Ru-Catalyzed highly site-selective C-H bond arylation of 9-(pyrimidin-2-yl)-9H-carbazole

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Contents

General Information:

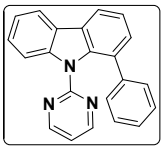
^{1}H NMR and ^{13}C NMR (Avance 300, Innova 400 MHz and Brucker Gemini 200 MHz) spectra were recorded in $CDCl_3$. Chemical shifts (δ) were reported in ppm, and spin-spin coupling constants (*J*) were in Hz. Melting points were determined on a Fischer-Johns melting point apparatus. IR and MS were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer and Finnegan MAT 1020 mass spectrometer operating at 70 eV.

General Procedure for Synthesis of and 9(Pyrimidin-2-yl)-9*H*-carbazole:[1]

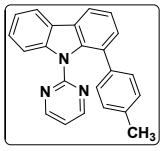
NaH (60% dispersion in mineral oil, 440 mg, 11.0 mmol) was added in portions at 0 ^{O}C to a stirred solution of carbazole (1.67 g, 10.0 mmol) in DMF (25mL). After stirring for 30 min at 0 ^{O}C, 2-chloropyrimidine (1.37 g, 12.0 mmol) was added and the mixture was stirred at 130 ^{O}C for 24 h. Then, the reaction mixture was cooled to ambient temperature, poured into H_2O (300 mL) and extracted with EtOAc (4 × 75 mL). The combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product which was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 4/1).

General Experimental Procedure for the synthesis of 1-phenyl-9-(pyrimidin-2-yl)-9H-carbazole: To a mixture of 9-(pyrimidin-2-yl)-9H-carbazole (0.25 mmol), phenylboronic acid (0.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol%), Ag_2O (1.0 mmol) and $AgSbF_6$ (20 mol%), THF(2ml) was added and Thereafter, the reaction mixture was stirred at 120 ^{o}C for 12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. The solvent was evaporated under vacuum to give the crude product was purified by column chromatography on silica gel. The purity of the product was confirmed by ^{1}H NMR, ^{13}C NMR and mass spectra.

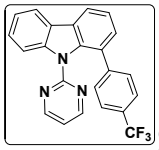
Spectroscopic Data:



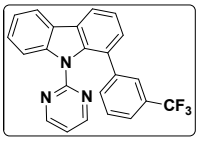
1-phenyl-9-(pyrimidin-2-yl)-9H-carbazole: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, J = 4.8 Hz, 2H), 8.12 (dd, J = 8.5, 3.4 Hz, 3H), 7.51 – 7.22 (m, 6H), 7.14 – 7.02 (m, 3H), 6.82 (t, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.1, 140.7, 128.5, 127.9, 127.4, 126.6, 125.9, 122.2, 121.8, 119.9, 119.1, 116.8, 112.0; ESI- MS: *m/z* 322[M+1].



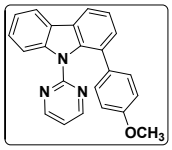
9-(pyrimidin-2-yl)-1-(p-tolyl)-9H-carbazole: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, *J* = 4.7Hz, 2H), 8.13-8.07 (m, 3H), 7.47-7.41 (m, 3H), 7.37-7.34 (m, 1H), 7.15-7.12 (m, 2H), 6.91 (d, *J* = 7.7 Hz, 2H), 6.82 (t, *J* = 4.7 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 157.1, 140.7, 138.2, 135.6, 128.5, 128.4, 127.3, 126.5, 125.0, 122.1, 121.8, 119.9, 118.8, 116.6, 112.0, 20.9; ESI- MS: *m/z* 336[M+1].



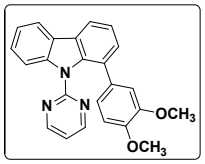
9-(pyrimidin-2-yl)-1-(4-(trifluoromethyl)phenyl)-9H-carbazole: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31(d, *J* = 4.7Hz, 2H), 8.17 - 8.12 (m, 3H), 7.51 - 7.43 (m, 3H), 7.41 - 7.32 (m, 5H), 6.84 (t, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.3, 140.6, 128.2, 127.7, 126.8, 124.7, 124.6, 122.2, 122.1, 120.0, 119.9, 117.0, 112.1; ESI- MS: *m/z* 390[M+1].



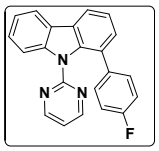
9-(pyrimidin-2-yl)-1-(3-(trifluoromethyl)phenyl)-9H-carbazole:^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, *J* = 4.8 Hz, 2H), 8.16 - 8.12 (m, 3H), 7.52 - 7.45 (m, 5H), 7.40 - 7.33 (m, 2H), 7.26 - 7.23 (m, 1H), 6.82 (t, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 142.2, 140.7, 136.5, 130.8, 130.1 , 128.5, 126.9, 126.7, 124.8, 124.3, 122.8, 122.1, 120.0, 117.1, 112.2; ESI- MS: *m/z* 390[M+1].



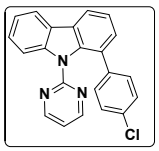
1-(4-methoxyphenyl)-9-(pyrimidin-2-yl)-9H-carbazole:^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 – 8.33 (m, 2H), 8.10 (ddd, *J* = 8.7, 6.7, 3.4 Hz, 3H), 7.49 – 7.41 (m, 3H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.21 – 7.14 (m, 2H), 6.87 (t, *J* = 4.8 Hz, 1H), 6.65 (dd, *J* = 8.5, 1.7 Hz, 2H), 3.75 (s,3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 157.48, 157.1, 141.3, 137.0, 133.8, 128.4, 128.0, 126.8, 126.6, 125.0, 122.2, 121.9, 120.0, 118.7, 116.8, 116.5, 113.4, 112.0, 55.3; ESI-MS: *m/z* 352[M+1].



1-(3,4-dimethoxyphenyl)-9-(pyrimidin-2-yl)-9H-carbazole:^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.8 Hz, 2H), 8.10 (t, *J* = 7.7 Hz, 3H), 7.53 – 7.28 (m, 4H), 6.86 (dt, *J* = 10.3, 3.3 Hz, 2H), 6.74 (d, *J* = 1.5 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 157.2, 148.3, 147.4, 140.8, 136.9, 134.1, 128.4, 128.0, 126.7, 124.9, 122.2, 121.9, 120.0, 118.9, 117.1, 112.0, 111.0, 110.6, 56.0, 55.6; ESI-MS: *m/z* 382 [M+1].

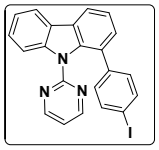


1-(4-fluorophenyl)-9-(pyrimidin-2-yl)-9H-carbazole:^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, *J* = 4.8Hz, 2H), 8.13 - 8.09 (m, 3H), 7.47 - 7.40 (m, 3H), 7.38 - 7.35 (m, 1H), 7.27 - 7.19(m, 2H), 6.88(t, *J* = 4.8Hz, 1H), 6.82 - 6.78 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ157.2, 140.7, 137.3, 129.0, 128.4, 126.7, 124.9, 122.0, 120.0, 119.2, 117.0, 114.6, 112.1; ESI- MS: *m/z* 340[M+1].

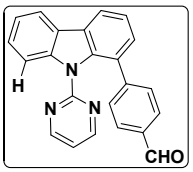


1-(4-chlorophenyl)-9-(pyrimidin-2-yl)-9H-carbazole: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37(d, *J* = 4.8Hz, 2H), 8.14 - 8.09 (m, 3H), 7.48 - 7.41 (m, 3H), 7.39 - 7.35 (m, 1H), 7.22 - 7.19 (m, 2H), 6.94 - 6.90 (m, 2H), 6.88 - 6.85 (m,1H); ^{13}C NMR (75 MHz, $CDCl_3$):

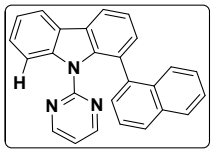
δ157.3, 156.6, 129.5, 129.1, 128.7, 128.2, 128.0, 127.5, 127.0, 126.7, 122.2, 120.7, 120.0, 119.6, 119.4, 117.0, 112.1; ESI- MS: *m/z* 356 [M+1].



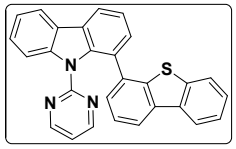
1-(4-iodophenyl)-9-(pyrimidin-2-yl)-9H-carbazole: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36(d, *J* = 4.8Hz, 2H), 8.13 - 8.09 (m, 3H), 7.48 - 7.40 (m, 4H), 7.39 - 7.35 (m, 1H), 7.29 - 7.26 (m,1H), 7.03 - 7.00 (m, 2H), 6.93 (t, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.3, 136.9, 130.2, 129.4, 128.1, 126.7,122.2, 120.0, 119.5, 117.0, 112.0; ESI- MS: *m/z* 448[M+1].



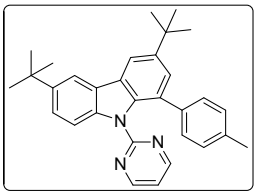
4-(9-(pyrimidin-2-yl)-9H-carbazol-1-yl)benzaldehyde:^{1}H NMR (300 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.30 - 8.29 (m, 2H), 8.17 - 8.13 (m, 3H), 7.63 (t, *J* = 6.5 Hz, 2H), 7.56 - 7.30 (m,6H), 6.80 - 6.79 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.8, 157.3, 140.6, 133.9, 129.3, 128.2, 127.9, 126.9, 124.8, 122.2, 120.0, 117.0, 112.2; ESI- MS: *m/z* 350[M+1].



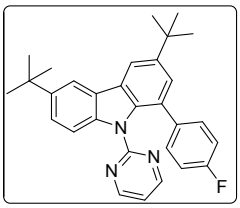
1-(naphthalen-1-yl)-9-(pyrimidin-2-yl)-9H-carbazole: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 -8.15 (m, 2H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 4.9 Hz, 2H), 7.72 - 7.20 (m, 11H), 6.49 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 129.7, 127.4, 126.9, 126.4, 125.9, 125.5, 125.2, 121.6, 119.9, 119.9, 116.5, 111.7; ESI- MS: *m/z* 372[M+1].



1-(dibenzo[b,d]thiophen-4-yl)-9-(pyrimidin-2-yl)-9H-carbazole: ^{1}HNMR (300 MHz, $CDCl_3$): δ 8.26 - 8.04 (m, 4H), 7.96 (d, *J* = 4.9 Hz, 2H), 7.89 (t, *J* = 4.5 Hz, 1H), 7.82 - 7.70 (m, 2H), 7.53 - 7.31 (m, 5H), 7.13 (d, *J* = 4.3 Hz, 2H), 6.57 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 156.6, 140.5, 136.2, 127.9, 126.7, 126.3, 126.6, 124.8, 124.2, 122.8, 121.9, 121.4, 120.0, 119.4, 116.6, 112.1; ESI- MS: *m/z* 428[M+1].



3,6-di-tert-butyl-9-(pyrimidin-2-yl)-1-(p-tolyl)-9H-carbazole: ^{1}HNMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 4.8 Hz, 2H), 8.12 – 8.04 (m, 3H), 7.54 – 7.45 (m, 2H), 7.28 – 7.13 (m, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.76 (t, *J* = 4.8 Hz, 1H), 2.26 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.0, 145.2, 144.9, 139.0, 135.5, 128.6, 127.7, 127.3, 127.0, 126.3, 125.2, 124.2, 116.2, 116.0, 115.0, 111.9, 34.8, 31.9, 21.0; ESI- MS: *m/z* 448 [M+1].



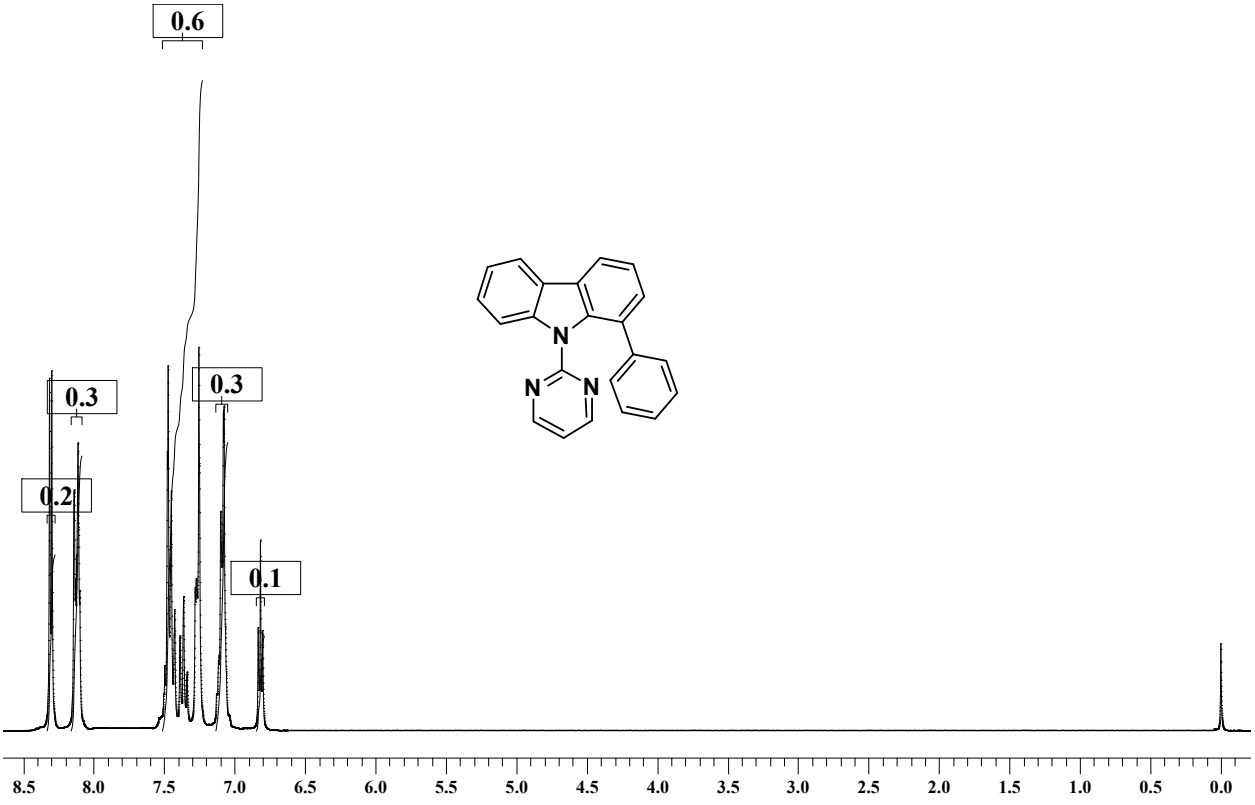
3,6-di-tert-butyl-1-(4-fluorophenyl)-9-(pyrimidin-2-yl)-9H-carbazole: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J* = 1.7 Hz, 1H), 7.89 (d, *J* = 4.8 Hz, 1H), 7.42 – 7.23 (m, 3H), 6.92 (dd, *J* = 8.5, 5.6 Hz, 3H), 6.66 (t, *J* = 8.7 Hz, 4H), 1.52 (d, *J* = 29.8 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.2, 160.1, 158.0 , 156.5, 143.6, 136.8, 136.0, 129.9, 127.1, 124.9, 117.8, 115.5, 114.4, 114.2, 34.7, 31.9; ESI-MS: *m/z* 452[M+1].

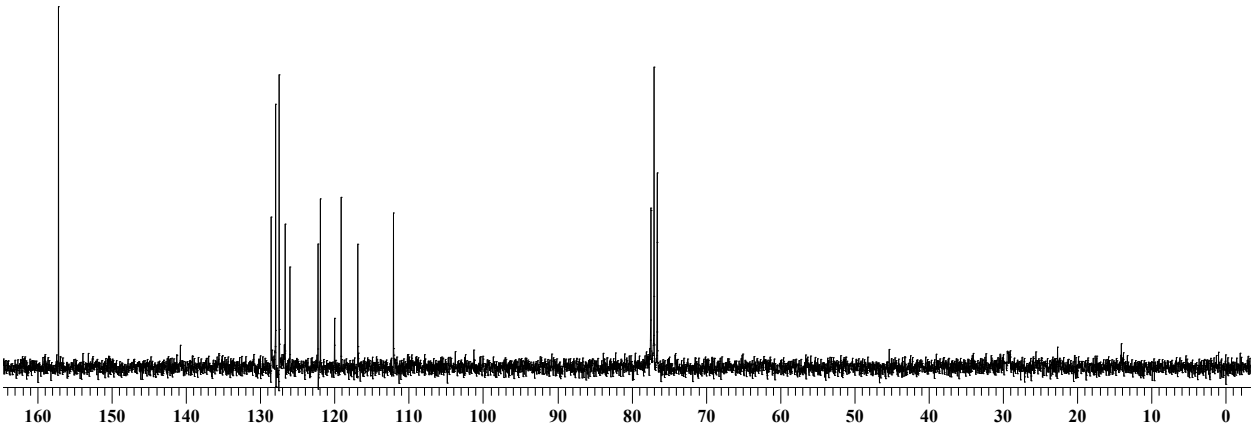
References:

(1) Ackermann, L.; Lygin, A. V. *Org. Lett.* **2011**, *13*, 3332.

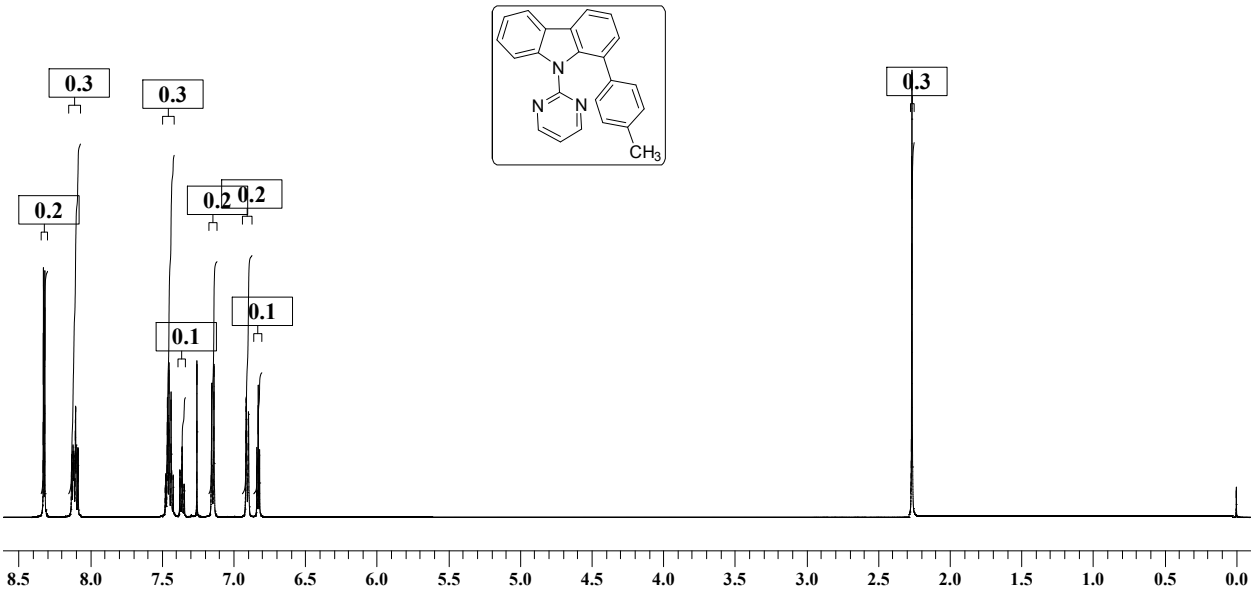
Copies of ^{1}H NMR and ^{13}C NMR of Compounds:

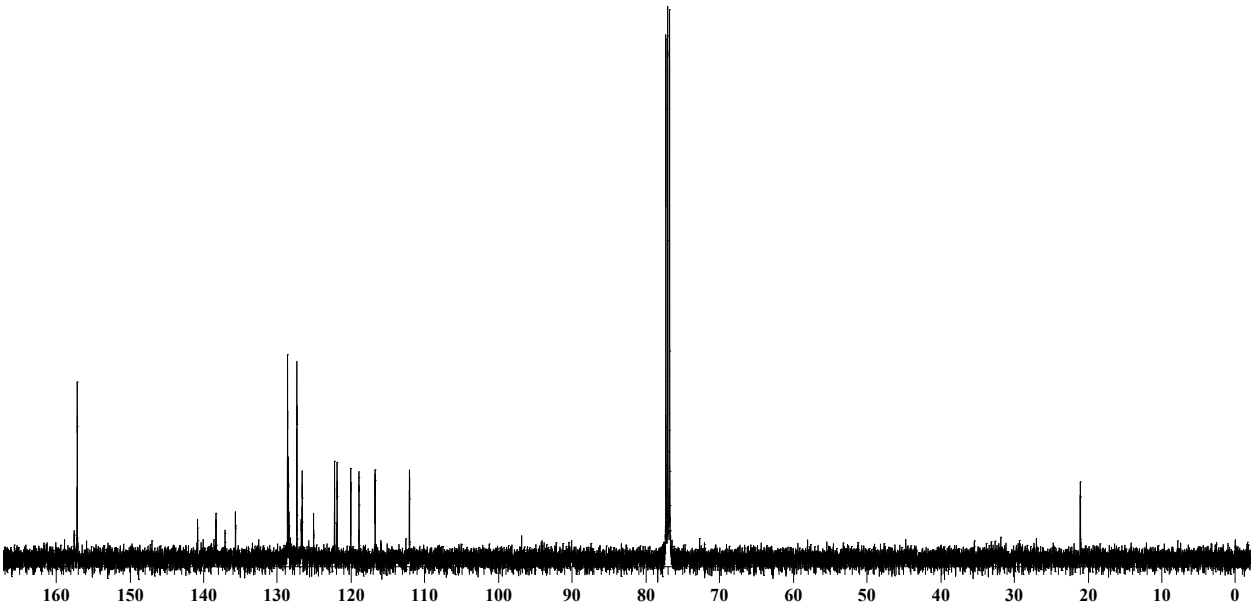
1-phenyl-9-(pyrimidin-2-yl)-9H-carbazole:



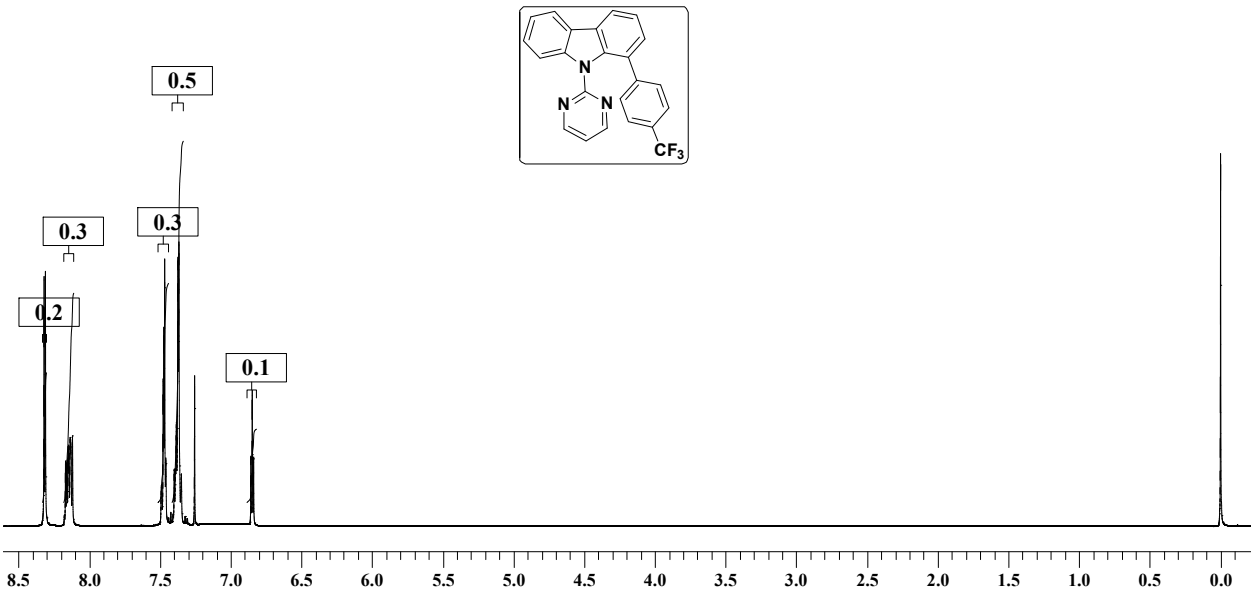


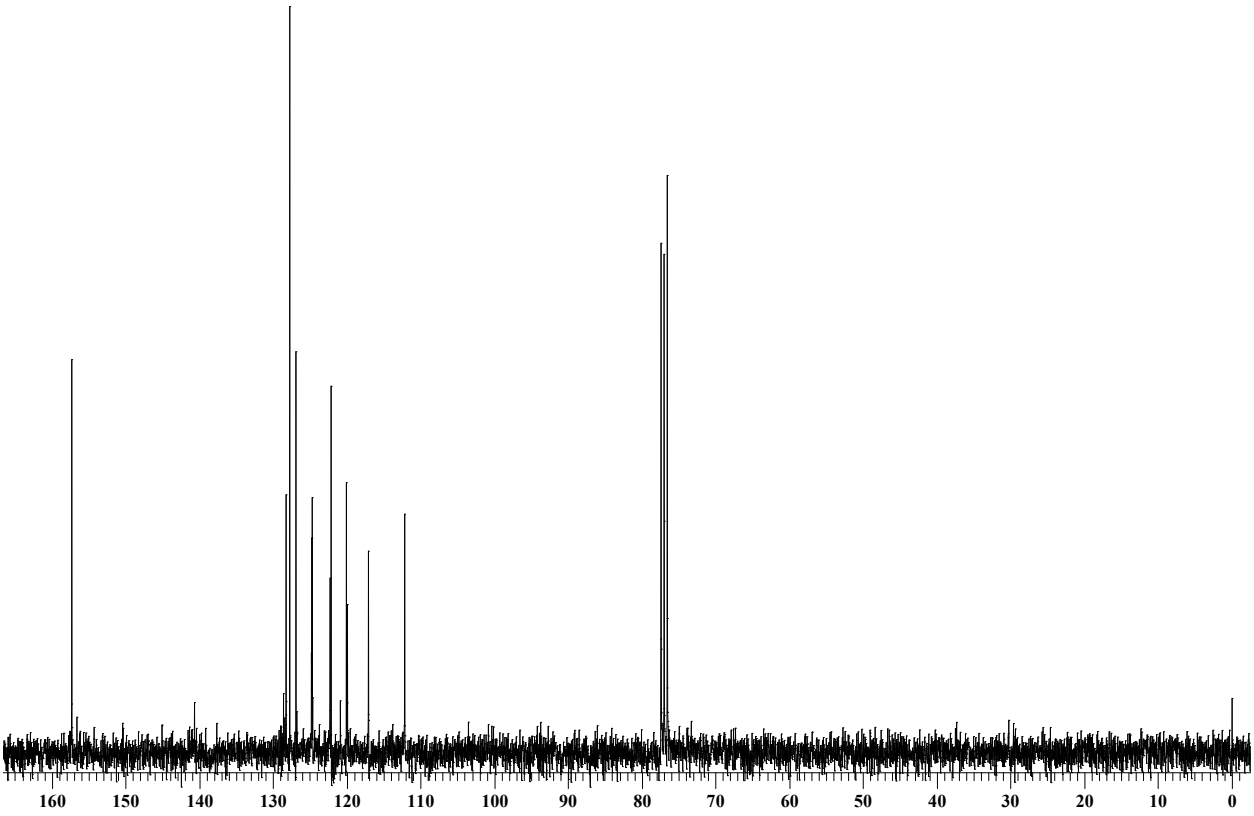
9-(pyrimidin-2-yl)-1-(p-tolyl)-9H-carbazole:



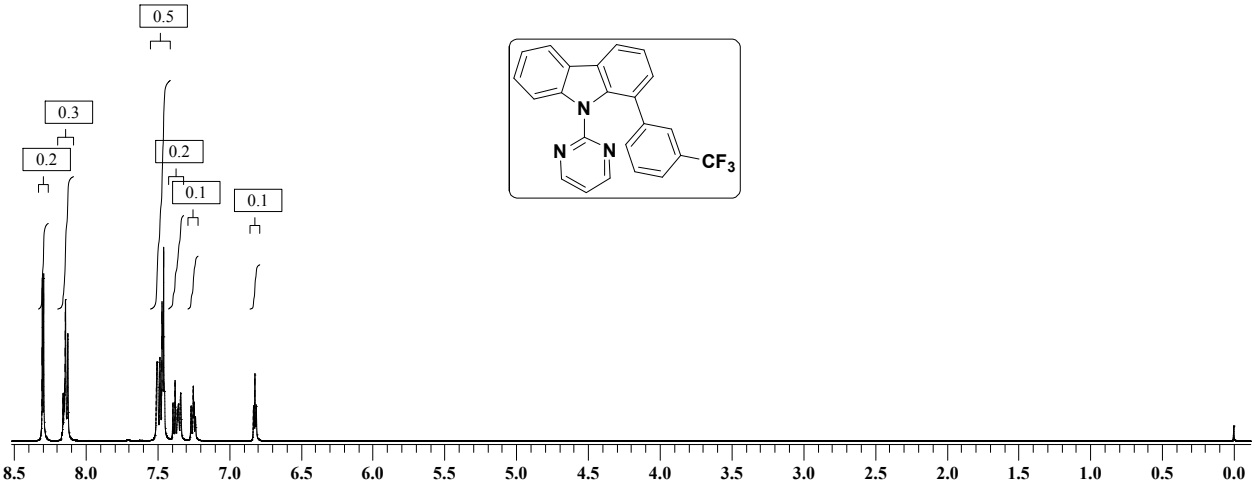


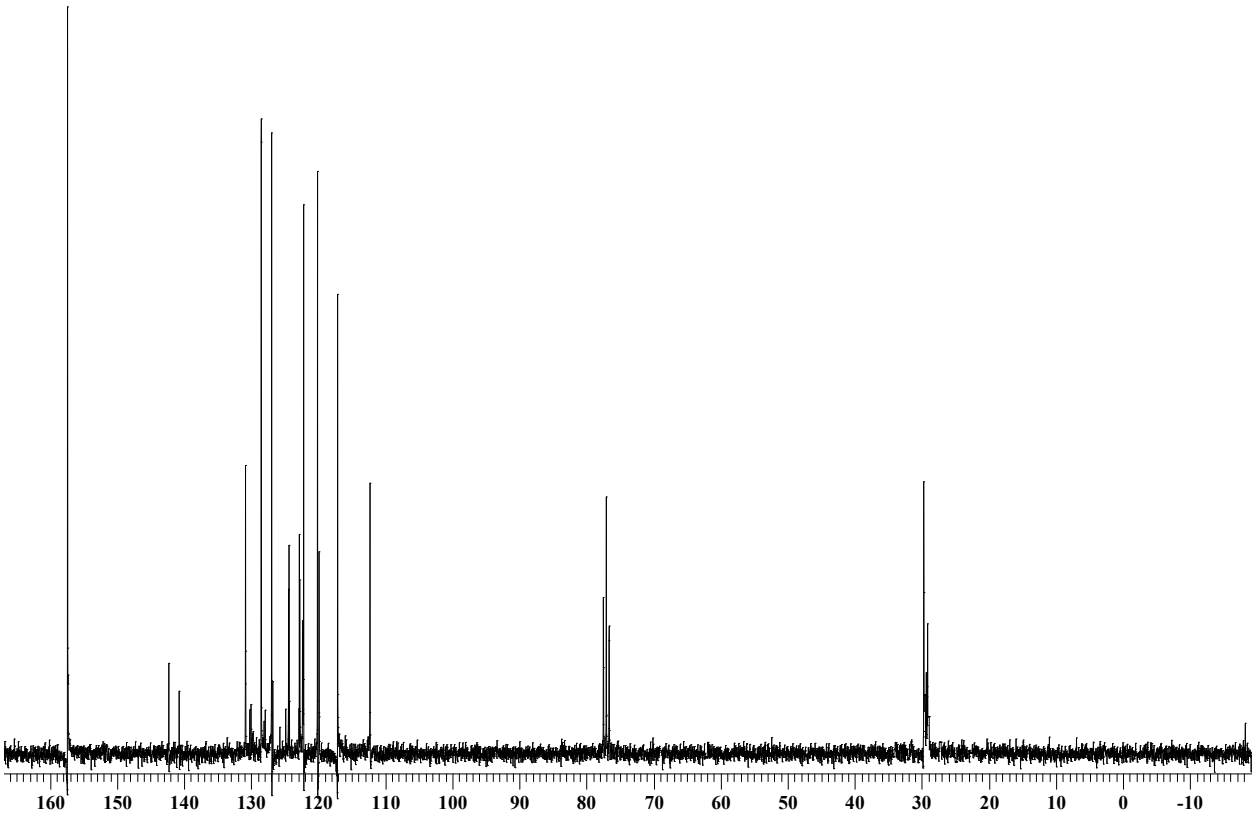
9-(pyrimidin-2-yl)-1-(4-(trifluoromethyl)phenyl)-9H-carbazole:



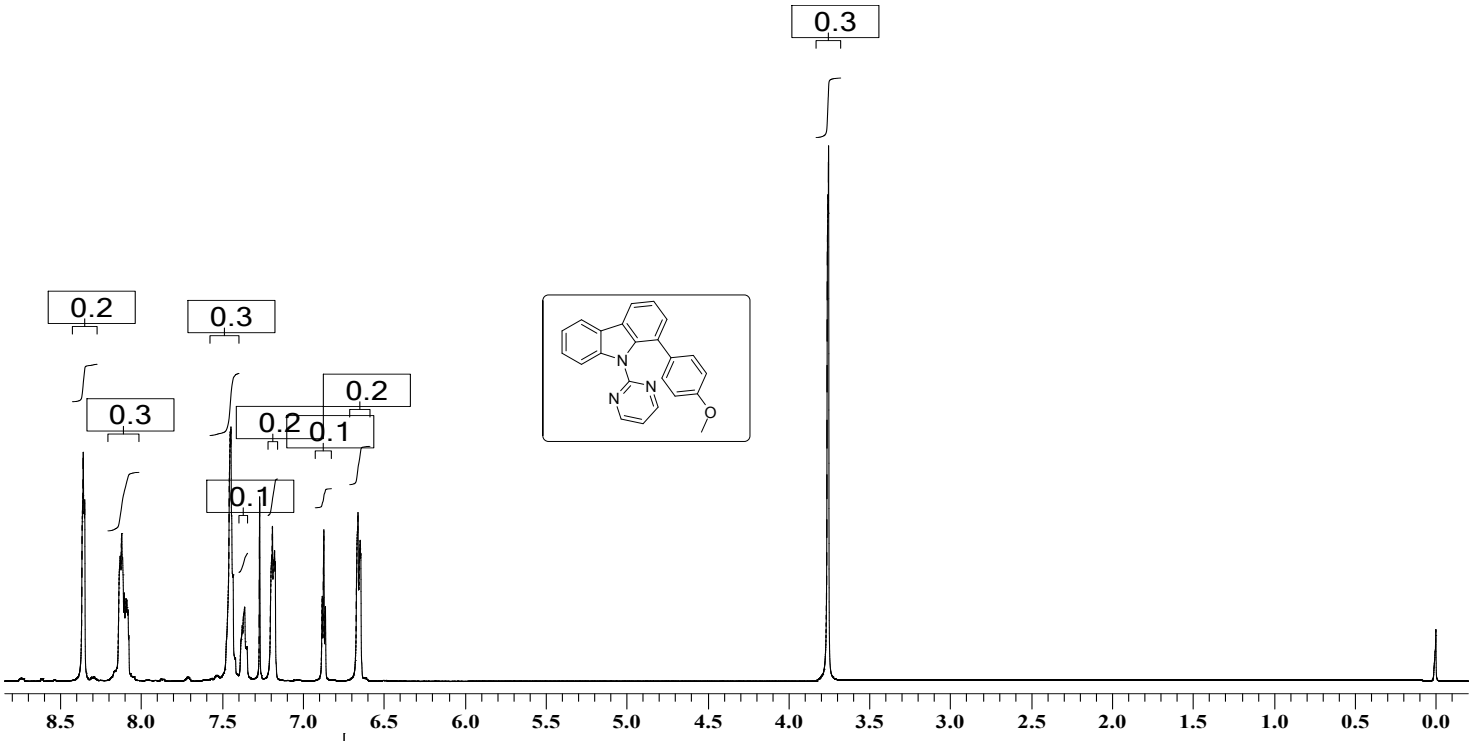


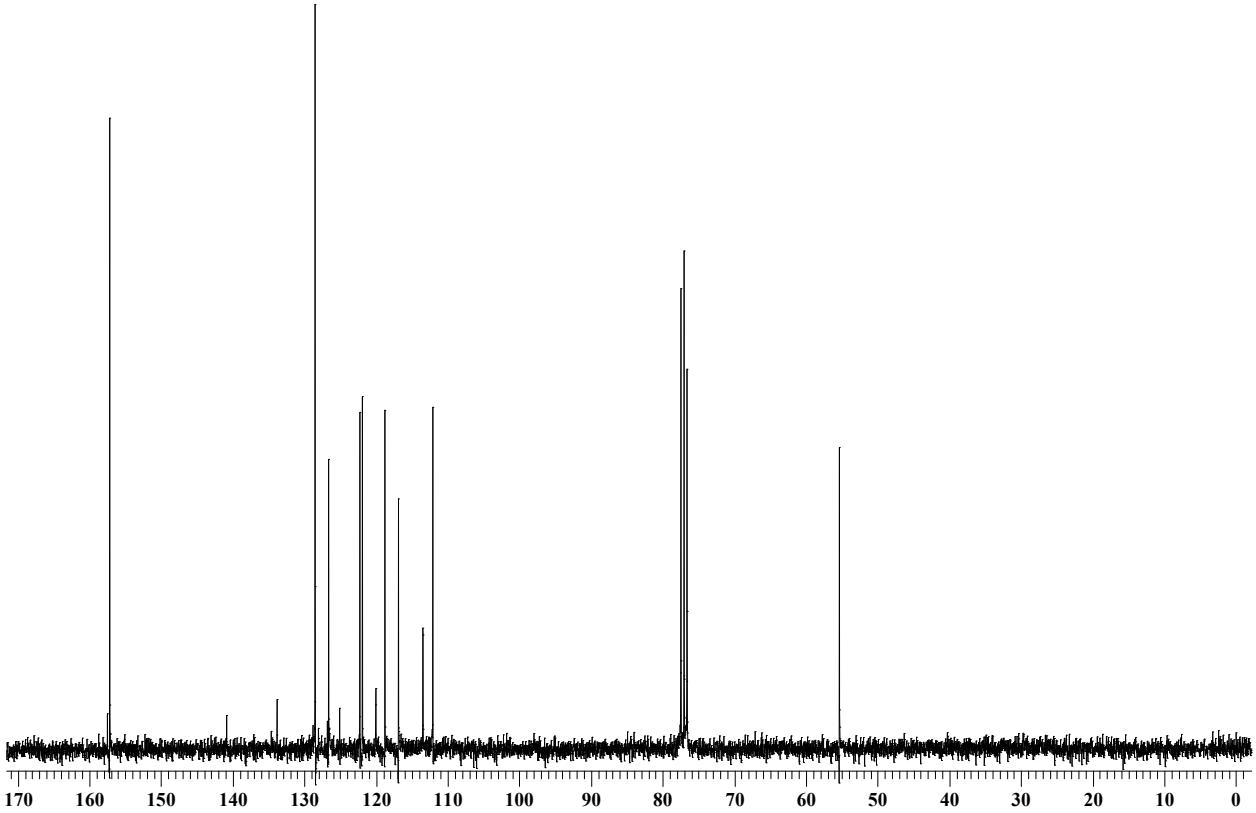
9-(pyrimidin-2-yl)-1-(3-(trifluoromethyl)phenyl)-9H-carbazole:



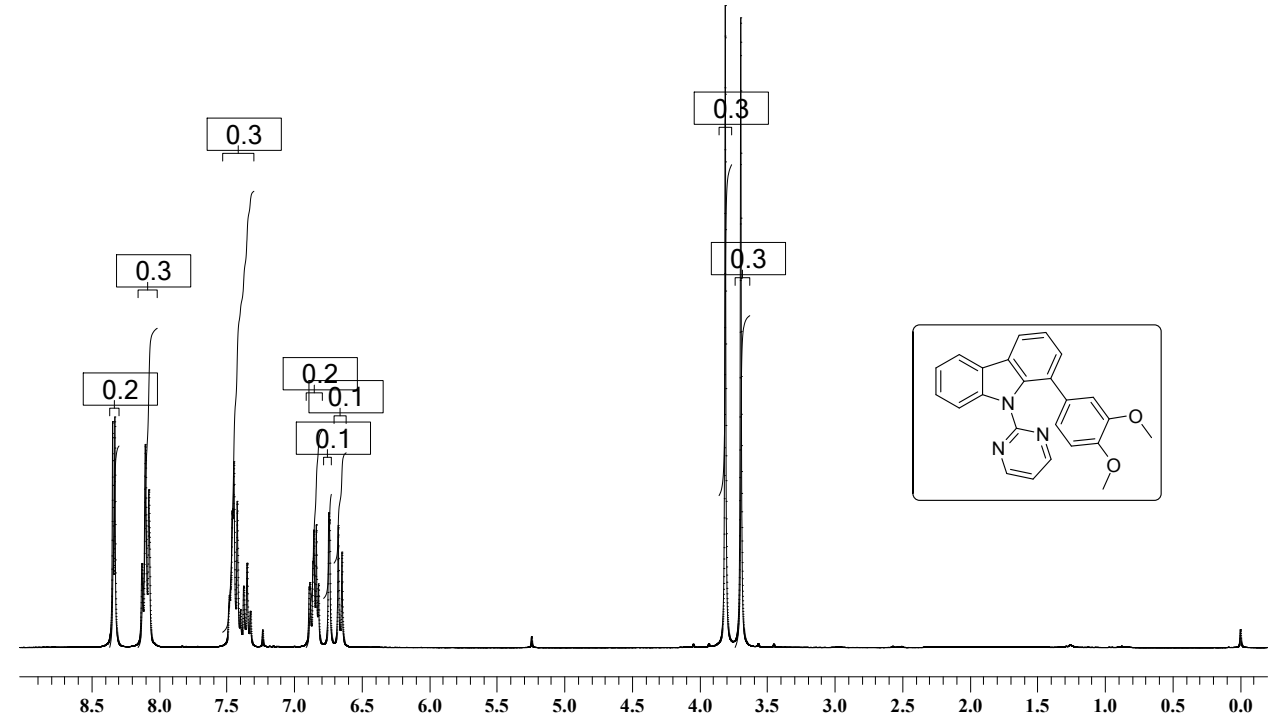


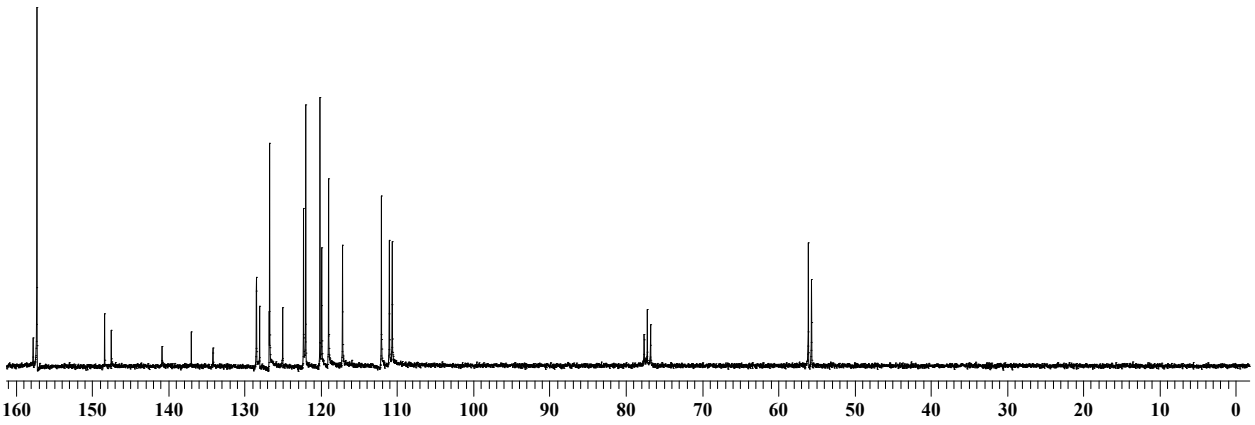
1-(4-methoxyphenyl)-9-(pyrimidin-2-yl)-9H-carbazole:





1-(3,4-dimethoxyphenyl)-9-(pyrimidin-2-yl)-9H-carbazole





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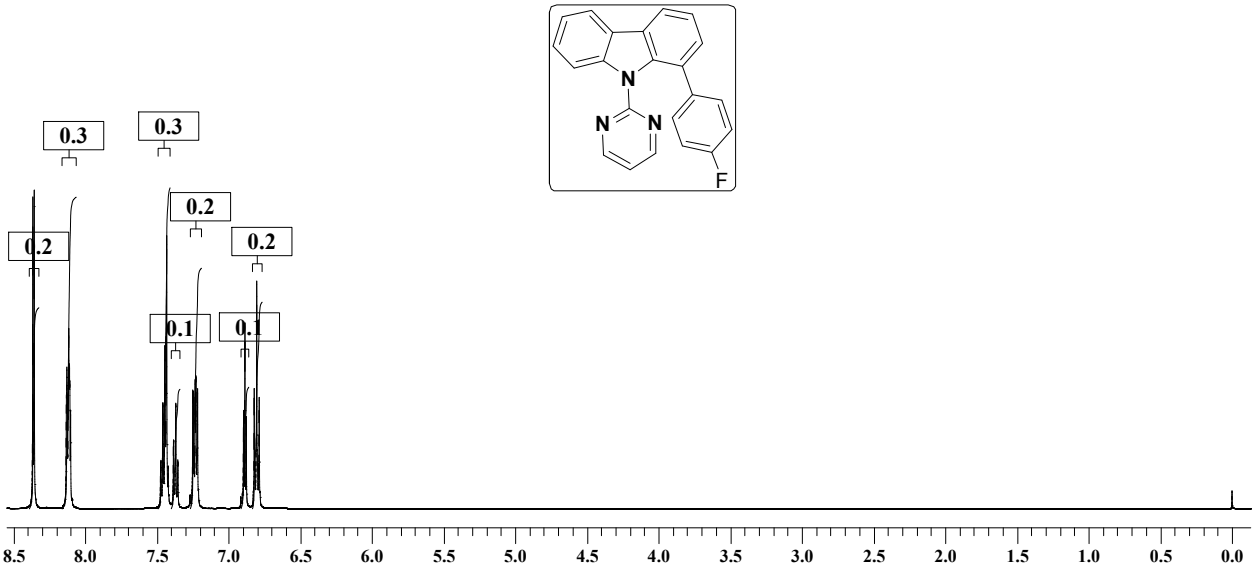
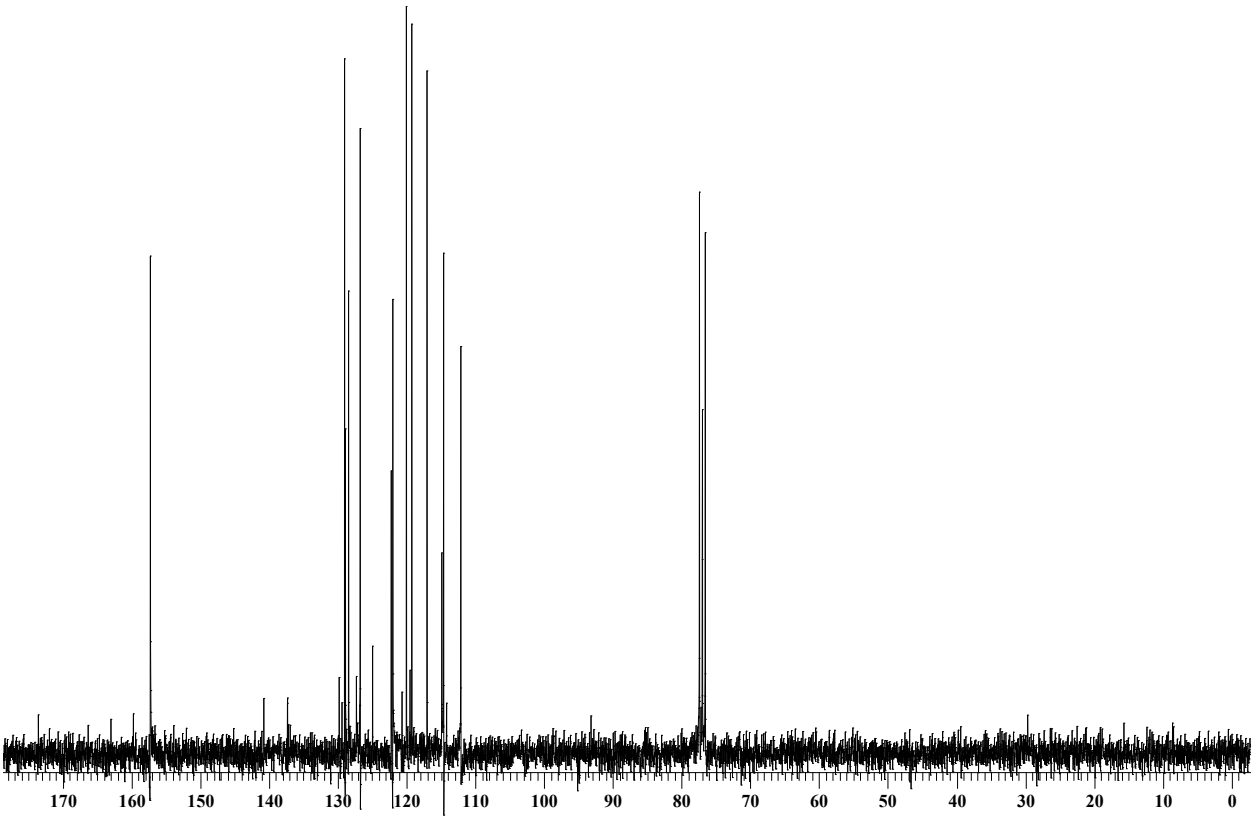
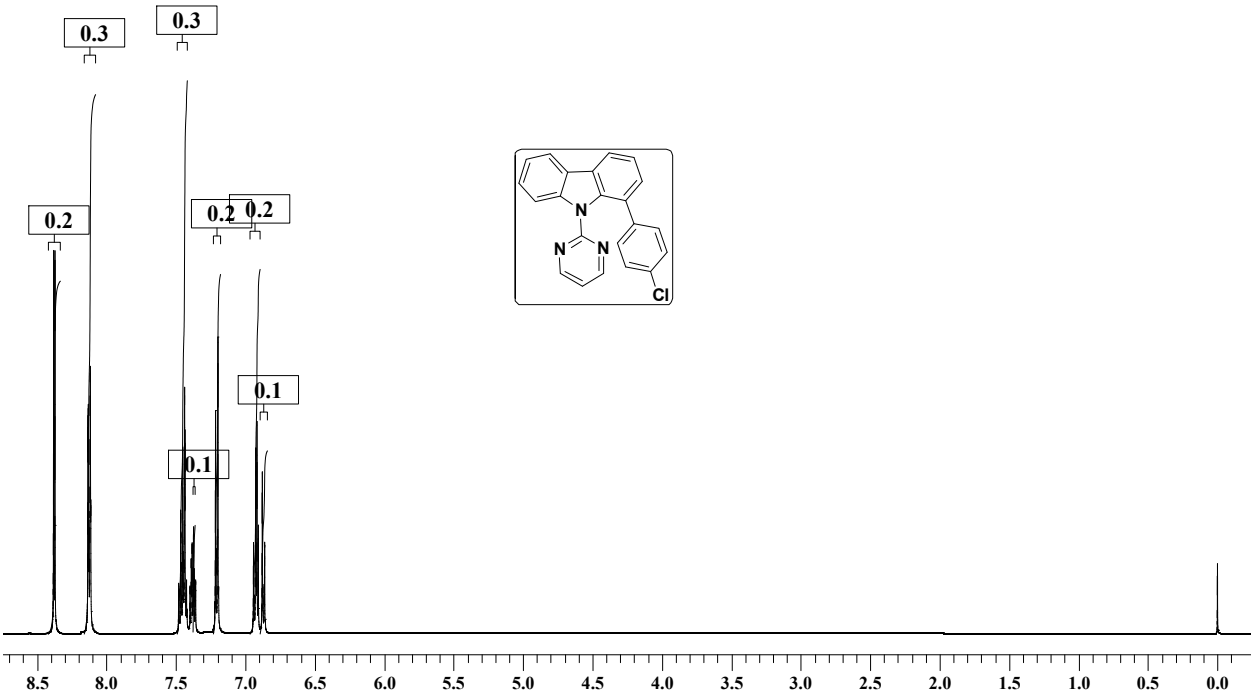
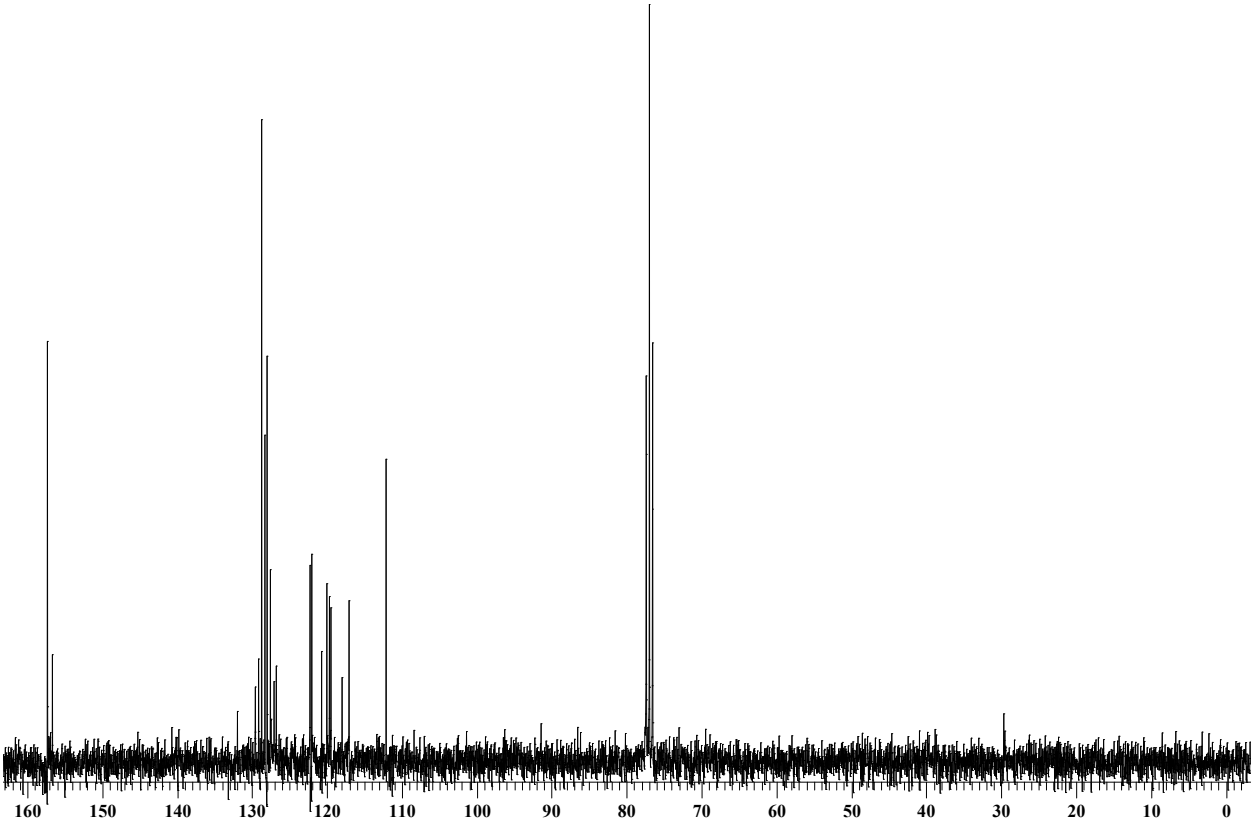


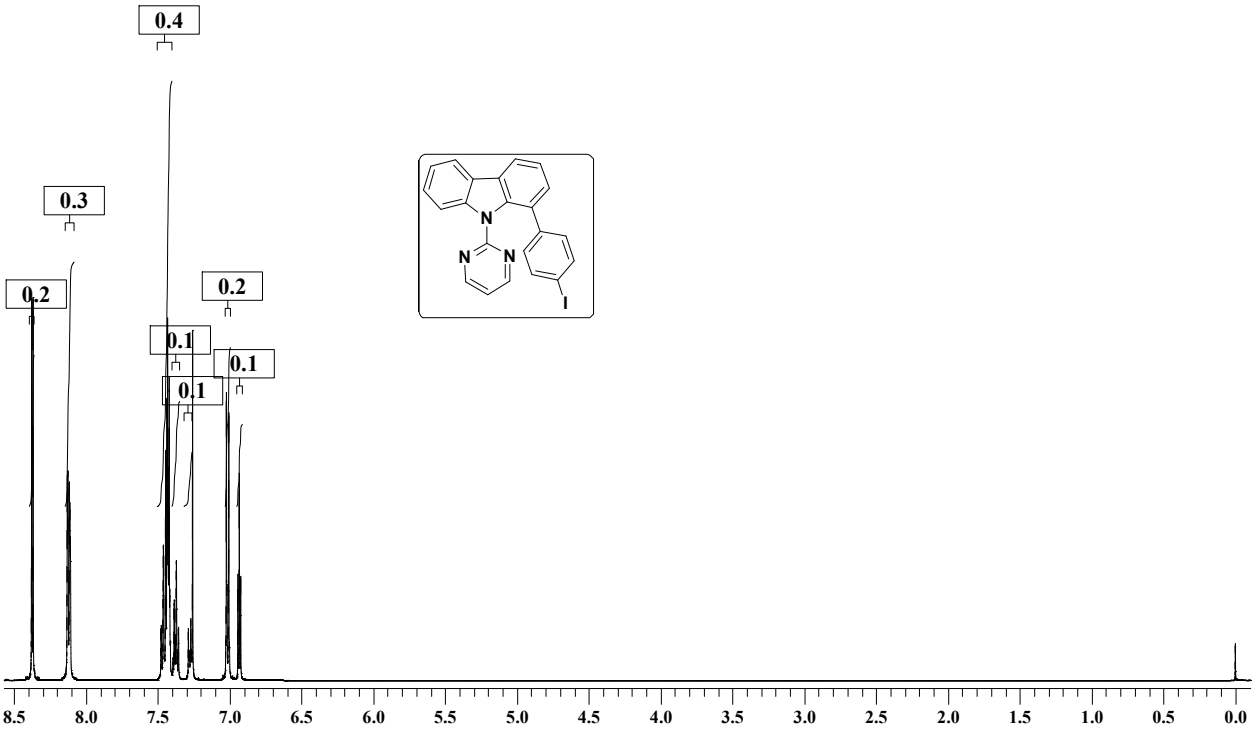


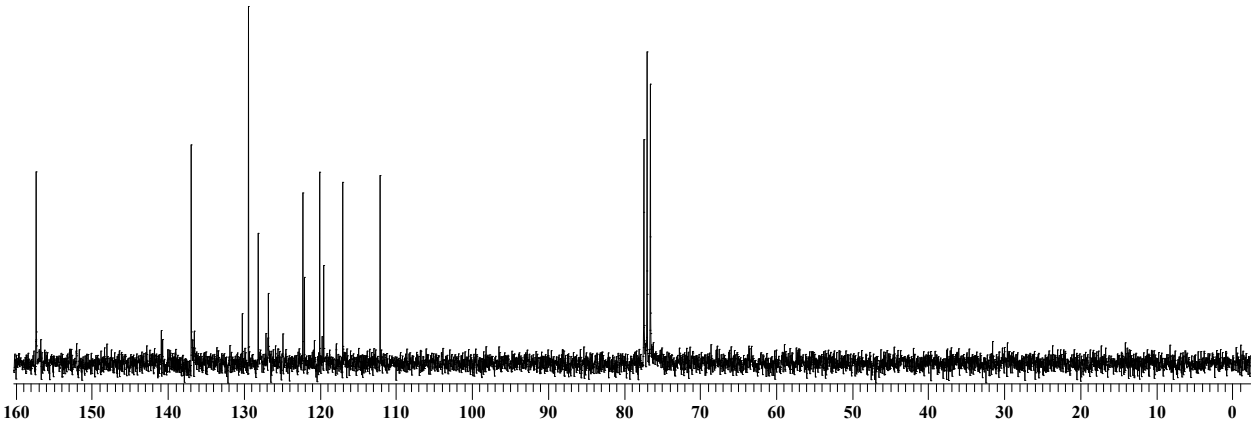
1-(4-chlorophenyl)-9-(pyrimidin-2-yl)-9H-carbazole:



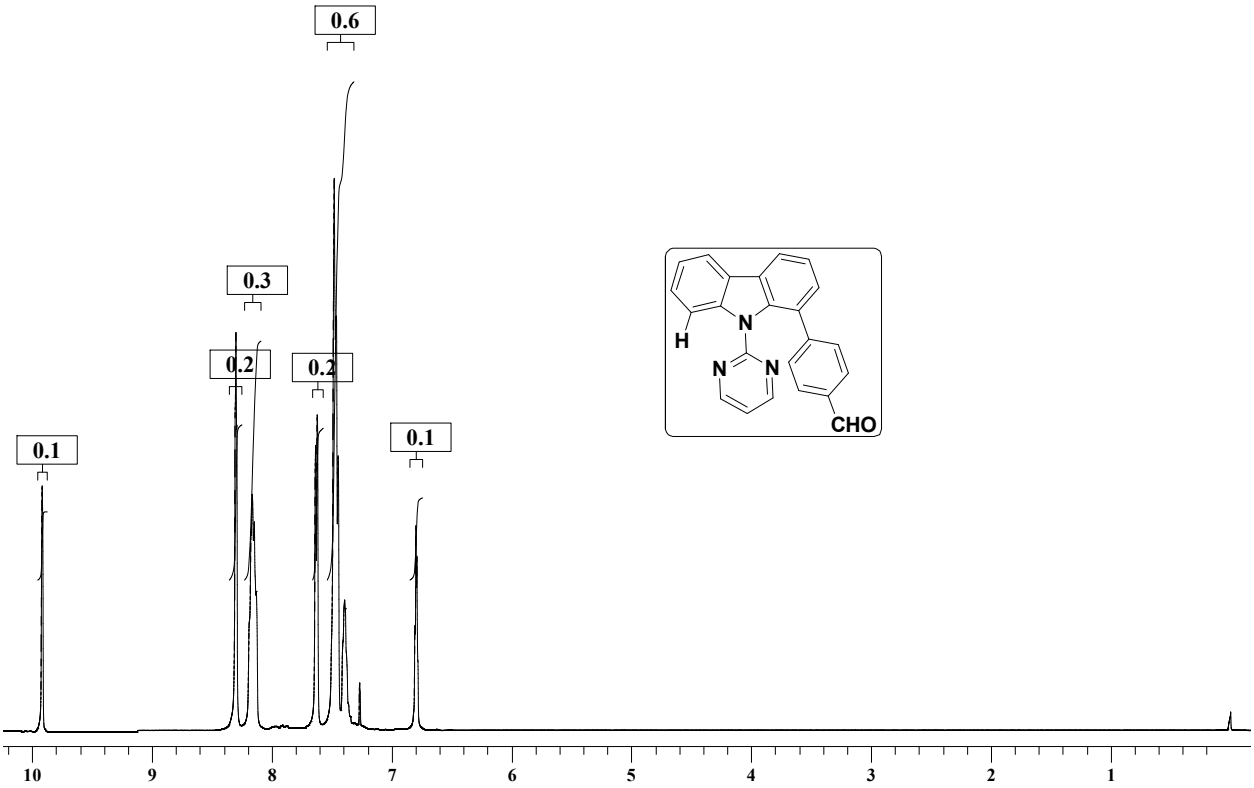


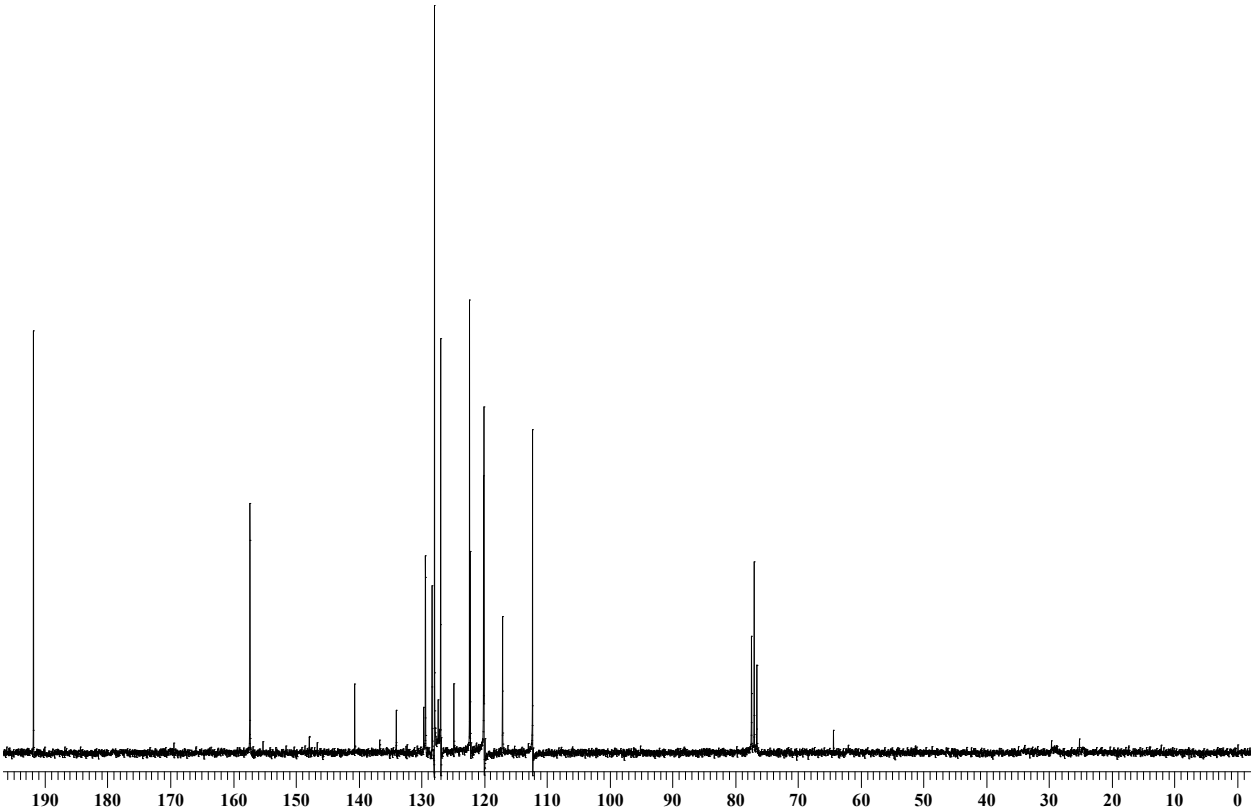
1-(4-iodophenyl)-9-(pyrimidin-2-yl)-9H-carbazole:



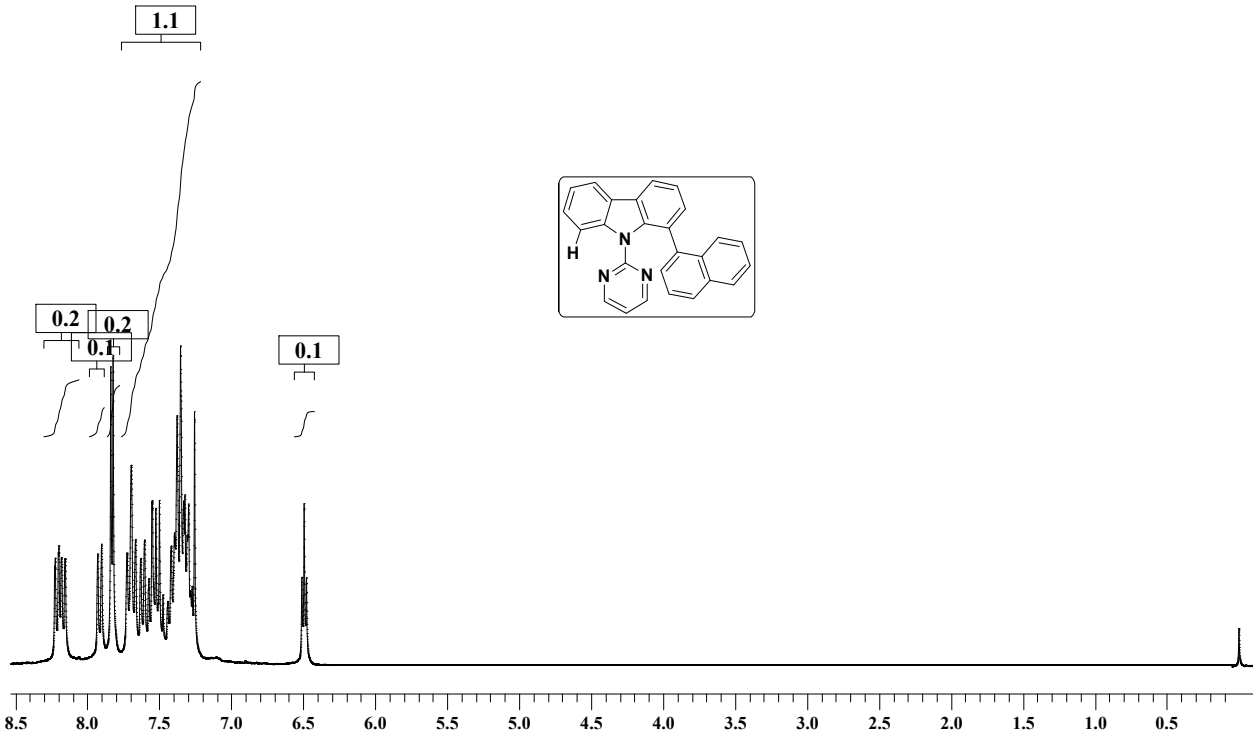


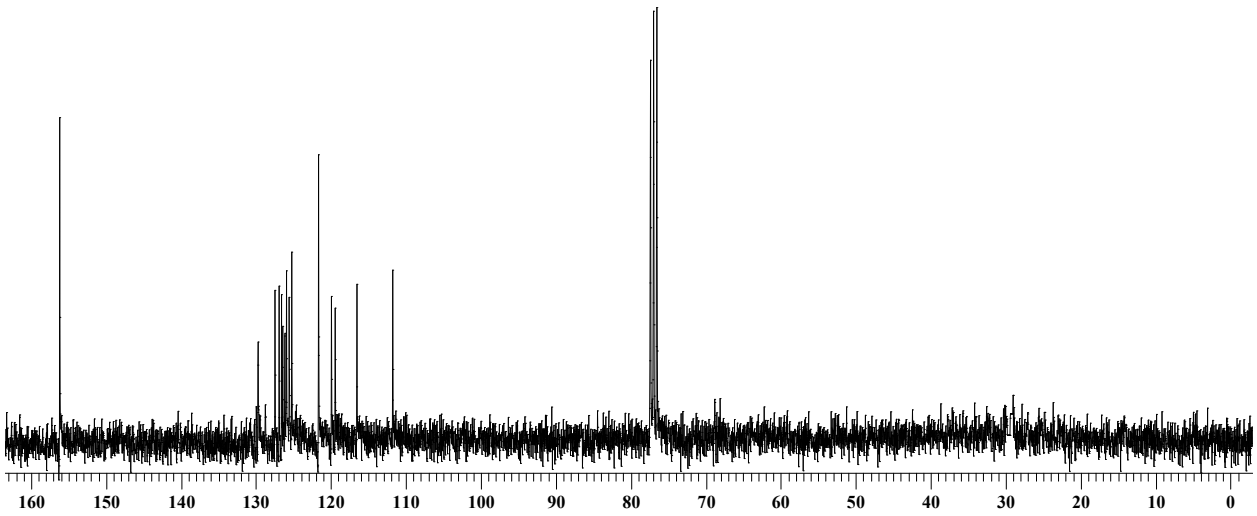
4-(9-(pyrimidin-2-yl)-9H-carbazol-1-yl)benzaldehyde:



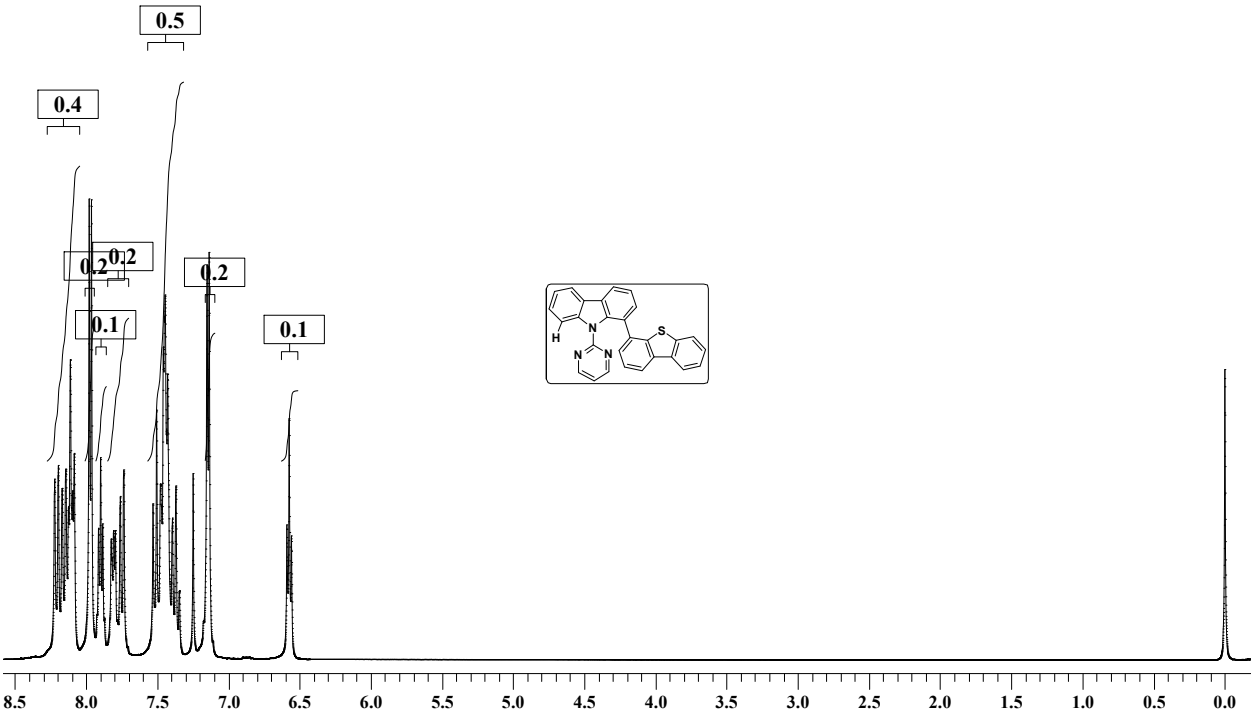


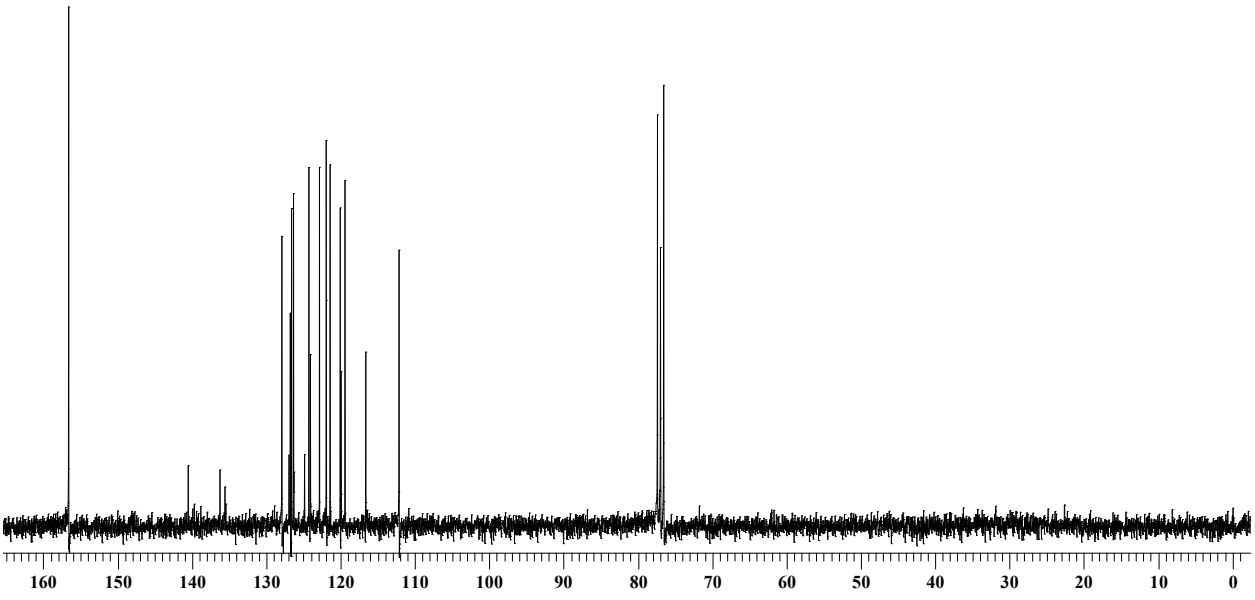
1-(naphthalen-1-yl)-9-(pyrimidin-2-yl)-9H-carbazole:



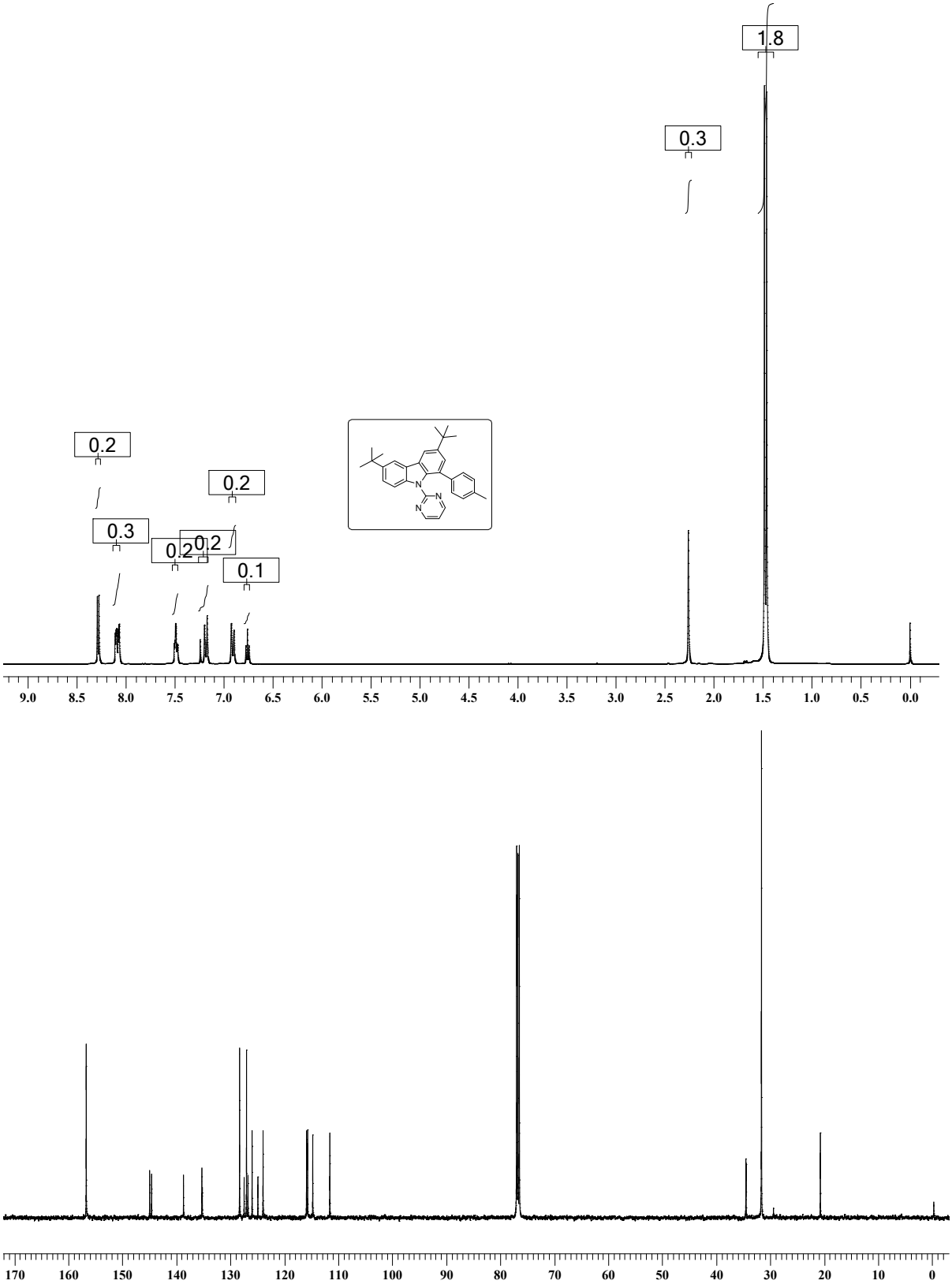


1-(dibenzo[b,d]thiophen-4-yl)-9-(pyrimidin-2-yl)-9H-carbazole:





3,6-di-tert-butyl-9-(pyrimidin-2-yl)-1-(p-tolyl)-9H-carbazole:



3,6-di-tert-butyl-1-(4-fluorophenyl)-9-(pyrimidin-2-yl)-9H-carbazole: