Supporting Information

Palladium-Catalyzed Carbonylative Cyclization of 2-Alkynylanilines and Aryl Iodides to Access *N*-Acyl Indoles

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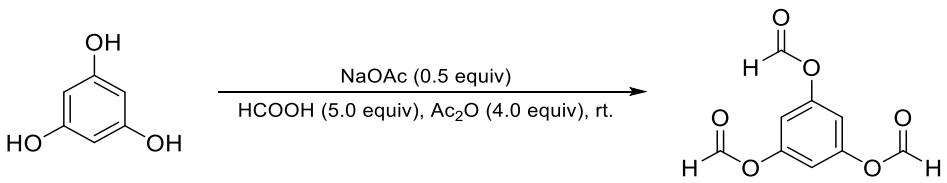
1. General experimental information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer.

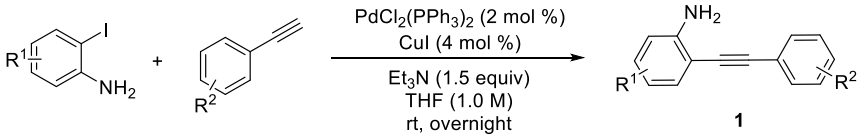
2. Preparation of benzene-1,3,5-triyl triformate (TFBen)[1]



Formic acid (8.4 mL, 222.8 mmol, 5.0 equiv) was added to acetic anhydride (16.8 mL, 178.2 mmol, 4.0 equiv) at rt. The mixture was stirred at 60 °C for 1 h and cooled to rt. The resulting solution was poured into a flask containing 1,3,5-trihydroxybenzene (5.62 g, 44.6 mmol, 1.0 equiv) and AcONa (1.83 g, 22.3 mmol, 0.5 equiv). The mixture was stirred for 4 h in a water bath and then diluted with toluene (100 mL), washed with H_2O (50 mL) twice. Keep the organic phase in fridge (2-8 °C) for overnight. Then filtered and dried in vacuo to afford the desired product benzene-1,3,5-triyl triformate (TFBen) as a white solid (5.1 g, 55%).

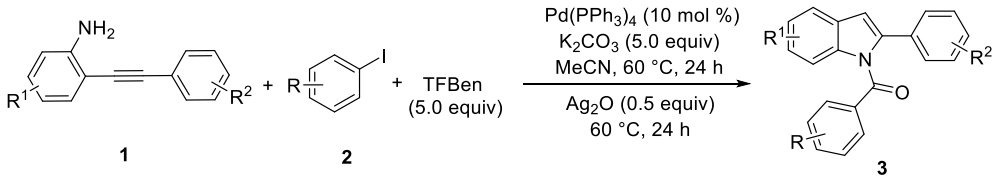
3. General procedure for the synthesis of 2-alkynylanilines (1a–f)

The 2-alkynylanilines **1a-f** were prepared according to a general procedure reported by Shi.[2]



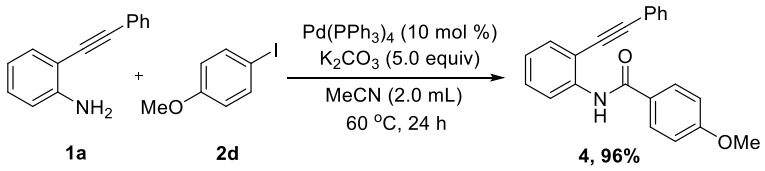
To a 50 mL flask charged with a 2-iodoaniline (5.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (70.2mg, 0.1 mmol, 2 mol %) and CuI (38.1 mg, 0.2 mmol, 4 mol %) in dry THF (5 mL) was added Et_3N (7.5 mmol, 1.5 equiv) and an aryl alkyne (6.0 mmol, 1.2 equiv) under N_2 atmosphere and the resulting solution was stirred at room temperature overnight. Upon completion, the solvent was removed under reduced pressure and the residue was extracted with ethyl acetate (3 × 5 mL), water (2 × 10 mL) and brine (10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica-gel column chromatography (petroleum ether / ethyl acetate = 20 / 1) to give the 2-alkynylaniline **1**.

4. General procedure for the synthesis of *N*-acyl indoles (3aa–an and 3ba–fa)



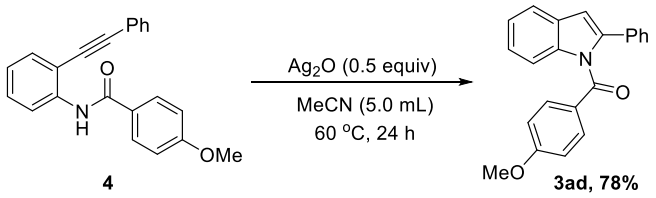
In an oven-dried *In-Ex* tube (15 mL), 2-alkynylaniline **1** (0.2 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol, 10 mol %) and K_2CO_3 (138.2 mg, 1.0 mmol, 5.0 equiv) were added to the *Ex* tube and TFBen (210.1 mg, 1.0 mmol, 5.0 equiv) was added to the *In* tube. Then the tube was placed under vacuum and refilled with nitrogen three times. An aryl iodide **2** (0.22 mmol, 1.1 equiv) and MeCN (2.0 mL) were added into the *Ex* tube via syringe. The tube was sealed and stirred at 60 °C for 24 h. Then, Ag_2O (23.2 mg, 0.1 mmol, 0.5 equiv) and MeCN (4.0 mL) were added to the *Ex* tube and the reaction was stirred at 60 °C for another 24 h. The resulting mixture was concentrated under vacuum and purified by silica-gel column chromatography (petroleum ether / ethyl acetate = 20 / 1) to obtain the product **3**.

5. Control experiments



1a **2d** **4, 96%**

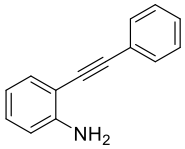
The 2-alkynylaniline **1a** (38.6 mg, 0.2 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol, 10 mol %), K_2CO_3 (138.2 mg, 1.0 mmol, 5.0 equiv) and a 1.5 mL vial containing TFBen (210.1 mg, 1.0 mmol, 5.0 equiv) were added to an oven-dried tube (15 mL). Then the tube was placed under vacuum and refilled with nitrogen three times. The aryl iodide **2d** (0.22 mmol, 1.1 equiv) and MeCN (2.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 60 °C for 24 h. The resulting mixture was concentrated under vacuum and purified by silica gel column chromatography (petroleum ether / ethyl acetate = 20 / 1) to obtain the product **4** (62.9 mg, 96% yield).



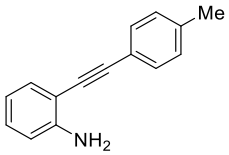
4 **3ad, 78%**

Compound **4** (65.5 mg, 0.2 mmol, 1.0 equiv) and Ag_2O (23.2 mg, 0.1 mmol, 0.5 equiv) were added to an oven-dried tube (15 mL). Then the tube was placed under vacuum and refilled with nitrogen three times. MeCN (5.0 mL) was added into the tube via syringe. The tube was sealed and stirred at 60 °C for 24 h. The resulting mixture was concentrated under vacuum and purified by silica gel column chromatography (petroleum ether / ethyl acetate = 20 / 1) to obtain the product **3ad** (51.1 mg, 78% yield).

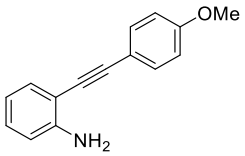
6. Characterization data of compounds 1a-f



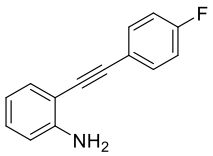
2-(phenylethynyl)aniline (1a).[3] Yellow solid in 73% yield, mp 81.5 – 84.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.41 – 7.33 (m, 4H), 7.19 – 7.11 (m, 1H), 6.76 – 6.71 (m, 2H), 4.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 132.3, 131.6, 129.9, 128.5, 128.3, 123.5, 118.1, 114.5, 108.1, 94.8, 86.0.



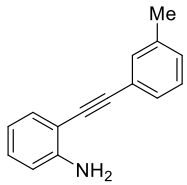
2-(*p*-tolylethynyl)aniline (1b).[4] Yellow solid in 81% yield, mp 89.5– 92.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.1 Hz, 2H), 7.40 (dd, J = 7.9, 1.4 Hz, 1H), 7.22 – 7.13 (m, 3H), 6.72 – 6.77 (m, 2H), 4.28 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 138.4, 132.2, 131.4, 129.6, 129.2, 120.3, 118.0, 114.4, 108.2, 95.0, 85.3, 21.6.



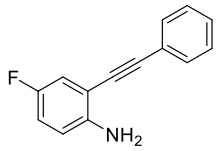
2-((4-methoxyphenyl)ethynyl)aniline (1c).[4] Yellow solid in 68% yield, mp 107.8 – 109.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.8 Hz, 2H), 7.37 (dd, J = 7.9, 1.3 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.75 – 6.68 (m, 2H), 4.06 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 147.7, 133.0, 132.1, 129.5, 118.1, 115.5, 114.4, 114.1, 108.5, 94.7, 84.5, 55.4.



2-((4-fluorophenyl)ethynyl)aniline (1d).[4] Yellow solid in 80% yield, mp 93.4 – 96.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.38 (dd, J = 7.9, 1.4 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.09 – 7.02 (m, 2H), 6.77 – 6.71 (m, 2H), 4.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 249.5 Hz, 1C), 147.9, 133.4 (d, J = 8.3 Hz, 1C), 132.2, 129.9, 119.5 (d, J = 3.4 Hz, 1C), 118.1, 115.8 (d, J = 22.1 Hz, 1C), 114.5, 107.8, 93.7, 85.7.

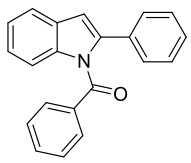


2-(*m*-tolylethynyl)aniline (1e).[4] Yellow solid in 86% yield, mp 45.6 – 47.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.32 (t, J = 7.3 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.83 – 6.76 (m, 2H), 4.34 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 138.2, 132.2, 132.1, 129.8, 129.2, 128.6, 128.4, 123.2, 118.1, 114.4, 108.1, 95.0, 85.6, 21.4.

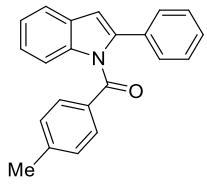


4-fluoro-2-(phenylethynyl)aniline (1f).[5] Yellow solid in 62% yield, mp 59.3 – 62.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 6.5, 2.9 Hz, 2H), 7.37 (dd, J = 6.9, 2.9 Hz, 3H), 7.08 (dd, J = 9.0, 2.9 Hz, 1H), 6.88 (td, J = 8.5, 2.9 Hz, 1H), 6.67 (dd, J = 8.8, 4.7 Hz, 1H), 4.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4 (d, J = 235.9 Hz, 1C), 144.3, 131.7, 128.7, 128.6, 122.9, 117.9 (d, J = 23.5 Hz, 1C), 117.0 (d, J = 22.8 Hz, 1C), 115.4 (d, J = 8.0 Hz, 1C), 108.8 (d, J = 9.2 Hz, 1C), 95.5, 85.1 (d, J = 2.8 Hz, 1C).

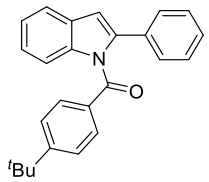
7. Characterization data of products 3aa–an, 3ba–fa, and 4



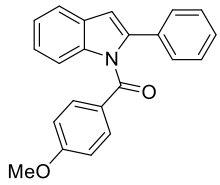
phenyl(2-phenyl-1*H*-indol-1-yl)methanone (3aa).[3] Yellow solid, 38.7 mg, 65% yield, mp 109.2 – 111.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 1H), 7.67 – 7.61 (m, 3H), 7.40 (t, J = 7.5 Hz, 1H), 7.33 – 7.24 (m, 6H), 7.19 (m, 2H), 7.15 – 7.10 (m, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 141.4, 138.3, 135.2, 133.1, 132.9, 130.4, 129.4, 128.44, 128.38, 128.3, 127.6, 124.3, 123.2, 120.8, 114.2, 109.6.



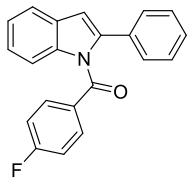
(2-phenyl-1*H*-indol-1-yl)(*p*-tolyl)methanone (3ab).[6] Yellow solid, 44.2 mg, 71% yield, mp 145.6 – 147.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 1H), 7.64 (d, J = 8.1 Hz, 3H), 7.42 – 7.37 (m, 2H), 7.34 – 7.19 (m, 5H), 7.15 (d, J = 8.1 Hz, 2H), 6.85 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 144.0, 141.5, 138.3, 133.1, 132.3, 130.6, 129.3, 129.2, 128.3, 127.6, 124.1, 123.0, 120.8, 114.0, 109.2, 21.8.



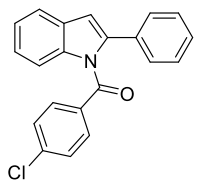
(4-(*tert*-butyl)phenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ac). Yellow oil, 53.7 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.58 – 7.55 (m, 2H), 7.29 – 7.23 (m, 6H), 7.19 – 7.13 (m, 2H), 7.12 – 7.08 (m, 1H), 6.80 – 6.74 (m, 1H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.8, 141.6, 138.4, 133.2, 132.2, 130.5, 129.4, 128.5, 128.2, 127.5, 125.3, 124.2, 123.1, 120.8, 114.2, 109.3, 35.2, 31.1; HRMS (ESI-TOF) Calcd. for $C_{25}H_{24}NO^+$ $[M+H]^+$: 354.1852; found: 354.1859.



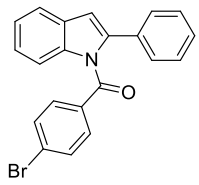
(4-methoxyphenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ad).[7] Yellow oil, 42.6 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 3H), 7.58 – 7.54 (m, 1H), 7.37 – 7.32 (m, 2H), 7.28 – 7.20 (m, 4H), 7.19 – 7.13 (m, 1H), 6.82 – 6.75 (m, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 163.6, 141.4, 138.3, 133.1, 132.9, 129.3, 128.3, 128.2, 127.6, 127.2, 124.0, 122.8, 120.8, 113.8, 108.8, 55.6.



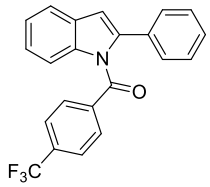
(4-fluorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ae). Yellow oil, 51.7 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 1H), 7.69 – 7.60 (m, 3H), 7.34 – 7.27 (m, 4H), 7.24 – 7.12 (m, 3H), 6.97 – 6.88 (m, 2H), 6.79 (d, J = 0.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.4 (d, J = 255.2 Hz, 1C), 141.1, 138.3, 132.9 (d, J = 9.1 Hz, 1C), 131.4 (d, J = 2.9 Hz, 1C), 129.3, 128.43, 128.39, 127.8, 124.5, 123.4, 120.9, 115.6 (d, J = 22.2 Hz, 1C), 109.6; HRMS (ESI-TOF) Calcd. for $C_{21}H_{15}FNO^+$ $[M+H]^+$: 316.1132; found: 316.1138.



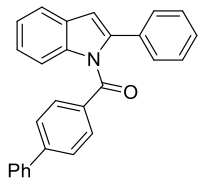
(4-chlorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3af).[8] Yellow oil, 37.8 mg, 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 1H), 7.68 – 7.63 (m, 1H), 7.57 – 7.52 (m, 2H), 7.32 – 7.25 (m, 4H), 7.23 – 7.13 (m, 5H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 141.1, 139.2, 138.2, 133.6, 132.9, 131.7, 129.3, 128.6, 128.45, 128.43, 127.9, 124.6, 123.5, 120.9, 114.2, 109.8.



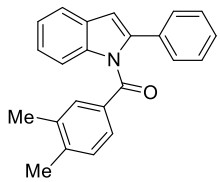
(4-bromophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ag).[9] Yellow oil, 41.4 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 1H), 7.66 – 7.60 (m, 1H), 7.47 – 7.43 (m, 2H), 7.39 – 7.34 (m, 2H), 7.31 – 7.23 (m, 4H), 7.21 – 7.12 (m, 3H), 6.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 141.1, 138.2, 134.0, 132.9, 131.7, 131.6, 129.3, 128.4, 127.9, 124.6, 123.6, 120.9, 114.2, 109.8.



(2-phenyl-1*H*-indol-1-yl)(4-(trifluoromethyl)phenyl)methanone (3ah). Yellow solid, 43.8 mg, 60% yield, mp 111.5 – 113.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 1H), 7.69 – 7.62 (m, 3H), 7.46 (d, J = 8.2 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.18 – 7.08 (m, 3H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 140.9, 138.6, 138.2, 133.8 (q, J = 32.7 Hz, 1C), 132.9, 130.4, 129.4, 128.7, 128.4, 127.9, 125.2 (d, J = 3.6 Hz, 1C), 124.9, 123.8, 123.5 (q, J = 272.7 Hz, 1C), 121.0, 114.5, 110.4; HRMS (ESI-TOF) Calcd. for $C_{22}H_{15}F_3NO^+$ $[M+H]^+$: 366.1100; found: 366.1101.

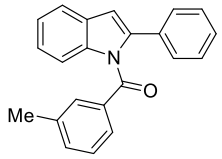


[1,1'-biphenyl]-4-yl(2-phenyl-1*H*-indol-1-yl)methanone (3ai). Yellow oil, 53.0 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 4H), 7.55 (d, J = 8.1 Hz, 2H), 7.52 – 7.38 (m, 5H), 7.36 (d, J = 8.0 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.22 (t, J = 7.5 Hz, 2H), 7.18 – 7.11 (m, 1H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 145.6, 141.4, 139.8, 138.3, 133.8, 133.1, 131.0, 129.4, 129.0, 128.5, 128.4, 128.3, 127.7, 127.3, 127.0, 124.3, 123.2, 120.9, 114.2, 109.5; HRMS (ESI-TOF) Calcd. for $C_{27}H_{20}NO^+$ $[M+H]^+$: 374.1539; found: 374.1543.

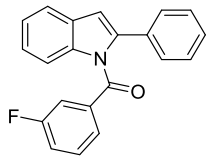


(3,4-dimethylphenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3aj). Yellow oil, 34.5 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 6.7, 1.8 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.38 – 7.15 (m,

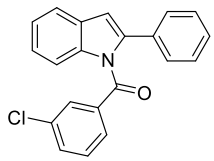
7H), 7.12 – 7.06 (m, 1H), 6.95 (s, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.76 (s, 1H), 2.40 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 142.2, 141.4, 138.6, 138.0, 133.4, 132.6, 132.0, 130.3, 129.5, 128.3, 128.0, 127.6, 126.4 124.4, 123.2, 120.8, 114.3, 110.1, 21.5, 19.8; HRMS (ESI-TOF) Calcd. for $C_{23}H_{20}NO^+$ $[M+H]^+$: 326.1539; found: 326.1541.



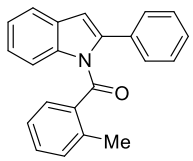
(2-phenyl-1*H*-indol-1-yl)(*m*-tolyl)methanone (3ak). Yellow oil, 36.7 mg, 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 (s, 1H), 7.34 – 7.25 (m, 4H), 7.24 – 7.12 (m, 5H), 6.79 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3 141.4, 138.3, 138.1, 135.0, 133.7, 133.3, 131.0, 129.3, 128.3, 128.2, 127.6, 124.3, 123.2, 120.8, 114.2, 109.5, 21.2; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}NO^+$ $[M+H]^+$: 312.1383; found: 312.1385.



(3-fluorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3al). Yellow oil, 35.9 mg, 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 1H), 7.69 – 7.63 (m, 1H), 7.40 – 7.26 (m, 6H), 7.23 – 7.11 (m, 4H), 7.09 – 7.02 (m, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 162.2 (d, *J* = 248.3 Hz, 1C), 141.0, 138.3, 137.3 (d, *J* = 7.0 Hz, 1C), 133.0, 130.0 (d, *J* = 7.8 Hz, 1C), 129.4, 128.5, 128.4, 127.8, 126.0 (d, *J* = 3.0 Hz, 1C), 124.7, 123.6, 120.9, 119.7 (d, *J* = 21.3 Hz, 1C), 117.1 (d, *J* = 23.1 Hz, 1C), 114.3, 110.0; HRMS (ESI-TOF) Calcd. for $C_{21}H_{15}FNO^+$ $[M+H]^+$: 316.1132; found: 316.1133.

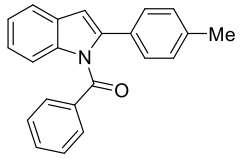


(3-chlorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3am). Yellow oil, 27.2 mg, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 1H), 7.68 – 7.61 (m, 1H), 7.53 – 7.40 (m, 2H), 7.36 – 7.24 (m, 5H), 7.22 – 7.09 (m, 4H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 141.0, 138.2, 136.9, 134.3, 133.0, 132.6, 130.3, 129.6, 129.3, 128.5, 128.4, 128.3, 127.9, 124.8, 123.7, 120.9, 114.4, 110.1; HRMS (ESI-TOF) Calcd. for $C_{21}H_{15}ClNO^+$ $[M+H]^+$: 332.0837; found: 332.0839.

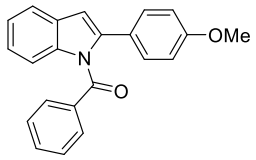


(2-phenyl-1*H*-indol-1-yl)(*o*-tolyl)methanone (3an). Yellow oil, 14.9 mg, 24% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.59 (m, 2H), 7.29 – 7.24 (m, 3H), 7.21 – 7.12 (m, 5H), 7.06 – 6.96 (m, 3H), 6.70 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 141.3, 138.1, 138.0, 135.6,

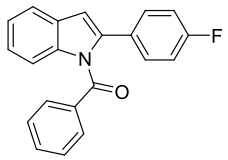
133.4, 131.5, 131.1, 129.8, 128.4, 128.0, 127.7, 125.6, 124.7, 123.5, 120.8, 114.5, 110.5, 19.8; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}NO^+$ $[M+H]^+$: 312.1383; found: 312.1385.



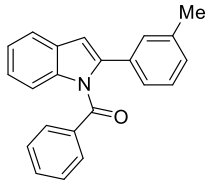
phenyl(2-(*p*-tolyl)-1*H*-indol-1-yl)methanone (3ba).[4] Yellow solid, 27.4 mg, 44% yield, mp 115.7 – 118.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 4H), 7.47 (t, J = 7.5 Hz, 1H), 7.36 – 7.23 (m, 6H), 7.05 (d, J = 7.9 Hz, 2H), 6.80 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.6, 138.2, 137.5, 135.2, 132.9, 130.4, 130.2, 129.5, 129.0, 128.4, 128.3, 124.1, 123.1, 120.7, 114.1, 109.1, 21.3.



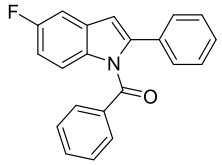
(2-(4-methoxyphenyl)-1*H*-indol-1-yl)(phenyl)methanone (3ca).[4] Yellow oil, 41.3 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 4H), 7.39 (t, J = 7.5 Hz, 1H), 7.29 – 7.19 (m, 6H), 6.74 – 6.67 (m, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.1, 141.2, 138.1, 135.2, 132.9, 130.3, 129.7, 129.5, 128.4, 125.7, 124.0, 123.1, 120.6, 114.1, 113.8, 108.6, 55.3.



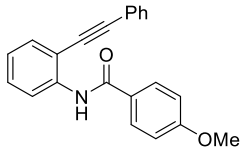
(2-(4-fluorophenyl)-1*H*-indol-1-yl)(phenyl)methanone (3da).[4] Yellow solid, 46.0 mg, 71% yield, mp 118.3 – 120.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 4H), 7.43 (t, J = 7.5 Hz, 1H), 7.31 – 7.22 (m, 6H), 6.88 (t, J = 8.6 Hz, 2H), 6.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 162.2 (d, J = 248.0 Hz, 1C), 140.2, 138.2, 135.1, 133.1, 130.3, 130.1 (d, J = 8.2 Hz, 1C), 129.3 (d, J = 3.4 Hz, 1C), 129.25, 128.5, 124.4, 123.3, 120.8, 115.4 (d, J = 21.8 Hz, 1C), 114.2, 109.7.



phenyl(2-(*m*-tolyl)-1*H*-indol-1-yl)methanone (3ea). Yellow solid, 43.0 mg, 69% yield, mp 104.3 – 106.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 1H), 7.67 – 7.60 (m, 3H), 7.39 (t, J = 7.4 Hz, 1H), 7.30 – 7.23 (m, 4H), 7.15 – 7.03 (m, 3H), 6.93 (d, J = 7.4 Hz, 1H), 6.78 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.5, 138.3, 137.8, 135.3, 133.0, 132.8, 130.2, 129.4, 129.3, 128.4, 128.3, 128.2, 125.5, 124.3, 123.2, 120.8, 114.2, 109.3, 21.4; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}NO^+$ $[M+H]^+$: 312.1383; found: 312.1385.



(5-fluoro-2-phenyl-1*H*-indol-1-yl)(phenyl)methanone (3fa). White solid, 51.7 mg, 82% yield, mp 94.3 – 95.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 9.1, 4.5 Hz, 1H), 7.57 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.31 – 7.20 (m, 5H), 7.19 – 7.10 (m, 3H), 6.99 (td, J = 9.1, 2.5 Hz, 1H), 6.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 159.6 (d, J = 239.2 Hz, 1C), 142.9, 134.9, 134.7, 133.0, 132.8 130.3, 130.1 (d, J = 10.2 Hz, 1C), 128.5, 128.4, 128.3, 127.9, 115.2 (d, J = 9.1 Hz, 1C), 112.2 (d, J = 25.3 Hz, 1C), 109.1 (d, J = 3.8 Hz, 1C), 106.1 (d, J = 23.8 Hz, 1C); HRMS (ESI-TOF) Calcd. for $C_{21}H_{15}FNO^{+}$ $[M+H]^{+}$: 316.1132; found: 316.1133.



4-methoxy-*N*-(2-(phenylethynyl)phenyl)benzamide (4).[10] Yellow solid, 62.9 mg, 96% yield, mp 112.8 – 114.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.62 (d, J = 8.3 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.58 – 7.50 (m, 3H), 7.44 – 7.38 (m, 4H), 7.10 (td, J = 7.6, 0.9 Hz, 1H), 6.99 – 6.93 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.8, 139.4, 131.6, 131.5, 130.0, 129.1, 129.0, 128.8, 127.3, 123.4, 122.4, 119.2, 114.2, 112.2, 97.0, 84.7, 55.6.

8. References

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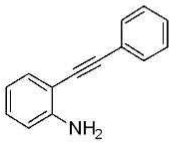
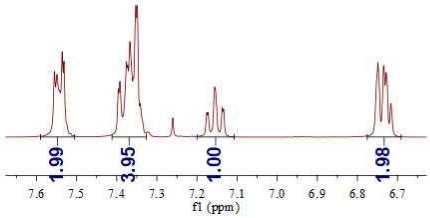
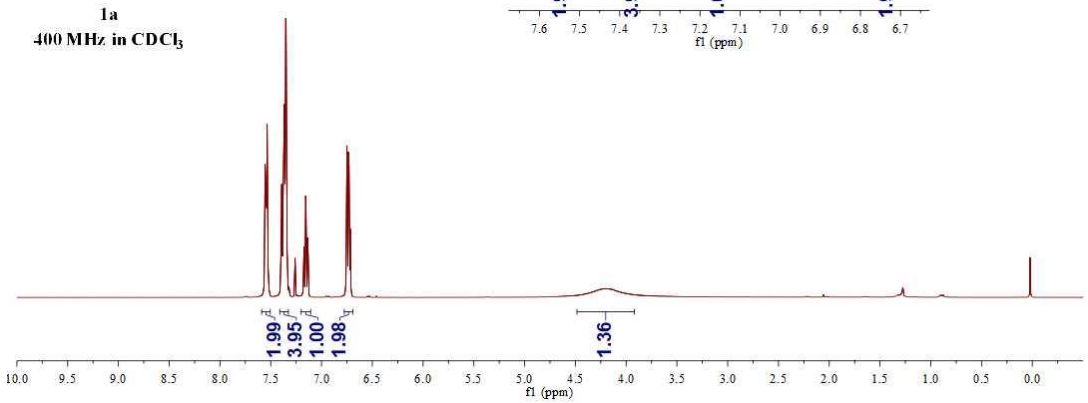
9. ^{1}H, ^{13}C spectra of 1a–f, 3aa–an, 3ba–fa, and 4

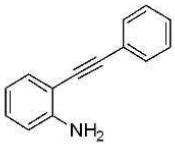


1a

400 MHz in $CDCl_3$

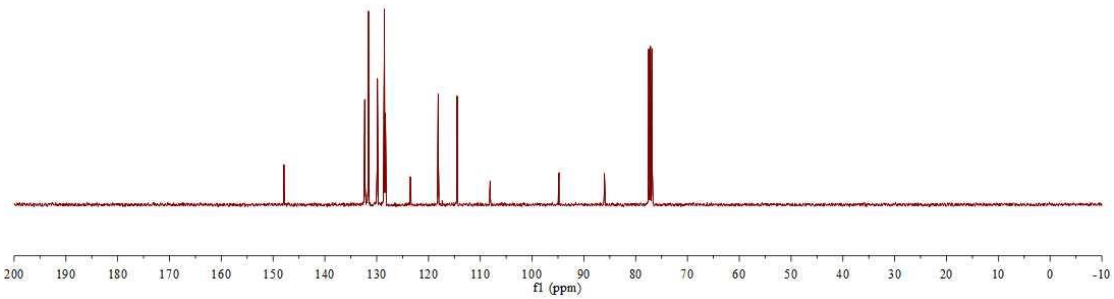


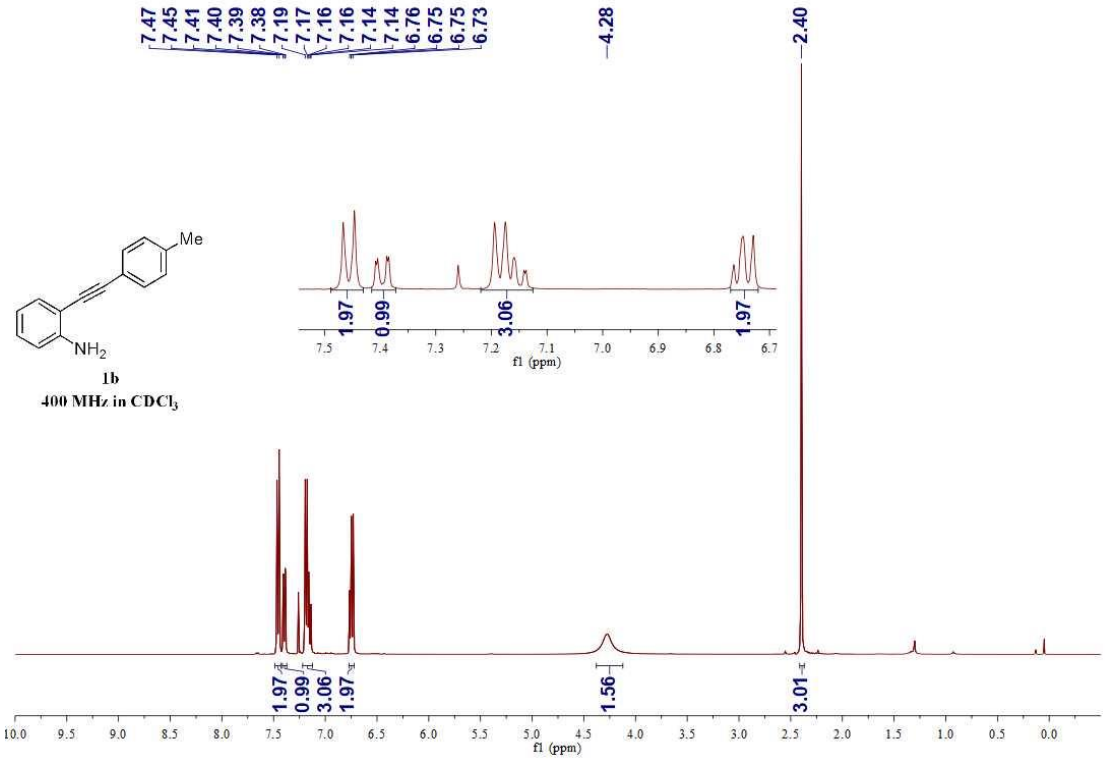




1a

100 MHz in $CDCl_3$

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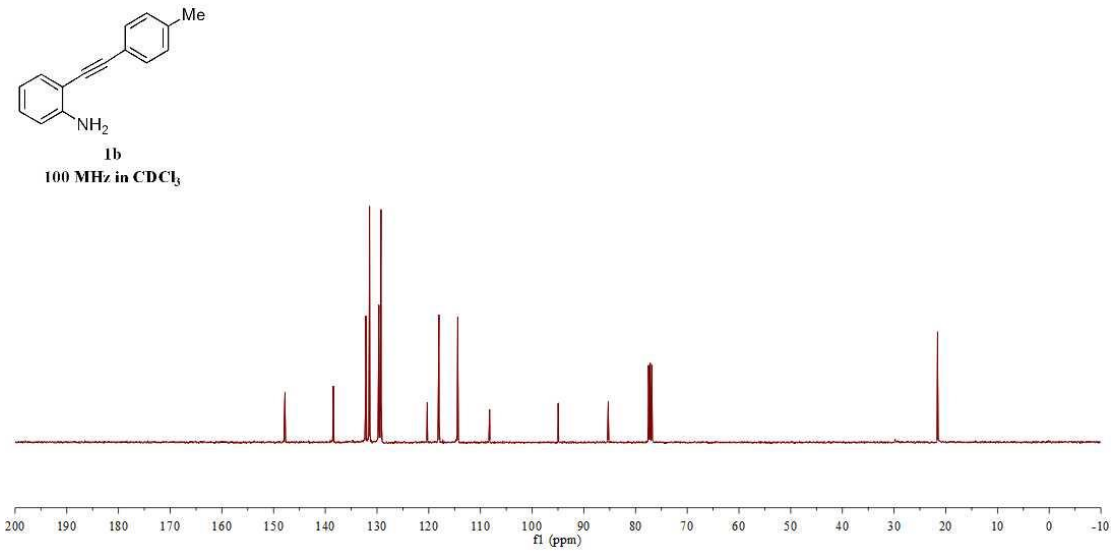
7.14
7.14
6.76
6.75
6.75
6.73
4.28
2.40
Me
NH2
1b
400 MHz in CDCl3
1.97
0.99
3.06
1.97
f1 (ppm)
1.97
0.99
3.06
1.97
1.56
3.01
f1 (ppm)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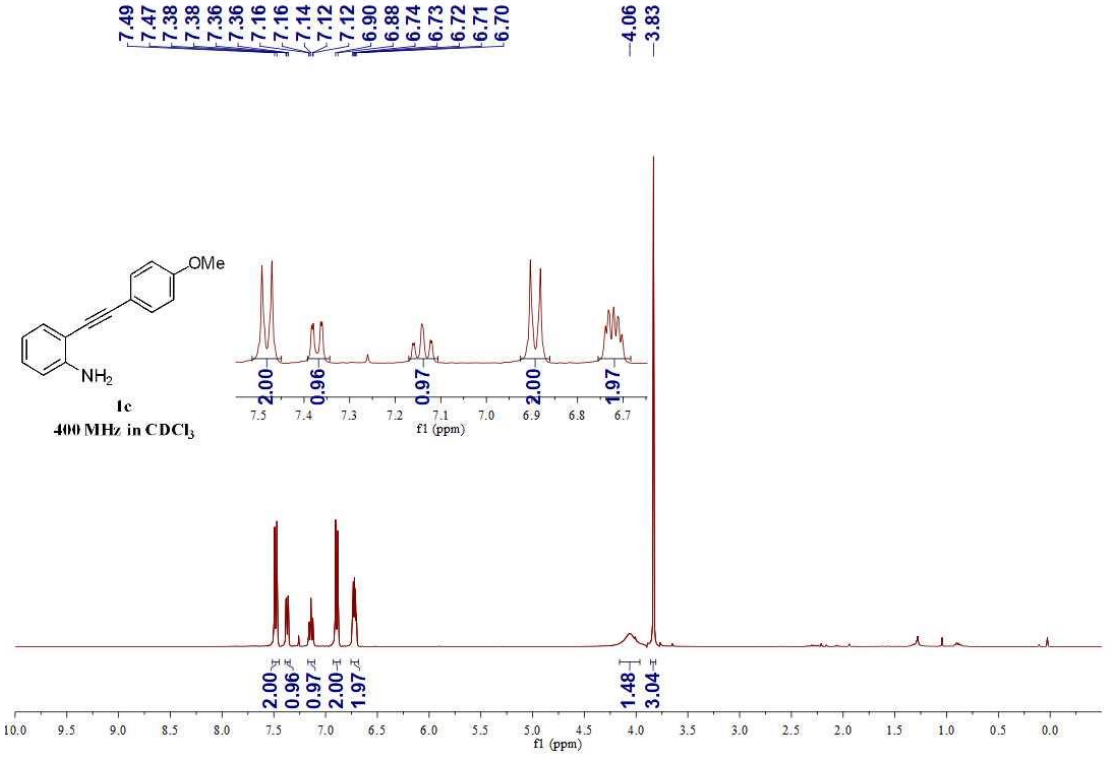
Me
NH2
1b
100 MHz in CDCl3
f1 (ppm)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6.73
6.72
6.71
6.70
4.06
3.83
OMe
NH2
1c
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2.00
0.96
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2.00
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f1 (ppm)
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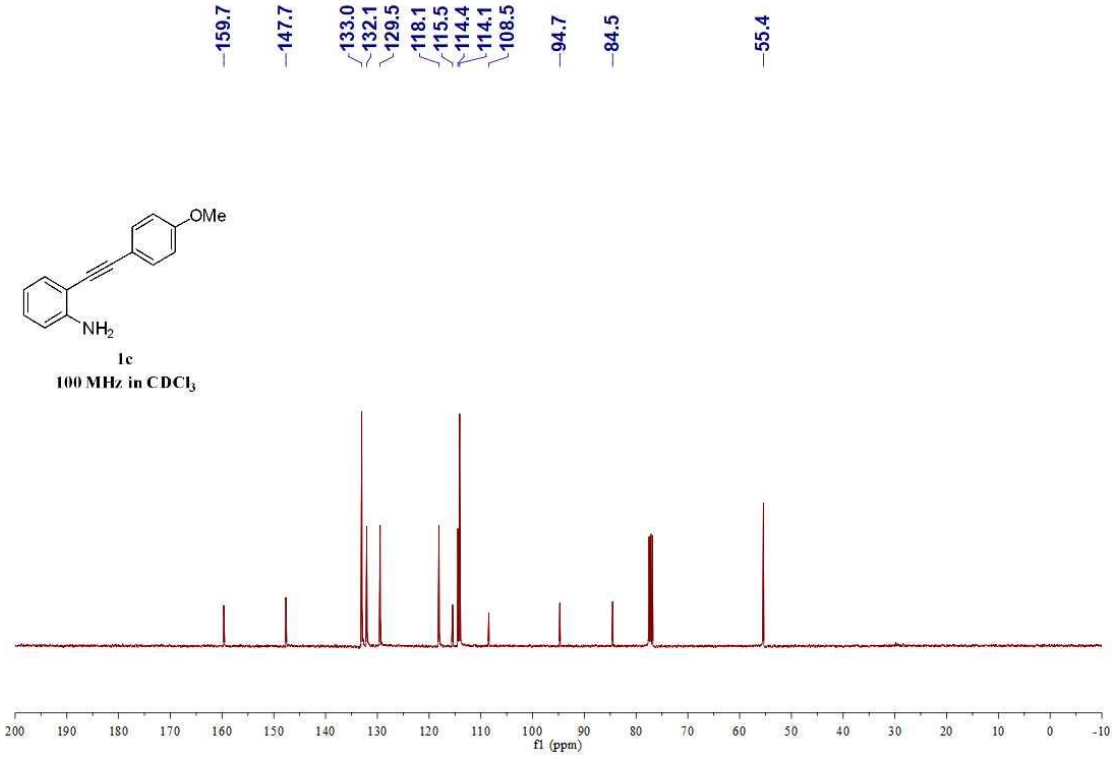
3.04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NH2
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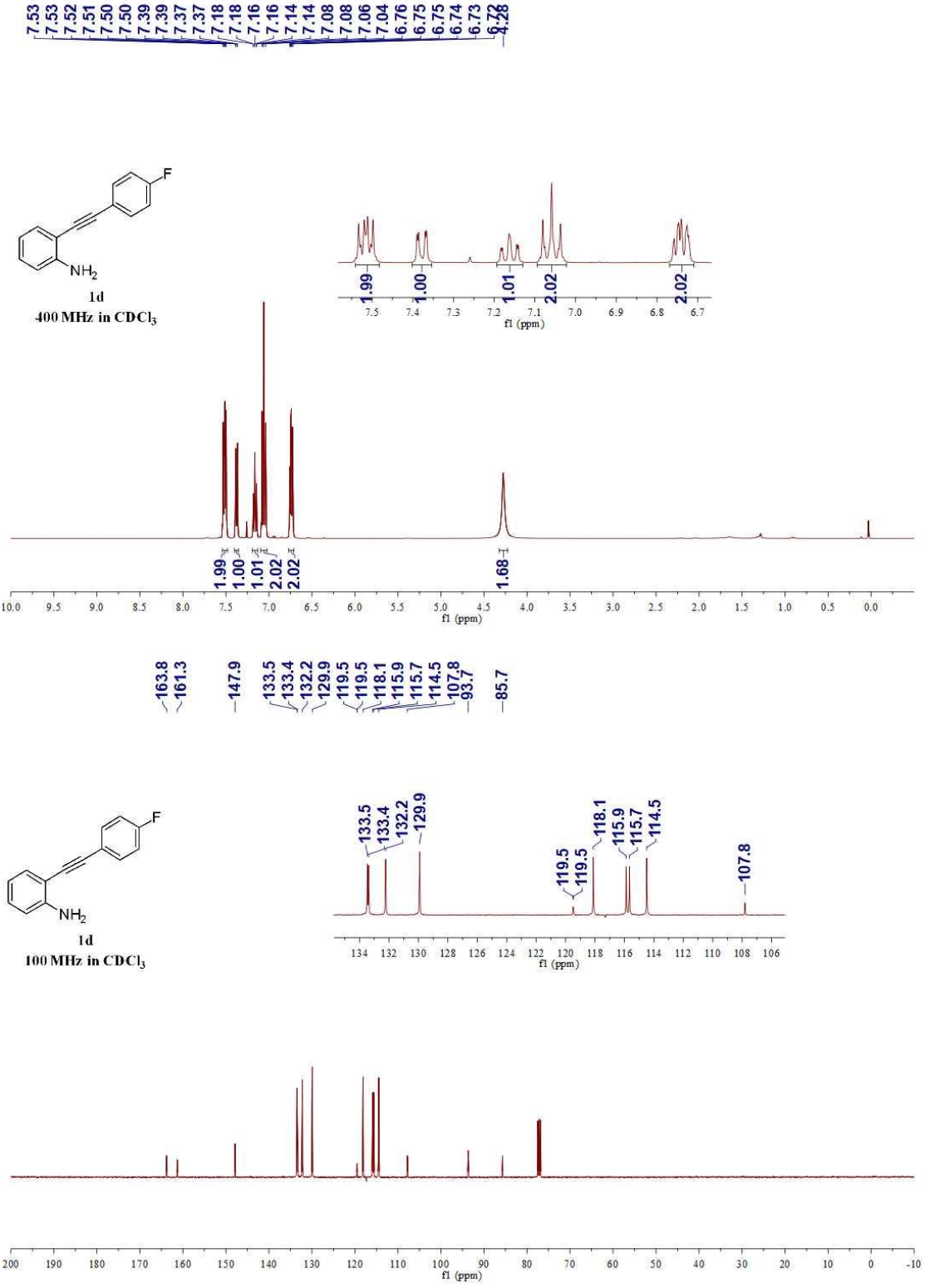
100 MHz in CDCl3
f1 (ppm)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7.16
7.14
7.14
7.08
7.08
7.06
7.04
6.76
6.75
6.74
6.73
4.28
F
NH2
1d
400 MHz in CDCl3
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1.00
1.01
2.02
2.02
1.68
f1 (ppm)
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161.3
147.9
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NH2
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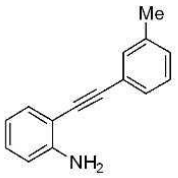
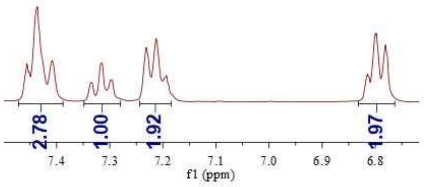
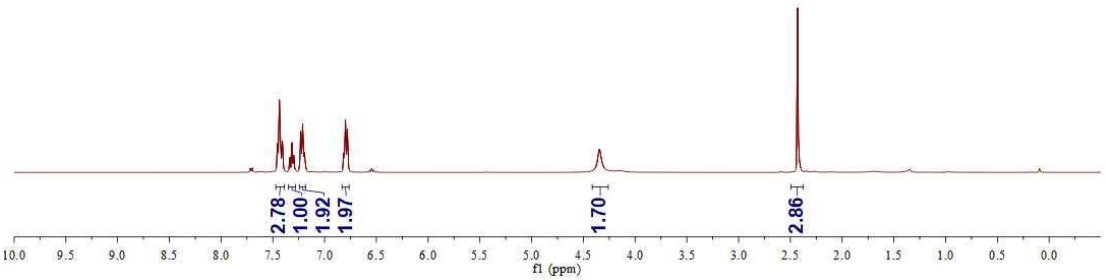
f1 (ppm)

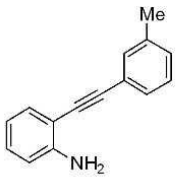


1e

400 MHz in $CDCl_3$

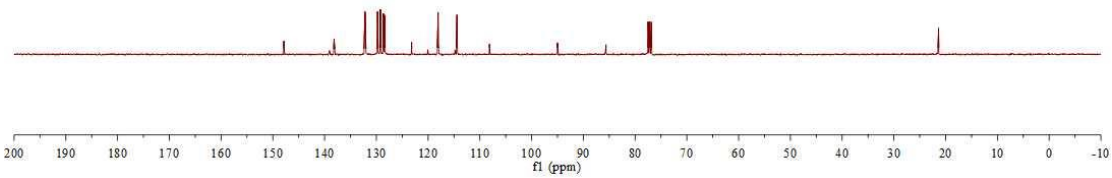


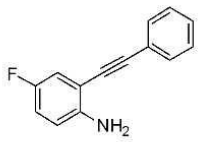




1e

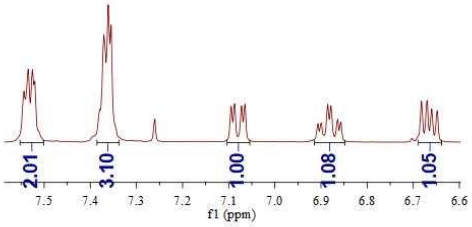
100 MHz in $CDCl_3$

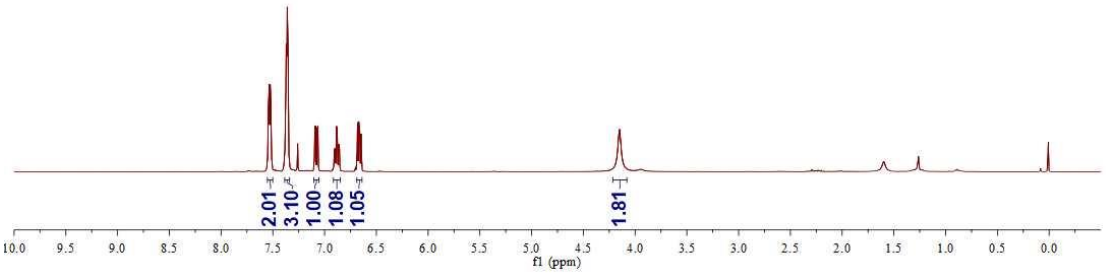


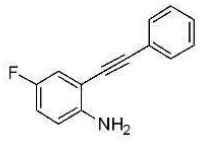


1f

400 MHz in $CDCl_3$

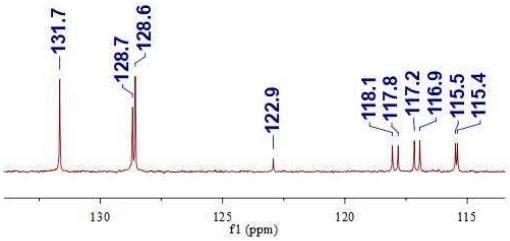


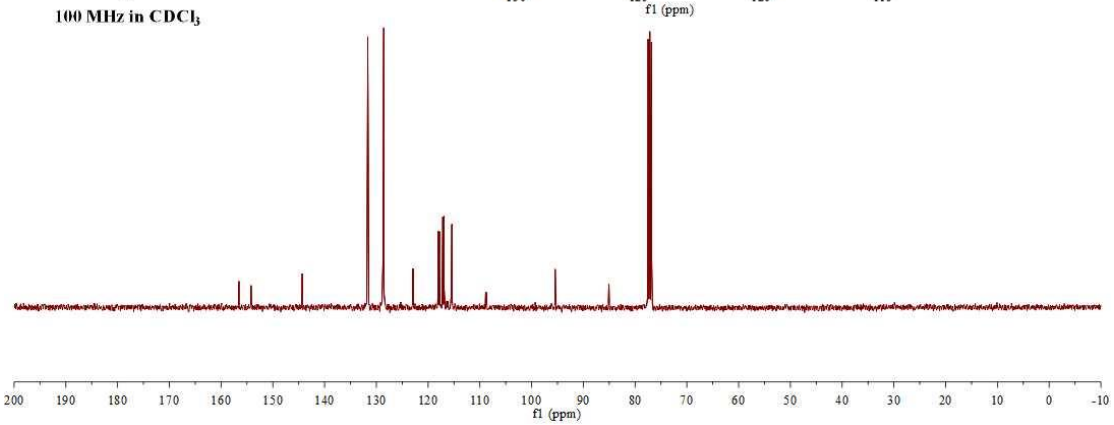


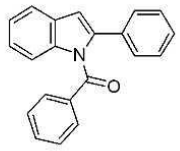


1f

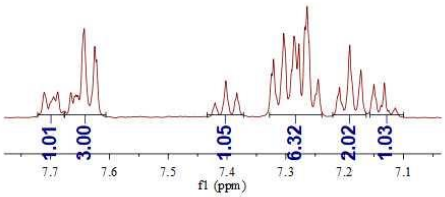
100 MHz in $CDCl_3$

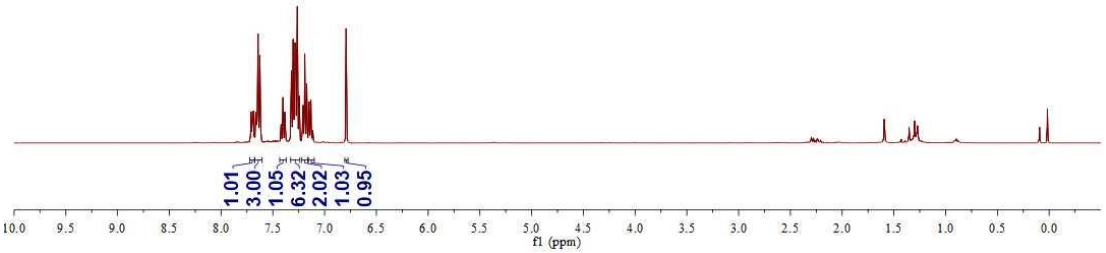


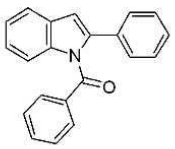




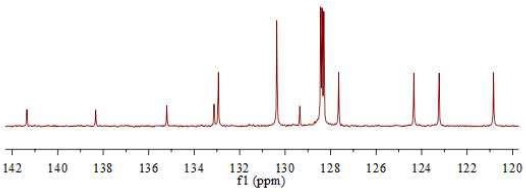
3aa
400 MHz in $CDCl_3$

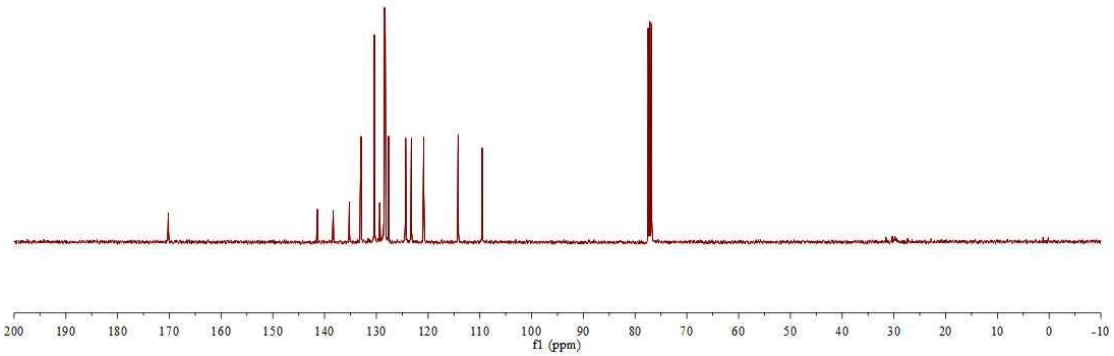






3aa
100 MHz in $CDCl_3$






7.71
7.70
7.69
7.69
7.65
7.63
7.40
7.40
7.40
7.38
7.38
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.25
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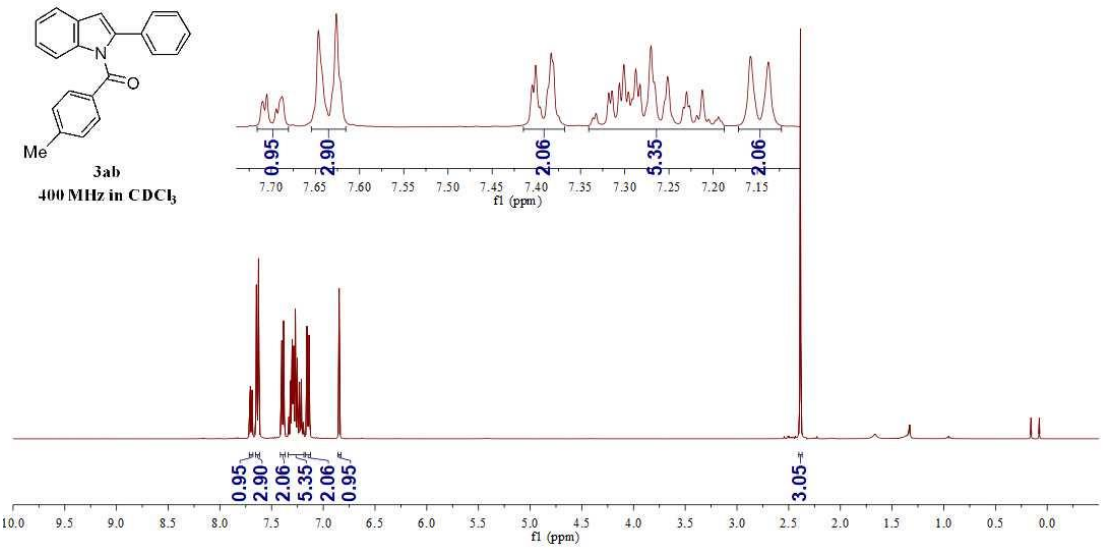
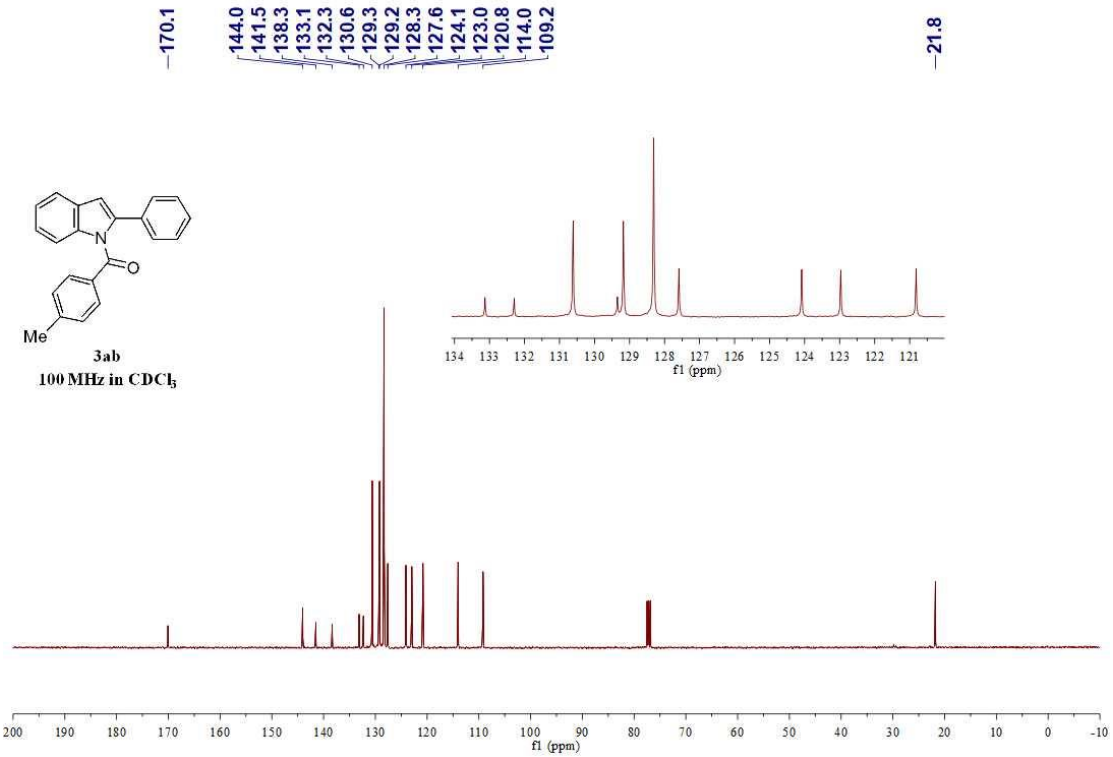
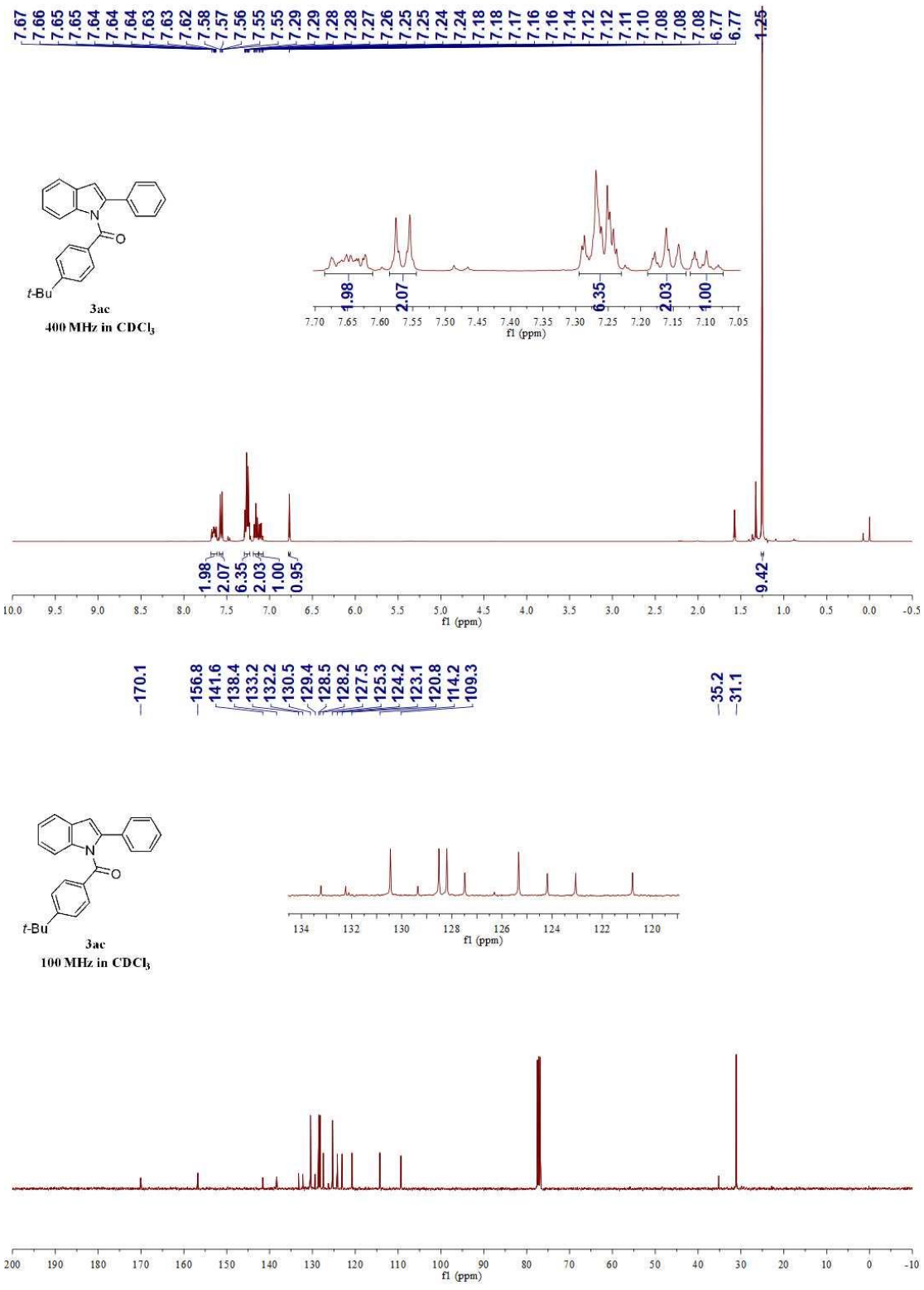
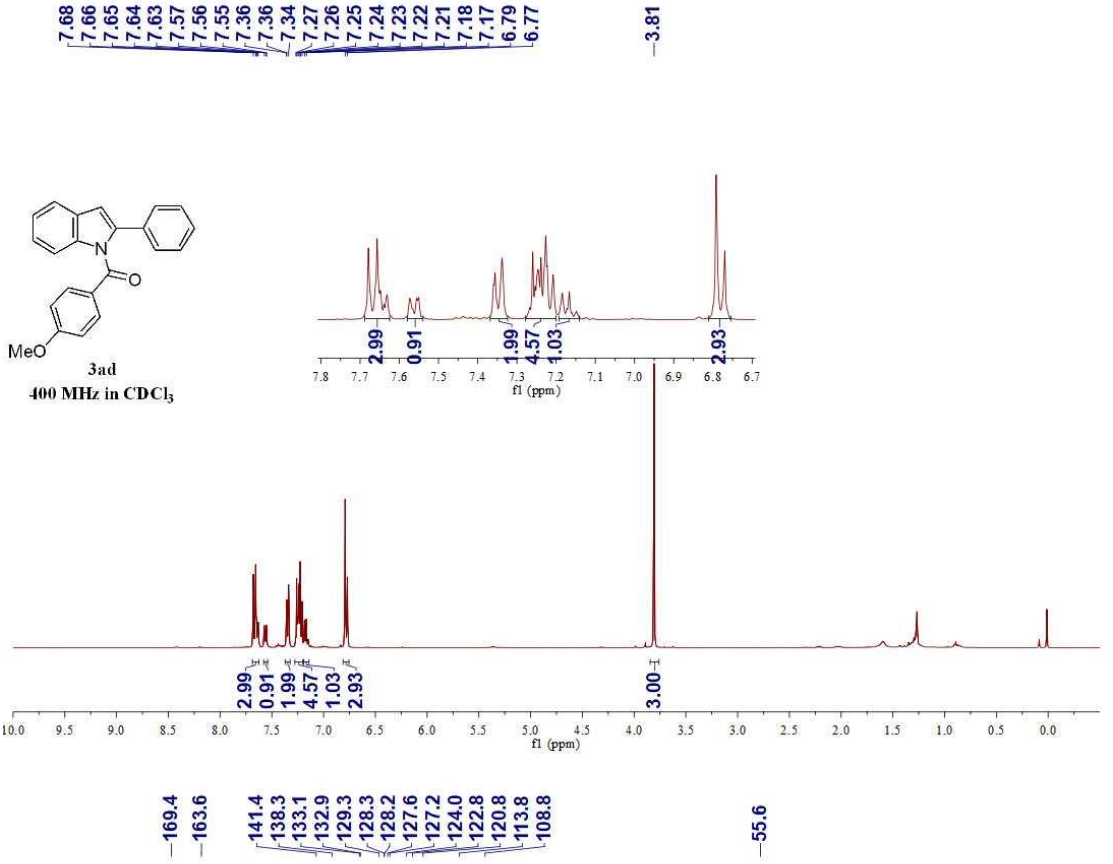
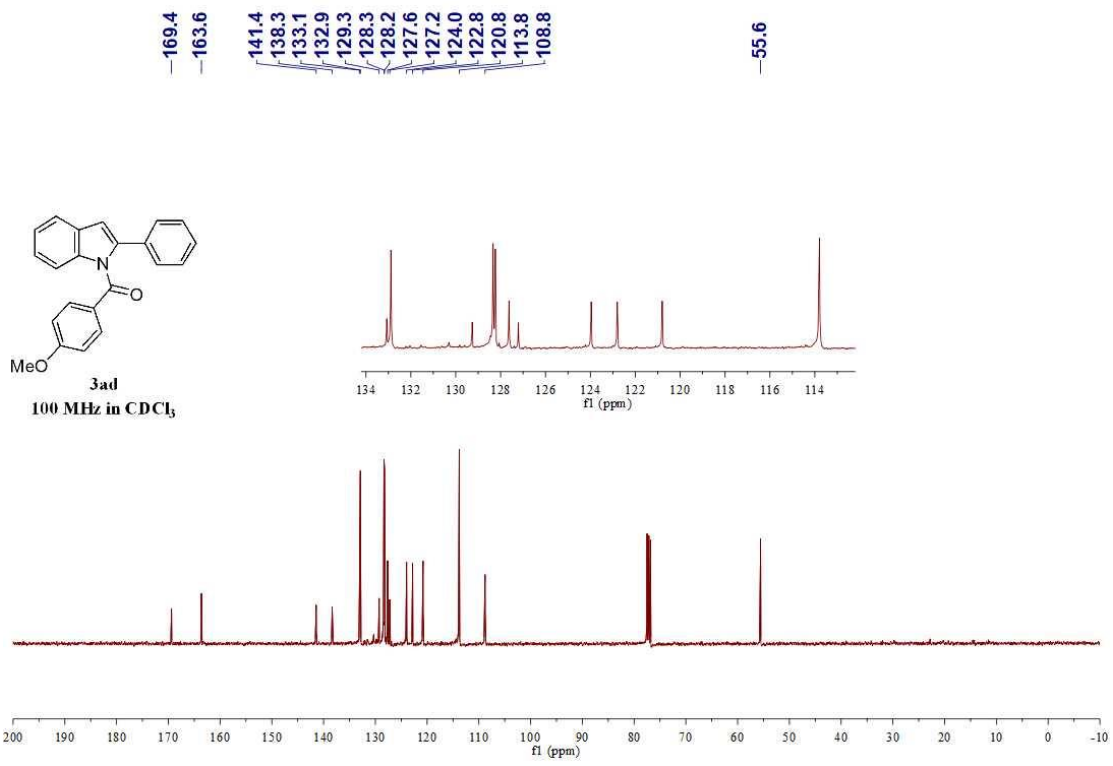
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.16
7.14
2.39


Me
3ab
400 MHz in CDCl3
0.95
2.90
2.06
5.35
2.06
f1 (ppm)
0.95
2.90
2.06
5.35
2.06
0.95
3.05
f1 (ppm)

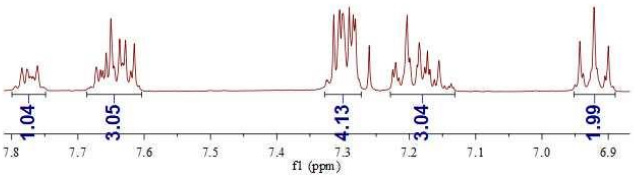

170.1
144.0
141.5
138.3
133.1
132.3
130.6
129.3
129.2
128.3
127.6
124.1
123.0
120.8
114.0
109.2
21.8
Me
3ab
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

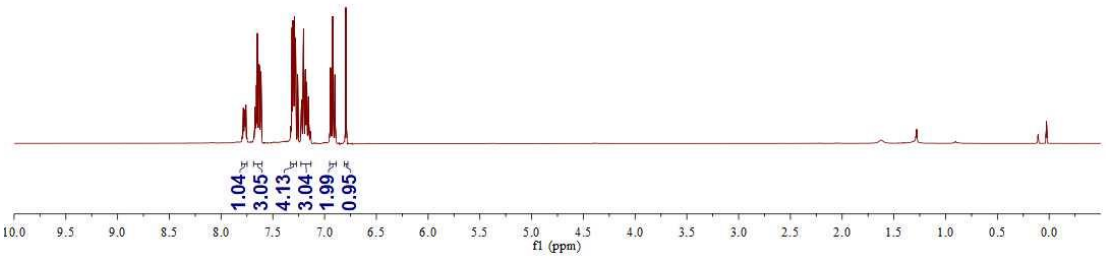

7.67 7.66 7.65 7.65 7.64 7.64 7.64 7.63 7.63 7.62 7.58 7.57 7.56 7.55 7.55 7.29 7.29 7.28 7.28 7.27 7.26 7.25 7.25 7.24 7.24 7.18 7.18 7.17 7.16 7.16 7.14 7.12 7.12 7.11 7.10 7.08 7.08 7.08 6.77 6.77 1.25
t-Bu
3ac
400 MHz in CDCl3
1.98 2.07 6.35 2.03 1.00
f1 (ppm)
1.98 2.07 6.35 2.03 1.00 0.95 9.42
f1 (ppm)
170.1 156.8 141.6 138.4 133.2 132.2 130.5 129.4 128.5 128.2 127.5 125.3 124.2 123.1 120.8 114.2 109.3 35.2 31.1
t-Bu
3ac
100 MHz in CDCl3
f1 (ppm)
f1 (ppm)

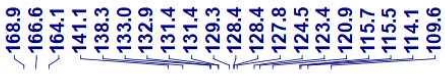

7.68
7.66
7.65
7.64
7.63
7.57
7.56
7.55
7.36
7.36
7.34
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.18
7.17
6.79
6.77
3.81
MeO
3ad
400 MHz in CDCl3
2.99
0.91
1.99
4.57
1.03
2.93
3.00
f1 (ppm)

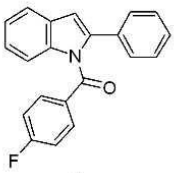

169.4
163.6
141.4
138.3
133.1
132.9
129.3
128.3
128.2
127.6
127.2
124.0
122.8
120.8
113.8
108.8
55.6
MeO
3ad
100 MHz in CDCl3
f1 (ppm)

3ae
400 MHz in $CDCl_3$

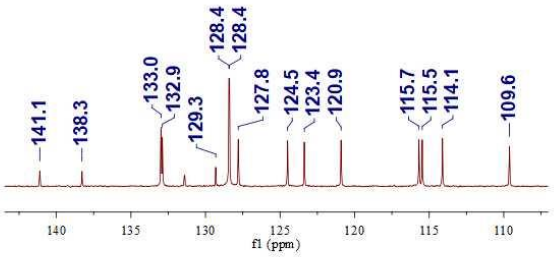


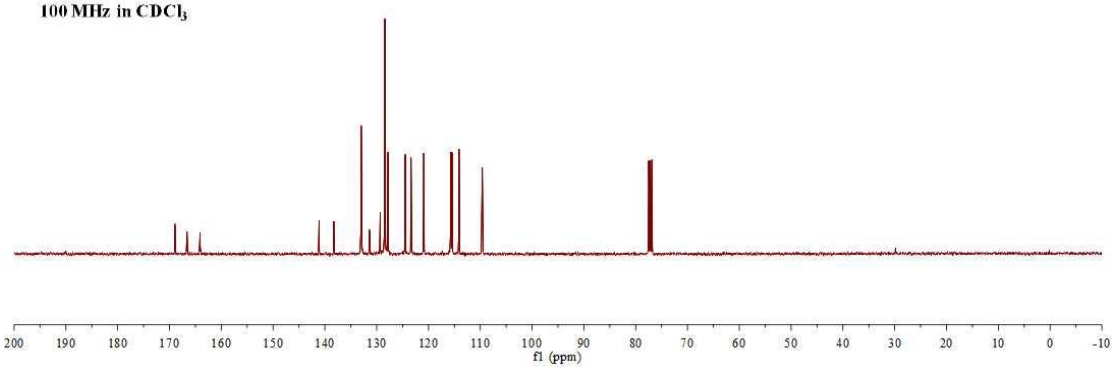


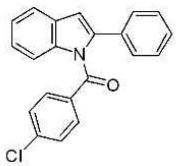




3ae
100 MHz in $CDCl_3$

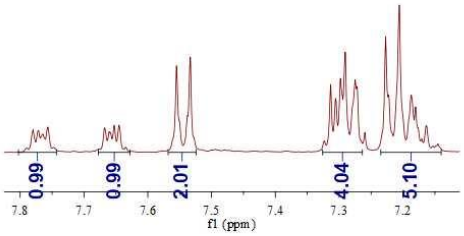


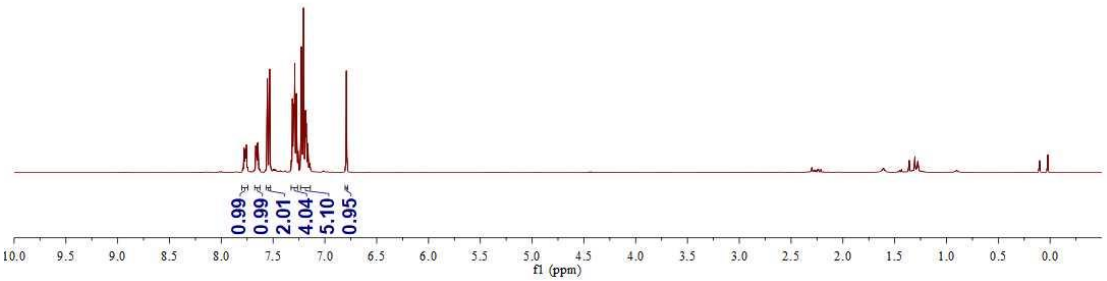


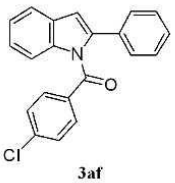


3af

400 MHz in $CDCl_3$

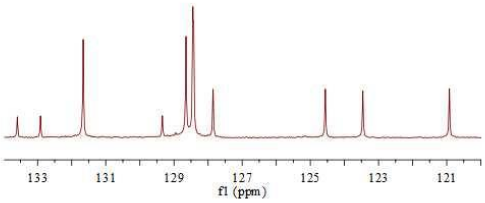


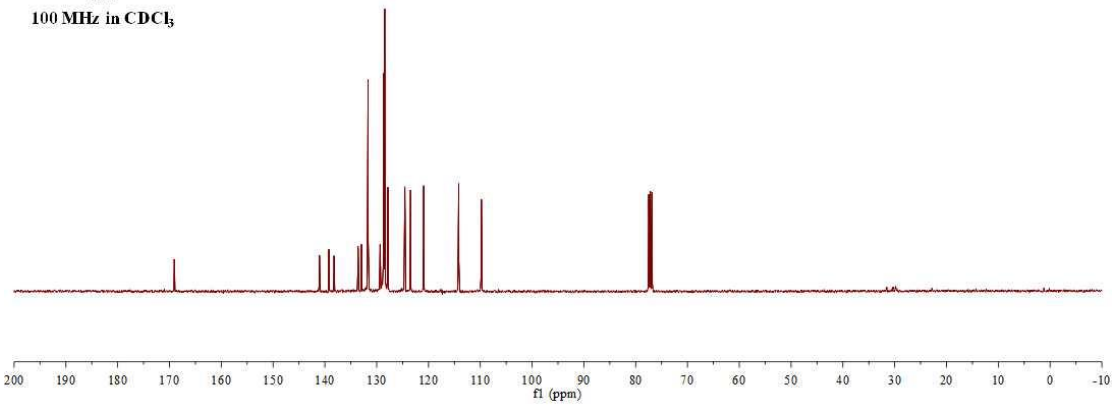


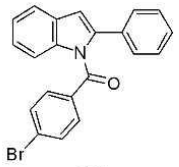


3af

100 MHz in $CDCl_3$

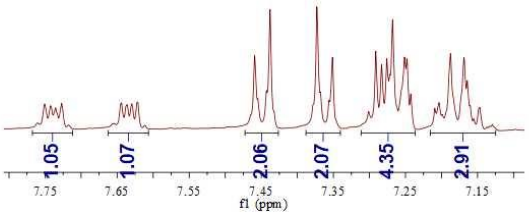


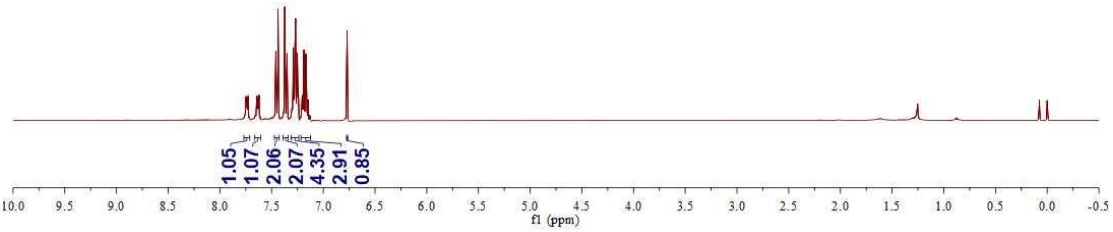


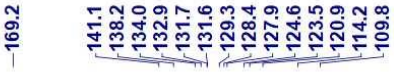


3ag

400 MHz in $CDCl_3$

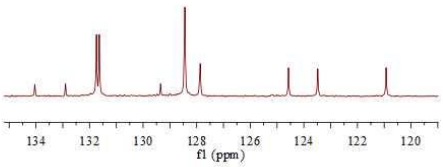


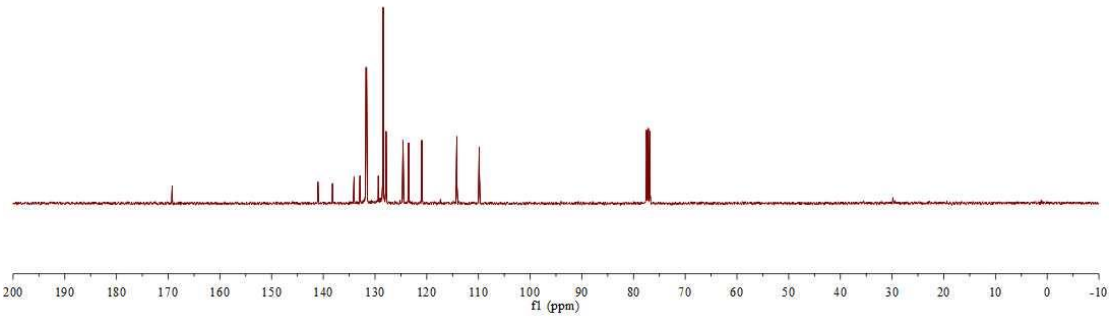


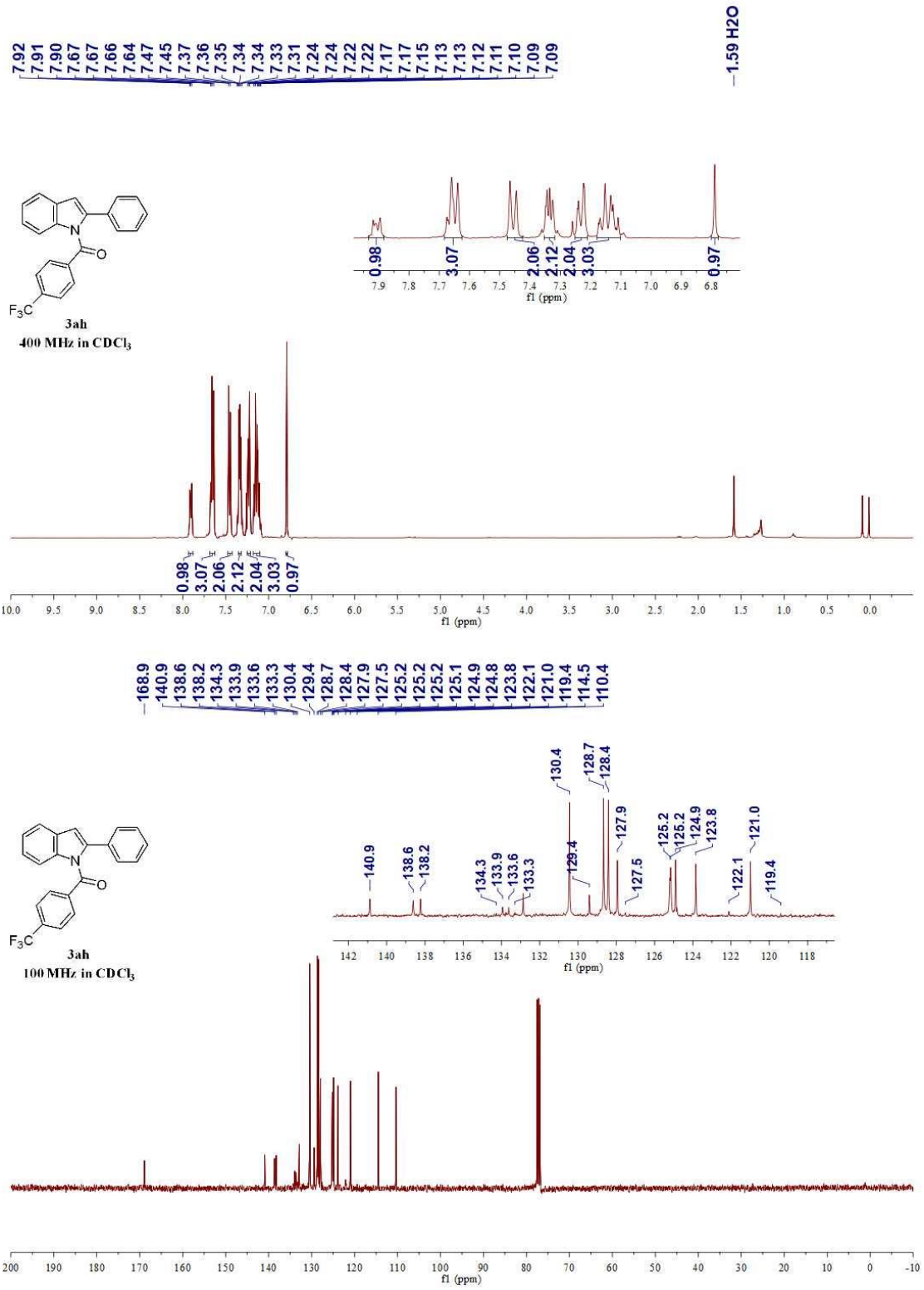


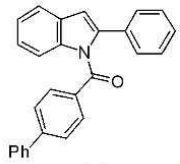
3ag

100 MHz in $CDCl_3$

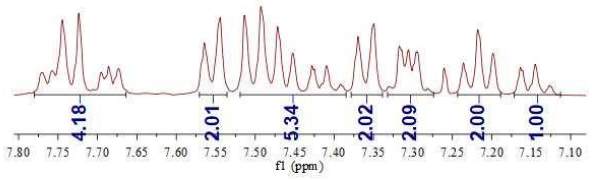


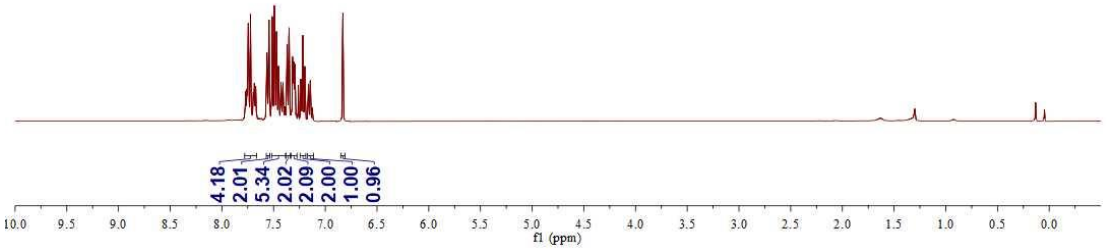


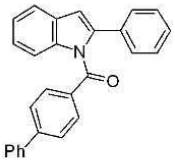

7.92
7.91
7.90
7.67
7.67
7.66
7.64
7.47
7.45
7.37
7.36
7.35
7.34
7.34
7.33
7.31
7.24
7.24
7.22
7.22
7.17
7.17
7.15
7.13
7.13
7.12
7.11
7.10
7.09
7.09
1.59 H2O
0.98
3.07
2.06
2.12
2.04
3.03
0.97
f1 (ppm)
3ah
400 MHz in CDCl3
f1 (ppm)
168.9
140.9
138.6
138.2
134.3
133.9
133.6
133.3
130.4
129.4
128.7
128.4
127.9
127.5
125.2
125.2
125.2
125.1
124.9
124.8
123.8
122.1
121.0
119.4
114.5
110.4
f1 (ppm)
3ah
100 MHz in CDCl3
f1 (ppm)



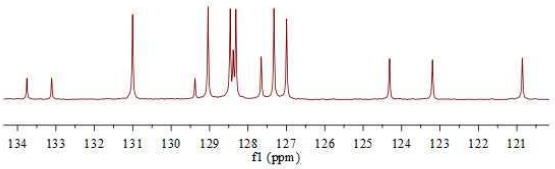
3ai
400 MHz in $CDCl_3$

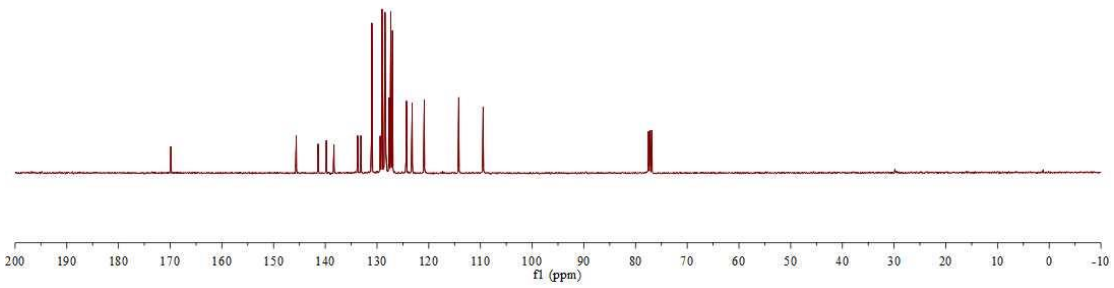


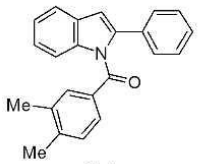




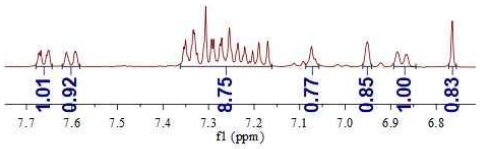
3ai
100 MHz in $CDCl_3$

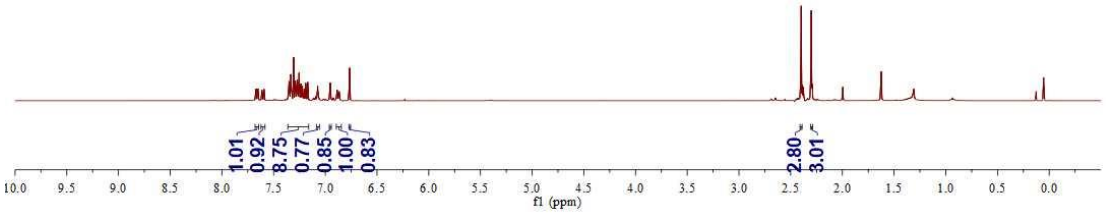


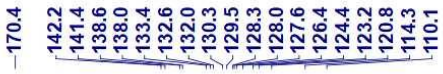


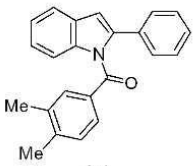


3aj
400 MHz in $CDCl_3$

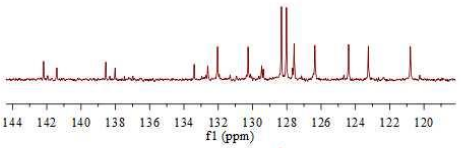


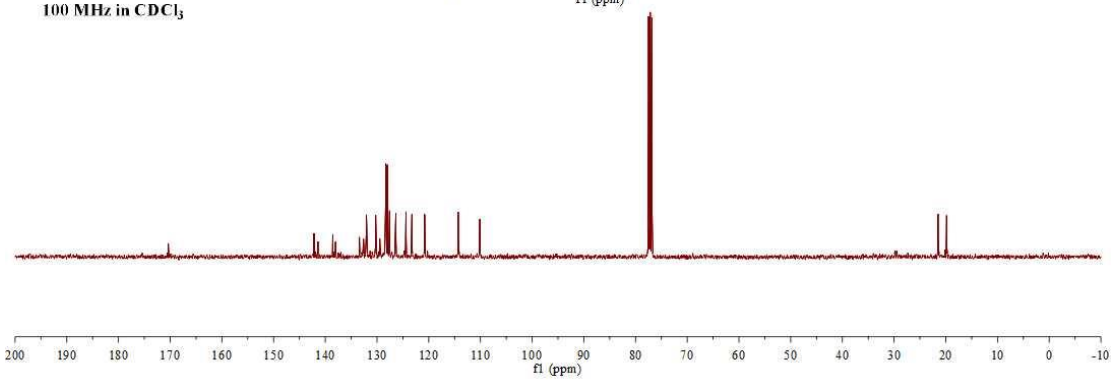


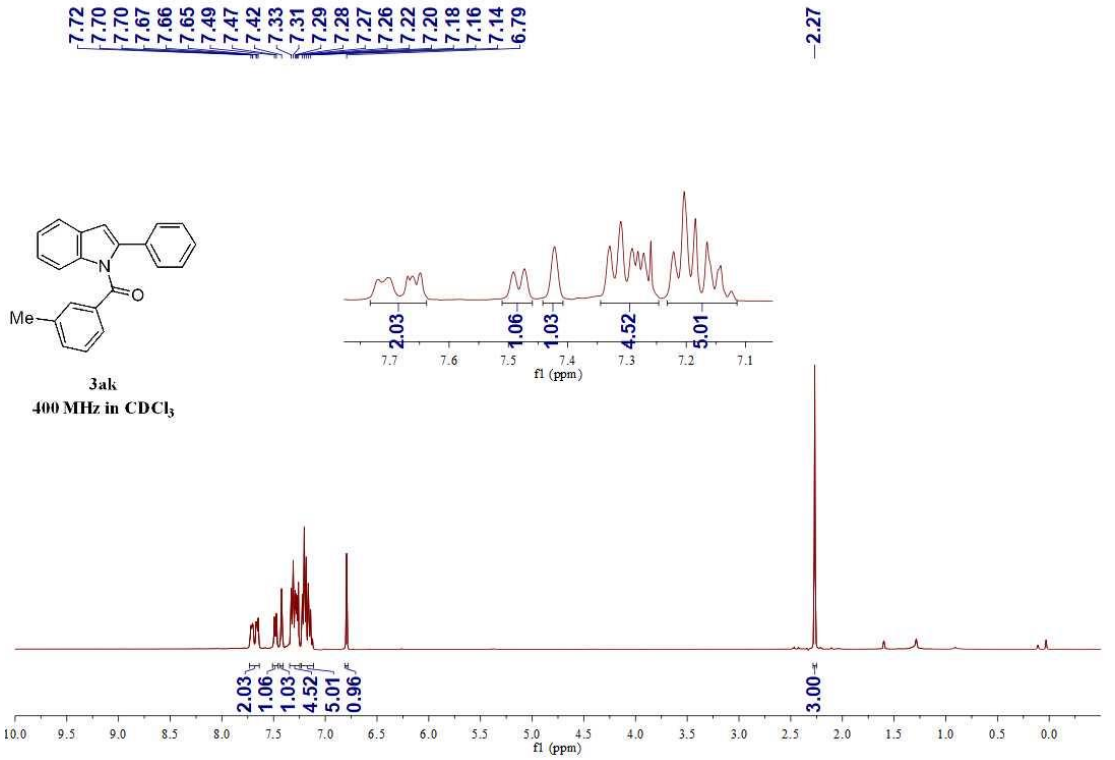


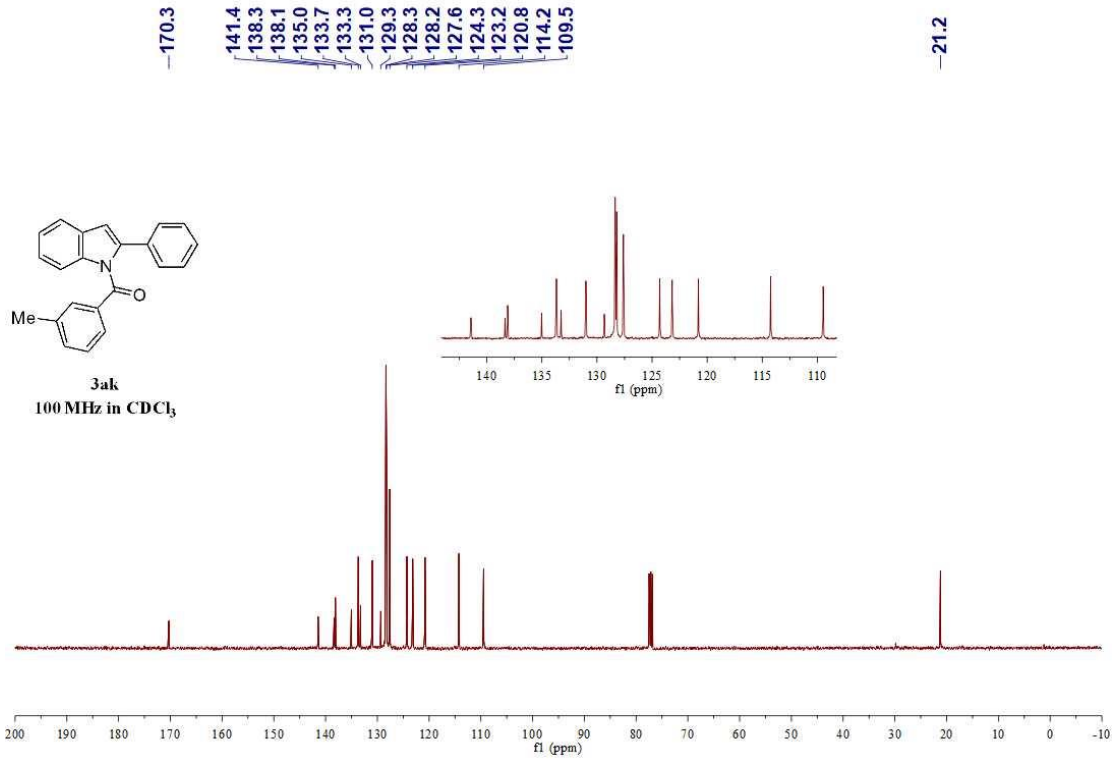


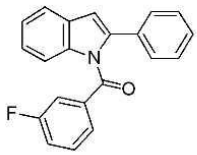
3aj
100 MHz in $CDCl_3$



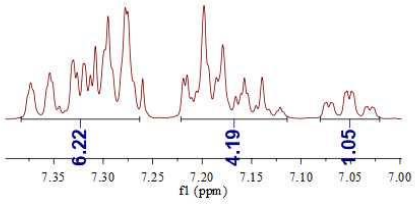


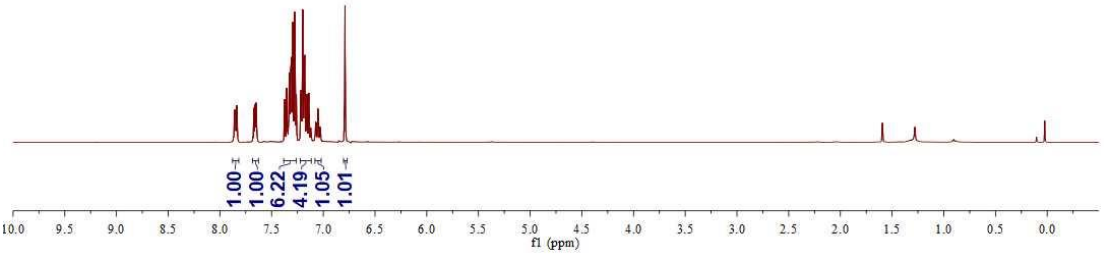

7.72
7.70
7.70
7.67
7.66
7.65
7.49
7.47
7.42
7.33
7.31
7.29
7.28
7.27
7.26
7.22
7.20
7.18
7.16
7.14
6.79
2.27
Me
3ak
400 MHz in CDCl3
2.03
1.06
1.03
4.52
5.01
f1 (ppm)
0.96
3.00

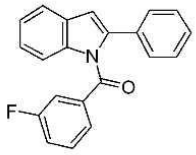

170.3
141.4
138.3
138.1
135.0
133.7
133.3
131.0
129.3
128.3
128.2
127.6
124.3
123.2
120.8
114.2
109.5
21.2
Me
3ak
100 MHz in CDCl3
f1 (ppm)



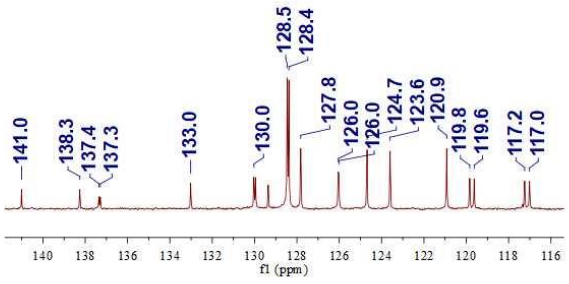
3al
400 MHz in $CDCl_3$

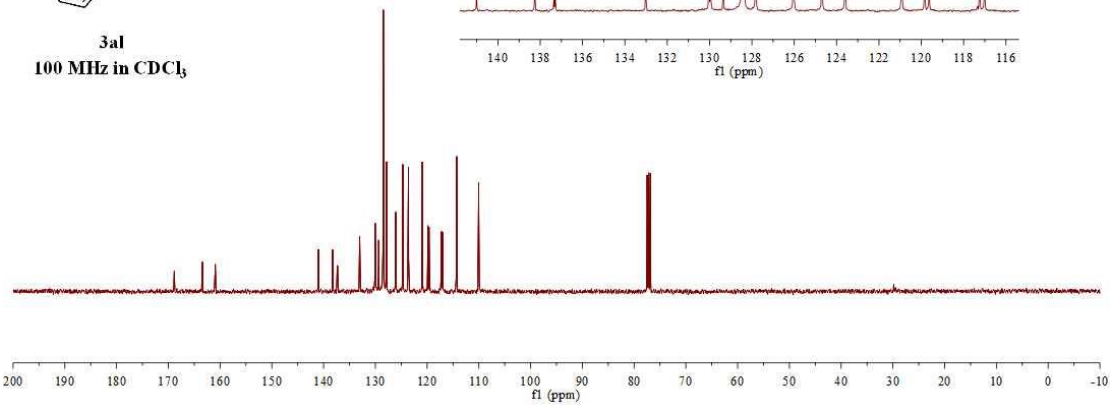


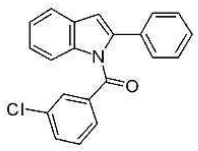




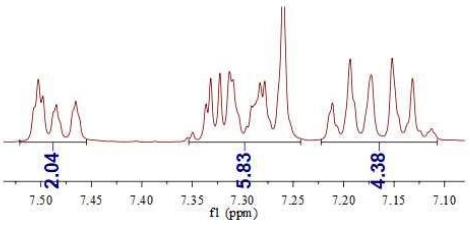
3al
100 MHz in $CDCl_3$

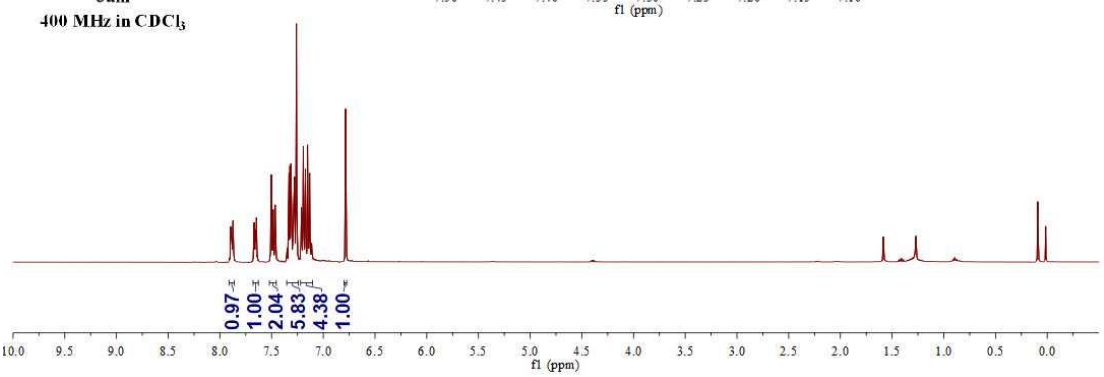


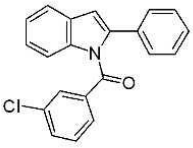




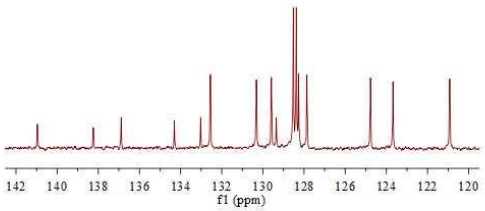
3am
400 MHz in $CDCl_3$

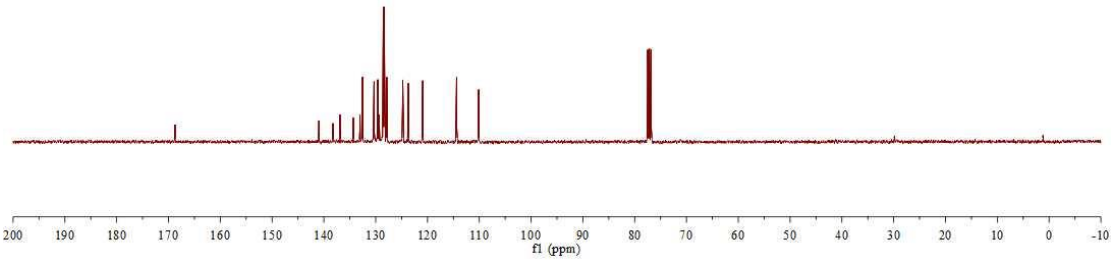


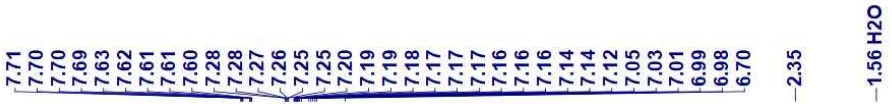


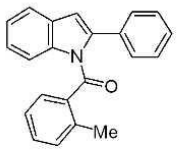


3am
100 MHz in $CDCl_3$

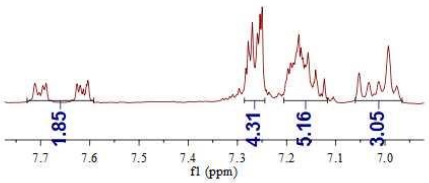


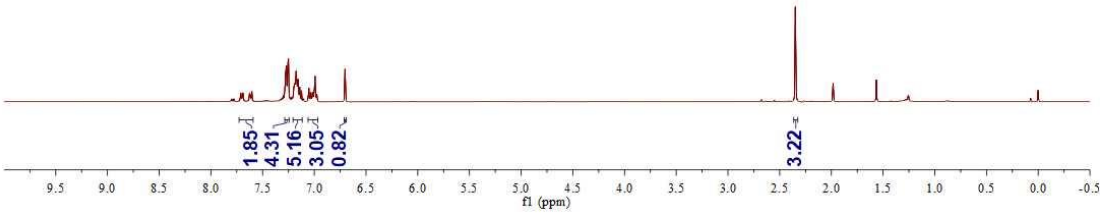


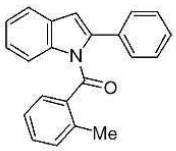




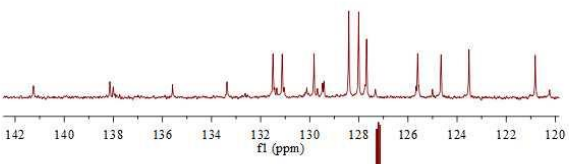
3an
400 MHz in $CDCl_3$

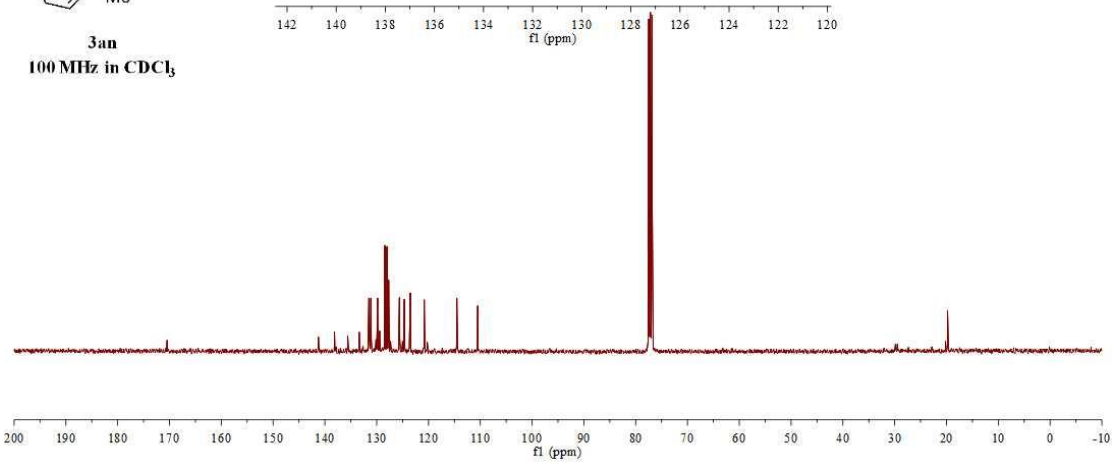


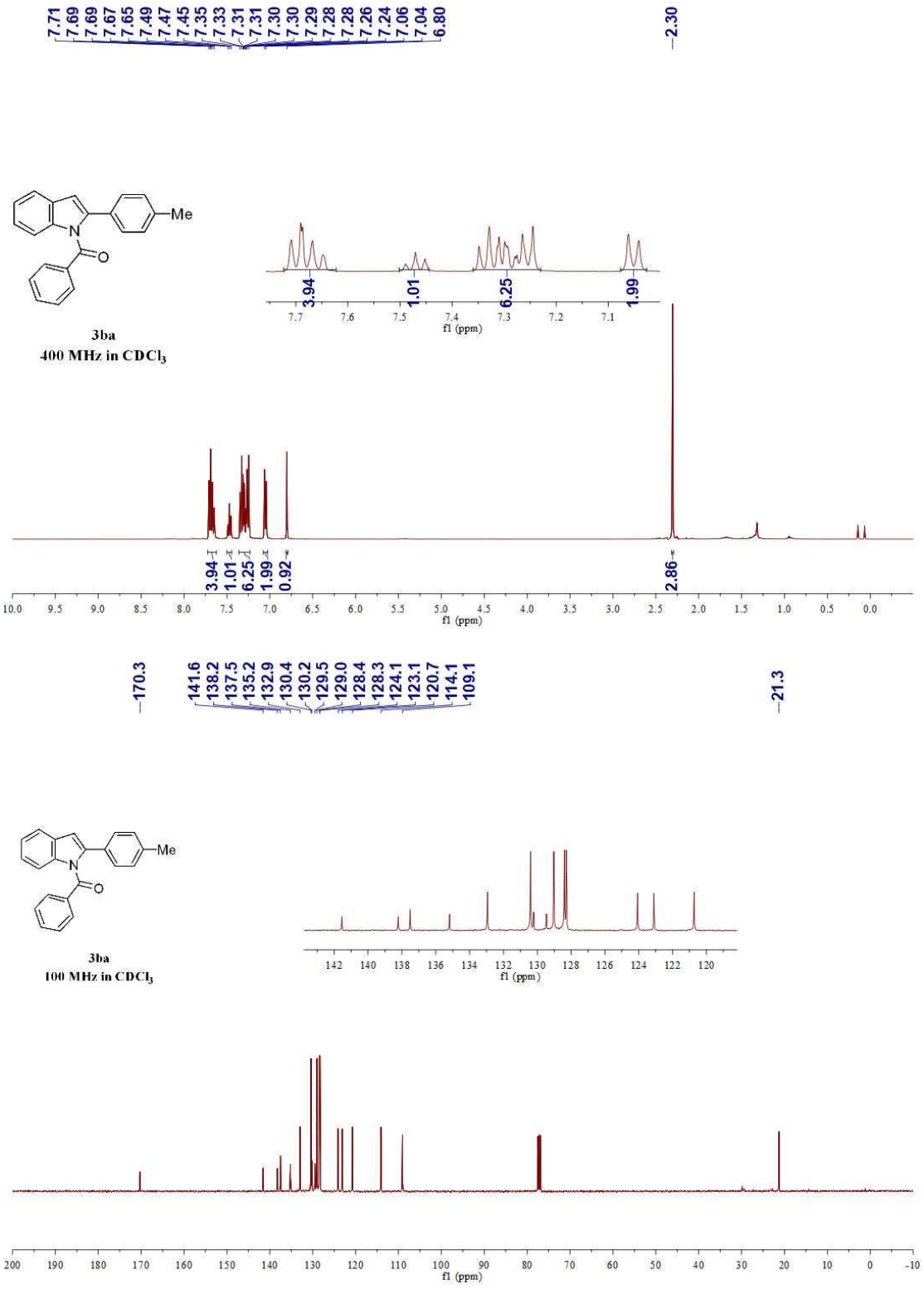


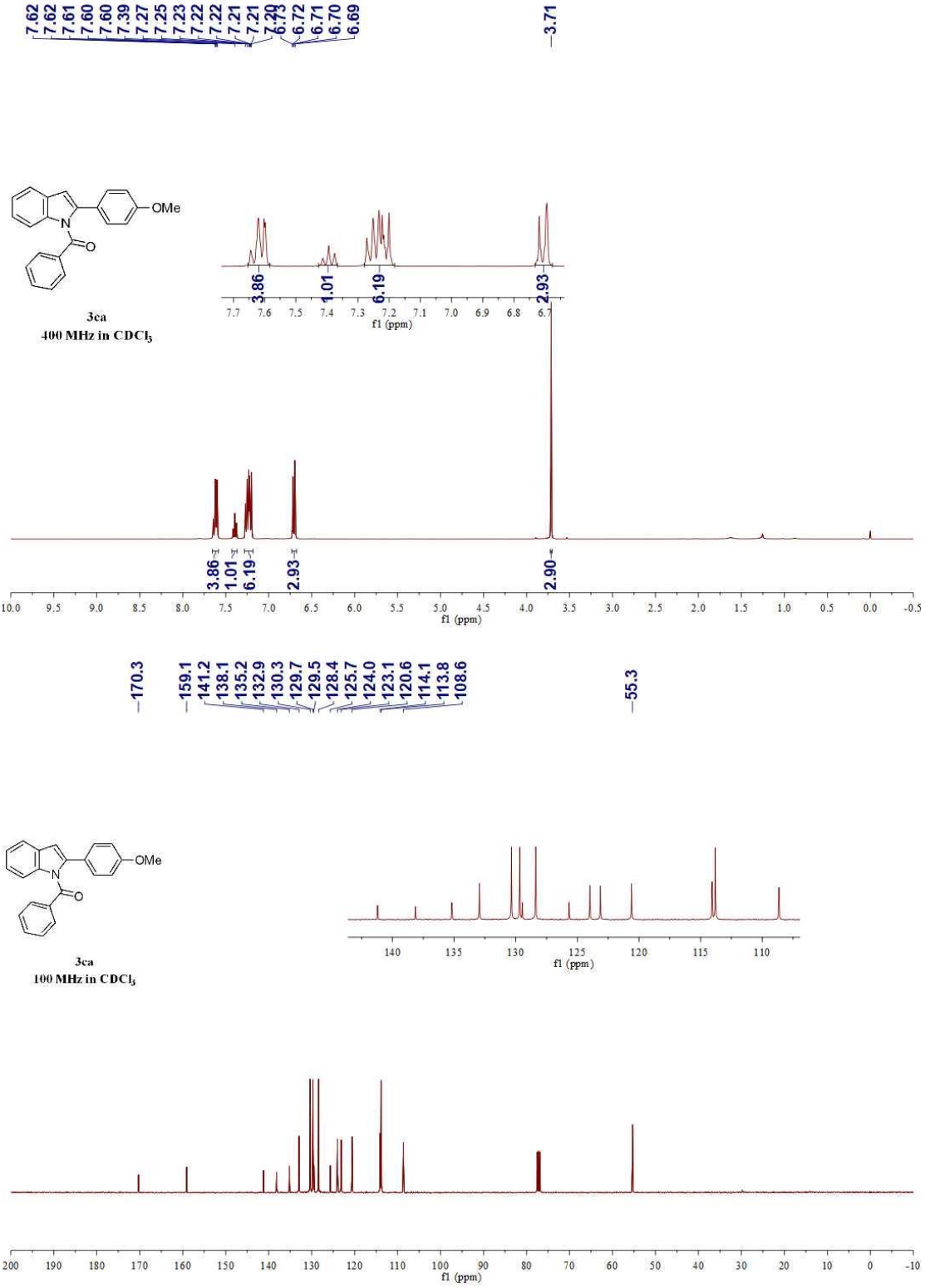


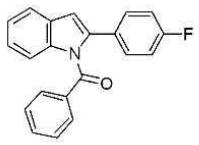
3an
100 MHz in $CDCl_3$



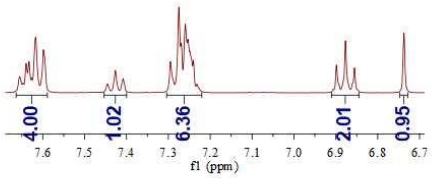


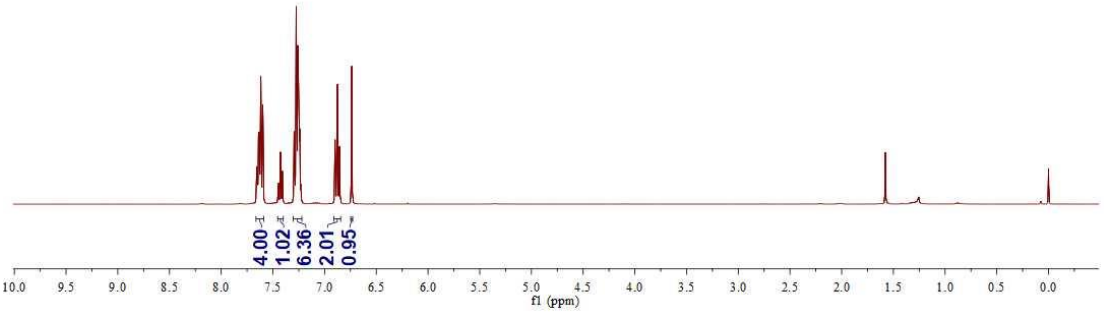

7.71
7.69
7.69
7.67
7.65
7.49
7.47
7.45
7.35
7.33
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.26
7.24
7.06
7.04
6.80
2.30
Me
N
O
3ba
400 MHz in CDCl3
3.94
1.01
6.25
1.99
0.92
2.86
f1 (ppm)
170.3
141.6
138.2
137.5
135.2
132.9
130.4
130.2
129.5
129.0
128.4
128.3
124.1
123.1
120.7
114.1
109.1
21.3
3ba
100 MHz in CDCl3

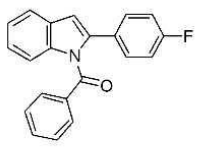

7.62
7.62
7.61
7.60
7.60
7.39
7.27
7.25
7.23
7.22
7.22
7.21
7.21
6.73
6.72
6.71
6.70
6.69
3.71
OMe
N
O
3ca
400 MHz in CDCl3
3.86
1.01
6.19
2.93
f1 (ppm)
2.90
170.3
159.1
141.2
138.1
135.2
132.9
130.3
129.7
129.5
128.4
125.7
124.0
123.1
120.6
114.1
113.8
108.6
55.3
3ca
100 MHz in CDCl3



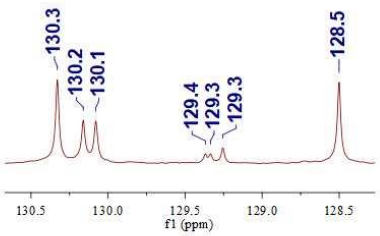
3da
400 MHz in $CDCl_3$

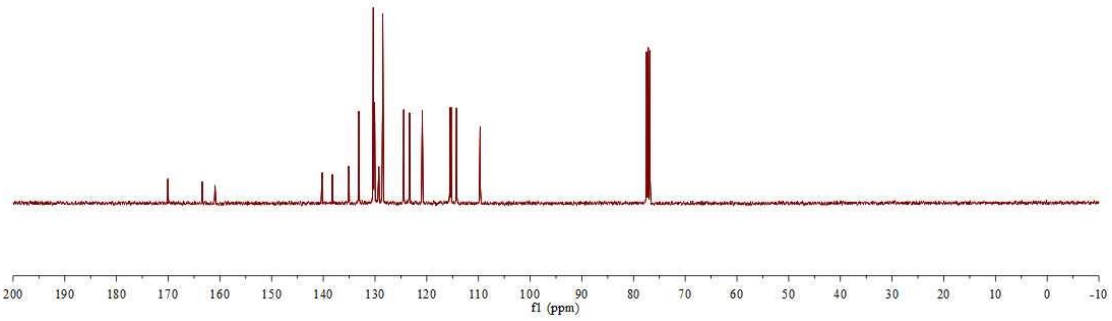


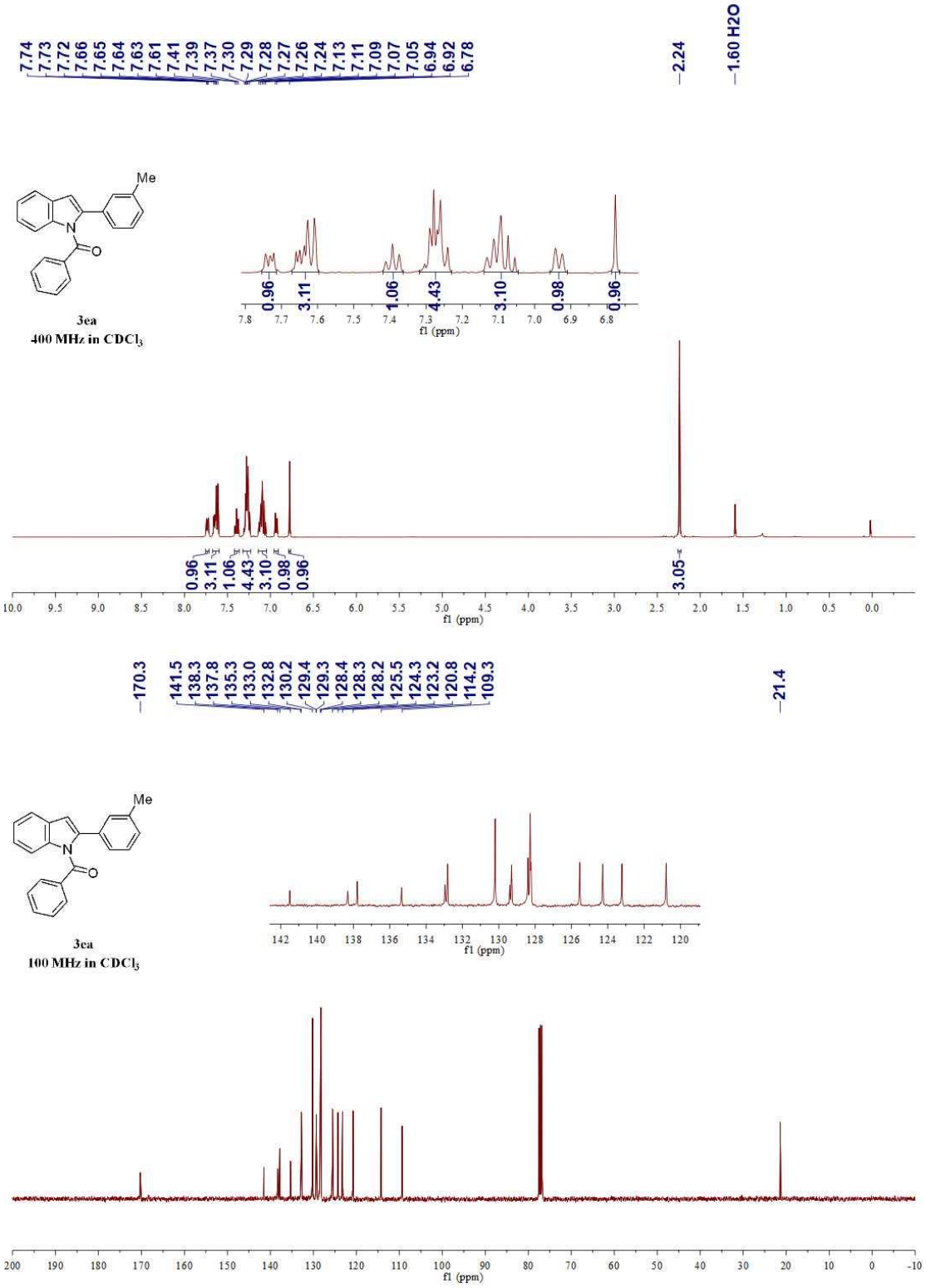


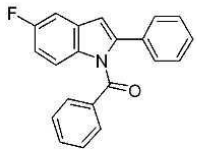


3da
100 MHz in $CDCl_3$

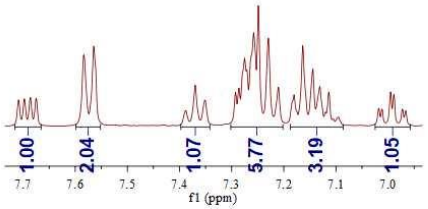


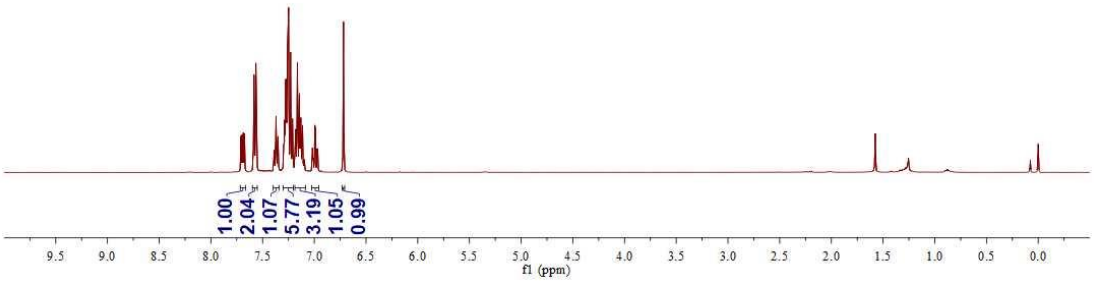


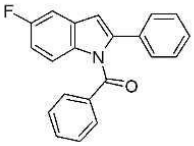

7.74
7.73
7.72
7.66
7.65
7.64
7.63
7.61
7.41
7.39
7.37
7.30
7.29
7.28
7.27
7.26
7.24
7.13
7.11
7.09
7.07
7.05
6.94
6.92
6.78
2.24
1.60 H2O
Me
N
O
3ea
400 MHz in CDCl3
0.96
3.11
1.06
4.43
3.10
0.98
0.96
f1 (ppm)
3.05
170.3
141.5
138.3
137.8
135.3
133.0
132.8
130.2
129.4
129.3
128.4
128.3
128.2
125.5
124.3
123.2
120.8
114.2
109.3
21.4
3ea
100 MHz in CDCl3



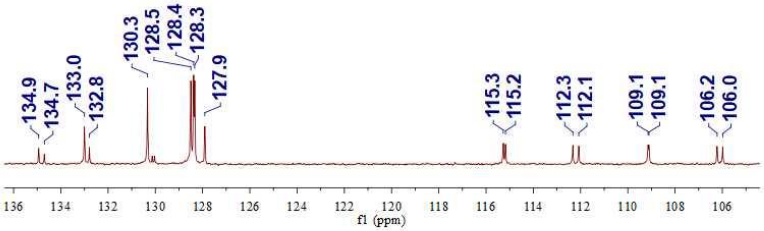
3fa
400 MHz in $CDCl_3$

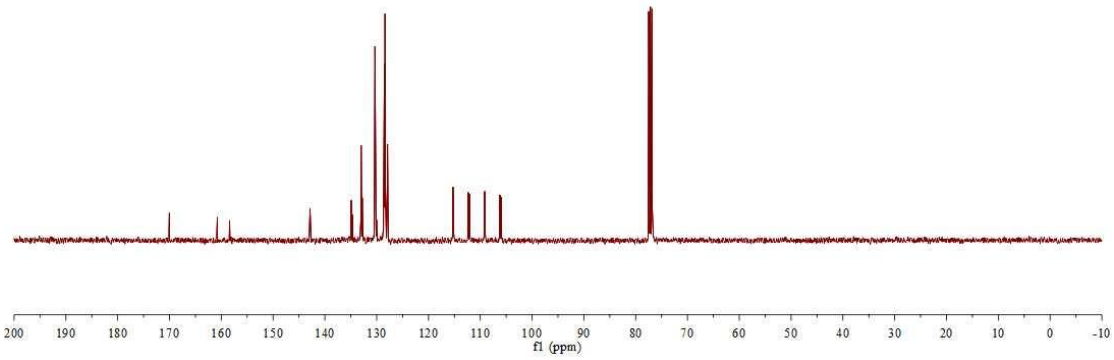


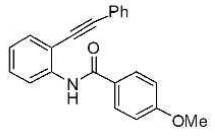




3fa
100 MHz in $CDCl_3$

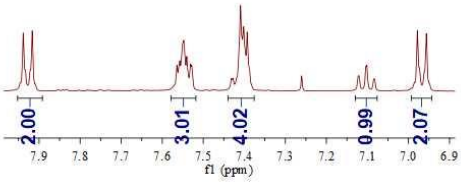


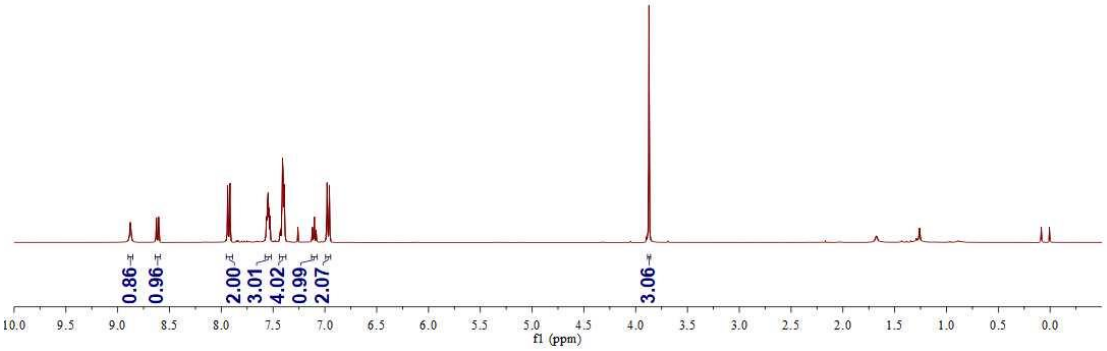


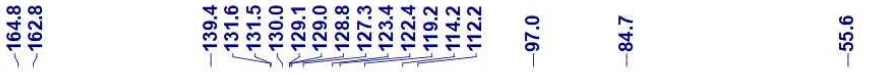


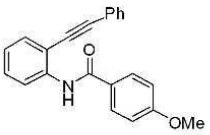
4

400 MHz in $CDCl_3$









4

100 MHz in $CDCl_3$