Supporting Information

Utilization of Nitriles as the Nitrogen Source: Practical and Economical Construction of 4-Aminopyrimidine and β-Enaminonitrile Skeleton

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1. General Information

Unless otherwise stated, the reaction was carried out in a Teflon screw-cap sealed tube (50 ml) under N\textsubscript{2} atmosphere. All the commercial liquid-nitriles were distilled before use. Other commercial-grade chemicals were used without further purification. DME were dried over Na and degassed before use. Flash chromatography was performed on silica gel (200-300 mesh). The single crystal data of compounds were collected by a Cu-Kα rotating anode source at 100 K, using a Supernova diffractometer with the o-scan method. ESI-MS were obtained using a Bruker Impact II quardrupole time-of-flight mass spectrometer. The \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were recorded on Bruker Avance III (400 MHz) and chemical shifts are expressed in δ ppm values with reference to tetramethylsilane (TMS) as internal standard. The NMR spectra were recorded in solvent of CDCl\textsubscript{3} except for the last compound 4ag, which was recorded in d\textsubscript{6}-DMSO. Product yields refer to isolated yields after column chromatography.

2. General Experimental Procedures

a) General experimental procedure for the synthesis of 4-aminopyrimidines

Alkyl nitrile 1 (0.20 mmol), aryl nitrile 2 (0.60 mmol), LiHMDS (0.20 mmol) and dried DME (1 ml) were mixed in a 50 mL Teflon screw-cap sealed tube. The tube was charged with N\textsubscript{2} and the mixture was vigorously stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and further concentrated under reduced pressure. The crude product was purified on a silica gel column (200-300 mesh) eluted with petroleum ether/acetone (10 : 1 v/v) to afford products 3.

b) General experimental procedure for the synthesis of β-enaminonitriles

Alkyl nitrile 1 (0.20 mmol), aryl nitrile 2 (0.30 mmol), LiHMDS (0.20 mmol) and dried DME (1 ml) were mixed in a 50 mL Teflon screw-cap sealed tube. The tube was charged with N\textsubscript{2} and the mixture was vigorously stirred at 40 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and further concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/acetone (8: 1 v/v) to afford products 4.

c) General experimental procedure for the synthesis of variable substitution 4-aminopyrimidines

Alkyl nitrile 1 (0.20 mmol), aryl nitrile 2 (0.30 mmol), LiHMDS (0.20 mmol) and dried DME (1 ml) were mixed in a 50 mL Teflon screw-cap sealed tube. The tube was charged with N\textsubscript{2} and the mixture was vigorously stirred at 40 °C for 24 h. The intermediate 4a was isolated on a silica column and mixed with a second portion of nitrile 2′ (0.3 mmol)/LiHMDS (0.20 mmol)/DME (1 ml) in a 50 mL Teflon screw-cap sealed tube. The tube was charged with N\textsubscript{2} again and the mixture was vigorously stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel. The crude product was purified on a silica gel column (200-300 mesh) eluted with petroleum ether/acetone (10 : 1 v/v) to afford the multi-substitution products 3.
3. Characterization Data for the Products

![5-benzyl-2,6-diphenyl-4-aminopyrimidine (3a)]

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.48 (dd, $J = 6.7$, 3.0 Hz, 2H), 7.65 (dt, $J = 9.3$, 3.3 Hz, 2H), 7.52 – 7.42 (m, 6H), 7.39 (t, $J = 7.3$ Hz, 2H), 7.31 (dd, $J = 12.9$, 5.6 Hz, 1H), 7.25 (d, $J = 7.2$ Hz, 2H), 4.91 (s, 2H), 4.05 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.21, 163.28, 162.27, 139.07, 138.17, 137.78, 130.11, 129.21, 128.88, 128.31, 128.11, 127.86, 127.01, 110.04, 33.28. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{23}$H$_{19}$N$_3$ + H$: 338.1657. Found, 338.1652.

![2,6-diphenyl-4-aminopyrimidine (3b)]

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.54 (dd, $J = 7.4$, 2.2 Hz, 2H), 8.15 (dd, $J = 7.3$, 2.2 Hz, 2H), 7.62 – 7.44 (m, 6H), 6.74 (d, $J = 2.0$ Hz, 1H), 5.09 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.53, 164.24, 163.63, 138.44, 137.80, 130.50, 130.38, 128.83, 128.52, 128.38, 127.14, 98.58. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{16}$H$_{13}$N$_3$ + H$: 248.1187. found, 248.1182.

![5-ethyl-2,6-diphenyl-4-aminopyrimidine (3c)]

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.56 – 8.41 (m, 2H), 7.68 – 7.58 (m, 2H), 7.58 – 7.43 (m, 6H), 5.33 (s, 2H), 2.53 (q, $J = 7.5$ Hz, 2H), 1.20 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.25, 162.74, 161.56, 139.74, 138.54, 130.04, 128.77, 128.61, 128.42, 128.34, 128.21, 114.28, 20.12, 12.83. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{18}$H$_{17}$N$_3$ + H$: 276.1500. found, 276.1495.

![5-propyl-2,6-diphenyl-4-aminopyrimidine (3d)]

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.53 – 8.38 (m, 2H), 7.60 (d, $J = 6.8$ Hz, 2H), 7.50 (dd, $J = 15.9$, 6.7 Hz, 6H), 5.24 (s, 2H), 2.63 – 2.41 (m, 2H), 1.73 – 1.51 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.57, 162.74, 161.40, 139.77, 138.36, 129.93, 128.77, 128.44, 128.29, 128.21, 128.10, 112.96, 28.95, 21.48, 14.27. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{19}$H$_{19}$N$_3$ + H$: 290.1657. found, 290.1653.
5-isopropyl-2,6-diphenyl-4-aminopyrimidine (3e)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 – 8.38 (m, 2H), 7.53 (tdd, $J$ = 3.9, 2.7, 1.4 Hz, 2H), 7.51 – 7.42 (m, 6H), 5.30 (s, 2H), 3.37 – 3.24 (m, 1H), 1.29 (s, 3H), 1.27 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.72, 162.23, 161.14, 140.48, 138.22, 129.92, 128.63, 128.33, 128.26, 128.24, 128.10, 117.38, 27.07, 20.03. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{19}$H$_{19}$N$_3$ + H$^+$: 290.1657. found, 290.1652.

5-decyl-2,6-diphenyl-4-aminopyrimidine (3f)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.51 – 8.41 (m, 2H), 7.65 – 7.57 (m, 2H), 7.56 – 7.42 (m, 6H), 5.29 (s, 2H), 2.58 – 2.42 (m, 2H), 1.55 (dt, $J$ = 22.8, 11.3 Hz, 2H), 1.32 (dd, $J$ = 32.1, 13.9 Hz, 14H), 1.01 – 0.89 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.46, 162.72, 161.37, 139.75, 138.39, 129.90, 128.78, 128.44, 128.28, 128.19, 128.11, 113.15, 31.96, 29.66, 29.60, 29.55, 29.37, 29.21, 28.05, 26.80, 22.75, 14.21. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{26}$H$_{33}$N$_3$ + H$^+$: 388.2752. found, 388.2747.

5-phenethyl-2,6-diphenyl-4-aminopyrimidine (3g)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.51 – 8.38 (m, 2H), 7.55 – 7.43 (m, 8H), 7.33 – 7.20 (m, 3H), 7.09 – 7.00 (m, 2H), 5.07 (s, 2H), 2.99 – 2.70 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.24, 162.66, 161.65, 140.80, 139.50, 138.22, 130.02, 128.68, 128.56, 128.47, 128.30, 128.25, 128.12, 126.39, 112.09, 34.28, 29.00. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{24}$H$_{21}$N$_3$ + H$^+$: 352.1813. found, 352.1810.

2,5,6-triphenyl-4-aminopyrimidine (3h)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (dt, $J$ = 5.1, 3.2 Hz, 2H), 7.50 – 7.40 (m, 5H), 7.40 – 7.28 (m, 3H), 7.26 – 7.17 (m, 5H), 5.00 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.86, 162.32, 162.26, 138.77, 138.18, 135.13, 130.32, 130.21, 129.86, 129.38, 128.47, 128.31, 128.17, 127.98, 127.69, 114.34. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{22}$H$_{17}$N$_3$ + H$^+$: 324.1500. found, 324.1495.
**2,6-diphenyl-5-(o-tolyl)-4-aminopyrimidine (3i)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (dd, $J = 7.1$, 2.0 Hz, 2H), 7.59 – 7.46 (m, 5H), 7.35 – 7.18 (m, 7H), 4.96 (s, 2H), 2.10 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.02, 162.34, 161.83, 138.87, 138.22, 137.35, 134.14, 131.02, 130.68, 129.31, 128.68, 128.57, 128.35, 128.17, 127.74, 126.89, 113.56, 19.55. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{23}$H$_{19}$N$_3$ + H$^+$: 338.1657. Found, 338.1652.

**2,6-diphenyl-5-(m-tolyl)-4-aminopyrimidine (3j)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.53 (dd, 2H), 7.57 – 7.45 (m, 5H), 7.32 – 7.21 (m, 4H), 7.16 (d, $J = 7.6$ Hz, 1H), 7.10 (s, 1H), 7.05 (d, $J = 7.5$ Hz, 1H), 5.05 (s, 2H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.73, 162.40, 162.02, 139.08, 138.84, 138.25, 135.02, 130.72, 130.16, 129.86, 129.27, 128.74, 128.45, 128.30, 128.16, 127.66, 127.37, 114.47, 21.46.

**2,6-diphenyl-5-(p-tolyl)-4-aminopyrimidine (3k)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.65 – 8.39 (m, 2H), 7.54 – 7.45 (m, 5H), 7.31 – 7.18 (m, 7H), 7.15 (d, $J = 8.1$ Hz, 2H), 5.03 (s, 2H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.69, 162.50, 162.16, 138.91, 138.24, 137.72, 131.93, 130.14, 130.10, 129.87, 128.39, 128.29, 128.14, 127.67, 114.33, 21.30. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{23}$H$_{19}$N$_3$ + H$^+$: 338.1657. Found, 338.1652.

**5-(4-(tert-buty1)phenyl)-2,6-diphenyl-4-aminopyrimidine (3l)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 – 8.44 (m, 2H), 7.53 – 7.44 (m, 5H), 7.44 – 7.38 (m, 2H), 7.31 – 7.22 (m, 3H), 7.20 (dd, $J = 8.4$, 5.2, 1.8 Hz, 2H), 5.04 (s, 2H), 1.35 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.68, 162.52, 162.12, 151.03, 138.87, 138.26, 131.89, 130.13, 129.90, 129.87, 128.39, 128.29, 128.13, 127.60, 126.26, 114.31, 34.66, 31.32. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{25}$H$_{25}$N$_3$ + H$^+$: 380.2126. Found, 380.2120.
1H NMR (400 MHz, CDCl$_3$) δ 8.59 – 8.48 (m, 2H), 7.70 – 7.61 (m, 4H), 7.55 – 7.45 (m, 7H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.37 – 7.32 (m, 2H), 7.26 (dd, $J = 8.8$, 5.1, 3.2 Hz, 3H), 5.06 (s, 2H).

13C NMR (101 MHz, CDCl$_3$) δ 162.89, 162.34, 140.60, 140.22, 138.77, 138.16, 134.08, 130.75, 130.24, 129.90, 128.92, 128.52, 128.32, 128.18, 127.95, 127.77, 127.67, 126.98, 113.97.

1H NMR (400 MHz, CDCl$_3$) δ 8.55 – 8.46 (m, 2H), 7.53 – 7.45 (m, 5H), 7.31 – 7.23 (m, 3H), 7.20 – 7.14 (m, 2H), 6.99 – 6.82 (m, 2H), 5.04 (s, 2H), 3.85 (d, $J = 6.1$ Hz, 3H).

13C NMR (101 MHz, CDCl$_3$) δ 162.67, 162.65, 162.27, 159.20, 138.92, 138.23, 131.45, 130.14, 129.85, 128.38, 128.30, 128.14, 127.71, 126.91, 114.84, 114.02, 55.28. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{23}$H$_{19}$ON$_3$ + H$^+$: 354.1606. found, 354.1600.

1H NMR (400 MHz, CDCl$_3$) δ 8.52 (dd, $J = 5.1$, 2.3 Hz, 2H), 7.51 (dd, $J = 6.9$, 3.3 Hz, 3H), 7.47 – 7.42 (m, 2H), 7.31 – 7.20 (m, 5H), 7.13 – 7.06 (m, 2H), 5.06 (s, 2H).

13C NMR (101 MHz, CDCl$_3$) δ 163.10, 162.58, 162.08, 138.48, 137.97, 134.00, 133.63, 131.75, 130.35, 129.79, 129.68, 128.65, 128.33, 128.18, 127.86, 113.10. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{22}$H$_{16}$FN$_3$ + H$^+$: 342.1406. found, 342.1402.

1H NMR (400 MHz, CDCl$_3$) δ 8.54 – 8.42 (m, 2H), 7.51 – 7.44 (m, 3H), 7.41 (ddd, $J = 6.4$, 5.3, 2.9 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.28 – 7.22 (m, 3H), 7.20 – 7.14 (m, 2H), 4.96 (s, 2H).

13C NMR (101 MHz, CDCl$_3$) δ 163.10, 162.58, 162.08, 138.48, 137.97, 134.00, 133.63, 131.75, 130.35, 129.79, 129.68, 128.65, 128.33, 128.18, 127.86, 113.10. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{22}$H$_{16}$ClN$_3$ + H$^+$: 358.1111. found, 358.1106.
5-(4-bromophenyl)-2,6-diphenyl-4-aminopyrimidine (3q)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.50 (dt, $J = 4.9, 2.8$ Hz, 2H), 7.56 – 7.47 (m, 5H), 7.43 (dt, $J = 11.6, 5.6$ Hz, 2H), 7.34 – 7.21 (m, 3H), 7.18 – 7.10 (m, 2H), 5.01 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.11, 162.52, 162.01, 138.46, 137.97, 134.13, 132.63, 132.06, 129.80, 128.67, 128.35, 128.19, 127.88, 122.16, 113.11.

5-(2-methoxyphenyl)-2,6-diphenyl-4-aminopyrimidine (3r)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (dt, $J = 5.2, 3.7$ Hz, 2H), 7.52 – 7.44 (m, 5H), 7.35 (ddd, $J = 9.1, 6.8, 2.7$ Hz, 1H), 7.27 – 7.19 (m, 3H), 7.15 (ddd, $J = 7.5, 1.7$ Hz, 1H), 6.98 (dd, $J = 7.5, 0.8$ Hz, 1H), 6.94 (dd, $J = 8.9, 4.6$ Hz, 1H), 4.95 (s, 2H), 3.64 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.22, 162.91, 162.44, 157.21, 139.40, 138.34, 131.74, 130.06, 129.91, 129.04, 128.34, 128.25, 128.16, 127.53, 123.70, 121.39, 111.54, 111.09, 55.43.

5-(naphthalen-1-yl)-2,6-diphenyl-4-aminopyrimidine (3s)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (dt, $J = 5.1, 3.1$ Hz, 2H), 7.93 (t, $J = 7.9$ Hz, 1H), 7.89 (d, $J = 8.3$ Hz, 1H), 7.78 (t, $J = 10.4$ Hz, 1H), 7.60 – 7.49 (m, 5H), 7.50 – 7.42 (m, 1H), 7.39 (dd, $J = 5.3, 3.3$ Hz, 2H), 7.34 – 7.29 (m, 1H), 7.21 – 7.14 (m, 1H), 7.13 – 7.06 (m, 2H), 4.77 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.33, 162.64, 138.79, 138.14, 133.91, 132.48, 131.65, 130.32, 129.09, 129.91, 128.80, 128.77, 128.57, 128.36, 128.20, 127.64, 127.08, 126.48, 126.12, 125.13, 112.40. HRMS m/z (ESI) [M + H$^+$] calcd for C$_{26}$H$_{19}$N$_3$ + H$: 374.1657$. found, 374.1652.

5-(naphthalen-2-yl)-2,6-diphenyl-4-aminopyrimidine (3t)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.61 – 8.49 (m, 2H), 7.92 – 7.79 (m, 4H), 7.58 – 7.47 (m, 7H), 7.29 (dd, $J = 8.1, 1.9$ Hz, 1H), 7.26 – 7.14 (m, 3H), 5.04 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.92, 162.46, 162.38, 138.72, 138.17, 133.64, 132.70, 132.67, 130.25, 129.90, 129.21, 128.52, 128.33, 128.20, 128.13, 127.97, 127.86, 127.77, 126.56, 126.53, 114.18.
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\text{\textbf{5-(3,5-dimethylphenyl)-2,6-diphenyl-4-aminopyrimidine (3u)}}
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\(^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.65 – 8.42 (m, 2H), 7.61 – 7.44 (m, 5H), 7.33 – 7.18 (m, 4H), 6.96 (d, \(J = 9.2\) Hz, 1H), 6.87 (s, 2H), 4.98 (s, 2H), 2.29 (s, 6H). \(^13\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 162.59, 162.43, 161.79, 138.92, 138.84, 138.27, 134.89, 130.10, 129.83, 129.60, 128.42, 128.28, 128.11, 127.79, 127.61, 114.58, 21.32.

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\text{\textbf{5-benzyl-2,6-di-m-tolyl-4-aminopyrimidine (3aa)}}
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\(^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.39 – 8.17 (m, 2H), 7.47 (d, \(J = 15.5\) Hz, 1H), 7.39 (dd, \(J = 14.0, 6.8\) Hz, 4H), 7.35 – 7.26 (m, 4H), 7.24 (d, \(J = 7.4\) Hz, 2H), 4.93 (s, 2H), 4.03 (s, 2H), 2.47 (s, 3H), 2.42 (s, 3H). \(^13\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 165.50, 163.20, 162.44, 139.06, 138.17, 138.04, 137.97, 137.87, 130.89, 129.60, 129.16, 128.69, 128.25, 128.11, 127.86, 126.94, 125.71, 125.34, 110.08, 33.30, 21.56. HRMS m/z (ESI) [M + H\(^+\)] calcd for C\(_{25}\)H\(_{23}\)N\(_3\) + H\(^+\): 366.1970. found, 366.1965.

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\text{\textbf{5-benzyl-2,6-di-p-tolyl-4-aminopyrimidine (3ab)}}
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\(^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.37 (d, \(J = 8.1\) Hz, 2H), 7.55 (d, \(J = 8.0\) Hz, 2H), 7.37 (t, \(J = 7.3\) Hz, 2H), 7.34 – 7.20 (m, 7H), 4.82 (s, 2H), 4.05 (s, 2H), 2.43 (d, \(J = 9.0\) Hz, 6H). \(^13\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 165.05, 163.24, 162.31, 153.18, 151.86, 138.05, 136.22, 135.53, 129.17, 128.95, 128.75, 128.02, 127.86, 126.92, 109.62, 33.33, 21.50, 21.34. HRMS m/z (ESI) [M + H\(^+\)] calcd for C\(_{31}\)H\(_{35}\)N\(_3\) + H\(^+\): 366.1970. found, 366.1965.

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\text{\textbf{5-benzyl-2,6-bis(4-(tert-butyl)phenyl)-4-aminopyrimidine (3ac)}}
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\(^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.38 (d, \(J = 8.2\) Hz, 2H), 7.61 (d, \(J = 7.9\) Hz, 2H), 7.47 (dd, \(J = 13.0, 8.3\) Hz, 4H), 7.39 (t, \(J = 7.4\) Hz, 2H), 7.32 (d, \(J = 7.1\) Hz, 1H), 7.29 – 7.24 (m, 2H), 4.86 (s, 2H), 4.08 (s, 2H), 1.38 (d, \(J = 8.8\) Hz, 18H). \(^13\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 165.05, 163.24, 162.31, 153.18, 151.86, 138.05, 136.22, 135.53, 129.17, 128.59, 127.90, 127.84, 126.93, 125.24, 125.20, 109.57, 34.80, 34.73, 33.39, 31.33. HRMS m/z (ESI) [M + H\(^+\)] calcd for C\(_{31}\)H\(_{35}\)N\(_3\) + H\(^+\): 450.2909. found, 450.2904.

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1H NMR (400 MHz, CDCl₃) δ 8.49 – 8.38 (m, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.31 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 7.2 Hz, 2H), 7.03 – 6.89 (m, 4H), 4.76 (s, 2H), 4.05 (d, J = 11.3 Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H).

13C NMR (101 MHz, CDCl₃) δ 164.71, 163.28, 161.95, 161.95, 160.25, 138.04, 131.64, 130.98, 130.37, 129.68, 129.26, 127.91, 127.01, 113.71, 113.62, 108.98, 55.43, 33.43. HRMS m/z (ESI) [M + H⁺] calcd for C₂₅H₂₃O₂N₃⁺ H⁺: 398.1868. found, 398.1862.

1H NMR (400 MHz, CDCl₃) δ 8.40 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.47 – 7.35 (m, 6H), 7.32 (t, J = 6.2 Hz, 1H), 7.22 (d, J = 7.2 Hz, 2H), 4.87 (s, 2H), 4.01 (s, 2H).

13C NMR (101 MHz, CDCl₃) δ 164.10, 163.34, 161.39, 137.32, 136.50, 136.41, 135.21, 130.24, 129.49, 129.40, 128.64, 128.58, 127.80, 127.27, 110.20, 33.27. HRMS m/z (ESI) [M + H⁺] calcd for C₂₃H₁₇Cl₂N₃⁺ H⁺: 406.0877. found, 406.0872.

1H NMR (400 MHz, CDCl₃) δ 8.33 (d, J = 8.5 Hz, 2H), 7.79 (dd, J = 11.6, 8.5 Hz, 4H), 7.41 – 7.30 (m, 5H), 7.21 (d, J = 7.2 Hz, 2H), 4.88 (s, 2H), 4.00 (s, 2H). 13C NMR (101 MHz, CDCl₃) δ 164.17, 163.27, 161.55, 138.32, 137.48, 137.23, 130.57, 129.82, 129.32, 127.72, 127.20, 110.23, 97.20, 95.33, 33.21.
1H NMR (400 MHz, CDCl3) δ 8.67 (d, J = 2.0 Hz, 1H), 8.41 (dd, J = 8.6, 2.1 Hz, 1H), 7.88 (d, J = 2.1 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.38 (t, J = 7.3 Hz, 2H), 7.31 (t, J = 5.8 Hz, 1H), 7.22 (d, J = 7.2 Hz, 2H), 6.98 (d, J = 8.7 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 4.85 (s, 2H), 4.03 (s, 2H), 3.98 (s, 3H), 3.94 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 163.38, 163.23, 160.72, 157.44, 156.46, 137.51, 134.03, 133.08, 132.63, 131.98, 129.28, 128.97, 128.56, 127.74, 127.10, 111.66, 111.57, 111.27, 111.24, 109.58, 56.36, 33.24.

1H NMR (400 MHz, CDCl3) δ 9.64 (s, 1H), 8.87 (t, J = 6.6 Hz, 1H), 8.75 – 8.65 (m, 3H), 8.02 – 7.90 (m, 1H), 7.40 (ddd, J = 9.8, 8.1, 5.4 Hz, 4H), 7.32 (t, J = 4.9 Hz, 1H), 7.23 (d, J = 7.0 Hz, 2H), 4.94 (d, J = 59.2 Hz, 2H), 4.05 (s, 2H).

13C NMR (101 MHz, CDCl3) δ 163.36, 162.18, 160.70, 150.95, 150.08, 149.76, 149.57, 136.81, 136.31, 135.45, 134.48, 133.30, 129.41, 127.70, 127.36, 123.25, 111.08, 33.14. HRMS m/z (ESI) [M + H]+ calcd for C21H17N5 + H+: 340.1562. found, 340.1557.

1H NMR (400 MHz, CDCl3) δ 7.99 (d, J = 3.6 Hz, 1H), 7.61 (dt, J = 8.2, 2.1 Hz, 3H), 7.59 – 7.57 (m, 1H), 7.44 (dd, J = 6.5, 3.7 Hz, 3H), 7.38 (t, J = 7.3 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 2H), 4.84 (s, 2H), 4.04 (s, 2H).

13C NMR (101 MHz, CDCl3) δ 165.12, 163.04, 159.01, 143.98, 138.67, 137.09, 131.41, 129.74, 129.23, 128.94, 128.74, 128.32, 127.81, 127.06, 124.74, 110.32, 33.28.

1H NMR (400 MHz, CDCl3) δ 7.99 (d, J = 3.6 Hz, 1H), 7.61 (dt, J = 6.6, 2.8 Hz, 2H), 7.46 – 7.40 (m, 4H), 7.37 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 5.0 Hz, 1H), 7.23 (d, J = 7.5 Hz, 2H), 7.16 – 7.10 (m, 1H), 4.83 (s, 2H), 4.02 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 165.12, 163.04, 159.01, 143.98, 138.67, 137.71, 129.20, 128.92, 128.79, 128.27, 128.22, 127.92, 127.81, 127.01, 109.71, 33.26.
1H NMR (400 MHz, CDCl₃) δ 7.64 – 7.57 (m, 2H), 7.49 – 7.41 (m, 3H), 7.40 – 7.34 (m, 4H), 7.33 – 7.26 (m, 1H), 4.43 (s, 2H), 3.60 (s, 2H).

13C NMR (101 MHz, CDCl₃) δ 157.51, 137.73, 136.06, 130.33, 128.91, 128.76, 128.04, 128.03, 126.94, 123.41, 78.15, 34.51. HRMS m/z (ESI) [M + H⁺] calcd for C₁₆H₁₄N₂⁺ H⁺: 235.1235. found, 235.1228.

1H NMR (400 MHz, CDCl₃) δ 7.54 (q, J = 2.0 Hz, 1H), 7.52 (t, J = 2.0 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.47 (t, J = 1.8 Hz, 1H), 5.16 – 4.84 (m, 2H), 4.28 (s, 1H).

13C NMR (101 MHz, CDCl₃) δ 161.52, 135.37, 130.99, 129.04, 126.02, 119.50, 63.82. HRMS m/z (ESI) [M + Na⁺] calcd for C₉H₈N₂⁺ Na⁺: 167.0585. found, 167.0580.

1H NMR (400 MHz, CDCl₃) δ 7.62 – 7.56 (m, 2H), 7.47 – 7.42 (m, 3H), 4.33 (s, 2H), 2.29 – 2.16 (m, 2H), 1.27 (dd, J = 9.6, 5.4 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ 155.56, 136.38, 130.07, 128.71, 127.96, 122.32, 81.94, 21.06, 12.25. HRMS m/z (ESI) [M + Na⁺] calcd for C₁₁H₁₂N₂⁺ Na⁺: 195.0898. found, 195.0893.

1H NMR (400 MHz, CDCl₃) δ 7.63 – 7.54 (m, 2H), 7.48 – 7.40 (m, 3H), 4.53 – 4.22 (m, 2H), 2.20 – 2.10 (m, 2H), 1.75 – 1.62 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ 156.22, 136.47, 130.04, 128.67, 127.99, 122.79, 80.19, 29.85, 21.12, 13.79. HRMS m/z (ESI) [M + Na⁺] calcd for C₁₂H₁₄N₂⁺ Na⁺: 209.1049. found, 209.1054.

1H NMR (400 MHz, CDCl₃) δ 7.63 – 7.54 (m, 2H), 7.48 – 7.40 (m, 3H), 4.34 (s, 2H), 2.55 (hept, J = 6.8 Hz, 1H), 1.25 (d, J = 6.7 Hz, 6H).

13C NMR (101 MHz, CDCl₃) δ 154.55, 136.66, 130.01, 128.68, 128.07, 120.91, 88.05, 26.49, 21.24. HRMS m/z (ESI) [M + Na⁺] calcd for C₁₂H₁₄N₂⁺ Na⁺: 209.1049. found, 209.1054.
2-(amino(phenyl)methylene)dodecanitrile (4f)

\[
\text{C}_{10}\text{H}_{21}\text{CN} \quad \text{Ph} \quad \text{NH}_2
\]

\(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.65 - 7.54 (m, 2H), 7.50 - 7.40 (m, 3H), 4.32 (s, 2H), 2.22 - 2.14 (m, 2H), 1.71 - 1.63 (m, 2H), 1.47 - 1.26 (m, 14H), 0.91 (t, \(J=6.8\) Hz, 3H).\(^{13}\text{C} \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 155.88, 136.44, 130.05, 128.69, 127.99, 122.64, 80.73, 31.93, 29.63, 29.49, 29.35, 27.94, 27.80, 22.71, 14.15. \text{HRMS m/z (ESI) [M + Na}^+\text{] caleed for C}_{19}\text{H}_{28}\text{N}_2 + \text{Na}^+: 307.2150. \text{found, 307.2145.}
\]

2-(amino(phenyl)methylene)-4-phenylbutanitrile (4g)

\[
\text{Ph} \quad \text{CN} \quad \text{Ph} \quad \text{NH}_2
\]

\(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.55 - 7.49 (m, 2H), 7.46 - 7.40 (m, 3H), 7.39 - 7.25 (m, 5H), 4.14 (s, 2H), 2.96 (t, \(J=7.6\) Hz, 2H), 2.48 (t, \(J=7.6\) Hz, 2H).\(^{13}\text{C} \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 156.85, 141.09, 136.40, 130.15, 128.70, 128.64, 128.62, 127.96, 126.39, 122.75, 79.36, 34.14, 30.43. \text{HRMS m/z (ESI) [M + Na}^+\text{] caleed for C}_{17}\text{H}_{16}\text{N}_2 + \text{Na}^+: 271.1211. \text{found, 271.1206.}
\]

3-amino-2,3-diphenylacrylonitrile (4h)

\[
\text{Ph} \quad \text{CH}_3 \quad \text{CN} \quad \text{Ph} \quad \text{NH}_2
\]

\(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.75 - 7.69 (m, 2H), 7.55 (ddd, \(J=5.2, 3.7, 1.8\) Hz, 2H), 7.53 - 7.44 (m, 5H), 7.36 - 7.30 (m, 1H), 4.92 (d, \(J=7.3\) Hz, 2H).\(^{13}\text{C} \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 156.97, 136.03, 133.99, 130.64, 129.45, 128.89, 128.68, 128.07, 127.52, 122.17, 81.96. \text{HRMS m/z (ESI) [M + Na}^+\text{] caleed for C}_{13}\text{H}_{12}\text{N}_2 + \text{Na}^+: 243.0898. \text{found, 243.0893.}
\]

3-amino-3-phenyl-2-(o-tolyl)acrylonitrile (4i)

\[
\text{Ph} \quad \text{CH}_3 \quad \text{CN} \quad \text{Ph} \quad \text{NH}_2
\]

\(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.79 - 7.73 (m, 2H), 7.54 - 7.49 (m, 3H), 7.43 - 7.39 (m, 1H), 7.36 - 7.29 (m, 3H), 4.41 (s, 2H), 2.45 (s, 3H).\(^{13}\text{C} \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 157.35, 138.18, 135.42, 131.94, 131.11, 130.78, 130.61, 128.88, 128.74, 128.02, 126.91, 121.46, 80.72, 19.50. \text{HRMS m/z (ESI) [M + Na}^+\text{] caleed for C}_{16}\text{H}_{14}\text{N}_2 + \text{Na}^+: 257.1054. \text{found, 257.1049.}
\]

3-amino-3-phenyl-2-(m-tolyl)acrylonitrile (4j)

\[
\text{Ph} \quad \text{CH}_3 \quad \text{CN} \quad \text{Ph} \quad \text{NH}_2
\]

\(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.75 - 7.67 (m, 2H), 7.54 - 7.46 (m, 3H), 7.40 - 7.33 (m, 3H), 7.14 (dd, \(J=5.6, 2.4\) Hz, 1H), 4.83 (s, 2H), 2.42 (s, 3H).\(^{13}\text{C} \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 156.91, 139.29, 136.09, 133.87, 130.57, 129.35, 129.28, 128.86, 128.30, 128.06, 125.55, 122.31, 81.94, 21.48.
3-amino-3-phenyl-2-(p-tolyl)acrylonitrile (4k)

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 – 7.68 (m, 2H), 7.53 – 7.47 (m, 3H), 7.44 (d, \(J = 8.1\) Hz, 2H), 7.28 (d, \(J = 8.7\) Hz, 2H), 4.78 (s, 2H), 2.41 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 156.68, 137.38, 136.10, 130.92, 130.54, 130.10, 128.85, 128.55, 128.06, 122.28, 81.90, 21.24.

HRMS m/z (ESI) [M + Na\(^{+}\)] calcd for C\(_{16}\)H\(_{14}\)N\(_{2}\) + Na\(^{+}\): 257.1054. found, 257.1049.

3-amino-2-(4-(4-tert-butylphenyl)-3-phenylacrylonitrile (4l)

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 – 7.68 (m, 2H), 7.52 – 7.46 (m, 7H), 4.82 (s, 2H), 1.37 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 156.72, 150.56, 136.14, 130.96, 130.53, 128.30, 128.08, 126.35, 125.09, 122.29, 81.83, 34.67, 31.30. HRMS m/z (ESI) [M + Na\(^{+}\)] calcd for C\(_{19}\)H\(_{20}\)N\(_{2}\) + Na\(^{+}\): 299.1524. found, 299.1520.

2-(1,1'-biphenyl)-4-yl)-3-amino-3-phenylacrylonitrile (4m)

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 – 7.68 (m, 4H), 7.68 – 7.62 (m, 4H), 7.55 – 7.47 (m, 5H), 7.44 – 7.40 (m, 1H), 4.90 (s, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.05, 140.37, 140.24, 136.05, 133.02, 130.70, 128.97, 128.92, 128.10, 128.07, 127.59, 127.03, 122.12, 81.70.

3-amino-2-(4-methoxyphenyl)-3-phenylacrylonitrile (4n)

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.79 – 7.66 (m, 2H), 7.56 – 7.42 (m, 5H), 7.04 – 6.93 (m, 2H), 4.71 (s, 2H), 3.86 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.88, 156.51, 136.04, 130.51, 130.10, 128.85, 128.04, 125.96, 122.30, 114.84, 81.65, 55.39. HRMS m/z (ESI) [M + Na\(^{+}\)] calcd for C\(_{16}\)H\(_{14}\)N\(_{2}\)O + Na\(^{+}\): 273.1004. found, 273.0098.
3-amino-2-(4-fluorophenyl)-3-phenylacrylonitrile (4o)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 – 7.68 (m, 2H), 7.57 – 7.47 (m, 5H), 7.23 – 7.10 (m, 2H), 4.75 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.62, 157.12, 135.76, 130.75, 130.72, 130.64, 129.80, 128.94, 8.01, 121.96, 116.60, 116.39, 81.01. HRMS m/z (ESI) [M + Na$^+$] calcd for C$_{13}$H$_{11}$FN$_2$ + Na$^+$: 261.0804. found, 261.0800.

3-amino-2-(4-chlorophenyl)-3-phenylacrylonitrile (4p)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 – 7.67 (m, 2H), 7.58 – 7.47 (m, 5H), 7.46 – 7.41 (m, 2H), 4.82 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.29, 135.75, 133.21, 132.47, 130.83, 130.03, 129.65, 128.96, 128.02, 121.74, 80.97. HRMS m/z (ESI) [M + Na$^+$] calcd for C$_{13}$H$_{11}$ClN$_2$ + Na$^+$: 277.0508. found, 277.0503.

3-amino-2-(4-bromophenyl)-3-phenylacrylonitrile (4q)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 – 7.67 (m, 2H), 7.63 – 7.57 (m, 2H), 7.56 – 7.48 (m, 3H), 7.48 – 7.41 (m, 2H), 4.82 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.25, 135.75, 132.98, 132.61, 130.85, 130.32, 128.97, 128.01, 121.26, 81.06.

3-amino-2-(2-methoxyphenyl)-3-phenylacrylonitrile (4r)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 – 7.73 (m, 2H), 7.52 – 7.45 (m, 4H), 7.37 (td, $J$ = 8.3, 1.7 Hz, 1H), 7.07 (dd, $J$ = 7.5, 1.0 Hz, 1H), 7.03 (dd, $J$ = 6.3, 4.7 Hz, 1H), 4.58 (s, 2H), 3.93 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.53, 157.06, 136.05, 131.53, 130.40, 129.72, 128.74, 128.21, 122.08, 121.90, 121.37, 112.13, 78.34, 55.94.

3-amino-2-(naphthalen-2-yl)-3-phenylacrylonitrile (4s)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (s, 1H), 7.95 (d, $J$ = 8.5 Hz, 1H), 7.87 (dd, $J$ = 9.4, 5.2 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.68 (dd, $J$ = 8.5, 1.8 Hz, 1H), 7.59 – 7.50 (m, 5H), 5.00 (d, $J$ = 68.7 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.18, 136.04, 133.74, 132.46, 131.40, 130.73, 129.27, 128.95, 128.11, 127.82, 127.78, 127.62, 126.67, 126.42, 126.32, 122.16, 82.14.
**2-(amino(phenyl)methylene)hexanedinitrile (4t)**

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 8.42 - 8.23 \text{ (m, 2H), 7.53 - 7.38 \text{ (m, 3H), 4.92 (s, 2H), 3.00 (t, J = 7.8 Hz, 2H), 2.74 (dd, J = 9.3, 5.5 Hz, 2H), 2.16 (qd, J = 7.7, 4.9 Hz, 2H).} \]

\[ \text{^13C NMR (101 MHz, CDCl}_3\text{) } \delta 173.20, 163.77, 159.54, 138.56, 129.78, 128.31, 128.01, 113.99, 34.30, 26.76, 21.60.} \]

HRMS m/z (ESI) [M + H\(^+\)] calcd for C\(_{13}\)H\(_{13}\)N\(_3\) + H\(^+\): 212.1188. found, 212.1182.

**3-amino-2-(3,5-dimethylphenyl)-3-phenylacrylonitrile (4u)**

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.74 - 7.67 \text{ (m, 2H), 7.54 - 7.46 \text{ (m, 3H), 7.18 (s, 2H), 6.96 (s, 1H), 4.82 (s, 2H), 2.37 (s, 6H).} \]

\[ \text{^13C NMR (101 MHz, CDCl}_3\text{) } \delta 156.75, 139.08, 136.16, 133.75, 130.52, 129.22, 128.86, 128.05, 126.28, 122.33, 82.12, 21.35.} \]

**3-amino-2-benzyl-3-(m-tolyl)acrylonitrile (4aa)**

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.41 \text{ (d, J = 2.4 Hz, 2H), 7.37 \text{ (t, J = 5.0 Hz, 4H), 7.35 - 7.31 \text{ (m, 1H), 7.29 (dd, J = 7.4, 6.1 Hz, 2H), 4.38 (s, 2H), 3.62 (s, 2H), 2.42 (s, 3H).} \]

\[ \text{^13C NMR (101 MHz, CDCl}_3\text{) } \delta 157.61, 138.54, 137.72, 136.01, 131.07, 128.92, 128.67, 128.00, 126.93, 125.12, 123.33, 78.10, 34.58, 21.40.} \]

HRMS m/z (ESI) [M + Na\(^+\)] calcd for C\(_{17}\)H\(_{16}\)N\(_2\) + Na\(^+\): 271.1211. found, 271.1206.

**3-amino-2-benzyl-3-(p-tolyl)acrylonitrile (4ab)**

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.52 \text{ (d, J = 8.1 Hz, 2H), 7.37 \text{ (t, J = 4.4 Hz, 4H), 7.29 (ddd, J = 12.8, 9.8, 6.0 Hz, 3H), 4.37 (s, 2H), 3.62 (s, 2H), 2.41 (s, 3H).} \]

\[ \text{^13C NMR (101 MHz, CDCl}_3\text{) } \delta 157.49, 140.57, 137.76, 133.14, 129.43, 128.91, 128.01, 127.88, 126.92, 123.51, 77.93, 34.61, 21.42.} \]

HRMS m/z (ESI) [M + Na\(^+\)] calcd for C\(_{17}\)H\(_{16}\)N\(_2\) + Na\(^+\): 271.1211. found, 271.1206.

**3-amino-2-benzyl-3-(4-(tert-butyl)phenyl)acrylonitrile (4ac)**

- 14 -
1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.54 (m, 2H), 7.50 – 7.45 (m, 2H), 7.37 (d, $J = 4.4$ Hz, 4H), 7.32 – 7.26 (m, 1H), 4.42 (d, $J = 35.2$ Hz, 2H), 3.63 (s, 2H), 1.36 (s, 9H). $\delta$ NMR (101 MHz, CDCl$_3$) $\delta$ 157.43, 153.63, 137.78, 133.06, 128.90, 128.00, 127.73, 126.91, 125.71, 123.60, 77.76, 34.86, 34.67, 31.23. HRMS m/z (ESI) [M + Na$^+$] calcd for C$_{20}$H$_{22}$N$_2$ + Na$: 313.1680$. found, 313.1675.

3-amino-2-benzyl-3-(4-methoxyphenyl)acrylonitrile (4ad)

1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 – 7.52 (m, 2H), 7.40 – 7.33 (m, 4H), 7.33 – 7.25 (m, 1H), 7.01 – 6.88 (m, 2H), 4.35 (s, 2H), 3.85 (s, 3H), 3.61 (s, 2H). $\delta$ C NMR (101 MHz, CDCl$_3$) $\delta$ 161.12, 157.18, 137.84, 129.48, 128.91, 128.21, 127.99, 126.91, 123.70, 114.08, 77.56, 55.40, 34.65. HRMS m/z (ESI) [M + Na$^+$] calcd for C$_{17}$H$_{16}$ON + Na$: 287.1160$. found, 287.1155.

3-amino-2-benzyl-3-(4-chlorophenyl)acrylonitrile (4ae)

1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 8.4$ Hz, 2H), 7.41 (dd, $J = 7.8, 4.7$ Hz, 2H), 7.36 (q, $J = 6.8$ Hz, 4H), 7.33 – 7.26 (m, 1H), 4.41 (s, 2H), 3.59 (s, 2H). $\delta$ C NMR (101 MHz, CDCl$_3$) $\delta$ 156.17, 137.43, 136.34, 134.38, 129.46, 129.05, 128.97, 128.00, 127.05, 122.98, 78.91, 34.49. HRMS m/z (ESI) [M + Na$^+$] calcd for C$_{16}$H$_{13}$ClN$_2$ + Na$: 291.0665$. found, 291.0659.

3-amino-2-benzyl-3-(4-bromophenyl)acrylonitrile (4af)

1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (dd, $J = 8.7, 2.1$ Hz, 2H), 7.47 (dd, $J = 8.7, 2.2$ Hz, 2H), 7.41 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 4.41 (s, 2H), 3.59 (s, 2H). $\delta$ C NMR (101 MHz, CDCl$_3$) $\delta$ 156.18, 137.40, 134.85, 132.02, 129.68, 128.97, 128.01, 127.06, 124.64, 122.94, 78.94, 34.49. HRMS m/z (ESI) [M + Na$^+$] calcd for C$_{18}$H$_{13}$BrN$_2$ + Na$: 335.0159$. found, 335.0154.

3-amino-2-benzyl-3-(pyridin-3-yl)acrylonitrile (4ag)

1H NMR (400 MHz, DMSO) $\delta$ 8.70 (d, $J = 1.8$ Hz, 1H), 8.65 (dd, $J = 4.8, 1.6$ Hz, 1H), 7.96 – 7.89 (m, 1H), 7.49 (dd, $J = 7.9, 4.9$ Hz, 1H), 7.40 – 7.30 (m, 4H), 7.24 (pd, $J = 5.5, 2.7$ Hz, 1H), 6.82 (s, 2H), 3.57 (s, 2H). $\delta$ C NMR (101 MHz, DMSO) $\delta$ 160.74, 155.59, 153.90, 144.59, 141.30, 138.03, 133.62, 133.45, 131.46, 128.63, 128.53, 81.42, 37.87.
4. The Characterization of MePhSO$_2$-SPhMe

Figure S1. The structure of MePhSO$_2$-SPhMe (Refcode: BILCOO)
5. $^1$H NMR and $^{13}$C NMR of Products

![H NMR and 13C NMR of Products](image)

**Product (3a)**

- **H NMR**
  - A (s) 3.32
  - B (s) 3.85
  - C (d) 7.25
  - D (dd) 7.31
  - E (t) 7.39
  - F (m) 7.47

- **C NMR**
  - A (s) 162.1
  - B (s) 162.2
  - C (s) 127.01
  - D (s) 127.86
  - E (s) 128.11
  - F (s) 128.31

- **Product (3b)**

  - H (s) 129.21
  - I (s) 137.78
  - J (s) 138.17
  - K (s) 138.17
  - L (s) 138.17

- **C NMR**
  - M (s) 162.27
  - O (s) 165.21
  - P (s) 163.28
  - Q (s) 163.28

- **Product (3c)**

  - H (s) 129.21
  - I (s) 137.78
  - J (s) 138.17
  - K (s) 138.17
  - L (s) 138.17

- **C NMR**
  - M (s) 162.27
  - O (s) 165.21
  - P (s) 163.28
  - Q (s) 163.28
\[
\text{N} = \text{N} \quad \text{Ph} (3r)
\]
(3ab)
(3ac)
\[
\text{Ph} \quad \text{CN} \quad \text{NH}_2(4d)
\]
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**13C NMR Data:**

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**1H NMR Data:**

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**Formula:**

\[
\text{Me} \quad \text{Ph} \quad \text{CN} \quad \text{NH}_2 \quad (4j)
\]

**Diagram:**

Aromatic ring with labeled peaks and chemical shifts.
$\text{Me-CN}$

$\text{Ph-CN}$

(4k)

\[ \begin{align*}
\text{C} & : 156.68 \\
\text{L} & : 156.68 \\
\text{I} & : 136.96 \\
\text{F} & : 128.85 \\
\text{J} & : 128.06 \\
\text{G} & : 122.23 \\
\text{K} & : 137.33 \\
\text{H} & : 139.97 \\
\text{B} & : 81.90 \\
\text{A} & : 21.24 \\
\end{align*} \]