## Electronic Supplementary Information

# The tuning of frontier orbital energy levels of dibenzosilole copolymers for their application in organic electronics

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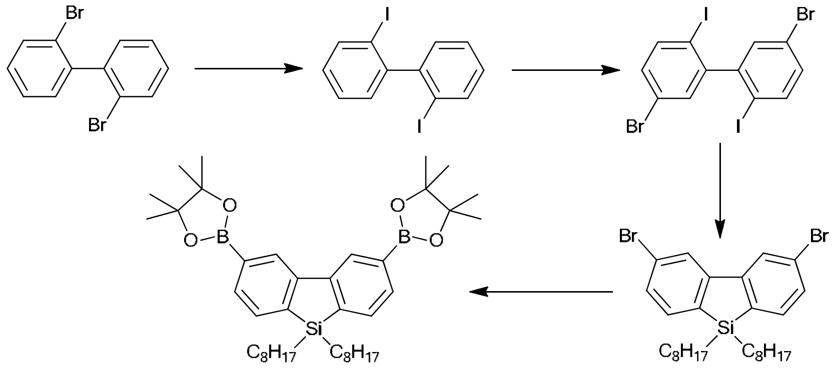
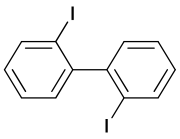
*S1: Synthetic route to dibenzosilole monomer* **1**[1]



## 1 - Experimental procedures – literature compounds

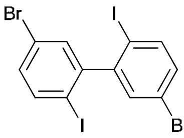
### ***2,2'-Diiodobiphenyl*** [2]



An oven-dried 2-necked flask was charged with 2,2'-dibromobiphenyl (5.00 g, 16.0 mmol) and dry diethyl ether (50 mL) under a nitrogen atmosphere. The solution was cooled to -78 ºC and n-butyllithium (23.0 mL, 36.9 mmol, 1.6 M in hexanes) was added dropwise over one hour. The mixture was stirred overnight, warming to room temperature. It was then cooled to 0 °C and a solution of iodine (9.35 g, 36.9 mmol) in dry diethyl ether (50 mL) was added dropwise. The reaction was stirred at room temperature for a further two hours before a solution of sodium thiosulphate (1 g) in distilled water (60 mL) was added to quench the reaction. The product was extracted with diethyl ether (3 x 100 mL) and the combined organic fractions were washed with brine (150 mL) then dried ($MgSO_4$). Removal of the solvent in vacuo gave an off-white solid. Purification by filtration through a pad of silica, using hexane as eluent, followed by recrystallisation from hexane afforded the title compound (4.16 g, 10.24 mmol, 64%) as colourless crystals.

Mp 112 - 114 °C (lit. mp 107-108 °C)[2]; δH(400 MHz, $CDCl_3$) 7.07 (2H, td, *J* 7.5, 1.5, Ar*H*), 7.18 (2H, dd, *J* 1.5, 7.5, Ar*H*), 7.40 (2H, t, *J* 6.5, Ar*H*), 7.93 (2H, d, *J* 7.5, Ar*H*). The δH data is in agreement with literature values.[2]

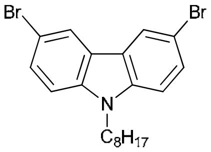
### ***5,5'-Dibromo-2,2'-diiodobiphenyl*** [1]



A multi-necked round-bottomed flask was charged with 2,2'-diiodobiphenyl (15.00 g, 36.9 mmol), iron powder (309 mg, 5.5 mmol) and carbon tetrachloride (350 mL). The mixture was stirred and de-gassed with nitrogen for 30 minutes, then bromine (8.52 mL, 166.2 mmol) was added via syringe. The reaction was stirred at 50 °C overnight under a nitrogen atmosphere then allowed to cool to room temperature. A solution of aqueous potassium hydroxide (10%, 200 mL) was added to quench excess bromine and the mixture was separated. The aqueous layer was extracted with carbon tetrachloride (1 x 100 mL), the combined organic layers were dried ($MgSO_4$) and the solvent was removed in vacuo. The product was washed thoroughly with DCM (200 mL) to afford the title compound (8.22 g, 14.6 mmol, 39%) as a white powder.

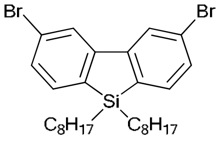
Mp 212 – 213 °C; (lit. mp 198-200 °C)[1] δH(400 MHz, $CDCl_3$) 7.22 (2H, dd, *J* 8.5, 2.5, Ar*H*), 7.30 (2H, d, *J* 2.5, Ar*H*), 7.76 (2H, d, *J* 8.5, Ar*H*). The δH data is in agreement with literature values.[1]

### *3,6-Dibromo-N-octyl-9H-carbazole* [3]



A round bottomed flask was charged with N-octyl-9H-carbazole (10.00 g, 35.78 mmol) and THF (200 mL). The solution was cooled to 0 °C in an ice bath and N-Bromosuccinimide (13.38 g, 75.15 mmol) was added portion-wise over a period of 10 min. The reaction mixture was stirred overnight, warming to room temperature. The crude product was extracted with DCM (3 x 200 mL) and the combined organic extracts were washed with distilled water (2 x 300 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by filtration through a silica plug, using hexane as eluent, followed by recrystallisation from ethanol gave the title compound (12.61 g, 28.83 mmol, 81%) as colourless crystals; RF (hexane-EtOAc, 5:1) 0.23; δH(400 MHz, $CDCl_3$) 0.86 (3H, t, *J* 6.9, C$H_3$), 1.23–1.31 (10H, m, C$H_2$), 1.80–1.84 (2H, m, C$H_2$), 4.23 (2H, t, *J* 7.2, NC$H_2$), 7.25 (2H, d, *J* 8.7, Ar*H*), 7.55 (2H, dd, *J* 1.8 8.7, Ar*H*), 8.14 (2H, d, *J* 1.8, Ar*H*). The δH data is in agreement with literature values.[3]

### *3,6-Dibromo-9,9-dioctyl-9H-dibenzosilole* [1]

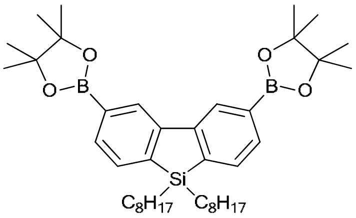


An oven dried multi-necked round-bottomed flask was evacuated and nitrogen filled, then charged with 5,5'-dibromo-2,2'-diiodobiphenyl (14.00 g, 24.8 mmol) and dry THF (250 mL) under nitrogen. The solution was cooled to -90 °C and stirred at this temperature for 25 minutes. t-Butyllithium (64.00 mL, 101.8 mmol, 1.6 M solution in hexanes) was added dropwise via cannula. The reaction was stirred at -90 °C for one hour before di-n-octyldichlorosilane (18.05 mL, 52.2 mmol) was added via syringe. The reaction was stirred overnight, allowing it to warm to room temperature. Distilled water (5 mL) was added to quench the reaction and the majority of the solvent was removed in vacuo. The material was extracted with diethyl ether (3 x 100 mL) and the combined organic layers were washed with aqueous sodium thiosulphate solution (10%, 2 x 200 mL) and brine (200 mL), then dried

($MgSO_4$). The solvent was removed in vacuo and purification by column chromatography on silica gel, using hexane as eluent, afforded the title compound (6.80 g, 12.0 mmol, 49%) as a colourless oil.

RF (hexane) 0.54; δH(400 MHz, $CDCl_3$) 0.83 (6H, t, *J* 7.0, C$H_3$), 0.85-0.93 (4H, m, C$H_2$), 1.12-1.32 (24H, m, C$H_2$), 7.37-7.45 (4H, m, Ar*H*), 7.88 (2H, d, *J* 1.5, Ar*H*). The δH data is in agreement with literature values.[1]

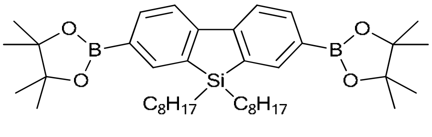
### *9,9-Dioctyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-dibenzosilole* (1) [1]



An oven dried multi-necked round-bottomed flask was evacuated and nitrogen filled. A solution of 3,6-dibromo-9,9-dioctyl-9H-dibenzosilole (6.80 g, 12.0 mmol) in dry THF (120 mL) was added via cannula under nitrogen. The flask was cooled to -78 °C and stirred for 10 minutes. t-Butyllithium (30.84 mL, 49.4 mmol, 1.6 M solution in hexanes) was added dropwise via cannula and the reaction was stirred for a further 30 minutes at -78 °C. 2-Isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaboralane (6.14 mL, 30.1 mmol) was added via syringe and the reaction was stirred overnight under nitrogen, allowing to warm to room temperature. Distilled water (5 mL) was added to quench the reaction and the majority of the solvent / water was removed in vacuo. The crude product was extracted with diethyl ether (3 x 100 mL) and the combined organic layers were washed with aqueous sodium thiosulphate (10%, 200 mL) and brine (200 mL), then dried ($MgSO_4$). The solvent was removed in vacuo and purification by column chromatography on silica, using EtOAc-hexane (1:9) was eluent, followed by recrystallisation from ethanol afforded the title compound (2.36 g, 3.6 mmol, 30%) as colourless crystals.

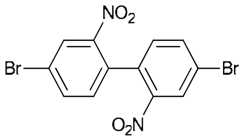
RF (EtOAc-hexane, 1:9) 0.32; mp 94 – 96 °C (lit. mp 87-89 °C)[1]; δH(400 MHz, $CDCl_3$) 0.82 (6H, t, *J* 7.0, C$H_3$), 0.85-0.91 (4H, m, C$H_2$), 1.13-1.36 (24H, m, C$H_2$), 1.37 (24H, s, C$H_3$), 7.59 (2H, d, *J* 7.0, Ar*H*), 7.69 (2H, d, *J* 7.5, Ar*H*), 8.34 (2H, s, Ar*H*). The δH data is in agreement with literature values.[1]

### **2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyldibenzosilole (2).**[4]



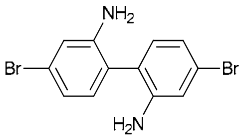
A dry 2-necked flask was charged with 2,7-dibromo-9,9-dioctyldibenzosilole (3.00 g, 5.3 mmol) and dry THF (60 mL) under a nitrogen atmosphere. The solution was cooled to -78 ºC and *t*-butyllithium (13.22 mL, 22.5 mmol, 1.7 M in hexanes) was added dropwise over 30 minutes. The mixture was stirred for a further 20 minutes at -78 ºC, then 2-isopropoxy-4,4’,5,5’-tetramethyl-1,3,2-dioxaboralane (2.71 mL, 13.3 mmol) was added dropwise to the mixture. The reaction was then stirred overnight, warming to room temperature. Distilled water was added to quench the reaction and the bulk of the solvents were removed *in vacuo*. The product was extracted with diethyl ether (3 x 100 mL) and the combined organic layers were washed with brine (150 mL), dried ($MgSO_4$) and evaporated to dryness. Purification by recrystallisation from isopropyl alcohol afforded the *title compound* (1.99 g, 3.0 mmol, 57%) as colourless crystals; mp 116-117°C (from isopropyl alcohol, lit. mp 115-116 °C)[4]; $\delta_H$(400 MHz, $CDCl_3$) 0.86 (6H, t, *J* 7.0, C$H_3$), 0.88-0.96 (4H, m, C$H_2$), 1.19-1.35 (24H, m, C$H_2$), 1.37 (24H, s, OCC$H_3$), 7.86 (2H, d, *J* 7.6, Ar*H*), 7.89 (2H, d, *J* 7.6, Ar*H*), 8.05 (2H, s, Ar*H*). The $\delta_H$ data is in agreement with literature values.[4]

**4,4’-Dibromo-2,2’-dinitrobiphenyl (3).**[5]



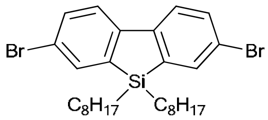
2,5-Dibromonitrobenzene (50.00 g, 178.0 mmol) was dissolved in dry DMF (200 mL). Copper powder (27.00 g, 424.0 mmol) was added to the solution, after which the reaction mixture was heated to 125 ºC for 3 h. Having allowed the mixture to cool to room temperature, toluene (200 mL) was added and any insoluble inorganic salts present in the mixture were removed by filtration through celite. The filtrate was evaporated to dryness *in vacuo* to give a solid, which was then washed with cold methanol (500 mL) and redissolved in toluene (200 mL). This solution was again filtered through celite, to remove any remaining inorganic salts, then evaporated to give the title compound (28.20 g, 70.0 mmol, 79 %) as yellow crystals; mp 147-149 ºC (lit. mp 146-148 °C)[6]; $\delta_H$(400 MHz, $CDCl_3$) 7.16 (2H, d, *J* 8.1, Ar*H*), 7.83 (2H, dd, *J* 8.2, 2.0, Ar*H*), 8.38 (2H, d, *J* 2.0, Ar*H*). The $\delta_H$ data is in agreement with literature values.[5]

**4,4’-Dibromobiphenyl-2,2’-diamine (4).**[7]



4,4’-Dibromo-2,2'-dinitrobiphenyl (50.00 g, 124.4 mmol) was dissolved in stirring abs. ethanol (600 mL). Subsequently, aqueous HCl (410 mL, 32% w/w) was added, followed by a cautious addition of tin powder (59.05 g, 497.5 mmol) over 10 minutes. The reaction mixture was heated at 100 ºC to reflux, whilst stirring, for 2 h. Having allowed the mixture to cool, it was poured into ice water (ca. 2000 mL). KOH pellets were added slowly until the mixture was pH-basic (pH > 9). Diethyl ether (1000 mL) was used to extract the crude product, which was washed with brine (500 mL) and dried ($MgSO_4$), before being filtered and evaporated to dryness. Purification by recrystallisation from ethanol yielded the *title* *compound* (10.87 g, 32.0 mmol, 92 %) as a light brown solid; mp 119 ºC (from EtOH, lit. mp 119-120 °C)[7]; $\delta_H$(400 MHz, $CDCl_3$) 3.72 (4H, br s, N*H*$_2$), 6.94 (6H, m, Ar*H*). The $\delta_H$ data is in agreement with literature values.[7]

### 2,7-Dibromo-9,9-di-n-octyldibenzosilole (6).[4]



An oven-dried 3-necked flask was charged with 4,4'-dibromo-2,2'-diiodobiphenyl (8.00 g, 14.2 mmol) and dry THF (200 mL) under a nitrogen atmosphere. The solution was cooled to -90 ºC using an ethanol / liquid nitrogen cooling bath. *t*-Butyllithium (34.25 mL, 58.2 mmol, 1.7 M in hexanes) was added dropwise, while maintaining the reaction temperature at -90 ºC. The mixture was stirred for a further 30 min at -90 ºC, then di-*n*-octyldichlorosilane (10.32 mL, 29.8 mmol) was added dropwise. The mixture was stirred overnight, warming to room temperature. Distilled water was added to quench the reaction and the THF / water was removed *in vacuo*. The crude product was extracted with diethyl ether (3 x 200 mL) and the combined organic layers were washed with aq. sodium thiosulphate (2 x 200 mL) and brine (2 x 150 mL). The organic layer was dried ($MgSO_4$) and evaporated to dryness to give a yellow/brown oil. Purification by column chromatography on silica gel, using hexane as eluent, yielded the *title compound* (6.44 g, 11.4 mmol, 81%) as a colourless oil; $R_F$ (hexane) 0.45; $\delta_H$(400 MHz, $CDCl_3$) 0.86 (6H, t, *J* 7.0, C*H*$_3$), 0.90-0.95 (4H, m, C*H*$_2$), 1.19-1.33 (24H, m, C*H*$_2$), 7.54 (2H, dd, *J* 8.3, 2.0, Ar*H*), 7.63 (2H, d, *J* 8.3, Ar*H*), 7.71 (2H, d, *J* 2.0, Ar*H*). The $\delta_H$ data is in agreement with literature values.[4]

### Purification of P8 by palladium scavenging agent

A solution of sodium diethyldithiocarbamate trihydrate (1.35 g, 6.0 mmol) in distilled water (10 mL) was added to a toluene solution of copolymer **P8** (400 mg in 30 mL). The mixture was vigorously stirred at room temperature in air for 48 hours. Distilled water (40 mL) and the organic layer extracted with toluene (3 x 30 mL) the combined organic layers washed with distilled water (50 mL) and brine (50 mL), then dried ($MgSO_4$). The solution was concentrated under vacuum, then added dropwise into a vigorously stirred flask of methanol (250 mL). The resulting precipitate was filtered and collected to give a light-yellow fibrous solid (378 mg).

## 2.1 – NMR spectra of precursor and monomer materials

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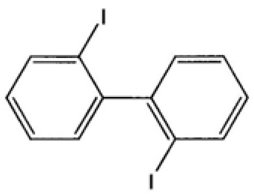
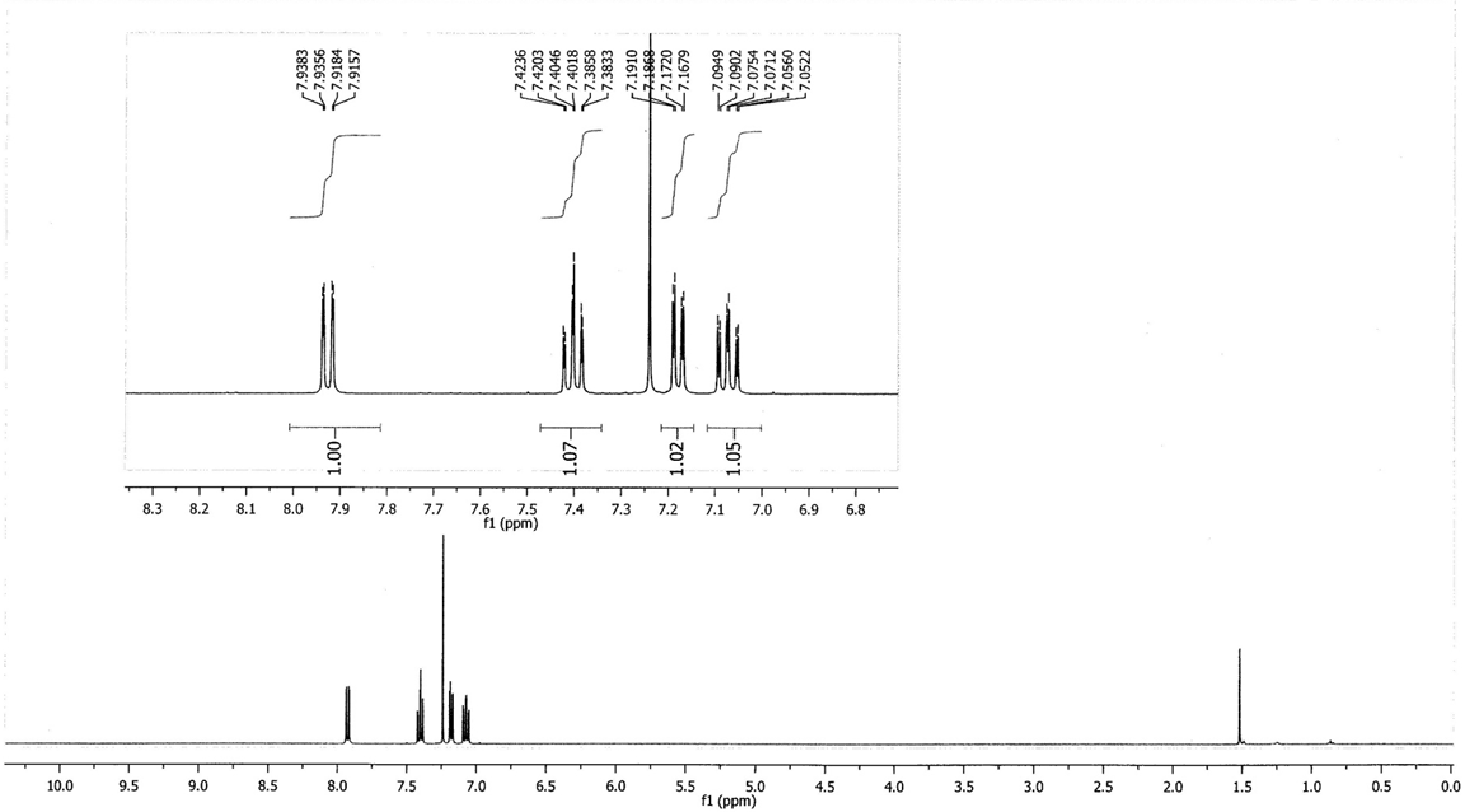
**2,2'-Diiodobiphenyl**





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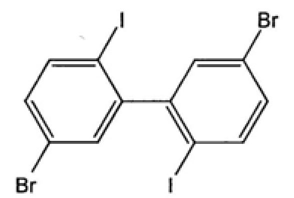
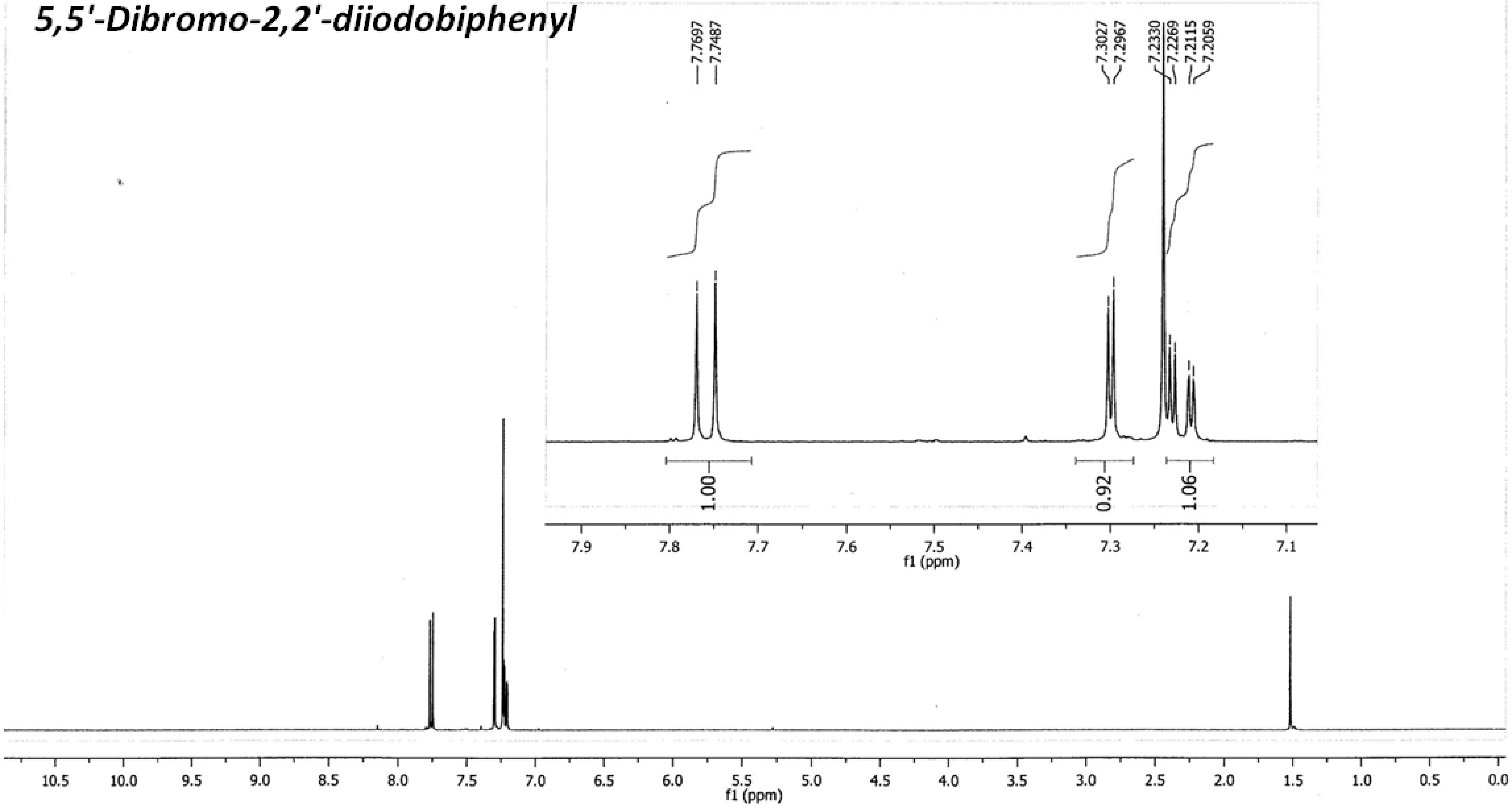
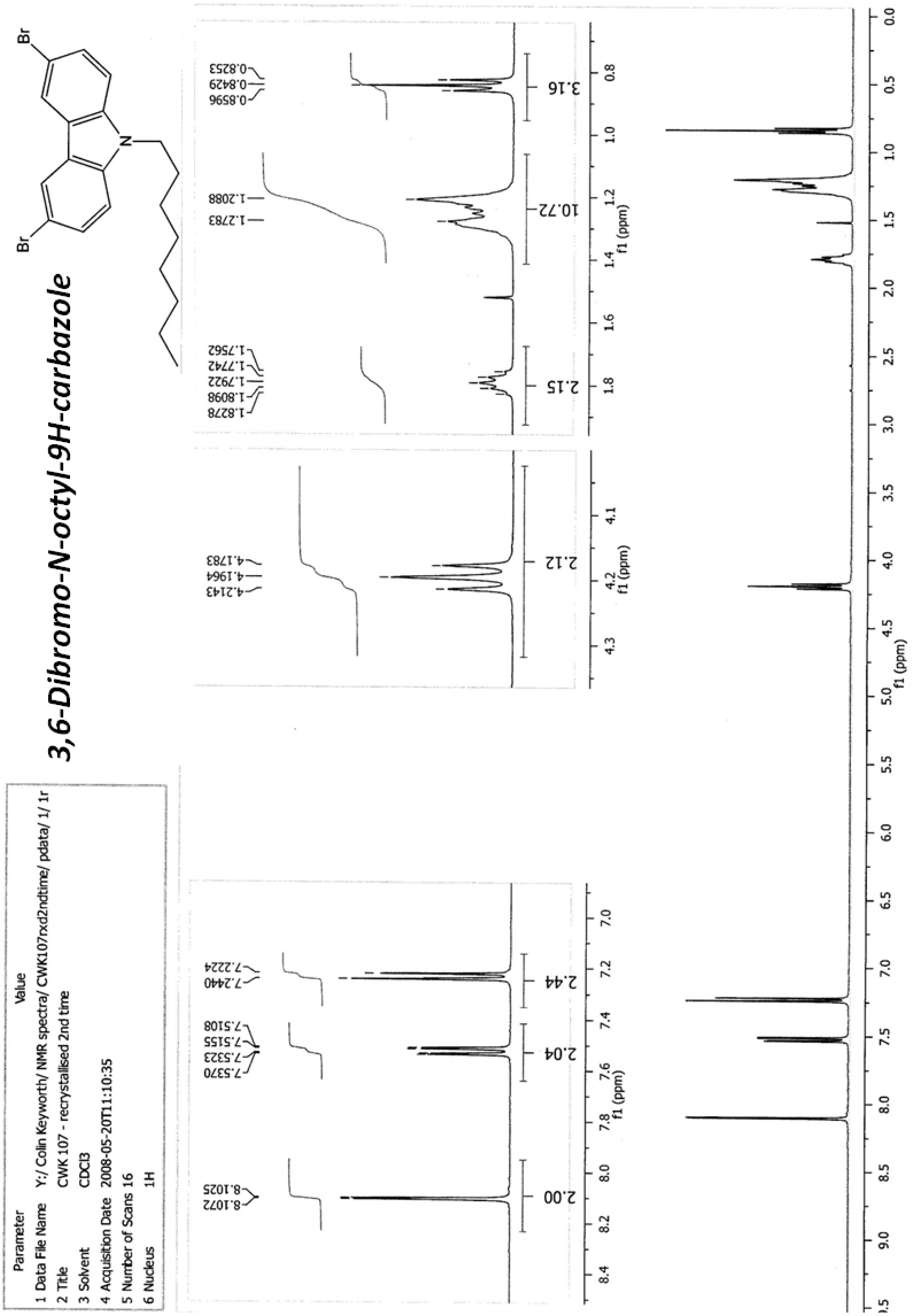


**5,5'-Dibromo-2,2'-diiodobiphenyl**





3,6-Dibromo-N-octyl-9H-carbazole

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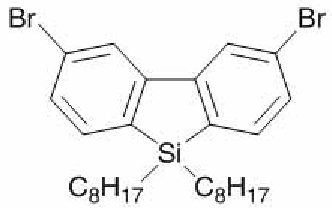

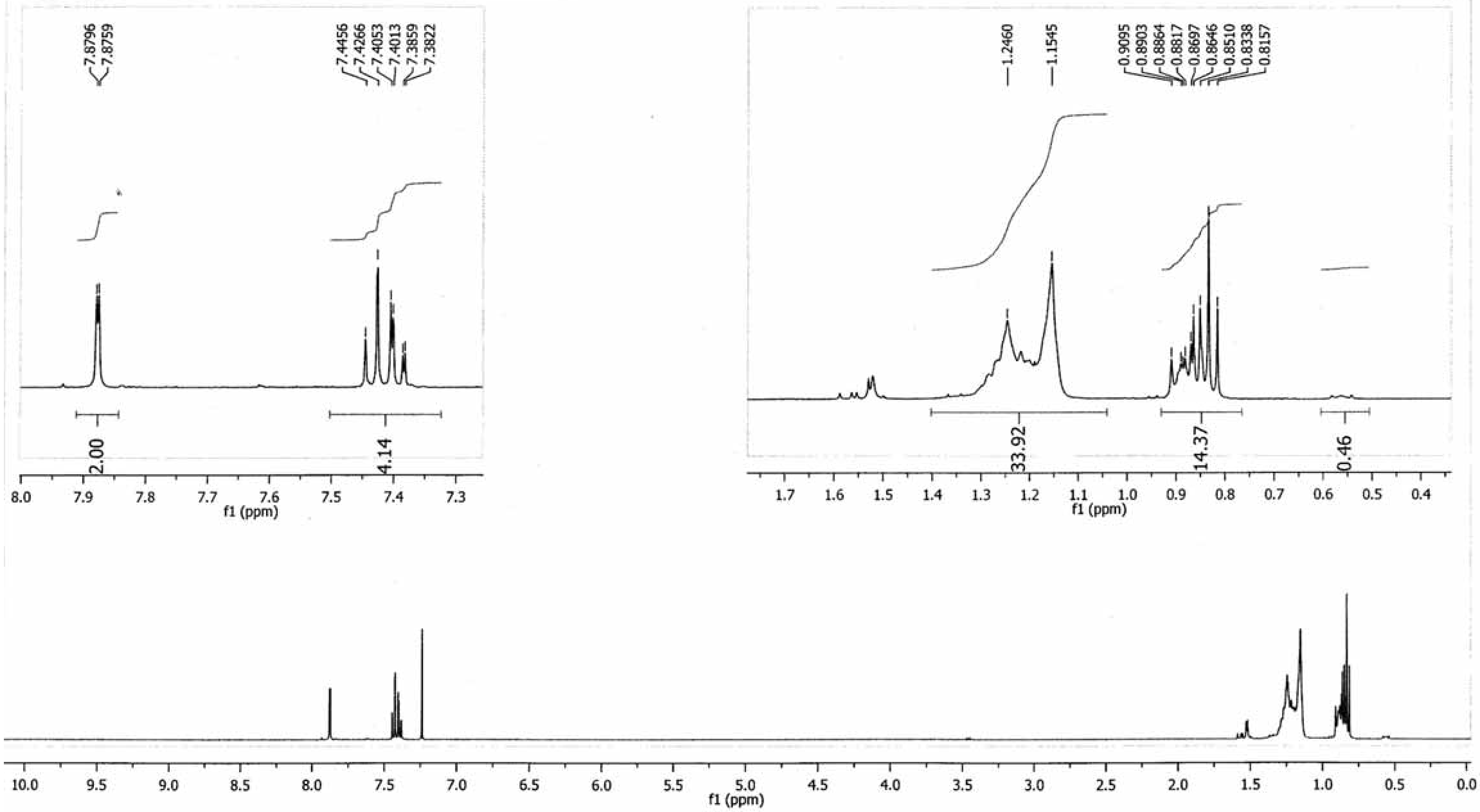

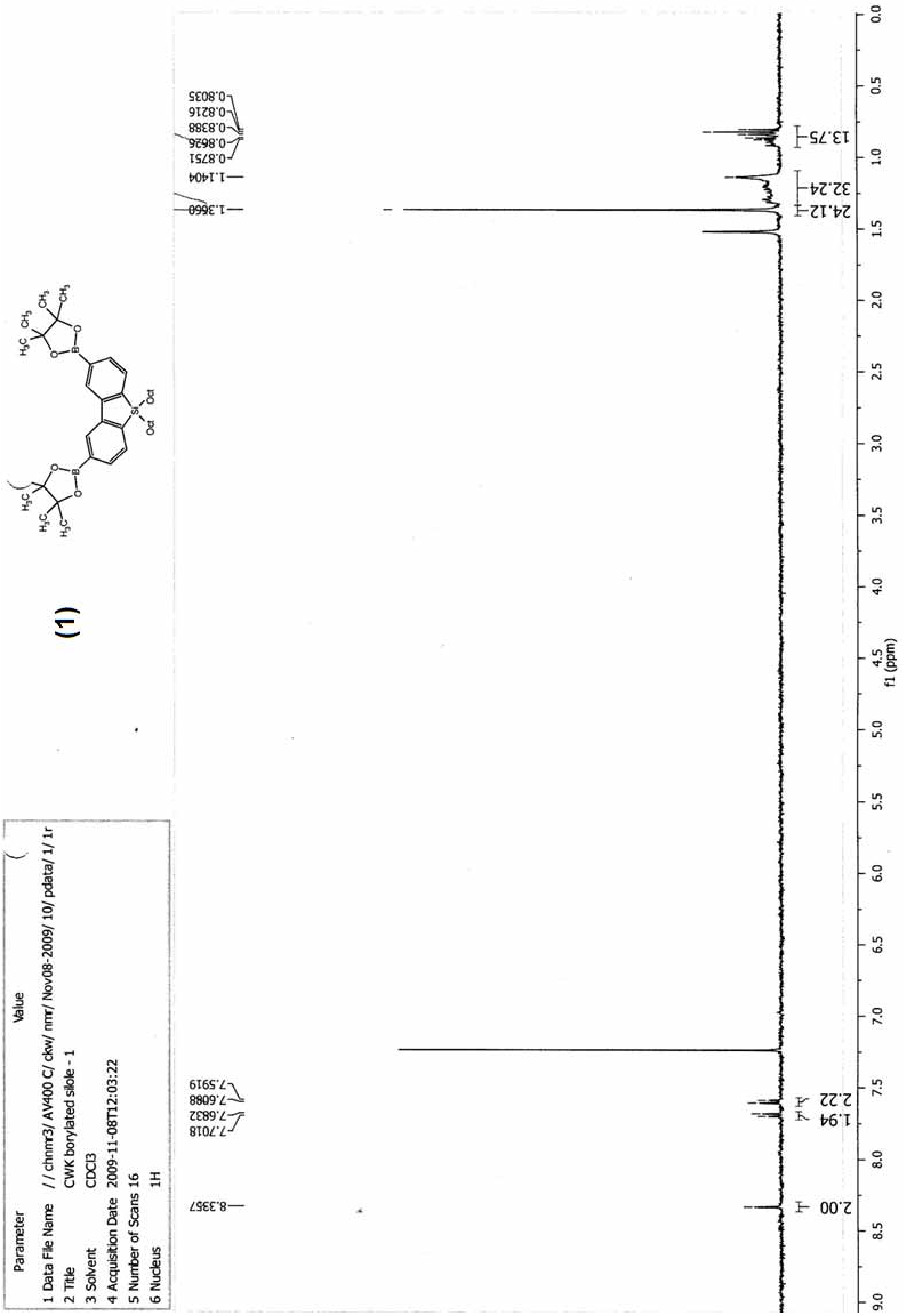

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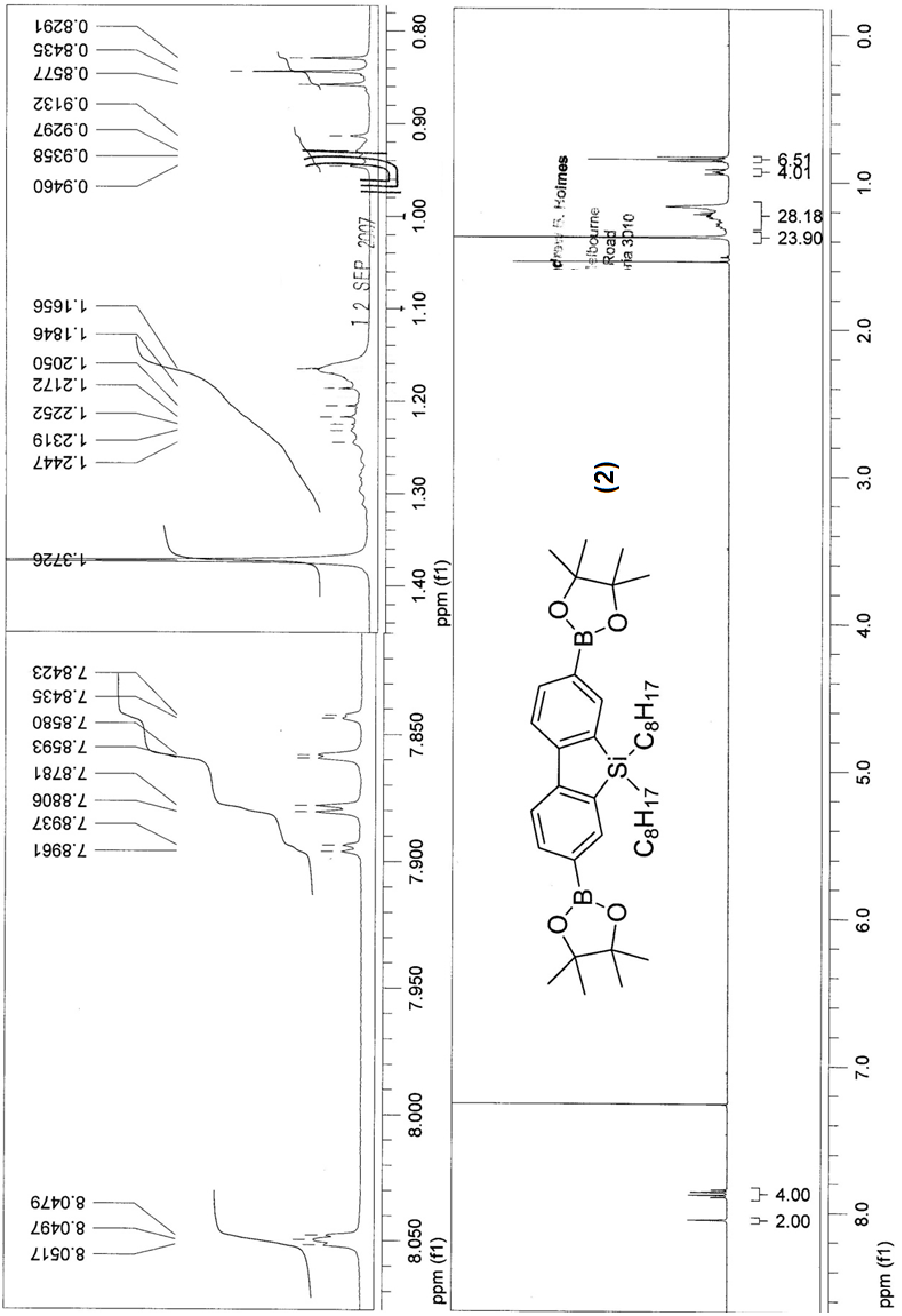
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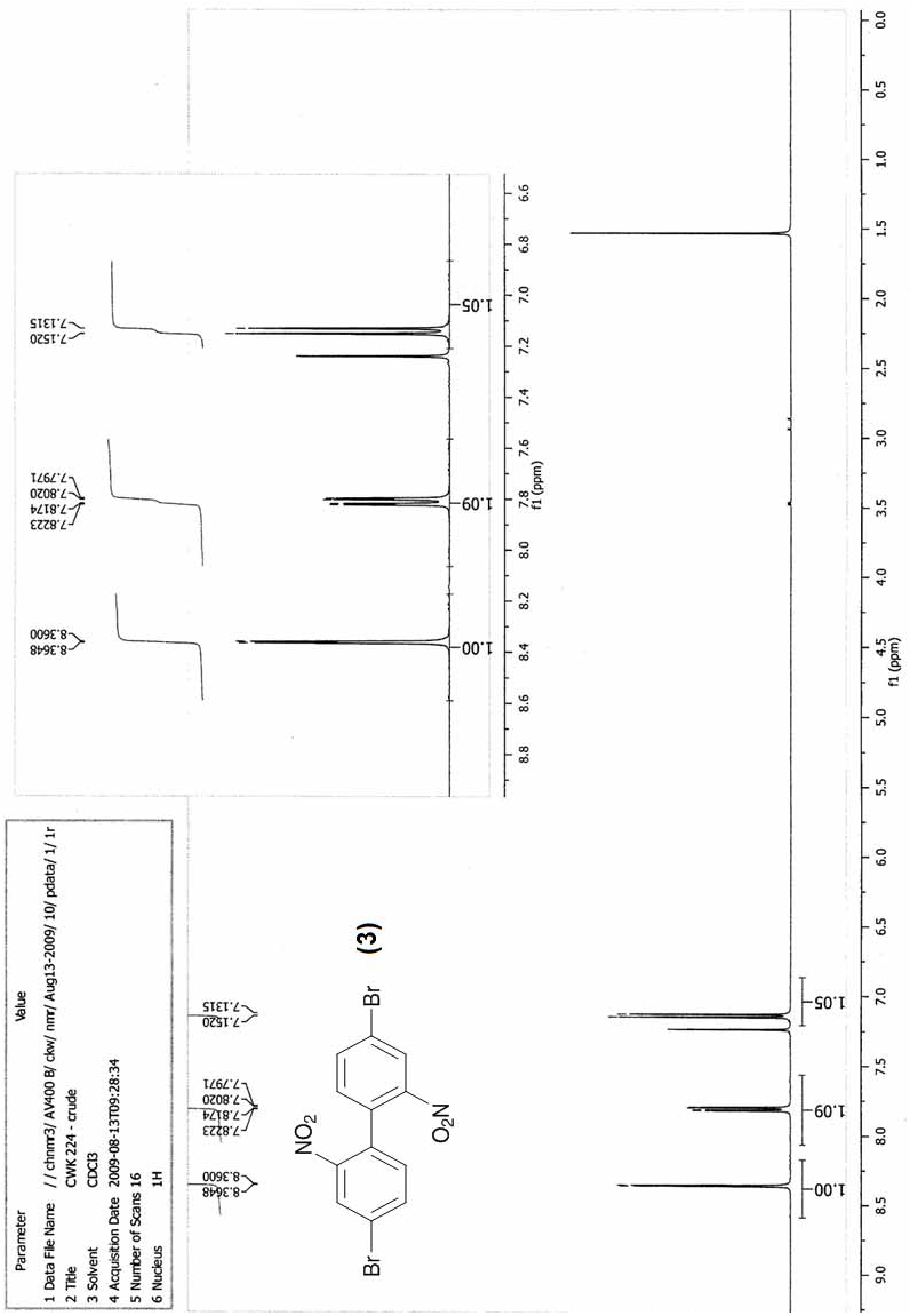

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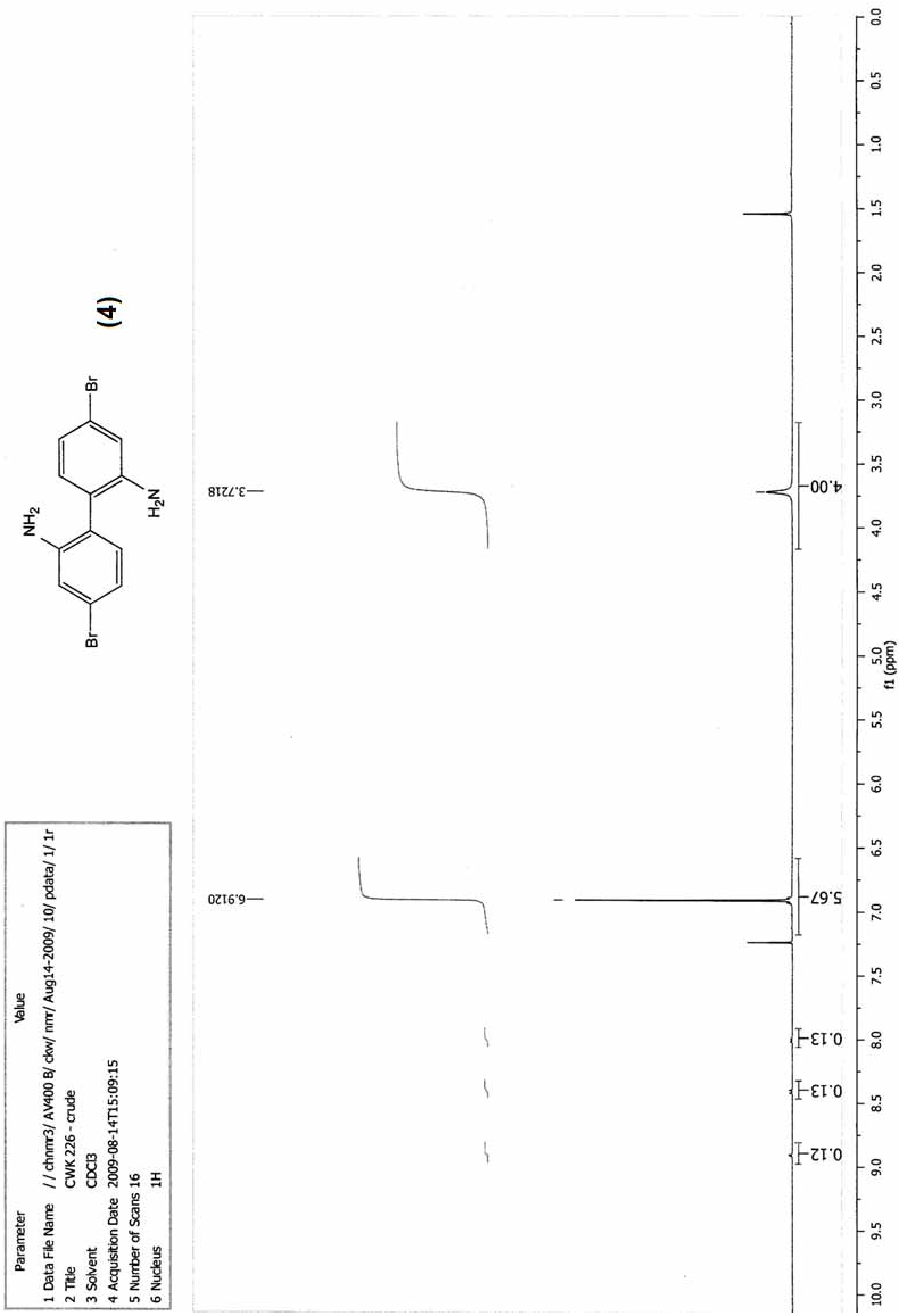

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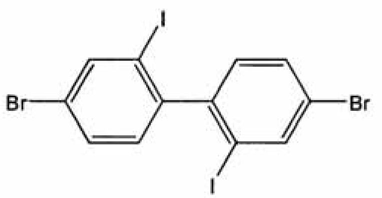
| 6 Nucleus | 1H |



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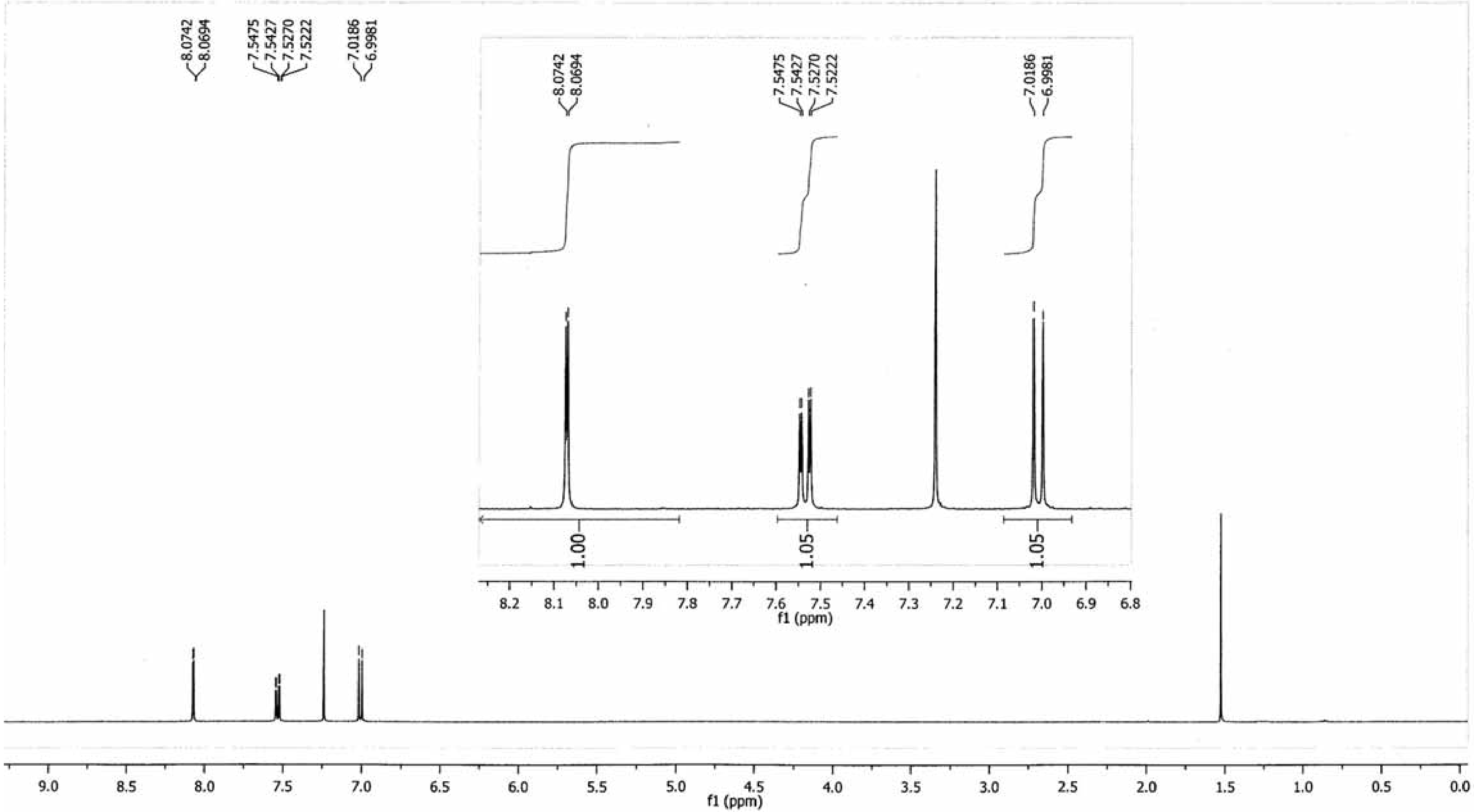

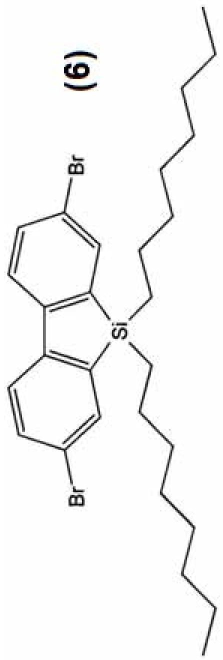

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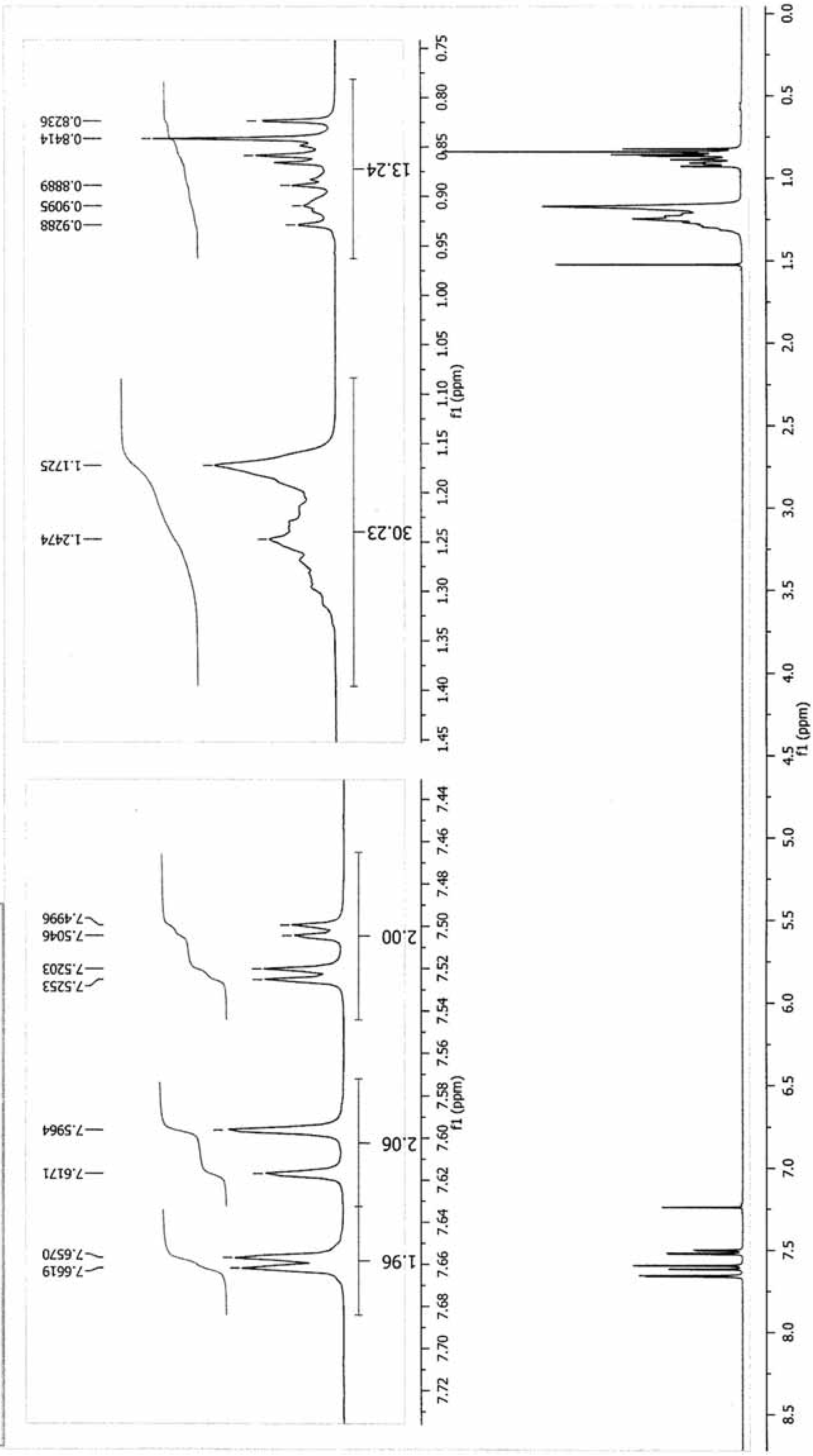
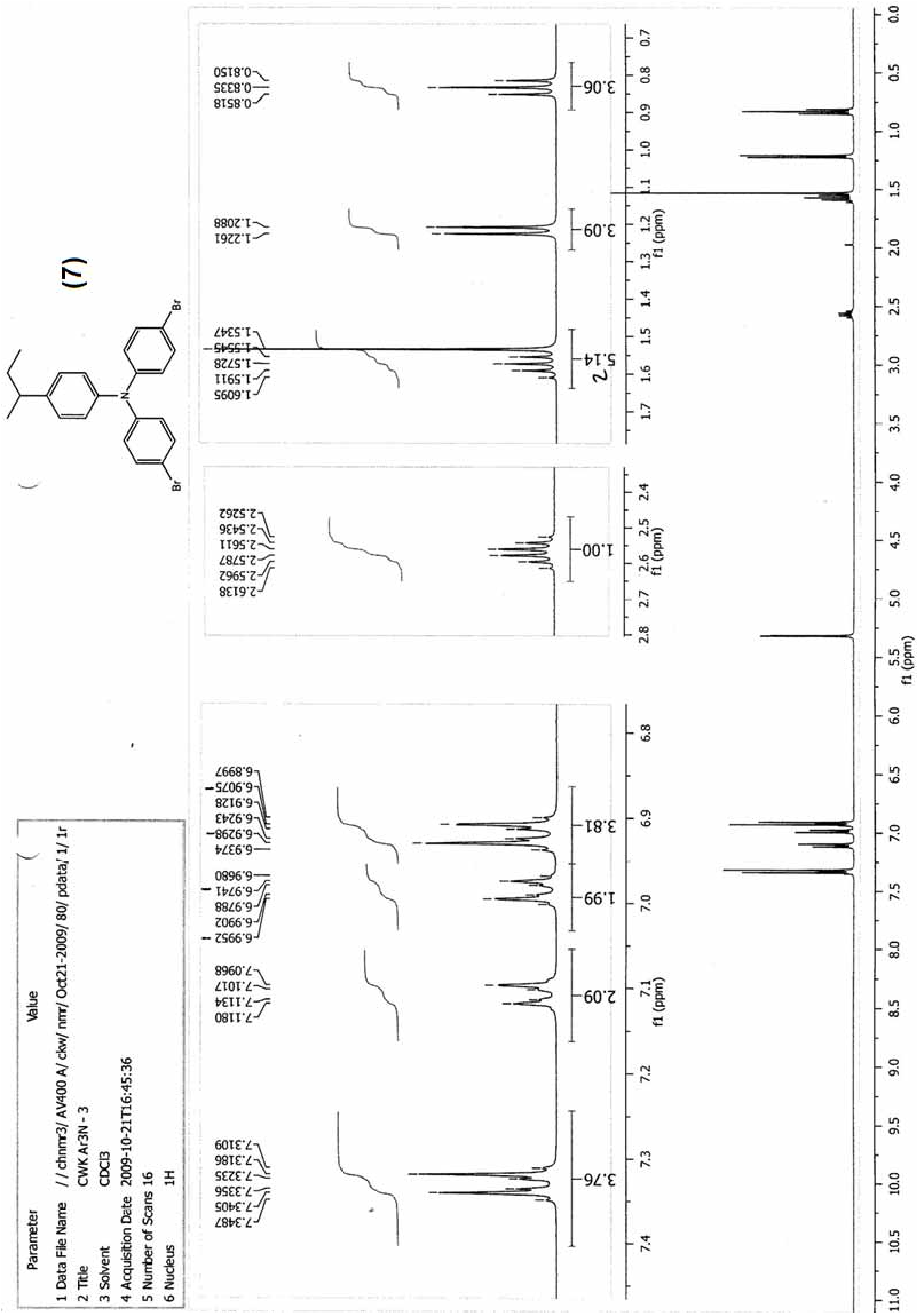
| 4 Acquisition Date | 2009-08-25T12:04:26 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |





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| 3 Solvent | CDCl3 |
| 4 Acquisition Date | 2009-10-21T16:45:36 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |

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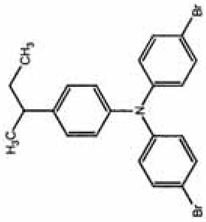

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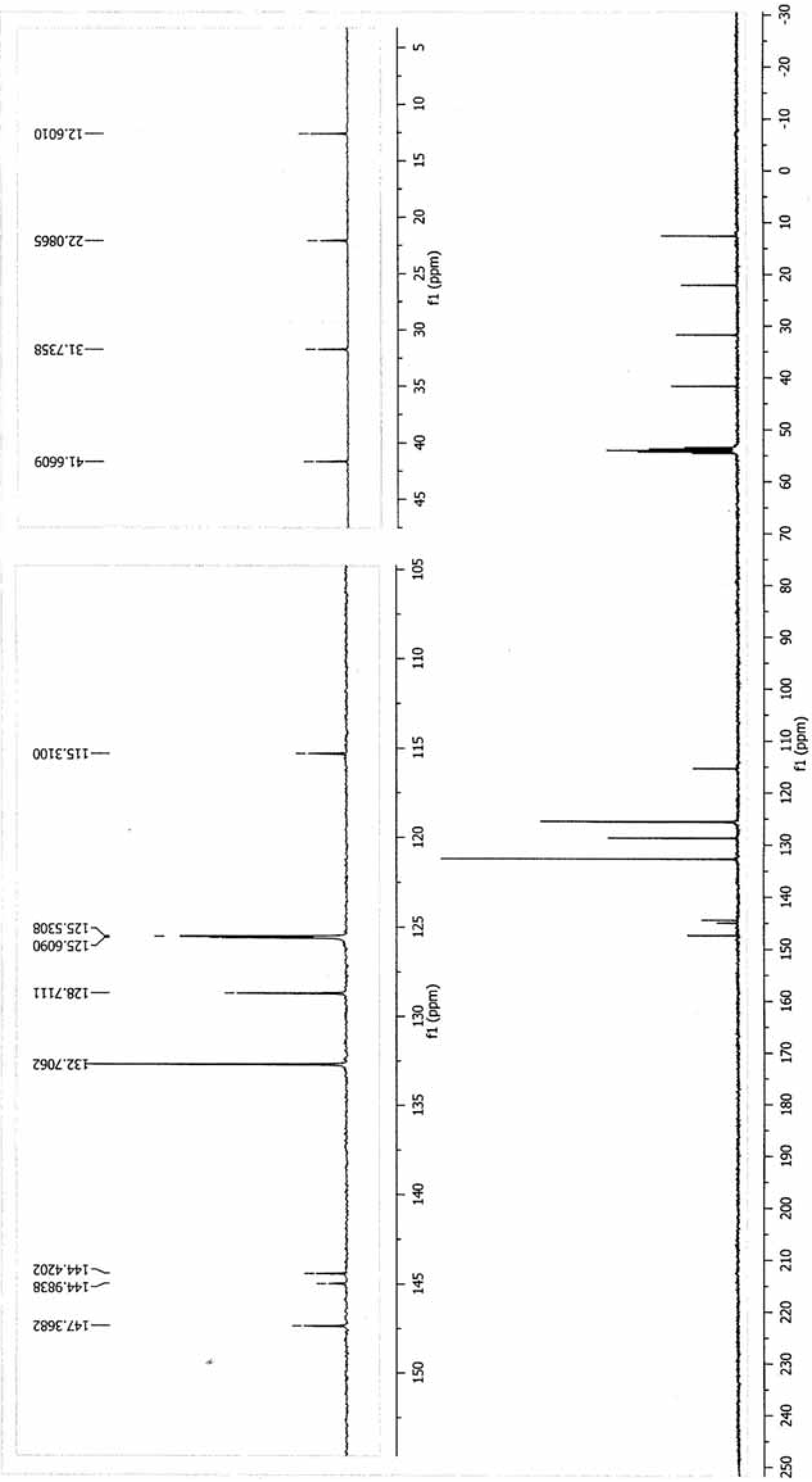

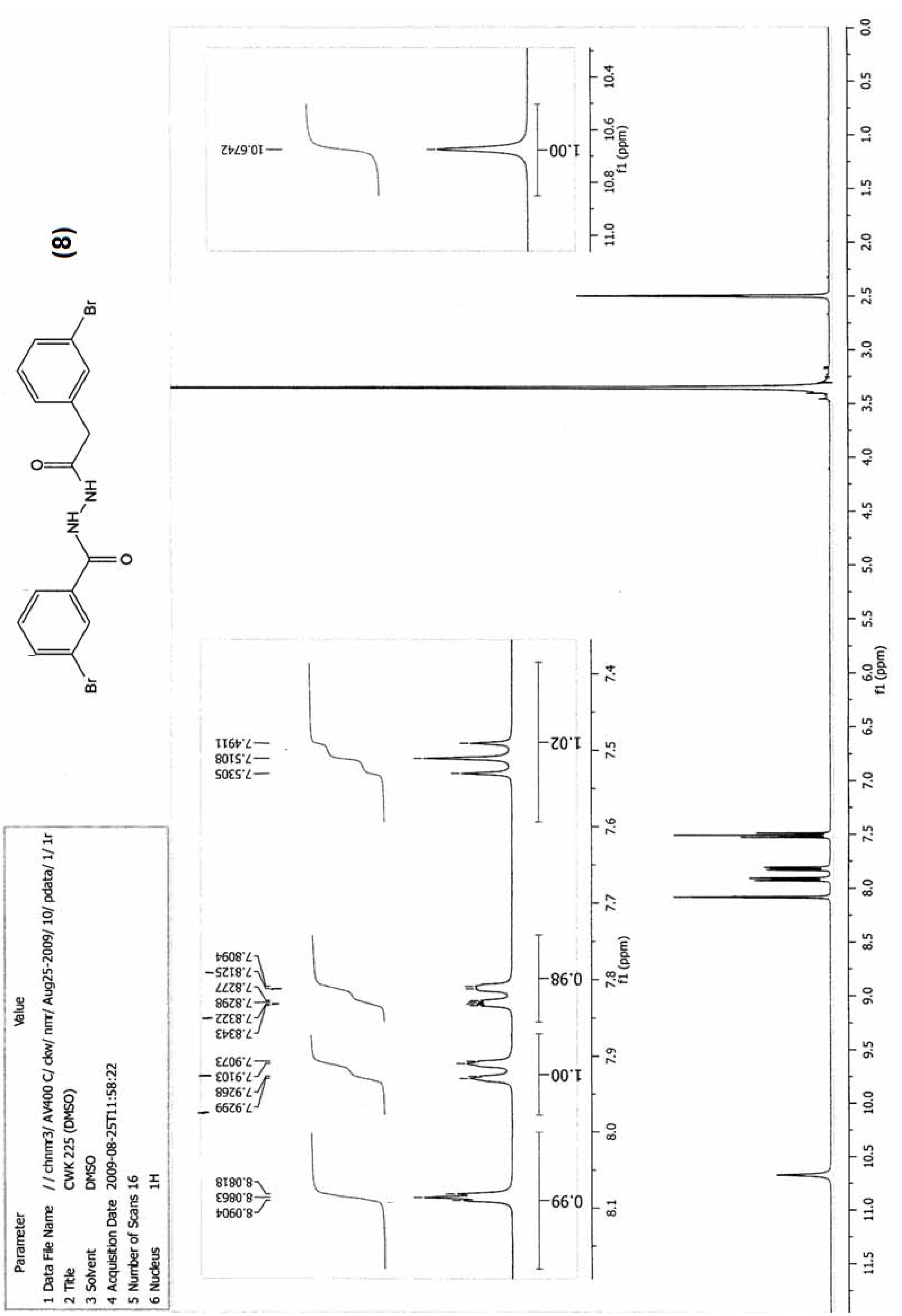

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| Parameter | Value |
|---|---|
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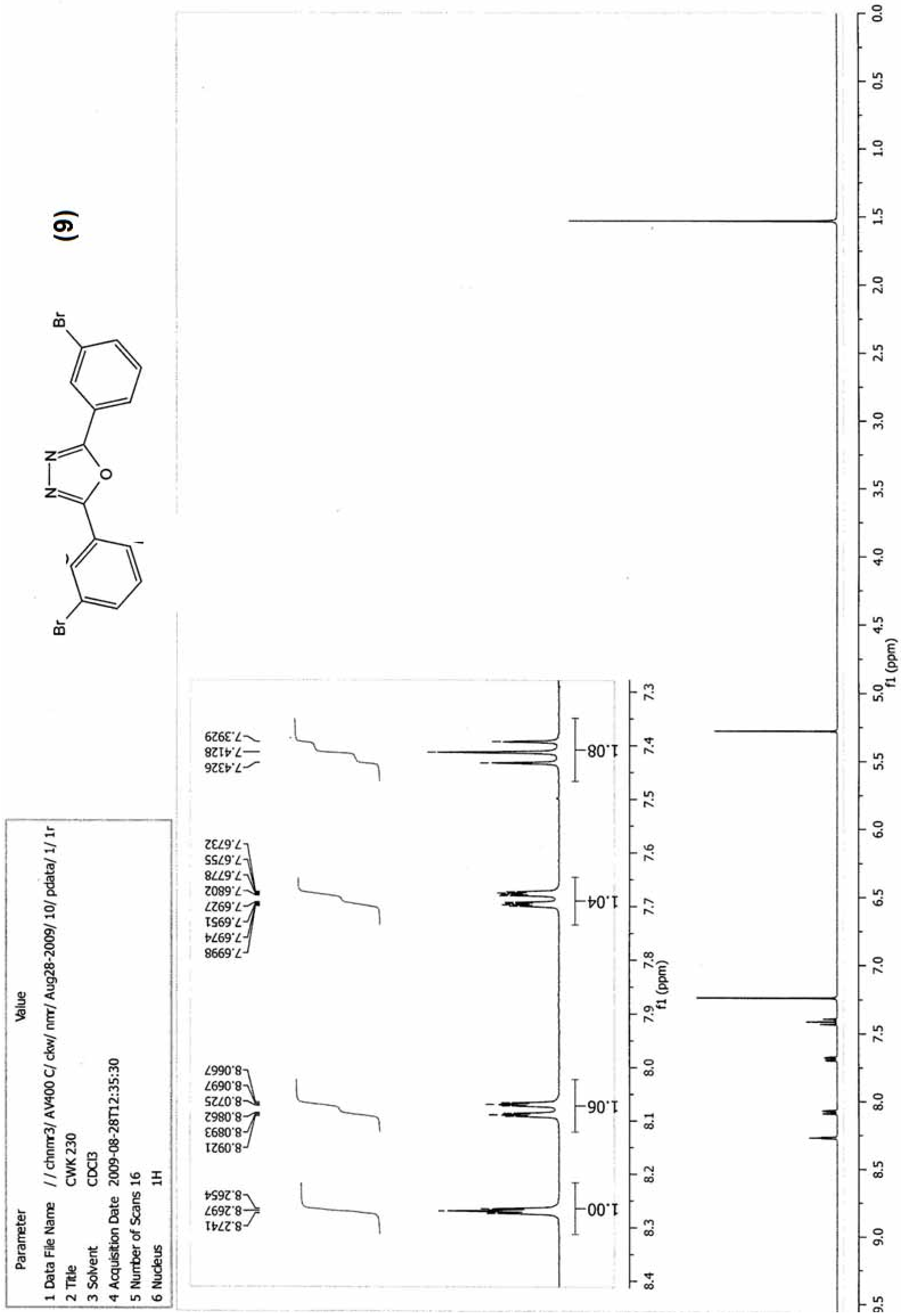
| 3 Solvent | DMSO |
| 4 Acquisition Date | 2009-08-25T11:58:22 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |

Keyworth *et al.*, ‘The tuning of frontier orbital energy levels of dibenzosilole....’



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| 2 Title | CWK 230 |
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| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |

| Parameter | Value |
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| 4 Acquisition Date | 2009-12-08T03:17:08 |
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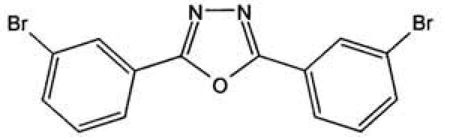
| 6 Nucleus | 13C |



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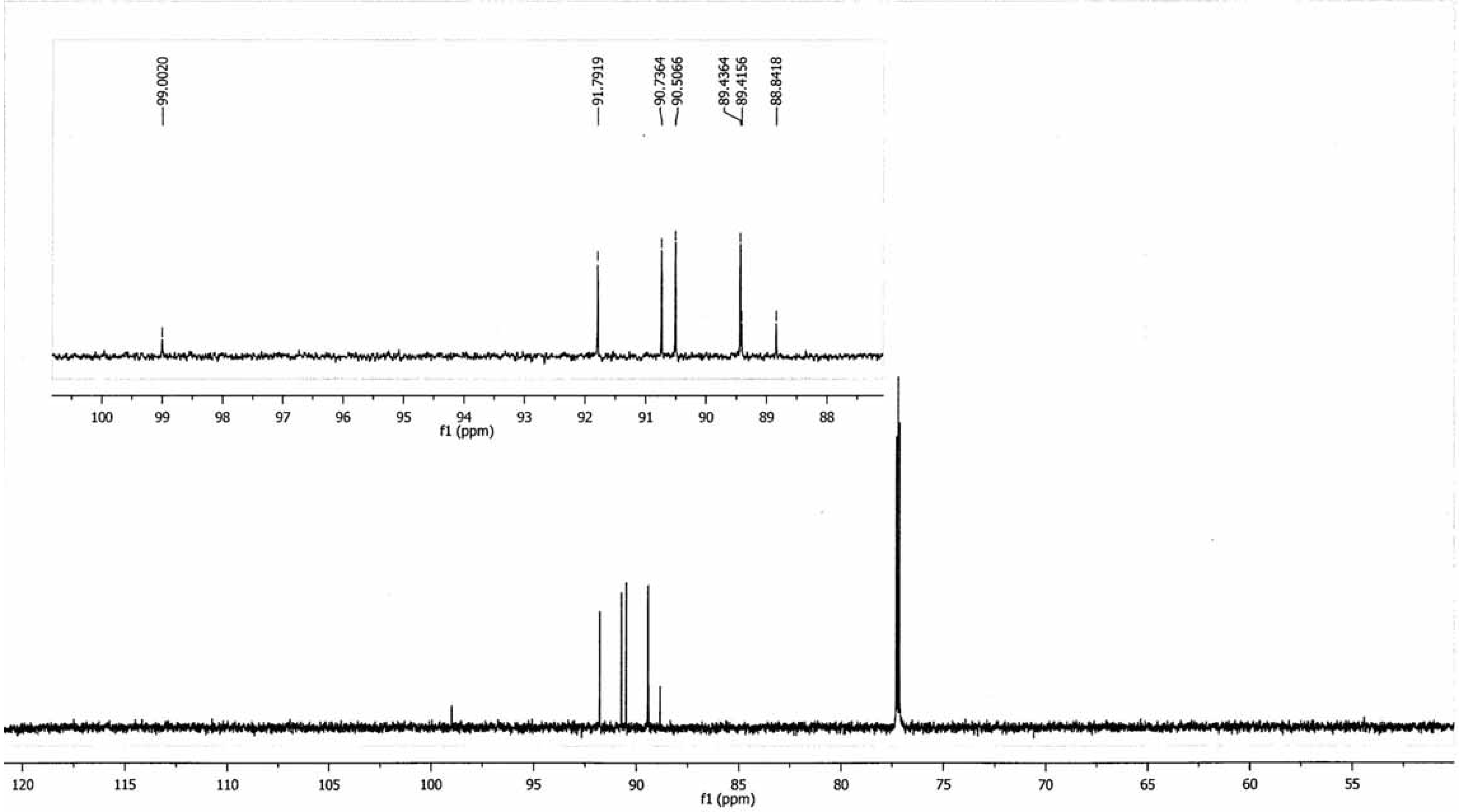

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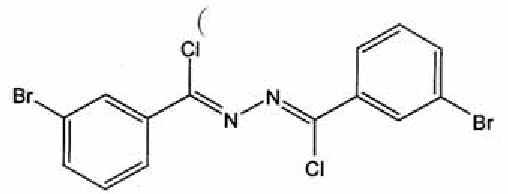
| 2 Title | CWK 253 - second reaction |
| 3 Solvent | DMSO |
| 4 Acquisition Date | 2009-10-21T16:22:26 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |



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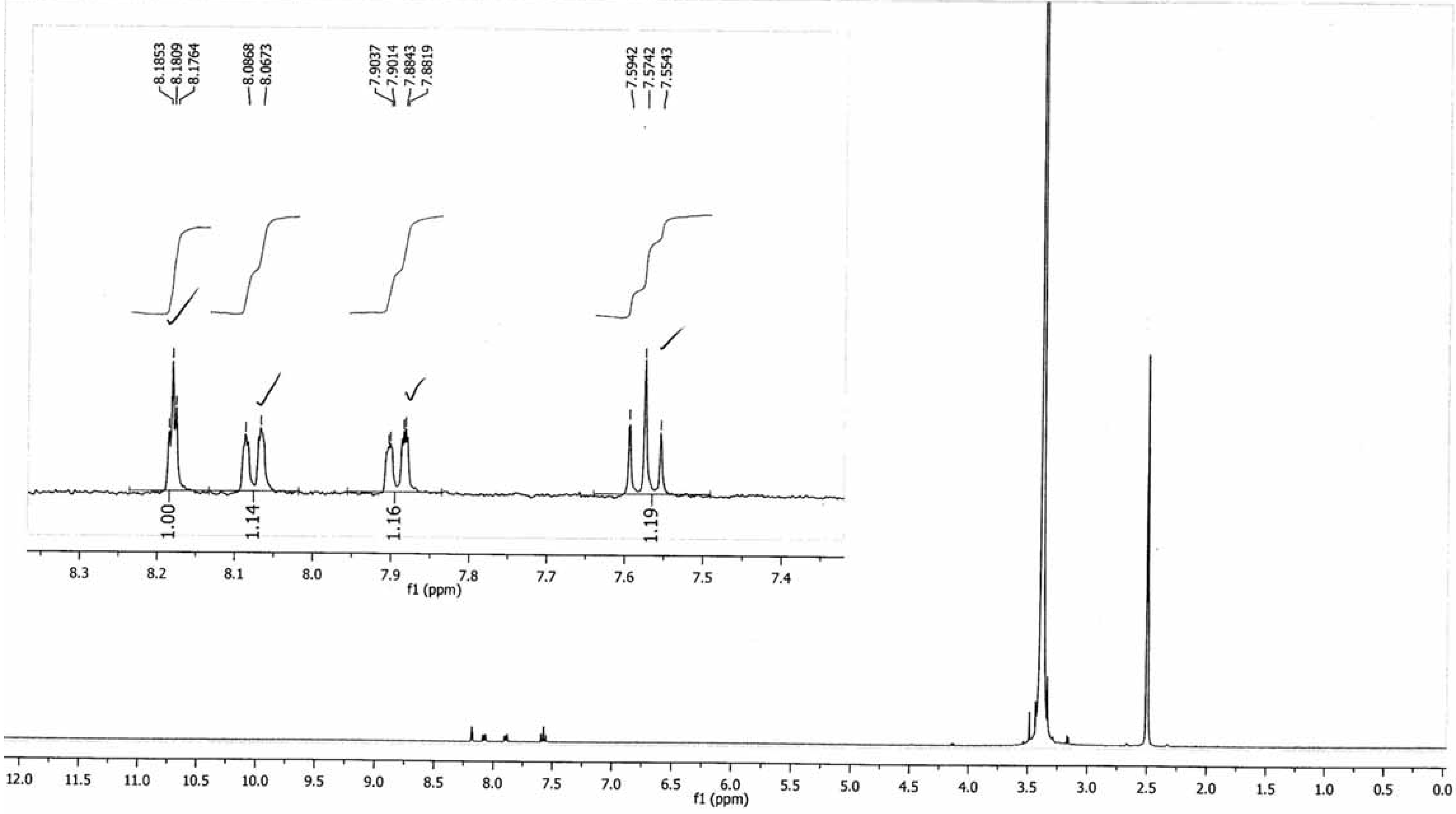

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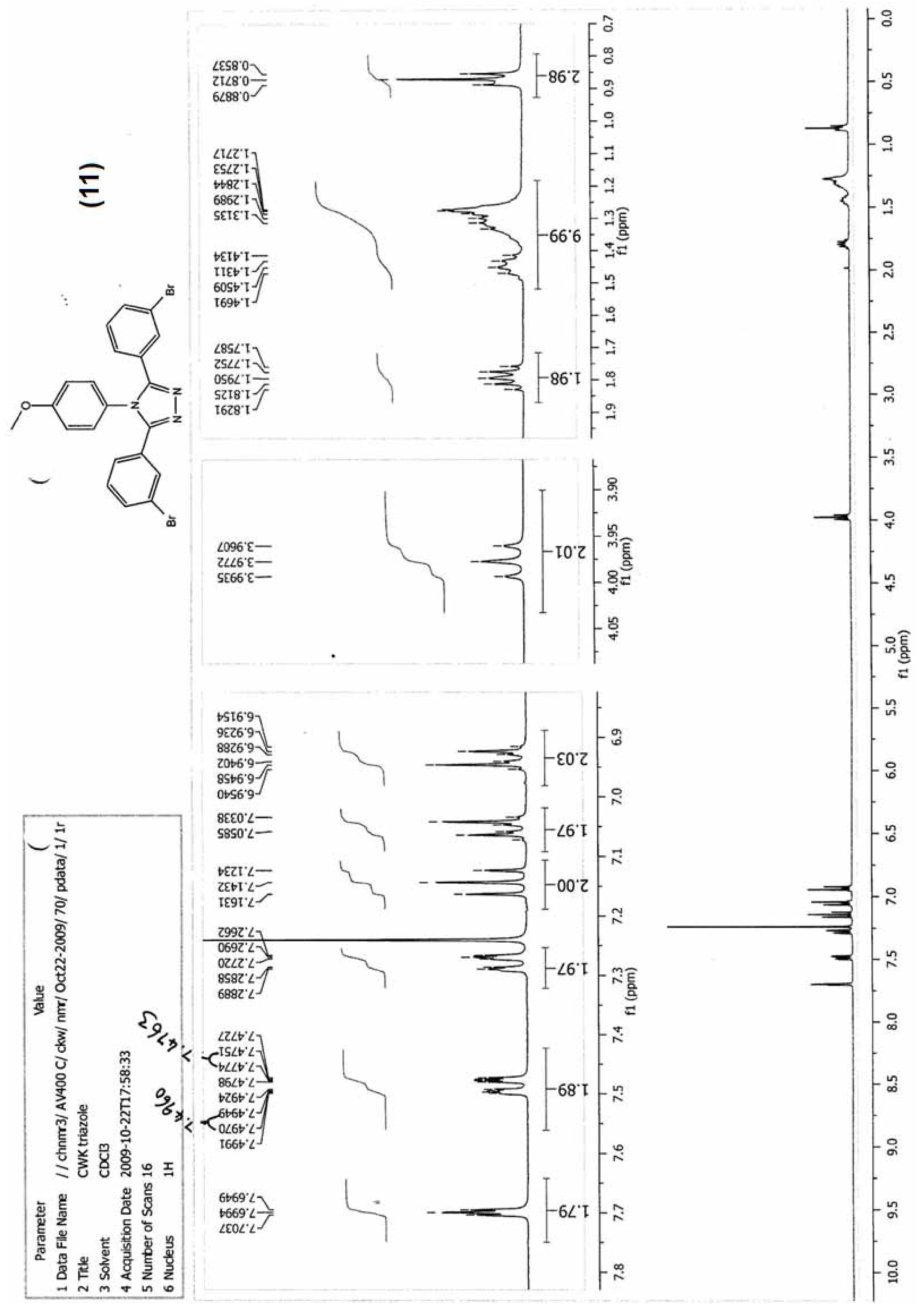

| Parameter | Value |
|---|---|
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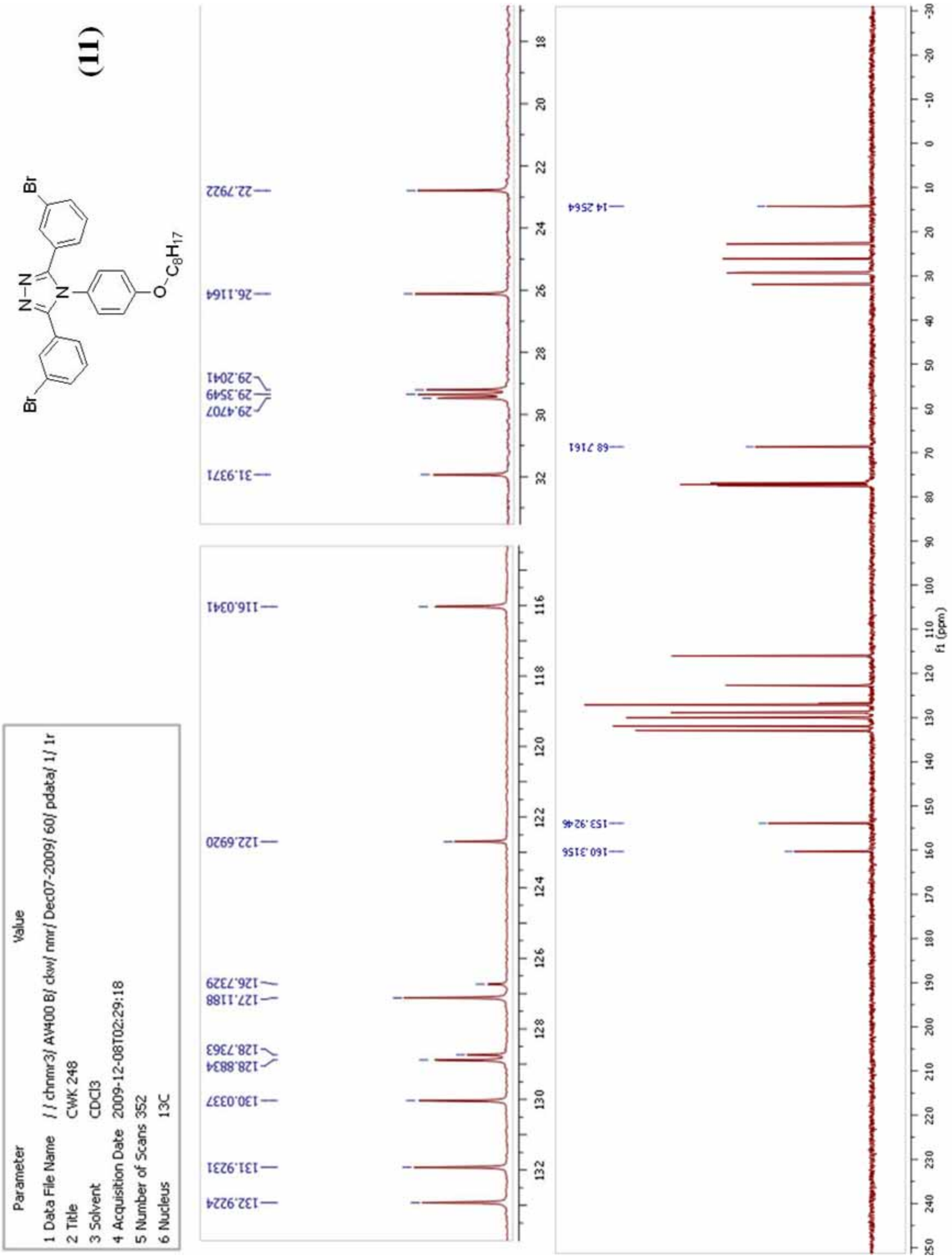
| 3 Solvent | CDCl3 |
| 4 Acquisition Date | 2009-10-22T17:58:33 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |



**(11)**

| Parameter | Value |
|---|---|
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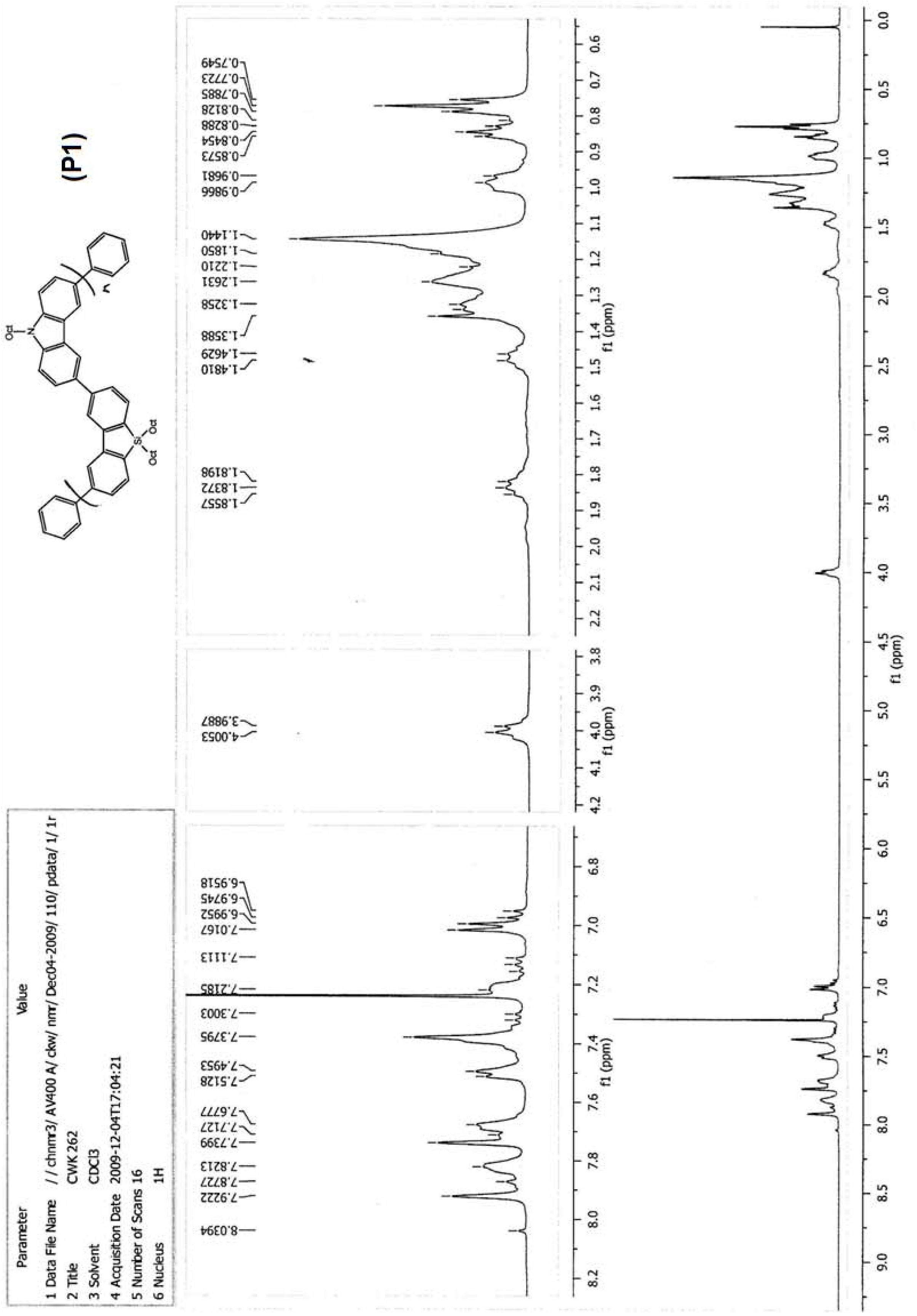
| 2 Title | CWK 248 |
| 3 Solvent | CDCl3 |
| 4 Acquisition Date | 2009-12-08T02:29:18 |
| 5 Number of Scans | 352 |
| 6 Nucleus | 13C |

## 2.2 – NMR spectra of polymers

**(P1)**



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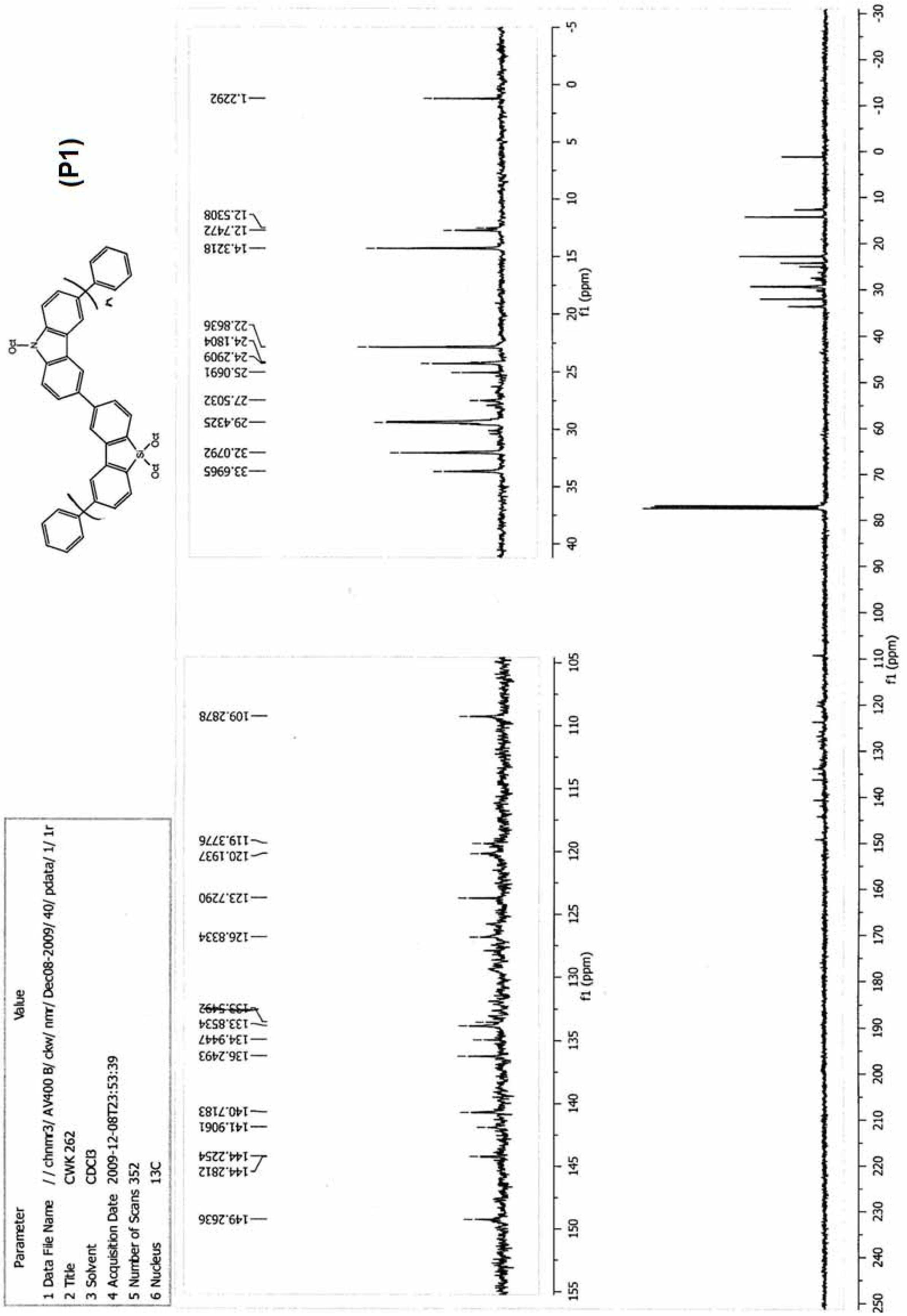
| 4 Acquisition Date | 2009-12-04T17:04:21 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |



| Parameter | Value |
|---|---|
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| 2 Title | CWK 262 |
| 3 Solvent | CDCl3 |
| 4 Acquisition Date | 2009-12-08T23:53:39 |
| 5 Number of Scans | 352 |
| 6 Nucleus | 13C |

|  | Parameter | Value |
|---|---|---|
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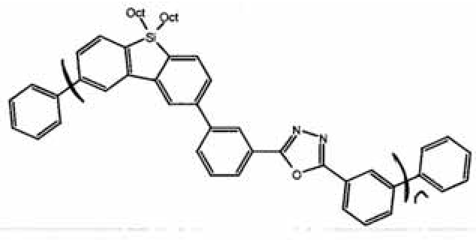
| 2 | Title | CWK 263 |
| 3 | Solvent | CDCl3 |
| 4 | Acquisition Date | 2009-12-04T17:09:12 |
| 5 | Number of Scans | 16 |
| 6 | Nucleus | 1H |



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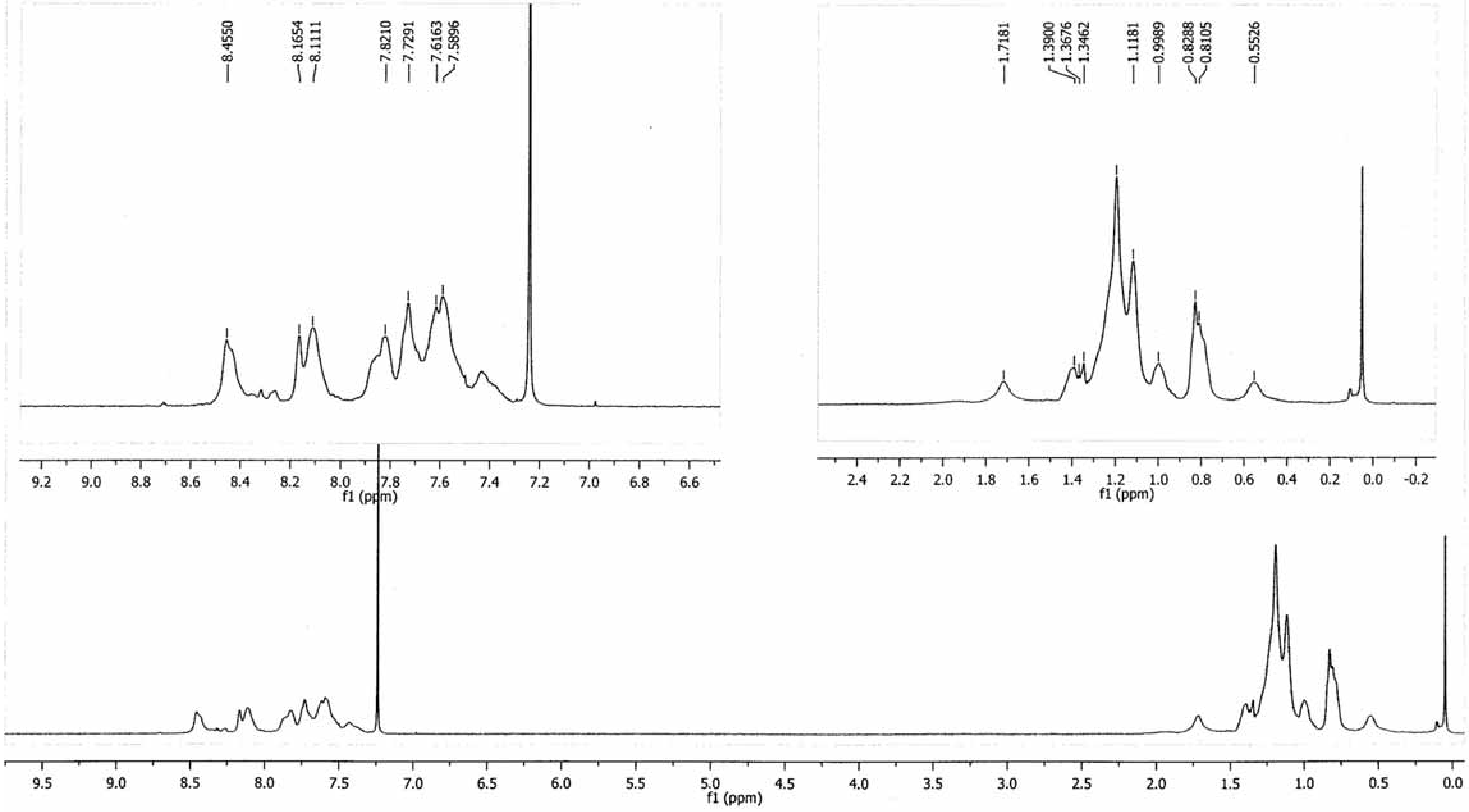

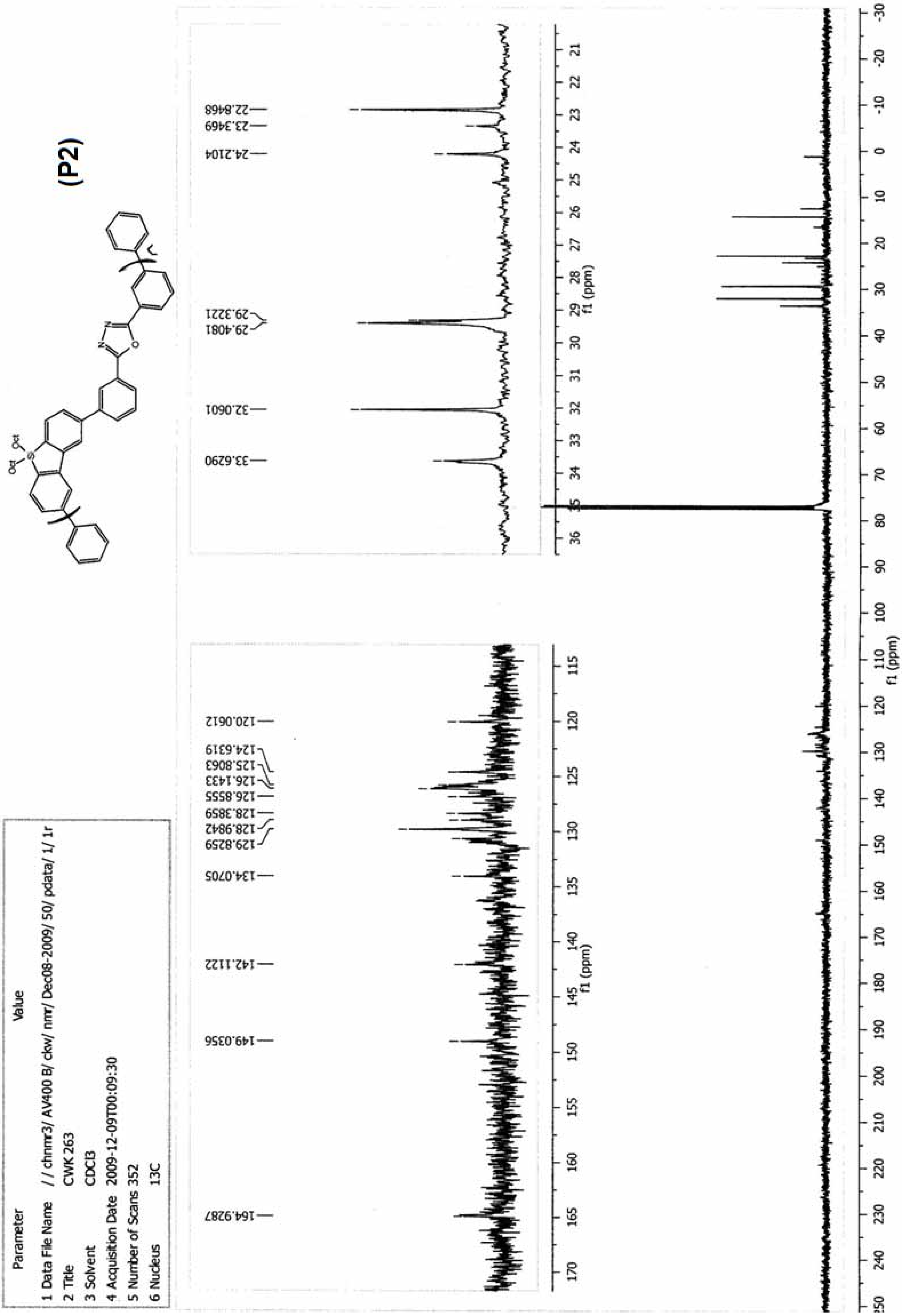

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| 5 Number of Scans | 352 |
| 6 Nucleus | 13C |

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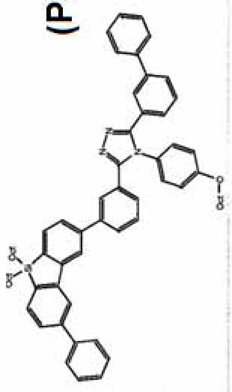

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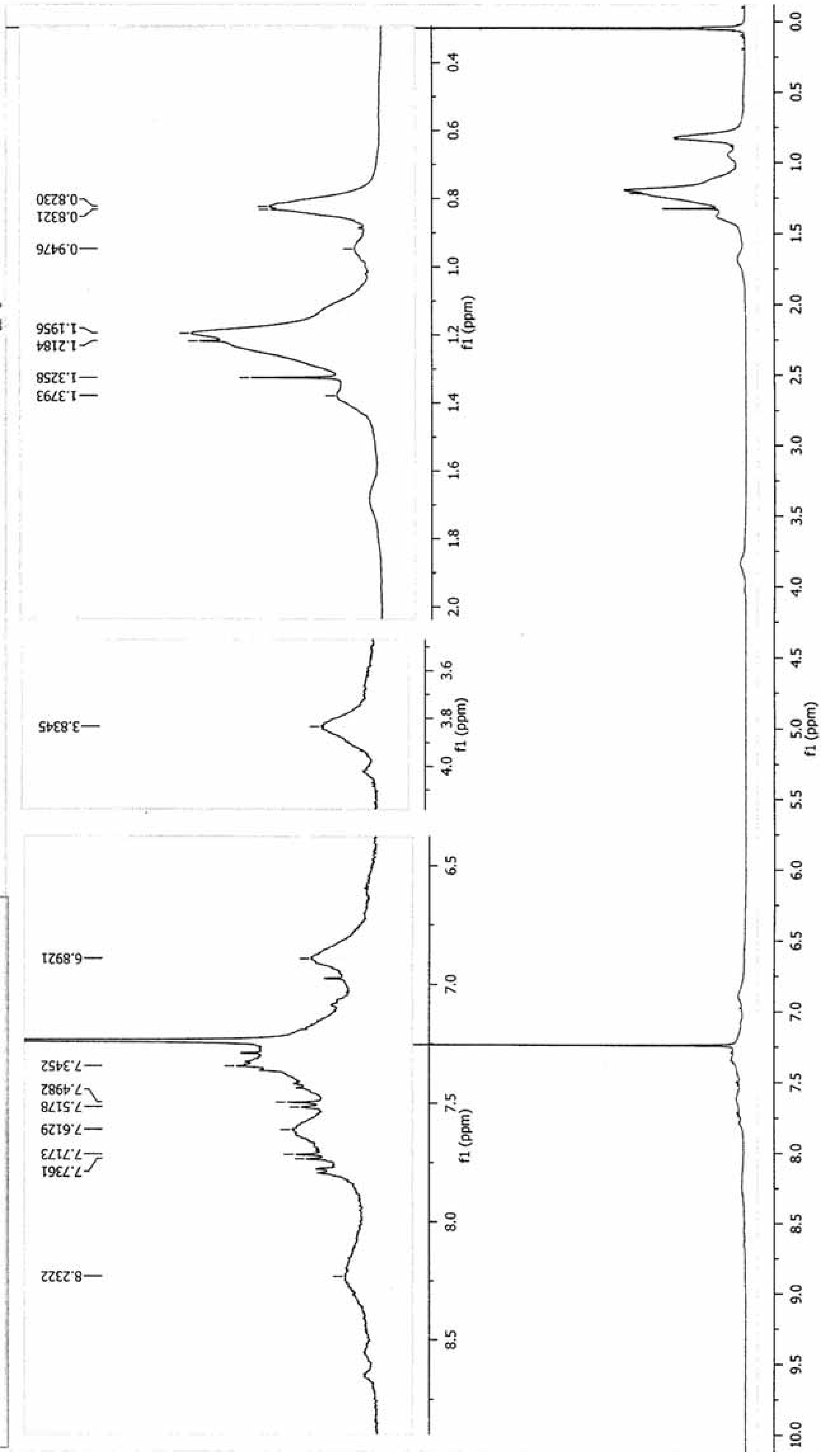
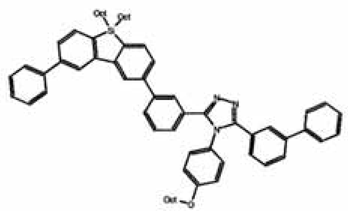
| 4 Acquisition Date | 2009-12-04T17:18:45 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |





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| 4 Acquisition Date | 2009-12-09T00:24:50 |
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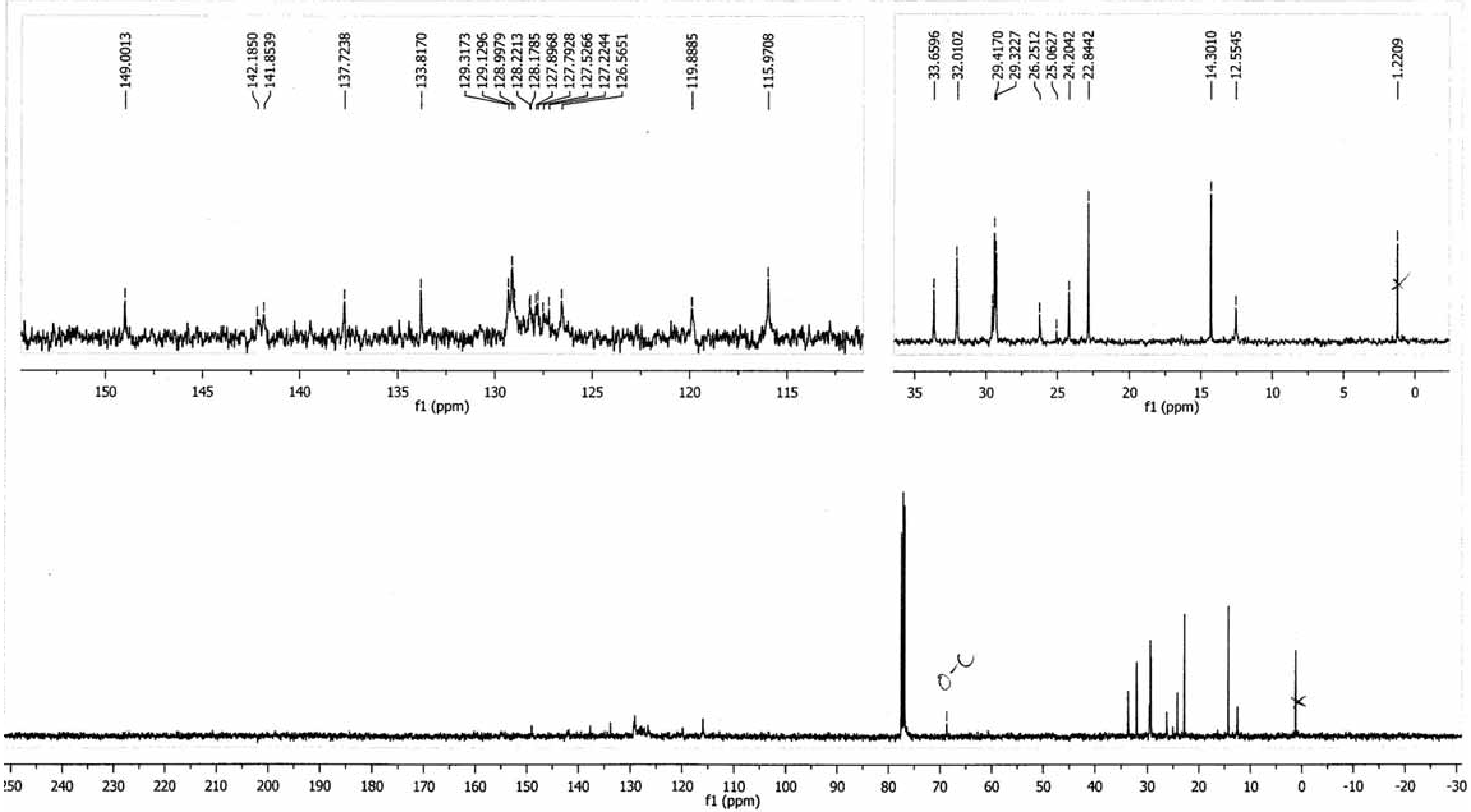
| 6 Nucleus | 13C |



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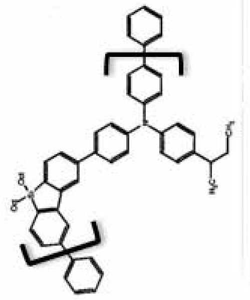

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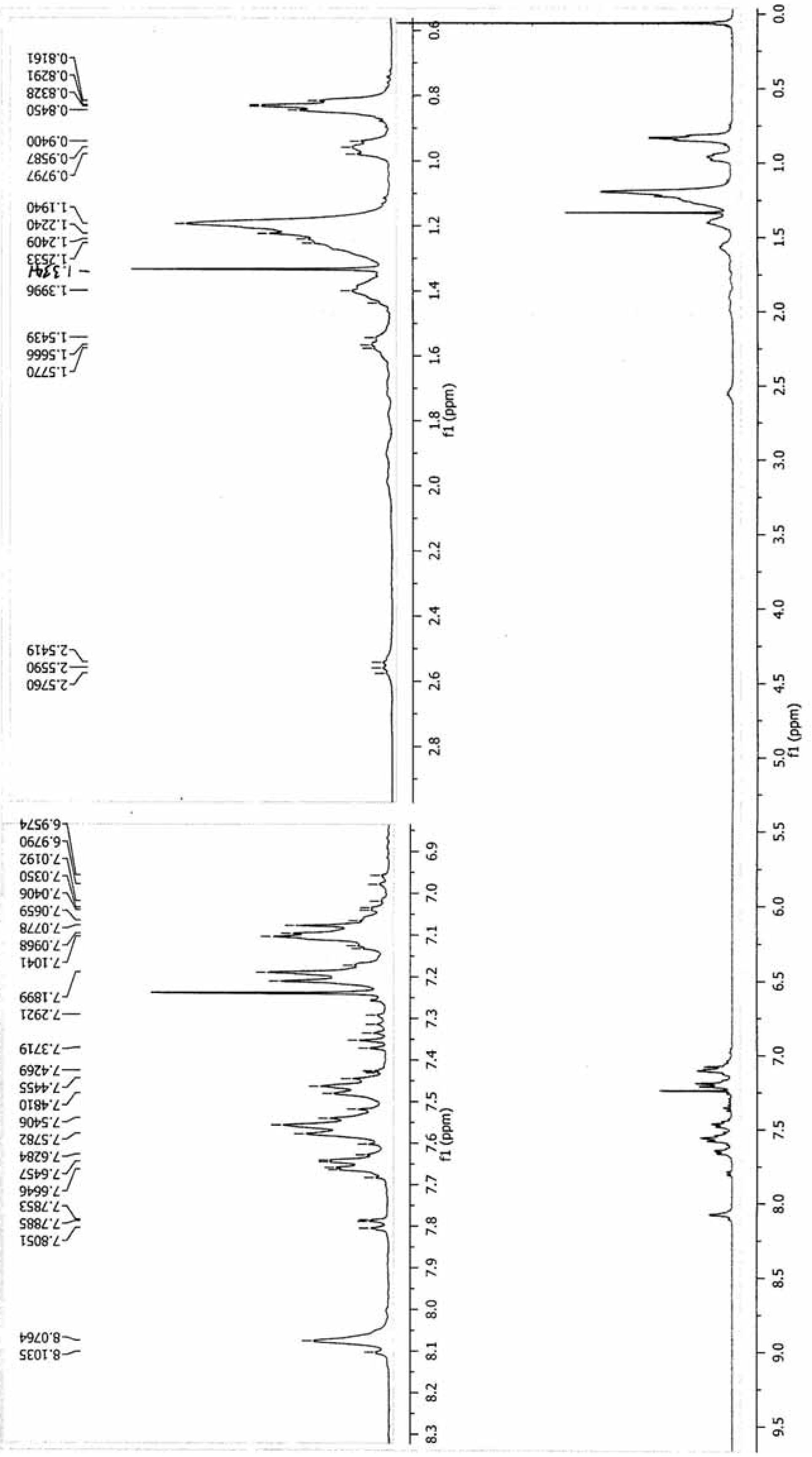
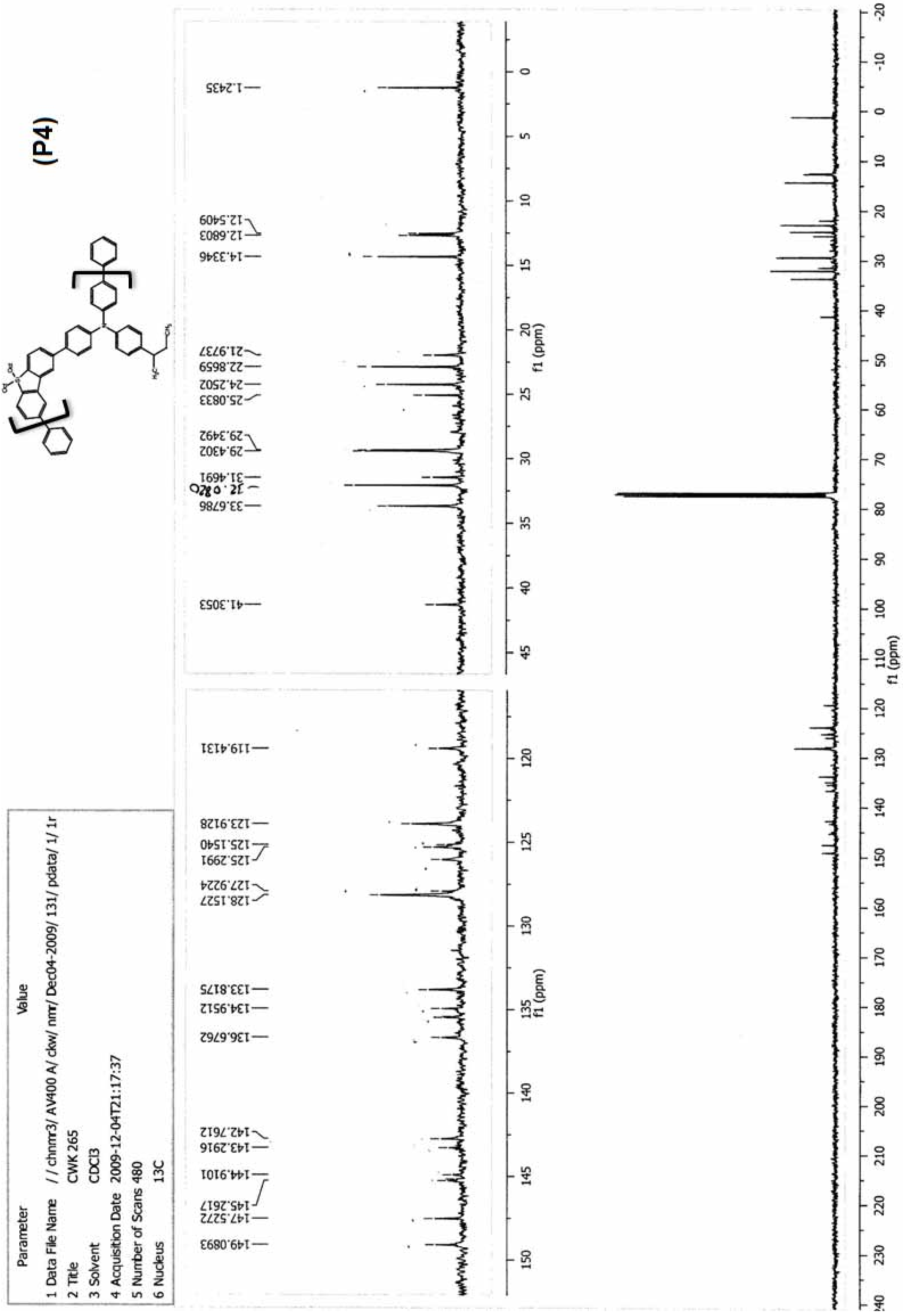
| 6 Nucleus | 1H |





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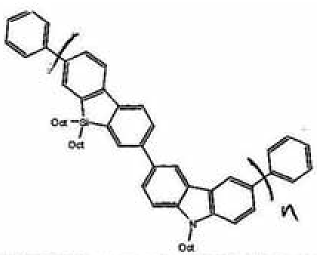
| 3 Solvent | CDCl3 |
| 4 Acquisition Date | 2009-12-04T21:17:37 |
| 5 Number of Scans | 480 |
| 6 Nucleus | 13C |

**(P5)**



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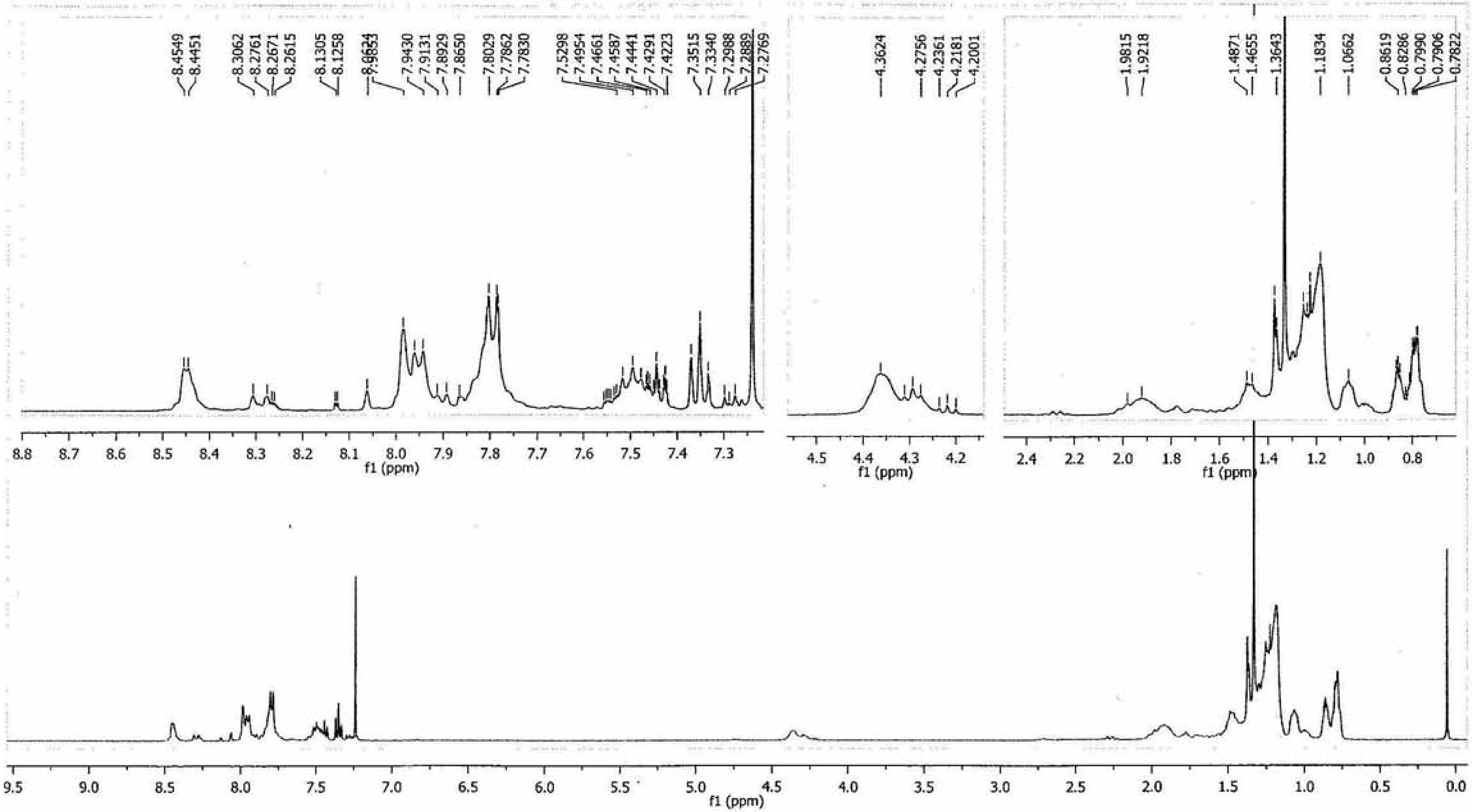
| 4 Acquisition Date | 2009-12-04T17:23:31 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |



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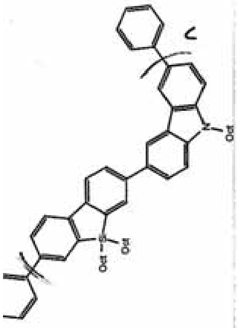

| Parameter | Value |
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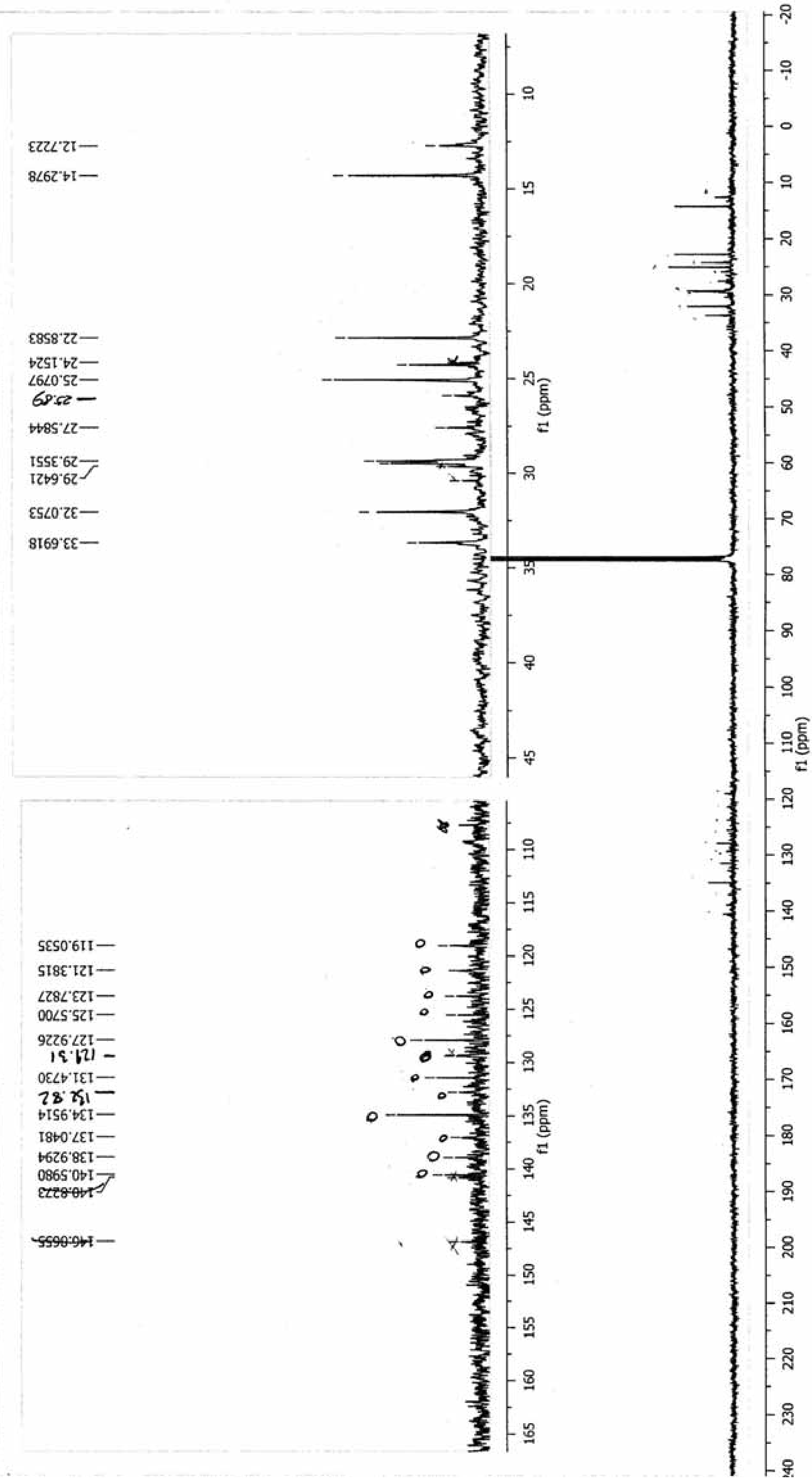
| 4 Acquisition Date | 2009-12-04T22:10:02 |
| 5 Number of Scans | 480 |
| 6 Nucleus | 13C |



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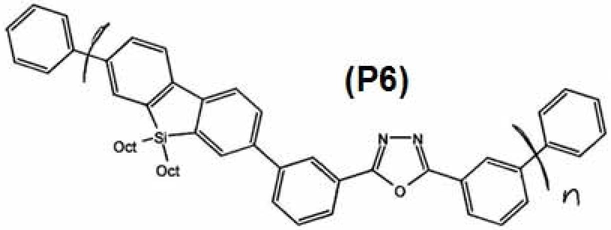

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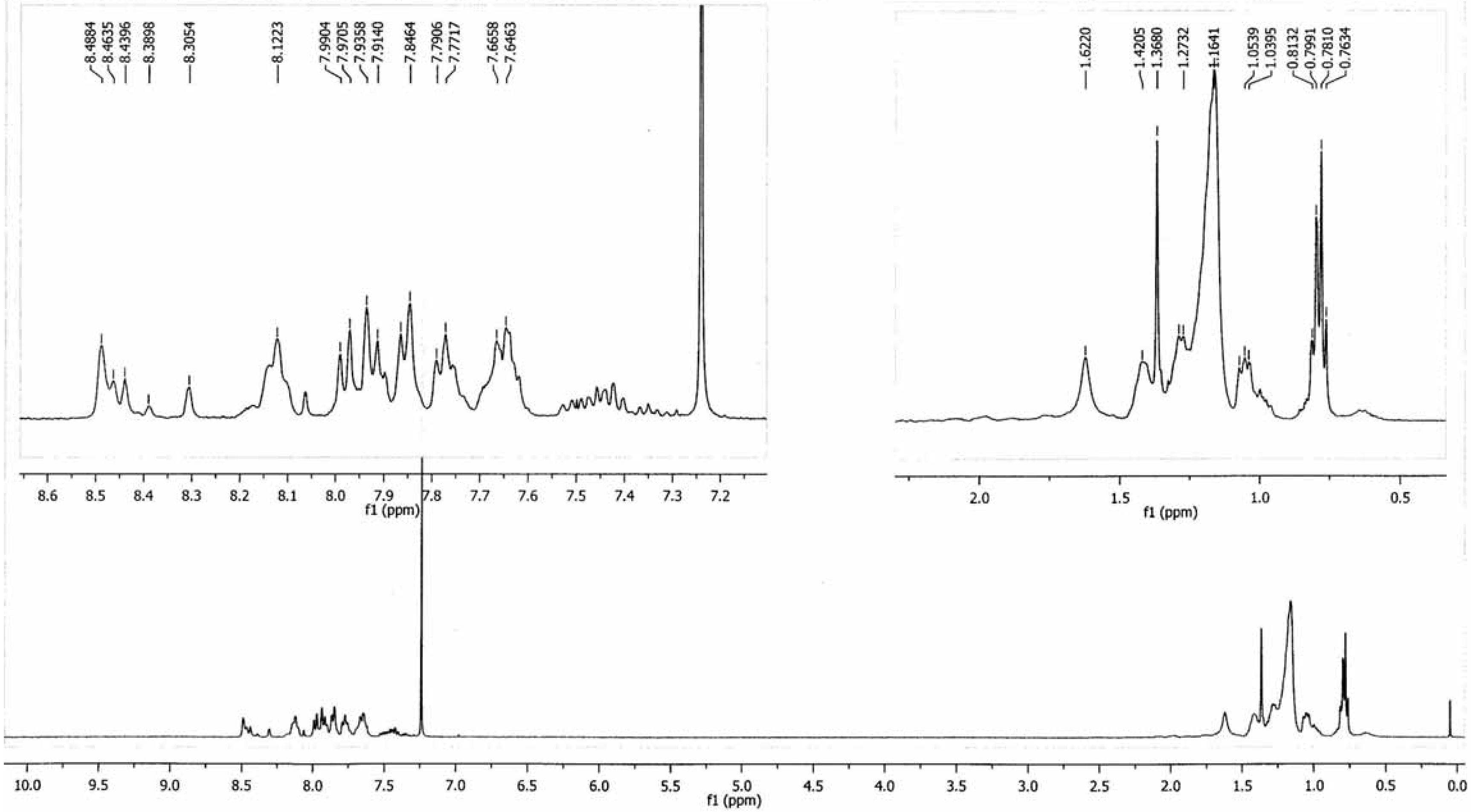
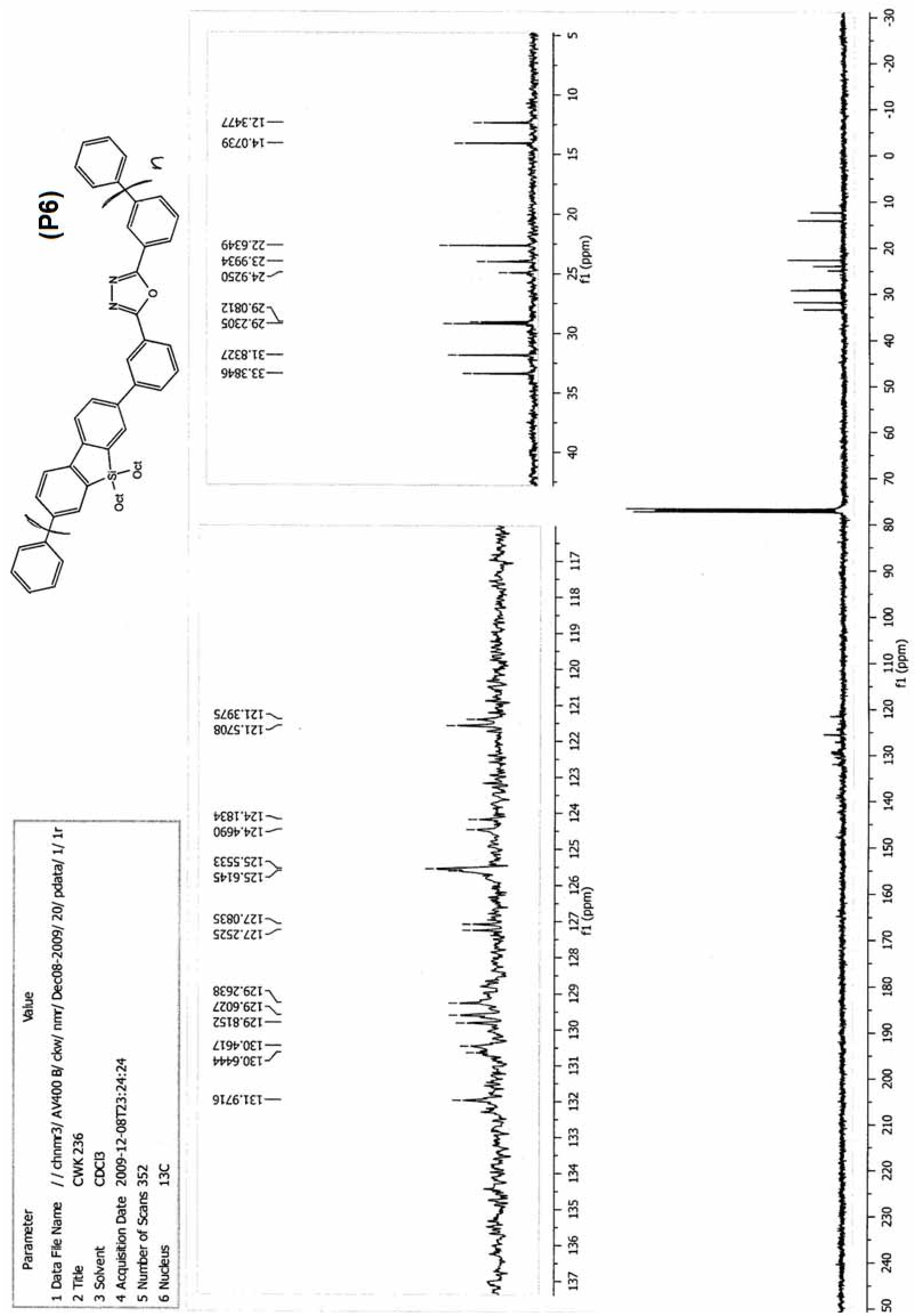
| 4 Acquisition Date | 2009-12-04T16:54:44 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |





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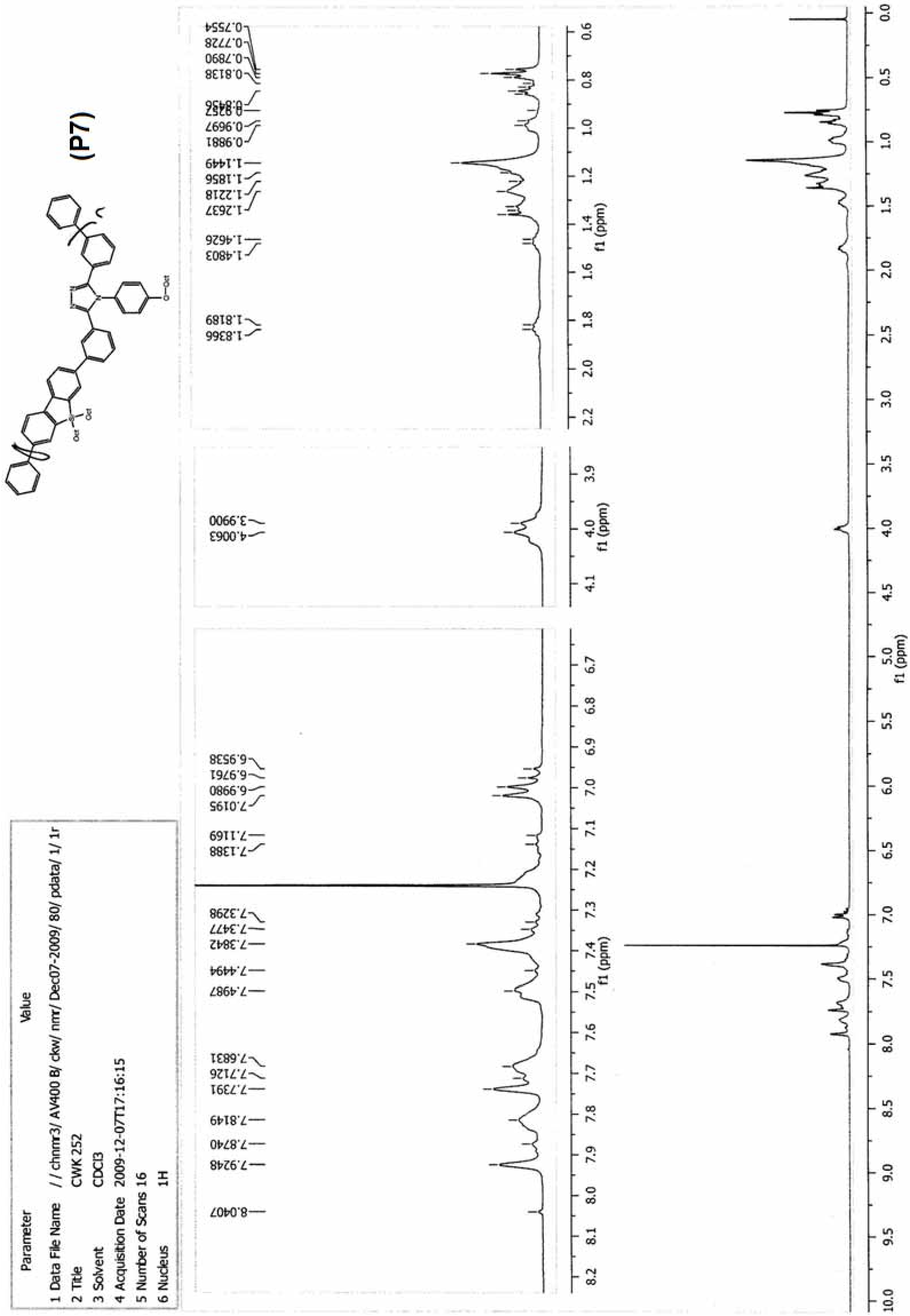
| 4 Acquisition Date | 2009-12-08T23:24:24 |
| 5 Number of Scans | 352 |
| 6 Nucleus | 13C |



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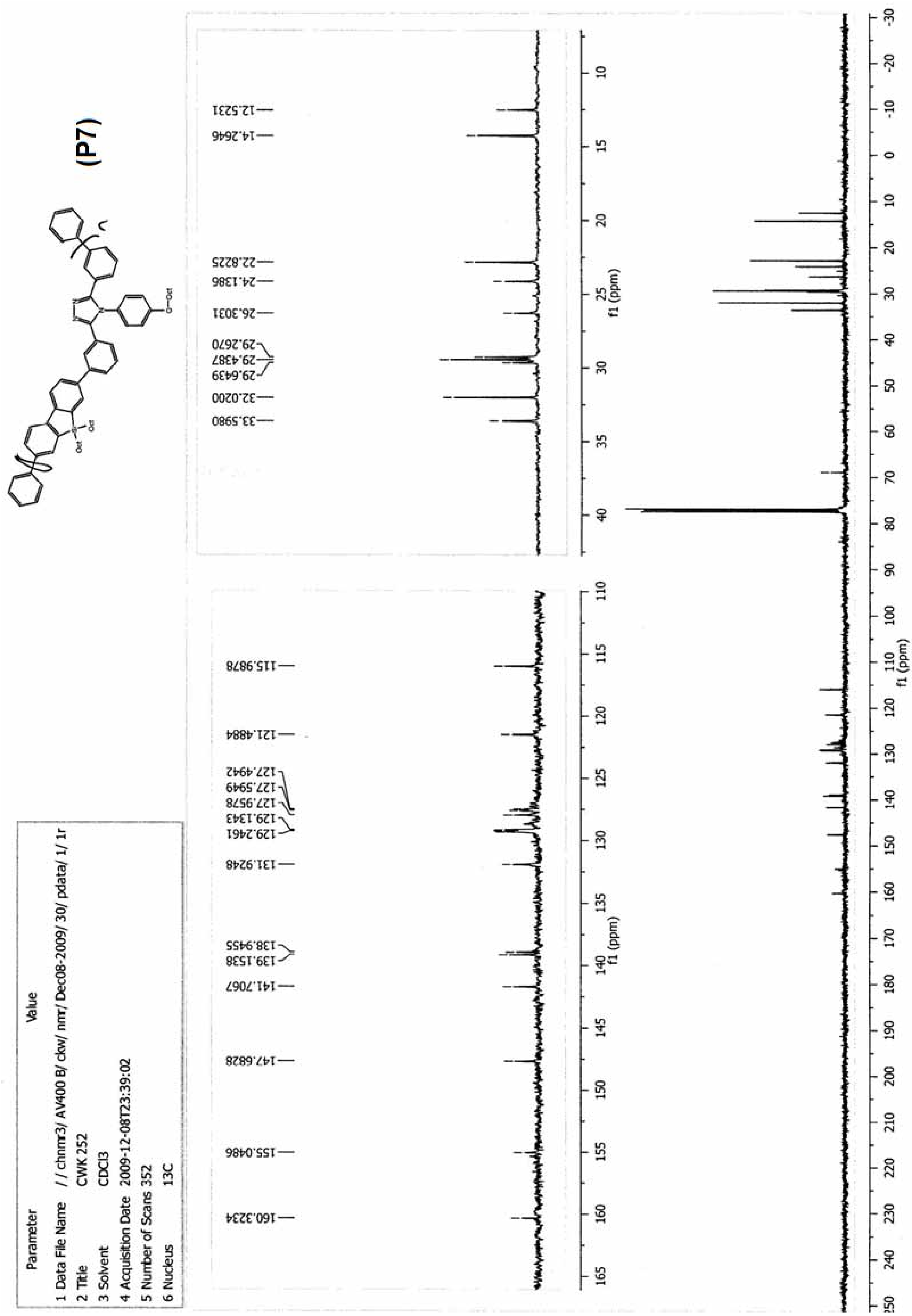
| 4 Acquisition Date | 2009-12-07T17:16:15 |
| 5 Number of Scans | 16 |
| 6 Nucleus | 1H |



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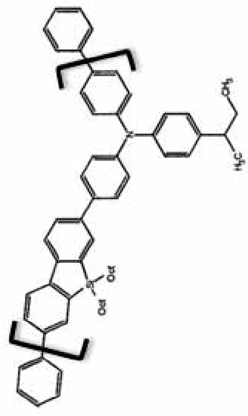
| 4 Acquisition Date | 2009-12-08T23:39:02 |
| 5 Number of Scans | 352 |
| 6 Nucleus | 13C |



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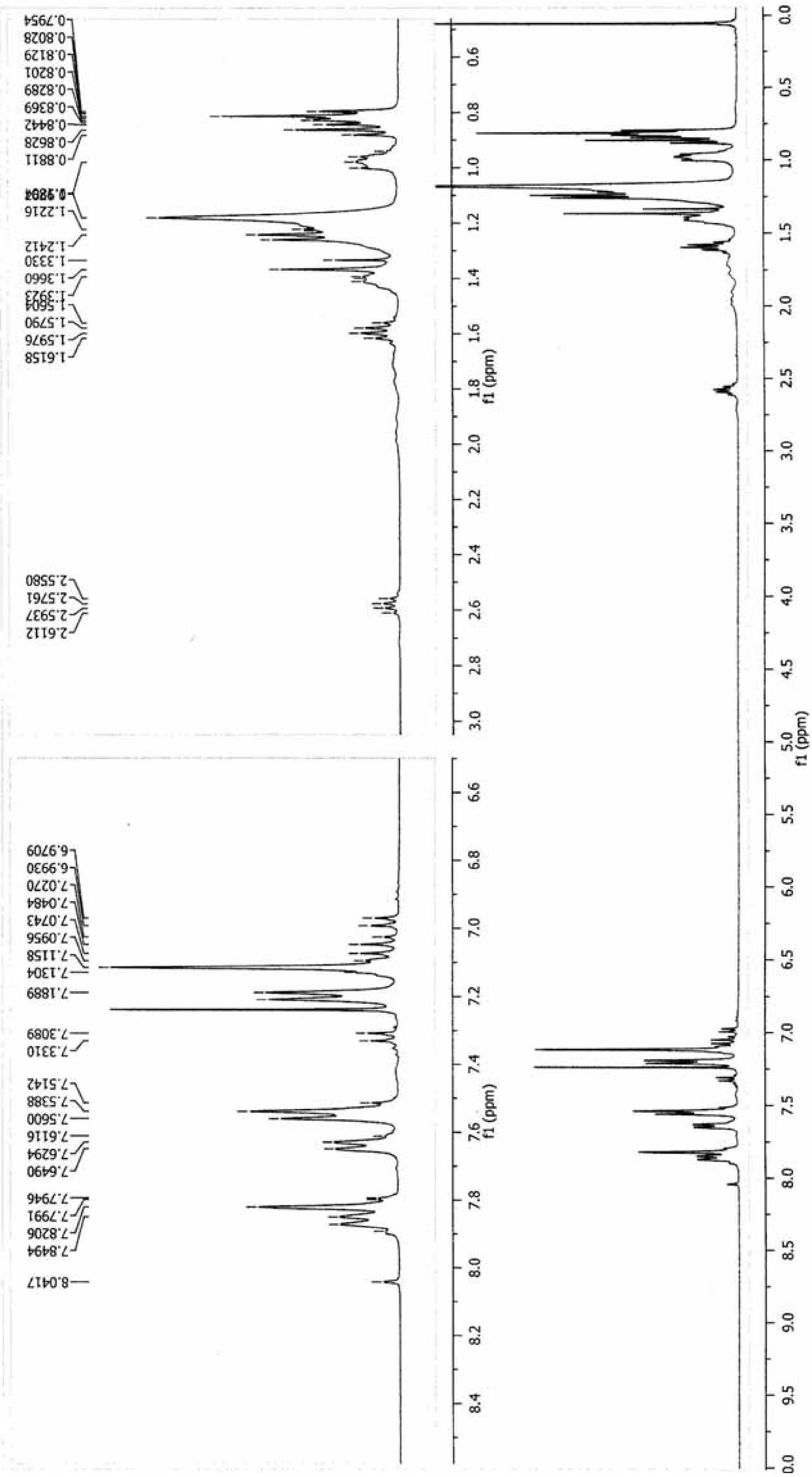

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| 2 | Title | CWK 251 |
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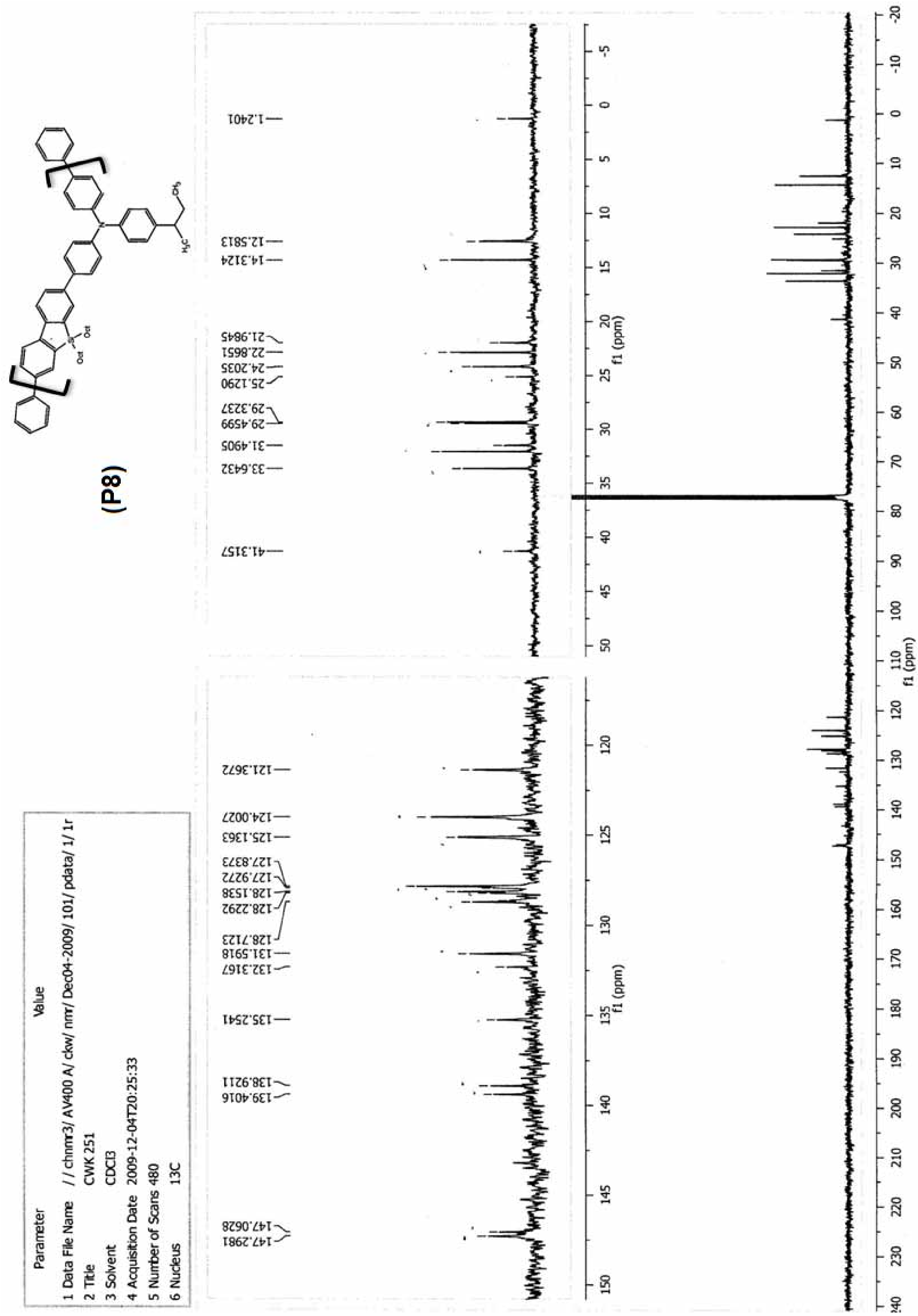
| 4 | Acquisition Date | 2009-12-04T16:59:28 |
| 5 | Number of Scans | 16 |
| 6 | Nucleus | 1H |



**(P8)**

| Parameter | Value |
|---|---|
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| 2 Title | CWK 251 |
| 3 Solvent | CDCl3 |
| 4 Acquisition Date | 2009-12-04T20:25:33 |
| 5 Number of Scans | 480 |
| 6 Nucleus | 13C |

## 3 - Cyclic Voltammograms

Co-polymers containing oxadiazole subunits (**P2** and **P6**) or triazole subunits (**P3** and **P7**) gave no observable reduction or oxidation responses. Co-polymers containing carbazole and triarylamine subunits gave a clear oxidation (HOMO) response, but both were irreversible (Figure S1). The oxidation waves observed for co-polymers **P1**, **P4** and **P8** were non-reproducible. For co-polymer **P8**, the response at 0.62 V becomes weaker with successive cycles, which could be due to dissolution of the sample from the working electrode surface, or to electro-decomposition to a redox-inactive species (Figure S2).

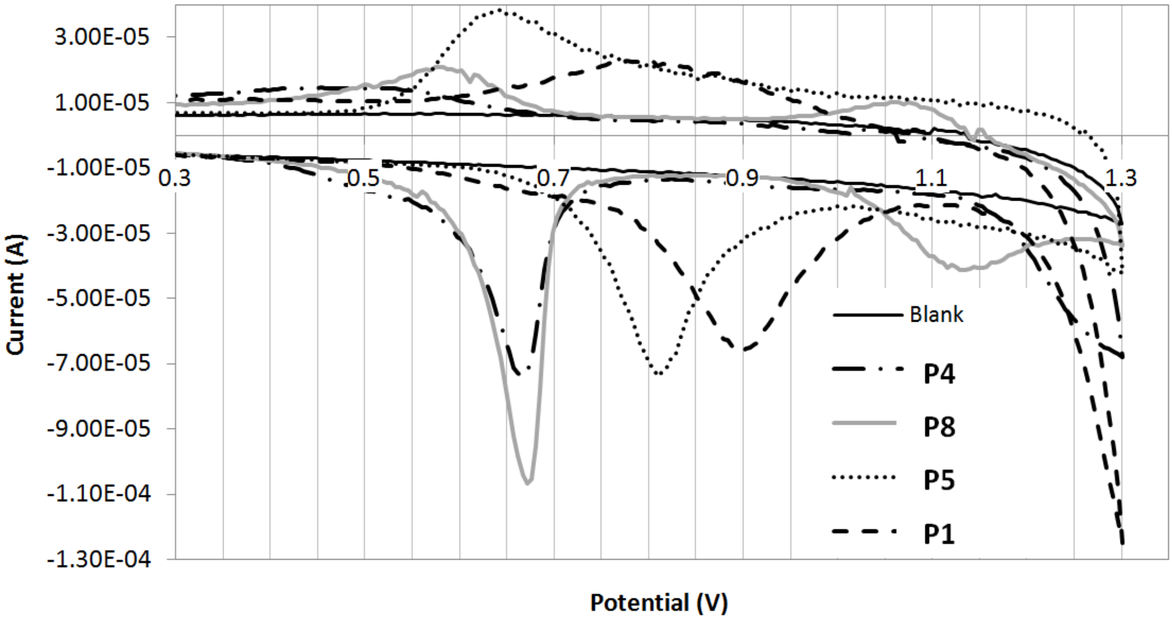


***Figure S1: Cyclic voltammogram showing oxidation sweeps for co-polymer samples on spin-coated thin films.***
***[Note: Glass-carbon working electrode. Ag/AgCl pseudo reference electrode, platinum wire counter electrode, 0.1 M tetrabutylammonium perchlorate in acetonitrile, under a blanket of argon. Oxidation sweeps performed at 1000mV/s and used to calculate HOMO]***

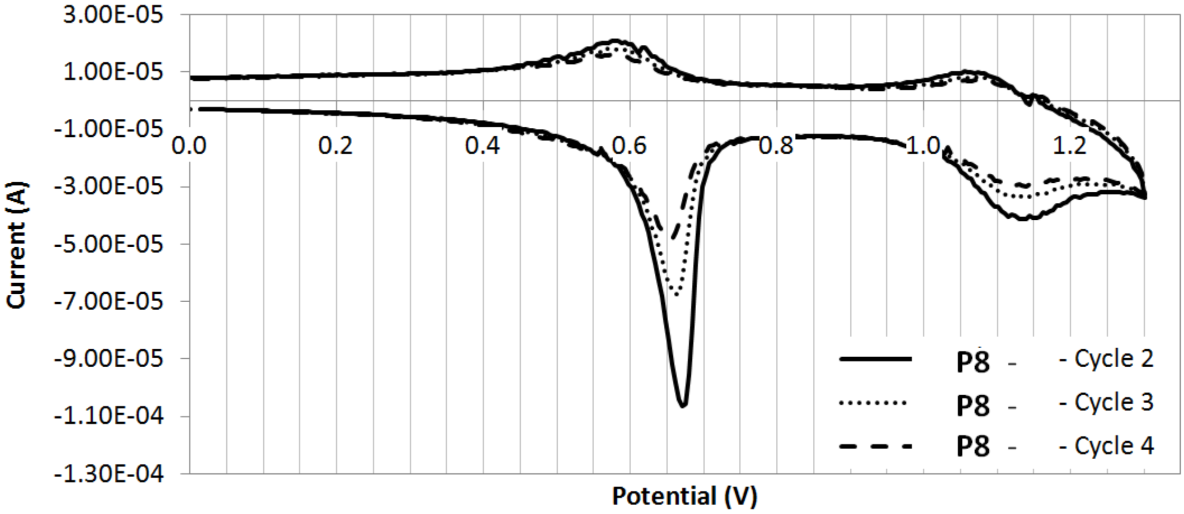


***Figure S2: Cyclic voltammogram showing oxidation sweeps for co-polymer P8 on spin-coated thin film.***
***[Note: Glass-carbon working electrode. Ag /AgCl pseudo reference electrode, platinum wire counter electrode, 0.1 M tetrabutylammonium perchlorate in acetonitrile, under a blanket of argon. Oxidation sweeps performed at 1000mV /s and used to calculate HOMO]***

For co-polymer samples **P1** and **P4** the waves were also non-reproducible. But in these cases, while the original peak decreases in intensity, a new peak is observed to increase in intensity during progressive sweeps. For co-polymer **P4** the peak at 0.62 V decreases, while the shoulder at 0.50 V increases (Figure S3); for co-polymer **P1** the peak at 0.90 V decreases while the shoulder at 0.70 V increases - Figure S4). This would indicate that an electrochemical reaction is taking place for these two co-polymers during the oxidation sweeps.

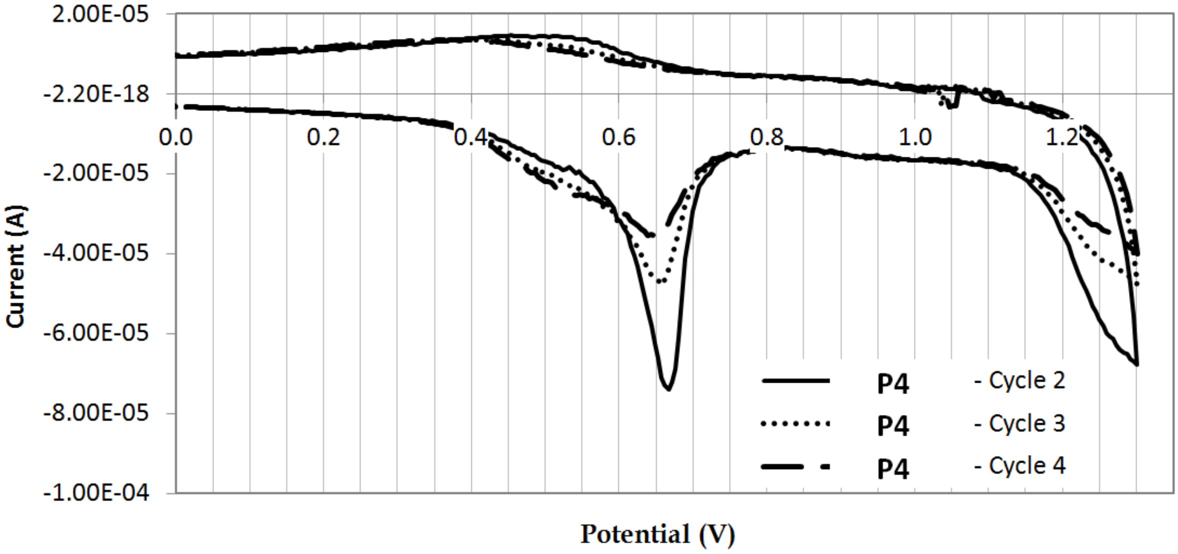


***Figure S3: Cyclic voltammogram showing oxidation sweeps for co-polymer P4 on spin-coated thin film.***
***[Note: Glass-carbon working electrode. Ag/AgCl pseudo reference electrode, platinum wire counter electrode, 0.1 M tetrabutylammonium perchlorate in acetonitrile, under a blanket of argon. Oxidation sweeps performed at 1000mV/s and used to calculate HOMO]***

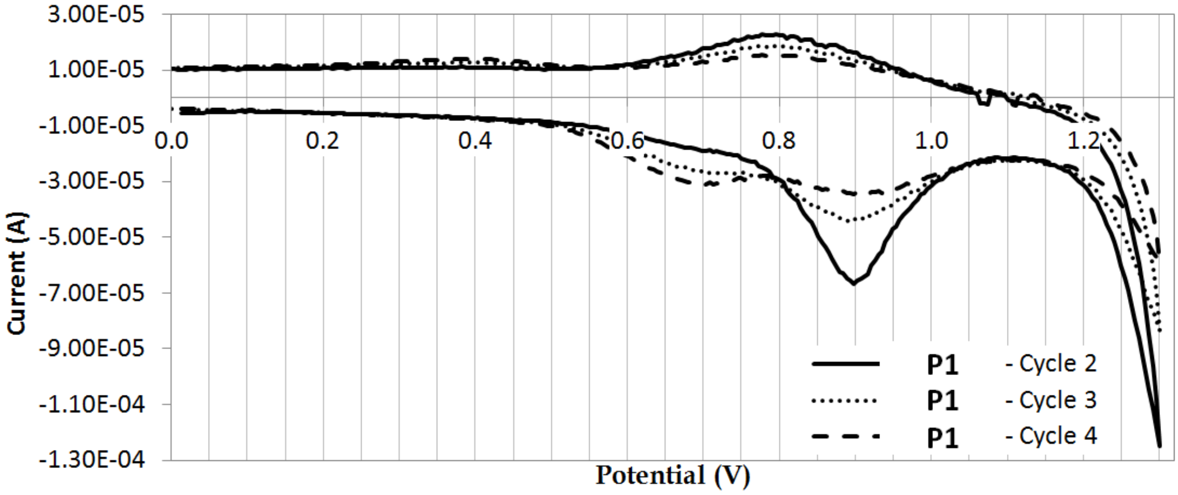


***Figure S4: Cyclic voltammogram showing oxidation sweeps for co-polymer P1 on spin-coated thin film.***
***[Note: Glass-carbon working electrode. Ag /AgCl pseudo reference electrode, platinum wire counter electrode, 0.1 M tetrabutylammonium perchlorate in acetonitrile, under a blanket of argon. Oxidation sweeps performed at 1000mV /s and used to calculate HOMO]***

## 4 - X-Ray Crystallographic data

### 4.1 - *N*,*N*-Bis(4-bromobenzene)-4-*sec*butylaniline (7)

*Crystal data for* **7**: $C_{22}H_{21}Br_2N$, $M$ = 459.22, triclinic, $P$–1 (no. 2), $a$ = 7.0740(3), $b$ = 10.1883(4), $c$ = 13.9770(5) Å, α = 80.255(3), β = 87.742(3), γ = 89.718(3)°, $V$ = 992.04(7) Å$^3$, $Z$ = 2, $D_c$ = 1.537 g cm$^{-3}$, μ(Cu-Kα) = 5.194 mm$^{-1}$, $T$ = 173 K, colourless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3929 independent measured reflections ($R_{int}$ = 0.0230), $F^2$ refinement, $R_1$(obs) = 0.0364, $wR_2$(all) = 0.1005, 3332 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 145°], 224 parameters. CCDC 803757.

The 4-*sec*butylaniline unit in the structure of **7** was found to be disordered (see Figs S5 and S6). Three discrete partial occupancy orientations were identified of *ca*. 43, 29 and 28% occupancy. The geometries of the three orientations were optimised (including treating the aryl rings as idealised hexagons), and all three orientations were refined isotropically.

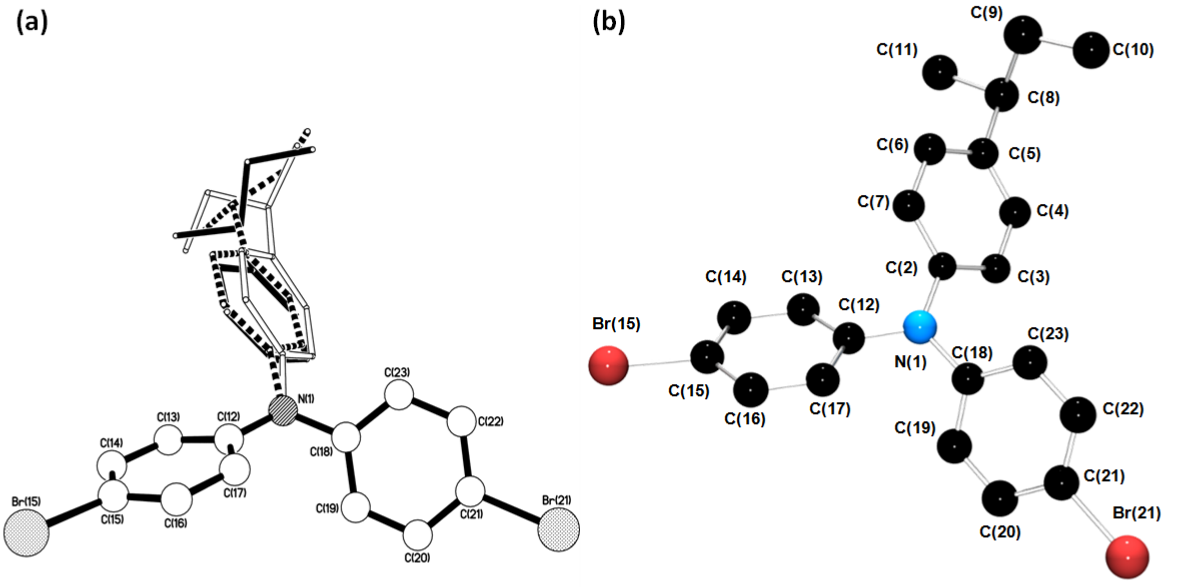


***Figure S5: X-ray crystal structure of triarylamine monomer* 7*, showing (a) three different partial occupancy orientations overlaid; (b) POV-ray image of major occupancy.***

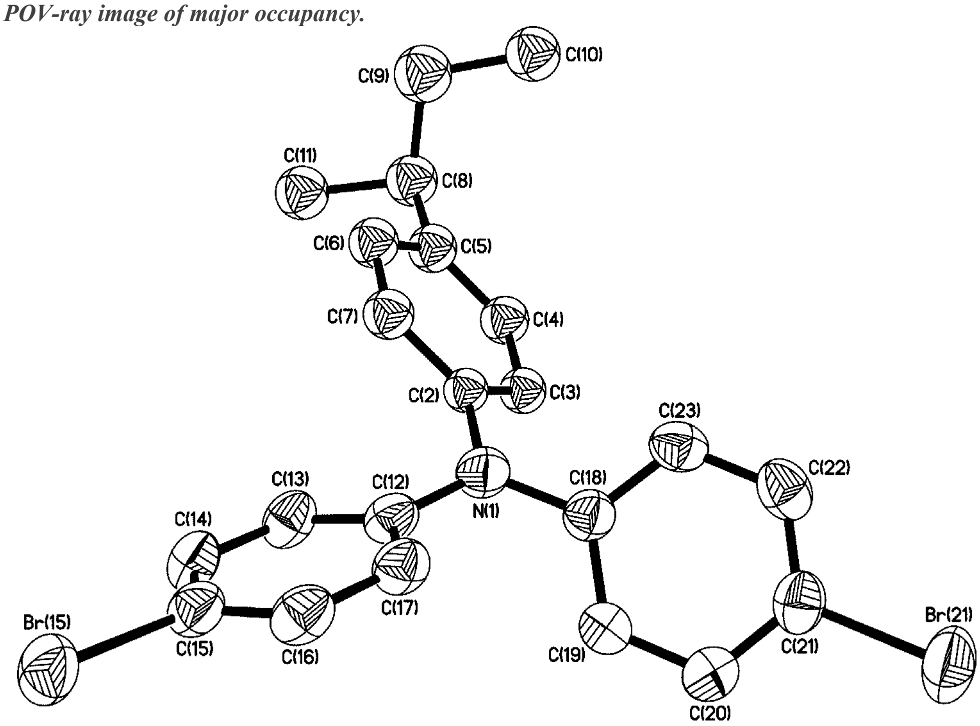


***Figure S6: The molecular structure of* 7 *(50% probability ellipsoids).***

## *Crystal Data and Structure Refinement*

| | | |
|---|---|---|
| Empirical formula | $C_{22}H_{21}Br_2N$ | |
| Formula weight | 459.22 | |
| Temperature | 173(2) K | |
| Diffractometer, wavelength | OD Xcalibur PX Ultra, 1.54184 Å | |
| Crystal system, space group | Triclinic, P-1 | |
| Unit cell dimensions | a = 7.0740(3) Å | α = 80.255(3)° |
| | b = 10.1883(4) Å | β = 87.742(3)° |
| | c = 13.9770(5) Å | γ = 89.718(3)° |
| Volume, Z | 992.04(7) Å$^3$, 2 | |
| Density (calculated) | 1.537 Mg/m$^3$ | |
| Absorption coefficient | 5.194 mm$^{-1}$ | |
| F(000) | 460 | |
| Crystal colour / morphology | Colourless needles | |
| Crystal size | 0.32 x 0.23 x 0.09 mm$^3$ | |
| θ Range for data collection | 3.21 to 72.57° | |
| Index ranges | -8<=h<=8, -12<=k<=12, -17<=l<=17 | |
| Reflns collected / unique | 12528 / 3929 [R(int) = 0.0230] | |
| Reflns observed [F>4σ(F)] | 3332 | |
| Absorption correction | Analytical | |
| Max. and min. transmission | 0.693 and 0.337 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3929 / 97 / 224 | |
| Goodness-of-fit on F$^2$ | 1.075 | |
| Final R indices [F>4σ(F)] | R1 = 0.0364, wR2 = 0.0963 | |
| R indices (all data) | R1 = 0.0436, wR2 = 0.1005 | |
| Extinction coefficient | 0.0020(3) | |
| Largest diff. peak, hole | 0.605, -0.582 eÅ$^{-3}$ | |

Mean and maximum shift/error 0.000 and 0.001

## *Bond Lengths [Å] and Angles [°]*

| Bond | Bond Length /Å |
|---|---|
| N(1)-C(12) | 1.416(4) |
| N(1)-C(18) | 1.419(4) |
| N(1)-C(2) | 1.421(4) |
| N(1)-C(2') | 1.445(5) |
| N(1)-C(2") | 1.488(5) |
| C(2)-C(3) | 1.3900 |
| C(2)-C(7) | 1.3900 |
| C(3)-C(4) | 1.3900 |
| C(4)-C(5) | 1.3900 |
| C(5)-C(6) | 1.3900 |
| C(5)-C(8) | 1.544(7) |
| C(6)-C(7) | 1.3900 |
| C(8)-C(9) | 1.517(9) |
| C(8)-C(11) | 1.625(9) |
| C(9)-C(10) | 1.551(10) |
| C(2')-C(3') | 1.3900 |
| C(2')-C(7') | 1.3900 |
| C(3')-C(4') | 1.3900 |
| C(4')-C(5') | 1.3900 |
| C(5')-C(6') | 1.3900 |
| C(5')-C(8') | 1.537(9) |
| C(6')-C(7') | 1.3900 |
| C(8')-C(9') | 1.521(11) |
| C(8')-C(11') | 1.579(11) |
| C(9')-C(10') | 1.562(12) |
| C(2")-C(3") | 1.3900 |
| C(2")-C(7") | 1.3900 |
| C(3")-C(4") | 1.3900 |
| C(4")-C(5") | 1.3900 |
| C(5")-C(6") | 1.3900 |
| C(5")-C(8") | 1.539(9) |
| C(6")-C(7") | 1.3900 |
| C(8")-C(9") | 1.516(11) |
| C(8")-C(11") | 1.530(11) |
| C(9")-C(10") | 1.542(12) |
| C(12)-C(13) | 1.392(4) |
| C(12)-C(17) | 1.398(4) |
| C(13)-C(14) | 1.381(4) |
| C(14)-C(15) | 1.383(4) |
| C(15)-C(16) | 1.381(4) |
| C(15)-Br(15) | 1.899(3) |
| C(16)-C(17) | 1.383(4) |
| C(18)-C(23) | 1.385(4) |
| C(18)-C(19) | 1.390(4) |
| C(19)-C(20) | 1.383(4) |
| C(20)-C(21) | 1.376(4) |
| C(21)-C(22) | 1.372(4) |
| C(21)-Br(21) | 1.912(3) |
| C(22)-C(23) | 1.387(4) |

| Bonds | Bond Angle /° |
|---|---|
| C(12)-N(1)-C(18) | 120.4(2) |
| C(12)-N(1)-C(2) | 119.3(4) |
| C(18)-N(1)-C(2) | 120.3(4) |
| C(12)-N(1)-C(2') | 126.8(4) |
| C(18)-N(1)-C(2') | 112.7(4) |
| C(12)-N(1)-C(2") | 115.5(4) |
| C(18)-N(1)-C(2") | 123.7(4) |
| C(3)-C(2)-C(7) | 120.0 |
| C(3)-C(2)-N(1) | 119.3(4) |
| C(7)-C(2)-N(1) | 120.7(4) |
| C(2)-C(3)-C(4) | 120.0 |
| C(5)-C(4)-C(3) | 120.0 |
| C(6)-C(5)-C(4) | 120.0 |
| C(6)-C(5)-C(8) | 120.1(4) |
| C(4)-C(5)-C(8) | 119.8(4) |
| C(5)-C(6)-C(7) | 120.0 |
| C(6)-C(7)-C(2) | 120.0 |
| C(9)-C(8)-C(5) | 113.1(5) |
| C(9)-C(8)-C(11) | 105.5(6) |
| C(5)-C(8)-C(11) | 109.1(5) |
| C(8)-C(9)-C(10) | 107.6(7) |
| C(3')-C(2')-C(7') | 120.0 |
| C(3')-C(2')-N(1) | 121.1(5) |
| C(7')-C(2')-N(1) | 118.7(5) |
| C(4')-C(3')-C(2') | 120.0 |
| C(3')-C(4')-C(5') | 120.0 |
| C(4')-C(5')-C(6') | 120.0 |
| C(4')-C(5')-C(8') | 119.1(5) |
| C(6')-C(5')-C(8') | 120.9(5) |
| C(7')-C(6')-C(5') | 120.0 |
| C(6')-C(7')-C(2') | 120.0 |
| C(9')-C(8')-C(5') | 113.9(7) |
| C(9')-C(8')-C(11') | 106.7(9) |
| C(5')-C(8')-C(11') | 111.1(8) |
| C(8')-C(9')-C(10') | 105.0(9) |
| C(3")-C(2")-C(7") | 120.0 |
| C(3")-C(2")-N(1) | 116.9(5) |
| C(7")-C(2")-N(1) | 123.0(5) |
| C(2")-C(3")-C(4") | 120.0 |
| C(5")-C(4")-C(3") | 120.0 |
| C(6")-C(5")-C(4") | 120.0 |
| C(6")-C(5")-C(8") | 120.4(5) |
| C(4")-C(5")-C(8") | 119.6(5) |
| C(5")-C(6")-C(7") | 120.0 |
| C(6")-C(7")-C(2") | 120.0 |
| C(9")-C(8")-C(11") | 110.6(9) |
| C(9")-C(8")-C(5") | 114.3(7) |
| C(11")-C(8")-C(5") | 111.6(7) |
| C(8")-C(9")-C(10") | 106.4(9) |
| C(13)-C(12)-C(17) | 118.4(3) |
| C(13)-C(12)-N(1) | 121.2(2) |
| C(17)-C(12)-N(1) | 120.4(2) |
| C(14)-C(13)-C(12) | 121.2(3) |
| C(13)-C(14)-C(15) | 119.4(3) |
| C(16)-C(15)-C(14) | 120.6(3) |
| C(16)-C(15)-Br(15) | 120.2(2) |
| C(14)-C(15)-Br(15) | 119.2(2) |
| C(15)-C(16)-C(17) | 119.8(3) |
| C(16)-C(17)-C(12) | 120.6(3) |
| C(23)-C(18)-C(19) | 119.2(3) |
| C(23)-C(18)-N(1) | 120.7(2) |
| C(19)-C(18)-N(1) | 120.1(3) |
| C(20)-C(19)-C(18) | 120.9(3) |
| C(21)-C(20)-C(19) | 118.8(3) |
| C(22)-C(21)-C(20) | 121.5(3) |
| C(22)-C(21)-Br(21) | 119.3(2) |
| C(20)-C(21)-Br(21) | 119.2(2) |
| C(21)-C(22)-C(23) | 119.6(3) |
| C(18)-C(23)-C(22) | 120.1(3) |

## 4.2 - 3,5-Bis(3-bromophenyl)-4-(4-(octyloxy)phenyl)-1,2,4-triazole (11)

*Crystal data for* **11**: $C_{28}H_{29}Br_2N_3O$, $M$ = 583.36, monoclinic, $C2/c$ (no. 15), $a$ = 19.3994(4), $b$ = 9.5710(2), $c$ = 28.8219(7) Å, $\beta$ = 100.402(2)°, $V$ = 5263.5(2) Å$^3$, $Z$ = 8, $D_c$ = 1.472 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 3.105 mm$^{-1}$, $T$ = 173 K, colourless blocks, Oxford Diffraction Xcalibur 3 diffractometer; 9031 independent measured reflections ($R_{int}$ = 0.0309), $F^2$ refinement, $R_1$(obs) = 0.0345, $wR_2$(all) = 0.0745, 5676 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 66°], 307 parameters. CCDC 803758.

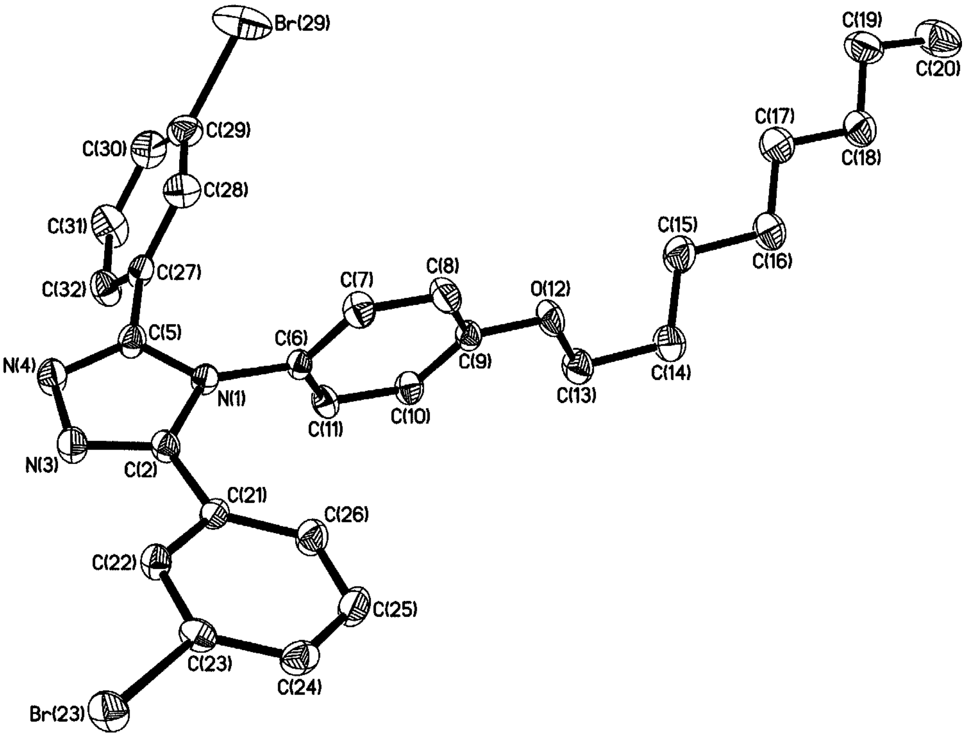


*Figure S7: The molecular structure of* **11** *(50% probability ellipsoids).*

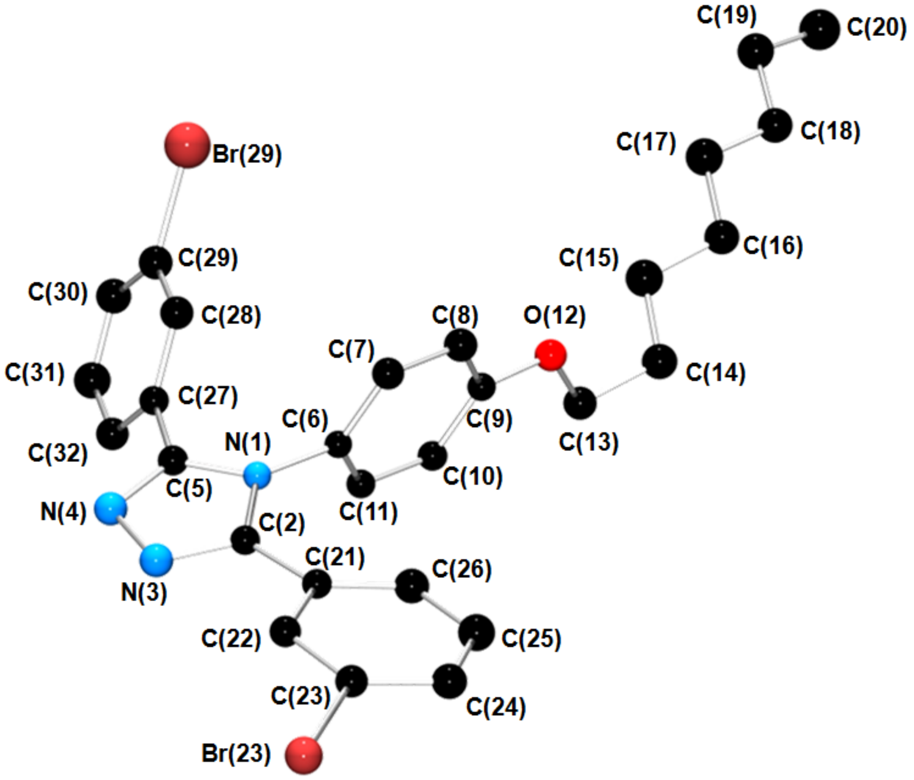


*Figure S8: X-ray crystal structure of triazole monomer* **11.**

## *Crystal Structure and Structure Refinement*

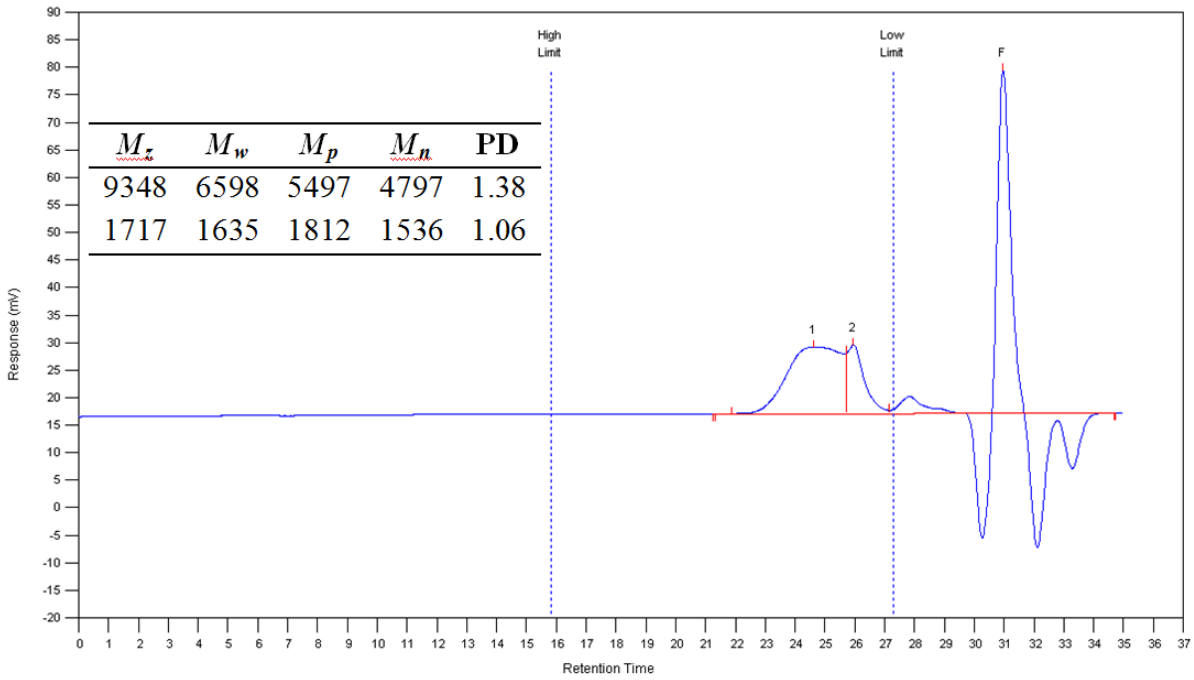
| | |
|---|---|
| Empirical formula | $C_{28}H_{29}Br_2N_3O$ |
| Formula weight | 583.36 |
| Temperature | 173(2) K |
| Diffractometer, wavelength | OD Xcalibur 3, 0.71073 Å |
| Crystal system, space group | Monoclinic, C2/c |
| Unit cell dimensions | a = 19.3994(4) Å α = 90°<br>b = 9.5710(2) Å β = 100.402(2)°<br>c = 28.8219(7) Å γ = 90° |
| Volume, Z | 5263.5(2) Å$^3$, 8 |
| Density (calculated) | 1.472 Mg/m$^3$ |
| Absorption coefficient | 3.105 mm$^{-1}$ |
| F(000) | 2368 |
| Crystal colour / morphology | Colourless blocks |
| Crystal size | 0.38 x 0.30 x 0.23 mm$^3$ |
| θ Range for data collection | 3.08 to 33.04° |
| Index ranges | -26<=h<=29, -13<=k<=14, -41<=l<=42 |
| Reflns collected / unique | 29084 / 9031 [R(int) = 0.0309] |
| Reflns observed [F>4σ(F)] | 5676 |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.588 and 0.412 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 9031 / 0 / 307 |
| Goodness-of-fit on F$^2$ | 0.925 |
| Final R indices [F>4σ(F)] | R1 = 0.0345, wR2 = 0.0714 |
| R indices (all data) | R1 = 0.0673, wR2 = 0.0745 |
| Largest diff. peak, hole | 0.803, -0.811 eÅ$^{-3}$ |
| Mean and maximum shift/error | 0.000 and 0.005 |

## *Bond Lengths [Å] and Angles [°]*

| Bond | Bond Length /Å |
|---|---|
| N(1)-C(5) | 1.365(2) |
| N(1)-C(2) | 1.377(2) |
| N(1)-C(6) | 1.447(2) |
| C(2)-N(3) | 1.316(2) |
| C(2)-C(21) | 1.470(2) |
| N(3)-N(4) | 1.3840(19) |
| N(4)-C(5) | 1.318(2) |
| C(5)-C(27) | 1.478(2) |
| C(6)-C(11) | 1.370(2) |
| C(6)-C(7) | 1.381(2) |
| C(7)-C(8) | 1.381(2) |
| C(8)-C(9) | 1.390(2) |
| C(9)-O(12) | 1.3657(18) |
| C(9)-C(10) | 1.389(2) |
| C(10)-C(11) | 1.391(2) |
| O(12)-C(13) | 1.442(2) |
| C(13)-C(14) | 1.518(2) |
| C(14)-C(15) | 1.490(3) |
| C(15)-C(16) | 1.528(3) |
| C(16)-C(17) | 1.524(3) |
| C(17)-C(18) | 1.515(3) |
| C(18)-C(19) | 1.516(3) |
| C(19)-C(20) | 1.505(3) |
| C(21)-C(26) | 1.394(2) |
| C(21)-C(22) | 1.401(2) |
| C(22)-C(23) | 1.378(2) |
| C(23)-C(24) | 1.378(2) |
| C(23)-Br(23) | 1.9015(15) |
| C(24)-C(25) | 1.378(2) |
| C(25)-C(26) | 1.383(2) |
| C(27)-C(32) | 1.384(2) |
| C(27)-C(28) | 1.384(2) |
| C(28)-C(29) | 1.381(2) |
| C(29)-C(30) | 1.373(3) |
| C(29)-Br(29) | 1.8915(18) |
| C(30)-C(31) | 1.382(3) |
| C(31)-C(32) | 1.389(3) |

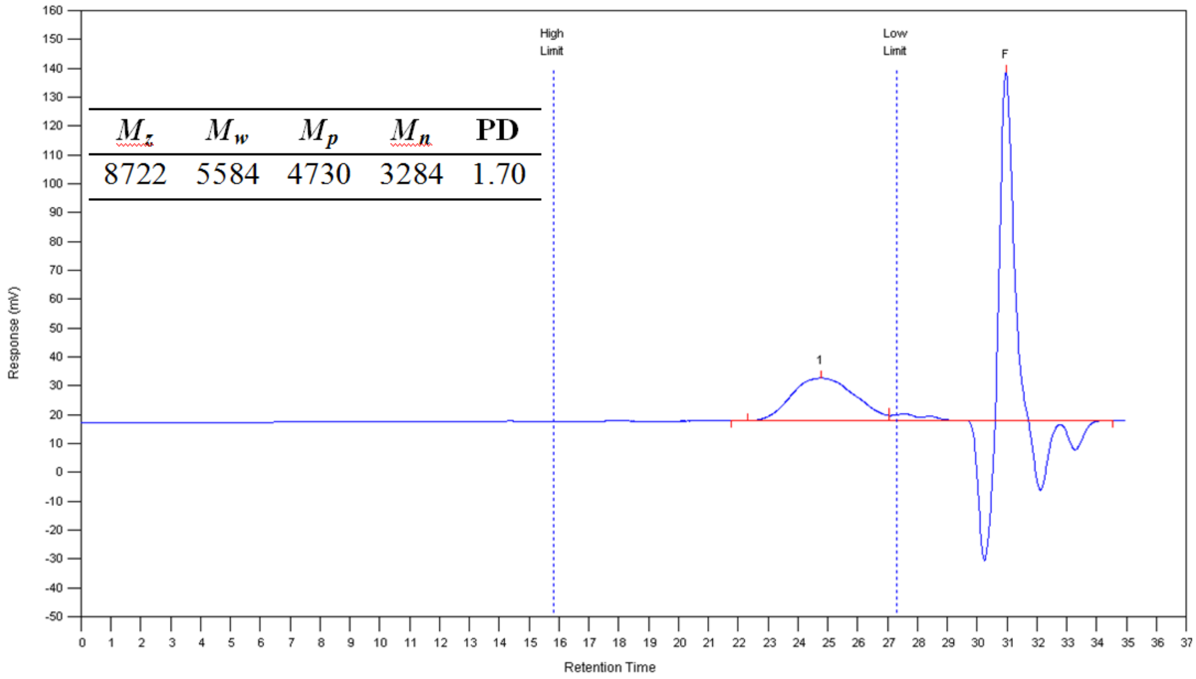
| Bonds | Bond Angle /° |
|---|---|
| C(5)-N(1)-C(2) | 104.76(13) |
| C(5)-N(1)-C(6) | 124.03(13) |
| C(2)-N(1)-C(6) | 130.08(14) |
| N(3)-C(2)-N(1) | 109.43(14) |
| N(3)-C(2)-C(21) | 122.42(14) |
| N(1)-C(2)-C(21) | 128.14(15) |
| C(2)-N(3)-N(4) | 108.41(13) |
| C(5)-N(4)-N(3) | 106.40(13) |
| N(4)-C(5)-N(1) | 110.99(14) |
| N(4)-C(5)-C(27) | 124.38(15) |
| N(1)-C(5)-C(27) | 124.62(14) |
| C(11)-C(6)-C(7) | 120.99(15) |
| C(11)-C(6)-N(1) | 117.66(15) |
| C(7)-C(6)-N(1) | 121.31(14) |
| C(8)-C(7)-C(6) | 119.20(16) |
| C(7)-C(8)-C(9) | 120.36(16) |
| O(12)-C(9)-C(10) | 123.80(15) |
| O(12)-C(9)-C(8) | 116.11(15) |
| C(10)-C(9)-C(8) | 120.09(15) |
| C(9)-C(10)-C(11) | 119.03(16) |
| C(6)-C(11)-C(10) | 120.32(16) |
| C(9)-O(12)-C(13) | 117.72(13) |
| O(12)-C(13)-C(14) | 106.71(15) |
| C(15)-C(14)-C(13) | 112.98(17) |
| C(14)-C(15)-C(16) | 113.69(17) |
| C(17)-C(16)-C(15) | 113.21(17) |
| C(18)-C(17)-C(16) | 113.62(17) |
| C(17)-C(18)-C(19) | 113.38(17) |
| C(20)-C(19)-C(18) | 112.73(18) |
| C(26)-C(21)-C(22) | 118.73(15) |
| C(26)-C(21)-C(2) | 124.74(15) |
| C(22)-C(21)-C(2) | 116.48(14) |
| C(23)-C(22)-C(21) | 119.66(15) |
| C(24)-C(23)-C(22) | 121.78(15) |
| C(24)-C(23)-Br(23) | 119.92(12) |
| C(22)-C(23)-Br(23) | 118.30(12) |
| C(25)-C(24)-C(23) | 118.42(16) |
| C(24)-C(25)-C(26) | 121.37(16) |
| C(25)-C(26)-C(21) | 120.01(16) |
| C(32)-C(27)-C(28) | 120.41(16) |
| C(32)-C(27)-C(5) | 118.71(16) |
| C(28)-C(27)-C(5) | 120.86(16) |
| C(29)-C(28)-C(27) | 118.96(17) |
| C(30)-C(29)-C(28) | 121.53(17) |
| C(30)-C(29)-Br(29) | 118.66(14) |
| C(28)-C(29)-Br(29) | 119.80(14) |
| C(29)-C(30)-C(31) | 119.20(17) |
| C(30)-C(31)-C(32) | 120.29(18) |
| C(27)-C(32)-C(31) | 119.59(17) |

## 5 - Gel Permeation Chromatography Traces



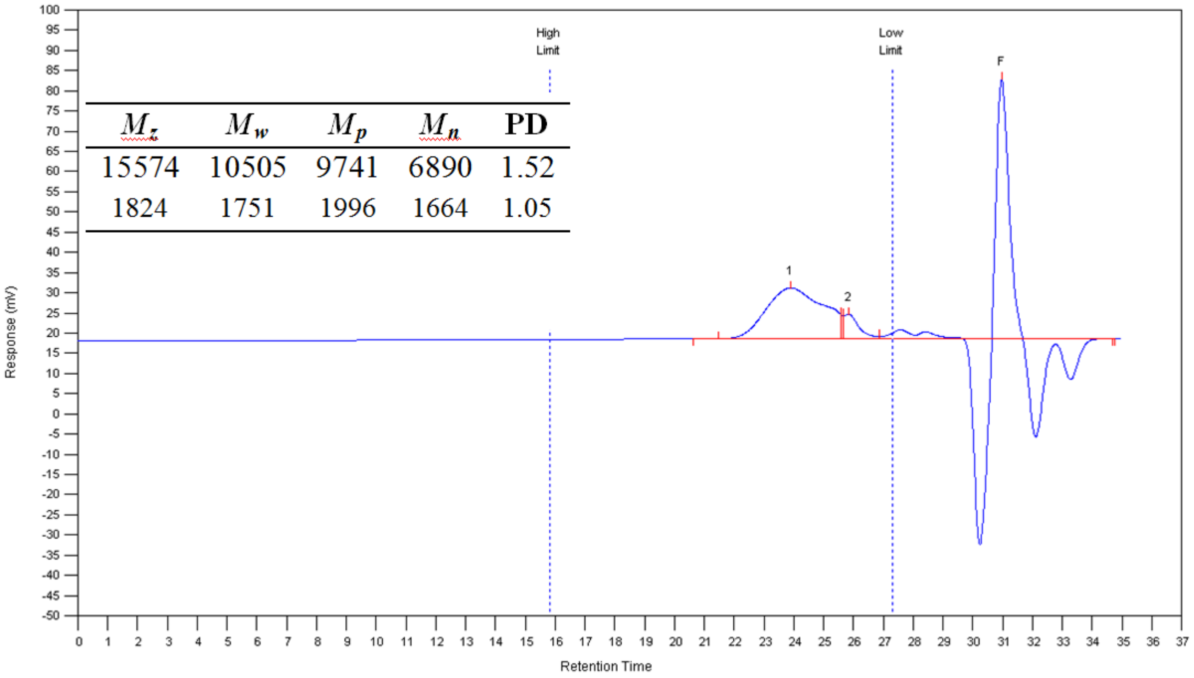
| $M_z$ | $M_w$ | $M_p$ | $M_n$ | PD |
|---|---|---|---|---|
| 9348 | 6598 | 5497 | 4797 | 1.38 |
| 1717 | 1635 | 1812 | 1536 | 1.06 |

*Figure S9: Gel permeation chromatogram for copolymer P1*



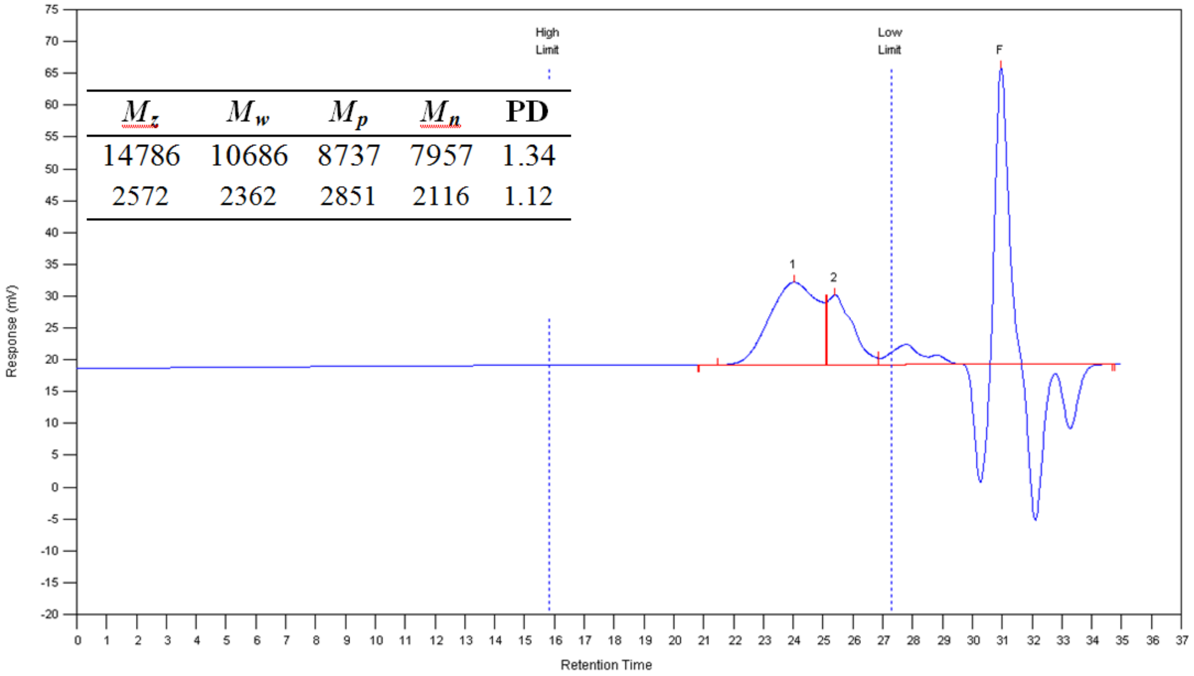
| $M_z$ | $M_w$ | $M_p$ | $M_n$ | PD |
|---|---|---|---|---|
| 8722 | 5584 | 4730 | 3284 | 1.70 |

*Figure S10: Gel permeation chromatogram for copolymer P2*



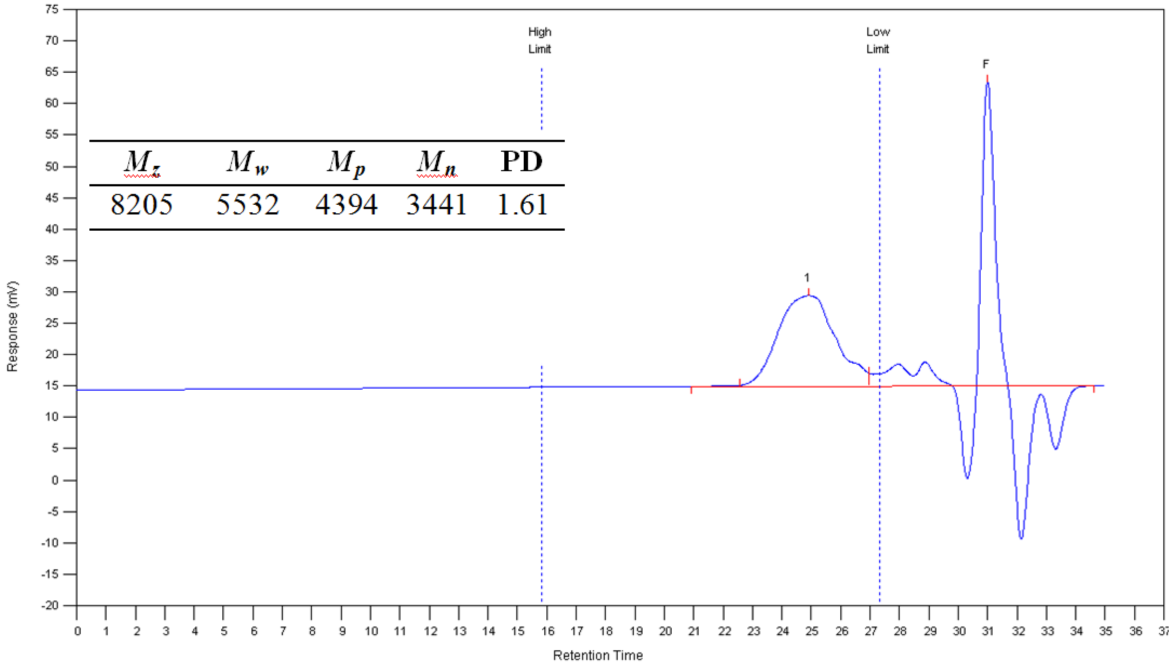
| $M_z$ | $M_w$ | $M_p$ | $M_n$ | PD |
|---|---|---|---|---|
| 15574 | 10505 | 9741 | 6890 | 1.52 |
| 1824 | 1751 | 1996 | 1664 | 1.05 |

*Figure S11: Gel permeation chromatogram for copolymer P3*



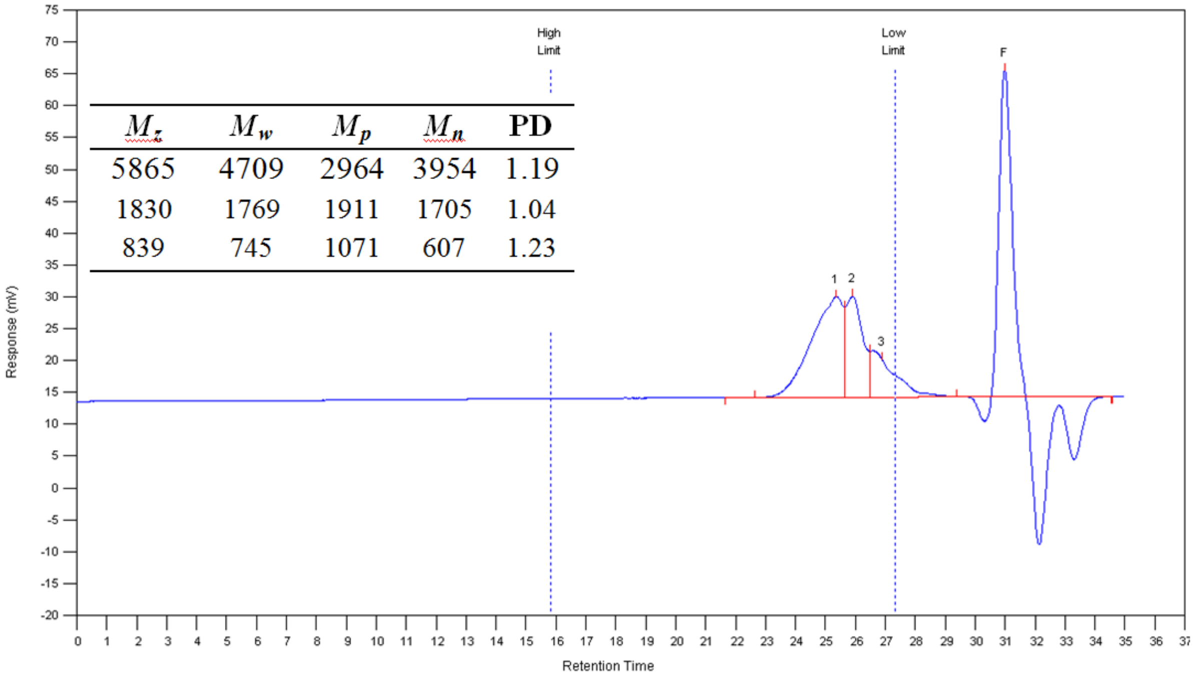
| $M_z$ | $M_w$ | $M_p$ | $M_n$ | PD |
|---|---|---|---|---|
| 14786 | 10686 | 8737 | 7957 | 1.34 |
| 2572 | 2362 | 2851 | 2116 | 1.12 |

*Figure S12: Gel permeation chromatogram for copolymer P4*



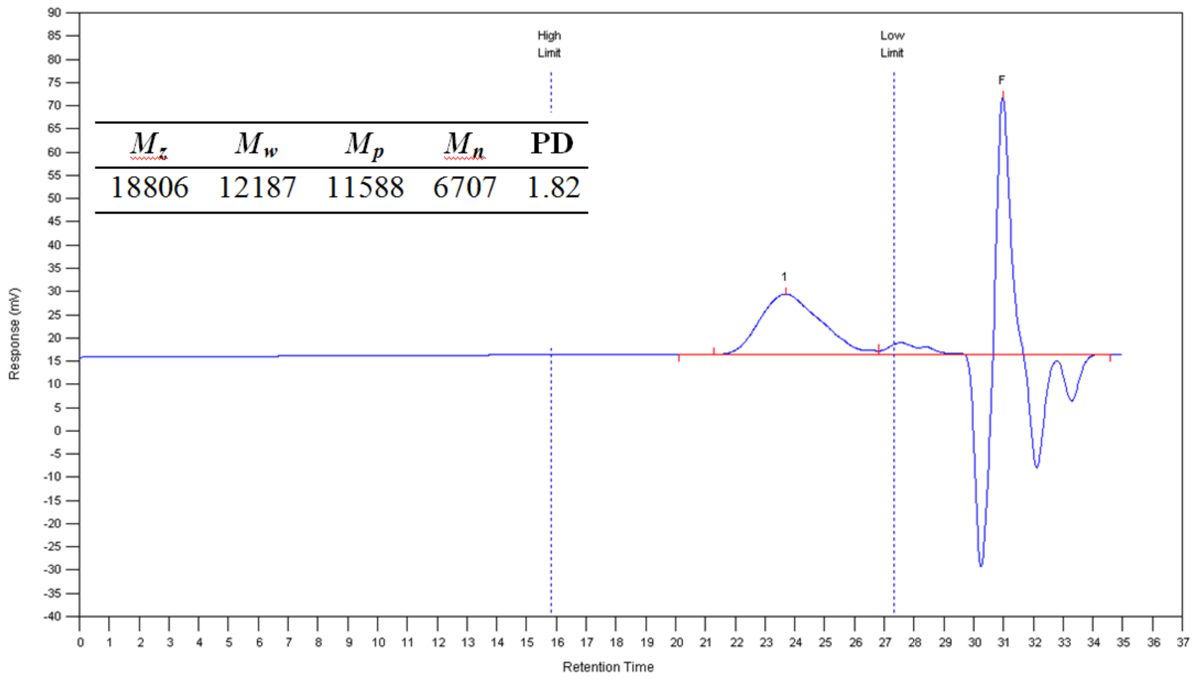
| $M_z$ | $M_w$ | $M_p$ | $M_n$ | PD |
|---|---|---|---|---|
| 8205 | 5532 | 4394 | 3441 | 1.61 |

*Figure S13: Gel permeation chromatogram for copolymer P5*



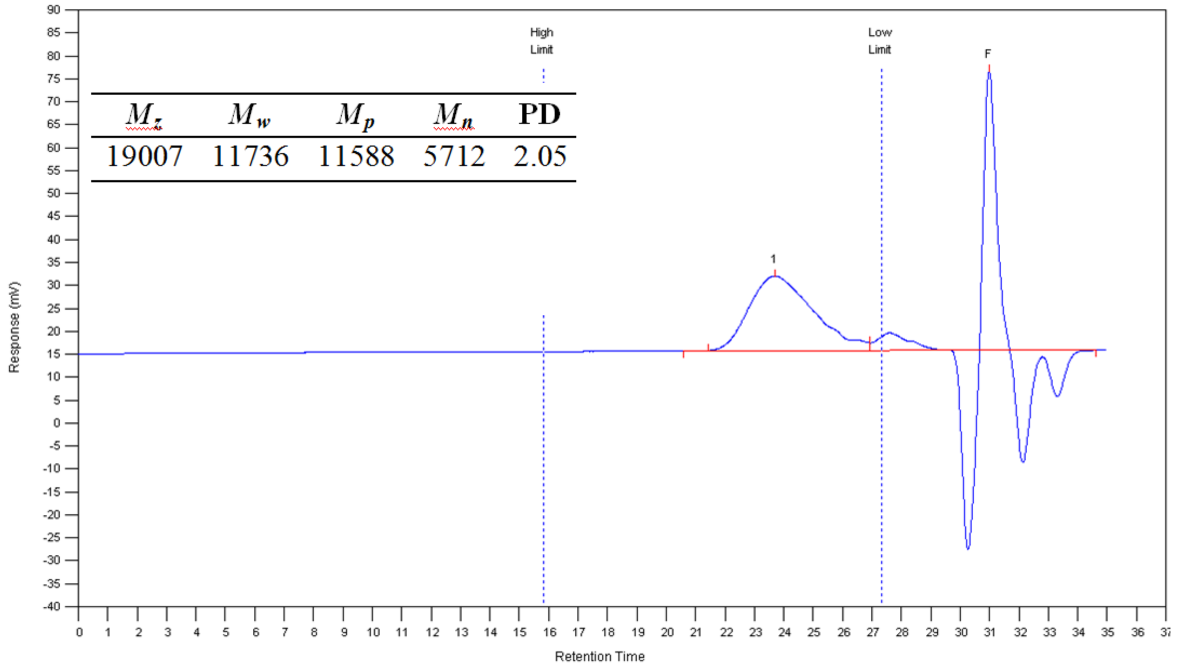
| $M_z$ | $M_w$ | $M_p$ | $M_n$ | PD |
|---|---|---|---|---|
| 5865 | 4709 | 2964 | 3954 | 1.19 |
| 1830 | 1769 | 1911 | 1705 | 1.04 |
| 839 | 745 | 1071 | 607 | 1.23 |

*Figure S14: Gel permeation chromatogram for copolymer P6*



| $M_z$ | $M_w$ | $M_p$ | $M_n$ | PD |
|---|---|---|---|---|
| 18806 | 12187 | 11588 | 6707 | 1.82 |

*Figure S15: Gel permeation chromatogram for copolymer P7*



| $M_z$ | $M_w$ | $M_p$ | $M_n$ | PD |
|---|---|---|---|---|
| 19007 | 11736 | 11588 | 5712 | 2.05 |

*Figure S16: Gel permeation chromatogram for copolymer P8*

## 6 - References

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