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

Margherita Barbero, Silvano Cadamuro, Stefano Dughera,* Roberta Torregrossa
Dipartimento di Chimica, Università di Torino, C.so Massimo d’Azeglio 48, 10125 Torino, Italy.

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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$_3$): $\delta$ = 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$_3$): $\delta$ = 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) $\nu$ (cm$^{-1}$): 3508, 3504 (NH$_2$), 1585, 1312 (NO$_2$).


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$_8$H$_9$IN$_2$O$_2$ requires: C 32.90; H 3.11; N 9.59%. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 8.44 (s, 1H), 6.16 (br s, 2H), 2.42 (s, 3H), 2.16 (s, 3H). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 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) $\nu$ (cm$^{-1}$): 3510, 3504 (NH$_2$), 1535, 1350 (NO$_2$).

2. Synthesis of Diiodonitro derivatives (7)

First HBF$_4$Et$_2$O (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$_2$O (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$_2$O-H$_2$O (100 mL, 1:1). The aqueous layer was separated and extracted with Et$_2$O (100 mL). The combined organic extracts were washed with H$_2$O (50 mL),
dried over Na$_2$SO$_4$ 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$_3$): $\delta = 7.68$ (s, 1H), 7.66 (s, 1H), 2.47 (s, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 147.2$, 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) $\nu$ (cm$^{-1}$): 1542, 1358 (NO$_2$)


**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$_8$H$_7$INO$_2$ requires: C 23.85; H 1.75; N 3.48%. $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.84$ (s, 1H), 2.64 (s, 3H), 2.57 (s, 3H). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 144.2$, 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) $\nu$ (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$_3$PO$_4$ (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$_2$O 4:1). Then, the reaction mixture was poured into CH$_2$Cl$_2$-H$_2$O (100 ml, 1:1). The aqueous layer was separated and extracted with CH$_2$Cl$_2$ (100 mL). The combined organic extracts were washed with H$_2$O (100 mL), dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The crude residue, purified in a chromatography column (PE/Et$_2$O 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$_3$): $\delta = 7.53$ (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$_3$): $\delta = 147.8$, 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) $\nu$ (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$_2$O) 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$_2$O/H$_2$O (100 mL, 1:1). The aqueous layer was separated and extracted with Et$_2$O (100 mL). The combined organic extracts were washed with H$_2$O (100 mL), dried over Na$_2$SO$_4$ 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$_3$): $\delta$ = 6.91 (s, 1H), 6.84 (s, 1H), 6.13 (br s, 2H), 2.15 (s, 3H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 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) $\nu$ (cm$^{-1}$): 3410, 3406 (NH$_2$).


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$_8$H$_9$I$_2$N requires: C 25.76; H 2.43; N 3.76%. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 7.11 (s, 1H), 4.00 (br s, 2H), 2.47 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 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) $\nu$ (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$_3$): $\delta = 7.32$–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$_3$): $\delta = 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) $\nu$ (cm$^{-1}$): 3416, 3410 (NH$_2$).

6. Synthesis of diiodoisatins 10

10 were prepared, starting from diidoanilines (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-diido-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$_2$SO$_4$ (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$_9$H$_5$I$_2$NO$_2$ requires: C 26.18; H 1.22; N 3.39%. $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.65$ (br s, 1H), 7.44 (s, 1H), 2.40 (s, 3H). $^{13}$C NMR (50 MHz, DMSO-d$_6$): $\delta = 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) $\nu$ (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$_7$I$_2$NO$_2$ requires: C 28.13; H 1.65; N 3.28%. $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.62$ (br s, 1H), 2.58 (s, 3H), 2.52 (s, 3H). $^{13}$C NMR (50 MHz, DMSO-d$_6$): $\delta = 183.5, 159.9, 154.5, 149.7, 135.3, 119.7, 101.2, 87.8, 28.7, 25.2. IR (neat) $\nu$ (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$_3$H (15 ml) and used without further purification. It was impossible to obtain 11b using H$_2$SO$_4$.

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$_3$): $\delta$ = 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$_3$): $\delta$ = 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$_2$O (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$_2$Cl$_2$/EtOAc, 9.8:0.2). The reaction mixture was then poured into CH$_2$Cl$_2$-H$_2$O (100 ml, 1:1). The aqueous layer was separated and extracted with CH$_2$Cl$_2$ (100 mL). The combined organic extracts were washed with H$_2$O (100 mL), dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The crude residue, purified in a chromatography column (CH$_2$Cl$_2$/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$_{16}$NO$_2$ requires: C 80.92; H 5.61; N 4.10%. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 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$_3$): $\delta$ = 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<sub>30</sub>H<sub>21</sub>NO<sub>2</sub> requires: C 84.29; H 4.95; N 3.28%.<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 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).<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 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, 126.1, 125.7, 125.4, 125.2, 125.1, 125.0, 124.1, 114.8, 19.2, 16.5. MS (ESI +) <sup>m/z</sup>: 428.26 (M + H)<sup>+</sup>. IR (neat) ν (cm<sup>−1</sup>): 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 <sup>1</sup>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<sub>22</sub>H<sub>21</sub>NO<sub>2</sub> requires: C 79.73; H 6.39; N 4.23%. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 7.28–7.09 (m, 8H), 6.35 (s, 1H), 2.13, 2.11, 2.05, 1.84 (4s, 9H).<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 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 +) <sup>m/z</sup>: 332.29 (M + H)<sup>+</sup>. IR (neat) ν (cm<sup>−1</sup>): 3408, 3403 (NH<sub>2</sub>), 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<sub>23</sub>H<sub>23</sub>NO<sub>2</sub> requires: C 79.97; H 6.71; N 4.05%. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 7.28–6.95 (m, 8H), 2.03, 2.02, 1.83, 1.71 (4s, 9H).<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 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 +) \textit{m/z}: 346.26 (M + H)^+. IR (neat) \nu (\text{cm}^{-1}): 3403, 3401 (NH), 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\textsubscript{29}H\textsubscript{23}NO\textsubscript{2} requires: C 83.43; H 5.55; N 3.35%.

1H NMR (200 MHz, CDCl\textsubscript{3}): \delta = 7.91–7.71 (m, 5H), 7.59–7.32 (m, 9H), 1.80 (s, 3H), 1.66 (s, 3H). 13C NMR (50 MHz, CDCl\textsubscript{3}): \delta = 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 +) \textit{m/z}: 418.46 (M + H)^+. IR (neat) \nu (\text{cm}^{-1}): 3407, 3404 (NH\textsubscript{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\textsubscript{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\textsubscript{2}O/H\textsubscript{2}O (100 mL, 1:1). The aqueous layer was separated and extracted with Et\textsubscript{2}O (100 mL). The combined organic extracts were washed with H\textsubscript{2}O (100 mL) and a saturated solution of Na\textsubscript{2}CO\textsubscript{3} (50 mL), dried over Na\textsubscript{2}SO\textsubscript{4} and evaporated under reduced pressure. The crude residue, purified by column chromatography (PE/Et\textsubscript{2}O 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 \textit{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\textsubscript{27}H\textsubscript{30}OS\textsubscript{2} requires: C 74.61; H 6.96; S 14.75%. \textit{1}H NMR (200 MHz, CDCl\textsubscript{3}): \delta = 7.29–7.13 (m, 8H), 6.84 (s, 1H), 6.55 and 6.53 (2s, 1H), 3.37 (t, \textit{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). 13C NMR (50 MHz, CDCl\textsubscript{3}): \delta = 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 +) \textit{m/z}: 435.29 (M + H)^+. 

8
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}O_{2}S_{2} requires: C 74.95; H 7.19; S 14.29%. ¹H NMR (200 MHz, CDCl₃): 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). ¹³C NMR (50 MHz, CDCl₃): 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 (C₅H₁₁)] (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}O_{2}S_{2} requires: C 78.42; H 6.19; S 12.31%. ¹H NMR (200 MHz, CDCl₃): 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, 6H). ¹³C NMR (50 MHz, CDCl₃): 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-tolyl)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)
11.11 4-Nitro-3,6-bis(o-toly)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-toly)-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

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

meso isomer + couple of enantiomers

meso isomer + couple of enantiomers
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

(-) enantiomer
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

mass isomer + couple of enantiomers
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

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### SAMPLE INFORMATION

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### Chromatogram

![Chromatogram](image)

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

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Vial: 1

Acq.Method: solfocloruro

Processed by: Breeze

Injection: #

Date processed: 8/12/2013 11:15:37 AM CEST

Injection volume: 6.00 ul

Channel name: 2998 Ch1 254nm@1.2nm

Run time: 25 minutes

Channel desc: 2998 Ch1 254nm@1.2nm

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12.4 Atropisomers of 14b

Sample Information

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Sample type: Unknown  
Vial: 1  
Injection: #  
Injection volume: 6.00 ul  
Run time: 25 minutes  
Sampling rate: 4.00 per sec

Acquired by: Breeze  
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Acq.Method: solfocloruro  
Processed by: Breeze  
Date processed: 8/14/2013 10:02:37 AM CEST  
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Vial: 1
Acq.Method: solfocloruro
Injection: #
Processed by: Breeze
Injection volume: 6.00 ul
Date processed: 3/10/2014 09:04:55 AM  CEST
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Sampling rate: 10.00 per sec
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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  
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Sampling rate: 12.00 per sec  
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## 12.7 Atropisomers of 14c

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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

### Peak Table

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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\(_3\)): \(\delta = 1.88\) (s, 3H), 4.28 (br s, 1H), 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\(_3\)): \(\delta = 33.5, 57.3, 115.9, 120.1, 121.0, 125.1, 128.8, 129.2, 129.4, 140.1, 143.7\). MS (EI) \(m/z\): (%) 222 [M\(^+\)](10), 195 (50), 180 (100), 77 (45). IR (CHCl\(_3\)) \(\nu\) (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\(_3\)): \(\delta = 1.94\) (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\(_3\)): \(\delta = 33.1, 55.7, 58.4, 114.6, 118.5, 121.3, 125.3, 128.8, 129.4, 137.5, 140.4, 154.2\). MS (EI) \(m/z\): (%) 225 [M\(^+\)-HCN](65), 210 (100). IR (CHCl\(_3\)) \(\nu\) (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\(_3\)): \(\delta = 1.95\) (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\(_3\)): \(\delta = 33.1, 56.7, 115.8, 120.0, 120.7, 124.8, 126.4, 129.3, 142.9, 147.3, 148.3\). MS (EI) \(m/z\): (%) 240 [M\(^+\)-HCN](72), 225 (100), 179 (60). IR (CHCl\(_3\)) \(\nu\) (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\(_3\)): \(\delta = 1.86\) (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 \(\delta\) (50 MHz, CDCl\(_3\)): \(\delta = 33.4, 57.3, 112.2, 117.5, 120.7, 125.0, 129.0, 129.6, 132.0, 139.4, 142.8\). MS (EI) \(m/z\): (%) 273 [M\(^+\)+2–HCN](65), 273 [M\(^+\)-HCN](65), 260 (100), 258 (100). IR (CHCl\(_3\)) \(\nu\) (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\(_3\)): \(\delta = 1.86\) (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\(_3\)): \(\delta = 33.3, 57.9, 115.6, 116.0, 117.6\) (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\(_3\)) \(\nu\) (cm\(^{-1}\)): 3431 (NH), 2256 (CN).
13.6 2-(2-Methoxyphenylamino)-2-phenylpropanenitrile (21f). Pale brown solid; mp 80–81 °C (EtOH; lit.\textsuperscript{10b} 80-81 °C). \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{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). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{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-\text{HCN}]\textsuperscript{+}(45), 210 (100). IR (CHCl\textsubscript{3}) ν (cm\textsuperscript{-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.\textsuperscript{16} 102–105 °C). \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{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). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{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-\text{HCN}]\textsuperscript{+}(60), 210 (100). IR (CHCl\textsubscript{3}) ν (cm\textsuperscript{-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.\textsuperscript{17} 126–128 °C). \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}): δ = 1.87 (s, 3H), 2.32 (s, 3H), 4.29 (br s, 1H), 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). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}): δ = 21.3, 33.6, 57.1, 115.9, 120.0, 125.0, 125.8, 126.6, 130.4, 135.7, 139.3, 149.4. MS (EI) m/z (%): 209 [M-\text{HCN}]\textsuperscript{+}(85), 194 (100), 77 (35). IR (CHCl\textsubscript{3}) ν (cm\textsuperscript{-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.\textsuperscript{10b} 102–103 °C). \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}): δ = 1.93 (s, 3H), 2.32 (s, 3H), 4.29 (br s, 1H), 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). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{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-\text{HCN}]\textsuperscript{+}(75), 239 (100), 193 (50). IR (CHCl\textsubscript{3}) ν (cm\textsuperscript{-1}): 3421 (NH), 2242 (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.\textsuperscript{10b} 88–89 °C). \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{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). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{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-\text{HCN}]\textsuperscript{+}(70), 225 (100). IR (CHCl\textsubscript{3}) ν (cm\textsuperscript{-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). 1H NMR (200 MHz, CDCl3): 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). 13C NMR (50 MHz, CDCl3): 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 (CHCl3) ν (cm⁻¹): 3424 (NH), 2251 (CN).

13.12 2-Phenyl-2-phenylaminoacetonitrile (21m). White solid; mp 79 °C (EtOH; lit.17 76–78 °C). 1H NMR (200 MHz, CDCl3): 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). 13C NMR (50 MHz, CDCl3): 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 (CHCl3) ν (cm⁻¹): 3415 (NH), 2240 (CN).

13.13 2-(4-Nitrophenyl)-2-phenylaminoacetonitrile (21n). Pale brown waxy solid. 1H NMR (200 MHz, CDCl3): δ = 4.18 (br s, 1H), 5.53 (s, 1H), 6.71 (d, J = 8.0 Hz, 2H), 6.86–6.92 (m, 1H), 7.20–7.26 (m, 2H), 7.77 (d, J = 8.0 Hz, 2H). 13C NMR (50 MHz, CDCl3): 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 (CHCl3) 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). 1H NMR (200 MHz, CDCl3): 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). 13C NMR (50 MHz, CDCl3): 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 (CHCl3) 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). 1H NMR (200 MHz, CDCl3): 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). 13C NMR (50 MHz, CDCl3): 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 (CHCl3) 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).
14.8 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 (21I)
14.13 2-Phenyl-2-phenylaminoacetonitrile (21m).
14.14 2-(4-Nitrophenyl)-2-phenylaminoacetonitrile (21n)

[Chemical structure image]

[Graph and spectra images]
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)
15.2 2-Phenyl-2-phenylaminopropanenitrile (21a), obtained at 0°C in the presence of catalyst 3a
15.3 2-Phenyl-2-phenylaminopropanenitrile (21a), obtained at -20°C in the presence of catalyst 3b
15.4 2-Phenyl-2-phenylaminopropanenitrile (21a), obtained at 0°C in the presence of catalyst 3b
15.5 2-Phenyl-2-phenylaminopropanenitrile (21a), obtained at -20 °C in the presence of catalyst 3b.
15.6 2-(4-Methoxyphenylamino)-2-phenylpropanenitrile (21b), obtained at -20°C in the presence of catalyst 3b

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15.8 2-(4-Bromophenylamino)-2-phenylpropanenitrile (21d), obtained at -20°C in the presence of catalyst 3b
15.9 2-(4-Fluorophenylamino)-2-phenylpropanenitrile (21e), obtained at -20°C in the presence of catalyst 3b
15.10 2-(2-Methoxyphenylamino)-2-phenylpropanenitrile (21f), obtained at -20°C in the presence of catalyst 3b

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15.12 2-Phenylamino-2-(4-tolyl)propanenitrile (21h), obtained at -20°C in the presence of catalyst 3b
15.13 2-(4-Nitrophenylamino)-2-(4-tolyl)propanenitrile (21i), obtained at -20°C in the presence of catalyst 3b
15.14 2-(4-Methoxyphenylamino)-2-(4-tolyl)propanenitrile (21j), obtained at -20°C in the presence of catalyst 3b
15.15 2-(4-Methoxyphenylamino)-2-(4-nitrophenyl)propanenitrile (21k), obtained at -20°C in the presence of catalyst 3b.
15.16 2-Methyl-2-(phenylamino)pentanenitrile (21l), obtained at -20°C in the presence of catalyst 3b
15.17 2-Phenyl-2-phenylaminoacetonitrile (21m), obtained at -20°C in the presence of catalyst 3b
15.18 2-(4-Nitrophenyl)-2-phenylaminoacetonitrile (21n), obtained at -20°C in the presence of catalyst 3b
15.19 2-Phenylamino-2-(4-tolyl)acetonitrile (21o), obtained at -20°C in the presence of catalyst 3b.
15.20 2-Phenylamino-2-thienylacetonitrile (21p), obtained at -20°C in the presence of catalyst 3b

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