Supporting Information

Generation and Application of Carbodiimide Anion: Efficient Construction for 2-aminopyrimidines via a Cascade [4+2] Annulation/Aromatization Sequence

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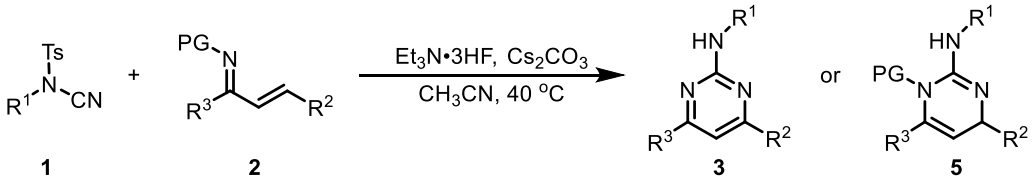
1. General Information

All reactions were performed in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. NMR spectra were recorded on a Bruker AM400 (400 MHz) spectrometer or Agilent DD2 (600 MHz) spectrometer. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ (δ 0.00) standard for ^{1}H NMR and chloroform-*d* (δ 77.16) or DMSO-d_6 (δ 39.52) for ^{13}C NMR. Data for ^{1}H NMR are recorded as follows: chemical shift (δ ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz) and integration. Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (HRMS) were recorded on a Thermo Q-Exactive Spectrometer (ESI source). Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Flash column chromatography was performed using silica gel (300-400 mesh). CCDC-2282332 (**3ea**), CCDC-2282334 (*trans*-**5as**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

N-Ts Cyanamides **1**[1] and 1-azadienes **2**[2] were synthesized employing literature procedures.

2. General Procedures and Characterization Data of the Products

2.1 General Procedures for the Reaction Between N-Ts Cyanamides 1 and 1-Azadienes 2



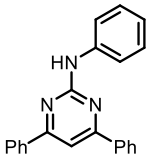
1 **2** **3** **5**

In a 10 mL test tube was sequentially added N-Ts cyanamides **1** (0.30 mmol, 1.5 equiv.), linear 1-azadienes **2** (0.20 mmol, 1.0 equiv.), Cs_2CO_3 (0.20 mmol, 1.0 equiv.),

$Et_3N·3HF$ (0.133 mmol, 0.67 equiv.) and MeCN (2.0 mL) under air atmosphere. The tube was sealed and stirred at 40 ℃. After the complete consumption of linear 1-azadienes **2**, the reaction mixture was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography (ethyl acetate/hexane) on silica gel to afford the pure products **3** or **5**. Compounds **3aa**[3], **3ba**[4], **3ca**[5] and **3af**[6] are known.

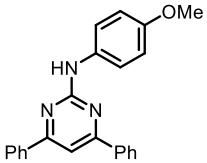
2.3 Characterization Data of Products

N,4,6-triphenylpyrimidin-2-amine (3aa)



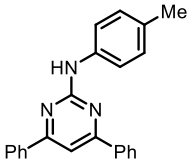
White solid (63 mg, 98% yield), purified by ethyl acetate:hexane = 1:40. m. p. 129-130 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.10 (m, 4H), 7.76 (d, J = 7.6 Hz, 2H), 7.56 (s, 1H), 7.53-7.49 (m, 6H), 7.40-7.34 (m, 3H), 7.04 (d, J = 7.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 160.6, 140.1, 137.7, 130.8, 129.00, 128.95, 127.3, 122.2, 119.1, 104.8 ppm; IR (KBr): v 3420, 3406, 2832, 1596, 1575, 1532, 1497, 1459, 1433, 1351, 1312, 1211, 1177, 1070, 1028, 988, 925, 760, 690, 604 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{18}N_3$ 324.1495, Found 324.1502.

N-(4-methoxyphenyl)-4,6-diphenylpyrimidin-2-amine (3ba)



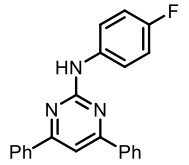
Yellow solid (58 mg, 82% yield), purified by ethyl acetate:hexane = 1:30. m. p. 117-119 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12-8.10 (m, 4H), 7.66 (d, J = 9.0 Hz, 2H), 7.54 (s, 1H), 7.52-7.48 (m, 6H), 7.24-7.23 (m, 1H), 6.93 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 160.8, 155.3, 137.9, 133.4, 130.7, 128.9, 127.3, 121.1, 114.3, 104.4, 55.7 ppm; IR (KBr): v 3421, 1589, 1572, 1533, 1507, 1458, 1440, 1415, 1354, 1244, 1181, 833, 759, 687, 576 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}N_3O$ 354.1601, Found 354.1610.

4,6-diphenyl-N-(p-tolyl)pyrimidin-2-amine (3ca)



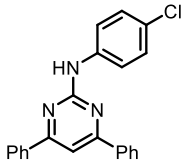
Yellow solid (56 mg, 83% yield), purified by ethyl acetate:hexane = 1:40. m. p. 136-138 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.11 (m, 4H), 7.66 (d, J = 8.4 Hz, 2H), 7.56 (s, 1H), 7.54-7.50 (m, 6H), 7.29 (s, 1H), 7.18 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 160.7, 137.8, 137.5, 131.8, 130.7, 129.5, 129.0, 127.3, 119.4, 104.6, 20.9 ppm; IR (KBr): v 3403, 2098, 1590, 1574, 1530, 1493, 1455, 1440, 1408, 1351, 1244, 1207, 1083, 1029, 988, 814, 760, 685, 583 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}N_3$ 338.1652, Found 338.1660.

N-(4-fluorophenyl)-4,6-diphenylpyrimidin-2-amine (3da)



White solid (67 mg, 98% yield), purified by ethyl acetate:hexane = 1:30. m. p. 140-141 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12-8.10 (m, 4H), 7.71-7.68 (m, 2H), 7.58 (s, 1H), 7.53-7.49 (m, 6H), 7.35 (s, 1H), 7.06 (t, J = 8.4 Hz, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 160.6, 158.4 (d, J = 241.6 Hz), 137.7, 136.1 (d, J = 1.5 Hz), 130.8, 129.0, 127.3, 120.8 (d, J = 9.1 Hz), 115.5 (d, J = 22.7 Hz), 104.9 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -121.1 ppm; IR (KBr): v 3434, 1589, 1544, 1528, 1455, 1409, 1364, 1213, 1180, 1156, 832, 777, 760, 694, 535 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}FN_3$ 342.1401, Found 342.1410.

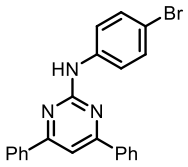
N-(4-chlorophenyl)-4,6-diphenylpyrimidin-2-amine (3ea)



White solid (59 mg, 83% yield), purified by ethyl acetate:hexane = 1:40. m. p. 167-168 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11-8.10 (m, 4H), 7.69 (d, J = 9.0 Hz, 2H), 7.59 (s, 1H), 7.53-7.50 (m, 6H), 7.39 (s, 1H), 7.30 (d, J = 9.0 Hz, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 160.4, 138.7, 137.6, 130.9, 129.0, 128.9, 127.3, 127.0, 120.3, 105.1 ppm; IR (KBr): v 3446, 3259, 2830, 1607, 1536, 1491, 1455,

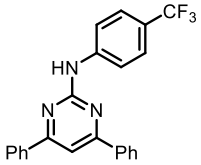
1405, 1356, 1247, 1089, 992, 826, 774, 759, 683 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}ClN_3$ 358.1106, Found 358.1112.

N-(4-bromophenyl)-4,6-diphenylpyrimidin-2-amine (3fa)



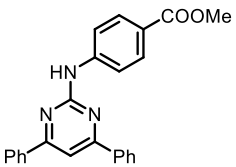
White solid (75 mg, 94% yield), purified by ethyl acetate:hexane = 1:40. m. p. 172-173 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.12-8.09 (m, 4H), 7.65 (d, J = 9.0 Hz, 2H), 7.59 (s, 1H), 7.54-7.50 (m, 6H), 7.45 (d, J = 8.4 Hz, 2H), 7.38 (s, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 160.3, 139.2, 137.6, 131.9, 130.9, 129.0, 127.3, 120.7, 114.4, 105.2 ppm; IR (KBr): ν 3181, 1610, 1534, 1489, 1456, 1438, 1402, 1355, 1248, 1090, 996, 830, 759, 683, 501 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}Br^{79}N_3$ 402.0600, Found 402.0602.

4,6-diphenyl-N-(4-(trifluoromethyl)phenyl)pyrimidin-2-amine (3ga)



White solid (57 mg, 73% yield), purified by ethyl acetate:hexane = 1:40. m. p. 167-168 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.13-8.11 (m, 4H), 7.87 (d, J = 9.0 Hz, 2H), 7.64 (s, 1H), 7.61-7.57 (m, 3H), 7.55-7.52 (m, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 160.1, 143.2, 137.4, 131.0, 129.1, 127.3, 126.3 (q, J = 3.0 Hz), 124.7 (q, J = 270.0 Hz), 123.7 (q, J = 33.2 Hz), 118.3, 105.7 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -61.6 ppm; IR (KBr): ν 3396, 1619, 1598, 1577, 1527, 1412, 1355, 1325, 1113, 1067, 762 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{17}F_3N_3$ 392.1369, Found 392.1378.

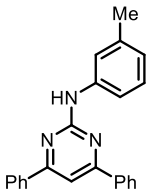
methyl 4-((4,6-diphenylpyrimidin-2-yl)amino)benzoate (3ha)



White solid (60 mg, 79% yield), purified by ethyl acetate:hexane = 1:20. m. p. 156-158 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.13-8.12 (m, 4H), 8.05 (d, J = 8.4 Hz,

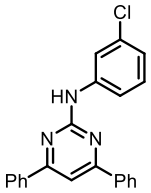
2H), 7.85 (d, *J* = 9.0 Hz, 2H), 7.66-7.62 (m, 2H), 7.53-7.52 (m, 6H), 3.90 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 166.0, 160.0, 144.5, 137.4, 131.0, 129.6, 129.1, 127.3, 123.2, 117.8, 105.6, 52.0 ppm; IR (KBr): *v* 3434, 3329, 2959, 2831, 2716, 1703, 1599, 1526, 1493, 1412, 1365, 1285, 1267, 1174, 1113, 989, 855, 775, 763, 690, 630 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{20}N_3O_2$ 382.1550, Found 382.1558.

4,6-diphenyl-N-(m-tolyl)pyrimidin-2-amine (3ia)



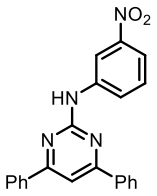
White solid (65 mg, 96% yield), purified by ethyl acetate:hexane = 1:40. m. p. 102-104 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.13 (m, 4H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.58 (s, 2H), 7.53-7.49 (m, 6H), 7.34 (s, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 160.6, 140.0, 138.7, 137.8, 130.8, 129.0, 128.9, 127.3, 123.1, 119.9, 116.3, 104.7, 21.8 ppm; IR (KBr): *v* 3384, 1598, 1587, 1572, 1533, 1497, 1444, 1362, 1347, 1096, 996, 830, 761, 688 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}N_3$ 338.1652, Found 338.1661.

N-(3-chlorophenyl)-4,6-diphenylpyrimidin-2-amine (3ja)



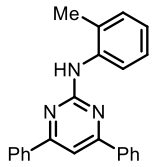
White solid (65 mg, 91% yield), purified by ethyl acetate:hexane = 1:40. m. p. 141-142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (m, 4H), 8.04 (t, *J* = 2.0 Hz, 1H), 7.62 (s, 2H), 7.56-7.50 (m, 7H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.03-7.01 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.9, 141.1, 137.2, 134.7, 131.1, 129.9, 129.1, 127.4, 122.2, 119.2, 117.1, 105.2 ppm; IR (KBr): *v* 3421, 3398, 3123, 2955, 2925, 1599, 1571, 1524, 1495, 1457, 1443, 1426, 1363, 1076, 761, 688, 627, 562 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}ClN_3$ 358.1106, Found 358.1115.

N-(3-nitrophenyl)-4,6-diphenylpyrimidin-2-amine (3ka)



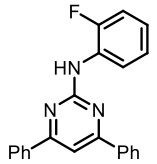
Yellow solid (73 mg, 99% yield), purified by ethyl acetate:hexane = 1:40. m. p. 137-138 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.17-8.15 (m, 4H), 7.85-7.83 (m, 1H), 7.80 (s, 1H), 7.67-7.65 (m, 2H), 7.55-7.51 (m, 6H), 7.41 (t, J = 8.4 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 160.0, 148.9, 141.3, 137.1, 131.2, 129.4, 129.1, 127.4, 124.0, 116.5, 113.6, 105.7 ppm; IR (KBr): v 3334, 1602, 1574, 1533, 1518, 1430, 1365, 1348, 1096, 996, 830, 761, 688 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}N_4O_2$ 369.1346, Found 369.1349.

4,6-diphenyl-N-(o-tolyl)pyrimidin-2-amine (3la)



White solid (55 mg, 82% yield), purified by ethyl acetate:hexane = 1:40. m. p. 102-103 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, J = 7.8 Hz, 1H), 8.12-8.11 (m, 4H), 7.56 (s, 1H), 7.52-7.48 (m, 6H), 7.31 (t, J = 7.8 Hz, 1H), 7.23-7.22 (m, 1H), 7.06-7.02 (m, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 161.0, 138.1, 137.8, 130.7, 130.5, 128.9, 127.7, 127.3, 126.7, 123.0, 121.1, 104.7, 18.4 ppm; IR (KBr): v 3443, 2831, 1602, 1528, 1496, 1480, 1464, 1445, 1402, 1366, 1350, 1311, 1180, 775, 753, 688, 628, 556 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}N_3$ 338.1652, Found 338.1663.

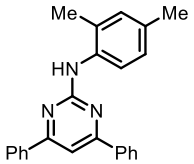
N-(2-fluorophenyl)-4,6-diphenylpyrimidin-2-amine (3ma)



White solid (68 mg, 99% yield), purified by ethyl acetate:hexane = 1:45. m. p. 125-126 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (t, J = 8.4 Hz, 1H), 8.14-8.12 (m, 4H), 7.61 (s, 1H), 7.54-7.50 (m, 7H), 7.21 (t, J = 7.8 Hz, 1H), 7.14-7.11 (m, 1H),

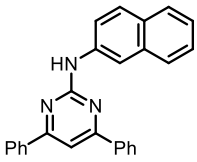
6.99-6.95 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 160.3, 152.5 (d, J = 241.6 Hz), 137.6, 130.9, 129.0, 128.7 (d, J = 9.1 Hz), 127.3, 124.4 (d, J = 3.0 Hz), 121.9 (d, J = 7.6 Hz), 120.5, 114.8 (d, J = 19.6 Hz), 105.3 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -131.8 ppm; IR (KBr): ν 3443, 1621, 1594, 1573, 1528, 1477, 1450, 1425, 1353, 1181, 780, 750, 688 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}FN_3$ 342.1401, Found 342.1410.

N-(2,4-dimethylphenyl)-4,6-diphenylpyrimidin-2-amine (3na)



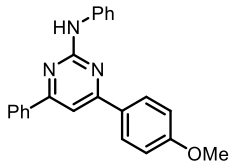
Yellow solid (48 mg, 68% yield), purified by ethyl acetate:hexane = 1:40. m. p. 116-117 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.10 (m, 5H), 7.55 (s, 1H), 7.52-7.47 (m, 6H), 7.11 (d, J = 7.8 Hz, 1H), 7.05 (s, 1H), 6.97 (s, 1H), 2.36 (s, 3H), 2,34 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 161.2, 137.9, 135.5, 132.7, 131.2, 130.7, 128.9, 128.3, 127.3, 127.1, 121.7, 104.4, 21.0, 18.3 ppm; IR (KBr): ν 3435, 1589, 1525, 1496, 1446, 1385, 1351, 1310, 1231, 1205, 1084, 988, 844, 758, 694, 627, 533 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{22}N_3$ 352.1808, Found 352.1816.

N-(naphthalen-2-yl)-4,6-diphenylpyrimidin-2-amine (3oa)



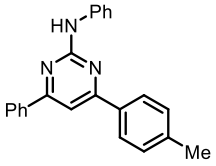
White solid (63 mg, 84% yield), purified by ethyl acetate:hexane = 1:40. m. p. 146-148 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, J = 1.8 Hz, 1H), 8.18-8.16 (m, 4H), 7.82-7.78 (m, 3H), 7.67 (dd, J = 9.0, 2.4 Hz, 1H), 7.62 (s, 1H), 7.55-7.50 (m, 7H), 7.46 (t, J = 7.8 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 160.6, 137.7, 137.6, 134.4, 130.8, 129.8, 129.0, 128.6, 127.7, 127.5, 127.4, 126.4, 124.2, 120.5, 114.8, 105.0 ppm; IR (KBr): ν 3401, 3130, 2831, 1605, 1590, 1528, 1491, 1471, 1456, 1399, 1357, 1251, 1084, 988, 854, 774, 759, 688, 569 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{20}N_3$ 374.1652, Found 374.1663.

4-(4-methoxyphenyl)-N,6-diphenylpyrimidin-2-amine (3ad)



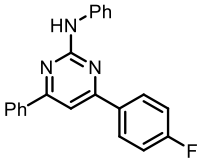
Yellow solid (49 mg, 69% yield), purified by ethyl acetate:hexane = 1:20. m. p. 146-147 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12-8.10 (m, 4H), 7.78 (d, J = 7.8 Hz, 2H), 7.52-7.48 (m, 4H), 7.37 (t, J = 7.8 Hz, 2H), 7.32 (s, 1H), 7.05-7.01 (m, 3H), 3.87 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 165.4, 161.9, 160.5, 140.2, 137.9, 130.6, 130.1, 129.0, 128.9, 128.8, 127.3, 122.2, 119.1, 114.3, 104.1, 55.5 ppm; IR (KBr): ν 3425, 3249, 3121, 1606, 1585, 1534, 1515, 1495, 1456, 1438, 1358, 1302, 1258, 1237, 1173, 1127, 1027, 990, 827, 772, 693, 582 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}N_3O$ 354.1601, Found 354.1612.

N,4-diphenyl-6-(p-tolyl)pyrimidin-2-amine (3ae)



White solid (53 mg, 79% yield), purified by ethyl acetate:hexane = 1:40. m. p. 119-120 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13-8.12 (m, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.56 (s, 1H), 7.53-7.49 (m, 3H), 7.38-7.31 (m, 5H), 7.04 (t, J = 8.4 Hz, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 165.8, 160.6, 141.1, 140.2, 137.9, 135.0, 130.7, 129.7, 129.0, 128.9, 127.3, 127.2, 122.2, 119.1, 104.6, 21.6 ppm; IR (KBr): ν 3415, 2832, 2717, 1715, 1597, 1536, 1497, 1434, 1364, 1222, 1084, 819, 775, 691, 531 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}N_3$ 338.1652, Found 338.1660.

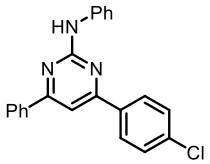
4-(4-fluorophenyl)-N,6-diphenylpyrimidin-2-amine (3af)



White solid (64 mg, 94% yield), purified by ethyl acetate:hexane = 1:40. m. p. 121-123 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.11 (m, 4H), 7.77 (d, J = 8.4 Hz, 2H), 7.53-7.51 (m, 4H), 7.38 (t, J = 7.8 Hz, 2H), 7.32 (d, J = 5.4 Hz, 1H), 7.19 (t, J = 8.4 Hz, 2H), 7.06 (t, J = 7.2 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1,

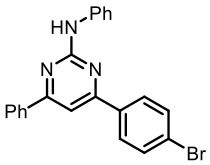
164.8, 164.6 (d, J = 250.7 Hz), 160.6, 140.0, 137.7, 133.9 (d, J = 3.0 Hz), 130.9, 129.3 (d, J = 9.1 Hz), 129.1, 129.0, 127.3, 122.4, 119.2, 116.0 (d, J = 21.1 Hz), 104.5 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.0 ppm; IR (KBr): v 3423, 2831, 1604, 1543, 1509, 1496, 1447, 1435, 1354, 1312, 1220, 1178, 1155, 1072, 1030, 1014, 990, 898, 831, 772, 760, 693, 570 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}FN_3$ 342.1401, Found 342.1413.

4-(4-chlorophenyl)-N,6-diphenylpyrimidin-2-amine (3ag)



White solid (59 mg, 83% yield), purified by ethyl acetate:hexane = 1:40. m. p. 150-152 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12-8.09 (m, 2H), 8.06 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.53-7.50 (m, 4H), 7.47 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 8.4 Hz, 2H), 7.32 (s, 1H), 7.06 (t, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 164.6, 160.6, 140.0, 137.6, 136.9, 136.2, 130.9, 129.2, 129.1, 129.0, 128.6, 127.3, 122.4, 119.2, 104.5 ppm; IR (KBr): v 3412, 3061, 2832, 1714, 1593, 1541, 1528, 1492, 1457, 1442, 1428, 1366, 1351, 1304. 1247, 1207, 1085, 1015, 989, 851, 827, 770, 759, 699, 690, 654, 560 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}ClN_3$ 358.1106, Found 358.1114.

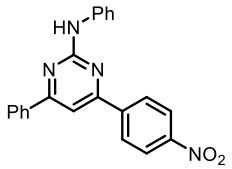
4-(4-bromophenyl)-N,6-diphenylpyrimidin-2-amine (3ah)



White solid (79 mg, 99% yield), purified by ethyl acetate:hexane = 1:40. m. p. 138-140 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12-8.10 (m, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 9.0 Hz, 2H), 7.53-7.51 (m, 4H), 7.38 (t, J = 7.8 Hz, 2H), 7.31 (s, 1H), 7.06 (t, J = 7.2 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 164.7, 160.6, 140.0, 137.6, 136.6, 132.2, 130.9, 129.1, 129.0, 128.8, 127.3, 125.3, 122.4, 119.2, 104.5 ppm; IR (KBr): v 3407, 3061, 2832, 1592, 1540, 1527, 1493, 1456, 1442, 1398, 1365, 1348, 1305, 1247, 1180, 1068, 1010, 988, 895, 824,

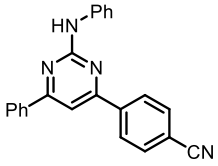
769, 728, 691, 561 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}Br^{79}N_3$ 402.0600, Found 402.0607.

4-(4-nitrophenyl)-N,6-diphenylpyrimidin-2-amine (3ai)



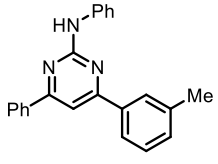
White solid (51 mg, 69% yield), purified by ethyl acetate:hexane = 1:9. m. p. 150-151 ^oC. ^1H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 9.0 Hz, 2H), 8.14-8.13 (m, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.61 (s, 1H), 7.55-7.54 (m, 3H), 7.40 (t, J = 7.8 Hz, 2H), 7.36 (s, 1H), 7.09 (t, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 163.4, 160.7, 149.3, 143.7, 139.7, 137.3, 131.2, 129.2, 129.1, 128.2, 127.4, 124.2, 122.8, 119.4, 105.3 ppm; IR (KBr): ν 3051, 2831, 1592, 1541, 1527, 1494, 1456, 1306, 1247, 1180, 1068, 1010, 988, 895, 824, 769, 728, 691, 561 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}N_4O_2$ 369.1346, Found 369.1354.

4-(6-phenyl-2-(phenylamino)pyrimidin-4-yl)benzonitrile (3aj)



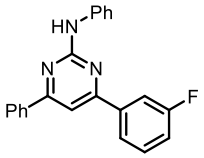
White solid (54 mg, 67% yield), purified by ethyl acetate:hexane = 1:7. m. p. 165-166 ^oC. ^1H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, J = 8.4 Hz, 2H), 8.13-8.12 (m, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 8.78 (s, 1H), 7.54-7.53 (m, 3H), 7.39 (t, J = 7.8 Hz, 2H), 7.34 (s, 1H), 7.09 (t, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 163.8, 160.7, 142.0, 139.7, 137.3, 132.8, 131.2, 129.13, 129.10, 127.9, 127.4, 122.8, 119.4, 118.7, 114.1, 105.1 ppm; IR (KBr): ν 3400, 3062, 2831, 1592, 1540, 1527, 1493, 1456, 1442, 1398, 1365, 1348, 1010, 988, 895, 824, 769, 728, 691, 561 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{17}N_4$ 349.1448, Found 349.1450.

N,4-diphenyl-6-(m-tolyl)pyrimidin-2-amine (3ak)



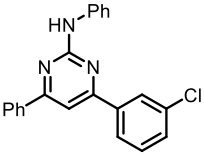
White solid (60 mg, 89% yield), purified by ethyl acetate:hexane = 1:40. m. p. 140-141 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.13 (m, 2H), 7.93-7.91 (m, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.57 (s, 1H), 7.53-7.48 (m, 3H), 7.41-7.31 (m, 5H), 7.05 (t, *J* = 7.2 Hz, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 165.8, 160.6, 140.2, 138.6, 137.8, 137.7, 131.5, 130.7, 129.02, 128.95, 128.88, 127.9, 127.3, 124.5, 122.2, 119.1, 104.9, 21.7 ppm; IR (KBr): *v* 3441, 3247, 2832, 1599, 1538, 1496, 1465, 1446, 1356, 1250, 1200, 1084, 835, 767, 723, 696, 657,631 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}N_3$ 338.1652, Found 338.1660.

4-(3-fluorophenyl)-N,6-diphenylpyrimidin-2-amine (3al)



White solid (62 mg, 91% yield), purified by ethyl acetate:hexane = 1:40. m. p. 126-128 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.86-7.84 (m, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.54-7.51 (m, 4H), 7.49-7.45 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.33 (s, 1H), 7.21-7.18 (m, 1H), 7.06 (t, *J* = 7.2 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 164.5 (d, *J* = 1.5 Hz), 163.4 (d, *J* = 247.6 Hz), 160.6, 140.1 (d, *J* = 7.6 Hz), 139.9, 137.5, 130.9, 130.5 (d, *J* = 7.6 Hz), 129.1, 129.0, 127.3, 122.9 (d, *J* = 1.5 Hz), 122.5, 119.2, 117.6 (d, *J* = 21.1 Hz), 114.3 (d, *J* = 22.7 Hz), 104.8 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.3 ppm; IR (KBr): *v* 3395, 2832, 1593, 1575, 1550, 1497, 1461, 1445, 1432, 1354, 1307, 1269, 1252, 1211, 1193, 1158, 1031, 976, 898, 872, 778, 769, 754, 672, 630, 580 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}FN_3$ 342.1401, Found 342.1410.

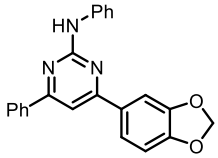
4-(3-chlorophenyl)-N,6-diphenylpyrimidin-2-amine (3am)



White solid (71 mg, 99% yield), purified by ethyl acetate:hexane = 1:40. m. p. 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (m, 3H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.54-7.51 (m, 4H), 7.49-7.34 (m, 5H), 7.07 (t, *J* = 7.2

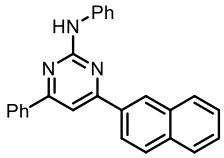
Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 164.5, 160.5, 139.9, 139.5, 137.5, 135.1, 131.0, 130.7, 130.2, 129.1, 129.0, 127.5, 127.4, 125.4, 122.5, 119.3, 104.8 ppm; IR (KBr): *v* 3390, 2831, 1598, 1547, 1497, 1457, 1444, 1433, 1363, 1352, 1302, 1268, 1294, 1185, 1119, 1068, 1031, 997, 895, 836, 799, 770, 757, 737, 672, 656, 585 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}ClN_3$ 358.1106, Found 358.1112.

4-(benzo[d][1,3]dioxol-5-yl)-N,6-diphenylpyrimidin-2-amine (3an)



White solid (59 mg, 80% yield), purified by ethyl acetate:hexane = 1:3. m. p. 118-119 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11-8.10 (m, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.68-7.65 (m, 2H), 7.52-7.47 (m, 4H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.32 (s, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.04 (s, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 165.2, 160.4, 150.0, 148.4, 140.1, 137.8, 132.0, 130.7, 129.0, 128.9, 127.3, 122.2, 121.9, 119.1, 108.6, 107.5, 104.2, 101.7 ppm; IR (KBr): *v* 3433, 2832, 2717, 1599, 1537, 1496, 1446, 1433, 1364, 1249, 1084, 1036, 933, 774, 697 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{18}N_3O_2$ 368.1394, Found 368.1401.

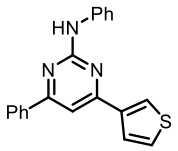
4-(naphthalen-2-yl)-N,6-diphenylpyrimidin-2-amine (3ao)



Yellow solid (46 mg, 62% yield), purified by ethyl acetate:hexane = 1:40. m. p. 131-133 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 6.0 Hz, 2H), 7.98-7.96 (m, 2H), 7.89-7.88 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.71 (s, 1H), 7.55-7.52 (m, 5H), 7.41-7.38 (m, 3H), 7.07 (t, *J* = 7.2 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 165.9, 160.7, 140.2, 137.9, 135.1, 134.7, 133.4, 130.8, 129.14, 129.07, 129.0, 128.7, 127.9, 127.5, 127.4 (3C), 126.7, 124.4, 122.3, 119.2, 105.1 ppm; IR (KBr): *v* 3404, 3055, 2832, 1660, 1593, 1571, 1532, 1495, 1470, 1455, 1435, 1385, 1364, 1326, 1245, 1212, 1193, 1134, 1074, 1014, 991, 965, 899, 867, 815, 774, 756, 718, 695, 669, 645 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for

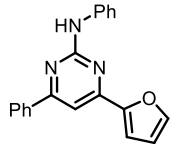
$C_{26}H_{20}N_3$ 374.1652, Found 374.1663.

N,4-diphenyl-6-(thiophen-3-yl)pyrimidin-2-amine (3ap)



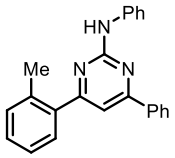
White solid (52 mg, 79% yield), purified by ethyl acetate:hexane = 1:40. m. p. 129-130 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09-8.08 (m, 2H), 7.80 (d, J = 3.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.52-7.48 (m, 4H), 7.44 (s, 1H), 7.36 (t, J = 7.8 Hz, 2H), 7.30 (s, 1H), 7.15-7.14 (m, 1H), 7.04 (t, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 160.4, 160.2, 143.4, 140.0, 137.6, 130.8, 129.5, 129.0, 128.9, 128.3, 127.3, 127.1, 122.3, 119.1, 103.0 ppm; IR (KBr): v 3381, 2832, 1593, 1575, 1531, 1519, 1494, 1458, 1444, 1426, 1354, 1338, 1243, 1210, 1179, 1072, 983, 888, 859, 833, 768, 759, 745, 718, 691, 631, 582 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{16}N_3S$ 330.1059, Found 330.1070.

4-(furan-2-yl)-N,6-diphenylpyrimidin-2-amine (3aq)



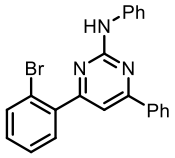
White solid (38 mg, 61% yield), purified by ethyl acetate:hexane = 1:45. m. p. 140-142 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.61 (s, 1H), 7.53-7.50 (m, 4H), 7.37 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 4.8 Hz, 1H), 7.26 (d, J = 3.6 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 6.59-6.58 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 160.3, 156.9, 152.5, 144.8, 140.1, 137.5, 130.9, 129.0, 128.9, 127.3, 122.3, 119.1, 112.5, 112.0, 102.7 ppm; IR (KBr): v 3405, 2925, 2832, 2716, 1599, 1538, 1497, 1482, 1445, 1433, 1365, 1342, 1251, 1166, 1072, 1011, 883, 823, 773, 755, 707, 692, 641 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{16}N_3O$ 314.1288, Found 314.1293.

N,4-diphenyl-6-(o-tolyl)pyrimidin-2-amine (3ar)



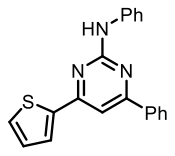
White solid (41 mg, 61% yield), purified by ethyl acetate:hexane = 1:45. m. p. 131-132 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12-8.10 (m, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.52-7.47 (m, 5H), 7.37-7.30 (m, 5H), 7.28 (s, 1H), 7.02 (t, J = 7.2 Hz, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 165.2, 160.1, 140.0, 138.9, 137.5, 136.1, 131.2, 130.8, 129.3, 128.98, 128.97, 127.3, 126.2, 122.3, 119.1, 108.8, 20.6 ppm; IR (KBr): v 3407, 2832, 1592, 1540, 1527, 1493, 1456, 1442, 1429, 1398, 1366, 1348, 1305, 1247, 1208, 1180, 1068, 1029, 1010, 989, 895, 824, 769, 728, 691, 638, 562 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}N_3$ 338.1652, Found 338.1662.

4-(2-bromophenyl)-N,6-diphenylpyrimidin-2-amine (3as)



White solid (60 mg, 75% yield), purified by ethyl acetate:hexane = 1:42. m. p. 131-132 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2H), 7.77 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 7.8 Hz, 1H), 7.62 (dd, J = 7.8, 1.8 Hz, 1H), 7.53-7.51 (m, 3H), 7.48-7.44 (m, 2H), 7.39-7.35 (m, 3H), 7.33-7.30 (m, 1H), 7.04 (t, J = 7.2 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 165.1, 160.3, 139.91, 139.85, 137.4, 133.8, 131.1, 130.9, 130.7, 129.1, 129.0, 127.8, 127.4, 122.4, 121.5, 119.1, 109.4 ppm; IR (KBr): v 3407, 2832, 1592, 1540, 1527, 1493, 1456, 1442, 1429, 1398, 1366, 1348, 1305, 1247, 1208, 1180, 1068, 1029, 1010, 989, 895, 824, 769, 728, 691, 638, 562 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{17}Br^{79}N_3$ 402.0600, Found 402.0609.

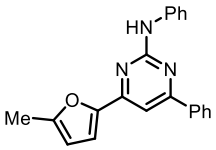
N,4-diphenyl-6-(thiophen-2-yl)pyrimidin-2-amine (3at)



White solid (58 mg, 88% yield), purified by ethyl acetate:hexane = 1:30. m. p.

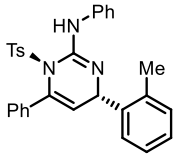
124-126 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10-8.09 (m, 2H), 7.80-7.76 (m, 3H), 7.51-7.45 (m, 5H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.31 (s, 1H), 7.16 (t, *J* = 4.2 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 160.4, 160.2, 143.4, 140.0, 137.6, 130.8, 129.6, 129.0, 128.9, 128.3, 127.3, 127.1, 122.3, 119.1, 103.0 ppm; IR (KBr): *v* 3389, 2831, 1593, 1576, 1531, 1519, 1495, 1458, 1444, 1426, 1355, 1244, 1210, 1155, 1072, 983, 888, 858, 769, 756, 746, 691, 640, 581 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{16}N_3S$ 330.1059, Found 330.1070.

4-(5-methylfuran-2-yl)-N,6-diphenylpyrimidin-2-amine (3au)



White solid (41 mg, 63% yield), purified by ethyl acetate:hexane = 1:30. m. p. 129-130 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.52-7.47 (m, 4H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.32-7.31 (m, 1H), 7.17 (d, *J* = 3.6 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 2.44 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 160.3, 156.9, 155.4, 150.9, 140.2, 137.6, 130.7, 129.0, 128.9, 127.3, 122.1, 119.0, 113.4, 109.0, 102.3, 14.2 ppm; IR (KBr): *v* 3431, 3259, 2832, 1609, 1578, 1538, 1518, 1497, 1459, 1438, 1364, 1254, 1207, 1136, 1083, 1028, 982, 845, 797, 773, 756, 691, 640 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{18}N_3O$ 328.1444, Found 328.1453.

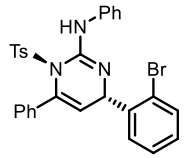
***trans*-N,6-diphenyl-4-(o-tolyl)-1-tosyl-1,4-dihydropyrimidin-2-amine (*trans*-5ar)**



White solid (61 mg, 62% yield), purified by ethyl acetate:hexane = 1:45. m. p. 114-116 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.47 (s, 1H), 7.40-7.37 (m, 2H), 7.35-7.29 (m, 6H), 7.18-7.04 (m, 4H), 5.90 (s, 1H), 3.73 (s, 1H), 2.42 (s, 3H), 2.00 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 143.1, 141.5, 139.8, 138.3, 136.8, 134.9, 134.1, 130.3, 130.2, 129.1, 128.8, 128.5, 128.1, 127.4, 127.2, 127.0, 126.5, 126.0, 122.9,

118.8, 54.5, 21.8, 19.0 ppm; IR (KBr): *v* 3410, 3261, 1668, 1598, 1525, 1496, 1462, 1440, 1358, 1301, 1252, 1121, 1068, 1017, 971, 921, 900, 772, 735, 664, 596 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{30}H_{28}N_3O_2S$ 494.1897, Found 494.1900.

***trans*-4-(2-bromophenyl)-N,6-diphenyl-1-tosyl-1,4-dihydropyrimidin-2-amine (*trans*-5as)**



White solid (88 mg, 79% yield), purified by ethyl acetate:hexane = 1:40. m. p. 171-173 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 7.2 Hz, 2H), 7.51-7.47 (m, 3H), 7.39 (t, J = 7.8 Hz, 2H), 7.36-7.33 (m, 3H), 7.30-7.26 (m, 3H), 7.09-7.06 (m, 2H), 5.89 (d, J = 2.4 Hz, 1H), 3.99 (s, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 143.6, 142.2, 139.6, 137.9, 136.8, 134.4, 132.5, 130.5, 129.6, 129.2, 128.8, 128.7, 128.5, 127.9 (3C), 126.6, 126.0, 123.1, 122.3, 119.0, 57.0, 21.9 ppm; IR (KBr): *v* 3378, 3057, 2924, 2832, 1663, 1601, 1538, 1497, 1467, 1442, 1378, 1365, 1311, 1281, 1247, 1186, 1171, 1126, 1087, 1017, 925, 915, 816, 767, 757, 746, 720, 706, 662, 631, 619, 574, 523 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{29}H_{25}Br^{79}N_3O_2S$ 558.0845, Found 558.0852.

Computational Details

All geometries were optimized with spin-restricted pure functional B3LYP including Grimme dispersion corrections (GD3BJ) with an all-electron 6-31G(d,p) basis set within the Gaussian16, D.01 suite of *ab initio* programs.[7] Transition structures were found through constrained optimizations along the desired reaction path. The frequency calculations were carried out at the same level to confirm the transition states with only one imaginary frequency. Meanwhile, the single imaginary frequency of each transition state displayed the desired displacement orientation indeed. The single-point calculations were performed with SMD model. According to the experimental reports, MeCN was selected as an effective solvent. The intrinsic reaction coordinate (IRC) calculations were performed to ensure that the transition states led to the expected reactants and products.

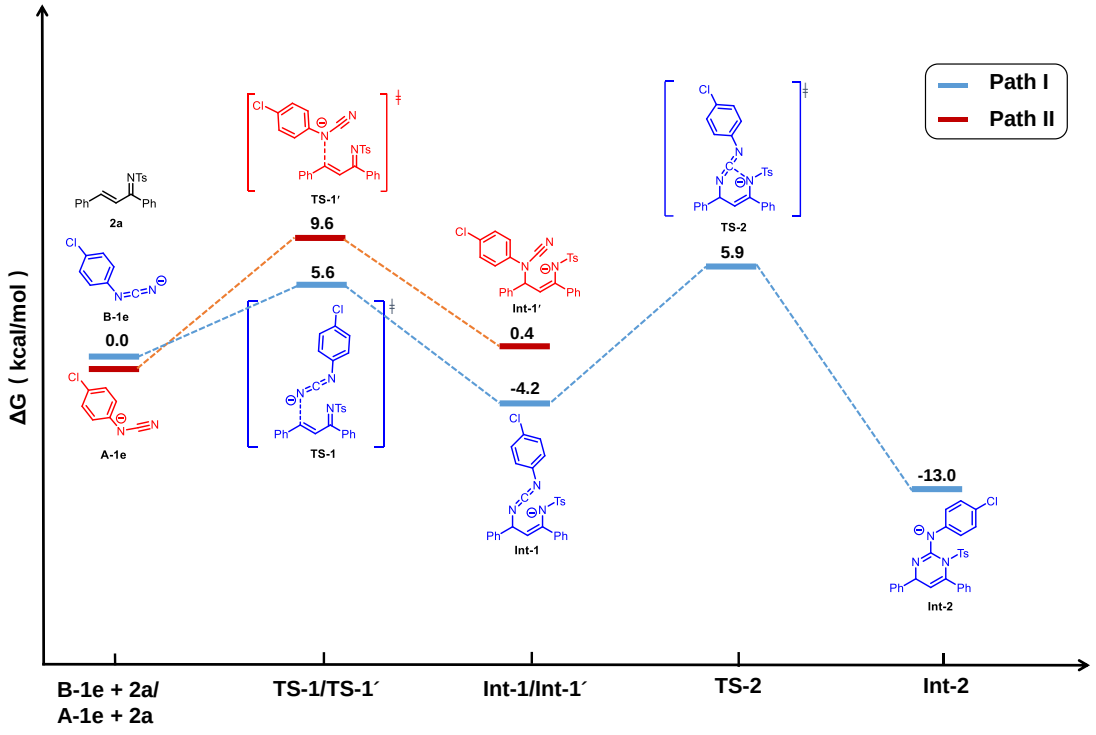


Figure S1. Computed energy profiles of selected key steps in the reaction of linear 1-azadiene **2a** with carbodiimide anion **B-1e** (path I) and cyanamide anion **A-1e** (path II).

Path I

B-1e+2a

C	-8.80209300	-0.39691400	1.07860700
C	-7.49789000	-0.68057300	1.48220900
C	-6.42609200	-0.26581700	0.69909600
C	-6.61838800	0.44772500	-0.51644300
C	-7.96409400	0.71342900	-0.88558300
C	-9.03780700	0.30131500	-0.10695400
Cl	-10.17648000	-0.92804700	2.08056600
C	-4.37357900	0.66508000	-1.04184700
N	-3.21257300	0.51360300	-0.85972400
C	0.75348600	1.62451800	0.15387400
C	2.20513600	1.60204300	0.42630100
C	0.42121200	-0.05577900	-1.76258800
C	-0.57359200	-0.93299600	-2.23889100
C	-0.28857000	-1.84246100	-3.25724000
C	0.97832200	-1.87358900	-3.84052500
C	1.96200100	-0.97953700	-3.40385600
C	1.68924300	-0.08047200	-2.37563800
C	2.85747600	2.94826700	0.45791700
C	2.45698900	3.89376000	-0.50332200
C	3.00745600	5.17259200	-0.51470500
C	3.94097400	5.53870800	0.45666400
C	4.32384600	4.61647900	1.43118300
C	3.79416700	3.32701000	1.43366300
N	2.73399600	0.43537800	0.65334100
C	4.34167700	-1.65825600	0.84139600
C	3.76494800	-2.37424300	-0.21034900
C	3.79326300	-3.76422700	-0.17786300
C	4.39572700	-4.45640400	0.88472300
C	4.97326100	-3.71346100	1.91951000
C	4.94881700	-2.31774900	1.90646600
C	4.39563800	-5.96628800	0.91314200
S	4.39098900	0.13792000	0.80370600
O	4.91827500	0.56065500	2.11738100
O	5.08951400	0.56261400	-0.42252100
H	-7.32252800	-1.22402600	2.40616900
H	-5.41033600	-0.48724400	1.01477400
H	-8.13442800	1.25730200	-1.81012200
H	-10.05610900	0.51900600	-0.41524900
H	0.21432900	2.36859100	0.73856300
H	-1.57154300	-0.86299300	-1.80949100
H	-1.06683300	-2.51551500	-3.60643400
H	1.19597800	-2.57308300	-4.64367600

H	2.94290800	-0.97578700	-3.87199000
H	2.46335100	0.61134900	-2.06291700
H	1.71743100	3.61200900	-1.24573000
H	2.70037600	5.88443800	-1.27532500
H	4.36291000	6.54002200	0.45719100
H	5.04064400	4.89906600	2.19674100
H	4.10288000	2.61687200	2.19016000
H	3.28379700	-1.85535700	-1.03152200
H	3.33358300	-4.32190100	-0.98983500
H	5.44506600	-4.23053000	2.75125000
H	5.38683200	-1.73825500	2.71099200
H	5.06415900	-6.35254600	1.68767000
H	3.39126300	-6.35695400	1.11668400
H	4.71331100	-6.38413600	-0.04822200
N	-5.61910900	0.88862500	-1.34211800
C	0.01758000	0.88574800	-0.70752000
H	-1.06586200	1.02292200	-0.65654500

TS-1

C	-4.38491300	2.04890000	0.71333400
C	-3.04816900	1.80307300	0.40049700
C	-2.26966300	1.04928300	1.27429100
C	-2.81419700	0.51315300	2.46304200
C	-4.17218200	0.77307800	2.73979800
C	-4.95358600	1.53808100	1.87912500
Cl	-5.38466500	3.01922800	-0.38853100
C	-0.84986500	-0.43726700	3.29220900
N	0.33118200	-0.63793100	3.34038400
C	0.20377500	-2.49427600	1.08523000
C	-0.01343500	-1.83676100	-0.15423200
C	2.47924500	-1.61148000	1.86343900
C	3.12204000	-0.69872600	2.71272900
C	4.46690100	-0.37734000	2.52721200
C	5.20514200	-0.96457500	1.49798600
C	4.57755400	-1.87612100	0.64650800
C	3.23165900	-2.19424900	0.82795500
C	-0.91787200	-2.56757600	-1.10678900
C	-0.66414300	-3.91690800	-1.39859300
C	-1.51244800	-4.63812700	-2.23669600
C	-2.64393100	-4.02577700	-2.77856600
C	-2.91372300	-2.68957400	-2.48031700
C	-2.05731200	-1.96011100	-1.65589200
N	0.51761800	-0.63494700	-0.36967700
C	1.68329500	1.44346700	-1.49390000
C	2.90874500	1.18993400	-0.87582400

C	3.81176700	2.23386100	-0.69650800
C	3.51665600	3.53468300	-1.13093500
C	2.28482100	3.76210900	-1.75394600
C	1.36711700	2.72625100	-1.93568500
C	4.49407800	4.66373500	-0.90067400
S	0.52056000	0.10932100	-1.84580700
O	-0.76313700	0.78614900	-2.15495200
O	1.11383000	-0.73551000	-2.90487200
H	-2.61347000	2.17160900	-0.52230200
H	-1.23209700	0.84905300	1.02314500
H	-4.59821500	0.35870000	3.64837400
H	-5.99639400	1.73397600	2.10740400
H	-0.51207200	-3.27396000	1.32698100
H	2.53801100	-0.23540700	3.49732900
H	4.93997900	0.33972400	3.19381700
H	6.25465600	-0.71632700	1.36055700
H	5.13316300	-2.34103000	-0.16385500
H	2.74940700	-2.90606100	0.16672000
H	0.21262000	-4.39142100	-0.96868900
H	-1.29091600	-5.67766100	-2.46473100
H	-3.31103900	-4.58688300	-3.42808600
H	-3.79665100	-2.20706000	-2.89016500
H	-2.26984300	-0.92174100	-1.43474200
H	3.14253400	0.19384200	-0.52078000
H	4.75848200	2.03271700	-0.20099700
H	2.03456500	4.76373300	-2.09626000
H	0.40555000	2.90051300	-2.40527800
H	5.52348000	4.35211600	-1.10859700
H	4.26713400	5.52563900	-1.53551500
H	4.46688800	5.00742600	0.14123600
N	-2.10953900	-0.27662800	3.36295000
C	1.09300500	-2.12972500	2.10446600
H	1.04203500	-2.77215700	2.97979000

Int-1

C	4.89426500	0.99965300	0.01164500
C	5.28561200	0.33328700	1.17194800
C	4.31032600	-0.11437000	2.06015800
C	2.94939000	0.11514300	1.80415800
C	2.57945000	0.79010300	0.62856600
C	3.54852000	1.22356200	-0.27323700
Cl	6.13792300	1.55581900	-1.12260000
C	0.82730500	-0.05650200	2.85254300
N	-0.27704100	0.24253300	3.24968100
C	-2.13349400	1.17581500	1.92641100

C	-1.72708700	1.46623300	0.64935200
C	-1.87912800	-1.39990400	2.22892800
C	-1.25316000	-2.49310700	2.84338700
C	-1.51893700	-3.79862800	2.42893200
C	-2.42214800	-4.03543100	1.39237000
C	-3.05452000	-2.95369700	0.77833200
C	-2.78748900	-1.64931700	1.19454600
C	-2.24150600	2.75544300	0.07001900
C	-1.37290600	3.65061700	-0.57493800
C	-1.83106500	4.88532300	-1.02944100
C	-3.16811200	5.25178700	-0.85910800
C	-4.04462500	4.36508600	-0.23252900
C	-3.58414900	3.13112100	0.22665400
N	-0.80644200	0.67599500	0.01054700
C	-0.47578500	-1.15590600	-1.88197500
C	0.58669300	-1.86709400	-1.31758500
C	0.71643900	-3.22824400	-1.57399000
C	-0.19736400	-3.90462800	-2.39705200
C	-1.24465600	-3.17126200	-2.96292100
C	-1.38870500	-1.80526600	-2.70922900
C	-0.05994800	-5.38937500	-2.64205100
S	-0.66299300	0.62230900	-1.60034300
O	0.62845700	1.22285300	-2.03193900
O	-1.87033800	1.02018100	-2.36565000
H	6.33762600	0.16208100	1.37407600
H	4.58997900	-0.64490600	2.96487500
H	1.52817700	0.94746700	0.39951900
H	3.23505300	1.70998000	-1.18999000
H	-2.70505000	1.93019800	2.45530300
H	-0.54858700	-2.32285500	3.65184500
H	-1.01656600	-4.63022700	2.91716200
H	-2.62652600	-5.05094100	1.06276400
H	-3.74743300	-3.12151100	-0.04167600
H	-3.27112300	-0.80812500	0.71170000
H	-0.33764700	3.36476900	-0.72854300
H	-1.13962700	5.56352800	-1.52312100
H	-3.52463200	6.21306700	-1.22107100
H	-5.09232600	4.62951500	-0.10856100
H	-4.26928400	2.43469100	0.70010600
H	1.30396400	-1.35808400	-0.68402500
H	1.54267000	-3.77773200	-1.12797000
H	-1.95925800	-3.67358600	-3.61208800
H	-2.19710900	-1.22901000	-3.14577400
H	-0.66556200	-5.71207600	-3.49477100

H	0.98017800	-5.67012500	-2.84229500
H	-0.38588900	-5.96971500	-1.76916400
N	2.01928800	-0.38263300	2.72730500
C	-1.66766000	0.02017100	2.77149200
H	-2.25676200	0.06849400	3.69706800

TS-2

C	-6.38025700	-0.71121300	-0.48247400
C	-5.79636900	0.17270000	0.42222600
C	-4.43537700	0.07248800	0.70101600
C	-3.63572600	-0.91006700	0.07644300
C	-4.25966100	-1.78599200	-0.83621400
C	-5.61851600	-1.69274900	-1.11617200
Cl	-8.11839400	-0.58870100	-0.83160000
C	-1.58486500	-0.29280700	1.00095500
N	-1.47425600	0.51239100	1.94706600
C	0.94827300	0.52780600	2.34916000
C	1.25442800	-0.40162600	1.40476300
C	-0.18274500	2.59189400	1.37105400
C	-0.56391800	2.61489000	0.02313400
C	-0.39458900	3.77333600	-0.74016900
C	0.15127700	4.92707300	-0.17491900
C	0.52871200	4.91525500	1.16911500
C	0.35817300	3.75878300	1.92949700
C	2.41811100	-1.31061000	1.63820300
C	3.64191400	-0.78247500	2.08111600
C	4.71746100	-1.61743400	2.38183800
C	4.59130900	-3.00031400	2.24000100
C	3.38173100	-3.53587500	1.79084500
C	2.30511000	-2.70332700	1.48881600
N	0.36739500	-0.51706400	0.34747200
C	2.32366900	-0.40969200	-1.56868700
C	2.49207600	0.97604200	-1.62493800
C	3.72251900	1.50211300	-2.00958600
C	4.79639800	0.66506600	-2.34859100
C	4.60127400	-0.71942600	-2.29387800
C	3.37447000	-1.25960500	-1.90460900
C	6.13543200	1.24842900	-2.73637900
S	0.70270100	-1.11091300	-1.13531000
O	-0.27163300	-0.51104600	-2.06369900
O	0.88118500	-2.58028600	-1.19927400
H	-6.40187000	0.93141000	0.90803300
H	-3.97354900	0.75150200	1.41027100
H	-3.64248500	-2.53356200	-1.32324300
H	-6.08422400	-2.37175600	-1.82299100

H	1.50573800	0.54927500	3.27935800
H	-0.97747600	1.72648600	-0.43952600
H	-0.69582000	3.76828200	-1.78447900
H	0.27560300	5.82644200	-0.77273700
H	0.94740400	5.80793500	1.62801300
H	0.64922300	3.75821600	2.97828600
H	3.74203000	0.29481800	2.17159800
H	5.65779200	-1.18635100	2.71714500
H	5.42945900	-3.65397600	2.46865800
H	3.27350500	-4.61129600	1.67447900
H	1.37518900	-3.12040400	1.12244300
H	1.66839400	1.63314200	-1.36741000
H	3.85138400	2.58157900	-2.05015000
H	5.42026700	-1.38561900	-2.55650900
H	3.21676000	-2.33105800	-1.85434600
H	6.01928600	2.13685600	-3.36645400
H	6.70906500	1.55463300	-1.85191700
H	6.74443200	0.52288100	-3.28443900
N	-2.28139100	-1.08924200	0.31446500
C	-0.32075300	1.35121400	2.26599800
H	-0.51665200	1.73789800	3.27344200

Int-2

C	6.32419000	-0.43022800	0.28490600
C	5.60969500	0.29594400	-0.66298600
C	4.22246300	0.17286000	-0.73817300
C	3.50847100	-0.68395600	0.14397300
C	4.28392000	-1.40411700	1.09179400
C	5.66478300	-1.28630900	1.16895400
Cl	8.09900000	-0.27288900	0.37061800
C	1.28410700	-0.25154700	-0.56089300
N	1.44318600	0.61900000	-1.52802300
C	-0.88055400	0.23264600	-2.23729000
C	-1.05725900	-0.68376100	-1.26623500
C	-0.19254900	2.52414900	-1.40296800
C	0.50461600	3.03225600	-0.30243700
C	0.09258500	4.21633900	0.31669100
C	-1.01735000	4.91539300	-0.15894200
C	-1.71437700	4.42121600	-1.26554900
C	-1.30272800	3.23853500	-1.87846600
C	-2.02265100	-1.80401300	-1.37861400
C	-3.28325100	-1.59827500	-1.96379800
C	-4.16713100	-2.65953500	-2.14754000
C	-3.81278800	-3.94680200	-1.73779200
C	-2.56763300	-4.15907300	-1.14149400

C	-1.67877800	-3.10075500	-0.95966100
N	-0.10904600	-0.65723100	-0.21603700
C	-2.22784000	-0.20296500	1.46152100
C	-2.47411300	1.16017600	1.27924800
C	-3.77861700	1.63362200	1.38256700
C	-4.84380000	0.76980500	1.68091500
C	-4.56614300	-0.58764500	1.87688700
C	-3.26493800	-1.08003300	1.76756900
C	-6.25689400	1.29678300	1.77070700
S	-0.52466400	-0.81248100	1.43290600
O	0.26538700	0.14580200	2.20898600
O	-0.58135100	-2.22206000	1.84714200
H	6.13543500	0.95655700	-1.34668300
H	3.66085500	0.72902300	-1.47737900
H	3.74943100	-2.05962100	1.77260900
H	6.22842400	-1.84863300	1.90722000
H	-1.43389700	0.14689500	-3.16749500
H	1.36680700	2.48463500	0.06096200
H	0.64300200	4.58912200	1.17674600
H	-1.33622700	5.83591900	0.32362600
H	-2.57918100	4.95773400	-1.64959400
H	-1.85515100	2.85826700	-2.73511500
H	-3.56981500	-0.59192000	-2.25378000
H	-5.13961100	-2.47894100	-2.59877500
H	-4.50406700	-4.77455200	-1.87345200
H	-2.28295600	-5.15627700	-0.81654000
H	-0.71620300	-3.26366700	-0.48897900
H	-1.65628400	1.83852600	1.06401200
H	-3.96922600	2.69330300	1.23200000
H	-5.37722400	-1.27111900	2.11640200
H	-3.04397200	-2.13084800	1.91484500
H	-6.30123500	2.22866000	2.34475400
H	-6.66406000	1.51381600	0.77508400
H	-6.92444900	0.57339000	2.24804200
N	2.15347900	-0.91446100	0.18021900
C	0.25874400	1.22743200	-2.11058700
H	0.53051200	1.53858700	-3.13149300

Path II

A-1e + 2a

C	7.75781500	-0.69490700	0.22647500
C	7.33002900	0.48739300	-0.37585900
C	5.97561000	0.68938600	-0.61886000
C	5.00051200	-0.28363100	-0.26907100
C	5.48222300	-1.47053600	0.34220400

C	6.83383800	-1.67657200	0.58741100
Cl	9.49141300	-0.95519200	0.53763300
C	3.17665800	0.93713300	-1.02579300
N	2.63737500	1.87871900	-1.49623100
C	0.01873300	0.94408900	0.88886000
C	-1.30572700	1.50708800	0.61580600
C	0.01480900	-1.62049300	0.38313500
C	-1.28347000	-2.09601300	0.64494300
C	-1.65131900	-3.38596400	0.26477700
C	-0.74061800	-4.22008100	-0.38628300
C	0.55453400	-3.76289700	-0.64648800
C	0.93564700	-2.48393700	-0.25373600
C	-1.27498700	2.95247000	0.22990600
C	-2.20278700	3.87186500	0.74861200
C	-2.11615600	5.22050700	0.41203300
C	-1.11346800	5.66715200	-0.45090700
C	-0.18464800	4.76037900	-0.96330400
C	-0.24865000	3.41156600	-0.61707100
N	-2.36562000	0.75126000	0.74781000
C	-4.62595400	-0.43064900	0.04150700
C	-4.66146900	-0.96933200	-1.24371800
C	-5.22809100	-2.22720900	-1.43916000
C	-5.76566000	-2.95447800	-0.36833300
C	-5.71988800	-2.38735300	0.91311800
C	-5.15780300	-1.12939000	1.12450000
C	-6.40821600	-4.30248700	-0.59633200
S	-3.92493800	1.20713300	0.29373600
O	-3.99213500	1.89916900	-1.00355700
O	-4.61567700	1.78356600	1.46490000
H	8.05445300	1.24732400	-0.65368400
H	5.64392700	1.61127000	-1.08808800
H	4.75685800	-2.22916300	0.62196200
H	7.17281600	-2.59491100	1.05725200
H	0.76300300	1.70796300	1.08782200
H	-1.98767900	-1.44860900	1.14817300
H	-2.65767300	-3.73600500	0.47726600
H	-1.03554200	-5.22333600	-0.68422700
H	1.27032000	-4.40700700	-1.15015200
H	1.93940000	-2.11248500	-0.45159700
H	-2.98022300	3.53598000	1.42559000
H	-2.83390600	5.92258200	0.82712000
H	-1.05163500	6.72006500	-0.71431500
H	0.60785900	5.09541800	-1.62560700
H	0.50797800	2.73188700	-1.00630200

H	-4.25289600	-0.40185900	-2.07240500
H	-5.25187200	-2.65170600	-2.43963800
H	-6.13427700	-2.93577500	1.75553000
H	-5.13672900	-0.68327700	2.11268100
H	-7.46215200	-4.19545600	-0.88319600
H	-5.90853800	-4.85261700	-1.39952000
H	-6.37786700	-4.91865500	0.30716800
N	3.65044800	-0.15627500	-0.48068200
C	0.53885400	-0.30553700	0.75883100
H	1.62433800	-0.32067600	0.85840200

TS-1'

C	-6.38783700	0.21571400	-0.32190200
C	-5.92662300	-0.62233700	-1.33546400
C	-4.55951800	-0.82580200	-1.49189100
C	-3.62130800	-0.18691900	-0.64927900
C	-4.12137000	0.66444900	0.36002800
C	-5.48970500	0.85874200	0.52663700
Cl	-8.13095100	0.47109200	-0.11618300
C	-1.79848100	-1.10209500	-1.78314200
N	-1.35493900	-1.74436500	-2.65949900
C	-0.29361100	-1.71299800	0.67131300
C	1.05928600	-1.69668300	0.27894400
C	-0.82722000	0.74110400	1.25265800
C	-0.22371700	1.67268000	0.39876200
C	0.10732900	2.94498700	0.86166500
C	-0.15626000	3.31196700	2.18338500
C	-0.76175800	2.39529600	3.04262000
C	-1.09929300	1.12421400	2.57551700
C	1.75229400	-3.02869000	0.39571800
C	1.72615000	-3.72756800	1.61149200
C	2.32033100	-4.98355200	1.72510900
C	2.93405700	-5.56874800	0.61633300
C	2.95499500	-4.88509300	-0.60025600
C	2.37420900	-3.62214500	-0.71273600
N	1.65109700	-0.59093200	-0.18216700
C	3.40343800	1.32978800	-0.52600400
C	3.02023100	1.95837400	-1.71230500
C	3.15383600	3.33965200	-1.83022500
C	3.68084100	4.10965000	-0.78154700
C	4.06385600	3.45502300	0.39475300
C	3.92914100	2.07192200	0.52739100
C	3.85907300	5.60257000	-0.93533100
S	3.28002300	-0.46513700	-0.37999800
O	3.73290100	-0.99165000	-1.68866600

O	4.06095800	-0.84242300	0.81968000
H	-6.63133800	-1.11918600	-1.99436900
H	-4.19864100	-1.48408600	-2.27566500
H	-3.42596300	1.19077200	1.00281700
H	-5.85498100	1.51852900	1.30679200
H	-0.71179500	-2.70317700	0.82041500
H	-0.01463700	1.38863000	-0.62319900
H	0.58651600	3.64783300	0.18657700
H	0.10709100	4.30487600	2.53897100
H	-0.97670400	2.66691700	4.07306300
H	-1.57497300	0.41304700	3.24709800
H	1.24489600	-3.26886700	2.46965300
H	2.30375400	-5.50475700	2.67906400
H	3.39396600	-6.55027500	0.70049000
H	3.42632400	-5.33530700	-1.46977300
H	2.40236700	-3.08886900	-1.65516200
H	2.62766200	1.36373800	-2.53008500
H	2.85071500	3.82953800	-2.75301100
H	4.47265800	4.03444800	1.21961100
H	4.22814100	1.55787000	1.43421400
H	4.78445800	5.84140700	-1.47563000
H	3.03369900	6.04936900	-1.49943000
H	3.91228100	6.10138100	0.03722600
N	-2.24297900	-0.36347500	-0.77720200
C	-1.21601400	-0.64747000	0.84276200
H	-2.10091600	-0.97240100	1.38935500

Int-1'

C	-5.78589200	-0.91949400	-0.53779500
C	-5.09760200	-0.90556300	-1.74885500
C	-3.71033900	-1.00125300	-1.75542200
C	-2.98561700	-1.11158000	-0.55240600
C	-3.70158000	-1.11374900	0.65876100
C	-5.09245900	-1.02098900	0.66314500
Cl	-7.55103800	-0.80140400	-0.52865600
C	-0.97180200	-1.27786600	-1.76093500
N	-0.56793100	-1.29912600	-2.85679700
C	0.55671700	-2.18640200	0.40203200
C	1.69413100	-1.50947600	0.01997400
C	-0.77911100	-0.44278100	1.69476800
C	-0.74739500	0.90397900	1.32300800
C	-0.72630000	1.90605800	2.29480500
C	-0.73858300	1.57829000	3.65089600
C	-0.77025100	0.23548600	4.03232700
C	-0.79144900	-0.76314700	3.05947300

C	2.94222800	-2.34649100	-0.06815500
C	3.31487100	-3.16361400	1.01015000
C	4.43175500	-3.99504500	0.92903400
C	5.19363100	-4.02920400	-0.23975100
C	4.83270500	-3.21898600	-1.31819300
C	3.72136500	-2.38072300	-1.23536500
N	1.64126700	-0.19223500	-0.31778600
C	2.09639500	2.35478800	-0.51357900
C	1.17542400	2.62436600	-1.53106900
C	0.56484600	3.87344300	-1.59086500
C	0.86774200	4.87697700	-0.65515700
C	1.79742700	4.58659300	0.34831200
C	2.41150200	3.33276400	0.42344200
C	0.21520400	6.23721400	-0.74846500
S	2.94428700	0.75974300	-0.45437600
O	3.63370700	0.65280600	-1.76738700
O	3.82403700	0.79321400	0.74106800
H	-5.63967700	-0.82366500	-2.68469200
H	-3.17910200	-0.99679700	-2.70002500
H	-3.18213700	-1.15732000	1.60583200
H	-5.62942900	-1.02042500	1.60543400
H	0.61828100	-3.26402800	0.49788900
H	-0.71913600	1.16497000	0.27301500
H	-0.68206900	2.94584600	1.98406700
H	-0.71933900	2.36124800	4.40458500
H	-0.77889900	-0.03509300	5.08526600
H	-0.80691500	-1.80913300	3.35942200
H	2.72176500	-3.12753600	1.91858700
H	4.70961500	-4.61158600	1.78078900
H	6.06539400	-4.67578000	-0.30722600
H	5.42135300	-3.23619900	-2.23193900
H	3.45819700	-1.73721600	-2.06600200
H	0.93457200	1.85005600	-2.25204400
H	-0.15909200	4.07778000	-2.37722000
H	2.04432500	5.34931600	1.08416600
H	3.12770400	3.09520300	1.20269400
H	0.59262300	6.80615100	-1.60795400
H	-0.87065200	6.15518600	-0.87275500
H	0.40565100	6.83382200	0.14892900
N	-1.57655900	-1.22716200	-0.56544200
C	-0.78873700	-1.59344100	0.68894500
H	-1.38632100	-2.39625500	1.13872100

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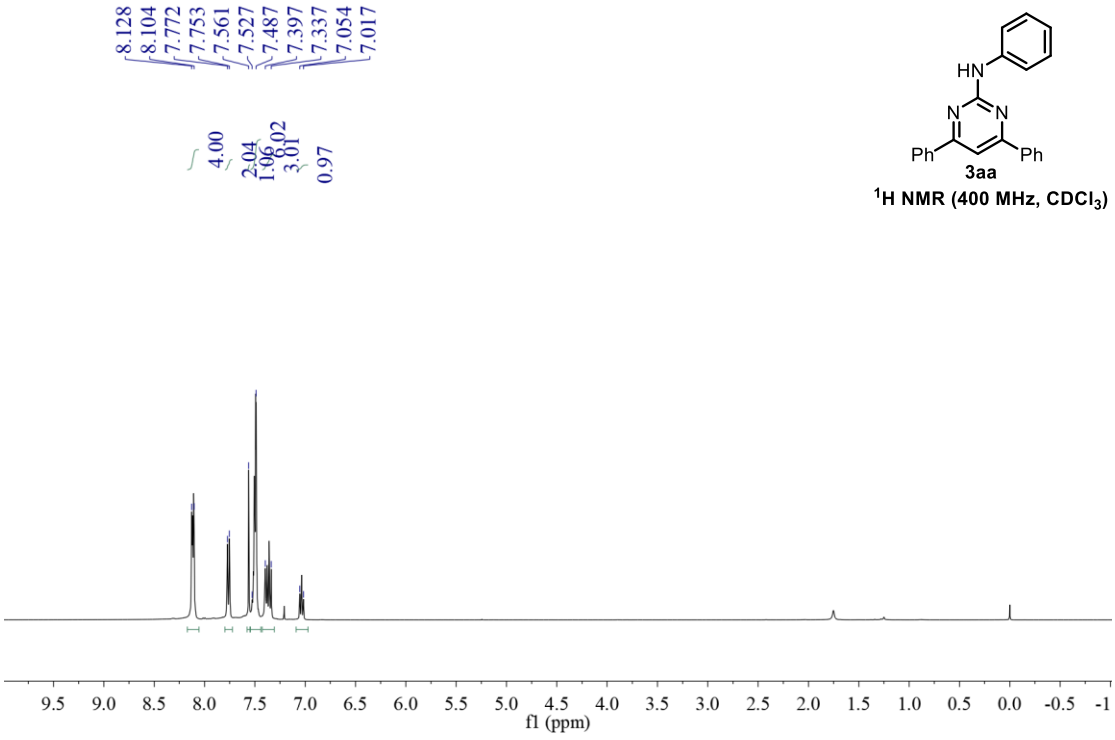
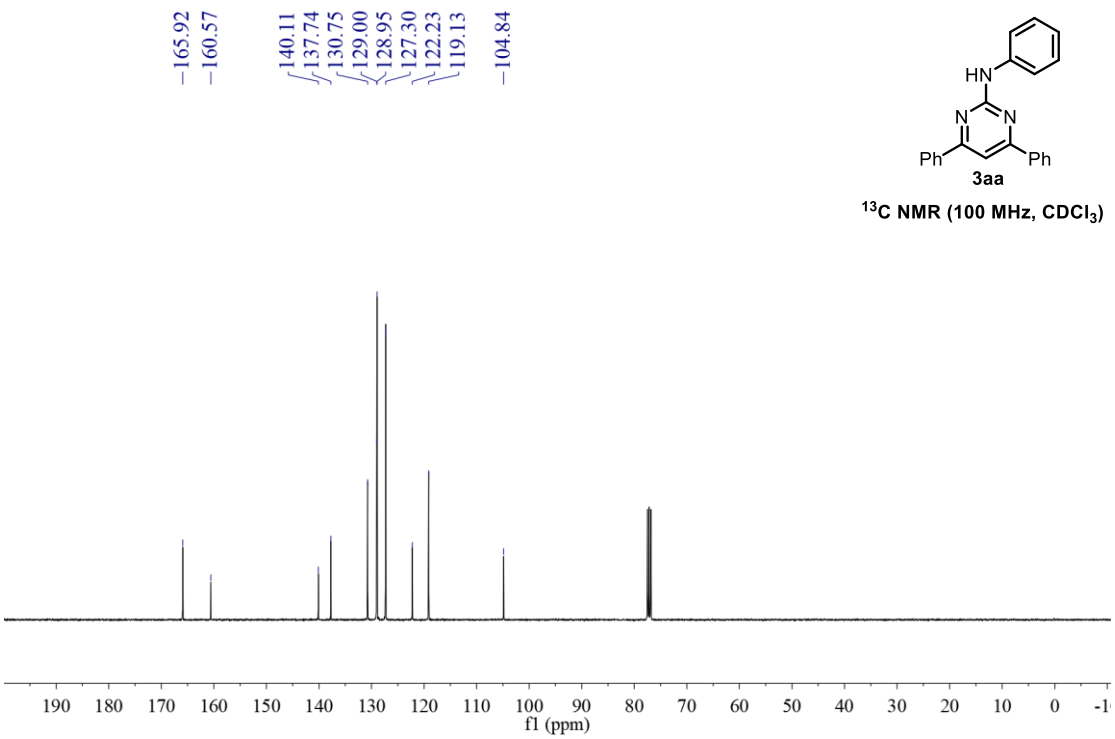
[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P.

Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta Jr., F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, revision C.01, Gaussian, Inc., Wallingford, CT, 2016.

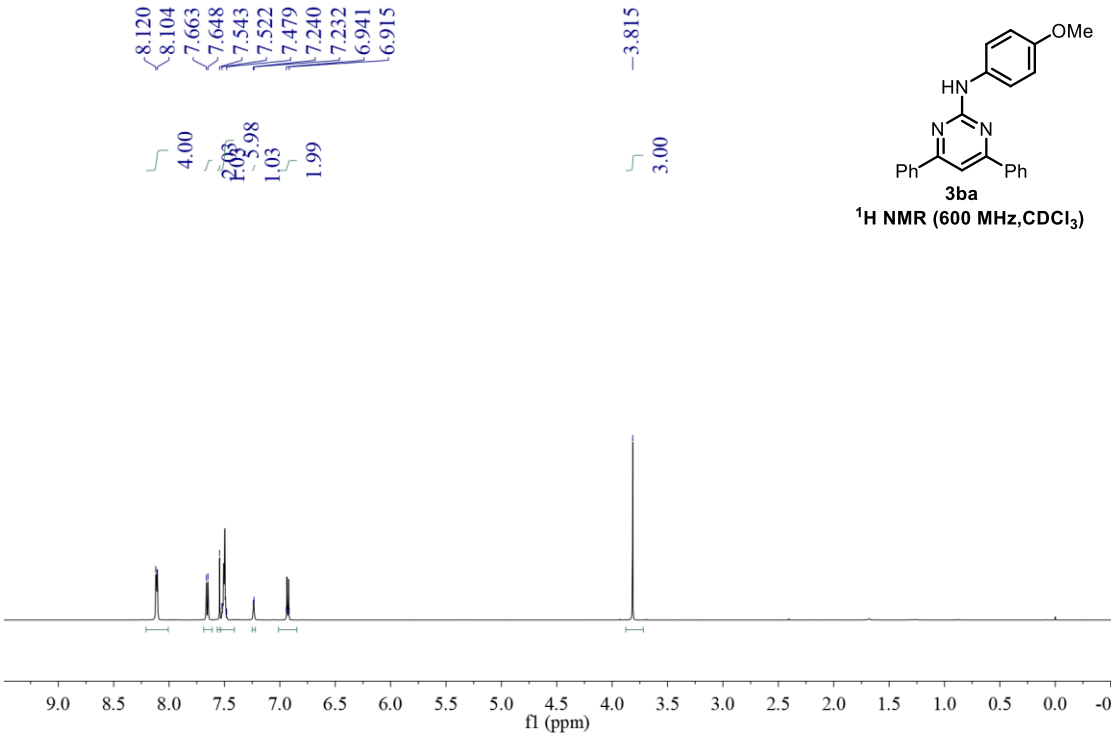
4. Copies of NMR Spectra



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)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7.522
7.479
7.240
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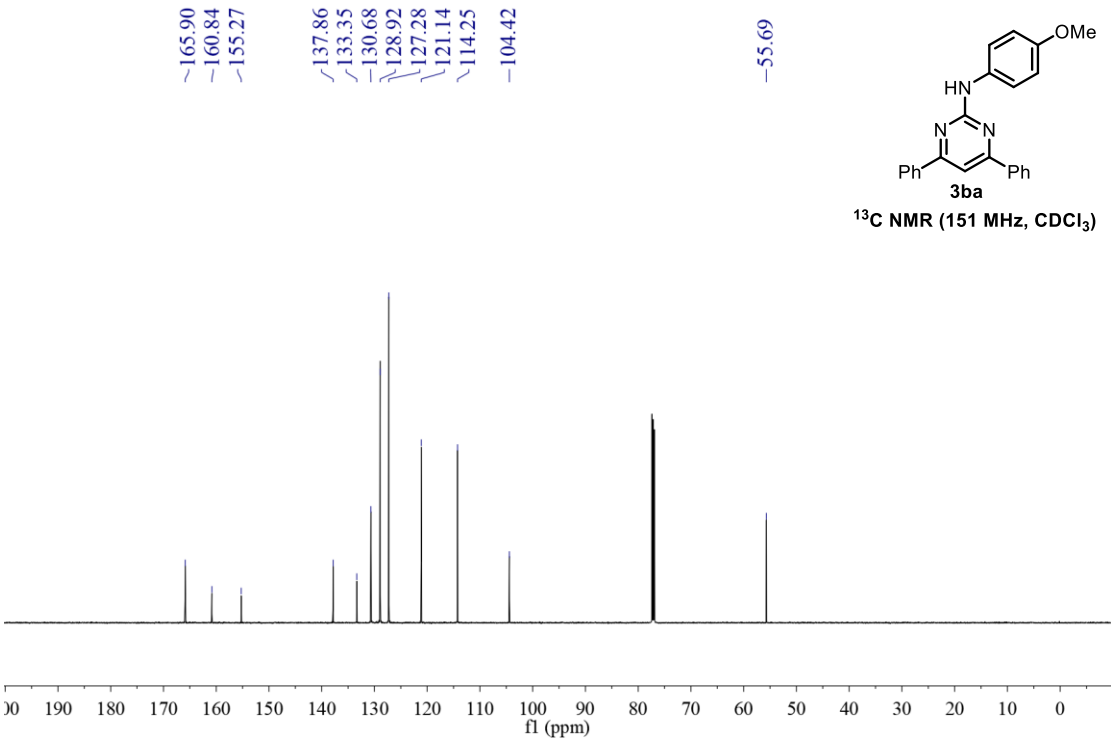
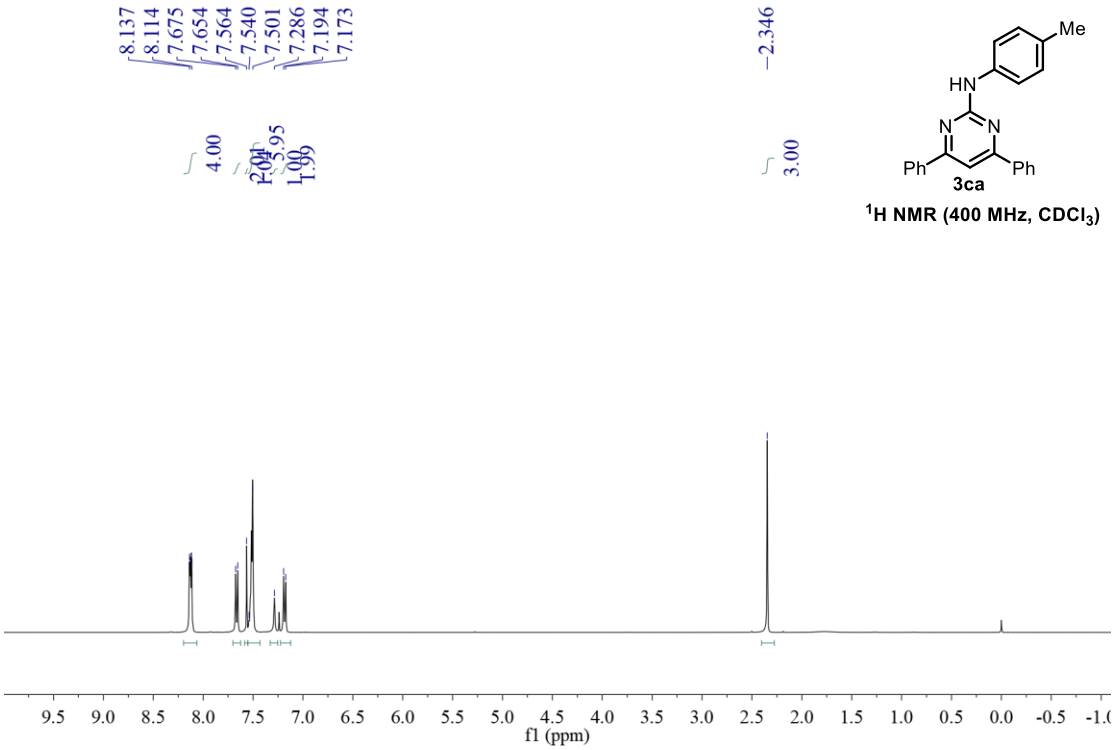
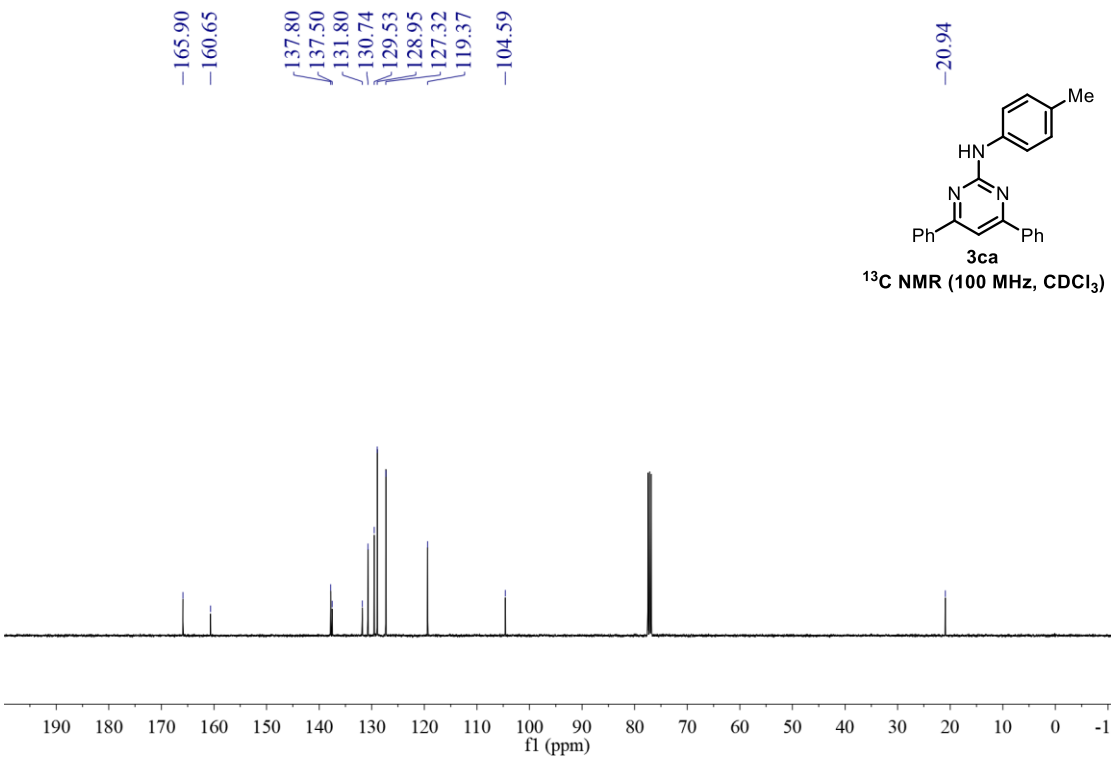
3.815
4.00
2.03
1.98
1.03
1.99
3.00
OMe
HN
N
N
Ph
Ph
3ba
^{1}H NMR (600 MHz,CDCl$_3$)
fl (ppm)

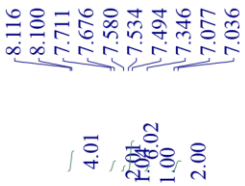

165.90
160.84
155.27
137.86
133.35
130.68
128.92
127.28
121.14
114.25
104.42
55.69
OMe
HN
N
N
Ph
Ph
3ba
^{13}C NMR (151 MHz, CDCl$_3$)
fl (ppm)

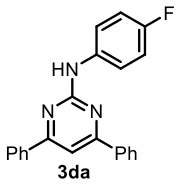


^{1}H NMR (400 MHz, $CDCl_3$)



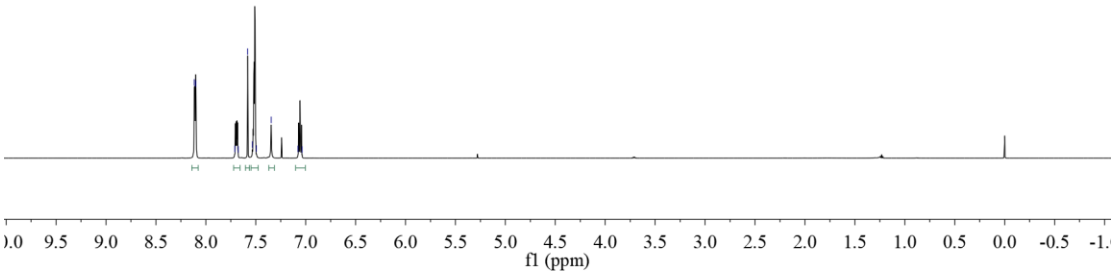
^{13}C NMR (100 MHz, $CDCl_3$)

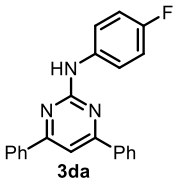




3da

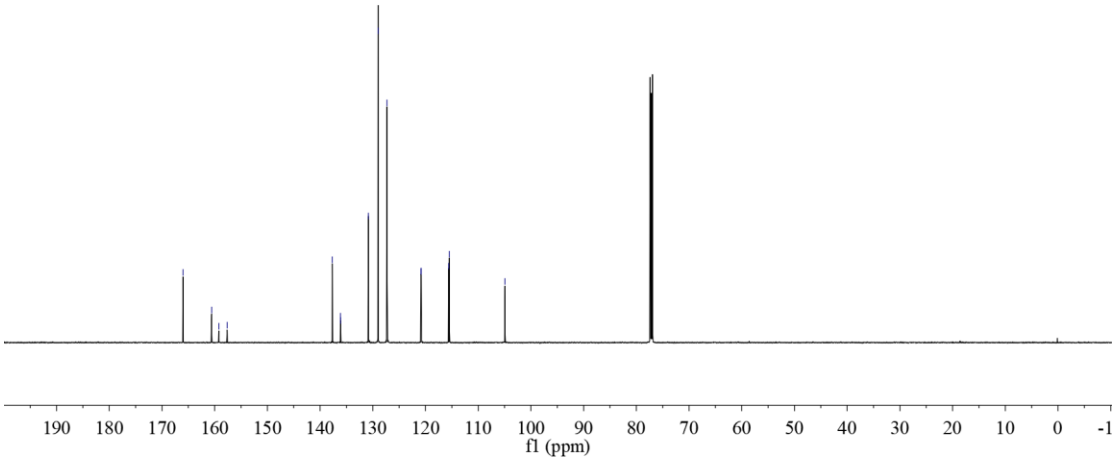
^{1}H NMR (600 MHz, $CDCl_3$)

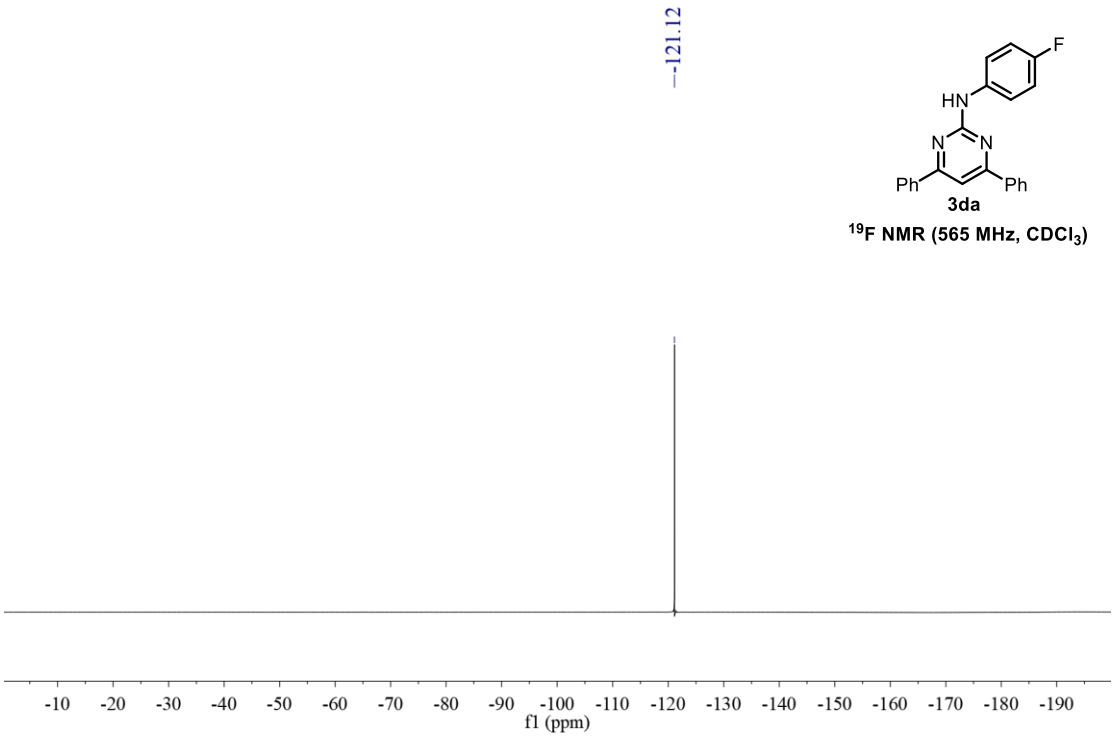




3da

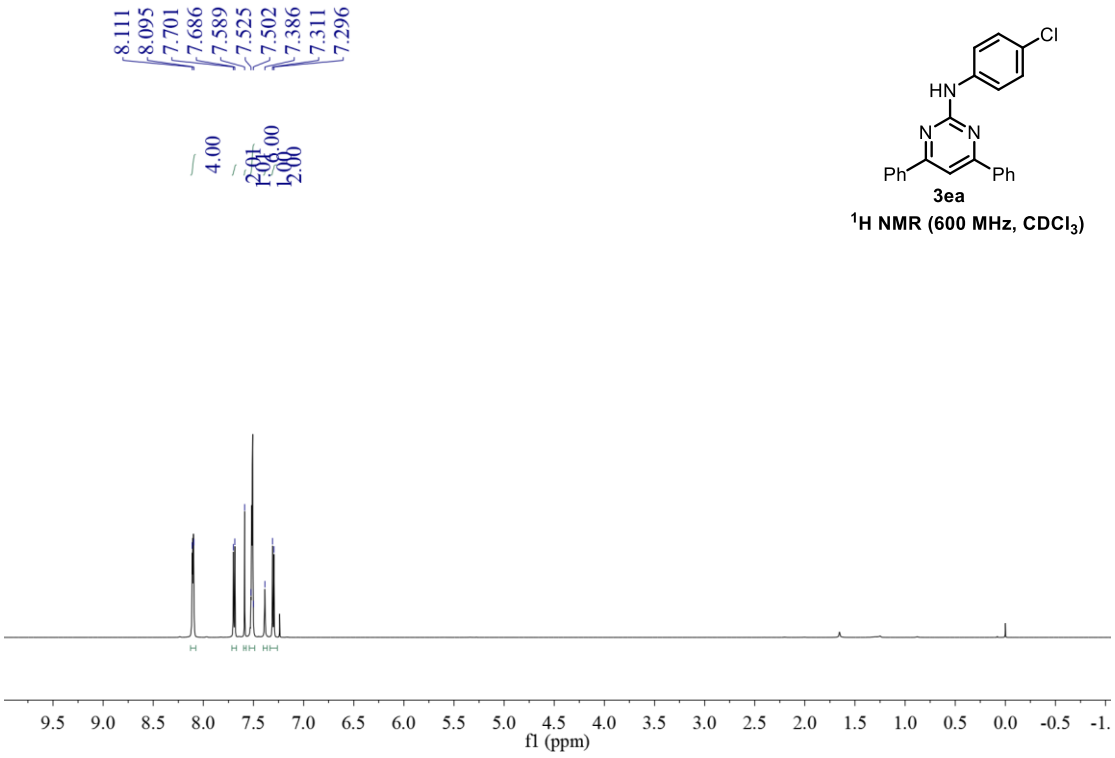
^{13}C NMR (151 MHz, $CDCl_3$)





3da

^{19}F NMR (565 MHz, $CDCl_3$)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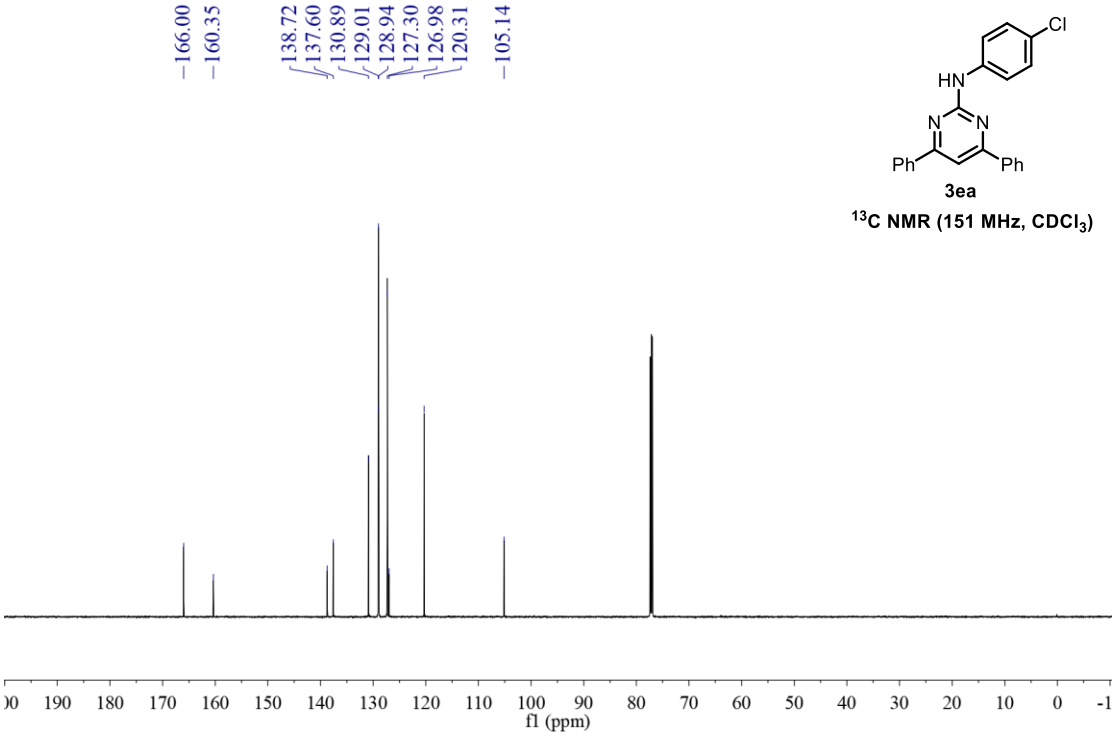
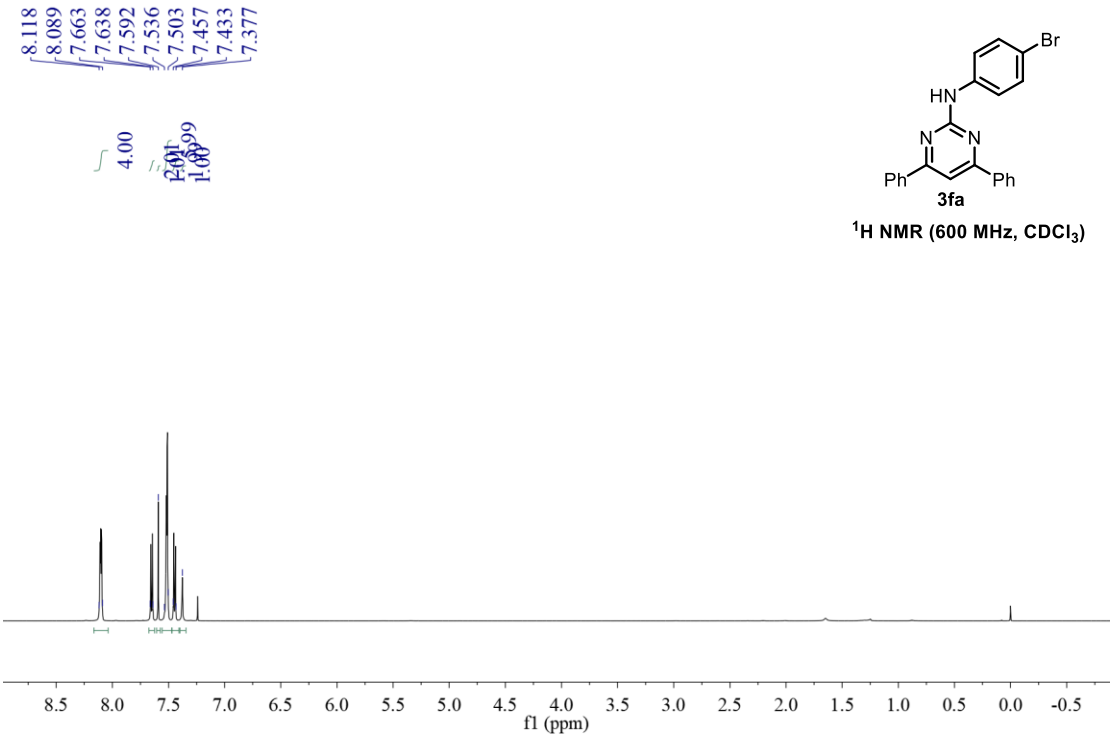
7.686
7.589
7.525
7.502
7.386
7.311
7.296
4.00
2.01
6.00
2.00
Cl
HN
N
N
Ph
Ph
3ea
^{1}H NMR (600 MHz, CDCl$_3$)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


166.00
160.35
138.72
137.60
130.89
129.01
128.94
127.30
126.98
120.31
105.14
Cl
HN
N
N
Ph
Ph
3ea
^{13}C NMR (151 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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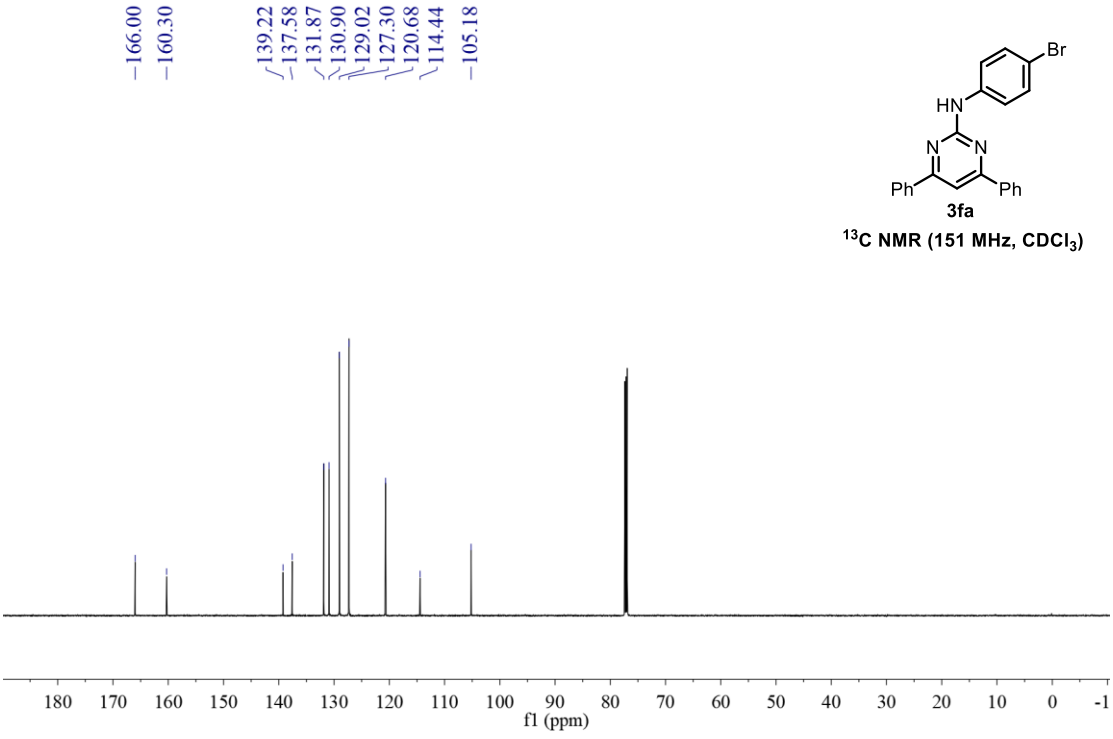
8.089
7.663
7.638
7.592
7.536
7.503
7.457
7.433
7.377
4.00
2.01
2.00
1.99
1.00
Br
HN
N
N
Ph
Ph
3fa
^{1}H NMR (600 MHz, CDCl$_3$)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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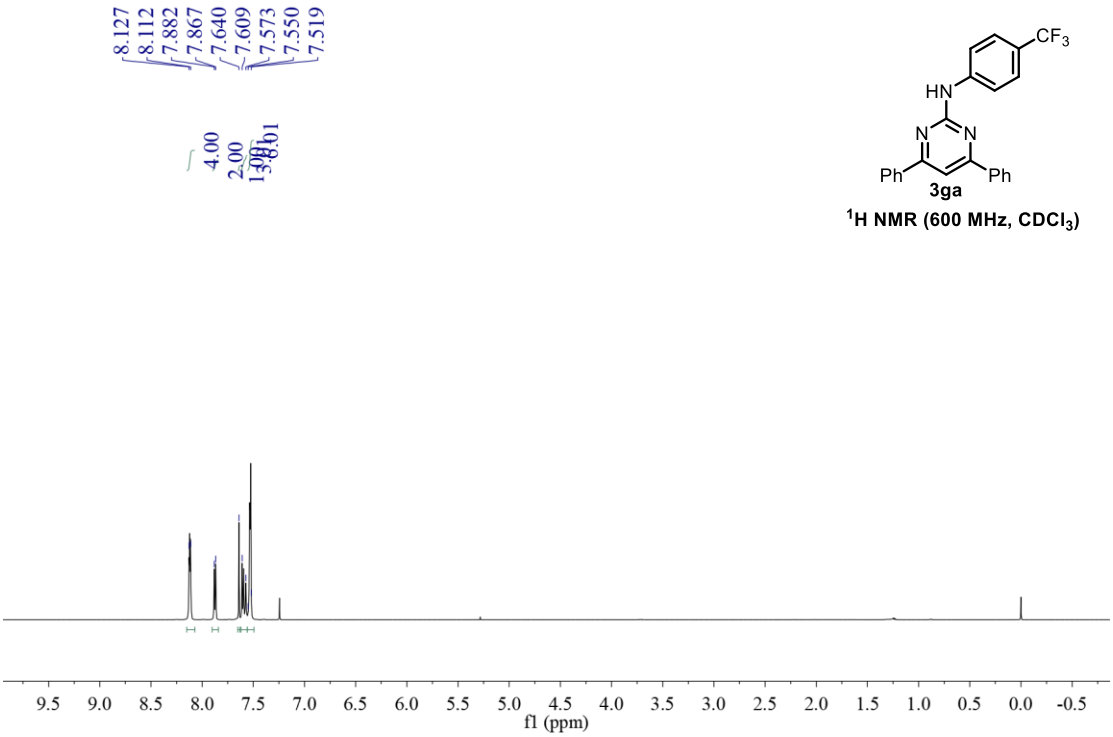
139.22
137.58
131.87
130.90
129.02
127.30
120.68
114.44
105.18
Br
HN
N
N
Ph
Ph
3fa
^{13}C NMR (151 MHz, CDCl$_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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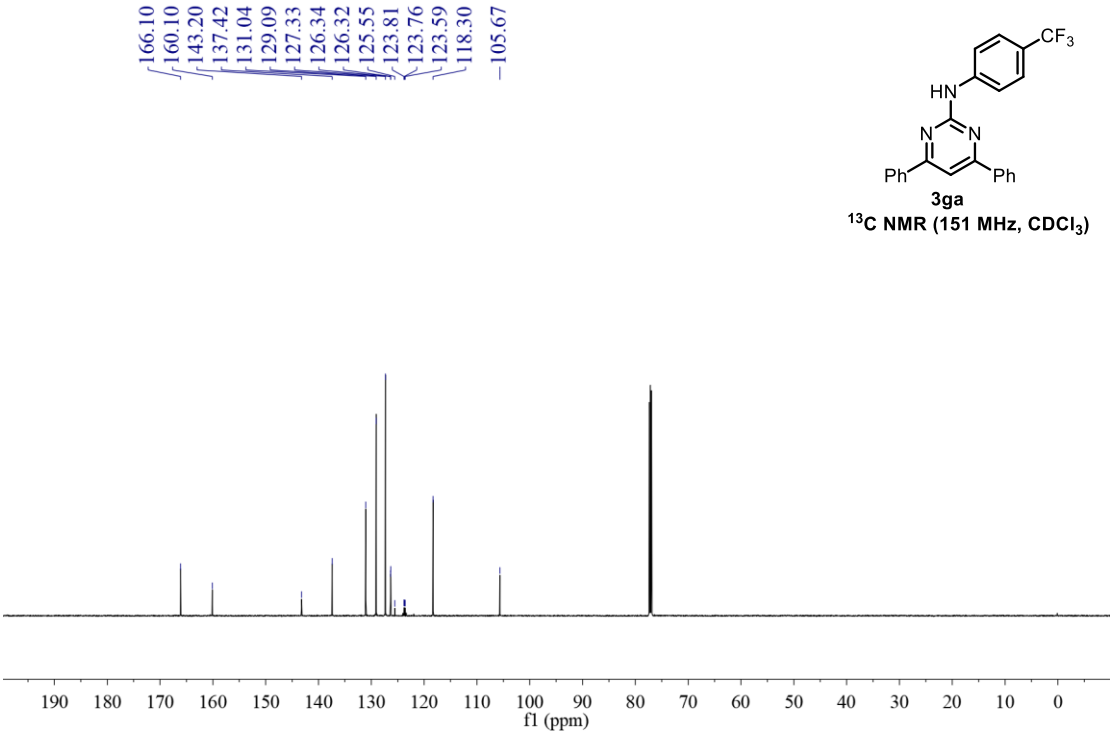
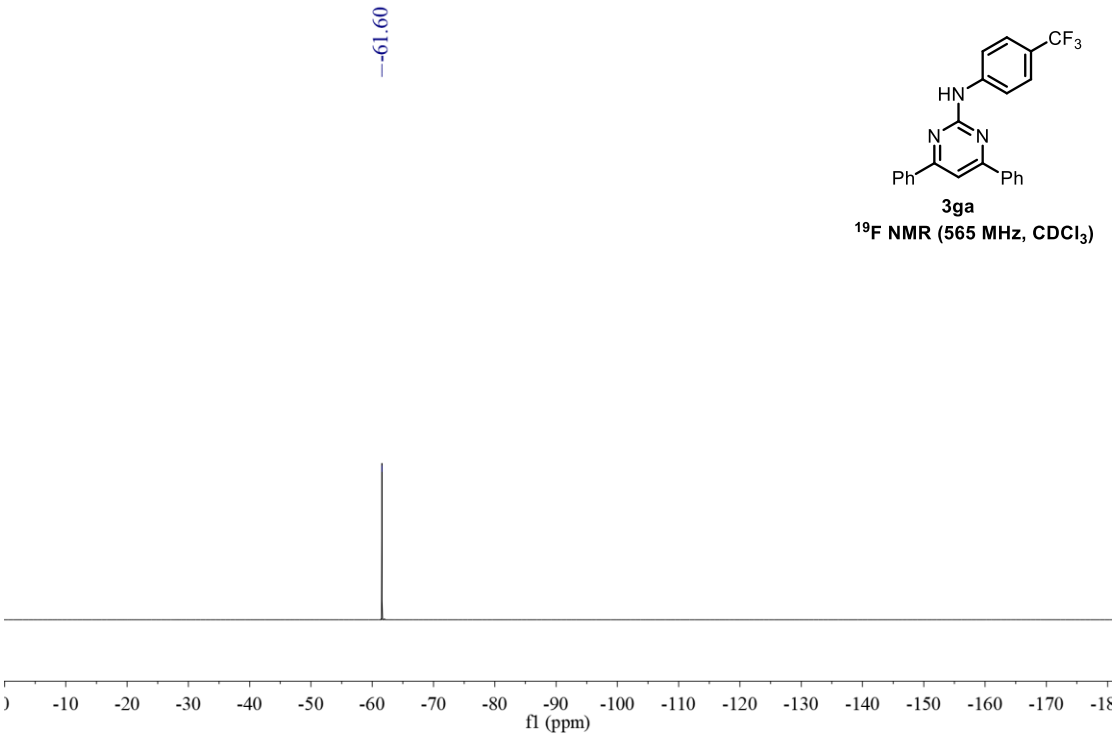
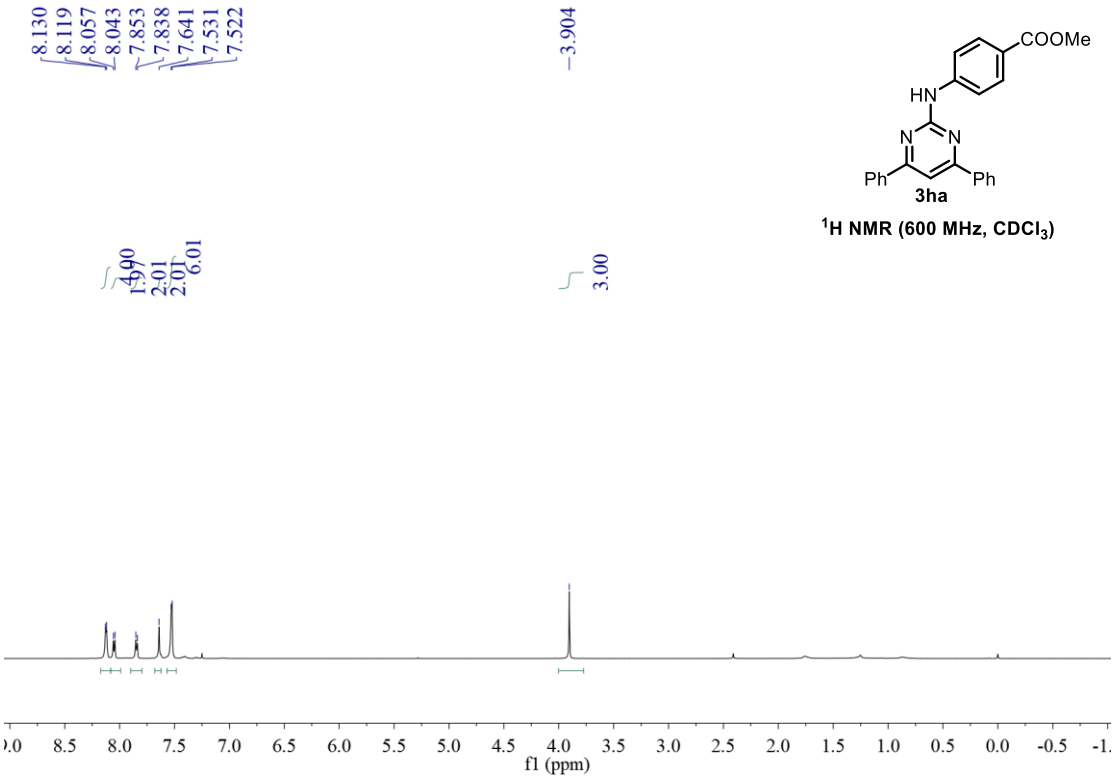
8.112
7.882
7.867
7.640
7.609
7.573
7.550
7.519
4.00
2.00
13.01
CF3
HN
N
N
Ph
Ph
3ga
1H NMR (600 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.10
160.10
143.20
137.42
131.04
129.09
127.33
126.34
126.32
125.55
123.81
123.76
123.59
118.30
105.67
CF3
HN
N
N
Ph
Ph
3ga
13C NMR (151 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

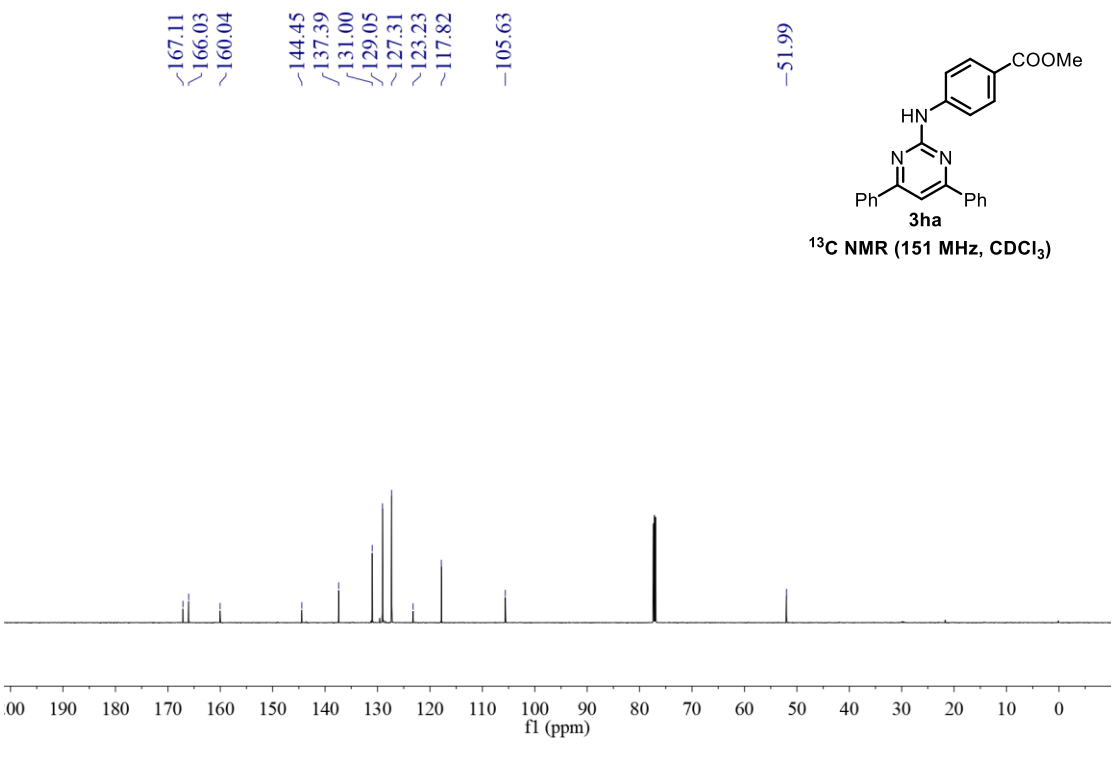


3ga

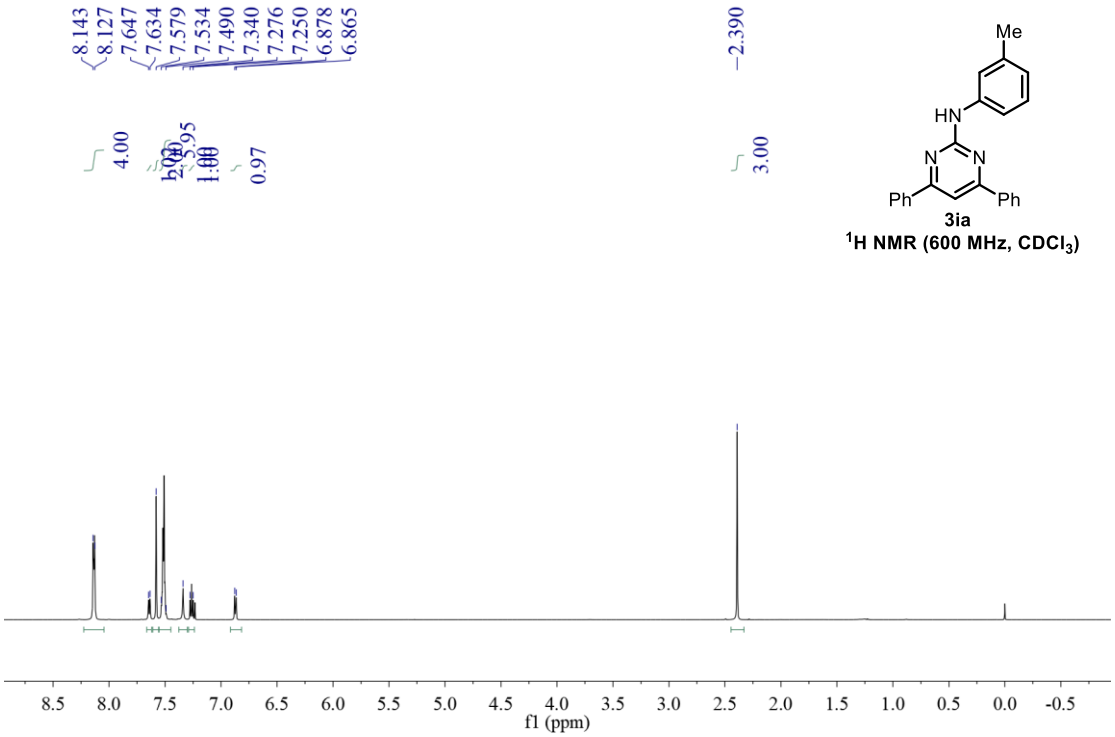
^{19}F NMR (565 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)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8.127
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7.579
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7.490
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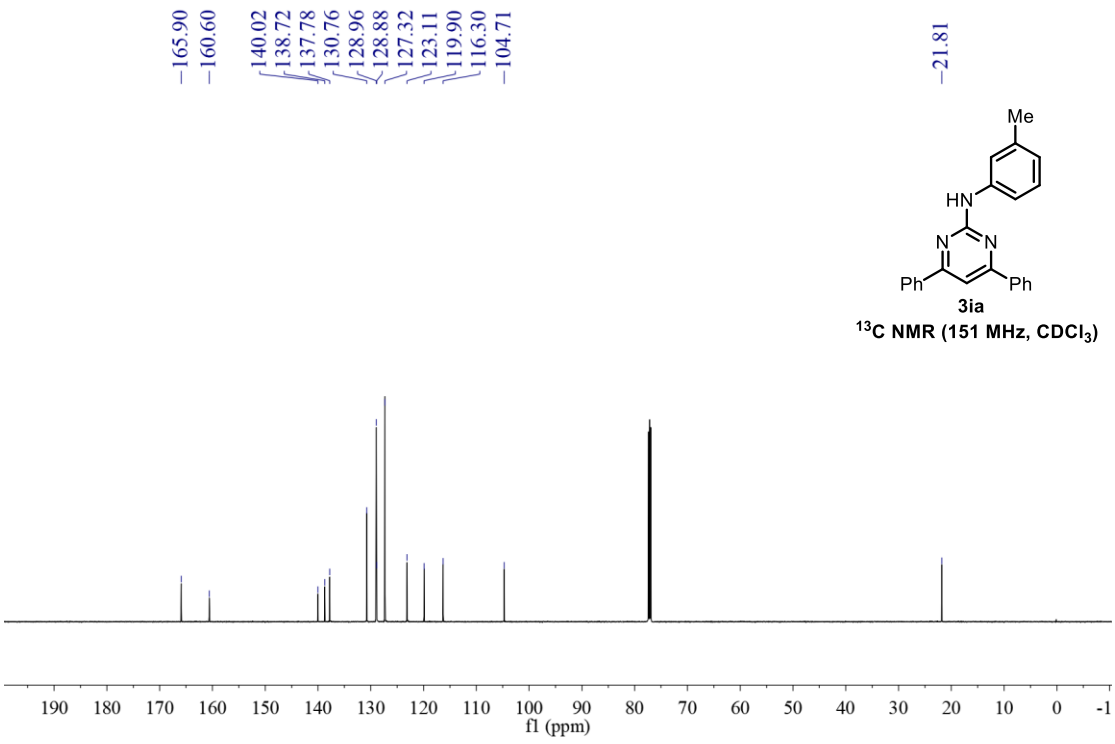
7.276
7.250
6.878
6.865
2.390
4.00
3.00
0.97
Me
HN
N
N
Ph
Ph
3ia
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)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137.78
130.76
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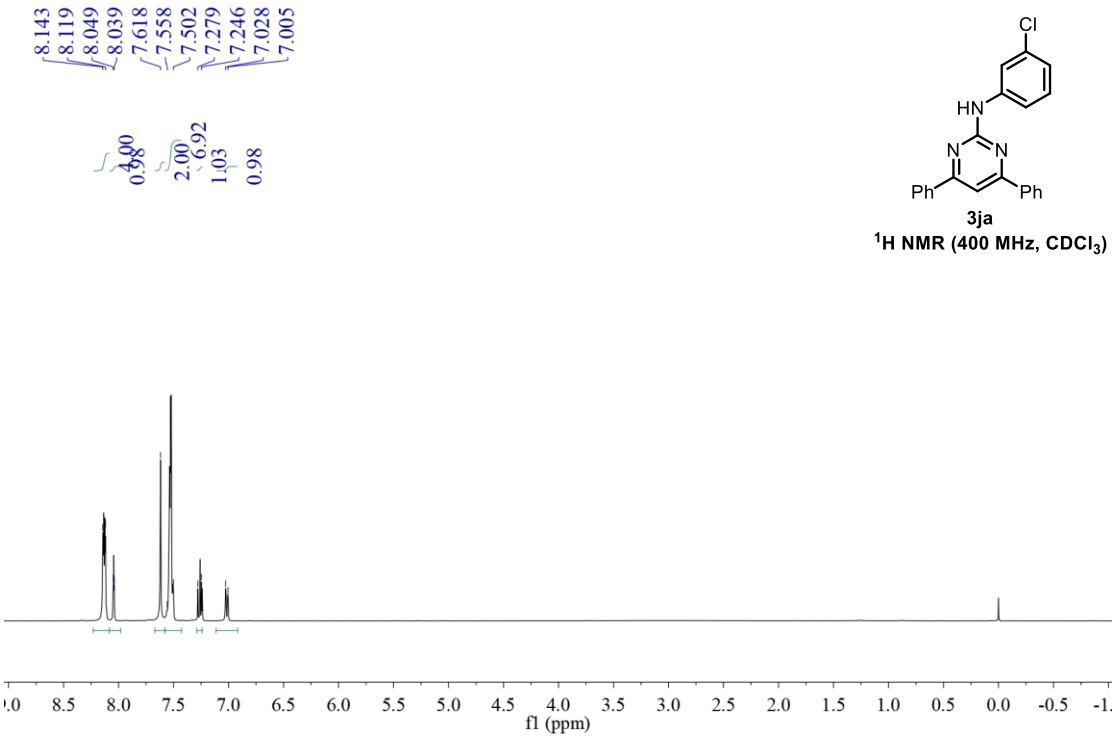
128.88
127.32
123.11
119.90
116.30
104.71
21.81
Me
HN
N
N
Ph
Ph
3ia
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)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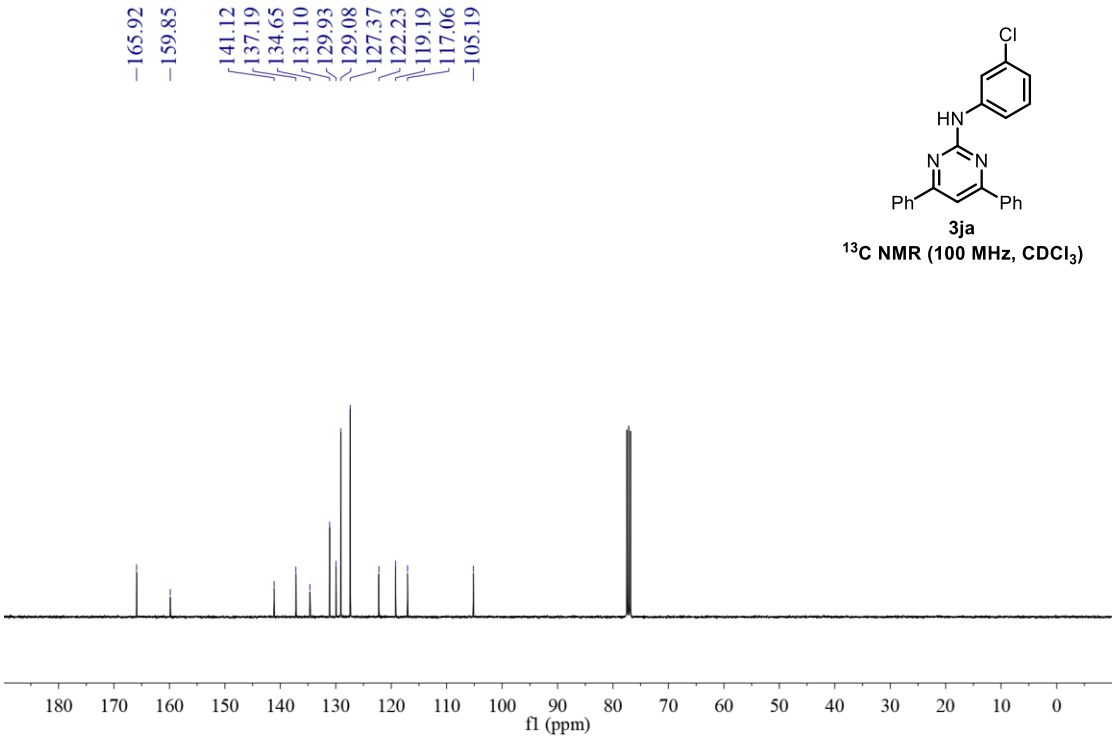
8.049
8.039
7.618
7.558
7.502
7.279
7.246
7.028
7.005
4.00
0.98
2.00
6.92
1.03
0.98
Cl
HN
N
N
Ph
Ph
3ja
1H NMR (400 MHz, CDCl3)
fl (ppm)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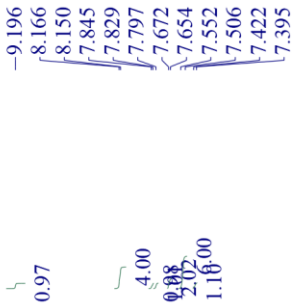
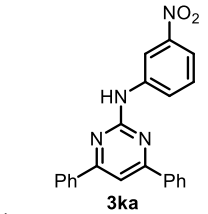
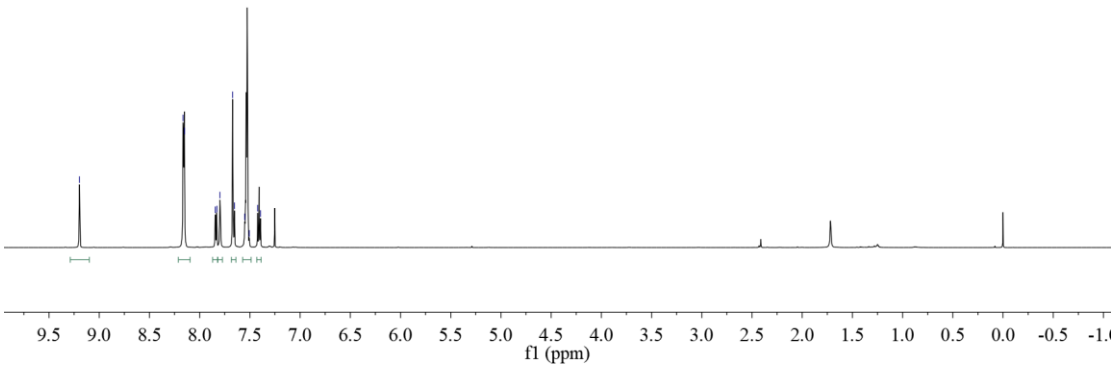
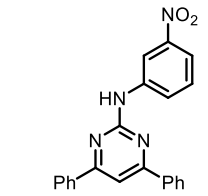
137.19
134.65
131.10
129.93
129.08
127.37
122.23
119.19
117.06
105.19
Cl
HN
N
N
Ph
Ph
3ja
13C NMR (100 MHz, CDCl3)
fl (ppm)



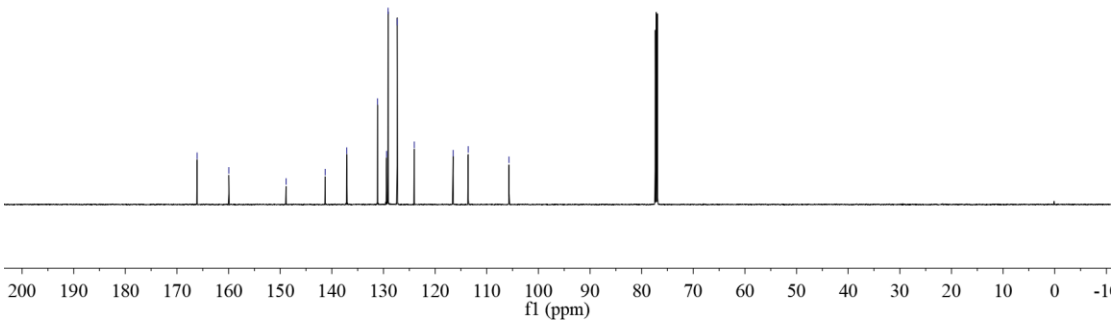


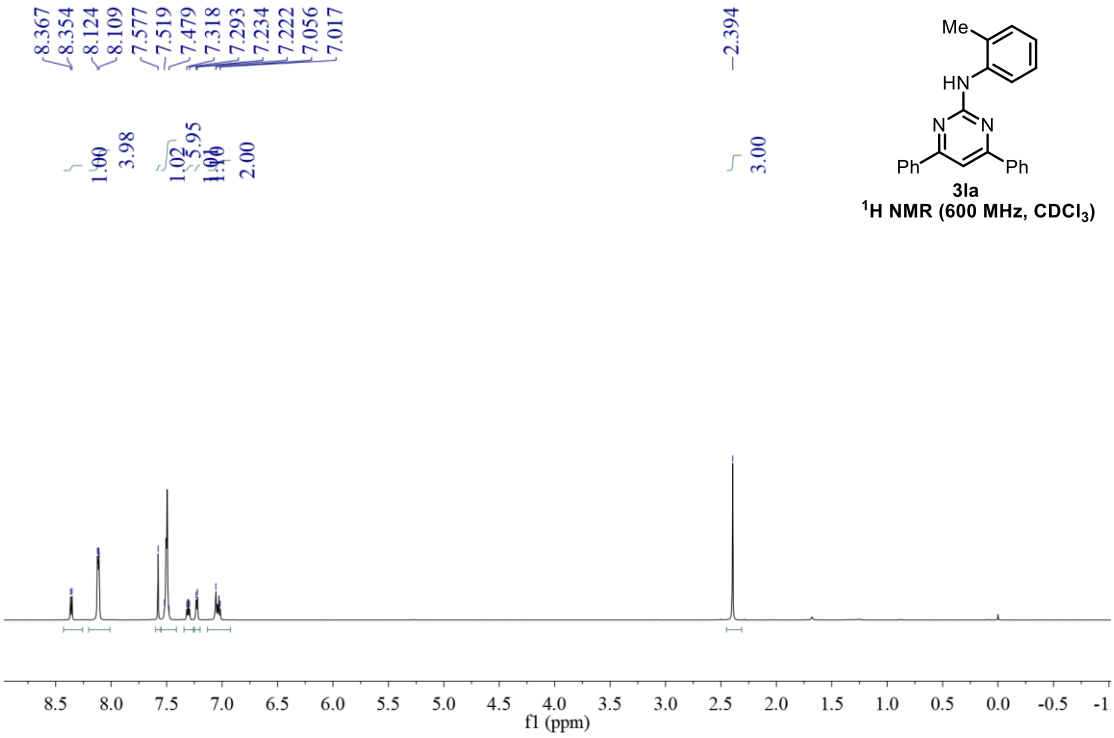
3ka
^{1}H NMR (600 MHz, $CDCl_3$)





3ka
^{13}C NMR (151 MHz, $CDCl_3$)

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8.109
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7.318
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7.234
7.222
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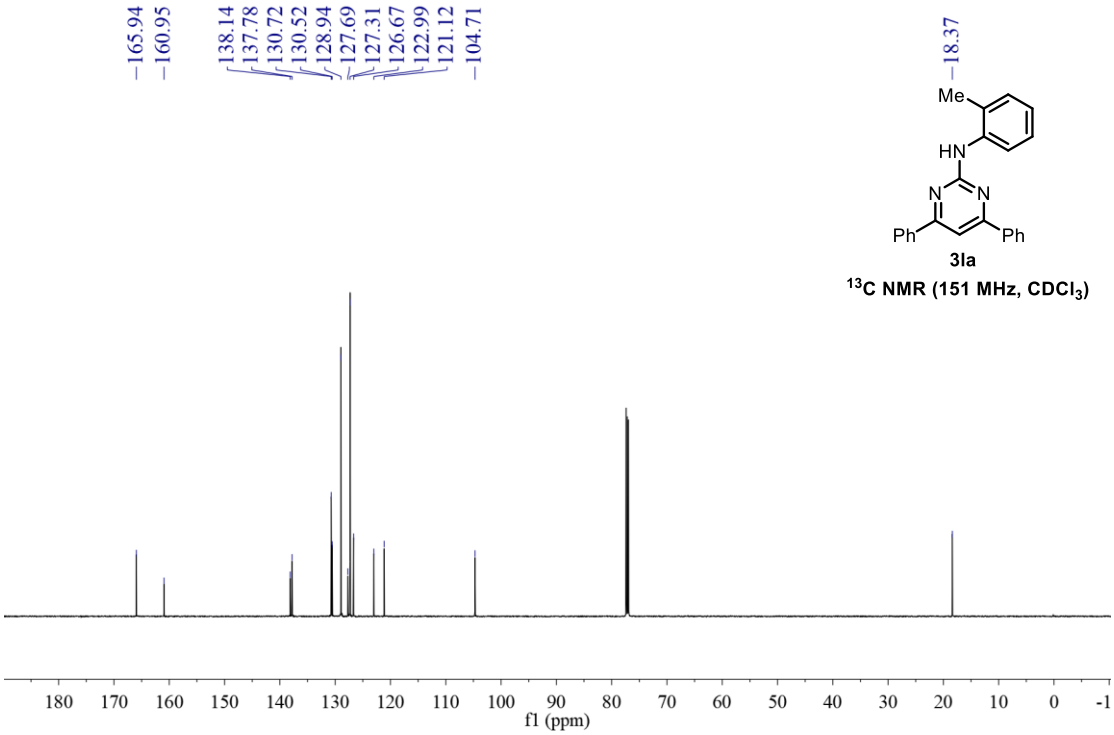
7.017
2.394
1.00
3.98
1.02
5.95
1.00
1.00
2.00
3.00
Me
HN
N
N
Ph
Ph
3la
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)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128.94
127.69
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126.67
122.99
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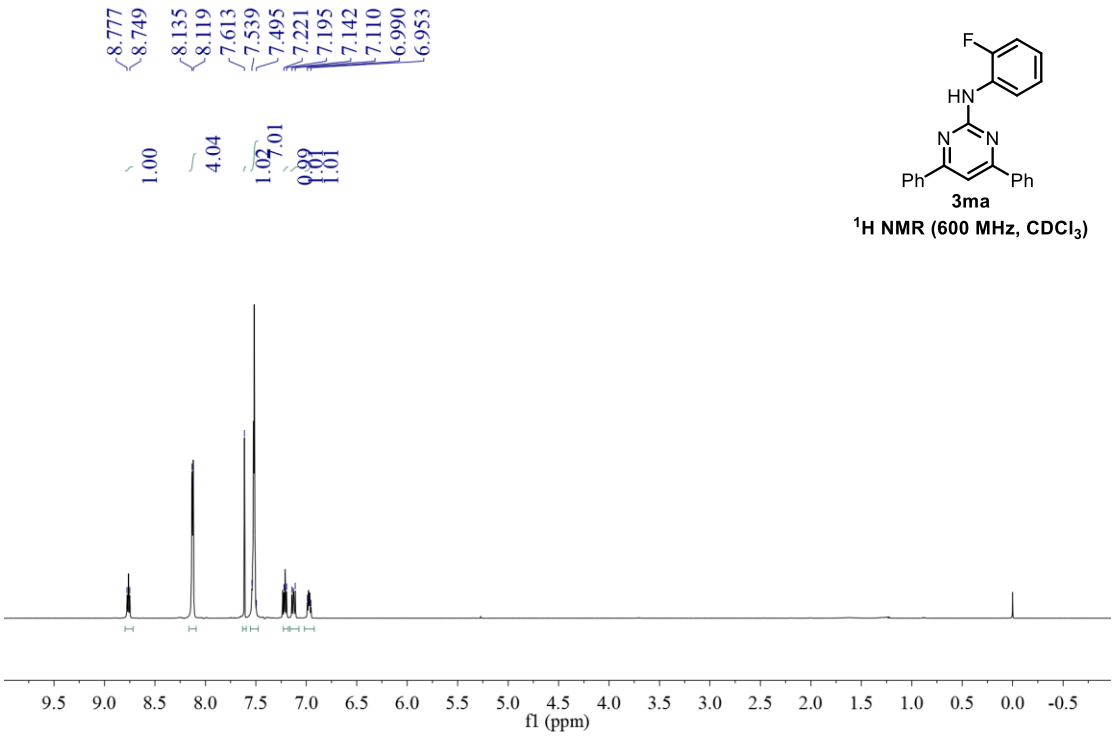
104.71
18.37
Me
HN
N
N
Ph
Ph
3la
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)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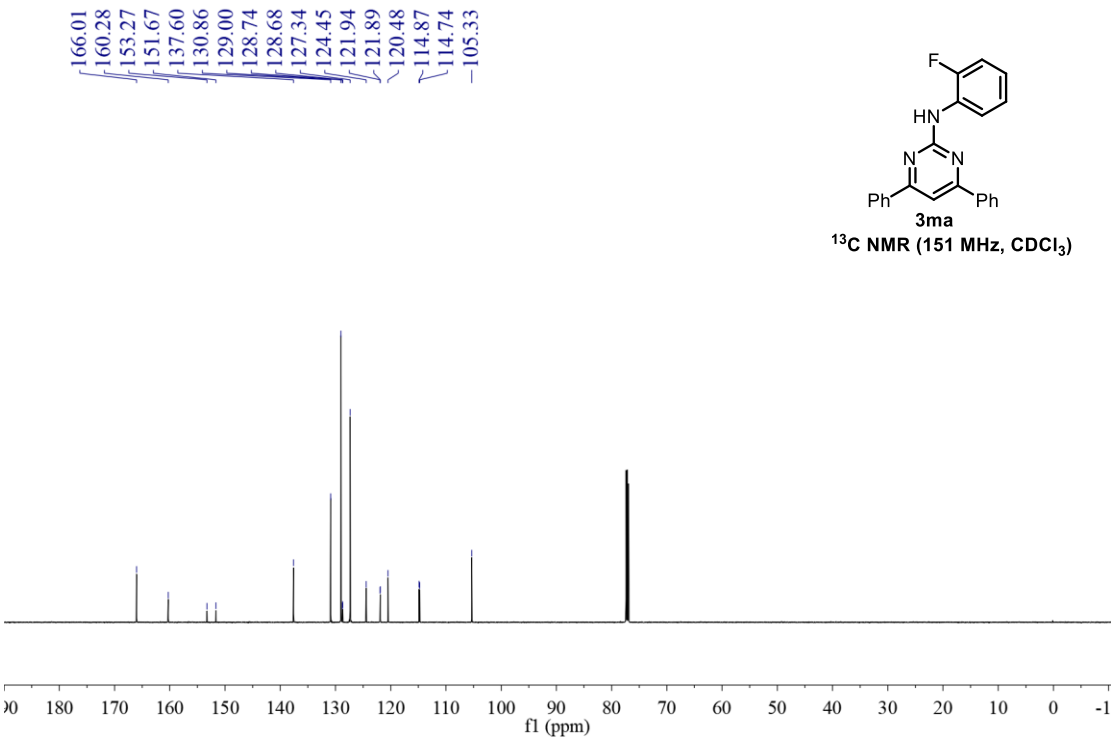
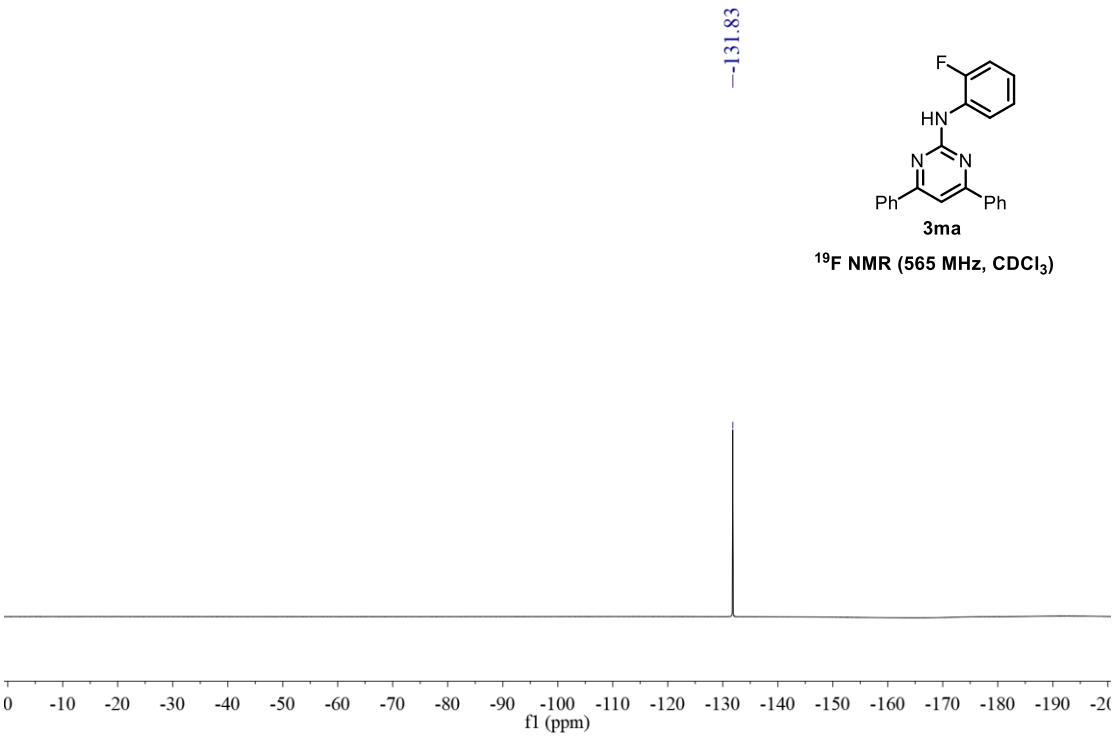
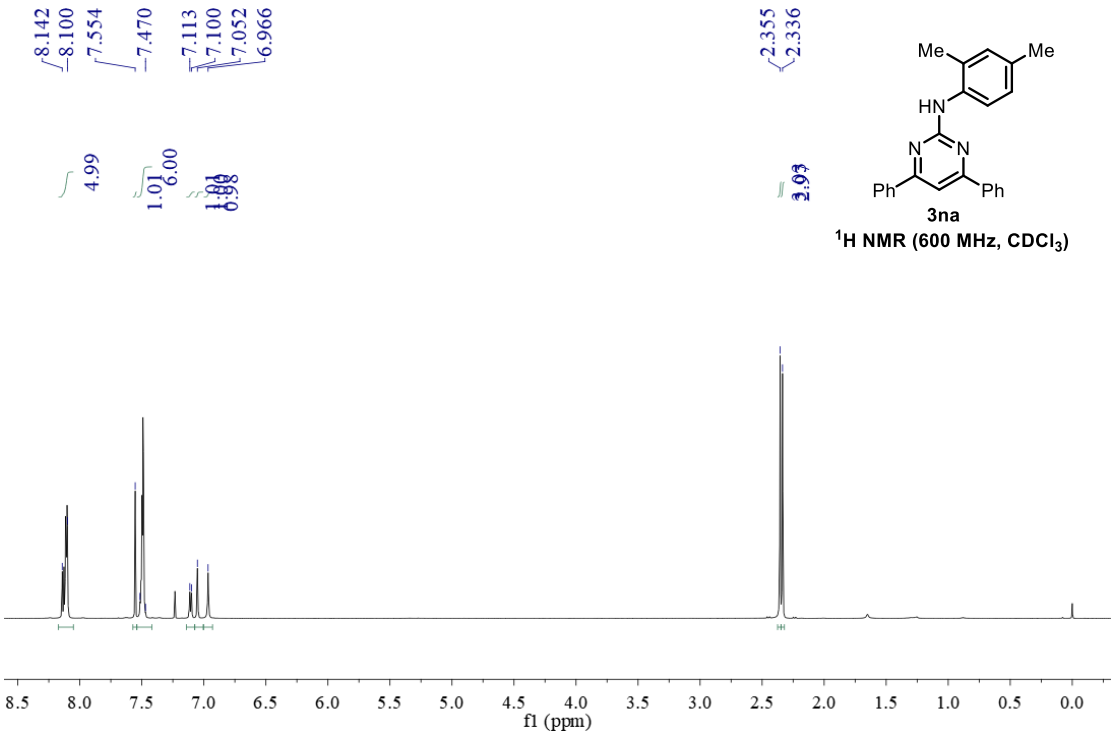
7.613
7.539
7.495
7.221
7.195
7.142
7.110
6.990
6.953
1.00
4.04
1.02
7.01
0.99
1.01
1.01
F
HN
N
N
Ph
Ph
3ma
^{1}H NMR (600 MHz, CDCl$_3$)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.01
160.28
153.27
151.67
137.60
130.86
129.00
128.74
128.68
127.34
124.45
121.94
121.89
120.48
114.87
114.74
105.33
F
HN
N
N
Ph
Ph
3ma
^{13}C NMR (151 MHz, CDCl$_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

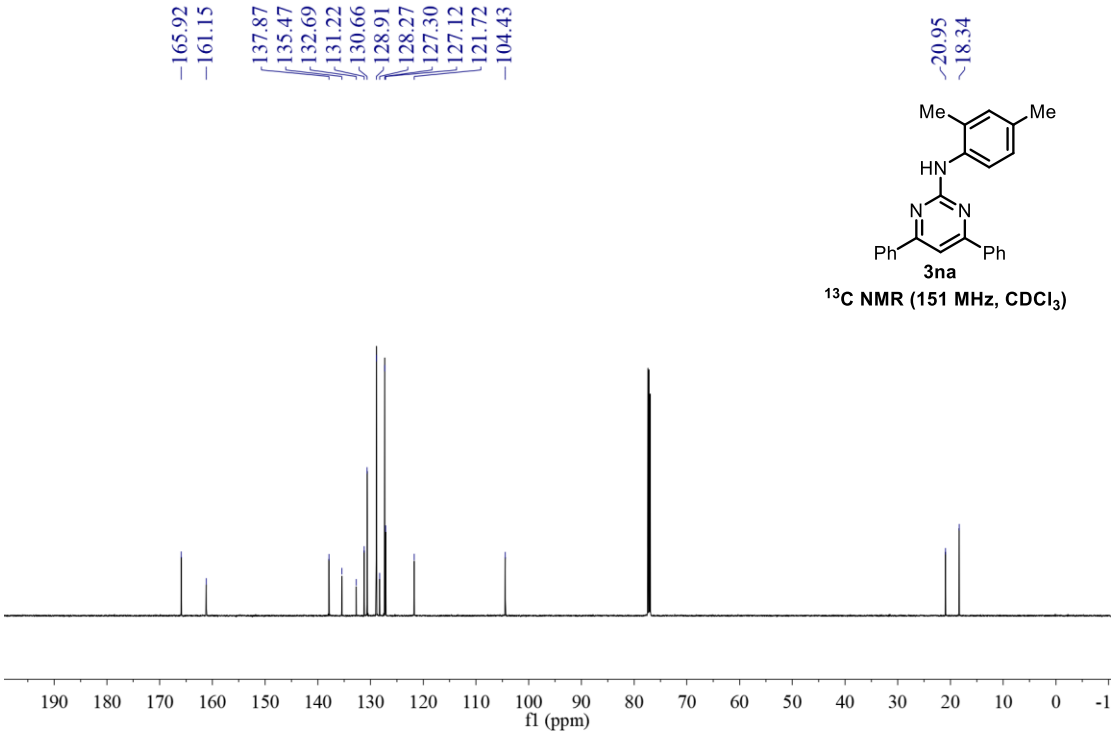


3ma

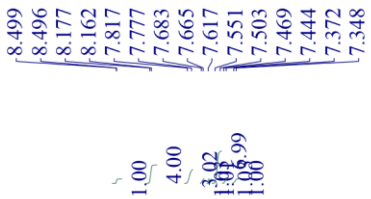
^{19}F NMR (565 MHz, $CDCl_3$)

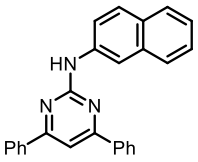


^{1}H NMR (600 MHz, $CDCl_3$)



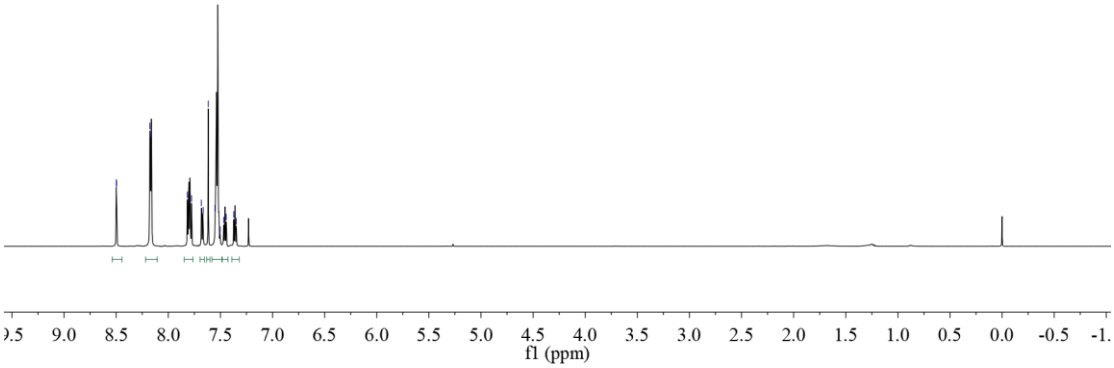
^{13}C NMR (151 MHz, $CDCl_3$)

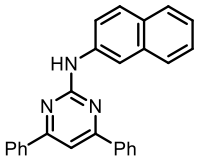




3oa

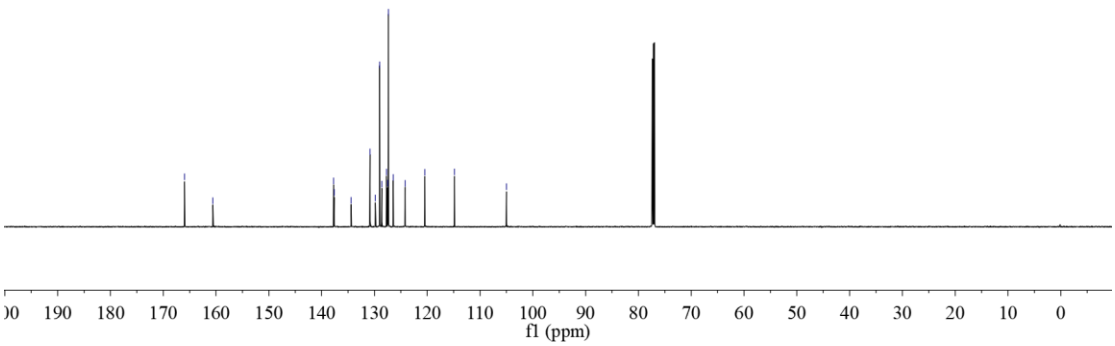
^{1}H NMR (600 MHz, $CDCl_3$)

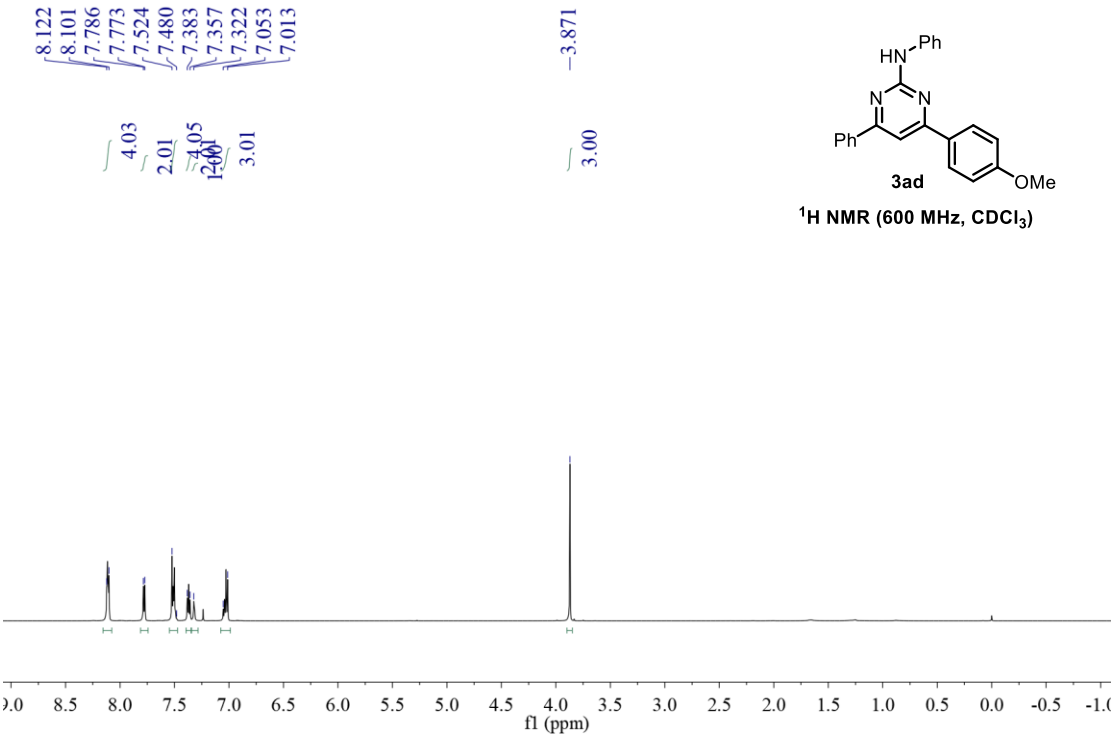




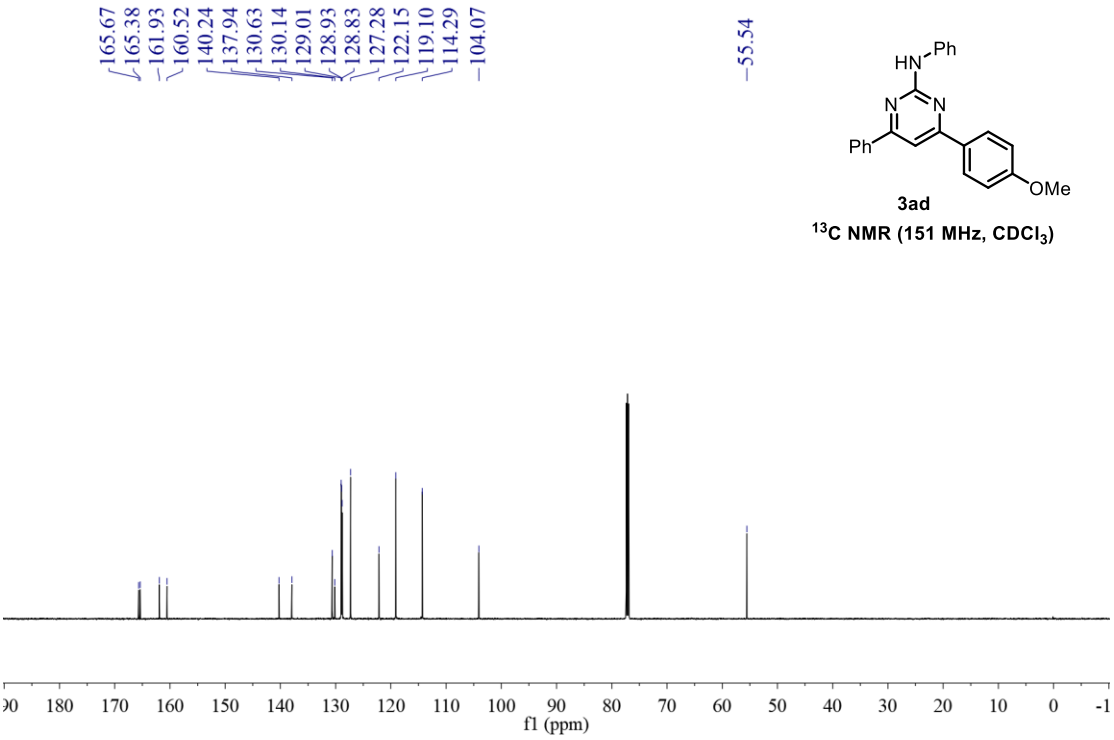
3oa

^{13}C NMR (151 MHz, $CDCl_3$)

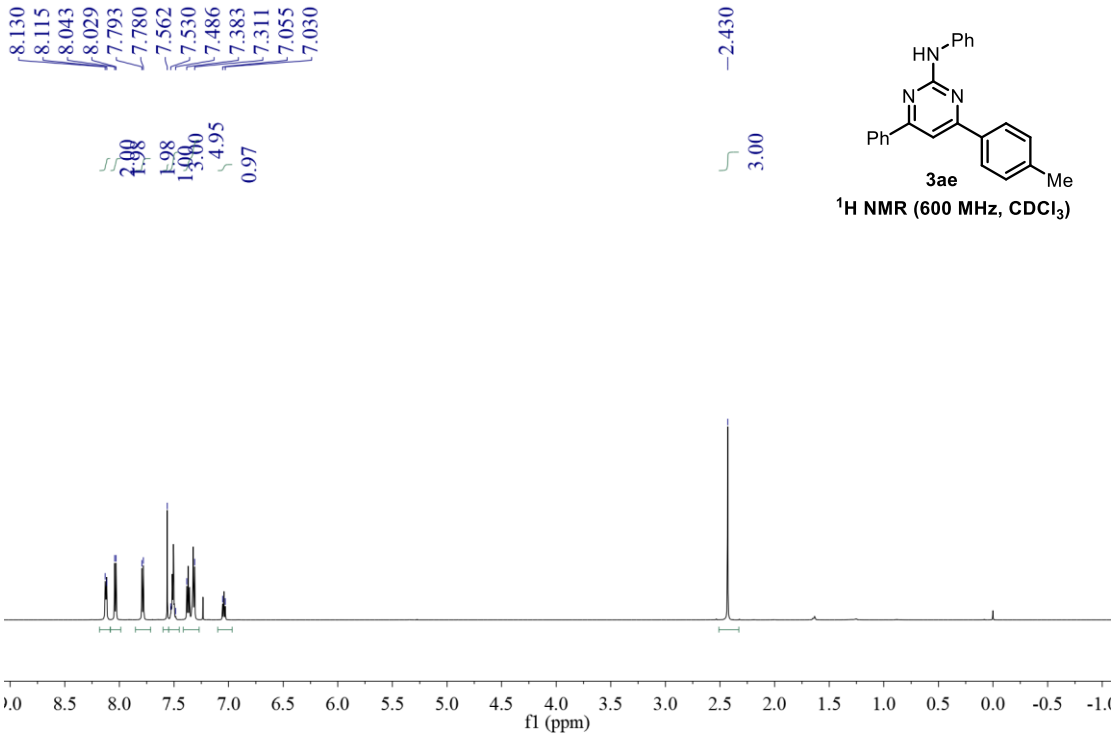




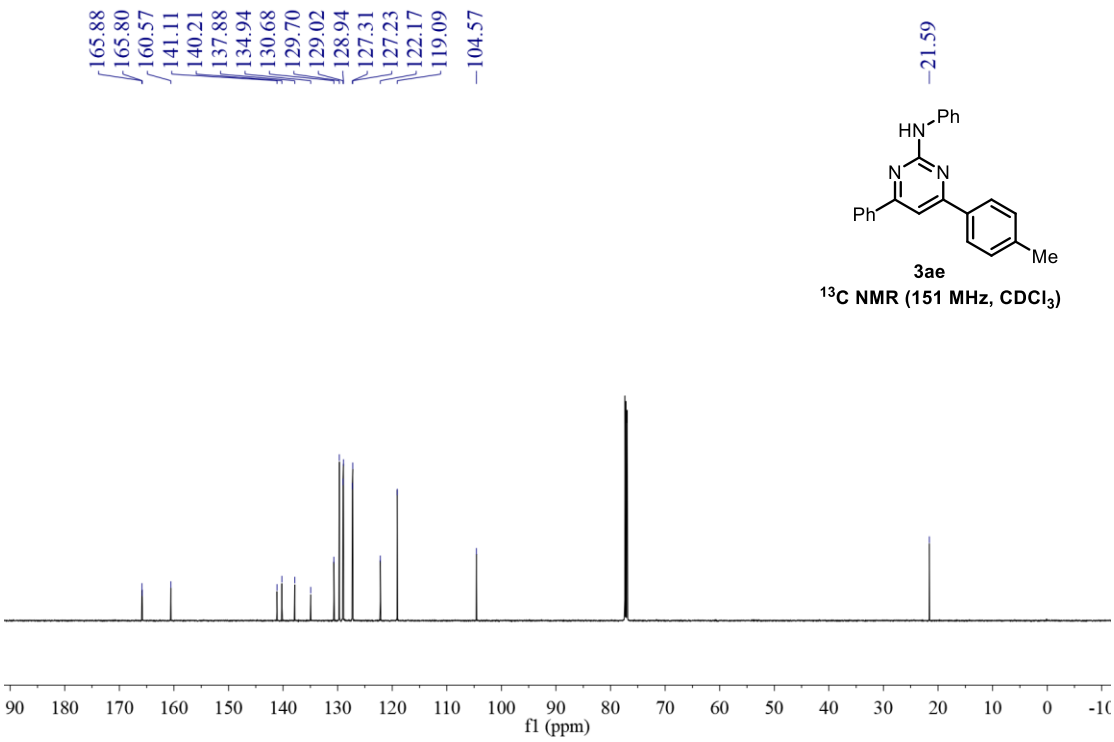
^{1}H NMR (600 MHz, $CDCl_3$)



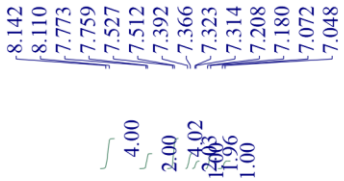
^{13}C NMR (151 MHz, $CDCl_3$)

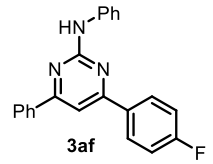


^{1}H NMR (600 MHz, $CDCl_3$)



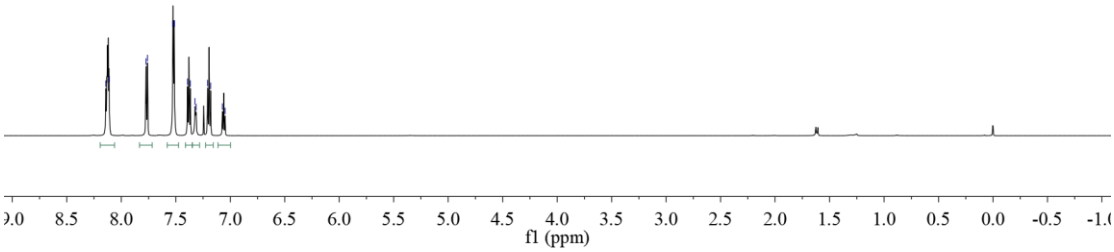
^{13}C NMR (151 MHz, $CDCl_3$)

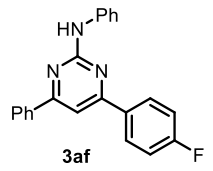




3af

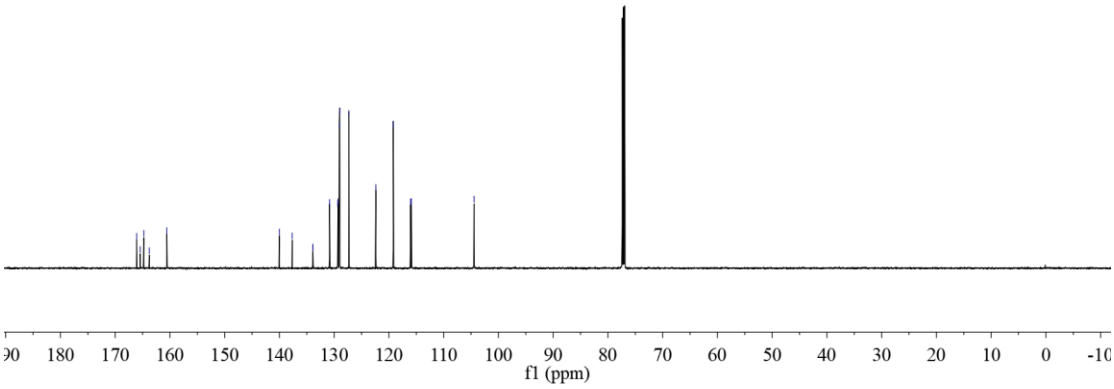
^{1}H NMR (600 MHz, $CDCl_3$)

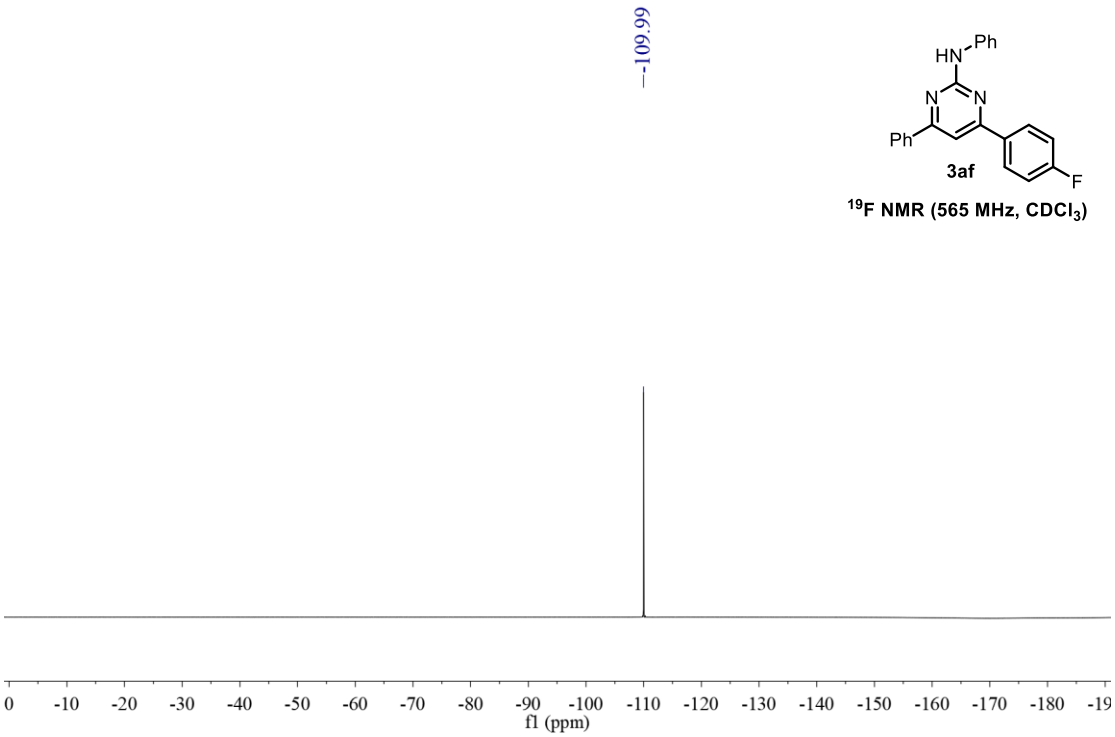




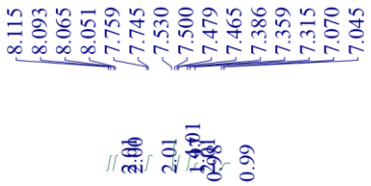
3af

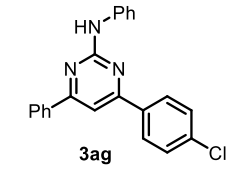
^{13}C NMR (151 MHz, $CDCl_3$)





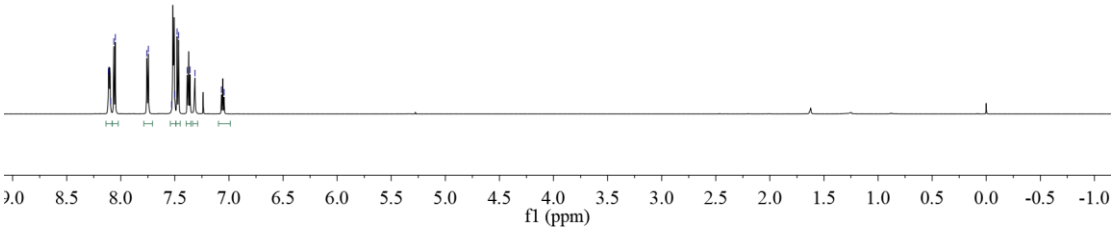
^{19}F NMR (565 MHz, $CDCl_3$)

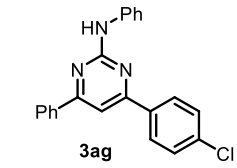




3ag

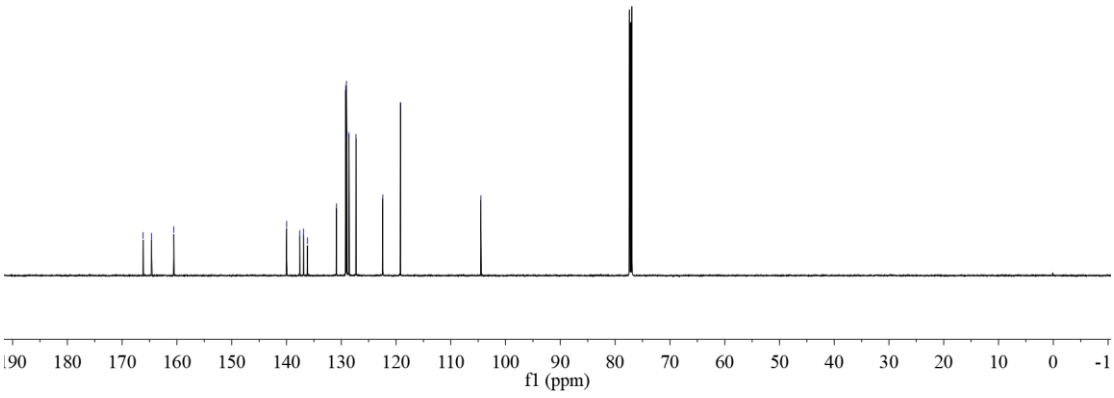
^{1}H NMR (600 MHz, $CDCl_3$)

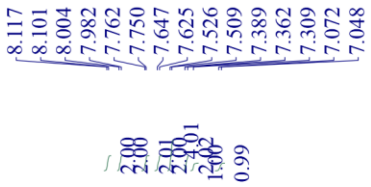


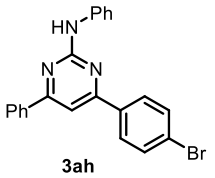


3ag

^{13}C NMR (151 MHz, $CDCl_3$)

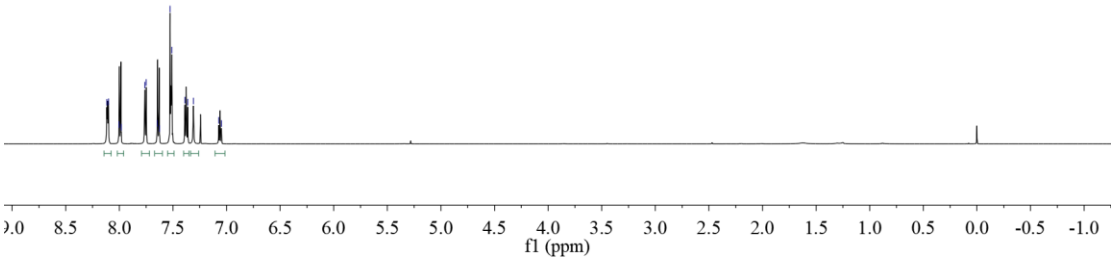


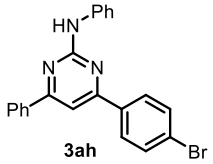




3ah

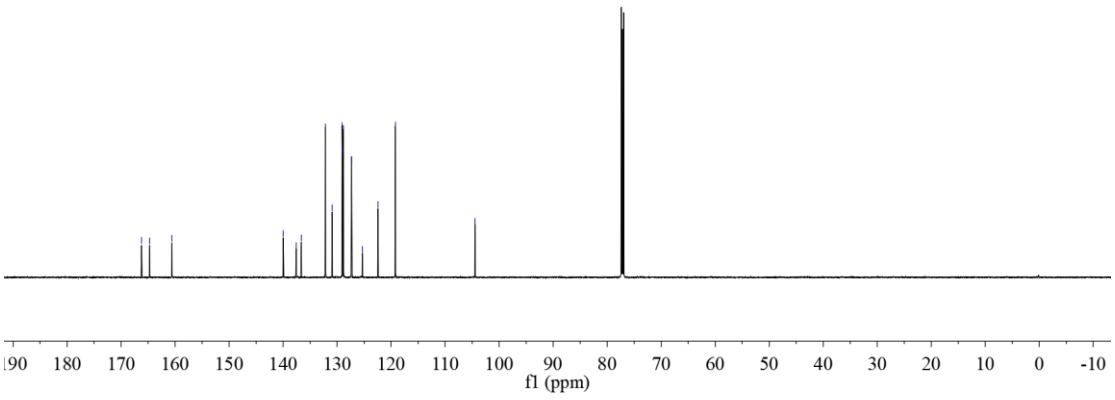
^{1}H NMR (600 MHz, $CDCl_3$)

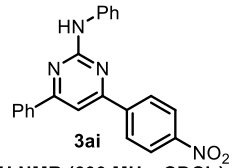




3ah

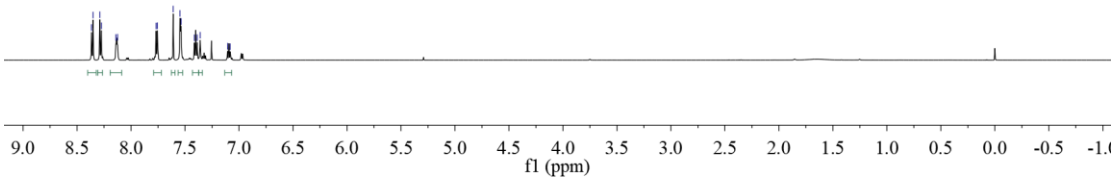
^{13}C NMR (151 MHz, $CDCl_3$)

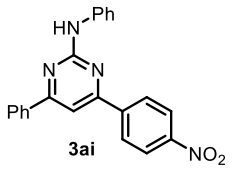




3ai

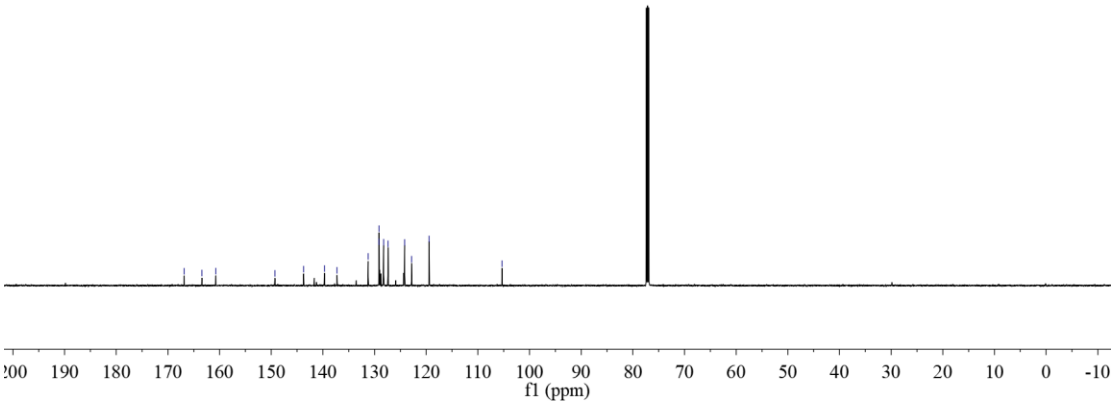
^{1}H NMR (600 MHz, $CDCl_3$)

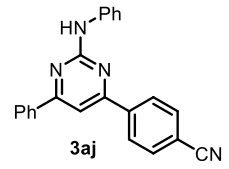




3ai

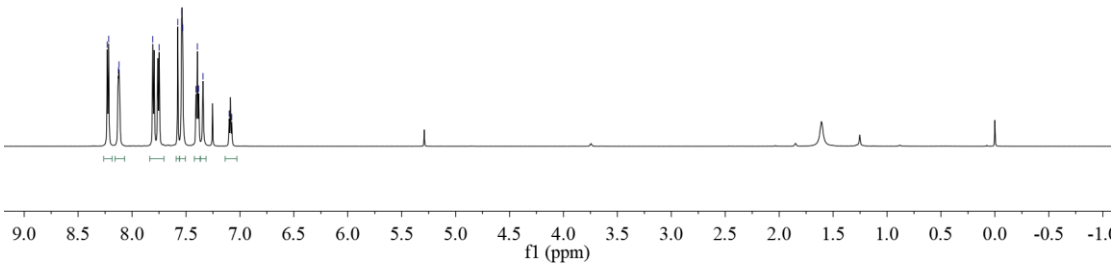
^{13}C NMR (151 MHz, $CDCl_3$)

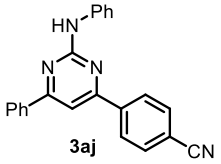




3aj

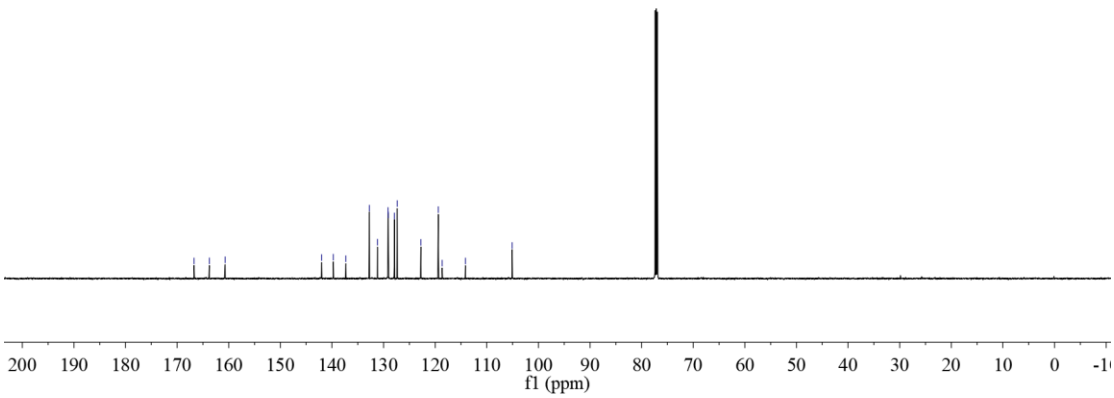
^{1}H NMR (600 MHz, $CDCl_3$)

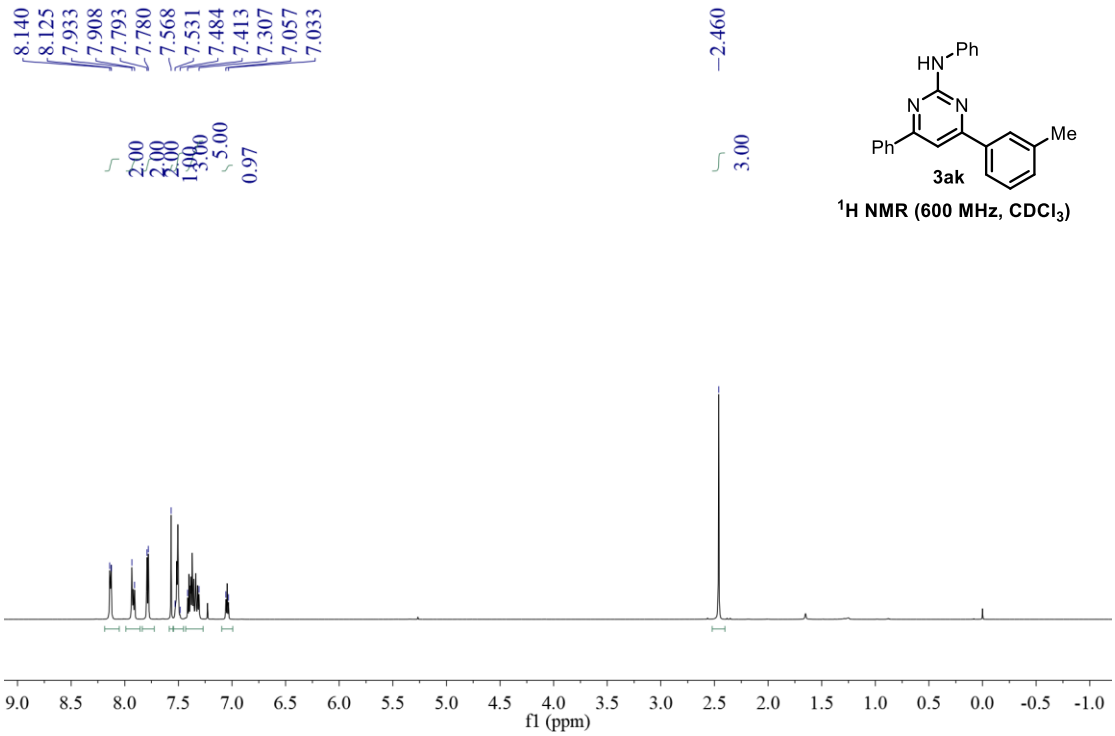




3aj

^{13}C NMR (151 MHz, $CDCl_3$)

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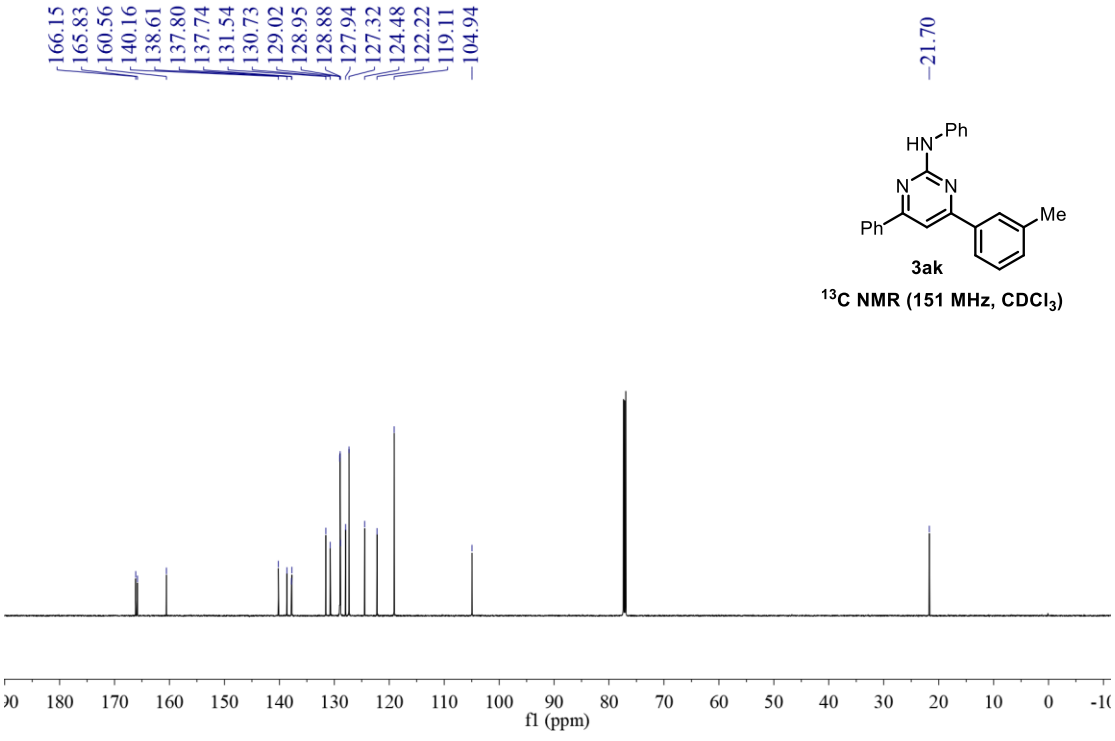
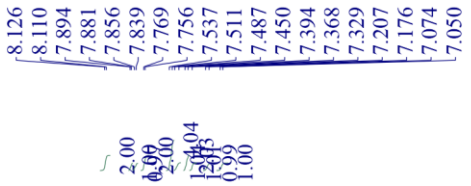
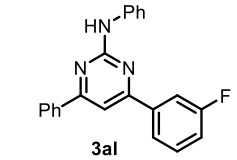
8.125
7.933
7.908
7.793
7.780
7.568
7.531
7.484
7.413
7.307
7.057
7.033
2.460
2.00
2.00
2.00
2.00
1.00
3.00
5.00
0.97
3.00
HN
Ph
N
N
Ph
Me
3ak
^{1}H NMR (600 MHz, CDCl$_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

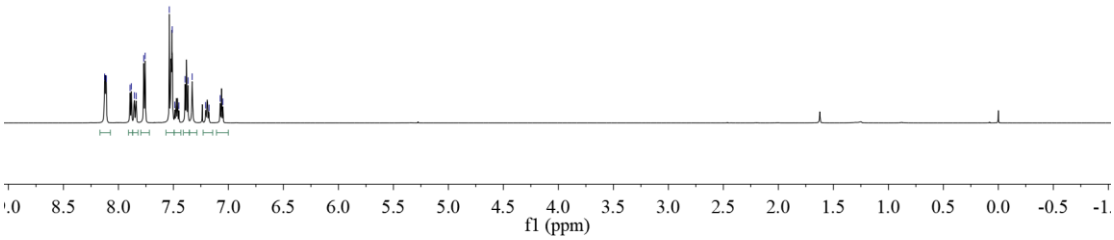

166.15
165.83
160.56
140.16
138.61
137.80
137.74
131.54
130.73
129.02
128.95
128.88
127.94
127.32
124.48
122.22
119.11
104.94
21.70
HN
Ph
N
N
Ph
Me
3ak
^{13}C NMR (151 MHz, CDCl$_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

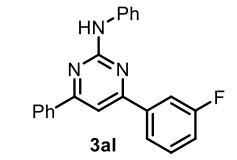




3al

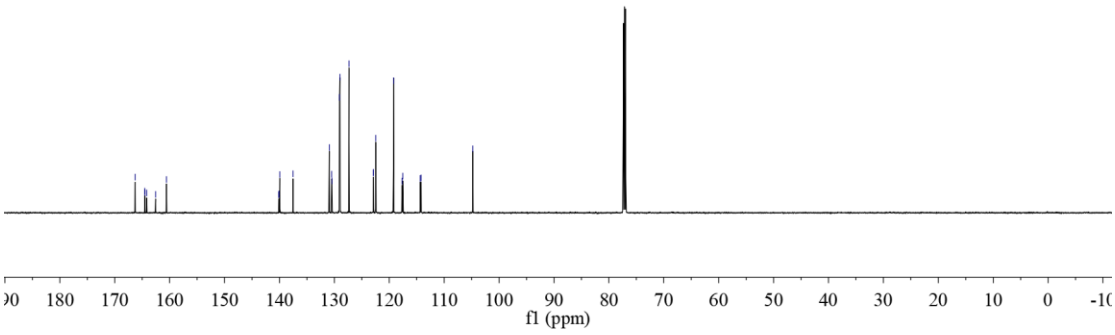
^{1}H NMR (600 MHz, $CDCl_3$)

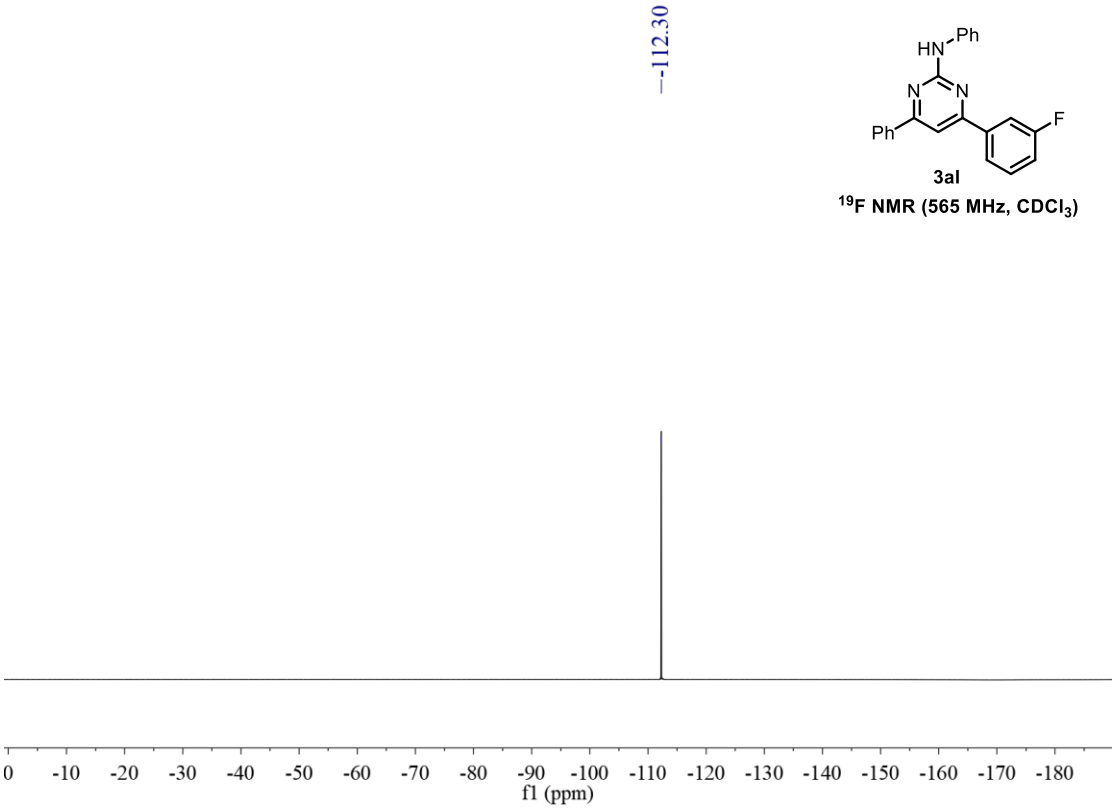




3al

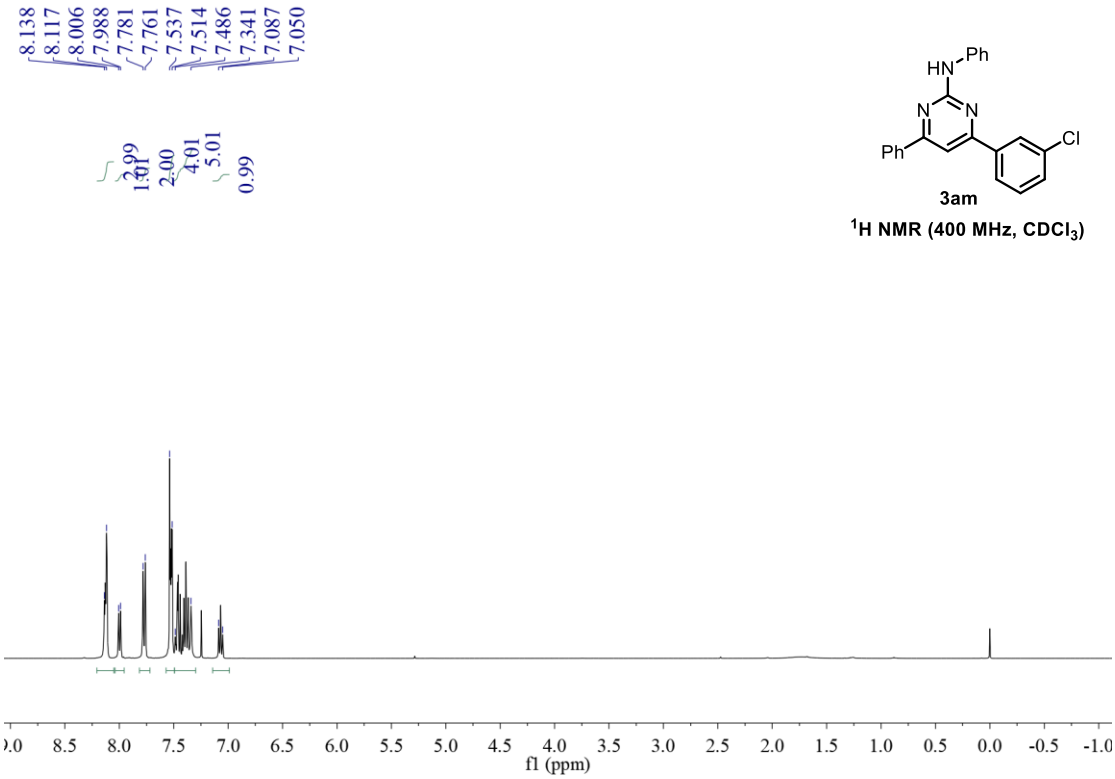
^{13}C NMR (151 MHz, $CDCl_3$)

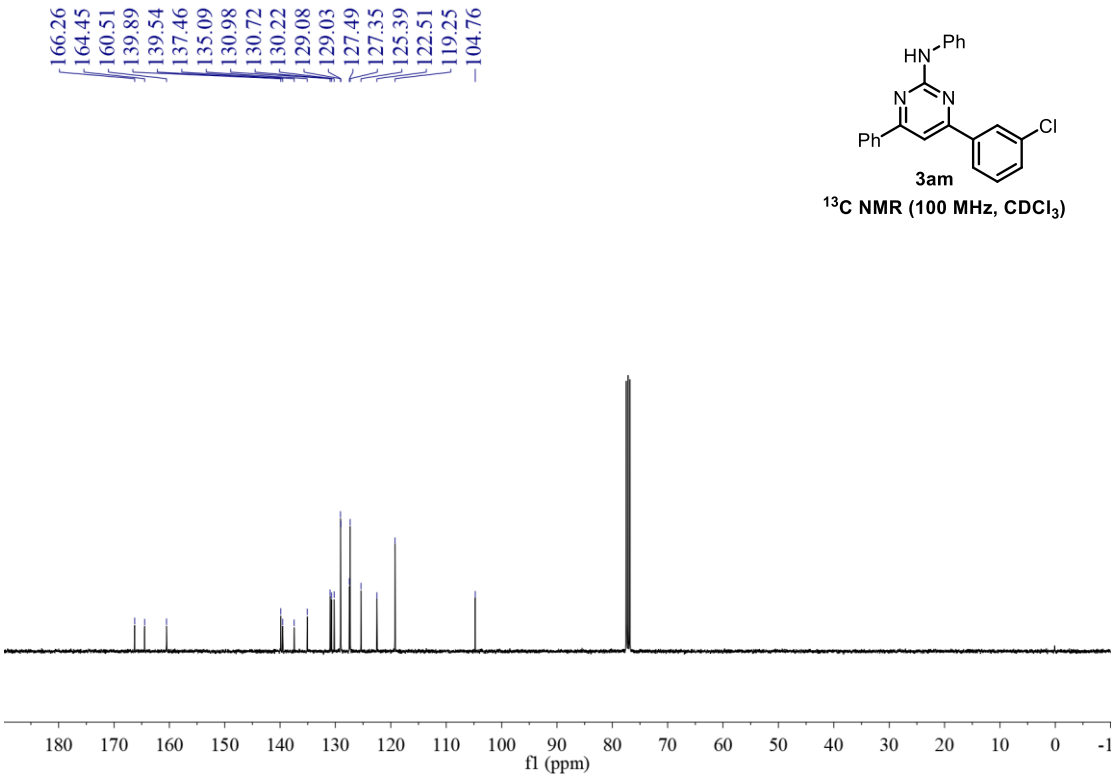


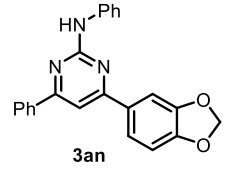


3al

^{19}F NMR (565 MHz, $CDCl_3$)

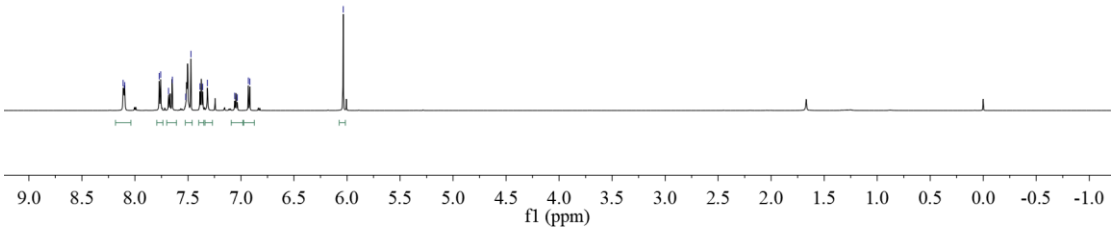

8.138
8.117
8.006
7.988
7.781
7.761
7.537
7.514
7.486
7.341
7.087
7.050
2.99
1.01
2.00
4.01
5.01
0.99
HN
Ph
N
N
Ph
Cl
3am
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

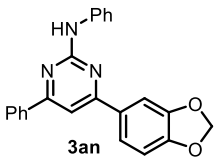

166.26
164.45
160.51
139.89
139.54
137.46
135.09
130.98
130.72
130.22
129.08
129.03
127.49
127.35
125.39
122.51
119.25
104.76
HN
Ph
N
N
Ph
Cl
3am
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



3an

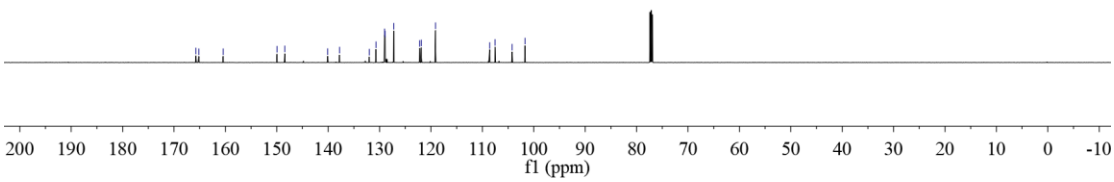
^{1}H NMR (600 MHz, $CDCl_3$)

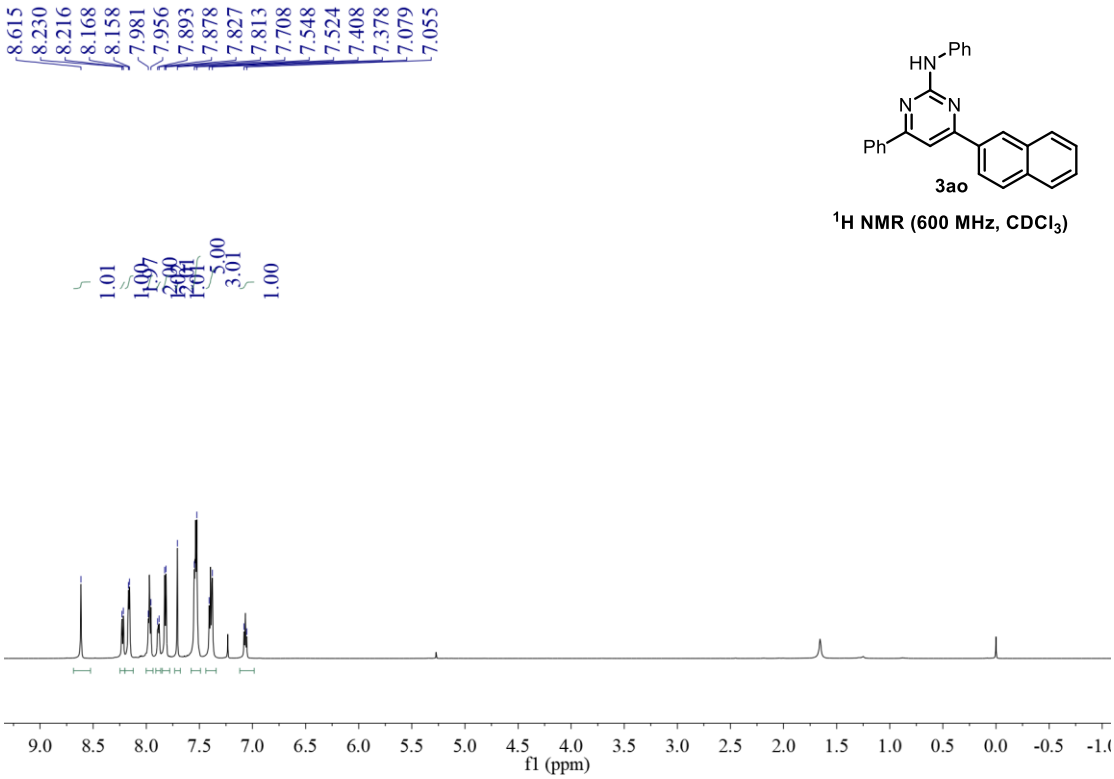




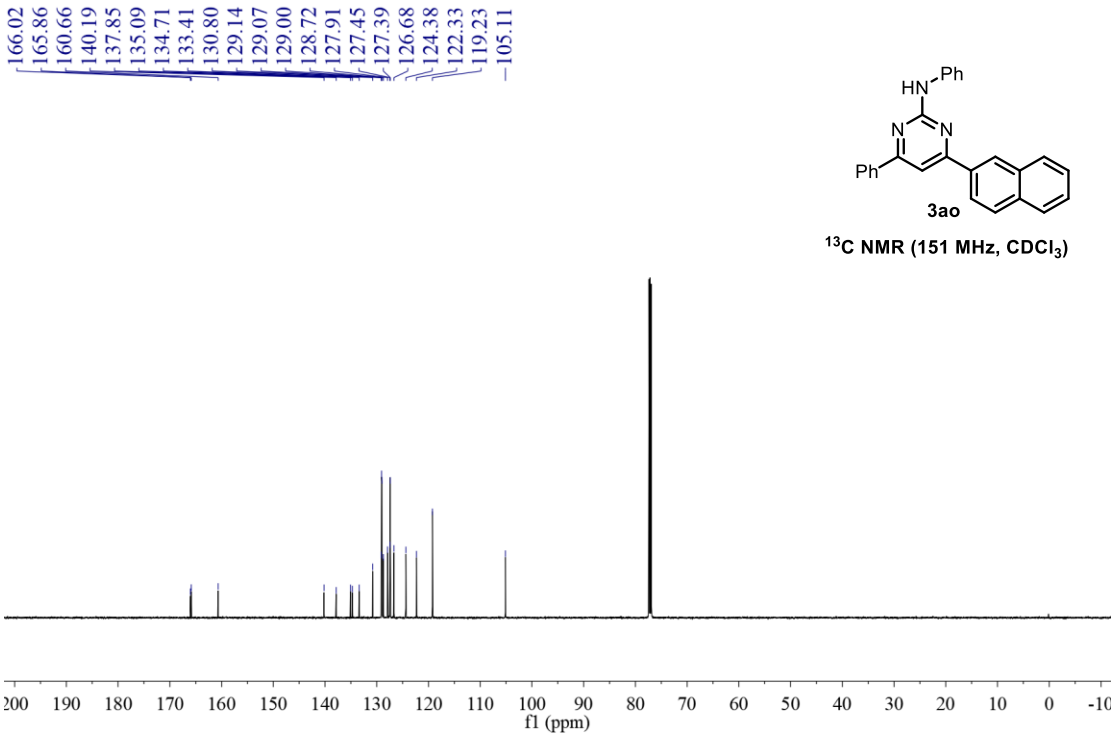
3an

^{13}C NMR (151 MHz, $CDCl_3$)

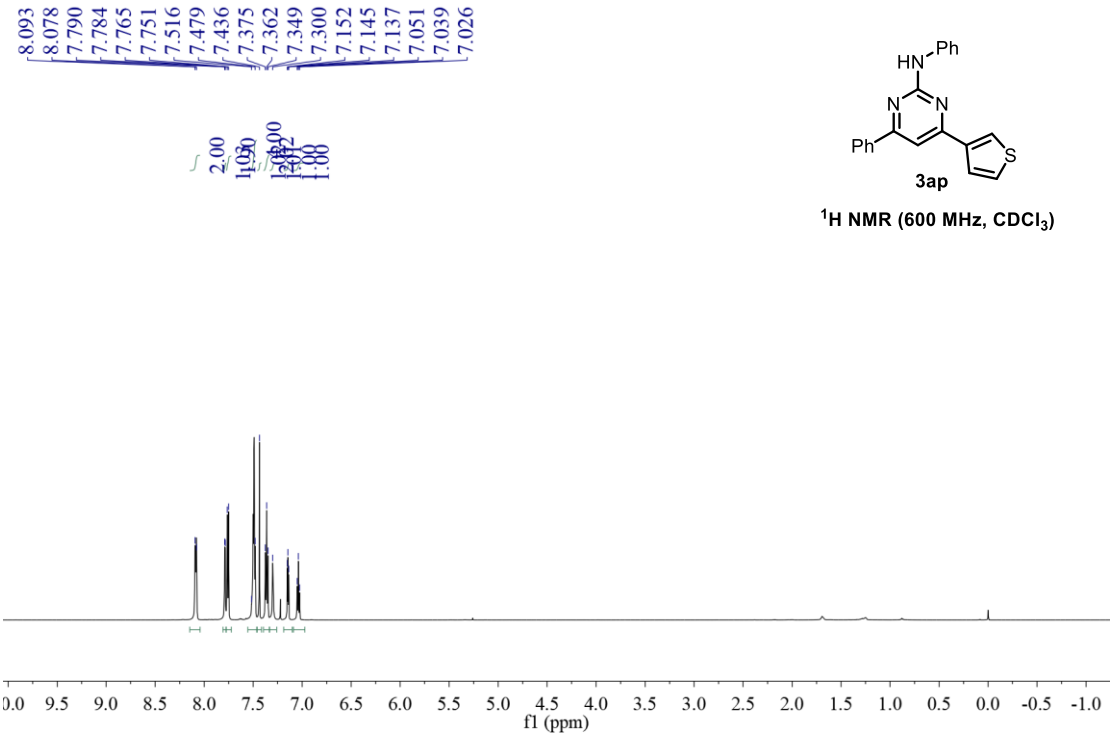




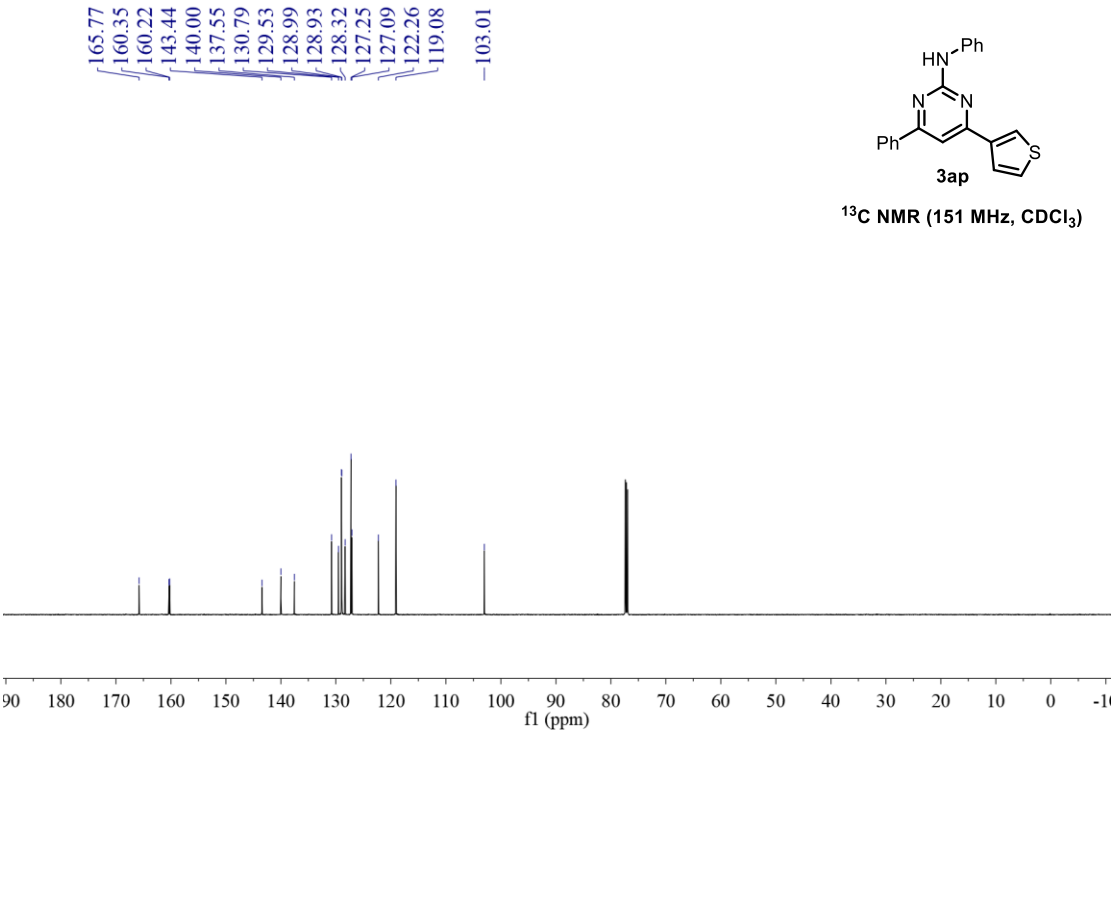
^{1}H NMR (600 MHz, $CDCl_3$)



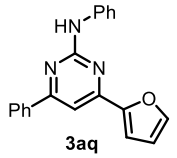
^{13}C NMR (151 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

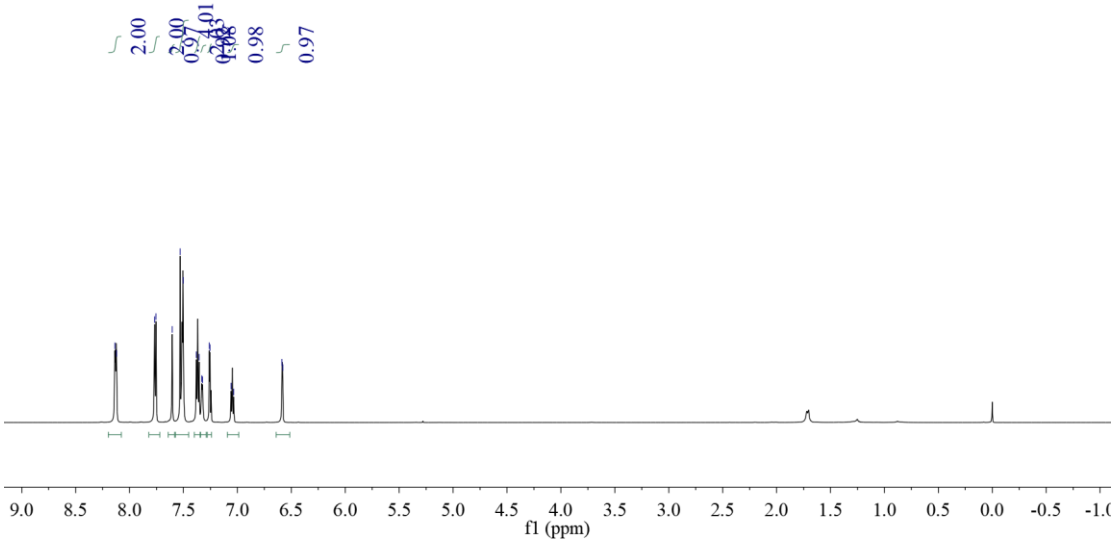


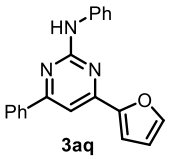
^{13}C NMR (151 MHz, $CDCl_3$)



3aq

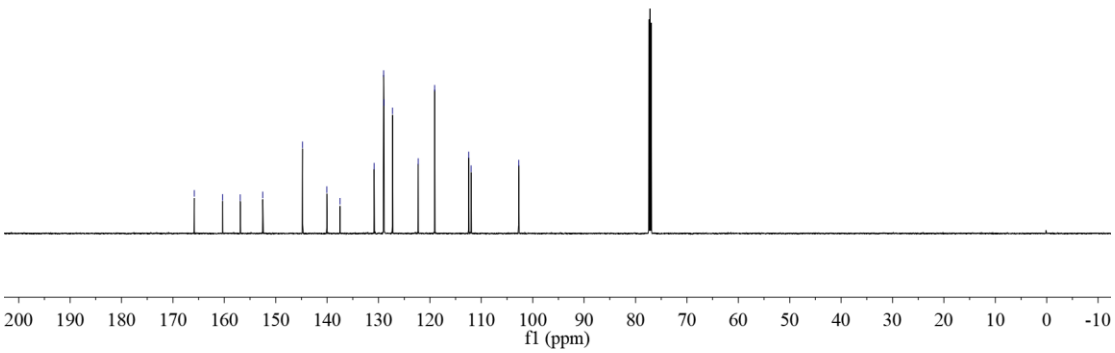
^{1}H NMR (600 MHz, $CDCl_3$)

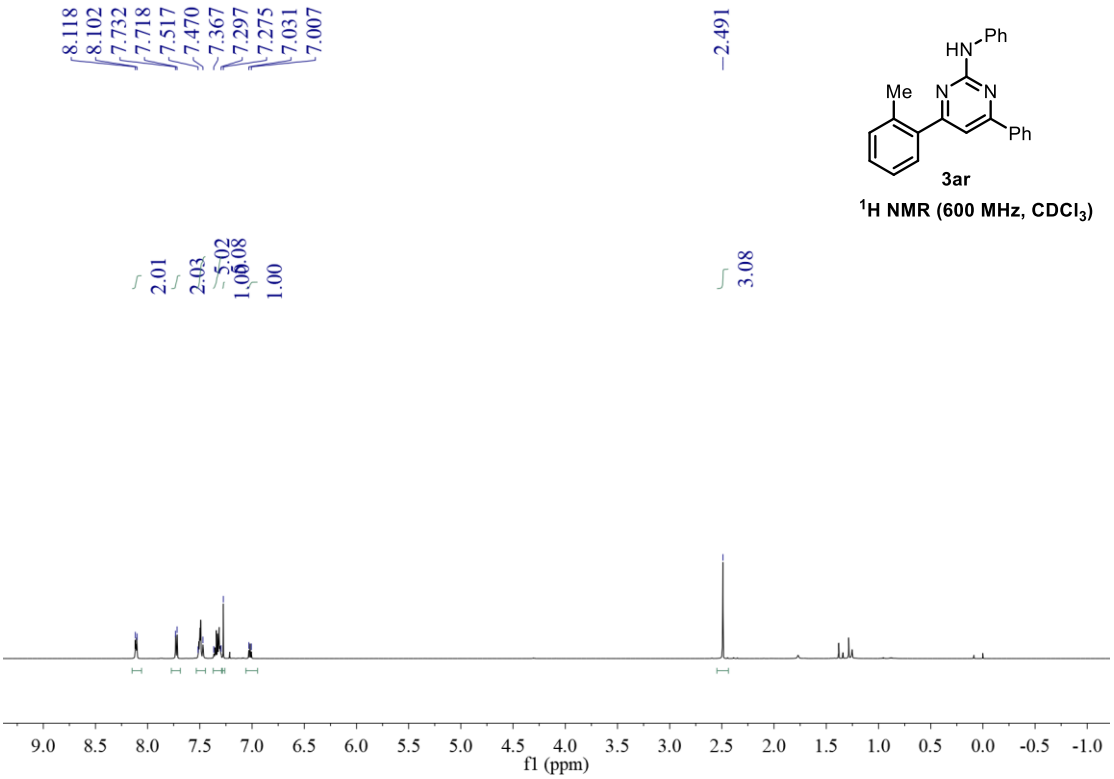




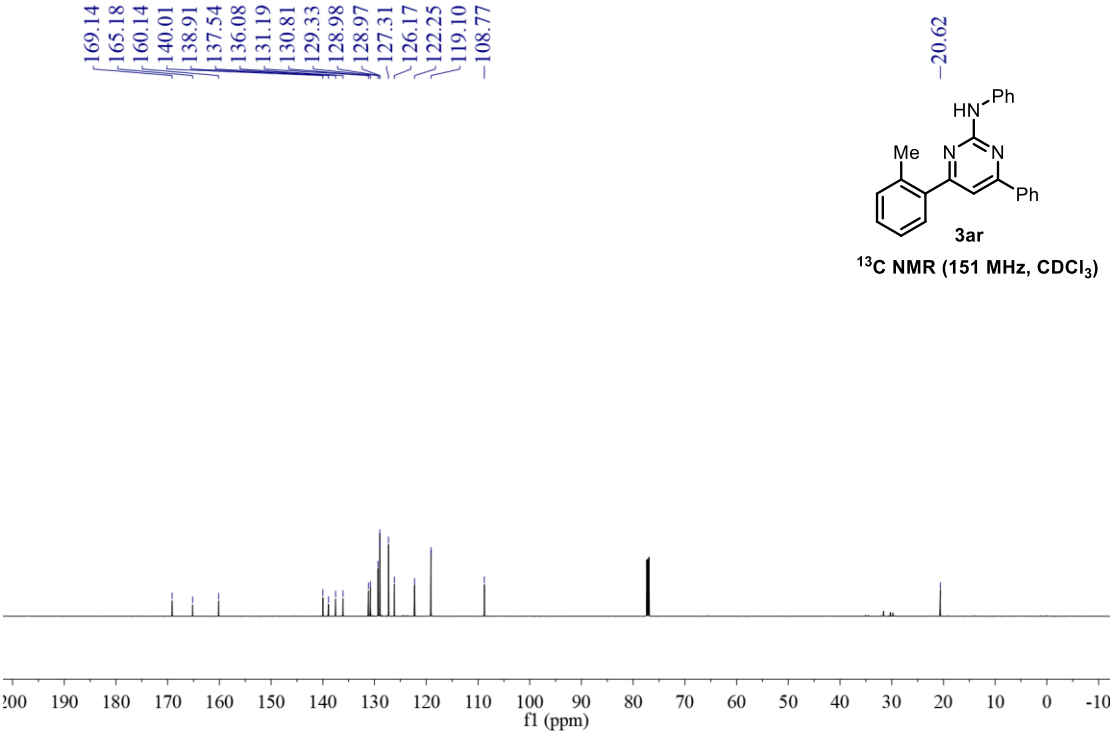
3aq

^{13}C NMR (151 MHz, $CDCl_3$)

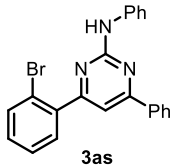




^{1}H NMR (600 MHz, $CDCl_3$)

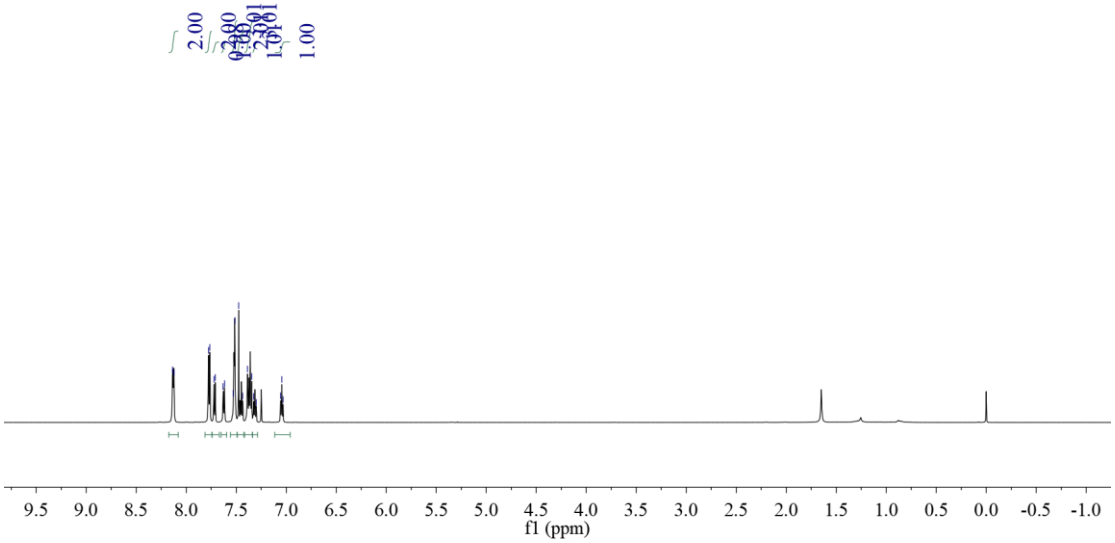


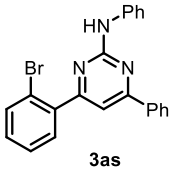
^{13}C NMR (151 MHz, $CDCl_3$)



3as

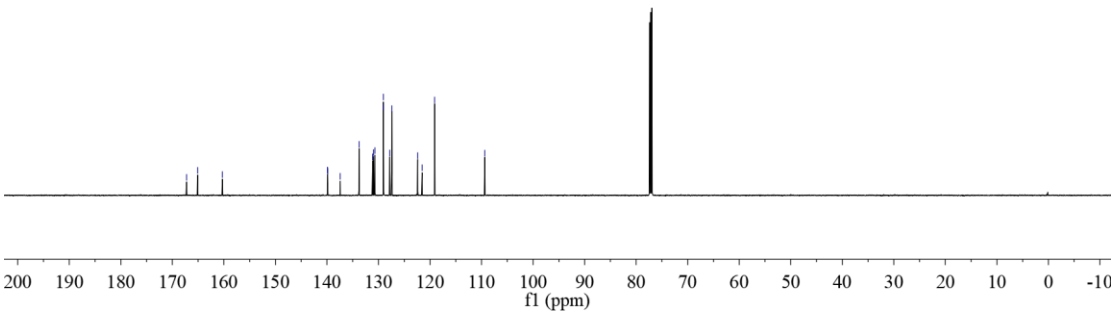
^{1}H NMR (600 MHz, $CDCl_3$)

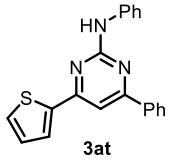




3as

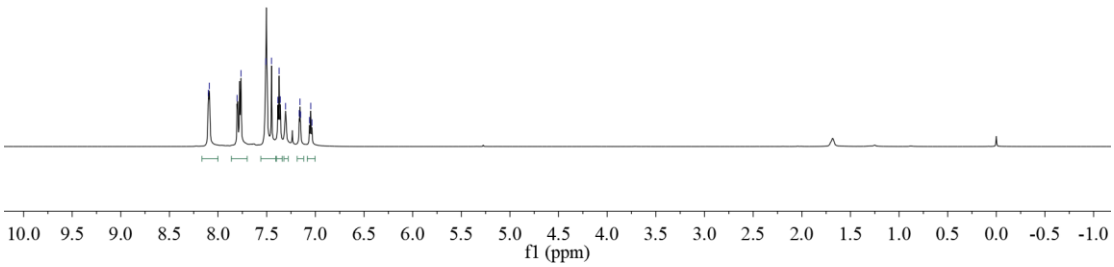
^{13}C NMR (151 MHz, $CDCl_3$)

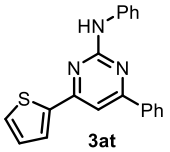




3at

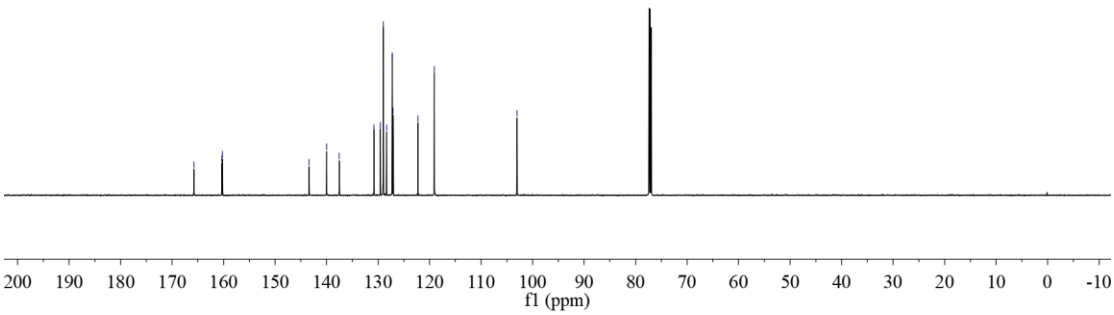
^{1}H NMR (600 MHz, $CDCl_3$)

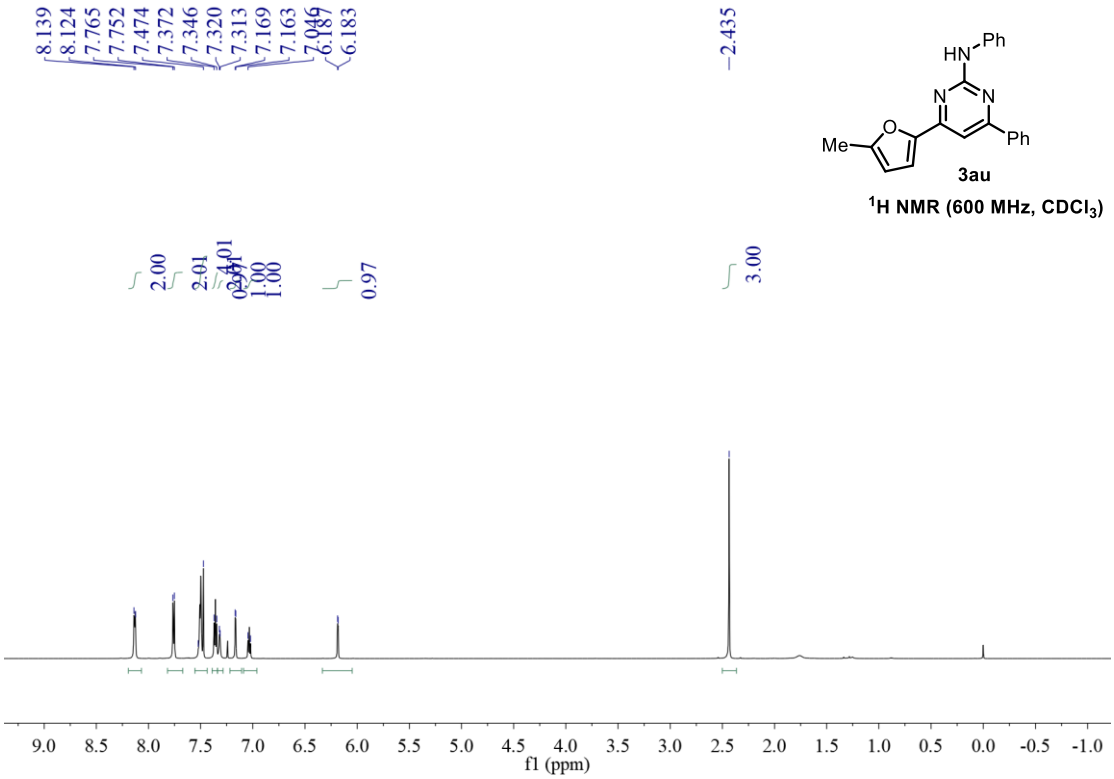




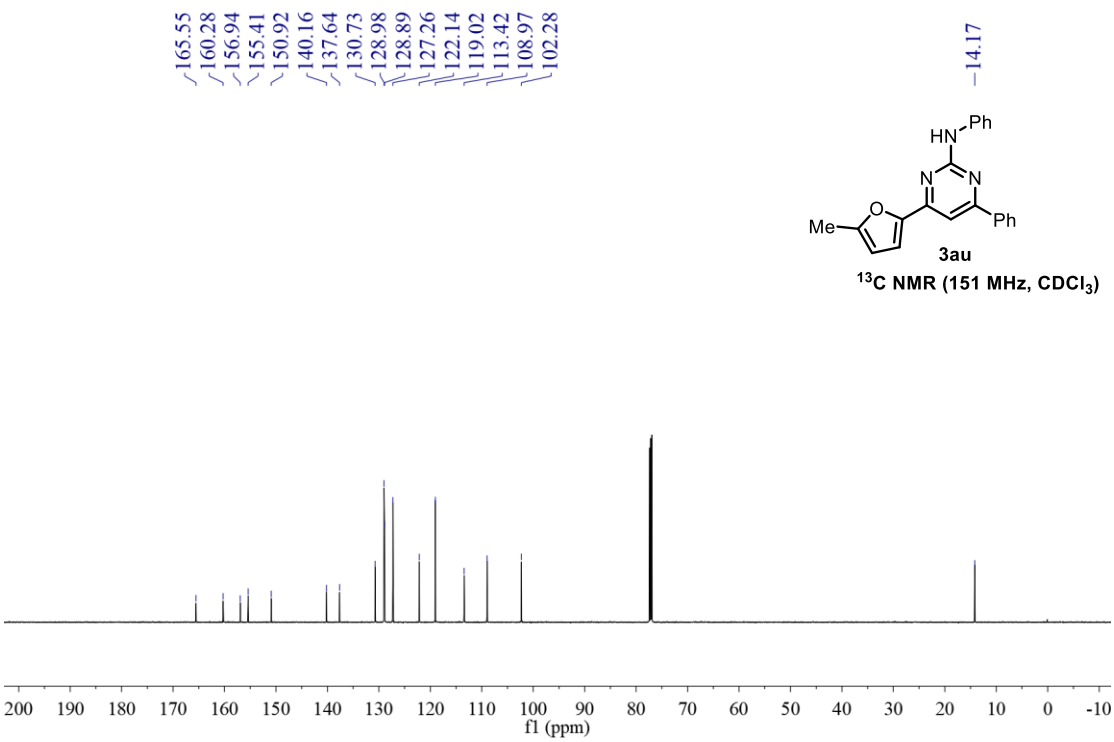
3at

^{13}C NMR (151 MHz, $CDCl_3$)

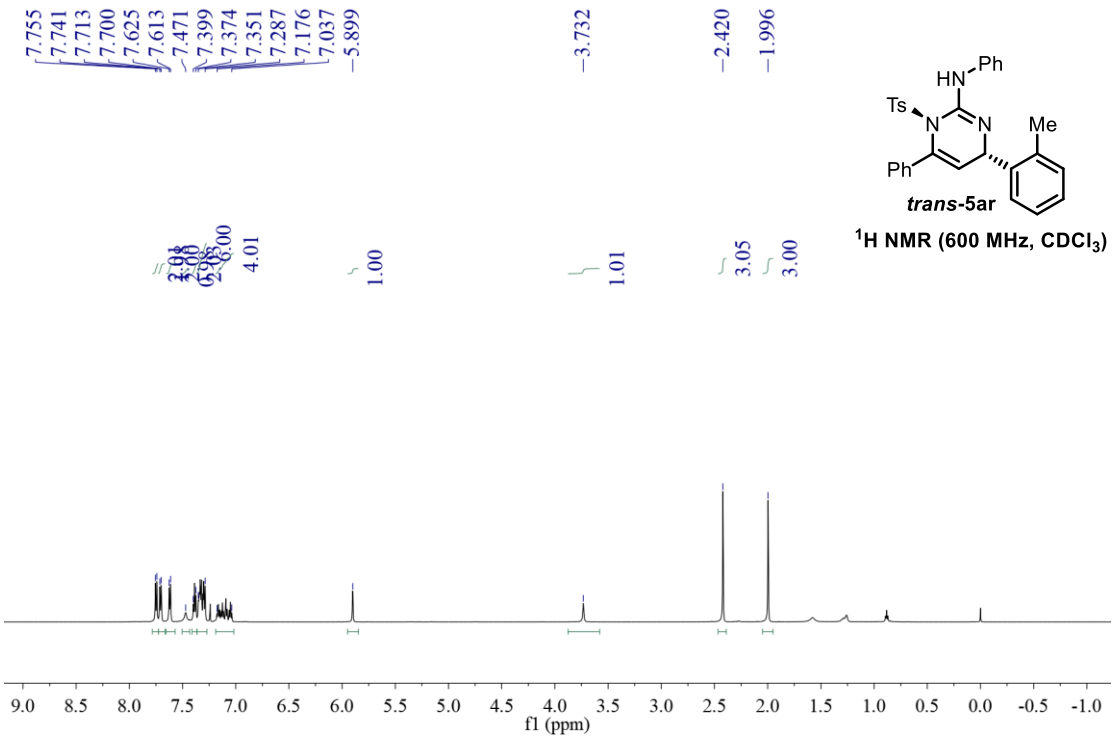


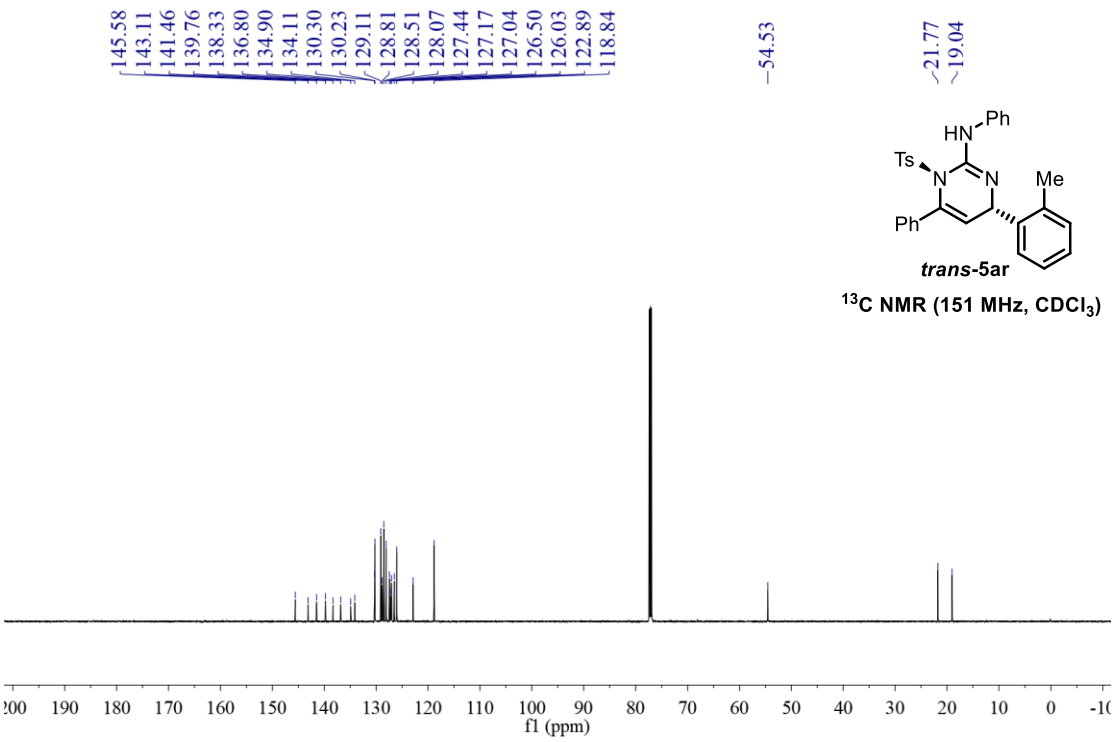


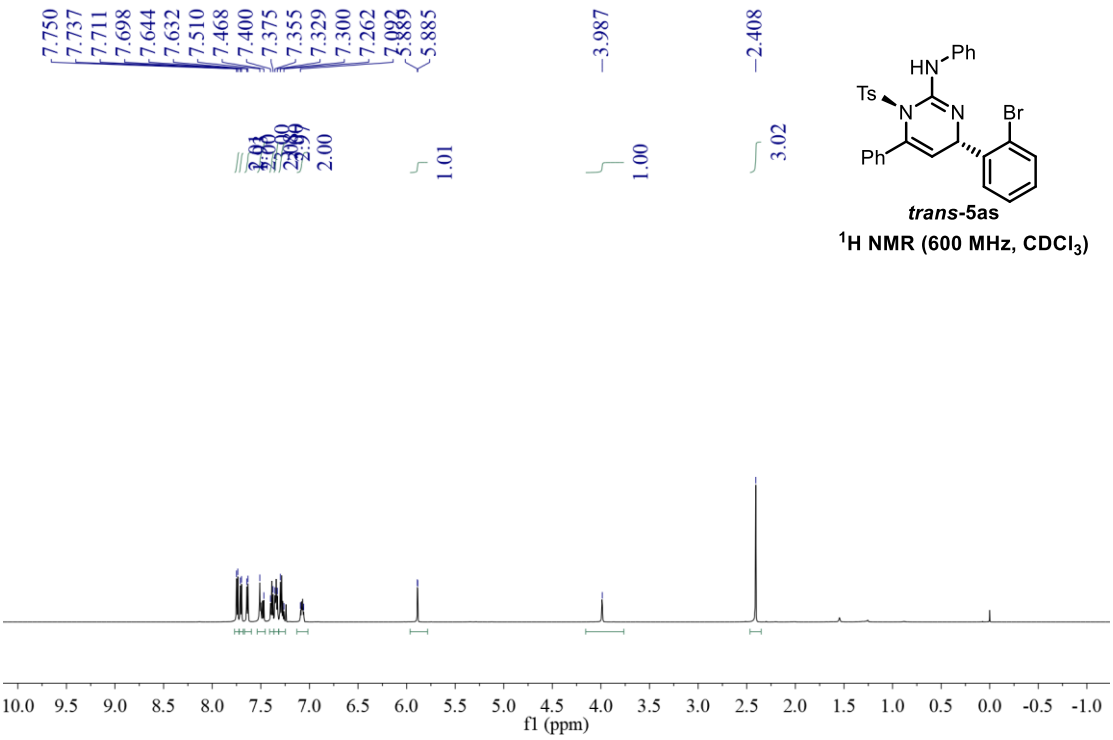
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

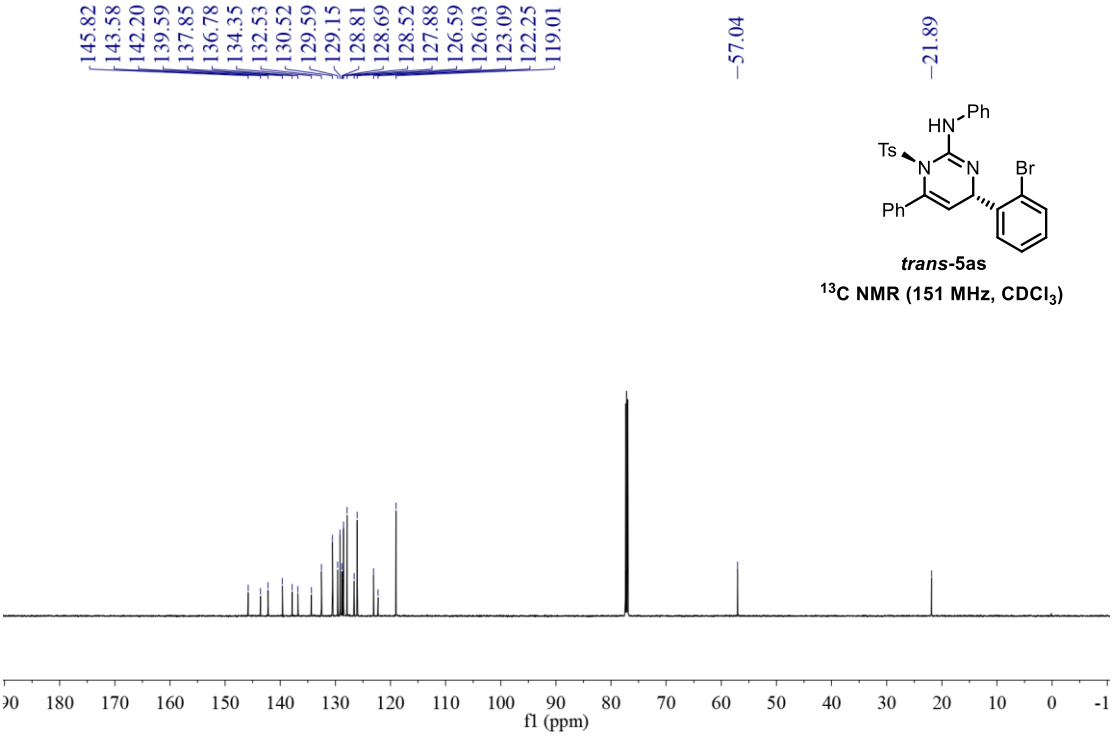

7.755
7.741
7.713
7.700
7.625
7.613
7.471
7.399
7.374
7.351
7.287
7.176
7.037
5.899
3.732
2.420
1.996
4.01
1.00
1.01
3.05
3.00
HN
Ph
Ts
N
N
Me
Ph
trans-5ar
1H NMR (600 MHz, CDCl3)
f1 (ppm)


145.58
143.11
141.46
139.76
138.33
136.80
134.90
134.11
130.30
130.23
129.11
128.81
128.51
128.07
127.44
127.17
127.04
126.50
126.03
122.89
118.84
54.53
21.77
19.04
HN
Ph
Ts
N
N
Me
Ph
trans-5ar
13C NMR (151 MHz, CDCl3)
f1 (ppm)



***trans*-5as**

^{1}H NMR (600 MHz, $CDCl_3$)



***trans*-5as**

^{13}C NMR (151 MHz, $CDCl_3$)

6. Single-Crystal X-Ray Diffraction Data

6.1 Single-Crystal X-Ray Diffraction Data of 3ea

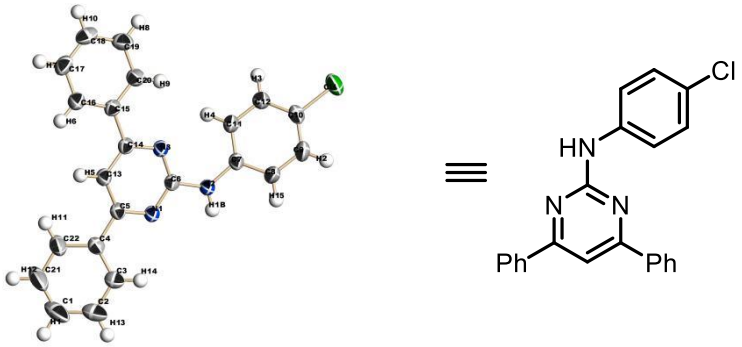


Figure S3. ORTEP drawing of **3ea (**CCDC 2282332**)** with 50% ellipsoid probability

Identification code	**3ea**
Chemical formula	$C_{22}H_{16}ClN_3$
Formula weight	357.83 g/mol
Temperature	301 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 24.3817(8) Å α = 90°
	b = 8.4440(3) Å β =120.586(1)°
	c = 19.9088(8) Å γ = 90°
Volume	3528.5(2) $Å^3$
Z	8
F(000)	1488
Theta range for data collection	2.38 to 28.32°
Index ranges	$-32 \le h \le 32$, $-11 \le k \le 11$, $-26 \le l \le 26$
wR2(reflections)	0.1236(4405)
Absorption correction	Multi-Scan
Diffractometer	d8 venture
Reflections collected	87504

6.2 Single-Crystal X-Ray Diffraction Data of *trans*-5as

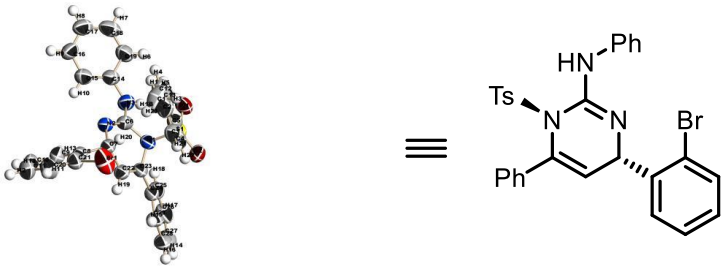


Figure S4. ORTEP drawing of *trans*-**5as** (CCDC 2282334) with 50% ellipsoid probability

Identification code	*trans*-**5as**	
Chemical formula	$C_{29}H_{24}BrN_3O_2S$	
Formula weight	558.48 g/mol	
Temperature	298(2) K	
Wavelength	1.54178 Å	
Crystal system, space group	Tetragonal, l 41 c d	
Unit cell dimensions	a = 32.9888(3) Å	α = 90°
	b = 32.9888(3) Å	β =90°
	c = 10.8474(2) Å	γ = 90°
Volume	11804.8(3) $Å^3$	
Z	16	
Absorption coefficient	2.781 mm^{-1}	
F(000)	4576	
Theta range for data collection	2.68 to 65.00°	
Index ranges	-38 ≤ h ≤ 38, -38 ≤ k ≤ 38, -12 ≤ l ≤ 12	
Absorption correction	Multi-Scan	
Data / restraints / parameters	4885 / 2 / 329	
Goodness-of-fit on F^2	0.973	
Final R indices [l>2sigma(l)]	R1 = 0.0467, wR2 = 0.1101	
R indices (all data)	R1 = 0.0720, wR2 = 0.1264	
Largest diff. peak and hole	0.156 and -0.434 e$Å^{-3}$	