Chiral Aryl Iodide Catalysts for the Enantioselective Synthesis of *p*-Quinols

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Supporting Information

Materials and Methods

Unless otherwise stated, reactions were performed in flame- or oven-dried glassware under an argon or nitrogen atmosphere using anhydrous solvents. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Methanol was dried over 3Å molecular sieves. 3-Chloroperoxybenzoic acid (≤ 77%) was purchased from Aldrich. Labeled ^{18}O water was obtained from Isoflex USA (98.03% enrichment). Unless otherwise stated, reactions were monitored using thin-layer chromatography (TLC) using plates precoated with silica gel XHL w/ UV254 (250 mm) and visualized by UV light or $KMnO_4$, phosphomolybdic acid, or anisaldehyde stains, followed by heating. Silica gel (particle size 32–63 mm) was used for flash column chromatography. ^1H and ^{13}C NMR spectra are reported relative to the residual solvent peak (δ 7.26 and δ 77.2 for ^1H and ^{13}C in $CDCl_3$, δ 3.31 and δ 49.0 for ^1H and ^{13}C in CD_3OD, respectively), or tetramethylsilane (δ 0.00 for ^1H) when the residual solvent peak is obscured. Data for ^1H NMR spectra are reported as follows: chemical shift (ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity is described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, app = apparent. IR samples were prepared on NaCl plates either neat or by evaporation from $CHCl_3$ or CH_2Cl_2.

Computational Methods

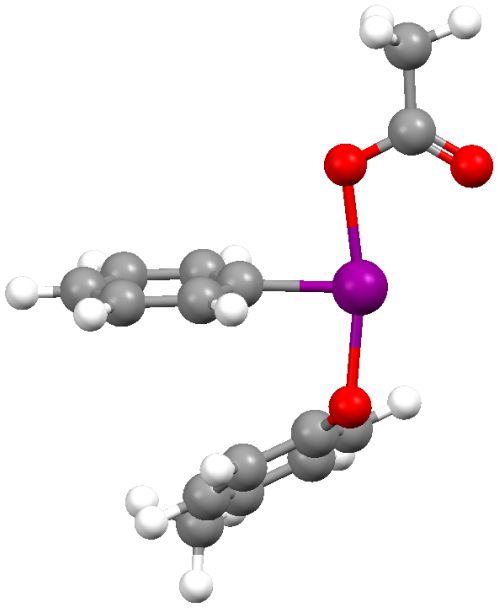
All geometries were fully optimized at the M06-2X level[1] of density functional theory. A mixed basis set comprised of 6–31G(d)[2] for C, H and O and the Stuttgart/Dresden basis set and pseudopotential (SDD)[3] for iodine. An ultrafine grid density was used for numerical integration.[4] Optimizations were performed with no frozen coordinates. The effects of CH_2Cl_2 (a lower polarity solvent that is commonly used in oxidative dearomatization reactions) and CH_3CN (a polar, non-nucleophilic solvent) solvation were included in the geometry optimizations using the SMD solvation model.[5] Energy minima and transition states were identified though frequency analysis. All calculations made use of the *Gaussian* 09 Rev A.02 suite[6] of electronic structure programs. The Gibbs energies are included below with the atomic coordinates.

(1) Y. Zhao, and D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215.
(2) W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
(3) A. Bergner, M. Dolg, W. Küchle, H. Stoll, and H. Preuß, *Mol. Phys.* 1993, **80**, 1431.
(4) S. E. Wheeler, and K. N. Houk, *J. Chem. Theory Comput.* 2010, **6**, 395.
(5) A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378.
(6) 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, T. Keith, 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. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, Rev A.02; Gaussian, Inc.: Wallingford, CT, 2010.

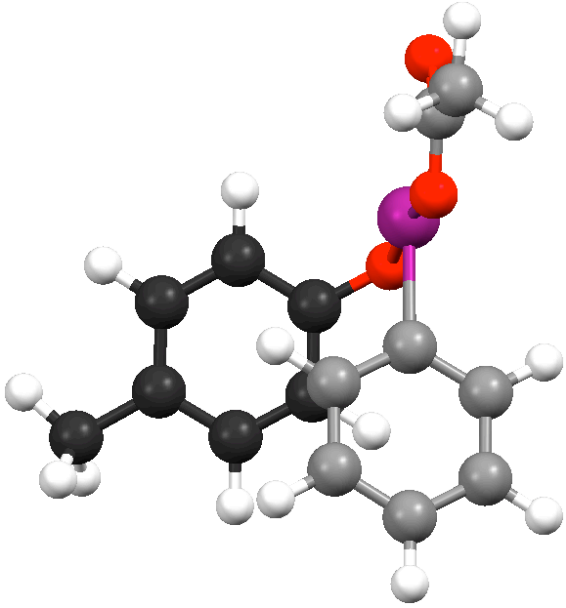
Final structures, coordinates, and energies for the calculated structure of 7.

The final optimized geometry of each species is given below, along with the following:
(i) Number of imaginary frequencies (frequency if present)
(ii) Free energy (G) at 298.15 K and 1 atm. All energies are quoted in Hartrees.

Compound 7 in CH_2Cl_2



(side view)



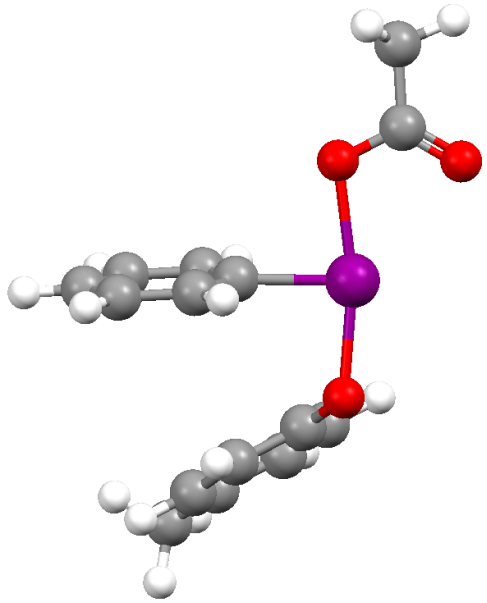
(top view, phenol is shaded darker)

I	-1.195000	-0.604700	-0.499300
C	-0.343400	1.292300	-0.093900
C	0.903300	3.701800	0.363800
C	-0.416000	2.275400	-1.073600
C	0.339000	1.471300	1.103900
C	0.965400	2.696900	1.326800
C	0.216400	3.493800	-0.831100
H	-0.948300	2.099900	-2.002700
H	0.391900	0.677700	1.842100
H	1.506400	2.858300	2.253600
H	0.169900	4.277300	-1.580700
H	1.396800	4.651700	0.543200
O	0.584300	-1.033700	-1.562500
C	1.737300	-1.008900	-0.847700
C	4.166500	-0.930700	0.590600
C	2.030300	-1.990500	0.105000
C	2.664700	0.017500	-1.071600
C	3.861300	0.046400	-0.364600
C	3.230000	-1.943900	0.812000
H	1.310800	-2.785900	0.283700
H	2.425500	0.786600	-1.800800

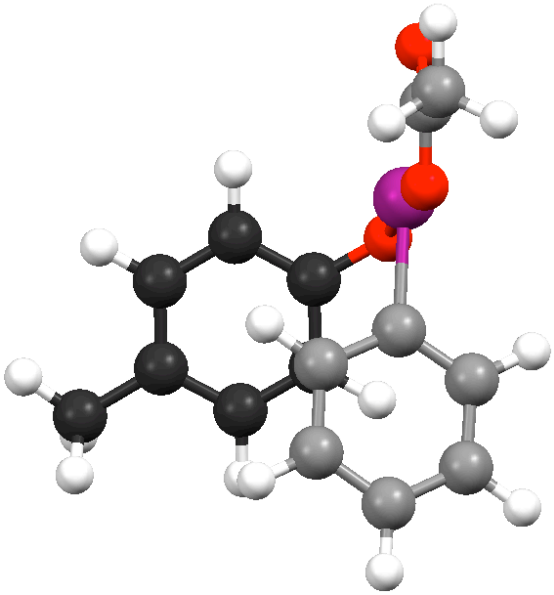
H	4.572300	0.848500	-0.550300
H	3.443800	-2.714900	1.548500
C	5.471600	-0.887800	1.344000
H	6.320500	-1.075300	0.676700
H	5.496200	-1.642400	2.135000
H	5.633500	0.092300	1.805100
O	-2.876400	0.245700	0.608500
C	-3.826000	-0.646600	0.738900
O	-3.736100	-1.782100	0.282700
C	-5.032700	-0.153300	1.499400
H	-5.430400	0.743000	1.016200
H	-4.735300	0.120800	2.515500
H	-5.796600	-0.930100	1.533400

*** 0 imaginary frequencies ***
G = -817.049054

Compound 7 in CH_3CN



(side view)



(top view, phenol is shaded darker)

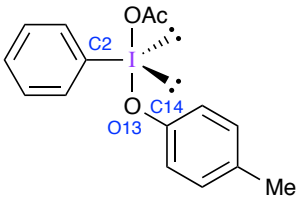
I	-1.266200	-0.614100	-0.473400
C	-0.226600	1.198400	-0.133400
C	1.303200	3.453300	0.241800
C	-0.122500	2.110800	-1.175800
C	0.413600	1.371600	1.088600
C	1.184100	2.519300	1.269800
C	0.651900	3.253000	-0.974000
H	-0.625500	1.938600	-2.121900
H	0.325100	0.630000	1.875800
H	1.696200	2.674600	2.213900
H	0.745400	3.982000	-1.772600
H	1.908600	4.342000	0.388900
O	0.486800	-1.273500	-1.475900
C	1.648700	-1.161300	-0.786600

C	4.085600	-0.879200	0.616300
C	1.911200	-1.939700	0.345800
C	2.615000	-0.239600	-1.213700
C	3.813500	-0.109000	-0.521600
C	3.114800	-1.793500	1.033700
H	1.162100	-2.651300	0.685000
H	2.403500	0.371000	-2.087000
H	4.552000	0.611900	-0.866200
H	3.303400	-2.405300	1.912700
C	5.385600	-0.715300	1.361800
H	6.244300	-0.918300	0.712600
H	5.439800	-1.396300	2.215500
H	5.500500	0.307200	1.738200
O	-2.871100	0.449600	0.558300
C	-3.903000	-0.339100	0.727300
O	-3.922800	-1.500100	0.330900
C	-5.057400	0.307600	1.452500
H	-5.386100	1.192900	0.901400
H	-4.729200	0.634800	2.443000
H	-5.882100	-0.398600	1.549300

*** 0 imaginary frequencies ***
G = -817.049128

Potential energy scan of compound 7

A relaxed scan of the C2–I–O13–C14 dihedral in **7** was performed to confirm that the originally obtained structures were indeed minima. Scans were performed in the gas phase and with CH_3CN and CH_2Cl_2. The scan involved stepping the dihedral angle in 30º increments starting at 0º. The plot for each scan is shown in Figures S1 and S2. In both cases, the global minimum corresponds to the originally obtained structures, or their enantiomer.



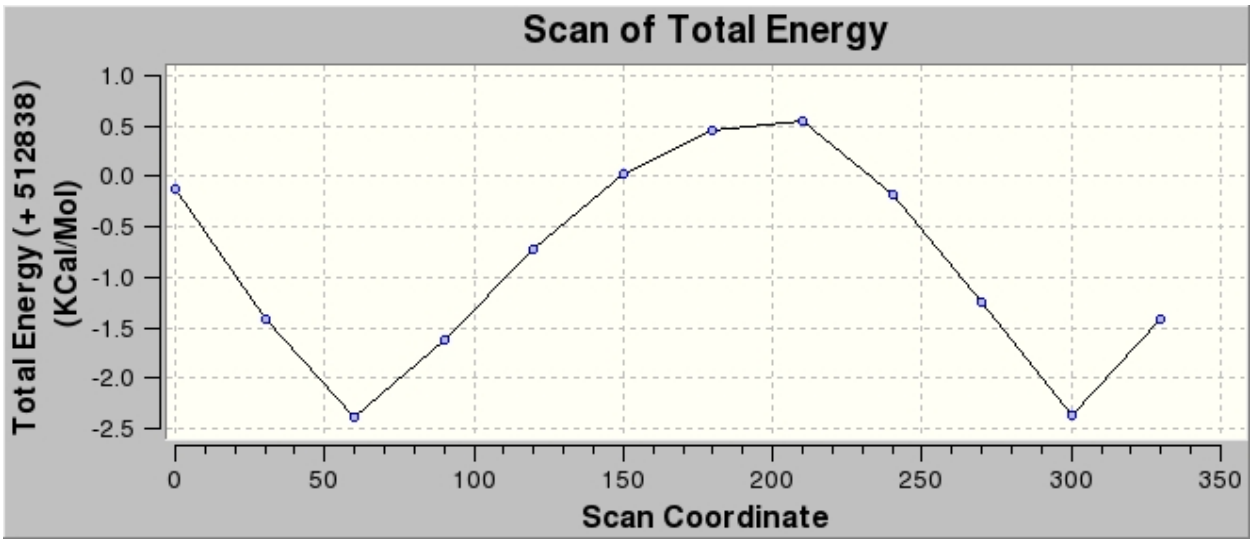


Figure S1. Relaxed scan of C2–I–O13–C14 dihedral with CH_3CN solvation.

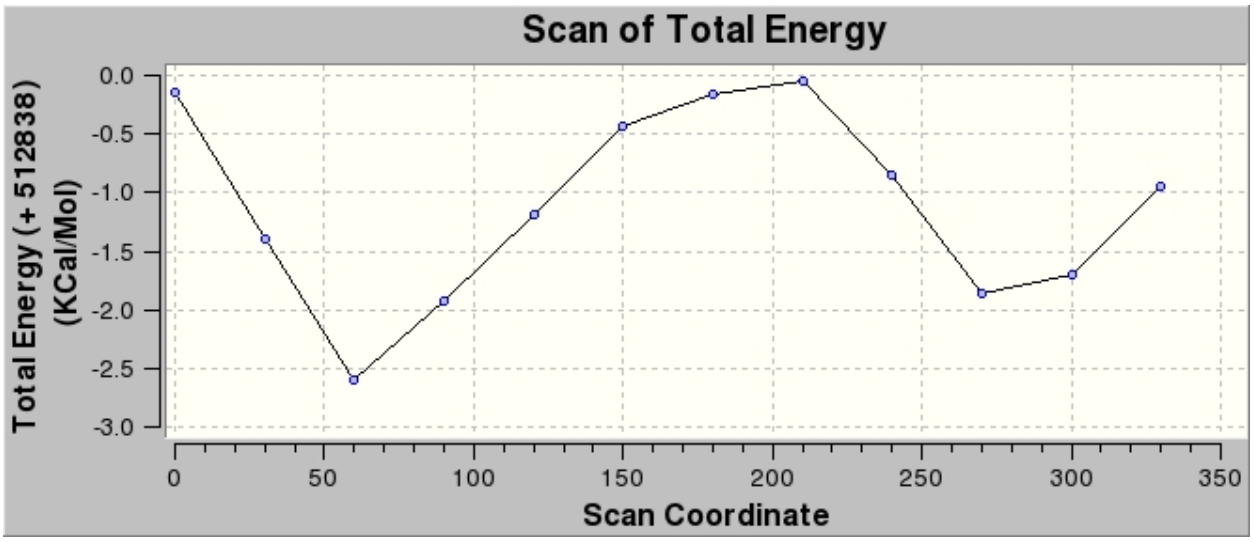
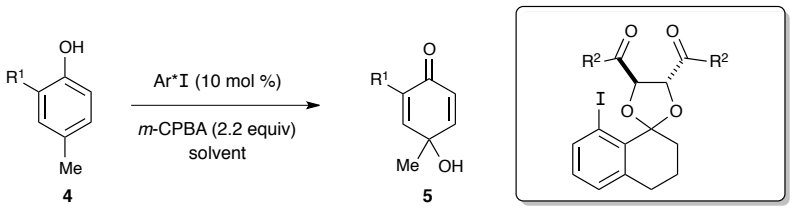


Figure S2. Relaxed scan of C2–I–O13–C14 dihedral with CH_2Cl_2 solvation.

Aryl Iodide Catalyst Scope

Table S1: Full Results of Iodotetralone Catalysts



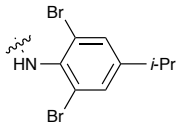
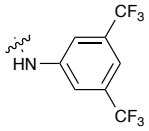
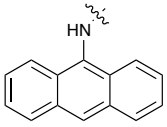
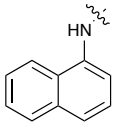
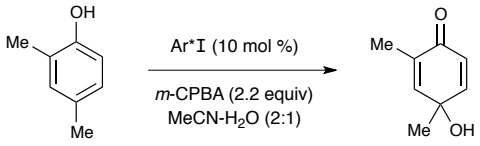
entry	R^1	R^2		temp	MeCN:H_2O	time (h)	yield (%)	er
1	Me	OH	(**8a**)	rt	2:1	1.5	36	60:40
2	Me	morpholine	(**8b**)	rt	3:1	1.5	33	59:41
3	Me	NHPh	(**8c**)	rt	3:1	1.5	19	60:40
4	Me	NHBn	(**8d**)	rt	3:1	1.5	34	61:39
5	Me	NHMes	(**8e**)	rt	2:1	1.5	47	63:37
6	Br	NHPh	(**8c**)	rt	9:1	16	48	40:60
7	Br	NHBn	(**8d**)	rt	2:1	1.5	20	40:60
8	Br	NHMes	(**8e**)	rt	2:1	0.3	45	35:65
9	Br		(**8f**)	rt	9:1	16	80	37:63
10	TMS			rt	9:1	16	94	28:72
11	Br		(**8g**)	rt	9:1	16	75	57:43
12	Br		(**8h**)	rt	9:1	16	70	37:63
13	Br		(**8i**)	rt	9:1	16	52	40:60

Table S2: Other Aryl Iodide Catalysts Results



4a **5a**

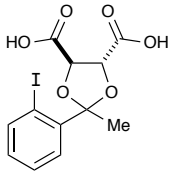
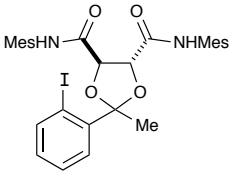
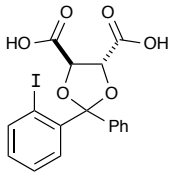
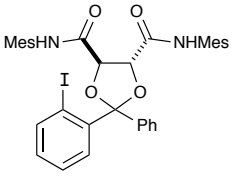
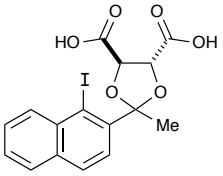
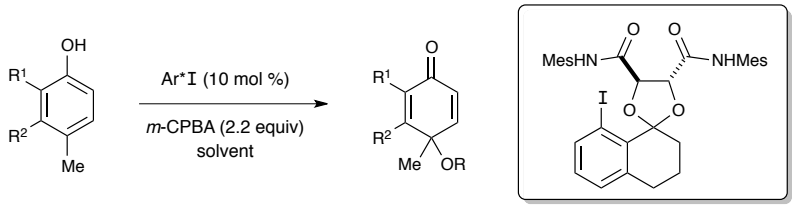
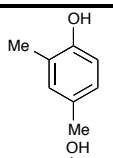
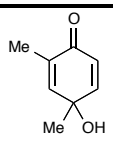
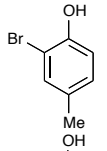
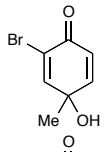
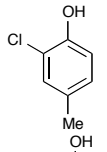
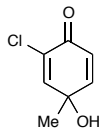
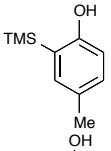
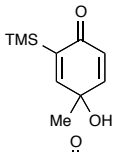
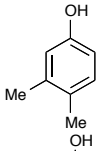
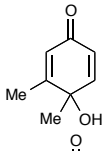
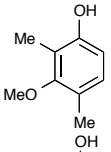
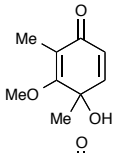
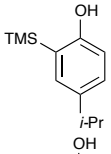
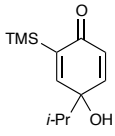
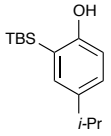
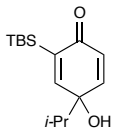
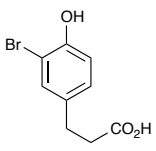
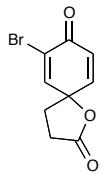
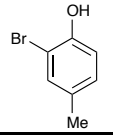
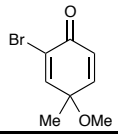
entry	Ar*I		temp (°C)	time (h)	yield (%)	er
1		(**S1**)	rt	1	27	44:56
2		(**S2**)	rt	1.5	29	46:54
3		(**S3**)	rt	1	28	47:53
4		(**S4**)	rt	1	35	46:54
5		(**S5**)	rt	1	39	45:55

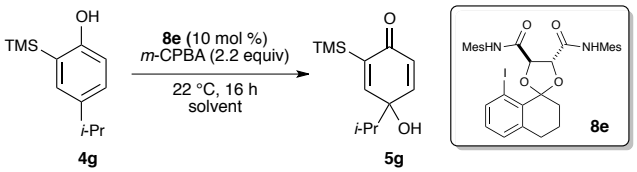
Table S3: Full Results of Substrate Scope



entry[a]	substrate	product	temp	solvent MeCN:H_2O	time (h)	yield (%)	er
1			rt rt	2:1 9:1	1.5 16	47 52	38:62 38:62
2			0 °C rt rt	2:1 2:1 9:1	3 0.3 16	21 45 52	32:68 35:65 35:65
3			0 °C rt	2:1 9:1	1 16	76 65	35:65 35:65
4			0 °C 0 °C rt	2:1 9:1 9:1	0.5 7 16	21 58 79	24:76[b] 21:79 25:75
5			0 °C rt	2:1 9:1	0.5 16	23 43	47:53[b] 50:50
6			0 °C	2:1	1	20	33:67
7			rt	9:1	16	53	67:33
8			rt	9:1	16	41	38:62
9			0 °C	1:0	1	27	40:60[c]
10			0 °C	MeOH	3	60	35:65

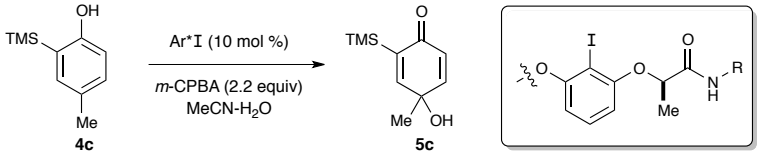
[a] all reactions carried out on a 0.17 mmol scale with 2.2 equiv of *m*-CPBA, 10 mol % catalyst.
[b] quinol product was converted to the *t*-butyl malonate derivative in order for separation on the HPLC
[c] spirolactone product was transesterified with aqueous MeOH–$NaHCO_3$ in order for separation on the HPLC

Table S4: Solvent Screen Results



entry	solvent (9:1)	yield (%)	er
1	MeCN-H_2O	53	67:33
2	THF-H_2O	33	62:38
3	CF_3CH_2OH-H_2O	<10	nd
4	$MeNO_2$-H_2O	62	53:47
5	acetone-H_2O	66	68:32

Table S5: Ishihara Catalysts with Phenol 4c



entry	R	temp	MeCN:H_2O	time [h]	yield [%]	er
1	3,5-dimethyl	0 °C	2:1	2	36	61:39
2	mesityl	rt	9:1	16	57	67:33

Experimental Procedures

Synthesis of Aryl Iodide Catalysts

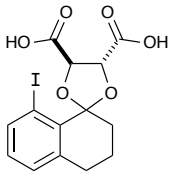
General Procedure A: Ketalization with (+)-Dimethyl L-tartrate

The aryl iodoketone (1 equiv) was dissolved in methanol (0.65 M) and treated with trimethyl orthoformate (5 equiv) followed by *p*-toluenesulfonic acid monohydrate (10 mol %). The mixture was refluxed overnight and then concentrated in vacuo. In the same flask, the residue was dissolved in toluene (0.2 M) and (+)-dimethyl L-tartrate (2.1 equiv) was added, followed by $BF_3 \cdot OEt_2$ (5 mol %). The mixture was heated and the methanol removed by azeotrope. After 3 h, the reaction was cooled to r.t., quenched with saturated aq. $NaHCO_3$, and extracted with EtOAc (3×). The combined organic layers were washed with brine and then concentrated under reduced pressure to give a viscous oil. The oil was treated with a 1:1 mixture of MeOH and 2 N NaOH for 1 hr, and then transferred to a separatory funnel. The aqueous layer was washed with ether, acidified with 10% aq. HCl, and then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure.

General Procedure B: Amide Synthesis

The aryl iodotartrate was dissolved in DCM (0.1 M) and treated with oxalyl chloride (3.5 equiv) and DMF (10 μL) at room temperature for 3 h. The resulting dark solution was concentrated in vacuo and re-dissolved in DCM (0.2 M). Into the same flask was added the respective aniline or amine (4 equiv) and pyridine (4 equiv). The mixture was stirred at r.t. overnight, then quenched with 10% aq. HCl and extracted with DCM. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (hexanes/EtOAc).

(4*R*,5*R*)-8'-iodo-3',4'-dihydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxylic acid (8a).



The iodo tetralone[7] (902 mg, 3.31 mmol) was dissolved in dry methanol (5 mL, 0.65 M) and to this was added trimethyl orthoformate (2.5 mL, 23 mmol), which was followed by *p*-toluenesulfonic acid monohydrate (2 mg). The reaction was refluxed overnight, concentrated in vacuo, and carried on immediately without isolation. Into the same flask was added dry benzene (4 mL), 3 Å molecular sieves, (+)-dimethyl L-tartrate (890 mg, 4.97 mmol), and scandium triflate (2 mg). The resulting mixture was stirred, heated to 90 °C, and left open to the atmosphere for 3 h. After such time, the reaction mixture was concentrated in vacuo and the resulting residue was dissolved in EtOAc, transferred to a separatory funnel and washed with saturated aq. $NaHCO_3$, H_2O, and brine. It was then dried (Na_2SO_4), filtered, and concentrated under reduced pressure, affording a viscous, colorless oil. This was treated with MeOH (2 mL) and 2 N NaOH (2 mL) for 1.5 h. After such time, the mixture was washed with EtOAc and the aqueous layer acidified with 10% aq. HCl. The product was extracted with EtOAc, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give a reddish orange solid (844 mg, 63% yield). No further purification was performed.

(7) P. Nguyen, E. Corpuz, T. M. Heidelbaugh, K. Chow, and M. E. Garst, *J. Org. Chem.* 2003, **68**, 10195.

IR (thin film) 3052, 2942, 2624, 1728, 1437, 1165, 1096 cm^{-1}

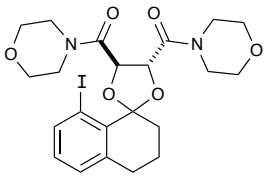
^{1}H NMR (300 MHz, CD_3OD): δ 7.85 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.16 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 5.19 (d, *J* = 7.0 Hz, 1H), 5.08 (d, *J* = 7.0 Hz, 1H), 5.00 (bs, exchangeable OHs), 2.85 (t, *J* = 6.1 Hz, 2H), 2.24–2.16 (m, 1H), 2.07 (dd, *J* = 7.9, 5.9 Hz, 1H), 1.85 (dt, *J* = 11.2, 5.6 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 174.1 (C), 171.5 (C), 143.7, (C) 141.9 (CH), 134.8 (C), 131.4 (CH), 130.6 (CH), 111.9 (C), 94.7 (C), 78.0 (CH), 35.7 (CH_2), 32.1 (CH_2), 20.8 (CH_2).

HRMS (ESI–) 402.9684 calculated for $C_{14}H_{12}IO_6$ found 402.9672

$[\alpha]_D^{24}$ – 10.2 (*c* 0.02, MeOH)

(4*R*,5*R*)-8'-iodo-3',4'-dihydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxylic acid (8b).



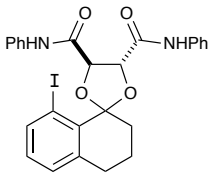
Using general procedure B, **8b** was synthesized from **8a** in 81% yield after flash column chromatography (4:1 hexanes/EtOAc).

IR (thin film) 2958, 2924, 2857, 1644, 1441, 1274, 1114, 978 cm^{-1}

^{1}H NMR (300 MHz, CDCl3): δ 7.87 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 5.77 (d, *J* = 6.8 Hz, 1H), 5.66 (d, *J* = 6.8 Hz, 1H), 3.92–3.49 (m, 16H), 2.84 (t, *J* = 6.2 Hz, 2H), 2.11–2.07 (m, 2H), 1.85–1.77 (m, 2H).

HRMS (ESI+) 565.0806 calculated for $C_{22}H_{27}IN_2NaO_6$ found 565.0799

(4*R*,5*R*)-8'-iodo-*N*^{4},*N*^{5}-diphenyl-3',4'-dihydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxamide (8c).



Using general procedure B, **8c** was obtained from **8a** and isolated as an orange solid in 74% yield after purification by flash column chromatography (4:1 hexanes/EtOAc).

IR (thin film) 3383, 3288, 3055, 2933, 1699, 1599, 1538, 1445, 1095 cm^{-1}

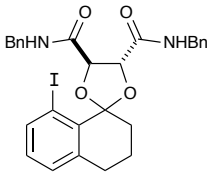
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.63 (s, 1H), 7.92 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.67–7.63 (m, 4H), 7.41–7.33 (m, 4H), 7.21–7.12 (m, 3H), 6.97 (t, *J* = 7.7 Hz, 1H), 5.25 (d, *J* = 7.6 Hz, 1H), 5.05 (d, *J* = 7.6 Hz, 1H), 2.91 (dq, *J* = 9.7, 5.1 Hz, 2H), 2.30–2.14 (m, 2H), 1.92 (qd, *J* = 9.1, 4.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 168.3 (C), 167.1 (C), 142.8 (C), 141.2 (CH), 137.6 (C), 136.6 (C), 133.0 (C), 130.8 (CH), 129.9 (CH), 129.3 (CH × 2), 129.2 (CH × 2), 125.3 (CH), 124.7 (CH), 120.5 (CH × 2), 119.8 (CH × 2), 111.5 (C), 94.0 (C), 78.4 (CH), 77.3 (CH), 34.9 (CH_2), 31.3 (CH_2), 19.9 (CH_2).

HRMS (ESI+) 577.0595 calculated for $C_{26}H_{23}IN_2NaO_4$ found 577.0641

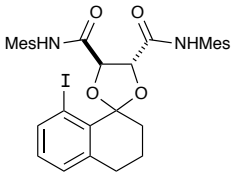
$[\alpha]_D^{25}$ – 37.2 (*c* 0.01, EtOAc)

(4*R*,5*R*)-*N*^{4},*N*^{5}-dibenzyl-8'-iodo-3',4'-dihydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxamide (8d).



Using general procedure B, **8d** was obtained from **8a** and isolated as a brown solid in 86% yield after purification by flash column chromatography (3:1 hexanes/EtOAc).

(4*R*,5*R*)-8'-iodo-*N*^{4},*N*^{5}-dimesityl-3',4'-dihydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxamide (8e).



Using general procedure B, **8e** was obtained from **8a** and isolated as a brown solid in 86% yield after purification by flash column chromatography (3:1 hexanes/EtOAc).

IR (thin film) 3368, 3267, 3006, 2947, 2920, 2863, 1704, 1510, 1093 cm^{-1}

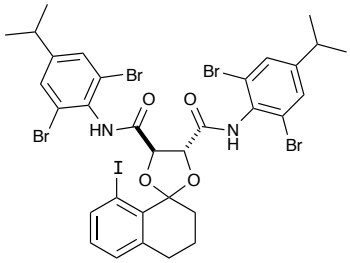
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 2H), 7.91 (d, *J* = 7.5 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.95–6.90 (m, 5H), 5.44 (d, *J* = 8.2 Hz, 1H), 5.13 (d, *J* = 8.2 Hz, 1H), 2.93–2.87 (m, 2H), 2.40–2.35 (m, 1H), 2.27 (s, 12H), 2.25 (s, 6H), 2.00–1.93 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 169.3 (C), 166.4 (C), 142.6 (C), 141.2 (CH), 137.3 (C), 135.0 (C × 2), 134.9 (C × 2), 133.2 (C), 130.7 (CH), 130.3 (C), 130.2 (C), 129.8 (CH), 129.2 (CH × 4), 111.1 (C), 94.1 (C), 78.0 (CH), 77.7 (CH), 34.8 (CH_2), 31.4 (CH_2), 21.0 (CH_3 × 2), 20.0 (CH_2), 19.1 (CH_3 × 2), 18.7 (CH_3 × 2).

HRMS (ESI+) 661.1534 calculated for $C_{32}H_{35}IN_2NaO_4$ found 661.1531

$[\alpha]_D^{24}$ + 4.4 (*c* 0.01, MeOH)

(4*R*,5*R*)-*N*^{4},*N*^{5}-bis(2,6-dibromo-4-isopropylphenyl)-8'-iodo-3',4'-dihydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxamide (8f).



Using general procedure B, **8f** was obtained from **8a** and isolated as a brown solid in 76% yield after purification by flash column chromatography (9:1 hexanes/EtOAc).

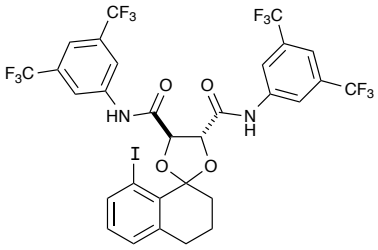
IR (thin film) 3379, 3258, 2961, 2869, 1724, 1681, 1501, 1096 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.63 (s, 1H), 7.91 (d, *J* = 8.0, 1H), 7.46 (s, 2H), 7.44 (s, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 5.56 (d, *J* = 8.1 Hz, 1H), 5.28 (d, *J* = 8.1 Hz, 1H), 2.95–2.83 (m, 4H), 2.40–2.27 (m, 2H), 1.98–1.95 (m, 2H), 1.232 (d, *J* = 6.9, 6H), 1.227 (d, *J* = 6.9).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT) δ 169.3 (C), 166.1 (C), 151.7 (C), 151.6 (C), 142.6 (C), 141.1 (CH), 133.1 (C), 131.11 (C), 131.05 (C), 130.74 (CH), 130.69 (CH), 129.6 (CH), 123.7 (C), 123.6 (C), 111.5 (C), 94.6 (C), 77.6 (CH), 77.2 (CH), 35.0 (CH_2), 33.75 (CH), 33.73 (CH), 31.4 (CH_2), 23.7 ($CH_3 \times 4$), 20.1 (CH_2).

HRMS (ESI+) 976.7917 calculated for $C_{32}H_{31}Br_4IN_2NaO_4$ found 976.7964

(4*R*,5*R*)-*N*^{4},*N*^{5}-bis(3,5-bis(trifluoromethyl)phenyl)-8'-iodo-3',4'-dihydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxamide (8g).



Using general procedure B, **8g** was obtained from **8a** and isolated as a yellow solid in 51% yield after purification by flash column chromatography (5:1 hexanes/EtOAc).

IR (thin film) 3267, 2924, 1708, 1381, 1278, 1137 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.77 (s, 1H), 8.15 (s, 4H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.70 (s, 1H), 7.66 (s, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 5.30 (d, *J* = 7.3 Hz, 1H), 5.11 (d, *J* = 7.3 Hz, 1H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.27–2.06 (m, 2H), 1.93 (t, *J* = 4.6 Hz, 2H).

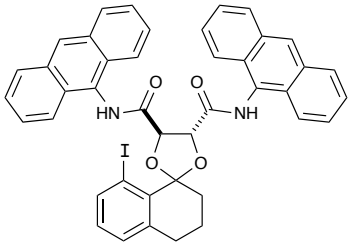
^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 168.8 (C), 167.7 (C), 142.8 (C), 141.2 (CH), 138.8 (C), 137.9 (C), 132.9 d, *J* = 18.8 Hz, C–CF_3), 132.6 (d, *J* = 18.8 Hz, C–CF_3), 131.2 (CH), 130.1 (CH),

123.15 (d, *J* = 271.3 Hz, CF_3), 123.08 (d, *J* = 272.5 Hz, CF_3), 120.0 (CH), 119.6 (CH), 118.8 (m, CH),[8] 118.2 (m, CH),[8] 112.19 (C), 78.3 (CH), 77.0 (CH), 34.9 (CH_2), 31.2 (CH_2), 19.8 (CH_2).

HRMS (ESI+) 849.0090 calculated for $C_{30}H_{19}F_{12}IN_2NaO_4$ found 849.0080

$[\alpha]_D^{25}$ – 4.0 (*c* 0.01, EtOAc)

(4R,5R)-N4,N5-di(anthracen-9-yl)-8'-iodo-3',4'-dihydro-2'H-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxamide (8h).



Using general procedure B, **8h** was obtained from **8a** and isolated as a yellow solid in 45% yield after purification by flash column chromatography (9:1 hexanes/EtOAc).

IR (thin film) 3358, 3053, 2924, 2853, 1670, 1496, 1354 cm^{-1}

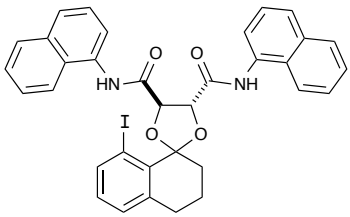
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.05 (s, 1H), 8.49 (s, 1H), 8.43 (s, 1H), 8.30 (d, *J* = 8.7 Hz, 2H), 8.13 (d, *J* = 8.7 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.00 (app d, *J* = 8.1 Hz, 2H, 1H), 7.58 (app t, *J* = 7.3 Hz, 2H), 7.52–7.44 (m, 6H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 5.98 (d, *J* = 8.0 Hz, 1H), 5.68 (d, *J* = 8.0 Hz, 1H), 3.02–2.92 (m, 2H), 2.60 (dt, *J* = 9.3, 4.4 Hz, 1H), 2.45 (td, *J* = 12.4, 3.3 Hz, 1H), 2.11–2.01 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 169.9 (C), 168.5 (C), 142.9 (C), 141.2 (CH), 133.2 (C), 131.71 (C), 131.66 (C), 130.8 (CH), 130.0 (CH), 128.9 (CH × 2), 128.8 (CH × 2), 128.2 (C), 128.0 (C), 127.7 (CH), 127.2 (CH), 126.8 (C), 126.7 (CH × 2), 126.6 (CH × 2), 126.1 (C), 125.5 (CH × 2), 125.4 (CH × 2), 123.4 (CH × 2), 123.2 (CH × 2), 111.9 (C), 94.2 (C), 78.6 (CH), 78.4 (CH), 35.0 (CH_2), 31.4 (CH_2), 20.1 (CH_2).

HRMS (ESI+) 777.1221 calculated for $C_{42}H_{31}IN_2NaO_4^+$ found 777.1296

$[\alpha]_D^{24}$ + 30.6 (*c* 0.004, EtOAc)

(4*R*,5*R*)-8'-iodo-*N*^{4},*N*^{5}-di(naphthalen-1-yl)-3',4'-dihydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalene]-4,5-dicarboxamide (8i).



Using general procedure B, **8i** was obtained from **8a** and isolated as a brown solid in 71% yield after purification by flash column chromatography (8:1 hexanes/EtOAc).

IR (thin film) 3296, 3054, 2925, 2854, 1711, 1670, 1598, 1503, 1260, 1095 cm^{-1}

(8) Complex splitting due to multiple C–F coupling interactions.

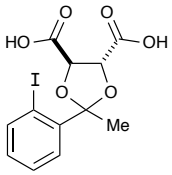
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (s, 1H), 9.17 (s, 1H), 8.26 (d, *J* = 7.5 Hz, 1H), 8.19 (d, *J* = 7.5 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.05–8.03 (m, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.90–7.88 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.56–7.50 (m, 6H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 5.59 (d, *J* = 7.7 Hz, 1H), 5.31 (d, *J* = 7.7 Hz, 1H), 3.00–2.90 (m, 2H), 2.35 (qt, *J* = 13.1, 6.3 Hz, 2H), 2.00 (dt, *J* = 11.3, 5.9 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT) δ 169.1 (C), 167.8 (C), 142.8 (C), 141.2 (CH), 134.3 (C), 134.2 (C), 133.2 (C), 132.2 (C), 131.4 (C), 130.8 (CH), 129.9 (CH), 128.9 (CH), 126.9 (C), 126.7 (CH), 126.6 (CH), 126.49 (C), 126.46 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 125.8 (CH), 125.6 (CH), 121.3 (CH), 120.8 (CH), 120.4 (CH), 119.5 (CH), 111.8 (C), 94.1 (C), 78.8 (CH), 78.0 (CH), 35.1 (CH_2), 31.4 (CH_2), 20.01 (CH_2).

HRMS (ESI+) 677.0908 calculated for $C_{34}H_{27}IN_2NaO_4^+$ found 677.0914

$[\alpha]_D^{26}$ – 51.6 (*c* 0.01, EtOAc)

(4*R*,5*R*)-2-(2-iodophenyl)-2-methyl-1,3-dioxolane-4,5-dicarboxylic acid (S1).



Using general procedure A, **S1** was synthesized from commercially available 2-iodoacetephenone. A yellow solid was obtained (38% yield).

IR (thin film) 3405, 3059, 2991, 2933, 1727, 1605, 1426, 1191, 1085 cm^{-1}

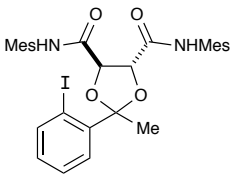
^{1}H NMR (300 MHz, CD_3OD): δ 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.33 (td, *J* = 7.6, 1.1 Hz, 1H), 6.96 (td, *J* = 7.6, 1.7 Hz, 1H), 5.04 (bs, exchangeable OHs), 4.61 (d, *J* = 8.0 Hz, 1H), 4.39 (d, *J* = 8.0 Hz, 1H), 1.84 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 173.4 (C), 173.1 (C), 144.8 (CH), 143.2 (C), 130.8 (CH), 129.4 (CH), 128.8 (CH), 112.5 (C), 93.5 (C), 78.4 (CH), 77.5 (CH), 26.6 (CH_3).

HRMS (ESI–) 376.9528 calculated for $C_{12}H_{10}IO_6$ found 376.9483

$[\alpha]_D^{26}$ + 28.6 (*c* 0.03, MeOH)

(4*R*,5*R*)-2-(2-iodophenyl)-*N*^{4},*N*^{5}-dimesityl-2-methyl-1,3-dioxolane-4,5-dicarboxamide (S2).



Compound **S2** was synthesized from **S1** using general procedure B and purified by flash column chromatography (1:0 hexanes → 4:1 hexanes/EtOAc) to obtain a brown solid (81% yield).

IR (thin film) 3358, 3269, 2919, 1695, 1506, 1189 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.48 (s, 1H), 7.94 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.02 (td, *J* = 7.6, 1.8 Hz, 1H), 6.88 (s, 2H),

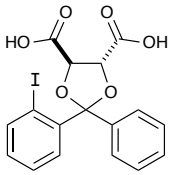
6.84 (s, 2H), 4.94 (d, *J* = 8.3 Hz, 1H), 4.77 (d, *J* = 8.3 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.22 (s, 6H), 2.07 (s, 3H), 1.87 (bs, 6H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 169.1 (C), 165.5 (C), 142.9 (C), 142.6 (CH), 137.6 (C), 136.9 (C), 135.0 (C), 134.8 (C), 130.5 (CH), 129.5 (C), 129.1 (CH), 129.0 (CH), 127.4 (CH), 112.5 (C), 93.7 (C), 78.4 (CH), 77.3 (CH), 26.6 (CH_3), 21.1 (CH_3), 18.6 (CH_3), 18.0 (CH_3).

HRMS (ESI+) 635.1277 calculated for $C_{30}H_{33}IN_2NaO_4$ found 635.1418

$[\alpha]_D^{25}$ + 12.3 (*c* 0.01, EtOAc)

(4*R*,5*R*)-2-(2-iodophenyl)-2-phenyl-1,3-dioxolane-4,5-dicarboxylic acid (S3).



Using general procedure A, **S3** was synthesized from known compound 2-iodoacetephenone.[9] A beige solid was obtained (37% yield).

IR (thin film) 3061, 2627, 1733, 1450, 1248, 1202, 1105 cm^{-1}

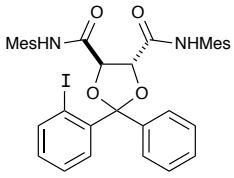
^{1}H NMR (300 MHz, CD_3OD) δ 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.45–7.37 (m, 3H), 7.32–7.30 (m, 3H), 7.03 (td, *J* = 7.6, 1.7 Hz, 1H), 5.06 (bs, exchangeable OHs), 4.88 (d, *J* = 6.9 Hz, 1H), 4.82 (d, *J* = 6.9 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 171.8 (C), 171.6 (C), 143.3 (CH), 143.0 (C), 140.5 (C), 131.28 (CH), 130.3 (CH), 129.9 (CH), 129.8 (CH), 128.8 (CH), 128.4 (CH), 114.1 (C), 96.2 (C), 78.8 (CH), 78.1 (CH).

HRMS (ESI–) 438.9684 calculated for $C_{17}H_{12}IO_6$ found 438.9621

$[\alpha]_D^{25}$ + 22.0 (*c* 0.01, EtOH)

(4*R*,5*R*)-2-(2-iodophenyl)-*N*^{4},*N*^{5}-dimesityl-2-phenyl-1,3-dioxolane-4,5-dicarboxamide (S4).



Using general procedure B, **S4** was synthesized from **S3** and purified by flash column chromatography (1:0 → 4:1 hexanes/EtOAc) to afford a beige solid (55% yield).

IR (thin film) 3370, 3267, 3059, 2919, 2857, 1699, 1506, 1201, 1100 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.39 (s, 1H), 8.03 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53–7.45 (m, 3H), 7.39–7.34 (m, 3H), 7.08 (td, *J* = 7.6, 1.7 Hz, 1H), 6.87 (s, 2H), 6.84 (s, 2H), 5.18 (d, *J* = 7.6 Hz, 1H), 5.07 (d, *J* = 7.6 Hz, 1H), 2.25 (d, *J* = 3.9 Hz, 6H), 2.16 (s, 6H), 1.92 (s, 6H).

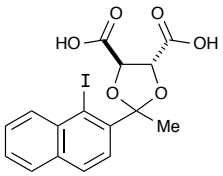
(9) E. A. Krasnokutskaya, N. I. Semenischeva, V. D. Filimonov, and P. Knochel, *Synthesis*, **2007**, 81.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 168.0 (C), 166.1 (C), 142.6 (CH), 141.4 (C), 138.4 (C), 137.4 (C), 137.1 (C), 135.0 (C), 134.9 (C), 130.9 (CH), 130.3 (C), 129.8 (C), 129.5 (CH), 129.1 (CH), 128.6 (CH), 128.3 (CH), 127.8 (CH), 113.5 (C), 95.8 (C), 79.1 (CH), 78.3 (CH), 21.0 (CH_3), 18.6 (CH_3), 18.2 (CH_3).

HRMS (ESI+) 697.1534 calculated for $C_{35}H_{35}IN_2NaO_4$ found 697.1580

$[\alpha]_D^{25}$ + 44.0 (*c* 0.004, EtOAc)

(4*R*,5*R*)-2-(1-iodonaphthalen-2-yl)-2-methyl-1,3-dioxolane-4,5-dicarboxylic acid (S5).



Compound **S5** was synthesized from known compound 1-(1-iodonaphthalen-2-yl)ethanone[10] using general procedure A, affording a brown solid (34% yield).

IR (thin film) 3057, 2934, 1734, 1224, 1092 cm^{-1}

^{1}H NMR (300 MHz, CD_3OD): δ 8.45 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.83–7.76 (m, 2H), 7.58–7.47 (m, 2H), 4.97 (bs, exchangeable OHs), 4.77 (d, *J* = 6.1 Hz, 1H), 4.72 (d, *J* = 6.1 Hz, 1H), 2.00 (s, 3H).

^{13}C NMR (75 MHz, CD_3OD, DEPT) δ 172.4 (C), 171.8 (C), 144.4 (C), 136.9 (C), 135.1 (CH), 134.8 (C), 129.8 (CH), 129.3 (CH), 128.7 (CH), 128.0 (CH), 126.0 (CH), 114.3 (C), 100.7 (C), 78.9 (CH), 77.3 (CH), 26.9 (CH_3).

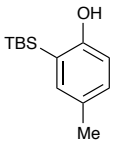
HRMS (ESI–) 426.9684 calculated for $C_{16}H_{12}IO_6$ found 426.9688

$[\alpha]_D^{26}$ + 45.4 (*c* 0.01, MeOH)

Synthesis of Phenol Substrates

Substrates **4a–f** were synthesized as previously described.[11]

2-(*tert*-butyldimethylsilyl)-4-methylphenol (4g).[12]



Into a round bottom flask was placed commercially available 2-bromo-4-methyl phenol (1.96 g, 10.5 mmol), imidazole (0.93 g, 13.6 mmol) and DCM (12 mL) and cooled to 0 °C. The TBS-Cl (1.9 g, 12.6 mmol) was then added and the reaction stirred overnight, allowing to slowly warm to r.t. The DCM was removed in vacuo, giving a colorless oil. Into the same flask

(10) U. H. Hirt, M. F. H. Schuster, A. N. French, O. G. Wiest, and T. Wirth, *Eur. J. Org. Chem*., 2001, 1569.
(11) R. Tello-Aburto, K. A. Kalstabakken, K. A. Volp, and A. M. Harned, *Org. Biomol. Chem.* 2011, **9**, 7849.
(12) Adapted from A. N. Thadani, Y. Huang, and V. H. Rawal. *Org. Lett.* **2007***, 9*, 3873.

was added THF (30 mL) and the solution was cooled to –78 °C under N_2. To this, *n*-BuLi (2.5 M, 4.2 mL) was slowly added. The reaction was allowed to slowly warm to r.t. and after 2 h was quenched with saturated aq. NH_4Cl. The mixture was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (1:0 hexanes → 9:1 hexanes/EtOAc) to give a pale yellow oil (1.99 g, 86% yield).

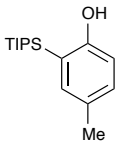
IR (thin film) 3537, 2953, 2927, 2855, 1493, 1388, 1254, 822 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 2.2 Hz, 1H), 7.05 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 4.68 (s, 1H), 2.30 (s, 3H), 0.94 (s, 9H), 0.34 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 158.5 (C), 137.2 (CH), 131.3 (CH), 129.1 (C), 122.5 (C), 114.9 (CH), 27.0 (CH_3 × 3), 20.7 (CH_3), 17.7 (C), -4.6 (CH_3 × 2).

LRMS (ESI+) 221.14 calculated for $C_{13}H_{21}NaOSi$ found 221.19

4-methyl-2-(triisopropylsilyl)phenol (4h).



Phenol **4h** was synthesized from 2-bromo-4-methyl phenol in the same fashion as **4g**, except that TIPS-Cl was used instead of TBS-Cl. A white solid (30% yield) was obtained after purification by flash column chromatography (50:1 hexanes/EtOAc).

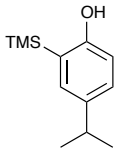
IR (thin film) 3522, 2942, 2861, 1492, 1386, 1175 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 2.1 Hz, 1H), 7.03 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 4.53 (s, 1H), 2.28 (s, 3H), 1.48 (sept, *J* = 7.5 Hz, 3H), 1.10 (d, *J* = 7.4 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 158.6 (C), 137.7 (CH), 130.9 (CH), 129.1 (C), 120.3 (C), 114.8 (CH), 19.03 (CH_3 × 7), 11.8 (CH × 3).

HRMS (ESI+) 263.1837 calculated for $C_{16}H_{27}NaOSi$ found 263.1211

4-isopropyl-2-(trimethylsilyl)phenol (4i).[11]



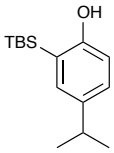
Phenol **4g** was synthesized from commercially available 2-bromo-4-isopropyl phenol. A colorless oil (61% yield) was obtained after purification by flash column chromatography (95:5 hexanes/EtOAc).

IR (thin film) 3535, 2958, 2898, 2870, 11596, 1403, 1314, 1245, 1074, 862, 838 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) 7.29 (d, *J* = 2.0 Hz, 1H), 7.17 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.84 (d, *J* = 3.3 Hz, 1H), 2.93 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 6H), 0.41 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 158.5 (C), 140.7 (C), 133.5 (CH), 128.4 (CH), 125.2 (C), 114.5 (CH), 33.5 (CH), 24.5 (CH_3 × 2), -0.72 (CH_3 × 3).

2-(*tert*-butyldimethylsilyl)-4-isopropylphenol (4j).[12]



Into a round bottom flask was placed commercially available 2-bromo-4-isopropyl phenol (763 mg, 3.55 mmol), imidazole (314 mg, 4.61 mmol) and DCM (3.5 mL) and cooled to 0 °C. The TBS-Cl (64 mg, 4.3 mmol) was then added and the reaction stirred overnight, allowing to slowly warm to r.t. The DCM was removed in vacuo, giving a colorless oil. Into the same flask was added THF (20 mL) and the solution was cooled to –78 °C under N_2. To this, *n*-BuLi (2.5 M, 1.4 mL) was slowly added. The reaction was allowed to slowly warm to r.t. and after 2 h was quenched with saturated aq. NH_4Cl. The mixture was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (1:0 hexanes → 9:1 hexanes/EtOAc) to give a pale yellow oil (696 mg, 78% yield).

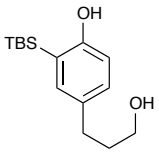
IR (thin film) 3610, 3011, 2957, 2927, 2856, 1595, 1487, 1402, 1314, 1176, 1073 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 2.3 Hz, 1H), 7.11 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 4.67 (s, 1H), 2.87 (hept, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 0.93 (s, 9H), 0.35 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 158.7 (C), 140.3 (C), 134.8 (CH), 128.4 (CH), 122.3 (C), 114.8 (CH), 33.5 (CH), 26.9 (CH_3 × 3), 24.4 (CH_3 × 2), 17.8 (C), -4.6 (CH_3 × 2).

LRMS (CI) 251 calculated for $C_{15}H_{27}OSi^+$ found 251

2-(*tert*-butyldimethylsilyl)-4-(3-hydroxypropyl)phenol (9).



Into a vial was placed 3-(3-bromo-4-hydroxyphenyl)propanoic acid (206 mg, 0.841 mmol) and dissolved in THF (4 mL). At 0 °C, BH_3•$S(CH_3)_2$ (110 μL) was added dropwise. The mixture was stirred for 2 h and MeOH was then added slowly until bubbling ceased. The mixture was diluted with EtOAc and washed with brine (3 × 2 mL), dried with Na_2SO_4, filtered and concentrated. The crude oil was dissolved in DCM (1 mL), cooled to 0 °C and treated with imidazole (143 mg, 2.10 mmol) followed by TBS-Cl (317 mg, 2.10 mmol). The mixture stirred overnight, slowly warming to rt. After such time, the mixture was diluted with EtOAc and filtered over a plug of celite. The solvent was removed and the crude oil was stirred in THF (5 mL) and cooled to –98 °C under N_2. n-BuLi (400 μL) was added slowly dropwise. The mixture was allowed to warm to rt slowly and stir for 1 h. After such time, a saturated solution of NH_4Cl was added and the product extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated. The crude product was dissolved in ethanol (8 mL) and pyridinium *p*-toluenesulfonate (21 mg, 0.084 mmol) was added and the mixture stirred rt overnight. After such time, the ethanol was removed in vacuo and the product was purified by flash column chromatography (4:1 hexanes/EtOAc). A white solid was obtained (66.0 mg) in 29% yield over four steps.

IR (thin film) 3335, 2951, 2928, 2855, 1509, 1471, 1401, 1254, 836 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.62 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.82 (s, 1H), 3.69-3.68 (m, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 1.86 (quintet, *J* = 6.6 Hz, 2H), 0.90 (s, 9H), 0.32 (s, 6H).

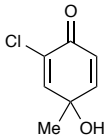
^{13}C NMR (125 MHz, $CDCl_3$, DEPT) δ 159.0 (C), 136.6 (CH), 133.1 (C), 130.6 (CH), 122.7 (C), 115.0 (CH), 62.6 (CH_2), 34.8 (CH_2), 31.5 (CH_2), 27.0 (CH_3 × 3), 17.8 (C), -4.6 (CH_3 × 2).

HRMS (ESI+) 289.1594 calculated for $C_{15}H_{26}NaO_2Si$ found 289.1595

Synthesis of Racemic Quinols

Quinols **5a, 5b, 5c, 5e,** and **5f** were prepared as previously described.[11]

2-chloro-4-hydroxy-4-methylcyclohexa-2,5-dienone (5d).



Commercially available 2-chloro-4-methyl phenol (20 μL, 0.16 mmol) was dissolved in a mixture of MeCN/H_2O (0.17 M, 2:1). (Diacetoxyiodo)benzene (56 mg, 0.17 mmol) was added and the mixture was stirred r.t. overnight. The mixture was then quenched with saturated aq. $NaHCO_3$ and extracted with EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (4:1 hexanes/EtOAc) and a yellow crystalline solid (18 mg, 67% yield) was isolated.

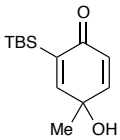
IR (thin film) 3406, 3047, 2981, 2930, 1673, 1644, 1603, 1130, 1057 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, *J* = 2.9 Hz, 1H), 6.90 (dd, *J* = 10.0, 2.9 Hz, 1H), 6.21 (d, *J* = 10.0 Hz, 1H), 2.44 (s, 1H), 1.53 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 178.5 (C), 152.4 (CH), 148.0 (CH), 131.7 (C), 126.2 (CH), 69.4 (C), 26.8 (CH_3).

HRMS (ESI+) 181.0027 calculated for $C_7H_7ClNaO_2^+$ found 181.0021

2-(*tert*-butyldimethylsilyl)-4-hydroxy-4-methylcyclohexa-2,5-dienone (5g).



Into a 1 dram vial was placed **4g** (48.1 mg, 0.22 mmol) and 4-iodotoluene (10 mol %, 7 mg) in a mixture of acetonitrile/H_2O (1.3 mL, 9:1). Last was added *m*-CPBA (107 mg, 0.41 mmol) and the mixture was capped and stirred overnight at r.t. After such time, the reaction was quenched with 10% aq $Na_2S_2O_3$ (1 mL) and stirred 5 min before saturated aq. $NaHCO_3$ (1 mL) was added. The mixture was extracted with EtOAc (3 × 1 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (5:1 hexanes/EtOAc). A white solid was obtained (23.5 mg, 46% yield).

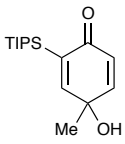
IR (thin film) 3384, 2954, 2928, 2856, 1655, 1618, 1363, 1249, 1058, 838 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 2.9 Hz, 1H), 6.82 (dd, *J* = 10.0, 2.9 Hz, 1H), 6.08 (d, *J* = 10.0 Hz, 1H), 2.11 (s, 1H), 1.45 (s, 3H), 0.87 (s, 9H), 0.17 (app d, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT) δ 188.0 (C), 161.6 (CH), 150.6 (CH), 137.6 (C), 128.4 (CH), 67.1 (C), 27.3 (CH_3). 27.2 (CH_3 × 3), 17.0 (C), -5.2 (CH_3), -5.3 (CH_3).

HRMS (ESI+) 261.1281 calculated for $C_{13}H_{22}NaO_2Si$ found 261.1297

4-hydroxy-4-methyl-2-(triisopropylsilyl)cyclohexa-2,5-dienone (5h).



Dienone **5h** was synthesized from **4h** in the same fashion as **5g**. A white solid (59% yield) was obtained after purification by flash column chromatography (5:1 hexanes/EtOAc).

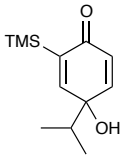
IR (thin film) 3383, 2944, 2889, 2866, 1654, 1617, 1464, 1228, 883 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 2.2 Hz, 1H), 6.83 (dd, *J* = 10.0, 2.2 Hz, 1H), 6.09 (d, *J* = 10.0 Hz, 1H), 2.24 (bs, 1H), 1.45 (s, 3H), 1.36 (dt, *J* = 7.5 Hz, 3H), 1.03 (dd, *J* = 7.3, 2.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 188.6 (C), 162.6 (CH), 150.6 (CH), 135.0 (C), 128.4 (CH), 67.2 (C), 27.5 (CH_3), 18.9 (CH_3 × 6), 11.2 (CH × 3).

HRMS (ESI+) 303.1751 calculated for $C_{16}H_{28}NaO_2Si$ found 303.1749

4-hydroxy-4-isopropyl-2-(trimethylsilyl)cyclohexa-2,5-dienone (5i).



Dienone **5i** was synthesized from **4i** in the same fashion as **5d**, except that a mixture of 3:1 acetonitrile-H_2O was used. A white crystalline solid (55% yield) was obtained after purification by flash column chromatography (9:1 hexanes/EtOAc).

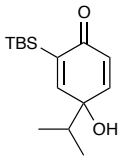
IR (thin film) 3373, 2961, 2549, 1694, 1650, 1304, 1263, 844 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (d, *J* = 3.2 Hz, 1H), 6.76 (dd, *J* = 10.1, 3.2 Hz, 1H), 6.19 (d, *J* = 10.1 Hz, 1H), 2.13 (bs, 1H), 1.97 (hept, 6.9 Hz, 1H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.18 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 188.7 (C), 158.0 (CH), 149.0 (CH), 141.7 (C), 130.1 (CH), 72.1 (C), 36.9 (CH), 17.2 (CH_3 × 3), 17.3 (CH_3), 17.1 (CH_3), -1.38 (CH_3 × 3).

HRMS (ESI+) 247.1125 calculated for $C_{12}H_{20}NaO_2Si^+$ found 247.1141

2-(*tert*-butyldimethylsilyl)-4-hydroxy-4-isopropylcyclohexa-2,5-dienone (5j).



Dienone **5j** was synthesized from **4j** in the same fashion as **5g**. A white crystalline solid (61% yield) was obtained after purification by flash column chromatography (1:0 → 9:1 hexanes/EtOAc).

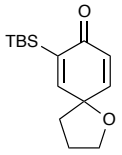
IR (thin film) 3385, 2958, 2928, 2881, 2856, 1653, 1617, 1470, 1363, 1249, 1004, 838 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (d, *J* = 3.2 Hz, 1H), 6.74 (dd, *J* = 10.1, 3.2 Hz, 1H), 6.18 (d, *J* = 10.1 Hz, 1H), 2.05 (bs, 1H), 1.97 (hept, *J* = 6.9 Hz, 1H), 0.94 (app t, *J* = 6.9 Hz, 3H), 0.89 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 188.4 (C), 159.9 (CH), 148.4 (CH), 139.9 (C), 130.3 (CH), 72.3 (C), 36.9 (CH), 27.3 (CH_3 × 3), 17.3 (CH_3), 17.1 (CH_3), 17.0 (C), -5.1 (CH_3), -5.2 (CH_3).

HRMS (ESI+) 289.1594 calculated for $C_{15}H_{26}NaO_2Si^+$ found 289.1593

7-(*tert*-butyldimethylsilyl)-1-oxaspiro[4.5]deca-6,9-dien-8-one (10).



Spirocycle **10** was obtained from **9** in the same fashion as **5g** except that MeCN was used as the solvent. A white solid was obtained in 34% yield after purification by flash column chromatography (6:1 hexanes/EtOAc).

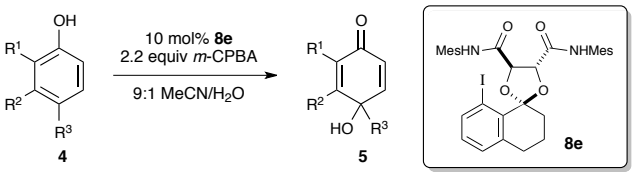
IR (thin film) 2953, 2927, 2856, 1656, 1628, 1248, 1229, 1035, 835 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (d, *J* = 3.1 Hz, 1H), 6.76 (dd, *J* = 10.0, 3.1 Hz, 1H), 6.08 (dd, *J* = 10.0, 0.6 Hz, 1H), 4.08 (t, *J* = 6.9 Hz, 2H), 2.15 (quintet, *J* = 6.9 Hz, 2H), 2.02 (t, *J* = 7.2 Hz, 2H), 0.87 (s, 9H), 0.16 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT) δ 188.4 (C), 159.5 (CH), 148.4 (CH), 137.6 (C), 128.2 (CH), 77.35 (C), 69.4 (CH_2), 37.6 (CH_2), 27.3 (CH_3 × 3), 27.1 (CH_2), 17.0 (C), -5.3 (CH_3 × 2).

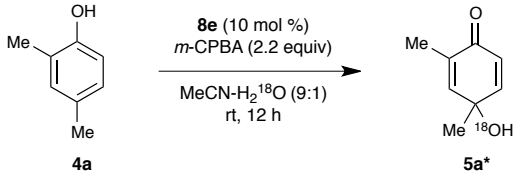
HRMS (ESI+) 287.1438 calculated for $C_{15}H_2NaO_2Si$ found 287.1429

General Procedure for the Synthesis of Enantioenriched Quinols 5a–h



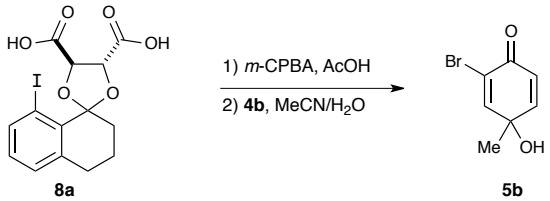
Into a 1 dram vial was placed phenol **4** (0.165 mmol) and iodine catalyst **8** (10 mol %) in a mixture of acetonitrile/H_2O (0.16 M, 9:1). Last was added *m*-CPBA (2.2 equiv) and the mixture was stirred overnight at r.t. After such time, the reaction was quenched with 10% aq $Na_2S_2O_3$ (1 mL) and stirred 5 min before saturated aq. $NaHCO_3$ (1 mL) was added. The mixture was extracted with EtOAc (3 × 1 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (1:0 → 9:1 hexanes/EtOAc) to afford quinol **5**.

Procedure for the synthesis of O^{18} labeled quinol 5a



Into a 1 dram vial was placed phenol **4a** (0.165 mmol, 19 μL) and iodine catalyst **8e** (10 mol %, 11.0 mg) in a mixture of acetonitrile (0.9 mL) and ^{18}O labeled water (0.1 mL). Last was added *m*-CPBA (0.364 mmol, 81.6 mg) and the mixture was stirred overnight at r.t. After such time, the reaction was quenched with 10% aq $Na_2S_2O_3$ (1 mL) and stirred 5 min before saturated aq. $NaHCO_3$ (1 mL) was added. The mixture was extracted with EtOAc (3 × 1 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (1:0 → 6:1 hexanes/EtOAc) to afford quinol **5a*** (9.5 mg, 41% yield) as a beige solid.

Stoichiometric Iodine Experiment

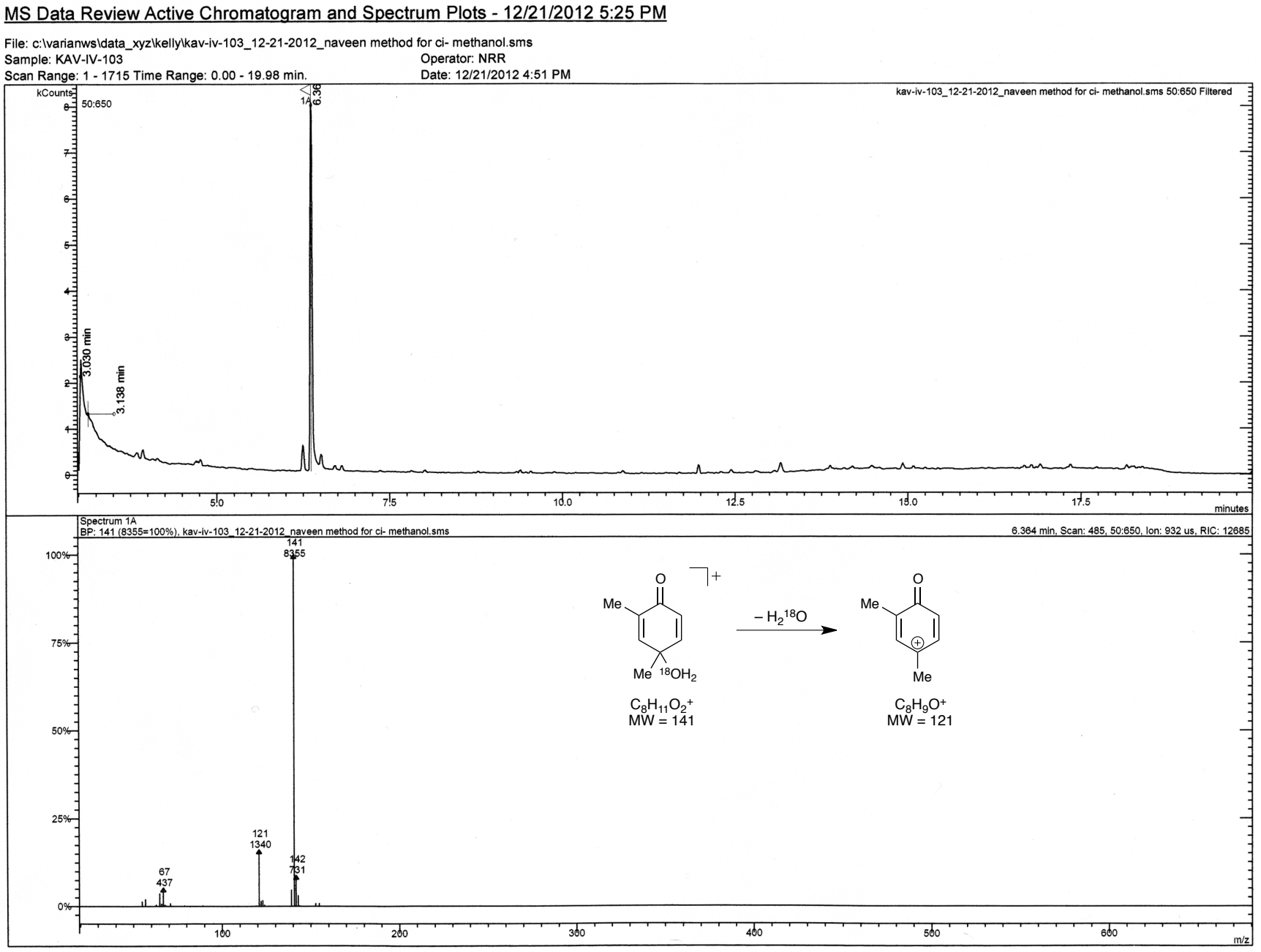


8a **5b**

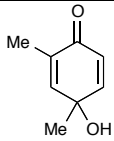
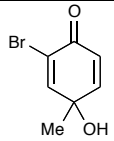
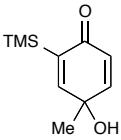
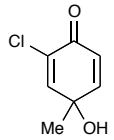
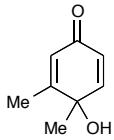
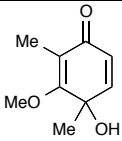
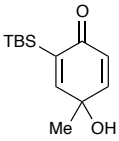
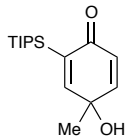
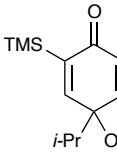
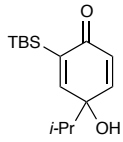
A literature procedure was adapted.[13] Aryl iodide **8a** (103 mg, 0.255 mmol) was stirred in acetic acid (0.25 mL) at rt. To this was added *m*-CPBA (63 mg, 0.280 mmol) and the homogenous mixture stirred for 2 h. After such time, the mixture became heterogeneous and was filtered. The filtrate was dried under vacuum to obtain a yellow solid, which was subsequently dissolved in a mixture of acetonitrile (440 μL) and water (50 μL). The mixture was treated with an excess of 2-bromo-4-methylphenol and stirred rt for 4 h. After such time, the reaction was quenched with 10% aq $Na_2S_2O_3$ (1 mL) and stirred 5 min before saturated aq. $NaHCO_3$ (1 mL) was added. The mixture was extracted with EtOAc (3 × 1 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (1:0 → 9:1 hexanes/EtOAc) to afford quinol **5**.

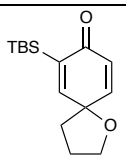
[13] M. Iinuma, K. Moriyama, and H. Togo, *Synlett* 2012, **23**, 2663.

Labelled Water Experiment Results – Mass Spectrum (CI with MeOH)



Summary of HPLC Data

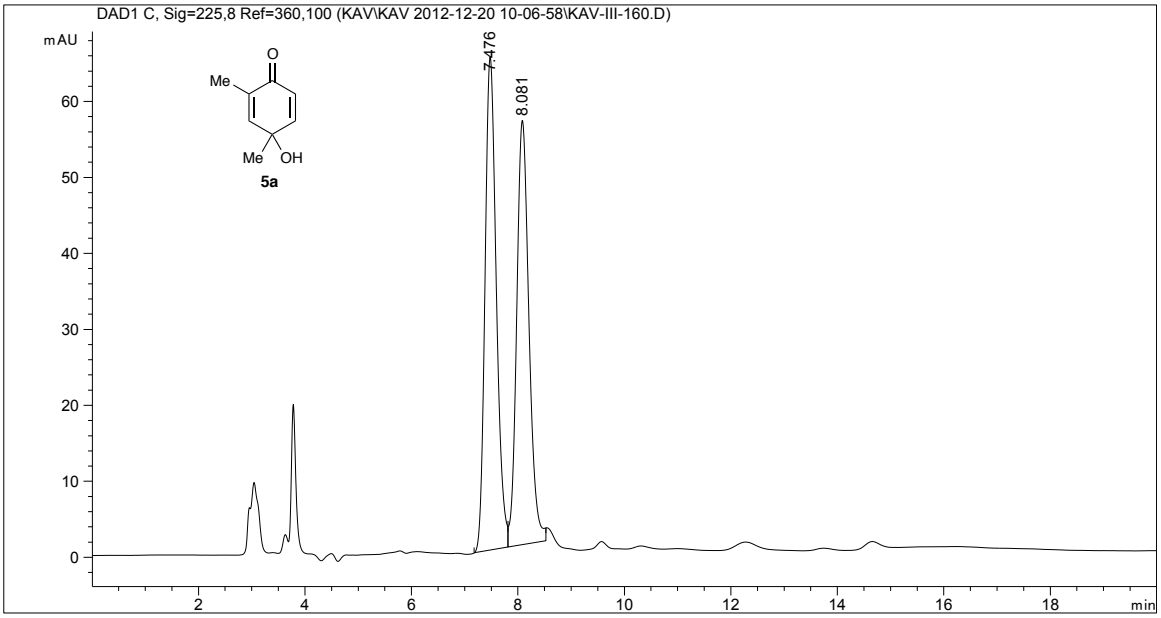
Entry	Compound	Sample Solution	HPLC Column	HPLC conditions	Retention Time Major Isomer (min)	Retention Time Minor Isomer (min)
1	 (**5a**)	*i*-PrOH	Chiralcel OD-H	8% *i*-PrOH in hexane isocratic, 1 mL/min	8.03	4.43
2	 (**5b**)	*i*-PrOH	Chiralcel OD-H	10% *i*-PrOH in hexane isocratic, 1 mL/min	8.59	7.65
3	 (**5c**)	100:1 hexane:*i*-PrOH	Chiralcel OD	2% EtOH in hexane isocratic, 0.3 mL/min	9.27	7.92
4	 (**5d**)	*i*-PrOH	Chiralcel OD-H	10% *i*-PrOH in hexane isocratic, 1 mL/min	31.01	28.92
5	 (**5e**)	100:1 hexane:*i*-PrOH	Chiralcel OJ	5% EtOH in hexane isocratic, 1 mL/min	11.0	11.9
6	 (**5f**)	*i*-PrOH	Chiralpak AS	10% *i*-PrOH in hexane isocratic, 1 mL/min	9.85	11.29
7	 (**5g**)	100:1 hexane:*i*-PrOH	Chiralcel OD-H	3% EtOH in hexane isocratic, 0.5 mL/min	13.34	12.04
8	 (**5h**)	100:1 hexane:*i*-PrOH	Chiralcel OD	2% EtOH in hexane isocratic, 0.3 mL/min	22.94	21.63
9	 (**5i**)	100:1 hexane:*i*-PrOH	Chiralcel OD	3% EtOH in hexane isocratic, 0.5 mL/min	11.53	12.22
10	 (**5j**)	100:1 hexane:*i*-PrOH	Chiralcel OJ	1% EtOH in hexane isocratic, 0.5 mL/min	12.01	11.27

11	 (**10**)	100:1 hexane:*i*-PrOH	Chiralcel OD-H	2% EtOH in hexane isocratic, 0.5 mL/min	8.91	9.82

HPLC Traces

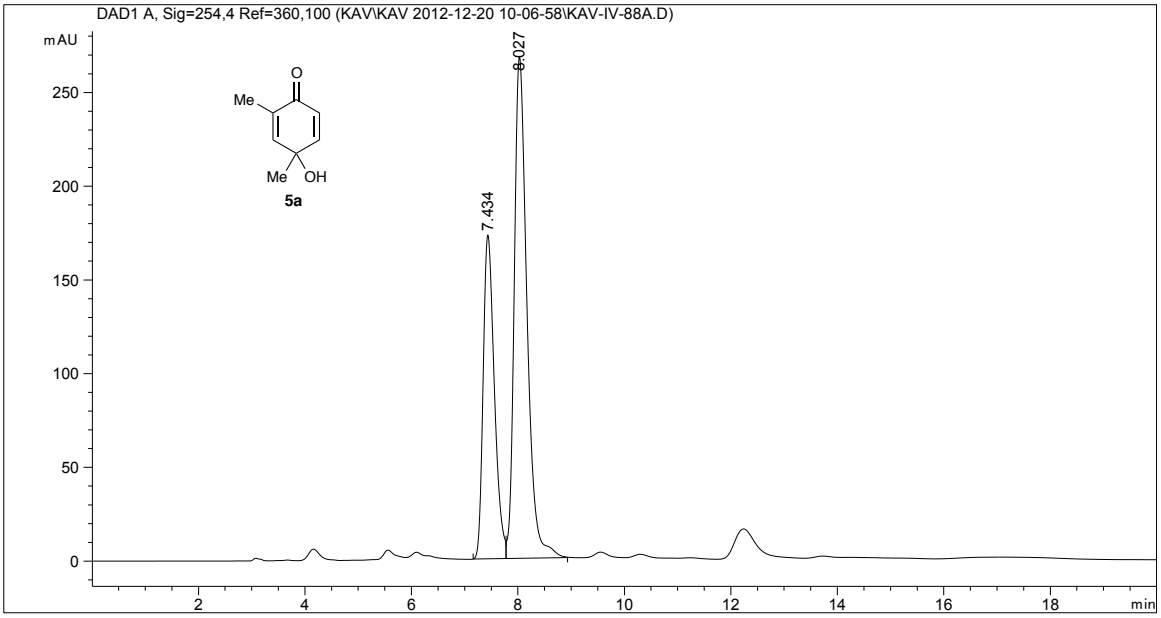
5a – racemic:

Retention Time (min)	Area Percent
7.5	51.7
8.1	48.3



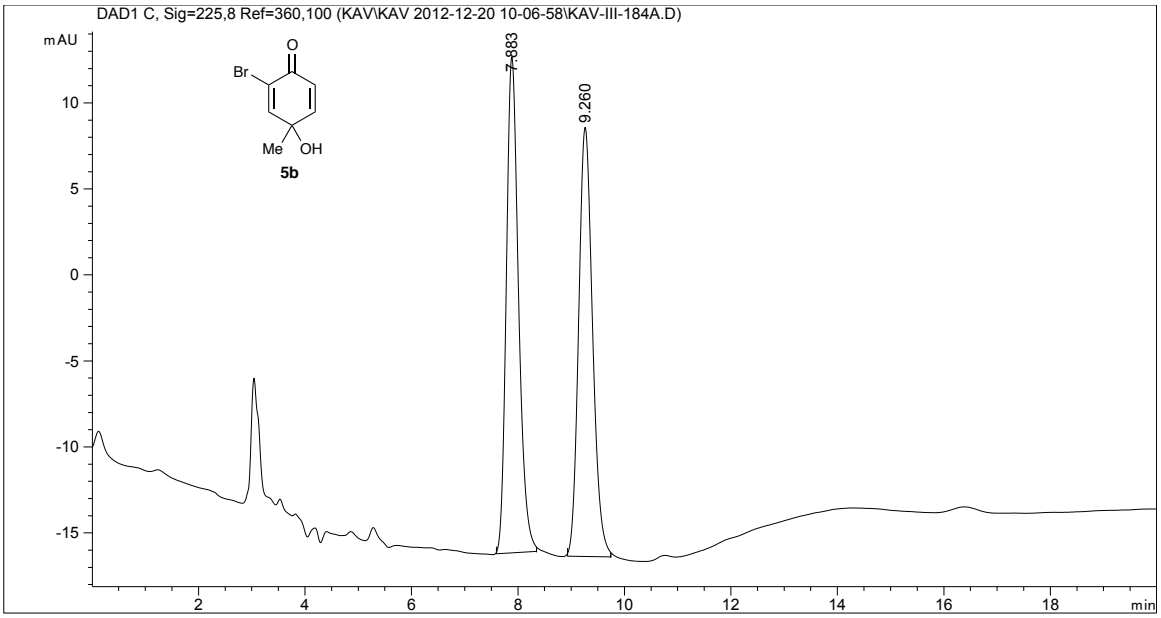
5a with catalyst **8e**:

Retention Time (min)	Area Percent
7.4	36.3
8.0	63.7



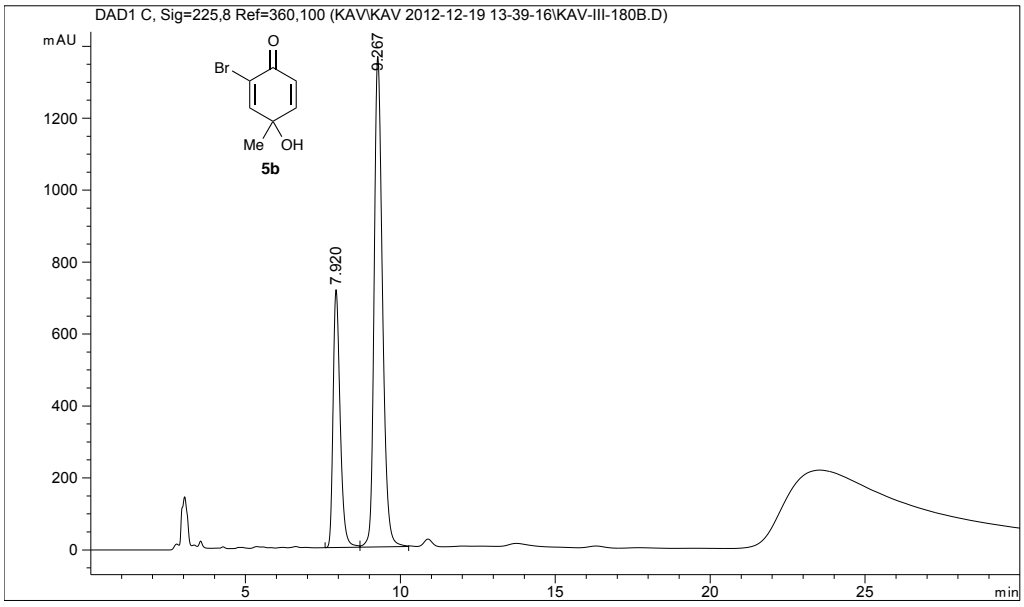
5b – racemic:

Retention Time (min)	Area Percent
7.9	50.4
9.3	49.6



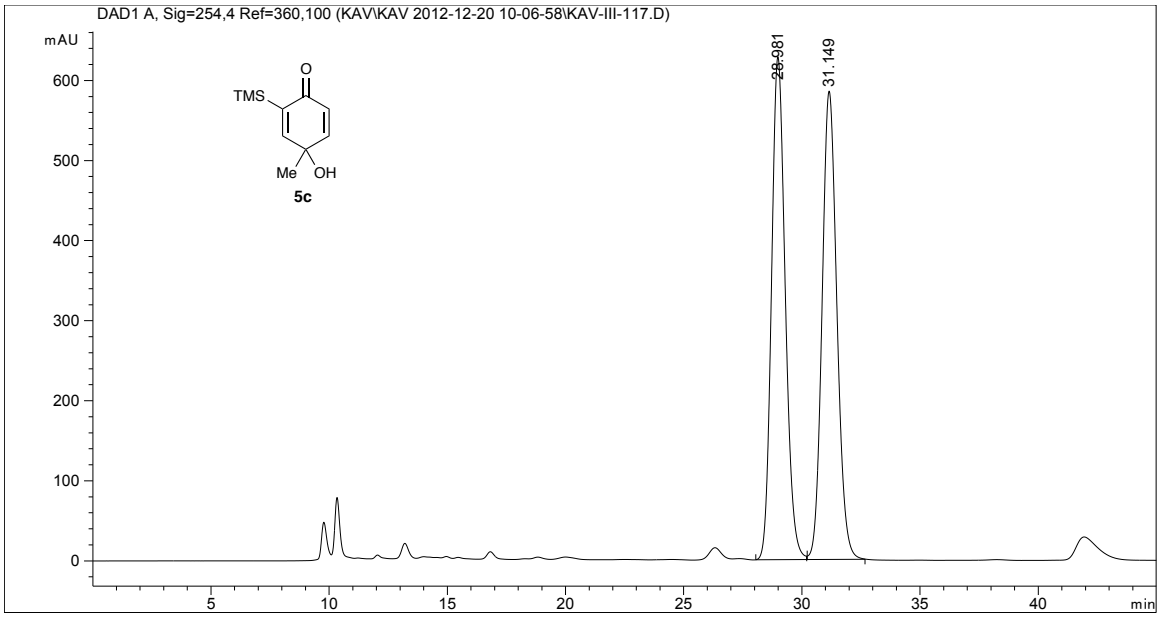
5b with catalyst **8e**:

Retention Time (min)	Area Percent
7.9	30.7
9.3	69.3



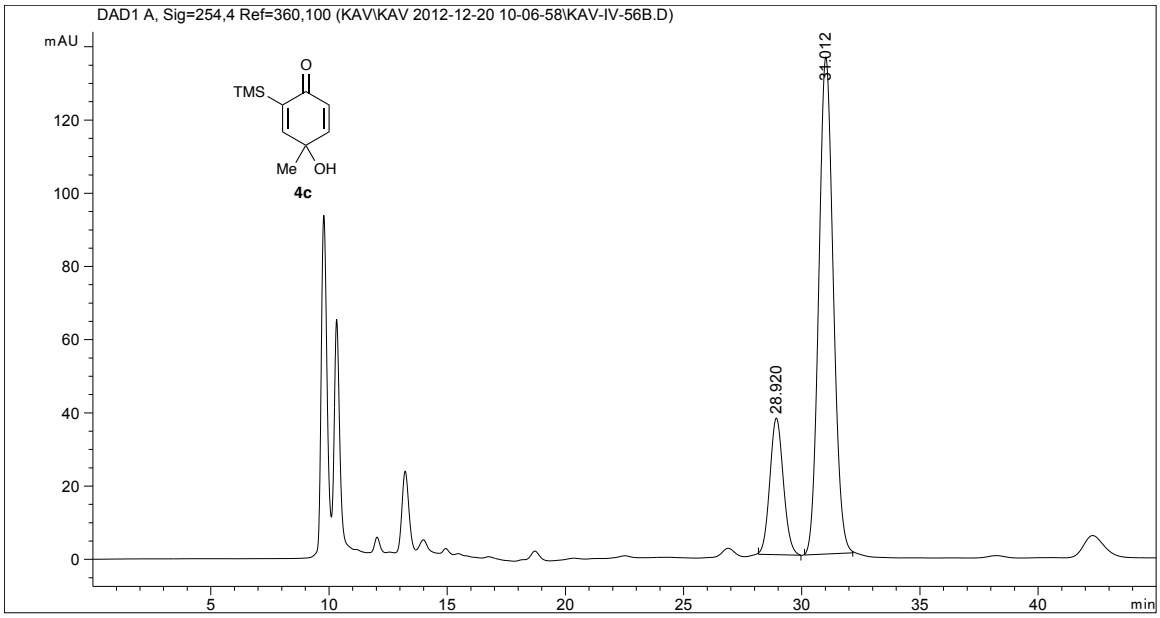
5c – racemic:

Retention Time (min)	Area Percent
29.0	50.0
31.1	50.0



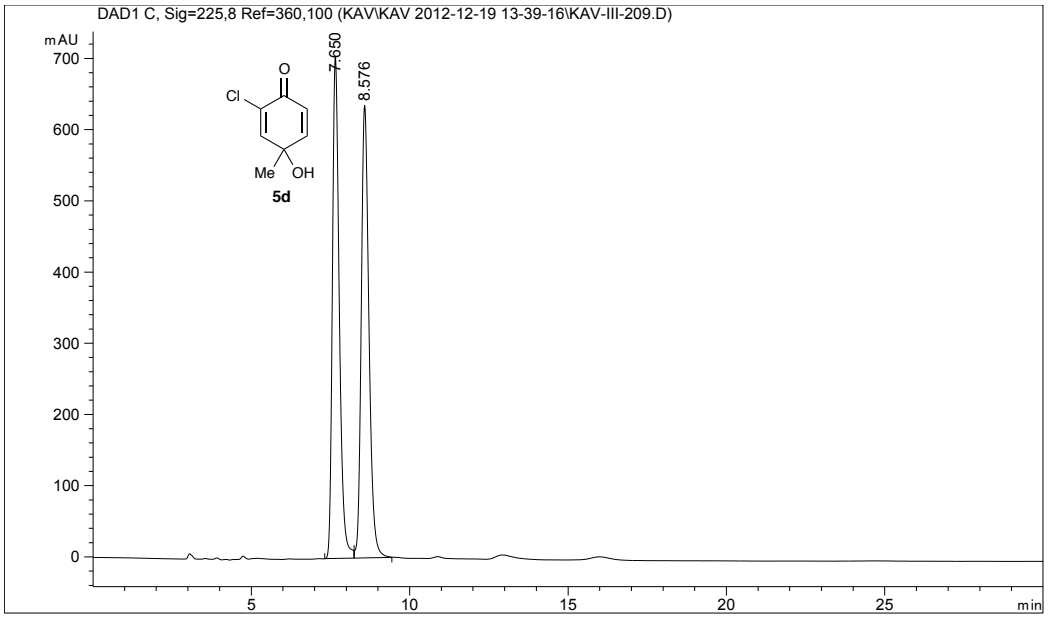
5c with catalyst **8e:**

Retention Time (min)	Area Percent
28.9	20.4
31.0	79.6



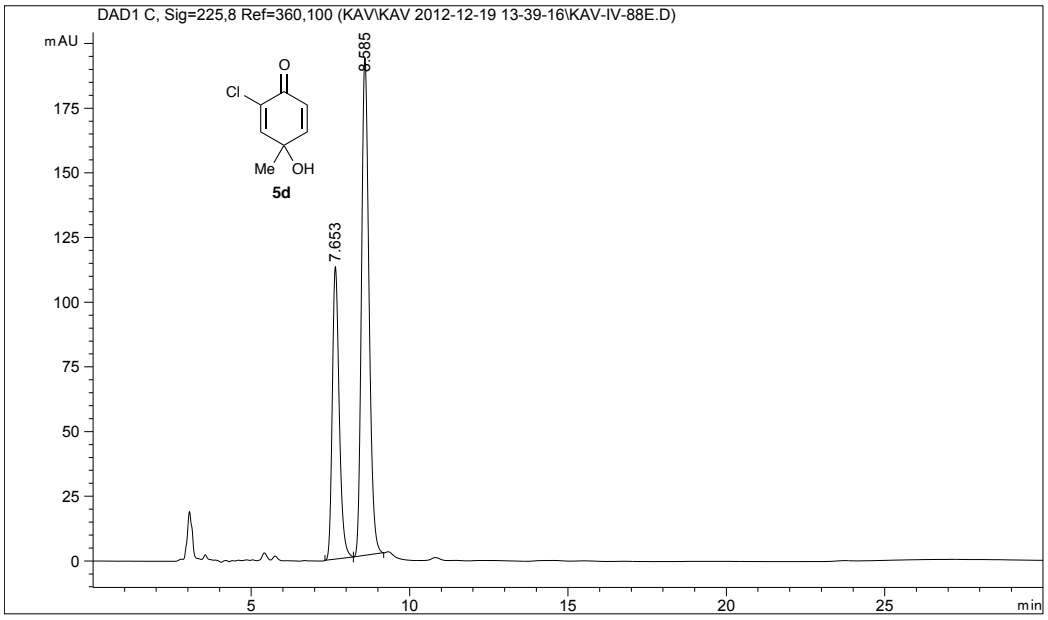
5d – racemic:

Retention Time (min)	Area Percent
7.7	49.8
8.6	50.2



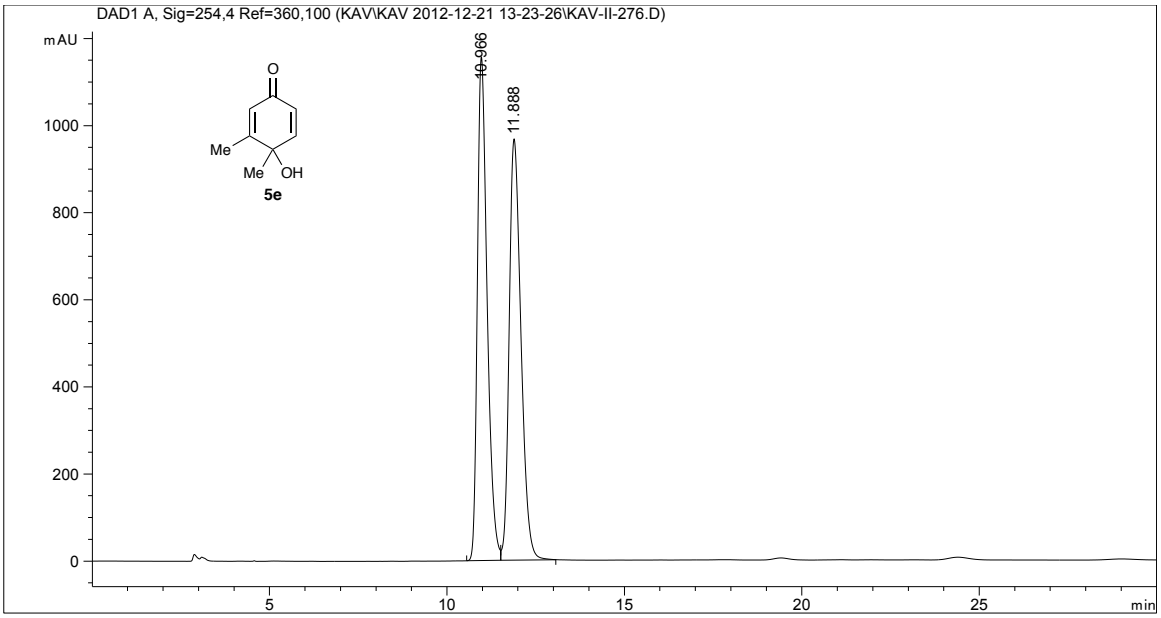
5d with catalyst **8e:**

Retention Time (min)	Area Percent
7.7	35.1
8.6	64.9



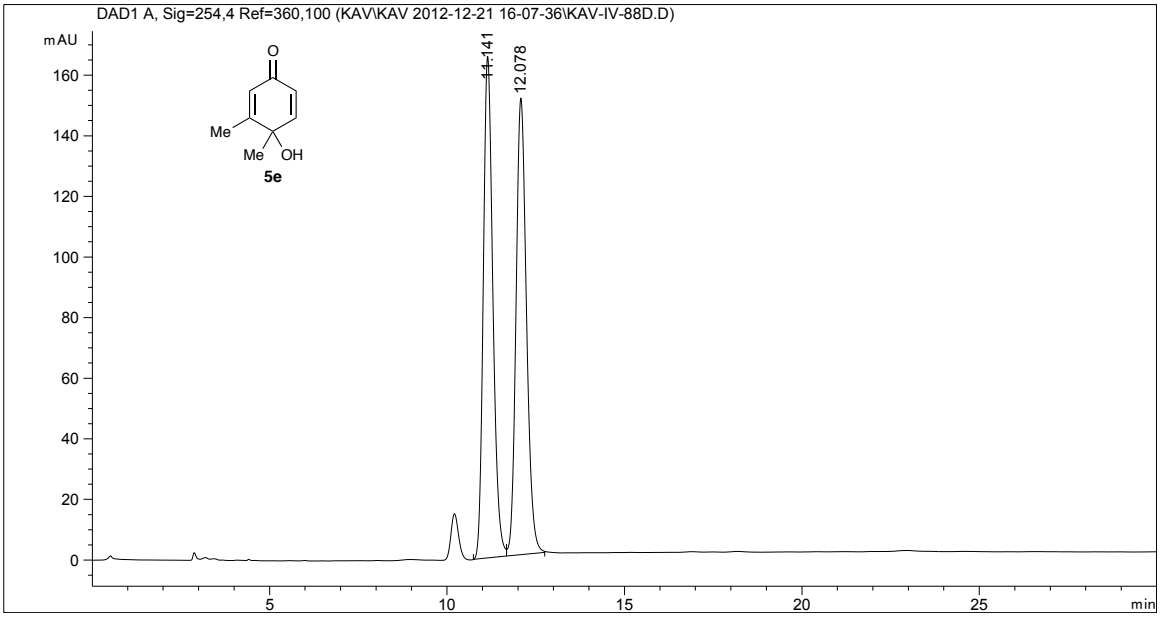
5e – racemic:

Retention Time (min)	Area Percent
11.0	49.7
11.9	50.3



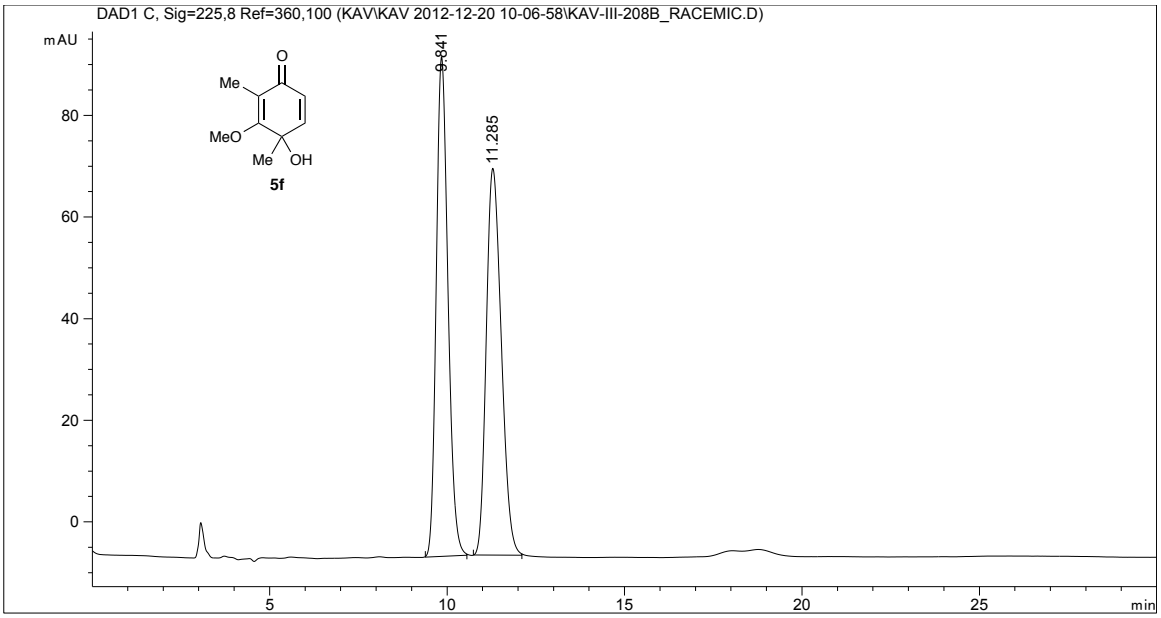
5e with catalyst **8e** at room temperature:

Retention Time (min)	Area Percent
11.1	50.2
12.1	49.8



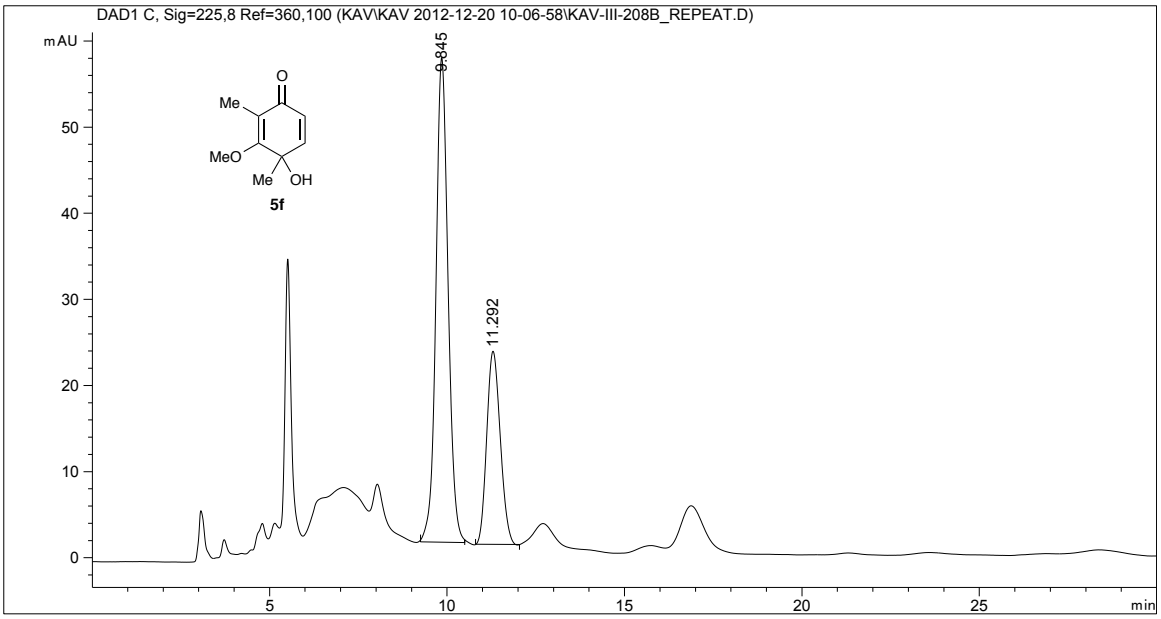
5f – racemic:

Retention Time (min)	Area Percent
9.8	50.2
11.3	49.8



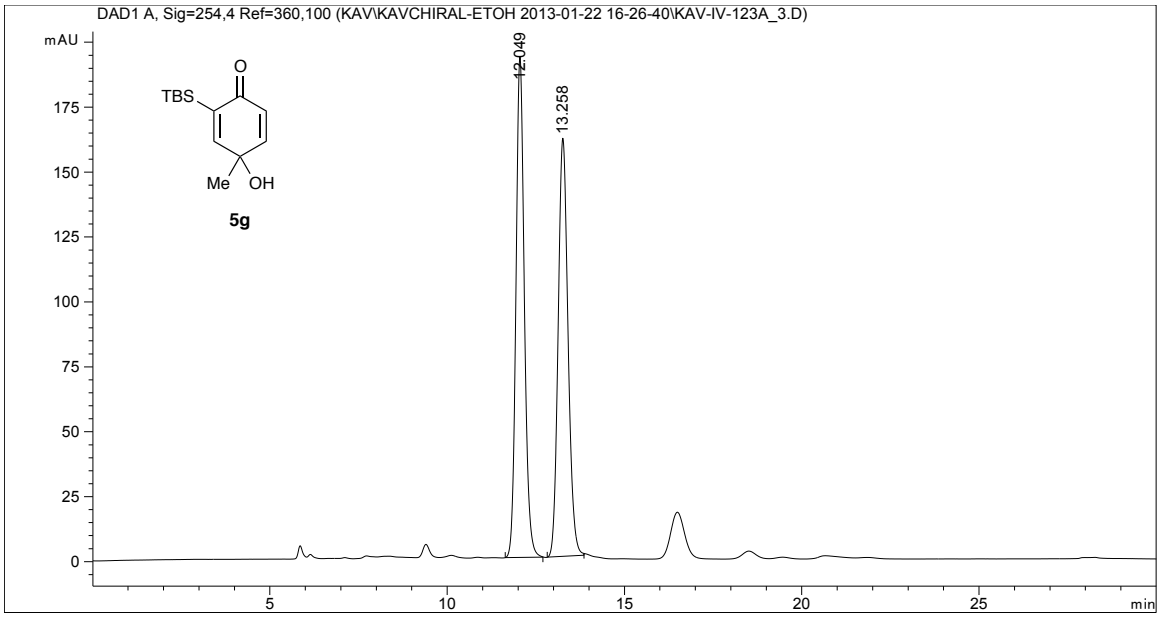
5f with catalyst **8e:**

Retention Time (min)	Area Percent
9.8	69.2
11.3	30.8



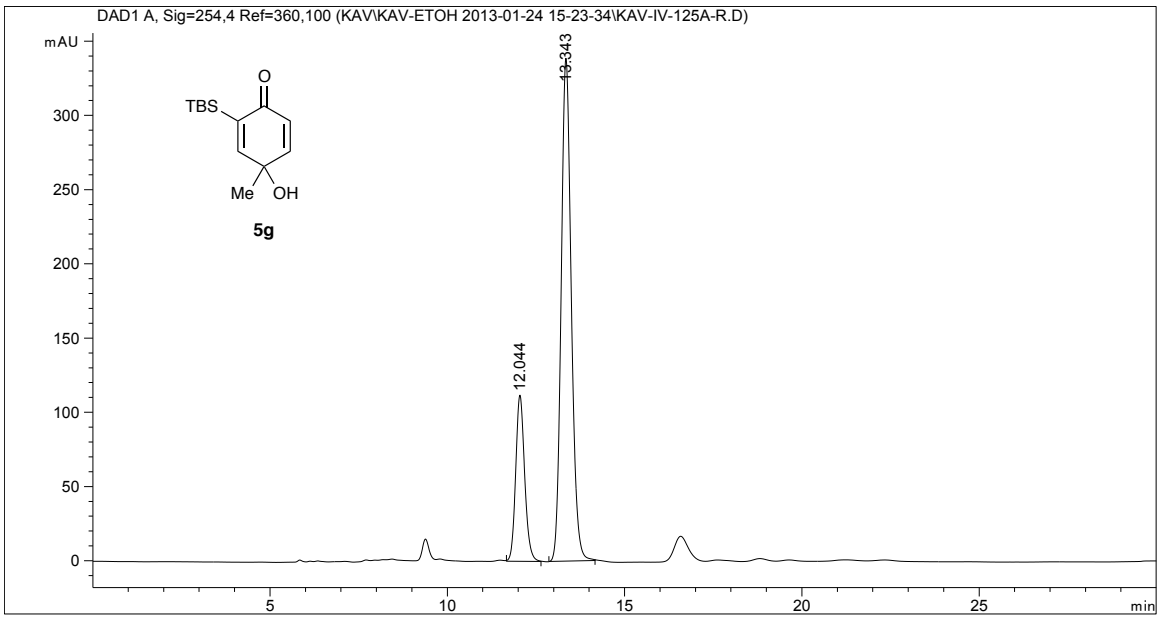
5g – racemic:

Retention Time (min)	Area Percent
12.0	50.4
13.3	49.6



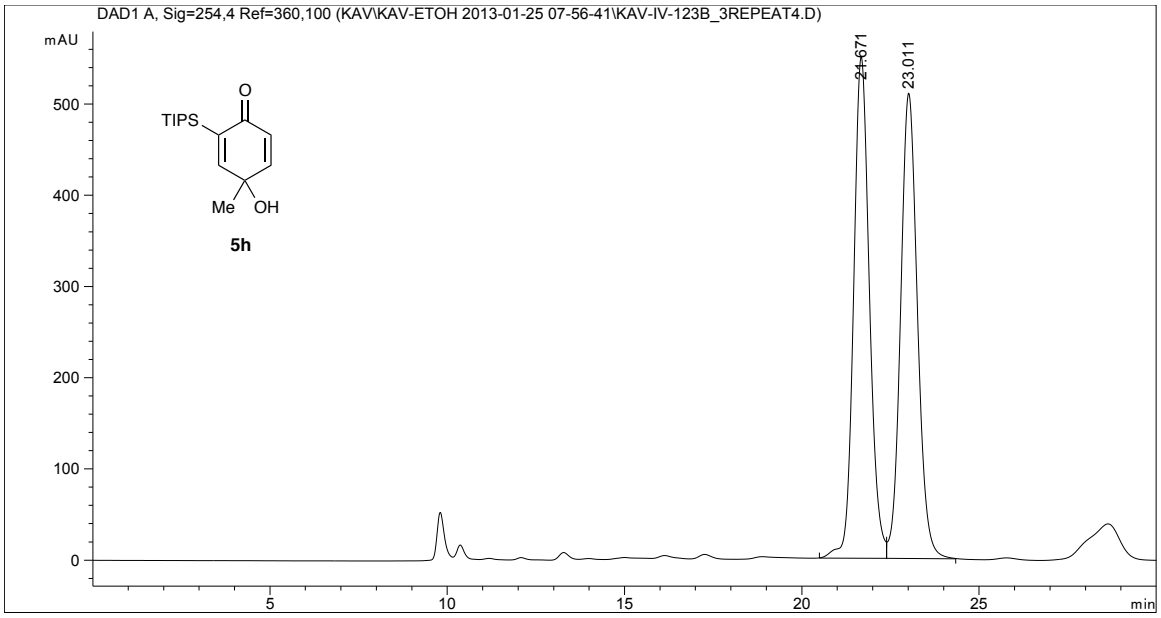
5g with catalyst **8e**:

Retention Time (min)	Area Percent
12.0	22.7
13.3	77.3



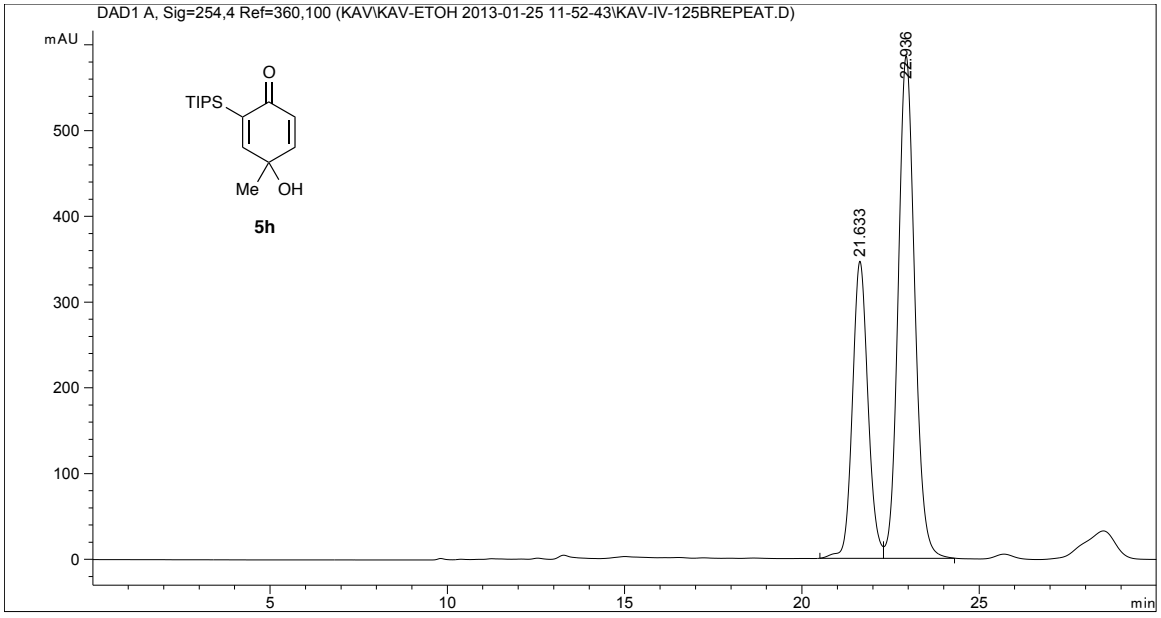
5h – racemic:

Retention Time (min)	Area Percent
21.7	50.4
23.0	49.6



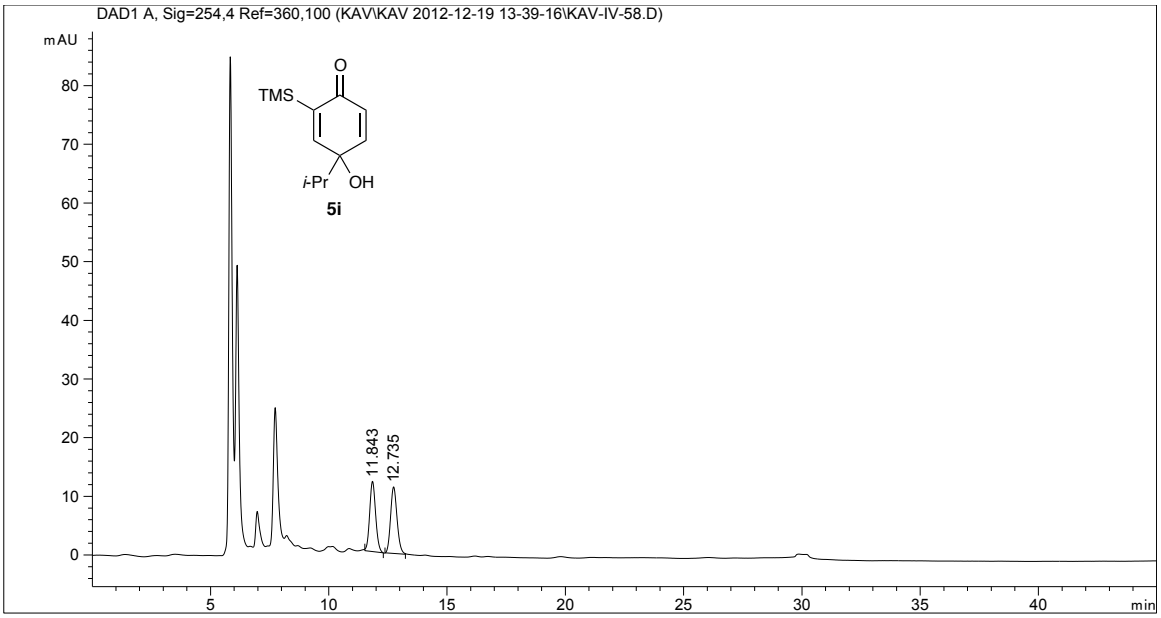
5h with catalyst **8e**:

Retention Time (min)	Area Percent
21.6	35.7
22.9	64.3



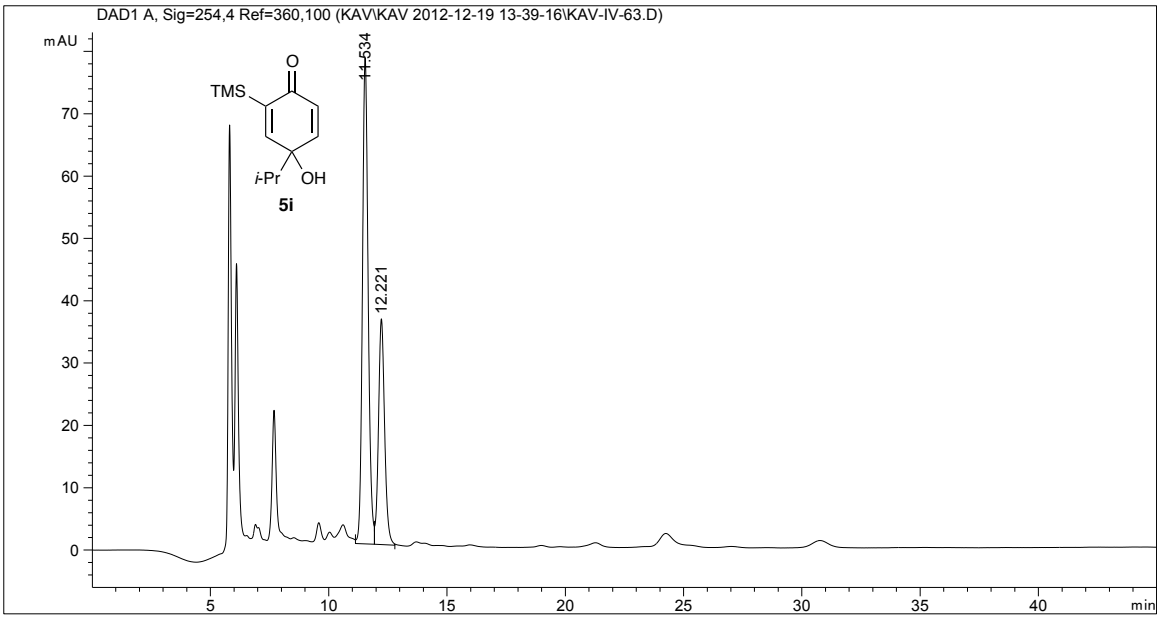
5i – racemic:

Retention Time (min)	Area Percent
11.8	49.3
12.7	50.7



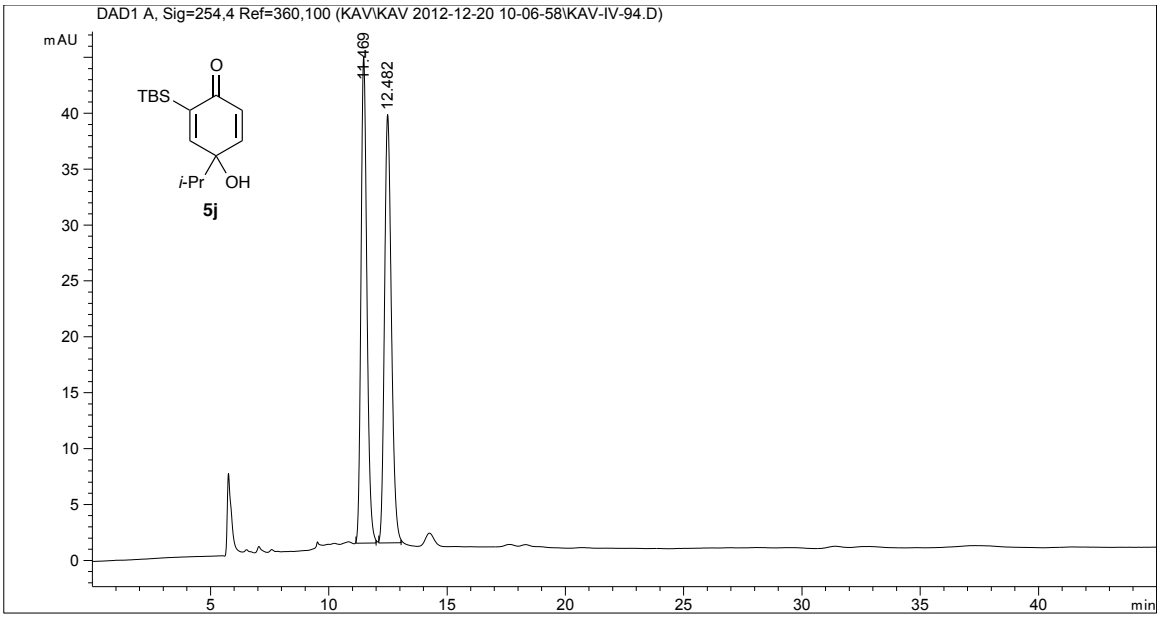
5i with catalyst **8e:**

Retention Time (min)	Area Percent
11.5	66.8
12.2	33.2



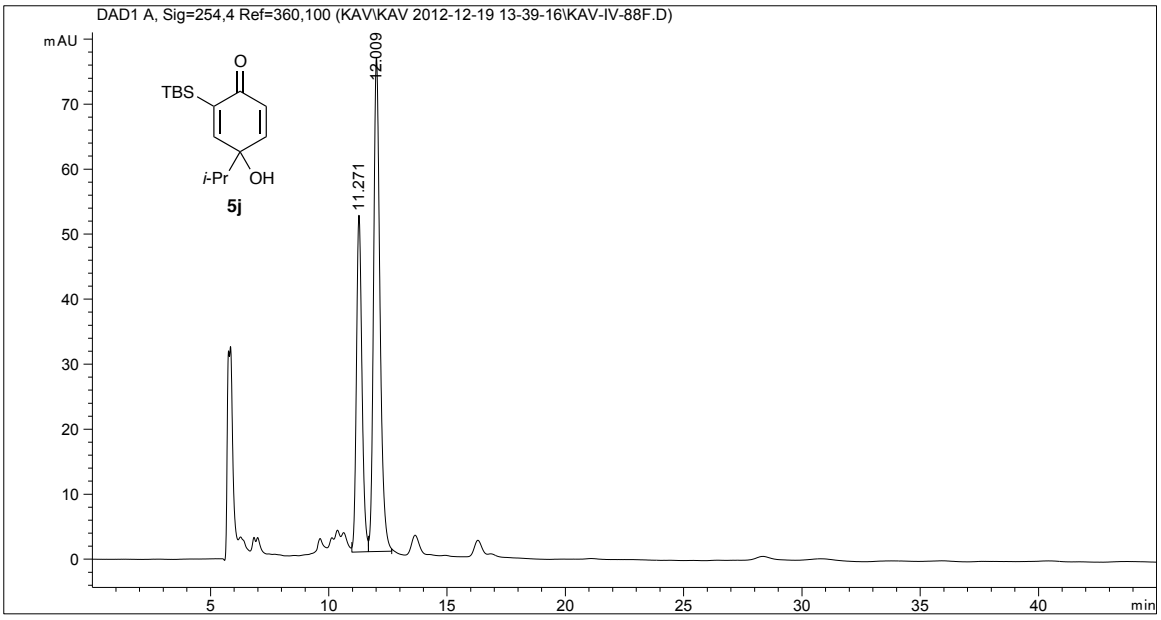
5j – racemic:

Retention Time (min)	Area Percent
11.5	49.3
12.5	50.7



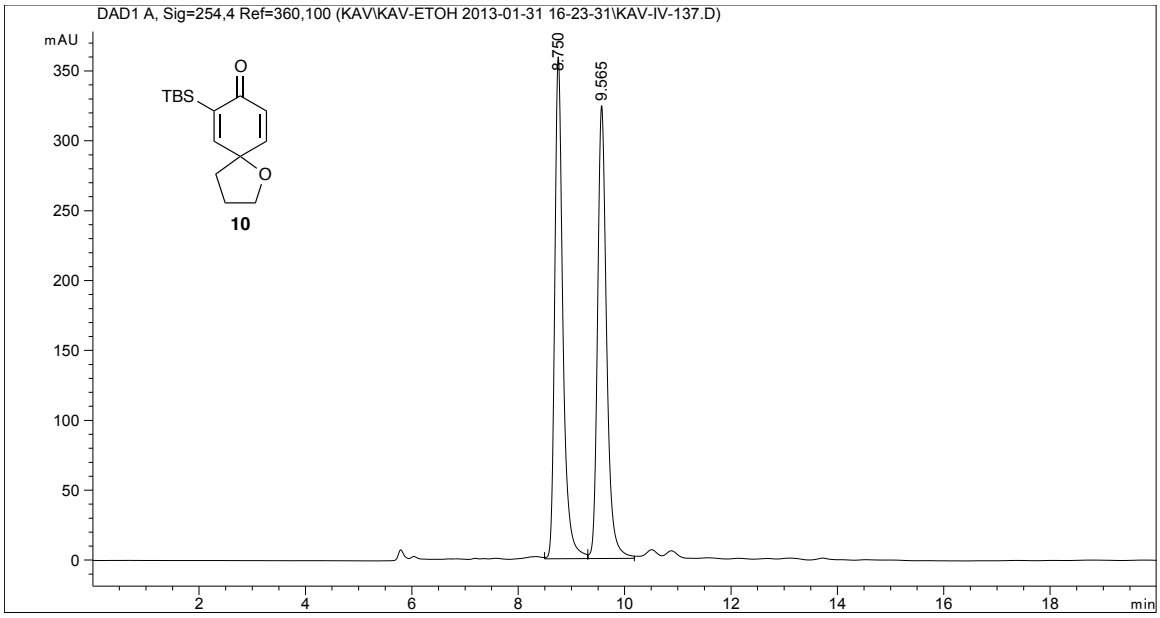
5j with catalyst **8e:**

Retention Time (min)	Area Percent
11.3	37.0
12.0	63.0



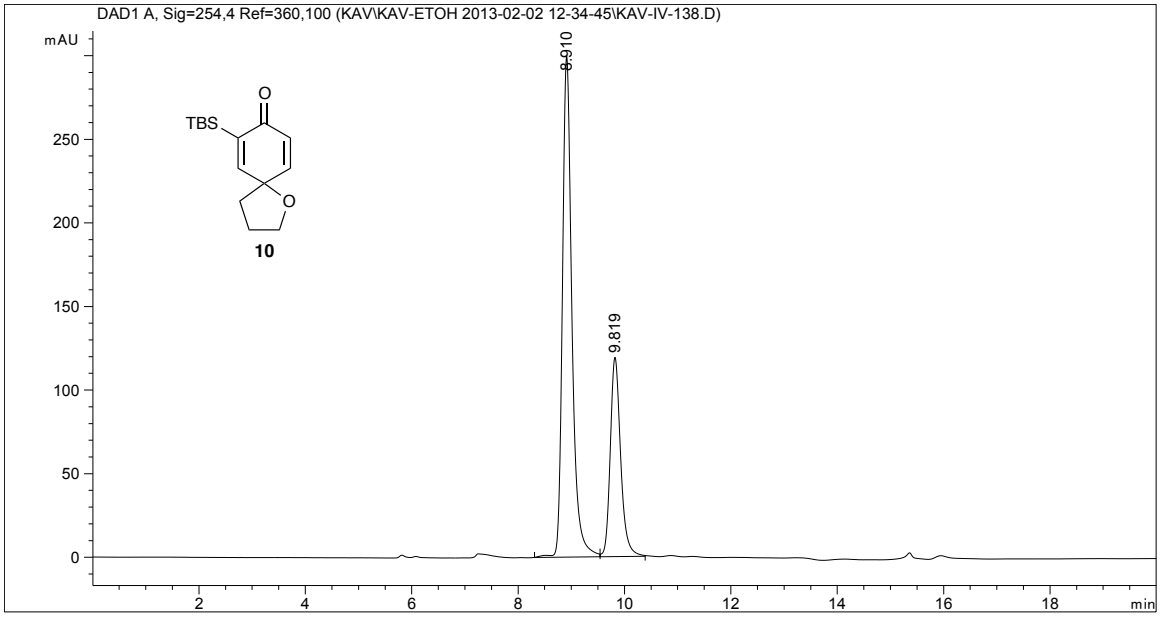
10 – racemic:

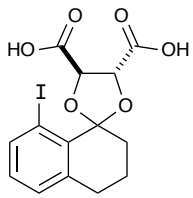
Retention Time (min)	Area Percent
8.8	50.1
9.6	49.9



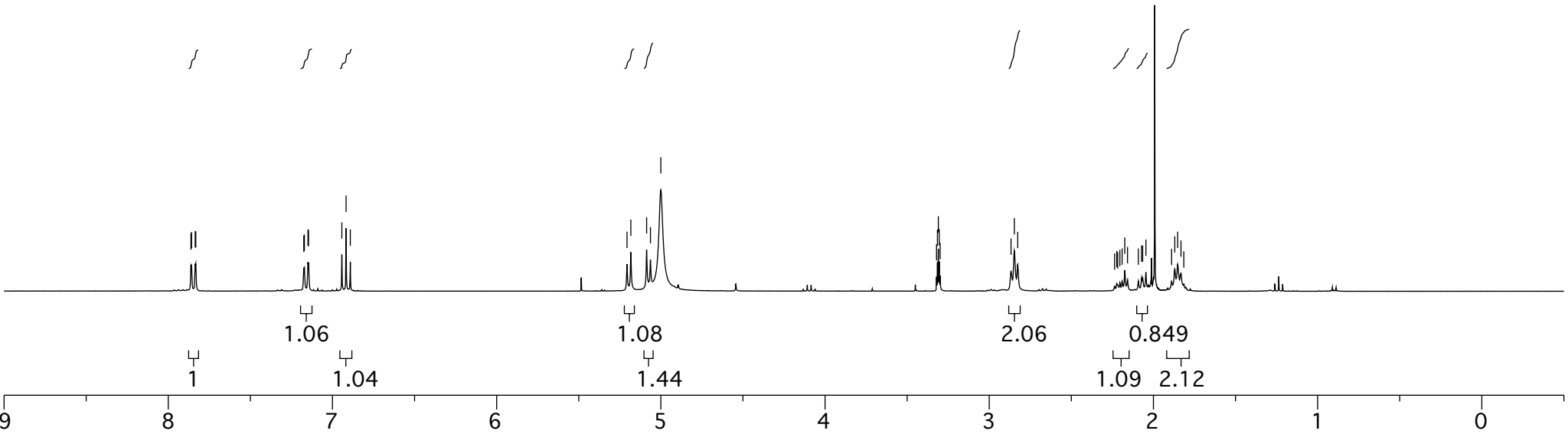
10 with catalyst **8e**:

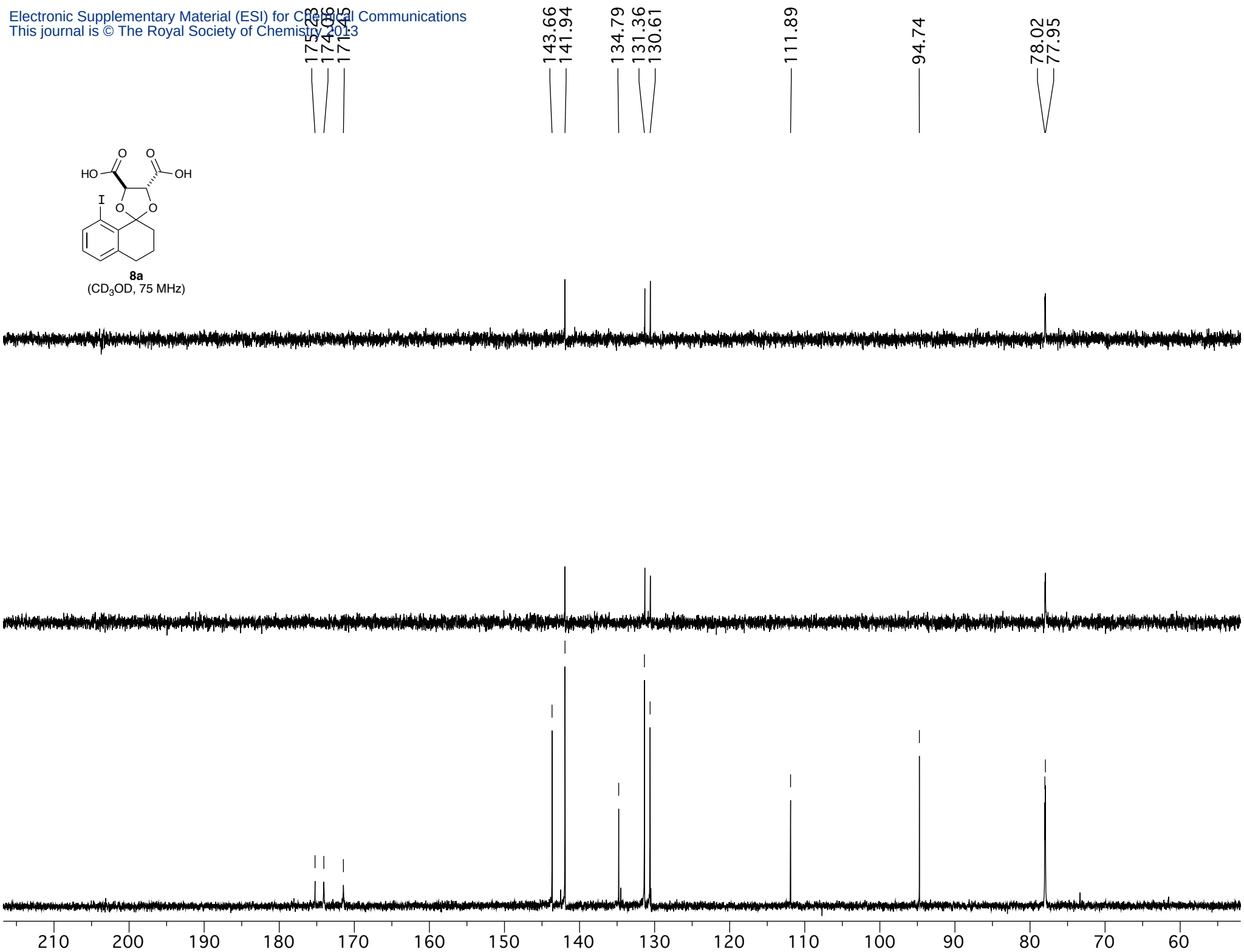
Retention Time (min)	Area Percent
8.9	69.8
9.8	30.2

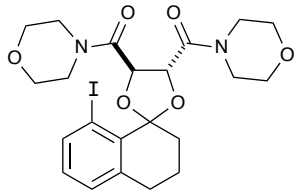




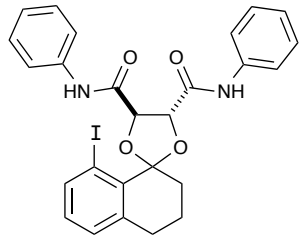
8a
(CD_3OD, 300 MHz)



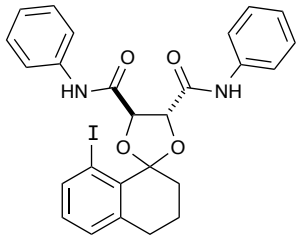




8b
($CDCl_3$, 300 MHz)

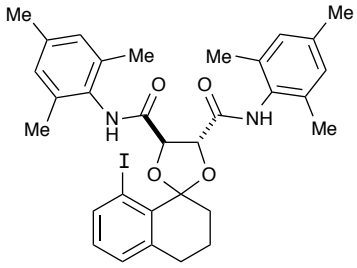


8c
($CDCl_3$, 300 MHz)



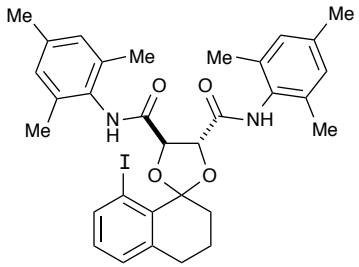
8c
($CDCl_3$, 75 MHz)

168.30
167.06
142.77
141.17
137.60
136.03
133.03
130.84
129.91
129.31
129.22
125.32
124.66
120.45
119.80
111.50
94.04
78.41
77.58
77.30
77.16
76.74
34.87
31.34
19.89



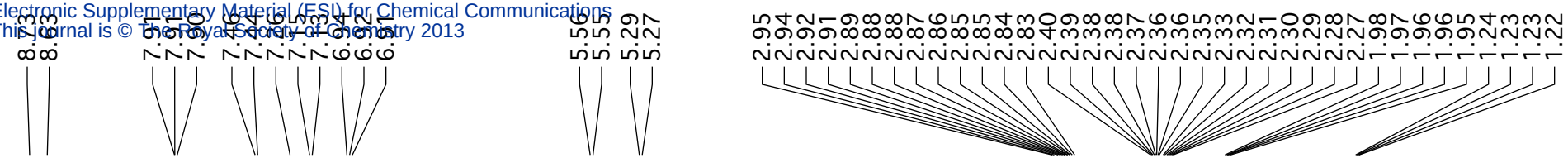
8e
($CDCl_3$, 500 MHz)

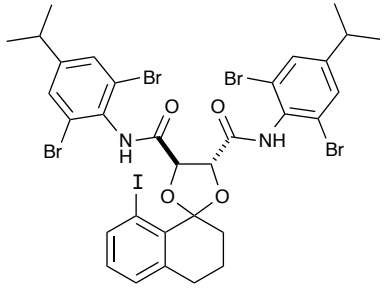
169.22
166.38
142.57
141.16
137.29
137.27
134.89
134.85
133.21
130.71
130.27
130.15
129.75
129.18
111.07
94.13
77.95
77.71
77.58
77.16
76.74
34.76
31.35
21.04
20.01
19.10
18.68



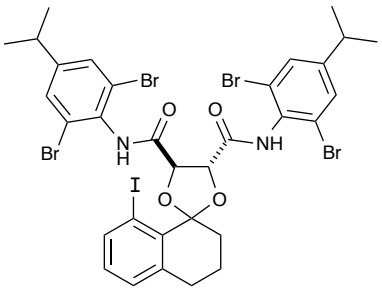
8e
($CDCl_3$, 75 MHz)

ppm 200 180 160 140 120 100 80 60 40 20 0





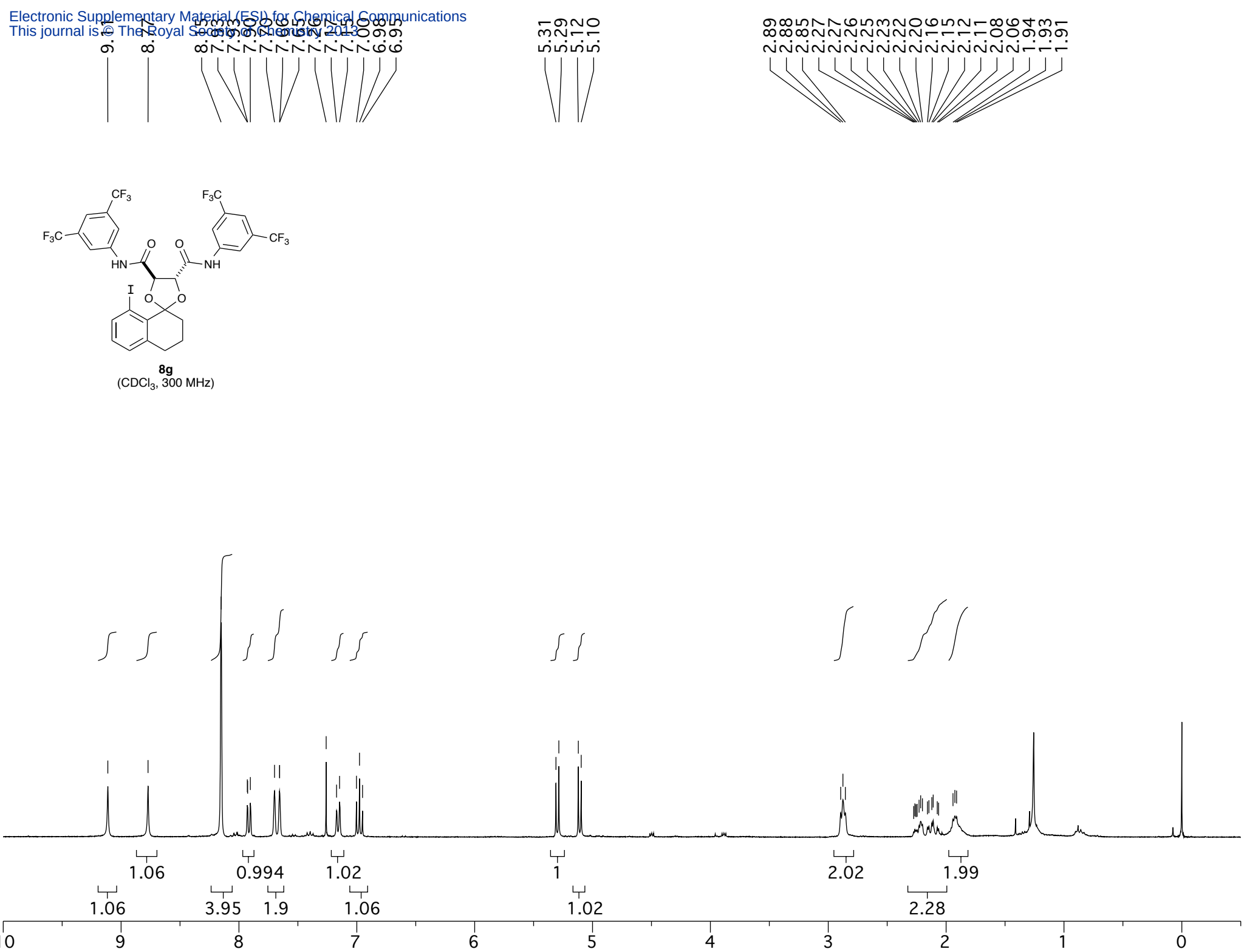
8f
($CDCl_3$, 500 MHz)



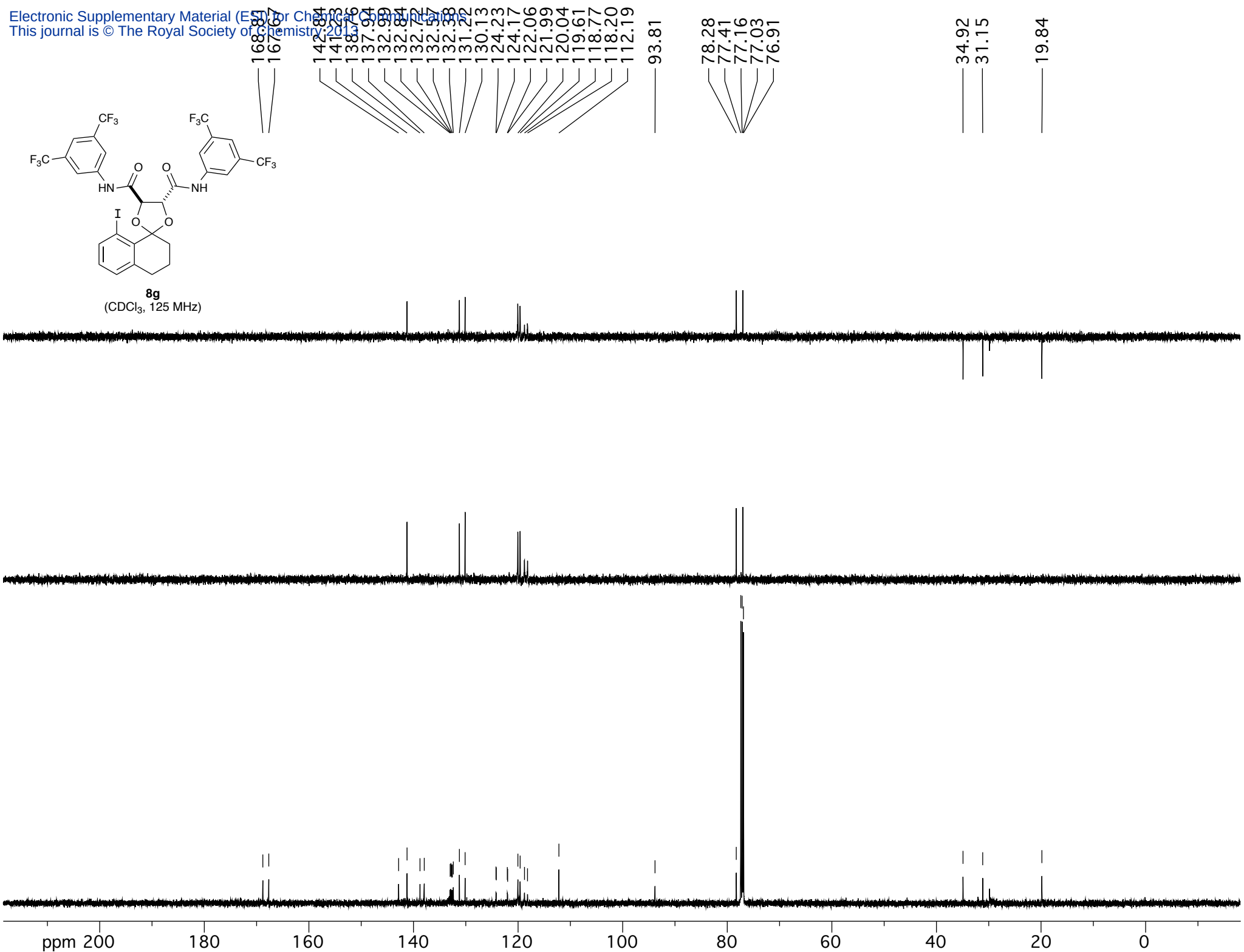
8f
($CDCl_3$, 125 MHz)

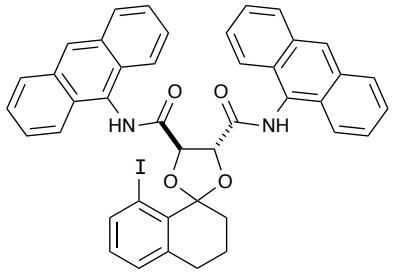
169.26
166.08
151.70
151.38
142.61
141.14
133.12
131.05
130.74
130.69
129.64
123.66
123.57
111.51
94.59
77.63
77.41
77.21
77.16
76.91
34.95
33.75
33.73
31.40
23.72
20.05

ppm 200 180 160 140 120 100 80 60 40 20 0

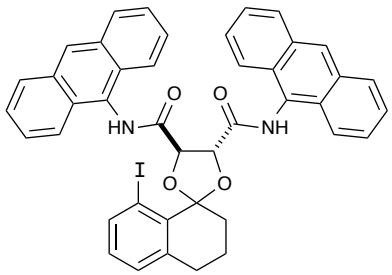


8g
($CDCl_3$, 300 MHz)



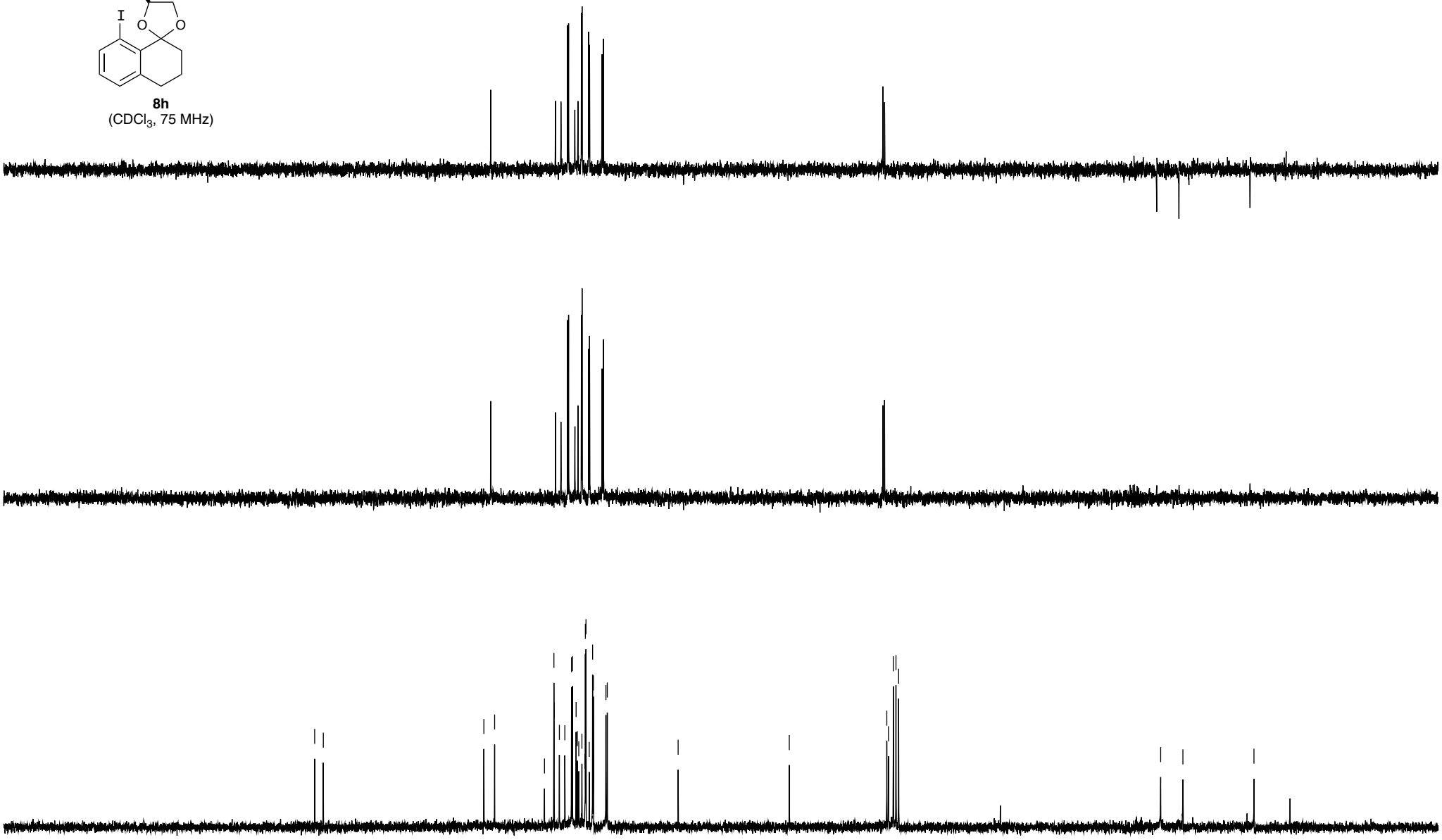


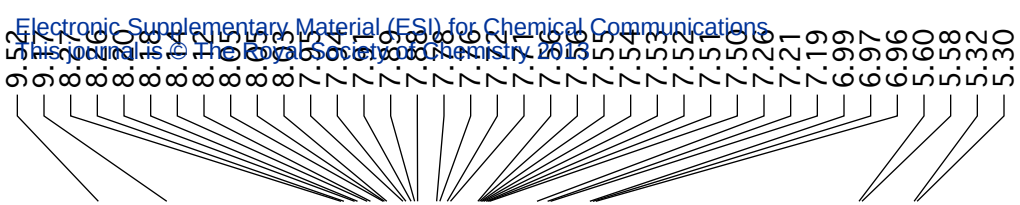
8h
($CDCl_3$, 500 MHz)

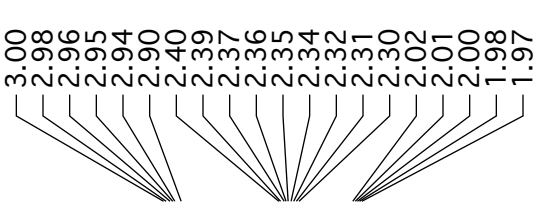


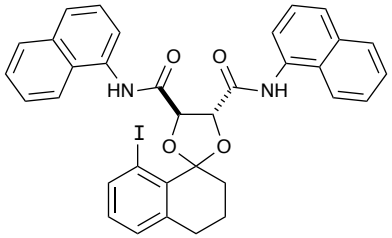
8h
($CDCl_3$, 75 MHz)

169.86
168.48
142.83
141.76
133.71
131.66
131.62
130.84
129.96
128.90
128.55
128.17
127.98
127.74
127.24
126.76
126.69
126.60
126.08
125.54
125.41
123.41
123.20
111.90
94.17
78.62
78.36
77.58
77.16
76.74
34.95
31.40
20.07

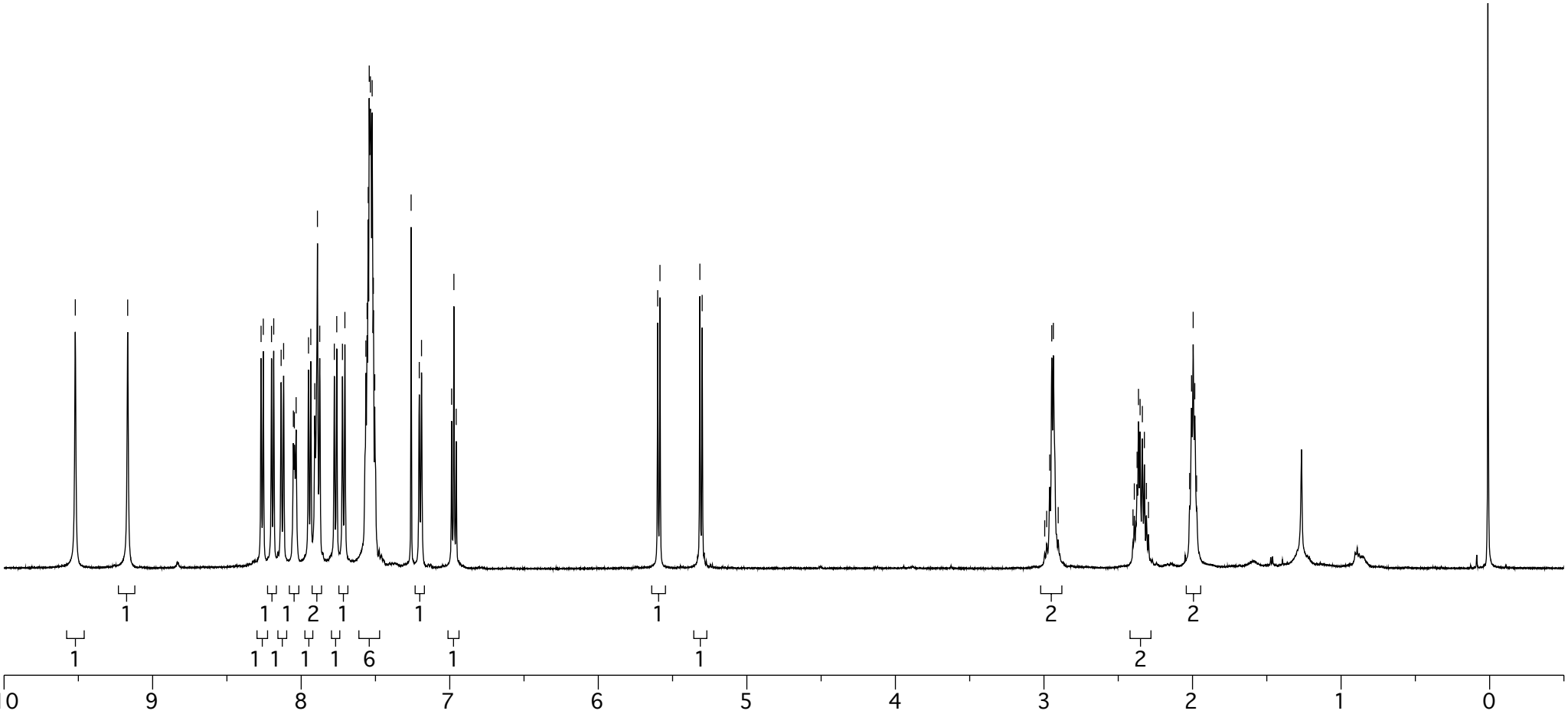


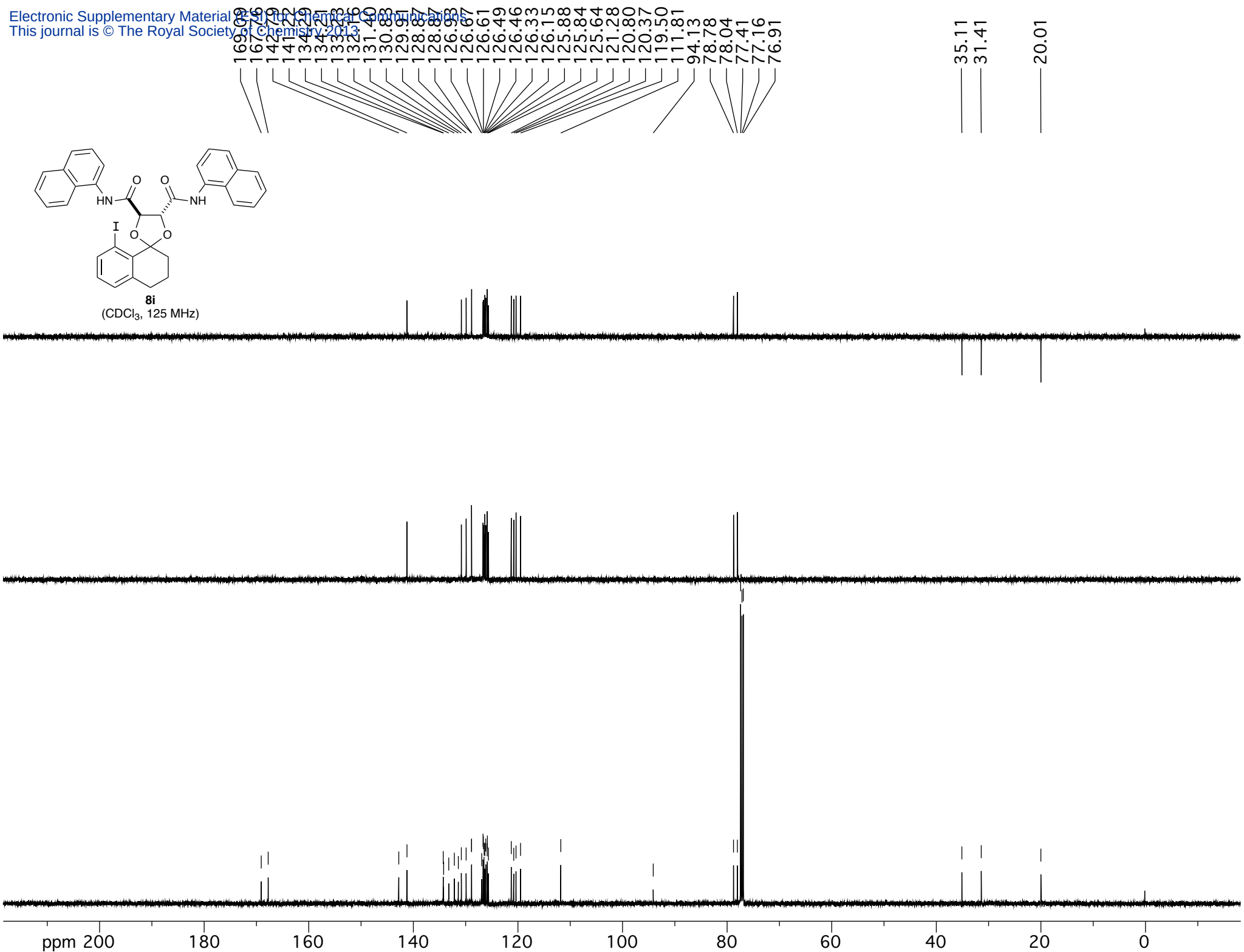


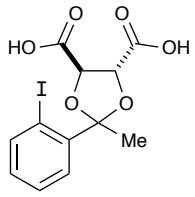




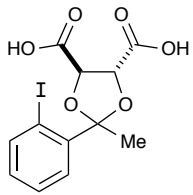
8i
($CDCl_3$, 500 MHz)



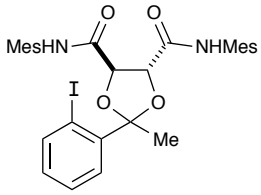




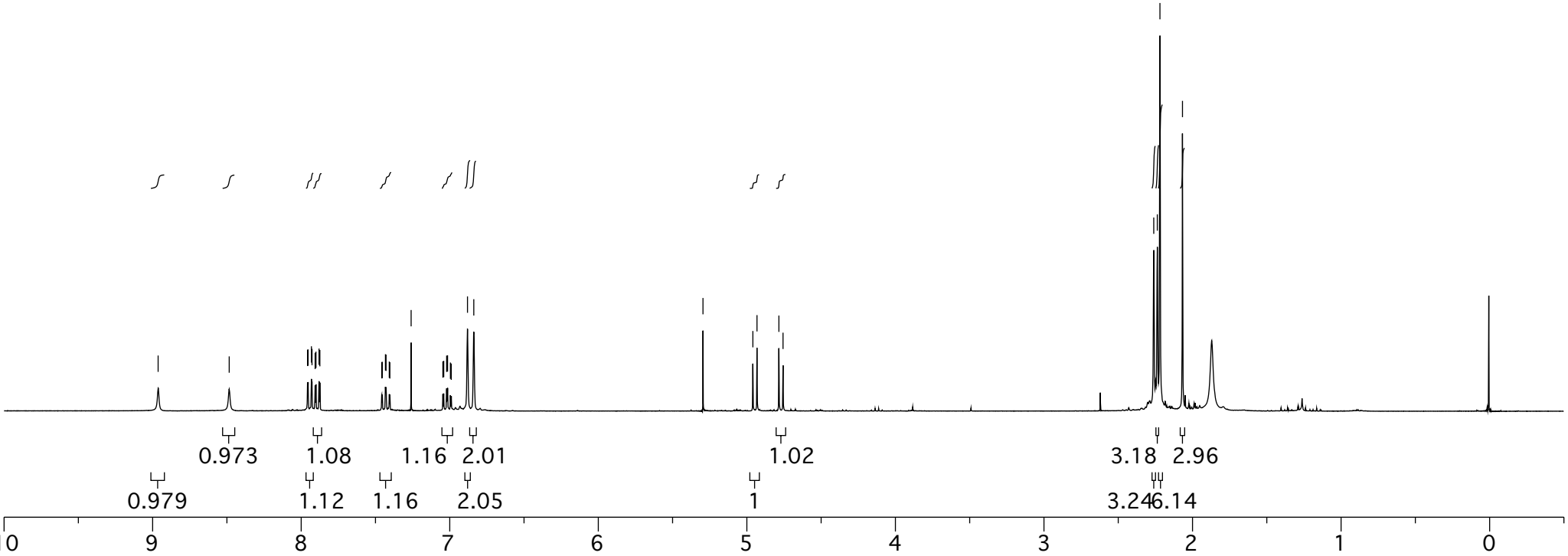
S1
(CD_3OD, 300 MHZ)

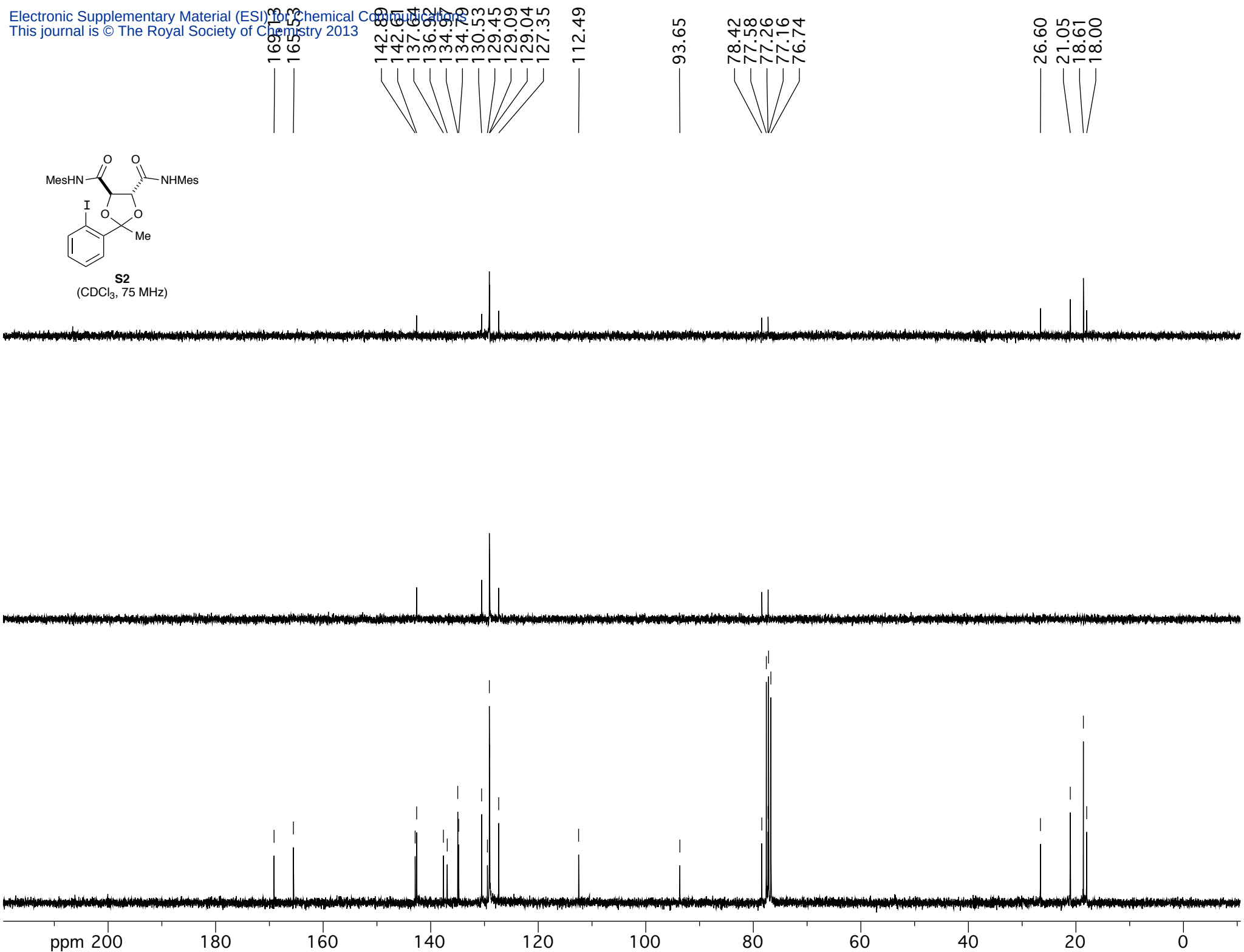


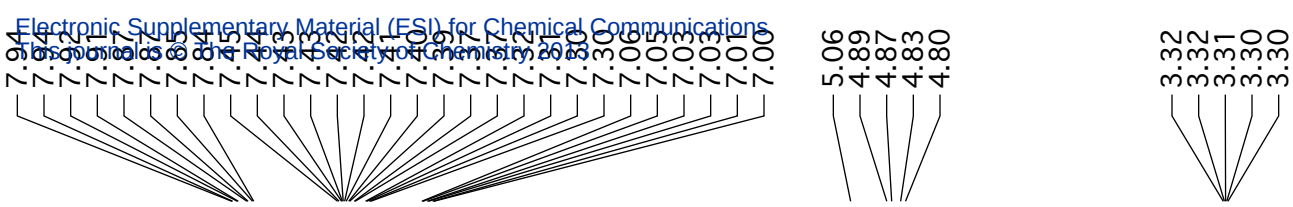
S1
(CD_3OD, 75 MHZ)

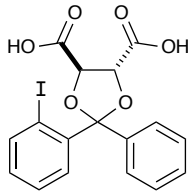


S2
($CDCl_3$, 300 MHz)

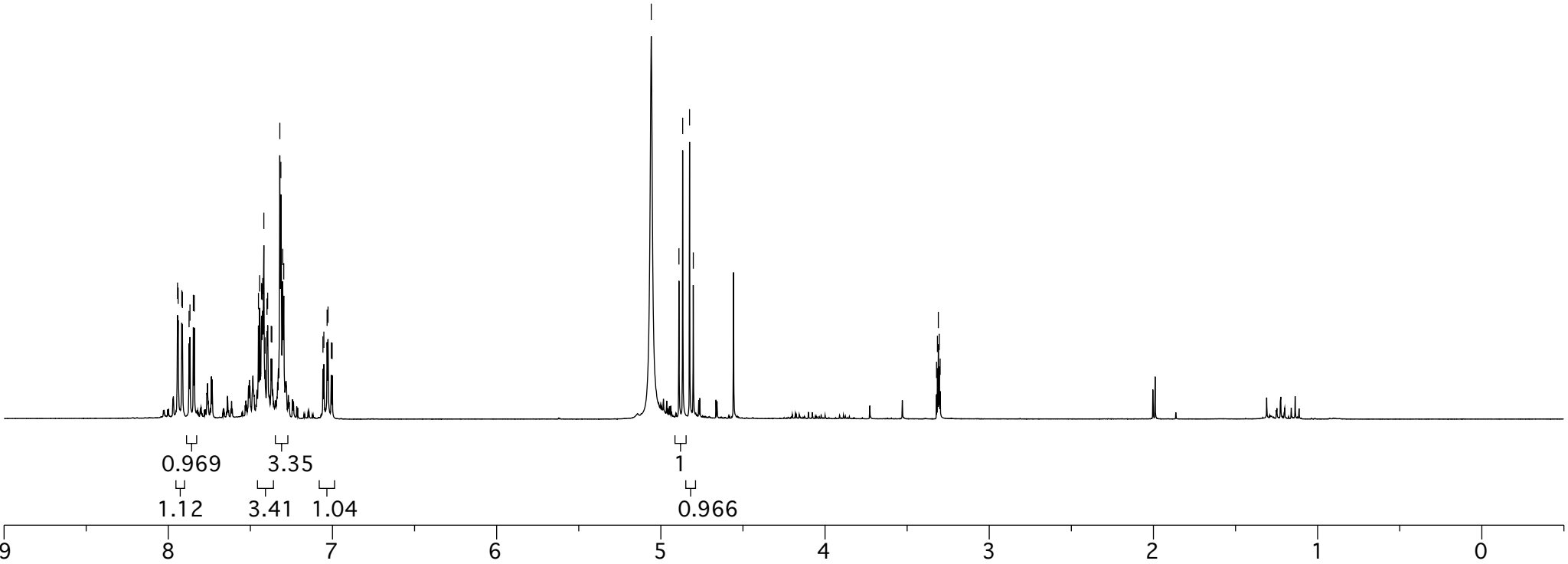


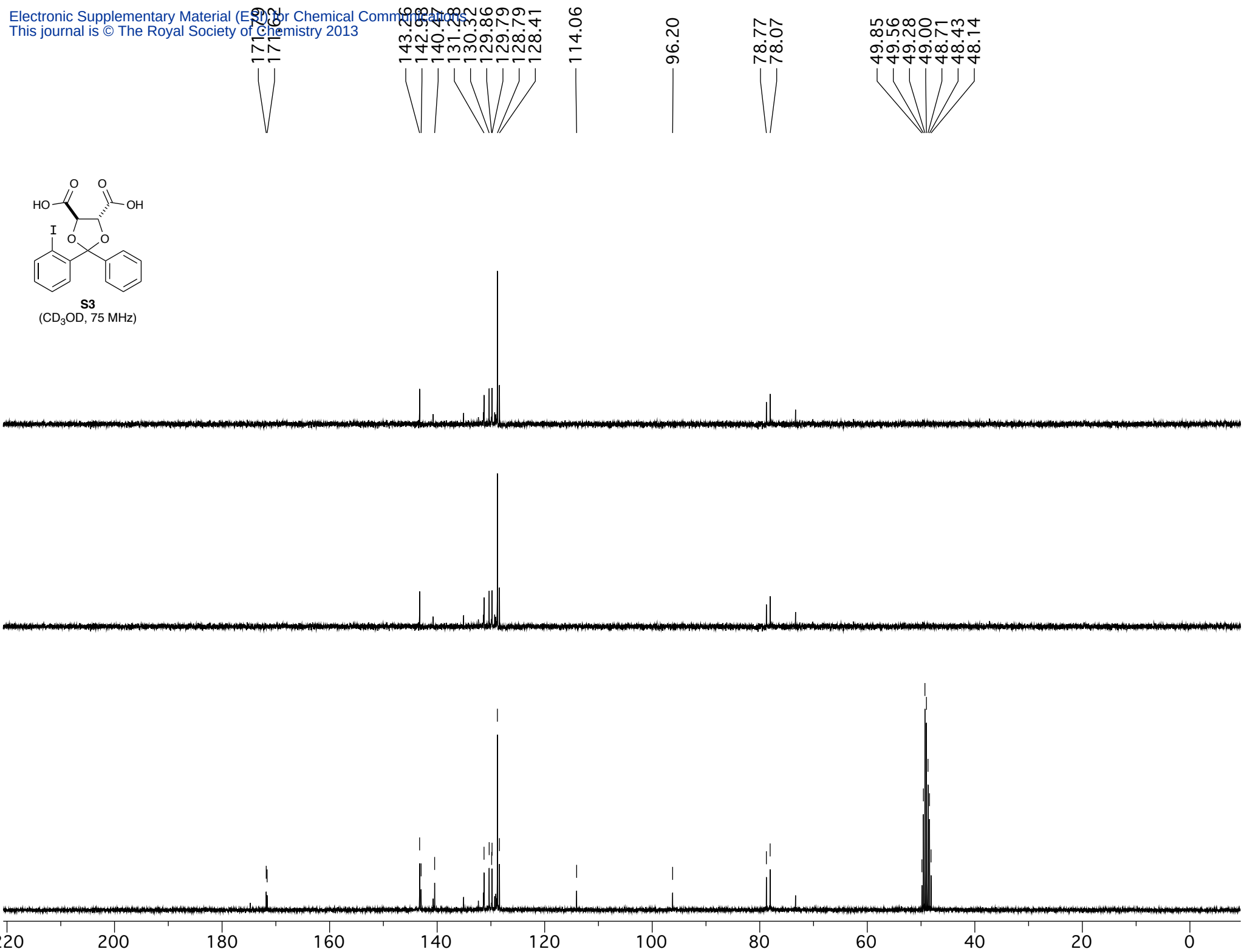




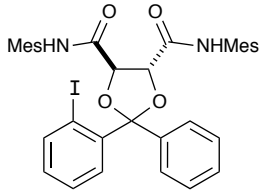


S3
(CD_3OD, 300 MHz)

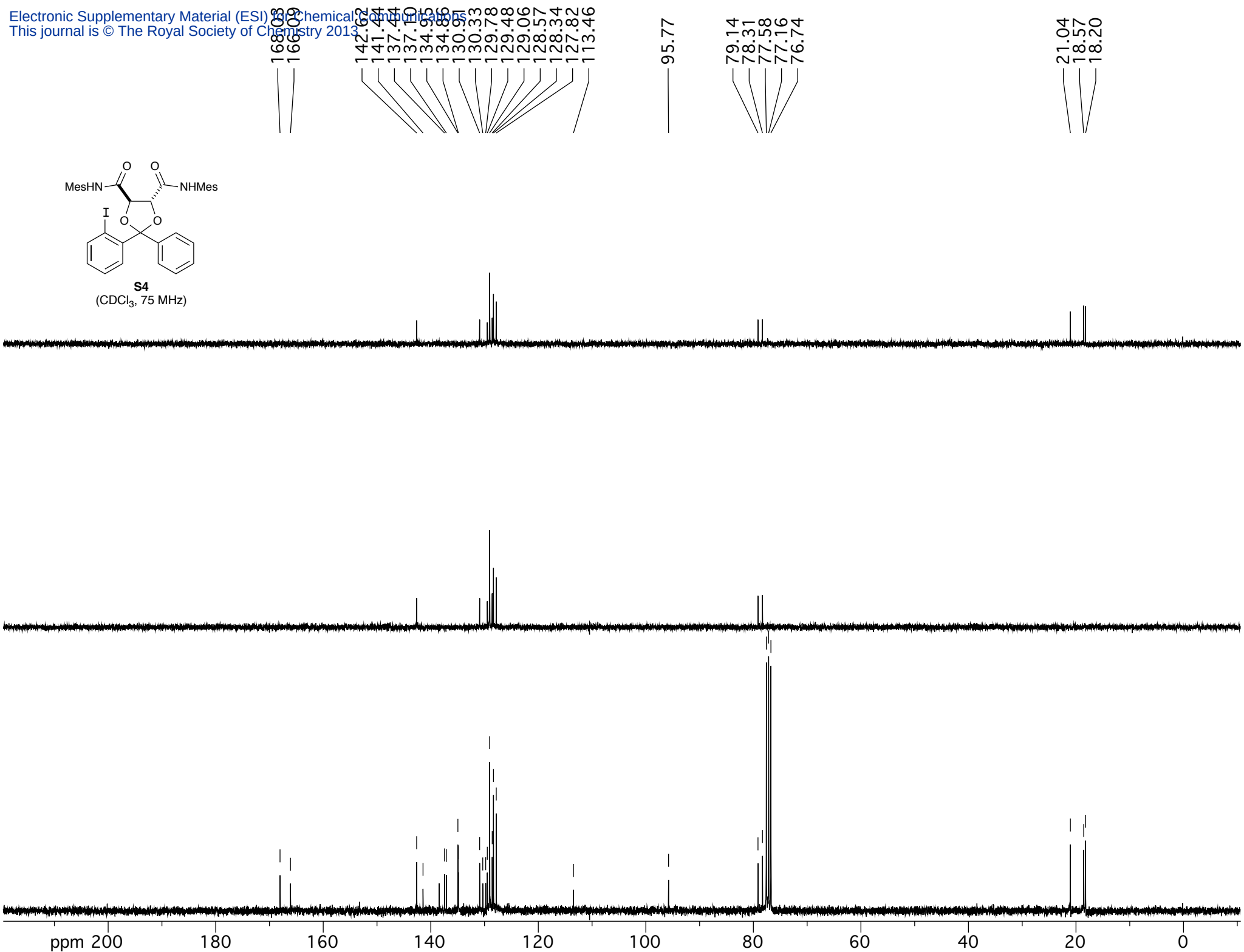


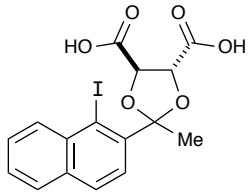


S3
(CD_3OD, 75 MHz)

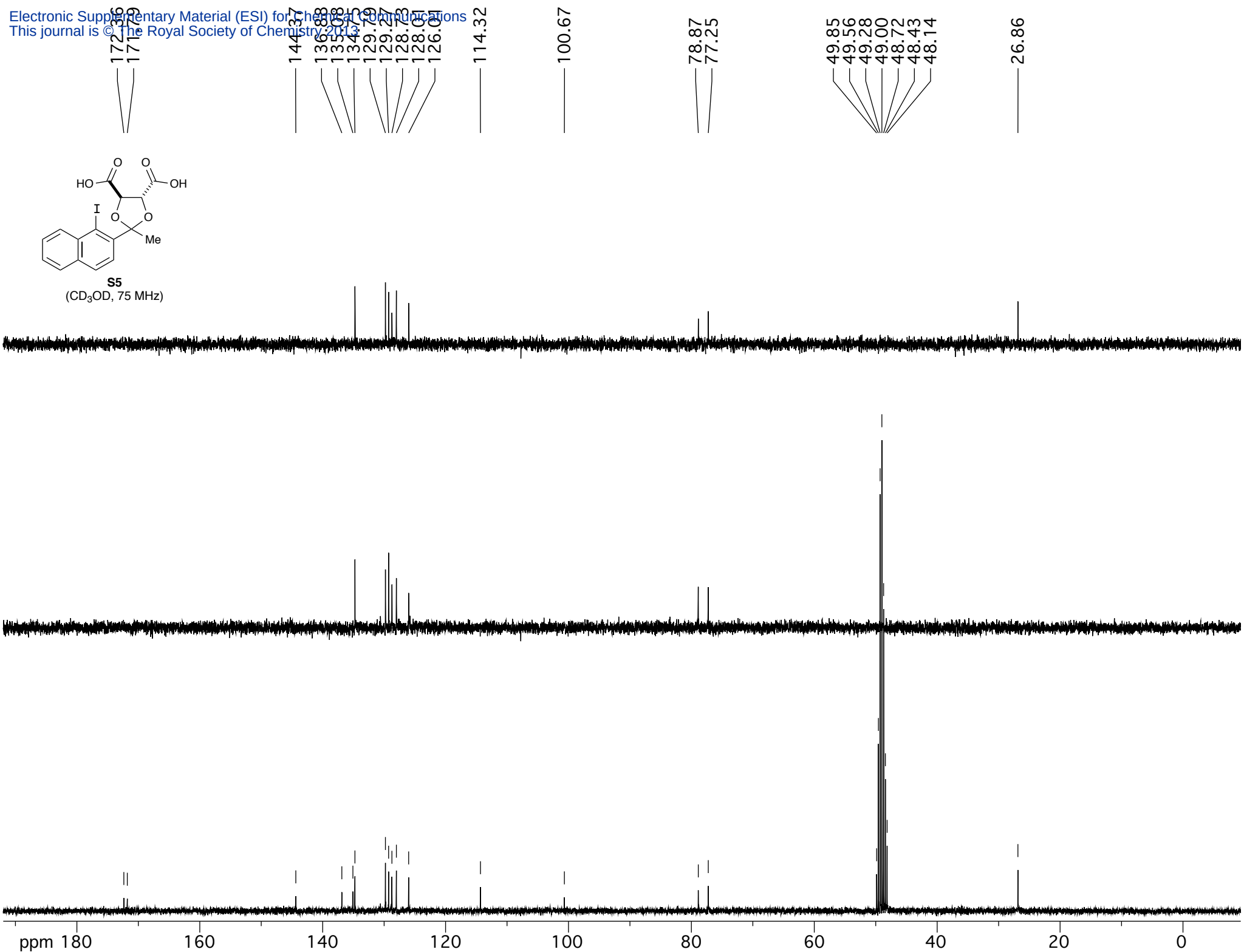


S4
($CDCl_3$, 300 MHz)

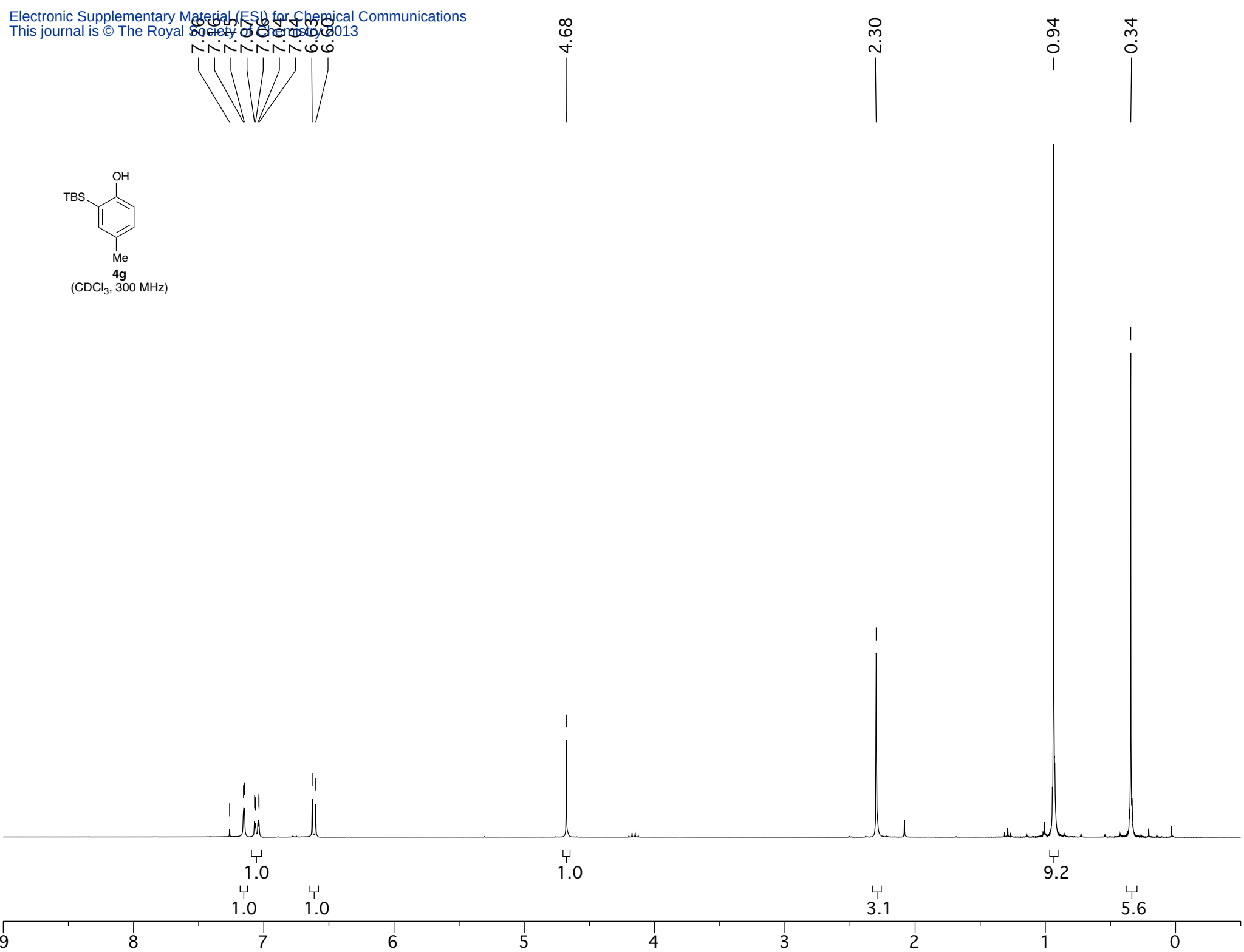


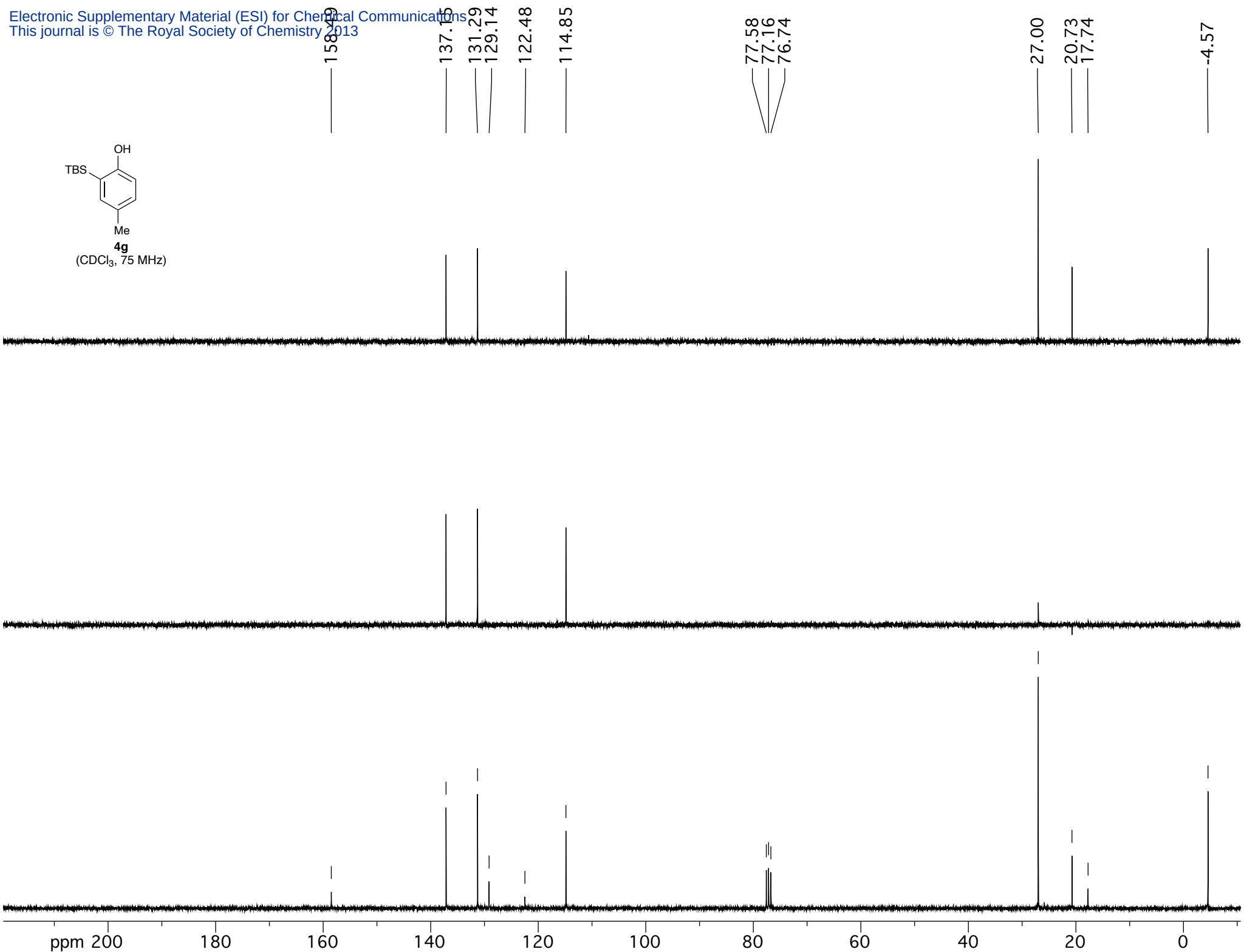


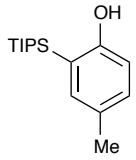
S5
(CD_3OD, 300 MHz)



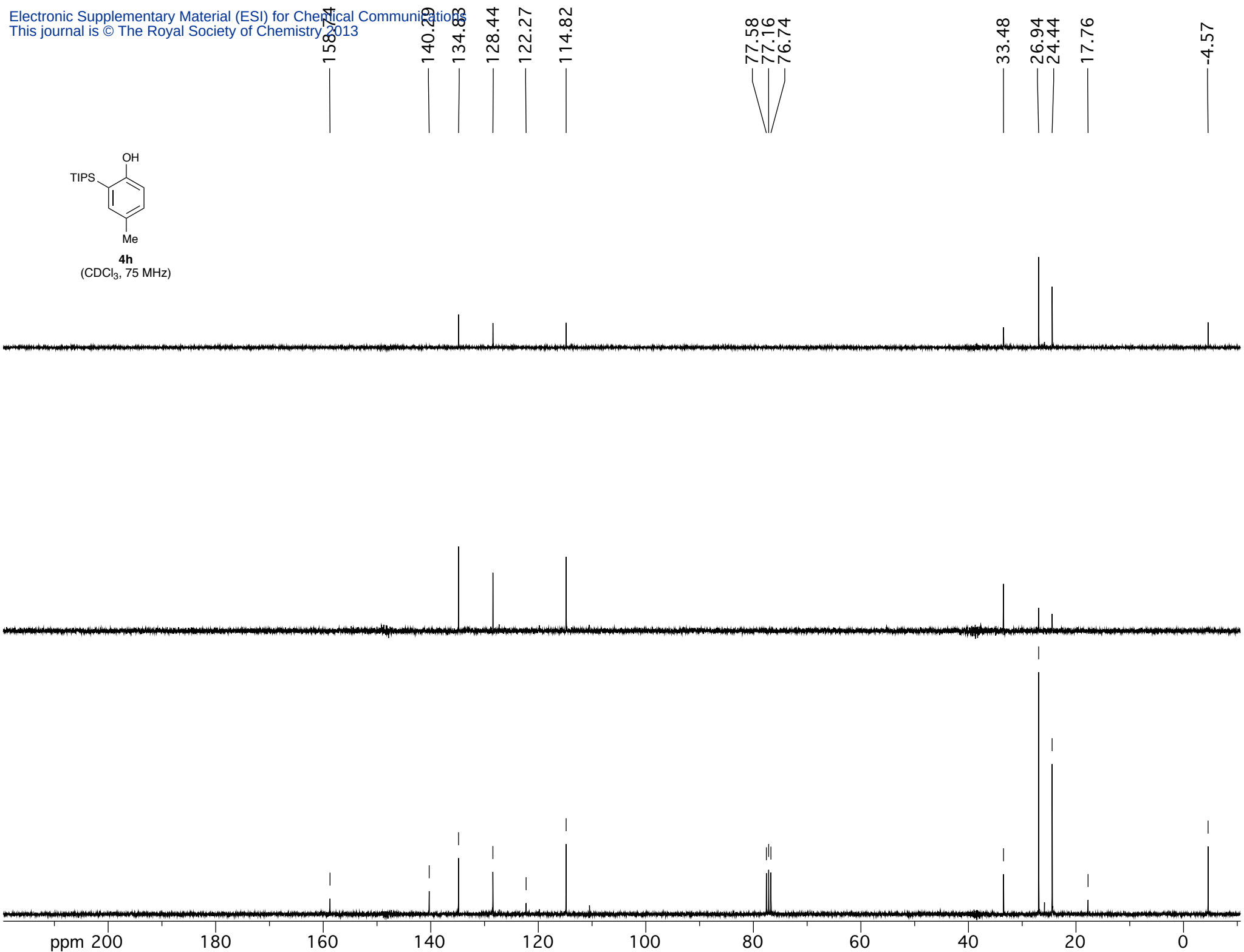
S5
(CD_3OD, 75 MHz)

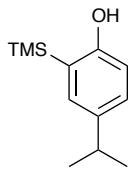






4h
($CDCl_3$, 75 MHz)



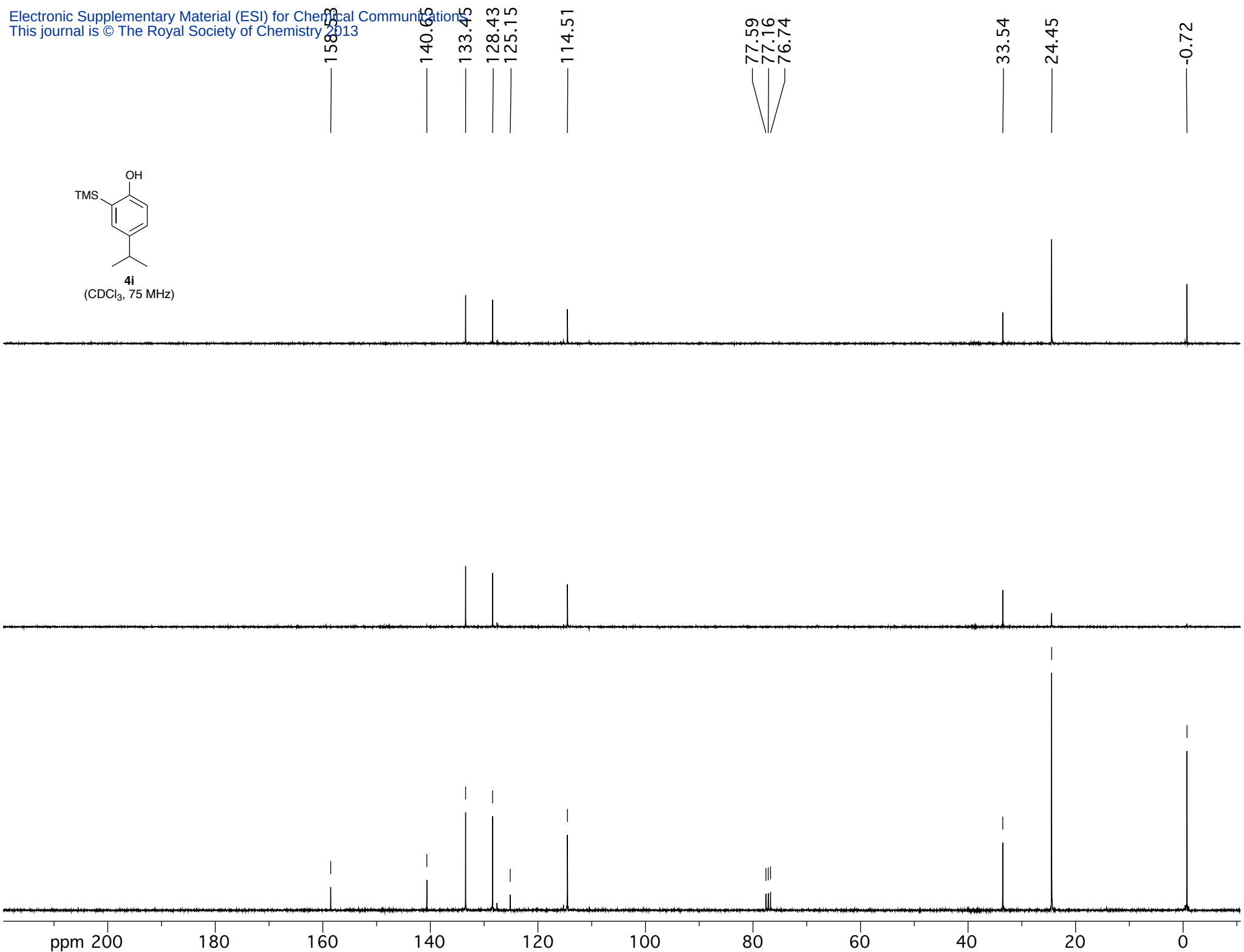


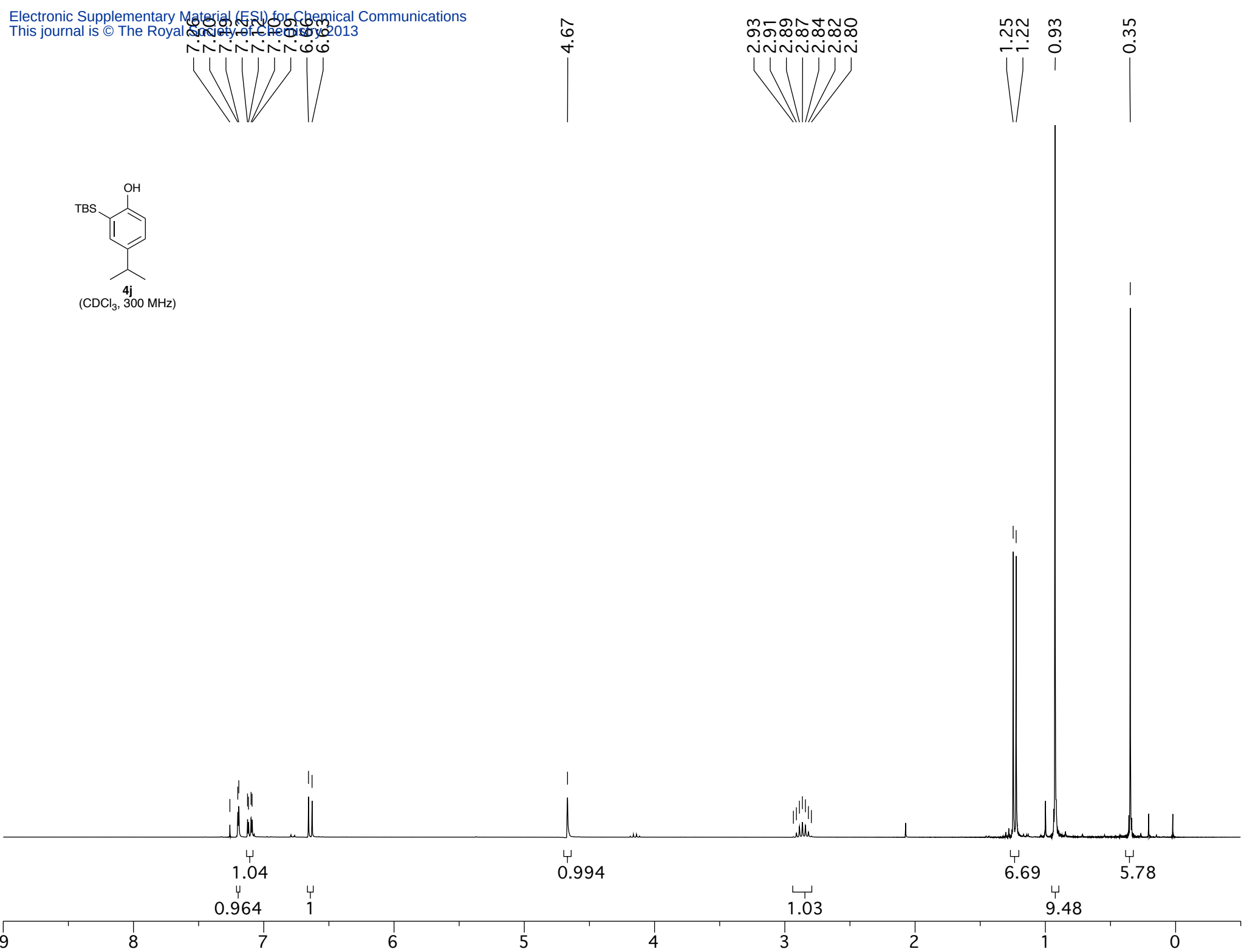
4i
($CDCl_3$, 300 MHz)

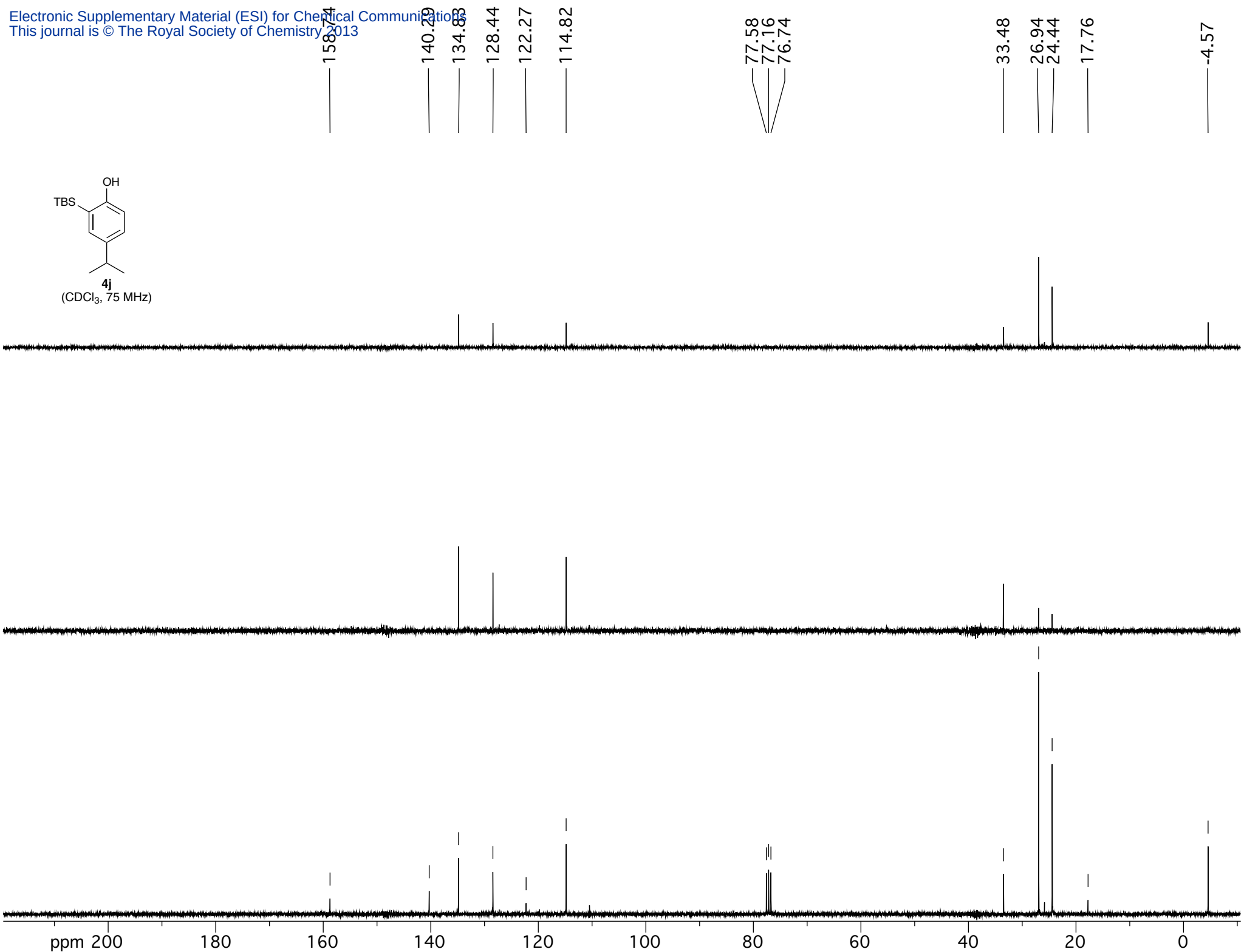
7.29
7.28
7.26
6.88
6.85
4.84
4.83
3.01
2.99
2.96
2.94
2.92
2.90
2.87
1.33
1.30
0.41

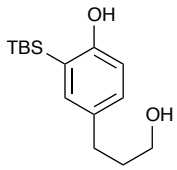
1
0.923
6.11
0.9
0.939
0.987
7.79

9 8 7 6 5 4 3 2 1 0

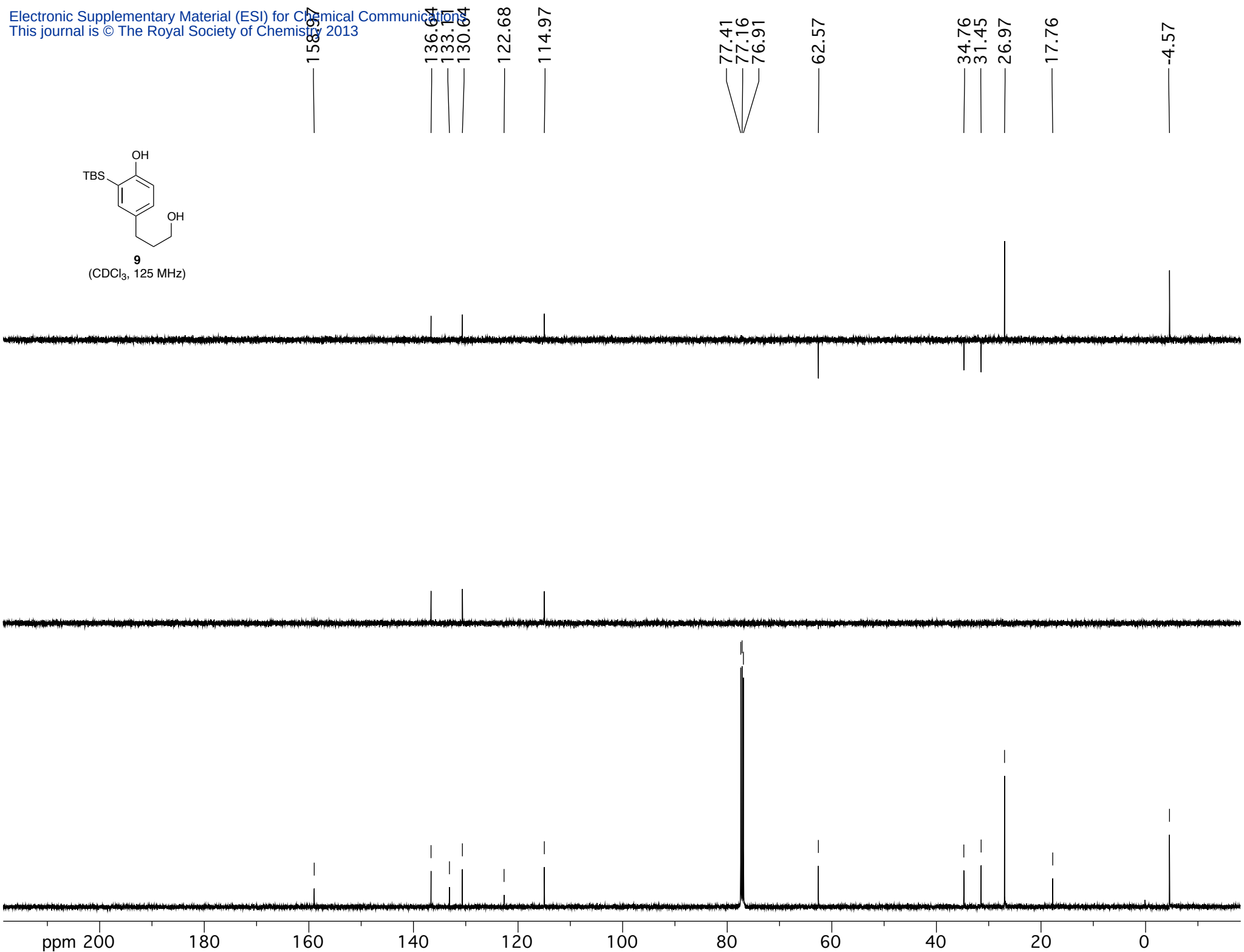


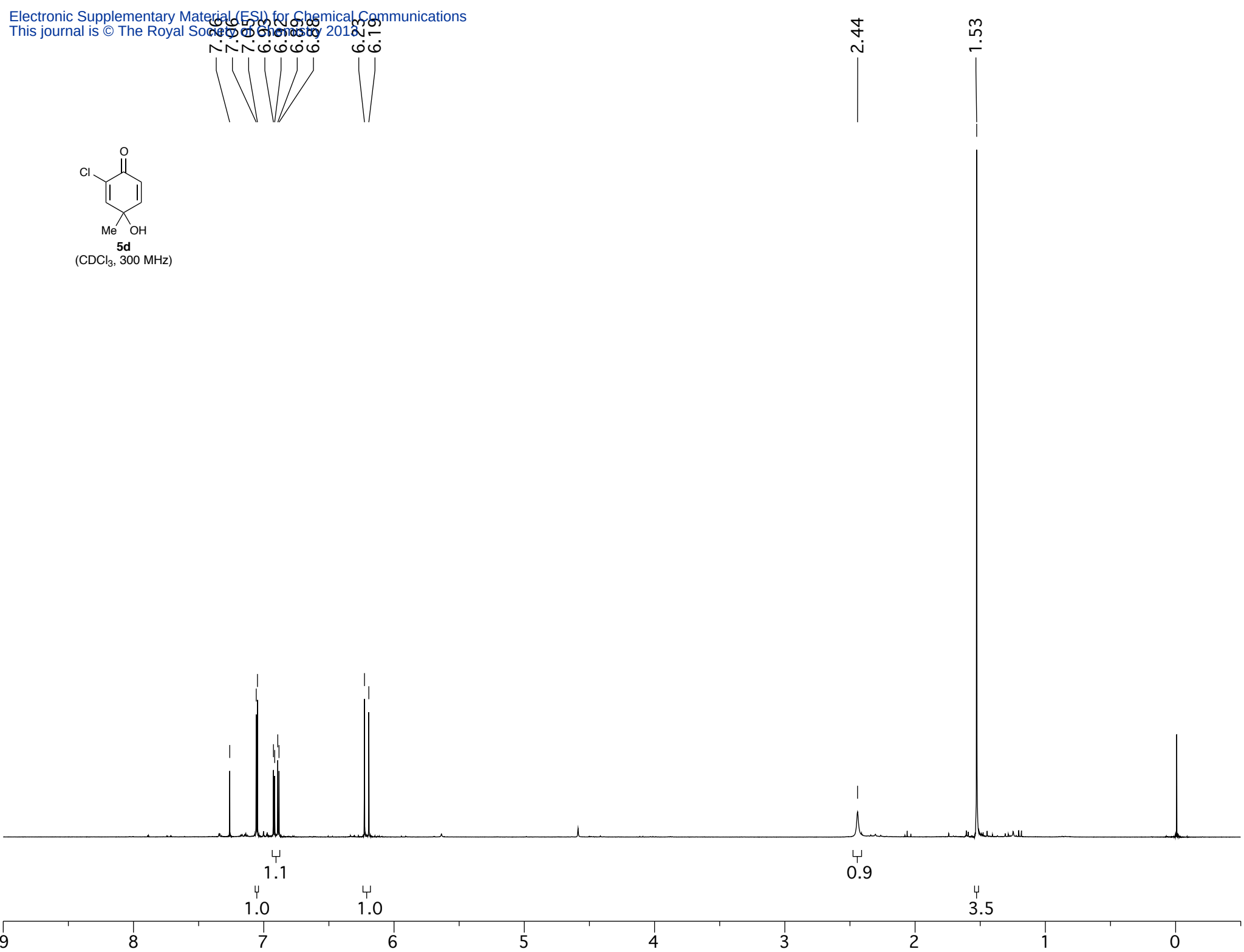


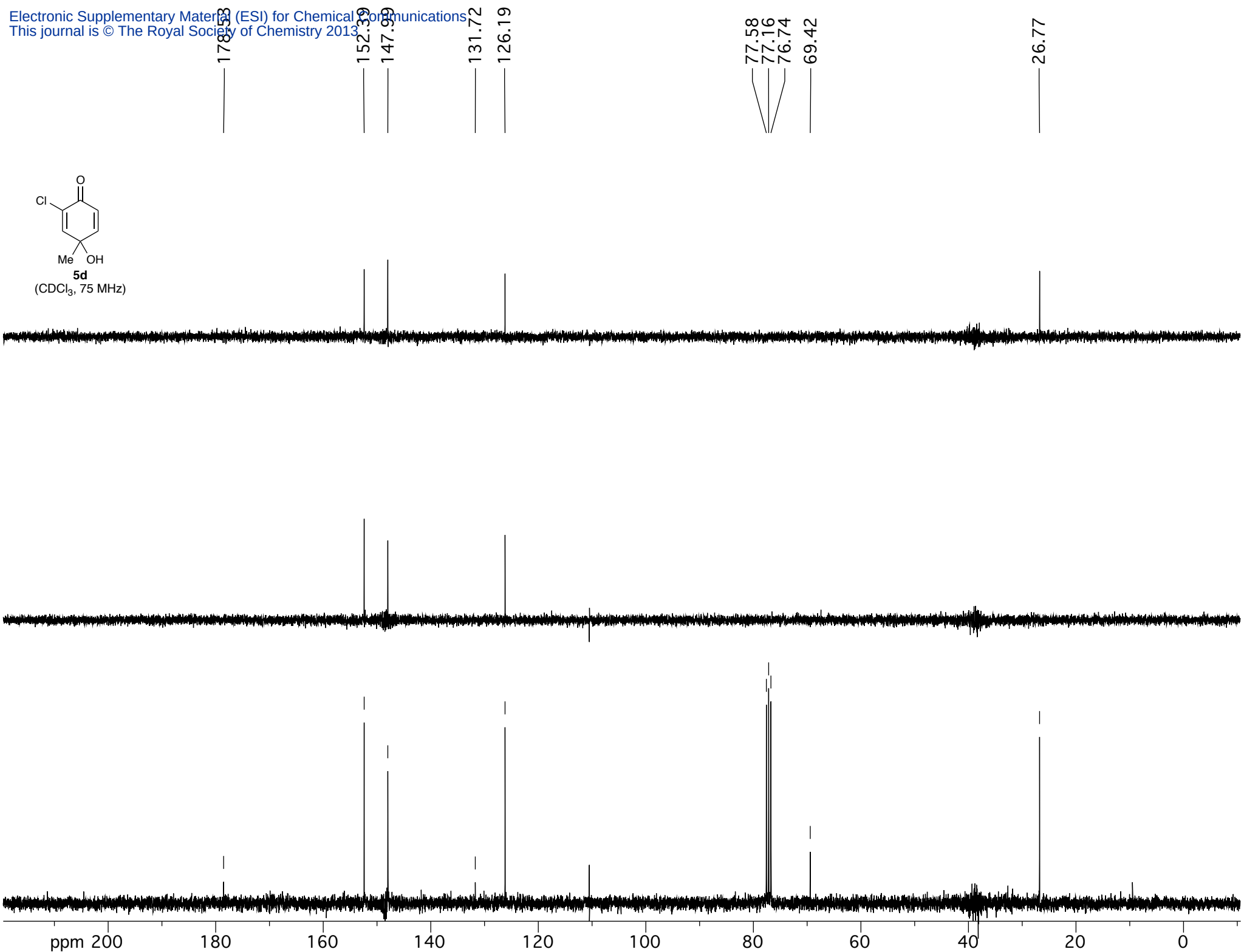


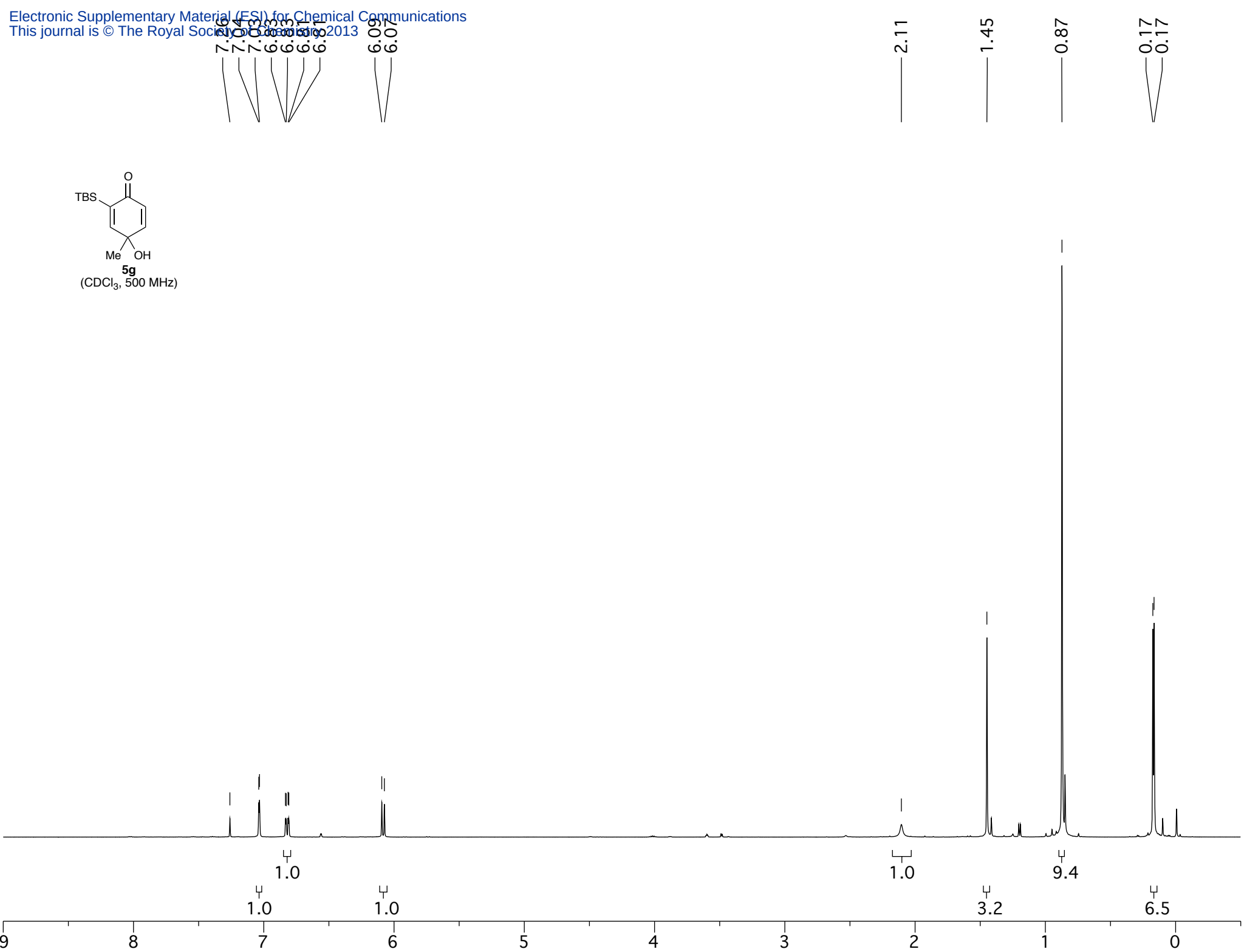


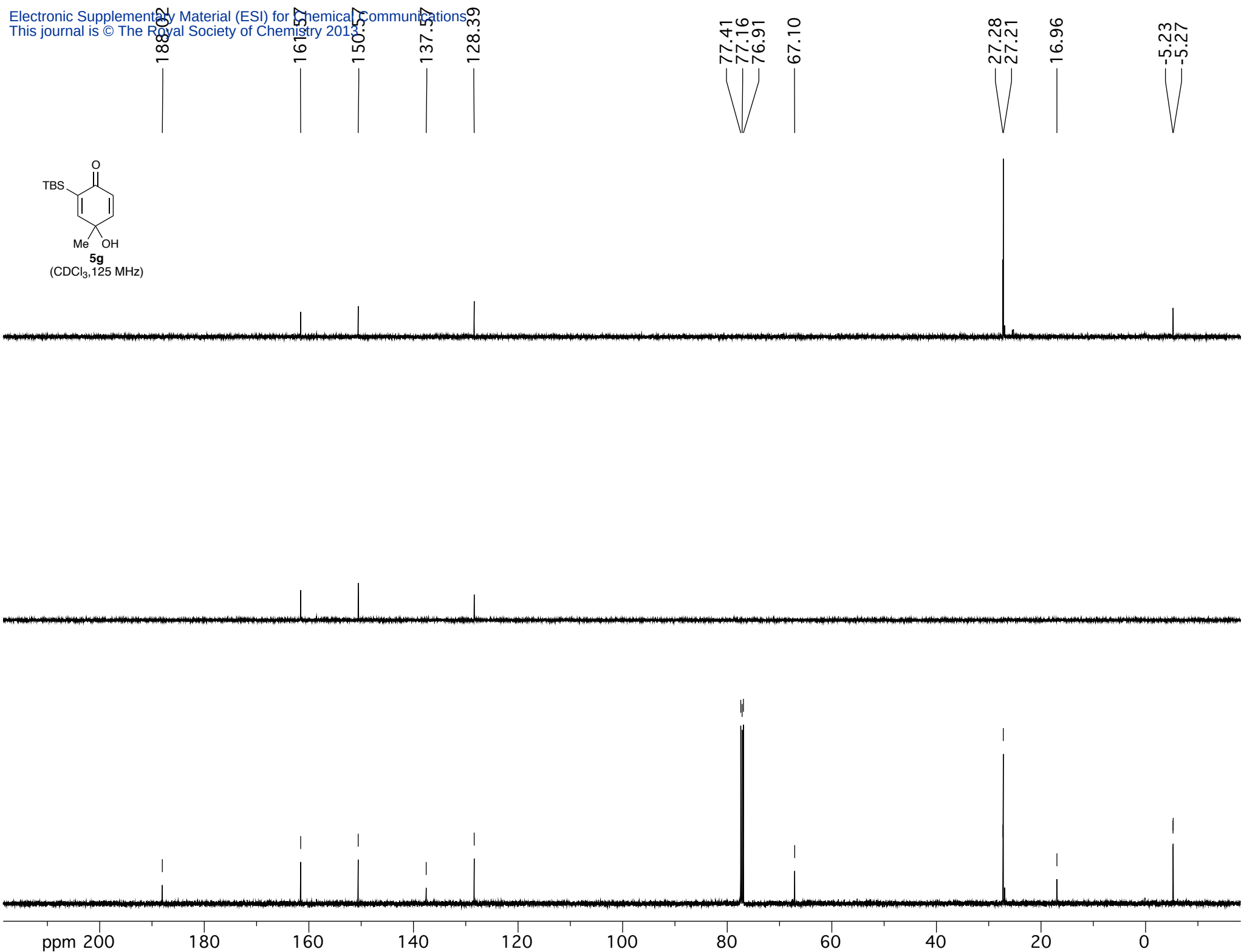
9
($CDCl_3$, 500 MHz)

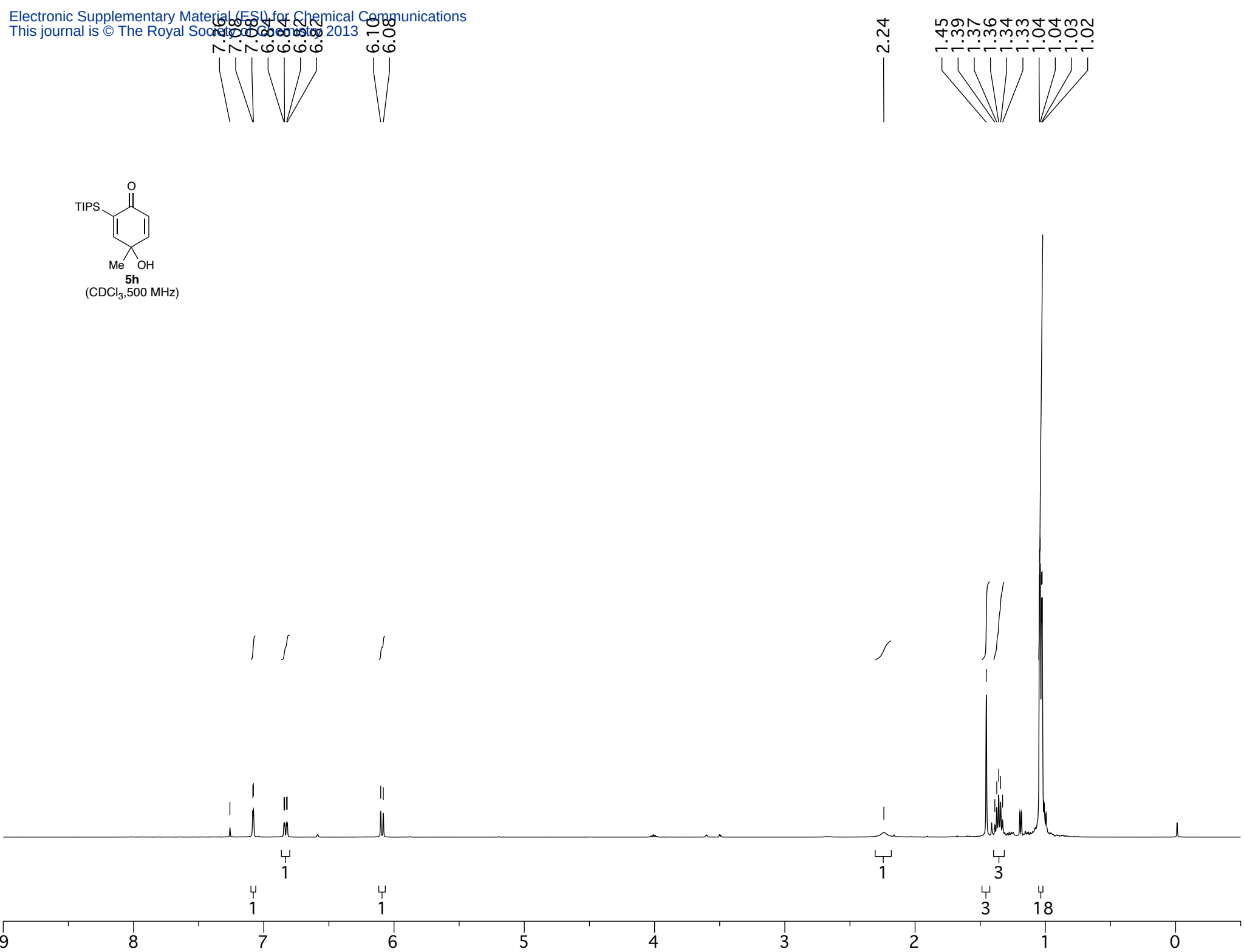


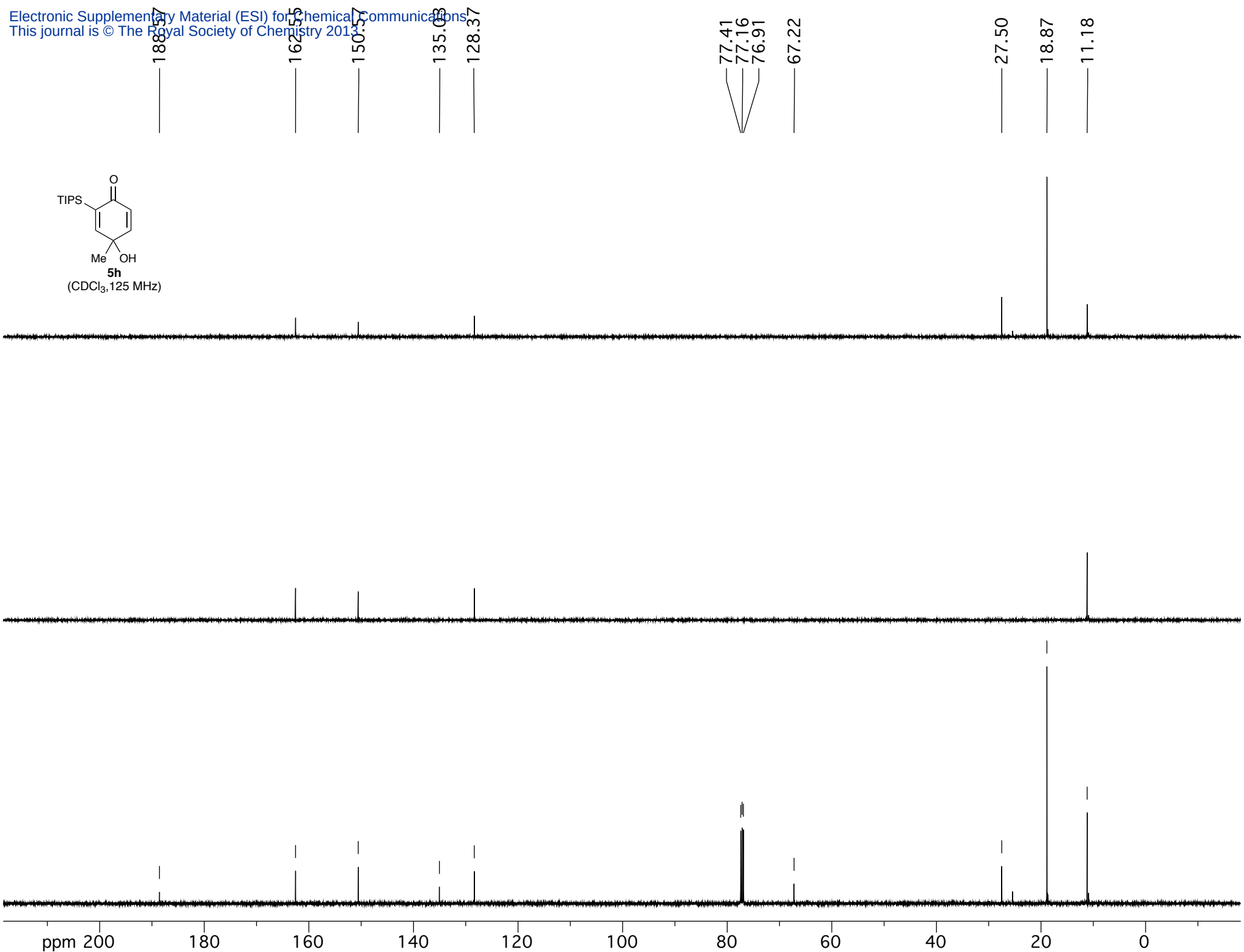


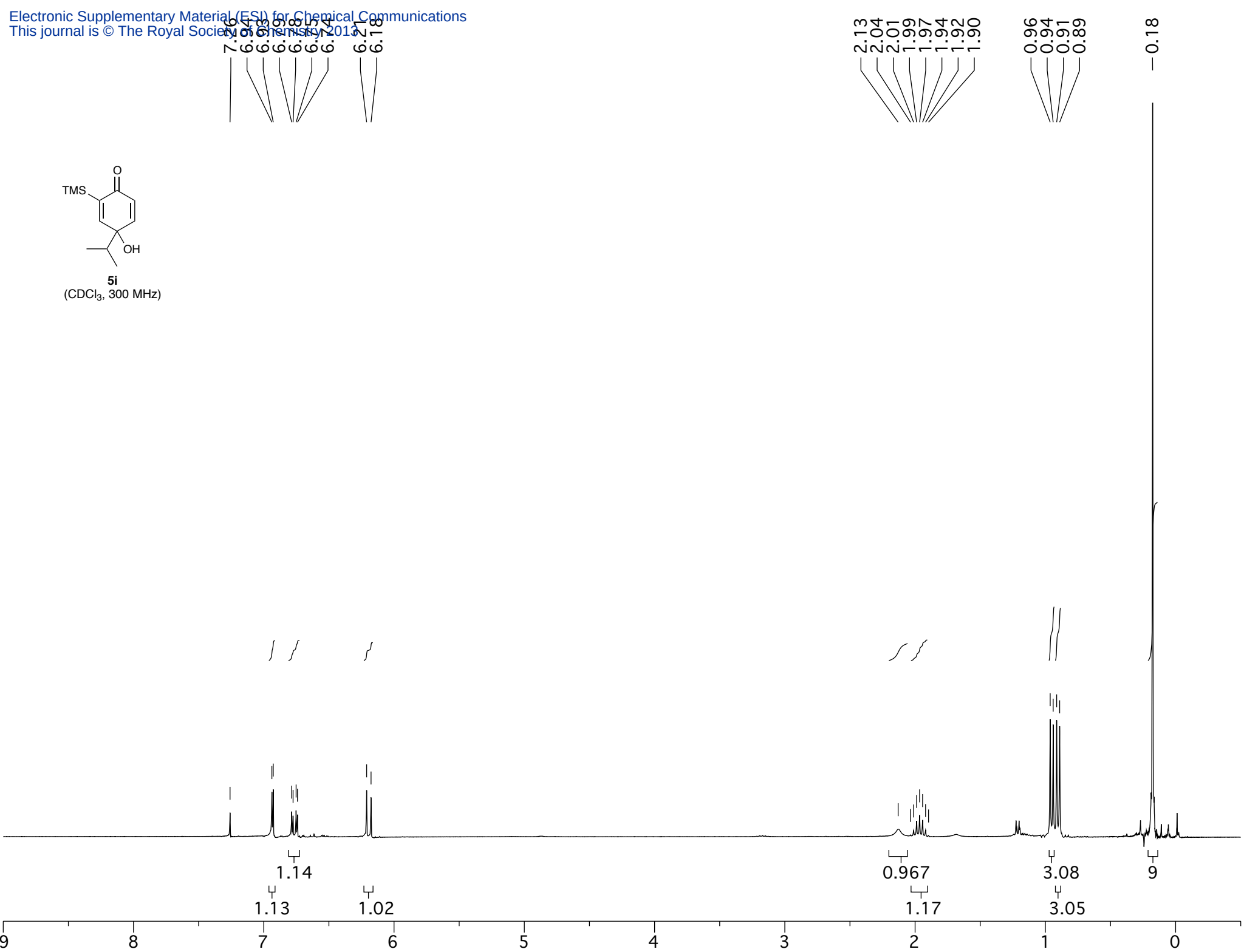




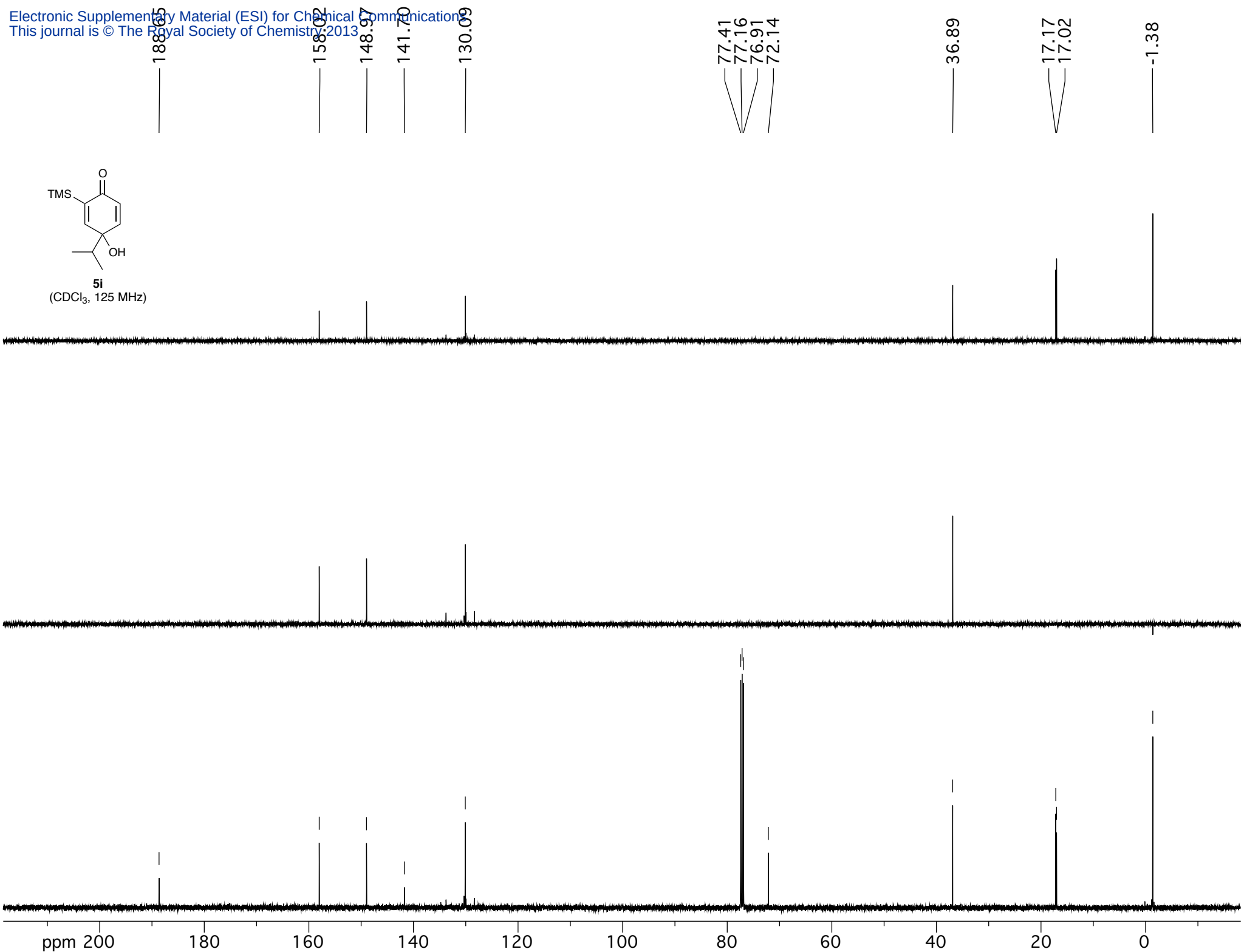


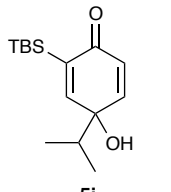




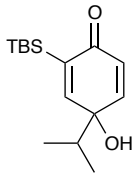


5i
($CDCl_3$, 300 MHz)

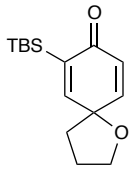




5j
($CDCl_3$, 300 MHz)



5j
($CDCl_3$, 75 MHz)



10
($CDCl_3$, 500 MHz)