The Iodination of Strongly Electron-Deficient Arenes under Electrochemical Conditions with I_2 and Catalytic Amounts of Chloride Anions

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Synthesis | DOI 10.1055/a-2811-7617 |

Supporting Information

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1. General Information

All solvents were commercially available and have been distilled under reduced pressure prior to use. Solvents were dried over 3 Å molecular sieves. All chemicals or reagents were purchased from commercial suppliers and used without further purification, if not otherwise stated, or were prepared according to known literature procedures. If water or air sensitive compounds have been used, the experiments were carried out in heat gun dried glassware using conventional SCHLENK techniques under nitrogen atmosphere. Electrochemical reactions were carried out using an AIM-TTI Instruments MX100T power supply. These reactions were performed in an divided cell (**Figure S1**), equipped with a stirring bar (700 rpm), a platinum anode (1.60 · 3.40 cm^2, active surface: 3.20 cm^2) and a carbon cathode (1.50 · 3.50 cm^2, active surface: 3.0 cm^2). All known compounds were characterized by ^1H and ^{13}C NMR. All unknown compounds were identified by ^1H NMR, ^{13}C NMR, and HRMS.

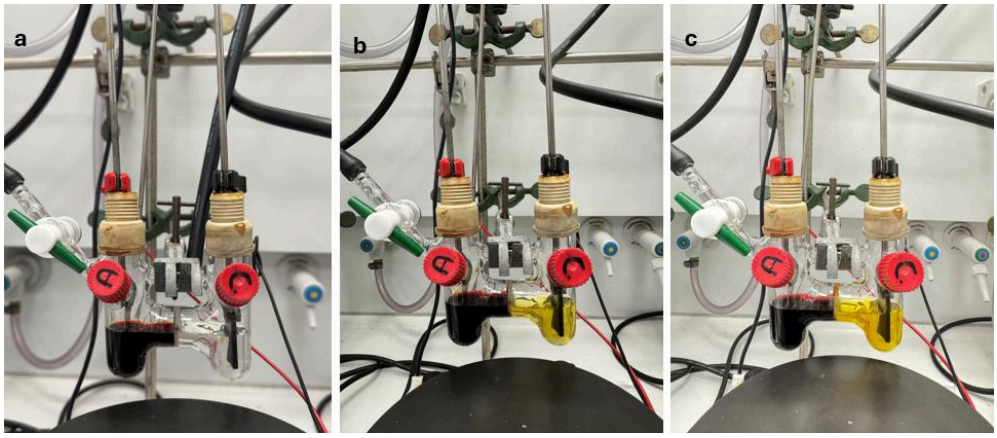

Figure S1: Color changes observed during electrochemical iodination of dimethyl isophthalate after (a) 0 *F* (b) 2.0 *F* and (c) 4.0 *F*.

NMR spectroscopy: ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 300 / 500 instruments. Chemical shifts are reported in parts per million (ppm). The spectra are referenced to the residual solvent peak of $CDCl_3$. In the ^1H NMR spectra this corresponds with the singlet of the solvent signal of $CDCl_3$ at δ = 7.26 ppm. The ^{13}C NMR spectra was referenced to the central line of the triplet of $CDCl_3$ at δ = 77.16 ppm.

Chromatography: Flash chromatography was carried out using Machery-Nagel silica gel 60 (0.040-0.063 mm). The thin layer chromatography was carried out on Merck TLC plates coated with silica gel 60 F254 with fluorescence indicator.

HRMS: HRMS spectra of products were obtained with a Waters Q-TOF Premier (ESI, pos. mode or APCI) or Thermo Scientific DFS (EI) spectrometers.

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IR: The IR spectra were obtained with a Shimadzu IR Spirit with a QATR-S cell. The wave numbers λ^{-1} is quoted in reciprocal centimeters (cm^{-1}).

2. Reaction Procedure

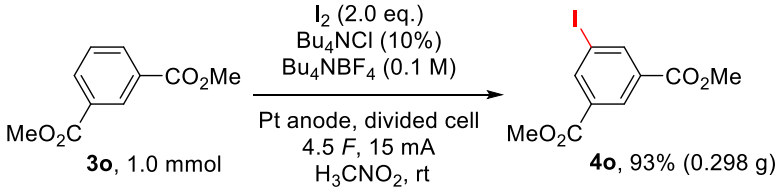
General procedure

In a divided-dried electrochemical cell (oven dried) and under nitrogen, the electrochemical cell was charged with tetrabutylammonium chloride ($n$$Bu_4NCl$) (6.9 mg, 0.025 mmol, 10 mol%) and tetrabutylammonium tetrafluoroborate ($n$$Bu_4NBF_4$) (0.1 M, 0.33 g). Then, the divided cell was evacuated for 10 min and flushed with nitrogen followed by addition of 10 mL of anhydrous nitromethane, iodine (I_2) (127 mg, 0.5 mmol, 2.0 equiv.) and the arene (0.25 mmol, 1.0 equiv.) in the anode compartment. The cathode compartment contained a solution of 2.0 mL of nitromethane, 8.0 mL of CH_2Cl_2 in the presence of $n$$Bu_4NBF_4$ (0.1 M, 0.33 g). Afterwards, the mixture was electrolyzed under constant current (10 mA, 2.0-8.0 *F*) utilizing a Pt plate electrode as anode (2.4 cm^2) and a graphite cathode at 20-35 °C under stirring (700 rpm). After completion of the reaction, 5.0 mL of saturated aqueous $Na_2S_2O_3$ solution was added to the anodic compartment solution. Then 100 mL of water was added and extracted with *n*-pentane (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Finally, the residue was either submitted to column chromatography (SiO_2) or all volatile compounds were removed under reduced pressure to furnish the respective iodoarenes.

Note: Pre-electrolysis of the reaction mixture and addition of the substrate led to the same iodinated products. However, the *in situ* electrolysis was preferred as the conversion could be easily monitored by GC analysis and the electrolysis prolonged until complete conversion was observed.

Procedure for the scale-up experiment:

According to the General Procedure dimethyl isophthalate (194 mg, 1.0 mmol, 1.0 equiv.) and iodine (508 mg, 2.0 mmol, 2.0 equiv.) were converted to furnish product **4o** as white solid (298 mg, 0.93 mmol, 93%) under constant current (15 mA) and after consumption of 4.5 *F*.



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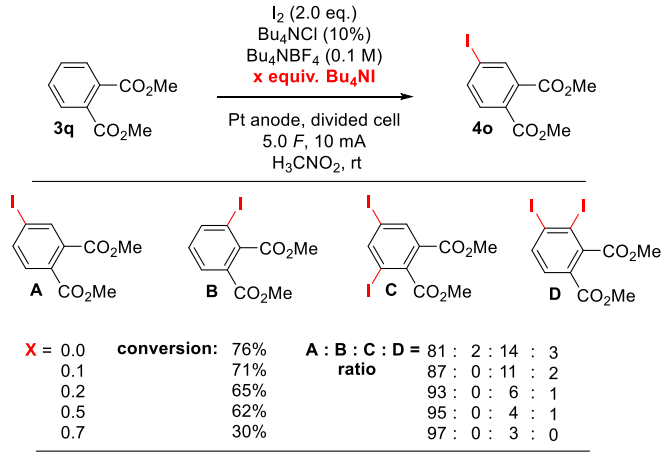
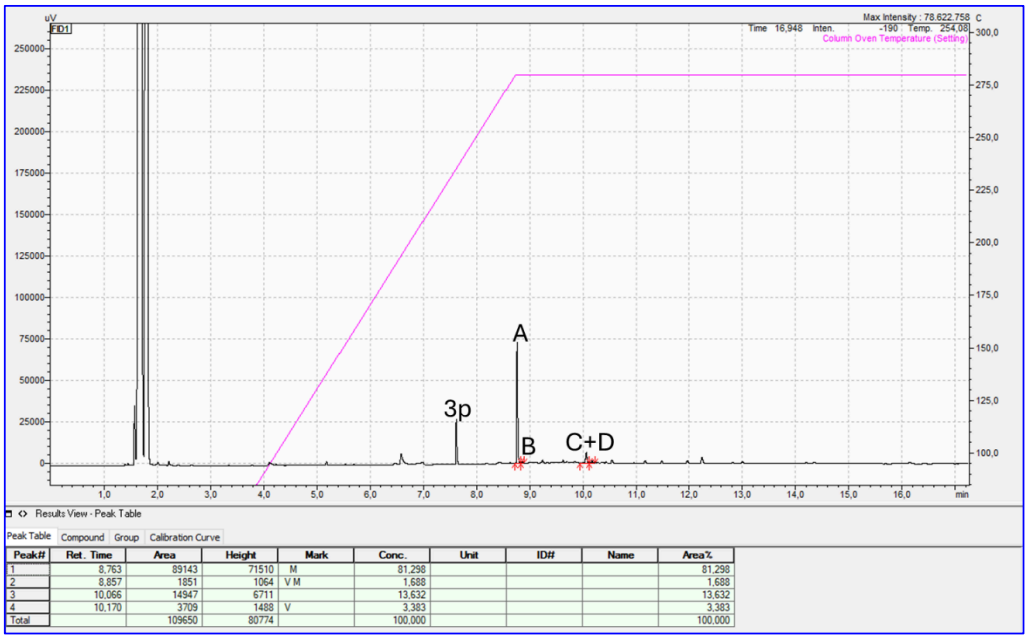
3. GC results concerning electrochemical iodination of 3p with the I_2/Cl^- system in the presence of additional Bu_4NI



X =	conversion:	A : B : C : D = ratio
0.0	76%	81 : 2 : 14 : 3
0.1	71%	87 : 0 : 11 : 2
0.2	65%	93 : 0 : 6 : 1
0.5	62%	95 : 0 : 4 : 1
0.7	30%	97 : 0 : 3 : 0



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	8,763	89143	71510	M	81,298				81,298
2	8,857	1851	1064	V M	1,688				1,688
3	10,066	14947	6711		13,632				13,632
4	10,170	3709	1488	V	3,383				3,383
Total		109650	80774		100,000				100,000

Figure S2: GC results concerning electrochemical iodination of **3p** in the absence of Bu_4NI

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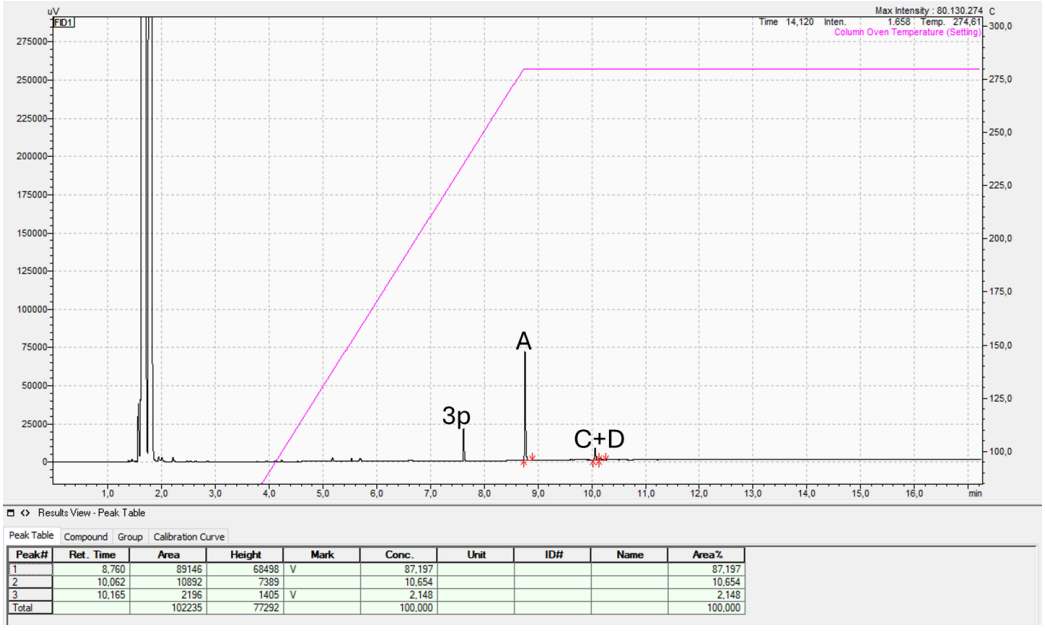
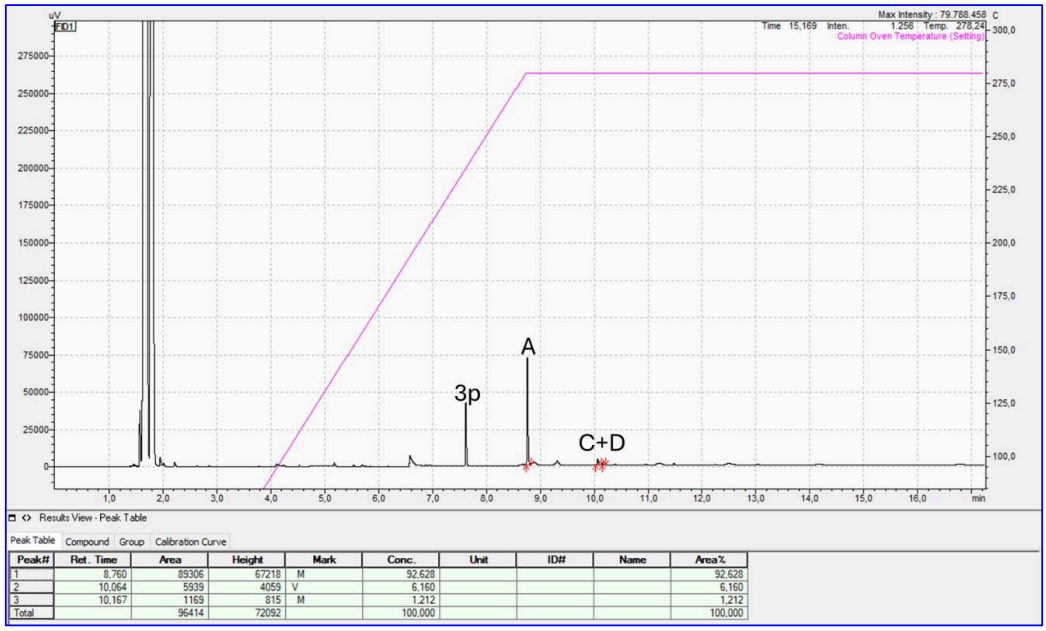


Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	8,760	89146	68498	V	87,197				87,197
2	10,062	10892	7389		10,654				10,654
3	10,165	2196	1405	V	2,148				2,148
Total		102235	77292		100,000				100,000

Figure S3: GC results concerning electrochemical iodination of **3p** in the presence of 0.1 equiv. of Bu_4NI



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	8,760	89306	67218	M	92,628				92,628
2	10,064	5939	4059	V	6,160				6,160
3	10,167	1169	815	M	1,212				1,212
Total		96414	72092		100,000				100,000

Figure S4: GC results concerning electrochemical iodination of **3p** in the presence of 0.2 equiv. of Bu_4NI

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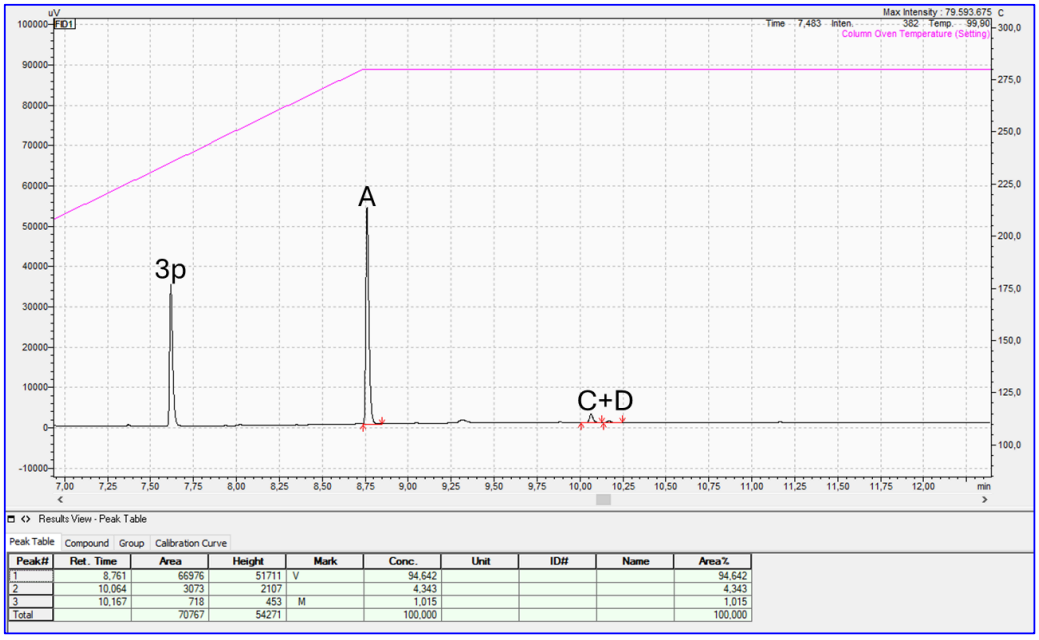
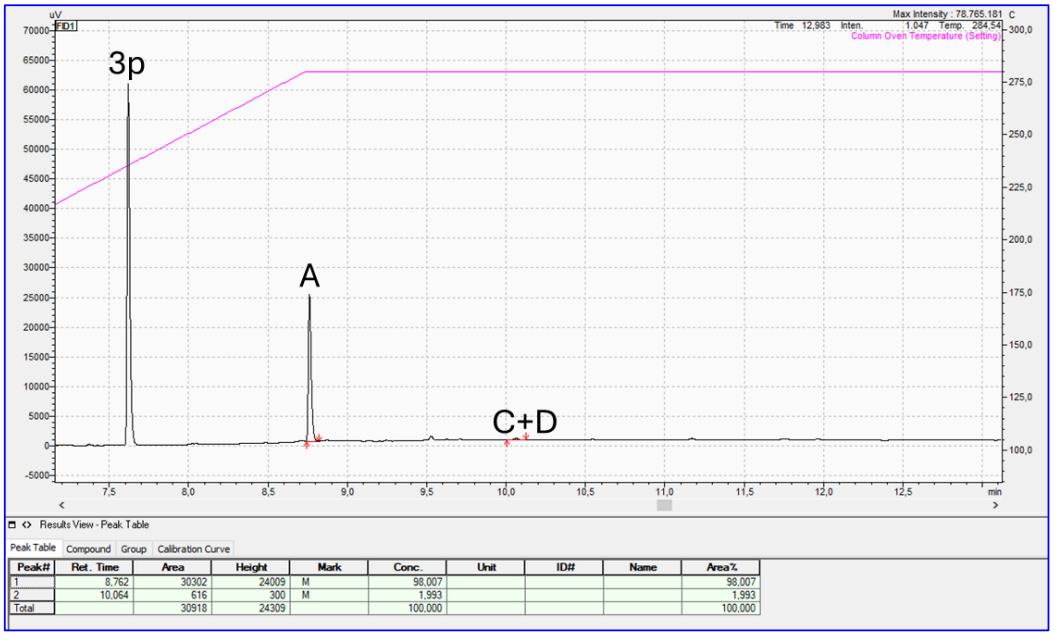


Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	8,761	66976	51711	V	94,642				94,642
2	10,064	3073	2107		4,343				4,343
3	10,167	718	453	M	1,015				1,015
Total		70767	54271		100,000				100,000

Figure S5: GC results concerning electrochemical iodination of **3p** in the presence of 0.5 equiv. of Bu_4NI



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	8,762	30302	24009	M	98,007				98,007
2	10,064	616	300	M	1,993				1,993
Total		30918	24309		100,000				100,000

Figure S6: GC results concerning electrochemical iodination of **3p** in the presence of 0.7 equiv. of Bu_4NI

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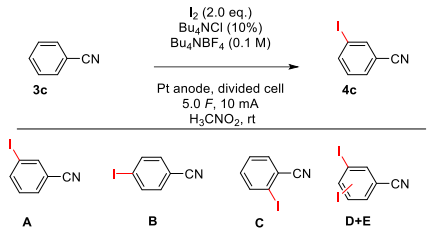
4. GC results concerning the electrochemical iodination of 3c with the I_2/Cl^- system



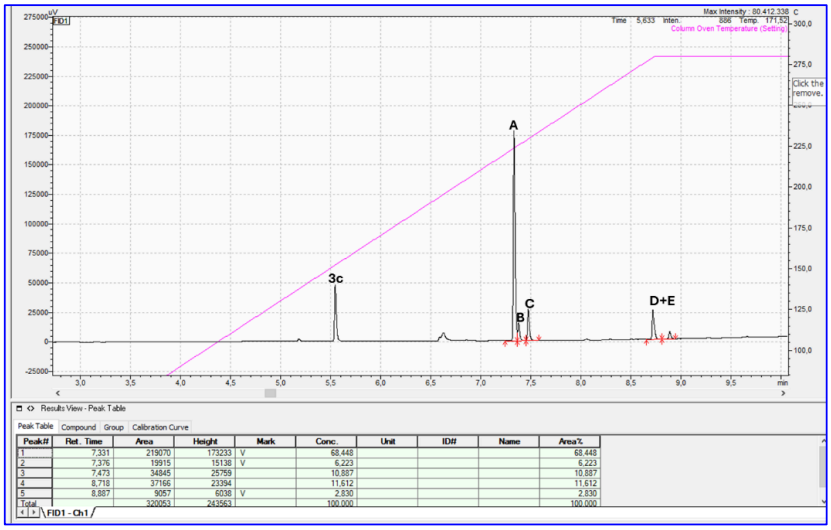


Figure S7: GC results concerning electrochemical iodination of **3c**

5. The electrochemical iodination of ethyl benzoate 1 with different combinations of reagents

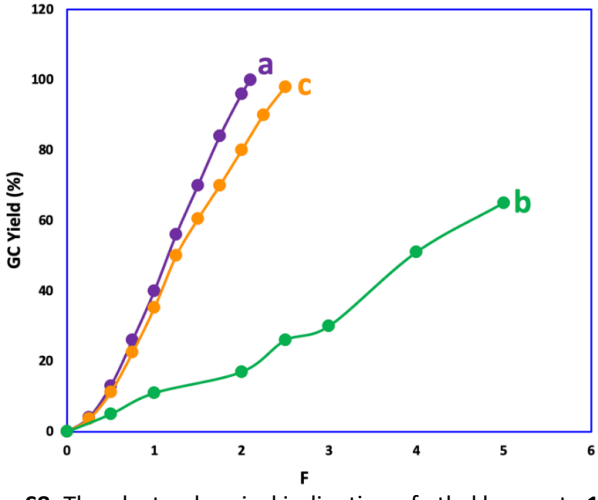


Figure S8: The electrochemical iodination of ethyl benzoate **1** with

(**a**) 2.1 eq. I_2 + 0.1 eq. Bu_4NCl

(**b**) 2.1 eq. I_2 + 0.1 eq. I-Cl (old sample of I-Cl)

(**c**) 2.1 eq. I_2 + 0.1 eq. I-Cl (new sample of I-Cl).

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The insufficient performance of the I_2 / I-Cl system in comparison with the I_2 /Cl^- system is caused by the sensitivity of the I-Cl towards light and moisture. When a fresh sample was used (curve b) a very similar performance of the I_2 / I-Cl system with respect to the I_2 / Cl^- system was observed. Based on this finding, the use of the I_2 /Cl^- system is much more convenient, the components are easier to handle and much less sensitive. Therefore, we prefer the I_2 / Cl^- system for preparative transformations.

Note: I-Cl is reported to be light-sensitive and as it is proposed to be generated *in situ*, care should be taken.

6. The distinction between the I^-/Cl^- and I_2/Cl^- systems for electrochemical iodination

To improve clarity, we have now added a concise comparative table (Table S1) that directly contrasts the performance of the I^-/Cl^- and I_2/Cl^- systems for key representative substrates. This addition facilitates a clearer overview of the advantages and limitations of both systems.

Table S1. Electrochemical iodination of the key substrate using two different systems

Substrate	Yield with the I_2/Cl^- system	Yield with the I^-/Cl^- system
Benzaldehyde	86%, single isomer	28%
Nitrobenzene	84%, single isomer	19%
Benzonitrile	62% (+32% over iodination)	30%

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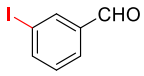
7. Analytical section

3-Iodobenzaldehyde (4a)



According to the General Procedure benzaldehyde (26.5 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4a** as a white solid (48 mg, 0.21 mmol, 86%) after column chromatography (SiO_2, *n*-pentane) and consumption of 7.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 8.12 (t, *J* = 1.7 Hz, 1H), 7.87 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.76 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H) ppm.

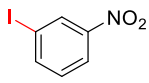
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 190.7, 143.2, 138.4, 138.0, 130.7, 128.9, 94.7 ppm.

GC/MS: m/z = 232 (100), 203 (18), 127 (4), 104 (11), 77 (46), 50 (49).

Melting point range: 55–57 °C.

The spectroscopic values are in accordance with literature values.[1]

1-Iodo-3-nitrobenzene (4b)



According to the General Procedure nitrobenzene (30.8 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4b** as pale-yellow solid (62mg, 0.21 mmol, 84%) after column chromatography (SiO_2, *n*-pentane:CH_2Cl_2 = 5:1) and consumption of 5.5 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.59 (t, *J* = 2.0 Hz, 1H), 8.24 (ddd, *J* = 8.3, 2.2, 1.0 Hz, 1H), 8.06 (ddd, *J* = 7.9, 1.6, 1.0 Hz, 1H), 7.33 (t, *J* = 8.1 Hz, 1H) ppm.

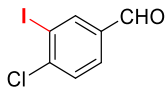
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 148.6, 143.5, 132.5, 130.8, 122.8, 93.5 ppm.

GC/MS: m/z = 249 (54), 203 (32), 76 (100), 50 (70).

Melting point range: 35–37 °C.

The spectroscopic values are in accordance with literature values.[2]

4-Chloro-3-iodobenzaldehyde (4d)



According to the General Procedure 4-chlorobenzaldehyde (35.0 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4d** as white solid (54 mg, 0.2 mmol, 80%) after column chromatography (SiO_2, *n*-pentane:CH_2Cl_2 = 2:1) and consumption of 4.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 8.34 (d, *J* = 1.9 Hz, 1H), 7.80 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 189.5, 145.1, 141.4, 135.7, 130.0, 123.0, 98.8 ppm.

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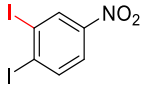
GC/MS: m/z = 268 (26), 267 (28), 266 (83), 265 (63), 237 (19), 110 (29), 75 (100).

Melting point range: 115–117 °C.

The spectroscopic values are in accordance with literature values.[3]

1,2-Diiodo-4-nitrobenzene (4e)



According to the General Procedure 1-iodo-4-nitrobenzene (62.3 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4e** as yellow solid (90 mg, 0.24mmol, 95%) after column chromatography (SiO_2, *n*-pentane:CH_2Cl_2 = 3:1) and consumption of 5.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 2.5 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.91 (dd, *J* = 8.7, 2.5 Hz, 1H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 147.6, 139.9, 133.8, 123.5, 117.1, 108.3 ppm.

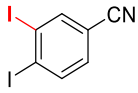
GC/MS: m/z = 375 (19), 329 (10), 202 (12), 75 (100).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_6H_3O_2NI_2Na$ 397.8151; Found 397.8150.

Melting point range: 109–111 °C.

The spectroscopic values are in accordance with literature values.[4]

3,4-Diiodobenzonitrile (4f)



According to the General Procedure 4-iodobenzonitrile (57.2 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) at 35 °C were converted to furnish product **4f** as yellow solid (74 mg, 0.21mmol, 83%) after column chromatography (SiO_2, *n*-pentane) and consumption of 4.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 1.9 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.2, 1.9 Hz, 1H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 141.8, 140.0, 131.7, 116., 114.8, 113.2, 108.6 ppm.

GC/MS: m/z = 355 (83), 254 (13), 228 (61), 127 (29), 101 (80), 75 (41), 50 (100).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_7H_3NI_2Na$ 377.8253; Found 377.8253.

IR (ATR): λ^{-1} = 3063, 2923, 2359, 1761, 1651, 1537, 1372, 1253, 1187, 1006, 959, 883, 807, 688, 574, 557, 524 cm^{-1}.

Melting point range: 157–159 °C.

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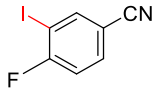
4-Fluoro-3-iodobenzonitrile (4g)



According to the General Procedure 4-fluorobenzonitrile (61.8 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) at 35 °C were converted to furnish product **4g** as colorless solid (56.2 mg, 0.23 mmol, 91%) after column chromatography (SiO_2, *n*-pentane) and consumption of 5.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (dd, *J* = 5.7, 2.1 Hz, 1H), 7.71-7.68 (m, 1H), 7.21 (dd, *J* = 8.5, 7.3 Hz, 1H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 164.4 (d, *J* = 255.3 Hz), 143.4 (d, *J* = 3.2 Hz), 134.3 (d, *J* = 9.0 Hz), 116.7, 116.5 (d, *J* = 3.5 Hz), 110.4 (d, *J* = 4.2 Hz), 82.2 (d, *J* = 27.5 Hz) ppm.

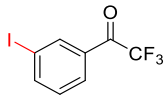
GC/MS: m/z = 247 (100), 120 (70), 100 (32), 75 (13).

^{19}F{^{1}H} NMR ($CDCl_3$): δ = −83.91 ppm.

Melting point range: 55–57 °C.

The spectroscopic values are in accordance with literature values.[5]

2,2,2-Trifluoro-1-(3-iodophenyl)ethan-1-one (4h)



According to the General Procedure 2,2,2-trifluoro-1-phenylethan-1-one (43.5 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4h** as yellow oil (70.0 mg, 0.24 mmol, 96%) after column chromatography (SiO_2, *n*-pentane:CH_2Cl_2 = 10:1) and consumption of 3.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 8.05 – 8.03 (m, 2H), 7.32 – 7.29 (t, *J* = 7.9 Hz, 1H) ppm.

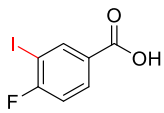
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 179.3 (q, *J* = 35.6 Hz), 144.3, 138.8, 131.6, 130.7, 129.1 (q, *J* = 2.3 Hz), 116.4 (q, *J* = 291.3 Hz), 94.5 ppm.

GC/MS: m/z = 300 (28), 231 (76), 203 (43), 76 (100), 50 (74).

^{19}F{^{1}H} NMR ($CDCl_3$): δ = -71.49 ppm.

The spectroscopic values are in accordance with literature values.[6]

4-Fluoro-3-iodobenzoic acid (4i)



According to the General Procedure ethyl 4-fluorobenzoic acid (35.0 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4i** as pale yellow solid (39.9 mg, 0.15 mmol, 60%) after an acid-base separation process to remove impurities and consumption of 2.0 *F*.

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^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.54 (dd, *J* = 6.1, 2.2 Hz, 1H), 8.12 – 8.07 (m, 1H), 7.16 (dd, *J* = 8.6, 7.5 Hz, 1H) ppm.

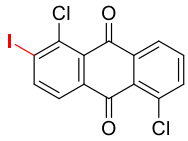
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 169.8, 165.4 (d, *J* = 254.2 Hz), 142.2 (d, *J* = 3.3 Hz), 132.7 (d, *J* = 8.9 Hz), 127.2 (d, *J* = 3.4 Hz), 115.8 (d, *J* = 24.8 Hz), 81.3 (d, *J* = 26.6 Hz) ppm.

GC/MS: m/z = 266 (100), 249 (51), 221 (16), 94 (46), 50 (17).

Melting point range: 170–172 °C.

The spectroscopic values are in accordance with literature values.[7]

1,5-Dichloro-2-iodoanthracene-9,10-dione (4j)



According to the General Procedure 1,5-dichloroanthracene-9,10-dione (69.3 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4j** as yellow solid (17.8 mg, 0.04 mmol, 18%) after column chromatography (SiO_2, *n*-pentane:CH_2Cl_2 = 2:1) and consumption of 8.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 8.3 Hz, 1H), 8.23 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.79 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H) ppm.

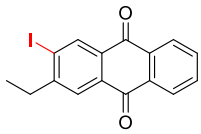
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 180.8, 180.6, 145.2, 138.0, 137.5, 136.9, 136.7, 134.7, 134.4, 130.1, 128.9, 127.5, 127.3, 111.6 ppm.

GC/MS: m/z = 402 (100), 374 (27), 219 (44), 184 (72), 149 (35), 74 (38).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_5Cl_2IO_2Na$ 424.8609; Found 424.8594.

Melting point range: 234–235 °C.

2-Ethyl-3-iodoanthracene-9,10-dione (4k)



According to the General Procedure 2-ethylanthracene-9,10-dione (51.9 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4k** as pale yellow solid (62.5 mg, 0.17 mmol, 70%) after column chromatography (SiO_2, *n*-pentane:CH_2Cl_2 = 4:1) and consumption of 6.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 8.25 – 8.23 (m, 2H), 8.01 (s, 1H), 7.78 – 7.76 (m, 2H), 2.84 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 183.1, 181.9, 153.6, 138.5, 134.4, 134.3, 133.5, 133.3, 133.2, 131.8, 127.3, 127.3, 126,5, 108.5, 34.8, 14.1 ppm.

GC/MS: m/z = 362 (100), 347 (22), 235 (46), 178 (39), 76 (22).

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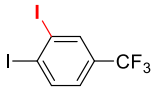
HRMS (ESI) m/z: [M+Na]$^+$ Calcd for $C_{16}H_{11}O_2INa$ 384.9702; Found 384.9702.

Melting point range: 167–168 °C.

1,2-Diiodo-4-(trifluoromethyl)benzene (4l)



According to the General Procedure 1-iodo-4-(trifluoromethyl)benzene (68 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) at 35 °C were converted to furnish product **4l** as white solid (95 mg, 0.24 mmol, 99%) after column chromatography (SiO_2, *n*-pentane) and consumption of 4.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 2.1 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.28 (m, 1H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 139.8, 135.9 (q, *J* = 3.8 Hz), 131.5 (q, *J* = 33.3 Hz), 125.8 (q, *J* = 3.6 Hz), 122.8 (q, *J* = 273 Hz), 112.9, 108.3.ppm.

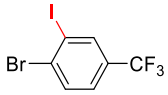
GC/MS: m/z = 398 (84), 271 (28), 254 (5), 144 (100), 94 (20), 75 (60), 50 (34).

^{19}F{^{1}H} NMR ($CDCl_3$): δ = −62.99 ppm.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd for $C_7H_3F_3I_2Na$ 420.8174; Found 397.8173.

Melting point range: 65–67 °C.

1-Bromo-2-iodo-4-(trifluoromethyl)benzene (4m)



According to the General Procedure 1-bromo-4-(trifluoromethyl)benzene (56.3 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) at 35 °C were converted to furnish product **4m** as pale-yellow oil (73 mg, 0.21 mmol, 85%) after column chromatography (SiO_2, *n*-pentane) and consumption of 5.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.50 (dd, *J* = 8.4, 2.2 Hz, 1H) ppm.

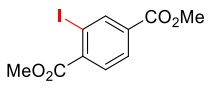
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 137.1 (q, *J* = 3.9 Hz), 134.2 (q, *J* = 1.6 Hz), 133.0, 130.8 (q, *J* = 33.3 Hz), 126.2 (q, *J* = 3.6 Hz), 122.7 (q, *J* = 272 Hz), 101.4 ppm.

GC/MS: m/z = 350 (100), 225 (31), 144 (89), 94 (22), 74 (53), 50 (37).

^{19}F{^{1}H} NMR ($CDCl_3$): δ = −62.99 ppm.

The spectroscopic values are in accordance with literature values.[8]

Dimethyl 2-iodoterephthalate (4n)



According to the General Procedure dimethyl terephthalate (48.5 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4n** as white solid (70 mg, 0.22 mmol, 90%) after consumption of 6.0 *F*.

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^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 1.6 Hz, 1H), 8.08 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 4.0 (s, 3H), 3.98 (s, 3H) ppm.

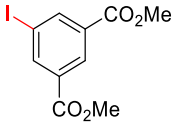
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 166.6, 164.8, 142.1, 139.2, 133.5, 130.5, 128.9, 93.4, 52.8, 52.7 ppm.

GC/MS: m/z = 320 (76), 289 (100), 261 (18), 103 (22), 75 (48).

Melting point range: 78–79 °C.

The spectroscopic values are in accordance with literature values.[9]

Dimethyl 5-iodoisophthalate (4o)



According to the General Procedure dimethyl isophthalate (48.5 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4o** as white solid (77 mg, 0.24 mmol, 96%) after consumption of 4.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.67 (t, *J* = 1.5 Hz, 1H), 8.58 (d, *J* = 1.6 Hz, 2H), 3.99 (s, 6H) ppm.

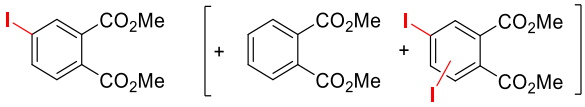
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 164.8, 142.5, 132.2, 129.9, 93.5, 52.7 ppm.

GC/MS: m/z = 320 (71), 289 (100), 261 (29), 134 (17), 75 (93).

Melting point range: 103-105 °C.

The spectroscopic values are in accordance with literature values.[10]

Dimethyl 4-iodophthalate (4p)



4p **3p** **4p'**

According to the General Procedure dimethyl phthalate (48.5 mg, 0.25 mmol, 1.0 equiv.), iodine (127 mg, 0.5 mmol, 2.0 equiv.) and 0.7 eq. of Bu_4NI (129 mg) were converted to furnish product **4p** (70% conversion) accompanied with 30% of starting material as inseparable mixture as a white solid (76 mg, 0.24 mmol, **4p**:(**3p** + **4p´**) = 97:3) after consumption of 14.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 1.8 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): (all resolved signals of the mixture) δ = 168.1, 167.3, 166.7, 143.3, 140.1, 137.7, 133.8, 132.0, 131.2, 130.9, 130.5, 130.4, 129.8, 129.1, 128.9, 97.7, 93.3, 53.1, 52.95, 52.87, 52.4, 52.7 ppm.

The spectroscopic values are in accordance with literature values.[10]

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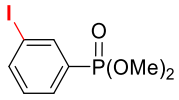
Dimethyl (3-iodophenyl)phosphonate (4s)



According to the General Procedure dimethyl phenylphosphonate (46.5 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4s** as pale yellow oil (77 mg, 0.24 mmol, 94%) after consumption of 4.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (dt, *J* = 13.2, 1.7 Hz, 1H), 7.88 (dm, *J* = 7.9 Hz, 1H), 7.74 (ddt, *J* = 13.0, 7.7, 1.3 Hz, 1H), 7.20 (td, *J* = 7.7, 4.7 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 141.7 (d, *J* = 3.2 Hz), 140.5 (d, *J* = 10.6 Hz), 131.0 (d, *J* = 9.6 Hz), 130.4 (d, *J* = 15.3 Hz), 129.8 (d, *J* = 187.6 Hz), 94.7 (d, *J* = 18.6 Hz), 53.0 (d, *J* = 5.3 Hz) ppm.

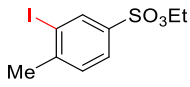
^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.63 ppm.

GC/MS: m/z = 312 (50), 217 (24), 185 (30), 91 (21), 76 (100).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_8H_{10}IO_3PNa$ 334.9310; Found 334.9305.

Melting point range: 117–118 °C.

Ethyl 3-iodo-4-methylbenzenesulfonate (4t)



According to the General Procedure ethyl 4-methylbenzenesulfonate (50.1 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4t** as white solid (75 mg, 0.23 mmol, 90%) after column chromatography (SiO_2, *n*-pentane) and consumption of 2.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 148.1, 137.9, 135.0, 130.1, 127.4, 100.8, 67.3, 28.5, 14.8 ppm.

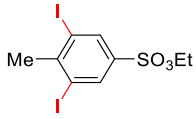
GC/MS: m/z = 326 (70), 298 (31), 217 (32), 171 (21), 90 (100), 63 (43).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_9H_{11}O_3ISNa$ 348.9372; Found 348.9365.

IR (ATR): λ^{-1} = 2987, 2905, 1580, 1368, 1260, 1176, 1097, 1034, 1000, 911, 817, 781, 681, 656, 588, 561, 518, 492 cm^{-1}.

Melting point range: 122–124 °C.

Ethyl 3,5-diiodo-4-methylbenzenesulfonate (4u)



According to the General Procedure ethyl 4-methylbenzenesulfonate (50.1 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4u** as white solid

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(99 mg, 0.22 mmol, 86%) after column chromatography (SiO_2, *n*-pentane:CH_2Cl_2 = 3:1) and consumption of 4.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.35 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.87 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 149.6, 138.1, 136.1, 98.9, 67.7, 35.4, 14.8 ppm.

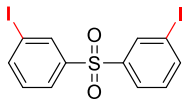
GC/MS: m/z = 452 (40), 424 (11), 344 (11), 217 (23), 89 (100), 63 (90).

HRMS (ESI) m/z: [M+Na]$^+$ Calcd for $C_9H_{10}O_3I_2SNa$ 474.8338; Found 474.8335.

IR (ATR): λ^{-1} = 3056, 2977, 1523, 1470, 1358, 1204, 1180, 1113, 1041, 1021, 903, 838, 781, 700, 683, 598, 567, 503 cm^{-1}.

Melting point range: 105–107 °C.

3,3'-Sulfonylbis(iodobenzene) (4v)



According to the General Procedure sulfonyldibenzene (54.6 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4v** as white solid (113 mg, 0.24 mmol, 96%) after column chromatography (SiO_2, *n*-pentane) and consumption of 6.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.35 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.87 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 142.7, 142.6, 136.3, 131.0, 127.0, 94.8 ppm.

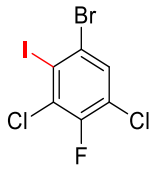
GC/MS: m/z = 470 (20), 251 (27), 203 (21), 96 (17), 76 (100), 50 (70).

HRMS (ESI) m/z: [M+Na]$^+$ Calcd for $C_{12}H_8O_2I_2SNa$ 492.8298; Found 492.8297.

IR (ATR): λ^{-1} = 1564, 1454, 1322, 1291, 1154, 1114, 990, 794, 765, 734, 574 cm^{-1}.

Melting point range: 121–123 °C.

1-Bromo-3,5-dichloro-4-fluoro-2-iodobenzene (4x)



According to the General Procedure 5-bromo-1,3-dichloro-2-fluorobenzene (61 mg, 0.25 mmol, 1.0 equiv.) and iodine (127 mg, 0.5 mmol, 2.0 equiv.) were converted to furnish product **4x** as white solid (81 mg, 0.22 mmol, 88%) after column chromatography (SiO_2, *n*-pentane) and consumption of 4.0 *F*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 6.7 Hz, 1H) ppm.

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$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 152.5 (d, *J* = 253.9 Hz), 131.3, 129.1 (d, *J* = 18.7 Hz), 125.3 (d, *J* = 5.0 Hz), 123.0 (d, *J* = 19.2 Hz), 105.8 ppm.

GC/MS: m/z = 370 (100), 243 (41), 162 (54), 127 (52), 92 (65), 61 (21).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C_6HFCl_2BrINa 390.7560; Found 390.7559.

IR (ATR): λ^{-1} = 3069, 1730, 1420, 1336, 1300, 1291, 1262, 1217, 1117, 1109, 1037, 941, 864, 820, 604, 591, 518, 490 cm^{-1}.

Melting point range: 39–41 °C.

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8. NMR spectra of all Synthesized Compounds

3-Iodobenzaldehyde (4a)

Figure S9: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4a**.

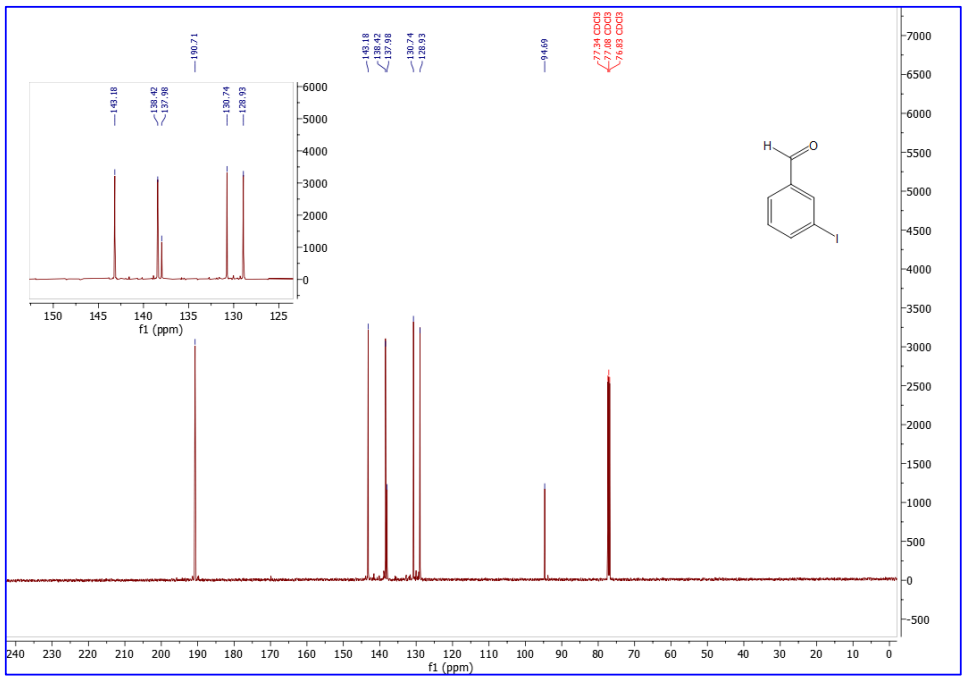

Figure S10: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4a**.

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1-Iodo-3-nitrobenzene (4b)

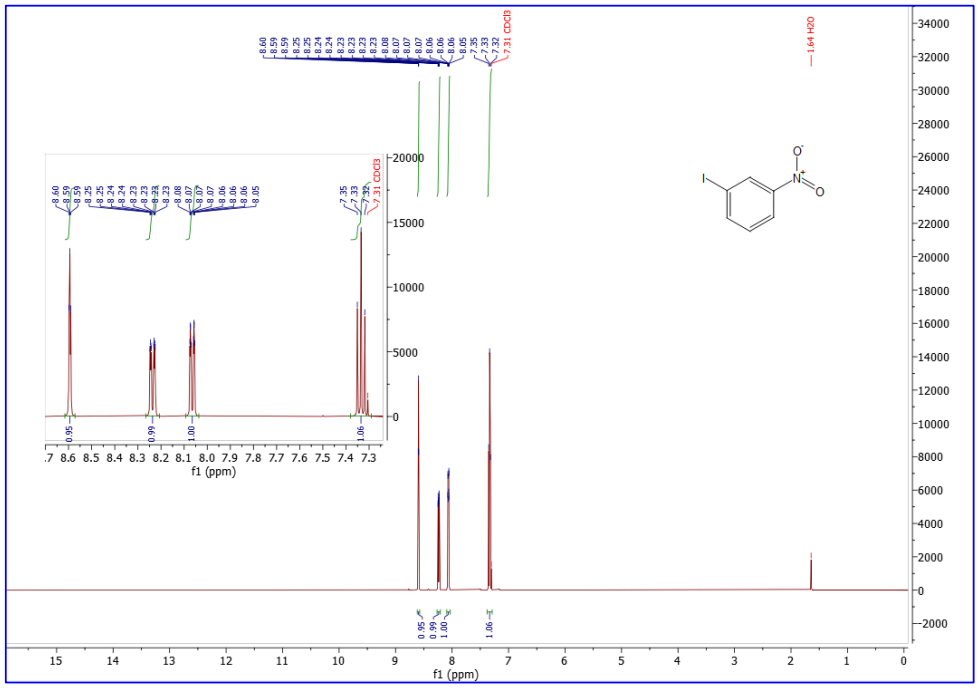

Figure S11: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4b**.

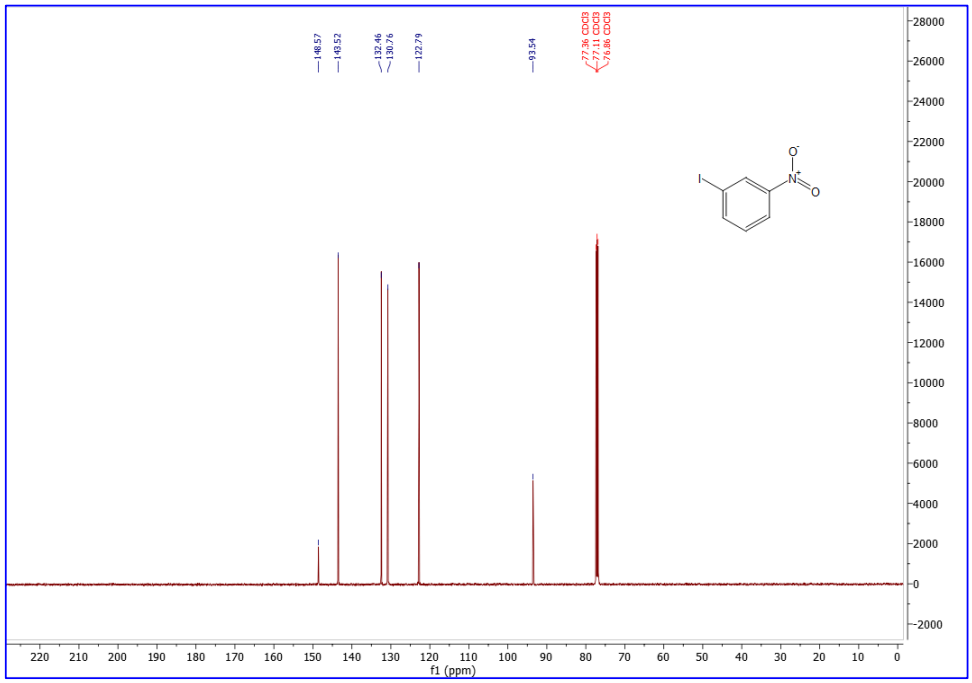

Figure S12: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4b**.

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4-Chloro-3-iodobenzaldehyde (4d)

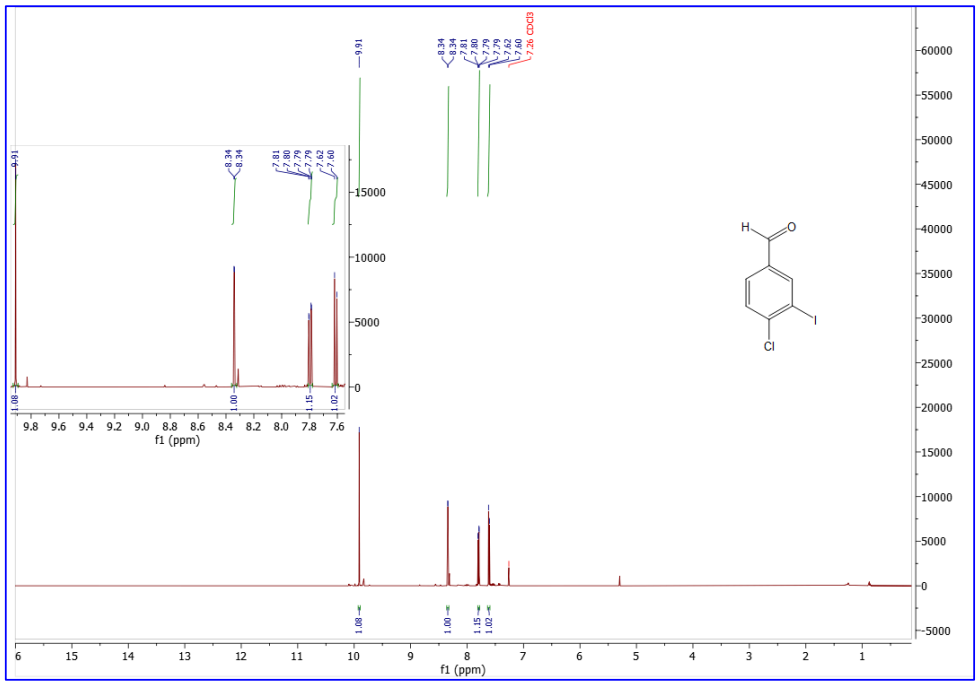

Figure S13: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4d**.

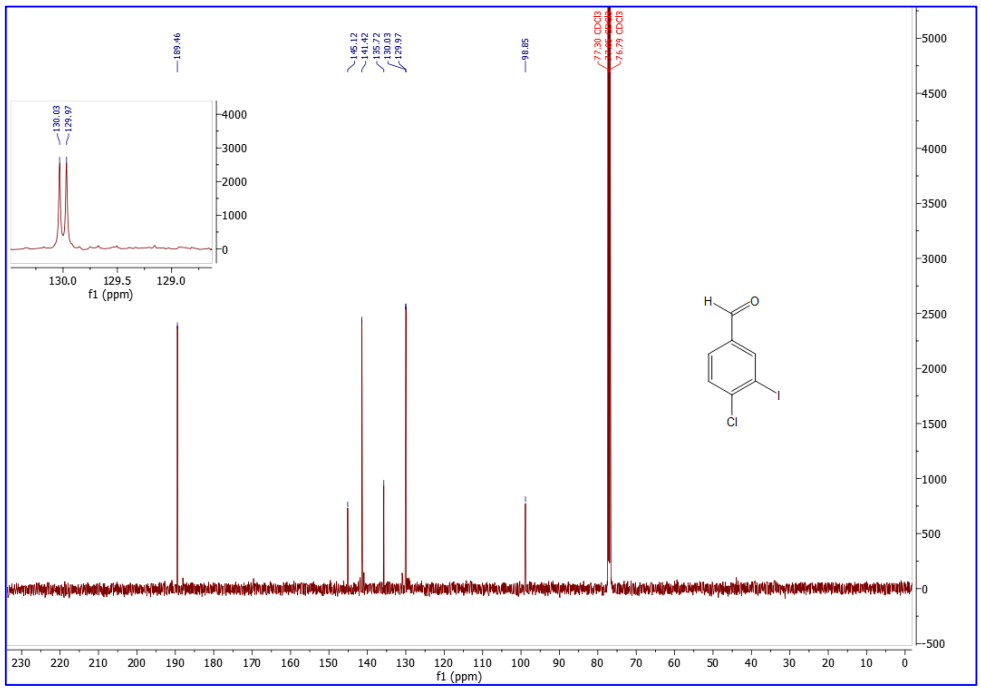

Figure S14: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4d**.

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1,2-Diiodo-4-nitrobenzene (4e)

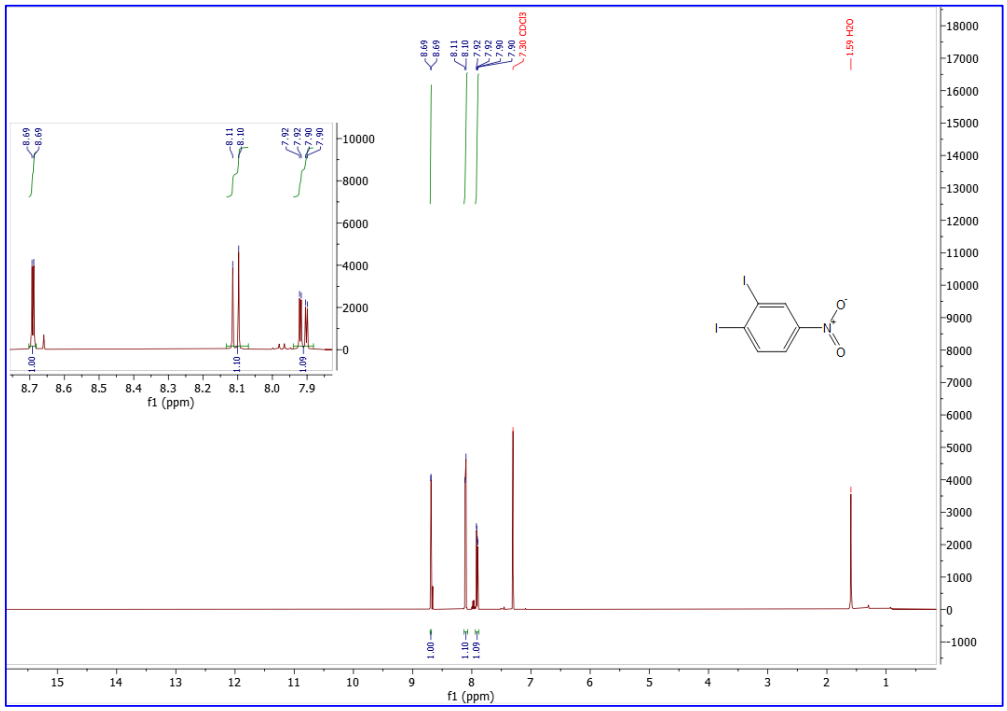

Figure S15: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4e.**

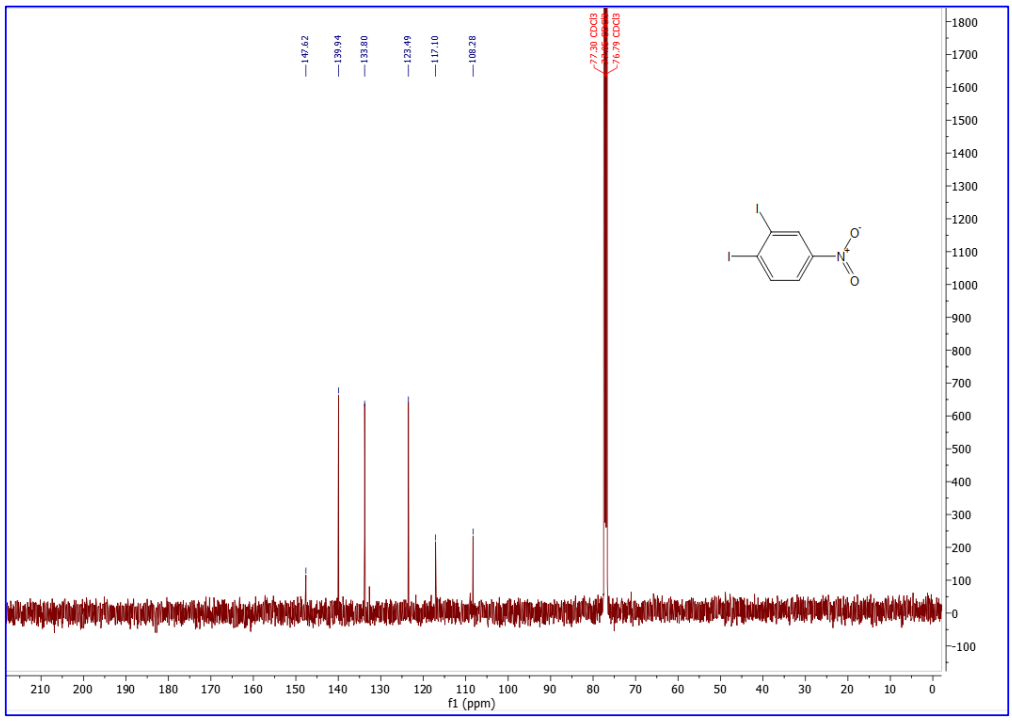

Figure S16: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4e.**

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3,4-Diiodobenzonitrile (4f)

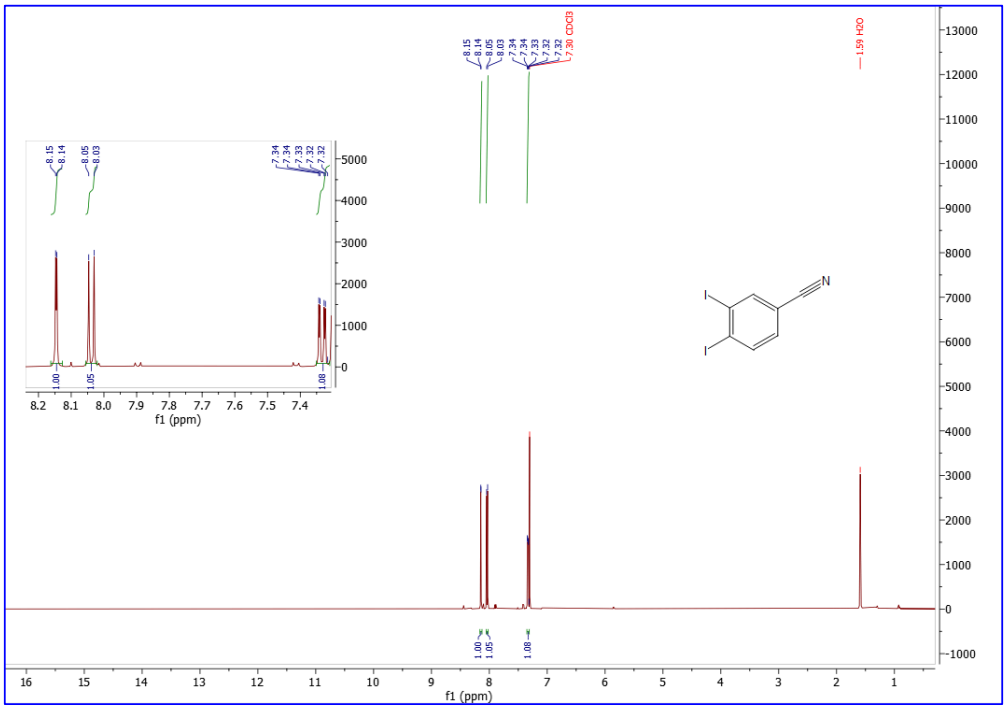

Figure S17: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4f**.

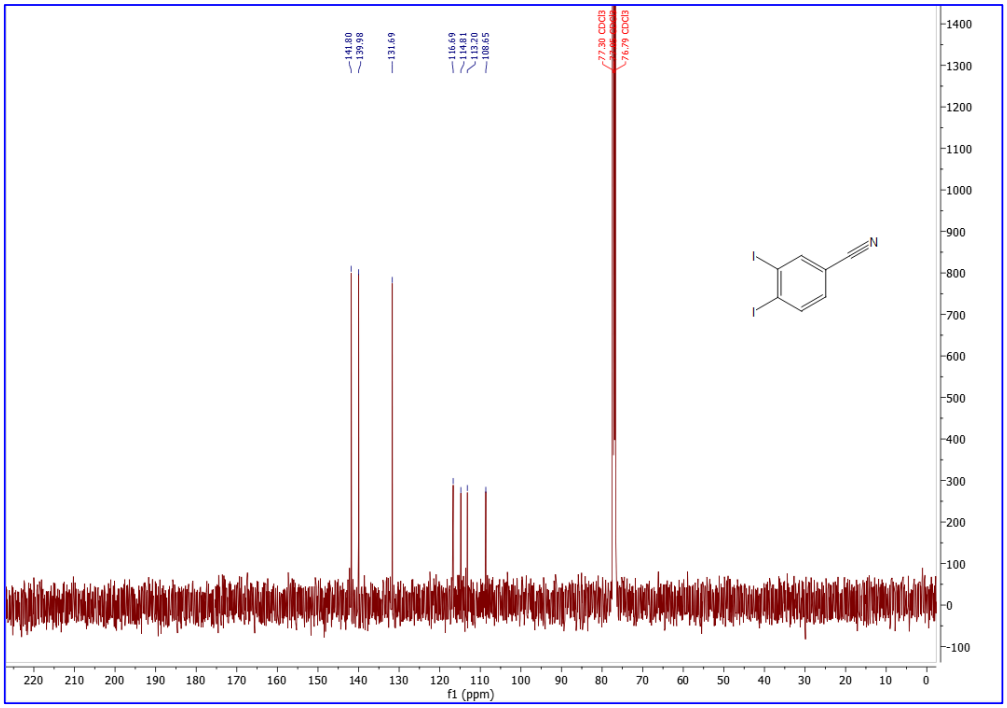

Figure S18: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4f**.

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4-Fluoro-3-iodobenzonitrile (4g)

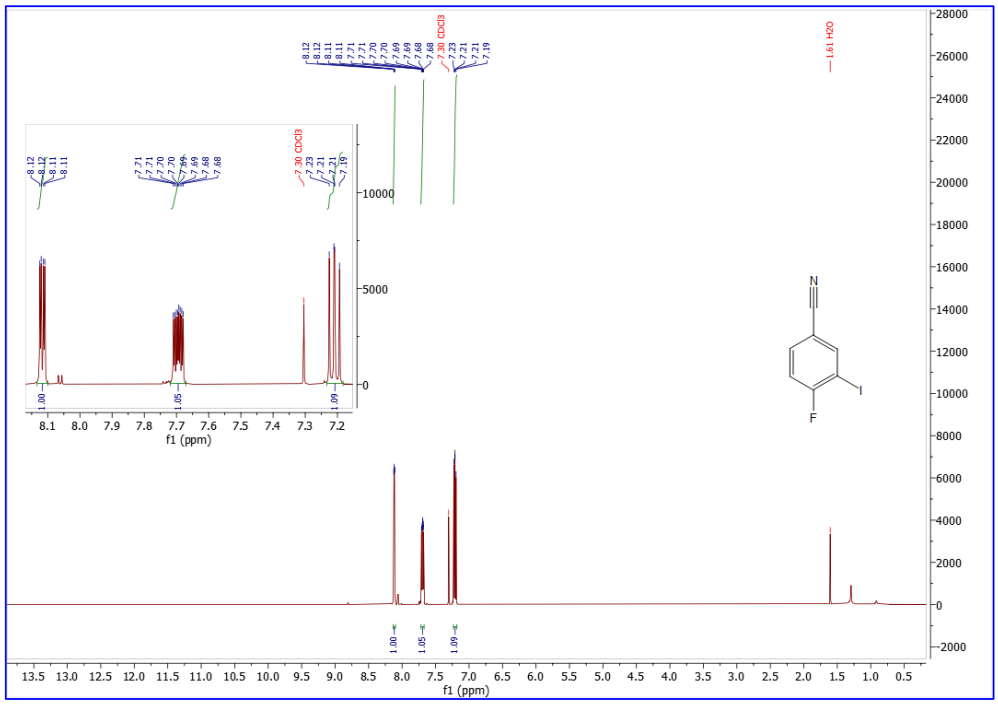

Figure S19: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4g**.

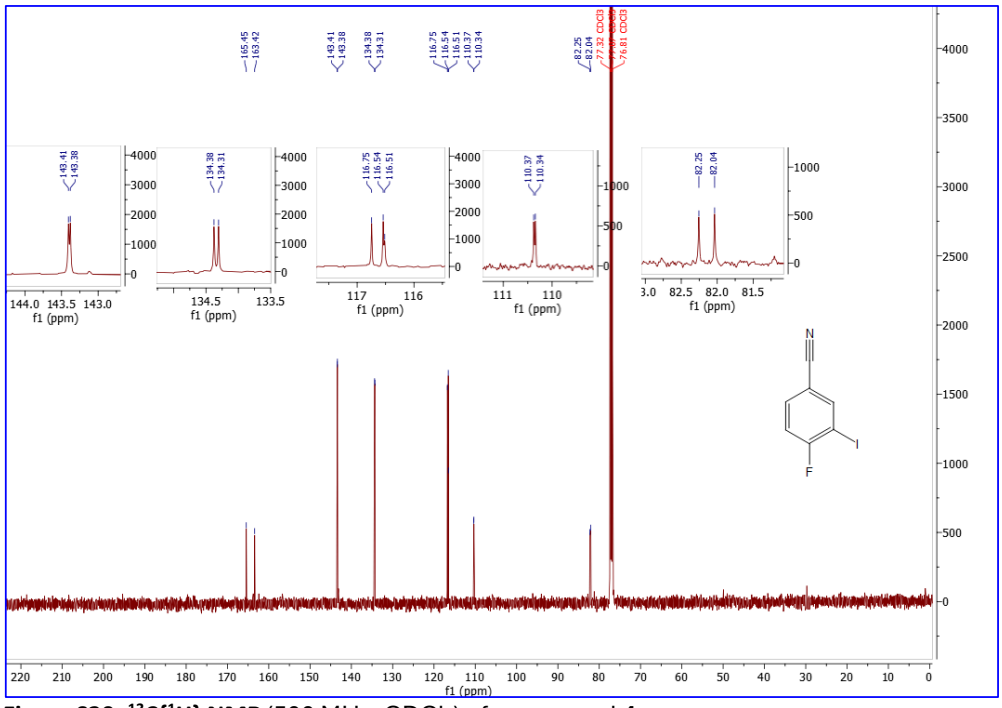

Figure S20: **$^{13}C\{^{1}H\}$ NMR** (500 MHz, $CDCl_3$) of compound **4g**.

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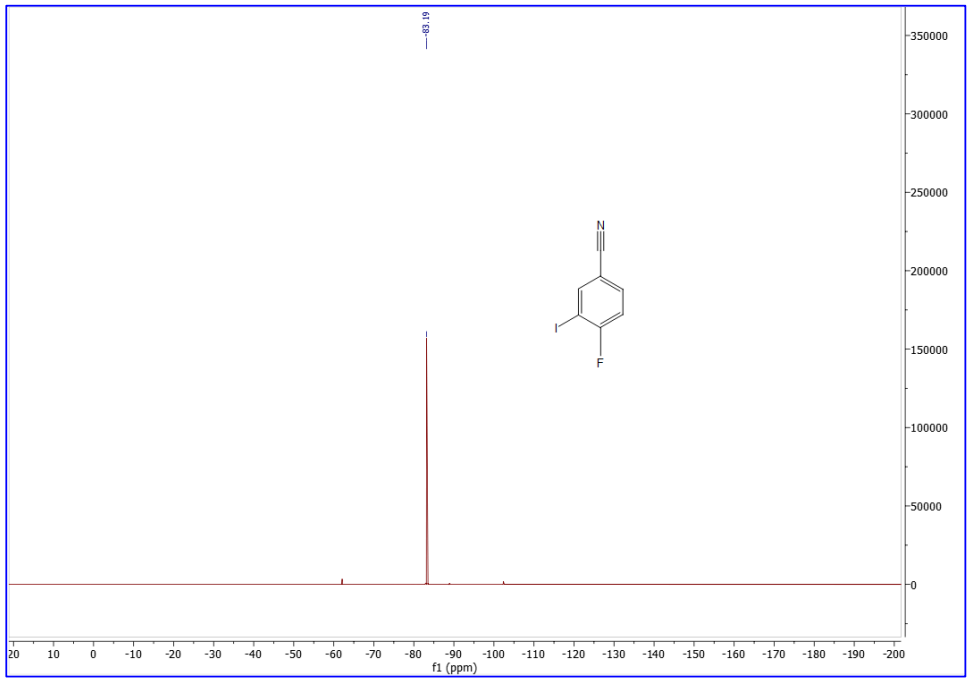

Figure S21: **^{19}F NMR** spectrum of compound **4g** in $CDCl_3$

2,2,2-Trifluoro-1-(3-iodophenyl)ethan-1-one (4h)

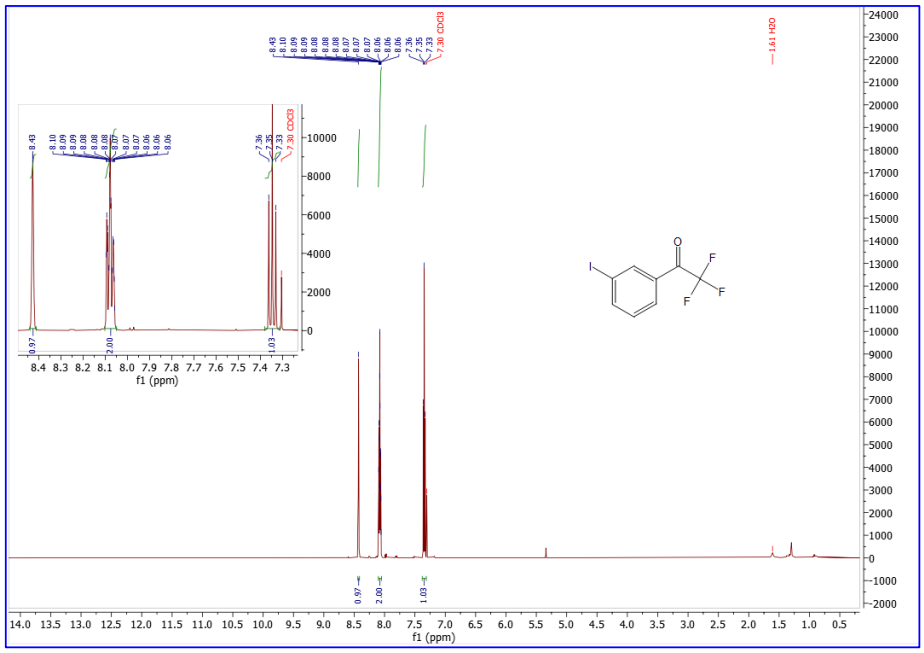

Figure S22: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4h**.

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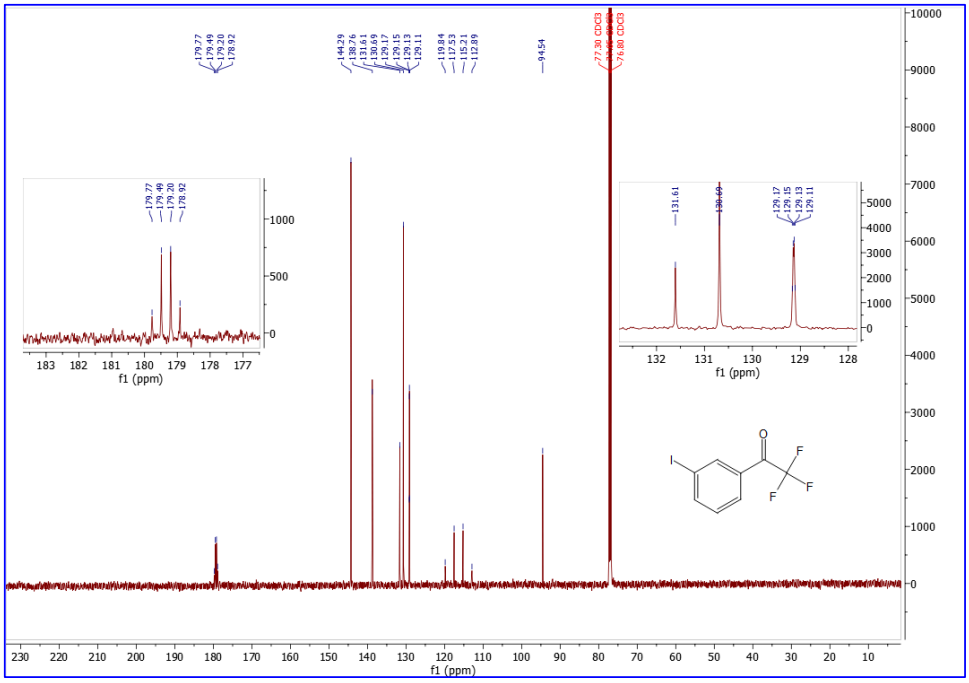

Figure S23: **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) of compound **4h**.

4-Fluoro-3-iodobenzoic acid (4i)

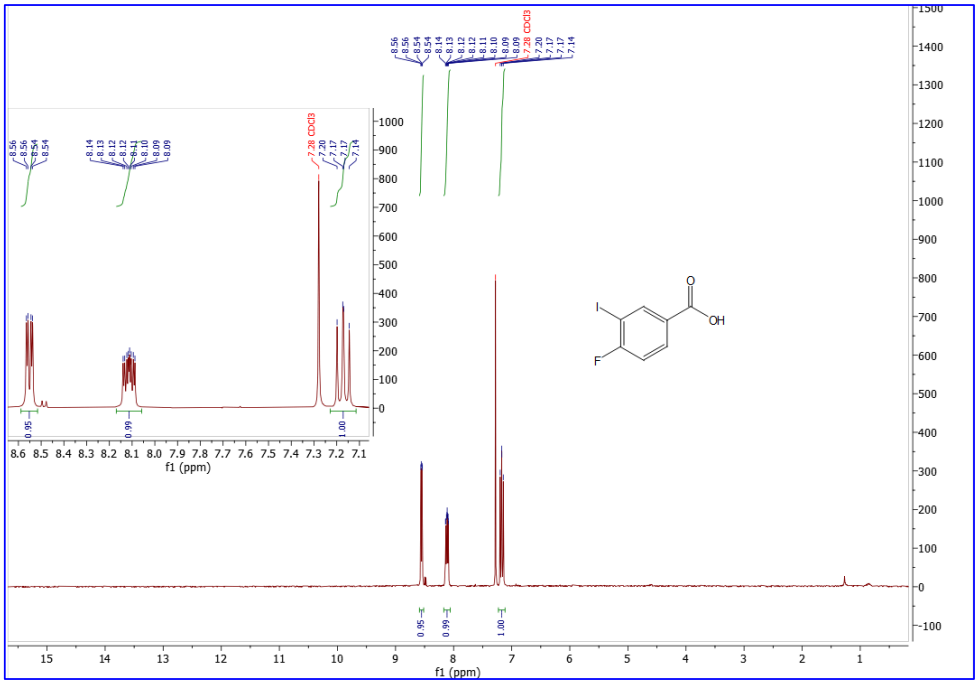

Figure S24: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4i**.

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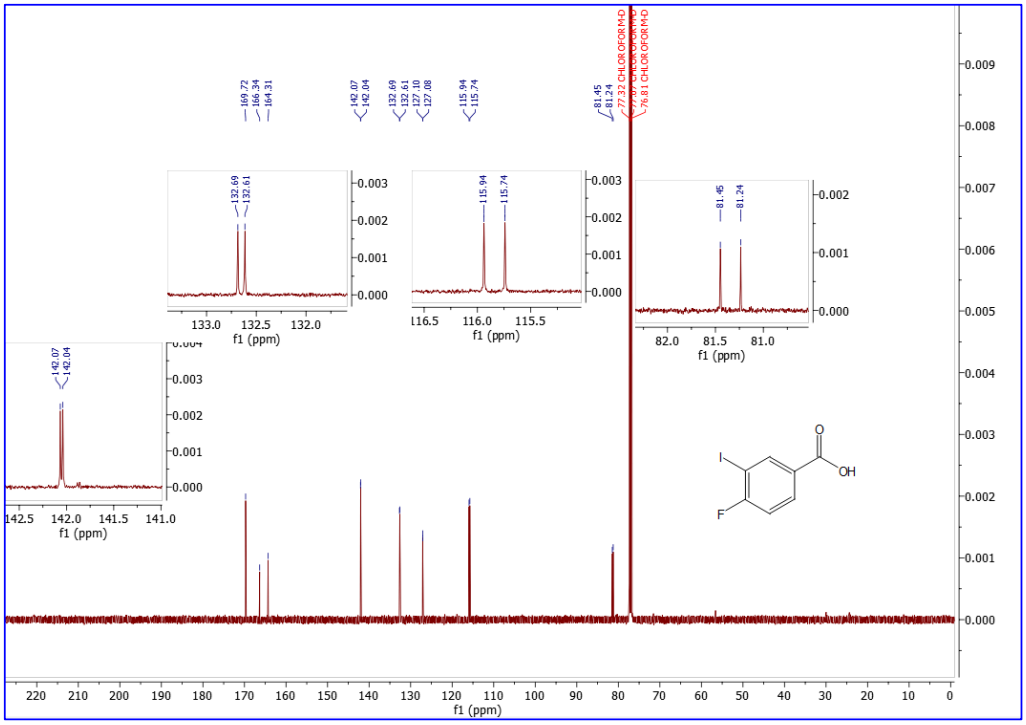

Figure S25: **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) of compound **4i**.

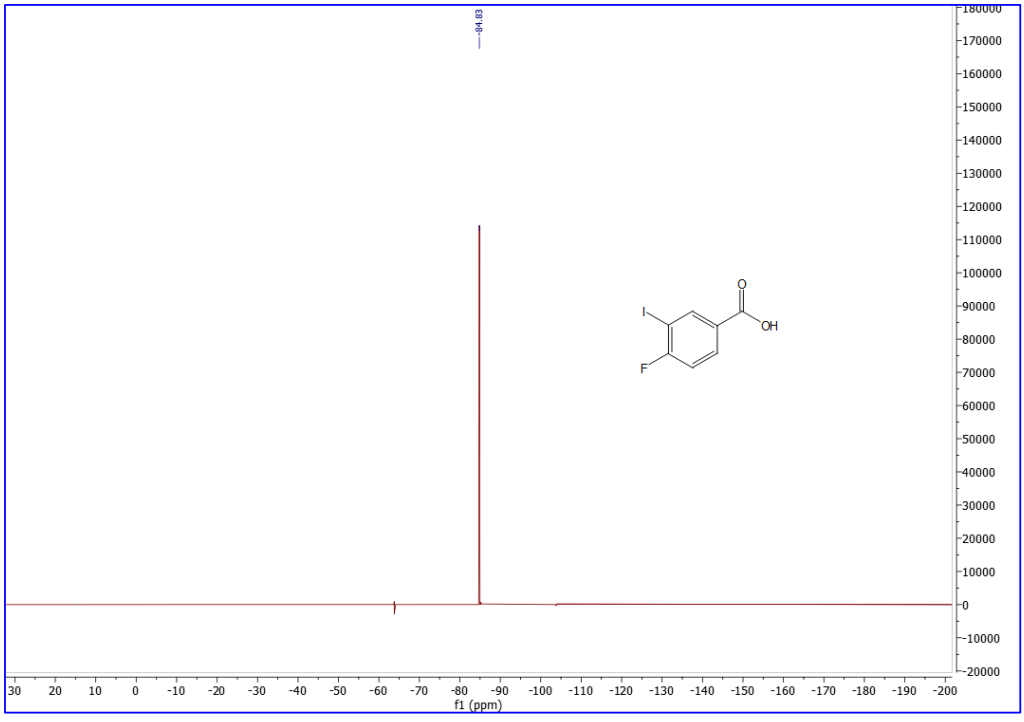

Figure S26: **^{19}F NMR** spectrum of compound **4i** in $CDCl_3$

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1,5-Dichloro-2-iodoanthracene-9,10-dione (4j)

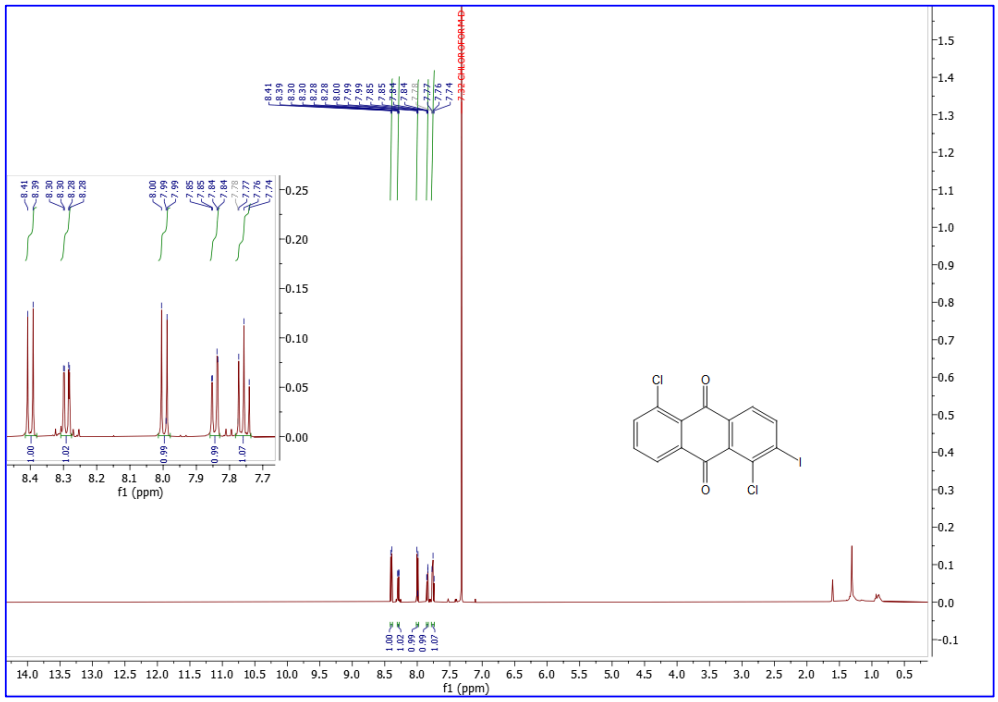

Figure S27: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4j**.

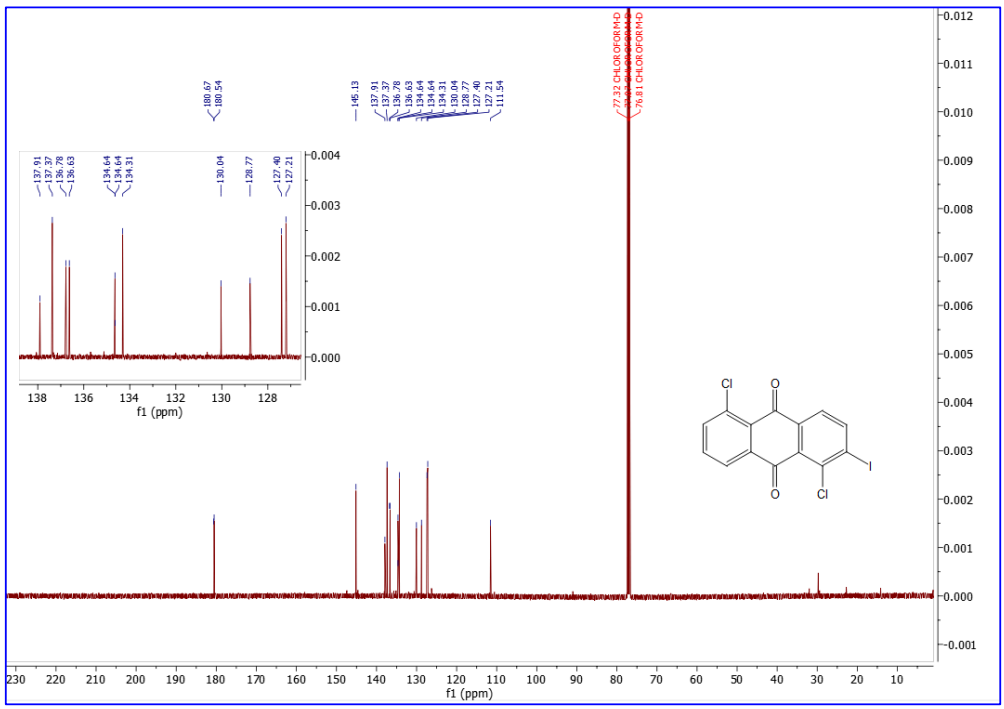

Figure S28: **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) of compound **4j**.

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2-Ethyl-3-iodoanthracene-9,10-dione (4k)

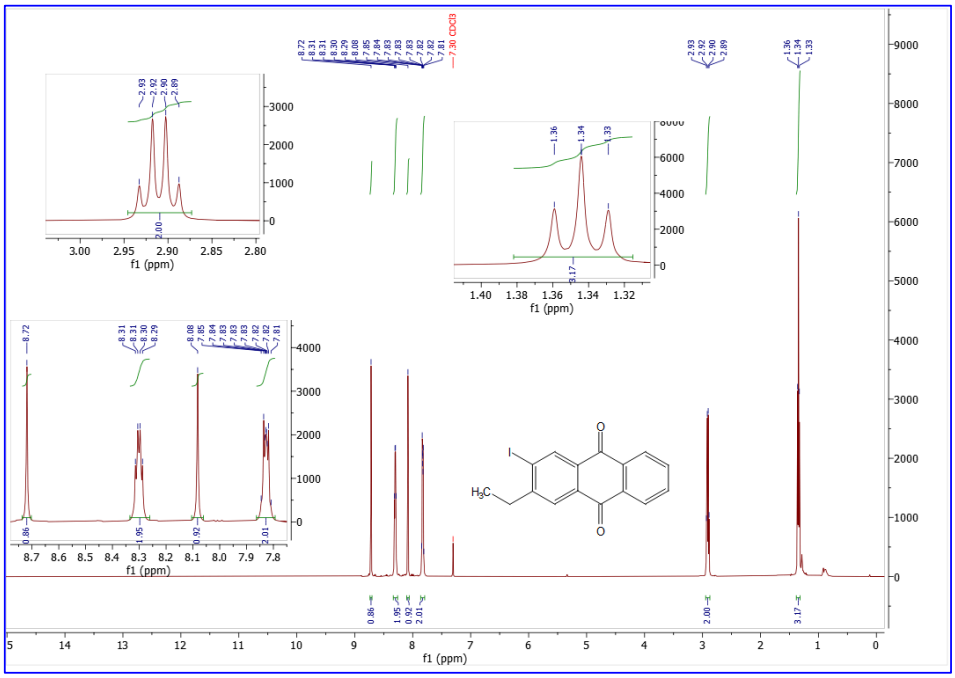

Figure S29: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4k.**

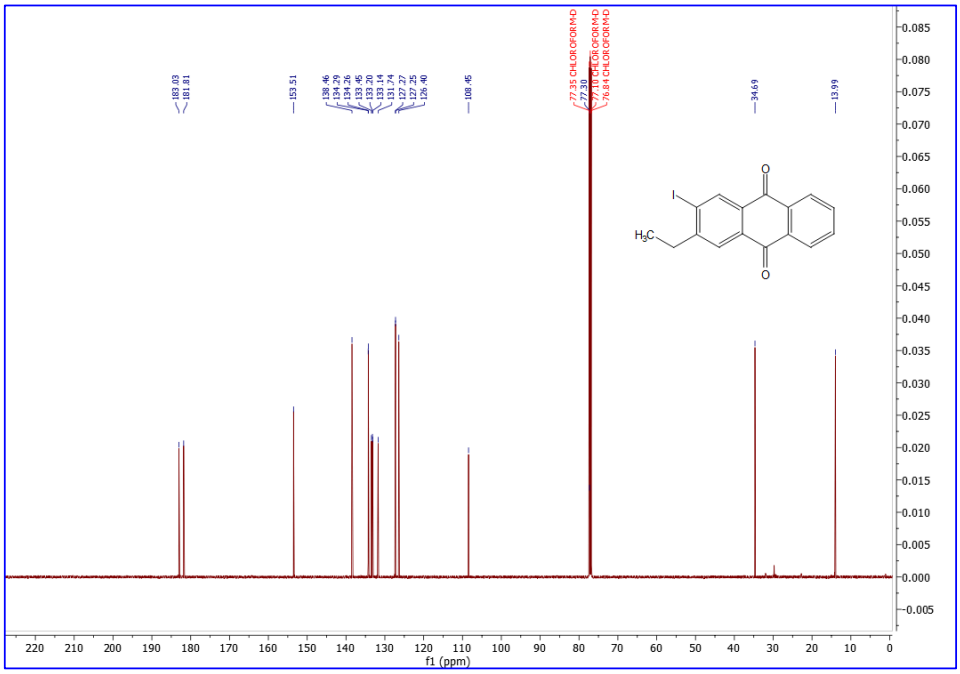

Figure S30: **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) of compound **4k.**

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1,2-Diiodo-4-(trifluoromethyl)benzene (4l)

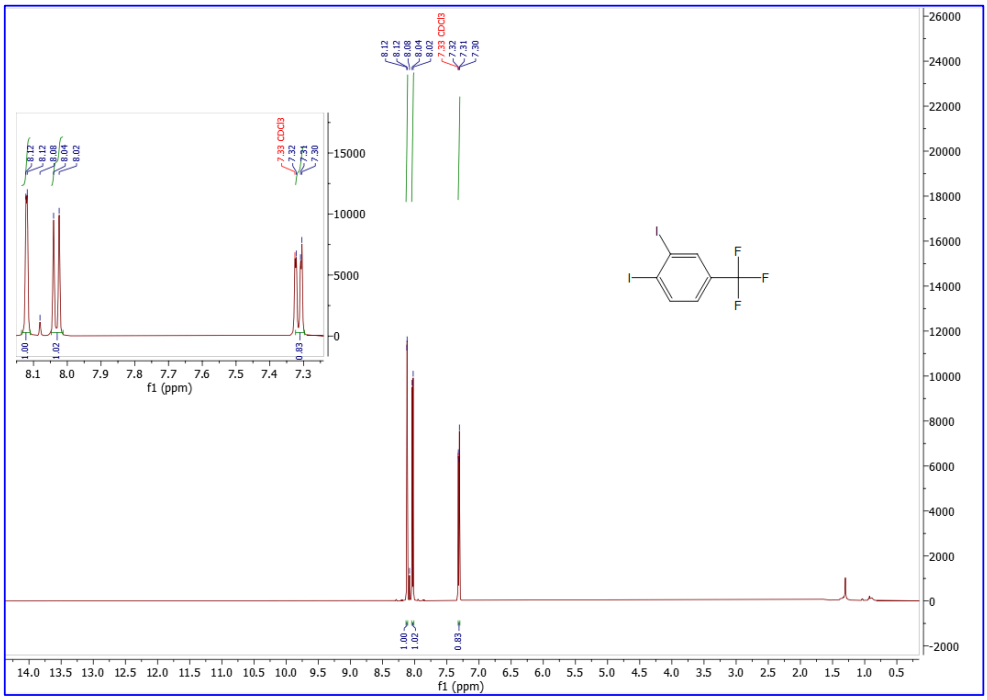

Figure S31: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4l**.

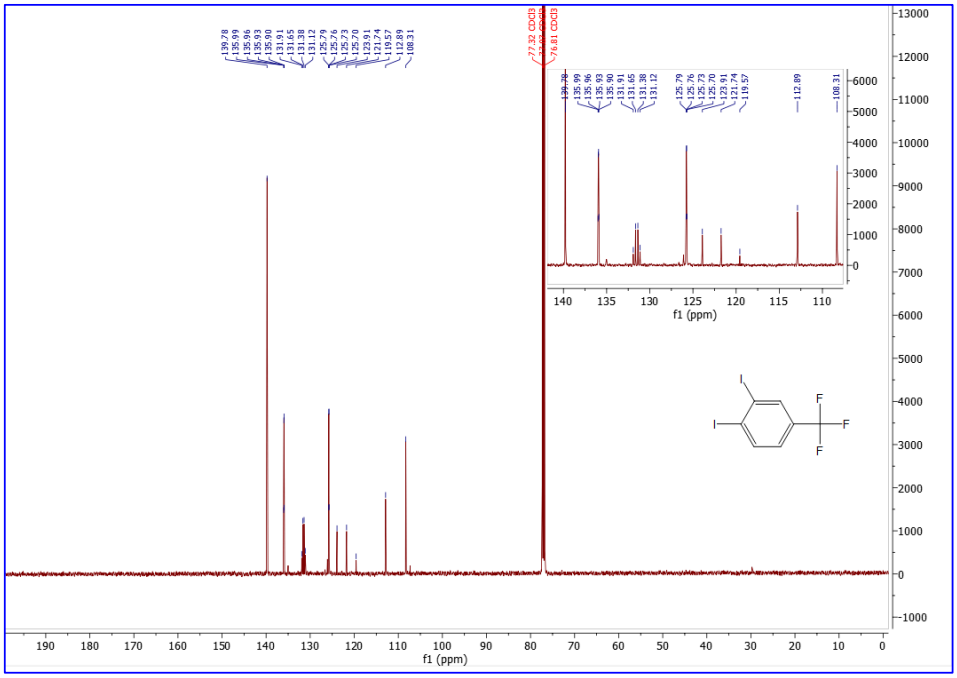

Figure S32: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4l**.

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1-Bromo-2-iodo-4-(trifluoromethyl)benzene (4m)

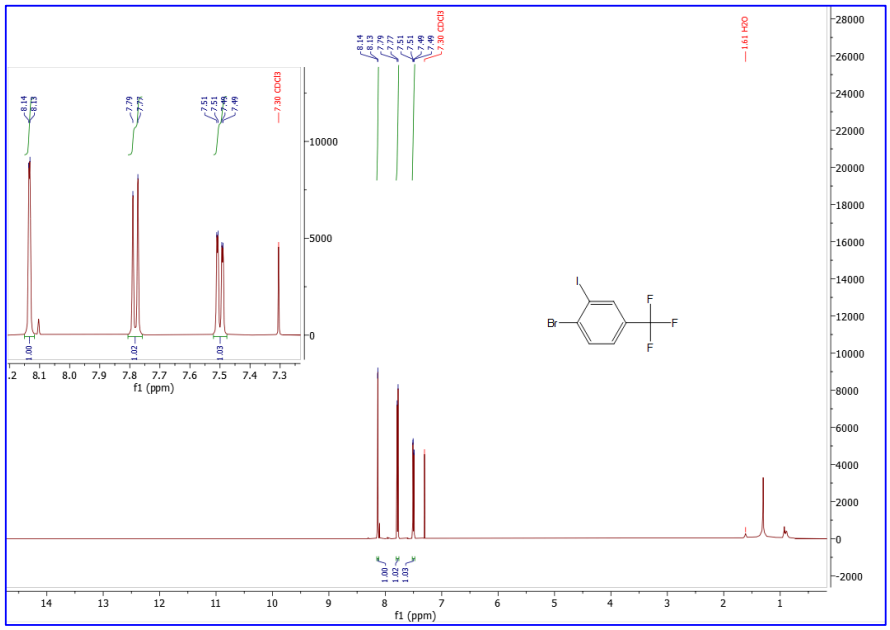

Figure S33: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4m**.

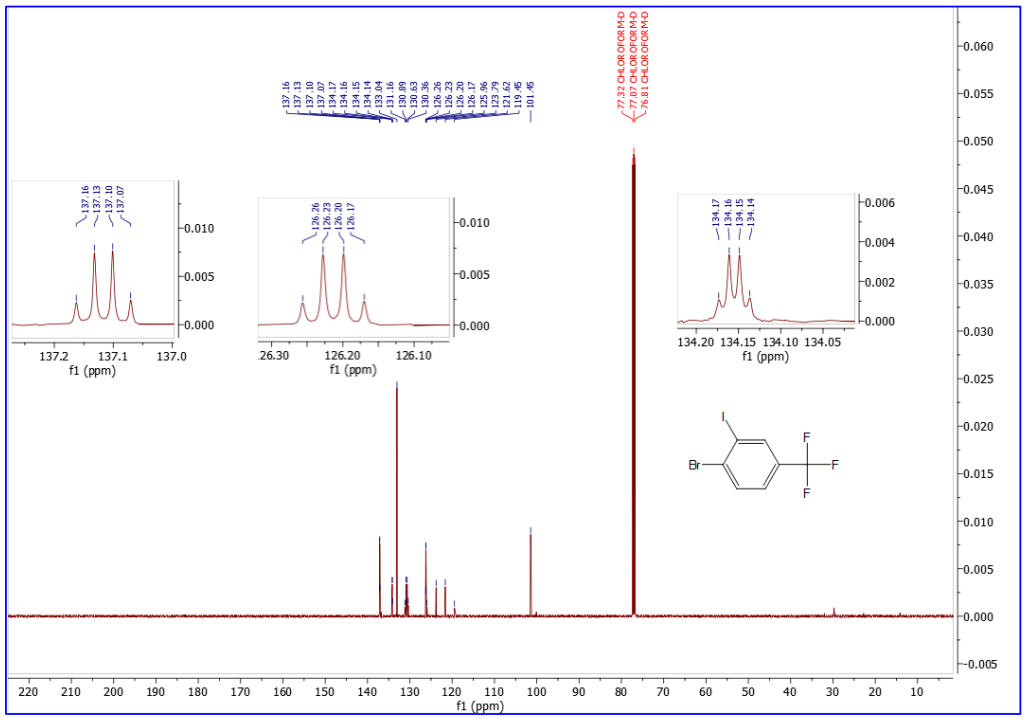

Figure S34: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4m**.

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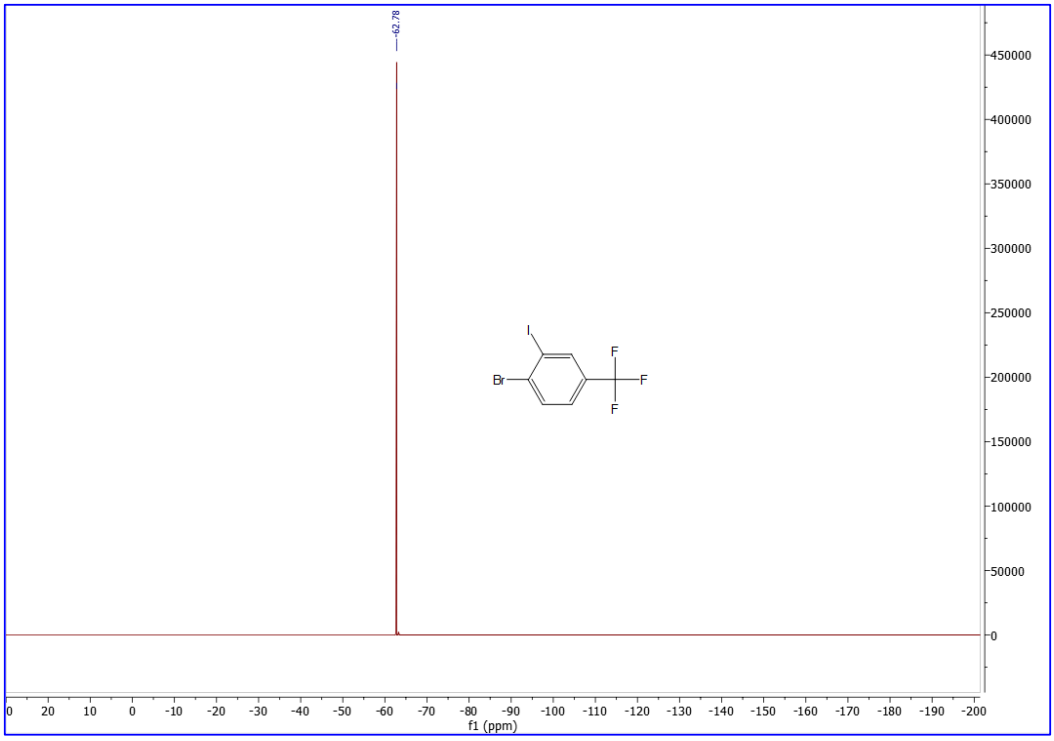

Figure S35: **^{19}F NMR** spectrum of compound **4m** in $CDCl_3$

Dimethyl 2-iodoterephthalate (4n)

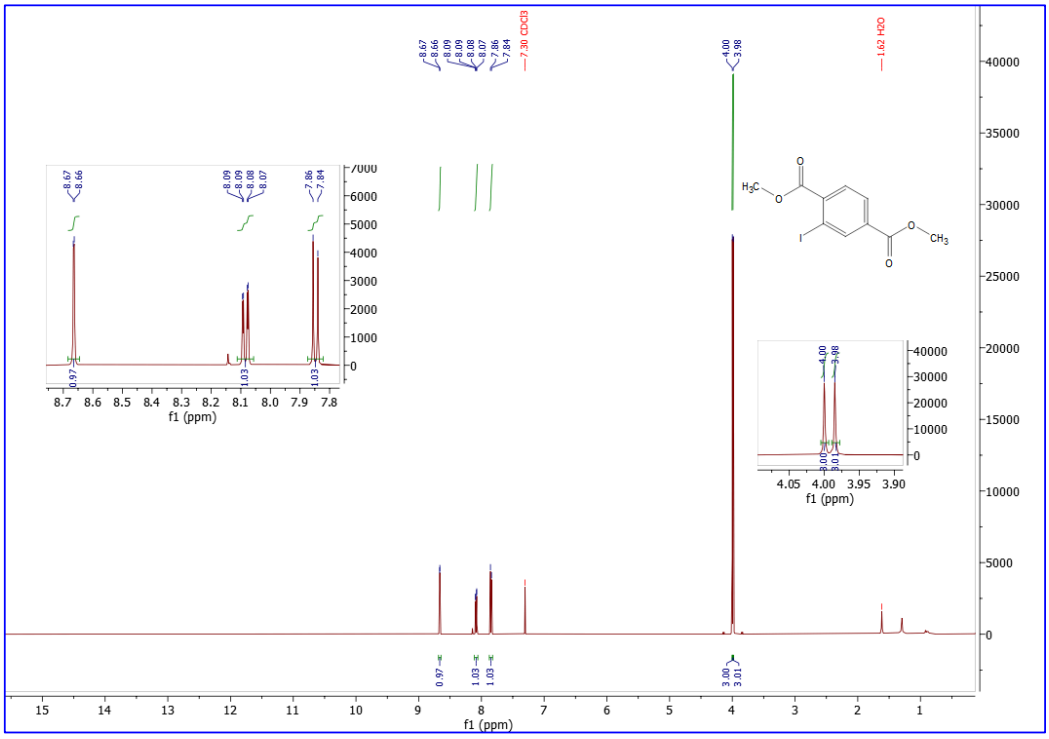

Figure S36: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4n**.

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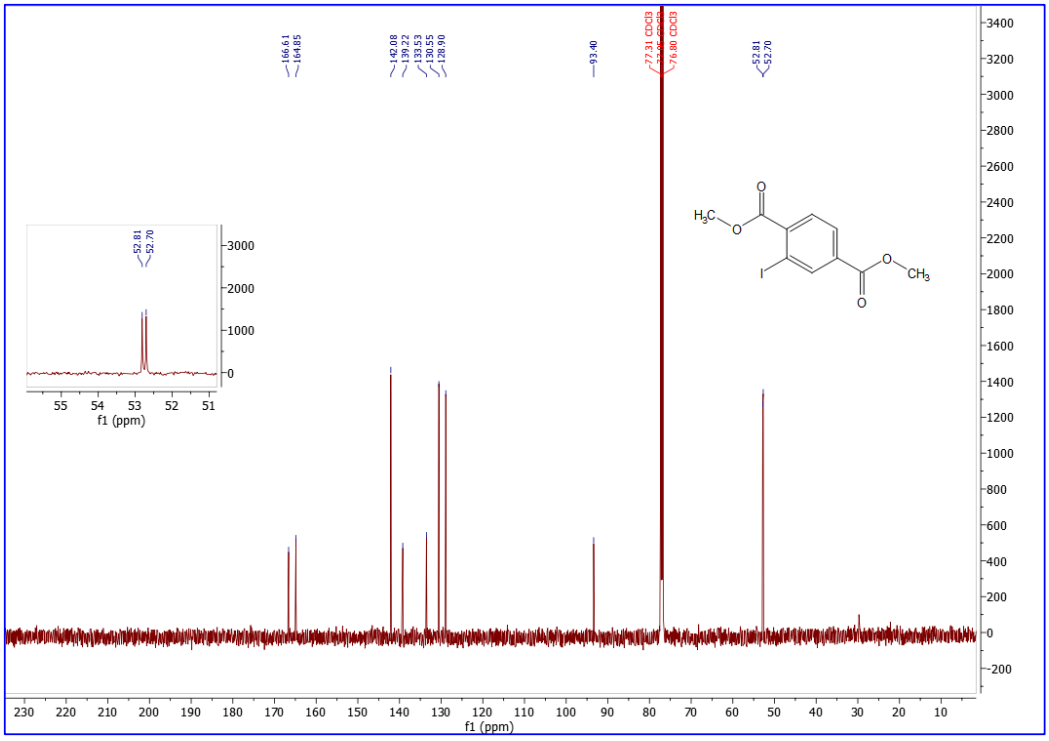

Figure S37: **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) of compound **4n**.

Dimethyl 5-iodoisophthalate (4o)

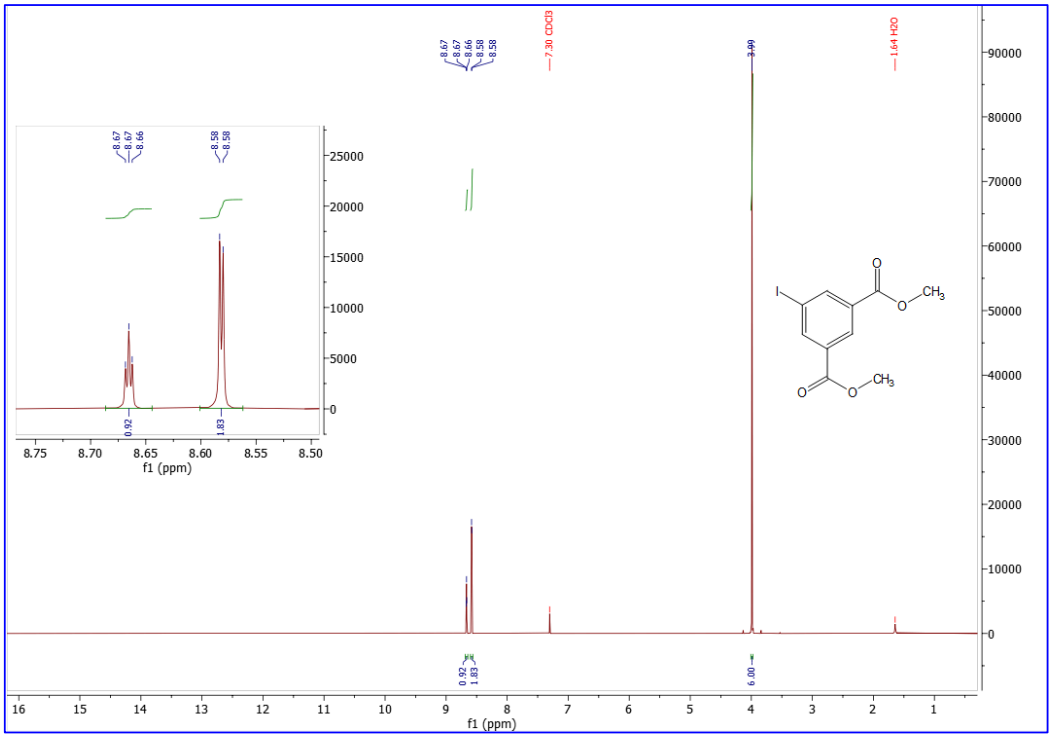

Figure S38: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4o**.

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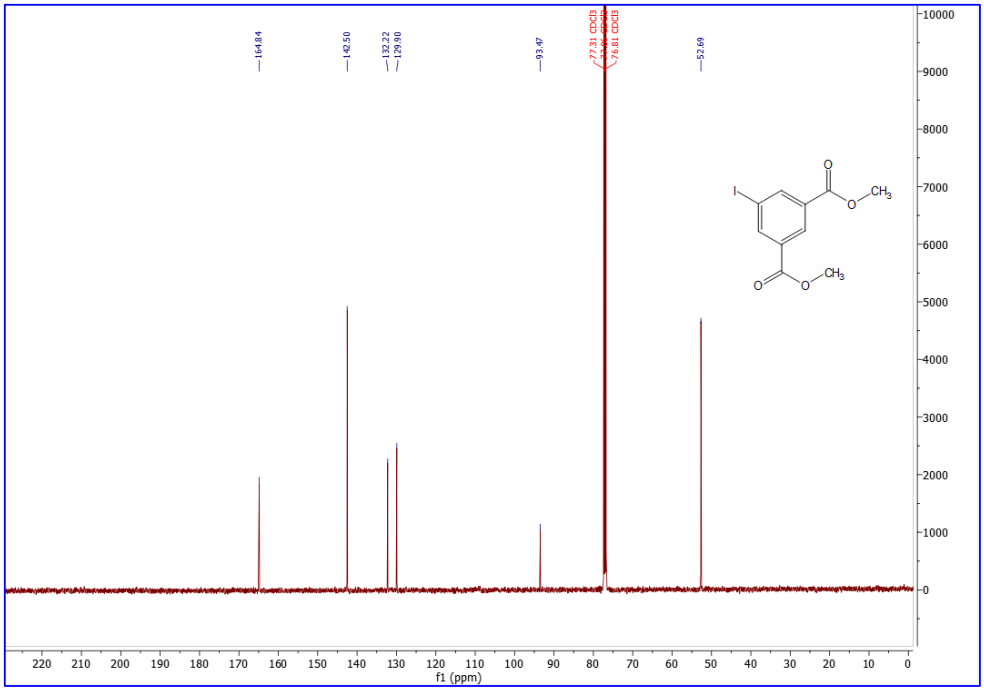

Figure S39: **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) of compound **4o**.

Dimethyl 4-iodophthalate (4p)

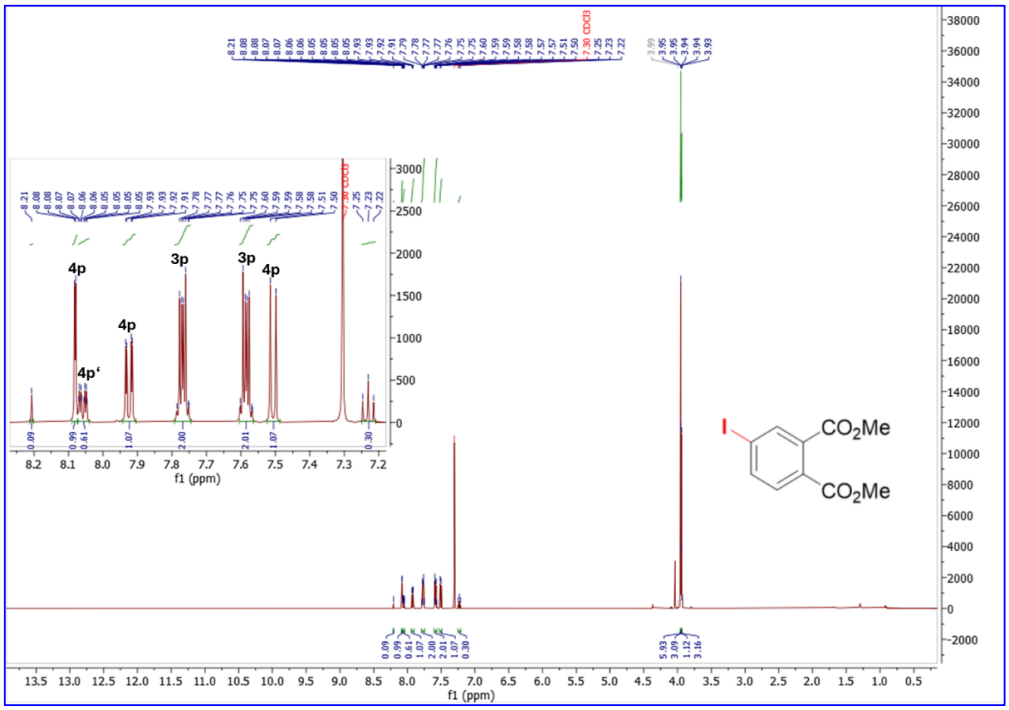

Figure S40: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4p**.

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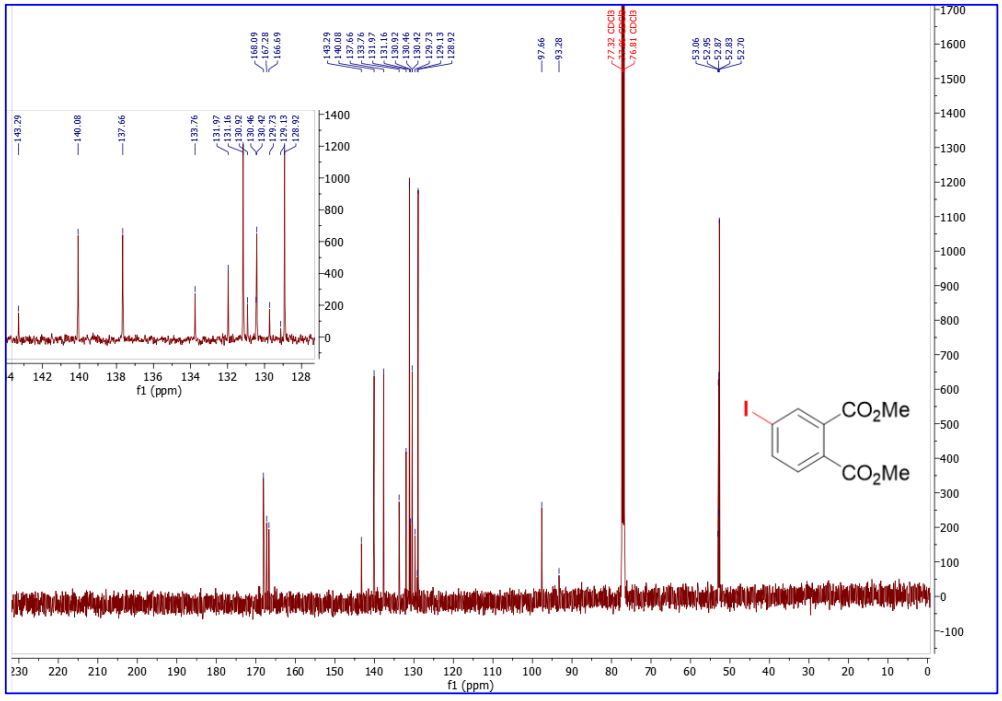

Figure S41: **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) of compound **4p**.

Dimethyl (3-iodophenyl)phosphonate (4s)

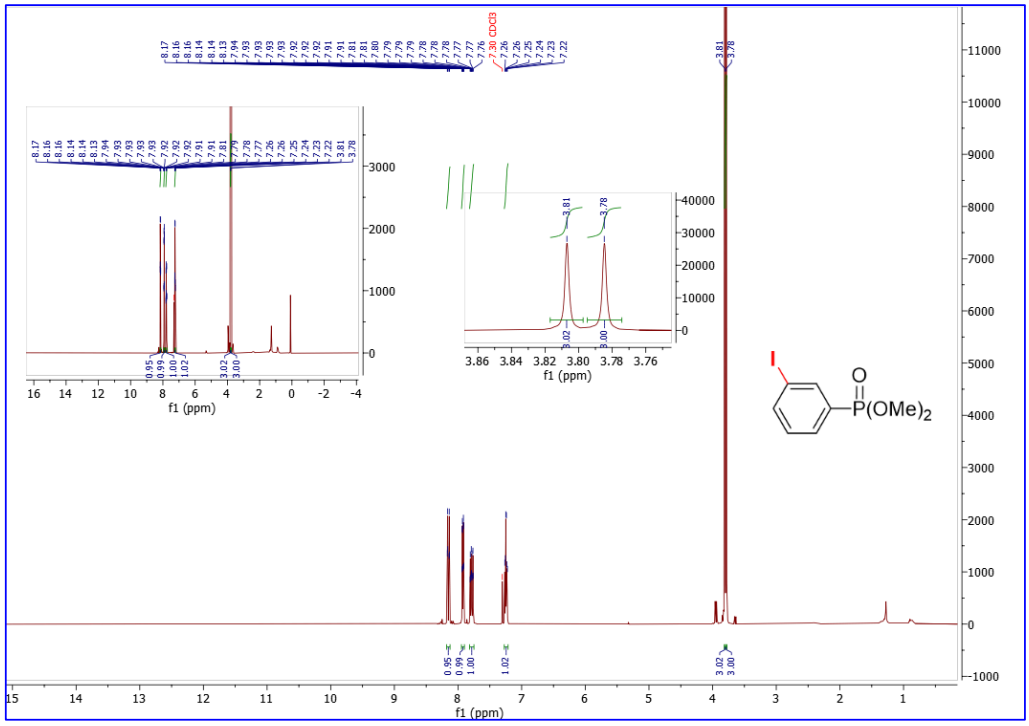

Figure S42: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4s**.

Synthesis | DOI 10.1055/a-2811-7617 | © The Author(s).

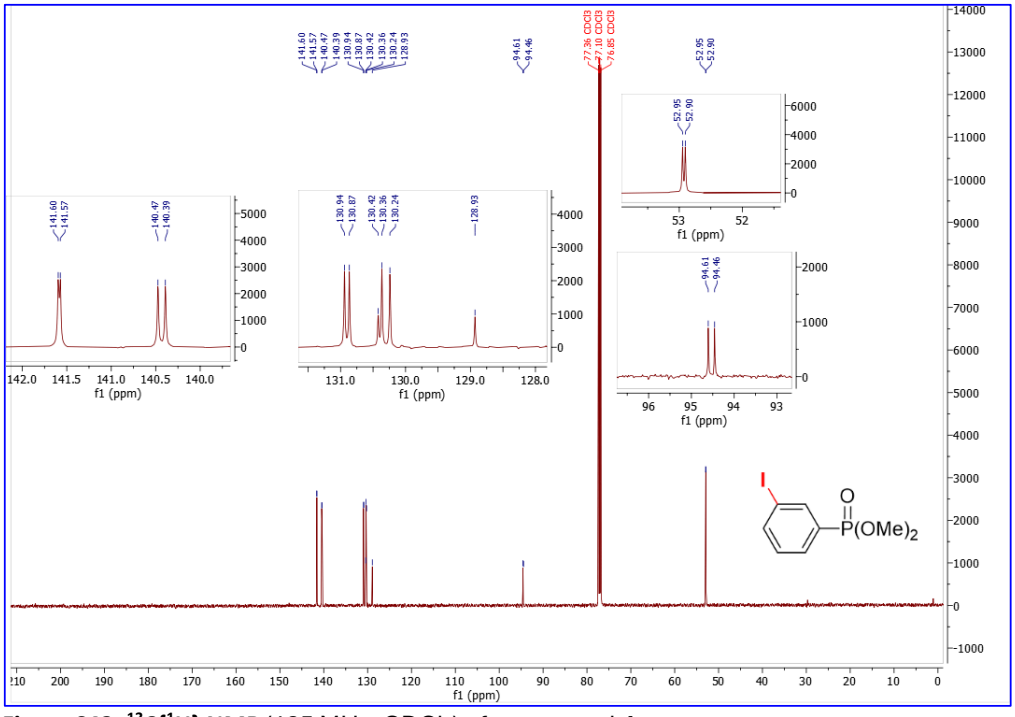

Figure S43: **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) of compound **4s**.

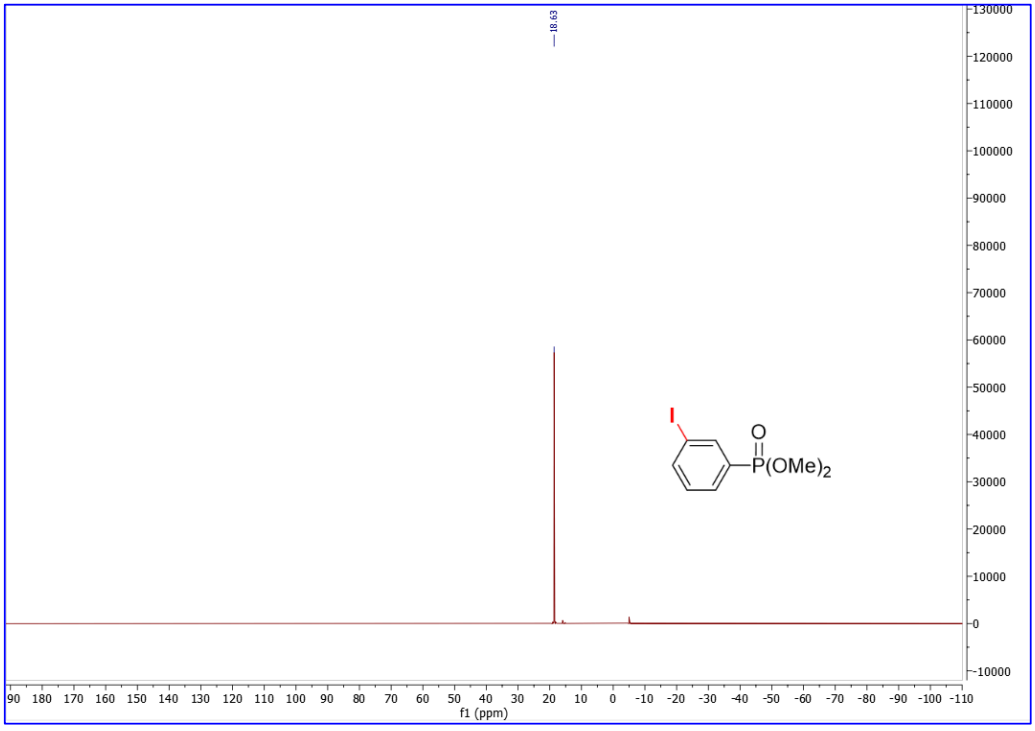

Figure S44: **^{31}P NMR** (202 MHz, $CDCl_3$): of compound **4s**.

Synthesis | DOI 10.1055/a-2811-7617 | © The Author(s).

Ethyl 3-iodo-4-methylbenzenesulfonate (4t)

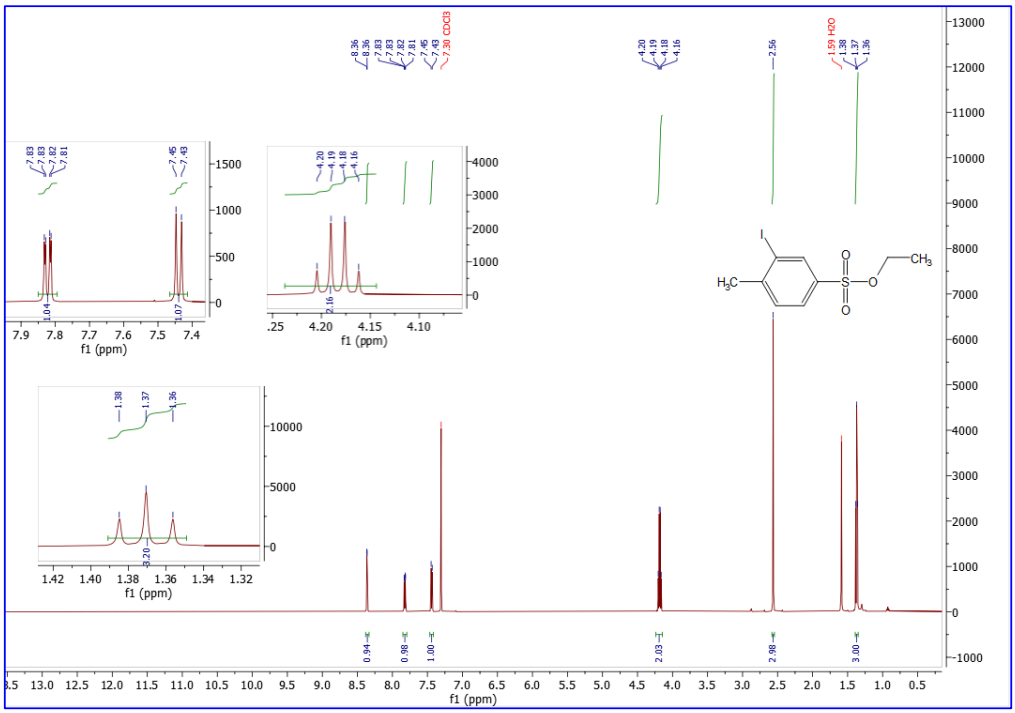

Figure S45: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4t**.

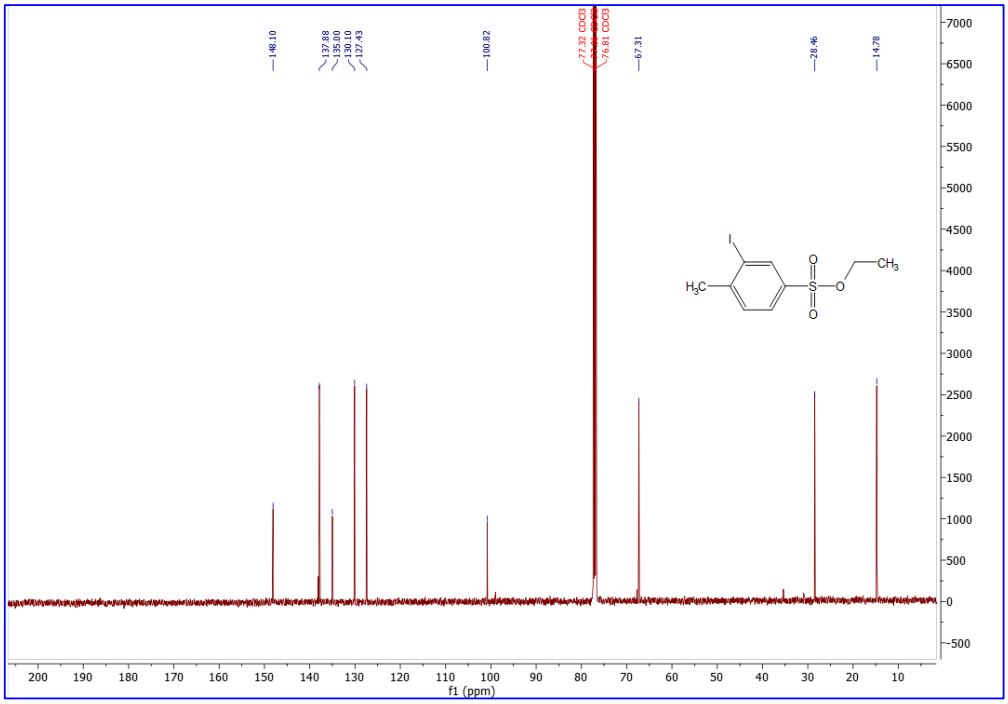

Figure S46: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4t**.

Synthesis | DOI 10.1055/a-2811-7617 | © The Author(s).

Ethyl 3,5-diiodo-4-methylbenzenesulfonate (4u)

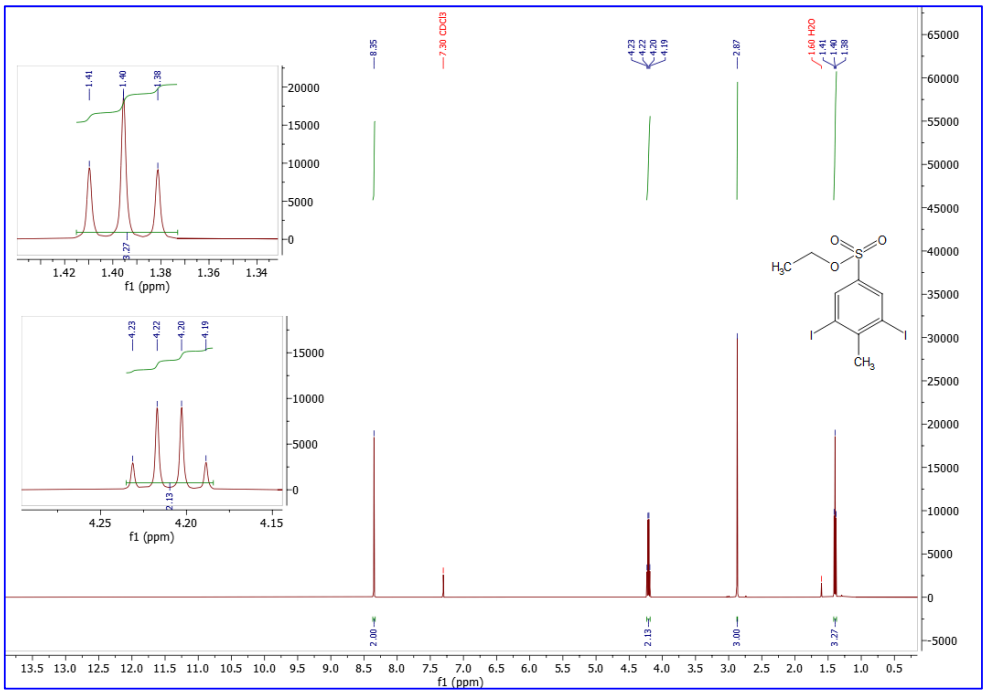

Figure S47: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4u**.

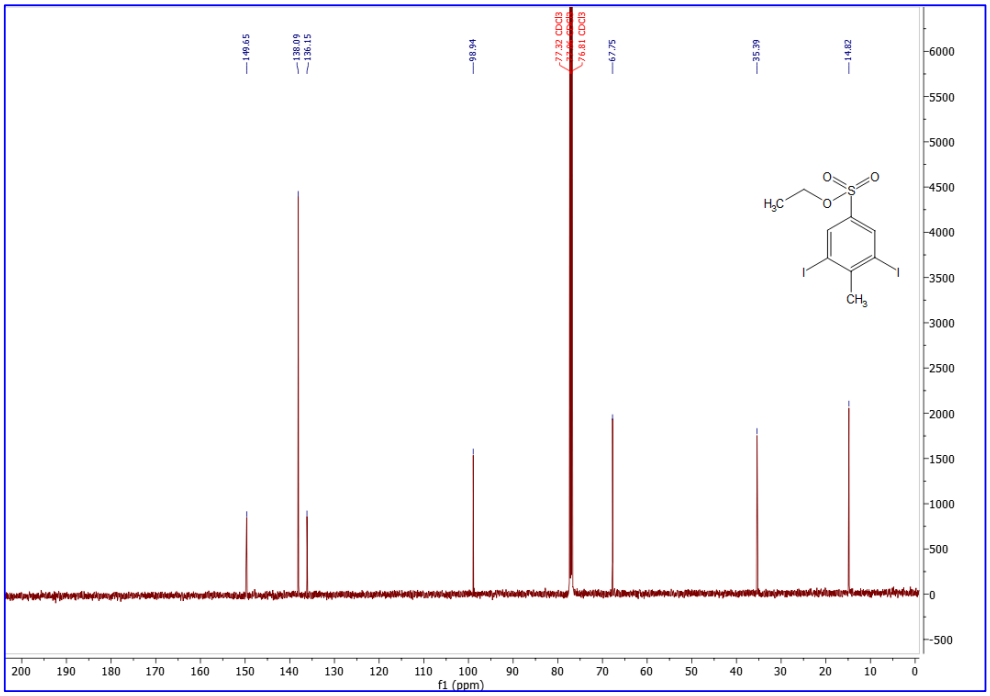

Figure S48: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4u**.

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3,3'-Sulfonylbis(iodobenzene) (4v)

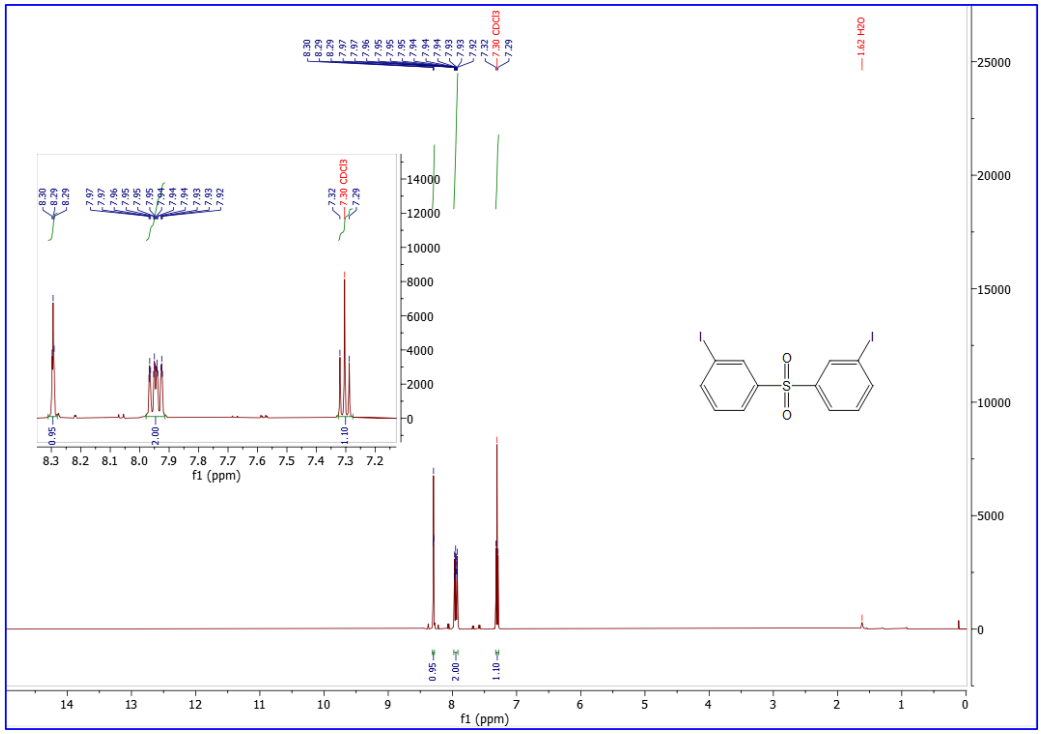

Figure S49: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4v**.

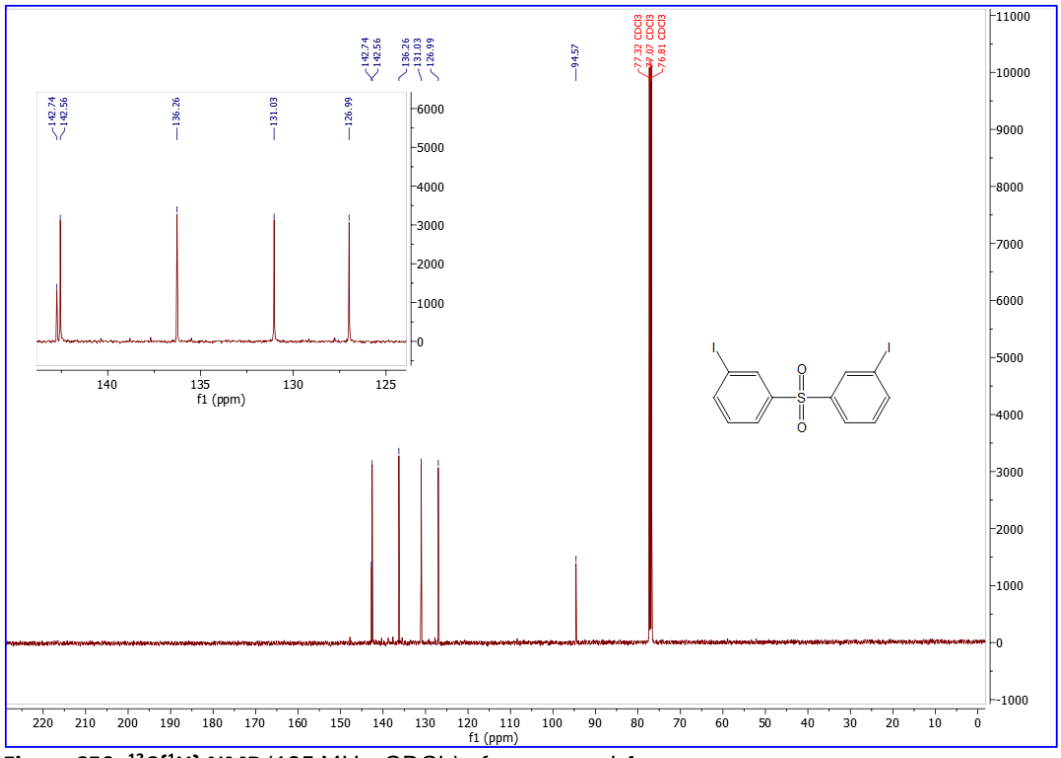

Figure S50: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4v**.

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1-Bromo-3,5-dichloro-4-fluoro-2-iodobenzene (4x)

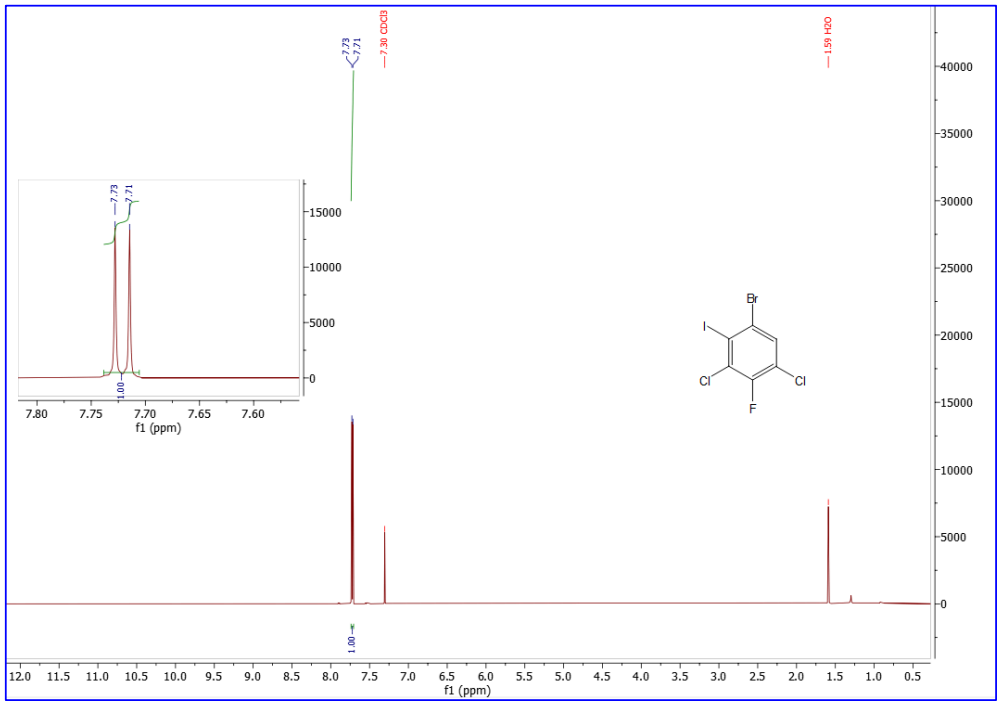

Figure S51: **^{1}H NMR** (500 MHz, $CDCl_3$) of compound **4x**.

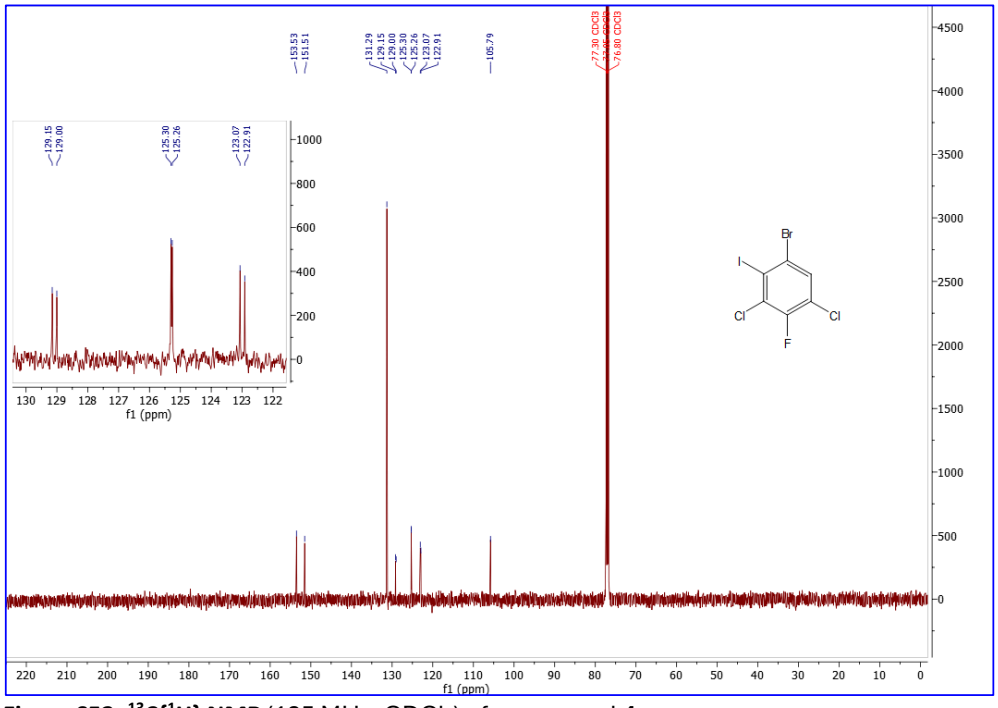

Figure S52: **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) of compound **4x**.

Synthesis | DOI 10.1055/a-2811-7617 | © The Author(s).

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