Supporting Information

Nickel-Catalyzed Cascade Carbonylative Synthesis of *N*-Benzoyl Indoles from 2-Nitroalkynes and Aryl Iodides

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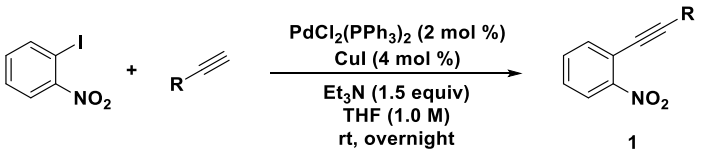
1. General experimental information

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 (101 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.

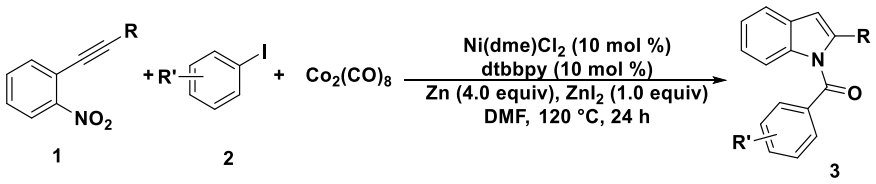
2. General procedure for the synthesis of 2-nitroalkynes (1a–i)

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



To a 50 mL flask charged with 1-iodo-2-nitrobenzene (5.0 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (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 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 = 30 / 1) to give the 2-nitroalkyne **1**.

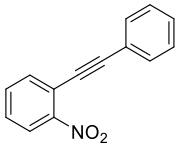
3. General procedure for the synthesis of *N*-acyl indoles (3aa–ar and 3ba–ia)



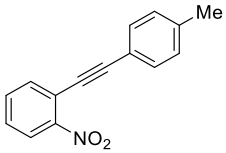
2-nitroalkyne **1** (0.3 mmol, 1.5 equiv), Ni(dme)Cl_2 (4.4 mg, 0.02 mmol, 10 mol%), dtbbpy (5.4 mg, 0.02 mmol, 10 mol%), Zn (52.3 mg, 0.8 mmol, 4.0 equiv), ZnI_2 (63.8 mg, 0.2 mmol, 1.0 equiv), and $Co_2(CO)_8$ (54.7 mg, 0.16 mmol, 0.8 equiv) were added to an oven-dried tube (15 mL). Then the tube was placed under vacuum and refilled with nitrogen three times. An aryl iodide **2** (0.2 mmol, 1.0 equiv) and DMF (2.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 120 °C for 24 h. The resulting mixture was purified by silica-gel column chromatography (petroleum ether / ethyl acetate = 50 / 1) to obtain the *N*-acyl indole **3**.

1 mmol scale: 2-nitroalkyne **1a** (1.5 mmol, 1.5 equiv), Ni(dme)Cl_2 (10 mol%), dtbbpy (10 mol%), Zn (4.0 equiv), ZnI_2 (1.0 equiv), and $Co_2(CO)_8$ (0.8 equiv) were added to an oven-dried tube (15 mL). Then the tube was placed under vacuum and refilled with nitrogen three times. An aryl iodide **2e** (1 mmol, 1.0 equiv) and DMF (5.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 120 °C for 24 h. The resulting mixture was purified by silica-gel column chromatography (petroleum ether / ethyl acetate = 50 / 1) to obtain the *N*-acyl indole **3ae** in 66% yield (215.6 mg).

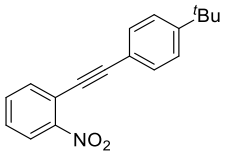
4. Characterization data of compounds 1a-i



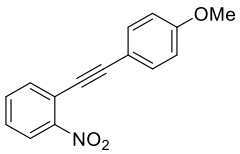
1-nitro-2-(phenylethynyl)benzene (1a).[2] Yellow oil in 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 1H), 7.71 (dd, J = 7.8, 1.0 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.49 – 7.42 (m, 1H), 7.40 – 7.35 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 134.6, 132.9, 132.1, 129.3, 128.6, 128.5, 124.8, 122.4, 118.7, 97.2, 84.9.



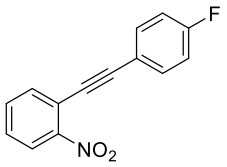
1-nitro-2-(*p*-tolylethynyl)benzene (1b).[3] Yellow solid in 68% yield, mp 58.7 – 59.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.3, 0.9 Hz, 1H), 7.69 (dd, J = 7.8, 1.2 Hz, 1H), 7.58 (td, J = 7.6, 1.1 Hz, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.46 – 7.39 (m, 1H), 7.18 (d, J = 7.9 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 139.7, 134.6, 132.9, 132.0, 129.3, 128.4, 124.8, 119.4, 119.1, 97.6, 84.4, 21.7.



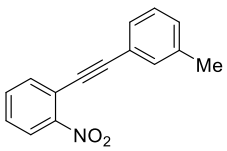
1-((4-(*tert*-butyl)phenyl)ethynyl)-2-nitrobenzene (1c).[3] Yellow solid in 80% yield, mp 83.4 – 85.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.3, 1.0 Hz, 1H), 7.71 (dd, J = 7.8, 1.2 Hz, 1H), 7.58 (td, J = 7.6, 1.2 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.47 – 7.38 (m, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 149.7, 134.7, 132.9, 131.9, 128.4, 125.6, 124.8, 119.5, 119.2, 97.7, 84.4, 35.0, 31.3.



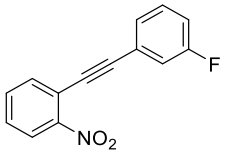
1-((4-methoxyphenyl)ethynyl)-2-nitrobenzene (1d).[3] Yellow solid in 73% yield, mp 66.8 – 68.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.3, 1.0 Hz, 1H), 7.68 (dd, J = 7.8, 1.3 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.46 – 7.38 (m, 1H), 6.94 – 6.84 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 149.5, 134.5, 133.8, 132.9, 128.2, 124.8, 119.3, 114.5, 114.2, 97.7, 84.0, 55.5.



1-((4-fluorophenyl)ethynyl)-2-nitrobenzene (1e).[3] Yellow solid in 62% yield, mp 78.4 – 79.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 1H), 7.70 (dd, J = 7.8, 1.1 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.50 – 7.44 (m, 1H), 7.07 (t, J = 8.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, J = 251.1 Hz, 1C), 149.7, 134.6, 134.2 (d, J = 8.6 Hz, 1C), 133.0, 128.7, 124.9, 118.8, 118.7 (d, J = 3.4 Hz, 1C), 116.0 (d, J = 22.2 Hz, 1C), 96.2, 84.7.

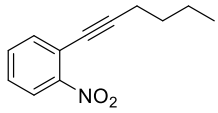


1-nitro-2-(*m*-tolylethynyl)benzene (1f).[3] Yellow oil in 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.3, 1.0 Hz, 1H), 7.68 (dd, J = 7.8, 1.3 Hz, 1H), 7.56 (td, J = 7.6, 1.2 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.25 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 138.3, 134.6, 132.9, 132.6, 130.2, 129.2, 128.5, 128.4, 124.8, 122.2, 118.9, 97.5, 84.5, 21.3.

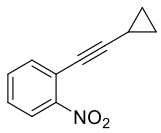


1-((3-fluorophenyl)ethynyl)-2-nitrobenzene (1g).[4] Yellow oil in 69% yield; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.08 (dd, J = 8.3, 1.0 Hz, 1H), 7.71 (dd, J = 7.8, 1.3 Hz, 1H), 7.61 (td, J = 7.6, 1.2 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.39 – 7.26 (m, 3H), 7.12 – 7.05 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, J = 247.1 Hz, 1C), 149.8, 134.7, 133.0, 130.2 (d, J = 8.6 Hz, 1C), 129.0, 128.0 (d, J = 3.0 Hz, 1C), 124.9, 124.3 (d, J = 9.5 Hz, 1C), 118.8 (d, J = 22.9 Hz, 1C), 118.4, 116.7 (d, J = 21.2 Hz, 1C), 95.7 (d, J = 3.4 Hz, 1C), 85.6.

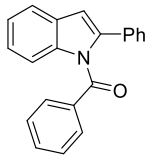


1-(hex-1-yn-1-yl)-2-nitrobenzene (1h).[2] Yellow oil in 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.2, 0.7 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.38 – 7.32 (m, 1H), 2.44 (t, J = 7.0 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.51 – 1.42 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 134.8, 132.6, 127.9, 124.4, 119.4, 99.4, 76.0, 30.4, 22.0, 19.5, 13.6.

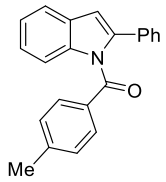


1-(cyclopropylethynyl)-2-nitrobenzene (1i).[2] Yellow oil in 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.2, 0.8 Hz, 1H), 7.58 – 7.45 (m, 2H), 7.39 – 7.32 (m, 1H), 1.56 – 1.45 (m, 1H), 1.00 – 0.83 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 134.7, 132.7, 127.7, 124.5, 119.5, 102.8, 71.3, 9.3, 0.8.

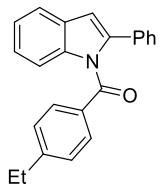
5. Characterization data of products 3aa–ar, 3ba–ia, and 4



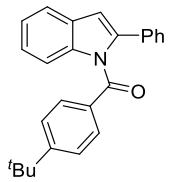
phenyl(2-phenyl-1*H*-indol-1-yl)methanone (3aa).[5] Yellow solid, 38.1 mg, 64% yield, mp 108.3 – 110.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 1H), 7.65 – 7.57 (m, 3H), 7.41 – 7.34 (m, 1H), 7.32 – 7.21 (m, 6H), 7.20 – 7.14 (m, 2H), 7.14 – 7.08 (m, 1H), 6.77 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 141.4, 138.4, 135.2, 133.1, 132.9, 130.4, 129.4, 128.45, 128.37, 128.3, 127.6, 124.3, 123.2, 120.8, 114.2, 109.5.



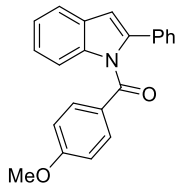
(2-phenyl-1*H*-indol-1-yl)(*p*-tolyl)methanone (3ab).[5] Yellow solid, 42.3 mg, 68% yield, mp 144.4 – 147.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 1H), 7.61 – 7.56 (m, 3H), 7.37 – 7.32 (m, 2H), 7.29 – 7.13 (m, 5H), 7.10 (d, J = 8.0 Hz, 2H), 6.80 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 144.0, 141.5, 138.4, 133.2, 132.3, 130.6, 129.4, 129.2, 128.33, 128.30, 127.6, 124.1, 123.0, 120.8, 114.0, 109.2, 21.7.



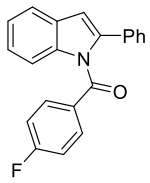
(4-ethylphenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ac). Yellow oil, 41.7 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 4H), 7.31 (dd, J = 5.2, 3.3 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.21 – 7.16 (m, 2H), 7.15 – 7.11 (m, 1H), 7.09 (d, J = 8.3 Hz, 2H), 6.77 (s, 1H), 2.61 (q, J = 7.6 Hz, 2H), 1.17 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 141.5, 138.4, 133.2, 132.6, 130.7, 129.4, 128.4, 128.3, 128.0, 127.6, 124.1, 123.0, 120.8, 114.1, 109.2, 29.1, 15.3 ; HRMS (ESI-TOF) Calcd. for $C_{23}H_{19}NONa^+$ $[M+Na]^+$: 348.1359; found: 348.1363.



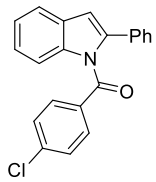
(4-(*tert*-butyl)phenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ad).[5] Yellow oil, 50.2mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.58 – 7.53 (m, 2H), 7.30 – 7.22 (m, 6H), 7.18 – 7.12 (m, 2H), 7.12 – 7.06 (m, 1H), 6.76 (s, 1H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 156.7, 141.6, 138.4, 133.2, 132.3, 130.4, 129.4, 128.5, 128.2, 127.5, 125.3, 124.2, 123.1, 120.8, 114.2, 109.3, 35.2, 31.1.



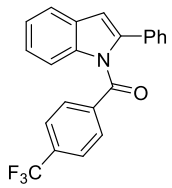
(4-methoxyphenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ae).[5] Yellow oil, 46.5 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 3H), 7.57 – 7.52 (m,1H), 7.35 – 7.30 (m, 2H), 7.26 – 7.18 (m, 4H), 7.17 – 7.12 (m, 1H), 6.79 – 6.73 (m, 3H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 163.6, 141.5, 138.4, 133.1, 132.9, 129.3, 128.35, 128.27, 127.6, 127.3, 124.0, 122.8, 120.8, 113.8, 108.8, 55.6.



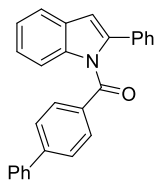
(4-fluorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3af).[5] Yellow oil, 32.8 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 1H), 7.68 – 7.60 (m, 3H), 7.32 – 7.27 (m, 4H), 7.22 – 7.13 (m, 3H), 6.92 (t, J = 8.6 Hz, 2H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 165.4 (d, J = 255.1 Hz, 1C), 141.1, 138.3, 133.0 (d, J = 9.5 Hz, 1C), 131.5 (d, J = 2.9 Hz, 1C), 129.3, 128.5, 128.4, 127.8, 124.5, 123.4, 120.9, 115.6 (d, J = 22.2 Hz, 1C), 114.1, 109.6.



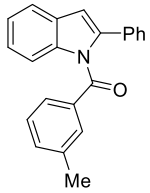
(4-chlorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ag).[5] Yellow oil, 35.8 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 1H), 7.68 – 7.63 (m, 1H), 7.56 – 7.52 (m, 2H), 7.33 – 7.27 (m, 4H), 7.23 – 7.13 (m, 5H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 141.1, 139.2, 138.2, 133.6, 132.9, 131.7, 129.4, 128.7, 128.5, 128.4, 127.9, 124.6, 123.5, 120.9, 114.2, 109.8.



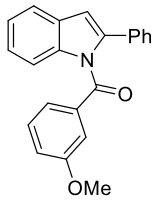
(2-phenyl-1*H*-indol-1-yl)(4-(trifluoromethyl)phenyl)methanone (3ah).[5] Yellow solid, 46.8 mg, 64% yield, mp 110.6 – 113.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 1H), 7.67 – 7.61 (m, 3H), 7.44 (d, J = 8.2 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.24 – 7.19 (m, 2H), 7.17 – 7.08 (m, 3H), 6.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 140.9, 138.6, 138.3, 133.8 (q, J = 32.8 Hz, 1C), 132.9, 130.5, 129.4, 128.7, 128.4, 128.0, 125.2 (q, J = 3.6 Hz, 1C), 124.9, 123.9, 121.0, 120.8 (q, J = 272.7 Hz, 1C), 114.5, 110.4.



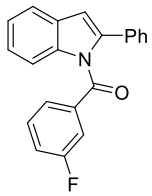
[1,1'-biphenyl]-4-yl(2-phenyl-1*H*-indol-1-yl)methanone (3ai).[5] Yellow oil, 40.3 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 4H), 7.54 (d, J = 7.2 Hz, 2H), 7.51 – 7.43 (m, 4H), 7.40 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.21 (t, J = 7.5 Hz, 2H), 7.13 (t, J = 7.3 Hz, 1H), 6.82 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 145.6, 141.4, 139.9, 138.4, 133.8, 133.2, 131.0, 129.4, 129.1, 128.5, 128.4, 128.3, 127.7, 127.3, 127.0, 124.3, 123.2, 120.9, 114.2, 109.5.



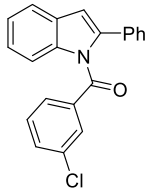
(2-phenyl-1*H*-indol-1-yl)(*m*-tolyl)methanone (3aj).[5] Yellow oil, 36.1 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 1H), 7.65 – 7.61 (m, 1H), 7.45 (d, J = 7.4 Hz, 1H), 7.39 (s, 1H), 7.31 – 7.23 (m, 4H), 7.21 – 7.09 (m, 5H), 6.76 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 141.4, 138.4, 138.1, 135.0, 133.7, 133.3, 131.0, 129.3, 128.4, 128.2, 127.6, 124.3, 123.2, 120.8, 114.2, 109.5, 21.2.



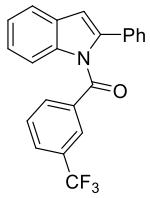
(3-methoxyphenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ak). Yellow oil, 45.2 mg, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 1H), 7.68 – 7.62 (m, 1H), 7.35 – 7.25 (m, 4H), 7.24 – 7.12 (m, 6H), 6.97 – 6.92 (m, 1H), 6.79 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 159.4, 141.4, 138.4, 136.4, 133.2, 129.5, 129.4, 128.34, 128.29, 127.7, 124.3, 123.2, 123.0, 120.8, 119.6, 114.7, 114.2, 109.6, 55.5; HRMS (ESI-TOF) Calcd. for $C_{22}H_{17}NO_2Na^+$ $[M+Na]^+$: 350.1151; found: 350.1155.



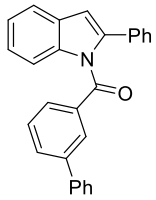
(3-fluorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3al).[5] Yellow oil, 37.8 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.66 – 7.60 (m, 1H), 7.36 – 7.32 (m, 1H), 7.31 – 7.23 (m, 5H), 7.20 – 7.08 (m, 4H), 7.06 – 6.99 (m, 1H), 6.76 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 162.2 (d, J = 248.3 Hz, 1C), 141.0, 138.3, 137.4 (d, J = 7.1 Hz, 1C), 133.1, 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 = 23.2 Hz, 1C), 114.3, 110.0.



(3-chlorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3am).[5] Yellow oil, 27.2 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 1H), 7.69 – 7.62 (m, 1H), 7.52 – 7.45 (m, 2H), 7.36 – 7.25 (m, 5H), 7.22 – 7.10 (m, 4H), 6.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 141.0, 138.2, 136.9, 134.3, 133.0, 132.5, 130.3, 129.6, 129.4, 128.5, 128.4, 128.3, 127.9, 124.8, 123.7, 120.9, 114.4, 110.1.

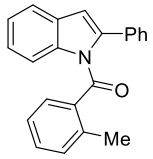


(2-phenyl-1*H*-indol-1-yl)(3-(trifluoromethyl)phenyl)methanone (3an). Yellow oil, 40.2 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.71 (s, 1H), 7.69 – 7.65 (m, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.25 – 7.21 (m, 2H), 7.16 – 7.05 (m, 3H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 140.7, 138.3, 136.2, 133.2, 132.9, 130.6 (q, J = 33.2 Hz, 1C), 129.4, 128.9, 128.8 (q, J = 3.7 Hz, 1C), 128.7, 128.4, 127.9, 127.1 (q, J = 3.7 Hz, 1C), 125.0, 123.9, 123.5 (q, J = 272.7 Hz, 1C), 121.0, 114.5, 110.4; HRMS (ESI-TOF) Calcd. for $C_{22}H_{14}F_3NONa^+$ [M+Na]$^+$: 388.0920; found: 388.0923.

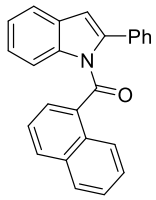


[1,1'-biphenyl]-3-yl(2-phenyl-1*H*-indol-1-yl)methanone (3ao). Yellow oil, 41.8 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 1H), 7.77 (t, J = 1.6 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.64 – 7.56 (m, 2H), 7.48 – 7.40 (m, 4H), 7.39 – 7.27 (m, 6H), 7.16 (t, J = 7.3 Hz, 2H), 7.13 – 7.07 (m, 1H), 6.80 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 141.4, 139.9, 138.4, 135.8, 133.1, 131.4, 129.4, 129.1, 129.02, 128.98, 128.9, 128.5, 128.3, 127.9, 127.7, 127.2, 124.5, 123.4, 120.9, 114.3, 109.7; HRMS (ESI-

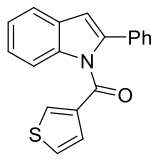
TOF) Calcd. for $C_{27}H_{19}NONa^+$ $[M+Na]^+$: 396.1359; found: 396.1364.



(2-phenyl-1*H*-indol-1-yl)(*o*-tolyl)methanone (3ap).[5] Yellow oil, 29.3 mg, 47% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 1H), 7.66 – 7.60 (m, 1H), 7.31 – 7.26 (m, 4H), 7.22 – 7.11 (m, 5H), 7.06 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.72 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.2, 138.1, 138.0, 135.6, 133.4, 131.5, 131.1, 129.8, 129.5, 128.4, 128.0, 127.7, 125.6, 124.6, 123.5, 120.8, 114.5, 110.5, 19.7.

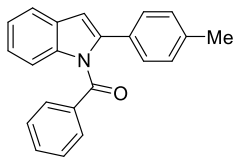


naphthalen-1-yl(2-phenyl-1*H*-indol-1-yl)methanone (3aq). Yellow oil, 35.4 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.77 – 7.71 (m, 2H), 7.68 – 7.63 (m, 1H), 7.55 – 7.43 (m, 3H), 7.36 – 7.30 (m, 2H), 7.21 (dd, J = 8.1, 7.3 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.92 – 6.84 (m, 3H), 6.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 141.5, 138.2, 133.4, 133.2, 133.0, 132.4, 131.0, 129.5, 129.3, 128.4, 128.3, 127.8, 127.6, 127.3, 126.5, 125.1, 124.8, 124.3, 123.7, 120.8, 115.1, 110.5; HRMS (ESI-TOF) Calcd. for $C_{25}H_{17}NONa^+$ $[M+Na]^+$: 370.1202; found: 370.1207.

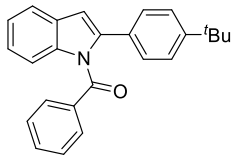


(2-phenyl-1*H*-indol-1-yl)(thiophen-3-yl)methanone (3ar). Yellow oil, 25.5 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 1H), 7.73 – 7.70 (m, 1H), 7.68 – 7.61 (m, 1H), 7.36 – 7.27 (m, 5H), 7.26 – 7.20 (m, 2H), 7.20 – 7.14 (m, 1H), 7.12 (dd, J = 5.1, 3.0 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 140.9, 138.3, 137.8, 134.5, 133.2, 129.3, 128.5, 128.4, 128.2, 127.7, 126.2, 124.4, 123.2, 120.9, 114.0, 109.5; HRMS (ESI-TOF) Calcd. for $C_{19}H_{13}NOSNa^+$

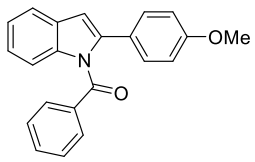
$[M+Na]^+$: 326.0610; found: 326.0612.



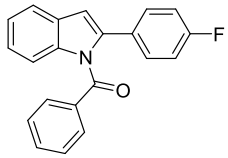
phenyl(2-(*p*-tolyl)-1*H*-indol-1-yl)methanone (3ba).[5] Yellow solid, 38.6 mg, 62% yield, mp 114.3 – 117.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 4H), 7.41 (t, J = 7.5 Hz, 1H), 7.29 – 7.17 (m, 6H), 6.99 (d, J = 7.9 Hz, 2H), 6.73 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 141.6, 138.3, 137.5, 135.3, 132.9, 130.4, 130.3, 129.5, 129.0, 128.4, 128.3, 124.1, 123.1, 120.7, 114.1, 109.1, 21.3.



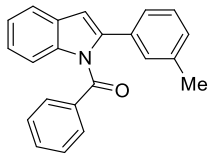
(2-(4-(*tert*-butyl)phenyl)-1*H*-indol-1-yl)(phenyl)methanone (3ca).[6] Yellow oil, 38.9 mg, 56% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.61 (m, 4H), 7.41 (t, J = 7.4 Hz, 1H), 7.33 – 7.19 (m, 8H), 6.80 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 150.6, 141.5, 138.3, 135.4, 132.7, 130.3, 130.2, 129.5, 128.4, 128.3, 125.1, 124.1, 123.2, 120.7, 114.3, 109.1, 34.6, 31.2.



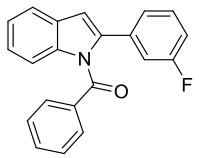
(2-(4-methoxyphenyl)-1*H*-indol-1-yl)(phenyl)methanone (3da).[5] Yellow oil, 39.3 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 4H), 7.41 (t, J = 7.5 Hz, 1H), 7.30 – 7.20 (m, 6H), 6.75 – 6.69 (m, 3H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 159.1, 141.2, 138.2, 135.2, 132.9, 130.4, 129.7, 129.5, 128.4, 125.7, 124.0, 123.1, 120.6, 55.4.



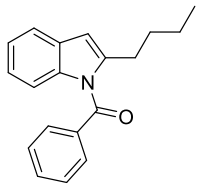
(2-(4-fluorophenyl)-1*H*-indol-1-yl)(phenyl)methanone (3ea).[5] Yellow solid, 29.6 mg, 47% yield, mp 117.9 – 120.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 4H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.32 – 7.21 (m, 6H), 6.88 (t, *J* = 8.4 Hz, 2H), 6.74 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.1, 162.2 (d, *J* = 248.1 Hz, 1C), 140.3, 138.3, 135.2, 133.1, 130.3, 130.2 (d, *J* = 8.2 Hz, 1C), 129.4 (d, *J* = 3.2 Hz, 1C), 129.3, 128.5, 124.5, 123.3, 120.9, 115.4 (d, *J* = 21.9 Hz, 1C), 114.2, 109.7.



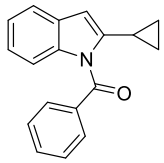
phenyl(2-(*m*-tolyl)-1*H*-indol-1-yl)methanone (3fa).[5] Yellow oil, 36.1 mg, 58% yield, mp 102.7 – 105.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.74 – 7.69 (m, 1H), 7.66 – 7.58 (m, 3H), 7.41 – 7.36 (m, 1H), 7.30 – 7.26 (m, 2H), 7.26 – 7.23 (m, 2H), 7.13 – 7.04 (m, 3H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.78 – 6.75 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.3, 141.5, 138.3, 137.8, 135.4, 133.0, 132.8, 130.2, 129.4, 129.3, 128.4, 128.3, 128.2, 125.6, 124.3, 123.2, 120.8, 114.2, 109.4, 21.4.



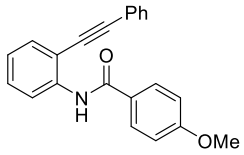
(2-(3-fluorophenyl)-1H-indol-1-yl)(phenyl)methanone (3ga). Yellow oil, 31.5 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.15 (td, *J* = 7.9, 5.9 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.86 – 6.79 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.0, 162.4 (d, *J* = 246.3 Hz, 1C), 140.0 (d, *J* = 2.3 Hz, 1C), 138.4, 135.3 (d, *J* = 8.4 Hz, 1C), 135.1, 133.1, 130.3, 129.9 (d, *J* = 8.5 Hz, 1C), 129.2, 128.5, 124.8, 124.2 (d, *J* = 2.8 Hz, 1C), 123.4, 121.1, 115.3 (d, *J* = 22.8 Hz, 1C), 114.5 (d, *J* = 21.2 Hz, 1C), 114.3, 110.3. HRMS (ESI-TOF) Calcd. for $C_{21}H_{14}FNONa^+$ [M+Na]$^+$: 338.0952; found: 338.0954.



(2-butyl-1*H*-indol-1-yl)(phenyl)methanone (3ha).[6] Yellow oil, 30.0 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.64 (dd, J = 10.6, 4.3 Hz, 1H), 7.50 (t, J = 7.5 Hz, 3H), 7.16 – 7.10 (m, 1H), 7.02 – 6.96 (m, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.49 (s, 1H), 2.89 – 2.81 (m, 2H), 1.68 – 1.58 (m, 2H), 1.35 (dd, J = 14.9, 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 143.2, 137.4, 135.6, 133.2, 130.0, 129.6, 128.9, 122.6, 122.5, 120.1, 114.2, 107.4, 31.3, 28.7, 22.5, 14.0.



(2-cyclopropyl-1*H*-indol-1-yl)(phenyl)methanone (3ia).[6] Yellow oil, 30.0 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 8.0 Hz, 3H), 7.31 (d, J = 8.1 Hz, 1H), 7.17 (td, J = 7.5, 1.0 Hz, 1H), 7.13 – 7.07 (m, 1H), 6.34 (s, 1H), 1.87 – 1.77 (m, 1H), 0.78 – 0.66 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 144.3, 137.5, 136.0, 132.8, 129.9, 129.3, 128.7, 123.2, 122.8, 120.1, 114.4, 105.9, 10.4, 8.5.



4-methoxy-*N*-(2-(phenylethynyl)phenyl)benzamide (4).[5] White solid, mp 111.5 – 113.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.61 (d, J = 8.4 Hz, 1H), 7.93 (dd, J = 8.8, 1.9 Hz, 2H), 7.60 – 7.51 (m, 3H), 7.44 – 7.37 (m, 4H), 7.10 (t, J = 7.6 Hz, 1H), 6.97 (dd, J = 8.8, 1.9 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 162.8, 139.5, 131.7, 131.6, 130.1, 129.1, 129.0, 128.8, 127.3, 123.4, 122.5, 119.2, 114.3, 112.2, 97.0, 84.8, 55.6.

6. References

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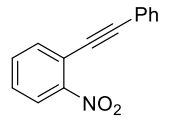
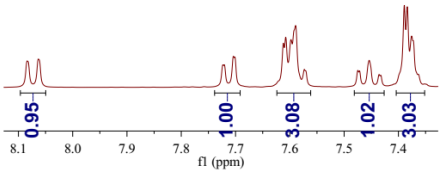
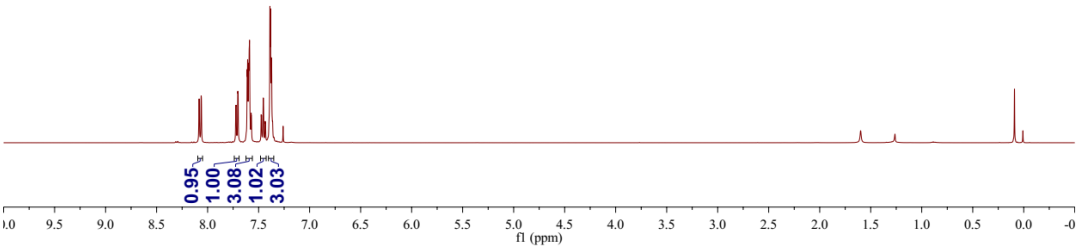
7. ^{1}H, ^{13}C spectra of 1a–i, 3aa–ar, 3ba–ia and 4

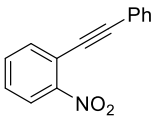


1a

400 MHz in $CDCl_3$

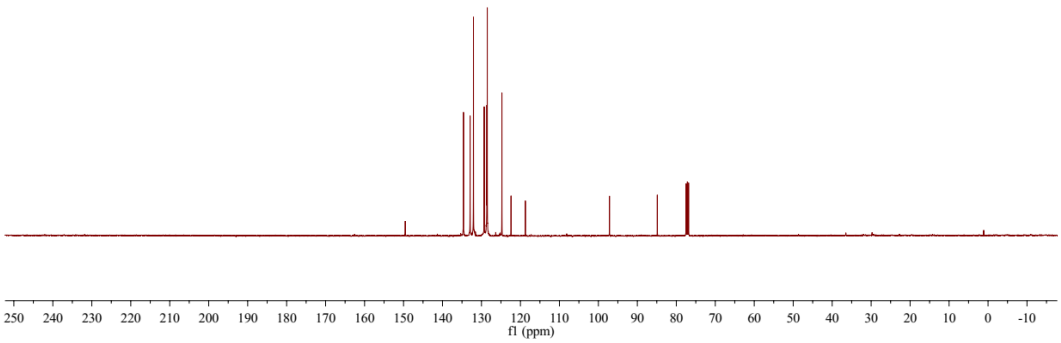


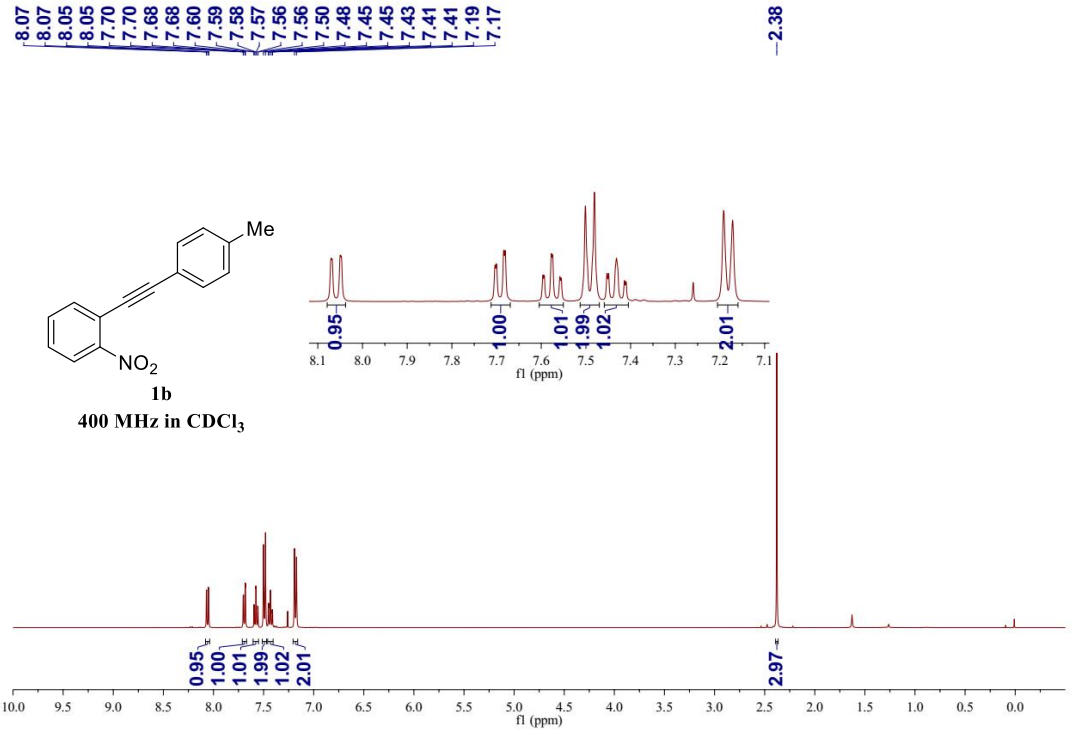




1a

101 MHz in $CDCl_3$





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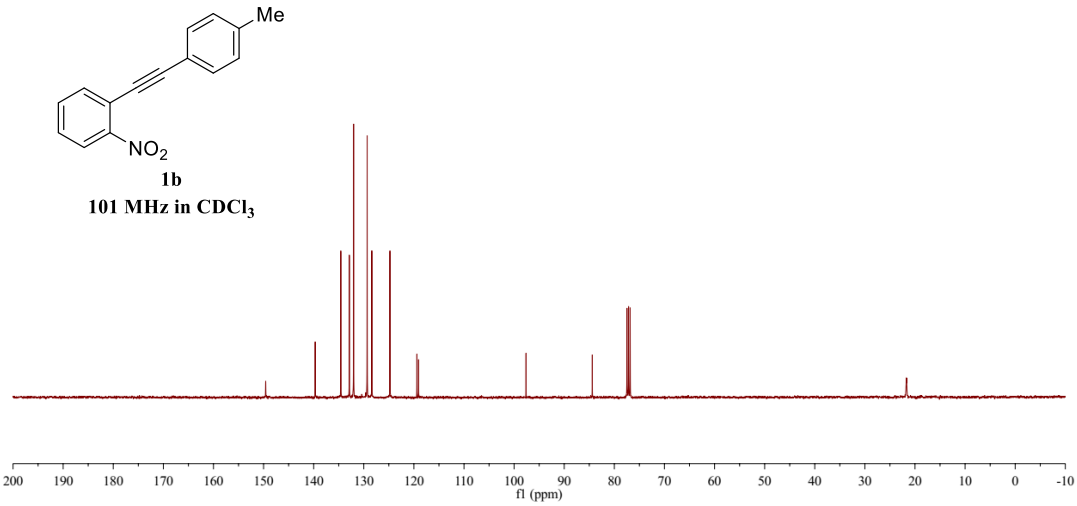

1b

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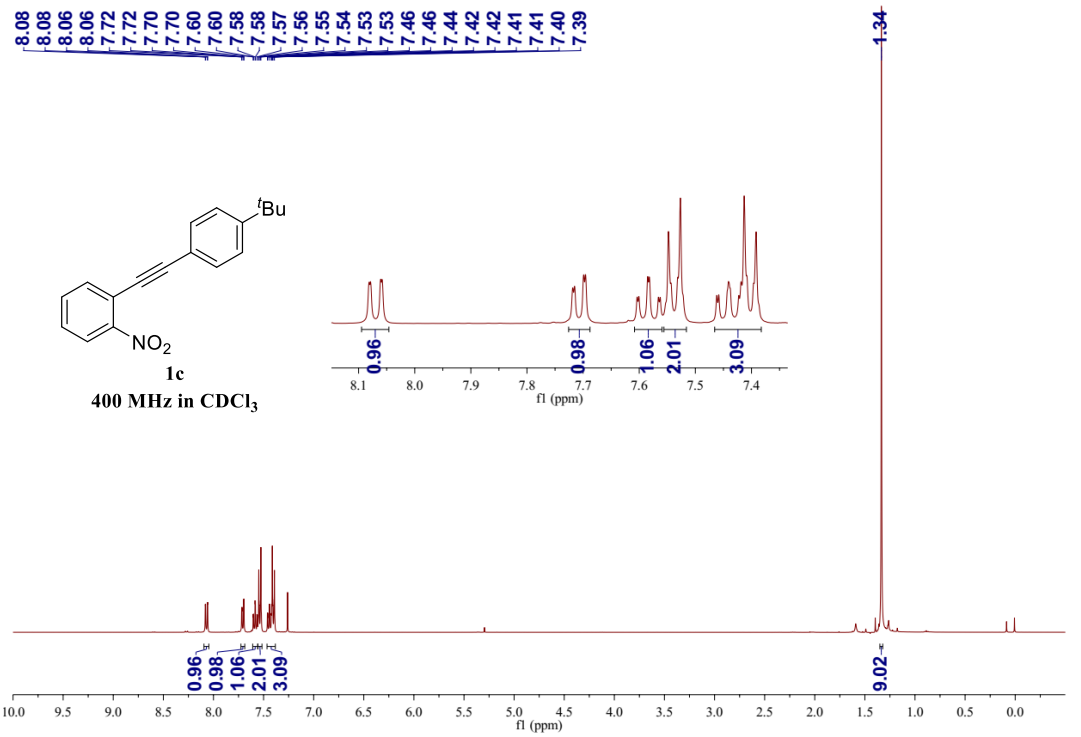
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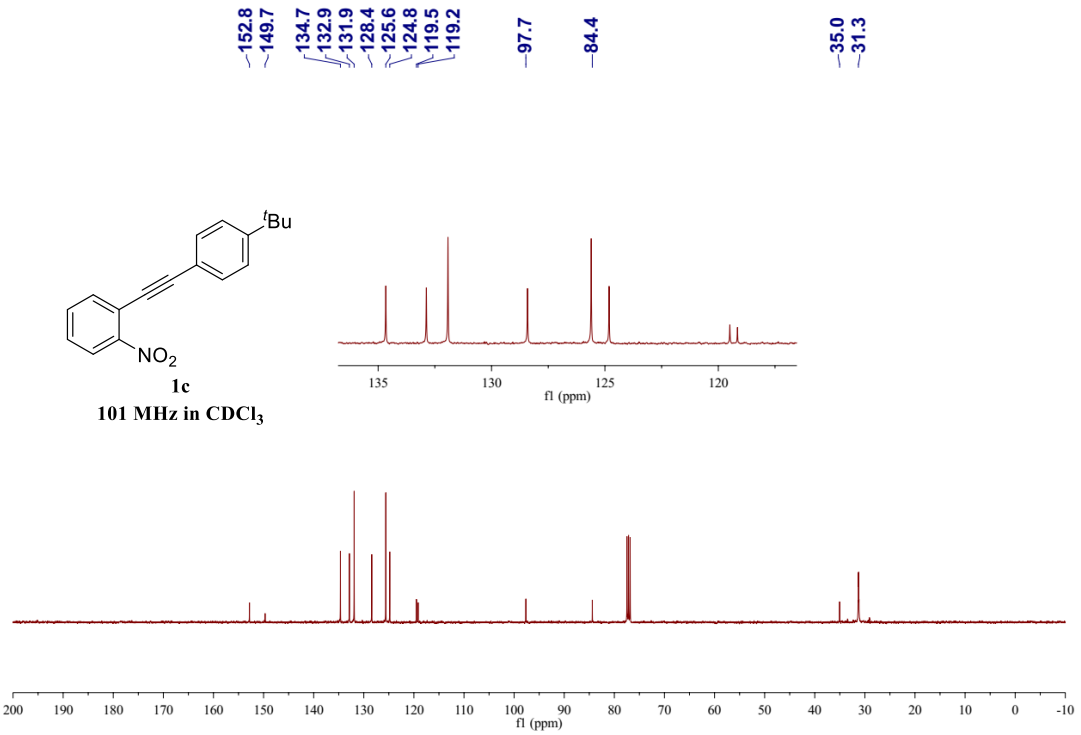
8.08
8.06
8.06
7.72
7.72
7.70
7.70
7.60
7.60
7.58
7.58
7.57
7.56
7.55
7.54
7.53
7.46
7.46
7.44
7.42
7.42
7.41
7.41
7.40
7.39
1.34
tBu
NO2
1c
400 MHz in CDCl3
0.96
0.98
1.06
2.01
3.09
9.02
f1 (ppm)


152.8
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132.9
131.9
128.4
125.6
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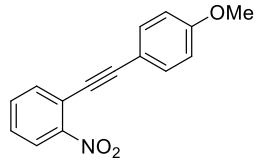
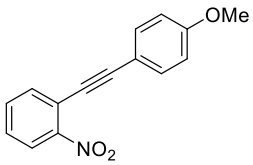
31.3
tBu
NO2
1c
101 MHz in CDCl3
f1 (ppm)



1d

400 MHz in $CDCl_3$



1d

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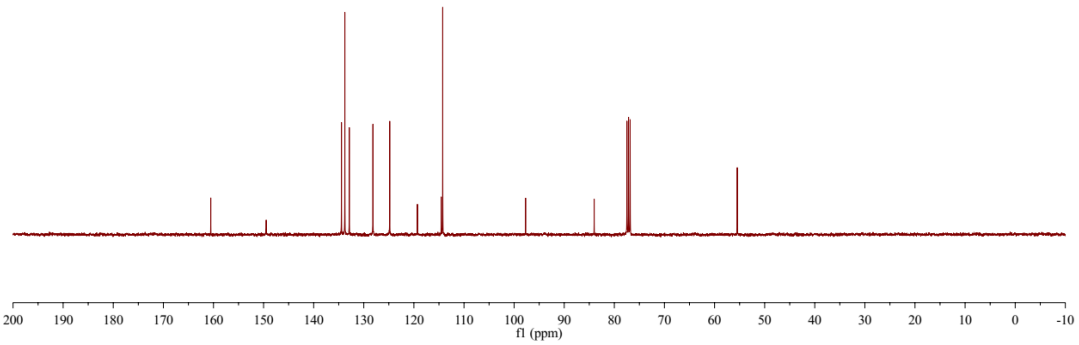

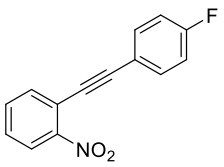

1e

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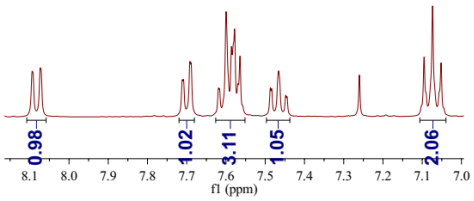

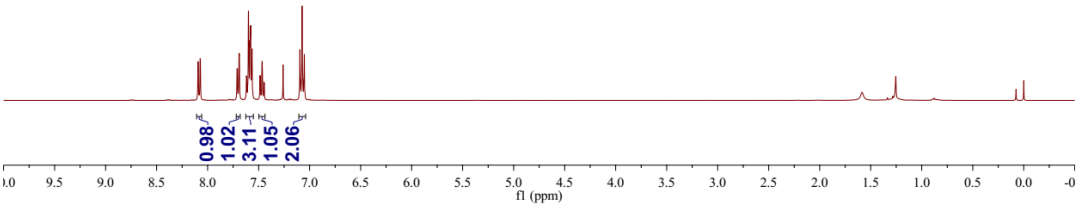

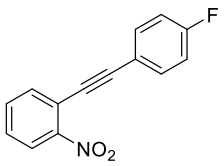

1e

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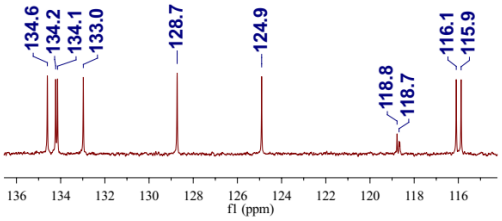

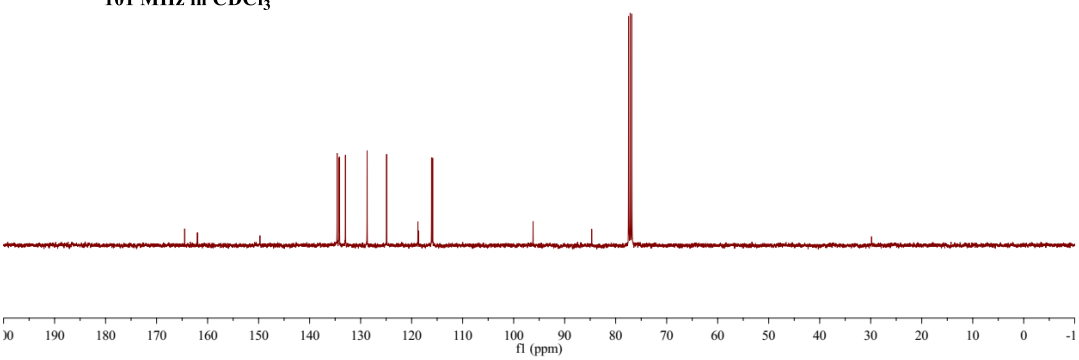

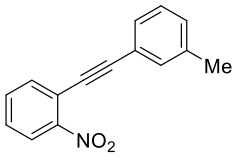

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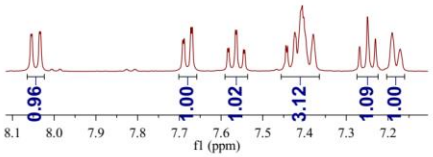

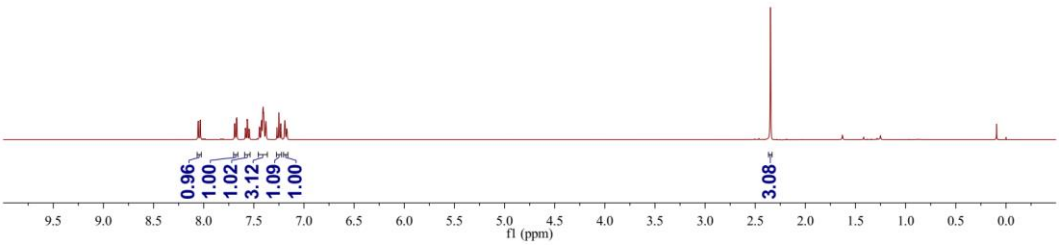

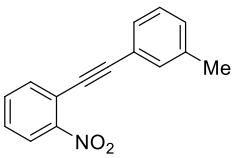

1f

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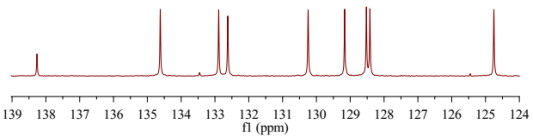

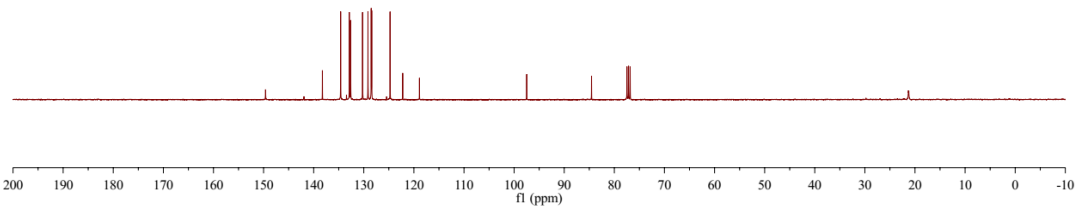

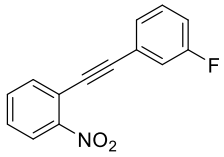

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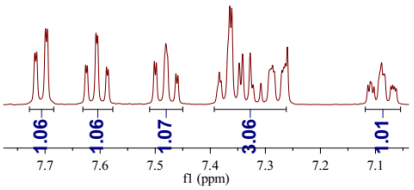

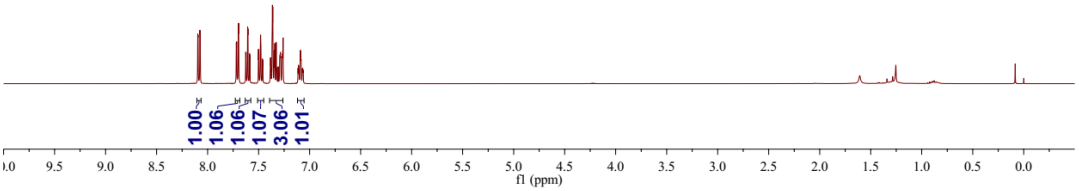

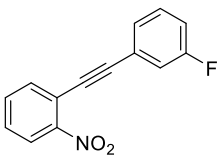

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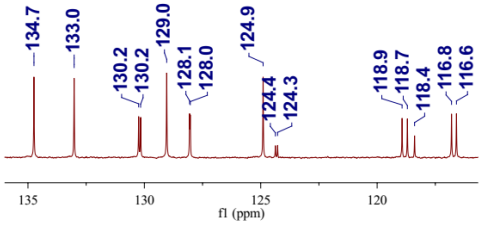

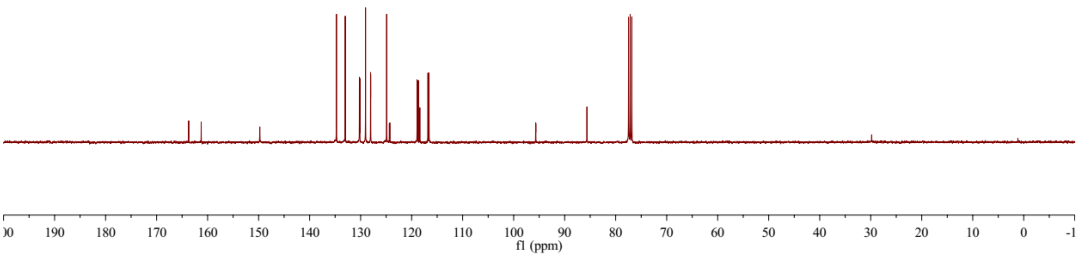

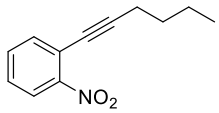

1h

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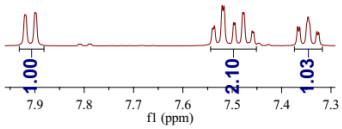

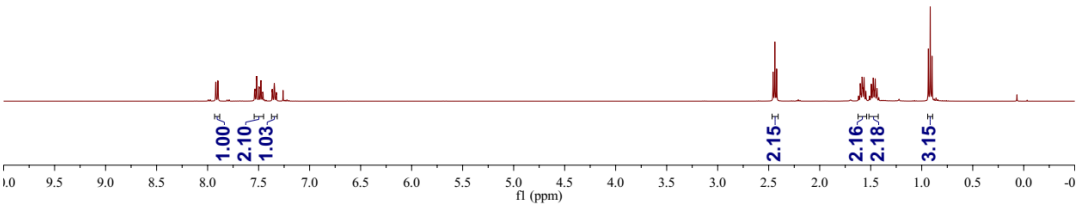

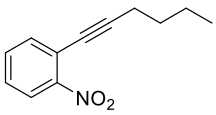

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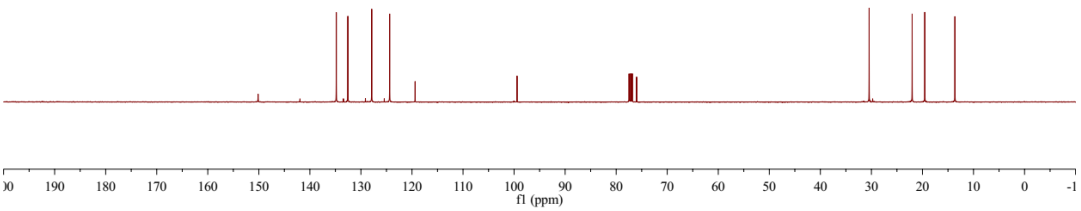

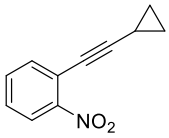

1i

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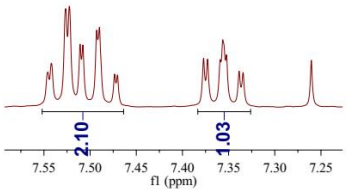

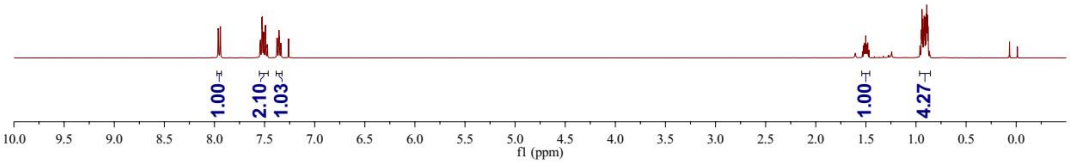

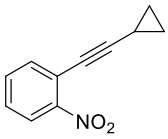

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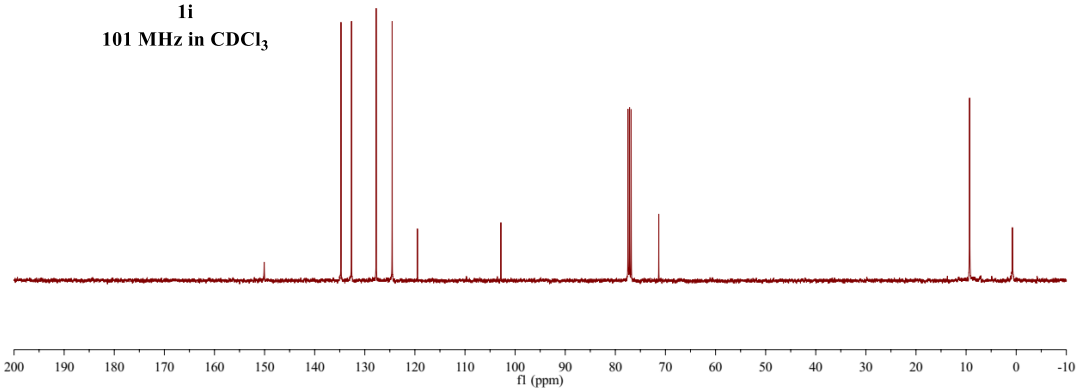

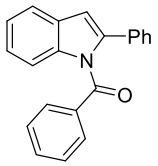

3aa

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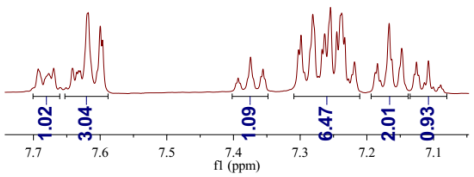

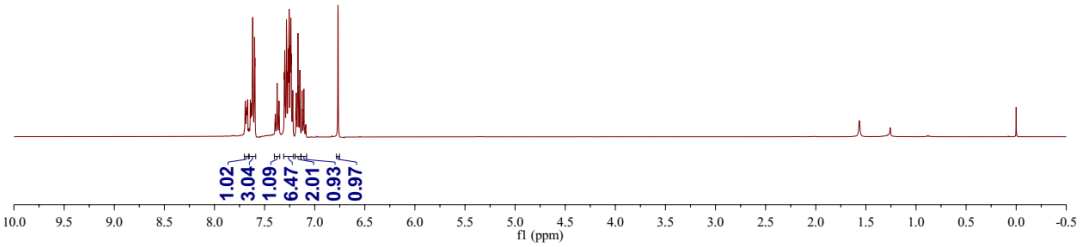

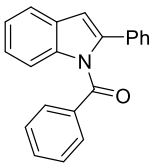

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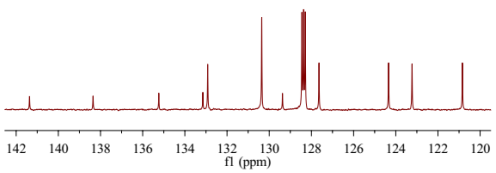

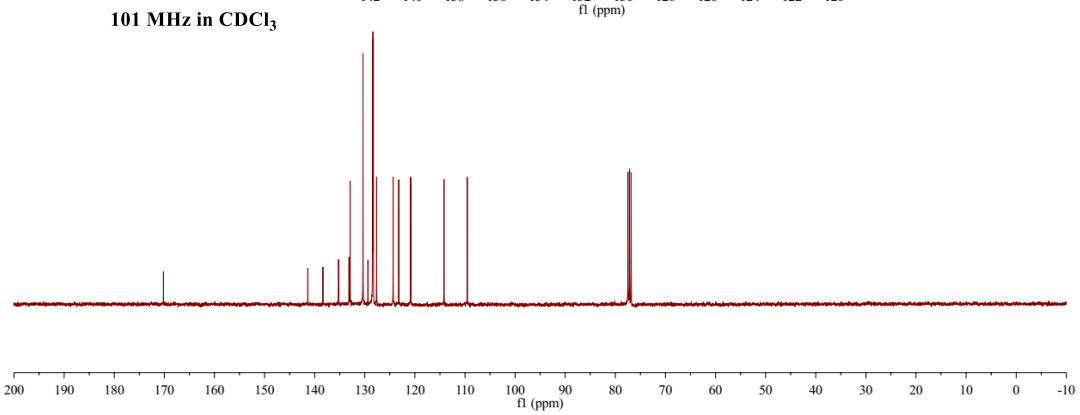

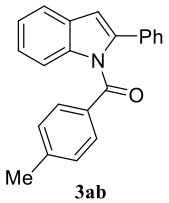

3ab

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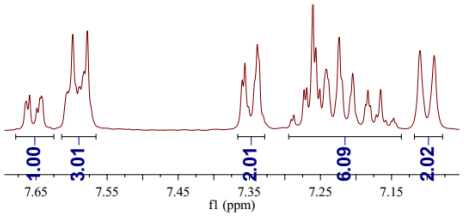

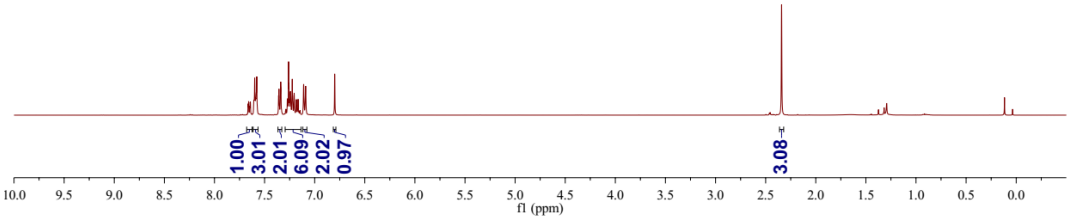

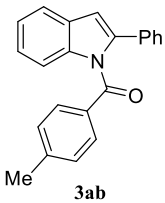

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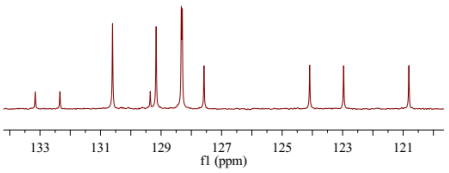
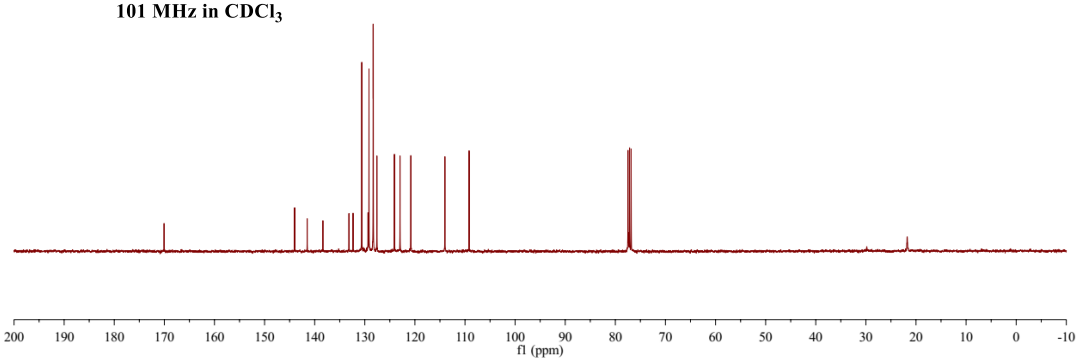
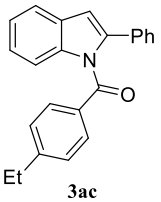
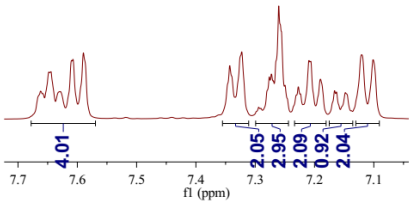


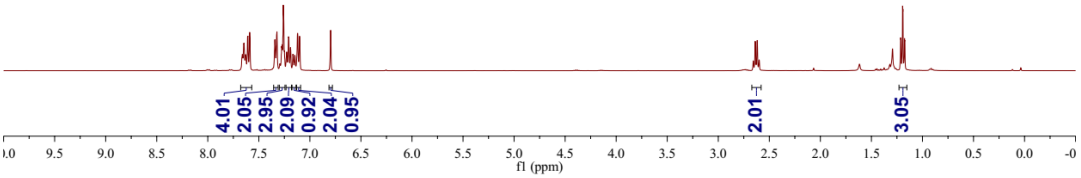


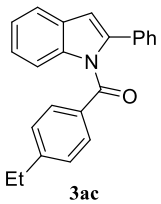


3ac

400 MHz in $CDCl_3$

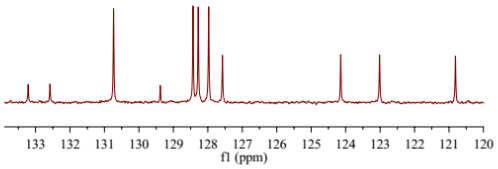


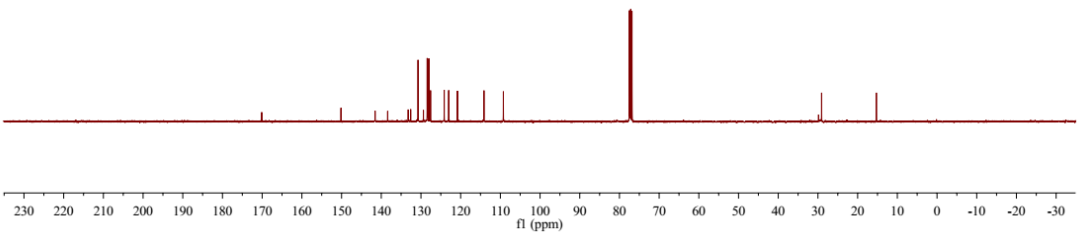


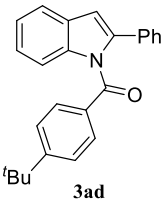


3ac

101 MHz in $CDCl_3$

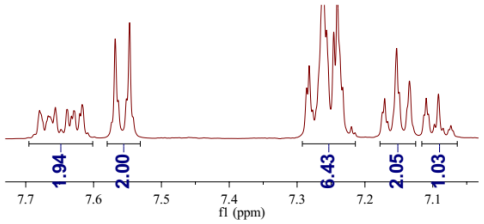


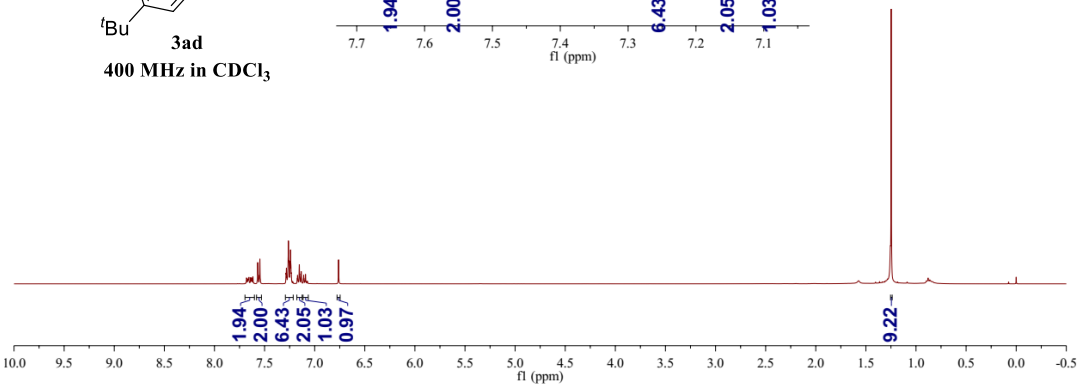


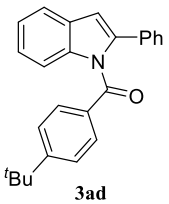


3ad

400 MHz in $CDCl_3$

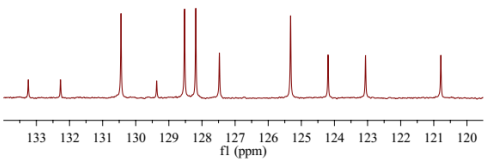


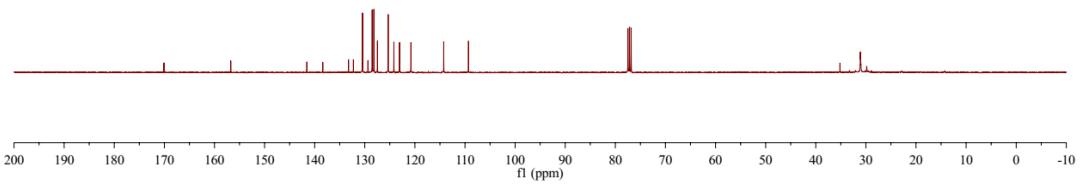


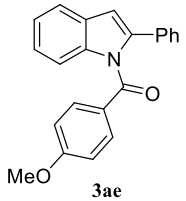


3ad

101 MHz in $CDCl_3$

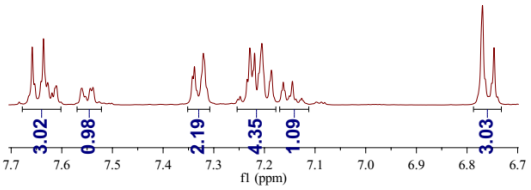


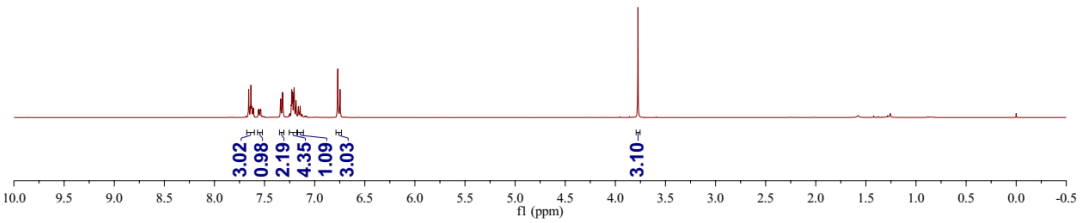


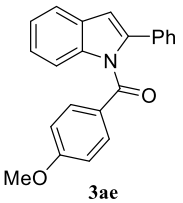


3ae

400 MHz in $CDCl_3$

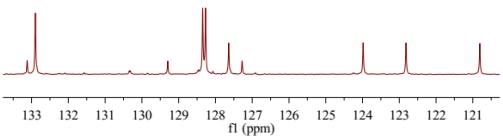


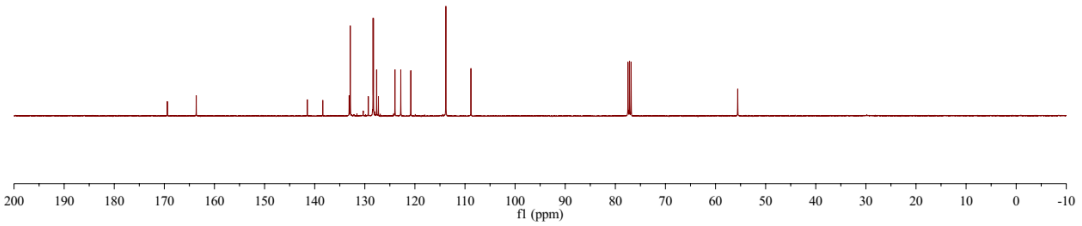


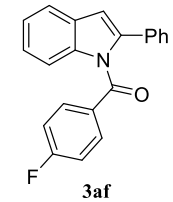


3ae

101 MHz in $CDCl_3$

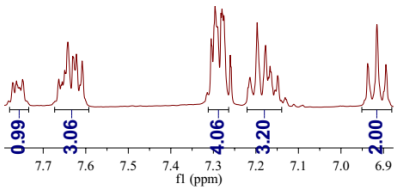


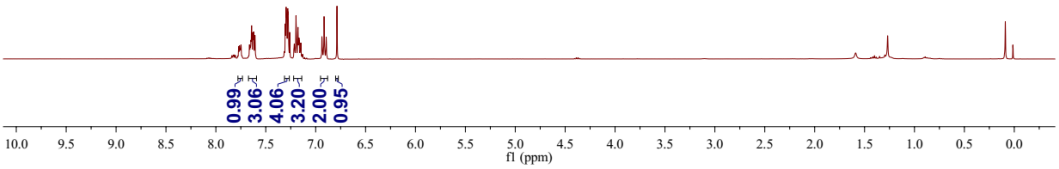


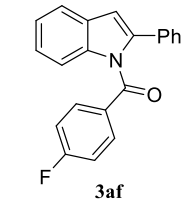


3af

400 MHz in $CDCl_3$

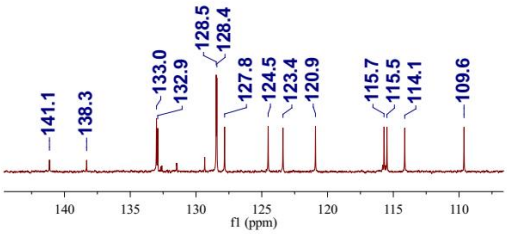


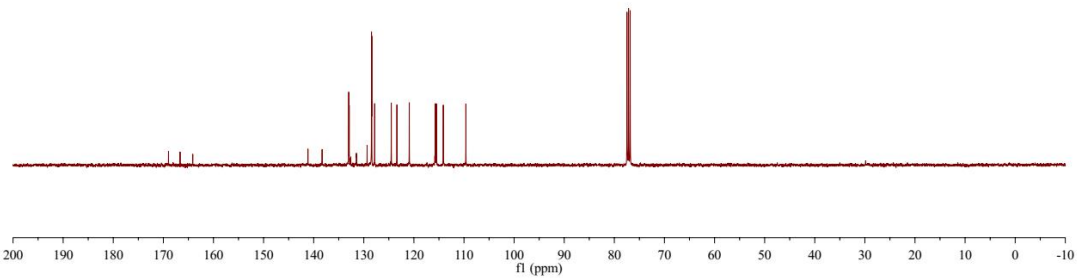


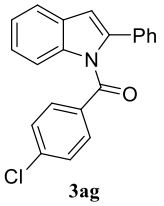


3af

101 MHz in $CDCl_3$

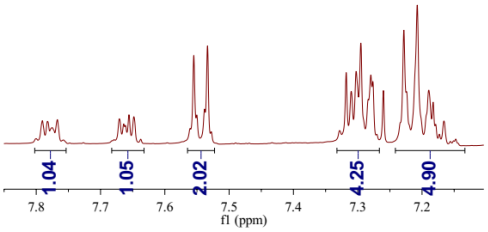


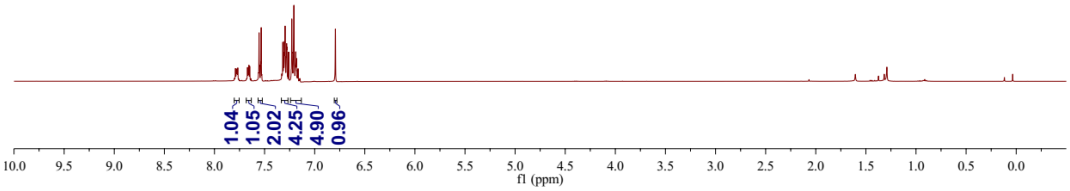


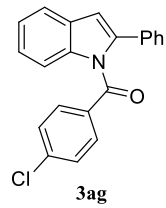


3ag

400 MHz in $CDCl_3$







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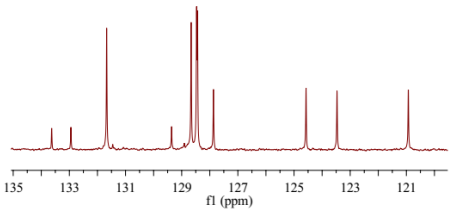
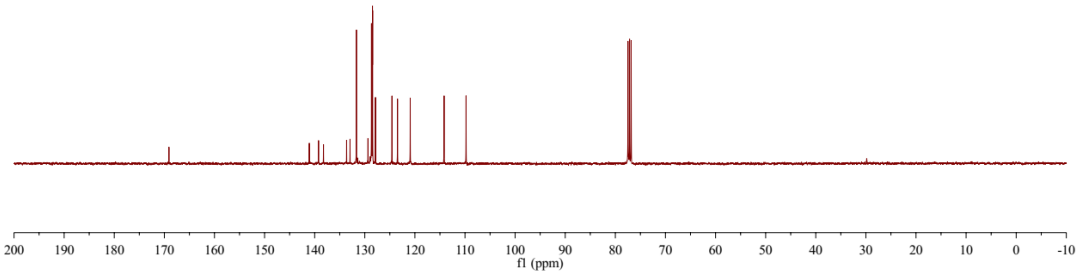
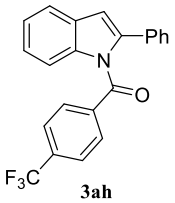
101 MHz in $CDCl_3$

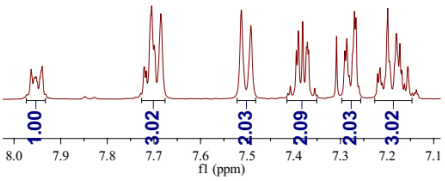


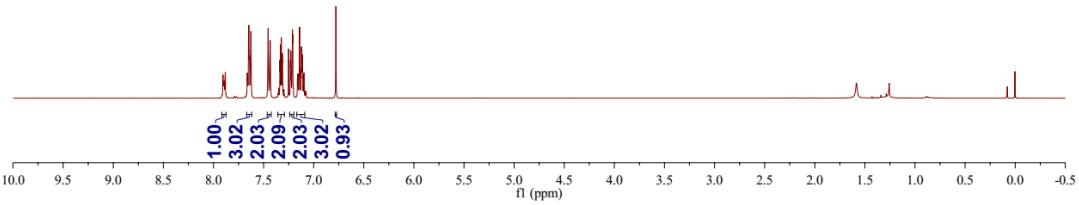


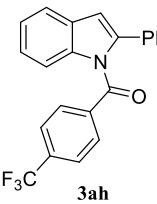


3ah

400 MHz in $CDCl_3$

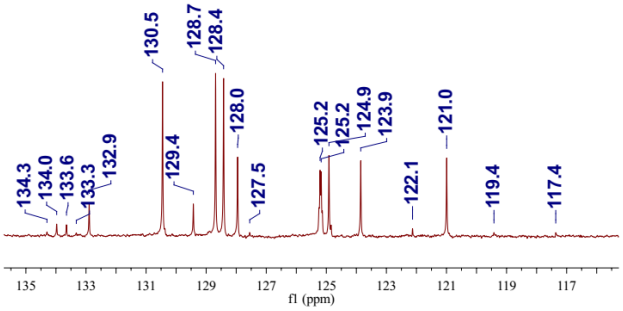


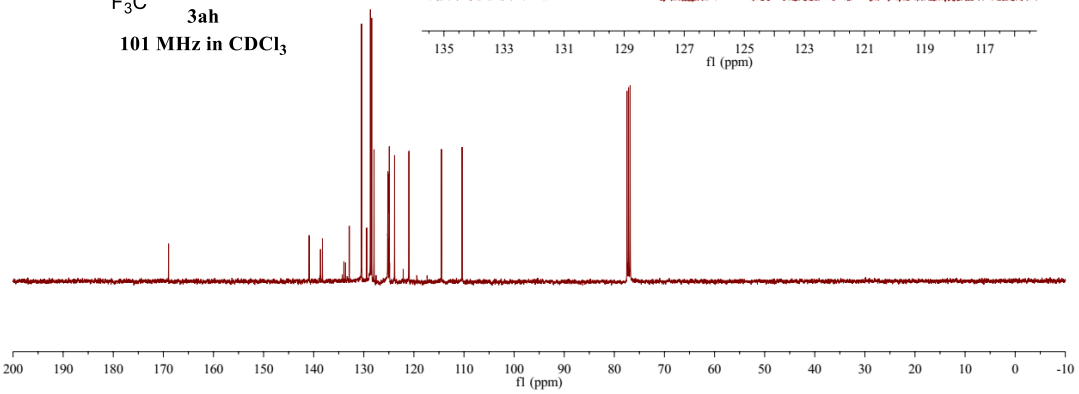


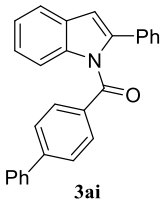


3ah

101 MHz in $CDCl_3$

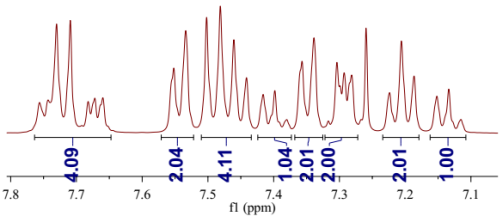


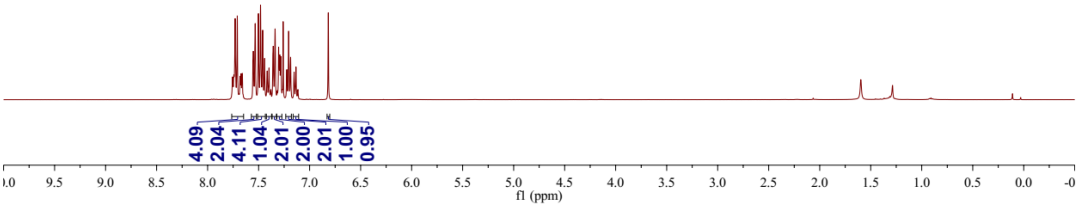


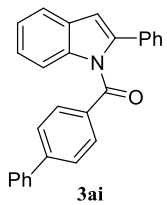


3ai

400 MHz in $CDCl_3$

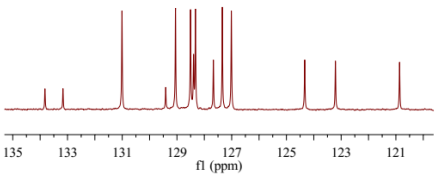


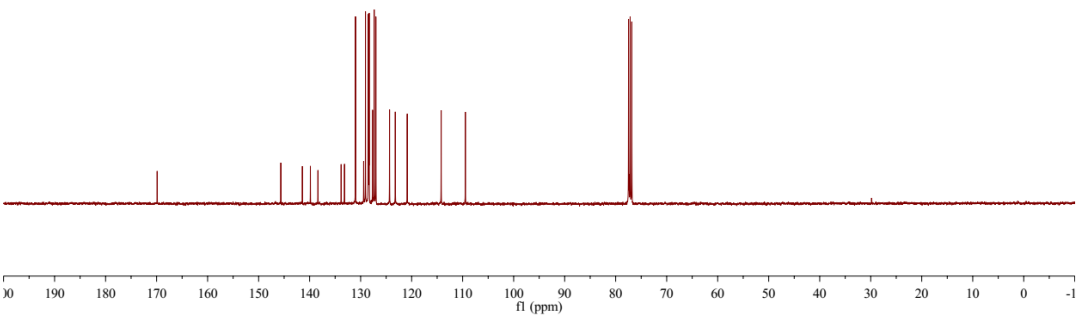


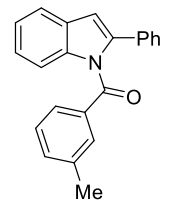


3ai

101 MHz in $CDCl_3$

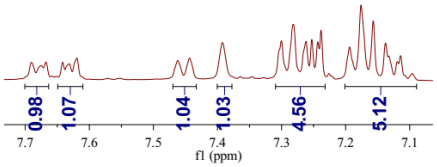


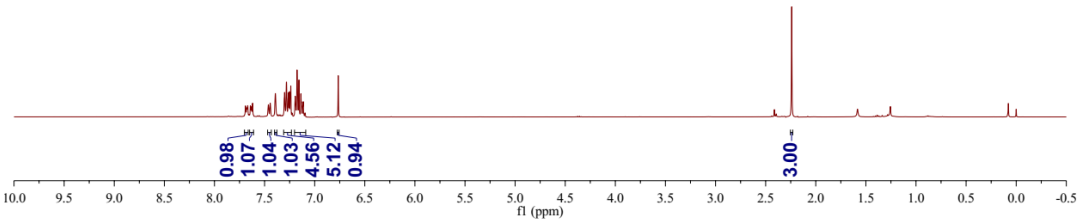


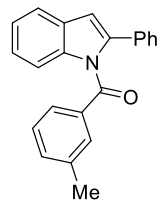


3aj

400 MHz in $CDCl_3$

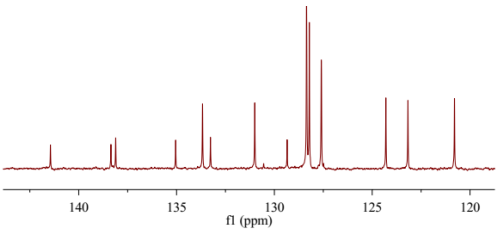


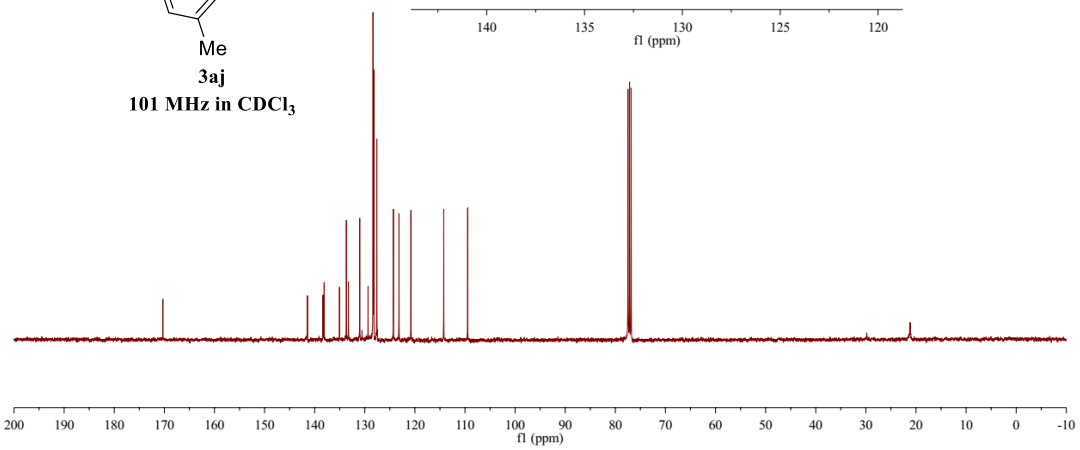


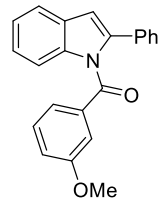


3aj

101 MHz in $CDCl_3$

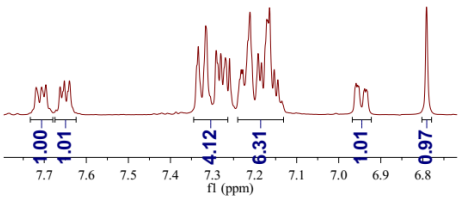


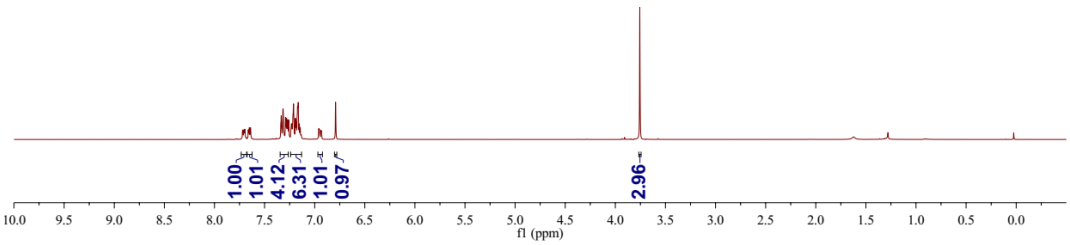


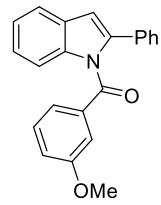


3ak

400 MHz in $CDCl_3$

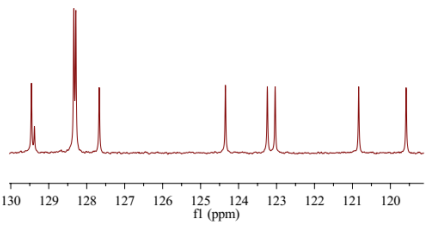


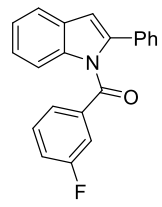




3ak

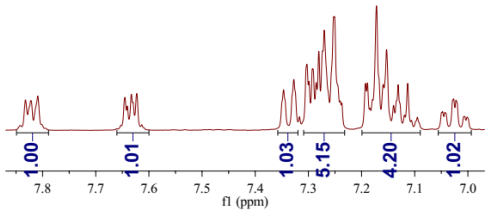
101 MHz in $CDCl_3$

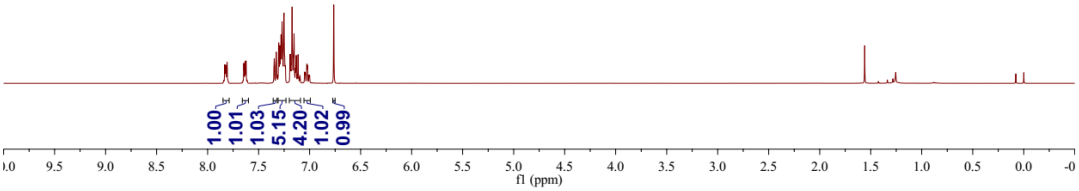


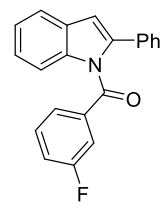


3al

400 MHz in $CDCl_3$

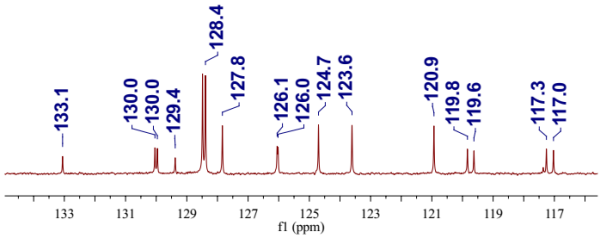


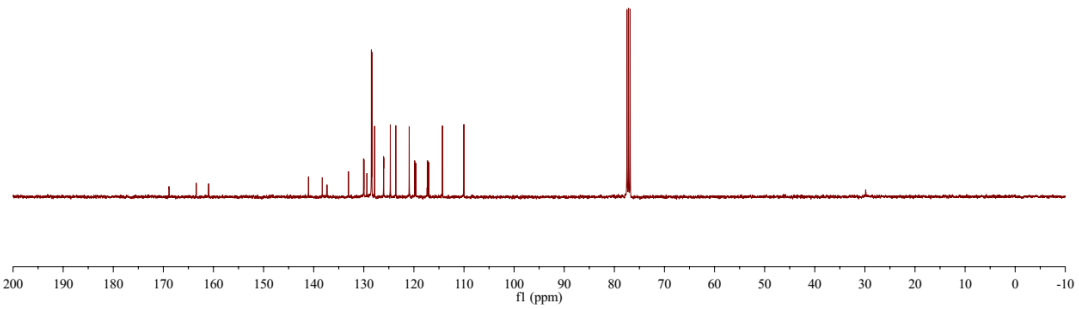


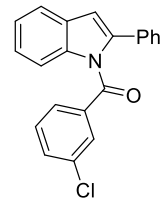


3al

101 MHz in $CDCl_3$

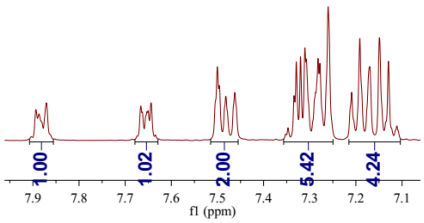


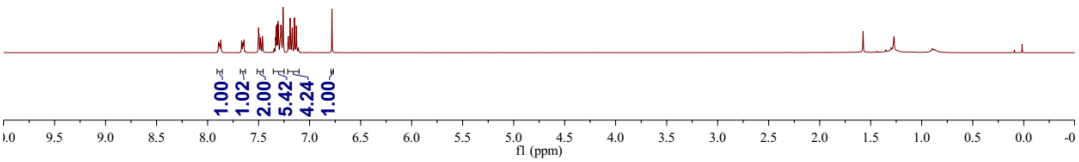


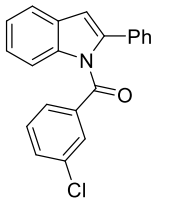


3am

400 MHz in $CDCl_3$

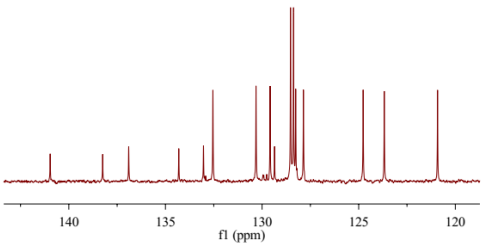


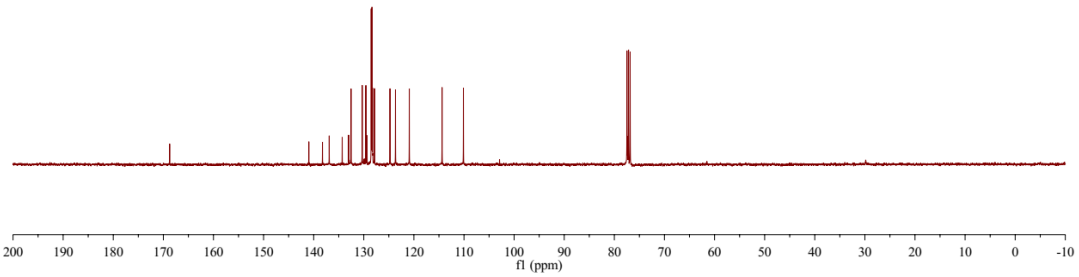


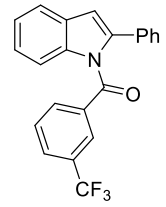


3am

101 MHz in $CDCl_3$

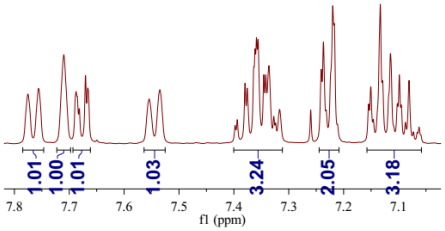


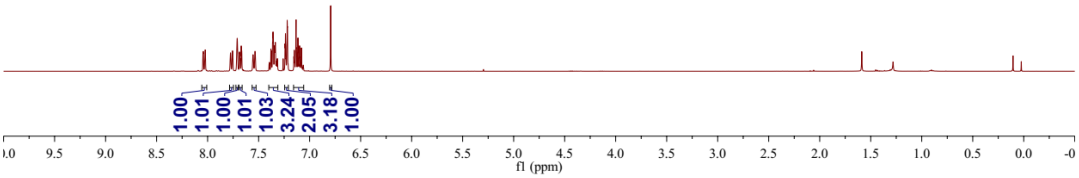


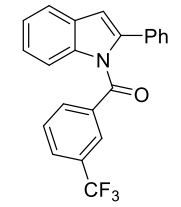


3an

400 MHz in $CDCl_3$

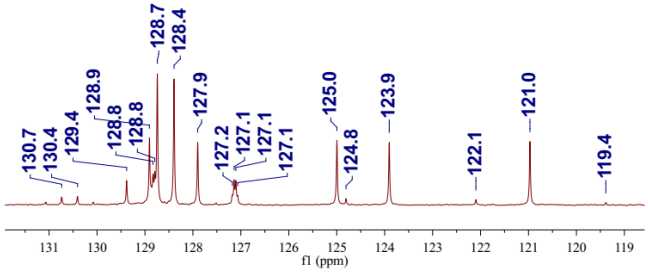


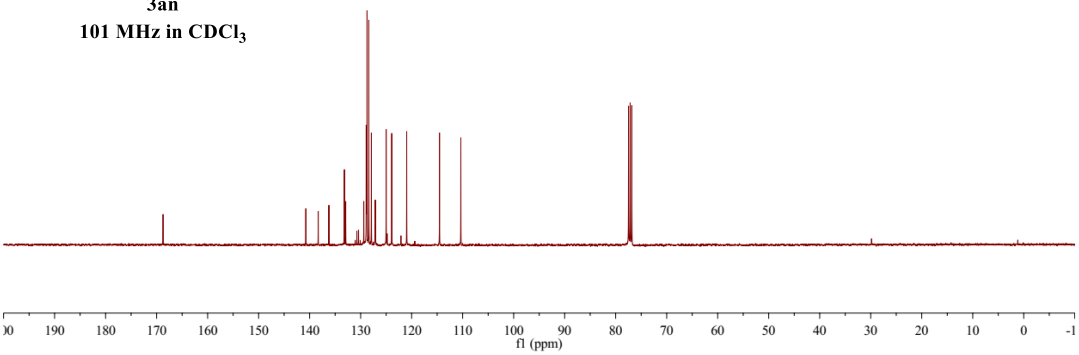


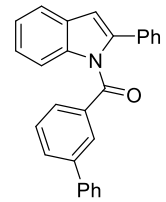


3an

101 MHz in $CDCl_3$

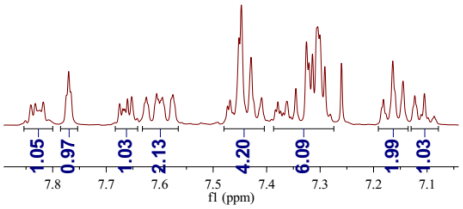


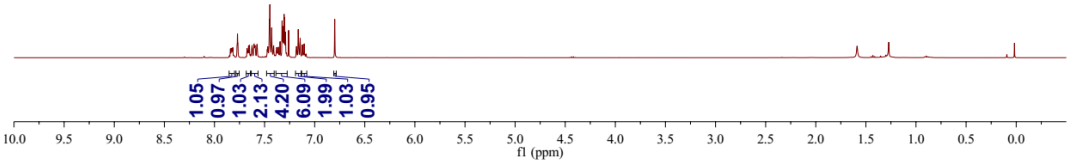


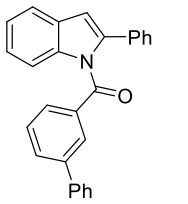


3ao

400 MHz in $CDCl_3$

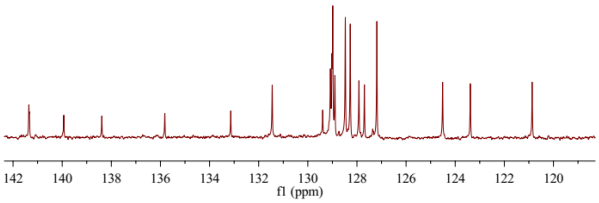


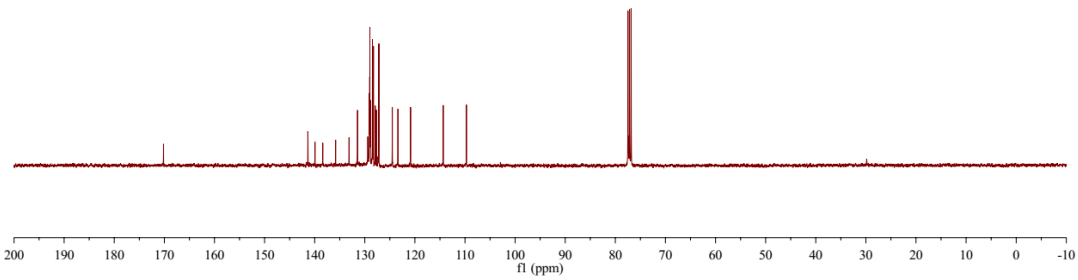


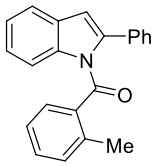


3ao

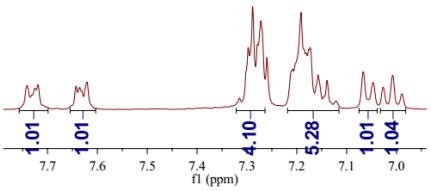
101 MHz in $CDCl_3$

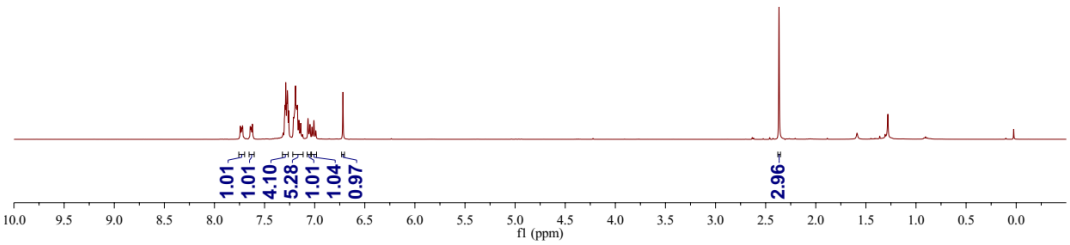


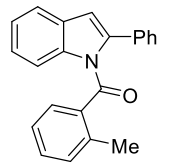




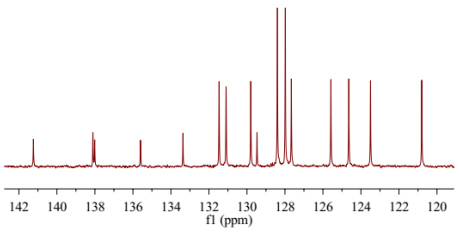
3ap
400 MHz in $CDCl_3$

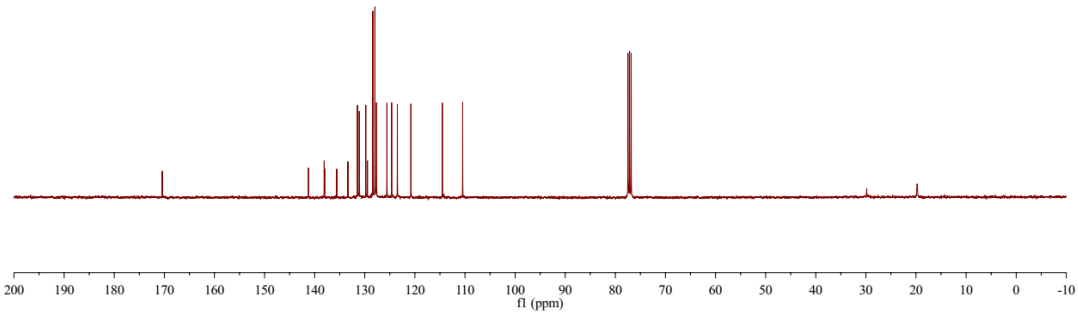


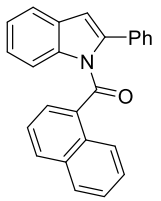




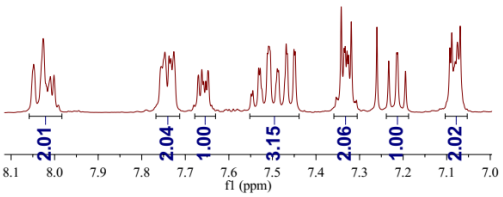
3ap
101 MHz in $CDCl_3$

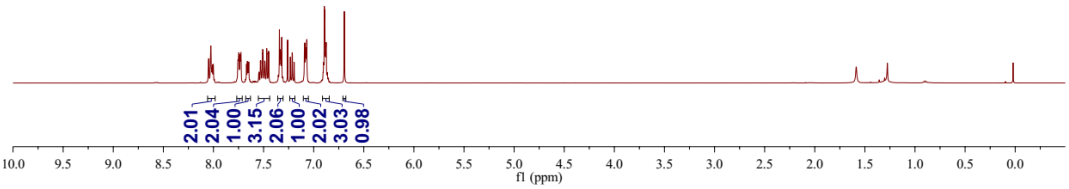


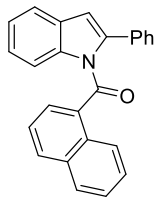




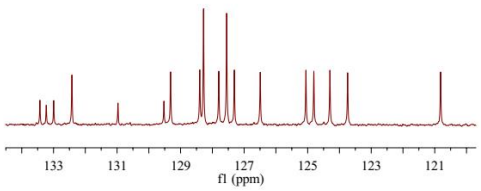
3aq
400 MHz in $CDCl_3$

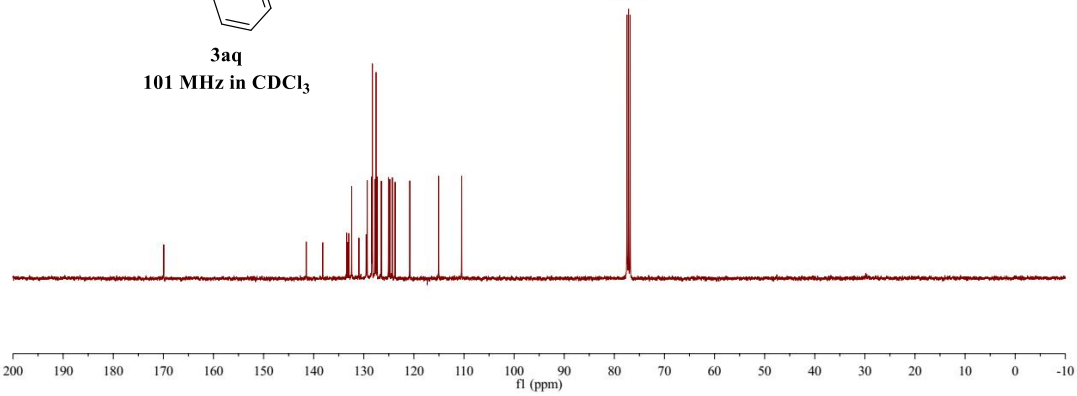


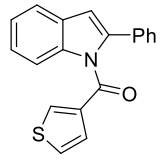




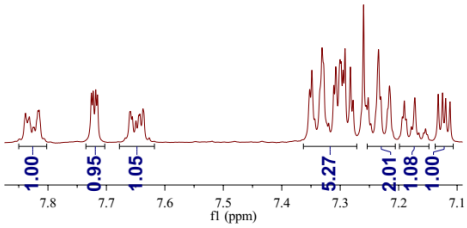
3aq
101 MHz in $CDCl_3$

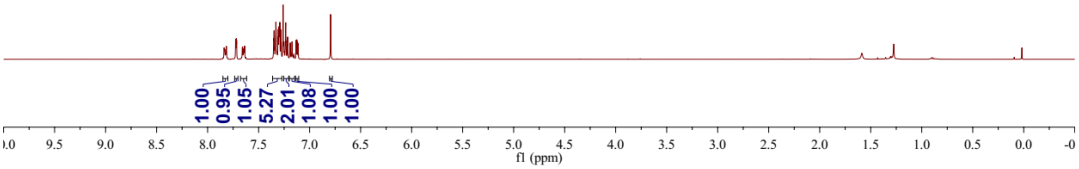


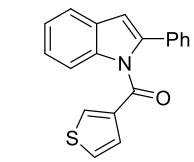




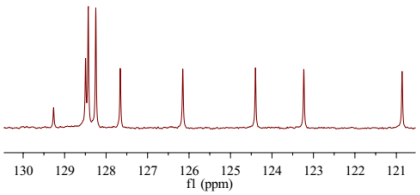
3ar
400 MHz in $CDCl_3$

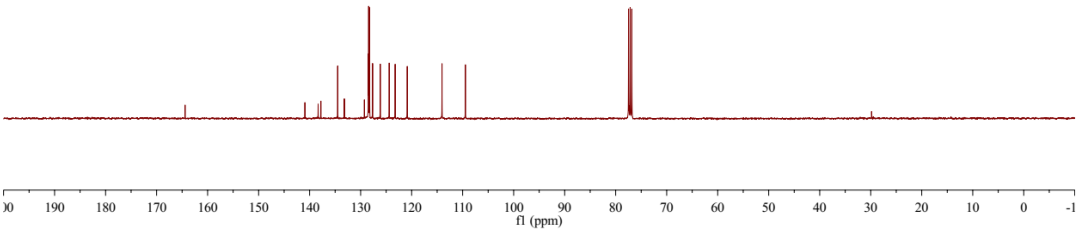


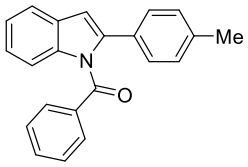




3ar
101 MHz in $CDCl_3$

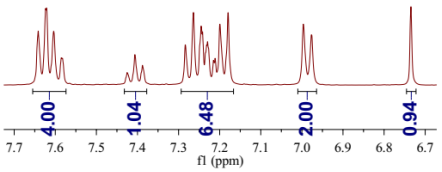


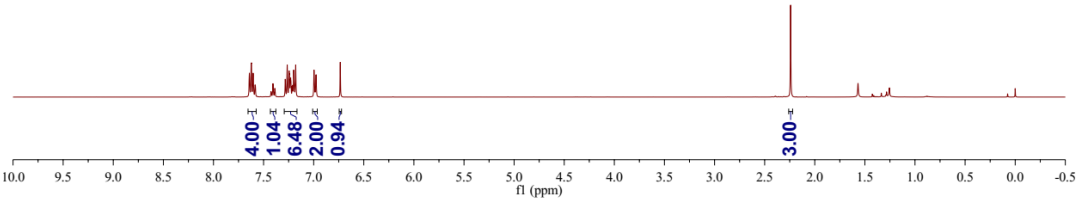


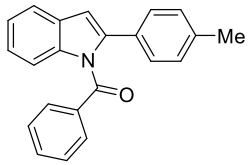


3ba

400 MHz in $CDCl_3$

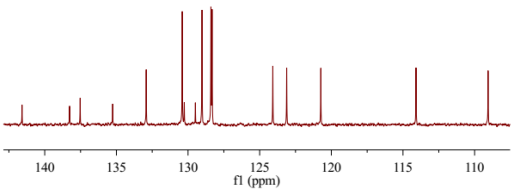


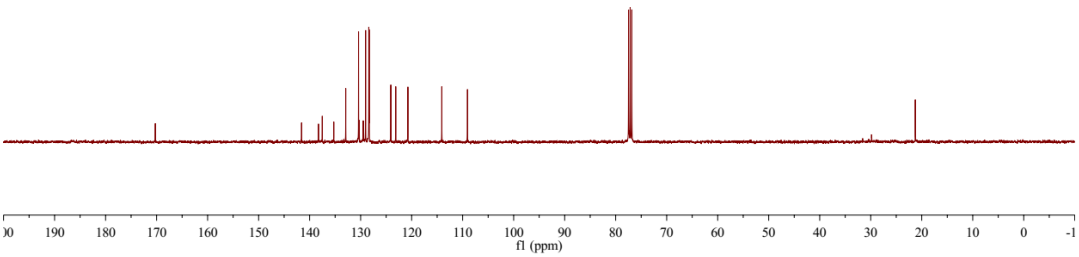


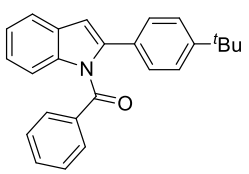


3ba

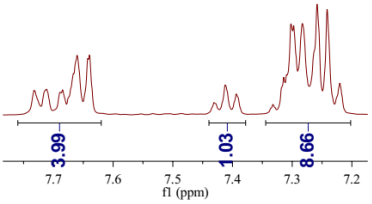
101 MHz in $CDCl_3$

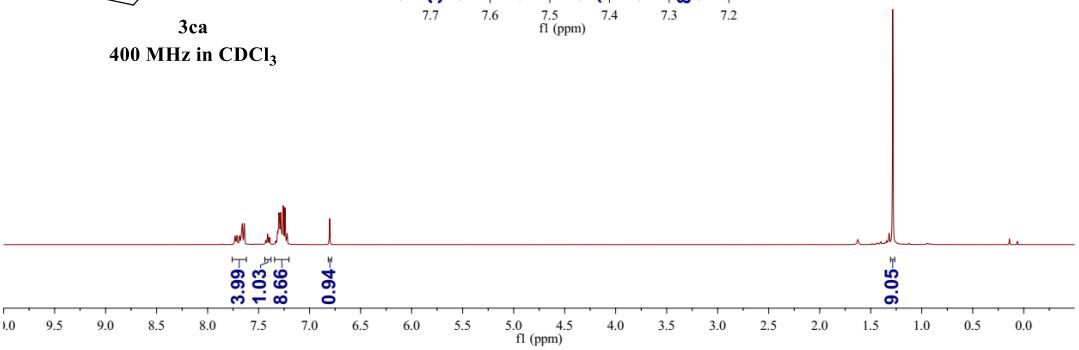


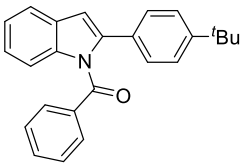




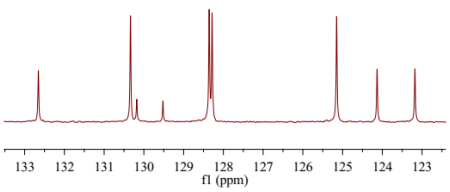
3ca
400 MHz in $CDCl_3$

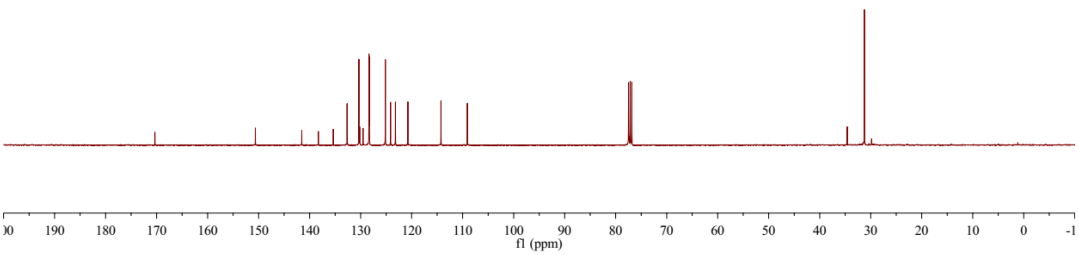


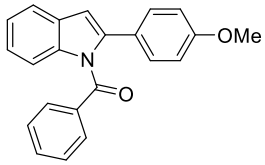




3ca
101 MHz in $CDCl_3$

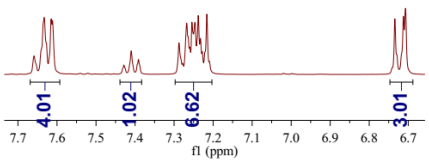


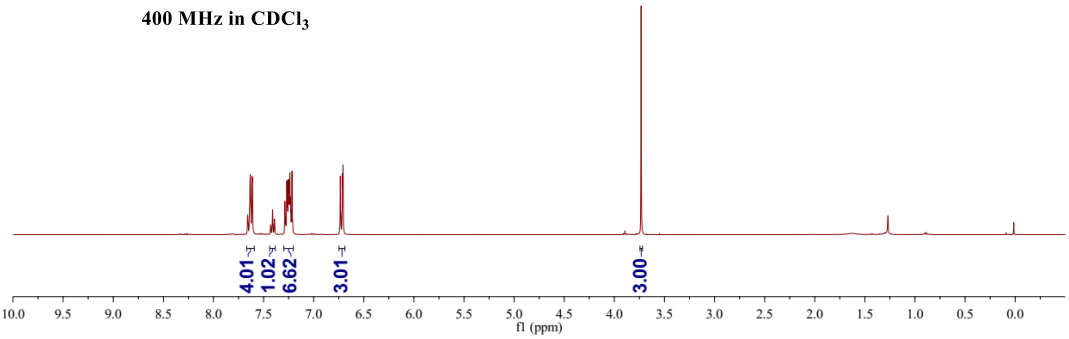


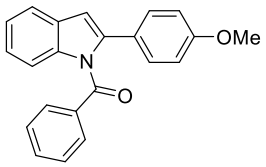


3da

400 MHz in $CDCl_3$

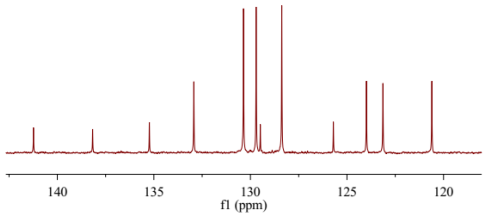


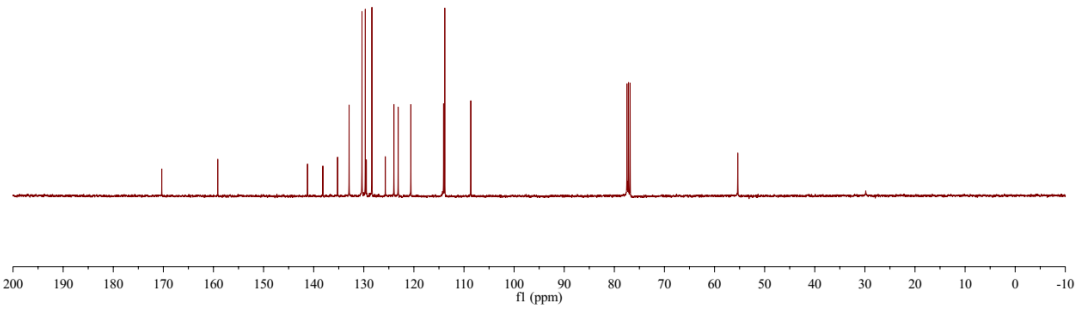


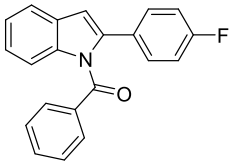


3da

101 MHz in $CDCl_3$

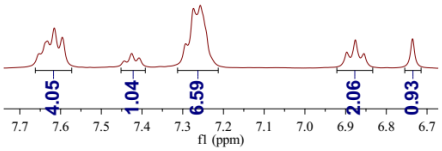


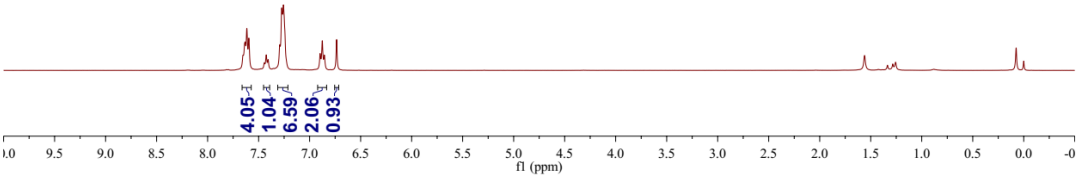


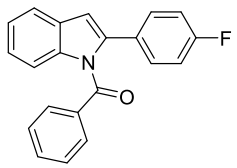


3ea

400 MHz in $CDCl_3$

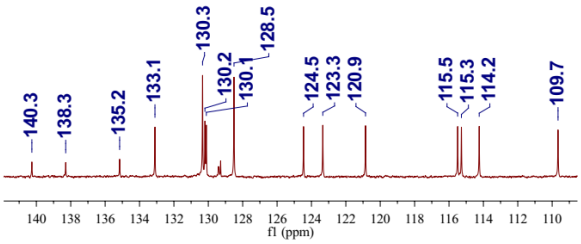


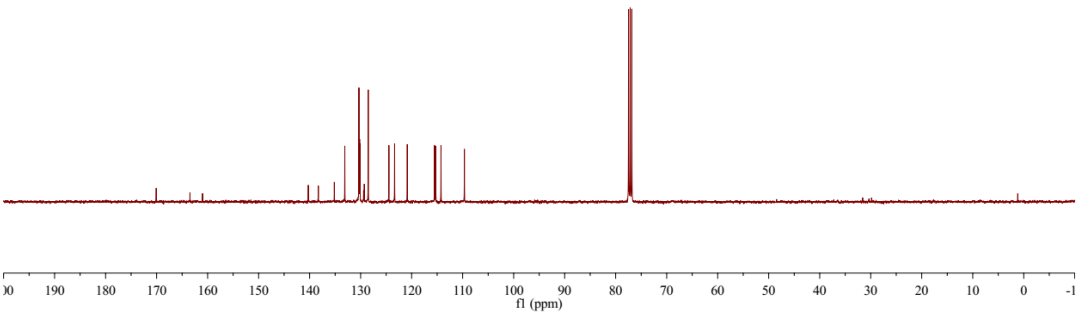


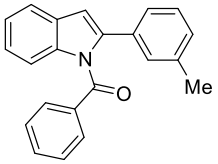


3ea

101 MHz in $CDCl_3$

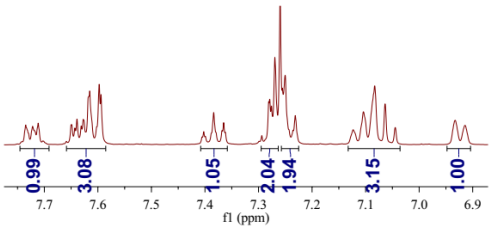


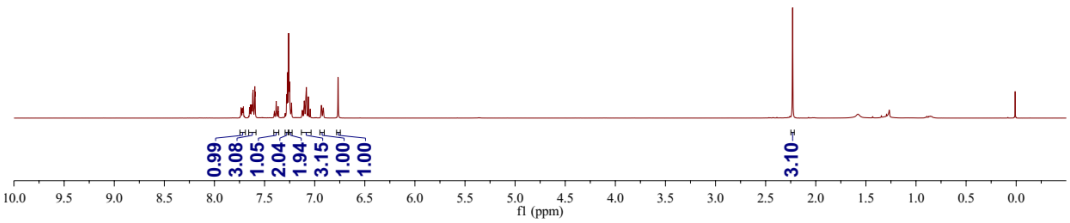


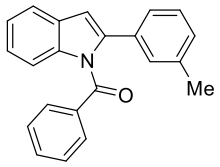


3fa

400 MHz in $CDCl_3$

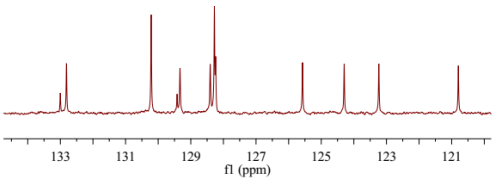


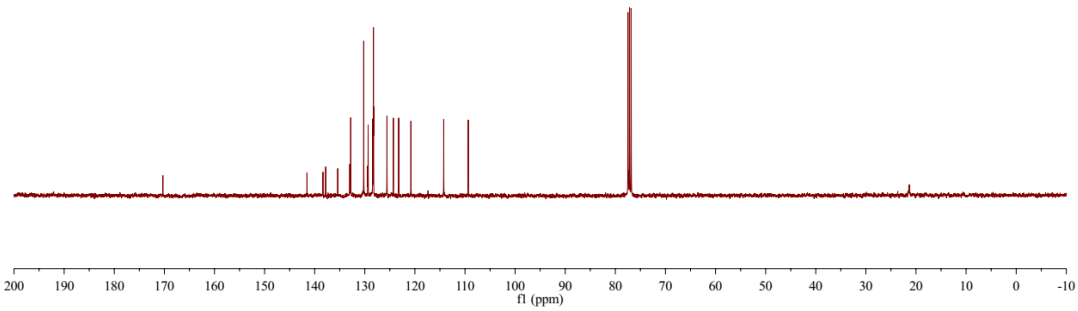


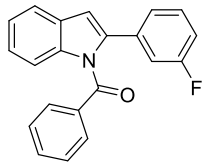


3fa

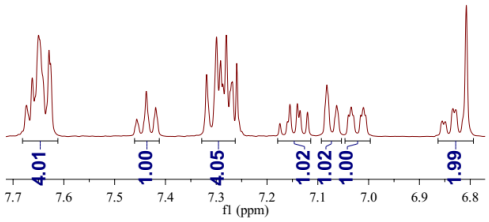
101 MHz in $CDCl_3$

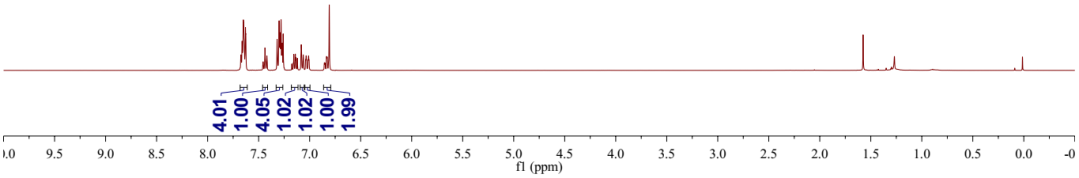


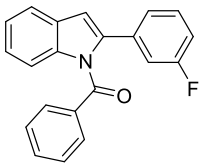




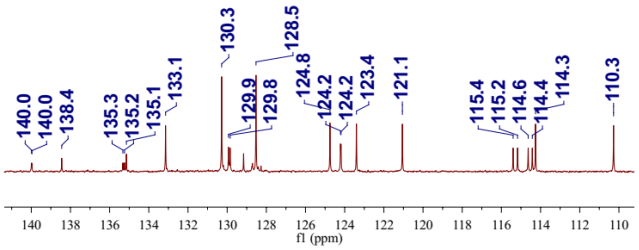
3ga
400 MHz in $CDCl_3$

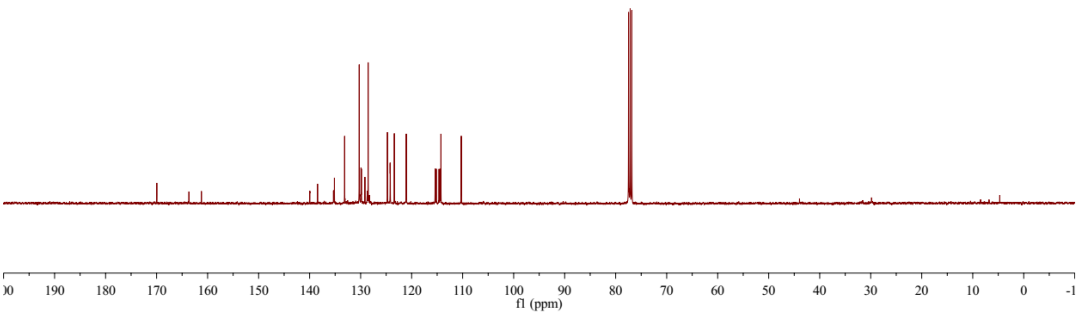


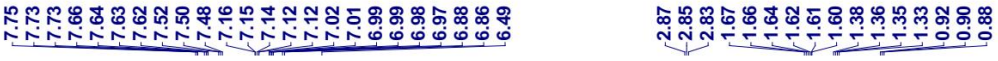


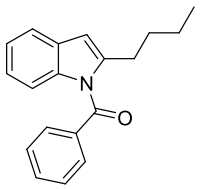


3ga
101 MHz in $CDCl_3$



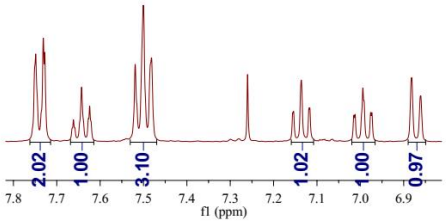


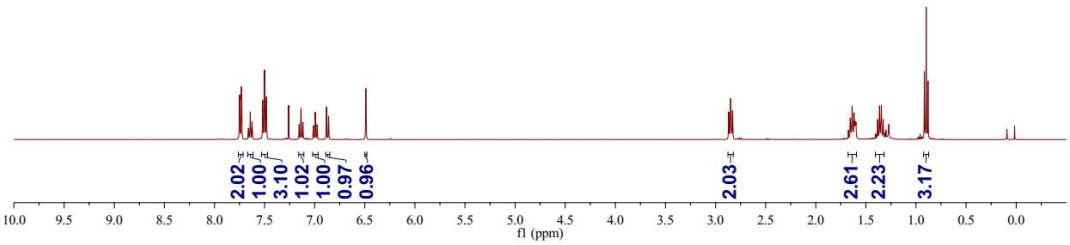


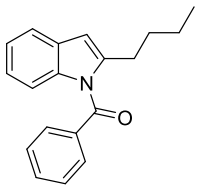


3ha

400 MHz in $CDCl_3$

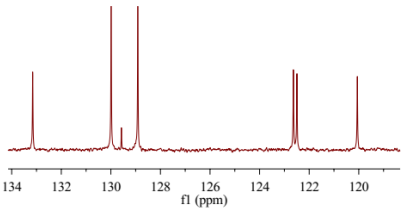


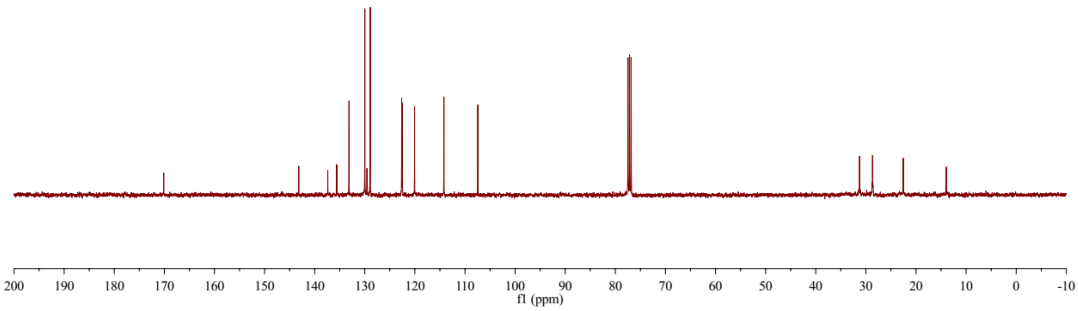


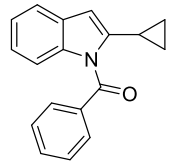


3ha

101 MHz in $CDCl_3$

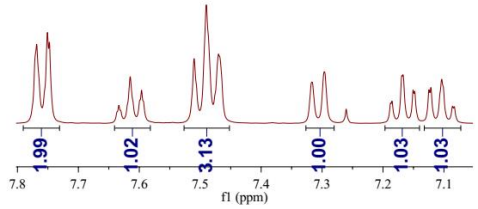


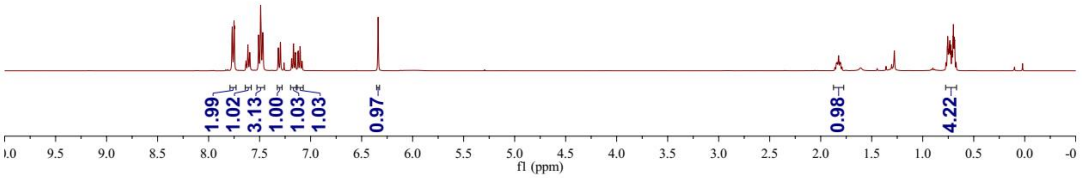


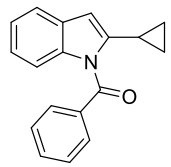


3ia

400 MHz in $CDCl_3$

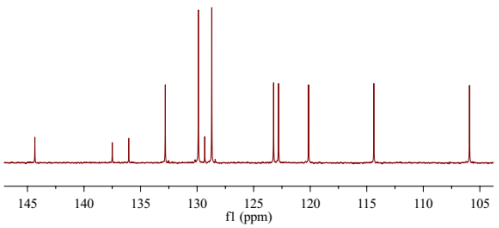


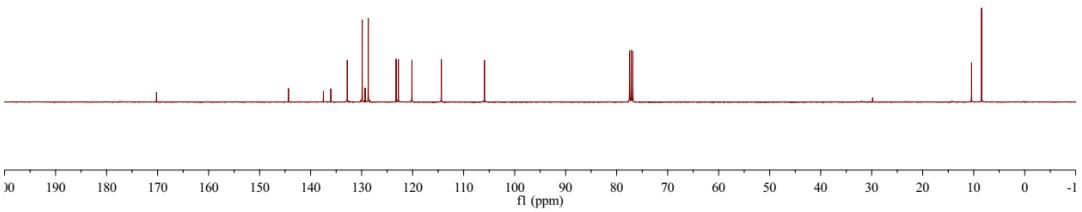


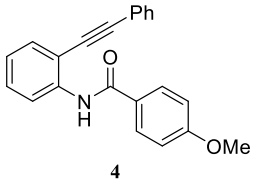


3ia

101 MHz in $CDCl_3$

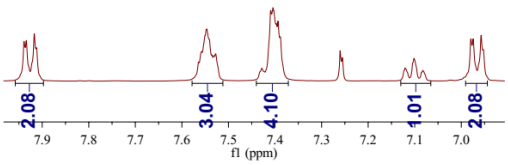


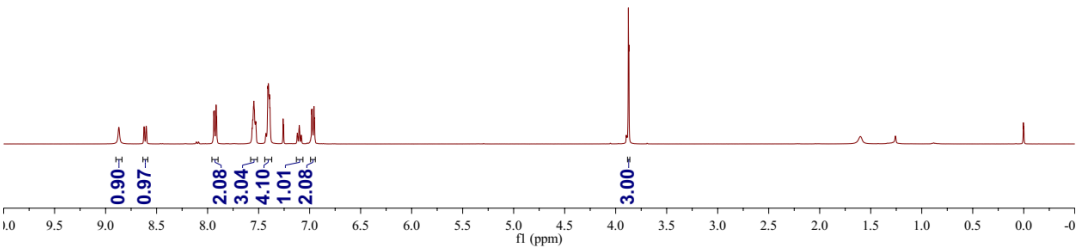


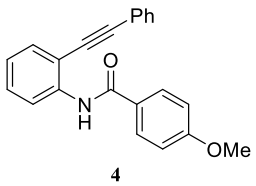


4

400 MHz in $CDCl_3$







4

101 MHz in $CDCl_3$