

ELECTRONIC SUPPLEMENTARY INFORMATION

Gold-Catalyzed Intermolecular Cyclocarboamination of Ynamides with 1,3,5-Triazinanes: En Route to Tetrahydropyrimidines

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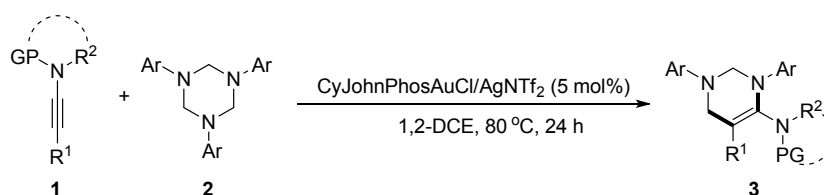
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1. General remarks

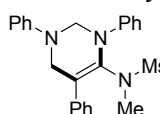
Chemicals were purchased from commercial suppliers and used without further purification. Reagents **1** and **2** could be easily prepared according to the previous literatures.^{1,2} Dry solvents were dispensed from the solvent purification system MB SPS-800. Deuterated solvents were bought from Euriso-Top. NMR spectra were, if not mentioned otherwise, recorded at room temperature on the following spectrometers: Bruker Avance-III-300 and Bruker Avance-III-500. Chemical shifts were referenced to residual solvent protons and reported in ppm and coupling constants in Hz. The following abbreviations were used for ¹H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). All ¹³C NMR spectra were measured with ¹H-decoupling. The multiplicities mentioned in these spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH₂-group), q (quartet, CH₃-group)] were determined by DEPT135. HRMS were determined at the chemistry department of the University of Heidelberg under the direction of Dr. J. Gross. EI⁺-spectra were measured on a JOEL JMS-700 spectrometer. For ESI⁺-spectra a Bruker ApexQu FT-ICR-MS spectrometer was applied. IR spectra were recorded on a Bruker Vector 22, and the absorption maxima were given in wavelength in cm⁻¹ units. X-ray crystal structure analyses were measured at the chemistry department of the University of Heidelberg under the direction of Dr. F. Rominger on a Bruker Smart CCD or Bruker APEX-II CCD instrument using Mo-K_α-radiation. The structures were solved and refined by Dr. F. Rominger using the SHELXTL software package. Thin-layer chromatography (TLC) was performed on precoated polyester sheets (POLYGRAM SIL G/UV254), and components were visualized by observation under UV light. Melting points were uncorrected.

2. General procedure and characterization data

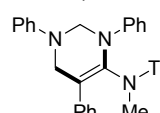


A round bottom flask equipped with a magnetic stirrer bar was charged with CyJohnPhosAuCl (5 mol%, 4.4 mg), AgNTf₂ (5 mol%, 2.9 mg), and 1,2-DCE (0.40 ml). The mixture was stirred for 5 minutes at room temperature. Ynamides **1** and 1,3,5-triazinanes **2** were added followed by 0.35 mL 1,2-DCE. The reaction mixture was then stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was concentrated and the residue was purified by chromatography on silica gel (eluent: PE/EA) to afford the desired product **3**.

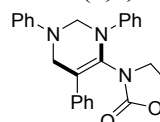
3aa: N-methyl-N-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide

 Yield 90%, light yellow solid, m.p.: 59–60 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.57–7.55 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37–7.32 (m, 3H), 7.18–7.13 (m, 5H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 2H), 5.04 (s, 1H), 4.75 (s, 1H), 4.29 (s, 1H), 4.03 (s, 1H), 2.69 (s, 3H), 2.36 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 147.6 (s), 146.1 (s), 137.2 (s), 137.1 (s), 129.4 (d), 129.2 (d), 128.8 (d), 128.4 (d), 127.6 (d), 124.7 (d), 124.0 (d), 119.3 (d), 117.7 (s), 115.0 (d), 69.4 (t), 51.0 (t), 39.9 (q), 37.6 (q) ppm; IR (ATR): $\tilde{\nu}$ 3057, 3028, 2928, 2853, 1685, 1639, 1595, 1494, 1451, 1416, 1340, 1220, 1146, 1078, 1041, 1001, 960, 879, 768, 734, 698, 637, 619 cm⁻¹; HRMS (EI) calcd for [C₂₄H₂₅N₃O₂S]⁺ (M)⁺: 419.1647; found: 419.1662.

3ba: N,4-dimethyl-N-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)benzenesulfonamide

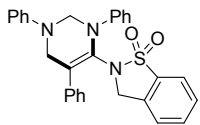
 Yield 65%, light yellow solid, m.p.: 89–90 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 7.9 Hz, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.95 (t, *J* = 8.8 Hz, 3H), 6.75–6.72 (m, 3H), 6.62 (d, *J* = 8.3 Hz, 2H), 4.80 (s, 2H), 4.14 (s, 2H), 2.77 (s, 3H), 2.32 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 147.6 (s), 145.9 (s), 142.5 (s), 137.9 (s), 137.3 (s), 137.2 (s), 129.2 (d), 128.9 (d), 128.7 (d), 128.5 (d), 128.4 (d), 127.5 (d), 126.7 (d), 123.7 (d), 123.5 (d), 119.0 (d), 118.2 (s), 114.7 (d), 69.2 (t), 51.0 (t), 38.6 (q), 21.4 (q) ppm; IR (ATR): $\tilde{\nu}$ 3416, 3058, 3029, 2960, 2926, 2872, 2852, 1638, 1600, 1494, 1448, 1341, 1287, 1215, 1154, 1088, 1078, 1029, 995, 961, 931, 863, 813, 761, 696, 668, 646, 607 cm⁻¹; HRMS (EI) calcd for [C₃₀H₂₉N₃O₂S]⁺ (M)⁺: 495.1975; found: 495.1978.

3ca: 3-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)oxazolidin-2-one

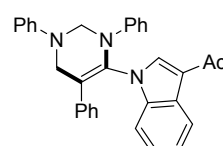
 Yield 70%, light yellow solid, m.p.: 82–83 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.42–7.37 (m, 4H), 7.33–7.28 (m, 3H), 7.19–7.11 (m, 5H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H), 4.90 (s, 2H), 4.20 (s, 2H), 4.01 (t, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 8.0 Hz, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 154.9 (s), 147.7 (s), 145.4 (s), 137.6 (s), 132.0 (s), 129.4 (d), 129.2 (d), 128.7 (d), 127.7 (d), 127.3 (d), 124.8 (d), 123.8 (d), 119.6 (d), 116.3 (s), 115.4 (d), 69.5 (t), 61.9 (t), 50.8 (t), 45.2 (t) ppm; IR (ATR): $\tilde{\nu}$ 3059, 3030, 2918, 2850,

1754, 1681, 1596, 1493, 1447, 1401, 1389, 1324, 1206, 1120, 1070, 1034, 992, 973, 933, 910, 804, 749, 696, 650 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_2\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$: 420.1682; found: 420.1686.

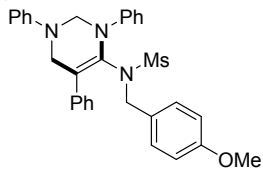
3da: 2-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide


Yield 94%, white solid, m.p.: 168–169 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.71 (s, 1H), 7.56 (d, $J = 6.6$ Hz, 2H), 7.42 (s, 2H), 7.32–7.12 (m, 10H), 6.98 (s, 1H), 6.80 (t, $J = 6.7$ Hz, 1H), 6.70 (d, $J = 7.5$ Hz, 2H), 4.98 (s, 2H), 4.26 (s, 2H), 4.20 (s, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.6 (s), 146.7 (s), 136.8 (s), 134.7 (s), 133.1 (s), 132.9 (s), 132.3 (d), 129.2 (d), 128.9 (d), 128.8 (d), 128.8 (d), 127.6 (d), 125.0 (d), 124.7 (d), 123.8 (d), 121.4 (d), 119.3 (d), 115.3 (s), 114.9 (d), 69.7 (t), 50.8 (t), 50.0 (t) ppm; IR (ATR): $\tilde{\nu}$ 3062, 2865, 2783, 1650, 1597, 1505, 1490, 1456, 1372, 1304, 1294, 1277, 1267, 1204, 1169, 1131, 1104, 1066, 1056, 1036, 992, 971, 933, 900, 827, 794, 754, 734, 700, 661, 624, 609 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{29}\text{H}_{25}\text{N}_3\text{O}_2\text{S}]^+$ (M) $^+$: 479.1662; found: 479.1668.

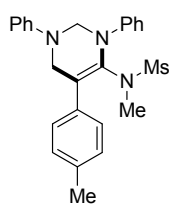
3ea: 1-(1-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-1H-indol-3-yl)ethanone


Yield 46%, white solid, m.p.: 96–97 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.19–8.17 (m, 1H), 7.56 (s, 1H), 7.53–7.50 (m, 1H), 7.24–7.21 (m, 2H), 7.17–7.08 (m, 7H), 7.04 (d, $J = 7.4$ Hz, 2H), 7.00–6.98 (m, 2H), 6.95 (t, $J = 7.2$ Hz, 1H), 6.86–6.80 (m, 3H), 5.10 (s, 2H), 4.40 (s, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 193.4 (s), 147.5 (s), 145.0 (s), 136.6 (s), 136.3 (s), 135.4 (d), 133.9 (s), 129.4 (d), 129.2 (d), 128.6 (d), 127.2 (d), 127.2 (d), 126.1 (s), 125.0 (d), 123.8 (d), 123.5 (d), 122.9 (d), 122.1 (d), 112.0 (d), 118.9 (s), 115.6 (d), 114.8 (s), 112.2 (d), 70.0 (t), 50.5 (t), 27.5 (q) ppm; IR (ATR): $\tilde{\nu}$ 3056, 3028, 2922, 1738, 1649, 1597, 1530, 1492, 1454, 1376, 1347, 1310, 1271, 1201, 1154, 1069, 1028, 1016, 996, 973, 932, 909, 748, 695, 637, 615 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{32}\text{H}_{27}\text{N}_3\text{O}]^+$ (M) $^+$: 469.2149; found: 469.2148.

3fa: N-(4-methoxybenzyl)-N-(1,3,5-triphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide

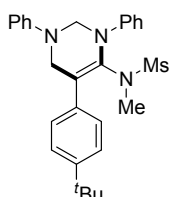

Yield 81%, white solid, m.p.: 73–74 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.41–7.36 (m, 4H), 7.33–7.27 (m, 3H), 7.22 (t, $J = 6.8$ Hz, 1H), 7.16–7.12 (m, 4H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 6.75 (t, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 8.5$ Hz, 2H), 4.93 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 12.1$ Hz, 1H), 4.16 (d, $J = 14.8$ Hz, 2H), 4.06–3.96 (m, 2H), 3.81 (s, 3H), 2.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 159.5 (s), 147.7 (s), 145.8 (s), 137.9 (s), 135.1 (s), 131.4 (d), 129.42 (d), 129.35 (d), 129.2 (d), 128.3 (d), 127.6 (s), 127.4 (d), 125.9 (d), 125.7 (d), 119.7 (s), 119.1 (d), 114.8 (d), 113.7 (d), 69.8 (t), 55.3 (q), 51.9 (t), 51.8 (t), 41.8 (q) ppm; IR (ATR): $\tilde{\nu}$ 3058, 3037, 2933, 2350, 2248, 1681, 1628, 1611, 1596, 1512, 1494, 1453, 1338, 1303, 1247, 1216, 1175, 1150, 1073, 1034, 962, 911, 834, 764, 730, 697, 647, 618 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{31}\text{H}_{31}\text{N}_3\text{O}_3\text{S}]^+$ (M) $^+$: 525.2081; found: 525.2067.

3ga: N-(1,3-diphenyl-5-(p-tolyl)-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



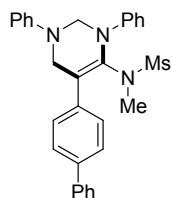
3ha: Yield 94%, white solid, m.p.: 69–70 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, $J = 7.9$ Hz, 2H), 7.35 (t, $J = 7.8$ Hz, 2H), 7.27–7.25 (m, 2H), 7.18–7.12 (m, 5H), 6.77 (t, $J = 7.2$ Hz, 1H), 6.68 (d, $J = 8.5$ Hz, 2H), 5.06 (s, 1H), 4.73 (s, 1H), 4.29 (s, 1H), 4.00 (s, 1H), 2.70 (s, 3H), 2.39 (s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.7 (s), 146.2 (s), 137.3 (s), 136.8 (s), 134.1 (s), 129.5 (d), 129.4 (d), 129.2 (d), 128.2 (d), 124.6 (d), 123.9 (d), 119.2 (d), 117.8 (s), 114.9 (d), 69.4 (t), 51.1 (t), 40.0 (q), 37.7 (q), 21.3 (q) ppm; IR (ATR): $\tilde{\nu}$ 3056, 3030, 2923, 2856, 2249, 1677, 1637, 1597, 1494, 1456, 1336, 1287, 1271, 1220, 1145, 1080, 1039, 996, 961, 931, 911, 867, 822, 798, 754, 731, 699, 648 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{24}\text{H}_{25}\text{N}_3\text{O}_2\text{S}]^+$ (M) $^+$: 433.1819; found: 433.1817.

3ha: N-(5-(4-(tert-butyl)phenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



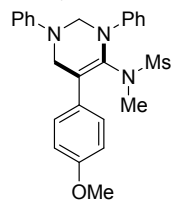
Yield 85%, white solid, m.p.: 176–177 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.48 (q, $J = 7.8$ Hz, 4H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.18–7.12 (m, 5H), 6.77 (t, $J = 7.2$ Hz, 1H), 6.68 (d, $J = 8.0$ Hz, 2H), 5.04 (s, 1H), 4.74 (s, 1H), 4.29 (s, 1H), 4.01 (s, 1H), 2.70 (s, 3H), 2.37 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 150.5 (s), 147.7 (s), 146.2 (s), 136.8 (s), 134.1 (s), 129.4 (d), 129.2 (d), 128.0 (d), 125.6 (d), 124.6 (d), 123.9 (d), 119.2 (d), 117.7 (s), 117.5 (s), 114.9 (d), 69.4 (t), 51.0 (t), 40.0 (q), 37.7 (q), 34.7 (s), 31.4 (q); IR (ATR): $\tilde{\nu}$ 2951, 2866, 1623, 1599, 1505, 1491, 1455, 1395, 1335, 1273, 1209, 1145, 1084, 1060, 1030, 998, 965, 931, 852, 837, 796, 782, 751, 695, 644 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{28}\text{H}_{33}\text{N}_3\text{O}_2\text{S}]^+$ (M) $^+$: 475.2288; found: 475.2273.

3ia: N-(5-([1,1'-biphenyl]-4-yl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



Yield 79%, white solid, m.p.: 159–160 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.70–7.62 (m, 6H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.38–7.34 (m, 3H), 7.18–7.13 (m, 5H), 6.77 (t, $J = 7.3$ Hz, 1H), 6.69 (d, $J = 8.0$ Hz, 2H), 5.07 (s, 1H), 4.74 (s, 1H), 4.35 (s, 1H), 4.04 (s, 1H), 2.74 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.6 (s), 146.1 (s), 140.5 (s), 140.1 (s), 137.3 (s), 136.1 (s), 129.4 (d), 129.2 (d), 128.9 (d), 128.7 (d), 127.4 (d), 127.3 (d), 127.0 (d), 124.7 (d), 123.9 (d), 119.3 (d), 117.1 (s), 115.0 (d), 69.4 (t), 50.9 (t), 40.0 (q), 37.8 (q) ppm; IR (ATR): $\tilde{\nu}$ 3060, 3029, 2954, 2924, 2852, 1633, 1598, 1502, 1488, 1454, 1339, 1279, 1212, 1147, 1082, 1032, 1006, 963, 932, 847, 766, 751, 730, 695, 643 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{24}\text{H}_{25}\text{N}_3\text{O}_2\text{S}]^+$ (M) $^+$: 495.1975; found: 495.1945.

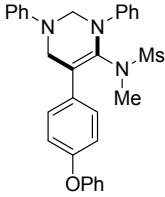
3ja: N-(5-(4-methoxyphenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



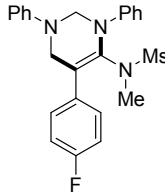
Yield 94%, white solid, m.p.: 145–146 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, $J = 8.6$ Hz, 2H), 7.35 (t, $J = 7.8$ Hz, 2H), 7.17–7.12 (m, 5H), 6.99 (d, $J = 8.7$ Hz, 2H), 6.76 (t, $J = 7.3$ Hz, 1H), 6.67 (d, $J = 8.2$ Hz, 2H), 5.06 (s, 1H), 4.70 (s, 1H), 4.28 (s, 1H), 3.97 (s, 1H), 3.85 (s, 3H), 2.70 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 159.0 (s), 147.6 (s), 146.3 (s), 136.7 (s), 129.5 (d), 129.4 (d), 129.3 (s), 129.2 (d), 124.6 (d), 123.8 (d), 119.2 (d), 117.5 (s), 114.9 (d), 114.1 (d), 69.4 (t), 55.3 (q), 51.1 (t), 40.1 (q), 37.7 (q) ppm; IR (ATR): $\tilde{\nu}$ 3030, 2933, 2838, 2254, 1738, 1641, 1598, 1504, 1494, 1460, 1336, 1278, 1246, 1217, 1205, 1179, 1145, 1081, 1032, 995, 961, 931, 911, 867, 835,

799, 755, 732, 702, 649, 615 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{25}\text{H}_{27}\text{N}_3\text{O}_3\text{S}]^+(\text{M})^+$: 449.1768; found: 419.1779.

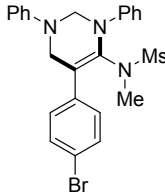
3ka: N-methyl-N-(5-(4-phenoxyphenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide


Yield 80%, light yellow solid, m.p.: 60–61 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.55–7.52 (m, 2H), 7.39–7.34 (m, 4H), 7.18–7.13 (m, 6H), 7.10–7.05 (m, 4H), 6.77 (t, $J = 7.3$ Hz, 1H), 6.68 (d, $J = 7.9$ Hz, 2H), 5.06 (s, 1H), 4.71 (s, 1H), 4.30 (s, 1H), 4.00 (s, 1H), 2.74 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 156.9 (s), 156.8 (s), 147.6 (s), 146.2 (s), 137.1 (s), 131.9 (s), 129.9 (d), 129.7 (d), 129.4 (d), 129.2 (d), 124.7 (d), 123.9 (d), 123.6 (d), 119.3 (d), 119.2 (d), 118.8 (d), 117.1 (s), 115.0 (d), 69.4 (t), 51.1 (t), 40.1 (q), 37.8 (q) ppm; IR (ATR): $\tilde{\nu}$ 3061, 3036, 2929, 2851, 2363, 2252, 1647, 1597, 1489, 1457, 1336, 1273, 1236, 1169, 1144, 1080, 1033, 995, 961, 932, 910, 868, 800, 750, 732, 694, 650 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{30}\text{H}_{29}\text{N}_3\text{O}_2\text{S}]^+(\text{M})^+$: 511.1924; found: 511.1920.

3la: N-(5-(4-fluorophenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

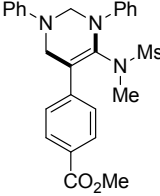

Yield 87%, light yellow solid, m.p.: 64–65 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.55–7.52 (m, 2H), 7.37–7.34 (m, 2H), 7.17–7.12 (m, 7H), 6.77 (t, $J = 7.3$ Hz, 1H), 6.66 (d, $J = 7.9$ Hz, 2H), 5.05 (s, 1H), 4.71 (s, 1H), 4.27 (s, 1H), 3.97 (s, 1H), 2.69 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 162.1 (s, d: $J_{\text{C-F}} = 247.1$ Hz), 147.5 (s), 146.1 (s), 137.4 (s), 133.0 (s, d: $J_{\text{C-F}} = 3.4$ Hz), 130.1 (d, d: $J_{\text{C-F}} = 8.0$ Hz), 129.4 (d), 129.2 (d), 124.8 (d), 123.9 (d), 119.4 (d), 116.8 (s), 115.7 (d, d: $J_{\text{C-F}} = 21.3$ Hz), 115.0 (d), 69.5 (t), 51.1 (t), 40.0 (q), 37.8 (q) ppm; ^{19}F NMR (282 MHz, CDCl_3) δ -114.16 ppm; IR (ATR): $\tilde{\nu}$ 3063, 2929, 1681, 1638, 1595, 1494, 1336, 1222, 1157, 1146, 1099, 1080, 1040, 961, 912, 840, 799, 761, 729, 696, 648, 613 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}_2\text{S}]^+(\text{M})^+$: 437.1568; found: 437.1557.

3ma: N-(5-(4-bromophenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

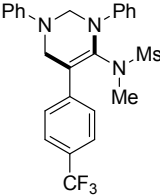

Yield 91%, white solid, m.p.: 165–166 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.18–7.12 (m, 5H), 6.78 (t, $J = 7.3$ Hz, 1H), 6.67 (d, $J = 8.2$ Hz, 2H), 5.05 (s, 1H), 4.70 (s, 1H), 4.29 (s, 1H), 3.98 (s, 1H), 2.70 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.5 (s), 146.0 (s), 137.6 (s), 136.1 (s), 131.9 (d), 130.0 (d), 129.5 (d), 129.3 (d), 124.9 (d), 124.0 (d), 121.5 (s), 119.5 (d), 116.4 (s), 115.0 (d), 69.4 (t), 50.8 (t), 39.9 (q), 37.8 (q) ppm; IR (ATR): $\tilde{\nu}$ 3067, 3035, 2862, 1641, 1599, 1490, 1461, 1424, 1385, 1362, 1329, 1295, 1283, 1199, 1142, 1080, 1041, 1008, 997, 963, 932, 893, 869, 833, 803, 789, 763, 733, 700, 658 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}_2\text{SBr}]^+(\text{M})^+$: 497.0767; found: 497.0745.

3na: methyl 4-(6-(N-methylmethanesulfonamido)-1,3-diphenyl-1,2,3,4-tetrahydropyrimidin-5-yl)benzoate

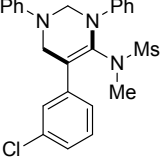
Yield 86%, white s solid, m.p.: 81–82 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.11 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.35 (t, $J = 7.9$ Hz, 2H), 7.18–7.12 (m, 5H), 6.78 (t, $J = 7.3$ Hz, 1H), 6.68


 (d, $J = 7.9$ Hz, 2H), 5.05 (s, 1H), 4.73 (s, 1H), 4.34 (s, 1H), 4.03 (s, 1H), 3.93 (s, 3H), 2.68 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 166.9 (s), 147.5 (s), 145.8 (s), 142.1 (s), 138.2 (s), 130.0 (d), 129.5 (d), 129.3 (d), 129.0 (s), 128.3 (d), 125.0 (d), 124.1 (d), 119.5 (d), 116.2 (s), 115.1 (d), 69.3 (t), 52.2 (q), 50.6 (t), 39.8 (q), 37.7 (q) ppm; IR (ATR): $\tilde{\nu}$ 2951, 1717, 1685, 1637, 1597, 1494, 1456, 1436, 1337, 1278, 1221, 1182, 1146, 1110, 1039, 1020, 960, 933, 862, 828, 772, 697, 647 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{26}\text{H}_{27}\text{N}_3\text{O}_4\text{S}]^+$ (M) $^+$: 477.1717; found: 477.1701.

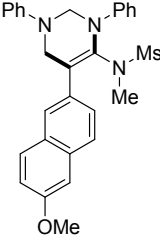
30a: N-(1,3-diphenyl-5-(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide


 Yield 80%, light yellow solid, m.p.: 139–140 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.71–7.67 (m, 4H), 7.36 (t, $J = 7.9$ Hz, 2H), 7.18–7.12 (m, 5H), 6.79 (t, $J = 7.3$ Hz, 1H), 6.68 (d, $J = 8.0$ Hz, 2H), 5.06 (s, 1H), 4.72 (s, 1H), 4.34 (s, 1H), 4.01 (s, 1H), 2.69 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.5 (s), 145.8 (s), 141.0 (s, d: $J_{\text{C-F}} = 1.1$ Hz), 138.3 (s), 129.5 (d), 129.4 (s, q: $J_{\text{C-F}} = 32.5$ Hz), 129.3 (d), 128.6 (d), 125.7 (d, q: $J_{\text{C-F}} = 3.7$ Hz), 125.0 (d), 124.15 (s, q: $J_{\text{C-F}} = 270.0$ Hz), 124.07 (d), 119.6 (d), 116.0 (s), 115.1 (d), 69.4 (t), 50.7 (t), 39.8 (q), 37.9 (q) ppm; ^{19}F NMR (470 MHz, CDCl_3) δ -62.459, -62.464 ppm; IR (ATR): $\tilde{\nu}$ 3029, 2924, 2849, 1599, 1493, 1455, 1411, 1337, 1277, 1213, 1148, 1114, 1066, 1033, 1016, 996, 963, 935, 862, 850, 794, 769, 754, 694, 609 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{25}\text{H}_{24}\text{N}_3\text{O}_2\text{SF}_3]^+$ (M) $^+$: 487.1536; found: 487.1522.

3pa: N-(5-(3-chlorophenyl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

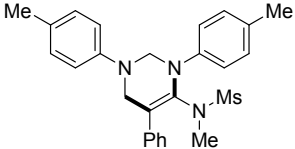

 Yield 82%, light yellow solid, m.p.: 78–79 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.52–7.48 (m, 2H), 7.39–7.29 (m, 4H), 7.18–7.12 (m, 5H), 6.78 (t, $J = 7.3$ Hz, 1H), 6.67 (d, $J = 7.9$ Hz, 2H), 5.03 (s, 1H), 4.71 (s, 1H), 4.27 (s, 1H), 4.00 (s, 1H), 2.71 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.5 (s), 145.9 (s), 139.1 (s), 137.9 (s), 134.4 (s), 130.1 (d), 129.5 (d), 129.2 (d), 128.1 (d), 127.6 (d), 126.9 (d), 124.9 (d), 124.1 (d), 119.5 (d), 116.1 (s), 115.1 (d), 69.4 (t), 50.8 (t), 39.8 (q), 37.7 (q) ppm; IR (ATR): $\tilde{\nu}$ 3063, 3030, 2929, 2854, 1639, 1594, 1562, 1493, 1411, 1336, 1285, 1205, 1145, 1080, 1033, 996, 962, 866, 787, 752, 721, 695, 611 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}_2\text{SCl}]^+$ (M) $^+$: 453.1272; found: 453.1265.

3qa: N-(5-(6-methoxynaphthalen-2-yl)-1,3-diphenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

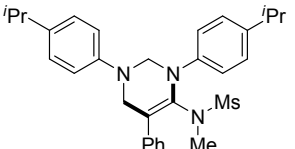

 Yield 40%, white solid, m.p.: 188–189 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 1.1$ Hz, 1H), 7.80 (t, $J = 9.3$ Hz, 2H), 7.71 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.37–7.34 (m, 2H), 7.19–7.12 (m, 7H), 6.77 (t, $J = 7.3$ Hz, 1H), 6.70 (d, $J = 7.9$ Hz, 2H), 5.10 (s, 1H), 4.75 (s, 1H), 4.44 (s, 1H), 4.06 (s, 1H), 3.94 (s, 3H), 2.67 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 157.9 (s), 147.7 (s), 146.2 (s), 137.3 (s), 133.8 (s), 132.3 (s), 129.6 (d), 129.4 (d), 129.2 (d), 128.9 (s), 127.2 (d), 127.1 (d), 126.6 (d), 124.6 (d), 123.8 (d), 119.3 (d), 119.2 (d), 117.5 (s), 114.9 (d), 105.7 (d), 69.3 (t), 55.4 (q), 51.0 (t), 40.0 (q), 37.8 (q) ppm; IR (ATR): $\tilde{\nu}$ 2932, 2236, 1627, 1599, 1485, 1392,

1340, 1268, 1214, 1156, 1026, 955, 914, 756, 696 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{29}\text{H}_{29}\text{N}_3\text{O}_2\text{S}]^+$ (M)⁺: 499.1924; found: 499.1926.

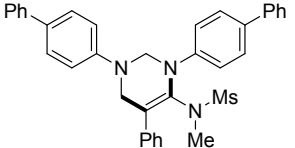
3ab: N-methyl-N-(5-phenyl-1,3-di-p-tolyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide

 Yield 86%, white solid, m.p.: 79–80 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.91 (s, 1H), 4.66 (s, 1H), 4.23 (s, 1H), 3.98 (s, 1H), 2.68 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H), 2.22 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.5 (s), 143.7 (s), 137.4 (s), 137.2 (s), 134.4 (s), 129.9 (d), 129.7 (d), 128.72 (s), 128.70 (d), 128.5 (s), 127.4 (d), 124.1 (d), 117.4 (s), 115.3 (d), 70.2 (t), 51.3 (t), 40.0 (q), 37.6 (q), 20.9 (q), 20.4 (q) ppm; IR (ATR): $\tilde{\nu}$ 3032, 3010, 2926, 2864, 2239, 1680, 1635, 1596, 1513, 1450, 1408, 1381, 1339, 1330, 1273, 1218, 1175, 1040, 961, 914, 876, 819, 769, 729, 703, 645 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_2\text{S}]^+$ (M)⁺: 447.1975; found: 447.1956.

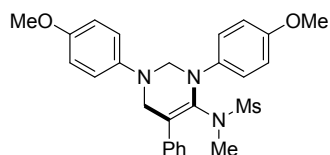
3ac: N-(1,3-bis(4-isopropylphenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

 Yield 73%, light yellow solid, m.p.: 140–141 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.35–7.32 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 4H), 6.67 (d, *J* = 8.1 Hz, 2H), 4.98 (s, 1H), 4.68 (s, 1H), 4.29 (s, 1H), 3.99 (s, 1H), 2.90 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.80 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.70 (s, 3H), 2.40 (s, 3H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.19 (d, *J* = 6.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.9 (s), 145.3 (s), 143.9 (s), 139.9 (s), 137.4 (s), 137.3 (s), 128.7 (d), 128.4 (d), 127.4 (d), 127.2 (d), 127.1 (d), 124.0 (d), 117.4 (s), 115.3 (d), 70.0 (t), 51.3 (t), 40.0 (q), 37.7 (q), 33.5 (q), 33.2 (q), 24.2 (q), 24.1 (q) ppm; IR (ATR): $\tilde{\nu}$ 3402, 3053, 3022, 2833, 1738, 1627, 1598, 1509, 1472, 1440, 1386, 1361, 1291, 1264, 1220, 1176, 1145, 1125, 1030, 980, 956, 935, 832, 809, 746, 702, 653, 619 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{30}\text{H}_{37}\text{N}_3\text{O}_2\text{S}]^+$ (M)⁺: 503.2601; found: 503.2590.

3ad: N-(1,3-di([1,1'-biphenyl]-4-yl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

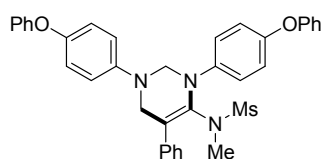
 Yield 70%, light yellow solid, m.p.: 150–151 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.61–7.57 (m, 6H), 7.49–7.32 (m, 13H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.12 (s, 1H), 4.80 (s, 1H), 4.35 (s, 1H), 4.10 (s, 1H), 2.72 (s, 3H), 2.42 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.9 (s), 145.3 (s), 140.8 (s), 140.1 (s), 137.4 (s), 137.1 (s), 137.0 (s), 132.1 (s), 128.9 (d), 128.8 (d), 128.7 (d), 128.4 (d), 128.0 (d), 127.9 (d), 127.6 (d), 127.3 (d), 126.8 (d), 126.5 (d), 124.0 (d), 117.9 (s), 115.1 (d), 69.1 (t), 51.0 (t), 40.1 (q), 37.7 (q) ppm; IR (reflection): $\tilde{\nu}$ 3055, 3030, 2924, 2852, 1681, 1637, 1609, 1523, 1486, 1449, 1337, 1297, 1263, 1215, 1176, 1145, 1077, 1041, 1007, 960, 931, 911, 841, 762, 728, 697, 649 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_2\text{SNa}]^+$ (M+Na)⁺: 594.2186; found: 594.2192.

3ae: N-(1,3-bis(4-methoxyphenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



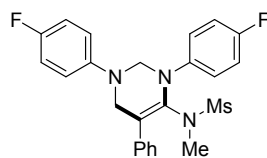
Yield 76%, light yellow solid, m.p.: 158–159 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.54–7.52 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.13–7.10 (m, 2H), 6.89–6.86 (m, 2H), 6.76–6.73 (m, 2H), 6.69–6.66 (m, 2H), 4.73 (s, 1H), 4.62 (s, 1H), 4.13 (s, 1H), 3.99 (s, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.68 (s, 3H), 2.33 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 157.0 (s), 153.6 (s), 142.0 (s), 139.4 (s), 137.6 (s), 137.2 (s), 128.7 (d), 128.6 (d), 127.4 (d), 126.0 (d), 117.6 (d), 117.1 (s), 114.6 (d), 114.4 (d), 71.9 (t), 55.6 (q), 55.4 (q), 52.1 (t), 39.7 (q), 37.4 (q) ppm; IR (ATR): $\tilde{\nu}$ 3058, 3039, 2988, 2958, 2914, 2837, 2788, 1654, 1608, 1581, 1508, 1455, 1445, 1479, 1331, 1295, 1240, 1194, 1143, 1107, 1088, 1064, 1032, 963, 933, 876, 837, 828, 770, 747, 699 cm⁻¹; HRMS (EI) calcd for [C₂₆H₂₉N₃O₄S]⁺ (M)⁺: 479.1873; found: 479.1874.

3af: N-(1,3-bis(4-phenoxyphenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



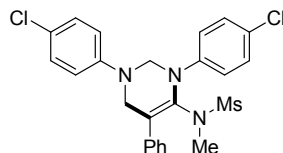
Yield 90%, white solid, m.p.: 75–76 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, *J* = 7.1 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34–7.28 (m, 5H), 7.13–7.08 (m, 3H), 7.04–6.96 (m, 5H), 6.91–6.88 (m, 4H), 6.74–6.72 (m, 2H), 4.88 (s, 1H), 4.75 (s, 1H), 4.22 (s, 1H), 4.07 (s, 1H), 2.69 (s, 3H), 2.36 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 158.4 (s), 157.2 (s), 154.2 (s), 149.8 (s), 144.3 (s), 141.5 (s), 137.3 (s), 136.9 (s), 129.8 (d), 129.6 (d), 128.8 (d), 128.5 (d), 127.6 (d), 125.7 (d), 123.4 (d), 122.4 (d), 120.7 (d), 119.6 (d), 118.7 (d), 117.6 (d), 117.4 (s), 117.2 (d), 70.9 (t), 51.8 (t), 39.8 (q), 37.4 (q) ppm; IR (ATR): $\tilde{\nu}$ 3059, 3039, 2931, 1643, 1589, 1504, 1487, 1338, 1291, 1234, 1198, 1144, 1105, 1076, 1023, 961, 931, 869, 841, 756, 692 cm⁻¹; HRMS (EI) calcd for [C₃₆H₃₃N₃O₄S]⁺ (M)⁺: 603.2186; found: 603.2183.

3ag: N-(1,3-bis(4-fluorophenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



Yield 83%, light yellow solid, m.p.: 154–155 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.50 (d, *J* = 7.1 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.18–7.14 (m, 2H), 7.03 (t, *J* = 8.5 Hz, 2H), 6.87 (t, *J* = 8.6 Hz, 2H), 6.67–6.62 (m, 2H), 4.74 (s, 2H), 4.09 (s, 2H), 2.69 (s, 13H), 2.26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.1 (s, d: *J*_{C-F} = 244.8 Hz), 157.1 (s, d: *J*_{C-F} = 239.0 Hz), 144.2 (s, d: *J*_{C-F} = 2.2 Hz), 142.1 (s, d: *J*_{C-F} = 2.8 Hz), 137.37 (s), 136.72 (s), 128.78 (d), 128.65 (d), 127.64 (d), 126.21 (d, d: *J*_{C-F} = 8.2 Hz), 117.53 (s), 117.19 (d, d: *J*_{C-F} = 7.6 Hz), 116.11 (d, d: *J*_{C-F} = 22.5 Hz), 115.69 (d, d: *J*_{C-F} = 22.3 Hz), 71.25 (t), 51.88 (t), 39.58 (q), 37.12 (q); ¹⁹F NMR (282 MHz, CD₃Cl₃) δ -122.45, -129.63 ppm; IR (ATR): $\tilde{\nu}$ 3063, 3032, 3012, 2868, 2799, 1648, 1598, 1506, 1462, 1453, 1441, 1425, 1375, 1330, 1293, 1275, 1224, 1197, 1171, 1154, 1141, 1098, 1081, 1065, 1025, 997, 962, 934, 911, 883, 843, 822, 774, 762, 752, 733, 723, 701, 642, 608 cm⁻¹; HRMS (ESI) calcd for [C₂₄H₂₃N₃O₂SF₂Na]⁺ (M+Na)⁺: 478.1371; found: 478.1376.

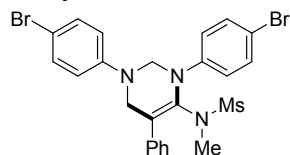
3ah: N-(1,3-bis(4-chlorophenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



Yield 55%, yellow solid, m.p.: 170–171 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, *J* = 7.1 Hz, 12H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35–7.30 (m, 3H), 7.11–7.09 (m, 4H), 6.58 (d, *J* = 8.9 Hz, 2H), 4.81 (s,

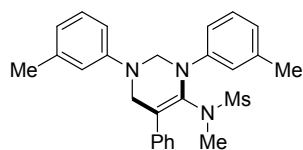
2H), 4.10 (s, 2H), 2.67 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 146.1 (s), 144.5 (s), 137.0 (s), 136.5 (s), 130.4 (s), 129.6 (d), 129.1 (d), 128.8 (d), 128.5 (d), 127.8 (d), 125.4 (d), 124.4 (s), 118.0 (s), 116.3 (d), 69.5 (t), 51.2 (t), 39.8 (q), 37.2 (q); IR (ATR): $\tilde{\nu}$ 3092, 3061, 2932, 2851, 1685, 1635, 1595, 1492, 1451, 1391, 1377, 1358, 1337, 1293, 1273, 1245, 1222, 1205, 1147, 1094, 1077, 1056, 1016, 1001, 961, 927, 910, 854, 836, 816, 800, 780, 766, 756, 731, 701, 661, 632, 621 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_2\text{S}\text{Cl}_2]^+$ (M) $^+$: 487.0883; found: 487.0877.

3ai: N-(1,3-bis(4-bromophenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



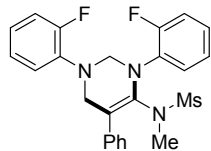
Yield 53%, light yellow solid, m.p.: 188–189 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.51–7.42 (m, 6H), 7.34 (t, $J = 7.3$ Hz, 1H), 7.26–7.23 (m, 2H), 7.05–7.03 (m, 2H), 6.53 (d, $J = 9.0$ Hz, 2H), 4.80 (s, 2H), 4.09 (s, 2H), 2.67 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 146.5 (s), 144.9 (s), 136.9 (s), 136.5 (s), 132.5 (d), 132.0 (d), 128.8 (d), 128.5 (d), 127.8 (d), 125.6 (d), 118.09 (s), 118.08 (s), 116.6 (d), 111.6 (s), 69.2 (t), 51.1 (t), 39.9 (q), 37.2 (q) ppm; IR (ATR): $\tilde{\nu}$ 3054, 3025, 2924, 2851, 1682, 1637, 1590, 1487, 1336, 1217, 1145, 1074, 1040, 1010, 961, 911, 872, 830, 768, 731, 701 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_2\text{S}^{79}\text{Br}^{81}\text{BrNa}]^+$ (M+Na) $^+$: 599.9749; found: 599.9759.

3aj: N-methyl-N-(5-phenyl-1,3-di-m-tolyl-1,2,3,6-tetrahydropyrimidin-4-yl)methanesulfonamide



Yield 86%, light yellow solid, m.p.: 149–150 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 7.9$ Hz, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H), 7.26–7.22 (m, 1H), 7.06 (t, $J = 7.7$ Hz, 1H), 6.96–6.85 (m, 3H), 6.61 (d, $J = 7.4$ Hz, 1H), 6.52–6.50 (m, 2H), 5.03 (s, 1H), 4.71 (s, 1H), 4.30 (s, 1H), 4.01 (s, 1H), 2.69 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 147.8 (s), 146.1 (s), 139.2 (s), 139.0 (s), 137.3 (s), 137.1 (s), 129.1 (d), 129.0 (d), 128.7 (d), 128.4 (d), 127.5 (d), 125.4 (d), 124.5 (d), 120.9 (d), 120.1 (d), 117.5 (s), 115.7 (d), 112.2 (d), 69.2 (t), 51.2 (t), 39.9 (q), 37.7 (q), 21.7 (q), 21.5 (q) ppm; IR (ATR): $\tilde{\nu}$ 3055, 3034, 3009, 2918, 1682, 1644, 1604, 1490, 1446, 1371, 1333, 1276, 1238, 1174, 1144, 1078, 1045, 1006, 962, 945, 894, 870, 858, 787, 766, 742, 704, 688, 659, 610 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_2\text{SNa}]^+$ (M+Na) $^+$: 470.1873; found: 470.1876.

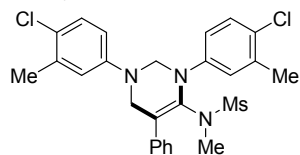
3ak: N-(1,3-bis(2-fluorophenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide



Yield 80%, white solid, m.p.: 160–161 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H), 7.10–7.08 (m, 3H), 7.04–6.98 (m, 3H), 6.89–6.85 (m, 2H), 4.84 (s, 1H), 4.71 (s, 1H), 4.19 (s, 1H), 4.14 (s, 1H), 2.68 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 157.0 (s, d: $J_{\text{C-F}} = 198.9$ Hz), 155.1 (s, d: $J = 197.5$ Hz), 137.4 (s), 136.3 (s, d: $J_{\text{C-F}} = 8.9$ Hz), 136.1 (s), 132.9 (s, d: $J_{\text{C-F}} = 9.7$ Hz), 128.8 (d), 127.6 (d), 127.2 (d), 126.4 (d, d: $J_{\text{C-F}} = 7.8$ Hz), 124.4 (d, d: $J_{\text{C-F}} = 3.6$ Hz), 124.0 (d, d: $J_{\text{C-F}} = 3.8$ Hz), 122.7 (d, d: $J_{\text{C-F}} = 7.8$ Hz), 119.6 (d), 119.6 (d), 117.3 (s), 116.2 (d, d: $J_{\text{C-F}} = 20.0$ Hz), 116.2 (d, d: $J_{\text{C-F}} = 20.0$ Hz), 72.5–67.8 (t, m), 52.5 (t), 39.5 (q), 37.0 (q) ppm; ^{19}F NMR (282 MHz, CDCl_3) δ -123.46, -124.26 ppm; IR (ATR): $\tilde{\nu}$ 3053, 2927, 2187, 1656, 1488, 1416, 1356, 1302, 1259, 1208, 1192, 1154, 1108, 1043,

1017, 980, 938, 883, 828, 793, 732, 714, 675, 612 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_2\text{SF}_2]^+$ (M)⁺: 455.1474; found: 455.1487.

3al: N-(1,3-bis(4-chloro-3-methylphenyl)-5-phenyl-1,2,3,6-tetrahydropyrimidin-4-yl)-N-methylmethanesulfonamide

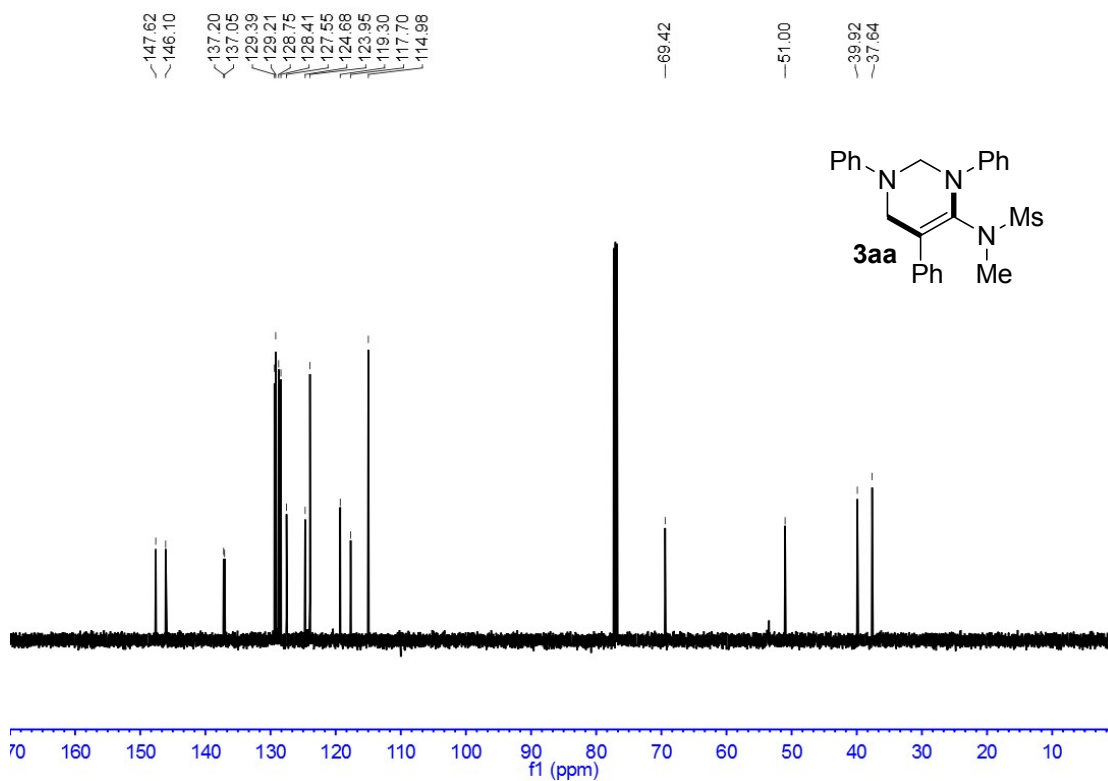
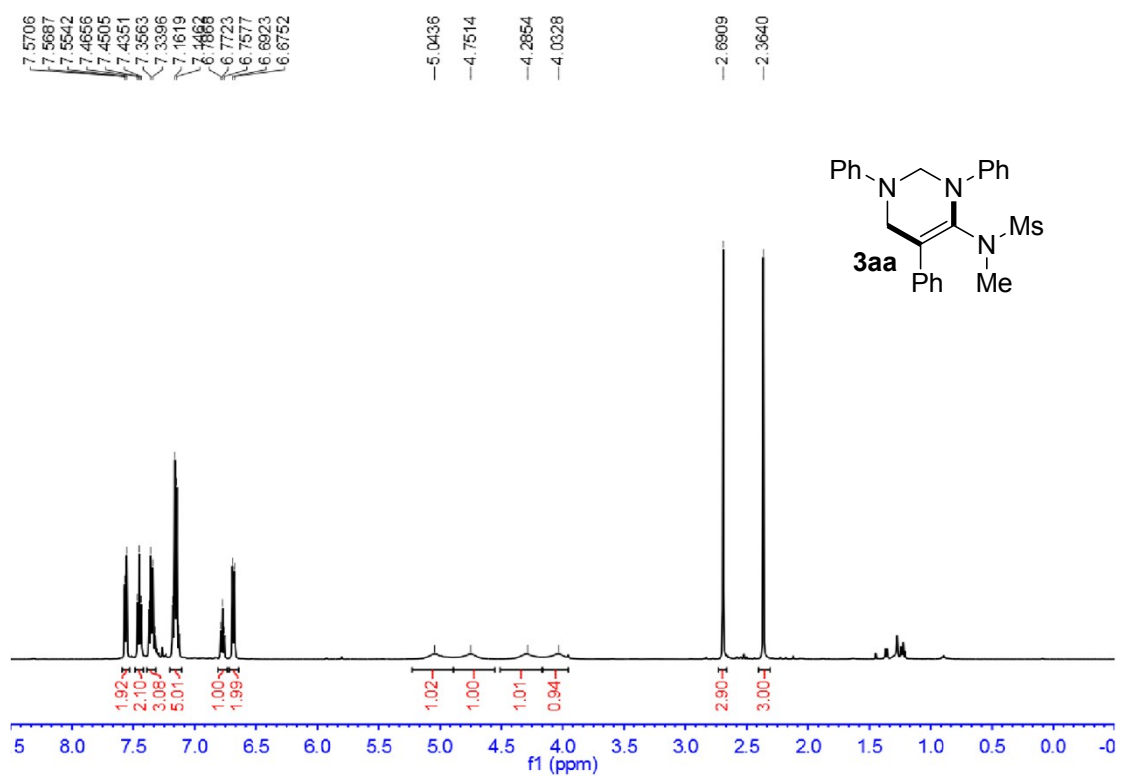


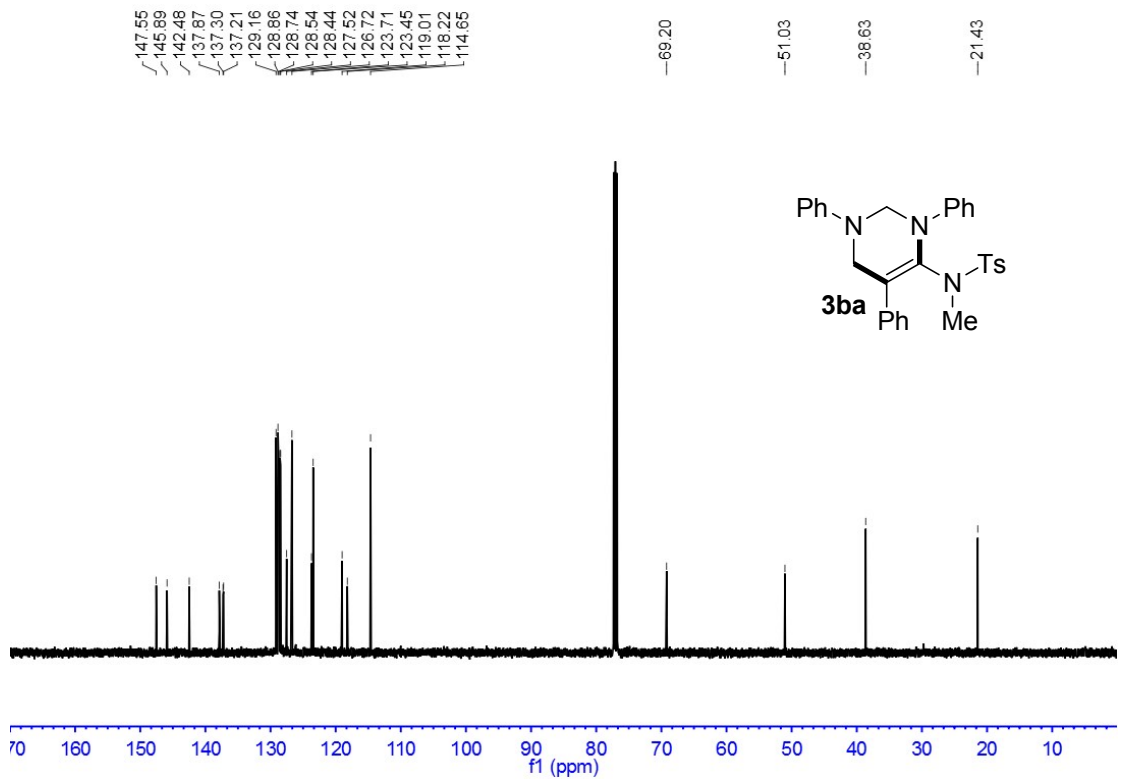
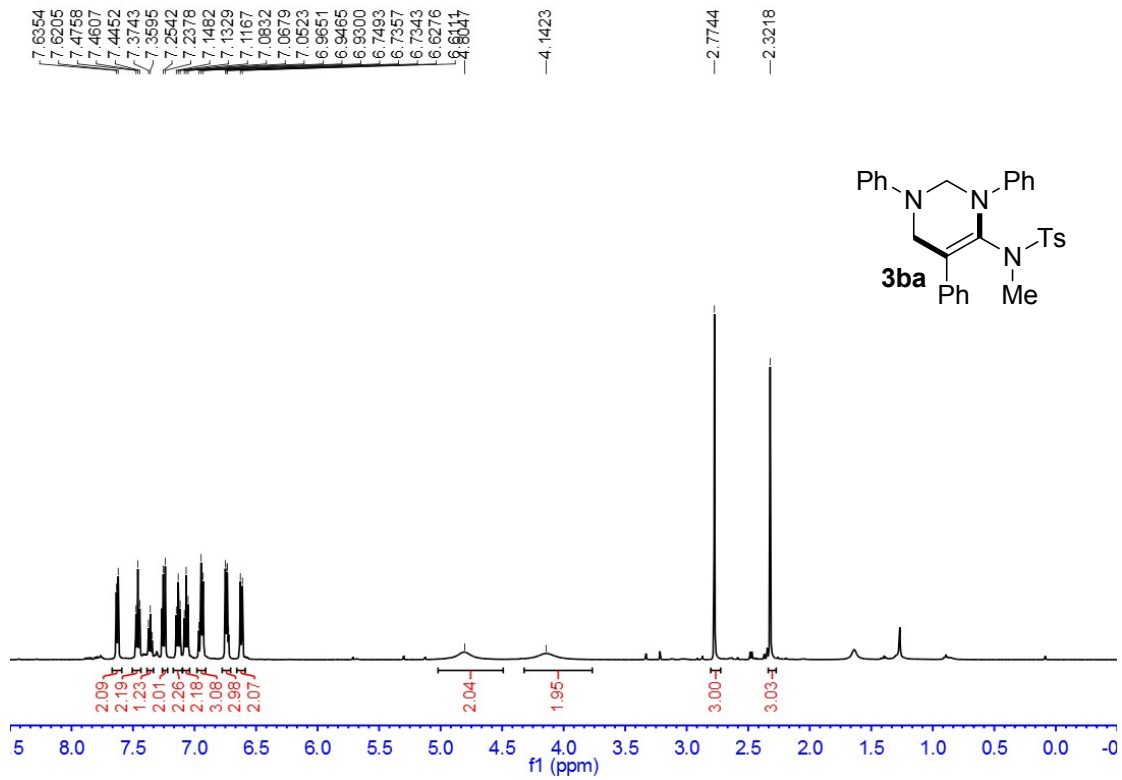
Yield 81%, light yellow solid, m.p.: 121–122 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.53–7.51 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.36–7.29 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.54 (d, *J* = 2.7 Hz, 1H), 6.45 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.79 (s, 2H), 4.10 (s, 2H), 2.68 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.3 (s), 144.4 (s), 137.2 (s), 137.1 (s), 136.5 (s), 130.4 (s), 129.8 (d), 129.4 (d), 128.8 (d), 128.5 (d), 127.7 (d), 126.4 (d), 124.8 (s), 122.6 (d), 117.8 (s), 117.6 (d), 114.1 (d), 69.4 (t), 51.4 (t), 39.9 (q), 37.2 (q), 20.4 (q), 20.3 (q) ppm; IR (ATR): $\tilde{\nu}$ 2927, 2856, 1640, 1597, 1482, 1446, 1413, 1336, 1230, 1145, 1089, 1046, 962, 862, 817, 767, 700 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{26}\text{H}_{27}\text{N}_3\text{O}_2\text{SCl}_2]^+$ (M)⁺: 515.1196; found: 515.1198.

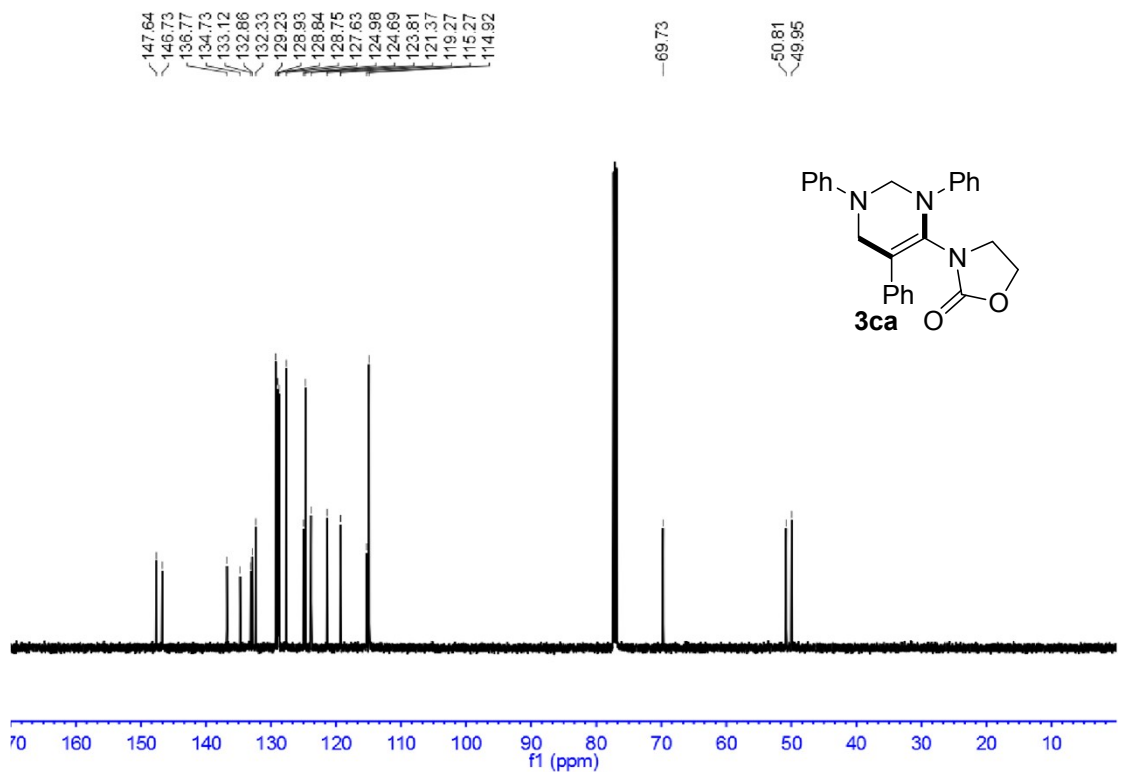
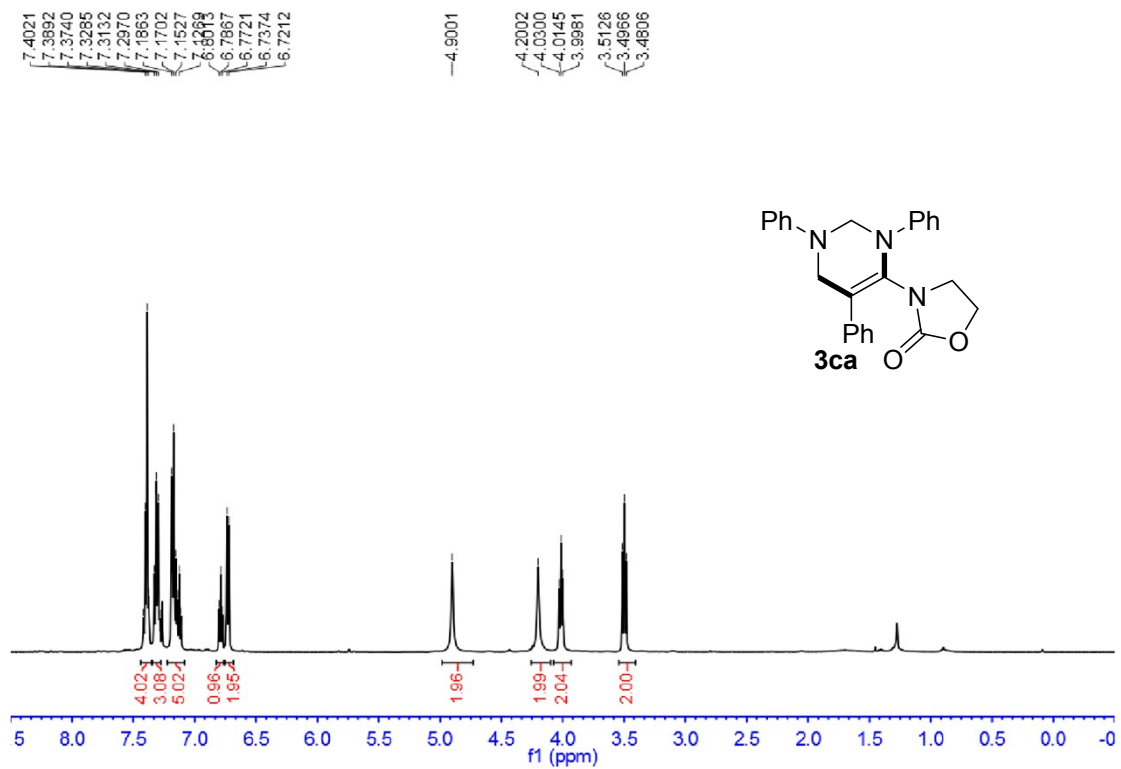
3. References

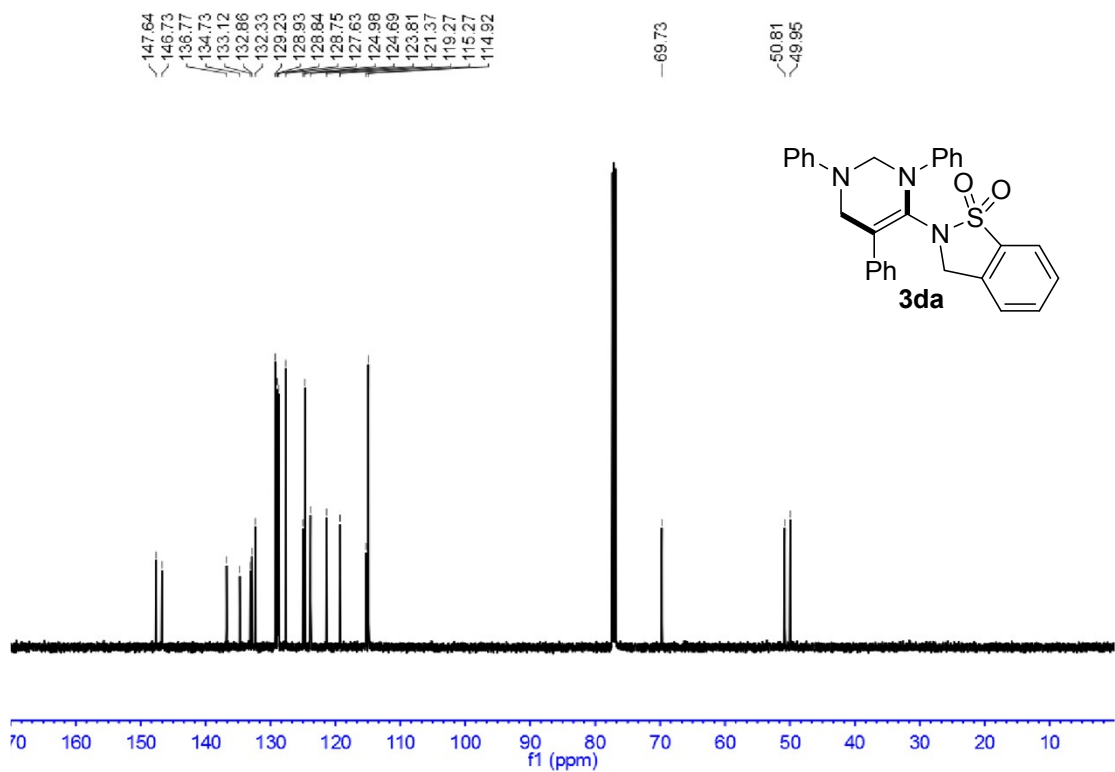
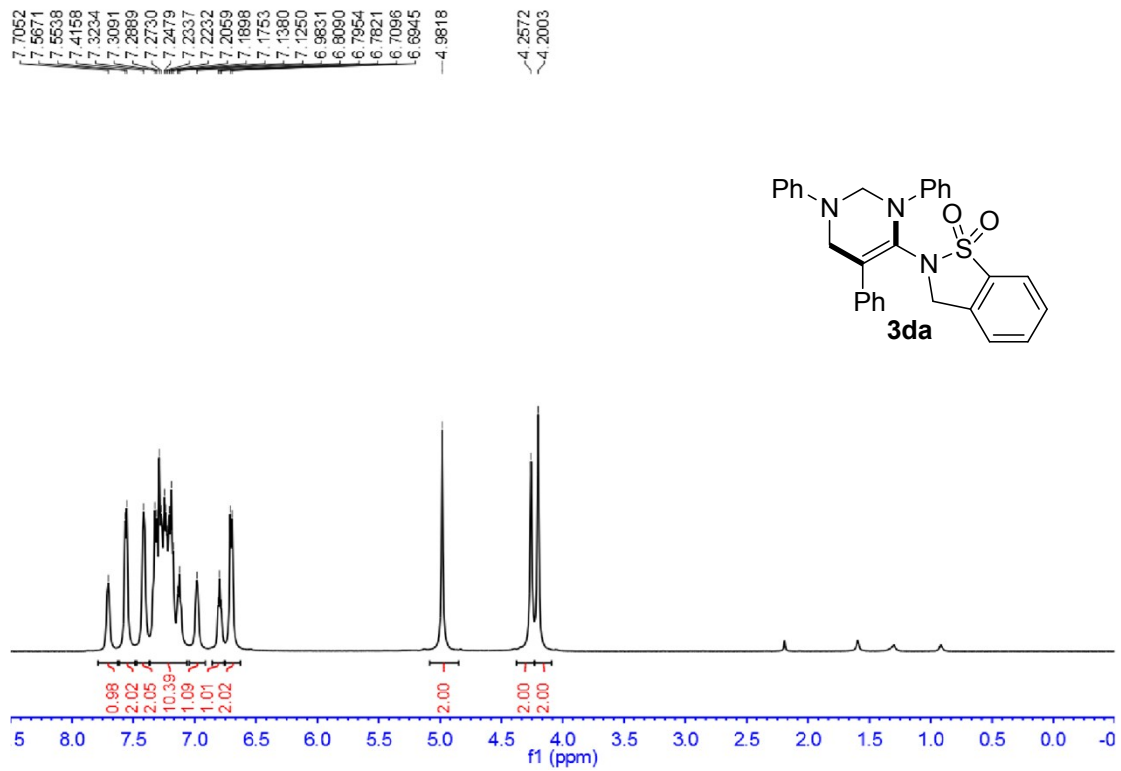
- 1 L. Zhu, Y. Yu, Z. Mao, and X. Huang, *Org. Lett.*, 2015, **17**, 30.
- 2 A. G. Giumanini, G. Verardo, E. Zangrando, and L. Lassiani, *J. Prakt. Chem.*, 1987, **329**, 1087.

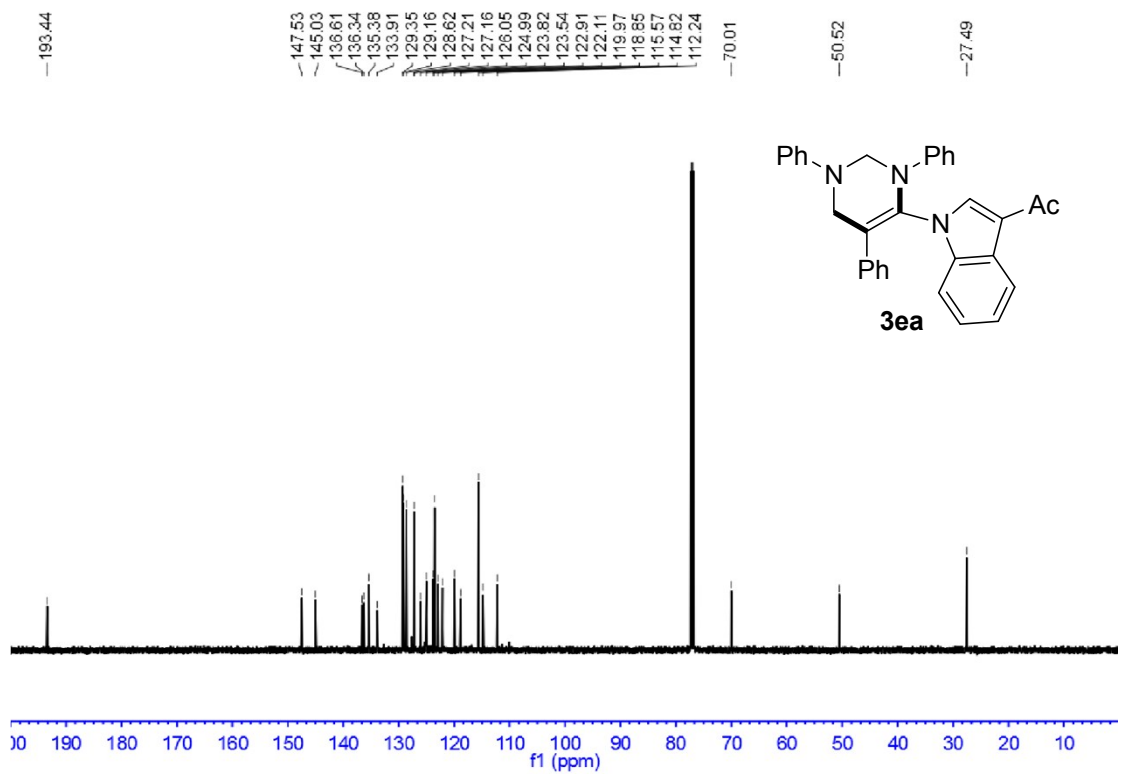
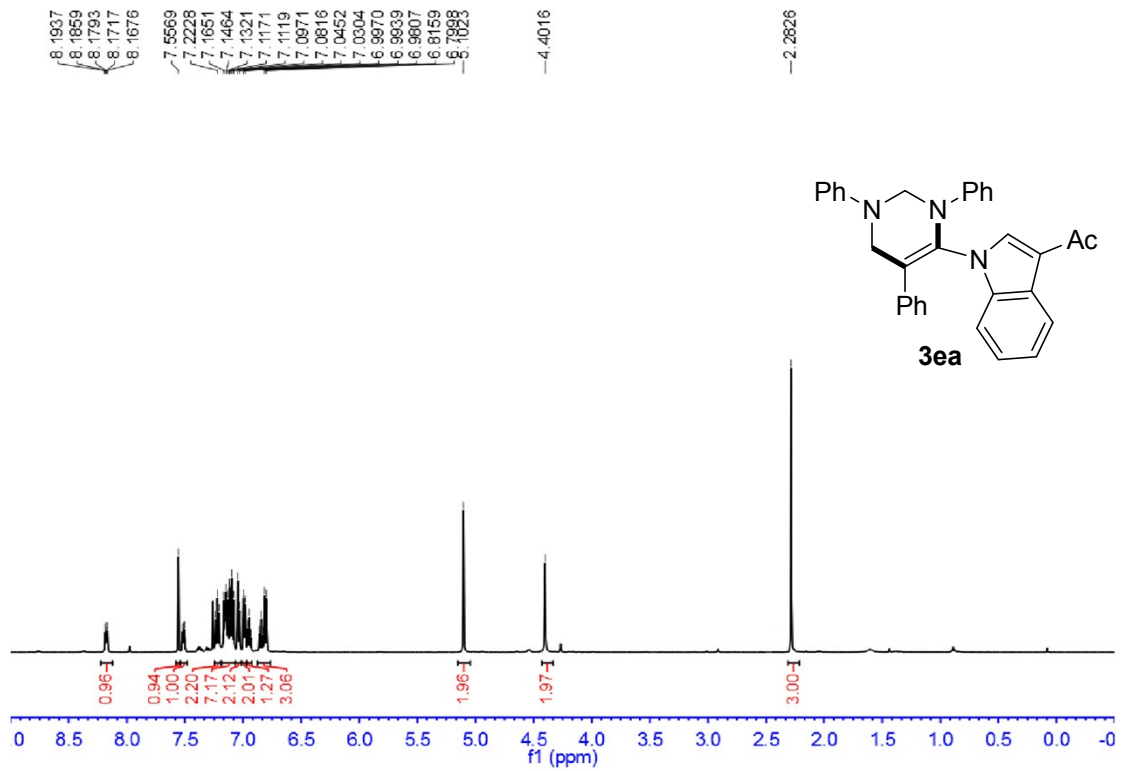
4. Copies of NMR spectra

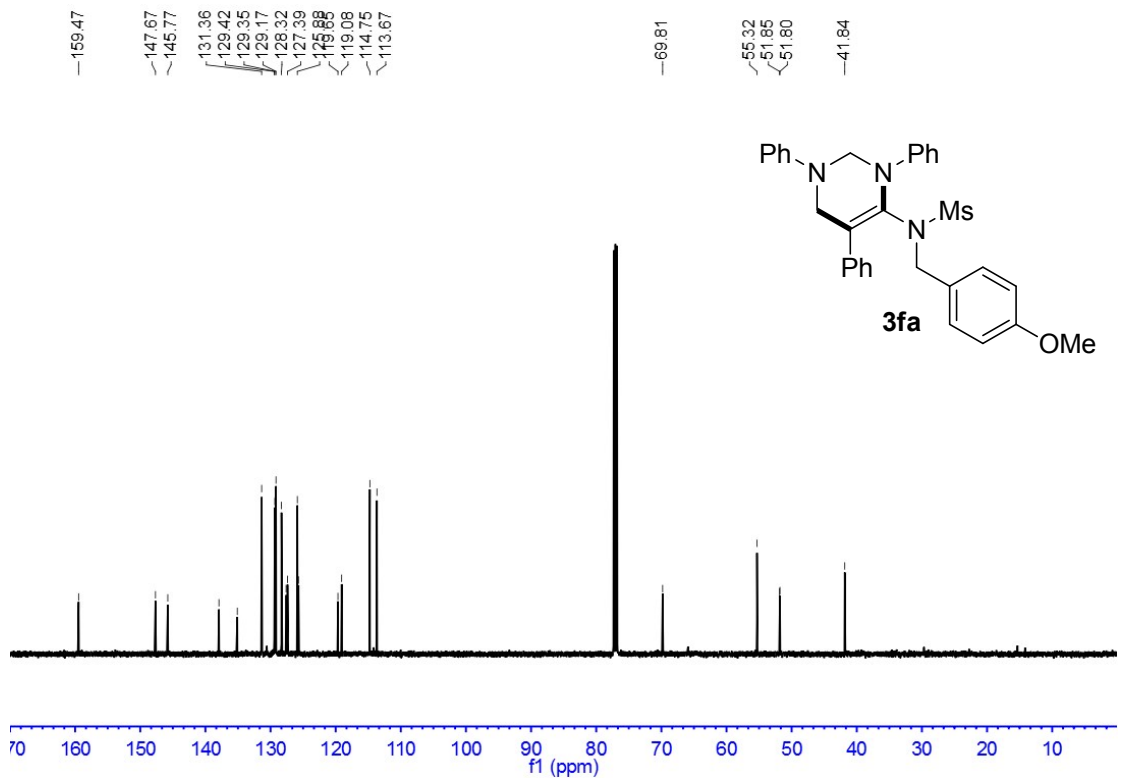
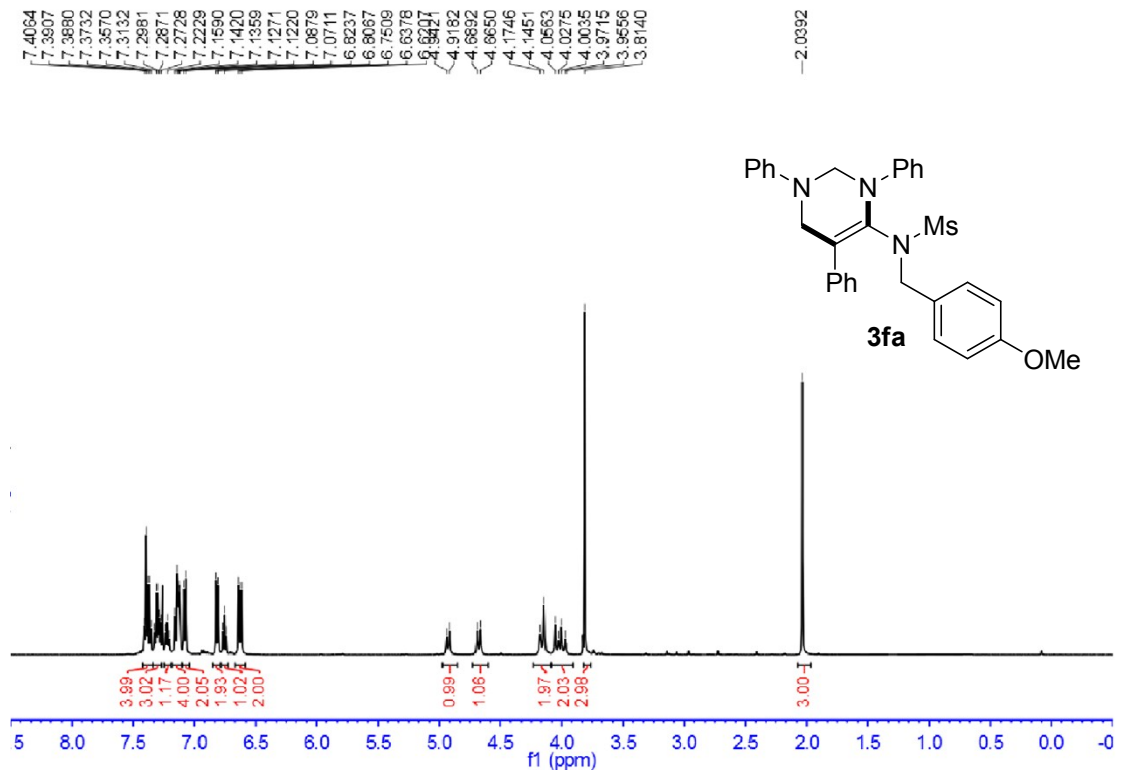


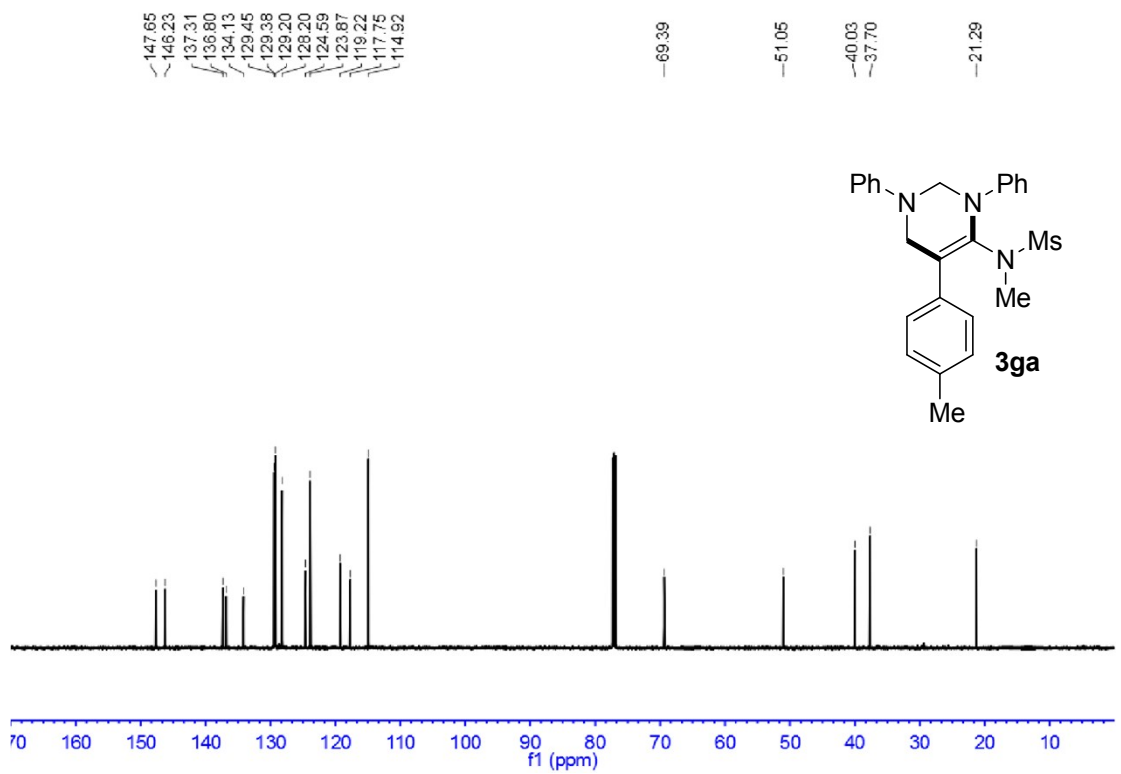
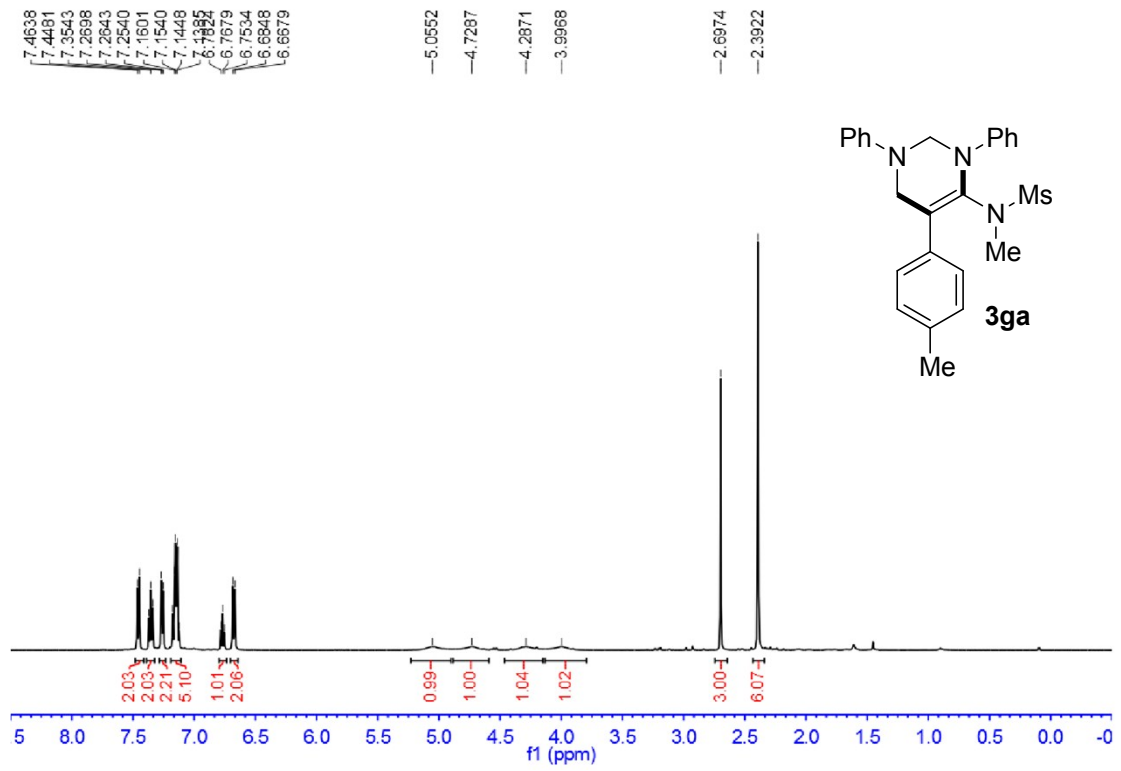


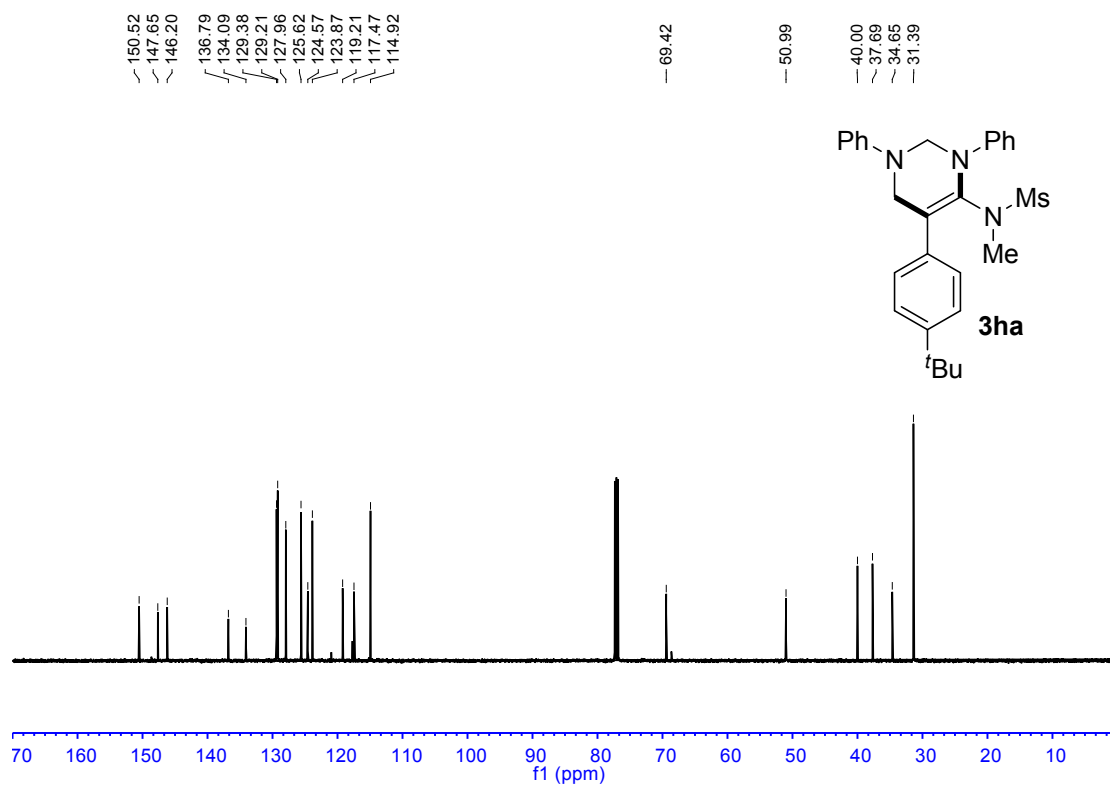
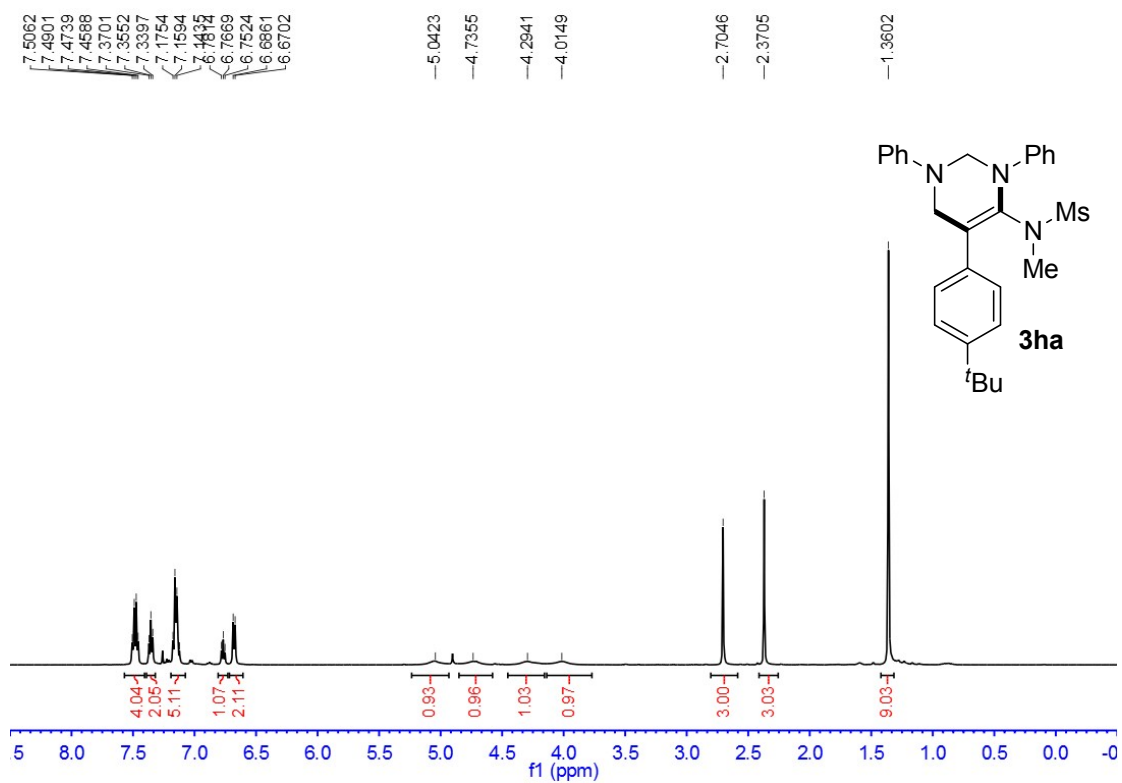


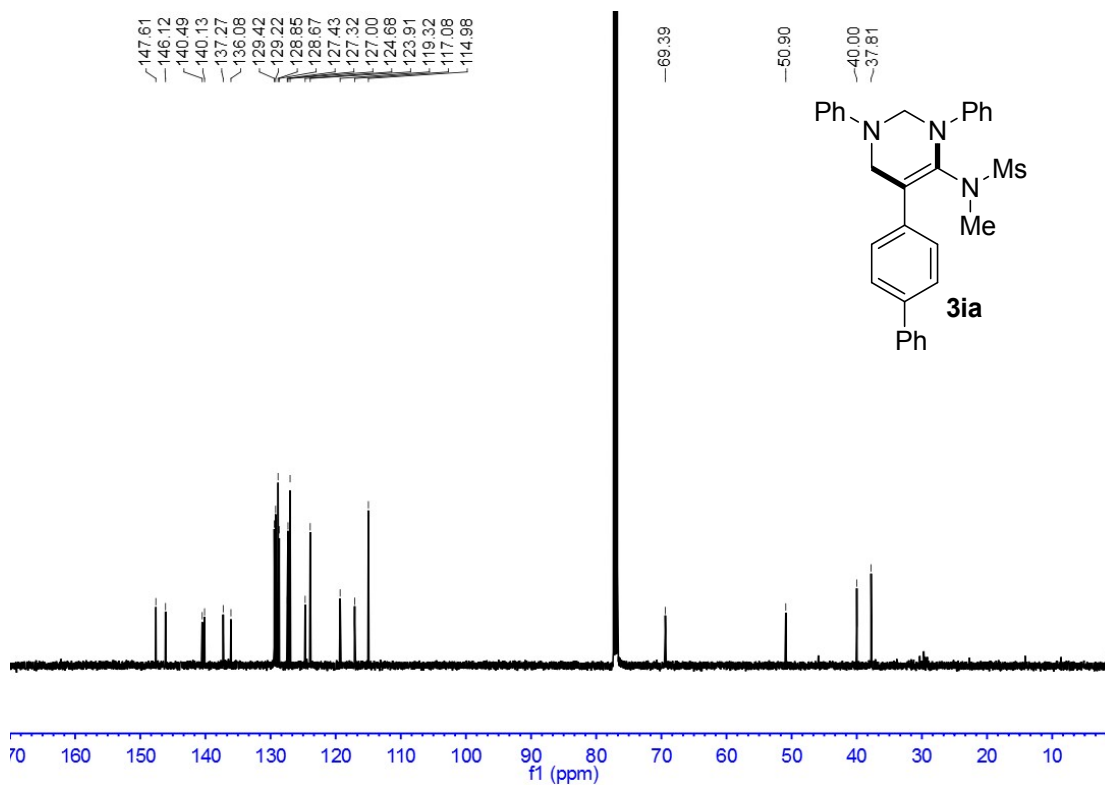
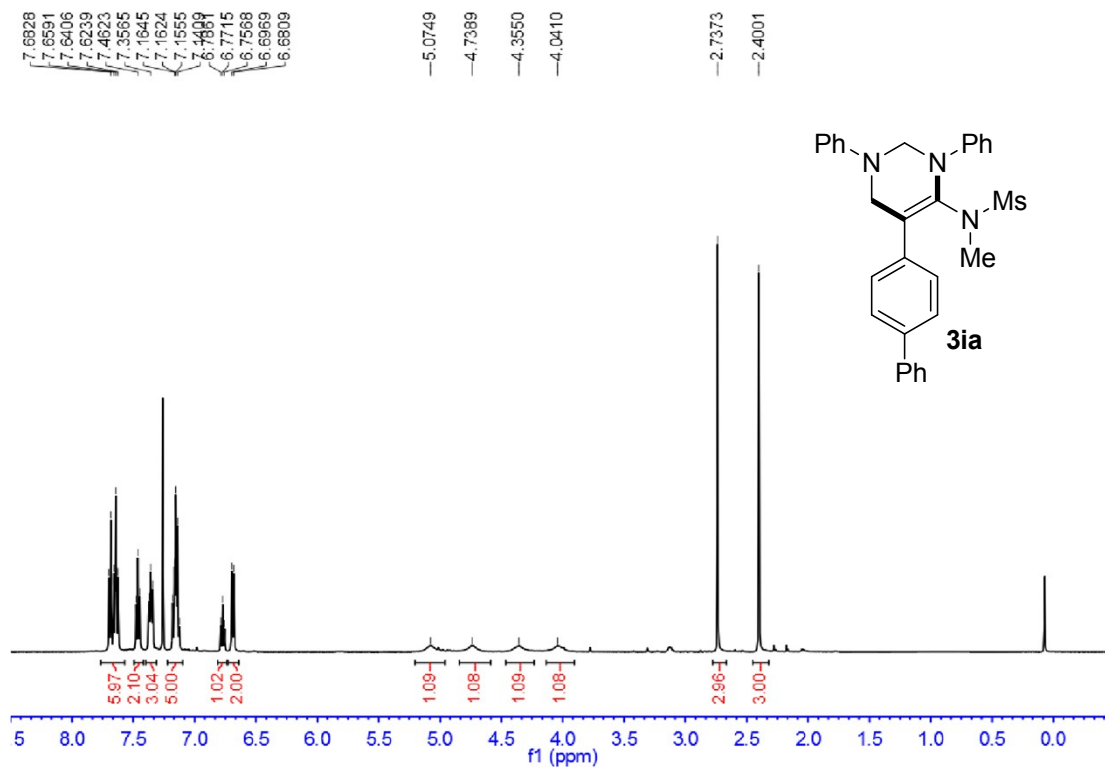


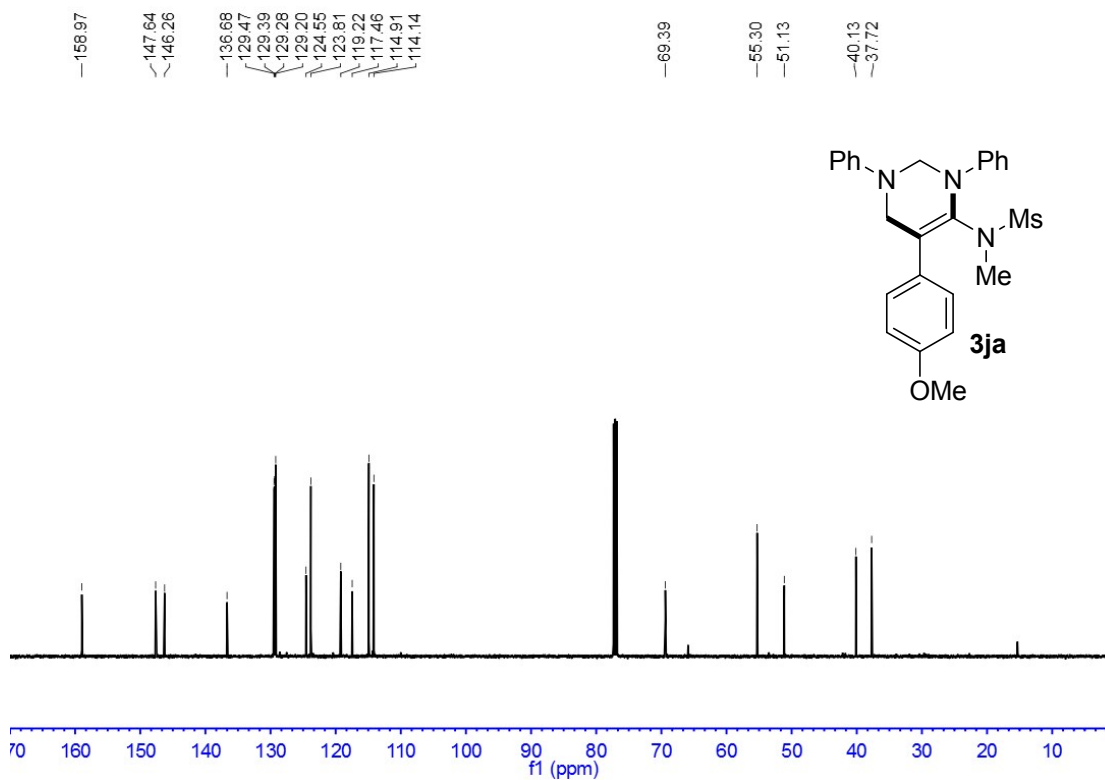
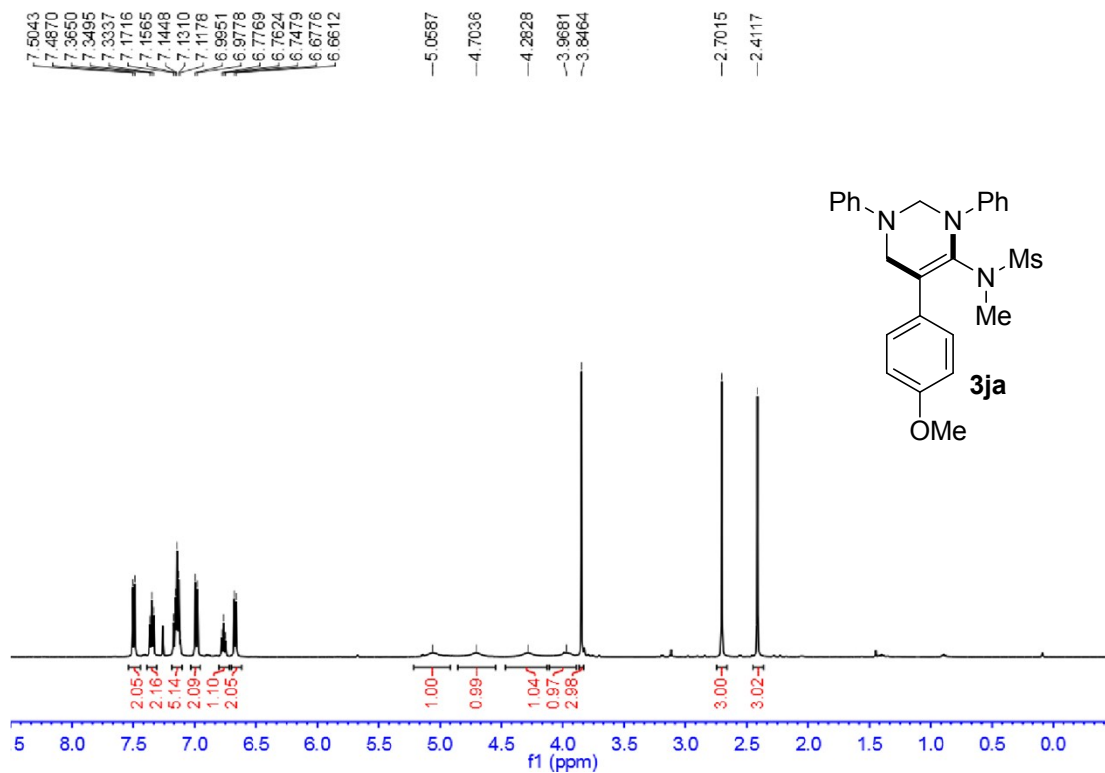


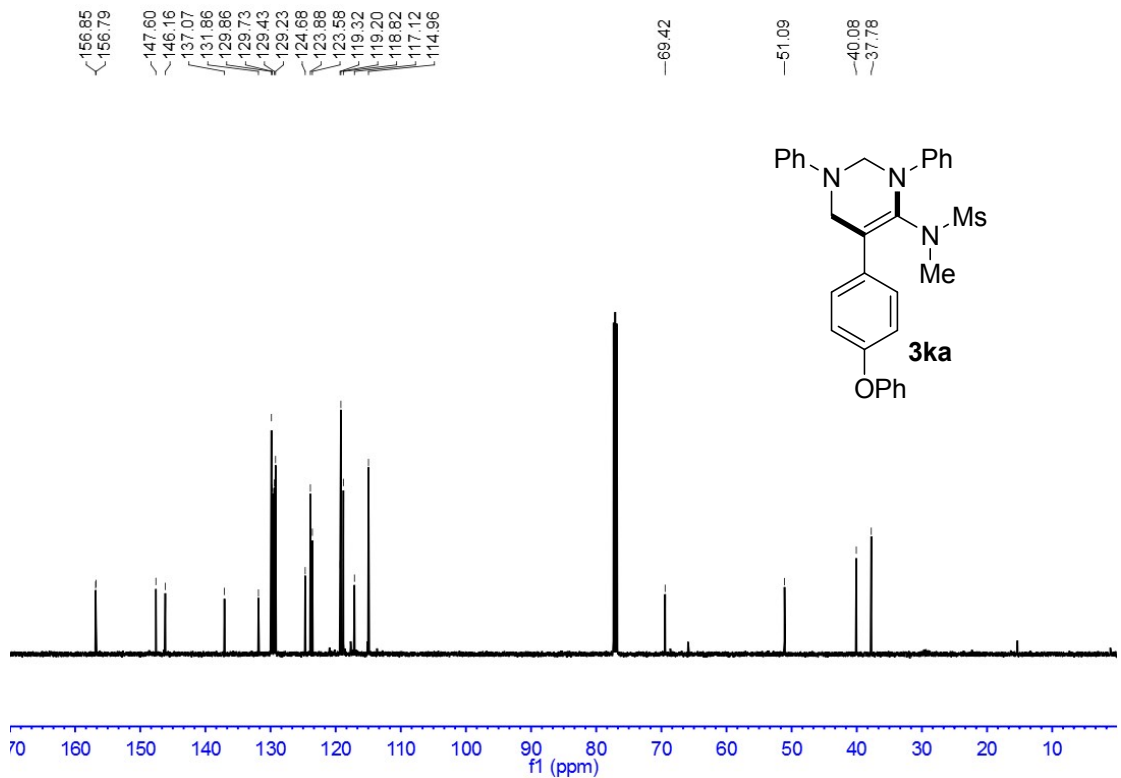
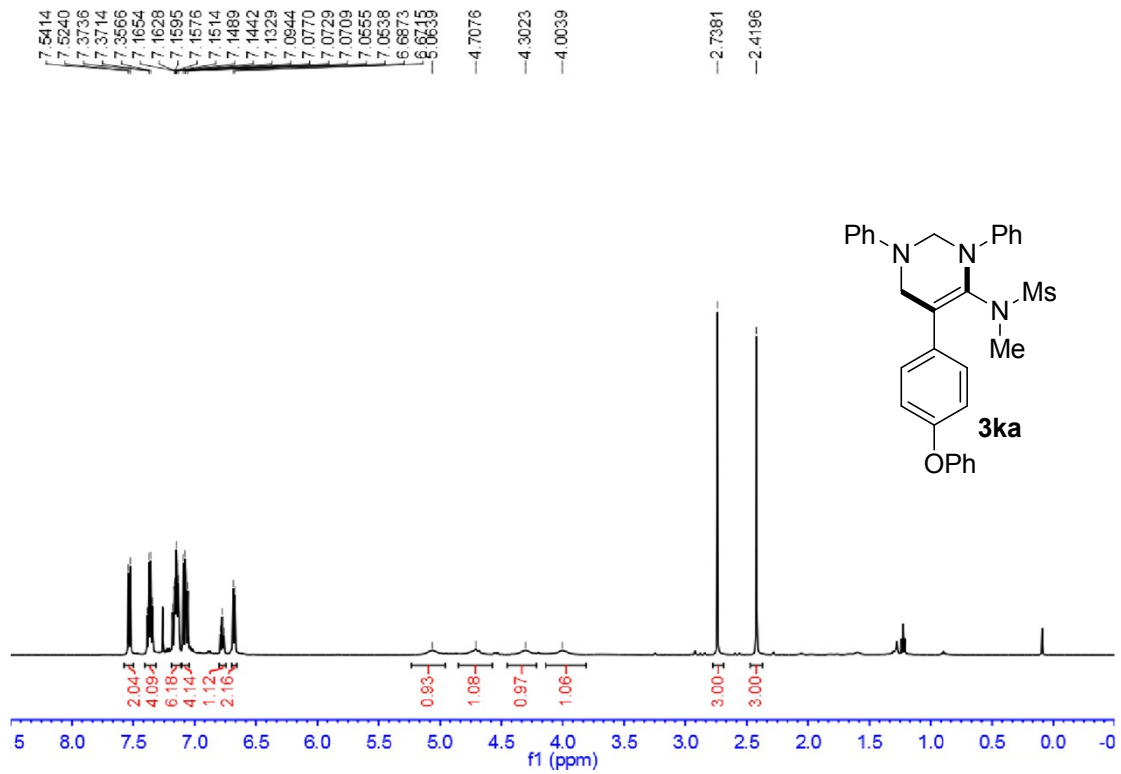


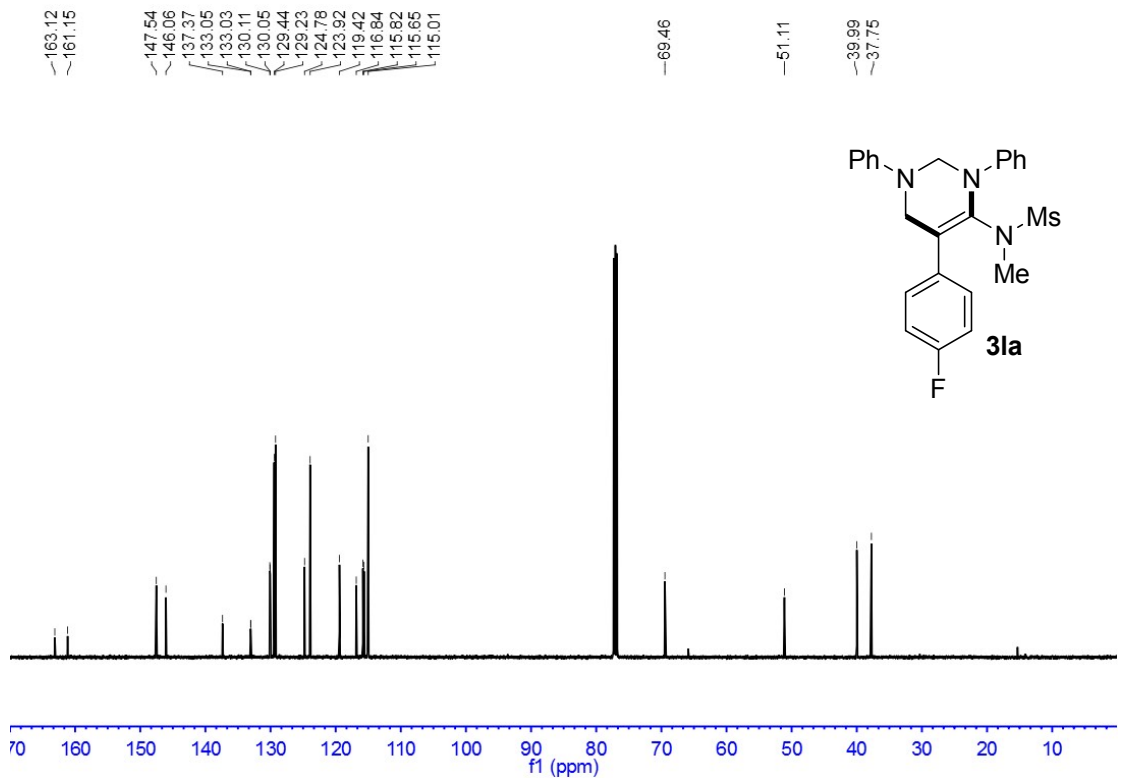
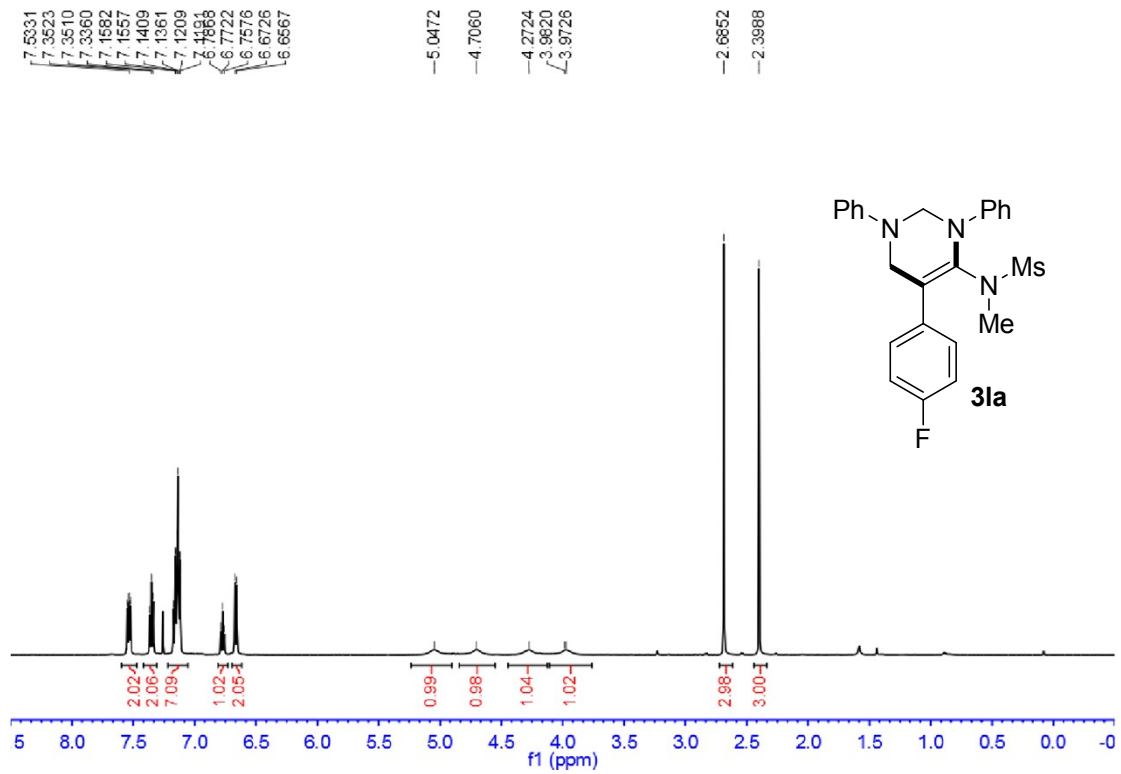


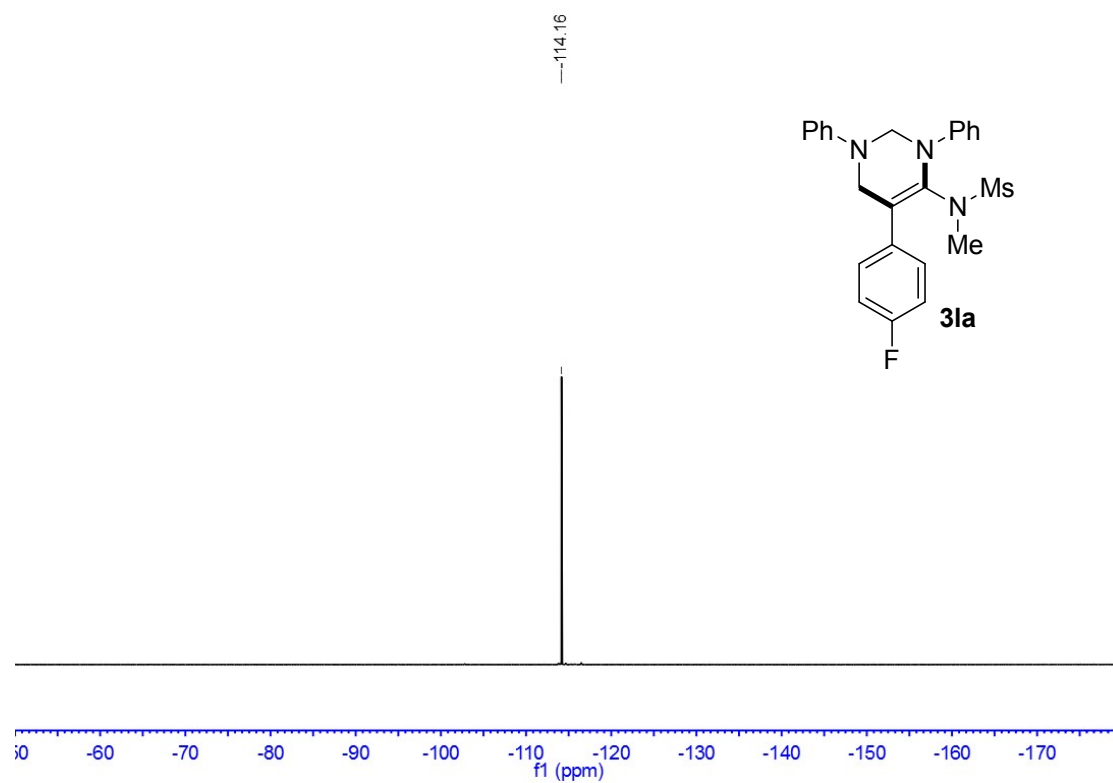


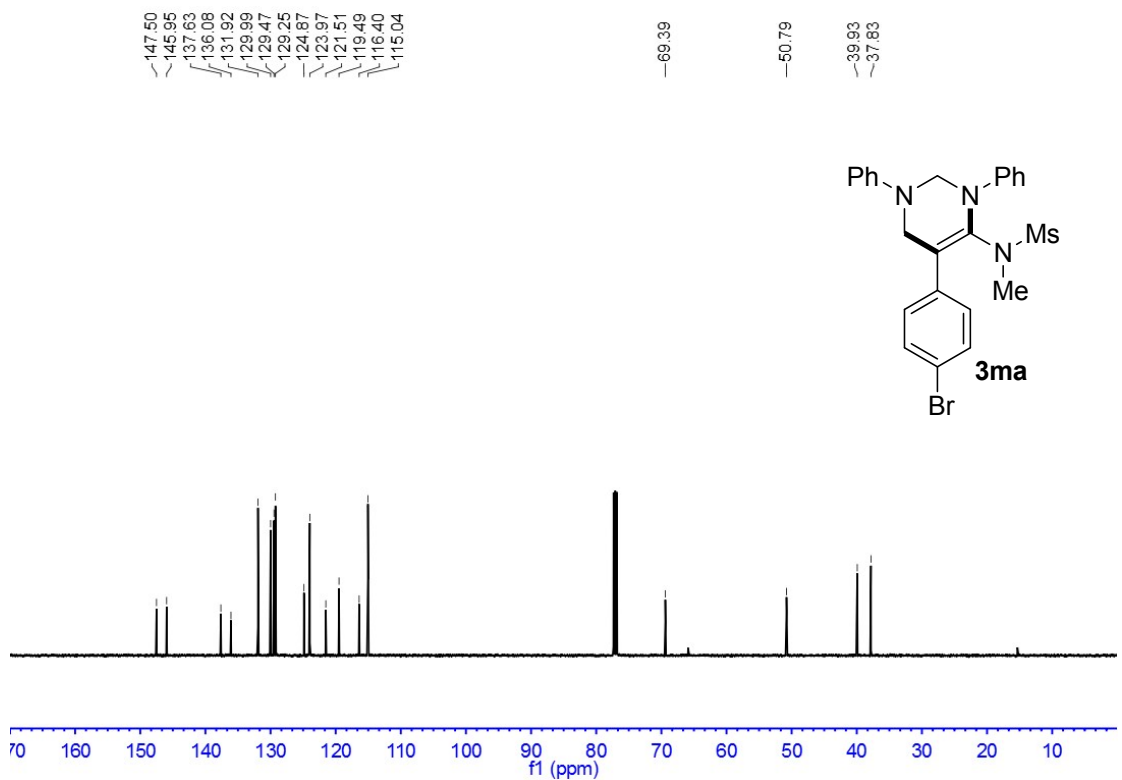
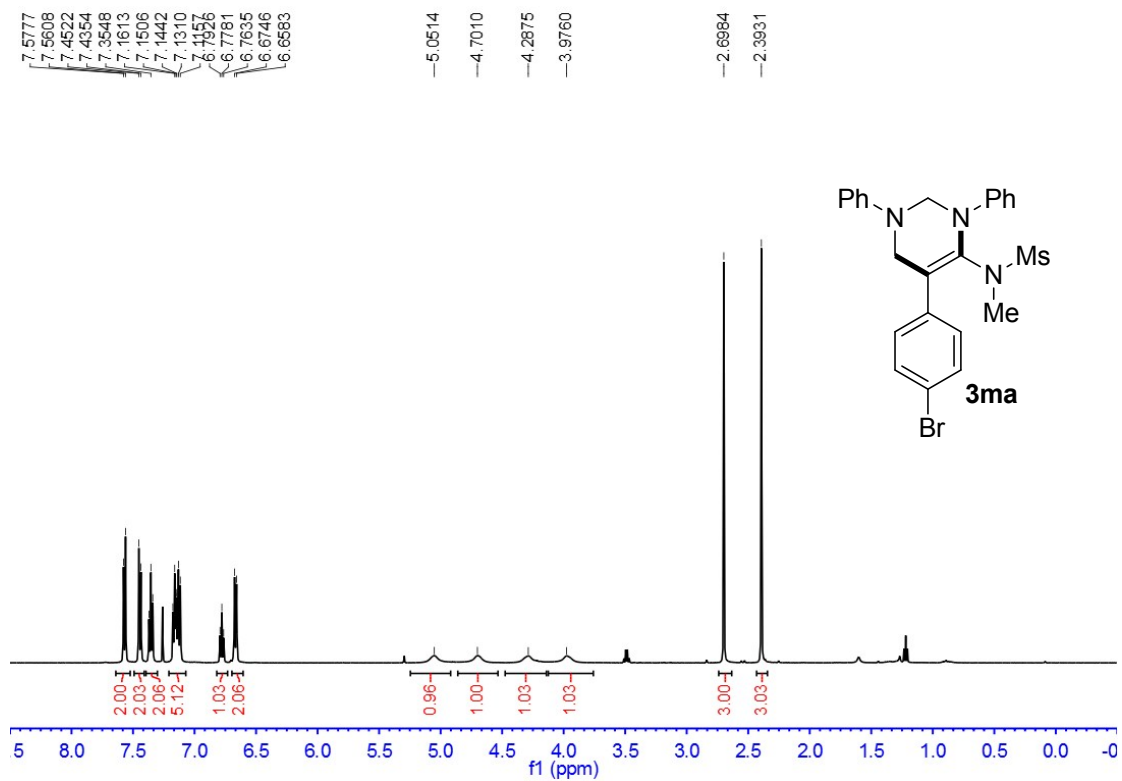


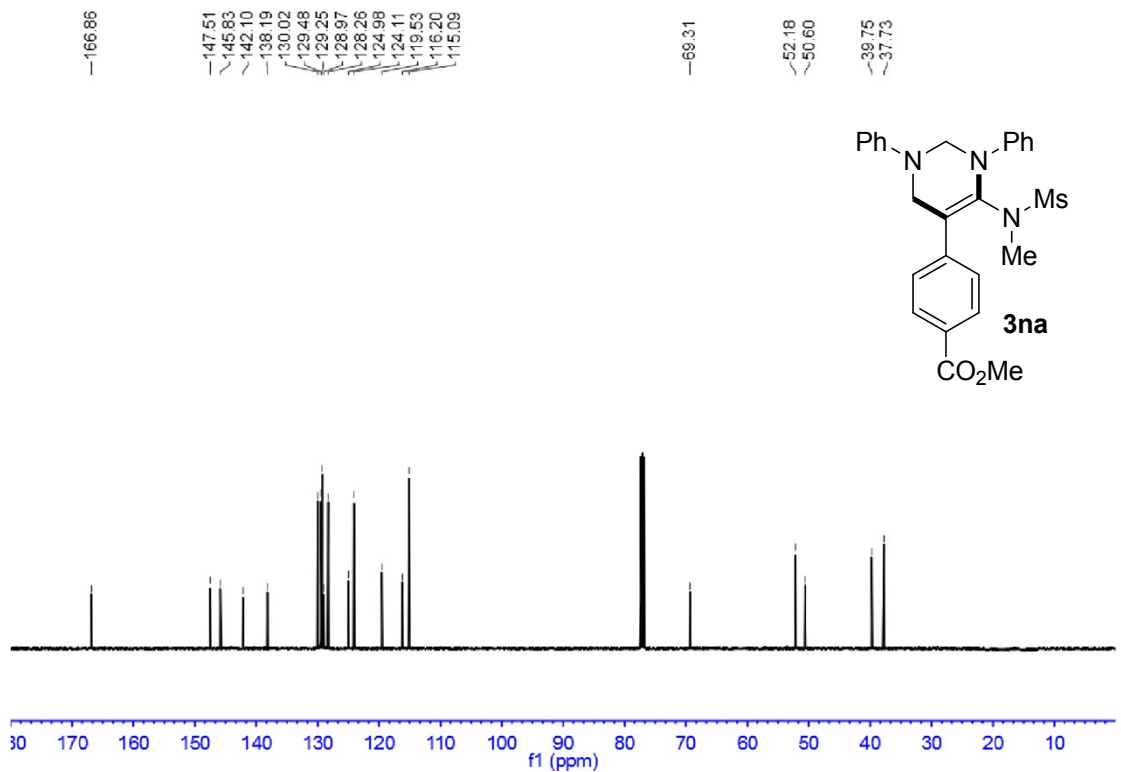
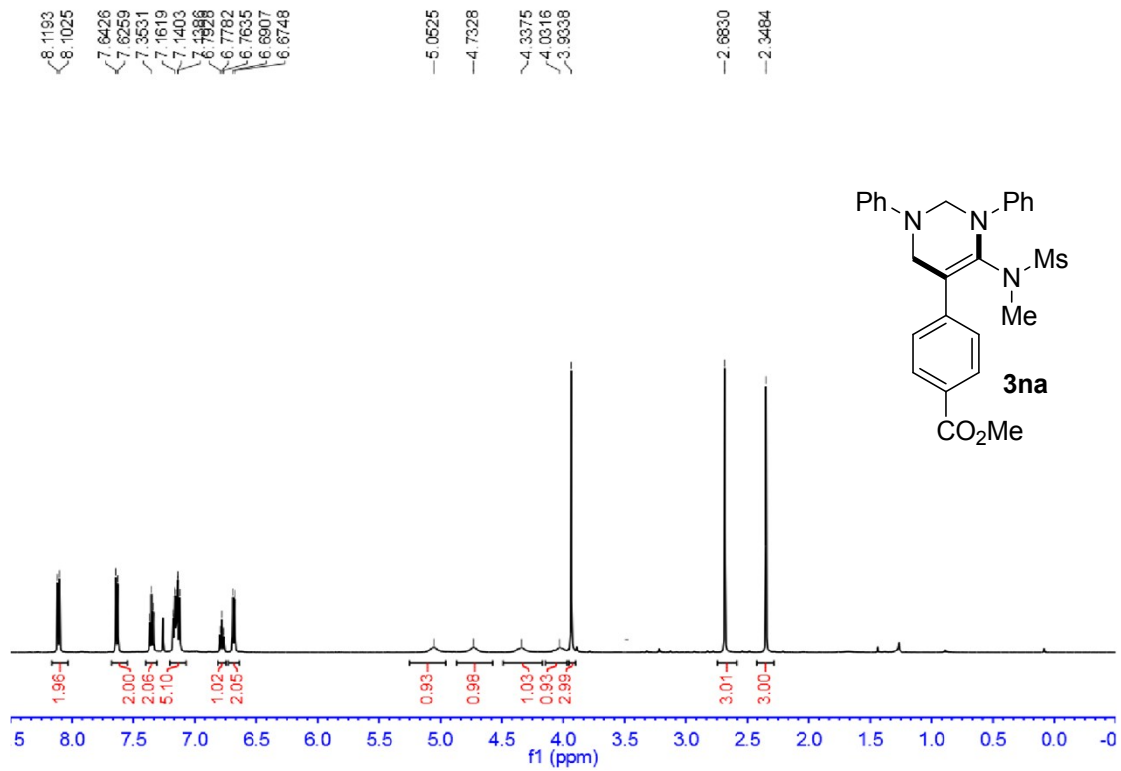


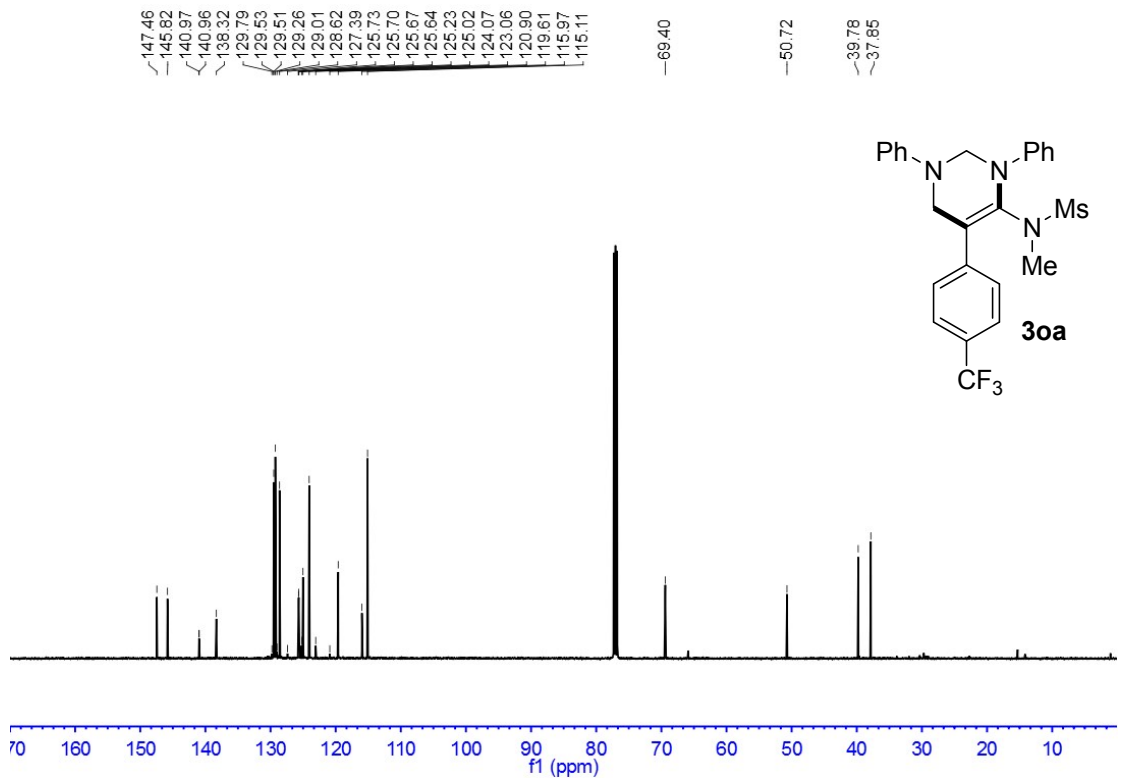
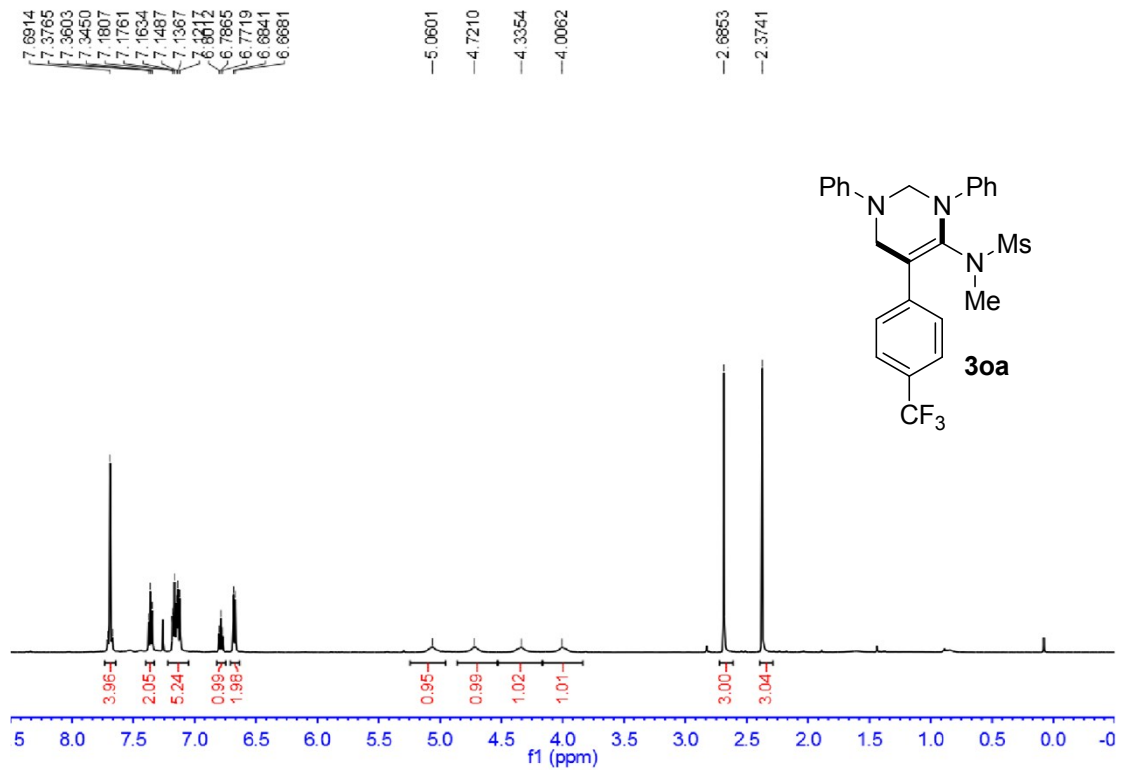


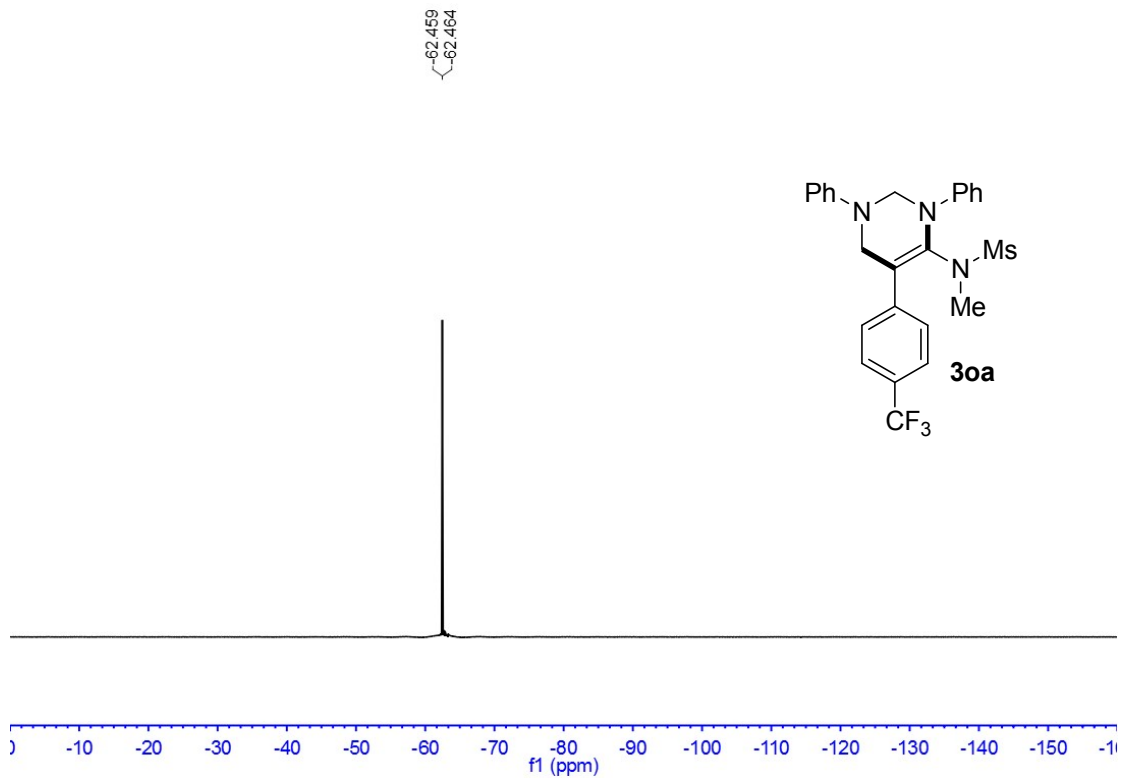


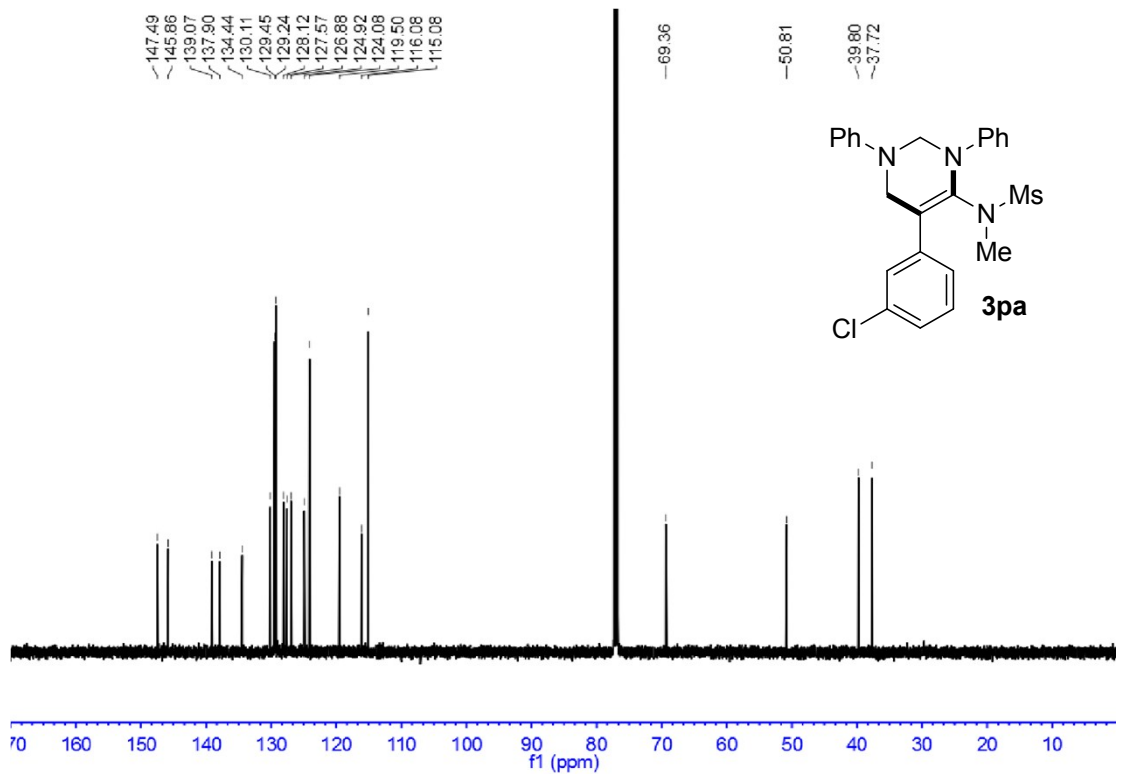
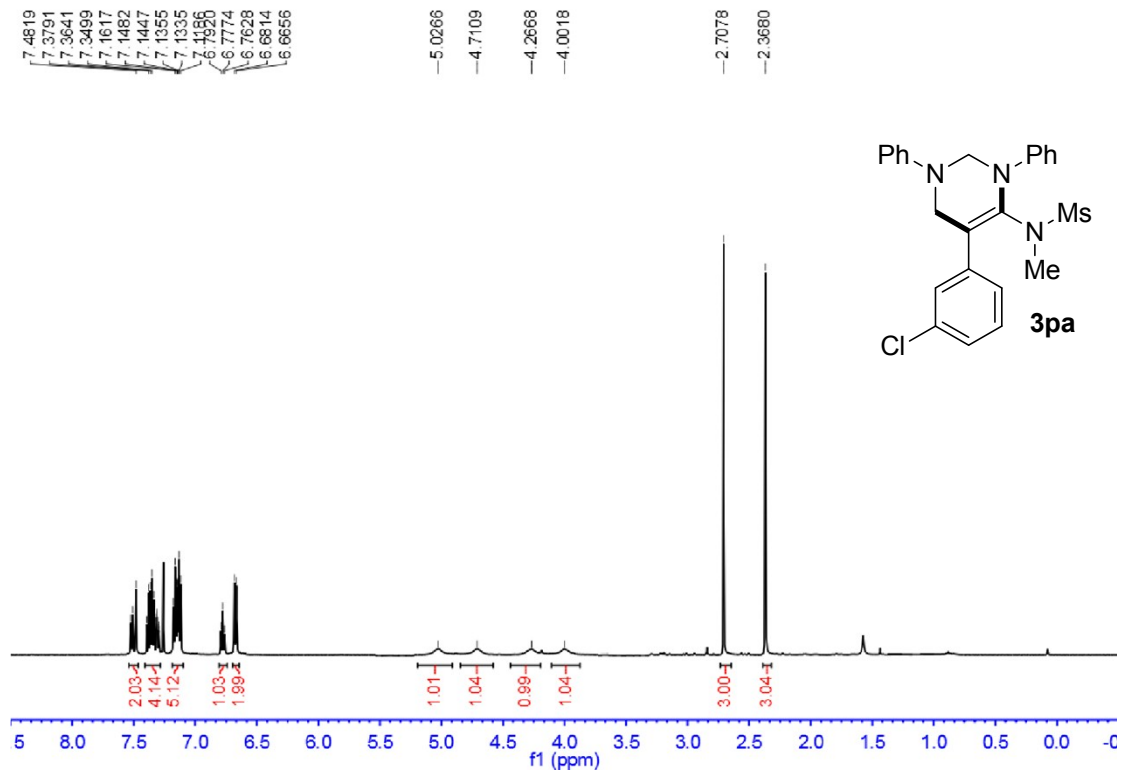


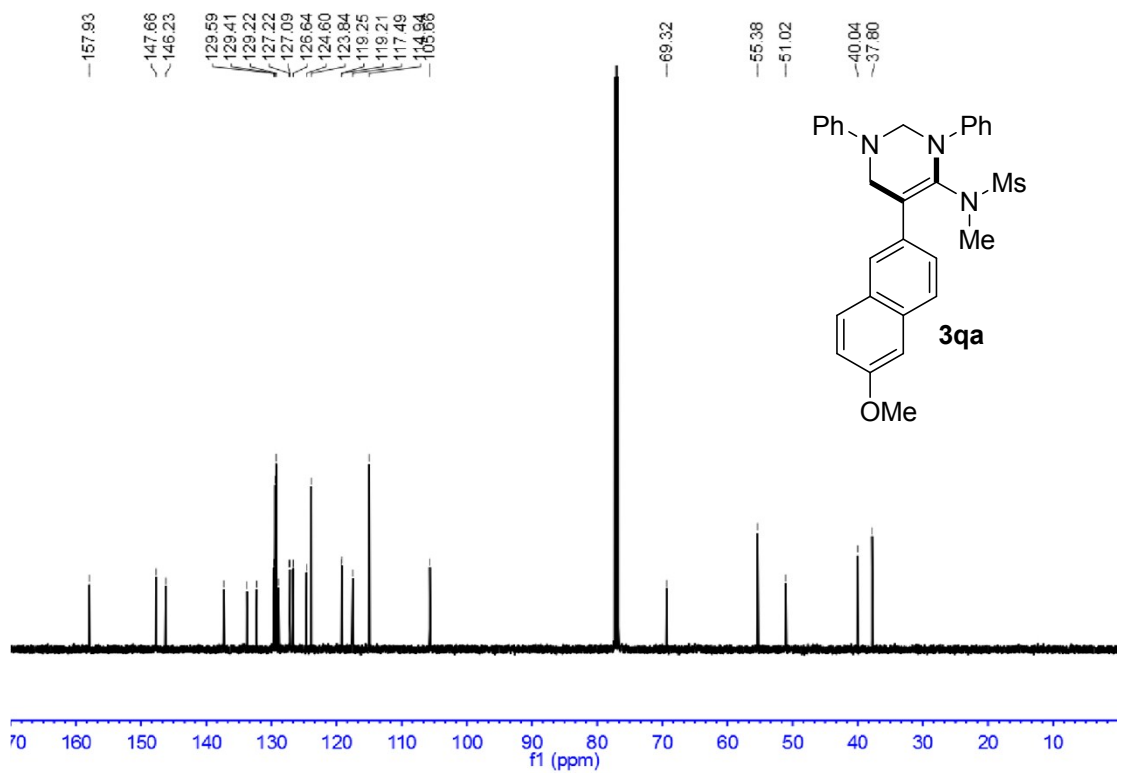
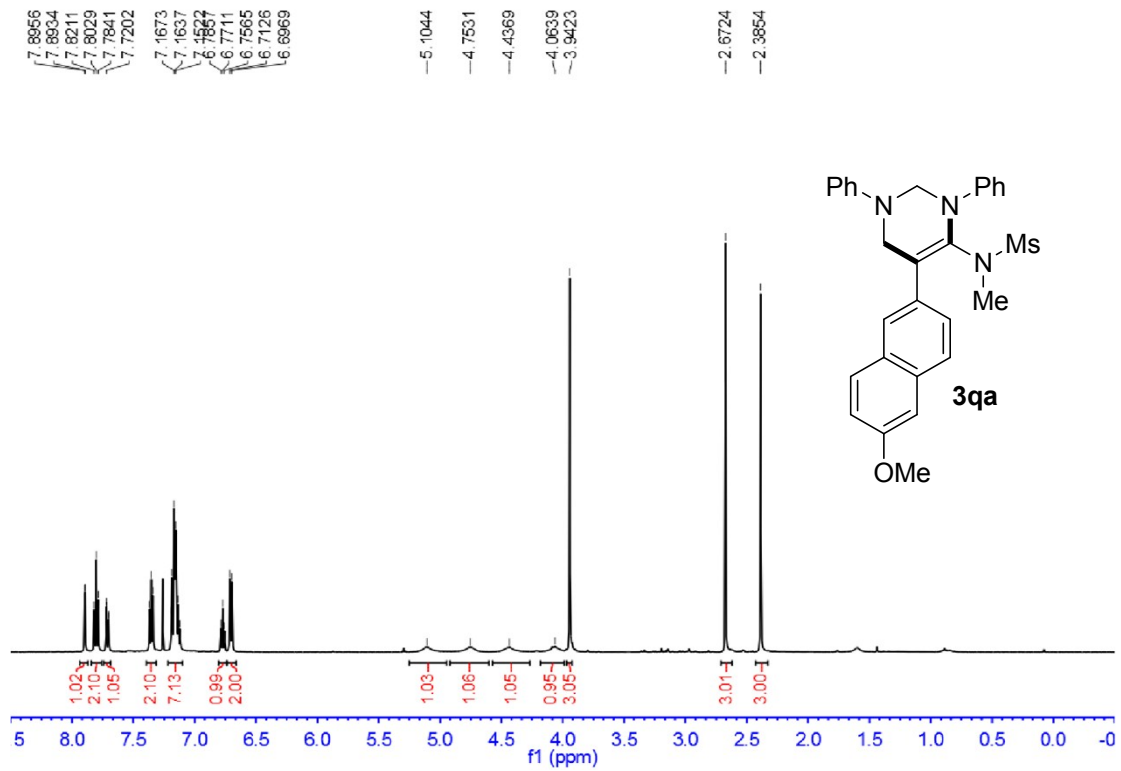


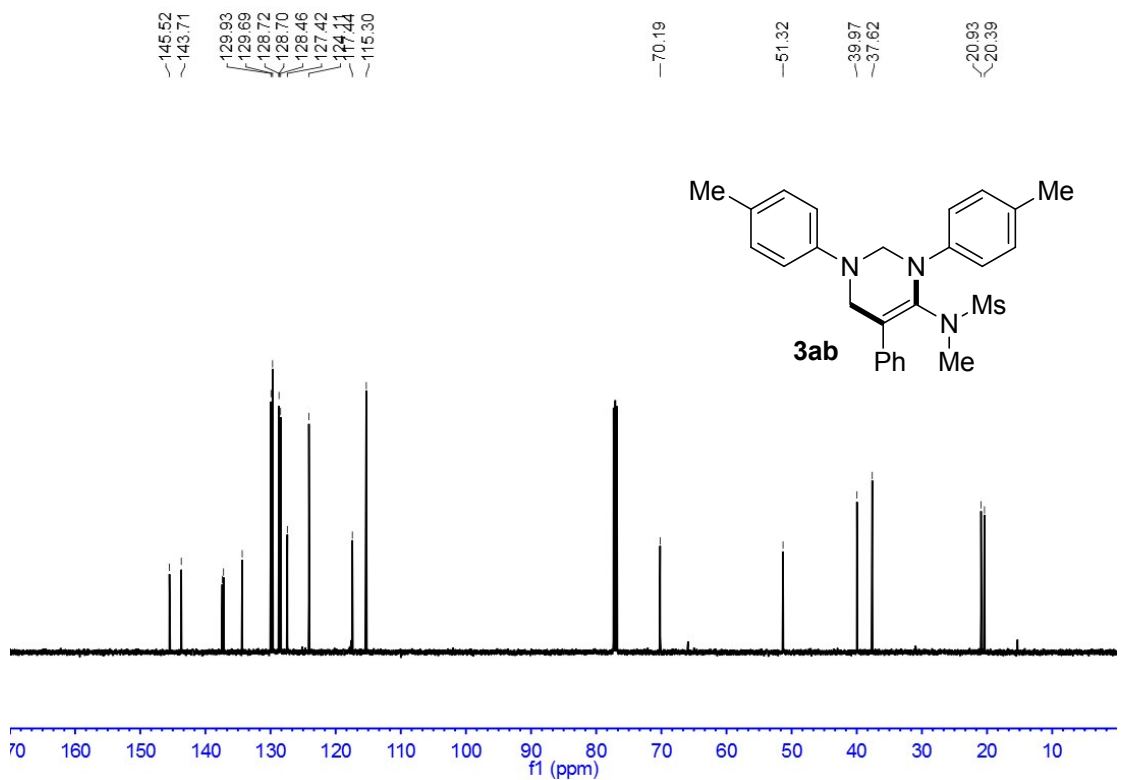
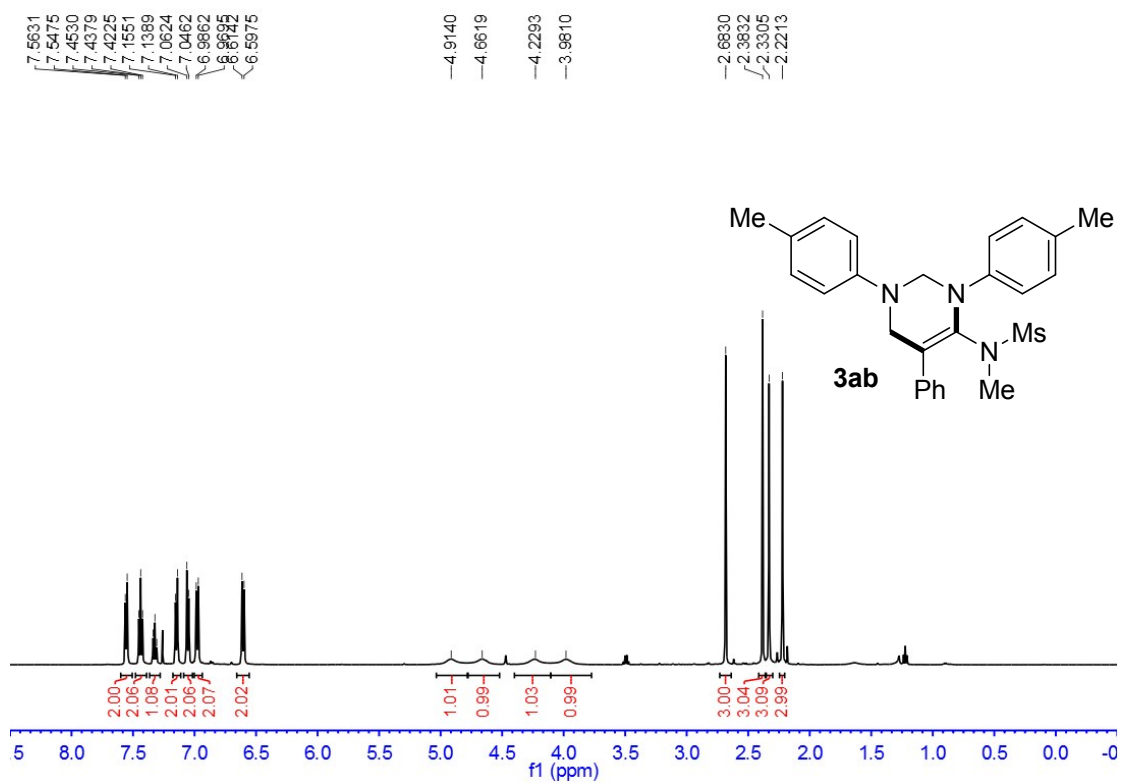


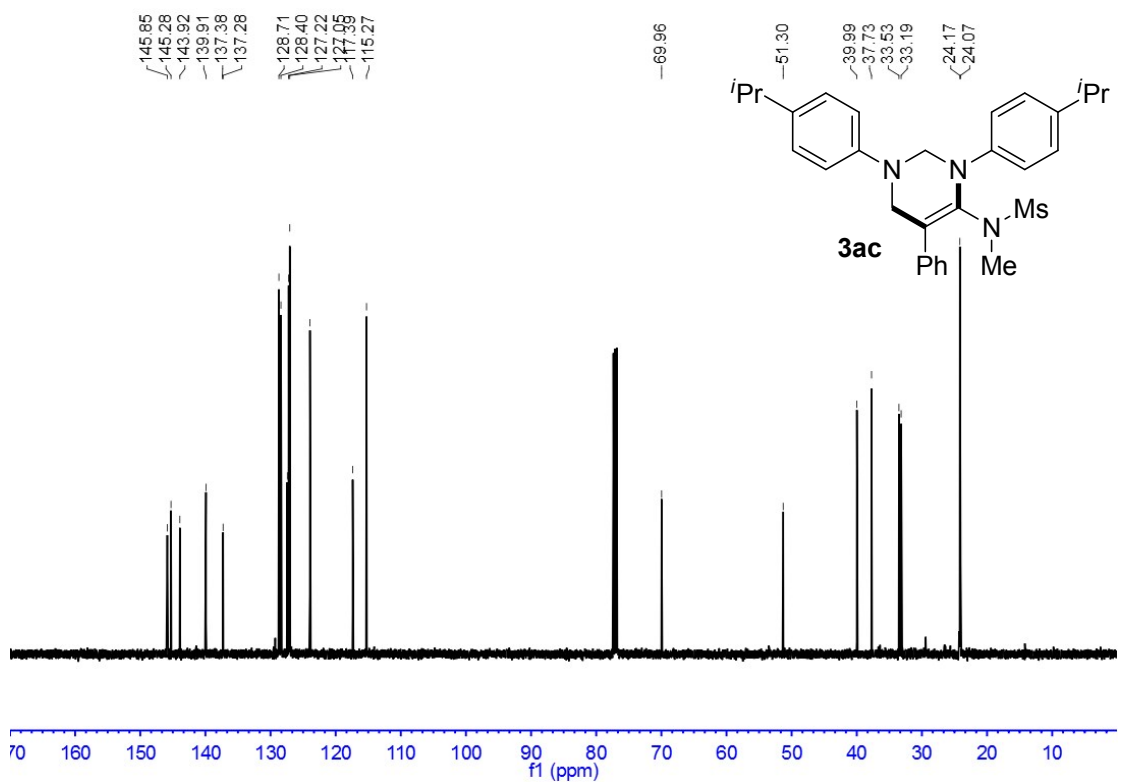
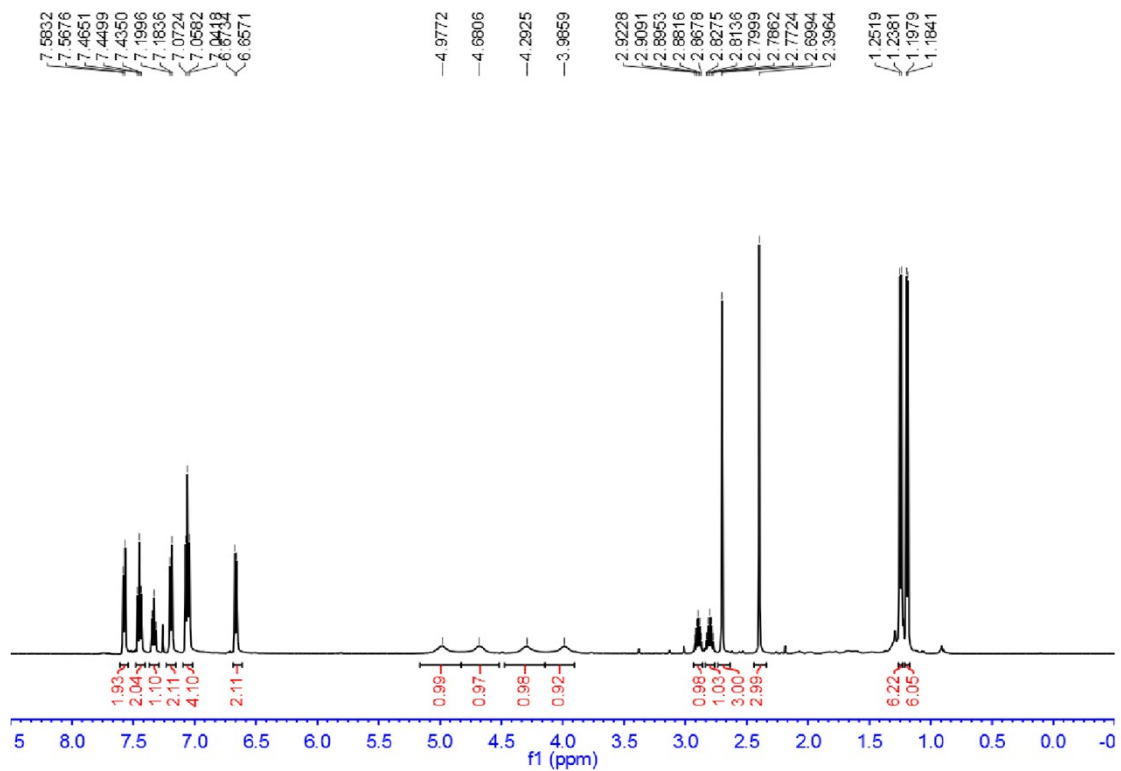


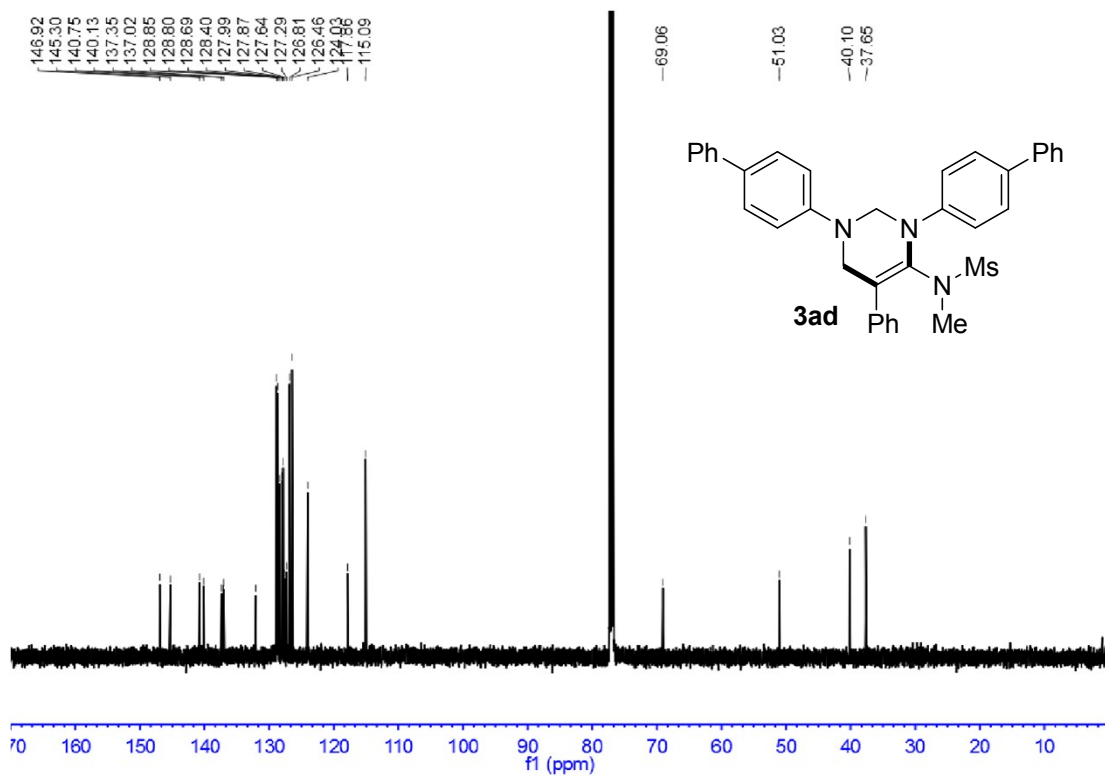
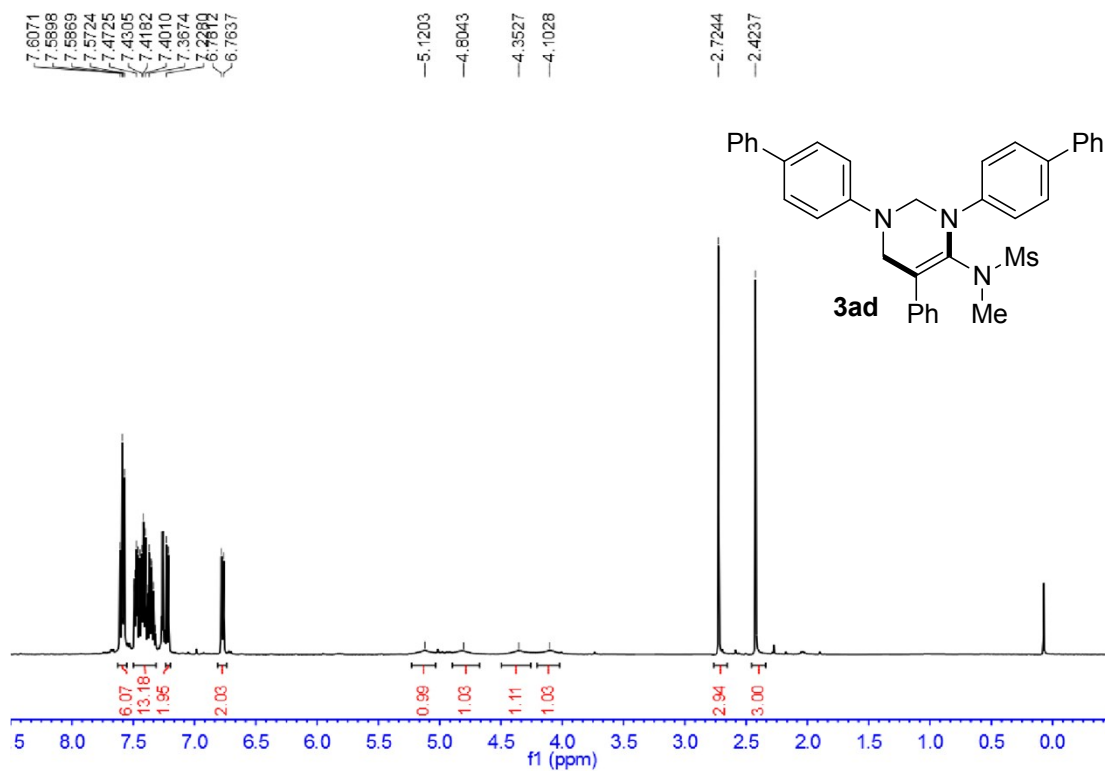


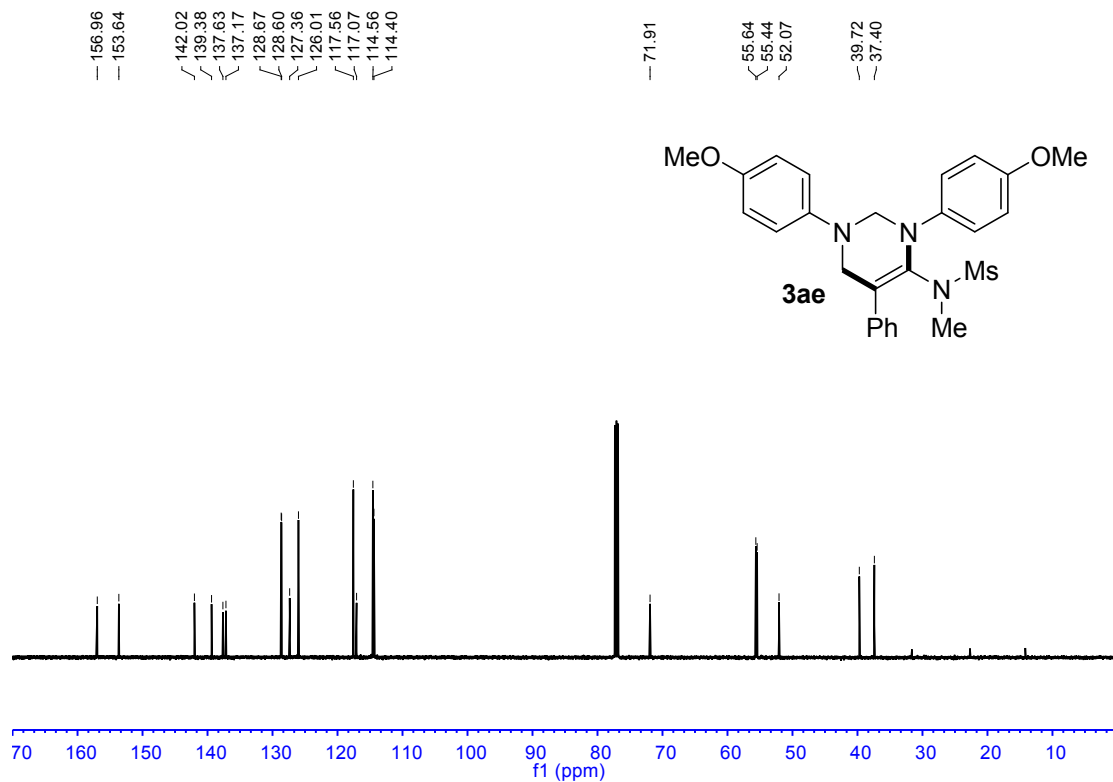
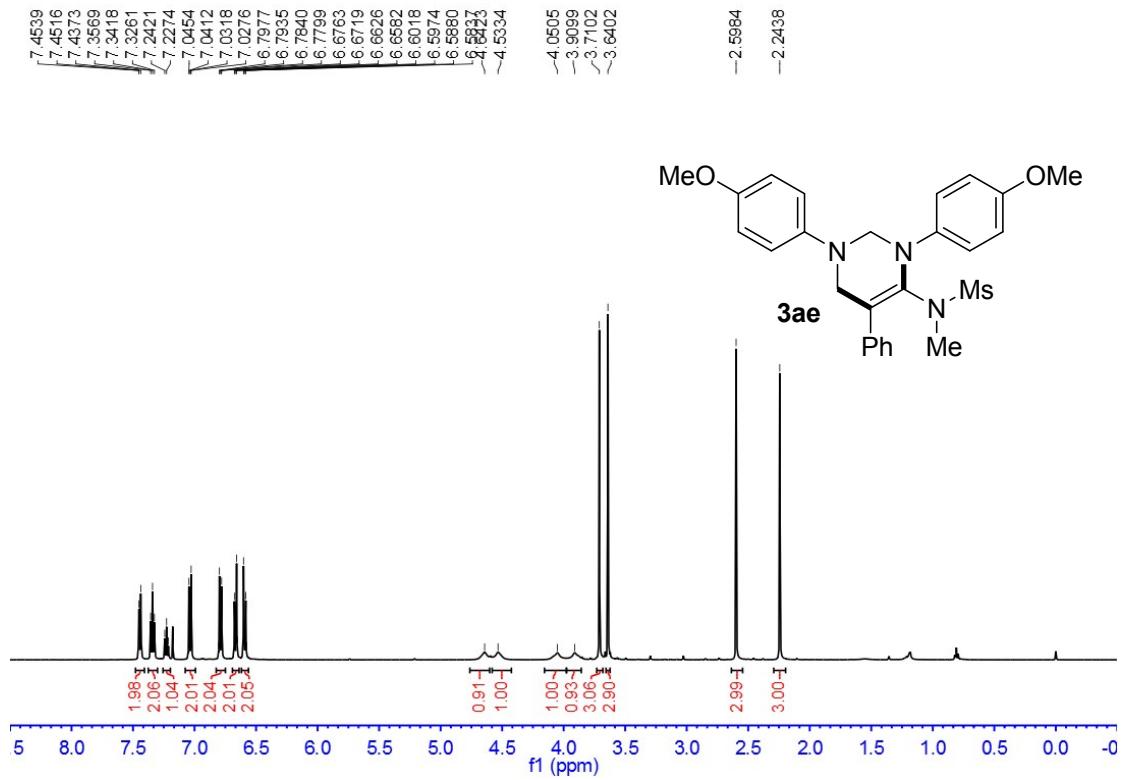


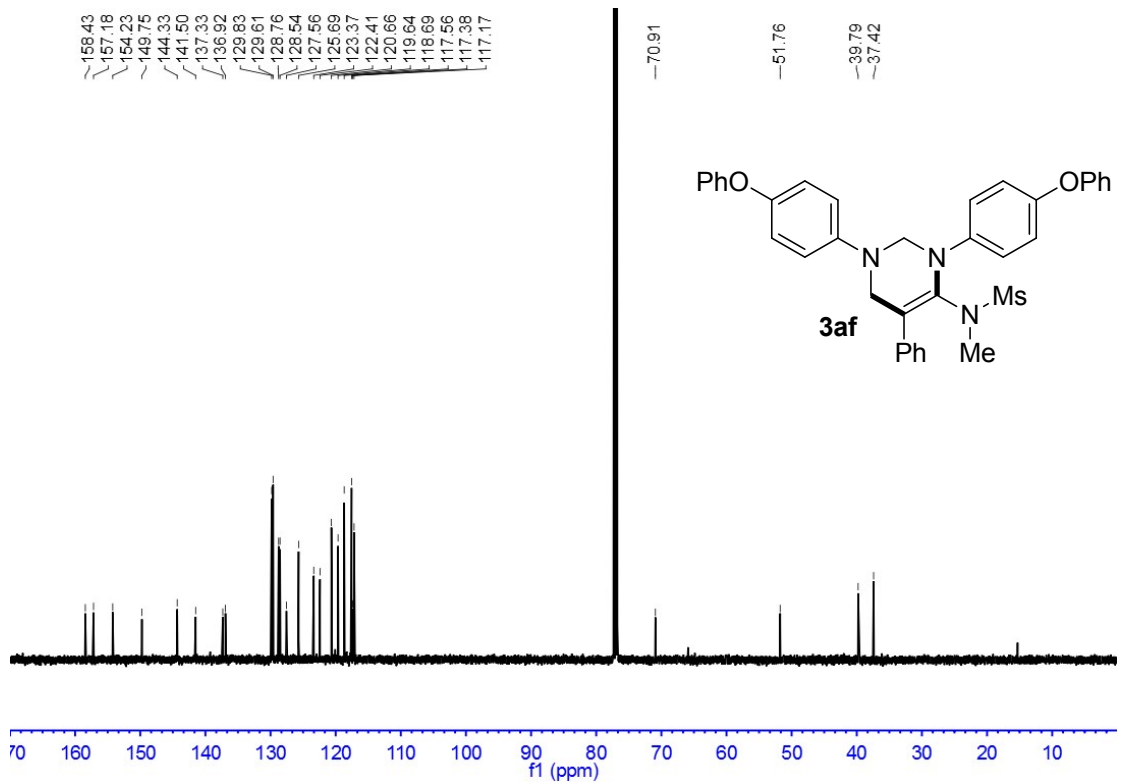
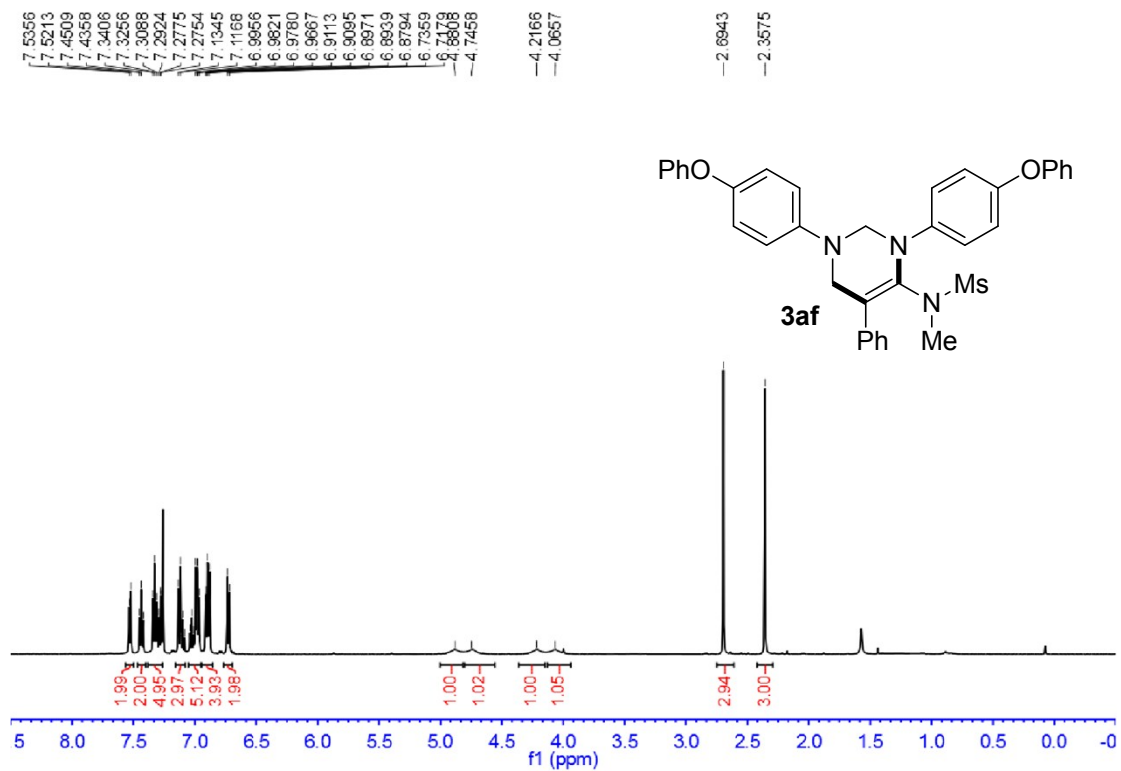


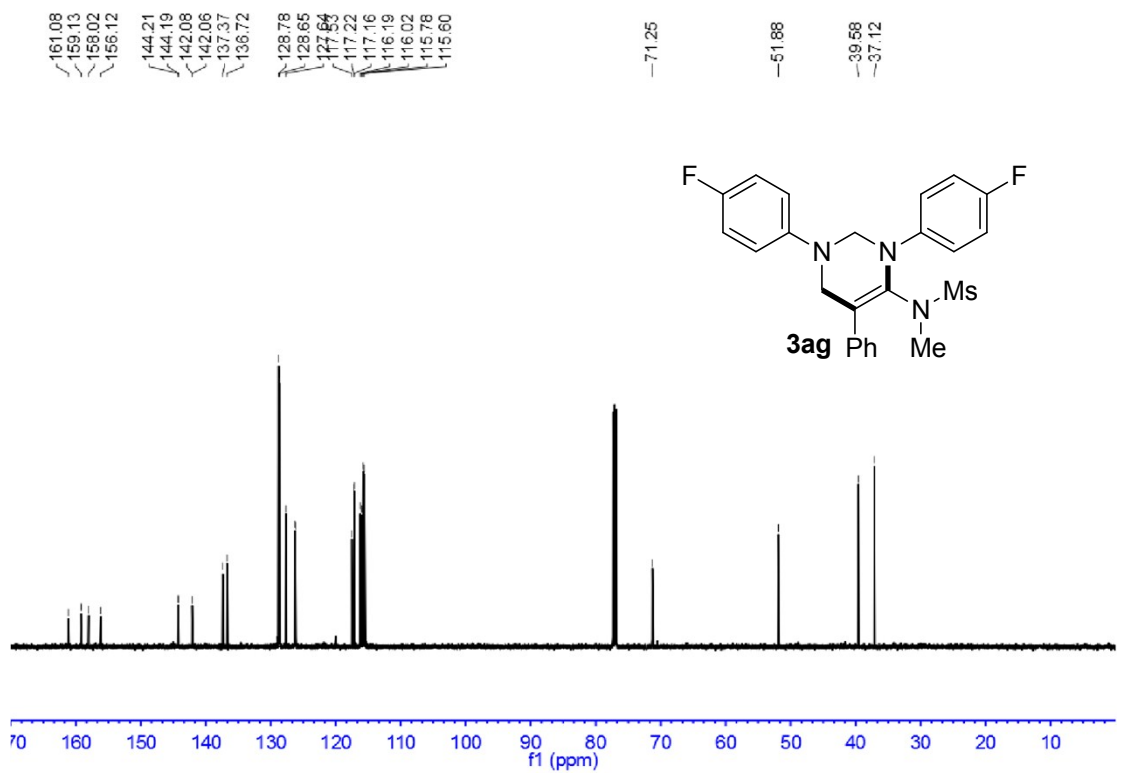
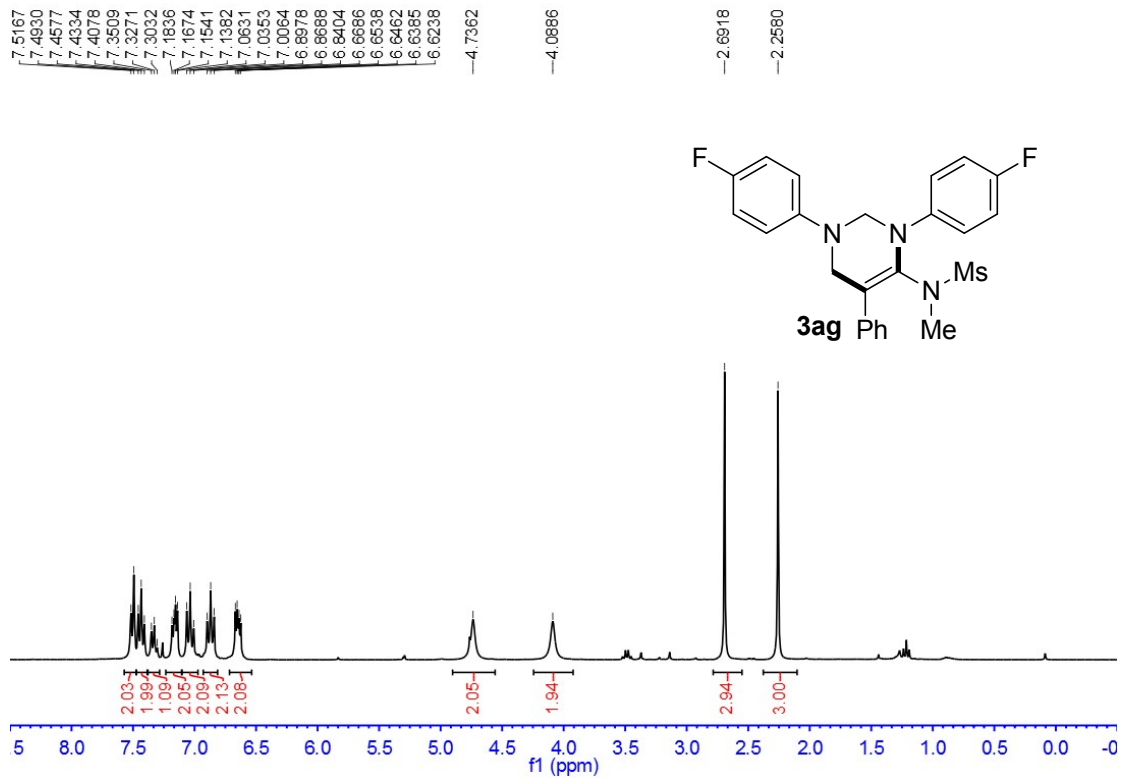


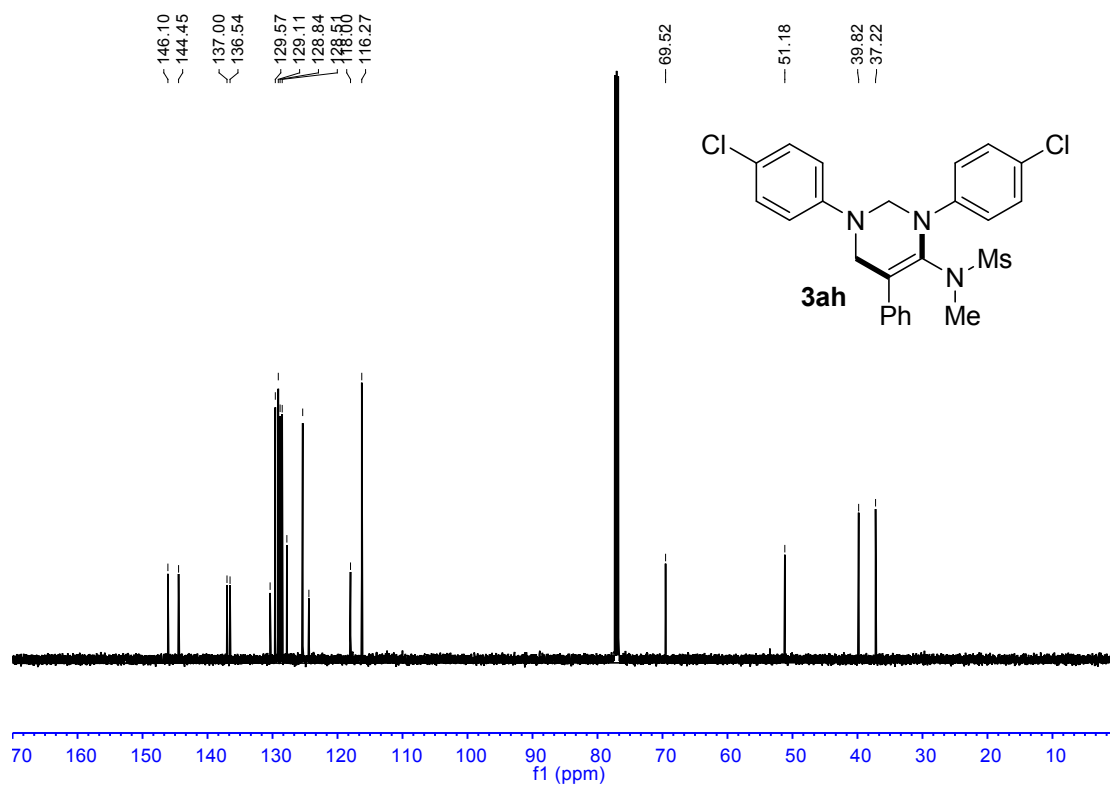
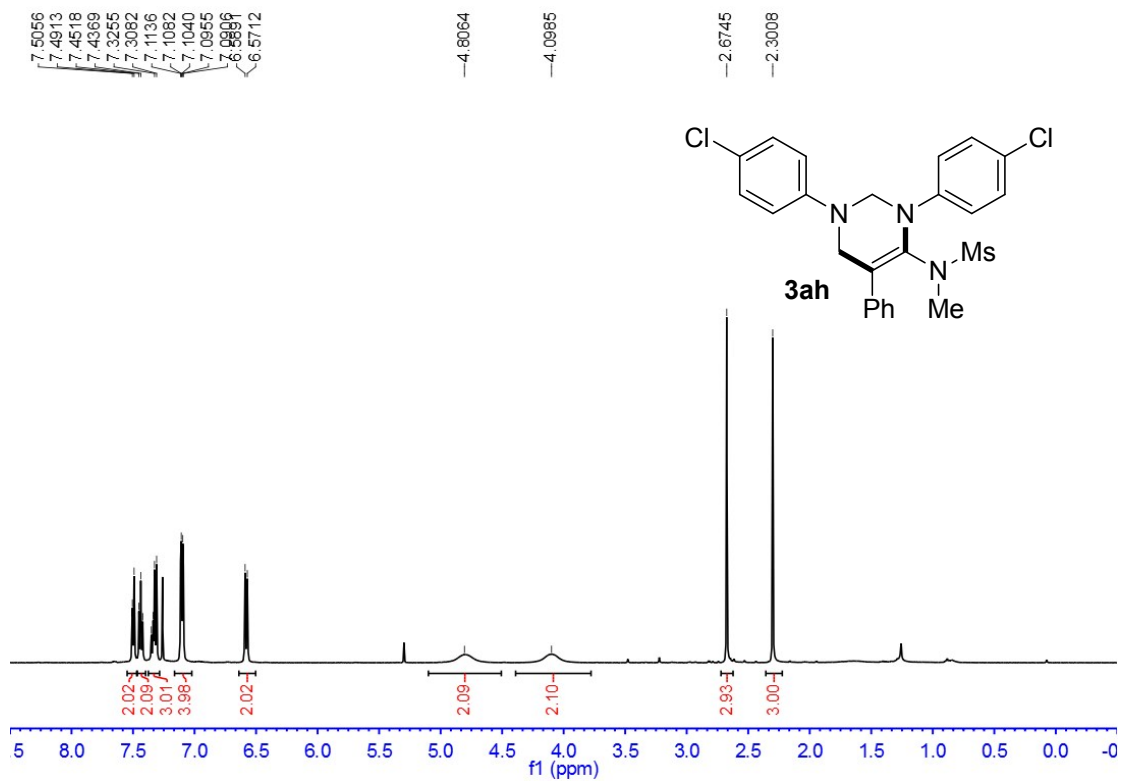


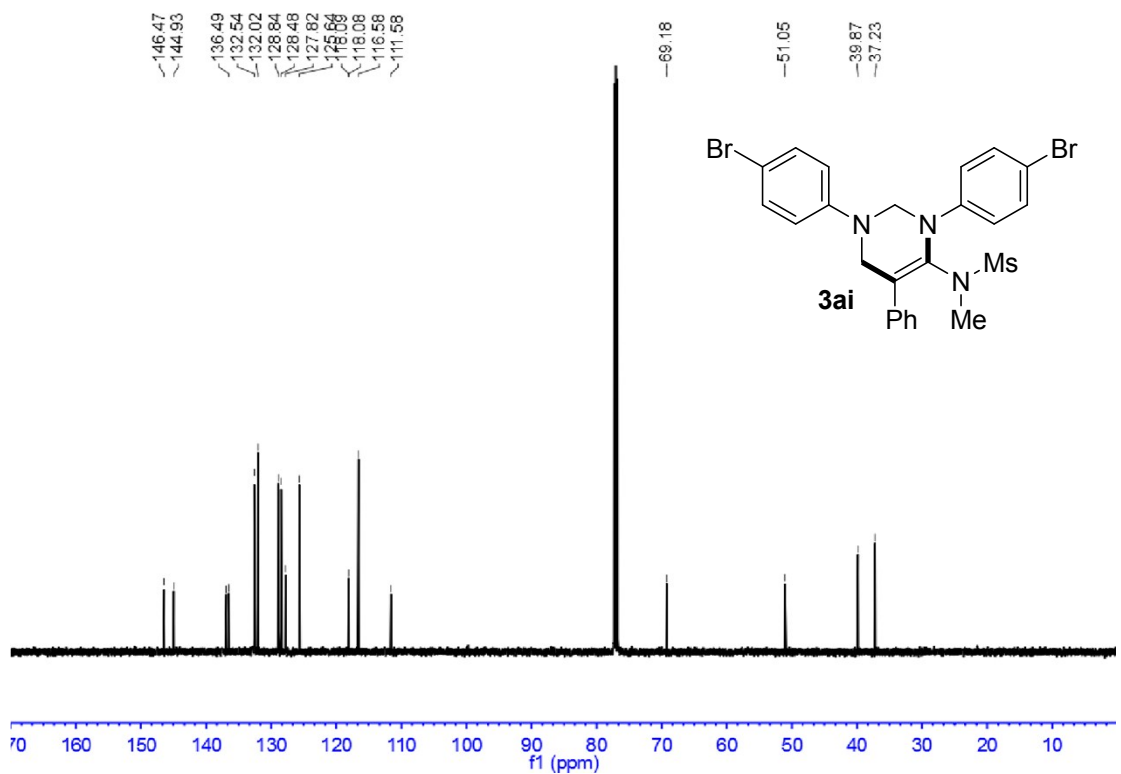
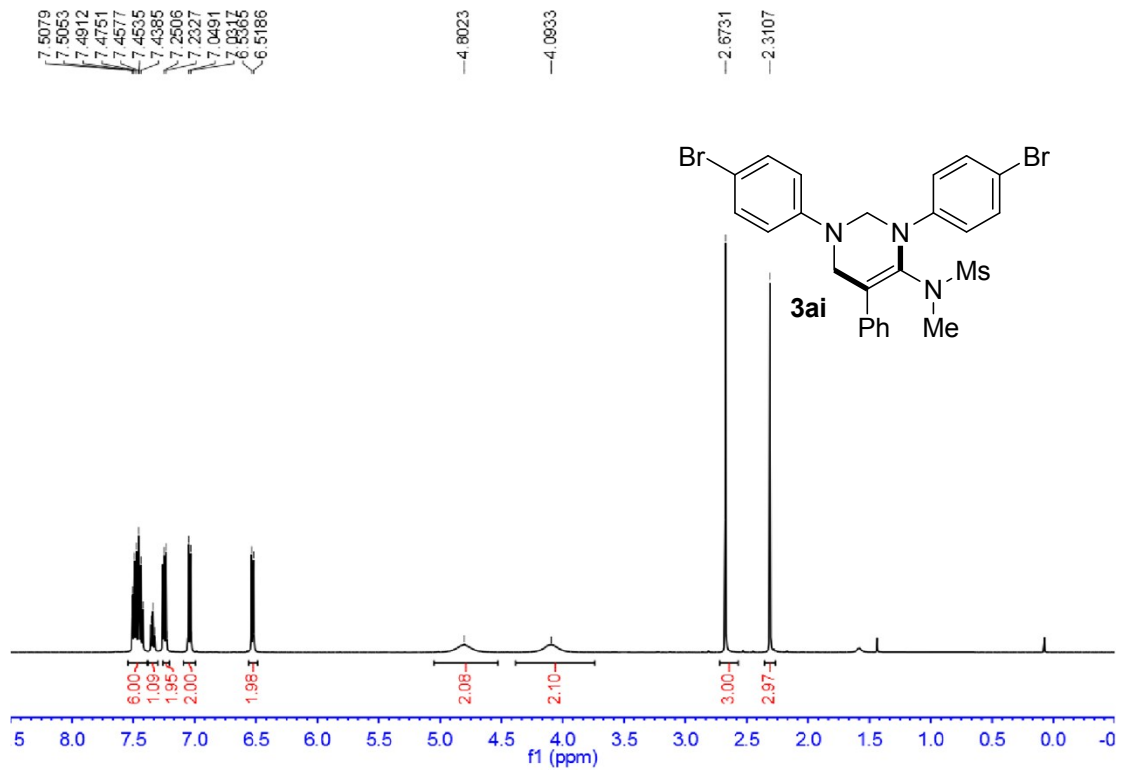


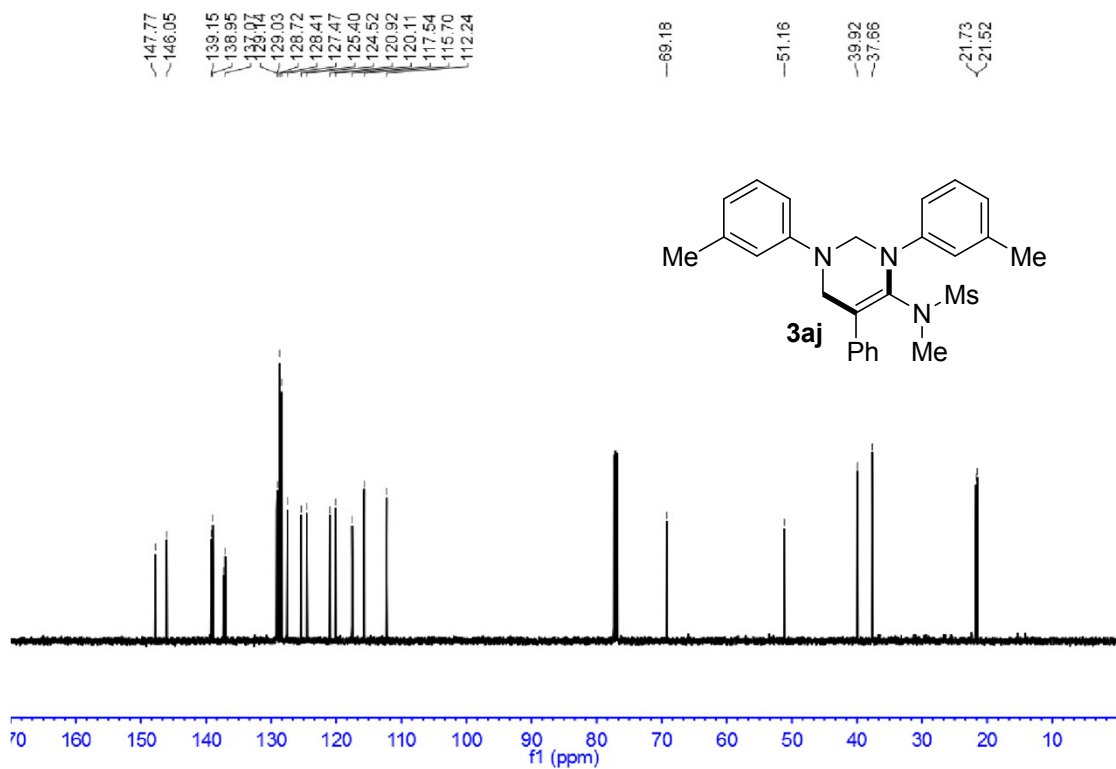
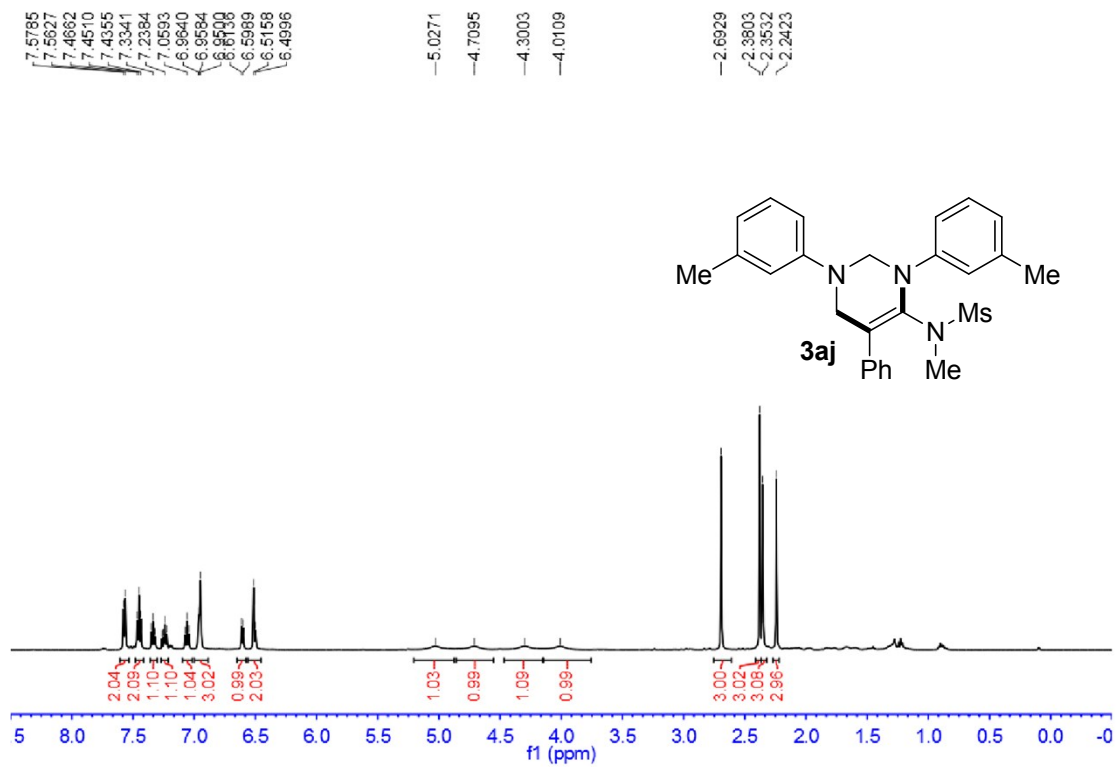


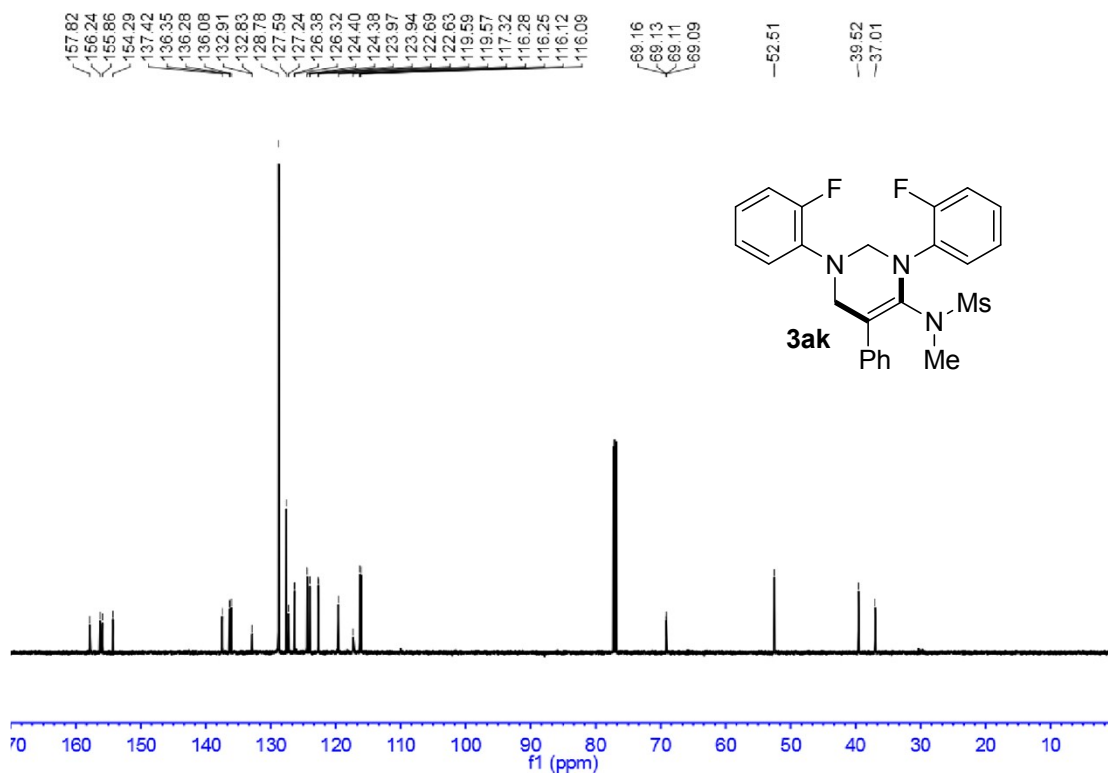
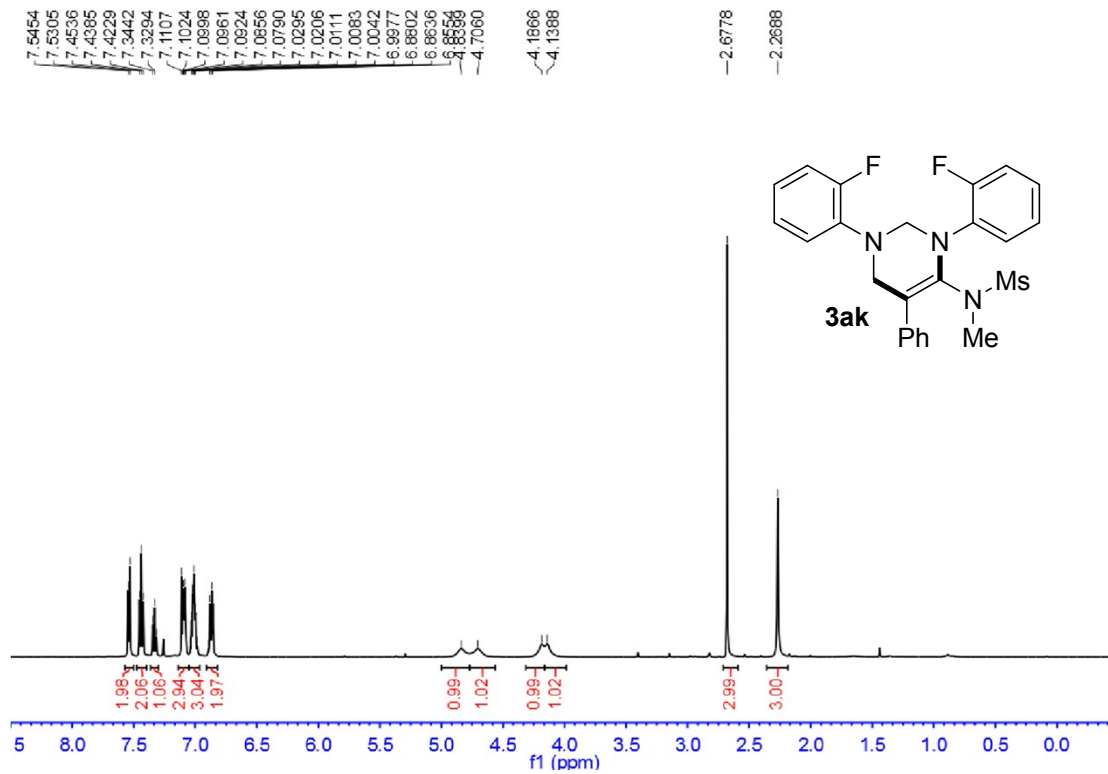


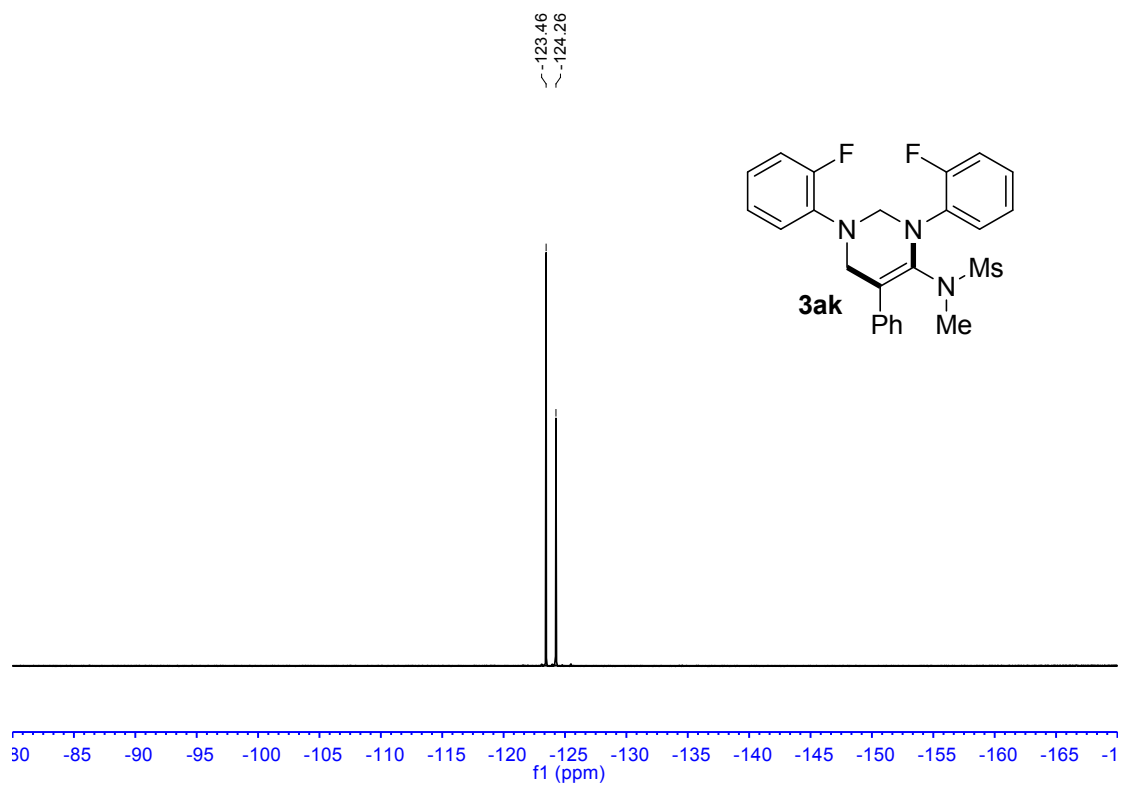


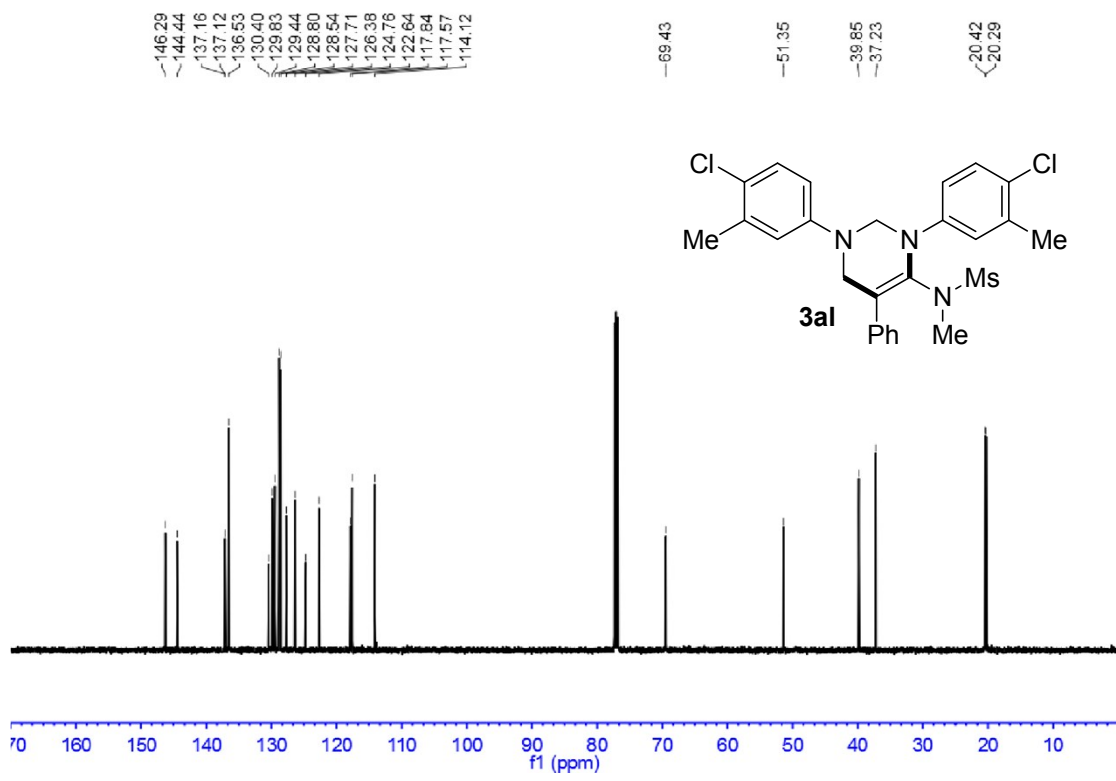
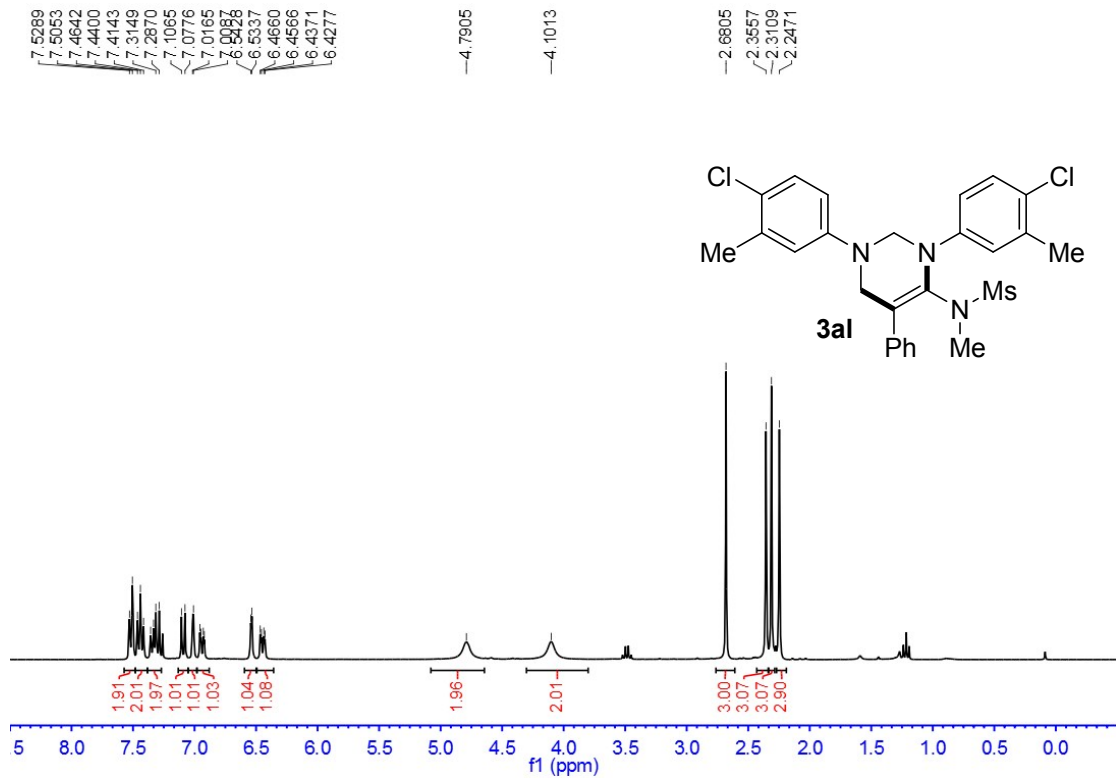






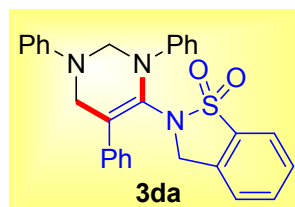
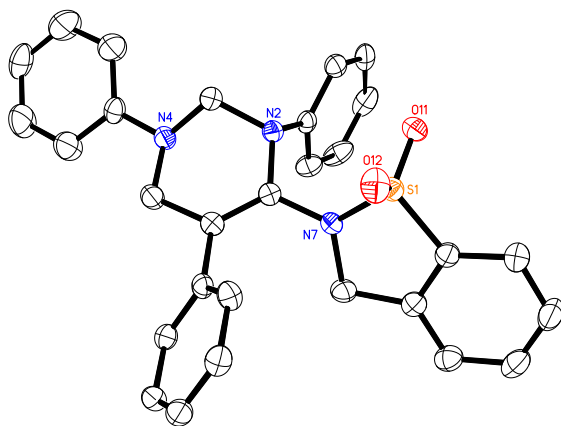




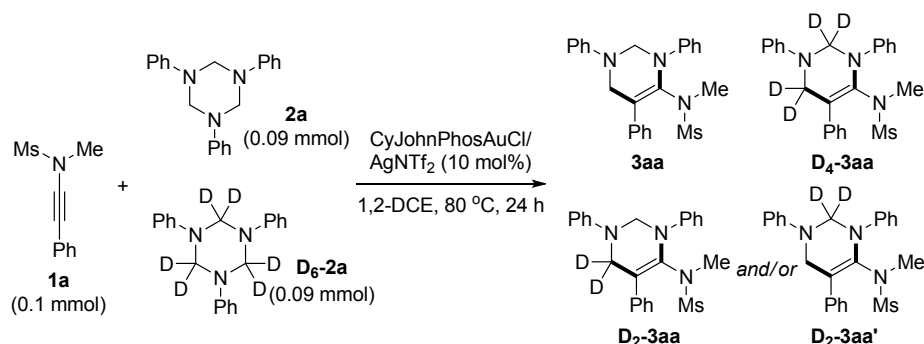


5. X-Ray crystal structure analysis

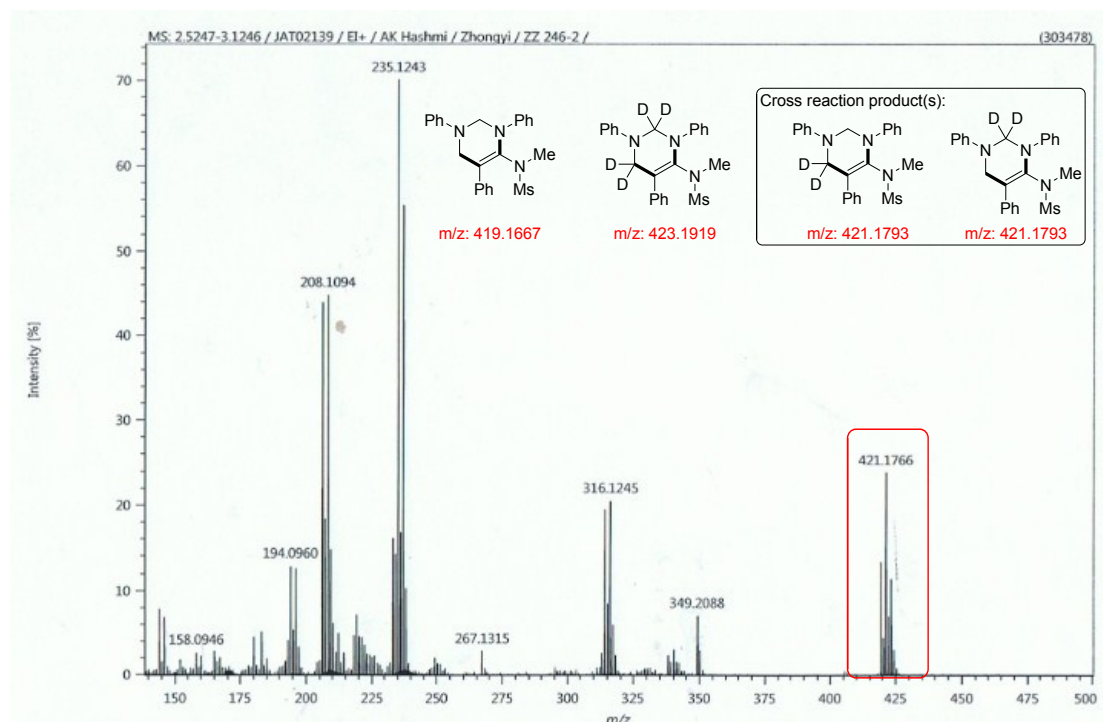
The crystallographic data of compound **3da** (CCDC 1525557) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



6. Mechanistic investigations

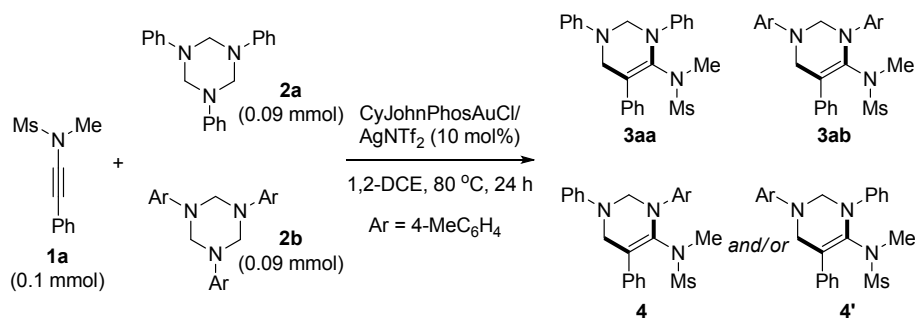


A round bottom flask equipped with a magnetic stirrer bar was charged with CyJohnPhosAuCl (10 mol%, 5.8 mg), AgNTf₂ (10 mol%, 3.9 mg), and 1,2-DCE (0.5 ml). The mixture was stirred for 5 minutes at room temperature. Ynamide **1a** (0.1 mmol, 2 equiv.), 1,3,5-triazinanes **2a** (0.09 mmol, 1.8 equiv.) and **D₆-2a** (0.09 mmol, 1.8 equiv.) were added followed by 0.5 mL 1,2-DCE. The reaction mixture was then stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was concentrated and the residue was purified by flash chromatography on silica gel (PE/EA = 5:1, v/v) to afford the crude product. Then such a crude product was subjected to HRMS analysis. The result showed that the formation of **3aa**, **D₄-3aa**, **D₂-3aa**, and/or **D₂-3aa'**. See the copies of the HRMS spectra below.

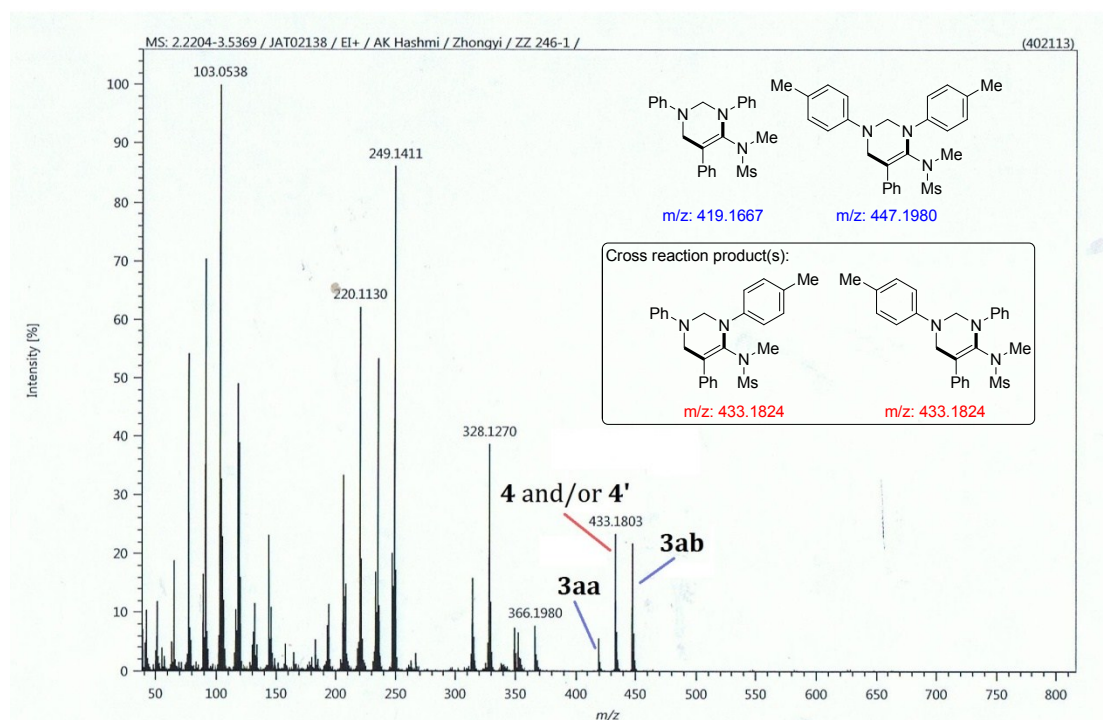


Results			
Mass	Formula	Calculated Mass	Mass Difference [mDa]
423.18815	C24 H21 N3 O2 S D4	423.19131	-3.16
	C24 H23 N3 O2 S D3	423.19285	-4.71
	C24 H25 N3 O2 S D2	423.19440	-6.25
	C24 H27 N3 O2 S D	423.19595	-7.80
422.18031	C24 H20 N3 O2 S D4	422.18348	-3.18
	C24 H22 N3 O2 S D3	422.18503	-4.72
	C24 H24 N3 O2 S D2	422.18658	-6.27
	C24 H26 N3 O2 S D	422.18813	-7.82
421.17665	C24 H21 N3 O2 S D3	421.17720	-0.56
	C24 H19 N3 O2 S D4	421.17566	0.99
	C24 H23 N3 O2 S D2	421.17875	-2.11
	C24 H25 N3 O2 S D	421.18030	-3.65
	C24 H27 N3 O2 S	421.18185	-5.20
420.16850	C24 H18 N3 O2 S D4	420.16783	0.67
	C24 H20 N3 O2 S D3	420.16938	-0.87
	C24 H22 N3 O2 S D2	420.17093	-2.42
	C24 H24 N3 O2 S D	420.17248	-3.97
	C24 H26 N3 O2 S	420.17402	-5.52
419.16463	C24 H23 N3 O2 S D	419.16465	-0.02
	C24 H21 N3 O2 S D2	419.16310	1.53
	C24 H25 N3 O2 S	419.16620	-1.57
	C24 H19 N3 O2 S D3	419.16155	3.08
	C24 H17 N3 O2 S D4	419.16001	4.63

Report list



A round bottom flask equipped with a magnetic stirrer bar was charged with CyJohnPhosAuCl (10 mol%, 5.8 mg), AgNTf₂ (10 mol%, 3.9 mg), and 1,2-DCE (0.5 ml). The mixture was stirred for 5 minutes at room temperature. Ynamide **1a** (0.1 mmol, 2 equiv.), 1,3,5-triazinanes **2a** (0.09 mmol, 1.8 equiv.) and **2b** (0.09 mmol, 1.8 equiv.) were added followed by 0.5 mL 1,2-DCE. The reaction mixture was then stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was concentrated and the residue was purified by flash chromatography on silica gel (PE/EA = 5:1, v/v) to afford the crude product. Then such a crude product was subjected to HRMS analysis. The result showed that the formation of **3aa**, **3ab**, **4** and/or **4'**. See the copy of the HRMS spectrum below.



Overall spectrum

Results

Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]
447.19577	C29 H25 N3 O2	447.19413	1.65	3.68
	C26 H29 N3 O2 S	447.19750	-1.72	-3.86
	C34 H25 N	447.19815	-2.38	-5.31
	C31 H29 N S	447.20152	-5.75	-12.85
	C30 H27 N2 S	447.18895	6.83	15.27
433.18029	C25 H27 N3 O2 S	433.18185	-1.56	-3.60
	C28 H23 N3 O2	433.17848	1.81	4.18
	C33 H23 N	433.18250	-2.21	-5.11
	C30 H27 N S	433.18587	-5.58	-12.89
	C29 H25 N2 S	433.17330	6.99	16.14
419.16536	C24 H25 N3 O2 S	419.16620	-0.84	-2.01
	C32 H21 N	419.16685	-1.49	-3.56
	C27 H21 N3 O2	419.16283	2.53	6.03
	C29 H25 N S	419.17022	-4.86	-11.61
	C28 H23 N2 S	419.15765	7.71	18.40

Report list