

Supporting Information for

***p*-TSA Catalyzed 6-Endo-Trig/Dig Cyclization of 5-Aminopyrazoles and 3⁰/2⁰-Propargylic alcohols: Access to Pyrazolo[1,5-*a*]dihydropyrimidines & Pyrazolo[3,4-*b*]pyridines**

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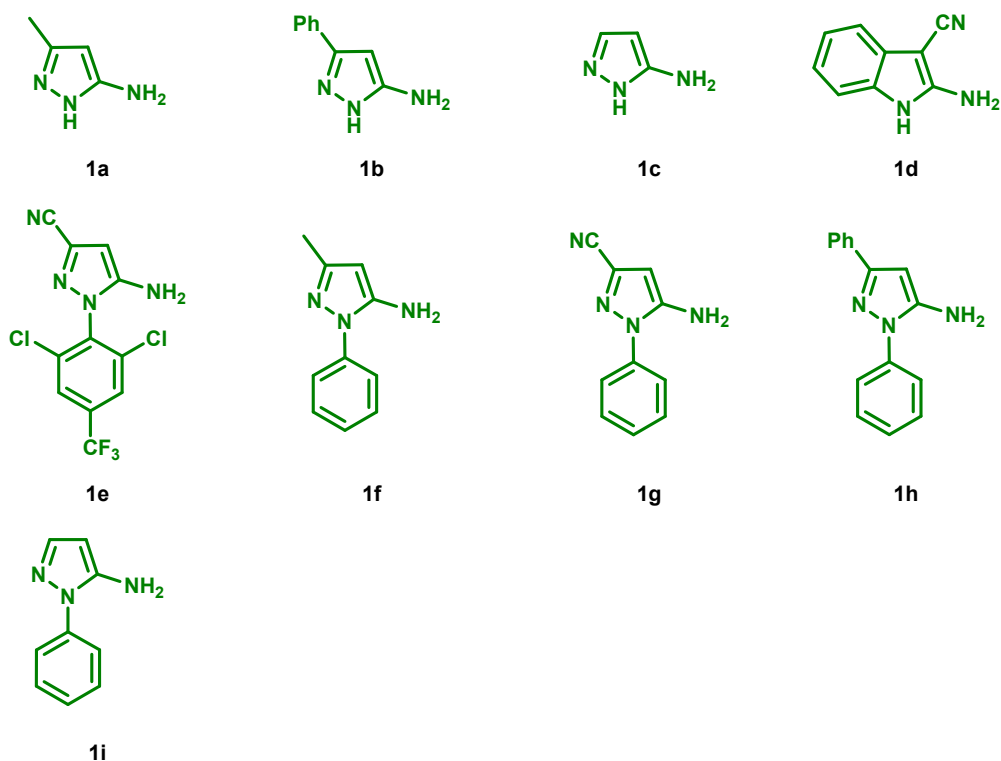
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Contents

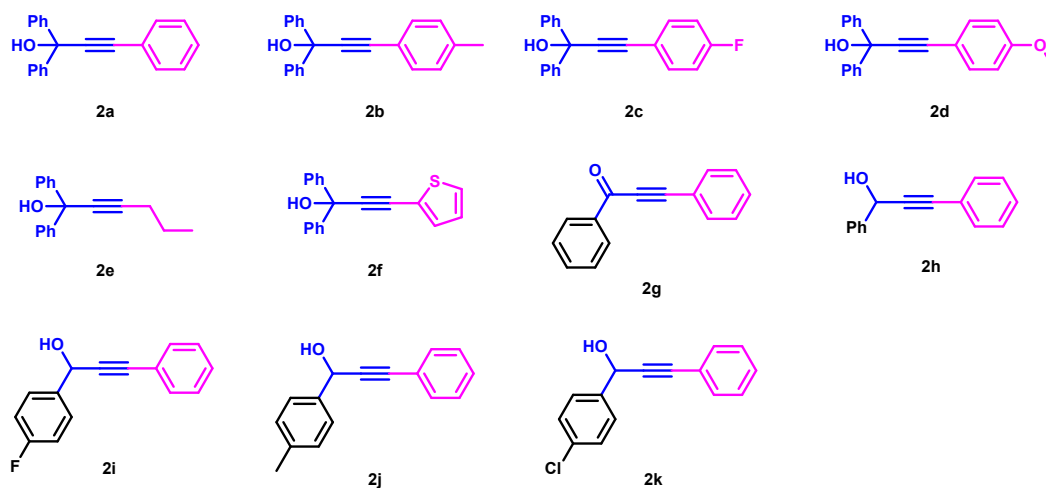
1.1.	Structures of starting materials	1
1.2.	Experimental Section	1
1.2.1.	General procedure for the synthesis of compounds 3a-3l and 3m-3t	2
1.2.2.	General procedure for the synthesis of compounds 7a-7i	2
1.3.	Spectroscopic data and copies ¹ H & ¹³ C of compounds 3a-3t , 6a-6b & 7a-7i	3-36

1.1. Structures of starting materials

1.1.1. Structures of Aminopyrazoles (1a-i)



1.1.2. Structures of 3°/2°-Propargylic alcohols (2a-k)



1.2. Experimental section

General

Melting points were measured by CINTEX programmable melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra of samples in CDCl_3 recorded on AVANCE- 300, 400,

500 MHz spectrometers. Chemical shifts (δ) are reported relative to TMS ($\delta = 0.0$) as the internal standard. Mass spectra were recorded in ESI spectrometers. All high-resolution mass spectra were recorded on QSTAR XL hybrid ms/ms system (Applied Bio systems/MDS sciex, foster city, USA), equipped with an ESI source (IICT, Hyderabad). TLC was performed on Merck 60 F-254 silica gel plates. The chemicals used in this work were obtained from commercial channels and were used without purification.

1.2.1. General Procedure for the Synthesis of dihydropyrazolo[1,5-*a*]pyrimidines (3a-3l) and pyrazolo[1,5-*a*]pyrimidines (3m-3t).

A mixture of *NH*-5-aminopyrazoles (**1a-d**, 82 mg, 1.2 mmol, 1.2 equiv.), substituted tert-propargylic alcohols (**2a-f**, 200 mg, 1 mmol, 1.0 equiv.)/1,3-diphenyl-2-yn-1-one (**2g**, 200 mg, 1 mmol, 1.0 equiv.), and *p*-TSA (40 mg, 0.3 mmol, 0.3 equiv.) in acetonitrile (15 mL) was stirred at reflux temperature for 3 h. After completion of the reaction ascertained by TLC, acetonitrile was evaporated under reduced pressure and the crude mass was purified by column chromatography (silica gel 60-120 mesh, hexane/EtOAc 7:3 as eluent) to afford the isolated yield of **3a** is 86% (215 mg). Similar procedure was adopted for all the corresponding products **3a-3t**.

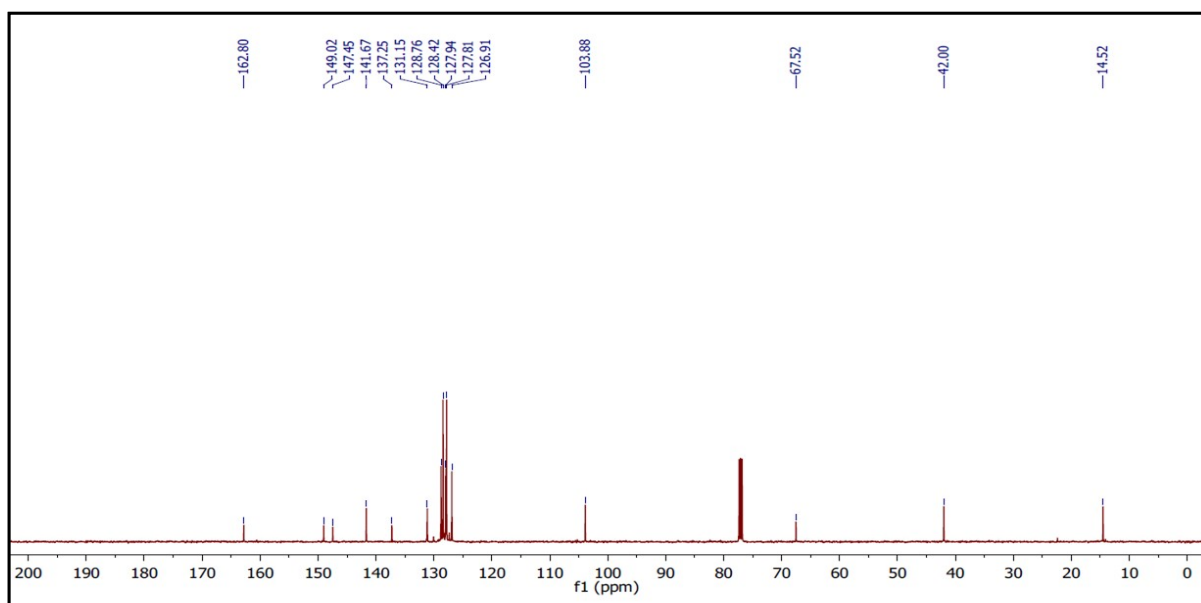
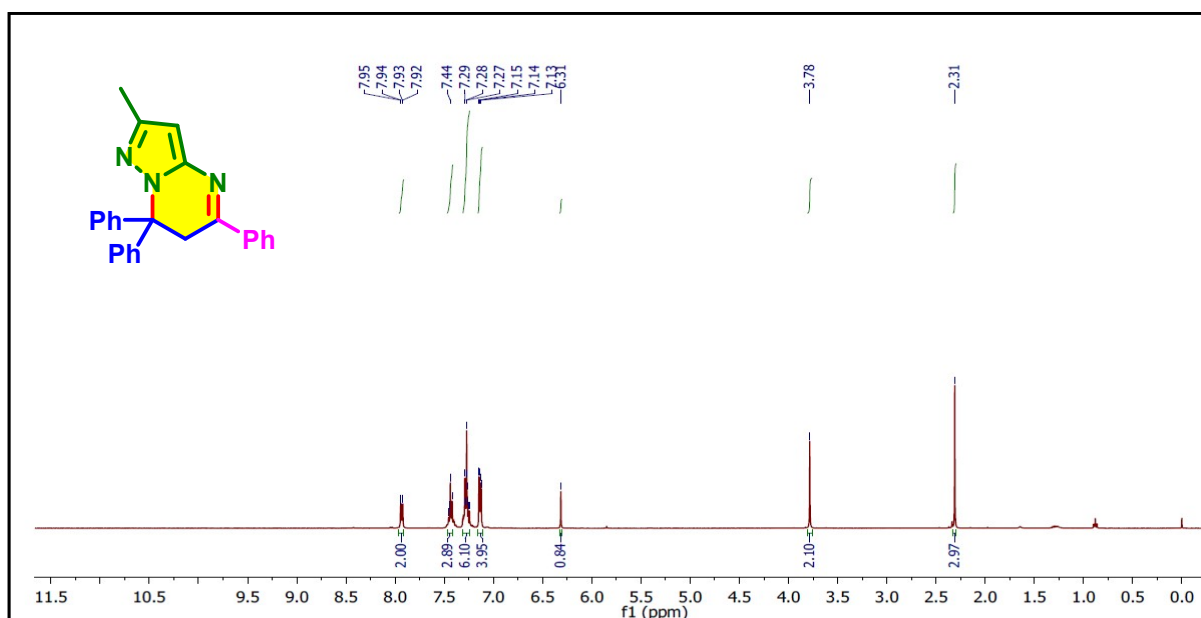
1.2.2. General Procedure for the Synthesis pyrazolo[3,4-*b*]pyridines (7a-7i).

A mixture of *N*-aryl-5-aminopyrazoles (**1e-i**, 370 mg, 1.2 mmol, 1.2 equiv.), sec-propargylic alcohols (**2h-k**, 200 mg, 1.0 mmol, 1.0 equiv.) and sequential addition of *p*-TSA (54 mg, 0.3 mmol, 0.3 equiv.) and K₂CO₃ (66 mg, 0.5 mmol, 0.5 equiv.) in acetonitrile (15 mL) was heated to reflux for 4 h. After completion of the reaction indicated by TLC, acetonitrile was evaporated under reduced pressure and worked up with water (20 mL) and ethyl acetate (30 mL). Further, separated organic layer dried over anhydrous sodium sulphate evaporated under reduced pressure, crude product was purified by column chromatography, (silica gel 60-120 mesh, hexane/EtOAc 9:1 as eluent) to afford the isolated yield of **7a** is 93% (455 mg) and similar procedure was followed for all the corresponding products **7a-7i**.

1.3 Spectroscopic data and copies ^1H & ^{13}C of compounds.

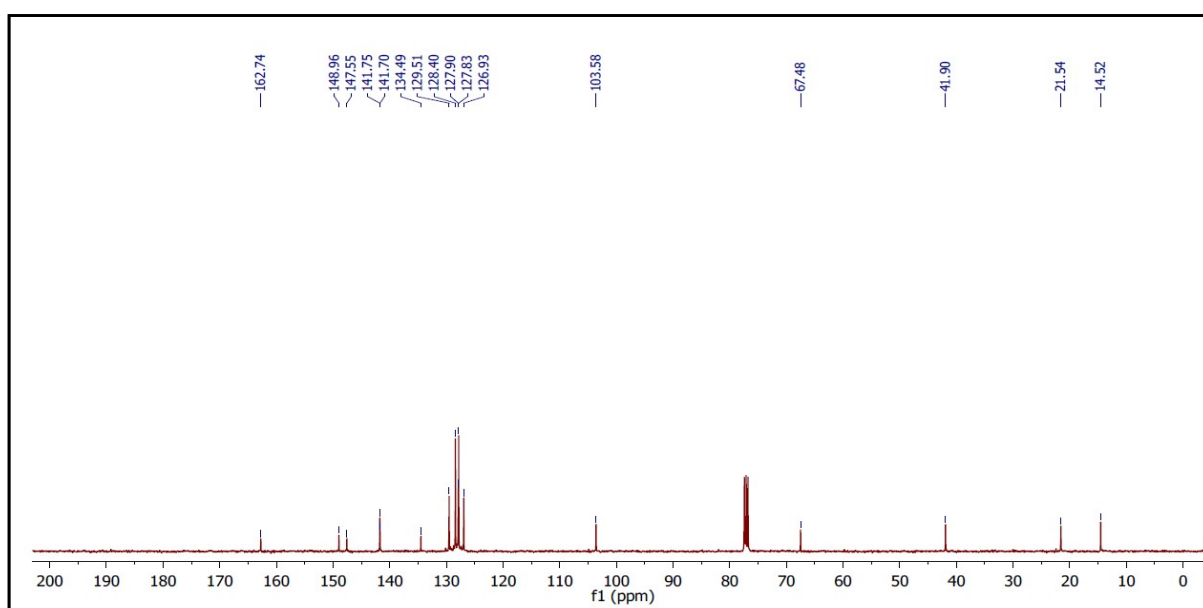
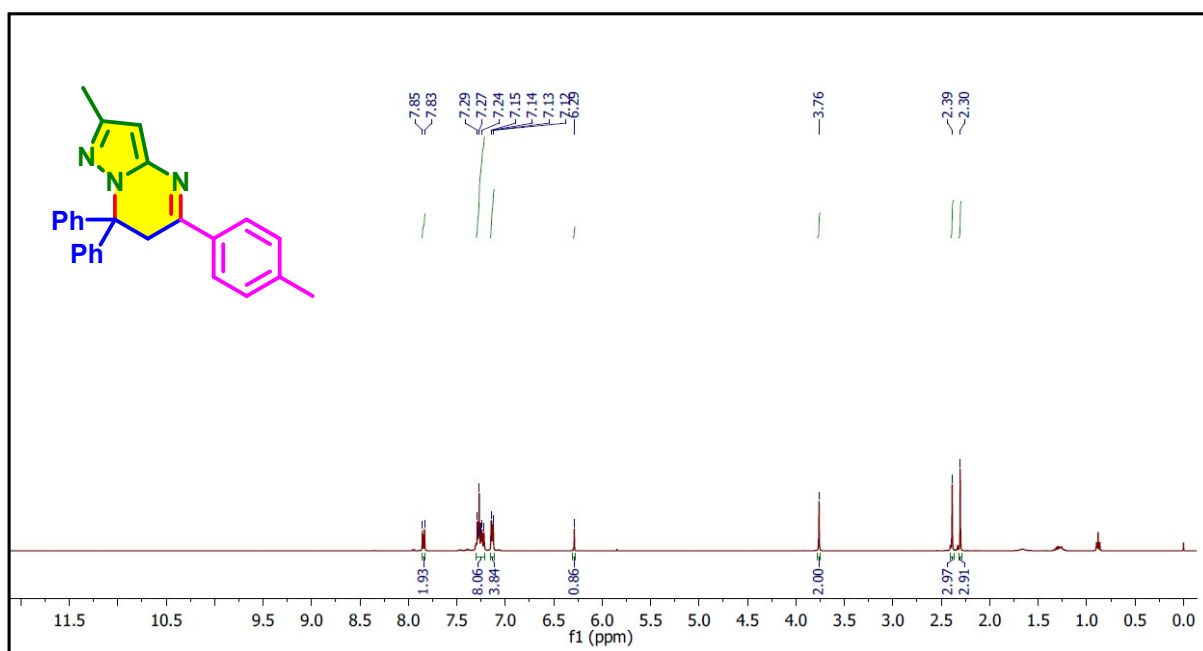
2-methyl-5,7,7-triphenyl-6,7-dihydropyrazolo[1,5-*a*]pyrimidine (3a)

Isolated as a yellow solid, yield 80% (215 mg), m.p 175-177 °C, IR (ATR): 3132, 3022, 2244, 1718, 1597, 1488, 1385, 1272, 1050, 843, 754 cm^{-1} , ^1H NMR (400 MHz, CDCl_3): δ 7.93 (dd, $J = 7.9, 1.7$ Hz, 2H), 7.44 (dd, $J = 7.9, 6.0$ Hz, 3H), 7.29-7.24 (m, 6H), 7.15-7.12 (m, 4H), 6.31 (s, 1H), 3.78 (s, 2H), 2.31 (s, 3H) ppm, ^{13}C NMR (125 MHz, CDCl_3): δ 162.80, 149.02, 147.45, 141.67, 137.25, 131.15, 128.76, 128.42, 127.94, 127.81, 126.91, 103.88, 67.52, 42.00, 14.52 ppm, ESI-MS: m/z 364 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{25}\text{H}_{22}\text{N}_3$ m/z 364.1808 $[\text{M}+\text{H}]^+$, found 364.1800.



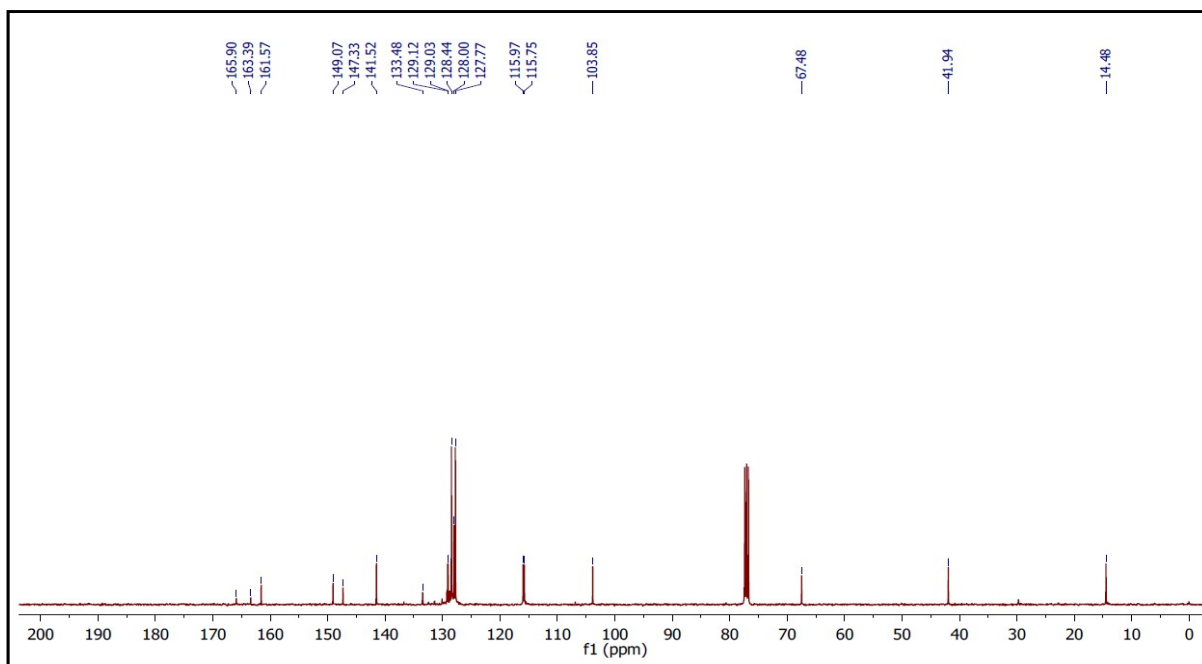
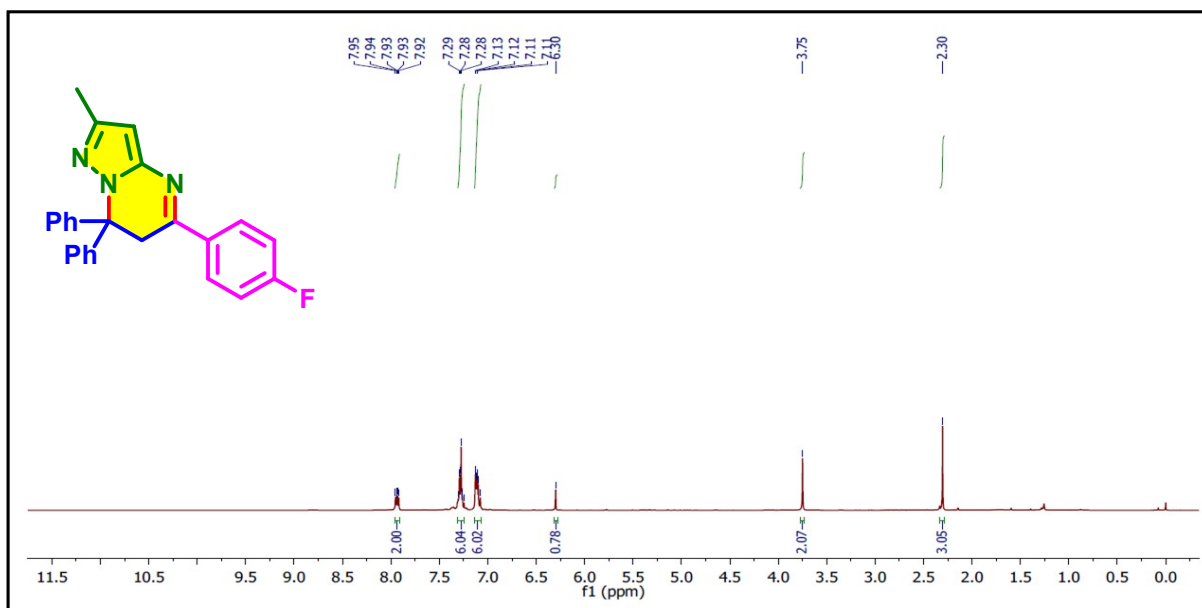
2-methyl-7,7-diphenyl-5-(*p*-tolyl)-6,7-dihydropyrazolo[1,5-*a*]pyrimidine (3b)

Isolated as a light yellow solid, yield 83% (210 mg), m.p 154-156 °C, IR (ATR): 3060, 3023, 2361, 1557, 1397, 1306, 1175, 1094, 932, 753 cm⁻¹, ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.21 (m, 8H), 7.13 (dd, *J* = 7.8, 1.6 Hz, 4H), 6.29 (s, 1H), 3.76 (s, 2H), 2.39 (s, 3H), 2.30 (s, 3H) ppm, ¹³C NMR (100 MHz, CDCl₃) δ 162.74, 148.96, 147.55, 141.75, 141.70, 134.49, 129.51, 128.40, 127.90, 127.83, 126.93, 103.58, 67.48, 41.90, 21.54, 14.52 ppm, ESI-MS: *m/z* 378 [M+H]⁺, HRMS (ESI) Anal. calcd. for C₂₆H₂₄N₃ *m/z* 378.1964 [M+H]⁺, found 378.1957.



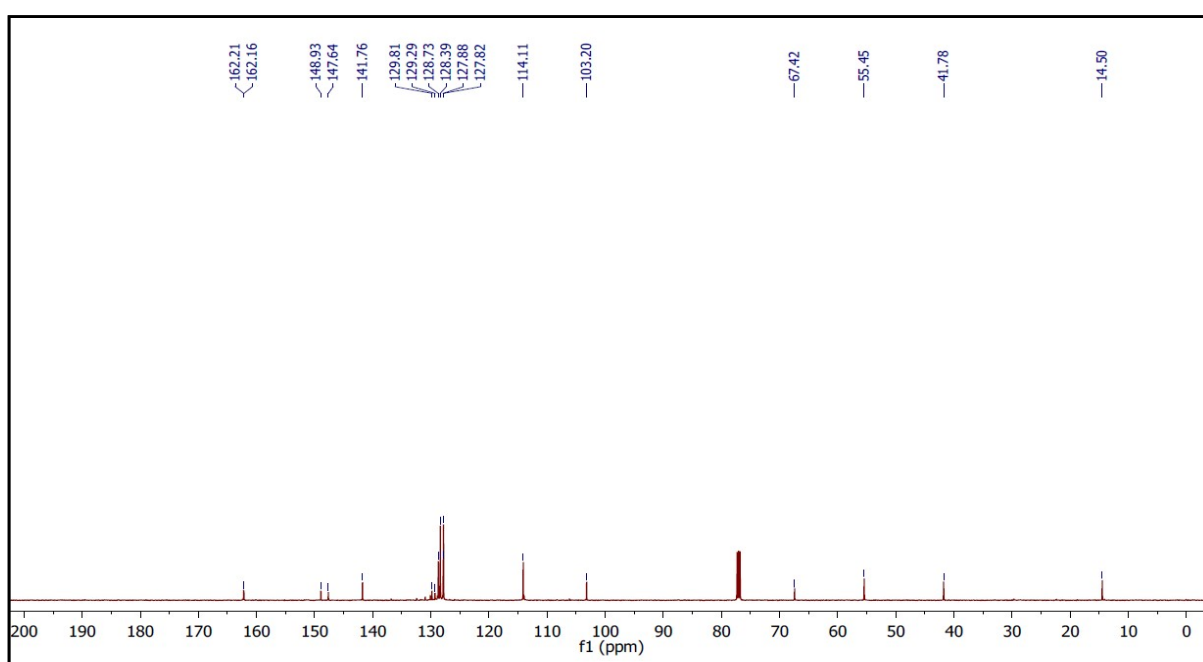
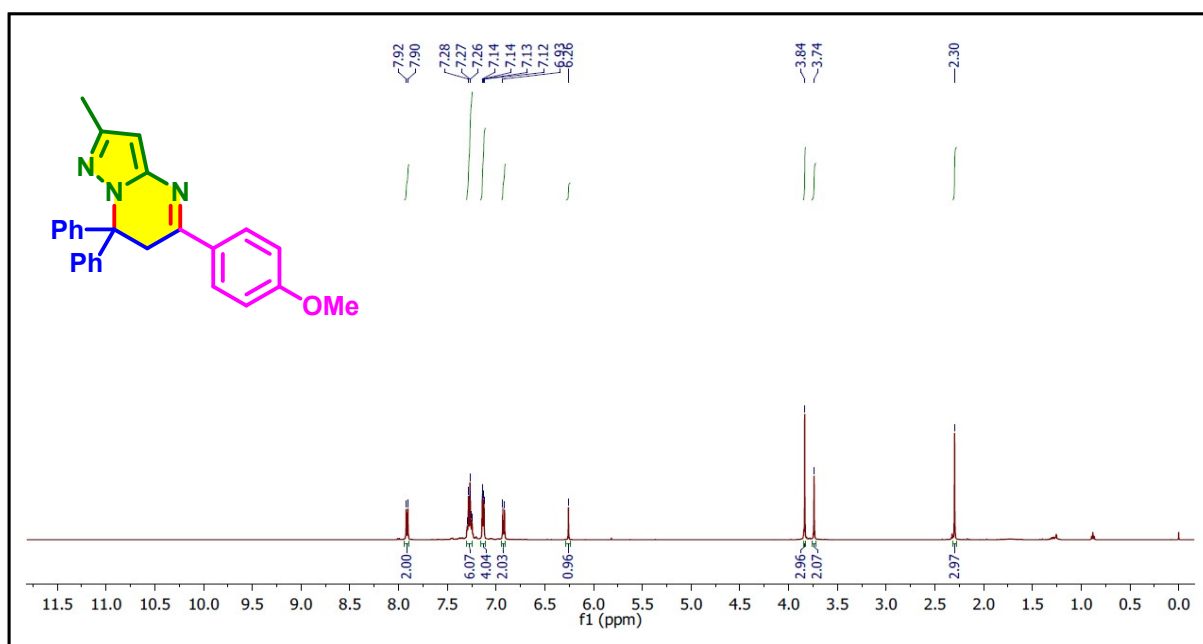
5-(4-fluorophenyl)-2-methyl-7,7-diphenyl-6,7-dihydropyrazolo[1,5-a]pyrimidine (3c)

Isolated as a red solid, yield 78% (197 mg), m.p 105-107 °C, IR (ATR): 3203, 2925, 2384, 2309, 1721, 1608, 1448, 1214, 1036, 909, 759 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 7.96 – 7.91 (m, 2H), 7.32 – 7.26 (m, 6H), 7.14 – 7.06 (m, 6H), 6.30 (s, 1H), 3.75 (s, 2H), 2.30 (s, 3H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 164.58 (d, $J= 252.72$ Hz), 161.57, 149.07, 147.33, 141.52, 133.48, 129.08 (d, $J= 8.8$ Hz), 128.44, 128.00, 127.77, 115.86 (d, $J= 22.0$ Hz), 103.85, 67.48, 41.94, 14.48 ppm, ESI-MS: m/z 382 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{25}\text{H}_{21}\text{FN}_3$ m/z 382.1714 $[\text{M}+\text{H}]^+$, found 382.1705.



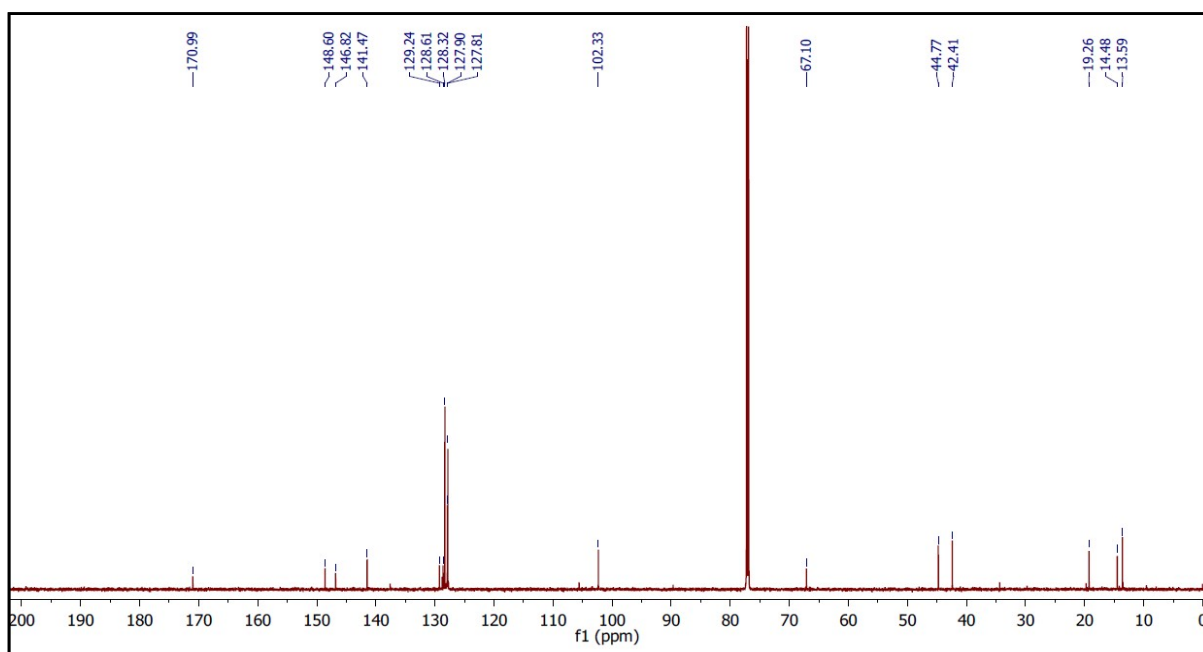
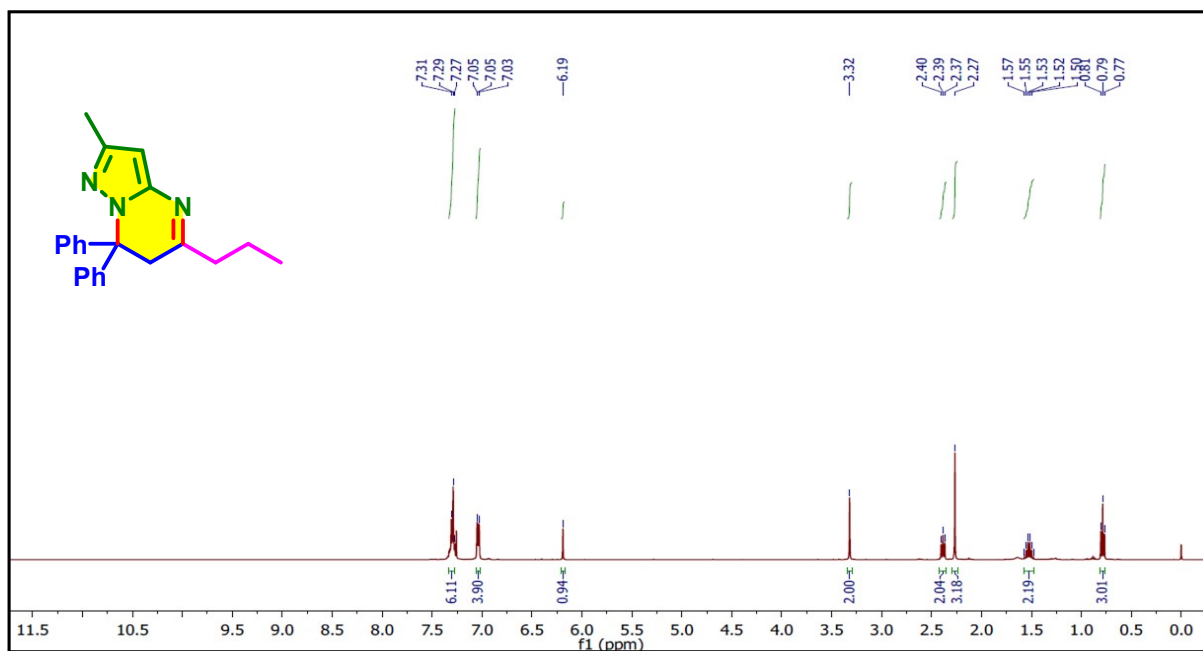
5-(4-methoxyphenyl)-2-methyl-7,7-diphenyl-6,7-dihydropyrazolo[1,5-a]pyrimidine (3d)

Isolated as a red solid, yield 85% (212 mg), m.p 175-177 °C, IR (ATR): 3050, 3018, 1707, 1640, 1554, 1448, 1214, 1073, 890, 745 cm^{-1} , ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, $J = 8.9$ Hz, 2H), 7.30 – 7.24 (m, 6H), 7.13 (m, 4H), 6.92 (d, $J = 8.9$ Hz, 2H), 6.26 (s, 1H), 3.84 (s, 3H), 3.74 (s, 2H), 2.30 (s, 3H) ppm, ^{13}C NMR (125 MHz, CDCl_3): δ 162.21, 162.16, 148.93, 147.64, 141.76, 129.81, 129.29, 128.73, 128.39, 127.88, 127.82, 114.11, 103.20, 67.42, 55.45, 41.78, 14.50 ppm, ESI-MS: m/z 394 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_3\text{O}$ m/z 394.1913 $[\text{M}+\text{H}]^+$, found 394.1906.



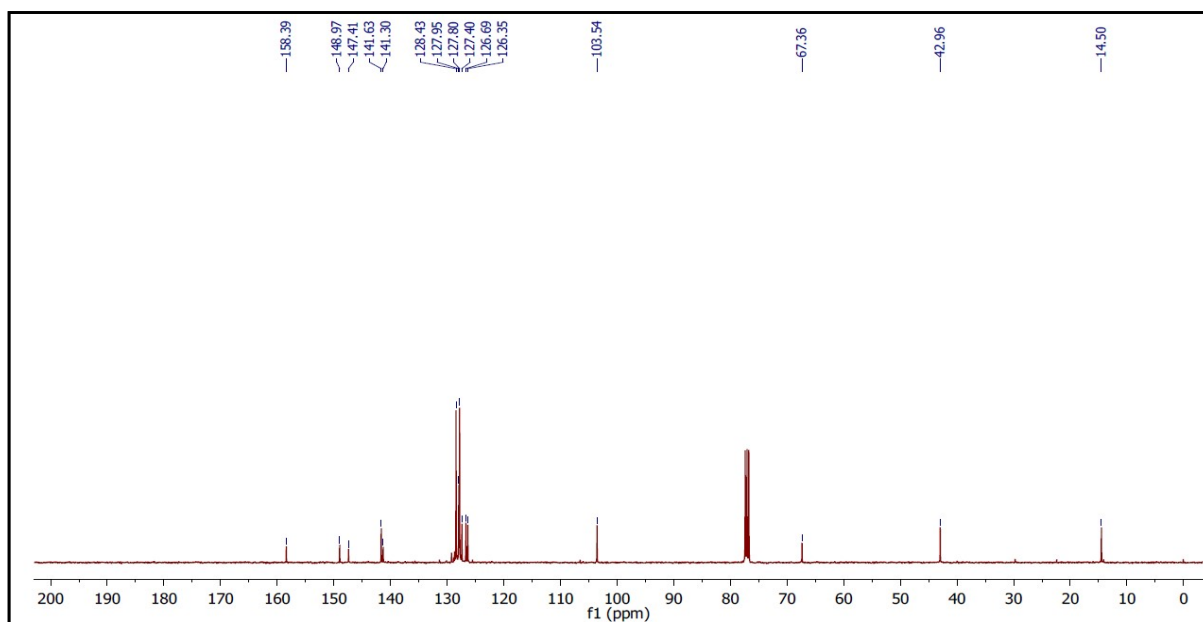
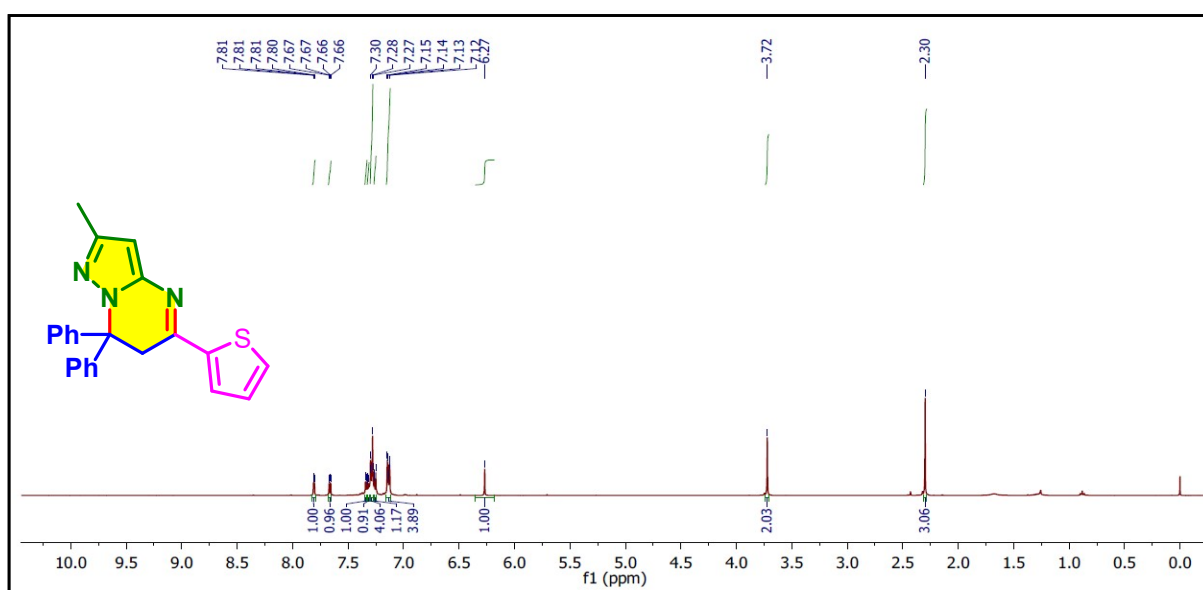
2-methyl-7,7-diphenyl-5-propyl-6,7-dihydropyrazolo[1,5-a]pyrimidine (3e)

Isolated as a brown solid, yield 72% (190 mg), m.p 137-139 °C, IR (ATR): 3216, 3025, 2957, 1599, 1486, 1269, 1158, 1062, 981, 755 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 7.29 (m, 6H), 7.06 – 7.02 (m, 4H), 6.19 (s, 1H), 3.32 (s, 2H), 2.39 (t, $J = 7.5$ Hz, 2H), 2.27 (s, 3H), 1.58 – 1.48 (m, 2H), 0.79 (t, $J = 7.4$ Hz, 3H) ppm, ^{13}C NMR (125 MHz, CDCl_3) δ 170.99, 148.60, 146.82, 141.47, 129.24, 128.61, 128.32, 127.90, 127.81, 102.33, 67.10, 44.77, 42.41, 19.26, 14.48, 13.59 ppm, ESI-MS: m/z 330 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_3$ m/z 330.1964 $[\text{M}+\text{H}]^+$, found 330.1960.



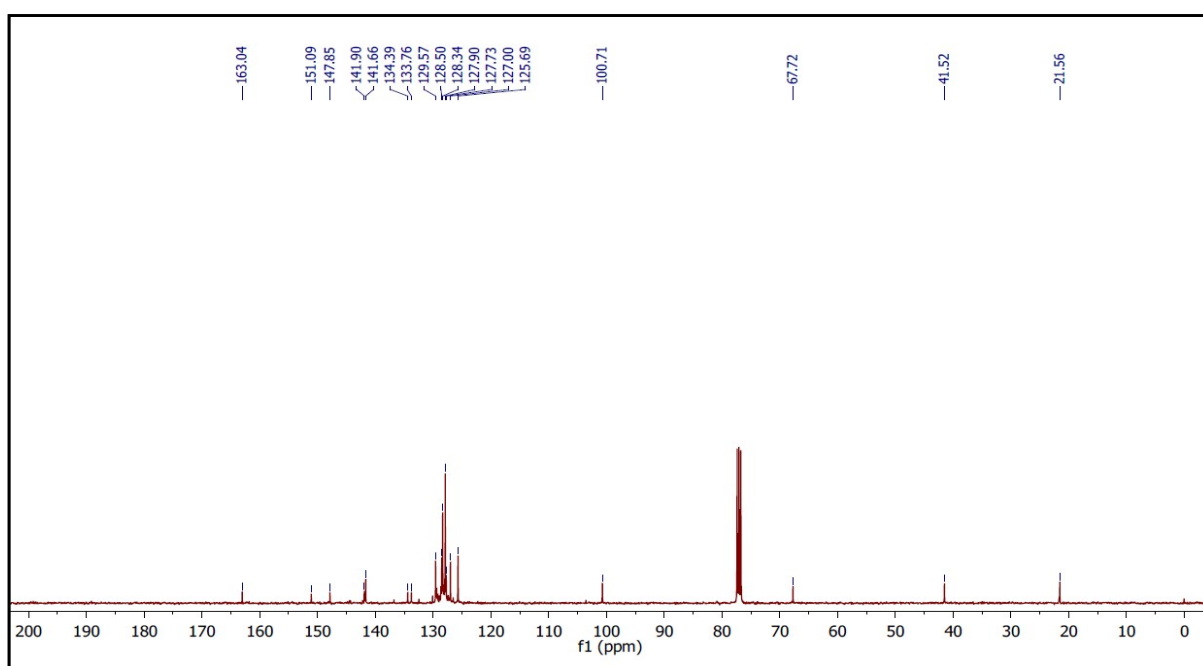
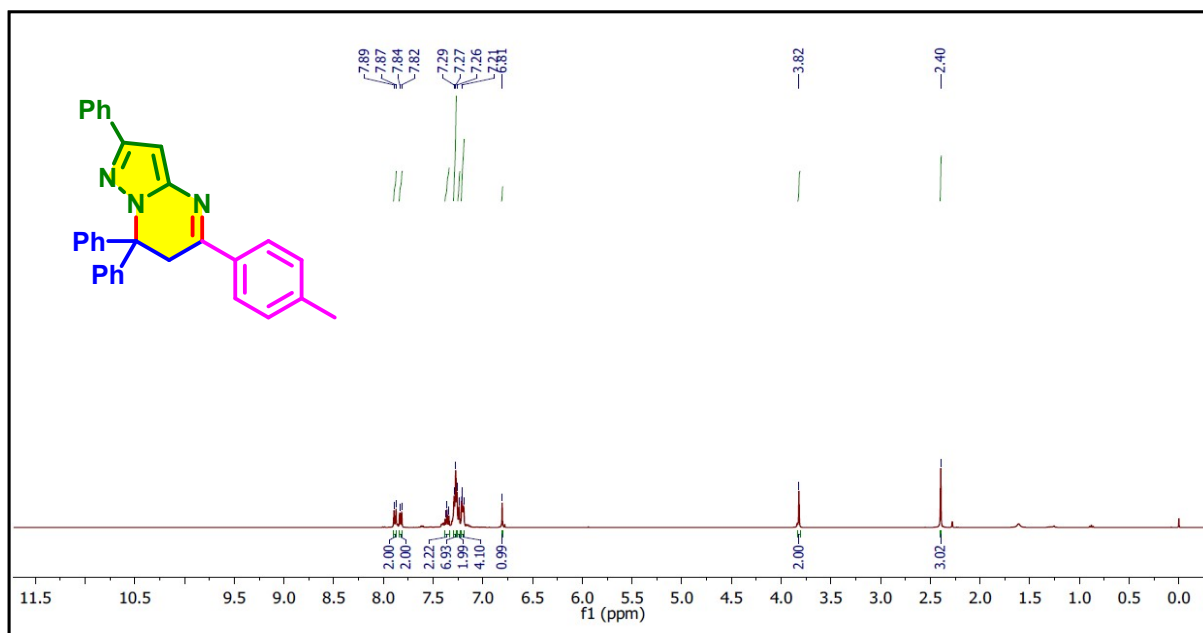
2-methyl-7,7-diphenyl-5-(thiophen-2-yl)-6,7-dihydropyrazolo[1,5-*a*]pyrimidine (3f)

Isolated as a red solid, yield 76% (193 mg), m.p 129-131 °C, IR (ATR): 3212, 2952, 2326, 1702, 1626, 1452, 1246, 1124, 856, 726 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 7.81 (dd, $J = 2.8, 1.2$ Hz, 1H), 7.66 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.35 – 7.33 (m, 1H), 7.33 – 7.31 (m, 1H), 7.30 – 7.28 (m, 4H), 7.27 – 7.25 (m, 1H), 7.16 – 7.12 (m, 4H), 6.27 (s, 1H), 3.72 (s, 2H), 2.30 (s, 3H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 158.39, 148.97, 147.41, 141.63, 141.30, 128.43, 127.95, 127.80, 127.40, 126.69, 126.35, 103.54, 67.36, 42.96, 14.50 ppm, ESI-MS: m/z 370 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{23}\text{H}_{20}\text{N}_3\text{S}$ m/z 370.1372 $[\text{M}+\text{H}]^+$, found 370.1382.



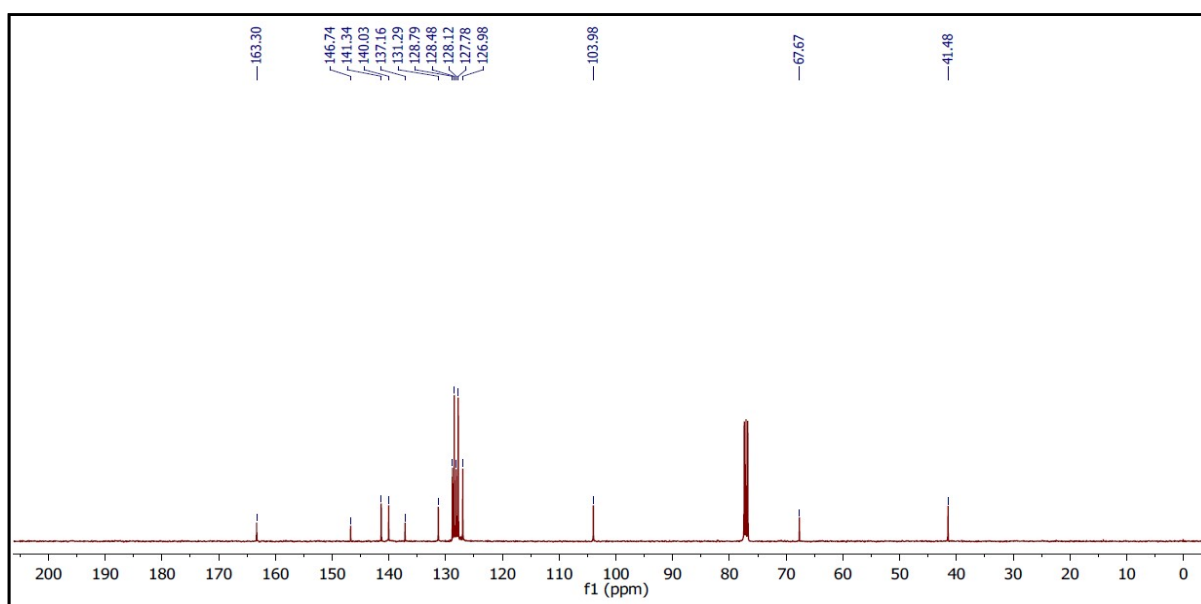
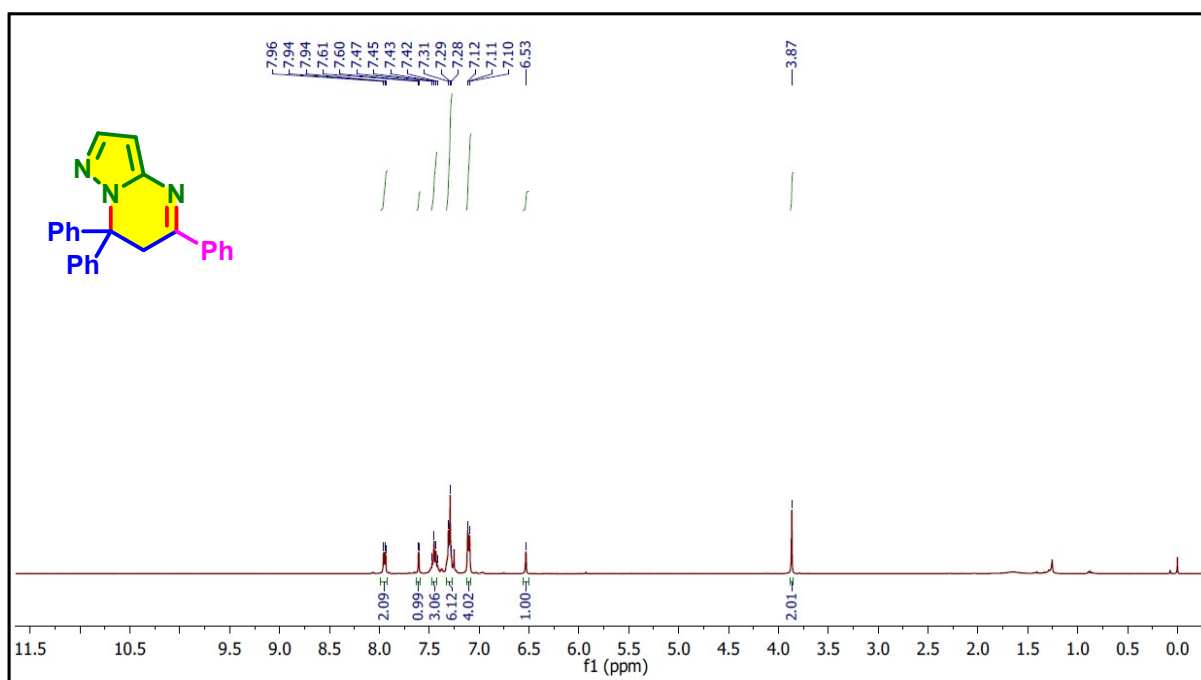
2,7,7-triphenyl-5-(*p*-tolyl)-6,7-dihydropyrazolo[1,5-*a*]pyrimidine (3g)

Isolated as a light yellow solid, yield 85% (250 mg), m.p 216-218 °C, IR (ATR): 3058, 3021, 1711, 1606, 1487, 1382, 1227, 1041, 914, 751, 698 cm⁻¹, ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (m, 7H), 7.24 (s, 2H), 7.22 – 7.19 (m, 4H), 6.81 (s, 1H), 3.82 (s, 2H), 2.40 (s, 3H) ppm, ¹³C NMR (100 MHz, CDCl₃) δ 163.04, 151.09, 147.85, 141.90, 141.66, 134.39, 133.76, 129.57, 128.50, 128.34, 127.90, 127.73, 127.00, 125.69, 100.71, 67.72, 41.52, 21.56 ppm, ESI-MS: *m/z* 440 [M+H]⁺, HRMS (ESI) Anal. calcd. for C₃₁H₂₆N₃ *m/z* 440.2121 [M+H]⁺, found 440.2110.



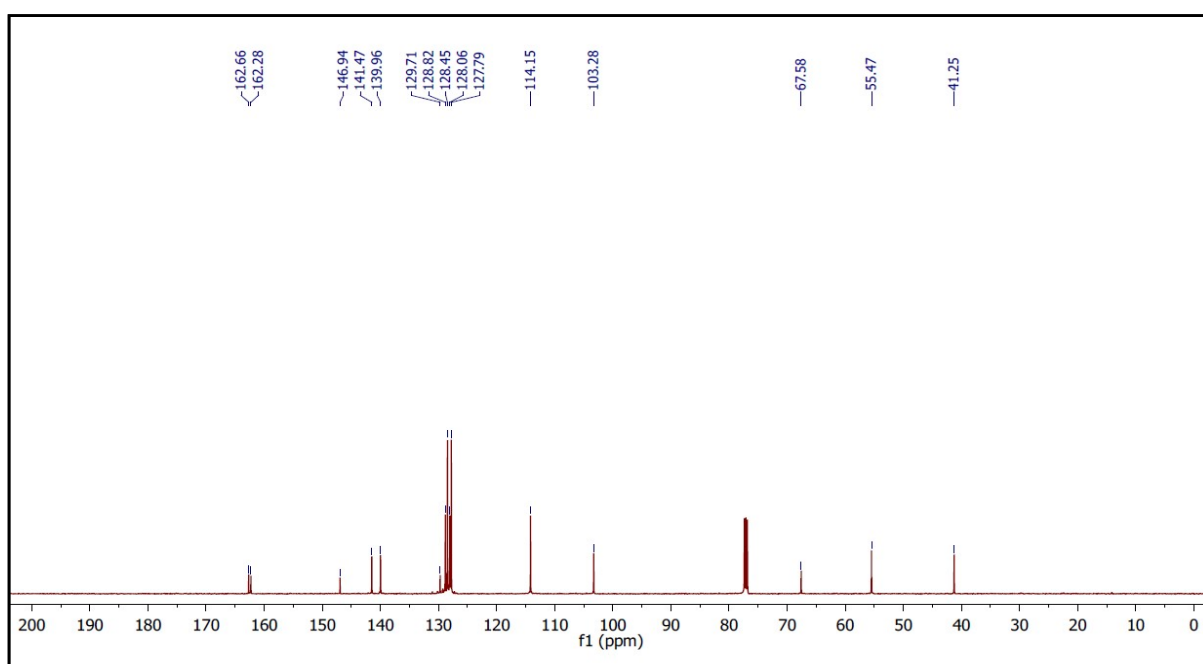
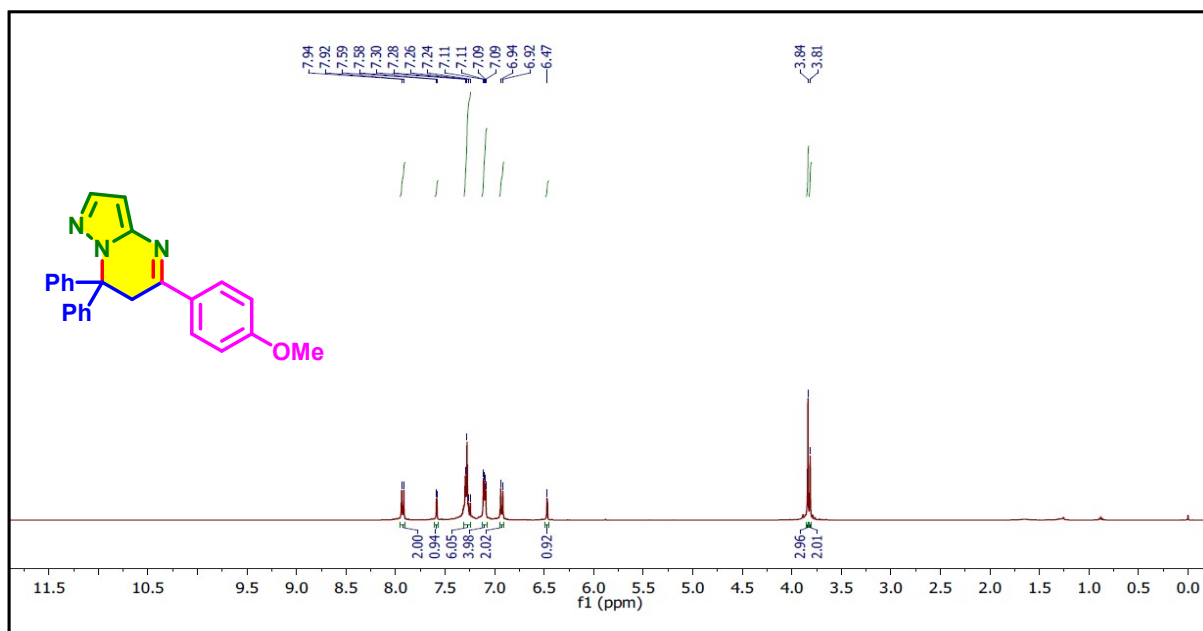
5,7,7-triphenyl-6,7-dihydropyrazolo[1,5-*a*]pyrimidine (3h)

Isolated as a yellow solid, yield 88% (216 mg), m.p 183-185 °C, IR (ATR): 3061, 3023, 2244, 1563, 1502, 1396, 1211, 1137, 1095, 816, 755 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.92 (m, 2H), 7.61 (d, $J = 1.8$ Hz, 1H), 7.47-7.42 (m, 3H), 7.31-7.28 (m, 6H), 7.13 – 7.08 (m, 4H), 6.53 (s, 1H), 3.87 (s, 2H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 163.30, 146.74, 141.34, 140.03, 137.16, 131.29, 128.79, 128.48, 128.12, 127.78, 126.98, 103.98, 67.67, 41.48 ppm, ESI-MS: m/z 350 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_3$ m/z 350.1651 $[\text{M}+\text{H}]^+$, found 350.1646.



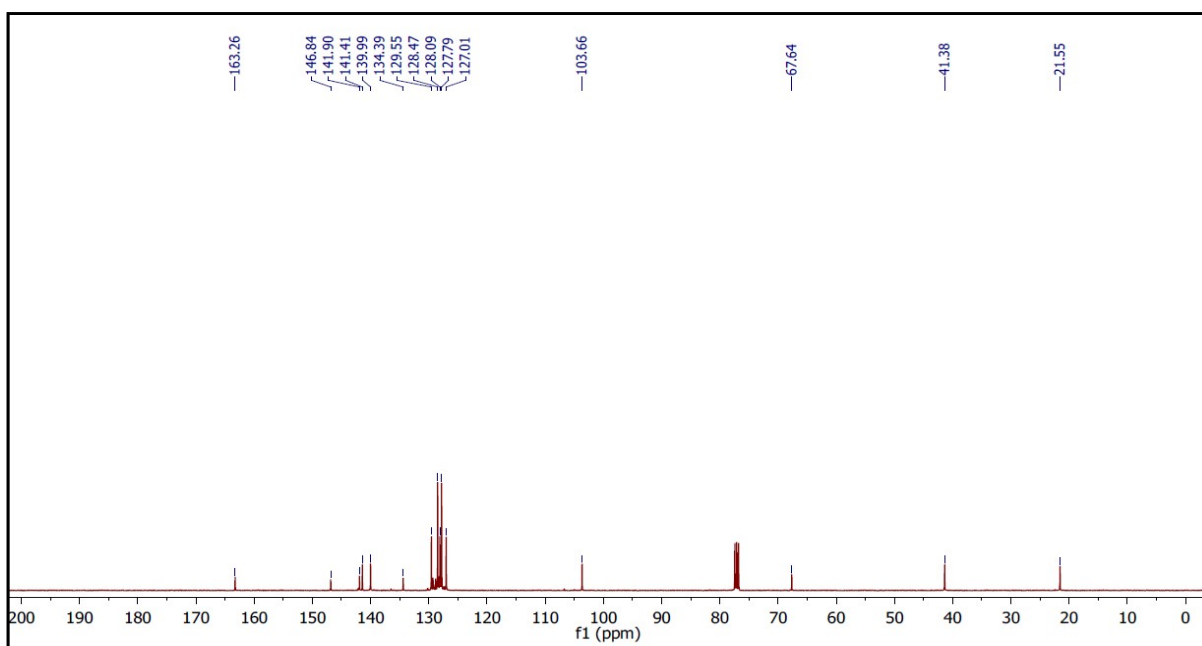
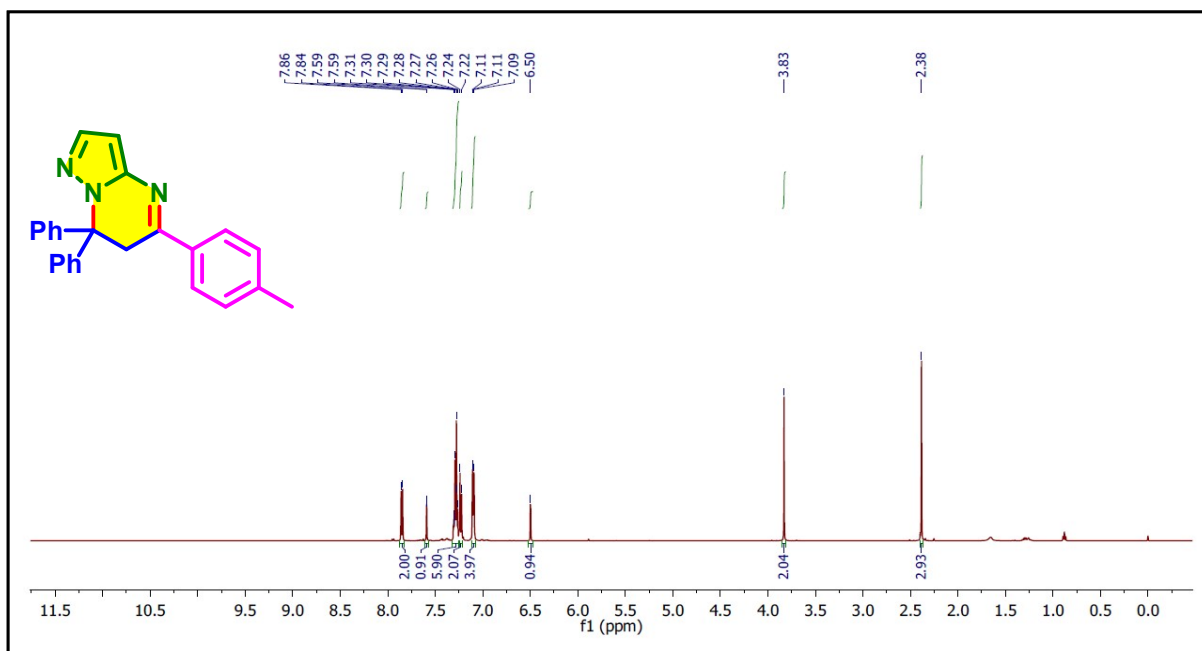
5-(4-methoxyphenyl)-7,7-diphenyl-6,7-dihydropyrazolo[1,5-a]pyrimidine (3i)

Isolated as a yellow solid, yield 86% (207 mg), m.p 200-202 °C, IR (ATR): 3281, 3023, 2307, 1663, 1514, 1477, 1270, 1215, 1037, 982, 749, 693 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.9$ Hz, 2H), 7.58 (d, $J = 1.8$ Hz, 1H), 7.31-7.24 (m, 6H), 7.13-7.09 (m, 4H), 6.93 (d, $J = 8.9$ Hz, 2H), 6.47 (s, 1H), 3.84 (s, 3H), 3.81 (s, 2H) ppm, ^{13}C NMR (125 MHz, CDCl_3) δ 162.66, 162.28, 146.94, 141.47, 139.96, 129.71, 128.82, 128.45, 128.06, 127.79, 114.15, 103.28, 67.58, 55.47, 41.25 ppm, ESI-MS: m/z 380 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{25}\text{H}_{22}\text{N}_3\text{O}$ m/z 380.1757 $[\text{M}+\text{H}]^+$, found 380.1750.



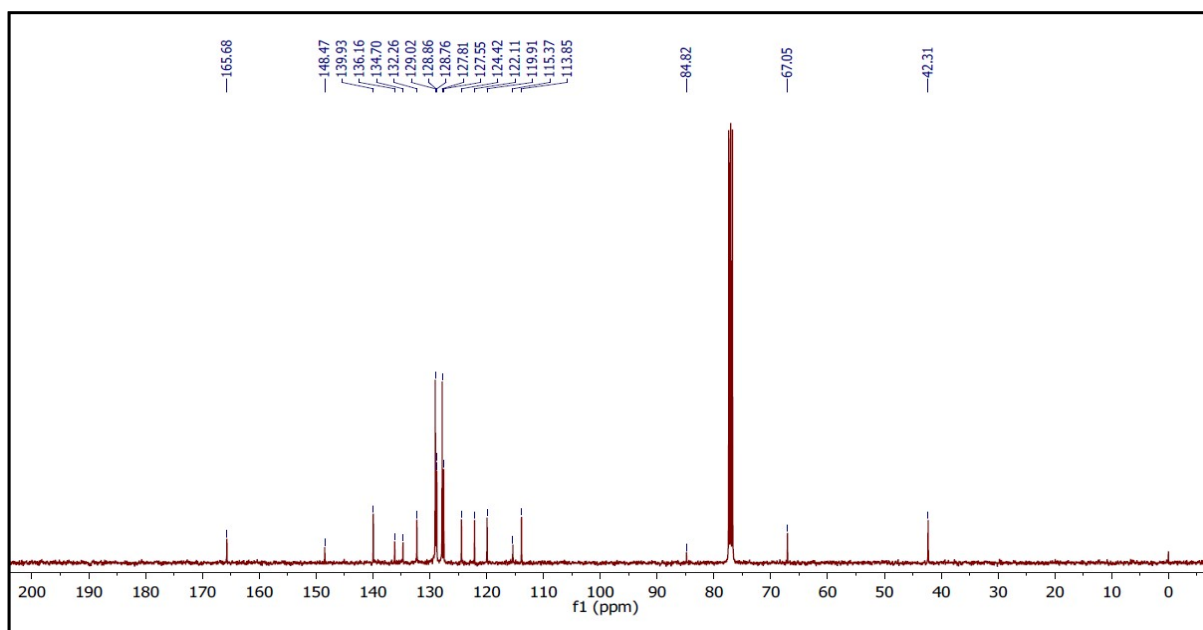
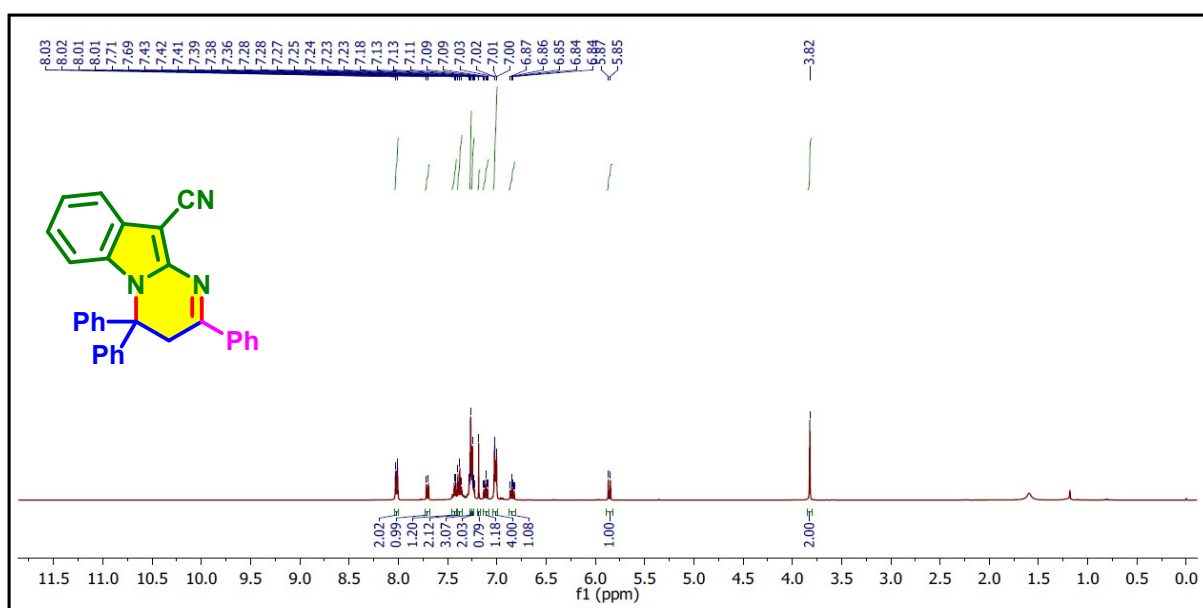
7,7-diphenyl-5-(*p*-tolyl)-6,7-dihydropyrazolo[1,5-*a*]pyrimidine (3j)

Isolated as a red solid, yield 83% (202 mg), m.p 172-174 °C, IR (ATR): 3021, 2959, 1597, 1488, 1412, 1269, 1214, 750, 668 cm^{-1} , ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 1.6$ Hz, 1H), 7.32 – 7.25 (m, 6H), 7.23 (d, $J = 8.3$ Hz, 2H), 7.12 – 7.08 (m, 4H), 6.50 (s, 1H), 3.83 (s, 2H), 2.38 (s, 3H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 163.26, 146.84, 141.90, 141.41, 139.99, 134.39, 129.55, 128.47, 128.09, 127.79, 127.01, 103.66, 67.64, 41.38, 21.55 ppm, ESI-MS: m/z 364 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{25}\text{H}_{22}\text{N}_3$ m/z 364.1808 $[\text{M}+\text{H}]^+$, found 364.1802.



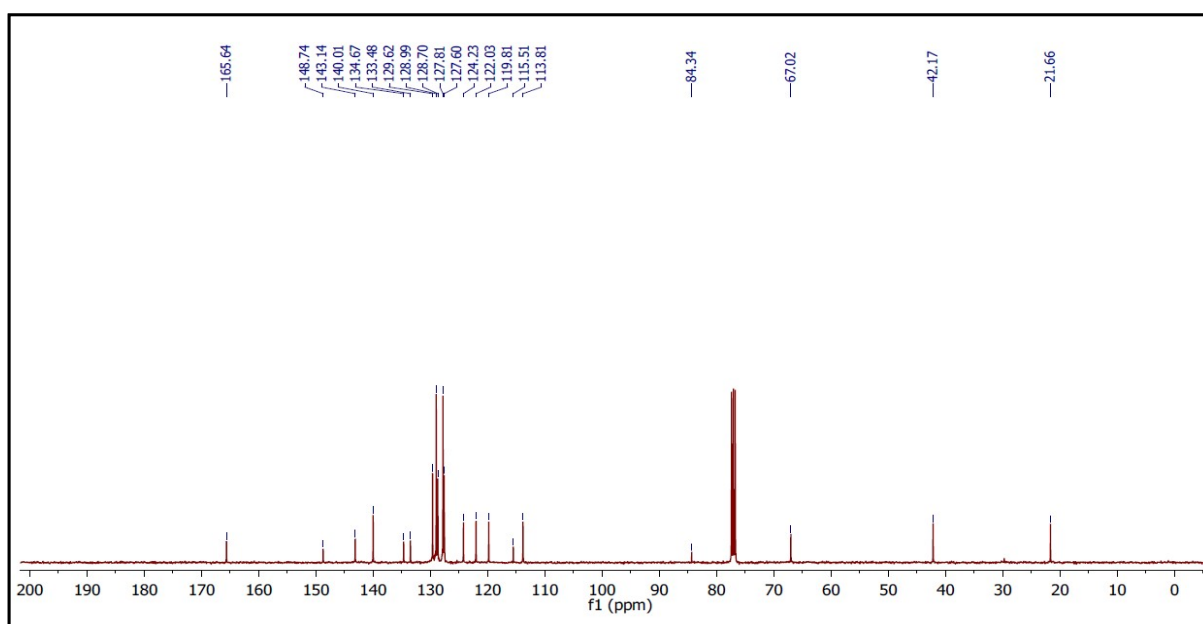
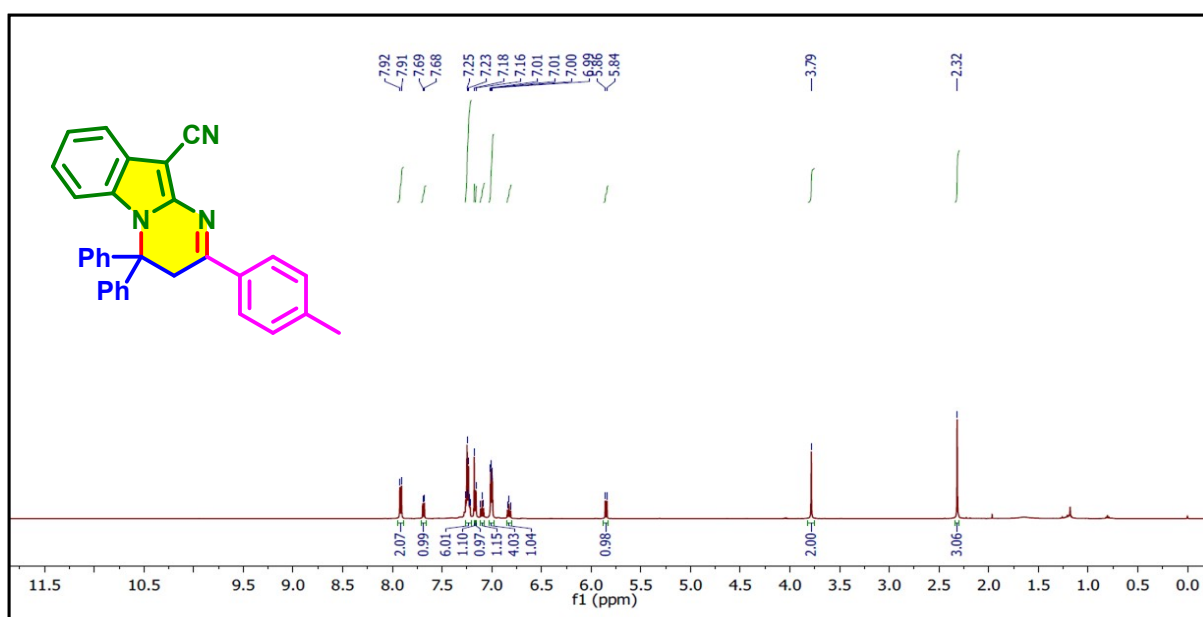
2,4,4-triphenyl-3,4-dihydropyrimido[1,2-*a*]indole-10-carbonitrile (3k)

Isolated as a light yellow solid, yield 75% (223 mg), m.p 289-291 °C, IR (ATR): 3254, 3020, 2134, 1709, 1560, 1445, 1254, 1080, 932, 753 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 8.04-8.01 (m, 2H), 7.70 (d, $J = 7.9$ Hz, 1H), 7.45 – 7.41 (m, 1H), 7.38 (m, 2H), 7.28-7.25 (s, 3H), 7.24 – 7.22 (m, 2H), 7.18 (s, 1H), 7.14 – 7.08 (m, 1H), 7.04-7.00 (m, 4H), 6.87-6.28 (m, 1H), 5.86 (d, $J = 8.5$ Hz, 1H), 3.82 (s, 2H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 165.68, 148.47, 139.93, 136.16, 134.70, 132.26, 129.02, 128.86, 128.76, 127.81, 127.55, 124.42, 122.11, 119.91, 115.37, 113.85, 84.82, 67.05, 42.31 ppm, ESI-MS: m/z 424 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{30}\text{H}_{22}\text{N}_3$ m/z 424.1808 $[\text{M}+\text{H}]^+$, found 424.1800.



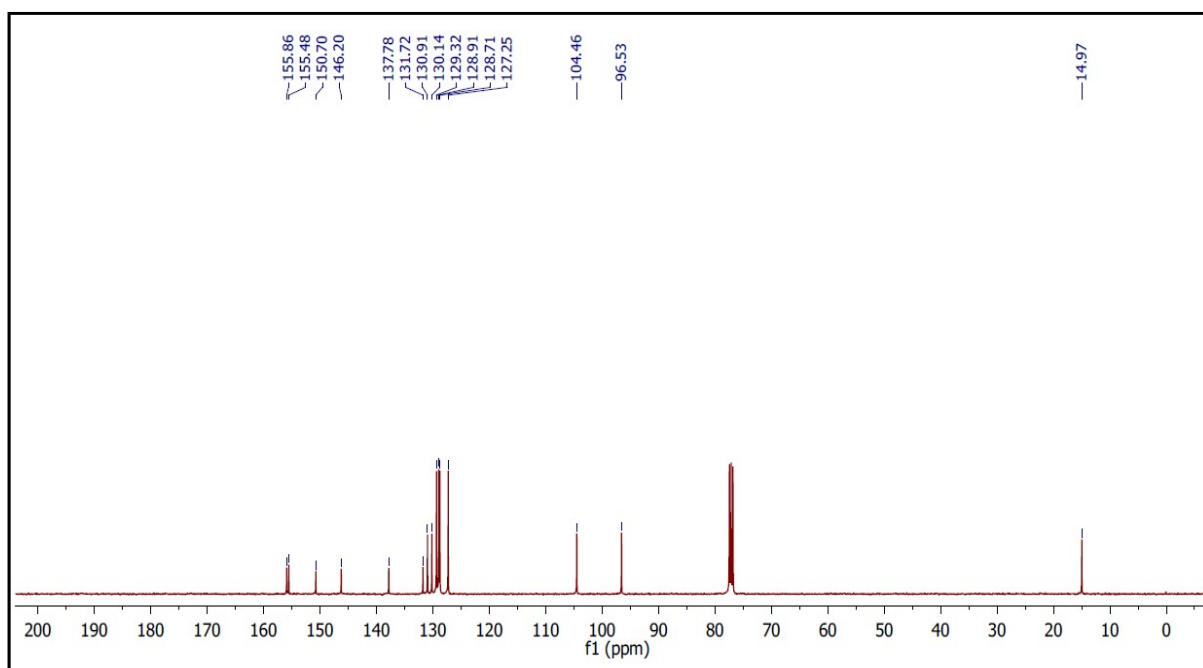
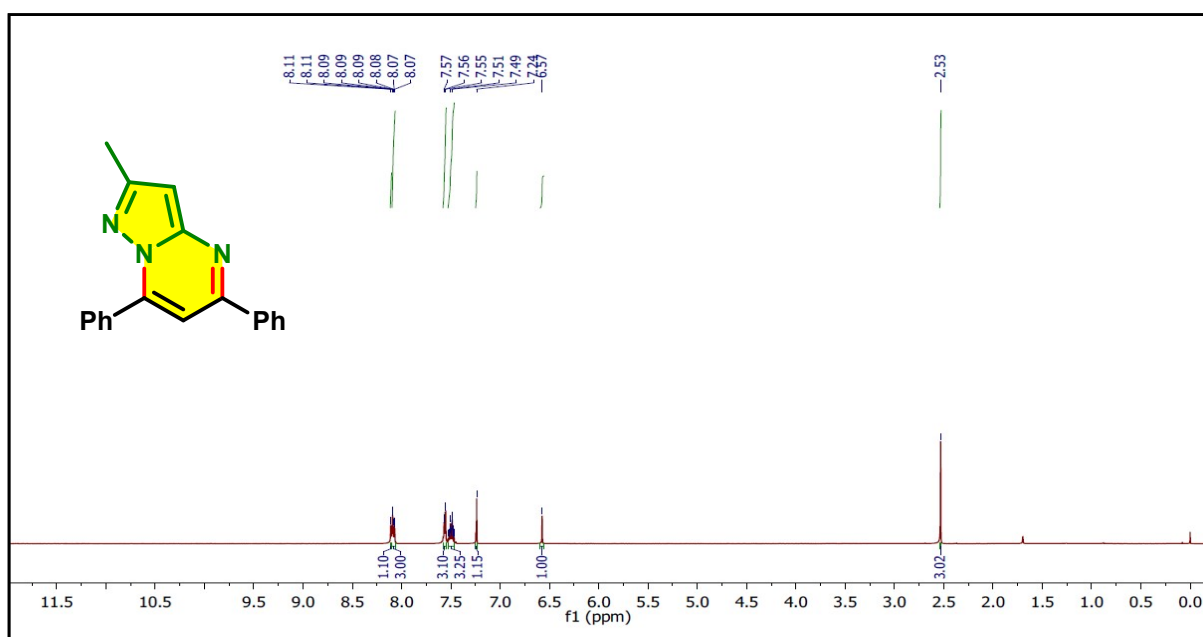
4,4-diphenyl-2-(p-tolyl)-3,4-dihydropyrimido[1,2-a]indole-10-carbonitrile (3I)

Isolated as a red solid, yield 78% (228 mg), m.p 270-272 °C, IR (ATR): 3289, 3017, 2105, 1669, 1549, 1475, 1219, 1044, 907, 753 cm^{-1} , ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 7.9$ Hz, 1H), 7.27 – 7.21 (m, 6H), 7.18 (s, 1H), 7.16 (s, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.03-6.99 (m, 4H), 6.85 – 6.80 (m, 1H), 5.85 (d, $J = 8.5$ Hz, 1H), 3.79 (s, 2H), 2.32 (s, 3H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 165.64, 148.74, 143.14, 140.01, 134.67, 133.48, 129.62, 128.99, 128.70, 127.81, 127.60, 124.23, 122.03, 119.81, 115.51, 113.81, 84.34, 67.02, 42.17, 21.66 ppm, ESI-MS: m/z 438 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{31}\text{H}_{24}\text{N}_3$ m/z 438.1964 $[\text{M}+\text{H}]^+$, found 438.1953.



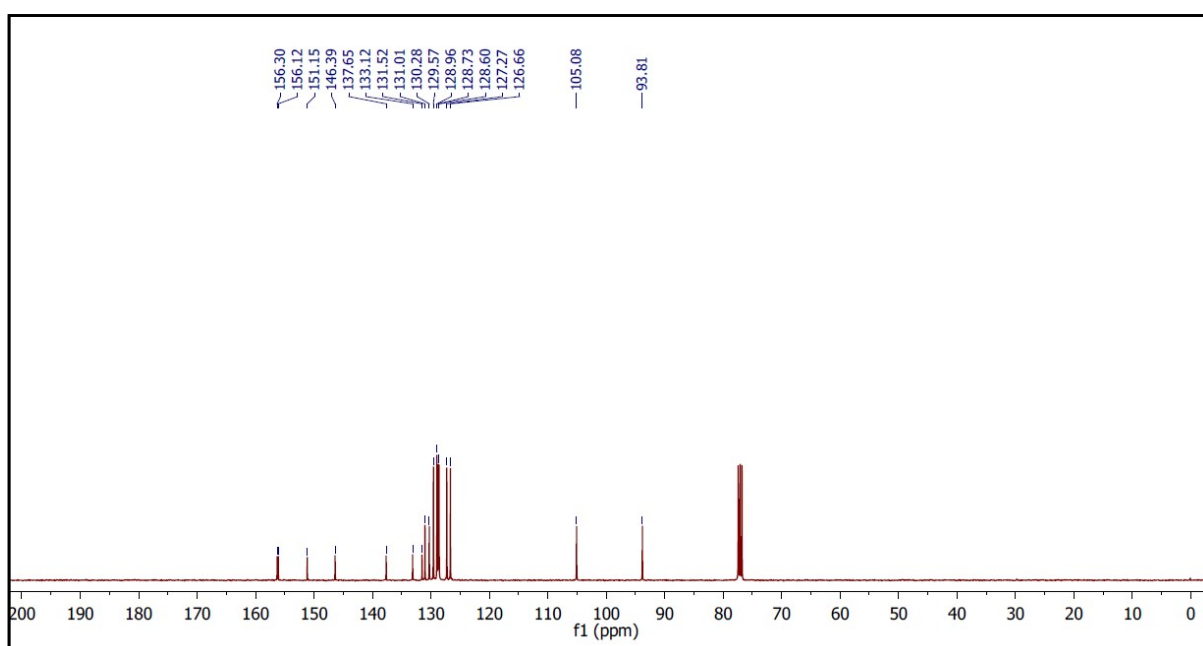
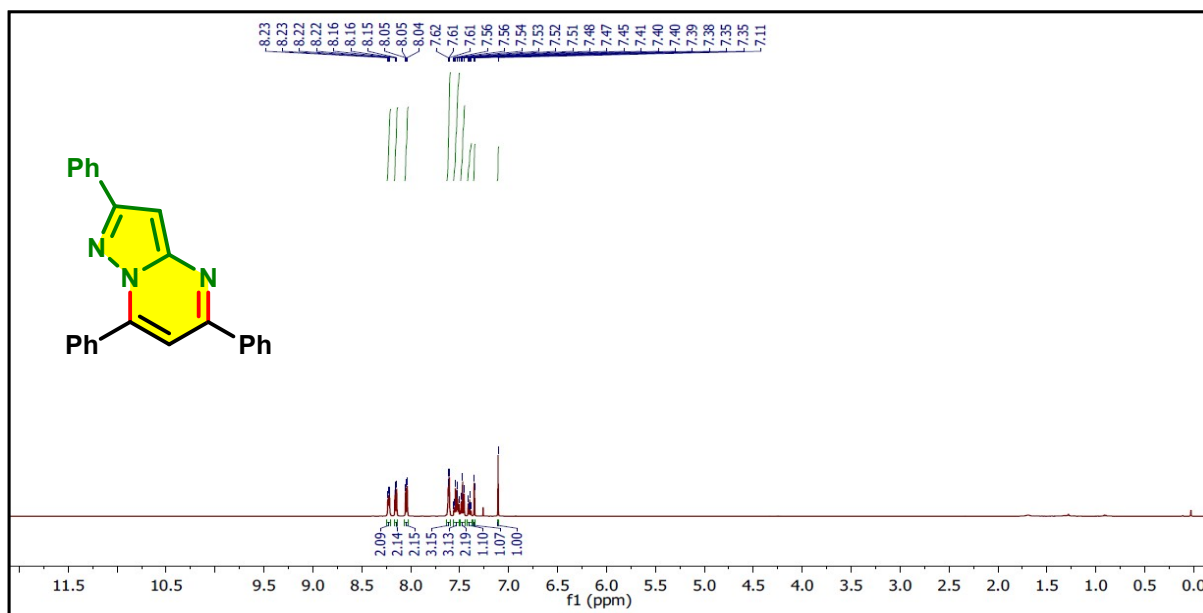
2-methyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine (3m)

Isolated as a cream solid, yield 95% (263 mg), m.p 118-120 °C, IR (ATR): 3279, 3006, 1659, 1570, 1264, 1065, 767, 684 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 1.8$ Hz, 1H), 8.10 – 8.06 (m, 3H), 7.57-7.53 (m, 3H), 7.53 – 7.46 (m, 3H), 7.24 (s, 1H), 6.57 (s, 1H), 2.53 (s, 3H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 155.86, 155.48, 150.70, 146.20, 137.78, 131.72, 130.91, 130.14, 129.32, 128.91, 128.71, 127.25, 104.46, 96.53, 14.97 ppm, ESI-MS: m/z 286 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_3$ m/z 286.1338 $[\text{M}+\text{H}]^+$, found 286.1335.



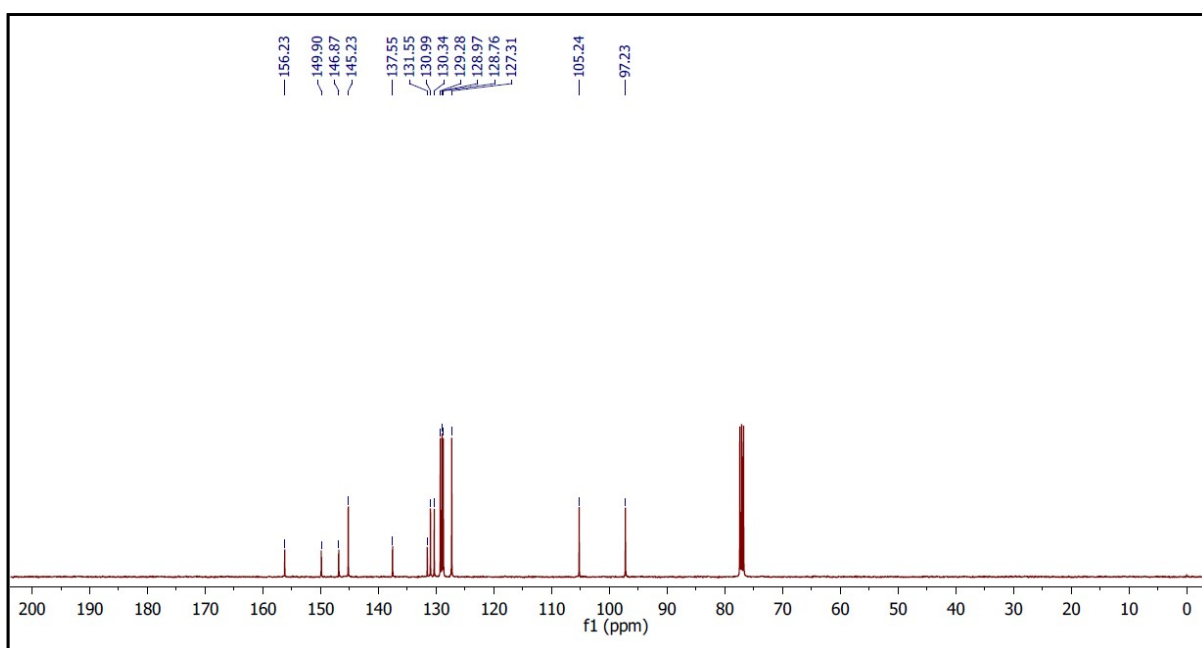
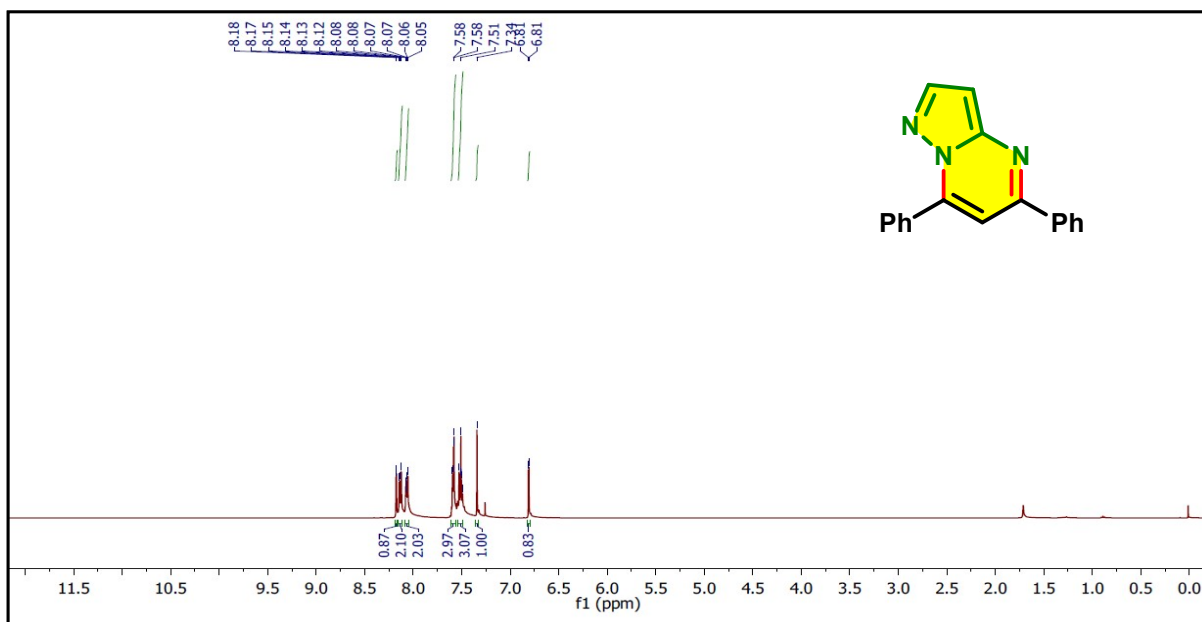
2,5,7-triphenylpyrazolo[1,5-a]pyrimidine (3n)

Isolated as a cream solid, yield 90% (303 mg), m.p 163-165 °C, IR (ATR): 3249, 3056, 1687, 1582, 1202, 1026, 732, 695 cm^{-1} , ^1H NMR (500 MHz, CDCl_3) δ 8.22 (m, 2H), 8.17 – 8.13 (m, 2H), 8.06 – 8.02 (m, 2H), 7.63 – 7.59 (m, 3H), 7.56 – 7.50 (m, 3H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.42 – 7.38 (m, 1H), 7.35 (m, 1H), 7.11 (s, 1H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 156.30, 156.12, 151.15, 146.39, 137.65, 133.12, 131.52, 131.01, 130.28, 129.57, 128.96, 128.73, 128.60, 127.27, 126.66, 105.08, 93.81 ppm, ESI-MS: m/z 348 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_3$ m/z 348.1495 $[\text{M}+\text{H}]^+$, found 348.1491.



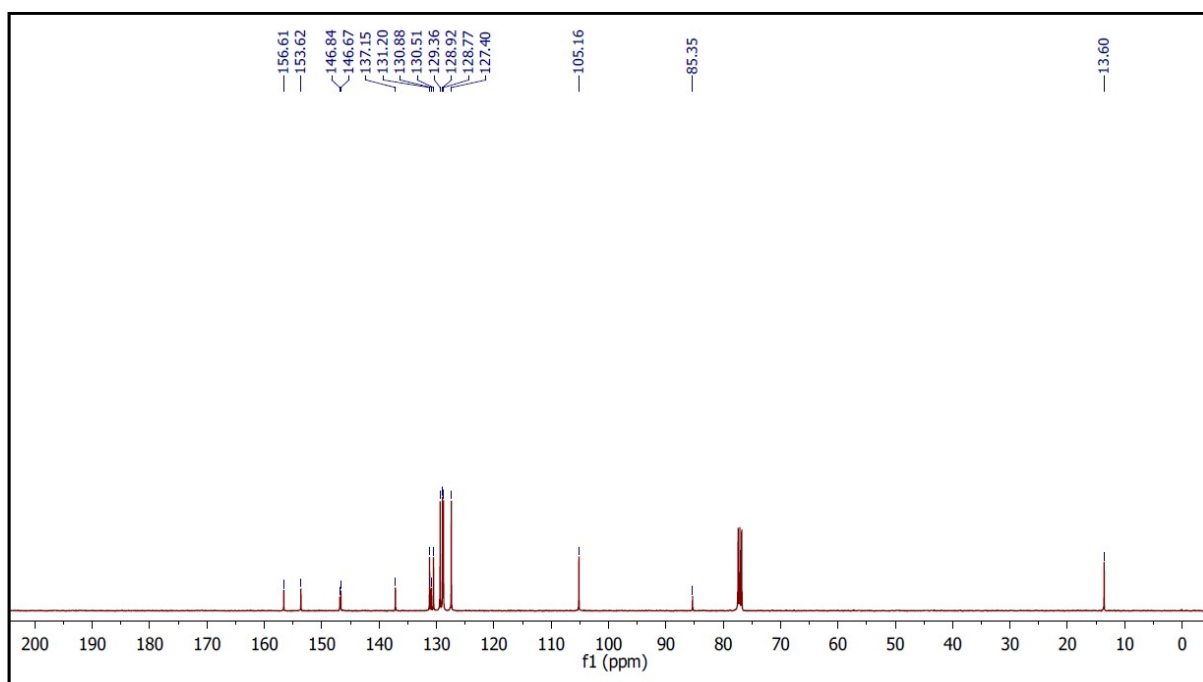
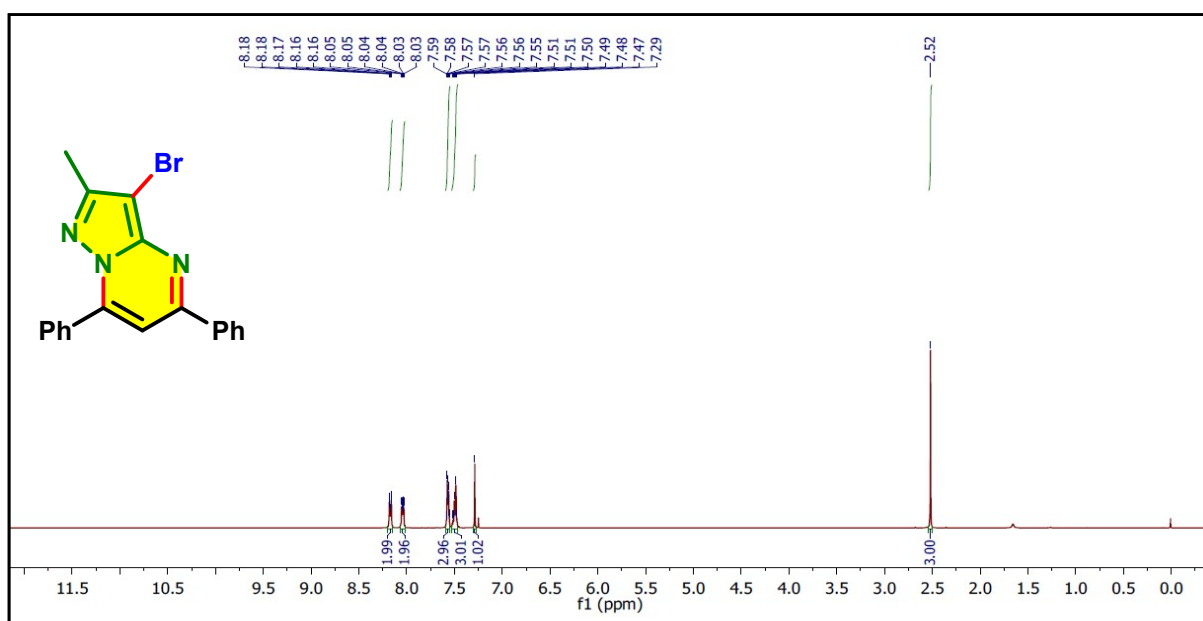
5,7-diphenylpyrazolo[1,5-a]pyrimidine (3o)

Isolated as a light yellow solid, yield 92% (242 mg), m.p 88-90 °C, IR (ATR): 3289, 3022, 1668, 1618, 1517, 1404, 1218, 1046, 905, 753 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 2.3$ Hz, 1H), 8.15-8.12 (m, 2H), 8.08 – 8.05 (m, 2H), 7.60-7.59 (m, 3H), 7.54 – 7.49 (m, 3H), 7.34 (s, 1H), 6.81 (d, $J = 2.3$ Hz, 1H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 156.23, 149.90, 146.87, 145.23, 137.55, 131.55, 130.99, 130.34, 129.28, 128.97, 128.76, 127.31, 105.24, 97.23 ppm, ESI-MS: m/z 272 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_3$ m/z 272.1182 $[\text{M}+\text{H}]^+$, found 272.1180.



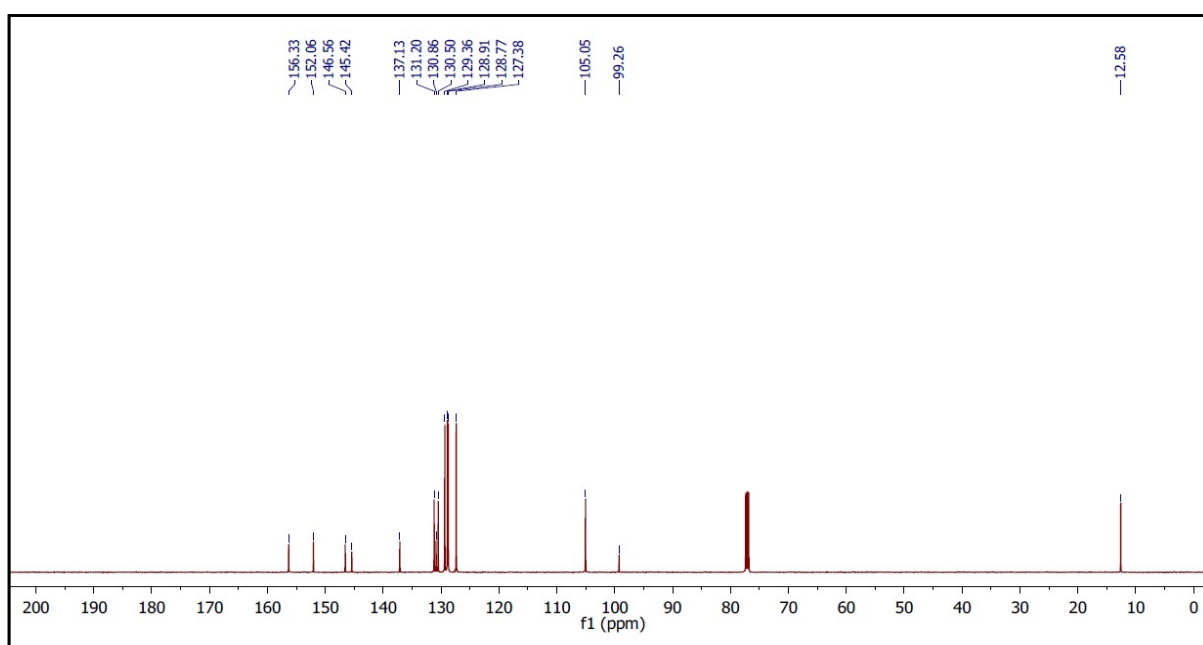
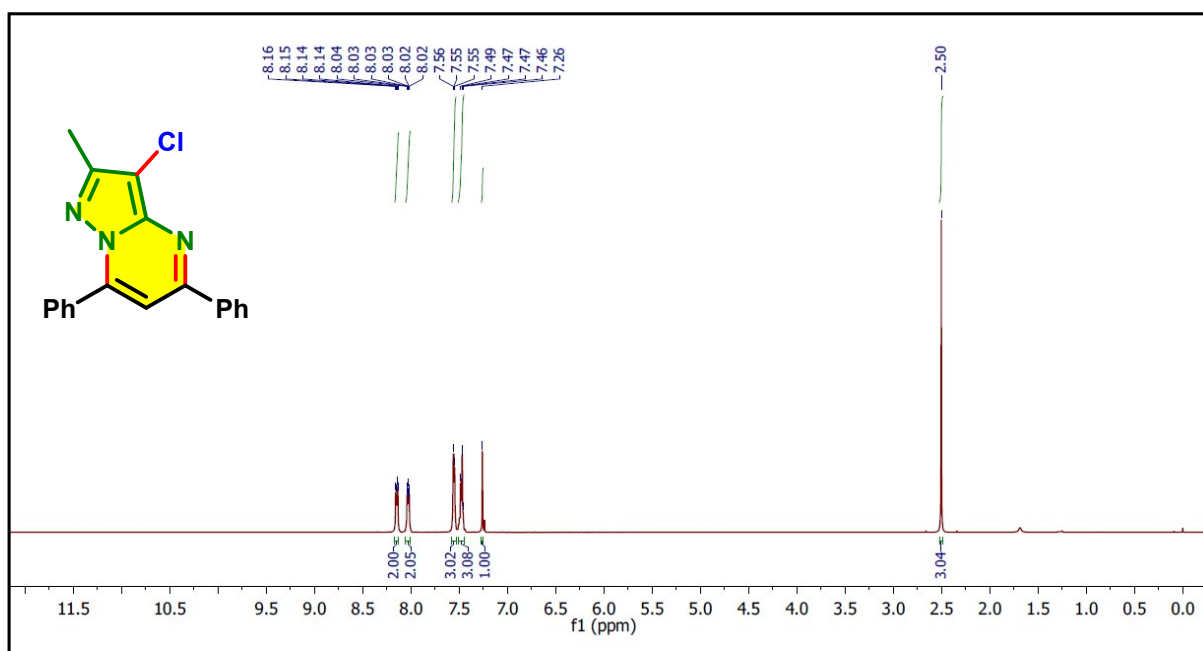
3-bromo-2-methyl-5,7-diphenylpyrazolo[1,5-a]pyrimidine (3p)

Isolated as a yellow solid, yield 86% (303 mg), m.p 147-149 °C, IR (ATR): 3289, 3020, 1669, 1618, 1549, 1516, 1214, 1045, 747, 667 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 8.20 – 8.15 (m, 2H), 8.07 – 8.02 (m, 2H), 7.59 – 7.55 (m, 3H), 7.53 – 7.46 (m, 3H), 7.29 (s, 1H), 2.52 (s, 3H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 156.61, 153.62, 146.84, 146.67, 137.15, 131.20, 130.88, 130.51, 129.36, 128.92, 128.77, 127.40, 105.16, 85.35, 13.60 ppm, ESI-MS: m/z 364 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{19}\text{H}_{15}\text{BrN}_3$ m/z 364.0443 $[\text{M}+\text{H}]^+$, found 364.0439.



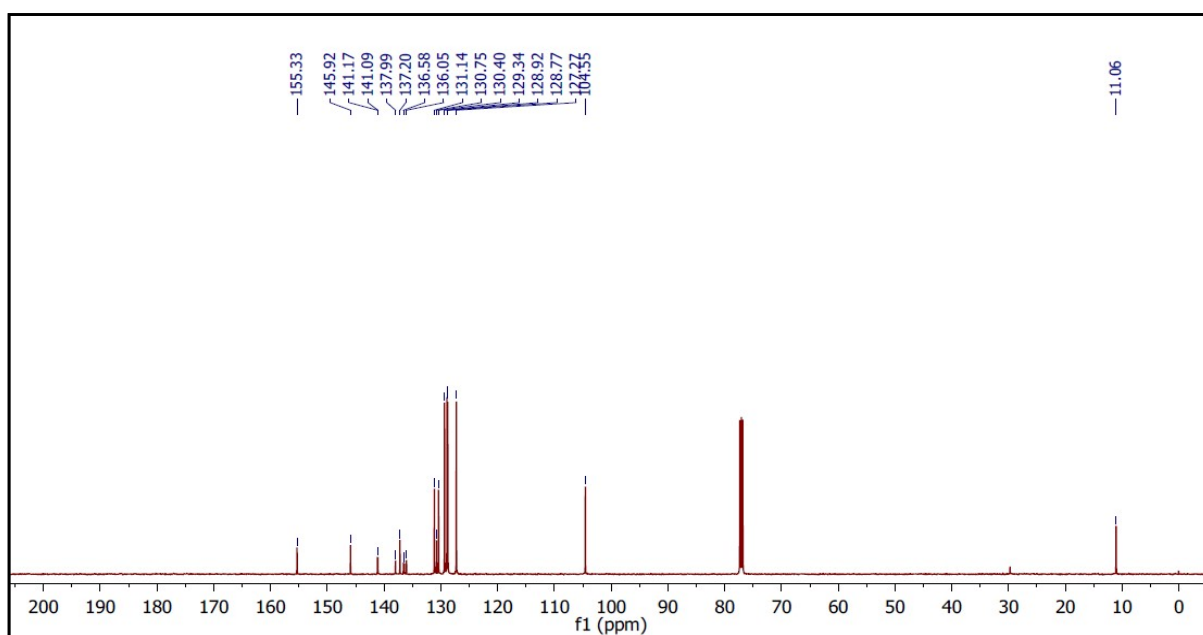
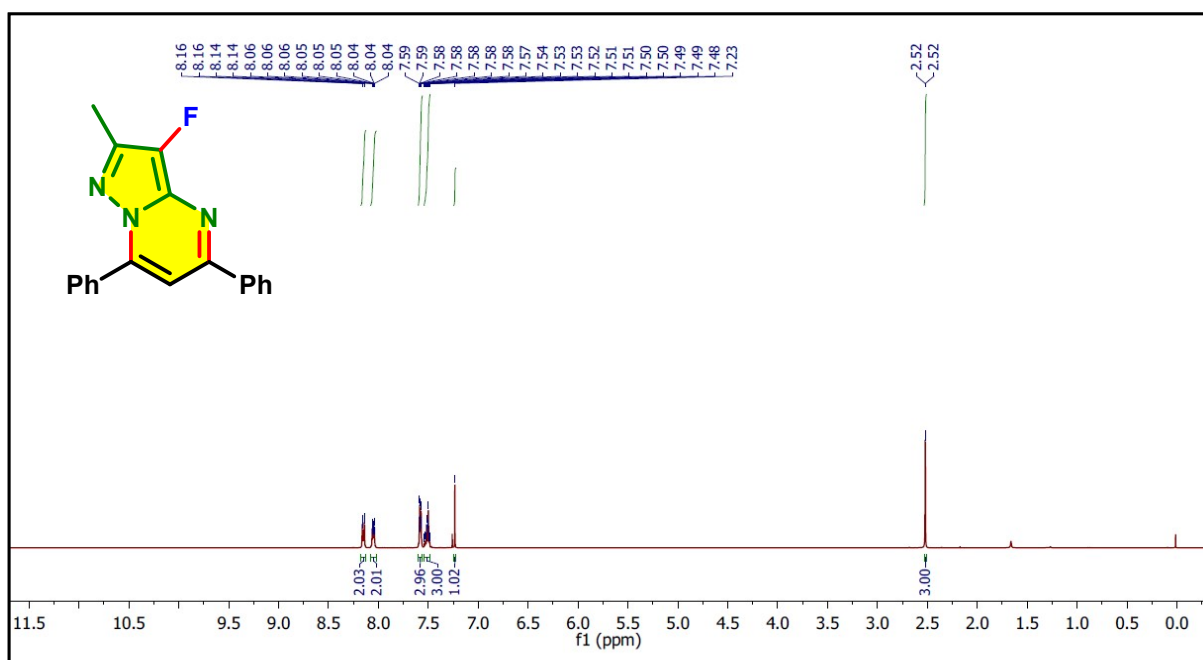
3-chloro-2-methyl-5,7-diphenylpyrazolo[1,5-a]pyrimidine (3q)

Isolated as a light yellow solid, yield 83% (257 mg), m.p 152-154 °C, IR (ATR): 3285, 3036, 1675, 1592, 1512, 1487, 1234, 1106, 987, 787, 665 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 8.16-8.14 (m, 2H), 8.06 – 8.00 (m, 2H), 7.58 – 7.53 (m, 3H), 7.49-7.46 (m, 3H), 7.26 (s, 1H), 2.50 (s, 3H) ppm, ^{13}C NMR (125 MHz, CDCl_3) δ 156.33, 152.06, 146.56, 145.42, 137.13, 131.20, 130.86, 130.50, 129.36, 128.91, 128.77, 127.38, 105.05, 99.26, 12.58 ppm, ESI-MS: m/z 320 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{19}\text{H}_{15}\text{ClN}_3$ m/z 320.0949 $[\text{M}+\text{H}]^+$, found 320.0947.



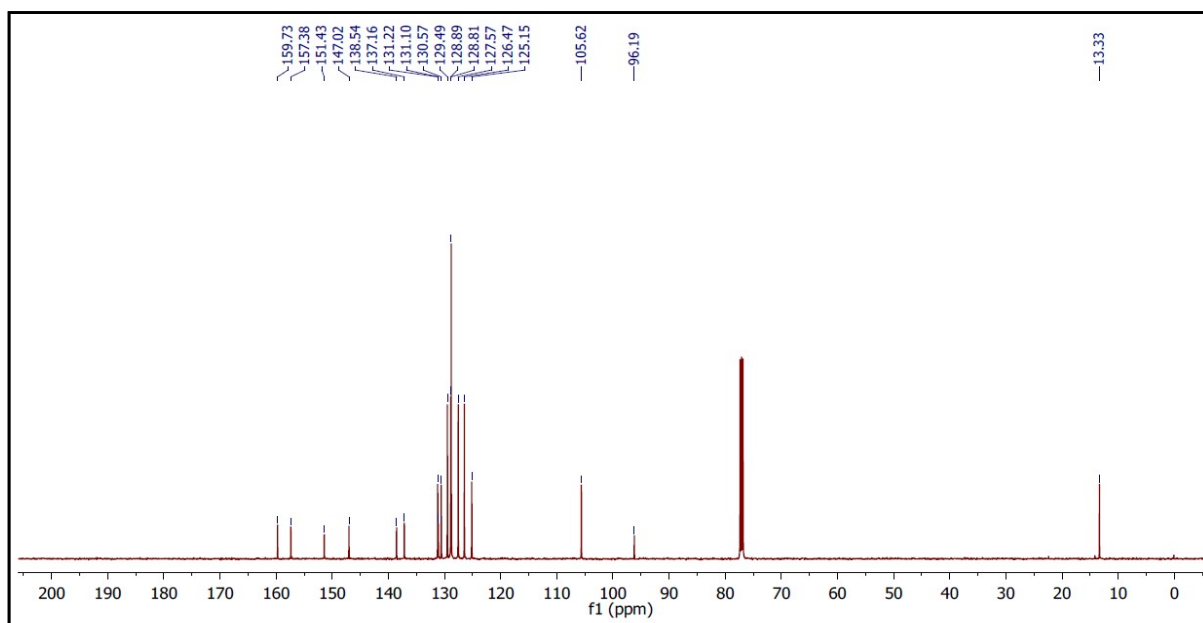
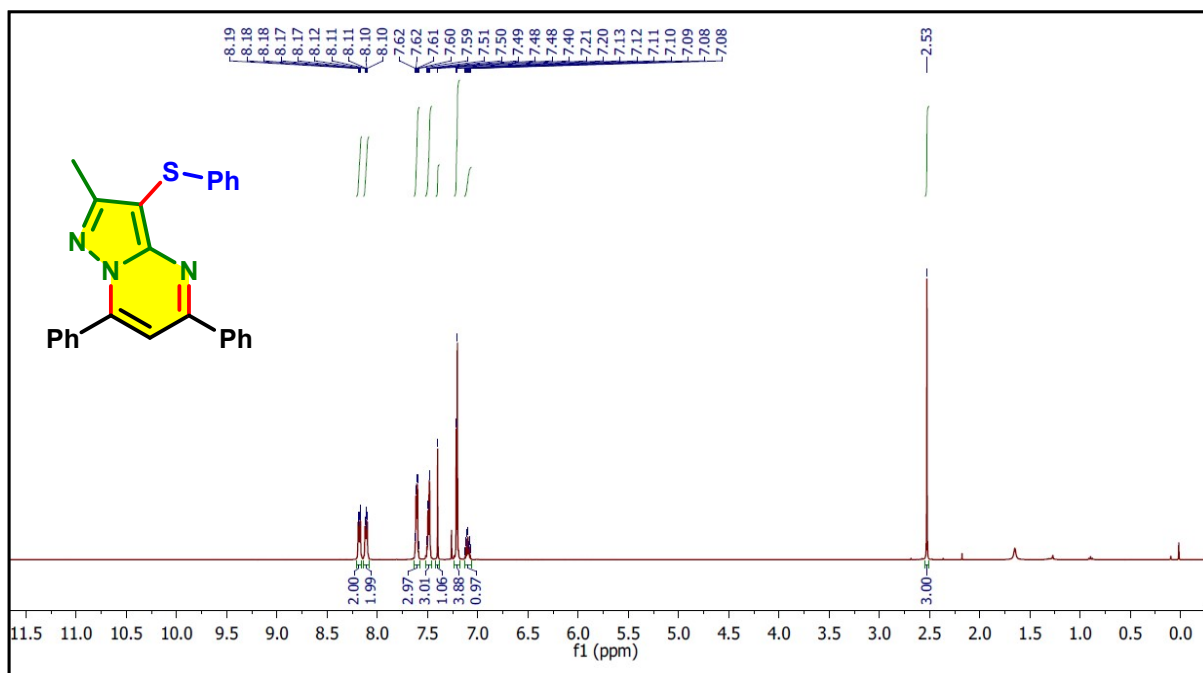
3-fluoro-2-methyl-5,7-diphenylpyrazolo[1,5-a]pyrimidine (3r)

Isolated as a yellow solid, yield 80% (236 mg), m.p 143-145 °C, IR (ATR): 3245, 3014, 1654, 1625, 1508, 1487, 1305, 1187, 1012, 765, 684 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 8.15 (m, 2H), 8.08 – 8.02 (m, 2H), 7.58 (m, 3H), 7.54 – 7.48 (m, 3H), 7.23 (s, 1H), 2.52 (s, 3H) ppm, ^{13}C NMR (125 MHz, CDCl_3) δ 155.33, 145.92, 141.13 (d, $J = 9.8$ Hz), 137.99, 137.20, 136.49 (d, $J = 23.1$ Hz), 136.05, 131.14, 130.75, 130.40, 129.34, 128.92, 128.77, 127.27, 104.55, 11.06 ppm, ESI-MS: m/z 304 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{19}\text{H}_{15}\text{FN}_3$ m/z 304.1244 $[\text{M}+\text{H}]^+$, found 304.1241.



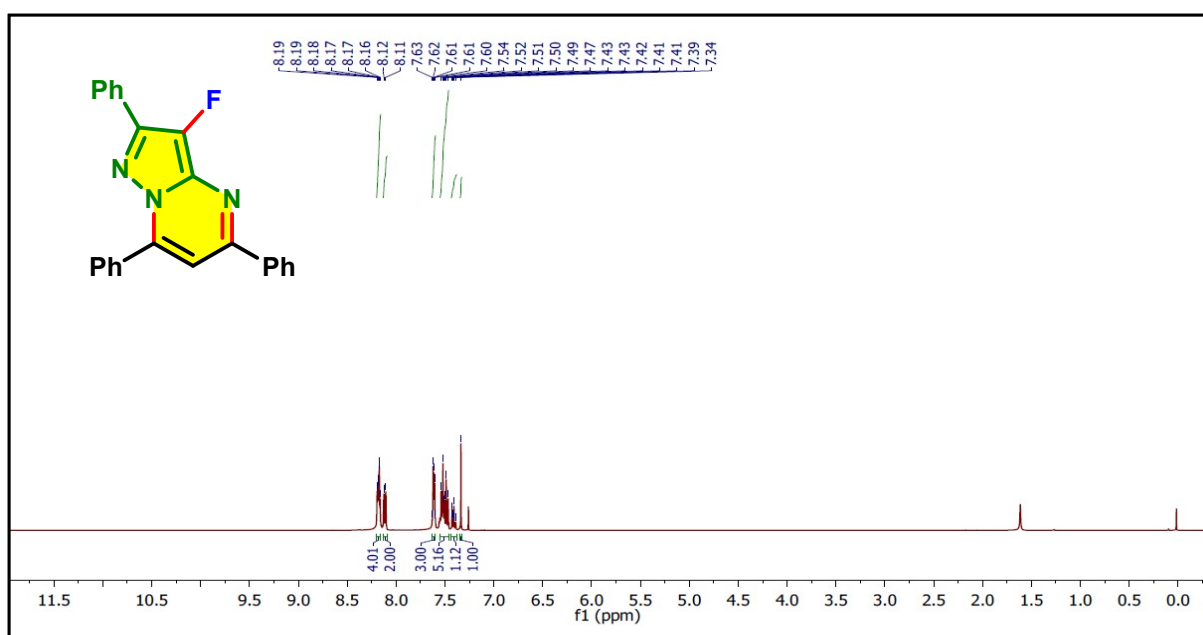
2-methyl-5,7-diphenyl-3-(phenylthio)pyrazolo[1,5-a]pyrimidine (3s)

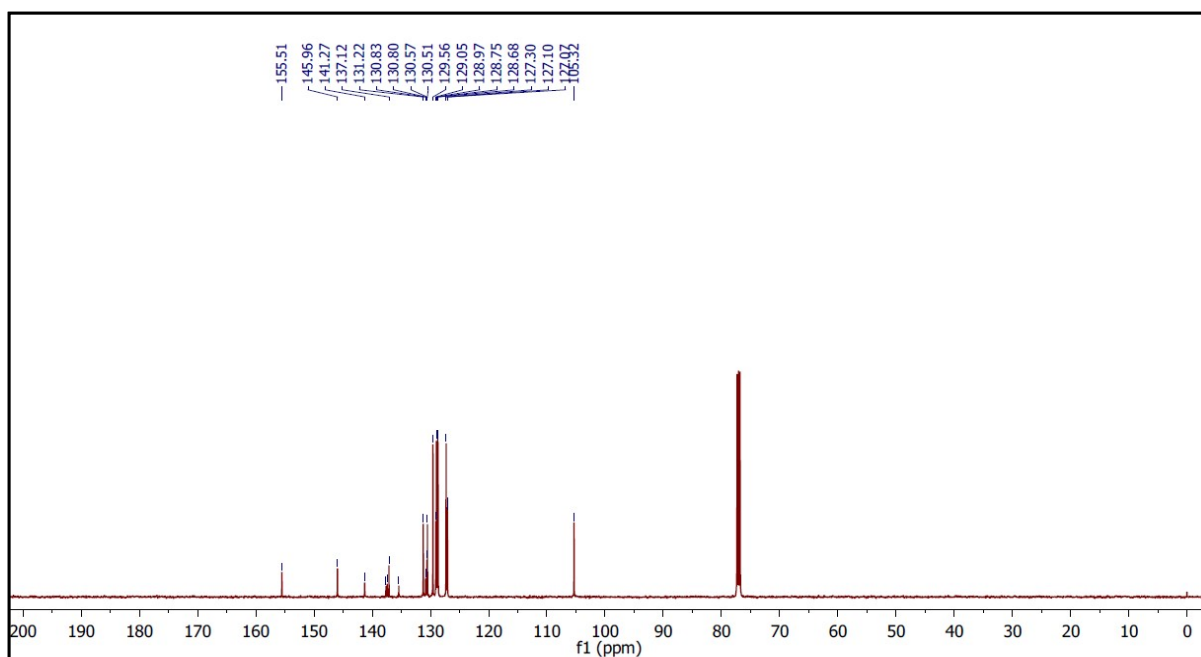
Isolated as a colourless solid, yield 78% (297 mg), m.p 180-182 °C, IR (ATR): 3423, 3257, 3031, 2945, 1635, 1602, 1517, 1207, 1132, 986, 875, 784, 675 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 8.21 – 8.16 (m, 2H), 8.14 – 8.08 (m, 2H), 7.64 – 7.58 (m, 3H), 7.52 – 7.46 (m, 3H), 7.40 (s, 1H), 7.21 (d, $J = 4.4$ Hz, 4H), 7.13 – 7.06 (m, 1H), 2.53 (s, 3H) ppm, ^{13}C NMR (125 MHz, CDCl_3) δ 159.73, 157.38, 151.43, 147.02, 138.54, 137.16, 131.22, 131.10, 130.57, 129.49, 128.89, 128.81, 127.57, 126.47, 125.15, 105.62, 96.19, 13.33 ppm, ESI-MS: m/z 394 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_3\text{S}$ m/z 394.1372 $[\text{M}+\text{H}]^+$, found 394.1366.



3-fluoro-2,5,7-triphenylpyrazolo[1,5-a]pyrimidine (3t)

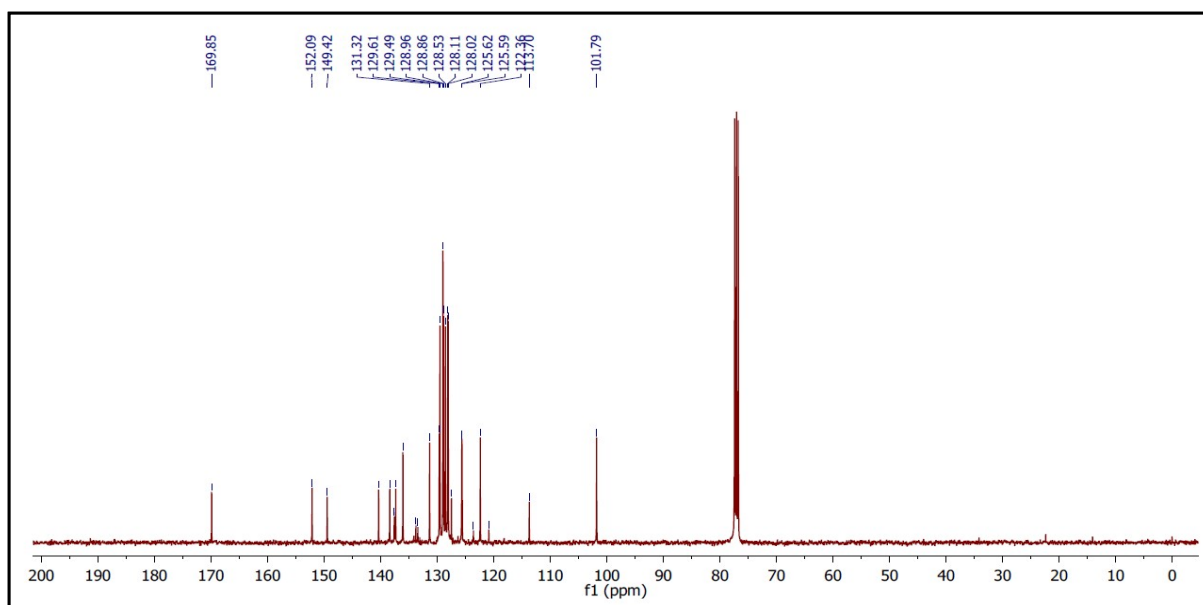
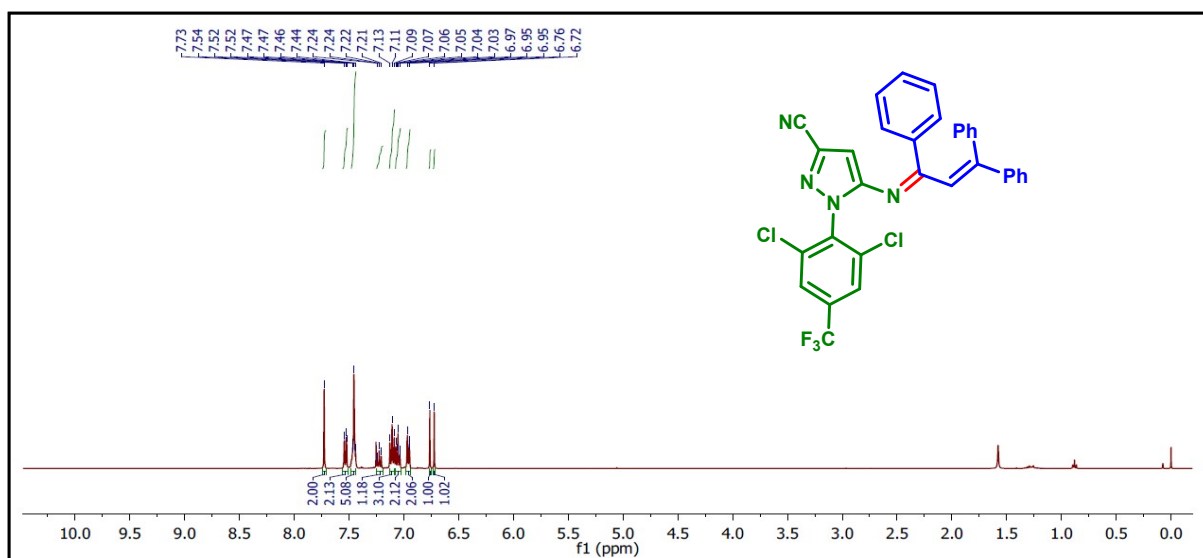
Isolated as a light yellow solid, yield 82% (290 mg), m.p 170-172 °C, IR (ATR): 3466, 3238, 3067, 2926, 1679, 1635, 1606, 1549, 1430, 1224, 1158, 978, 845, 754, 692 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 8.19-8.16 (m, 4H), 8.11 (d, $J = 7.4$ Hz, 2H), 7.63 – 7.60 (m, 3H), 7.54-7.47 (m, 5H), 7.43-7.39 (m, 1H), 7.34 (s, 1H) ppm, ^{13}C NMR (125 MHz, CDCl_3) δ 155.51, 145.96, 141.30, 141.27, 137.64, 137.42, 137.12, 135.43, 131.22, 130.83, 130.80, 130.57, 130.51, 129.56, 129.05, 128.97, 128.75, 128.68, 127.30, 127.10, 127.07, 105.32 ppm, ESI-MS: m/z 366 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{24}\text{H}_{17}\text{FN}_3$ m/z 366.1401 $[\text{M}+\text{H}]^+$, found 366.1400.





(Z)-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-5-((1,3,3-triphenylallylidene)amino)-1H-pyrazole-3-carbonitrile (6aa)

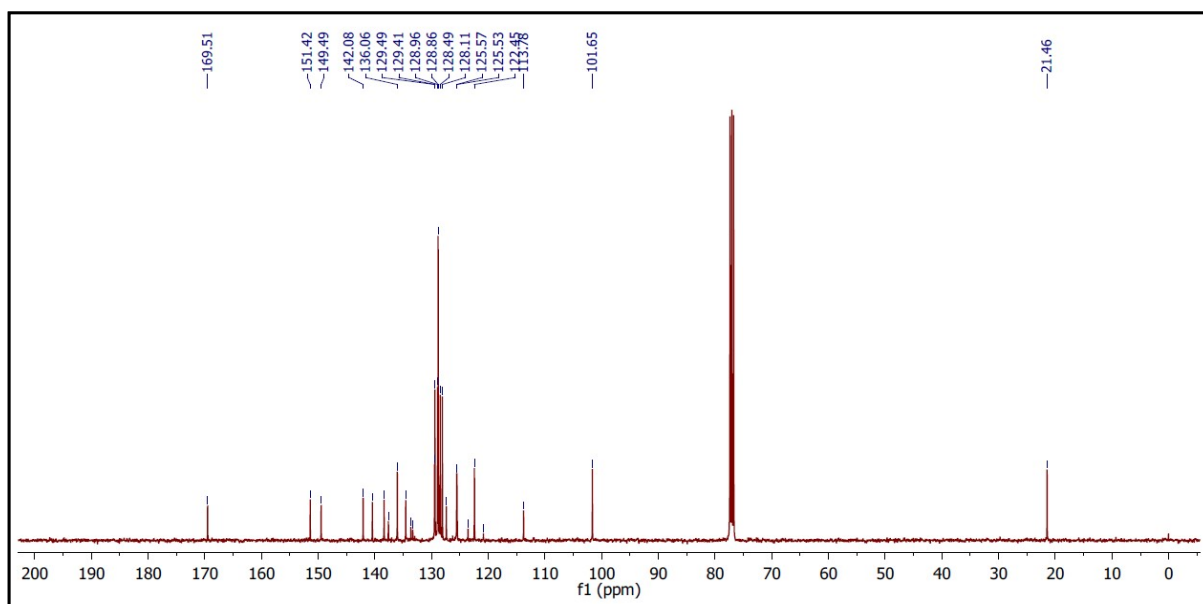
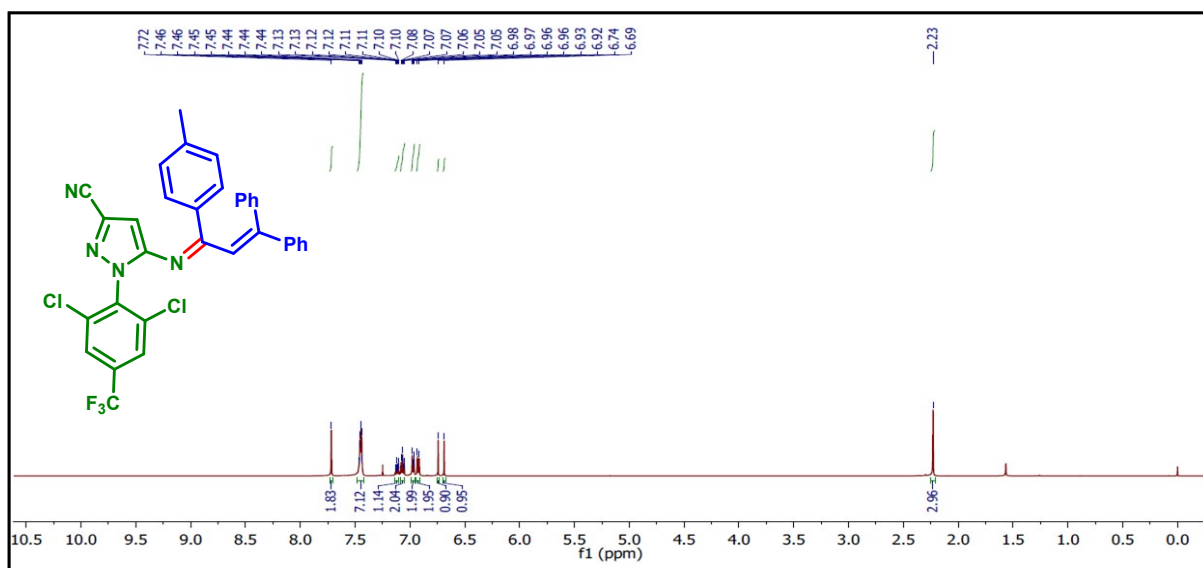
Isolated as a yellow solid, yield 95% (392 mg), m.p 233-235 °C, IR (ATR): 3061, 3023, 2244, 1563, 1502, 1396, 1308, 1137, 1095, 816, 755 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 2H), 7.56 – 7.51 (m, 2H), 7.49 – 7.43 (m, 5H), 7.23-7.21 (m, 1H), 7.13-7.09 (m, 3H), 7.07 – 7.03 (m, 2H), 6.98 – 6.94 (m, 2H), 6.76 (s, 1H), 6.72 (s, 1H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 169.85, 152.09, 149.42, 140.33, 138.37, 137.56, 137.31, 136.04, 133.53 (q, $J=34.47$ Hz), 131.32, 129.61, 129.49, 128.96, 128.86, 128.53, 128.11, 128.02, 127.45, 125.62, 125.59, 122.36, 122.08 (d, $J=273.62$ Hz), 113.70, 101.79 ppm, ESI-MS: m/z 587 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{32}\text{H}_{20}\text{Cl}_2\text{F}_3\text{N}_4$ m/z 587.1011 $[\text{M}+\text{H}]^+$, found 587.1022.



(Z)-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-5-((3,3-diphenyl-1-(*p*-tolyl)allylidene)amino)-1*H*-pyrazole-3-carbonitrile (6ab)

Isolated as a yellow solid, yield 92% (371 mg), m.p 246-248 °C, IR (ATR): 3060, 3023, 2244, 1557, 1503, 1397, 1306, 1175, 1137, 1094, 880, 819, 753 cm⁻¹, ¹H NMR (500 MHz, CDCl₃) δ 7.71 (s, 2H), 7.48 – 7.42 (m, 7H), 7.14 – 7.10 (m, 1H), 7.09 – 7.05 (m, 2H), 6.97-6.95 (m, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.74 (s, 1H), 6.69 (s, 1H), 2.23 (s, 3H) ppm, ¹³C NMR (100 MHz, CDCl₃) δ 169.51, 151.42, 149.49, 142.08, 140.46, 138.39, 137.63, 136.06, 134.57, 133.43 (q, *J*=34.11 Hz), 129.49, 129.41, 128.96, 128.86, 128.49, 128.11, 127.40, 125.57, 125.53, 122.45, 122.10 (d, *J*=273.26 Hz), 113.78, 101.65, 21.46 ppm, ESI-MS: *m/z* 601

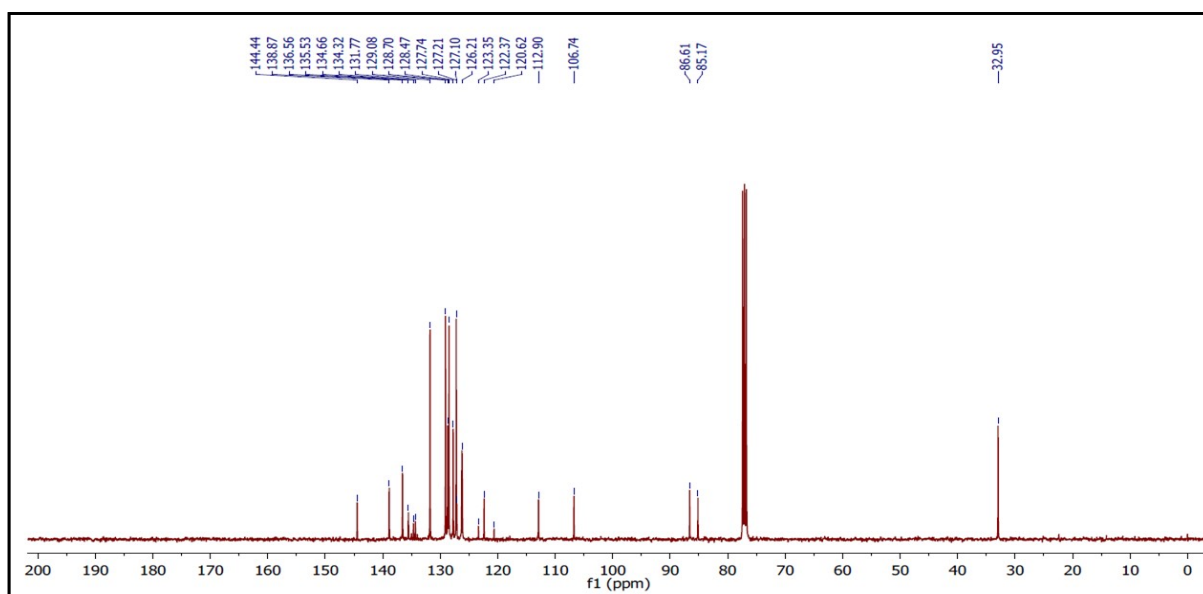
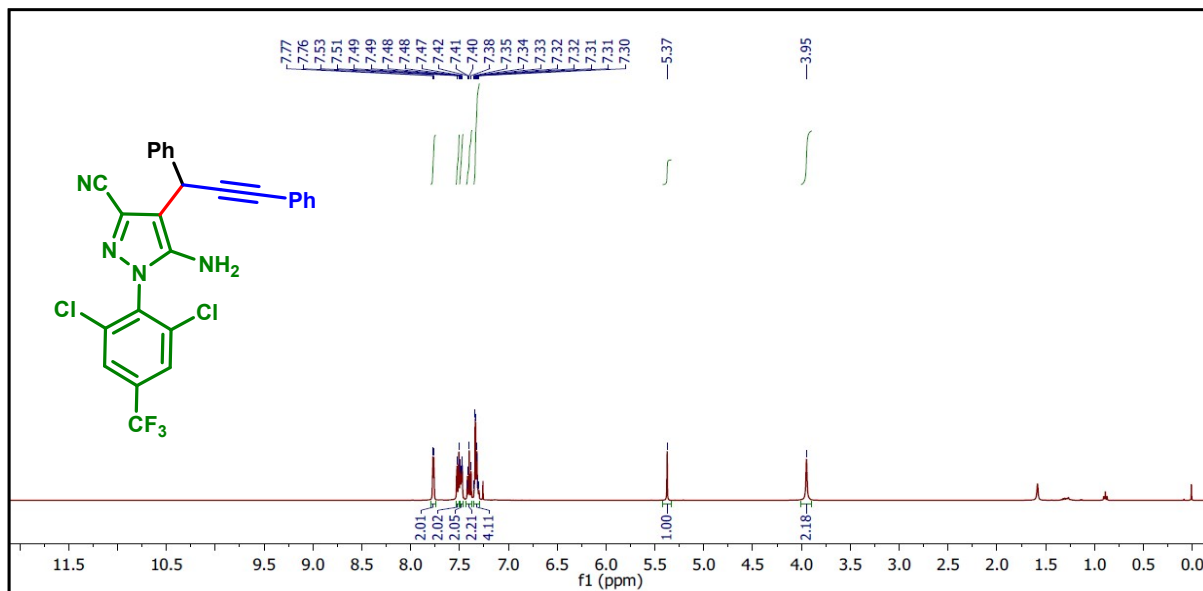
[M+H]⁺, HRMS (ESI) Anal. calcd. for C₃₃H₂₂Cl₂F₃N₄ m/z 601.1168 [M+H]⁺, found 601.1143.



5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(1,3-diphenylprop-2-yn-1-yl)-1H-pyrazole-3-carbonitrile (6a)

Isolated as a yellow solid, yield 80% (393 mg), m.p 189-191 °C, IR (ATR): 3339, 3073, 2241, 1623, 1572, 1492, 1388, 1315, 1142, 818, 755 cm⁻¹, ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 3.1 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.42-7.38 (m, 2H), 7.35 – 7.30 (m, 4H), 5.37 (s, 1H), 3.95 (s, 2H) ppm, ¹³C NMR (100 MHz, CDCl₃) δ 144.44, 138.87, 136.56, 135.53, 134.49 (q, *J* = 34.47 Hz), 131.77, 129.08, 128.70, 128.47, 127.74, 127.21,

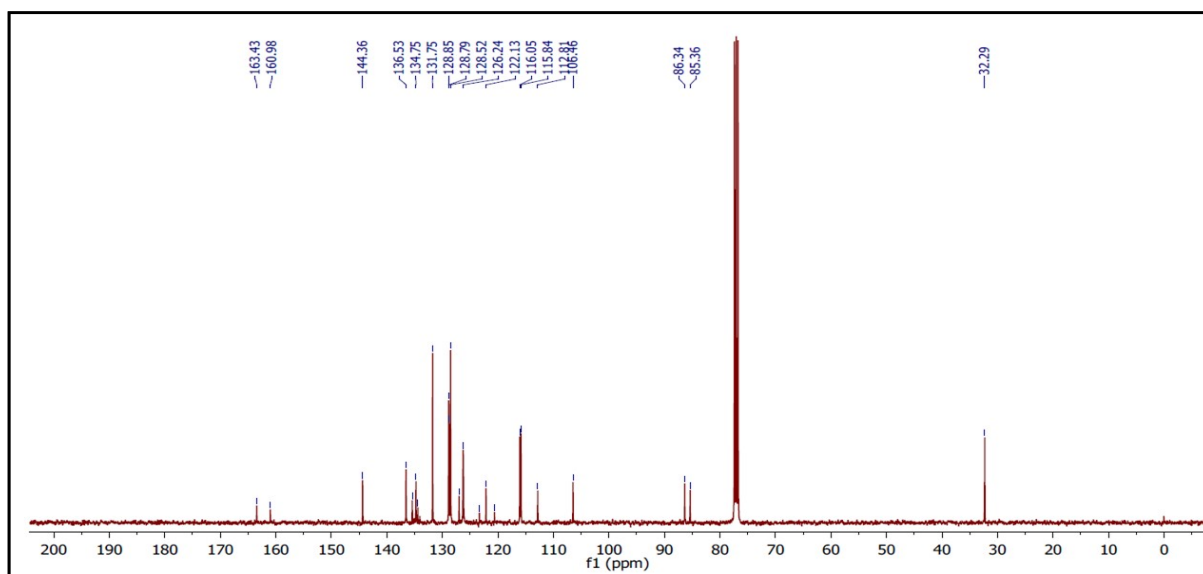
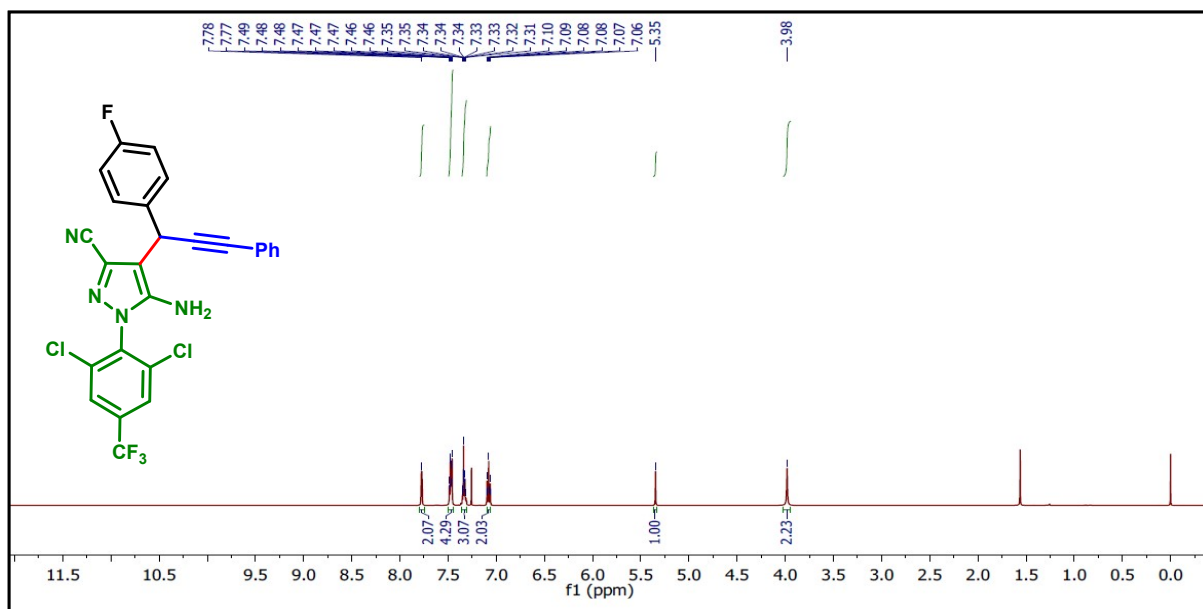
127.10, 126.21, 122.37, 121.62 (d, $J = 273.62$ Hz), 112.90, 106.74, 86.61, 85.17, 32.95 ppm, ESI-MS: m/z 511 $[M+H]^+$, HRMS (ESI) Anal. calcd. for $C_{26}H_{16}Cl_2F_3N_4$ m/z 511.0698 $[M+H]^+$, found 511.0682.



5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl)-1H-pyrazole-3-carbonitrile (6b)

Isolated as a yellow solid, yield 89% (416 mg), m.p 203-205 °C, IR (ATR): 3339, 3078, 2241, 1624, 1620, 1506, 1387, 1317, 1175, 1143, 816, 757 cm^{-1} , 1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, $J = 2.8$ Hz, 2H), 7.49-7.46 (m, 4H), 7.36 – 7.31 (m, 3H), 7.10 – 7.06 (m, 2H), 5.35 (s, 1H), 3.98 (s, 2H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.43, 160.98, 144.36, 136.53,

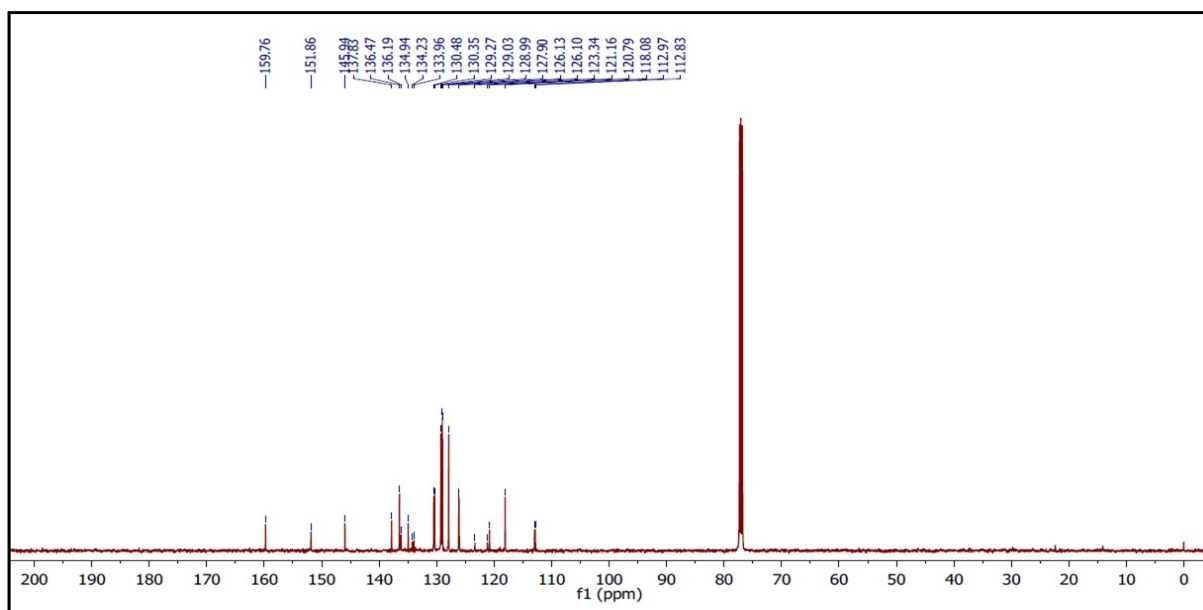
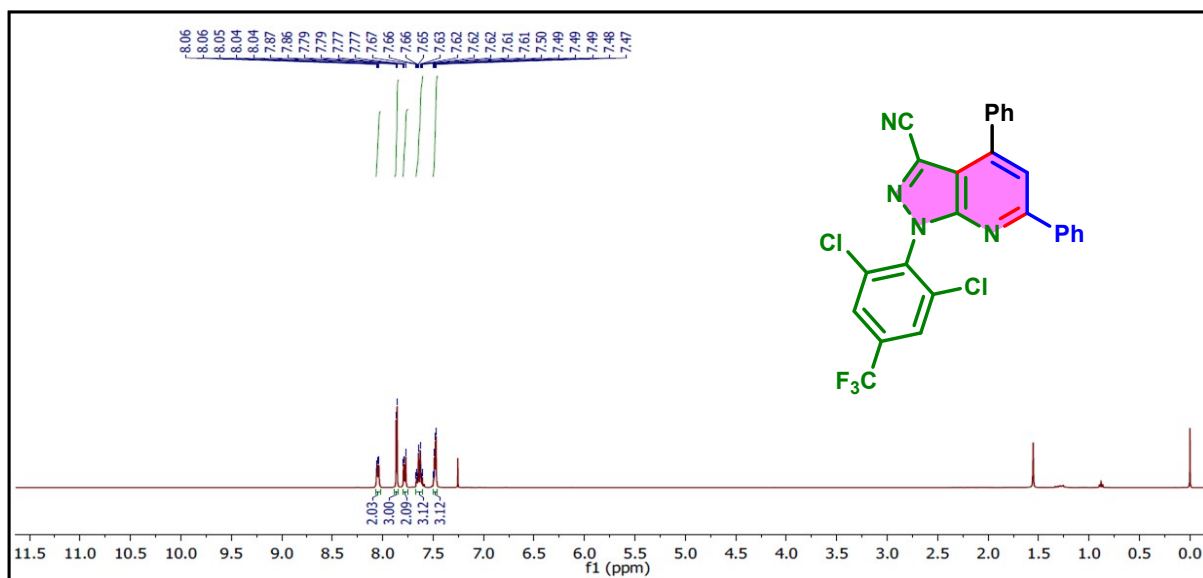
135.42, 134.49 (q, $J = 34.84$ Hz), 131.75, 128.85, 128.79, 128.52, 126.99, 126.24, 122.13, 121.62 (d, $J = 273.99$ Hz), 116.05, 115.84, 112.81, 106.46, 86.34, 85.36, 32.29 ppm, ESI-MS: m/z 529 $[M+H]^+$, HRMS (ESI) Anal. calcd. for $C_{26}H_{15}Cl_2F_4N_4$ m/z 529.0604 $[M+H]^+$, found 529.0588.



1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4,6-diphenyl-1*H*-pyrazolo[3,4-*b*]pyridine-3-carbonitrile (7a)

Isolated as a cream solid, yield 93% (455 mg), m.p 149-151 °C, IR (ATR): 3066, 2241, 1567, 1317, 1179, 1142, 878, 758 cm^{-1} , 1H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H), 7.86 (d, $J = 4.1$ Hz, 3H), 7.78 (m, 2H), 7.67 – 7.60 (m, 3H), 7.50 – 7.46 (m, 3H) ppm, ^{13}C NMR (125

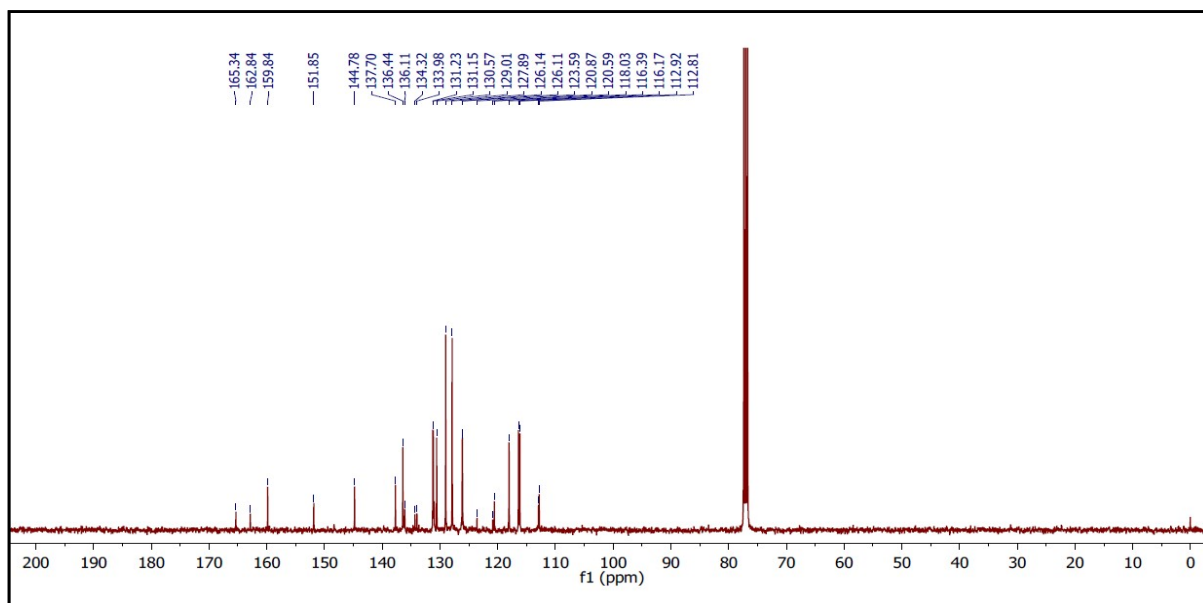
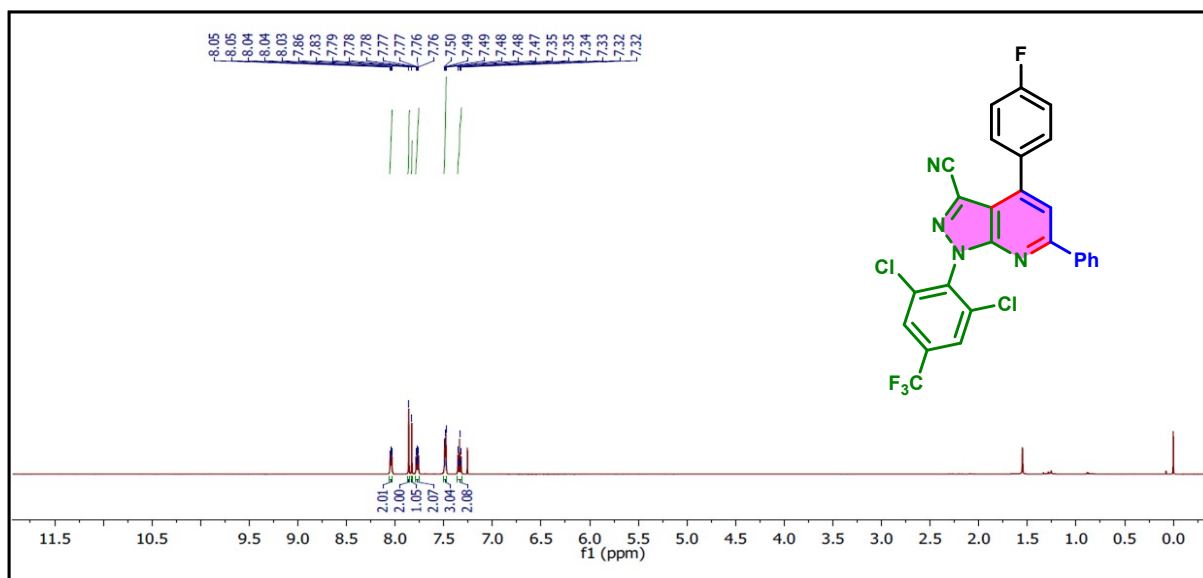
MHz, CDCl₃) δ 159.76, 151.86, 145.94, 137.83, 136.47, 136.19, 134.94, 134.09 (d, *J* = 34.3 Hz), 130.48, 130.35, 129.27, 129.03, 128.99, 127.90, 126.13, 126.10, 122.25 (q, *J* = 273.6 Hz), 120.79, 118.08, 112.97, 112.83 ppm, ESI-MS: *m/z* 509 [M+H]⁺, HRMS (ESI) Anal. calcd. for C₂₆H₁₄Cl₂F₃N₄ *m/z* 509.0542 [M+H]⁺, found 509.0524.



1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(4-fluorophenyl)-6-phenyl-1H-pyrazolo[3,4-*b*]pyridine-3-carbonitrile (7b)

Isolated as a colourless solid, yield 90% (419 mg), m.p 158-160 °C, IR (ATR): 3052, 2241, 1528, 1372, 1305, 1205, 1123, 806, 772 cm⁻¹, ¹H NMR (500 MHz, CDCl₃) δ 8.06 – 8.03 (m, 2H), 7.86 (s, 2H), 7.83 (s, 1H), 7.79 – 7.75 (m, 2H), 7.50 – 7.47 (m, 3H), 7.36 – 7.32 (m, 2H) ppm, ¹³C NMR (100 MHz, CDCl₃) δ 164.09 (d, *J* = 251.0 Hz), 159.84, 151.85, 144.78,

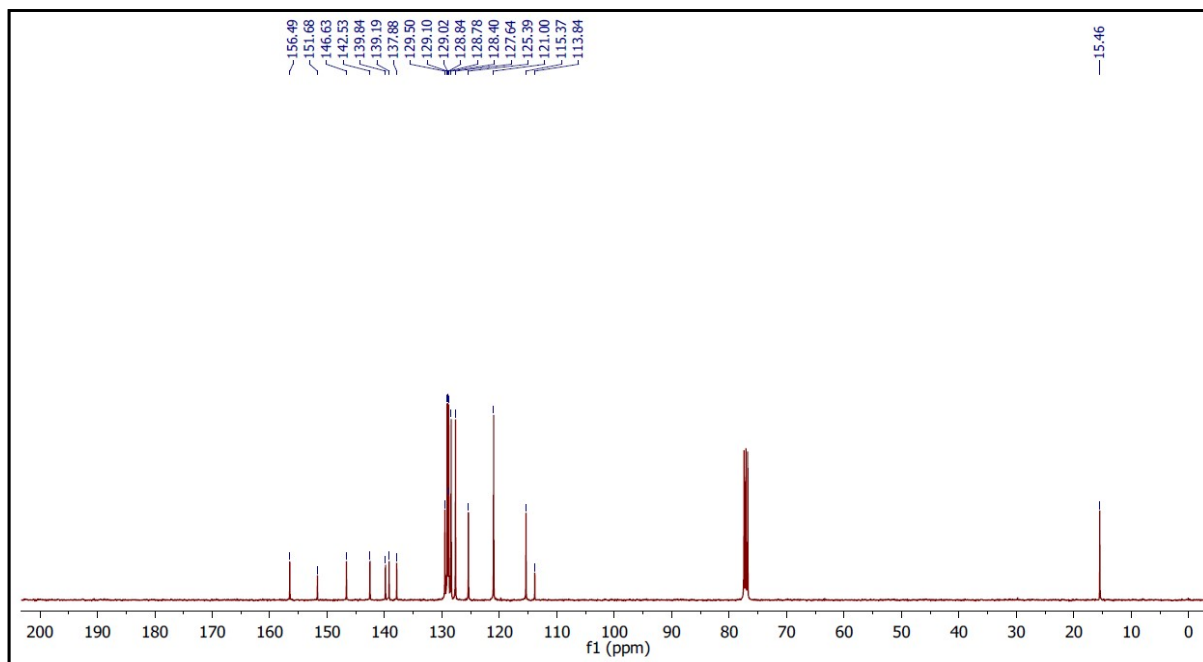
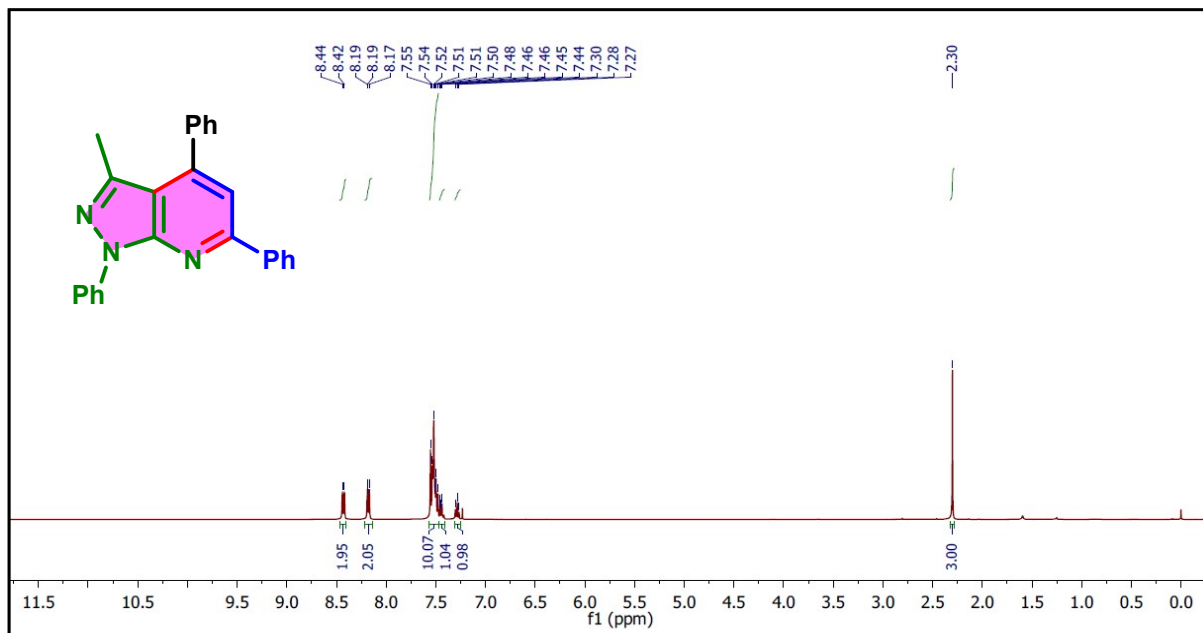
137.70, 136.44, 136.11, 134.15 (d, $J = 34.6$ Hz), 131.23, 131.15, 130.57, 129.01, 127.89, 126.14, 126.11, 122.23 (q, $J = 273.8$ Hz), 120.59, 118.03, 116.39, 116.17, 112.92, 112.81 ppm, ESI-MS: m/z 527 $[M+H]^+$, HRMS (ESI) Anal. calcd. for $C_{26}H_{13}Cl_2F_4N_4$ m/z 527.0447 $[M+H]^+$, found 527.0427.



3-methyl-1,4,6-triphenyl-1H-pyrazolo[3,4-b]pyridine (7c)

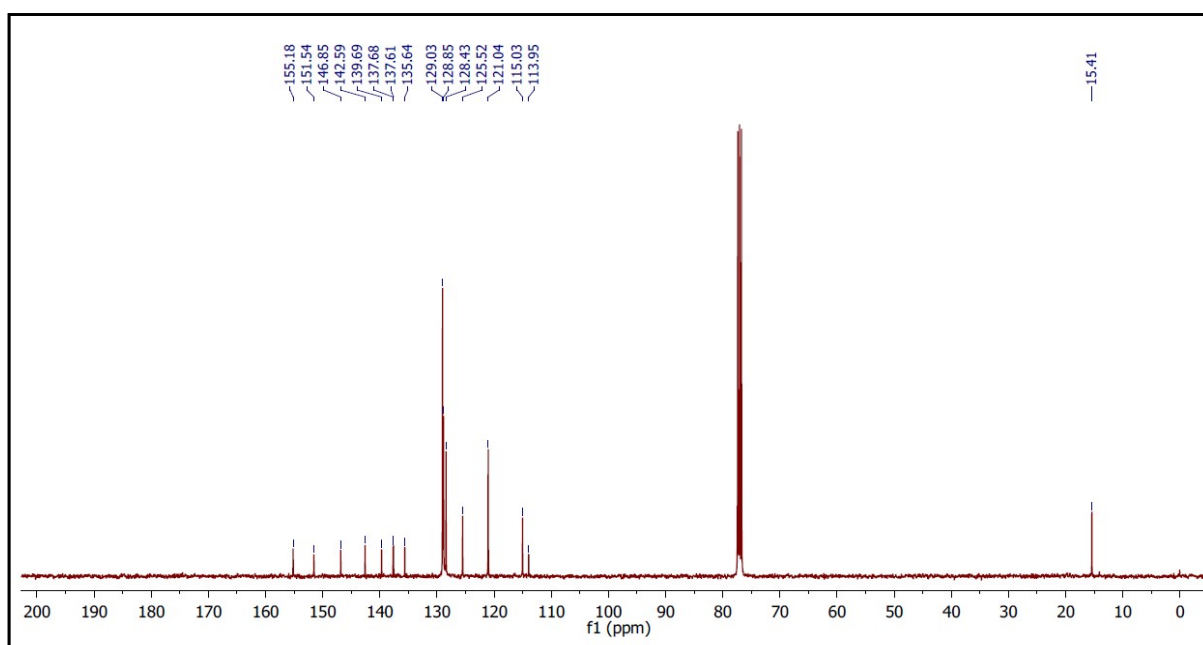
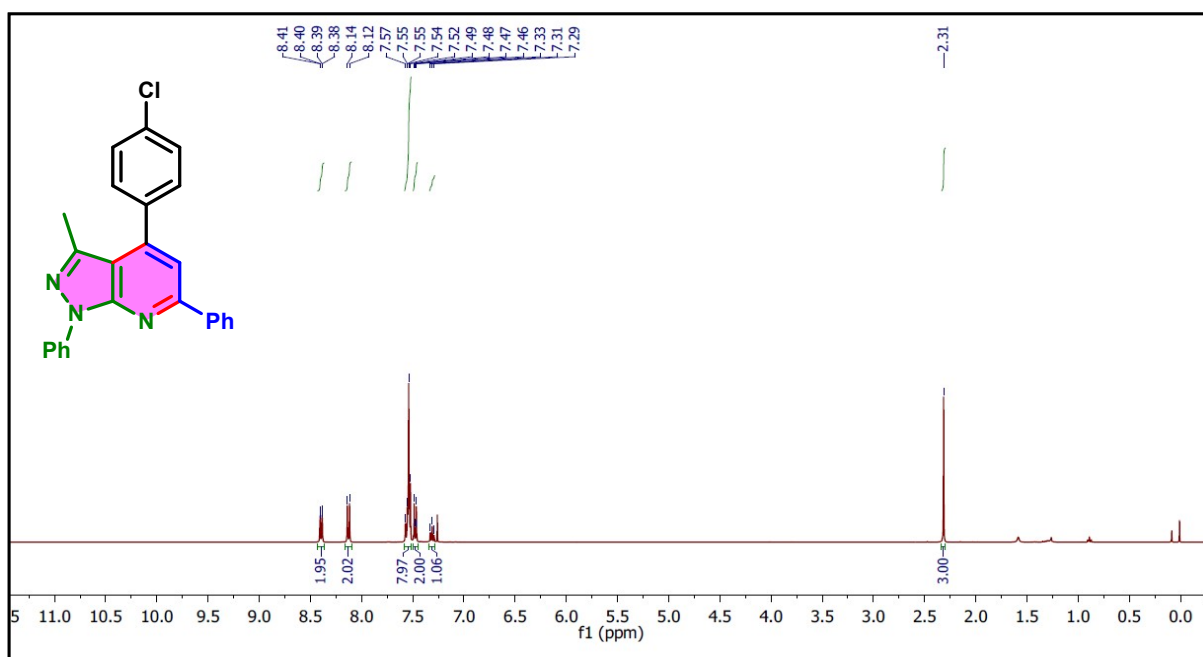
Isolated as a light yellow solid, yield 92% (319 mg), m.p 190-192 °C, IR (ATR): 3023, 2873, 1689, 1657, 1492, 1385, 1218, 1147, 871, 752 cm^{-1} , 1H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, $J = 7.7$ Hz, 2H), 8.22 – 8.14 (m, 2H), 7.56 – 7.47 (m, 10H), 7.46-7.44 (m, 1H), 7.28 (t, $J = 7.4$ Hz, 1H), 2.30 (s, 3H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.49, 151.68, 146.63, 142.53,

139.84, 139.19, 137.88, 129.50, 129.10, 129.02, 128.84, 128.78, 128.40, 127.64, 125.39, 121.00, 115.37, 113.84, 15.46 ppm, ESI-MS: m/z 362 $[M+H]^+$, HRMS (ESI) Anal. calcd. for $C_{25}H_{20}N_3$ m/z 362.1651 $[M+H]^+$, found 362.1646.



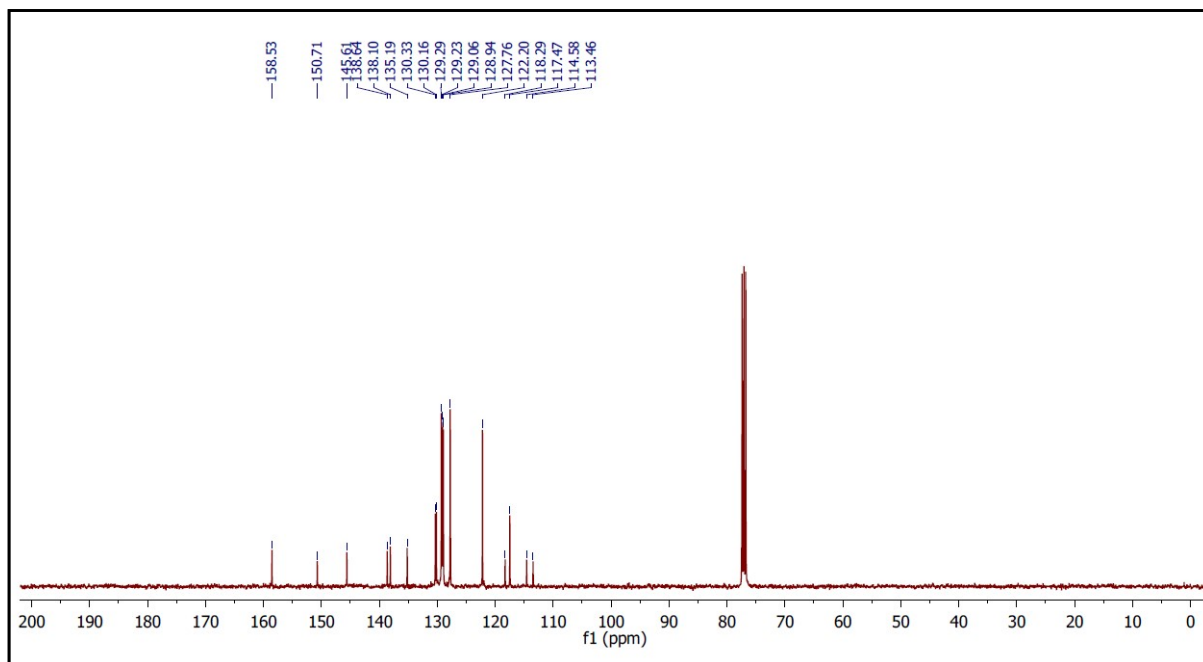
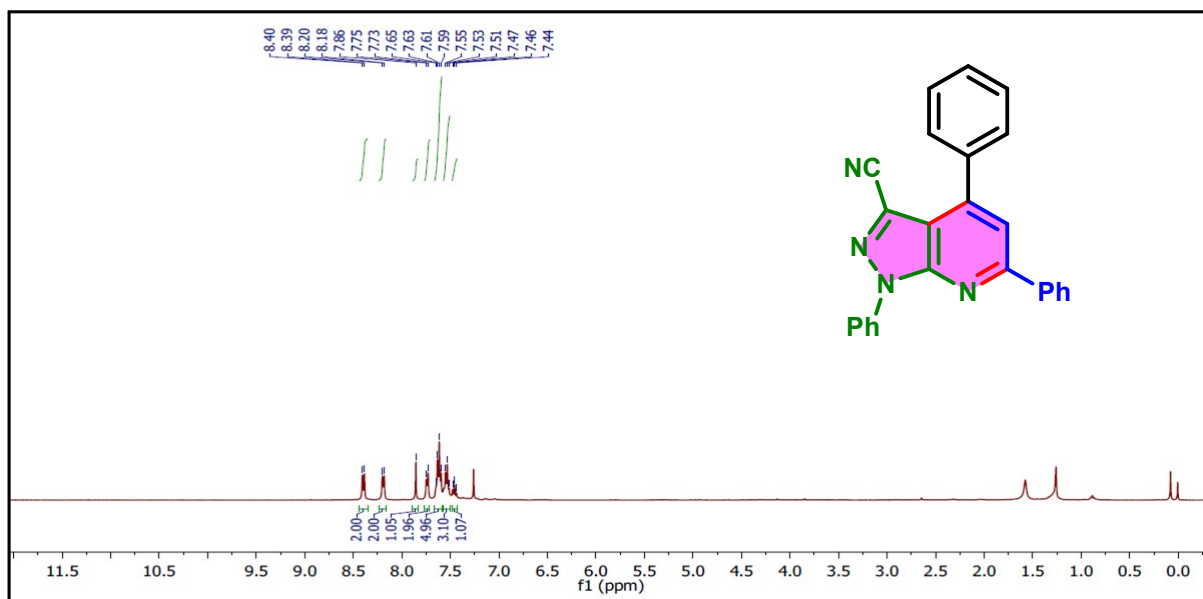
4-(4-chlorophenyl)-3-methyl-1,6-diphenyl-1*H*-pyrazolo[3,4-*b*]pyridine (7d)

Isolated as a colourless solid, yield 87% (284 mg), m.p 212-214 °C, IR (ATR): 3032, 2912, 1652, 1625, 1523, 1402, 1283, 1123, 932, 782 cm⁻¹, ¹H NMR (400 MHz, CDCl₃) δ 8.40 (m, 2H), 8.13 (d, *J* = 8.6 Hz, 2H), 7.58 – 7.51 (m, 8H), 7.50 – 7.45 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 2.31 (s, 3H) ppm, ¹³C NMR (100 MHz, CDCl₃) δ 155.18, 151.54, 146.85, 142.59, 139.69, 137.68, 137.61, 135.64, 129.03, 128.85, 128.43, 125.52, 121.04, 115.03, 113.95, 15.41 ppm, ESI-MS: *m/z* 396 [M+H]⁺, HRMS (ESI) Anal. calcd. for C₂₅H₁₉ClN₃ *m/z* 396.1262 [M+H]⁺, found 396.1252.



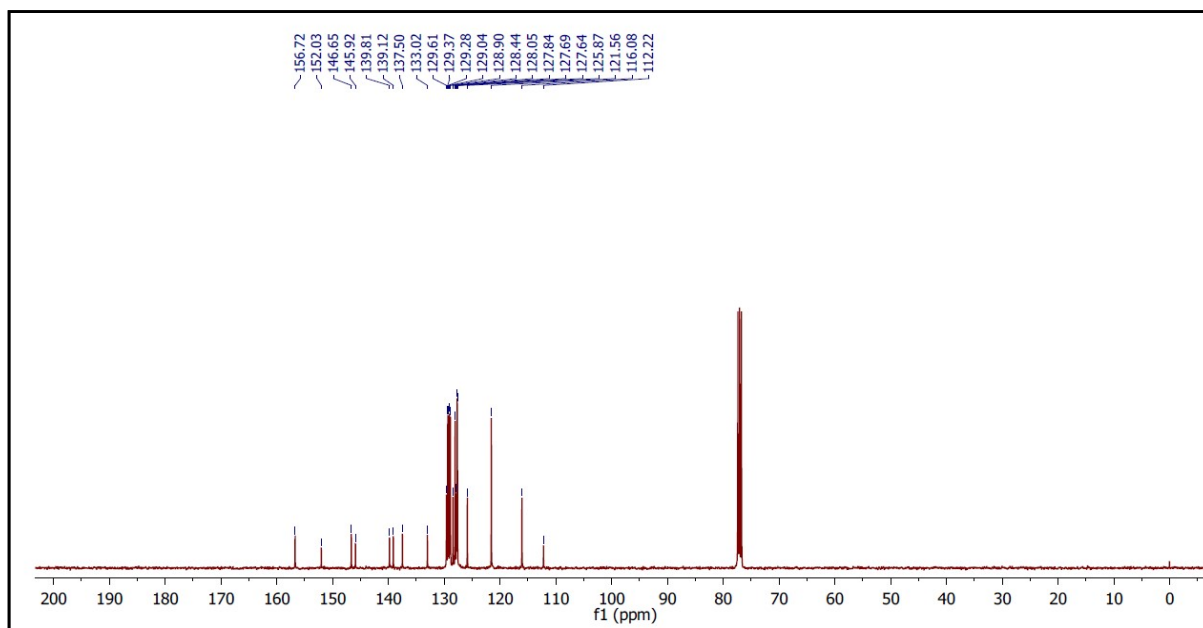
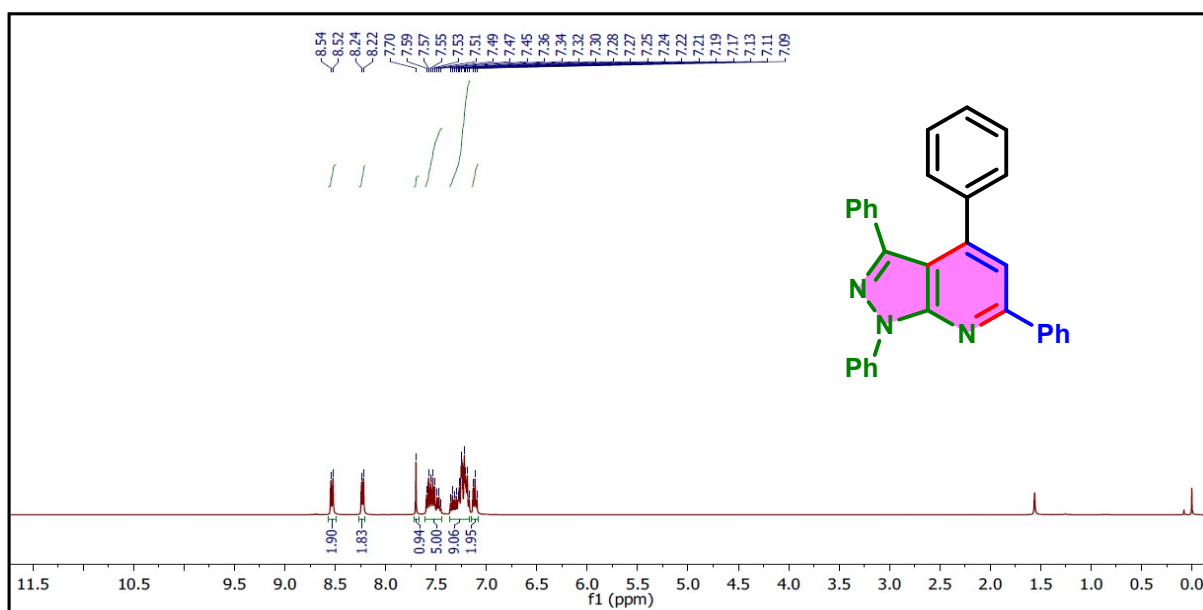
1,4,6-triphenyl-1*H*-pyrazolo[3,4-*b*]pyridine-3-carbonitrile (7e)

Isolated as a brown solid, yield 85% (304 mg), m.p 207-209 °C, IR (ATR): 3058, 3027, 2924, 1954, 1602, 1548, 1493, 1447, 1236, 1176, 915, 756, 698 cm⁻¹, ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 7.8 Hz, 2H), 8.19 (d, *J* = 6.5 Hz, 2H), 7.86 (s, 1H), 7.74 (d, *J* = 6.4 Hz, 2H), 7.65-7.59 (m, 5H), 7.53 (t, *J* = 7.4 Hz, 3H), 7.46 (t, *J* = 7.4 Hz, 1H) ppm, ¹³C NMR (100 MHz, CDCl₃) δ 158.53, 150.71, 145.61, 138.64, 138.10, 135.19, 130.33, 130.16, 129.29, 129.23, 129.06, 128.94, 127.76, 122.20, 118.29, 117.47, 114.58, 113.46 ppm, ESI-MS: *m/z* 373 [M+H]⁺, HRMS (ESI) Anal. calcd. for C₂₅H₁₇N₄ *m/z* 373.1447 [M+H]⁺, found 373.1439.



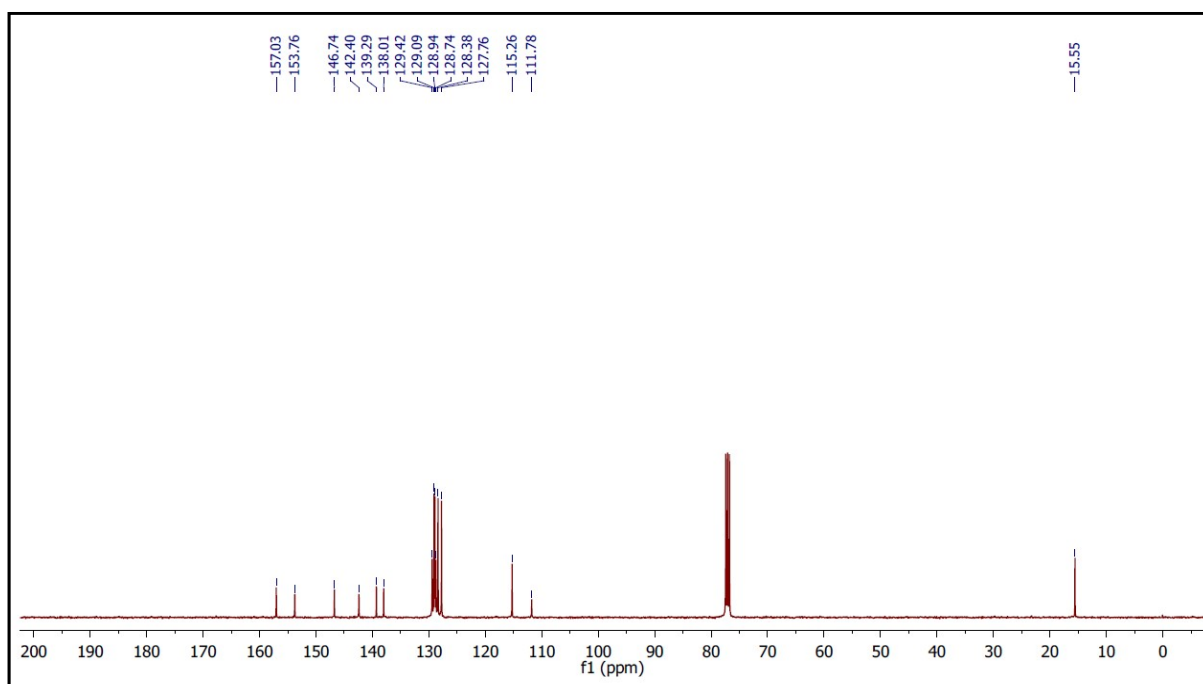
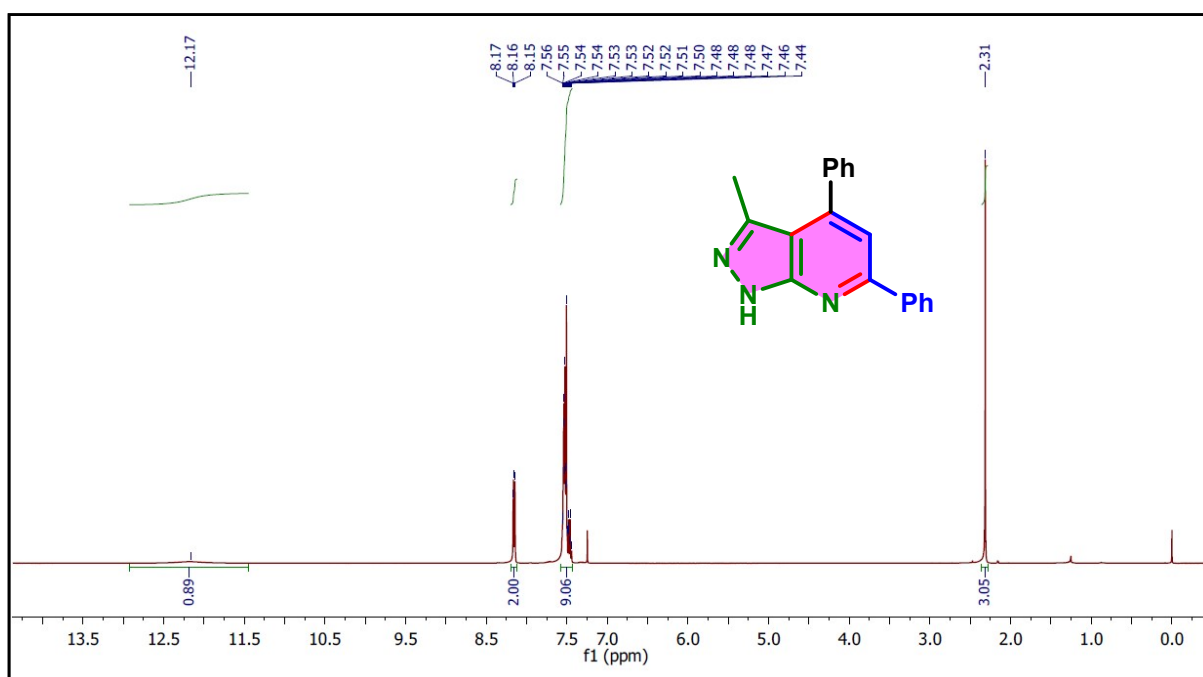
1,3,4,6-tetraphenyl-1*H*-pyrazolo[3,4-*b*]pyridine (7f)

Isolated as a light yellow solid, yield 82% (333 mg), m.p 206-208 °C, IR (ATR): 3227, 3055, 2957, 2869, 1635, 1589, 1483, 1272, 1157, 926, 756 cm⁻¹, ¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, *J* = 7.8 Hz, 2H), 8.23 (d, *J* = 7.2 Hz, 2H), 7.70 (s, 1H), 7.70-7.45 (m, 5H), 7.36 – 7.16 (m, 9H), 7.11 (t, *J* = 7.5 Hz, 2H) ppm, ¹³C NMR (100 MHz, CDCl₃) δ 156.72, 152.03, 146.65, 145.92, 139.81, 139.12, 137.50, 133.02, 129.61, 129.37, 129.28, 129.04, 128.90, 128.44, 128.05, 127.84, 127.69, 127.64, 125.87, 121.56, 116.08, 112.22 ppm, ESI-MS: *m/z* 424 [M+H]⁺, HRMS (ESI) Anal. calcd. for C₃₀H₂₂N₃ *m/z* 424.1808 [M+H]⁺, found 424.1801.



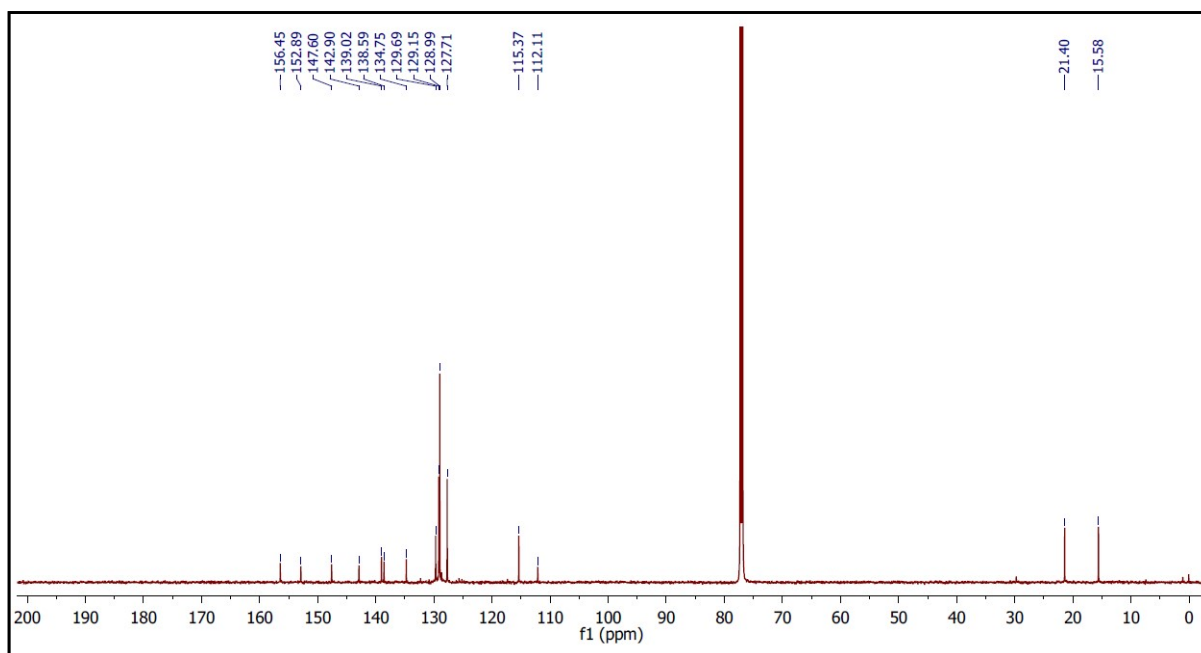
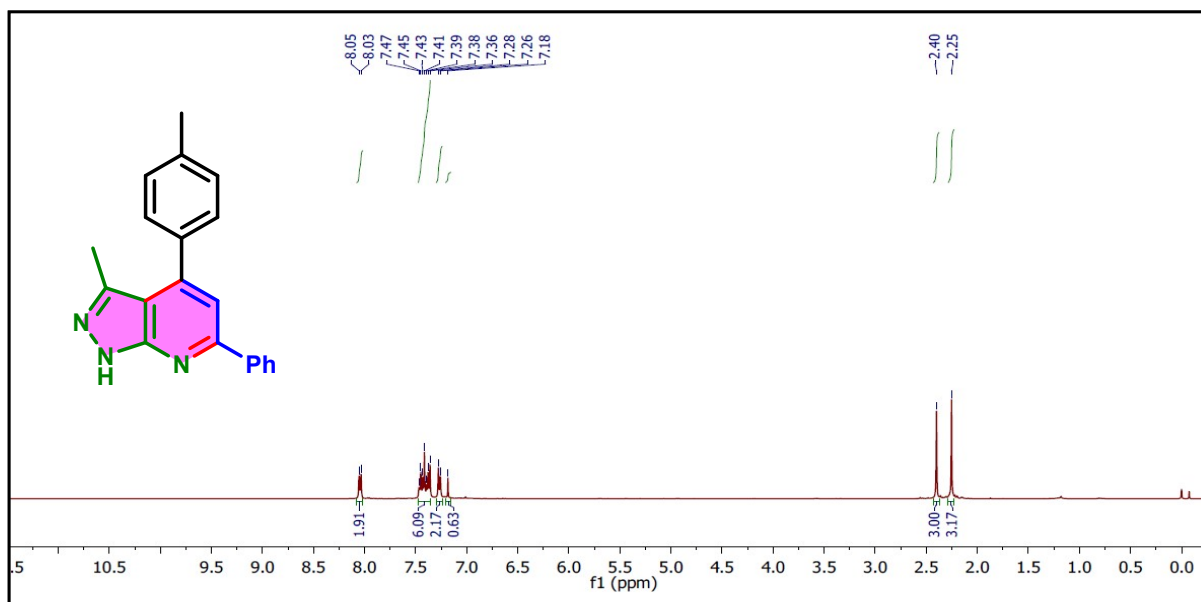
3-methyl-4,6-diphenyl-1H-pyrazolo[3,4-b]pyridine (7g)

Isolated as a light yellow solid, yield 36% (98 mg), m.p 198-200 °C, IR (ATR): 3107, 3023, 2932, 2035, 1683, 1567, 1438, 1302, 1232, 976, 857 cm^{-1} , ^1H NMR (400 MHz, CDCl_3) δ 12.17 (br (NH), 1H), 8.20 – 8.12 (m, 2H), 7.58 – 7.43 (m, 9H), 2.31 (s, 3H) ppm, ^{13}C NMR (100 MHz, CDCl_3) δ 157.03, 153.76, 146.74, 142.40, 139.29, 138.01, 129.42, 129.09, 128.94, 128.74, 128.38, 127.76, 115.26, 111.78, 15.55 ppm, ESI-MS: m/z 286 $[\text{M}+\text{H}]^+$, HRMS (ESI) Anal. calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_3$ m/z 286.1338 $[\text{M}+\text{H}]^+$, found 286.1335.



3-methyl-6-phenyl-4-(*p*-tolyl)-1*H*-pyrazolo[3,4-*b*]pyridine (7h)

Isolated as a light yellow solid, yield 42% (113 mg), m.p 185-187 °C, IR (ATR): 3135, 3005, 2952, 2011, 1632, 1522, 1467, 1295, 1202, 1023, 962, 878 cm⁻¹, ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.36 (m, 6H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.18 (br (NH), 1H), 2.40 (s, 3H), 2.25 (s, 3H) ppm, ¹³C NMR (125 MHz, CDCl₃) δ 156.45, 152.89, 147.60, 142.90, 139.02, 138.59, 134.75, 129.69, 129.15, 128.99, 127.71, 115.37, 112.11, 21.40, 15.58 ppm, ESI-MS: *m/z* 300 [M+H]⁺, HRMS (ESI) Anal. calcd. for C₂₀H₁₈N₃ *m/z* 300.1491 [M+H]⁺, found 300.1495.



1,4,6-triphenyl-1*H*-pyrazolo[3,4-*b*]pyridine (7i)

Isolated as a white solid, yield 82% (273 mg), m.p 158-160 °C, IR (ATR): 3140, 3012, 2930, 2023, 1643, 1563, 1432, 1284, 1212, 1062, 973, 867 cm⁻¹, ¹H NMR (400 MHz, CDCl₃): δ 8.45 (d, *J* = 7.8 Hz, 2H), 8.31 (s, 1H), 8.20 (d, *J* = 7.1 Hz, 2H), 7.84 – 7.75 (m, 3H), 7.61 – 7.44 (m, 8H), 7.33 (t, *J* = 7.4 Hz, 1H) ppm, ¹³C NMR (125 MHz, CDCl₃): δ 157.27, 151.24, 144.80, 139.86, 139.30, 137.60, 133.48, 129.59, 129.49, 129.31, 129.09, 128.89, 128.50, 127.70, 125.92, 121.27, 114.64, 113.98 ppm, ESI-MS: *m/z* 348 [M+H]⁺, HRMS (ESI) Anal. calcd. for C₂₄H₁₇N₃ *m/z* 348.1506 [M+H]⁺, found 348.1485.

