Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Facile Synthesis of Penta-substituted Pyrroles and Pyrrole-fused Piperidin-4-ones *via* Four Component Reactions of 2,3-Diketoesters, Anilines and Enaminones

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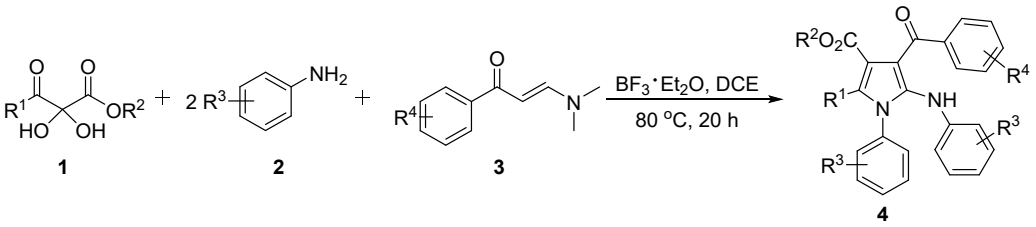
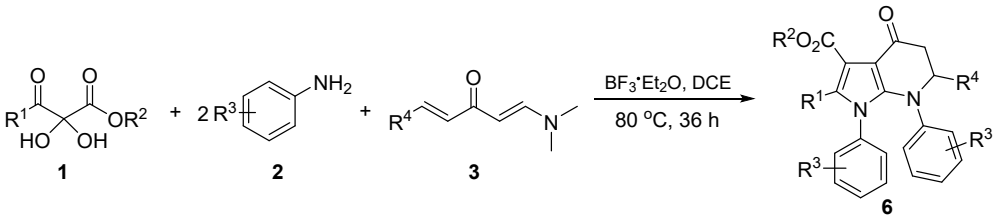
General. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance III 400 MHz spectrometer or JNM-ECZ500R JEOL-500 MHz spectrometer. Chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz (Hz). The peak information is described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. High-resolution mass spectra (HRMS) were performed on a microTOF-ESI mass spectrometer using CsOAc as the standard. Melting points were obtained uncorrected from an Electrothermo Mel-Temp DLX 104 device. Unless otherwise noted, all reagents and solvents (AR grade) were obtained from commercial sources (aladdin, energy-chemical, J&K chemical) and used directly without purification. Unless otherwise noted, all reactions were performed under N_2 using standard Schlenk techniques. 2,3-Diketoesters[1] and enaminones[2] were synthesized according to literature.

General procedure for the synthesis of 4



A Schlenk tube with a magnetic stir bar charged with 2,3-diketoesters **1** (0.20 mmol), anilines **2** (0.40 mmol, 2.0 equiv.), enaminones **3** (0.20 mmol), $BF_3 \cdot Et_2O$ (0.24 mmol, 1.2 equiv.), and 1,2-dichloroethane (DCE, 2.0 mL). The reaction mixture was then heated to 80 °C and stirred for 20 hours. The reaction mixture was then allowed to cool to ambient temperature and all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography, eluding with petroleum/ethyl acetate, to provide penta-substituted pyrroles **4**.

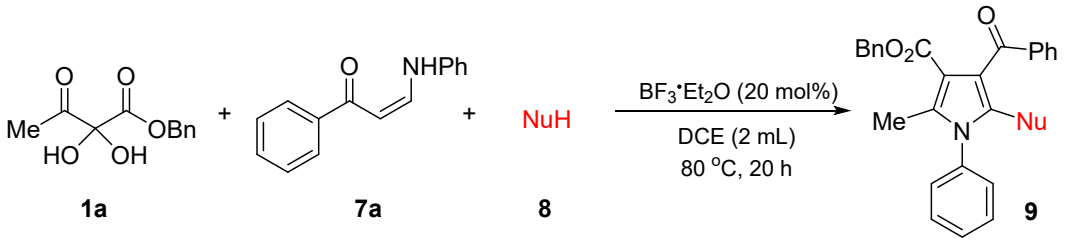
General procedure for the synthesis of 6



A Schlenk tube with a magnetic stir bar charged with 2,3-diketoesters **1** (0.20 mmol), anilines **2**

(0.40 mmol, 2.0 equiv.), enaminones **3** (0.20 mmol), $BF_3 \cdot Et_2O$ (0.24 mmol, 1.2 equiv.), and 1,2-dichloroethane (DCE, 2.0 mL). The reaction mixture was then heated to 80 °C and stirred for 36 hours. The reaction mixture was then allowed to cool to ambient temperature and all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography, eluding with petroleum/ethyl acetate, to provide 6,7-dihydro-4*H*-pyrrolo[2,3-*b*]pyridin-4-ones **6**.

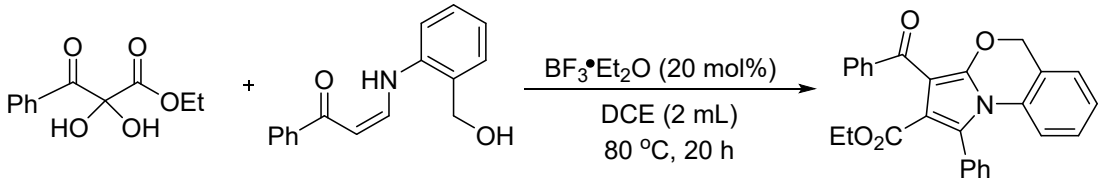
General procedure for the synthesis of 9



1a **7a** **8** **9**

A Schlenk tube with a magnetic stir bar charged with benzyl 2,2-dihydroxy-3-oxobutanoate (**1a**, 0.20 mmol), (*Z*)-1-phenyl-3-(phenylamino)prop-2-en-1-one (**7a**, 0.20 mmol), nucleophilic reagent (**8**, 0.40 mmol), $BF_3 \cdot Et_2O$ (0.04 mmol, 0.2 equiv.), and 1,2-dichloroethane (DCE, 2.0 mL). The reaction mixture was then heated to 80 °C and stirred for 20 hours. The reaction mixture was then allowed to cool to ambient temperature and all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography, eluding with petroleum/ethyl acetate, to provide product **9**.

General procedure for the synthesis of 11



1h **10** **11**, 48% yield

A Schlenk tube with a magnetic stir bar charged with ethyl 2,2-dihydroxy-3-oxo-3-phenylpropanoate (**1h**, 0.20 mmol), (*Z*)-3-((2-(hydroxymethyl)phenyl) amino)-1-phenylprop-2-en-1-one (**10**, 0.20 mmol), $BF_3 \cdot Et_2O$ (0.04 mmol, 0.2 equiv.), and 1,2-dichloroethane (DCE, 2.0 mL). The reaction mixture was then heated to 80 °C and stirred for 20 hours. The reaction mixture was then allowed to cool to ambient temperature and all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography, eluding with petroleum/ethyl acetate, to provide product **11**.

Biological assays

Antifungal activities test of 6 selected compounds was carried out using mycelia growth inhibitory rate methods. Most of the compounds were tested with the concentration of 50 μg/mL, Streptobromo and Boscalid were used as the positive control. The tested fungi were provided by the Laboratory of Plant Disease Control, Nanjing Agricultural University, and the experimental procedure of the antifungal activity was performed according to the paper from Department of Plant Pathology, Nanjing Agricultural University.[3] The strains were activated in PDA at 25 °C for 2-15 days to obtain new mycelia, the edge of the mycelia was punched before the antifungal activity assay. The results of the test on the target compounds against *Botrytis cinrea, Alternaria solani*, *Gibberella zeae, Rhizoctonia solani, Gibberella zeae, Colletotrichum lagenarium, Alternaria leaf spot* were listed in **Table 1**.

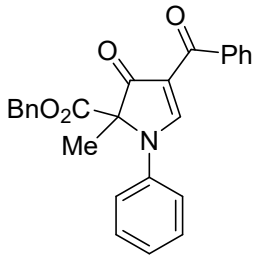
Table 1. Antifungal activity of the six selected compounds

Entry	BOT[a]	ALS[a]	GIB[a]	RHI[a]	COL[a]	ALL[a]
4g	1.00%[b]	1.69%	14.99%	15.38%	1.00%	15.89%
4v	4.61%	3.18%	1.00%	8.33%	1.00%	9.11%
4w	6.75%	4.93%	1.00%	3.21%	1.00%	1.00%
4ae	1.00%	3.93%	1.00%	14.74%	1.00%	1.00%
6a	7.02%	1.94%	1.29%	13.78%	1.00%	1.00%
6b[c]	18.01%	16.37%	**46.00%**	**43.27%**	13.33%	4.17%
Streptobromo	100.00%	63.13%	91.21%	82.37%	33.33%	28.91%
Boscalid	100.00%	49.74%	25.30%	93.54%	19.01%	NT[d]

[a] BOT, *Botrytis cinerea*; ALS, *Alternaria solani*; GIB, *Gibberella zeae*; RHI, *Rhizoctorzia solani*; COL, *Colletotrichum lagenarium*; ALL, *Alternaria Leaf Spot*. [b] All the data was the average value of three replications, 1.00% means data equal to or below 1.00% control. [c] Under the concentration of 20 μg/mL. [d] No test.

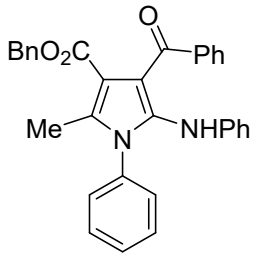
Characterization data of 4, 5a, 6, 7a

Benzyl 4-benzoyl-2-methyl-3-oxo-1-phenyl-2,3-dihydro-1*H*-pyrrole-2-carboxylate (5a)



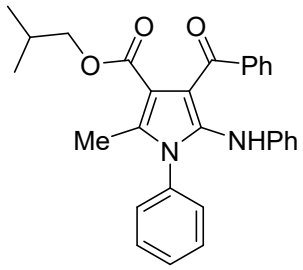
Light yellow solid, m.p. 97.7-98.9 °C; R_f = 0.24 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.82-7.80 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.37-7.28 (m, 8H), 7.02 (d, *J* = 7.8 Hz, 2H), 5.28 (d, *J* = 12.8 Hz, 1H), 5.23 (d, *J* = 12.4 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 188.3, 167.2, 165.5, 138.0, 137.2, 134.6, 132.4, 130.1, 129.2, 128.74, 128.68, 128.64, 128.0, 127.2, 120.3, 113.5, 77.3, 68.5, 18.8; HRMS (ESI) *m/z* calculated for $[C_{26}H_{21}NO_4+H]^+$ $[M+H]^+$ 412.1549, found: 412.1543.

Benzyl 4-benzoyl-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4a)



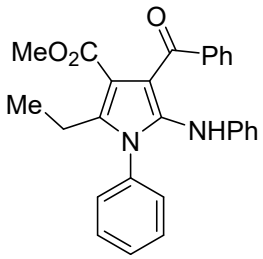
80.7 mg, 83% yield, Light yellow solid, m.p. 134.7-136.6 °C; R_f = 0.79 (PE/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.56 (s, 1H), 7.46-7.42 (m, 1H), 7.36-7.33 (m, 2H), 7.28-7.18 (m, 8H), 7.01-7.00 (m, 2H), 6.94-6.90 (m, 2H), 6.70-6.66 (m,1H), 6.53 (d, *J* = 7.9 Hz, 2H), 4.61 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 165.0, 142.8, 140.4, 139.0, 135.71, 135.68, 133.6, 129.0, 128.6, 128.5, 128.3, 128.24, 128.17, 127.9, 127.8, 121.5, 118.4, 112.4, 111.7, 65.8, 12.4; HRMS (ESI) *m/z* calculated for $[C_{32}H_{26}N_2O_3+H]^+$ $[M+H]^+$ 487.2022, found: 487.2018.

Isobutyl 4-benzoyl-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4b)



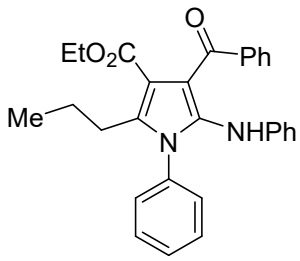
78.5 mg, 87% yield, Light yellow solid, m.p. 122.0-123.8 °C; R_f = 0.65 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.0 Hz, 2H), 7.48 (s, 1H), 7.47-7.44 (m, 1H), 7.41-7.38 (m, 2H), 7.28-7.25 (m, 2H), 7.22-7.19 (m, 3H), 6.94-6.90 (m, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 3.39 (d, *J* = 6.8 Hz, 2H), 2.31 (s, 3H), 1.39 (hept, *J* = 6.7 Hz, 1H), 0.70 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 165.3, 143.0, 140.2, 138.3, 135.7, 133.3, 131.7, 129.0, 128.8, 128.5, 128.1, 127.8, 121.3, 118.1, 112.8, 112.1, 70.3, 27.3, 19.2, 12.3; HRMS (ESI) *m/z* calculated for $[C_{29}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 453.2178, found: 453.2176.

Methyl 4-benzoyl-2-ethyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4c)



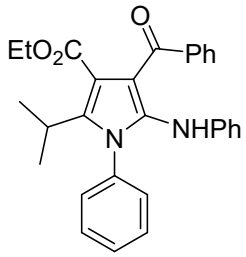
49.5 mg, 58% yield, Light yellow solid, m.p. 167.4-169.3 °C; R_f = 0.57 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.79 (m, 2H), 7.47-7.40 (m, 4H), 7.26-7.21 (m, 5H), 6.96-6.92 (m, 2H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 3.13 (s, 3H), 2.76 (q, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 165.3, 143.1, 140.7, 139.4, 138.9, 135.7, 131.5, 129.0, 128.6, 128.5, 128.3, 128.2, 128.1, 121.5, 118.5, 112.6, 111.0, 50.5, 18.6, 14.5; HRMS (ESI) *m/z* calculated for $[C_{27}H_{24}N_2O_3+H]^+$ $[M+H]^+$ 425.1865, found: 425.1860.

Ethyl 4-benzoyl-1-phenyl-5-(phenylamino)-2-propyl-1*H*-pyrrole-3-carboxylate (4d)



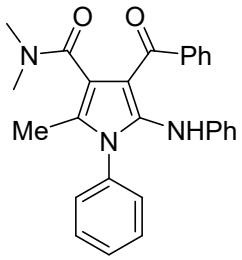
68.7 mg, 76% yield, Light yellow solid, m.p. 104.4-107.6 °C; R_f = 0.65 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.48-7.39 (m, 4H), 7.29-7.19 (m, 5H), 6.95-6.91 (m, 2H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 2H), 3.67 (q, *J* = 7.2 Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 2H), 1.42-1.33 (m, 2H), 0.76 (t, *J* = 7.1 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 165.1, 143.2, 140.5, 138.6, 137.9, 135.7, 131.7, 128.9, 128.7, 128.6, 128.5, 128.2, 128.1, 121.4, 118.3, 112.8, 111.8, 59.9, 27.0, 23.1, 13.8, 13.5; HRMS (ESI) *m/z* calculated for $[C_{29}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 453.2178, found: 453.2178.

Ethyl 4-benzoyl-2-isopropyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4e)



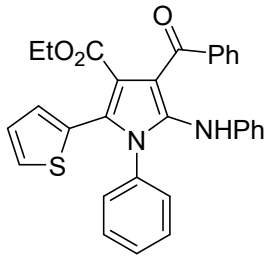
20.0 mg, 22% yield, Light yellow solid, m.p. 168.7-170.8 °C; R_f = 0.65 (PE/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.46-7.44 (m, 1H), 7.42-7.39 (m, 2H), 7.26-7.24 (m, 3H), 7.18-7.16 (m, 3H), 6.94-6.91 (m, 2H), 6.70-6.67 (m, 1H), 6.49 (d, *J* = 7.6 Hz, 2H), 3.59 (q, *J* = 7.2 Hz, 2H), 3.02 (hept, *J* = 7.2 Hz, 1H), 1.25 (d, *J* = 7.2 Hz, 6H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 165.5, 143.6, 141.5, 140.3, 137.9, 136.2, 131.8, 128.9, 128.8, 128.70, 128.66, 128.55, 128.3, 121.4, 118.3, 113.8, 111.4, 60.2, 26.4, 21.4, 13.6; HRMS (ESI) *m/z* calculated for $[C_{29}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 453.2178, found: 453.2179.

4-Benzoyl-*N*,*N*,2-trimethyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxamide (4f)



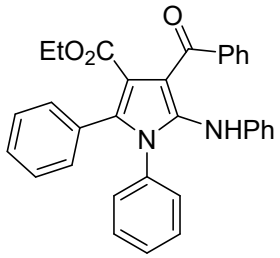
27.5 mg, 33% yield, Light yellow solid, m.p. 179.2-181.3 °C; R_f = 0.19 (PE/EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.77 (d. *J* = 6.6 Hz, 2H), 7.47-7.42 (m, 3H), 7.26-7.15 (m, 5H), 6.93 (t, *J* = 7.7 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 2.71 (s, 3H), 2.38 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 167.4, 142.5, 141.2, 139.8, 136.1, 131.3, 128.9, 128.5, 128.4, 128.2, 127.9, 127.5, 126.8, 122.4, 120.2, 115.5, 108.3, 38.5, 34.3, 12.0; HRMS (ESI) *m/z* calculated for $[C_{27}H_{25}N_3O_3+H]^+$ $[M+H]^+$ 424.2025, found: 424.2020.

Ethyl 4-benzoyl-1-phenyl-5-(phenylamino)-2-(thiophen-2-yl)-1*H*-pyrrole-3-carboxylate (4g)



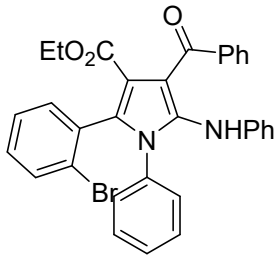
44.7 mg, 45% yield, Light yellow solid, m.p. 174.8-176.3 °C; R_f = 0.56 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.90 (d, *J* = 6.9 Hz, 2H), 7.52-7.43 (m, 3H), 7.25 (d, *J* = 4.2 Hz, 1H), 7.11-7.06 (m, 6H), 6.92 (t, *J* = 7.8 Hz, 2H), 6.87 (dd, *J* = 5.0 Hz, 3.7 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 3.54 (q, *J* = 7.1 Hz, 2H), 0.73 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 164.2, 142.1, 140.9, 140.3, 135.8, 131.8, 129.8, 128.59, 128.56, 128.49, 128.3, 128.2, 128.1, 128.0, 126.6, 126.1, 122.0, 119.1, 115.8, 111.8, 100.0, 60.5, 13.4; HRMS (ESI) *m/z* calculated for $[C_{30}H_{24}N_2O_3S+H]^+$ $[M+H]^+$ 493.1586, found: 493.1580.

Ethyl 4-benzoyl-1,2-diphenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4h)



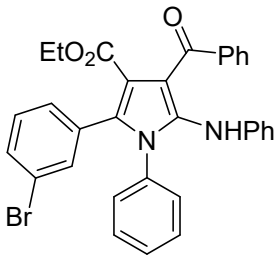
39.5 mg, 41% yield, Light yellow solid, m.p. 185.3-187.2 °C; R_f = 0.50 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.88 (s, 1H), 7.51-7.42 (m, 3H), 7.29-7.26 (m, 2H), 7.23-7.18 (m, 3H), 7.06-7.00 (m, 5H), 6.92 (t, *J* = 8.1 Hz, 2H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 2H), 3.52 (q, *J* = 7.2 Hz, 2H), 0.68 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 164.4, 142.6, 140.4, 139.8, 135.9, 134.6, 131.9, 131.8, 129.8, 128.7, 128.51, 128.48, 128.4, 128.3, 127.9, 127.8, 127.3, 121.6, 118.5, 113.7, 112.3, 60.2, 13.4; HRMS (ESI) *m/z* calculated for $[C_{32}H_{26}N_2O_3+H]^+$ $[M+H]^+$ 487.2022, found: 487.2019.

Ethyl 4-benzoyl-2-(2-bromophenyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4i)



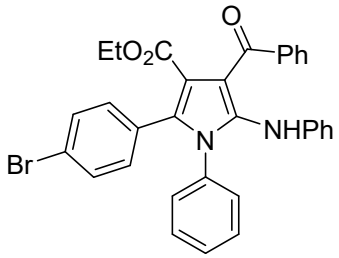
20.4 mg, 18% yield, Light yellow solid, m.p. 170.2-171.6 °C; R_f = 0.40 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.76 (s, 1H), 7.53-7.43 (m, 4H), 7.24 (dd, *J* = 7.4 Hz, 1.8 Hz, 1H), 7.19 (dd, *J* = 7.4 Hz, 1.3 Hz, 1H), 7.16-7.11 (m, 3H), 7.06-7.01 (m, 3H), 6.97-6.93 (m, 2H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 2H), 3.58 (q, *J* = 7.2 Hz, 2H), 0.64 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 163.6, 142.6, 140.4, 139.4, 135.6, 134.1, 133.1, 132.4, 132.1, 131.8, 130.4, 128.8, 128.6, 128.4, 128.2, 128.0, 127.5, 126.7, 126.6, 121.6, 118.3, 114.2, 112.0, 60.0, 13.3; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}BrN_2O_3+H]^+$ $[M+H]^+$ 565.1127, found: 565.1125.

Ethyl 4-benzoyl-2-(3-bromophenyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4j)



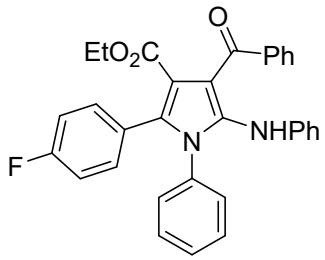
82.6 mg, 73% yield, Light yellow solid, m.p. 160.2-161.5 °C; R_f = 0.50 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 3H), 7.53 (d, *J* = 1.3 Hz, 1H), 7.49-7.42 (m, 3H), 7.34 (dd, *J* = 7.9 Hz, 0.9 Hz, 1H), 7.13 (dd, *J* = 7.8 Hz, 0.9 Hz, 1H), 7.08-7.01 (m, 6H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.1 Hz, 2H), 3.55 (q, *J* = 7.2 Hz, 2H), 0.72 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 164.2, 142.5, 140.3, 140.1, 135.6, 134.9, 132.5, 131.9, 131.8, 131.4, 130.4, 128.8, 128.69, 128.66, 128.6, 128.3, 128.1, 127.9, 121.8, 121.3, 118.7, 114.3, 112.4, 60.4, 13.4; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}BrN_2O_3+H]^+$ $[M+H]^+$ 565.1127, found: 565.1125.

Ethyl 4-benzoyl-2-(4-bromophenyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4k)



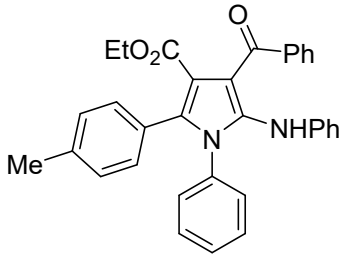
82.8 mg, 73% yield, Light yellow solid, m.p. 223.8-225.0 °C; R_f = 0.52 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 3H), 7.51-7.41 (m, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.08-7.00 (m, 5H), 6.93-6.89 (m, 2H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 2H), 3.52 (q, *J* = 7.2 Hz, 2H), 0.69 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 164.3, 142.4, 140.3, 140.0, 135.7, 133.5, 133.1, 131.9, 130.6, 128.72, 128.69, 128.65, 128.5, 128.3, 128.0, 127.9, 122.9, 121.8, 118.6, 114.0, 112.4, 60.4, 13.4; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}BrN_2O_3+H]^+$ $[M+H]^+$ 565.1127, found: 565.1121.

Ethyl 4-benzoyl-2-(4-fluorophenyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4l)



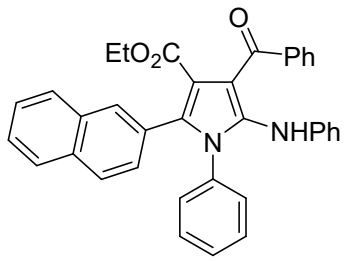
49.6 mg, 49% yield, Light yellow solid, m.p. 148.9-151.3 °C; R_f = 0.52 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 3H), 7.91 (d, *J* = 7.0 Hz, 2H), 7.51-7.42 (m, 3H), 7.28-7.25 (m, 2H), 7.06-7.01 (m, 5H), 6.94-6.87 (m, 4H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.1 Hz, 2H), 3.52 (q, *J* = 7.0 Hz, 2H), 0.69 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 164.3, 162.6 (d, *J* = 249.7 Hz), 142.5, 140.3, 139.9, 135.8, 133.8 (d, *J* = 8.4 Hz), 133.5, 131.8, 128.7, 128.6, 128.5, 128.3, 127.93, 127.89, 125.8 (d, *J* = 3.4 Hz), 121.7, 118.6, 114.5 (d, *J* = 21.7 Hz), 113.9, 112.2, 60.3, 13.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.38; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}FN_2O_3+H]^+$ $[M+H]^+$ 505.1927, found: 505.1925.

Ethyl 4-benzoyl-1-phenyl-5-(phenylamino)-2-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate (4m)



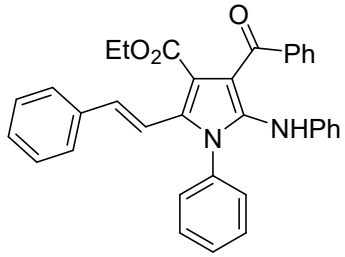
57.3 mg, 57% yield, Light yellow solid, m.p. 174.3-175.9 °C; R_f = 0.52 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.91 (m, 2H), 7.88 (s, 1H), 7.48-7.41 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.04-6.99 (m, 7H), 6.93-6.89 (m, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 3.51 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 0.67 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 164.4, 142.7, 140.4, 139.6, 138.2, 136.0, 134.9, 131.7, 128.7, 128.5, 128.3, 128.1, 127.9, 127.7, 126.7, 121.5, 118.5, 113.5, 112.4, 60.2, 21.4, 13.4; HRMS (ESI) *m/z* calculated for $[C_{33}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 501.2178, found: 501.2177.

Ethyl 4-benzoyl-2-(naphthalen-2-yl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4n)



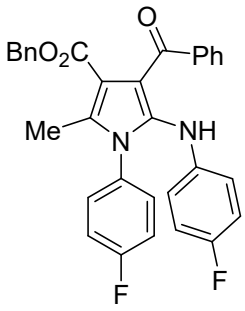
76.7 mg, 72% yield, Light yellow solid, m.p. 190.0-191.7 °C; R_f = 0.46 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 4H), 7.76-7.71 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.49-7.41 (m, 5H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 6.9 Hz, 2H), 7.01-6.95 (m, 3H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 2H), 3.49 (q, *J* = 7.2 Hz, 2H), 0.66 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 164.5. 142.6, 140.4, 136.0, 134.3, 132.8, 132.5, 132.0, 131.8, 128.8, 128.7, 128.6, 128.5, 128.34, 128.32, 127.9, 127.8, 127.6, 127.1, 126.7, 126.6, 126.1, 121.7, 118.6, 114.2, 112.4, 60.3, 13.4; HRMS (ESI) *m/z* calculated for $[C_{36}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 537.2178, found: 537.2177.

Ethyl (E)-4-benzoyl-1-phenyl-5-(phenylamino)-2-styryl-1*H*-pyrrole-3-carboxylate (4o)



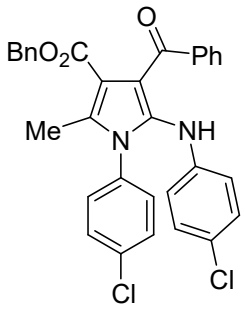
34.8 mg, 34% yield, Light yellow solid, m.p. 164.2-165.9 °C; R_f = 0.58 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.81 (m, 3H), 7.50-7.44 (m, 3H), 7.29-7.26 (m, 5H), 7.24-7.16 (m, 5H), 7.08 (d, *J* = 16.7 Hz, 1H), 6.97-6.93 (m, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 16.7 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 3.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 165.4, 142.3, 141.3, 140.6, 137.1, 136.3, 133.61, 131.59, 131.4, 129.1, 128.7, 128.58, 128.55, 128.3, 128.2, 128.0, 126.5, 122.2, 119.5, 115.6, 113.6, 112.8, 50.9; HRMS (ESI) *m/z* calculated for $[C_{34}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 513.2178, found: 513.2175.

Benzyl 4-benzoyl-1-(4-fluorophenyl)-5-((4-fluorophenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4p)



74.1 mg, 71% yield, Light yellow solid, m.p. 112.3-113.5 °C; R_f = 0.50 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.70 (s, 1H), 7.47-7.43 (m, 1H), 7.38-7.34 (m, 2H), 7.25-7.23 (m, 3H), 7.13-7.10 (m, 2H), 7.01-6.93 (m, 4H), 6.67-6.63 (m, 2H), 6.52-6.49 (m, 2H), 4.59 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 164.9, 162.1 (d, *J* = 250.7 Hz), 158.4 (d, *J* = 242.3 Hz), 140.4, 140.3, 138.6 (d, *J* = 2.4 Hz), 135.6, 133.4, 131.7, 131.6 (d, *J* = 3.3 Hz), 129.6 (d, *J* = 8.9 Hz), 128.5, 128.28, 128.27, 128.2, 127.9, 121.0 (d, *J* = 8.1 Hz), 116.2 (d, *J* = 23.1 Hz), 115.3 (d, *J* = 22.8 Hz), 111.8, 111.5, 65.9, 12.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.6, -120.9; HRMS (ESI) *m/z* calculated for $[C_{32}H_{24}F_2N_2O_3+H]^+$ $[M+H]^+$ 523.1833, found: 523.1828.

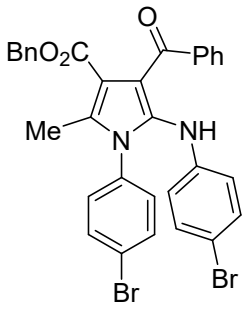
Benzyl 4-benzoyl-1-(4-chlorophenyl)-5-((4-chlorophenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4q)



106.5 mg, 96% yield, Light yellow solid, m.p. 156.8-158.7 °C; R_f = 0.50 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.47-7.43 (m, 1H), 7.36-7.32 (m, 2H), 7.29-7.22 (m, 6H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.00-6.98 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 8.6 Hz, 2H), 4.63 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 164.6, 141.9, 139.8, 137.2, 135.5, 134.8, 134.0, 133.7, 132.0, 129.5, 129.0, 128.7, 128.6, 128.30, 128.26, 128.0, 126.4, 118.7, 113.8, 112.1, 65.9, 12.3; HRMS (ESI) *m/z* calculated for $[C_{32}H_{24}Cl_2N_2O_3+H]^+$ $[M+H]^+$ 555.1242, found: 555.1239.

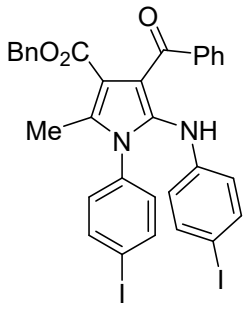
Benzyl 4-benzoyl-1-(4-bromophenyl)-5-((4-bromophenyl)amino)-2-methyl-1*H*-pyrrole-3-

carboxylate (4r)



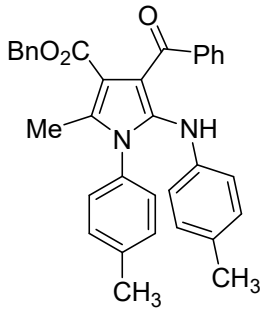
109.1 mg, 85% yield, Light yellow solid, m.p. 163.4-165.7 ºC; R_f = 0.46 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.50-7.47 (m, 3H), 7.39-7.35 (m, 2H), 7.29-7.25 (m, 3H), 7.22 (s, 1H), 7.11-7.08 (m, 4H), 7.03-7.00 (m, 2H), 6.42 (d, *J* = 8.7 Hz, 2H), 4.65 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 164.6, 142.5, 139.8, 136.8, 135.5, 134.5, 133.7, 132.5, 132.0, 131.7, 129.2, 128.6, 128.30, 128.26, 128.0, 122.9, 119.0, 114.0, 113.8, 112.1, 66.0, 12.3; HRMS (ESI) *m/z* calculated for $[C_{32}H_{24}Br_2N_2O_3+H]^+$ $[M+H]^+$ 643.0232, found: 643.0221.

Benzyl 4-benzoyl-1-(4-iodophenyl)-5-((4-iodophenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4s)



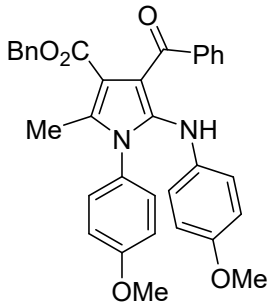
115.0 mg; 78% yield, Light yellow solid, m.p. 137.0-138.9 ºC; R_f = 0.46 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.46-7.42 (m, 1H), 7.36-7.31 (m, 2H), 7.24-7.19 (m, 5H), 7.12 (s, 1H), 6.99-6.97 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.25 (d, *J* = 8.5 Hz, 2H), 4.64 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 164.5, 143.6, 139.6, 138.5, 137.5, 135.8, 135.5, 135.1, 133.8, 132.1, 129.5, 128.7, 128.32, 128.28, 128.26, 128.0, 118.9, 114.8, 112.1, 94.6, 83.3, 66.0, 12.4; HRMS (ESI) *m/z* calculated for $[C_{32}H_{24}I_2N_2O_3+H]^+$ $[M+H]^+$ 738.9955, found: 738.9955.

Benzyl 4-benzoyl-2-methyl-1-(*p*-tolyl)-5-(*p*-tolylamino)-1*H*-pyrrole-3-carboxylate (4t)



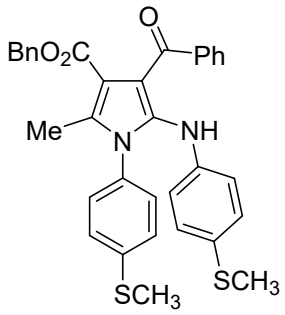
82.2 mg, 80% yield, Light yellow solid, m.p. 129.8-132.0 °C; R_f = 0.60 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.54 (s, 1H), 7.44-7.40 (m, 1H), 7.35-7.31 (m, 2H), 7.24-7.22 (m, 3H), 7.09-7.01 (m, 4H), 7.04-7.00 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.44 (d, *J* = 8.2 Hz, 2H), 4.59 (s, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 165.1, 140.6, 140.4, 140.0, 138.4, 135.7, 133.7, 133.2, 131.5, 131.0, 129.6, 129.0, 128.6, 128.25, 128.23, 128.1, 127.8, 127.5, 118.7, 111.8, 111.5, 65.8, 21.1, 20.1, 12.3; HRMS (ESI) *m/z* calculated for $[C_{34}H_{30}N_2O_3+H]^+$ $[M+H]^+$ 515.2335, found: 515.2330.

Benzyl 4-benzoyl-1-(4-methoxyphenyl)-5-((4-methoxyphenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4u)



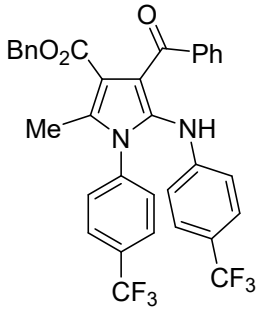
79.7 mg, 73% yield, Light yellow solid, m.p. 113.5-115.3 °C; R_f = 0.27 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.45-7.42 (m, 1H), 7.37-7.34 (m, 2H), 7.25-7.22 (m, 3H), 7.01-6.99 (m, 4H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 9.0 Hz, 2H), 6.49 (d, *J* = 9.0 Hz, 2H), 4.56 (s, 2H), 3.72 (s, 3H), 3.63 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 165.3, 159.3, 155.4, 142.7, 140.9, 135.7, 135.5, 133.7, 131.3, 129.0, 128.5, 128.2, 128.1, 127.8, 122.3, 114.2, 113.8, 111.3, 109.8, 65.7, 55.4, 12.1; HRMS (ESI) *m/z* calculated for $[C_{34}H_{30}N_2O_5+H]^+$ $[M+H]^+$ 547.2233, found: 547.2229.

Benzyl 4-benzoyl-2-methyl-1-(4-(methylthio)phenyl)-5-((4-(methylthio)phenyl)amino)-1*H*-pyrrole-3-carboxylate (4v)



70.1 mg, 61% yield, Light yellow solid, m.p. 57.9-59.3 °C; R_f = 0.34 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.46-7.42 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.25-7.22 (m, 3H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.01-6.98 (m, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.47 (d, *J* = 8.6 Hz, 2H), 4.61 (s, 2H), 2.41 (s, 3H), 2.30 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 164.9, 141.3, 140.2, 139.8, 138.5, 135.6, 133.8, 132.3, 131.7, 129.9, 128.9, 128.6, 128.3, 128.24, 128.19, 128.0, 127.9, 126.4, 118.9, 112.7, 111.7, 65.8, 17.6, 15.5, 12.3; HRMS (ESI) *m/z* calculated for $[C_{34}H_{30}N_2O_3S_2+H]^+$ $[M+H]^+$ 579.1776, found: 579.1770.

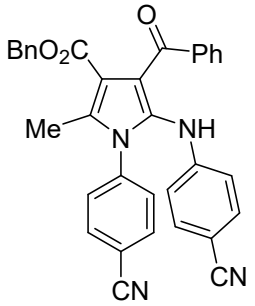
Benzyl 4-benzoyl-2-methyl-1-(4-(trifluoromethyl)phenyl)-5-((4-(trifluoromethyl)phenyl) amino)-1*H*-pyrrole-3-carboxylate (4w)



106..1 mg, 85% yield, Light yellow solid, m.p. 134.9-136.0 °C; R_f = 0.44 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.49-7.45 (m, 1H), 7.36-7.32 (m, 4H), 7.25-7.21 (m, 3H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 1H), 7.00-6.98 (m, 2H), 6.50 (d, *J* = 8.4 Hz, 2H), 4.70 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 164.3, 146.9, 139.2, 138.4, 135.4, 133.99, 133.92, 132.4, 131.1 (q, *J* = 33.2 Hz), 128.8, 128.33, 128.27, 128.2, 128.0, 126.5 (q, *J* = 3.7 Hz), 126.2 (q, *J* = 3.8 Hz), 125.2 (q, *J* = 85.3 Hz), 122.6 (q, *J* = 32.9 Hz), 122.5 (q, *J* = 86.8 Hz), 116.3, 115.5, 112.4, 66.1, 12.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.7, -62.8; HRMS (ESI) *m/z* calculated for $[C_{34}H_{24}F_6N_2O_3+H]^+$ $[M+H]^+$ 623.1769, found: 623.1760.

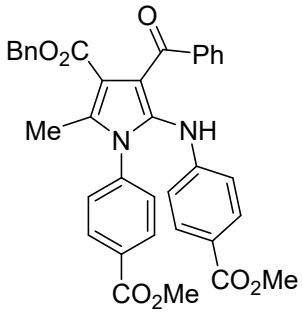
Benzyl 4-benzoyl-1-(4-cyanophenyl)-5-((4-cyanophenyl)amino)-2-methyl-1*H*-pyrrole-3-

carboxylate (4x)



57.0 mg, 53% yield, Light yellow solid, m.p. 184.6-186.9 °C; R_f = 0.40 (PE/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.52-7.48 (m, 1H), 7.38-7.33 (m, 4H), 7.26-7.17 (m, 6H), 6.98 (d, *J* = 7.1 Hz, 2H), 6.44 (d, *J* = 7.6 Hz, 2H), 4.74 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 163.9, 148.3, 138.9, 138.6, 135.3, 134.2, 133.4, 133.3, 132.9, 131.4, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 119.2, 118.2, 117.5, 114.8, 113.2, 112.7, 102.7, 66.2, 12.5; HRMS (ESI) *m/z* calculated for $[C_{34}H_{24}N_4O_3+H]^+$ $[M+H]^+$ 537.1927, found: 537.1925.

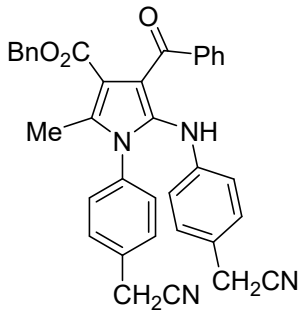
Benzyl 4-benzoyl-1-(4-(methoxycarbonyl)phenyl)-5-((4-(methoxycarbonyl)phenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4y)



89.2 mg, 74% yield, Light yellow solid, m.p. 160.3-162.9 °C; R_f = 0.49 (PE/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.47-7.43 (m, 1H), 7.35-7.29 (m, 4H), 7.23-7.21 (m, 4H), 7.00-6.98 (m, 2H), 6.44 (d, *J* = 8.6 Hz, 2H), 4.71 (s, 2H), 3.87 (s, 3H), 3.76 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 166.7, 165.8, 164.3, 148.3, 139.22, 139.18, 135.5, 134.1, 133.3, 132.4, 130.9, 130.6, 130.5, 128.8, 128.3, 128.2, 127.9, 127.7, 121.8, 116.7, 114.6, 112.3, 66.0, 52.4, 51.7, 12.5; HRMS (ESI) *m/z* calculated for $[C_{36}H_{30}N_2O_7+H]^+$ $[M+H]^+$ 603.2131, found: 603.2129.

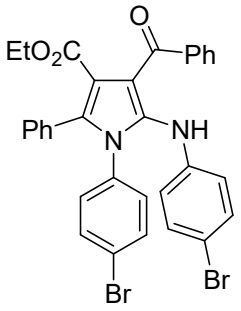
Benzyl 4-benzoyl-1-(4-(cyanomethyl)phenyl)-5-((4-(cyanomethyl)phenyl)amino)-2-methyl-

1*H*-pyrrole-3-carboxylate (4z)



89.4 mg, 79% yield, Light yellow solid, m.p. 68.5-70.1 °C; R_f = 0.23 (PE/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39 (s, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.26-7.19 (m, 7H), 7.01-6.98 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 8.4 Hz, 2H), 4.63 (s, 2H), 3.66 (s, 2H), 3.47 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 164.7, 143.0, 139.9, 131.2, 135.6, 135.4, 133.6, 132.0, 130.7, 128.8, 128.6, 128.5, 128.4, 128.31, 128.26, 128.2, 127.9, 122.5, 118.3, 118.0, 117.4, 113.6, 112.0, 65.9, 23.2, 22.8, 12.4; HRMS (ESI) *m/z* calculated for $[C_{36}H_{28}N_4O_3+H]^+$ $[M+H]^+$ 565.2240, found: 565.2238.

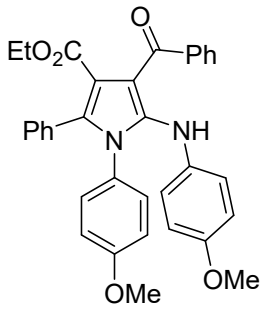
Ethyl 4-benzoyl-1-(4-bromophenyl)-5-((4-bromophenyl)amino)-2-phenyl-1*H*-pyrrole-3-carboxylate (4aa)



92.5 mg, 72% yield, Light yellow solid, m.p. 247.0-248.3 °C; R_f = 0.42 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 1H), 7.55 (s, 1H), 7.53-7.49 (m, 1H), 7.46-7.42 (m, 2H), 7.26-7.21 (m, 7H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.45 (d, *J* = 8.6 Hz, 2H), 3.54 (q, *J* = 7.1 Hz, 2H), 0.67 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 164.0, 142.3, 139.8, 137.9, 134.78, 134.73, 132.2, 132.0, 131.8, 131.7, 129.32, 129.29, 128.71, 128.70, 127.6, 122.1, 119.2, 114.1, 113.9, 113.8, 60.4, 13.3; HRMS (ESI) *m/z* calculated for $[C_{32}H_{24}Br_2N_2O_3+H]^+$ $[M+H]^+$ 643.0232, found: 643.0232.

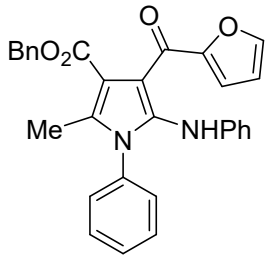
Ethyl 4-benzoyl-1-(4-methoxyphenyl)-5-((4-methoxyphenyl)amino)-2-phenyl-1*H*-pyrrole-3-

carboxylate (4ab)



82.0 mg, 75% yield, Light yellow solid, m.p. 48.2-50.8 °C; R_f = 0.29 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.91-7.89 (m, 2H), 7.48-7.42 (m, 3H), 7.26-7.18 (m, 5H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.52-6.48 (m, 4H), 3.63 (s, 3H), 3.62 (s, 3H), 3.48 (q, *J* = 7.2 Hz, 2H), 0.68 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 164.7, 158.7, 155.4, 143.2, 140.9, 135.4, 134.5, 131.8, 131.5, 129.9, 129.2, 128.8, 128.5, 128.2, 127.3, 122.2, 113.8, 113.6, 113.4, 109.9, 60.2, 55.4, 55.3, 13.4; HRMS (ESI) *m/z* calculated for $[C_{34}H_{30}N_2O_5+H]^+$ $[M+H]^+$ 547.2233, found: 547.2229.

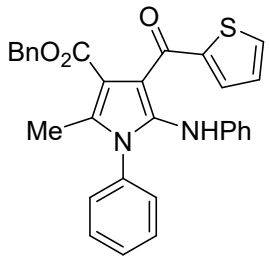
Benzyl 4-(furan-2-carbonyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ac)



76.2 mg, 80% yield, Light yellow solid, m.p. 148.3-149.2 °C; R_f = 0.37 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.39 (s, 1H), 7.27-7.25 (m, 3H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.20-7.13 (m, 5H), 7.08 (d, *J* = 3.5 Hz, 1H), 6.91 (t, *J* = 7.7 Hz, 2H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 1.9 Hz, 1H), 4.97 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 165.5, 154.3, 145.1, 142.3, 139.6, 135.8, 135.7, 133.6, 129.0, 128.5, 128.4, 128.4, 128.0, 127.7, 121.8, 118.8, 116.3, 112.2, 111.5, 110.9, 66.3, 12.3; HRMS (ESI) *m/z* calculated for $[C_{30}H_{24}N_2O_4+H]^+$ $[M+H]^+$ 477.1814, found: 477.1817.

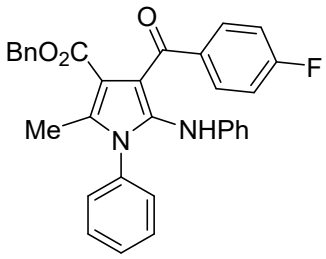
Benzyl 2-methyl-1-phenyl-5-(phenylamino)-4-(thiophene-2-carbonyl)-1*H*-pyrrole-3-

carboxylate (4ad)



25.1 mg, 26% yield, Light yellow solid, m.p. 184.9-186.9 °C; R_f = 0.42 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.7 Hz, 1H), 7.49 (d, *J* = 4.9 Hz, 1H), 7.29-7.23 (m, 6H), 7.19-7.17 (m, 2H), 7.10 (s, 1H), 7.08-7.06 (m, 2H), 7.00-6.98 (m, 1H), 6.92 (t, *J* = 7.7 Hz, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.87 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.5, 165.1, 146.2, 143.1, 137.2, 135.62, 135.59, 134.2, 132.2, 132.1, 129.0, 128.6, 128.5, 128.3, 127.9, 127.8, 127.6, 121.2, 117.8, 113.4, 111.2, 100.0, 66.2, 12.4; HRMS (ESI) *m/z* calculated for $[C_{30}H_{24}N_2O_3S+H]^+$ $[M+H]^+$ 493.1586, found: 493.1589.

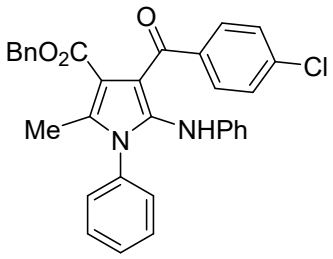
Benzyl 4-(4-fluorobenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ae)



74.3 mg, 74% yield, Light yellow solid, m.p. 170.3-172.0 °C; R_f = 0.49 (PE/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.8 Hz, 5.5 Hz, 2H), 7.38 (s, 1H), 7.27-7.22 (m, 6H), 7.19-7.18 (m, 2H), 7.05-7.03 (m, 2H), 6.95-6.91 (m, 4H), 6.69-6.66 (m, 1H), 6.51 (dd, *J* = 8.6 Hz, 1.1 Hz, 2H), 4.74 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 164.88, 164.87 (d, *J* = 251.1 Hz), 142.9, 138.5, 136.5 (d, *J* = 2.9 Hz), 135.7, 135.6, 134.1, 131.1 (d, *J* = 9.0 Hz), 129.1, 128.7, 128.6, 128.41, 128.37, 128.1, 127.9, 121.5, 118.2, 115.2 (d, *J* = 21.6 Hz), 112.6, 111.4, 66.0, 12.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -107.38; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}FN_2O_3+H]^+$ $[M+H]^+$ 505.1927, found: 505.1925.

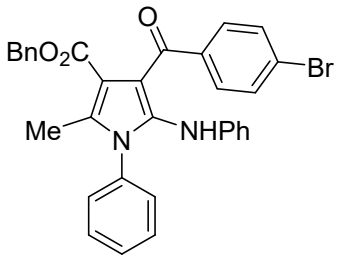
Benzyl 4-(4-chlorobenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate

(4af)



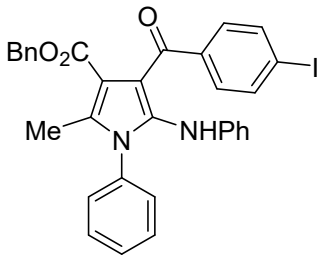
52.0 mg, 50% yield, Light yellow solid, m.p. 158.7-159.4 °C; R_f = 0.53 (PE/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.49 (s, 1H), 7.27-7.25 (m, 5H), 7.23-7.21 (m, 3H), 7.19-7.17 (m, 2H), 7.04-7.02 (m, 2H), 6.94-6.90 (m, 2H), 6.70-6.67 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 2H), 4.73 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 164.8, 142.7, 139.0, 138.7, 137.8, 135.7, 135.5, 134.2, 130.0, 128.7, 128.6, 128.45, 128.40, 128.38, 128.1, 127.8, 121.7, 118.5, 112.2, 111.4, 66.1, 12.5; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}ClN_2O_3+H]^+$ $[M+H]^+$ 521.1632, found: 521.1624.

Benzyl 4-(4-bromobenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ag)



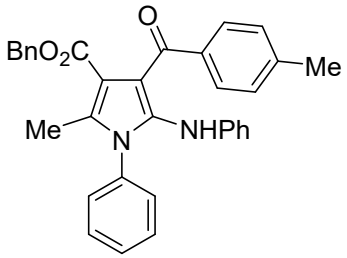
76.7 mg, 68% yield, Light yellow solid, m.p. 146.2-147.6 °C; R_f = 0.54 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.51 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.28-7.21 (m, 6H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.04-7.02 (m, 2H), 6.92 (t, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 2H), 4.73 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 164.8, 142.6, 139.06, 139.02, 135.6, 135.5, 134.1, 131.3, 130.1, 129.1, 128.63, 128.56, 128.4, 128.3, 128.0, 127.8, 126.4, 121.7, 118.4, 112.1, 111.3, 66.0, 12.4; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}BrN_2O_3+H]^+$ $[M+H]^+$ 565.1127, found: 565.1128.

Benzyl 4-(4-iodobenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ah)



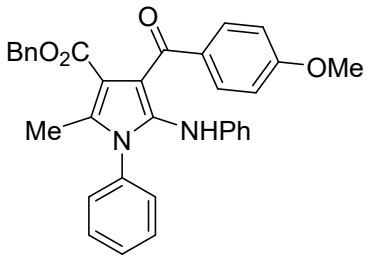
87.8 mg, 72% yield, Light yellow solid, m.p. 173.5-174.6 °C; R_f = 0.54 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.28-7.24 (m, 5H), 7.22-7.19 (m, 1H), 7.18-7.16 (m, 2H), 7.04-7.02 (m, 2H), 6.92 (t, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 4.72 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 164.8, 142.6, 139.6, 139.1, 137.3, 135.6, 135.5, 134.1, 130.0, 129.1, 128.63, 128.56, 128.39, 128.35, 128.1, 127.8, 121.7, 118.5, 112.0, 111.3, 99.1, 66.1, 12.4; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}IN_2O_3+H]^+$ $[M+H]^+$ 613.0988, found: 613.0986.

Benzyl 2-methyl-4-(4-methylbenzoyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ai)



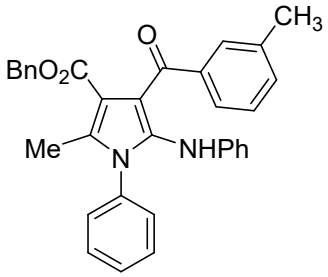
80.0 mg, 80% yield, Light yellow solid, m.p. 159.8-161.3 °C; R_f = 0.49 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.39 (s, 1H), 7.26-7.20 (m, 8H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.02-7.00 (m, 2H), 6.93-6.89 (m, 2H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 4.67 (s, 2H), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 165.1, 143.1, 142.2, 138.1, 137.6, 135.74, 135.71, 133.6, 129.0, 128.8, 128.5, 128.3, 128.2, 127.83, 127.81, 121.3, 118.0, 113.0, 111.7, 65.9, 21.7, 12.4; HRMS (ESI) *m/z* calculated for $[C_{33}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 501.2178, found: 501.2177.

Benzyl 4-(4-methoxybenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4aj)



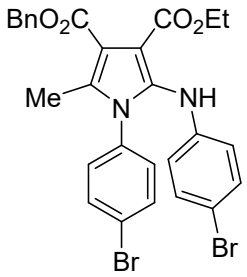
74.7 mg, 72% yield, Light yellow solid, m.p. 176.9-179.8 °C; R_f = 0.28 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.28-7.18 (m, 8H), 7.15 (s, 1H), 7.03-7.01 (m, 2H), 6.91 (t, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 2H), 4.75 (s, 2H), 3.81 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 165.0, 162.5, 143.5, 137.1, 135.7, 133.8, 132.9, 130.9, 129.0, 128.5, 128.3, 128.2, 127.0, 121.0, 117.5, 113.8, 113.4, 111.5, 65.9, 55.4, 12.4; HRMS (ESI) *m/z* calculated for $[C_{33}H_{28}N_2O_4+H]^+$ $[M+H]^+$ 517.2127, found: 517.2126.

Benzyl 2-methyl-4-(3-methylbenzoyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ak)



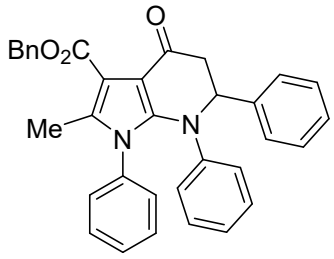
89.5 mg, 90% yield, Light yellow solid, m.p. 123.6-125.1 °C; R_f = 0.49 (PE/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.57 (m, 3H), 7.26-7.21 (m, 7H), 7.20-7.17 (m, 3H), 7.02-6.98 (m, 2H), 6.94-6.90 (m, 2H), 6.69-6.65 (m, 1H), 6.54-6.52 (m, 2H), 4.62 (s, 2H), 2.31 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 165.2, 142.9, 140.4, 139.0, 138.0, 135.8, 135.7, 133.5, 132.5, 129.2, 129.1, 128.6, 128.30, 128.27, 128.1,, 127.91, 127.85, 126.1, 121.6, 118.5, 112.5, 111.9, 66.0, 21.4, 12.4; HRMS (ESI) *m/z* calculated for $[C_{33}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 501.2178, found: 501.2177.

3-Benzyl 4-ethyl 1-(4-bromophenyl)-5-((4-bromophenyl)amino)-2-methyl-1*H*-pyrrole-3,4-dicarboxylate (4al)



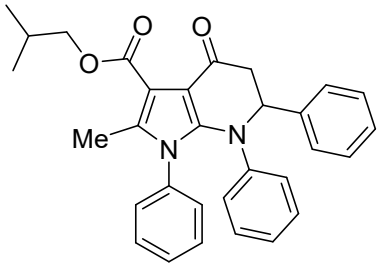
85.4 mg, 70% yield, Light yellow solid, m.p. 49.1-51.8 °C; R_f = 0.35 (PE/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 4H), 7.41-7.34 (m, 3H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.44 (d, *J* = 8.7 Hz, 2H), 6.41 (s, 1H), 5.34 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.21 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 164.7, 143.2, 136.1, 134.4, 132.5, 132.2, 131.7, 129.3, 128.5, 128.3, 128.1, 122.9, 118.5, 113.5, 111.9, 106.5, 66.4, 60.4, 14.1, 12.2; HRMS (ESI) *m/z* calculated for $[C_{32}H_{25}BrN_2O_3+H]^+$ $[M+H]^+$ 565.1127, found: 565.1128; HRMS (ESI) *m/z* calculated for $[C_{28}H_{24}Br_2N_2O_4+H]^+$ $[M+H]^+$ 611.0181, found: 611.0077.

Benzyl 2-methyl-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b]pyridine-3-carboxylate (6a)



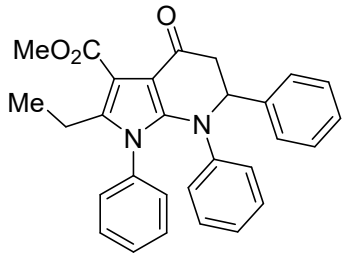
52.5 mg, 51% yield, Light yellow solid, m.p. 128.3-130.3 °C; R_f = 0.28 (PE/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.38-7.33 (m, 4H), 7.31-7.27 (m, 2H), 7.18-7.11 (m, 3H), 7.06-7.02 (m, 2H), 6.94-6.91 (m, 1H), 6.87-6.70 (m ,4H), 5.38 (d, *J* = 12.6 Hz, 1H), 5.34 (d, *J* = 12.6 Hz, 1H), 4.92 (t, *J* = 4.4 Hz, 1H), 3.18 (dd, *J* = 13.2 Hz, 5.3 Hz, 1H), 2.93 (dd, *J* = 13.2 Hz, 3.8 Hz, 1H), 3.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.0, 165.0, 147.2, 146.0, 140.0, 136.7, 135.7, 135.2, 129.0, 128.83, 128.81, 128.54, 128.53, 128.4, 128.3, 127.8, 127.2, 124.9, 124.3, 109.44, 109.40, 67.0, 66.4, 39.4, 12.2; HRMS (ESI) *m/z* calculated for $[C_{34}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 513.2178, found: 513.2179.

Isobutyl 2-methyl-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b]pyridine-3-carboxylate (6b)



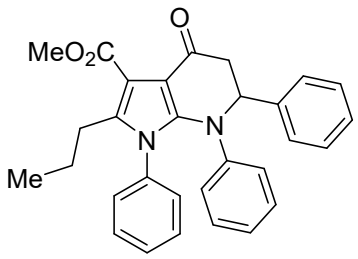
44.9 mg, 47% yield, Light yellow solid, m.p. 124.5-125.6 °C; R_f = 0.35 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.38-7.35 (m, 2H), 7.31-7.26 (m, 1H), 7.23-7.14 (m, 2H), 7.06-7.03 (m, 3H), 6.94-6.91 (m, 1H), 6.83-6.80 (m, 4 H), 4.92 (t, *J* = 4.4 Hz, 1H), 4.11 (dd, *J* = 10.6 Hz, 6.6 Hz, 1H), 4.06 (dd, *J* = 10.6 Hz, 6.8 Hz, 1H), 3.17 (dd, *J* = 17.3 Hz, 3.0 Hz, 1H), 2.91 (dd, *J* = 17.3 Hz, 3.8 Hz, 1H), 2.14-2.06 (m, 1H), 2.10 (s, 3H), 1.04 (d, *J* = 3.3 Hz, 3H), 1.03 (d, *J* = 3.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.0, 165.4, 147.0, 146.1, 140.1, 135.4, 135.3, 129.0, 128.6, 127.9, 127.3, 124.8, 124.2, 109.9, 109.5, 70.9, 67.0, 39.4, 28.0, 19.52, 19.49, 12.2; HRMS (ESI) *m/z* calculated for $[C_{31}H_{30}N_2O_3+H]^+$ $[M+H]^+$ 479.2335, found: 479.2334.

Methyl 2-ethyl-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b]pyridine-3-carboxylate (6c)



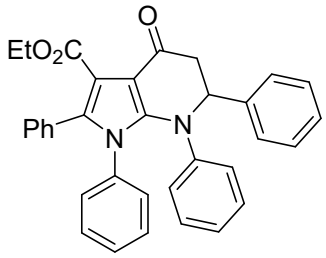
30.4 mg, 34% yield, Light yellow solid, m.p. 46.9-49.7 °C; R_f = 0.17 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.37-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.18 (m, 1H), 7.07-7.04 (m, 3H), 6.97-6.89 (m, 2H), 6.81-6.78 (m, 2H), 6.77-6.69 (m, 1H), 4.89 (t, *J* = 4.6 Hz, 1H), 3.90 (s, 3H), 3.17 (dd, *J* = 17.3 Hz, 5.3 Hz, 1H), 2.93 (dd, *J* = 17.1 Hz, 4.3 Hz, 1H), 2.61-2.44 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.4, 165.6, 147.6, 146.3, 141.7, 140.0, 135.2, 129.0, 128.7, 128.6, 127.9, 127.3, 125.1, 124.7, 109.2, 108.6, 67.1, 51.6, 39.6, 18.8, 14.3; HRMS (ESI) *m/z* calculated for $[C_{29}H_{26}N_2O_3+H]^+$ $[M+H]^+$ 451.2022, found: 451.2019.

Methyl 4-oxo-1,6,7-triphenyl-2-propyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*b*]pyridine-3-carboxylate (6d)



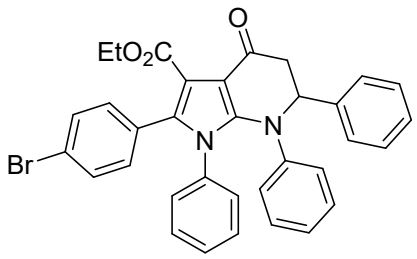
34.4 mg, 36% yield, Light yellow solid, m.p. 44.2-46.0 °C; R_f = 0.24 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.36-7.33 (m, 2H), 7.30-7.29 (m, 2H), 7.21-7.18 (m, 1H), 7.06-7.03 (m, 3H), 6.96-6.93 (m, 2H), 6.79-6.72 (m, 3H), 4.89 (t, *J* = 4.7 Hz, 1H), 4.39-4.34 (m, 2H), 3.16 (dd, *J* = 17.1 Hz, 5.3 Hz, 1H), 2.92 (dd, *J* = 17.1 Hz, 4.3 Hz, 1H), 2.55-2.49 (m, 1H), 2.44-2.38 (m, 1H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.34-1.29 (m, 2H), 0.70 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.3, 165.2, 147.6, 146.4, 140.1, 139.8, 135.3, 129.0, 128.65, 128.56, 127.8, 127.3, 125.0, 124.7, 109.6, 109.4, 100.0, 67.2, 60.4, 39.6, 27.2, 23.2, 14.4, 13.9; HRMS (ESI) *m/z* calculated for $[C_{30}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 479.2335, found: 479.2329.

Ethyl 4-oxo-1,2,6,7-tetraphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b]pyridine-3-carboxylate (6e)



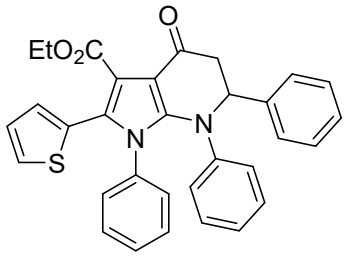
47.2 mg, 46% yield, Light yellow solid, m.p. 170.7-172.8 °C; R_f = 0.20 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.40-7.37 (m, 2H), 7.33-7.30 (m, 1H), 7.14-6.96 (m, 1H), 6.90-6.85 (m, 3H), 6.77-6.62 (m, 1H), 5.00 (t, *J* = 4.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.24 (dd, *J* = 17.0 Hz, 5.3 Hz, 1H), 2.96 (dd, *J* = 17.0 Hz, 3.9 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.7, 165.1, 147.2, 146.2, 140.1, 135.6, 135.1, 130.7, 129.9, 129.0, 128.7, 128.6, 128.4, 128.1, 128.0, 127.6, 127.3, 124.8, 124.3, 111.9, 109.7, 67.6, 60.8, 39.5, 13.9; HRMS (ESI) *m/z* calculated for $[C_{34}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 513.2178, found: 513.2175.

Ethyl 2-(4-bromophenyl)-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*b*] pyridine-3- carboxylate (6f)



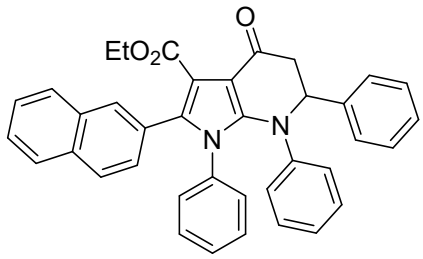
38.9 mg, 33% yield, Light yellow solid, m.p. 179.3-181.0 °C; R_f = 0.48 (PE/EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.40-7.37 (m, 2H), 7.33-7.30 (m, 1H), 7.24-7.22 (m, 2H), 7.03-6.83 (m, 11H), 6.69-6.67 (m, 1H), 4.99 (t, *J* = 4.5 Hz, 1H), 4.21 (dq, *J* = 7.2 Hz, 1.6 Hz, 2H), 3.22 (dd, *J* = 17.1 Hz, 4.8 Hz, 1H), 2.95 (dd, *J* = 17.1 Hz, 4.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.6, 164.9, 147.4, 146.0, 140.0, 135.4, 133.6, 132.3, 130.9, 129.1, 128.83, 128.76, 128.6, 128.2, 128.0, 127.3, 125.0, 124.4, 122.6, 112.2, 109.7, 67.5, 61.0, 39.5, 14.0; HRMS (ESI) *m/z* calculated for $[C_{34}H_{27}BrN_2O_3+H]^+$ $[M+H]^+$ 591.1283, found: 591.1279.

Ethyl 4-oxo-1,6,7-triphenyl-2-(thiophen-2-yl)-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*b*]pyridine-3-carboxylate (6g)



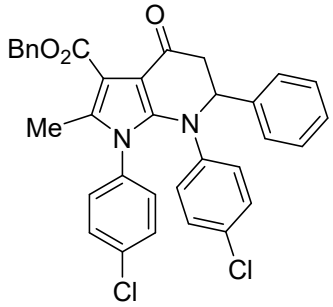
37.3 mg, 36% yield, Brown solid, m.p. 138.8-140.3 °C; R_f = 0.24 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.40-7.37 (m, 2H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 4.8 Hz, 1.5 Hz, 1H), 7.08-7.01 (m, 6H), 6.93-6.90 (m, 1H), 6.87-6.85 (m, 2H), 6.81-6.78 (m, 3H), 4.98 (t, *J* = 4.7 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.22 (dd, *J* = 17.1 Hz, 5.3 Hz, 1H), 2.96 (dd, *J* = 17.1 Hz, 4.3 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.3, 165.0, 147.5, 145.9, 139.9, 135.3, 130.01, 129.97, 128.9, 128.7, 128.4, 128.3, 127.9, 127.4, 127.2, 126.3, 125.0, 124.6, 109.4, 67.5, 61.1, 39.6, 14.0; HRMS (ESI) *m/z* calculated for $[C_{32}H_{26}N_2O_3S+H]^+$ $[M+H]^+$ 519.1742, found: 519.1739.

Ethyl 2-(naphthalen-2-yl)-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b] pyridine-3-carboxylate (6h)



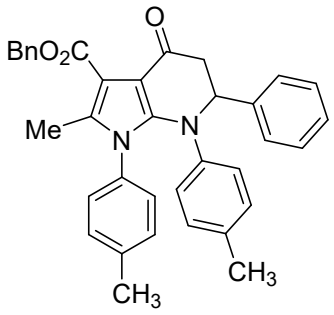
42.5 mg, 38% yield, Light yellow solid, m.p. 140.0-141.0 °C; R_f = 0.42 (PE/EtOAc = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.67 (m, 1H), 7.64-7.61 (m, 2H), 7.54-7.52 (m, 3H), 7.42-7.37 (m, 4H), 7.35-7.32 (m, 1H), 7.08 (dd, *J* = 8.5 Hz, 1.8 Hz, 1H), 7.04-7.01 (m, 2H), 6.96-6.69 (m, 8H), 5.02 (t, *J* = 4.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.27 (dd, *J* = 17.1 Hz, 5.3 Hz, 1H), 2.97 (dd, *J* = 17.0 Hz, 3.9 Hz, 1H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.7, 165.2, 147.3, 146.2, 140.1, 135.6, 134.7, 132.7, 132.6, 130.5, 129.0, 128.8, 128.6, 128.5, 128.2, 128.02, 128.01, 127.9, 127.6, 127.33, 127.31, 127.1, 126.5, 126.2, 124.9, 124.3, 112.3, 109.9, 67.6, 60.9, 39.4, 14.0; HRMS (ESI) *m/z* calculated for $[C_{38}H_{30}N_2O_3+H]^+$ $[M+H]^+$ 563.2335, found: 563.2331.

Benzyl 1,7-bis(4-chlorophenyl)-2-methyl-4-oxo-6-phenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b] pyridine-3-carboxylate (6i)



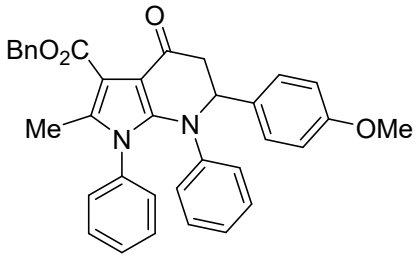
57.1 mg, 49% yield, Light yellow solid, m.p. 199.1-200.9 °C; R_f = 0.24 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.41-7.38 (m, 3H), 7.37-7.34 (m, 3H), 7.33-7.28 (m, 3H), 7.26-7.17 (m, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.81-6.68 (m, 4H), 5.37 (d, *J* = 12.5 Hz, 1H), 5.34 (d, *J* = 12.5 Hz, 1H), 4.89 (t, *J* = 4.8 Hz, 1H), 3.10 (dd, *J* = 17.3 Hz, 5.1 Hz, 1H), 2.95 (dd, *J* = 17.3 Hz, 4.5 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.0, 164.8, 146.7, 144.5, 139.3, 136.5, 135.6, 135.0, 133.6, 130.6, 129.5, 129.4, 129.3, 128.7, 128.5, 128.4, 128.2, 128.0, 127.4, 125.6, 109.90, 109.87, 67.3, 66.6, 39.4, 12.2; HRMS (ESI) *m/z* calculated for $[C_{34}H_{26}Cl_2N_2O_3+H]^+$ $[M+H]^+$ 581.1399, found: 581.1396.

Benzyl 2-methyl-4-oxo-6-phenyl-1,7-di-p-tolyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*b*]pyridine-3-carboxylate (6j)



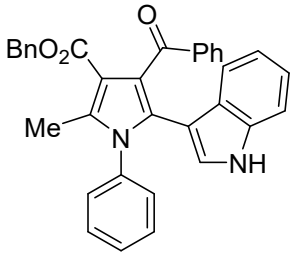
40.1 mg, 37% yield, Light yellow solid, m.p. 157.3-159.1 °C; R_f = 0.23 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.38-7.26 (m, 7H), 7.03-6.83 (m, 4H), 6.72-6.59 (m, 3H), 5.37 (d, *J* = 12.6 Hz, 1H), 5.34 (d, *J* = 12.5 Hz, 1H), 4.85 (t, *J* = 4.6 Hz, 1H), 3.16 (dd, *J* = 17.2 Hz, 5.2 Hz, 1H), 2.91 (dd, *J* = 17.2 Hz, 4.1 Hz, 1H), 2.25 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.2, 165.1, 148.0, 143.7, 140.2, 138.5, 136.8, 136.1, 134.7, 132.7, 129.5, 128.51, 128.48, 128.4, 127.9, 127.8, 127.3, 124.4, 109.22, 109.15, 67.1, 66.4, 39.4, 21.2, 20.9, 12.2; HRMS (ESI) *m/z* calculated for $[C_{36}H_{32}N_2O_3+H]^+$ $[M+H]^+$ 541.2491, found: 541.2487.

Benzyl 6-(4-methoxyphenyl)-2-methyl-4-oxo-1,7-diphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo [2,3-b]pyridine-3-carboxylate (6k)



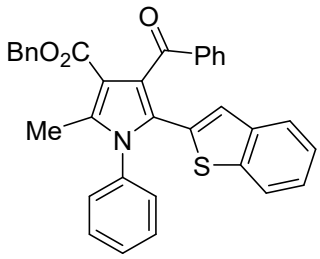
41.2 mg, 38% yield, Light yellow solid, R_f = 0.14 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.54 (m, 2H), 7.40-7.35 (m, 4H), 7.31-7.28 (m, 1H), 7.18-7.15 (m, 2H), 7.05-7.02 (m, 3H), 6.93-6.90 (m, 1H), 6.88-6.86 (m, 3H), 6.80-6.78 (m, 3H), 5.38 (d, *J* = 12.5 Hz, 1H), 5.35 (d, *J* = 12.5 Hz, 1H), 4.89 (t, *J* = 4.4 Hz, 1H), 3.79 (s, 3H), 3.14 (dd, *J* = 17.3 Hz, 5.1 Hz, 1H), 2.90 (dd, *J* = 17.3 Hz, 4.0 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.5, 165.1, 159.1, 147.2, 145.9, 136.7, 135.8, 135.2, 129.0, 128.61, 128.57, 128.5, 128.4, 127.9, 124.8, 124.3, 113.9, 109.5, 109.4, 66.53, 66.46, 55.4, 39.5, 12.3; HRMS (ESI) *m/z* calculated for $[C_{35}H_{30}N_2O_4+H]^+$ $[M+H]^+$ 543.2284, found: 543.2284.

Benzyl 4-benzoyl-5-(1*H*-indol-3-yl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (7a)



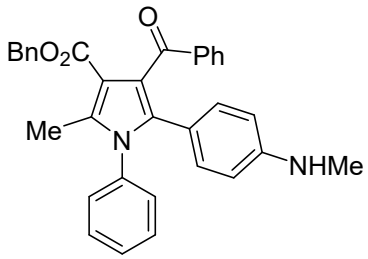
20.4 mg, 20% yield, Yellow solid, R_f = 0.33 (PE/EtOAc = 8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.61 (s, 1H), 7.49-7.46 (m, 1H), 7.40-7.36 (m, 2H), 7.32-7.21 (m, 8H), 7.05-7.02 (m, 2H), 6.97-6.94 (m, 2H), 6.73-6.70 (m, 1H), 6.57 (d, *J* = 7.7 Hz, 2H), 4.63 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 165.0, 142.7, 140.4, 139.0, 135.7, 135.6, 133.6, 131.6, 129.0, 128.6, 128.5, 128.27, 128.26, 128.2, 127.9, 127.8, 121.6, 118.5, 112.2, 111.7, 65.8, 12.4; HRMS (ESI) *m/z* calculated for $[C_{34}H_{26}N_2O_3+H]^+$ $[M+H]^+$ 511.2022, found: 511.2025.

Benzyl 5-(benzo[*b*]thiophen-2-yl)-4-benzoyl-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (7b)



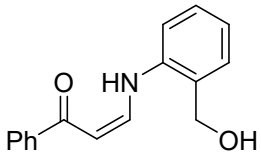
25.3 mg, 24% yield, Light yellow oil, R_f = 0.30 (PE/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.77 (m, 2H), 7.54 (brs, 1H), 7.46-7.43 (m, 1H), 7.37-7.33 (m, 2H), 7.29-7.26 (m, 2H), 7.24-7.22 (m, 3H), 7.21-7.19 (m, 2H), 7.02-7.00 (m, 2H), 6.94-6.91 (m, 2H), 6.70-6.67 (m, 1H), 6.54-6.53 (m, 2H), 4.60 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 165.1, 142.8, 140.4, 139.1, 135.8, 135.7, 133.7, 131.7, 129.1, 128.7, 128.58, 128.56, 128.31, 128.30, 128.2, 127.9, 127.8, 121.6, 118.5, 111.8, 100.0, 65.9, 12.4; HRMS (ESI) *m/z* calculated for $[C_{34}H_{25}NO_3S+H]^+$ $[M+H]^+$ 528.1633, found: 528.1635.

Benzyl 4-benzoyl-2-methyl-5-(4-(methylamino)phenyl)-1-phenyl-1*H*-pyrrole-3-carboxylate (7c)



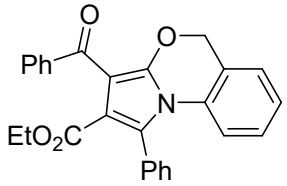
29.1 mg, 29% yield, White solid, R_f = 0.39 (PE/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.43-7.39 (m, 1H), 7.33-7.27 (m, 5H), 7.23-7.19 (m, 3H), 7.12-7.11 (m, 2H), 7.02-6.97 (m, 4H), 6.61-6.58 (m, 1H), 6.42-6.40 (m, 2H), 4.81 (s, 2H), 3.02 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 164.4, 148.2, 139.1, 136.5, 135.84, 135.77, 134.8, 132.2, 129.2, 129.0, 128.6, 128.32, 128.25, 128.1, 127.9, 127.8, 119.3, 118.2, 113.1, 111.0, 65.8, 40.3, 12.4; HRMS (ESI) *m/z* calculated for $[C_{33}H_{28}N_2O_3+H]^+$ $[M+H]^+$ 501.2178, found: 501.2181.

(*Z*)-3-((2-(hydroxymethyl)phenyl)amino)-1-phenylprop-2-en-1-one (10)



52% yield, Yellow solid, R_f = 0.51 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.52 (d, *J* = 12.2 Hz, 1H), 7.92 (dd, *J* = 8.2 Hz, 1.5 Hz, 2H), 7.52-7.47 (m, 2H), 7.44-7.41 (m, 2H), 7.34-7.30 (m, 1H), 7.27-7.25 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.04 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.05 (d, *J* = 7.9 Hz, 1H), 4.84 (s, 2H), 2.39 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 145.3, 139.9, 139.3, 131.7, 129.8, 129.4, 129.1, 128.5, 127.5, 123.6, 115.2, 94.5, 63.3; HRMS (ESI) *m/z* calculated for $[C_{16}H_{15}NO_2+H]^+$ $[M+H]^+$ 254.1181, found: 254.1180.

Ethyl 3-benzoyl-1-phenyl-5*H*-benzo[d]pyrrolo[2,1-*b*][1,3]oxazine-2-carboxylate (11)



40.6 mg, 48% yield, Light yellow oil, R_f = 0.69 (PE/EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.53-7.49 (m, 3H), 7.46-7.43 (m, 5H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.16-7.13 (m, 1H), 7.07-7.03 (m, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 5.18 (s, 2H), 7.07-7.03 (m, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 5.18 (s, 2H), 3.84 (q, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 164.4, 146.5, 139.4, 132.6, 132.3, 130.6, 130.4, 129.3, 129.0, 128.9, 128.6, 128.2, 128.0, 125.8, 125.7, 123.8, 118.6, 116.1, 103.8, 68.8, 60.7, 13.6; HRMS (ESI) *m/z* calculated for $[C_{27}H_{21}NO_4+H]^+$ $[M+H]^+$ 424.1549, found: 424.1547.

References

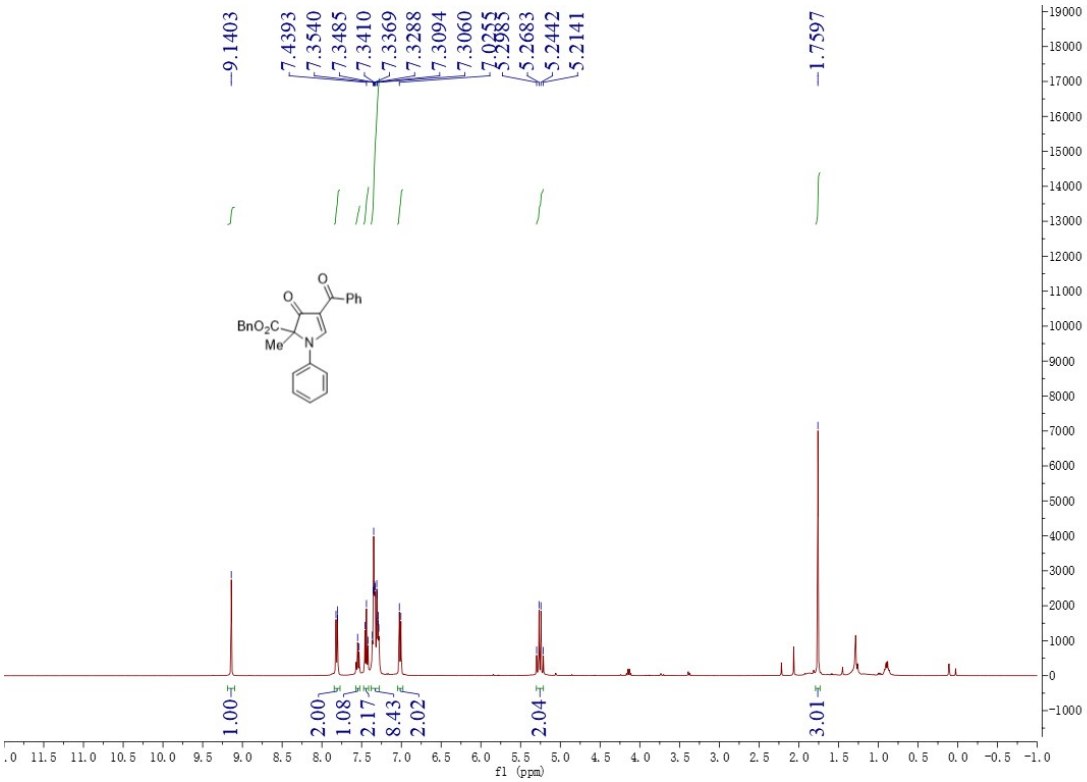
1. P. M. Truong, P. Y. Zavalij, M. P. Doyle. *Angew. Chem. Int. Ed*. **2014**, *53*, 6468−6472.

2. K. X, Luo, S. Mao, K. He, X. L. Yu, J. H. Pan, J. Lin, Z. H. Shao, Y. Jin. *ACS Catal*. **2020**, *10*, 3733−3740.
3. Y. Liu, Z. Chen, T. B. Ng, J. Zhang, M. Zhou, F. Song, F. Lu, Y. Liu. *Peptides*, **2007**, *28*, 553−559.

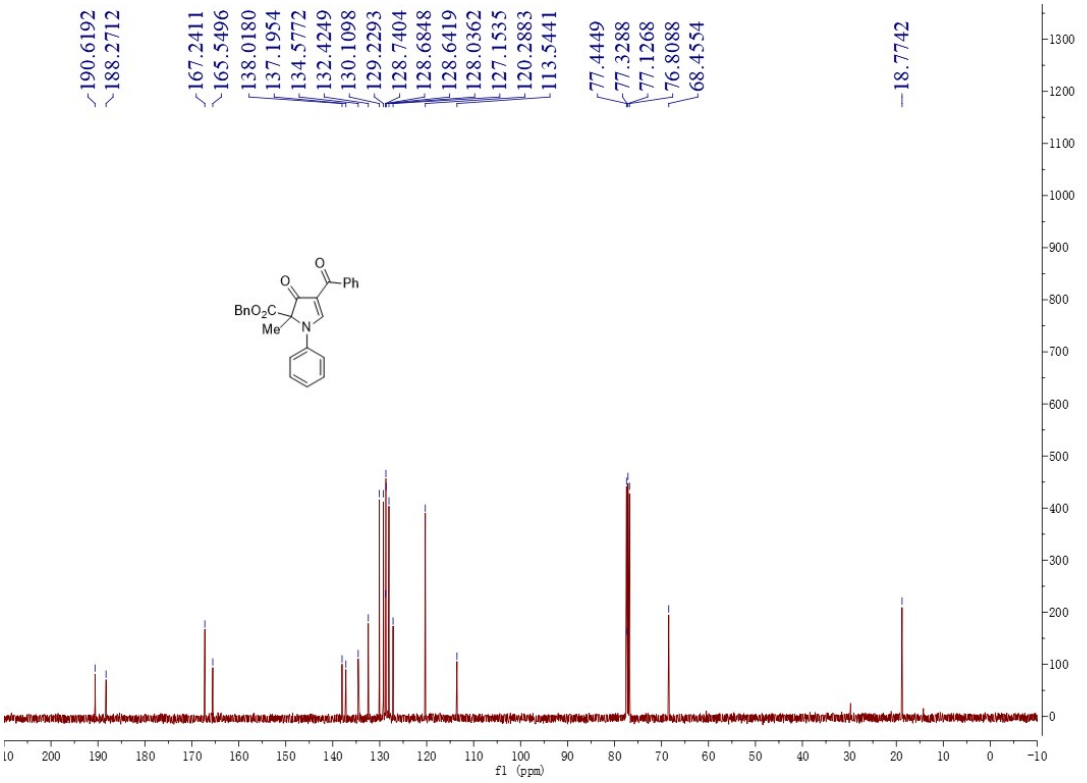
^{1}H, ^{13}C and ^{19}F spectra

Benzyl 4-benzoyl-2-methyl-3-oxo-1-phenyl-2,3-dihydro-1*H*-pyrrole-2-carboxylate (5a)

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

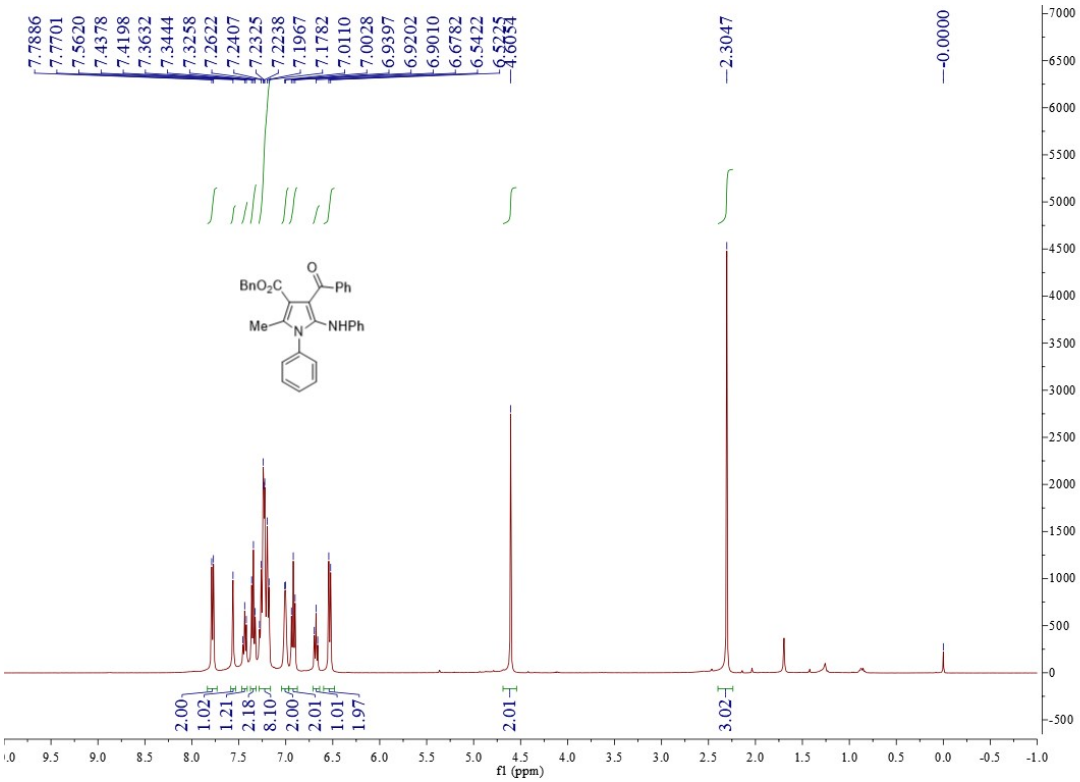


^{13}C NMR (101 MHz, $CDCl_3$)

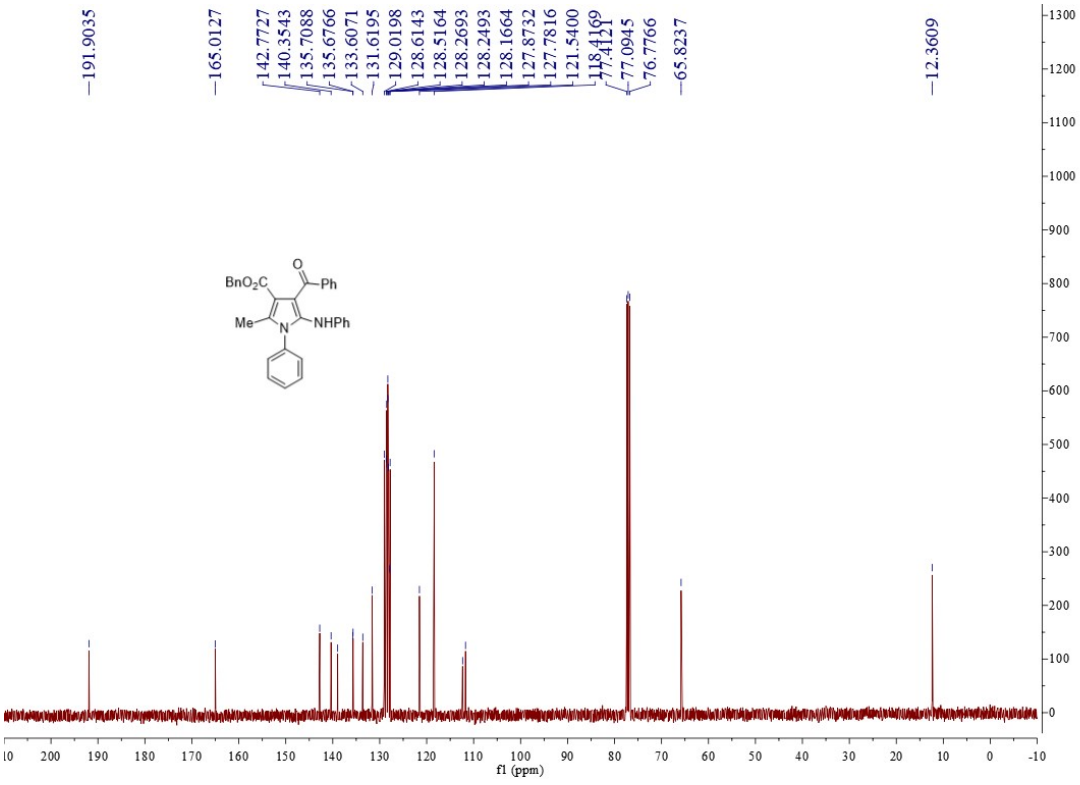


Benzyl 4-benzoyl-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4a)

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

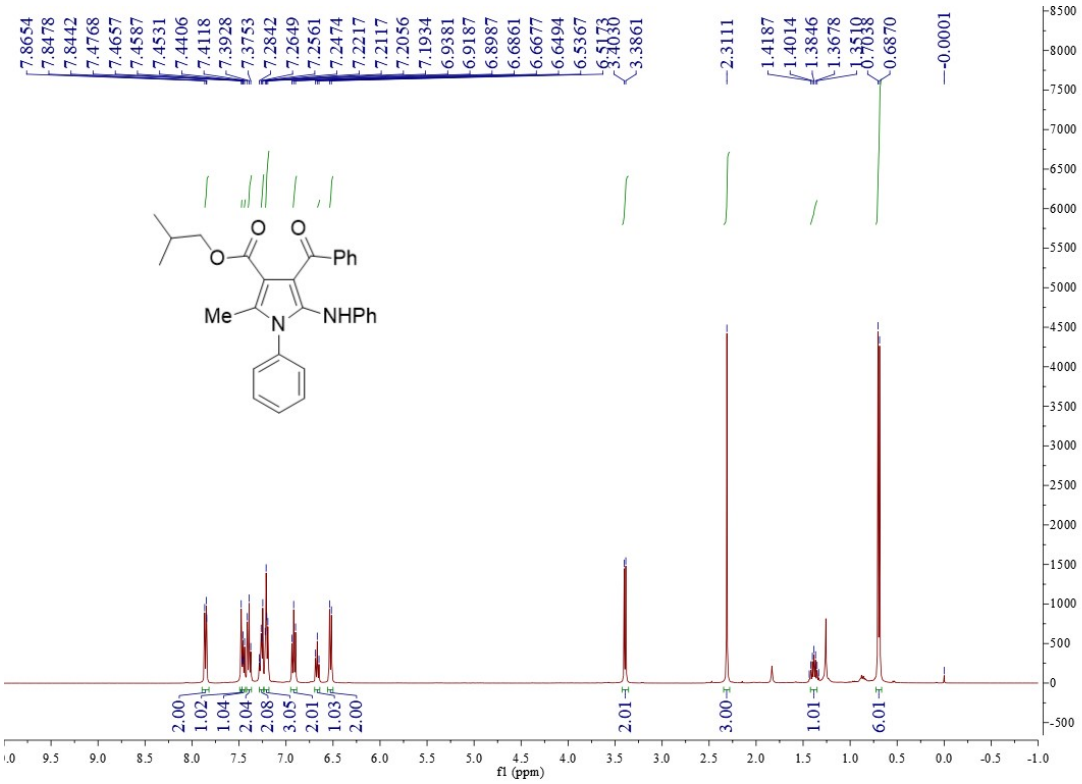


^{13}C NMR (101 MHz, $CDCl_3$)

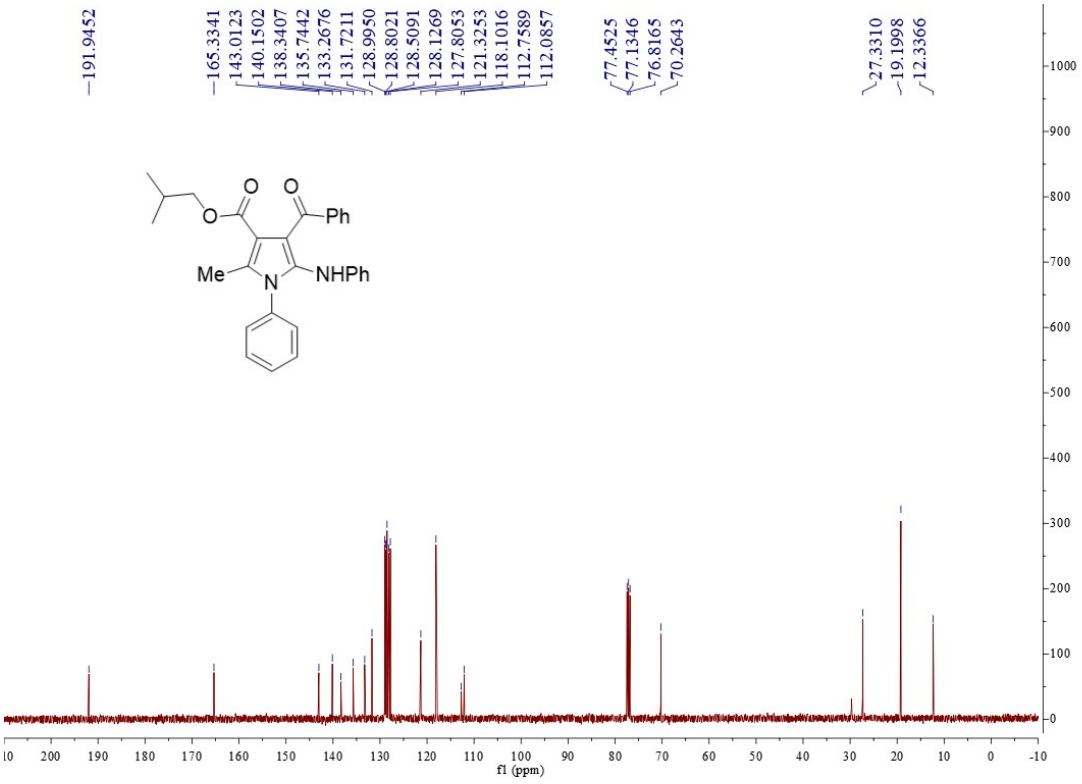


Isobutyl 4-benzoyl-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4b)

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

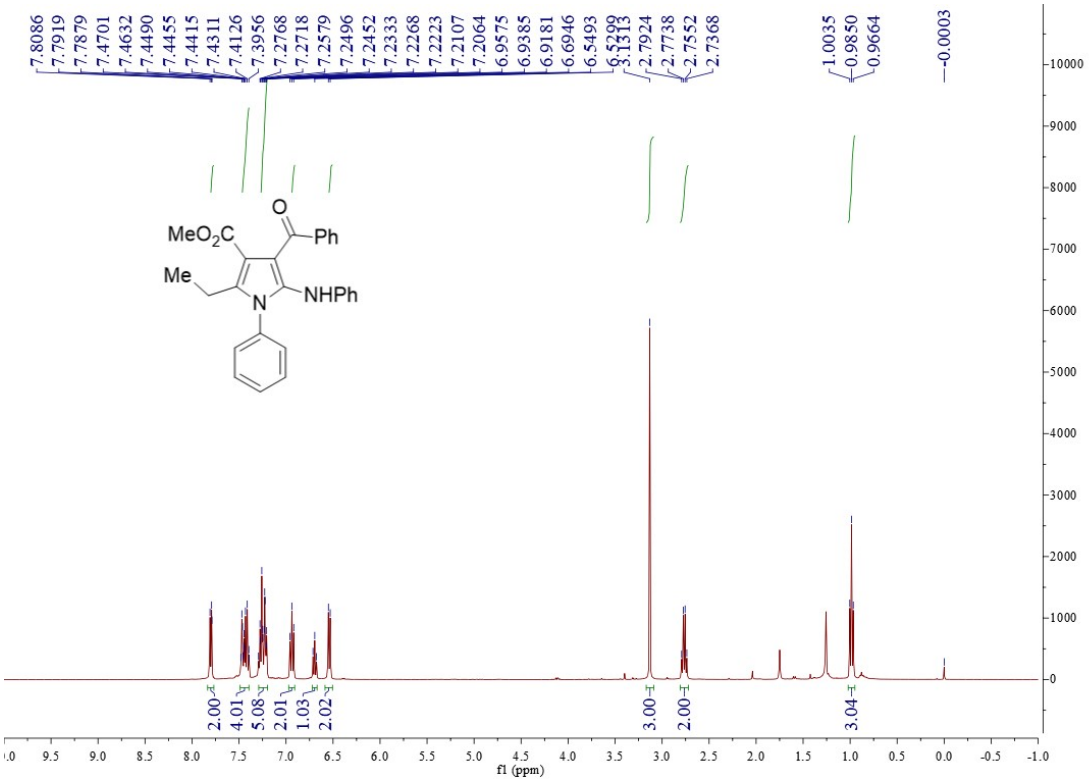


^{13}C NMR (101 MHz, $CDCl_3$)

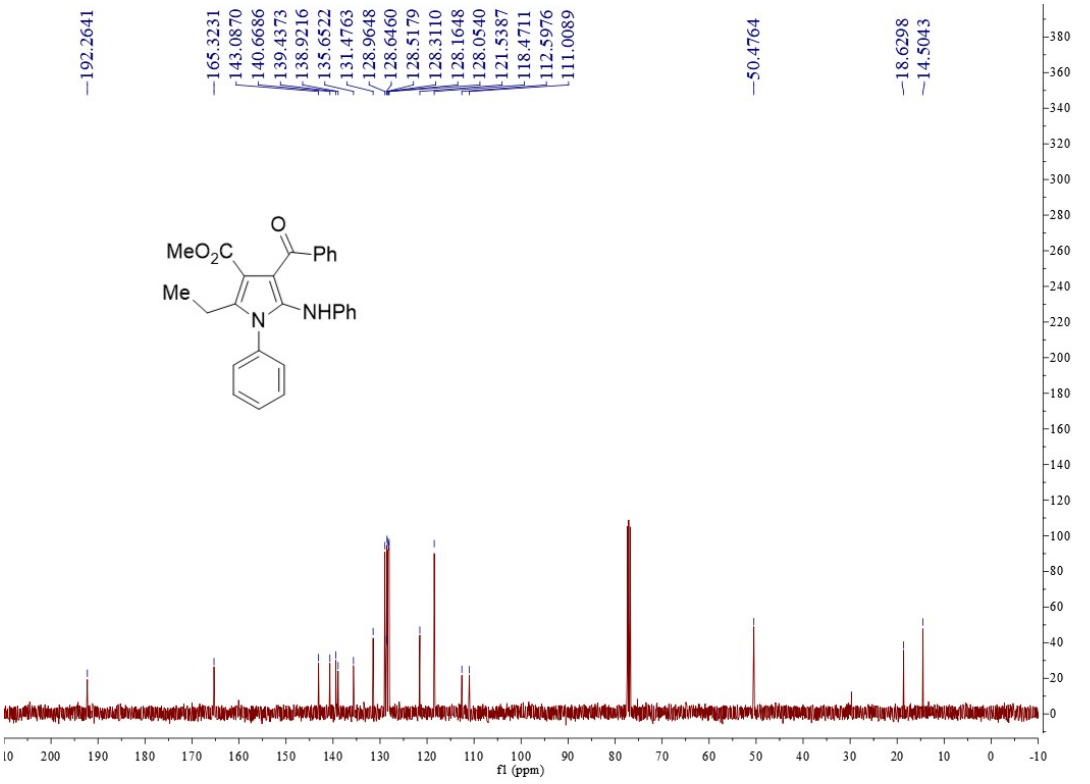


Methyl 4-benzoyl-2-ethyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4c)

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

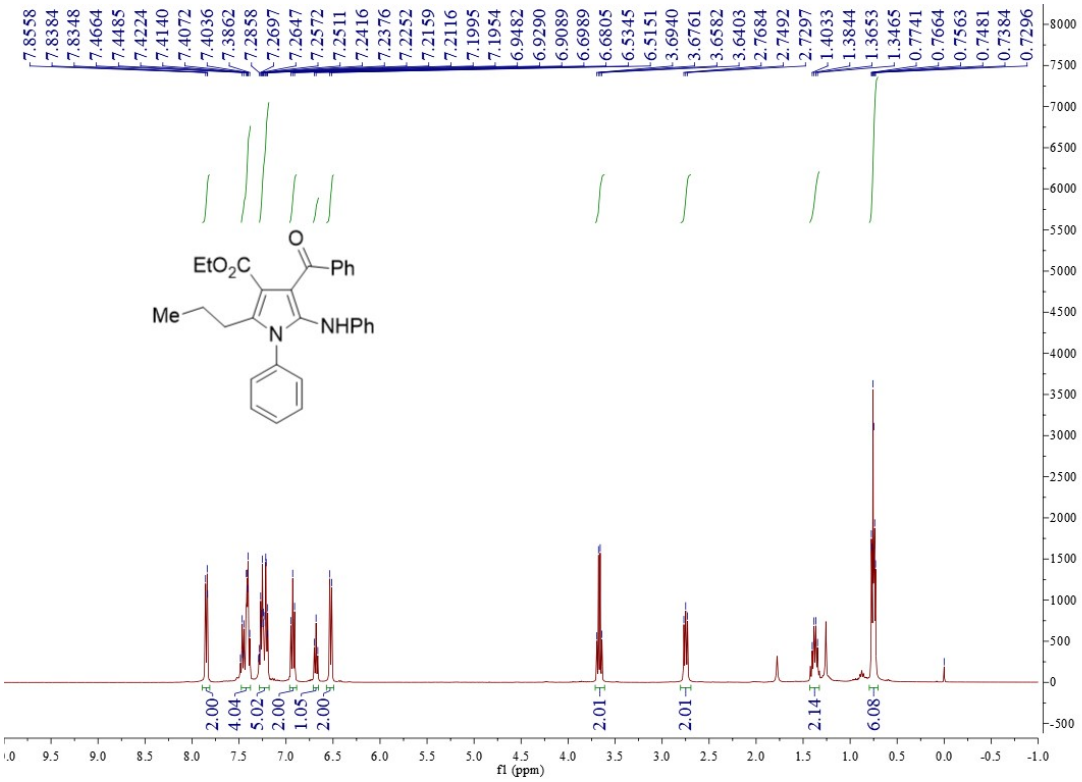


^{13}C NMR (101 MHz, $CDCl_3$)

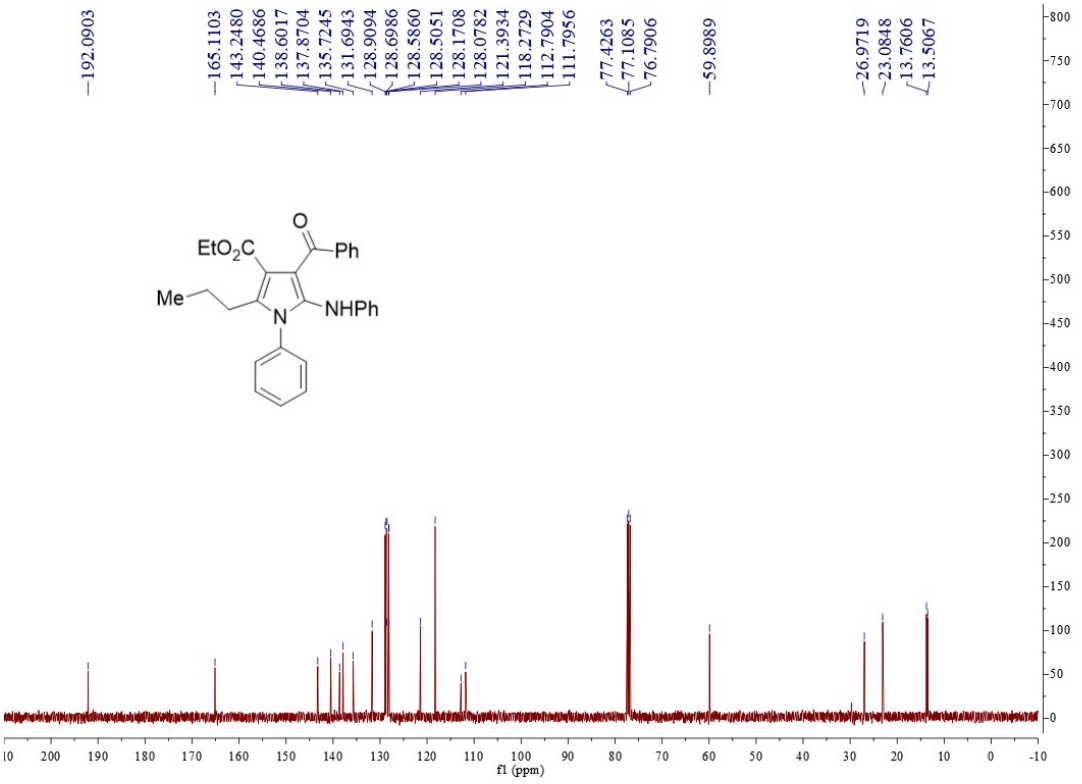


Ethyl 4-benzoyl-1-phenyl-5-(phenylamino)-2-propyl-1*H*-pyrrole-3-carboxylate (4d)

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

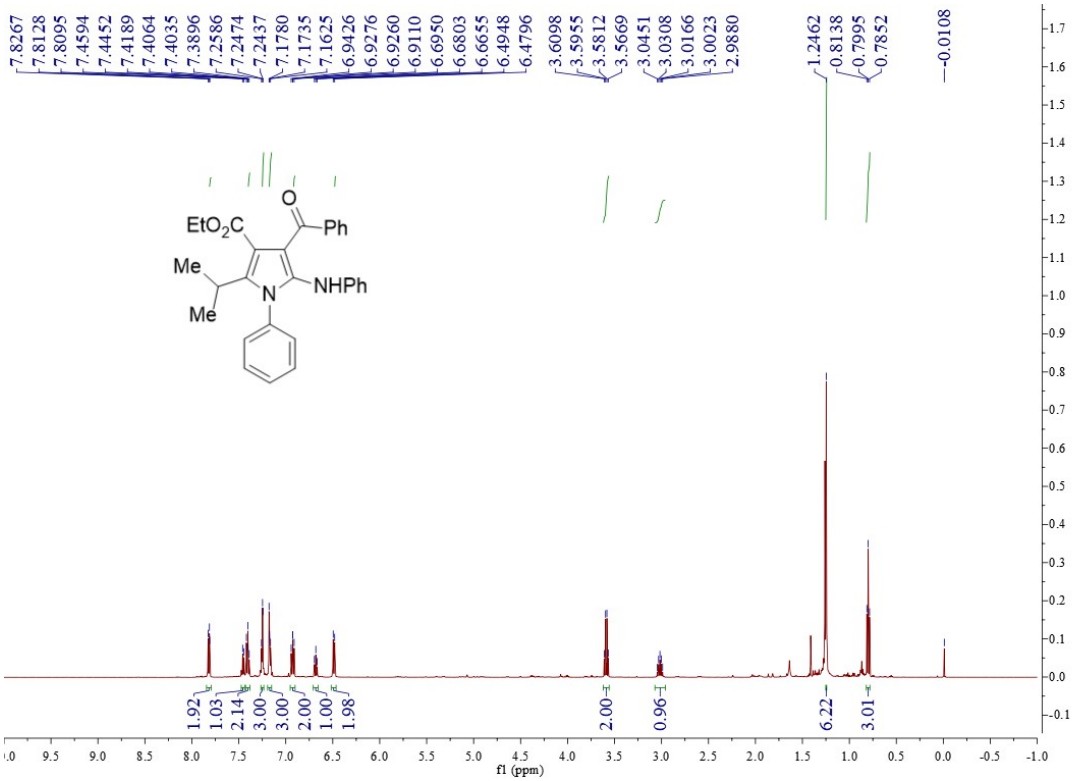


^{13}C NMR (101 MHz, $CDCl_3$)

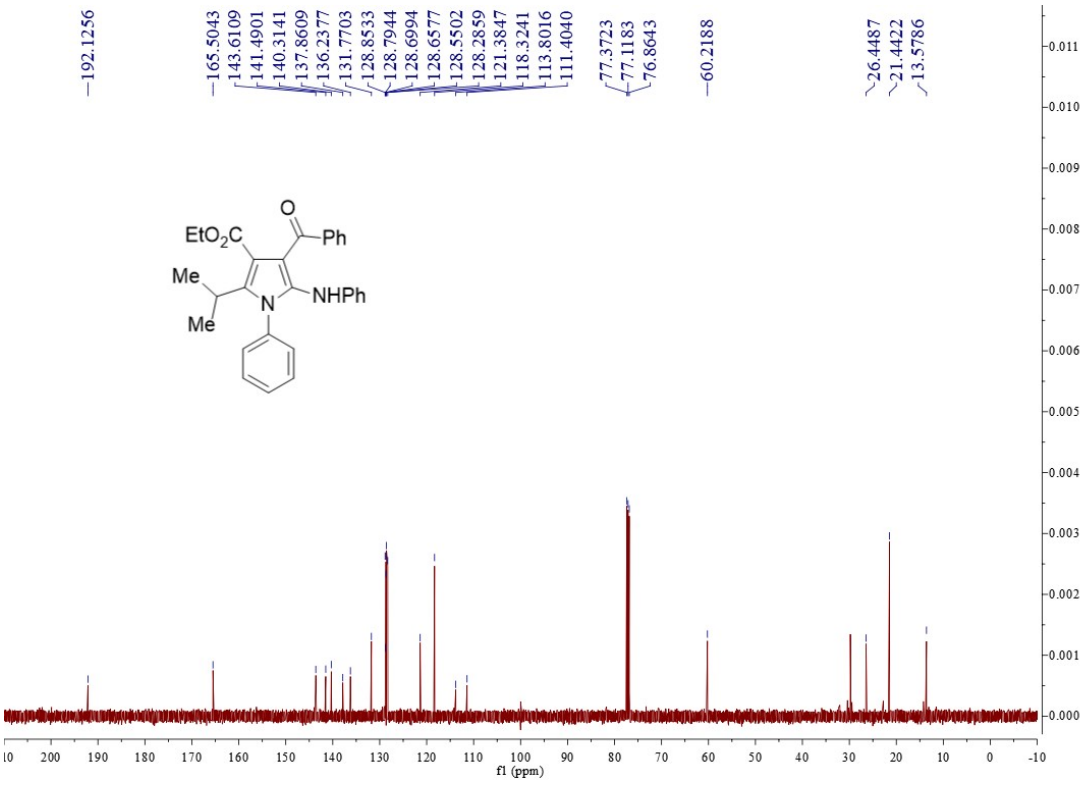


Ethyl 4-benzoyl-2-isopropyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4e)

^{1}H NMR (500 MHz, $CDCl_3$)

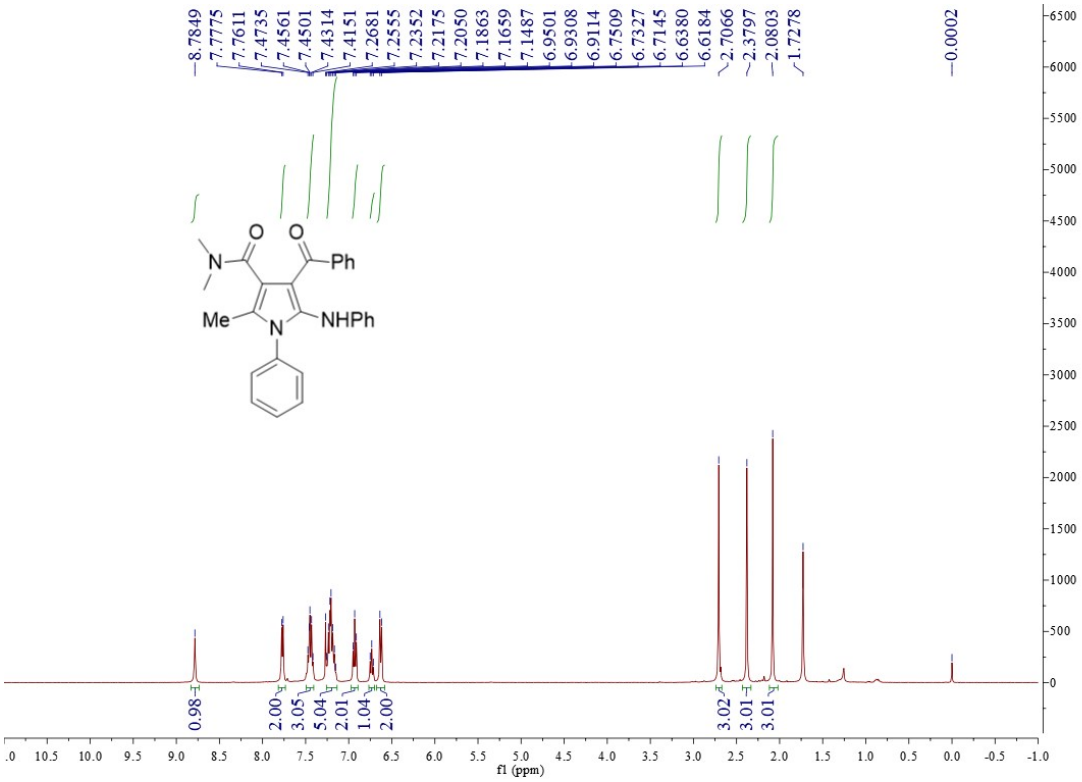


^{13}C NMR (125 MHz, $CDCl_3$)

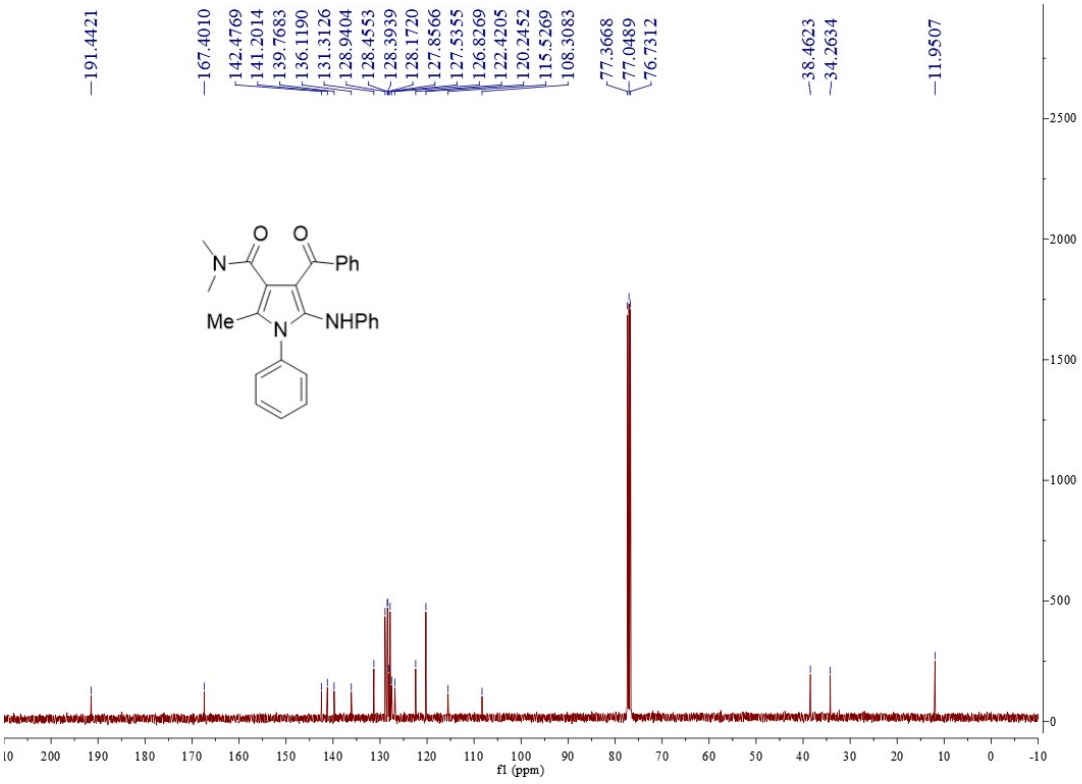


4-Benzoyl-*N*,*N*,2-trimethyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxamide (4f)

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

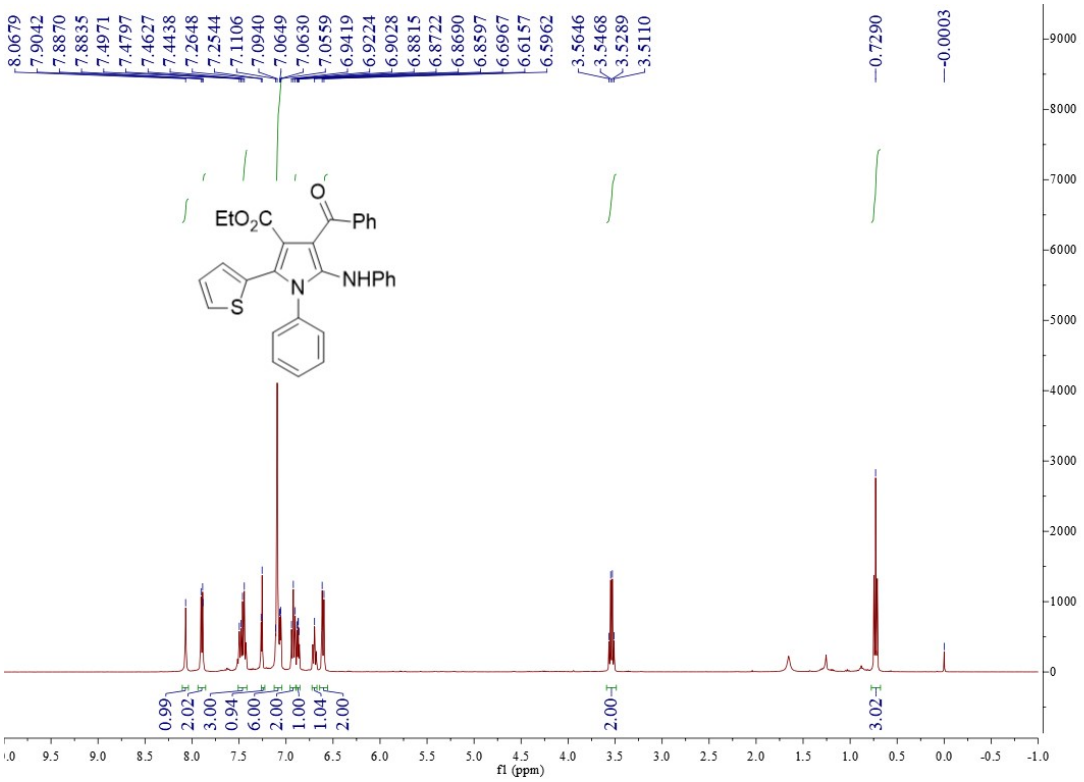


^{13}C NMR (101 MHz, $CDCl_3$)

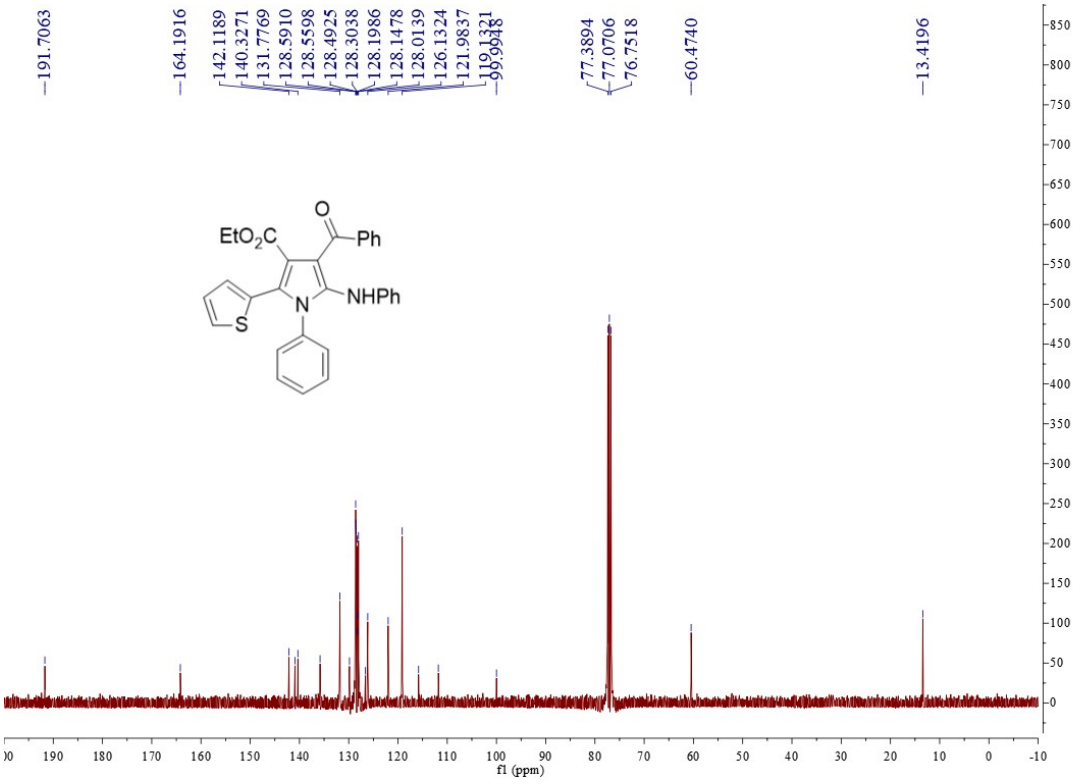


Ethyl 4-benzoyl-1-phenyl-5-(phenylamino)-2-(thiophen-2-yl)-1*H*-pyrrole-3-carboxylate (4g)

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

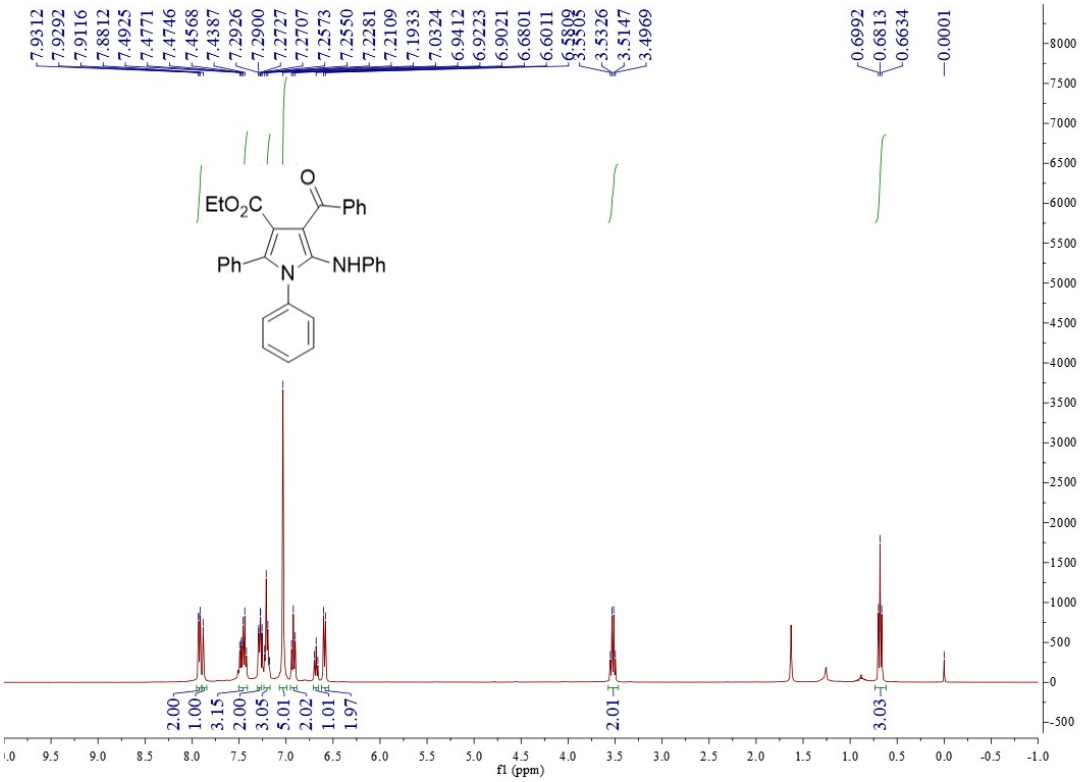


^{13}C NMR (101 MHz, $CDCl_3$)

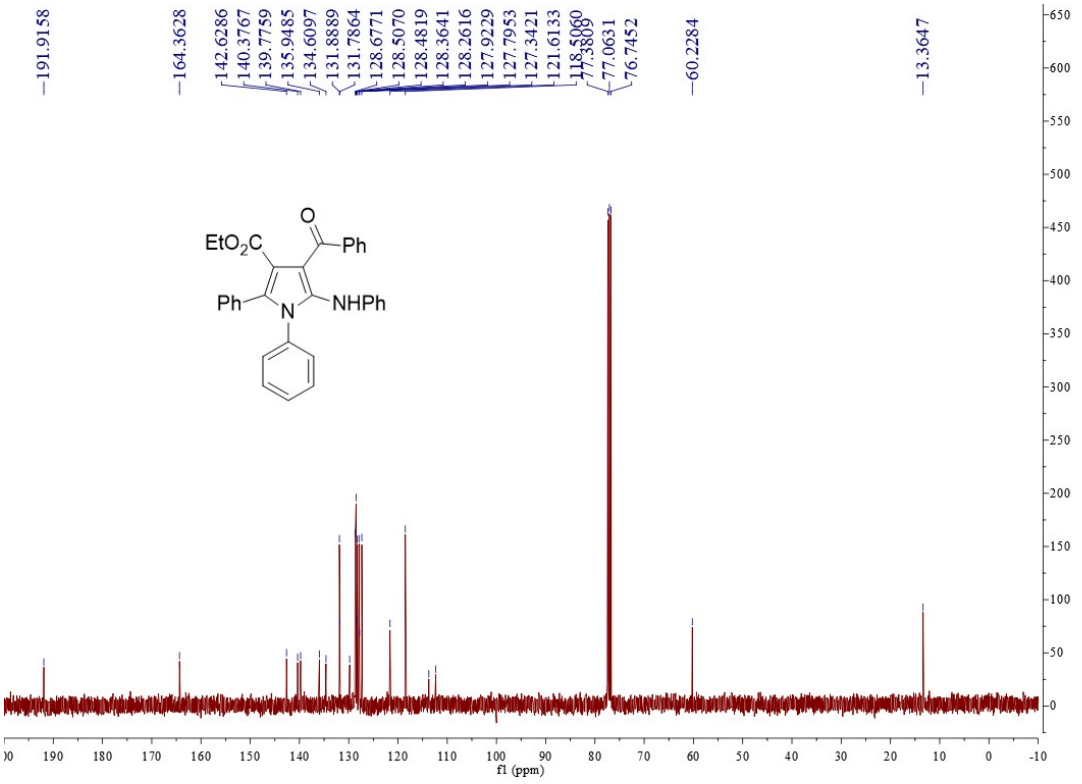


Ethyl 4-benzoyl-1,2-diphenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4h)

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

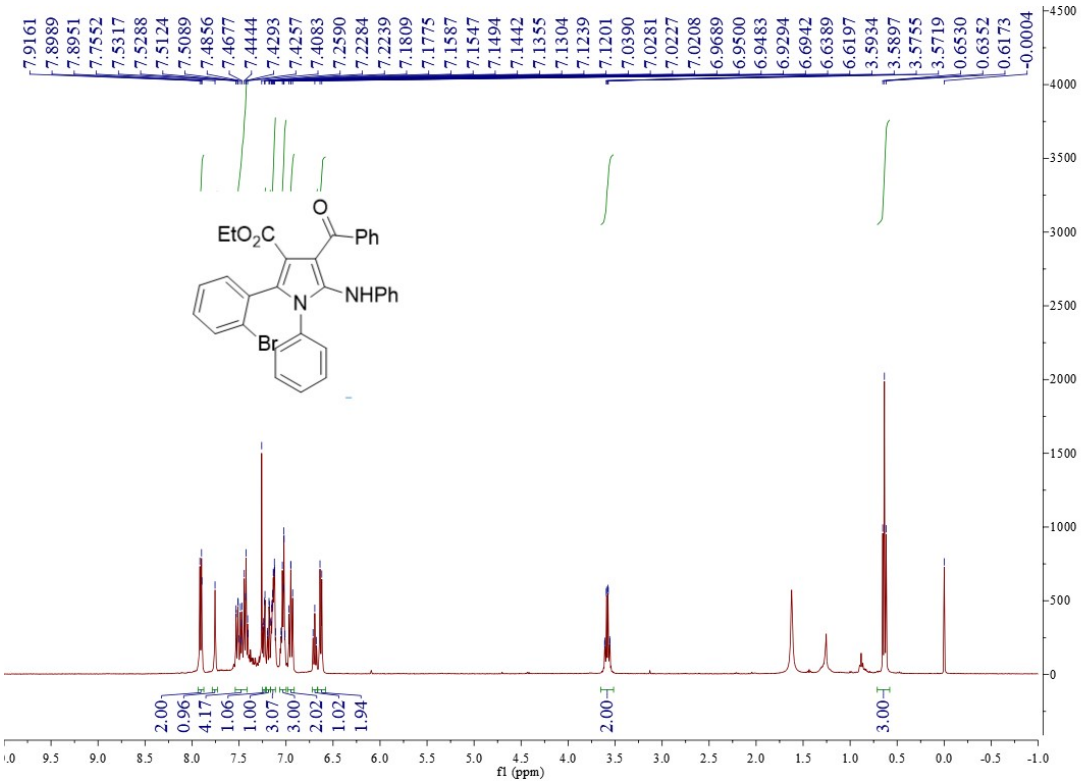


^{13}C NMR (101 MHz, $CDCl_3$)

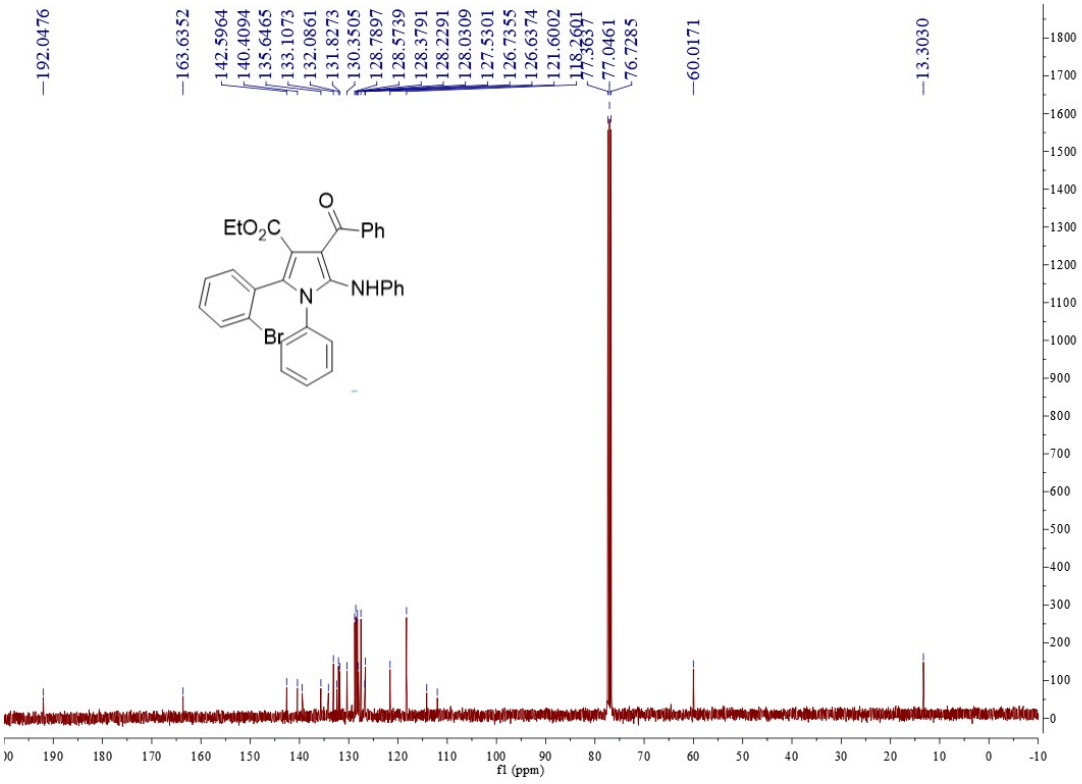


Ethyl 4-benzoyl-2-(2-bromophenyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4i)

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

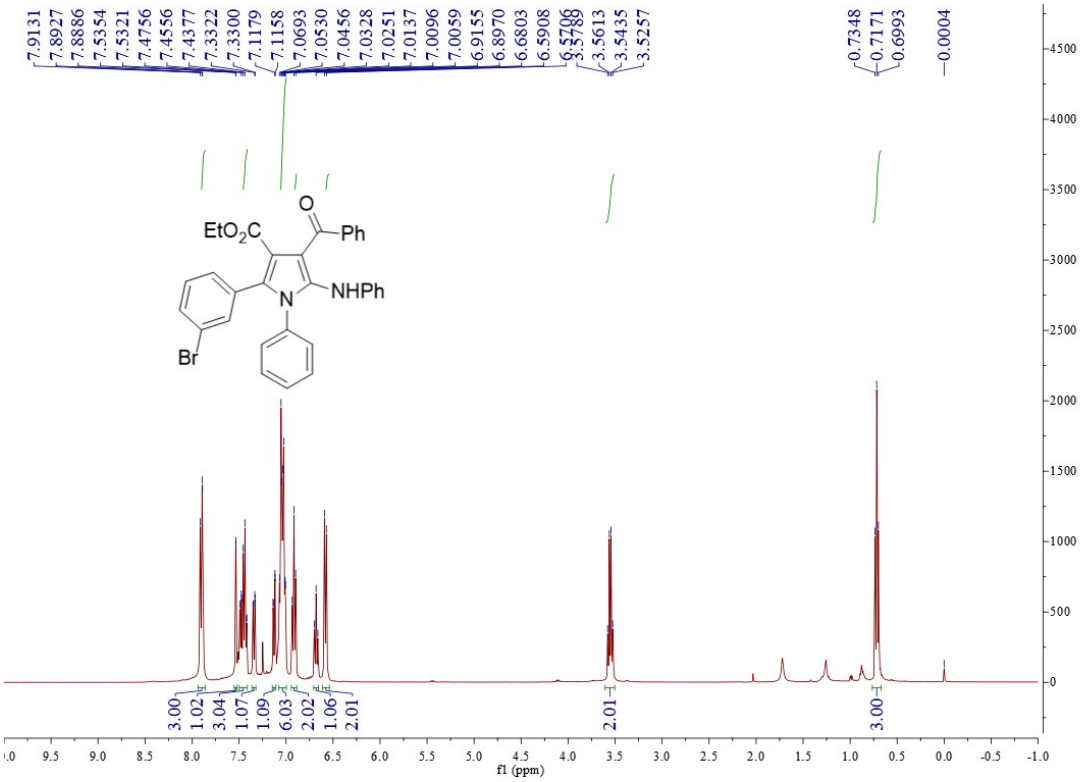


^{13}C NMR (101 MHz, $CDCl_3$)

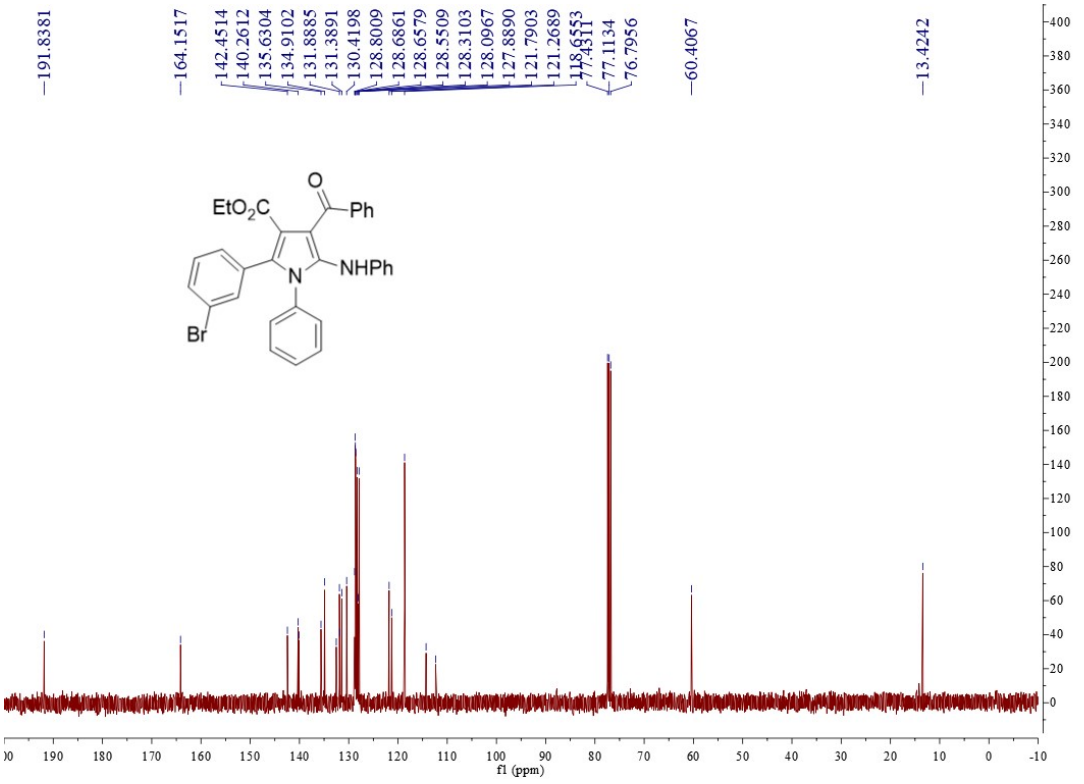


Ethyl 4-benzoyl-2-(3-bromophenyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4j)

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

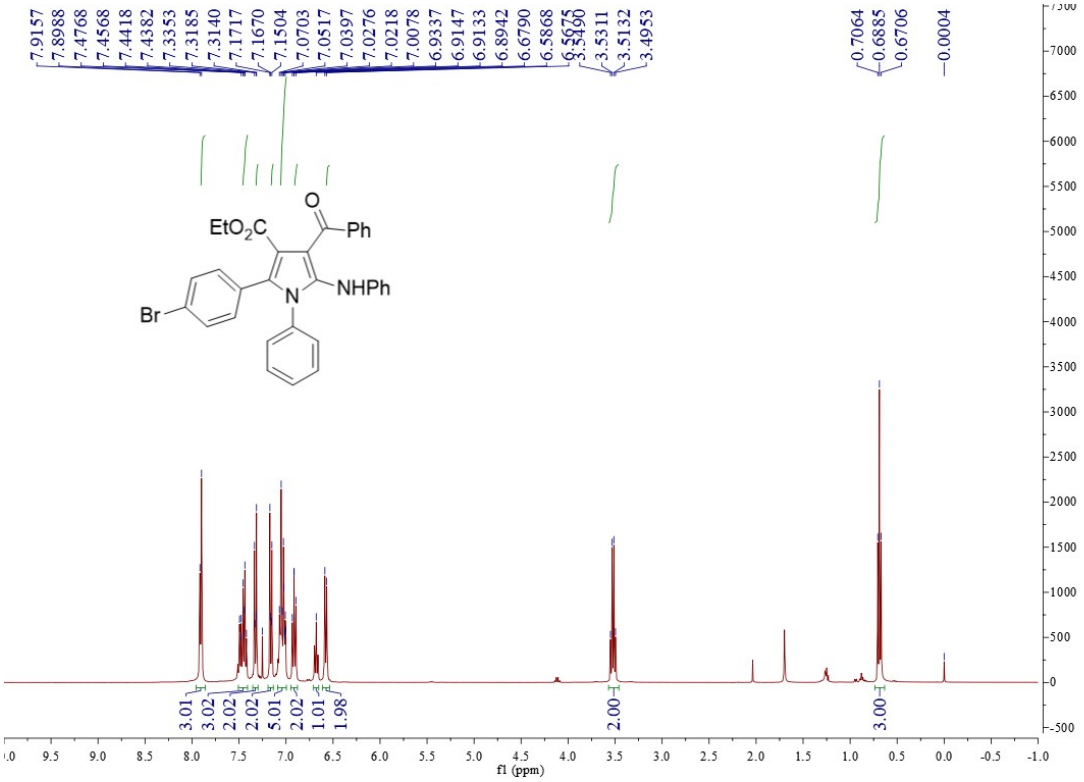


^{13}C NMR (101 MHz, $CDCl_3$)

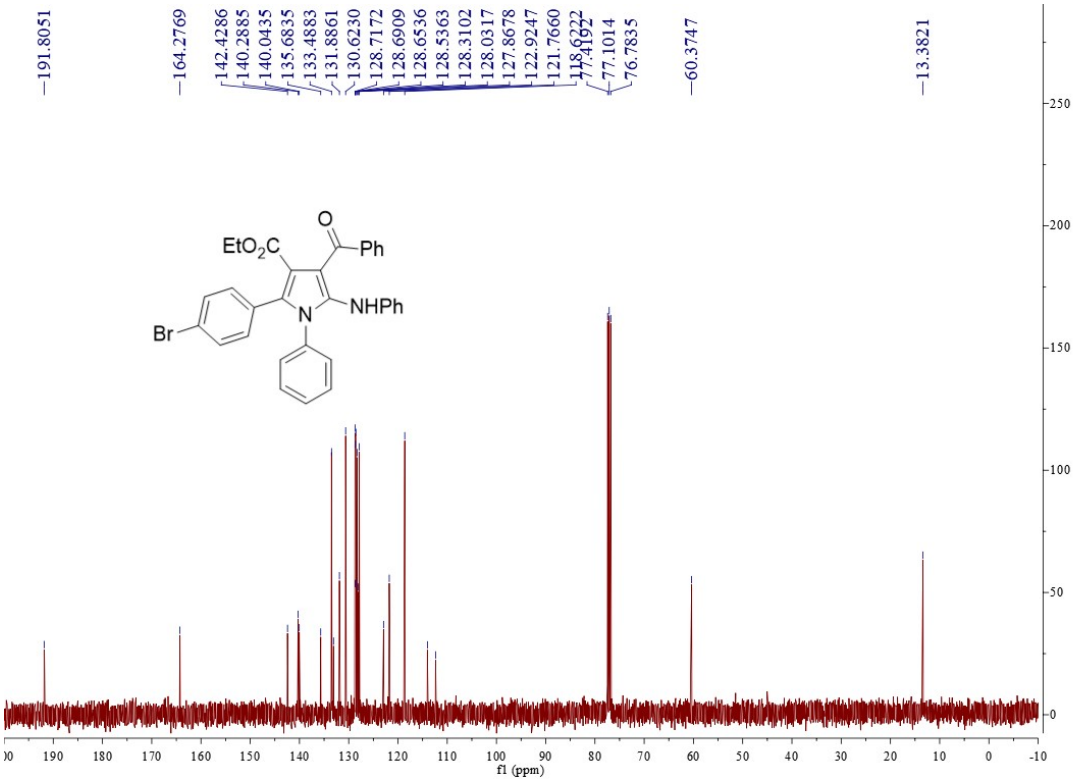


Ethyl 4-benzoyl-2-(4-bromophenyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4k)

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

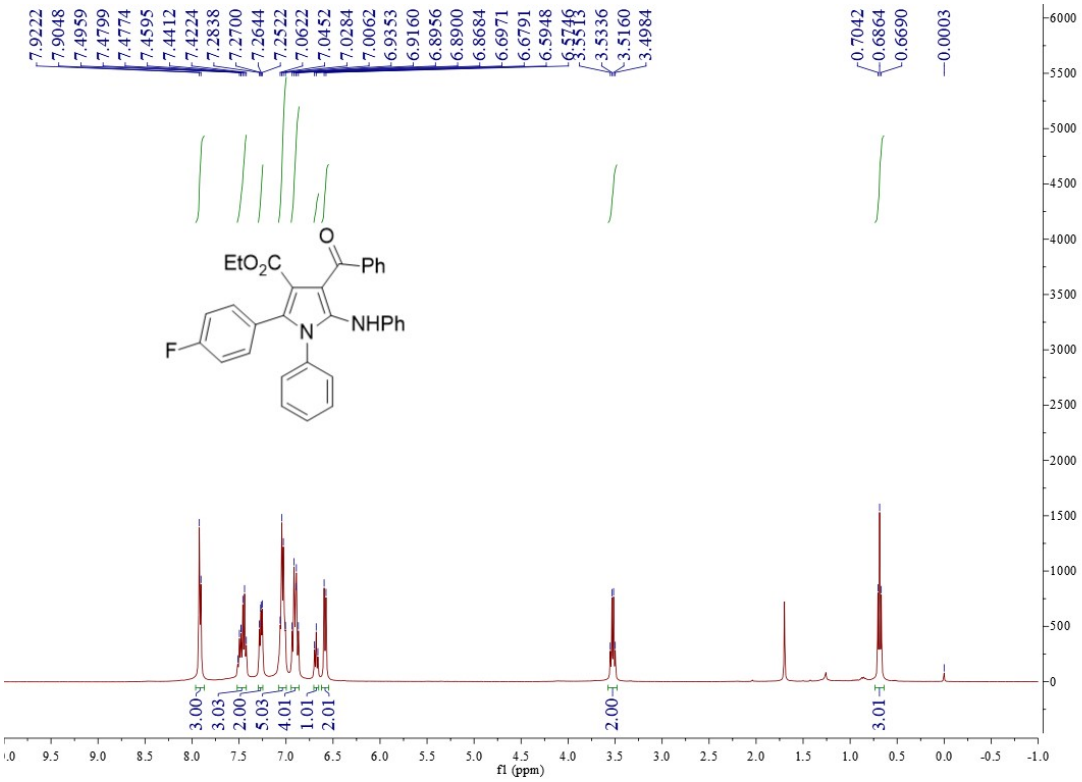


^{13}C NMR (101 MHz, $CDCl_3$)

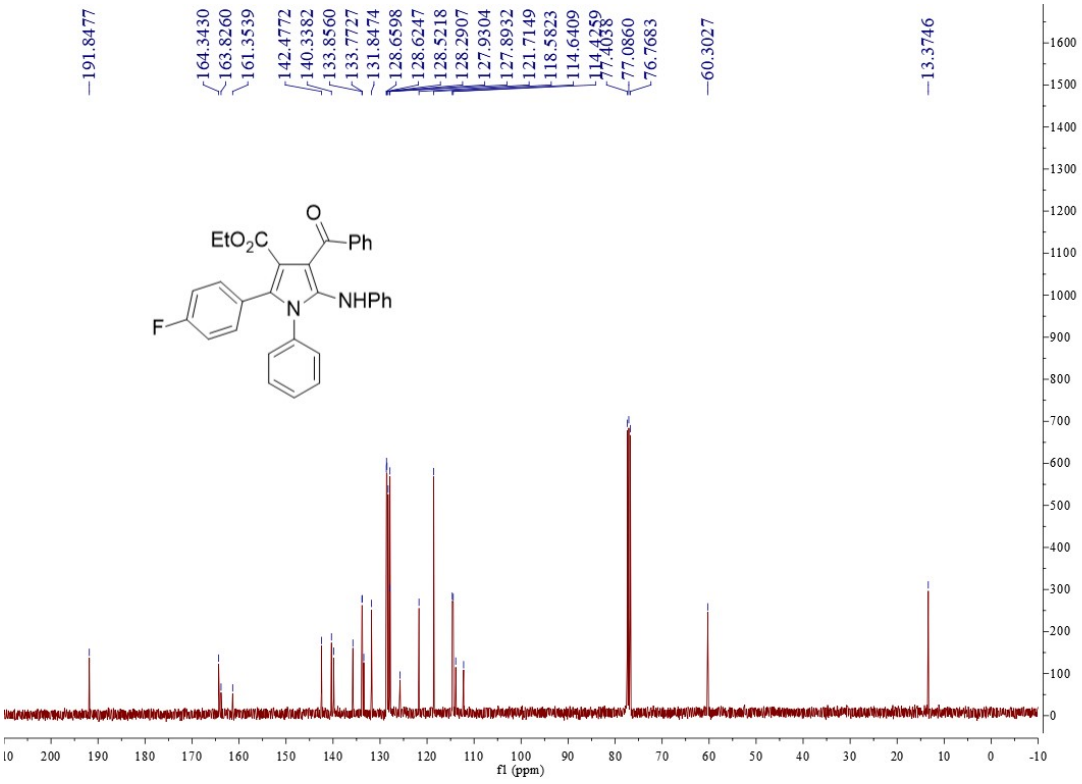


Ethyl 4-benzoyl-2-(4-fluorophenyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4l)

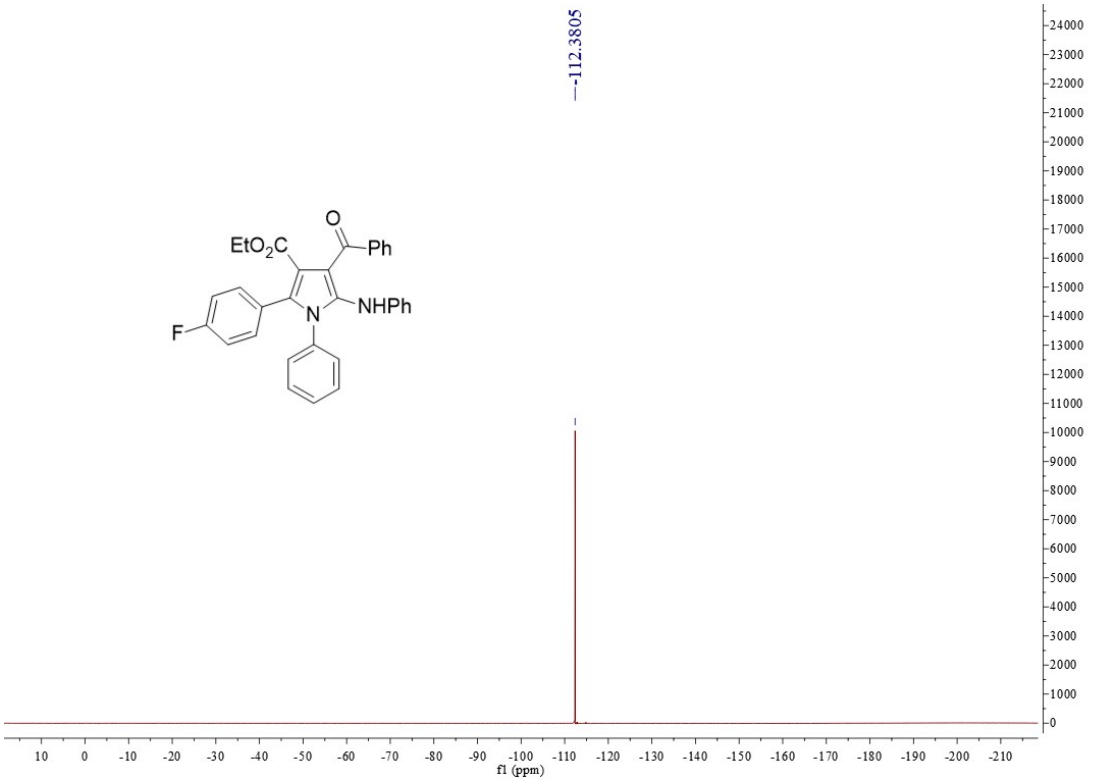
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

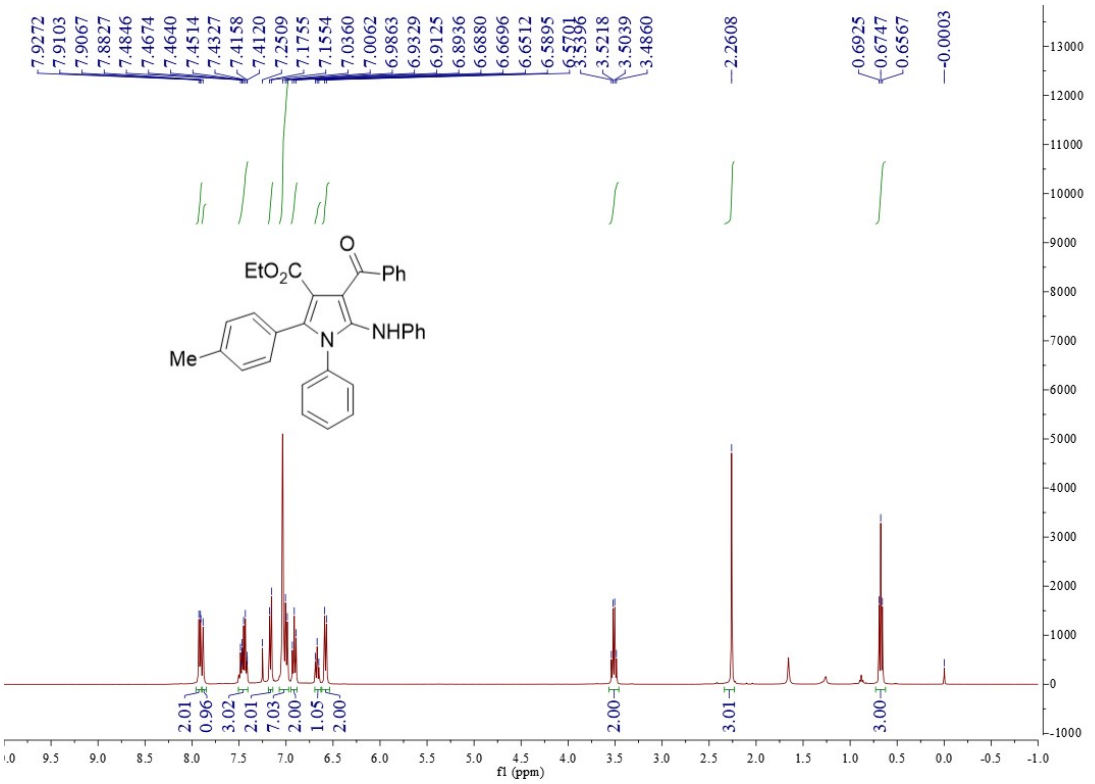


^{19}F NMR (376 MHz, $CDCl_3$)

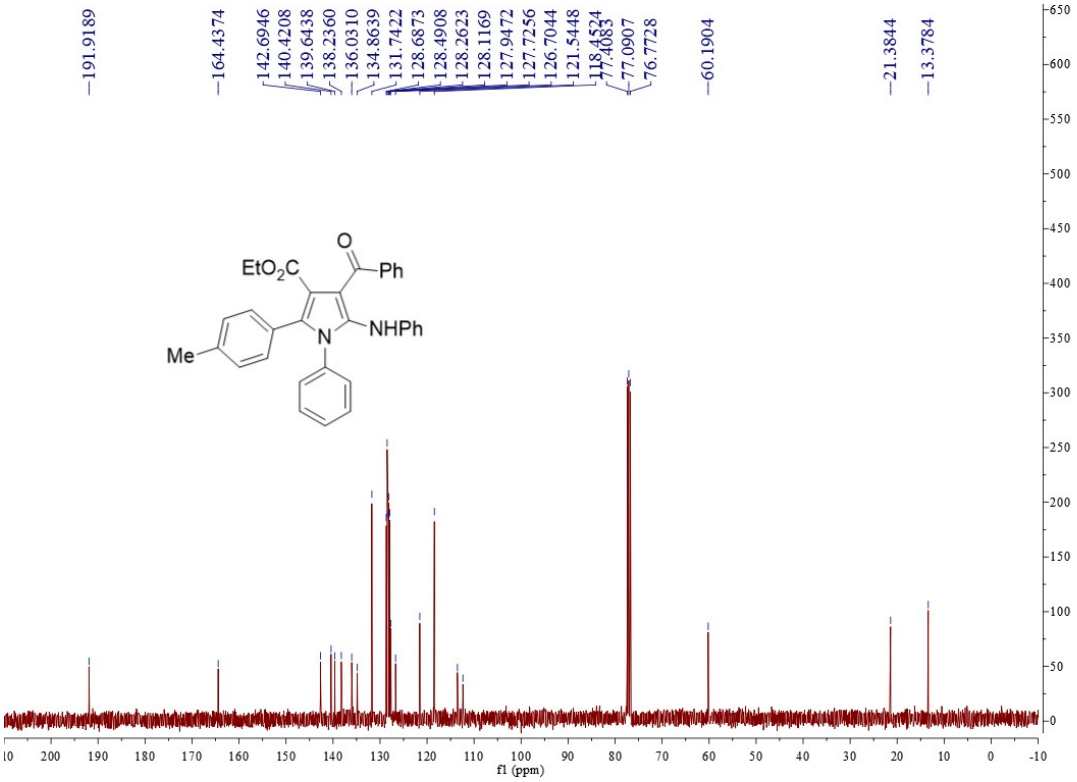


Ethyl 4-benzoyl-1-phenyl-5-(phenylamino)-2-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate (4m)

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

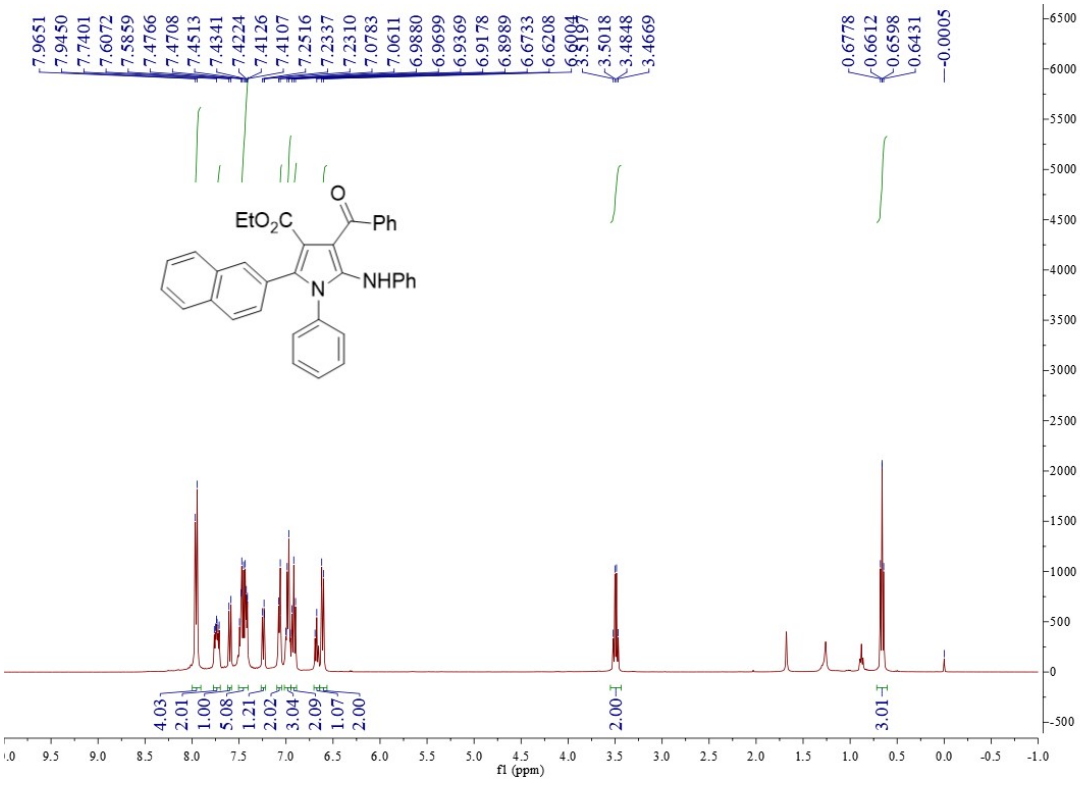


^{13}C NMR (101 MHz, $CDCl_3$)

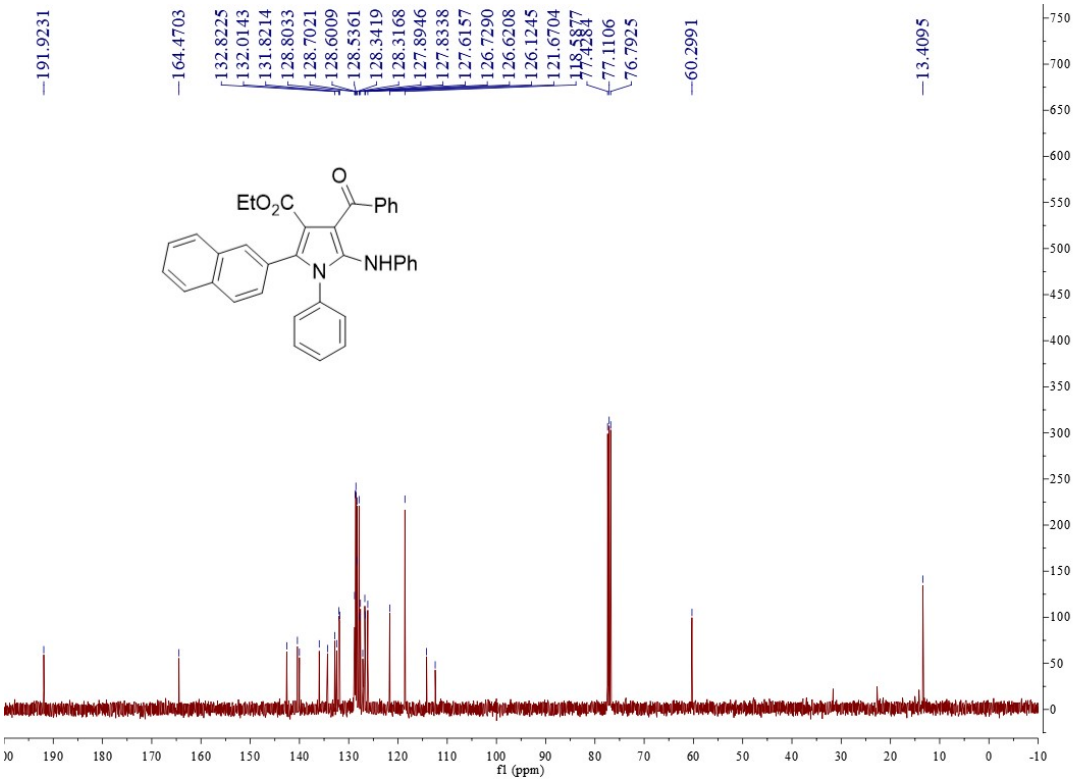


Ethyl 4-benzoyl-2-(naphthalen-2-yl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4n)

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

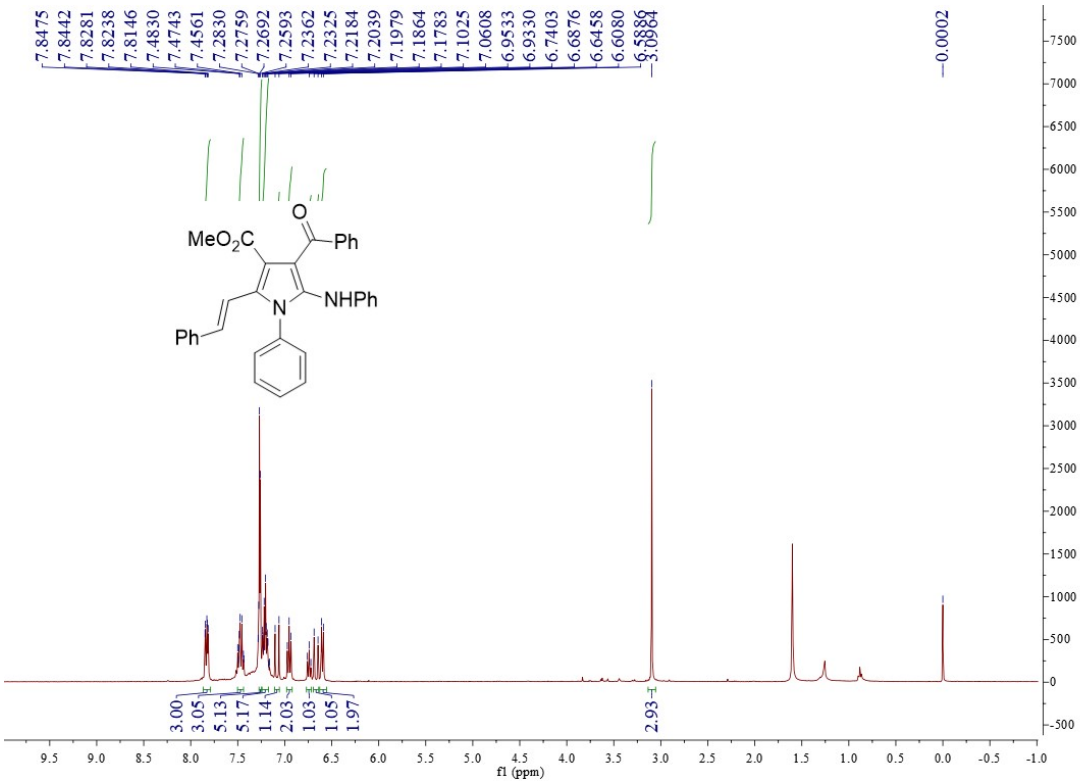


^{13}C NMR (101 MHz, $CDCl_3$)

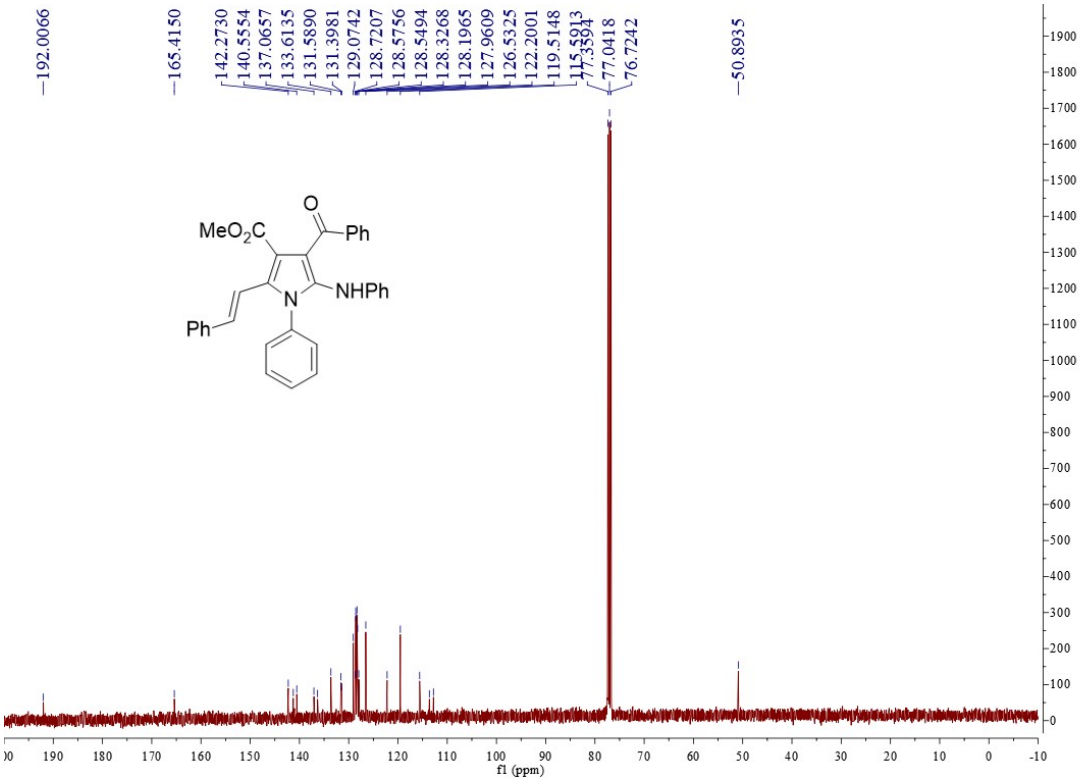


Ethyl (E)-4-benzoyl-1-phenyl-5-(phenylamino)-2-styryl-1*H*-pyrrole-3-carboxylate (4o)

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

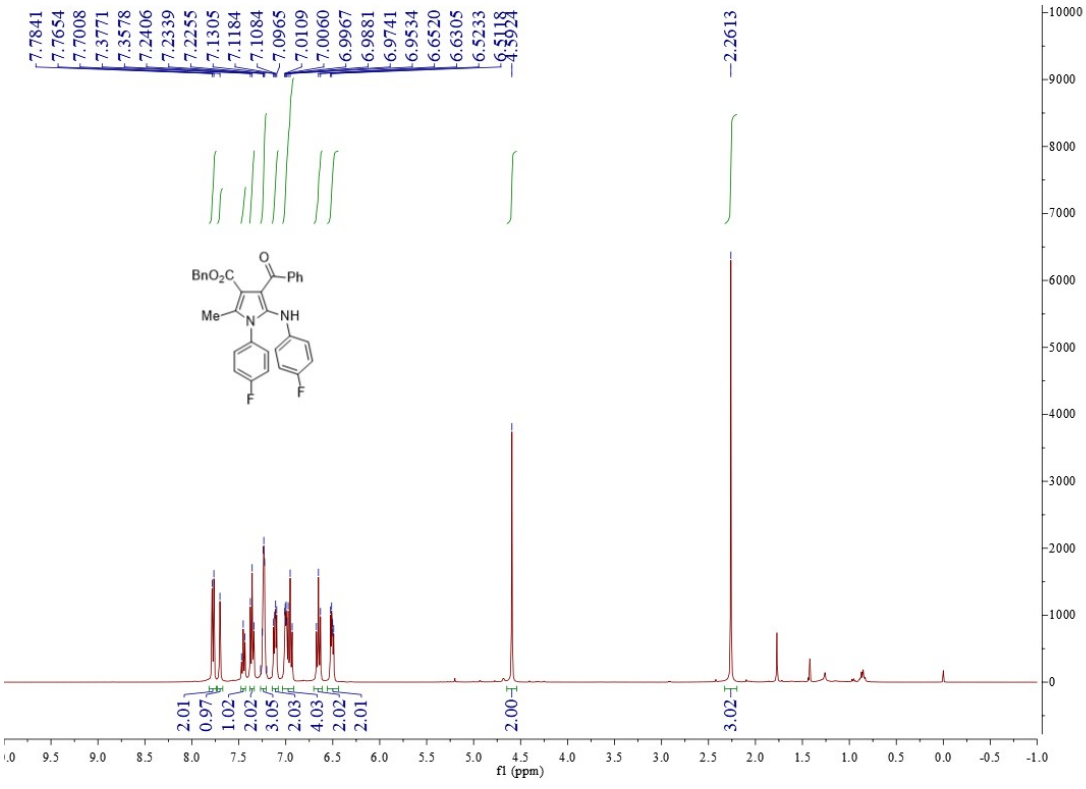


^{13}C NMR (101 MHz, $CDCl_3$)

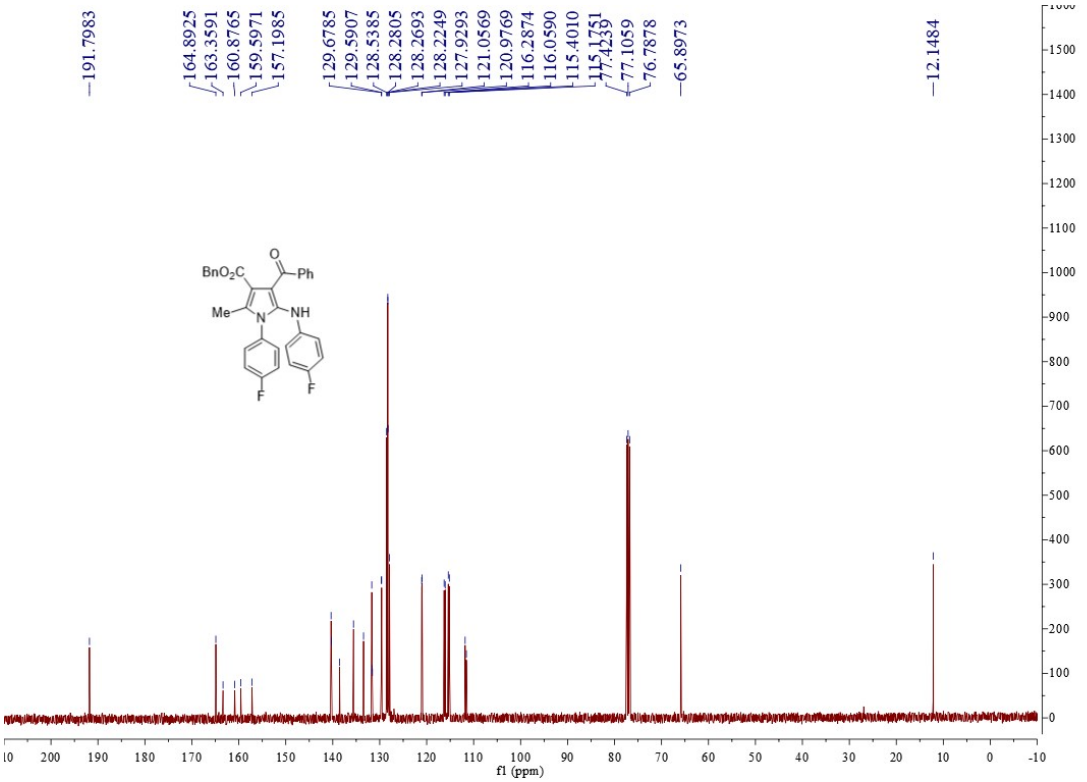


Benzyl 4-benzoyl-1-(4-fluorophenyl)-5-((4-fluorophenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4p)

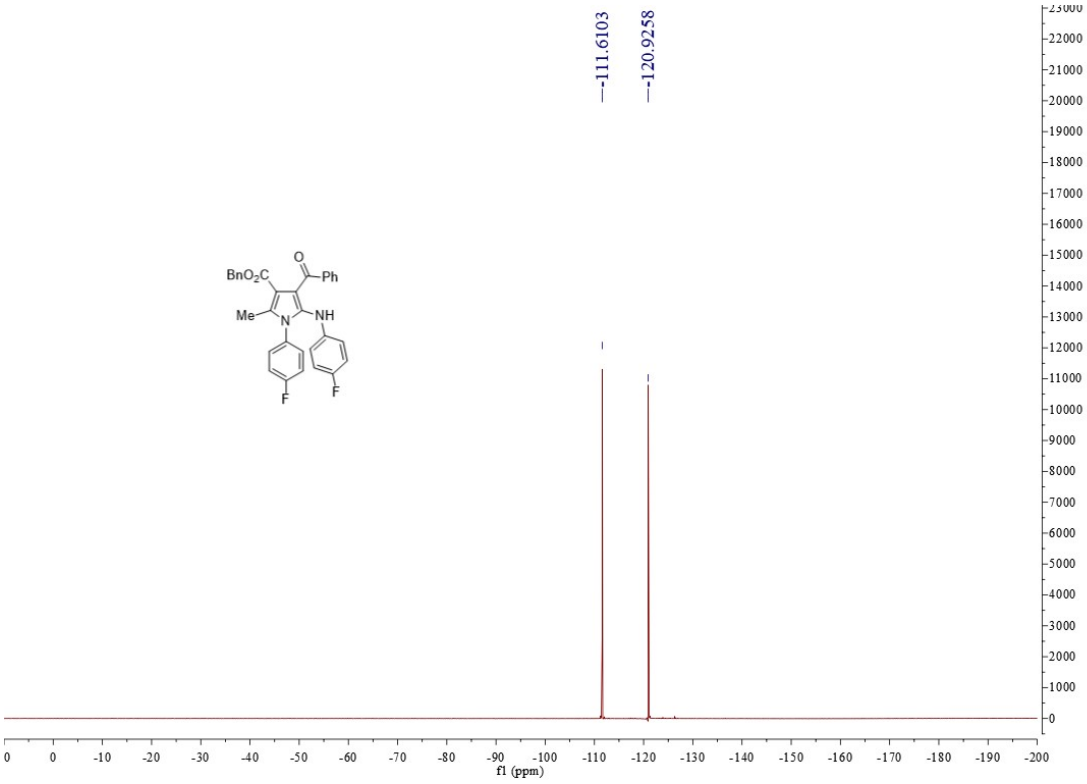
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



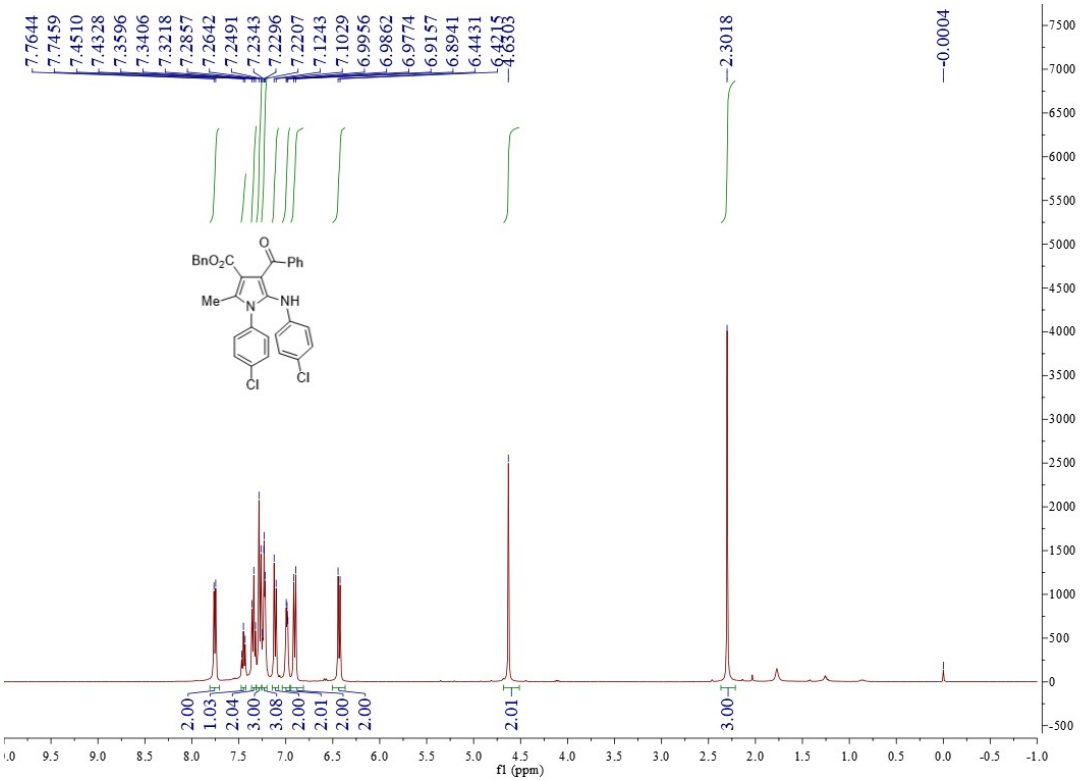
^{19}F NMR (376 MHz, $CDCl_3$)



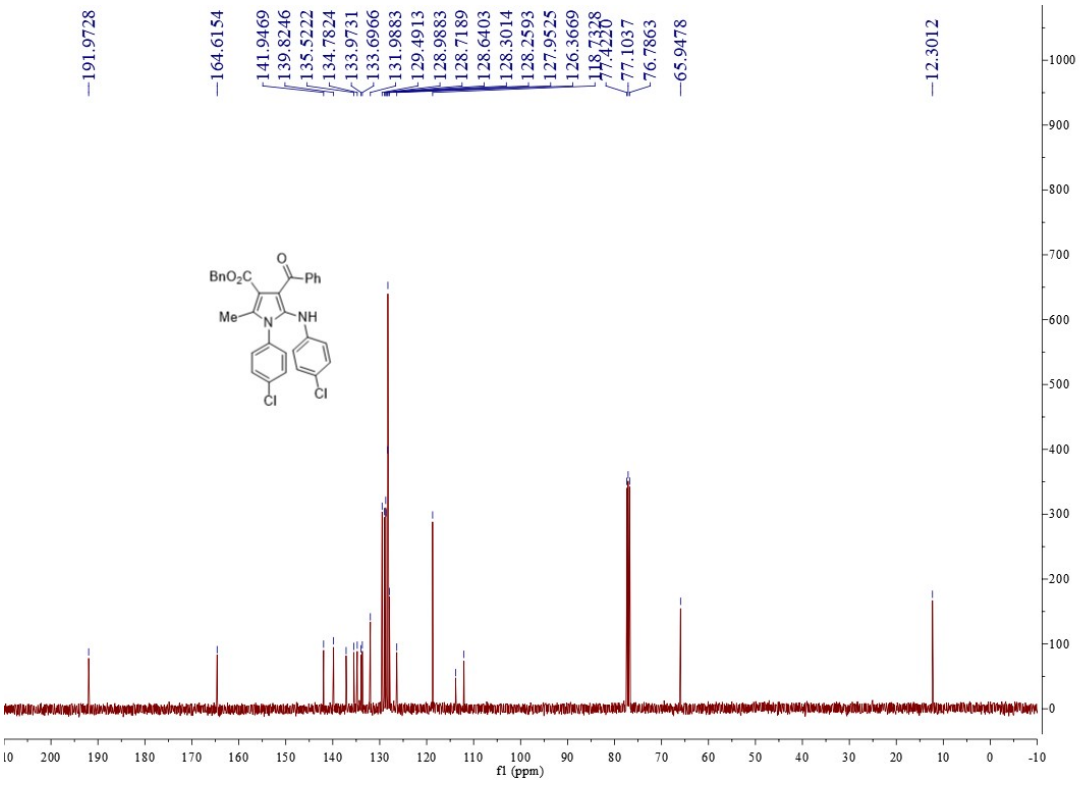
Benzyl 4-benzoyl-1-(4-chlorophenyl)-5-((4-chlorophenyl)amino)-2-methyl-1*H*-pyrrole-3-

carboxylate (4q)

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



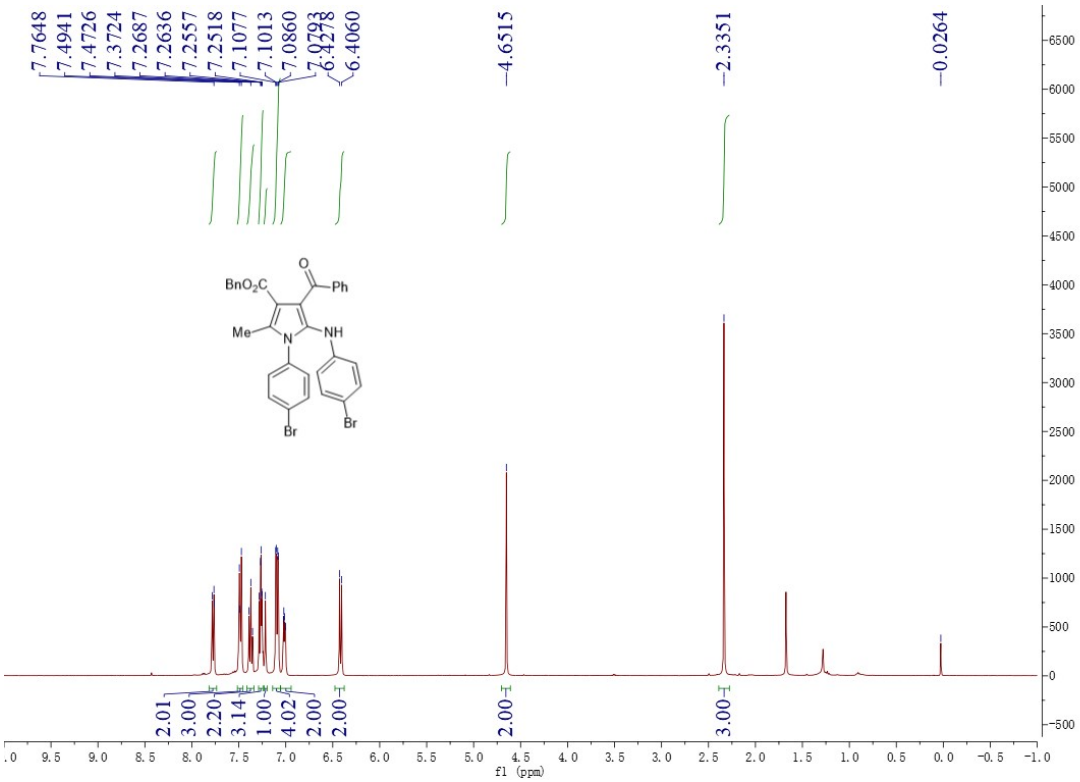
^{13}C NMR (101 MHz, $CDCl_3$)



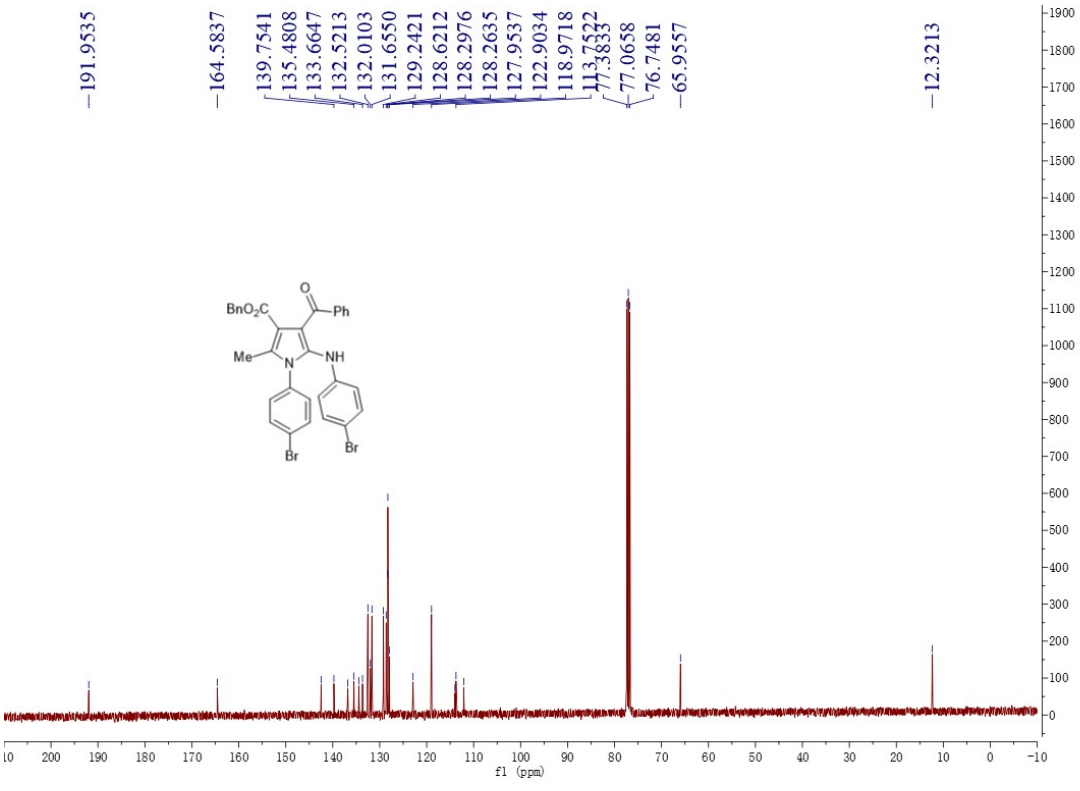
Benzyl 4-benzoyl-1-(4-bromophenyl)-5-((4-bromophenyl)amino)-2-methyl-1*H*-pyrrole-3-

carboxylate (4r)

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



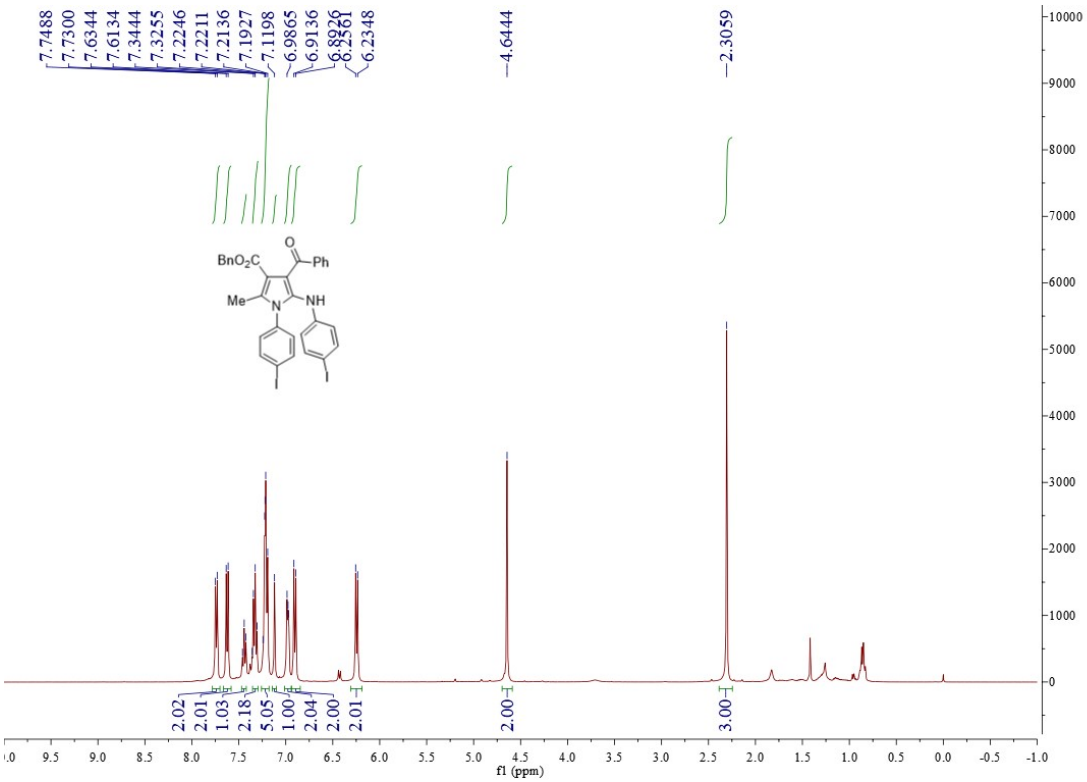
^{13}C NMR (101 MHz, $CDCl_3$)



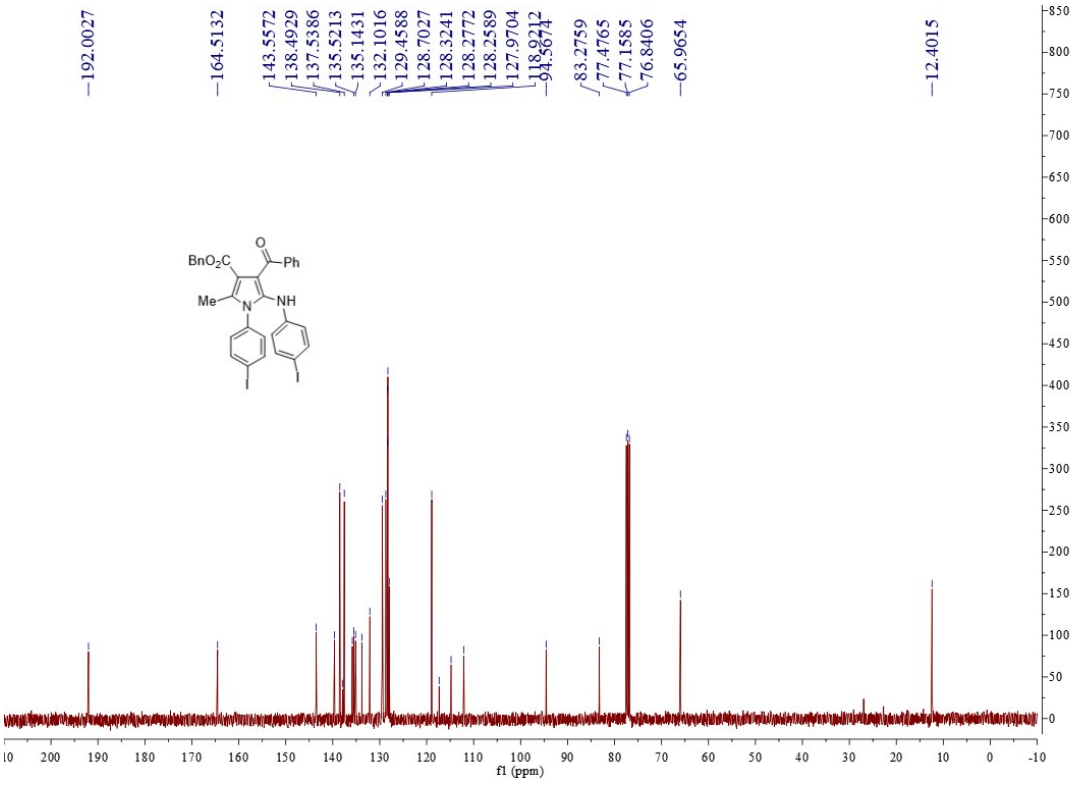
Benzyl 4-benzoyl-1-(4-iodophenyl)-5-((4-iodophenyl)amino)-2-methyl-1*H*-pyrrole-3-

carboxylate (4s)

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

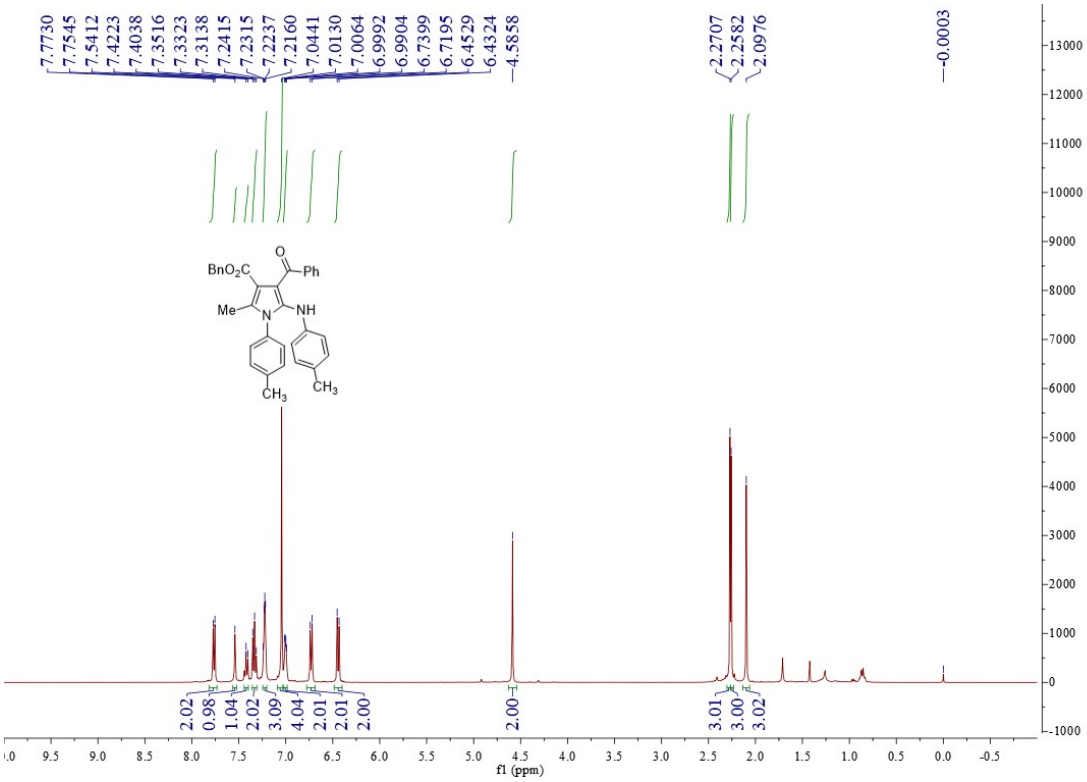


^{13}C NMR (101 MHz, $CDCl_3$)

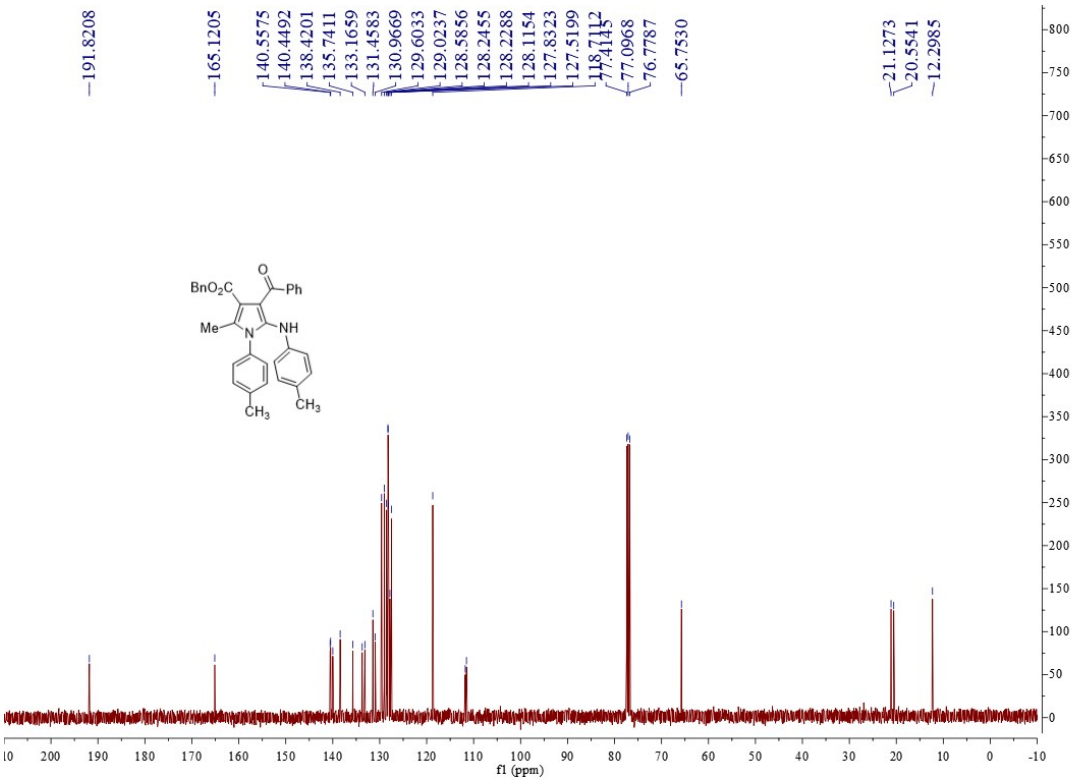


Benzyl 4-benzoyl-2-methyl-1-(*p*-tolyl)-5-(*p*-tolylamino)-1*H*-pyrrole-3-carboxylate (4t)

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



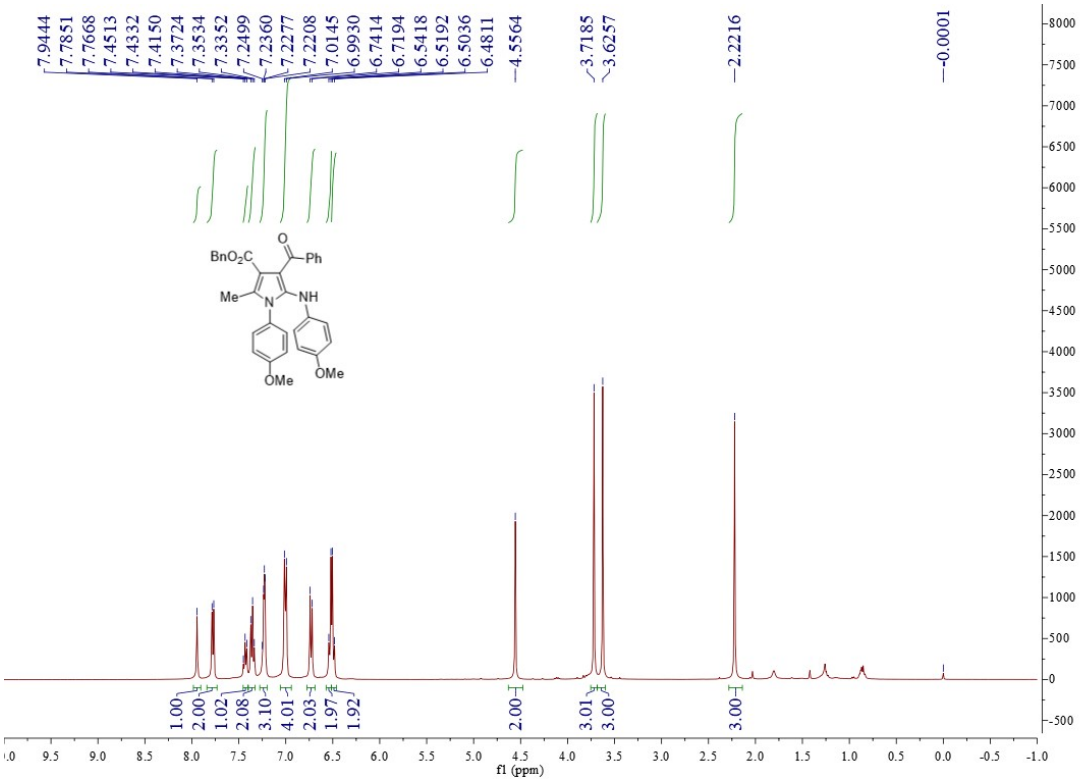
^{13}C NMR (101 MHz, $CDCl_3$)



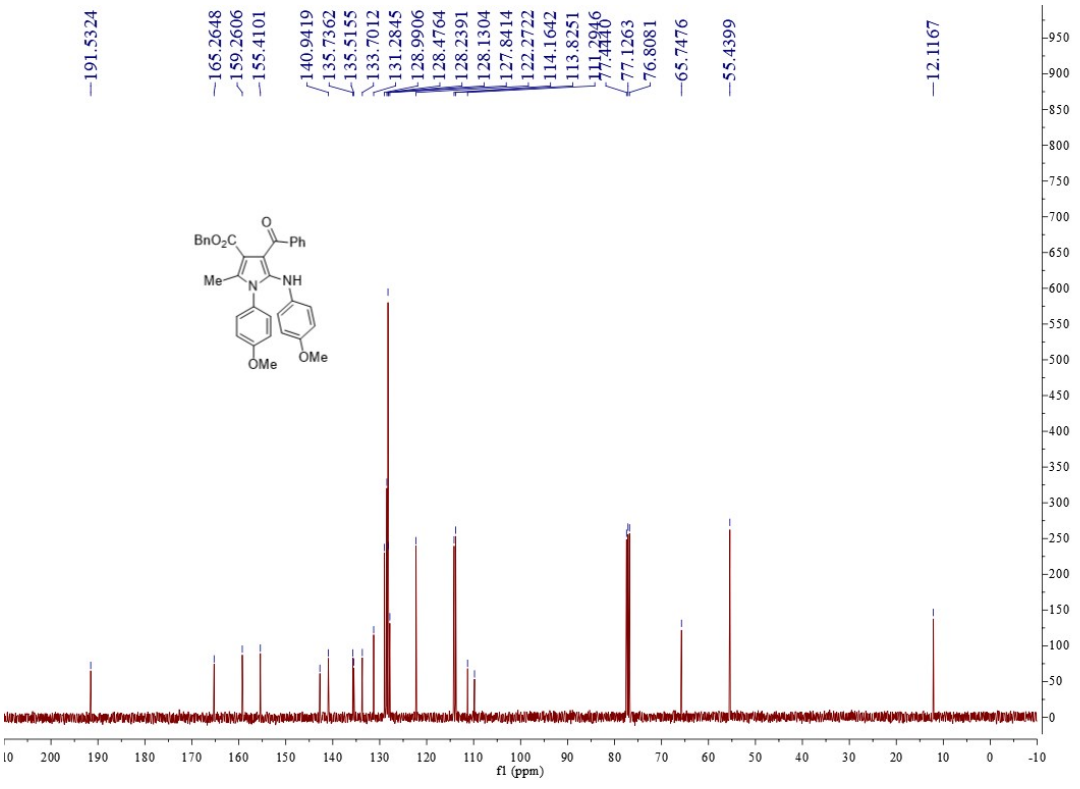
Benzyl 4-benzoyl-1-(4-methoxyphenyl)-5-((4-methoxyphenyl)amino)-2-methyl-1*H*-pyrrole-3-

carboxylate (4u)

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



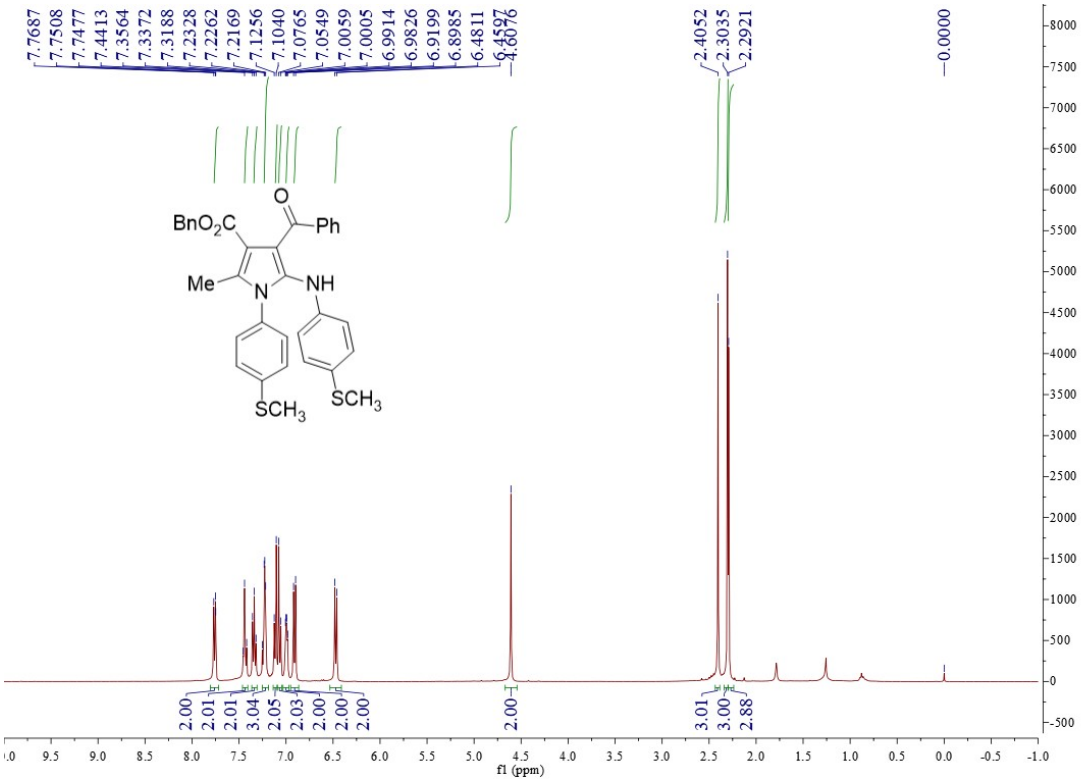
^{13}C NMR (101 MHz, $CDCl_3$)



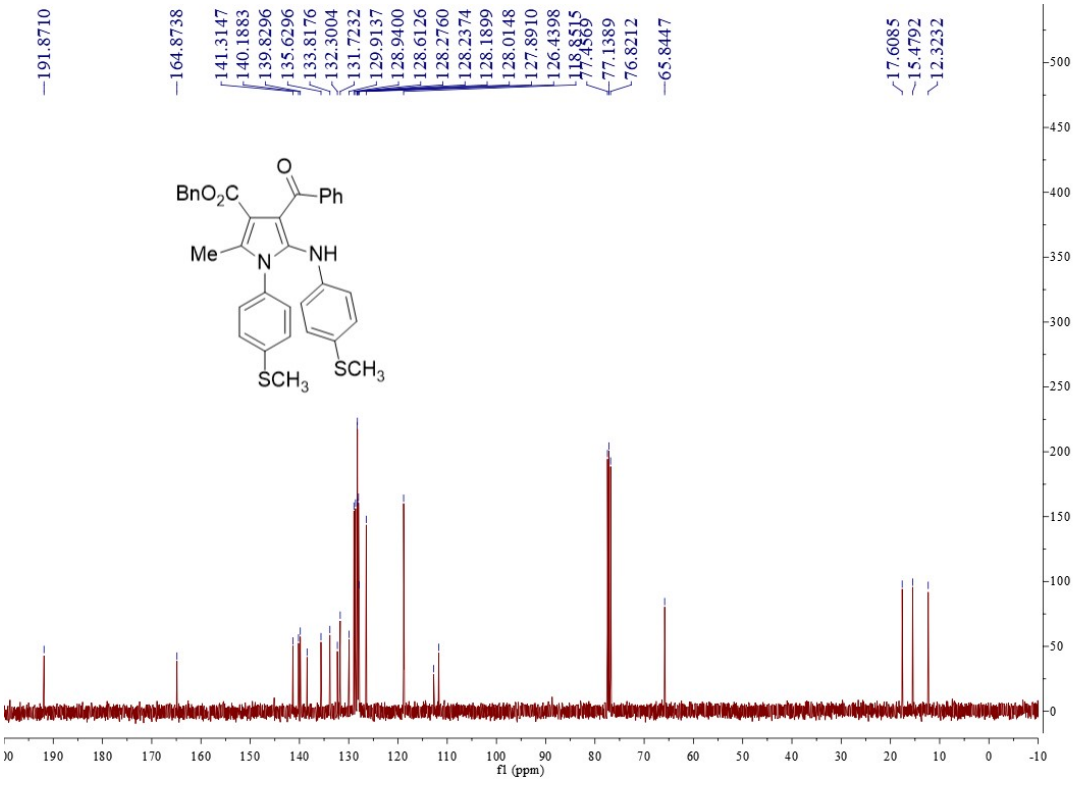
Benzyl 4-benzoyl-2-methyl-1-(4-(methylthio)phenyl)-5-((4-(methylthio)phenyl)amino)-1*H*-

pyrrole-3-carboxylate (4v)

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



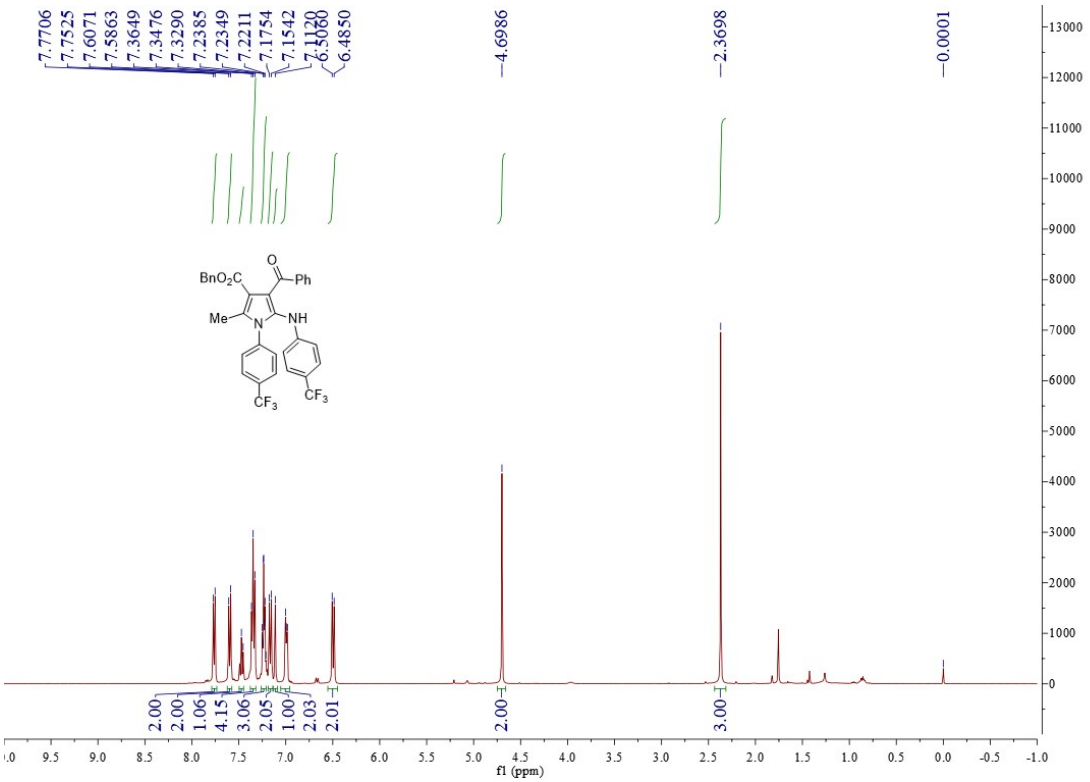
^{13}C NMR (101 MHz, $CDCl_3$)



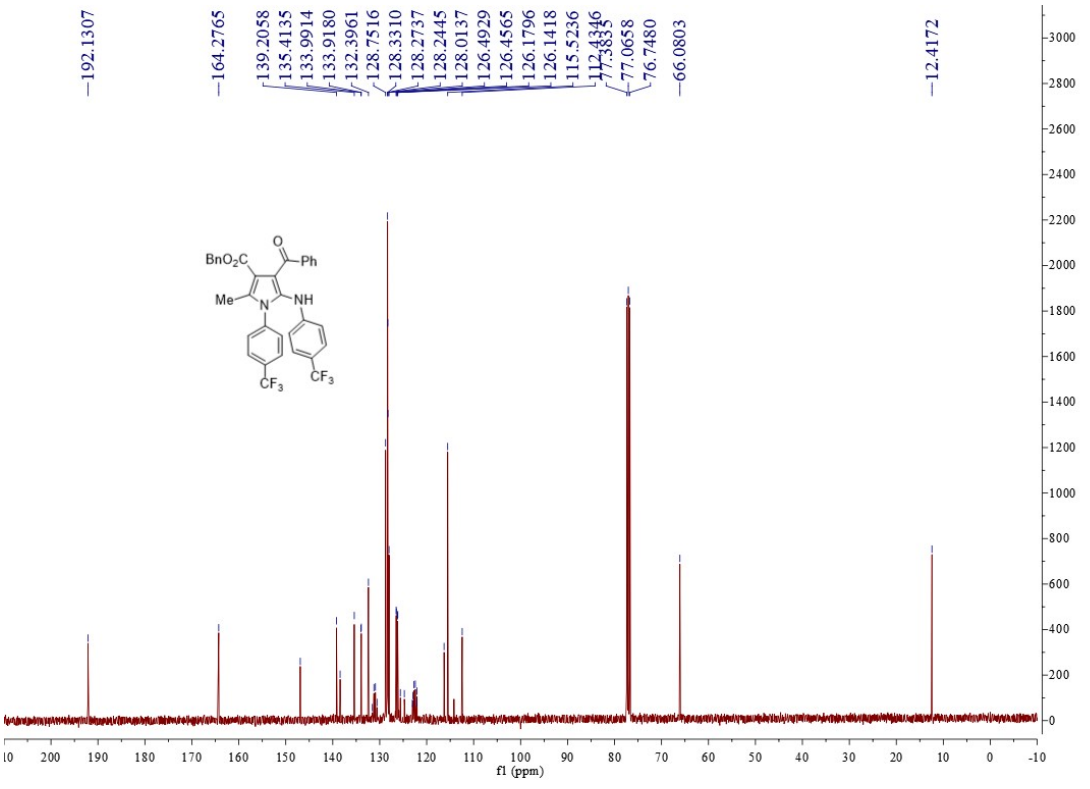
Benzyl 4-benzoyl-2-methyl-1-(4-(trifluoromethyl)phenyl)-5-((4-(trifluoromethyl)phenyl)

amino)-1*H*-pyrrole-3-carboxylate (4w)

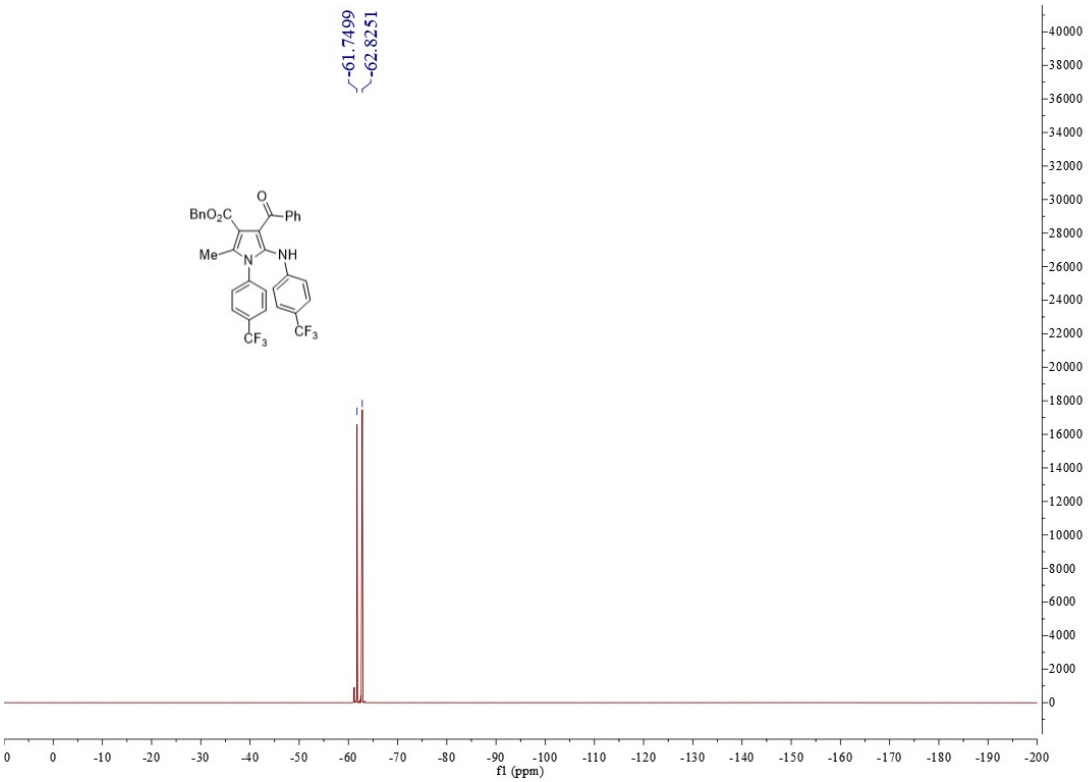
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

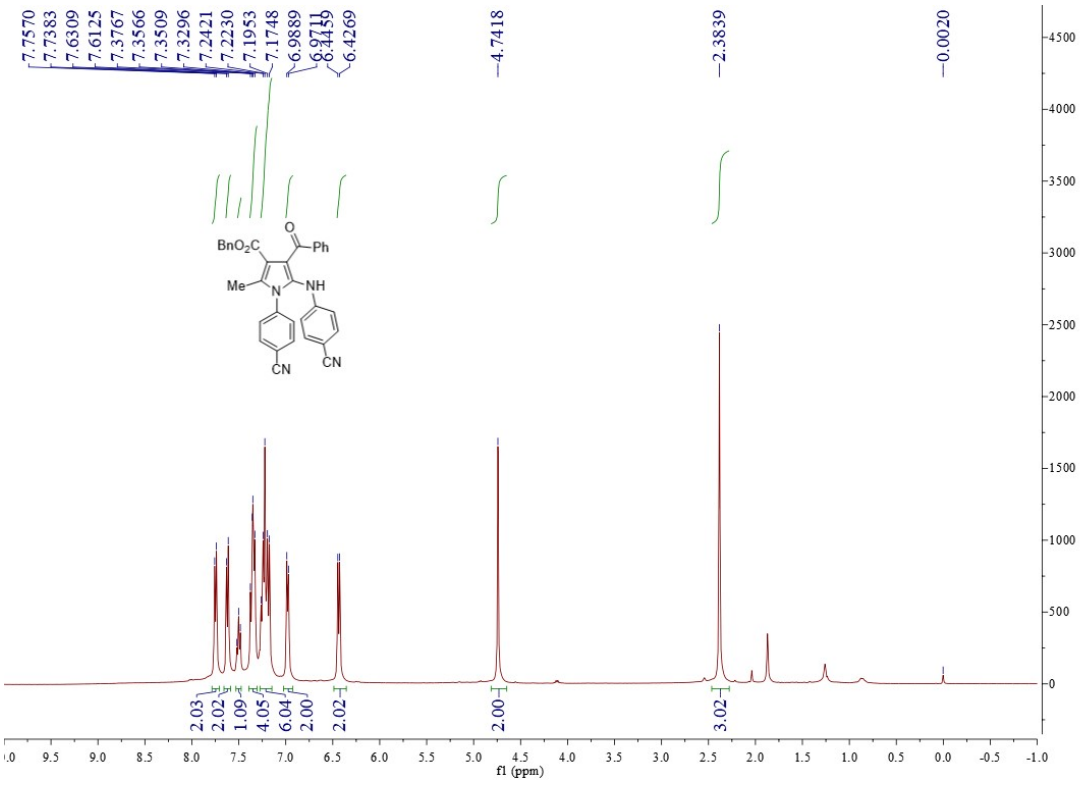


^{19}F NMR (376 MHz, $CDCl_3$)

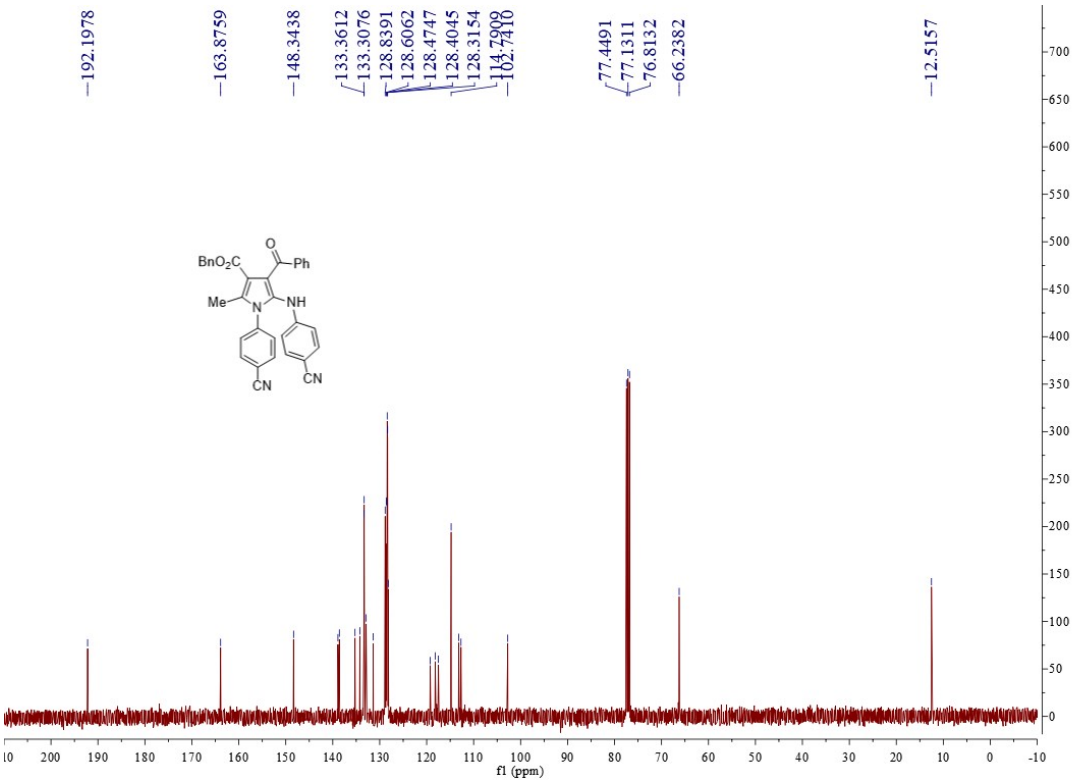


Benzyl 4-benzoyl-1-(4-cyanophenyl)-5-((4-cyanophenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4x)

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

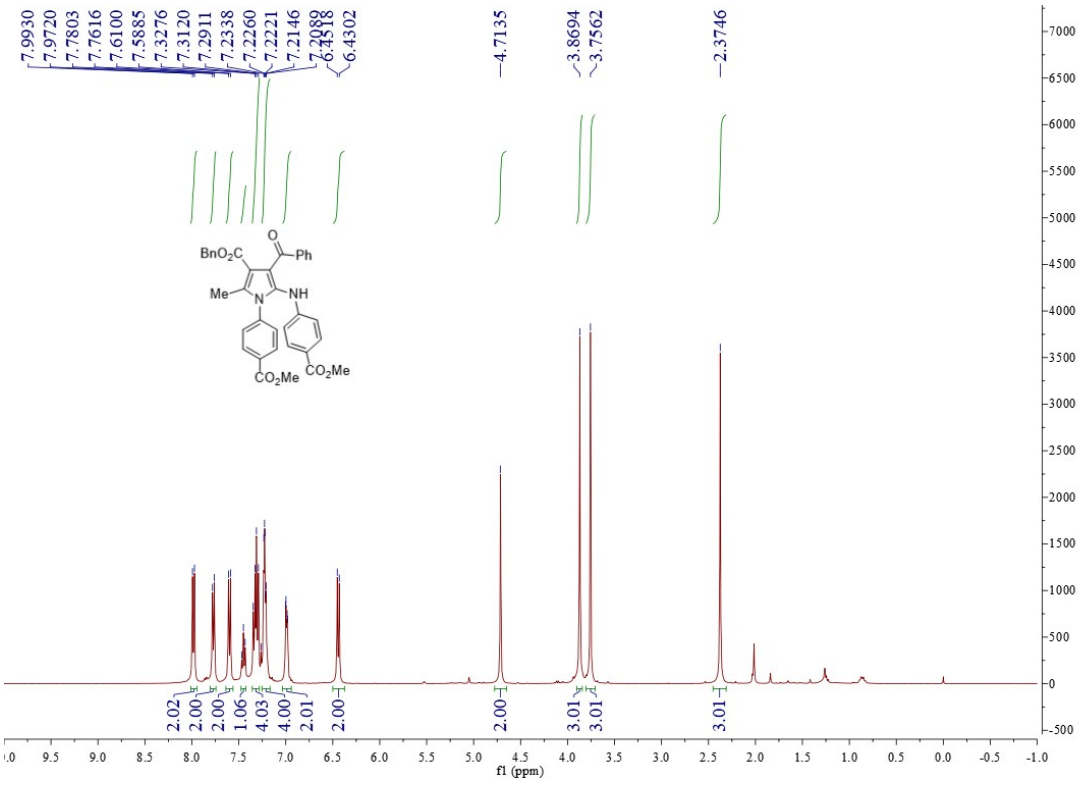


^{13}C NMR (101 MHz, $CDCl_3$)

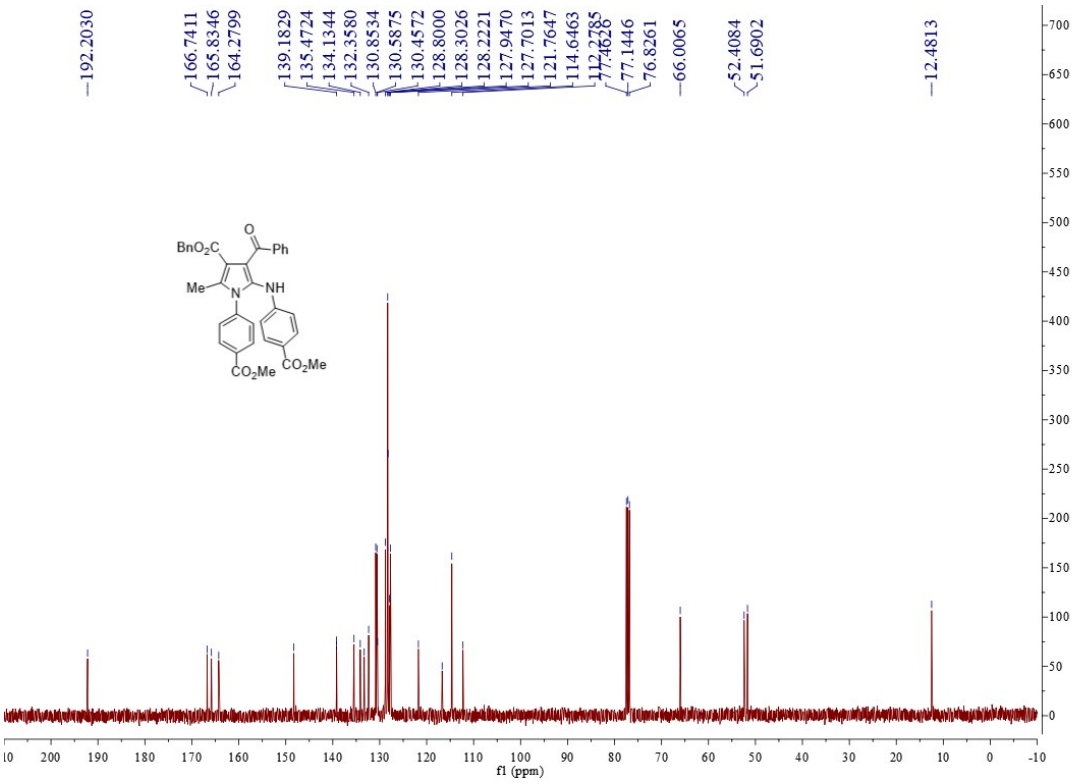


Benzyl 4-benzoyl-1-(4-(methoxycarbonyl)phenyl)-5-((4-(methoxycarbonyl)phenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4y)

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

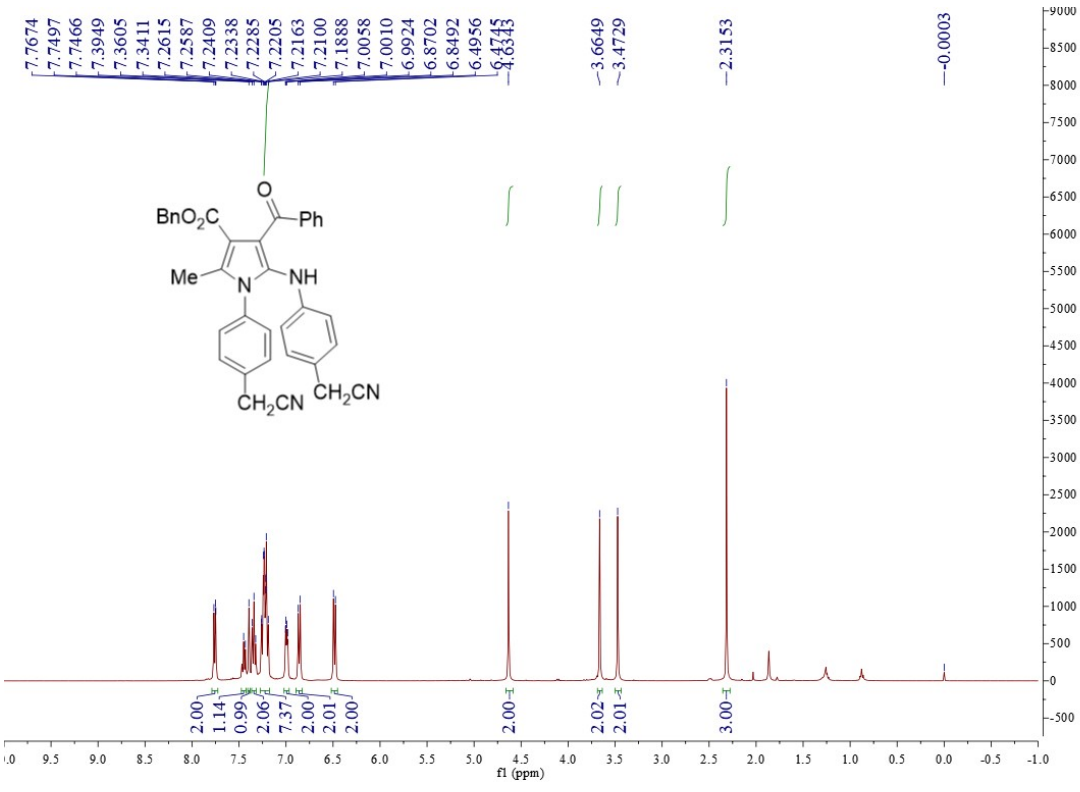


^{13}C NMR (101 MHz, $CDCl_3$)

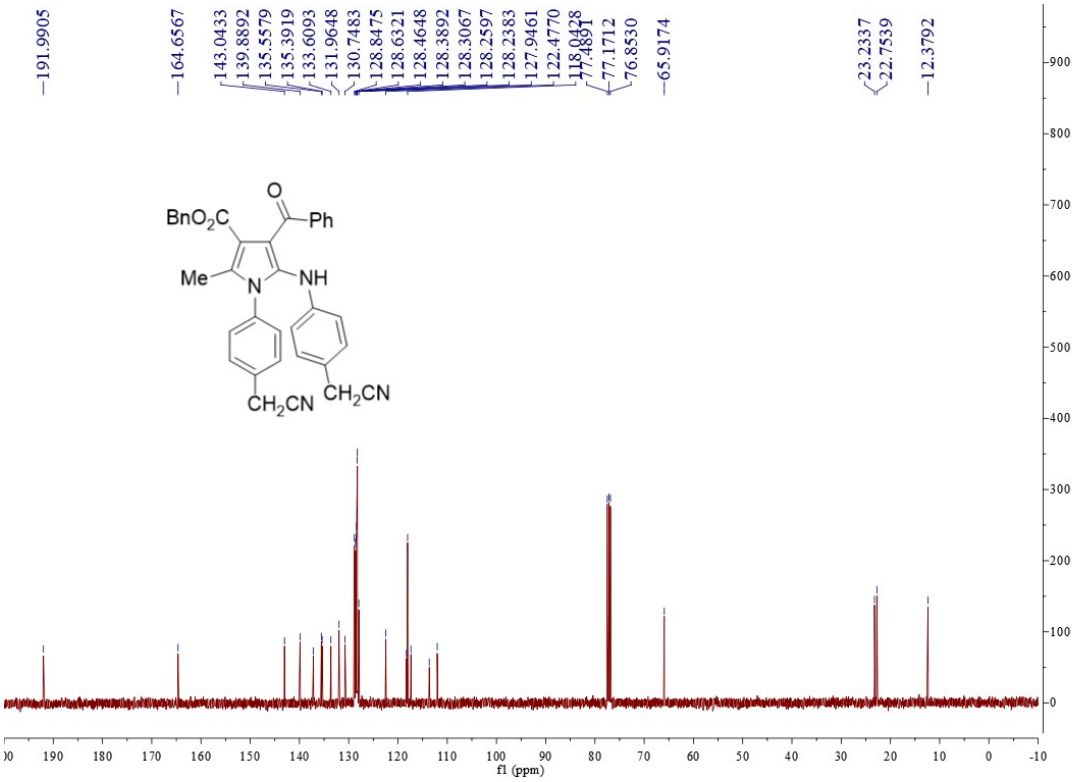


Benzyl 4-benzoyl-1-(4-(cyanomethyl)phenyl)-5-((4-(cyanomethyl)phenyl)amino)-2-methyl-1*H*-pyrrole-3-carboxylate (4z)

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

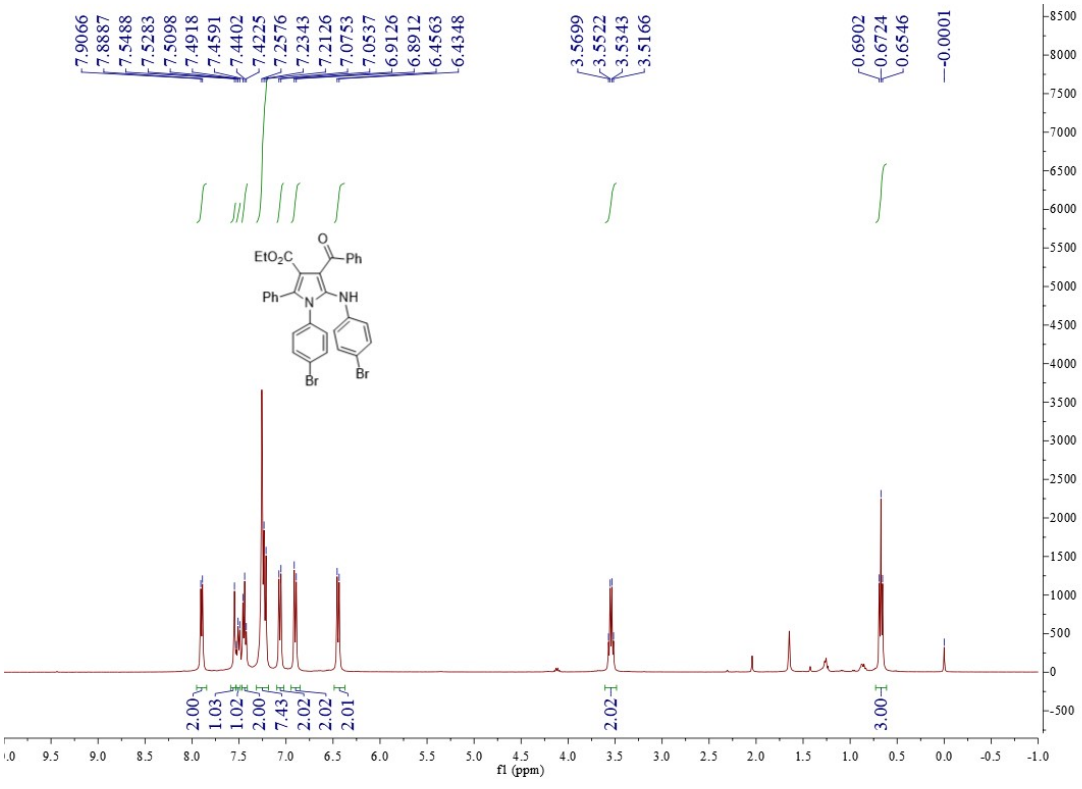


^{13}C NMR (101 MHz, $CDCl_3$)

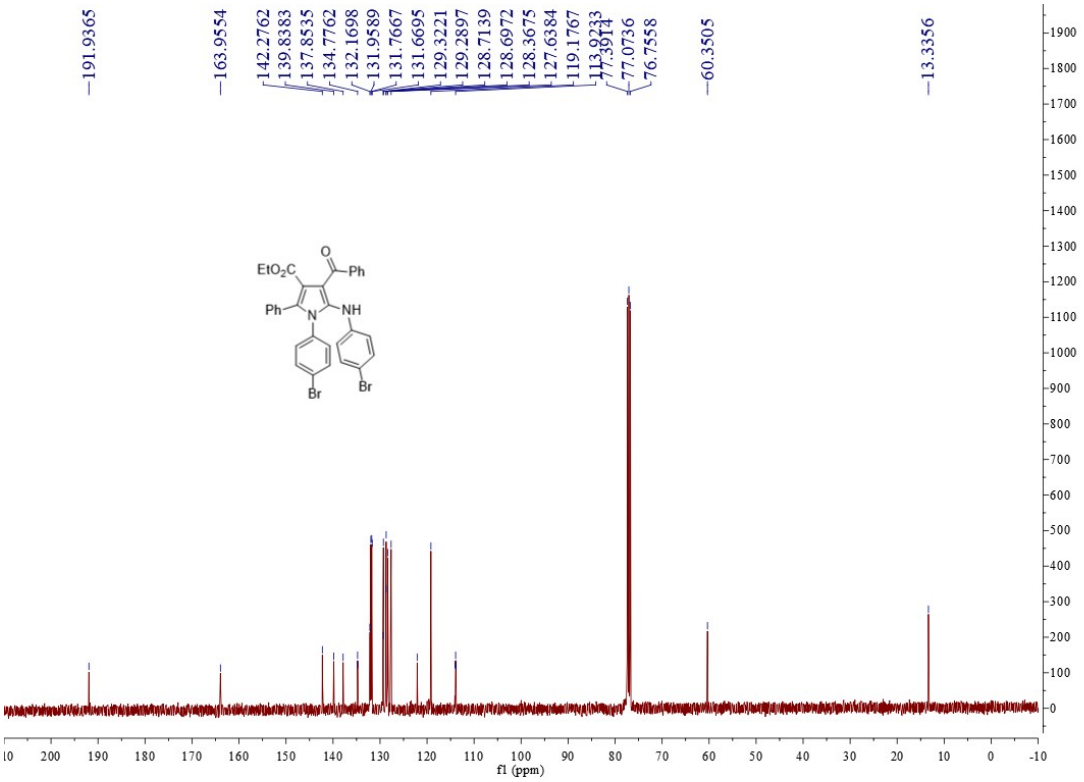


Ethyl 4-benzoyl-1-(4-bromophenyl)-5-((4-bromophenyl)amino)-2-phenyl-1*H*-pyrrole-3-carboxylate (4aa)

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

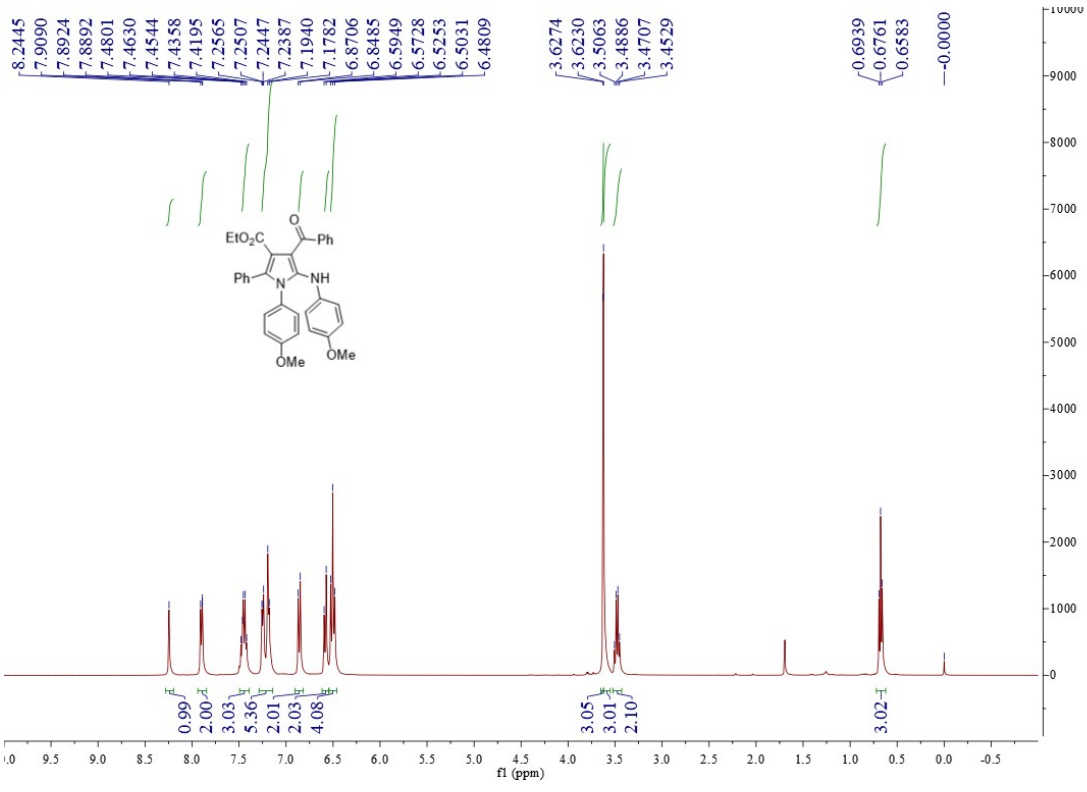


^{13}C NMR (101 MHz, $CDCl_3$)

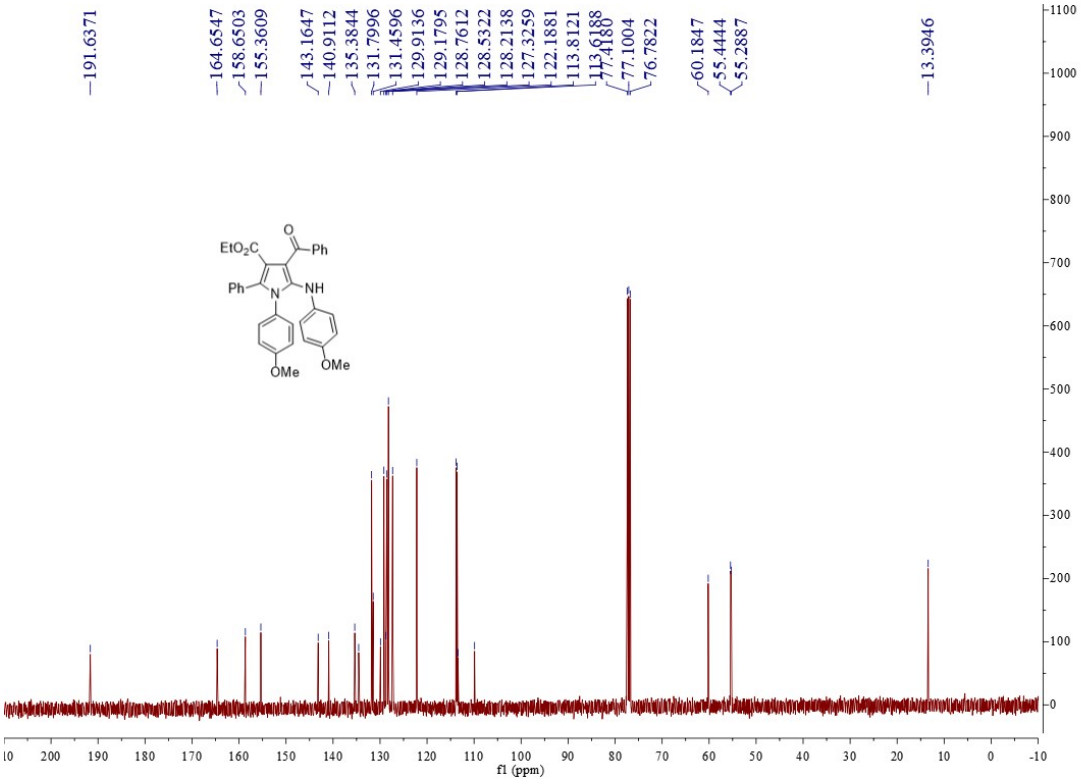


Ethyl 4-benzoyl-1-(4-methoxyphenyl)-5-((4-methoxyphenyl)amino)-2-phenyl-1*H*-pyrrole-3-carboxylate (4ab)

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

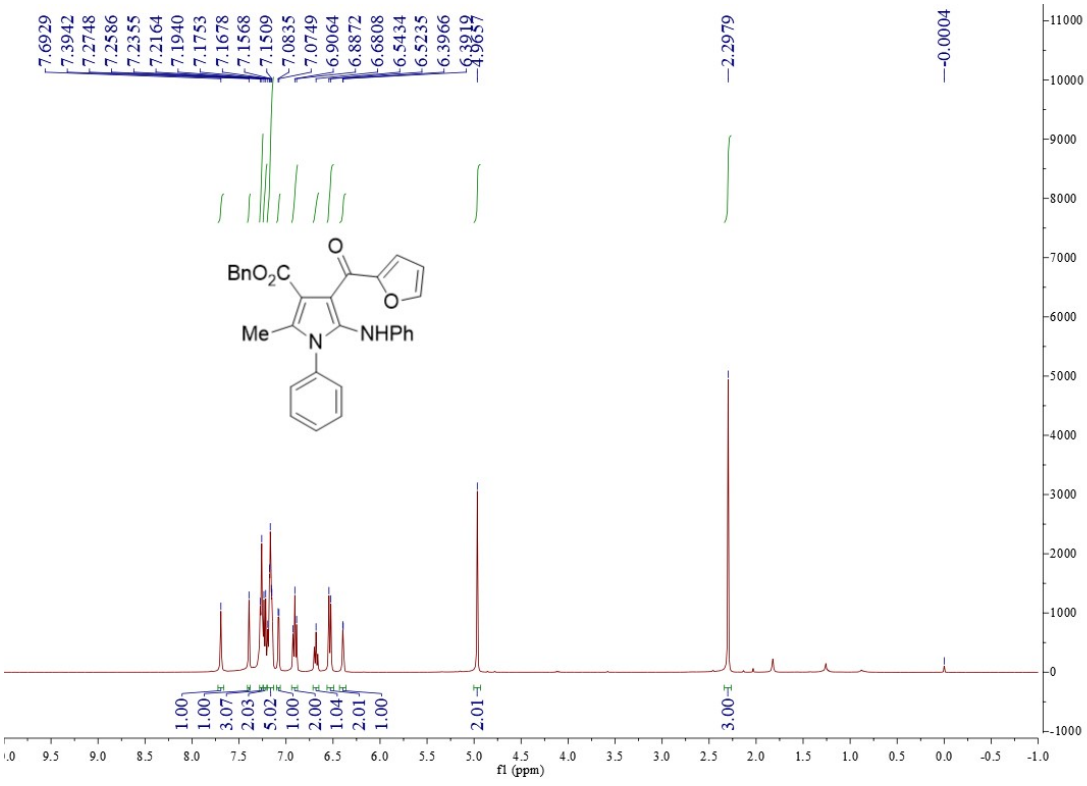


^{13}C NMR (101 MHz, $CDCl_3$)

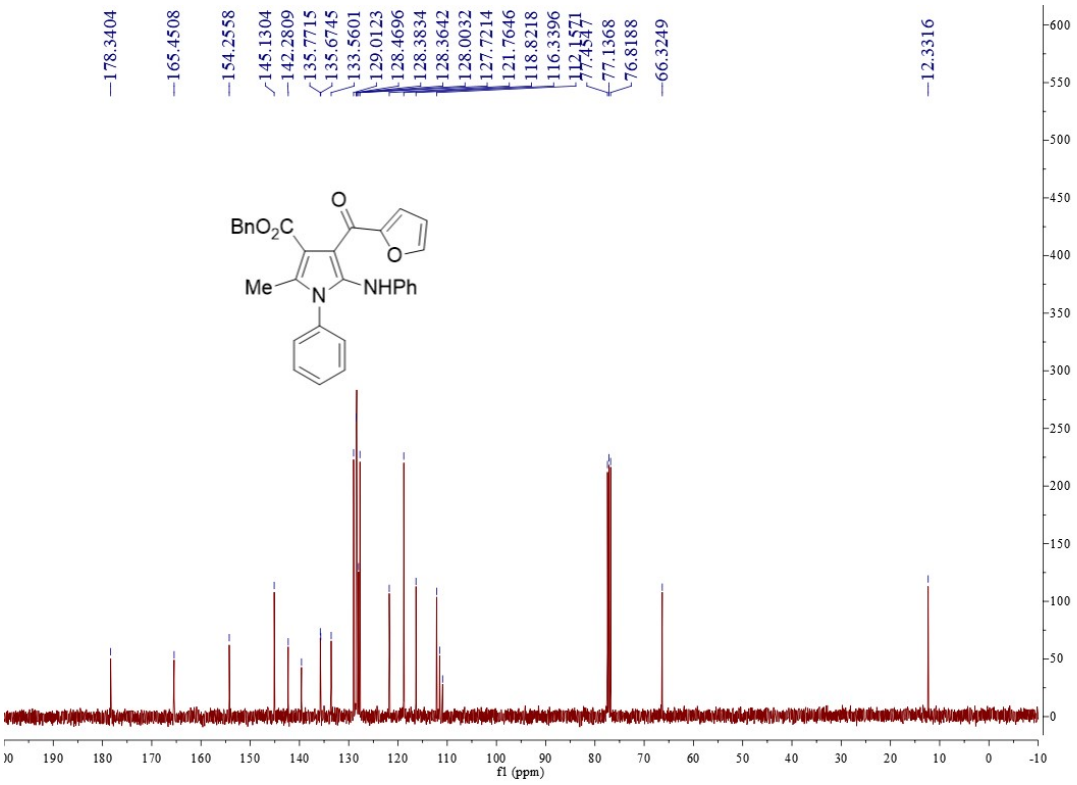


Benzyl 4-(furan-2-carbonyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ac)

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

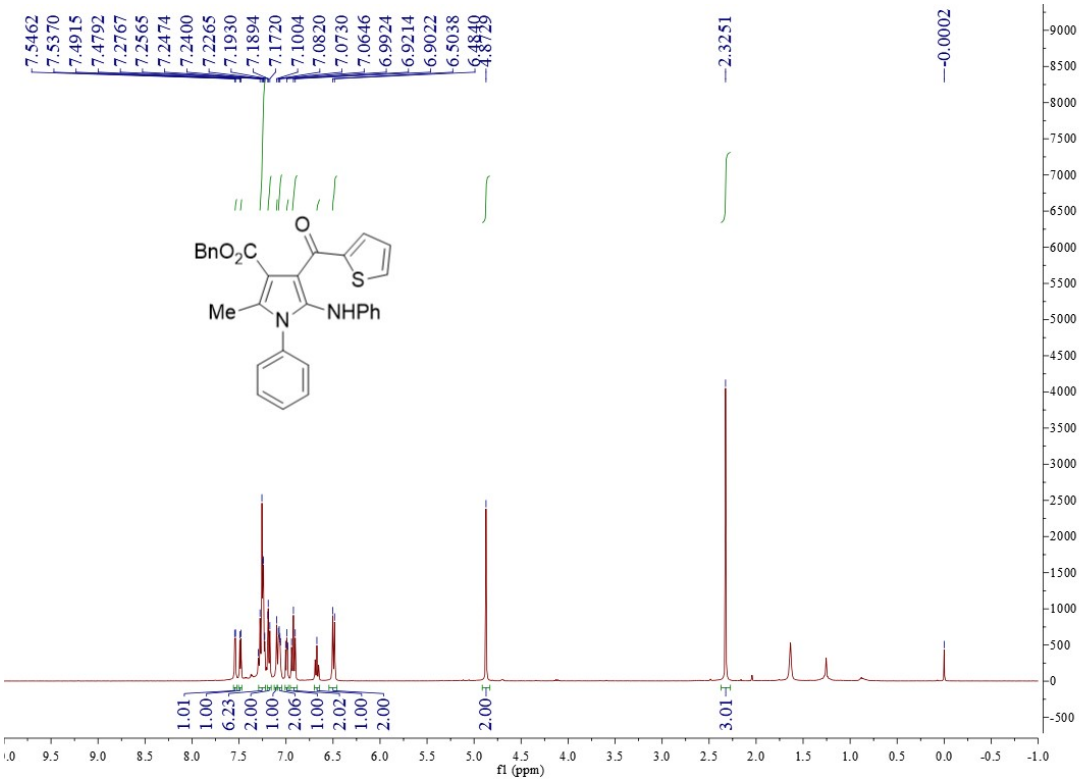


^{13}C NMR (101 MHz, $CDCl_3$)

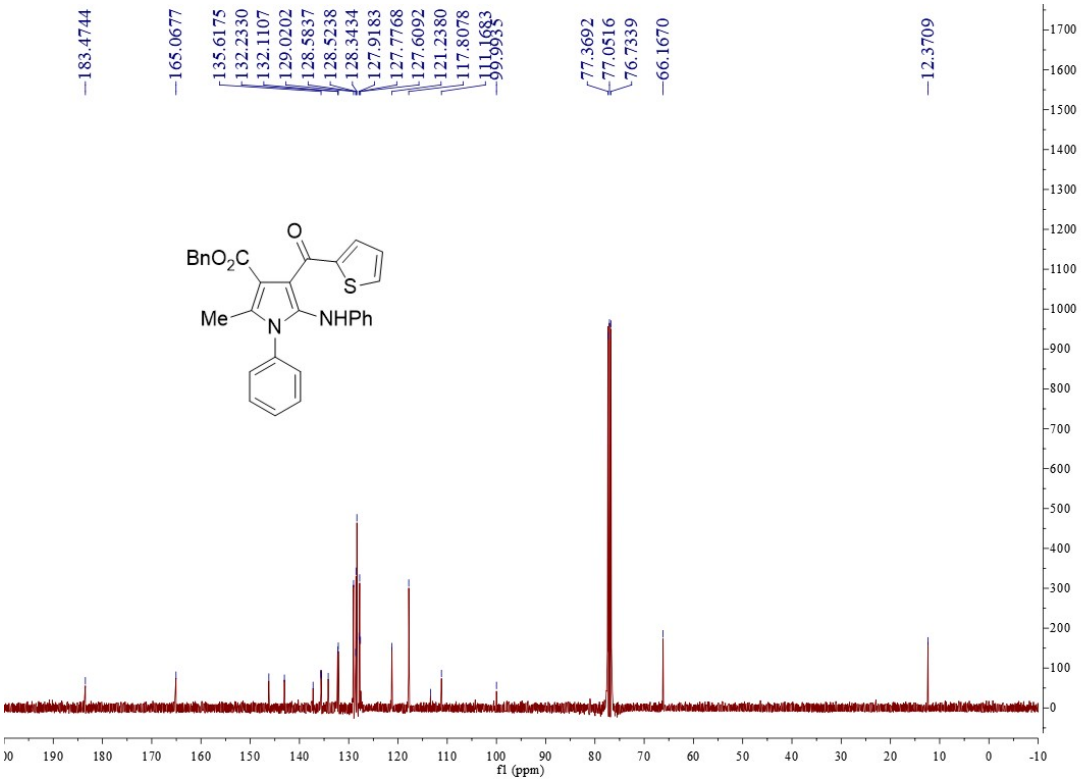


Benzyl 2-methyl-1-phenyl-5-(phenylamino)-4-(thiophene-2-carbonyl)-1*H*-pyrrole-3-carboxylate (4ad)

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

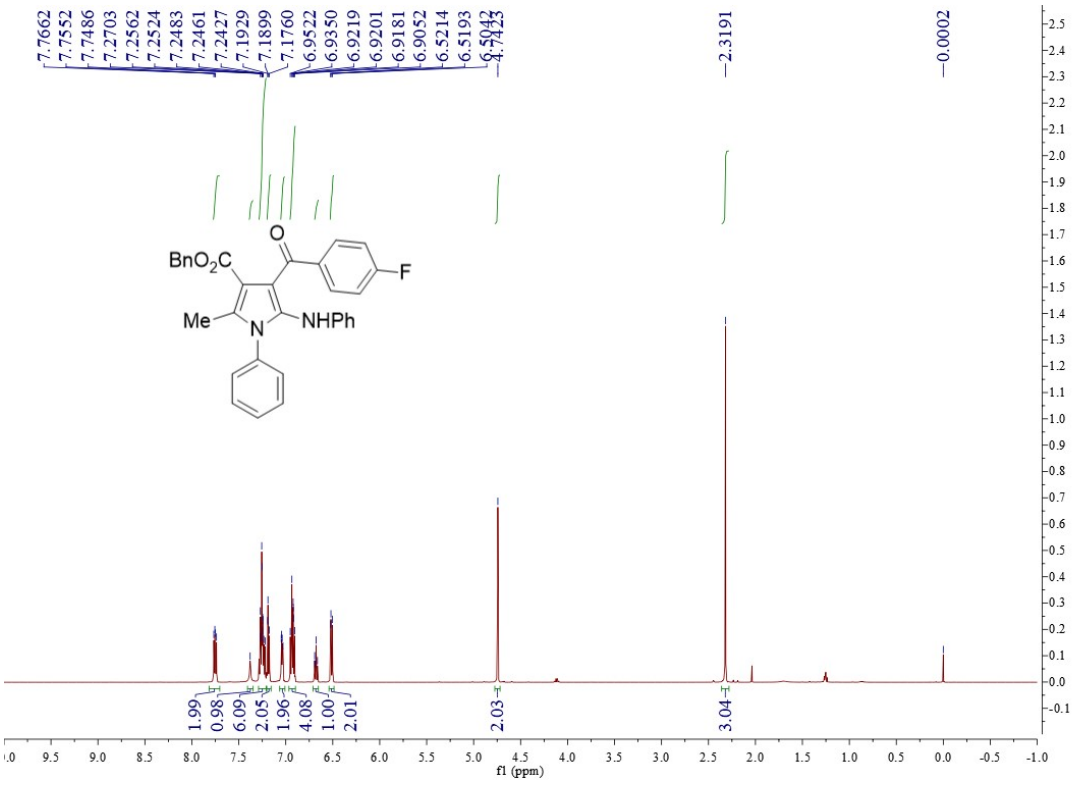


^{13}C NMR (101 MHz, $CDCl_3$)

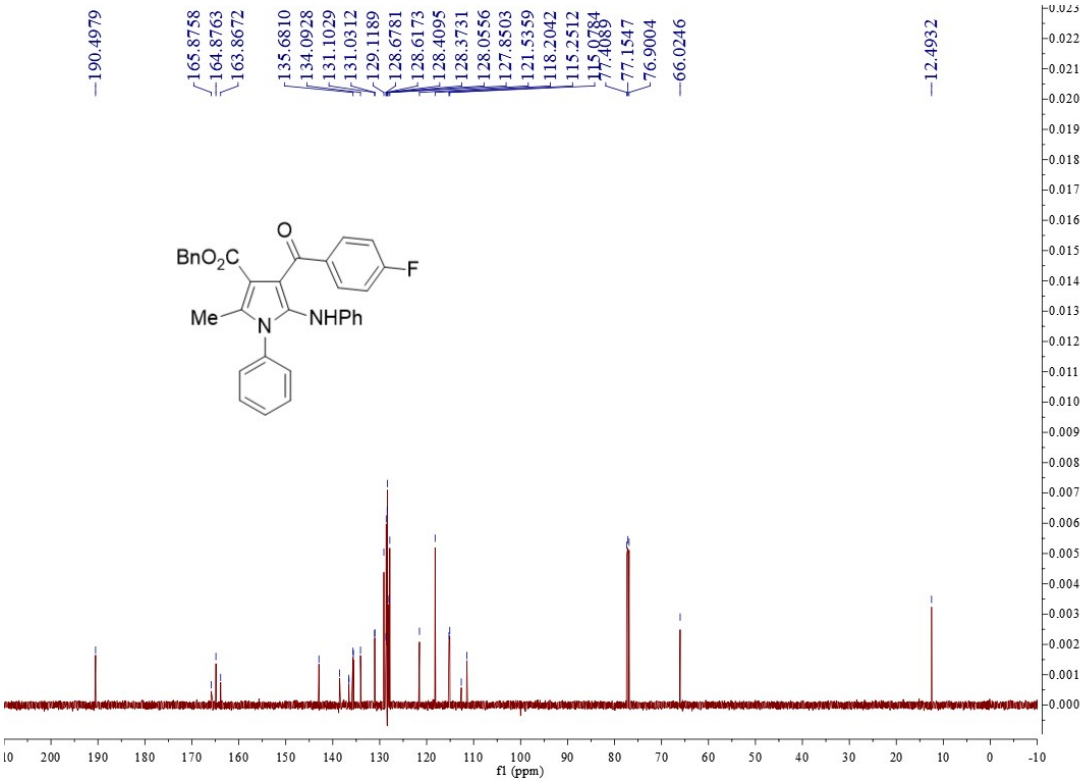


Benzyl 4-(4-fluorobenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ae)

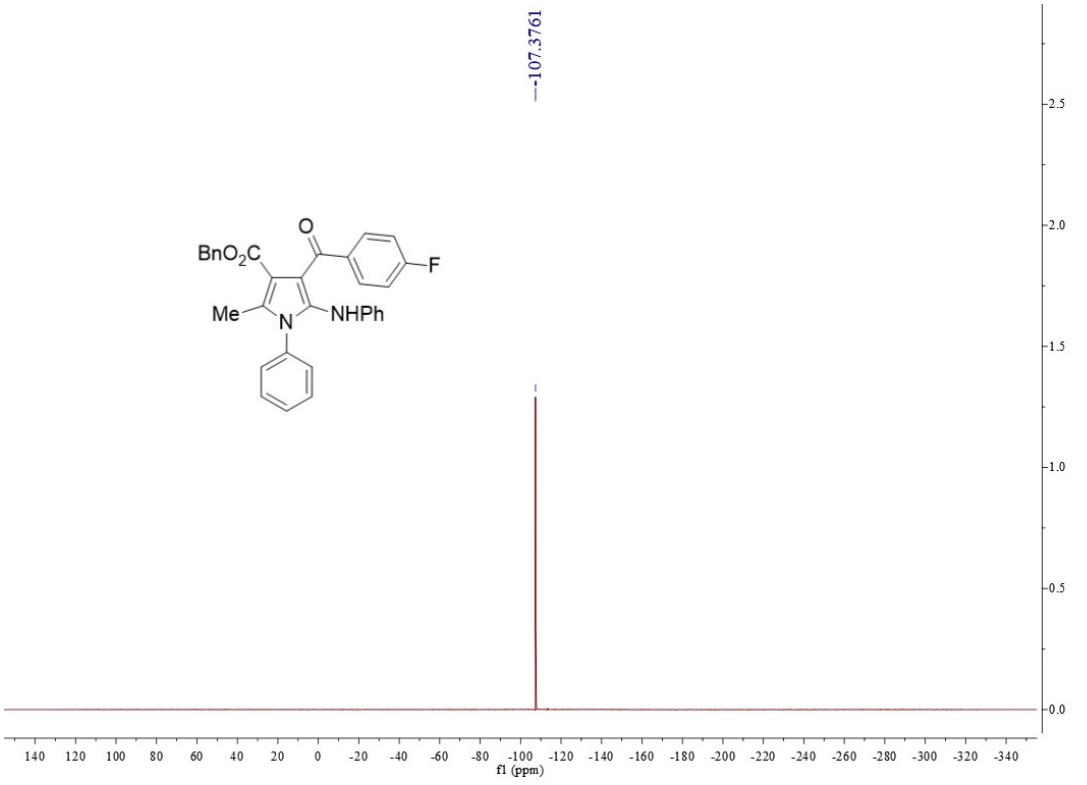
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



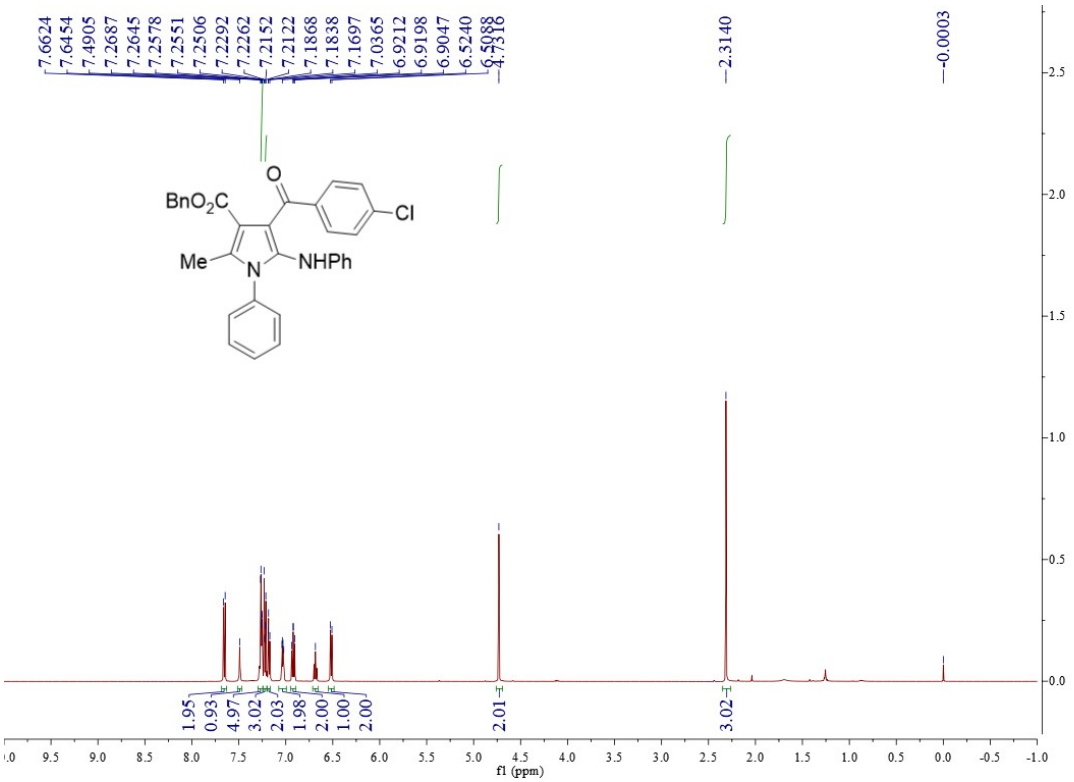
^{19}F NMR (470 MHz, $CDCl_3$)



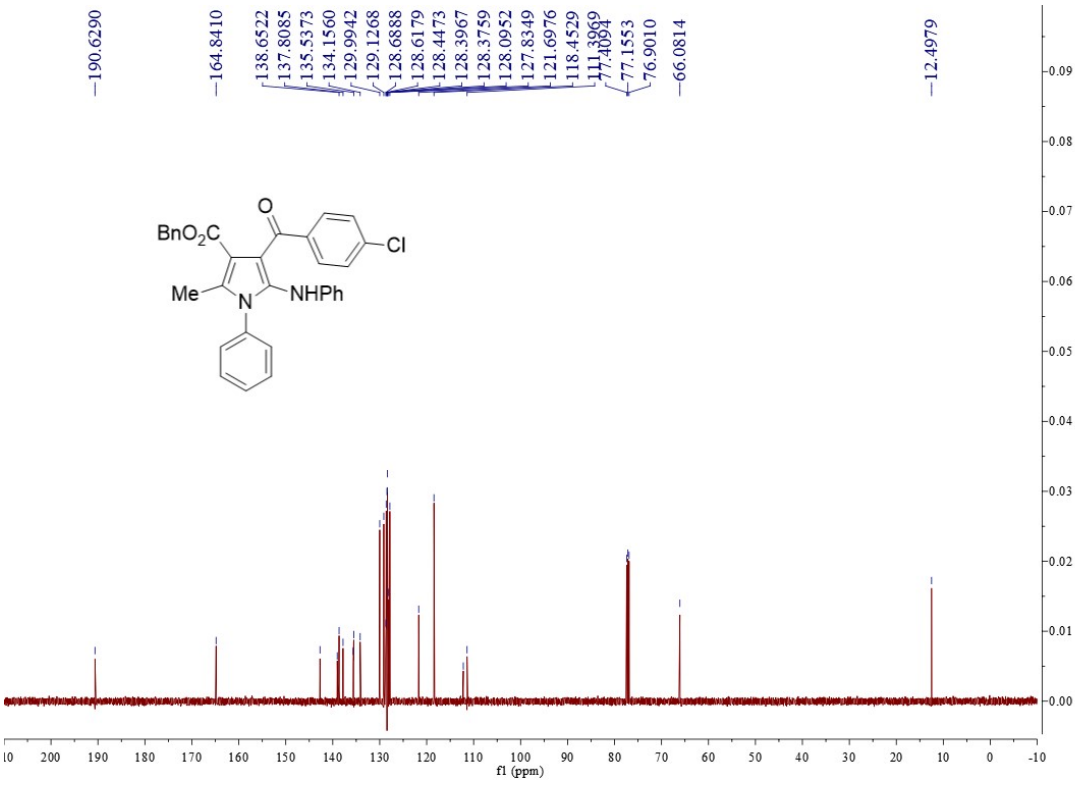
Benzyl 4-(4-chlorobenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate

(4af)

^{1}H NMR (500 MHz, $CDCl_3$)

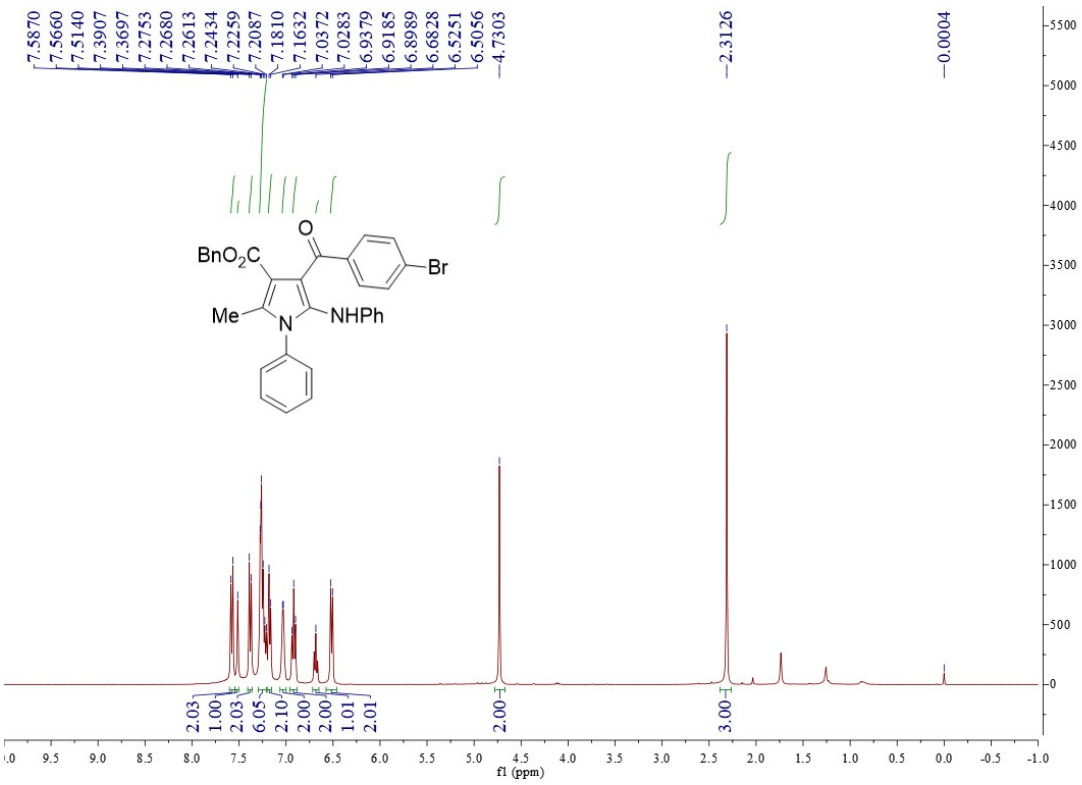


^{13}C NMR (125 MHz, $CDCl_3$)

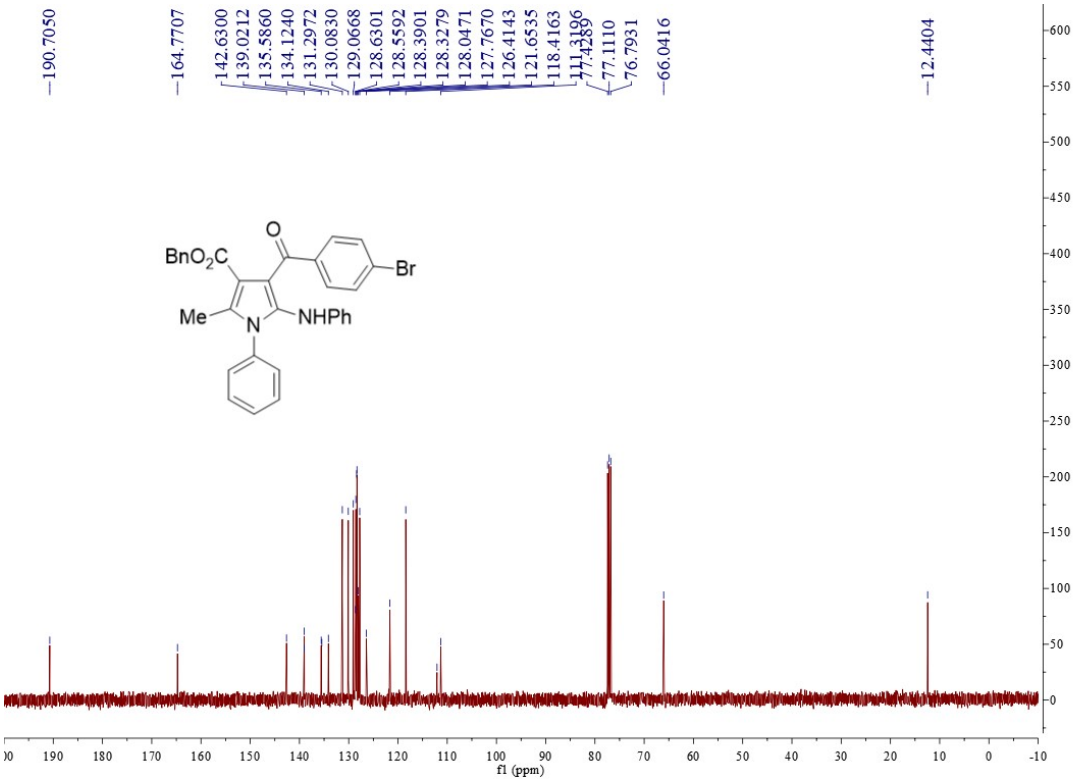


Benzyl 4-(4-bromobenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ag)

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

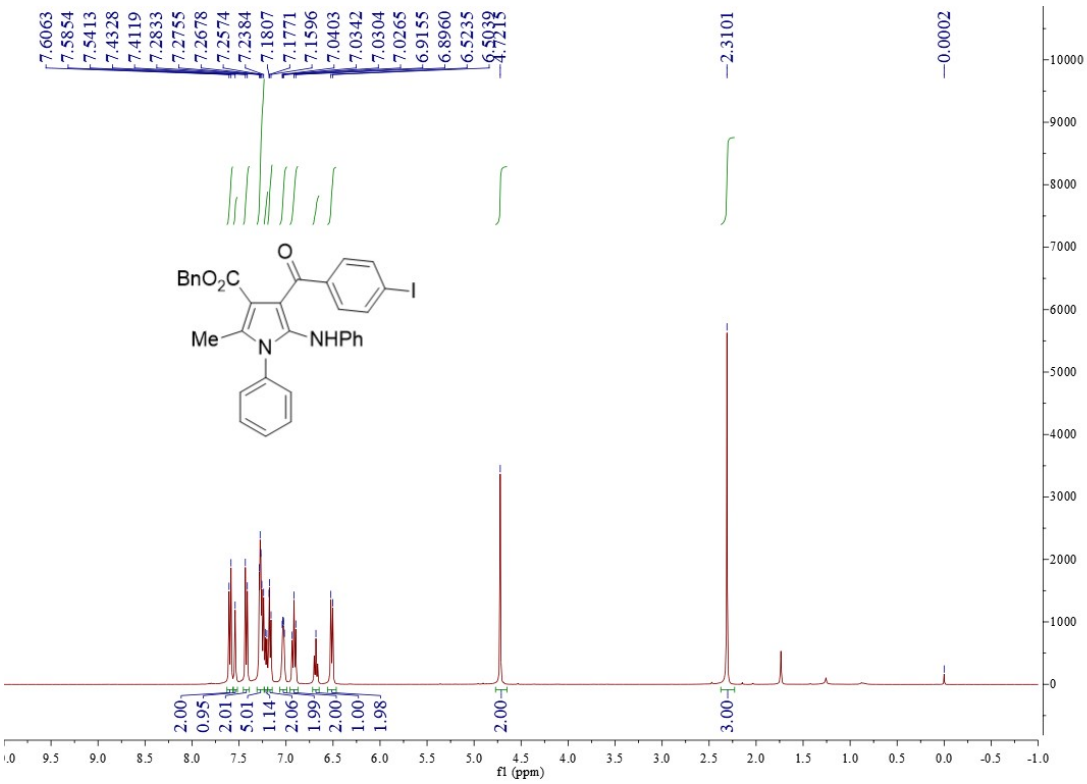


^{13}C NMR (101 MHz, $CDCl_3$)

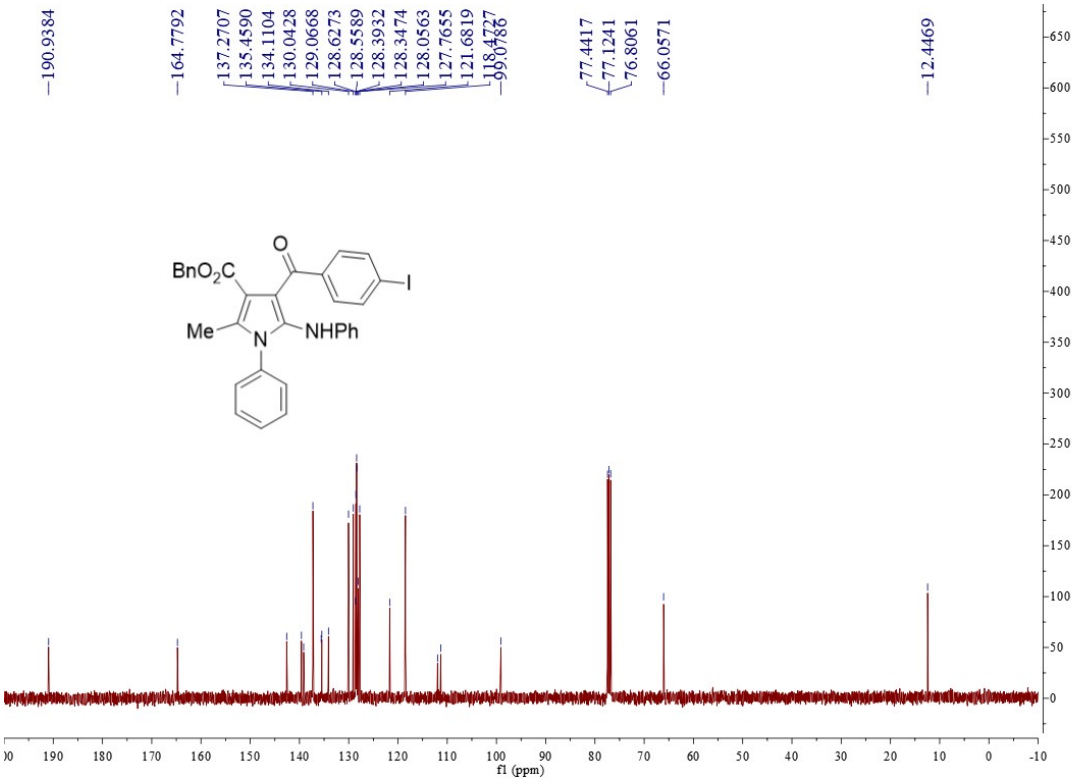


Benzyl 4-(4-iodobenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ah)

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



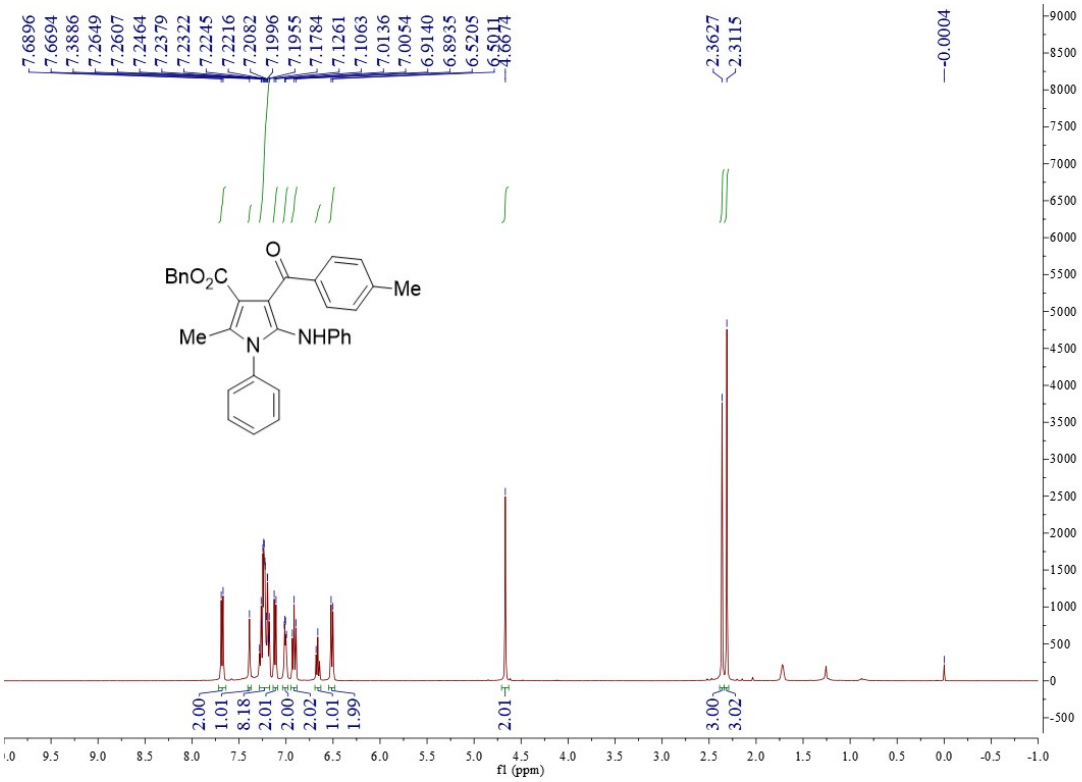
^{13}C NMR (101 MHz, $CDCl_3$)



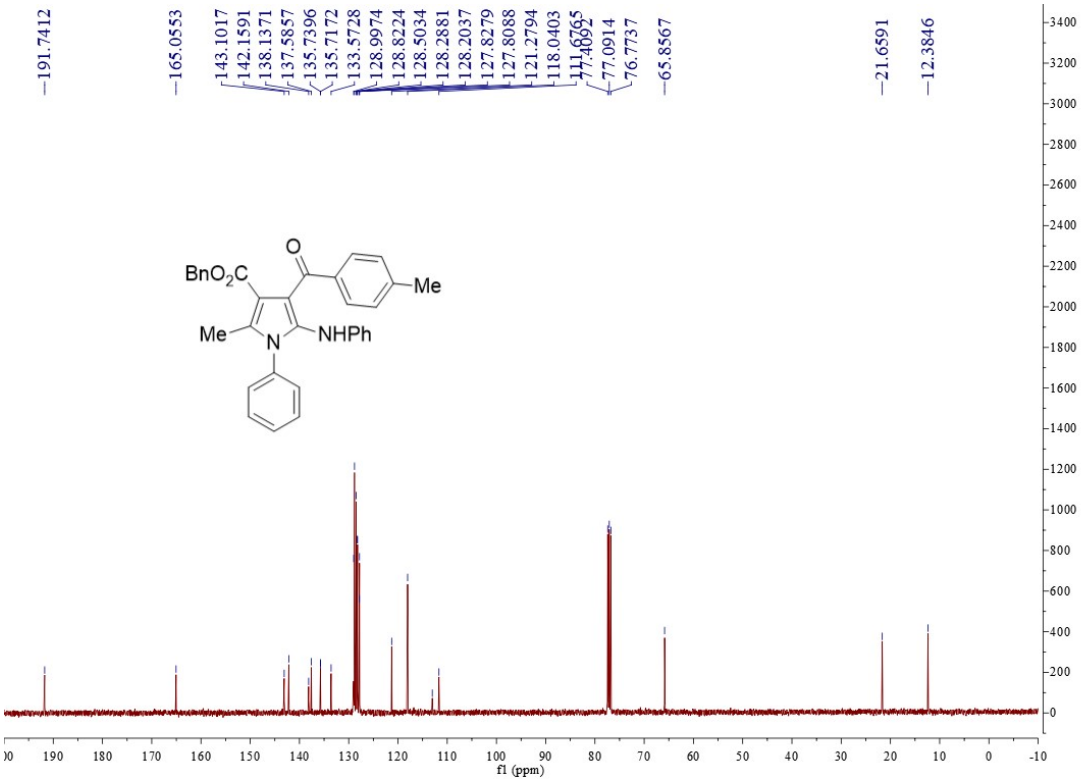
Benzyl 2-methyl-4-(4-methylbenzoyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate

(4ai)

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



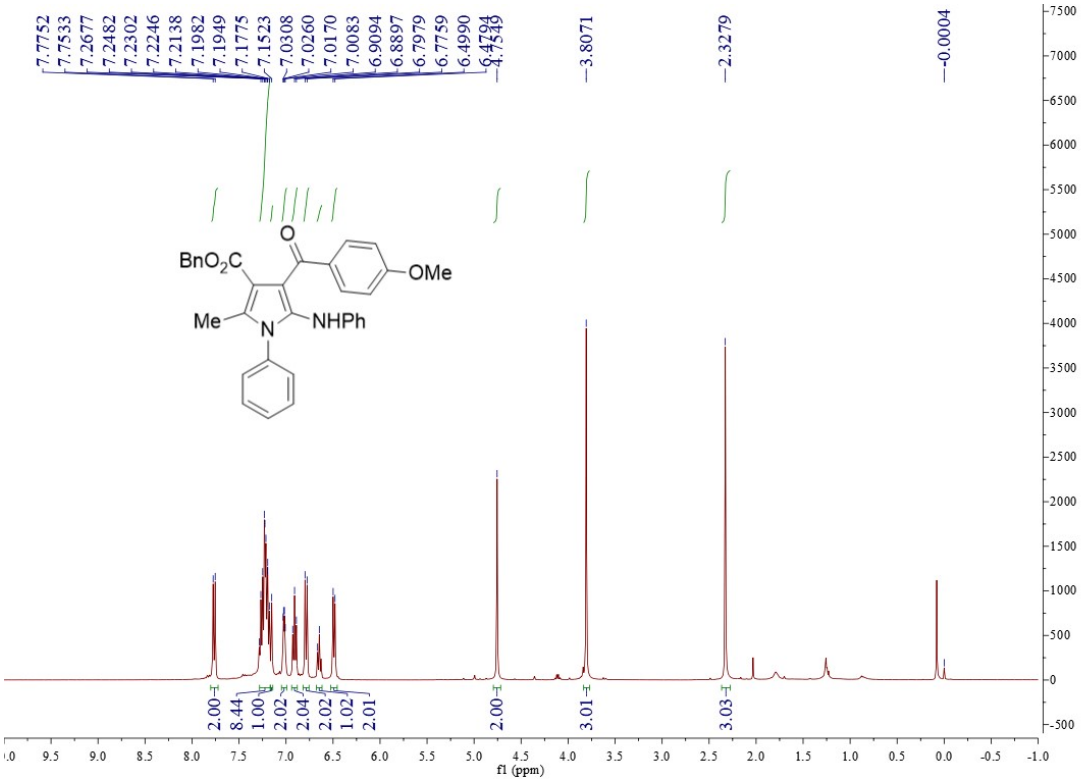
^{13}C NMR (101 MHz, $CDCl_3$)



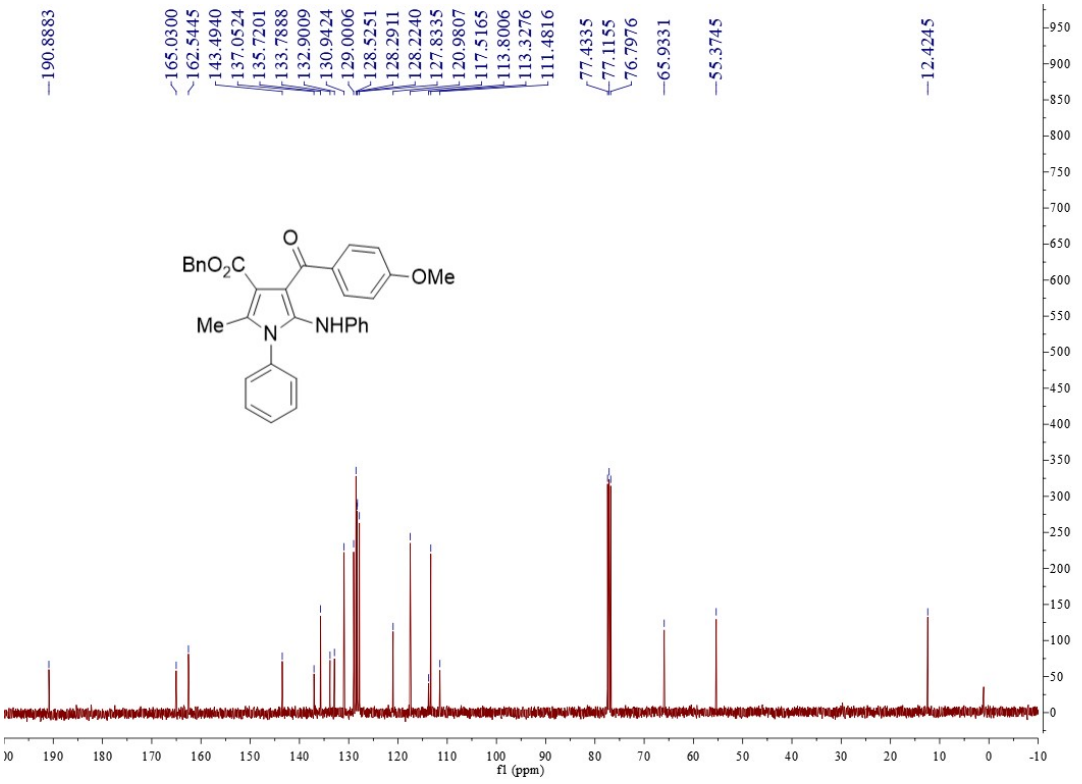
Benzyl 4-(4-methoxybenzoyl)-2-methyl-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate

(4aj)

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

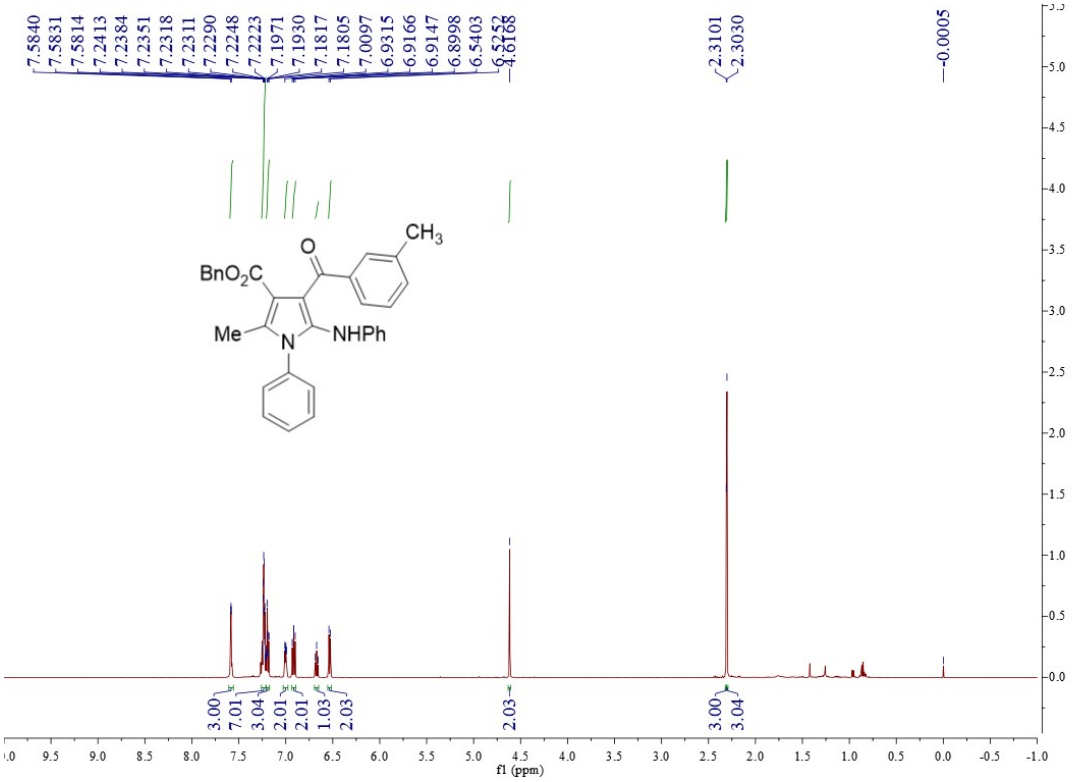


^{13}C NMR (101 MHz, $CDCl_3$)

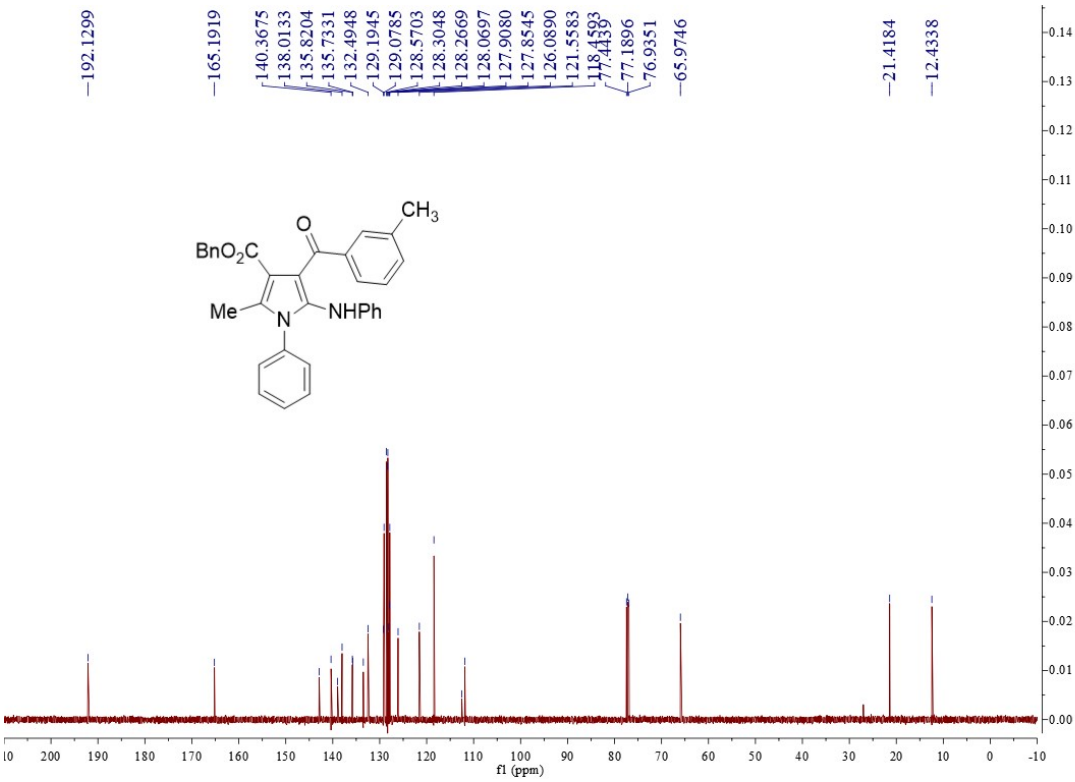


Benzyl 2-methyl-4-(3-methylbenzoyl)-1-phenyl-5-(phenylamino)-1*H*-pyrrole-3-carboxylate (4ak)

^{1}H NMR (500 MHz, $CDCl_3$)

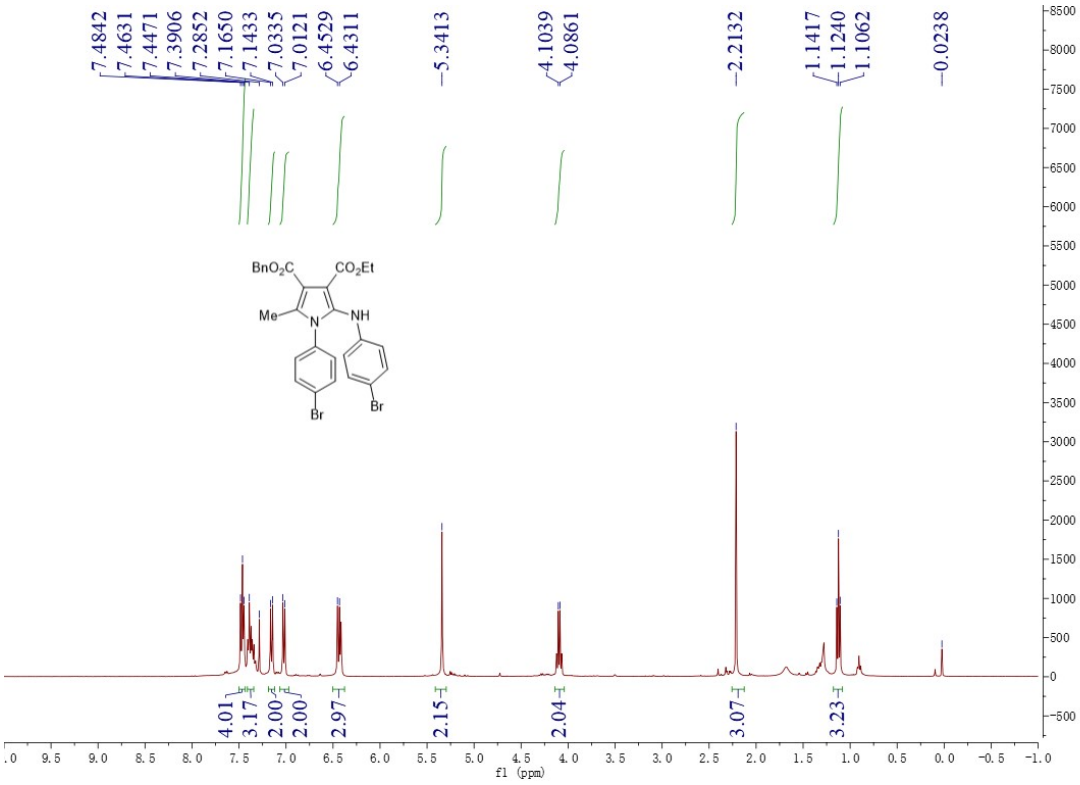


^{13}C NMR (125 MHz, $CDCl_3$)

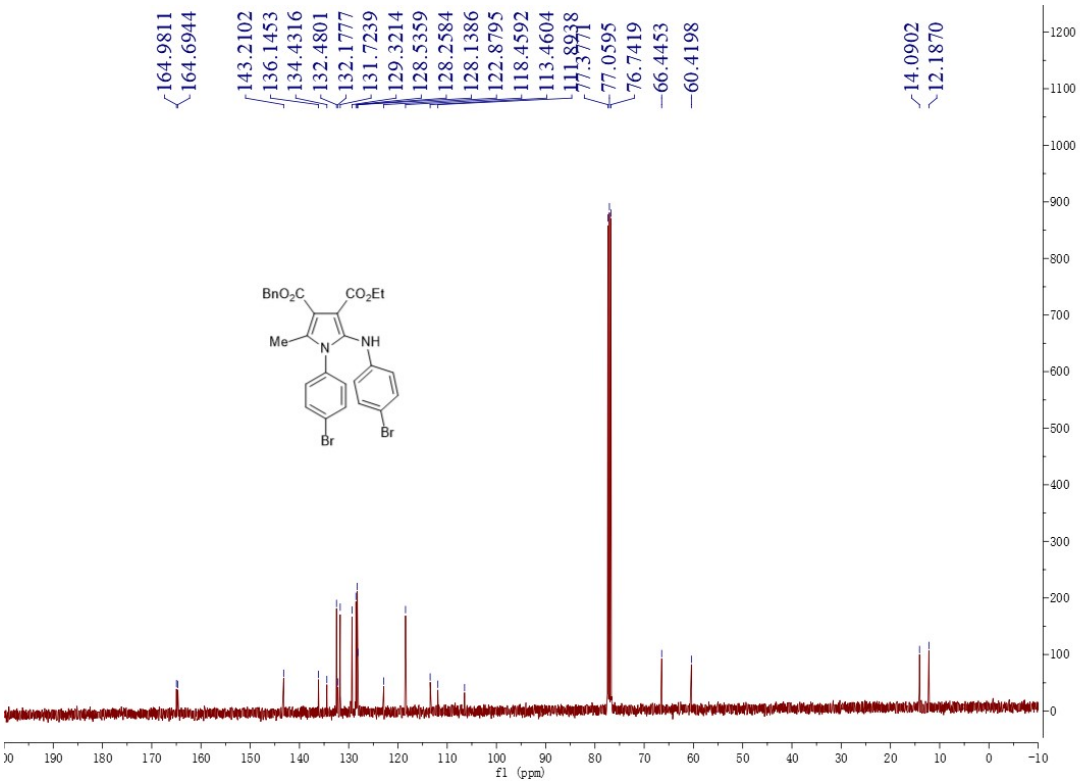


3-Benzyl 4-ethyl 1-(4-bromophenyl)-5-((4-bromophenyl)amino)-2-methyl-1*H*-pyrrole-3,4-dicarboxylate (4al)

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



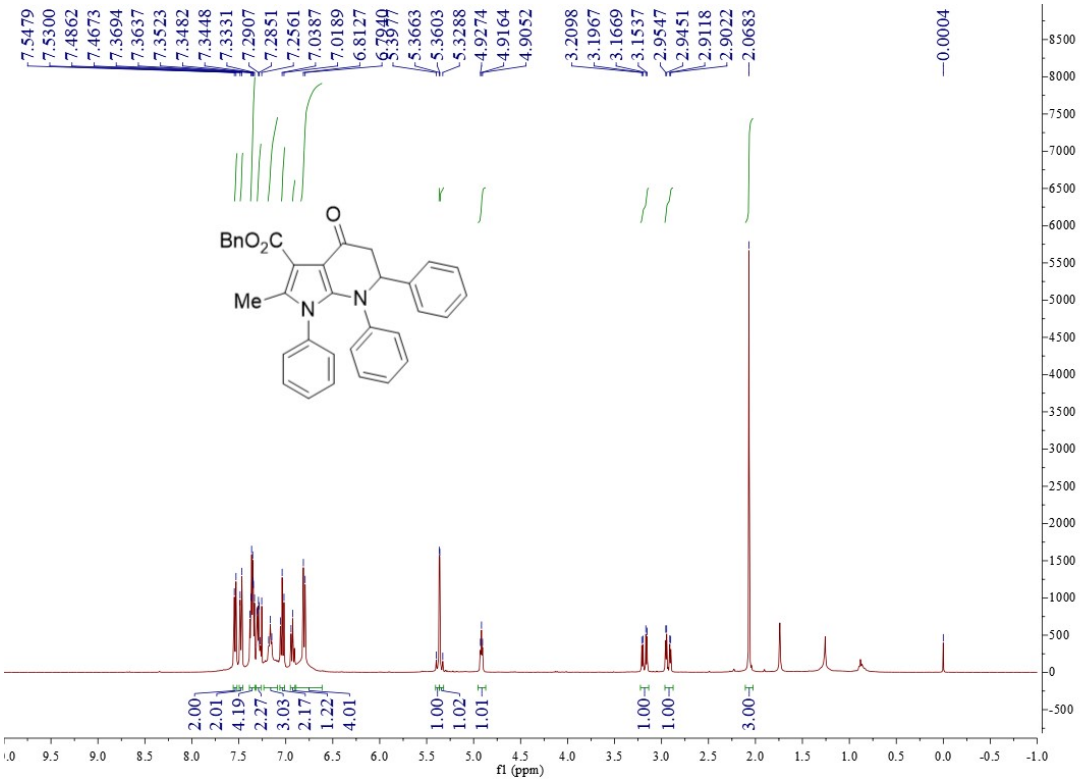
^{13}C NMR (101 MHz, $CDCl_3$)



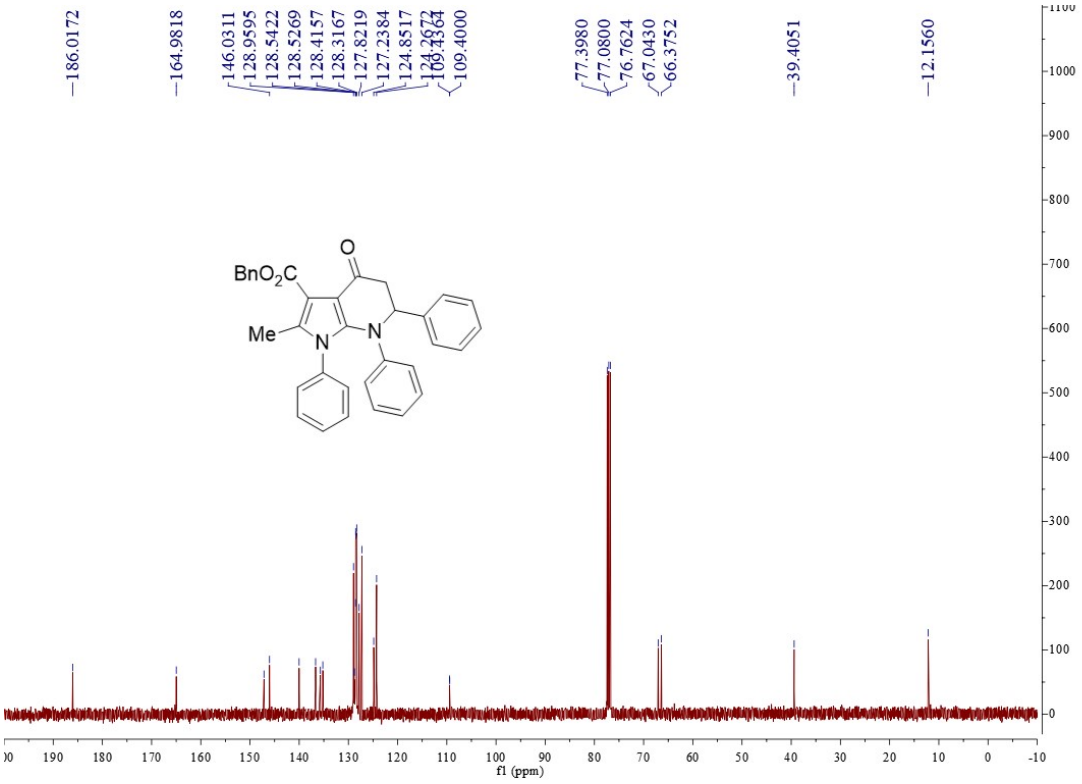
Benzyl 2-methyl-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b]pyridine-3-

carboxylate (6a)

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

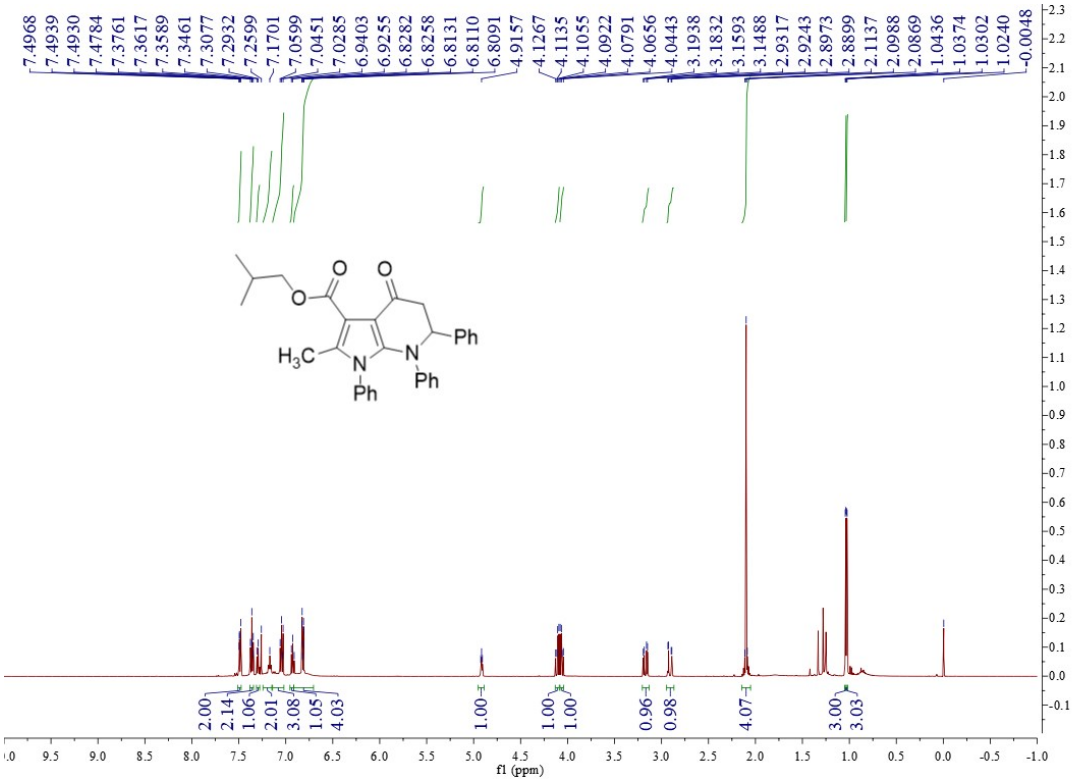


^{13}C NMR (101 MHz, $CDCl_3$)

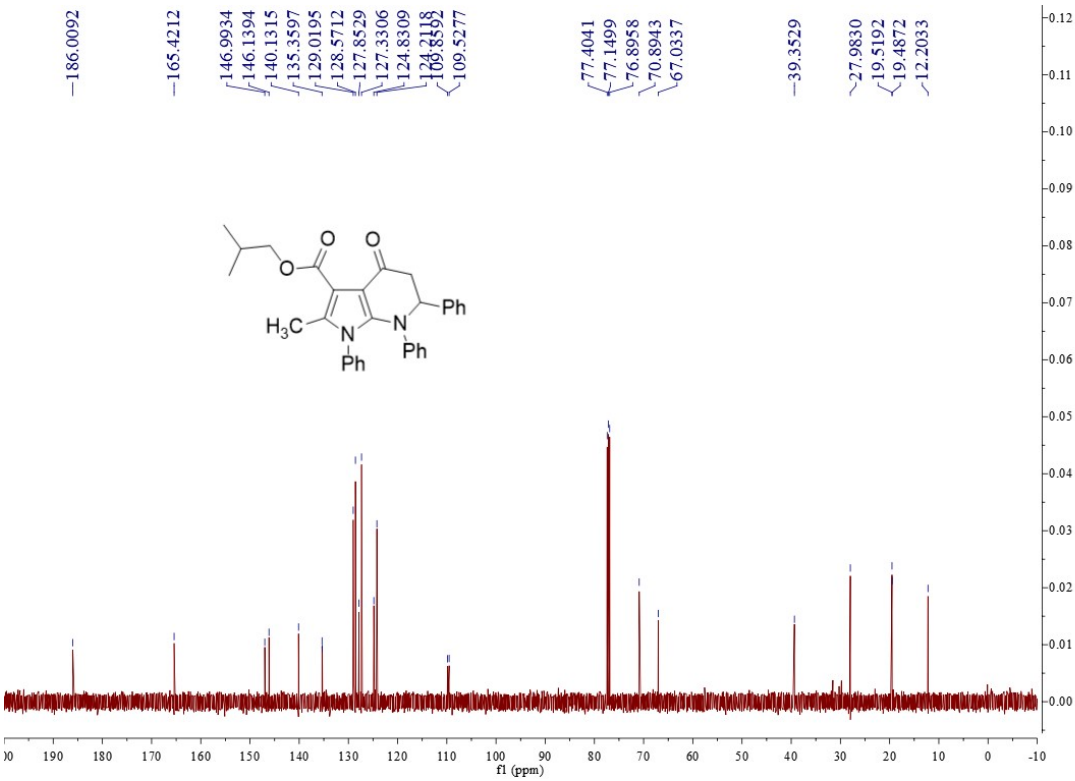


Isobutyl 2-methyl-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b]pyridine-3-carboxylate (6b)

^{1}H NMR (500 MHz, $CDCl_3$)

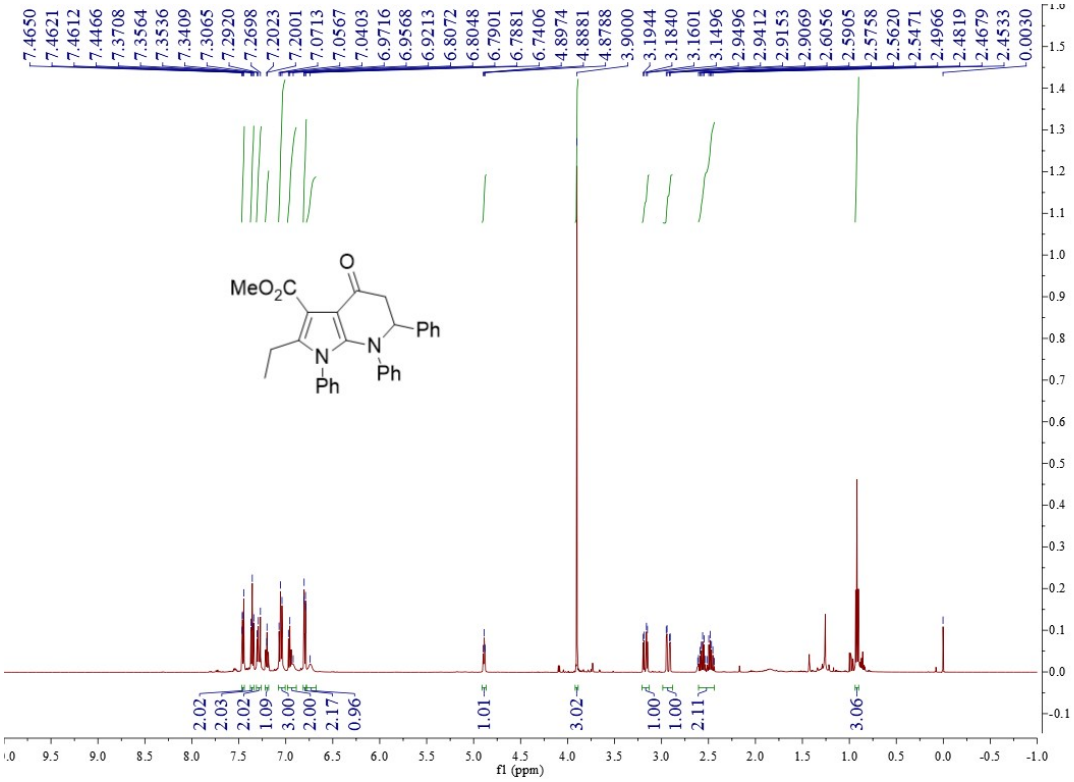


^{13}C NMR (125 MHz, $CDCl_3$)

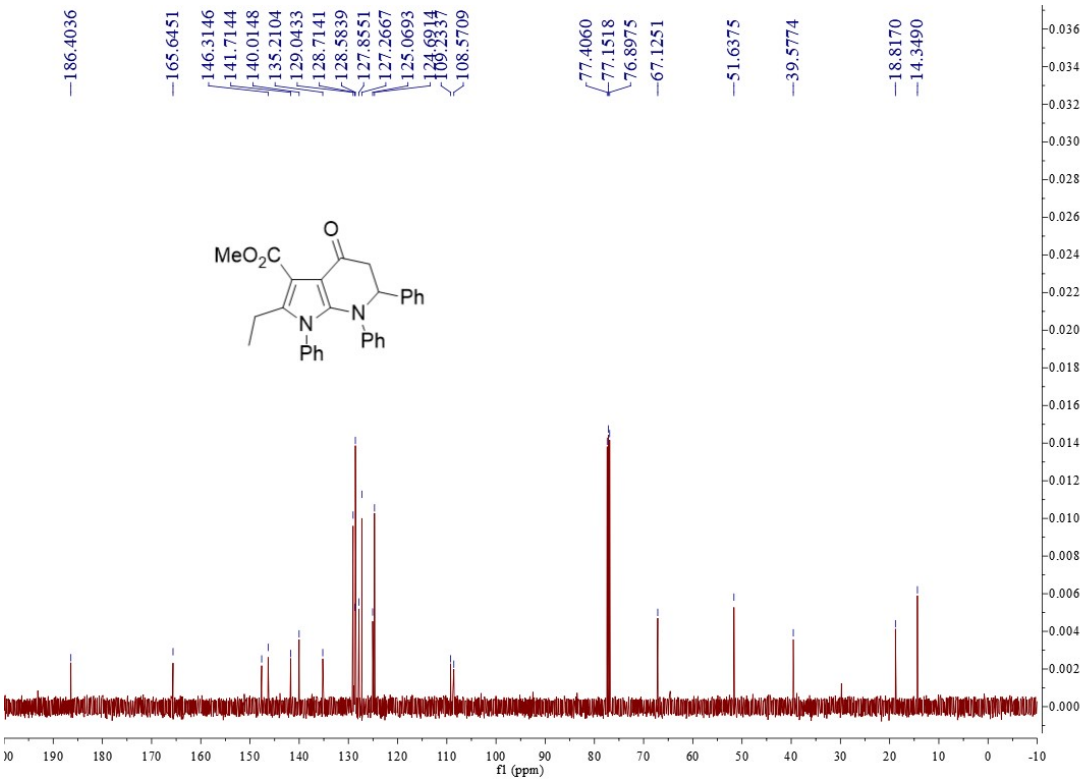


Methyl 2-ethyl-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b]pyridine-3-carboxylate (6c)

^{1}H NMR (500 MHz, $CDCl_3$)

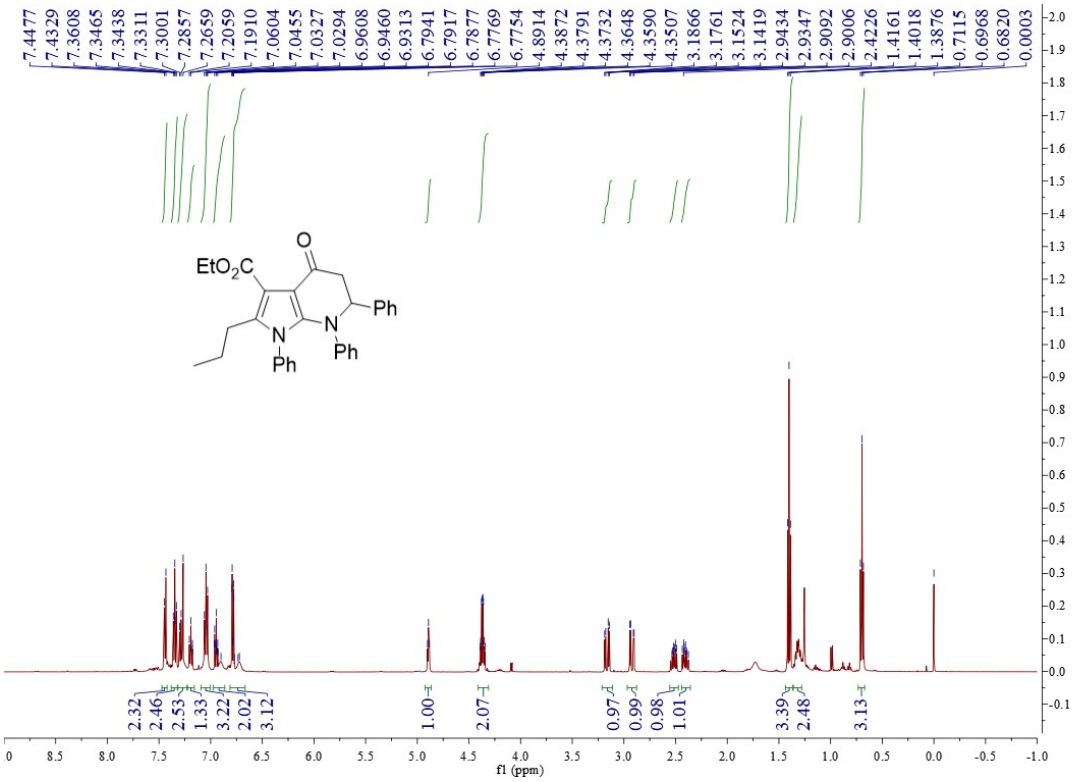


^{13}C NMR (125 MHz, $CDCl_3$)

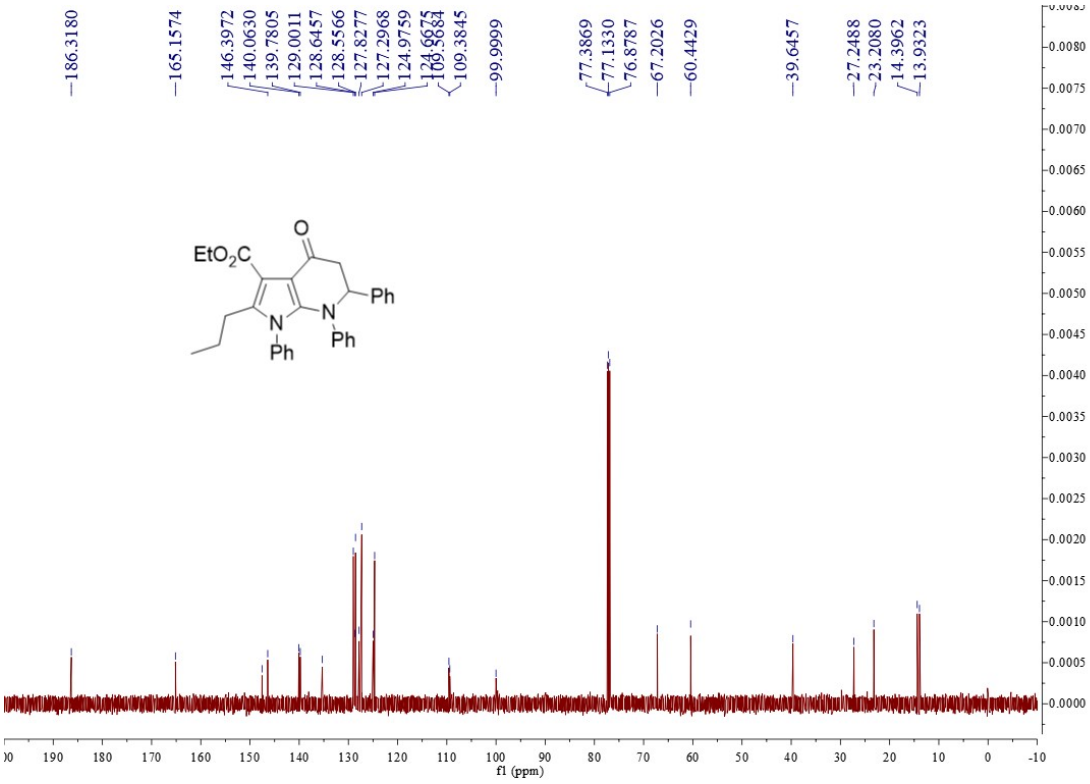


Methyl 4-oxo-1,6,7-triphenyl-2-propyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*b*]pyridine-3-carboxylate (6d)

^{1}H NMR (500 MHz, $CDCl_3$)

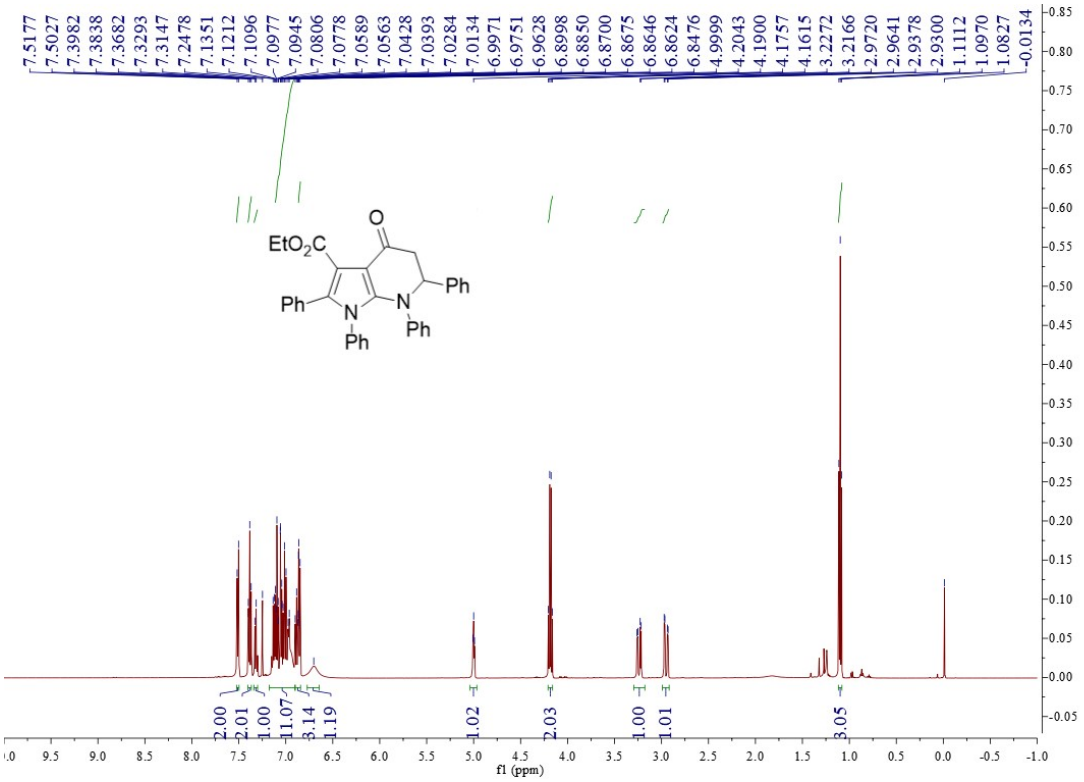


^{13}C NMR (125 MHz, $CDCl_3$)

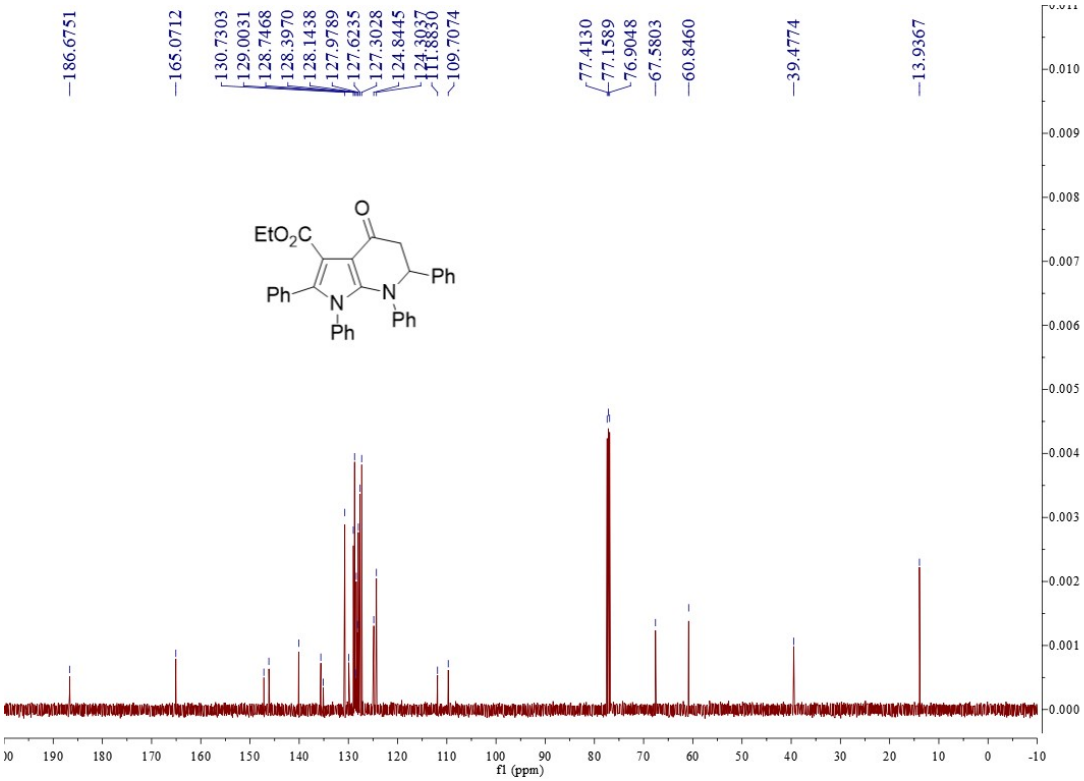


Ethyl 4-oxo-1,2,6,7-tetraphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b]pyridine-3- carboxylate (6e)

^{1}H NMR (500 MHz, $CDCl_3$)

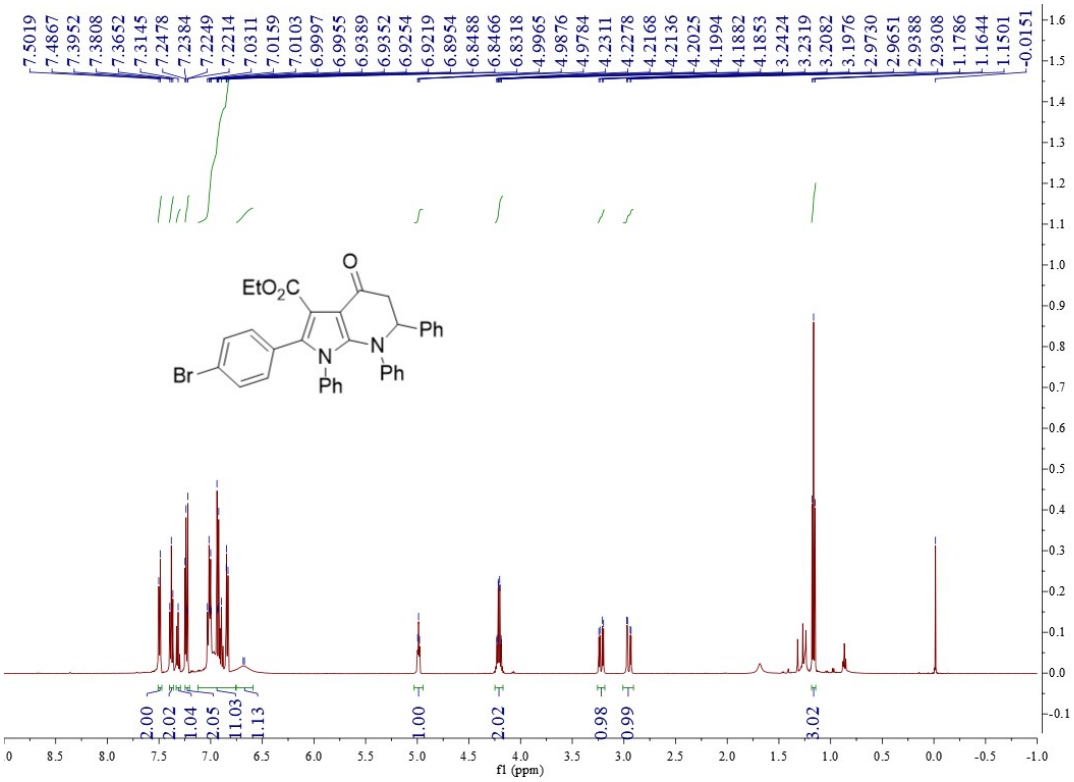


^{13}C NMR (125 MHz, $CDCl_3$)

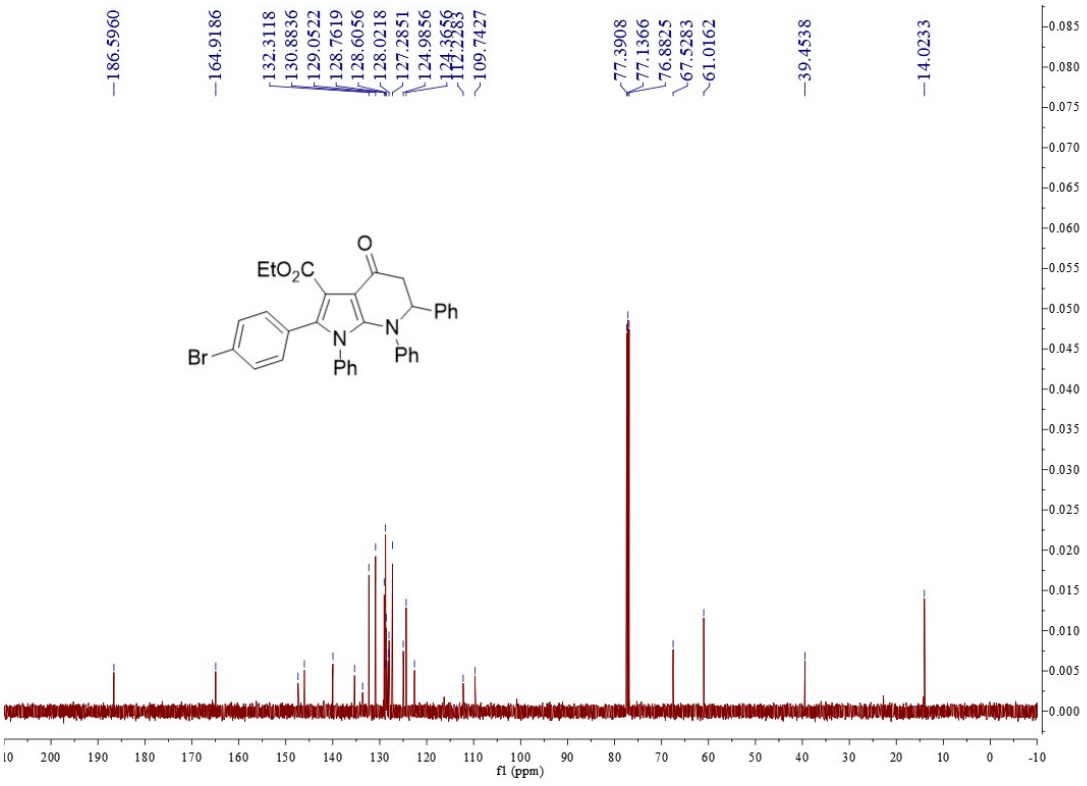


Ethyl 2-(4-bromophenyl)-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*b*] pyridine-3- carboxylate (6f)

^{1}H NMR (500 MHz, $CDCl_3$)

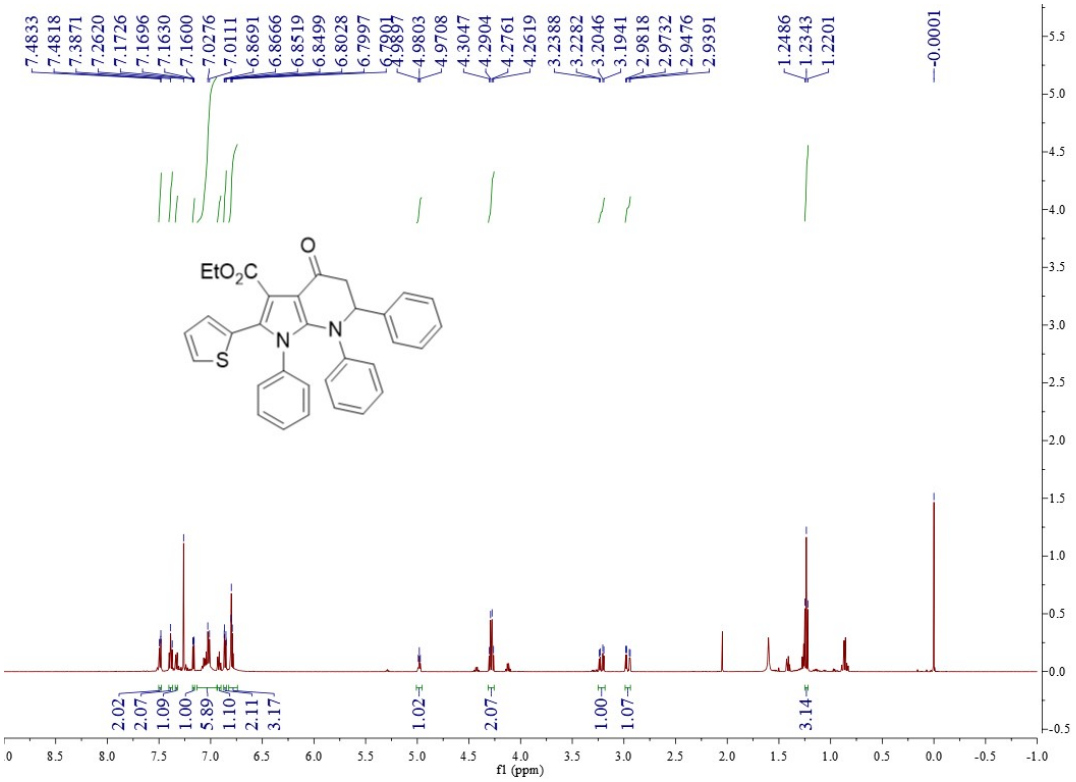


^{13}C NMR (125 MHz, $CDCl_3$)

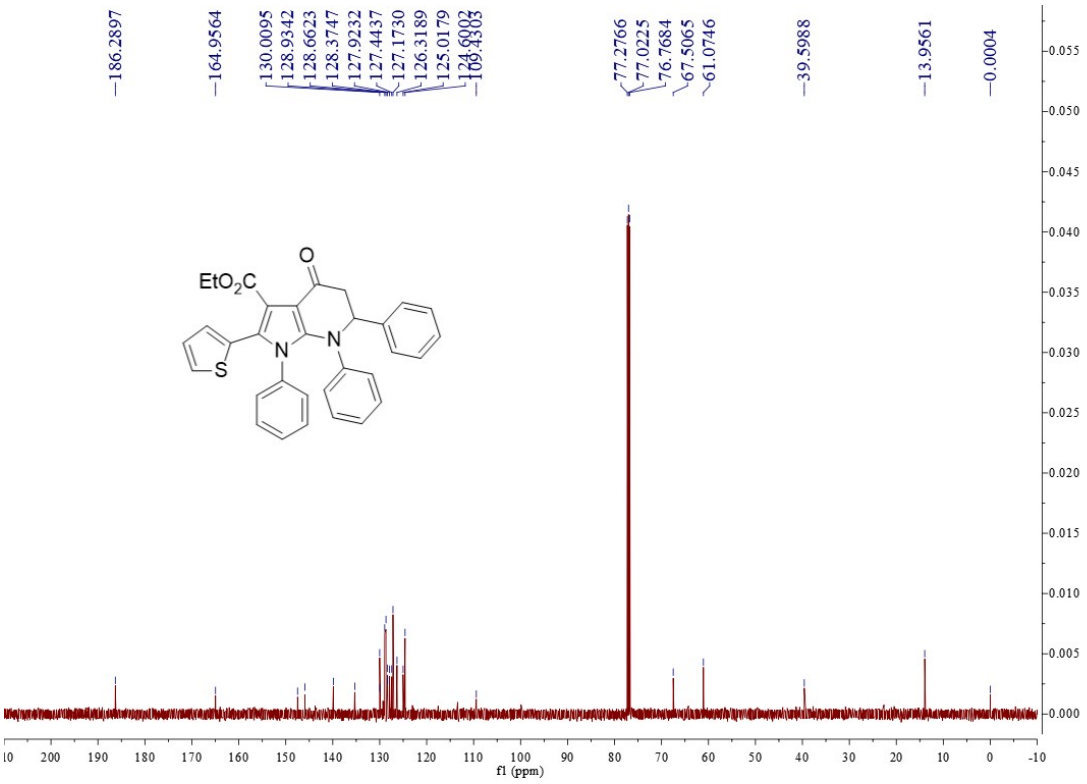


Ethyl 4-oxo-1,6,7-triphenyl-2-(thiophen-2-yl)-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*b*]pyridine-3-carboxylate (6g)

^{1}H NMR (500 MHz, $CDCl_3$)

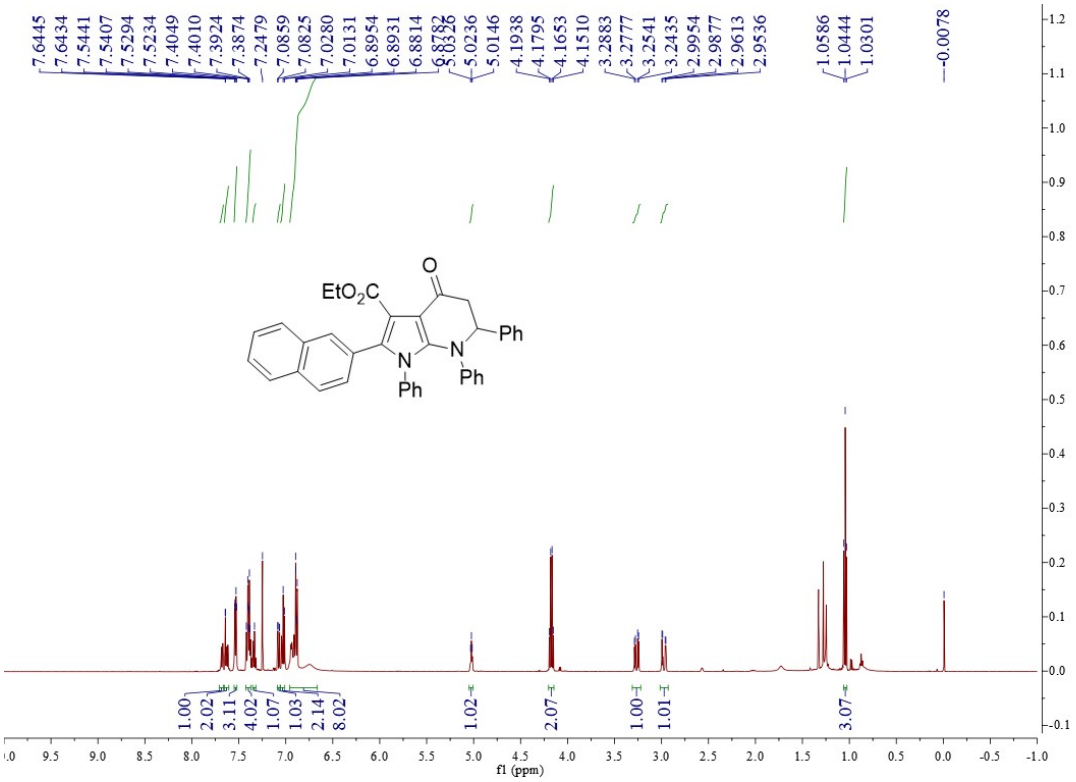


^{13}C NMR (125 MHz, $CDCl_3$)

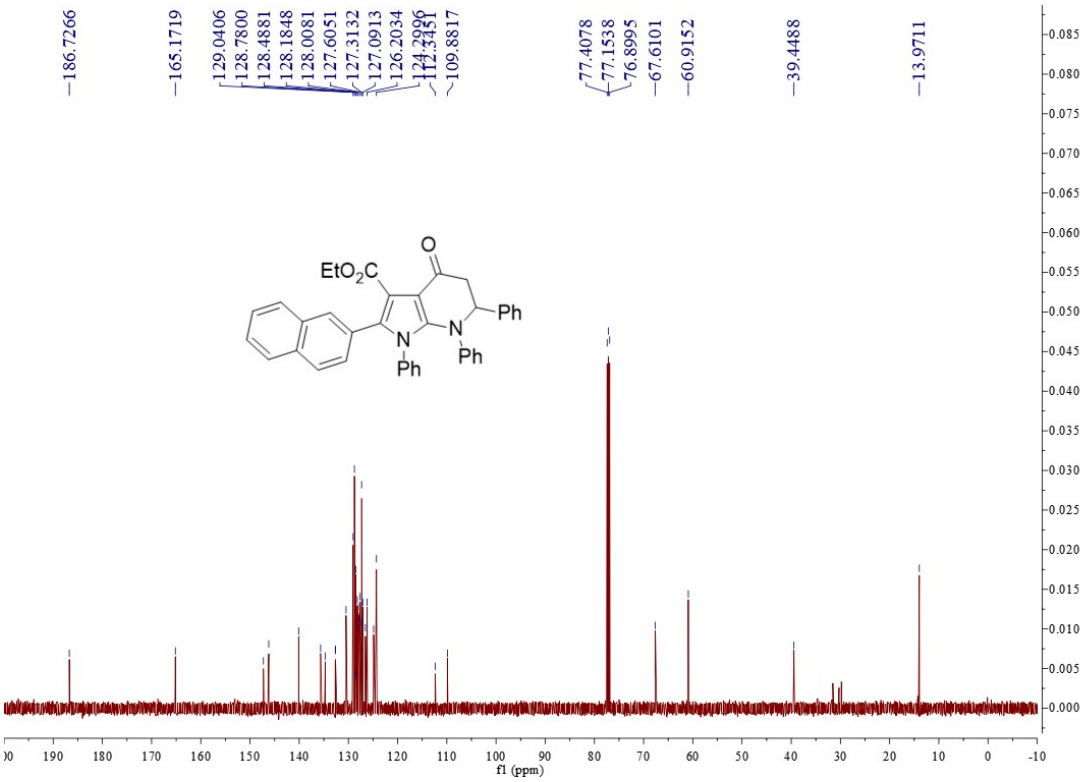


Ethyl 2-(naphthalen-2-yl)-4-oxo-1,6,7-triphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b] pyridine-3-carboxylate (6h)

^{1}H NMR (500 MHz, $CDCl_3$)

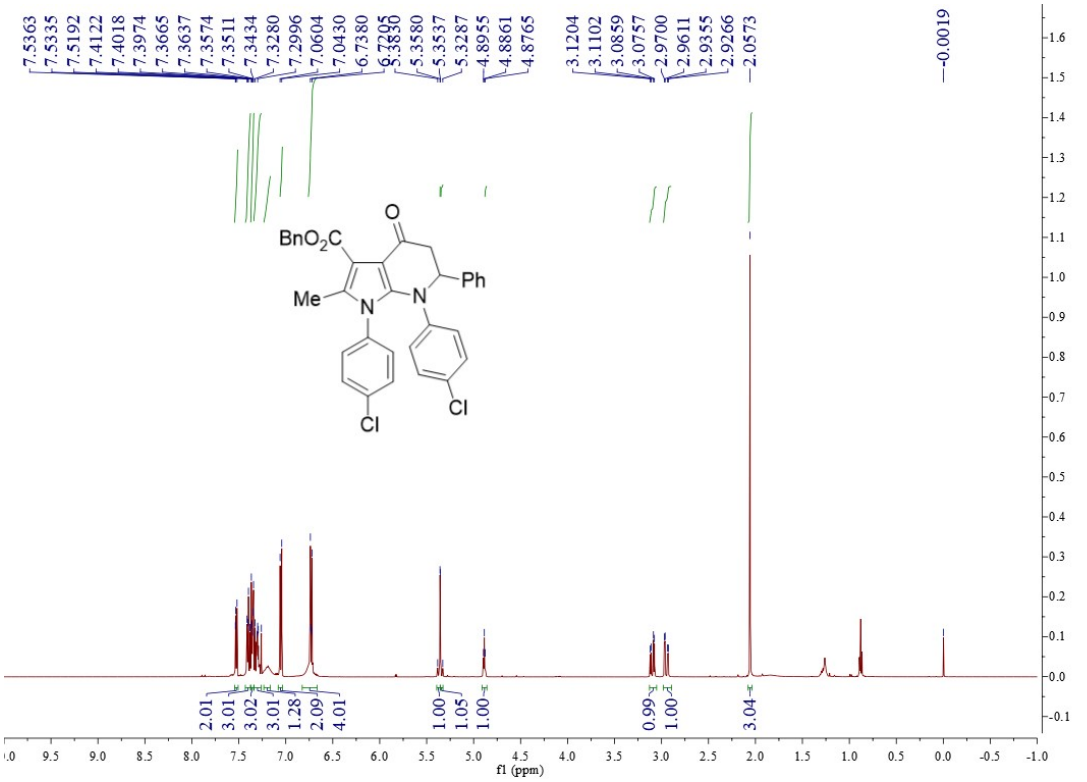


^{13}C NMR (125 MHz, $CDCl_3$)

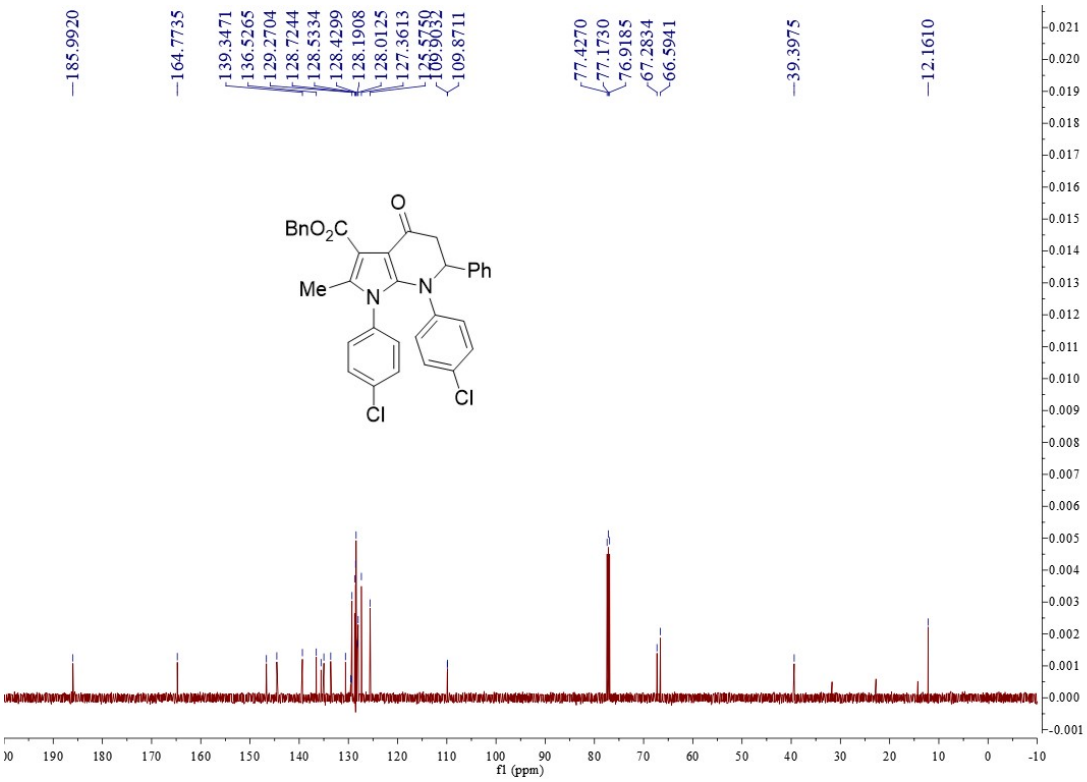


Benzyl 1,7-bis(4-chlorophenyl)-2-methyl-4-oxo-6-phenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-b] pyridine-3-carboxylate (6i)

^{1}H NMR (500 MHz, $CDCl_3$)

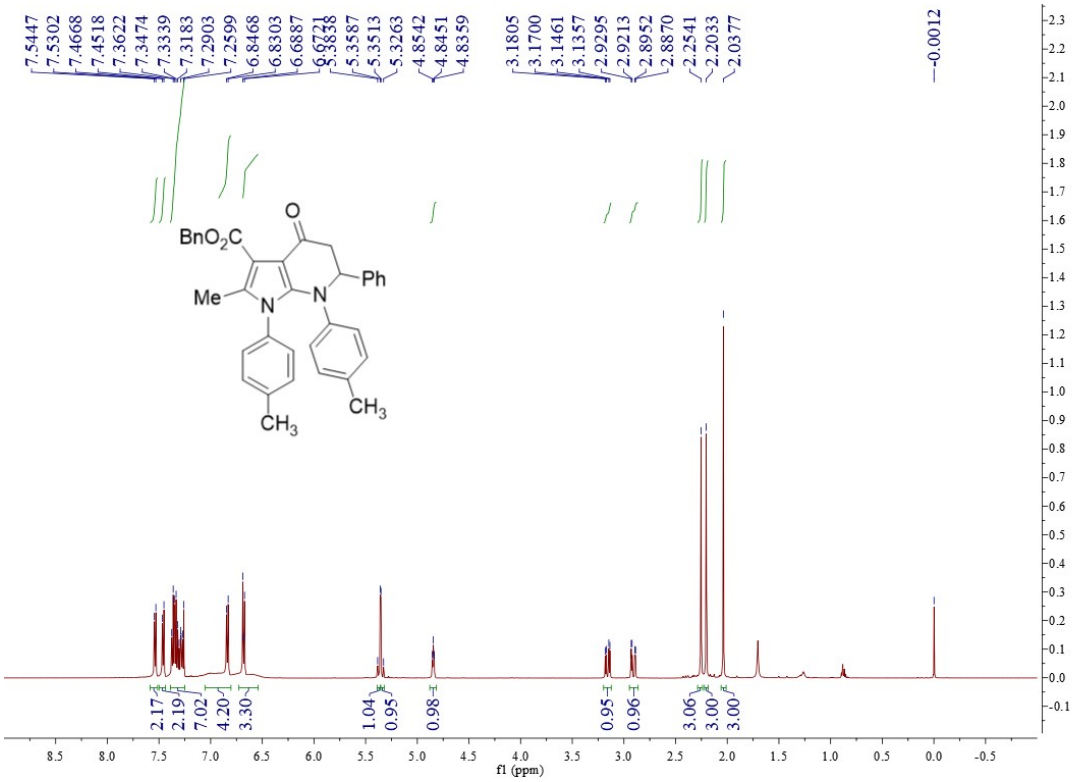


^{13}C NMR (125 MHz, $CDCl_3$)

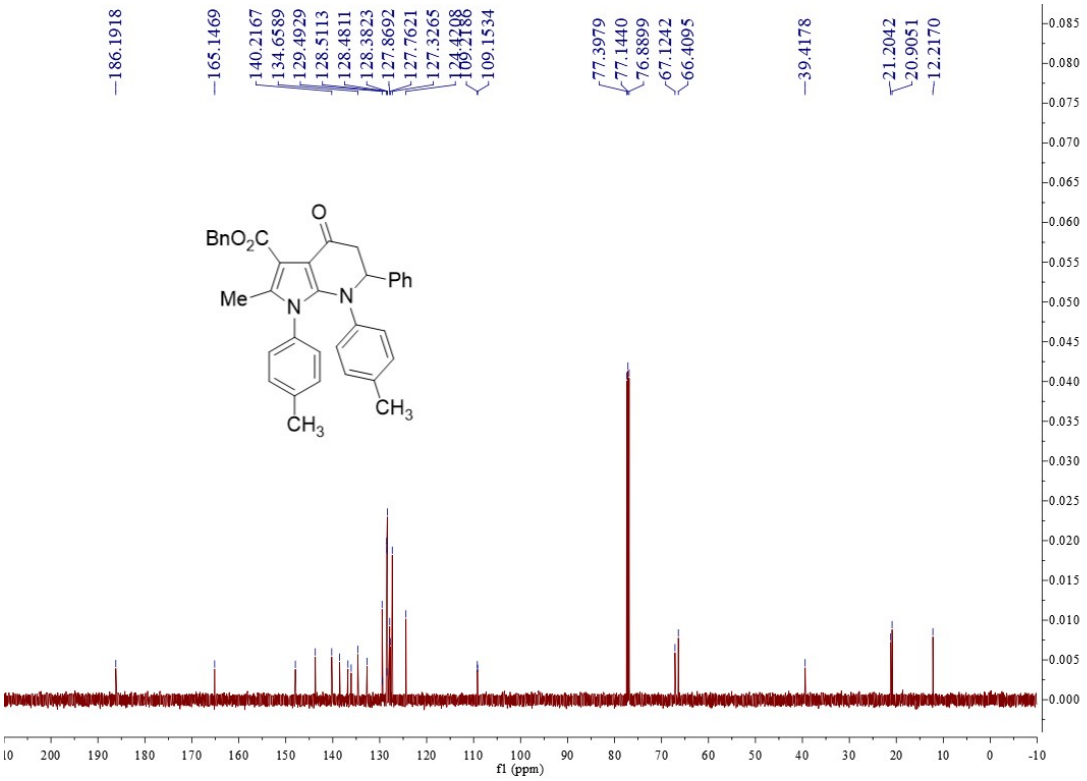


Benzyl 2-methyl-4-oxo-6-phenyl-1,7-di-p-tolyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*b*]pyridine-3-carboxylate (6j)

^{1}H NMR (500 MHz, $CDCl_3$)

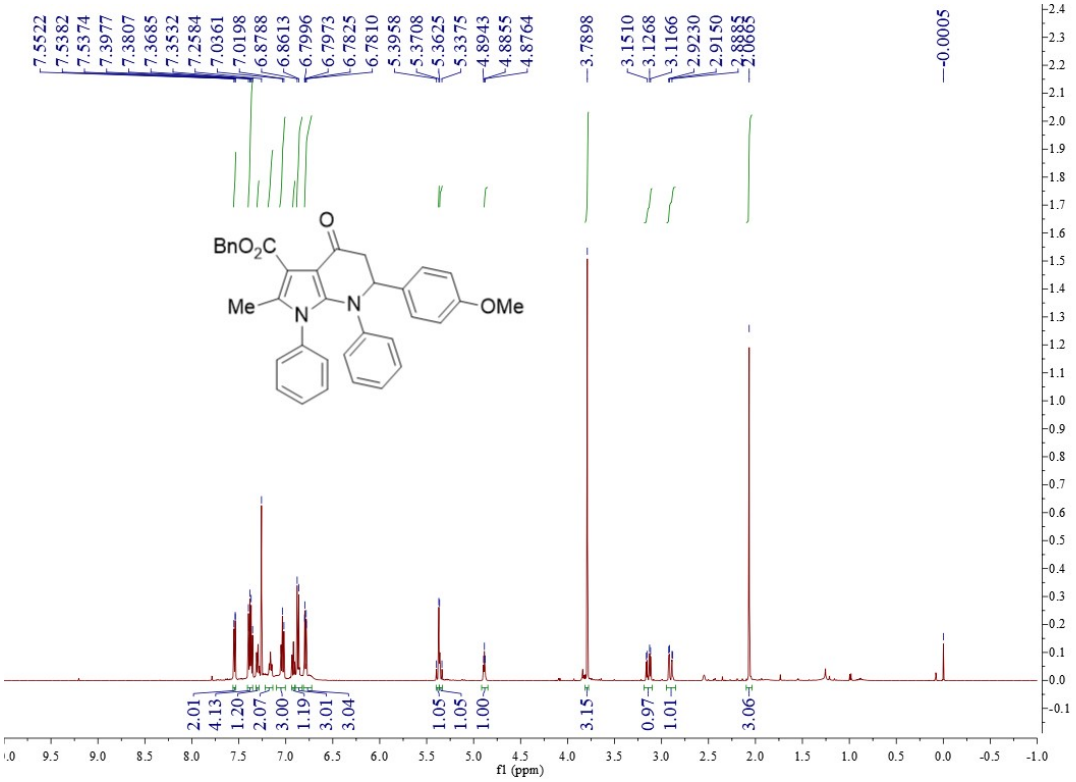


^{13}C NMR (125 MHz, $CDCl_3$)

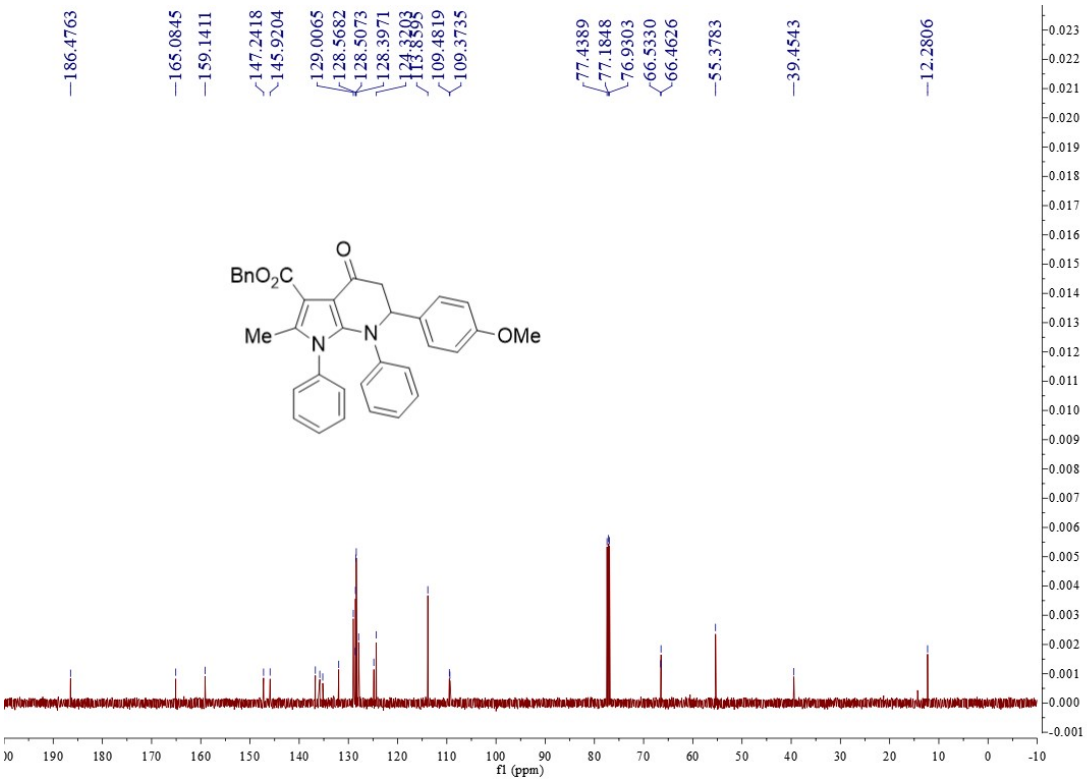


Benzyl 6-(4-methoxyphenyl)-2-methyl-4-oxo-1,7-diphenyl-4,5,6,7-tetrahydro-1*H*-pyrrolo [2,3-b]pyridine-3-carboxylate (6k)

^{1}H NMR (500 MHz, $CDCl_3$)

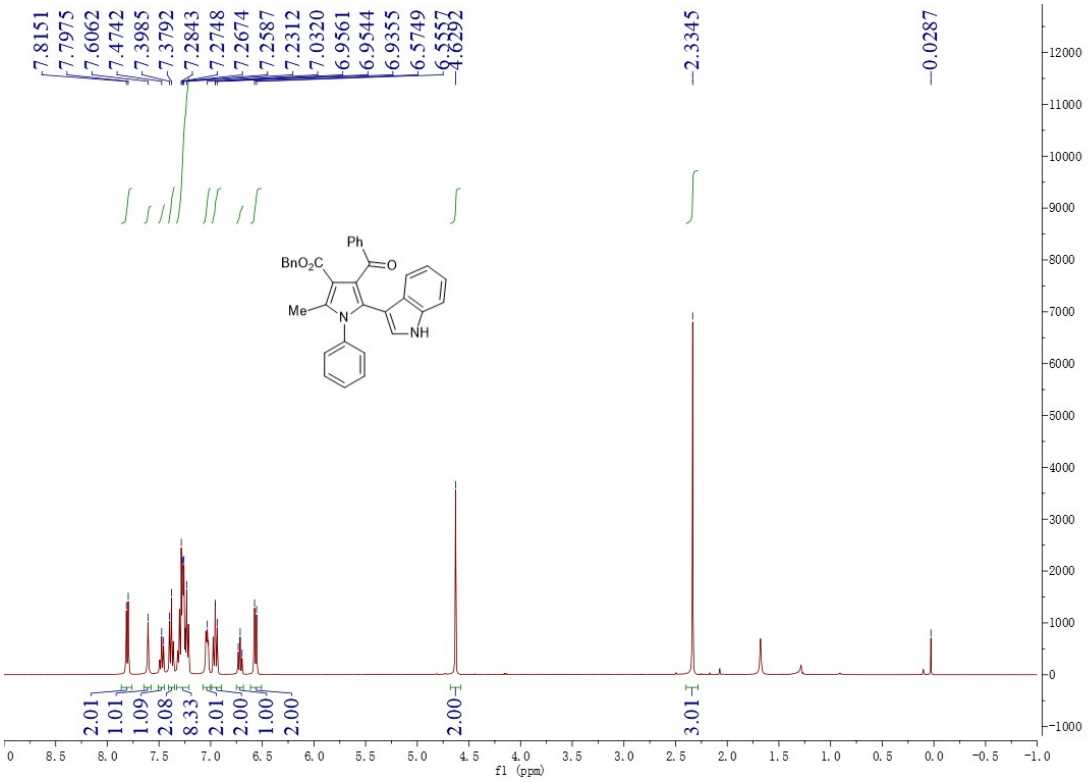


^{13}C NMR (125 MHz, $CDCl_3$)

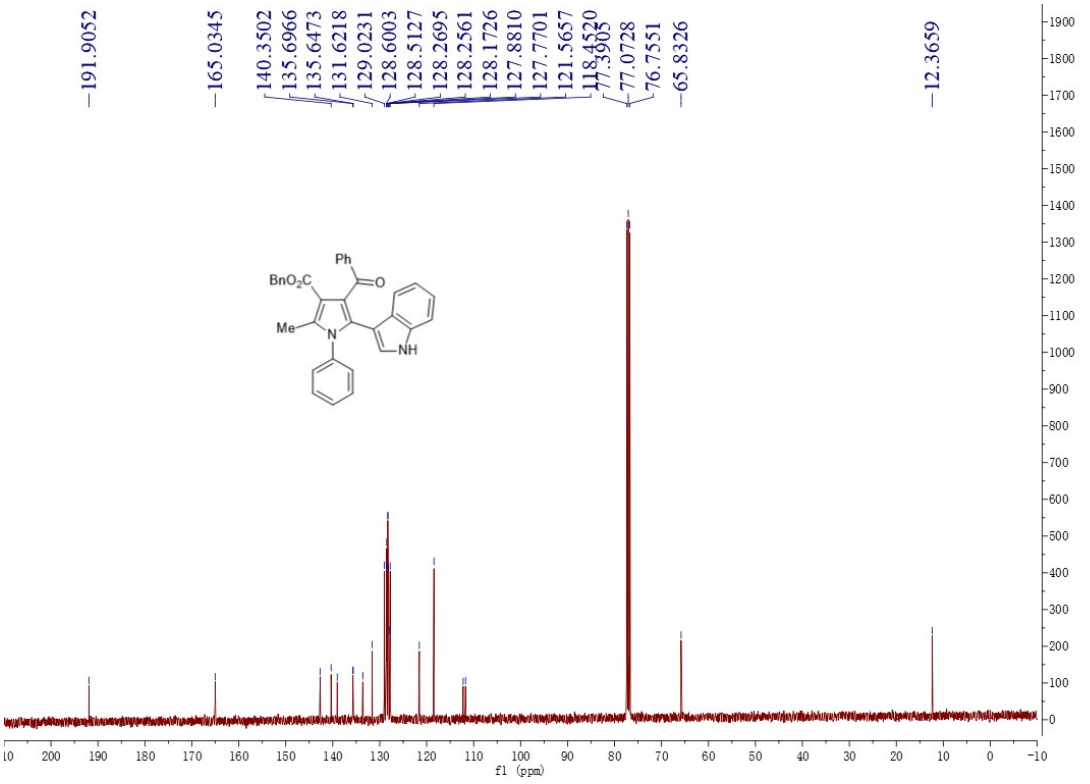


Benzyl 4-benzoyl-5-(1*H*-indol-3-yl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (9a)

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

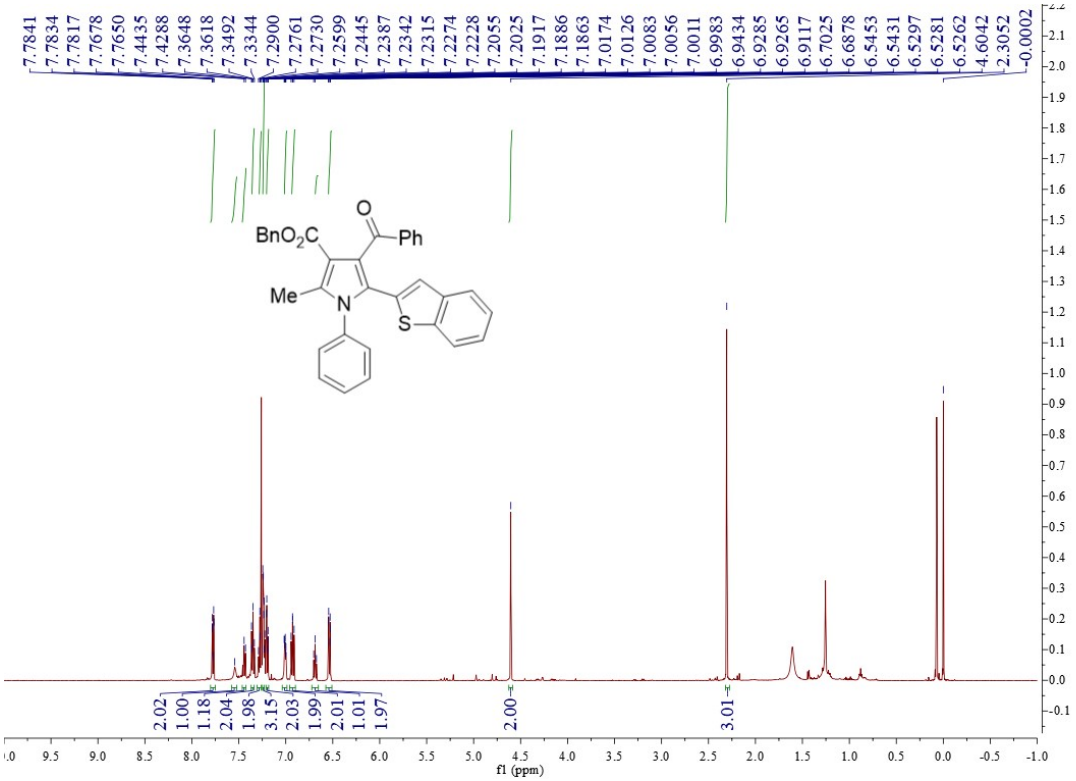


^{13}C NMR (101 MHz, $CDCl_3$)

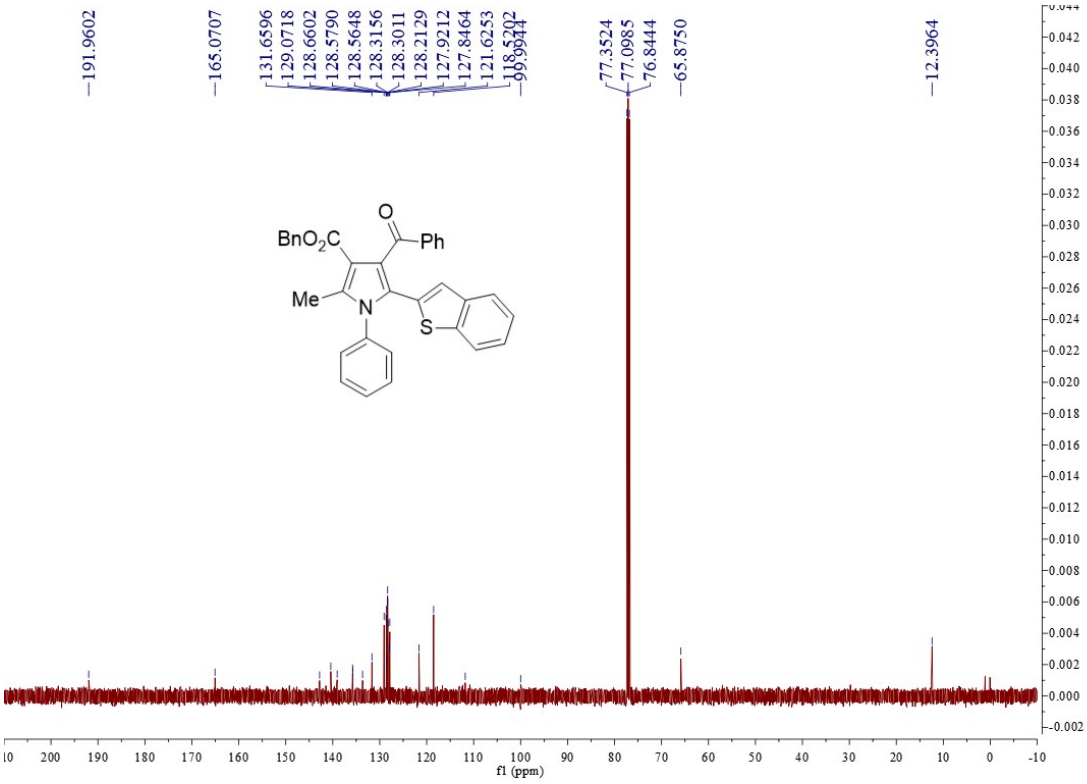


Benzyl 5-(benzo[*b*]thiophen-2-yl)-4-benzoyl-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (9b)

^{1}H NMR (500 MHz, $CDCl_3$)

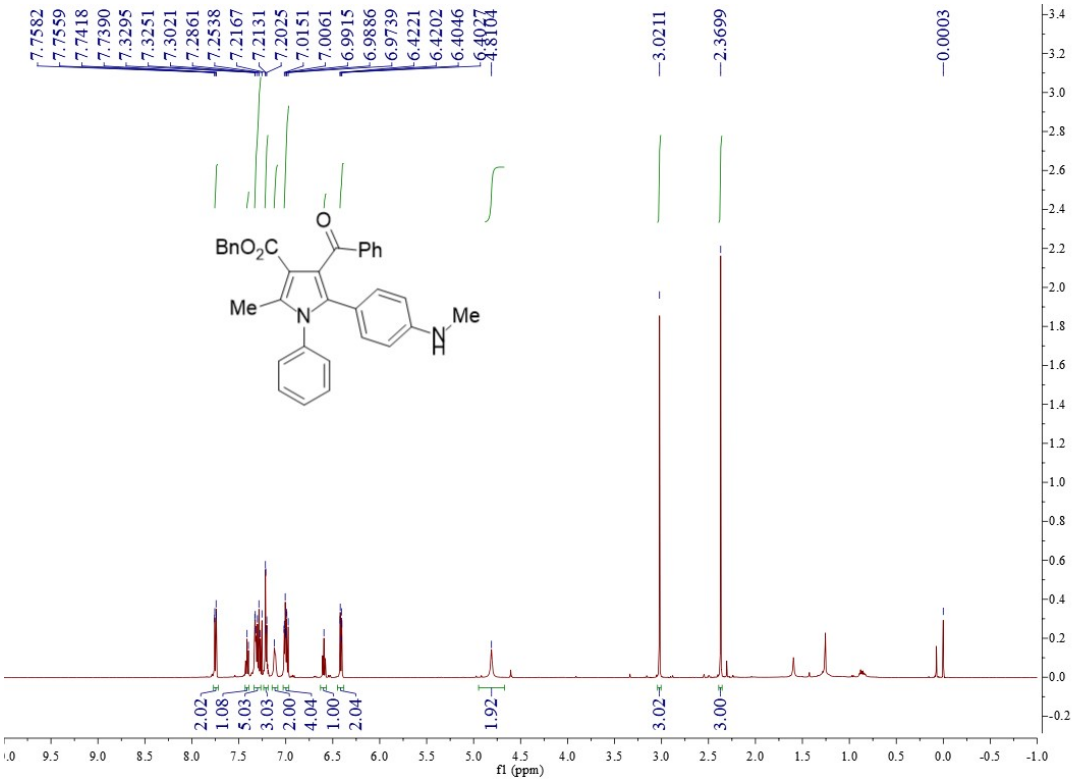


^{13}C NMR (125 MHz, $CDCl_3$)

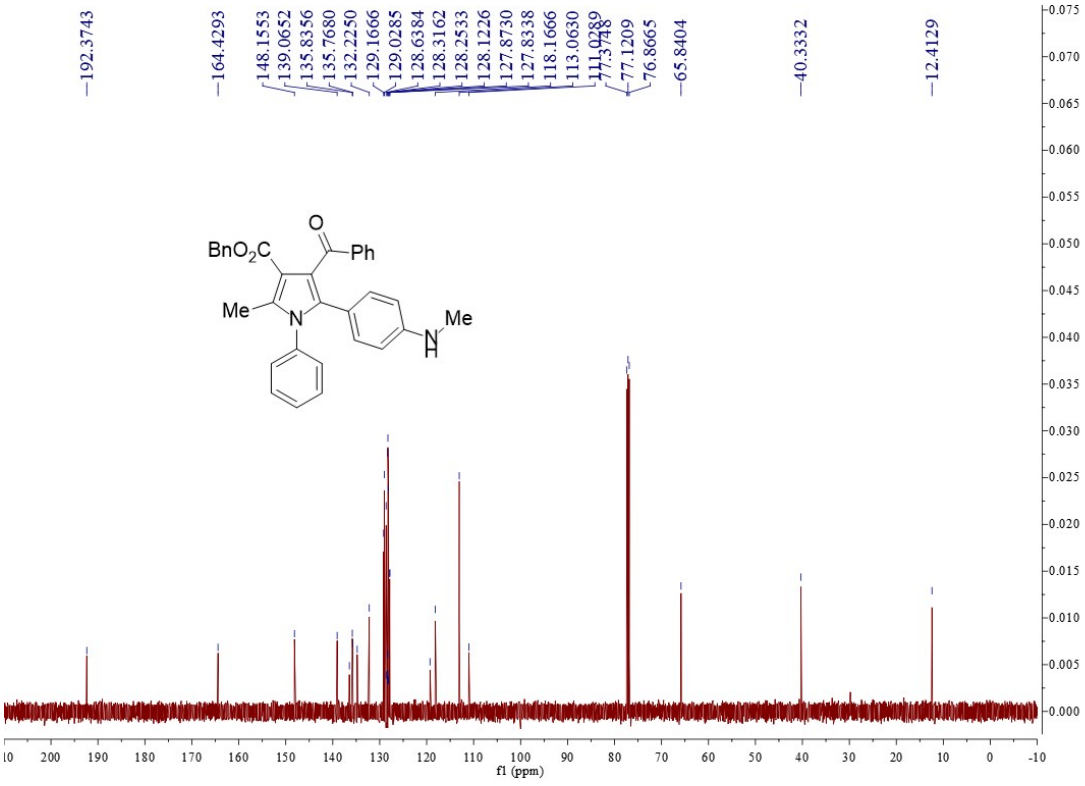


Benzyl 4-benzoyl-2-methyl-5-(4-(methylamino)phenyl)-1-phenyl-1*H*-pyrrole-3-carboxylate (9c)

^{1}H NMR (500 MHz, $CDCl_3$)

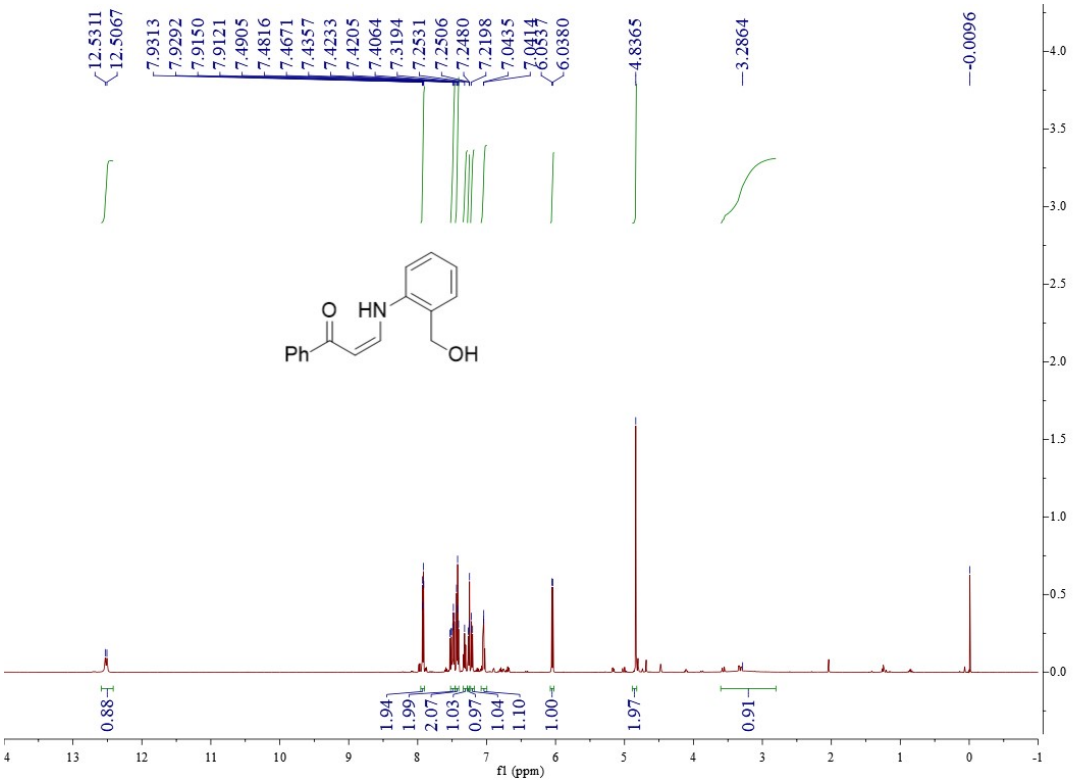


^{13}C NMR (125 MHz, $CDCl_3$)

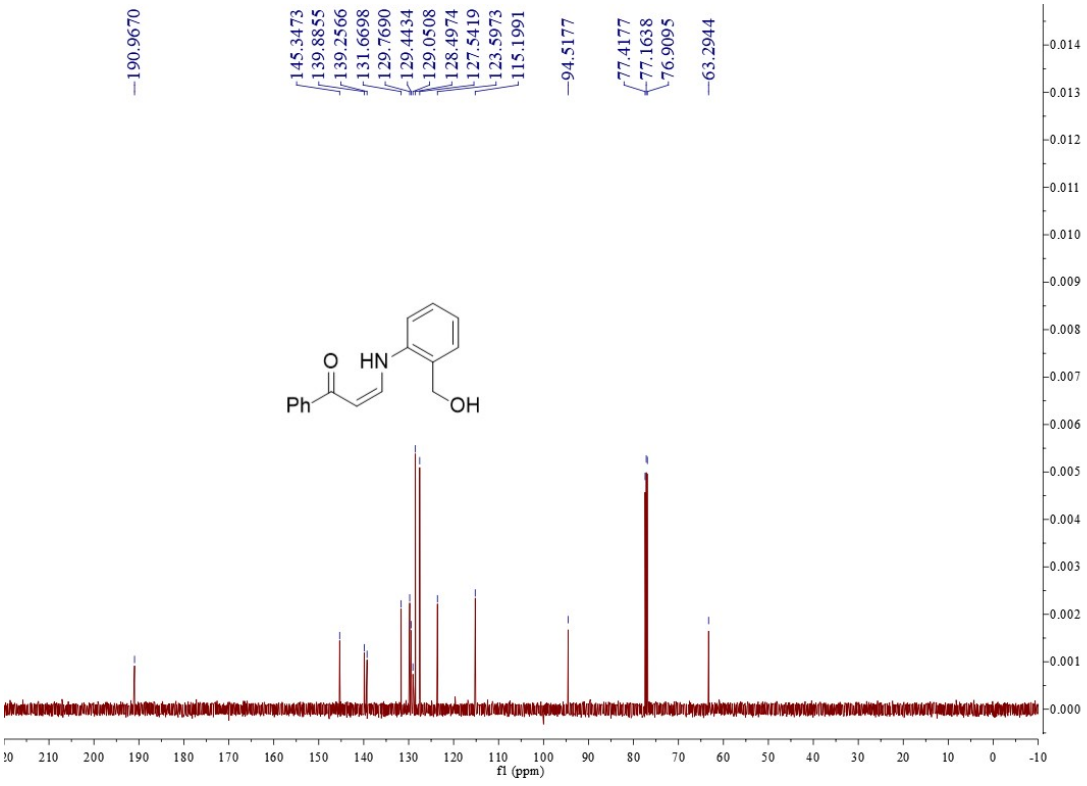


(*Z*)-3-((2-(hydroxymethyl)phenyl)amino)-1-phenylprop-2-en-1-one (10)

^{1}H NMR (500 MHz, $CDCl_3$)

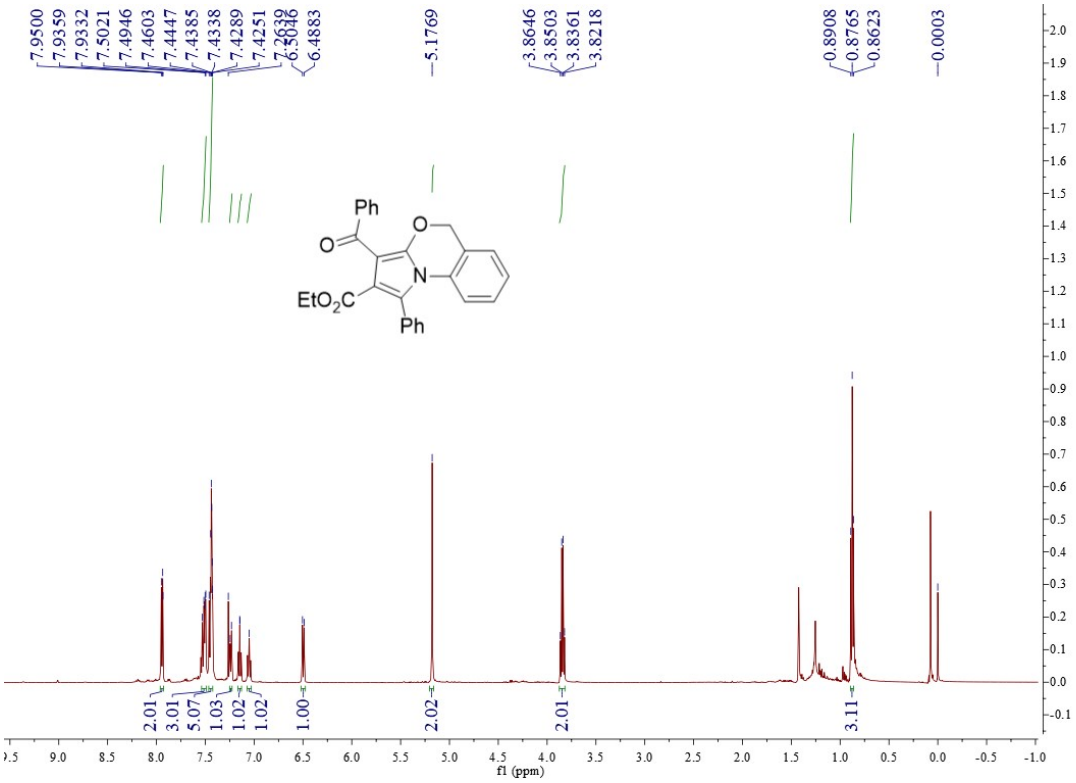


^{13}C NMR (125 MHz, $CDCl_3$)

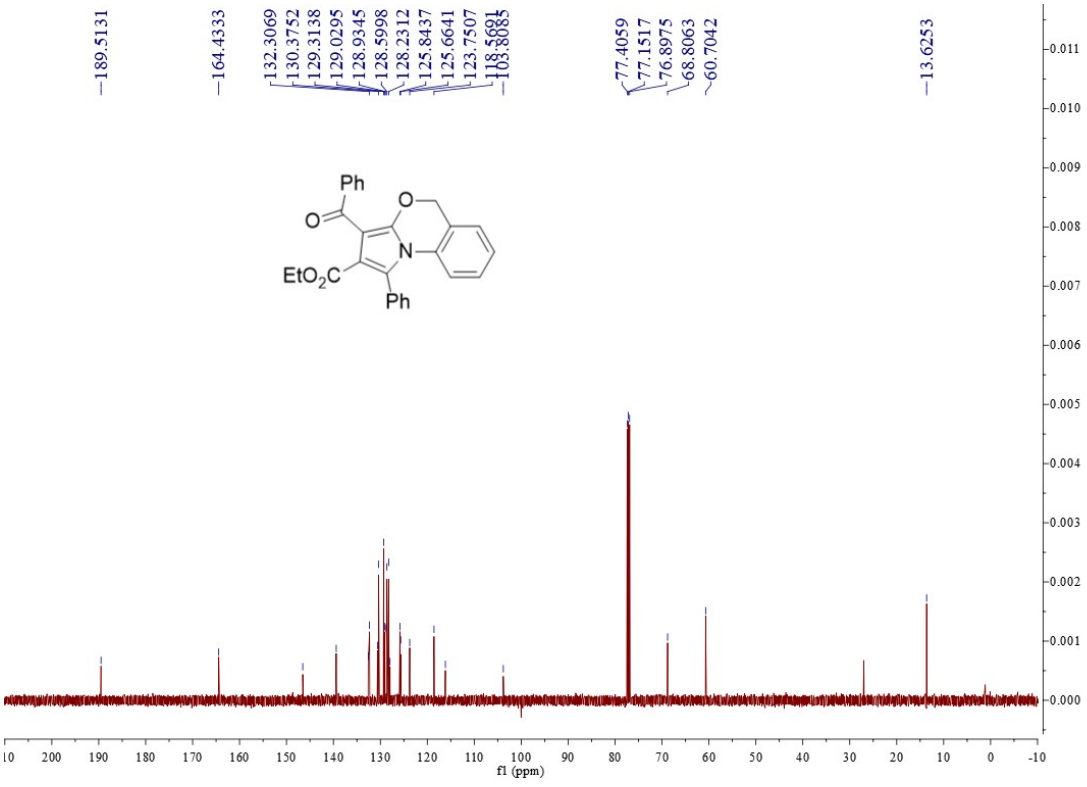


Ethyl 3-benzoyl-1-phenyl-5*H*-benzo[d]pyrrolo[2,1-*b*][1,3]oxazine-2-carboxylate (11)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



Crystallographic data for compounds 4j and 6a

Table 1. Crystal data and structure refinement for **4j**.

Identification code	**4j**	
Empirical formula	C32 H25 Br N2 O3	
Formula weight	565.45	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.305(3) Å	α= 92.405(9)°.
	b = 13.363(3) Å	β= 105.012(8)°.
	c = 19.885(5) Å	γ = 111.457(7)°.
Volume	2669.0(12) $Å^3$	
Z	4	
Density (calculated)	1.407 Mg/m^3	
Absorption coefficient	1.577 mm^{-1}	
F(000)	1160	
Crystal size	0.250 x 0.230 x 0.220 mm^3	
Theta range for data collection	2.474 to 27.564°.	
Index ranges	-14<=h<=14, -17<=k<=17, -25<=l<=25	
Reflections collected	38991	
Independent reflections	12200 [R(int) = 0.0421]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6899	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12200 / 23 / 687	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0502, wR2 = 0.1067	
R indices (all data)	R1 = 0.1101, wR2 = 0.1267	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.461 and -0.780 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **4j**.

Br(1)-C(13)	1.897(3)
C(1)-N(1)	1.380(3)
C(1)-C(2)	1.381(4)
C(1)-C(11)	1.482(3)
C(2)-C(3)	1.431(4)
C(2)-C(17)	1.472(4)
C(3)-C(4)	1.369(4)
C(3)-C(20)	1.479(4)
C(4)-N(1)	1.387(3)
C(4)-N(2)	1.395(3)
C(5)-C(10)	1.363(4)
C(5)-C(6)	1.378(4)
C(5)-N(1)	1.441(3)
C(6)-C(7)	1.374(4)
C(6)-H(6)	0.9300
C(7)-C(8)	1.356(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.370(5)
C(8)-H(8)	0.9300
C(9)-C(10)	1.383(5)
C(9)-H(9)	0.9300
C(10)-H(10)	0.9300
C(11)-C(16)	1.376(4)
C(11)-C(12)	1.391(4)
C(12)-C(13)	1.381(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.360(4)
C(14)-C(15)	1.379(4)
C(14)-H(14)	0.9300
C(15)-C(16)	1.376(4)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-O(2)	1.198(3)
C(17)-O(1)	1.329(4)
C(18)-C(19)	1.478(6)
C(18)-O(1)	1.483(4)

C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-O(3)	1.222(3)
C(20)-C(21)	1.482(4)
C(21)-C(26)	1.383(4)
C(21)-C(22)	1.391(4)
C(22)-C(23)	1.374(5)
C(22)-H(22)	0.9300
C(23)-C(24)	1.352(5)
C(23)-H(23)	0.9300
C(24)-C(25)	1.370(5)
C(24)-H(24)	0.9300
C(25)-C(26)	1.377(4)
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300
C(27)-C(32)	1.389(4)
C(27)-C(28)	1.390(4)
C(27)-N(2)	1.392(3)
C(28)-C(29)	1.374(4)
C(28)-H(28)	0.9300
C(29)-C(30)	1.377(5)
C(29)-H(29)	0.9300
C(30)-C(31)	1.366(5)
C(30)-H(30)	0.9300
C(31)-C(32)	1.375(4)
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300
N(2)-H(2)	0.8600
Br(2)-C(45)	1.887(3)
C(33)-N(3)	1.374(3)
C(33)-C(34)	1.382(4)
C(33)-C(43)	1.479(4)
C(34)-C(35)	1.429(3)
C(34)-C(49)	1.469(4)
C(35)-C(36)	1.370(4)

C(35)-C(52)	1.481(4)
C(36)-N(3)	1.385(3)
C(36)-N(4)	1.398(3)
C(37)-C(42)	1.353(5)
C(37)-C(38)	1.362(4)
C(37)-N(3)	1.446(3)
C(38)-C(39)	1.388(5)
C(38)-H(38)	0.9300
C(39)-C(40)	1.341(5)
C(39)-H(39)	0.9300
C(40)-C(41)	1.355(5)
C(40)-H(40)	0.9300
C(41)-C(42)	1.391(5)
C(41)-H(41)	0.9300
C(42)-H(42)	0.9300
C(43)-C(44)	1.373(4)
C(43)-C(48)	1.377(4)
C(44)-C(45)	1.378(4)
C(44)-H(44)	0.9300
C(45)-C(46)	1.358(4)
C(46)-C(47)	1.366(5)
C(46)-H(46)	0.9300
C(47)-C(48)	1.370(5)
C(47)-H(47)	0.9300
C(48)-H(48)	0.9300
C(49)-O(5)	1.200(3)
C(49)-O(4)	1.339(3)
C(50)-C(51)	1.456(5)
C(50)-O(4)	1.470(4)
C(50)-H(50A)	0.9700
C(50)-H(50B)	0.9700
C(51)-H(51A)	0.9600
C(51)-H(51B)	0.9600
C(51)-H(51C)	0.9600
C(52)-O(6)	1.214(3)
C(52)-C(53)	1.484(4)
C(53)-C(54)	1.384(4)
C(53)-C(58)	1.391(4)

C(54)-C(55)	1.383(4)
C(54)-H(54)	0.9300
C(55)-C(56)	1.372(5)
C(55)-H(55)	0.9300
C(56)-C(57)	1.359(5)
C(56)-H(56)	0.9300
C(57)-C(58)	1.374(4)
C(57)-H(57)	0.9300
C(58)-H(58)	0.9300
C(59)-C(60)	1.377(4)
C(59)-C(64)	1.388(4)
C(59)-N(4)	1.396(4)
C(60)-C(61)	1.377(5)
C(60)-H(60)	0.9300
C(61)-C(62)	1.366(5)
C(61)-H(61)	0.9300
C(62)-C(63)	1.371(6)
C(62)-H(62)	0.9300
C(63)-C(64)	1.369(5)
C(63)-H(63)	0.9300
C(64)-H(64)	0.9300
N(4)-H(4)	0.8600

N(1)-C(1)-C(2)	107.4(2)
N(1)-C(1)-C(11)	121.6(2)
C(2)-C(1)-C(11)	130.1(2)
C(1)-C(2)-C(3)	107.6(2)
C(1)-C(2)-C(17)	125.9(2)
C(3)-C(2)-C(17)	126.3(2)
C(4)-C(3)-C(2)	107.5(2)
C(4)-C(3)-C(20)	123.4(2)
C(2)-C(3)-C(20)	129.0(2)
C(3)-C(4)-N(1)	107.9(2)
C(3)-C(4)-N(2)	131.0(2)
N(1)-C(4)-N(2)	120.6(2)
C(10)-C(5)-C(6)	120.3(3)
C(10)-C(5)-N(1)	120.0(2)
C(6)-C(5)-N(1)	119.7(2)

C(7)-C(6)-C(5)	119.4(3)
C(7)-C(6)-H(6)	120.3
C(5)-C(6)-H(6)	120.3
C(8)-C(7)-C(6)	120.9(3)
C(8)-C(7)-H(7)	119.6
C(6)-C(7)-H(7)	119.6
C(7)-C(8)-C(9)	119.7(3)
C(7)-C(8)-H(8)	120.1
C(9)-C(8)-H(8)	120.1
C(8)-C(9)-C(10)	120.2(3)
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-H(9)	119.9
C(5)-C(10)-C(9)	119.5(3)
C(5)-C(10)-H(10)	120.2
C(9)-C(10)-H(10)	120.2
C(16)-C(11)-C(12)	118.8(2)
C(16)-C(11)-C(1)	120.1(2)
C(12)-C(11)-C(1)	121.1(2)
C(13)-C(12)-C(11)	118.9(2)
C(13)-C(12)-H(12)	120.6
C(11)-C(12)-H(12)	120.6
C(14)-C(13)-C(12)	122.4(3)
C(14)-C(13)-Br(1)	118.3(2)
C(12)-C(13)-Br(1)	119.3(2)
C(13)-C(14)-C(15)	118.5(3)
C(13)-C(14)-H(14)	120.7
C(15)-C(14)-H(14)	120.7
C(16)-C(15)-C(14)	120.2(3)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(11)-C(16)-C(15)	121.2(3)
C(11)-C(16)-H(16)	119.4
C(15)-C(16)-H(16)	119.4
O(2)-C(17)-O(1)	122.5(3)
O(2)-C(17)-C(2)	125.3(3)
O(1)-C(17)-C(2)	112.1(2)
C(19)-C(18)-O(1)	108.5(3)
C(19)-C(18)-H(18A)	110.0

O(1)-C(18)-H(18A)	110.0
C(19)-C(18)-H(18B)	110.0
O(1)-C(18)-H(18B)	110.0
H(18A)-C(18)-H(18B)	108.4
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(3)-C(20)-C(3)	119.2(2)
O(3)-C(20)-C(21)	121.3(2)
C(3)-C(20)-C(21)	119.5(2)
C(26)-C(21)-C(22)	118.5(3)
C(26)-C(21)-C(20)	122.1(2)
C(22)-C(21)-C(20)	119.4(3)
C(23)-C(22)-C(21)	120.3(3)
C(23)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8
C(24)-C(23)-C(22)	120.4(3)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(25)	120.5(3)
C(23)-C(24)-H(24)	119.8
C(25)-C(24)-H(24)	119.8
C(24)-C(25)-C(26)	120.0(3)
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-H(25)	120.0
C(25)-C(26)-C(21)	120.3(3)
C(25)-C(26)-H(26)	119.8
C(21)-C(26)-H(26)	119.8
C(32)-C(27)-C(28)	118.7(3)
C(32)-C(27)-N(2)	122.1(2)
C(28)-C(27)-N(2)	119.3(2)
C(29)-C(28)-C(27)	120.0(3)
C(29)-C(28)-H(28)	120.0
C(27)-C(28)-H(28)	120.0
C(28)-C(29)-C(30)	121.2(3)

C(28)-C(29)-H(29)	119.4
C(30)-C(29)-H(29)	119.4
C(31)-C(30)-C(29)	118.8(3)
C(31)-C(30)-H(30)	120.6
C(29)-C(30)-H(30)	120.6
C(30)-C(31)-C(32)	121.2(3)
C(30)-C(31)-H(31)	119.4
C(32)-C(31)-H(31)	119.4
C(31)-C(32)-C(27)	120.2(3)
C(31)-C(32)-H(32)	119.9
C(27)-C(32)-H(32)	119.9
C(1)-N(1)-C(4)	109.6(2)
C(1)-N(1)-C(5)	127.5(2)
C(4)-N(1)-C(5)	122.7(2)
C(27)-N(2)-C(4)	122.6(2)
C(27)-N(2)-H(2)	118.7
C(4)-N(2)-H(2)	118.7
C(17)-O(1)-C(18)	117.2(2)
N(3)-C(33)-C(34)	107.4(2)
N(3)-C(33)-C(43)	122.5(2)
C(34)-C(33)-C(43)	129.5(2)
C(33)-C(34)-C(35)	107.7(2)
C(33)-C(34)-C(49)	123.1(2)
C(35)-C(34)-C(49)	128.5(2)
C(36)-C(35)-C(34)	107.1(2)
C(36)-C(35)-C(52)	123.2(2)
C(34)-C(35)-C(52)	129.6(2)
C(35)-C(36)-N(3)	108.1(2)
C(35)-C(36)-N(4)	130.7(2)
N(3)-C(36)-N(4)	120.8(2)
C(42)-C(37)-C(38)	120.7(3)
C(42)-C(37)-N(3)	119.8(3)
C(38)-C(37)-N(3)	119.5(3)
C(37)-C(38)-C(39)	119.2(3)
C(37)-C(38)-H(38)	120.4
C(39)-C(38)-H(38)	120.4
C(40)-C(39)-C(38)	120.3(3)
C(40)-C(39)-H(39)	119.8

C(38)-C(39)-H(39)	119.8
C(39)-C(40)-C(41)	120.4(3)
C(39)-C(40)-H(40)	119.8
C(41)-C(40)-H(40)	119.8
C(40)-C(41)-C(42)	120.0(4)
C(40)-C(41)-H(41)	120.0
C(42)-C(41)-H(41)	120.0
C(37)-C(42)-C(41)	119.2(3)
C(37)-C(42)-H(42)	120.4
C(41)-C(42)-H(42)	120.4
C(44)-C(43)-C(48)	118.1(3)
C(44)-C(43)-C(33)	121.7(2)
C(48)-C(43)-C(33)	120.2(2)
C(43)-C(44)-C(45)	119.7(2)
C(43)-C(44)-H(44)	120.2
C(45)-C(44)-H(44)	120.2
C(46)-C(45)-C(44)	122.2(3)
C(46)-C(45)-Br(2)	118.1(2)
C(44)-C(45)-Br(2)	119.7(2)
C(45)-C(46)-C(47)	118.2(3)
C(45)-C(46)-H(46)	120.9
C(47)-C(46)-H(46)	120.9
C(46)-C(47)-C(48)	120.5(3)
C(46)-C(47)-H(47)	119.8
C(48)-C(47)-H(47)	119.8
C(47)-C(48)-C(43)	121.4(3)
C(47)-C(48)-H(48)	119.3
C(43)-C(48)-H(48)	119.3
O(5)-C(49)-O(4)	122.9(3)
O(5)-C(49)-C(34)	124.6(3)
O(4)-C(49)-C(34)	112.4(2)
C(51)-C(50)-O(4)	110.0(3)
C(51)-C(50)-H(50A)	109.7
O(4)-C(50)-H(50A)	109.7
C(51)-C(50)-H(50B)	109.7
O(4)-C(50)-H(50B)	109.7
H(50A)-C(50)-H(50B)	108.2
C(50)-C(51)-H(51A)	109.5

C(50)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(50)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
O(6)-C(52)-C(35)	119.6(2)
O(6)-C(52)-C(53)	121.2(2)
C(35)-C(52)-C(53)	119.2(2)
C(54)-C(53)-C(58)	119.0(3)
C(54)-C(53)-C(52)	122.3(2)
C(58)-C(53)-C(52)	118.7(3)
C(55)-C(54)-C(53)	119.9(3)
C(55)-C(54)-H(54)	120.1
C(53)-C(54)-H(54)	120.1
C(56)-C(55)-C(54)	120.1(3)
C(56)-C(55)-H(55)	120.0
C(54)-C(55)-H(55)	120.0
C(57)-C(56)-C(55)	120.5(3)
C(57)-C(56)-H(56)	119.8
C(55)-C(56)-H(56)	119.8
C(56)-C(57)-C(58)	120.2(3)
C(56)-C(57)-H(57)	119.9
C(58)-C(57)-H(57)	119.9
C(57)-C(58)-C(53)	120.4(3)
C(57)-C(58)-H(58)	119.8
C(53)-C(58)-H(58)	119.8
C(60)-C(59)-C(64)	118.3(3)
C(60)-C(59)-N(4)	122.5(3)
C(64)-C(59)-N(4)	119.2(3)
C(59)-C(60)-C(61)	120.9(3)
C(59)-C(60)-H(60)	119.6
C(61)-C(60)-H(60)	119.6
C(62)-C(61)-C(60)	120.3(4)
C(62)-C(61)-H(61)	119.9
C(60)-C(61)-H(61)	119.9
C(61)-C(62)-C(63)	119.4(4)
C(61)-C(62)-H(62)	120.3
C(63)-C(62)-H(62)	120.3

C(64)-C(63)-C(62)	120.8(4)
C(64)-C(63)-H(63)	119.6
C(62)-C(63)-H(63)	119.6
C(63)-C(64)-C(59)	120.3(3)
C(63)-C(64)-H(64)	119.8
C(59)-C(64)-H(64)	119.8
C(33)-N(3)-C(36)	109.5(2)
C(33)-N(3)-C(37)	125.6(2)
C(36)-N(3)-C(37)	124.8(2)
C(59)-N(4)-C(36)	121.1(2)
C(59)-N(4)-H(4)	119.5
C(36)-N(4)-H(4)	119.5
C(49)-O(4)-C(50)	116.2(2)

Symmetry transformations used to generate equivalent atoms:

Table 3. Hydrogen bonds for **4j** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(28)-H(28)...O(6)	0.93	2.61	3.417(4)	145.7
C(32)-H(32)...Br(2)#1	0.93	3.09	3.916(3)	148.3
N(2)-H(2)...O(6)	0.86	2.41	3.228(3)	159.3
C(60)-H(60)...Br(1)#2	0.93	3.06	3.807(3)	138.4
C(64)-H(64)...O(3)	0.93	2.62	3.417(4)	144.6
N(4)-H(4)...O(3)	0.86	2.42	3.219(3)	155.6

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 x-1,y-1,z

Table 1. Crystal data and structure refinement for **6a**.

Identification code	**6a**	
Empirical formula	C34 H28 N2 O3	
Formula weight	512.58	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.0614(8) Å	α= 77.467(2)°.
	b = 13.7806(9) Å	β= 77.052(2)°.
	c = 25.8567(17) Å	γ = 86.513(2)°.
Volume	4088.3(5) $Å^3$	
Z	6	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	1620	
Crystal size	0.230 x 0.210 x 0.080 mm^3	
Theta range for data collection	1.733 to 27.640°.	
Index ranges	-15<=h<=15, -17<=k<=17, -33<=l<=32	
Reflections collected	64708	
Independent reflections	18839 [R(int) = 0.0697]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6899	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18839 / 48 / 1057	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0692, wR2 = 0.1296	
R indices (all data)	R1 = 0.1766, wR2 = 0.1622	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.235 and -0.237 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **6a**.

C(1)-C(2)	1.377(3)
C(1)-N(1)	1.393(2)
C(1)-C(34)	1.482(3)
C(2)-C(3)	1.444(3)
C(2)-C(26)	1.462(3)
C(3)-C(4)	1.375(3)
C(3)-C(7)	1.461(3)
C(4)-N(1)	1.374(2)
C(4)-N(2)	1.387(2)
C(5)-N(2)	1.494(2)
C(5)-C(20)	1.521(3)
C(5)-C(6)	1.523(3)
C(5)-H(5)	0.9800
C(6)-C(7)	1.518(3)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-O(1)	1.223(2)
C(8)-C(9)	1.372(3)
C(8)-C(13)	1.375(3)
C(8)-N(1)	1.444(2)
C(9)-C(10)	1.386(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.360(4)
C(10)-H(10)	0.9300
C(11)-C(12)	1.365(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.387(3)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-C(15)	1.382(3)
C(14)-C(19)	1.382(3)
C(14)-N(2)	1.433(2)
C(15)-C(16)	1.389(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.365(3)
C(16)-H(16)	0.9300

C(17)-C(18)	1.367(4)
C(17)-H(17)	0.9300
C(18)-C(19)	1.381(3)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-C(21)	1.378(3)
C(20)-C(25)	1.381(3)
C(21)-C(22)	1.377(4)
C(21)-H(21)	0.9300
C(22)-C(23)	1.360(5)
C(22)-H(22)	0.9300
C(23)-C(24)	1.368(4)
C(23)-H(23)	0.9300
C(24)-C(25)	1.386(4)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9300
C(26)-O(3)	1.194(3)
C(26)-O(2)	1.341(3)
C(27)-O(2)	1.447(3)
C(27)-C(28)	1.479(4)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(28)-C(29)	1.370(3)
C(28)-C(33)	1.414(4)
C(29)-C(30)	1.379(4)
C(29)-H(29)	0.9300
C(30)-C(31)	1.358(4)
C(30)-H(30)	0.9300
C(31)-C(32)	1.342(4)
C(31)-H(31)	0.9300
C(32)-C(33)	1.389(4)
C(32)-H(32)	0.9300
C(33)-H(33)	0.9300
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600
C(35)-C(36)	1.373(3)
C(35)-N(3)	1.392(3)

C(35)-C(68)	1.484(3)
C(36)-C(37)	1.441(3)
C(36)-C(60)	1.463(3)
C(37)-C(38)	1.378(3)
C(37)-C(41)	1.454(3)
C(38)-N(3)	1.372(2)
C(38)-N(4)	1.382(3)
C(39)-N(4)	1.491(3)
C(39)-C(54)	1.518(3)
C(39)-C(40)	1.524(3)
C(39)-H(39)	0.9800
C(40)-C(41)	1.518(3)
C(40)-H(40A)	0.9700
C(40)-H(40B)	0.9700
C(41)-O(4)	1.225(3)
C(42)-C(43)	1.373(3)
C(42)-C(47)	1.376(3)
C(42)-N(3)	1.443(3)
C(43)-C(44)	1.386(3)
C(43)-H(43)	0.9300
C(44)-C(45)	1.363(4)
C(44)-H(44)	0.9300
C(45)-C(46)	1.371(4)
C(45)-H(45)	0.9300
C(46)-C(47)	1.394(4)
C(46)-H(46)	0.9300
C(47)-H(47)	0.9300
C(48)-C(53)	1.378(3)
C(48)-C(49)	1.385(3)
C(48)-N(4)	1.429(3)
C(49)-C(50)	1.382(3)
C(49)-H(49)	0.9300
C(50)-C(51)	1.364(4)
C(50)-H(50)	0.9300
C(51)-C(52)	1.371(4)
C(51)-H(51)	0.9300
C(52)-C(53)	1.381(3)
C(52)-H(52)	0.9300

C(53)-H(53)	0.9300
C(54)-C(55)	1.380(3)
C(54)-C(59)	1.388(3)
C(55)-C(56)	1.383(4)
C(55)-H(55)	0.9300
C(56)-C(57)	1.362(5)
C(56)-H(56)	0.9300
C(57)-C(58)	1.370(5)
C(57)-H(57)	0.9300
C(58)-C(59)	1.384(4)
C(58)-H(58)	0.9300
C(59)-H(59)	0.9300
C(60)-O(6)	1.200(3)
C(60)-O(5)	1.337(3)
C(61)-O(5)	1.447(3)
C(61)-C(62)	1.480(4)
C(61)-H(61A)	0.9700
C(61)-H(61B)	0.9700
C(62)-C(63)	1.360(4)
C(62)-C(67)	1.371(4)
C(63)-C(64)	1.371(6)
C(63)-H(63)	0.9300
C(64)-C(65)	1.324(7)
C(64)-H(64)	0.9300
C(65)-C(66)	1.371(6)
C(65)-H(65)	0.9300
C(66)-C(67)	1.387(5)
C(66)-H(66)	0.9300
C(67)-H(67)	0.9300
C(68)-H(68A)	0.9600
C(68)-H(68B)	0.9600
C(68)-H(68C)	0.9600
C(69)-C(70)	1.375(3)
C(69)-N(5)	1.395(2)
C(69)-C(102)	1.480(3)
C(70)-C(71)	1.439(3)
C(70)-C(94)	1.464(3)
C(71)-C(72)	1.382(3)

C(71)-C(75)	1.451(3)
C(72)-N(6)	1.377(2)
C(72)-N(5)	1.380(2)
C(73)-N(6)	1.497(2)
C(73)-C(88)	1.520(3)
C(73)-C(74)	1.523(3)
C(73)-H(73)	0.9800
C(74)-C(75)	1.511(3)
C(74)-H(74A)	0.9700
C(74)-H(74B)	0.9700
C(75)-O(7)	1.226(2)
C(76)-C(81)	1.374(3)
C(76)-C(77)	1.376(3)
C(76)-N(5)	1.441(2)
C(77)-C(78)	1.390(3)
C(77)-H(77)	0.9300
C(78)-C(79)	1.362(4)
C(78)-H(78)	0.9300
C(79)-C(80)	1.372(4)
C(79)-H(79)	0.9300
C(80)-C(81)	1.381(3)
C(80)-H(80)	0.9300
C(81)-H(81)	0.9300
C(82)-C(87)	1.380(3)
C(82)-C(83)	1.383(3)
C(82)-N(6)	1.430(2)
C(83)-C(84)	1.384(3)
C(83)-H(83)	0.9300
C(84)-C(85)	1.364(4)
C(84)-H(84)	0.9300
C(85)-C(86)	1.370(4)
C(85)-H(85)	0.9300
C(86)-C(87)	1.378(3)
C(86)-H(86)	0.9300
C(87)-H(87)	0.9300
C(88)-C(89)	1.372(3)
C(88)-C(93)	1.378(3)
C(89)-C(90)	1.382(3)

C(89)-H(89)	0.9300
C(90)-C(91)	1.357(4)
C(90)-H(90)	0.9300
C(91)-C(92)	1.361(3)
C(91)-H(91)	0.9300
C(92)-C(93)	1.378(3)
C(92)-H(92)	0.9300
C(93)-H(93)	0.9300
C(94)-O(9)	1.193(2)
C(94)-O(8)	1.345(2)
C(95)-O(8)	1.427(3)
C(95)-C(96)	1.501(3)
C(95)-H(95A)	0.9700
C(95)-H(95B)	0.9700
C(96)-C(101)	1.371(3)
C(96)-C(97)	1.374(3)
C(97)-C(98)	1.380(3)
C(97)-H(97)	0.9300
C(98)-C(99)	1.363(4)
C(98)-H(98)	0.9300
C(99)-C(100)	1.367(3)
C(99)-H(99)	0.9300
C(100)-C(101)	1.378(3)
C(100)-H(100)	0.9300
C(101)-H(101)	0.9300
C(102)-H(10A)	0.9600
C(102)-H(10B)	0.9600
C(102)-H(10C)	0.9600

C(2)-C(1)-N(1)	107.79(17)
C(2)-C(1)-C(34)	131.44(19)
N(1)-C(1)-C(34)	120.59(17)
C(1)-C(2)-C(3)	107.95(17)
C(1)-C(2)-C(26)	122.5(2)
C(3)-C(2)-C(26)	129.17(19)
C(4)-C(3)-C(2)	106.00(17)
C(4)-C(3)-C(7)	118.53(19)
C(2)-C(3)-C(7)	135.12(19)

N(1)-C(4)-C(3)	109.66(17)
N(1)-C(4)-N(2)	122.24(17)
C(3)-C(4)-N(2)	128.01(18)
N(2)-C(5)-C(20)	108.90(17)
N(2)-C(5)-C(6)	109.43(17)
C(20)-C(5)-C(6)	114.82(18)
N(2)-C(5)-H(5)	107.8
C(20)-C(5)-H(5)	107.8
C(6)-C(5)-H(5)	107.8
C(7)-C(6)-C(5)	114.63(18)
C(7)-C(6)-H(6A)	108.6
C(5)-C(6)-H(6A)	108.6
C(7)-C(6)-H(6B)	108.6
C(5)-C(6)-H(6B)	108.6
H(6A)-C(6)-H(6B)	107.6
O(1)-C(7)-C(3)	126.1(2)
O(1)-C(7)-C(6)	119.7(2)
C(3)-C(7)-C(6)	114.16(19)
C(9)-C(8)-C(13)	120.7(2)
C(9)-C(8)-N(1)	120.51(19)
C(13)-C(8)-N(1)	118.83(18)
C(8)-C(9)-C(10)	119.1(2)
C(8)-C(9)-H(9)	120.4
C(10)-C(9)-H(9)	120.4
C(11)-C(10)-C(9)	120.5(2)
C(11)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
C(10)-C(11)-C(12)	120.3(2)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-C(13)	120.2(3)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
C(8)-C(13)-C(12)	119.2(2)
C(8)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
C(15)-C(14)-C(19)	119.1(2)
C(15)-C(14)-N(2)	121.25(19)

C(19)-C(14)-N(2)	119.69(19)
C(14)-C(15)-C(16)	120.1(2)
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	120.3(2)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(18)	120.0(2)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(17)-C(18)-C(19)	120.4(2)
C(17)-C(18)-H(18)	119.8
C(19)-C(18)-H(18)	119.8
C(18)-C(19)-C(14)	120.2(2)
C(18)-C(19)-H(19)	119.9
C(14)-C(19)-H(19)	119.9
C(21)-C(20)-C(25)	118.2(2)
C(21)-C(20)-C(5)	123.1(2)
C(25)-C(20)-C(5)	118.7(2)
C(22)-C(21)-C(20)	121.0(3)
C(22)-C(21)-H(21)	119.5
C(20)-C(21)-H(21)	119.5
C(23)-C(22)-C(21)	120.5(3)
C(23)-C(22)-H(22)	119.7
C(21)-C(22)-H(22)	119.7
C(22)-C(23)-C(24)	119.6(3)
C(22)-C(23)-H(23)	120.2
C(24)-C(23)-H(23)	120.2
C(23)-C(24)-C(25)	120.2(3)
C(23)-C(24)-H(24)	119.9
C(25)-C(24)-H(24)	119.9
C(20)-C(25)-C(24)	120.5(3)
C(20)-C(25)-H(25)	119.7
C(24)-C(25)-H(25)	119.7
O(3)-C(26)-O(2)	122.7(2)
O(3)-C(26)-C(2)	126.7(2)
O(2)-C(26)-C(2)	110.6(2)
O(2)-C(27)-C(28)	110.6(2)

O(2)-C(27)-H(27A)	109.5
C(28)-C(27)-H(27A)	109.5
O(2)-C(27)-H(27B)	109.5
C(28)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	108.1
C(29)-C(28)-C(33)	117.6(3)
C(29)-C(28)-C(27)	121.1(3)
C(33)-C(28)-C(27)	121.3(3)
C(28)-C(29)-C(30)	121.1(3)
C(28)-C(29)-H(29)	119.5
C(30)-C(29)-H(29)	119.5
C(31)-C(30)-C(29)	120.9(3)
C(31)-C(30)-H(30)	119.6
C(29)-C(30)-H(30)	119.6
C(32)-C(31)-C(30)	119.8(3)
C(32)-C(31)-H(31)	120.1
C(30)-C(31)-H(31)	120.1
C(31)-C(32)-C(33)	121.2(3)
C(31)-C(32)-H(32)	119.4
C(33)-C(32)-H(32)	119.4
C(32)-C(33)-C(28)	119.5(3)
C(32)-C(33)-H(33)	120.2
C(28)-C(33)-H(33)	120.2
C(1)-C(34)-H(34A)	109.5
C(1)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(1)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(4)-N(1)-C(1)	108.60(15)
C(4)-N(1)-C(8)	124.88(16)
C(1)-N(1)-C(8)	126.22(16)
C(4)-N(2)-C(14)	118.72(16)
C(4)-N(2)-C(5)	109.94(15)
C(14)-N(2)-C(5)	117.96(16)
C(26)-O(2)-C(27)	116.7(2)
C(36)-C(35)-N(3)	108.16(18)
C(36)-C(35)-C(68)	131.1(2)

N(3)-C(35)-C(68)	120.51(19)
C(35)-C(36)-C(37)	107.74(18)
C(35)-C(36)-C(60)	121.6(2)
C(37)-C(36)-C(60)	130.3(2)
C(38)-C(37)-C(36)	106.12(18)
C(38)-C(37)-C(41)	118.8(2)
C(36)-C(37)-C(41)	134.6(2)
N(3)-C(38)-C(37)	109.56(18)
N(3)-C(38)-N(4)	122.86(18)
C(37)-C(38)-N(4)	127.50(19)
N(4)-C(39)-C(54)	108.75(18)
N(4)-C(39)-C(40)	109.07(17)
C(54)-C(39)-C(40)	115.01(19)
N(4)-C(39)-H(39)	107.9
C(54)-C(39)-H(39)	107.9
C(40)-C(39)-H(39)	107.9
C(41)-C(40)-C(39)	114.27(19)
C(41)-C(40)-H(40A)	108.7
C(39)-C(40)-H(40A)	108.7
C(41)-C(40)-H(40B)	108.7
C(39)-C(40)-H(40B)	108.7
H(40A)-C(40)-H(40B)	107.6
O(4)-C(41)-C(37)	125.6(2)
O(4)-C(41)-C(40)	120.0(2)
C(37)-C(41)-C(40)	114.25(19)
C(43)-C(42)-C(47)	120.7(2)
C(43)-C(42)-N(3)	120.7(2)
C(47)-C(42)-N(3)	118.6(2)
C(42)-C(43)-C(44)	119.0(3)
C(42)-C(43)-H(43)	120.5
C(44)-C(43)-H(43)	120.5
C(45)-C(44)-C(43)	121.2(3)
C(45)-C(44)-H(44)	119.4
C(43)-C(44)-H(44)	119.4
C(44)-C(45)-C(46)	119.5(3)
C(44)-C(45)-H(45)	120.2
C(46)-C(45)-H(45)	120.2
C(45)-C(46)-C(47)	120.3(3)

C(45)-C(46)-H(46)	119.8
C(47)-C(46)-H(46)	119.8
C(42)-C(47)-C(46)	119.2(2)
C(42)-C(47)-H(47)	120.4
C(46)-C(47)-H(47)	120.4
C(53)-C(48)-C(49)	119.1(2)
C(53)-C(48)-N(4)	119.6(2)
C(49)-C(48)-N(4)	121.2(2)
C(50)-C(49)-C(48)	120.0(2)
C(50)-C(49)-H(49)	120.0
C(48)-C(49)-H(49)	120.0
C(51)-C(50)-C(49)	120.4(2)
C(51)-C(50)-H(50)	119.8
C(49)-C(50)-H(50)	119.8
C(50)-C(51)-C(52)	119.8(2)
C(50)-C(51)-H(51)	120.1
C(52)-C(51)-H(51)	120.1
C(51)-C(52)-C(53)	120.4(2)
C(51)-C(52)-H(52)	119.8
C(53)-C(52)-H(52)	119.8
C(48)-C(53)-C(52)	120.2(2)
C(48)-C(53)-H(53)	119.9
C(52)-C(53)-H(53)	119.9
C(55)-C(54)-C(59)	118.2(2)
C(55)-C(54)-C(39)	122.8(2)
C(59)-C(54)-C(39)	119.0(2)
C(54)-C(55)-C(56)	120.5(3)
C(54)-C(55)-H(55)	119.8
C(56)-C(55)-H(55)	119.8
C(57)-C(56)-C(55)	120.7(3)
C(57)-C(56)-H(56)	119.7
C(55)-C(56)-H(56)	119.7
C(56)-C(57)-C(58)	119.9(3)
C(56)-C(57)-H(57)	120.0
C(58)-C(57)-H(57)	120.0
C(57)-C(58)-C(59)	119.8(3)
C(57)-C(58)-H(58)	120.1
C(59)-C(58)-H(58)	120.1

C(58)-C(59)-C(54)	120.9(3)
C(58)-C(59)-H(59)	119.5
C(54)-C(59)-H(59)	119.5
O(6)-C(60)-O(5)	121.5(2)
O(6)-C(60)-C(36)	125.2(2)
O(5)-C(60)-C(36)	113.2(2)
O(5)-C(61)-C(62)	108.8(2)
O(5)-C(61)-H(61A)	109.9
C(62)-C(61)-H(61A)	109.9
O(5)-C(61)-H(61B)	109.9
C(62)-C(61)-H(61B)	109.9
H(61A)-C(61)-H(61B)	108.3
C(63)-C(62)-C(67)	118.6(3)
C(63)-C(62)-C(61)	120.1(4)
C(67)-C(62)-C(61)	121.3(3)
C(62)-C(63)-C(64)	121.9(4)
C(62)-C(63)-H(63)	119.1
C(64)-C(63)-H(63)	119.1
C(65)-C(64)-C(63)	119.4(5)
C(65)-C(64)-H(64)	120.3
C(63)-C(64)-H(64)	120.3
C(64)-C(65)-C(66)	121.1(5)
C(64)-C(65)-H(65)	119.5
C(66)-C(65)-H(65)	119.5
C(65)-C(66)-C(67)	119.6(5)
C(65)-C(66)-H(66)	120.2
C(67)-C(66)-H(66)	120.2
C(62)-C(67)-C(66)	119.5(4)
C(62)-C(67)-H(67)	120.2
C(66)-C(67)-H(67)	120.2
C(35)-C(68)-H(68A)	109.5
C(35)-C(68)-H(68B)	109.5
H(68A)-C(68)-H(68B)	109.5
C(35)-C(68)-H(68C)	109.5
H(68A)-C(68)-H(68C)	109.5
H(68B)-C(68)-H(68C)	109.5
C(38)-N(3)-C(35)	108.40(17)
C(38)-N(3)-C(42)	125.03(17)

C(35)-N(3)-C(42)	126.06(17)
C(38)-N(4)-C(48)	120.13(17)
C(38)-N(4)-C(39)	110.82(16)
C(48)-N(4)-C(39)	119.54(17)
C(60)-O(5)-C(61)	115.4(2)
C(70)-C(69)-N(5)	107.71(17)
C(70)-C(69)-C(102)	130.98(19)
N(5)-C(69)-C(102)	120.99(17)
C(69)-C(70)-C(71)	108.04(17)
C(69)-C(70)-C(94)	122.45(19)
C(71)-C(70)-C(94)	128.42(18)
C(72)-C(71)-C(70)	106.51(17)
C(72)-C(71)-C(75)	118.86(19)
C(70)-C(71)-C(75)	133.69(18)
N(6)-C(72)-N(5)	124.23(17)
N(6)-C(72)-C(71)	126.66(18)
N(5)-C(72)-C(71)	108.79(17)
N(6)-C(73)-C(88)	110.21(17)
N(6)-C(73)-C(74)	108.83(17)
C(88)-C(73)-C(74)	114.35(17)
N(6)-C(73)-H(73)	107.7
C(88)-C(73)-H(73)	107.7
C(74)-C(73)-H(73)	107.7
C(75)-C(74)-C(73)	113.37(18)
C(75)-C(74)-H(74A)	108.9
C(73)-C(74)-H(74A)	108.9
C(75)-C(74)-H(74B)	108.9
C(73)-C(74)-H(74B)	108.9
H(74A)-C(74)-H(74B)	107.7
O(7)-C(75)-C(71)	124.8(2)
O(7)-C(75)-C(74)	121.23(19)
C(71)-C(75)-C(74)	113.88(18)
C(81)-C(76)-C(77)	120.7(2)
C(81)-C(76)-N(5)	118.89(19)
C(77)-C(76)-N(5)	120.4(2)
C(76)-C(77)-C(78)	118.9(2)
C(76)-C(77)-H(77)	120.6
C(78)-C(77)-H(77)	120.6

C(79)-C(78)-C(77)	120.7(2)
C(79)-C(78)-H(78)	119.6
C(77)-C(78)-H(78)	119.6
C(78)-C(79)-C(80)	119.9(2)
C(78)-C(79)-H(79)	120.1
C(80)-C(79)-H(79)	120.1
C(79)-C(80)-C(81)	120.4(3)
C(79)-C(80)-H(80)	119.8
C(81)-C(80)-H(80)	119.8
C(76)-C(81)-C(80)	119.5(2)
C(76)-C(81)-H(81)	120.3
C(80)-C(81)-H(81)	120.3
C(87)-C(82)-C(83)	119.2(2)
C(87)-C(82)-N(6)	119.10(19)
C(83)-C(82)-N(6)	121.73(19)
C(82)-C(83)-C(84)	119.8(2)
C(82)-C(83)-H(83)	120.1
C(84)-C(83)-H(83)	120.1
C(85)-C(84)-C(83)	120.6(2)
C(85)-C(84)-H(84)	119.7
C(83)-C(84)-H(84)	119.7
C(84)-C(85)-C(86)	119.8(2)
C(84)-C(85)-H(85)	120.1
C(86)-C(85)-H(85)	120.1
C(85)-C(86)-C(87)	120.2(3)
C(85)-C(86)-H(86)	119.9
C(87)-C(86)-H(86)	119.9
C(86)-C(87)-C(82)	120.4(2)
C(86)-C(87)-H(87)	119.8
C(82)-C(87)-H(87)	119.8
C(89)-C(88)-C(93)	117.2(2)
C(89)-C(88)-C(73)	123.5(2)
C(93)-C(88)-C(73)	119.27(19)
C(88)-C(89)-C(90)	121.2(2)
C(88)-C(89)-H(89)	119.4
C(90)-C(89)-H(89)	119.4
C(91)-C(90)-C(89)	120.5(2)
C(91)-C(90)-H(90)	119.8

C(89)-C(90)-H(90)	119.8
C(90)-C(91)-C(92)	119.5(2)
C(90)-C(91)-H(91)	120.3
C(92)-C(91)-H(91)	120.3
C(91)-C(92)-C(93)	120.0(2)
C(91)-C(92)-H(92)	120.0
C(93)-C(92)-H(92)	120.0
C(92)-C(93)-C(88)	121.6(2)
C(92)-C(93)-H(93)	119.2
C(88)-C(93)-H(93)	119.2
O(9)-C(94)-O(8)	121.9(2)
O(9)-C(94)-C(70)	126.9(2)
O(8)-C(94)-C(70)	111.11(19)
O(8)-C(95)-C(96)	108.84(19)
O(8)-C(95)-H(95A)	109.9
C(96)-C(95)-H(95A)	109.9
O(8)-C(95)-H(95B)	109.9
C(96)-C(95)-H(95B)	109.9
H(95A)-C(95)-H(95B)	108.3
C(101)-C(96)-C(97)	118.1(2)
C(101)-C(96)-C(95)	122.7(2)
C(97)-C(96)-C(95)	119.2(2)
C(96)-C(97)-C(98)	120.8(3)
C(96)-C(97)-H(97)	119.6
C(98)-C(97)-H(97)	119.6
C(99)-C(98)-C(97)	120.7(2)
C(99)-C(98)-H(98)	119.7
C(97)-C(98)-H(98)	119.7
C(98)-C(99)-C(100)	118.8(3)
C(98)-C(99)-H(99)	120.6
C(100)-C(99)-H(99)	120.6
C(99)-C(100)-C(101)	120.7(3)
C(99)-C(100)-H(100)	119.6
C(101)-C(100)-H(100)	119.6
C(96)-C(101)-C(100)	120.9(2)
C(96)-C(101)-H(101)	119.6
C(100)-C(101)-H(101)	119.6
C(69)-C(102)-H(10A)	109.5

C(69)-C(102)-H(10B)	109.5
H(10A)-C(102)-H(10B)	109.5
C(69)-C(102)-H(10C)	109.5
H(10A)-C(102)-H(10C)	109.5
H(10B)-C(102)-H(10C)	109.5
C(72)-N(5)-C(69)	108.92(15)
C(72)-N(5)-C(76)	125.44(16)
C(69)-N(5)-C(76)	125.42(16)
C(72)-N(6)-C(82)	122.06(16)
C(72)-N(6)-C(73)	110.97(15)
C(82)-N(6)-C(73)	118.15(16)
C(94)-O(8)-C(95)	116.87(18)

Symmetry transformations used to generate equivalent atoms:

Table 3. Hydrogen bonds for **6a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9)...O(9)	0.93	2.48	3.300(3)	146.9
C(34)-H(34A)...O(3)	0.96	2.35	3.027(3)	126.7
C(34)-H(34B)...O(9)	0.96	2.51	3.458(3)	171.5
C(43)-H(43)...O(6)#1	0.93	2.44	3.295(3)	152.8
C(68)-H(68A)...O(6)	0.96	2.35	3.025(3)	126.9
C(68)-H(68C)...O(6)#1	0.96	2.45	3.378(3)	162.5
C(102)-H(10A)...O(9)	0.96	2.41	3.094(3)	127.6
C(102)-H(10C)...O(3)	0.96	2.58	3.527(3)	168.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1