Supporting Information

for

Diels–Alder cycloadditions of \(N\)-arylpyrroles via arylene intermediates using diaryliodonium salts

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Experimental procedures and characterization data of all products, copies of \(^1\)H, \(^{13}\)C, \(^{19}\)F NMR and HRMS spectra of all compounds
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Part 1. General Information

a. Methods:

$^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded in CDCl$_3$ or DMSO-$d_6$ (with tetramethylsilane as an internal standard) on a Bruker AVANCE 400 spectrometer, operating at 400 MHz, 100 MHz, and 376 MHz respectively. Chemical shifts (δ) are reported in ppm, and coupling constants ($J$) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; High resolution mass spectrometry (HRMS) was performed on an ESI–TOF spectrometer; reactions were monitored by TLC (detection with UV light); Column chromatography was performed with silica gel (200–300 mesh ASTM).

b. Materials:

All solvents were dried and/or distilled by standard methods. All reagents were purchased from commercial sources and used without further purification. The diaryliodonium salts were synthesized according to the literature procedures$^{[1-3]}$. 1-Phenyl-$^1$H-pyrrole, tert-butyl 1$^H$-pyrrole-1-carboxylate, 1-tosyl-$^1$H-pyrrole, and 1-methyl-$^1$H-pyrrole were commercially available and were used as received. The preparation of all other materials is described in detail below.
Part 2. Synthesis and characterization of \( N \)-substituted pyrroles.

General procedure 1: Synthesis of \( N \)-aryl pyrroles.\(^4\)

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{H} \\
\text{R} \\
\text{Cu(OAc)}_2 \cdot \text{H}_2 \text{O (1 mol\%)} \\
\text{Cs}_2 \text{CO}_3, \text{DMF, 110 °C} \\
\end{array}
\]

An oven-dried Schlenk tube was charged with \( \text{Cu(OAc)}_2 \cdot \text{H}_2 \text{O} \) (0.1 mmol, 0.01 equiv), \( \text{Cs}_2 \text{CO}_3 \) (20 mmol, 2 equiv), and aryl iodide (if solid, 12 mmol, 1.2 equiv). The tube was degassed with argon for three times. Then DMF (20 mL), pyrrole (10 mmol, 1 equiv), and aryl iodide (if liquid, 12 mmol, 1.2 equiv) were added via syringe under room temperature. The mixture was stirred at 110 °C for 24 h, and then cooled down to room temperature. The reaction mixture was quenched with water (40 mL) and extracted with ethyl ether (20 mL) for three times. The combined organic layers were dried with \( \text{Na}_2 \text{SO}_4 \), filtered and concentrated. The crude products were purified using flash column chromatography on silica gel to afford the desired product.

1-(\( p \)-Tolyl)\( \text{H} \)-pyrrole (1b)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 75\% (1.18 g) as a white solid. Spectral data is consistent with that of previous reported.\(^5\)

\(^1\text{H NMR (400 MHz, CDCl}_3\)) \( \delta \) 7.34 – 7.29 (m, 2H), 7.26 (t, \( J = 9.1 \text{ Hz, 2H}) \), 7.09 (t, \( J = 2.2 \text{ Hz, 2H}) \), 6.37 (t, \( J = 2.2 \text{ Hz, 2H}) \), 2.41 (s, 3H).

\(^{13}\text{C NMR (100 MHz, CDCl}_3\)) \( \delta \) 138.5, 135.4, 130.1, 120.6, 119.4, 110.1, 20.9.

1-(4-(\text{tert-Butyl})phenyl)\( \text{H} \)-pyrrole (1c)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 79\% (1.58 g) as a white solid. Spectral data is consistent with that of previous reported.\(^6\)

\(^1\text{H NMR (400 MHz, CDCl}_3\)) \( \delta \) 7.48 (d, \( J = 8.6 \text{ Hz, 2H}) \), 7.37 (d, \( J = 8.6 \text{ Hz, 2H}) \), 7.12 (t, \( J = 2.0 \text{ Hz, 2H}) \), 1.56 (q, \( J = 7.3 \text{ Hz, 2H}) \), 1.22 (s, 9H).
Hz, 2H), 6.38 (t, \( J = 2.0 \) Hz, 2H), 1.40 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 148.7, 138.4, 126.4, 120.3, 119.4, 110.1, 34.5, 31.4.

1-(4-Methoxyphenyl)-1H-pyrrole (1d)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 63% (1.09 g) as a white solid. Spectral data is consistent with that of previous reported.\(^5\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.27 – 7.20 (m, 2H), 6.92 (t, \( J = 2.2 \) Hz, 2H), 6.90 – 6.83 (m, 2H), 6.25 (t, \( J = 2.2 \) Hz, 2H), 3.76 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 157.7, 134.5, 122.2, 119.7, 114.6, 109.9, 55.6.

1-(4-Fluorophenyl)-1H-pyrrole (1e)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 83% (1.33 g) as a white solid. Spectral data is consistent with that of previous reported.\(^7\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.46 – 7.30 (m, 2H), 7.23 – 7.09 (m, 2H), 7.05 (t, \( J = 2.2 \) Hz, 2H), 6.38 (t, \( J = 2.2 \) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 160.6 (d, \( J_{C,F} = 243.4 \) Hz), 137.16, 122.3 (d, \( J_{C,F} = 8.1 \) Hz), 119.64, 116.3 (d, \( J_{C,F} = 22.7 \) Hz), 110.47.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -117.10 (s, 1F).

1-(4-Chlorophenyl)-1H-pyrrole (1f)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 87% (1.54 g) as a colorless solid. Spectral data is consistent with that of previous reported.\(^5\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.42 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 7.04 (t, \( J = 2.2 \) Hz, 2H), 6.35 (t, \( J = 2.2 \) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 139.3, 131.0, 129.6, 121.6, 119.3, 110.8.
1-(4-Bromophenyl)-1H-pyrrole (1g)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 83% (1.85 g) as a white solid. Spectral data is consistent with that of previous reported.\[8\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 – 7.48 (m, 2H), 7.32 – 7.20 (m, 2H), 7.04 (t, $J = 2.2$ Hz, 2H), 6.35 (t, $J = 2.2$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.8, 132.6, 122.0, 119.2, 118.7, 110.9.

1-(4-(Trifluoromethyl)phenyl)-1H-pyrrole (1h)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 95% (2.00 g) as a white solid. Spectral data is consistent with that of previous reported.\[9\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.17 (t, $J = 2.2$ Hz, 2H), 6.43 (t, $J = 2.2$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.2, 127.4 (q, $J_{C,F} = 32.7$ Hz), 126.9 (q, $J_{C,F} = 3.7$ Hz), 124.0 (q, $J_{C,F}$ = 270.1 Hz), 120.0, 119.1, 111.5.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.20 (s, 3F).

1-(4-(Trifluoromethoxy)phenyl)-1H-pyrrole (1i)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 95% (2.15 g) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.32 (m, 2H), 7.27 (d, $J = 8.6$ Hz, 2H), 7.05 (t, $J = 2.1$ Hz, 2H), 6.36 (t, $J = 2.1$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.7, 139.4, 122.3, 121.6, 120.5 (q, $J_{C,F} = 255.7$ Hz), 119.2, 110.9.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -58.10 (s, 3F).
4-(1H-Pyrrol-1-yl)benzonitrile (1j)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 89% (1.50 g) as a white solid. Spectral data is consistent with that of previous reported.[7]

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 – 7.61 (m, 2H), 7.57 – 7.37 (m, 2H), 7.13 (t, $J = 2.2$ Hz, 2H), 6.40 (t, $J = 2.2$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.7, 133.8, 120.0, 118.9, 118.5, 112.2, 108.6.

1-([1,1'-Biphenyl]-4-yl)-1H-pyrrole (1k)

Prepared according to the general procedure 1 on 10.0 mmol scale and obtained an isolated yield of 82% (1.79 g) as a white solid. Spectral data is consistent with that of previous reported.[5]

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 – 7.59 (m, 4H), 7.51 (m, 4H), 7.46 – 7.36 (m, 1H), 7.19 (t, $J = 2.2$ Hz, 2H), 6.44 (t, $J = 2.2$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.2, 140.0, 138.6, 128.9, 128.2, 127.4, 127.0, 120.7, 119.3, 110.6.
Part 3. Synthesis and characterization of products from cycloaddition reactions.

General procedure 2: Synthesis of Diels–Alder reaction products.
To an oven-dried Schlenk tube was added iodonium salts (0.5 mmol, 1 equiv) and substituted pyrrole (if solid, 2.5 mmol, 5 equiv). The tube was degassed with argon for three times. Then the tube was placed in an ice bath. Toluene (4.25 mL) and substituted pyrrole (if liquid, 2.5 mmol, 5 equiv) were added sequentially via syringe. After being stirred for approximately 10 minutes, LiHMDS (0.75 mL (1 M in toluene), 0.75 mmol, 1.5 equiv) was added via syringe and the mixture was allowed to warm up to room temperature gradually. After TLC indicated that the iodonium salts were completely consumed, the reaction mixture was quenched by addition of an aqueous solution of ammonium chloride (5 mL) and extracted with DCM (10 mL) for three times. The combined organic layers were dried with Na$_2$SO$_4$, filtered and concentrated. The crude products were purified using flash column chromatography on silica gel to afford the desired product.

9-Phenyl-1,4-dihydro-1,4-epiminonaphthalene (3aa)

![Chemical Structure]

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 85% (93 mg) as a pale brown solid. Spectral data is consistent with that of previous reported.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 (m, 2H), 7.17 (m, 2H), 6.97 – 6.88 (m, 4H), 6.87 – 6.78 (m, 3H), 5.43 (t, $J$ = 1.4 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.6, 146.9, 141.9, 128.8, 124.9, 121.5, 120.8, 118.0, 69.3.

HRMS (ESI) calculated for C$_{16}$H$_{14}$N [M+H]$^+$ 220.1126, found 220.1127.

6-Methyl-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3ab)

![Chemical Structure]

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 63% (74 mg) as a pale brown oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.08 (ddd, $J$ = 13.6, 6.2, 4.8 Hz, 1H), 7.01 (s, 1H), 6.90 – 6.80 (m, 2H), 6.79 – 6.68 (m, 3H), 6.64 (dd, $J$ = 7.2, 0.5 Hz, 1H), 5.36 – 5.24 (m, 2H), 2.16 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.8, 147.0, 145.6, 142.2, 141.7, 134.6, 128.8, 125.0, 122.9, 121.2, 120.8, 118.0, 69.3, 69.0, 21.3.

HRMS (ESI) calculated for C$_{17}$H$_{16}$N [M+H]$^+$ 234.1283, found 234.1276.
6-(tert-Butyl)-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3ac)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 57% (78 mg) as a pale yellow oil.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.27 (d, \(J = 1.5\) Hz, 1H), 7.10 (m, 3H), 6.86 (dd, \(J = 7.5, 1.7\) Hz, 1H), 6.80 (m, 2H), 6.78 – 6.73 (m, 3H), 5.33 (m, 2H), 1.19 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.5, 148.1, 147.0, 145.4, 141.6, 141.4, 128.8, 121.2, 120.8, 120.6, 119.1, 118.1, 69.6, 69.2, 34.7, 31.6.

HRMS (ESI) calculated for C\(_{20}\)H\(_{22}\)N \([M+H]^+\) 276.1752, found 276.1749.

6-Fluoro-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3ad)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 77% (92 mg) as a pale yellow oil.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.13 – 7.03 (m, 3H), 6.92 (dd, \(J = 7.8, 2.3\) Hz, 1H), 6.90 – 6.81 (m, 2H), 6.80 – 6.68 (m, 3H), 6.50 (ddd, \(J = 10.0, 7.8, 2.3\) Hz, 1H), 5.38 – 5.24 (m, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.5 (d, \(J_{CF} = 242.9\) Hz), 151.4 (d, \(J_{CF} = 9.0\) Hz), 146.63, 143.8 (d, \(J_{CF} = 3.0\) Hz), 142.45, 141.44, 128.91, 121.9 (d, \(J_{CF} = 9.0\) Hz), 121.07, 117.95, 110.7 (d, \(J_{CF} = 25.0\) Hz), 110.4 (d, \(J_{CF} = 22.0\) Hz), 69.3 (d, \(J_{CF} = 3.0\) Hz), 68.78.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -117.76 (s, 1F).

HRMS (ESI) calculated for C\(_{16}\)H\(_{13}\)NF \([M+H]^+\) 238.1032, found 238.1038.

6-Chloro-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3ae)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 87% (110 mg) as a pale brown oil.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.15 (m, 1H), 7.12 – 7.04 (m, 3H), 6.88 – 6.79 (m, 3H), 6.79 – 6.74 (m, 1H), 6.72 (m, 2H), 5.31 (m, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.9, 147.1, 146.5, 142.2, 141.6, 130.6, 128.9, 124.6, 122.5, 122.3, 121.1, 117.9, 69.1, 68.8.

HRMS (ESI) calculated for C\(_{16}\)H\(_{13}\)NCl \([M+H]^+\) 254.0737, found 254.0730.
6-Bromo-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3af)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 96% (143 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 1.6$ Hz, 1H), 7.13 – 7.06 (m, 2H), 7.03 (d, $J = 7.5$ Hz, 1H), 6.98 (dd, $J = 7.5$, 1.7 Hz, 1H), 6.90 – 6.81 (m, 2H), 6.80 – 6.74 (m, 1H), 6.74 – 6.69 (m, 2H), 5.35 – 5.24 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.2, 147.7, 146.4, 142.2, 141.7, 128.9, 127.6, 125.2, 122.8, 121.1, 118.6, 117.9, 69.1, 68.9.

HRMS (ESI) calculated for C$_{16}$H$_{13}$NBr [M+H]$^+$ 298.0231, found 298.0231.

9-Phenyl-1,4-dihydro-1,4-epiminophthalene-6-carbonitrile (3ag)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 71% (87 mg) as a white solid.

m.p.: 187-188 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (s, 1H), 7.26 (m, 1H), 7.22 (m, 1H), 7.15 – 7.06 (m, 2H), 6.94 – 6.85 (m, 2H), 6.79 (t, $J = 7.4$ Hz, 1H), 6.72 (dd, $J = 8.6$, 0.9 Hz, 2H), 5.54 – 5.10 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.2, 150.0, 145.9, 142.1, 141.5, 130.8, 129.0, 124.1, 122.0, 121.5, 119.3, 117.8, 108.6, 69.2, 68.8.

HRMS (ESI) calculated for C$_{17}$H$_{13}$N$_2$ [M+H]$^+$ 245.1079, found 245.1070.

6-Nitro-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3ah)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 70% (92 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 1.9$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.17 – 7.04 (m, 2H), 6.93 (d, $J = 2.4$ Hz, 1H), 6.89 (d, $J = 2.4$ Hz, 1H), 6.78 (t, $J = 7.4$ Hz, 1H), 6.72 (m, 2H), 5.43 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.2, 150.8, 145.9, 145.7, 142.5, 141.4, 129.1, 122.3, 121.5, 121.4, 117.8, 116.5, 69.0, 69.0.

HRMS (ESI) calculated for C$_{16}$H$_{14}$NO$_2$ [M-H]$^-$ 263.0821, found 263.0825.
9-Phenyl-6- (trifluoromethyl)-1,4-dihydro-1,4-epiminonaphthalene (3ai)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 77% (110 mg) as a pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (s, 1H), 7.24 (d, $J = 7.4$ Hz, 1H), 7.18 – 7.13 (m, 1H), 7.10 (t, $J = 7.9$ Hz, 2H), 6.90 – 6.81 (m, 2H), 6.81 – 6.69 (m, 3H), 5.39 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.8, 149.8, 146.3, 142.0, 141.6, 129.0, 127.3 (q, $J_{C,F} = 31.7$ Hz), 124.3 (q, $J_{C,F} = 270.5$ Hz), 122.9 (q, $J_{C,F} = 4.0$ Hz), 121.3, 121.2, 118.1 (q, $J_{C,F} = 4.0$ Hz), 117.9, 69.1.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -61.84 (s, 3F).

HRMS (ESI) calculated for C$_{17}$H$_{13}$NF$_3$ [M+H]$^+$ 288.1000, found 288.1003.

9-Phenyl-6- (trifluoromethoxy)-1,4-dihydro-1,4-epiminonaphthalene (3aj)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 88% (134 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.14 – 7.07 (m, 3H), 7.05 (s, 1H), 6.87 – 6.80 (m, 2H), 6.80 – 6.75 (m, 1H), 6.75 – 6.66 (m, 3H), 5.34 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.2, 147.2, 146.5, 146.4, 142.0, 141.6, 129.0, 121.7, 121.2, 120.5 (q, $J_{C,F} = 255.1$ Hz), 118.0, 117.1, 115.6, 69.3, 69.0.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.88 (s, 3F).

HRMS (ESI) calculated for C$_{17}$H$_{13}$NOF$_3$ [M+H]$^+$ 304.0949, found 304.0944.

6,9-Diphenyl-1,4-dihydro-1,4-epiminonaphthalene (3ak)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 89% (131 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (m, 3H), 7.30 (m, 2H), 7.20 (m, 2H), 7.14 – 7.01 (m, 3H), 6.91 – 6.81 (m, 2H), 6.75 (m, 3H), 5.42 – 5.31 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.5, 147.6, 146.9, 141.9, 141.8, 141.4, 138.4, 128.9, 128.7, 127.2, 127.1, 124.0, 121.6, 121.0, 120.8, 118.1, 69.4, 69.2.

HRMS (ESI) calculated for C$_{22}$H$_{18}$N [M+H]$^+$ 296.1439, found 296.1432.
5,9-Diphenyl-1,4-dihydro-1,4-epiminonaphthalene (3a)

Prepared according to the **general procedure 2** on 0.5 mmol scale and obtained an isolated yield of 82% (121 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.35 (m, 2H), 7.35 – 7.27 (m, 3H), 7.17 (dd, $J = 5.4, 2.6$ Hz, 1H), 7.08 – 7.00 (m, 2H), 6.96 (dd, $J = 5.4, 2.2$ Hz, 1H), 6.95 – 6.88 (m, 3H), 6.76 – 6.69 (m, 1H), 6.66 (dd, $J = 8.6, 1.0$ Hz, 2H), 5.46 (m, 1H), 5.42 – 5.37 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.7, 146.8, 146.4, 142.2, 141.6, 140.0, 135.9, 128.8, 128.3, 127.4, 125.2, 120.9, 118.0, 69.6, 68.4.

HRMS (ESI) calculated for C$_{22}$H$_{18}$N $[M+H]^+$ 296.1439, found 296.1436.

3-Chloro-9-phenyl-5,8-dihydro-5,8-epiminoisoquinoline (3am)

Prepared according to the **general procedure 2** on 0.5 mmol scale and obtained an isolated yield of 80% (102 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (s, 1H), 7.14 (s, 1H), 7.14 – 7.08 (m, 2H), 6.91 (m, 1H), 6.85 – 6.76 (m, 2H), 6.70 (m, 2H), 5.40 (m, 1H), 5.34 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.1, 148.4, 145.6, 143.2, 142.7, 140.5, 140.1, 129.1, 121.7, 118.6, 117.7, 68.6, 66.7.

HRMS (ESI) calculated for C$_{15}$H$_{10}$N$_2$Cl [M-H]$^-$ 253.0533, found 253.0536.

9-Phenyl-1,4-dihydro-1,4-epiminonaphthalene-5-carbonitrile (3an)

Prepared according to the **general procedure 2** on 0.5 mmol scale and obtained an isolated yield of 71% (86 mg) as a pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, $J = 7.1$ Hz, 1H), 7.15 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 6.96 – 6.86 (m, 3H), 6.83 – 6.75 (m, 1H), 6.75 – 6.70 (m, 2H), 5.60 (m, 1H), 5.41 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.3, 150.3, 145.8, 142.8, 141.2, 129.1, 127.0, 126.0, 125.2, 121.5,
117.8, 117.2, 106.3, 69.5, 68.3.

HRMS (ESI) calculated for C_{17}H_{13}N_{2} [M+H]^+ 245.1079, found 245.1070.

5-Fluoro-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3ao)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 78% (92 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 – 7.03 (m, 2H), 6.95 (d, $J = 7.0$ Hz, 1H), 6.90 – 6.86 (m, 2H), 6.82 – 6.76 (m, 1H), 6.76 – 6.70 (m, 3H), 6.54 (td, $J = 8.4$, 0.6 Hz, 1H), 5.60 (m, 1H), 5.35 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.4 (d, $J_{C,F} = 244.3$ Hz), 152.3 (d, $J_{C,F} = 4.6$ Hz), 146.5, 142.3, 141.6, 133.0 (d, $J_{C,F} = 20.5$ Hz), 129.0, 127.3 (d, $J_{C,F} = 6.0$ Hz), 121.2, 117.9, 117.7 (d, $J_{C,F} = 2.6$ Hz), 113.6 (d, $J_{C,F} = 22.1$ Hz), 69.6, 65.7.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -121.42 (s, 1F).

HRMS (ESI) calculated for C_{16}H_{13}NF [M+H]^+ 238.1032, found 238.1026.

5-Methyl-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3ap)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 60% (70 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.08 (m, 2H), 7.00 (d, $J = 6.8$ Hz, 1H), 6.84 (s, 2H), 6.74 (m, 4H), 6.65 (d, $J = 7.7$ Hz, 1H), 5.44 (m, 1H), 5.33 (m, 1H), 2.26 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.2, 147.1, 146.9, 142.0, 141.4, 130.8, 128.8, 126.6, 124.9, 120.8, 119.0, 118.0, 110.5, 69.7, 67.4, 18.2.

HRMS (ESI) calculated for C_{16}H_{16}N [M+H]^+ 234.1283, found 234.1281.

5,7-Difluoro-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3aq)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 48% (62 mg) as a yellow oil.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.13 – 7.06 (m, 2H), 6.90 (qdd, $J = 5.5$, 2.4, 0.4 Hz, 2H), 6.80 – 6.74 (m, 2H), 6.73 – 6.69 (m, 2H), 6.29 (ddd, $J = 9.6$, 8.2, 1.9 Hz, 1H), 5.62 – 5.49 (m, 1H), 5.38 – 5.25 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.0 (dd, $J_{C,F} = 246.9$, 9.2 Hz), 156.4 (dd, $J_{C,F} = 246.2$, 12.7 Hz), 153.9 (dd, $J_{C,F} = 9.4$, 6.0 Hz), 146.2, 142.1, 141.8, 129.0, 128.6 (dd, $J_{C,F} = 21.1$, 3.2 Hz), 121.4, 117.8, 107.3 (dd, $J_{C,F} = 25.0$, 4.0 Hz), 100.6 (t, $J_{C,F} = 26.2$ Hz), 69.7, 65.4 (d, $J_{C,F} = 1.4$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -113.42 (d, $J = 5.6$ Hz, 1F), -117.91 (d, $J = 5.6$ Hz, 1F).

HRMS (ESI) calculated for C$_{16}$H$_{12}$NF$_2$ [M+H]$^+$ 256.0938, found 256.0947.

5,6-Dimethyl-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3ar)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 62% (76 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 (m, 2H), 6.99 (d, $J = 7.1$ Hz, 1H), 6.95 – 6.87 (m, 2H), 6.85 – 6.76 (m, 3H), 6.69 (d, $J = 7.1$ Hz, 1H), 5.52 (m, 1H), 5.37 (m, 1H), 2.25 (s, 3H), 2.15 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.2, 145.6, 142.3, 141.3, 133.6, 130.2, 128.8, 125.6, 120.7, 118.0, 69.6, 67.1, 21.2, 18.1.

HRMS (ESI) calculated for C$_{18}$H$_{18}$N [M+H]$^+$ 248.1439, found 248.1448.

5,7-Dimethyl-9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (3as)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 58% (72 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 – 7.12 (m, 2H), 6.94 – 6.89 (m, 3H), 6.84 – 6.77 (m, 3H), 6.54 (s, 1H), 5.47 (m, 1H), 5.36 (m, 1H), 2.29 (s, 3H), 2.20 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.5, 147.2, 143.9, 141.8, 141.7, 134.5, 130.5, 128.8, 126.8, 120.7, 120.4, 118.0, 69.6, 67.1, 21.2, 18.1.

HRMS (ESI) calculated for C$_{18}$H$_{18}$N [M+H]$^+$ 248.1439, found 248.1442.
9-(p-Tolyl)-1,4-dihydro-1,4-epiminonaphthalene (3ba)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 81% (94 mg) as a pale brown solid.

m.p.: 123-125°C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.25 (m, 2H), 7.02 (d, $J = 8.2$ Hz, 2H), 6.99 – 6.93 (m, 4H), 6.78 (d, $J = 8.4$ Hz, 2H), 5.43 (t, $J = 1.3$ Hz, 2H), 2.25 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.6, 144.6, 141.8, 130.1, 129.4, 124.9, 121.5, 118.1, 69.5, 20.6.

HRMS (ESI) calculated for C$_{17}$H$_{16}$N $[\text{M+H}]^+$ 234.1283, found 234.1281.

9-(4-(tert-Butyl)phenyl)-1,4-dihydro-1,4-epiminonaphthalene (3ca)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 83% (114 mg) as a white solid.

m.p.: 107-109°C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.28 (m, 2H), 7.24 – 7.22 (m, 1H), 7.22 – 7.19 (m, 1H), 6.97 (dd, $J = 5.1$, 3.0 Hz, 2H), 6.95 (t, $J = 1.4$ Hz, 2H), 6.82 – 6.80 (m, 1H), 6.79 – 6.77 (m, 1H), 5.44 (t, $J = 1.3$ Hz, 2H), 1.28 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.8, 144.3, 143.4, 141.8, 125.6, 124.8, 121.4, 117.7, 69.5, 34.0, 31.4.

HRMS (ESI) calculated for C$_{20}$H$_{22}$N $[\text{M+H}]^+$ 276.1752, found 276.1745.

9-(4-Methoxyphenyl)-1,4-dihydro-1,4-epiminonaphthalene (3da)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 62% (77 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (dd, $J = 5.1$, 3.0 Hz, 2H), 6.86 – 6.80 (m, 4H), 6.70 – 6.62 (m, 4H), 5.24 (t, $J = 1.4$ Hz, 2H), 3.61 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.1, 148.6, 141.7, 140.7, 124.9, 121.5, 119.4, 114.2, 69.9, 55.4.

HRMS (ESI) calculated for C$_{17}$H$_{16}$NO $[\text{M+H}]^+$ 250.1232, found 250.1233.
9-(4-Fluorophenyl)-1,4-dihydro-1,4-epiminonaphthalene (3ea)

\[
\begin{align*}
\text{F} & \\
\text{N} & \\
\text{N} & \\
\text{F} & \\
\end{align*}
\]

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 82% (97 mg) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 – 7.10 (m, 2H), 6.87 – 6.82 (m, 4H), 6.78 (t, \(J = 8.7\) Hz, 2H), 6.73 – 6.61 (m, 2H), 5.26 (t, \(J = 1.4\) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.7 (d, \(J_{C,F} = 237.7\) Hz), 148.3, 143.3 (d, \(J_{C,F} = 2.4\) Hz), 141.8, 125.0, 121.6, 119.2 (d, \(J_{C,F} = 7.6\) Hz), 115.4 (d, \(J_{C,F} = 22.1\) Hz), 69.8.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -123.68 (s, 1F).

HRMS (ESI) calculated for C\(_{16}\)H\(_{13}\)NF [M+H]\(^+\) 238.1032, found 238.1042.

9-(4-Chlorophenyl)-1,4-dihydro-1,4-epiminonaphthalene (3fa)

\[
\begin{align*}
\text{Cl} & \\
\text{N} & \\
\text{N} & \\
\end{align*}
\]

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 81% (103 mg) as a yellow solid.

m.p.: 139–141 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.21 – 7.14 (m, 2H), 7.06 – 7.04 (m, 1H), 7.03 – 7.01 (m, 1H), 6.90 – 6.81 (m, 4H), 6.70 – 6.66 (m, 1H), 6.66 – 6.64 (m, 1H), 5.29 (t, \(J = 1.4\) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.2, 145.6, 141.9, 128.8, 125.9, 125.1, 121.6, 119.2, 69.4.

HRMS (ESI) calculated for C\(_{16}\)H\(_{13}\)NCl [M+H]\(^+\) 254.0737, found 254.0739.

9-(4-Bromophenyl)-1,4-dihydro-1,4-epiminonaphthalene (3ga)

\[
\begin{align*}
\text{Br} & \\
\text{N} & \\
\text{N} & \\
\end{align*}
\]

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 71% (106 mg) as a yellow solid.

m.p.: 147–148 °C.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.06 (m, 4H), 6.98 – 6.77 (m, 4H), 6.64 – 6.61 (m, 1H), 6.61 – 6.59 (m, 1H), 5.29 (t, $J = 1.4$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.2, 146.1, 141.9, 131.7, 125.1, 121.6, 119.6, 113.3, 69.3.

HRMS (ESI) calculated for C$_{16}$H$_{13}$NBr [M+H]$^+$ 298.0231, found 298.0223.

9-(4-(Trifluoromethyl)phenyl)-1,4-dihydro-1,4-epiminonaphthalene (3ha)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 90% (129 mg) as a pale yellow solid.

m.p.: 97-99°C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, $J = 8.5$ Hz, 2H), 7.20 (dd, $J = 5.1$, 3.0 Hz, 2H), 6.93 – 6.84 (m, 4H), 6.79 (d, $J = 8.4$ Hz, 2H), 5.40 (t, $J = 1.4$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.7, 148.0, 142.0, 126.2 (q, $J_{C,F} = 3.7$ Hz), 125.2, 124.5 (q, $J_{C,F} = 269.4$ Hz), 122.4 (q, $J_{C,F} = 32.4$ Hz), 121.6, 117.2, 68.9.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -61.57 (s, 3F).

HRMS (ESI) calculated for C$_{17}$H$_{13}$NF$_3$ [M+H]$^+$ 288.1000, found 288.0992.

9-(4-(Trifluoromethoxy)phenyl)-1,4-dihydro-1,4-epiminonaphthalene (3ia)

Prepared according to the general procedure 2 on 0.5 mmol scale and obtained an isolated yield of 83% (126 mg) as a pale yellow solid.

m.p.: 74-76°C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.21 (m, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 6.98 – 6.90 (m, 4H), 6.81 – 6.79 (m, 1H), 6.79 – 6.75 (m, 1H), 5.38 (t, $J = 1.3$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.20, 145.71, 143.02, 141.86, 125.09, 121.83, 121.67, 121.56, 119.28, 118.69, 69.45.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.2, 145.7, 143.0, 141.9, 125.1, 121.7, 121.6, 120.6 (q, $J_{C,F} = 254.4$ Hz), 118.7, 69.4.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -58.16 (s, 3F).

HRMS (ESI) calculated for C$_{17}$H$_{13}$NOF$_3$ [M+H]$^+$ 304.0949, found 304.0950.
4-(1,4-Dihydro-1,4-epiminonaphthalen-9-yl)benzonitrile (3ja)

Prepared according to the **general procedure 2** on 0.5 mmol scale and obtained an isolated yield of 93\% (114 mg) as a white solid.
m.p.: 191-193 °C.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 – 7.42 (m, 1H), 7.42 – 7.39 (m, 1H), 7.31 – 7.22 (m, 2H), 6.98 (t, \(J = 1.5\) Hz, 2H), 6.94 (dd, \(J = 5.1,\) 3.0 Hz, 2H), 6.86 – 6.82 (m, 1H), 6.82 – 6.79 (m, 1H), 5.49 (t, \(J = 1.4\) Hz, 2H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.4, 147.8, 142.1, 133.2, 125.3, 121.6, 119.6, 117.3, 103.0, 68.5.
HRMS (ESI) calculated for C\(_{17}\)H\(_{13}\)N\(_2\) [M+H]\(^+\) 245.1079, found 245.1080.

9-([1,1'-Biphenyl]-4-yl)-1,4-dihydro-1,4-epiminonaphthalene (3ka)

Prepared according to the **general procedure 2** on 0.5 mmol scale and obtained an isolated yield of 40\% (59 mg) as a pale brown solid.
m.p.: 146-148 °C.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53 – 7.46 (m, 2H), 7.41 (dd, \(J = 8.6,\) 1.9 Hz, 2H), 7.35 (m, 2H), 7.29 – 7.25 (m, 2H), 7.25 – 7.21 (m, 1H), 6.98 – 6.91 (m, 4H), 6.88 (dd, \(J = 8.6,\) 1.6 Hz, 2H), 5.45 (m, 2H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.6, 146.3, 142.0, 140.8, 133.6, 128.7, 127.5, 126.6, 125.0, 121.5, 118.3, 69.3.
HRMS (ESI) calculated for C\(_{22}\)H\(_{18}\)N [M+H]\(^+\) 296.1439, found 296.1440.
Part 4. Synthesis and characterization of products from isomerization reaction.

**General procedure 3: Synthesis of N-phenylamine derivatives.**

To an oven-dried Schlenk tube was added 9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (0.5 mmol, 1 equiv) and TsOH·H₂O (0.1 mmol, 0.2 equiv). The tube was degassed with argon for three times. Then DCE (4 mL) was added via syringe under room temperature. The mixture was stirred at 80 °C until TLC indicated that the starting materials were completely consumed. Then the reaction mixture was cooled down to room temperature and it was quenched with water (20 mL) and extracted with ethyl ether (10 mL) for three times. The combined organic layers were dried with Na₂SO₄, filtered and concentrated. The crude products were purified using flash column chromatography on silica gel to afford the desired product.

**N-Phenynaphthalen-1-amine (4)**

![N-Phenynaphthalen-1-amine](image)

Prepared according to the **general procedure 3** on 0.5 mmol scale and obtained an isolated yield of 93% (102 mg) as a light gray solid. Spectral data is consistent with that of previous reported.¹⁰⁰

¹H NMR (400 MHz, DMSO) δ 8.30 – 8.08 (m, 2H), 7.89 (m, 1H), 7.59 – 7.44 (m, 3H), 7.40 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.9 Hz, 2H), 7.13 – 6.99 (m, 2H), 6.82 (t, J = 7.3 Hz, 1H).

¹³C NMR (100 MHz, DMSO) δ 145.0, 139.4, 134.4, 129.0, 127.0, 126.1, 126.0, 125.0, 122.8, 121.4, 119.5, 117.0, 114.1.

**3-Chloro-N-phenylisoquinolin-5-amine (5)**

![3-Chloro-N-phenylisoquinolin-5-amine](image)

Prepared according to the **general procedure 3** on 0.5 mmol scale and obtained an isolated yield of 75% (96 mg) as a yellow solid.

m.p.: 157-159 °C.

¹H NMR (400 MHz, DMSO) δ 9.16 (s, 1H), 8.45 (s, 1H), 8.25 (s, 1H), 7.67 (m, 1H), 7.60 – 7.50 (m, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.23 – 7.13 (m, 2H), 6.95 (t, J = 7.3 Hz, 1H).

¹³C NMR (100 MHz, DMSO) δ 153.1, 144.0, 143.1, 138.7, 130.4, 129.2, 128.4, 128.3, 121.1, 119.3, 118.5, 115.5, 115.0.

HRMS (ESI) calculated for C₁₅H₁₂N₂Cl [M+H]⁺ 255.0689, found 255.0692.
Part 5. Synthesis and characterization of products from hydrogenation reaction.

General procedure 4: Synthesis of hydrogenation products.
To a stirred solution of 9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (0.5 mmol) in EtOH (20 mL) was carefully added wet Pd/C catalyst (0.05 mmol) under argon atmosphere. The tube was degassed with hydrogen for three times. The mixture was stirred at room temperature until TLC indicated that the starting materials were completely consumed. Then the solid was filtered off and the filtrate was concentrated in vacuo. The crude products were purified using flash column chromatography on silica gel to afford the desired product.

9-Phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene (6)

Prepared according to the general procedure 4 on 0.5 mmol scale and obtained an isolated yield of 63% (70 mg) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.19 (m, 2H), 7.19 – 7.05 (m, 4H), 6.94 – 6.81 (m, 2H), 6.81 – 6.70 (m, 1H), 5.06 (dd, $J = 2.5$, 1.8 Hz, 2H), 2.26 – 2.08 (m, 2H), 1.37 – 1.29 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.4, 145.0, 129.0, 126.4, 120.1, 120.1, 117.2, 63.7, 26.0.

HRMS (ESI) calculated for C$_{16}$H$_{16}$N [M+H]$^+$ 222.1283, found 222.1277.
Part 6. References

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Part 7. Copies of $^1$H, $^{13}$C, $^{19}$F NMR and HRMS (ESI) spectra
S27
S52
A: $^1$H NMR spectrum of the product recorded at 400 MHz in DMSO-$d_6$ at 298K; B: $^1$H NMR spectrum of the product recorded at 400 MHz in DMSO-$d_6$ (major) / D$_2$O (minor) at 298 K.
$^1$H–$^1$H NOSY spectrum of the product recorded at 400 MHz in DMSO-d$_6$ at 298 K
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotop peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
18 formulas evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.44  H: 0.57  N: 0.3

ECUST Institute of Fine Chem

Minimum:  50.0  50.0  105.0
Maximum:  50.0  50.0  105.0

Mass  Calc. Mass  mDe  PPM  DBE  i-FIT  i-FIT (Norm) Formula
234.1276  234.1283  -0.7  -0.5  10.5  55.5  0.0  C17 H16 N
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM  /  DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 30.0  H: 0.0  N: 0.1  F: 0.0

C80 H80 N20

29-Jun-2017
Wang

Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM  /  DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.0  H: 0.13  N: 0.1  F: 0.1

C8 H8 N2 F

30-Jun-2017
Wang
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-16  H: 0-100  N: 0-1  Cl: 0-1
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WL-CH2-112 44 (0.628) Cmp (42.45)

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|------|------------|-----|-----|-----|-------|--------------|---------|
| 254.0730 | 254.0737 | -0.7 | -2.8 | 10.5 | 28.8 | 0.0 | C16 H13 N Cl |

Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-19  H: 0-57  N: 0-1  Br: 0-1
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WL-CH3-111 02 (1.922) Cmp (59.60)

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|------|------------|-----|-----|-----|-------|--------------|---------|
| 291.0291 | 299.0291 | 0.0 | 0.0 | 10.5 | 24.1 | 0.0 | C16 H13 N Br |
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron ions
6 formulae(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-17  H: 0-100  N: 0-2
LM-WANG
ECUST institute of Fine Chem
WL-CHO:114 15 (0.26) Cm (10.16)

Minimum: 35.0 50.0 100.0
Maximum: 35.0 50.0 100.0

Mass  Calcd. Mass  m/z  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
265.0825  265.0821  0.4  1.5  12.8  17.8  0.0  C16  H11  N2  O2

Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron ions
13 formulae(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-16  H: 0-50  N: 0-2  O: 0-2
LM-WANG
ECUST institute of Fine Chem
WL-CHO:115 11 (0.312) Cm (10.11)

Minimum: 35.0 50.0 100.0
Maximum: 35.0 50.0 100.0

Mass  Calcd. Mass  m/z  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
265.0825  265.0821  0.4  1.5  12.8  17.8  0.0  C16  H11  N2  O2

S73
Elemental Composition Report

**Single Mass Analysis**

Tolerance = 50.0 PPM / DBE: min = -15, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-17  H: 0-100  N: 0-1  F: 0-3

MW-1CH1=1-7 170 (0.457) cm (20.30)

| Mass | Calc. Mass | m/z | PPm | DBE | i-FIT | i-FIT (Norm) | Formula |
|------|------------|-----|-----|-----|-------|--------------|---------|
| 288.1003 | 288.1003 | 0.3 | 1.0 | 10.6 | 311.5 | 0.0 | C17 H13 N F3 |

Elemental Composition Report

**Single Mass Analysis**

Tolerance = 50.0 PPM / DBE: min = -15, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-17  H: 0-100  N: 0-1  O: 0-1  F: 0-3

MW-1CH2=1-2 14 (0149) cm (2-4)

| Mass | Calc. Mass | m/z | PPm | DBE | i-FIT | i-FIT (Norm) | Formula |
|------|------------|-----|-----|-----|-------|--------------|---------|
| 304.0944 | 304.0944 | -0.5 | -1.6 | 10.5 | 54.7 | 0.0 | C17 H13 N O F3 |
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for 1-FIT = 3

Monoisotopic Mass, Even Electron Ions
5 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.22  H: 0-100  N: 0-1

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Minimum:  35.0  50.0  100.0
Maximum:  35.0  50.0  100.0

Mass  Calc. Mass  mDa  PPM  DBE  1-FIT  1-FIT (Norm)  Formula
296.1436  296.1459  -0.7  -2.4  14.5  18.0  0.0  C22 H18 N

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## Elemental Composition Report

### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Even Electron Ions**

1 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

- **C**: 0-17
- **H**: 0-13
- **N**: 0-2

**Formula**: C15H10N2Cl

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### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Even Electron Ions**

1 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

- **C**: 0-17
- **H**: 0-13
- **N**: 0-2

**Formula**: C17H13N2
**Elemental Composition Report**

**Single Mass Analysis**

Tolerance = 30.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: ON

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:
C: 0.18  H: 0.23  N: 0.1

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WL-CH3127 (0.251) Cm (4.6)

Minimum:

| Mass | Calc. Mass | mDa | PPM | DBE | 1-FIT | 1-FIT (Norm) | Formula |
|------|------------|-----|-----|-----|-------|-------------|---------|
| 248.1442 | 248.1439 | 0.3 | 1.2 | 10.5 | 52.3 | 0.0 | C18 H18 N |

Minimum:

| Mass | Calc. Mass | mDa | PPM | DBE | 1-FIT | 1-FIT (Norm) | Formula |
|------|------------|-----|-----|-----|-------|-------------|---------|
| 234.1281 | 234.1283 | -0.2 | -0.9 | 10.5 | 30.9 | 0.0 | C17 H16 N |

05-JUL-2017
1: TOF MS ESI+
4.55e-005
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-20  H: 0-25  N: 0-2

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Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-17  H: 0-20  N: 0-1  O: 0-1

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Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-16  H: 0-20  N: 0-1  Cl: 0-1

MW: 363.37  C: 21.5  H: 3.9  Cl: 1.5

Minimum: 258.1052  Maximum: 258.1052

Mass  Calcd. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
258.1052  258.1052  1.0  4.2  10.5  32.8  0.0  C16 H13 N F

Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-10  H: 0-35  N: 0-1  Cl: 0-1

MW: 263.35  C: 14.1  H: 4.4  Cl: 1.0

Minimum: 254.0775  Maximum: 254.0775

Mass  Calcd. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
254.0775  254.0775  0.1  0.8  10.5  29.9  0.0  C16 H13 N Cl

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Elemental Composition Report

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.16 H: 0.36 N: 0.1 Br: 0.1

LM WANG
ECUST Institute of Fine Chem

W. CHG-165.23 (0.376) Cm (23.25)

Minimum: 298.0223
Maximum: 302.3025
Calc. Mass: 300.0000
Ppm: 0.0
DBE: 1-FIT: 1-FIT (Norm) Formula

C16 H13 N Br

Elemental Composition Report

Single Mass Analysis

Tolerance = 30.0 PPM / DBE: min = -1.6, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.17 H: 0.15 N: 0.1 F: 0.3

LM WANG
ECUST Institute of Fine Chem

W. CHG-165.13 (0.496) Cm (13.15)

Minimum: 290.0982
Maximum: 299.0982
Calc. Mass: 296.0000
Ppm: 0.0
DBE: 1-FIT: 1-FIT (Norm) Formula

C17 H13 N F3
Elemental Composition Report

Single Mass Analysis
- Tolerance = 30.0 PPM / DBE: min = -1.6, max = 100.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|------|------------|-----|-----|-----|-------|--------------|---------|
| 304.0880 | 304.0849 | 0.1 | 0.8 | 10.5 | 82.4 | 0.0 | C17 H13 N 0 F3 |

Elemental Composition Report

Single Mass Analysis
- Tolerance = 30.0 PPM / DBE: min = -1.5, max = 100.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|------|------------|-----|-----|-----|-------|--------------|---------|
| 245.1080 | 245.1079 | 0.1 | 0.4 | 12.5 | 197.9 | 0.0 | C17 H13 N2 |
Elemental Composition Report

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.6, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 3 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C 0.27  H 0.81  N 0.2

ECUST Institute of Fine Chem
WL-CHG-468 10 (0.227) Cm (10:12)

Minimum:
Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
296.1440  296.1639  0.1  0.3  14.5  15.9  0.0  C12 H18 N

Elemental Composition Report

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.6, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
79 formul(a) evaluated with 3 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C 0.38  H 0.92  N 0.4  Cl 0.4

ECUST Institute of Fine Chem
WL-CHG-182 182 (2.440) Cm (106:194)

Minimum:
Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
255.0692  255.0499  0.3  1.1  10.5  22.6  0.0  C16 H12 N2 Cl1
Elemental Composition Report

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for 1-FIT = 3

Monoisotopic Mass. Even Electron ion
10 formulas) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.38  H: 0.82  N: 0.4

Elemental Composition:

Mass  Calcd. Mass  nDa  PPM  DBE  1-FIT  1-FIT (Norm)  Formula
222.1277  222.1283  -0.6  -2.7  9.5  24.4  0.0  C16  H16  N