095899
28	6	0	-2.317230	-1.557785	-0.095274
29	6	0	-3.572950	-1.664895	-0.690893
30	6	0	-2.114277	-1.903156	1.242699
31	6	0	-4.649389	-2.115385	0.075263
32	1	0	-3.694722	-1.400758	-1.735513
33	6	0	-3.198050	-2.341079	2.001283
34	1	0	-1.126652	-1.829262	1.687797
35	6	0	-4.463838	-2.447888	1.417667
36	1	0	-5.632410	-2.203426	-0.378361
37	1	0	-3.053658	-2.605577	3.044871
38	1	0	-5.305141	-2.794015	2.011644
39	6	0	5.692728	0.150229	0.279389
40	9	0	6.096273	-0.540934	1.369300
41	9	0	6.270084	-0.438421	-0.793382
42	9	0	6.214241	1.394386	0.371803

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8. Cyclic voltammograms of **1** (Figure S2) and **2a** (Figures S3 and S4)

The reduction potentials (vs Fc/Fc^{+}) were measured in CH_2Cl_2 and MeCN (1.0×10^{-4} M, 100 mV/s scan rate, 0.1 M Bu_4NPF_6) by use of a glassy carbon as the working electrode, a Pt counter electrode, and an Ag/Ag^{+} reference electrode (0.01 M $AgNO_3$ and 0.1 M tetrabutylammonium perchlorate in acetonitrile) in 0.1 M $LiClO_4$/acetonitrile. E_{LUMO} was calculated by the following equation.[S4]

$$E_{LUMO} = -4.80 - E_{1/2}^{red} \text{ [eV]}$$

Figure S2. The CV profile of **1** in reduction (CH_2Cl_2)

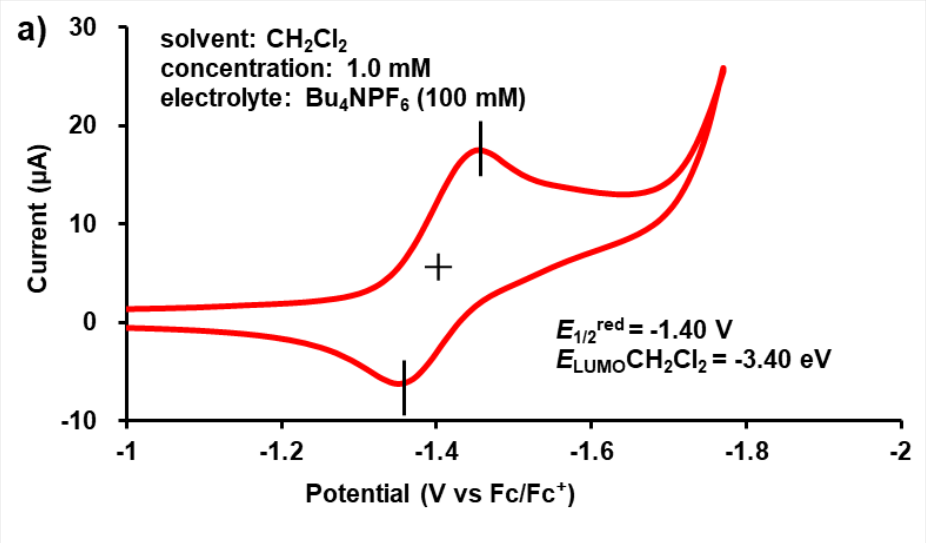


Figure S3. The CV profile of **2a** in reduction (CH_2Cl_2)

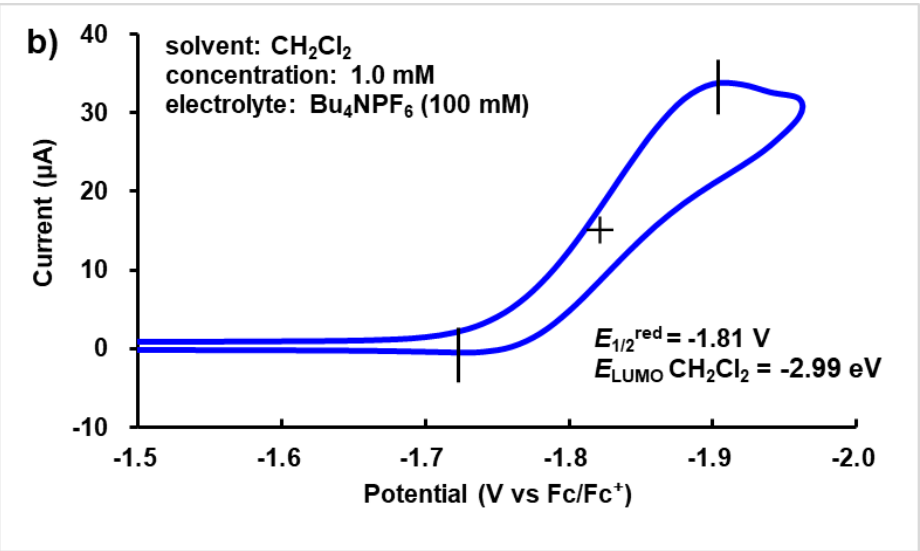
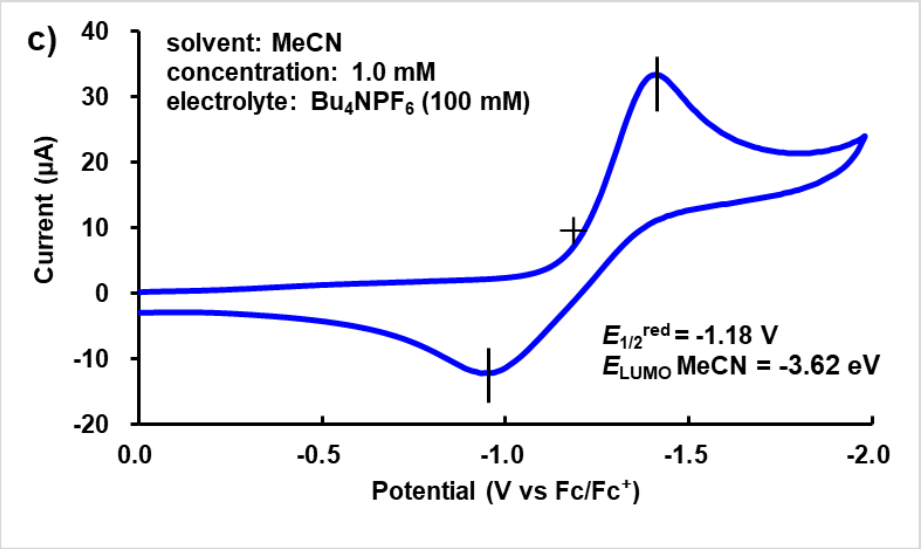
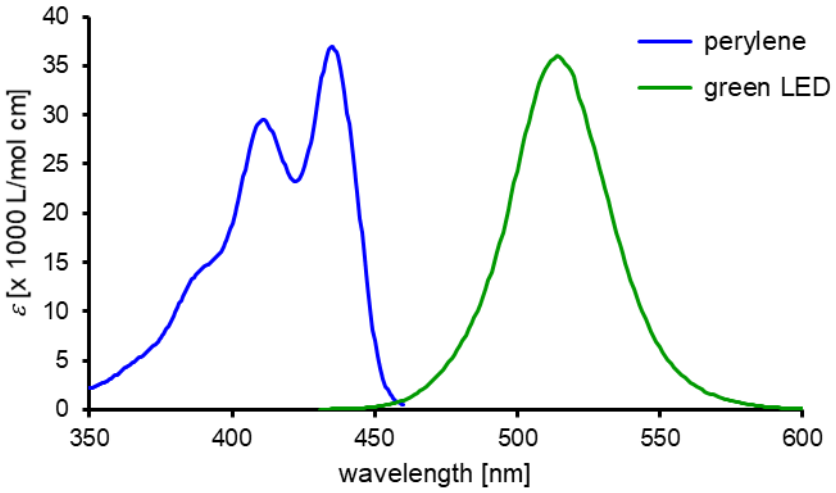


Figure S4. The CV profile of **2a** in reduction (MeCN)



9. UV-vis absorption of perylene and emission spectra of green-LED (Figure S5)



10. UV-vis absorption and photoluminescence spectra of **4** in $CHCl_3$ (Figure S6)

Aminodiyne **4** was synthesized according to the literature.[S5]

Figure S6. UV-vis absorption and photoluminescence spectra of **4**

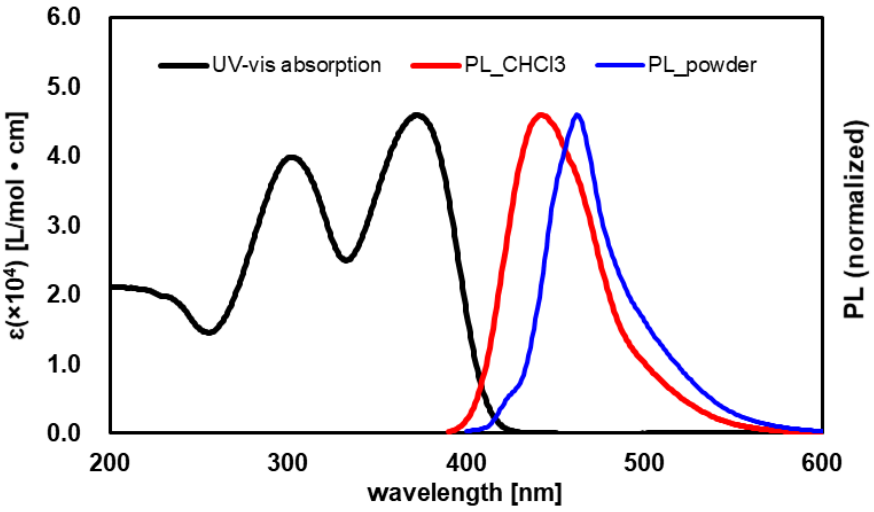


Table S4. Summary of UV-vis absorption and photoluminescence of **4**

	UV-vis absorption (1.0×10^{-5} M) [nm] ($\varepsilon(10^4)$ L/mol·cm)	photoluminescence	
		In $CHCl_3$ (1.0×10^{-7} M) [nm] (Φ_F)[a]	powdery state [nm] (Φ_F)[a]
4	373 (4.6)	442 (0.92)	462 (0.53)

[a]Absolute fluorescence quantum yield measured by integrated sphere system (Hamamatsu photonics C9920-02).

11. DFT calculations for transformation of **2a anionic radical** to **3.**

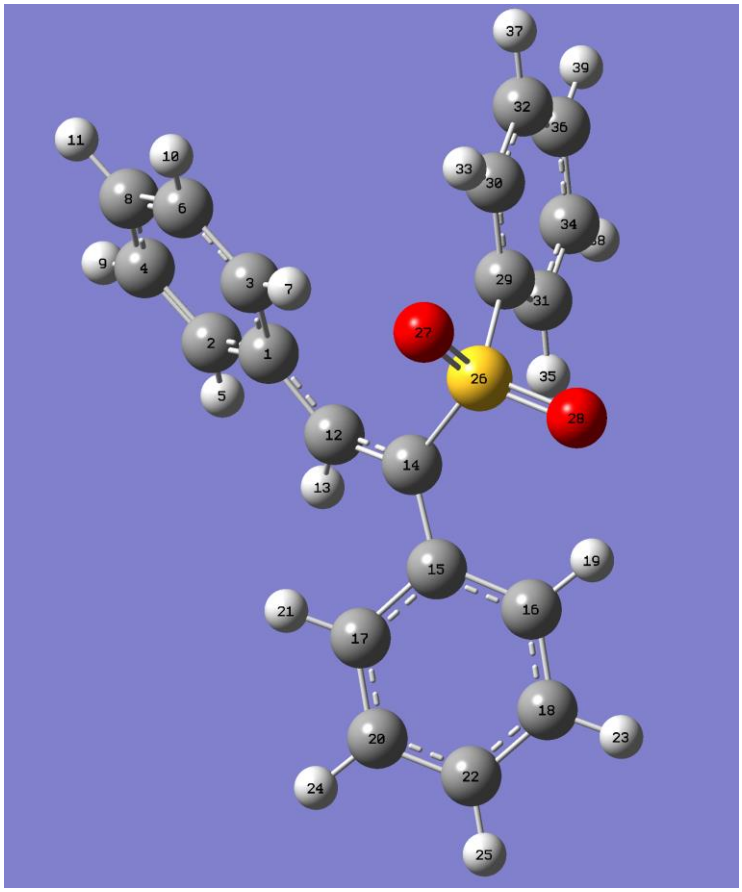
Table S5. The heats of formation (HOFs) simulated for **2**·⁻, **7**·, **7**⁻, **3a**, and $PhSO_2^-$ at the B3LYP/6-31G(d) level of theory.

stage	Chemical species	HOF [kcal/mol] (Hartree)	$\Delta(\Sigma HOF)$ [kcal/mol][a]
1	**2a**·⁻	-828523.2 (-1320.33574900)	0.0
2	**7**· (radical)	-828879.7 (-1320.90388274)	-356.5
3	**7**⁻ (anion)	-828904.4 (-1320.94318120)	-381.2
4	**3** $PhSO_2^-$	-339300.6 (-540.70996388) -489627.7 (-780.27136535)	-405.1

(a) $\Delta(\Sigma HOF)$ was calculated by the following equation.

$$\Delta(\Sigma HOF) = \Sigma HOF(\text{stage x}) - HOF(\text{stage 1})$$

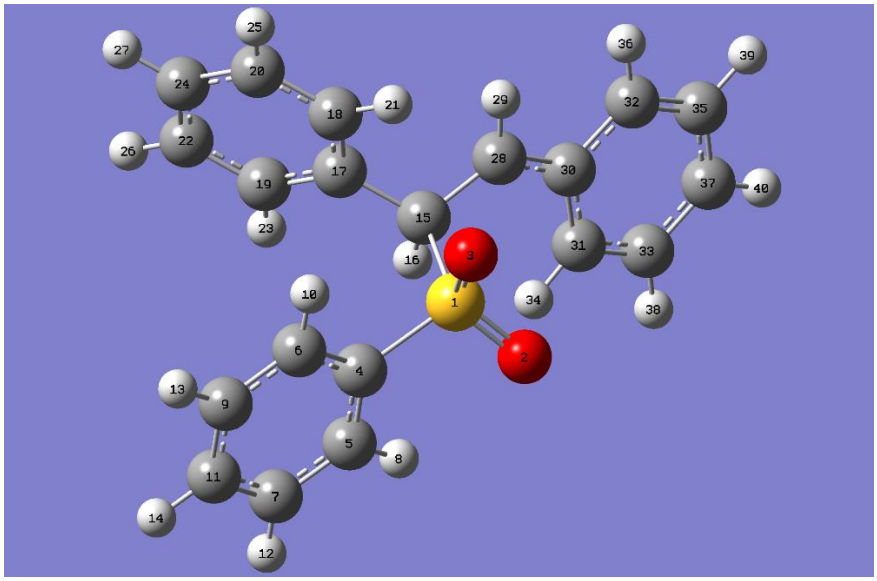
Cartesian coordinates for optimized structure of **2a**·⁻ (anionic radical).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000005604	0.000005792	0.000004079
2	6	0.000004586	-0.000002940	-0.000003426
3	6	0.000011325	0.000004872	-0.000001890
4	6	-0.000002318	-0.000004518	-0.000006834
5	1	0.000000721	-0.000003072	-0.000005988
6	6	-0.000003170	-0.000003539	-0.000004605
7	1	-0.000002487	0.000003329	-0.000001410
8	6	0.000002812	0.000003088	-0.000003708
9	1	0.000000870	-0.000003853	-0.000007250
10	1	0.000000043	0.000004740	-0.000001894
11	1	0.000000321	-0.000001167	-0.000005720
12	6	0.000003212	-0.000011848	-0.000017117
13	1	-0.000000294	0.000003822	-0.000001221
14	6	-0.000009780	-0.000006383	0.000015056
15	6	0.000001919	0.000002963	-0.000001555
16	6	-0.000002477	0.000003478	-0.000004272
17	6	0.000010332	-0.000008339	0.000001420
18	6	0.000002678	-0.000001183	0.000000372
19	1	-0.000001483	0.000001246	0.000002966
20	6	-0.000002931	0.000000540	-0.000004429
21	1	0.000002838	0.000004216	-0.000007718
22	6	-0.000002288	0.000004225	0.000001095
23	1	0.000000060	0.000000031	0.000003408
24	1	0.000001535	0.000001794	-0.000005364
25	1	0.000001534	0.000000775	-0.000002599
26	16	-0.000037098	0.000010878	0.000015019
27	8	0.000012500	0.000006572	-0.000011168
28	8	0.000016322	0.000005450	-0.000002516
29	6	0.000004733	-0.000005611	0.000014833
30	6	-0.000009111	0.000009297	0.000006112
31	6	0.000018661	-0.000008136	-0.000009501
32	6	0.000008255	-0.000006286	-0.000008051

33	1	0.000000942	0.000000772	0.000003577
34	6	-0.000026602	0.000004315	0.000007083
35	1	-0.000005870	-0.000001493	0.000002535
36	6	0.000009764	-0.000004160	0.000023630
37	1	-0.000002896	0.000000551	0.000008074
38	1	0.000000801	-0.000006000	0.000004943
39	1	-0.000002356	-0.000004221	0.000004035

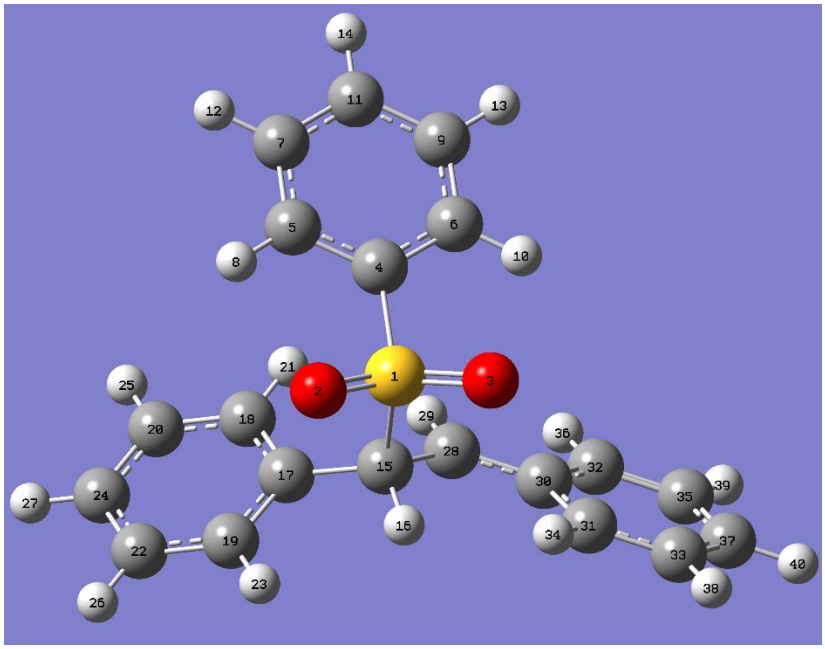
Cartesian coordinates for optimized structure of **7**· (radical).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	16	-0.000000244	0.000001145	-0.000003986
2	8	-0.000002368	0.000001550	-0.000001496
3	8	-0.000000804	0.000001802	0.000001862
4	6	-0.000003190	-0.000004316	-0.000000485
5	6	-0.000002477	-0.000000730	-0.000002339
6	6	-0.000001002	-0.000001086	-0.000001049
7	6	-0.000003096	-0.000003271	-0.000003271
8	1	-0.000003292	-0.000001659	-0.000002706

9	6	-0.000001737	-0.000002874	-0.000002637
10	1	-0.000000995	-0.000002078	-0.000000880
11	6	-0.000002909	-0.000004186	-0.000003106
12	1	-0.000003877	-0.000004236	-0.000003916
13	1	-0.000001373	-0.000004351	-0.000002093
14	1	-0.000003027	-0.000005704	-0.000003570
15	6	-0.000002534	0.000000502	0.000002385
16	1	0.000000546	0.000001525	-0.000000474
17	6	0.000004352	-0.000001503	-0.000003726
18	6	-0.000001516	-0.000002703	0.000004283
19	6	0.000005188	-0.000000670	0.000002388
20	6	0.000005929	-0.000000511	0.000003616
21	1	0.000001657	0.000001766	0.000000674
22	6	0.000000485	-0.000006291	0.000002266
23	1	0.000000823	-0.000003124	0.000000271
24	6	0.000002673	-0.000002294	-0.000002182
25	1	0.000003315	-0.000001340	0.000001854
26	1	0.000003810	-0.000004491	0.000001119
27	1	0.000004874	-0.000004185	0.000002799
28	6	0.000002402	0.000002707	0.000001454
29	1	-0.000000040	0.000002685	0.000002845
30	6	-0.000002420	0.000001262	0.000000583
31	6	0.000000128	0.000005851	-0.000000194
32	6	0.000003591	0.000003019	0.000001563
33	6	-0.000002064	0.000003339	0.000000663
34	1	-0.000000464	0.000002067	-0.000001503
35	6	0.000000187	0.000005294	0.000002465
36	1	0.000001555	0.000005083	0.000002500
37	6	0.000000579	0.000005710	0.000000644
38	1	-0.000001966	0.000003515	-0.000000236
39	1	0.000000619	0.000006685	0.000002616
40	1	-0.000001317	0.000006098	0.000001001

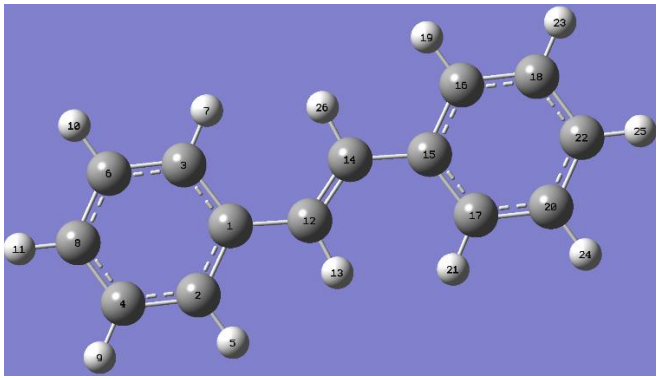
Cartesian coordinates for optimized structure of **7**$^{-}$ (anion).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	16	0.000618722	-0.009955837	-0.009314274
2	8	-0.015657915	0.002787538	0.017240729
3	8	0.002890813	0.008781759	0.006996354
4	6	-0.000922656	0.003621180	0.007660603
5	6	0.001765057	0.002078575	-0.001859060
6	6	0.001501662	-0.001068762	-0.001756203
7	6	-0.000959942	-0.001210234	0.000406723
8	1	0.000476212	-0.000600950	0.000354096
9	6	-0.002191228	0.000250283	-0.001147408
10	1	-0.000674759	-0.000845900	0.000711297
11	6	0.001820263	0.001096508	-0.000506684
12	1	-0.000970460	0.000444812	-0.000163220
13	1	0.000338851	0.000380163	-0.000791272
14	1	-0.000393346	0.000698579	-0.000572955
15	6	0.021550761	-0.000416767	-0.028817227
16	1	-0.000977917	0.000703814	0.003742811
17	6	0.006158987	0.004809024	0.004730878
18	6	-0.003414018	-0.000229791	-0.001279200

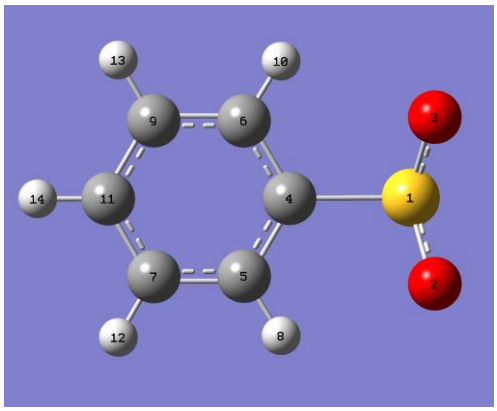
19	6	-0.003062718	-0.001596313	-0.001422627
20	6	0.001801994	0.000239220	0.000972618
21	1	0.001037661	-0.000487734	0.001315349
22	6	0.001020902	0.000101430	-0.000924642
23	1	0.000097198	0.000858390	0.000095916
24	6	-0.001579050	-0.001511666	-0.000148510
25	1	-0.000588146	0.000244632	-0.000735852
26	1	-0.000649766	-0.000924307	0.000396576
27	1	-0.001008795	-0.000457414	-0.000200105
28	6	-0.009340445	-0.006234115	0.006473788
29	1	-0.000551307	-0.000570770	-0.000752924
30	6	-0.018550988	-0.001545429	-0.001370945
31	6	0.007680598	-0.000223304	0.000974596
32	6	0.008165672	0.000519495	0.000168699
33	6	-0.003581695	-0.000167818	-0.004939963
34	1	-0.000637893	0.000660710	0.000347346
35	6	-0.004000899	-0.000949481	0.004226465
36	1	-0.001074746	0.000052538	-0.000772220
37	6	0.009209552	0.000145206	0.000505889
38	1	0.001272296	-0.000369621	0.001933927
39	1	0.001467798	0.000551977	-0.001913337
40	1	0.001913692	0.000340382	0.000133968

Cartesian coordinates for optimized structure of **3a**.



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.940347	-0.186150	0.000002
2	6	0	-2.829346	-1.277577	-0.000057
3	6	0	-2.493580	1.109755	0.000058
4	6	0	-4.210002	-1.088447	-0.000054
5	1	0	-2.424761	-2.287179	-0.000100
6	6	0	-3.871602	1.299524	0.000050
7	1	0	-1.839970	1.976943	0.000109
8	6	0	-4.739020	0.202583	-0.000004
9	1	0	-4.872504	-1.950034	-0.000094
10	1	0	-4.273498	2.309429	0.000097
11	1	0	-5.814783	0.355135	-0.000006
12	6	0	-0.498643	-0.453914	0.000004
13	1	0	-0.243224	-1.512570	-0.000006
14	6	0	0.498623	0.453878	0.000005
15	6	0	1.940342	0.186123	0.000002
16	6	0	2.829315	1.277565	-0.000057
17	6	0	2.493612	-1.109772	0.000059
18	6	0	4.209978	1.088471	-0.000054
19	1	0	2.424707	2.287159	-0.000099
20	6	0	3.871638	-1.299506	0.000050
21	1	0	1.840035	-1.976981	0.000110
22	6	0	4.739029	-0.202541	-0.000005
23	1	0	4.872458	1.950075	-0.000095
24	1	0	4.273562	-2.309399	0.000096
25	1	0	5.814796	-0.355065	-0.000007
26	1	0	0.243198	1.512535	-0.000003

Cartesian coordinates for optimized structure of $PhSO_2^-$ (anion).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	16	-0.000064689	-0.000049993	-0.000002288
2	8	0.000002631	0.000000889	-0.000004209
3	8	0.000057703	0.000048697	0.000006354
4	6	0.000005930	-0.000016689	0.000021529
5	6	0.000006318	0.000005660	-0.000006158
6	6	-0.000012919	0.000014511	-0.000015609
7	6	0.000000196	0.000005482	-0.000003199
8	1	-0.000003441	0.000001656	-0.000001516
9	6	0.000008974	-0.000001744	0.000004189
10	1	0.000000749	0.000001851	-0.000000877
11	6	-0.000009019	-0.000001980	-0.000004458
12	1	0.000001507	-0.000004643	0.000003340
13	1	0.000004035	-0.000002510	0.000000670
14	1	0.000002026	-0.000001187	0.000002229

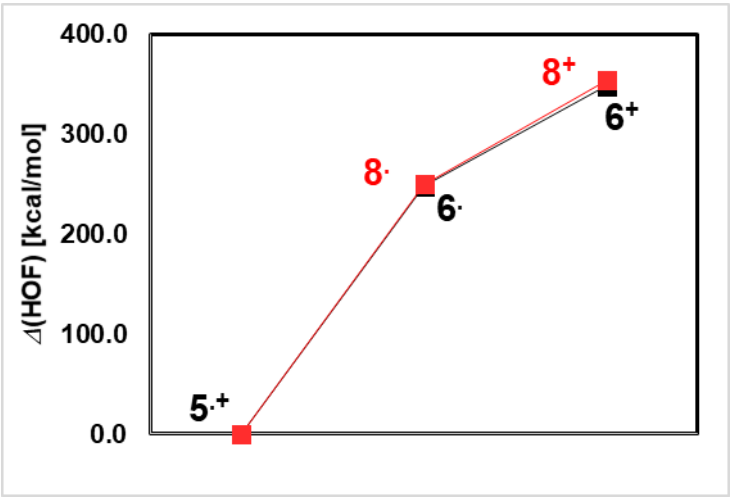
Table S6. The heats of formation (HOFs) simulated for **5** derivatives at the B3LYP/6-31G(d) level of theory.

stage	Chemical species	HOF [kcal/mol] (Hartree)	Δ(HOF) [kcal/mol][a]
1	**5**$^{\cdot+}$	-232670.7 (-370.78439105)	0.0
2	**6**$^{\cdot}$	-232423.1 (-370.38984393)	+247.6
3	**6**$^{+}$	-232322.8 (-370.22998015)	+347.9
2'	**8**$^{\cdot}$	-232421.0 (-370.38634735)	+249.8
3'	**8**$^{+}$	-232317.1 (-370.22087328)	+353.6

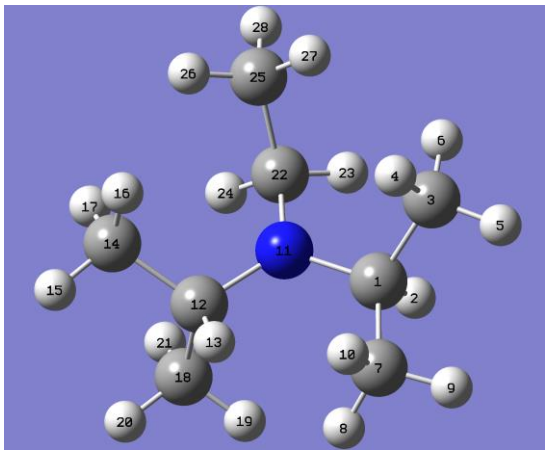
(a) Δ(HOF) was calculated by the following equation.

$$\Delta(\text{HOF}) = \text{HOF(stage x)} - \text{HOF(stage 1)}$$

Figure S7. An energy diagram in transformation of **5**$^{\cdot+}$ to **6**$^{+}$ and **8**$^{+}$.



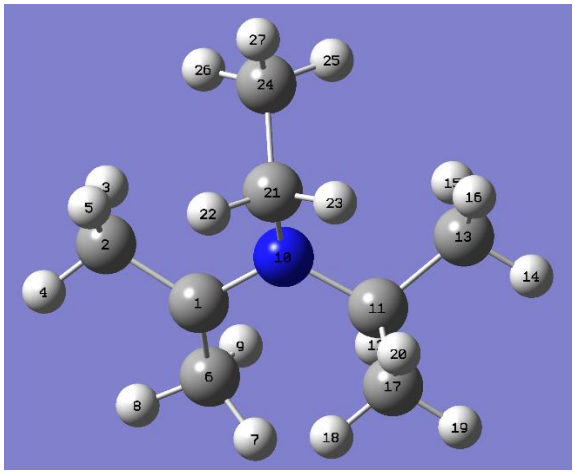
Cartesian coordinates for optimized structure of **5**$^{\cdot+}$ (cationic radical).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000007136	0.000005761	0.000003481
2	1	0.000000315	-0.000000855	-0.000000441
3	6	0.000003915	-0.000006577	0.000003547
4	1	-0.000000719	0.000000347	0.000000580
5	1	-0.000000768	-0.000001133	0.000002026
6	1	-0.000000182	0.000000999	0.000000773
7	6	-0.000003365	-0.000004946	-0.000001525
8	1	0.000002036	-0.000000186	-0.000000901
9	1	0.000001584	0.000000736	0.000000927
10	1	0.000000943	-0.000000272	-0.000000168
11	7	-0.000016455	0.000015057	0.000010508
12	6	0.000013107	-0.000004147	-0.000006711
13	1	-0.000002251	0.000001672	-0.000000263
14	6	-0.000004276	-0.000006240	0.000002378
15	1	-0.000000213	0.000002580	-0.000001978
16	1	-0.000000948	0.000002618	-0.000000625
17	1	0.000001474	0.000002330	-0.000002488
18	6	0.000000496	-0.000001402	-0.000002804
19	1	0.000002209	0.000001255	-0.000000749
20	1	0.000001100	0.000000793	-0.000002229
21	1	0.000000492	0.000000999	-0.000001516

22	6	0.000000574	-0.000013685	-0.000006228
23	1	0.000000161	0.000000289	0.000000539
24	1	0.000000942	0.000000981	0.000000804
25	6	-0.000001208	0.000003545	0.000002483
26	1	-0.000003243	0.000000272	-0.000000499
27	1	-0.000001810	-0.000000041	0.000000142
28	1	-0.000001048	-0.000000751	0.000000936

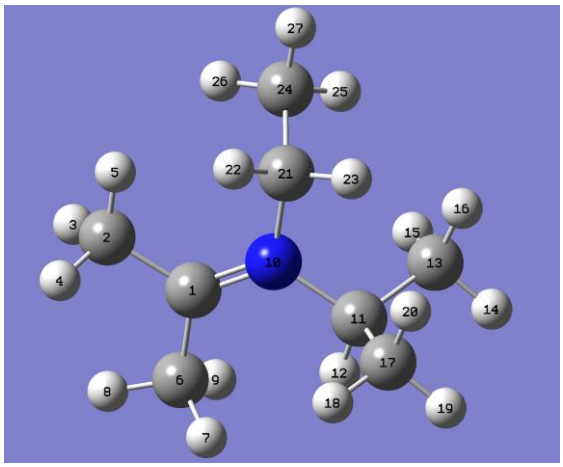
Cartesian coordinates for optimized structure of **6**· (radical).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000004435	-0.000001974	-0.000009471
2	6	-0.000009206	-0.000009540	-0.000010869
3	1	0.000003522	0.000004927	-0.000003183
4	1	0.000002015	0.000001389	-0.000005915
5	1	-0.000001451	-0.000004333	-0.000005447
6	6	0.000003843	0.000010512	-0.000004136
7	1	0.000002868	0.000002809	0.000002977
8	1	0.000003992	0.000001333	-0.000001021
9	1	0.000004883	0.000002707	0.000001822
10	7	0.000007403	0.000008982	0.000001550

11	6	0.000000788	-0.000005782	0.000000958
12	1	-0.000001666	0.000006341	0.000005323
13	6	0.000000990	-0.000004053	0.000004465
14	1	0.000001913	0.000000816	0.000009015
15	1	0.000005321	0.000003113	0.000003926
16	1	0.000001448	-0.000002898	0.000005622
17	6	-0.000003964	-0.000004311	0.000007562
18	1	-0.000002316	-0.000002098	0.000006387
19	1	-0.000001455	-0.000002337	0.000008752
20	1	-0.000003676	-0.000003506	0.000006749
21	6	0.000000338	-0.000003996	0.000000634
22	1	-0.000004197	-0.000002900	-0.000004851
23	1	-0.000004182	-0.000001026	-0.000002915
24	6	-0.000003715	0.000003850	-0.000004416
25	1	0.000002816	0.000000809	-0.000004653
26	1	-0.000000319	0.000001117	-0.000005843
27	1	-0.000001559	0.000000047	-0.000003022

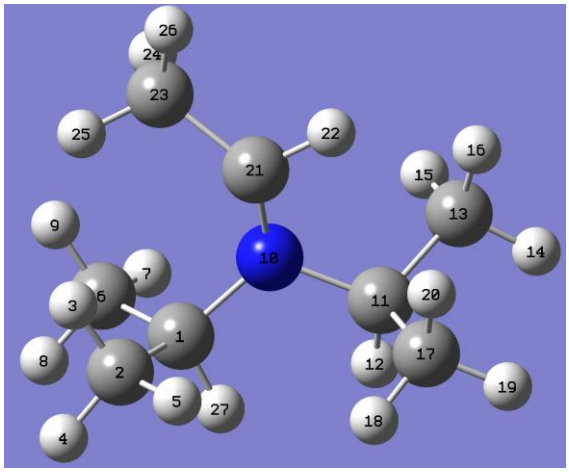
Cartesian coordinates for optimized structure of **6**$^{+}$ (cation).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000020974	0.000012916	0.000015515

2	6	-0.000001264	0.000004304	0.000004909
3	1	-0.000002805	0.000001152	0.000000914
4	1	0.000003505	0.000001852	0.000000386
5	1	0.000000392	0.000000619	-0.000000029
6	6	-0.000007482	-0.000001586	-0.000000020
7	1	-0.000000341	0.000000252	-0.000001063
8	1	0.000000413	0.000002791	0.000001698
9	1	0.000000521	0.000001869	0.000000593
10	7	-0.000001542	-0.000011328	-0.000005070
11	6	-0.000018737	-0.000004274	-0.000013235
12	1	-0.000000547	0.000000704	-0.000002836
13	6	0.000003264	-0.000003940	-0.000001215
14	1	-0.000002852	0.000000604	-0.000003491
15	1	-0.000001472	0.000001104	-0.000001080
16	1	0.000000868	-0.000000099	-0.000001931
17	6	-0.000003124	0.000007532	0.000003379
18	1	0.000002889	-0.000002530	-0.000001686
19	1	-0.000001196	-0.000001874	-0.000008389
20	1	-0.000000002	0.000003145	-0.000003965
21	6	-0.000000690	-0.000005452	0.000008934
22	1	0.000003722	0.000001089	0.000004182
23	1	0.000003211	-0.000009409	0.000001632
24	6	0.000003619	0.000006600	-0.000002056
25	1	-0.000000137	0.000001720	-0.000000238
26	1	-0.000001879	-0.000005329	0.000003723
27	1	0.000000695	-0.000002433	0.000000441

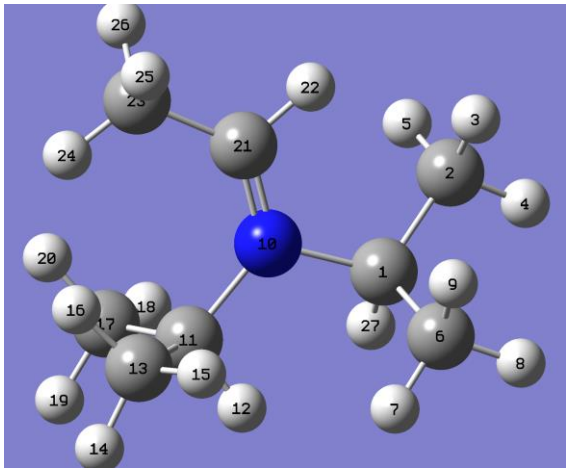
Cartesian coordinates for optimized structure of **8**· (radical).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000014499	-0.000011100	0.000006643
2	6	0.000000974	0.000003620	-0.000002492
3	1	-0.000002002	-0.000002025	-0.000004560
4	1	0.000001264	-0.000003402	-0.000003849
5	1	-0.000005269	-0.000003135	-0.000002009
6	6	0.000011099	0.000005021	0.000001116
7	1	0.000000014	0.000000855	-0.000003112
8	1	0.000001518	-0.000000363	-0.000005817
9	1	0.000001546	-0.000001158	-0.000004226
10	7	0.000003607	0.000012536	-0.000026858
11	6	0.000016190	-0.000005640	0.000020891
12	1	-0.000001594	0.000008064	-0.000002390
13	6	-0.000007115	0.000000739	0.000003421
14	1	0.000001569	0.000002722	0.000003386
15	1	0.000002234	0.000001732	0.000002335
16	1	0.000000954	0.000001460	0.000003181
17	6	-0.000005942	-0.000003220	-0.000006215
18	1	0.000000023	0.000000320	0.000000518
19	1	-0.000001630	0.000000191	0.000004246
20	1	-0.000003014	-0.000000457	0.000005722
21	6	0.000002754	-0.000001345	0.000013775
22	1	-0.000000106	-0.000004593	0.000002619

23	6	-0.000003374	-0.000002115	-0.000004989
24	1	0.000001839	0.000001593	0.000000125
25	1	-0.000000464	0.000000114	0.000000500
26	1	0.000001528	-0.000000033	0.000001269
27	1	-0.000002104	-0.000000378	-0.000003230

Cartesian coordinates for optimized structure of 8^{+} (cation).



Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000016869	-0.000013379	-0.000003267
2	6	0.000012165	0.000002889	-0.000001112
3	1	0.000000098	0.000001017	0.000000884
4	1	0.000000697	-0.000001784	0.000002439
5	1	0.000000360	0.000001318	0.000001551
6	6	0.000001101	0.000009334	0.000009377
7	1	-0.000000344	-0.000000250	-0.000001886
8	1	-0.000001406	-0.000002530	0.000001913
9	1	-0.000002685	-0.000001410	-0.000000668
10	7	0.000017387	-0.000000348	0.000004207
11	6	0.000002283	0.000004736	-0.000005757
12	1	-0.000011274	-0.000003040	0.000001219

13	6	-0.000003589	0.000007556	0.000001841
14	1	-0.000001295	-0.000001695	0.000000171
15	1	-0.000002228	-0.000002040	-0.000000770
16	1	0.000000492	-0.000001243	-0.000003605
17	6	-0.000000260	-0.000001277	0.000003655
18	1	0.000001650	0.000001344	-0.000001138
19	1	-0.000000246	0.000001081	-0.000000727
20	1	0.000003704	-0.000000168	-0.000001287
21	6	-0.000004786	0.000000345	0.000002289
22	1	-0.000004242	0.000001024	-0.000001851
23	6	0.000000991	-0.000004648	-0.000022294
24	1	-0.000001158	0.000000524	0.000002236
25	1	0.000002297	0.000001261	0.000004823
26	1	-0.000002139	0.000001079	0.000004836
27	1	0.000009298	0.000000304	0.000002922

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12. References for Supporting Information

(S1) Han, C. C.; Yang, L. H.; Raghunath, P.; Lin, M. C.; Kumar, R.; Lin, H. C. *RSC Adv.* **2016**, *6*, 110482.

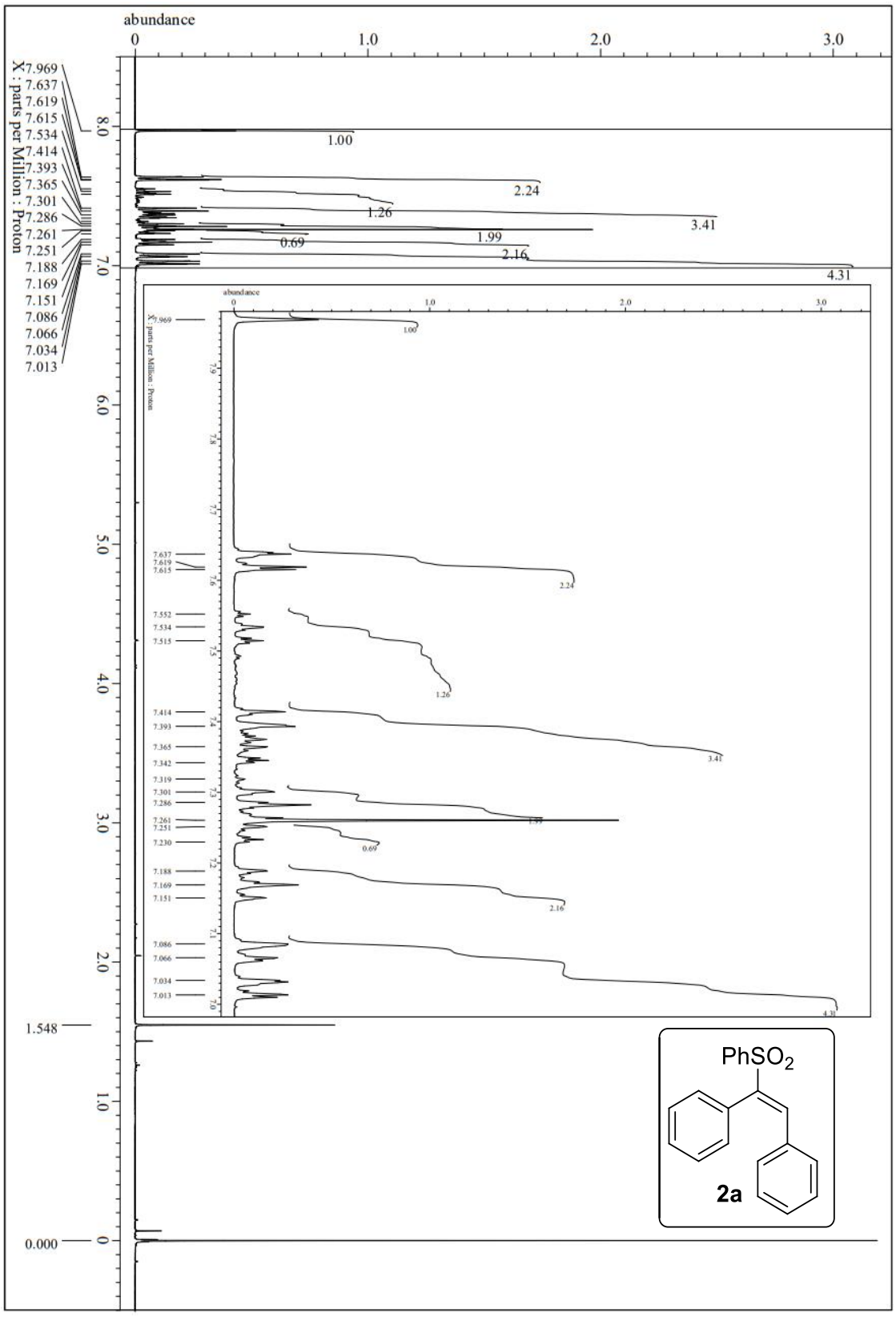
(S2) Aldred, M. P.; Hudson, R.; Kitney, S. P.; Vlachos, P.; Liedtke, A.; Woon, K. L.; O'Neill, O.; Kelly, S. M. *Liq Cryst.* **2008**, *35*, 413.

(S3) Gaussian09; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V.

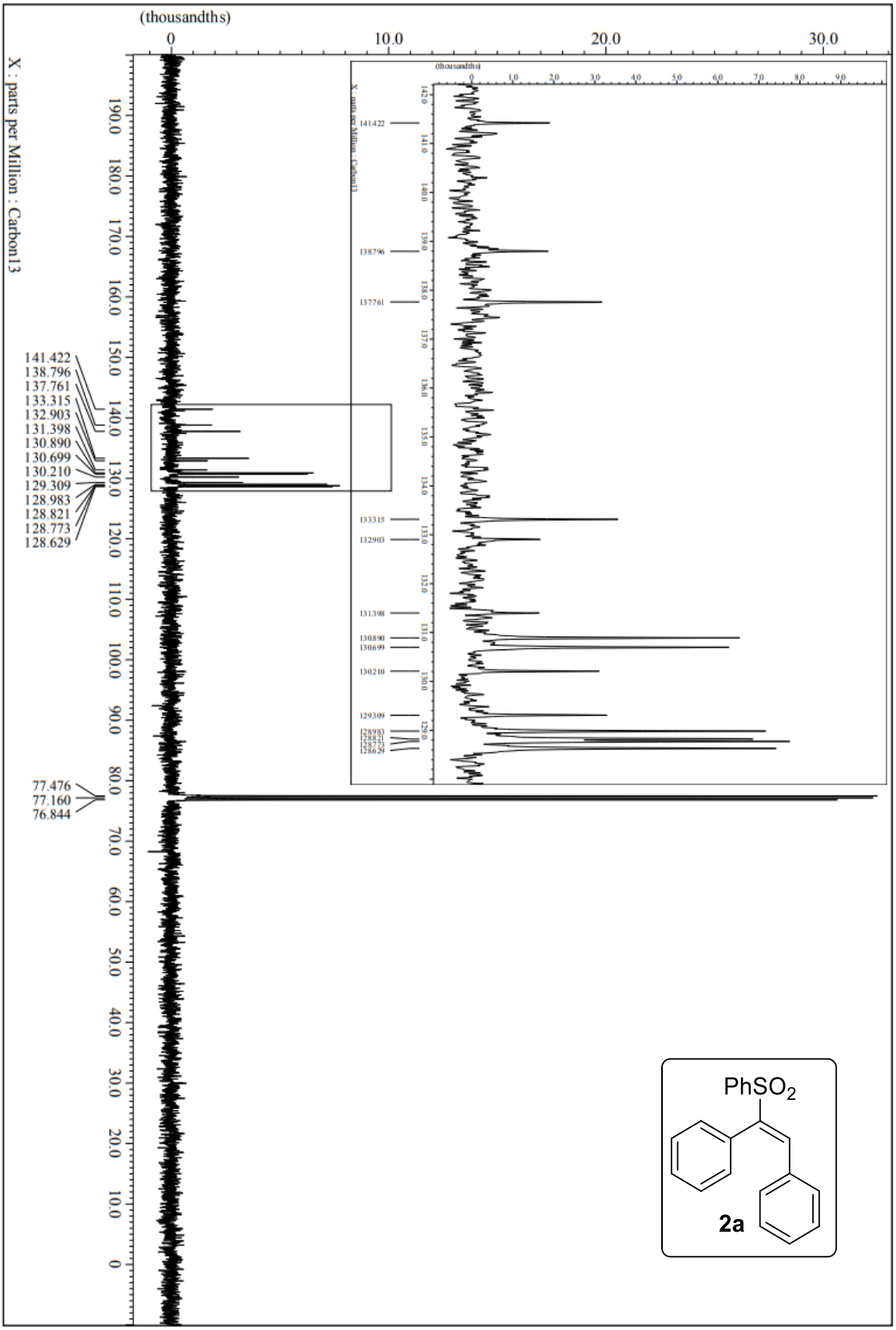
(S4) Liu, S-Y.; Shi, M-M.; Huang, J-C.; Jin, Z-N.; Hu, X-L.; Pan, J-Y.; Li, H-Y.; Jen, A. K.-Y.; Chen, H-Z. *J. Mater. Chem. A*, **2013**, *1*, 2795.

(S5) Fang, J-K.; An, D-L.; Wakamatsu, K.; Ishikawa, T.; Iwanaga, T.; Toyota, S.; Matsuo, D.; Orita, A.; Otera, J. *Tetrahedron Lett.* **2010**, *51*, 917.

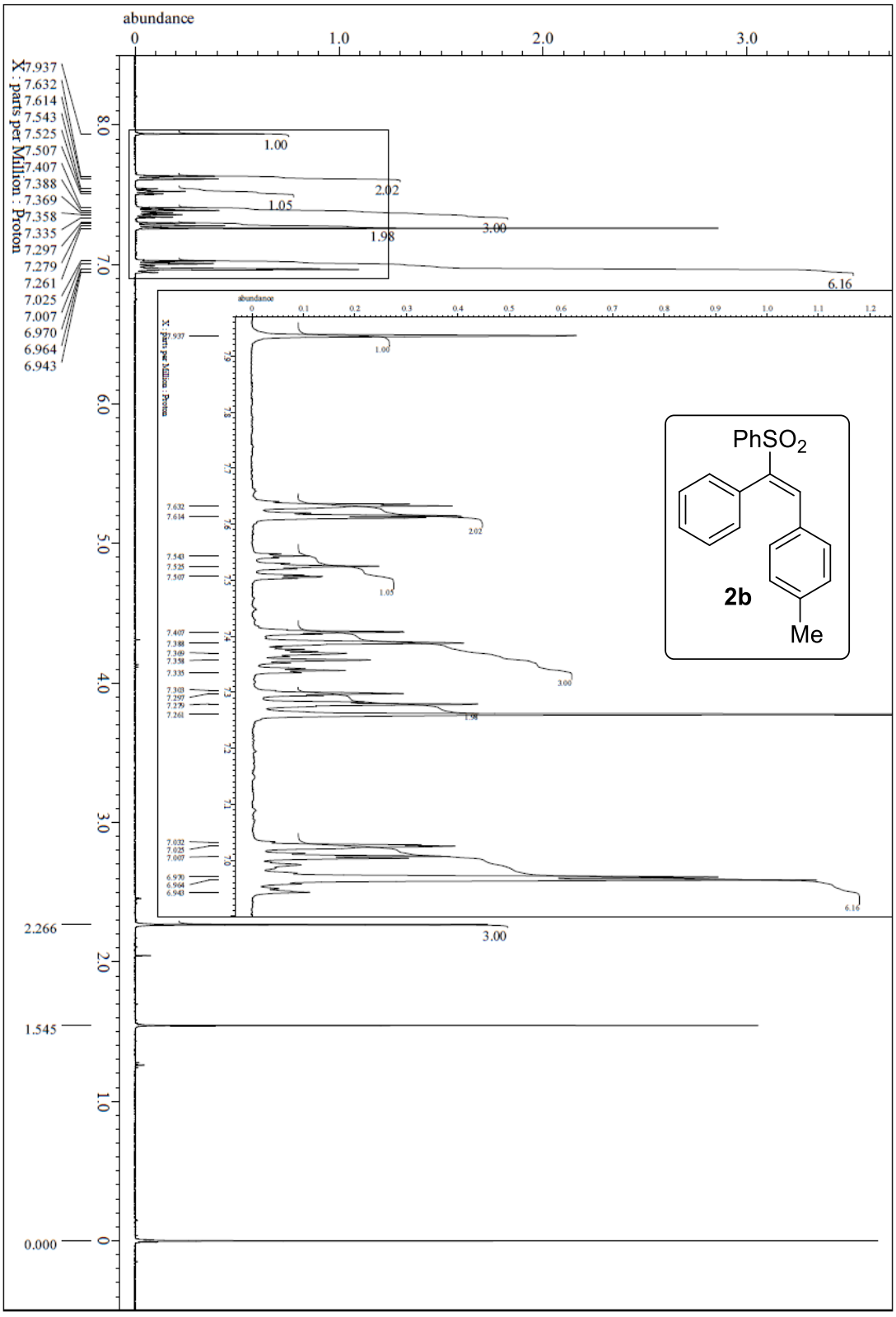
11. NMR charts



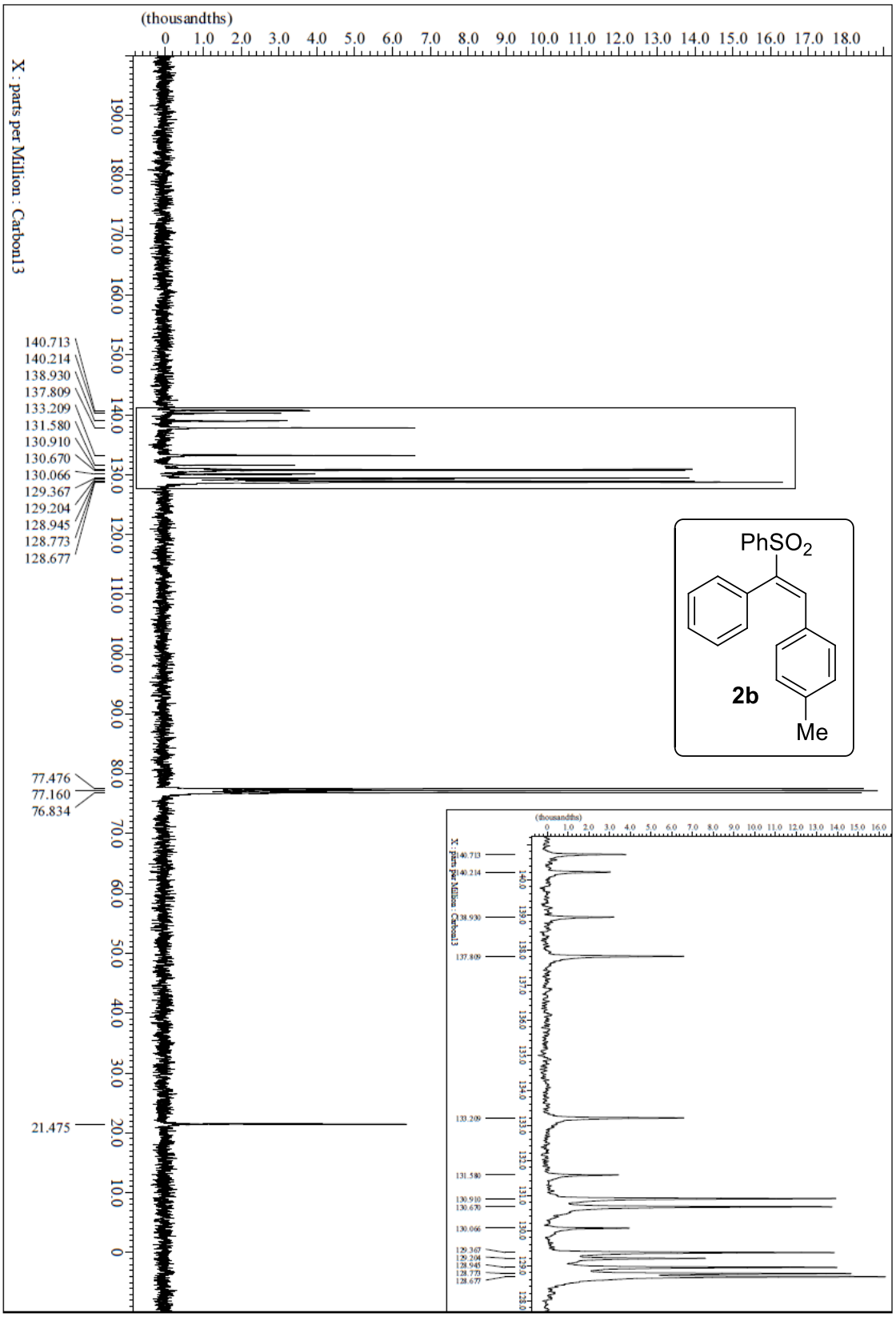
^{1}H NMR (400 MHz) spectrum of **2a** ($CDCl_3$, rt)



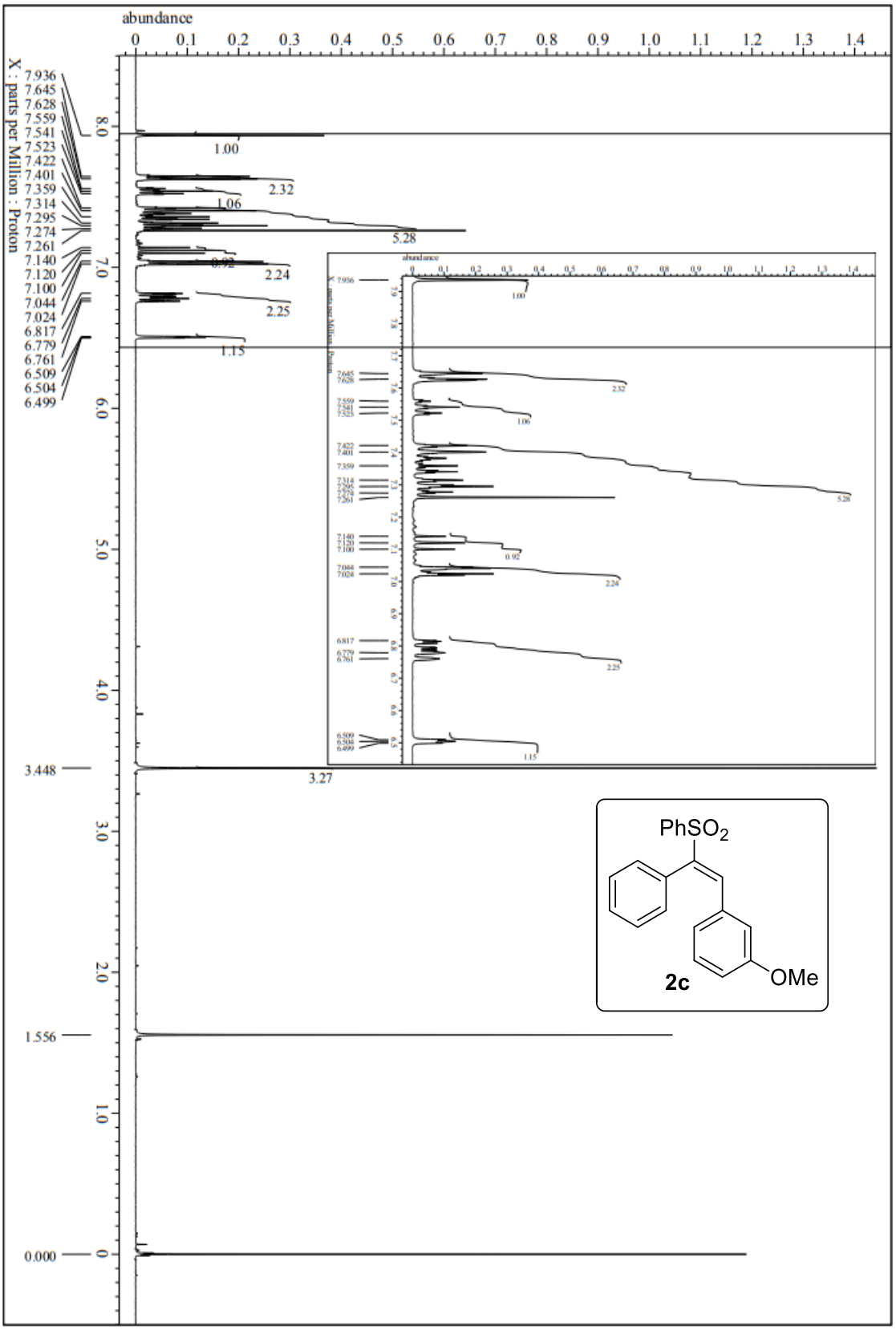
^{13}C NMR (101 MHz) spectrum of **2a** ($CDCl_3$, rt)



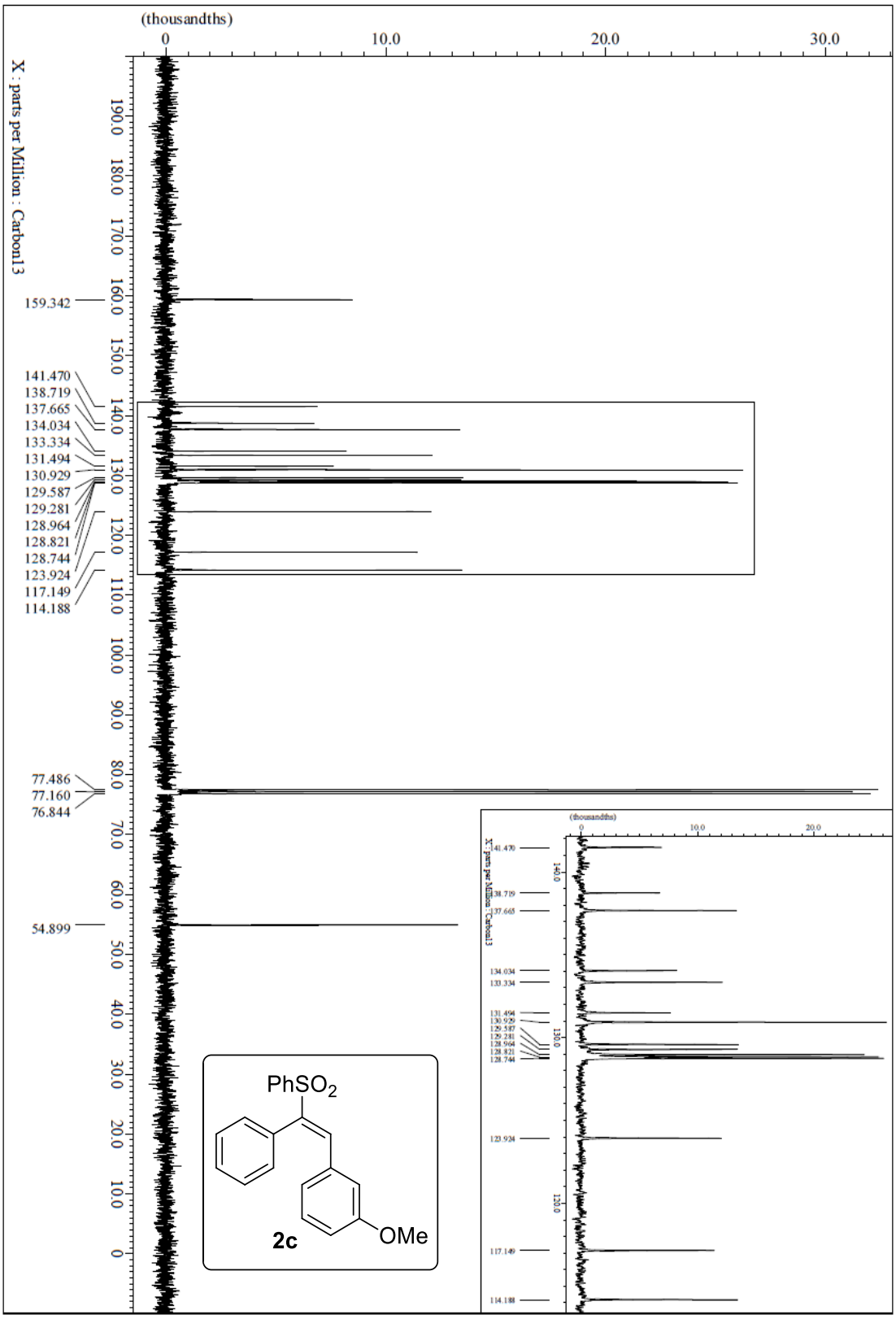
^{1}H NMR (400 MHz) spectrum of **2b** ($CDCl_3$, rt)



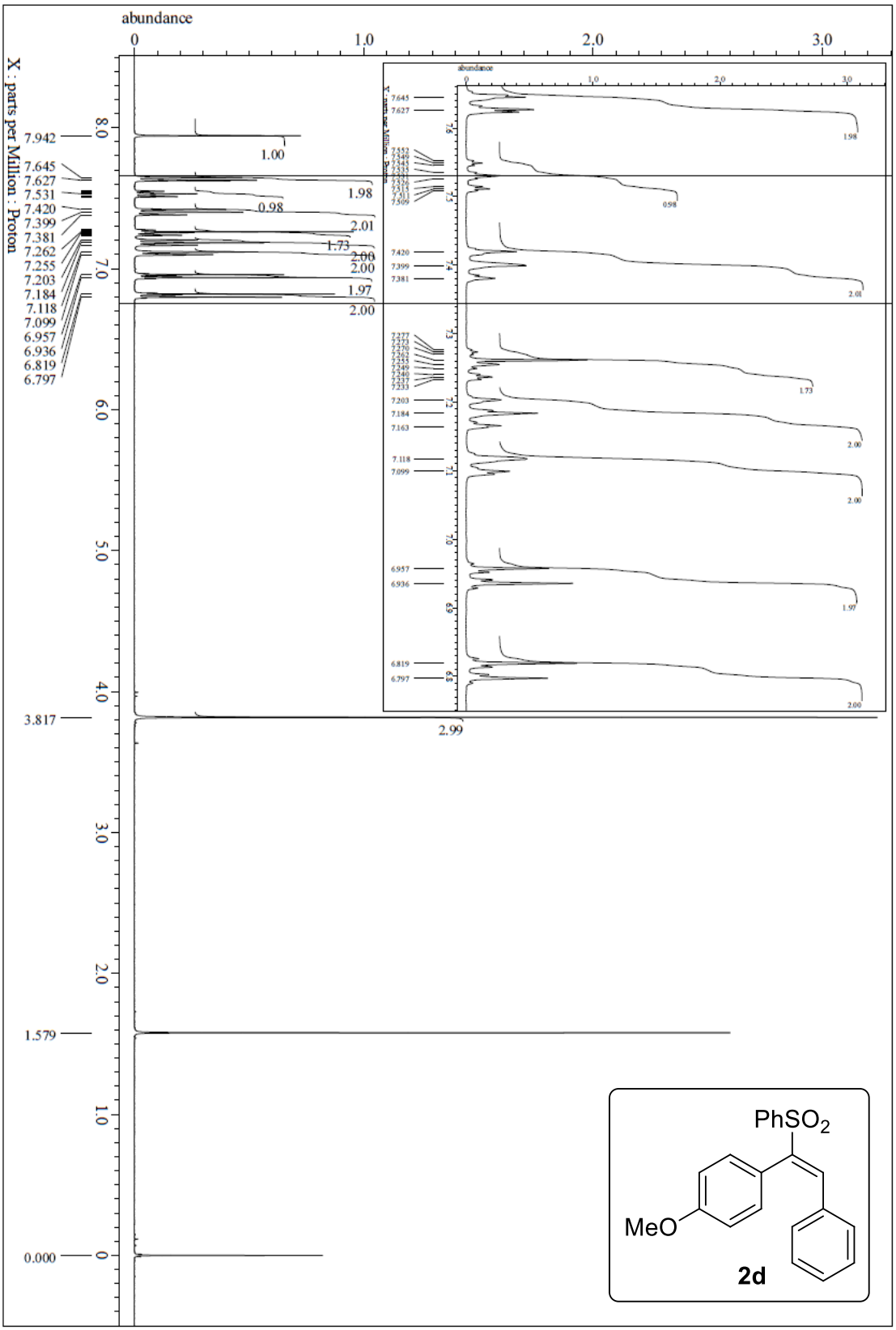
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2b** ($CDCl_3$, rt)



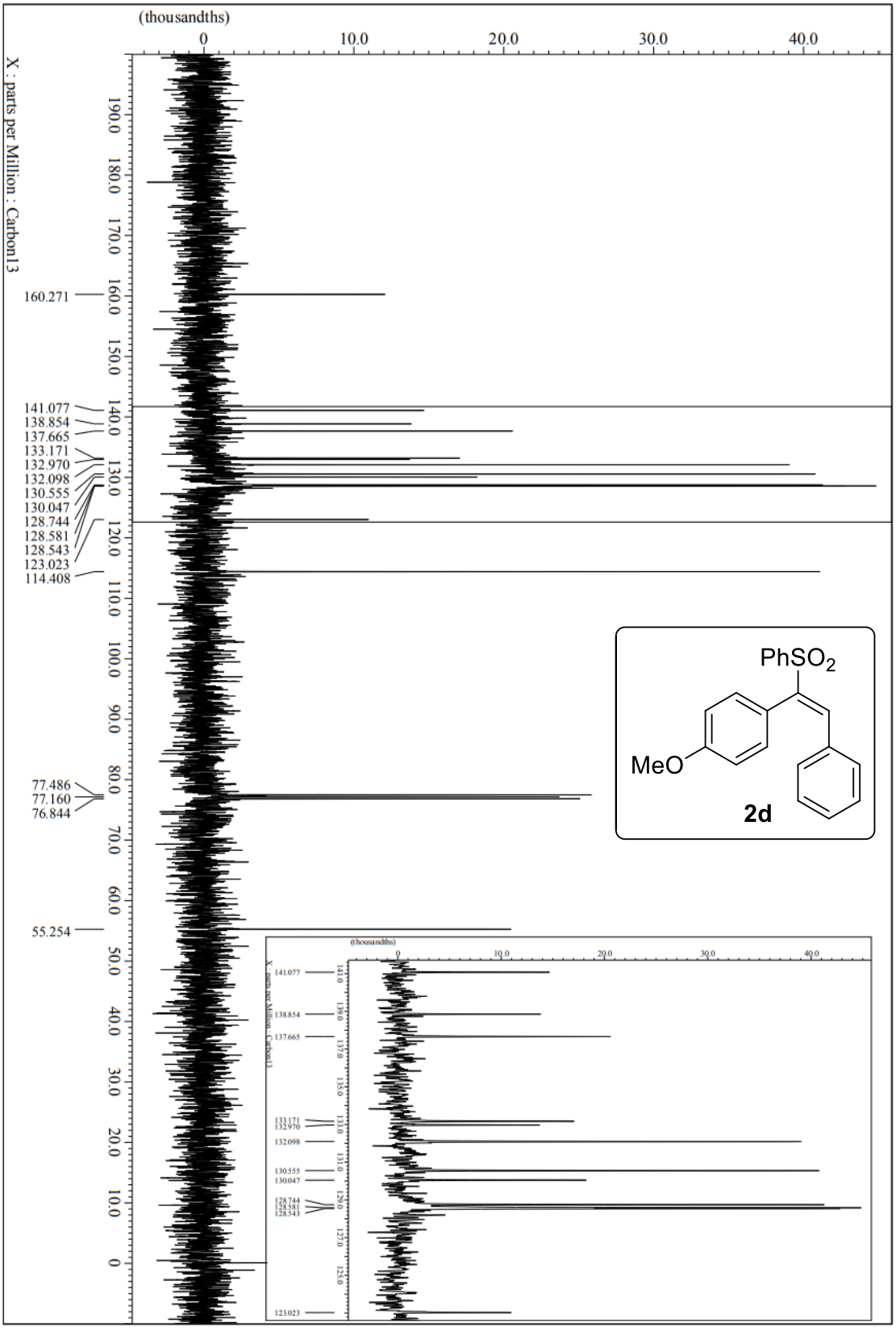
^{1}H NMR (400 MHz) spectrum of **2c** ($CDCl_3$, rt)



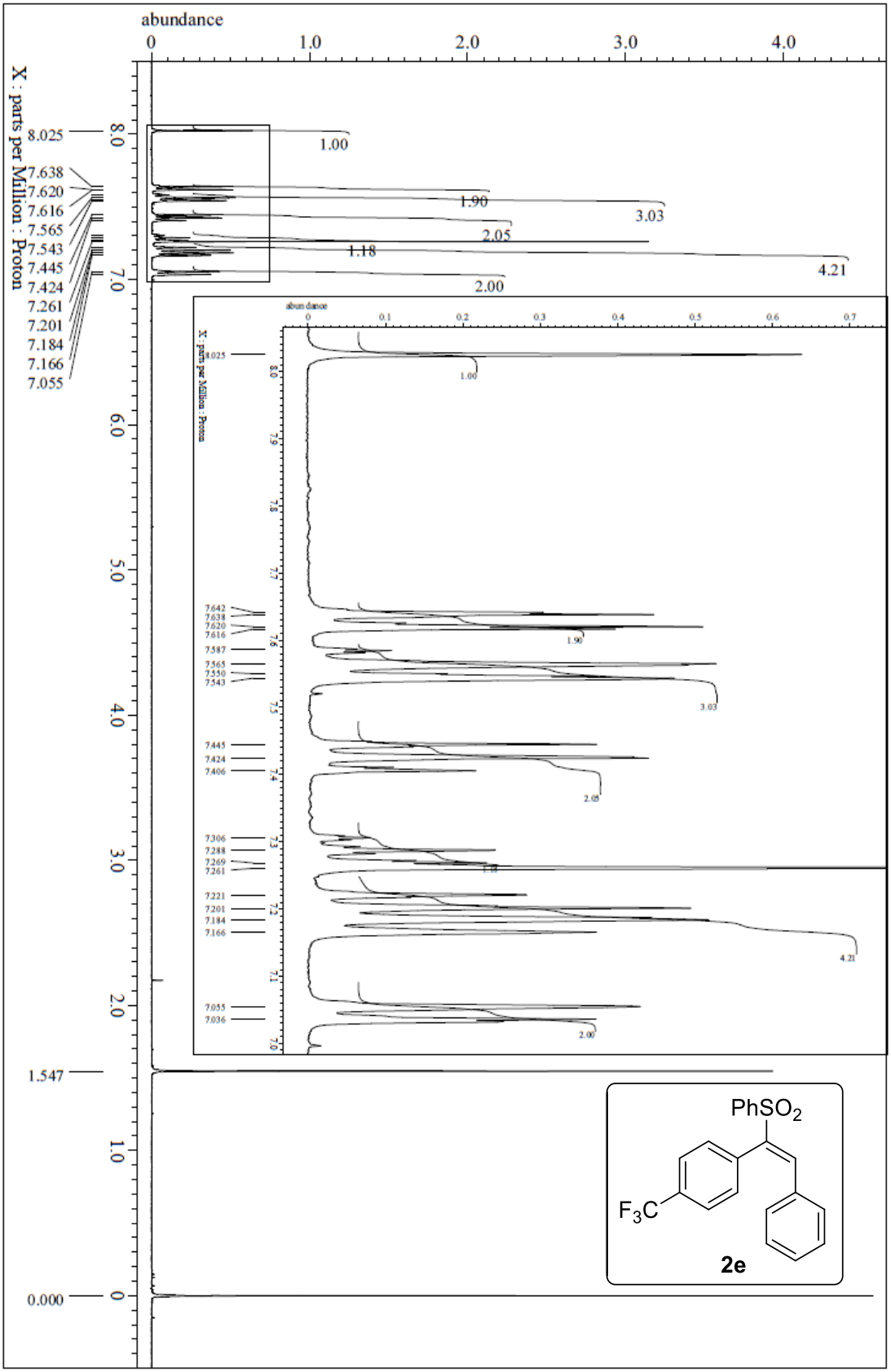
^{13}C NMR (101 MHz) spectrum of **2c** ($CDCl_3$, rt)



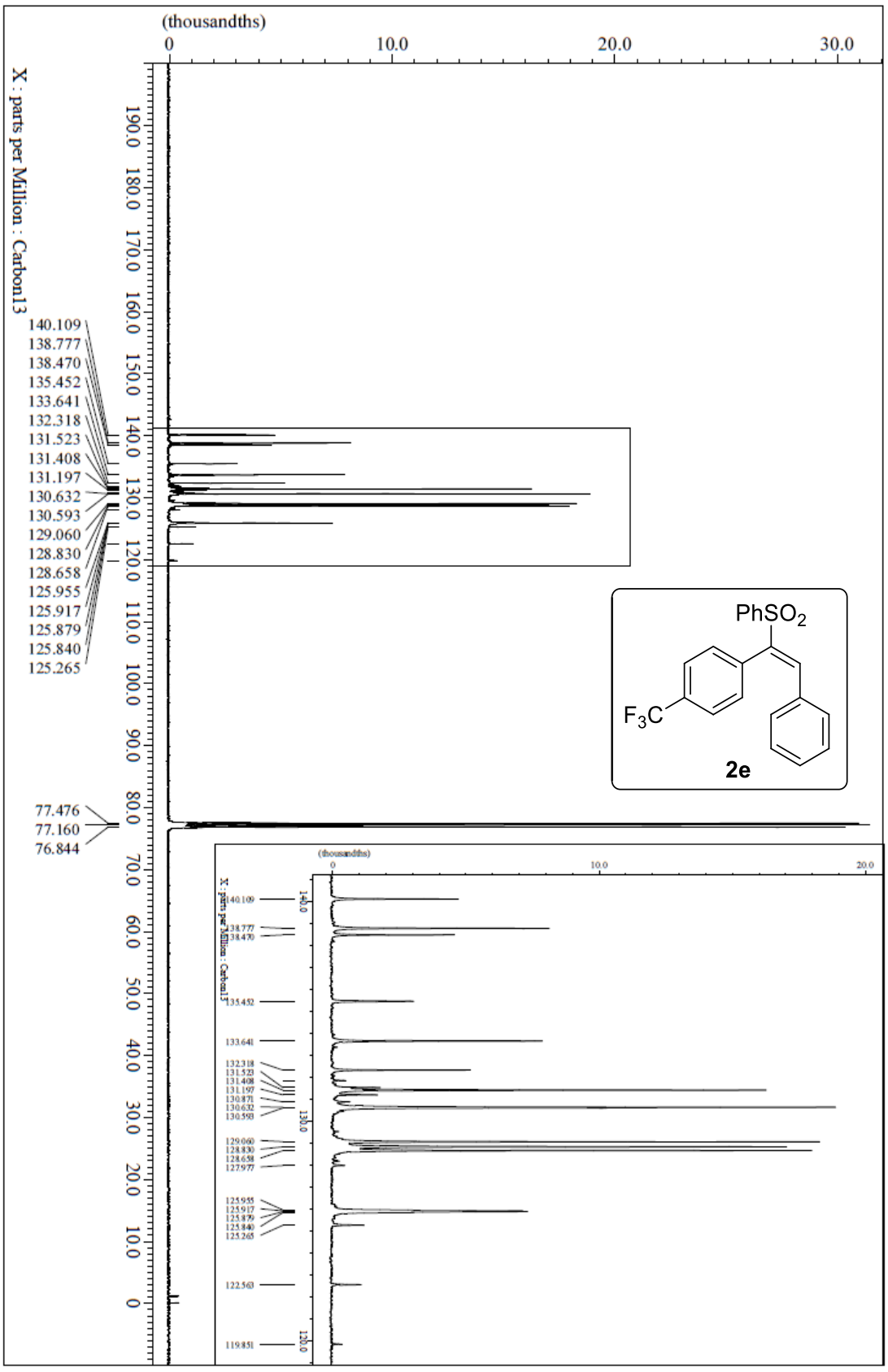
^{1}H NMR (400 MHz) spectrum of **2d** ($CDCl_3$, rt)



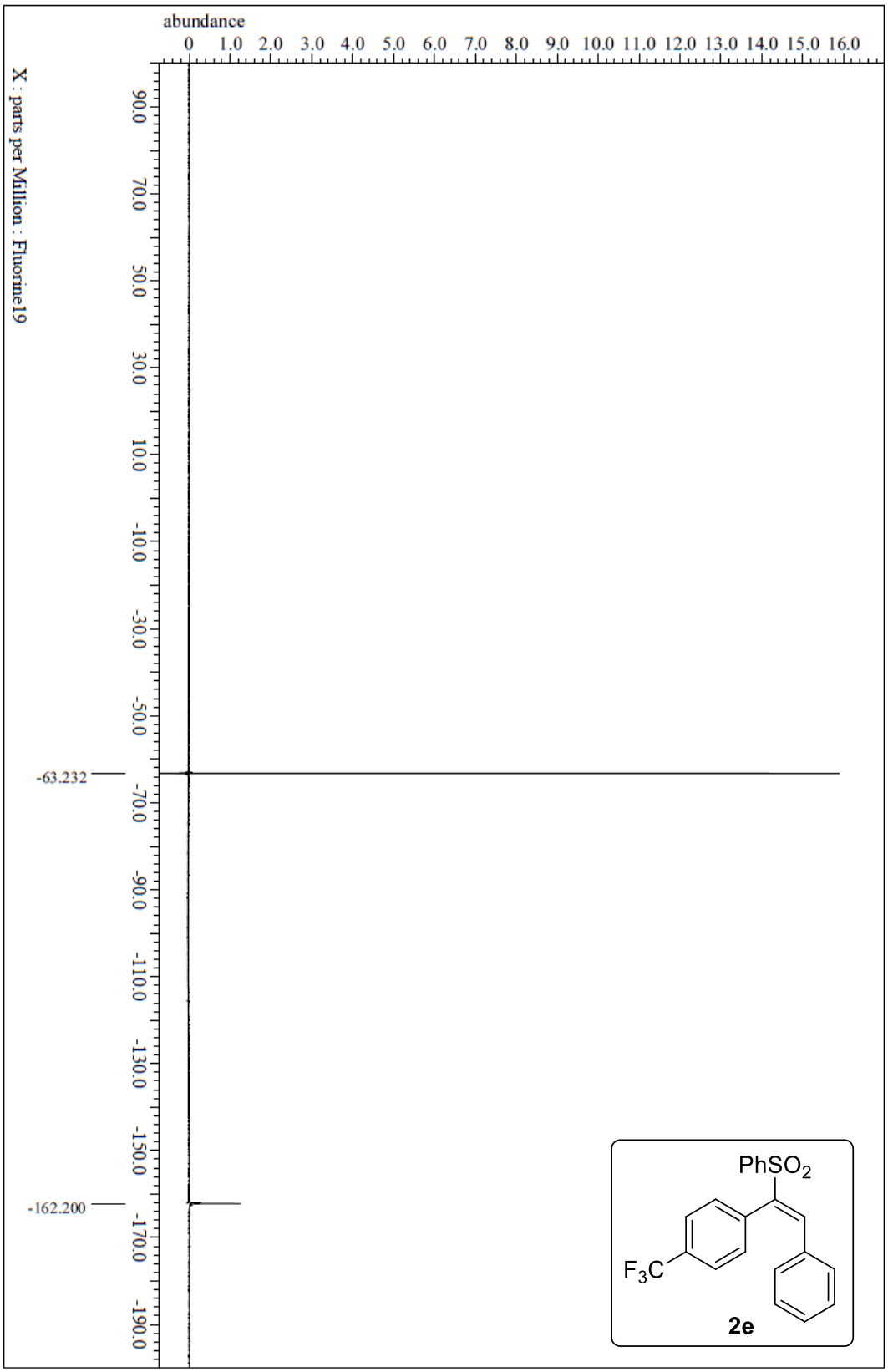
^{13}C NMR (101 MHz) spectrum of **2d** ($CDCl_3$, rt)



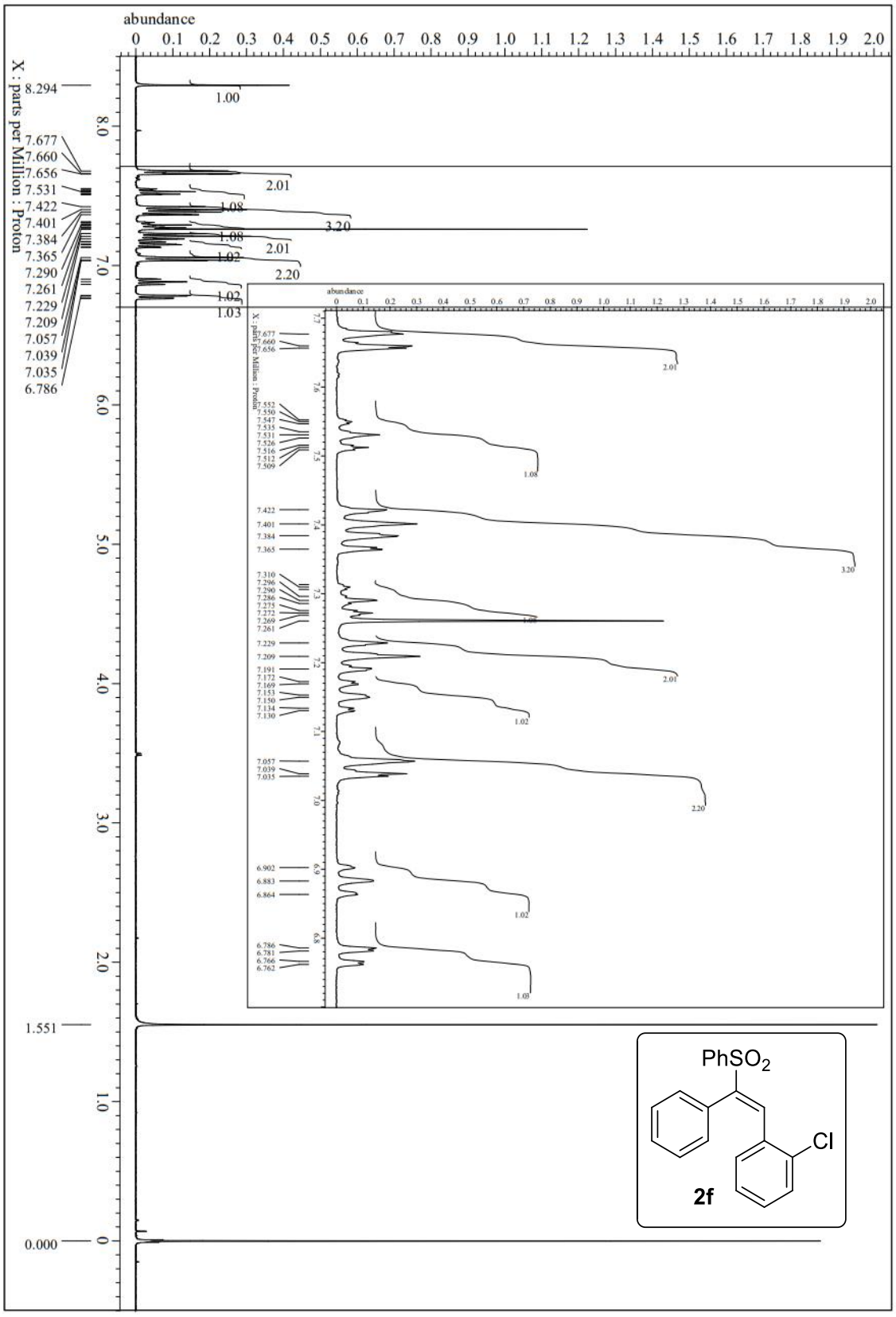
^{1}H NMR (400 MHz) spectrum of **2e** ($CDCl_3$, rt)



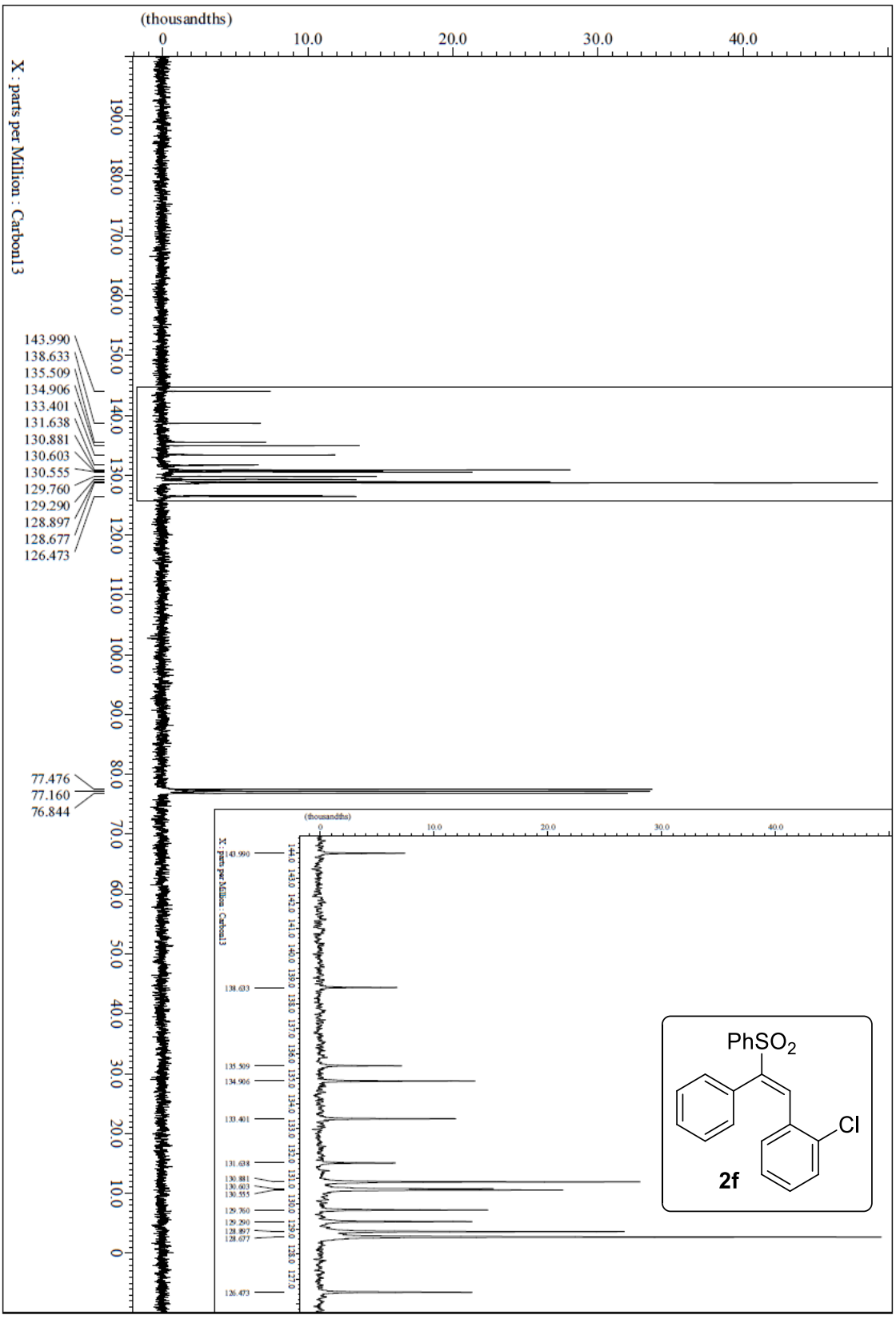
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2e** ($CDCl_3$, rt)



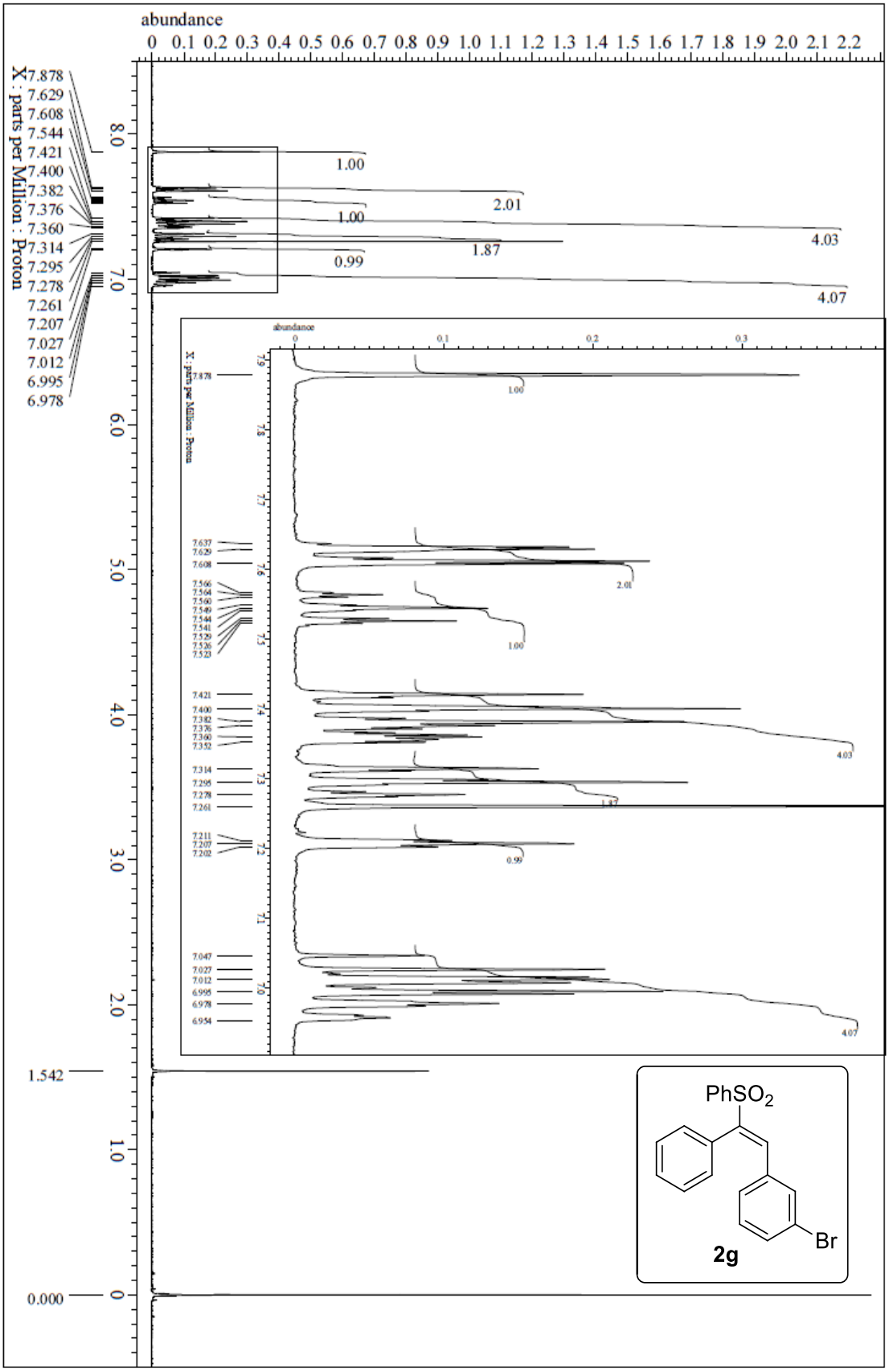
$^{19}F\{^{1}H\}$ NMR (376 MHz) spectrum of **2e** ($CDCl_3$, rt)



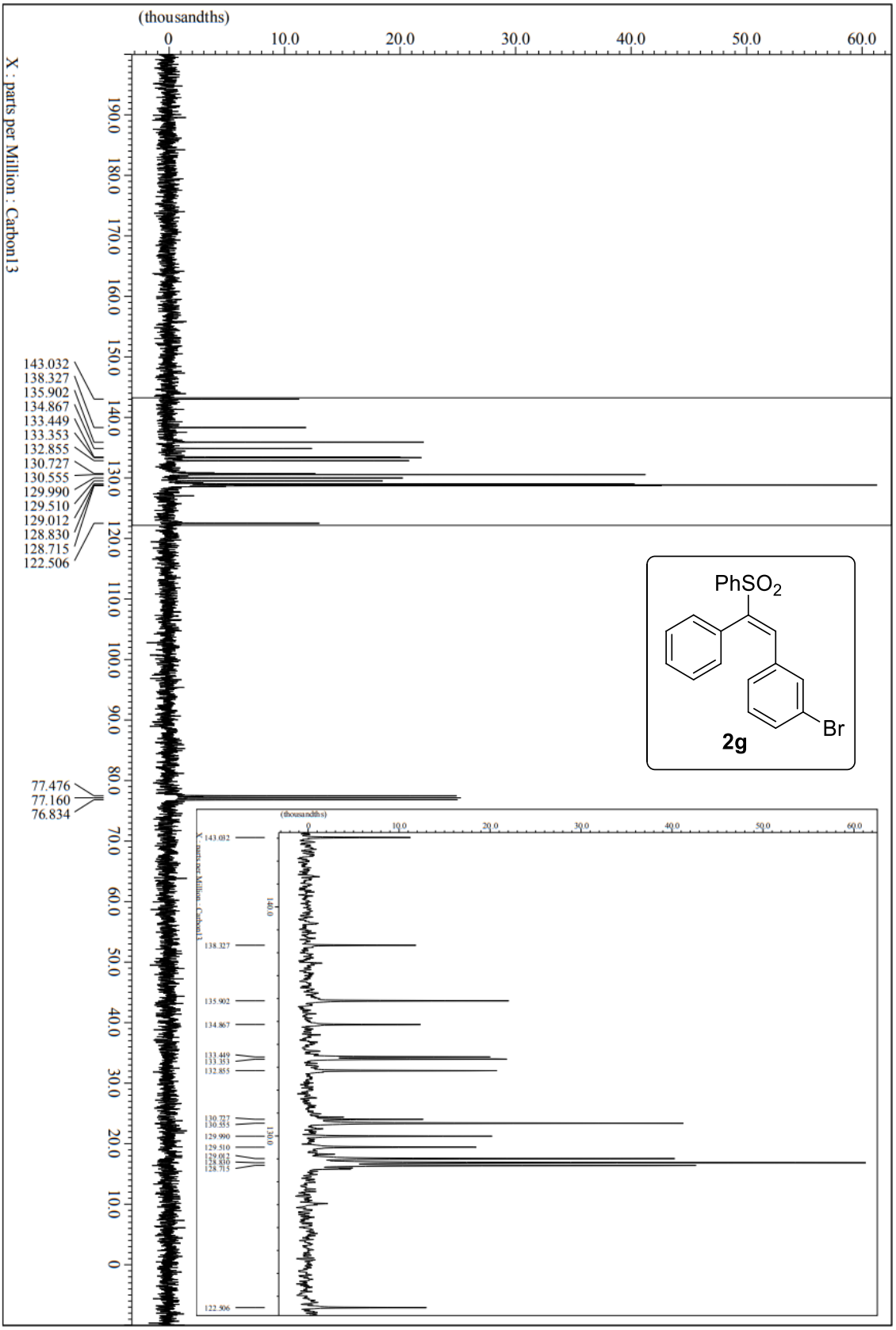
^{1}H NMR (400 MHz) spectrum of **2f** ($CDCl_3$, rt)



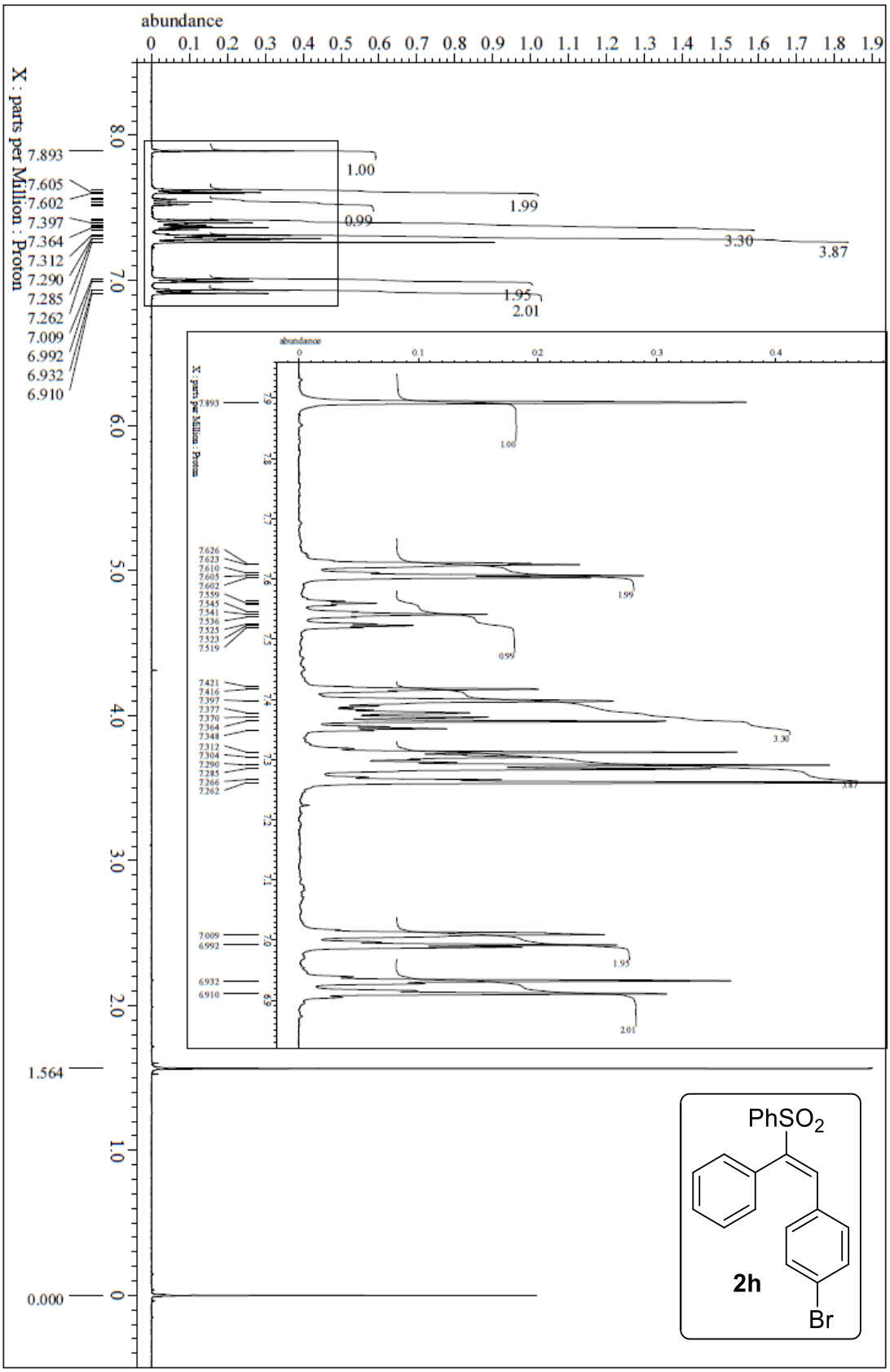
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2f** ($CDCl_3$, rt)



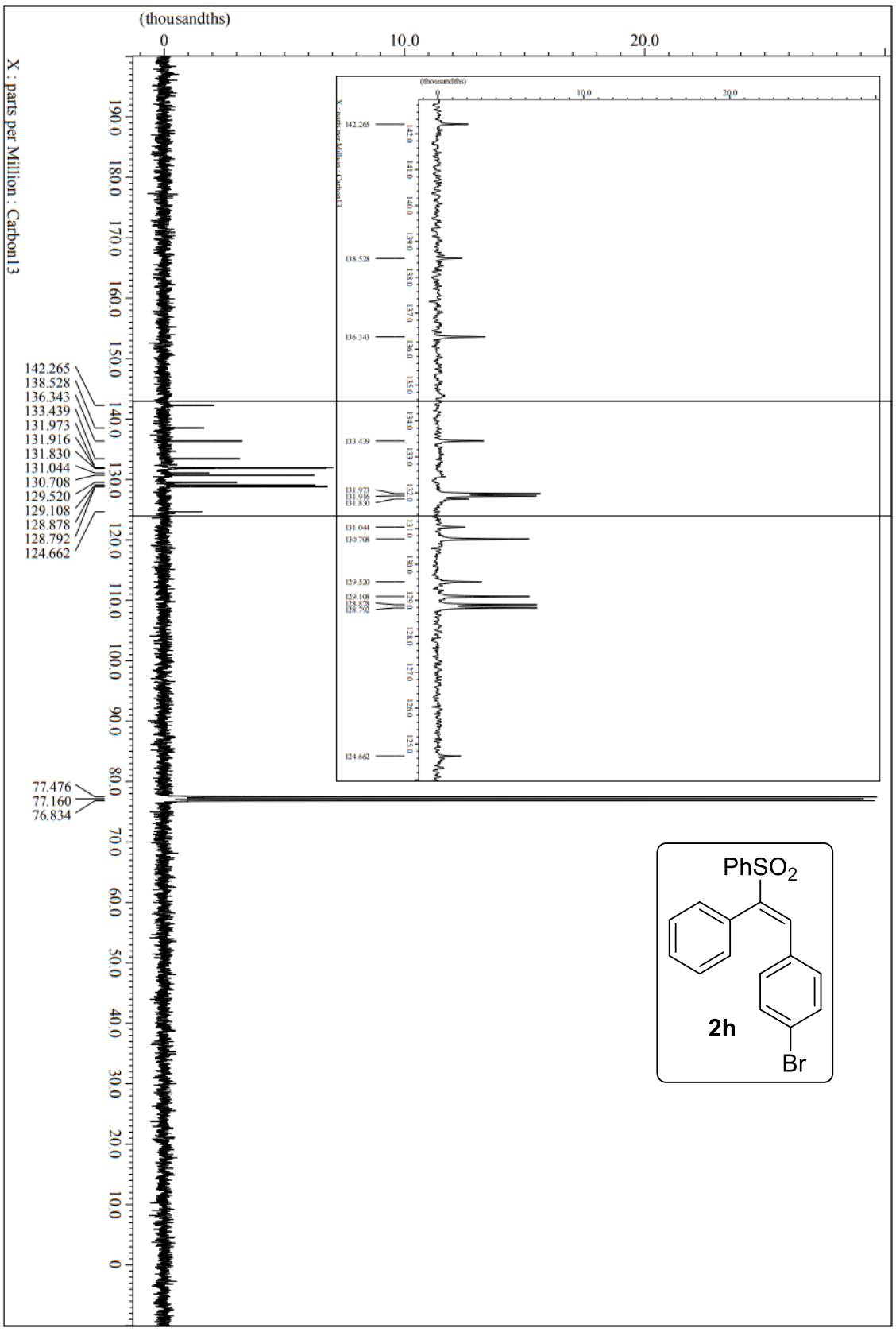
^{1}H NMR (400 MHz) spectrum of **2g** ($CDCl_3$, rt)



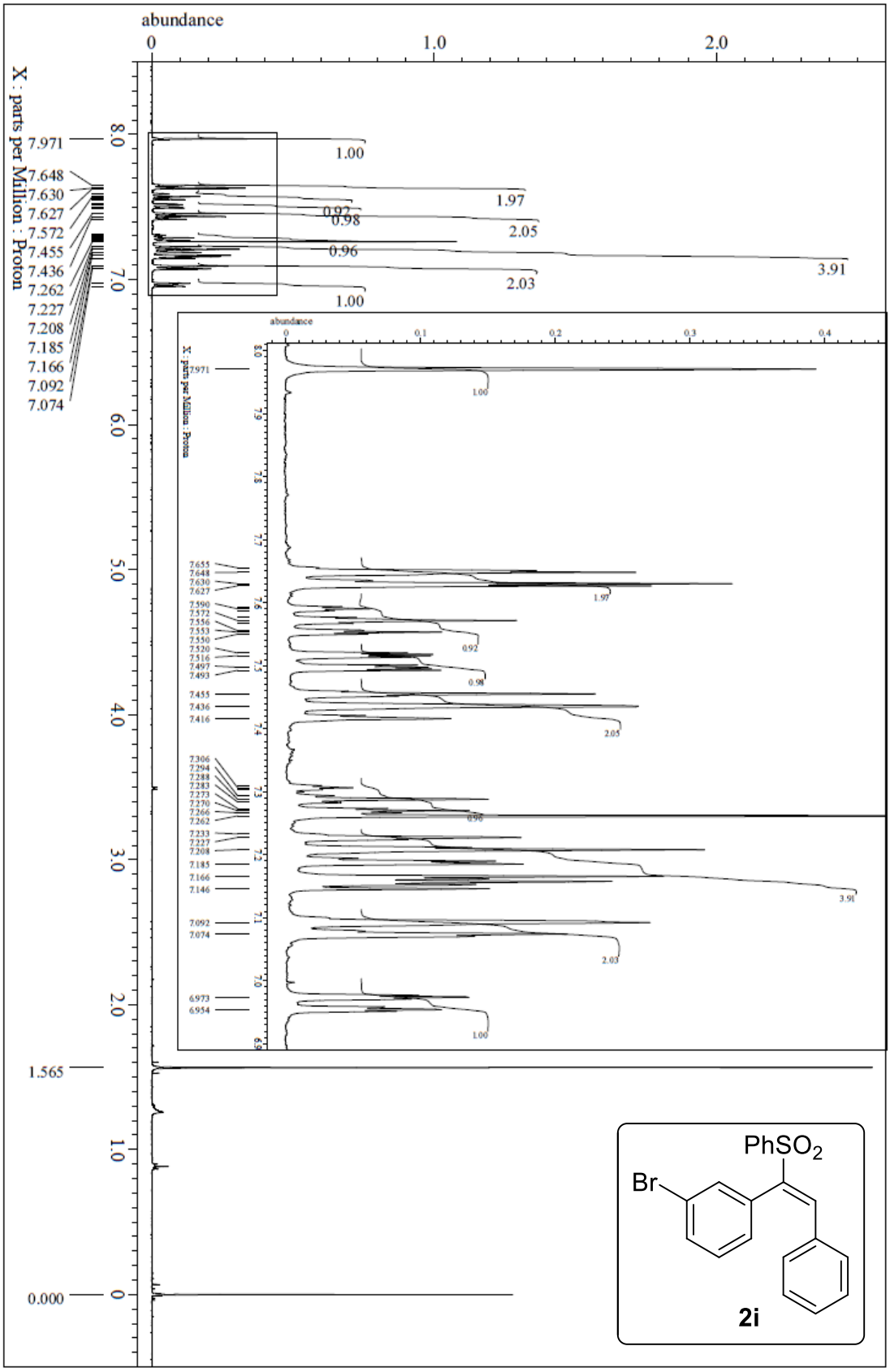
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2g** ($CDCl_3$, rt)



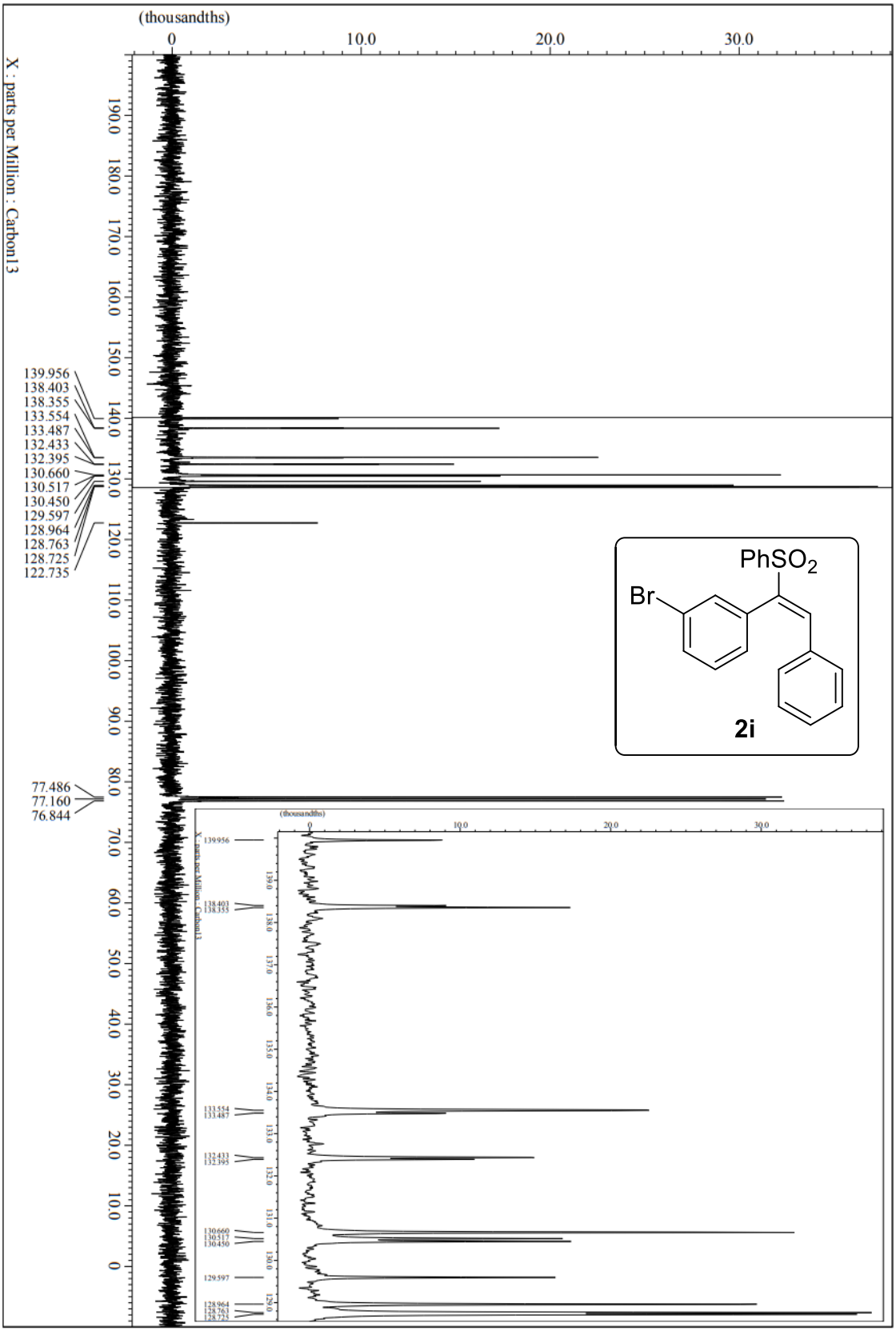
^{1}H NMR (400 MHz) spectrum of **2h** ($CDCl_3$, rt)



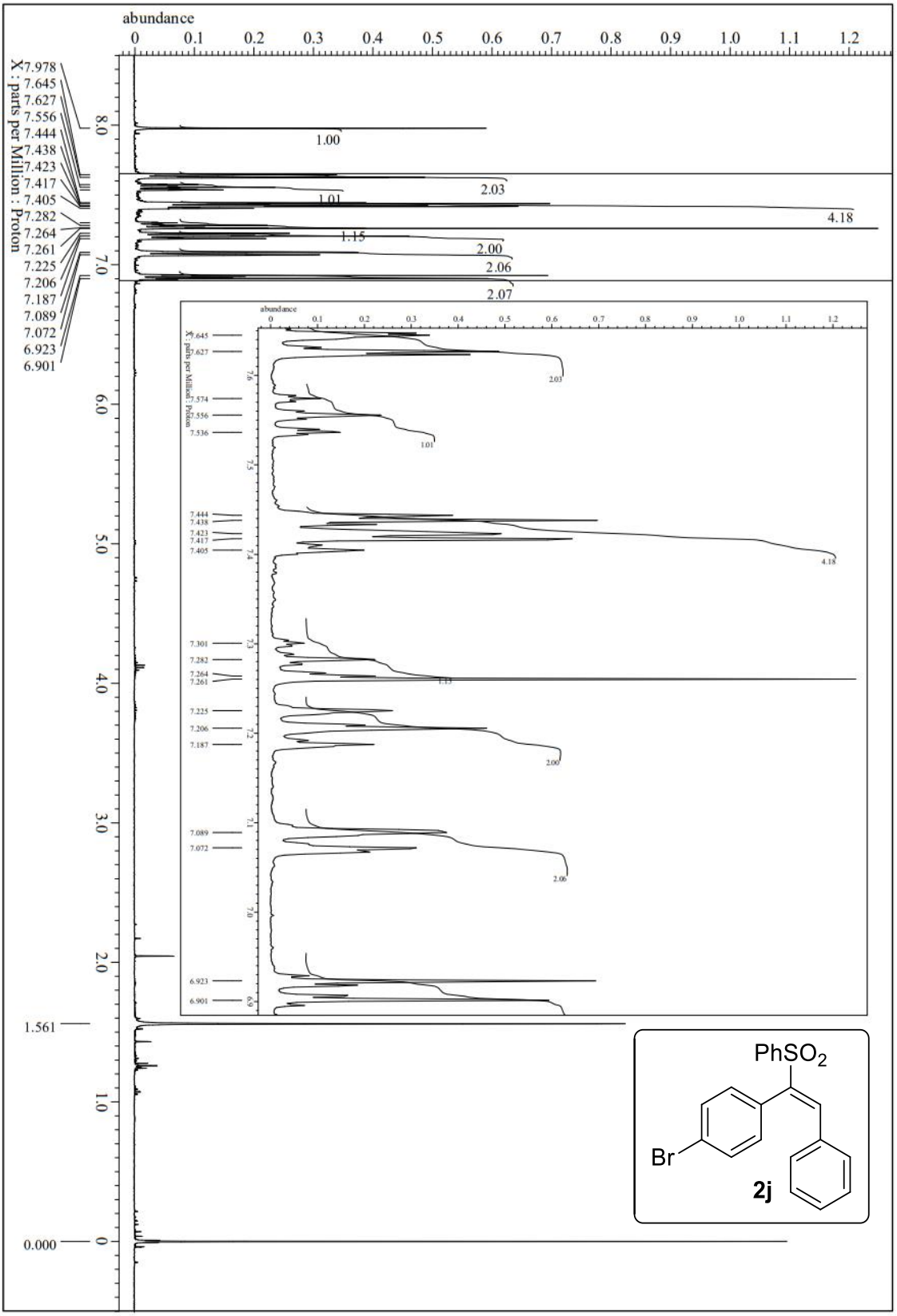
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2h** ($CDCl_3$, rt)



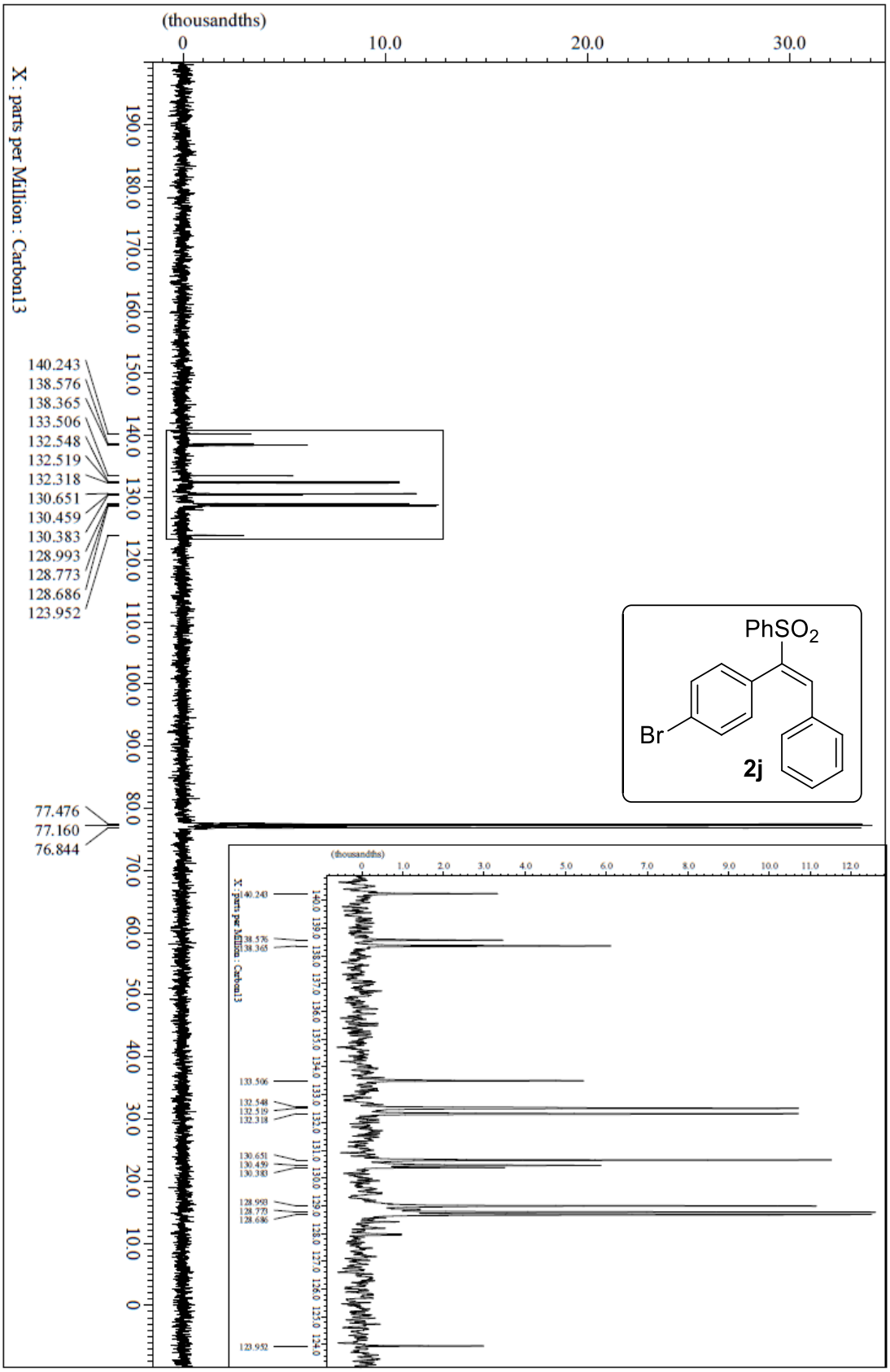
^{1}H NMR (400 MHz) spectrum of **2i** ($CDCl_3$, rt)



$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2i** ($CDCl_3$, rt)



^{1}H NMR (400 MHz) spectrum of **2j** ($CDCl_3$, rt)



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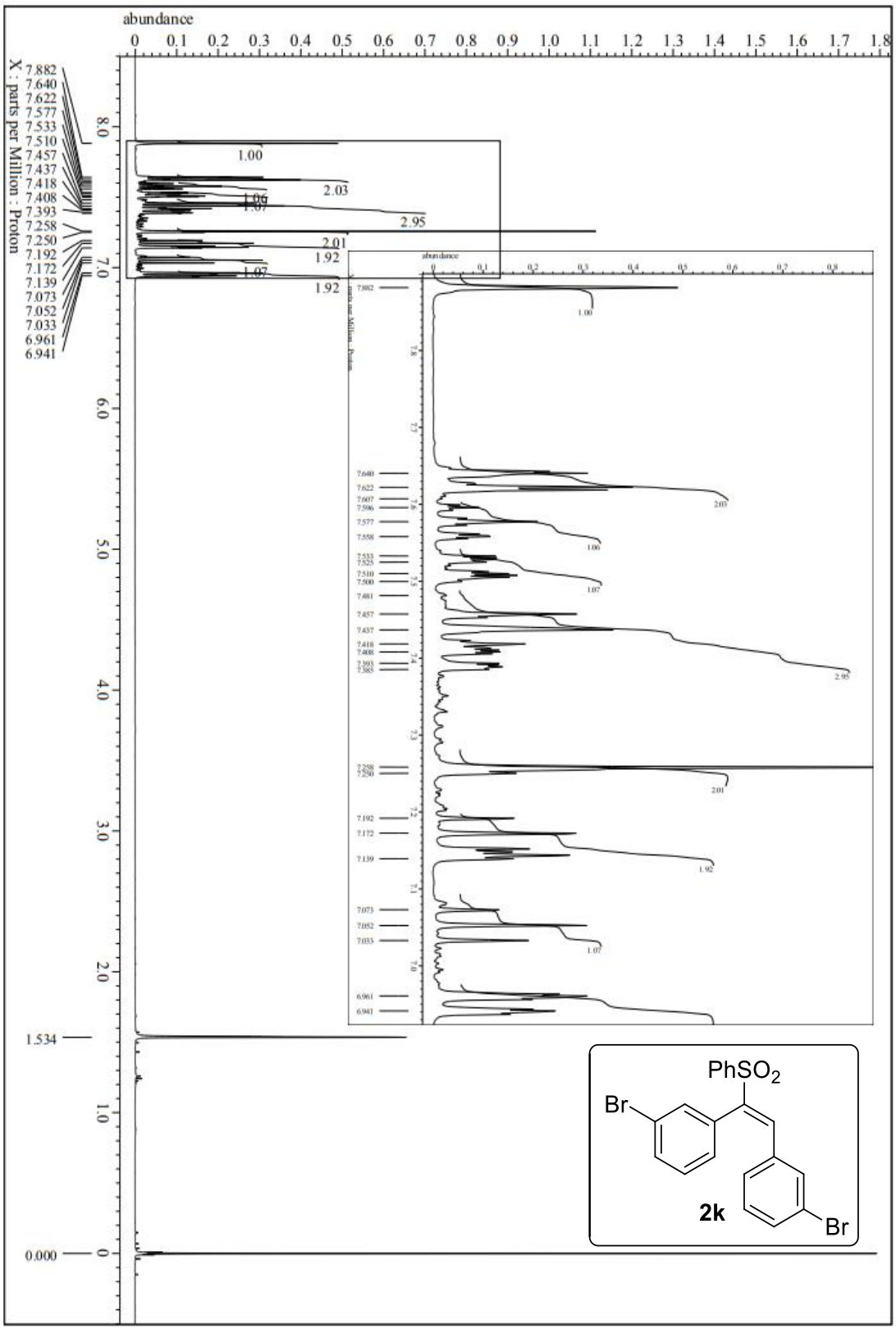
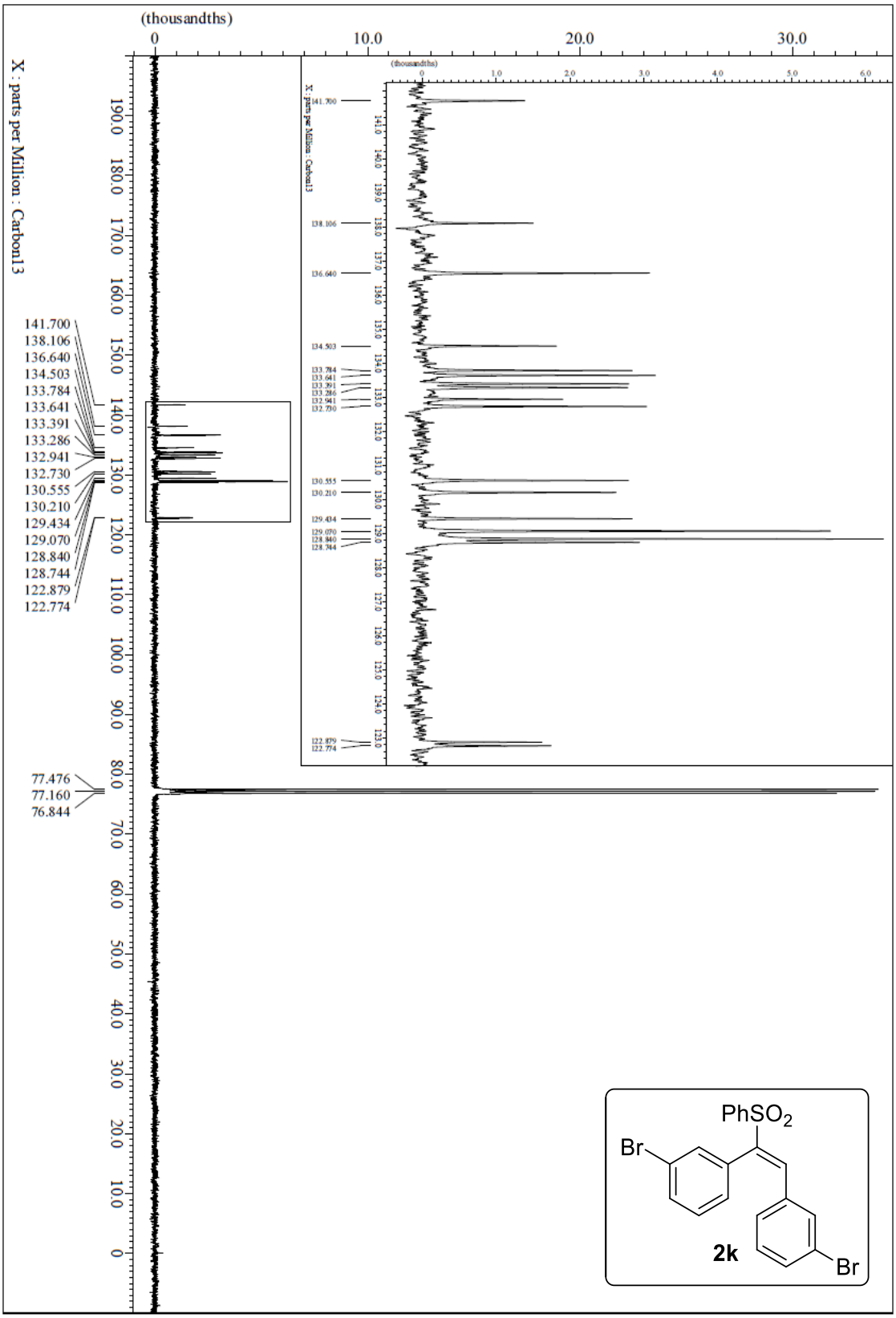
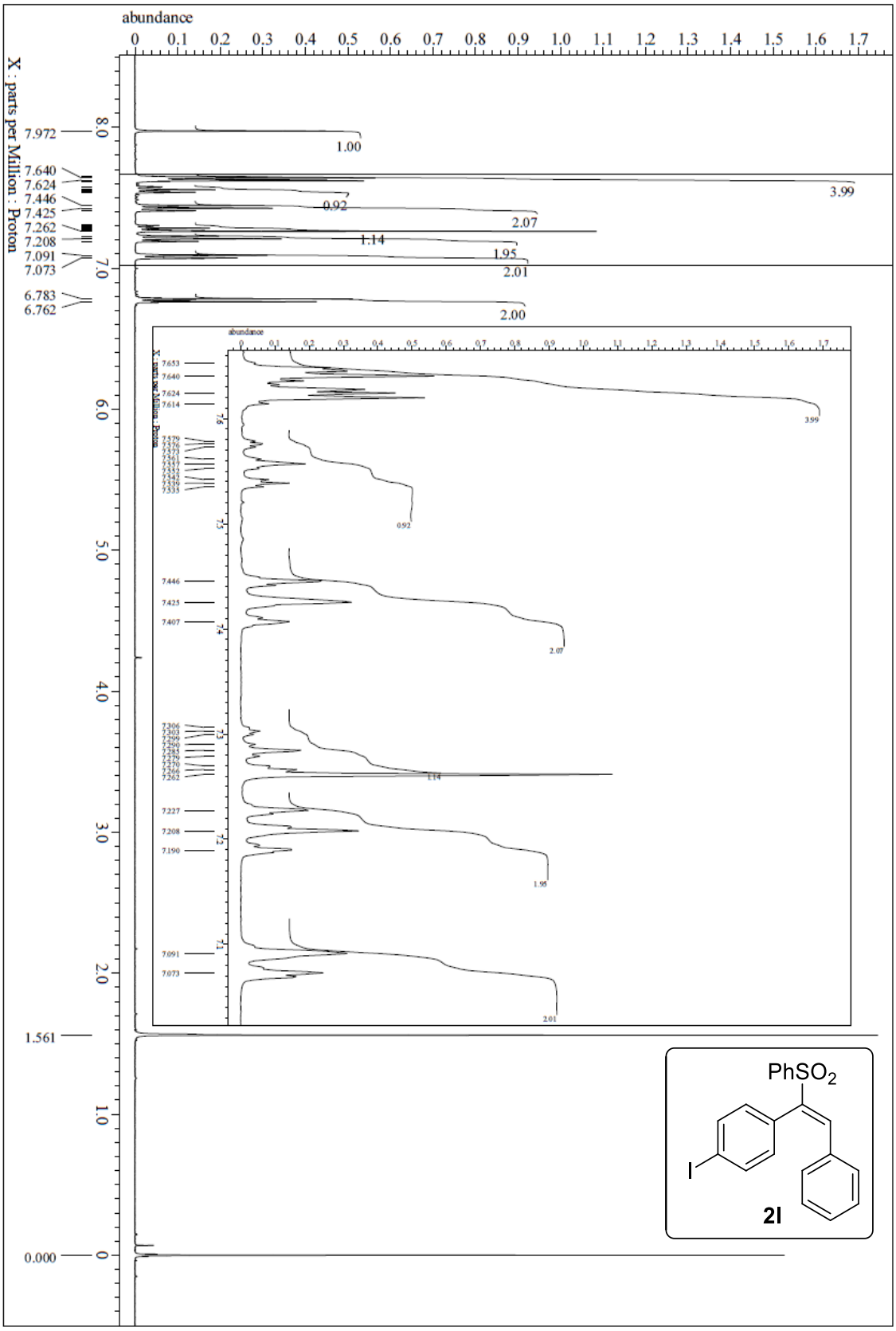


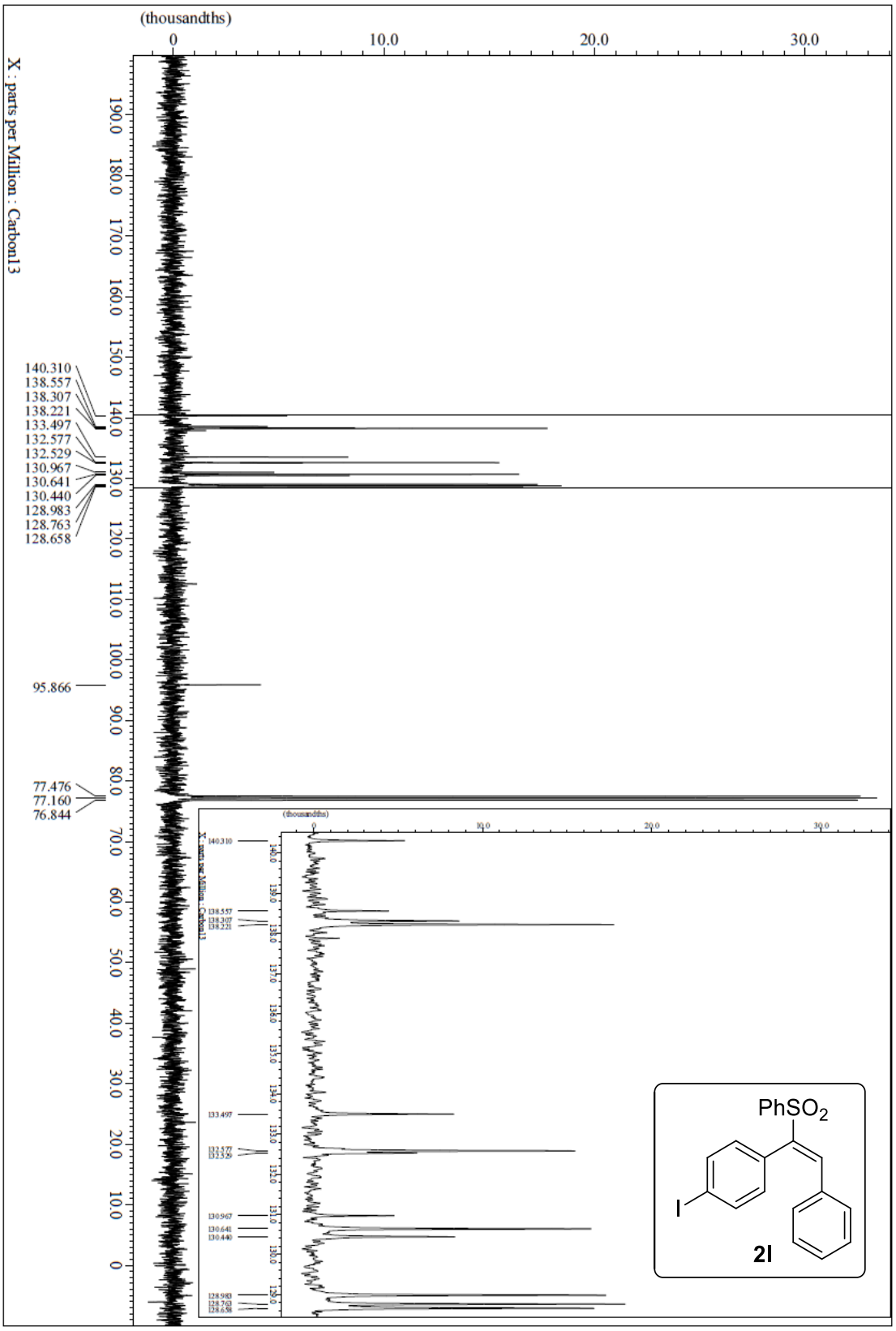
^{1}H NMR (400 MHz) spectrum of **2k** ($CDCl_3$, rt)



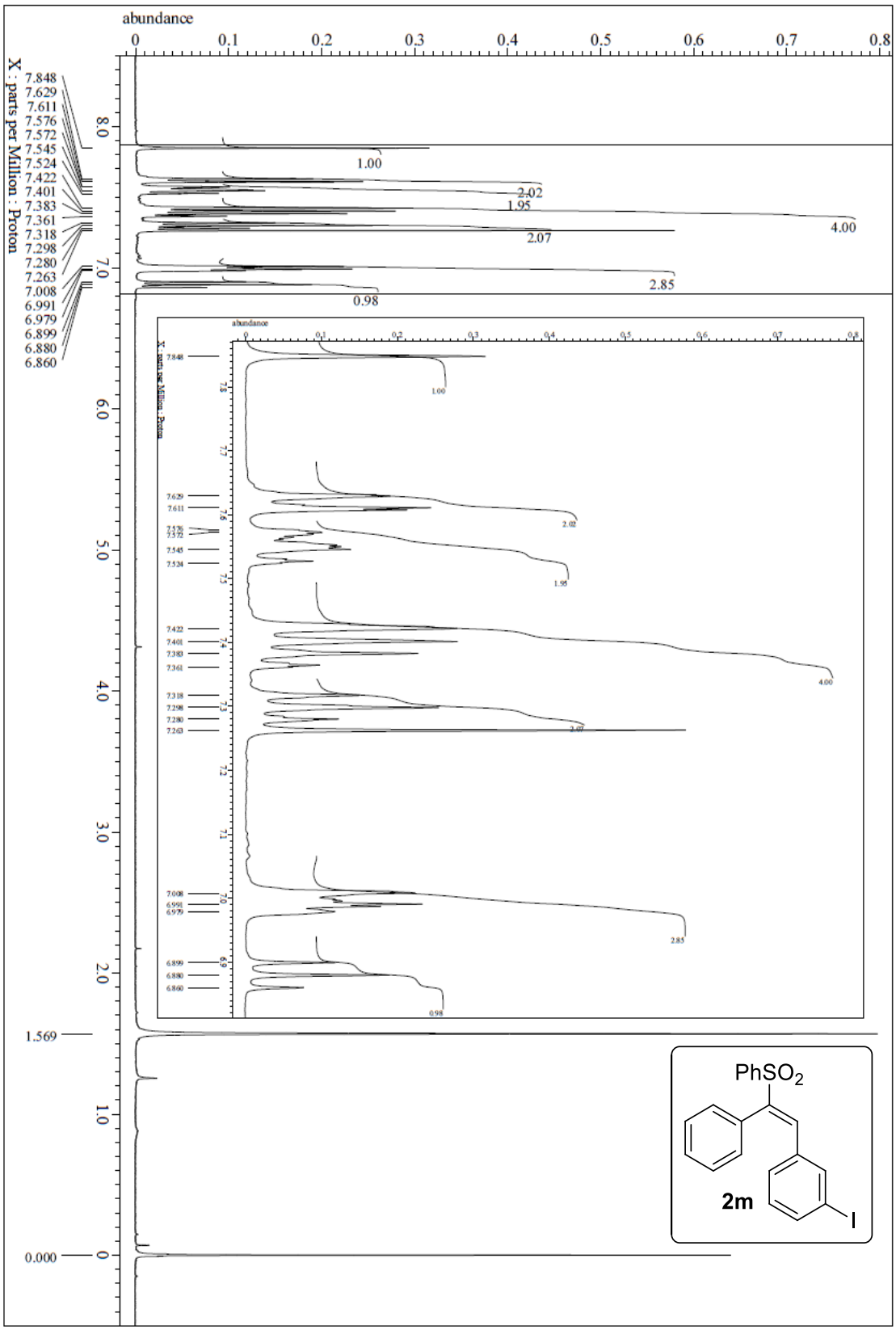
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2k** ($CDCl_3$, rt)



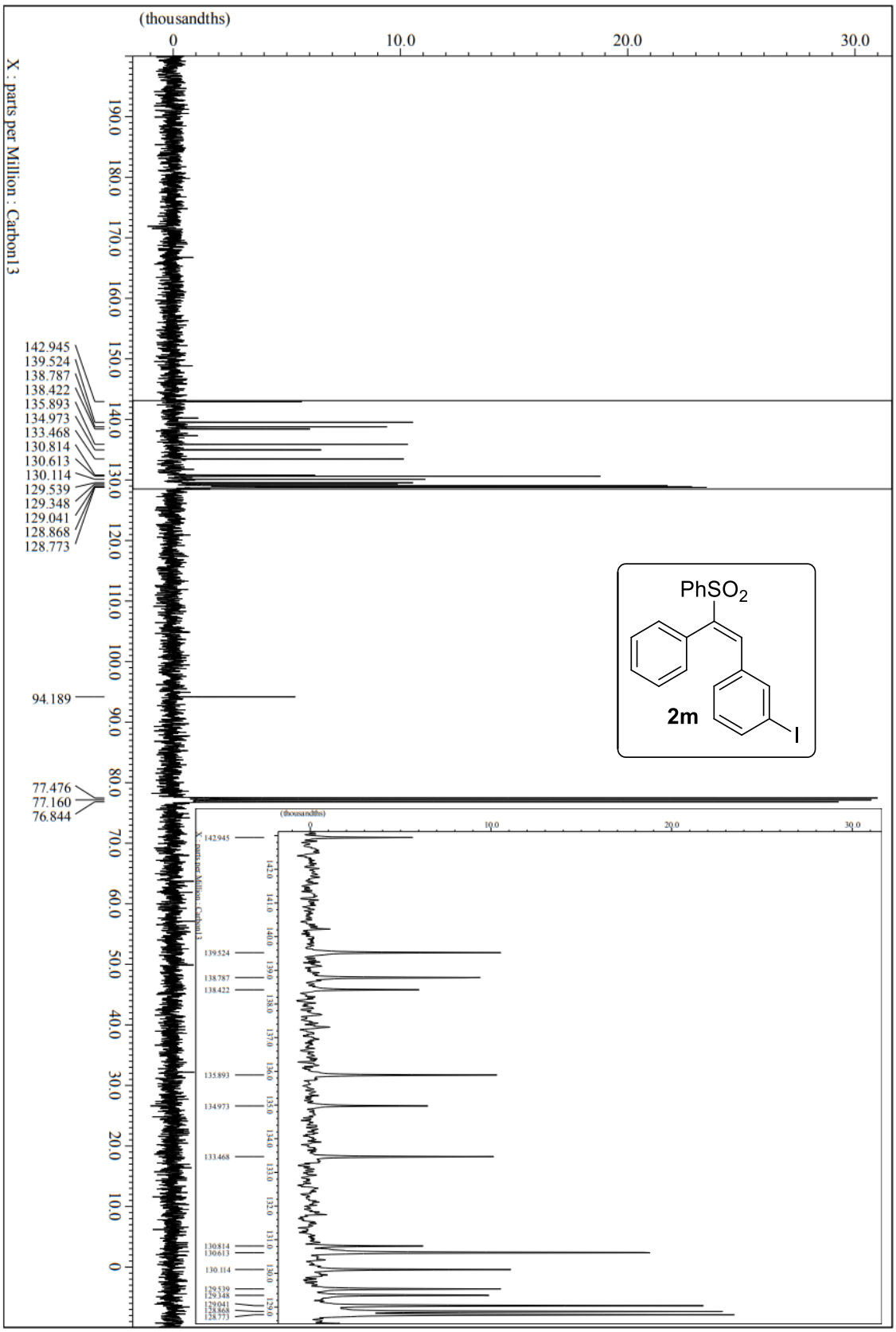
^{1}H NMR (400 MHz) spectrum of **2l** ($CDCl_3$, rt)



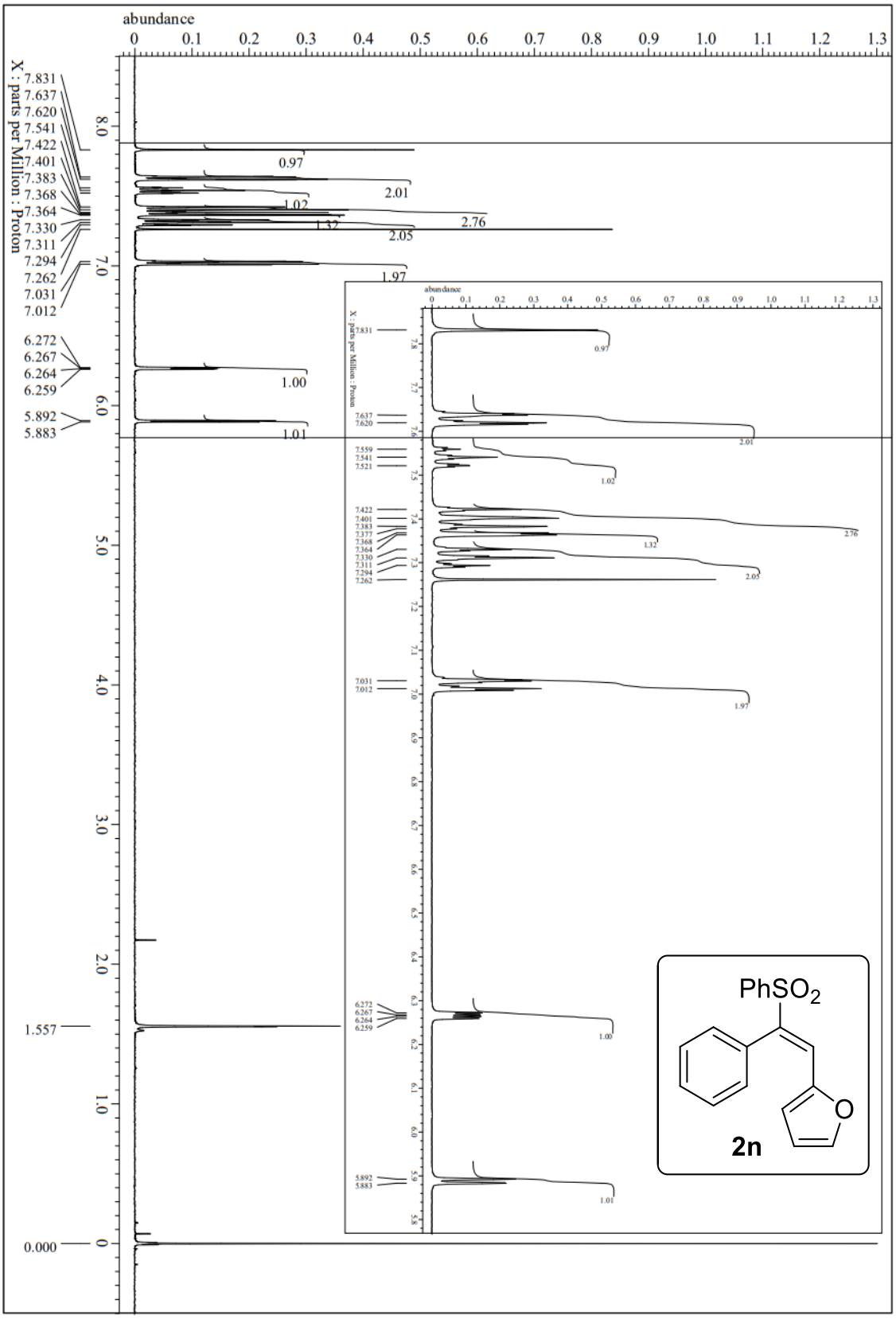
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2l** ($CDCl_3$, rt)



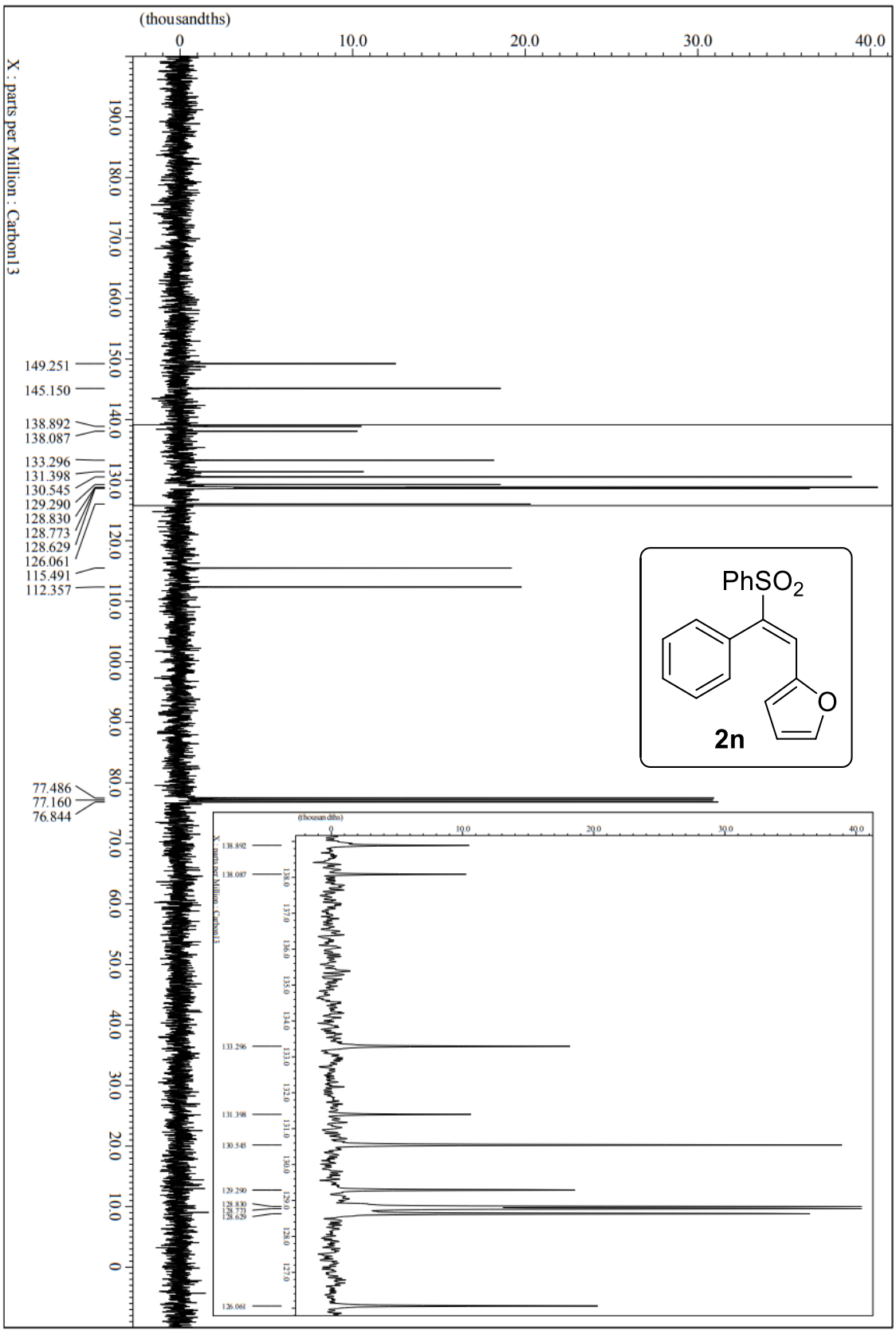
^{1}H NMR (400 MHz) spectrum of **2m** ($CDCl_3$, rt)



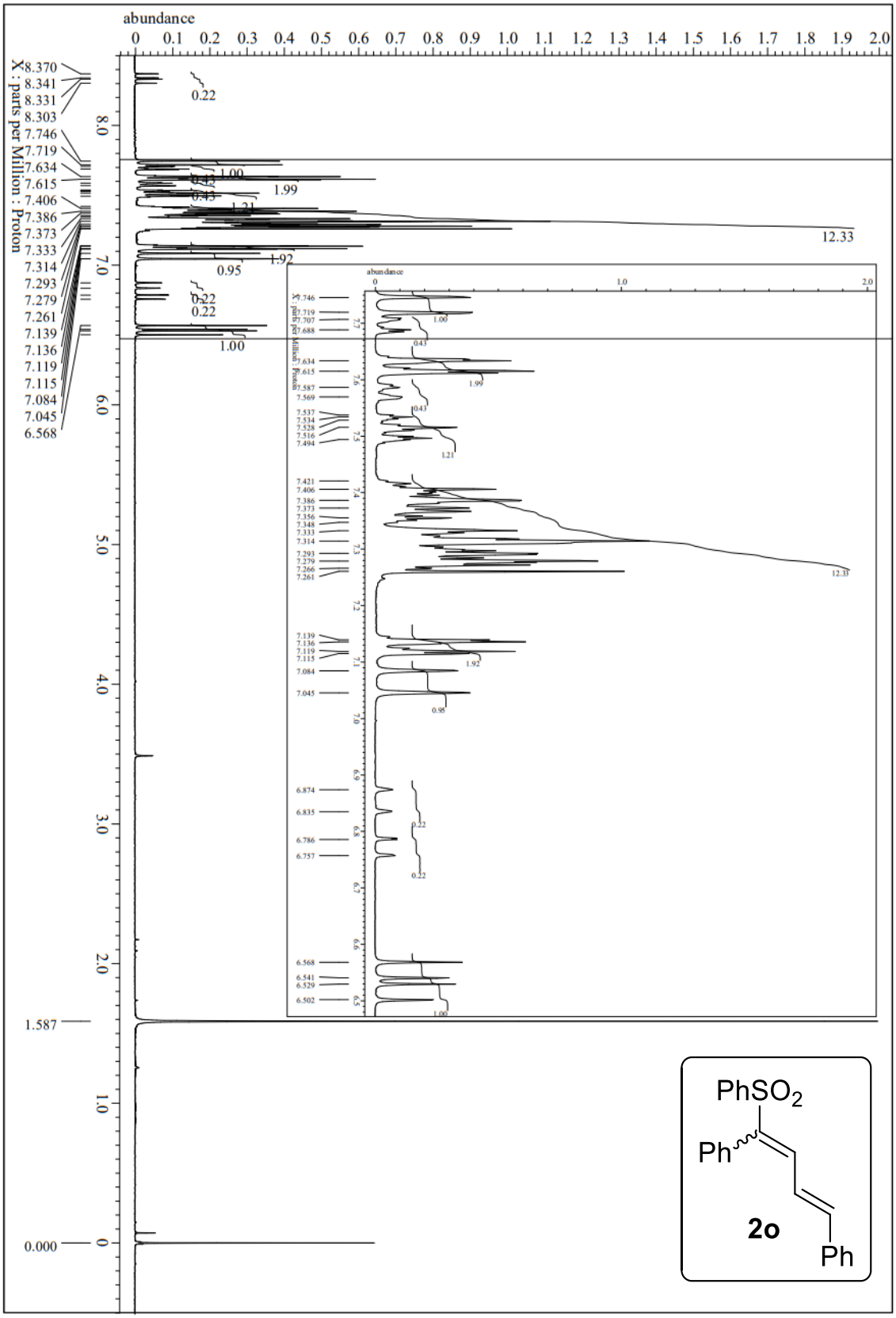
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2m** ($CDCl_3$, rt)



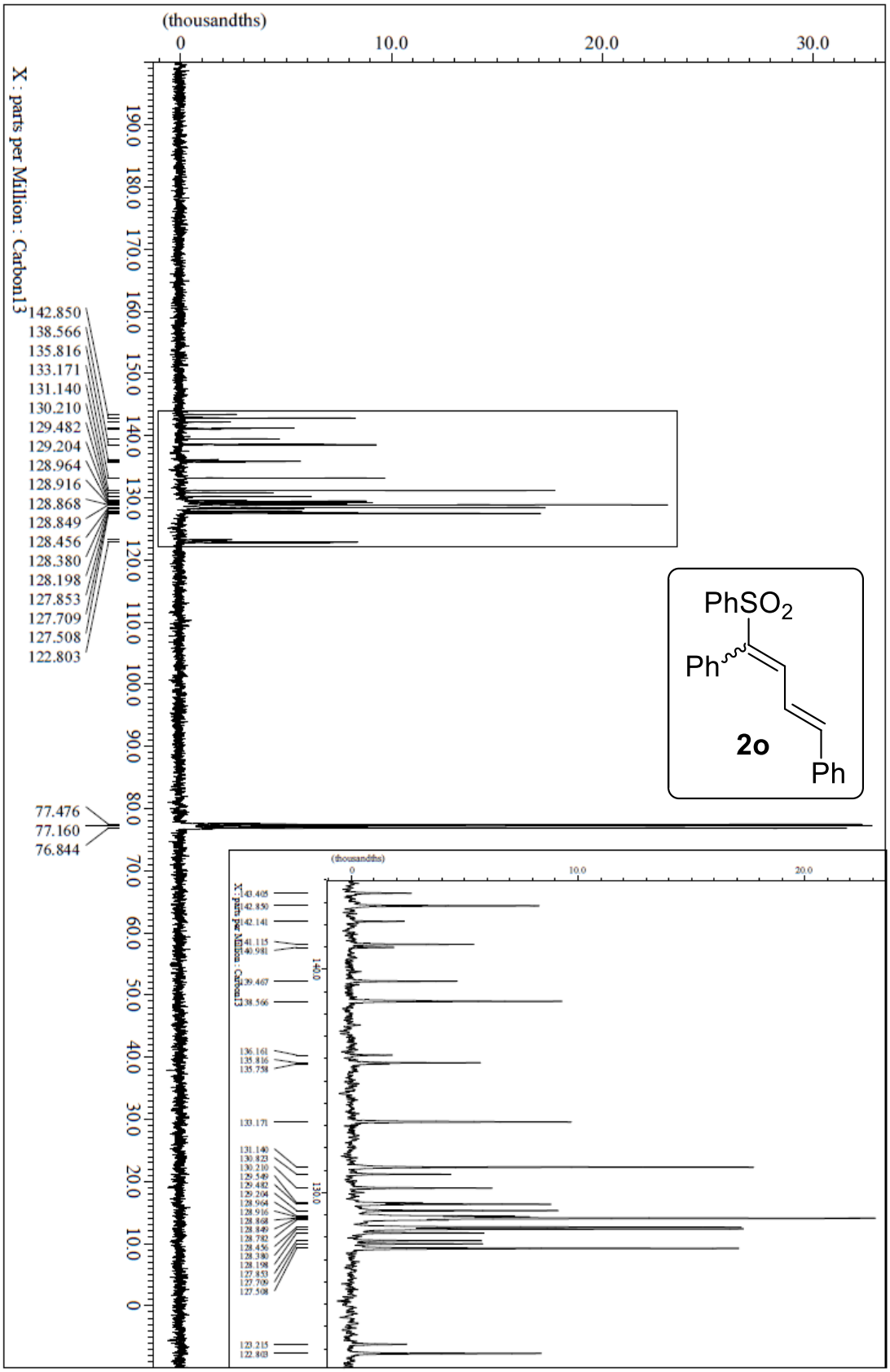
^{1}H NMR (400 MHz) spectrum of **2n** ($CDCl_3$, rt)



$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2n** ($CDCl_3$, rt)



^{1}H NMR (400 MHz) spectrum of **2o** ($CDCl_3$, rt)



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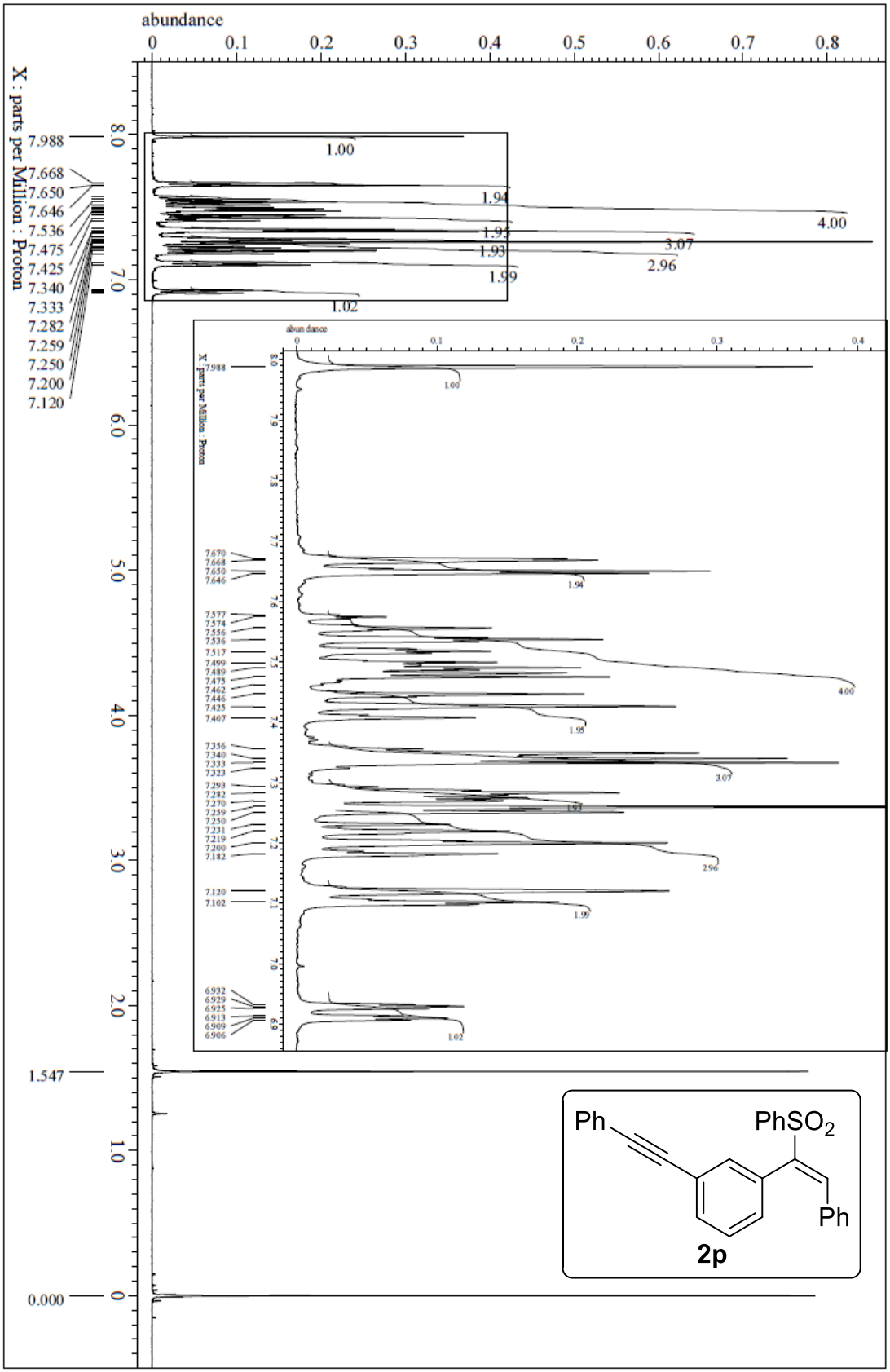
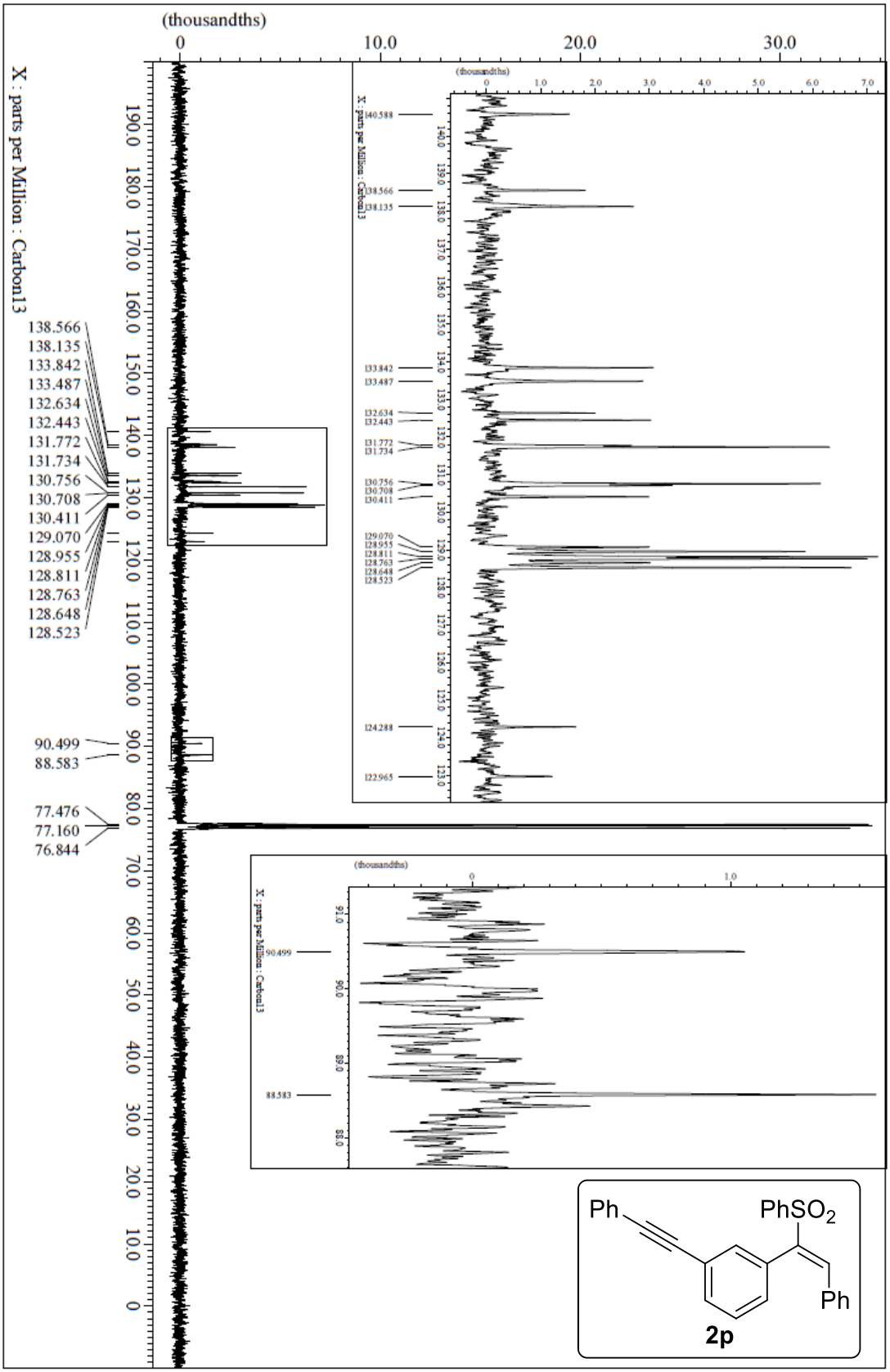


^{1}H NMR (400 MHz) spectrum of **2p** ($CDCl_3$, rt)



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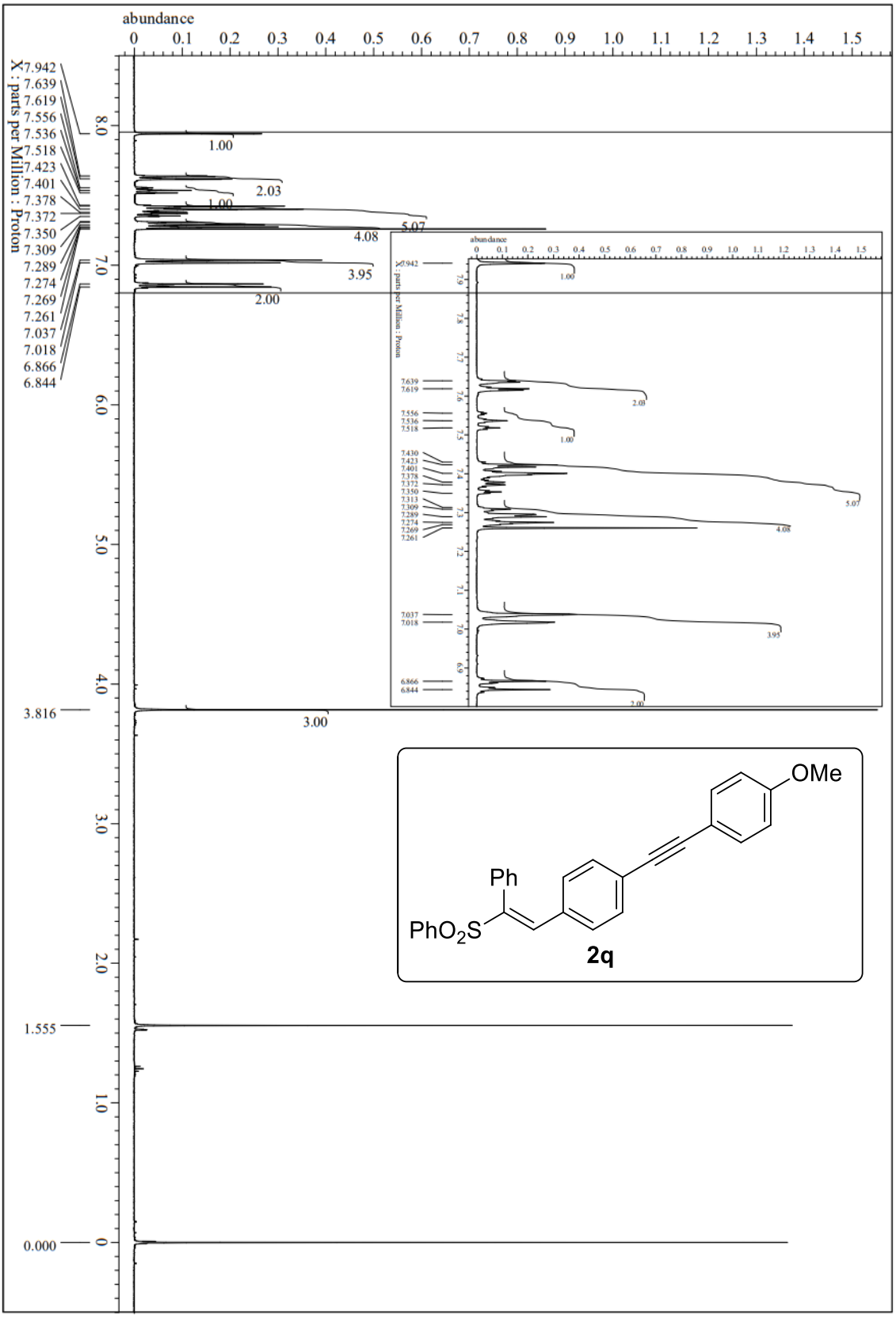
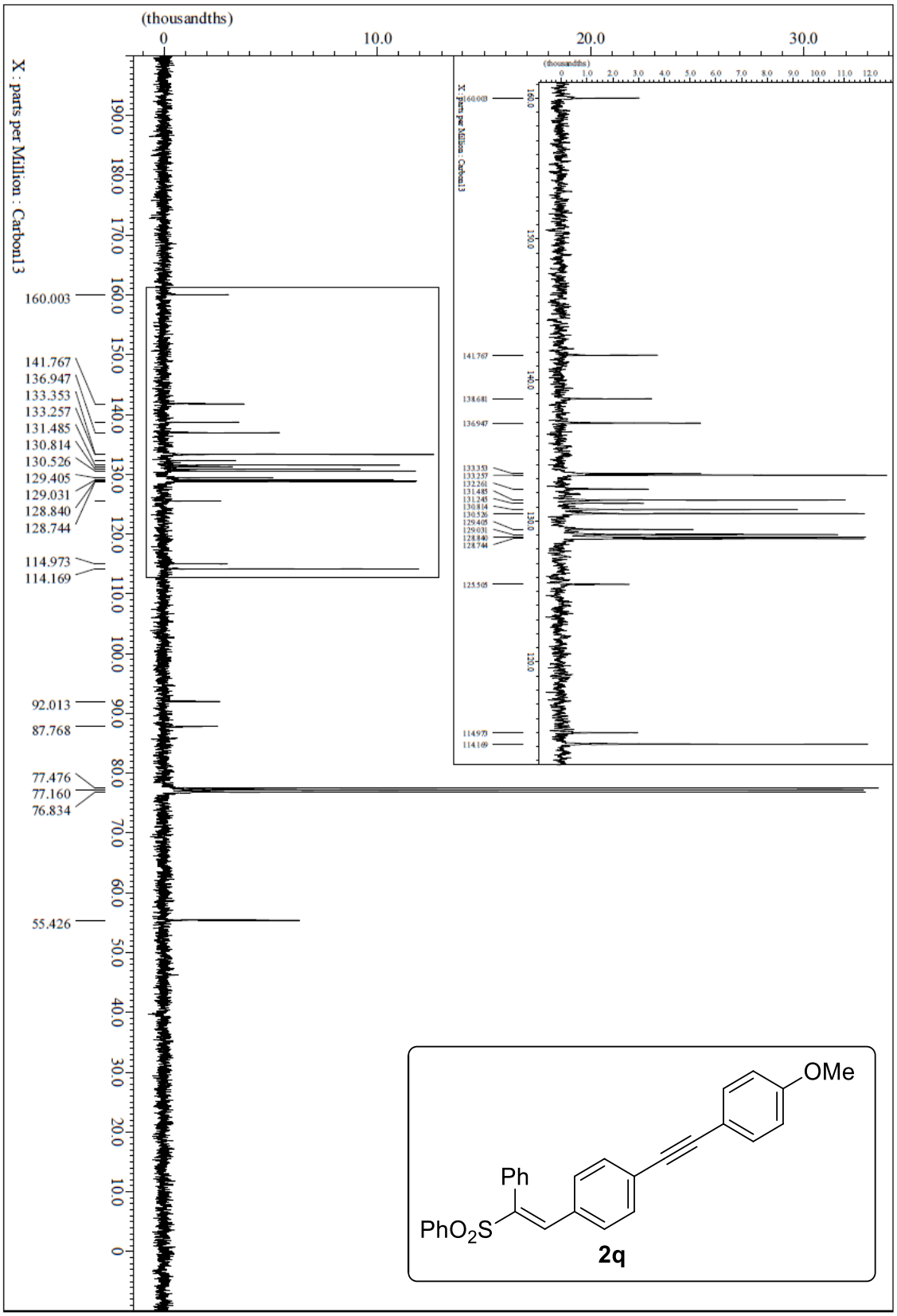
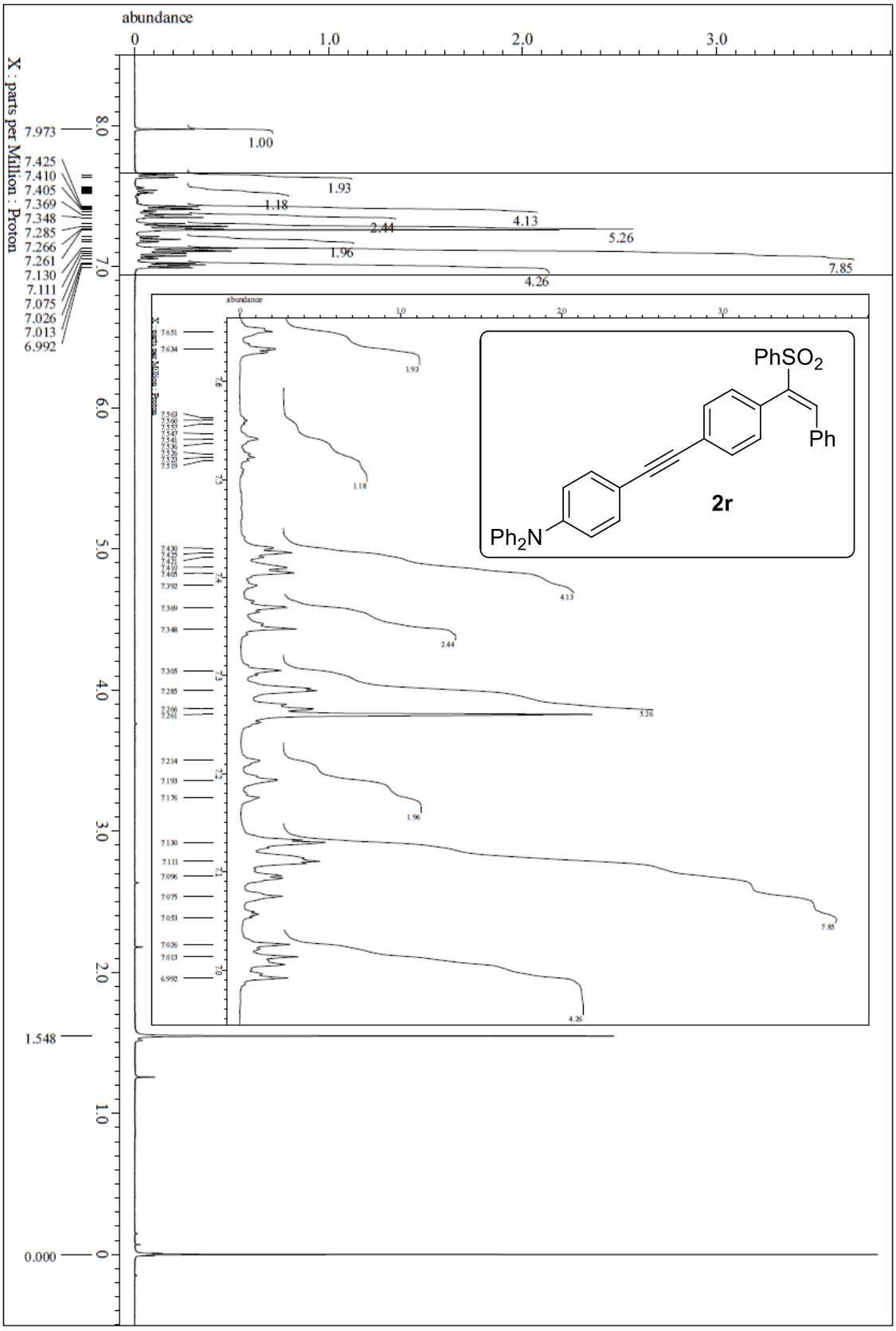


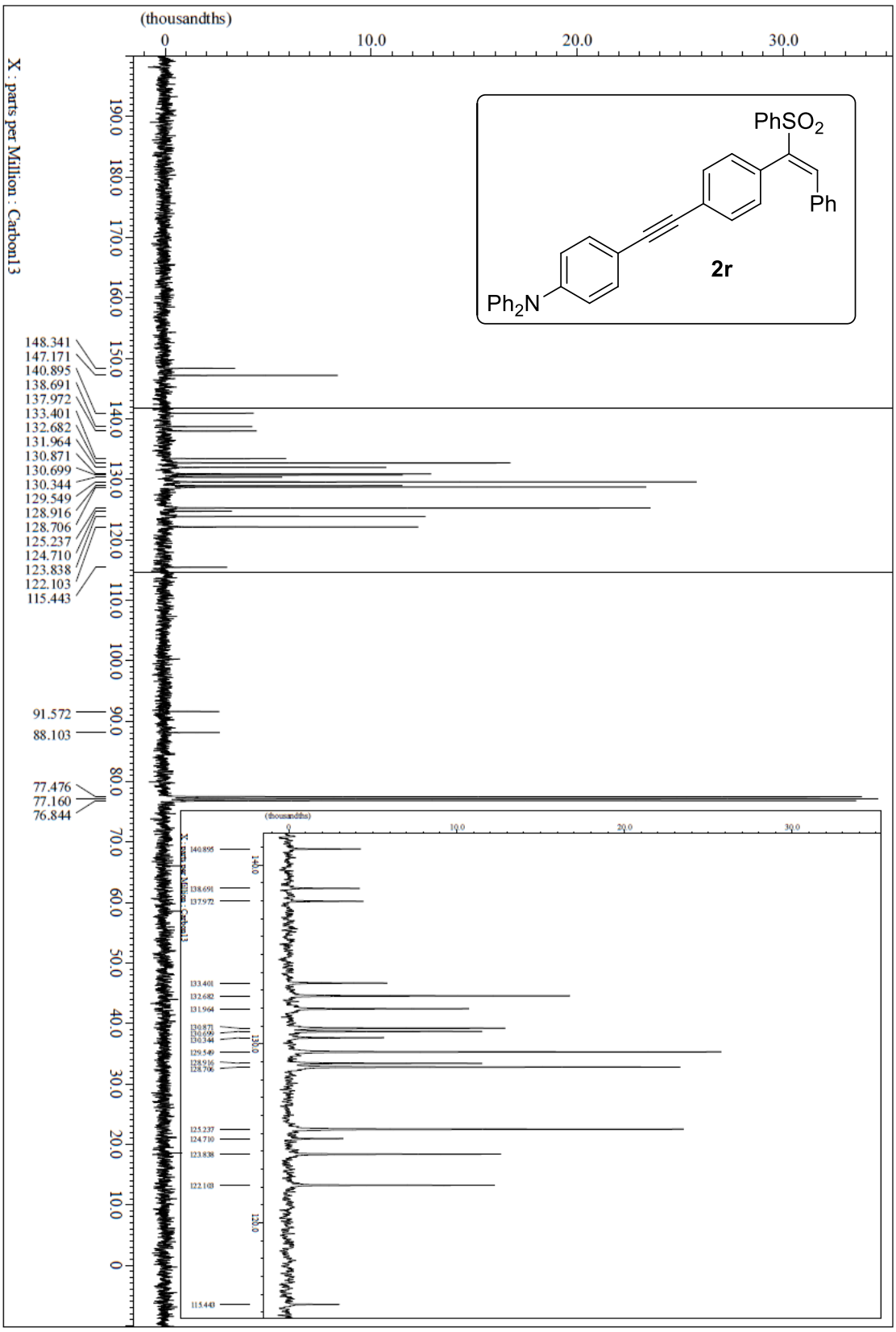
^{1}H NMR (400 MHz) spectrum of **2q** ($CDCl_3$, rt)



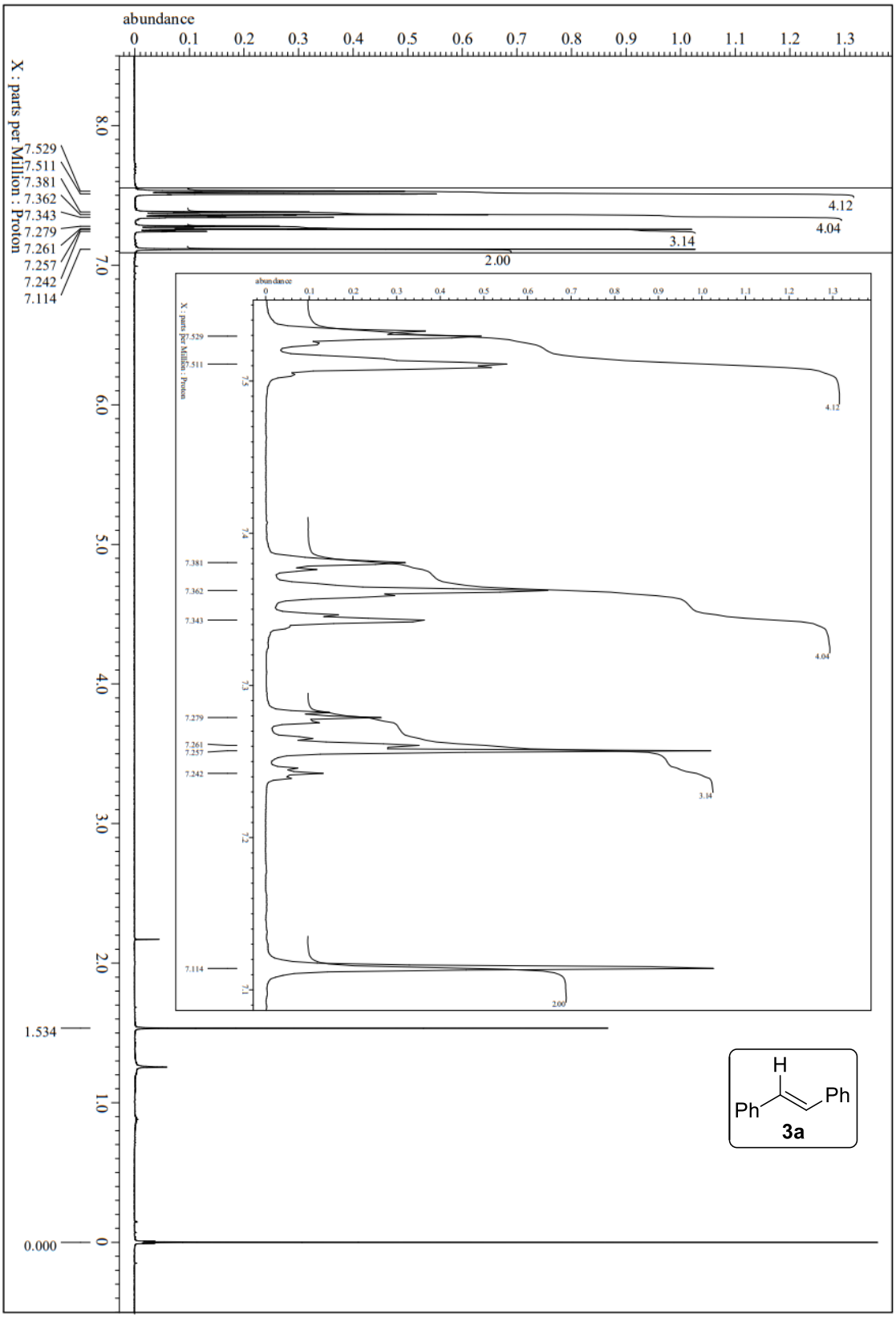
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2q** ($CDCl_3$, rt)



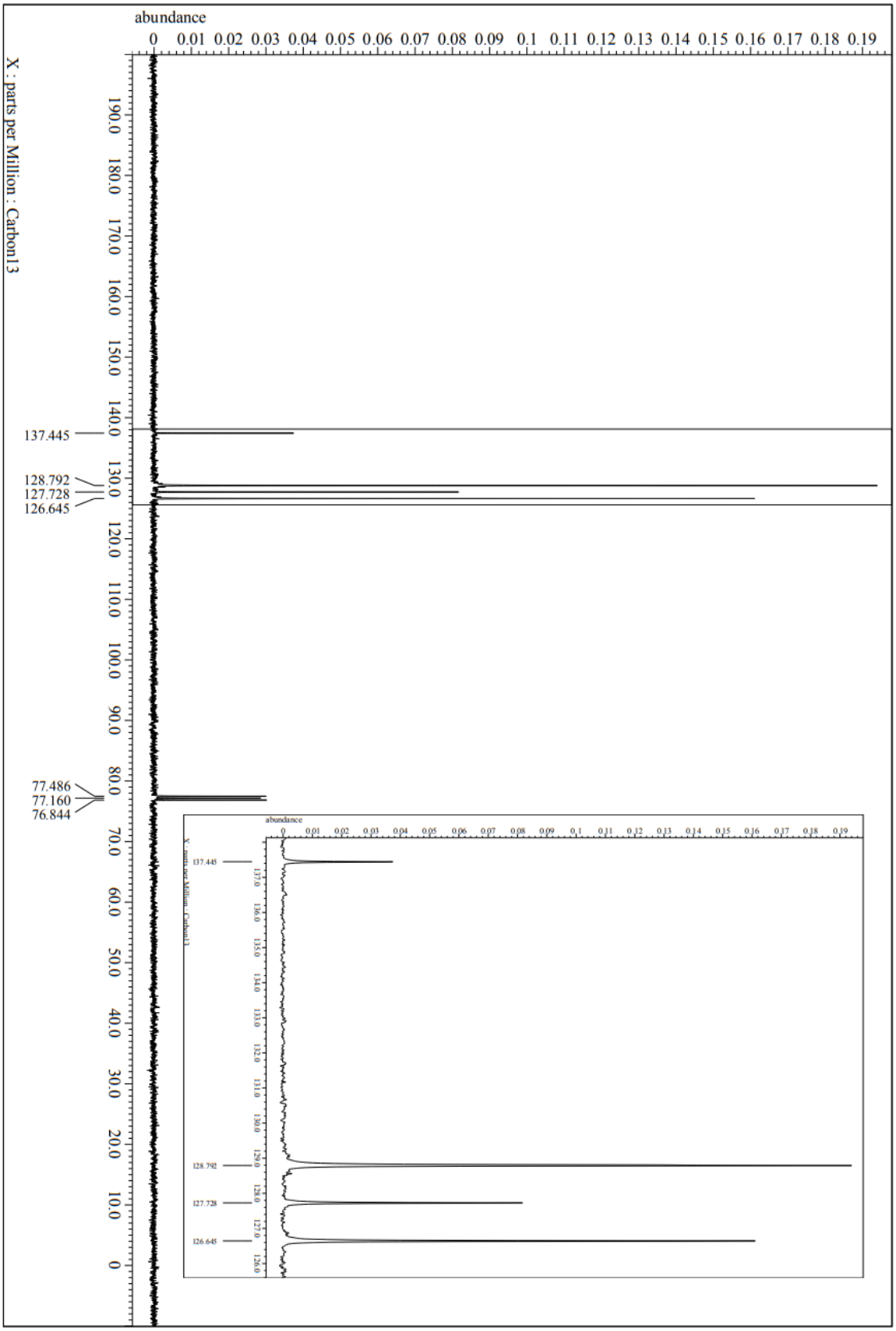
^{1}H NMR (400 MHz) spectrum of **2r** ($CDCl_3$, rt)



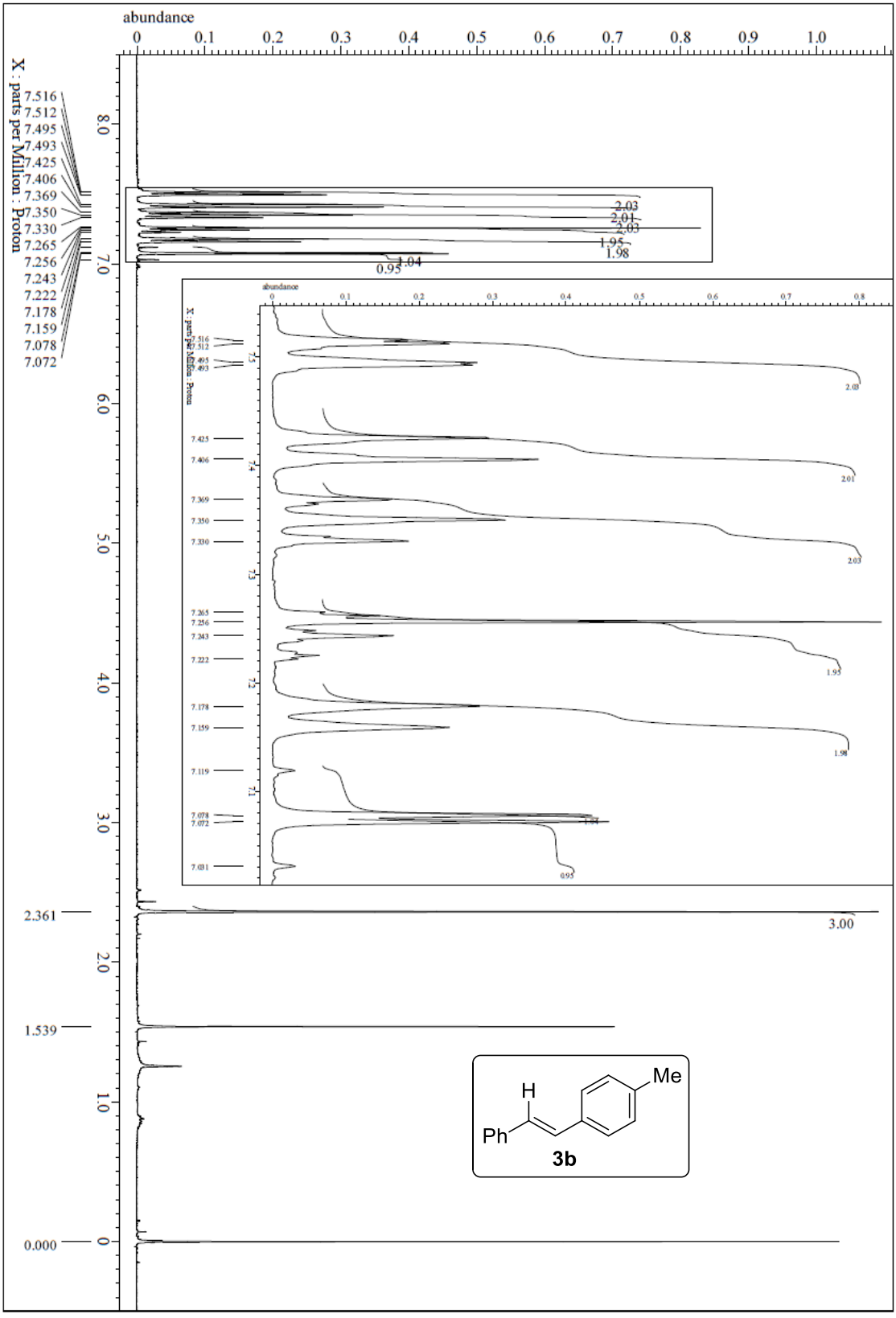
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2r** ($CDCl_3$, rt)



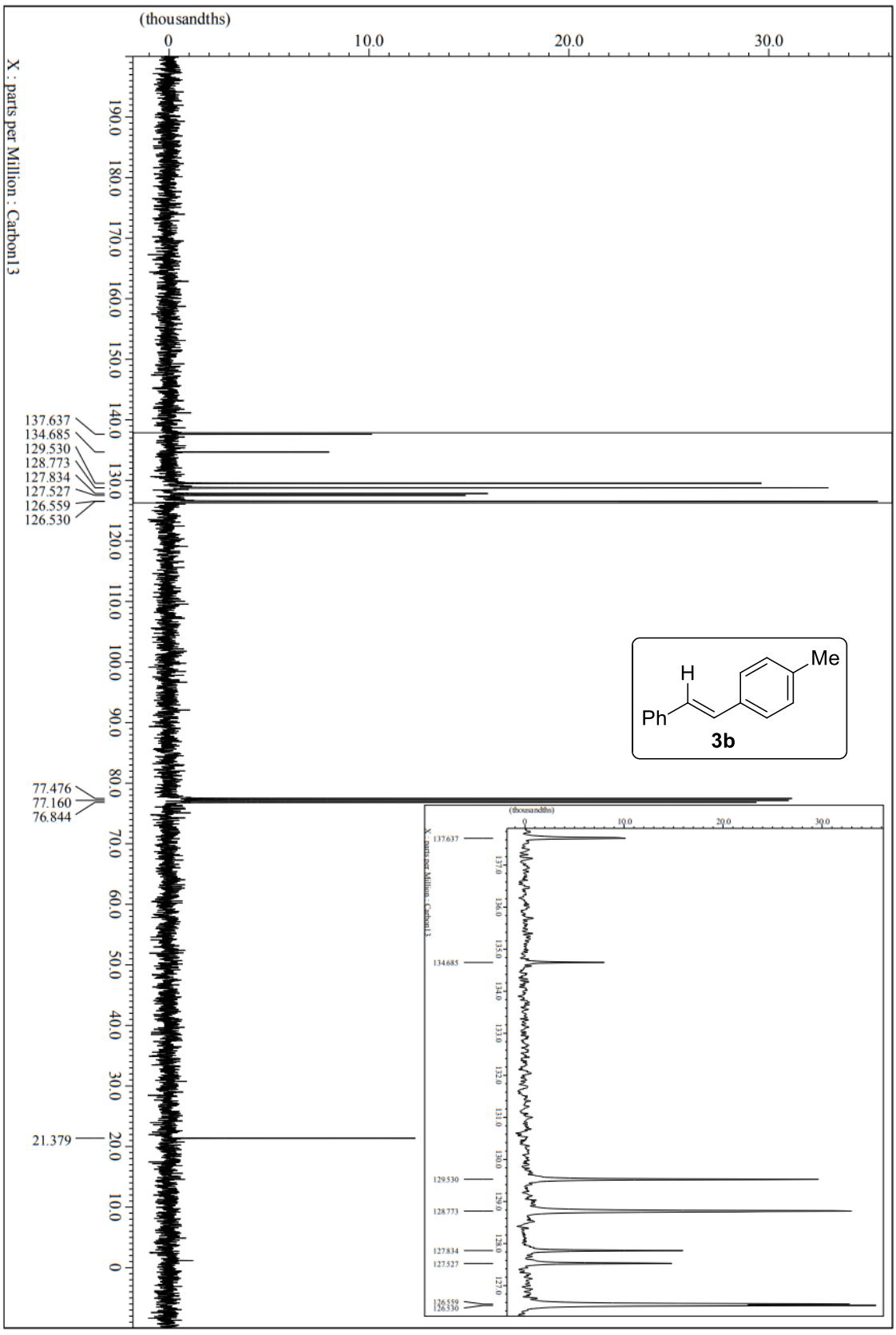
^{1}H NMR (400 MHz) spectrum of **3a** ($CDCl_3$, rt)



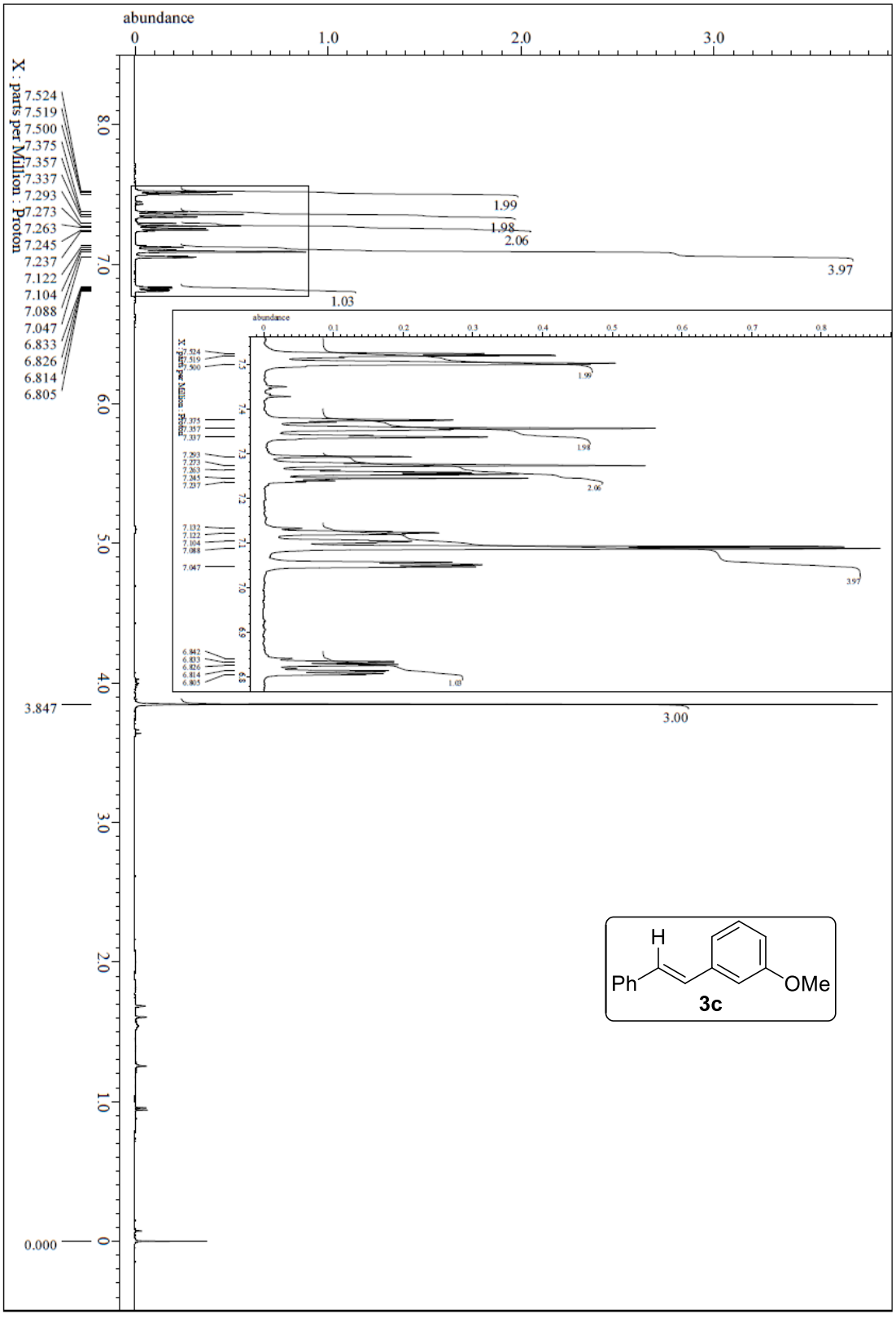
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3a** ($CDCl_3$, rt)



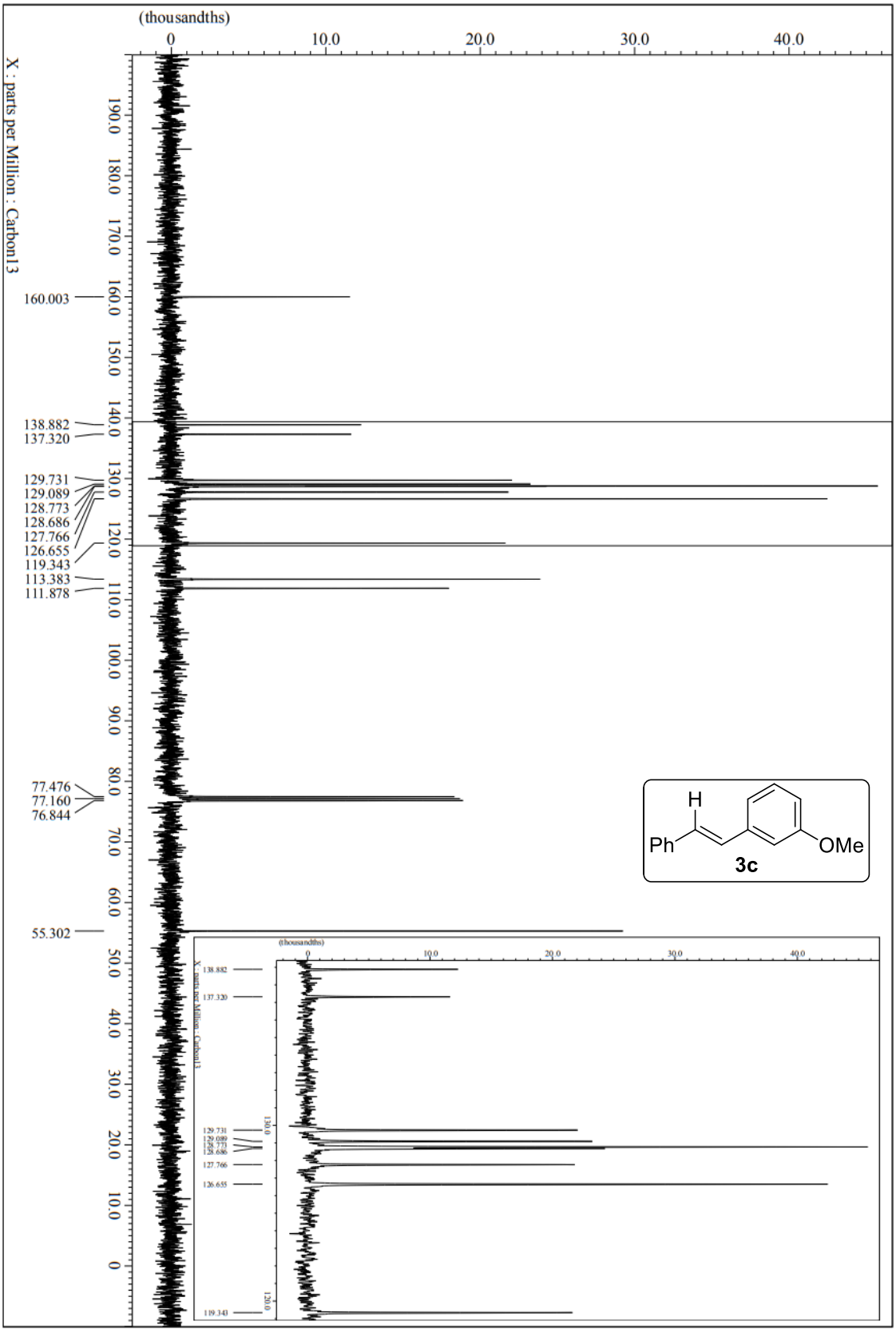
^{1}H NMR (400 MHz) spectrum of **3b** ($CDCl_3$, rt)



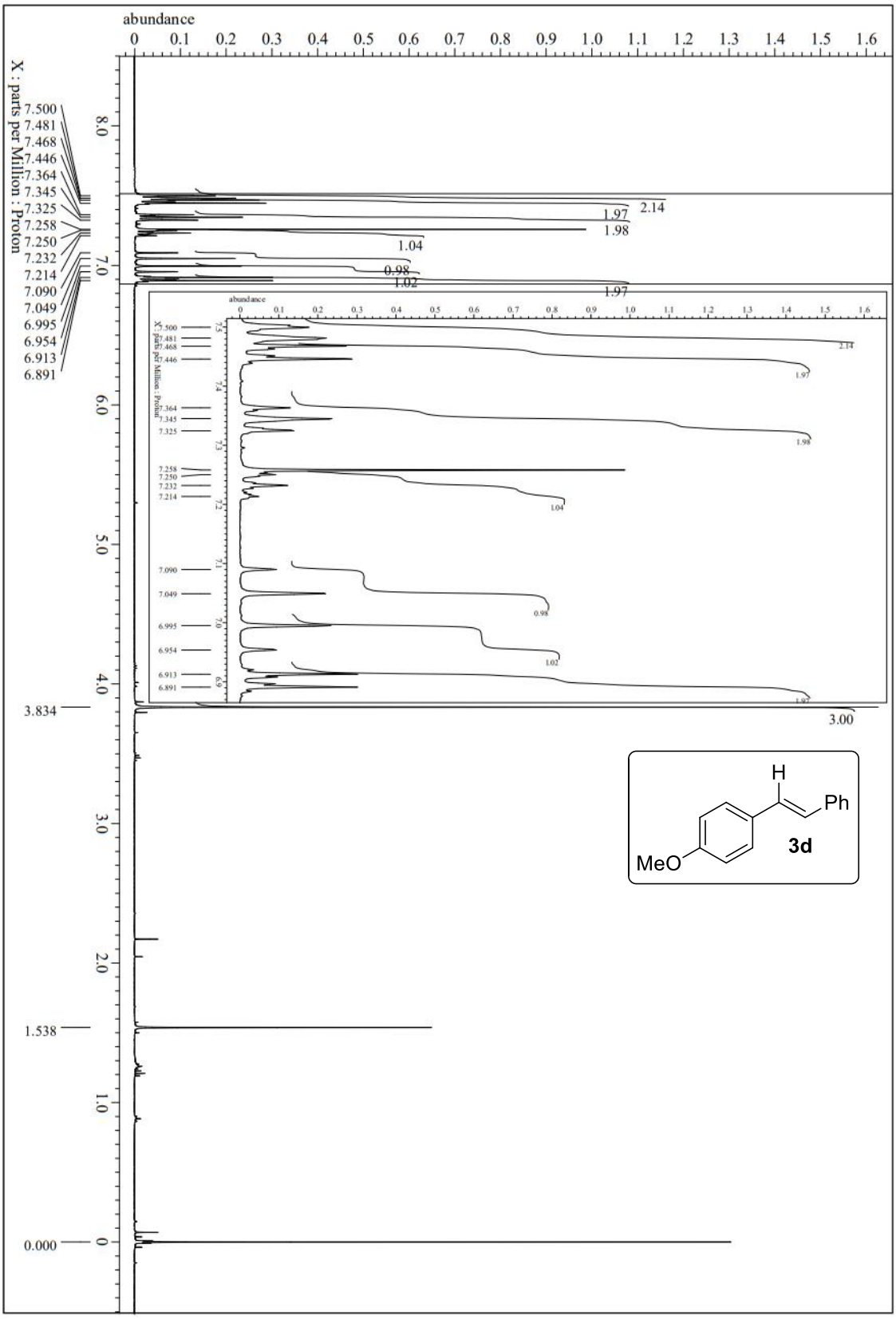
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3b** ($CDCl_3$, rt)



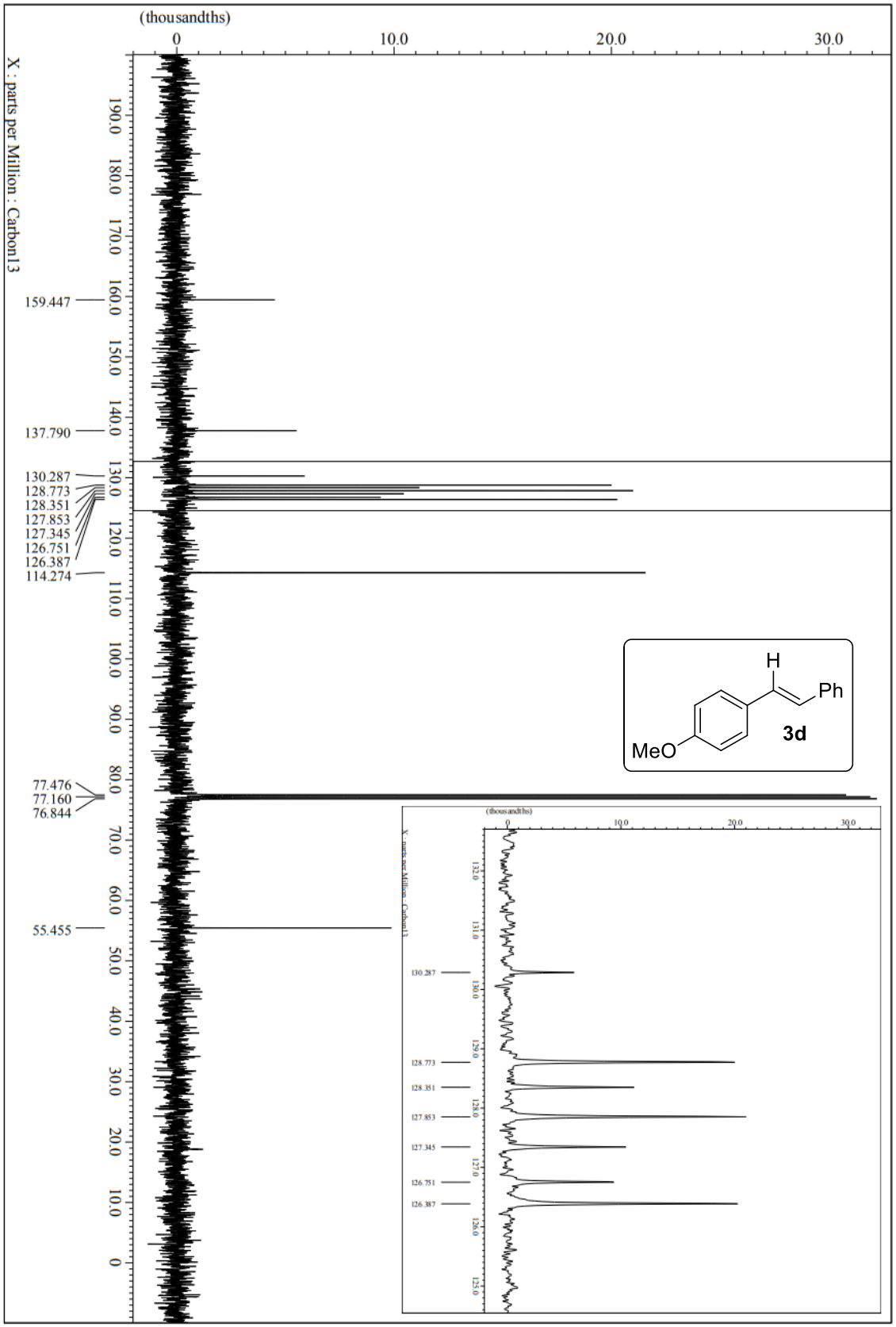
^{1}H NMR (400 MHz) spectrum of **3c** ($CDCl_3$, rt)



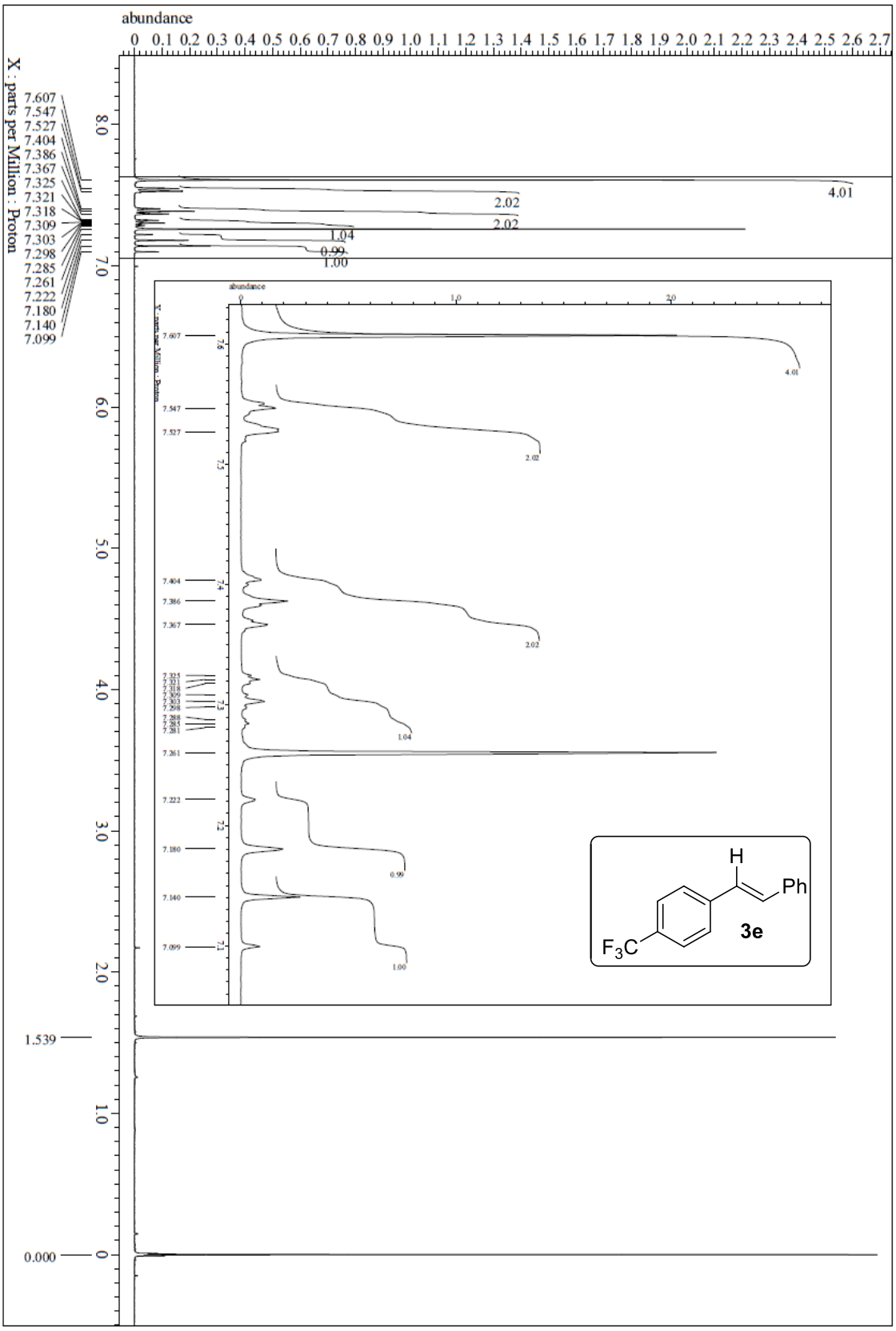
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3c** ($CDCl_3$, rt)



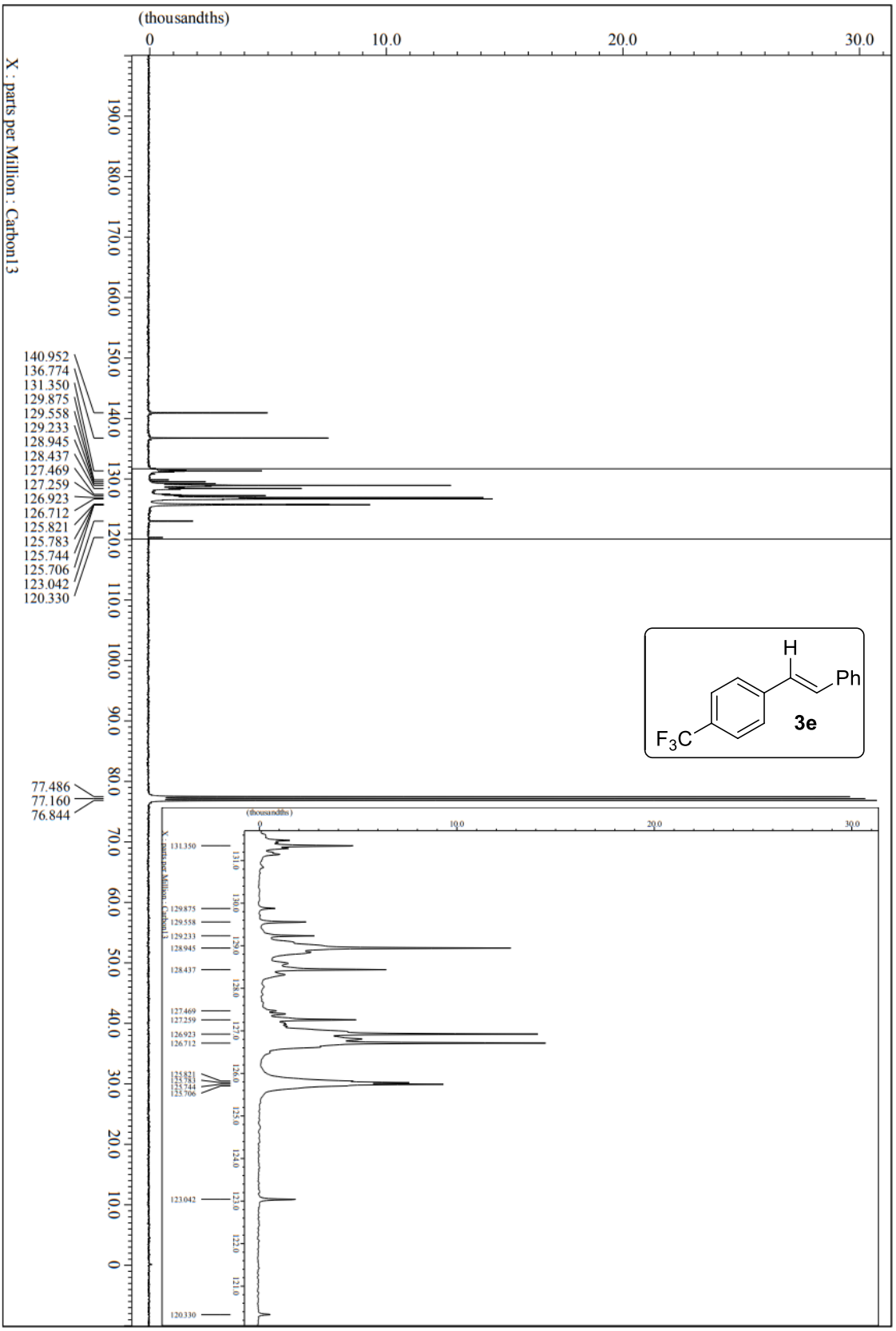
^{1}H NMR (400 MHz) spectrum of **3d** ($CDCl_3$, rt)



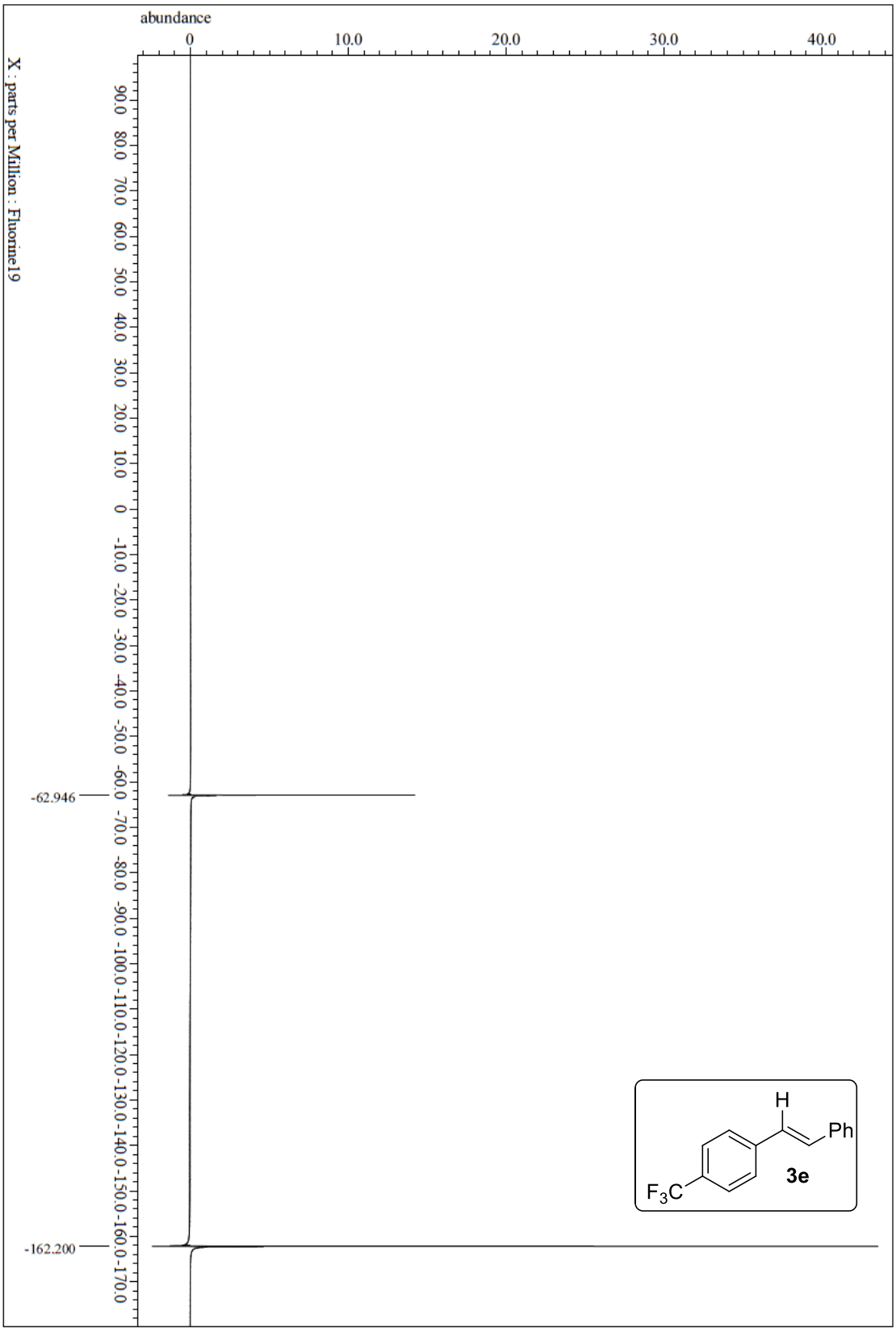
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3d** ($CDCl_3$, rt)



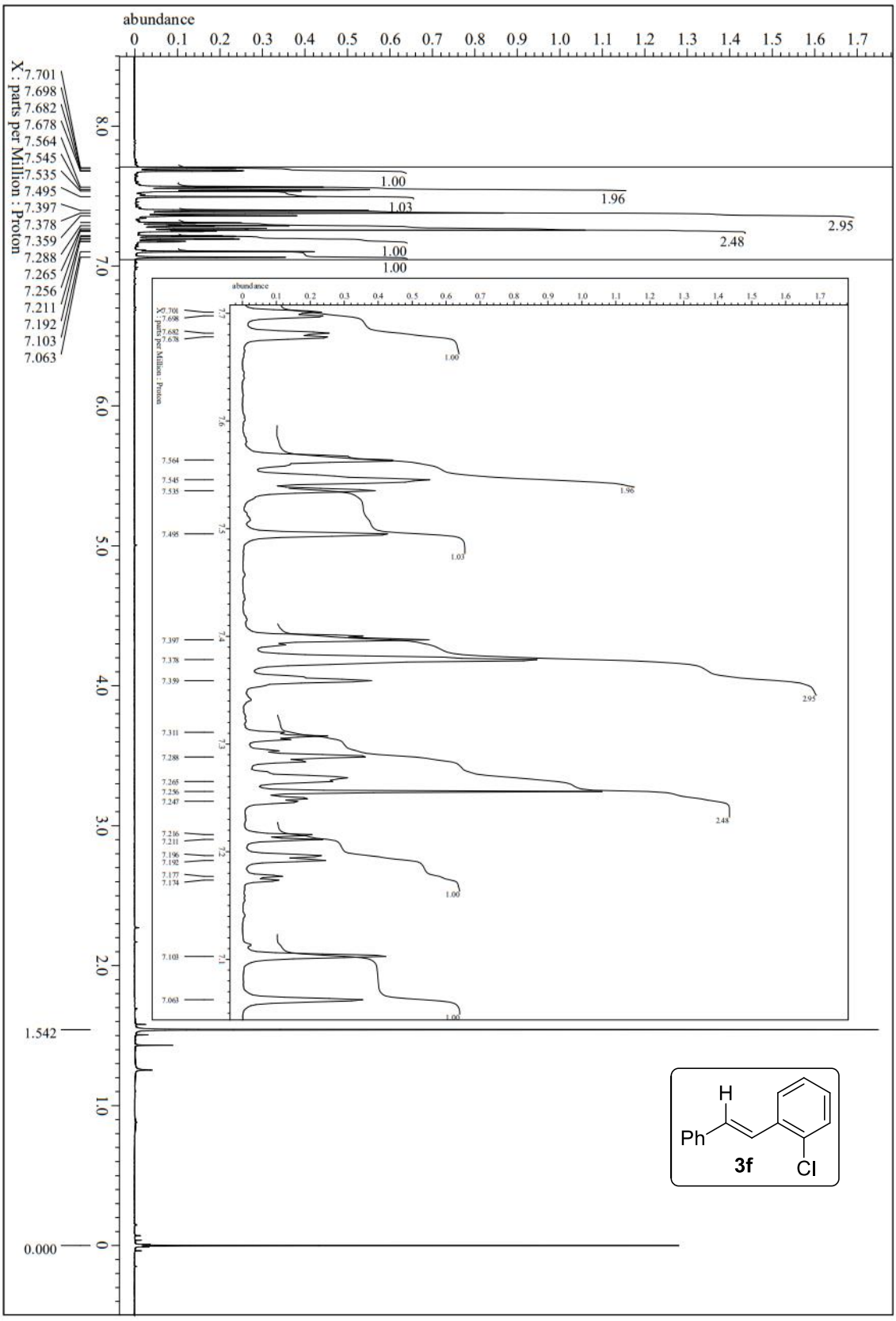
^{1}H NMR (400 MHz) spectrum of **3e** ($CDCl_3$, rt)



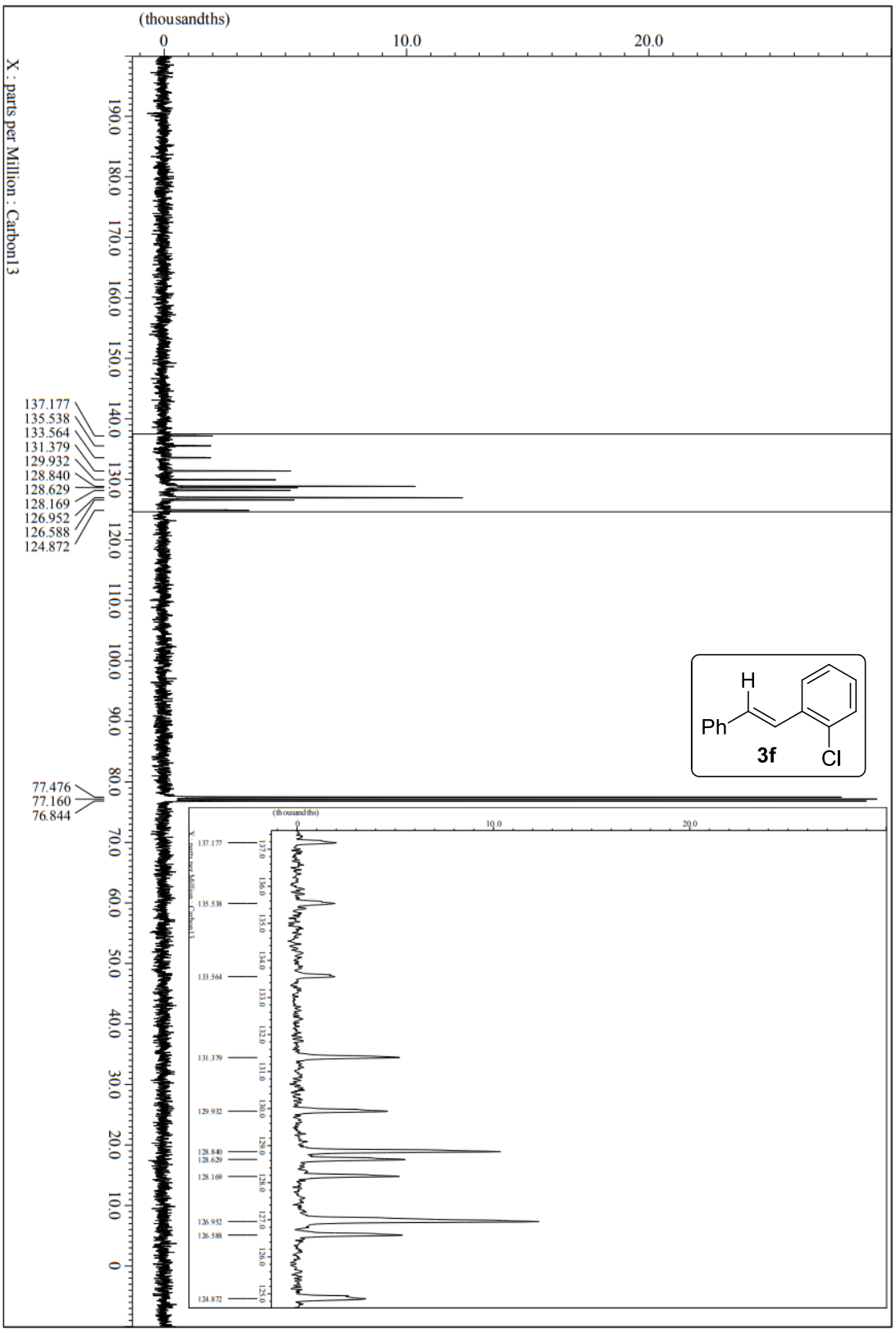
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3e** ($CDCl_3$, rt)



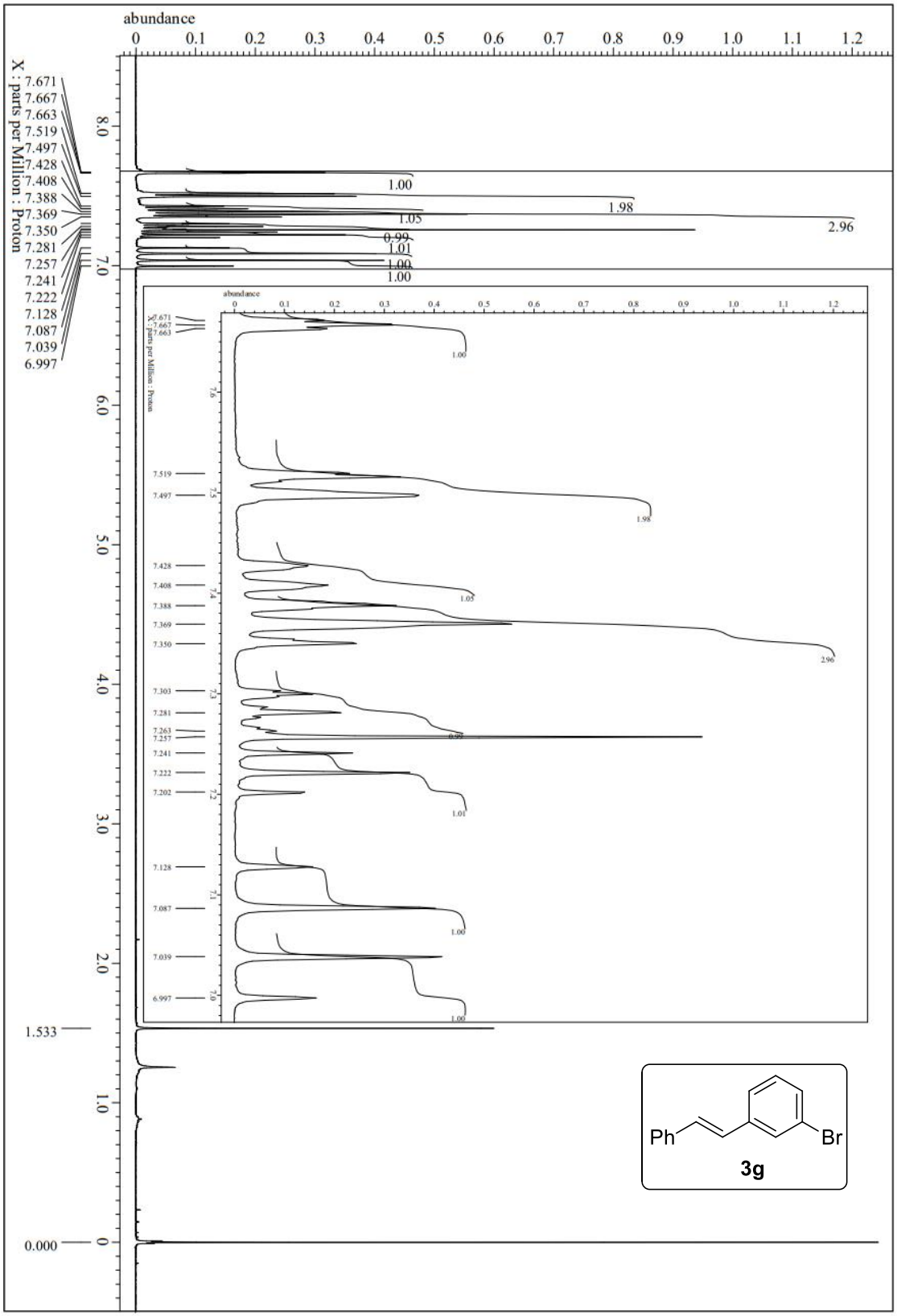
$^{19}F\{^{1}H\}$ NMR (376 MHz) spectrum of **3e** ($CDCl_3$, rt)



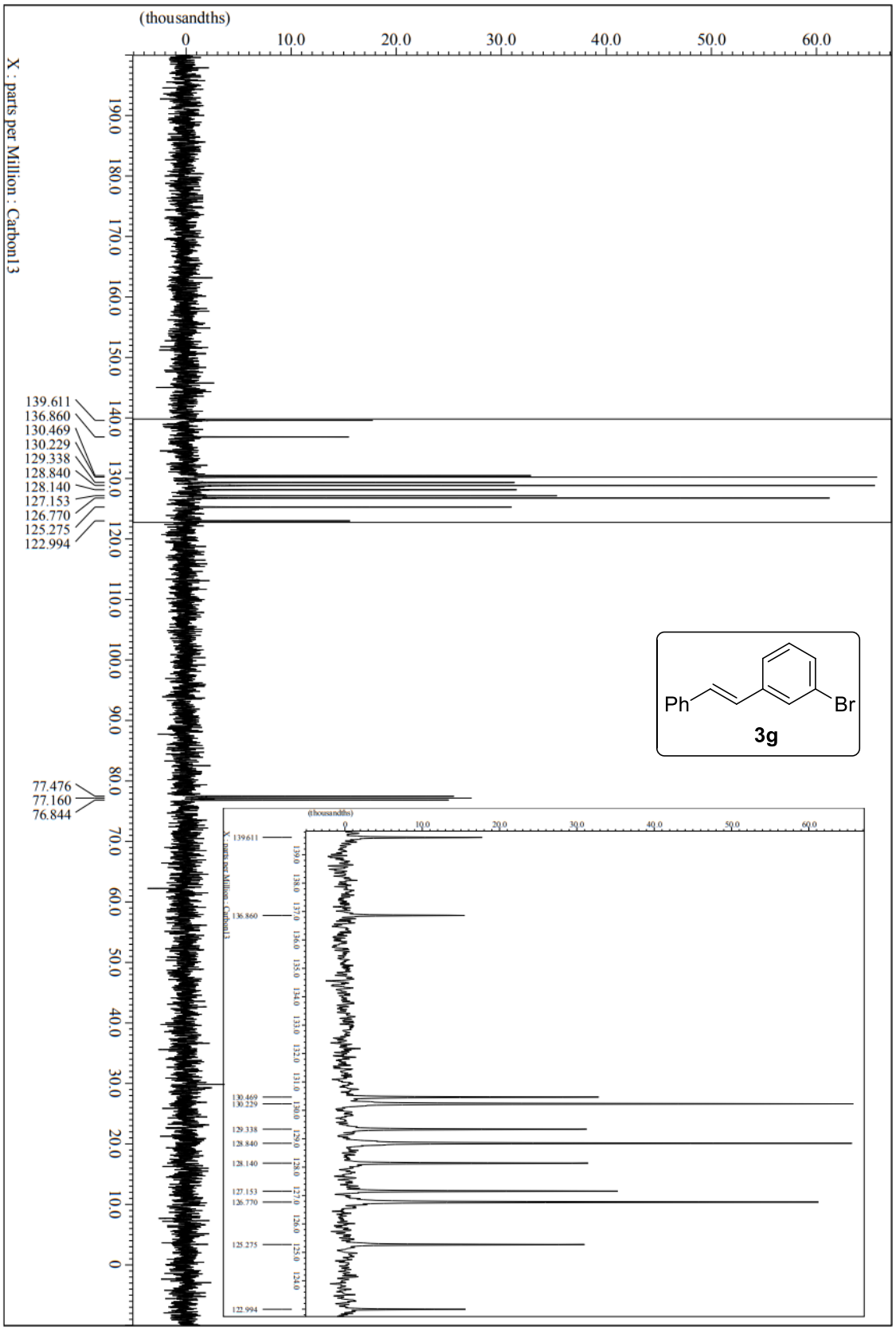
^{1}H NMR (400 MHz) spectrum of **3f** ($CDCl_3$, rt)



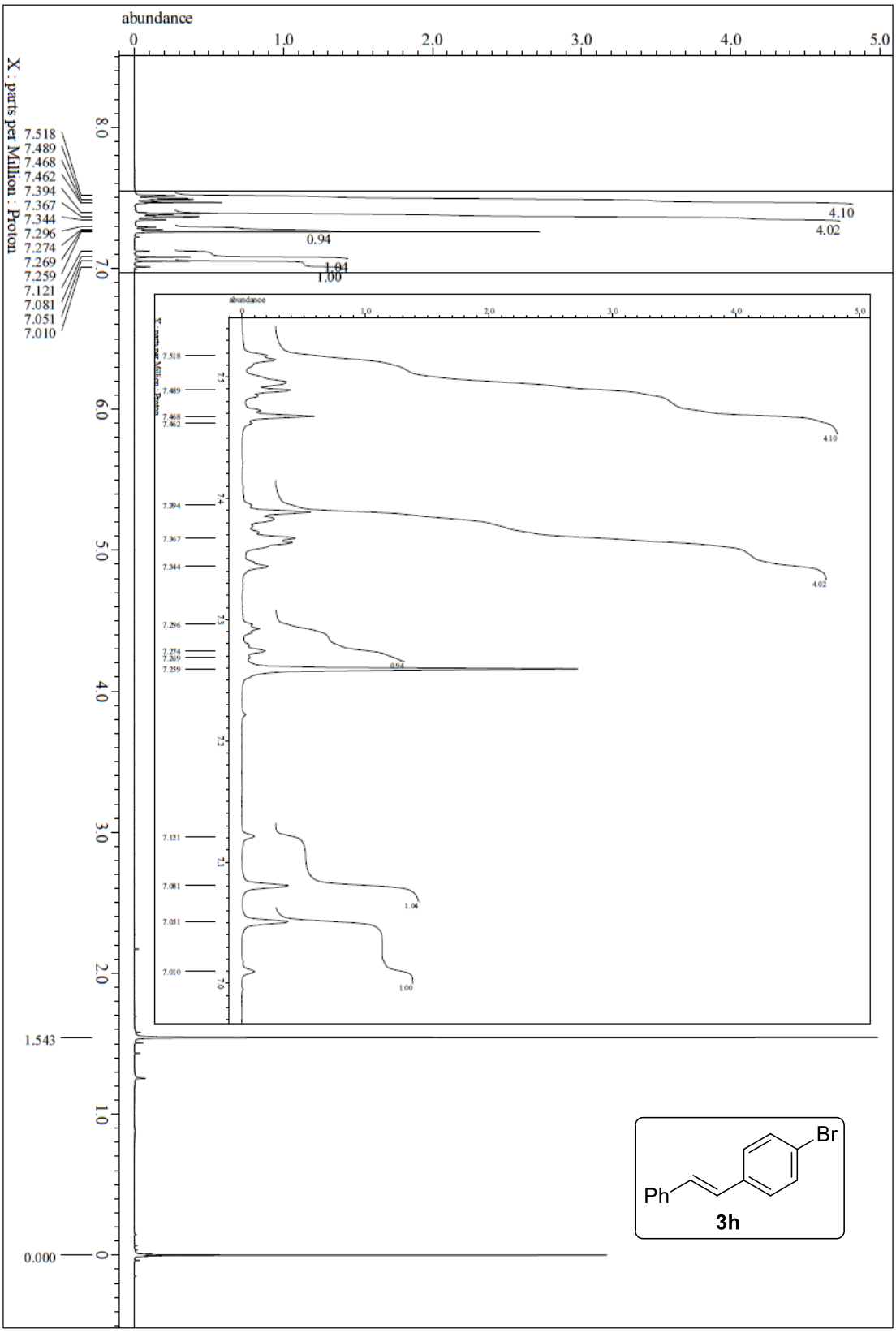
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3f** ($CDCl_3$, rt)



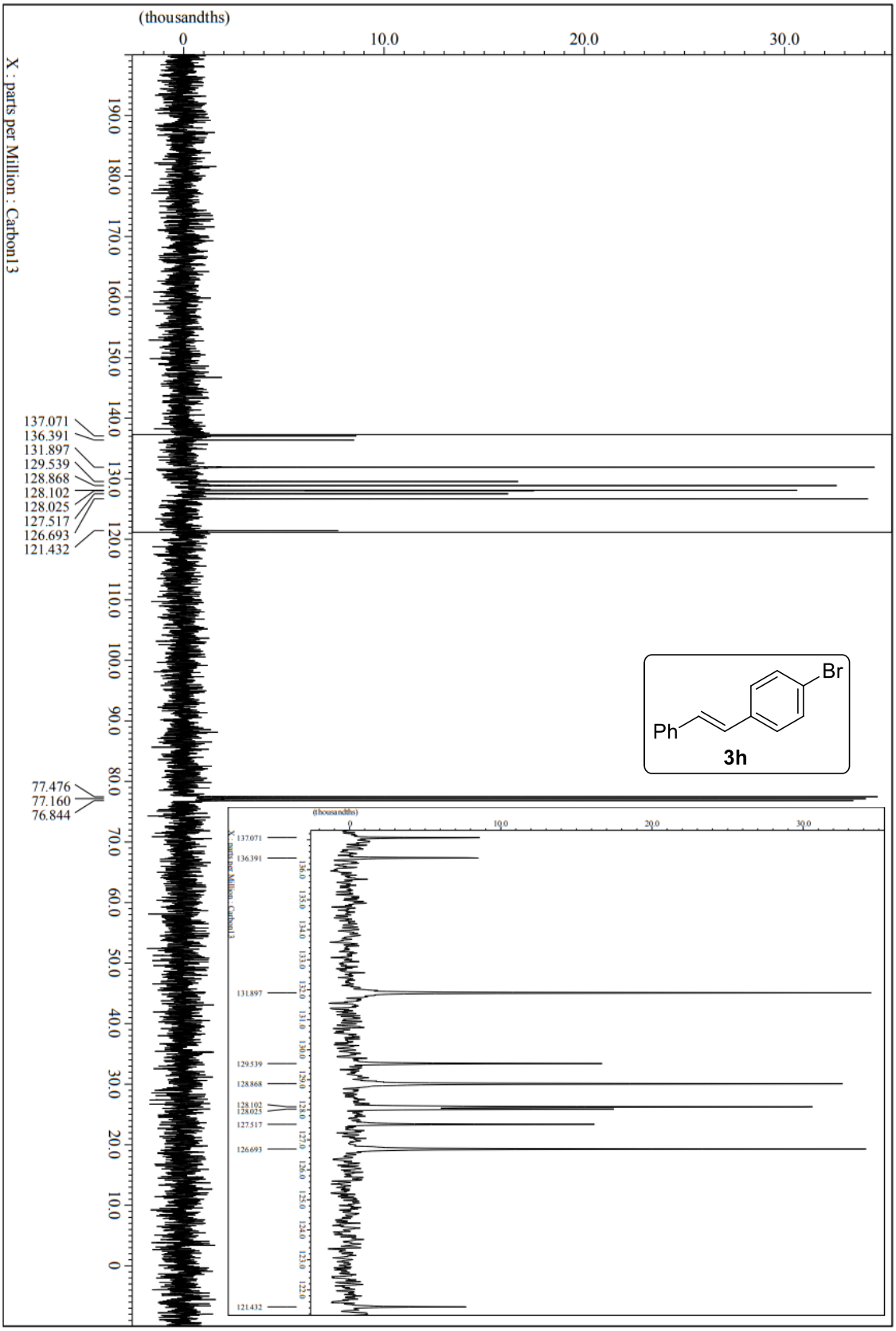
^{1}H NMR (400 MHz) spectrum of **3g** ($CDCl_3$, rt)



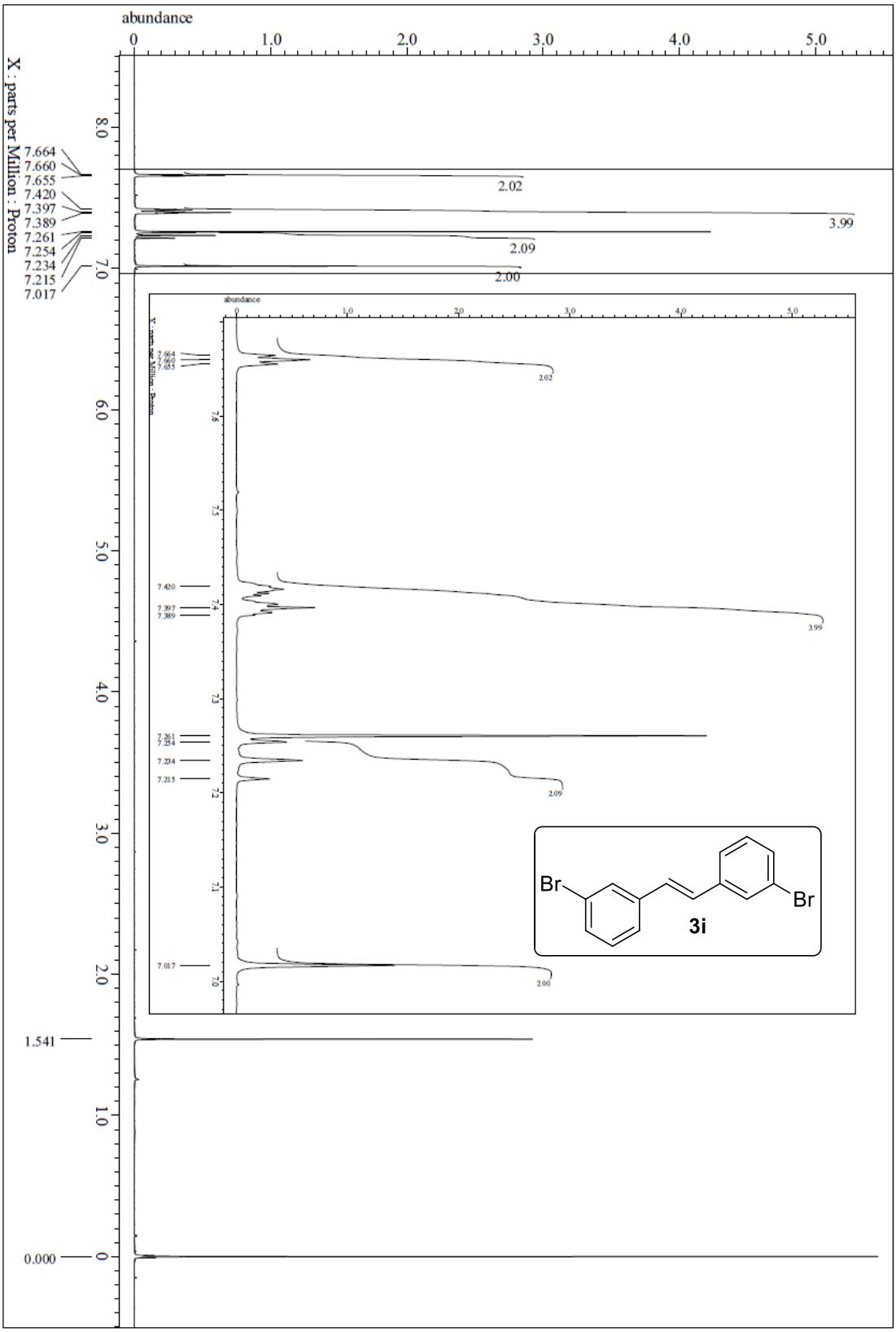
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3g** ($CDCl_3$, rt)



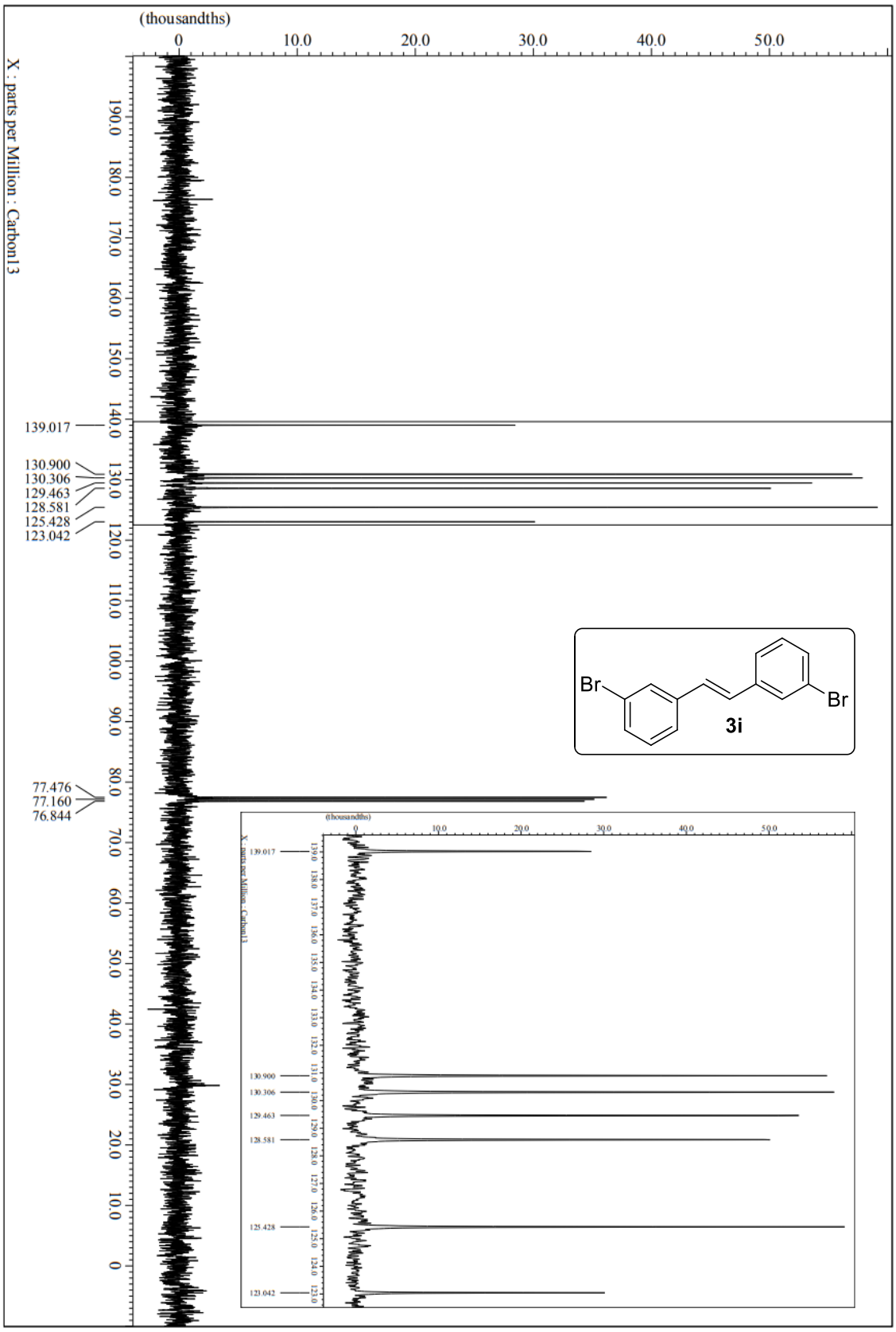
^{1}H NMR (400 MHz) spectrum of **3h** ($CDCl_3$, rt)



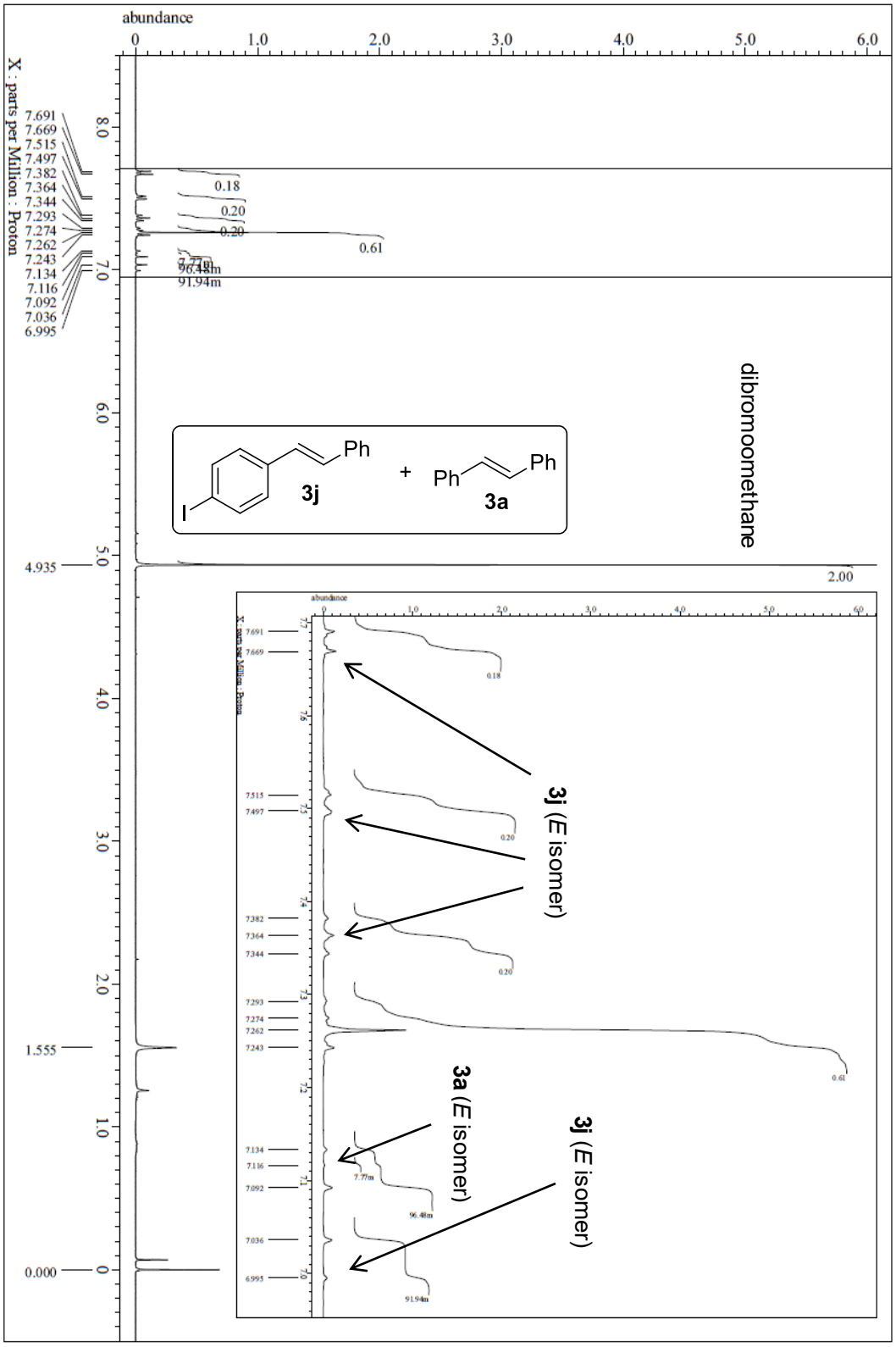
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3h** ($CDCl_3$, rt)



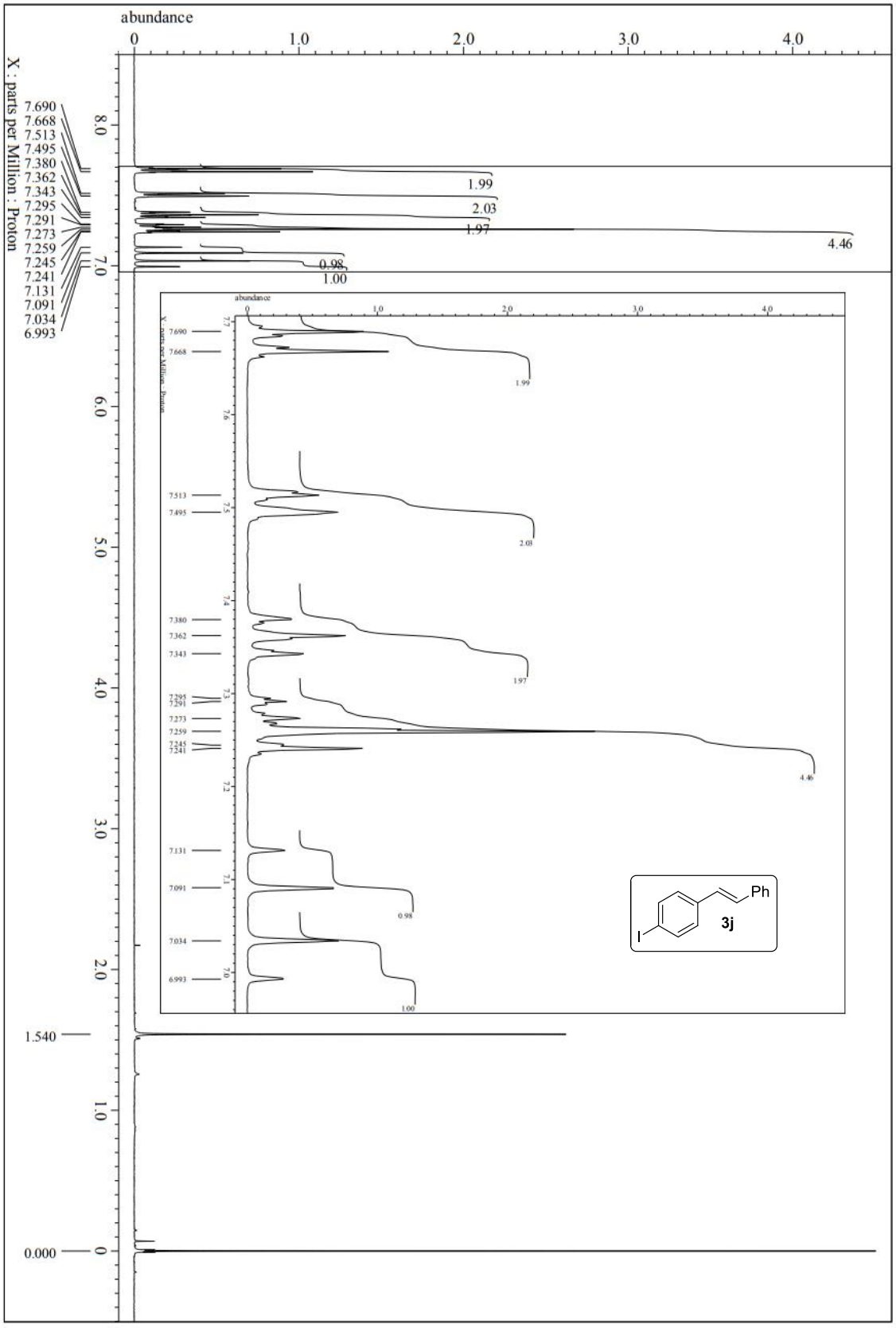
^{1}H NMR (400 MHz) spectrum of **3i** ($CDCl_3$, rt)



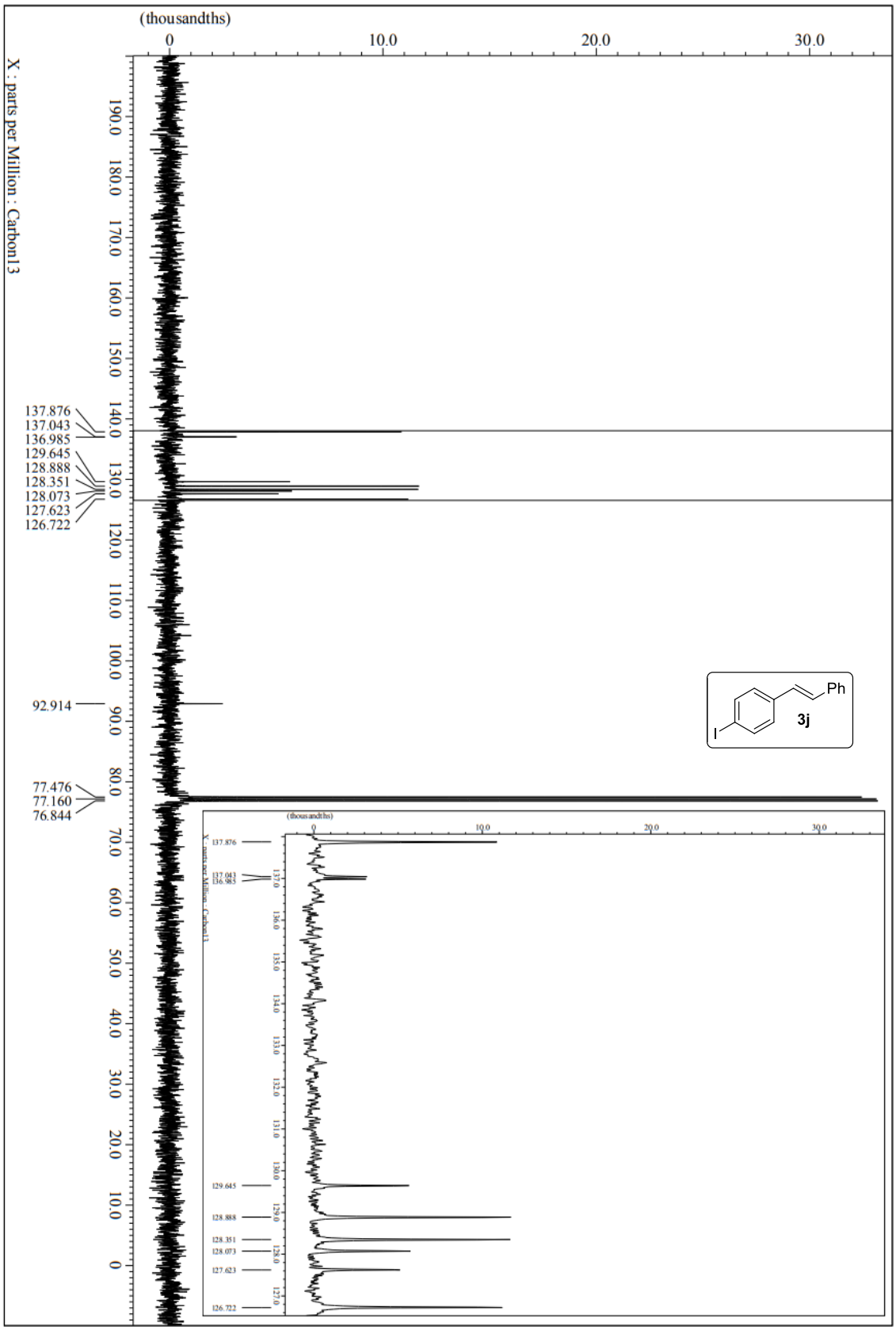
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3i** ($CDCl_3$, rt)



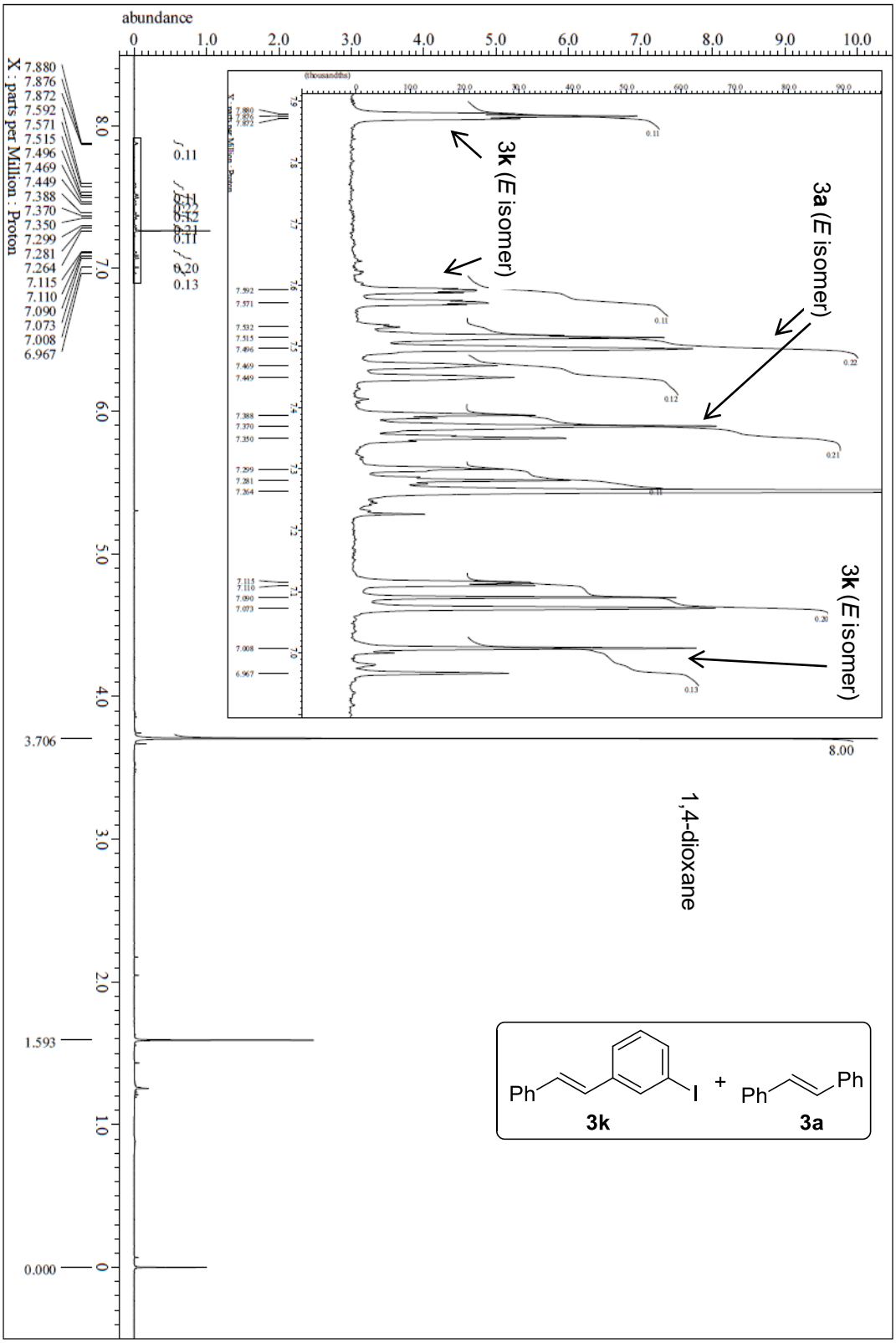
^{1}H NMR (400 MHz) spectrum to estimate the NMR yield of **3j** ($CDCl_3$, rt, internal standaed: dibromomethane)



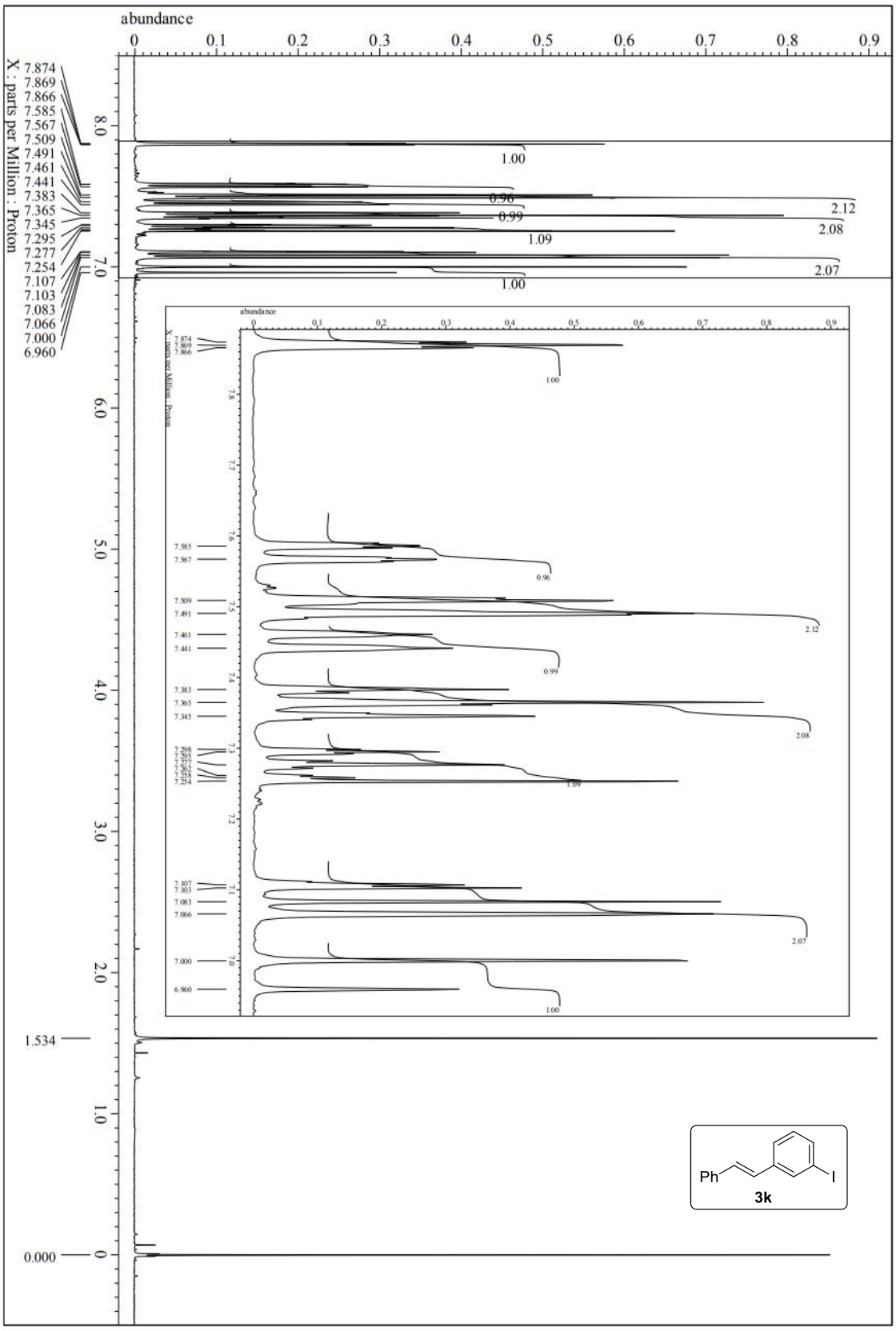
^{1}H NMR (400 MHz) spectrum of **3j** ($CDCl_3$, rt) *authentic sample*



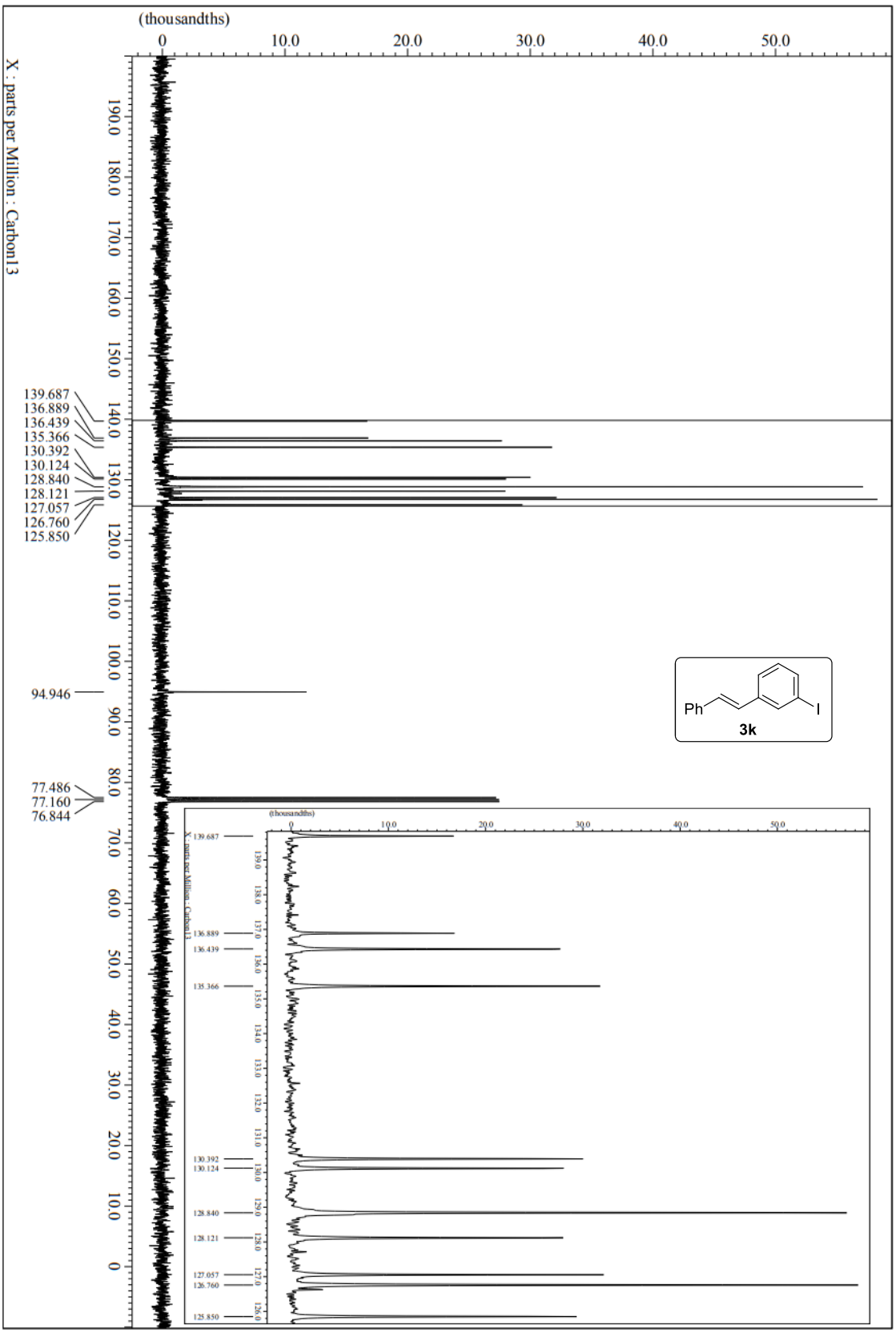
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3j** ($CDCl_3$, rt) *authentic sample*



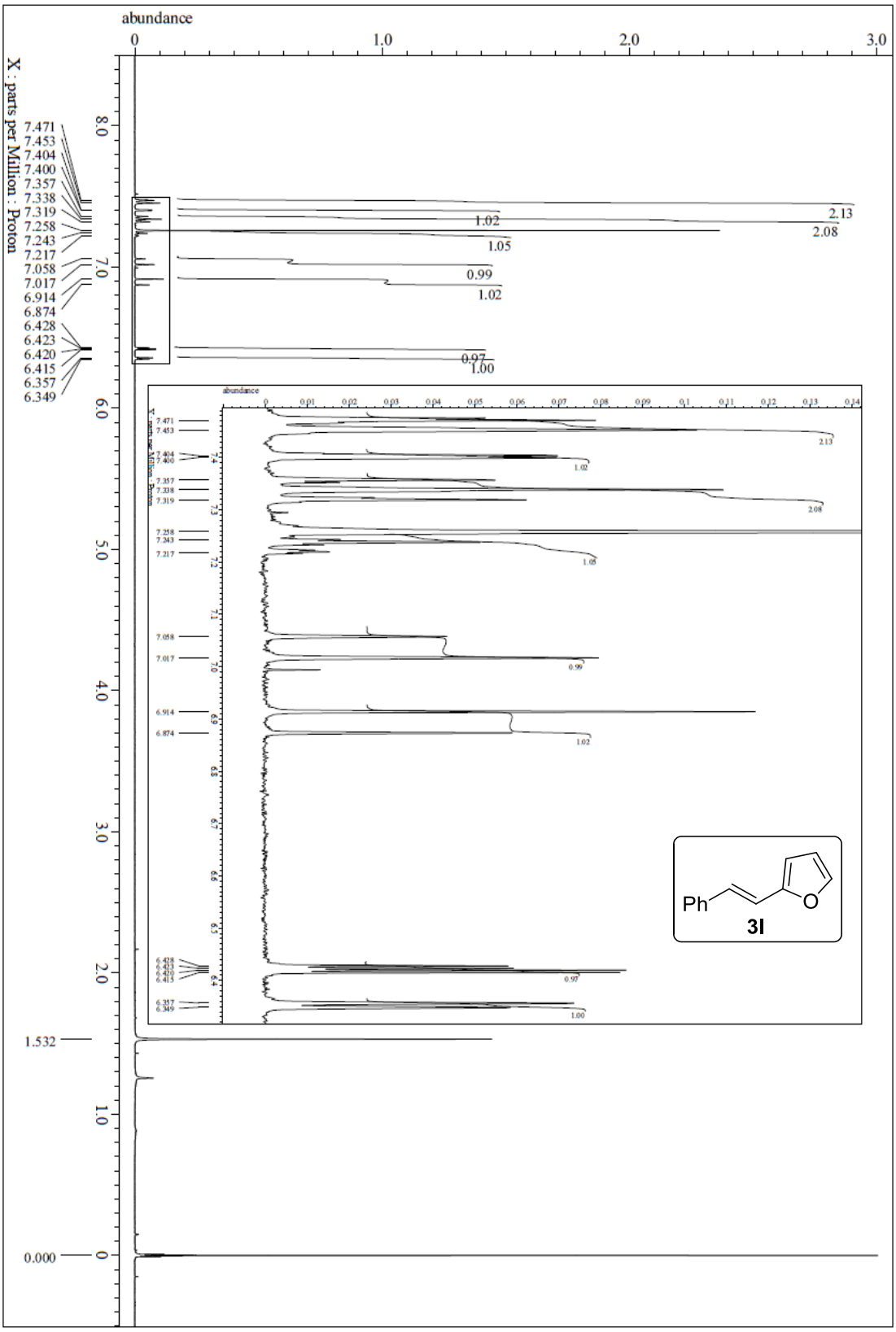
^{1}H NMR (400 MHz) spectrum to estimate the NMR yield of **3k** ($CDCl_3$, rt, internal standard: 1,4-dioxane)



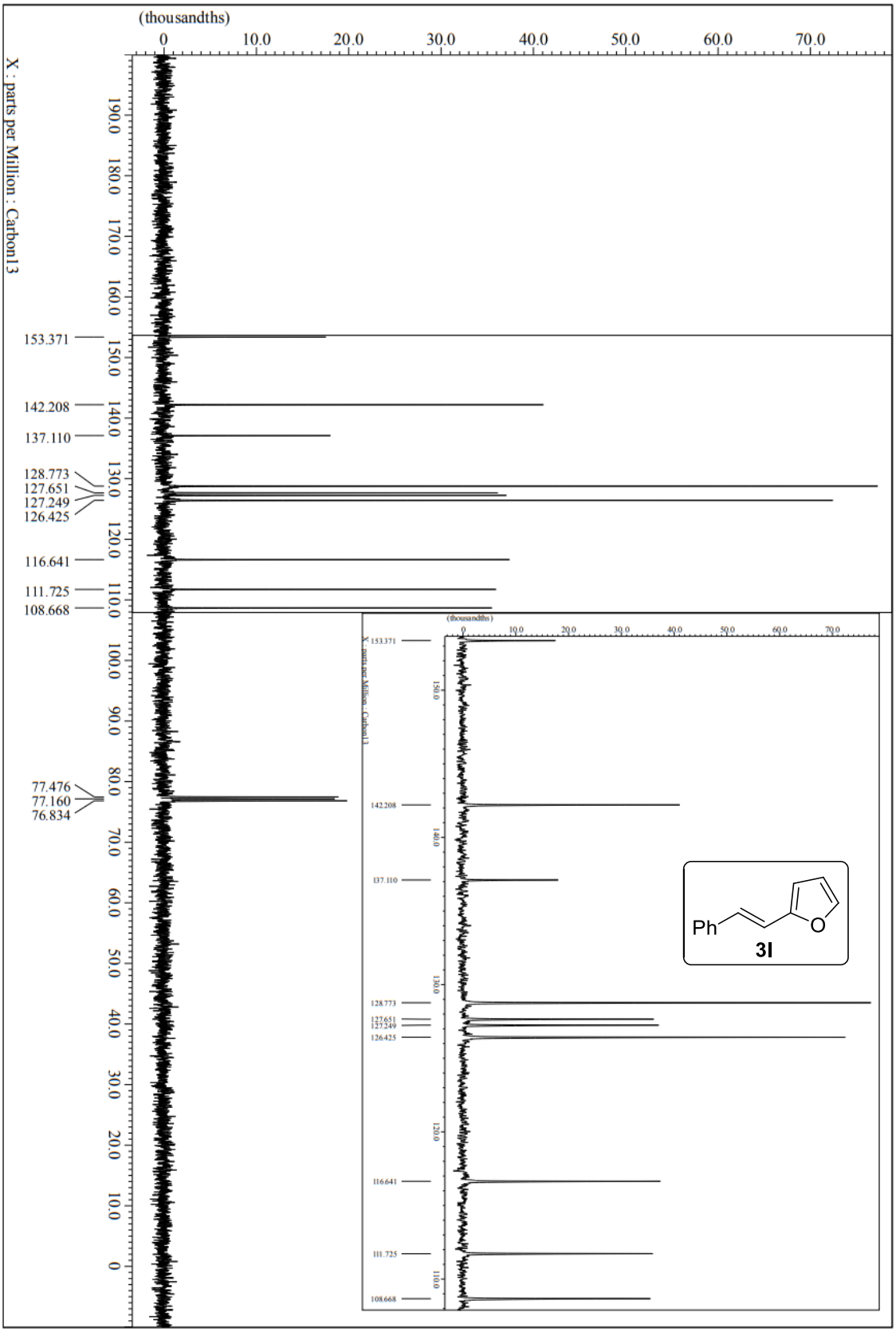
^{1}H NMR (400 MHz) spectrum of **3k** ($CDCl_3$, rt) *authentic sample*



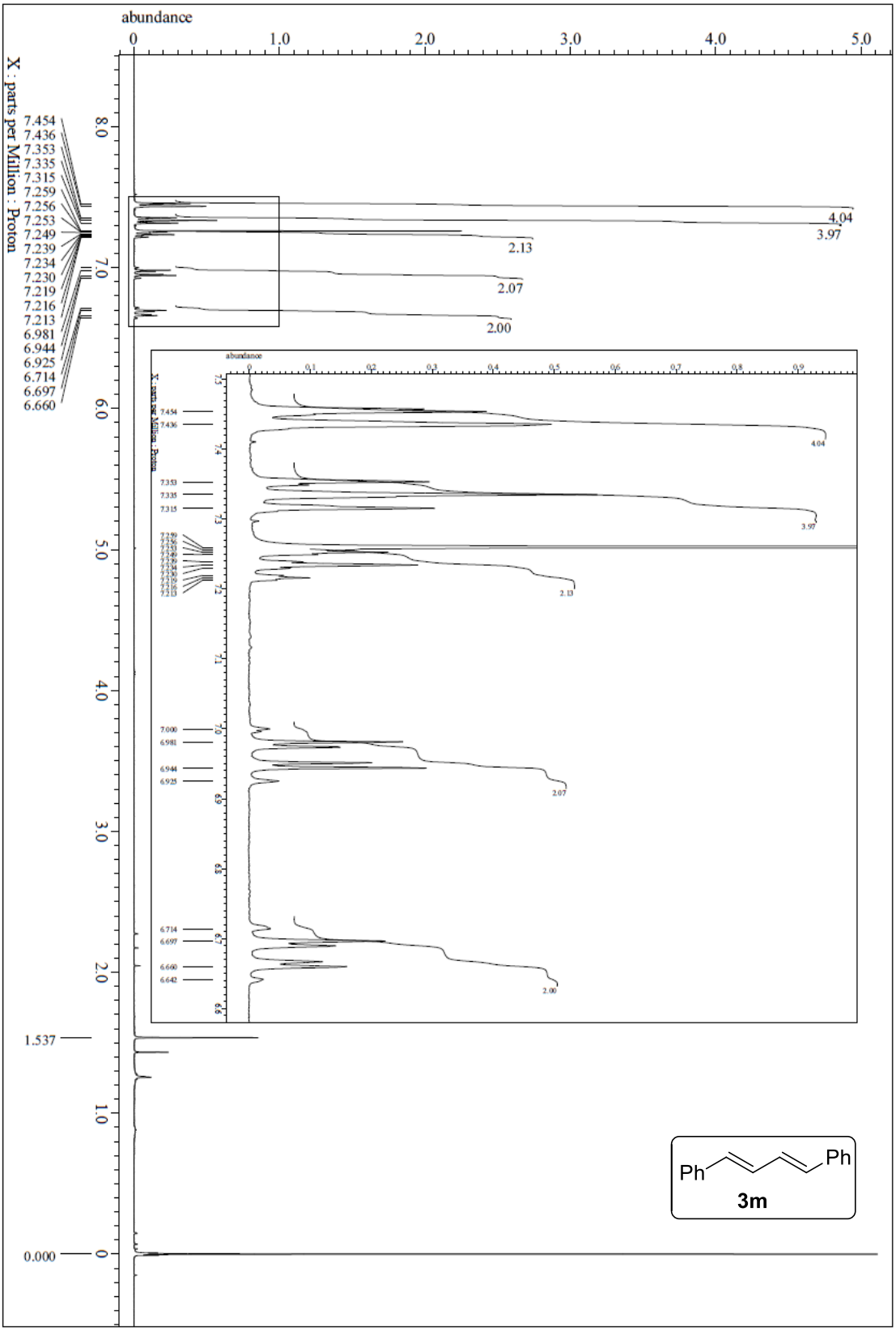
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3k** ($CDCl_3$, rt) *authentic sample*



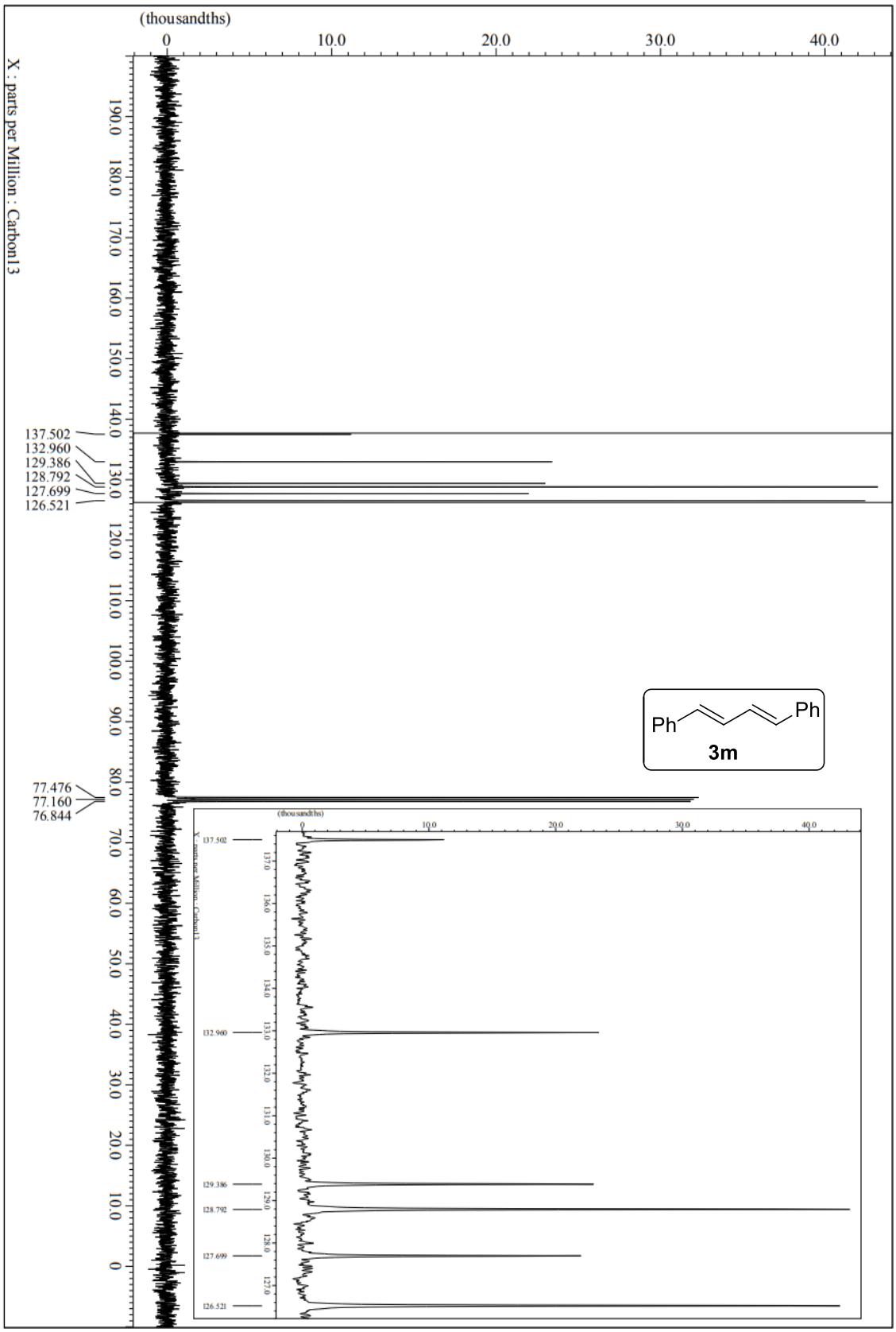
^{1}H NMR (400 MHz) spectrum of **3l** ($CDCl_3$, rt)



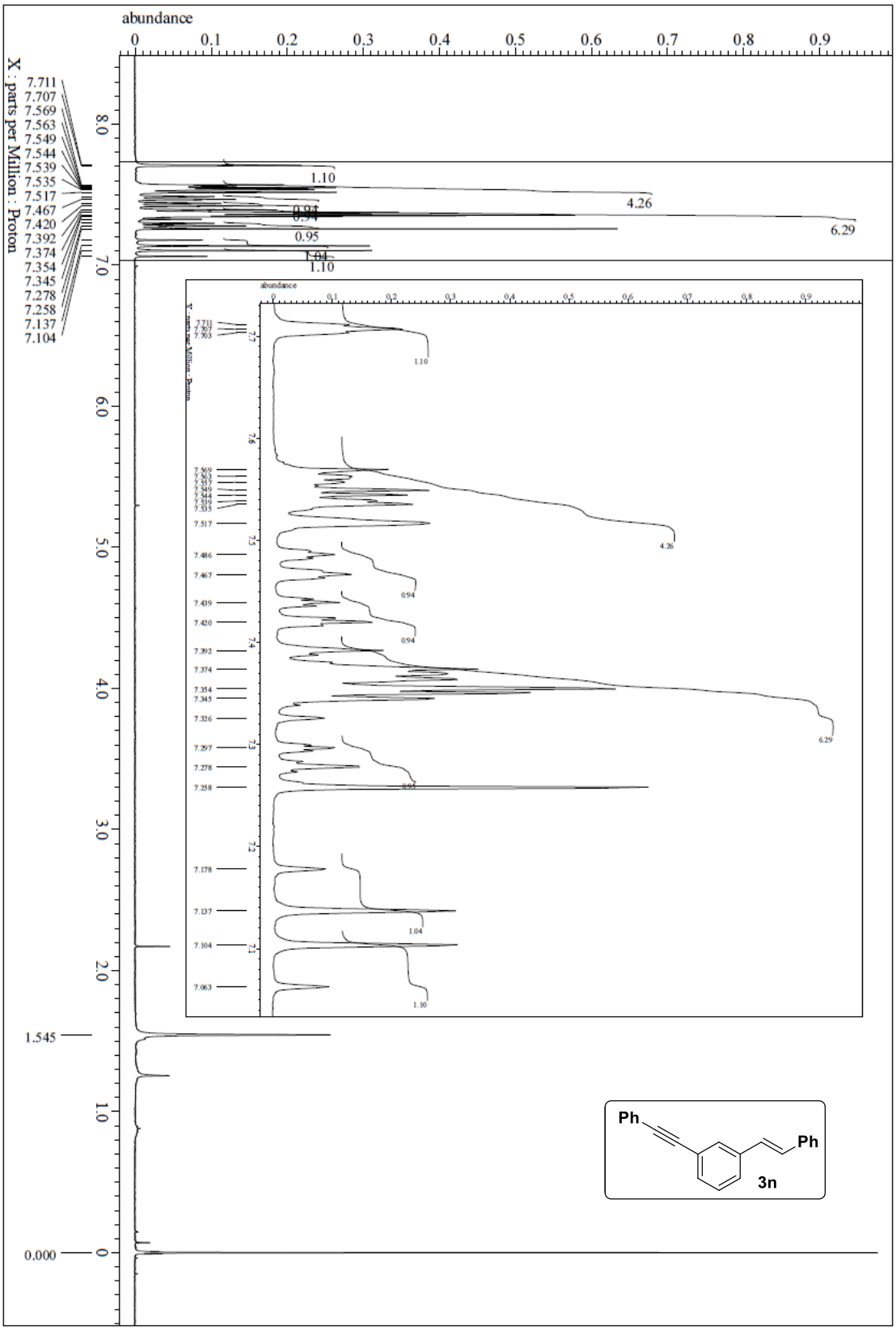
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3l** ($CDCl_3$, rt)



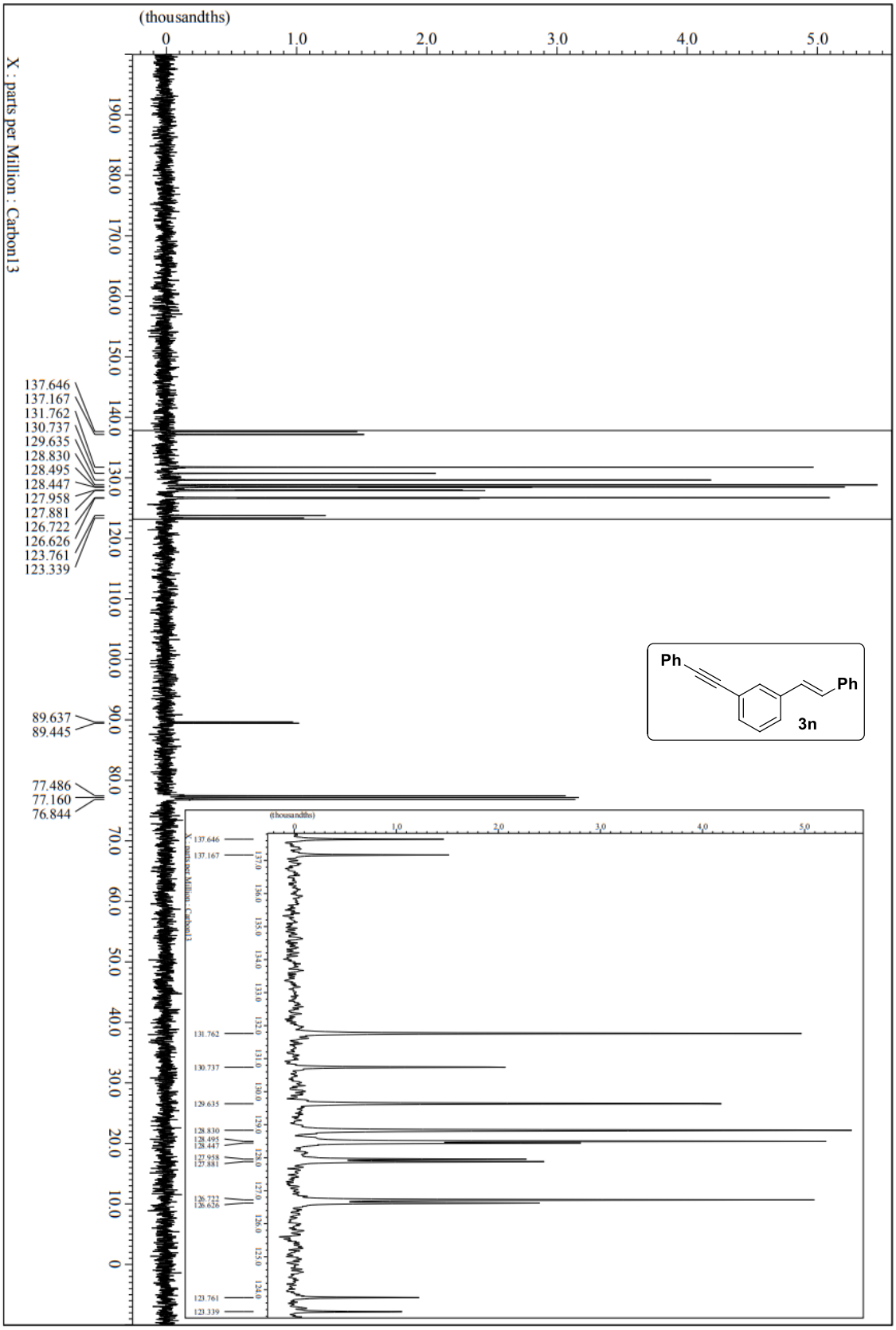
^{1}H NMR (400 MHz) spectrum of **3m** ($CDCl_3$, rt)



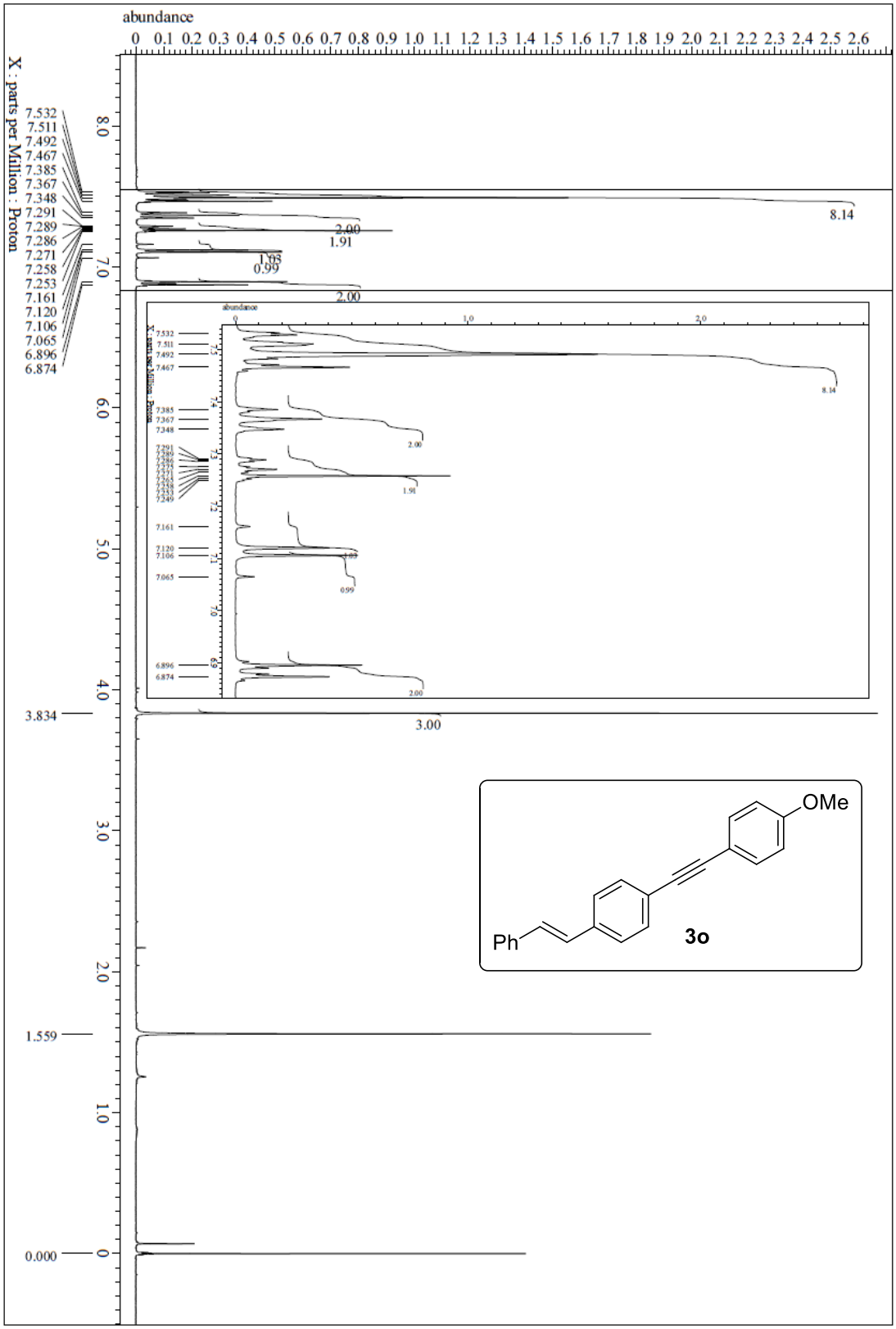
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3m** ($CDCl_3$, rt)



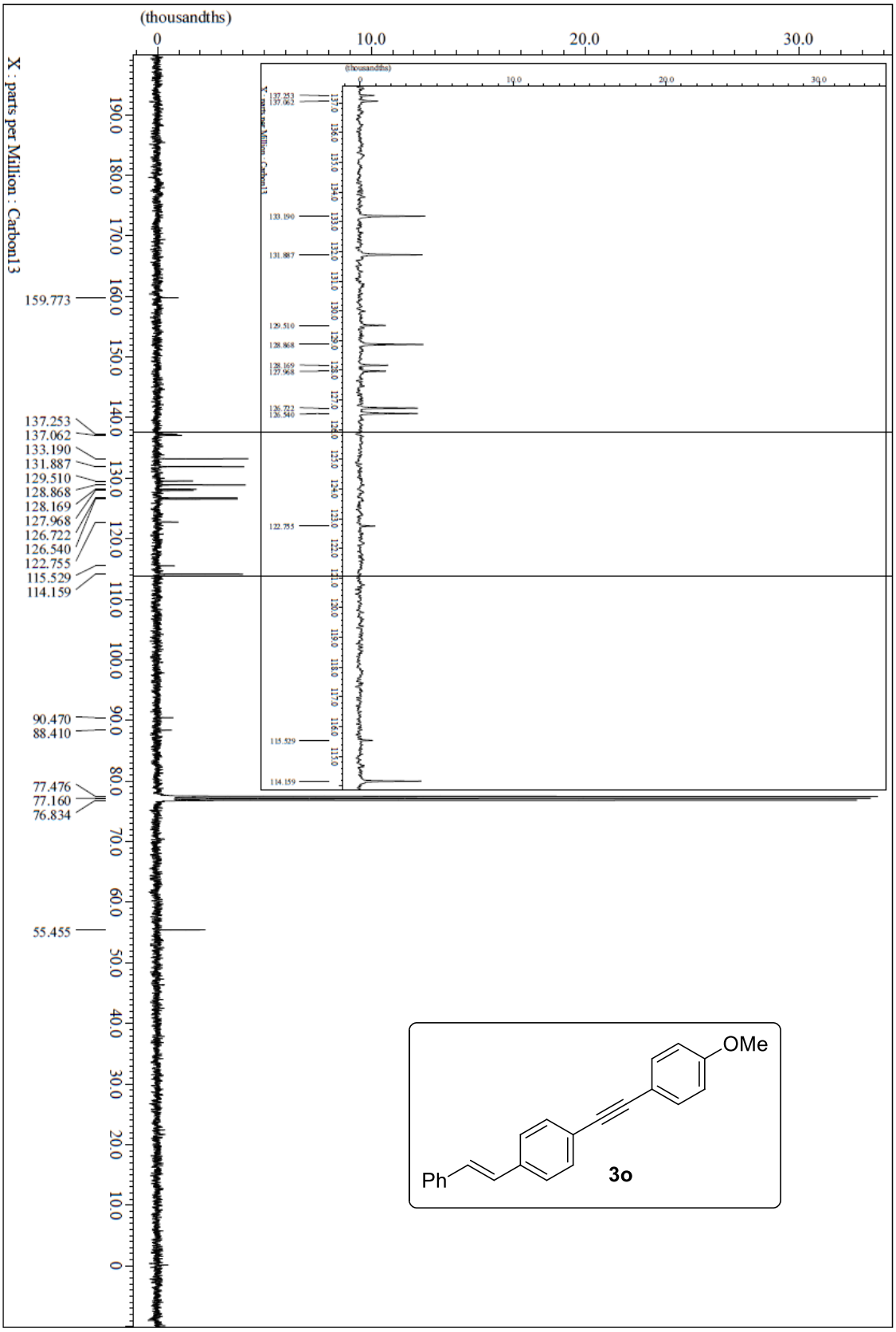
^{1}H NMR (400 MHz) spectrum of **3n** ($CDCl_3$, rt)



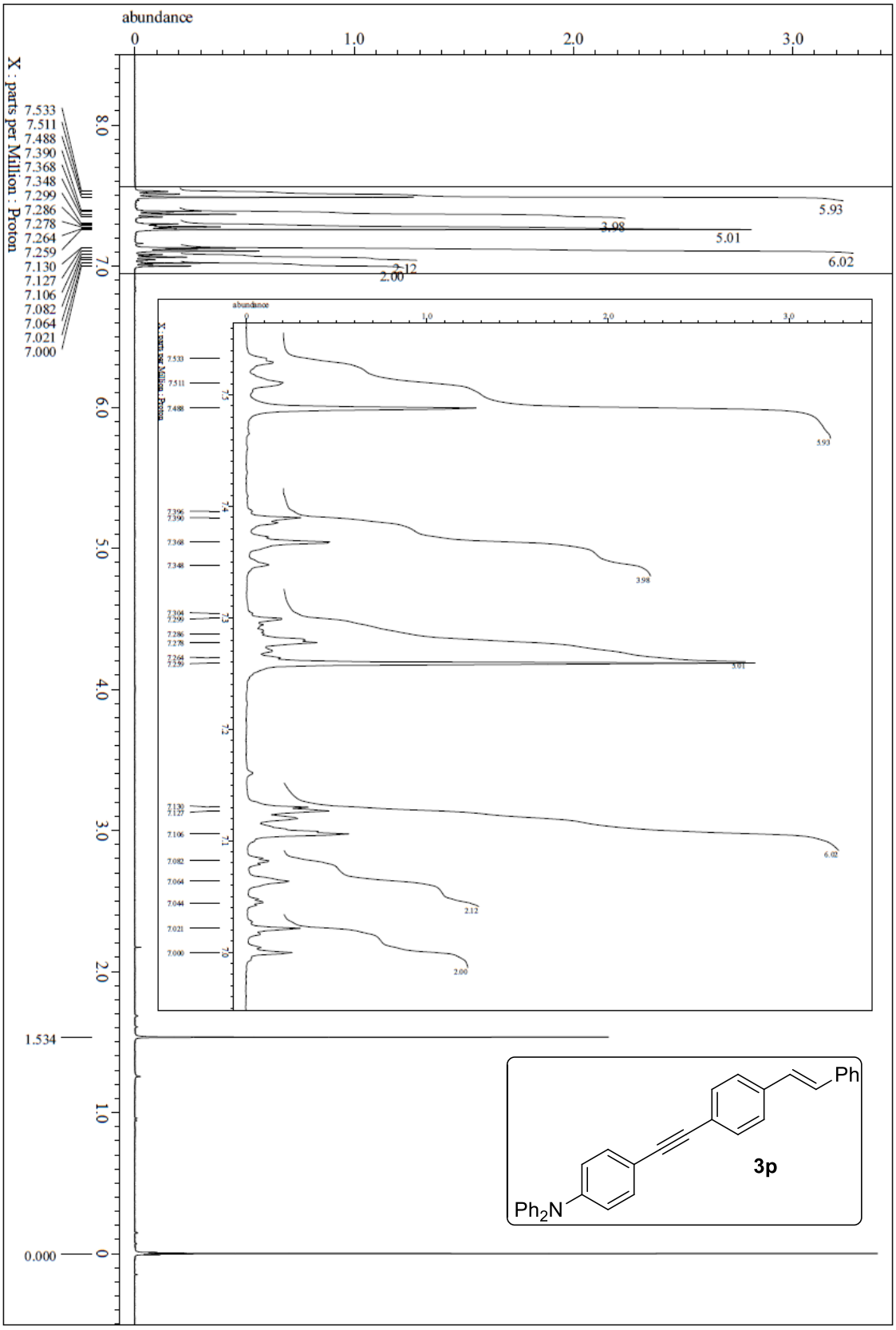
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3n** ($CDCl_3$, rt)



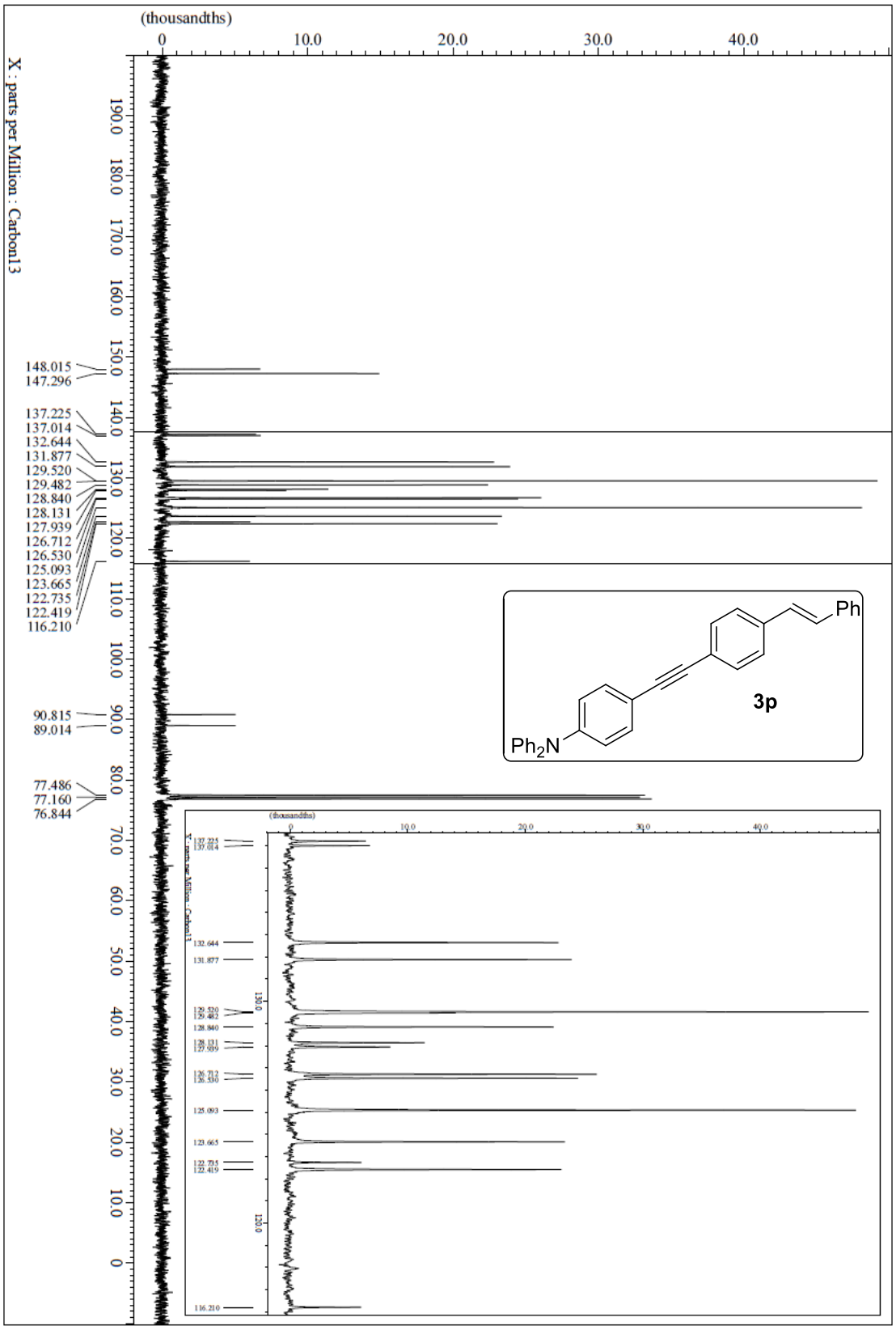
^{1}H NMR (400 MHz)NMR spectrum of **3o** ($CDCl_3$, rt)



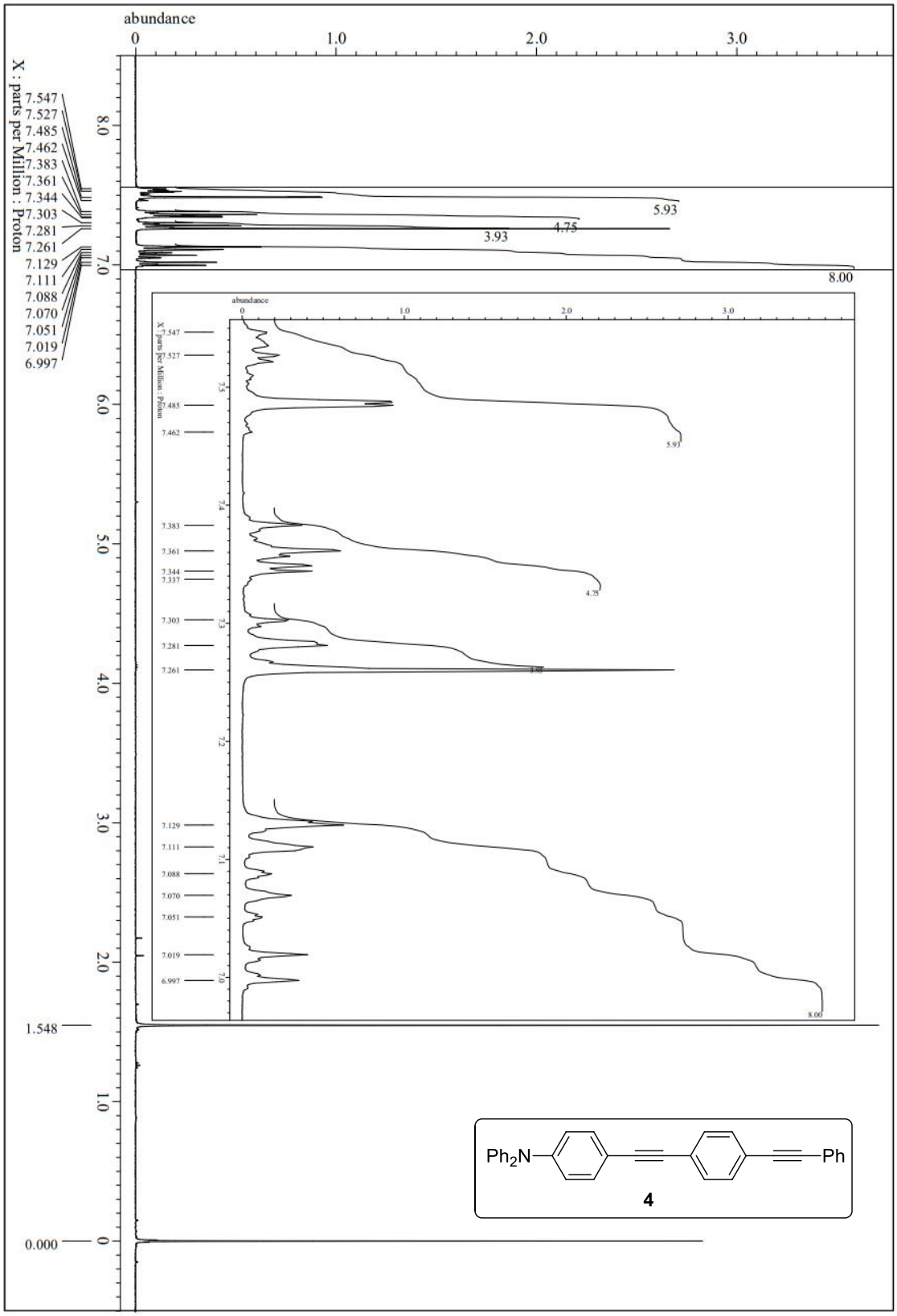
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3o** ($CDCl_3$, rt)



^{1}H NMR (400 MHz) spectrum of **3p** ($CDCl_3$, rt)



$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3p** ($CDCl_3$, rt)



^{1}H NMR (400 MHz) spectrum of **4** ($CDCl_3$, rt)