Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Re^{I}-Catalyzed Highly Regio- and Stereoselective C–H Addition to Terminal and Internal Alkynes

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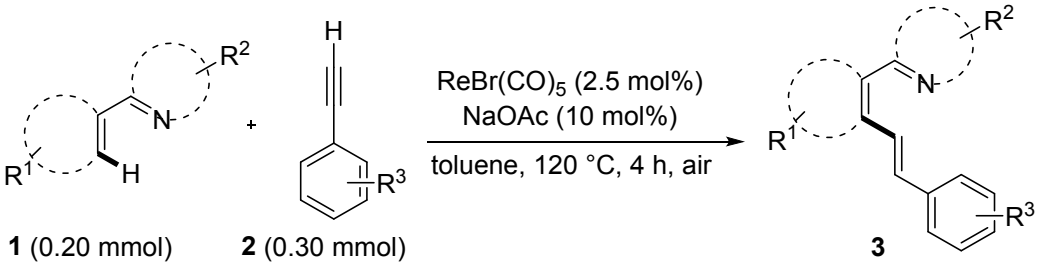
General Considerations

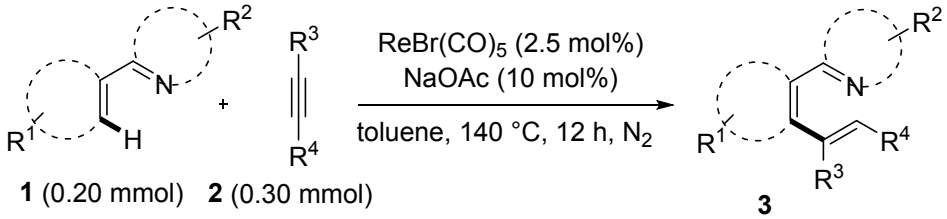
Unless otherwise mentioned, all reactions were performed under air atmosphere. Solvents were not dried and not distilled prior to use, unless specifically mentioned.[1] Starting materials 2-arylpyridines[2], *N*-pyrimidyl indoles[3], alkynes[4] and **D$_5$-1a**[2] were synthesized according to the reported methods. $ReBr(CO)_5$ was synthesized from $Re_2(CO)_{10}$ according to the reported method.[5] Other reagents were commercially available and used as purchased.

General Procedure for the Rhenium(I)-Catalyzed C–H Alkenylation of Heterocycles with Terminal Alkynes



To a screw-capped sealed tube was added $ReBr(CO)_5$ (0.005 mmol) and NaOAc (0.02 mmol). Then, *N*-heterocycles **1** (0.2 mmol), terminal alkynes **2** (0.3 mmol) followed by toluene (1.0 mL) was added to the system and the reaction mixture was allowed to be stirred at 120 ℃ for 4 h. When the reaction was completed, the reaction mixture was cooled and diluted with dichloromethane (10 mL). The mixture was filtered through short Celite pad and washed with dichloromethane (10 mL). The filtrate was concentrated and purified by silica gel column chromatography using hexane/EtOAc as eluent to give the corresponding pure alkenylated *N*-heterocycles (**3**).

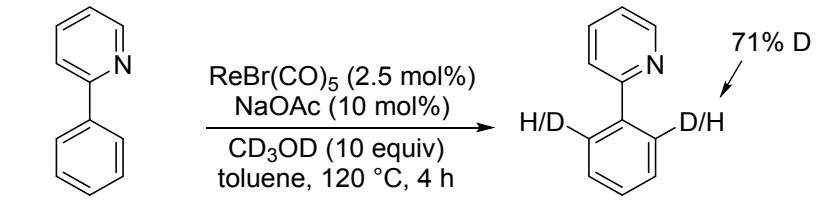
General Procedure for the Rhenium(I)-Catalyzed C–H Alkenylation of Heterocycles with Internal Alkynes



To a screw-capped sealed tube was added $ReBr(CO)_5$ (0.005 mmol) and NaOAc (0.02 mmol). The sealed tube was evacuated and purged with nitrogen three times. Then *N*-heterocycles **1** (0.2 mmol), internal alkynes **2** (0.3 mmol) and dry toluene (1.0 mL) were added to the system and the reaction mixture was allowed to be stirred at 140 ℃ for 12 h. When the reaction was completed, the reaction mixture was cooled and diluted with dichloromethane (10 mL). The mixture was filtered through short Celite pad and washed with dichloromethane (10 mL). The filtrate was concentrated and purified by silica gel column chromatography using hexane/EtOAc as eluent to give the corresponding pure alkenylated *N*-heterocycles (**3**).

Mechanistic Studies

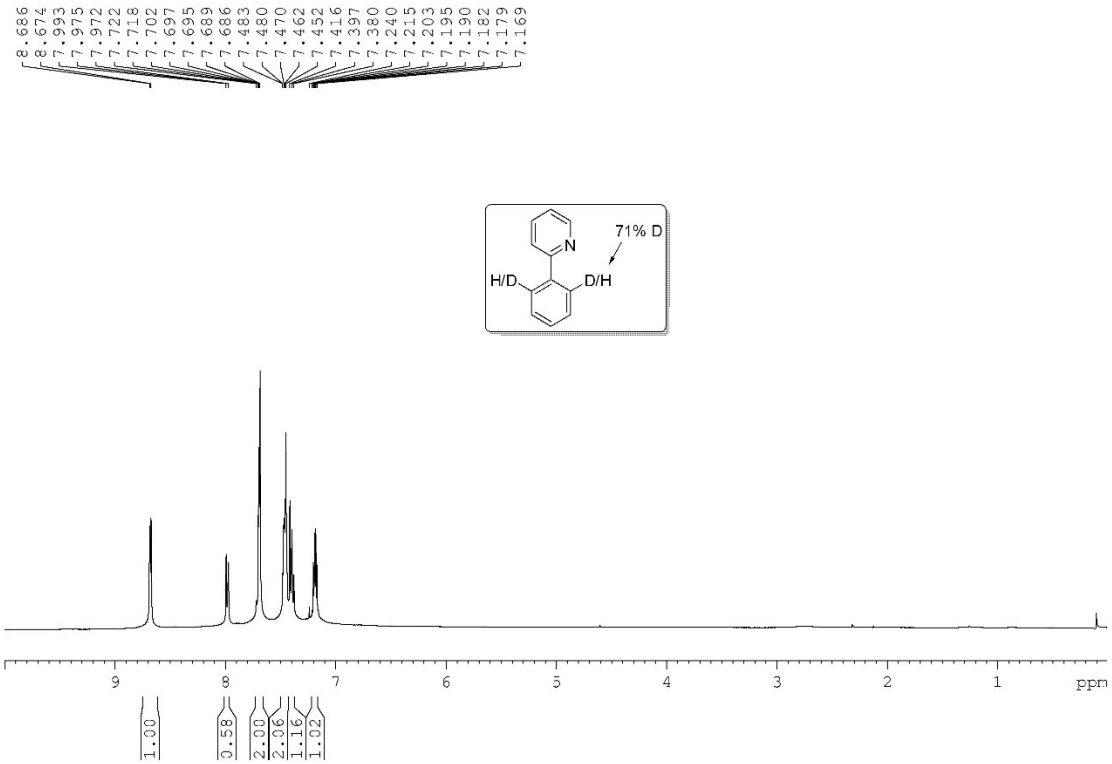
D/H Exchange Studies



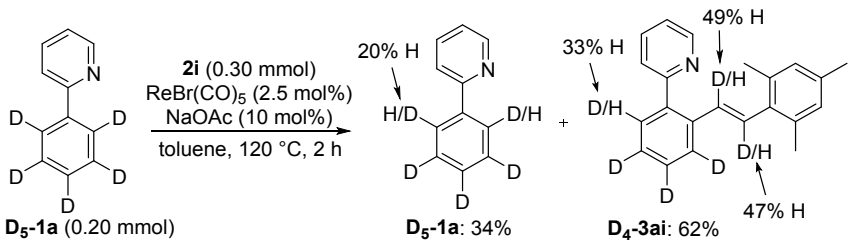
1a (0.20 mmol) **D$_2$-1a**: 91%

To a screw-capped sealed tube was added $ReBr(CO)_5$ (0.005 mmol) and NaOAc (0.02 mmol). Then 2-phenyl pyridine **1a** (0.2 mmol), CD_3OD (0.08 mL, 10 equiv) followed by toluene (1.0 mL), was added to the system and the reaction mixture was allowed to be stirred at 120 ℃ for 4 h. The reaction mixture was then cooled and diluted with dichloromethane (10 mL). The mixture was filtered through a short Celite pad and washed with dichloromethane (10 mL). The filtrate was concentrated and purified by silica gel column chromatography using hexane/EtOAc as eluent. The D/H-incorporation in **D$_2$-1a** was determined by ^{1}H-NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **D_2-1a**

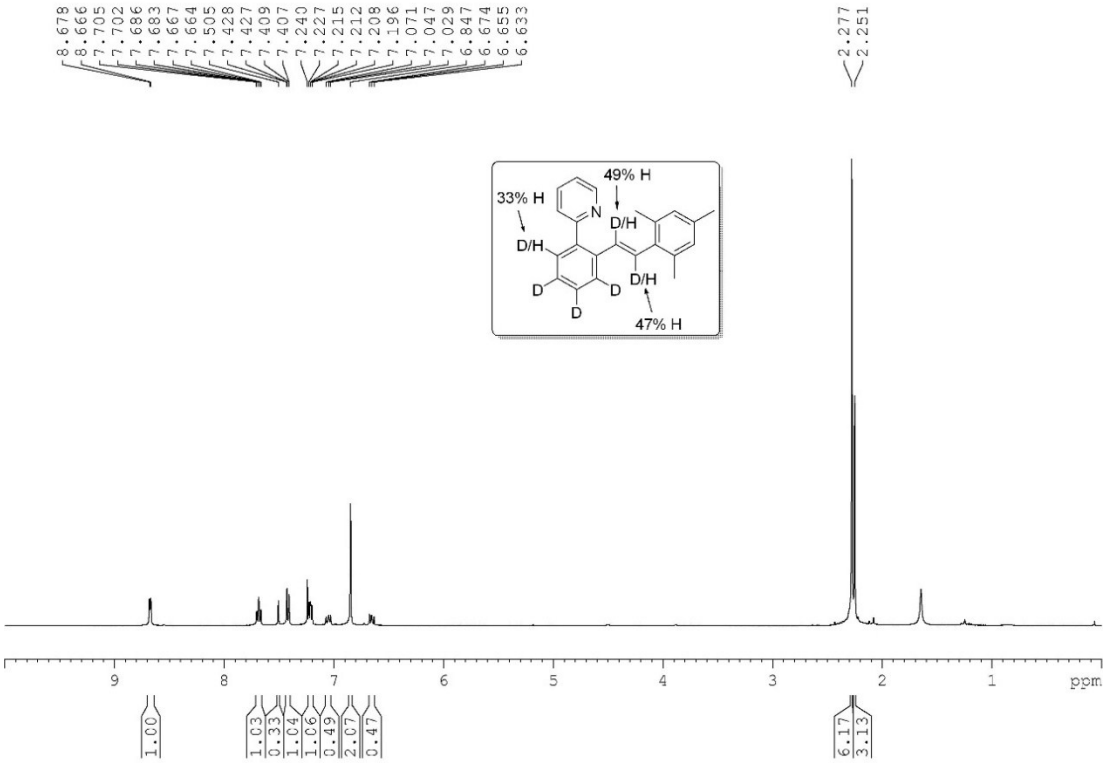


Rhenium(I)-Catalyzed Alkenylation of D_5-1a

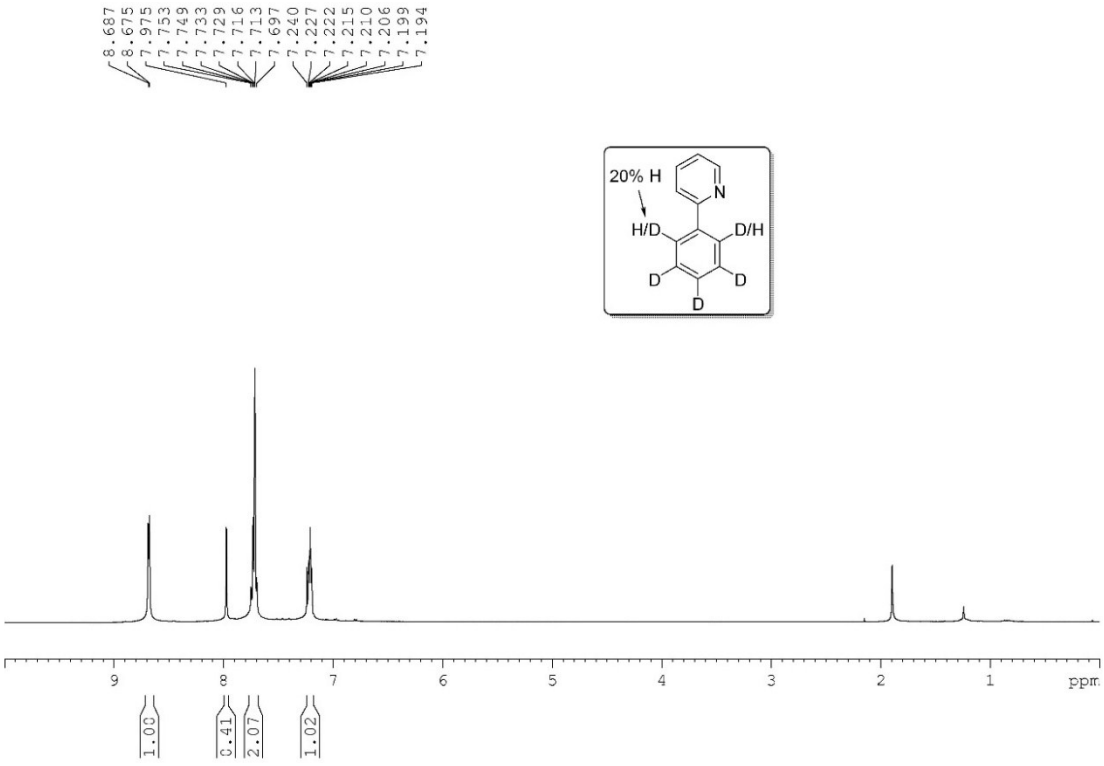


To a screw-capped sealed tube was added $ReBr(CO)_5$ (0.005 mmol) and NaOAc (0.02 mmol). Then **D_5-1a** (0.2 mmol) and mesitylacetylene **2i** (0.3 mmol) followed by toluene (1.0 mL) were added to the system and stirred at 120 ℃ for 2 h. When the reaction completed, the reaction mixture was cooled and diluted with dichloromethane (10 mL). The mixture was filtered through a short Celite pad and washed with dichloromethane (10 mL). The filtrate was concentrated and purified by silica gel column chromatography using hexane/EtOAc as eluent to give the desired product **D_4-3ai** in 62% yield. The D/H-incorporation in **D_4-3ai** and the recovered **D_5-1a** were determined by ^{1}H-NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **D_4-3ai**

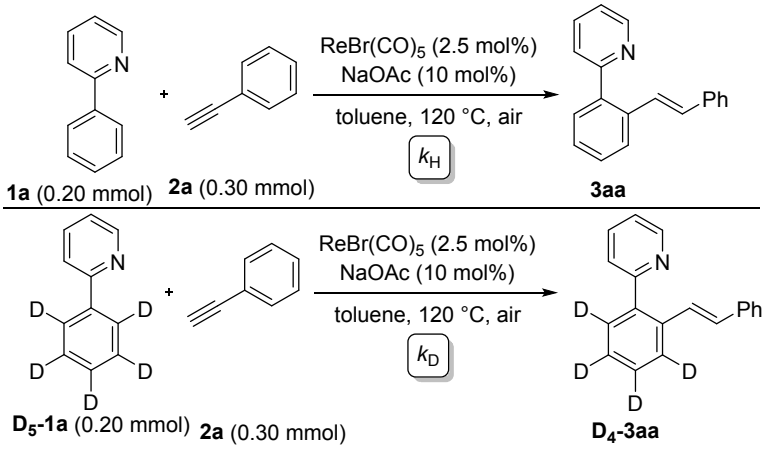


^{1}H NMR (400 MHz, $CDCl_3$) spectra of recovered compound **D_5-1a**

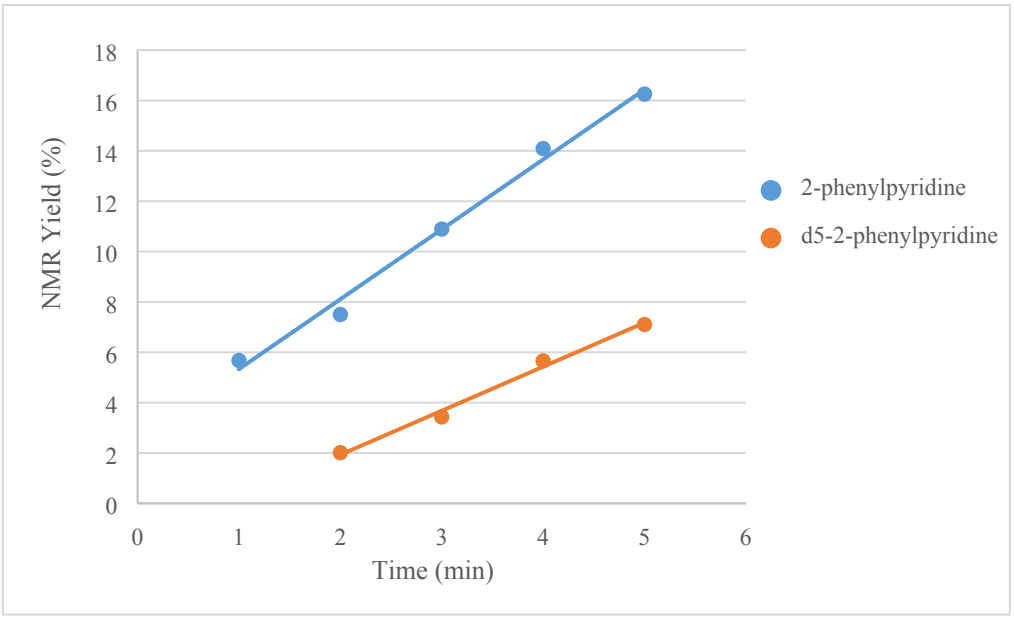


Kinetic Isotopic Experiments

Parallel experiments

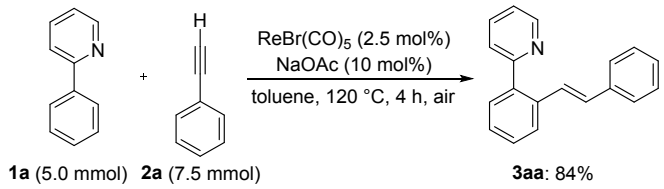


By following the general procedure, the two parallel experiments were conducted separately. Each reaction was stirred at 120 ℃ for 1 to 5 min. After immediately cooling in an ice bath, the reaction mixture was concentrated, and the yield of the products was determined by the ^{1}H NMR integration method using mesitylene as the internal standard. The product yields vs. time t (min) were plotted to give two linear graphs with slopes of 2.78 for **3aa** and 1.75 for **D_4-3aa**. The k_H/k_D value calculated from the slopes is 1.59.



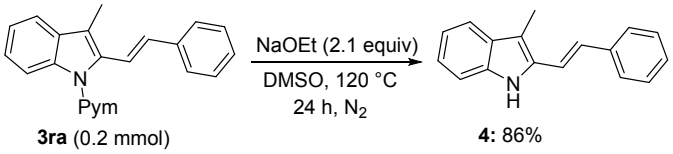
Applications

Gram Scale Reaction of 1a with 2a



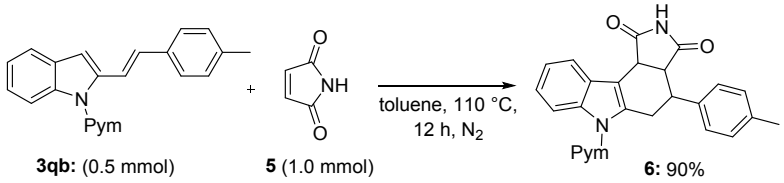
To a screw-cap sealed tube (100 mL) was added $ReBr(CO)_5$ (0.125 mmol) and NaOAc (0.5 mmol). Then 2-phenylpyridine (**1a**, 5.0 mmol), phenylacetylene (**2a**, 7.5 mmol) followed by toluene (25 mL) was added to the tube and stirred at 120 ℃ for 4 h. When the reaction was completed, the reaction mixture was cooled and diluted with dichloromethane (25 mL). The mixture was filtered through short Celite pad and washed with dichloromethane (20 mL). The filtrate was concentrated and purified by silica gel column chromatography using hexane/EtOAc as an eluent to give the desired product **3aa** (1.08g, 84%).

Typical Procedure for the Synthesis of (*E*)-3-Methyl-2-styryl-1*H*-indole (4)



A mixture of **3ra** (62.2 mg, 0.20 mmol) and NaOEt (28.6 mg, 0.42 mmol) in DMSO (4 mL) was stirred at 120 ℃ for 24 h under a nitrogen atmosphere. When the reaction was complted, the reaction mixture was cooled and quenched with water (5 mL), then extracted with EtOAc (3×10 mL). The combined organic layer was dried over $MgSO_4$. Then, the organic layer was filtered and concentrated by vacuum and the residue was purified by silica gel column chromatography to give the desired product **4** (40.0 mg, 86%) as a yellow solid.

Typical Procedure for the Synthesis of 6-(Pyrimidin-2-yl)-4-(*p*-tolyl)-4,5,6,10c-tetrahydropyrrolo[3,4-*c*]carbazole-1,3(2*H*,3a*H*)-dione (6)



3qb: (0.5 mmol) **5** (1.0 mmol) **6:** 90%

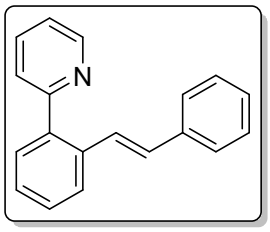
A mixture of **3qb** (155.7 mg, 0.5 mmol) and maleimide **5** (97.1 mg, 1.0 mmol) in toluene (5 mL) was stirred at 110 ℃ for 12 h under a nitrogen atmosphere. When the reaction was completed, the reaction mixture was cooled and concentrated by vacuum and the residue was purified by silica gel column chromatography to give the desired product **6** (148 mg, 90%) as an off-white solid.

References

1. Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 7th ed.; ButterworthHeinemann: Oxford, **2012**.
2. Rao, X.; Liu, C.; Qiu, J.; Jin, Z. *Org. Biomol. Chem.* **2012**, *10*, 7875-7883.
3. Mayuko, N.; Koji, H.; Tetsuya, S.; Masahiro, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 6993-6997.
4. Kumpan, K.; Nathubhai, A.; Zhang, C.; Wood, P. J.; Lloyd, M. D.; Thompson, A. S.; Haikarainen, T.; Lehtiö, L.; Threadgill, M. D. *Bioorganic Med. Chem.* **2015**, *23*, 3013, 3032.
5. Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorganic Synthesis,* **1990**, *28*, 160-165.

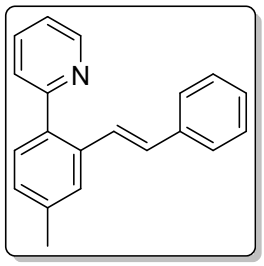
1. Spectral Data

(*E*)-2-(2-Styrylphenyl)pyridine (3aa)



Yellow oil (45 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.4 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.66 (td, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.60 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.45-7.38 (m, 5 H), 7.35-7.28 (m, 3 H), 7.24-7.20 (m, 2 H), 7.10 (d, *J* = 16.4 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 149.2, 139.2, 137.2, 135.7, 135.3, 129.9, 129.7, 128.3(3), 128.3(0), 127.3, 127.2, 126.3, 125.9, 124.7, 121.5; **HRMS** (ESI, m/z) calcd for $C_{19}H_{16}N$ $[M+H]^+$: 258.1283, found 258.1298; **IR** (thin film): 3057, 2960, 1584, 1495, 1460, 1424, 1265, 1151, 962, 795, 761, 749, and 692 cm^{-1}.

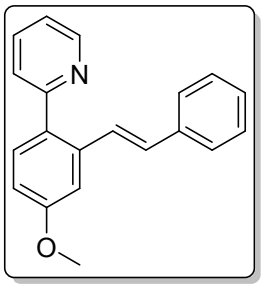
(*E*)-2-(4-Methyl-2-styrylphenyl)pyridine (3ba)



Yellow oil (46 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.8 Hz, 1 H), 7.68 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.59 (s, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.44-7.40 (m, 3 H), 7.33-7.26 (m, 4 H), 7.24-7.20 (m, 2 H), 7.07 (d, *J* = 16.4 Hz, 1 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 149.1, 138.0, 137.3, 136.7, 135.6, 135.2, 129.9, 129.5, 128.3, 127.4, 127.2, 126.5, 126.3, 124.7, 121.4, 21.4; **HRMS** (ESI, m/z)

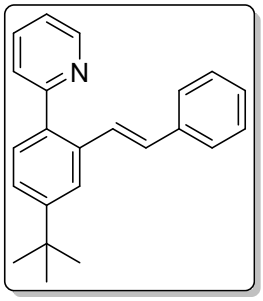
calcd for $C_{20}H_{18}N$ $[M+H]^+$: 272.1439, found 272.1450; **IR** (thin film): 3024, 2922, 1585, 1498, 1462, 1427, 1364, 1150, 1026, 962, 826, 786, 750, 727 and 692 cm^{-1}.

(*E*)-2-(4-Methoxy-2-styrylphenyl)pyridine (3ca)



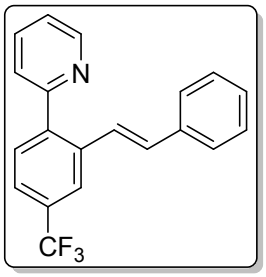
Colorless oil (51 mg, 89%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 1 H), 7.68 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 7.40 (d, *J* = 7.6 Hz, 3 H), 7.33-7.7.26 (m, 4 H), 7.24-7.20 (m, 2 H), 7.06 (d, *J* = 16.0 Hz, 1 H), 6.95 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1 H), 3.89 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.5, 158.2, 149.1, 137.1, 136.7, 135.6, 132.4, 131.4, 129.9, 128.4, 127.4, 127.3, 126.4, 124.7, 121.2, 113.4, 110.9, 55.3; **HRMS** (ESI, m/z) calcd for $C_{20}H_{18}NO$ $[M+H]^+$: 238.1388, found 238.1390; **IR** (thin film): 3059, 2962, 2834, 1600, 1568, 1499, 1462, 1426, 1282, 1213, 1167, 1151, 1119, 1062, 1045, 1018, 962, 840, 786, 751, 725 and 693 cm^{-1}.

(*E*)-2-(4-(*tert*-Butyl)-2-styrylphenyl)pyridine (3da)



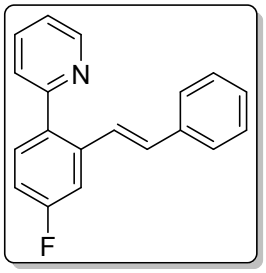
Off-white solid (58 mg, 92%); m.p. 91-93 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 1 H), 7.76 (d, *J* = 1.6 Hz, 1 H), 7.69 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.45-7.40 (m, 4 H), 7.32-7.26 (m, 3 H), 7.24-7.19 (m, 2 H), 7.05 (d, *J* = 16.4 Hz, 1 H), 1.41 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 151.3, 149.2, 137.4, 136.7, 135.7, 135.0, 129.8, 129.5, 128.4, 128.1, 127.2, 126.4, 124.9, 124.8, 122.9, 121.5, 34.8, 31.4; **HRMS** (ESI, m/z) calcd for $C_{23}H_{24}N$ $[M+H]^+$: 314.1909, found 314.1900; **IR** (thin film): 3054, 2962, 2867, 1586, 1463, 1428, 1363, 1264, 1024, 963, 790, 749, 734 and 692 cm^{-1}.

(*E*)-2-(2-Styryl-4-(trifluoromethyl)phenyl)pyridine (3ea)



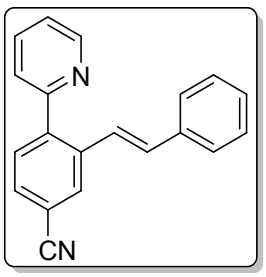
White solid (45 mg, 69%); m.p. 70-72 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.8 Hz, 1 H), 8.01 (s, 1 H), 7.76 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.61 (d, *J* = 8.0 Hz, 1 H), 7.46 (dd, *J* = 7.6 Hz, *J* = 0.4 Hz, 1 H), 7.41 (d, *J* = 7.6 Hz, 2 H), 7.34-7.30 (m, 3 H), 7.27-7.21 (m, 2 H), 7.12 (d, *J* = 16.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.2, 149.5, 142.2, 136.7, 136.3, 136.1, 131.5, 130.7, 130.6, 130.4, 128.5, 127.9, 126.6, 125.9, 124.8, 123.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 122.4; **HRMS** (ESI, m/z) calcd for $C_{20}H_{15}F_3N$ $[M+H]^+$: 326.1157 found 326.1137; **IR** (thin film): 3060, 2969, 1586, 1465, 1413, 1326, 1249, 1166, 1121, 1085, 962, 925, 839, 791, 750, 735, and 692 cm^{-1}.

(*E*)-2-(4-Fluoro-2-styrylphenyl)pyridine (3fa)



Yellow oil (44 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.72 (d, J = 4.8 Hz, 1 H), 7.71 (td, J = 7.6 Hz, J = 1.6 Hz, 1 H), 7.51 (dd, J = 8.4 Hz, J = 6.0 Hz, 1 H), 7.44-7.36 (m, 4 H), 7.31-7.22 (m, 4 H), 7.20-7.16 (m, 1 H), 7.07-7.01 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.8 (d, $J_{C\text{-}F}$ = 245.6 Hz), 157.8, 149.4, 137.8 (d, $J_{C\text{-}F}$ = 7.9 Hz), 136.9, 136.0, 135.6, 132.0 (d, $J_{C\text{-}F}$ = 8.5 Hz), 131.0, 128.6, 127.8, 126.6, 126.4, 124.9, 121.8, 114.5 (d, $J_{C\text{-}F}$ = 21.6 Hz), 112.3 (d, $J_{C\text{-}F}$ = 22.0 Hz); **HRMS** (ESI, m/z) calcd for $C_{19}H_{15}FN$ $[M+H]^+$: 276.1189 found 276.1123; **IR** (thin film): 3056, 2921, 2848, 1604, 1586, 1497, 1462, 1428, 1290, 1254, 1199, 1160, 962, 880, 847, 822, 786, 750, 722 and 691 cm^{-1}.

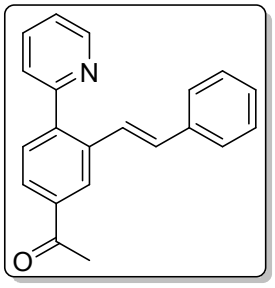
(*E*)-4-(Pyridin-2-yl)-3-styrylbenzonitrile (3ga)



White solid (35 mg, 62%); m.p. 117-119 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (d, J = 4.8 Hz, 1 H), 8.02 (s, 1 H), 7.78 (td, J = 7.6 Hz, J = 1.0 Hz, 1 H), 7.66-7.61 (m, 2 H), 7.46 (d, J = 7.6 Hz, 1 H), 7.40-7.26 (m, 6 H), 7.15 (d, J = 16.0 Hz, 1 H), 7.08 (d, J = 16.4 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.7, 149.7, 143.1, 136.8, 136.4, 136.3, 132.2, 130.9, 130.3, 130.1, 128.6, 128.2, 126.7, 125.2, 124.8, 122.7, 118.6, 112.4;

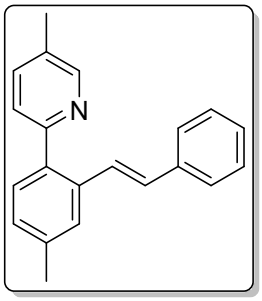
HRMS (ESI, m/z) calcd for $C_{20}H_{15}N_2$ $[M+H]^+$: 283.1235 found 283.1241; **IR** (thin film): 3057, 2916, 2229, 1585, 1568, 1496, 1463, 1429, 1152, 1024, 964, 901, 838, 790, 751, 729 and 692 cm^{-1}.

(*E*)-1-(4-(Pyridin-2-yl)-3-styrylphenyl)ethan-1-one (3ha)



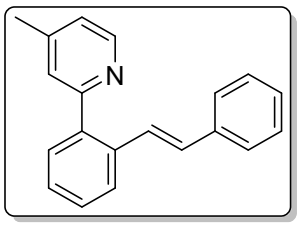
Off-white solid (41 mg, 68%); m.p. 78-80 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.4 Hz, 1 H), 8.33 (d, *J* = 1.6 Hz, 1 H), 7.92 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1 H), 7.75 (td, *J* = 8.0 Hz, *J* = 2.0 Hz, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.40-7.38 (m, 2 H), 7.32-7.29 (m, 3 H), 7.25-7.20 (m, 2 H), 7.14 (d, *J* = 16.0 Hz, 1 H), 2.68 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.6, 157.5, 149.5, 143.3, 136.9, 136.8, 136.0, 131.1, 130.4, 128.5, 127.7, 127.1, 126.5, 126.4, 126.1, 124.8, 122.3, 26.9; **HRMS** (ESI, m/z) calcd for $C_{21}H_{18}NO$ $[M+H]^+$: 300.1388 found 300.1382; **IR** (thin film): 3057, 2921, 1683, 1584, 1496, 1463, 1430, 1407, 1356, 1283, 1231, 1022, 963, 790,751, 731 and 695 cm^{-1}.

(*E*)-5-Methyl-2-(4-methyl-2-styrylphenyl)pyridine (3ia)



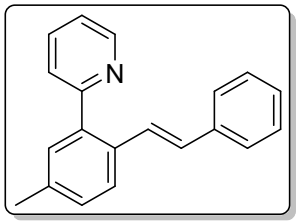
Light-green oil (47 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.56 (s, 1 H), 7.57 (s, 1 H), 7.51 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.40 (d, *J* = 7.6 Hz, 2 H), 7.33-7.31 (m, 3 H), 7.28 (d, *J* = 1.6 Hz, 1 H), 7.22 (d, *J* = 6.8 Hz, 1 H), 7.19 (d, *J* = 8.0 Hz, 1 H), 7.05 (d, *J* = 16.4 Hz, 1 H), 2.44 (s, 3 H), 2.38 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.7, 149.6, 137.9, 137.5, 136.7, 136.3, 135.2, 130.9, 129.9, 129.3, 128.4, 128.3, 127.7, 127.2, 126.5, 126.4, 124.3, 21.4, 18.3; **HRMS** (ESI, m/z) calcd for $C_{21}H_{20}N$ $[M+H]^+$: 286.1596 found 286.1600; **IR** (thin film): 3025, 2919, 1598, 1474, 1376, 1031, 963, 844, 816, 769, 750 and 692 cm^{-1}.

(*E*)-4-Methyl-2-(2-styrylphenyl)pyridine (3ja)



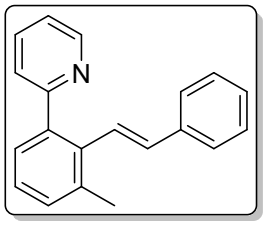
Yellow oil (46 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 5.2 Hz, 1 H), 7.77 (d, *J* = 7.2 Hz, 1 H), 7.52 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1 H), 7.44-7.34 (m, 4 H), 7.32-7.28 (m, 3 H), 7.25-7.20 (m, 2 H), 7.10 (d, *J* = 5.2 Hz, 1 H), 7.06 (d, *J* = 16.4 Hz, 1 H), 2.38 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 148.9, 146.9, 139.5, 137.4, 135.4, 129.9, 129.6, 128.4, 128.3, 127.4, 127.2, 126.4, 125.9, 125.7, 122.7, 21.2; **HRMS** (ESI, m/z) calcd for $C_{20}H_{18}N$ $[M+H]^+$: 272.1439 found 272.1400; **IR** (thin film): 3023, 2919, 1600, 1557, 1495, 1448, 1398, 1039, 963, 829, 760 and 692 cm^{-1}.

(*E*)-2-(5-Methyl-2-styrylphenyl)pyridine (3ka)



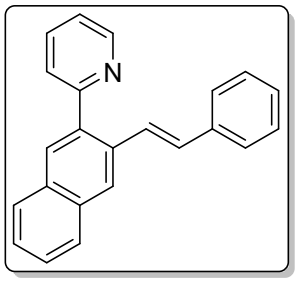
Yellow oil (39 mg, 72%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.8 Hz, 1 H), 7.72 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.39-7.36 (m, 3 H), 7.31-7.27 (m, 2 H), 7.25-7.17 (m, 4 H), 7.02 (d, *J* = 16.0 Hz, 1 H), 2.41 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 149.2, 139.1, 137.4(4), 137.4(3), 135.8, 132.6, 130.6, 129.4, 129.1, 128.4, 127.2, 127.1, 126.3, 126.0, 125.0, 121.7, 21.3; **HRMS** (ESI, m/z) calcd for $C_{20}H_{18}N$ $[M+H]^+$: 272.1439 found 272.1434; **IR** (thin film): 3023, 2921, 1585, 1565, 1498, 1463, 1426, 1151, 964, 813, 788, 750, and 692 cm^{-1}.

(*E*)-2-(3-Methyl-2-styrylphenyl)pyridine (3ka')



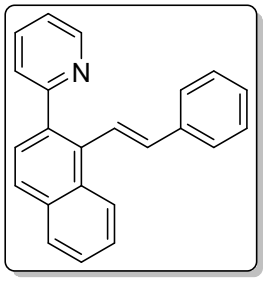
Yellow oil (8 mg, 15%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.8 Hz, 1 H), 7.63 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.41-7.36 (m, 2 H), 7.28-7.25 (m, 6 H), 7.22-7.16 (m, 2 H), 7.10 (d, *J* = 16.4 Hz, 1 H), 6.26 (d, *J* = 16.4 Hz, 1 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.7, 148.7, 139.6, 137.3, 136.7, 135.9, 135.6, 134.9, 130.5, 128.4, 127.9, 127.4, 126.9, 126.5, 126.1, 125.3, 121.4, 21.3; **HRMS** (ESI, m/z) calcd for $C_{20}H_{18}N$ $[M+H]^+$: 272.1439 found 272.1428; **IR** (thin film): 3056, 2921, 2855, 1585, 1563, 1495, 1459, 1427, 1150, 969, 802, 772, 755 and 693 cm^{-1}.

(*E*)-2-(3-Styrylnaphthalen-2-yl)pyridine (3la)



Yellow oil (38 mg, 62%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.8 Hz, 1 H), 8.19 (s, 1 H), 8.03 (s, 1 H), 7.88 (dd, *J* = 12.0 Hz, *J* = 7.6 Hz, 2 H), 7.74 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.52-7.46 (m, 2 H), 7.44-7.42 (m, 2 H), 7.35 (d, *J* = 10.8 Hz, 1 H), 7.33-7.27 (m, 3 H), 7.25-7.22 (m, 1 H), 7.17 (d, *J* = 16.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.6, 149.3, 137.8, 137.4, 135.9, 133.9, 133.1, 132.6, 130.1, 129.4, 128.5, 127.9, 127.7, 127.6, 127.4, 126.5, 126.4, 126.0, 125.2, 124.9, 121.8; **HRMS** (ESI, m/z) calcd for $C_{23}H_{18}N$ $[M+H]^+$: 308.1439 found 308.1432; **IR** (thin film): 3054, 2924, 1584, 1563, 1495, 1474, 1452, 1425, 1274, 1150, 960, 893, 786, 745 and 692 cm^{-1}.

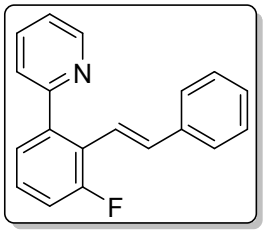
(*E*)-2-(1-Styrylnaphthalen-2-yl)pyridine (3la')



Yellow oil (12 mg, 20%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 1 H), 8.33-8.30 (m, 1 H), 7.90-7.86 (m, 2 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 7.64 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.53-7.45 (m, 4 H), 7.39-7.31 (m, 4 H), 7.27-7.25 (m, 1 H), 7.19 (ddd, *J* = 7.2 Hz, *J* = 5.2 Hz, *J* = 0.8 Hz, 1 H), 6.62 (d, *J* = 16.8 Hz, 1 H); **^{13}C NMR** (100

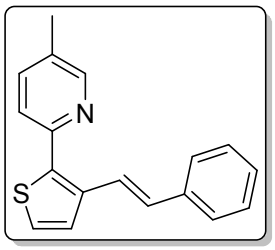
MHz, $CDCl_3$): δ 159.6, 149.3, 137.2, 136.7, 136.4, 135.5, 133.7, 133.4, 131.8, 128.5, 128.2, 127.6, 127.4(8), 127.4(7), 126.2, 126.1, 126.0, 125.9, 125.8, 125.6, 121.4; **HRMS** (ESI, m/z) calcd for $C_{23}H_{18}N$ $[M+H]^+$: 308.1439 found 308.1433; **IR** (thin film): 3055, 2929, 1585, 1567, 1475, 1433, 1376, 1250, 1150, 990, 969, 823, 792, 770, 748 and 693 cm^{-1}.

(*E*)-2-(3-Fluoro-2-styrylphenyl)pyridine (3ma)



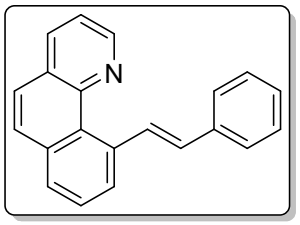
Pale yellow oil (50 mg, 91%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.72 (d, J = 4.8 Hz, 1 H), 7.69 (td, J = 7.6 Hz, J = 1.6 Hz, 1 H), 7.42 (d, J = 8.0 Hz, 1 H), 7.33-7.30 (m, 3 H), 7.29-7.25 (m, 4 H), 7.22-7.14 (m, 2 H), 7.10 (d, J = 16.8 Hz, 1 H), 6.93 (d, J = 16.8 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.7 (d, $J_{C\text{-}F}$ = 247.3 Hz), 157.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 149.3, 141.8 (d, $J_{C\text{-}F}$ = 3.5 Hz), 137.4, 135.9, 134.8 (d, $J_{C\text{-}F}$ = 11.3 Hz), 128.4, 127.8 (d, $J_{C\text{-}F}$ = 9.4 Hz), 127.6, 126.3, 125.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 124.9, 123.6 (d, $J_{C\text{-}F}$ = 12.4 Hz), 122.0, 120.9, 115.8 (d, $J_{C\text{-}F}$ = 23.4 Hz); **HRMS** (ESI, m/z) calcd for $C_{19}H_{15}FN$ $[M+H]^+$: 276.1189 found 276.1133; **IR** (thin film): 3053, 2965, 1585, 1562, 1452, 1425, 1242, 1213, 991, 968, 917, 803, 775, 752 and 691 cm^{-1}.

(*E*)-5-Methyl-2-(3-styrylthiophen-2-yl)pyridine (3na)



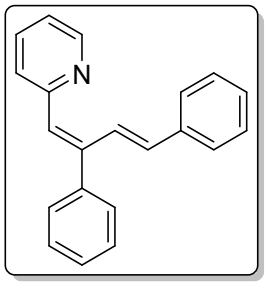
Yellow oil (47 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.52 (s, 1 H), 7.55-7.51 (m, 2 H), 7.48-7.43 (m, 3 H), 7.39 (d, *J* = 5.2 Hz, 1 H), 7.36-7.31 (m, 3 H), 7.26-7.23 (m, 1 H), 7.04 (d, *J* = 16.4 Hz, 1 H), 2.36 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.0(4), 150.0(1), 139.4, 137.3, 136.9, 136.1, 131.3, 130.2, 128.5, 127.3, 126.5, 126.3, 125.6, 122.5, 122.4, 18.3; **HRMS** (ESI, m/z) calcd for $C_{18}H_{16}NS$ $[M+H]^+$: 278.1003 found 278.0942; **IR** (thin film): 3026, 2920, 1596, 1562, 1479, 1373, 1230, 1028, 960, 831, 759 and 692 cm^{-1}.

(*E*)-10-Styrylbenzo[*h*]quinoline (3oa)



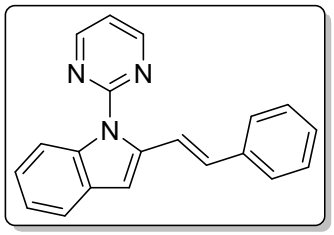
Off-white solid (50 mg, 89%); m.p. 83-85 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.15 (d, *J* = 16.0 Hz, 1 H), 9.06 (dd, *J* = 4.4 Hz, *J* = 2.0 Hz, 1 H), 8.13 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1 H), 7.93 (d, *J* = 7.2 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.82-7.75 (m, 3 H), 7.71-7.64 (m, 2 H), 7.48-7.45 (m, 3 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 7.00 (d, *J* = 16.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.8, 147.6, 138.6, 138.3, 135.3, 134.7, 134.5, 128.6, 128.4, 128.3, 128.0, 127.9, 127.5, 127.4, 127.3, 126.8, 126.6, 125.5, 120.6; **HRMS** (ESI, m/z) calcd for $C_{21}H_{16}N$ $[M+H]^+$: 282.1283 found 282.1214; **IR** (thin film): 3049, 2947, 1587, 1566, 1493, 1447, 1417, 1394, 1325, 1125, 951, 833, 761, 726 and 692 cm^{-1}.

2-((1*E*,3*E*)-2,4-Diphenylbuta-1,3-dien-1-yl)pyridine (3pa)



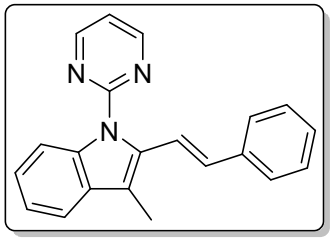
Brown oil (33 mg, 58%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.8 Hz, 1 H), 8.37 (d, *J* = 16.4 Hz, 1 H), 7.66 (td, *J* = 8.0 Hz, *J* = 2.0 Hz, 1 H), 7.48-7.46 (m, 2 H), 7.43-7.37 (m, 5 H), 7.33-7.29 (m, 3 H), 7.24-7.20 (m, 1 H), 7.14 (ddd, *J* = 7.2 Hz, *J* = 4.8 Hz, *J* = 0.8 Hz, 1 H), 6.58 (d, *J* = 16.4 Hz, 1 H), 6.54 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.4, 149.3, 144.5, 141.7, 137.4, 135.9, 135.7, 129.2, 129.1, 128.4, 128.0, 127.7, 127.5, 127.3, 126.8, 125.2, 121.1; **HRMS** (ESI, m/z) calcd for $C_{21}H_{18}N$ $[M+H]^+$: 284.1439 found 284.1446; **IR** (thin film): 3057, 3024, 2924, 1582, 1552, 1490, 1469, 1447, 1424, 1200, 1151, 1026, 971, 894, 870, 763, 742 and 694 cm^{-1}.

(*E*)-1-(Pyrimidin-2-yl)-2-styryl-1*H*-indole (3qa)



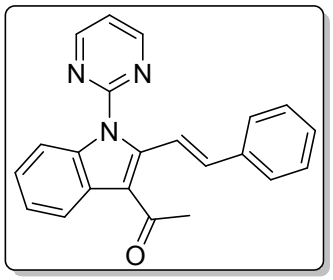
Red oil (54 mg, 91%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 4.8 Hz, 2 H), 8.32 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 16.4 Hz, 1 H), 7.63 (d, *J* = 6.8 Hz, 1 H), 7.51 (d, *J* = 7.6 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 2 H), 7.31-7.22 (m, 3 H), 7.19-7.12 (m, 2 H), 7.03 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 157.8, 138.6, 137.2, 137.1, 129.4, 129.2, 128.4, 127.4, 126.4, 123.3, 122.1, 120.5, 120.2, 117.1, 113.8, 105.1; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}N_3$ $[M+H]^+$: 298.1344 found 298.1340; **IR** (thin film): 3043, 2927, 1562, 1450, 1423, 1347, 1207, 1149, 954, 803, 749, 713 and 693 cm^{-1}.

(*E*)-3-Methyl-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (3ra)



White solid (52 mg, 84%); m.p. 119-121 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.8 Hz, 2 H), 8.31 (d, *J* = 8.0 Hz, 1 H), 7.61 (d, *J* = 7.2 Hz, 1 H), 7.55-7.50 (m, 3 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.34-7.25 (m, 3 H), 7.09 (t, *J* = 4.8 Hz, 1 H), 6.79 (d, *J* = 16.4 Hz, 1 H), 2.54 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 157.9, 137.6, 136.3, 133.7, 131.1, 130.6, 128.4, 127.3, 126.2, 123.8, 121.7, 120.6, 118.6, 116.7, 115.5, 113.5, 10.8; **HRMS** (ESI, m/z) calcd for $C_{21}H_{18}N_3$ $[M+H]^+$: 312.1501 found 312.1489; **IR** (thin film): 3043, 2917, 1573, 1560, 1455, 1424, 1344, 1200, 1152, 1074, 1018, 954, 805, 748 and 693 cm^{-1}.

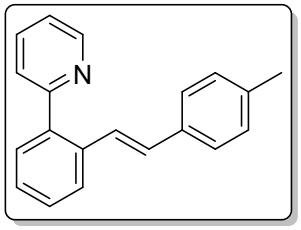
(*E*)-1-(1-(Pyrimidin-2-yl)-2-styryl-1*H*-indol-3-yl)ethan-1-one (3sa)



Pale yellow solid (64 mg, 94%); m.p. 143-145 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 4.8 Hz, 2 H), 8.25-8.22 (m, 1 H), 7.97-7.94 (m, 1 H), 7.81 (d, *J* = 16.4 Hz, 1 H), 7.41 (d, *J* = 7.2 Hz, 2 H), 7.35-7.27 (m, 5 H), 7.22 (t, *J* = 4.8 Hz, 1 H), 6.50 (d, *J* = 16.4 Hz, 1 H), 2.62 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.2, 158.3, 157.4, 142.2, 138.0, 136.4, 136.0, 128.5, 128.4, 127.0, 126.6, 124.3, 123.4, 121.4, 119.3, 119.1,

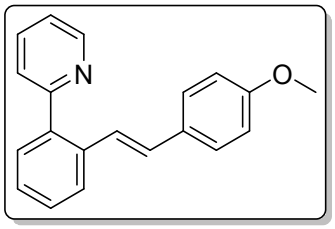
118.7, 112.6, 31.4; **HRMS** (ESI, m/z) calcd for $C_{22}H_{18}N_3O$ $[M+H]^+$: 340.1450 found 340.1448; **IR** (thin film): 3057, 2926, 1647, 1565, 1454, 1418, 1381, 1342, 1190, 1067, 967, 814, 751 and 698 cm^{-1}.

(*E*)-2-(2-(4-Methylstyryl)phenyl)pyridine (3ab)



Yellow oil (50 mg, 93%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.2 Hz, 1 H), 7.75-7.69 (m, 2 H), 7.54 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.45-7.33 (m, 3 H), 7.29-7.24 (m, 3 H), 7.17 (d, *J* = 16.0 Hz, 1 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 7.02 (d, *J* = 16.0 Hz, 1 H), 2.32 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.7, 149.3, 139.3, 137.3, 135.8, 135.7, 134.6, 130.0, 129.9, 129.2, 128.5, 127.3, 126.3(9), 126.3(6), 126.0, 124.9, 121.7, 21.4; **HRMS** (ESI, m/z) calcd for $C_{20}H_{18}N$ $[M+H]^+$: 272.1439 found 272.1448; **IR** (thin film): 3056, 3024, 2920, 2852, 1583, 1513, 1460, 1424, 1297, 1150, 1022, 964, 805, 752 and 692 cm^{-1}.

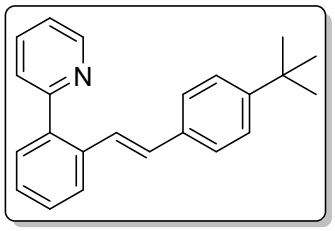
(*E*)-2-(2-(4-Methoxystyryl)phenyl)pyridine (3ac)



Yellow oil (53 mg, 92%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.8 Hz, 1 H), 7.74-7.68 (m, 2 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.45-7.34 (m, 3 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.26-7.23 (m, 1 H), 7.10 (d, *J* = 16.0 Hz, 1 H), 7.00 (d, *J* = 16.4 Hz, 1 H), 6.83 (d,

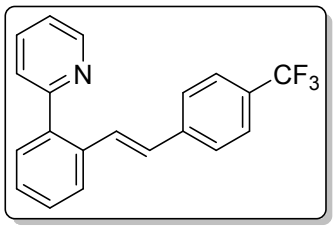
J = 8.8 Hz, 2 H), 3.77 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.9, 158.6, 149.2, 139.0, 135.7, 135.6, 130.1, 130.0, 129.3, 128.4, 127.6, 127.1, 125.8, 125.1, 124.8, 121.6, 113.8, 55.2; **HRMS** (ESI, m/z) calcd for $C_{20}H_{18}N$ $[M+H]^+$: 288.1388 found 288.1391; **IR** (thin film): 3056, 3003, 2931, 2835, 1604, 1583, 1511, 1461, 1441, 1424, 1302, 1286, 1250, 1175, 1032, 963, 820, 752 and 692 cm^{-1}.

(*E*)-2-(2-(4-(*tert*-Butyl)styryl)phenyl)pyridine (3ad)



Yellow oil (50 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.8 Hz, 1 H), 7.79 (d, *J* = 7.6 Hz, 1 H), 7.72 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.60 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.45-7.38 (m, 6 H), 7.29-7.24 (m, 2 H), 7.09 (d, *J* = 16.0 Hz, 1 H), 1.35 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 150.4, 149.2, 139.2, 135.7, 135.6, 134.5, 129.9, 129.6, 128.4, 127.3, 126.5, 126.1, 126.0, 125.3, 124.9, 121.6, 34.6, 31.3; **HRMS** (ESI, m/z) calcd for $C_{23}H_{24}N$ $[M+H]^+$: 314.1909 found 314.1899; **IR** (thin film): 3056, 2962, 2907, 2867, 1584, 1515, 1461, 1424, 1364, 1151, 1109, 1023, 965, 818, 796, 750 and 693 cm^{-1}.

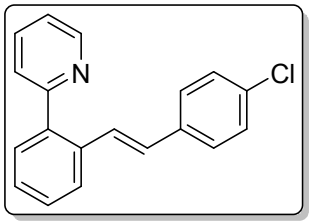
(*E*)-2-(2-(4-(Trifluoromethyl)styryl)phenyl)pyridine (3ae)



Yellow oil (50 mg, 76%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.8 Hz, 1 H), 7.77-7.72 (m, 2 H), 7.56-7.52 (m, 3 H), 7.46-7.38 (m, 5 H), 7.33 (d, *J* = 16.0 Hz, 1 H), 7.28 (ddd, *J* = 7.2 Hz, *J* = 4.8 Hz, *J* = 0.8 Hz, 1 H), 7.06 (d, *J* = 16.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 149.3, 140.8 (d, J_{C-F} = 1.4 Hz), 139.7, 136.0, 134.9,

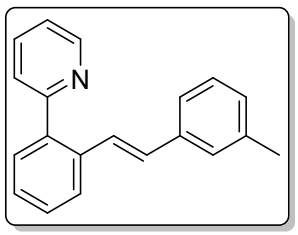
130.1, 130.0, 128.8, 128.6, 128.2, 128.1, 126.5, 126.2, 125.4 (q, J_{C-F} = 3.8 Hz), 124.8, 122.7, 121.9; **HRMS** (ESI, m/z) calcd for $C_{20}H_{15}F_3N$ $[M+H]^+$: 326.1157 found 326.1138; **IR** (thin film): 3062, 2924, 1614, 1585, 1461, 1425, 1322, 1164, 1120, 1067, 1016, 965, 862, 822, 795, 751 and 692 cm^{-1}.

(*E*)-2-(2-(4-Chlorostyryl)phenyl)pyridine (3af)



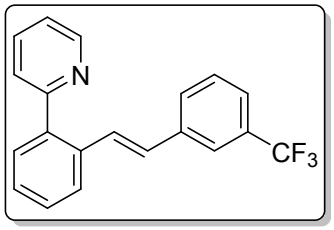
Yellow oil (52 mg, 89%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.8 Hz, 1 H), 7.74-70 (m, 2 H), 7.51 (dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 1 H), 7.42-7.33 (m, 3 H), 7.28-7.22 (m, 5 H), 7.18 (d, *J* = 16.0 Hz, 1 H), 6.97 (d, *J* = 16.4 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.6, 149.3, 139.5, 135.9(3), 135.9(0), 135.2, 132.9, 130.1, 128.6, 128.5(3), 128.5(0), 128.0, 127.7, 127.6, 126.0, 124.8, 121.8; **HRMS** (ESI, m/z) calcd for $C_{19}H_{15}ClN$ $[M+H]^+$: 292.0893 found 292.0823; **IR** (thin film): 3058, 2996, 1584, 1492, 1460, 1425, 1151, 1089, 1011, 963, 811, 795, 750 and 684 cm^{-1}.

(*E*)-2-(2-(3-Methylstyryl)phenyl)pyridine (3ag)



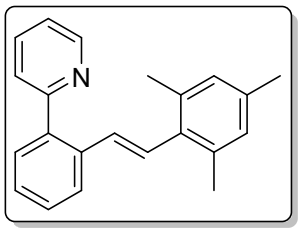
Yellow oil (46 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.8 Hz, 1 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 7.73 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.59 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.48-7.38 (m, 3 H), 7.29-7.21 (m, 5 H), 7.08-7.04 (m, 2 H), 2.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 149.2, 139.2, 137.9, 137.2, 135.7, 135.5, 129.9(9), 129.9(8), 128.4, 128.3, 128.2, 127.4, 127.2, 127.1, 126.0, 124.9, 123.4, 121.6, 21.5; **HRMS** (ESI, m/z) calcd for $C_{20}H_{18}N$ $[M+H]^+$: 272.1439 found 272.1380; **IR** (thin film): 3058, 2920, 2853, 1601, 1583, 1490, 1460, 1424, 1376, 1150, 1091, 1022, 962, 878, 781, 751 and 691 cm^{-1}.

(*E*)-2-(2-(3-(Trifluoromethyl)styryl)phenyl)pyridine (3ah)



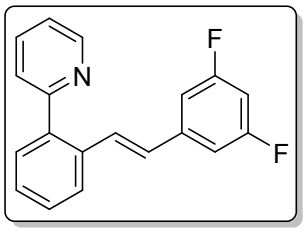
Yellow oil (46 mg, 70%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.8 Hz, 1 H), 7.76-7.72 (m, 2 H), 7.61 (s, 1 H), 7.57-7.53 (m, 2 H), 7.46-7.43 (m, 3 H), 7.42-7.37 (m, 2 H), 7.33 (d, *J* = 16.4 Hz, 1 H), 7.28 (ddd, *J* = 7.6 Hz, *J* = 4.8 Hz, *J* = 1.2 Hz, 1 H), 7.05 (d, *J* = 16.4 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 149.2, 139.6, 138.2, 136.0, 134.9, 130.9, 130.6, 130.1, 129.3, 129.2 (d, $J_{C\text{-}F}$ = 1.3 Hz), 128.8, 128.5, 128.2, 128.0, 126.2, 124.7, 123.8 (q, $J_{C\text{-}F}$ = 3.5 Hz), 123.2 (q, $J_{C\text{-}F}$ = 3.8 Hz), 121.8; **HRMS** (ESI, m/z) calcd for $C_{20}H_{15}F_3N$ $[M+H]^+$: 326.1157 found 326.1135; **IR** (thin film): 3062, 2920, 1585, 1461, 1425, 1335, 1248, 1164, 1123, 1095, 1071, 961, 898, 796, 751 and 696 cm^{-1}.

(*E*)-2-(2-(2,4,6-Trimethylstyryl)phenyl)pyridine (3ai)



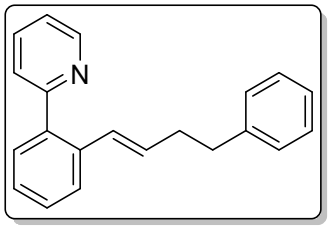
Pale yellow oil (44 mg, 74%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.8 Hz, 1 H), 7.82 (d, *J* = 7.6 Hz, 1 H), 7.70 (td, *J* = 8.0 Hz, *J* = 2.0 Hz, 1 H), 7.55-7.52 (m, 1 H), 7.48-7.43 (m, 2 H), 7.41-7.37 (m, 1 H), 7.24-7.21 (m, 1 H), 7.08 (d, *J* = 16.4 Hz, 1 H), 6.88 (s, 2 H), 6.69 (d, *J* = 16.4 Hz, 1 H), 2.31 (s, 6 H), 2.28 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.7, 149.2, 139.3, 136.1, 136.0, 135.9, 135.8, 134.0, 132.1, 129.9, 128.4(4), 128.4(1), 128.1, 127.3, 125.9, 124.7, 121.6, 21.1, 21.0; **HRMS** (ESI, m/z) calcd for $C_{22}H_{22}N$ $[M+H]^+$: 300.1752 found 300.1744; **IR** (thin film): 3062, 2946, 2918, 1610, 1584, 1460, 1441, 1424, 1376, 1150, 1024, 973, 849, 795, 752 and 693 cm^{-1}.

(*E*)-2-(2-(3,5-Difluorostyryl)phenyl)pyridine (3aj)



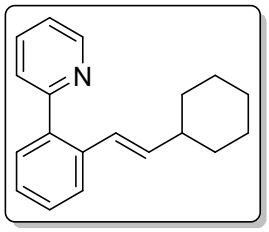
Off-white solid (42 mg, 72%); m.p. 76-78 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.74 (d, J = 4.4 Hz, 1 H), 7.77-7.71 (m, 2 H), 7.54 (dd, J = 6.8 Hz, J = 1.6 Hz, 1 H), 7.44-7.38 (m, 3 H), 7.30-7.23 (m, 2 H), 6.93 (d, J = 16.4 Hz, 1 H), 6.86 (d, J = 6.8 Hz, 2 H), 6.64 (tt, J = 9.2 Hz, J = 2.0 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.9 (d, $J_{C\text{-}F}$ = 245.2 Hz), 162.8 (d, $J_{C\text{-}F}$ = 245.1 Hz), 158.4, 149.3, 140.8 (t, $J_{C\text{-}F}$ = 9.5 Hz), 139.7, 136.1, 134.6, 130.1 (d, $J_{C\text{-}F}$ = 8.7 Hz), 128.6, 128.2, 127.5 (t, $J_{C\text{-}F}$ = 2.9 Hz), 126.2, 124.7, 121.9, 109.0 (dd, $J_{C\text{-}F}$ = 18.4 Hz, $J_{C\text{-}F}$ = 6.8 Hz), 102.5 (t, $J_{C\text{-}F}$ = 25.5 Hz); **HRMS** (ESI, m/z) calcd for $C_{19}H_{14}F_2N$ $[M+H]^+$: 294.1094 found 294.1018; **IR** (thin film): 3060, 2969, 1617, 1587, 1460, 1445, 1426, 1337, 1317, 1141, 1117, 981, 961, 870, 838, 795, 750 and 670 cm^{-1}.

(*E*)-2-(2-(4-Phenylbut-1-en-1-yl)phenyl)pyridine (3ak)



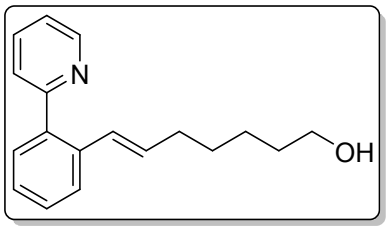
Yellow oil (45 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.70 (d, J = 4.8 Hz, 1 H), 7.64 (td, J = 7.6 Hz, J = 1.6 Hz, 1 H), 7.57 (d, J = 7.6 Hz, 1 H), 7.49 (d, J = 7.2 Hz, 1 H), 7.37-7.26 (m, 5 H), 7.23-7.18 (m, 4 H), 6.47 (d, J = 15.6 Hz, 1 H), 6.20 (dt, J = 15.6 Hz, J = 6.8 Hz, 1 H), 2.76 (t, J = 7.6 Hz, 2 H), 2.49 (q, J = 6.8 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.6, 149.1, 141.5, 138.6, 135.7, 135.6, 131.2, 129.8, 128.9, 128.3, 128.2, 128.1, 126.9, 126.1, 125.6, 124.8, 121.4, 35.7, 35.0; **HRMS** (ESI, m/z) calcd for $C_{21}H_{20}N$ $[M+H]^+$: 286.1596 found 286.1603; **IR** (thin film): 3059, 3026, 2918, 2842, 1584, 1496, 1460, 1424, 1150, 1025, 967, 795, 748 and 699 cm^{-1}.

(*E*)-2-(2-(2-Cyclohexylvinyl)phenyl)pyridine (3al)



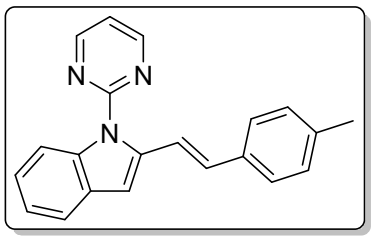
Pale yellow oil (48 mg, 91%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.8 Hz, 1 H), 7.69 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.56 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 7.2 Hz, 1 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.35-7.26 (m, 2 H), 7.24-7.20 (m, 1 H), 6.42 (d, *J* = 16.0 Hz, 1 H), 6.09 (dd, *J* = 16.0 Hz, *J* = 6.8 Hz, 1 H), 2.09-2.02 (m, 1 H), 1.74-1.62 (m, 4 H), 1.27-1.09 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.8, 149.1, 138.6, 138.1, 136.1, 135.5, 129.8, 128.2, 126.7, 126.0, 125.7, 124.8, 121.5, 41.2, 32.8, 26.2, 26.0; **HRMS** (ESI, m/z) calcd for $C_{19}H_{22}N$ $[M+H]^+$: 264.1752 found 264.1762; **IR** (thin film): 3064, 2923, 2849, 1584, 1460, 1448, 1424, 1299, 1260, 1149, 1023, 967, 893, 795, 749 and 692 cm^{-1}.

(*E*)-7-(2-(Pyridin-2-yl)phenyl)hept-6-en-1-ol (3am)



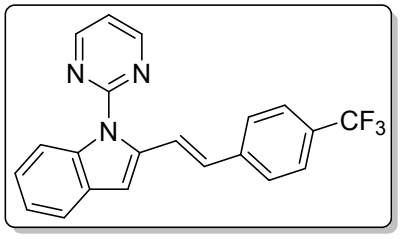
Pale yellow oil (25 mg, 47%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 4.8 Hz, 1 H), 7.73 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.56 (d, *J* = 7.2 Hz, 1 H), 7.45-7.40 (m, 2 H), 7.36-7.25 (m, 3 H), 6.41 (d, *J* = 15.6 Hz, 1 H), 6.13 (dt, *J* = 16.0 Hz, *J* = 6.8 Hz, 1 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 2.14 (q, *J* = 6.8 Hz, 2 H), 1.80 (s, OH), 1.54 (quint, *J* = 6.8 Hz, 2 H), 1.47-1.40 (m, 2 H), 1.39-1.34 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.8, 148.9, 138.3, 135.9(6), 135.9(5), 132.2, 129.8, 128.4, 128.3, 126.8, 126.1, 124.9, 121.6, 62.9, 33.1, 32.6, 29.0, 25.3; **HRMS** (ESI, m/z) calcd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1701 found 268.1692; **IR** (thin film): 3357, 2930, 2854, 1586, 1569, 1462, 1426, 1261, 1151, 1054, 1024, 967, 796 and 751 cm^{-1}.

(*E*)-2-(4-Methylstyryl)-1-(pyrimidin-2-yl)-1*H*-indole (3qb)



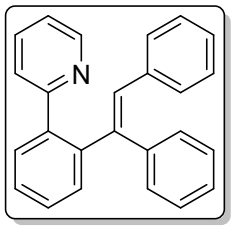
Colorless oil (55 mg, 89%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 4.8 Hz, 2 H), 8.33 (d, *J* = 8.0 Hz, 1 H), 7.68 (d, *J* = 16.4 Hz, 1 H), 7.64 (d, *J* = 7.6 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.32-7.24 (m, 2 H), 7.19-7.15 (m, 3 H), 7.11 (t, *J* = 4.8 Hz, 1 H), 7.03 (s, 1 H), 2.39 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.9, 157.7, 138.7, 137.3, 137.0, 134.4, 129.4, 129.2, 129.1, 126.3, 123.2, 122.1, 120.1, 119.4, 117.0, 113.7, 104.8, 21.3; **HRMS** (ESI, m/z) calcd for $C_{21}H_{18}N_3$ $[M+H]^+$: 312.1501 found 312.1486; **IR** (thin film): 3048, 2920, 1562, 1510, 1450, 1423, 1347, 1203, 1150, 957, 852, 806, 746 and 701 cm^{-1}.

(*E*)-1-(Pyrimidin-2-yl)-2-(4-(trifluoromethyl)styryl)-1*H*-indole (3qe)



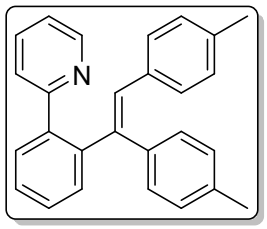
Colorless solid (57 mg, 78%); m.p. 97-99 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 4.8 Hz, 2 H), 8.35 (d, *J* = 8.4 Hz, 1 H), 7.78 (d, *J* = 16.4 Hz, 1 H), 7.62 (d, *J* = 7.6 Hz, 1 H), 7.59-7.53 (m, 4 H), 7.33-7.29 (m, 1 H), 7.26-7.23 (m, 1 H), 7.17-7.11 (m, 2 H), 7.04 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 157.7, 140.7 (d, $J_{C\text{-}F}$ = 1.3 Hz), 137.8, 137.2, 129.0, 128.8 (d, $J_{C\text{-}F}$ = 32.3 Hz), 127.5, 126.4, 125.4, 125.3 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.8, 123.0, 122.3, 120.4, 117.1, 114.0, 105.9; **HRMS** (ESI, m/z) calcd for $C_{21}H_{15}F_3N_3$ $[M+H]^+$: 366.1218 found 366.1209; **IR** (thin film): 3047, 2930, 1612, 1574, 1563, 1450, 1425, 1347, 1322, 1163, 1109, 1066, 1015, 947, 861, 820, 806 and 747 cm^{-1}.

(*E*)-2-(2-(1,2-Diphenylvinyl)phenyl)pyridine (3an)



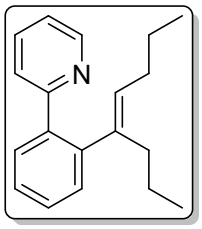
Yellow oil (55 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 4.8 Hz, 1 H), 7.74 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.49 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.40 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1 H), 7.38-7.37 (m, 2 H), 7.30 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.23-7.12 (m, 8 H), 7.01-6.94 (m, 3 H), 6.91 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.9, 148.8, 142.5, 141.5, 140.4, 138.4, 136.9, 135.0, 131.3, 130.3, 129.0, 128.9, 128.6, 128.0, 127.8(3), 127.8(2), 127.0, 126.9, 126.7, 123.3, 121.1; **HRMS** (ESI, m/z) calcd for $C_{25}H_{20}N$ $[M+H]^+$: 334.1596 found 334.1586; **IR** (thin film): 3058, 3020, 2918, 1585, 1492, 1461, 1446, 1424, 1266, 1151, 1077, 1023, 989, 920, 876, 796, 749 and 694 cm^{-1}.

(*E*)-2-(2-(1,2-Di-*p*-tolylvinyl)phenyl)pyridine (3ao)



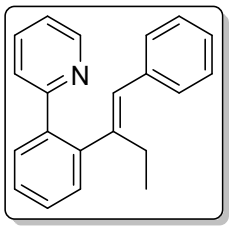
Off-white solid (62 mg, 86%); m.p. 117-119 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 4.8 Hz, 1 H), 7.74 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1 H), 7.48 (td, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.40-7.34 (m, 3 H), 7.27 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 6.98 (m, 3 H), 6.92 (d, *J* = 8.0 Hz, 2 H), 6.86-6.84 (m, 3 H), 2.26 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 148.8, 140.4, 140.3, 139.8, 138.8, 136.7, 136.4, 135.0, 134.2, 131.2, 130.3, 128.9, 128.7, 128.6, 128.5, 128.1, 127.9, 126.7, 123.3, 121.1, 21.3, 21.2; **HRMS** (ESI, m/z) calcd for $C_{27}H_{24}N$ $[M+H]^+$: 362.1909 found 362.1897; **IR** (thin film): 3048, 3021, 2919, 2859, 1585, 1512, 1460, 1424, 1185, 1021, 887, 819, 797 and 751 cm^{-1}.

(*E*)-2-(2-(Oct-4-en-4-yl)phenyl)pyridine (3ap)



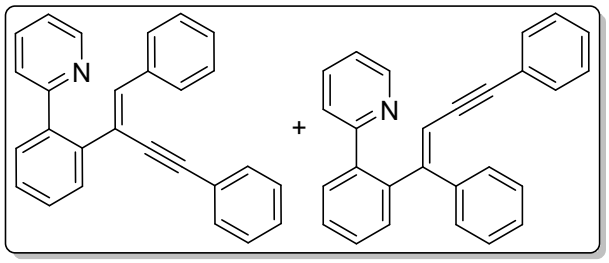
Colorless oil (42 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.8 Hz, 1 H), 7.59 (td, *J* = 8.0 Hz, *J* = 2.0 Hz, 1 H), 7.55-7.50 (m, 2 H), 7.35-7.28 (m, 2 H), 7.22-7.20 (m, 1 H), 7.18-7.15 (m, 1 H), 5.46 (t, *J* = 7.6 Hz, 1 H), 2.06 (q, *J* = 7.2 Hz, 2 H), 1.83 (t, *J* = 7.2 Hz, 2 H), 1.38 (sex, *J* = 7.2 Hz, 2 H), 1.13 (sex, *J* = 7.2 Hz, 2 H), 0.90 (t, *J* = 7.2 Hz, 3 H), 0.70 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.5, 149.1, 143.2, 141.2, 138.3, 135.2, 131.5, 130.0, 129.7, 127.9, 126.7, 124.1, 121.3, 33.5, 30.5, 22.9, 21.7, 14.1, 14.0; **HRMS** (ESI, m/z) calcd for $C_{19}H_{24}N$ $[M+H]^+$: 266.1909 found 266.1903; **IR** (thin film): 3065, 2958, 2930, 2870, 1585, 1459, 1423, 1150, 1094, 1061, 1022, 989, 896, 797 and 749 cm^{-1}.

(*E*)-2-(2-(1-Phenylbut-1-en-2-yl)phenyl)pyridine (3aq)



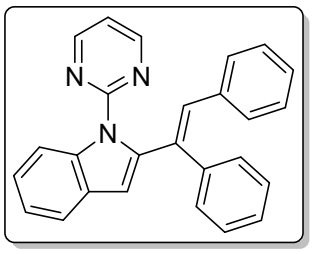
Pale yellow oil (35 mg, 61%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 4.8 Hz, 1 H), 7.64-7.57 (m, 3 H), 7.43-7.31 (m, 5 H), 7.23-7.16 (m, 4 H), 6.48 (s, 1 H), 2.19 (q, *J* = 7.6 Hz, 2 H), 0.82 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.2, 149.3, 145.5, 142.3, 138.6, 137.8, 135.5, 130.1, 129.9, 129.8, 128.4, 128.1, 128.0, 127.2, 126.3, 124.1, 121.5, 25.1, 13.1; **HRMS** (ESI, m/z) calcd for $C_{21}H_{20}N$ $[M+H]^+$: 286.1596 found 286.1590; **IR** (thin film): 3059, 3010, 2964, 2874, 1584, 1492, 1460, 1423, 1295, 1149, 1059, 1023, 989, 938, 868, 796, 749, 713 and 697 cm^{-1}.

(*E*)-2-(2-(1,4-diphenylbut-1-en-3-yn-2-yl)phenyl)pyridine (3ar)



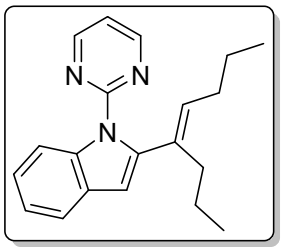
White solid; **HRMS** (ESI, m/z) calcd for $C_{27}H_{20}N$ $[M+H]^+$: 358.1596 found 358.1592.

(*E*)-2-(1,2-Diphenylvinyl)-1-(pyrimidin-2-yl)-1*H*-indole (3qn)



White solid (70 mg, 94%); 151-153 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.4 Hz, 2 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 7.2 Hz, 1 H), 7.31-7.23 (m, 2 H), 7.17-7.10 (m, 8 H), 7.03-7.02 (m, 3 H), 6.91 (s, 1 H), 6.86 (t, *J* = 4.8 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.7, 157.2, 142.4, 138.2, 137.5, 136.8, 135.1, 130.2, 129.5, 128.5, 127.7, 127.4, 127.0, 126.7, 123.6, 121.8, 120.4, 116.9, 112.6, 109.9; **HRMS** (ESI, m/z) calcd for $C_{26}H_{20}N_3$ $[M+H]^+$: 374.1657 found 374.1655; **IR** (thin film): 3051, 3023, 2927, 2851, 1562, 1493, 1452, 1425, 1347, 1258, 1151, 1028 806, 781, 745, 711 and 696 cm^{-1}.

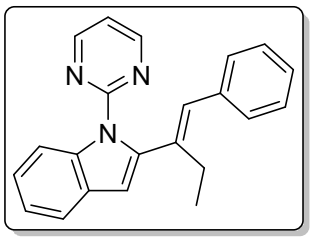
(*E*)-2-(Oct-4-en-4-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3qp)



Colorless oil (54 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.8 Hz, 2 H), 8.16 (d, *J* = 8.0 Hz, 1 H), 7.59 (d, *J* = 7.6 Hz, 1 H), 7.27-7.19 (m, 2 H), 7.10 (t, *J* = 3.2

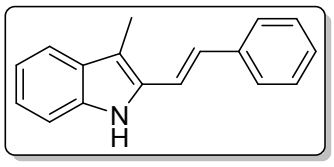
Hz, 1 H), 6.59 (s, 1 H), 5.64 (t, *J* = 7.2 Hz, 1 H), 2.20-2.14 (m, 4 H), 1.48-1.33 (m, 4 H), 0.96 (t, *J* = 7.6 Hz, 3 H), 0.85 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 157.9, 143.1, 137.1, 133.7, 130.8, 129.0, 122.7, 121.6, 119.9, 117.1, 112.8, 106.8, 33.0, 30.3, 22.8, 21.9, 14.1, 13.9; **HRMS** (ESI, m/z) calcd for $C_{20}H_{24}N_3$ $[M+H]^+$: 306.1970 found 306.1959; **IR** (thin film): 3043, 2957, 2930, 2869, 1562, 1453, 1422, 1348, 1309, 1258, 1213, 1150, 893, 805 and 744 cm^{-1}.

(*E*)-2-(1-Phenylbut-1-en-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3qq)



White solid (60 mg, 92%); m.p. 105-107 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.8 Hz, 2 H), 8.25 (d, *J* = 8.0 Hz, 1 H), 7.64 (d, *J* = 7.2 Hz, 1 H), 7.39-7.24 (m, 7 H), 7.10 (t, *J* = 3.6 Hz, 1 H), 6.76 (s, 1 H), 6.62 (s, 1 H), 2.51 (q, *J* = 7.2 Hz, 2 H), 1.07 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.0, 157.9, 142.4, 137.8, 137.5, 137.4, 129.0, 128.7, 128.5, 128.0, 126.4, 123.2, 121.9, 120.2, 117.2, 113.1, 107.8, 24.9, 13.3; **HRMS** (ESI, m/z) calcd for $C_{22}H_{20}N_3$ $[M+H]^+$: 326.1657 found 326.1653; **IR** (thin film): 3042, 2968, 2932, 1562, 1452, 1422, 1348, 1216, 1149, 1077, 1018, 919, 805, 746 and 701 cm^{-1}.

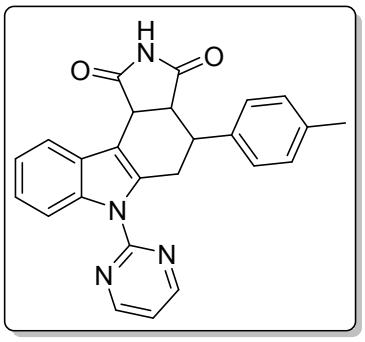
(*E*)-3-Methyl-2-styryl-1*H*-indole (4)



Yellow solid (40 mg, 86%); m.p. 110-112 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00 (s, 1 H), 7.57-7.52 (m, 3 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 7.26-7.21 (m, 2 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 6.77 (d, *J* = 16.4 Hz, 1 H), 2.42 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.0, 136.3, 132.1, 129.5, 128.6, 127.3, 126.0, 125.5, 123.0, 119.4, 118.8, 117.1, 112.5, 110.3, 8.9; **HRMS** (EI^+) calcd for $C_{17}H_{15}N$: 233.1204 found

233.1197; **IR** (thin film): 3349, 3059, 2921, 1654, 1581, 1523, 1450, 1336, 1315, 1248, 1180, 1096, 954, 753, 742 and 696 cm^{-1}.

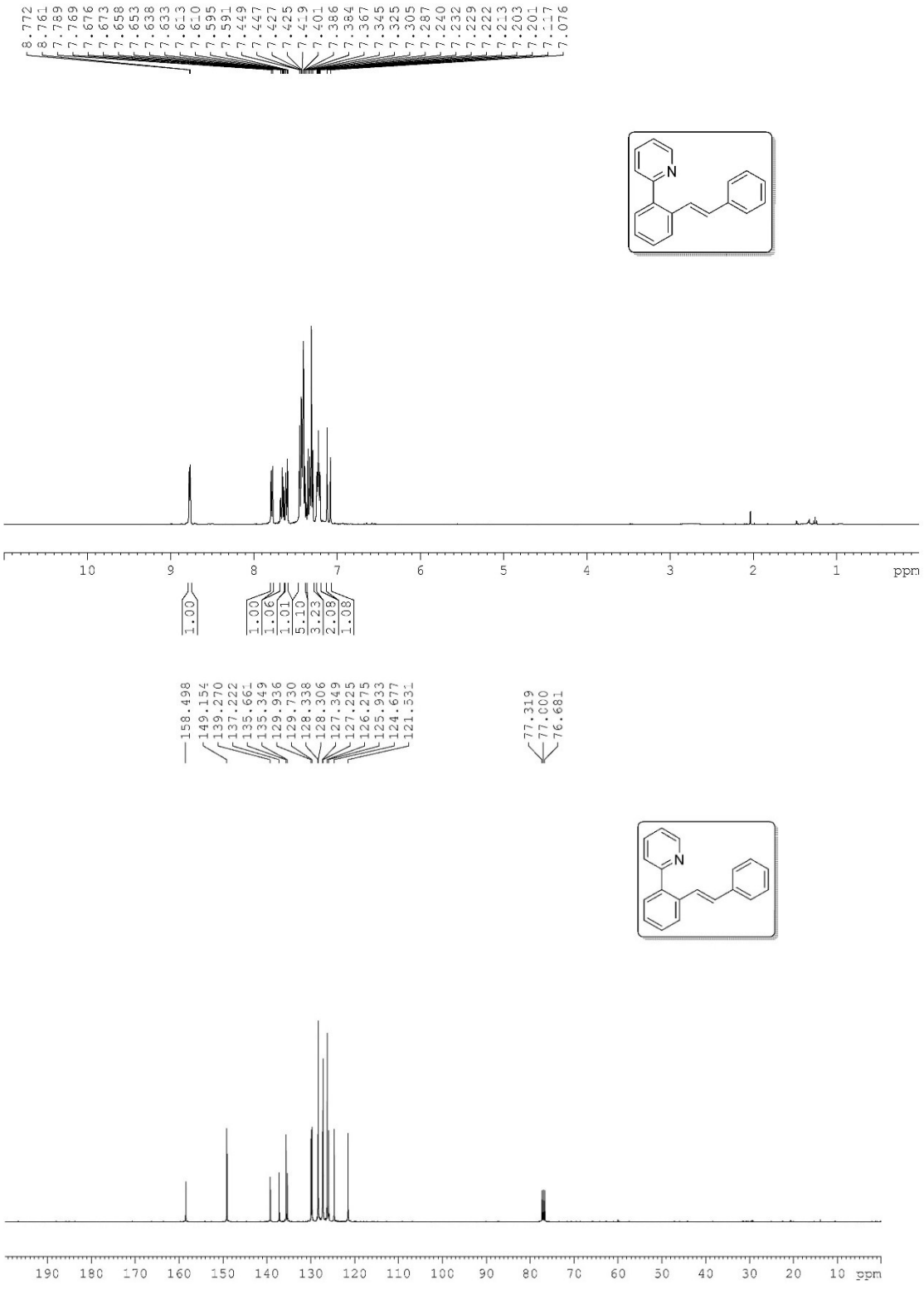
6-(Pyrimidin-2-yl)-4-(*p*-tolyl)-4,5,6,10c-tetrahydropyrrolo[3,4-c]carbazole-1,3(2*H*,3a*H*)-dione (6)



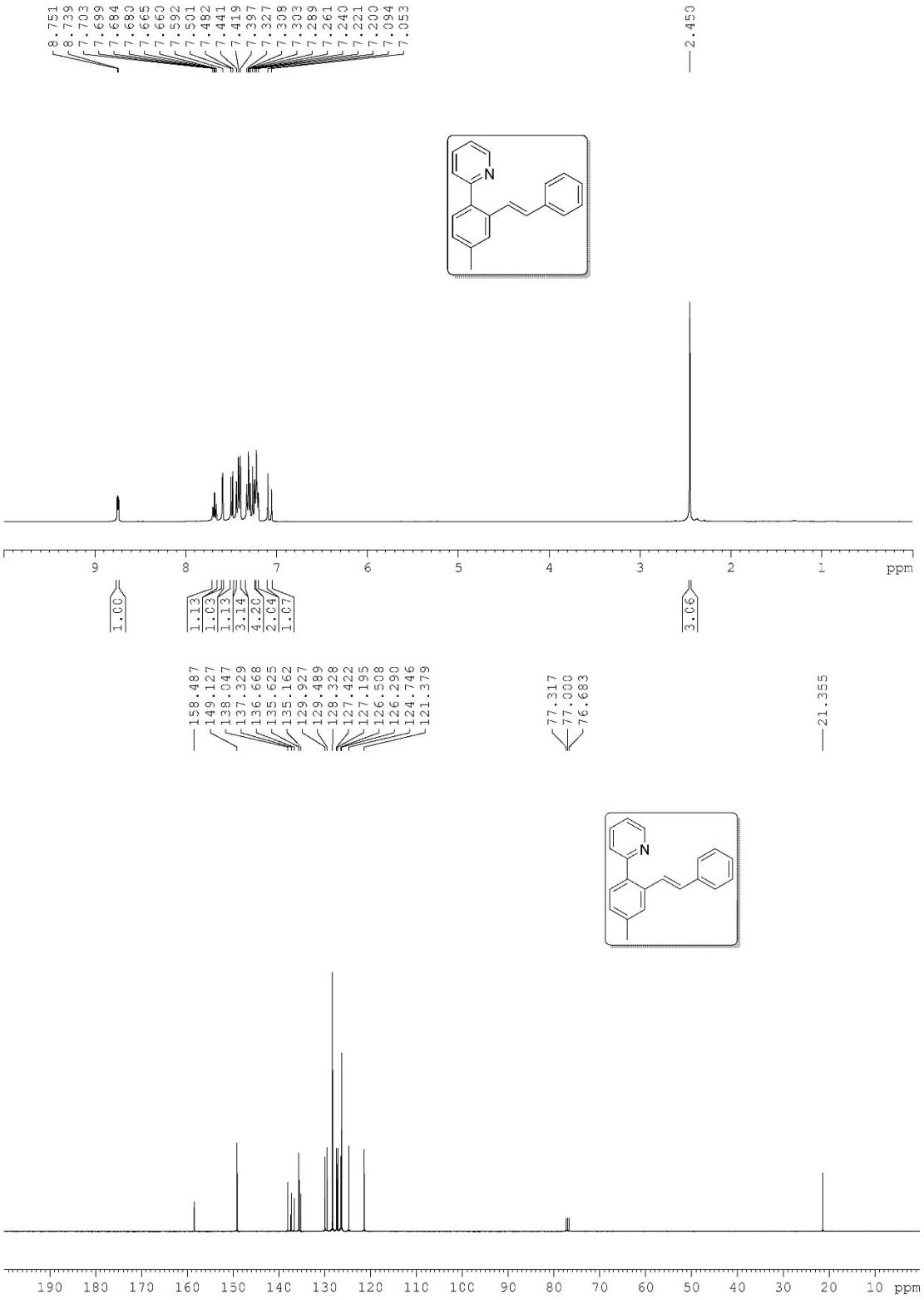
Off-white solid (148 mg, 90%); m.p. 256-258 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.92 (s, 1 H), 8.92 (d, *J* = 4.8 Hz, 2 H), 8.33-8.31 (m, 1 H), 7.88-7.86 (m, 1 H), 7.40 (t, *J* = 4.8 Hz, 1 H), 7.27-7.21 (m, 4 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 4.42 (d, *J* = 7.6 Hz, 1 H), 3.94 (dd, *J* = 7.2 Hz, *J* = 4.0 Hz, 1 H), 3.44-3.40 (m, 2 H), 2.25 (s, 3 H), One proton (1 H) is merging with DMSO-water peak; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 178.4, 177.4, 158.8, 156.9, 138.6, 136.3, 135.7, 135.2, 128.5, 127.9, 127.6, 123.0, 121.7, 120.0, 117.9, 113.9, 110.0, 45.9, 42.3, 38.5, 27.9, 20.6; **HRMS** (ESI, m/z) calcd for $C_{25}H_{20}N_4NaO_2$ $[M+Na]^+$: 431.1484 found 431.1491; **IR** (thin film): 3204, 3048, 2917, 1776, 1715, 1562, 1516, 1456, 1429, 1347, 1262, 1177, 1117, 799 and 745 cm^{-1}.

2. NMR Spectra

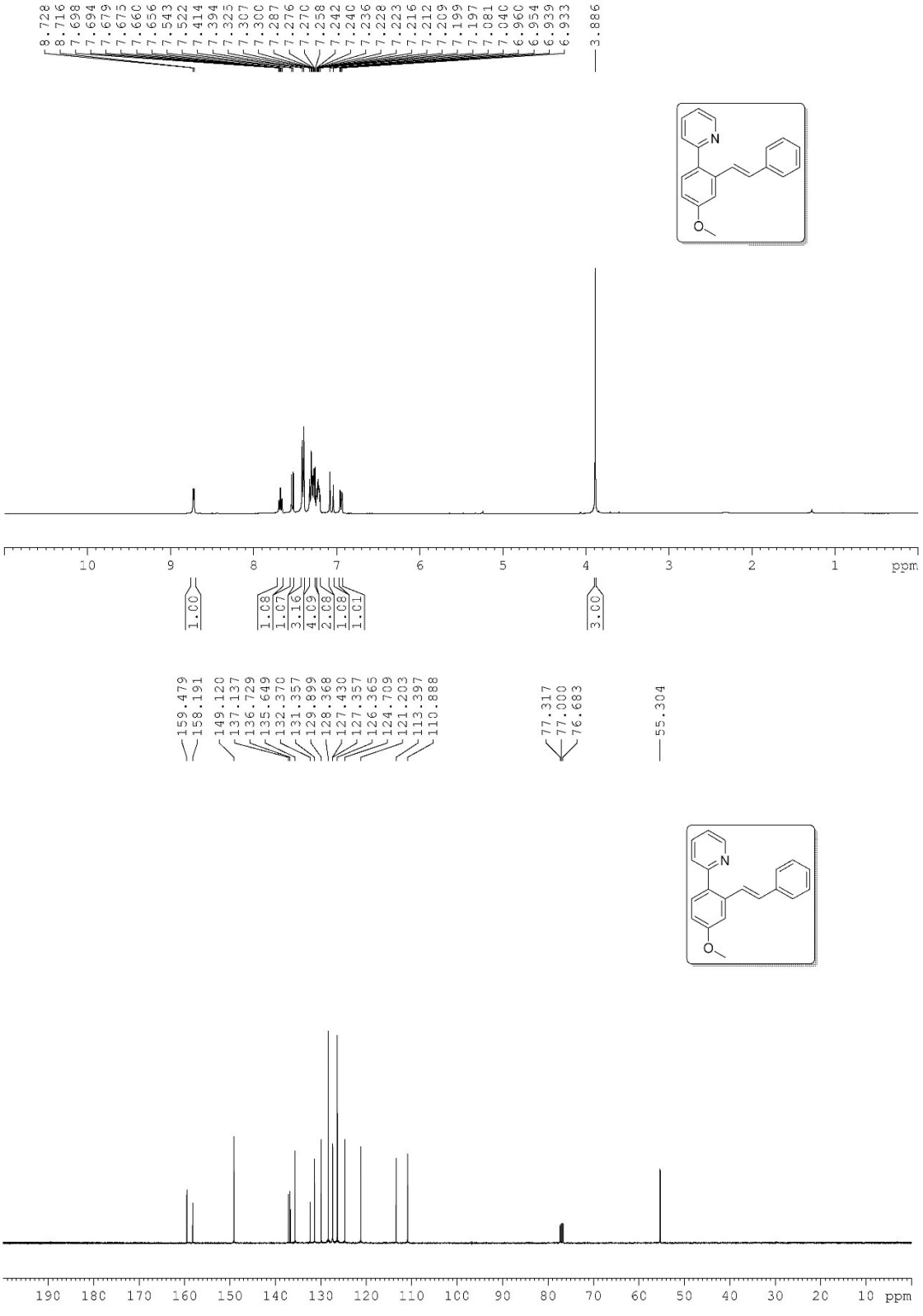
^{1}H and ^{13}C NMR spectra of compound **3aa**.



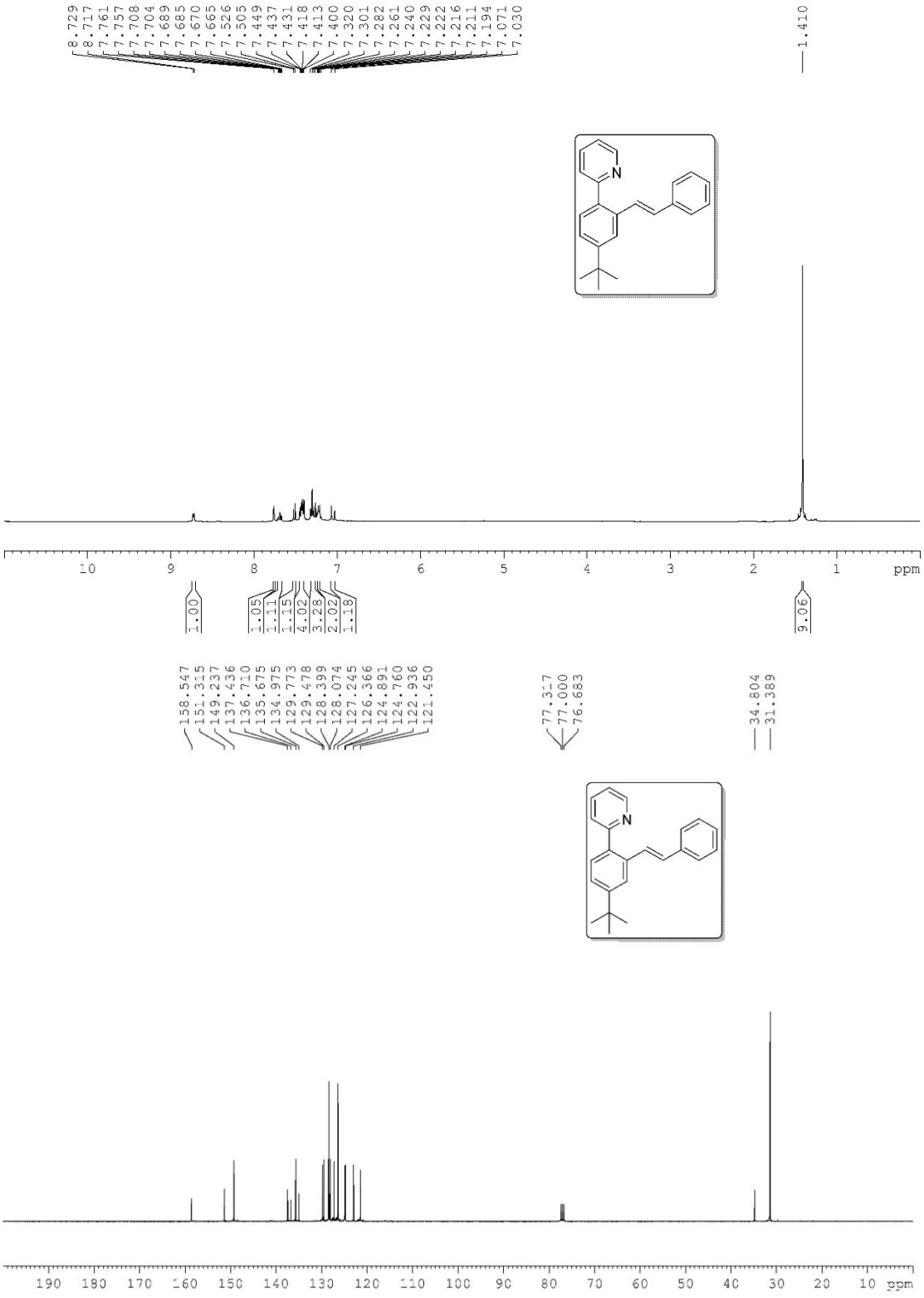
^{1}H and ^{13}C NMR spectra of compound **3ba**.



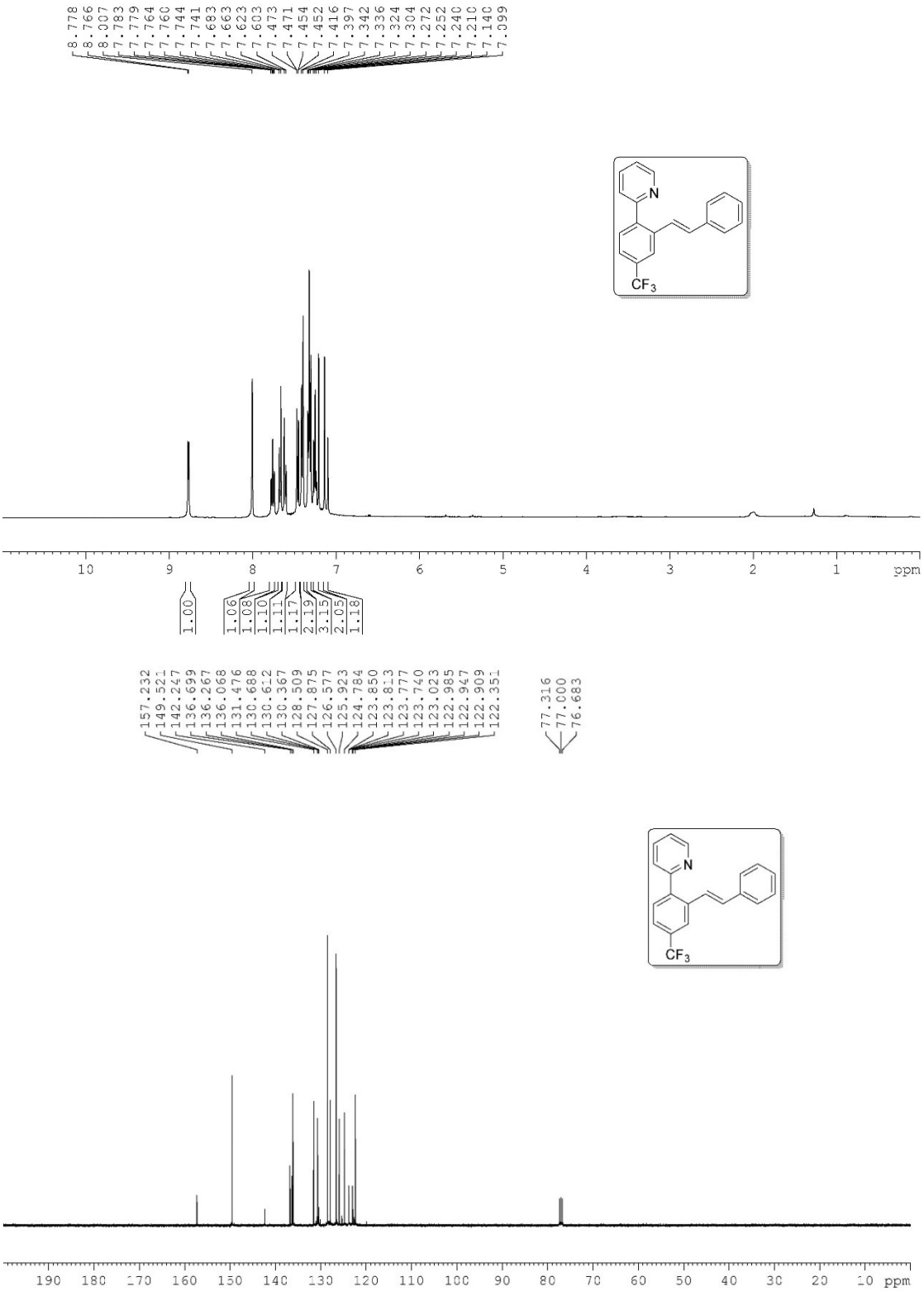
^{1}H and ^{13}C NMR spectra of compound **3ca**.



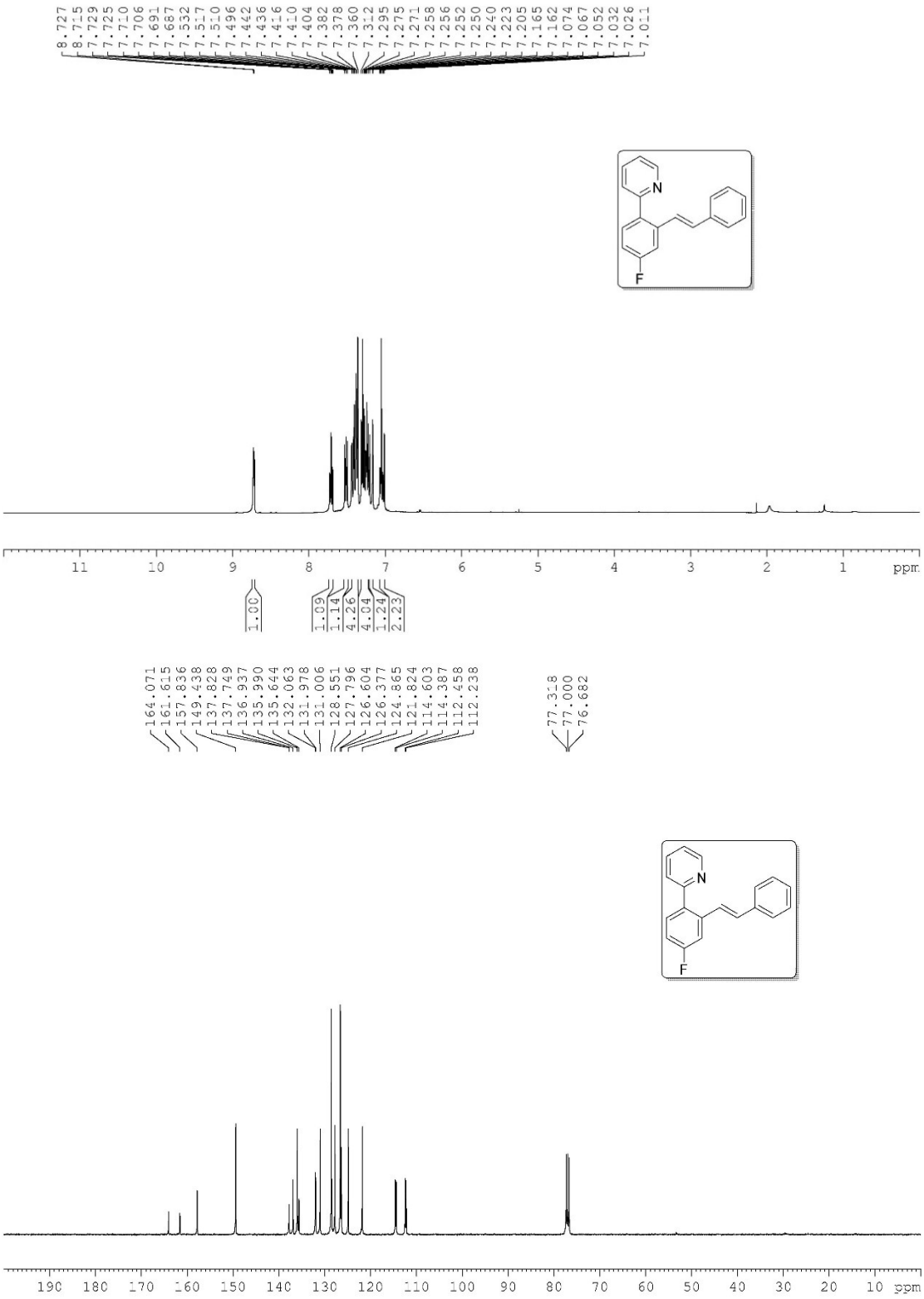
^{1}H and ^{13}C NMR spectra of compound **3da**.



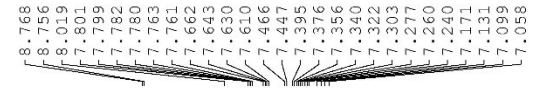
^{1}H and ^{13}C NMR spectra of compound **3ea**.

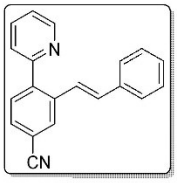


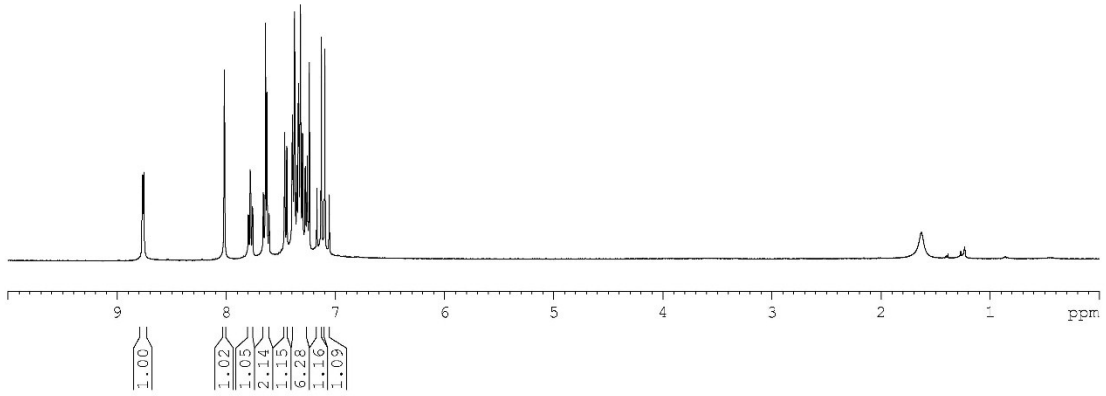
^{1}H and ^{13}C NMR spectra of compound **3fa**.

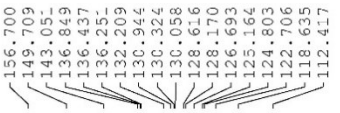


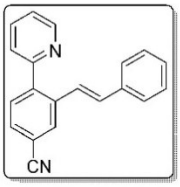
^{1}H and ^{13}C NMR spectra of compound **3ga**.

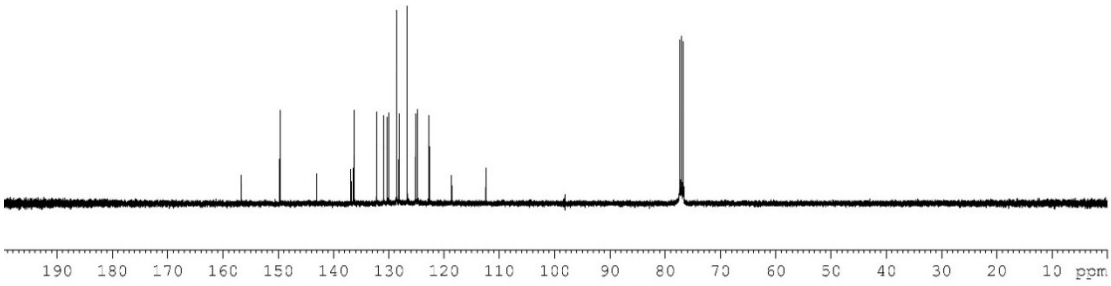




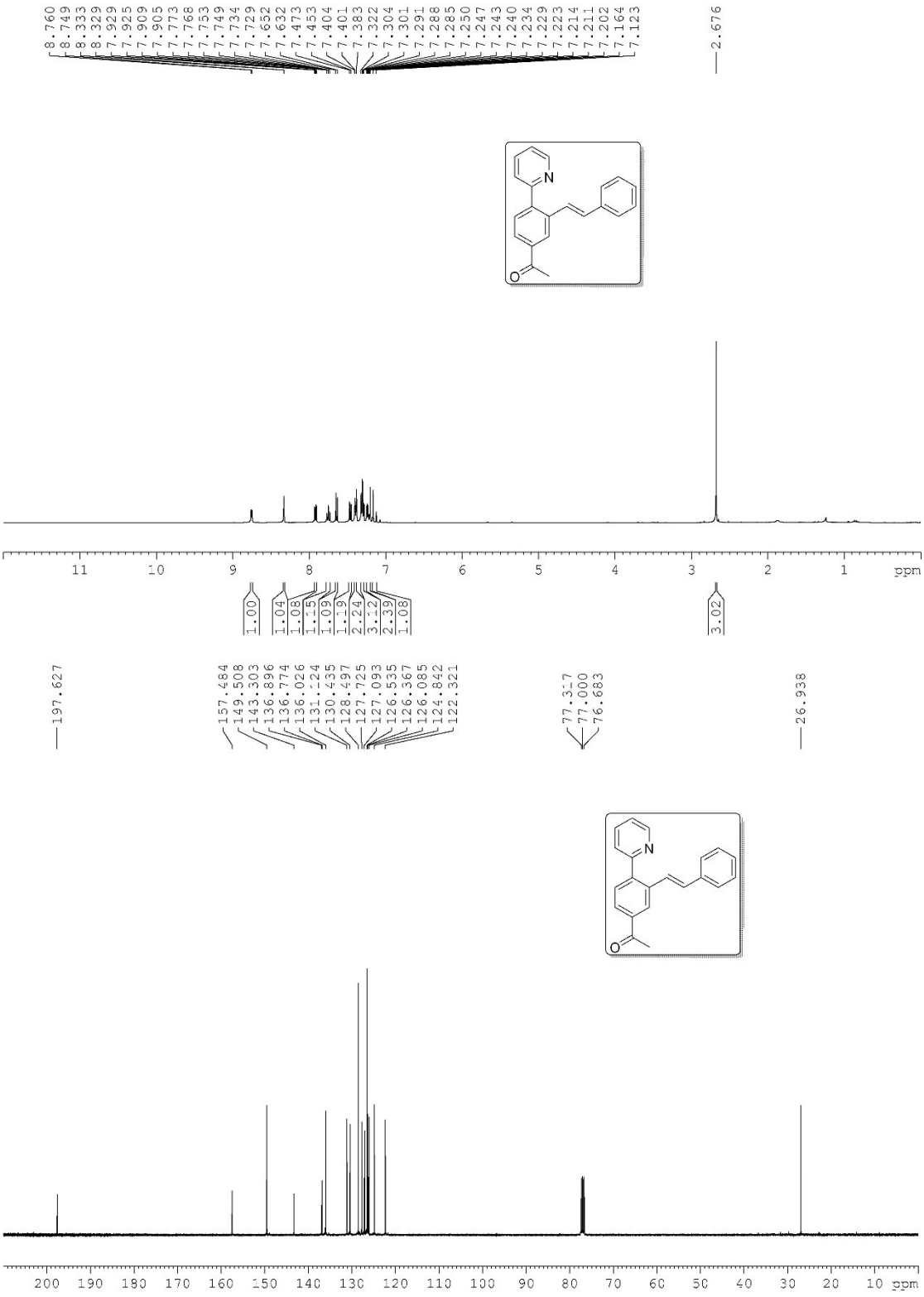




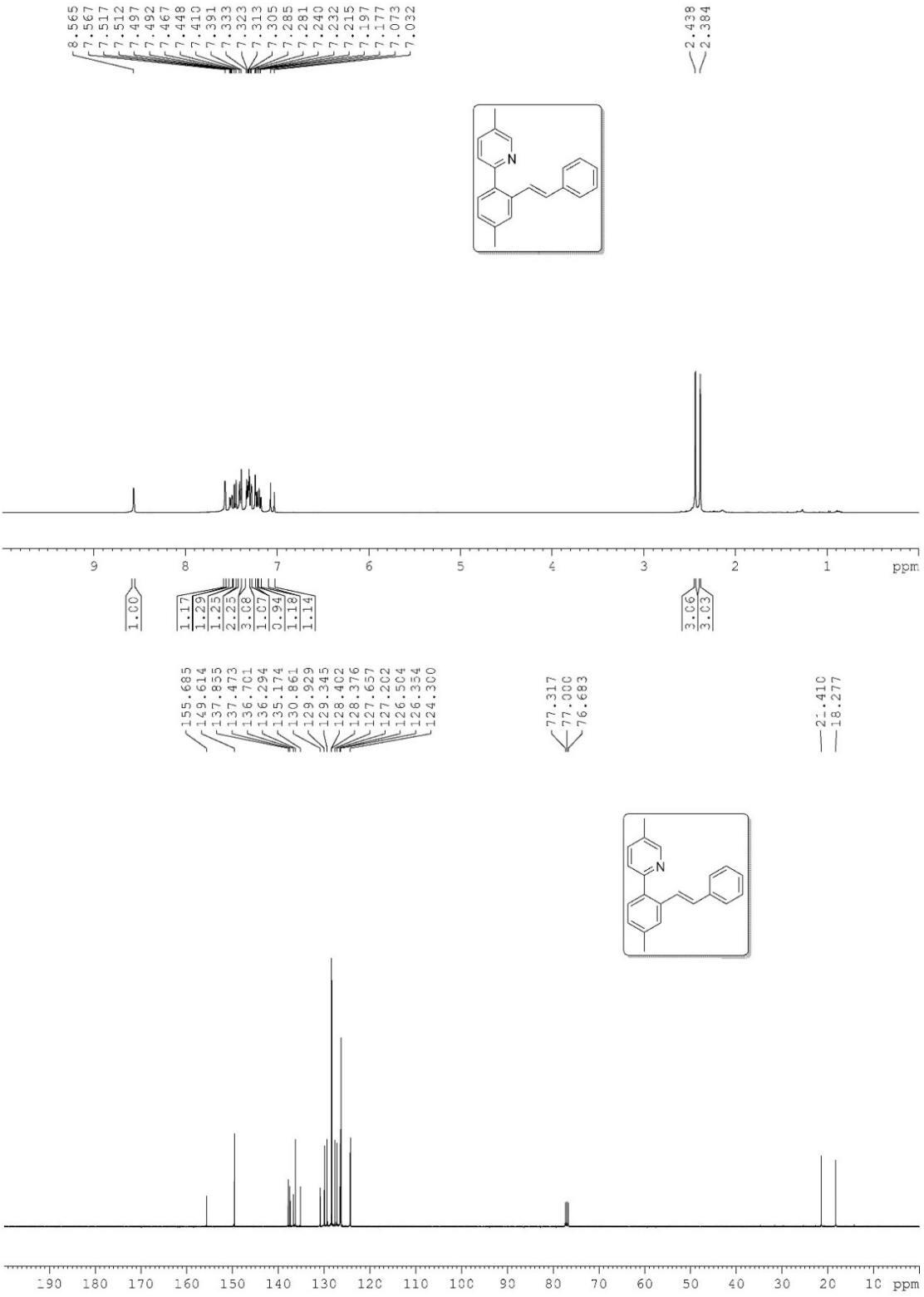




^{1}H and ^{13}C NMR spectra of compound **3ha**.

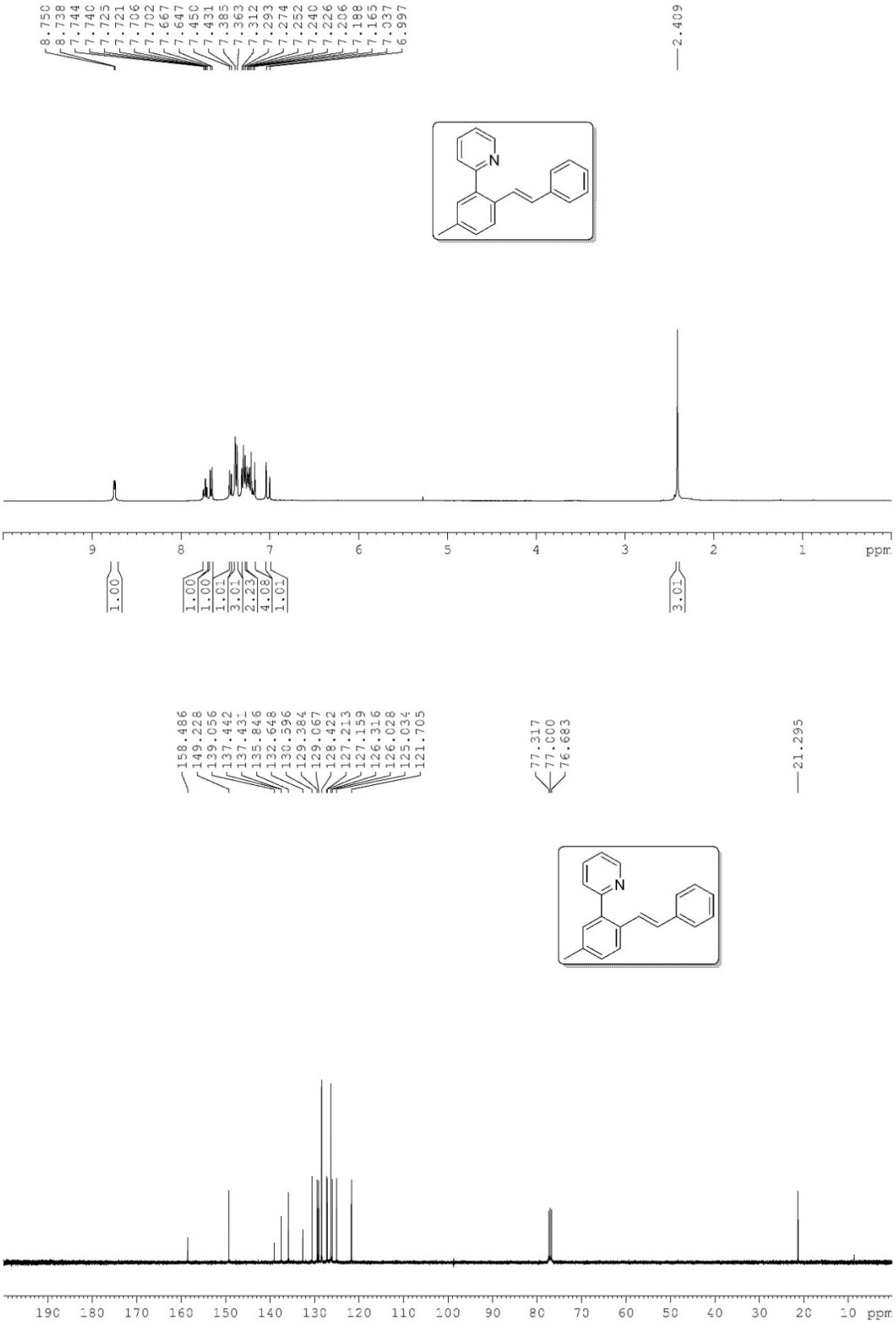


^{1}H and ^{13}C NMR spectra of compound **3ia**.

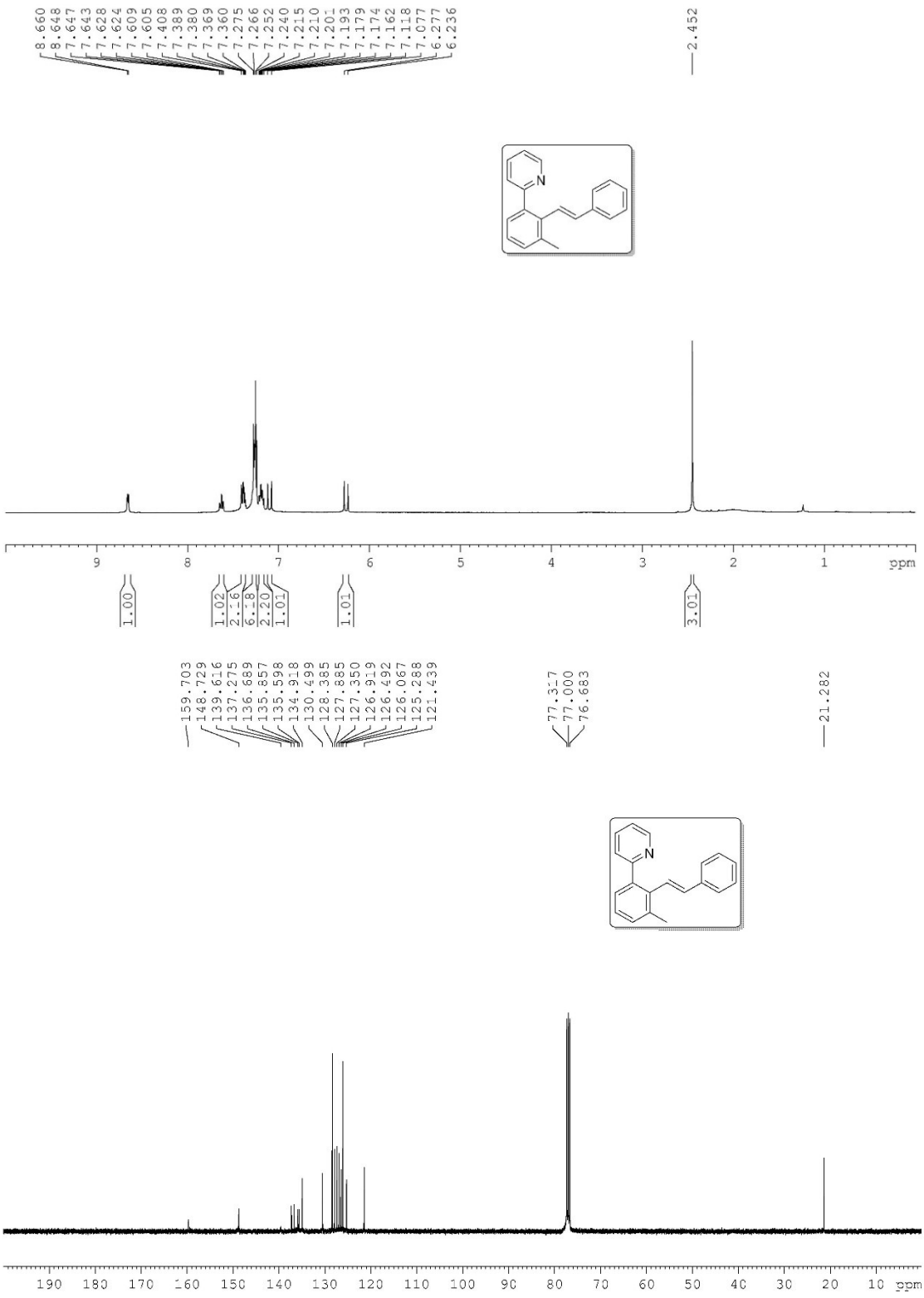


^{1}H and ^{13}C NMR spectra of compound **3ja**.

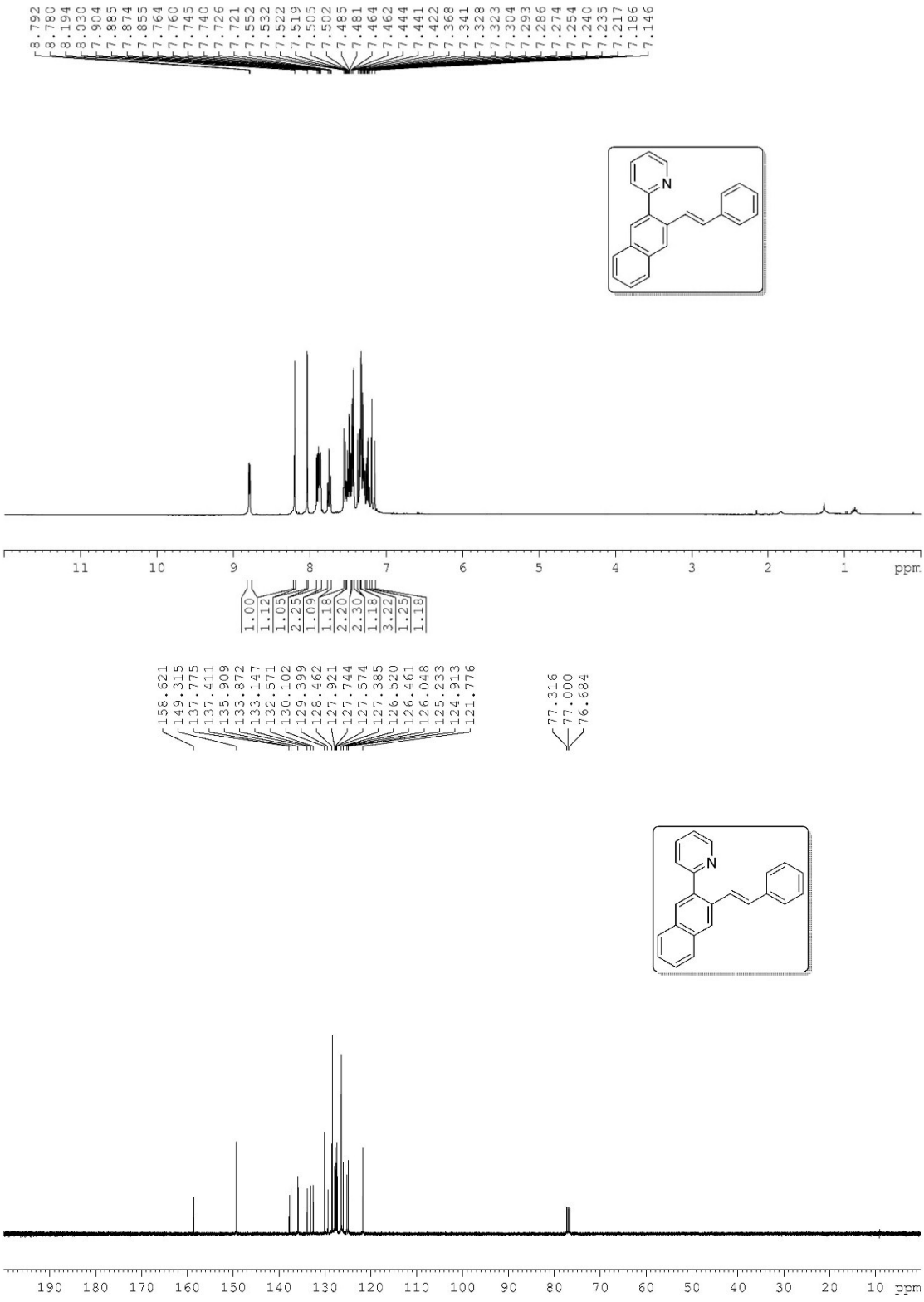
^{1}H and ^{13}C NMR spectra of compound **3ka**.



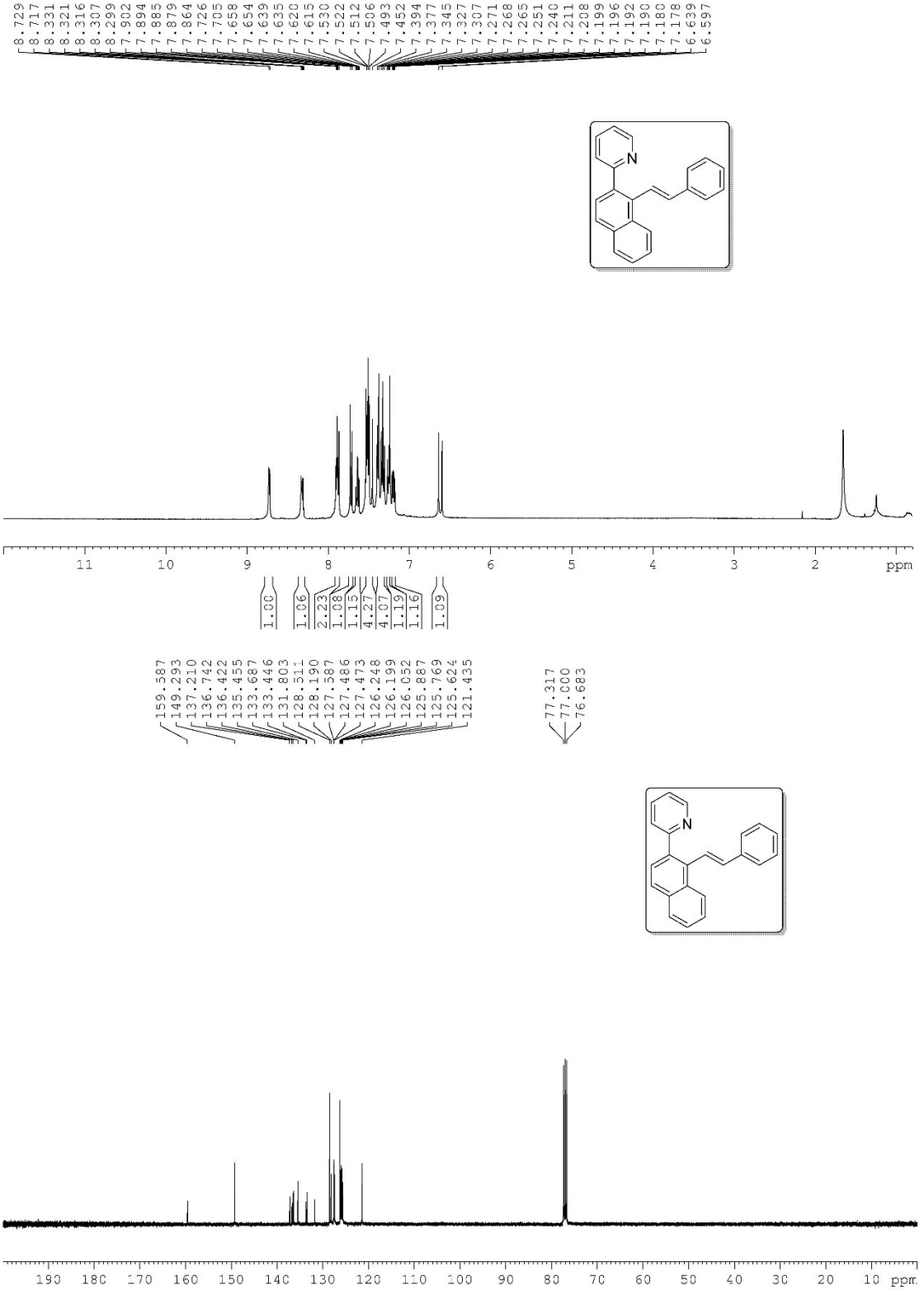
^{1}H and ^{13}C NMR spectra of compound **3ka'**.



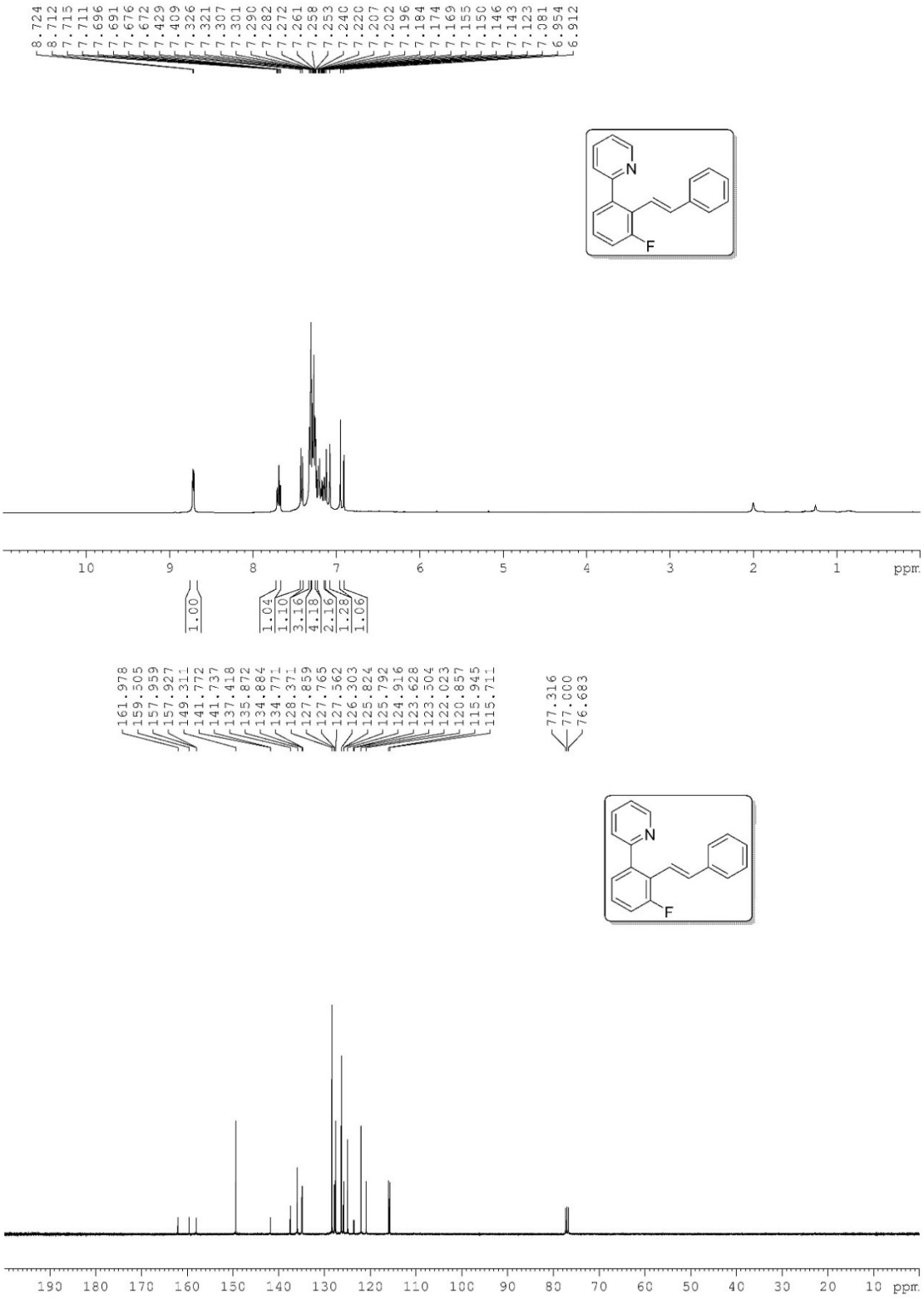
^{1}H and ^{13}C NMR spectra of compound **3la**.



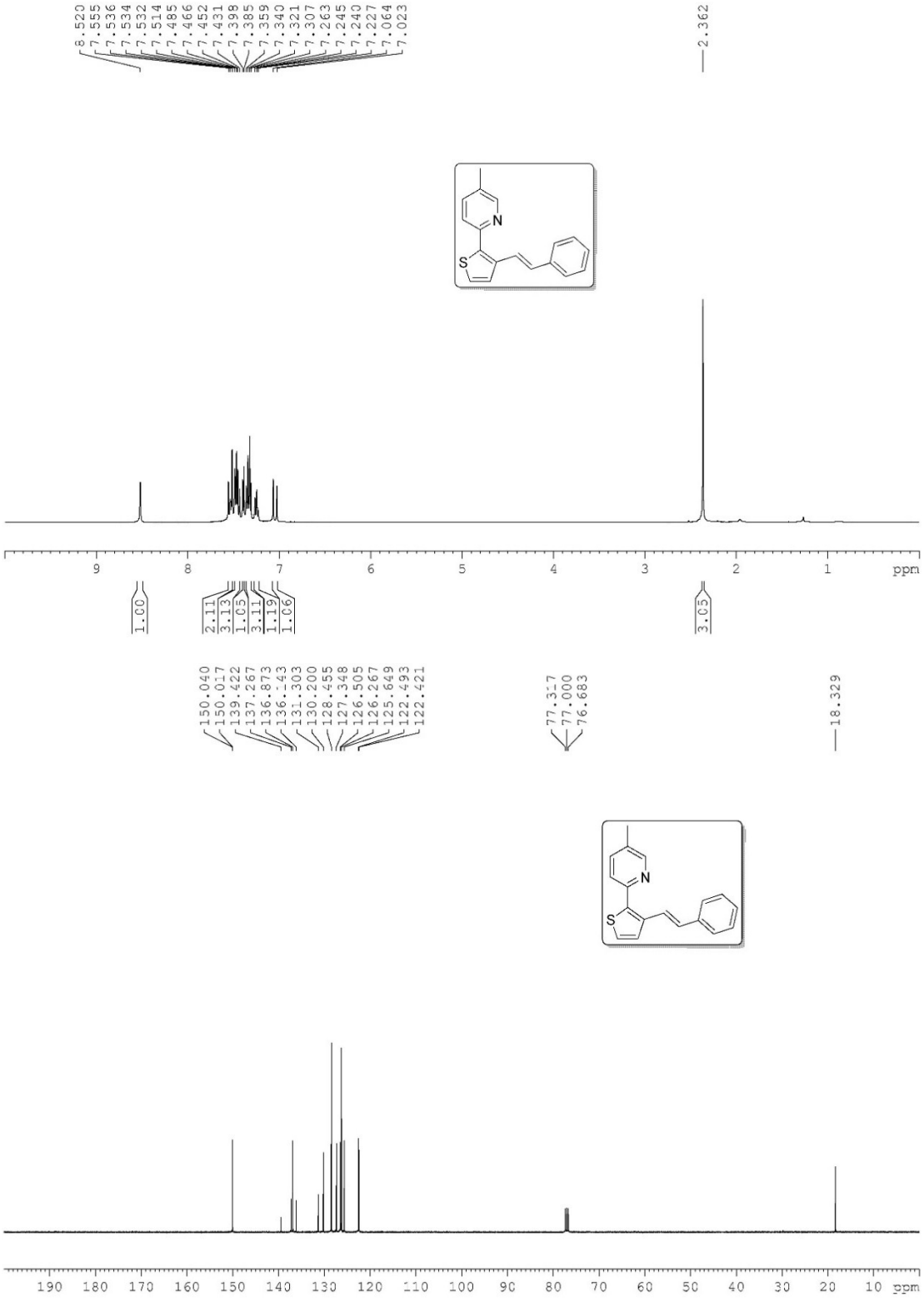
^{1}H and ^{13}C NMR spectra of compound **3la'**.



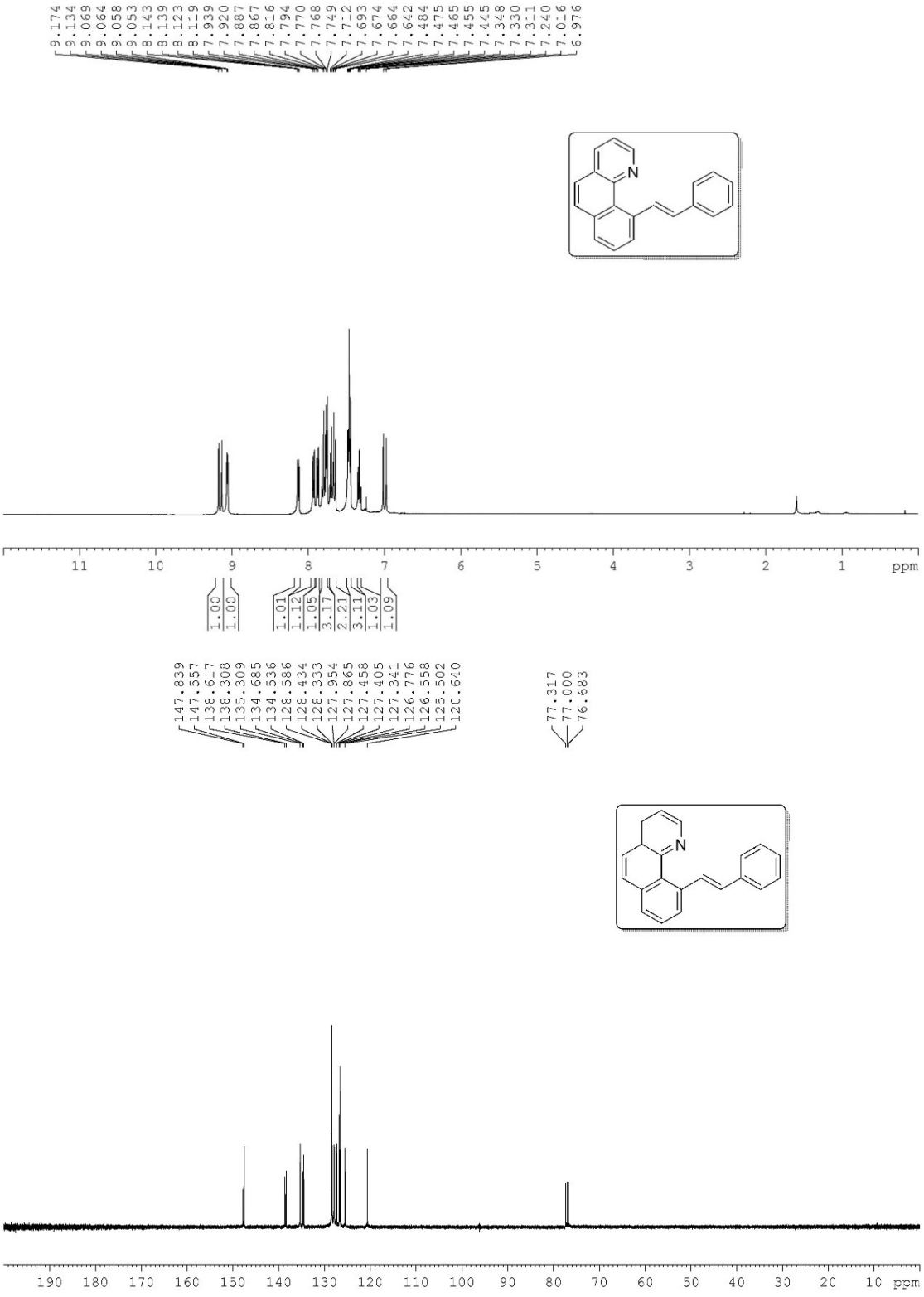
^{1}H and ^{13}C NMR spectra of compound **3ma**.



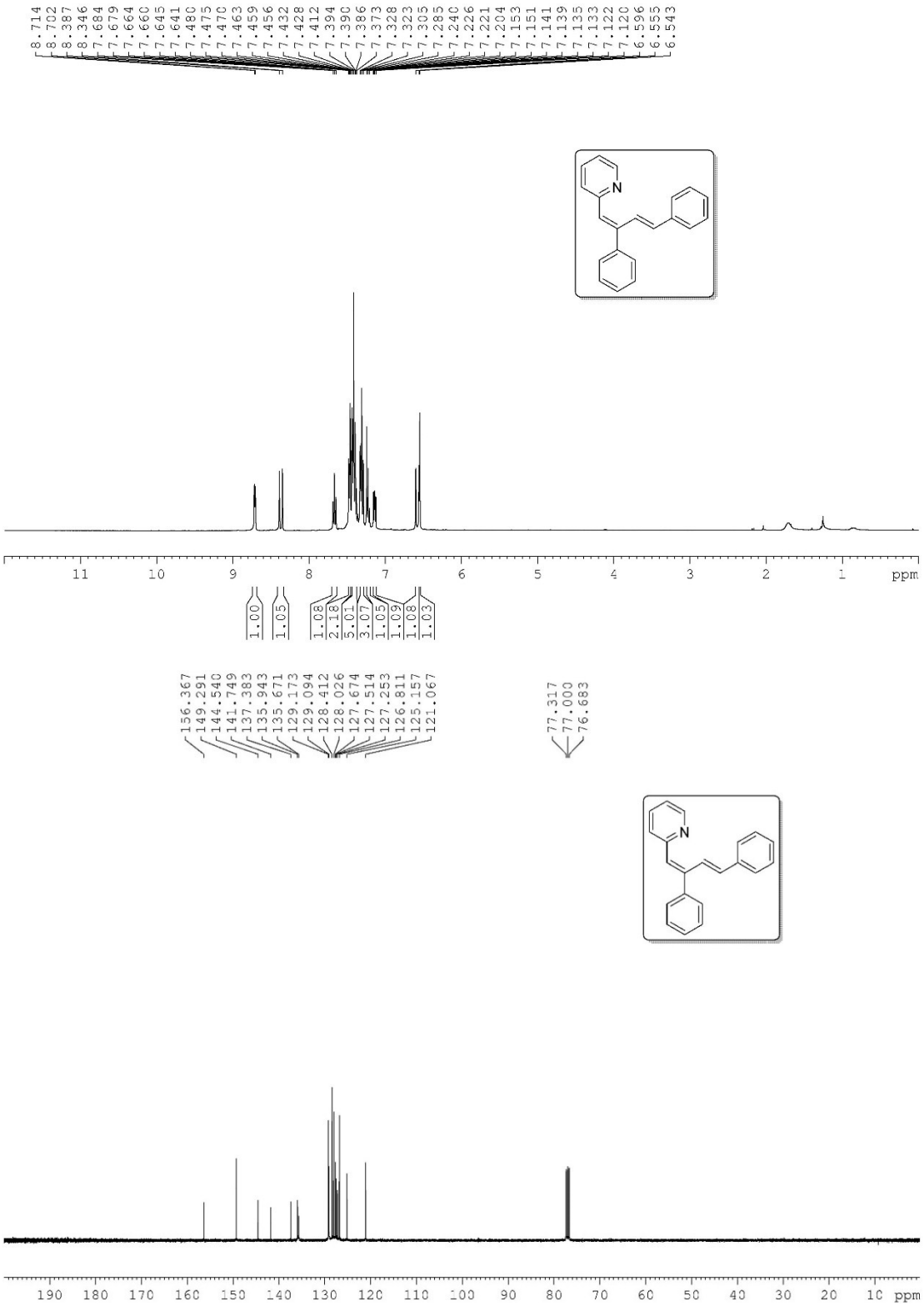
^{1}H and ^{13}C NMR spectra of compound **3na.**



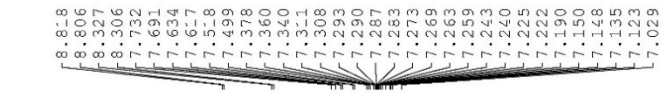
^{1}H and ^{13}C NMR spectra of compound **3oa**.

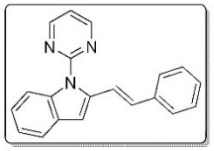


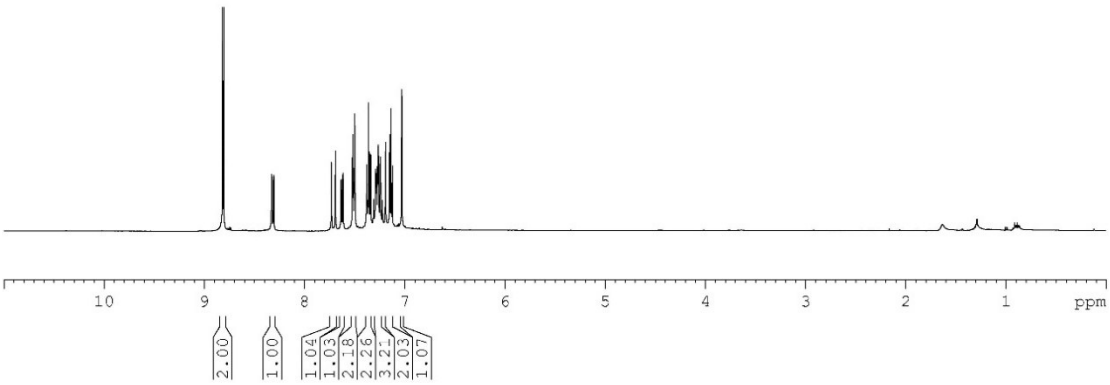
^{1}H and ^{13}C NMR spectra of compound **3pa**.

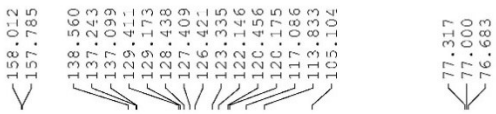


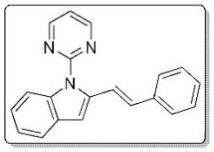
^{1}H and ^{13}C NMR spectra of compound **3qa**.

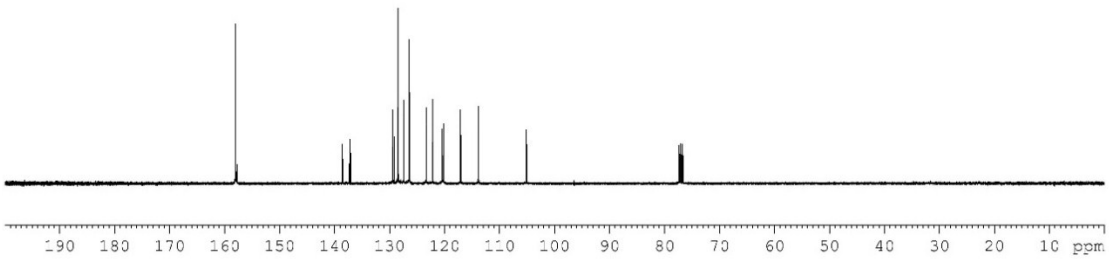




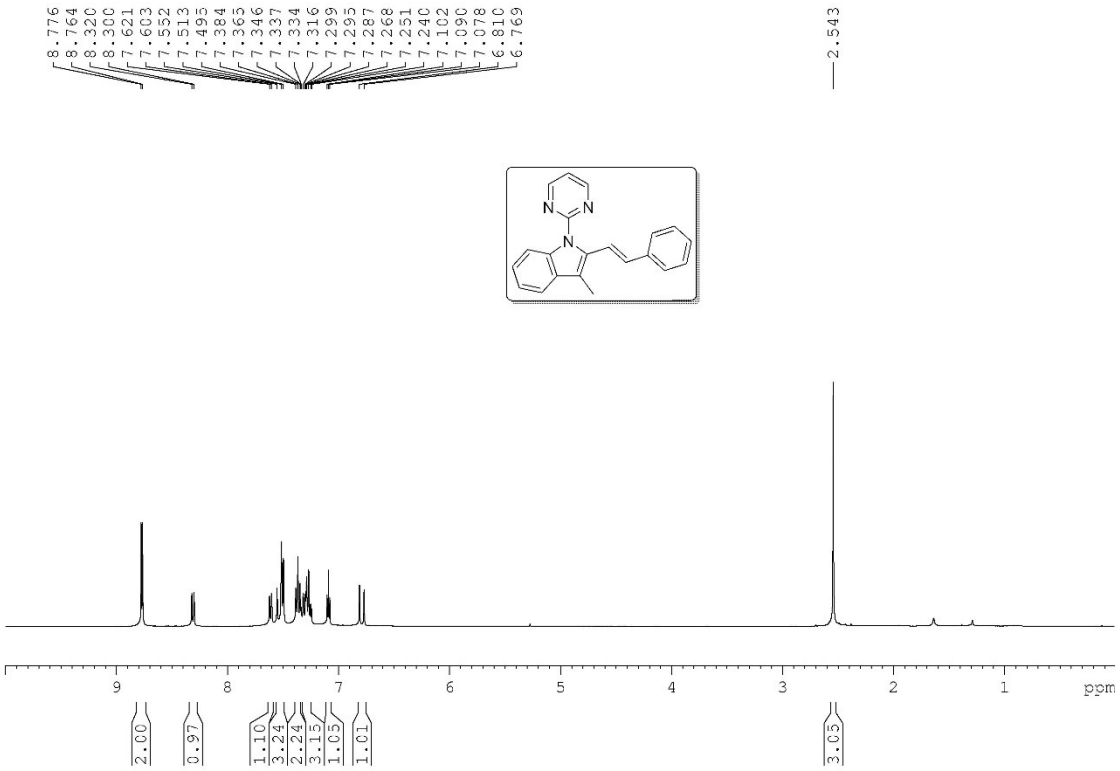


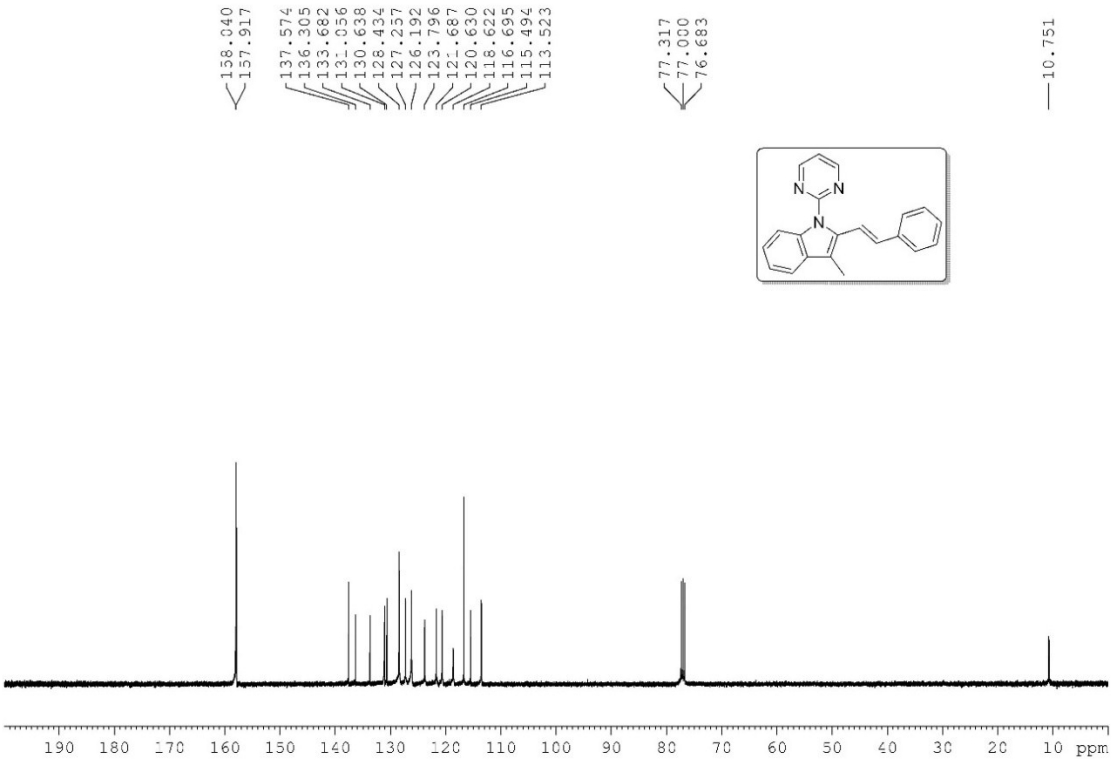




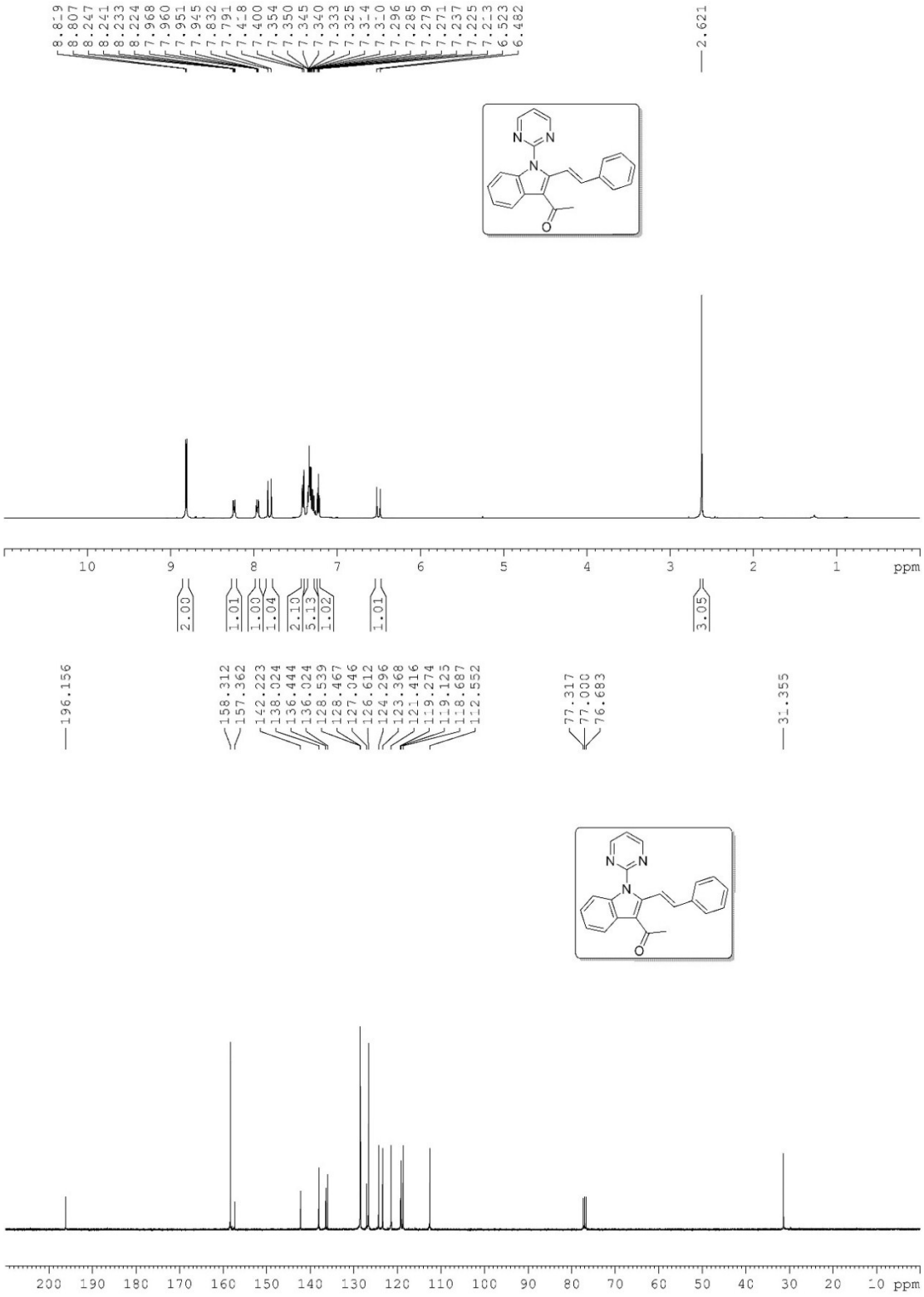


^{1}H and ^{13}C NMR spectra of compound **3ra**.

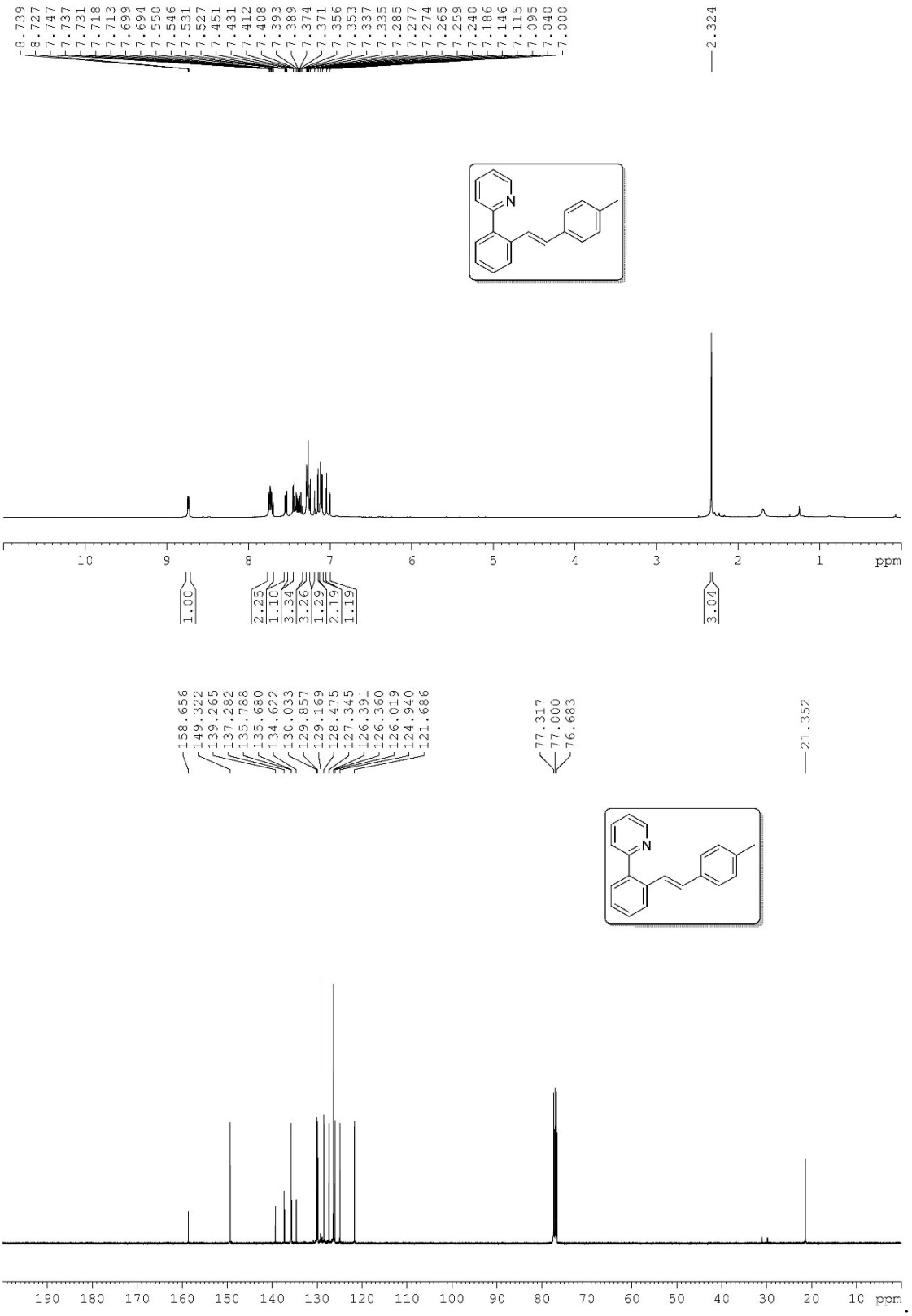




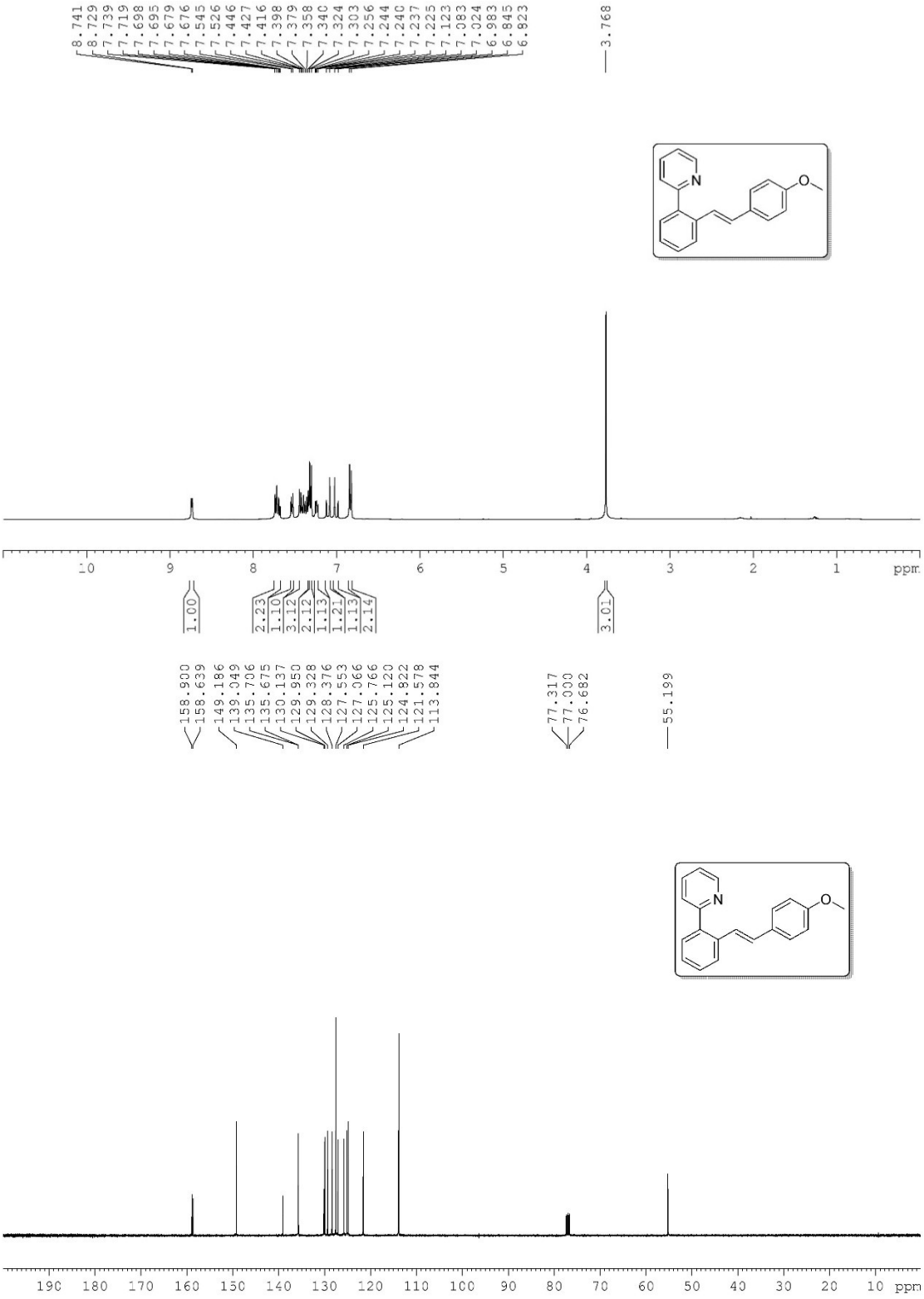
^{1}H and ^{13}C NMR spectra of compound **3sa.**



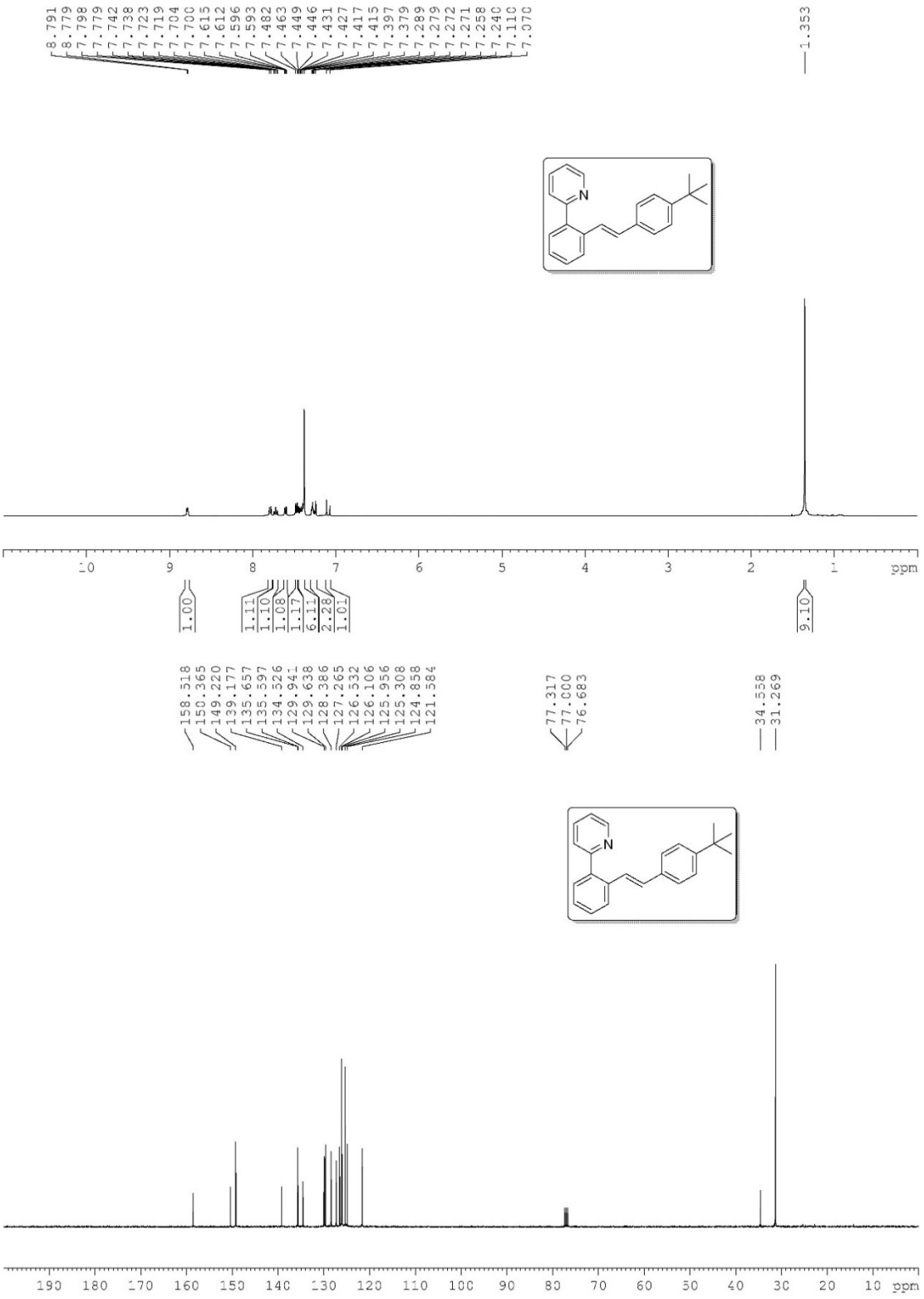
^{1}H and ^{13}C NMR spectra of compound **3ab**



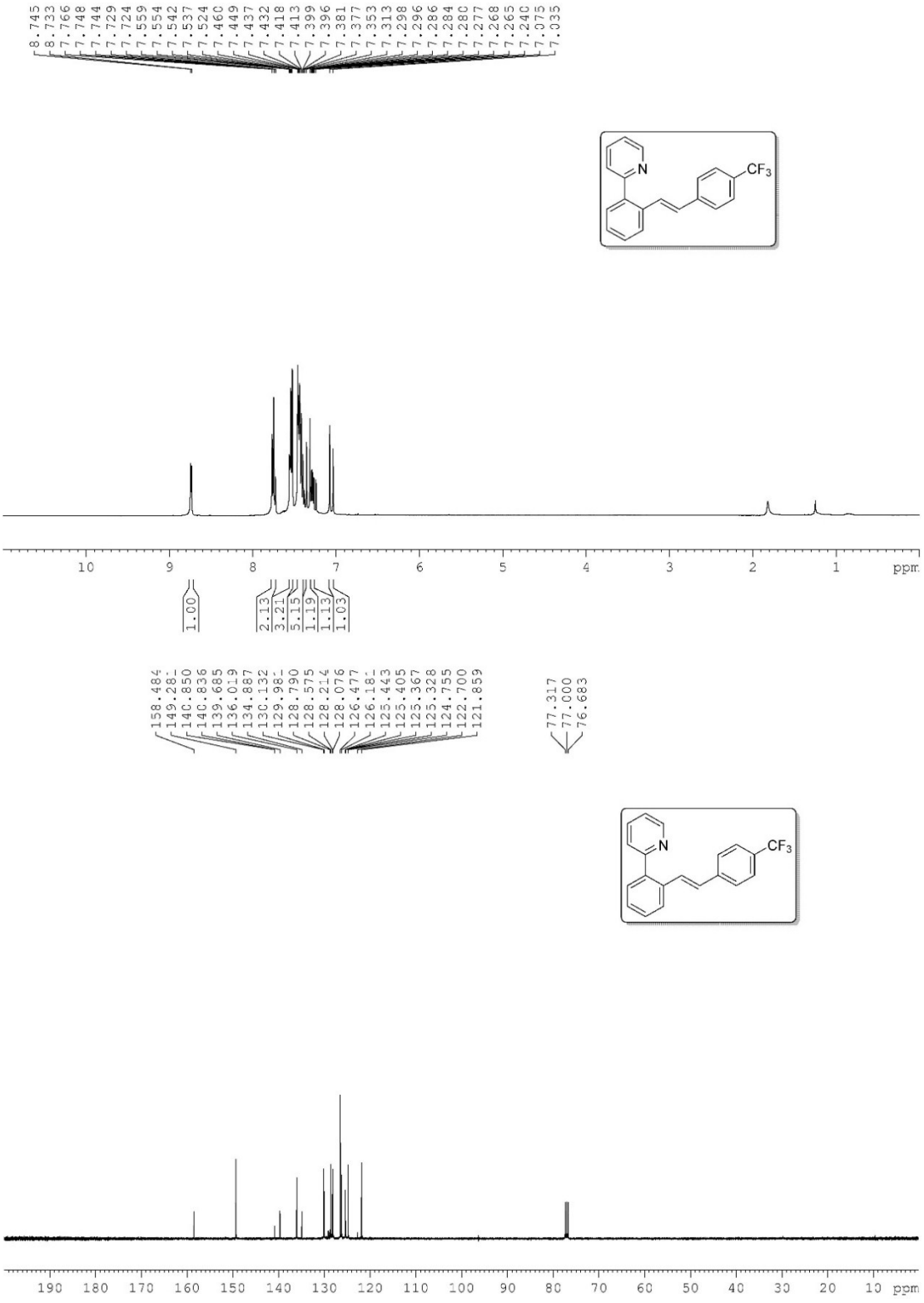
^{1}H and ^{13}C NMR spectra of compound **3ac**.



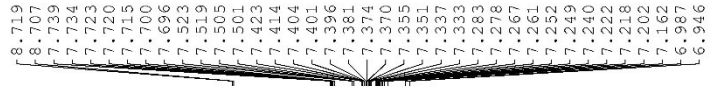
^{1}H and ^{13}C NMR spectra of compound **3ad**.

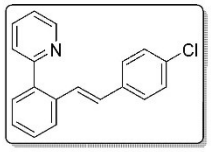


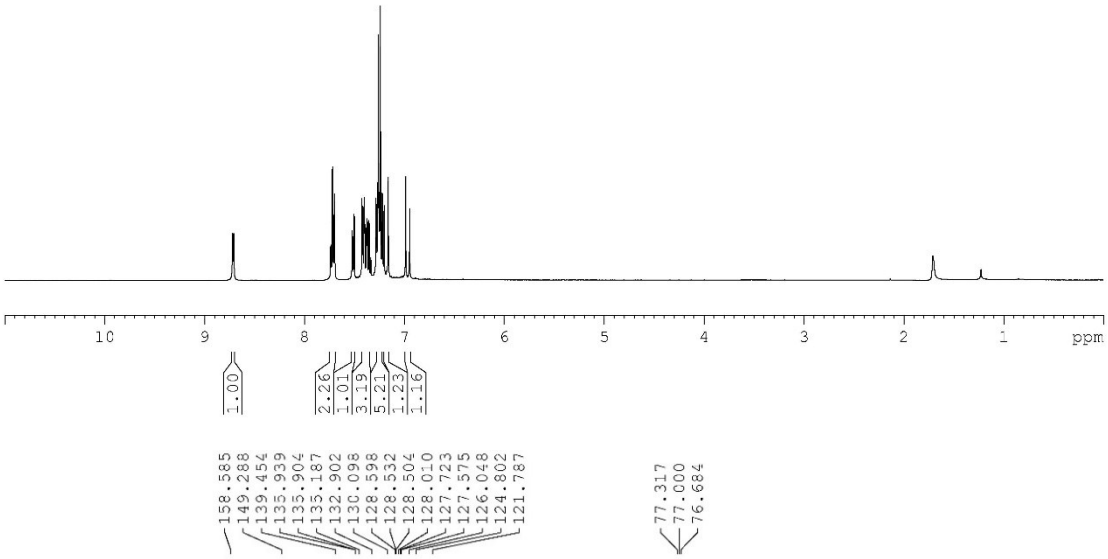
^{1}H and ^{13}C NMR spectra of compound **3ae**.

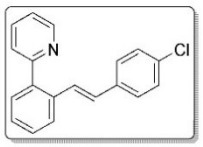


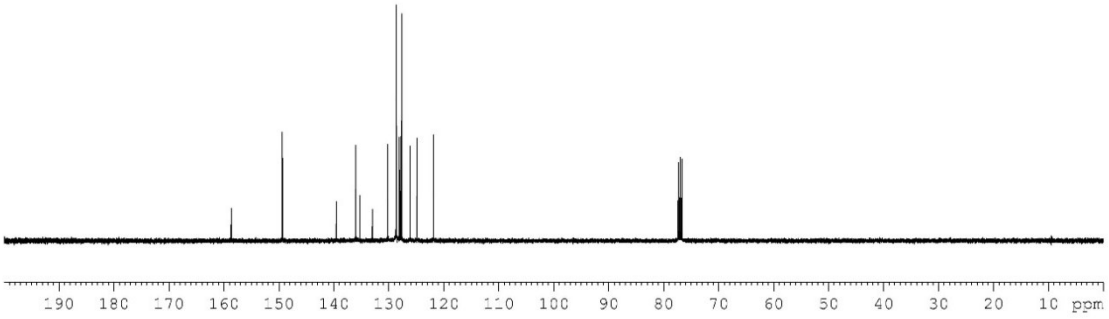
^{1}H and ^{13}C NMR spectra of compound **3af**.



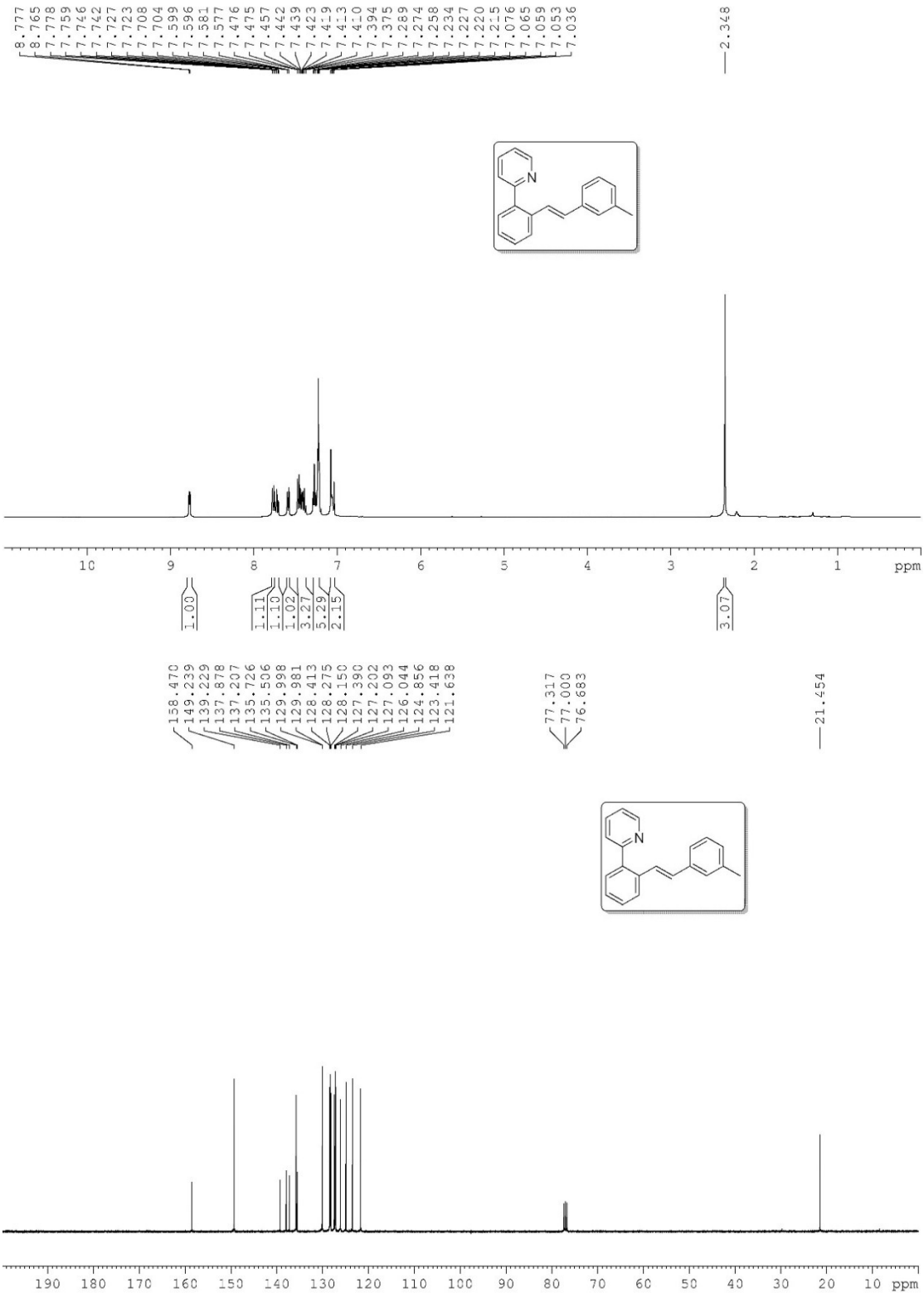




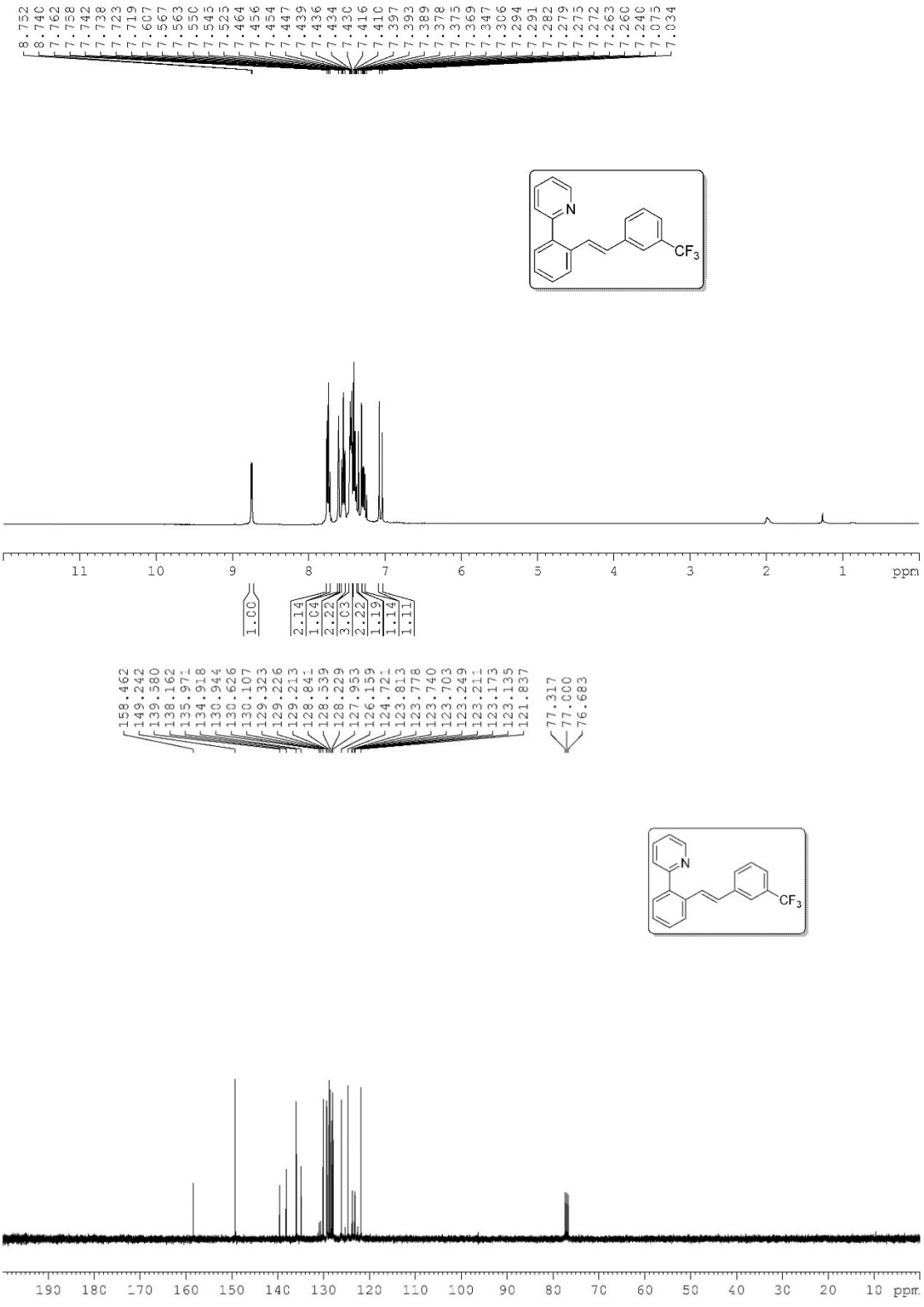




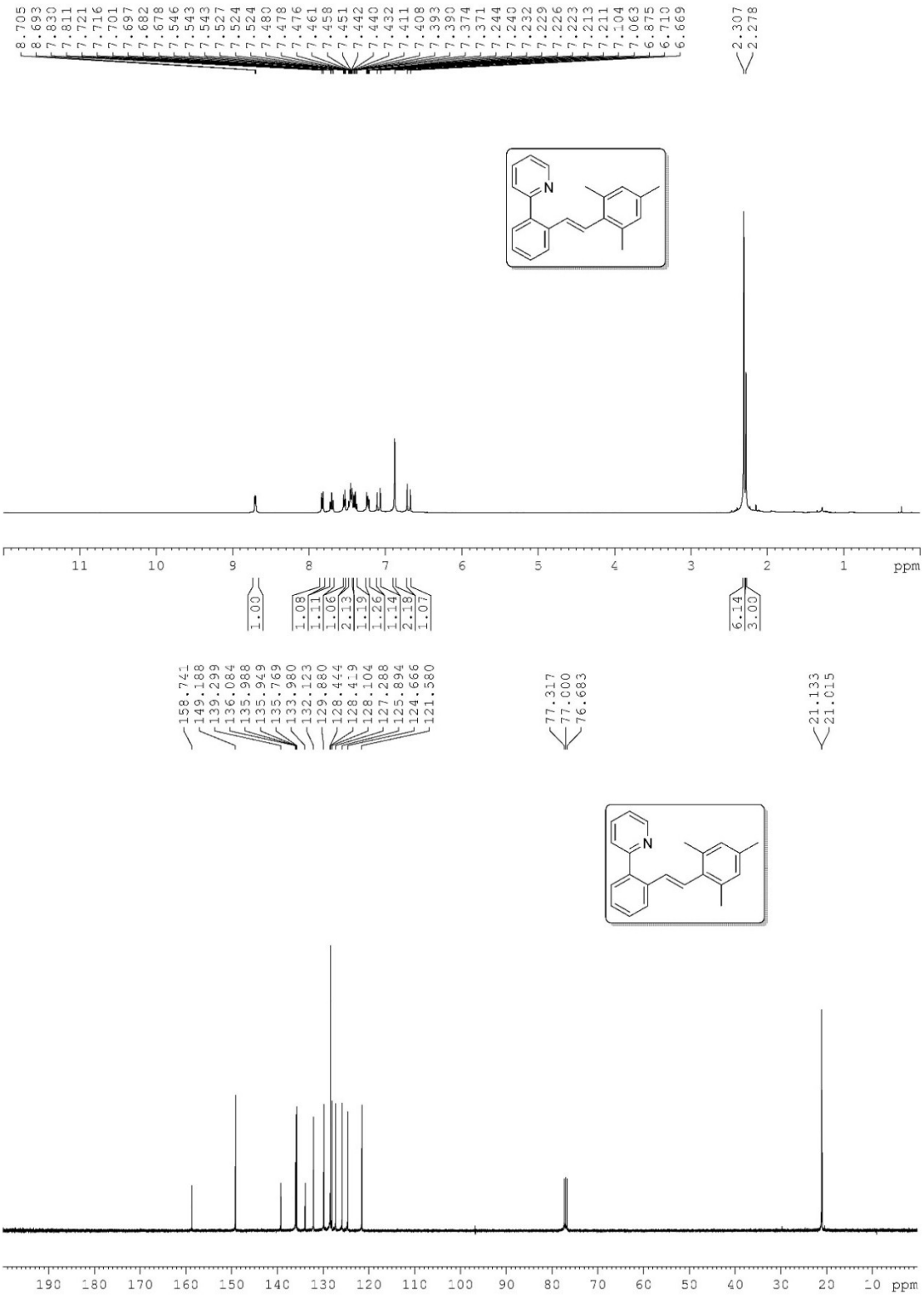
^{1}H and ^{13}C NMR spectra of compound **3ag**.



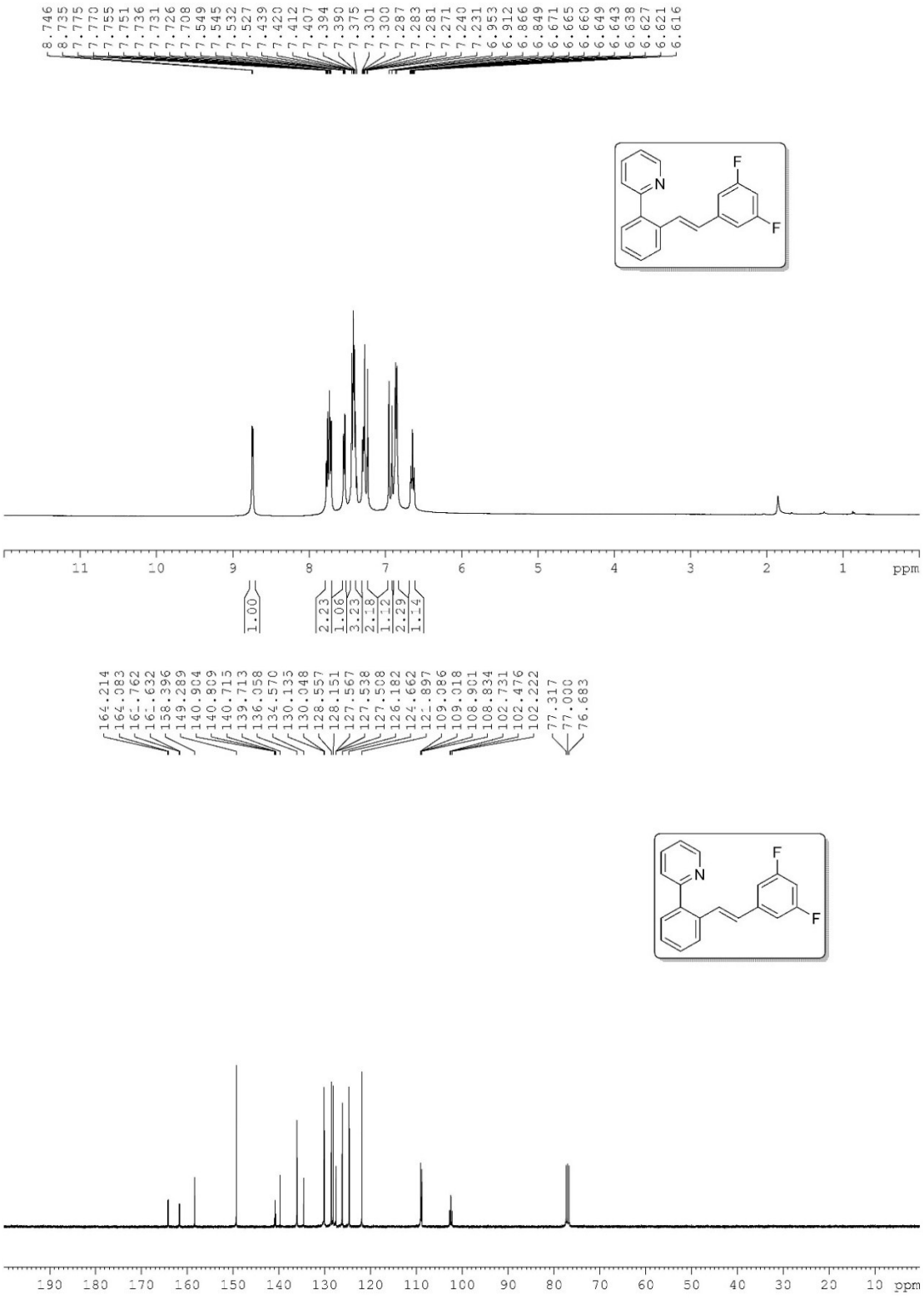
^{1}H and ^{13}C NMR spectra of compound **3ah**.



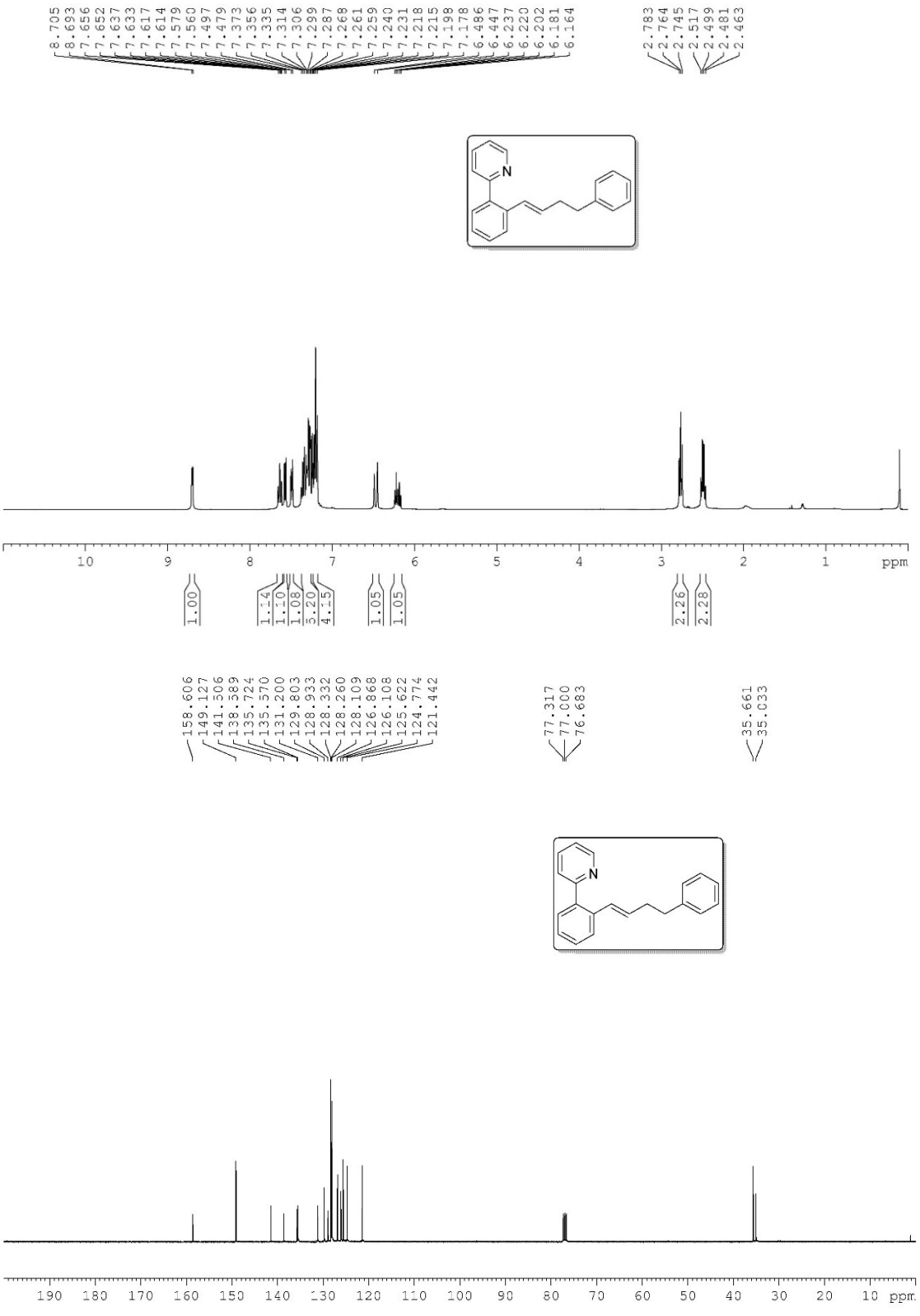
^{1}H and ^{13}C NMR spectra of compound **3ai**.



^{1}H and ^{13}C NMR spectra of compound **3aj**.

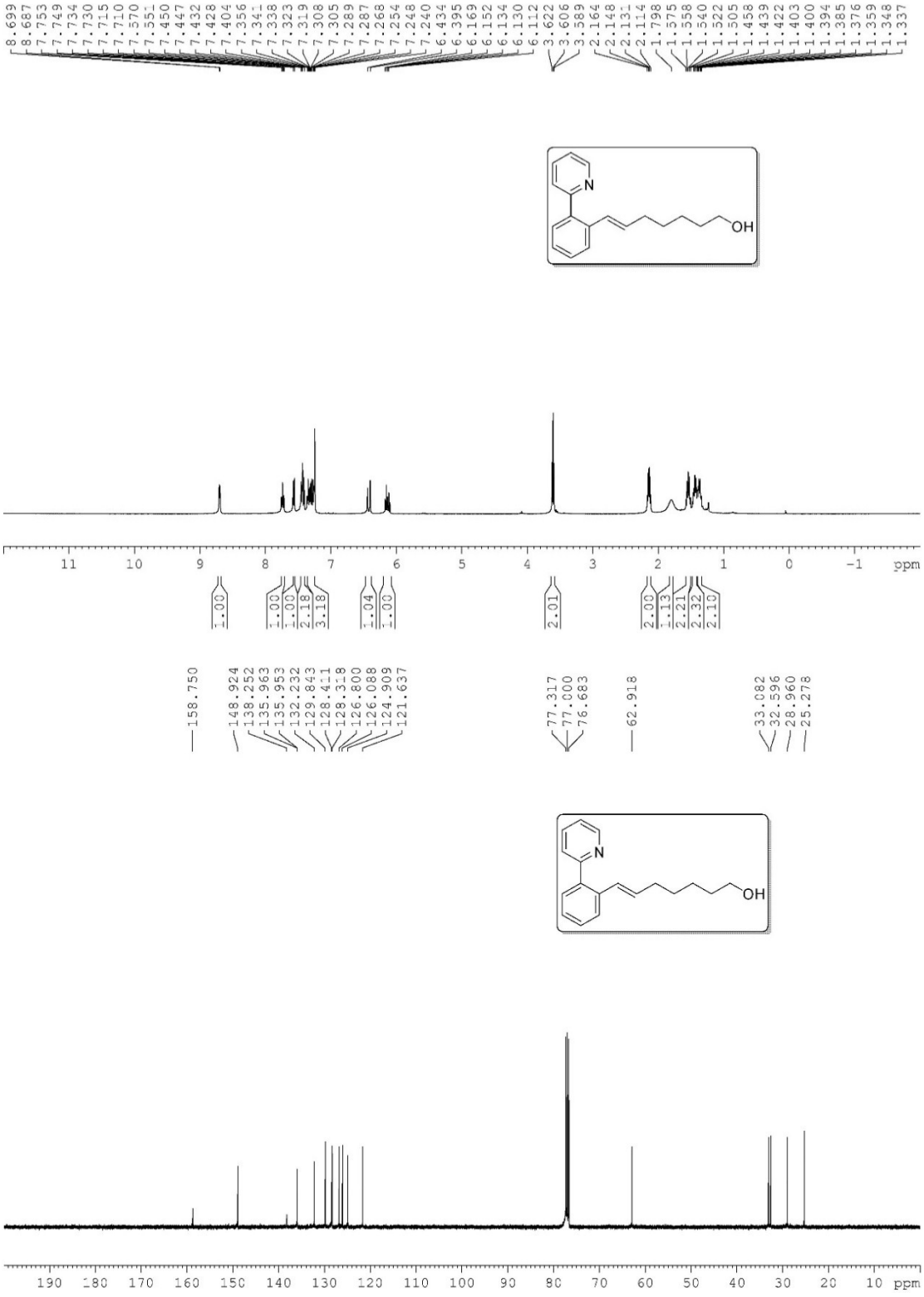


^{1}H and ^{13}C NMR spectra of compound **3ak**.

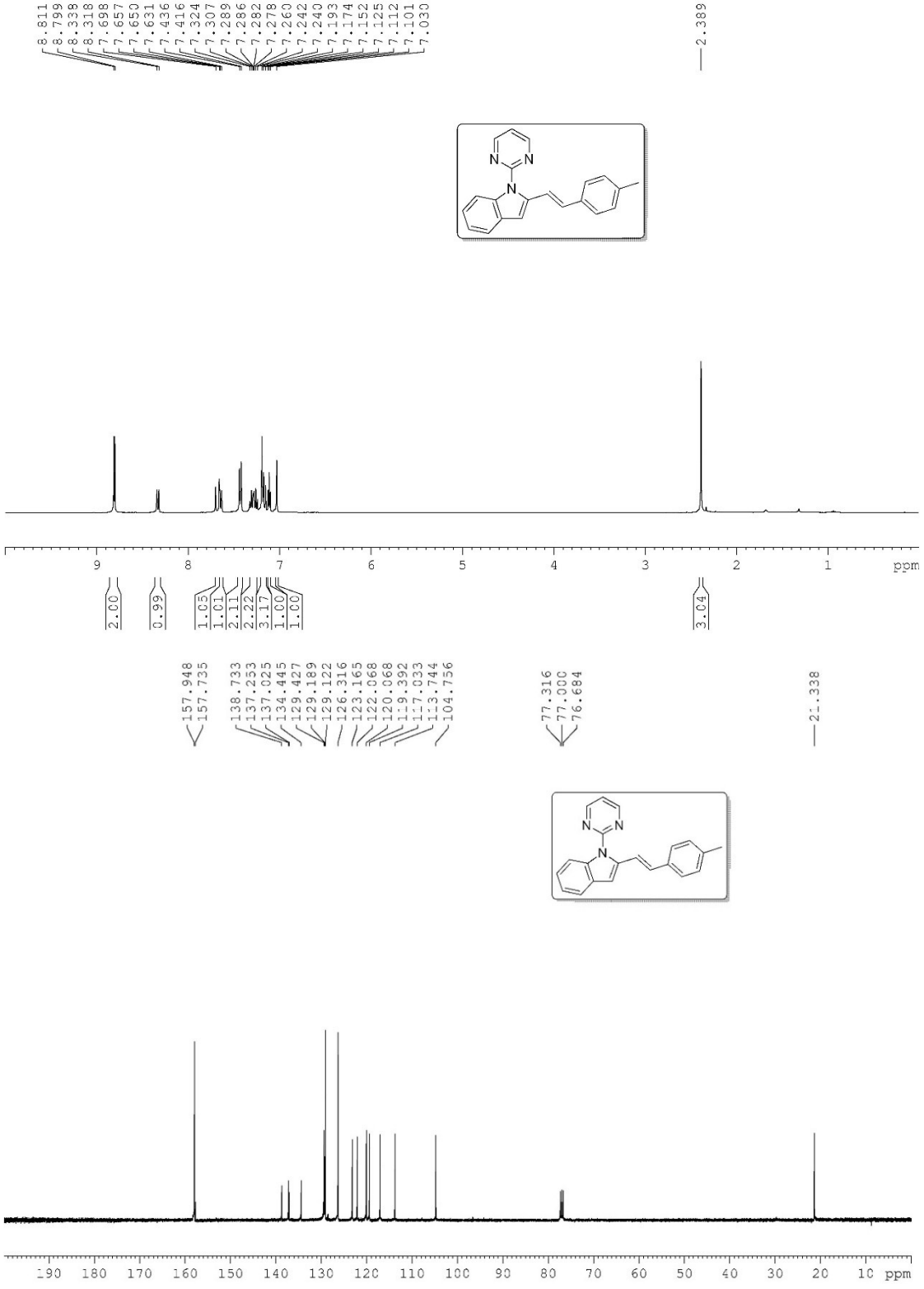


^{1}H and ^{13}C NMR spectra of compound **3al**.

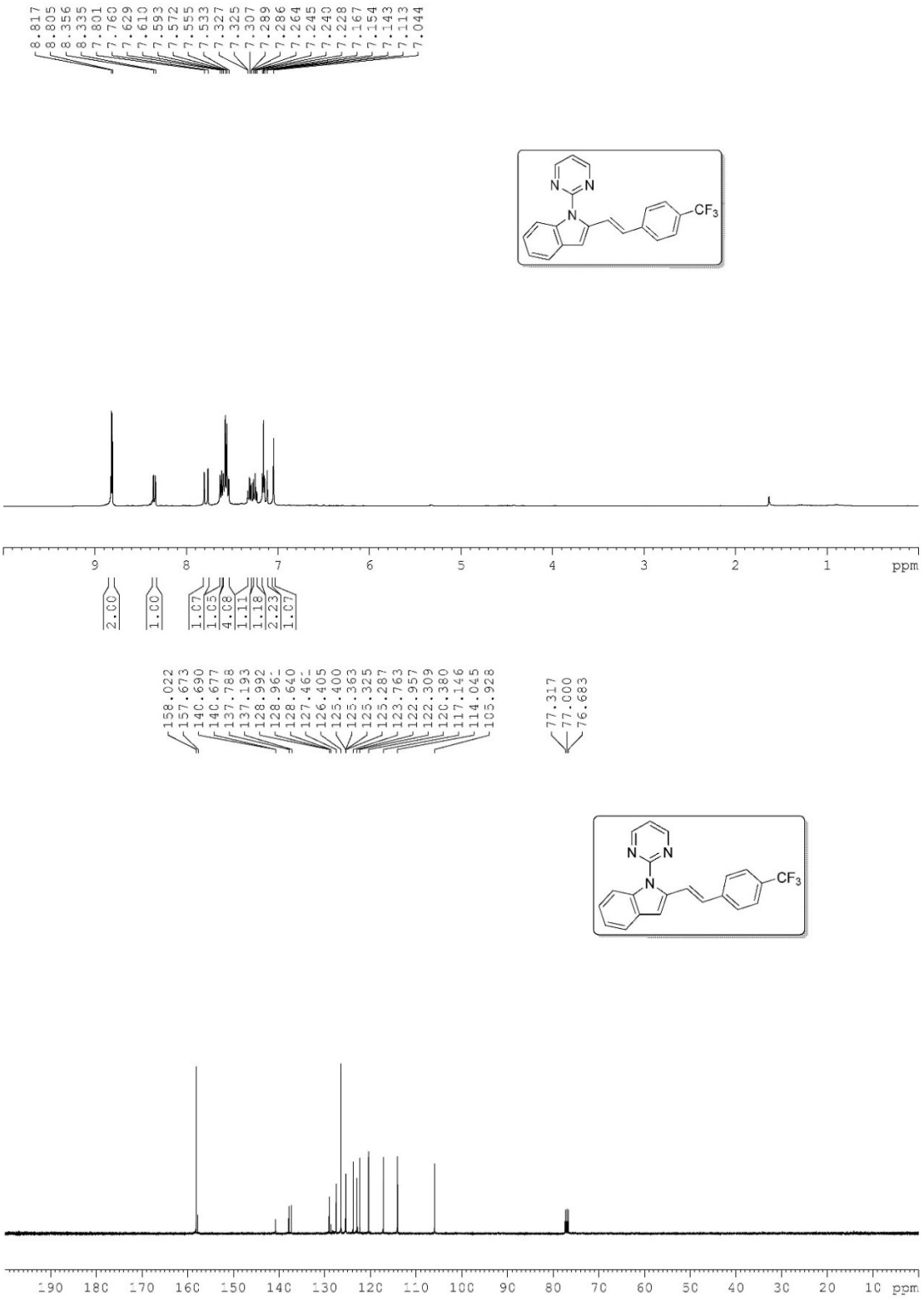
^{1}H and ^{13}C NMR spectra of compound **3am**.



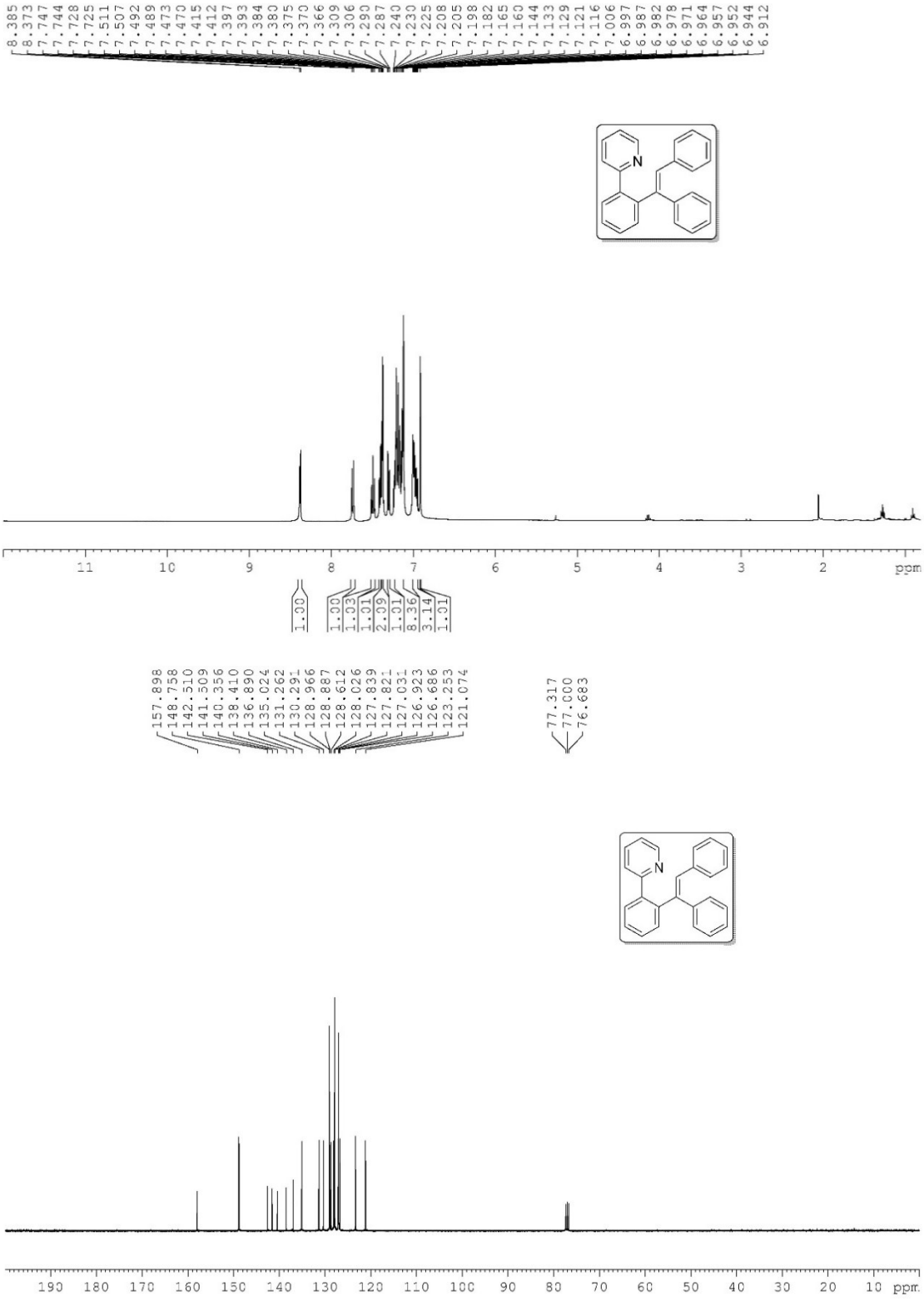
^{1}H and ^{13}C NMR spectra of compound **3qb**.



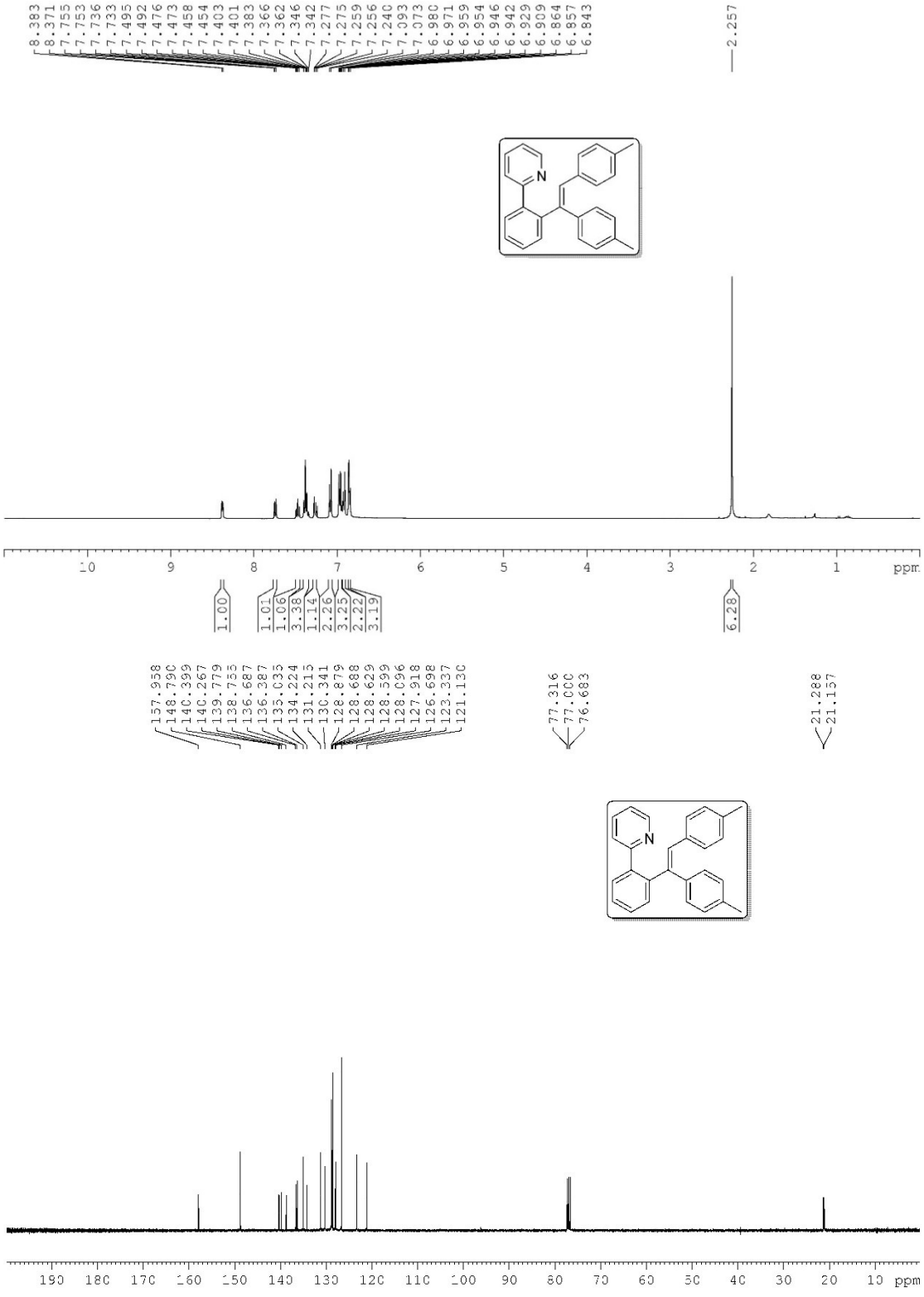
^{1}H and ^{13}C NMR spectra of compound **3qe**.



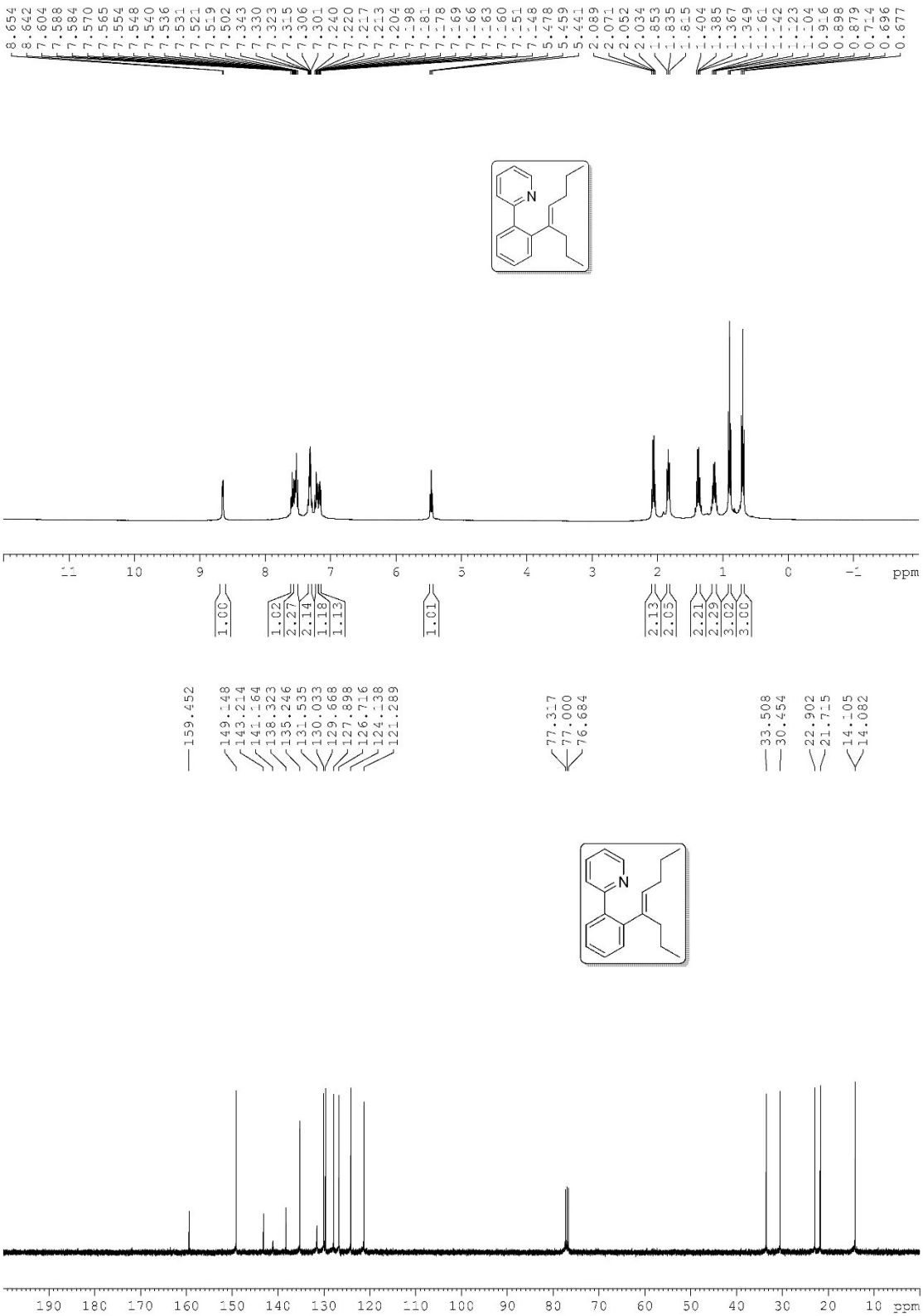
^{1}H and ^{13}C NMR spectra of compound **3an**.



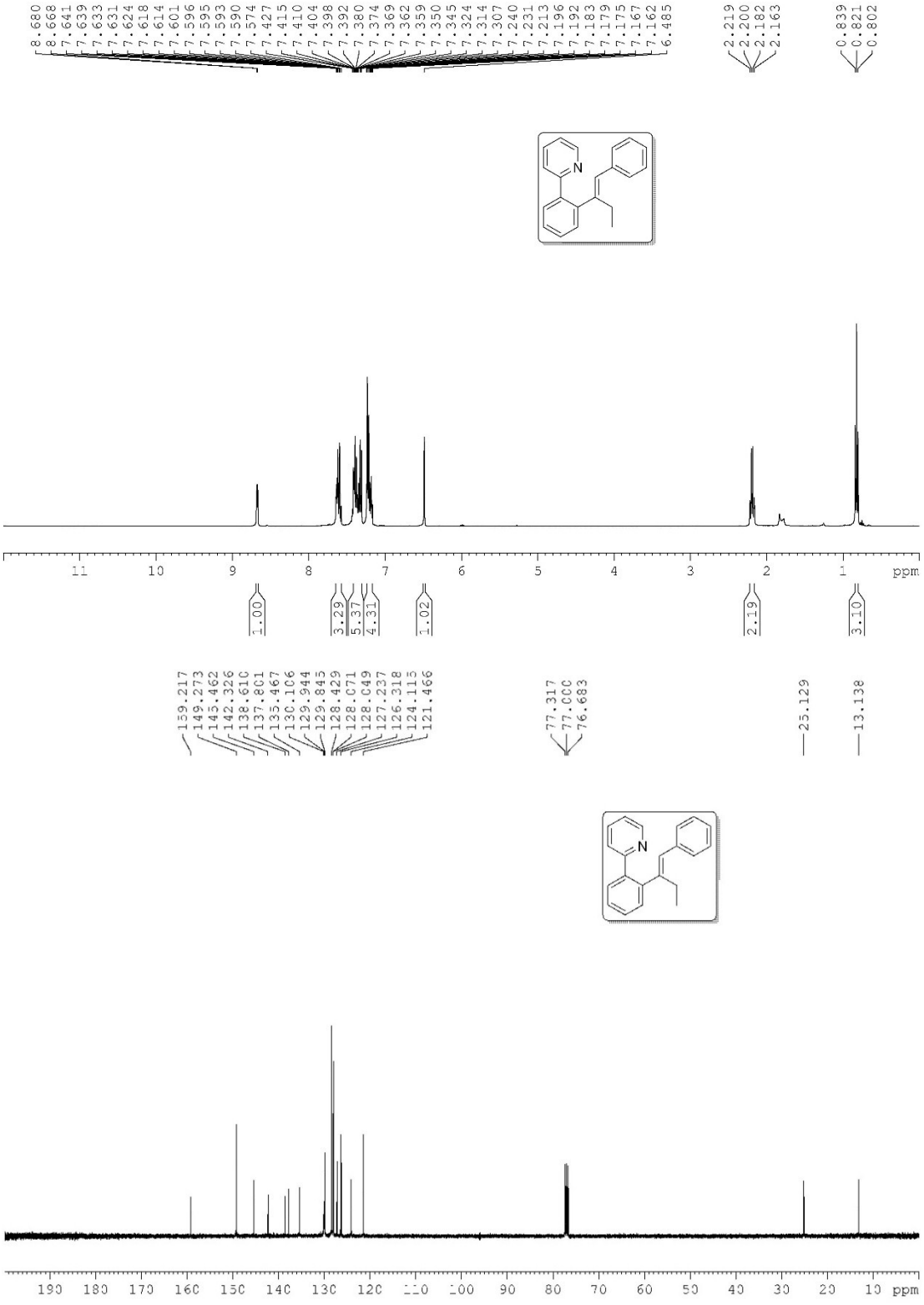
^{1}H and ^{13}C NMR spectra of compound **3ao**.



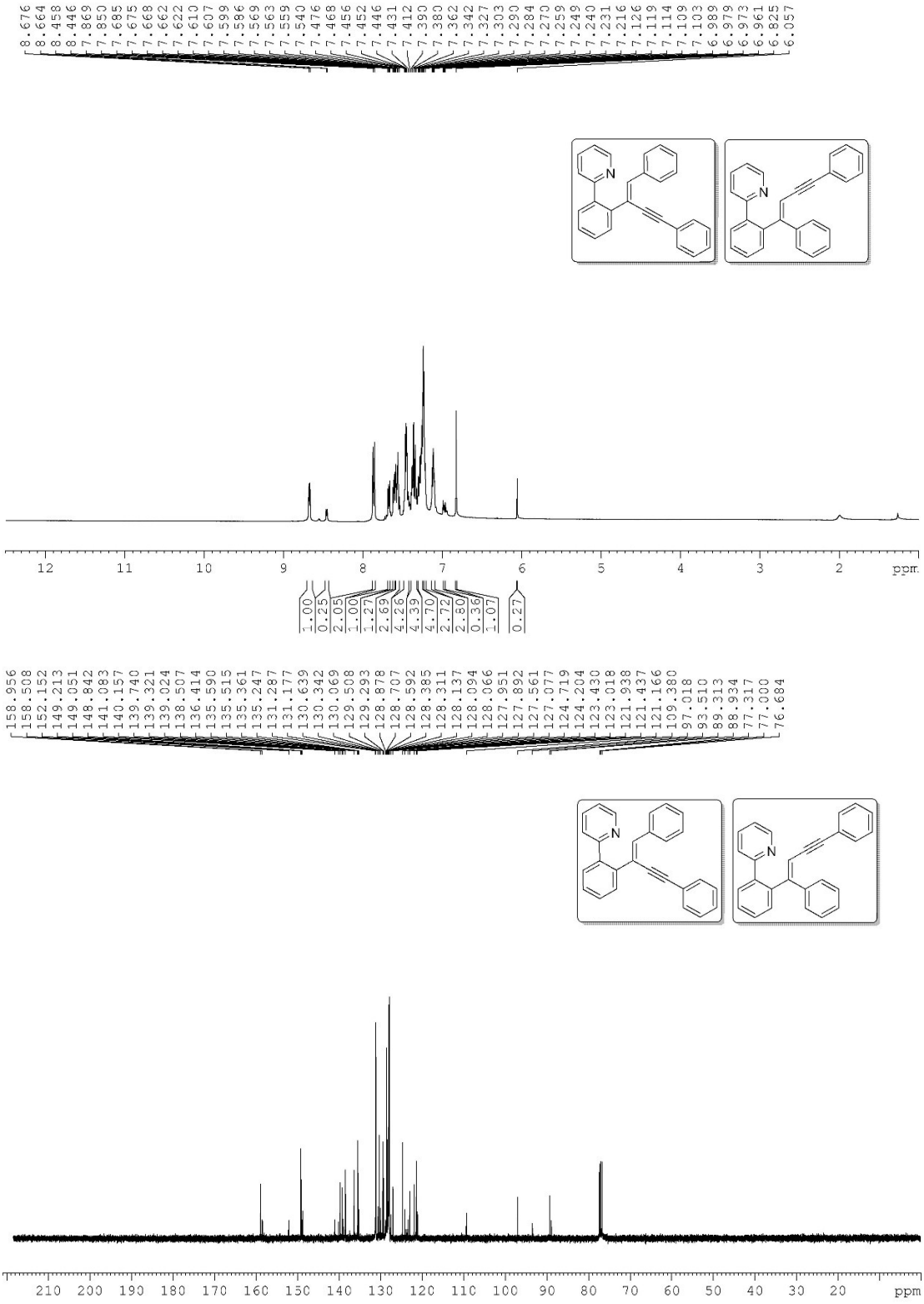
^{1}H and ^{13}C NMR spectra of compound **3ap**.



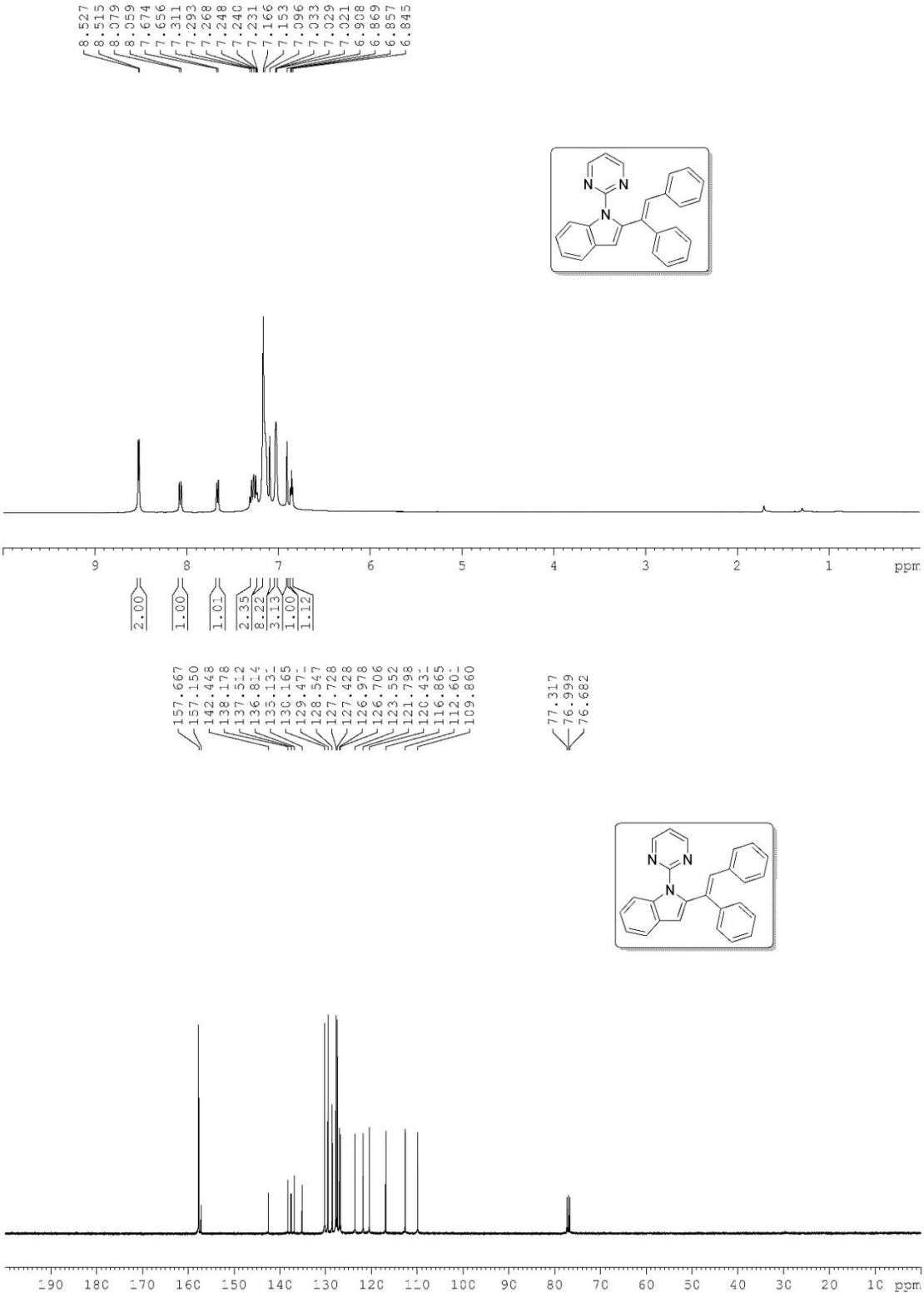
^{1}H and ^{13}C NMR spectra of compound **3aq**.



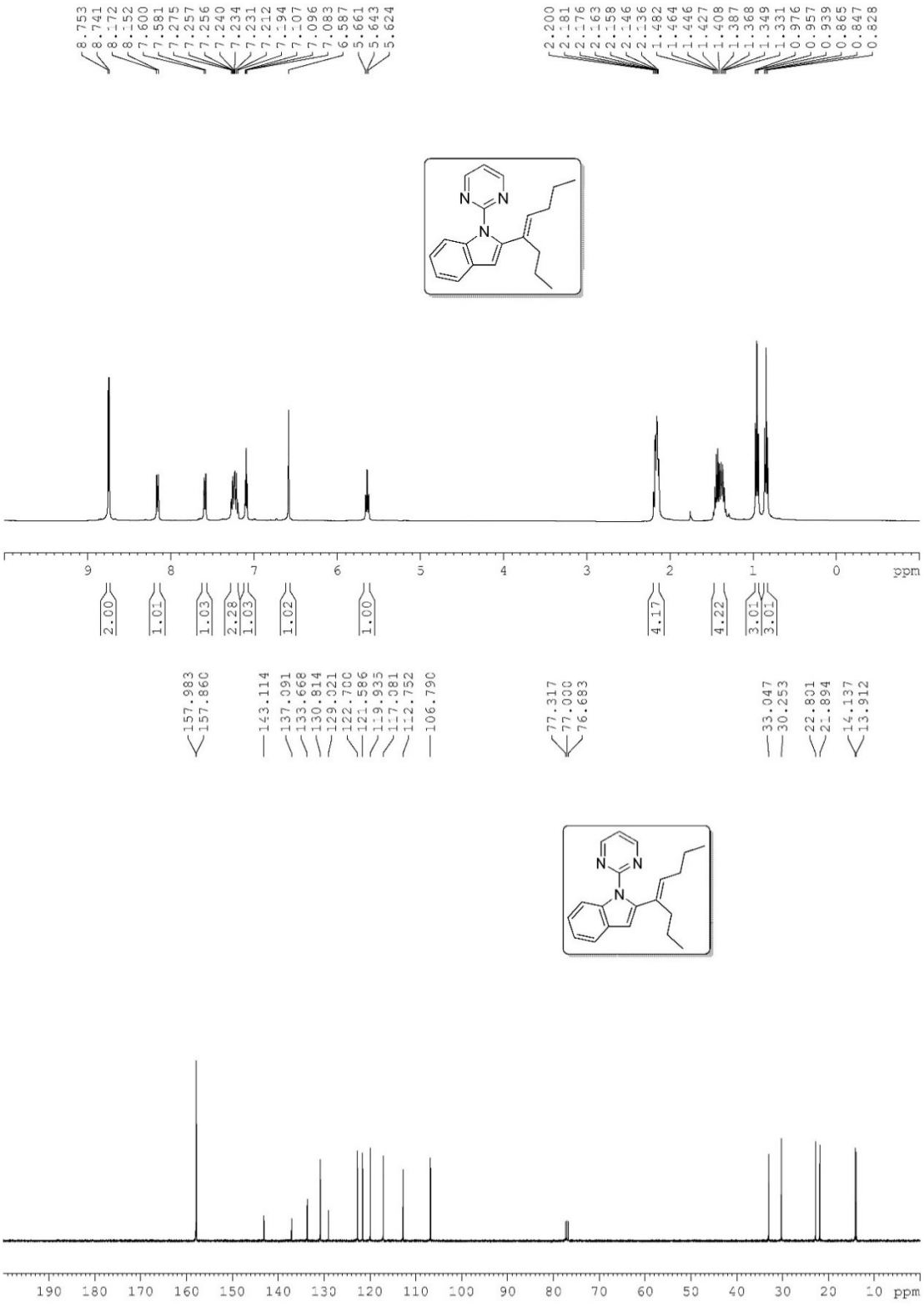
^{1}H and ^{13}C NMR spectra of compound **3ar+3ar'**.



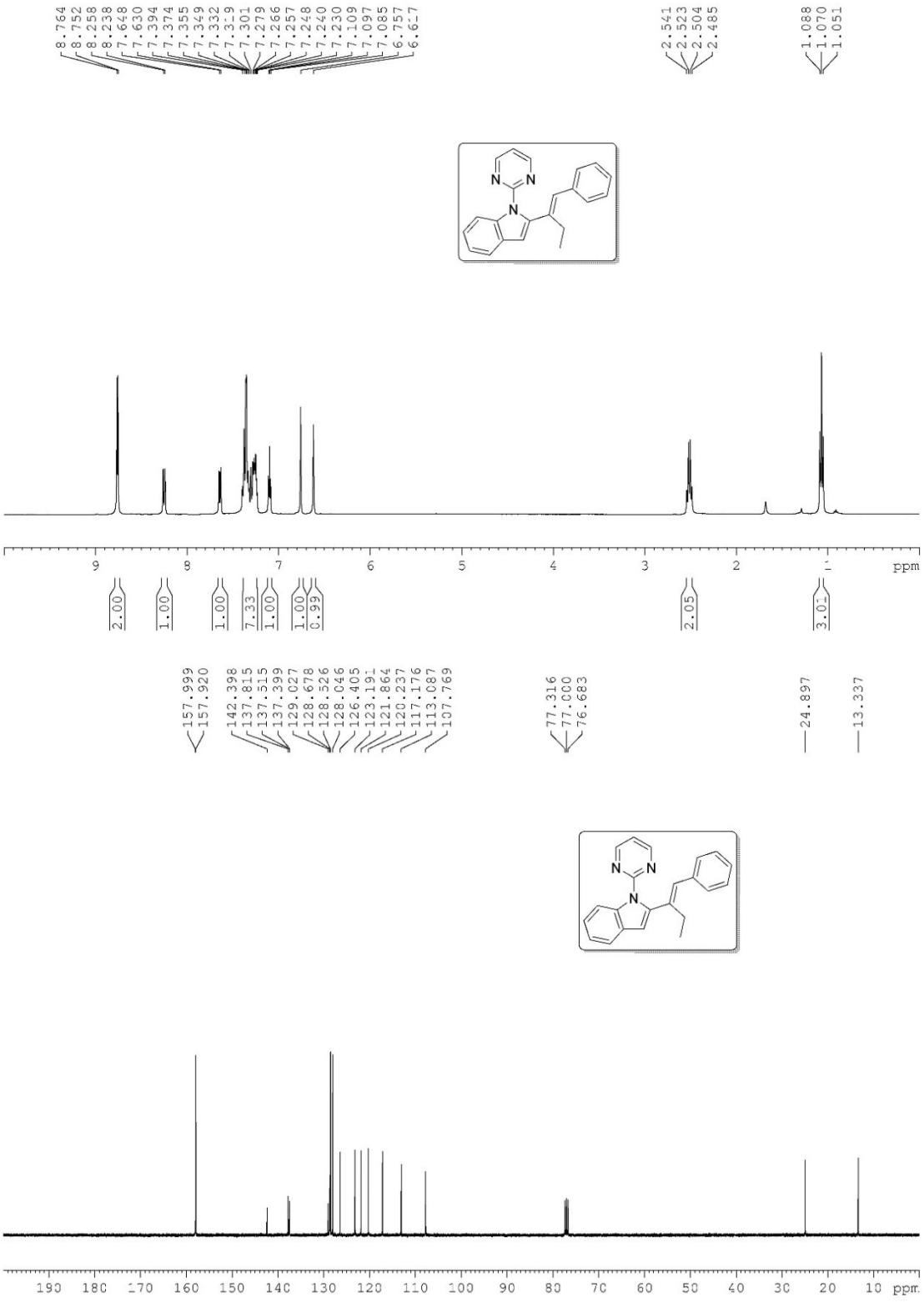
^{1}H and ^{13}C NMR spectra of compound **3qn**.



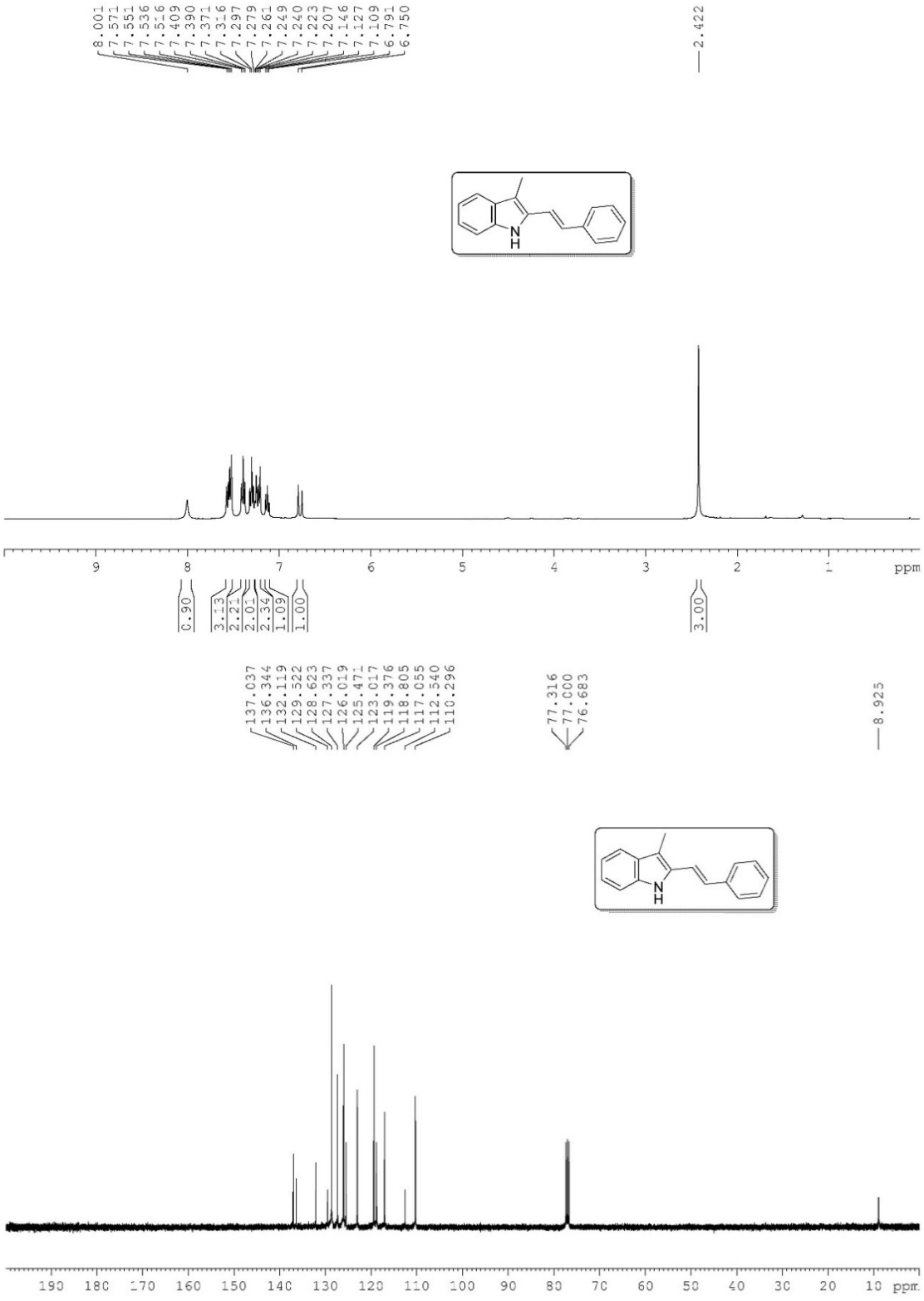
^{1}H and ^{13}C NMR spectra of compound **3qp**.



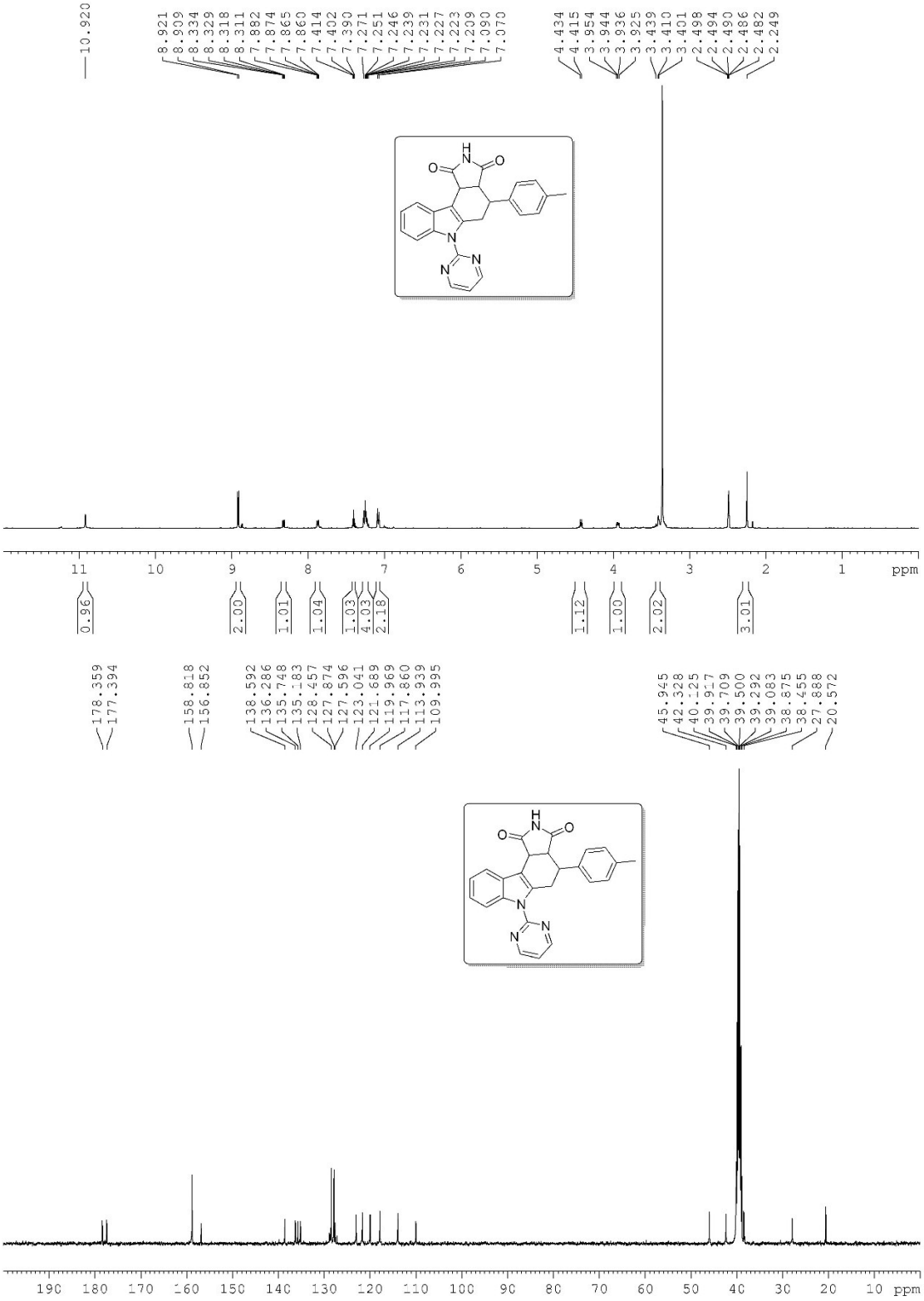
^{1}H and ^{13}C NMR spectra of compound **3qq**.



^{1}H and ^{13}C NMR spectra of compound **4**.

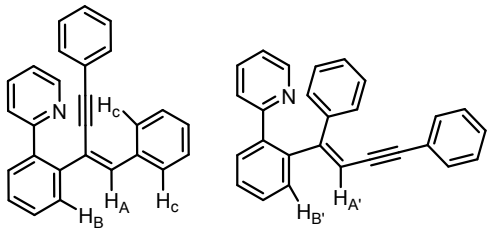


^{1}H and ^{13}C NMR spectra of compound **6**.



3. NOE analysis of 3ar+3ar'.

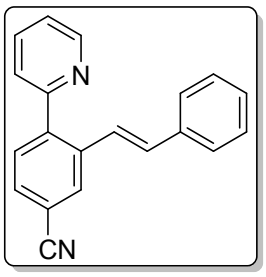
NOE data for **3ar+3ar'**.



Irradiation	Intensity increase
H_A (δ 6.83)	H_B (δ 7.62-7.60, 1.89%)
	H_C (δ 7.86, 2.95%)
H_B (δ 7.62-7.60)	H_A (δ 6.83, 0.73%)
H_C (δ 7.86)	H_A (δ 6.83, 1.16%)
$H_{A'}$ (δ 6.06)	$H_{B'}$ (δ 7.43-7.41, 1.76%)
$H_{B'}$ (δ 7.43-7.41)	$H_{A'}$ (δ 6.06, 0.77%)

4. Crystallographic Data

X-ray crystallographic data of compound **3ga**.



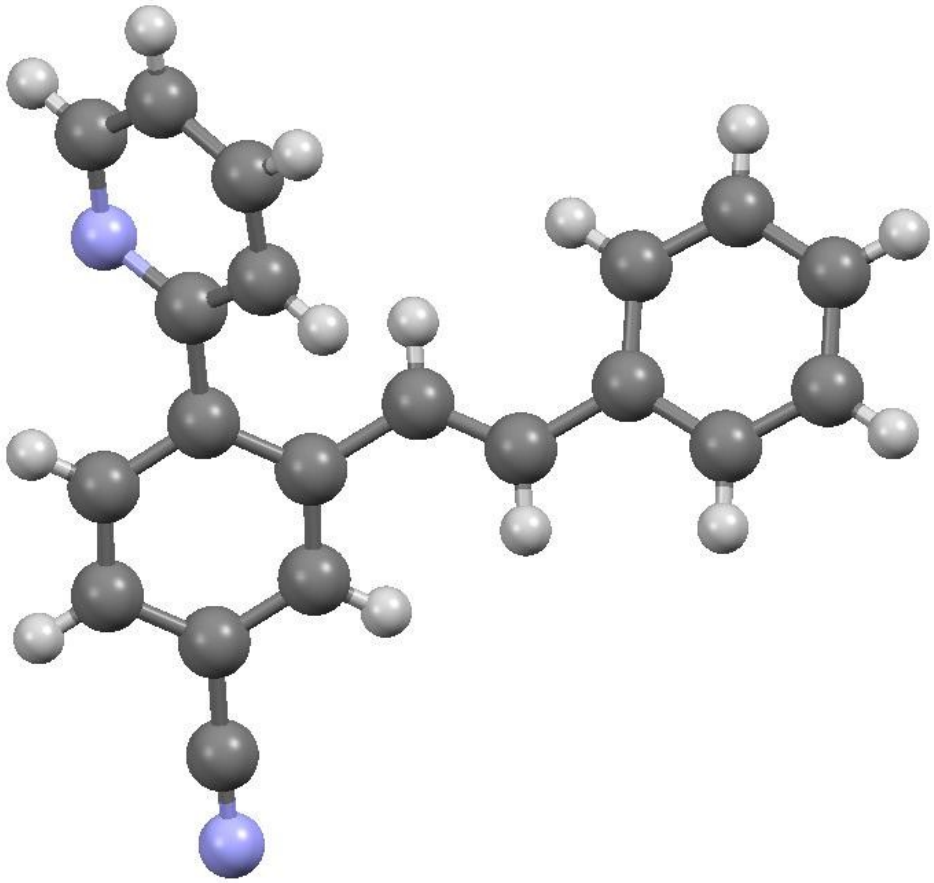
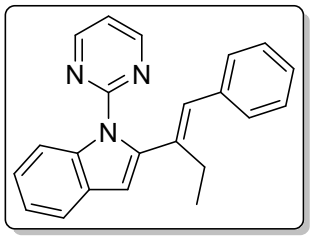


Table 1. Crystal data and structure refinement for mo_180141LT_0m_a (CCDC No. 1825212) (**3ga**).

Identification code	mo_180141LT_0m_a	
Empirical formula	C20 H14 N2	
Formula weight	282.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 3.9188(4) Å	α= 101.080(5)°.
	b = 12.5127(13) Å	β= 96.416(5)°.
	c = 15.3057(15) Å	γ = 92.665(5)°.
Volume	730.13(13) $Å^3$	
Z	2	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	296	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Theta range for data collection	1.366 to 26.623°.	
Index ranges	-4<=h<=4, -15<=k<=15, -19<=l<=19	
Reflections collected	25856	
Independent reflections	2993 [R(int) = 0.0436]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9485 and 0.8530	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2993 / 0 / 200	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1268	
R indices (all data)	R1 = 0.0531, wR2 = 0.1325	
Extinction coefficient	0.010(7)	
Largest diff. peak and hole	0.467 and -0.507 $e.Å^{-3}$	

X-ray crystallographic data of compound **3qq**.



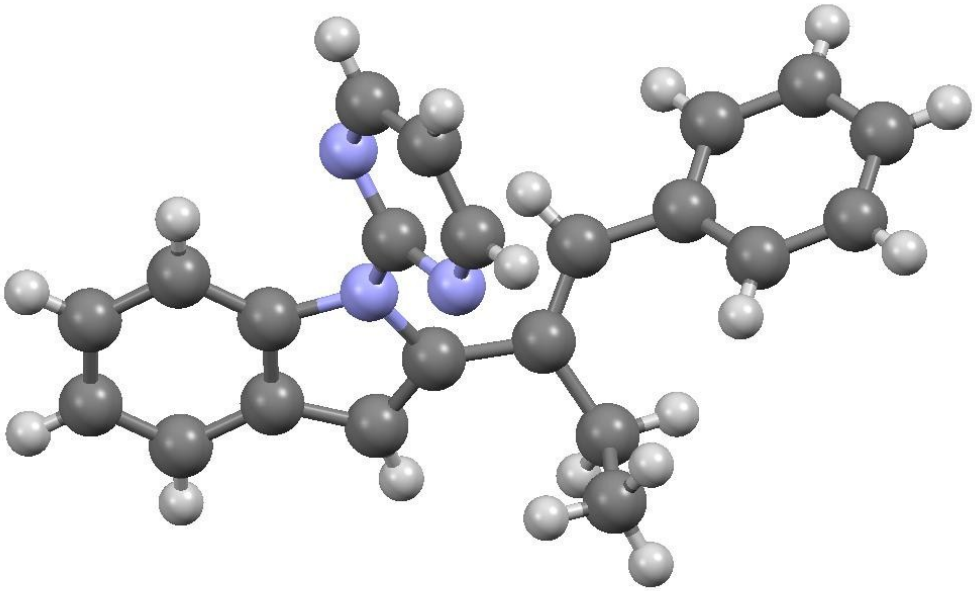
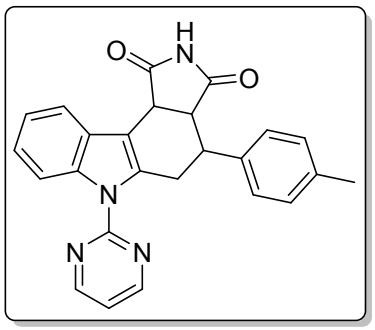


Table 1. Crystal data and structure refinement for 180303lt_0m (CCDC No. 1831607) (**3qq**).

Identification code	180303LT_0m	
Empirical formula	C22 H19 N3	
Formula weight	325.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.5762(7) Å	α= 90°.
	b = 7.8869(6) Å	β= 91.535(3)°.
	c = 19.9879(16) Å	γ = 90°.
Volume	1666.7(2) $Å^3$	
Z	4	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	688	
Crystal size	0.20 x 0.10 x 0.03 mm^3	
Theta range for data collection	2.038 to 26.423°.	
Index ranges	-13<=h<=11, -9<=k<=9, -24<=l<=25	
Reflections collected	13644	
Independent reflections	3412 [R(int) = 0.0335]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9485 and 0.8664	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3412 / 0 / 227	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0832	
R indices (all data)	R1 = 0.0480, wR2 = 0.0897	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.189 and -0.190 $e.Å^{-3}$	

X-ray crystallographic data of compound **6**.



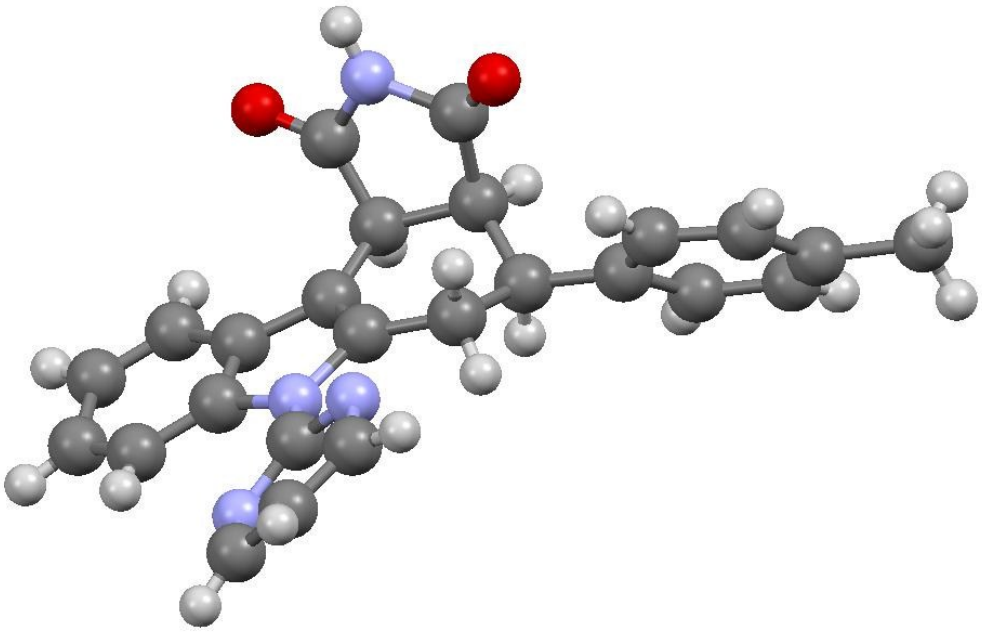


Table 1. Crystal data and structure refinement for 180446LT_a_sq (CCDC No. 1841353) (**6**).

Identification code	180446lt_a_sq	
Empirical formula	C25 H20 N4 O2	
Formula weight	408.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1577(9) Å	α= 106.893(3)°.
	b = 10.7173(7) Å	β= 91.497(4)°.
	c = 13.3021(10) Å	γ = 91.349(3)°.
Volume	1248.12(18) $Å^3$	
Z	2	
Density (calculated)	1.087 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	428	
Crystal size	0.20 x 0.20 x 0.15 mm^3	
Theta range for data collection	1.601 to 26.437°.	
Index ranges	-11<=h<=11, -13<=k<=13, -16<=l<=16	
Reflections collected	19906	
Independent reflections	5120 [R(int) = 0.0291]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9485 and 0.8548	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5120 / 0 / 281	
Goodness-of-fit on F^2	1.101	
Final R indices [I>2sigma(I)]	R1 = 0.1087, wR2 = 0.2187	
R indices (all data)	R1 = 0.1257, wR2 = 0.2278	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.974 and -0.882 $e.Å^{-3}$	