Chiral Derivatives of 1,2-Benzenedisulfonimide as efficient Brønsted acid catalysts in Strecker reaction.

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Electronic Supplementary Information (ESI)

1. Synthesis of 4-Iodonitroanilines 5

ICl 1M in MeCOOH (20 ml) was added to a MeCOOH (5 ml) solution of nitroaniline **4** (5 mmol). The mixture was stirred at 30 °C for 3 h until GC and GC-MS analyses showed the complete disappearance of the starting compound and the complete formation of iodinate product **5**. The reaction mixture was poured into a cold 10% aqueous $NaHCO_3$ solution (15 ml). A precipitate was formed and was gathered on a Buchner funnel and washed with further $NaHCO_3$ solution (15 ml) in order to remove completely MeCOOH. The resulting solid was the virtually pure **5**.

4-Iodo-6-methyl-2-nitroaniline (5a). Brown solid (1.39 g; 100% yield). Mp 140–141 °C (EtOH; lit 139–140 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.46 (s, 1H), 6.12 (br s, 2H), 2.15 (s, 3H); ^{1}H NMR data identical to that reported in the literature.[15] ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.1, 143.1, 132.6, 131.7, 123.8, 75.7, 17.4. MS (EI) *m/z*: (%) 278 [M^+] (100), 232 (35), 105 (35). IR (neat) ν (cm^{-1}): 3508, 3504 (NH_2), 1585, 1312 (NO_2).
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4-Iodo-5,6-dimethyl-2-nitroaniline (5b). Brown solid (1.46 g; 100% yield). Mp 158–159 °C (from EtOH). Found: C 32.94; H 3.07; N 9.54. $C_8H_9IN_2O_2$ requires: C 32.90; H 3.11; N 9.59%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 6.16 (br s, 2H), 2.42 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.2, 143.2, 141.7, 133.5, 123.6, 85.6, 26.9, 15.2. MS (EI) *m/z*: (%) 292 [M^+] (100), 246 (25), 119 (25). IR (neat) ν (cm^{-1}): 3510, 3500 (NH_2), 1535, 1350 (NO_2)

2. Synthesis of Diiodonitro derivatives (7)

First HBF_4·Et_2O (54 %; 6 mmol, 0.97 g) and then *i*-pentyl nitrite (6 mmol, 0.70 g) were added to a cooled (5 °C) suspension of iodonitroaniline **5** (5 mmol) in MeCOOH (20 ml). A clear solution was obtained; it was stirred for about 30 min at rt. Then, anhydrous Et_2O (50 ml) was added to this solution, previously cooled (5° C); a white precipitate was formed and it was gathered on a Buchner funnel. This solid was the corresponding diazonium tetrafluoroborate **6** and it was reacted immediately in the next step without further purification.
6 was added at rt to a stirred MeCN (20 mL) solution of tetra-*n*-butylammonium iodide (5.5 mmol, 2.03 g). Stirring was maintained for about 30 minutes until the complete disappearance of **6**. The reaction mixture was poured into Et_2O-H_2O (100 mL, 1:1). The aqueous layer was separated and extracted with Et_2O (100 mL). The combined organic extracts were washed with H_2O (50 mL),

dried over Na_2SO_4 and evaporated under reduced pressure. The obtained solid was the virtually pure **7**.

2,5-Diiodo-3-nitrotoluene (7a). Brown solid (1.78 g, 91% yield). Mp 93–94 °C (EtOH; lit 95 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.68 (s, 1H), 7.66 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.2, 141.7, 130.5, 118.9, 92.7, 92.5, 29.2. MS (EI) *m/z*: (%) 389 [M^+] (100), 343 (15), 216 (35). IR (neat) ν (cm^{-1}): 1542, 1358 (NO_2)
H. L. Wheeler, *Am. Chem. J.,* 1911, **44**, 493.

3,6-Diiodo-4-nitro-*o*-xylene (7b). Grey solid (1.90 g; 94% yield). Mp 117–118 °C (EtOH). Found: C 23.92; H 1.77; N 3.44. $C_8H_7INO_2$ requires: C 23.85; H 1.75; N 3.48%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 2.64 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.2, 143.3, 141.8, 132.1, 101.0, 93.6, 29.0, 28.1. MS (EI) *m/z*: (%) 403 [M^+] (100), 357 (15), 230 (25), 103 (15). IR (neat) ν (cm^{-1}): 1522, 1351 (NO_2)

3. Synthesis of 4-nitro-3,6-bis(*o*-tolyl)-*o*-xylene (15)

o-Tolylboronic acid (4.5 mmol, 0.61 g) and then K_3PO_4 (12 mmol, 2.54 g) were added to a stirring mixture of 3,6-diiodo-4-nitro-*o*-xylene (**7b**, 2 mmol, 0.81 g), tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) as a catalyst (0.04 mmol; 37 mg and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos) as a ligand (0.32 mmol; 0.132 g) in anhydrous toluene (15 mL). The mixture was stirred at reflux until the disappearance of **7b** as monitored by TLC (PE/Et_2O 4:1). Then, the reaction mixture was poured into CH_2Cl_2-H_2O (100 ml, 1:1). The aqueous layer was separated and extracted with CH_2Cl_2 (100 mL). The combined organic extracts were washed with H_2O (100 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue, purified in a chromatography column (PE/Et_2O 4:1), afforded pure **15**.

4-Nitro-3,6-bis(*o*-tolyl)-*o*-xylene (15). Mixture of diastereomers. Yellow solid (0.63 g, 95% yield). Mp 124–125 °C (EtOH). Found: C 79.72; H 6.45; N 4.20. $C_{22}H_{21}NO_2$ requires: C 79.73; H 6.39; N 4.23%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.26–6.97 (m, 8H), 2.08, 2.06, 2.05, 2.04, 1.95 (5s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.8, 141.8, 140.8, 140.2, 138.1, 136.9, 136.7, 136.1, 136.0, 134.1, 130.3, 130.2, 129.5, 129.4, 128.5, 128.4, 128.2, 126.2, 122.3, 20.2, 20.1, 18.0,17.6. MS (EI) *m/z*: (%) 331 [M^+] (90), 314 (100), 301 (95), 284 (100), 269 (85), 253 (85), 239 (55). IR (neat) ν (cm^{-1}): 1520, 1355 (NO_2).

We also performed the reaction using 1-naphthylboronic acid (4.5 mmol, 0.77 g). It was not possible to isolate 4-nitro-3,6-bis(1-naphthyl)-*o*-xylene in acceptable purity.

4. Synthesis of diiodoanilines 8

Fe powder (15 mmol, 0.84 g) and $CaCl_2$ (5 mmol, 0.55 g; dissolved in 2 ml of H_2O) were added to a stirred EtOH solution (15 mL) of nitroderivative **7** (5 mmol). Stirring was maintained for about 6 hours until its complete disappearance. The crude residue was filtered on a Buchner funnel in order to remove the excess Fe and EtOH was evaporated under reduced pressure. The crude residue was poured into Et_2O/H_2O (100 mL, 1:1). The aqueous layer was separated and extracted with Et_2O (100 mL). The combined organic extracts were washed with H_2O (100 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The obtained solid was the virtually pure **8**.

2,5-Diiodo-3-methylaniline (8a). Brown solid (1.65 g, 92% yield). Mp 84–85 °C (EtOH; lit 82 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.91 (s, 1H), 6.84 (s, 1H), 6.13 (br s, 2H), 2.15 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.7, 144.4, 128.0, 120.3, 94.1, 90.9, 24.4. MS (EI) *m/z*: (%) 359 [M^+] (100), 232 (15), 105 (20). IR (neat) ν (cm^{-1}): 3410, 3406 (NH_2).
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2,5-Diiodo-3,4-dimethylaniline (8b). Pale red waxy solid (1.55 g; 83% yield). Found: C 25.81; H 2.44; N 3.67. $C_8H_9I_2N$ requires: C 25.76; H 2.43; N 3.76%. ^{1}H NMR (200 MHz, CDCl3): δ = 7.11 (s, 1H), 4.00 (br s, 2H), 2.47 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.8, 146.1, 141.8, 122.4, 102.7, 93.9, 28.5, 26.7. MS (EI) *m/z*: (%) 373 [M^+] (100), 357 (15), 246 (25), 118 (15). IR (neat) ν (cm^{-1}): 3418, 3412 (NH_2).

5. Synthesis of 2,5-bis(*o*-tolyl)-3,4-dimethylaniline (16)

The same protocol as the synthesis of diiodoanilines **8** was used, starting from 4-nitro-3,6-bis(2-tolyl)benzene (**15**; 5 mmol, 1.65 g). The only difference was the use of Zn (15 mmol, 0.98 g) instead of Fe.

2,5-Bis(*o*-tolyl)-3,4-dimethylaniline (16). Mixture of diastereomers. Pale brown solid (1.35 g; 90% yield). Mp 158–159 °C (EtOH). Found: C 87.68; H 7.62; N 4.70. $C_{22}H_{23}N$ requires: C 87.66; H

7.69; N 4.65%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.32–7.07 (m, 9H), 6.51 (br s, 2H), 2.07, 2.05, 2.03, 2.03, 1.86, 1.84 (6s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.0, 142.9, 141.5, 141.4, 140.9, 140.7, 138.6, 138.5, 137.5, 137.4, 136.3, 136.2, 135.4, 135.2, 130.6, 130.4, 130.3, 129.8, 129.7, 129.6, 127.7, 127.0, 126.7, 125.6, 124.6, 114.0, 20.2, 20.0, 19.8, 19.6, 17.5,16.4. MS (EI) *m/z*: (%) 301 [M^+] (100), 286 (15), 271(15). IR (neat) ν (cm^{-1}): 3416, 3410 (NH_2).

6. Synthesis of diiodoisatins 10

10 were prepared, starting from diiodoanilines (**8**, 5 mmol), as described in the literature (V. Lisowski, M. Robba and S. Rault, *J. Org. Chem.*, 2000, **65**, 4193.) The intermediates *N*-(2,5-diiodo-3-methylphenyl)hydroxyiminoacetamide (**9a**), MS (EI) *m/z*: (%) 385 [M^+ - CH_2=NOH] (40), 359 (100), 232 (15), 105 (15) and *N*-(2,5-diiodo-3,4-dimethylphenyl)hydroxyiminoacetamide (**9b**), MS (EI) *m/z*: (%) 399 [M^+ -CH_2=NOH] (35), 373 (100), 246 (15) were converted into **10** upon heating to 35 °C in H_2SO_4 (15 ml) and were used without further purification. At higher temperatures the decomposition of these intermediates was observed.

4,7-Diiodo-5-methylisatin (10a). Red solid (1.60 g, 77% yield). Mp 159 °C (EtOH). Found: C 26.13; H 1.21; N 3.33. $C_9H_5I_2NO_2$ requires: C 26.18; H 1.22; N 3.39%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.65 (br s, 1H), 7.44 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (50 MHz, DMSO-d6): δ = 183.2, 160.6, 156.1, 153.3, 134.6, 119.6, 93.2, 85.9, 28.5. MS (EI) *m/z*: (%) 413 [M^+] (65), 385(100), 258 (25), 230 (20). IR (neat) ν (cm^{-1}): 3298 (NH), 1731 (CO), 1578 (CONH).

4,7-Diiodo-5,6-dimethylisatin (10b). Red solid (0.55 g, 26% yield). Mp 233 °C (EtOH). Found: C 28.18; H 1.61; N 3.31. $C_{10}H_7I_2NO_2$ requires: C 28.13; H 1.65; N 3.28%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.62 (br s, 1H), 2.58 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (50 MHz, DMSO-d6): δ = 183.5, 159.9, 154.5, 149.7, 135.3, 119.7, 101.2, 87.8, 28.7, 25.2. IR (neat) ν (cm^{-1}): 3305 (NH), 1729 (CO), 1576 (CONH).

7. Synthesis of 5,6-dimethyl-4,7-bis(*o*-tolyl)isatin (11b)

11b was prepared from 2,5-bis(*o*-tolyl)-3,4-dimethylaniline (**16**; 1.51 g, 5 mmol), as described in the literature (V. Lisowski, M. Robba and S. Rault, *J. Org. Chem.*, 2000, **65**, 4193).
The intermediate *N*-[2,5-bis(*o*-tolyl)-3,4-dimethylphenyl]hydroxyiminoacetamide (**17**), MS (EI) *m/z*: (%) 327 [M^+- CH_2=NOH] (100), 312 (20), 298 (15), 284 (25) was converted into the title

compound upon heating to 50 °C in $MeSO_3H$ (15 ml) and used without further purification. It was impossible to obtain **11b** using H_2SO_4.

5,6-Dimethyl-4,7-bis(*o*-tolyl)isatin (11b). Mixture of diastereomers. Orange solid (1.58 g; 89% yield). Mp 126–127 °C (EtOH). Found: C 81.03; H 6.00; N 3.93. $C_{24}H_{21}NO_2$ requires: C 81.10; H 5.96; N 3.94%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.34–6.96 (m, 9H), 2.11, 2.09, 2.03, 2.00, 1.99, 1.88 (6s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 181.8, 159.3, 147.4, 145.4, 140.6, 137.0, 136.9, 136.4, 135.6, 135.5, 133.8, 131.5, 131.1, 130.2, 129.9, 129.8, 129.2, 128.4, 128.3, 127.0, 126.1, 125.0, 113.9, 19.8, 19.7, 18.8, 16.1. MS (EI) *m/z*: (%) 355 [M^+] (55), 340 (15), 327 (15), 312 (100), 297 (25). IR (neat) ν (cm^{-1}): 3312 (NH), 1729 (CO), 1585 (CONH).

8. Synthesis of diarylisatins 11

o-Tolylboronic acid (4.5 mmol, 0.61 g) or 1-naphthylboronic acid (4.5 mmol, 0.77 g) and then CsF (5 mmol, 0.76 g), dissolved in H_2O (8 mL), were added to a stirring mixture of diiodoisatine (**10**, 2 mmol), $Pd(OAc)_2$ (0.4 mmol; 48 mg) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos) as a ligand (0.4 mmol; 0.16 g) in DME (10 mL). The mixture was stirred at reflux until the disappearance of **10**, as monitored by TLC (CH_2Cl_2/EtOAc, 9.8:0.2).The reaction mixture was then poured into CH_2Cl_2-H_2O (100 ml, 1:1). The aqueous layer was separated and extracted with CH_2Cl_2 (100 mL). The combined organic extracts were washed with H_2O (100 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue, purified in a chromatography column (CH_2Cl_2/EtOAc, 98:2), afforded pure **11**.

5-Methyl-4,7-bis(*o*-tolyl)isatin (11a). Red solid (0.58 g, 85% yield). Mp 79–80 °C (EtOH). Found: C 80.99; H 5.55; N 4.13. $C_{23}H_{19}NO_2$ requires: C 80.92; H 5.61; N 4.10%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.34–7.10 (m, 8H), 7.02 (br s, 1H), 6.82 (s, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 181.6, 159.2, 148.3, 147.4, 141.5, 136.9, 136.7, 136.1, 133.0, 131.2, 130.3, 129.7, 129.1, 128.7, 127.5, 127.1, 125.8, 124.4, 114.0, 21.0, 19.9, 19.7. MS (EI) *m/z*: (%) 341 [M^+] (85), 326(35), 313 (25), 298 (100), 283 (25), 270 (15), 254 (40). IR (neat) ν (cm^{-1}): 3313 (NH), 1727 (CO), 1574 (CONH).

5,6-Dimethyl-4,7-bis(*o*-tolyl)isatin (11b). Orange solid (0.20 g, 28%).
11b was also prepared as reported above for the synthesis of **15**. We obtained 0.62 g (87% yield).

5,6-Dimethyl-4,7-bis(1-naphthyl)isatin (11c). Mixture of diastereomers.Red waxy solid (0.25 g; 29% yield). Found: C 84.24; H 4.94; N 3.31. $C_{30}H_{21}NO_2$ requires: C 84.29; H 4.95; N 3.28%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98–7.90 (m, 4H), 7.62–7.28 (m, 10H), 6.87 (br s, 1H), 2.05 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 181.8, 159.1, 148.2, 146.6, 137.8, 137.6, 134.6, 134.2, 133.9, 133.8, 133.6, 132.5, 132.0, 131.8, 131.7, 129.5, 129.1, 128.7, 128.4, 128.1, 127.5, 127.1, 126.9, 126.7, 126.6, 126.1, 125.7, 125.4, 125.2, 125.1, 125.0, 124.1, 114.8, 19.2, 16.5. MS (ESI +) *m/z*: 428.26 $(M + H)^+$. IR (neat) ν (cm^{-1}): 3308 (NH), 1726 (CO), 1582(CONH).
11c was also prepared as reported above for the synthesis of **15**. We obtained 0.77 g (89% yield).

9. Synthesis of 2-aminobenzoic acids 12

A 30% hydrogen peroxide aqueous solution (10 mL) and 5% aqueous NaOH solution (10 mL) were slowly added to a stirred solution of isatin (**11**; 2 mmol) in 1,4-dioxane (5 mL) at 50 °C. The reaction mixture was stirred at 80 °C for 30 min and then was taken to rt, while stirring for other 30 min. The reaction mixture was filtered, and the resulting solution was acidified with 1M HCl until pH 3-4; the resulting solid, the virtually pure **12**, was collected by filtration on a Buchner funnel.

2-Amino-4-methyl-3,6-bis(*o*-tolyl)benzoic acid (12a). Mixture (1:1) of two diastereomers. The diastereomer ratio was determined by ^{1}H NMR analysis. In particular, the ratio was deduced by comparing the integration area of the signal centred at 2.13 ppm (pertinent to one of the Me bonded to aromatic rings) of one diastereomer, with the signal centred at 2.11 ppm of the other diastereomer. Pale yellow solid. (0.59 g, 89% yield). Mp 201–202 °C (EtOH). Found: C 79.68; H 6.35; N 4.33. $C_{22}H_{21}NO_2$ requires: C 79.73; H 6.39; N 4.23%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.28–7.09 (m, 8H), 6.35 (s, 1H), 2.13, 2.11, 2.05, 1.84 (4s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.4, 148.3, 143.7, 143.4, 141.3, 137.6, 137.4, 136.5, 135.5, 135.4, 130.9, 130.3, 130.2, 129.6, 128.5, 128.3, 127.1, 126.9, 126.7, 125.2, 121.7, 20.7, 20.3, 20.2, 19.4, 19.3. MS (ESI +) *m/z*: 332.29 $(M + H)^+$. IR (neat) ν (cm^{-1}): 3408, 3403 (NH_2), 2911 (OH), 1702 (CO).

2-Amino-4,5-dimethyl-3,6-bis(*o*-tolyl)benzoic acid (12b). Mixture of diastereomers. Pale yellow solid (0.59 g; 86% yield). Mp 168–171 °C (EtOH). Found: C 79.98; H 6.65; N 4.03. $C_{23}H_{23}NO_2$ requires: C 79.97; H 6.71; N 4.05%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.28–6.95 (m, 8H), 2.03, 2.02, 1.83, 1.71 (4s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.9, 144.7, 141.9, 140.5, 137.6, 136.5, 136.4, 131.2, 130.8, 130.4, 130.3, 129.6, 128.7, 128.6, 128.2, 127.5, 127.1, 125.7, 124.2, 120.8,

20.0, 19.9, 19.6, 19.4, 18.3, 16.5. MS (ESI +) *m/z*: 346.26 $(M + H)^+$. IR (neat) ν (cm^{-1}): 3403, 3401 (NH_2), 2915 (OH), 1704 (CO).

2-Amino-4,5-dimethyl-3,6-bis(1-naphthyl)benzoic acid (12c). Mixture of diastereomers. Pale yellow waxy solid (0.74 g; 89% yield). Found: C 83.51; H 5.50; N 3.33. $C_{29}H_{23}NO_2$ requires: C 83.43; H 5.55; N 3.35%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.91–7.71 (m, 5H), 7.59–7.32 (m, 9H), 1.80 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.4, 145.4, 145.3, 141.3, 140.7, 140.4, 136.0, 134.4, 133.5, 132.8, 132.2, 128.7, 128.5, 128.4, 128.3, 127.2, 126.9, 126.8, 126.6, 126.4, 126.3, 126.1, 125.7, 125.6, 125.5, 125.4, 18.7, 17.1. MS (ESI +) *m/z*: 418.46 $(M + H)^+$. IR (neat) ν (cm^{-1}): 3407, 3404 (NH_2), 2911 (OH), 1702 (CO).

10. Synthesis of 1,3-benzodithioles 13

3-Methylbutyl nitrite (4.8 mmol, 0.56 g), 3-methylbutan-1-ol (4 mmol, 0.35 g) and CS_2 (33.2 mmol, 2.52 g) were dissolved in 1,2-dichloroethane (40 mL) and heated to reflux at 82 °C. 2-Amino-benzoic acid (**12**; 2 mmol) dissolved in 1,4-dioxane (12 mL) was added dropwise to the previously prepared mixture. The resulting mixture was stirred first at reflux for 45 min and then at rt for 1 h. The reaction mixture was poured into Et_2O/H_2O (100 mL, 1:1). The aqueous layer was separated and extracted with Et_2O (100 mL). The combined organic extracts were washed with H_2O (100 mL) and a saturated solution of Na_2CO_3 (50 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue, purified by column chromatography (PE/Et_2O 95:5), afforded pure **13**.

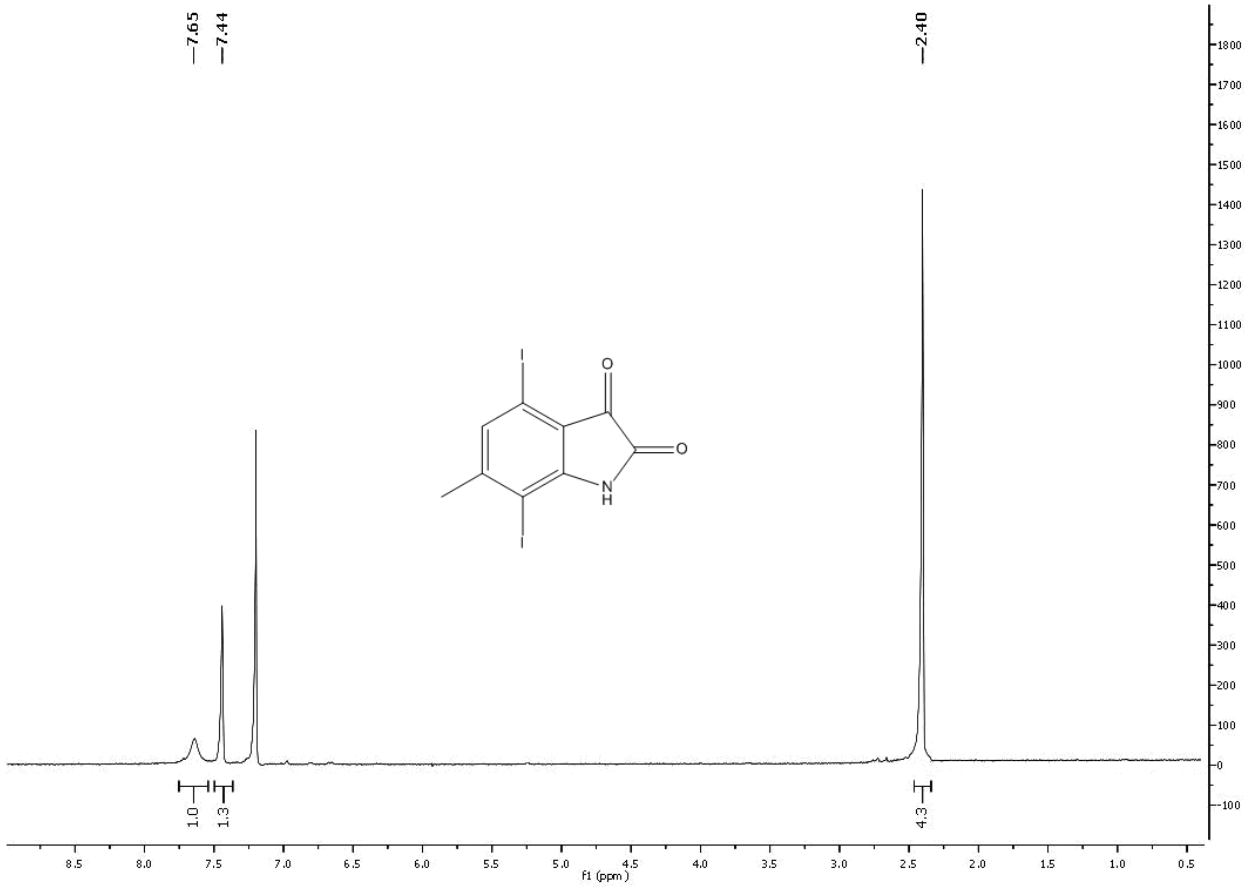
5-Methyl-2-(3-methylbutoxy)-4,7-bis(*o*-tolyl)-1,3-benzodithiole (13a). Mixture of two diastereomers. The diastereomer ratio was determined by ^{1}H NMR analysis. In particular, the ratio was deduced by comparing the integration area of the signal centred at 6.55 ppm (pertinent to the H of the C bound to two S) of one diastereomer, with the signal centred at 6.53 ppm of the other diastereomer. Viscous pale yellow oil (0.75 g, 86% yield). Found: C 74.57; H 6.95; S 14.83. $C_{27}H_{30}OS_2$ requires: C 74.61; H 6.96; S 14.75%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.29–7.13 (m, 8H), 6.84 (s, 1H), 6.55 and 6.53 (2s, 1H), 3.37 (t, J = 6.7 Hz, 2H), 2.24–1.94 (m, 9H), 1.67–1.37 (m, 1H), 1.33–1.27 (m, 2H), 0.79–0.74 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.8, 141.1, 140.3, 136.2, 135.7, 135.6, 134.9, 134.8, 134.3, 133.6, 133.5, 130.5, 130.4, 129.3, 129.1, 129.0, 128.9, 128.6, 128.3, 128.2, 126.5. 126.0, 88.6, 88.5, 48.8, 38.8, 37.9, 25.3, 25.1, 24.9, 22.6, 20.2, 20.0, 19.5. MS (ESI +) *m/z*: 435.29 $(M + H)^+$.

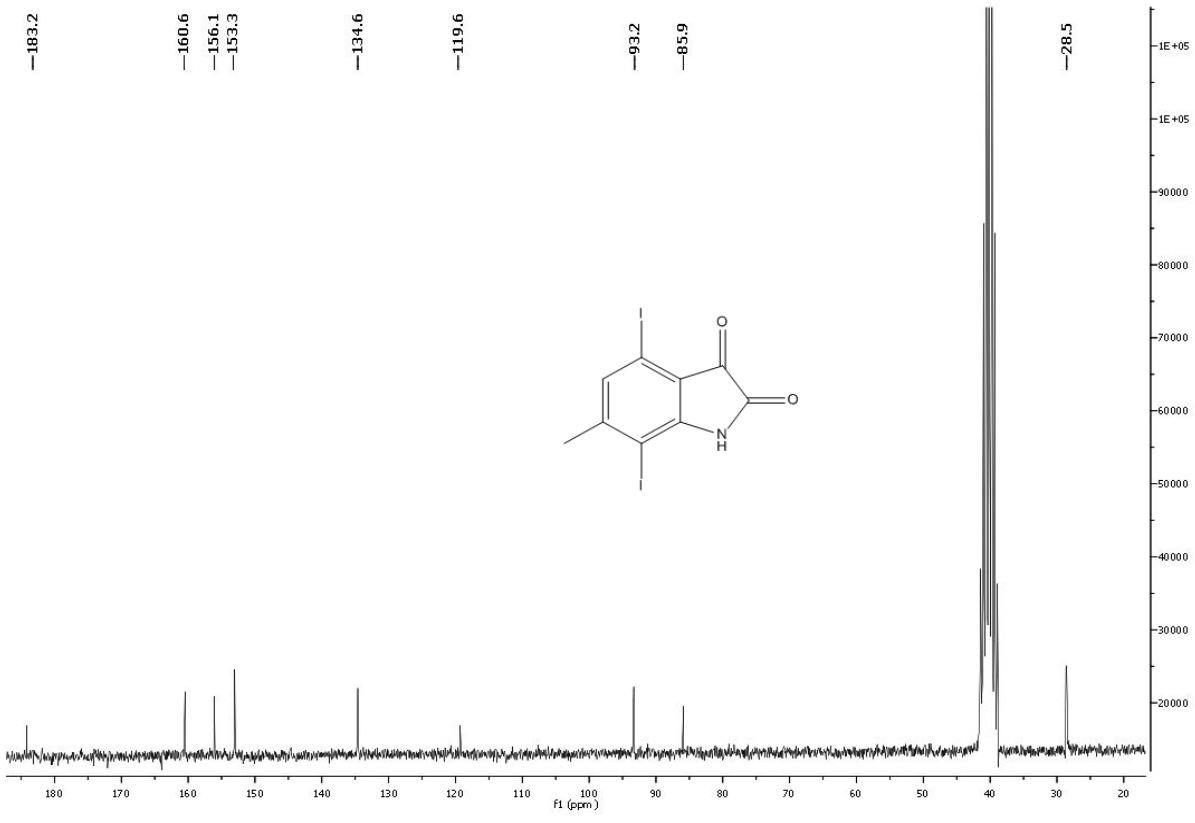
5,6-Dimethyl-2-(3-methylbutoxy)-4,7-bis(*o*-tolyl)-1,3-benzodithiole (13b). Complex mixture of diastereomers. Viscous pale yellow oil (0.78 g; 87% yield). Found: C 74.99; H 7.13; S 14.32. $C_{28}H_{32}OS_2$ requires: C 74.95; H 7.19; S 14.29%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.29–7.22 and 7.08–7.04 (2m, 8H), 6.48 and 6.47 (2s, 1H), 3.40–3.32 (m, 2H), 2.12, 2.10, 2.04, 2.02, 1.89 (5s, 12H), 1.58–1.41 (m, 1H), 1.38–1.29 (m, 2H), 0.77–0.73 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.4, 136.3, 136.2, 135.9, 135.7, 134.5, 134.4, 134.1, 134.0, 132.6, 132.5, 130.5, 130.3, 130.1, 129.5, 129.2, 129.1, 128.9, 128.2, 127.4, 128.2, 126.6. 126.2, 125.8, 88.3, 88.2, 88.0, 41.6, 39.1, 38.1, 37.7, 25.5, 25.3, 25.2, 24.9, 22.9, 22.8, 20.1, 19.9, 19.7, 19.5, 17.1. MS (EI) *m/z*: (%) 377 [M^+-71 (C_5H_{11})] (100). MS (ESI +) *m/z*: 449.51 $(M + H)^+$.

5,6-Dimethyl-2-(3-methylbutoxy)-4,7-bis(1-naphthyl)-1,3-benzodithiole (13c). Complex mixture of diastereomers. Viscous pale yellow oil (0.90 g; 87% yield) Found: C 78.45; H 6.09; S 12.35. $C_{34}H_{32}OS_2$ requires: C 78.42; H 6.19; S 12.31%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.92–7.90 (m, 4H), 7.56–7.38 (2m, 10H), 6.45, 6.41 and 6.37 (3s, 1H) 3.51–3.25 (m, 2H), 1.94 (s, 3H), 1.93 (s, 3H), 1.56–1.14 (m, 3H), 0.89–0.71 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.4, 139.2, 135.1, 135.0, 134.9, 133.9, 133.8, 133.6, 133.5, 133.2, 131.3, 130.9, 128.6, 128.5, 128.2, 128.1, 126.8, 126.7, 126.4, 126.1, 125.7, 125.6, 125.4, 125.3, 125.1, 88.3, 87.8, 87.4, 37.7, 37.5, 28.5, 24.9, 22.5, 17.2. MS (ESI +) *m/z*: 521.31 $(M + H)^+$.

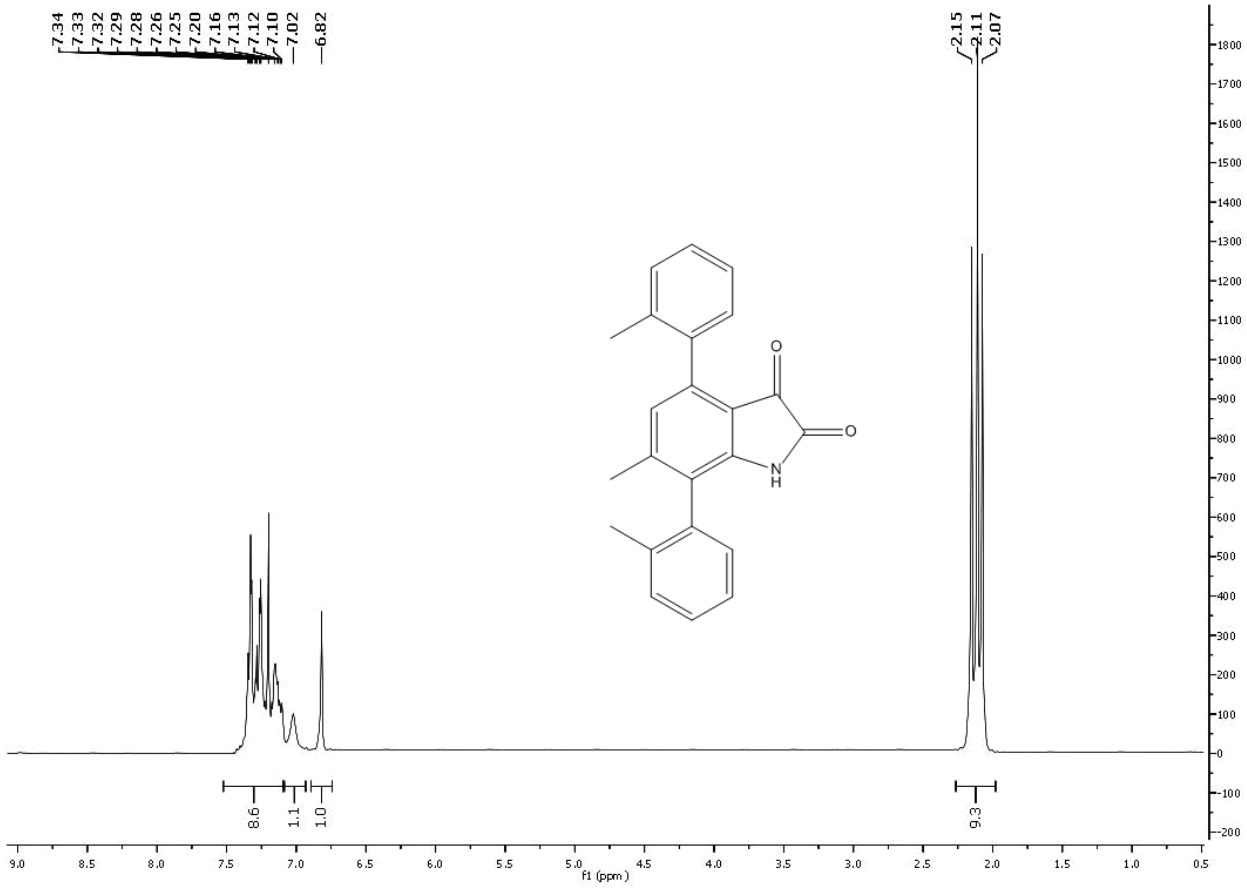
11. ^{1}H NMR and ^{13}C NMR spectra of unknown products.

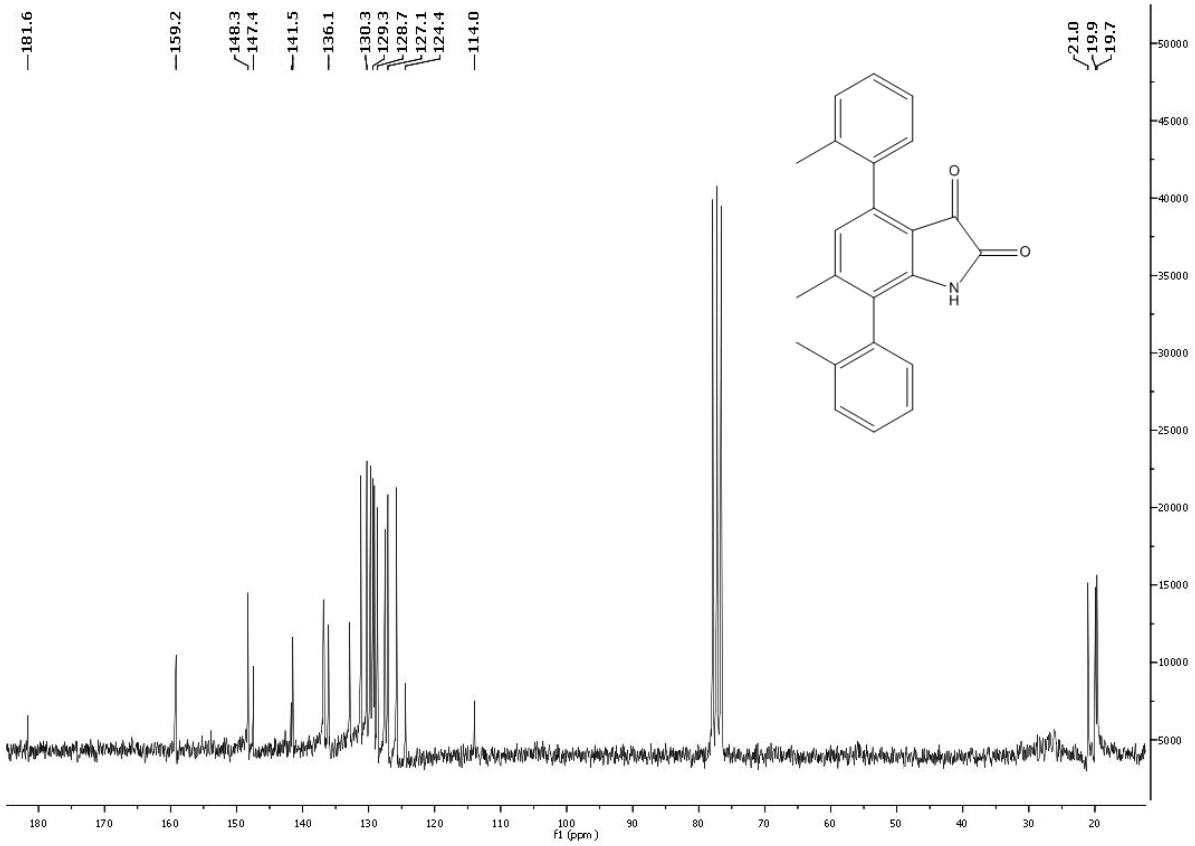
11.1 4,7-Diiodo-5-methylsatin (10a)



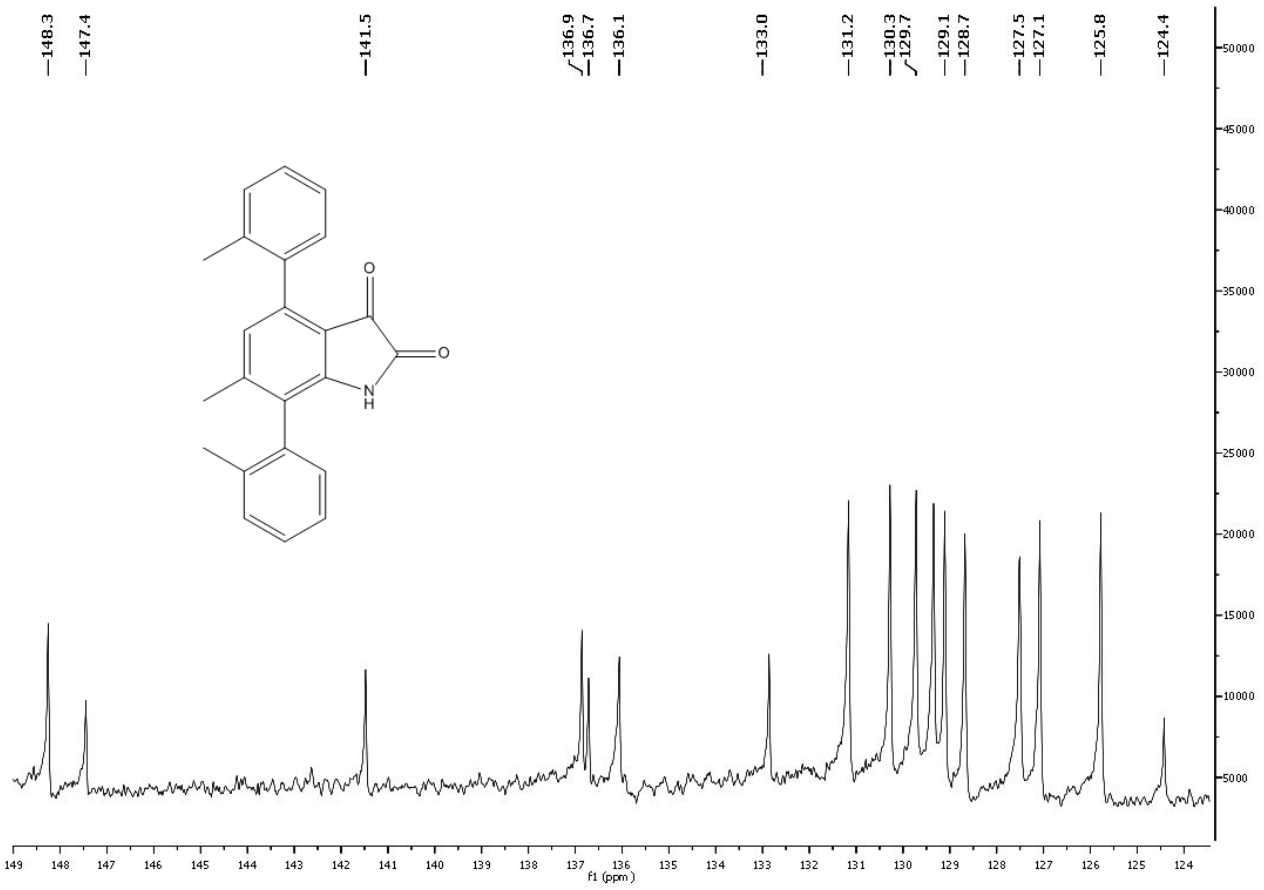


11.2 5-Methyl-4,7-bis(*o*-tolyl)isatin (11a)

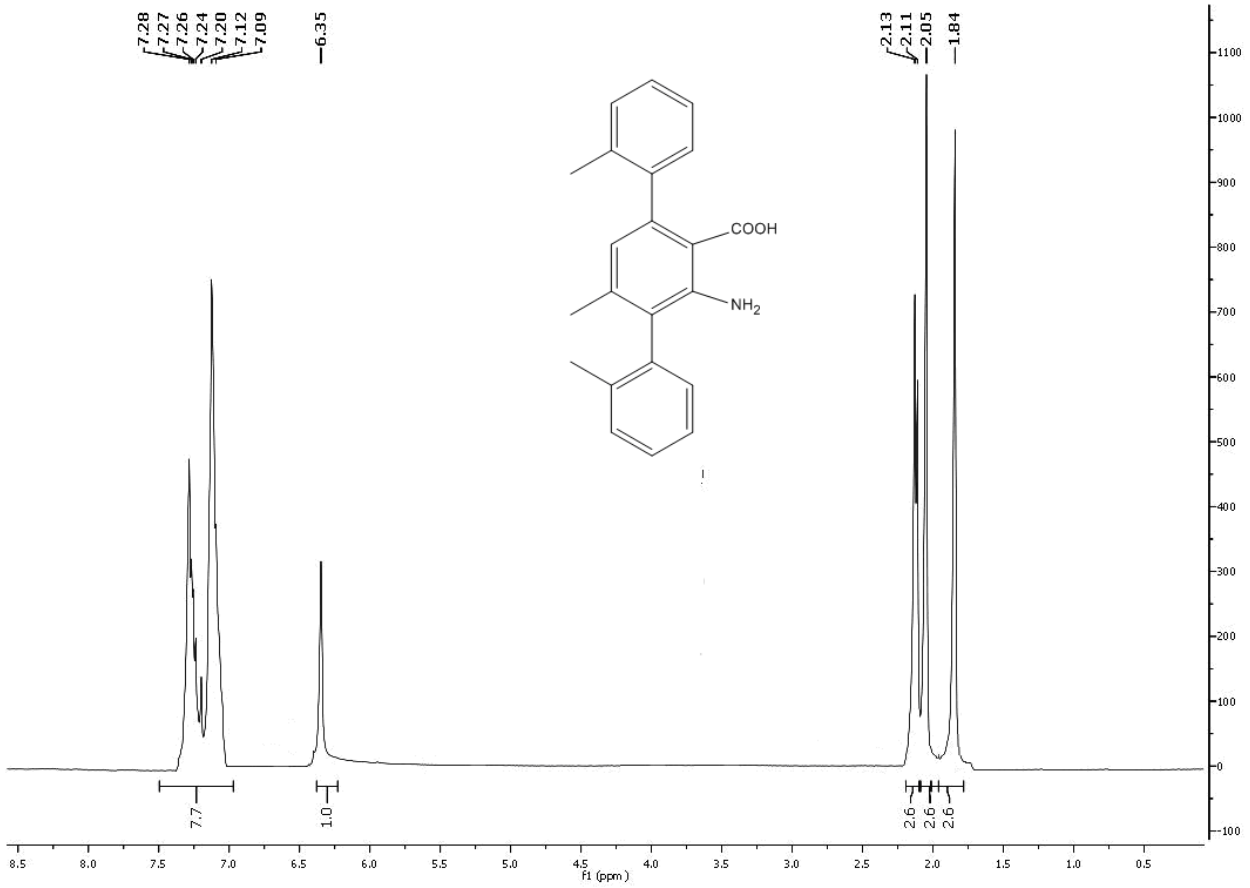


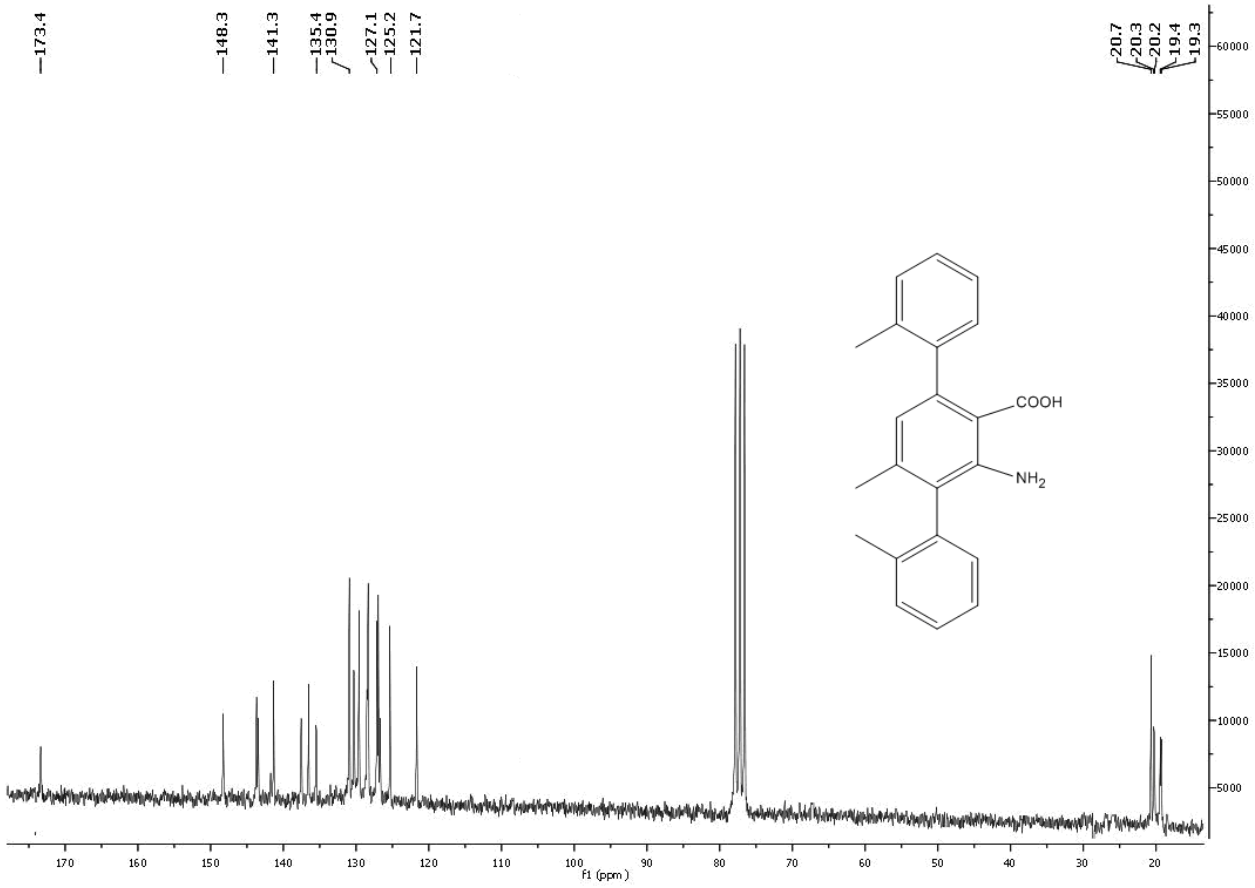


Expansion between 149-124 ppm

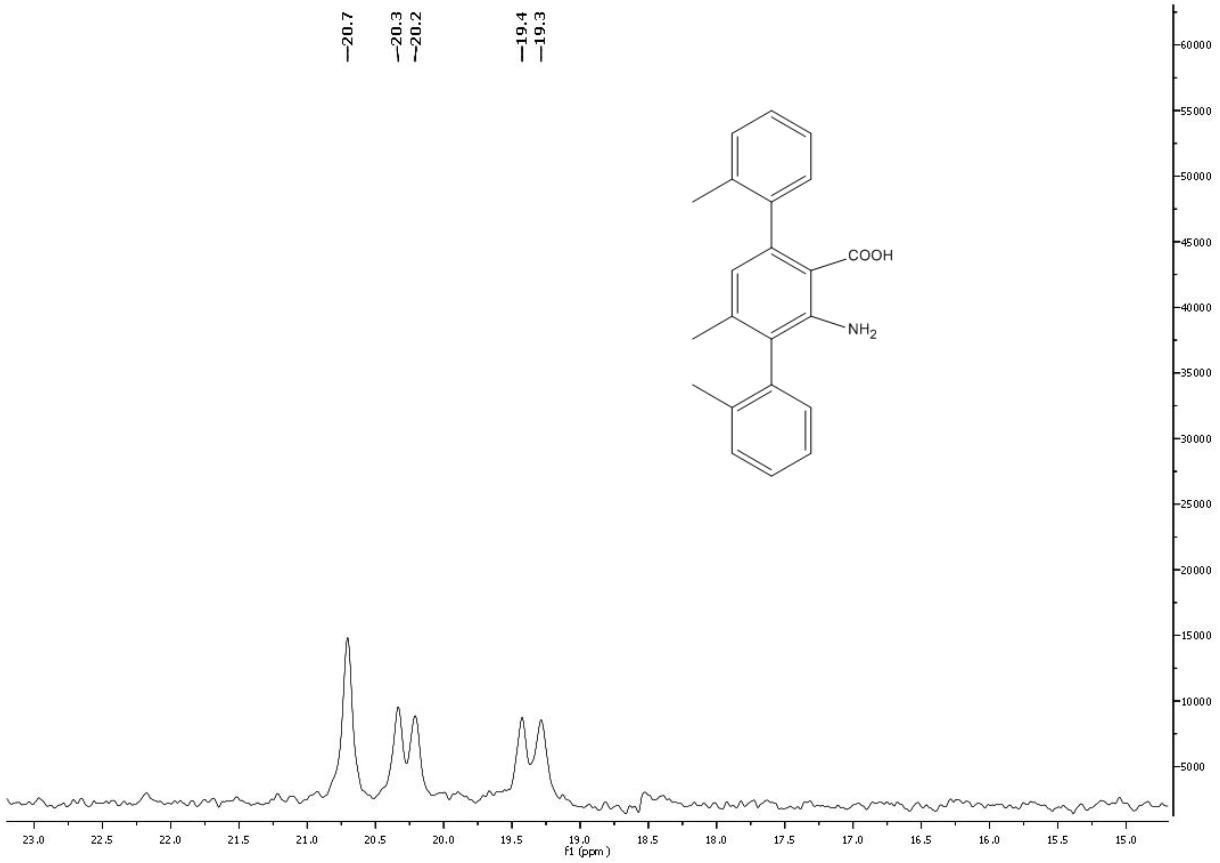


11.3 2-Amino-4-methyl-3,6-bis(*o*-toliyl)benzoic acid (12a)

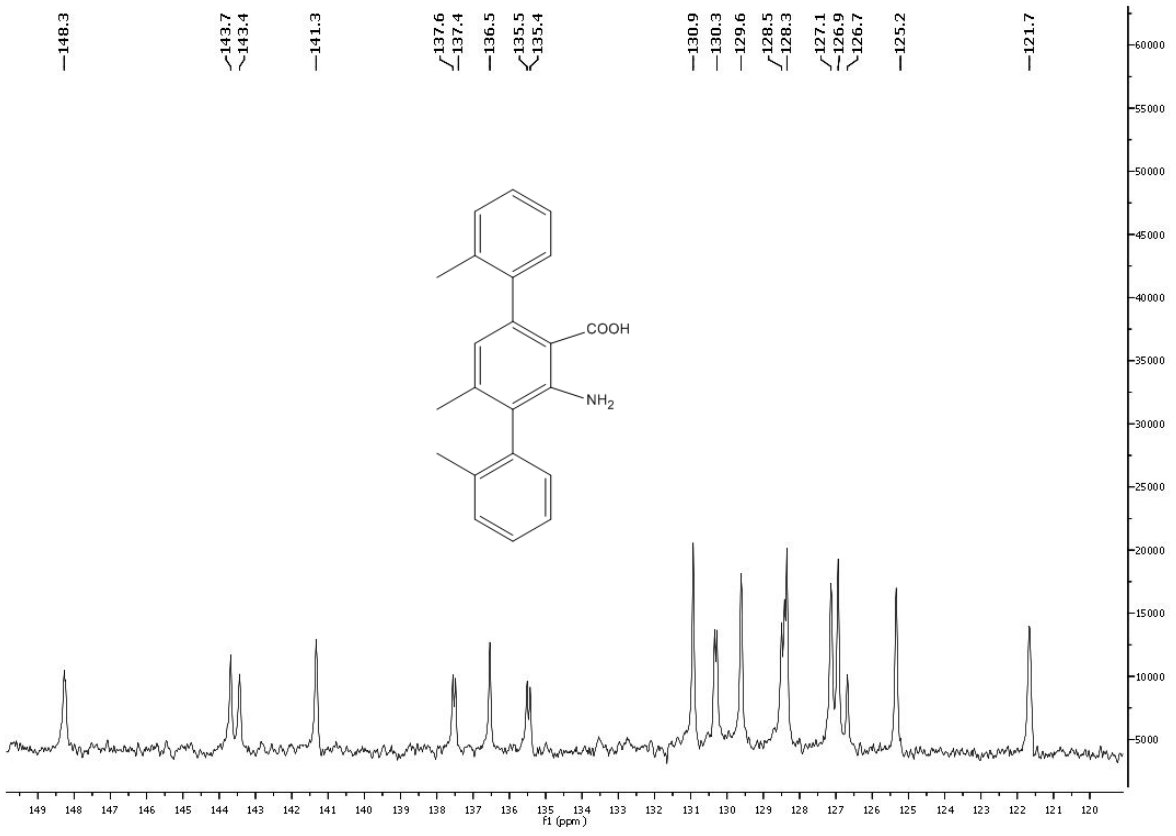




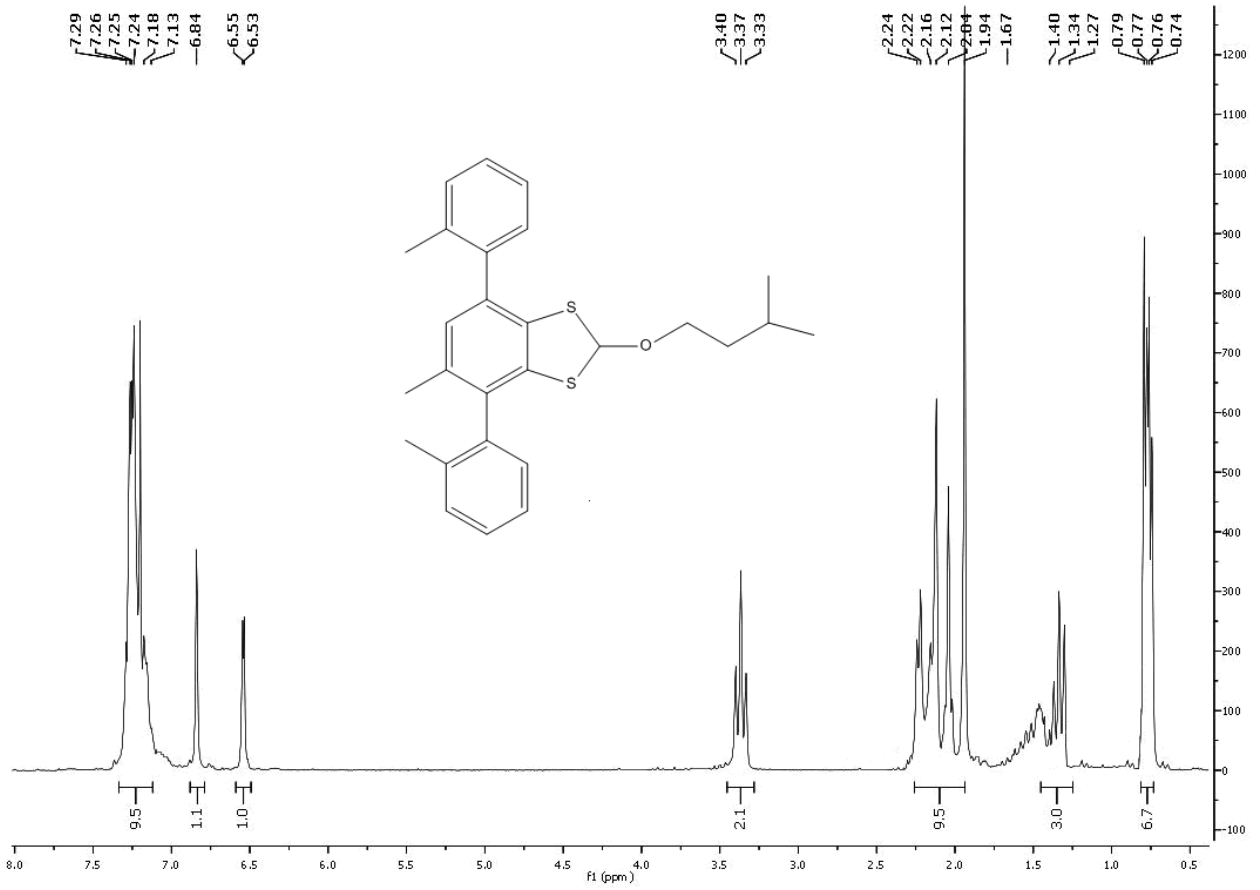
Expansion between 23-15 ppm

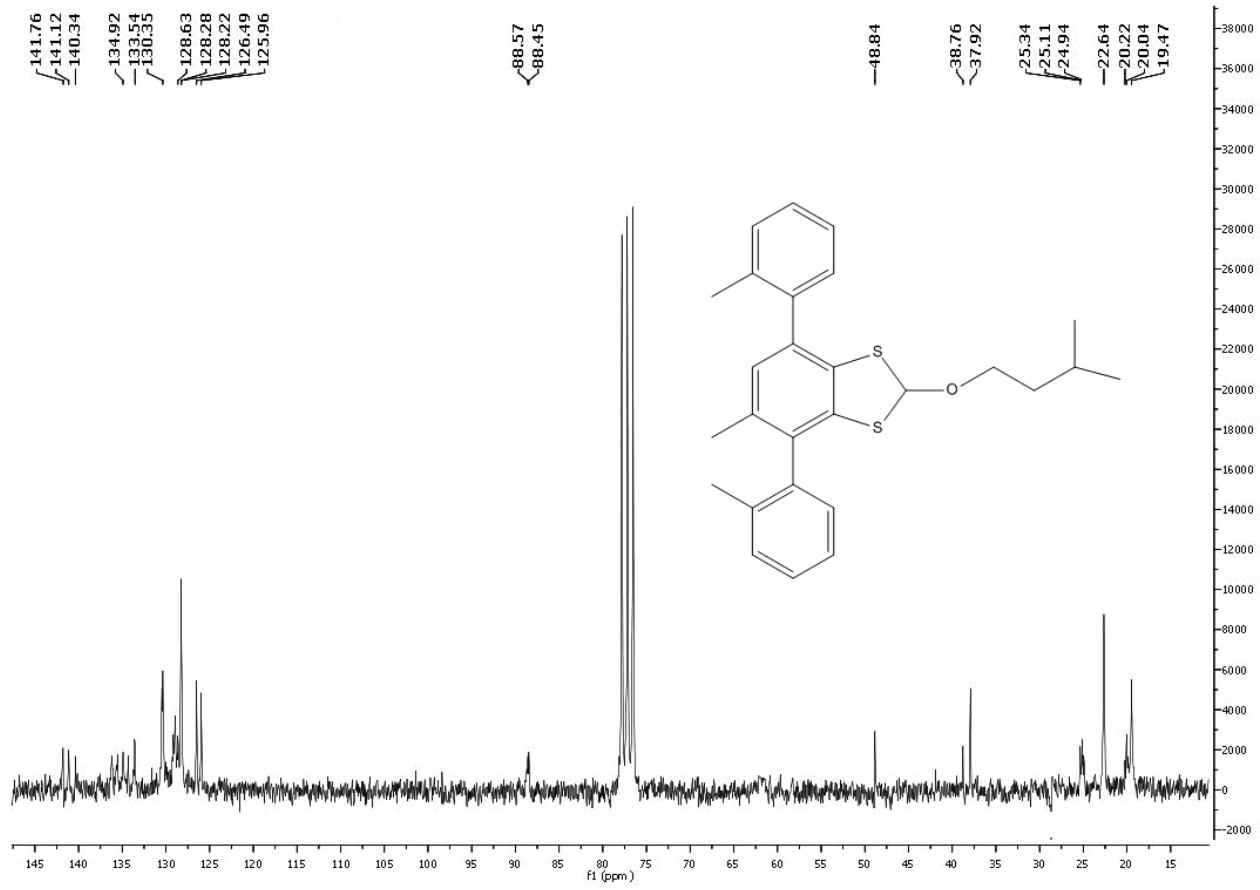


Expansion between 149-120 ppm

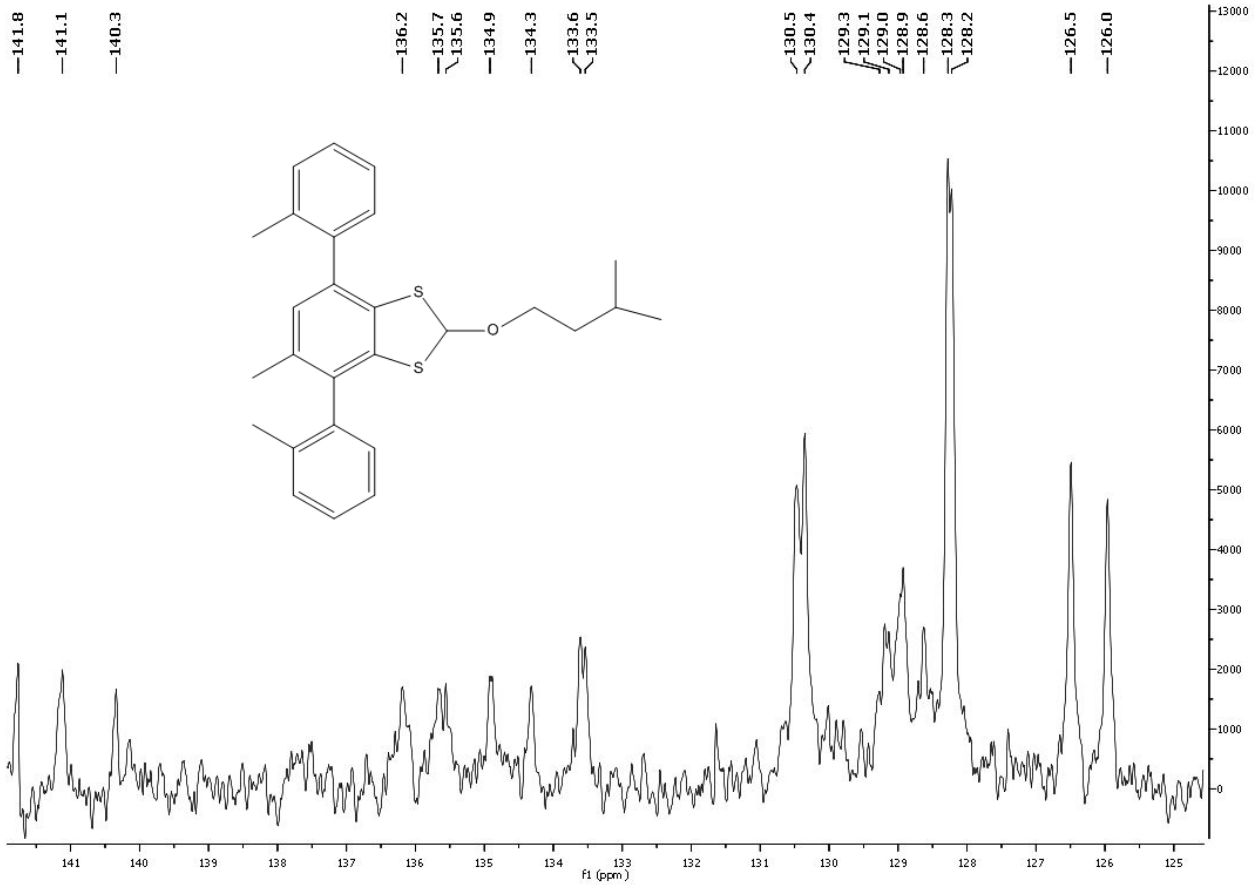


11.4 5-Methyl-2-(3-methylbutoxy)-4,7-bis(*o*-tolyl)-1,3-benzodithiole (13a)

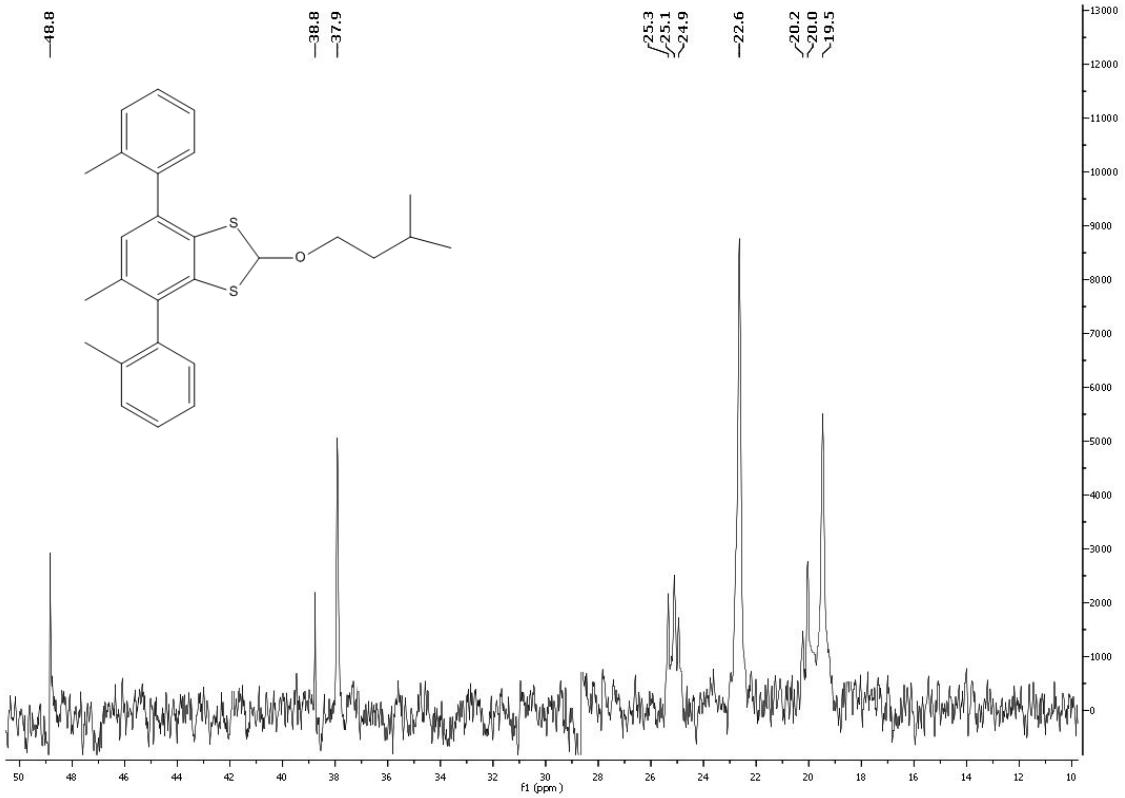




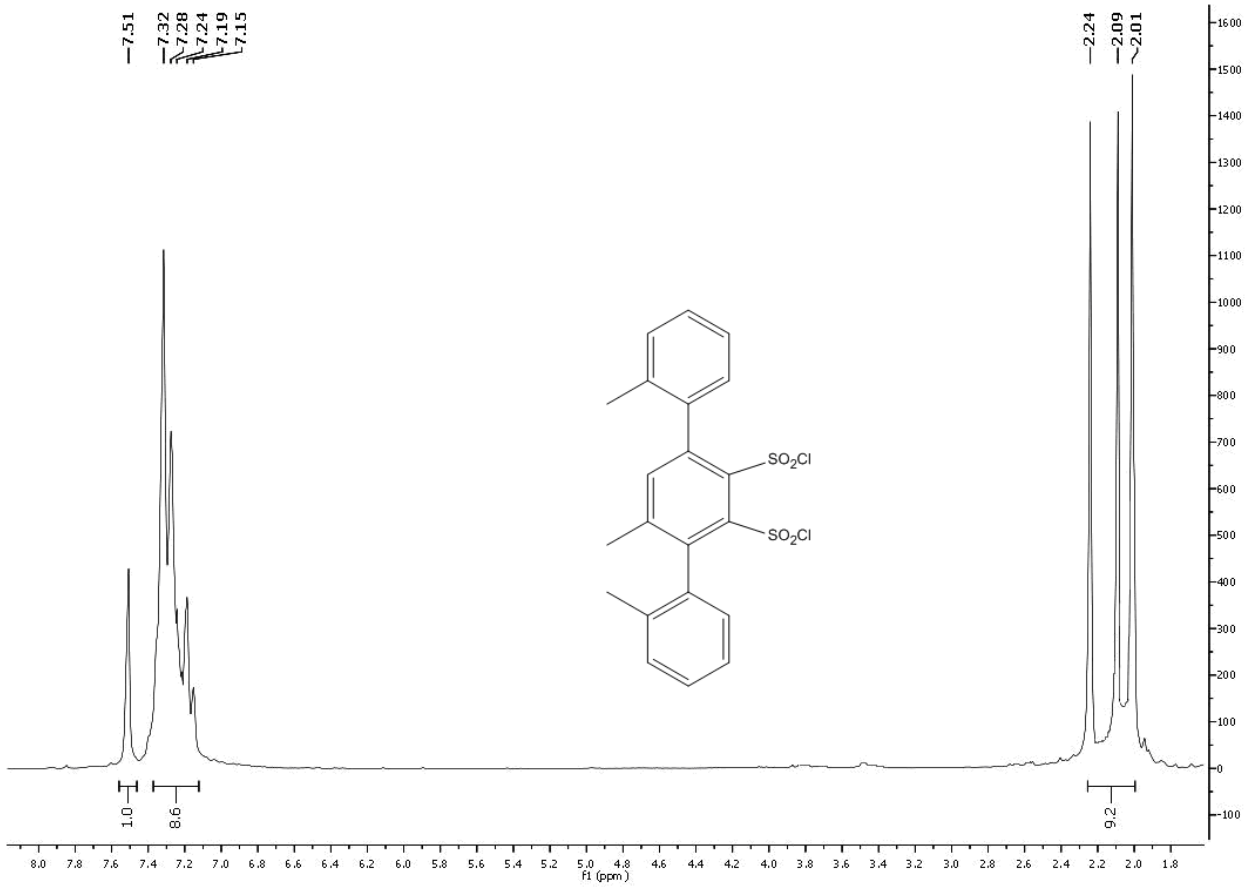
Expansion between 142-125 ppm

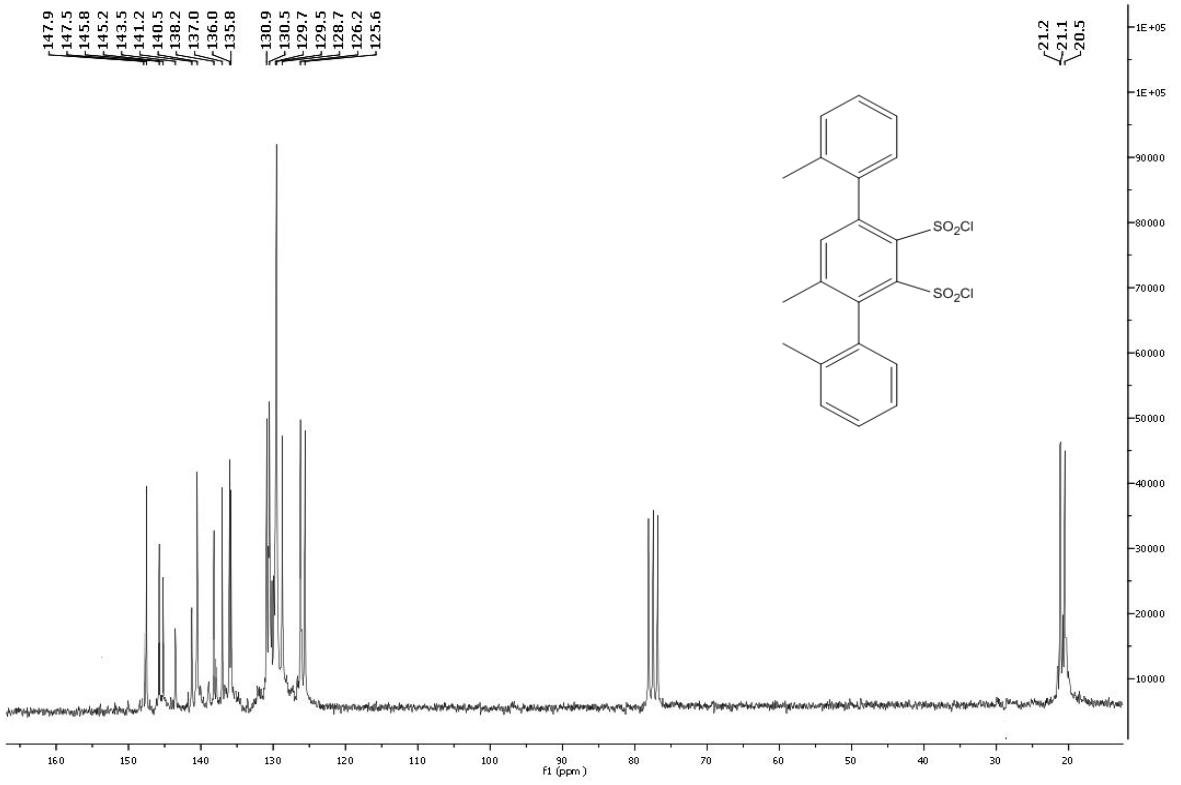


Expansion between 50-10 ppm

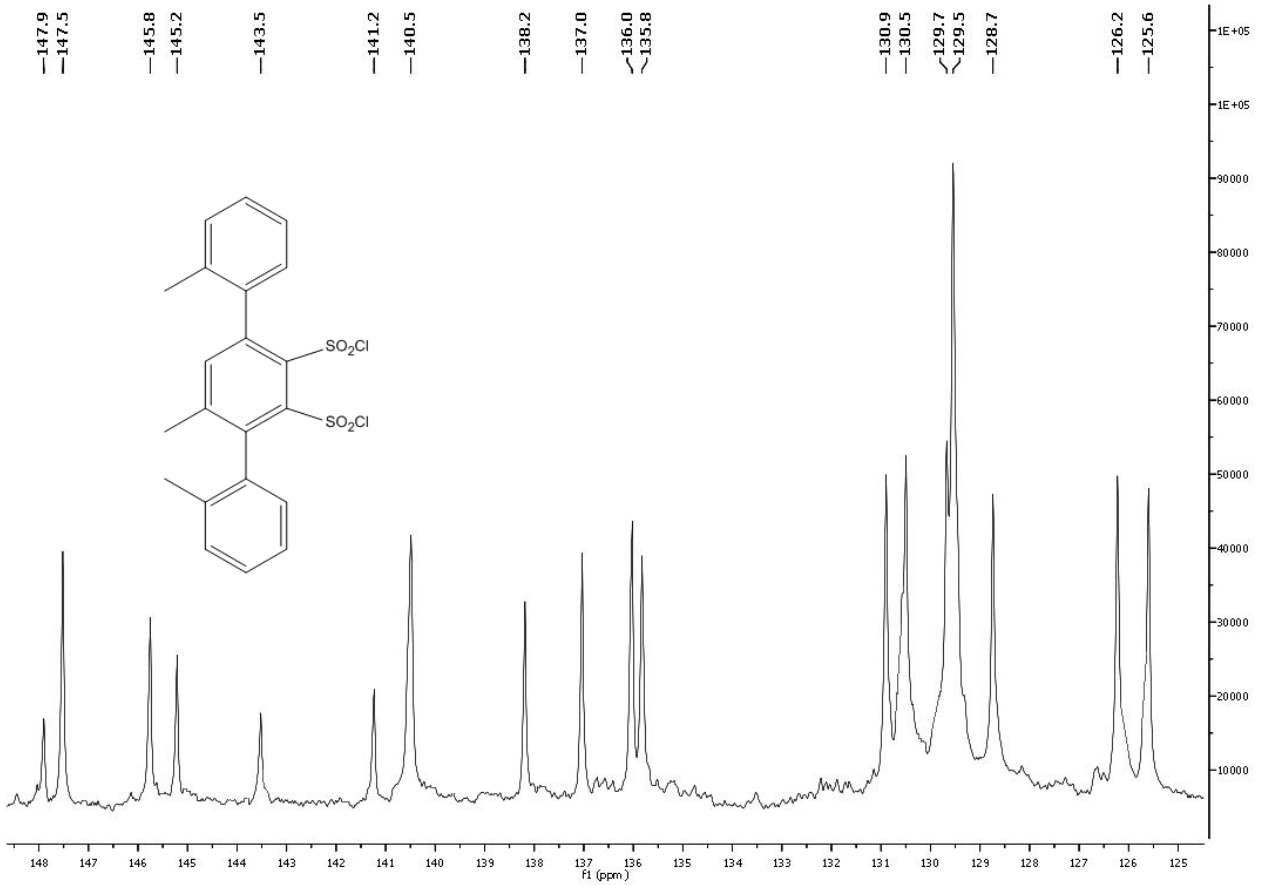


11.5 4-Methyl-3,6-bis(*o*-tolyl)-1,2-benzenedisulfonyl chloride (racemic mixture; 14a)

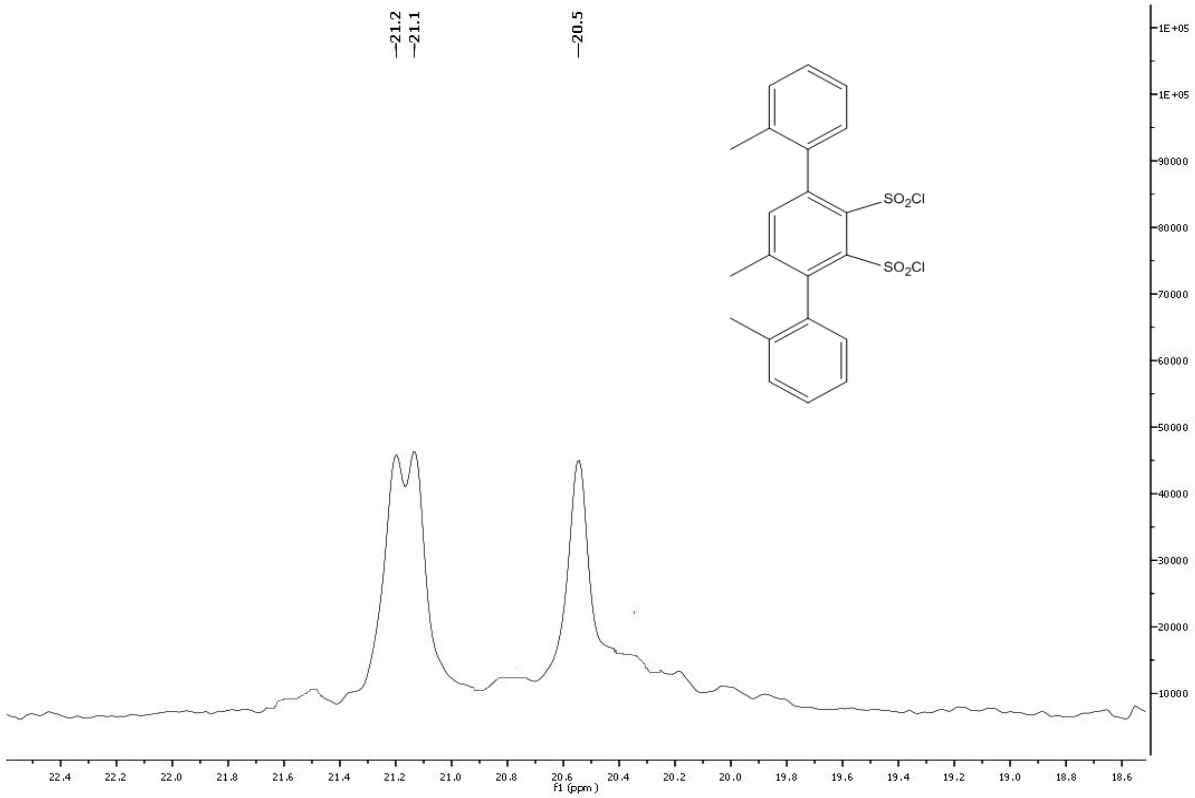




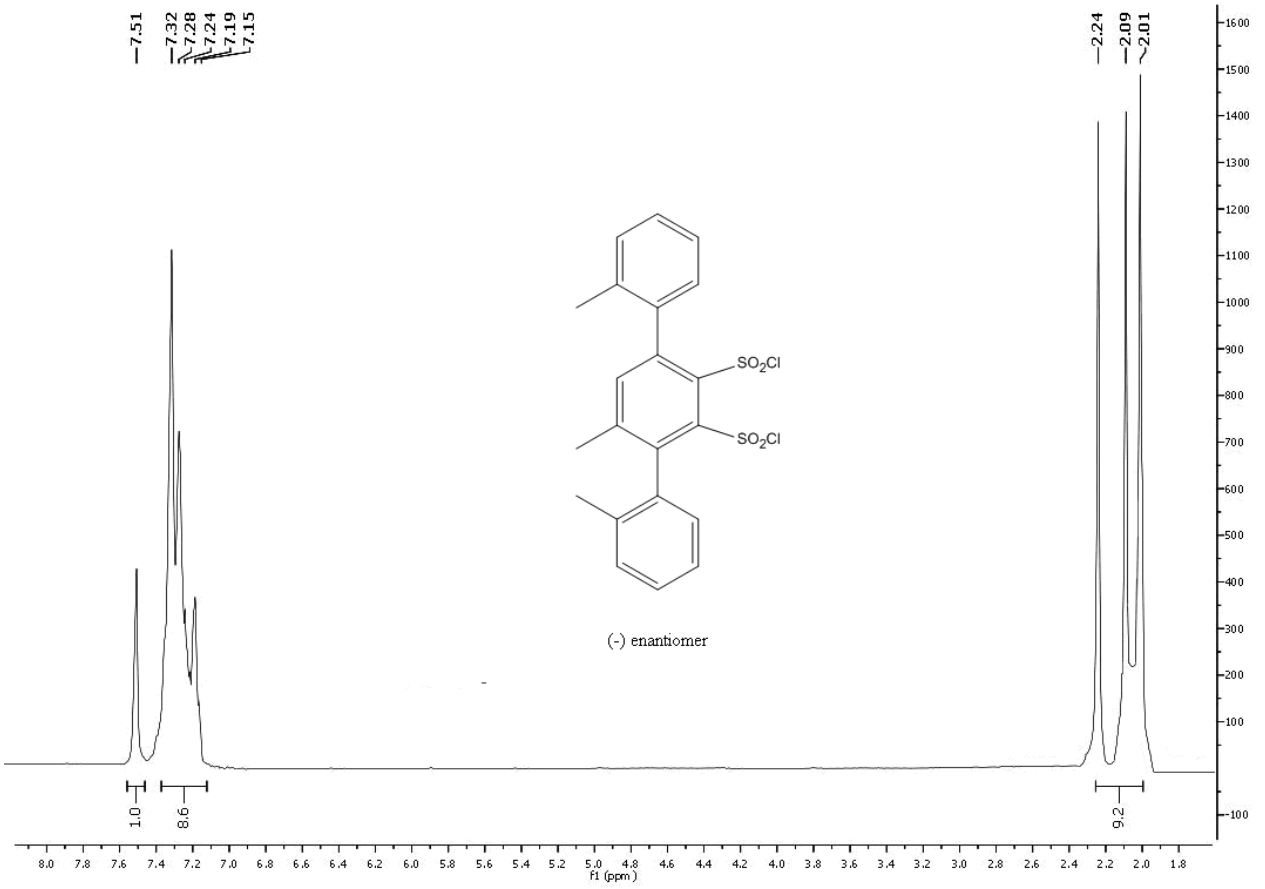
Expansion between 148-124 ppm

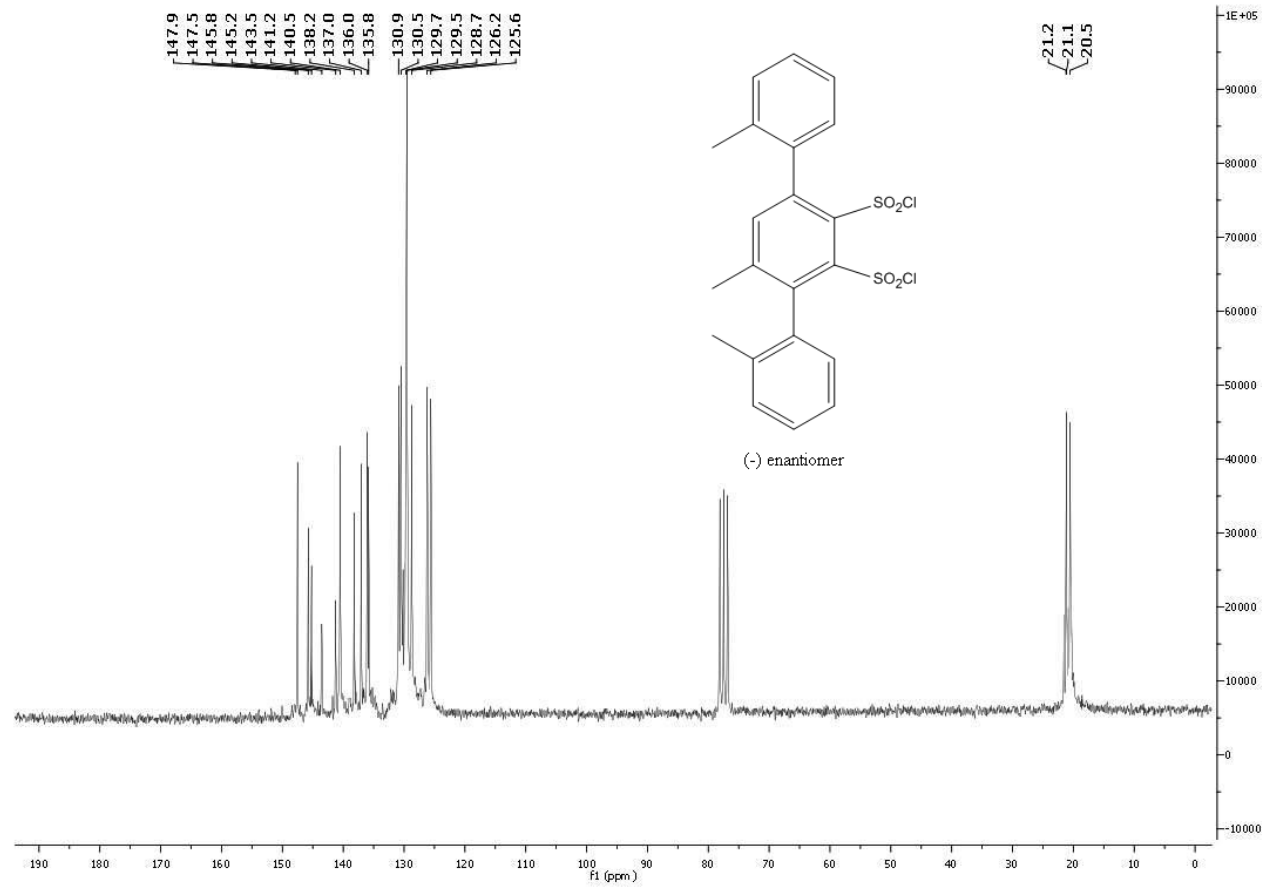


Expansion between 23-18 ppm

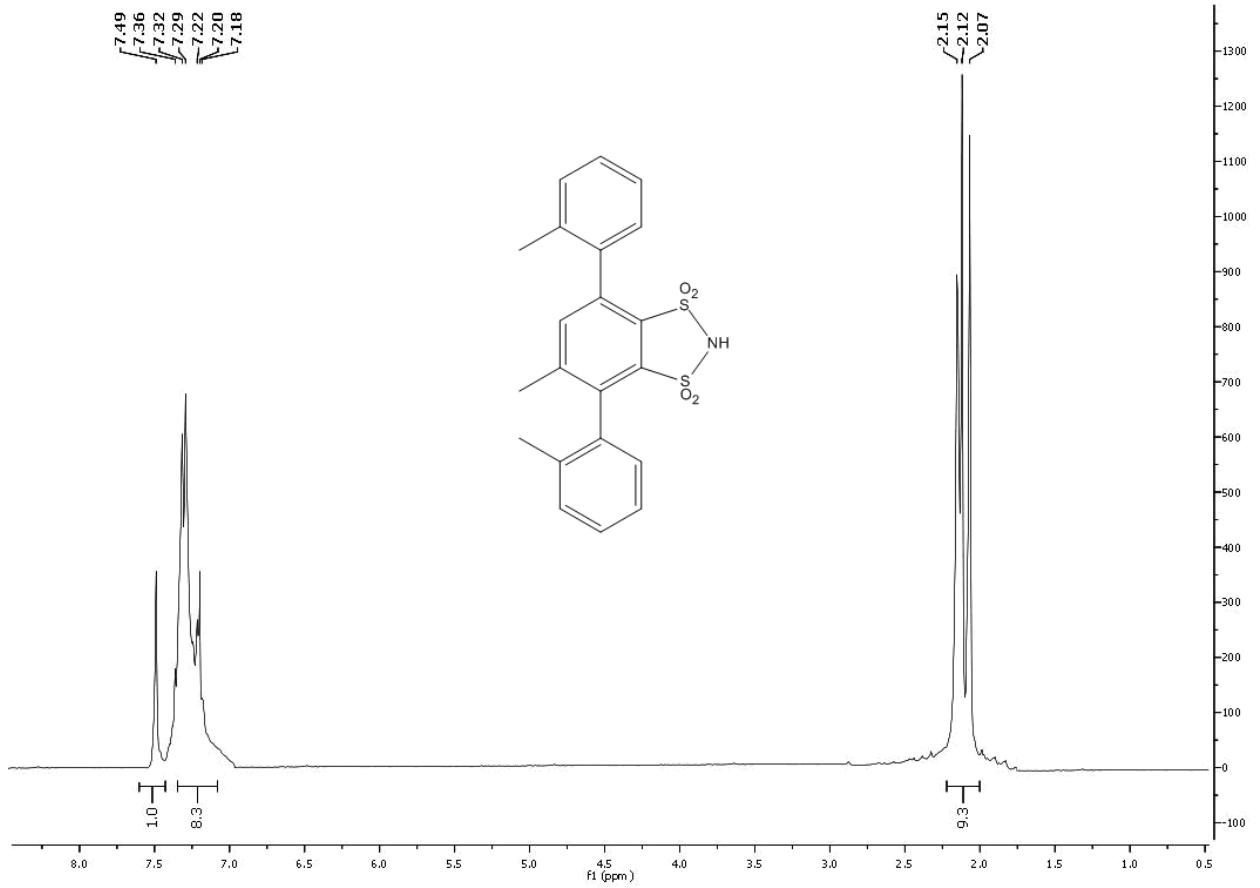


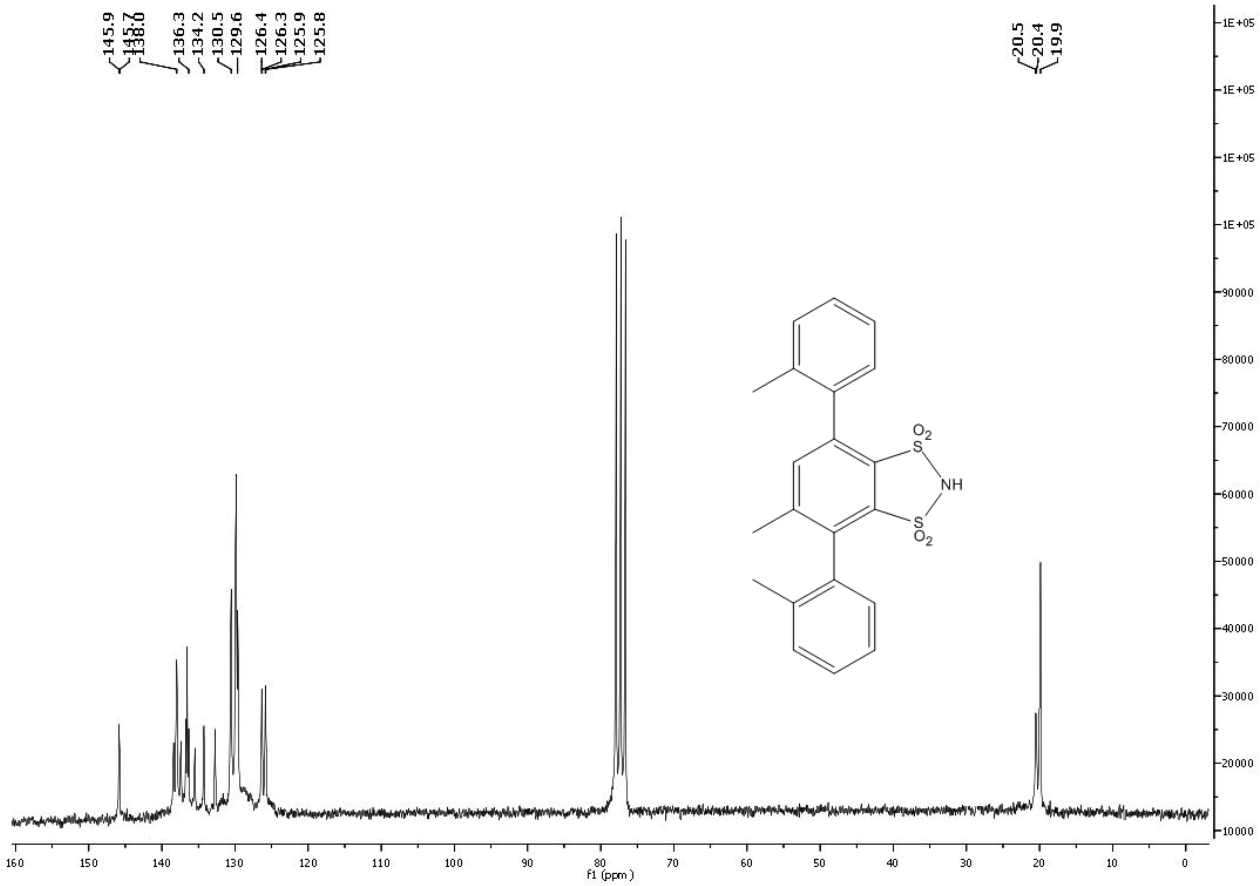
11.6 (-) 4-Methyl-3,6-bis(*o*-tolyl)-1,2-benzenedisulfonyl chloride (14a)



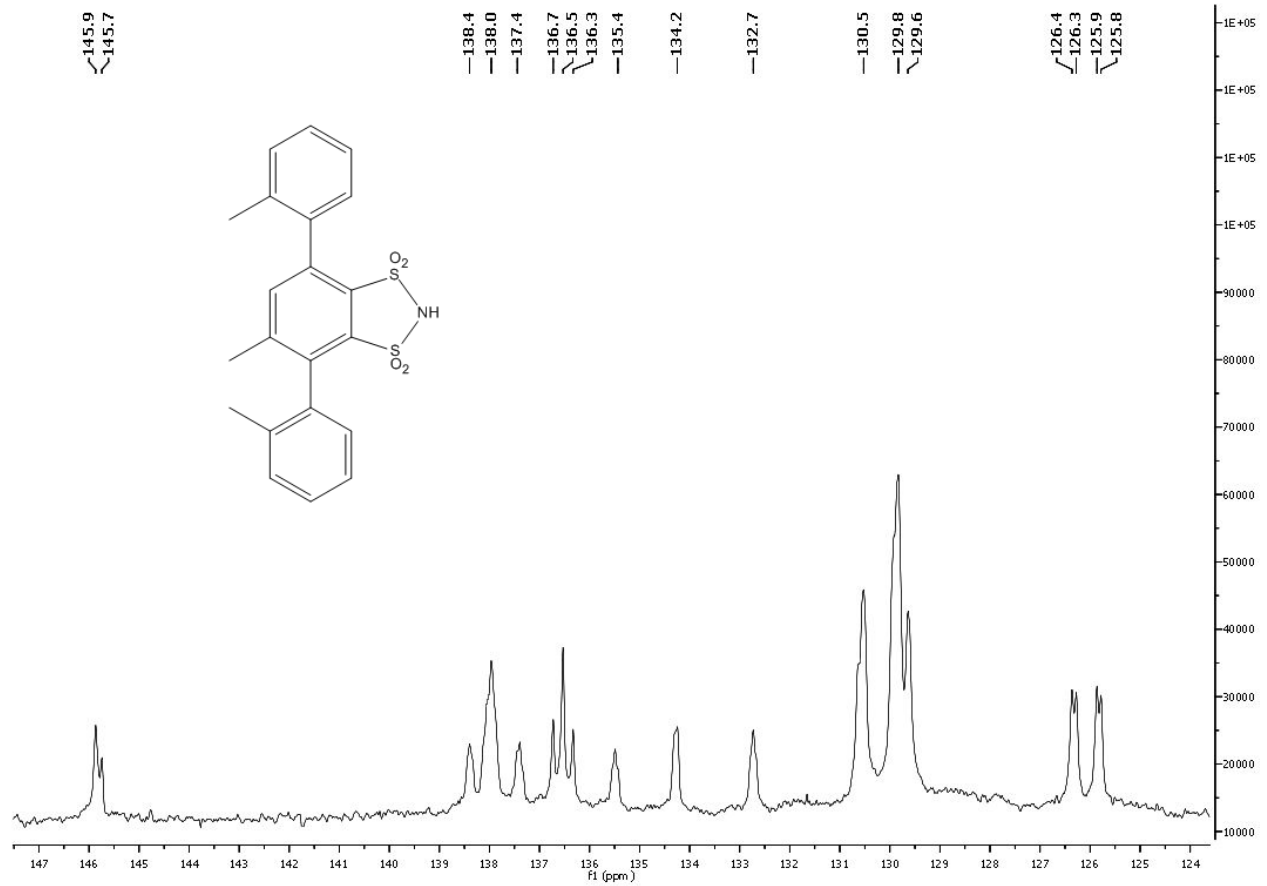


11.7 4-Methyl- 3,6-bis(*o*-tolyl)-1,2-benzenedisulfonimide (3a); racemic mixture

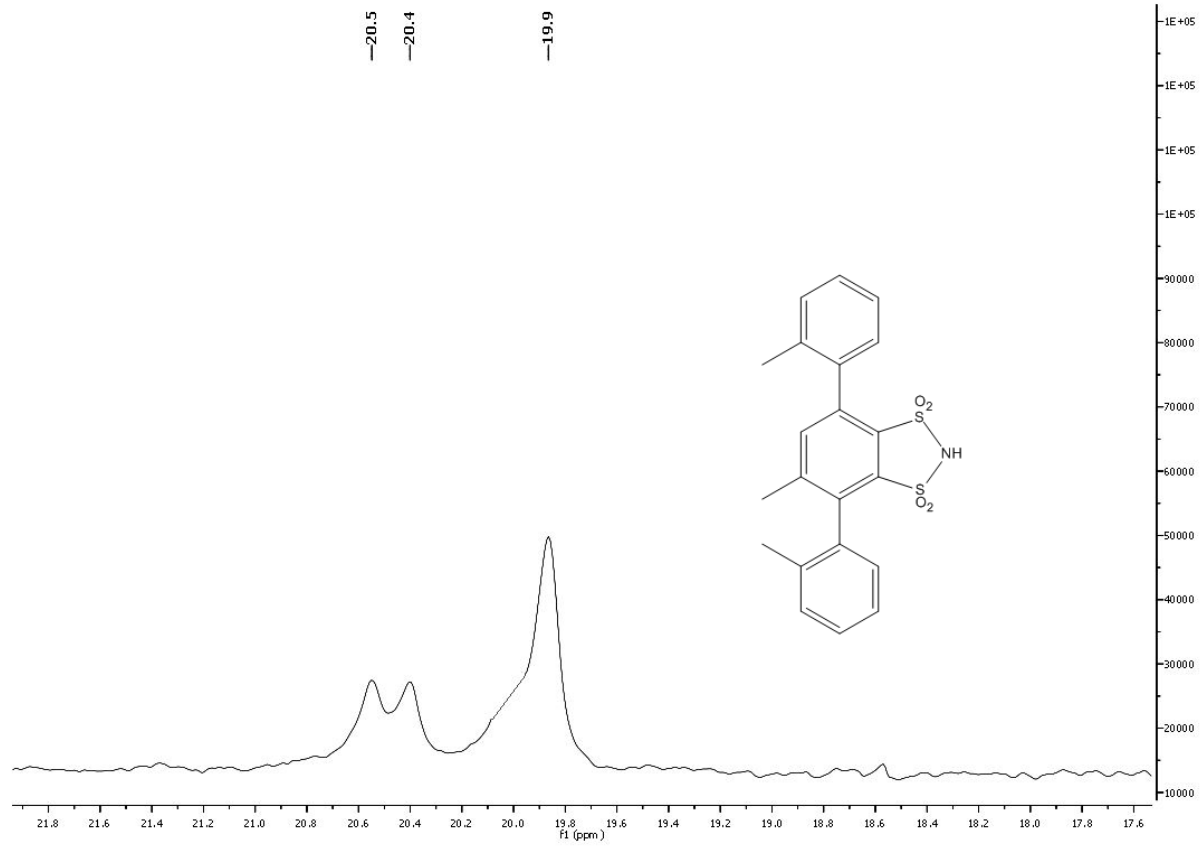




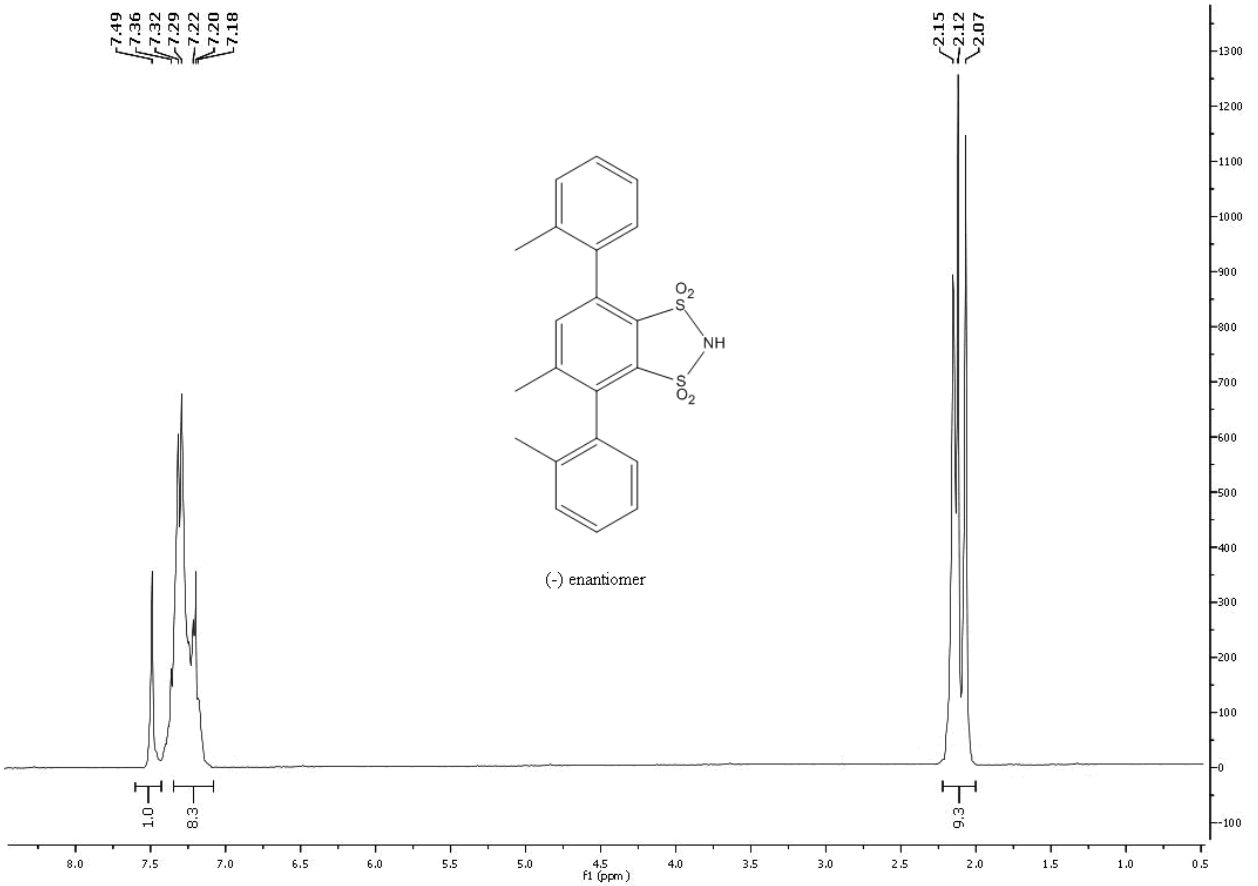
Expansion between 148-124 ppm

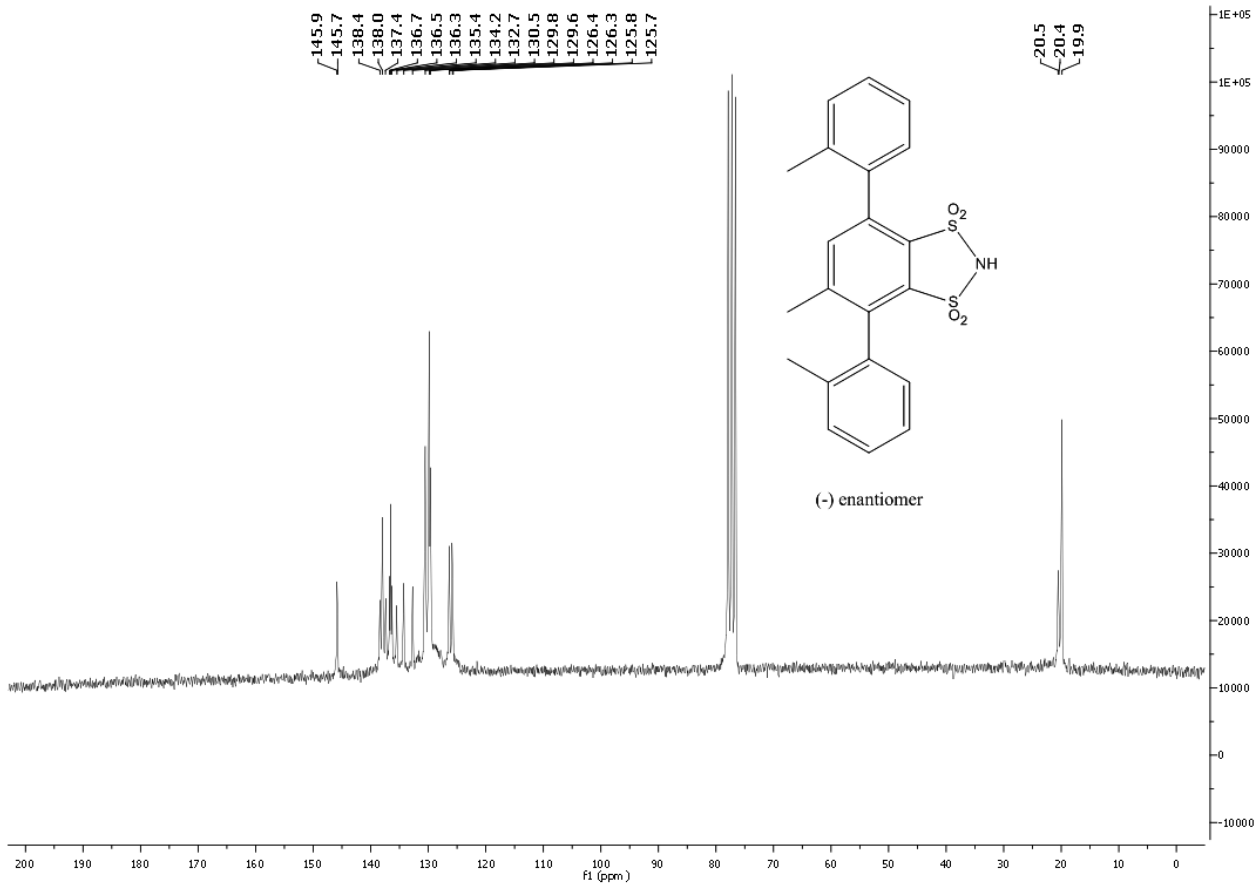


Expansion between 21-16 ppm

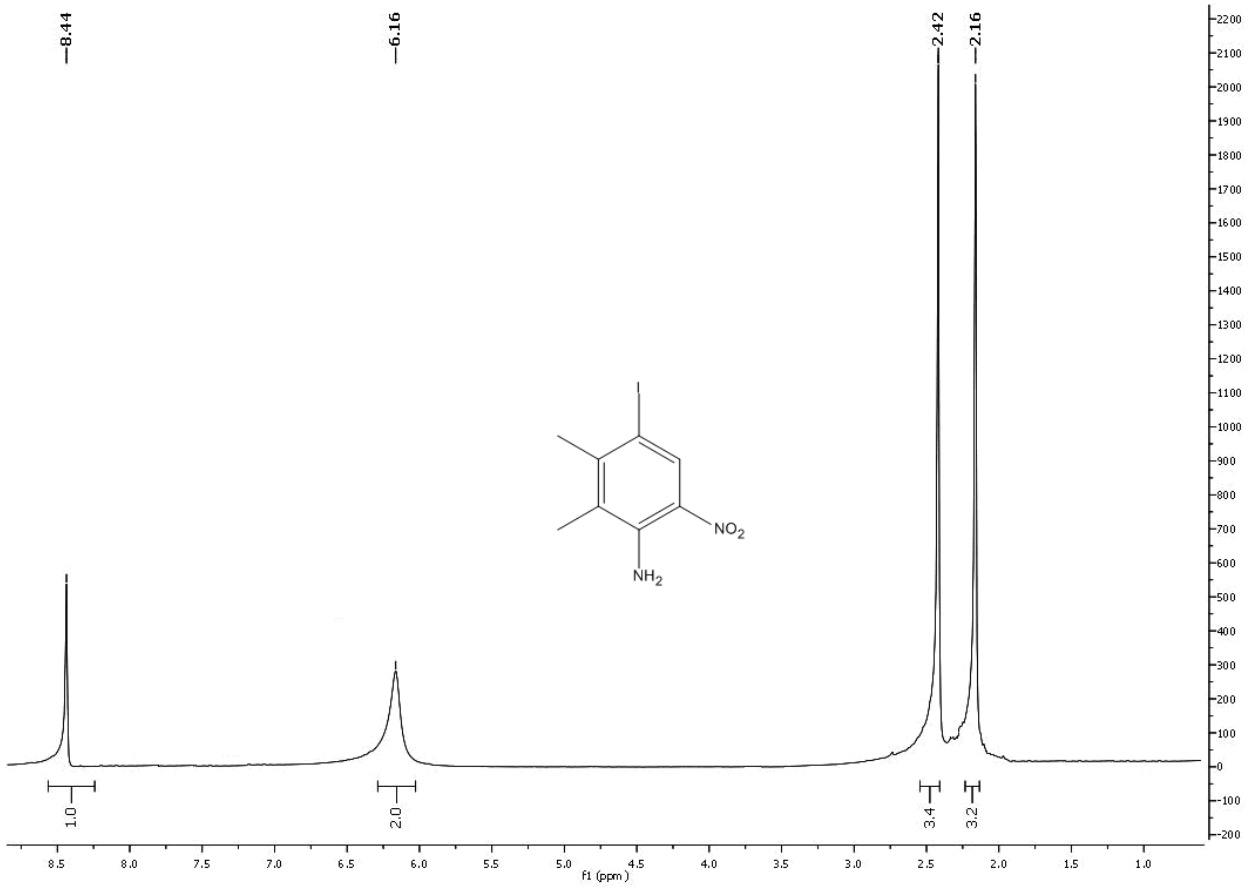


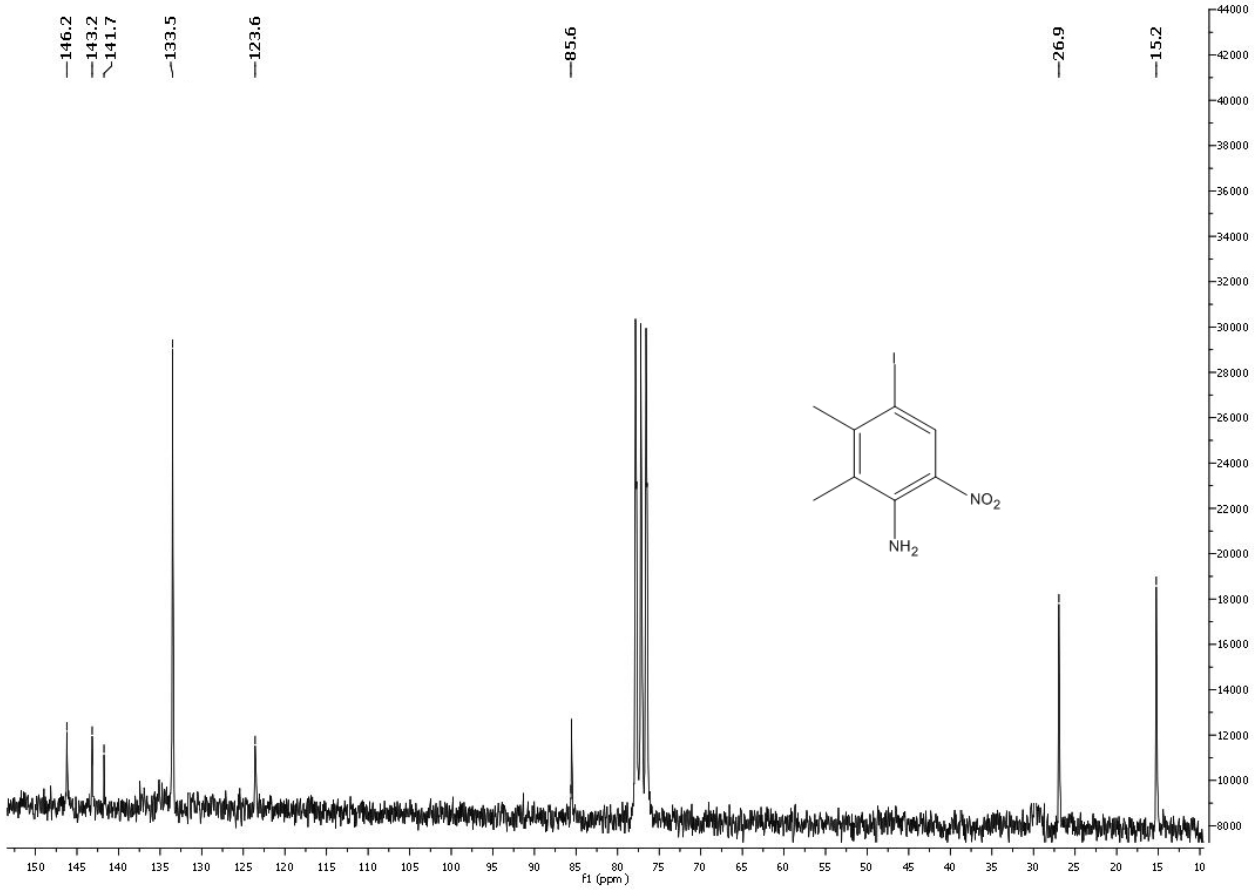
11.8 (-) 4-Methyl- 3,6-bis(*o*-tolyl)-1,2-benzenedisulfonimide (3a)



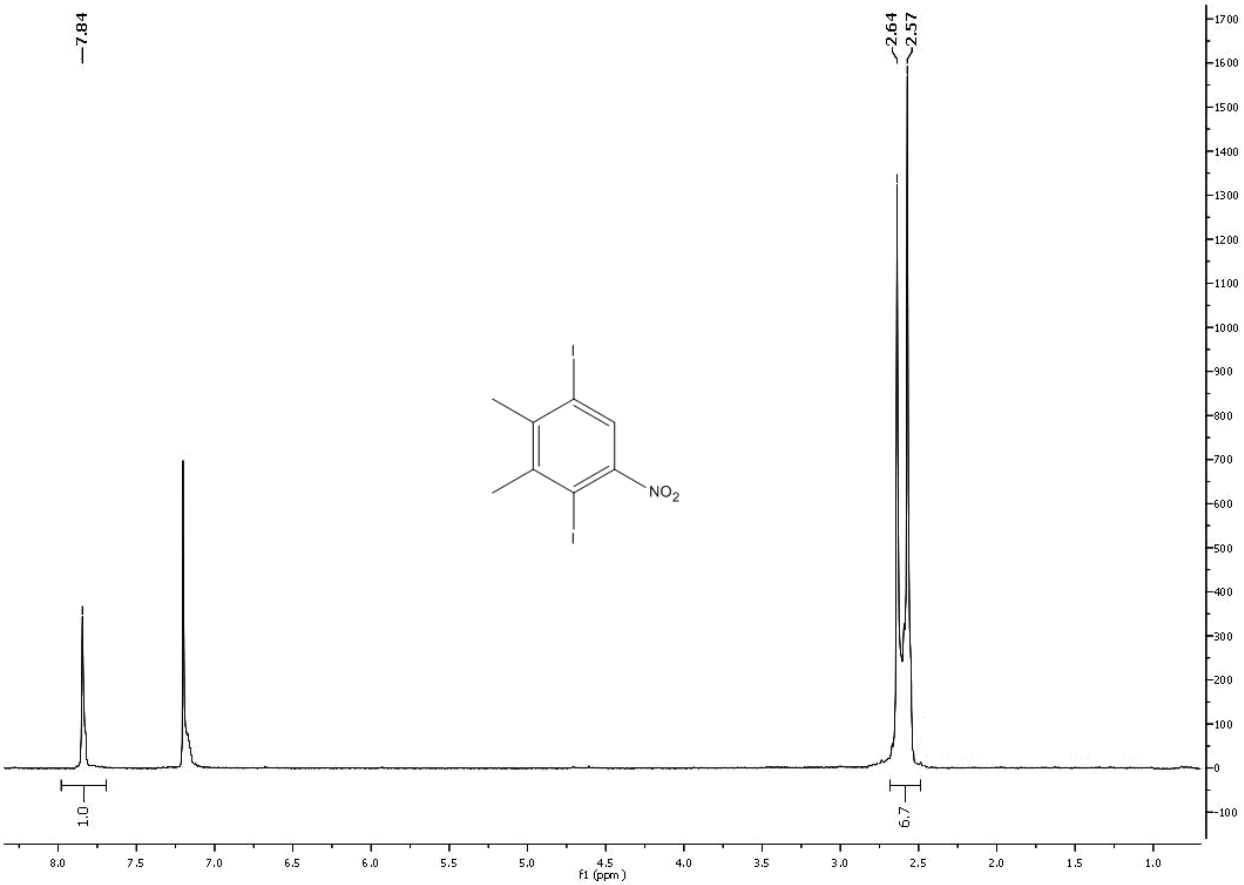


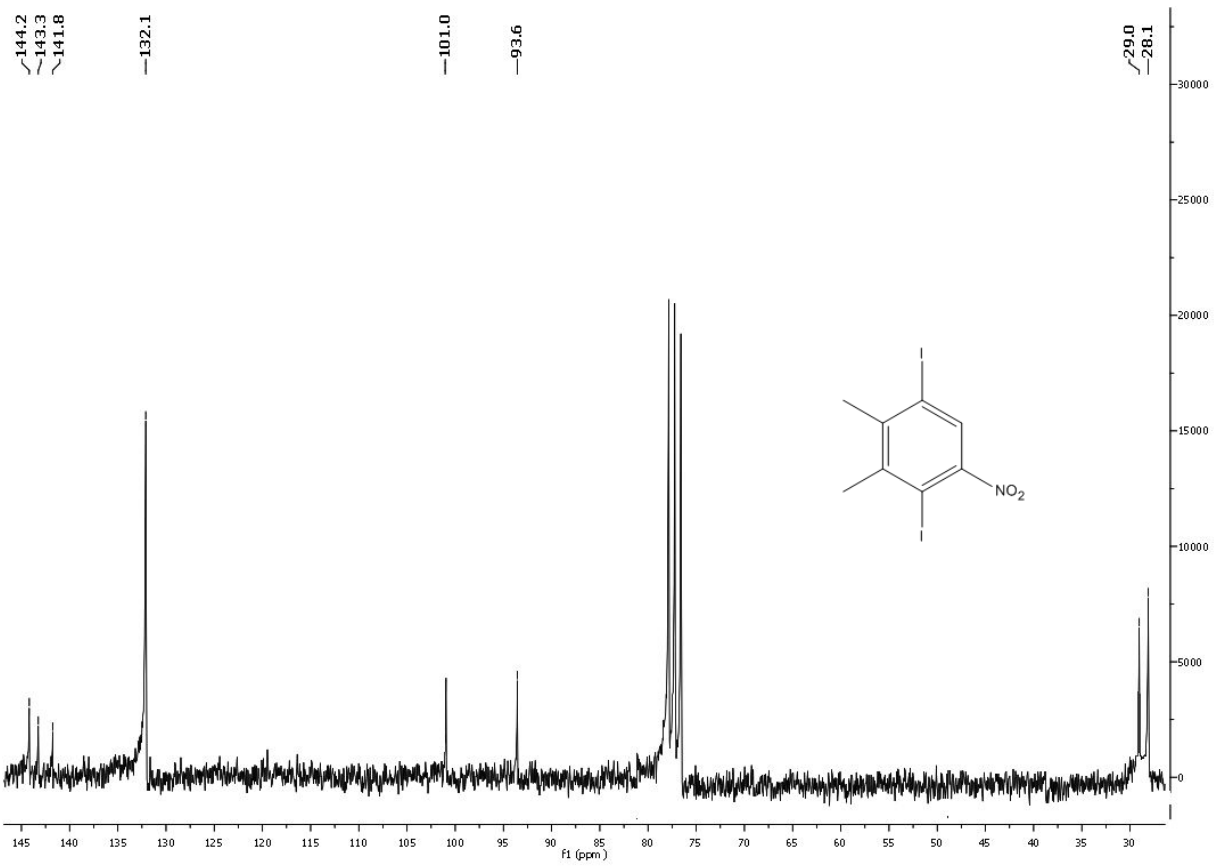
11.9 4-Iodo-5,6-dimethyl-2-nitroaniline (5b)



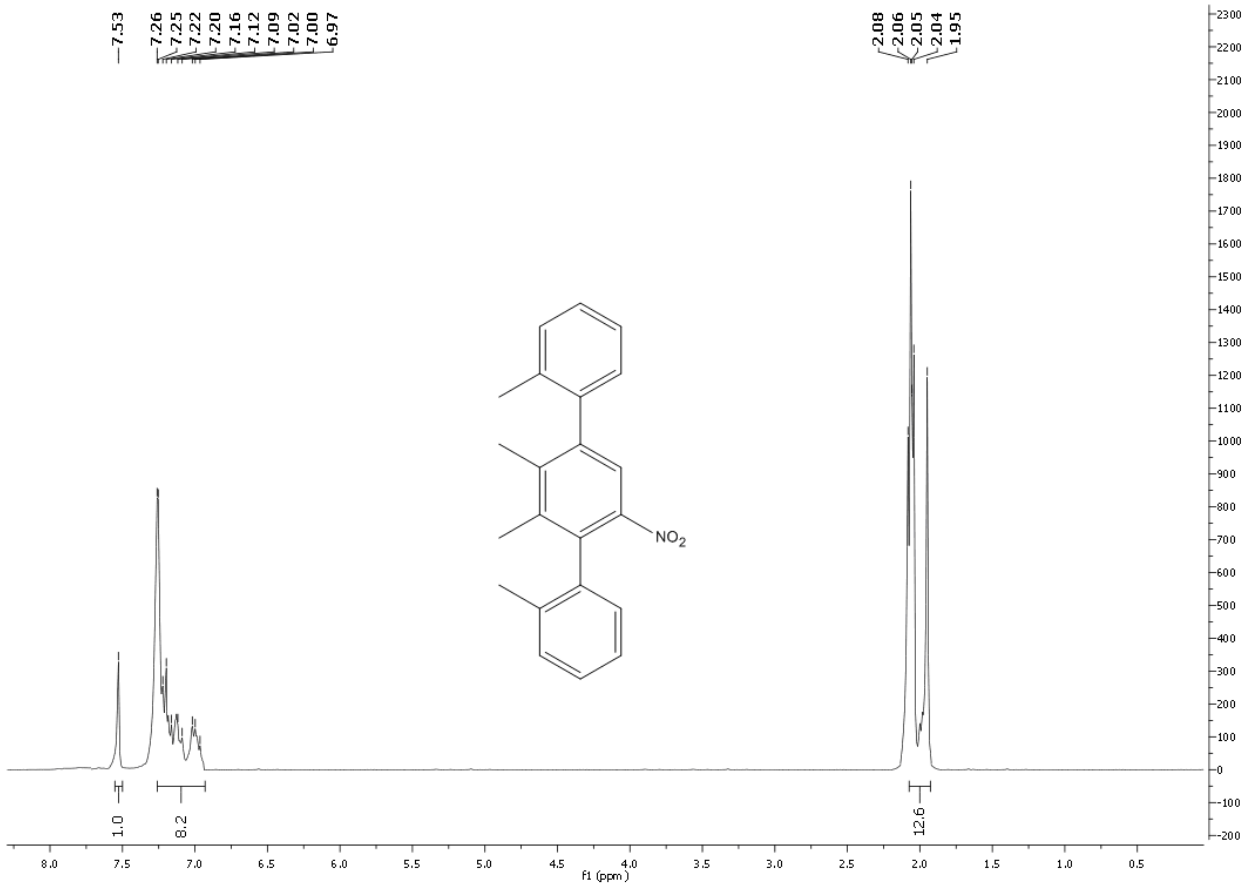


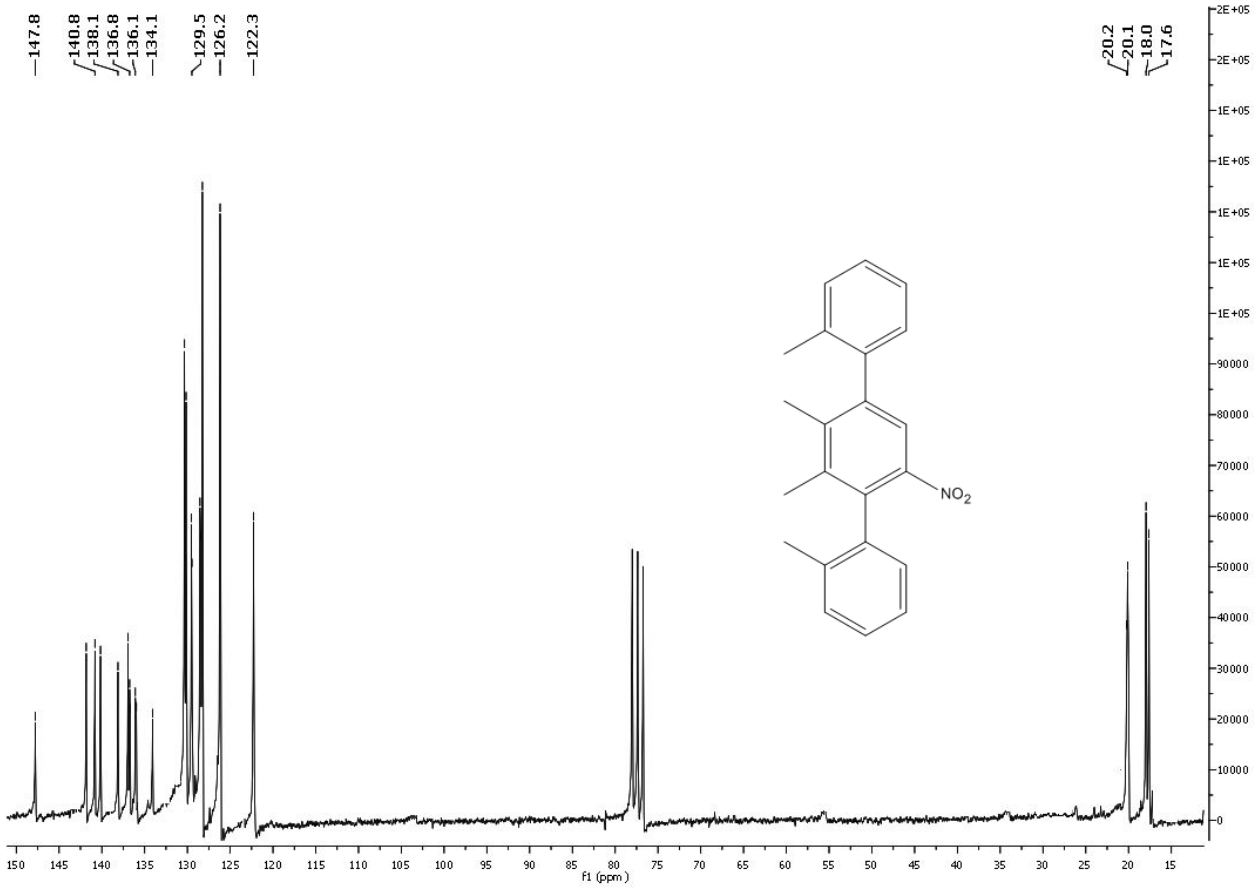
11.10 3,6-Diiodo-4-nitro-*o*-xylene (7b)



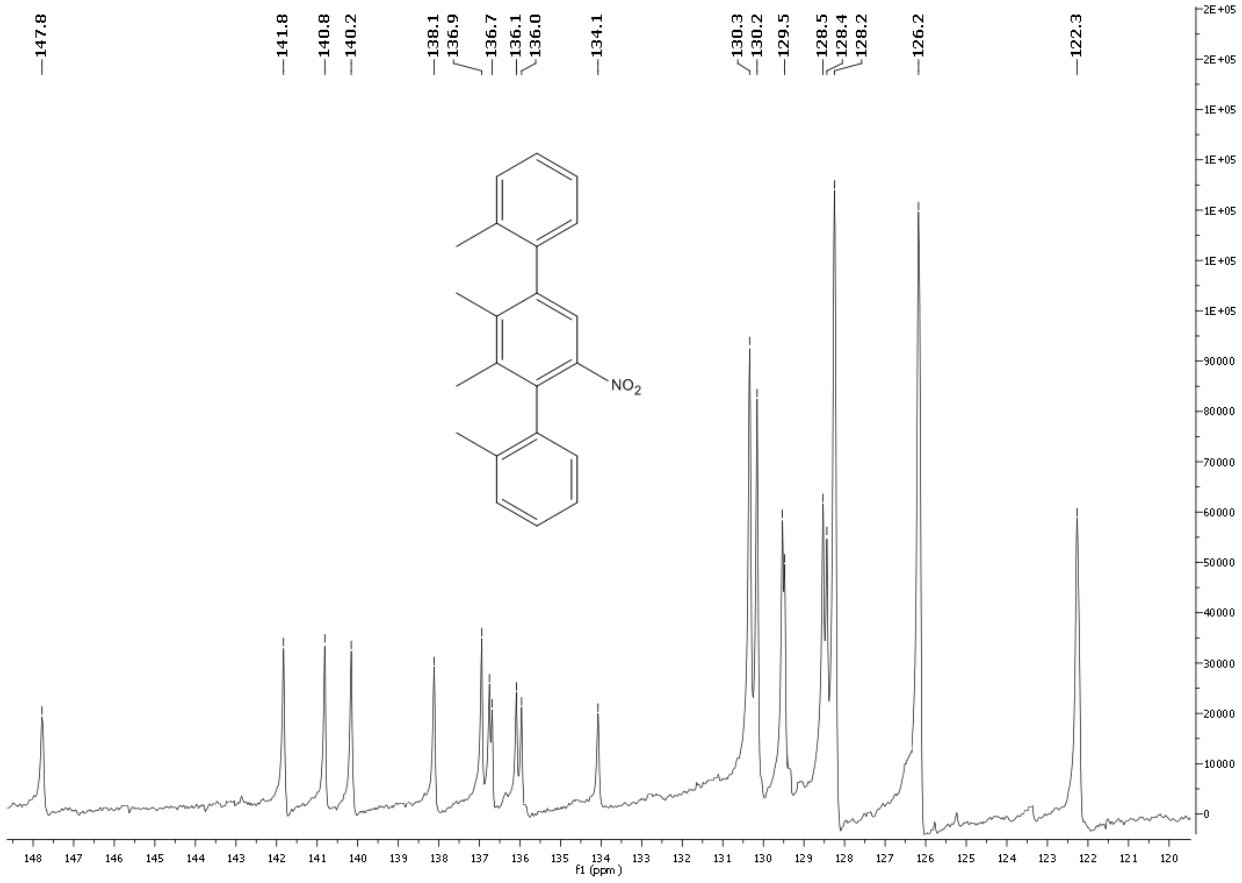


11.11 4-Nitro-3,6-bis(*o*-tolyl)benzene (15)

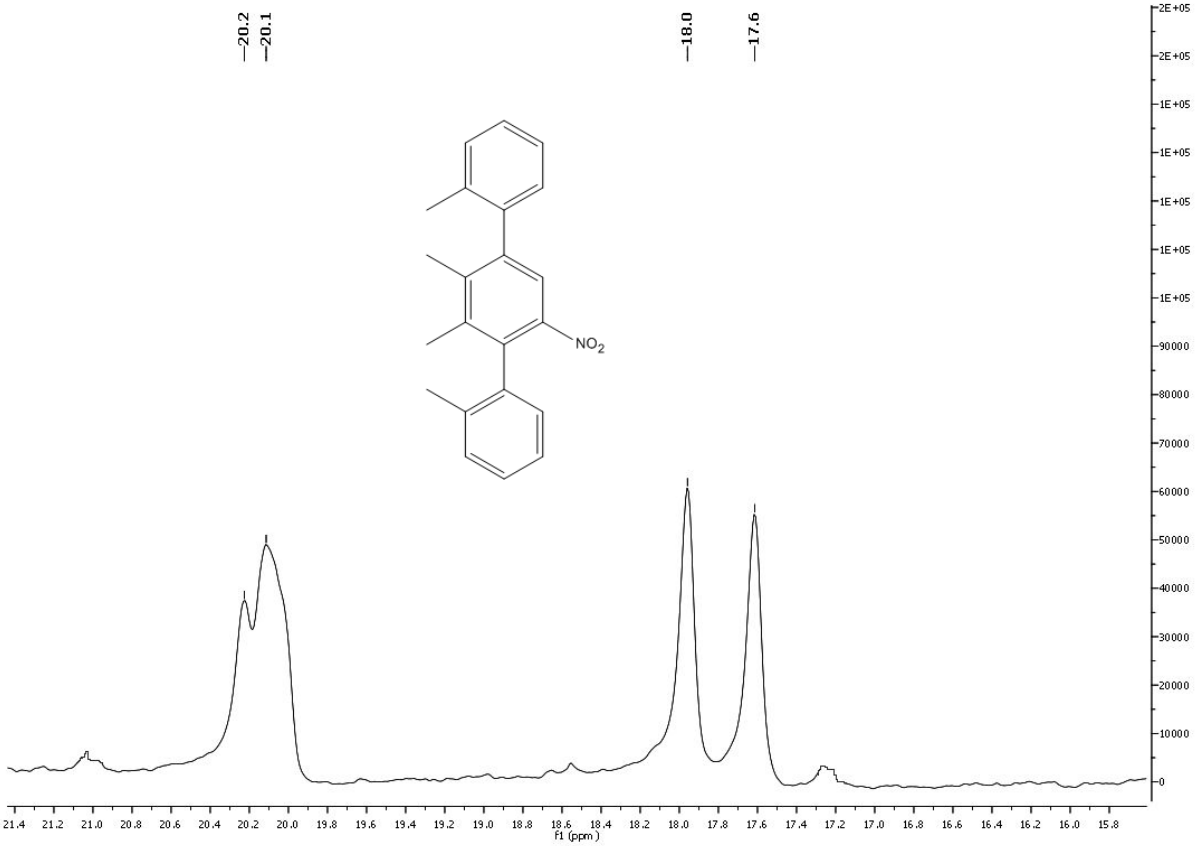




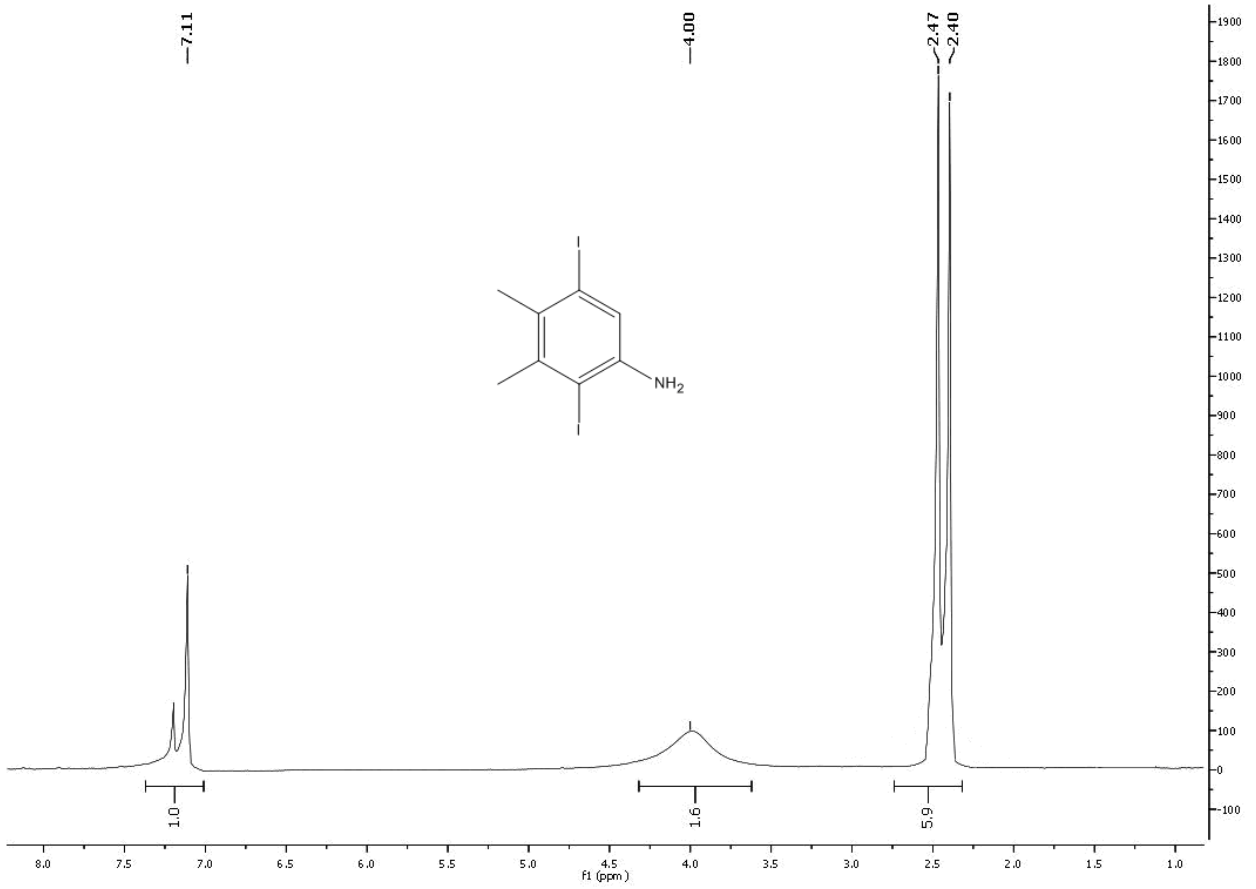
Expansion between 148-120 ppm

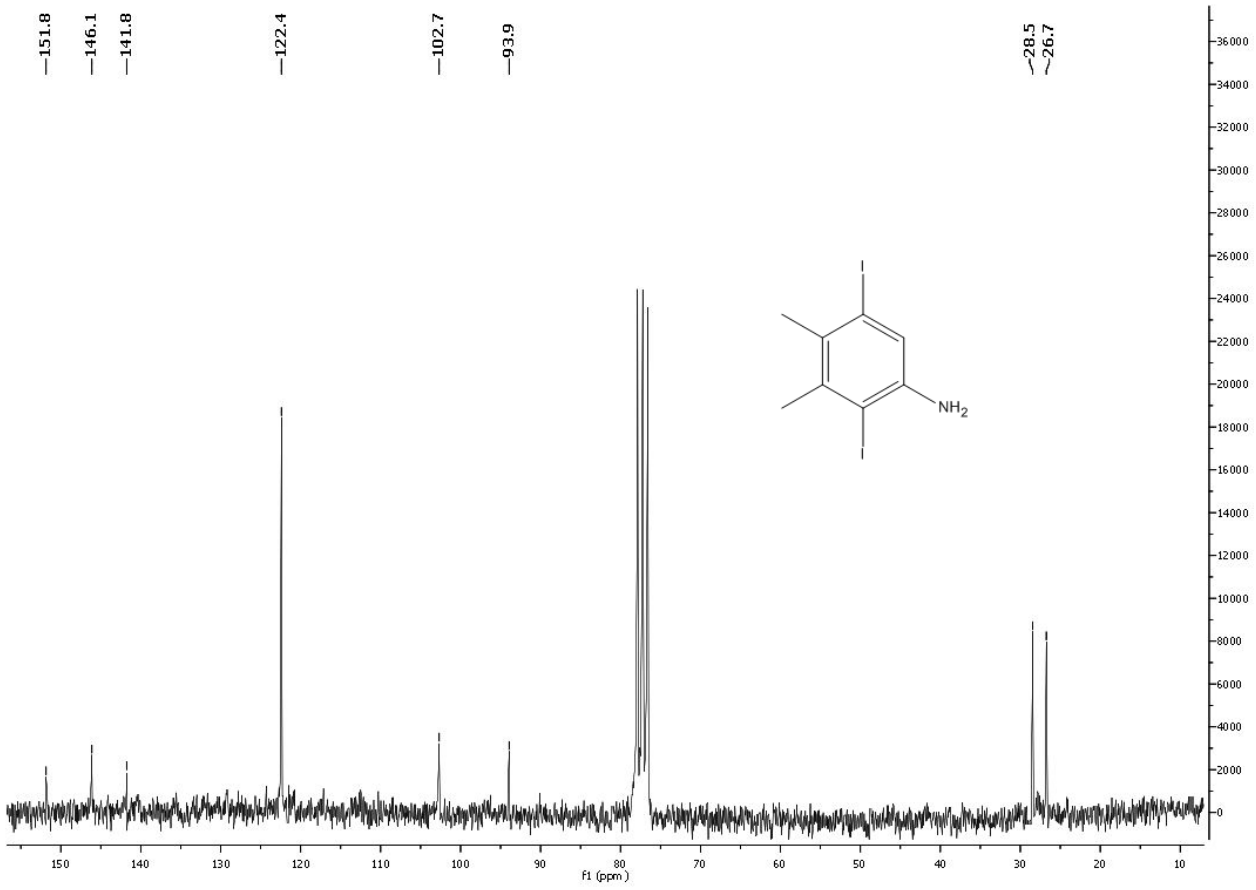


Expansion between 22-15 ppm

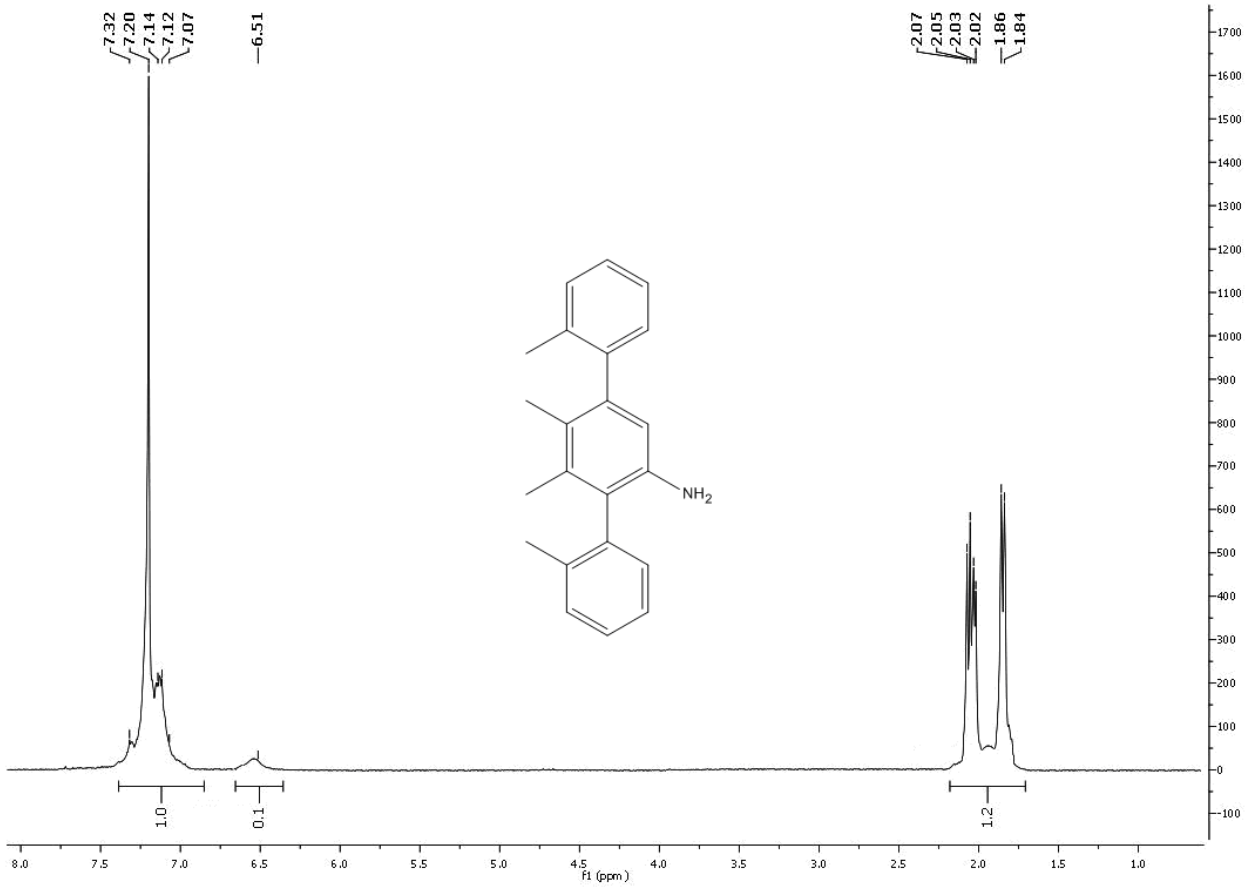


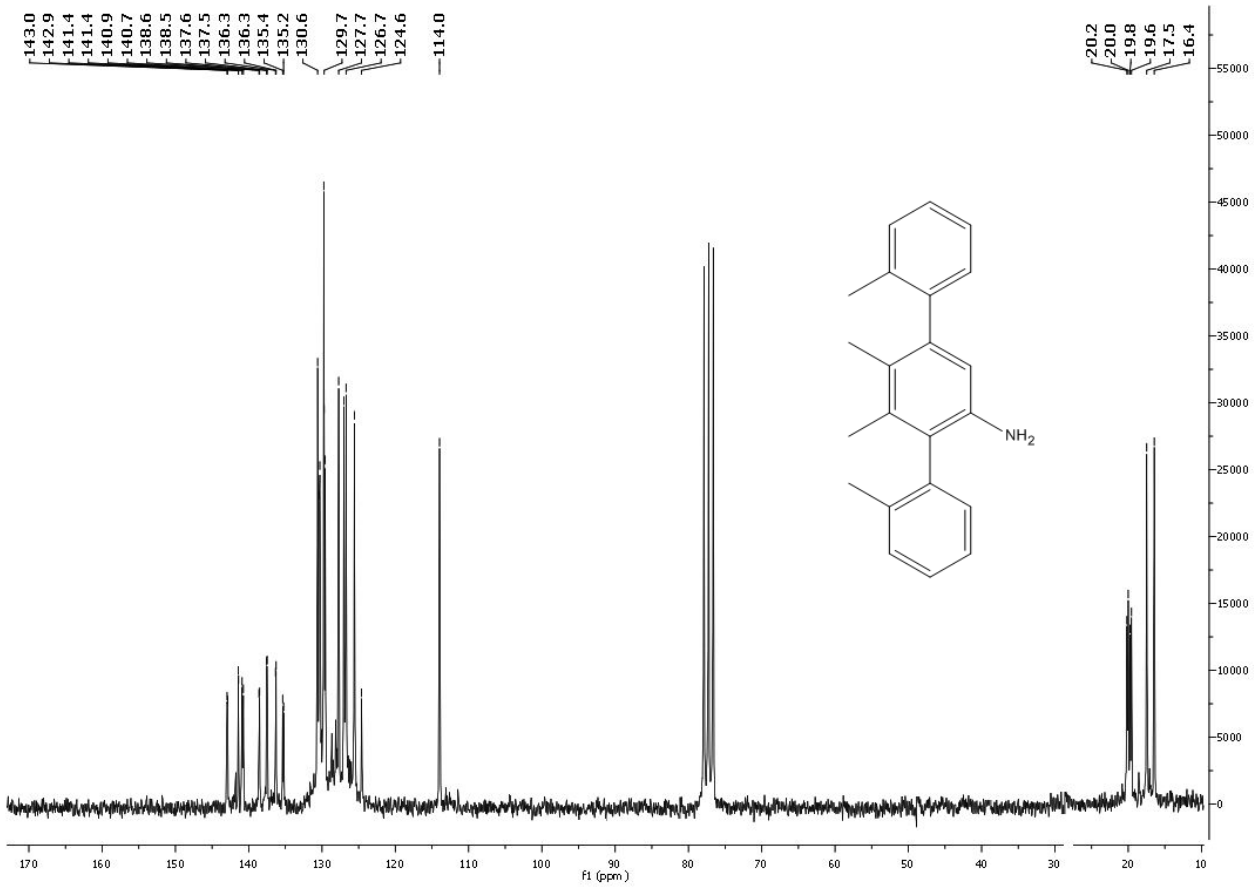
11.12 2,5-Diiodo-3,4-dimethylaniline (8b)



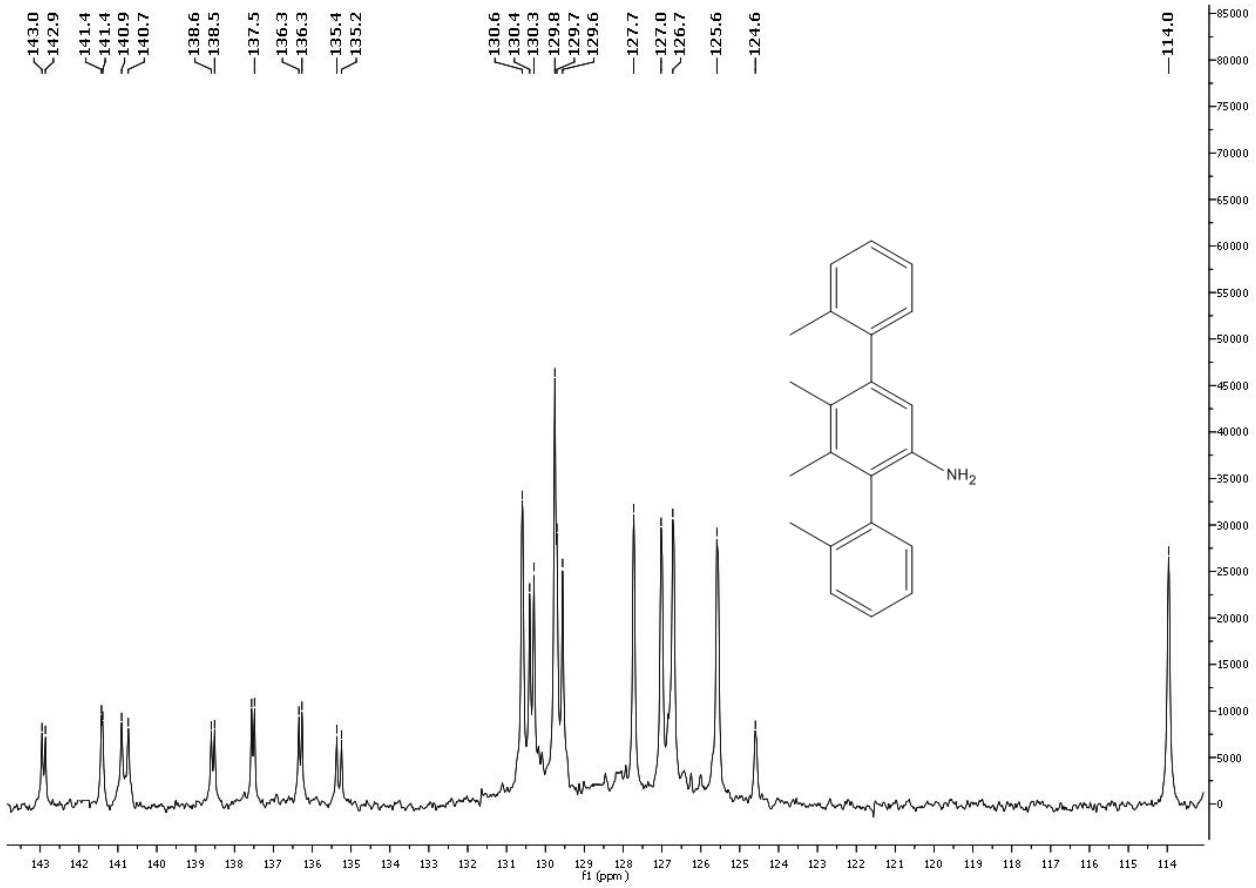


11.13 2,5-Bis(*o*-tolyl)-3,4-dimethylaniline (16)

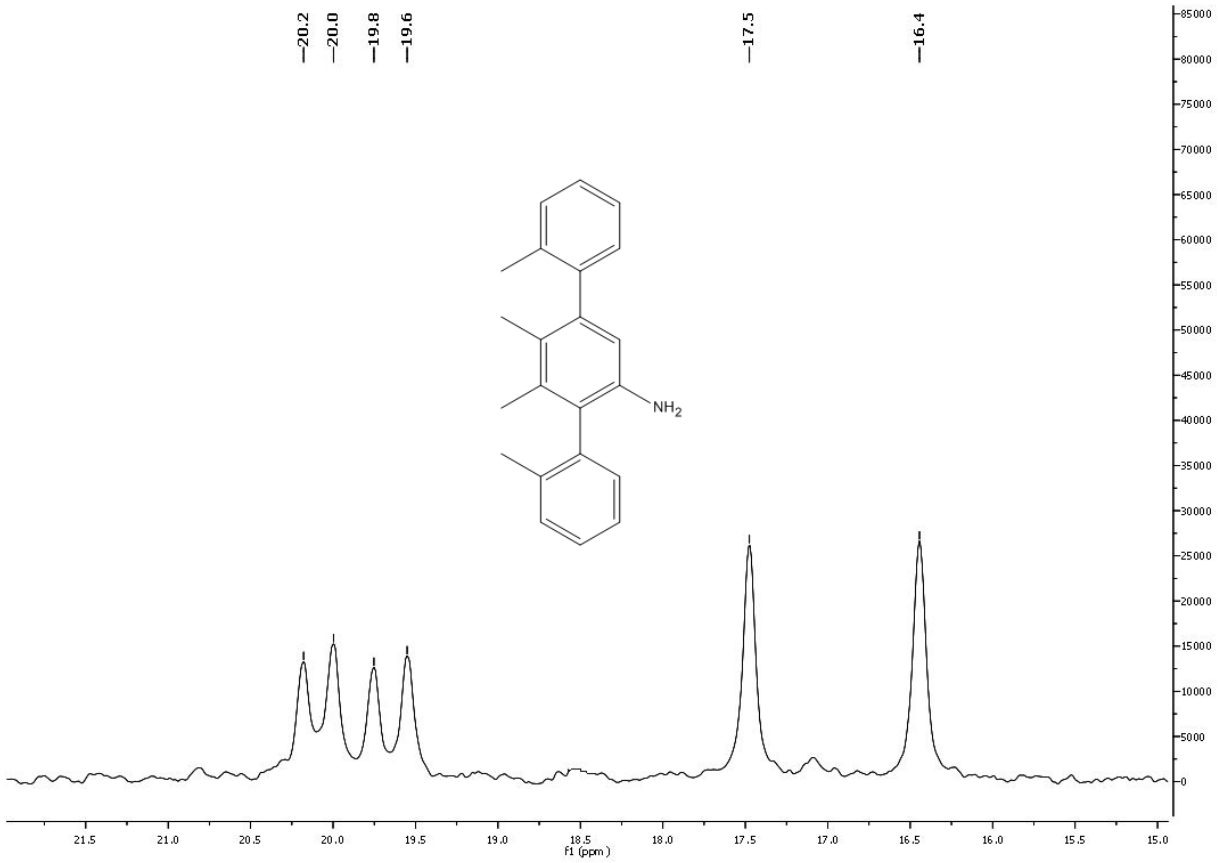




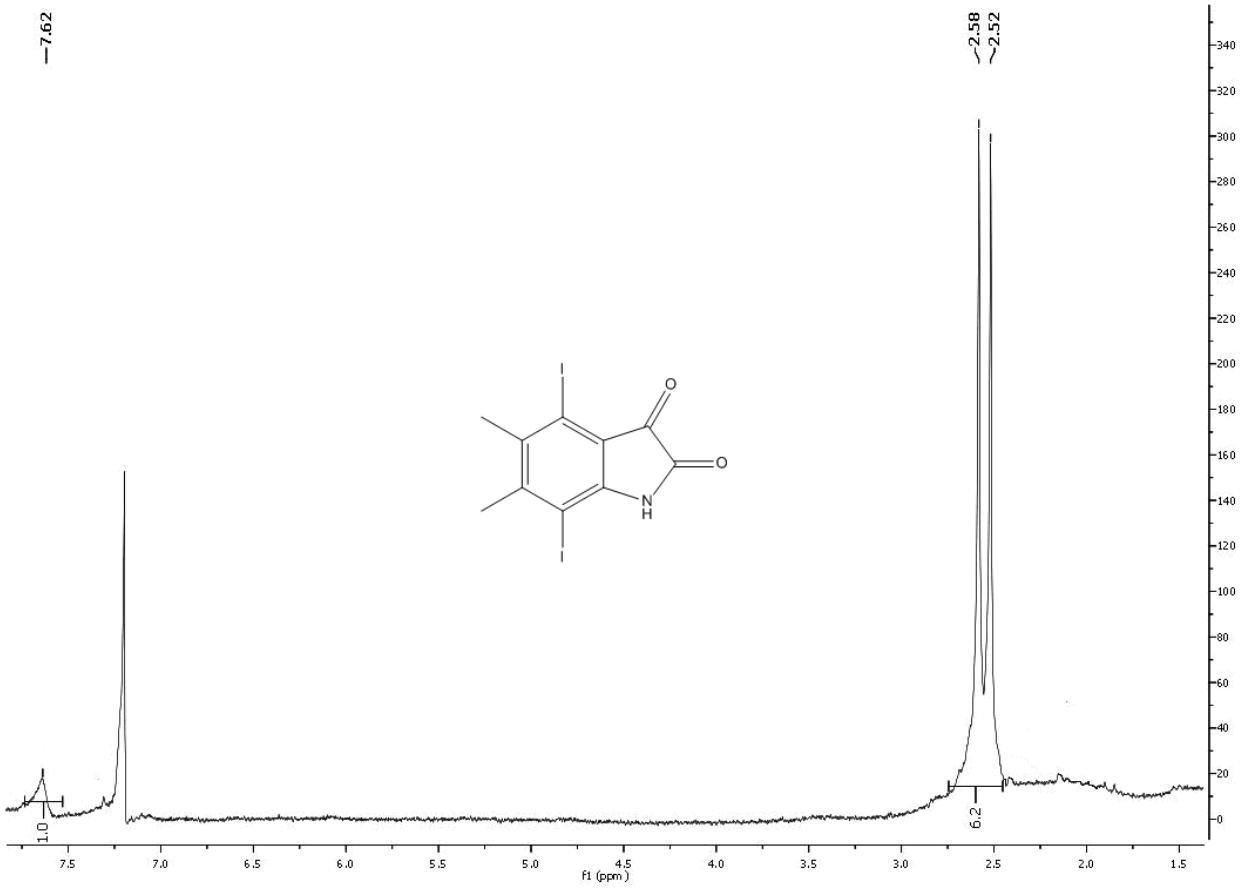
Expansion between 144-113 ppm

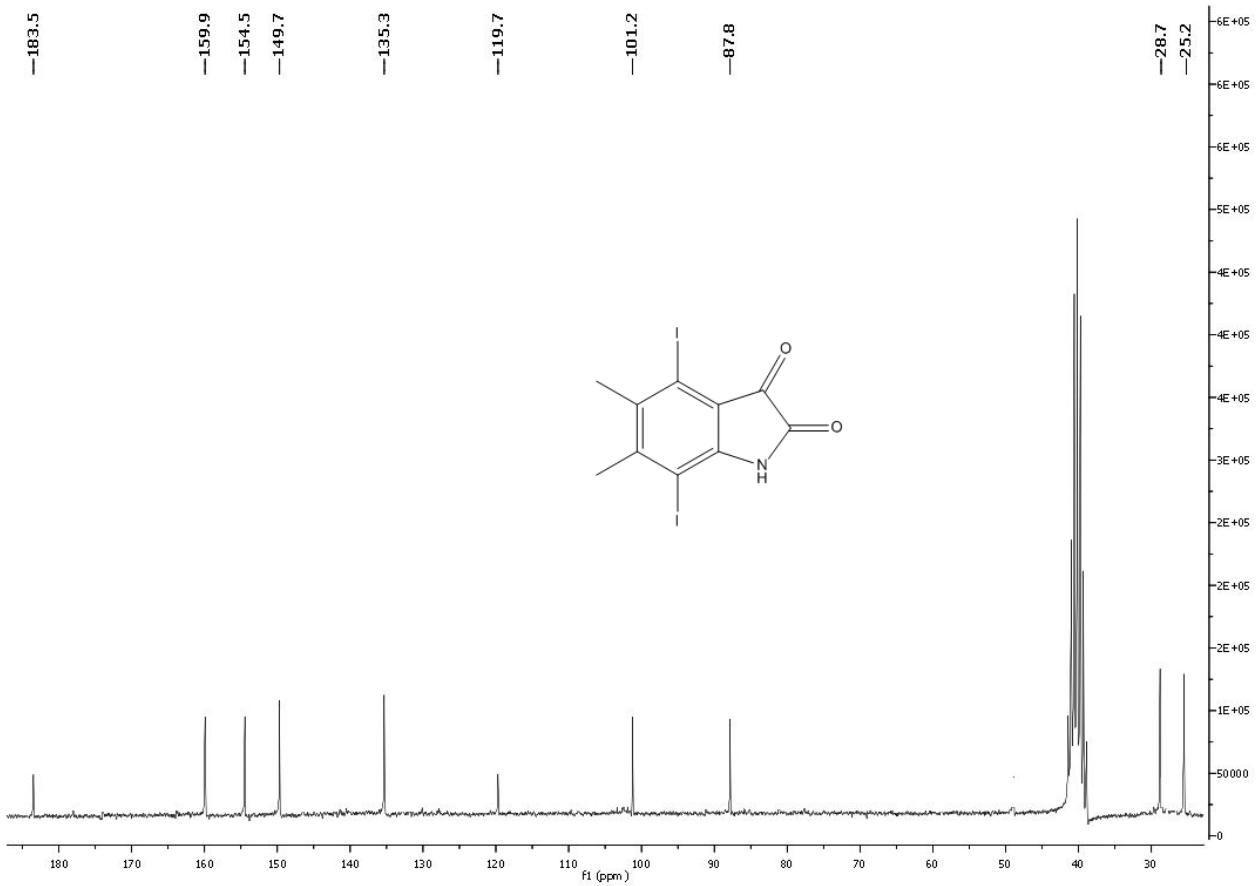


Expansion between 22-15 ppm

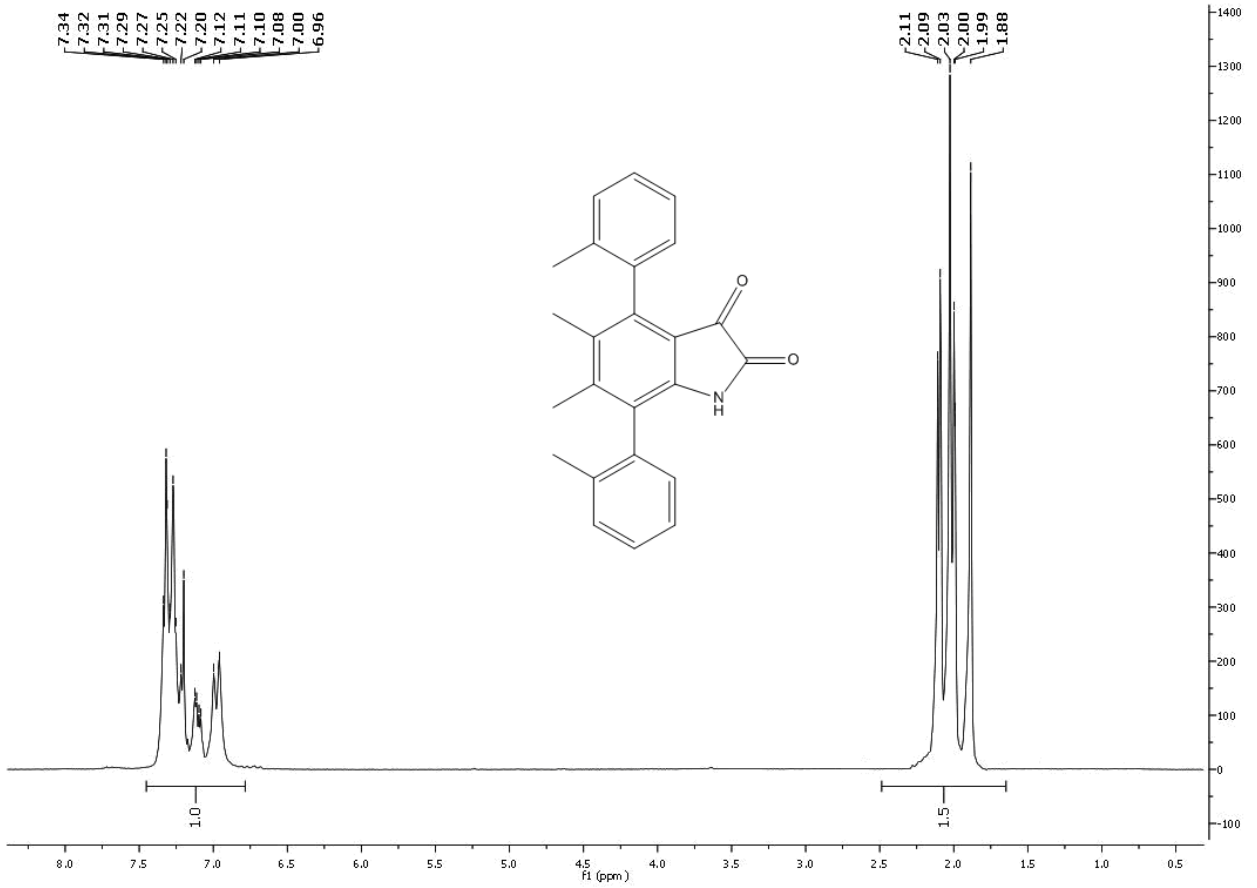


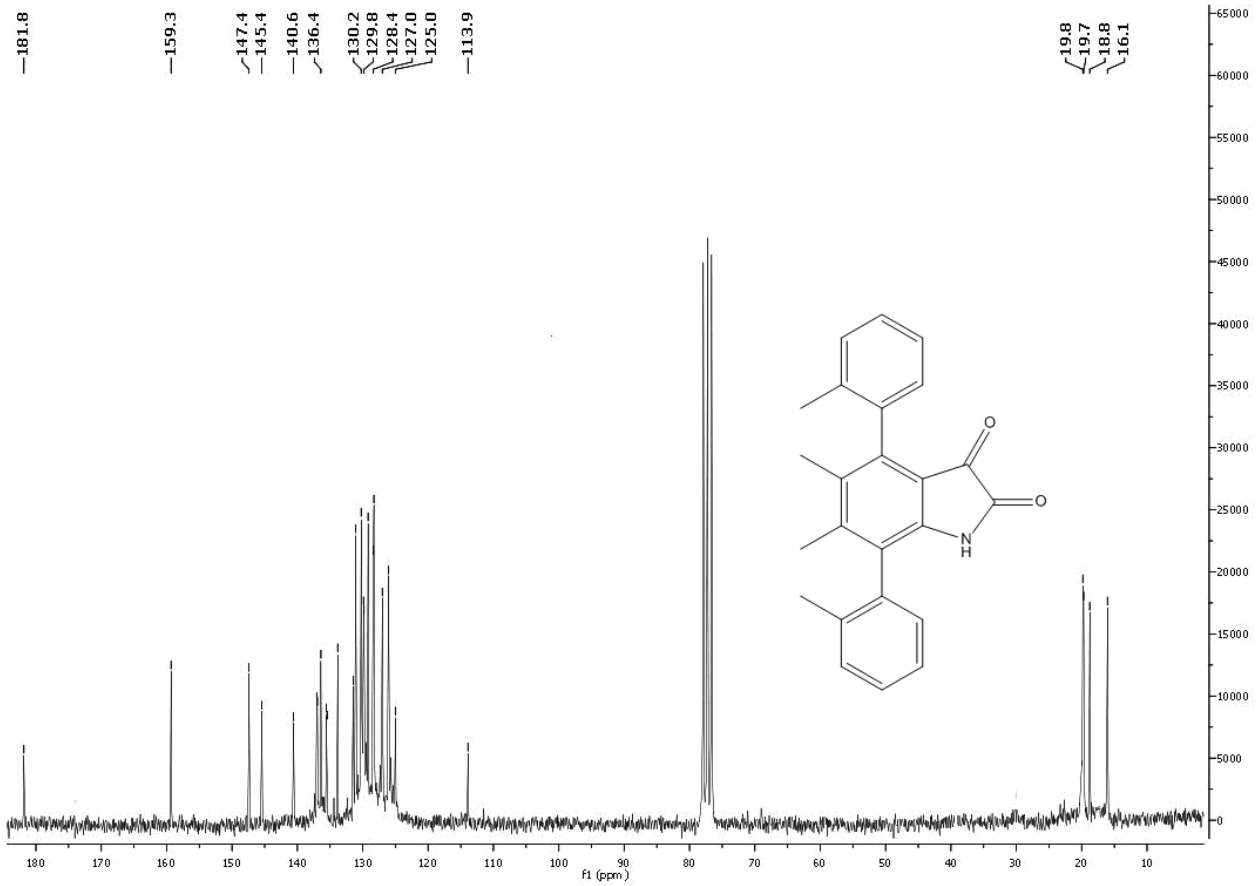
11.14 4,7-Diiodo-5,6-dimethylsatin (10b)



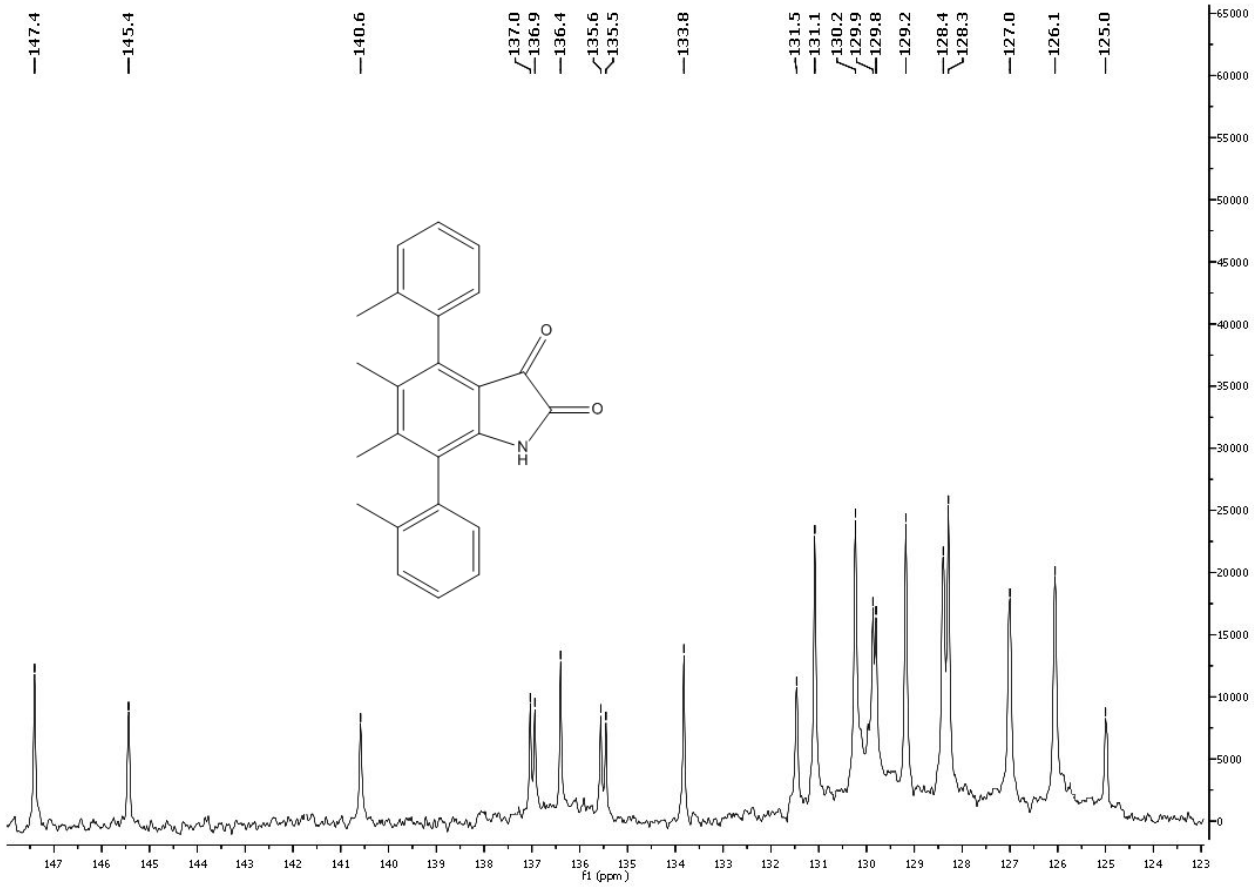


11.15 5,6-Dimethyl-4,7-bis(*o*-tolyl)isatin (11b)

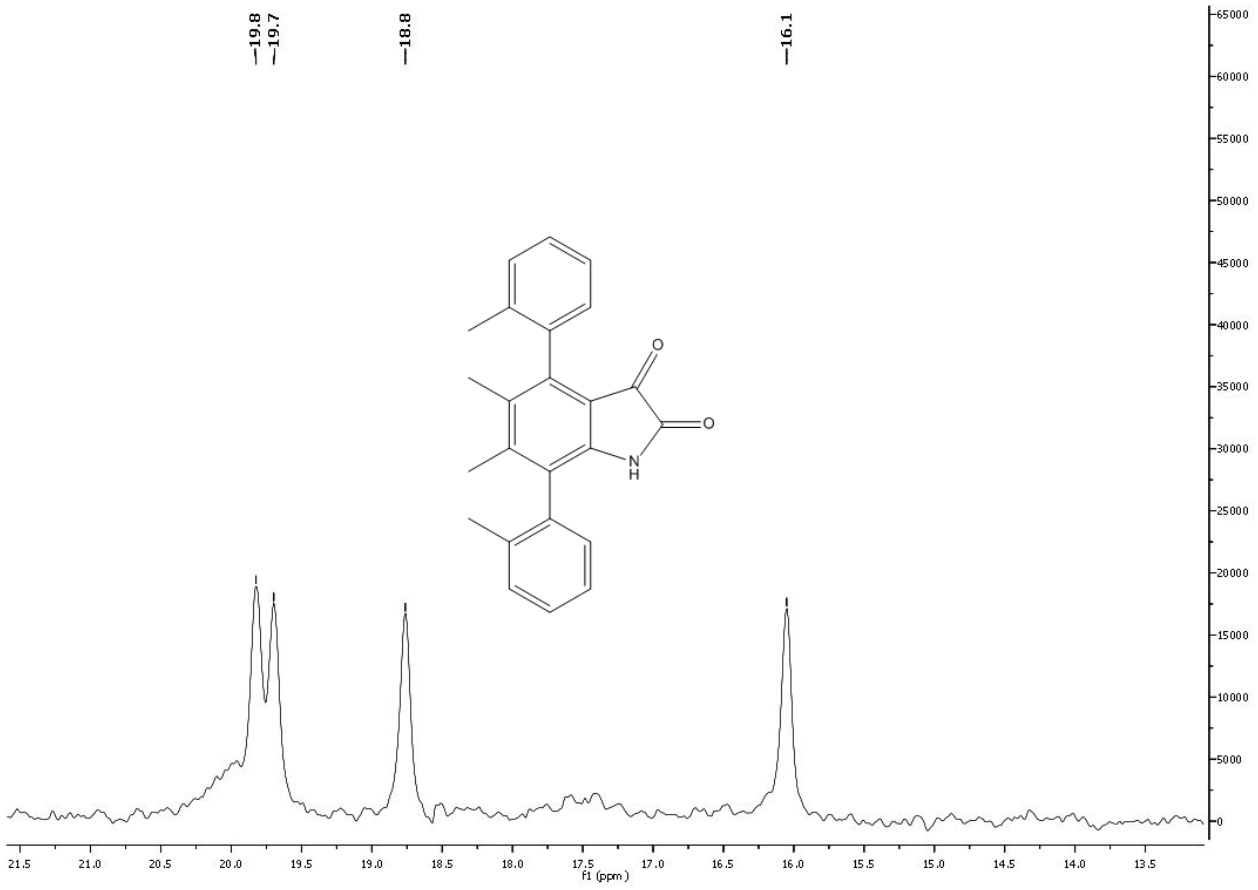




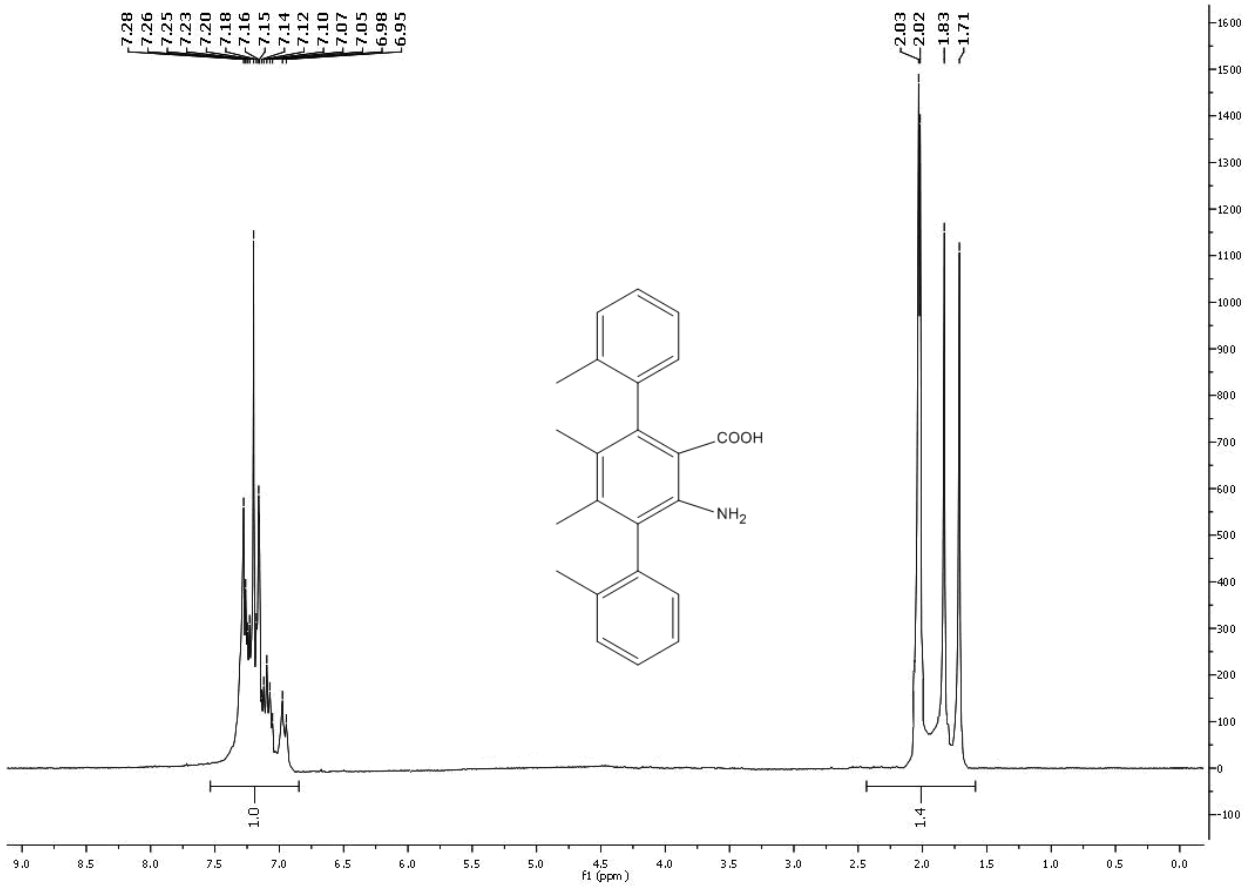
Expansion between 147-123 ppm

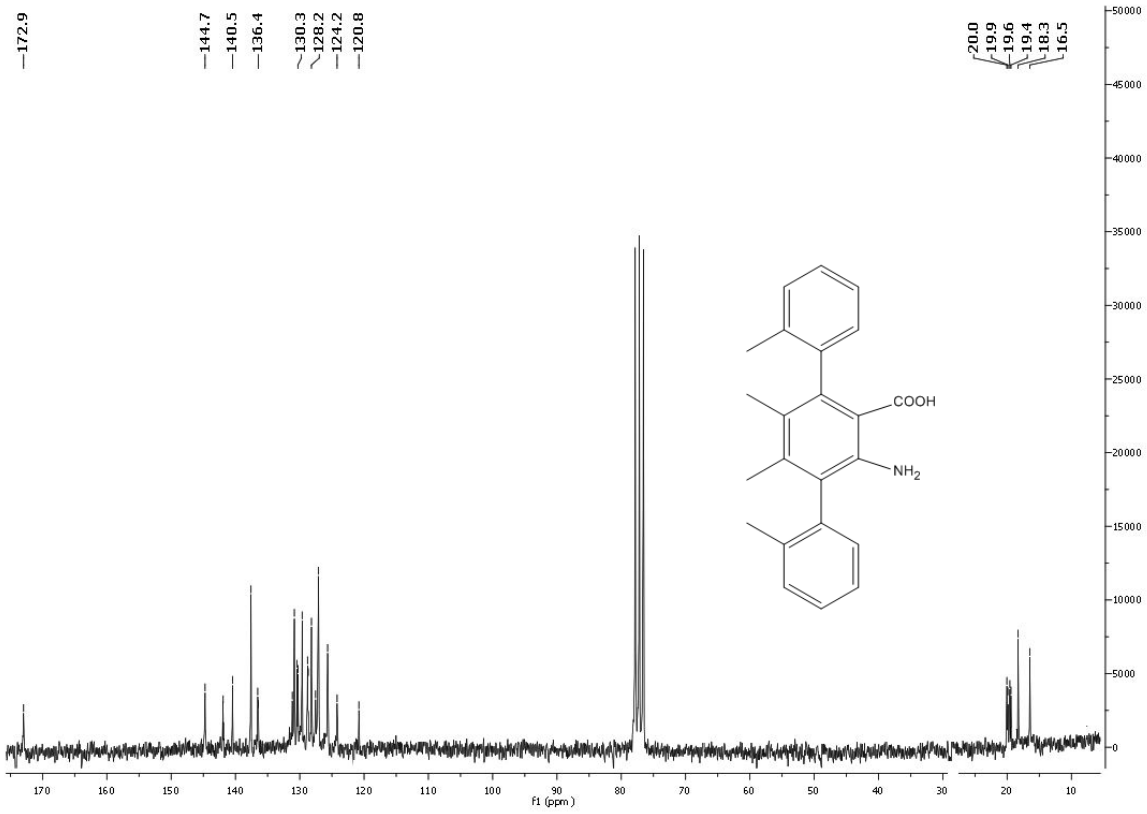


Expansion between 21-13 ppm

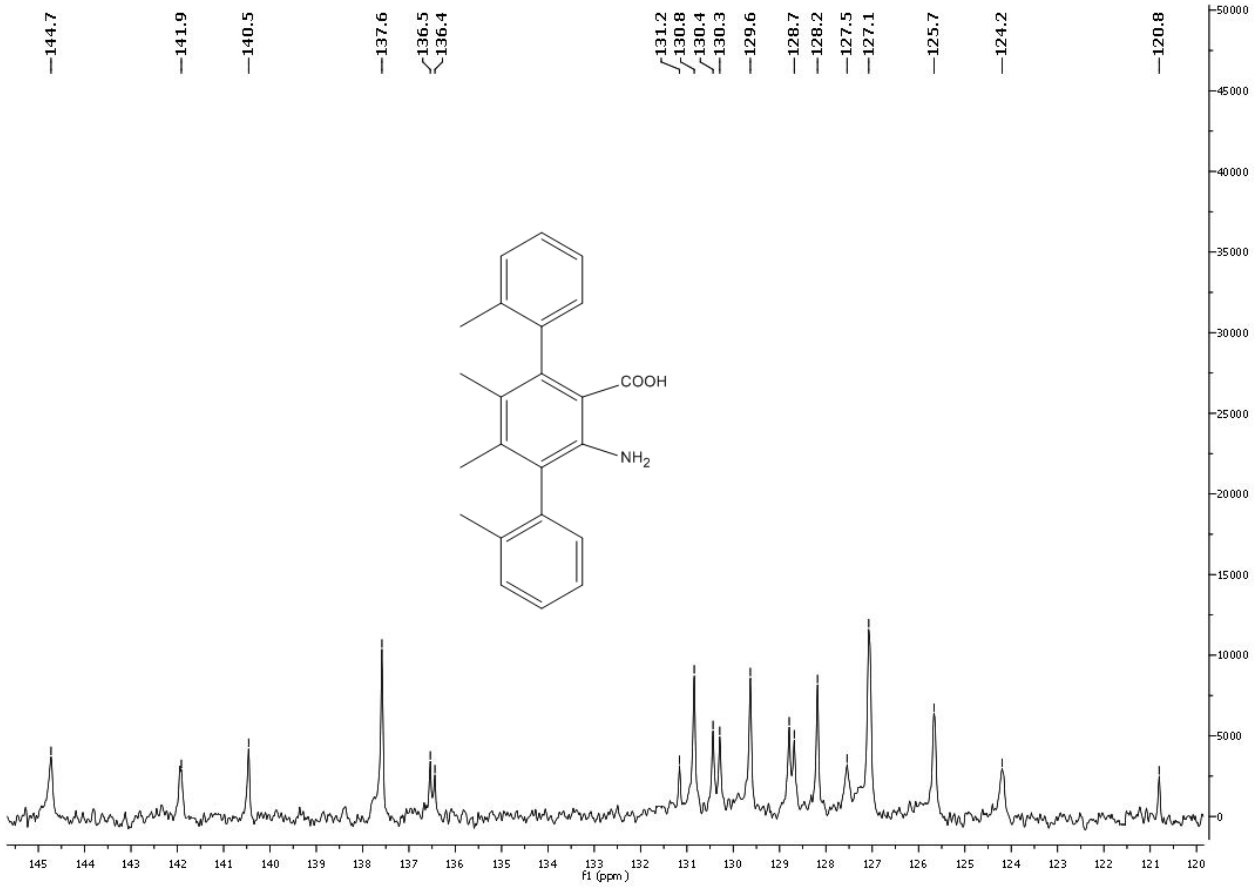


11.16 2-Amino-4,5-dimethyl-3,6-bis(*o*-tolyl)benzoic acid (12b)

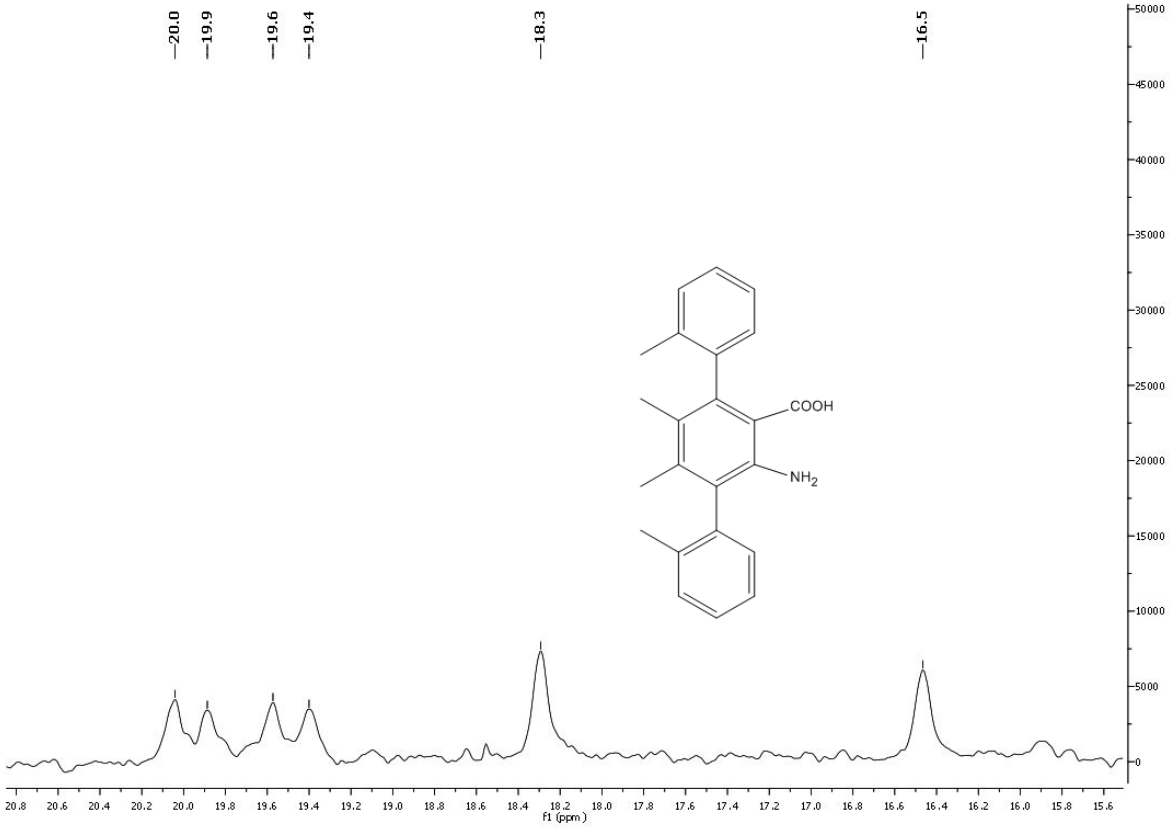




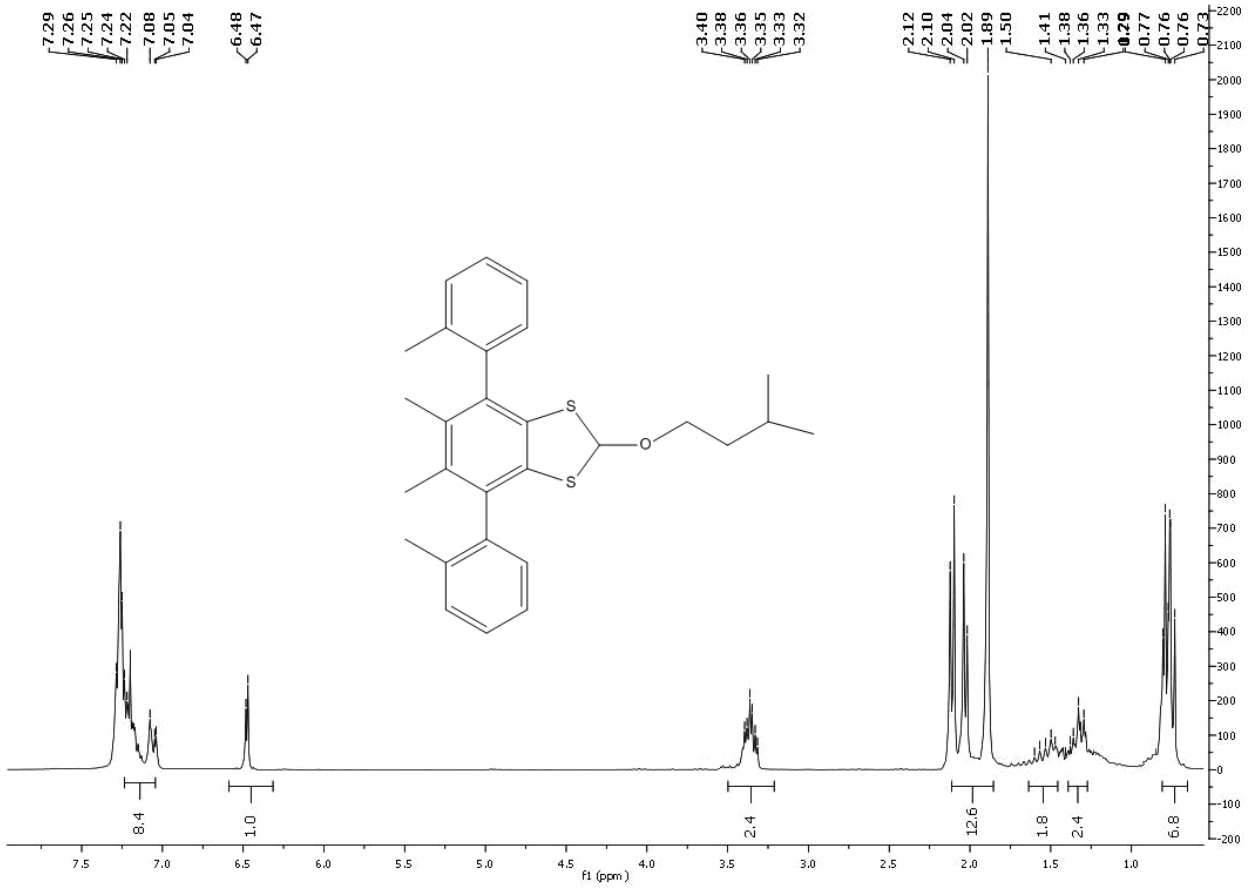
Expansion between 145-120 ppm

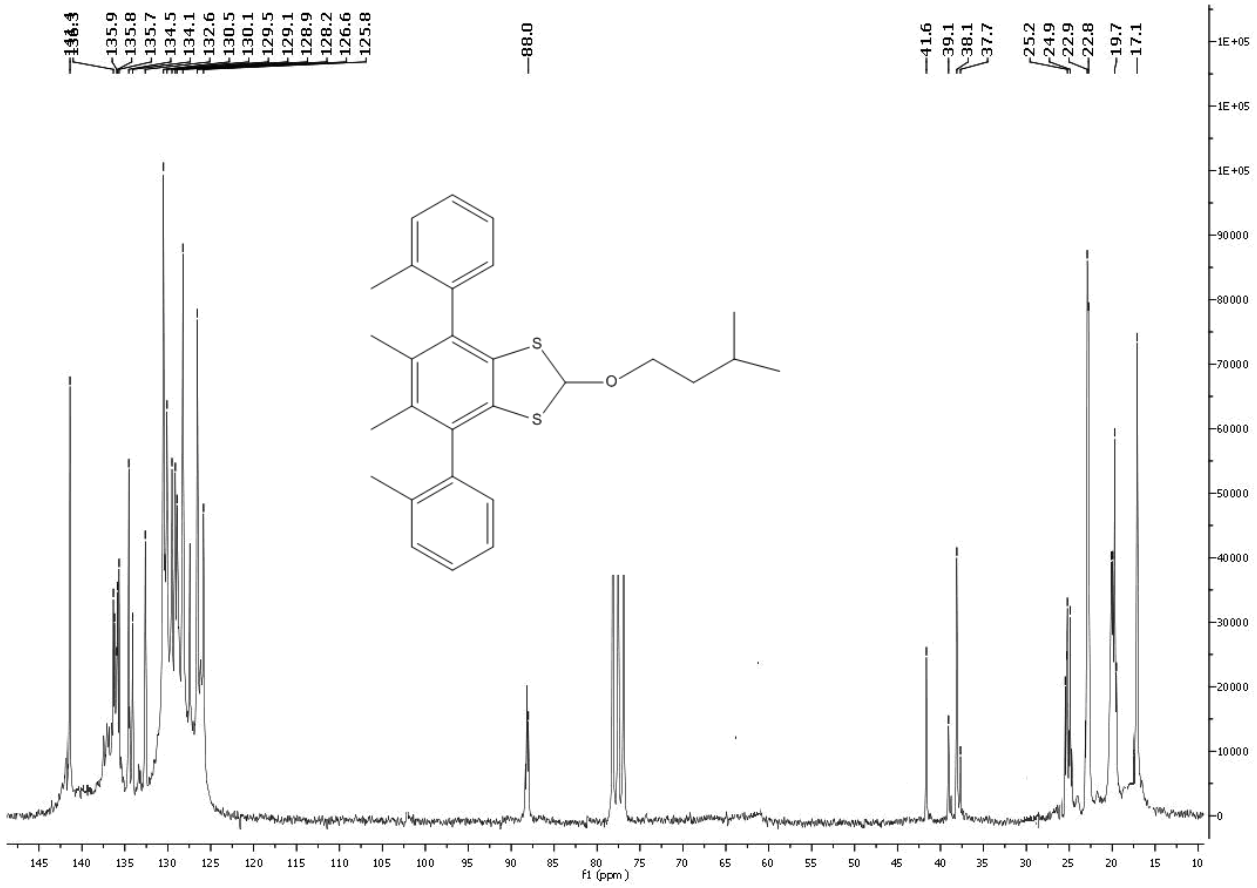


Expansion between 22-15 ppm

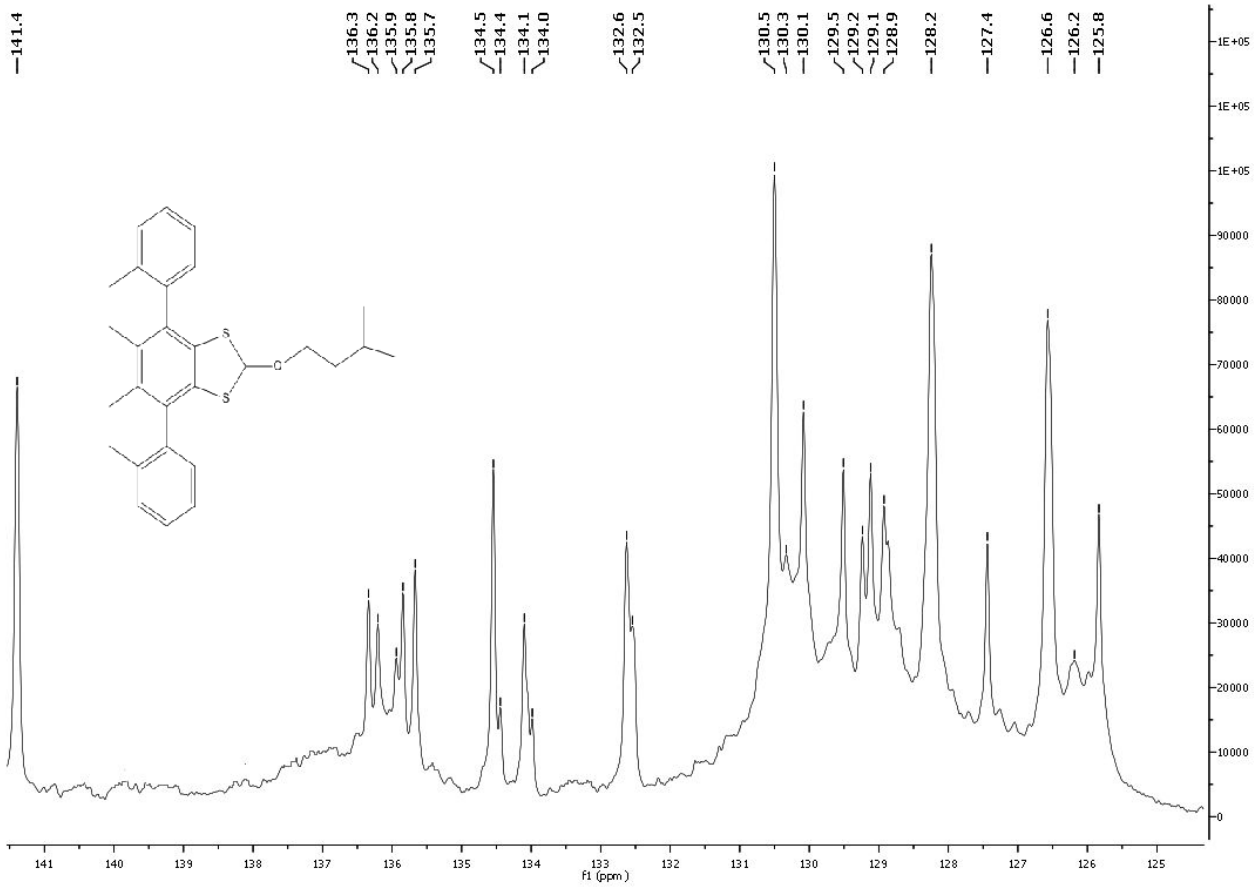


11.17 5,6-Dimethyl-2-(3-methylbutoxy)- 4,7-bis(*o*-tolyl)-1,3-benzodithiole (13b)

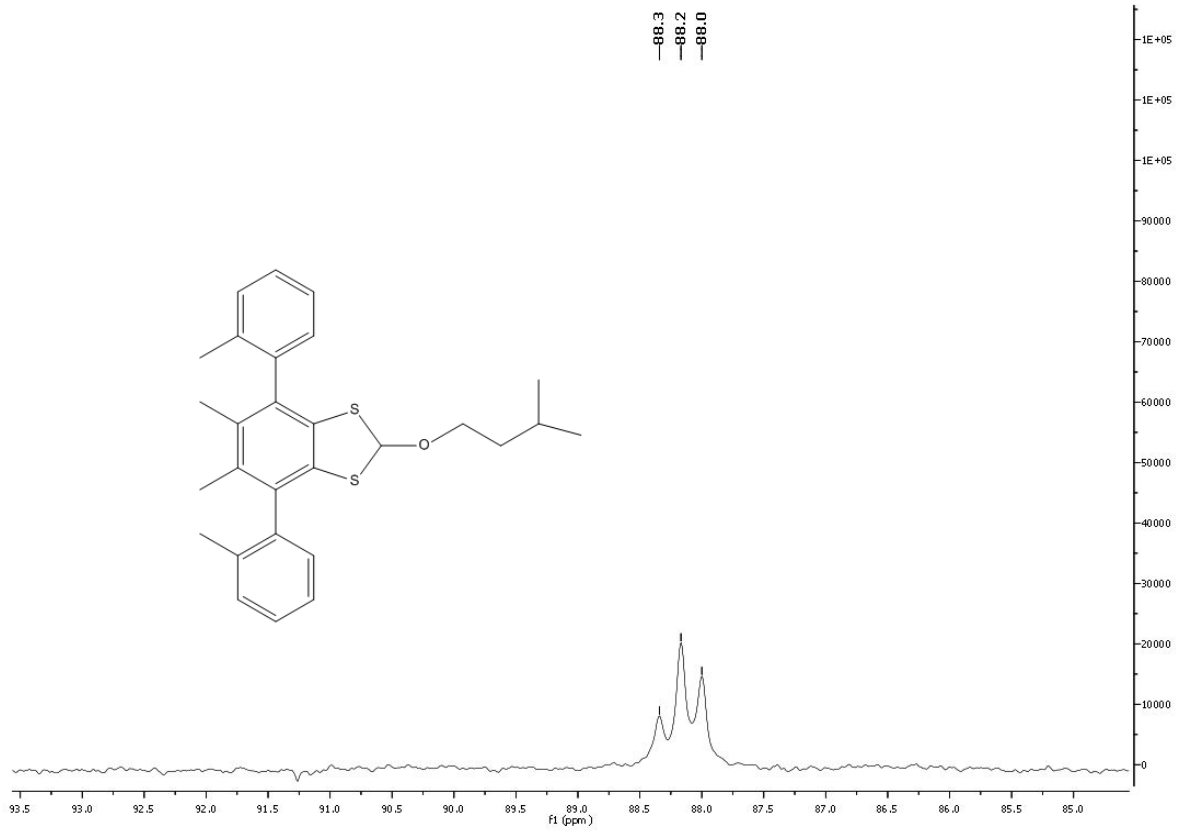




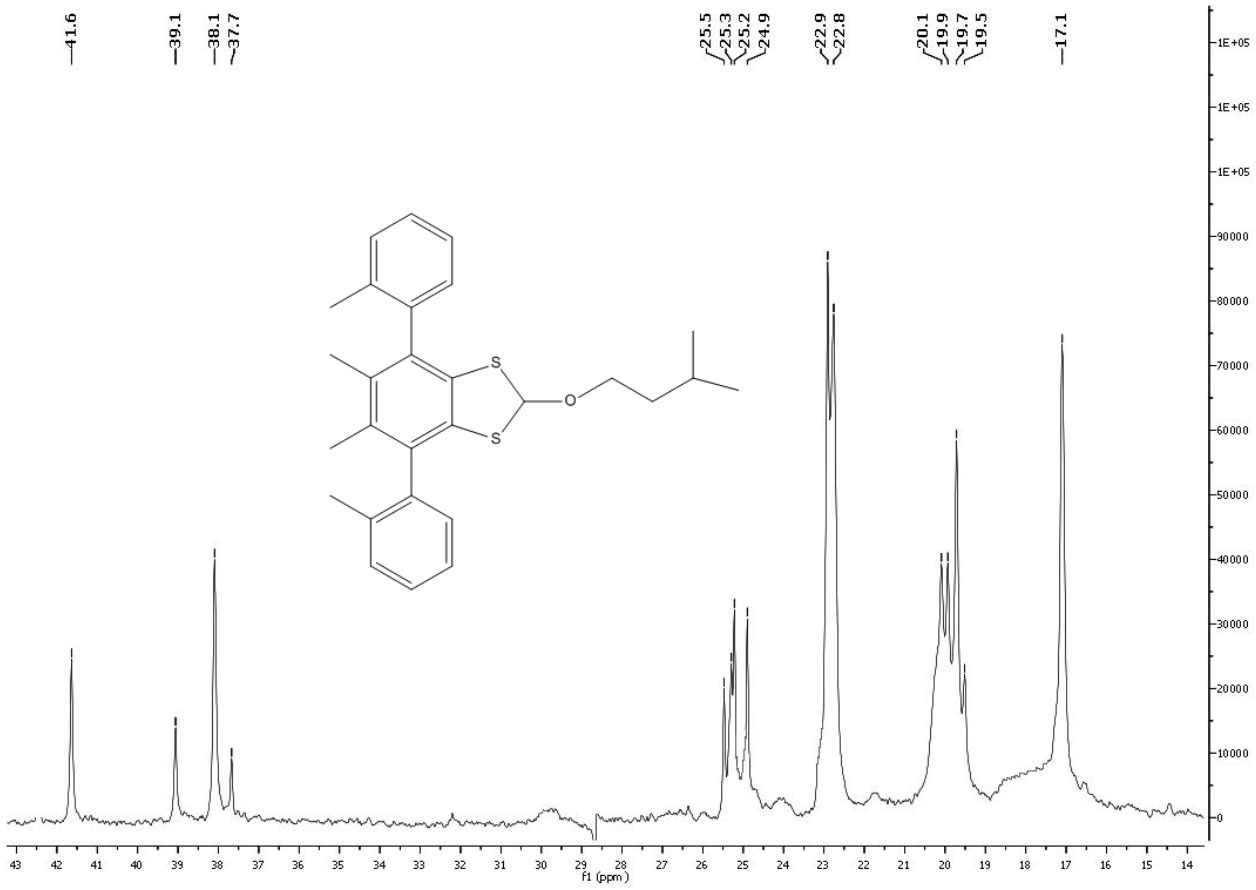
Expansion between 142-125 ppm



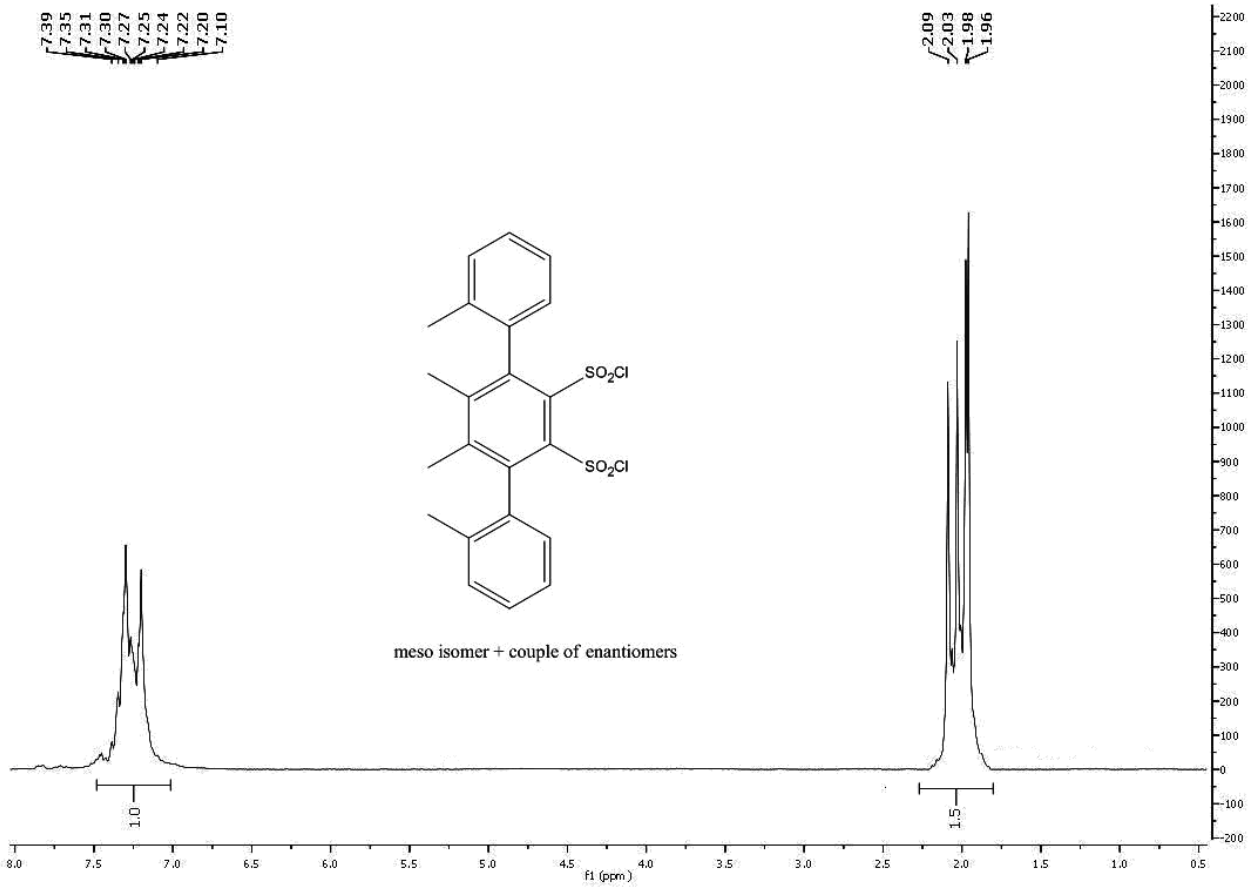
Expansion between 90-85 ppm

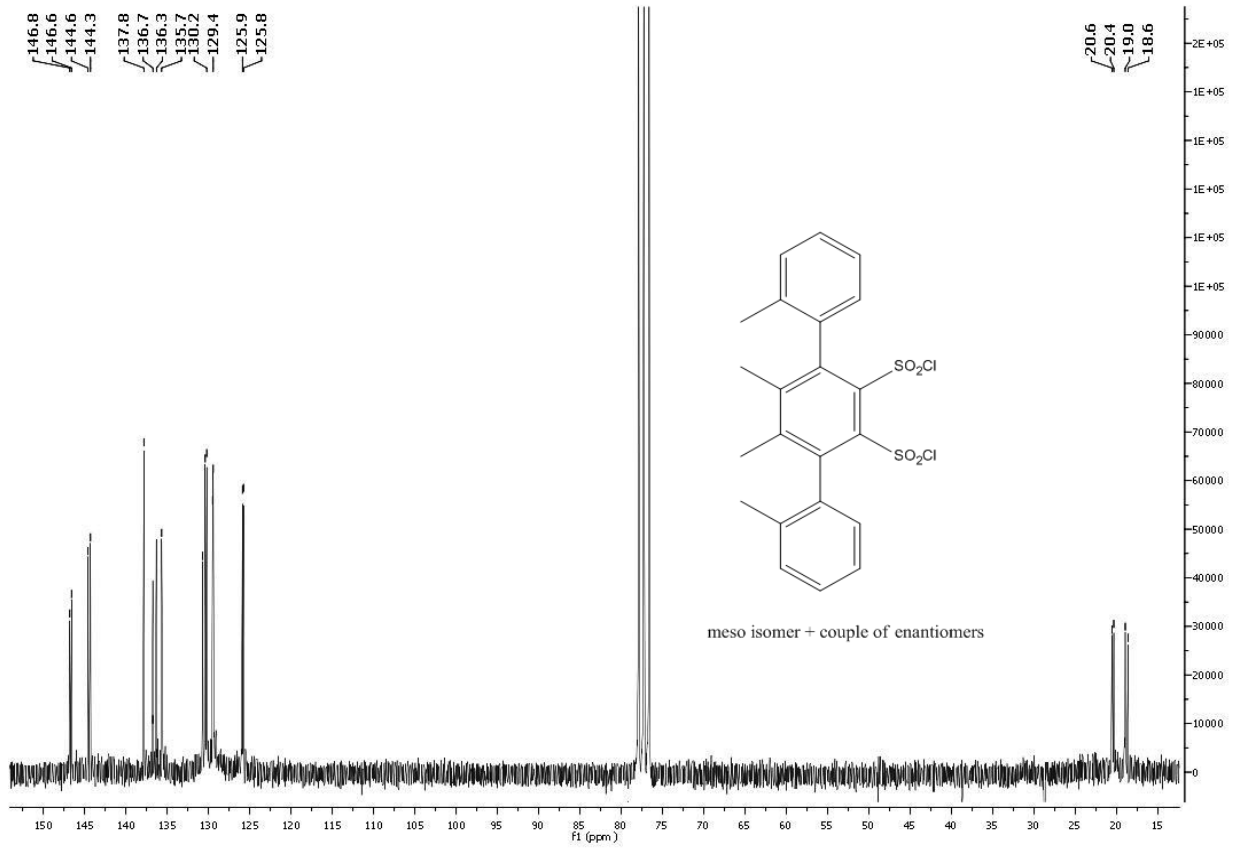


Expansion between 43-14 ppm

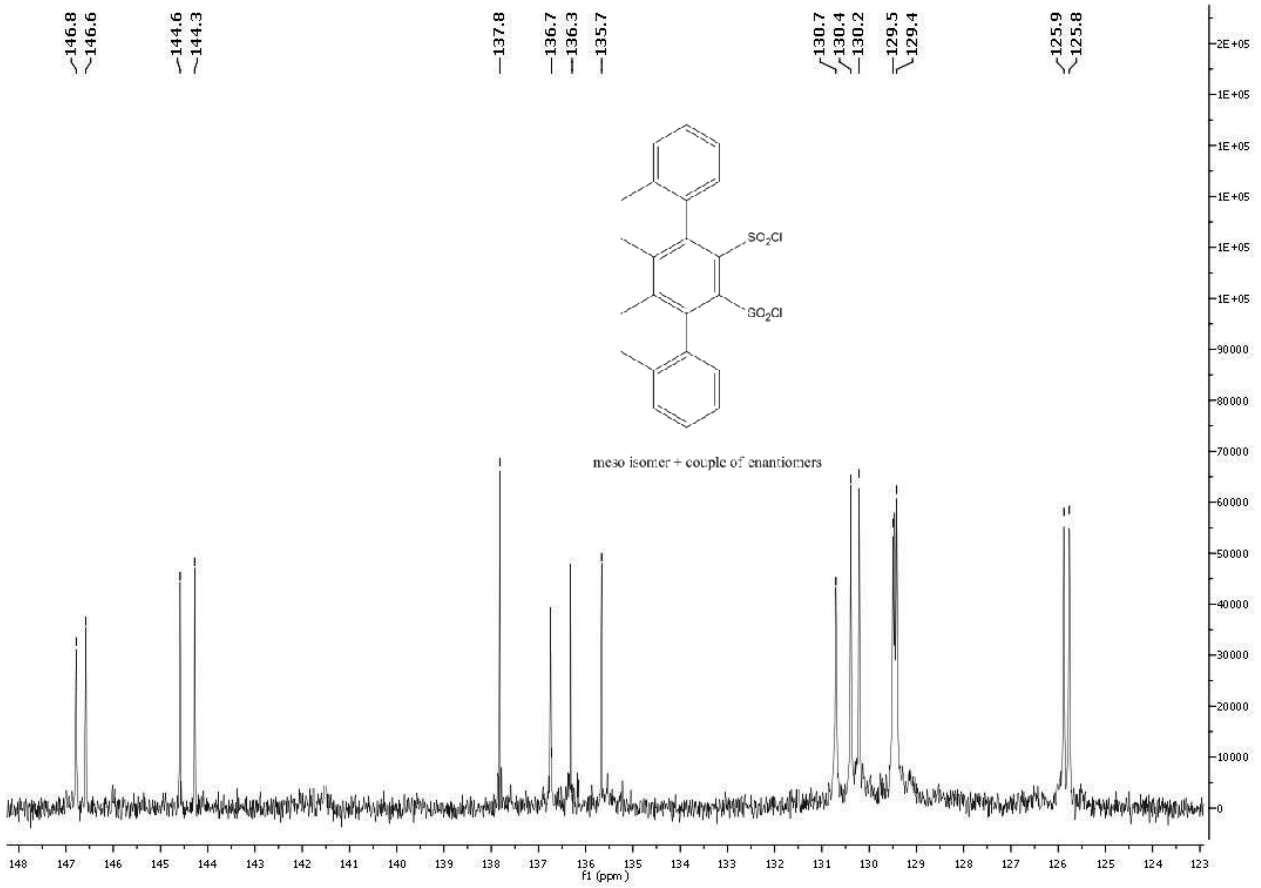


11.18 4,5-Dimethyl-3,6-bis(*o*-tolyl)-1,2-benzenedisulfonyl chloride (mixture of meso form and couple of atropisomers; 14b)

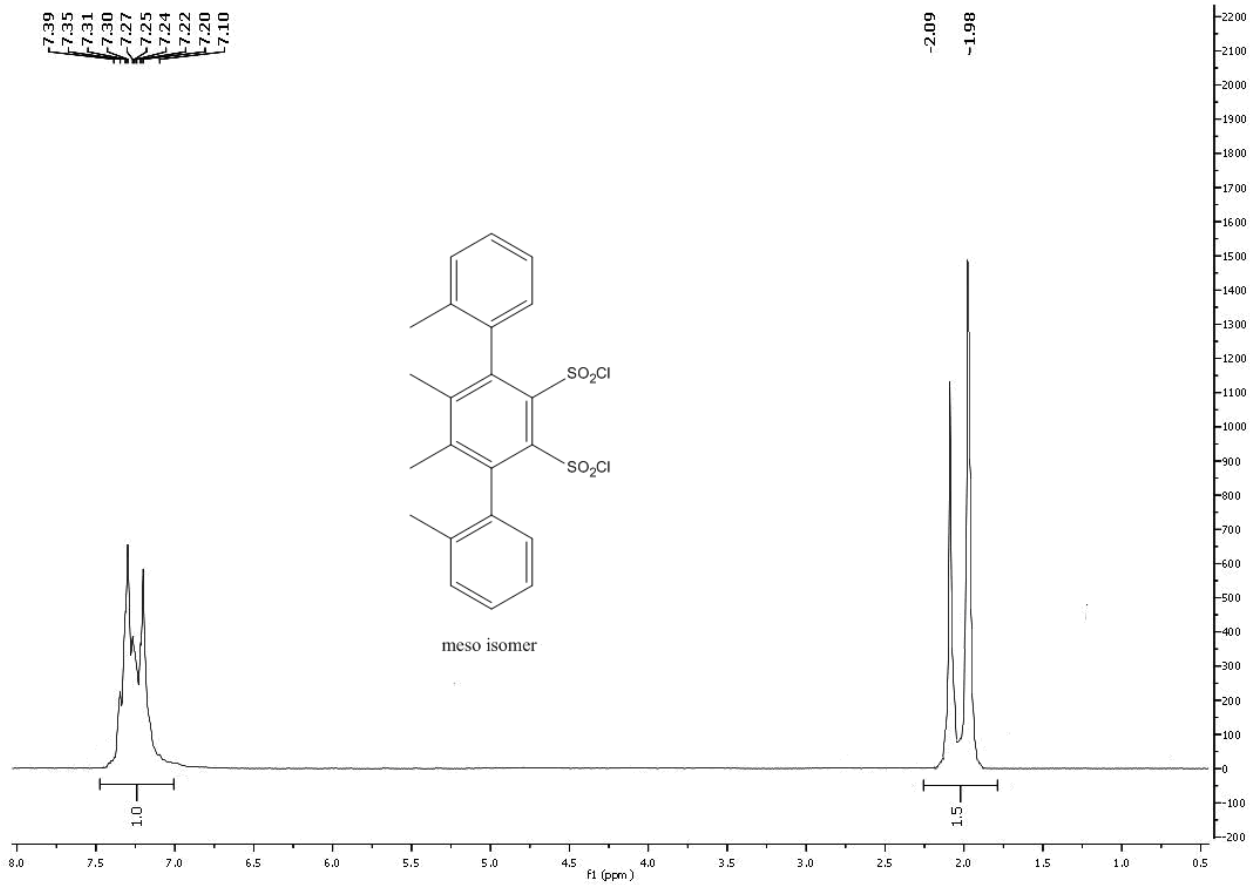


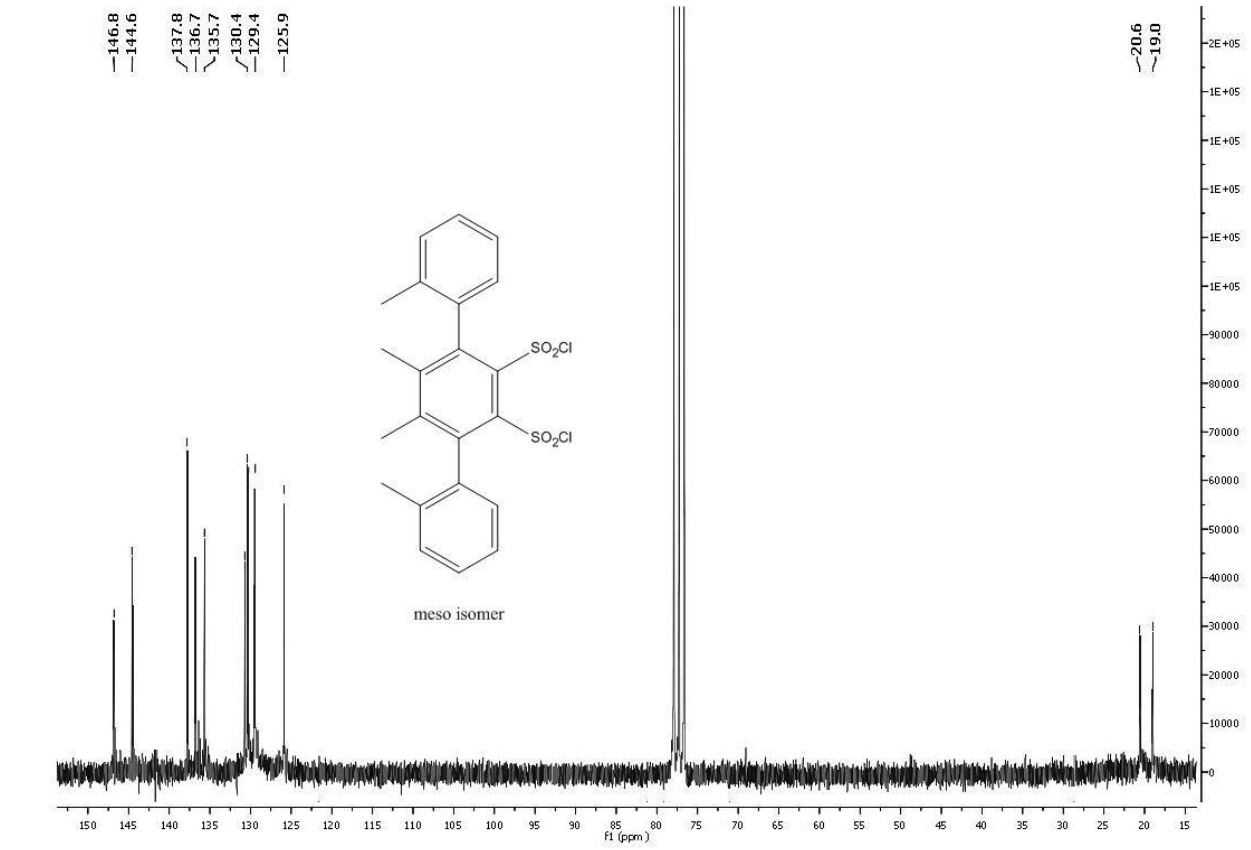


Expansion between 148-123 ppm

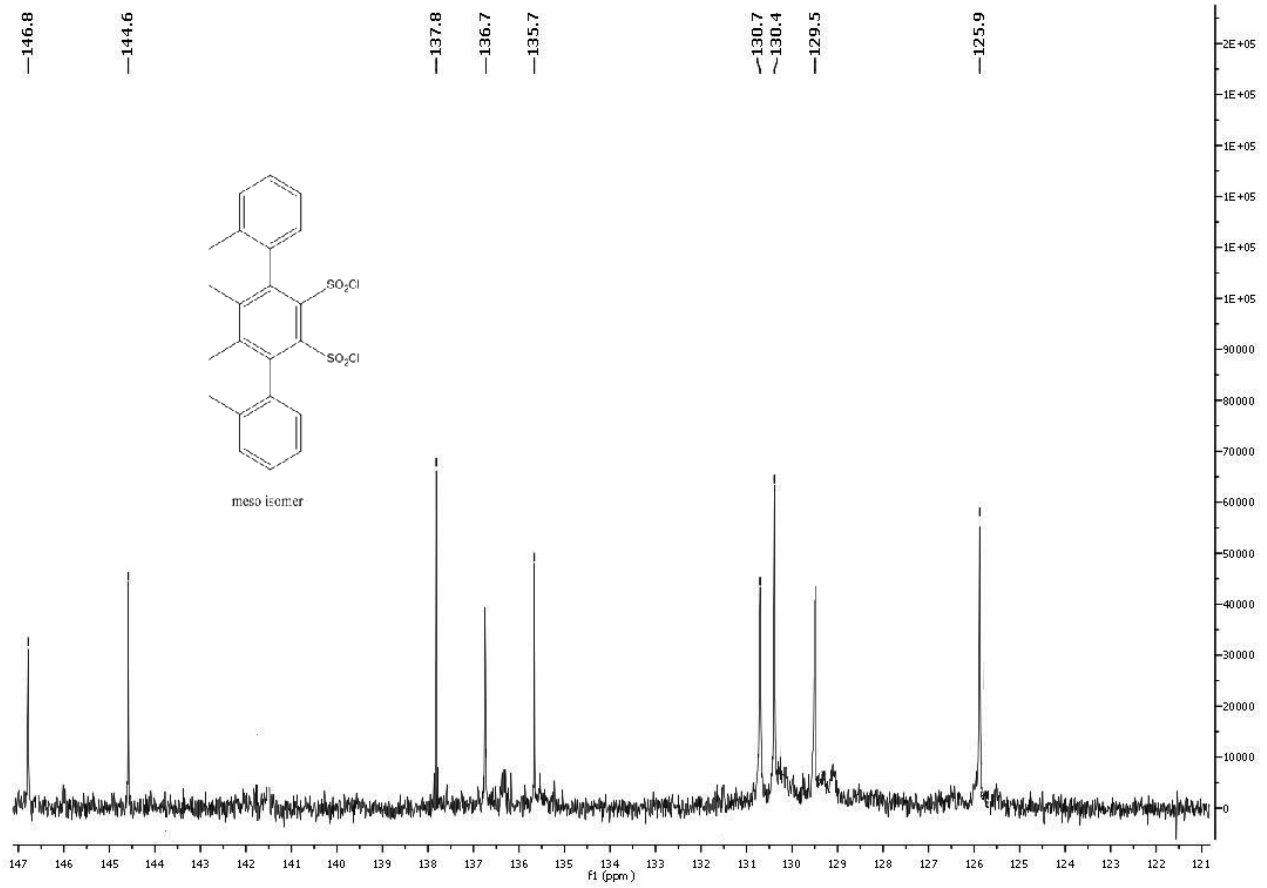


11.19 *meso* 4,5-Dimethyl-3,6-bis(*o*-tolyl)-1,2-benzenedisulfonyl chloride (14b)

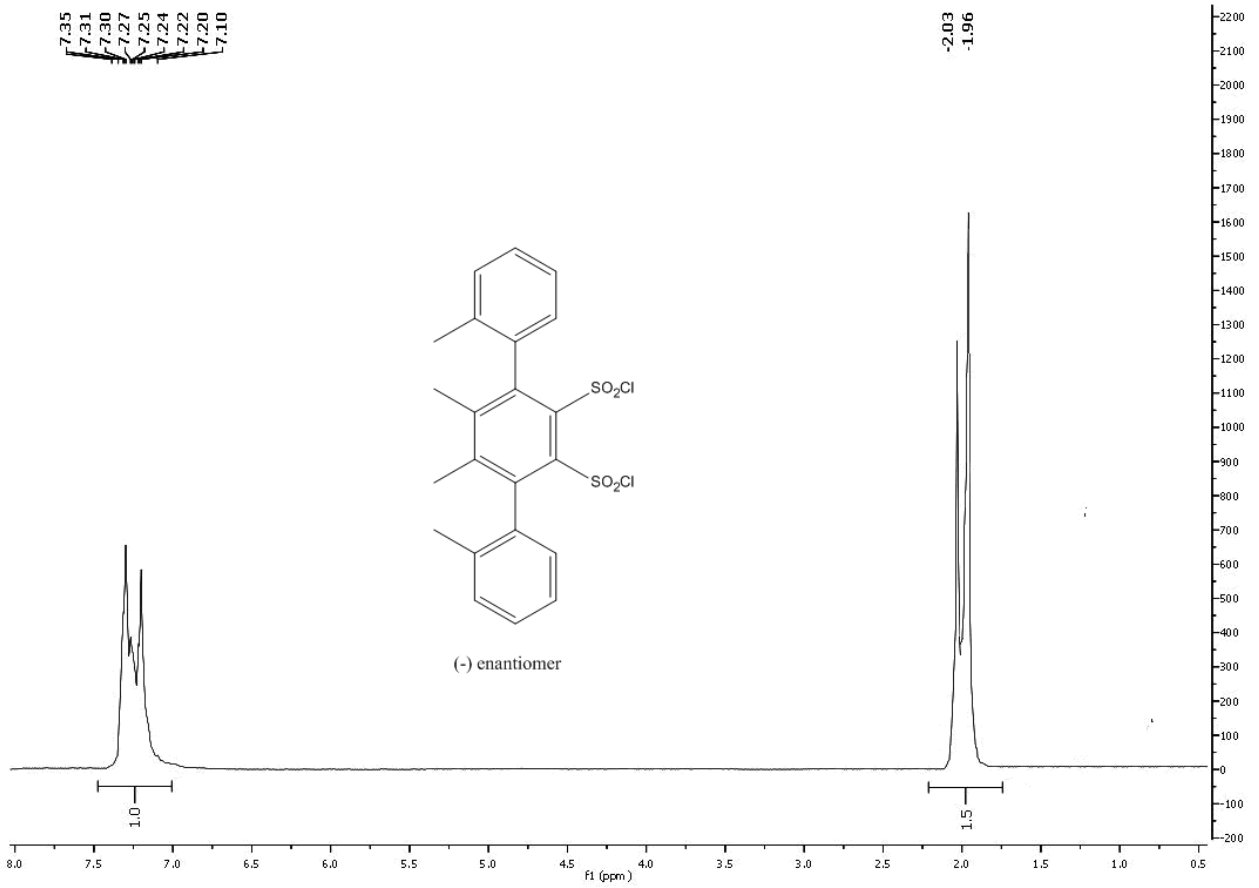


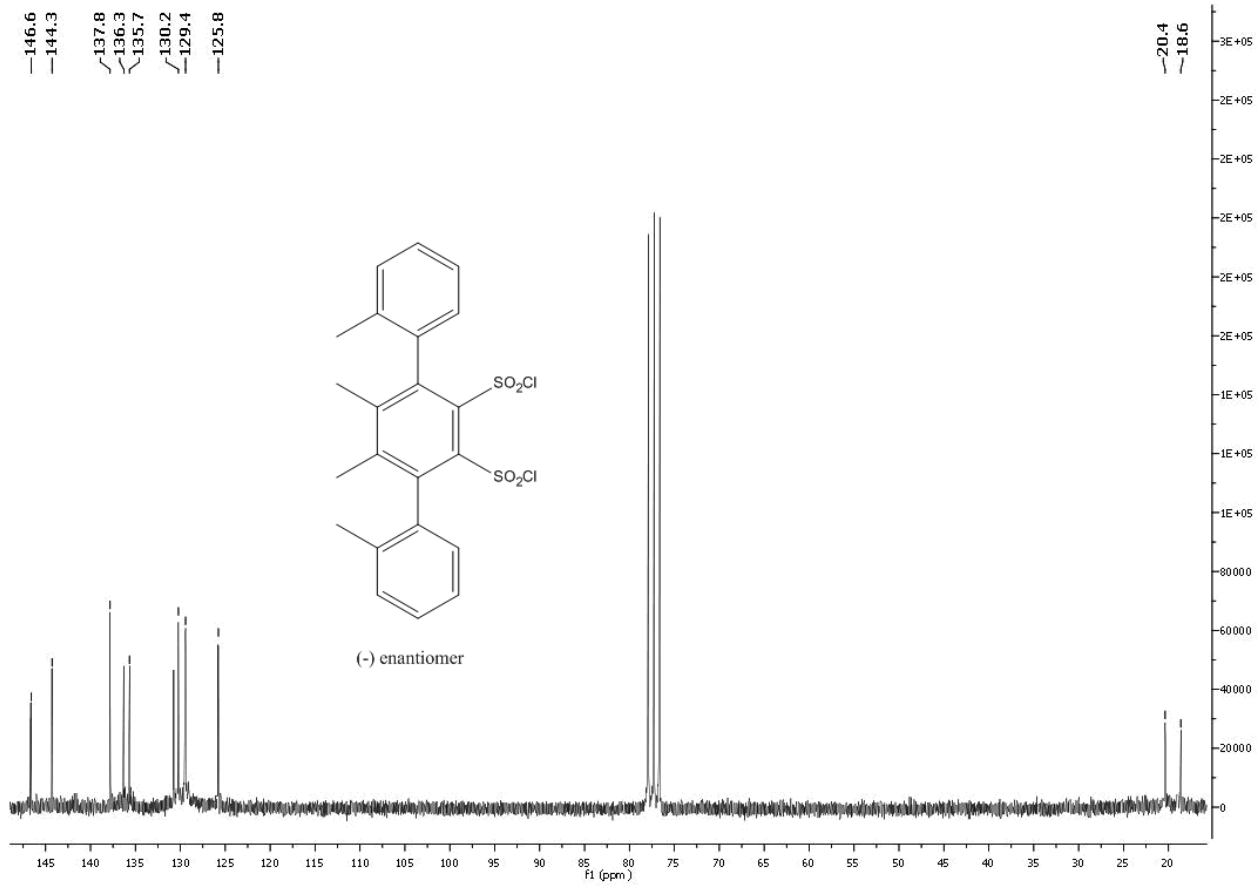


Expansion between 147-121 ppm

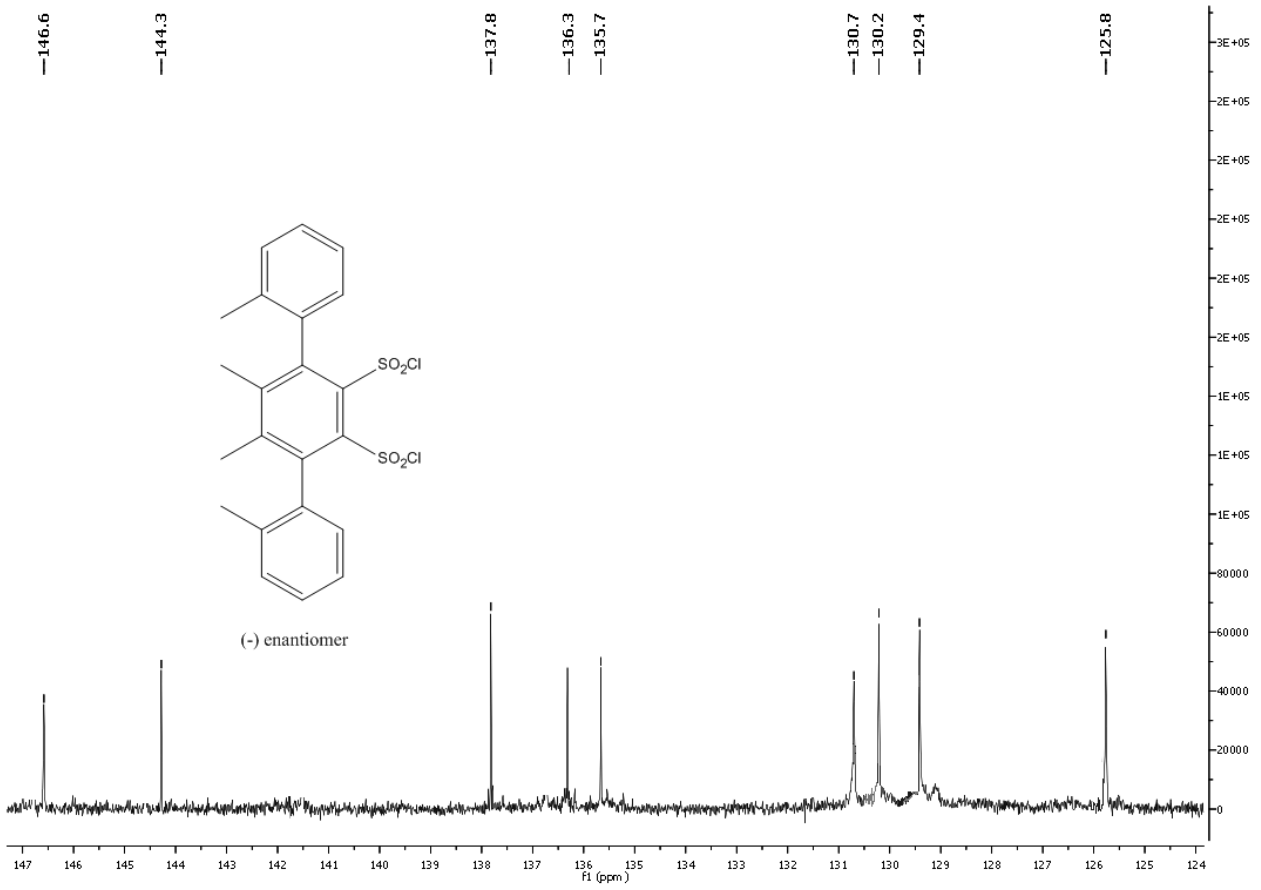


11.20 (-) 4,5-Dimethyl- 3,6-(bis-2-tolyl)-1,2-benzenedisulfonyl chloride (14b)

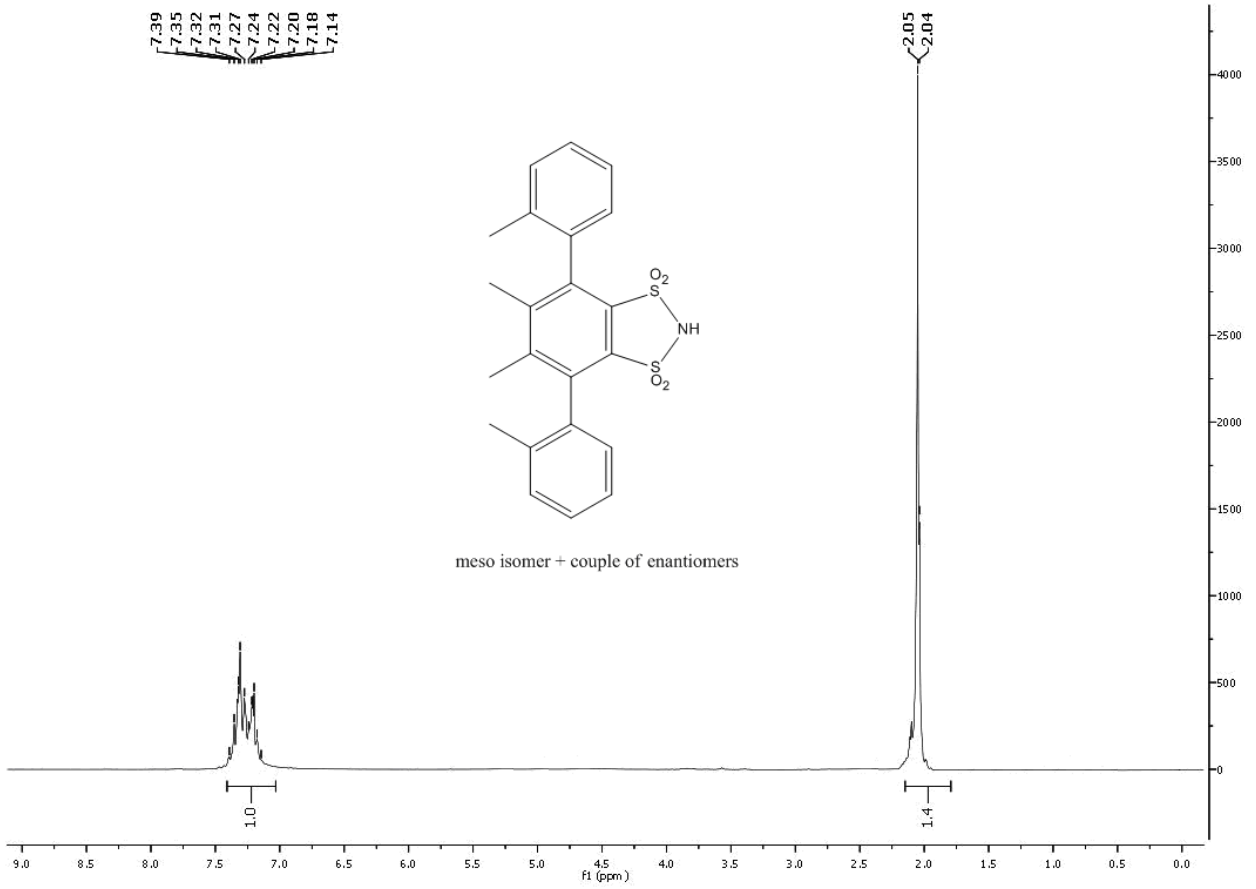


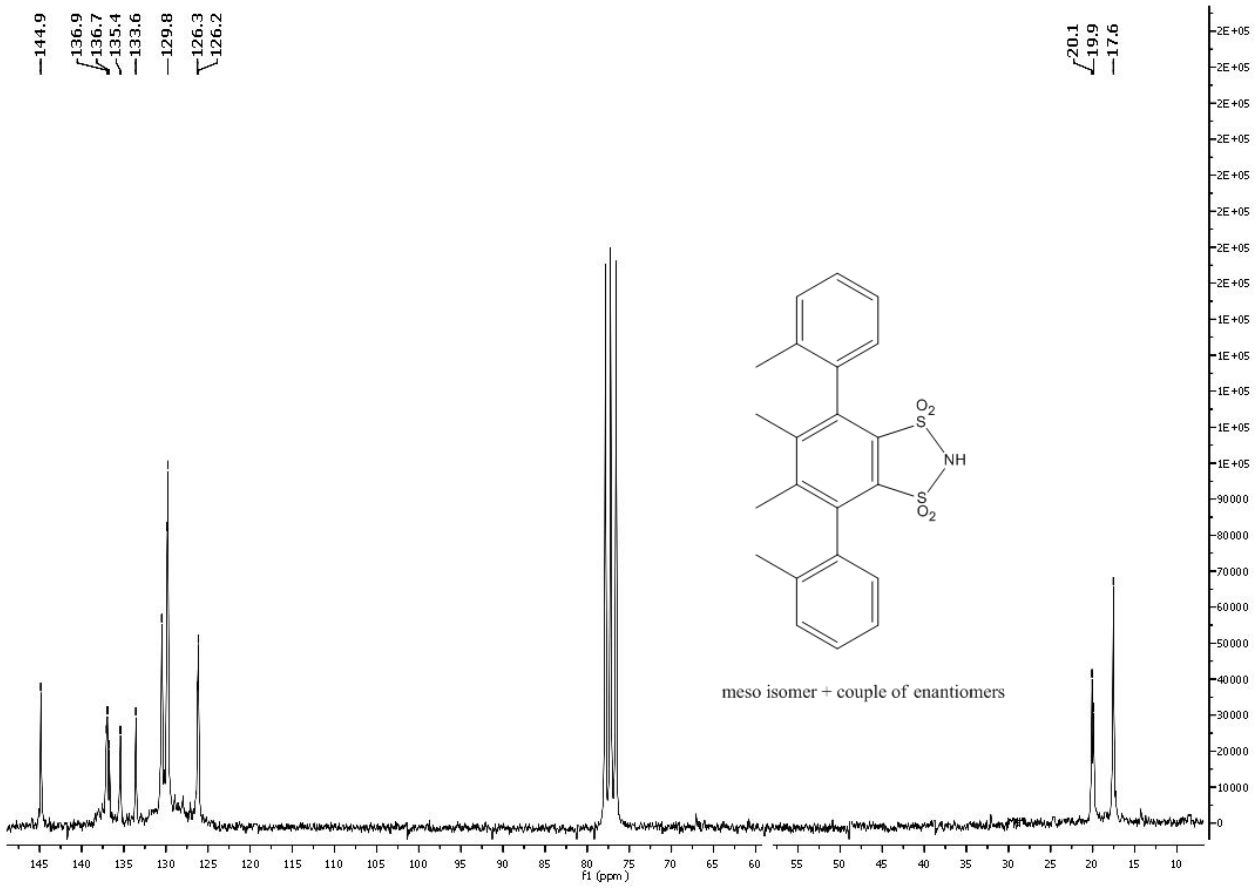


Expansion between 147-124 ppm

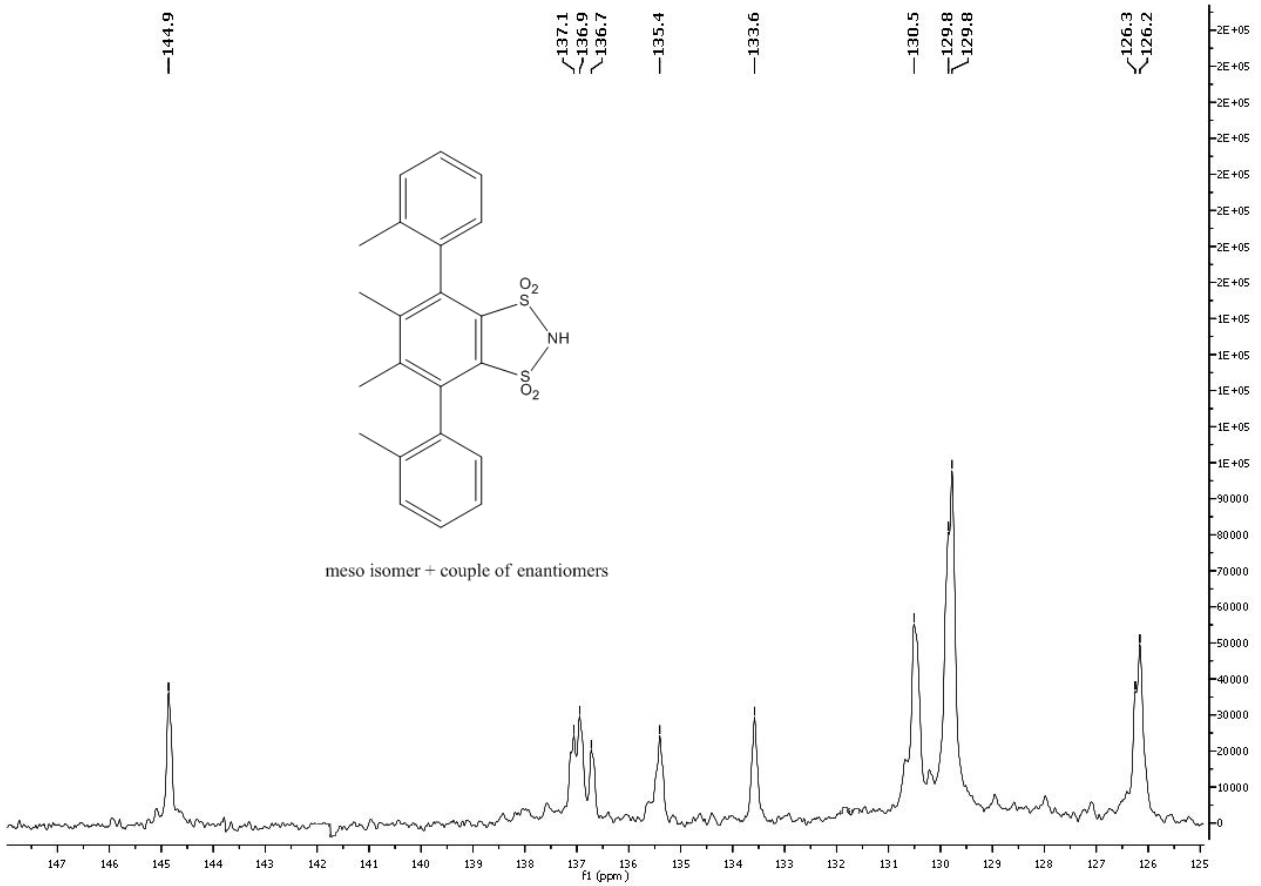


11.21 4,5-Dimethyl- 3,6-bis(*o*-tolyl)-1,2-benzenedisulfonimide (mixture of meso form and couple of atropisomers (3b)

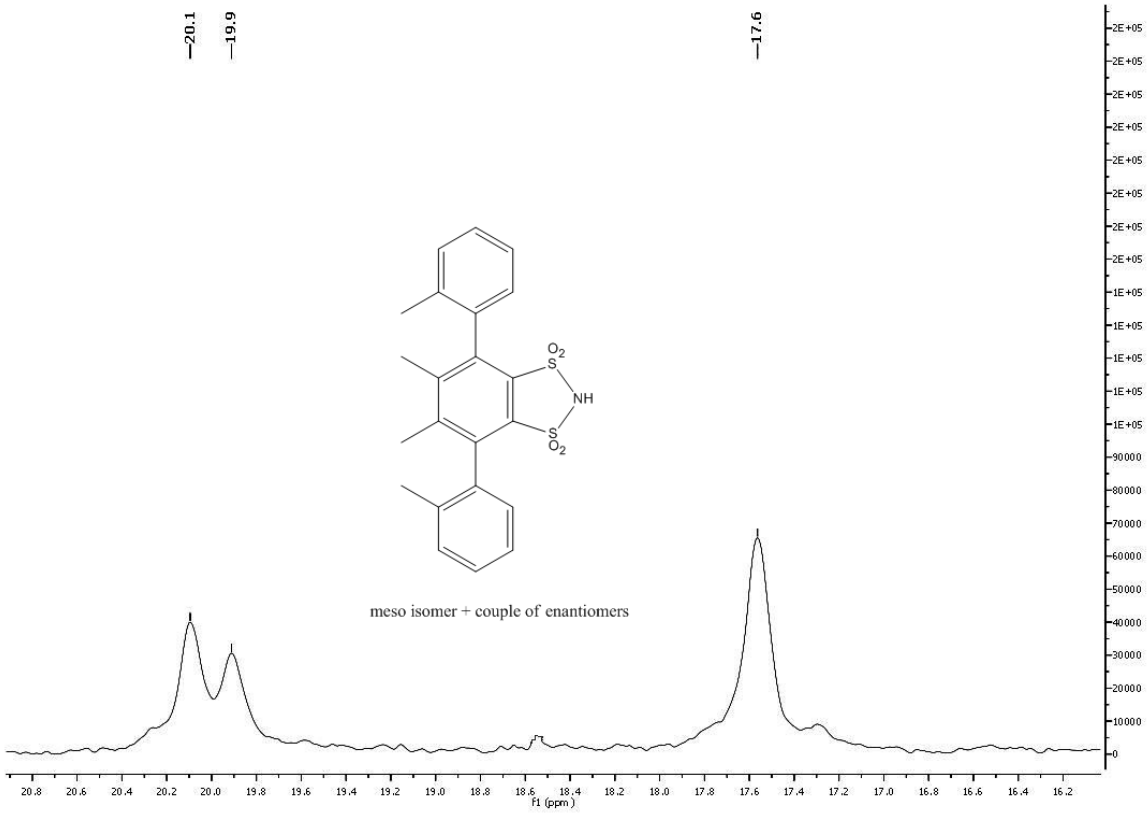




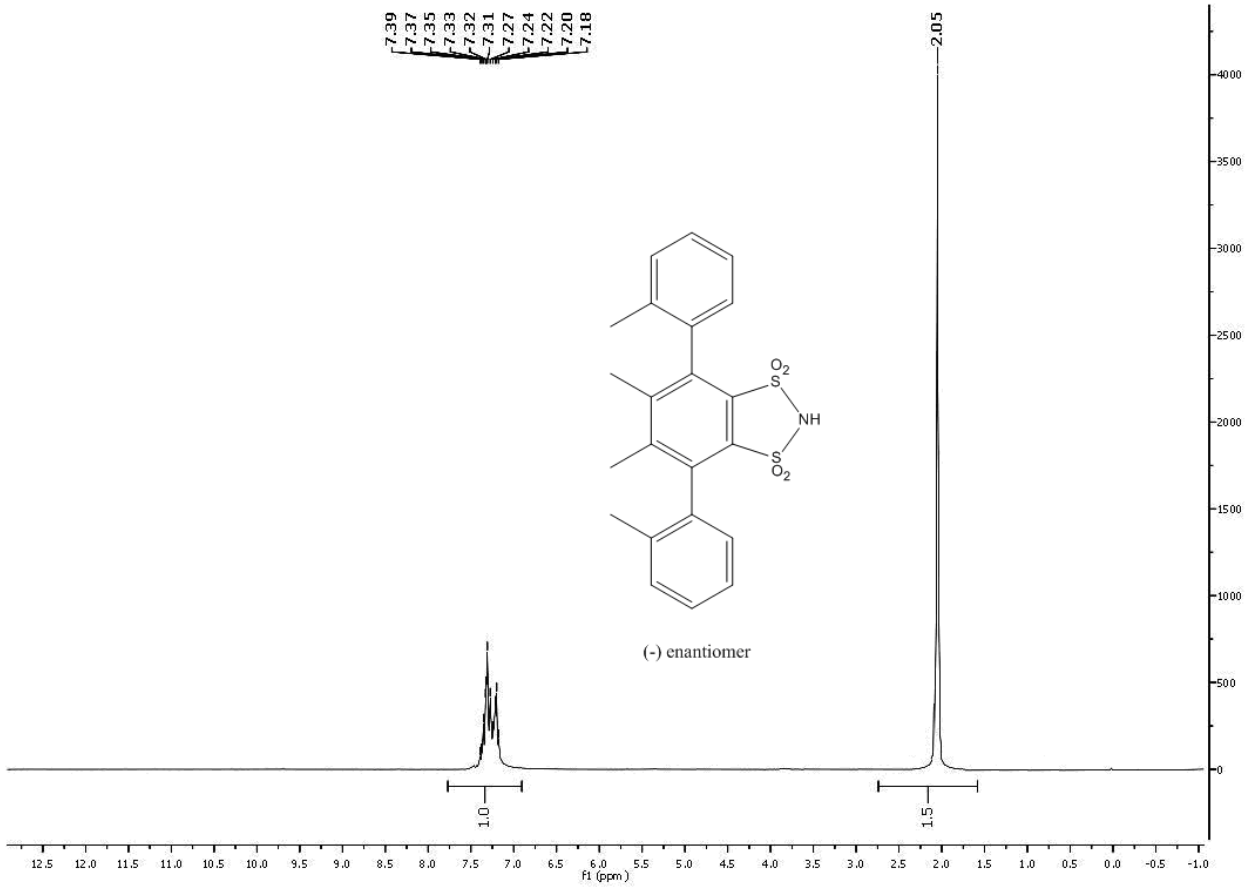
Expansion between 147-125 ppm

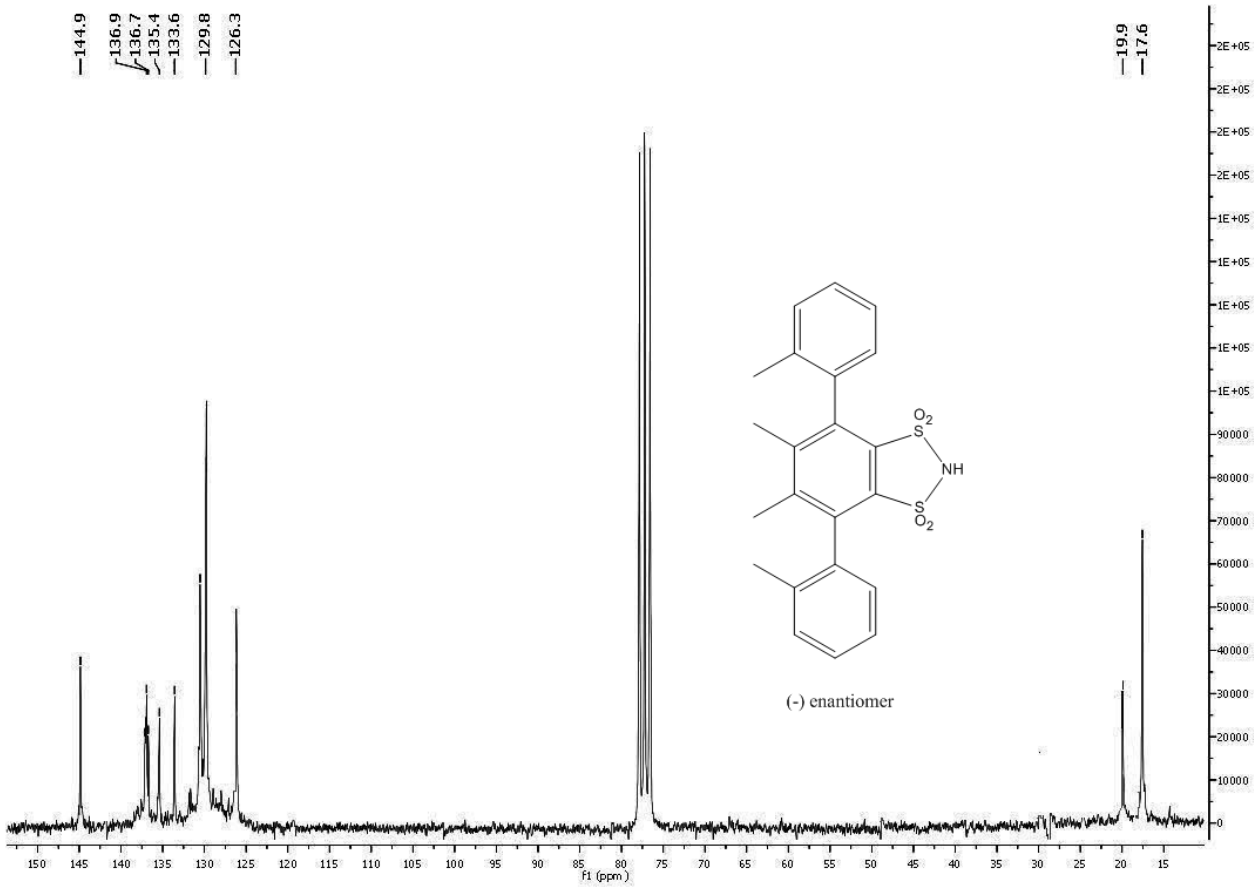


Expansion between 21-16 ppm

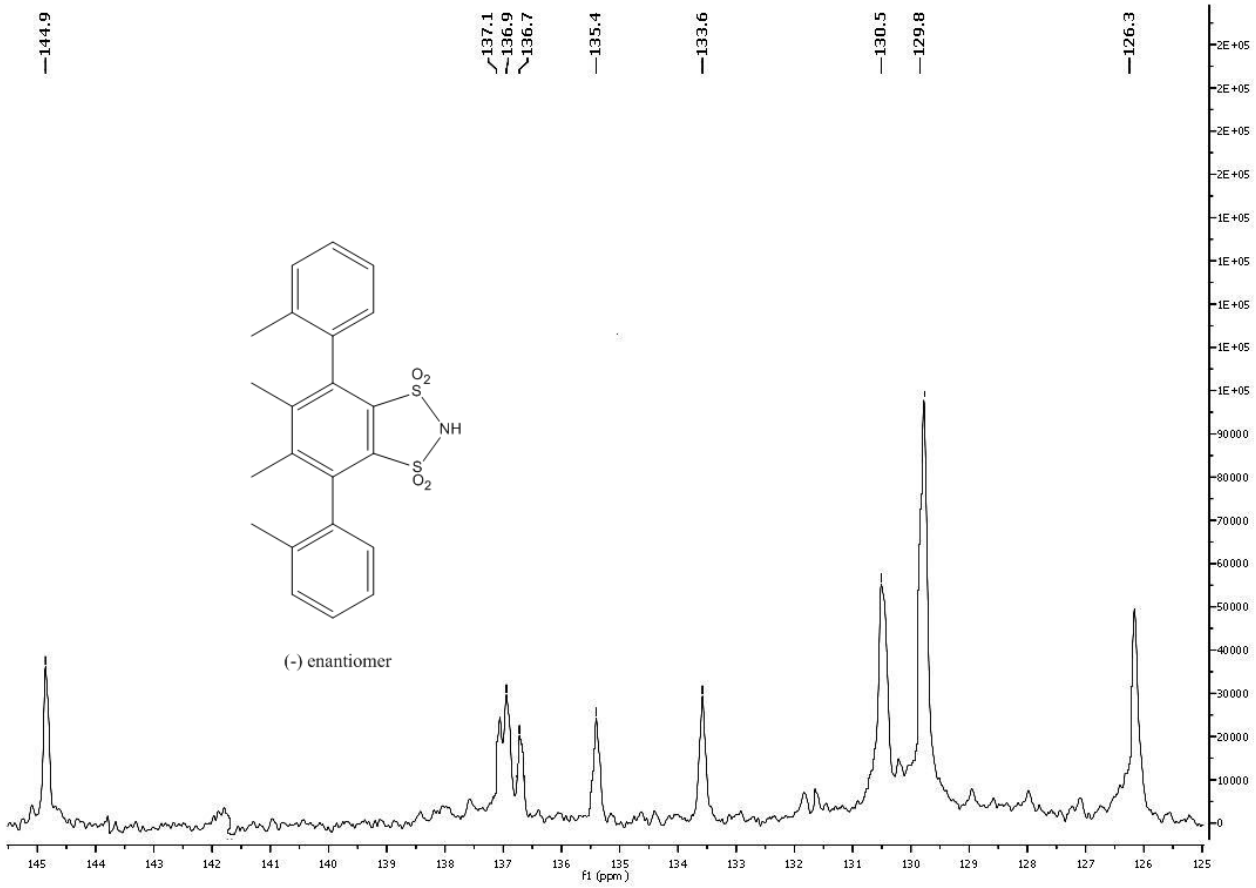


11.22 (-) 4,5-Dimethyl- 3,6-bis(*o*-tolyl)-1,2-benzenedisulfonimide (3b)

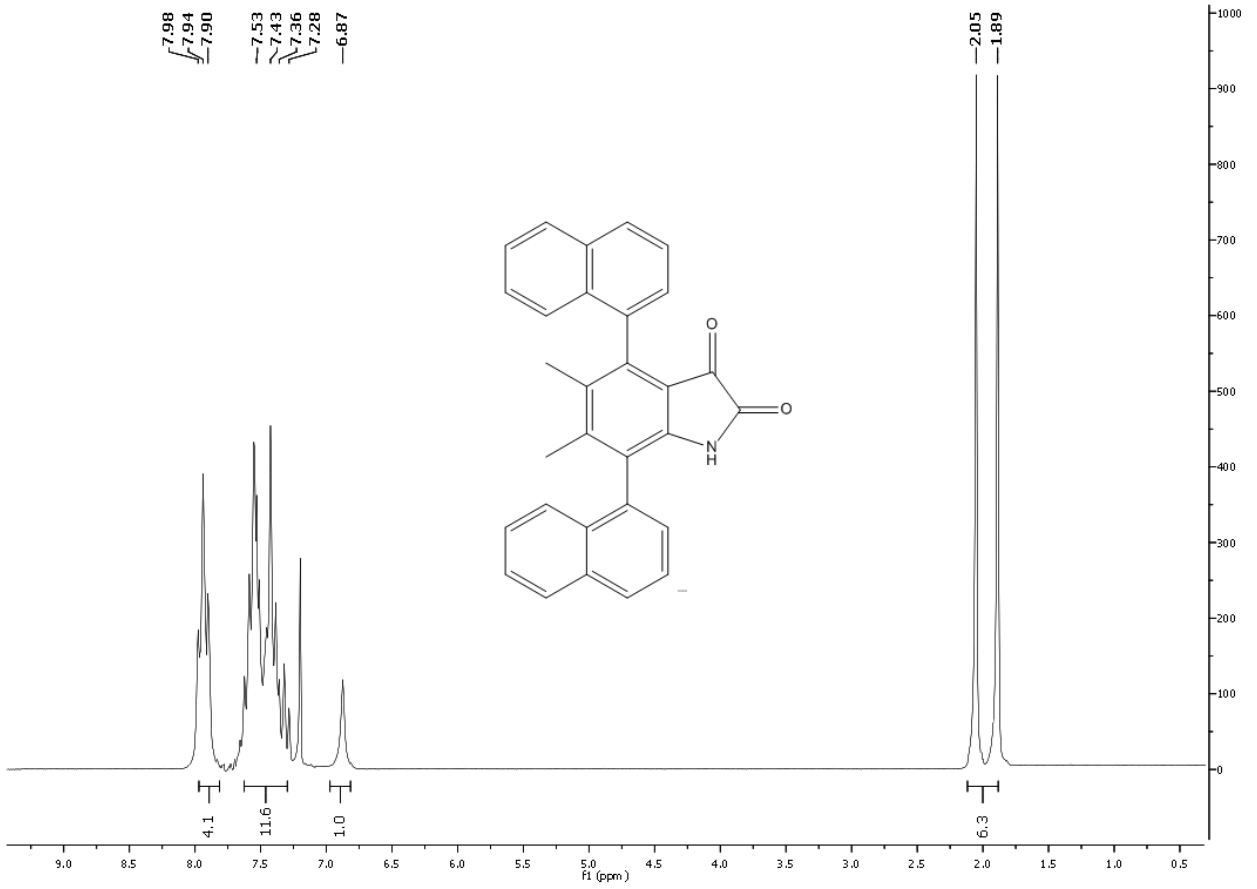


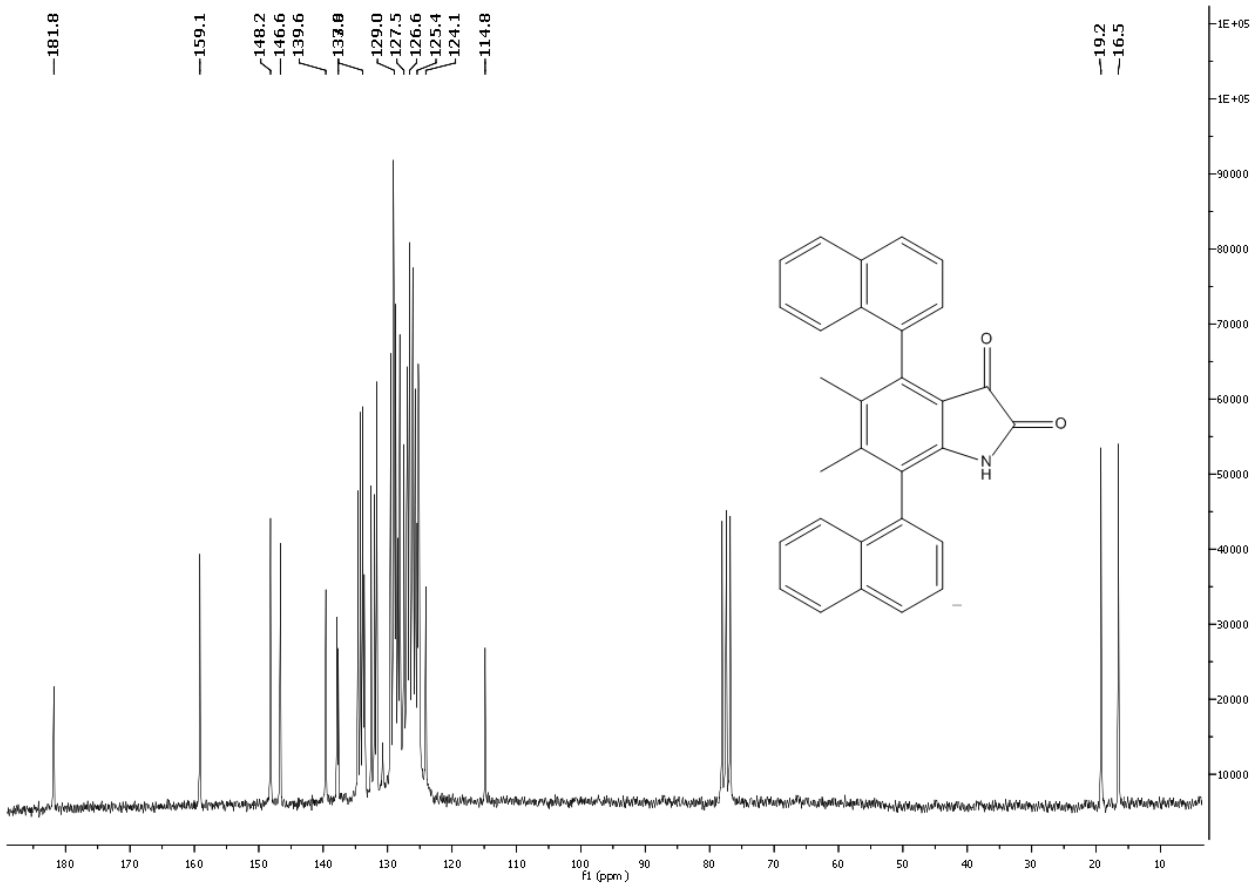


Expansion between 146-125 ppm

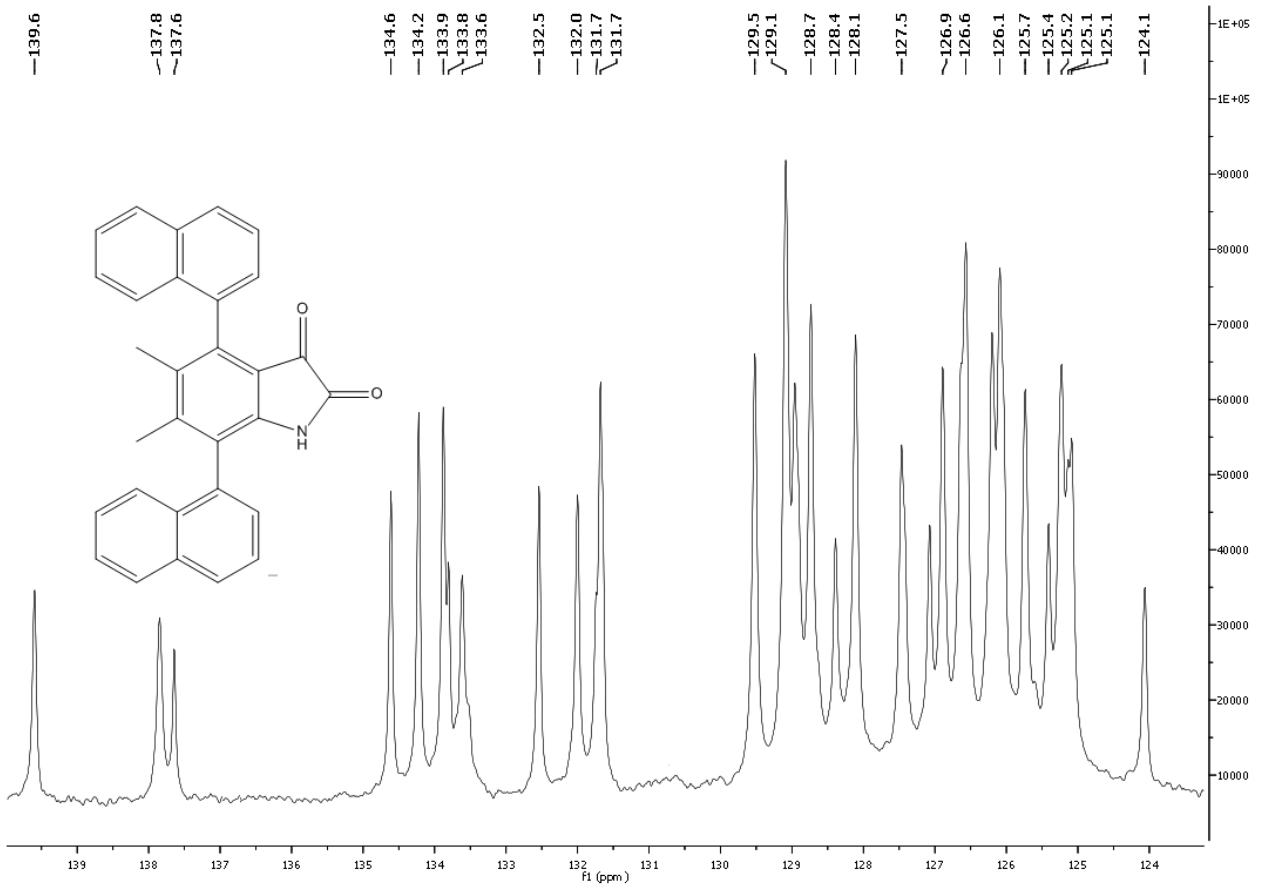


11.23 5,6-Dimethyl-4,7-bis(1-naphthyl)isatine (11c)

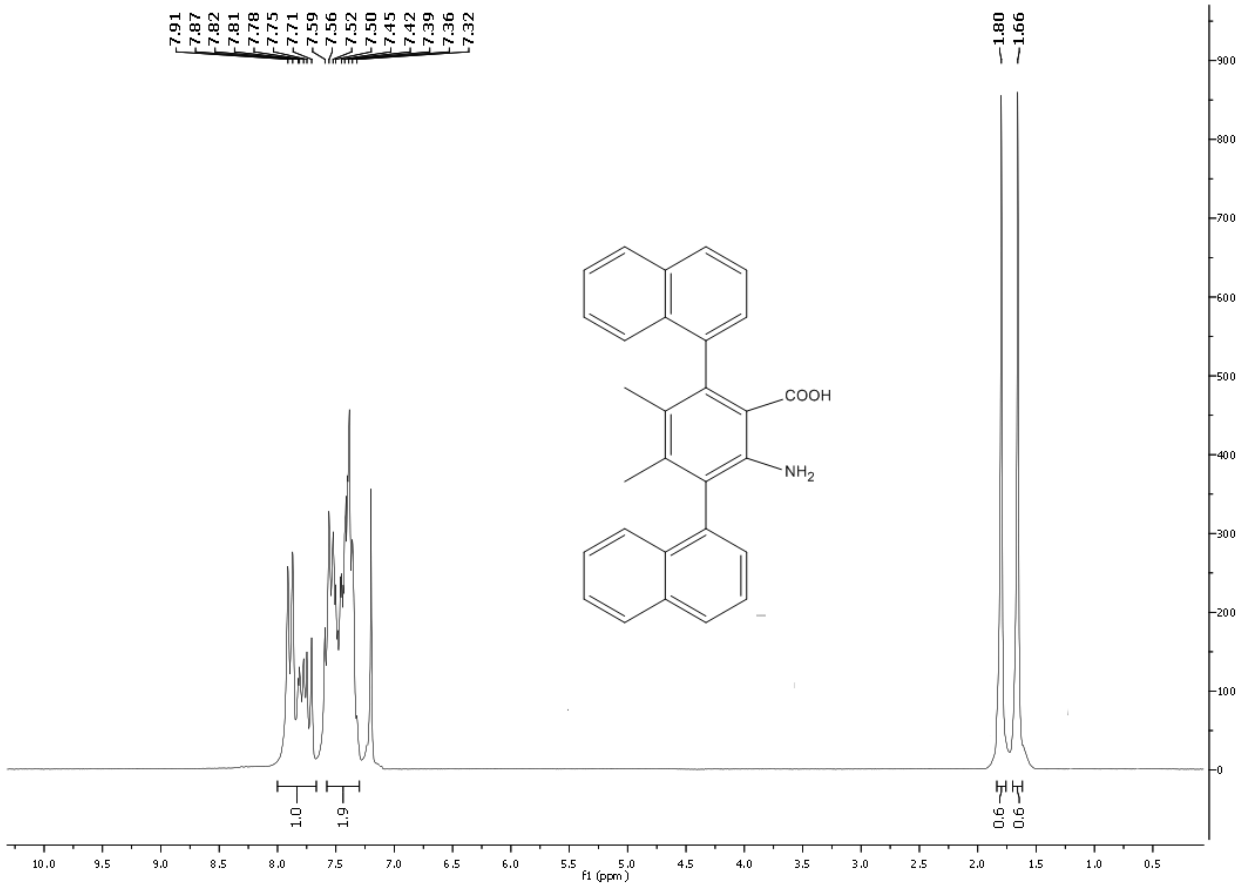


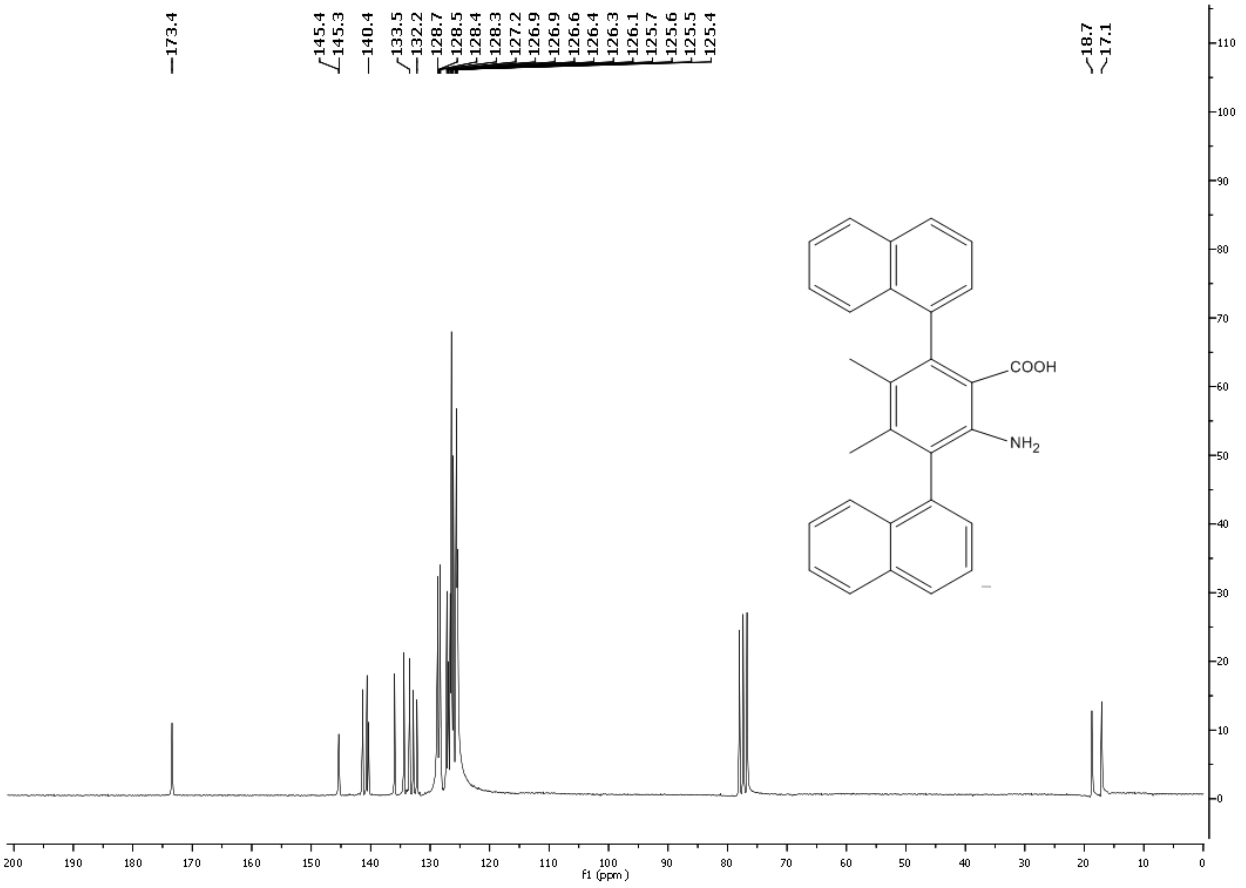


Expansion between 139-124 ppm

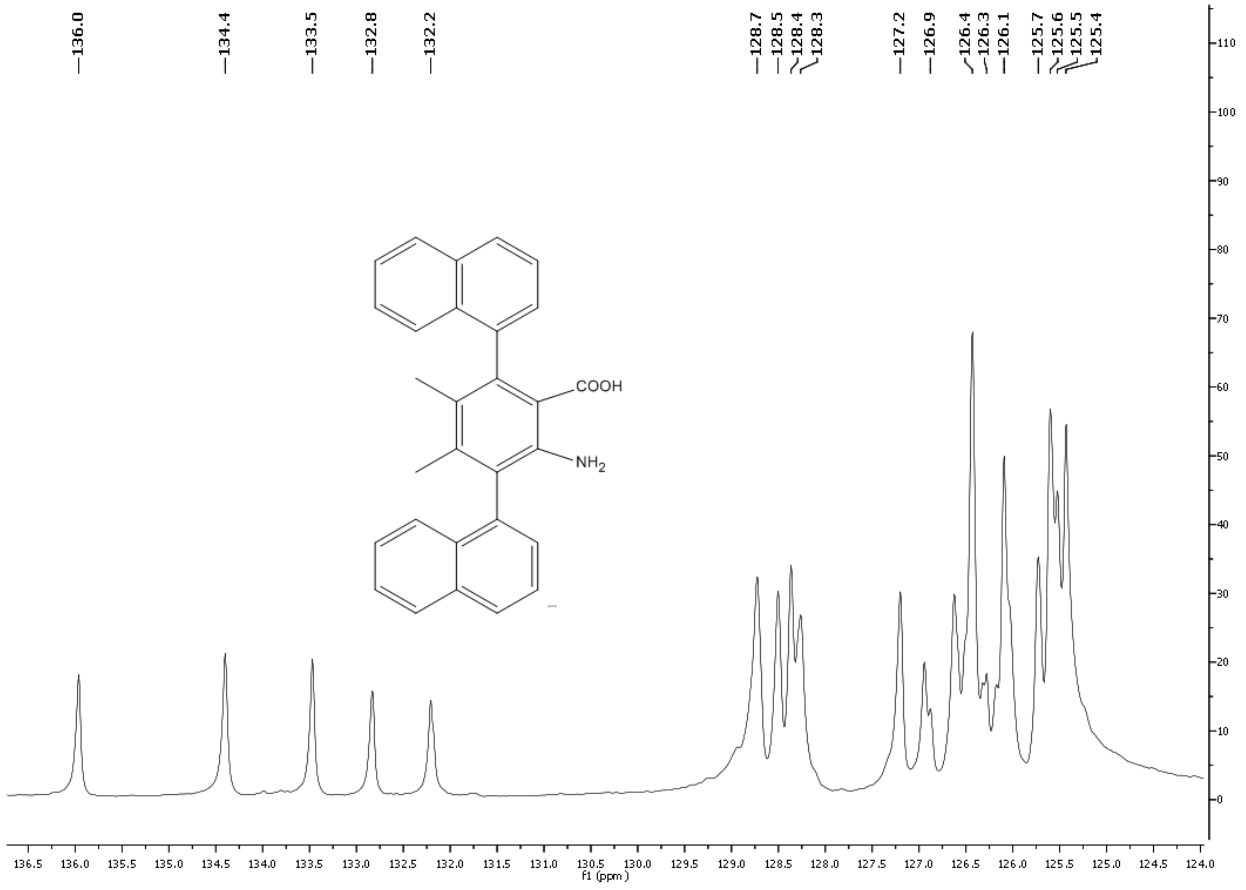


11.24 2-Amino-4,5-dimethyl-3,6-bis(1-naphthyl)benzoic acid (12c)

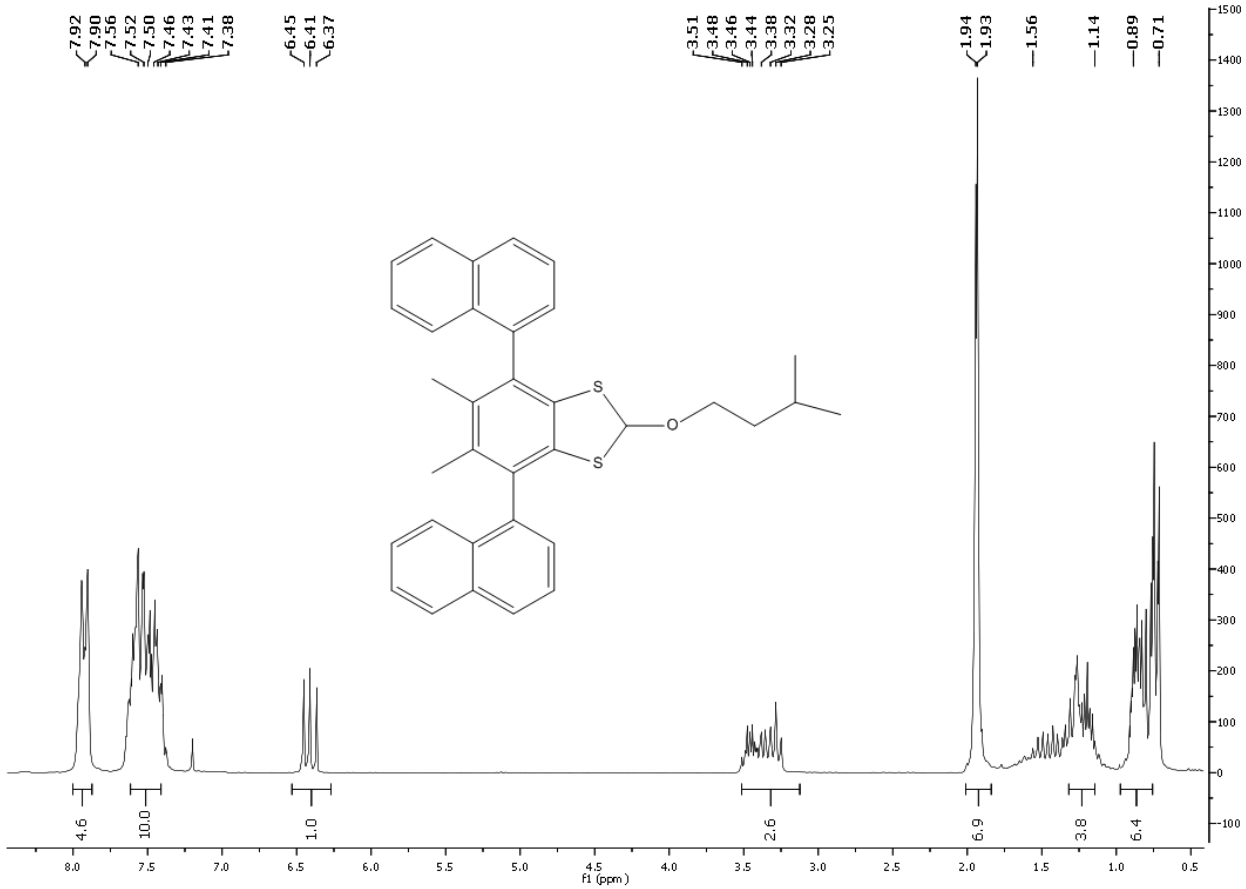


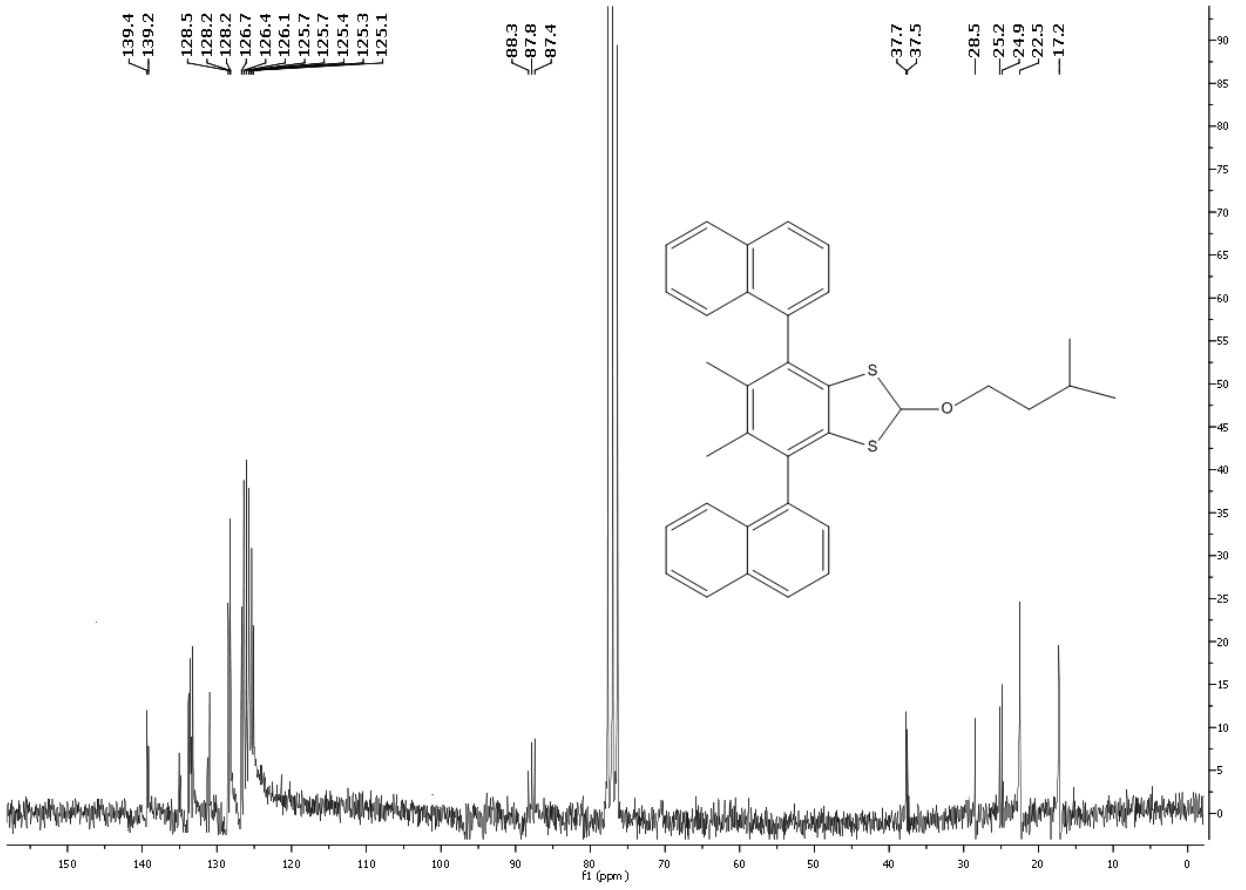


Expansion between 136-124 ppm

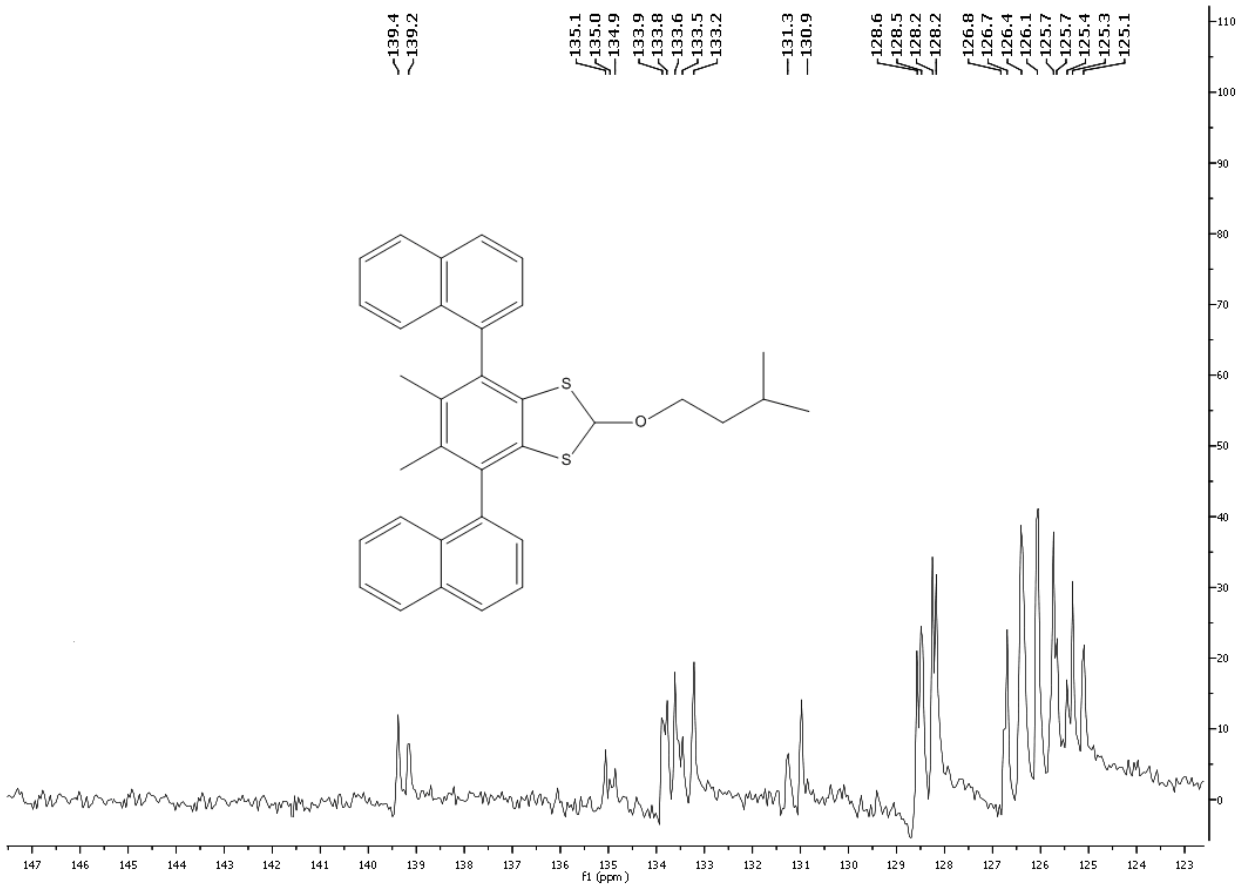


11.25 5,6-Dimethyl-2-(3-methylbutoxy)- 4,7-bis(1-naphthyl)-1,3-benzodithiole (13c)

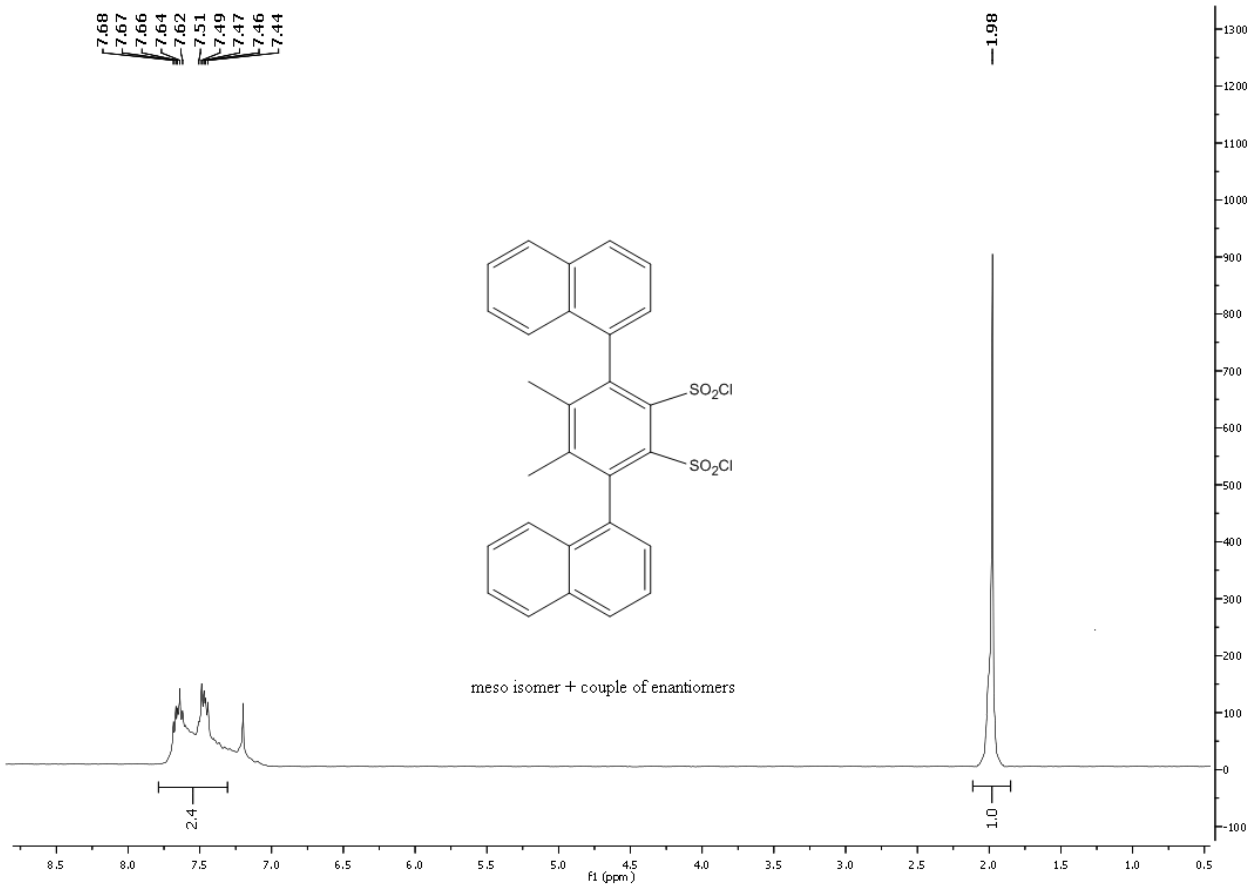


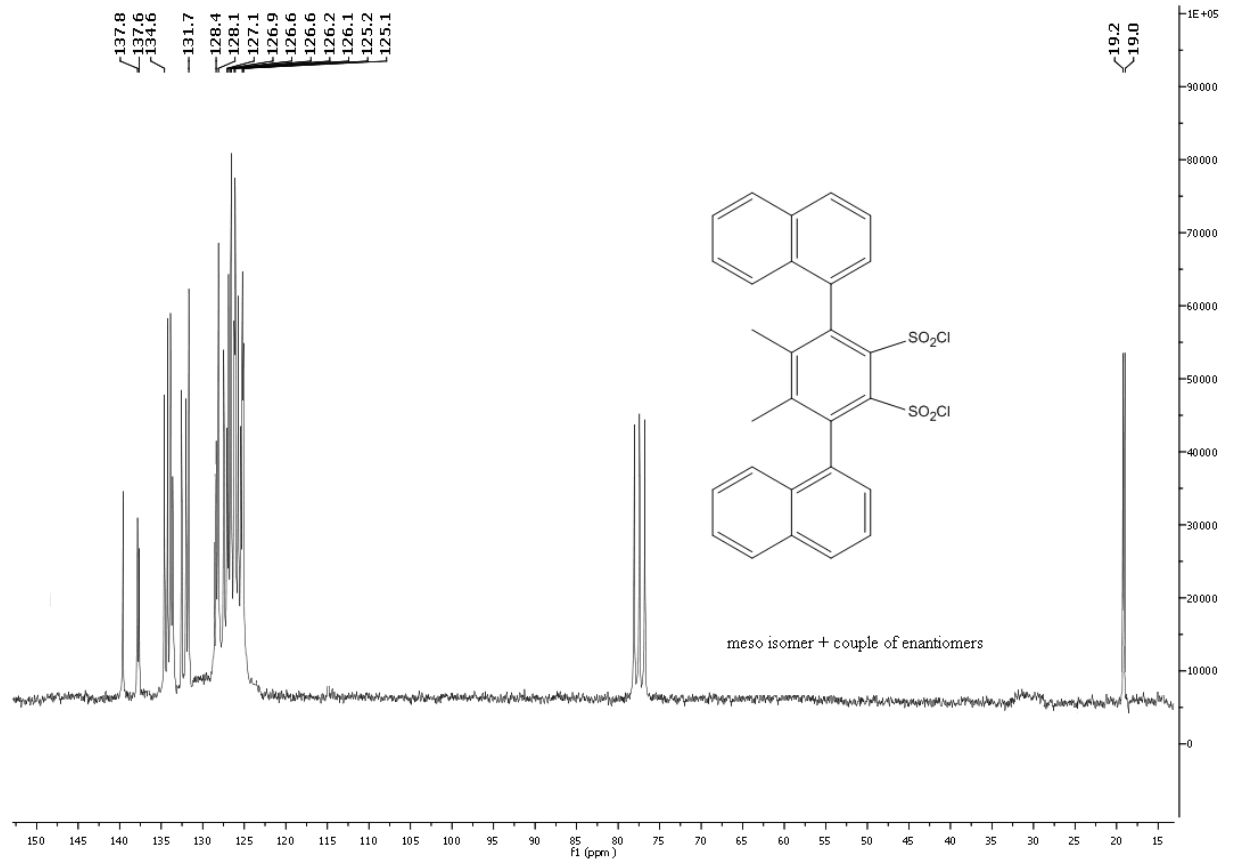


Expansion between 139-124 ppm

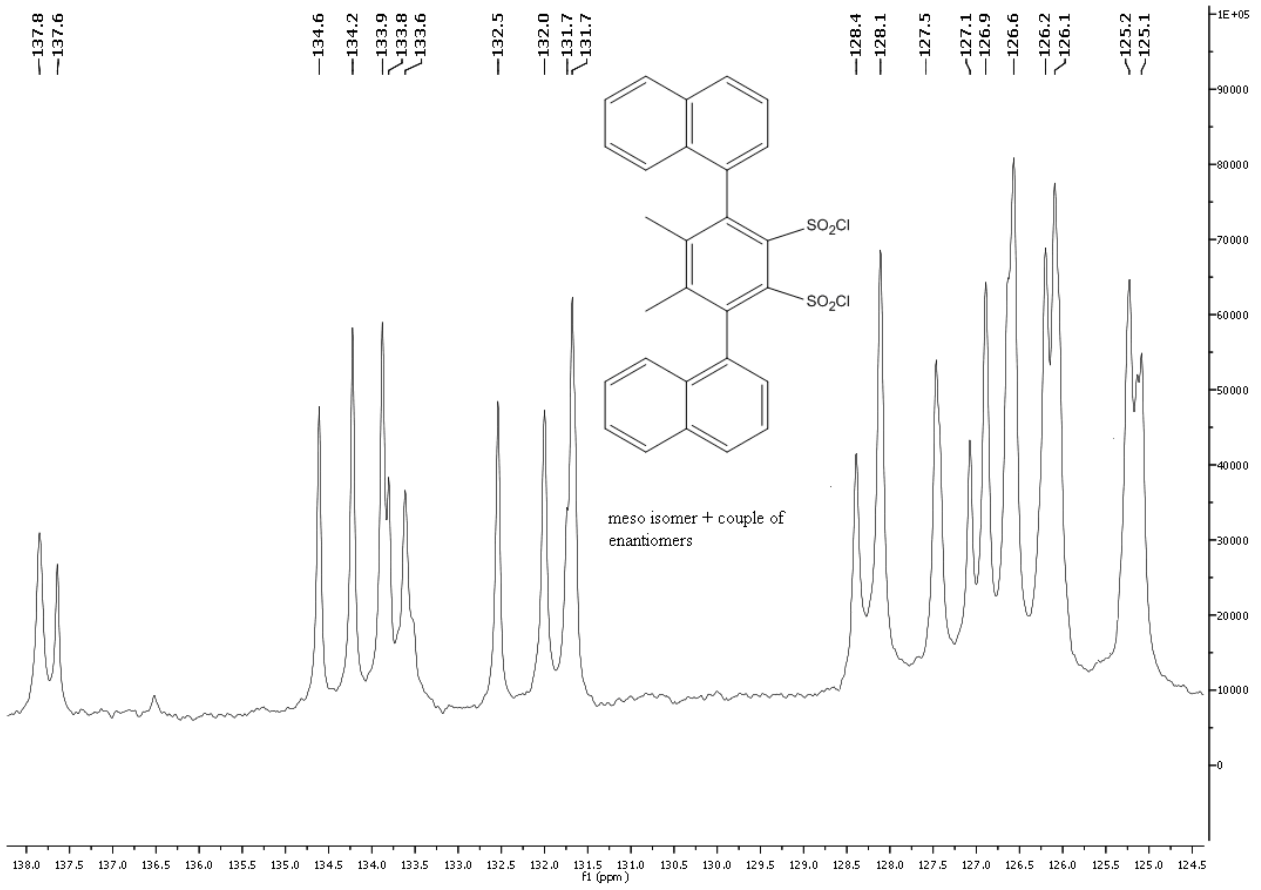


11.26 4,5-Dimethyl-3,6-bis(1-naphthyl)-1,2-benzenedisulfonyl chloride (mixture of meso form and couple of atropisomers; 14c)

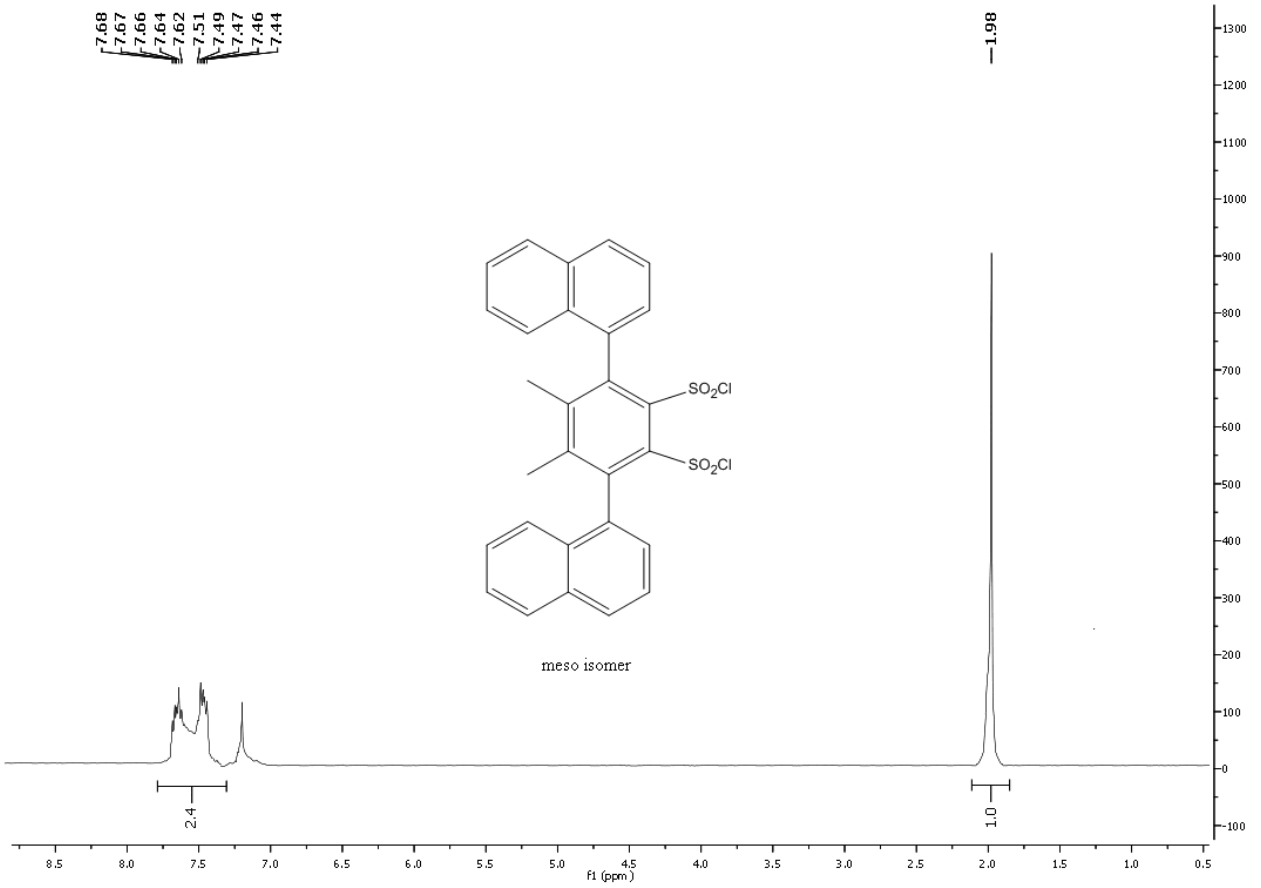


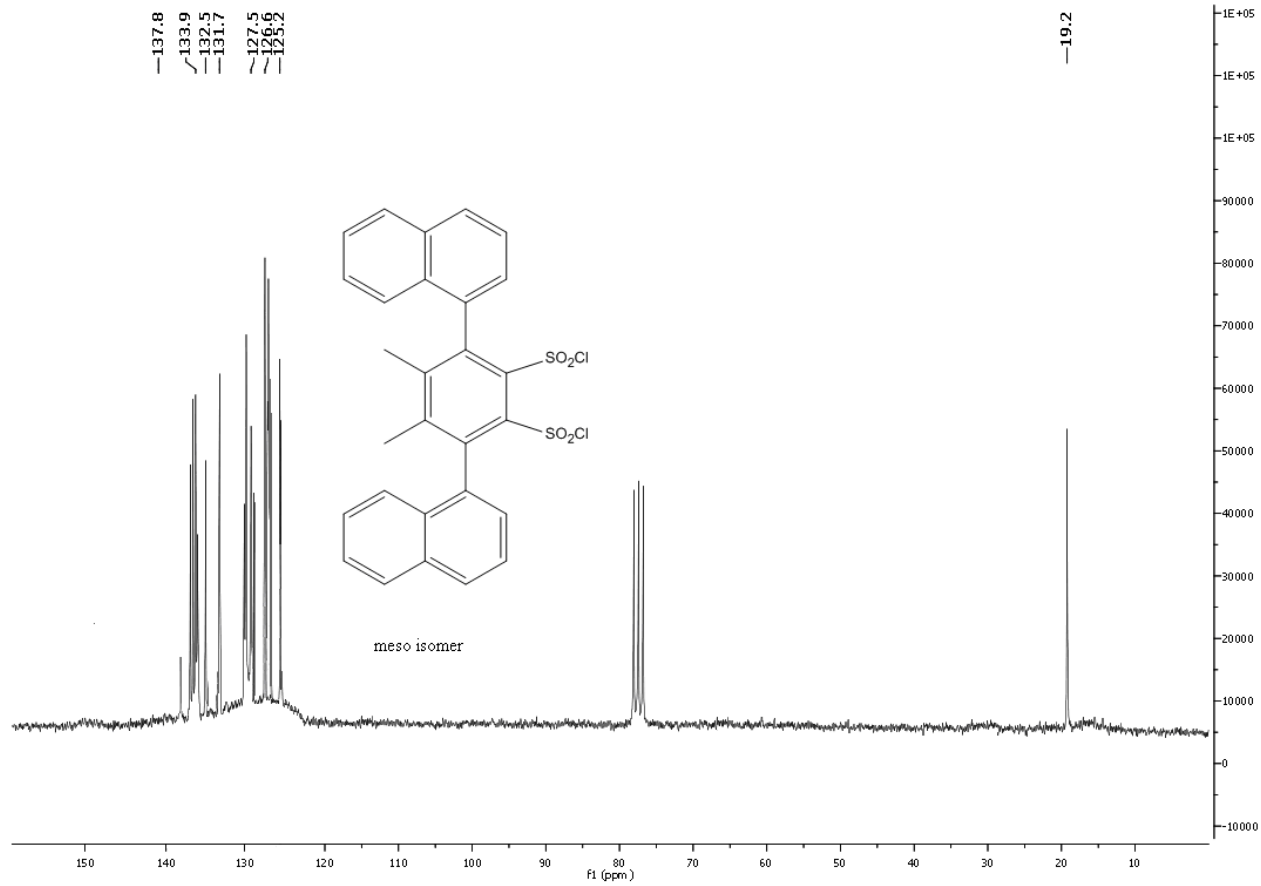


Expansion between 138-124 ppm

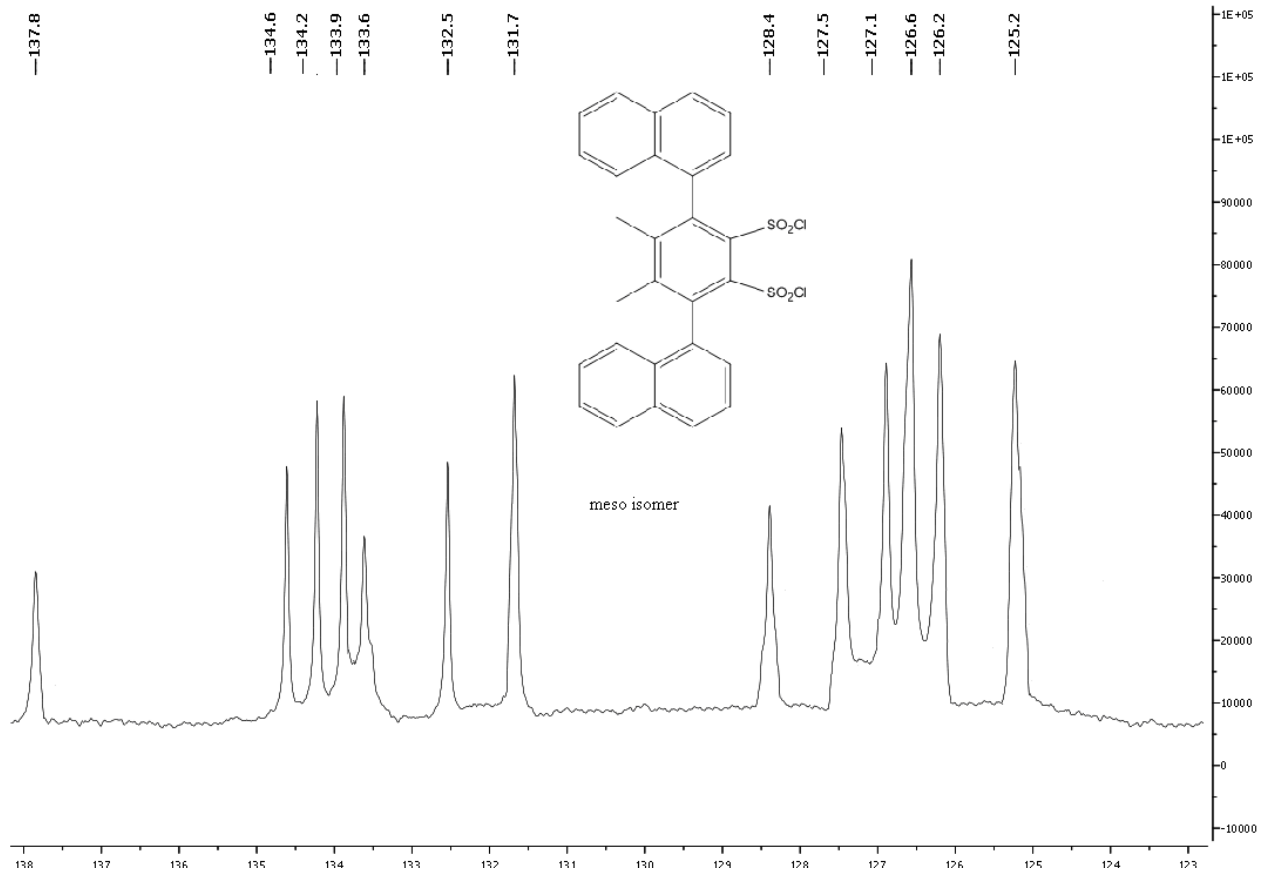


11.27 *meso* 4,5-Dimethyl-3,6-bis(1-naphthyl)-1,2-benzenedisulfonyl chloride (14c)

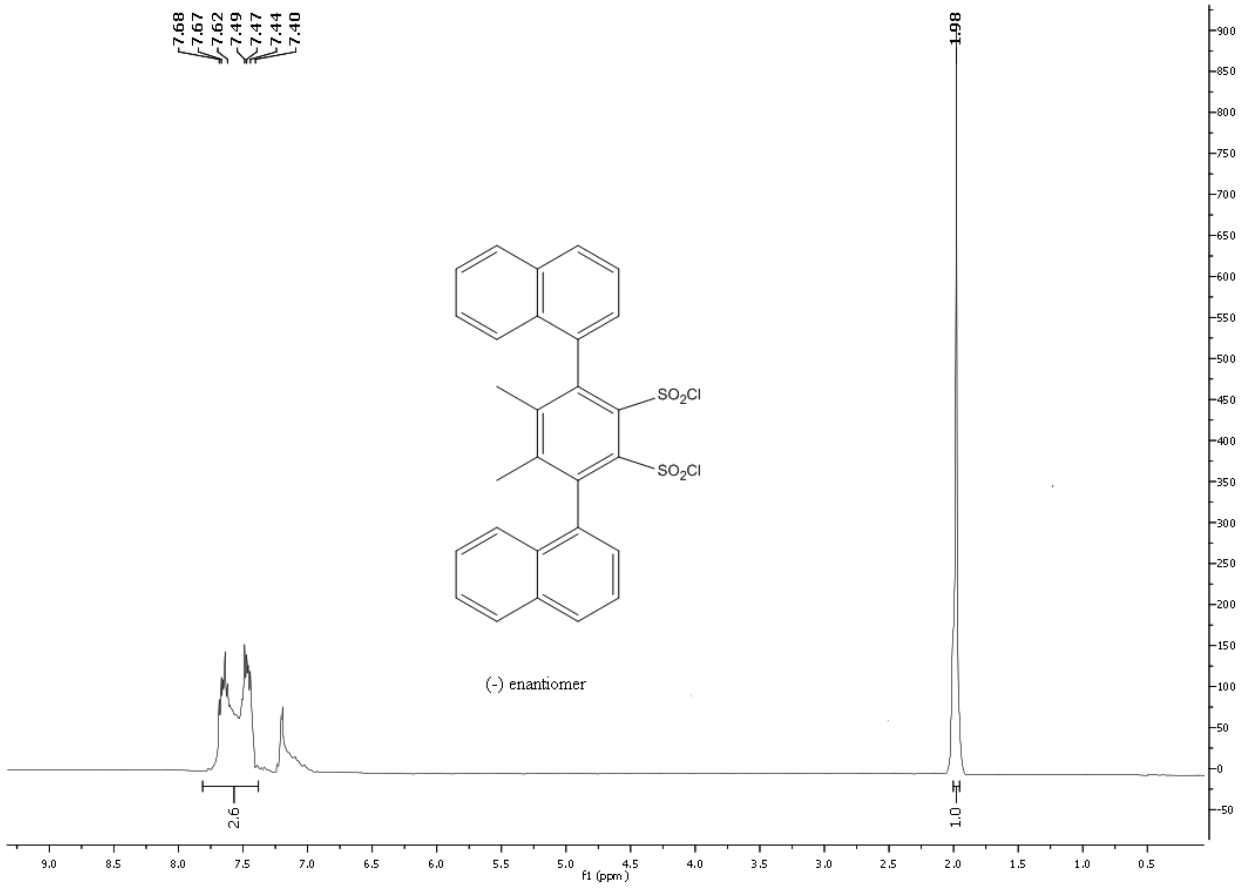


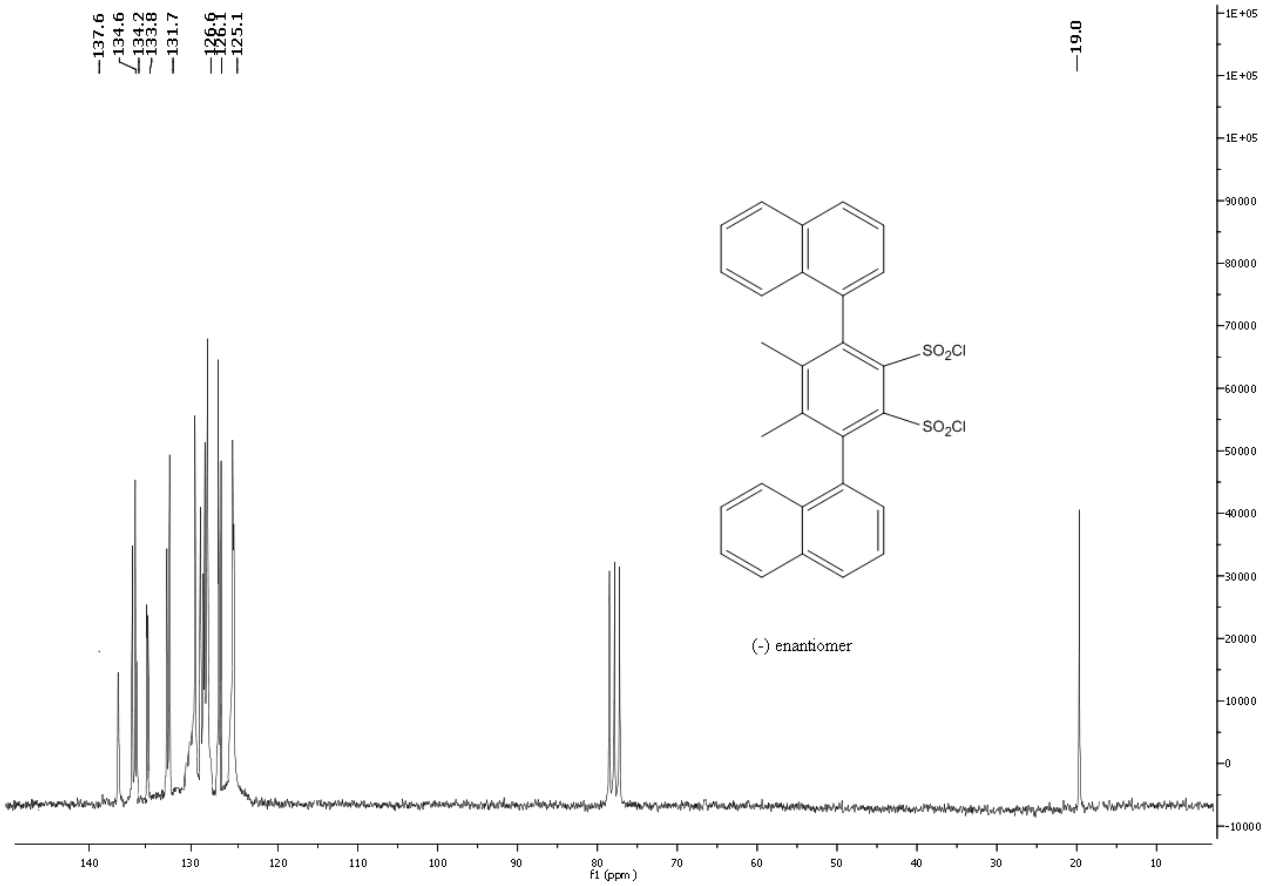


Expansion between 138-123 ppm

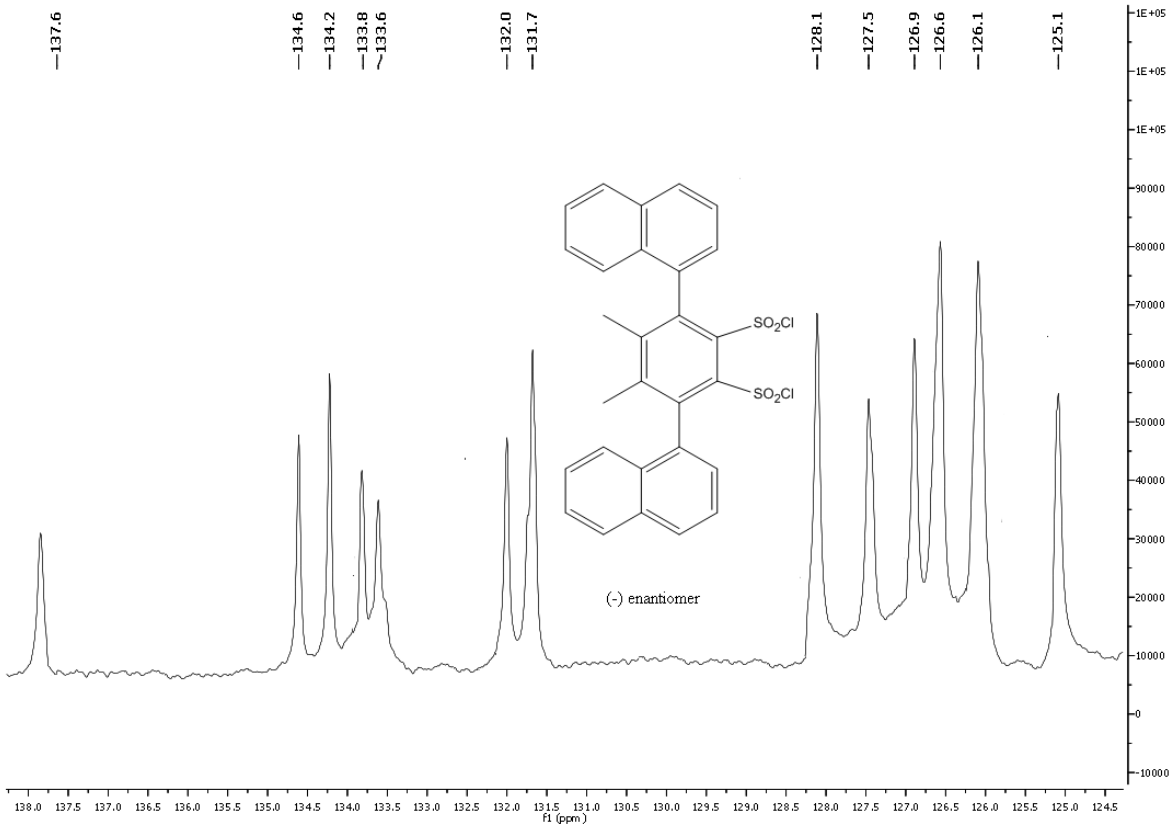


11.28 (-) 4,5-Dimethyl-3,6-bis(1-naphthyl)-1,2-benzenedisulfonyl chloride (14c)

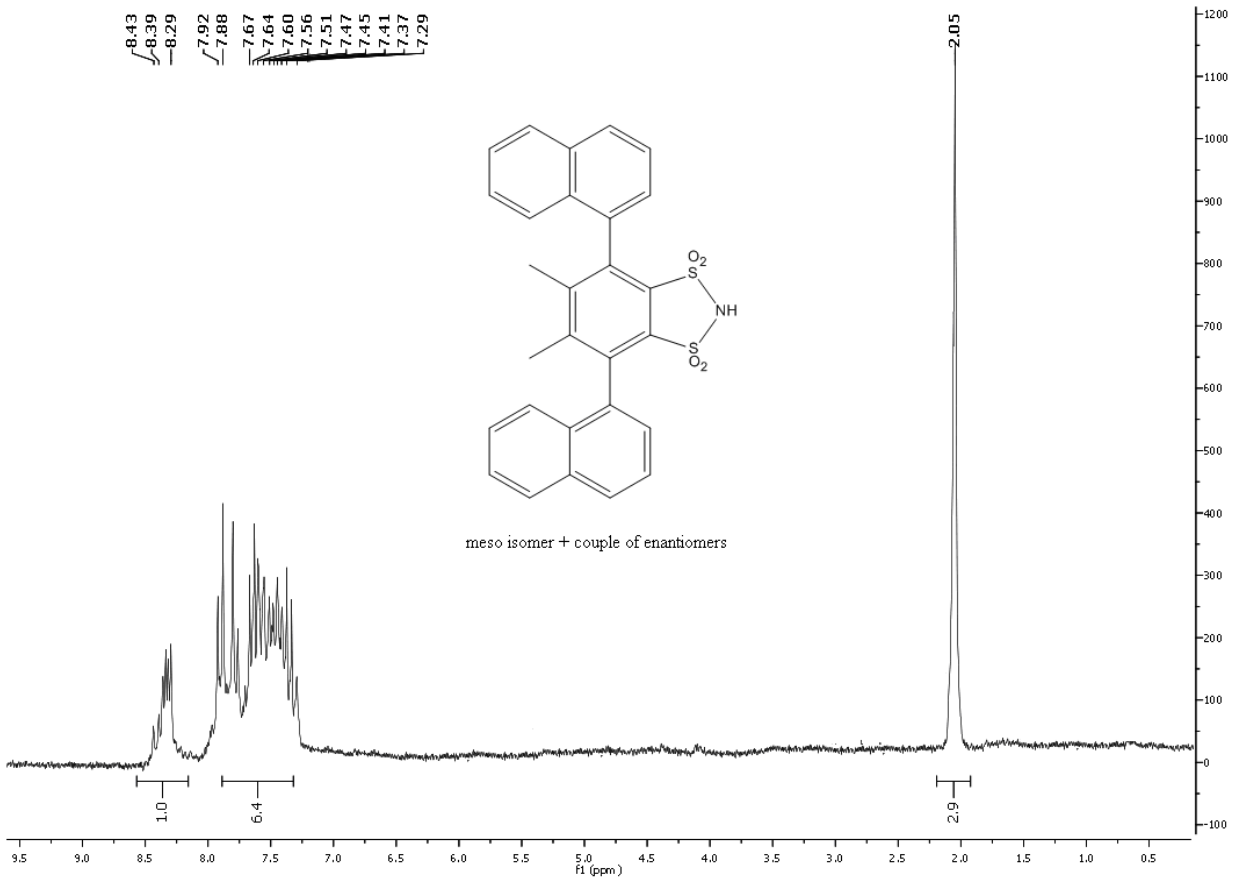


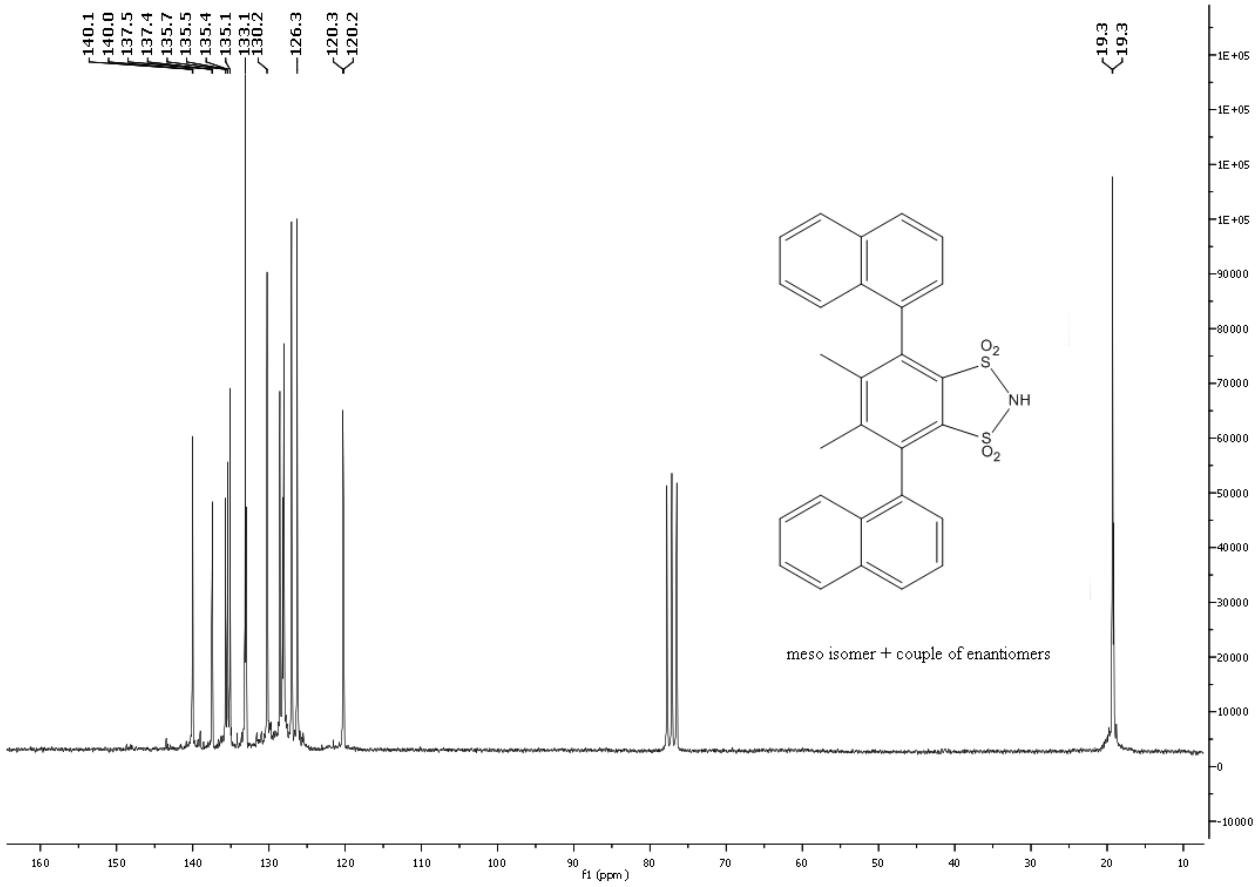


Expansion between 138-123 ppm

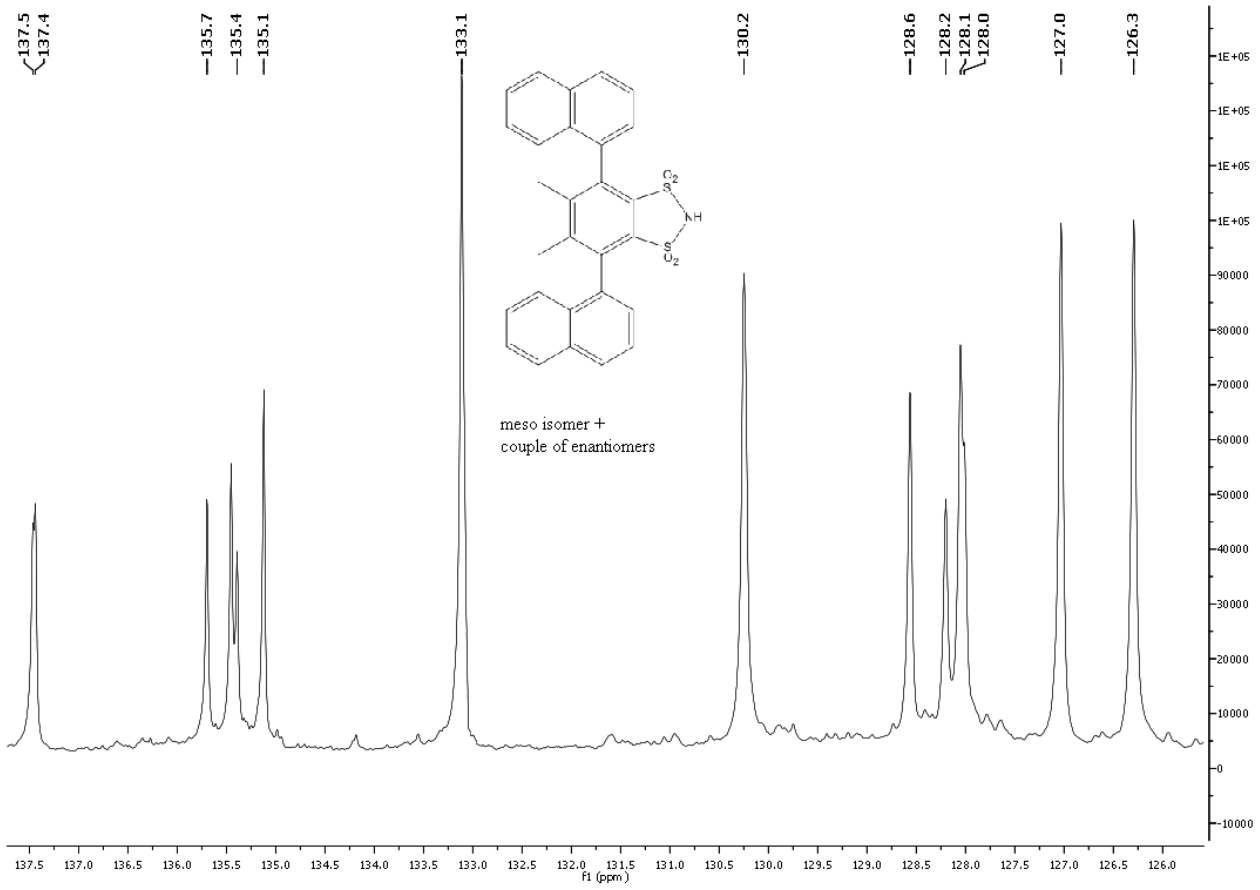


11.29 4,5-Dimethyl- 3,6-bis(1-naphthyl)-1,2-benzenedisulfonimide (mixture of meso form and couple of atropisomers; 3c)

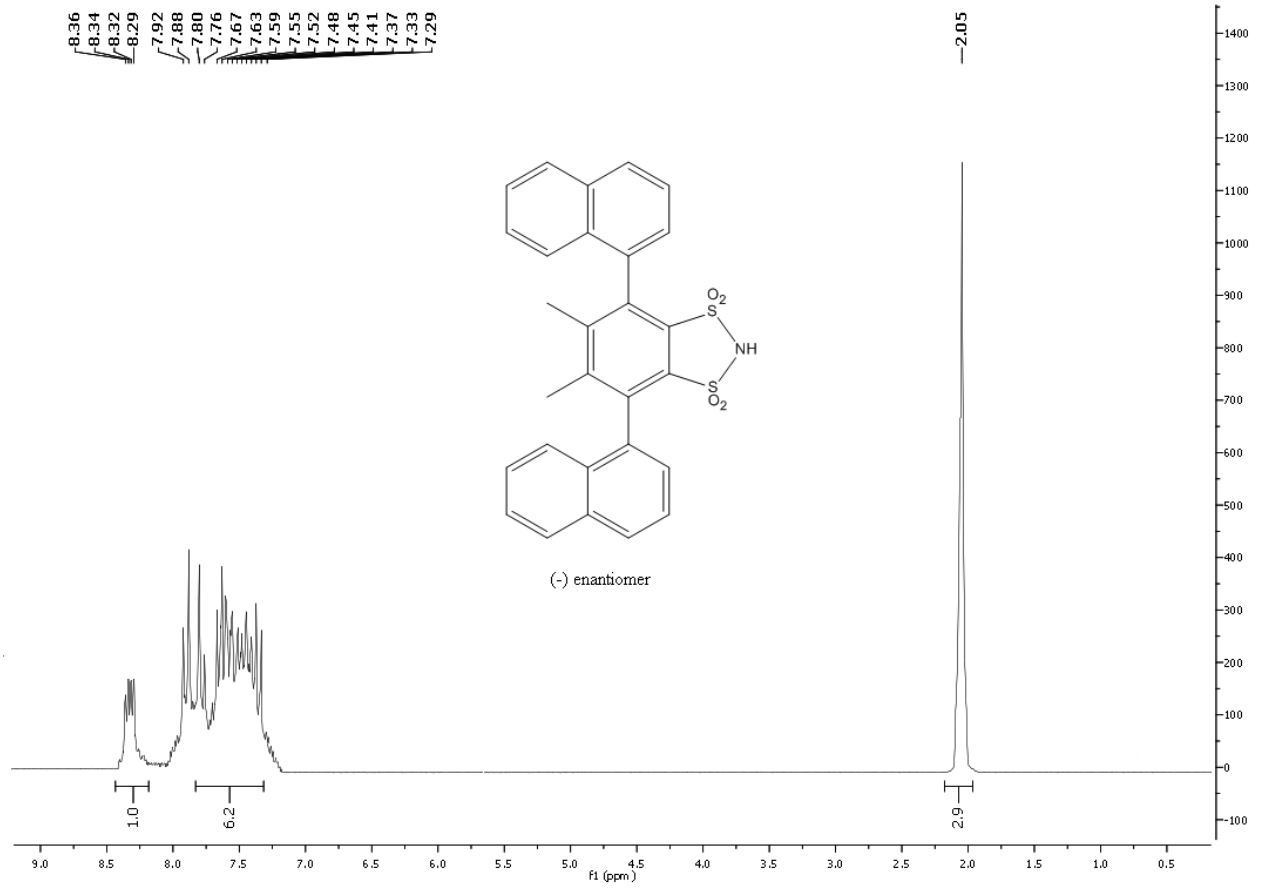


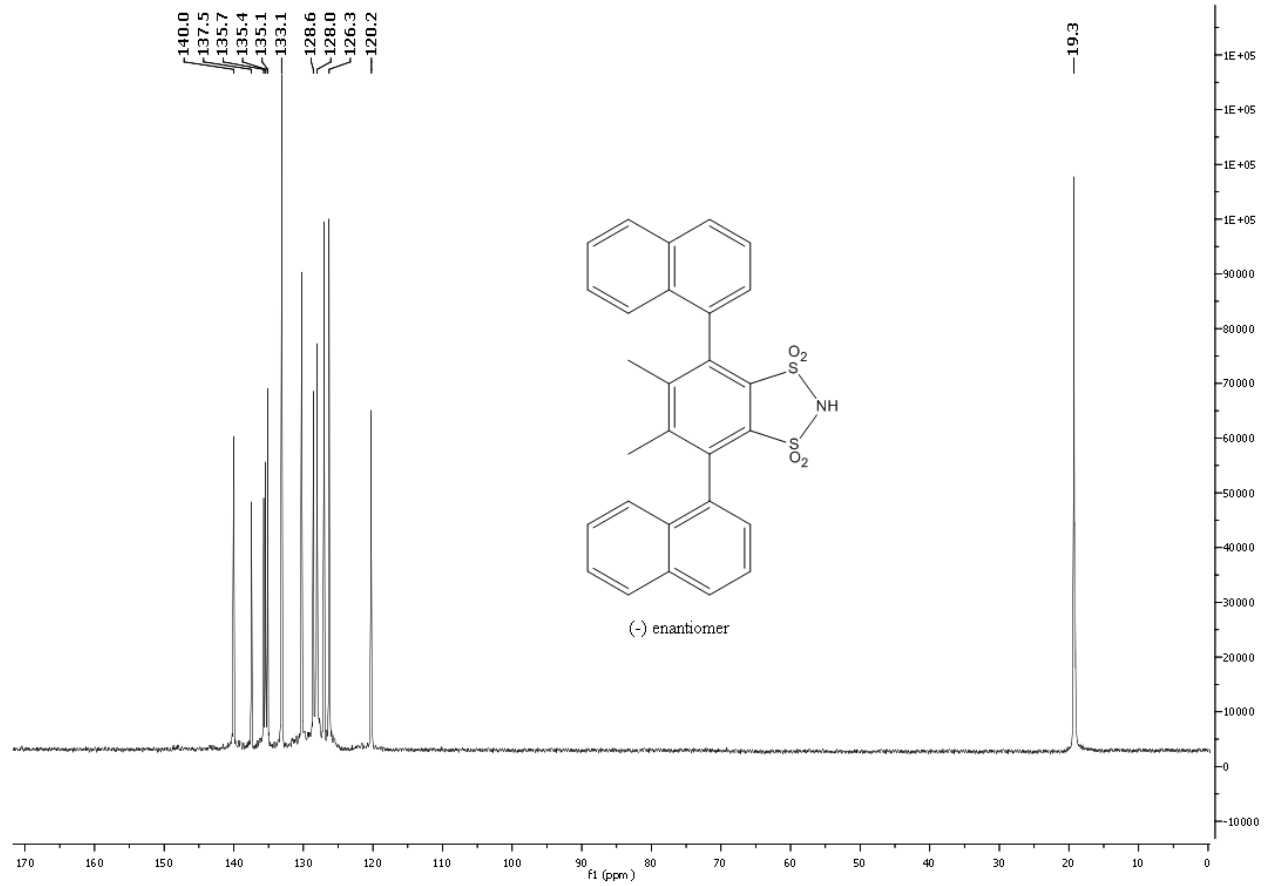


Expansion between 137-126 ppm

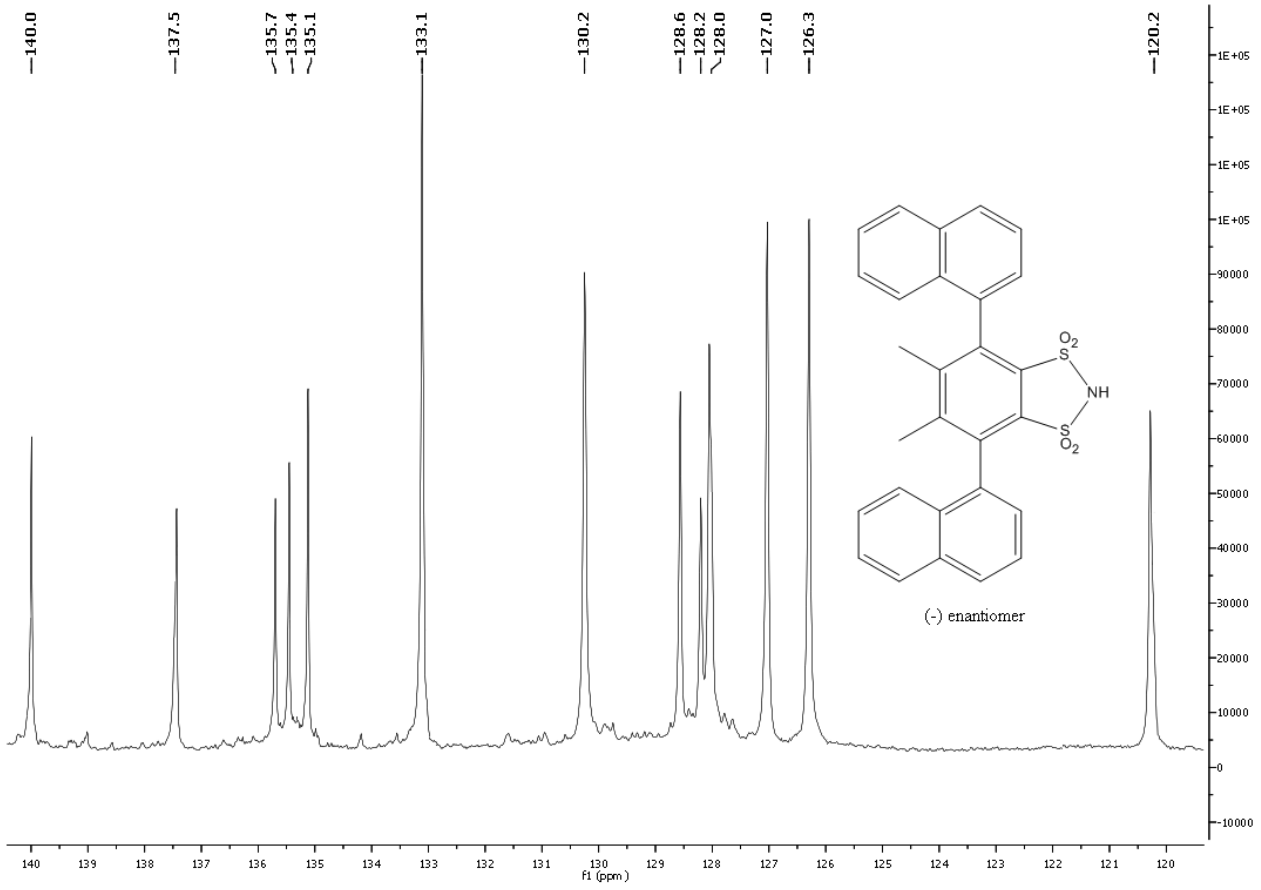


11.30 (-) 4,5-Dimethyl- 3,6-bis(1-naphthyl)-1,2-benzenedisulfonimide (3c)





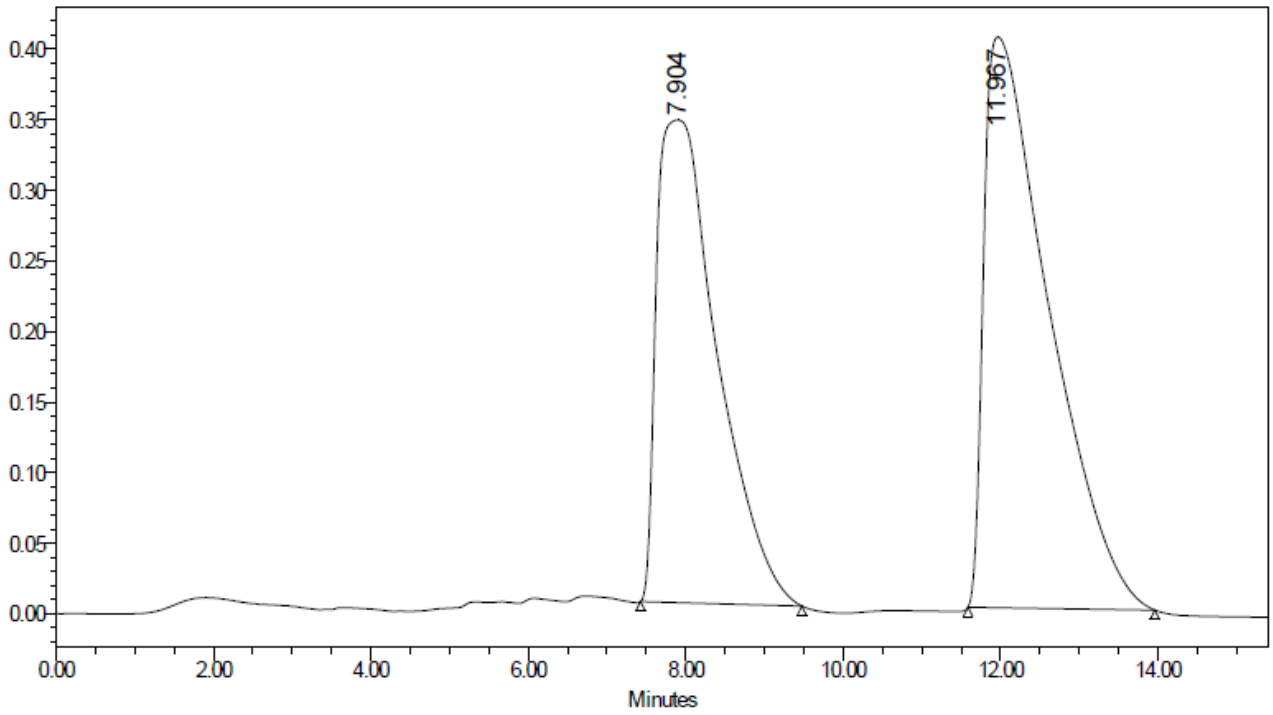
Expansion between 141-120 ppm



12. HPLC spectra of sulfonyl chlorides 14.

12.1 Atropisomers of 14a

SAMPLE INFORMATION	
Sample name: **Atropisomeri solfocloruro monometile**	Acquired by: Breeze
Sample type: Unknown	Date acquired: 5/11/2012 15:12:33 AM CEST
Vial: 1	Acq.Method: solfocloruro
Injection: #	Processed by: Breeze
Injection volume: 6.00 ul	Date processed: 5/11/2012 16:11:36 AM CEST
Run time: 25 minutes	Channel name: 2998 Ch1 254nm@1.2nm
Sampling rate: 10.00 per sec	Channel desc: 2998 Ch1 254nm@1.2nm

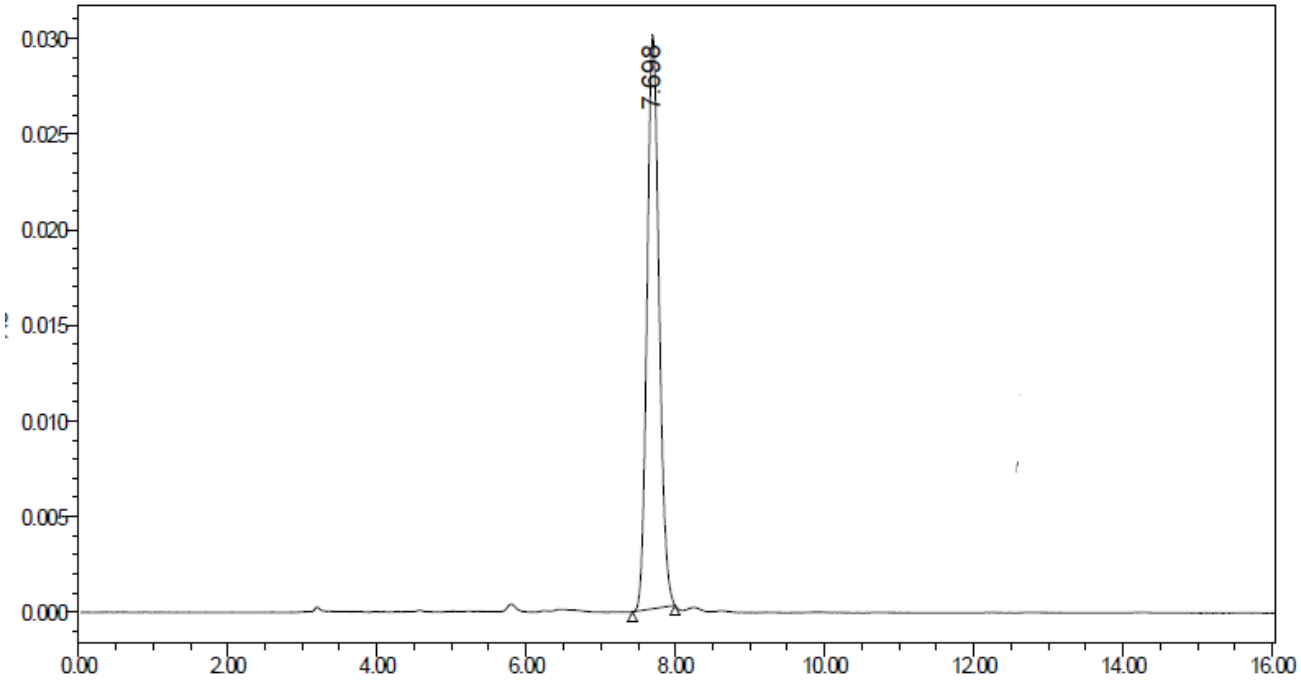


	RT(min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	Integration Type	Points Across Peaks	Start Time (min)	End Time (min)
1	7.904	**Atrop 1**	18315282	44.01	87770	BB	1670	7.428	9.477
2	11.967	**Atrop 2**	23301643	55.99	43695	BB	3141	11.588	13.962

12.2 Atropisomer (-)14a

SAMPLE INFORMATION

Sample name: **Enantiomeri solfocloruro monometile**	Acquired by: Breeze
Sample type: Unknown	Date acquired: 3/11/2014 08:32:15 AM CEST
Vial: 1	Acq.Method: solfocloruro
Injection: #	Processed by: Breeze
Injection volume: 6.00 ul	Date processed: 3/11/2014 09:10:37 AM CEST
Run time: 25 minutes	Channel name: 2998 Ch1 254nm@1.2nm
Sampling rate: 10.00 per sec	Channel desc: 2998 Ch1 254nm@1.2nm

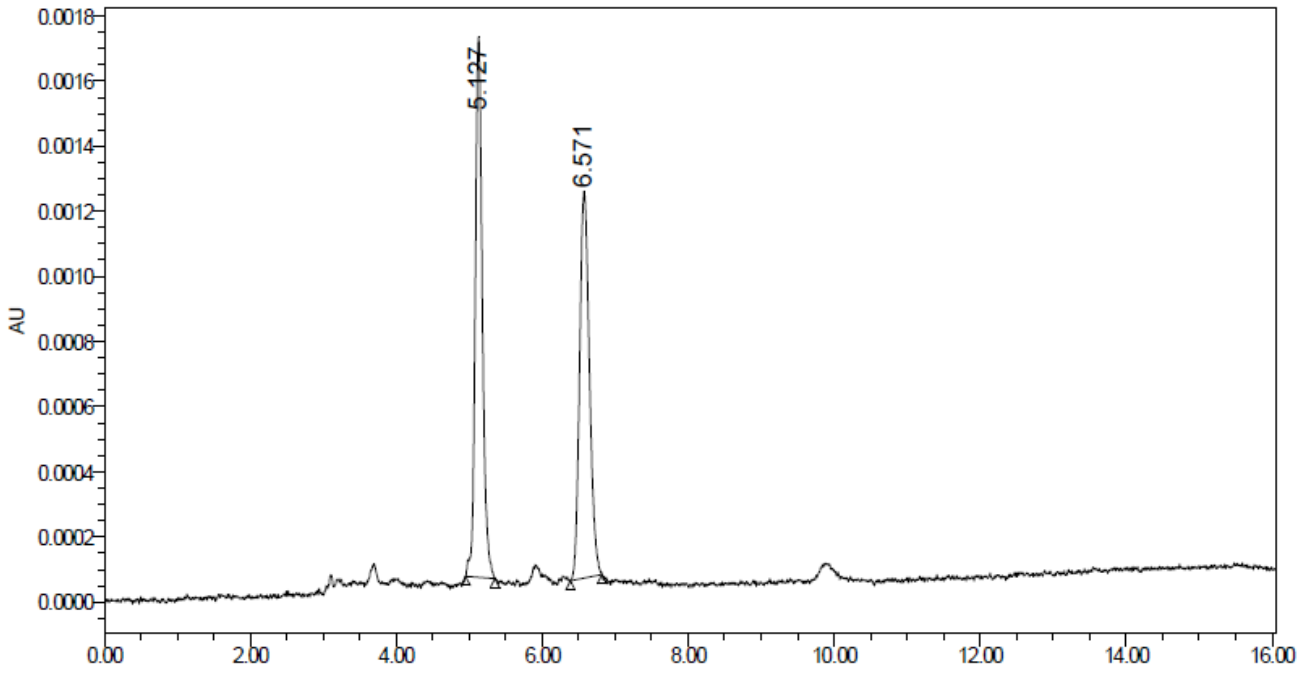


	RT(min)	Peak Type	Area (μV*sec)	Area %	Height (μV)	Integration Type	Points Across Peaks	Start Time (min)	End Time (min)
1	7.698	**(-)14a**	337038	100.0	29981	BB	342	7.425	7.995

12.3 Mixture of meso isomer and couple of atropisomers of 14b

SAMPLE INFORMATION

Sample name: **Atropisomeri solfocloruro**	Acquired by: Breeze
Sample type: Unknown	Date acquired: 8/12/2013 10:00:12 AM CEST
Vial: 1	Acq.Method: solfocloruro
Injection: #	Processed by: Breeze
Injection volume: 6.00 ul	Date processed: 8/12/2013 11:15:37 AM CEST
Run time: 25 minutes	Channel name: 2998 Ch1 254nm@1.2nm
Sampling rate: 10.00 per sec	Channel desc: 2998 Ch1 254nm@1.2nm

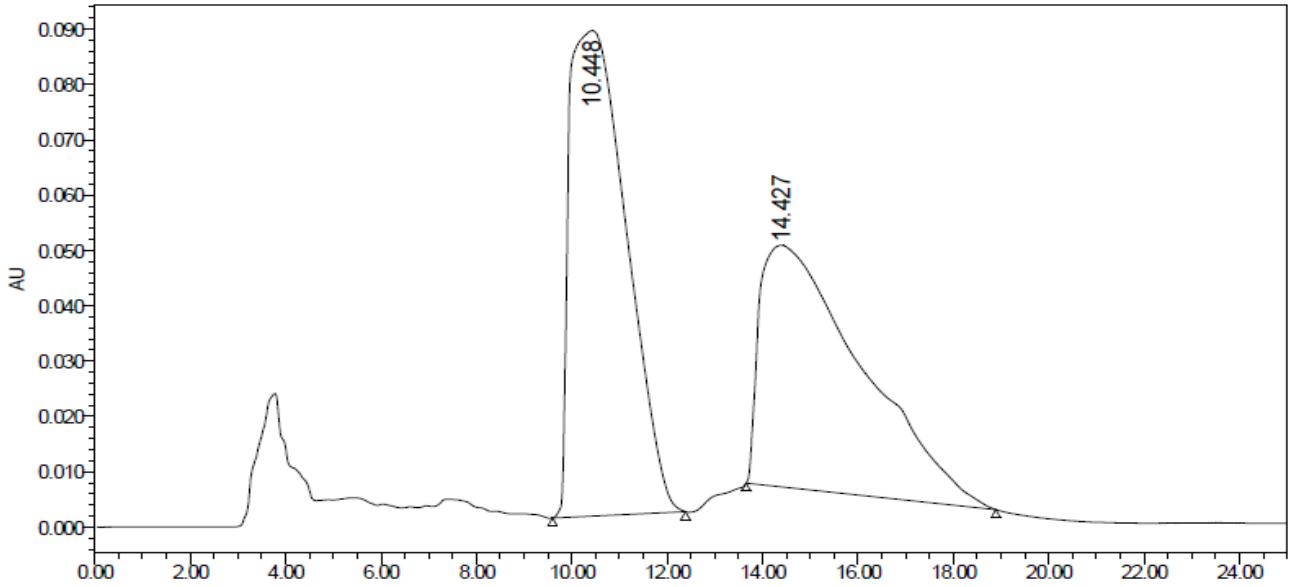


	RT(min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	Integration Type	Points Across Peaks	Start Time (min)	End Time (min)
1	5.127	**Forma meso**	11174	50.34	1659	BB	240	4.952	5.352
2	6.571	**Atrop**	11020	49.66	1187	BB	259	6.387	6.818

12.4 Atropisomers of 14b

SAMPLE INFORMATION

Sample name: **Atropisomeri solfocloruro**	Acquired by: Breeze
Sample type: Unknown	Date acquired: 8/14/2013 09:08:29 AM CEST
Vial: 1	Acq.Method: solfocloruro
Injection: #	Processed by: Breeze
Injection volume: 6.00 ul	Date processed: 8/14/2013 10:02:37 AM CEST
Run time: 25 minutes	Channel name: 2998 Ch1 254nm@1.2nm
Sampling rate: 4.00 per sec	Channel desc: 2998 Ch1 254nm@1.2nm

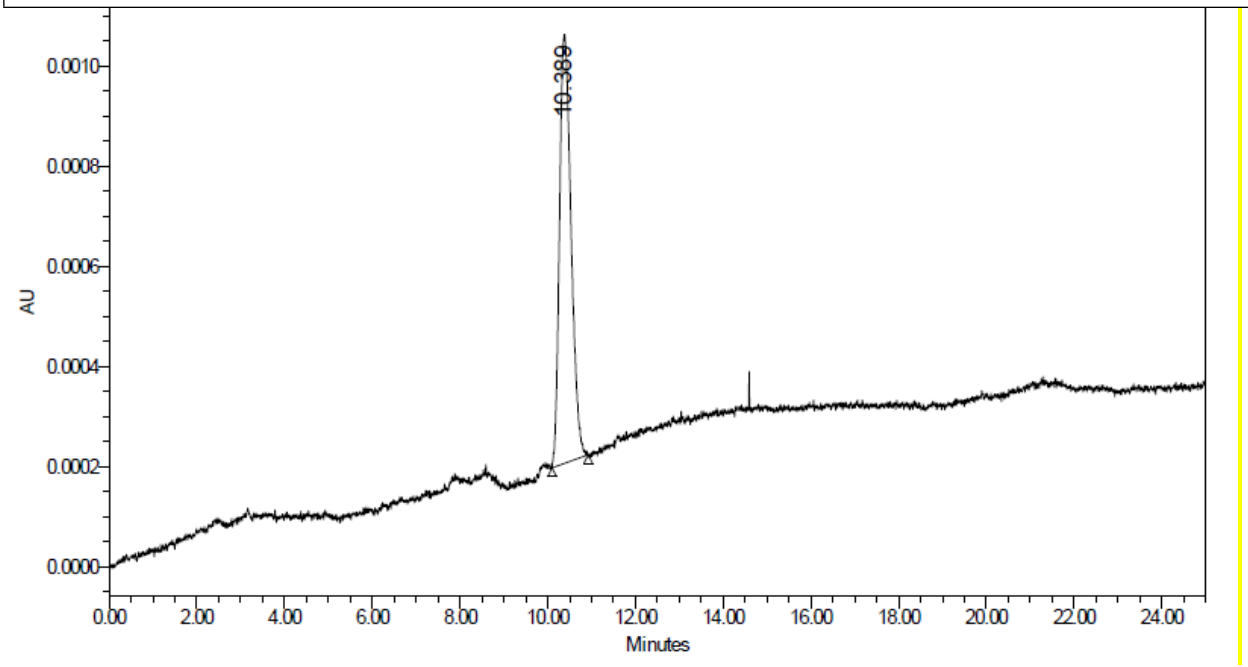


	RT(min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	Integration Type	Points Across Peaks	Start Time (min)	End Time (min)
1	10.448	**Atrop 1**	7277304	52.72	87770	BB	1670	9.568	12.382
2	14.427	**Atrop 2**	6527146	47.28	43695	BB	3141	13.665	18.890

12.5 Atropisomer (-)14b

SAMPLE INFORMATION

Sample name: **Enantiomeri solfocloruro**	Acquired by: Breeze
Sample type: Unknown	Date acquired: 3/10/2014 08:12:37 AM CEST
Vial: 1	Acq.Method: solfocloruro
Injection: #	Processed by: Breeze
Injection volume: 6.00 ul	Date processed: 3/10/2014 09:04:55 AM CEST
Run time: 25 minutes	Channel name: 2998 Ch1 254nm@1.2nm
Sampling rate: 10.00 per sec	Channel desc: 2998 Ch1 254nm@1.2nm

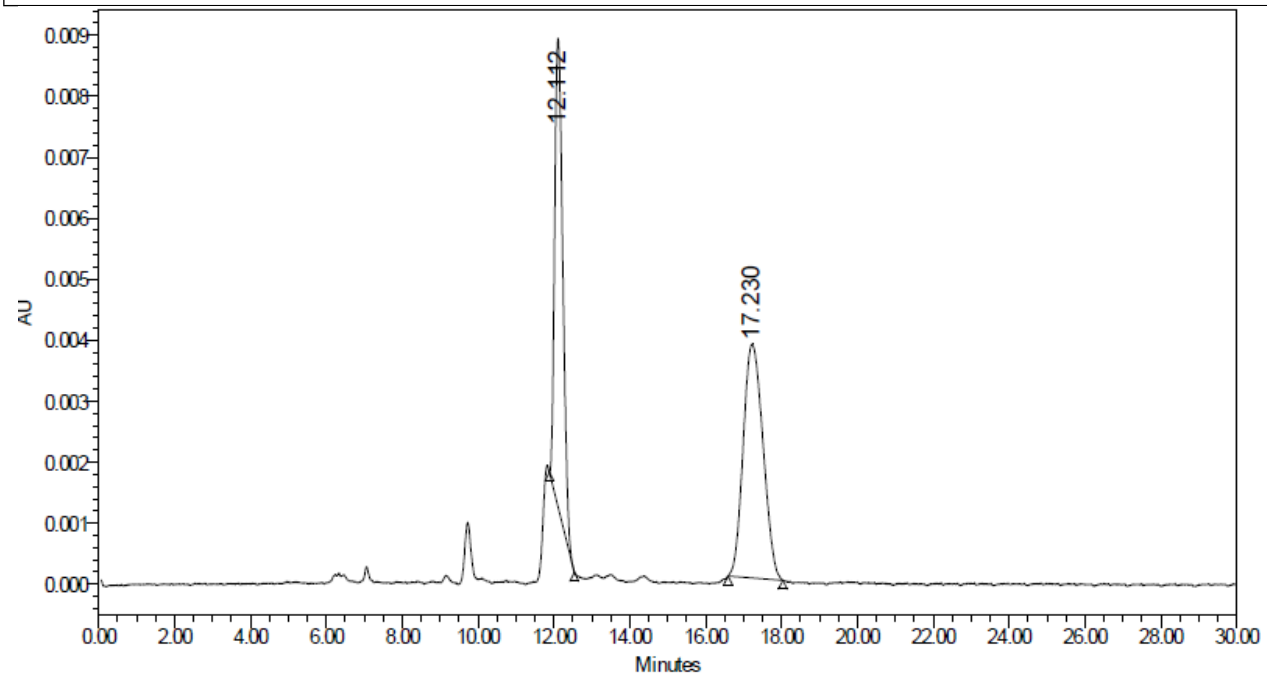


	RT(min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	Integration Type	Points Across Peaks	Start Time (min)	End Time (min)
1	10.389	**(-)14b**	15651	100.0	856	BB	495	10.100	10.925

12.6 Mixture of meso isomer and couple of atropisomers of 14c

SAMPLE INFORMATION

Sample name: **Atropisomeri solfocloruro naftile**	Acquired by: Breeze
Sample type: Unknown	Date acquired: 12/11/2013 08:16:42 AM CEST
Vial: 1	Acq.Method: solfocloruro naftile
Injection: #	Processed by: Breeze
Injection volume: 6.00 ul	Date processed: 12/11/2013 10:14:59 AM CEST
Run time: 25 minutes	Channel name: 2998 Ch1 254nm@1.2nm
Sampling rate: 12.00 per sec	Channel desc: 2998 Ch1 254nm@1.2nm

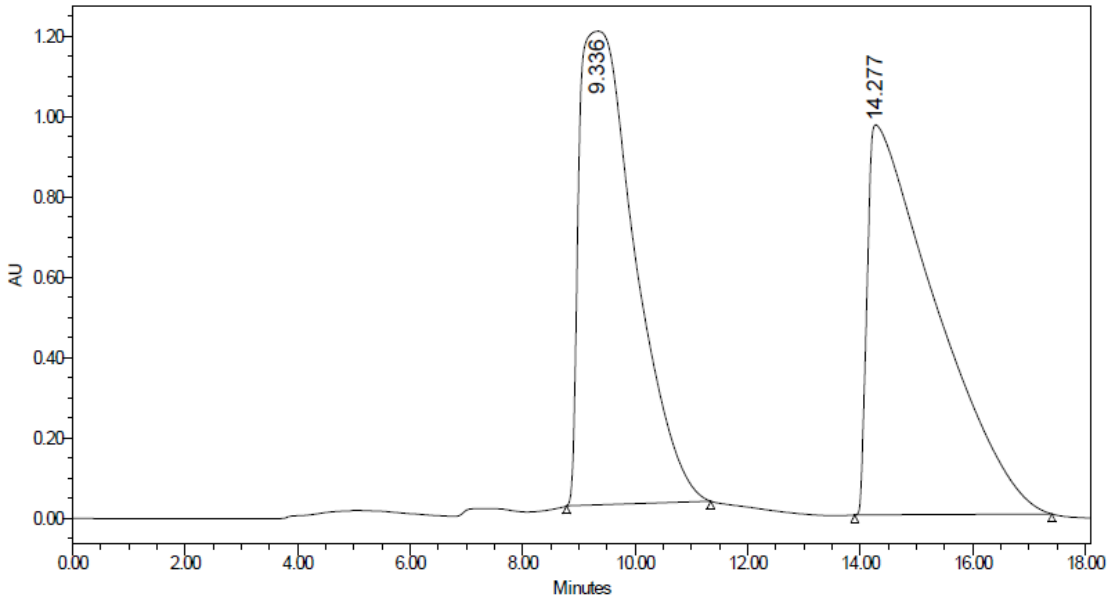


	RT(min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	Integration Type	Points Across Peaks	Start Time (min)	End Time (min)
1	12.112	**Forma meso**	133710	49.01	7687	BB	393	11.883	12.538
2	17.230	**RS + SR**	139105	50.99	3837	BB	869	16.587	18.035

12.7 Atropisomers of 14c

SAMPLE INFORMATION

Sample name: **Atropisomeri solfocloruro naftile**	Acquired by: Breeze
Sample type: Unknown	Date acquired: 12/18/2013 14:16:44 AM CEST
Vial: 1	Acq.Method: solfocloruro naftile
Injection: #	Processed by: Breeze
Injection volume: 6.00 ul	Date processed: 12/18/2013 16:22:00 AM CEST
Run time: 25 minutes	Channel name: 2998 Ch1 254nm@1.2nm
Sampling rate: 6.00 per sec	Channel desc: 2998 Ch1 254nm@1.2nm

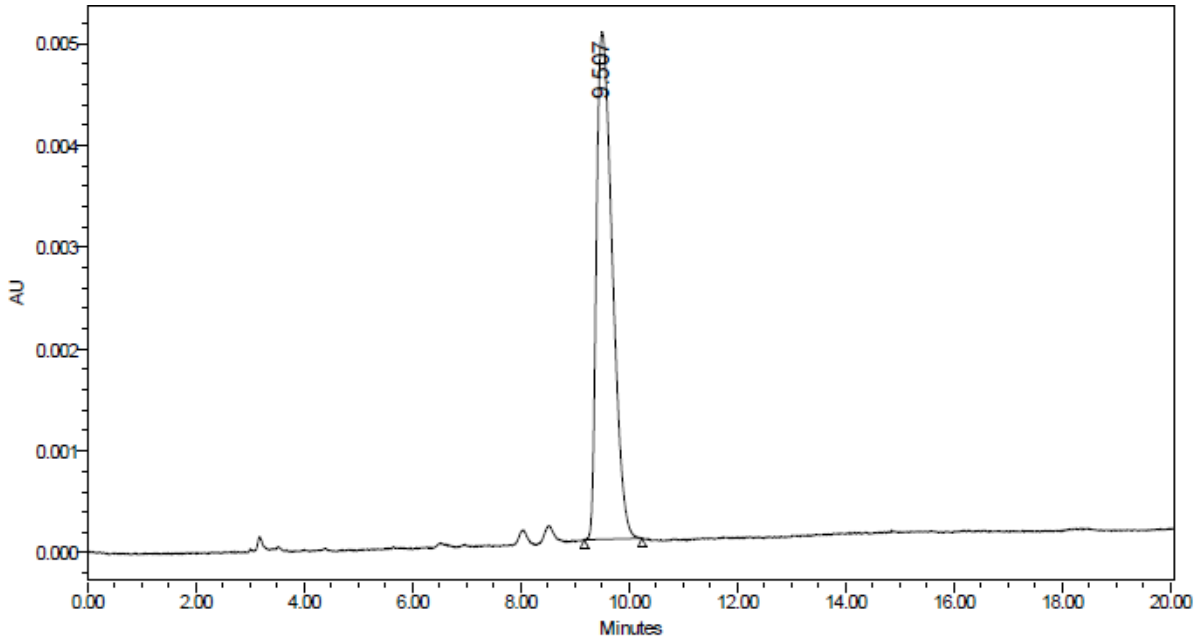


	RT(min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	Integration Type	Points Across Peaks	Start Time (min)	End Time (min)
1	9.336	**atrop**	8089847	49.42	1178	BB	1536	8.783	11.343
2	14.277	**atrop**	8279335	50.58	9704	BB	2102	13.903	17.407

12. 8 Atropisomer (-)14c

SAMPLE INFORMATION

Sample name: **Enantiomeri solfocloruro naftile**	Acquired by: Breeze
Sample type: Unknown	Date acquired: 03/07/2014 15:36:40 AM CEST
Vial: 1	Acq.Method: solfocloruro naftile
Injection: #	Processed by: Breeze
Injection volume: 6.00 ul	Date processed: 03/07/2014 16:44:55 AM CEST
Run time: 25 minutes	Channel name: 2998 Ch1 254nm@1.2nm
Sampling rate: 6.00 per sec	Channel desc: 2998 Ch1 254nm@1.2nm



	RT(min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	Integration Type	Points Across Peaks	Start Time (min)	End Time (min)
1	9.507	**(-)14c**	101312	100.0	4986	BB	639	9.175	10.240

13. Spectral and physical data of nitriles 21.

13.1 2-Phenyl-2-phenylaminopropanenitrile (**21a**). White solid; mp 140–141 °C (EtOH; lit.[15] 139–140 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.88 (s, 3H), 4.28 (br s, 1 H), 6.51 (d, J = 8.2 Hz, 2H), 6.72 (t, J = 7.4 Hz, 1H), 7.03–7.11 (m, 2H), 7.33–7.36 (m, 3H), 7.59 (d, J = 8.2 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.5, 57.3, 115.9, 120.1, 121.0, 125.1, 128.8, 129.2, 129.4, 140.1, 143.7. MS (EI) *m/z*: (%) 222 [M^+](10), 195 (50), 180 (100), 77 (45). IR ($CHCl_3$) ν (cm^{-1}): 3419 (NH), 2254 (CN).

13.2 2-(4-Methoxyphenylamino)-2-phenylpropanenitrile (**21b**). Pale brown solid; mp 102–103 °C (EtOH; lit.[16] 101–102 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 3.65 (s, 3H), 6.46–6.51 (m, 2H), 6.62–6.67 (m, 2H), 7.31–7.36 (m, 3H), 7.56 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.1, 55.7, 58.4, 114.6, 118.5, 121.3, 125.3, 128.8, 129.4, 137.5, 140.4, 154.2. MS (EI) *m/z*: (%) 225 [M^+ -HCN](65), 210 (100). IR ($CHCl_3$) ν (cm^{-1}): 3425 (NH), 2251 (CN).

13.3 2-(4-Nitrophenylamino)-2-phenylpropanenitrile (**21c**). Yellow solid; mp 134–135 °C (EtOH; lit.[10b] 134–135 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.95 (s, 3H), 5.21 (br s, 1H), 6.50 (d, J = 9.2 Hz, 2H), 7.33–7.52 (m, 5H), 7.95 (d, J = 9.2 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.1, 56.7, 115.8, 120.0, 120.7, 124.8, 126.4, 129.3, 142.9, 147.3, 148.3. MS (EI) *m/z*: (%) 240 [M^+ -HCN](72), 225 (100), 179 (60). IR ($CHCl_3$) ν (cm^{-1}): 3429 (NH), 2248 (CN).

13.4 2-(4-Bromophenylamino)-2-phenylpropanenitrile (**21d**). Brown solid; 1.10 g (yield 73 %); mp 122–123 °C (EtOH; lit.[10b] 122–123 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (s, 3H), 4.49 (br s 1H), 6.36 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.31–7.40 (m, 3H), 7.51–7.55 (m, 2H). ^{13}C NMR δ (50 MHz, $CDCl_3$): δ = 33.4, 57.3, 112.2, 117.5, 120.7, 125.0, 129.0, 129.6, 132.0, 139.4, 142.8. MS (EI) *m/z*: (%) 273 [M^++2 –HCN](65), 273 [M^+ -HCN](65), 260 (100), 258 (100). IR ($CHCl_3$) ν (cm^{-1}): 3433 (NH), 2254 (CN).

13.5 2-(4-Fluorophenylamino)-2-phenylpropanenitrile (**21e**). Pale grey solid; 1.10 g (yield 92%); mp 125–126 °C (EtOH; lit.[10b] 125–126 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (s, 3H), 6.41–6.48 (m, 2H), 6.72–6.81 (m, 2H), 7.30–7.40 (m, 3H), 7.54–7.58 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.3, 57.9, 115.6, 116.0, 117.6 (d, J_2 = 7.6 Hz), 120.8, 125.1, 128.9, 129.5, 139.8, 157.5 (d, J_1 = 236.5 Hz). MS (EI) *m/z*: (%) 213 [M^+ -HCN](65), 198 (100). IR ($CHCl_3$) ν (cm^{-1}): 3431 (NH), 2256 (CN).

13.6 2-(2-Methoxyphenylamino)-2-phenylpropanenitrile (**21f**). Pale brown solid; mp 80–81 °C (EtOH; lit.[10b] 80-81 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 3.86 (s, 3H), 4.90 (br s, 1H), 6.19–6.23 (m, 1H), 6.56–6.79 (m, 3H), 7.29–7.38 (m, 3H), 7.55–7.60 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.6, 55.7, 57.1, 109.8, 114.3, 119.4, 120.9, 125.1, 128.7, 129.4, 133.5, 140.4, 147.5. MS (EI) *m/z*: (%) 225 [M^+ -HCN](45), 210 (100). IR ($CHCl_3$) ν (cm^{-1}): 3430 (NH), 2258 (CN).

13.7 2-(3-Methoxyphenylamino)-2-phenylpropanenitrile (**21g**). Pale brown solid; 1.06 g (yield 84 %); mp 105 °C (EtOH; lit.[16] 102–105 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (s, 3H), 3.58 (s, 3H), 6.08–6.11 (m, 2H), 6.30–6.35 (m, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 7.28–7.35 (m, 3H), 7.57–7.61 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.4, 55.2, 57.4, 102.0, 105.5, 108.7, 121.0, 125.0, 128.8, 129.5, 130.0, 140.3, 145.3, 160.5. MS (EI) *m/z*: (%) 225 [M^+ -HCN](60), 210 (100). IR ($CHCl_3$) ν (cm^{-1}): 3440 (NH), 2251 (CN).

13.8 2-Phenylamino-2-(4-tolyl)propanenitrile (21h): pale grey solid; 1.04 g (yield 88 %); mp 129–130 °C (EtOH; lit.[17] 126–128 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.87 (s, 3H), 2.32 (s, 3H), 4.29 (br s, 1 H), 6.53 (d, *J* = 8.4 Hz, 2H), 6.72 (t, *J* = 7.7 Hz, 1H), 7.04–7.18 (m, 4H), 7.47 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 33.6, 57.1, 115.9, 120.0, 125.0, 128.7, 129.2, 130.1, 137.2, 138.6, 143.9. MS (EI) *m/z*: (%) 209 [M^+ -HCN](85), 194 (100), 77 (35). IR ($CHCl_3$) ν (cm^{-1}): 3428 (NH), 2242 (CN).

13.9 2-(4-Nitrophenylamino)-2-(4-tolyl)propanenitrile (21i). Yellow solid; 1.15 g (yield 82 %); mp 102–103 °C (EtOH; lit.[10b] 102–103 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 2.30 (s, 3H), 3.93 (br s, 1H), 6.50 (d, *J* = 9.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2, 33.2, 56.7, 113.6, 114.5, 124.7, 125.8, 126.6, 130.4, 135.7, 139.3, 149.4. MS (EI) *m/z*: (%) 254 [M^+ -HCN](75), 239 (100), 193 (50). IR ($CHCl_3$) ν (cm^{-1}): 3421 (NH), 2255 (CN).

13.10 2-(4-Methoxyphenylamino)-2-(4-tolyl)propanenitrile (21j). Pale grey solid; 1.13 g (yield 85%); mp 88–89 °C (EtOH; lit.[10b] 88–89 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83 (s, 3H), 2.32 (s, 3H), 3.64 (s, 3H), 4.05 (br s, 1H), 6.50 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 33.4, 55.7, 58.1, 114.6, 115.0, 118.4, 125.2, 128.7, 129.5, 130.0, 138.6, 154.1. MS (EI) *m/z*: (%) 239 [M^+ -HCN](70), 225 (100). IR ($CHCl_3$) ν (cm^{-1}): 3438 (NH), 2241 (CN).

13.11 2-(4-Methoxyphenylamino)-2-(4-nitrophenyl)propanenitrile (21k). Pale yellow solid; 1.25 g (yield 84 %); mp 109–111 °C (EtOH; lit.[16] 107 –109 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (s, 3H), 3.63 (s, 3H), 4.24 (br s, 1H), 6.43 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.8, 55.7, 57.9, 114.8, 118.3, 120.3, 124.7, 126.6, 136.7, 147.6, 148.2 154.5. MS (EI) *m/z*: (%) 270 [M^+ -HCN](100), 255 (100), 209 (40). IR ($CHCl_3$) ν (cm^{-1}): 3424 (NH), 2251 (CN).

13.12 2-Phenyl-2-phenylaminoacetonitrile (21m). White solid; mp 79 °C (EtOH; lit.[18] 76–78 °C). ^{1}H NMR (200 MHz, $CDCl_3$): *δ* = 4.09 (br s, 1H), 5.37 (s, 1H), 6.72–6.75 (m, 2H), 6.88 (t, *J* = 7.7 Hz, 1H), 7.21–7.29 (m, 2H), 7.34–7.41 (m, 3H), 7.54–7.56 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* = 50.3, 114.4, 118.6, 120.4, 127.5, 129.6, 129.7, 129.8, 134.2, 145.0. MS (EI) *m/z*: (%) 208 [M^+] (15), 181 (90), 180 (100), 116 (15), 77 (20). IR ($CHCl_3$) ν (cm^{-1}): 3415 (NH), 2240 (CN).

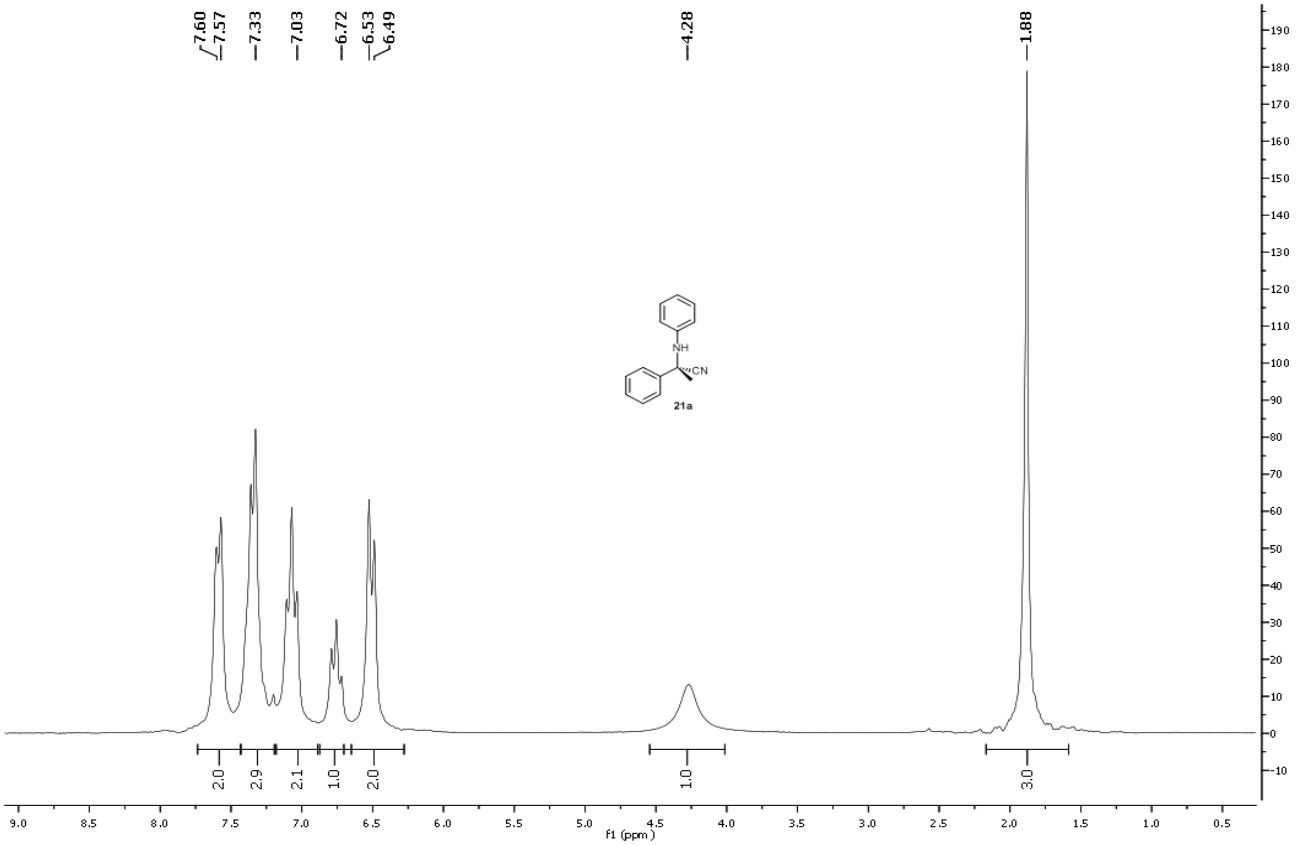
13.13 2-(4-Nitrophenyl)-2-phenylaminoacetonitrile (21n). Pale brown waxy solid. ^{1}H NMR (200 MHz, $CDCl_3$): *δ* = 4.18 (br s, 1H), 5.53 (s, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.85–6.92 (m, 1H), 7.20–7.26 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 8.25 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* = 49.9, 114.7, 117.6, 127.3, 128.4, 129.6, 129.8, 130.7, 141.1, 144.3. MS (EI) *m/z*: (%) 253 [M^+] (10), 226 (90), 225 (100), 77(20). IR ($CHCl_3$) ν (cm^{-1}): 3419 (NH), 2238 (CN).

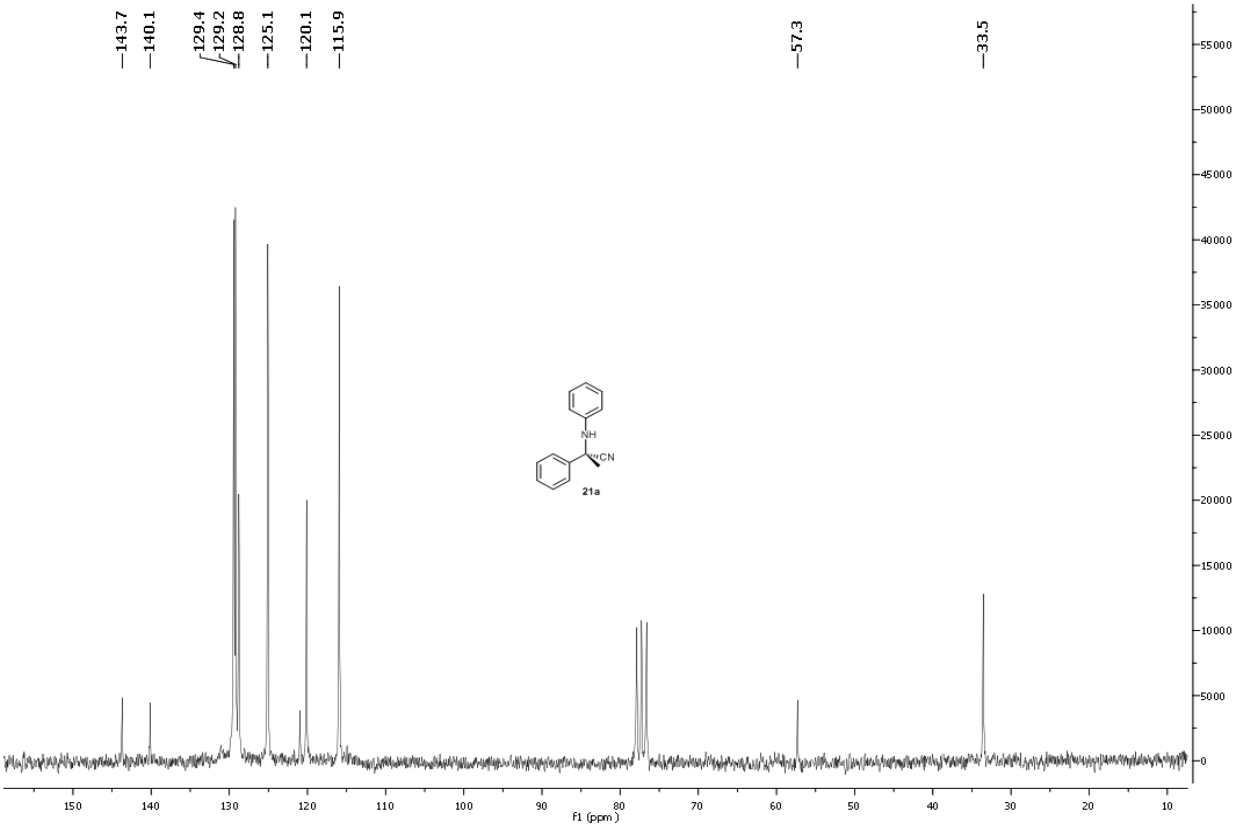
13.14 2-Phenylamino-2-(4-tolyl)acetonitrile (21o). White solid; mp 77–78 °C ((EtOH; lit.[20] 76–78 °C). ^{1}H NMR (200 MHz, $CDCl_3$): *δ* = 2.36 (s, 3H), 4.09 (br s, 1H), 5.33 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 7.20–7.28 (m, 4H), 7.44 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* = 21.1, 50.1, 114.4, 118.7, 120.4, 127.4, 129.4, 130.2, 131.2, 139.8, 145.0. MS (EI) *m/z*: (%) 222 [M^+] (10), 195 (85), 194 (100), 77 (20). IR ($CHCl_3$) ν (cm^{-1}): 3416 (NH), 2231 (CN).

13.15 2-Phenylamino-2-(2-thienyl)acetonitrile (21p). Pale yellow solid; mp 101–102 °C (EtOH; lit.[21] 100–102 °C). ^{1}H NMR (200 MHz, $CDCl_3$): *δ* = 4.08 (br s, 1H), 5.59 (s, 1H), 6.73–6.77 (m, 2H), 6.84–6.92 (m, 1H), 6.97–7.02 (m, 1H), 7.20–7.34 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* = 46.4, 114.9, 117.7, 121.0, 127.3, 127.4, 127.5, 129.8, 136.9, 144.2. MS (EI) *m/z*: (%) 214 [M^+] (5), 187 (90), 186 (100), 77 (10). IR ($CHCl_3$) ν (cm^{-1}): 3411 (NH), 2232 (CN).

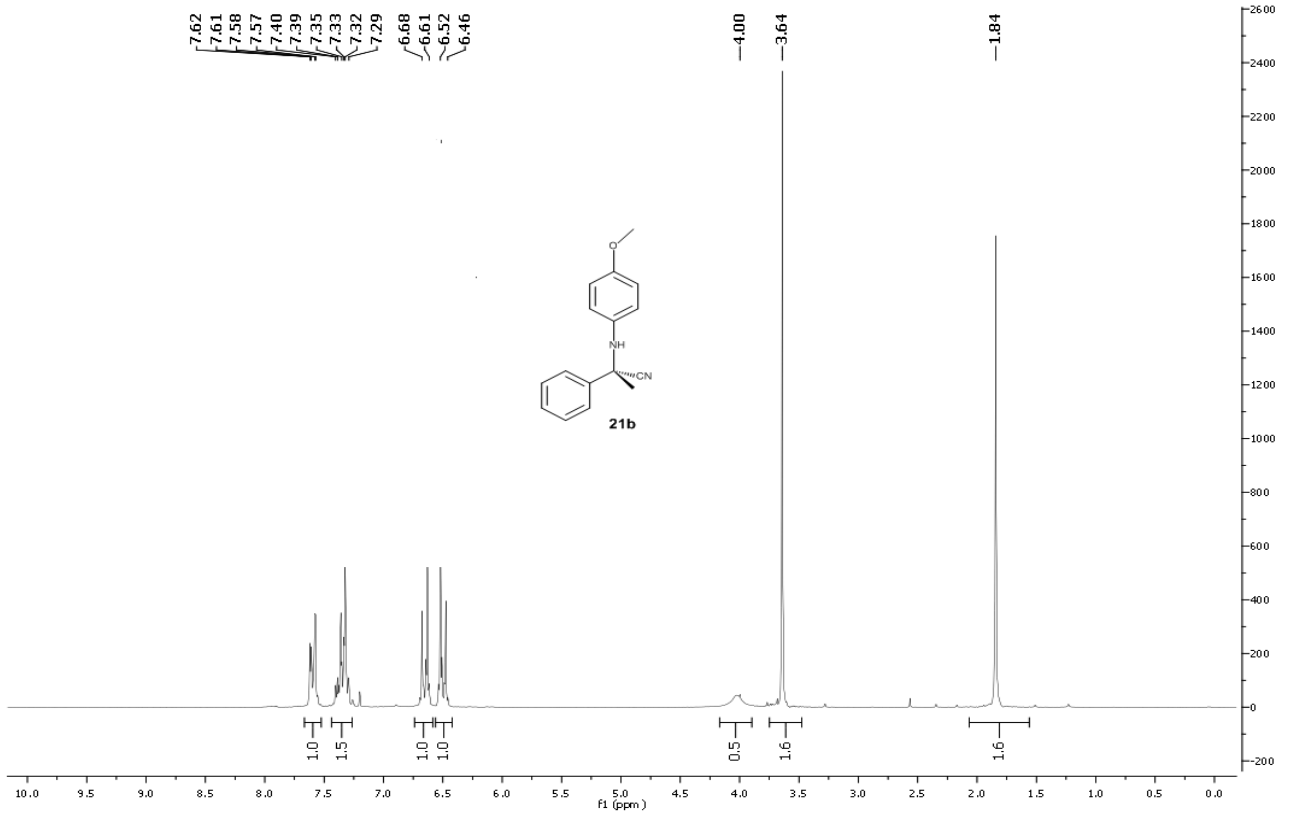
14. ^{1}H and $^{13}CNMR$ spectra of nitriles 21

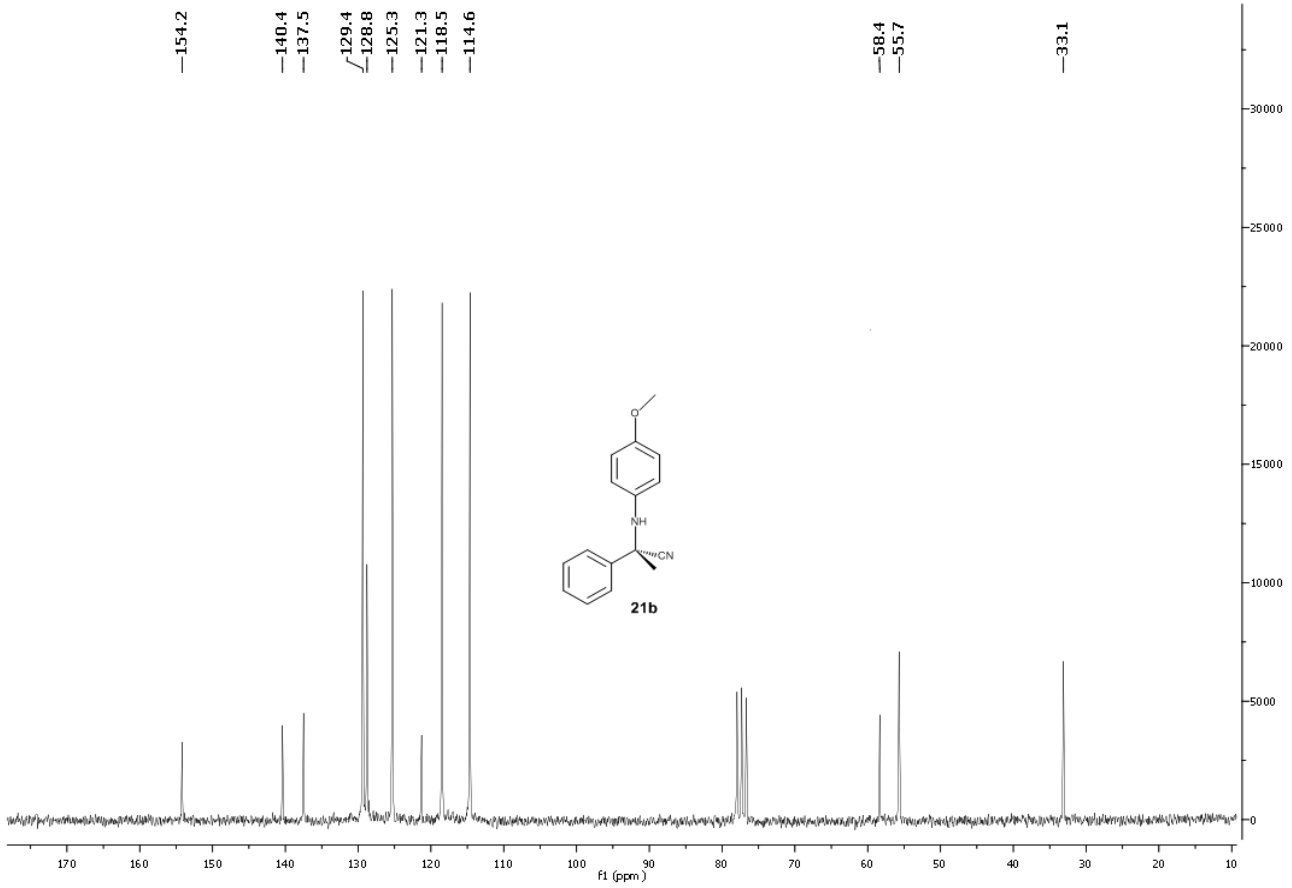
14.1 2-Phenyl-2-phenylaminopropanenitrile (21a).



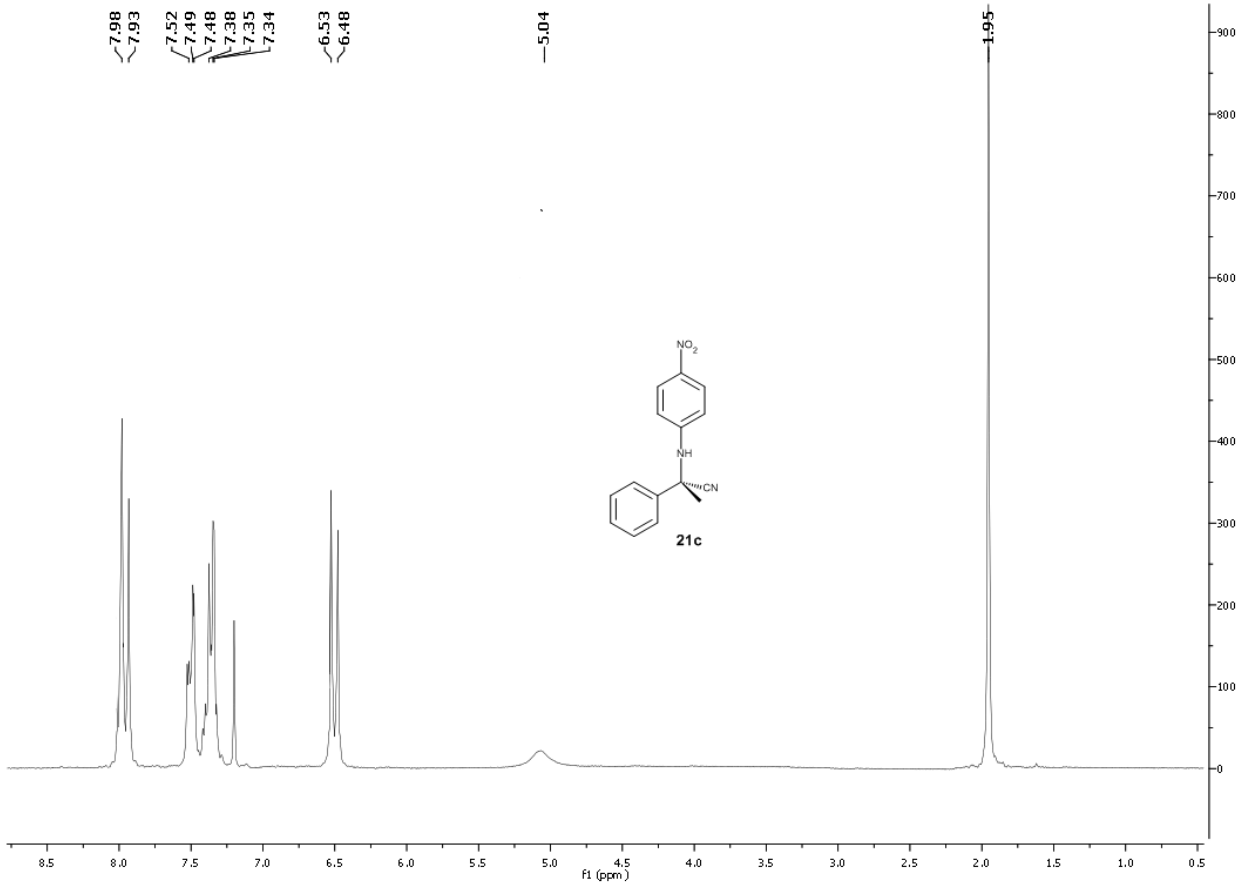


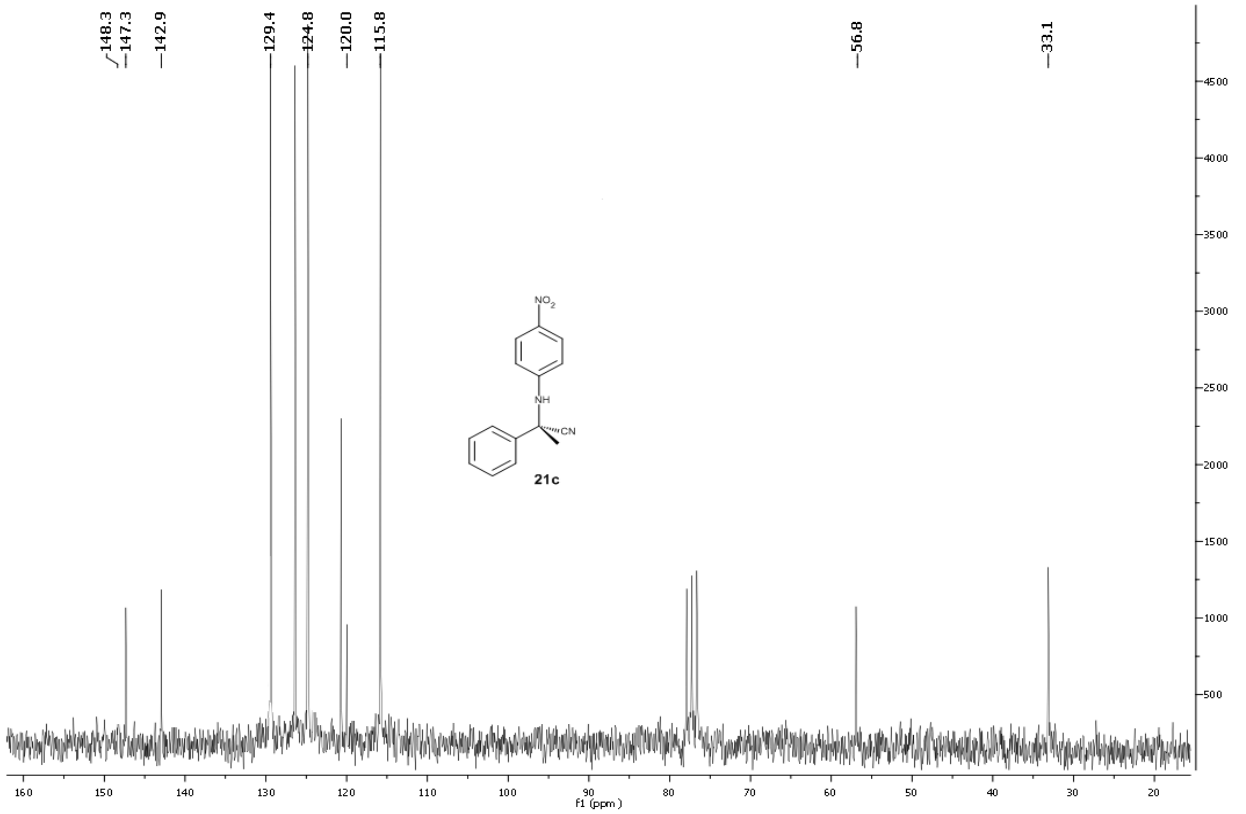
14.2 2-(4-Methoxyphenylamino)-2-phenylpropanenitrile (21b).



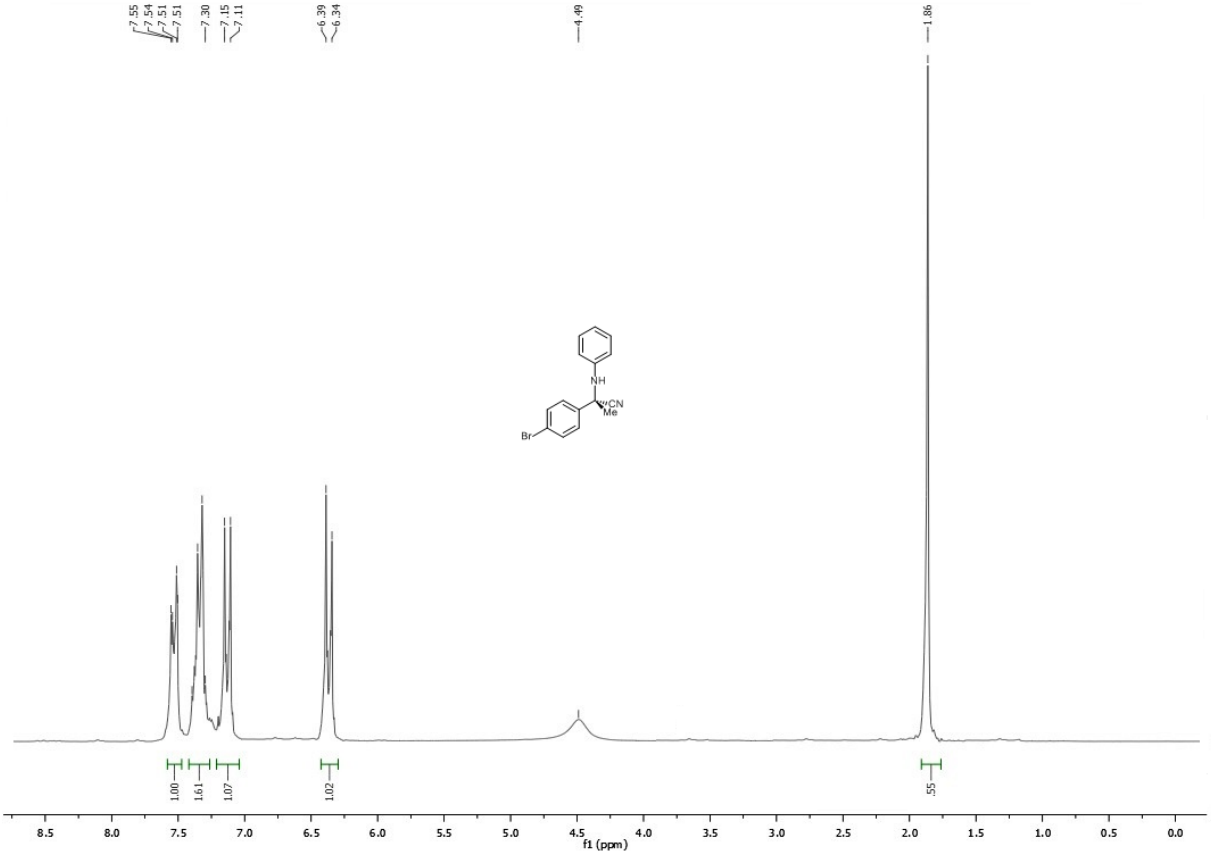


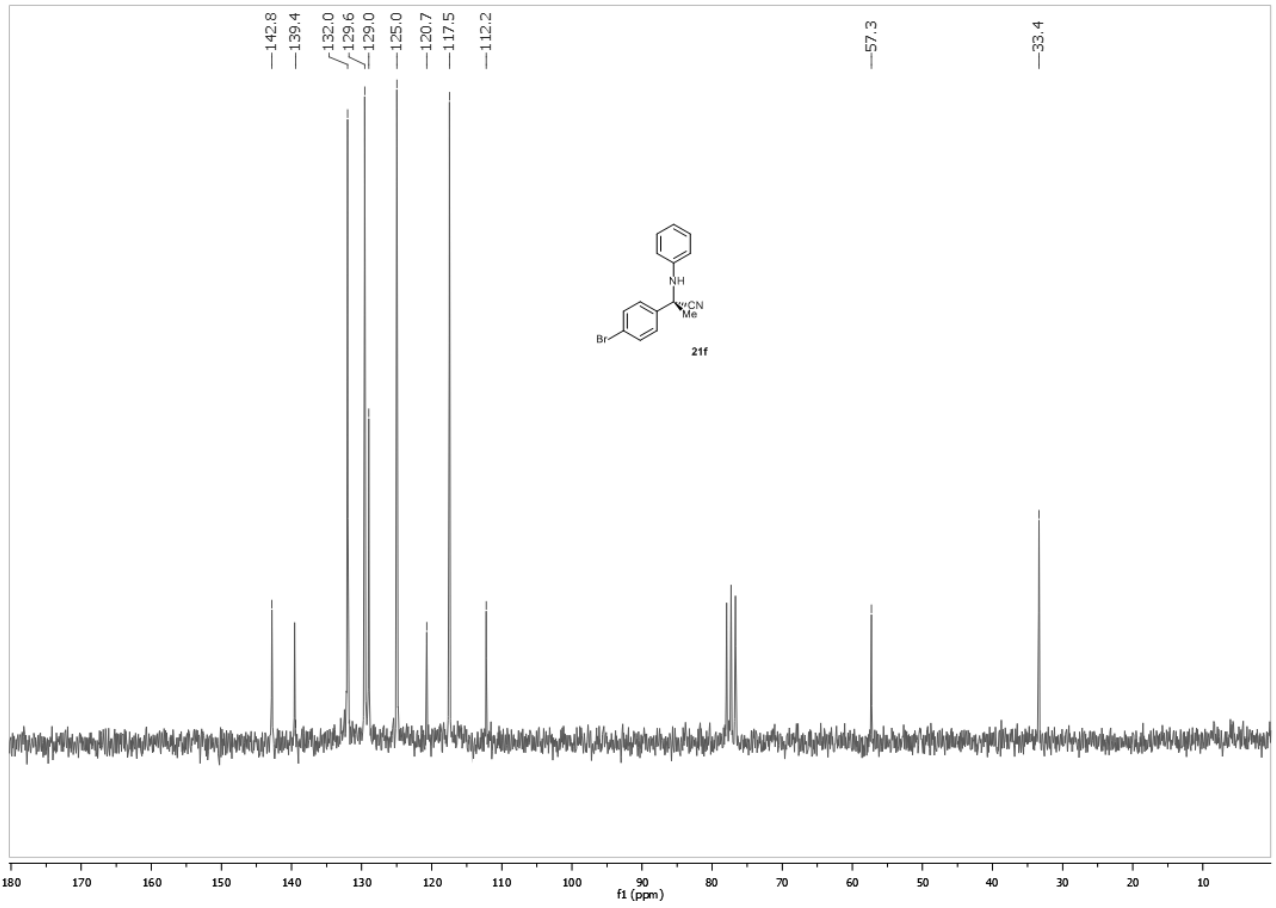
14.3 2-(4-Nitrophenylamino)-2-phenylpropanenitrile (**21c**).



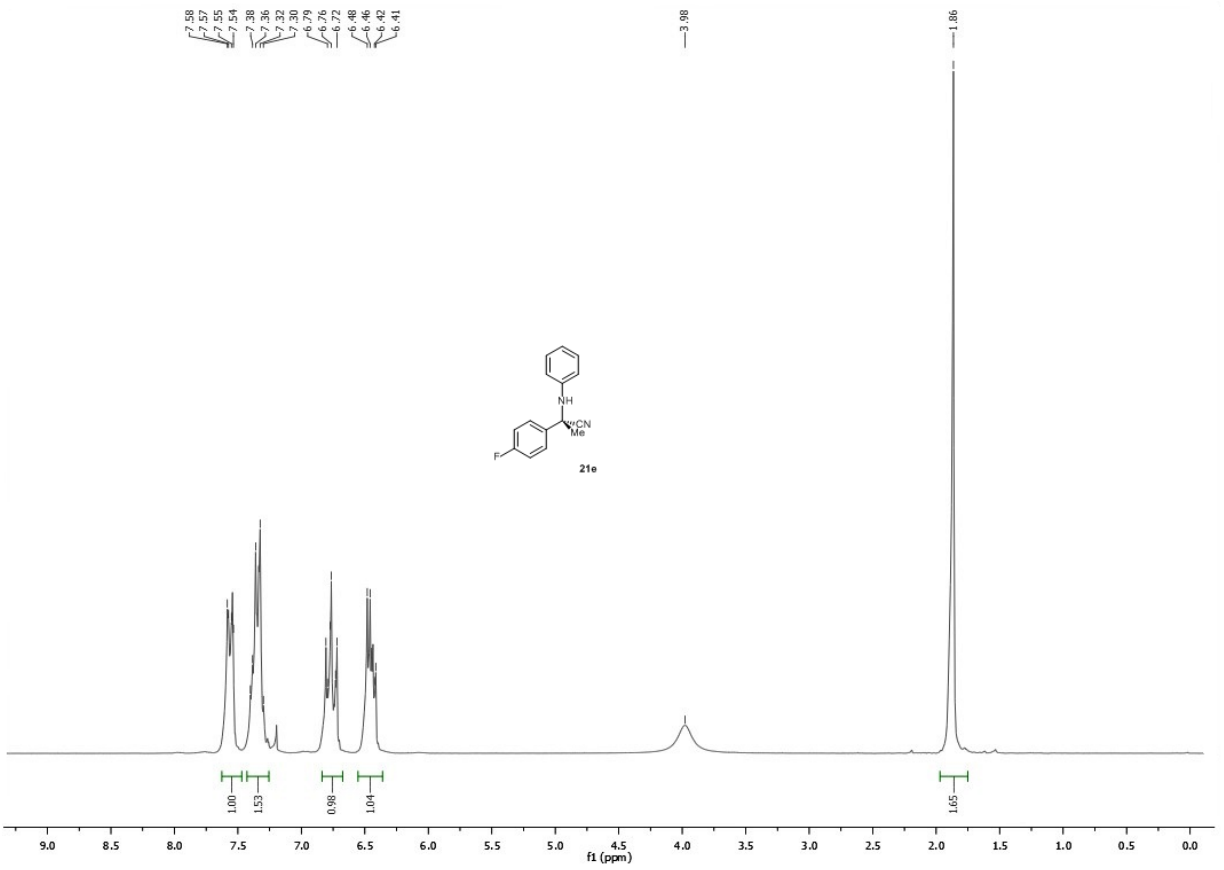


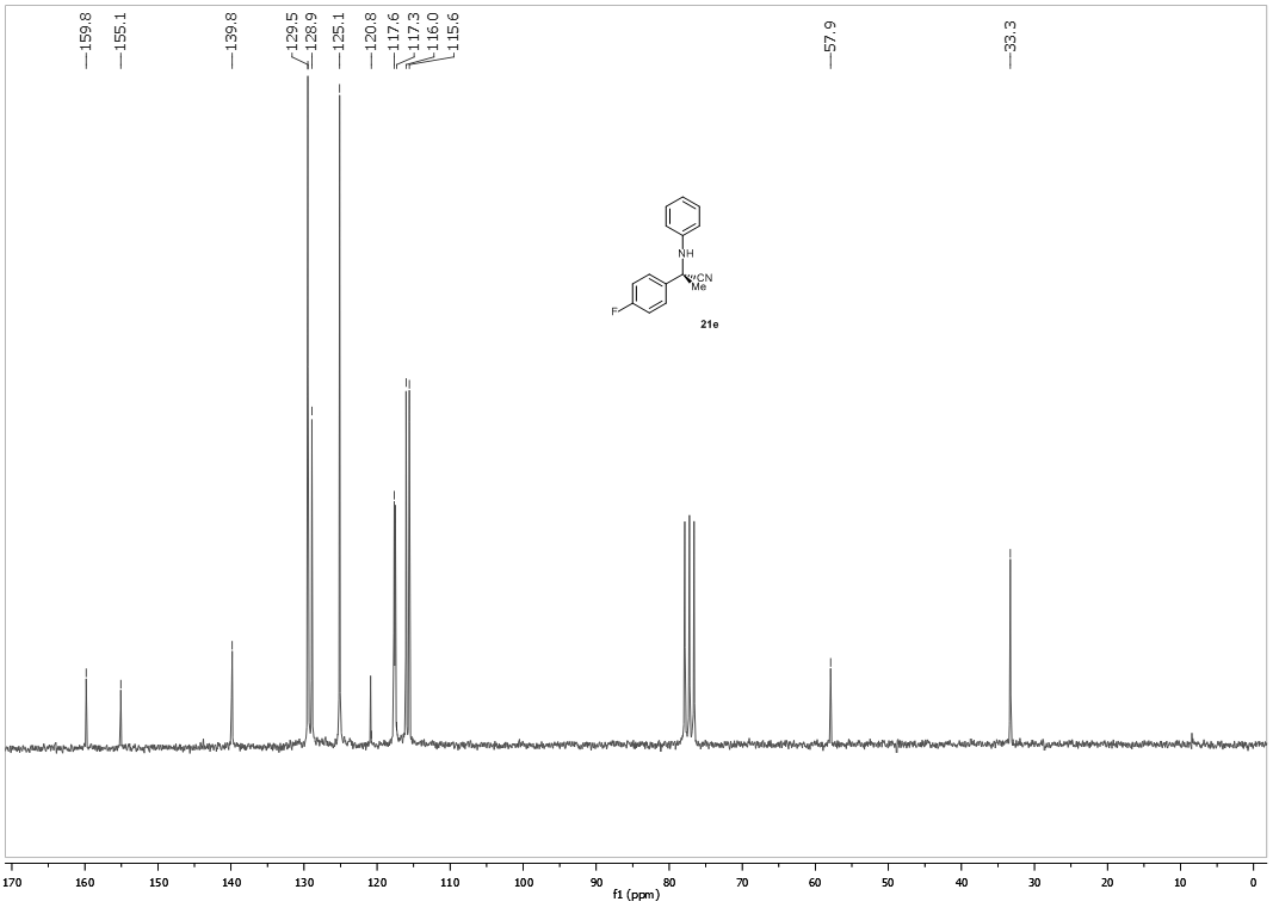
14.4 2-(4-Bromophenylamino)-2-phenylpropanenitrile (21d).



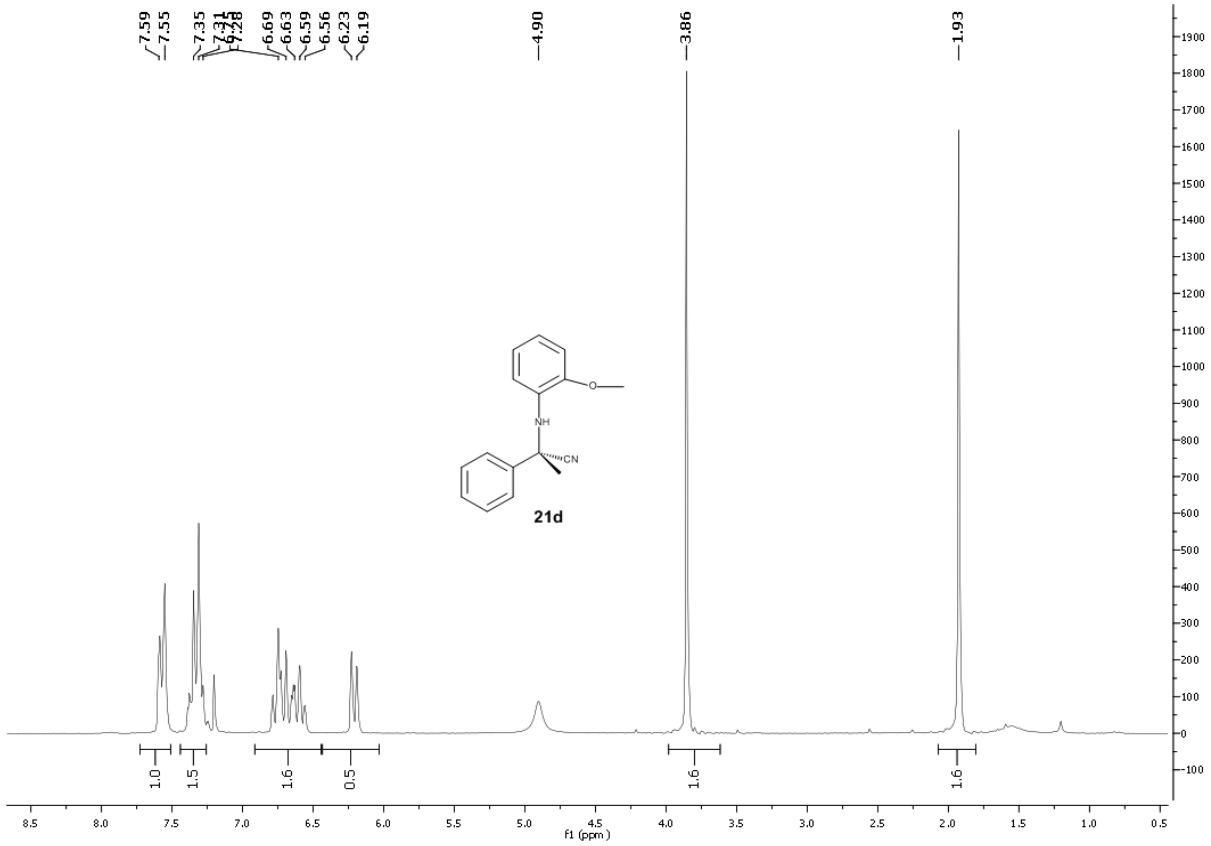


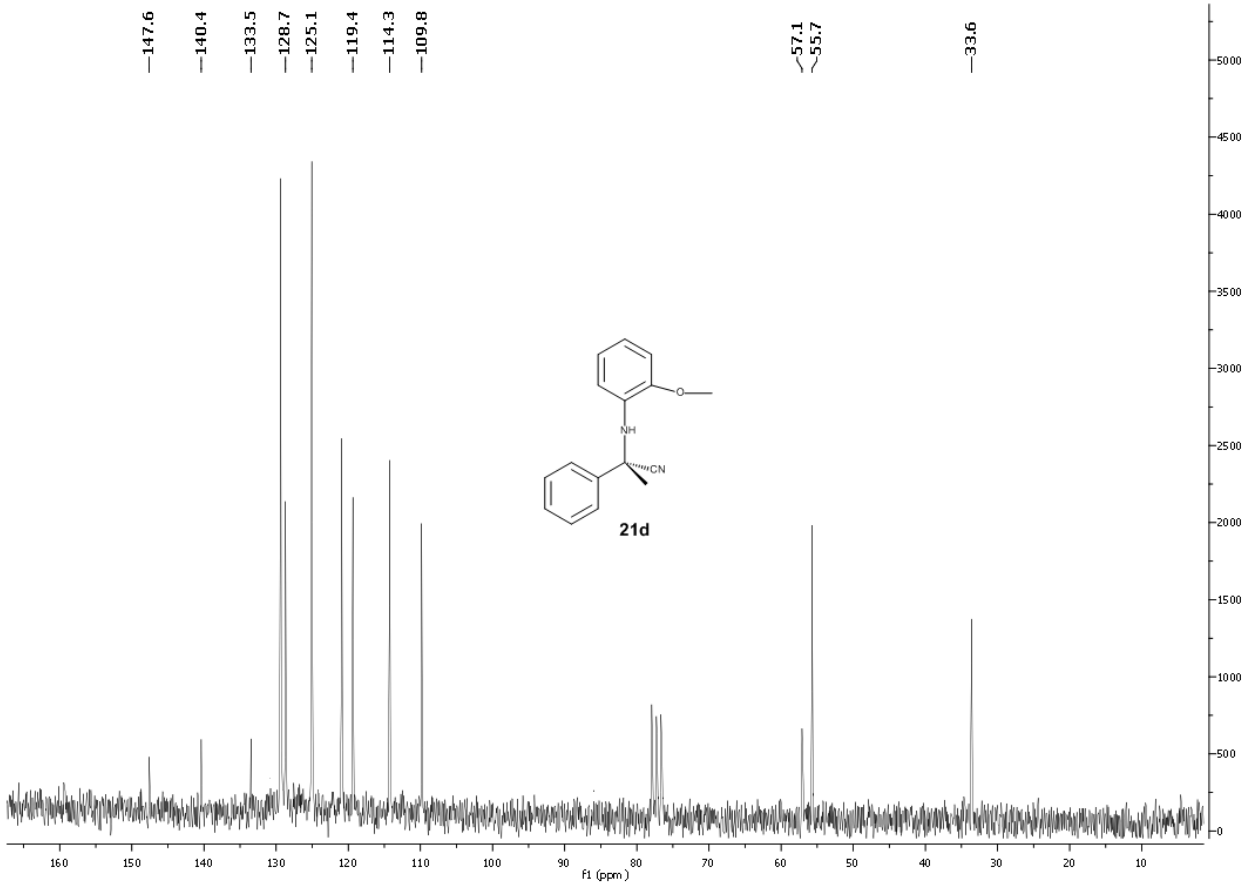
14.5 2-(4-Fluorophenylamino)-2-phenylpropanenitrile (21e).



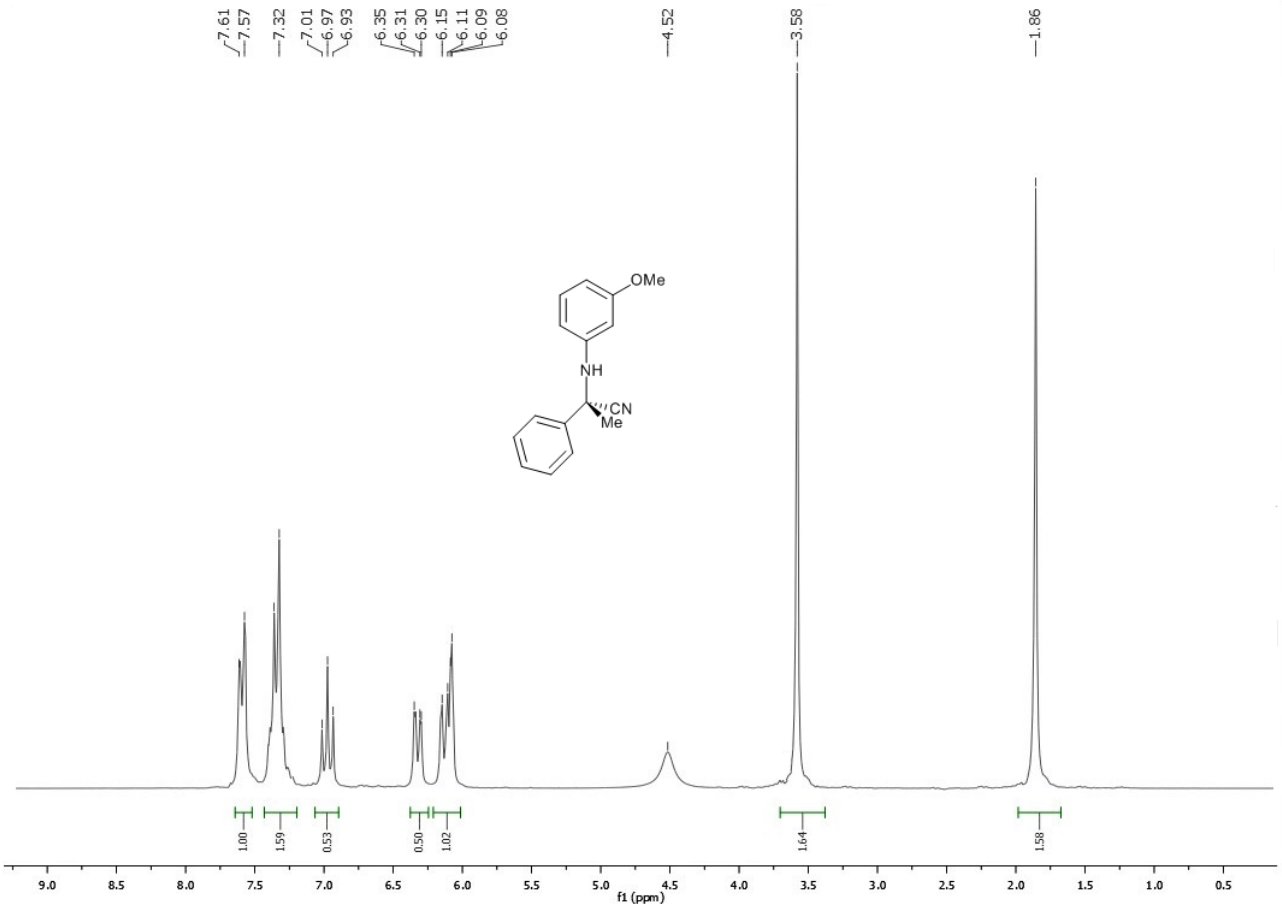


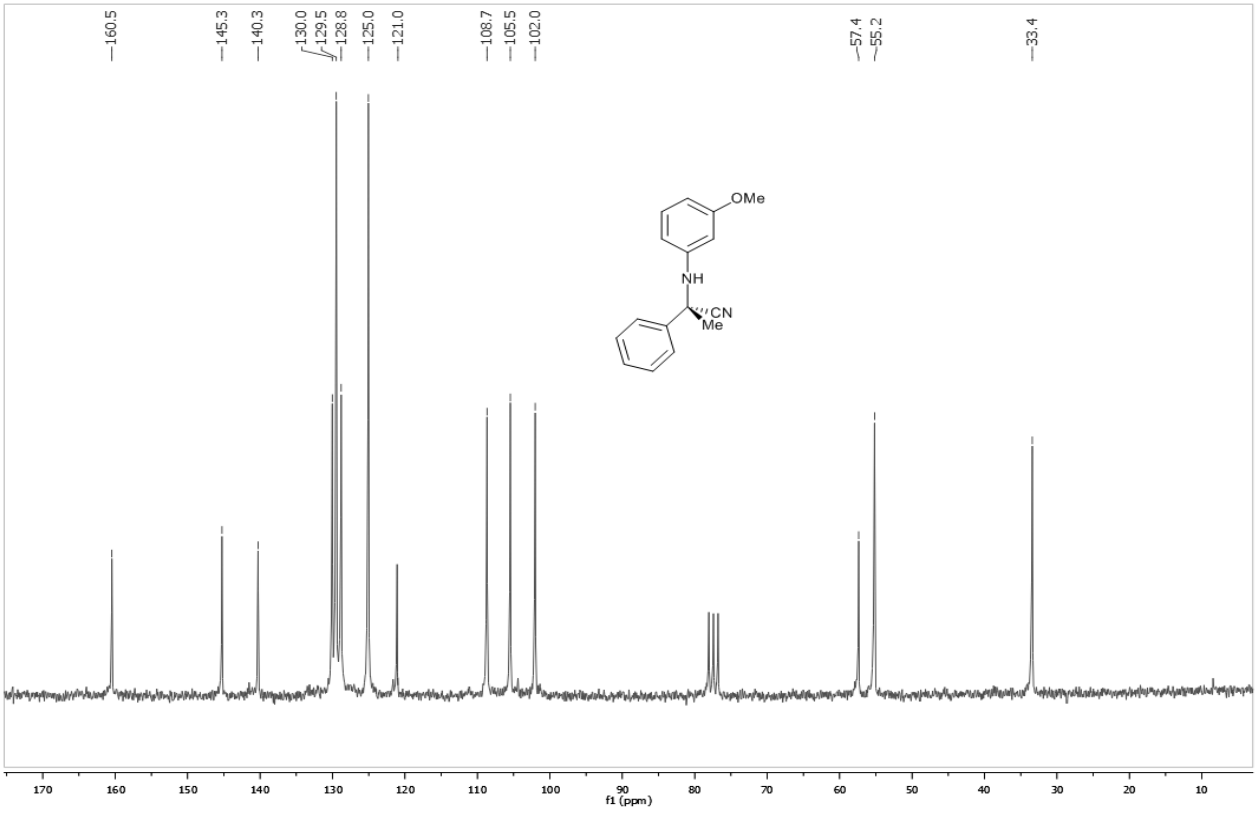
14.6 2-(2-Methoxyphenylamino)-2-phenylpropanenitrile (21f).



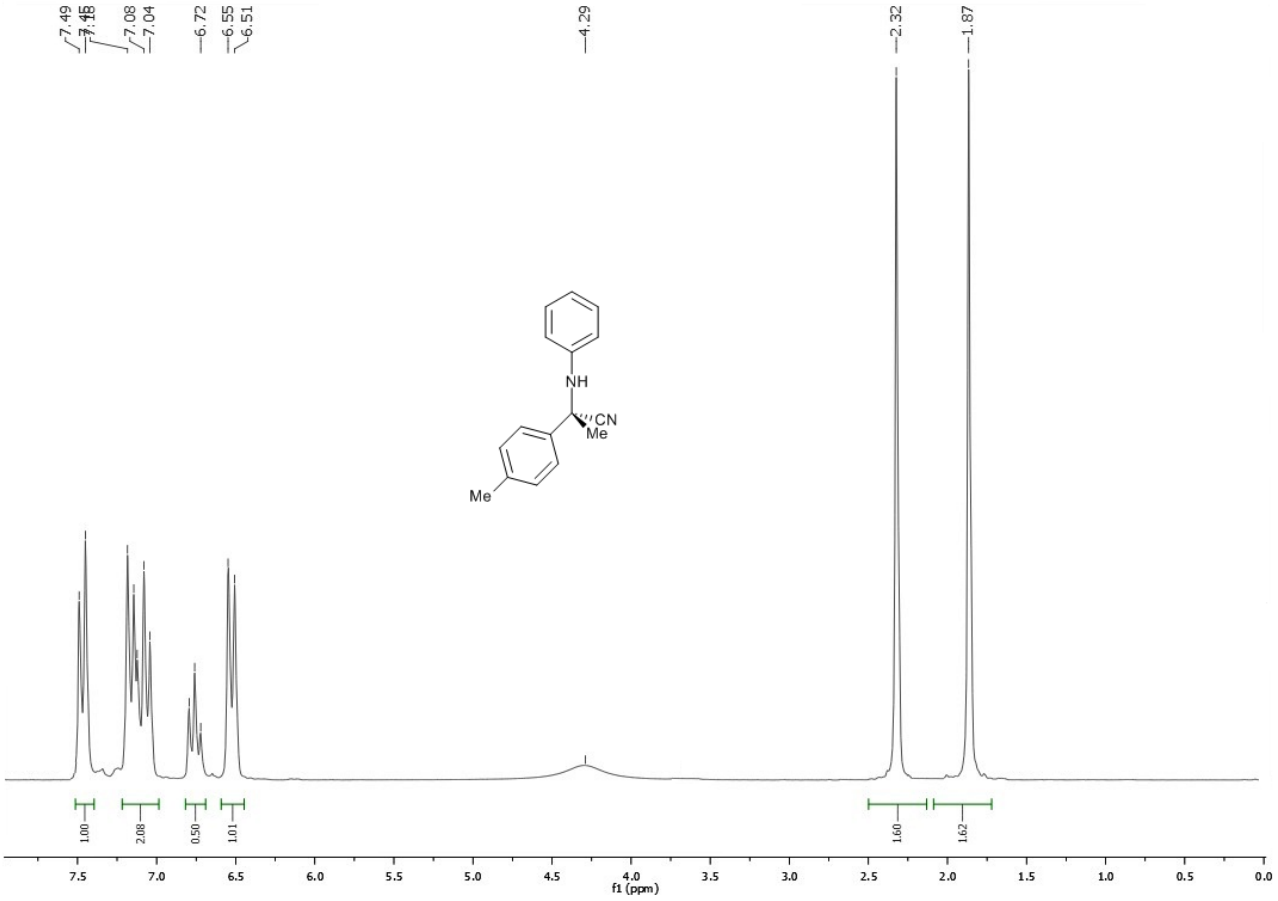


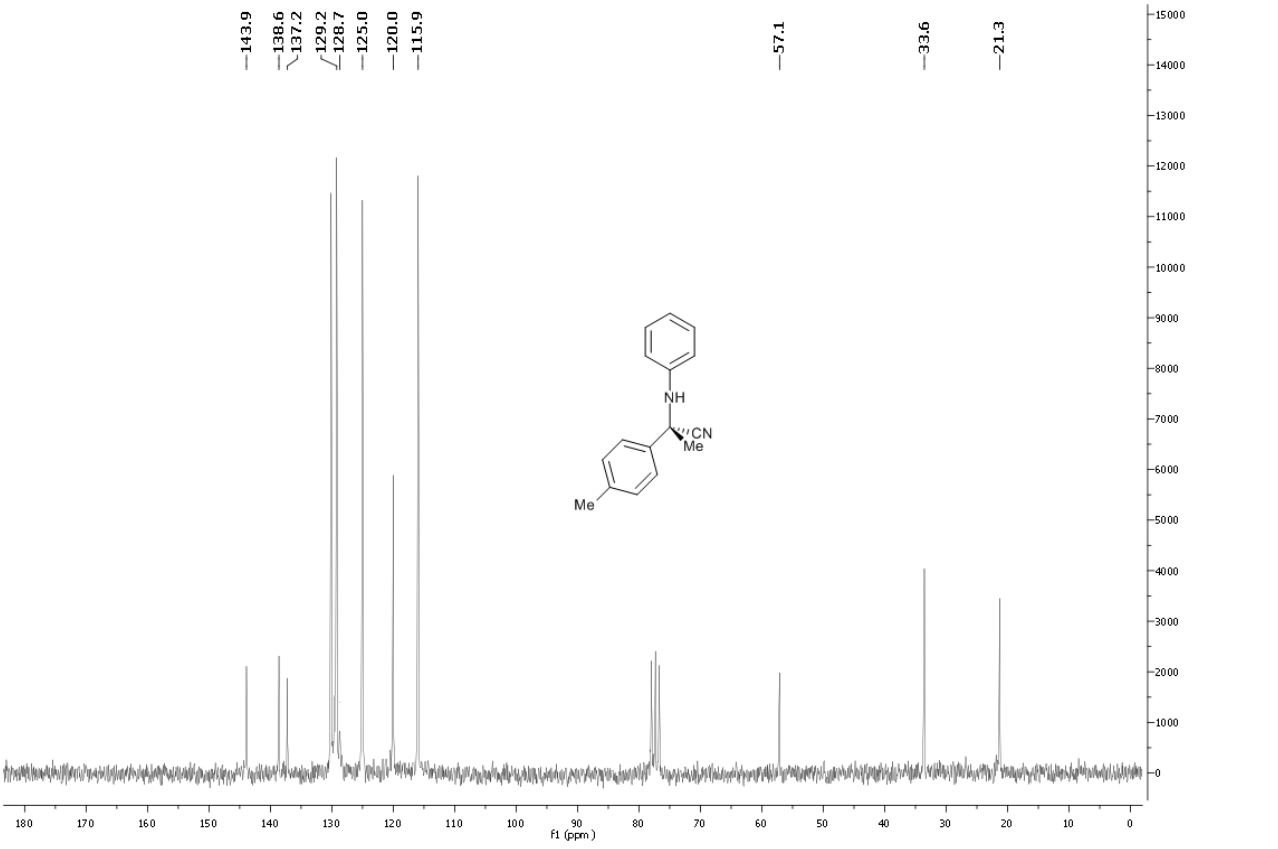
14.7 2-(3-Methoxyphenylamino)-2-phenylpropanenitrile (21g)



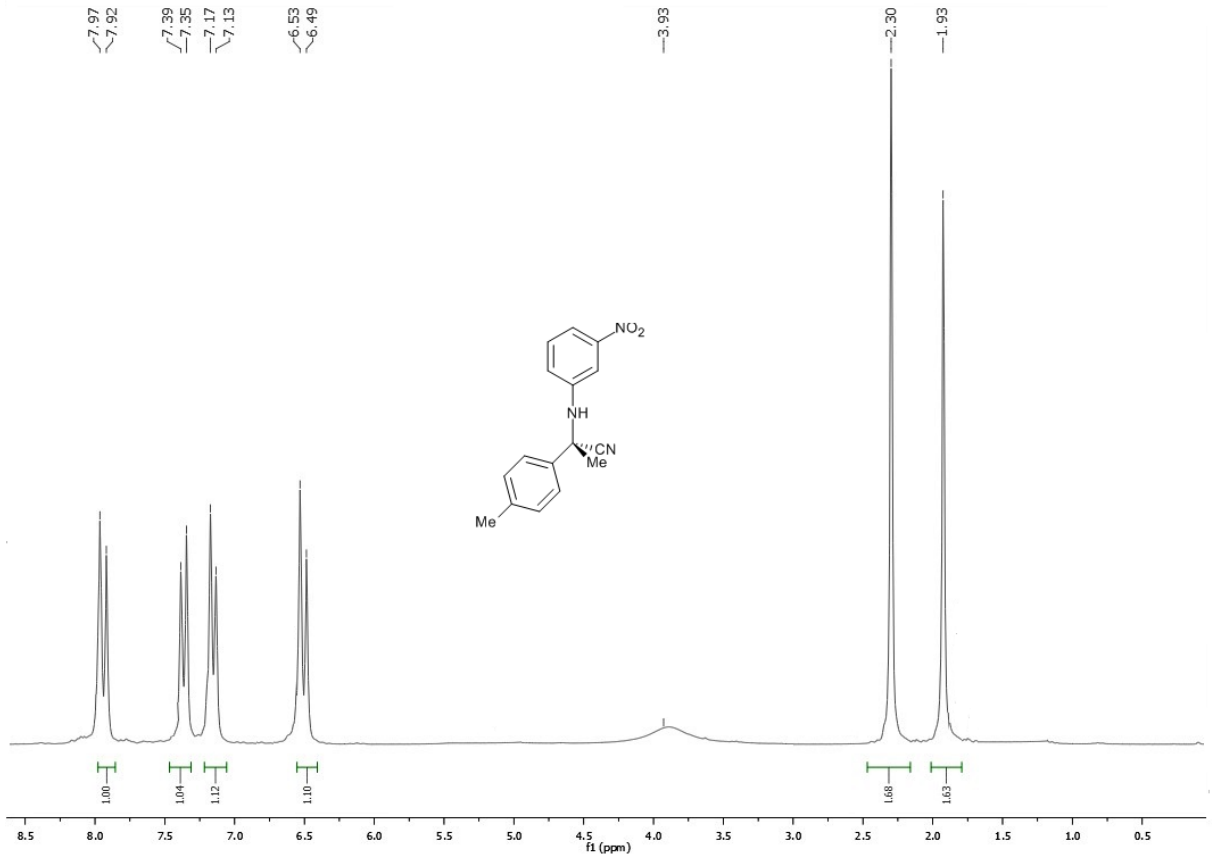


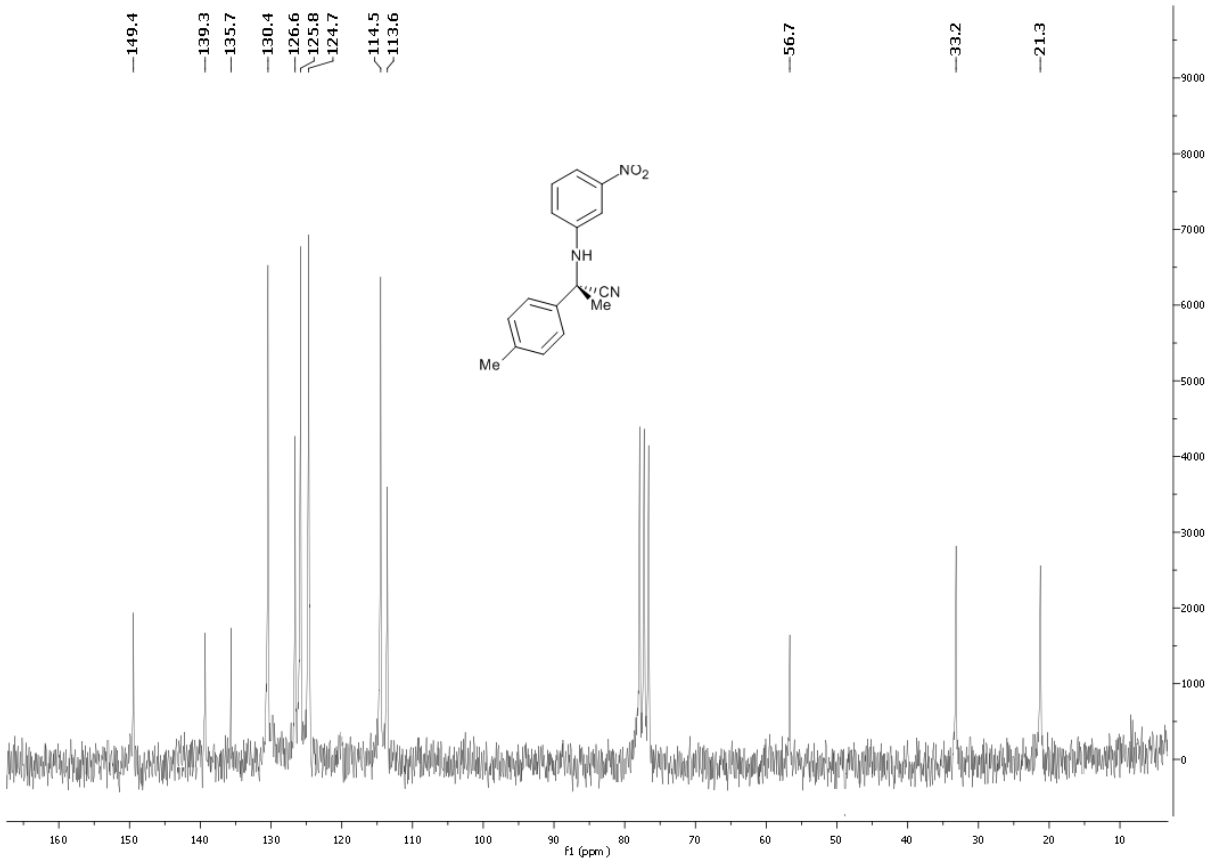
14.8 2-Phenylamino-2-(4-tolyl)propanenitrile (21h)



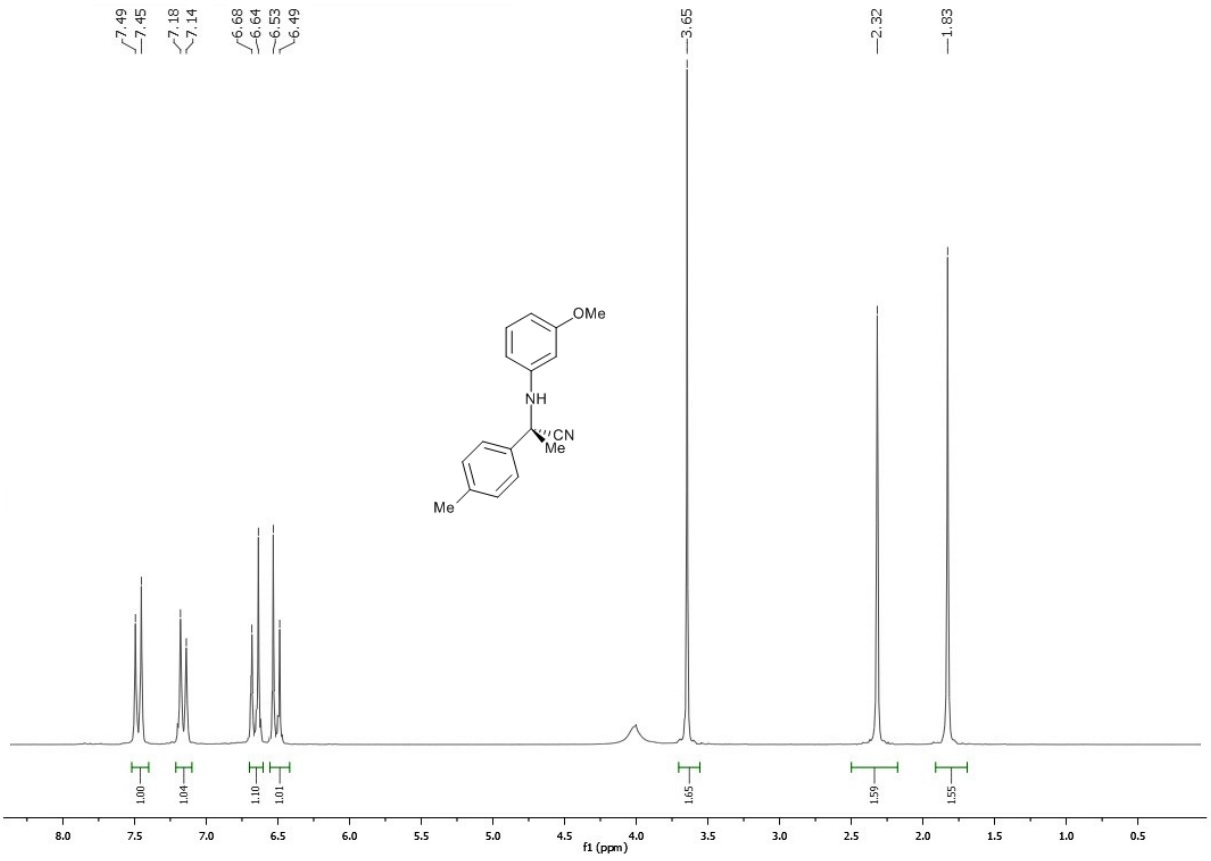


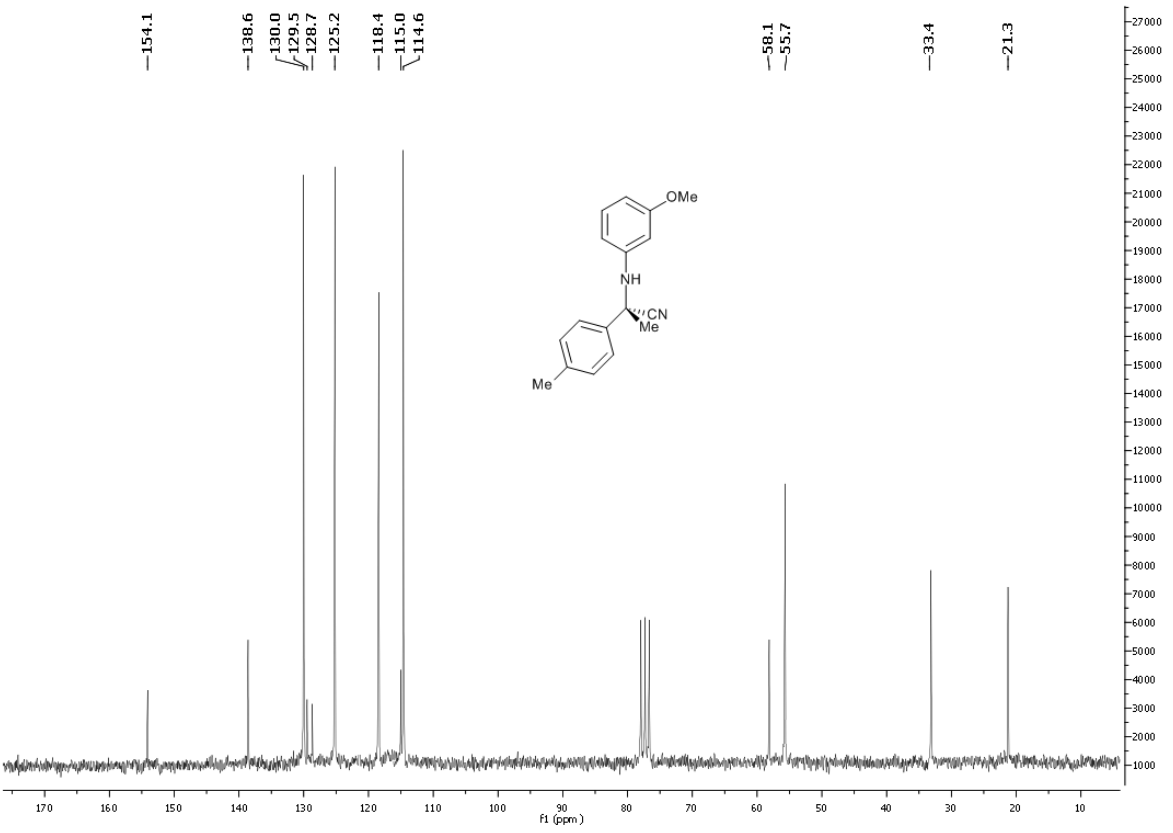
14.9 2-(4-Nitrophenylamino)-2-(4-tolyl)propanenitrile (21i)



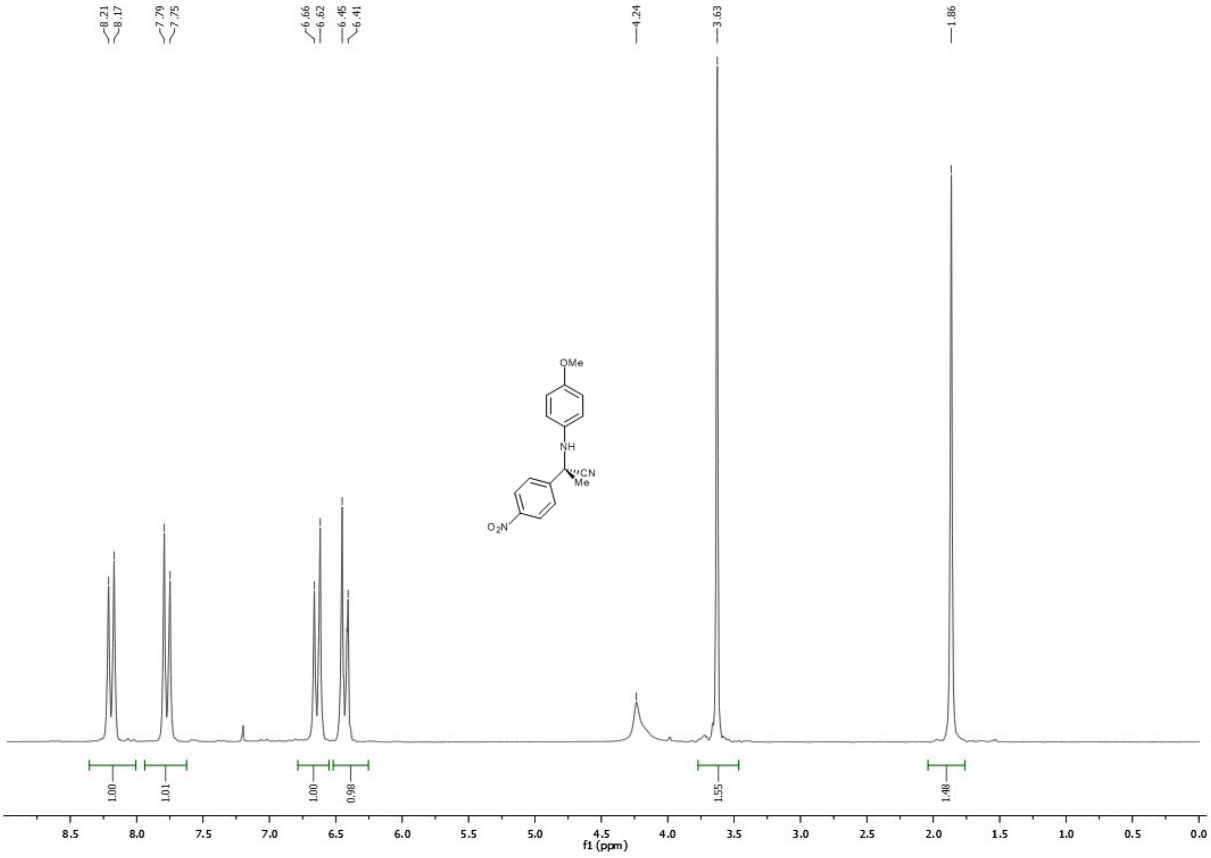


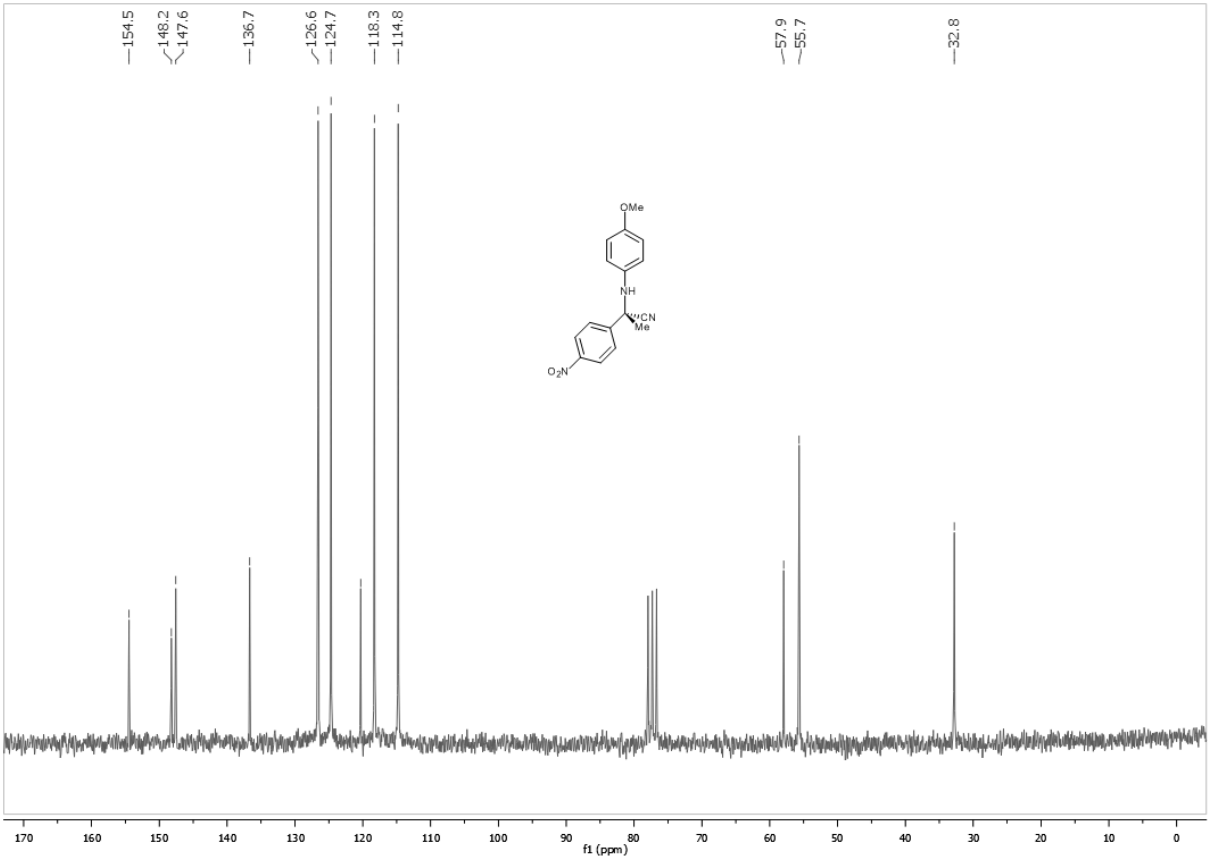
14.10 2-(4-Methoxyphenylamino)-2-(4-tolyl)propanenitrile (21j)



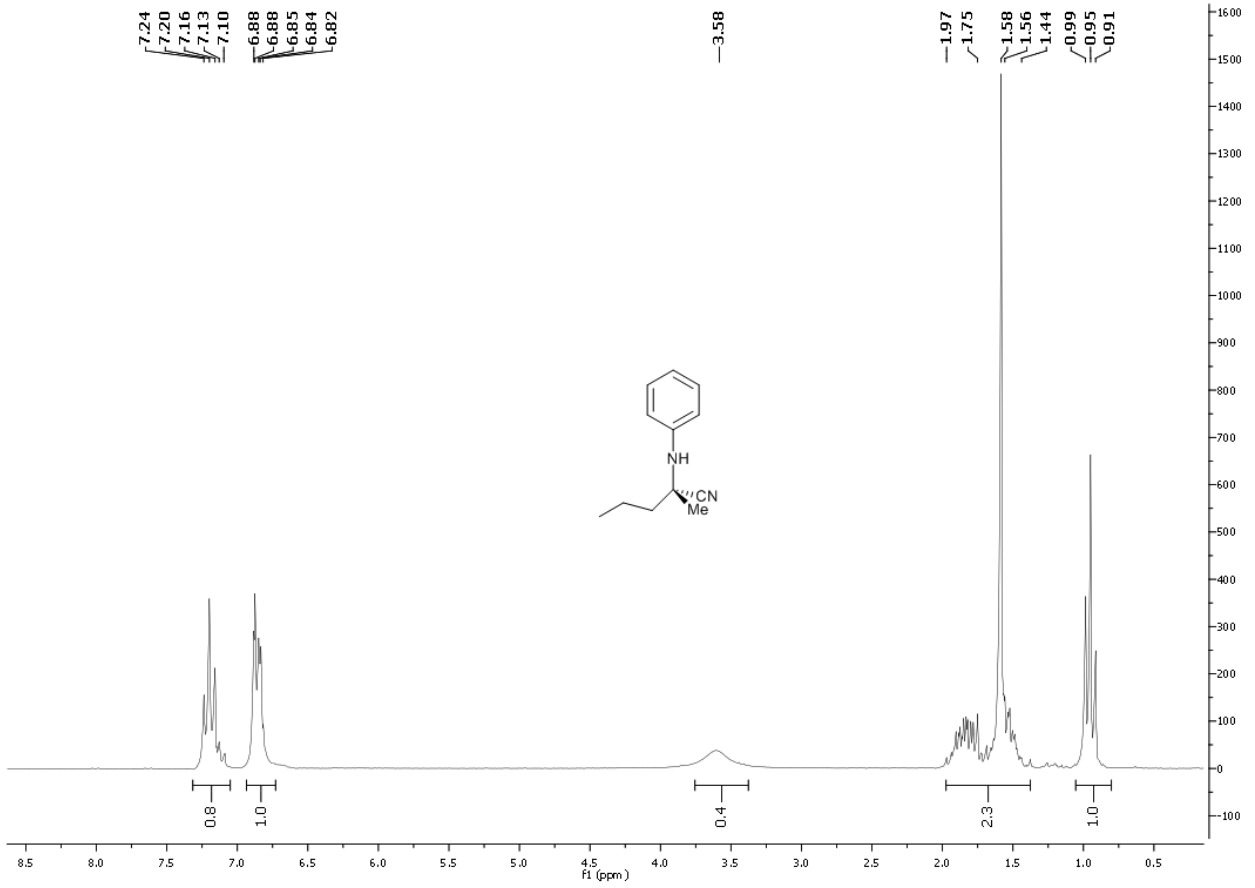


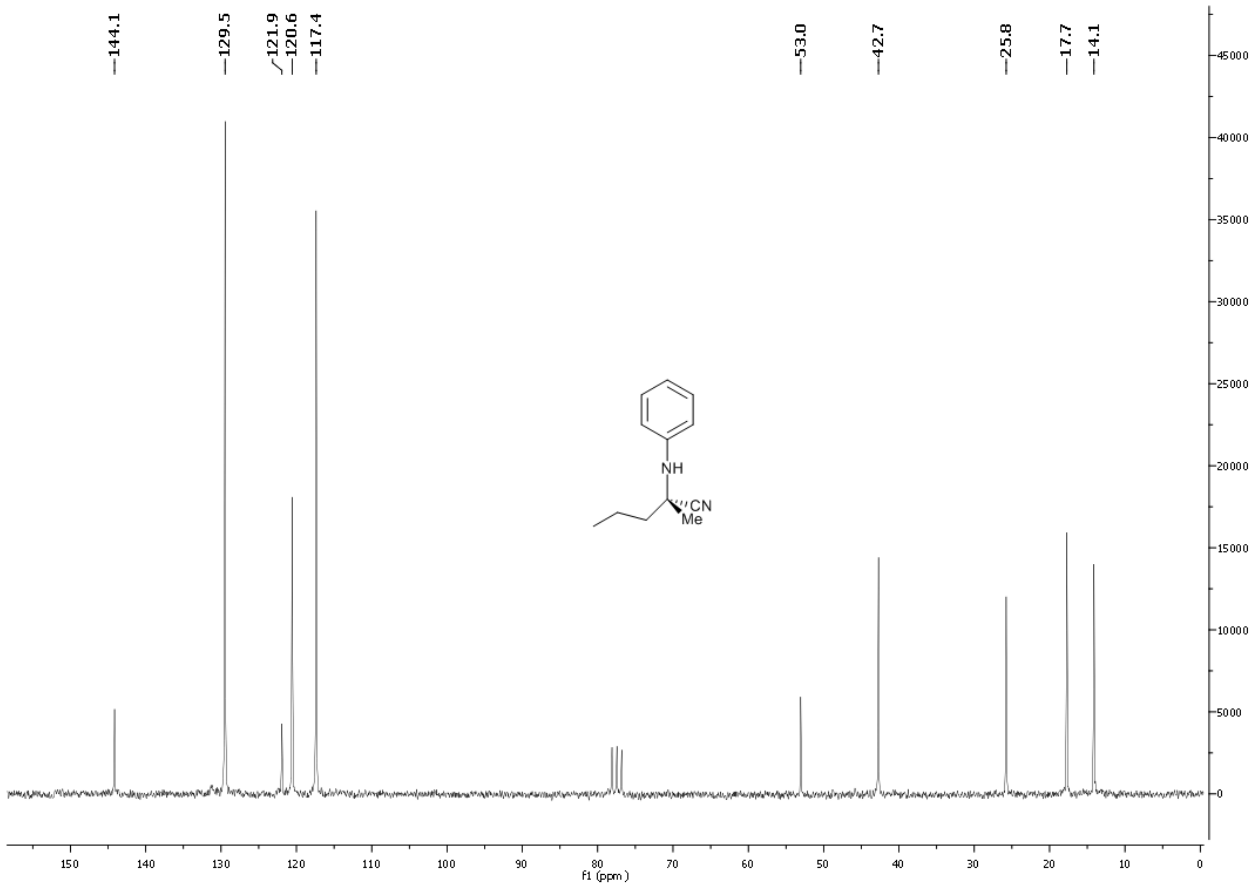
14.11 2-(4-Methoxyphenylamino)-2-(4-Nitrophenyl)propanenitrile (21k)



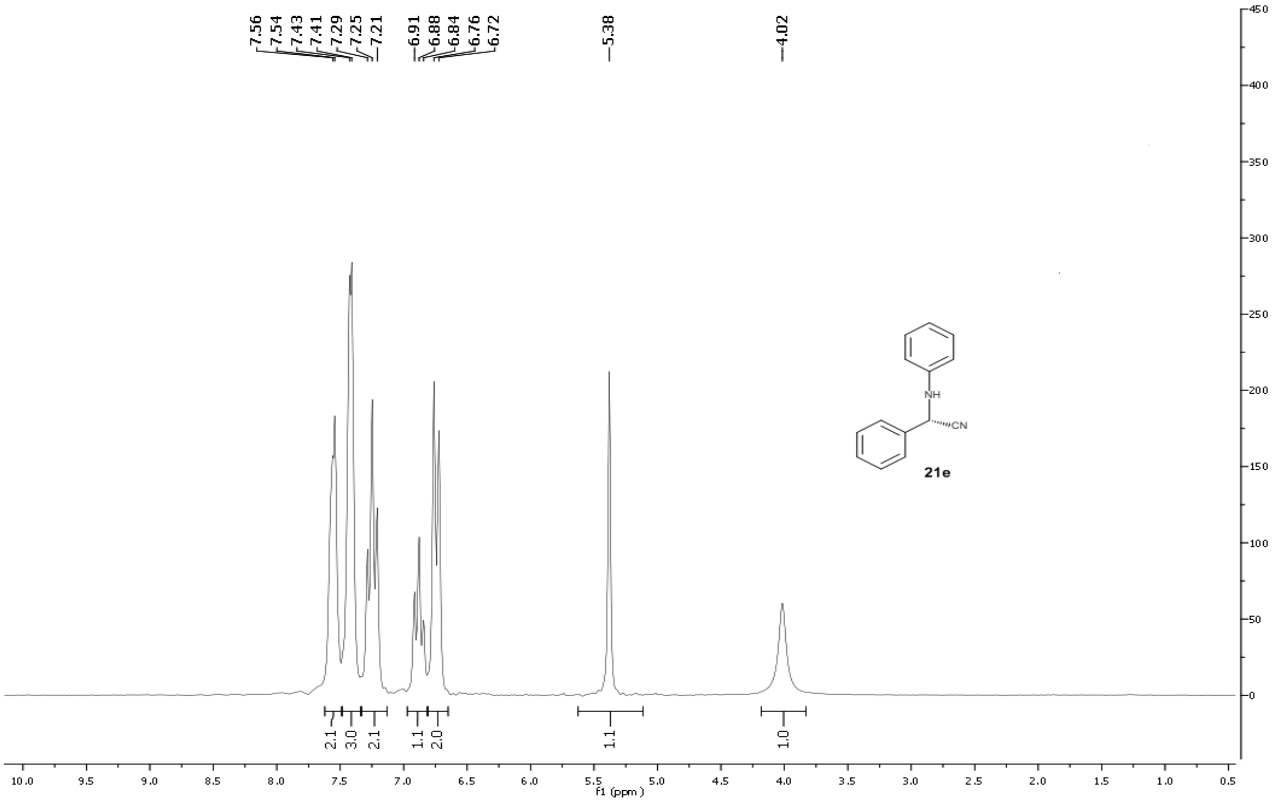


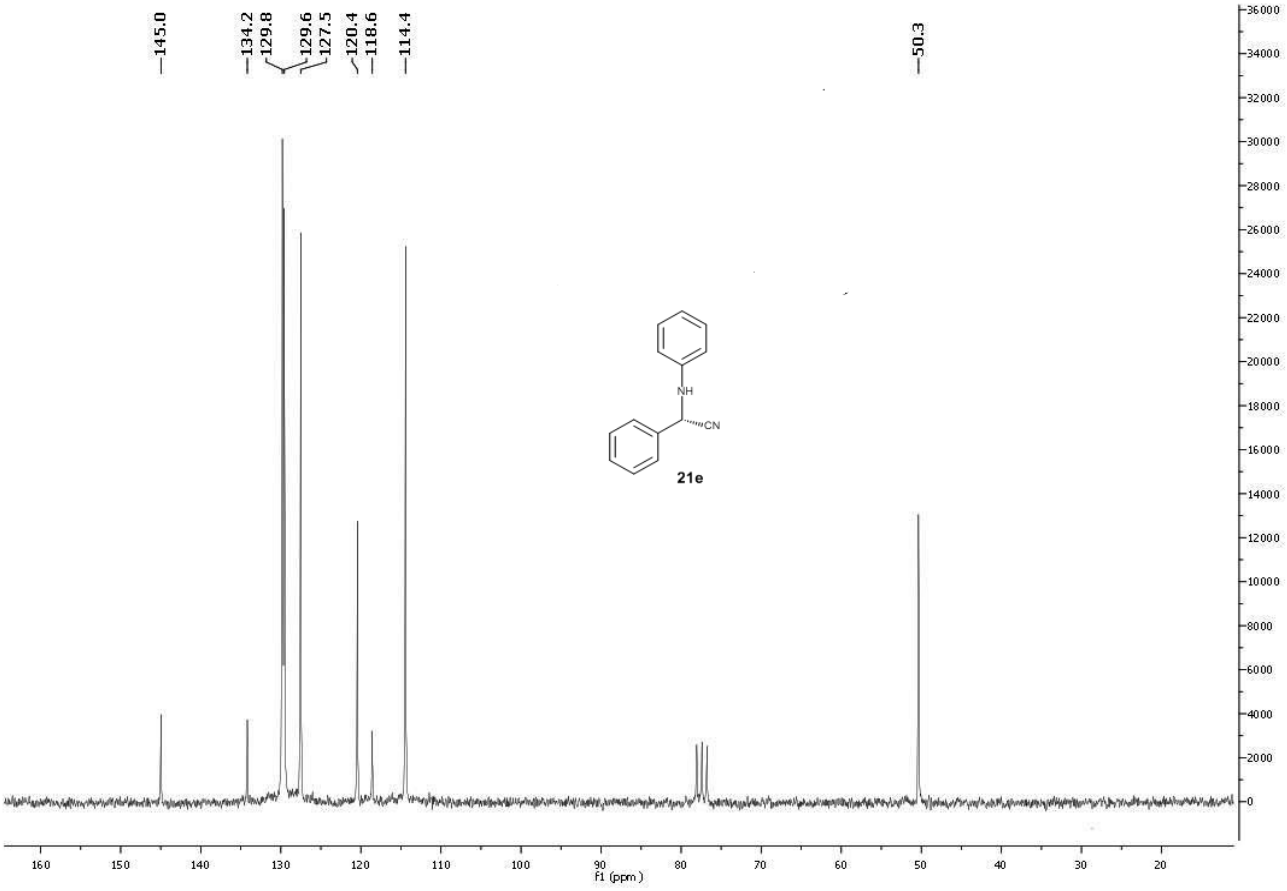
14.12 2-Methyl-2-phenylaminopentanenitrile (21l)



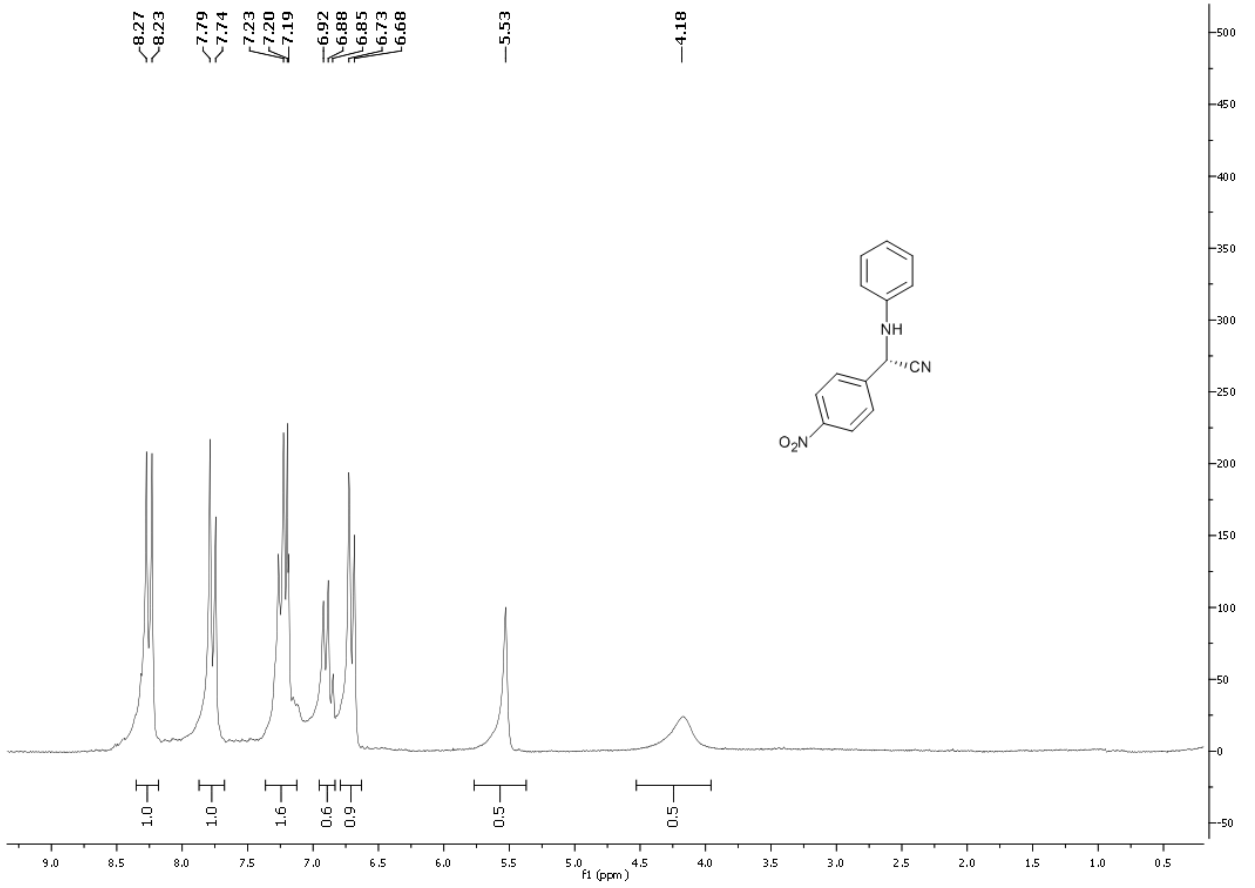


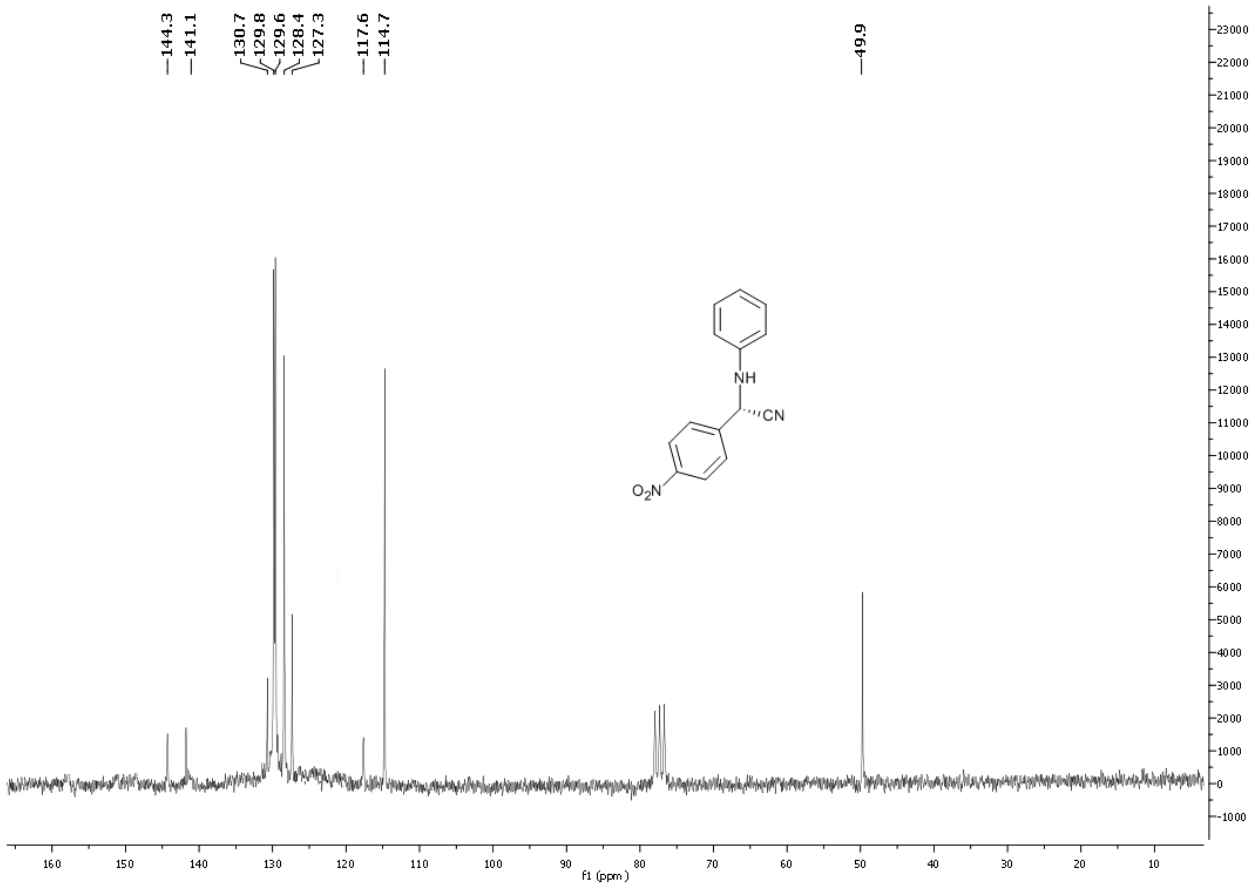
14.13 2-Phenyl-2-phenylaminoacetonitrile (21m).



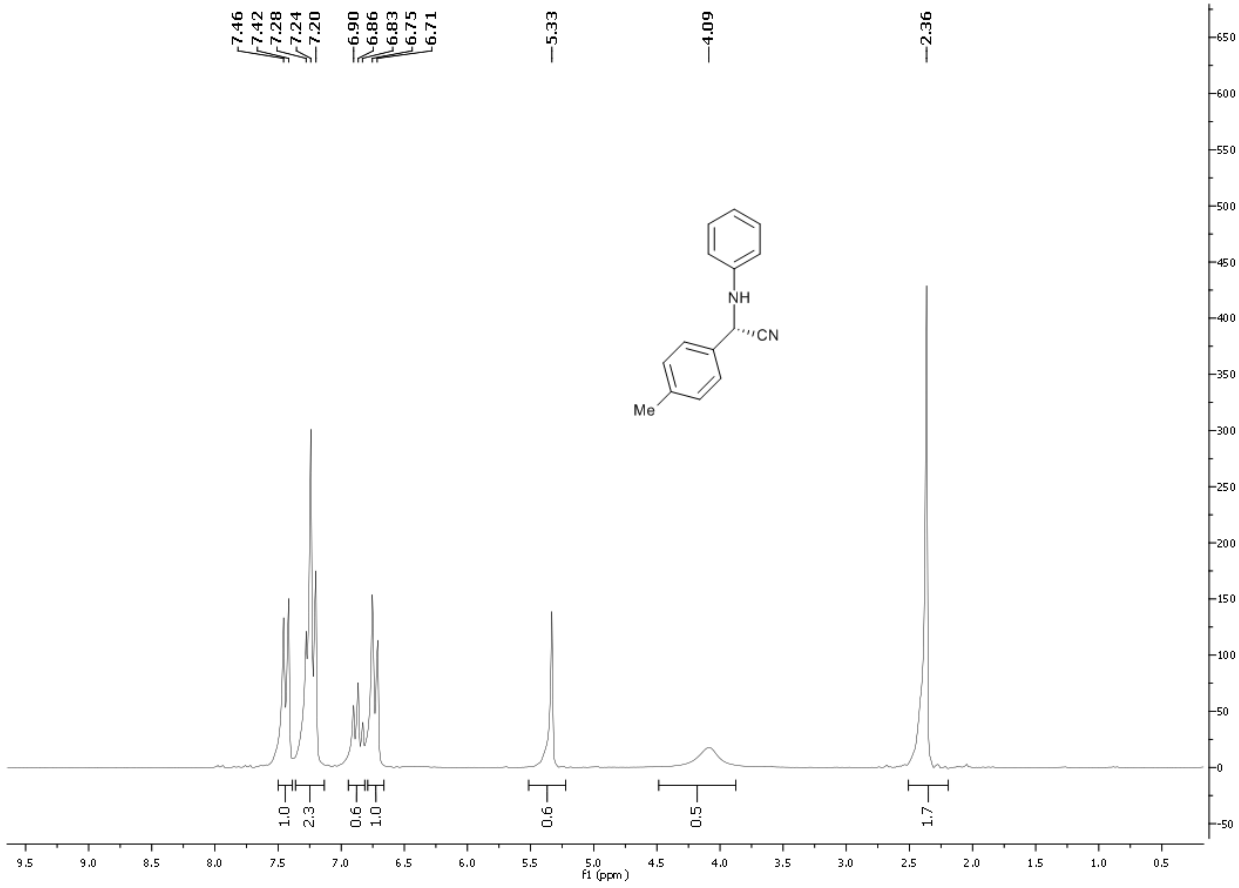


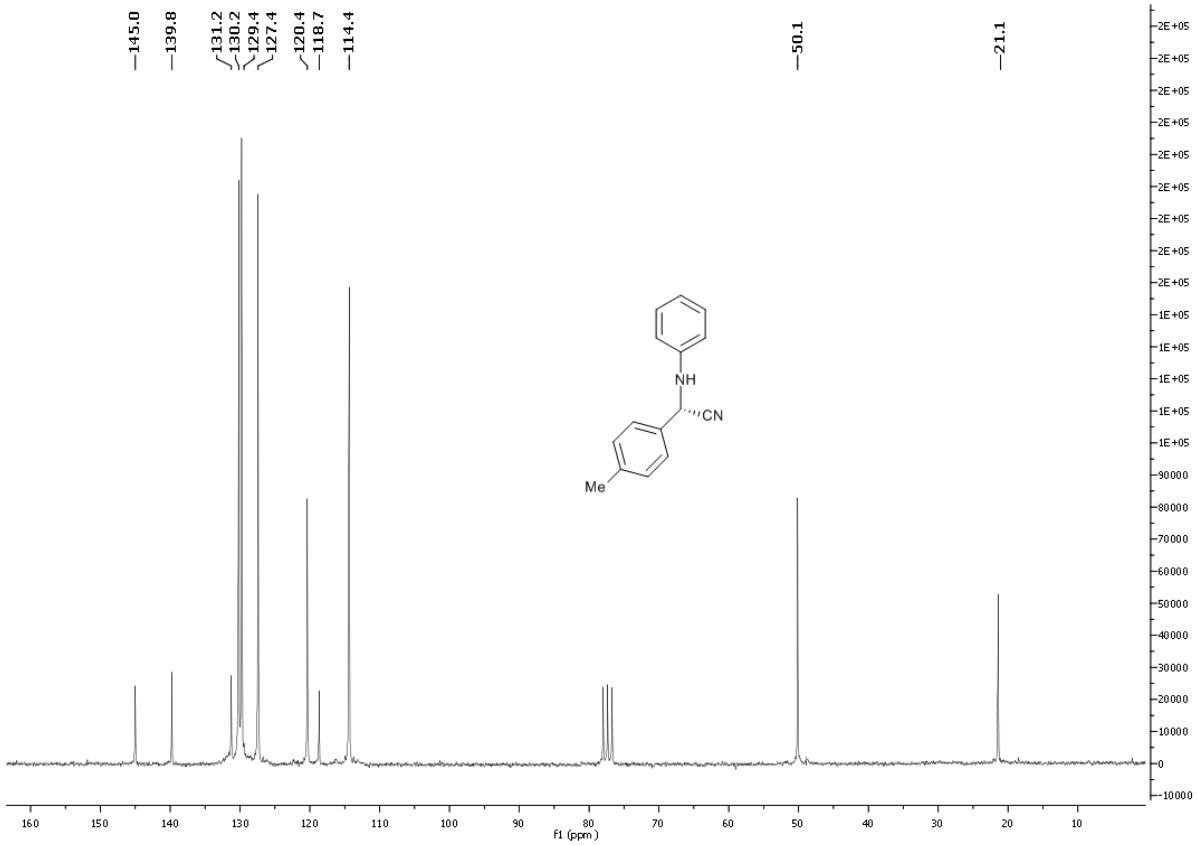
14.14 2-(4-Nitrophenyl)-2-phenylaminoacetonitrile (21n)



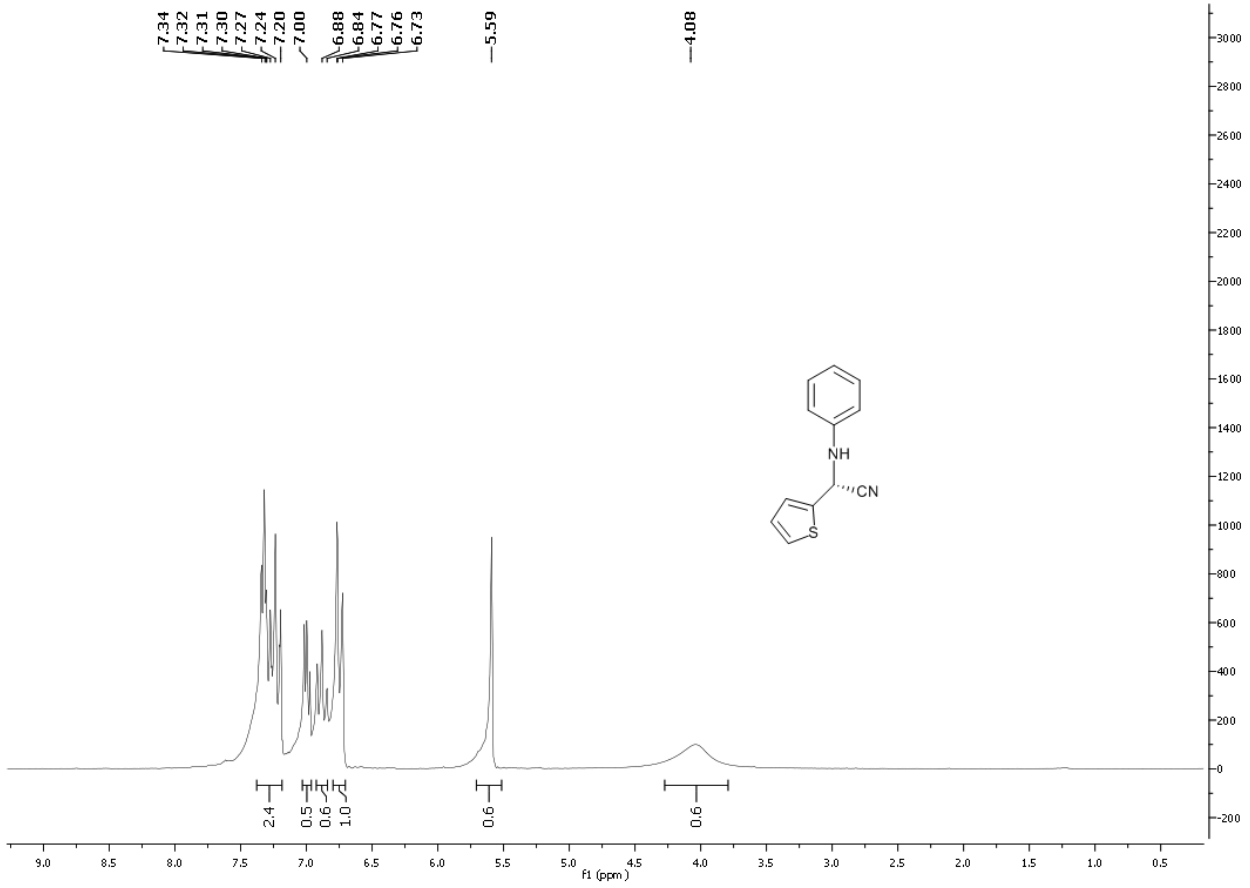


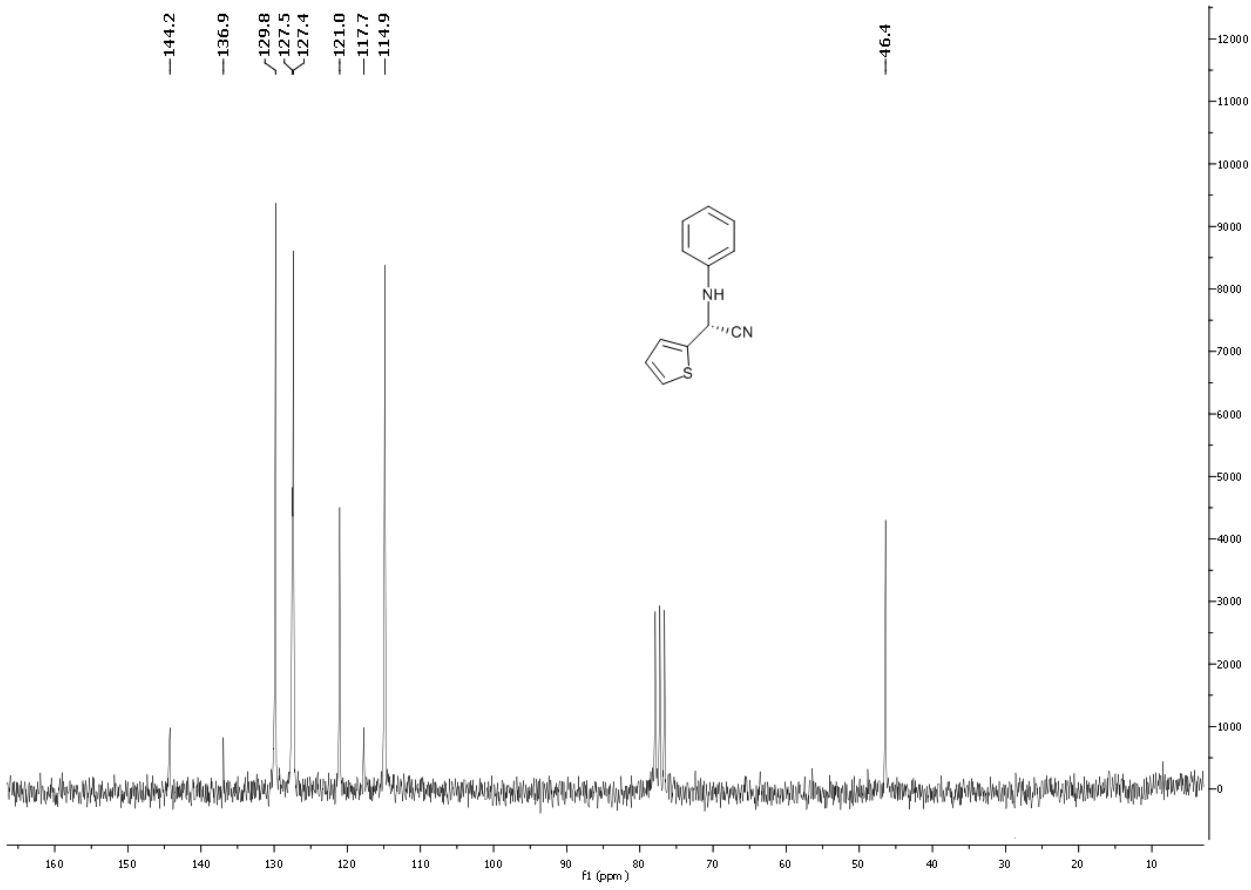
14.15 2-Phenylamino-2-(4-tolyl)acetonitrile (21o)





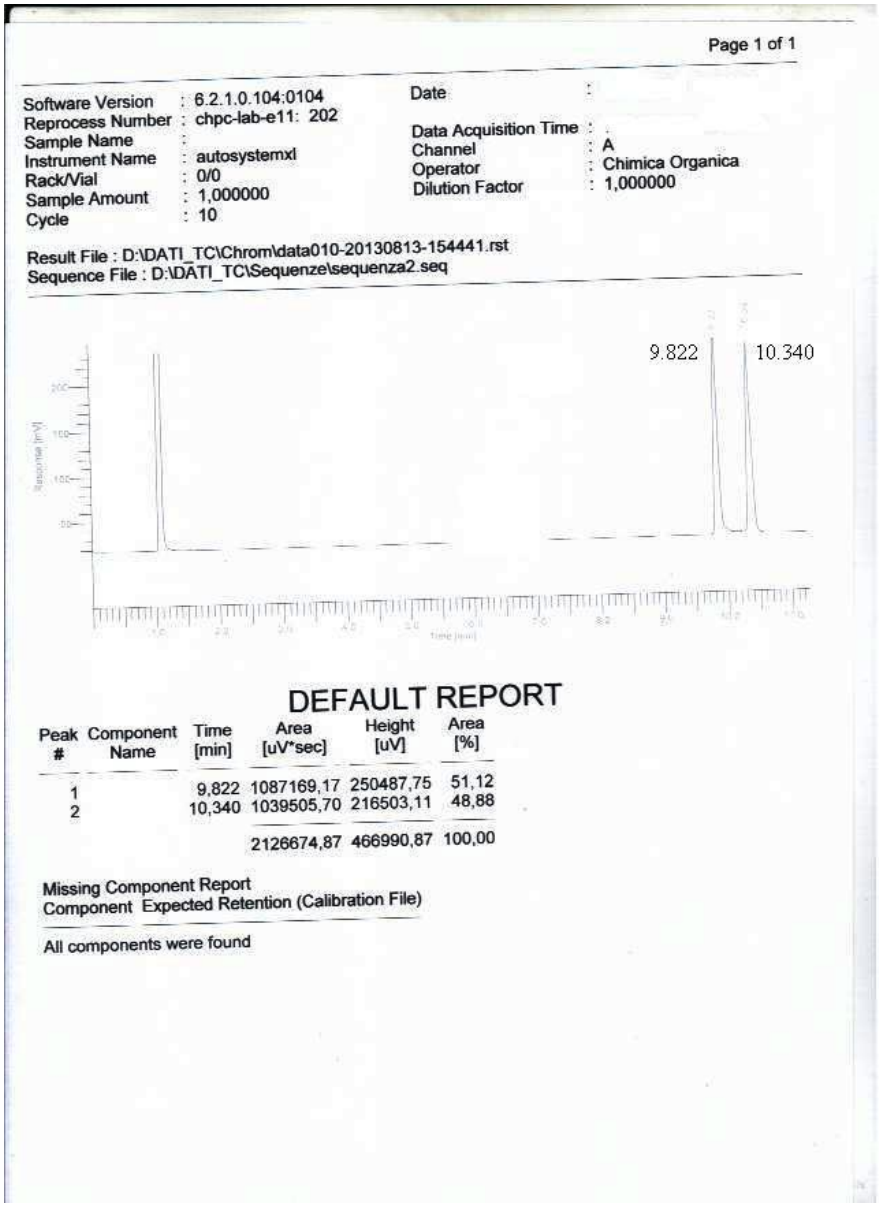
14.16 2-Phenylamino-2-(2-thienyl)acetonitrile (21o)





15. Chiral GC spectra of nitriles 21

15.1 Enantiomers of 2-phenyl-2-phenylaminopropanenitrile (21a)



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Software Version : 6.2.1.0.104:0104
Reprocess Number : chpc-lab-e11: 202
Sample Name :
Instrument Name : autosystemxl
Rack/Vial : 0/0
Sample Amount : 1,000000
Cycle : 10

Date :
Data Acquisition Time :
Channel : A
Operator : Chimica Organica
Dilution Factor : 1,000000

Result File : D:\DATI_TC\Chrom\data010-20130813-154441.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9,822	1087169,17	250487,75	51,12
2		10,340	1039505,70	216503,11	48,88
			2126674,87	466990,87	100,00

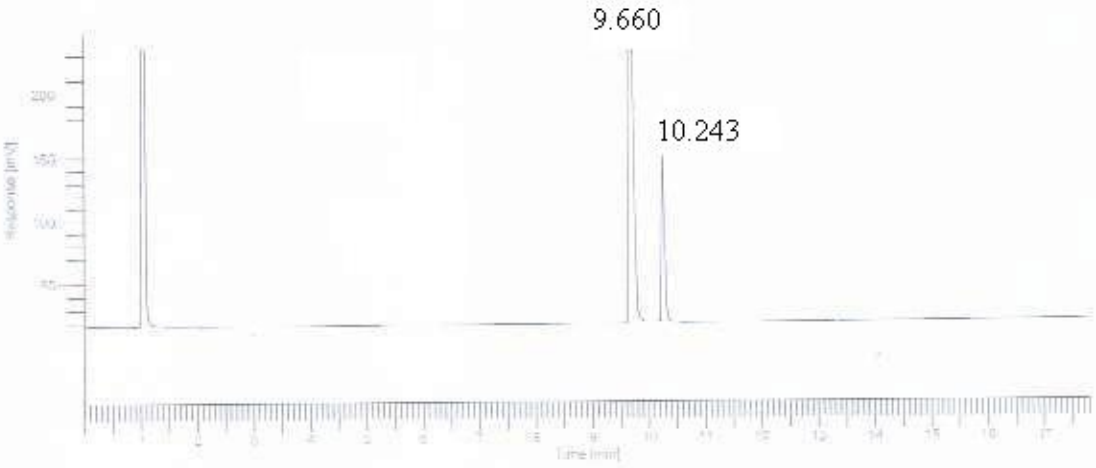
Missing Component Report
Component Expected Retention (Calibration File)

All components were found

15.2 2-Phenyl-2-phenylaminopropanenitrile (21a), obtained at 0°C in the presence of catalyst 3a

Software Version	: 6.2.1.0.104:0104	Date	:
Reprocess Number	: chpc-lab-e11: 204		
Sample Name	:	Data Acquisition Time	: .
Instrument Name	: autosystemxl	Channel	: A
Rack/Vial	: 0/0	Operator	: Chimica Organica
Sample Amount	: 1,000000	Dilution Factor	: 1,000000
Cycle	: 2		

Result File : D:\DATI_TC\Chrom\data002-20130814-092758.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9,660	2183530,04	432596,93	82,13
2		10,243	475254,56	118333,38	17,87
			2658784,61	550930,30	100,00

Missing Component Report

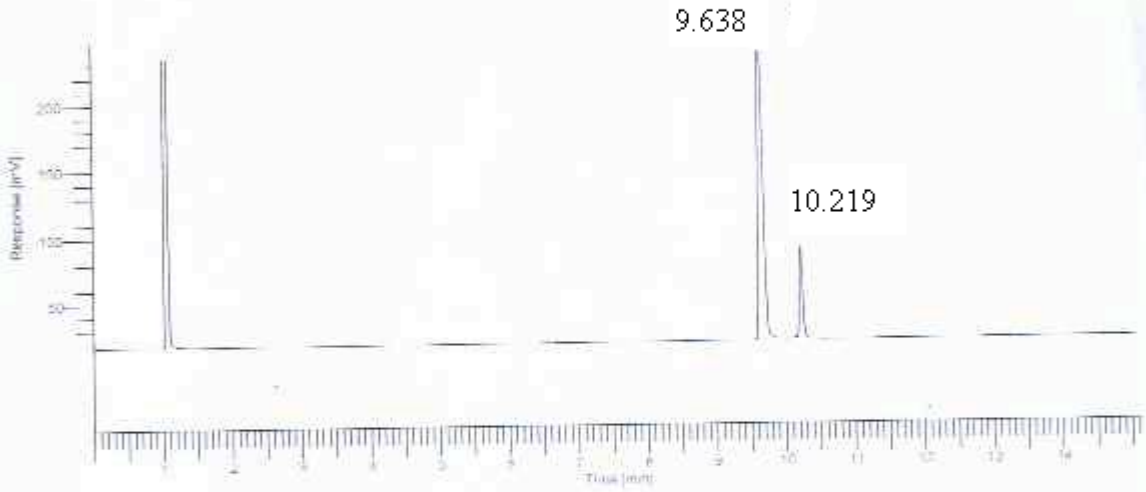
Component	Expected Retention (Calibration File)

All components were found

15.3 2-Phenyl-2-phenylaminopropanenitrile (21a), obtained at -20°C in the presence of catalyst 3b

Software Version	: 6.2.1.0.104:0104	Date	: 14/08/2013 11.42.38
Reprocess Number	: chpc-lab-e11: 209		
Sample Name	:	Data Acquisition Time	: 14/08/2013 11.27.23
Instrument Name	: autosystemxl	Channel	: A
Rack/Vial	: 0/0	Operator	: Chimica Organica
Sample Amount	: 1,000000	Dilution Factor	: 1,000000
Cycle	: 7		

Result File : D:\DATI_TC\Chrom\data007-20130814-114237.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq



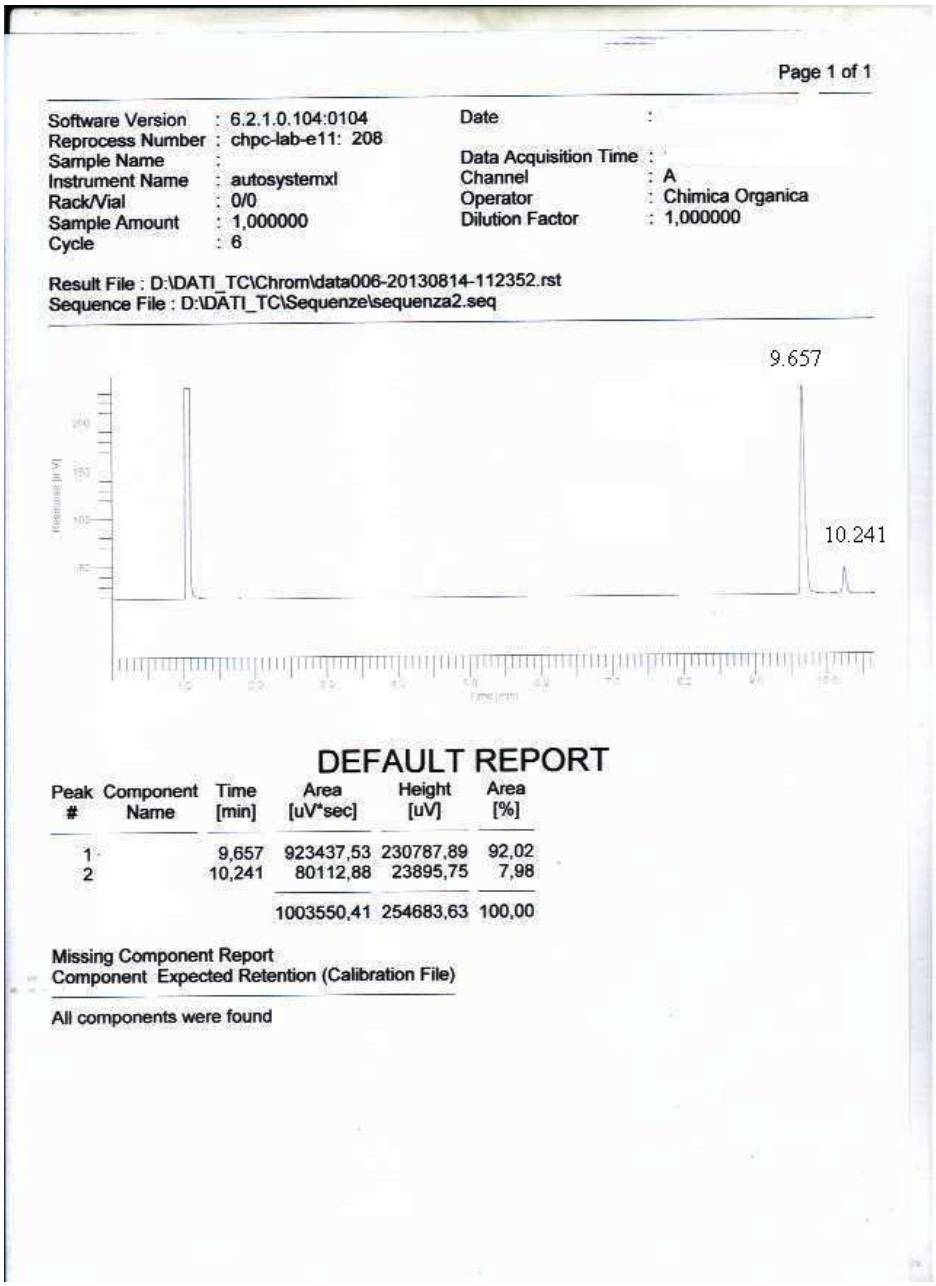
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9,638	1270518,50	297457,86	84,51
2		10,219	232931,09	68529,69	15,49
			1503449,59	365987,55	100,00

Missing Component Report
Component Expected Retention (Calibration File)

All components were found

15.4 2-Phenyl-2-phenylaminopropanenitrile (21a), obtained at 0°C in the presence of catalyst 3b



Software Version	: 6.2.1.0.104:0104	Date	:
Reprocess Number	: chpc-lab-e11: 208		
Sample Name	:	Data Acquisition Time	:
Instrument Name	: autosystemxl	Channel	: A
Rack/Vial	: 0/0	Operator	: Chimica Organica
Sample Amount	: 1,000000	Dilution Factor	: 1,000000
Cycle	: 6		

Result File : D:\DATI_TC\Chrom\data006-20130814-112352.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9,657	923437,53	230787,89	92,02
2		10,241	80112,88	23895,75	7,98
			1003550,41	254683,63	100,00

Missing Component Report
Component Expected Retention (Calibration File)

All components were found

15.5 2-Phenyl-2-phenylaminopropanenitrile (21a), obtained at -20 °C in the presence of catalyst 3b

Software Version	: 6.2.1.0.104:0104	Date	:
Reprocess Number	: chpc-lab-e11: 213		
Sample Name	:	Data Acquisition Time	:
Instrument Name	: autosystemxl	Channel	: A
Rack/Vial	: 0/0	Operator	: Chimica Organica
Sample Amount	: 1,000000	Dilution Factor	: 1,000000
Cycle	: 4		

Result File : D:\DATI_TC\Chrom\data004-20131118-121808.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9,665	515090,97	133054,96	97,36
2		10,249	13967,16	4333,00	2,64
			529058,13	137387,96	100,00

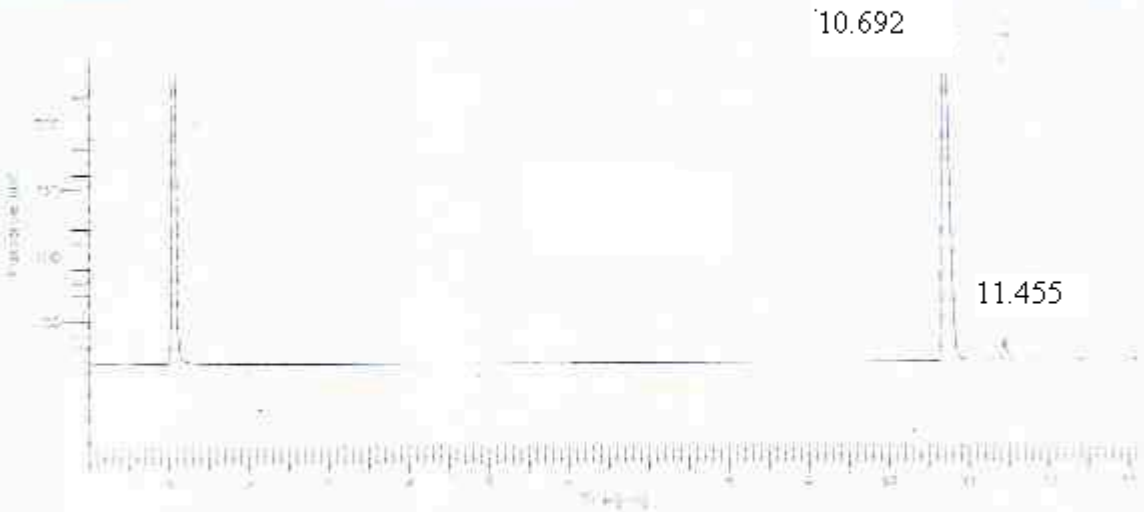
Missing Component Report
Component Expected Retention (Calibration File)

All components were found

15.6 2-(4-Methoxyphenylamino)-2-phenylpropanenitrile (21b), obtained at -20°C in the presence of catalyst 3b

Software Version	: 6.2.1.0.104:0104	Date	: 10/12/2013 11.30.03
Reprocess Number	: chpc-lab-e11: 225		
Sample Name	:	Data Acquisition Time	: 10/12/2013 11.16.47
Instrument Name	: autosystemxl	Channel	: A
Rack/Vial	: 0/0	Operator	: Chimica Organica
Sample Amount	: 1,000000	Dilution Factor	: 1,000000
Cycle	: 4		

Result File : D:\DATI_TC\Chrom\data004-20131210-113002.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq



DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		10,692	1786914,72	331963,43	97,38
2		11,455	48108,37	14194,39	2,62
			1835023,10	346157,82	100,00

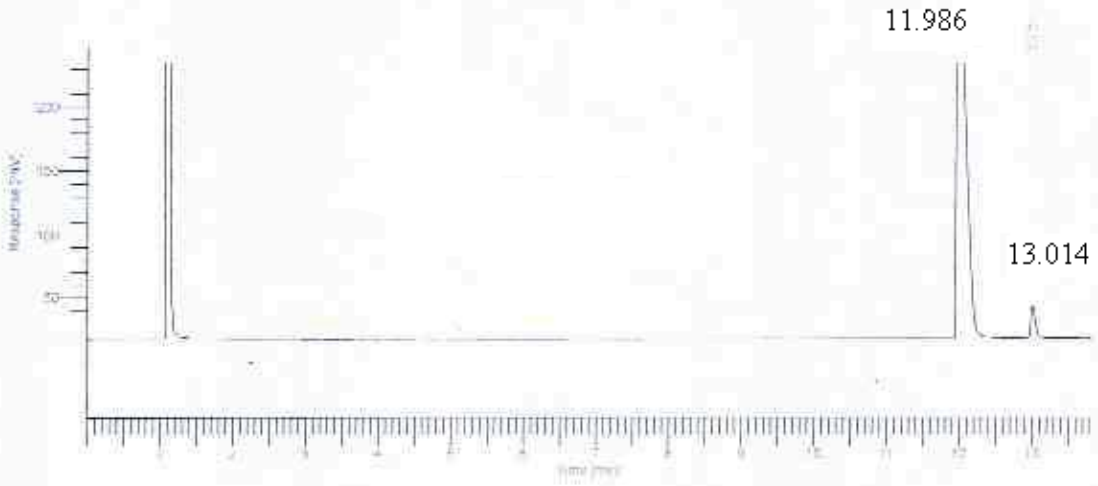
Missing Component Report
Component Expected Retention (Calibration File)

All components were found

15.7 2-(4-Nitrophenylamino)-2-phenylpropanenitrile (21c), obtained at -20°C in the presence of catalyst 3b

Software Version	: 6.2.1.0.104:0104	Date	: 10/12/2013 13.30.28
Reprocess Number	: chpc-lab-e11: 226		
Sample Name	:	Data Acquisition Time	: 10/12/2013 13.16.28
Instrument Name	: autosystemxl	Channel	: A
Rack/Vial	: 0/0	Operator	: Chimica Organica
Sample Amount	: 1,000000	Dilution Factor	: 1,000000
Cycle	: 5		

Result File : D:\DATI_TC\Chrom\data005-20131210-133027.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq



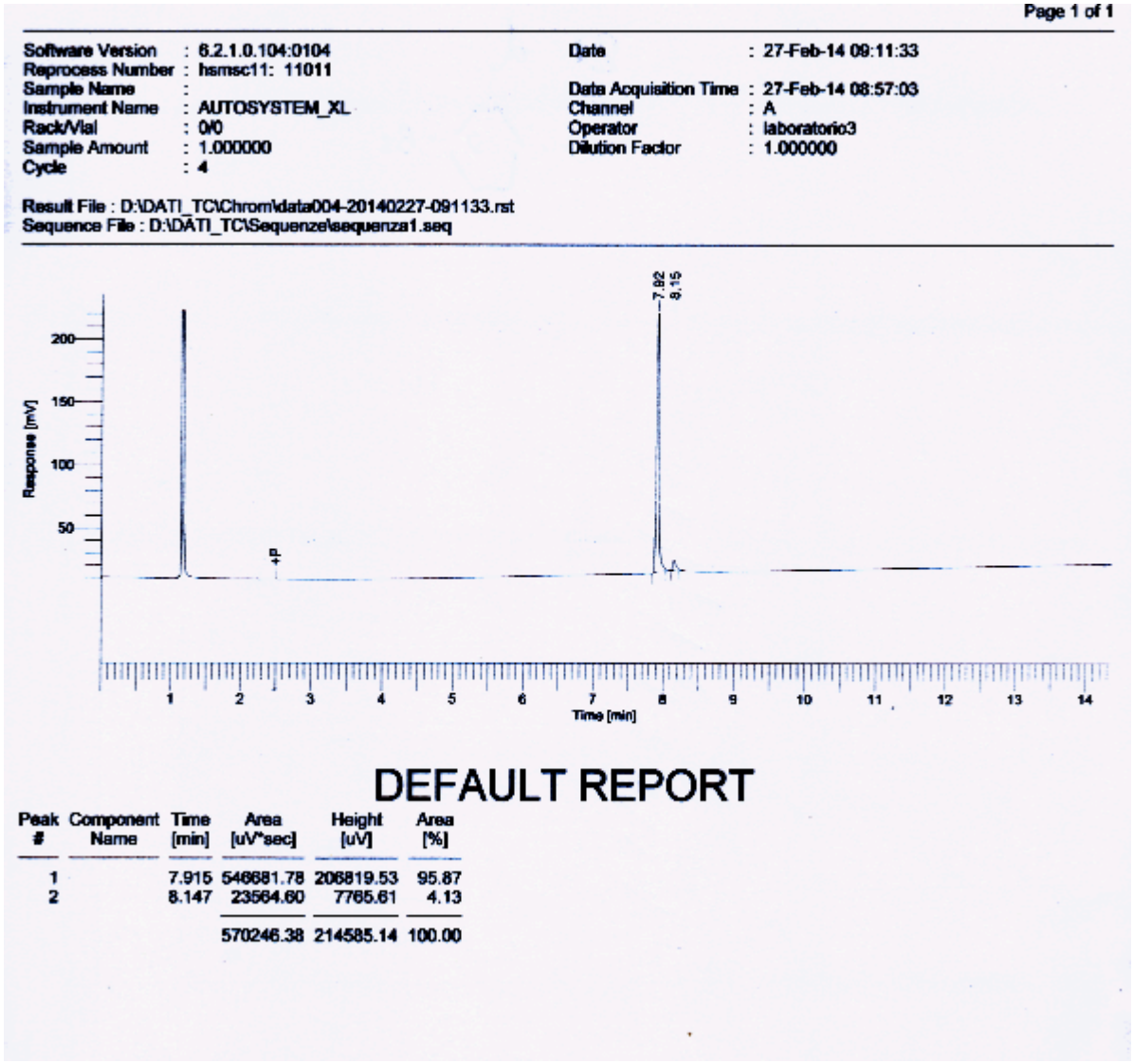
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		11,986	2883604,07	369290,20	96,59
2		13,014	101944,84	23837,85	3,41
			2985548,91	393128,05	100,00

Missing Component Report
Component Expected Retention (Calibration File)

All components were found

15.8 2-(4-Bromophenylamino)-2-phenylpropanenitrile (21d), obtained at -20°C in the presence of catalyst 3b



Software Version : 6.2.1.0.104:0104
Reprocess Number : hsmsc11: 11011
Sample Name :
Instrument Name : AUTOSYSTEM_XL
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 4

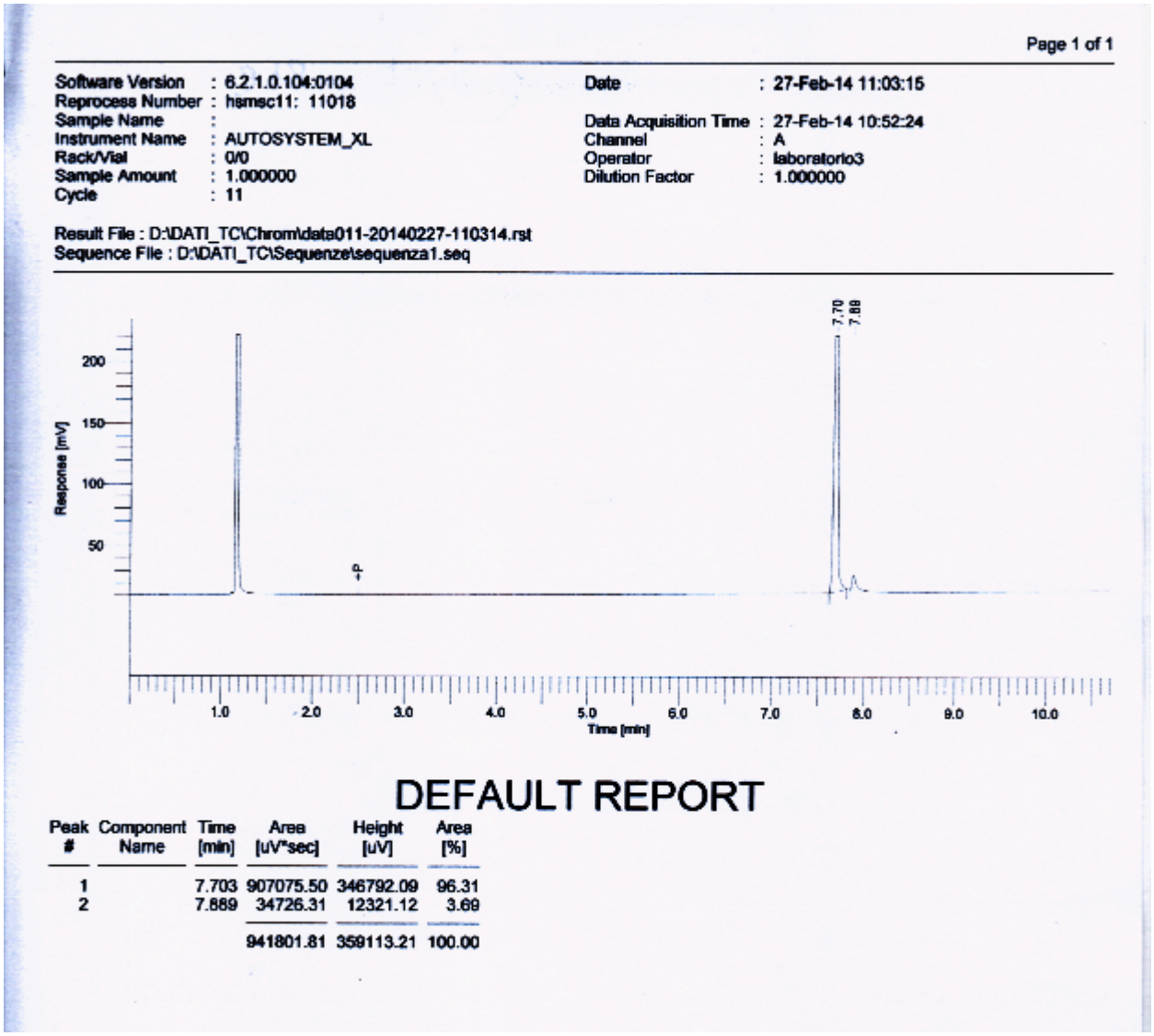
Date : 27-Feb-14 09:11:33
Data Acquisition Time : 27-Feb-14 08:57:03
Channel : A
Operator : laboratorio3
Dilution Factor : 1.000000

Result File : D:\DATI_TC\Chrom\data004-20140227-091133.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.915	546681.78	206819.53	95.87
2		8.147	23564.60	7765.61	4.13
			570246.38	214585.14	100.00

15.9 2-(4-Fluorophenylamino)-2-phenylpropanenitrile (21e), obtained at -20°C in the presence of catalyst 3b



Page 1 of 1

Software Version : 6.2.1.0.104:0104
Reprocess Number : hsmsc11: 11018
Sample Name :
Instrument Name : AUTOSYSTEM_XL
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 11

Date : 27-Feb-14 11:03:15
Data Acquisition Time : 27-Feb-14 10:52:24
Channel : A
Operator : laboratorio3
Dilution Factor : 1.000000

Result File : D:\DATI_TC\Chrom\data011-20140227-110314.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

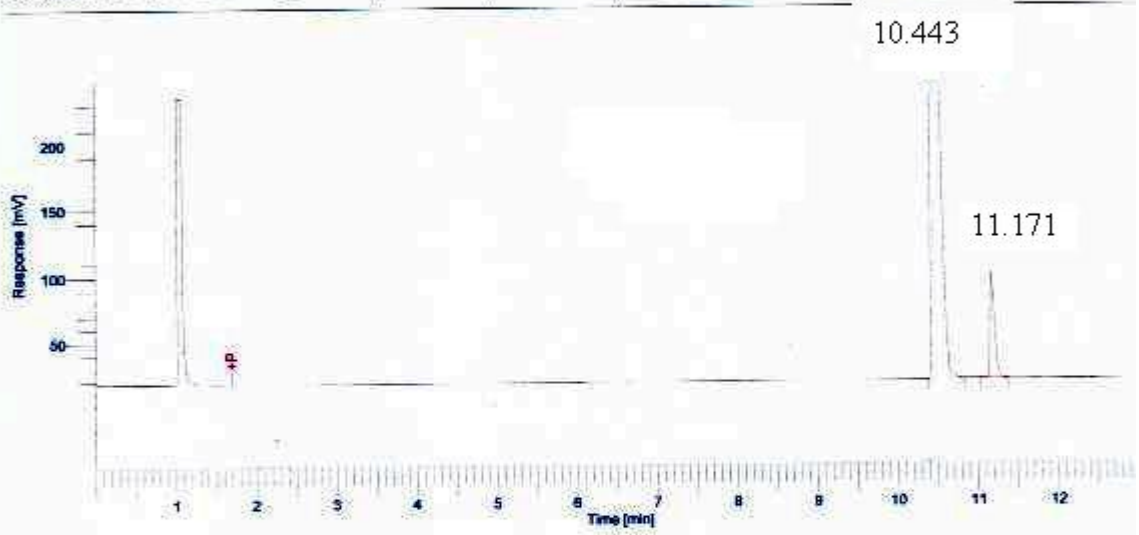
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.703	907075.50	346792.09	96.31
2		7.889	34726.31	12321.12	3.69
			941801.81	359113.21	100.00

15.10 2-(2-Methoxyphenylamino)-2-phenylpropanenitrile (21f), obtained at -20°C in the presence of catalyst 3b

Software Version	: 6.2.1.0.104:0104	Date	: 10/12/2013 14.10.06
Reprocess Number	: chpc-lab-e11: 228		
Sample Name	:	Data Acquisition Time	: 10/12/2013 13.56.53
Instrument Name	: autosystemxl	Channel	: A
Rack/Vial	: 0/0	Operator	: Chimica Organica
Sample Amount	: 1,000000	Dilution Factor	: 1,000000
Cycle	: 7		

Result File : D:\DATI_TC\Chrom\data007-20131210-141005.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq



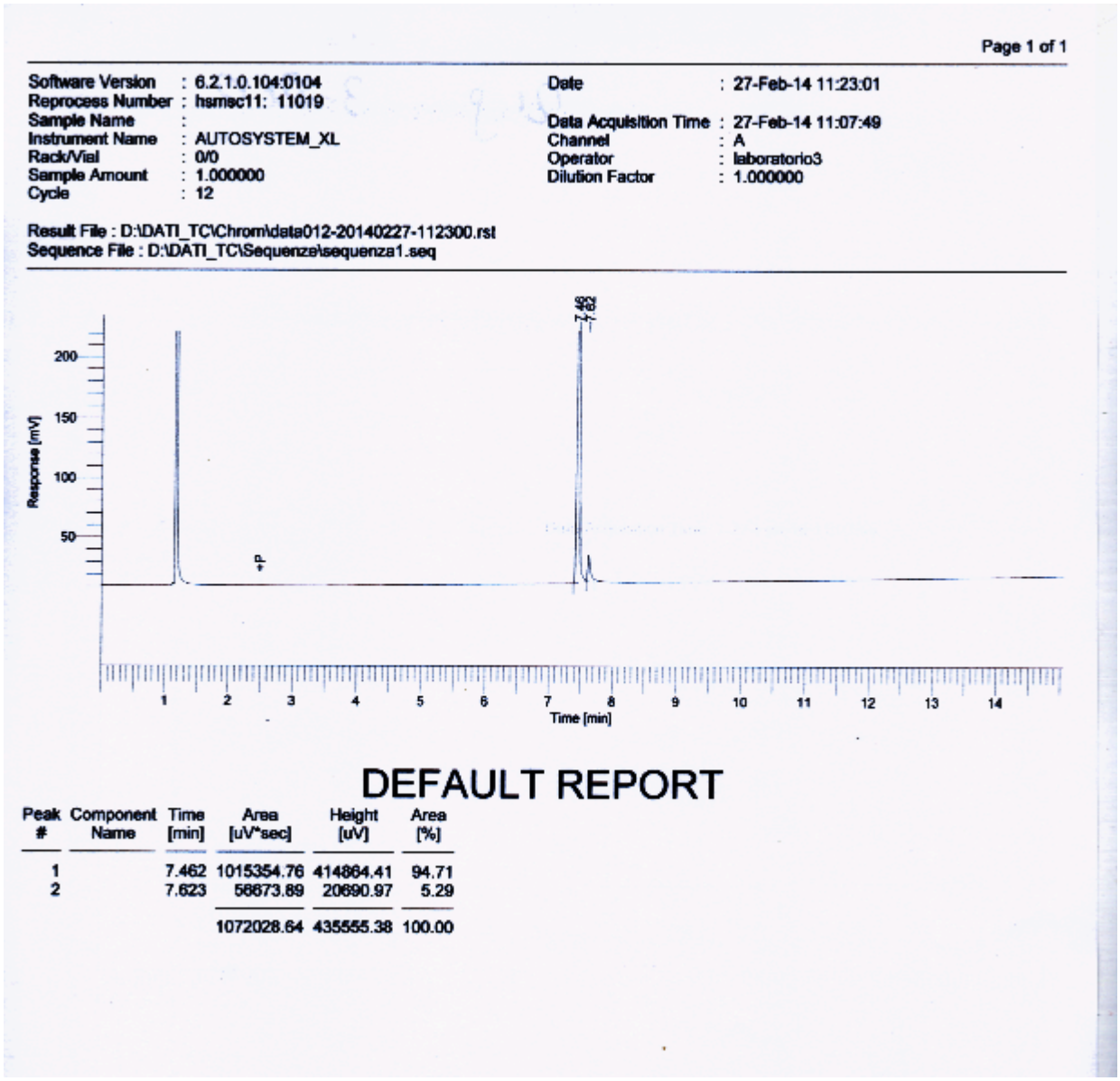
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		10,443	3278544,56	540019,98	91,19
2		11,171	316589,49	81383,74	8,81
			3595134,06	621403,72	100,00

Missing Component Report
Component Expected Retention (Calibration File)

All components were found

15.11 2-(3-Methoxyphenylamino)-2-phenylpropanenitrile (21g), obtained at -20°C in the presence of catalyst 3b



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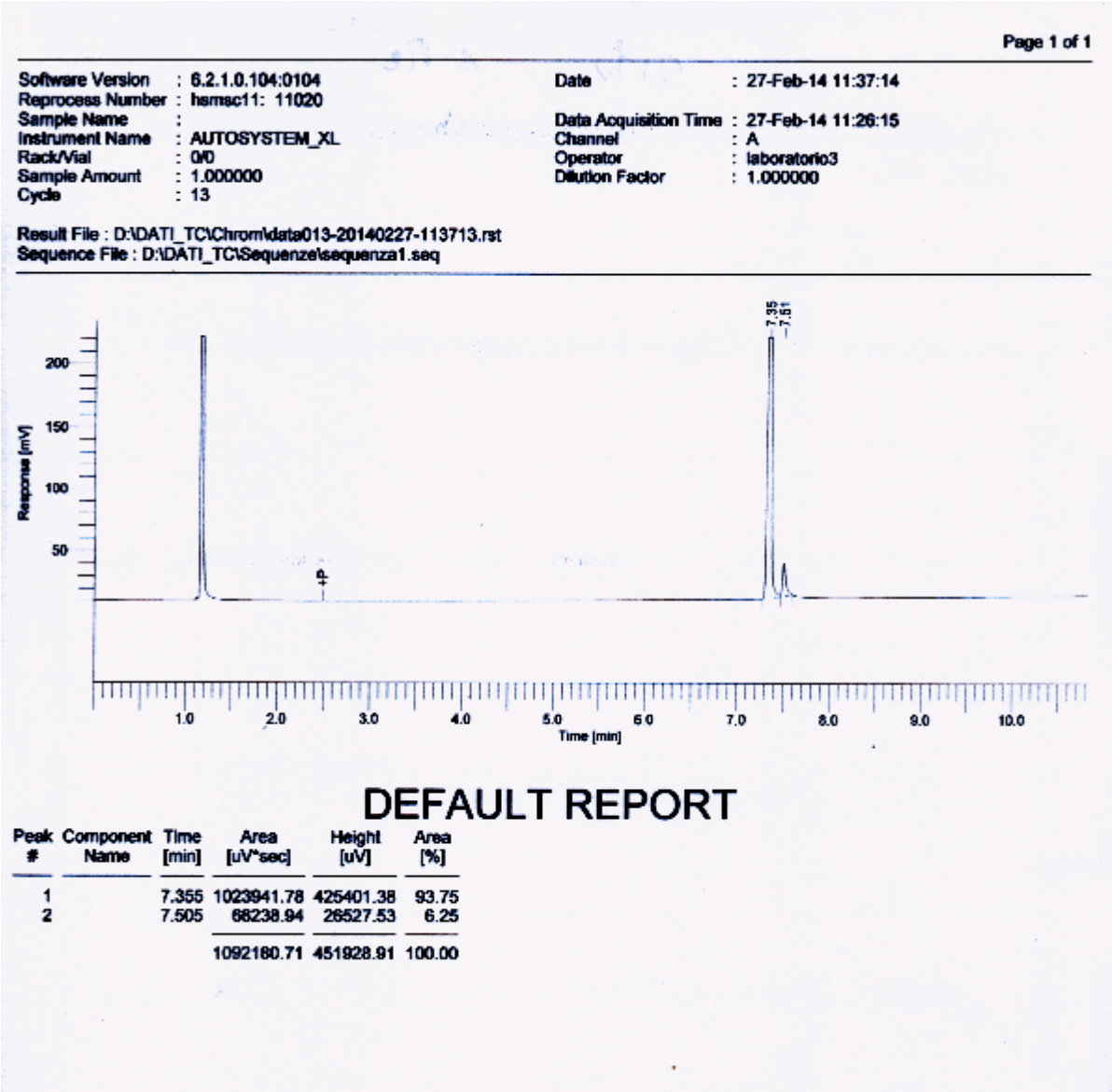
Software Version	: 6.2.1.0.104:0104	Date	: 27-Feb-14 11:23:01
Reprocess Number	: hsmsc11: 11019		
Sample Name	:	Data Acquisition Time	: 27-Feb-14 11:07:49
Instrument Name	: AUTOSYSTEM_XL	Channel	: A
Rack/Vial	: 0/0	Operator	: laboratorio3
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 12		

Result File : D:\DATI_TC\Chrom\data012-20140227-112300.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.462	1015354.76	414864.41	94.71
2		7.623	56673.89	20690.97	5.29
			1072028.64	435555.38	100.00

15.12 2-Phenylamino-2-(4-tolyl)propanenitrile (21h), obtained at -20°C in the presence of catalyst 3b



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Software Version : 6.2.1.0.104:0104
Reprocess Number : hsmsc11: 11020
Sample Name :
Instrument Name : AUTOSYSTEM_XL
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 13

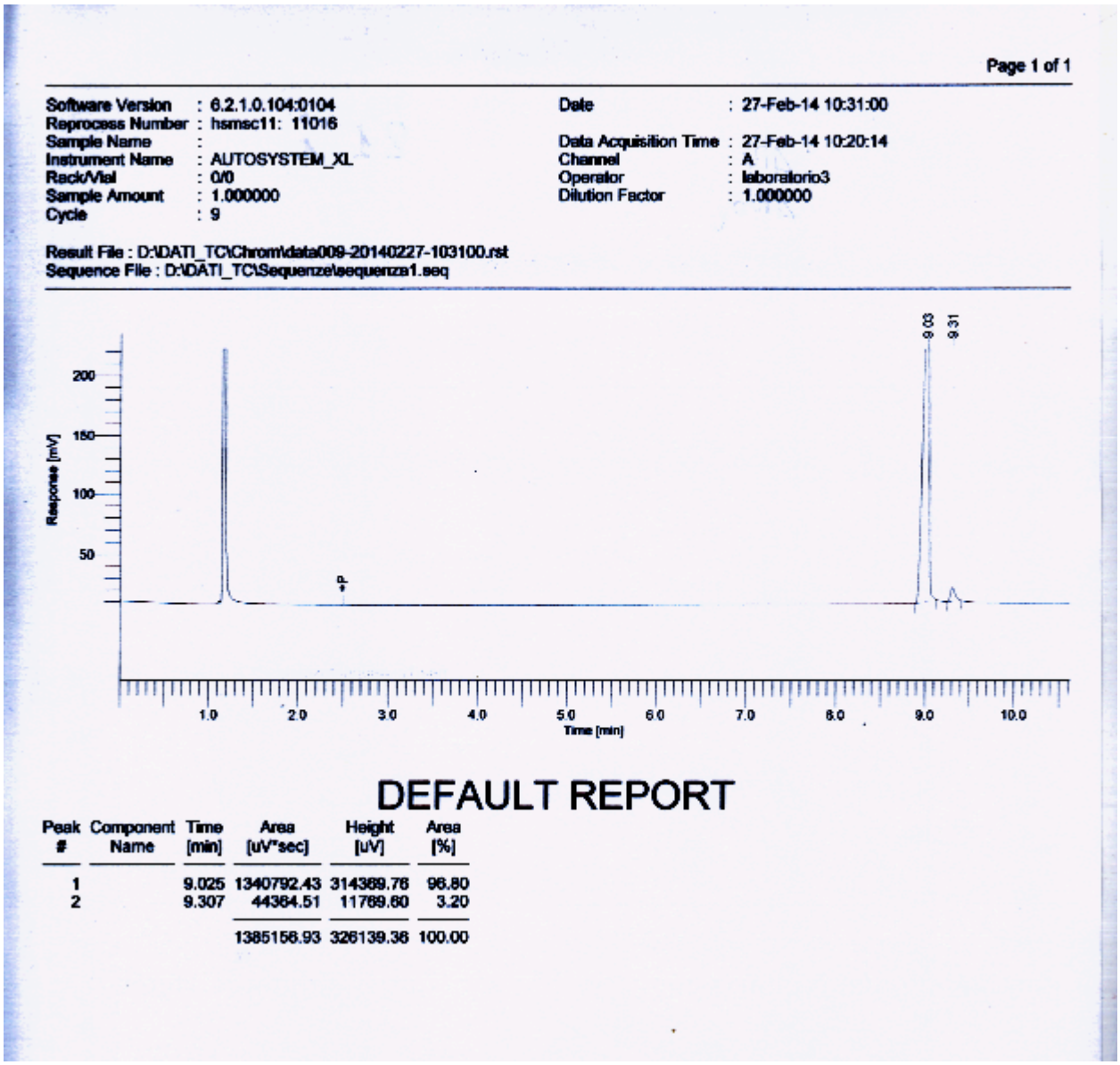
Date : 27-Feb-14 11:37:14
Data Acquisition Time : 27-Feb-14 11:26:15
Channel : A
Operator : laboratorio3
Dilution Factor : 1.000000

Result File : D:\DATI_TC\Chrom\data013-20140227-113713.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.355	1023941.78	425401.38	93.75
2		7.505	68238.94	26527.53	6.25
			1092180.71	451928.91	100.00

15.13 2-(4-Nitrophenylamino)-2-(4-tolyl)propanenitrile (21i), obtained at -20°C in the presence of catalyst 3b



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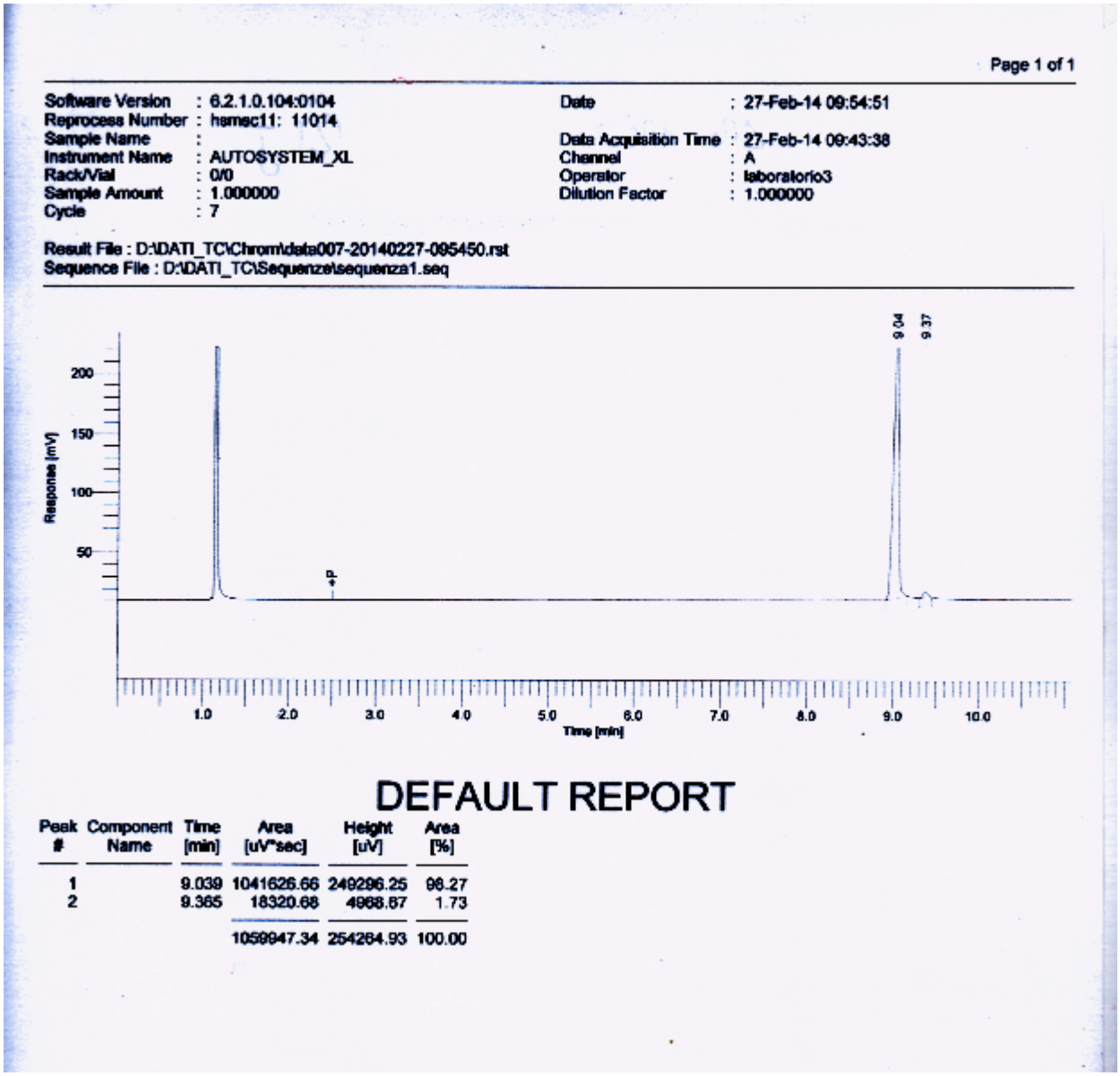
Software Version	: 6.2.1.0.104:0104	Date	: 27-Feb-14 10:31:00
Reprocess Number	: hsmsc11: 11016		
Sample Name	:	Data Acquisition Time	: 27-Feb-14 10:20:14
Instrument Name	: AUTOSYSTEM_XL	Channel	: A
Rack/Vial	: 0/0	Operator	: laboratorio3
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 9		

Result File : D:\DATI_TC\Chrom\data009-20140227-103100.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9.025	1340792.43	314389.76	96.80
2		9.307	44364.51	11769.60	3.20
			1385156.93	326139.36	100.00

15.14 2-(4-Methoxyphenylamino)-2-(4-tolyl)propanenitrile (21j), obtained at -20°C in the presence of catalyst 3b



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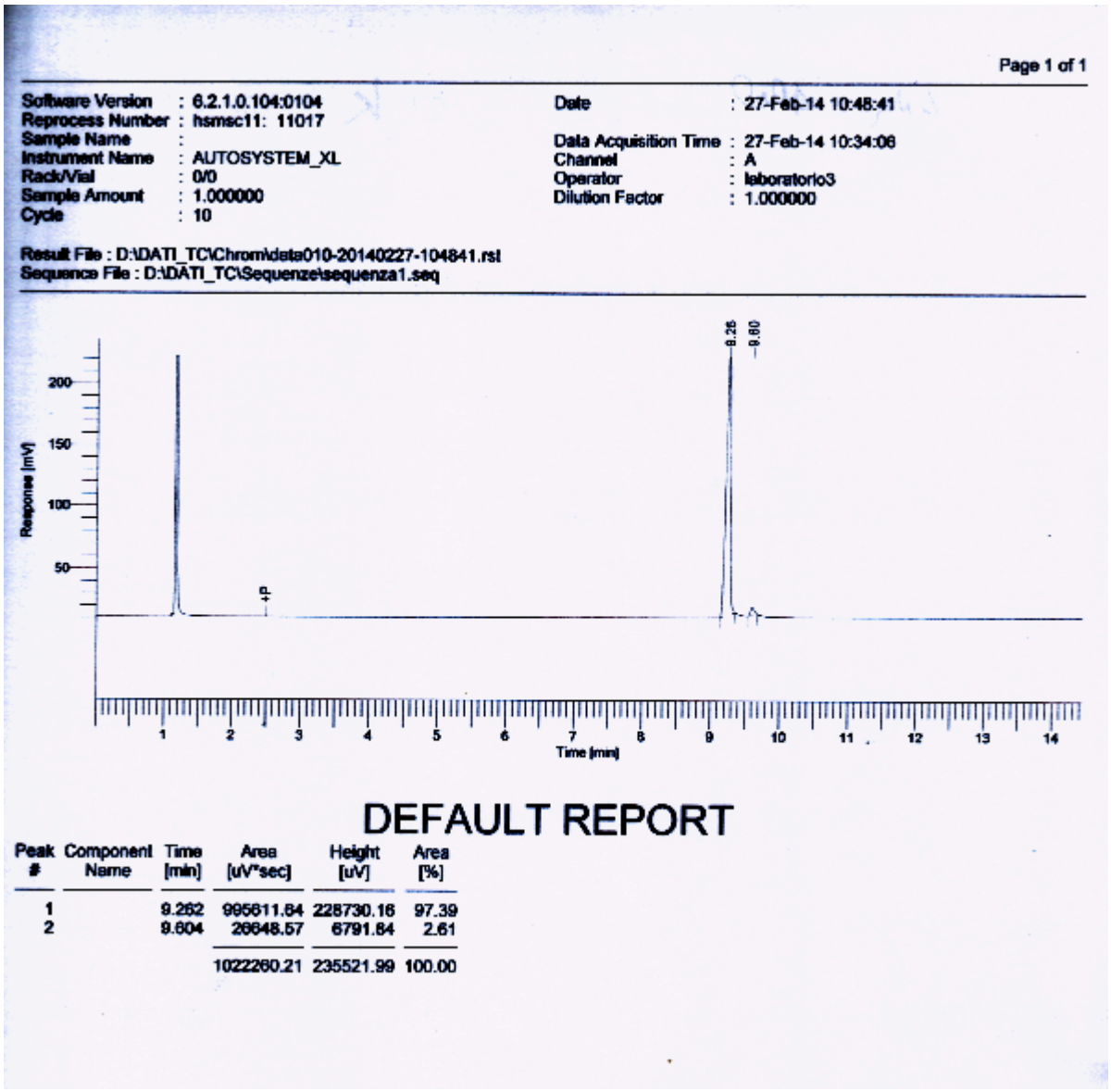
Software Version	: 6.2.1.0.104:0104	Date	: 27-Feb-14 09:54:51
Reprocess Number	: hsmsc11: 11014		
Sample Name	:	Data Acquisition Time	: 27-Feb-14 09:43:38
Instrument Name	: AUTOSYSTEM_XL	Channel	: A
Rack/Vial	: 0/0	Operator	: laboratorio3
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 7		

Result File : D:\DATI_TC\Chrom\data007-20140227-095450.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9.039	1041626.66	249296.25	98.27
2		9.365	18320.68	4968.67	1.73
			1059947.34	254264.93	100.00

15.15 2-(4-Methoxyphenylamino)-2-(4-nitrophenyl)propanenitrile (21k), obtained at -20°C in the presence of catalyst 3b



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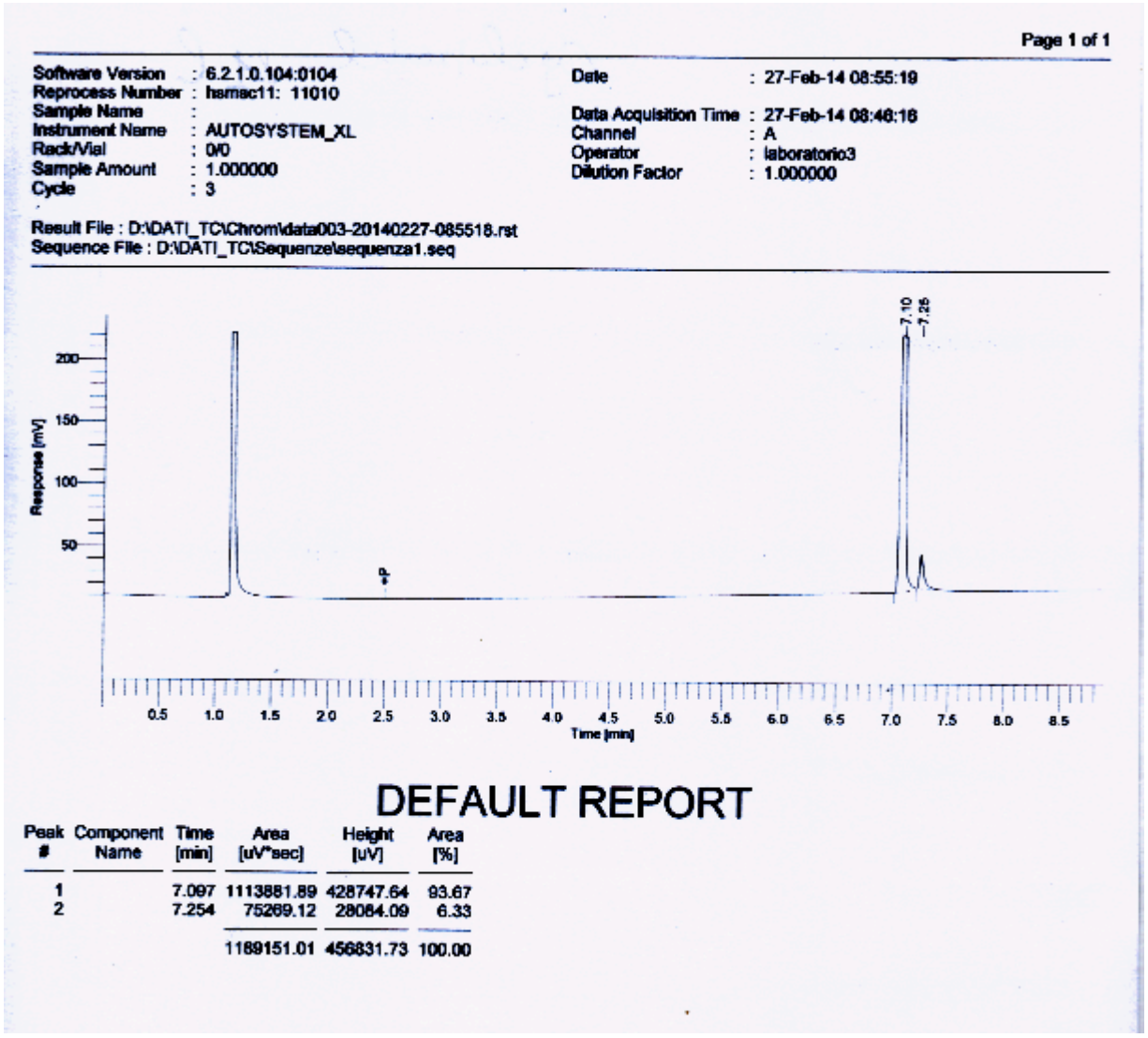
Software Version	: 6.2.1.0.104:0104	Date	: 27-Feb-14 10:48:41
Reprocess Number	: hsmsc11: 11017		
Sample Name	:	Data Acquisition Time	: 27-Feb-14 10:34:06
Instrument Name	: AUTOSYSTEM_XL	Channel	: A
Rack/Vial	: 0/0	Operator	: laboratorio3
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 10		

Result File : D:\DATI_TC\Chrom\data010-20140227-104841.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9.262	995611.64	228730.16	97.39
2		9.604	26648.57	6791.84	2.61
			1022260.21	235521.99	100.00

15.16 2-Methyl-2-(phenylamino)pentanenitrile (21l), obtained at -20°C in the presence of catalyst 3b



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Software Version : 6.2.1.0.104:0104
Reprocess Number : hsmac11: 11010
Sample Name :
Instrument Name : AUTOSYSTEM_XL
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 3

Date : 27-Feb-14 08:55:19
Data Acquisition Time : 27-Feb-14 08:46:16
Channel : A
Operator : laboratorio3
Dilution Factor : 1.000000

Result File : D:\DATI_TC\Chrom\data003-20140227-085518.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

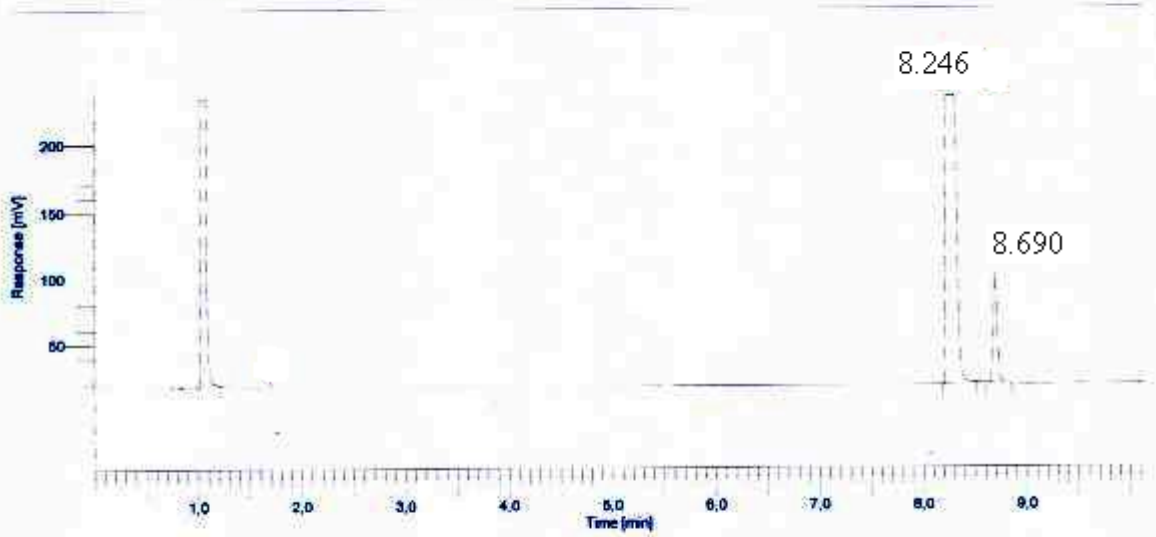
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.097	1113881.89	428747.64	93.67
2		7.254	75269.12	28084.09	6.33
			1189151.01	456831.73	100.00

15.17 2-Phenyl-2-phenylaminoacetonitrile (21m), obtained at -20°C in the presence of catalyst 3b

Software Version	: 6.2.1.0.104:0104	Date	: 10/12/2013 16.32.09
Reprocess Number	: chpc-lab-e11: 229		
Sample Name	:	Data Acquisition Time	: 10/12/2013 16.21.54
Instrument Name	: autosystemxl	Channel	: A
Rack/Vial	: 0/0	Operator	: Chimica Organica
Sample Amount	: 1,000000	Dilution Factor	: 1,000000
Cycle	: 8		

Result File : D:\DATI_TC\Chrom\data008-20131210-163209.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza2.seq



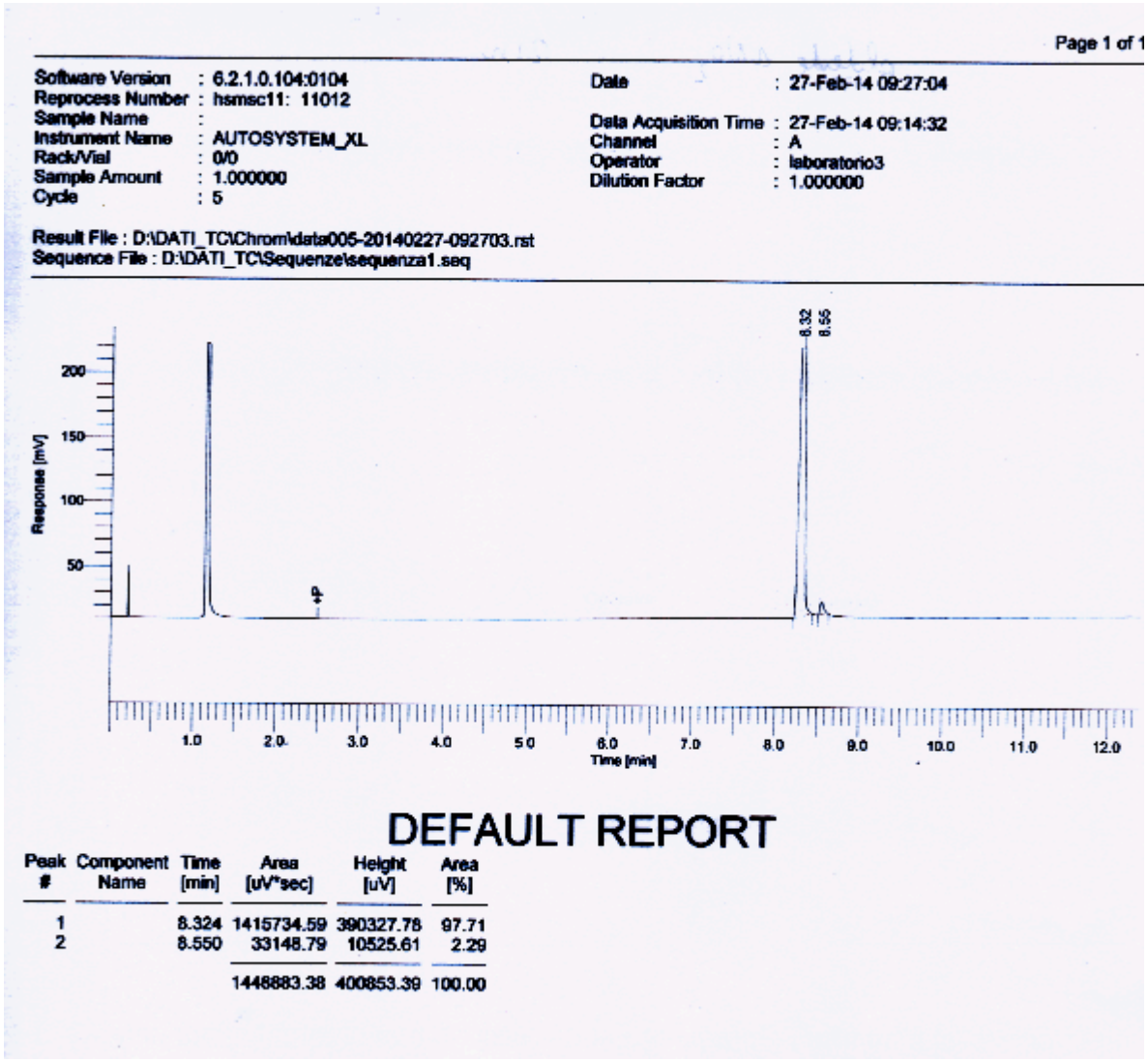
DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		8,246	2910594,99	644336,89	93,37
2		8,690	206567,42	68883,30	6,63
			3117162,41	713220,19	100,00

Missing Component Report
Component Expected Retention (Calibration File)

All components were found

15.18 2-(4-Nitrophenyl)-2-phenylaminoacetonitrile (21n), obtained at -20°C in the presence of catalyst 3b



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Software Version : 6.2.1.0.104:0104
Reprocess Number : hsmsc11: 11012
Sample Name :
Instrument Name : AUTOSYSTEM_XL
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 5

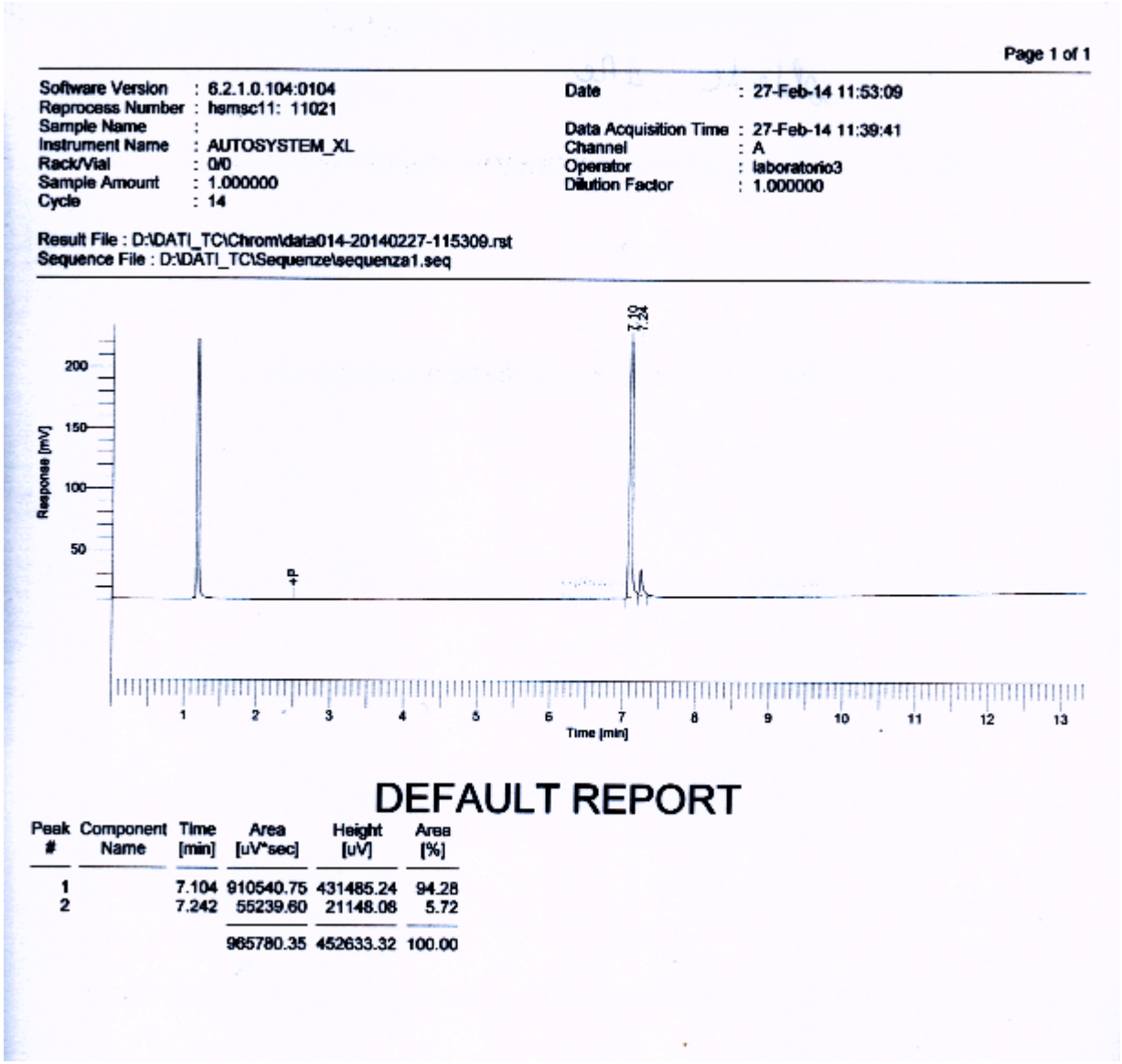
Date : 27-Feb-14 09:27:04
Data Acquisition Time : 27-Feb-14 09:14:32
Channel : A
Operator : laboratorio3
Dilution Factor : 1.000000

Result File : D:\DATI_TC\Chrom\data005-20140227-092703.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		8.324	1415734.59	390327.78	97.71
2		8.550	33148.79	10525.61	2.29
			1448883.38	400853.39	100.00

15.19 2-Phenylamino-2-(4-tolyl)acetonitrile (21o), obtained at -20°C in the presence of catalyst 3b



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Software Version : 6.2.1.0.104:0104
Reprocess Number : hsmsc11: 11021
Sample Name :
Instrument Name : AUTOSYSTEM_XL
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 14

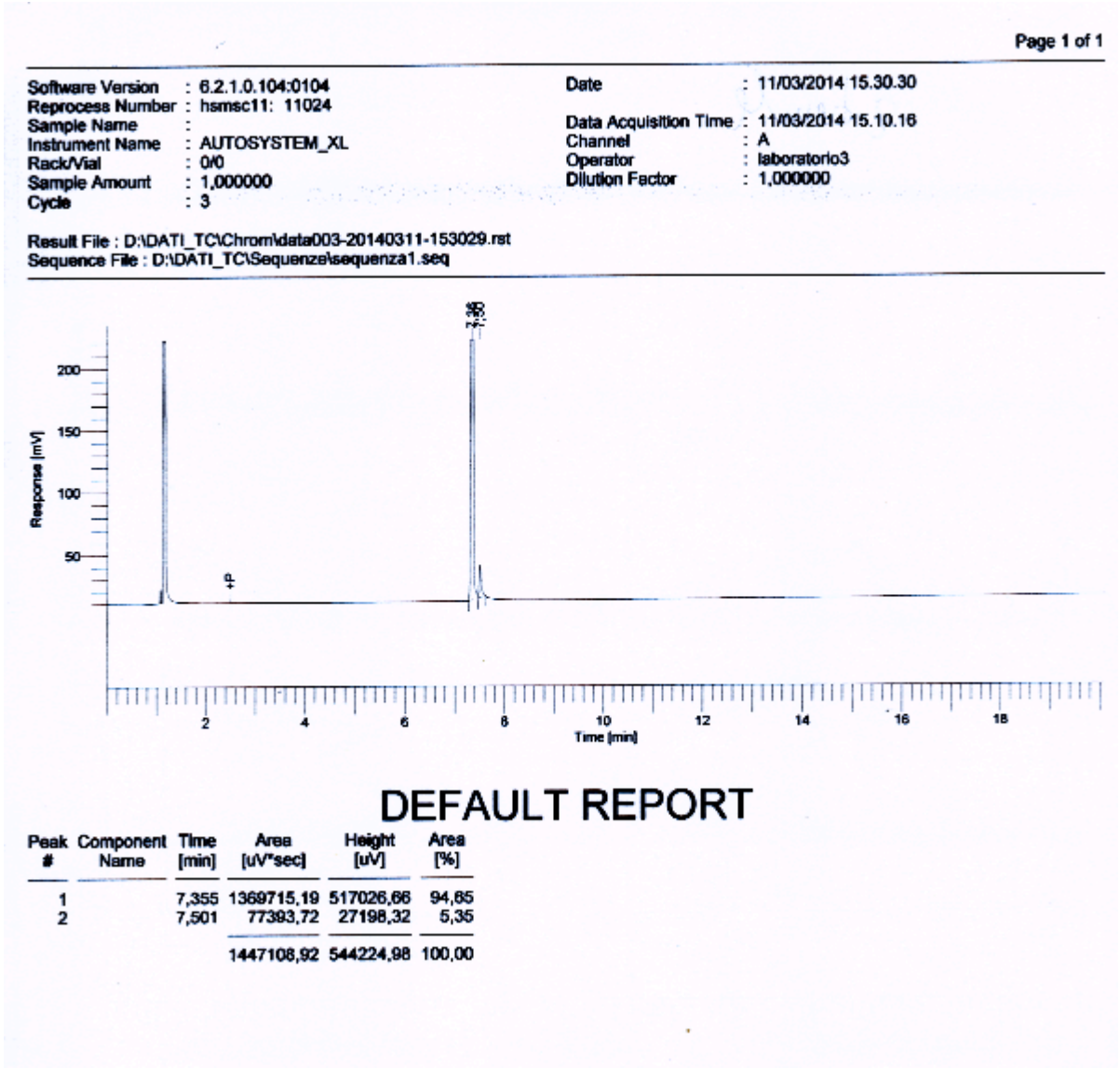
Date : 27-Feb-14 11:53:09
Data Acquisition Time : 27-Feb-14 11:39:41
Channel : A
Operator : laboratorio3
Dilution Factor : 1.000000

Result File : D:\DATI_TC\Chrom\data014-20140227-115309.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.104	910540.75	431485.24	94.28
2		7.242	55239.60	21148.08	5.72
			965780.35	452633.32	100.00

15.20 2-Phenylamino-2-thienylacetonitrile (21p), obtained at -20°C in the presence of catalyst 3b



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Software Version : 6.2.1.0.104:0104
Reprocess Number : hsmsc11: 11024
Sample Name :
Instrument Name : AUTOSYSTEM_XL
Rack/Vial : 0/0
Sample Amount : 1,000000
Cycle : 3

Date : 11/03/2014 15.30.30
Data Acquisition Time : 11/03/2014 15.10.16
Channel : A
Operator : laboratorio3
Dilution Factor : 1,000000

Result File : D:\DATI_TC\Chrom\data003-20140311-153029.rst
Sequence File : D:\DATI_TC\Sequenze\sequenza1.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7,355	1369715,19	517026,66	94,65
2		7,501	77393,72	27198,32	5,35
			1447108,92	544224,98	100,00