Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supplementary Information

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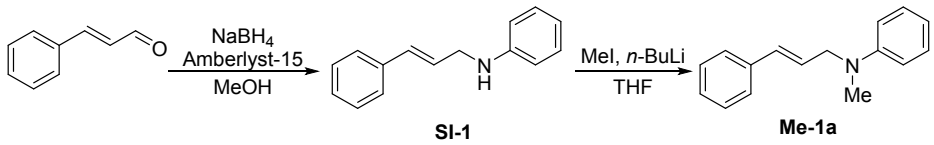
1. General Information:

Unless otherwise noted, reactions were carried out in oven-dried glassware or sealed tube under atmosphere of nitrogen. Toluene and acetonitrile (CH_3CN) were distilled from calcium hydride. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried and distilled from sodium. Methanol (MeOH) was dried under reflux with magnesium and then distilled. *N*, *N*-Dimethylformamide (DMF) was dried over calcium hydride and distilled under vacuum. Reactions were monitored by analytical thin-layer chromatography (TLC) on Merck silica gel 60 F_{254} plates (0.25 mm), visualized by ultraviolet light (254 nm) or by staining with ceric ammonium molybdate or basic potassium permanganate solutions as appropriate. ^{1}H NMR spectra were obtained on an Agilent 400MR or 600MR DD2 spectrometer at ambient temperature. Data were reported as follows: chemical shift on the δ scale using residual proton solvent as internal standard [δ 7.26 ($CDCl_3$); TMS: 0.00 ppm], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), integration, and coupling constant (*J*) in hertz (Hz). ^{13}C NMR spectra were obtained with proton decoupling on an Agilent 400MR DD2 (100 MHz) spectrometer and were reported in ppm with residual solvent for internal standard [δ 77.16 ($CDCl_3$)]. High resolution mass spectra were obtained on a Bruker SolariX 7.0T spectrometer.

2. Synthesis of Starting Materials:

2.1 General Scheme for the Synthesis of Directed Groups:

2.1.1 Synthesis of *N*-cinnamyl-*N*-methylaniline (Me-1a):

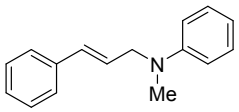


SI-1 **Me-1a**

Procedure SI-A[1]:

Cinnamaldehyde (1.0 g, 1.0 equiv) and aniline (0.70 g, 1.0 equiv) were mixed in THF (20 mL), and then Amberlyst 15 (0.2 g) was added. The mixture was vigorously stirred at room temperature, and $NaBH_4$ (1 mmol) was added. After completion of the reaction as indicated by TLC, the mixture was filtered, and the residue was washed with Et_2O (2x15 mL). The solvent was evaporated, and the residual oil was loaded on a silica gel column and eluted with 1:20 to 1:5 ethyl acetate/petroleum ether to afford the corresponding product **SI-1** (1.02 g, 65%) as a pale yellow oil. R_f = 0.50 (silica, hexanes: EtOAc, 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 – 7.08 (m, 7H), 6.67 – 6.51 (m, 4H), 6.24 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.85 (d, *J* = 5.6 Hz, 2H), 3.26 (brs, 1H).

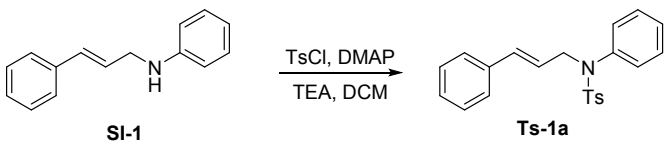
***N*-cinnamyl-*N*-methylaniline**



Me-1a

To a stirred solution of **SI-1** (800.0 mg, 1.0 equiv) in dry THF was added *n*-BuLi (2.5 M in hexanes, 38.7 mL, 96.7 mmol) slowly at −78 ºC. After 1 h, MeI (0.40 mL, 1.5 equiv) was added 0 ºC. After completion of reaction as monitored by TLC, H_2O was added dropwise and the reaction mixture was stirred for 10 min at 0 ºC. The aqueous phase was extracted with EtOAc (20 mL x 3) and the combined organic extracts were dried over Na_2SO_4 and concentrated, then the crude material was purified by flash column chromatography (SiO_2, Hexanes / EtOAc) to afford the title compound **Me-1a** (0.5 g, 59%) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28 – 7.11 (m, 7H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.17 (dt, *J* = 15.9, 5.5 Hz, 1H), 4.00 (dd, *J* = 5.5, 1.6 Hz, 2H), 2.90 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 149.6, 137.0, 131.4, 129.3, 128.6, 127.5, 126.4, 125.8, 116.7, 112.7, 55.0, 38.1; **HRMS** (ESI): calcd for $C_{16}H_{18}N^+$ [M+H$^+$]: 224.1433, found 224.1433.

2.1.2 Synthesis of *N*-cinnamyl-4-methyl-*N*-phenylbenzenesulfonamide:

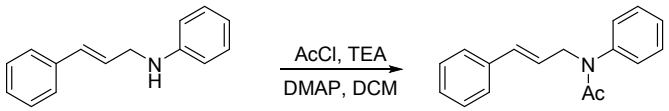


SI-1 **Ts-1a**

To a solution of amine **SI-1** (0.30 g, 1.0 equiv) in CH_2Cl_2 (0.3 M) at 0 ºC was added triethylamine (3 equiv)

followed by 4-metylbenzenesulfonyl chloride (0.27 g, 1.0 equiv) and the reaction allowed to room temperature. After stirring overnight, and water was added (equivalent to amount of CH_2Cl_2 solvent in reaction), the layers separated, and the organic layer extracted once with CH_2Cl_2. The combined organics were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography, using silica gel and Hexane / AcOEt afforded to yield the corresponding *p*-toluenesulfonyl -protected amine **Ts-1a** (312 mg, 60%) as a white solid. **m.p.** = 132.5-134.0 °C; R_f = 0.40 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.09 (m, 10H), 7.00 – 6.97 (m, 2H), 6.28 (d, *J* = 15.8 Hz, 1H), 6.01 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.25 (dd, *J* = 6.6, 1.4 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.5, 139.3, 136.4, 135.7, 133.8, 129.5, 129.0, 128.9, 128.5, 127.9, 127.8, 127.8, 126.5, 124.1, 53.3, 21.6. **HRMS** (ESI): calcd for $C_{22}H_{21}NNaO_2S^+$ [M+Na$^+$]: 386.1184, found 386.1185.

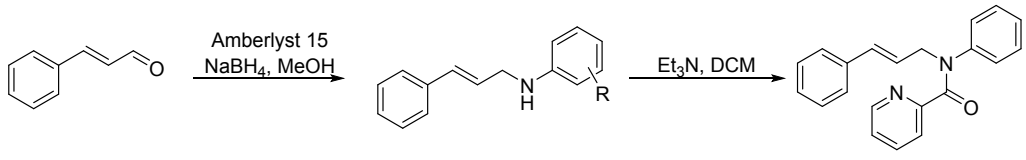
2.1.3 Synthesis of *N*-cinnamyl-*N*-phenylacetamide:



SI-1 **Ac-1a**

To a solution of amine **SI-1** (0.29 g, 1.0 equiv) in CH_2Cl_2 (0.3 M) at 0 ºC was added triethylamine (3 equiv) followed by acetyl chloride (0.28 g, 1.0 equiv) and the reaction allowed to room temperature. After stirring overnight, water was added (equivalent to amount of CH_2Cl_2 solvent in reaction), the layers separated, and the organic layer extracted once with CH_2Cl_2. The combined organics were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography, using silica gel and Hexane / AcOEt afforded to yield the corresponding *p*-toluenesulfonyl -protected amine **Ac-1a** (184.0 mg, 53%) as a pale brown liquid. R_f = 0.40 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.33 – 7.08 (m, 10H), 6.29 (d, *J* = 15.7 Hz, 1H), 6.22 – 6.15 (m, 1H), 4.36 (d, *J* = 6.5 Hz, 2H), 1.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.3, 143.0, 136.8, 133.3, 129.9, 129.7, 128.6, 128.4, 128.3, 128.0, 127.7, 126.5, 126.5, 124.55, 51.6, 22.8. **HRMS** (ESI): calcd for $C_{17}H_{17}NNaO^+$ [M+Na$^+$]: 274.1205, found 274.1202.

2.2.1 General Scheme for the Synthesis of 1a-s:



SI 1-9, 13,14 **1a-u**

Procedure SI-B[1]: for the Synthesis of SI 1-9, 13 and 14

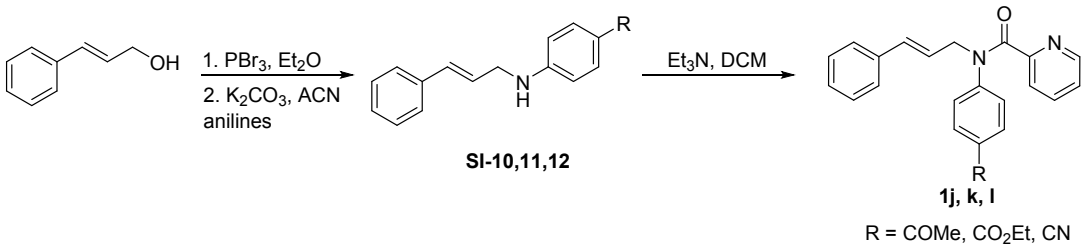
Cinnamaldehyde (1 mmol) and aniline (1 mmol) were mixed in THF (5 mL), and then Amberlyst 15 (0.1 g) was

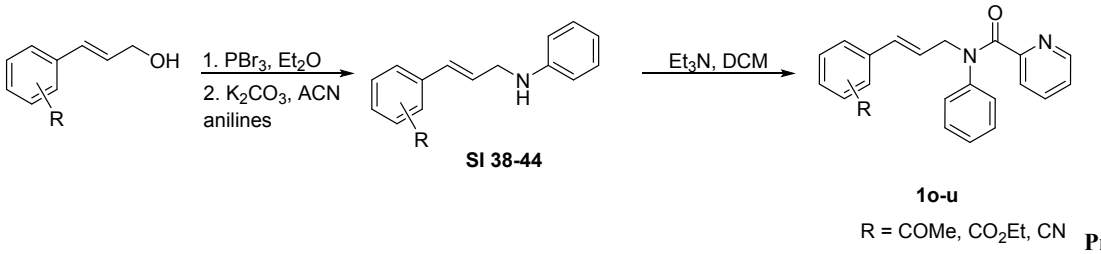
added. The mixture was vigorously stirred at room temperature, and $NaBH_4$ (1 mmol) was added. The mixture was stirred again. After completion of the reaction as indicated by TLC, the mixture was filtered, and the residue was washed with Et_2O (2 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was loaded on a silica gel column and eluted with 1:20 to 1:5 ethyl acetate/petroleum ether to afford the corresponding product **(SI-1-9, 13 and 14).**

Procedure SI-C[3]: for the Synthesis of 1a-u

To a solution of the picolinic acid (2.50 mmol) in DCM (20 mL) at room temperature was added $SOCl_2$ (2 mL) and one drop of dry DMF. The reaction was allowed to stir at 40 °C for 4 hours. The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride. Then DCM (20 mL) was added and the solution was cooled to 0°C followed by dropwise addition of NEt_3 (1.5 mL), DMAP (0.25 mmol) and amine (2.50 mmol, 1.0 eq). The reaction mixture was stirred at room temperature overnight, extracted by DCM, the organic layer was dried over Na_2SO_4 and the solvent was evaporated, then purified by flash chromatography(petroleum ether/ EtOAc = 2 : 1) to afford the corresponding product **(1a-u)**.

2.2.2 General Scheme for the Synthesis of 1J-l and 1o-u: [2]





Procedure SI-D[2]: for the Synthesis of SI-10,11,12 and SI 38-44

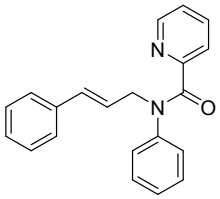
The cinnamylalcohol (1.00 equiv) is dissolved in Et_2O (16 mL/mmol) and the resulting mixture cooled to 0 °C. PBr_3 (1.05 equiv) is added and stirred at 0 °C for approximately 1 h. After completion of the reaction (monitored by TLC) the reaction is poured into ice-cooled sat. aq. NH_4Cl-solution (15 mL/mmol). The aqueous layer is extracted with Et_2O. The combined organic layers are washed with water, sat. aq. NaCl, dried over Na_2SO_4 and filtered. All volatiles are removed under reduced pressuret to afford cinnamylbromide, which was used for next

step without further purification. To a stirred solution of aniline (5 mmol) in dry CH_3CN (15 mL) was added K_2CO_3 (7.5 mmol) and stirred well at room temperature. To this solution, cinnamylbromide (5 mmol) in dry CH_3CN (10 mL) was added drop wise and stirred at room temperature for 3 h. After completion of the reaction, the reaction mixture was evaporated under reduced pressure to remove CH_3CN. The crude mixture obtained was diluted with water (10 mL) and extracted with ethyl acetate (3X10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ EtOAc = 20 : 1) to afford corresponding product (**SI-10, 11, 12 and SI 38-44**).

Procedure SI-E[3]: for the Synthesis of 1J-l and 1o-u

To a solution of the picolinic acid (2.50 mmol) in DCM (20 mL) at room temperature was added $SOCl_2$ (2 mL) and one drop of dry DMF. The reaction was allowed to stir at 40 °C for 4 hours. The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride. Then DCM (20 mL) was added and the solution was cooled to 0 °C followed by dropwise addition of NEt_3 (1.5 mL), DMAP (0.25 mmol) and amine (2.50 mmol, 1.0 eq). The reaction mixture was stirred at room temperature overnight, extracted by DCM, the organic layer was dried over Na_2SO_4 and the solvent was evaporated, then purified by flash chromatography(petroleum ether/ EtOAc = 2 : 1) to afford corresponding product **(1J-l and 1o-u)**.

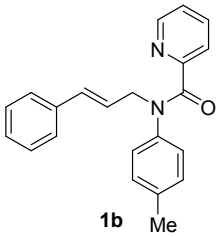
***N*-cinnamyl-*N*-phenylpicolinamide (1a):**



1a

Prepared according to general procedure **SI-C** from N-cinnamylaniline **SI-01** (500 mg, 2.39 mmol, 1.00 equiv) to yield **1a** (638 mg, 85%) as a pale yellow oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.49 (s, 1H), 7.36 (s, 1H), 7.27 – 7.01 (m, 11H), 6.45 – 6.28 (m, 2H), 4.62 (d, *J* = 6.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.5, 154.3, 148.5, 142.9, 136.7, 136.2, 133.5, 129.0, 128.6, 127.7, 126.8, 126.6, 124.2, 124.0, 123.7, 52.6; **HRMS** (ESI): calcd for $C_{21}H_{18}N_2NaO^+$ [M+Na$^+$]: 337.1314, found 337.1311.

***N*-cinnamyl-*N*-(p-tolyl)picolinamide (1b):**

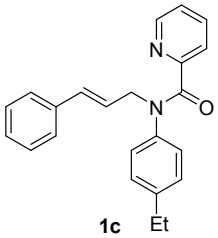


1b

Prepared according to general procedure **SI-C** from N-cinnamyl-4-methylaniline **SI-02** (500 mg, 2.24 mmol, 1.00 equiv) to yield **1b** (595 mg, 81%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.50 (s, 1H), 7.28 – 7.14 (m, 6H), 7.06 (s, 1H), 6.88 (s, 4H), 6.45 – 6.28 (m, 2H), 4.60 (d, *J* = 6.4 Hz, 2H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.5, 154.4, 148.5, 136.8, 136.7, 136.3, 133.5, 129.7, 128.6, 128.4, 127.7, 127.6, 126.6, 125.9, 124.3, 123.9, 123.7, 52.6, 21.1; **HRMS** (ESI): calcd for $C_{22}H_{20}N_2NaO^+$ [M+Na$^+$]:

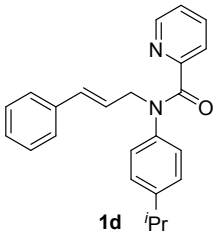
351.1469, found 351.1467.

***N*-cinnamyl-*N*-(4-ethylphenyl)picolinamide (1c):**



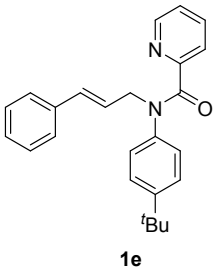
Prepared according to general procedure **SI-C** from N-cinnamyl-4-ethylaniline **SI-03** (500 mg, 2.10 mmol, 1.00 equiv) to yield **1c** (577 mg, 80%) as a pale yellow oil. R_f= 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.28 (s, 1H), 7.47 (s, 1H), 7.31 – 7.14 (m, 6H), 7.03 (s, 1H), 6.89 (s, 4H), 6.46 – 6.29 (m, 2H), 4.60 (d, *J* = 6.4 Hz, 2H), 2.46 (q, *J* = 7.6 Hz, 2H), 1.07 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.6, 154.5, 148.6, 142.9, 140.4, 136.8, 136.1, 133.4, 128.6, 128.4, 127.7, 127.6, 126.6, 124.3, 123.8, 123.6, 52.6, 28.3, 15.3; **HRMS** (ESI): calcd for $C_{23}H_{22}N_2NaO^+$ [M+Na$^+$]: 365.1625, found 365.1624.

***N*-cinnamyl-*N*-(4-isopropylphenyl)picolinamide (1d):**



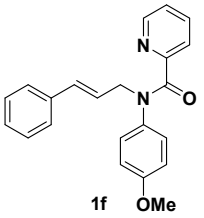
Prepared according to general procedure **SI-C** from N-cinnamyl-4-isopropylaniline **SI-04** (500 mg, 1.99 mmol, 1.00 equiv) to yield **1d** (496 mg, 70%) as a pale yellow oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.28 (s, 1H), 7.47 (s, 1H), 7.28 – 7.14 (m, 6H), 7.03 (s, 1H), 6.92 (s, 4H), 6.47 – 6.31 (m, 2H), 4.60 (d, *J* = 6.3 Hz, 2H), 2.72 (t, *J* = 6.4 Hz, 1H), 1.08 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.6, 154.5, 148.6, 147.5, 140.5, 136.8, 136.1, 133.3, 128.6, 128.4, 127.7, 127.5, 126.9, 126.6, 124.4, 123.8, 123.6, 52.5, 33.6, 23.9; **HRMS** (ESI): calcd for $C_{24}H_{24}N_2NaO^+$ [M+Na$^+$]: 379.1782, found 379.1780.

***N*-(4-(tert-butyl)phenyl)-*N*-cinnamylpicolinamide (1e):**



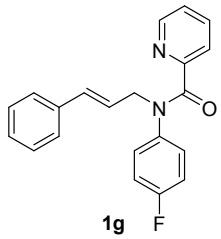
Prepared according to general procedure **SI-C** from 4-(tert-butyl)-N-cinnamylaniline **SI-05** (500 mg, 1.88 mmol, 1.00 equiv) to yield **1e** (439 mg, 63%) as a pale brown oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.28 (s, 1H), 7.48 (s, 1H), 7.28 – 7.08 (m, 9H), 6.90 (s, 2H), 6.48 – 6.32 (m, 2H), 4.60 (d, *J* = 6.3 Hz, 2H), 1.15 (s, 9H).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.5, 154.5, 149.8, 148.5, 140.1, 136.8, 136.2, 133.3, 128.6, 128.4, 127.7, 127.1, 126.6, 125.9, 124.4, 123.9, 123.7, 52.5, 34.5, 31.3; **HRMS** (ESI): calcd for $C_{25}H_{26}N_2NaO^+$ [M+Na$^+$]: 393.1936, found 393.1937.

***N*-cinnamyl-*N*-(4-methoxyphenyl)picolinamide (1f):**



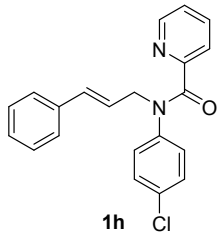
Prepared according to general procedure **SI-C** from N-cinnamyl-4-methoxyaniline **SI-06** (500 mg, 2.09 mmol, 1.00 equiv) to yield **1f** (510 mg, 71%) as a pale brown solid. **m.p.** = 98.0-99.5 °C; R*f* = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.13 (m, 6H), 7.03 (t, *J* = 6.3 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.3 Hz, 2H), 6.44 – 6.28 (m, 2H), 4.57 (d, *J* = 6.5 Hz, 2H), 3.63 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.6, 158.2, 154.5, 148.7, 136.8, 136.2, 135.5, 133.7, 129.2, 128.6, 128.4, 127.7, 126.6, 124.2, 123.7, 123.5, 114.1, 55.4, 52.6; **HRMS** (ESI): calcd for $C_{22}H_{21}N_2O_2^+$ [M+H$^+$]: 345.1600, found 345.1597.

***N*-cinnamyl-*N*-(4-fluorophenyl)picolinamide (1g):**



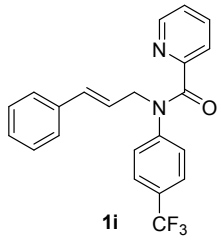
Prepared according to general procedure **SI-C** from N-cinnamyl-4-fluoroaniline **SI-07** (500 mg, 2.20 mmol, 1.00 equiv) to yield **1g** (658 mg, 90%) as a colorless oil. R$_f$ = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.54 (s, 1H), 7.40 (s, 1H), 7.27 – 7.15 (m, 5H), 7.06 (s, 1H), 6.97 (s, 2H), 6.78 (s, 2H), 4.58 (d, *J* = 6.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.4, 162.4, 159.9, 154.0, 148.4, 138.9, 136.6, 136.5, 133.9, 129.7, 128.6, 127.9, 126.6, 124.1, 123.8, 116.0, 115.8, 52.7; **HRMS** (ESI): calcd for $C_{21}H_{18}FN_2O^+$ [M+H$^+$]: 333.1400, found 333.1397.

***N*-(4-chlorophenyl)-*N*-cinnamylpicolinamide (1h):**



Prepared according to general procedure **SI-C** from 4-chloro-N-cinnamylaniline **SI-08** (500 mg, 2.05 mmol, 1.00 equiv) to yield **1h** (615 mg, 86%) as a colorless oil. R$_f$ = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.56 (s, 1H), 7.46 (s, 1H), 7.27 – 7.07 (m, 8H), 6.95 (s, 2H), 6.43 – 6.25 (m, 2H), 4.59 (d, *J* = 6.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.3, 153.9, 148.51, 141.6, 136.6, 133.9, 132.5, 129.2, 129.0, 128.6, 127.9, 126.6, 124.3, 123.9, 52.7; **HRMS** (ESI): calcd for $C_{21}H_{17}ClN_2NaO^+$ [M+Na$^+$]: 371.0921, found 371.0921.

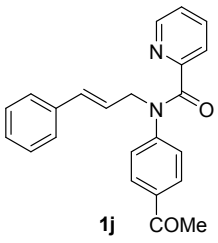
***N*-cinnamyl-*N*-(4-(trifluoromethyl)phenyl)picolinamide (1i):**



Prepared according to general procedure **SI-C** from N-cinnamyl-4-(trifluoromethyl)aniline **SI-09** (500 mg, 1.80 mmol, 1.00 equiv) to yield **1i** (413 mg, 60%) as a pale yellow oil. R$_f$ = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 7.56 (s, 1H), 7.48 (s, 1H), 7.27 – 6.96 (m, 10H), 6.44 – 6.26 (m, 2H), 4.60 (d, *J* = 6.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.4, 153.8, 148.4, 147.5, 147.5, 141.6, 138.8, 136.5, 133.8, 129.1, 128.6, 127.9, 126.6, 124.3, 124.2, 124.0, 123.9, 121.7, 121.3, 119.1, 52.8; **HRMS** (ESI): calcd for

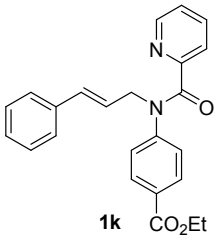
$C_{22}H_{17}F_3N_2NaO_2^+$ [M+Na$^+$]: 421.1137, found 421.1134.

***N*-(4-acetylphenyl)-*N*-cinnamylpicolinamide (1J):**



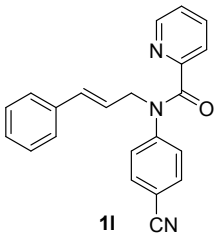
Prepared according to general procedure **SI-E** from 1-(4-(cinnamylamino)phenyl)ethan-1-one **SI-10** (500 mg, 1.99 mmol, 1.00 equiv) to yield **1j** (503 mg, 71%) as a pale brown oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 4.7 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.25 – 7.06 (m, 8H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.32 – 6.25 (m, 1H), 4.65 (d, *J* = 6.3 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 197.0, 168.3, 153.6, 148.4, 147.5, 136.6, 136.4, 134.8, 133.6, 129.1, 128.5, 127.8, 127.1, 126.5, 124.5, 124.1, 123.8, 52.6, 26.5; **HRMS** (ESI): calcd for $C_{23}H_{20}N_2NaO_2^+$ [M+Na$^+$]: 379.1419, found 379.1417.

Ethyl 4-(*N*-cinnamylpicolinamido)benzoate (1k):



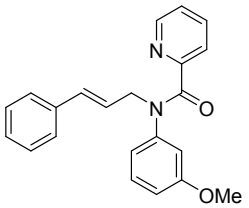
Prepared according to general procedure **SI-E** from ethyl 4-(cinnamylamino)benzoate **SI-11** (500 mg, 1.77 mmol, 1.00 equiv) to yield **1k** (453 mg, 66%) as a pale yellow oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 4.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.48 (m, 2H), 7.25 – 7.04 (m, 8H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.32 – 6.25 (m, 1H), 4.64 (d, *J* = 6.3 Hz, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.3, 165.8, 153.7, 148.4, 147.2, 136.5, 136.4, 133.7, 130.3, 128.5, 128.4, 127.8, 127.0, 126.5, 124.4, 124.0, 123.8, 61.1, 52.6, 14.3; **HRMS** (ESI): calcd for $C_{24}H_{22}N_2NaO_3^+$ [M+Na$^+$]: 409.1526, found 409.1522.

***N*-cinnamyl-*N*-(4-cyanophenyl)picolinamide (1l):**



Prepared according to general procedure **SI-E** from 4-(cinnamylamino)benzonitrile **SI-12** (500 mg, 2.13 mmol, 1.00 equiv) to yield **1l** (478 mg, 66%) as a white solid. **m.p.** = 115.0-116.5 °C; R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 4.7 Hz, 1H), 7.70 (s, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.16 (m, 8H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.38 – 6.31 (m, 1H), 4.72 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.2, 153.1, 148.3, 147.6, 136.9, 136.3, 133.9, 132.9, 128.6, 128.0, 127.7, 126.6, 124.9, 124.5, 123.6, 118.3, 110.0, 52.8; **HRMS** (ESI): calcd for $C_{22}H_{18}N_3O^+$ [M+H$^+$]: 340.1441, found 340.1444.

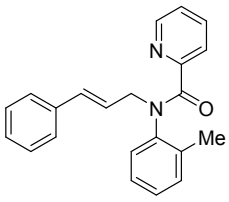
***N*-cinnamyl-N-(3-methoxyphenyl)picolinamide (1m):**



1m

Prepared according to general procedure **SI-B** from N-cinnamyl-3-methoxyaniline **SI-13** (500 mg, 2.09 mmol, 1.00 equiv) to yield **1m** (582 mg, 81%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.58 (s, 1H), 7.43 (s, 1H), 7.35 – 7.20 (m, 7H), 6.66 (d, *J* = 9.0 Hz, 3H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.43 – 6.36 (m, 1H), 4.6 (d, *J* = 6.3 Hz, 2H), 3.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.4, 159.8, 154.3, 148.5, 143.8, 136.5, 136.1, 133.3, 129.5, 128.2, 128.2, 127.6, 126.4, 124.2, 123.9, 123.4, 119.7, 113.2, 112.4, 55.2, 52.4; **HRMS** (ESI): calcd for $C_{22}H_{20}N_2NaO_2^+$ [M+Na$^+$]: 367.1420, found 367.1417.

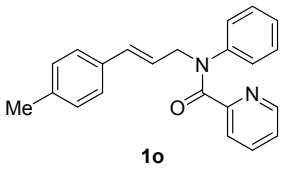
***N*-cinnamyl-*N*-(o-tolyl)picolinamide (1n):**



1n

Prepared according to general procedure **SI-B** from N-cinnamyl-2-methylaniline **SI-14** (500 mg, 2.24 mmol, 1.00 equiv) to yield **1n** (514 mg, 70%) as a pale yellow oil. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 4.8 Hz, 1H), 7.45 (td, *J* = 7.7, 1.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.27 – 7.14 (m, 6H), 7.01 – 6.92 (m, 5H), 6.36 (s, 1H), 4.87 – 4.83 (m, 1H), 4.16 – 4.11 (m, 1H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.54, 154.81, 154.19, 148.40, 141.29, 137.20, 136.84, 134.11, 133.42, 131.22, 130.92, 129.94, 128.63, 128.47, 127.83, 127.79, 126.61, 126.54, 126.41, 125.00, 124.81, 124.00, 123.74, 123.13, 54.92, 52.06, 18.34, 17.99; **HRMS** (ESI): calcd for $C_{22}H_{20}N_2NaO^+$ [M+Na$^+$]: 351.1468, found 351.1467.

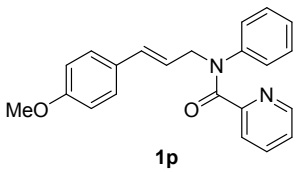
(*E*)-*N*-phenyl-*N*-(3-(p-tolyl)allyl)picolinamide (1o):



1o

Prepared according to general procedure **SI-E** from (*E*)-*N*-(3-(p-tolyl)allyl)aniline **SI-38** (500 mg, 2.24 mmol, 1.00 equiv) to yield **1o** (603 mg, 82%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 7.47 (s, 1H), 7.35 (s, 1H), 7.17-7.00 (m, 10H), 6.40 – 6.23 (m, 2H), 4.60 (d, *J* = 6.3 Hz, 2H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.5, 154.4, 148.5, 142.9, 137.5, 136.2, 136.2, 133.9, 133.4, 129.2, 128.9, 127.7, 126.8, 126.4, 123.9, 123.7, 123.1, 52.6, 21.2; **HRMS** (ESI): calcd for $C_{22}H_{20}N_2NaO^+$ [M+Na$^+$]: 351.1467, found 351.1467.

(*E*)-*N*-(3-(4-methoxyphenyl)allyl)-*N*-phenylpicolinamide (1p):

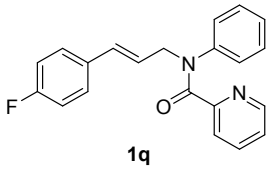


1p

Prepared according to general procedure **SI-E** from (*E*)-*N*-(3-(4-methoxyphenyl)allyl)aniline **SI-39** (500 mg, 2.09 mmol, 1.00 equiv) to yield **1p** (539 mg, 75%) as a pale yellow oil. R_f = 0.40 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.57 (s, 1H), 7.43 (s, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.17 – 7.08 (m, 6H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.1, 6.6 Hz, 1H), 4.66 (d, *J* = 6.6 Hz, 2H),

3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.5, 159.3, 154.4, 149.3, 148.5, 142.9, 136.2, 133.0, 129.5, 128.9, 127.7, 126.8, 123.9, 123.7, 121.9, 113.9, 55.3, 52.7; **HRMS** (ESI): calcd for $C_{22}H_{20}N_2NaO_2^+$ [M+Na$^+$]: 367.1418, found 367.1417.

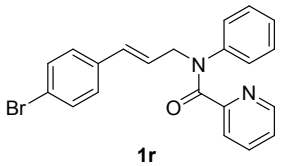
(*E*)-*N*-(3-(4-fluorophenyl)allyl)-*N*-phenylpicolinamide (1q):



1q

Prepared according to general procedure **SI-E** from (*E*)-*N*-(3-(4-fluorophenyl)allyl)aniline **SI-40** (500 mg, 2.20 mmol, 1.00 equiv) to yield **1q** (519 mg, 71%) as a pale yellow oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.58 (s, 1H), 7.44 (s, 1H), 7.30 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.19 – 7.05 (m, 6H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.68 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.6, 163.6, 161.2, 154.3, 148.5, 142.9, 136.3, 132.9, 132.3, 129.0, 128.0, 127.7, 126.8, 124.0, 123.7, 115.6, 115.4, 52.5; **HRMS** (ESI): calcd for $C_{21}H_{17}FN_2NaO^+$ [M+Na$^+$]: 355.1214, found 355.1217.

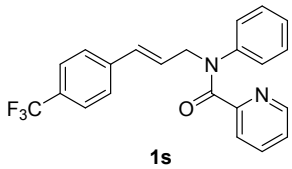
(*E*)-*N*-(3-(4-bromophenyl)allyl)-*N*-phenylpicolinamide (1r):



1r

Prepared according to general procedure **SI-E** from (*E*)-*N*-(3-(4-bromophenyl)allyl)aniline **SI-41** (500 mg, 1.74 mmol, 1.00 equiv) to yield **1r** (491 mg, 72%) as a pale brown oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 7.48 (s, 1H), 7.36 – 7.29 (m, 3H), 7.11 – 6.98 (m, 8H), 6.38 – 6.26 (m, 2H), 4.59 (d, *J* = 5.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.5, 154.1, 148.5, 142.8, 136.2, 135.5, 132.1, 131.6, 129.0, 128.0, 127.5, 126.8, 125.0, 124.0, 123.6, 121.4, 52.4; **HRMS** (ESI): calcd for $C_{21}H_{17}BrN_2NaO^+$ [M+Na$^+$]: 415.0414, found 415.0416.

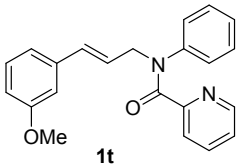
(*E*)-*N*-phenyl-*N*-(3-(4-(trifluoromethyl)phenyl)allyl)picolinamide (1s):



1s

Prepared according to general procedure **SI-E** from (*E*)-*N*-(3-(4-(trifluoromethyl)phenyl)allyl)aniline **SI-42** (500 mg, 1.80 mmol, 1.00 equiv) to yield **1s** (448 mg, 65%) as a pale yellow oil. R_f = 0.45 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.59 – 7.42 (m, 6H), 7.19 – 7.07 (m, 6H), 6.58 – 6.46 (m, 2H), 4.72 (d, *J* = 5.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.6, 154.1, 148.6, 142.8, 140.1, 136.3, 132.0, 129.6, 129.3, 129.1, 127.6, 126.9, 126.7, 125.4, 124.1, 123.7, 122.8, 52.4; **HRMS** (ESI): calcd for $C_{22}H_{17}F_3N_2NaO^+$ [M+Na$^+$]: 405.1181, found 405.1185.

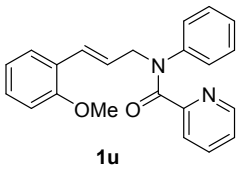
(*E*)-*N*-(3-(3-methoxyphenyl)allyl)-*N*-phenylpicolinamide (1t):



1t

Prepared according to general procedure **SI-E** from (*E*)-*N*-(3-(3-methoxyphenyl)allyl)aniline **SI-43** (500 mg, 2.09 mmol, 1.00 equiv) to yield **1t** (561 mg, 78%) as a colorless oil. R_f = 0.40 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.48 (s, 1H), 7.35 (s, 1H), 7.13-7.01 (m, 7H), 6.85 – 6.80 (m, 2H), 6.69 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.41 – 6.28 (m, 2H), 4.61 (d, *J* = 5.8 Hz, 2H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.5, 156.7, 154.4, 148.5, 142.8, 136.1, 128.9, 128.7, 128.3, 127.8, 127.0, 126.7, 125.7, 124.7, 123.8, 123.6, 120.6, 110.9, 55.5, 52.8; **HRMS** (ESI): calcd for $C_{22}H_{20}N_2NaO_2^+$ [M+Na$^+$]: 367.1418, found 367.1417.

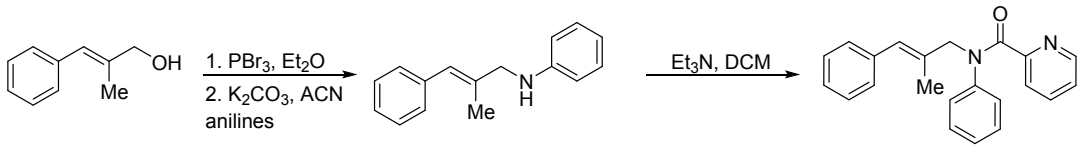
(*E*)-*N*-(3-(2-methoxyphenyl)allyl)-*N*-phenylpicolinamide (1u):



1u

Prepared according to general procedure **SI-E** from (*E*)-*N*-(3-(2-methoxyphenyl)allyl)aniline **SI-44** (500 mg, 2.09 mmol, 1.00 equiv) to yield **1u** (474 mg, 66%) as a colorless oil. R_f = 0.40 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.57 (s, 1H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.10 (m, 7H), 6.91 – 6.79 (m, 3H), 6.41 – 6.32 (m, 1H), 4.71 (d, *J* = 6.6 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.5, 159.8, 154.3, 148.6, 142.8, 138.1, 136.2, 133.4, 129.5, 129.0, 127.7, 126.8, 124.5, 124.0, 123.7, 119.3, 113.6, 111.6, 55.3, 52.5; **HRMS** (ESI): calcd for $C_{22}H_{20}N_2NaO_2^+$ [M+Na$^+$]: 367.1416, found 367.1417.

2.3 General Scheme for the Synthesis of 3a-i:



SI-15 to 23 **3a-i**

Procedure SI-F[2]:

The corresponding allylic alcohol (1.00 equiv) is dissolved in Et_2O (16 mL/mmol) and the resulting mixture cooled to 0 °C. PBr_3 (1.05 equiv) is added and stirred at 0 °C for approximately 1 h. After completion of the reaction (monitored by TLC) the reaction is poured into ice-cooled sat. aq. NH_4Cl-solution (15 mL/mmol). The aqueous layer is extracted with Et_2O (3 x 10 mL/mmol). The combined organic layers are washed with water (5x 15 mL/mmol), sat. aq. NaCl (15 mL/mmol), dried over Na_2SO_4 and filtered. All volatiles are removed under reduced pressure to afford allylic bromides, which were used for next step without further purification.

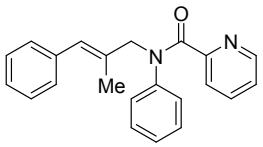
To a stirred solution of aniline (5 mmol) in dry CH_3CN (15 mL) was added K_2CO_3 (7.5 mmol) and stirred well at room temperature. To this solution, allylic bromides (5 mmol) in dry CH_3CN (10 mL) was added drop wise and stirred at room temperature for 3 h. After completion of the reaction, the reaction mixture was evaporated under

reduced pressure to remove CH_3CN. The crude mixture obtained was diluted with water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ EtOAc = 20 : 1) to afford corresponding product (**SI 15-23**).

Procedure SI-G[3]:

To a solution of the picolinic acid (2.50 mmol) in DCM (20 mL) at room temperature was added $SOCl_2$ (2 mL) and one drop of dry DMF. The reaction was allowed to stir at 40 °C for 4 hours. The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride. Then DCM (20 mL) was added and the solution was cooled to 0 °C followed by dropwise addition of NEt_3 (1.5 mL), DMAP (0.25 mmol) and amine (2.50 mmol, 1.0 eq). The reaction mixture was stirred at room temperature overnight, extracted by DCM, the organic layer was dried over Na_2SO_4 and the solvent was evaporated, then purified by flash chromatography(petroleum ether/ EtOAc = 2 : 1) to afford corresponding product **(3a-i)**.

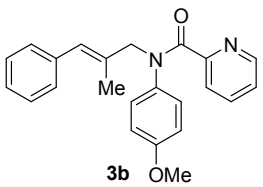
(*E*)-*N*-(2-methyl-3-phenylallyl)-*N*-phenylpicolinamide (3a):



3a

Prepared according to general procedure **SI-G** from (*E*)-*N*-(2-methyl-3-phenylallyl)aniline **SI-15** (500 mg, 2.24 mmol, 1.00 equiv) to yield **3a** (669 mg, 91%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, Benzene-d_6): δ = 8.01 (d, *J* = 4.9 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 5.0 Hz, 4H), 7.05 – 6.98 (m, 3H), 6.92 – 6.87 (m, 3H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.44 (s, 1H), 6.36 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.67 (s, 2H), 1.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.9, 154.6, 148.6, 142.7, 137.5, 136.2, 133.8, 128.9, 128.8, 128.4, 128.1, 127.5, 126.7, 126.5, 123.9, 123.6, 57.2, 16.2; **HRMS** (ESI): calcd for $C_{22}H_{20}N_2NaO^+$ [M+Na$^+$]: 351.1472, found 351.1467.

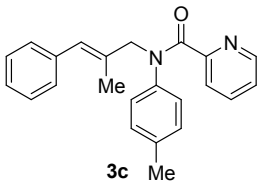
(*E*)-*N*-(4-methoxyphenyl)-*N*-(2-methyl-3-phenylallyl)picolinamide (3b):



3b

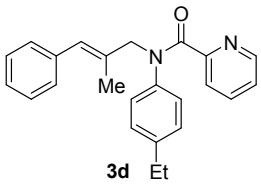
Prepared according to general procedure **SI-G** from (*E*)-4-methoxy-*N*-(2-methyl-3-phenylallyl)aniline **SI-16** (500 mg, 1.97 mmol, 1.00 equiv) to yield **3b** (587 mg, 83%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 4.9 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.22 (m, 3H), 7.12 (dt, *J* = 31.4, 7.0 Hz, 4H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 8.3 Hz, 2H), 6.30 (s, 1H), 4.63 (s, 2H), 3.67 (s, 3H), 1.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.9, 158.1, 154.8, 148.6, 137.6, 136.2, 135.3, 133.8, 128.9, 128.7, 128.1, 126.5, 123.7, 123.4, 114.0, 57.4, 55.4, 16.3; **HRMS** (ESI): calcd for $C_{23}H_{22}N_2NaO_2^+$ [M+Na$^+$]: 381.1575, found 381.1573.

(*E*)-*N*-(2-methyl-3-phenylallyl)-*N*-(p-tolyl)picolinamide (3c):



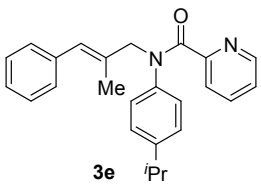
Prepared according to general procedure **SI-G** from (*E*)-4-methyl-*N*-(2-methyl-3-phenylallyl)aniline **SI-17** (500 mg, 2.10 mmol, 1.00 equiv) to yield **3c** (541 mg, 75%) as a pale yellow oil. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.30 (s, 1H), 7.48 (s, 1H), 7.30 (s, 1H), 7.24 – 7.17 (m, 2H), 7.13 – 7.00 (m, 4H), 6.87 (s, 4H), 6.27 (s, 1H), 4.60 (s, 2H), 2.15 (s, 3H), 1.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.9, 154.8, 148.6, 140.0, 137.6, 136.5, 136.2, 133.9, 129.5, 128.9, 128.3, 128.1, 127.3, 126.5, 123.8, 123.5, 57.3, 21.0, 16.3; **HRMS** (ESI): calcd for $C_{23}H_{22}N_2NaO^+$ [M+Na$^+$]: 365.1626, found 365.1624.

(*E*)-*N*-(4-ethylphenyl)-*N*-(2-methyl-3-phenylallyl)picolinamide (3d):



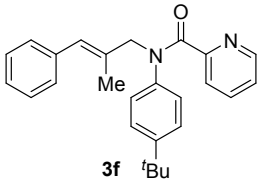
Prepared according to general procedure **SI-G** from (*E*)-4-ethyl-*N*-(2-methyl-3-phenylallyl)aniline **SI-18** (500 mg, 1.99 mmol, 1.00 equiv) to yield **3d** (574 mg, 81%) as a pale yellow oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, Benzene-d_6): δ = 8.05 (d, *J* = 4.7 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.12 – 7.10 (m, 4H), 7.03 – 7.00 (m, 3H), 6.92 – 6.88 (m, 1H), 6.78 (d, *J* = 7.9 Hz, 2H), 6.46 (s, 1H), 6.35 (t, *J* = 6.2 Hz, 1H), 4.70 (s, 2H), 2.25 (q, *J* = 7.6 Hz, 2H), 1.95 (s, 3H), 0.92 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.0, 154.8, 148.7, 142.7, 140.2, 137.6, 136.1, 133.9, 128.9, 128.2, 128.1, 127.3, 126.5, 123.7, 123.5, 57.2, 28.3, 16.2, 15.3; **HRMS** (ESI): calcd for $C_{24}H_{24}N_2NaO^+$ [M+Na$^+$]: 379.1782, found 379.1780.

(*E*)-*N*-(4-isopropylphenyl)-*N*-(2-methyl-3-phenylallyl)picolinamide (3e):



Prepared according to general procedure **SI-G** from (*E*)-4-isopropyl-*N*-(2-methyl-3-phenylallyl)aniline **SI-19** (500 mg, 1.88 mmol, 1.00 equiv) to yield **3e** (565 mg, 81%) as a pale yellow oil. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, Benzene-d_6): δ = 8.05 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 4.6 Hz, 4H), 7.03 – 6.99 (m, 3H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 2H), 6.48 (s, 1H), 6.35 (t, *J* = 6.3 Hz, 1H), 4.70 (s, 2H), 2.53 (p, *J* = 6.9 Hz, 1H), 1.94 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.0, 154.8, 148.6, 147.4, 140.3, 137.6, 136.0, 133.9, 128.9, 128.1, 127.2, 126.7, 126.5, 123.7, 123.6, 57.2, 33.6, 23.9, 16.2; **HRMS** (ESI): calcd for $C_{25}H_{27}N_2O^+$ [M+H$^+$]: 371.2120, found 371.2117.

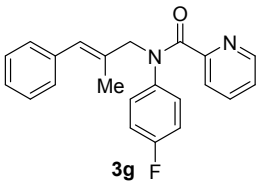
(*E*)-*N*-(4-(tert-butyl)phenyl)-*N*-(2-methyl-3-phenylallyl)picolinamide (3f):



Prepared according to general procedure **SI-G** from (*E*)-4-(tert-butyl)-*N*-(2-methyl-3-

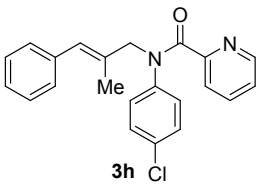
phenylallyl)aniline **SI-20** (500 mg, 1.79 mmol, 1.00 equiv) to yield **3f** (488 mg, 71%) as a pale yellow oil. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.31 (s, 1H), 7.22 – 7.18 (m, 2H), 7.12 – 7.08 (m, 6H), 6.89 (s, 2H), 6.29 (s, 1H), 4.61 (s, 2H), 1.88 (s, 3H), 1.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.9, 154.8, 149.6, 148.5, 140.0, 137.6, 136.1, 133.9, 128.9, 128.1, 126.8, 126.4, 125.7, 123.8, 123.6, 57.2, 34.5, 31.3, 16.2; **HRMS** (ESI): calcd for $C_{26}H_{28}N_2NaO^+$ [M+Na$^+$]: 407.2094, found 407.2093.

(*E*)-*N*-(4-fluorophenyl)-*N*-(2-methyl-3-phenylallyl)picolinamide (3g):



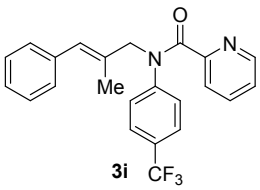
Prepared according to general procedure **SI-G** from (*E*)-4-fluoro-*N*-(2-methyl-3-phenylallyl)aniline **SI-21** (500 mg, 2.07 mmol, 1.00 equiv) to yield **3g** (617 mg, 86%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.52 (s, 1H), 7.39 (s, 1H), 7.21 (q, *J* = 7.1, 6.7 Hz, 2H), 7.13 – 6.95 (m, 6H), 6.77 (s, 2H), 6.24 (s, 1H), 4.59 (s, 2H), 1.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.8, 162.2, 159.8, 154.4, 148.5, 138.7, 137.4, 136.4, 133.5, 129.4, 128.9, 128.2, 128.1, 126.6, 124.0, 123.7, 115.8, 115.6, 57.4, 16.2; **HRMS** (ESI): calcd for $C_{22}H_{19}FN_2NaO^+$ [M+Na$^+$]: 369.1375, found 369.1373.

(*E*)-*N*-(4-chlorophenyl)-*N*-(2-methyl-3-phenylallyl)picolinamide (3h):



Prepared according to general procedure **SI-G** from (*E*)-4-chloro-*N*-(2-methyl-3-phenylallyl)aniline **SI-22** (500 mg, 1.94 mmol, 1.00 equiv) to yield **3h** (612 mg, 87%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.21 (q, *J* = 7.8 Hz, 2H), 7.13 – 7.07 (m, 6H), 6.94 (s, 2H), 6.26 (s, 1H), 4.59 (s, 2H), 1.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.7, 154.2, 148.5, 141.4, 137.3, 136.5, 133.5, 132.3, 129.0, 128.9, 128.7, 128.2, 126.7, 124.2, 123.9, 57.4, 16.2; **HRMS** (ESI): calcd for $C_{22}H_{19}ClN_2NaO^+$ [M+Na$^+$]: 385.1080, found 385.1078.

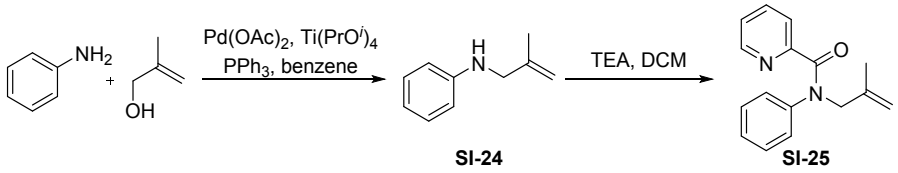
(*E*)-*N*-(2-methyl-3-phenylallyl)-*N*-(4-(trifluoromethyl)phenyl)picolinamide (3i):



Prepared according to general procedure **SI-G** from (*E*)-*N*-(2-methyl-3-phenylallyl)-4-(trifluoromethyl)aniline **SI-23** (500 mg, 1.71 mmol, 1.00 equiv) to yield **3i** (619 mg, 91%) as a pale brown oil. R_f = 0.40 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 4.8 Hz, 1H), 7.60 (td, *J* = 7.6, 1.6 Hz, 1H), 7.54 (d, *J*

= 7.7 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.18 – 7.06 (m, 6H), 6.31 (s, 1H), 4.65 (s, 2H), 1.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.7, 153.8, 148.4, 146.4, 137.2, 136.7, 133.5, 128.9, 128.4, 128.2, 127.2, 126.7, 126.0, 125.9, 125.2, 124.6, 124.2, 122.5, 57.5, 16.2; **HRMS** (ESI): calcd for $C_{23}H_{19}F_3N_2NaO^+$ [M+Na^+]: 419.1342, found 419.1341.

2.4 General Scheme for the Synthesis of SI-24 and SI-25:



SI-24 **SI-25**

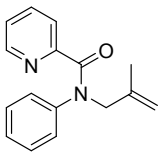
2.4.1 Procedure SI-H:

***N*-(2-methylallyl)aniline (SI-24) [4]:**

A mixture of aniline (300 mg, 1 mmol), 2-butene-1-ol (278 mg, 1.2 mmol), $Pd(OAc)_2$ (7.2 mg, 0.01 mmol), PPh_3 (33.8 mg, 0.04 mmol), $Ti(OPr^i)_4$ (229 mg, 0.25 mmol), MS4A (600 mg) and benzene (15ml) was refluxed under nitrogen at 50 °C for 3 h. After cooling, the reaction mixture was poured into aq. 10% HCl and extracted with ether. The ether layer was combined, dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography (petroleum ether/ EtOAc = 9 : 1) to afford corresponding product **SI-24** (298 mg, 63%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.16 (dd, *J* = 8.5, 7.2 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 4.97 (s, 1H), 4.88 (s, 1H), 3.86 (s, 1H), 3.68 (s, 2H), 1.78 (s, 3H).

2.4.2 Procedure SI-I[3]:

***N*-(2-methylallyl)-*N*-phenylpicolinamide (SI-25):**

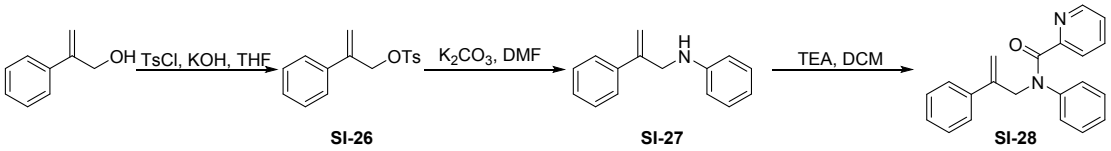


SI-25

To a solution of the picolinic acid (185 mg, 1.50 mmol) in DCM (10 mL) at room temperature was added $SOCl_2$ (2 mL) and one drop of dry DMF. The reaction was allowed to stir at 40 °C for 4 hours. The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride. Then DCM (20 mL) was added and the solution was cooled to 0 °C followed by dropwise addition of NEt_3 (0.95 mL, 5.0 eq.), DMAP (16.5 mg, 0.13 mmol, .1 eq.) and amine **(SI-24)** (200 mg, 1.36 mmol, 1.0 eq). The reaction mixture was stirred at room temperature overnight, extracted by DCM, the organic layer was dried over Na_2SO_4 and the solvent was evaporated, then purified by flash chromatography (petroleum ether/ EtOAc = 2 : 1) to afford **SI-25** (233 mg, 68%) as a brown solid. **m.p.** = 75.5-77.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.58 (s, 1H), 7.44 (s, 1H), 7.16 – 7.05 (m, 6H), 4.91 (d, *J* = 12.7 Hz, 2H), 4.54 (s, 2H), 1.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.6, 154.4, 148.4, 143.0, 140.6, 136.1, 128.7, 126.9, 126.3, 123.8,

123.5, 112.9, 55.3, 20.4; **HRMS** (ESI): calcd for $C_{16}H_{16}N_2NaO^+$ [M+Na$^+$]: 275.1155, found 275.1154.

2.5 General Scheme for the Synthesis of SI-26, SI-27 and SI-28:



SI-26 **SI-27** **SI-28**

2.5.1 Procedure SI-*J*:

2-phenylallyl 4-methylbenzenesulfonate (SI-26) [5]:

To a THF (60 mL) solution of alcohol (3.0 g, 18.6 mmol) and *p*-toluenesulfonyl chloride (5.34 g, 28.0 mmol) was added KOH (7.30 g 130.2 mmol) at 0 °C, and the mixture was stirred at 0 °C for 1 h and at room temperature for 3 h. The reaction was quenched by the addition of water and extracted with EtOAc. The organic extract was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified on a silica gel column chromatography (hexane/EtOAc = 10:1), which furnished tosylate **SI-26** (6.1 g, 95% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.23 (m, 7H), 5.54 (s, 1H), 5.35 (s, 1H), 4.92 (s, 2H), 2.44 (s, 3H).

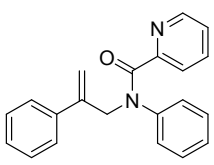
2.5.2 Procedure SI-K:

***N*-(2-phenylallyl)aniline (SI-27) [6]:**

To a solution of **SI-26** (508 mg, 2.0 mmol) in dry DMF (6 mL) was added aniline (783 mg, 2.2 mmol), K_2CO_3 (331 mg, 2.4 mmol). The resulting mixture was heated to 80 °C for 12 h. The mixture was cooled to room temperature, diluted with H_2O and extracted with Et_2O for two times. The combined organic phases were washed with brine, dried over Na_2SO_4. Filtration and evaporation led to a residue. Purification of the residue by flash chromatography on silica gel using PE/EA as the eluent provided the desired product **SI-27** (313 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48 – 7.45 (m, 2H), 7.38 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 6.74 – 6.70 (m, 1H), 6.63 (dd, *J* = 8.5, 2.4 Hz, 2H), 5.48 (d, *J* = 3.3 Hz, 1H), 5.34 (d, *J* = 2.9 Hz, 1H), 4.16 (s, 2H), 3.88 (s, 1H).

2.5.3 Procedure SI-L:

***N*-phenyl-*N*-(2-phenylallyl)picolinamide (SI-28) [3]:**

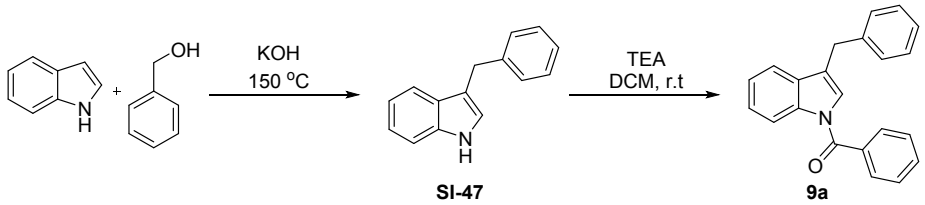


SI-28

To a solution of the picolinic acid (160 mg, 1.3 mmol) in DCM (20 mL) at room temperature was added $SOCl_2$ (2 mL) and one drop of dry DMF. The reaction was allowed to stir at 40 °C for 4 hours. The solvent was then removed under reduced pressure

to afford the corresponding crude acid chloride. Then DCM (20 mL) was added and the solution was cooled to 0 °C followed by dropwise addition of NEt_3 (0.83 mL, 5.0 equiv), DMAP (14.5 mg, 0.1 equiv) and amine **SI-27** (250 mg, 1.0 equiv). The reaction mixture was stirred at room temperature overnight, extracted by DCM, the organic layer was dried over Na_2SO_4 and the solvent was evaporated, then purified by flash chromatography(petroleum ether/ EtOAc = 2 : 1) to afford the corresponding product **SI-28** (6.1 g, 82% yield) as a white solid. **m.p.** = 89.0-91.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.30 (s, 1H), 7.54 (s, 1H), 7.44 (s, 2H), 7.34 – 7.28 (m, 4H), 7.07 (s, 4H), 6.86 (s, 2H), 5.43 (s, 1H), 5.28 (s, 1H), 5.08 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.6, 154.4, 148.4, 143.5, 142.3, 138.8, 136.1, 128.6, 128.4, 127.9, 127.4, 126.5, 126.4, 123.8, 123.5, 115.2, 52.6; **HRMS** (ESI): calcd for $C_{21}H_{18}N_2NaO^+$ [M+Na$^+$]: 337.1314, found 337.1311.

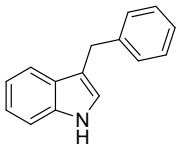
2.6 General Scheme for the Synthesis of SI-47 and 9a:



SI-47 **9a**

2.6.1 Procedure SI-N:

3-Benzyl-1*H*-indole (SI-47):

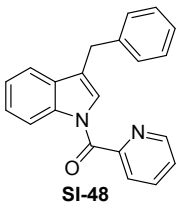


SI-47

To a stirred mixture of indole (500 mg, 4.26 mmol, 1.0 equiv) and KOH (311.3 mg, 5.54 mmol, 1.3 equiv), was added benzyl alcohol (1.38 g, 12.80 mmol, 3.0 equiv). The resulting mixture was stirred at 150 ºC for 24 hours. The resulting mixture was quenched with deionized water and extracted with EtOAc (3 × 20 mL). The organic phases were dried over Na_2SO_4, followed by evaporation under reduced pressure to remove the solvent. The residue was purified by silica gel flash chromatography to give the desired product **SI-47** (812 mg) in 91% yield. The characterization data of **SI-47** matched those previously reported.[7]

2.6.2 Procedure SI-O:

(3-benzyl-1*H*-indol-1-yl)(phenyl)methanone (9a):



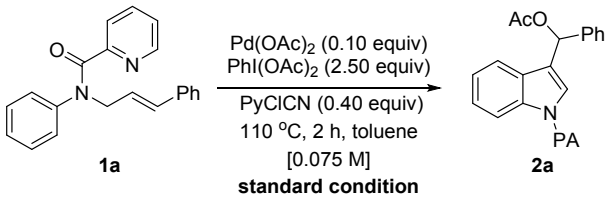
SI-48

To a solution of the picolinic acid (2.50 mmol) in DCM (20 mL) at room temperature was added $SOCl_2$ (2 mL) and one drop of dry DMF. The reaction was allowed to stir at 40 °C for 4 hours. The solvent was then removed under reduced pressure to afford the corresponding

crude acid chloride. Then DCM (20 mL) was added and the solution was cooled to 0 °C followed by dropwise addition of NEt_3 (1.5 mL), DMAP (0.25 mmol) and indole (2.50 mmol, 1.0 eq). The reaction mixture was stirred at room temperature overnight, extracted by DCM, the organic layer was dried over Na_2SO_4 and the solvent was evaporated, then the residue was purified by silica gel flash chromatography to give the desired product **9a** (704 mg) in 91% yield. R_f = 0.5 (silica gel, petroleum ether : EtOAc = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.7 Hz, 1H), 8.41 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.77 (td, *J* = 7.7, 1.7 Hz, 1H), 7.67 (s, 1H), 7.35 – 7.30 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.12 (m, 5H), 7.09 – 7.06 (m, 1H), 3.94 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 152.5, 148.5, 139.5, 137.4, 137.1, 130.9, 128.6, 128.5, 126.3, 126.1, 126.0, 125.7, 125.1, 124.0, 121.9, 121.7, 119.4, 117.1, 31.5. **HRMS** (ESI): calcd for $C_{21}H_{16}N_2NaO^+$ [M^+Na^+]: 335.1156, found 335.1154.

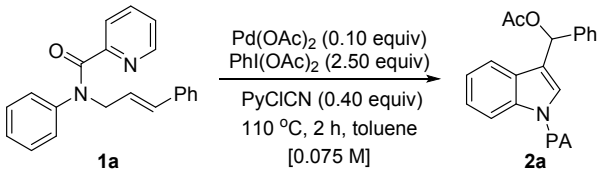
3. Optimization and Substrate Scope of Cinnamyl Aniline Compounds.

Table 1. Optimization using other oxidants of the arylacetoxylation reaction[a,b]



entry	oxidant	result
1	Dess-Martin reagent (2.50 equiv)	25%, some SM remained
2	iodoso-benzen (2.50 equiv)	no reaction
3	$NaIO_4$ (2.50 equiv)	no reaction
4	NFSI (2.50 equiv)	no reaction
5	Oxone (2.50 equiv)	no reaction
6	TBHP (2.50 equiv)	no reaction
7	benzoquinone (2.50 equiv)	no reaction
8	$Cu(OAc)_2$ (2.50 equiv)	no reaction

[a]Reactions conditions: **1** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), oxidant (0.75 mmol), 2-Chloro-4-cyanopyridine (0.12 mmol), toluene (4 mL), N_2, 2 h. [b]Yield is that of the isolated product.

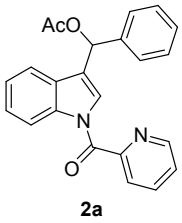


Scheme 1. Synthesis of indole derivatives.

General Procedure A: To a solution of **1** (0.3 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.015 mmol, 0.1 equiv) in anhydrous toluene (4 mL) at r.t. was added $PhI(OAc)_2$ (0.75 mmol, 2.5 equiv), 2-chloroisonicotinonitrile (16.6mg, 0.12 mmol, 0.4 equiv) in a 15 mL flame-dried sealed tube (purged with N_2, sealed with PTFE cap). The mixture was heated at 110 °C for 2 hours. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (petroleum ether / EtOAc) to give the product.

General Procedure B: To a solution of **1** (0.3 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.015 mmol, 0.1 equiv) in anhydrous toluene (4 mL) at r.t. was added $PhI(OAc)_2$ (0.75 mmol, 2.5 equiv), 2-chloroisonicotinonitrile (16.6mg, 0.12 mmol, 0.4 equiv), $AcOH/Ac_2O$ (0.1 mL/0.1 mL, 5 equiv./5 equiv.) in a 15 mL flame-dried sealed tube (purged with N_2, sealed with PTFE cap). The mixture was heated at 110 °C for 2 hours. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (petroleum ether / EtOAc) to give the product.

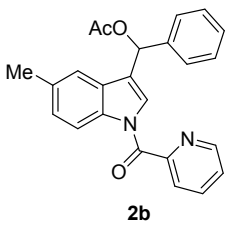
Phenyl(1-picolinoyl-1*H*-indol-3-yl)methyl acetate (2a):



2a

Prepared according to general procedure **A** from **1a** (48.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2a** (38.4 mg, 68%) as a colorless oil. When scale up of the reaction from **1a** (500.0 mg, 1.59 mmol, 1.00 equiv) and $Pd(OAc)_2$ (35.6 mg, 0.10 equiv) at 110 °C for 2 hours afforded **2a** (388.8 mg, 66%) as a colorless oil. R_f = 0.5 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.94 (s, 1H), 7.86 (td, *J* = 7.8, 1.8 Hz, 1H), 7.44 (ddd, *J* = 7.7, 4.7, 1.2 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.30 – 7.24 (m, 3H), 7.21 – 7.14 (m, 2H), 7.09 (s, 1H), 2.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.6, 152.2, 148.6, 138.8, 137.5, 137.3, 128.8, 128.6, 128.3, 127.5, 127.2, 126.4, 126.0, 125.4, 124.3, 121.4, 120.1, 117.2, 71.1, 21.3; **HRMS** (ESI): calcd for $C_{23}H_{18}N_2NaO_3^+$ [M+Na$^+$]: 393.1210, found 393.1209.

(5-methyl-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2b):

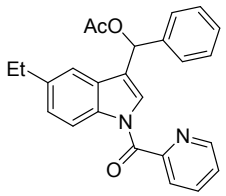


2b

Prepared according to general procedure **A** from **1b** (50.0 mg, 0.15 mmol, 1.00 equiv)

and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2b** (42.7 mg, 73%) as a colorless oil. R_f = 0.5 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 4.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.94 – 7.90 (m, 1H), 7.52 – 7.50 (m, 1H), 7.49 – 7.44 (m, 2H), 7.37 – 7.30 (m, 3H), 7.20 – 7.18 (m, 2H), 7.14 (s, 1H), 2.40 (s, 3H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.3, 165.4, 152.1, 148.5, 138.7, 137.5, 135.4, 133.9, 128.9, 128.5, 128.2, 127.5, 127.2, 126.7, 126.3, 125.9, 121.2, 119.9, 116.8, 71.0, 21.6, 21.3; **HRMS** (ESI): calcd for $C_{24}H_{20}N_2NaO_3^+$ [M+Na$^+$]: 407.1365, found 407.1366.

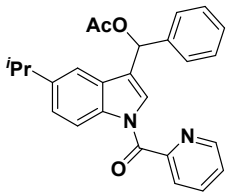
(5-ethyl-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2c):



2c

Prepared according to general procedure **A** from **1c** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2c** (44.1 mg, 73%) as a pale yellow oil. R_f = 0.55 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 4.4 Hz, 1H), 8.39 (d, *J* = 9.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.95 (s, 1H), 7.93 – 7.89 (m, 1H), 7.50 – 7.45 (m, 3H), 7.36 – 7.29 (m, 3H), 7.22 – 7.20 (m, 2H), 7.15 (s, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.14 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.3, 165.4, 152.2, 148.5, 140.5, 138.8, 137.5, 135.5, 129.0, 128.5, 128.2, 127.6, 127.3, 126.3, 125.9, 125.6, 121.4, 118.7, 116.9, 71.1, 29.0, 21.3, 16.1; **HRMS** (ESI): calcd for $C_{25}H_{22}N_2NaO_3^+$ [M+Na$^+$]: 421.1525, found 421.1522.

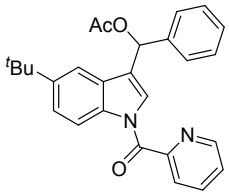
(5-isopropyl-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2d):



2d

Prepared according to general procedure **A** from **1d** (54.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2d** (44.3 mg, 71%) as a colorless oil. R_f = 0.6 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 4.8 Hz, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.92 – 7.87 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 3H), 7.36 – 7.24 (m, 5H), 7.16 (s, 1H), 3.00 – 2.90 (m, 1H), 2.14 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.3, 165.3, 152.1, 148.5, 145.1, 138.7, 137.4, 135.6, 128.9, 128.5, 128.2, 127.5, 127.3, 126.3, 125.9, 124.2, 121.5, 117.3, 116.9, 71.1, 34.1, 24.4, 24.3, 21.3; **HRMS** (ESI): calcd for $C_{26}H_{24}N_2NaO_3^+$ [M+Na$^+$]: 435.1681, found 435.1679.

(5-(tert-butyl)-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2e):

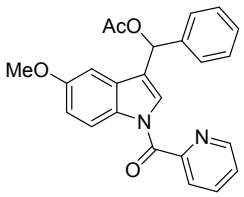


2e

Prepared according to general procedure **A** from **1e** (56.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2e** (43.8 mg, 68%) as a

pale yellow oil. R*f* = 0.6 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 4.8 Hz, 1H), 8.37 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.95 (s, 1H), 7.93 – 7.89 (m, 1H), 7.50 – 7.47 (m, 3H), 7.43 – 7.30 (m, 5H), 7.16 (s, 1H), 2.15 (s, 3H), 1.30 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.3, 165.4, 152.2, 148.5, 147.4, 138.8, 137.4, 135.2, 128.6, 128.5, 128.3, 127.4, 127.3, 126.3, 125.9, 123.2, 121.7, 116.6, 116.3, 71.2, 34.8, 31.54, 21.3; **HRMS** (ESI): calcd for $C_{27}H_{26}N_2NaO_3^+$ [M+Na$^+$]: 449.1834, found 449.1835.

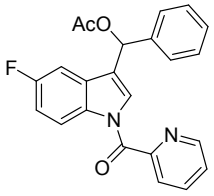
(5-methoxy-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2f):



2f

Prepared according to general procedure **A** from **1f** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2f** (48.9 mg, 81%) as a colorless oil. R$_f$ = 0.4 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.70 – 8.68 (m, 1H), 8.41 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 8.01 (s, 1H), 7.91 (dt, *J* = 6.0, 1.6 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.37 – 7.29 (m, 3H), 7.13 (s, 1H), 6.96 (dd, *J* = 6.3, 2.2 Hz, 1H), 6.86 (d, *J* = 2.4 Hz, 1H), 3.77 (s, 3H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.1, 156.8, 152.2, 148.5, 138.7, 137.4, 131.8, 129.8, 128.6, 128.3, 127.2, 126.3, 125.9, 121.3, 118.0, 113.2, 103.4, 71.0, 55.7, 21.3; **HRMS** (ESI): calcd for $C_{24}H_{20}N_2NaO_4^+$ [M+Na$^+$]: 423.1315, found 423.1315.

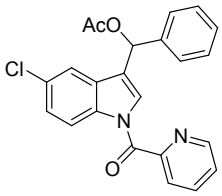
(5-fluoro-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2g):



2g

Prepared according to general procedure **A** from **1g** (50.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2g** (37.9 mg, 65%) as a pale yellow solid. **m.p.** = 110.0-111.5 °C; R$_f$ = 0.4 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 4.6 Hz, 1H), 8.48 (q, *J* = 4.6 Hz, 1H), 8.11 (t, *J* = 7.8, 7.2 Hz, 2H), 7.93 (t, *J* = 7.7 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.08 (t, *J* = 12.0, 8.8 Hz, 3H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.2, 161.1, 158.7, 151.8, 148.6, 138.4, 137.6, 133.6, 133.6, 129.9, 129.8, 129.1, 128.7, 128.4, 127.1, 126.5, 126.1, 121.1, 121.0, 118.4, 118.3, 113.2, 112.9, 106.2, 105.9, 70.9, 21.3; **HRMS** (ESI): calcd for $C_{23}H_{17}FN_2NaO_3^+$ [M+Na$^+$]: 411.1115, found 411.1115.

(5-chloro-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2h):

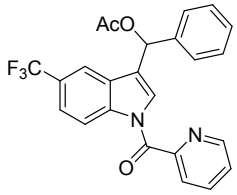


2h

Prepared according to general procedure **A** from **1h** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2h** (41.8 mg, 68%) as a colorless oil. R$_f$ = 0.4 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ =

8.67 (d, *J* = 4.7 Hz, 1H), 8.44 (d, *J* = 8.8 Hz, 1H), 8.12 – 8.08 (m, 2H), 7.94 – 7.90 (m, 1H), 7.52 – 7.49 (m, 1H), 7.43 – 7.29 (m, 7H), 7.10 (s, 1H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.3, 151.7, 148.6, 138.4, 137.6, 135.7, 130.0, 129.9, 128.9, 128.7, 128.4, 127.1, 126.6, 126.2, 125.6, 120.7, 119.8, 118.2, 70.8, 21.3; **HRMS** (ESI): calcd for $C_{23}H_{17}ClN_2NaO_3^+$ [M+Na$^+$]: 427.0817, found 427.0819.

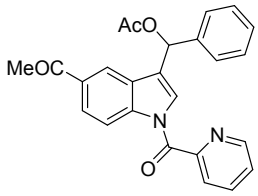
Phenyl(1-picolinoyl-5-(trifluoromethyl)-1*H*-indol-3-yl)methyl acetate (2i):



2i

Prepared according to general procedure **A** from **1i** (58.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2i** (43.8 mg, 66%) as a pale brown oil. R_f = 0.4 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 5.6 Hz, 1H), 8.53 (d, *J* = 8.8 Hz, 1H), 8.16 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.55 – 7.51 (m, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.25 – 7.22 (m, 2H), 7.12 (s, 1H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.3, 151.5, 148.6, 138.3, 137.6, 135.5, 129.3, 128.7, 128.5, 127.1, 126.7, 126.2, 121.0, 118.6, 118.1, 112.7, 70.8, 21.2; **HRMS** (ESI): calcd for $C_{19}H_{15}N_4O_6^+$ [M+H$^+$]: 395.0991, found 395.0986.

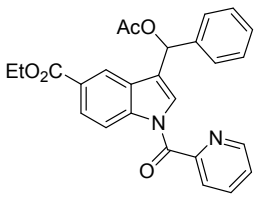
(5-acetyl-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2*J*):



2j

Prepared according to general procedure **B** from **1j** (54.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2j** (34.3 mg, 55%) as a colorless oil. R_f = 0.40 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 4.0 Hz, 1H), 8.54 (d, *J* = 8.7 Hz, 1H), 8.17 (s, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.03 (s, 1H), 8.00–7.94 (m, 2H), 7.56–7.53 (m, 1H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.38–7.31 (m, 3H), 7.18 (s, 1H), 2.58 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 197.8, 170.2, 165.5, 151.6, 148.7, 140.0, 138.6, 137.7, 133.5, 129.0, 128.8, 128.7, 128.7, 128.5, 127.2, 126.9, 126.8, 126.3, 125.7, 121.8, 121.0, 117.0, 70.9, 26.8, 21.3; **HRMS** (ESI): calcd for $C_{25}H_{20}N_2NaO_4^+$ [M+Na$^+$]: 435.1316, found 435.1315.

Ethyl 3-(acetoxy(phenyl)methyl)-1-picolinoyl-1*H*-indole-5-carboxylate (2k):

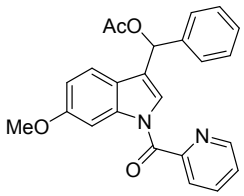


2k

Prepared according to general procedure **B** from **1k** (58.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2k** (33.8 mg, 51%) as a colorless oil. R_f = 0.45 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz,

$CDCl_3$): δ = 8.71 (d, *J* = 4.5 Hz, 1H), 8.52 (d, *J* = 8.7 Hz, 1H), 8.16 (d, *J* = 1.3 Hz, 1H), 8.12 (t, *J* = 4.1, 3.6 Hz, 1H), 8.07 (dd, *J* = 7.1, 1.6 Hz, 1H), 7.94 (dt, *J* = 6.2, 1.5 Hz, 2H), 7.55–7.51 (m, 1H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.16 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.15 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 166.8, 165.5, 151.6, 148.6, 139.9, 138.6, 137.6, 128.7, 128.6, 128.6, 128.4, 127.2, 126.7, 126.7, 126.5, 126.2, 122.1, 121.7, 116.8, 71.0, 61.0, 21.3, 14.4; **HRMS** (ESI): calcd for $C_{26}H_{22}N_2NaO_5^+$ [M+Na$^+$]: 465.1424, found 465.1420.

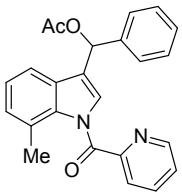
(6-methoxy-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2m):



2m

Prepared according to general procedure **A** from **1m** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2m** (45.3 mg, 75%) as a colorless oil. R_f = 0.45 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 8.13 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.94–7.88 (m, 2H), 7.51 – 7.43 (m, 3H), 7.34–7.25 (m, 4H), 7.11 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 3H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.8, 158.6, 152.3, 148.6, 138.8, 138.3, 137.5, 128.6, 128.2, 128.0, 127.7, 127.2, 126.5, 126.3, 126.3, 126.2, 126.0, 125.9, 125.9, 122.4, 121.4, 120.5, 113.4, 110.0, 105.4, 101.5, 71.8, 71.2, 55.8, 55.3, 21.3; **HRMS** (ESI): calcd for $C_{24}H_{20}N_2NaO_4^+$ [M+Na$^+$]: 423.1318, found 423.1315.

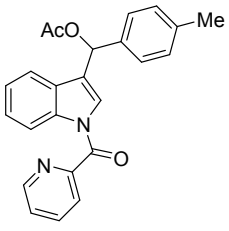
(7-methyl-1-picolinoyl-1*H*-indol-3-yl)(phenyl)methyl acetate (2n):



2n

Prepared according to general procedure **A** from **1n** (50.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2n** (38.6 mg, 66%) as a pale yellow oil. R_f = 0.6 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 4.6 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.57 – 7.53 (m, 1H), 7.46 – 7.42 (m, 3H), 7.34 – 7.26 (m, 4H), 7.18 – 7.14 (m, 3H), 2.47 (s, 3H), 2.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.3, 165.0, 151.2, 149.2, 138.8, 137.5, 136.6, 130.1, 128.5, 128.5, 128.2, 127.2, 127.90, 126.7, 126.5, 124.4, 120.8, 117.8, 71.0, 21.9, 21.3; **HRMS** (ESI): calcd for $C_{24}H_{20}N_2NaO_3^+$ [M+Na$^+$]: 407.1368, found 407.1366.

(1-picolinoyl-1*H*-indol-3-yl)(p-tolyl)methyl acetate (2o):

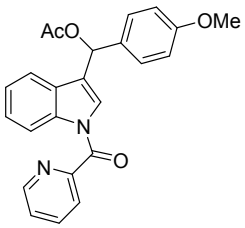


2o

Prepared according to general procedure **B** from **1o** (50.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2o** (32.7 mg, 56%) as a colorless oil. R_f = 0.5 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ =

8.64 (d, *J* = 4.5 Hz, 1H), 8.41 (d, *J* = 8.3 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.93 (s, 1H), 7.85 (td, *J* = 7.8, 1.8 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.34 – 7.25 (m, 4H), 7.16 (d, *J* = 6.7 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 3H), 2.24 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.6, 152.2, 148.6, 138.1, 137.5, 137.3, 135.8, 129.3, 128.8, 127.3, 127.2, 126.3, 126.0, 125.4, 124.3, 121.6, 120.1, 117.1, 71.1, 21.3, 21.2; **HRMS** (ESI): calcd for $C_{24}H_{20}N_2NaO_3^+$ [M+Na$^+$]: 407.1364, found 407.1366.

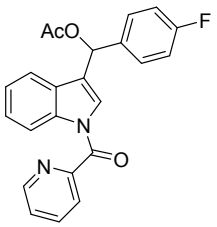
(4-methoxyphenyl)(1-picolinoyl-1*H*-indol-3-yl)methyl acetate (2p):



2p

Prepared according to general procedure **B** from **1p** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2p** (36.8 mg, 61%) as a colorless oil. R_f = 0.40 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 8.42 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.92 (s, 1H), 7.88 – 7.84 (m, 1H), 7.44 (t, *J* = 6.3 Hz, 1H), 7.31 (dd, *J* = 7.3, 4.7 Hz, 3H), 7.17 (d, *J* = 7.4 Hz, 2H), 7.04 (s, 1H), 6.79 (d, *J* = 8.3 Hz, 2H), 3.71 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.3, 165.6, 159.6, 152.2, 148.6, 137.5, 137.3, 131.6, 130.9, 128.9, 128.8, 127.0, 126.4, 126.0, 125.4, 124.3, 121.7, 120.1, 117.2, 114.0, 114.0, 113.8, 71.0, 55.4, 21.3; **HRMS** (ESI): calcd for $C_{24}H_{20}N_2NaO_4^+$ [M+Na$^+$]: 423.1315, found 423.1315.

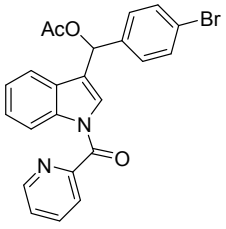
(4-fluorophenyl)(1-picolinoyl-1*H*-indol-3-yl)methyl acetate (2q):



2q

Prepared according to general procedure **B** from **1q** (50.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2q** (32.1 mg, 55%) as a pale brown oil. R_f = 0.5 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 4.7 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.94 (s, 1H), 7.85 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.38 – 7.34 (m, 2H), 7.29 (ddd, *J* = 7.5, 6.3, 1.5 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.05 (s, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 2.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.5, 163.8, 161.4, 152.0, 148.5, 137.5, 137.3, 134.6, 129.2, 128.5, 127.4, 126.4, 126.0, 125.5, 124.3, 121.2, 119.9, 117.2, 115.6, 115.4, 70.5, 21.3; **HRMS** (ESI): calcd for $C_{23}H_{17}FN_2NaO_3^+$ [M+Na$^+$]: 411.1112, found 411.1115.

(4-bromophenyl)(1-picolinoyl-1*H*-indol-3-yl)methyl acetate (2r):

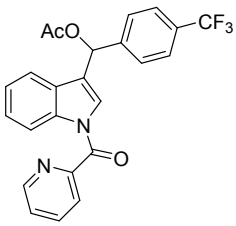


2r

Prepared according to general procedure **B** from **1r** (59.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2r** (32.3 mg, 48%) as a pale brown oil. R_f = 0.5 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ =

8.63 (d, *J* = 4.8 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.96 (s, 1H), 7.85 (td, *J* = 7.8, 1.8 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.32 – 7.23 (m, 4H), 7.19 – 7.14 (m, 1H), 7.02 (s, 1H), 2.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.1, 165.5, 151.9, 148.5, 137.8, 137.5, 137.2, 131.7, 128.9, 128.4, 127.6, 126.5, 126.0, 125.5, 124.3, 122.3, 120.7, 119.9, 117.2, 70.5, 21.2; **HRMS** (ESI): calcd for $C_{23}H_{17}BrN_2NaO_3^+$ [M+Na$^+$]: 471.0310, found 471.0314.

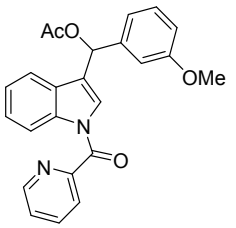
(1-picolinoyl-1*H*-indol-3-yl)(4-(trifluoromethyl)phenyl)methyl acetate (2s):



2s

Prepared according to general procedure **B** from **1s** (58.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2s** (33.9 mg, 51%) as a pale yellow oil. R_f = 0.40 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 4.8 Hz, 1H), 8.44 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.99 (s, 1H), 7.87 (td, *J* = 7.8, 1.8 Hz, 1H), 7.52 (d, *J* = 3.2 Hz, 4H), 7.46 – 7.43 (m, 1H), 7.31 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.20 – 7.16 (m, 1H), 7.10 (s, 1H), 2.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.1, 165.4, 151.9, 148.5, 142.8, 137.6, 137.3, 130.5, 130.2, 128.4, 127.9, 127.4, 126.5, 126.1, 125.6, 124.4, 120.5, 119.8, 117.3, 70.4, 21.2; **HRMS** (ESI): calcd for $C_{24}H_{17}F_3N_2NaO_3^+$ [M+Na$^+$]: 461.1079, found 461.1083.

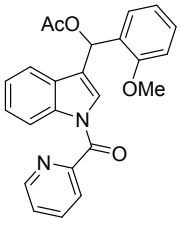
(3-methoxyphenyl)(1-picolinoyl-1*H*-indol-3-yl)methyl acetate (2t):



2t

Prepared according to general procedure **B** from **1t** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2t** (31.4 mg, 52%) as a pale yellow oil. R_f = 0.45 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 4.8 Hz, 1H), 8.46 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.39 – 7.33 (m, 1H), 7.30 – 7.25 (m, 2H), 6.96 – 6.87 (m, 2H), 3.83 (s, 3H), 2.12 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.0, 165.6, 156.7, 152.3, 148.5, 137.4, 137.1, 129.4, 129.2, 127.7, 127.3, 127.2, 126.3, 125.9, 125.2, 124.3, 121.6, 120.6, 120.0, 117.1, 110.9, 65.9, 55.7, 21.3; **HRMS** (ESI): calcd for $C_{24}H_{20}N_2NaO_4^+$ [M+Na$^+$]: 423.1314, found 423.1315.

(2-methoxyphenyl)(1-picolinoyl-1*H*-indol-3-yl)methyl acetate (2u):

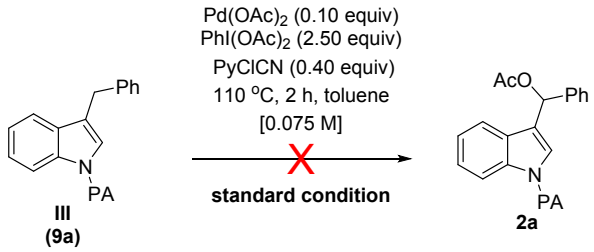


2u

Prepared according to general procedure **B** from **1u** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **2u** (30.8 mg, 51%) as a cplorless oil. R_f = 0.45 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.63

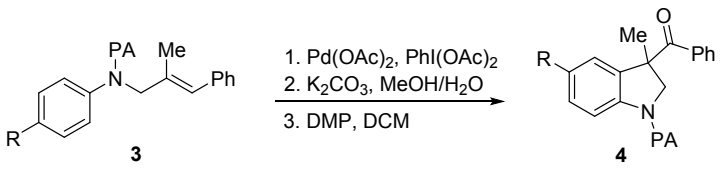
(d, J = 4.8 Hz, 1H), 8.42 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.93 (s, 1H), 7.86 – 7.82 (m, 1H), 7.44 – 7.36 (m, 2H), 7.31 – 7.27 (m, 1H), 7.19 – 7.15 (m, 2H), 7.05 (s, 1H), 6.97 – 6.93 (m, 2H), 6.75 (dd, J = 8.2, 2.6 Hz, 1H), 3.69 (s, 3H), 2.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.2, 165.5, 159.8, 152.1, 148.5, 140.3, 137.5, 137.2, 129.6, 128.7, 127.5, 126.4, 126.0, 125.4, 124.3, 121.3, 120.0, 119.5, 117.1, 113.5, 113.0, 70.9, 55.3, 21.3; **HRMS** (ESI): calcd for $C_{24}H_{20}N_2NaO_4^+$ [M+Na$^+$]: 423.1321, found 423.1315.

Attempted acetoxylation on 3-benzylindole (9a):



Procedure D: To a solution of **9a** (0.3 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.015 mmol, 0.1 equiv) in anhydrous toluene (4 mL) at r.t. was added $PhI(OAc)_2$ (0.75 mmol, 2.5 equiv), 2-chloroisonicotinonitrile (0.12 mmol, 0.4 equiv) in a 15 mL flame-dried sealed tube (purged with N_2, sealed with PTFE cap). After heating at 110 °C for 2 hours, by TLC analysis, starting material remained and observed multiple spots. Heating for longer time at same temperature did not afford the desired product.

4. Optimization and Substrate Scope of 2-methyl cinnamyl Anilines



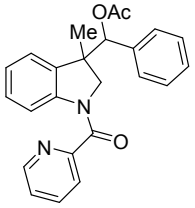
Scheme 2. Synthesis of indoline derivatives.

4.1 Procedure SI-M:

To a solution of **3** (0.3 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.015 mmol, 0.1 equiv) in anhydrous toluene (4 mL) at r.t. was added $PhI(OAc)_2$ (0.75 mmol, 2.5 equiv), 2-chloroisonicotinonitrile (16.6mg, 0.12 mmol, 0.4 equiv) in a 15 mL flame-dried sealed tube (purged with N_2, sealed with PTFE cap). The mixture was heated at 110 °C for 2 hours. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The resulting residue was

purified by silica gel flash chromatography (petroleum ether / EtOAc) to give the corresponding product **(SI 29-37)**.

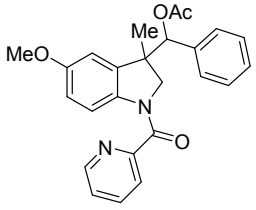
(3-methyl-1-picolinoylindolin-3-yl)(phenyl)methyl acetate (SI-29):



SI-29

Prepared according to general procedure **SI-M** from **3a** (50.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-29** (44.1 mg, 75%) as a colorless oil in 2:1 dr. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 8.04 (dd, *J* = 20.5, 8.1 Hz, 1H), 7.78 (q, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.34 (q, *J* = 5.8 Hz, 1H), 7.26 – 7.02 (m, 6H), 6.79 (dd, *J* = 25.5, 7.5 Hz, 2H), 5.67 (s, 1H), 4.36 (dd, *J* = 20.2, 11.9 Hz, 1H), 3.94 (dd, *J* = 12.0, 8.7 Hz, 1H), 1.95 (d, *J* = 34.6 Hz, 3H), 1.37 (d, *J* = 15.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.8, 169.7, 165.3, 165.2, 154.2, 154.2, 148.0, 147.9, 143.7, 143.6, 137.0, 136.6, 136.4, 135.7, 135.5, 128.6, 128.5, 128.3, 128.1, 127.9, 127.6, 127.5, 126.9, 125.1, 124.4, 124.2, 124.1, 124.0, 118.1, 118.0, 80.0, 79.5, 60.1, 59.7, 48.2, 48.0, 22.9, 22.3, 21.1, 21.0; **HRMS** (ESI): calcd for $C_{24}H_{22}N_2NaO_3^+$ [M+Na$^+$]: 409.1510, found 409.1522.

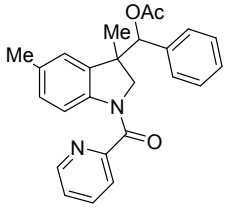
(5-methoxy-3-methyl-1-picolinoylindolin-3-yl)(phenyl)methyl acetate (SI-30)



SI-30

Prepared according to general procedure **SI-M** from **3b** (54.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-30** (57.1 mg, 91%) as a colorless oil in 3:2 dr. Rf = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.61 (dt, *J* = 8.0, 3.1 Hz, 1H), 8.05 (dd, *J* = 18.2, 8.8 Hz, 1H), 7.83 (dtd, *J* = 9.6, 7.7, 1.8 Hz, 1H), 7.73 (dd, *J* = 11.1, 7.8 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.24 – 7.10 (m, 3H), 6.93 – 6.80 (m, 3H), 6.65 (dd, *J* = 9.7, 2.7 Hz, 1H), 5.74 (d, *J* = 5.0 Hz, 1H), 4.45 (dd, *J* = 22.8, 12.1 Hz, 1H), 4.00 (dd, *J* = 12.1, 2.3 Hz, 1H), 3.79 (d, *J* = 4.0 Hz, 3H), 2.02 (d, *J* = 29.7 Hz, 3H), 1.42 (d, *J* = 13.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.8, 169.7, 164.7, 164.5, 156.7, 156.6, 154.3, 154.2, 148.0, 147.8, 137.3, 137.2, 137.1, 137.0, 136.9, 136.6, 136.3, 128.3, 128.1, 127.8, 127.6, 127.5, 126.9, 125.0, 124.4, 124.2, 118.9, 118.7, 113.5, 113.3, 110.2, 109.9, 79.9, 79.4, 60.3, 60.0, 55.7, 55.7, 48.3, 48.1, 22.8, 22.2, 21.1, 21.0; **HRMS** (ESI): calcd for $C_{25}H_{24}N_2NaO_4^+$ [M+Na$^+$]: 439.1624, found 439.1628.

(3,5-dimethyl-1-picolinoylindolin-3-yl)(phenyl)methyl acetate (SI-31):

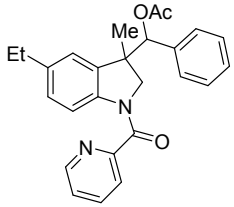


SI-31

Prepared according to general procedure **SI-M** from **3c** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-31** (50.4 mg, 83%) as a colorless oil in 3:2 dr. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.61 (t, *J* = 6.1 Hz, 1H), 7.99 (dd, *J* = 28.0, 8.2 Hz, 1H), 7.83 (tt, *J* = 8.1, 4.1

Hz, 1H), 7.72 (t, *J* = 5.4 Hz, 1H), 7.38 (dq, *J* = 8.6, 4.6 Hz, 1H), 7.24 – 7.09 (m, 4H), 6.93 – 6.89 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.73 (s, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.97 (t, *J* = 12.0 Hz, 1H), 2.36 (d, *J* = 5.2 Hz, 3H), 2.01 (d, *J* = 36.2 Hz, 3H), 1.41 (d, *J* = 22.8 Hz, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.9, 169.8, 165.1, 164.8, 154.4, 154.3, 148.0, 147.9, 141.4, 141.2, 136.9, 136.7, 136.4, 135.7, 135.7, 133.9, 133.8, 129.1, 129.0, 128.3, 128.1, 127.8, 127.5, 126.8, 125.0, 124.6, 124.5, 124.4, 124.2, 117.8, 117.7, 79.9, 79.5, 60.1, 59.8, 48.2, 48.0, 22.8, 22.3, 21.3, 21.3, 21.1, 21.0; **HRMS** (ESI): calcd for $C_{25}H_{24}N_2NaO_3^+$ [M+Na$^+$]: 423.1677, found 423.1679.

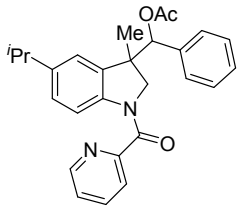
(5-ethyl-3-methyl-1-picolinoylindolin-3-yl)(phenyl)methyl acetate (SI-32):



SI-32

Prepared according to general procedure **SI-M** from **3d** (54.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-32** (52.1 mg, 83%) as a pale yellow oil in 2:1 dr. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.62 (t, *J* = 7.0 Hz, 1H), 8.03 (dd, *J* = 25.0, 8.2 Hz, 1H), 7.87 – 7.71 (m, 2H), 7.38 (q, *J* = 5.9 Hz, 1H), 7.24 – 7.09 (m, 4H), 6.92 – 6.82 (m, 3H), 5.73 (s, 1H), 4.44 (t, *J* = 12.1 Hz, 1H), 3.98 (t, *J* = 12.7 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.00 (d, *J* = 31.2 Hz, 3H), 1.42 (d, *J* = 16.9 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.9, 169.8, 165.1, 164.9, 154.4, 154.3, 148.0, 147.9, 141.6, 141.4, 140.5, 140.4, 137.0, 136.7, 136.4, 135.6, 135.6, 128.2, 128.1, 128.0, 127.8, 127.6, 127.0, 125.0, 124.4, 124.2, 123.5, 123.4, 117.9, 117.7, 80.1, 79.4, 60.3, 60.1, 48.3, 48.0, 28.7, 22.5, 22.3, 21.1, 21.0, 16.0; **HRMS** (ESI): calcd for $C_{26}H_{26}N_2NaO_3^+$ [M+Na$^+$]: 437.1845, found 437.1835.

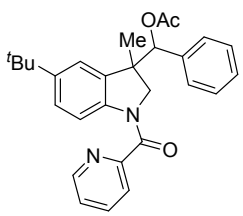
(5-ethyl-3-methyl-1-picolinoylindolin-3-yl)(phenyl)methyl acetate (SI-33):



SI-33

Prepared according to general procedure **SI-M** from **3e** (56.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-33** (52.4 mg, 81%) as a pale yellow oil in 2:1 dr. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 5.1 Hz, 1H), 8.04 (dd, *J* = 22.9, 8.3 Hz, 1H), 7.88 – 7.74 (m, 2H), 7.38 (q, *J* = 6.3 Hz, 1H), 7.17 (ddd, *J* = 24.8, 12.2, 7.3 Hz, 4H), 6.93 – 6.82 (m, 3H), 5.74 (s, 1H), 4.45 (dd, *J* = 19.0, 12.0 Hz, 1H), 4.00 (t, *J* = 12.7 Hz, 1H), 2.91 (p, *J* = 7.2 Hz, 1H), 2.00 (d, *J* = 35.3 Hz, 3H), 1.42 (d, *J* = 12.3 Hz, 3H), 1.28 – 1.20 (m, 6H).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.0, 169.7, 165.2, 164.9, 154.4, 154.3, 148.0, 147.9, 145.1, 145.0, 141.7, 141.4, 137.0, 136.7, 136.4, 135.5, 135.4, 128.2, 128.1, 127.8, 127.6, 127.6, 127.1, 126.8, 126.6, 125.0, 124.5, 124.2, 122.0, 121.9, 117.8, 117.7, 80.3, 79.3, 60.4, 60.3, 48.4, 48.0, 33.9, 24.5, 23.9, 21.2, 21.0; **HRMS** (ESI): calcd for $C_{27}H_{28}N_2NaO_3^+$ [M+Na$^+$]: 451.1988, found 451.1992.

(5-(tert-butyl)-3-methyl-1-picolinoylindolin-3-yl)(phenyl)methyl acetate (SI-34):

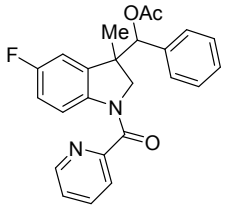


SI-34

Prepared according to general procedure **SI-M** from **3f** (58.0 mg, 0.15 mmol, 1.00

equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-34** (47.3 mg, 71%) as a pale brown oil in 2:1 dr. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 8.06 (dd, *J* = 18.4, 8.5 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.41 – 7.11 (m, 5H), 6.98 – 6.84 (m, 3H), 5.74 (s, 1H), 4.46 (dd, *J* = 26.8, 11.9 Hz, 1H), 4.01 (t, *J* = 11.3 Hz, 1H), 2.00 (d, *J* = 31.9 Hz, 3H), 1.30 (d, *J* = 12.1 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.0, 169.7, 165.2, 165.0, 154.3, 154.3, 148.0, 147.9, 147.3, 147.2, 141.4, 141.1, 137.0, 136.8, 136.5, 135.0, 134.9, 128.2, 128.1, 127.8, 127.6, 127.1, 125.5, 125.3, 125.0, 124.5, 124.2, 121.3, 121.1, 117.5, 117.3, 80.4, 79.2, 60.6, 60.5, 48.5, 48.1, 34.7, 31.5, 22.3, 22.0, 21.1, 21.0; **HRMS** (ESI): calcd for $C_{28}H_{30}N_2NaO_3^+$ [M+Na$^+$]: 465.2145, found 465.2148.

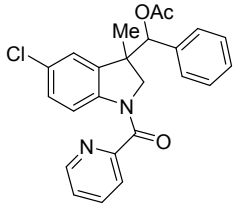
(5-fluoro-3-methyl-1-picolinoylindolin-3-yl)(phenyl)methyl acetate (SI-35):



SI-35

Prepared according to general procedure **SI-M** from **3g** (52.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-35** (45.5 mg, 75%) as a colorless oil in 3:2 dr. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.62 (dd, *J* = 10.7, 4.8 Hz, 1H), 8.08 (td, *J* = 6.1, 4.9, 2.1 Hz, 1H), 7.90 – 7.68 (m, 2H), 7.44 – 7.36 (m, 1H), 7.19 (dt, *J* = 33.2, 7.3 Hz, 3H), 6.99 (qd, *J* = 8.8, 2.6 Hz, 1H), 6.93 – 6.76 (m, 3H), 5.71 (d, *J* = 6.0 Hz, 1H), 4.48 (dd, *J* = 43.0, 12.1 Hz, 1H), 4.04 (dd, *J* = 12.1, 8.6 Hz, 1H), 2.03 (d, *J* = 20.0 Hz, 3H), 1.43 (d, *J* = 4.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.8, 169.7, 165.0, 158.5, 158.4, 154.0, 153.9, 148.0, 147.9, 139.7, 137.8, 137.8, 137.1, 137.0, 136.3, 136.1, 128.5, 128.3, 128.0, 127.8, 127.4, 126.9, 125.3, 125.2, 124.5, 124.3, 119.2, 119.1, 119.0, 118.9, 115.2, 115.1, 115.0, 114.9, 111.6, 111.4, 111.2, 79.7, 79.4, 60.5, 60.2, 48.2, 48.1, 22.9, 22.0, 21.1, 21.0; **HRMS** (ESI): calcd for $C_{24}H_{21}FN_2NaO_3^+$ [M+Na$^+$]: 427.1424, found 427.1428.

(5-chloro-3-methyl-1-picolinoylindolin-3-yl)(phenyl)methyl acetate (SI-36):

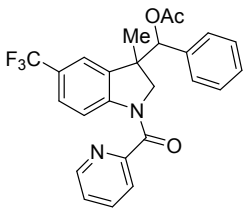


SI-36

Prepared according to general procedure **SI-M** from **3h** (55.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-36** (49.7 mg, 78%) as a colorless oil in 3:2 dr. R_f = 0.60 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.61 (ddd, *J* = 10.3, 4.8, 1.6 Hz, 1H), 8.05 (dd, *J* = 8.7, 3.0 Hz, 1H), 7.87 – 7.68 (m, 2H), 7.44 – 7.37 (m, 1H), 7.29 – 7.11 (m, 5H), 6.89 (t, *J* = 7.7 Hz, 2H), 5.71 (d, *J* = 9.5 Hz, 1H),

4.48 (dd, *J* = 41.6, 12.1 Hz, 1H), 4.04 (t, *J* = 6.1 Hz, 1H), 2.03 (d, *J* = 17.2 Hz, 3H), 1.42 (d, *J* = 4.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.7, 169.7, 165.1, 153.8, 153.7, 148.0, 147.9, 142.3, 137.6, 137.4, 137.1, 137.0, 136.3, 136.0, 129.1, 129.0, 128.6, 128.5, 128.3, 128.0, 127.8, 127.4, 127.0, 125.3, 125.3, 124.5, 124.4, 119.1, 118.9, 79.7, 79.4, 60.4, 60.1, 48.2, 48.1, 22.8, 22.0, 21.0, 21.0; **HRMS** (ESI): calcd for $C_{24}H_{21}ClN_2NaO_3^+$ [M+Na^+]: 443.1129, found 443.1132.

(3-methyl-1-picolinoyl-5-(trifluoromethyl)indolin-3-yl)(phenyl)methyl acetate (SI-37):

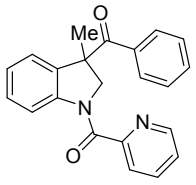


SI-37

Prepared according to general procedure **SI-M** from **3i** (60.0 mg, 0.15 mmol, 1.00 equiv) and $Pd(OAc)_2$ (3.4 mg, 0.10 equiv) at 110 °C for 2 hours to yield **SI-37** (46.7 mg, 68%) as a pale yellow oil in 3:2 dr. R_f = 0.50 (silica, hexanes: EtOAc, 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.63 (dd, *J* = 11.6, 4.7 Hz, 1H), 8.22 (s, 1H), 7.87 – 7.82 (m, 2H), 7.58 (s, 1H), 7.45 – 7.40 (m, 1H), 7.27 – 7.14 (m, 4H), 6.88 (dd, *J* = 29.3, 7.5 Hz, 2H), 5.73 (d, *J* = 10.6 Hz, 1H), 4.55 (dd, *J* = 57.0, 12.1 Hz, 1H), 4.09 (t, *J* = 14.1 Hz, 1H), 2.02 (d, *J* = 14.4 Hz, 3H), 1.47 (d, *J* = 3.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.7, 169.6, 165.7, 165.7, 153.5, 153.4, 148.1, 148.0, 146.6, 146.5, 138.9, 137.2, 137.1, 136.1, 135.9, 128.6, 128.4, 128.0, 127.8, 127.3, 127.1, 126.1, 126.0, 125.60, 125.5, 124.6, 124.4, 123.0, 121.6, 121.5, 117.8, 117.7, 79.7, 79.3, 60.6, 60.4, 48.1, 47.9, 22.5, 21.8, 21.0, 20.9; **HRMS** (ESI): calcd for $C_{25}H_{21}F_3N_2NaO_3^+$ [M+Na^+]: 477.1392, found 477.1396.

4.2 General Procedure C: To a solution of SM **(SI-29-37)** (0.10 mmol, 1.0 equiv) in MeOH/H_2O (1:1, 0.1 M) was added K_2CO_3 (0.30 mmol, 3.0 equiv) and stirred for 3h at room temperature. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with H_2O and extracted into EtOAc. The combined organics were dried over Na_2SO_4 and concentrated in vacuo to yield the crude hydroxyl compound which was used in next step without purification. The residue was dissolved in DCM (0.05 M) and added DMP (0.15 mmol, 1.50 equiv) at °C. The reaction was stirred at room temperature for 2 hours. Then water was added, the layers separated, and the aqueous layer extracted once with DCM (5 mL). The combined organics were dried over Na_2SO_4, concentrated and purified by flash chromatography (petroleum ether/ EtOAc = 10:1) to afford the corresponding product.

(3-benzoyl-3-methylindolin-1-yl)(pyridin-2-yl)methanone (4a):

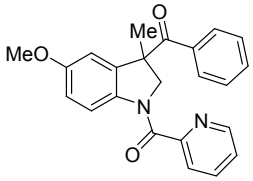


4a

Prepared according to general procedure **C** from **SI-29** (39.0 mg, 0.10 mmol, 1.00 equiv) to yield **4a** (29.3 mg, 85%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 4.7 Hz, 1H), 8.37 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.32 (dt, *J* = 18.9, 7.0 Hz, 3H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.02 (s, 2H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.29 (d, *J* = 12.3 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 200.8, 166.0, 153.8, 148.0, 142.8, 137.3, 136.9, 132.2, 129.1, 128.5, 125.4, 124.6, 123.8, 118.7, 61.9, 56.3, 26.6; HRMS (ESI): calcd for $C_{22}H_{18}N_2NaO_2^+$ [M+Na^+]: 365.1260, found 365.1260.

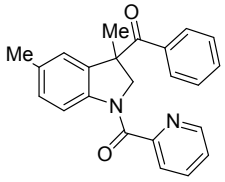
(3-benzoyl-5-methoxy-3-methylindolin-1-yl)(pyridin-2-yl)methanone (4b):



4b

Prepared according to general procedure **C** from **SI-30** (42.0 mg, 0.10 mmol, 1.00 equiv) to yield **4b** (33.0 mg, 88%) as a pale yellow oil. R_f = 0.40 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 4.8 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.72 (td, *J* = 7.8, 1.8 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.29 – 7.17 (m, 3H), 6.83 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.56 (d, *J* = 2.6 Hz, 1H), 4.86 (d, *J* = 12.4 Hz, 1H), 4.31 (d, *J* = 12.4 Hz, 1H), 3.66 (s, 3H), 1.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.7, 165.4, 157.4, 153.9, 147.9, 138.3, 137.1, 136.5, 135.9, 132.2, 129.1, 128.5, 125.2, 124.6, 119.5, 114.0, 109.4, 62.1, 56.4, 55.7, 26.5; **HRMS** (ESI): calcd for $C_{23}H_{20}N_2NaO_3^+$ [M+Na^+]: 395.1366, found 395.1366.

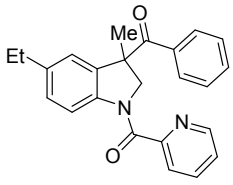
(3-benzoyl-3,5-dimethylindolin-1-yl)(pyridin-2-yl)methanone (4c):



4c

Prepared according to general procedure **C** from **SI-31** (40.0 mg, 0.1 mmol, 1.00 equiv) to yield **4c** (30.6 mg, 86%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 4.8 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.83 (s, 1H), 4.84 (d, *J* = 12.4 Hz, 1H), 4.28 (d, *J* = 12.3 Hz, 1H), 2.20 (s, 3H), 1.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.9, 165.7, 153.9, 148.0, 140.5, 137.2, 136.9, 136.0, 135.1, 132.2, 129.6, 129.1, 128.4, 125.3, 124.6, 124.2, 118.4, 62.0, 56.3, 26.7, 21.2; **HRMS** (ESI): calcd for $C_{23}H_{21}N_2O_2^+$ [M+H^+]: 357.1599, found 357.1597.

(3-benzoyl-5-ethyl-3-methylindolin-1-yl)(pyridin-2-yl)methanone (4d):

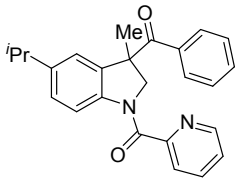


4d

Prepared according to general procedure **C** from **SI-32** (42.0 mg, 0.10 mmol, 1.00 equiv) to yield **4d** (32.6 mg, 87%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 4.7 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.85 (s, 1H), 4.83 (d, *J* = 12.3 Hz,

1H), 4.29 (d, *J* = 12.3 Hz, 1H), 2.51 (q, *J* = 7.6 Hz, 2H), 1.55 (s, 3H), 1.08 (t, *J* = 7.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 201.2, 165.7, 153.9, 148.0, 141.6, 140.7, 137.2, 136.8, 136.2, 132.1, 129.0, 128.4, 125.3, 124.6, 123.1, 118.4, 62.0, 56.4, 28.6, 26.6, 15.7; **HRMS** (ESI): calcd for $C_{24}H_{22}N_2NaO_2^+$ [M+Na$^+$]: 393.1574, found 393.1573.

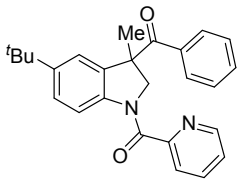
(3-benzoyl-5-isopropyl-3-methylindolin-1-yl)(pyridin-2-yl)methanone (4e):



4e

Prepared according to general procedure **C** from **SI-33** (43.0 mg, 0.10 mmol, 1.00 equiv) to yield **4e** (33.5 mg, 87%) as a pale yellow oil. R_f = 0.60 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 4.8 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.69 (m, 1H), 7.35 (dd, *J* = 19.4, 7.6 Hz, 3H), 7.27 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.23 – 7.14 (m, 3H), 6.86 (d, *J* = 1.8 Hz, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 4.28 (d, *J* = 12.3 Hz, 1H), 2.76 (h, *J* = 6.9 Hz, 1H), 1.55 (s, 3H), 1.09 (t, *J* = 6.3 Hz, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 165.7, 153.9, 148.0, 146.4, 140.8, 137.2, 136.7, 136.3, 132.0, 129.0, 128.4, 127.0, 125.3, 124.6, 121.7, 118.4, 62.0, 56.5, 33.9, 26.4, 24.1; HRMS (ESI): calcd for $C_{25}H_{24}N_2NaO_2^+$ [M+Na$^+$]: 407.1731, found 407.1730.

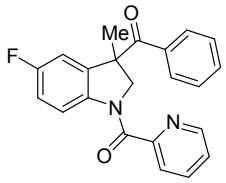
(3-benzoyl-5-(tert-butyl)-3-methylindolin-1-yl)(pyridin-2-yl)methanone (4f):



4f

Prepared according to general procedure **C** from **SI-34** (45.0 mg, 0.10 mmol, 1.00 equiv) to yield **4f** (33.6 mg, 83%) as a pale yellow oil. R_f = 0.60 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 4.9 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.25 (m, 5H), 7.21 – 7.17 (m, 2H), 7.00 (s, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 4.29 (d, *J* = 12.3 Hz, 1H), 1.55 (s, 3H), 1.16 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 201.6, 165.7, 153.9, 148.7, 148.0, 140.5, 137.1, 136.4, 132.0, 128.9, 128.3, 125.9, 125.3, 124.6, 120.7, 118.0, 62.0, 56.6, 34.7, 31.5, 26.4; **HRMS** (ESI): calcd for $C_{26}H_{26}N_2NaO_2^+$ [M+Na$^+$]: 421.1886, found 421.1886.

(3-benzoyl-5-fluoro-3-methylindolin-1-yl)(pyridin-2-yl)methanone (4g):

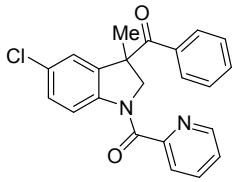


4g

Prepared according to general procedure **C** from **SI-35** (41.0 mg, 0.10 mmol, 1.00 equiv) to yield **4g** (28.1 mg, 77%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 4.8 Hz, 1H), 8.42 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.82 (td, *J* = 7.7, 1.8 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.39 – 7.28 (m, 3H), 7.06 (td, *J* = 8.9, 2.7 Hz, 1H), 6.81 (dd, *J* = 7.9, 2.7 Hz, 1H), 5.00 (d, *J* = 12.4

Hz, 1H), 4.43 (d, *J* = 12.4 Hz, 1H), 1.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.1, 165.8, 161.3, 158.8, 153.5, 148.0, 138.9, 138.8, 138.7, 137.3, 135.5, 132.5, 129.0, 128.6, 125.5, 124.7, 119.7, 119.6, 115.6, 115.4, 111.4, 111.2, 62.1, 56.2, 26.7; **HRMS** (ESI): calcd for $C_{22}H_{18}FN_2O_2^+$ [M+Na$^+$]: 361.1348, found 361.1346.

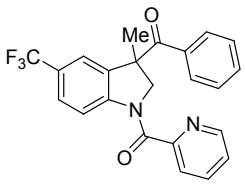
(3-benzoyl-5-chloro-3-methylindolin-1-yl)(pyridin-2-yl)methanone (4h):



4h

Prepared according to general procedure **C** from **SI-36** (42.0 mg, 0.10 mmol, 1.00 equiv) to yield **4h** (30.0 mg, 80%) as a colorless oil. R_f = 0.50 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 4.8 Hz, 1H), 8.39 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.29 (m, 4H), 7.08 (d, *J* = 2.2 Hz, 1H), 5.00 (d, *J* = 12.4 Hz, 1H), 4.43 (d, *J* = 12.4 Hz, 1H), 1.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.8, 165.8, 153.2, 147.9, 141.3, 138.5, 137.1, 135.3, 132.3, 129.8, 128.9, 128.4, 125.4, 124.6, 124.0, 119.3, 61.9, 55.9, 26.7; **HRMS** (ESI): calcd for $C_{22}H_{17}ClN_2NaO_2^+$ [M+Na$^+$]: 399.0872, found 399.0870.

(3-benzoyl-3-methyl-5-(trifluoromethyl)indolin-1-yl)(pyridin-2-yl)methanone (4i):

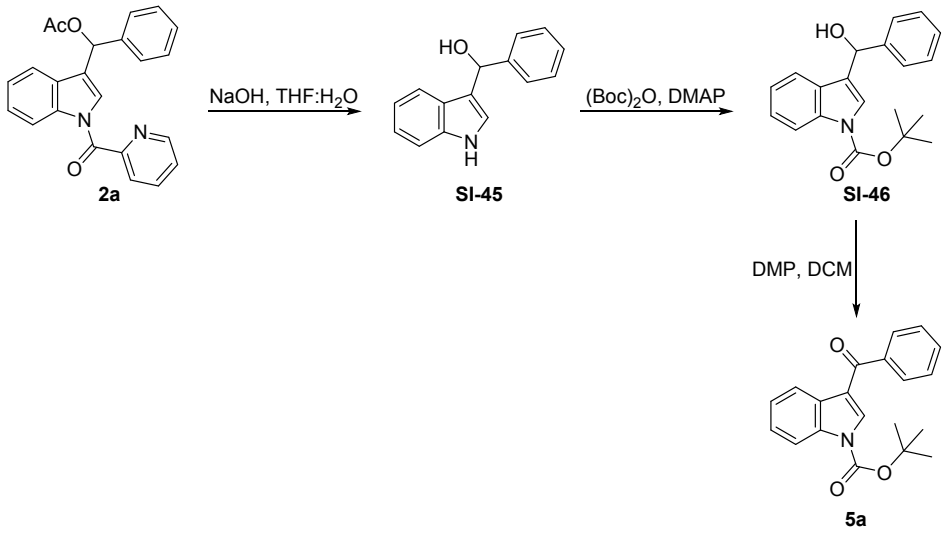


4i

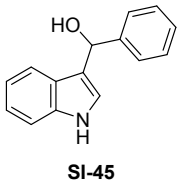
Prepared according to general procedure **C** from **SI-37** (46.0 mg, 0.10 mmol, 1.00 equiv) to yield **4i** (34.4 mg, 83%) as a pale brown oil. R_f = 0.45 (silica, hexanes: EtOAc, 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 4.9 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (td, *J* = 7.7, 1.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.28 (m, 7H), 5.05 (d, *J* = 12.3 Hz, 1H), 4.51 (s, 0H), 1.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 200.1, 166.4, 153.1, 148.2, 137.3, 135.5, 132.5, 128.9, 128.6, 126.6, 125.8, 125.4, 124.8, 122.7, 121.3, 118.3, 62.1, 56.0, 27.0; **HRMS** (ESI): calcd for $C_{23}H_{17}F_3N_2NaO_2$+ [M$^+$Na$^+$]: 433.1134, found 433.1134.

5. Versatile Transformations of the Product

5.1 General Scheme for the Synthesis of 5a:

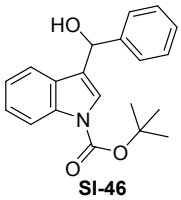


(1*H*-indol-3-yl)(phenyl)methanol (SI-45):



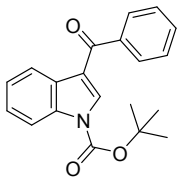
To a mixture of THF/H_2O (1.0/1.0 mL) was added compound **2a** (200 mg, 0.27 mmol, 1.0 equiv) and NaOH (43.2 mg, 1.08 mmol, 2.0 equiv) at 0 °C. The mixture was stirred at same temperature for 1 hour. Water was added and the mixture was extracted with EtOAc. The combined organic layers was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give the desired product **SI-45** (66.2 mg) in 55% yield. R_f = 0.4 (silica gel, petroleum ether : EtOAc = 2 : 1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.85 (s, 1H), 7.46 (dd, *J* = 7.7, 4.6 Hz, 3H), 7.32 – 7.26 (m, 3H), 7.23 – 7.15 (m, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.91 – 6.87 (m, 1H), 5.95 (d, *J* = 4.4 Hz, 1H), 5.56 (d, *J* = 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 146.2, 136.9, 128.2, 126.8, 126.7, 126.0, 123.0, 121.3, 120.0, 119.9, 118.7, 111.7, 69.3.

***tert*-butyl 3-(hydroxy(phenyl)methyl)-1*H*-indole-1-carboxylate (SI-46):**



Indole **SI-45** (38.0 mg, 17 mmol, 1.0 equiv) was dissolved in dry THF (10 mL) followed by the addition of DMAP (2.0 mg, 0.17 mmol, 0.1 equiv) and $(Boc)_2O$ (41 mg, 18.7 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 2 h, after which it was purified by silica gel flash chromatography to give the desired product **SI-46** (42.9 mg) in 78% yield. R_f = 0.6 (silica gel, petroleum ether : EtOAc = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.42 (m, 4H), 7.36 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.08 (d, *J* = 3.7 Hz, 1H), 2.19 (d, *J* = 4.1 Hz, 1H), 1.66 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 142.5, 136.0, 128.6, 128.0, 126.8, 124.6, 123.6, 122.7, 120.1, 115.4, 83.9, 70.5, 28.3.

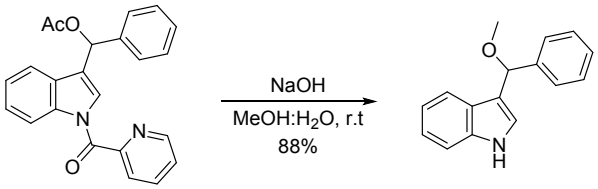
***tert*-butyl 3-benzoyl-1H-indole-1-carboxylate 5a:**



The hydroxyl compound **SI-46** (40.0 mg, 12 mmol, 1.0 equiv) was dissolved in DCM (10 mL)

and added DMP (157.0 mg, 0.37 mmol, 3.0 equiv) at 0 °C. The reaction was stirred at same temperature for 3 hours, after which it was purified by silica gel flash chromatography to give the desired product **5a** (36.1 mg) in 91% yield. R_f = 0.6 (silica gel, petroleum ether : EtOAc = 3 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.06 (s, 1H), 7.88 – 7.85 (m, 2H), 7.61 – 7.56 (m, 1H), 7.51 (td, *J* = 7.3, 6.8, 1.4 Hz, 2H), 7.44 – 7.36 (m, 2H), 1.68 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.4, 149.3, 139.7, 135.6, 134.0, 132.1, 129.0, 128.6, 128.4, 125.7, 124.4, 122.7, 119.5, 115.1, 85.5, 28.2. **HRMS** (ESI): calcd for $C_{20}H_{19}NNaO_3^+$ [M^+Na^+]: 344.1259, found 344.1257.

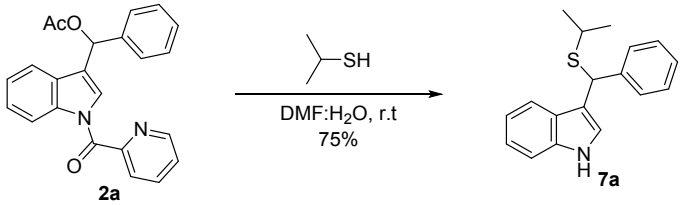
5.2 Synthesis of 6a:



2a **6a**

To a solution of compound **2a** (50 mg, 0.13 mmol, 1.0 equiv) in MeOH/H_2O (1.0/1.0 mL) was added NaOH (10.8 mg, 0.26 mmol, 2.0 equiv) and the mixture was stirred for 1 hour. Water was added and the mixture was extracted with EtOAc. The combined organic layers was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give the desired product **6a** (28.1 mg) in 88% yield. R_f = 0.6 (silica gel, petroleum ether : EtOAc = 2 : 1); **^{1}H NMR** (400 MHz, CD_3CN) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.38 – 7.36 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.11 – 7.07 (m, 2H), 6.98 – 6.95 (m, 1H), 5.56 (s, 1H), 3.32 (s, 3H). **^{13}C NMR** (101 MHz, CD_3CN) δ 143.7, 137.8, 129.1, 129.0, 128.0, 127.7, 126.8, 124.5, 122.7, 120.5, 120.0, 117.7, 112.4, 80.2, 56.7. **HRMS** (ESI): calcd for $C_{16}H_{15}NNaO^+$ [M^+Na^+]: 260.1046, found 260.1045.

5.3 Synthesis of 7a:

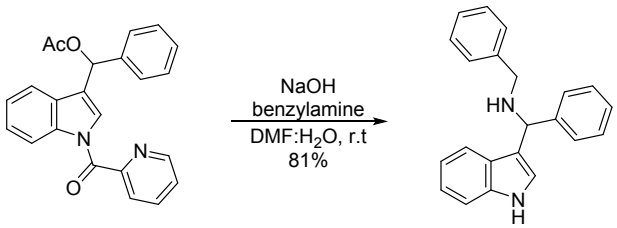


2a **7a**

To a solution of compound **2a** (50 mg, 0.13 mmol, 1.0 equiv) and propane-2-thiol (102.9 mg, 1.35 mmol, 10.0 equiv) in DMF/H_2O (1.0/1.0 mL) was added NaOH (10.8 mg, 0.26 mmol, 2.0 equiv) and the mixture was stirred for 3 hour. Water was added and the mixture was extracted with EtOAc. The combined organic layers was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica

gel flash chromatography to give the desired product **7a** (28.1 mg) in 75% yield. R_f = 0.6 (silica gel, petroleum ether : EtOAc = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.24 (q, *J* = 7.7 Hz, 3H), 7.12 (dt, *J* = 18.3, 7.6 Hz, 2H), 7.07 – 6.94 (m, 2H), 5.41 (s, 1H), 2.69 (hept, *J* = 6.7 Hz, 1H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4, 136.7, 128.5, 128.4, 127.0, 126.5, 123.2, 122.4, 119.7, 119.7, 117.2, 111.2, 45.1, 35.1, 23.4, 23.3. **HRMS** (ESI): calcd for $C_{18}H_{19}NNaS^+$ [M^+Na^+]: 304.1133, found 304.1130.

5.4 Synthesis of 8a:



2a **8a**

To a solution of compound **2a** (50 mg, 0.13 mmol, 1.0 equiv) and benzylamine (144.7 mg, 1.35 mmol, 10.0 equiv) in DMF/H_2O (1.0/1.0 mL) was added NaOH (10.8 mg, 0.26 mmol, 2.0 equiv) and the mixture was stirred for 3 hour. Water was added and the mixture was extracted with EtOAc. The combined organic layers was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give the desired product **8a** (28.1 mg) in 81% yield. R_f = 0.4 (silica gel, petroleum ether : EtOAc = 2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.28 (m, 6H), 7.25 – 7.20 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.07 – 7.02 (m, 2H), 5.17 (s, 1H), 3.81 (d, *J* = 2.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 140.8, 136.6, 128.5, 128.3, 127.7, 127.0, 127.0, 126.3, 122.2, 122.2, 119.8, 119.6, 119.6, 111.2, 59.2, 52.0. **HRMS** (ESI): calcd for $C_{22}H_{21}N_2^+$ [M^+]: 313.1700, found 313.1699.

6. X-ray Crystallographic Data of Compound 2h:

The crystal **2n** were prepared from the solution of **2h** in DCM/ hexane at ambient temperature

6.1 X-ray Crystallographic Data of Compound **2h:**

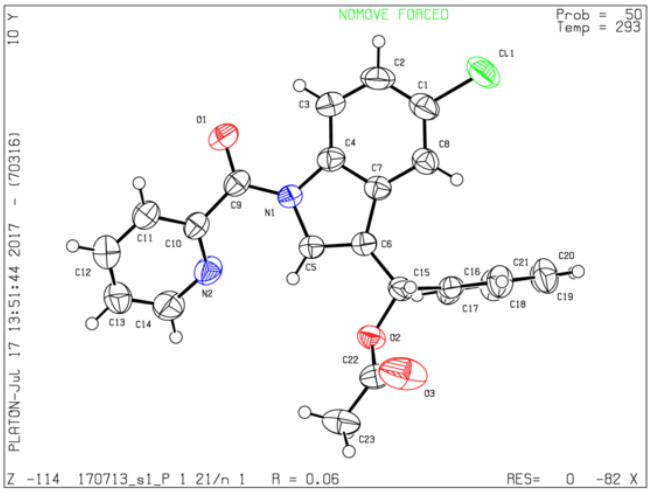


Figure 1. X-ray derived ORTEP representation of **2h**

Crystal data and structure refinement for 2h (CCDC: 1562681)

Identification code	**$C_{23}H_{17}ClN_2O_3$**
Empirical formula	**$C_{23}H_{17}ClN_2O_3$**
Formula weight	**404.09**
Temperature/K	**293.15**
Crystal system	**monoclinic**
Space group	**P 2_1/n**
a/Å	**9.6917(10)**
b/Å	**7.5033(7)**
c/Å	**27.151(2)**
α/°	**90**
β/°	**93.018(8)**
γ/°	**90**
Volume/Å3	**1971.7(3)**
Z	**4**
Dx,g cm-3	**1.364**

μ/mm-1	**0.221**
F(000)	**840.0**
Crystal size/mm3	**0.4 × 0.15 × 0.04**
Radiation	**MoK$^{\alpha}$ (λ = 0.71073)**
2Θ range for data collection/°	**6.004 to 52.742**
Index ranges	**-12 ≤ h ≤ 10, -9 ≤ k ≤ 9, -32 ≤ l ≤ 33**
Reflections collected	**10239**
Independent reflections	**4036 [R_{int} = 0.0339, R_{sigma} = 0.0541]**
Data/restraints/parameters	**4036/0/263**
Goodness-of-fit on F^2	**1.027**
Final R indexes [I>=2σ (I)]	**R1 = 0.0575, wR_2 = 0.1291**
Final R indexes [all data]	**R1 = 0.0949, wR_2 = 0.1509**
Largest diff. peak/hole / e Å^{-3}	**0.24/-0.24**

7. X-ray Crystallographic Data of Compound 4e:

The crystal **2n** were prepared from the solution of **4e** in DCM/ hexane at ambient temperature

7.1 X-ray Crystallographic Data of Compound **4e**:

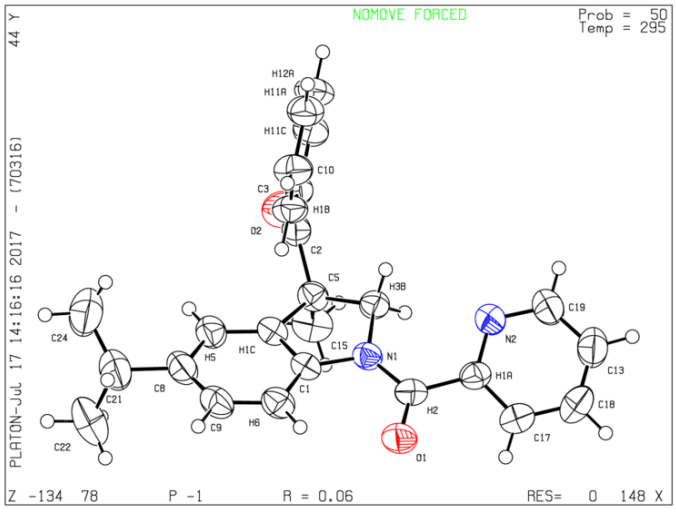


Figure 2. X-ray derived ORTEP representation of **4e**

Crystal data and structure refinement for 2h (CCDC: 1562684)

Identification code	**$C_{25}H_{24}N_2O_2$**
Empirical formula	**$C_{25}H_{24}N_2O_2$**
Formula weight	**384.46**
Temperature/K	**295 (2)**
Crystal system	**triclinic**
Space group	**P 1**
a/Å	**8.3765(5)**
b/Å	**11.2190(6)**
c/Å	**12.1776(7)**
α/°	**70.266 (5)**
β/°	**73.173(5)**
γ/°	**82.063(4)**
Volume/Å3	**1030.04(11)**
Z	**2**
Dx,g cm-3	**1.240**
μ/mm-1	**0.079**
F(000)	**408.0**
Crystal size/mm3	**0.45 × 0.43 × 0.4**
Radiation	**MoK$^{\alpha}$ (λ = 0.71073)**
2Θ range for data collection/°	**7.014 to 52.736**
Index ranges	**-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -15 ≤ l ≤15**
Reflections collected	**13983**
Independent reflections	**4213 [R_{int} = 0.0270, R_{sigma} = 0.0281]**
Data/restraints/parameters	**4213/0/265**
Goodness-of-fit on F^2	**1.045**
Final R indexes [I>=2σ (I)]	**R1 = 0.0578, wR_2 = 0.1476**
Final R indexes [all data]	**R1 = 0.0782, wR_2 = 0.1648**
Largest diff. peak/hole / e Å^{-3}	**0.34/-0.26**

8. References:

[1] H. Alinezhad, M. Tajbakhsh and N. Mahdavi, *Synth. Commun.,* 2010, **40***,* 951 - 956.

[2] T. N. T. Nguyen, N. O. Thiel, F. Pape and J. F. Teichert, *Org. Lett.,* 2016, **18**, 2455 - 2458.

[3] J. Zhou, B. Li, Z.-C. Qian and B.-F. Shi, *Adv. Synth. Catal.,* 2014*,* **356***,* 1038 - 1046.

[4] S.-C. Yang and C.-W. Hung, *J. Org. Chem.,* 1999, **64**, 5000 - 5001.

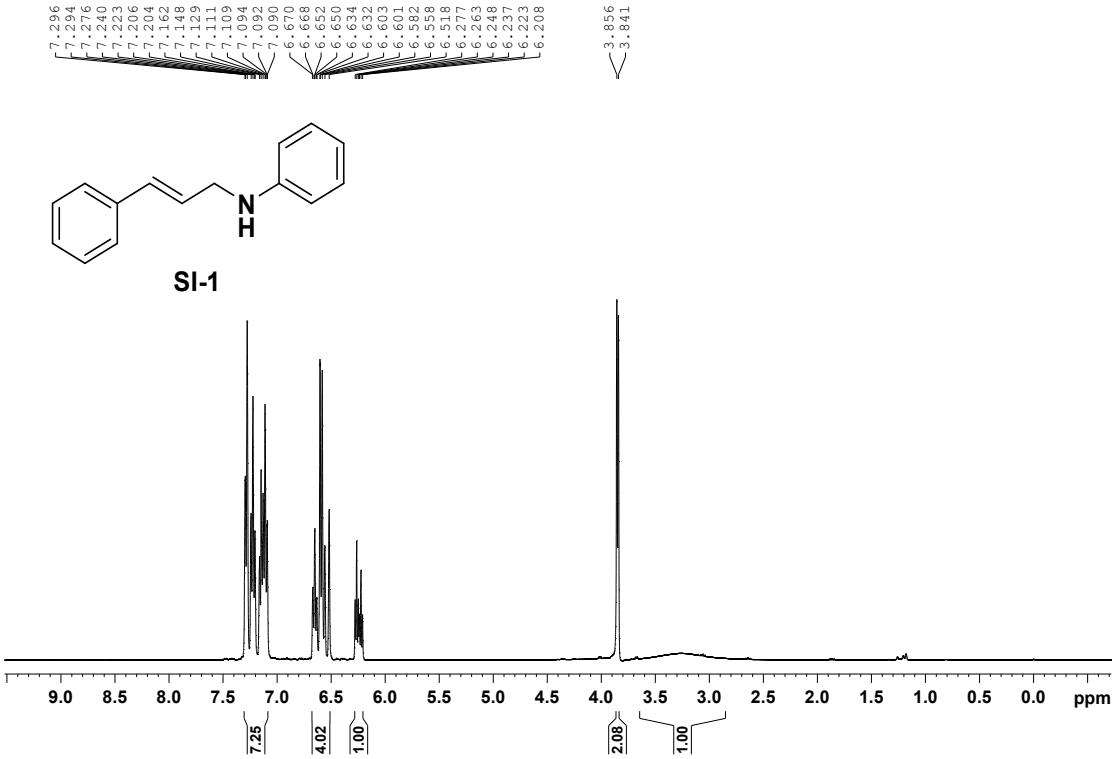
[5] E. Okazaki, R. Okamoto, Y. Shibata, K. Noguchi and K. Tanaka, *Angew. Chem. Int. Ed*., 2012, **51**, 6722 - 6727.

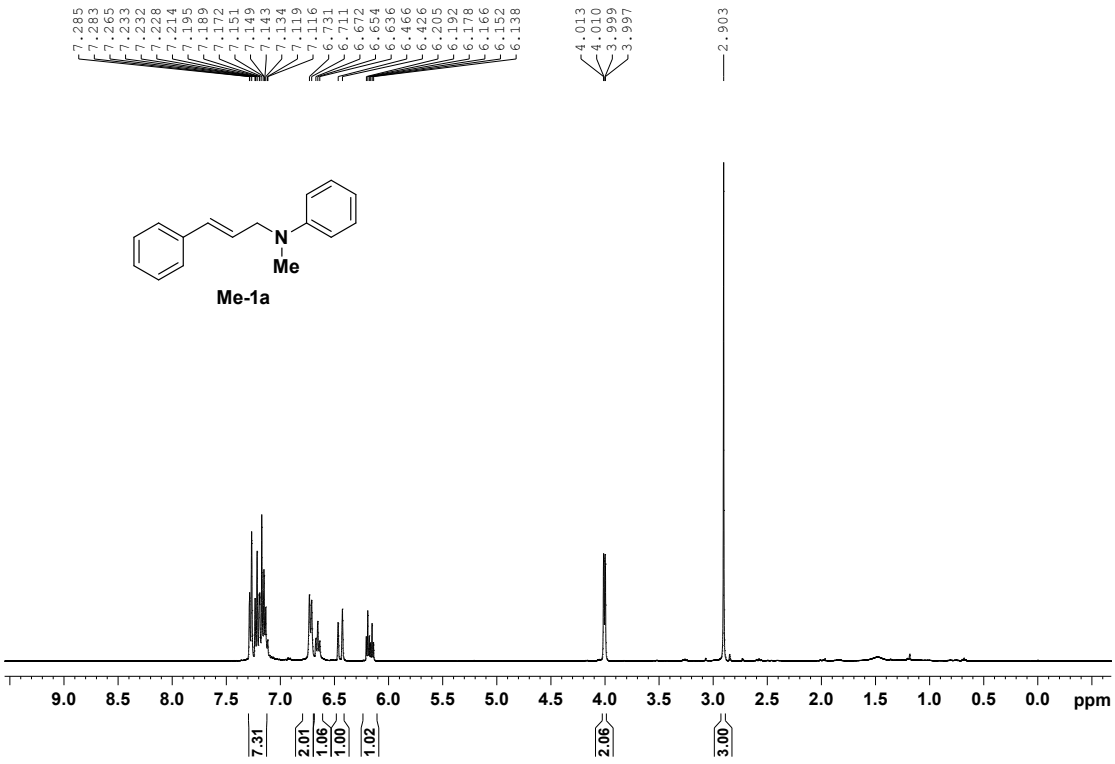
[6] W. Guo, L. Martínez-Rodríguez, R. Kuniyil, E. Martin, E. C. Escudero-Adán, F. Maseras and A. W. Kleij, *J. Am. Chem. Soc.,* 2016, **138**, 11970 - 11978.

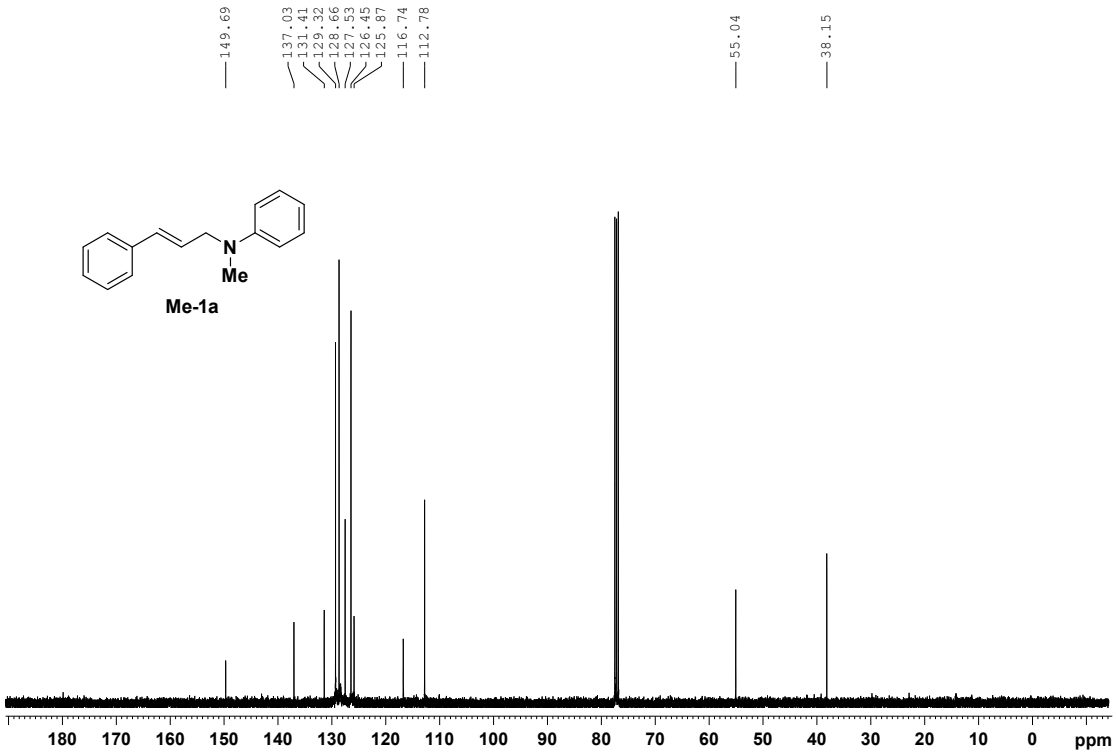
[7] R. Cano. M, Yus, D. J. Ramón, *Tetrahedron Letters,* 2013, **54**, 3394 - 3397.

9. Experimental Spectra:

9.1 Experimental Spectra of Arylacetoxylation 1.



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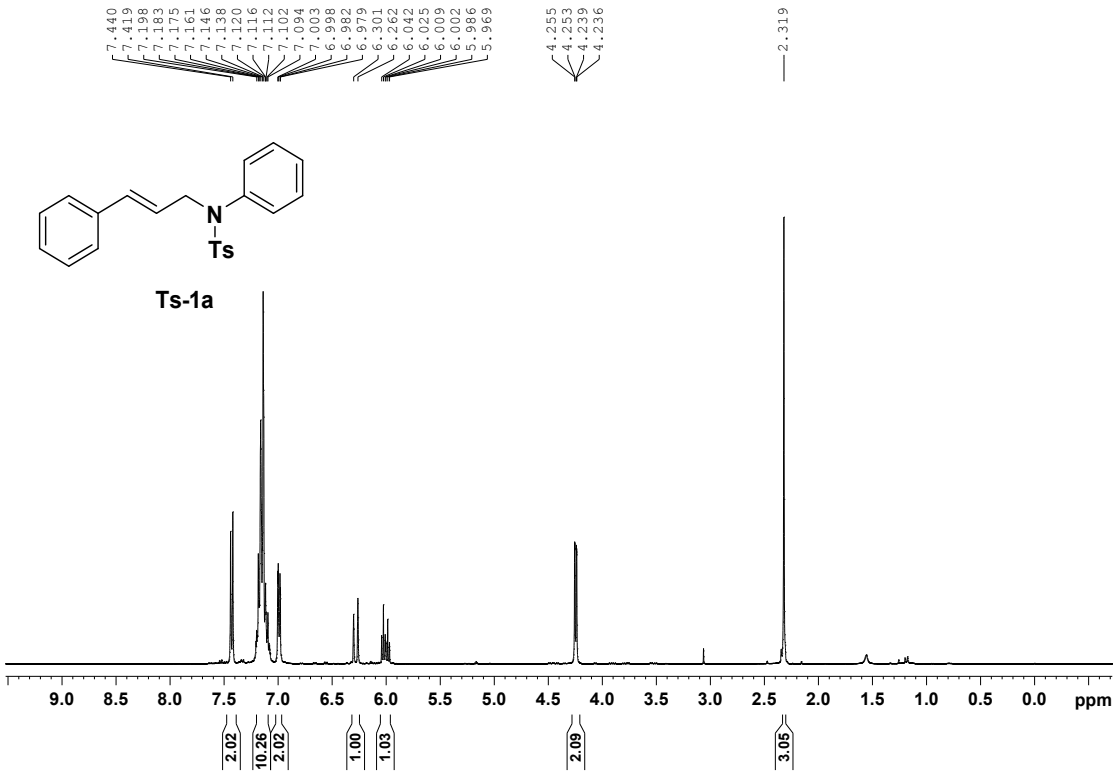
137.03
131.41
129.32
128.66
127.53
126.45
125.87
116.74
112.78
55.04
38.15
N
Me
Me-1a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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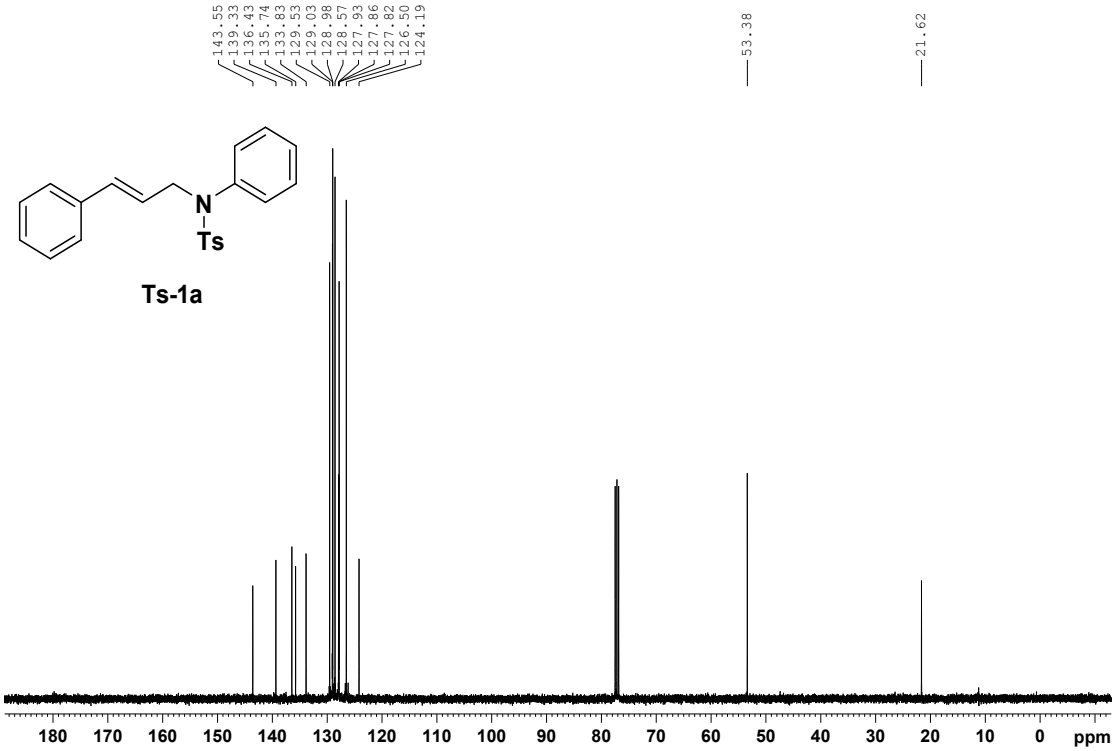
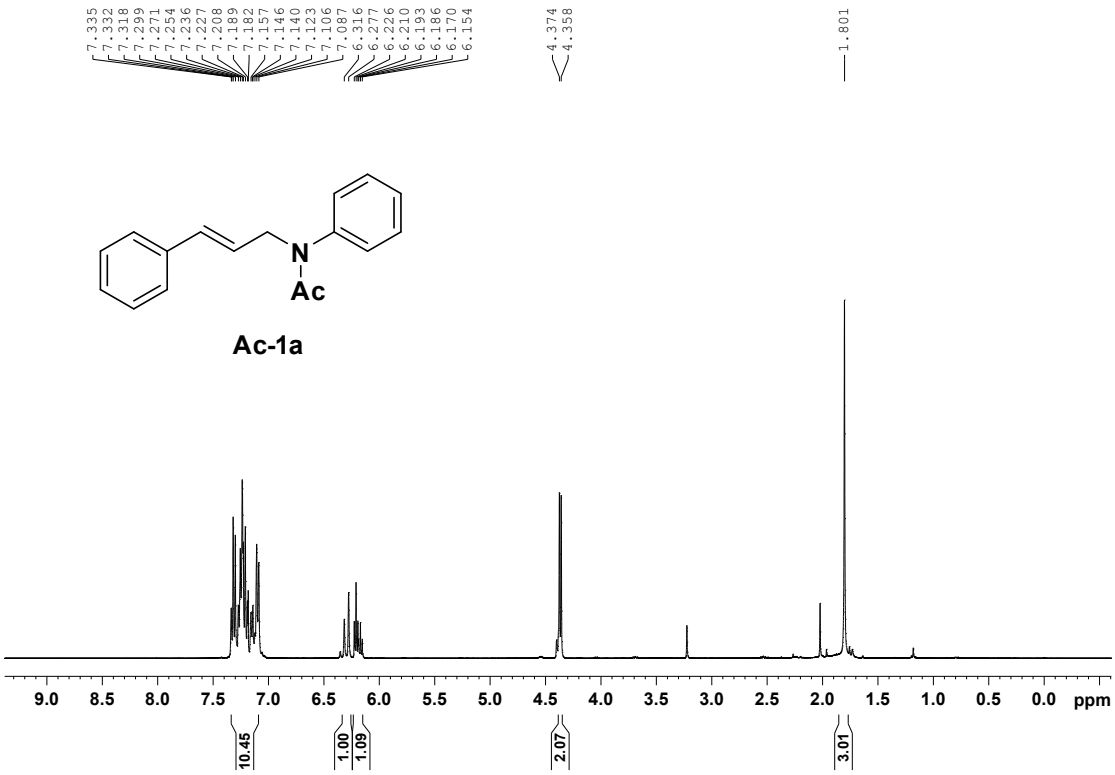
7.419
7.198
7.183
7.175
7.161
7.146
7.138
7.120
7.116
7.112
7.102
7.094
7.003
6.998
6.982
6.979
6.301
6.262
6.042
6.025
6.009
6.002
5.986
5.969
4.255
4.253
4.239
4.236
2.319
N
Ts
Ts-1a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
10.26
2.02
1.00
1.03
2.09
3.05


143.55
139.33
136.43
135.74
133.83
129.53
129.03
128.98
128.57
127.93
127.86
127.82
126.50
124.19
53.38
21.62
N
Ts
Ts-1a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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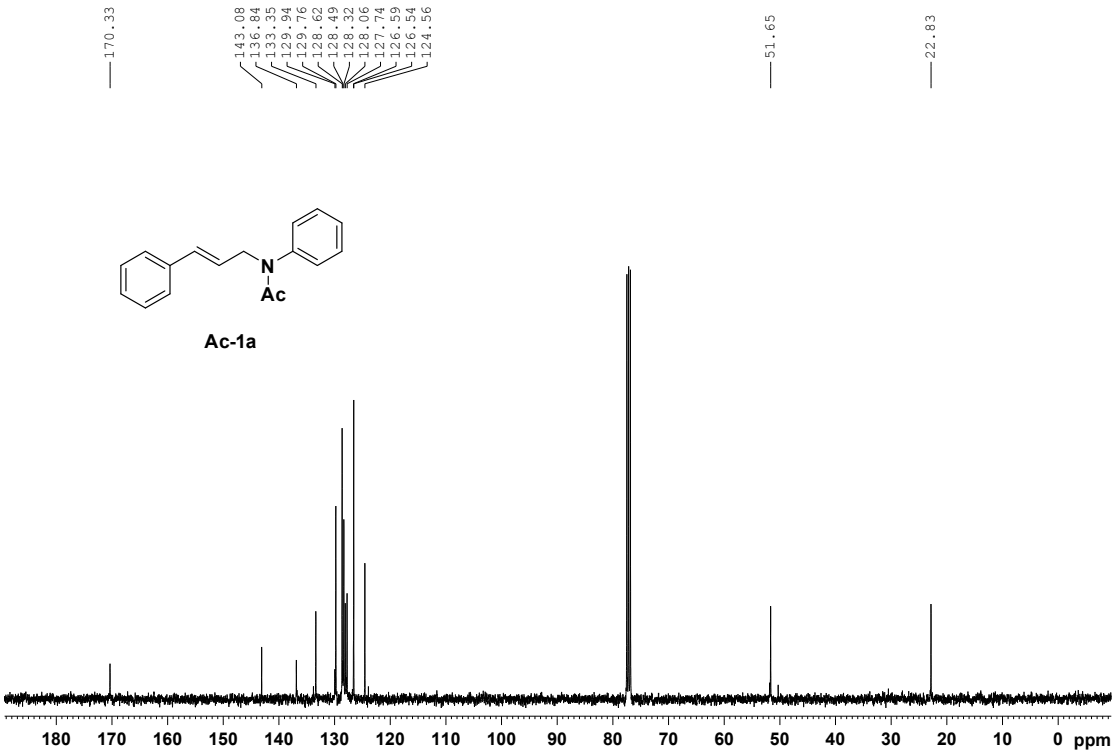
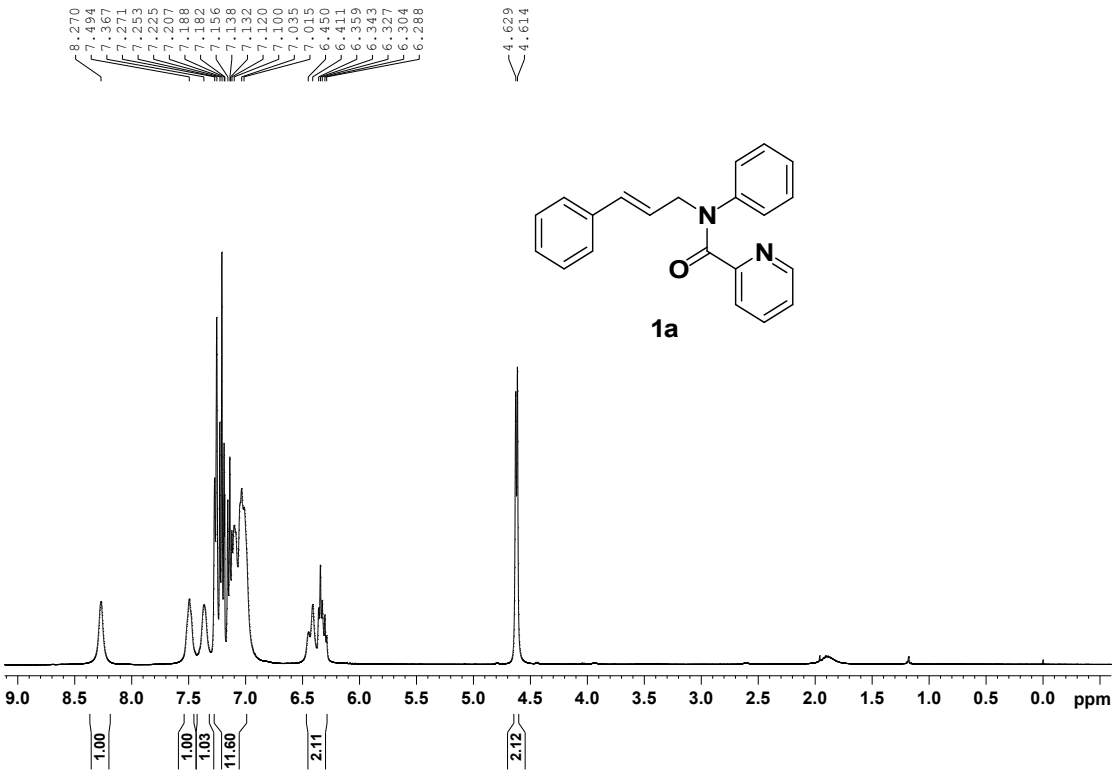
7.332
7.318
7.299
7.271
7.254
7.236
7.227
7.208
7.189
7.182
7.157
7.146
7.140
7.123
7.106
7.087
6.316
6.277
6.226
6.210
6.193
6.186
6.170
6.154
4.374
4.358
1.801
N
Ac
Ac-1a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
10.45
1.00
1.09
2.07
3.01


170.33
143.08
136.84
133.35
129.94
129.76
128.62
128.49
128.32
128.06
127.74
126.59
126.54
124.56
51.65
22.83
N
Ac
Ac-1a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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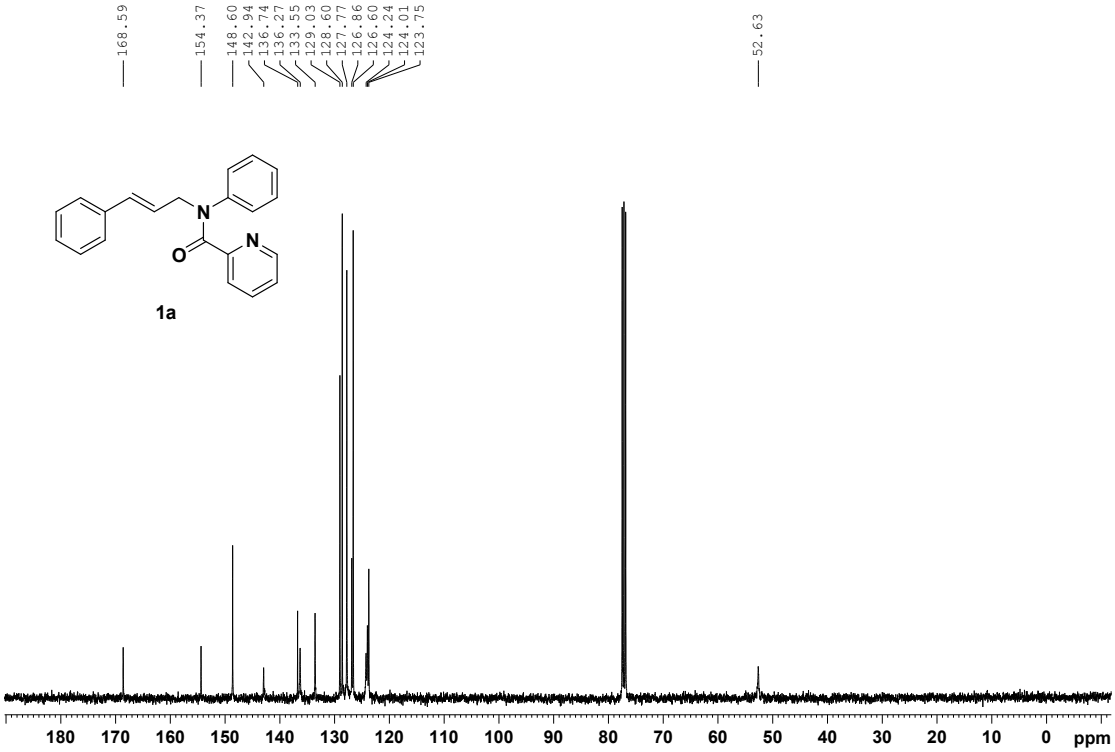
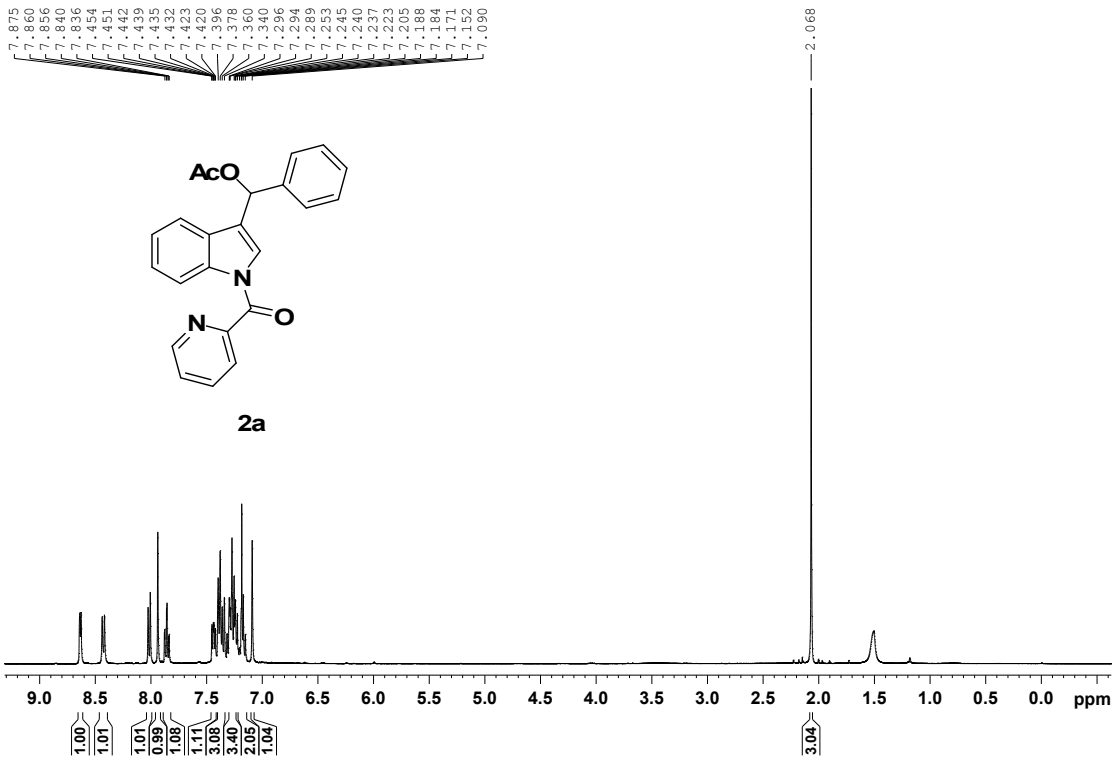
7.253
7.225
7.207
7.188
7.182
7.156
7.138
7.132
7.120
7.100
7.035
7.015
6.450
6.411
6.359
6.343
6.327
6.304
6.288
4.629
4.614
N
O
N
1a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
1.03
11.60
2.11
2.12


168.59
154.37
148.60
142.94
136.74
136.27
133.55
129.03
128.60
127.77
126.86
126.60
124.24
124.01
123.75
52.63
1a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.435
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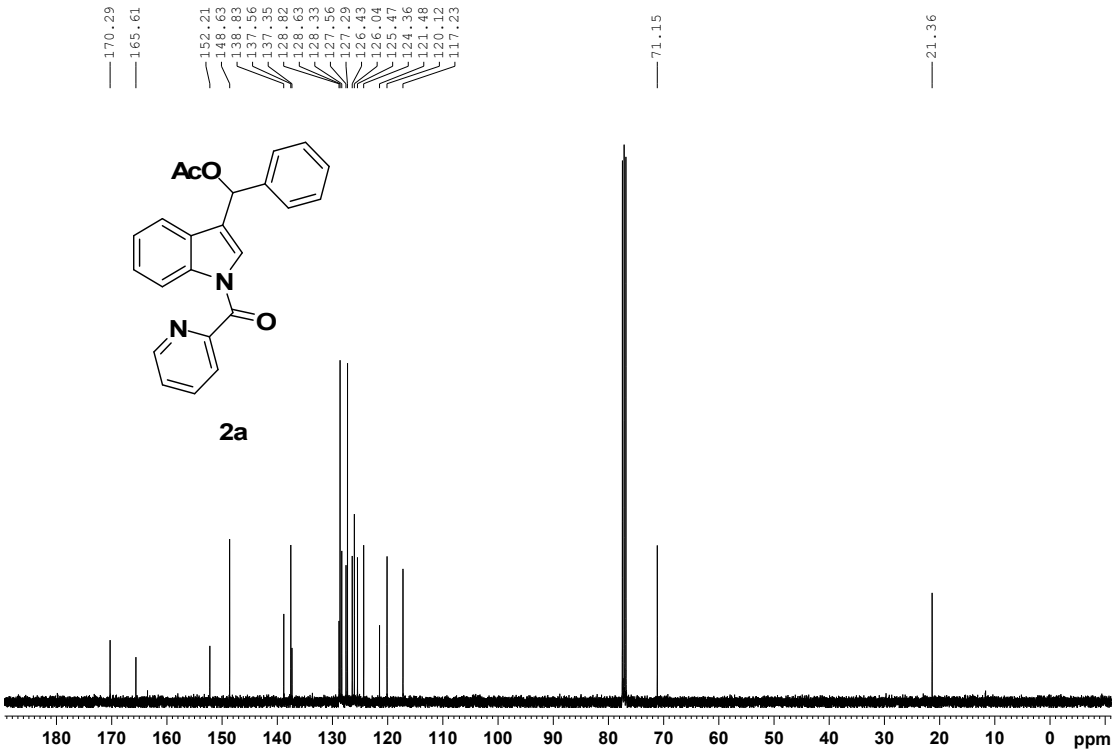
7.423
7.420
7.396
7.378
7.360
7.340
7.296
7.294
7.289
7.253
7.245
7.240
7.237
7.223
7.205
7.188
7.184
7.171
7.152
7.090
2.068
AcO
2a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.01 1.01 0.99 1.08 1.11 3.08 3.40 2.05 1.04 3.04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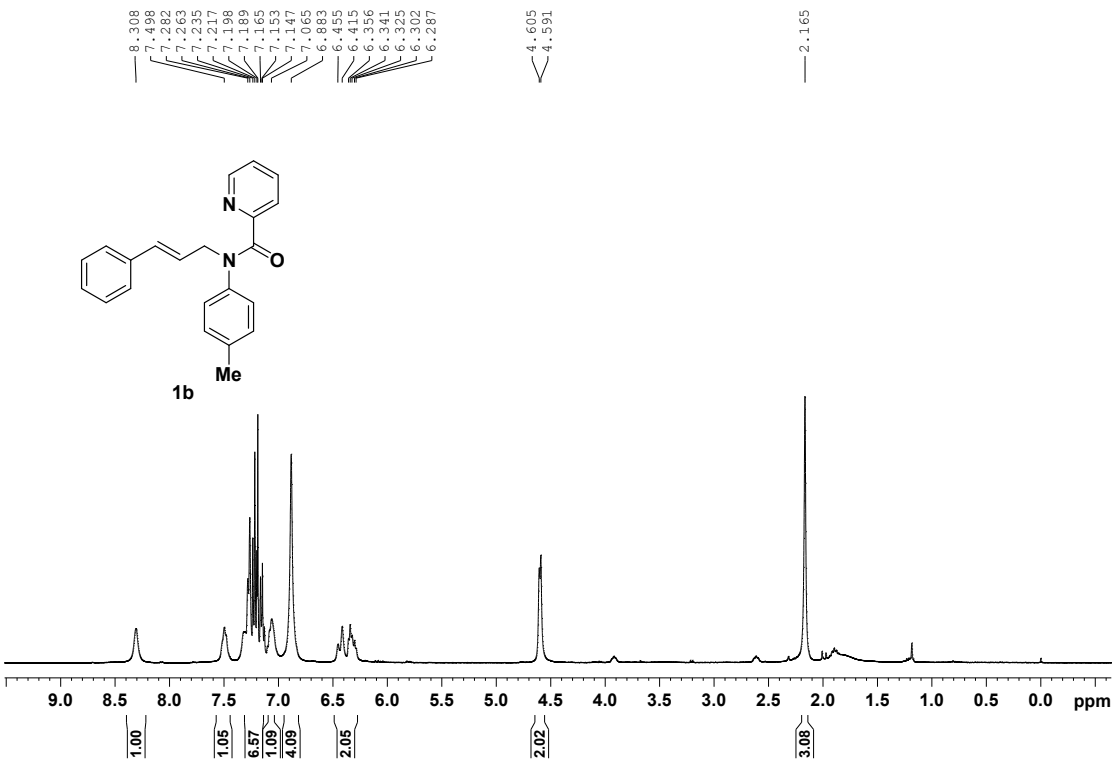
165.61
152.21
148.63
138.83
137.56
137.35
128.82
128.63
128.33
127.56
127.29
126.43
126.04
125.47
124.36
121.48
120.12
117.23
71.15
21.36
AcO
N
N
O
2a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.235
7.217
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7.189
7.165
7.153
7.147
7.065
6.883
6.455
6.415
6.356
6.341
6.325
6.302
6.287
4.605
4.591
2.165
N
N
O
Me
1b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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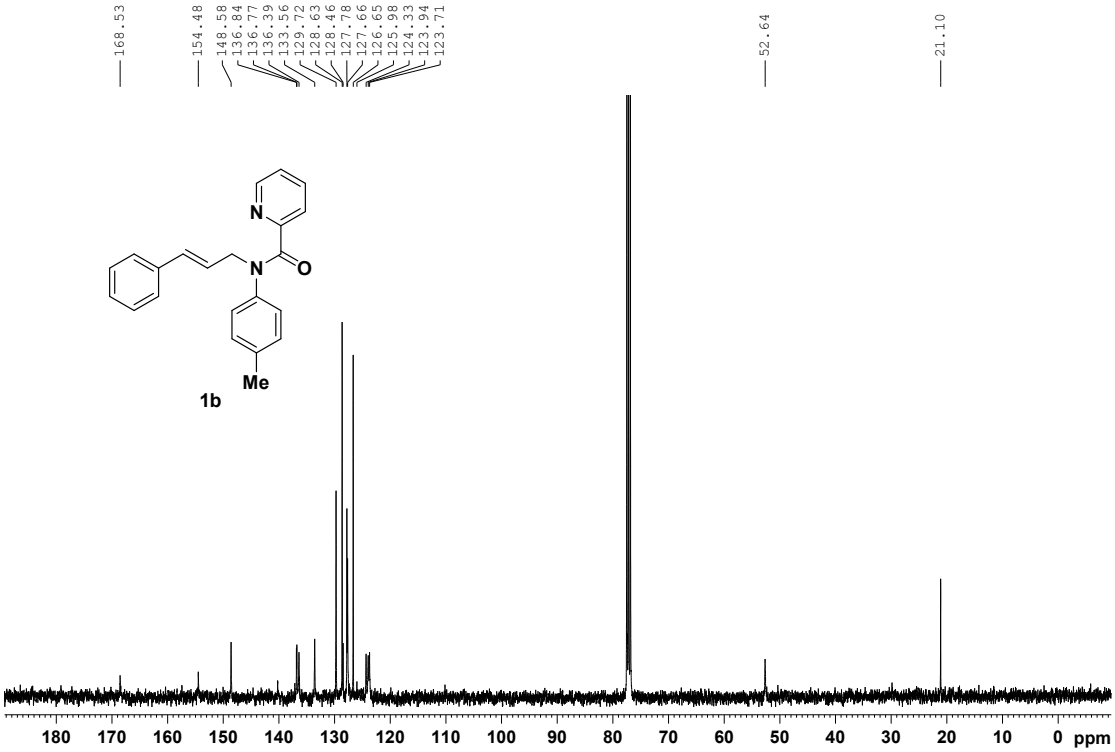
1.0
0.5
0.0
ppm
1.00
1.05
6.57
1.09
4.09
2.05
2.02
3.08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136.77
136.39
133.56
129.72
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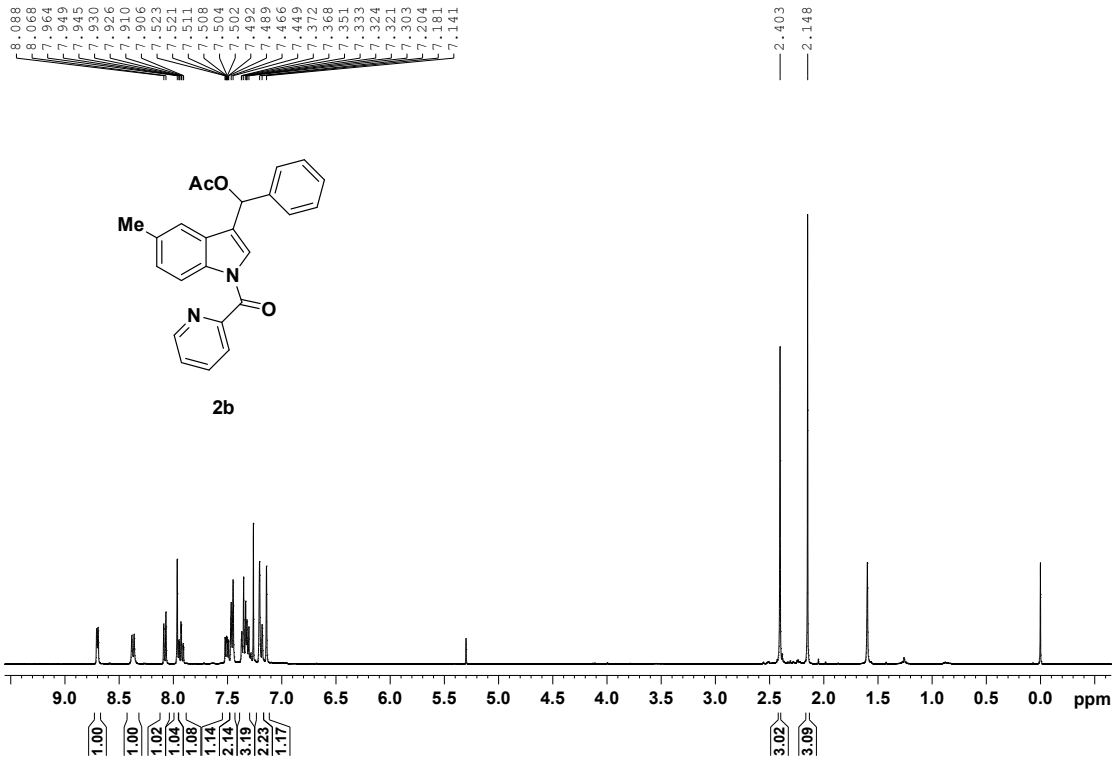
128.46
127.78
127.66
126.65
125.98
124.33
123.94
123.71
52.64
21.10
N
N
O
Me
1b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.906
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7.521
7.511
7.508
7.504
7.502
7.492
7.489
7.466
7.449
7.372
7.368
7.351
7.333
7.324
7.321
7.303
7.204
7.181
7.141
2.403
2.148
AcO
Me
N
N
O
2b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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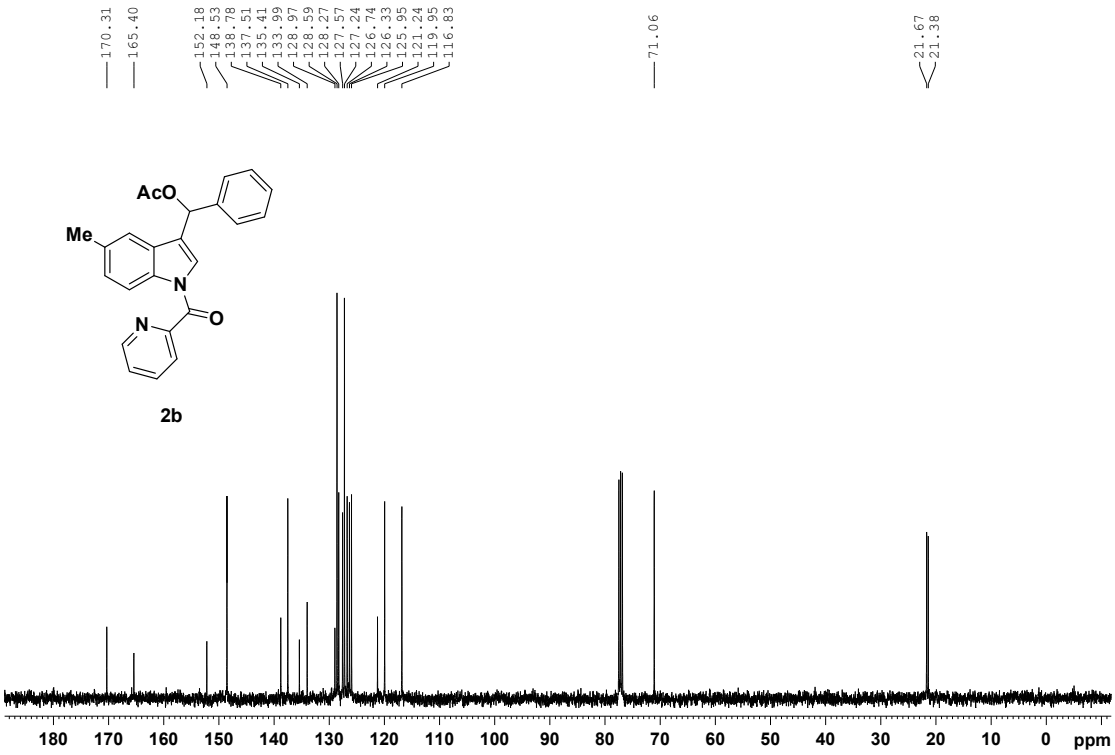
1.00
1.02
1.04
1.08
1.14
2.14
3.19
2.23
1.17
3.02
3.09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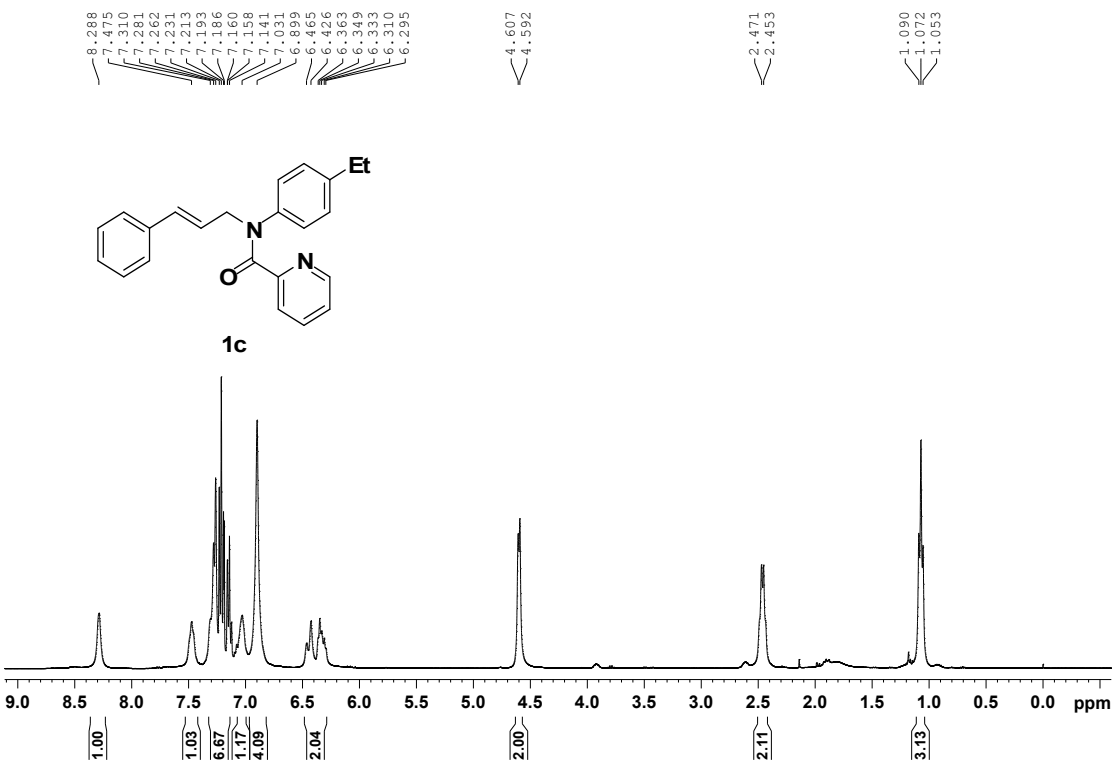
127.24
126.74
126.33
125.95
121.24
119.95
116.83
71.06
21.67
21.38
AcO
Me
N
O
N
2b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.160
7.158
7.141
7.031
6.899
6.465
6.426
6.363
6.349
6.333
6.310
6.295
4.607
4.592
2.471
2.453
1.090
1.072
1.053
Et
N
O
N
1c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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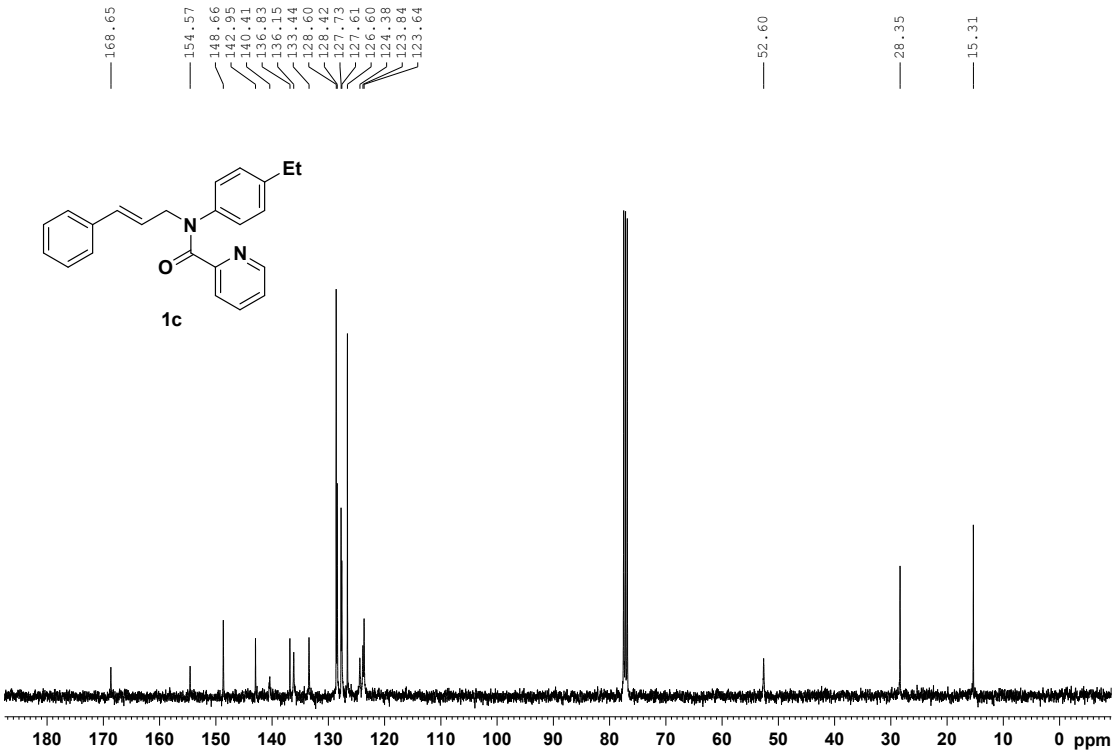
1.17
4.09
2.04
2.00
2.11
3.13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154.57
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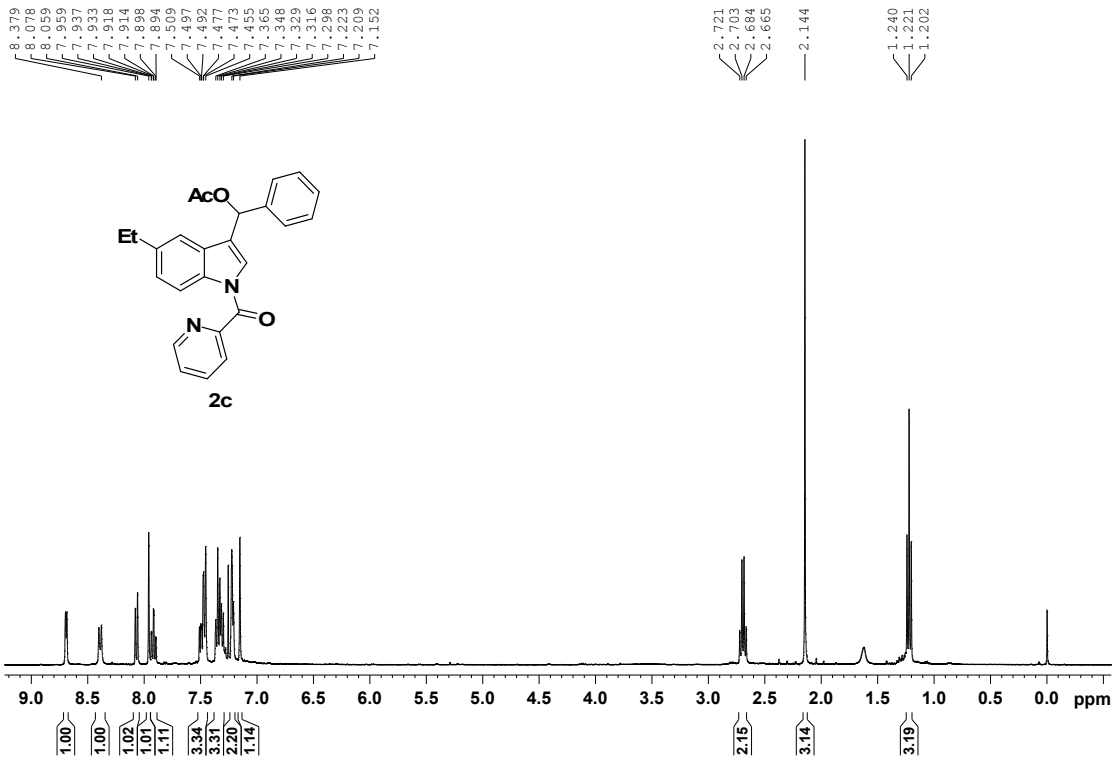
140.41
136.83
136.15
133.44
128.60
128.42
127.73
127.61
126.60
124.38
123.84
123.64
52.60
28.35
15.31
Et
N
O
N
1c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.937
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7.894
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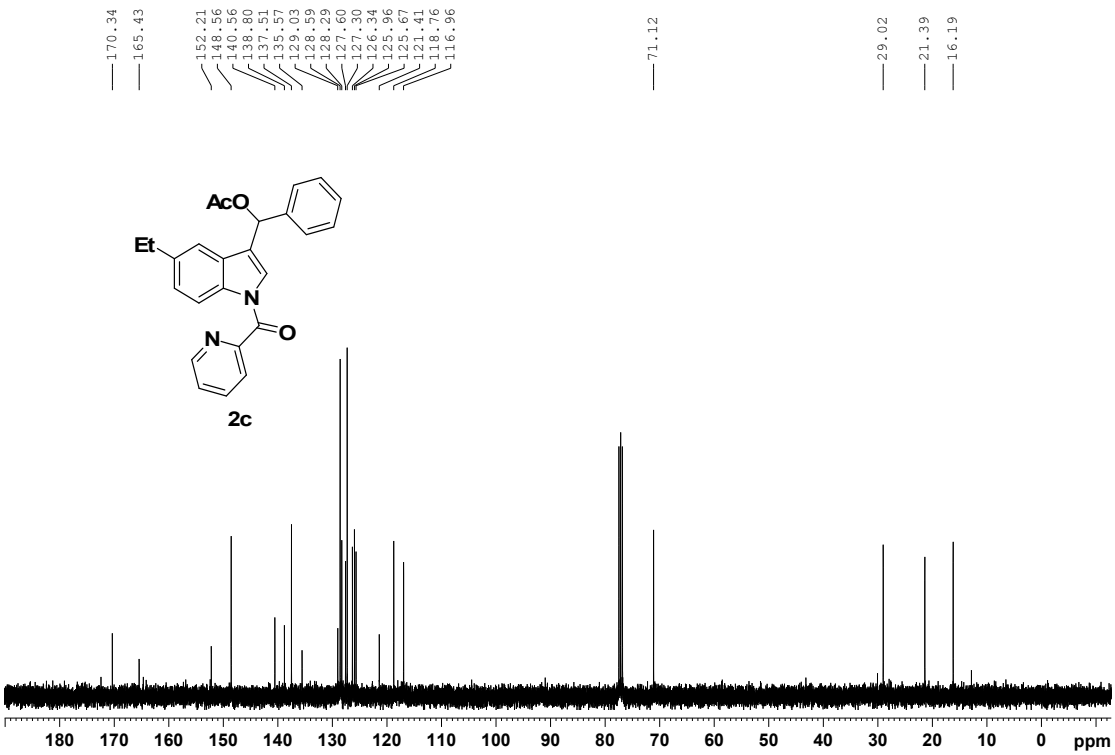
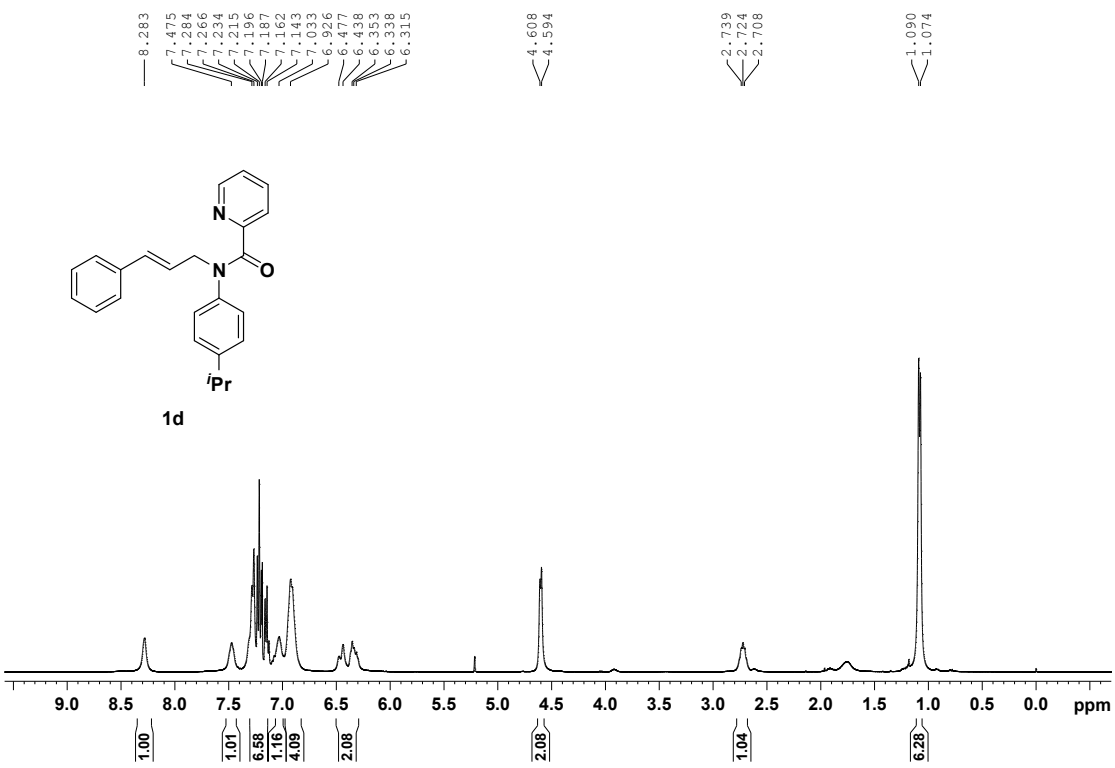
7.497
7.492
7.477
7.473
7.455
7.365
7.348
7.329
7.316
7.298
7.223
7.209
7.152
2.721
2.703
2.684
2.665
2.144
1.240
1.221
1.202
AcO
Et
N
N
O
2c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
1.02
1.01
1.11
3.34
3.31
2.20
1.14
2.15
3.14
3.19


170.34
165.43
152.21
148.56
140.56
138.80
137.51
135.57
129.03
128.59
128.29
127.60
127.30
126.34
125.96
125.67
121.41
118.76
116.96
71.12
29.02
21.39
16.19
AcO
Et
N
N
O
2c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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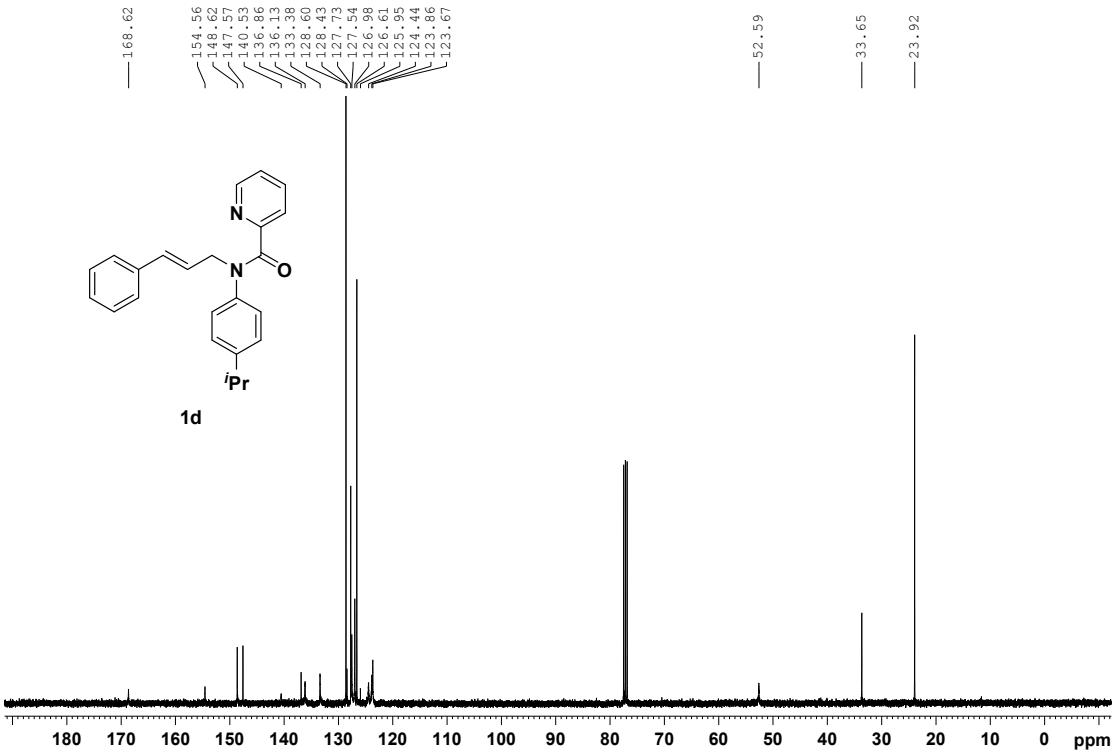
7.284
7.266
7.234
7.215
7.196
7.187
7.162
7.143
7.033
6.926
6.477
6.438
6.353
6.338
6.315
4.608
4.594
2.739
2.724
2.708
1.090
1.074
N
N
O
iPr
1d
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.01
6.58
1.16
4.09
2.08
2.08
1.04
6.28


168.62
154.56
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140.53
136.86
136.13
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128.60
128.43
127.73
127.54
126.98
126.61
125.95
124.44
123.86
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33.65
23.92
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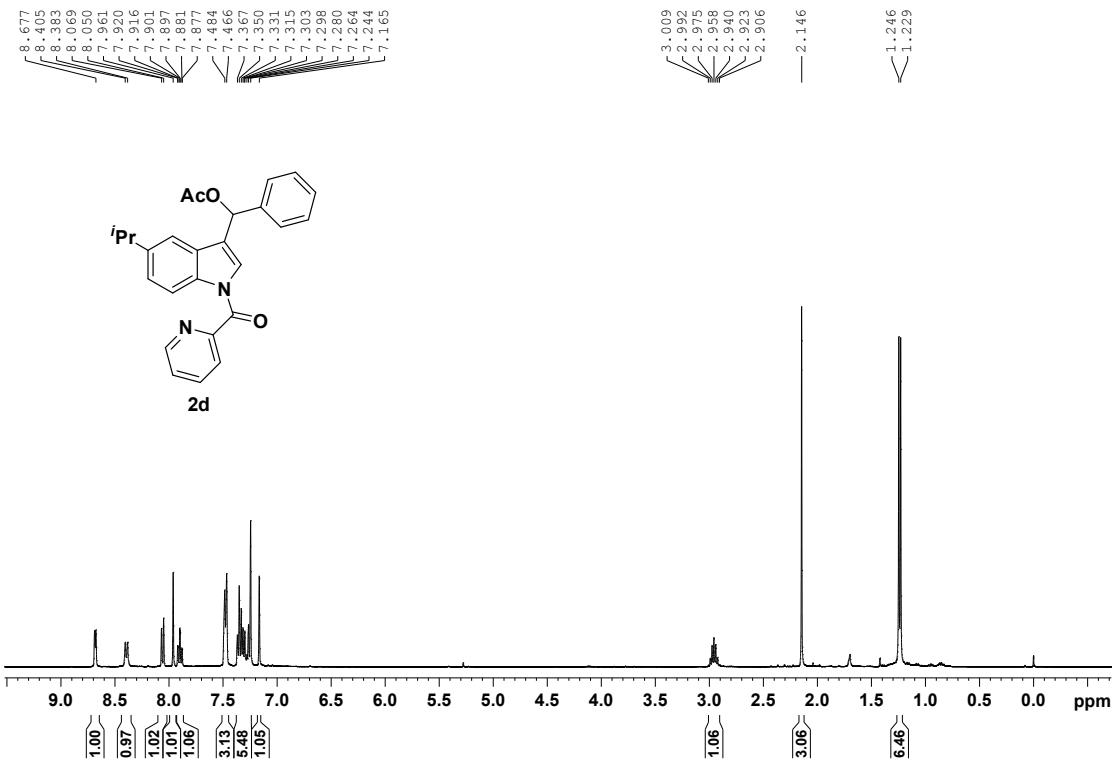
N
O
iPr
1d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.920
7.916
7.901
7.897
7.881
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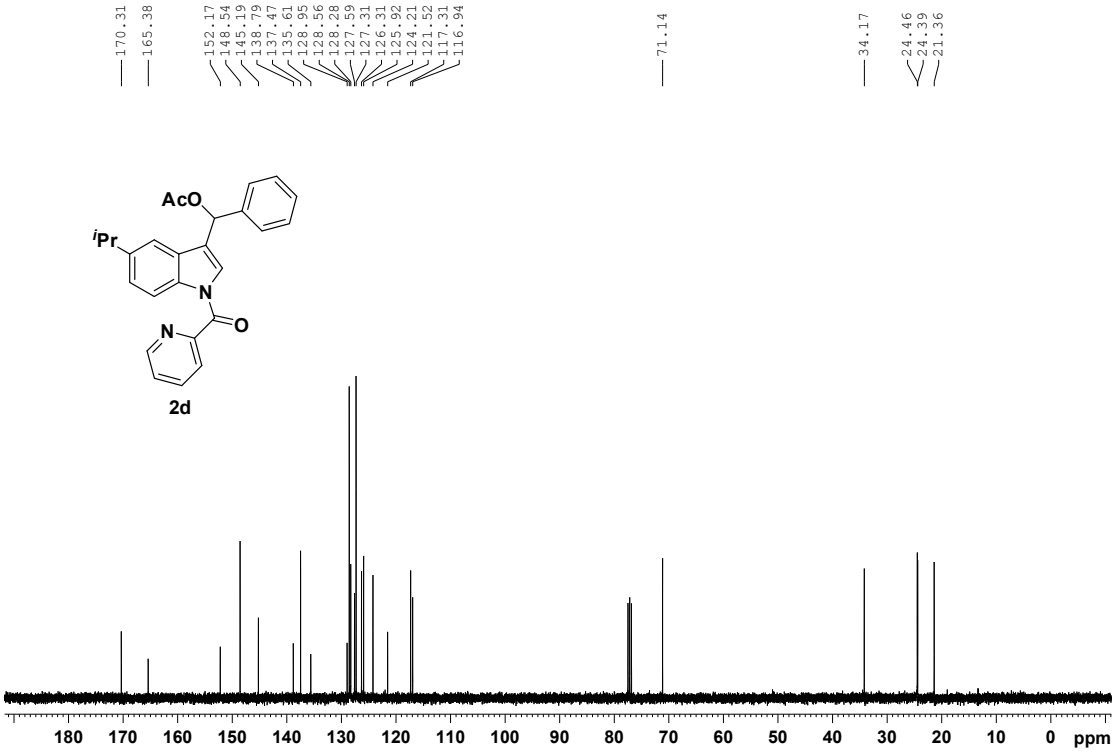
7.484
7.466
7.367
7.350
7.331
7.315
7.303
7.298
7.280
7.264
7.244
7.165
3.009
2.992
2.975
2.958
2.940
2.923
2.906
2.146
1.246
1.229
AcO
iPr
N
N
O
2d
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.97
1.02
1.01
1.06
3.13
5.48
1.05
1.06
3.06
6.46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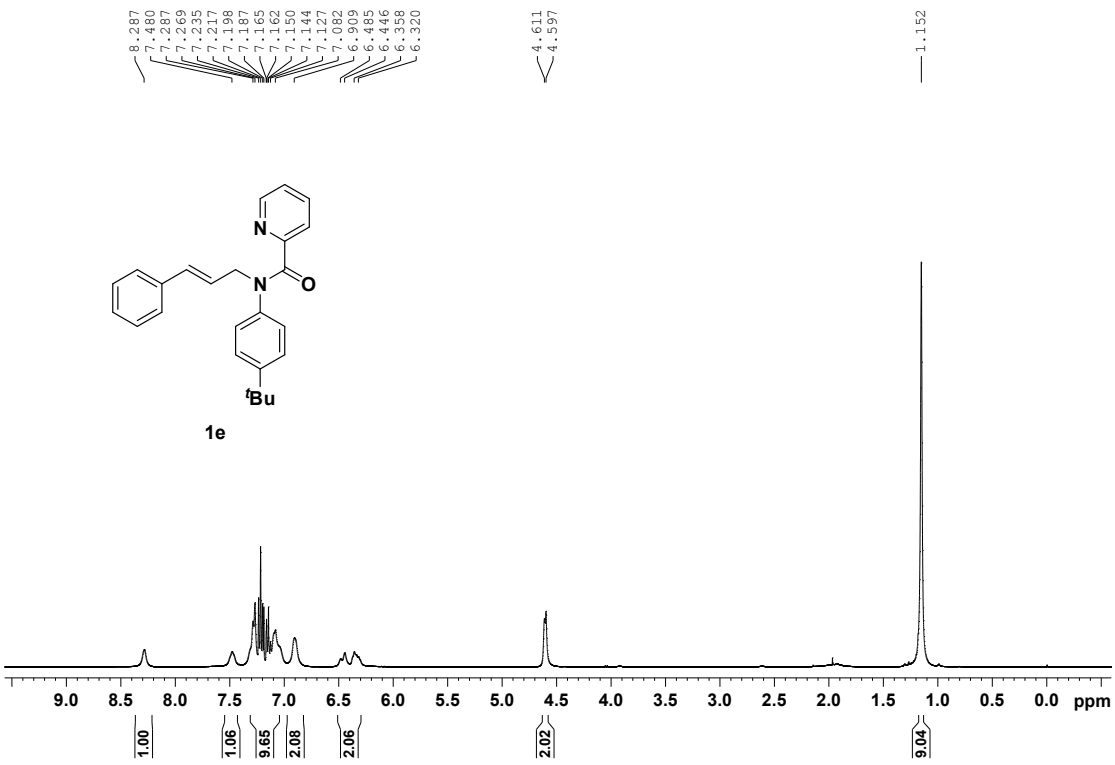
165.38
152.17
148.54
145.19
138.79
137.47
135.61
128.95
128.56
128.28
127.59
127.31
126.31
125.92
124.21
121.52
117.31
116.94
71.14
34.17
24.46
24.39
21.36
AcO
iPr
N
O
N
2d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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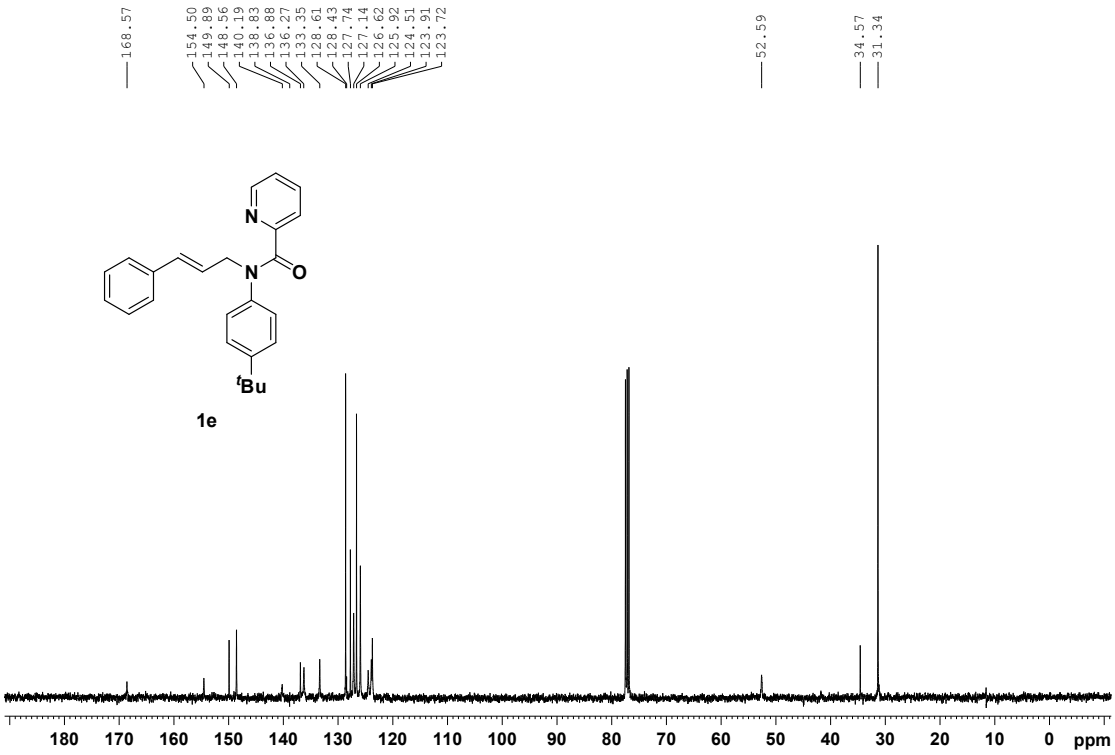
7.287
7.269
7.235
7.217
7.198
7.187
7.165
7.162
7.150
7.144
7.127
7.082
6.909
6.485
6.446
6.358
6.320
4.611
4.597
1.152
N
N
O
tBu
1e
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.06
9.65
2.08
2.06
2.02
9.04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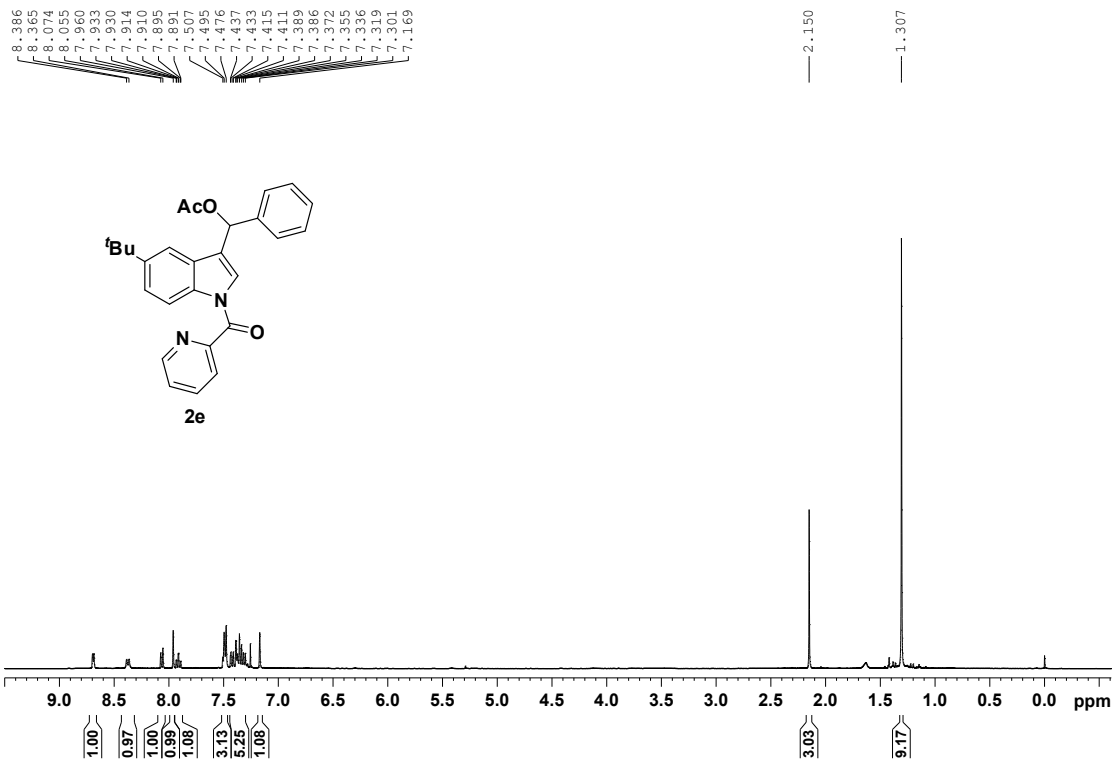
154.50
149.89
148.56
140.19
138.83
136.88
136.27
133.35
128.61
128.43
127.74
127.14
126.62
125.92
124.51
123.91
123.72
52.59
34.57
31.34
N
N
O
tBu
1e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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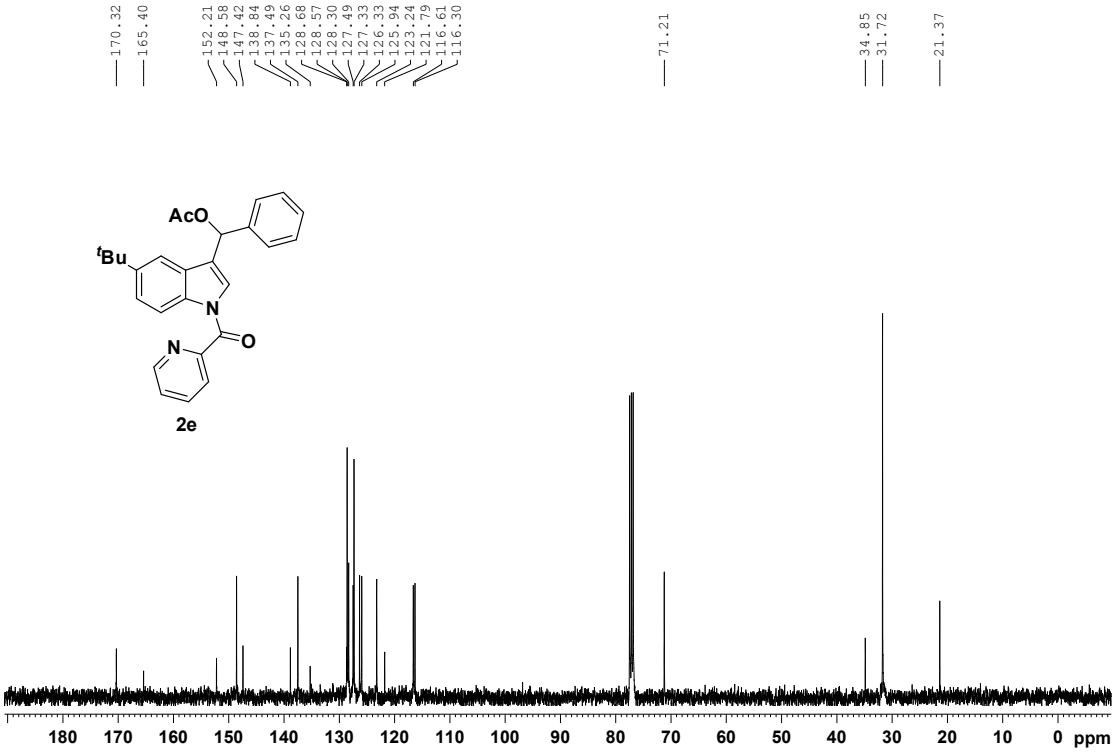
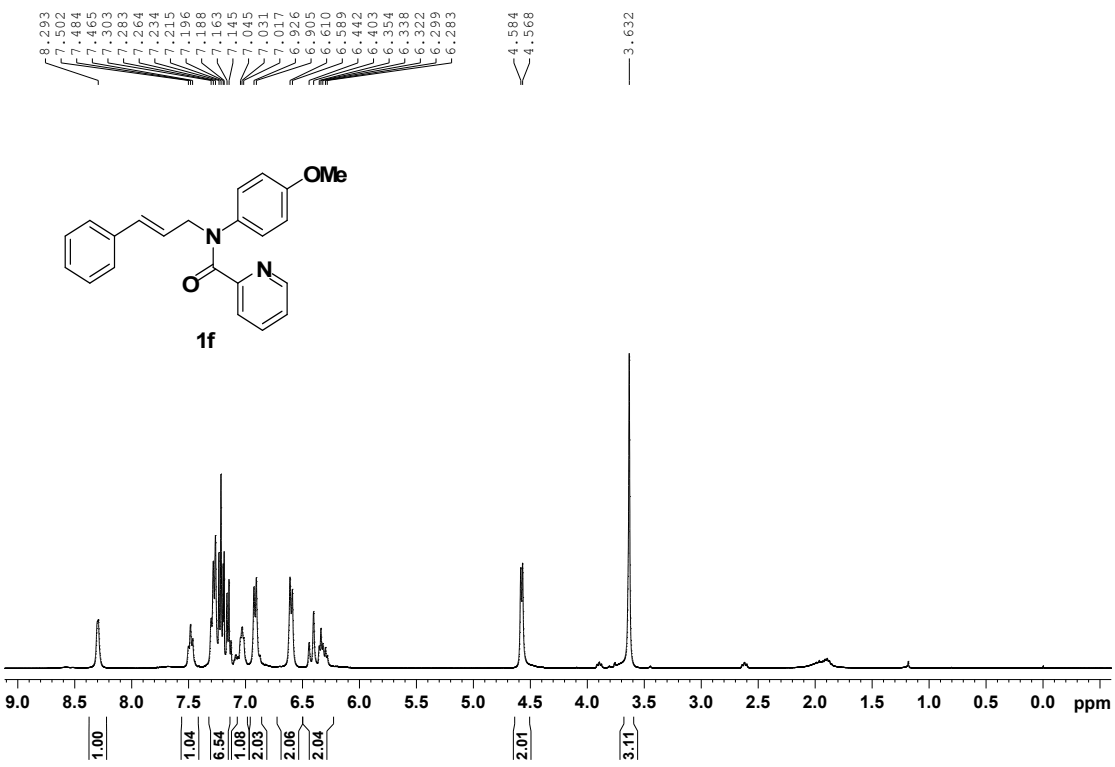
8.365
8.074
8.055
7.960
7.933
7.930
7.914
7.910
7.895
7.891
7.507
7.495
7.476
7.437
7.433
7.415
7.411
7.389
7.386
7.372
7.355
7.336
7.319
7.301
7.169
2.150
1.307
AcO
tBu
N
N
O
2e
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.97
1.00
0.99
1.08
3.13
5.25
1.08
3.03
9.17


170.32
165.40
152.21
148.58
147.42
138.84
137.49
135.26
128.68
128.57
128.30
127.49
127.33
126.33
125.94
123.24
121.79
116.61
116.30
71.21
34.85
31.72
21.37
AcO
tBu
N
O
N
2e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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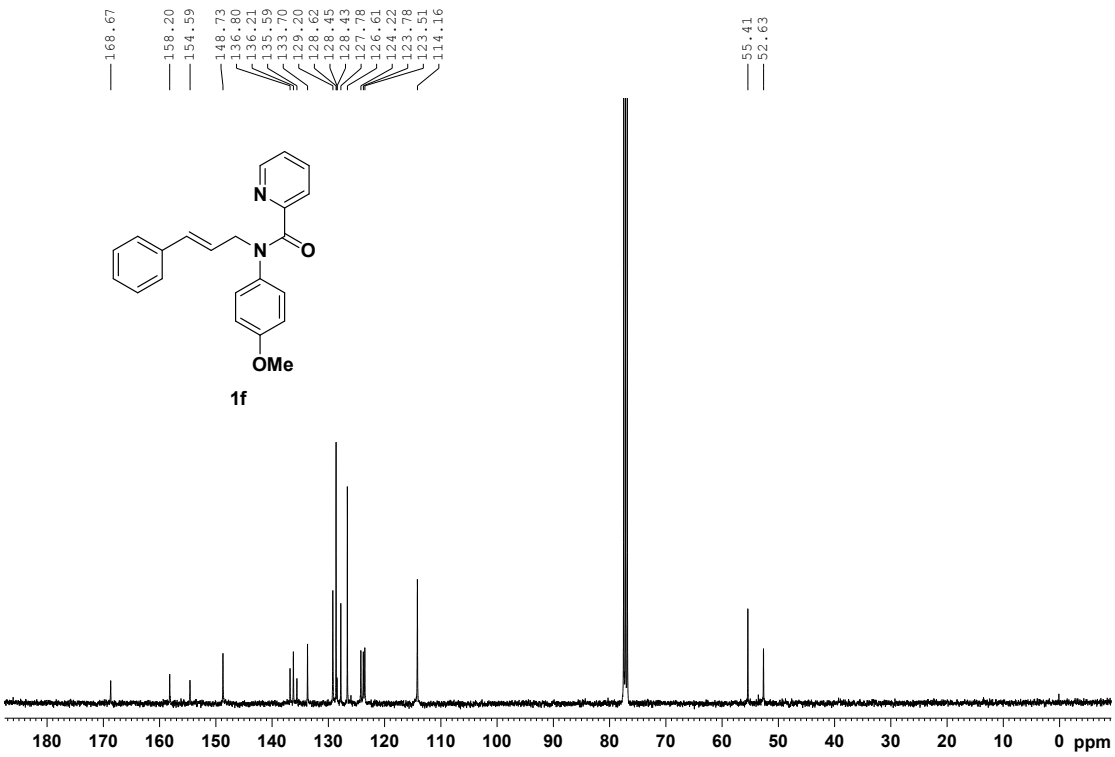
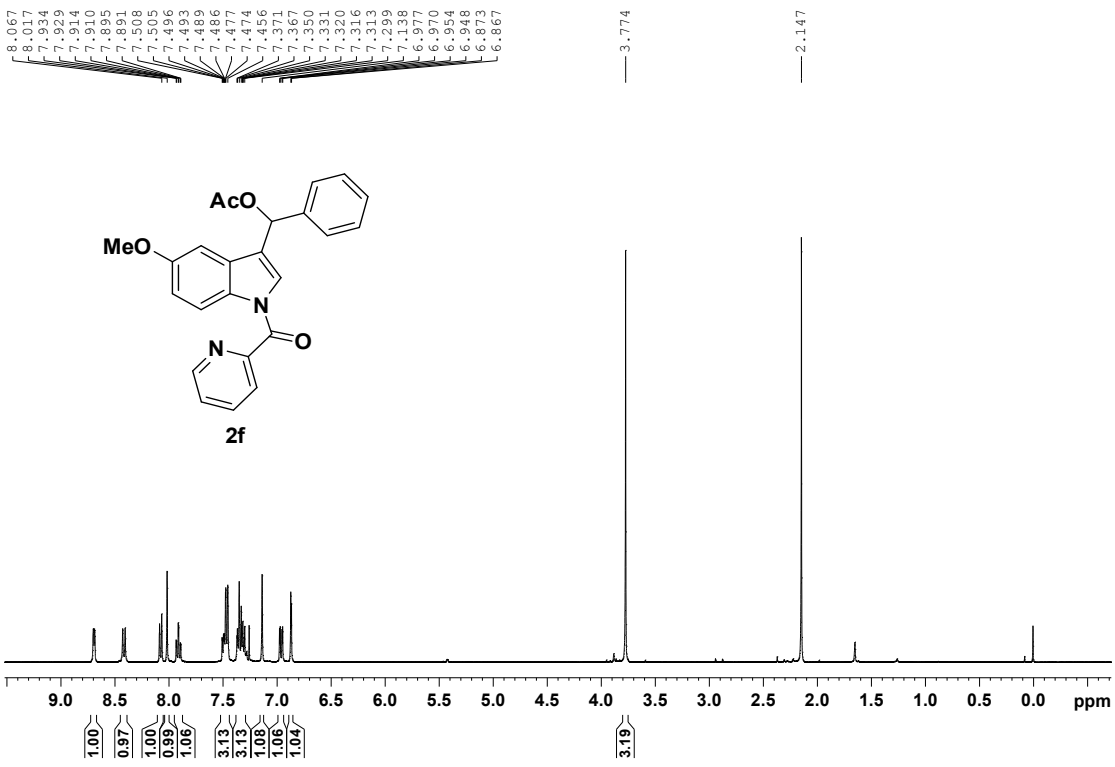
7.502
7.484
7.465
7.303
7.283
7.264
7.234
7.215
7.196
7.188
7.163
7.145
7.045
7.031
7.017
6.926
6.905
6.610
6.589
6.442
6.403
6.354
6.338
6.322
6.299
6.283
4.584
4.568
3.632
OMe
N
O
N
1f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.04
6.54
1.08
2.03
2.06
2.04
2.01
3.11


168.67
158.20
154.59
148.73
136.80
136.21
135.59
133.70
129.20
128.62
128.45
128.43
127.78
126.61
124.22
123.78
123.51
114.16
55.41
52.63
N
N
O
OMe
1f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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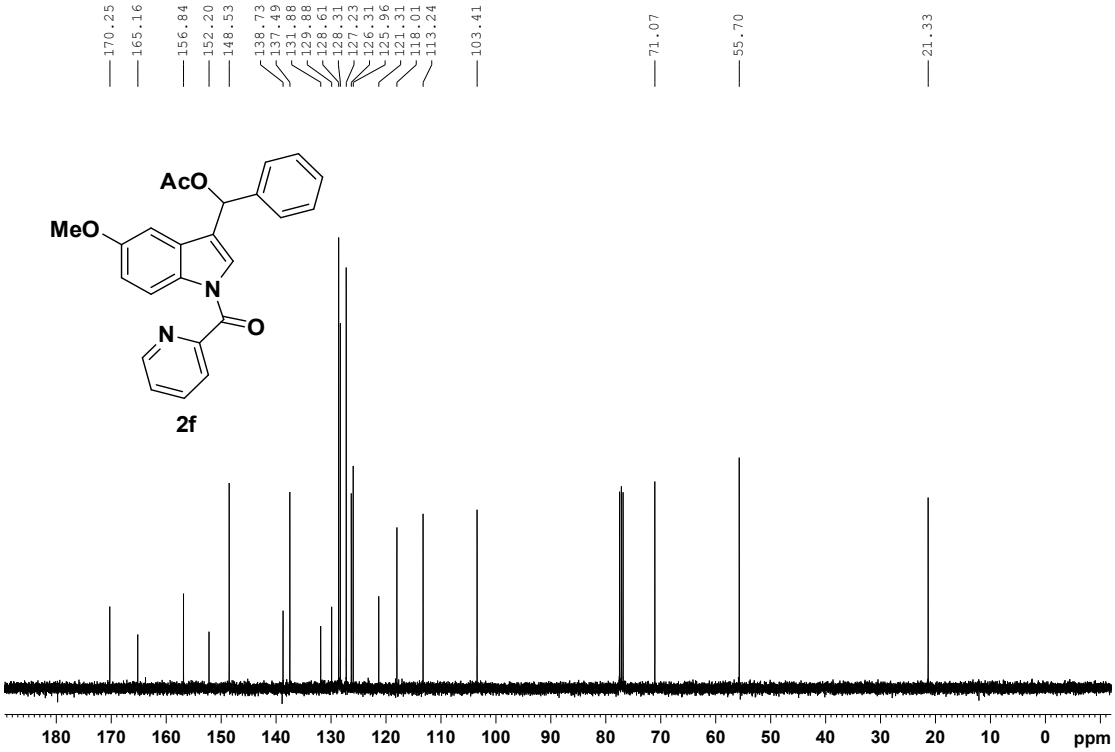
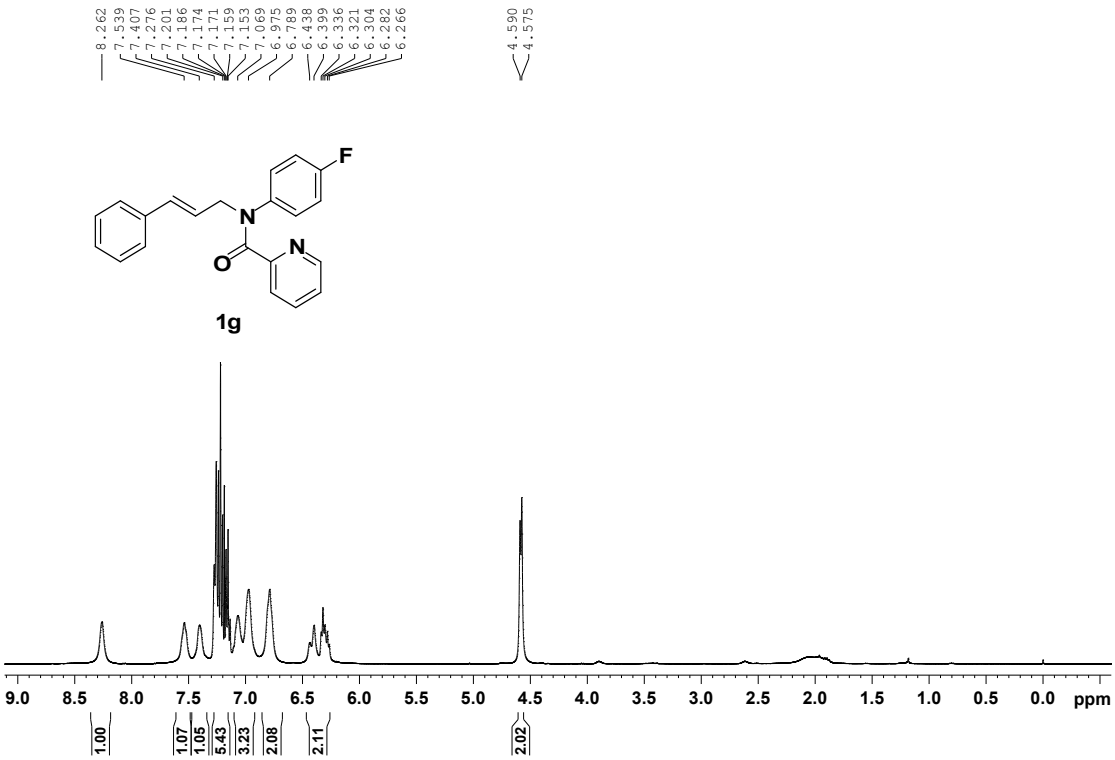
8.017
7.934
7.929
7.914
7.910
7.895
7.891
7.508
7.505
7.496
7.493
7.489
7.486
7.477
7.474
7.456
7.371
7.367
7.350
7.331
7.320
7.316
7.313
7.299
7.138
6.977
6.970
6.954
6.948
6.873
6.867
3.774
2.147
AcO
MeO
N
N
O
2f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.97
1.00
0.99
1.06
3.13
3.13
1.08
1.06
1.04
3.19


170.25
165.16
156.84
152.20
148.53
138.73
137.49
131.88
129.88
128.61
128.31
127.23
126.31
125.96
121.31
118.01
113.24
103.41
71.07
55.70
21.33
AcO
MeO
N
O
N
2f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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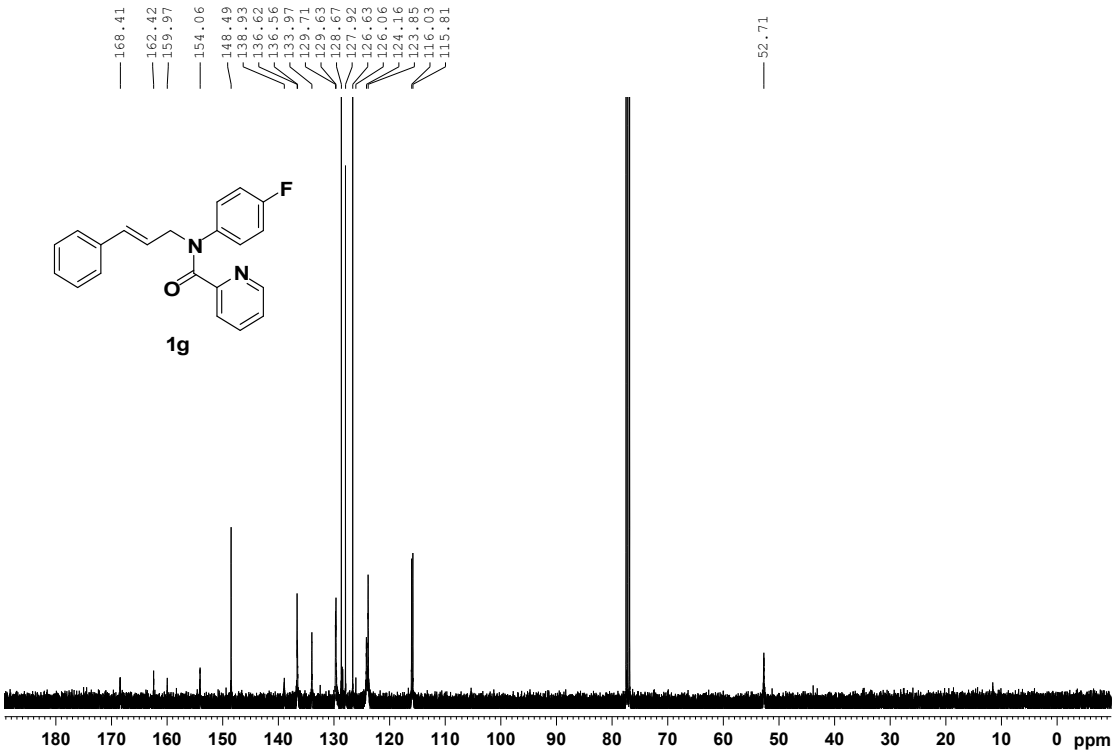
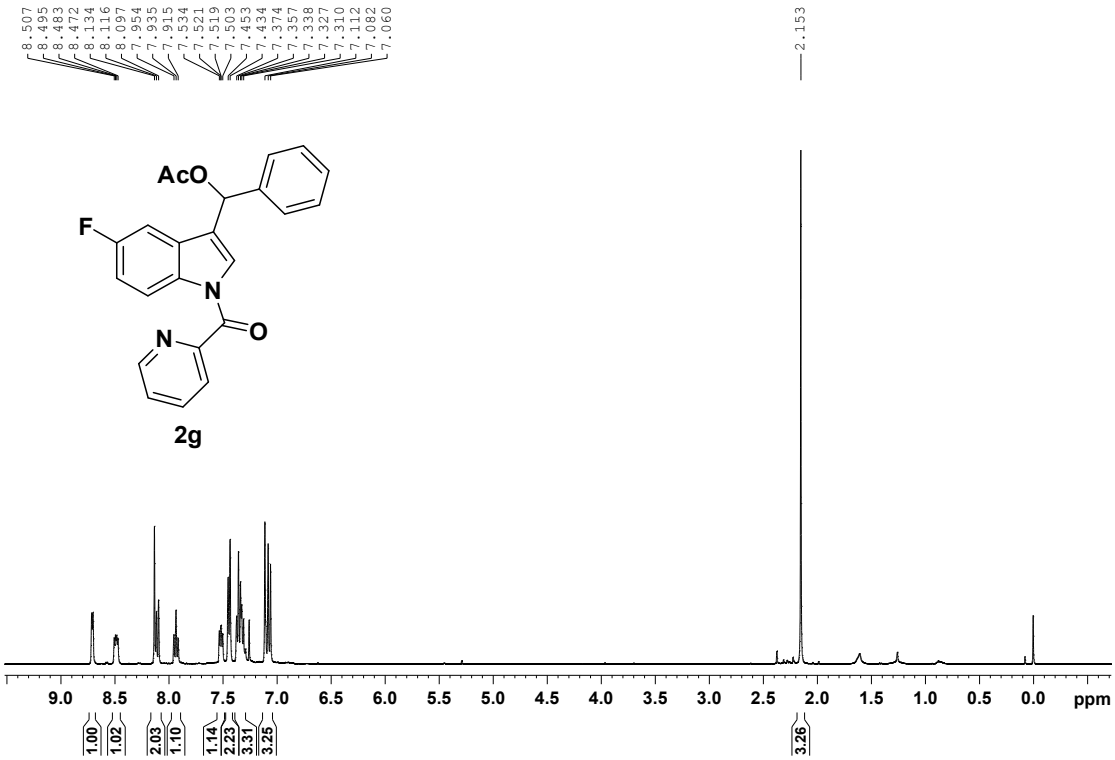
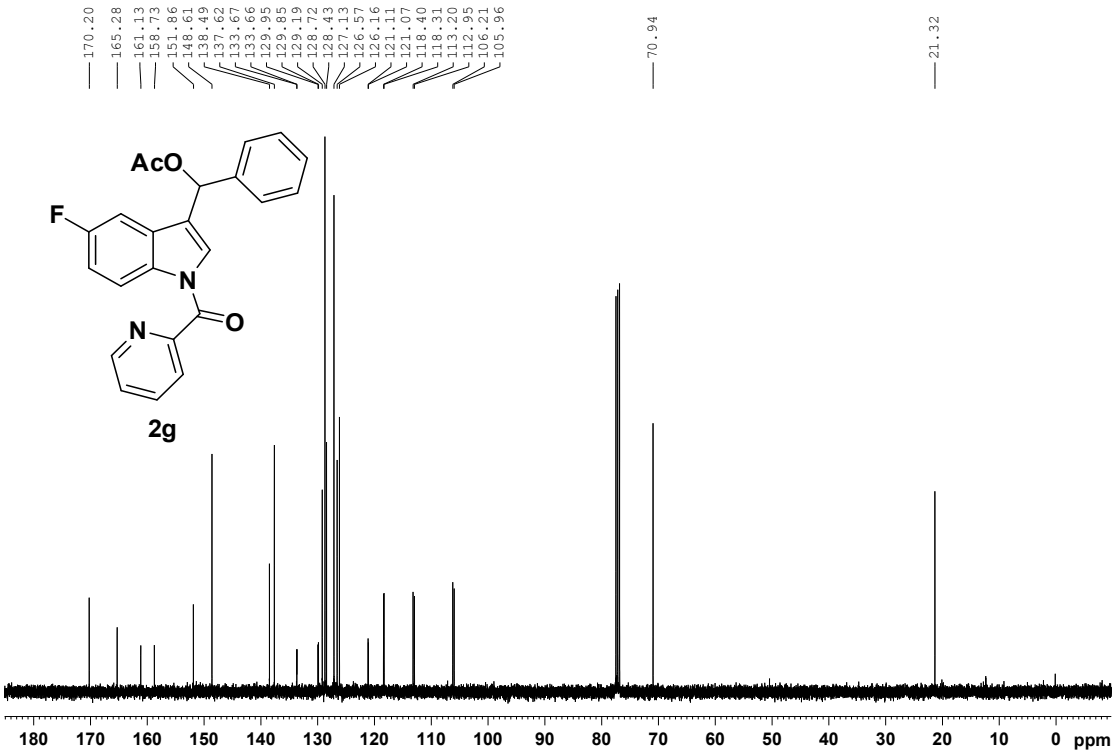
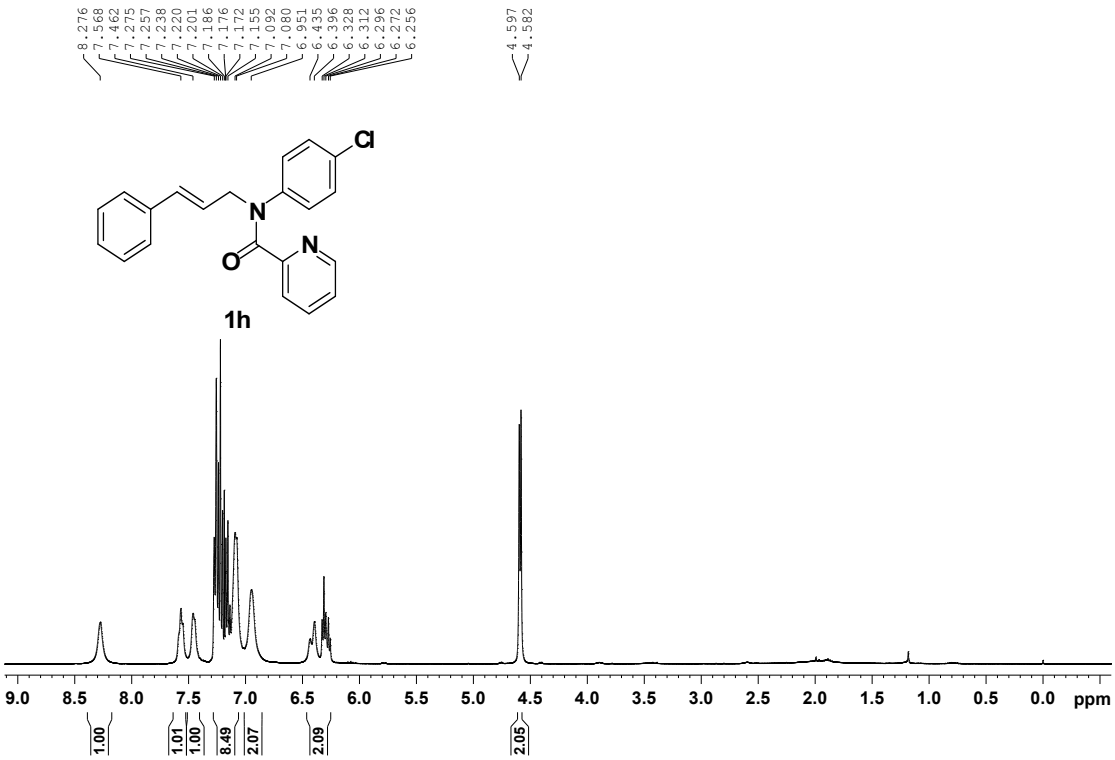
7.539
7.407
7.276
7.201
7.186
7.174
7.171
7.159
7.153
7.069
6.975
6.789
6.438
6.399
6.336
6.321
6.304
6.282
6.266
4.590
4.575
F
N
O
N
1g
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.07
1.05
5.43
3.23
2.08
2.11
2.02


168.41
162.42
159.97
154.06
148.49
138.93
136.62
136.56
133.97
129.71
129.63
128.67
127.92
126.63
126.06
124.16
123.85
116.03
115.81
52.71
F
N
O
N
1g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.507
8.495
8.483
8.472
8.134
8.116
8.097
7.954
7.935
7.915
7.534
7.521
7.519
7.503
7.453
7.434
7.374
7.357
7.338
7.327
7.310
7.112
7.082
7.060
2.153
AcO
F
N
N
O
2g
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
2.03
1.10
1.14
2.23
3.31
3.25
3.26


170.20
165.28
161.13
158.73
151.86
148.61
138.49
137.62
133.67
133.66
129.95
129.85
129.19
128.72
128.43
127.13
126.57
126.16
121.11
121.07
118.40
118.31
113.20
112.95
106.21
105.96
70.94
21.32
AcO
F
N
O
N
2g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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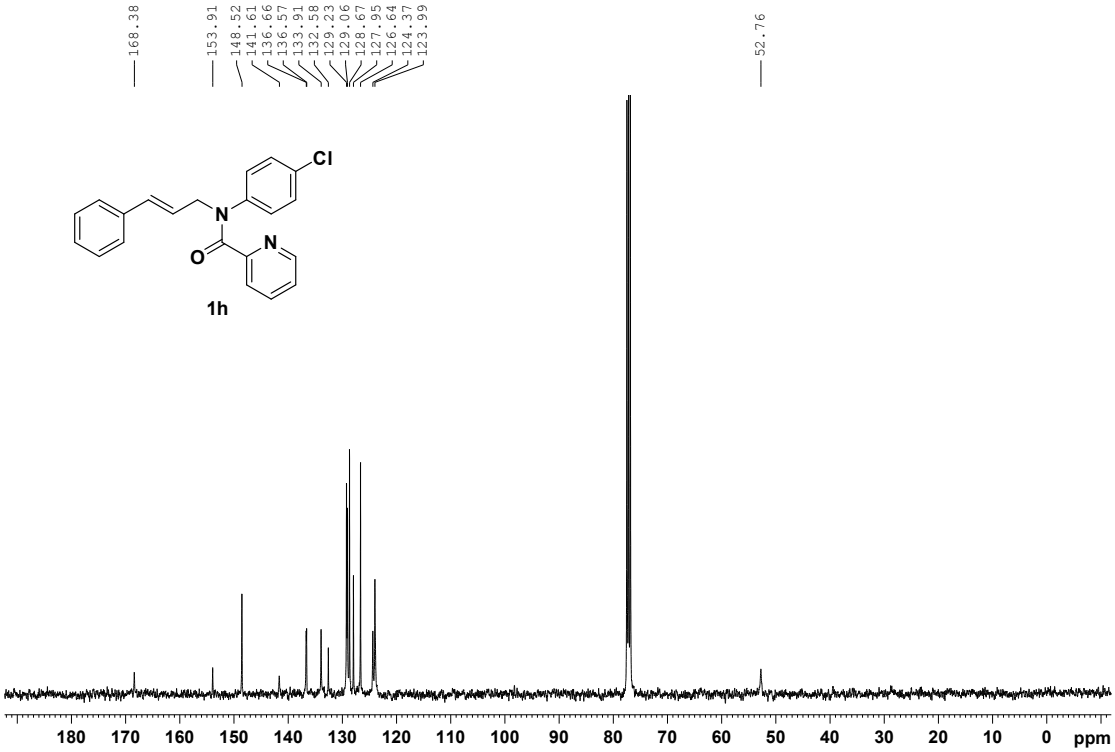
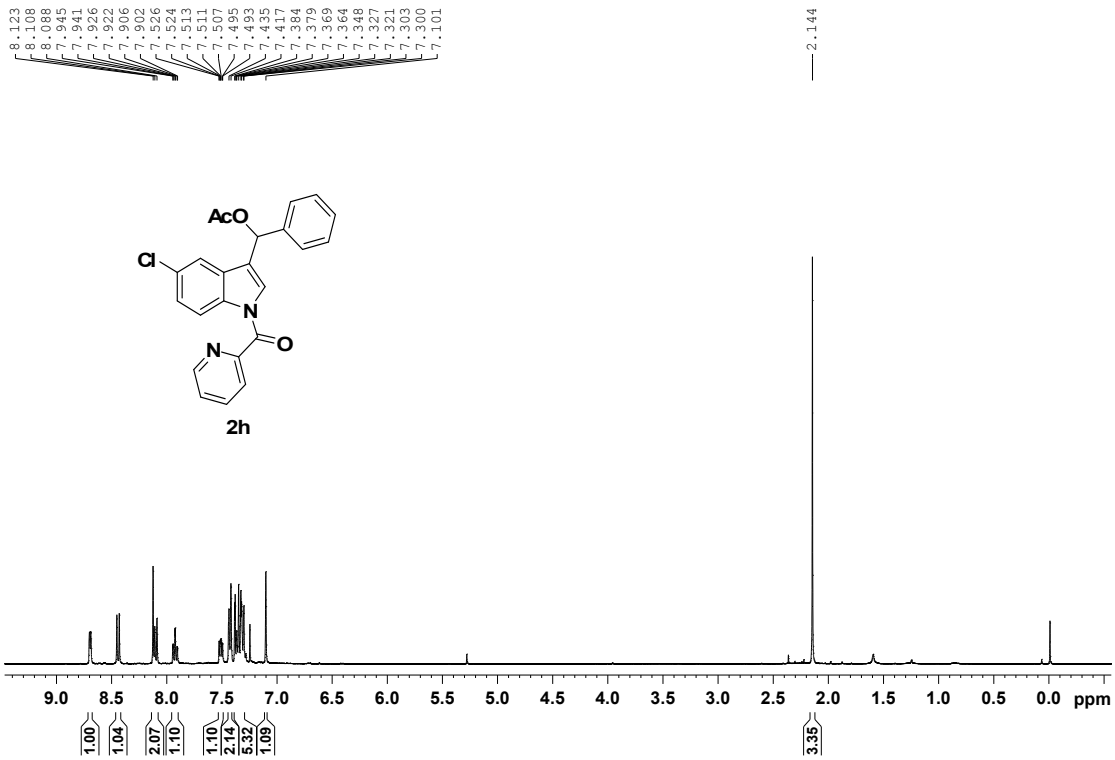
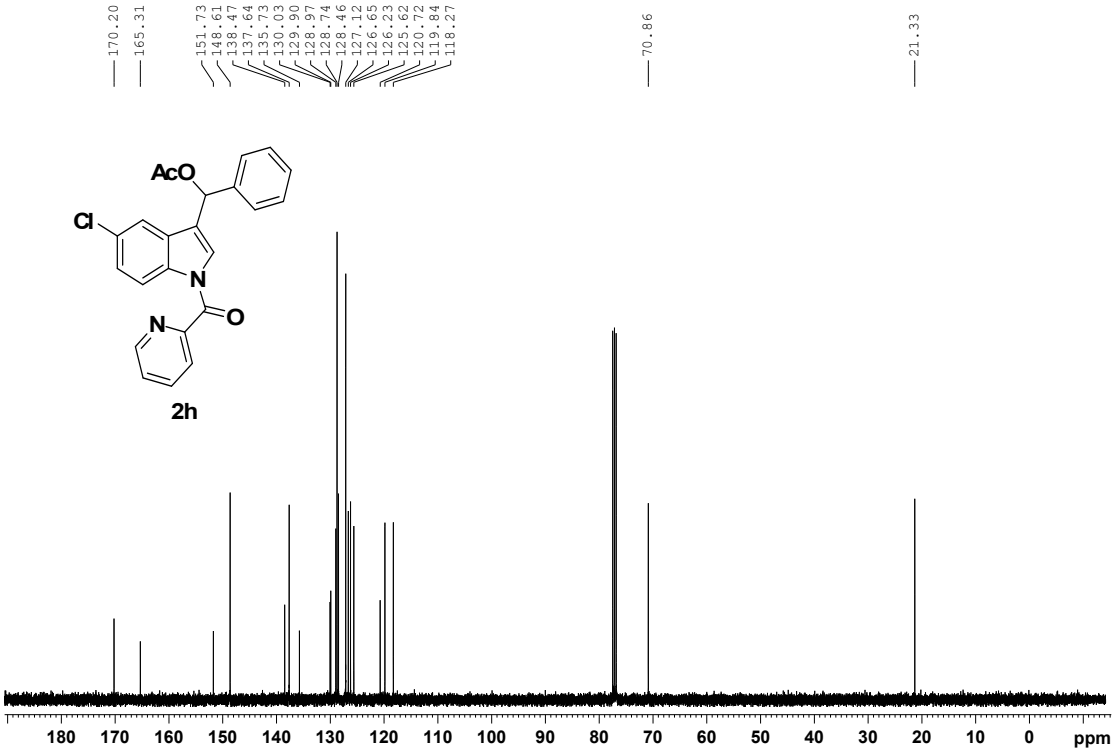
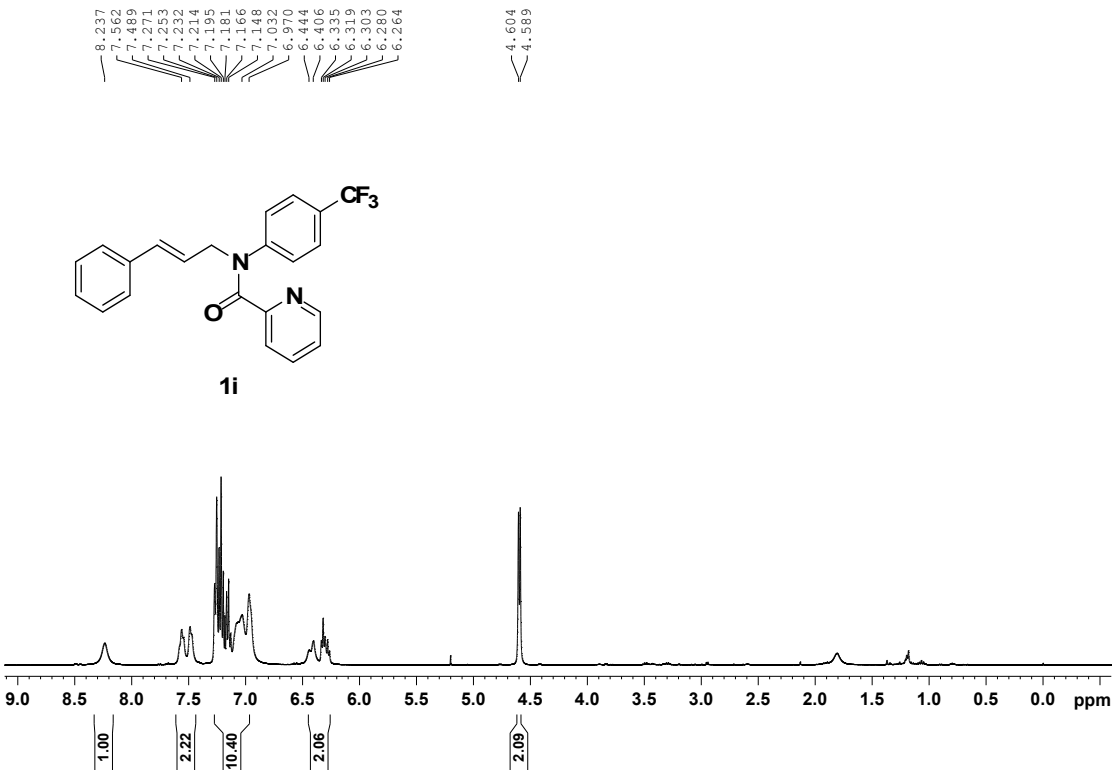
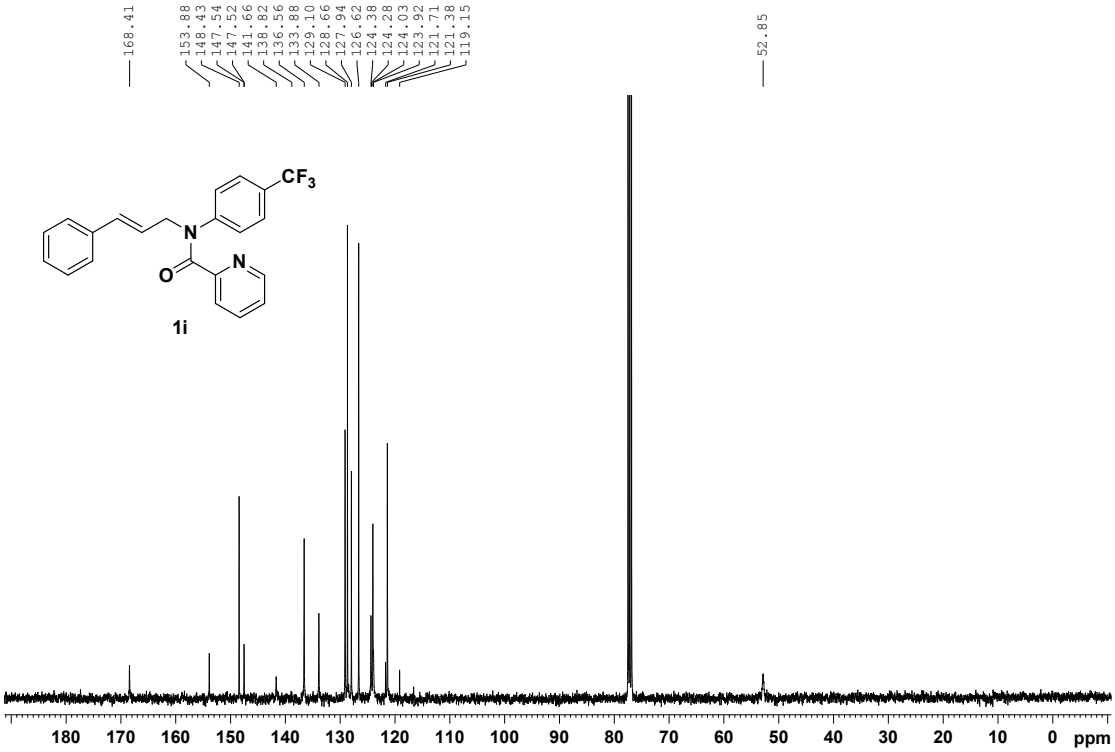
7.568
7.462
7.275
7.257
7.238
7.220
7.201
7.186
7.176
7.172
7.155
7.092
7.080
6.951
6.435
6.396
6.328
6.312
6.296
6.272
6.256
4.597
4.582
Cl
N
O
N
1h
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.01
1.00
8.49
2.07
2.09
2.05

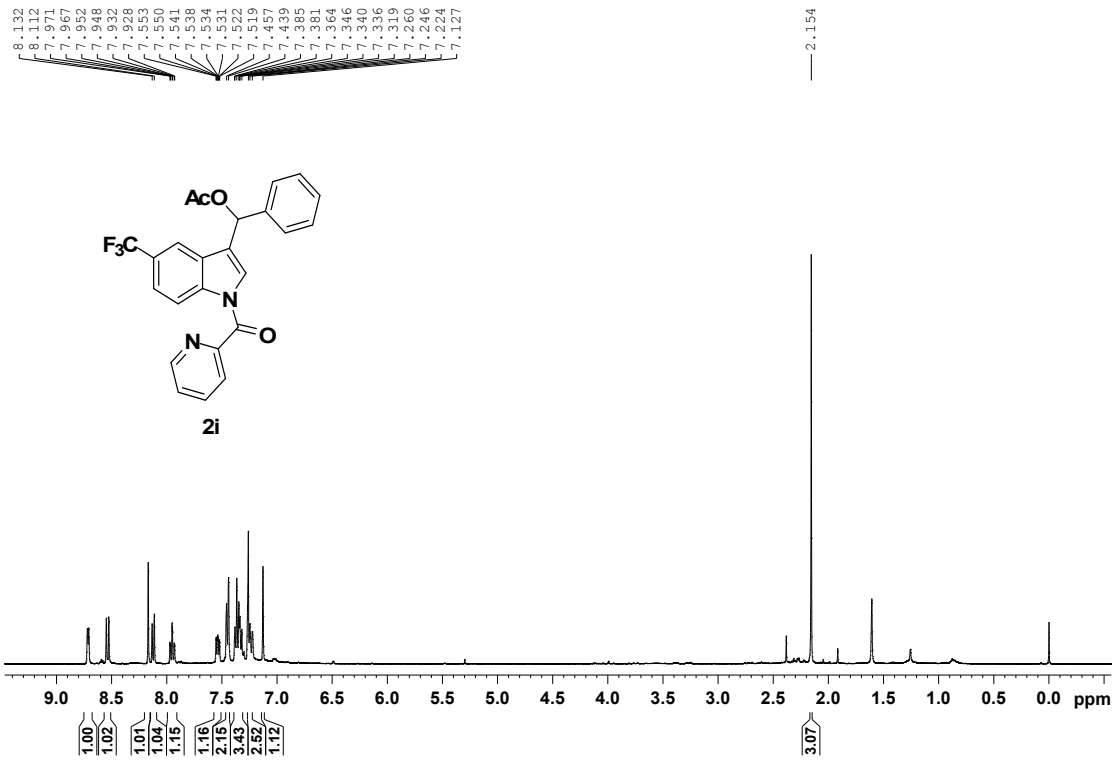

168.38
153.91
148.52
141.61
136.66
136.57
133.91
132.58
129.23
129.06
128.67
127.95
126.64
124.37
123.99
52.76
Cl
N
O
N
1h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

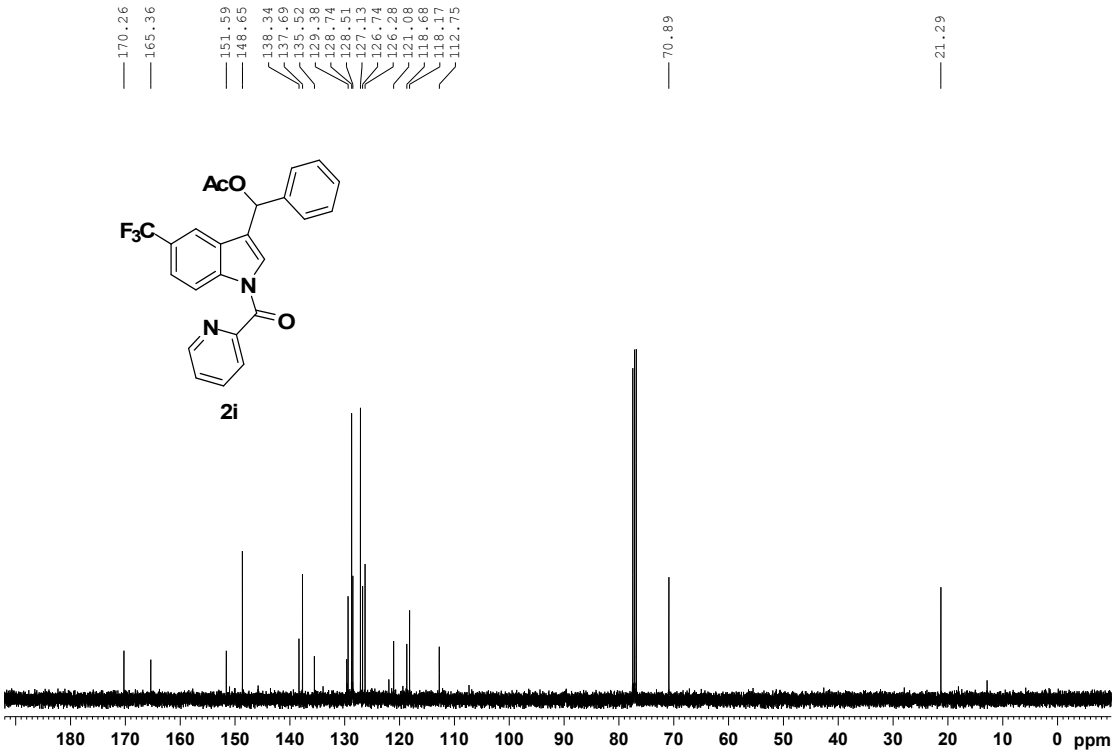

8.123
8.108
8.088
7.945
7.941
7.926
7.922
7.906
7.902
7.526
7.524
7.513
7.511
7.507
7.495
7.493
7.435
7.417
7.384
7.379
7.369
7.364
7.348
7.327
7.321
7.303
7.300
7.101
2.144
AcO
Cl
N
N
O
2h
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.04
2.07
1.10
1.10
2.14
5.32
1.09
3.35

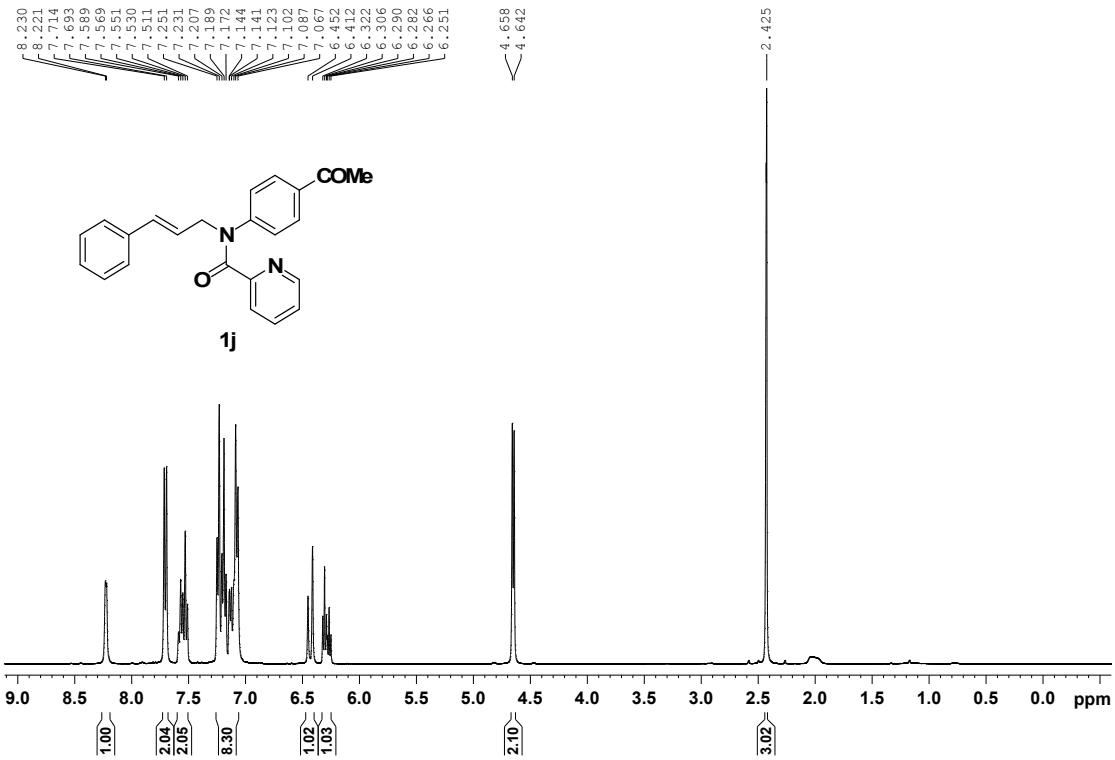

170.20
165.31
151.73
148.61
138.47
137.64
135.73
130.03
129.90
128.97
128.74
128.46
127.12
126.65
126.23
125.62
120.72
119.84
118.27
70.86
21.33
AcO
Cl
N
O
N
2h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

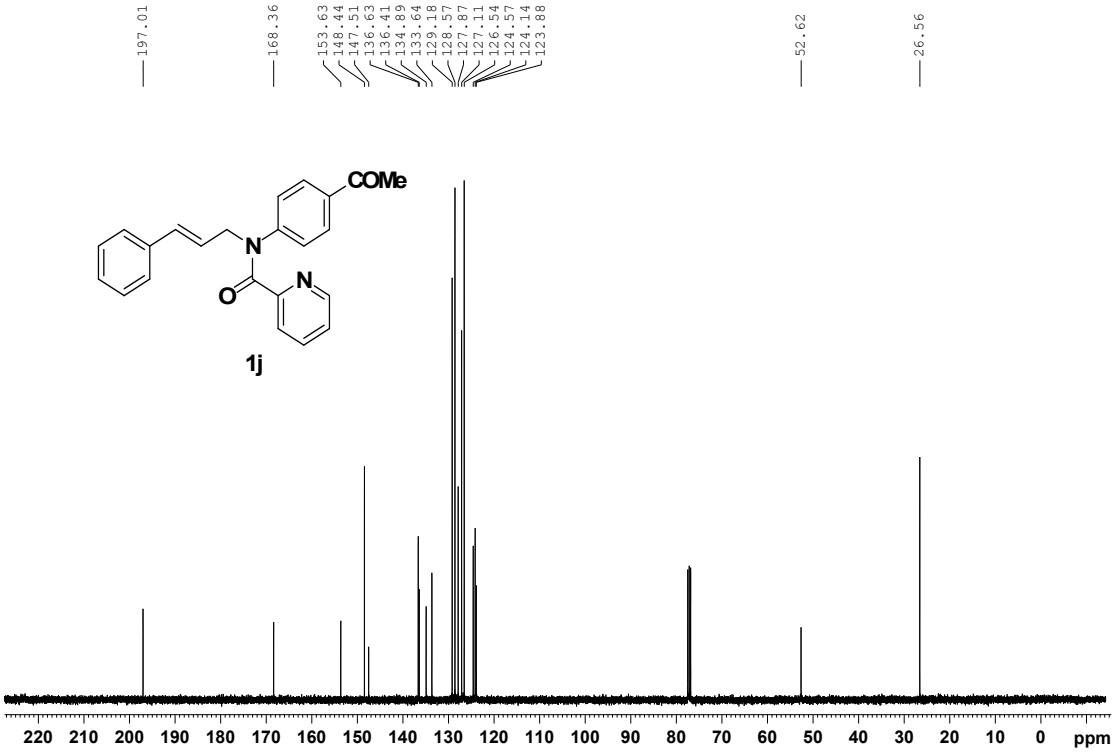

8.237
7.562
7.489
7.271
7.253
7.232
7.214
7.195
7.181
7.166
7.148
7.032
6.970
6.444
6.406
6.335
6.319
6.303
6.280
6.264
4.604
4.589
CF3
N
O
N
1i
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.22
10.40
2.06
2.09

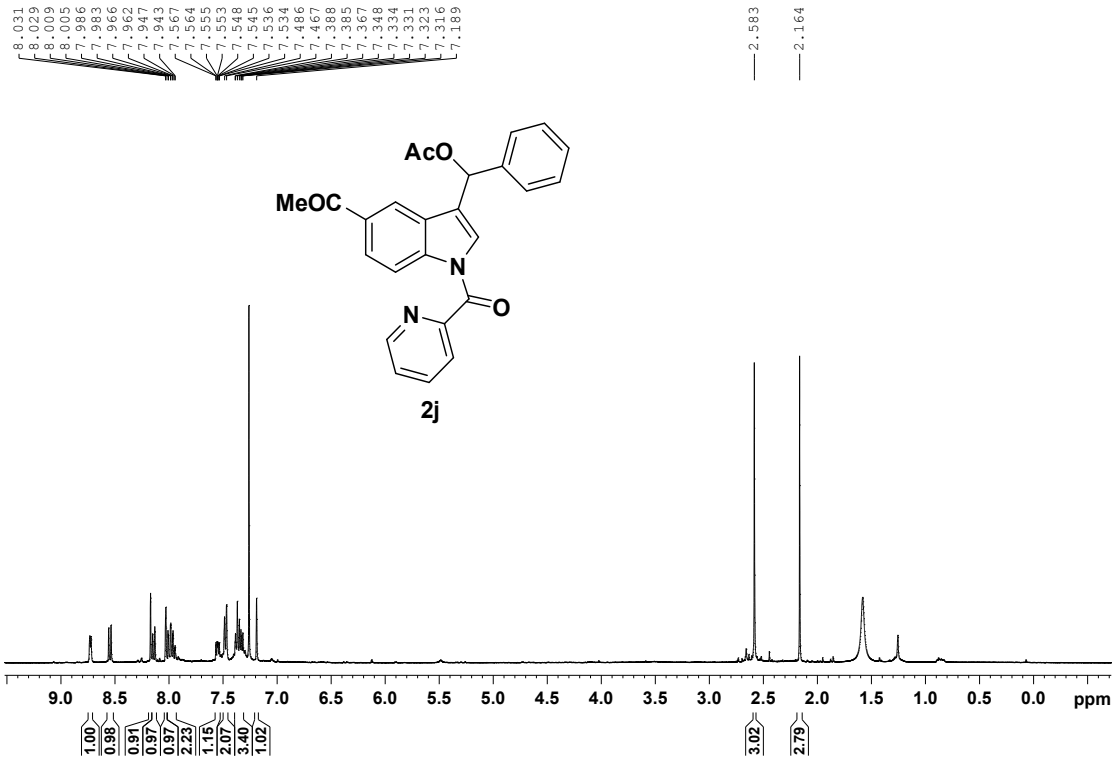

168.41
153.88
148.43
147.54
147.52
141.66
138.82
136.56
133.88
129.10
128.66
127.94
126.62
124.38
124.28
124.03
123.92
121.71
121.38
119.15
52.85
CF3
N
O
N
1i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

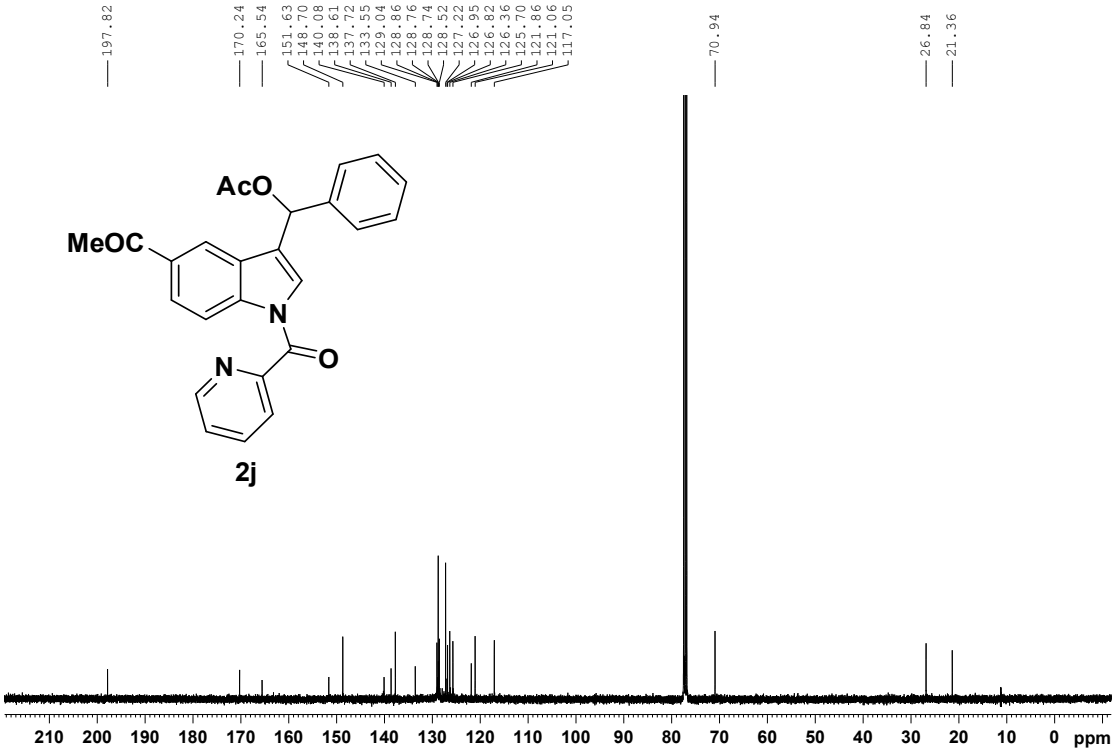

8.132
8.112
7.971
7.967
7.952
7.948
7.932
7.928
7.553
7.550
7.541
7.538
7.534
7.531
7.522
7.519
7.457
7.439
7.385
7.381
7.364
7.346
7.340
7.336
7.319
7.260
7.246
7.224
7.127
2.154
AcO
F3C
N
N
O
2i
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
1.01
1.04
1.15
1.16
2.15
3.43
2.52
1.12
3.07


170.26
165.36
151.59
148.65
138.34
137.69
135.52
129.38
128.74
128.51
127.13
126.74
126.28
121.08
118.68
118.17
112.75
70.89
21.29
AcO
F3C
N
O
N
2i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.230
8.221
7.714
7.693
7.589
7.569
7.551
7.530
7.511
7.251
7.231
7.207
7.189
7.172
7.144
7.141
7.123
7.102
7.087
7.067
6.452
6.412
6.322
6.306
6.290
6.282
6.266
6.251
4.658
4.642
2.425
COMe
N
O
N
1j
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.04
2.05
8.30
1.02
1.03
2.10
3.02


197.01
168.36
153.63
148.44
147.51
136.63
136.41
134.89
133.64
129.18
128.57
127.87
127.11
126.54
124.57
124.14
123.88
52.62
26.56
COMe
N
O
N
1j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.031
8.029
8.009
8.005
7.986
7.983
7.966
7.962
7.947
7.943
7.567
7.564
7.555
7.553
7.548
7.545
7.536
7.534
7.486
7.467
7.388
7.385
7.367
7.348
7.334
7.331
7.323
7.316
7.189
2.583
2.164
AcO
MeOC
N
N
O
2j
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.98
0.91
0.97
0.97
2.23
1.15
2.07
3.40
1.02
3.02
2.79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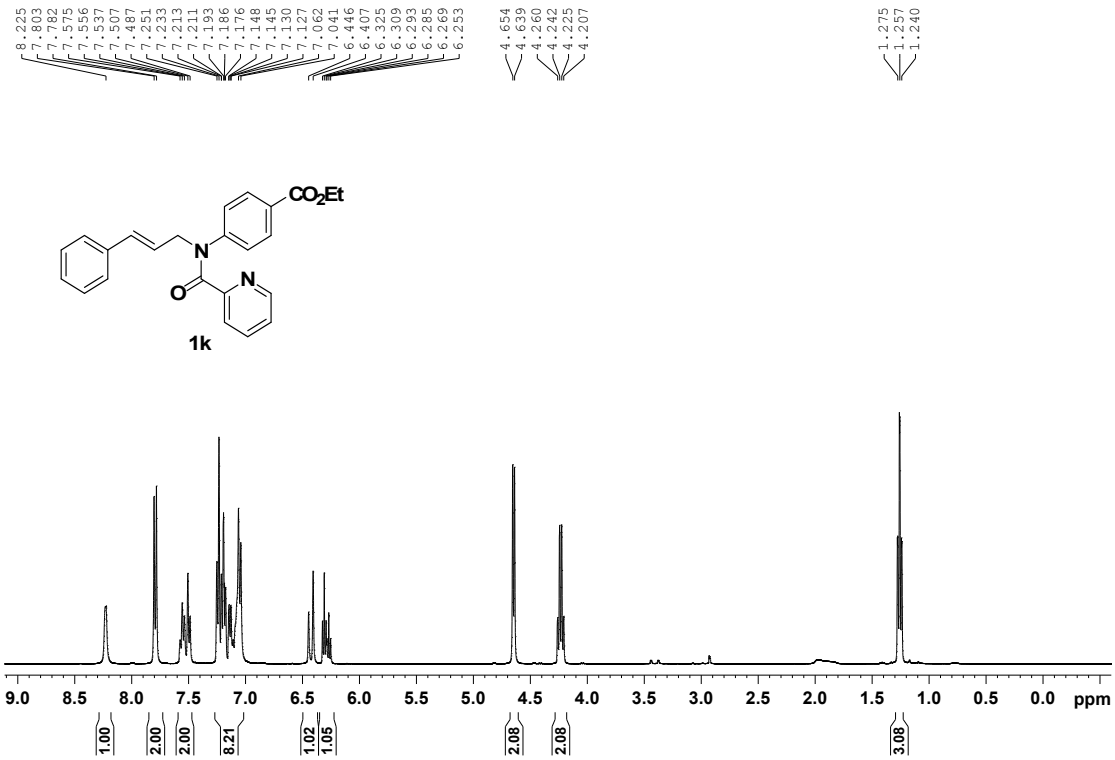
170.24
165.54
151.63
148.70
140.08
138.61
137.72
133.55
129.04
128.86
128.76
128.74
128.52
127.22
126.95
126.82
126.36
125.70
121.86
121.06
117.05
70.94
26.84
21.36
AcO
MeOC
N
N
O
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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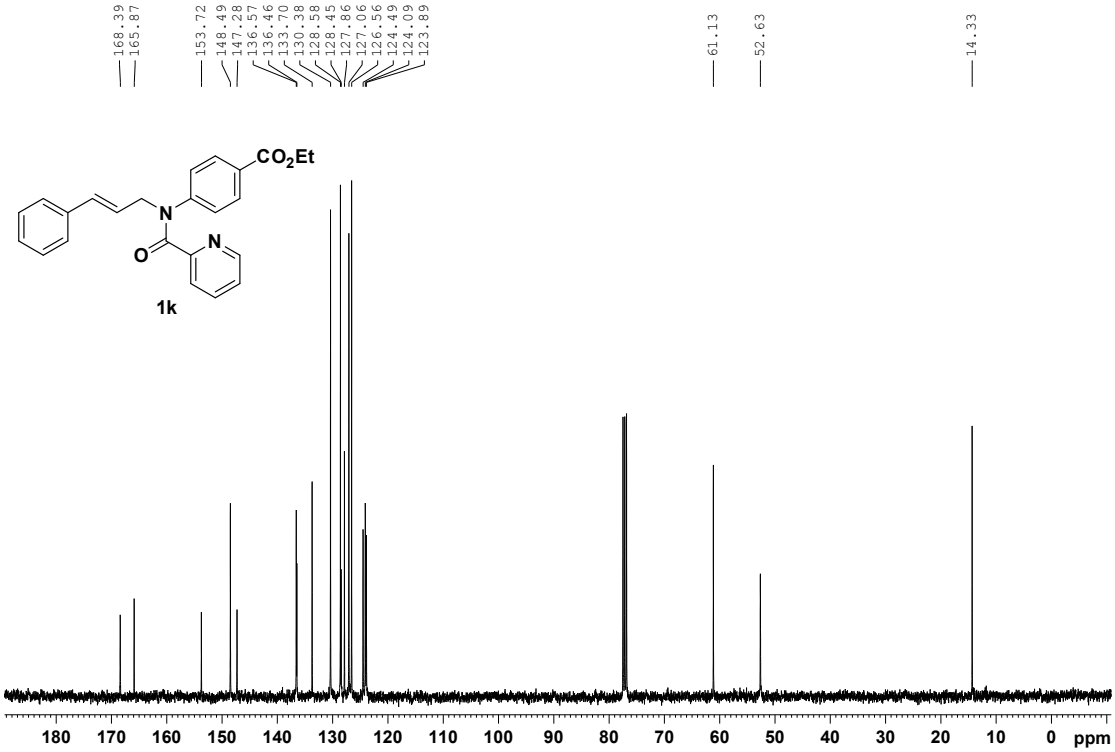
7.803
7.782
7.575
7.556
7.537
7.507
7.487
7.251
7.233
7.213
7.211
7.193
7.186
7.176
7.148
7.145
7.130
7.127
7.062
7.041
6.446
6.407
6.325
6.309
6.293
6.285
6.269
6.253
4.654
4.639
4.260
4.242
4.225
4.207
1.275
1.257
1.240
CO2Et
N
O
N
1k
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.00
2.00
8.21
1.02
1.05
2.08
2.08
3.08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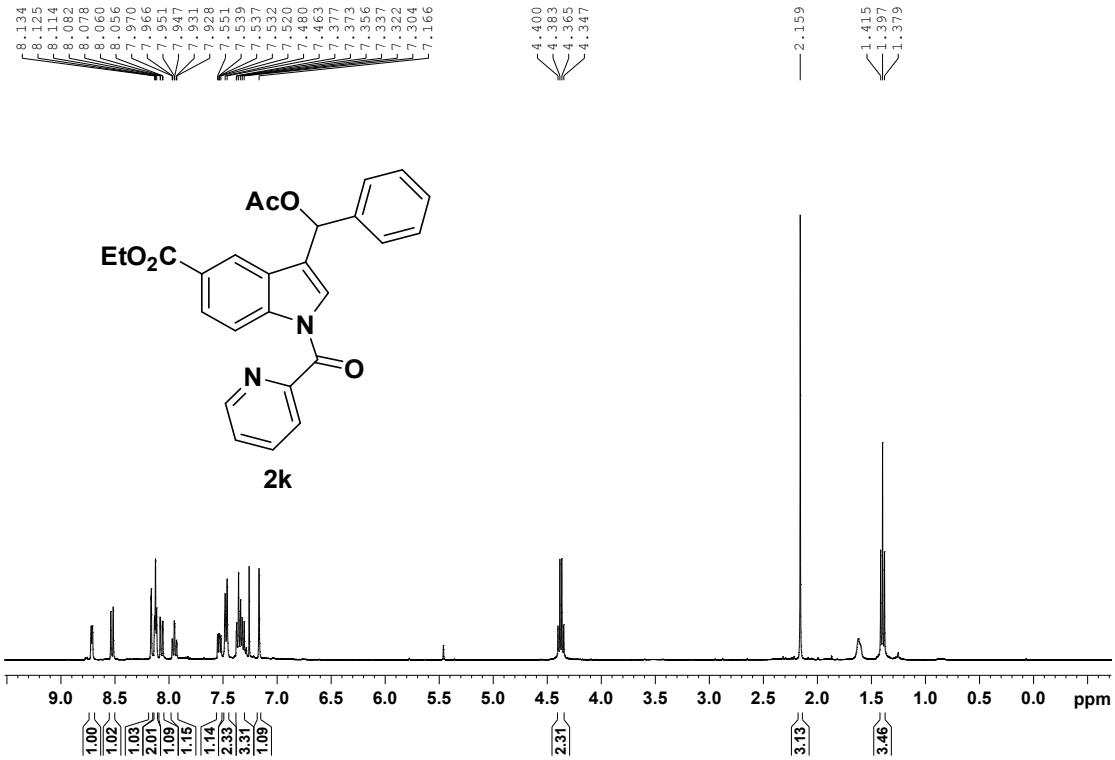
165.87
153.72
148.49
147.28
136.57
136.46
133.70
130.38
128.58
128.45
127.86
127.06
126.56
124.49
124.09
123.89
61.13
52.63
14.33
CO2Et
N
O
N
1k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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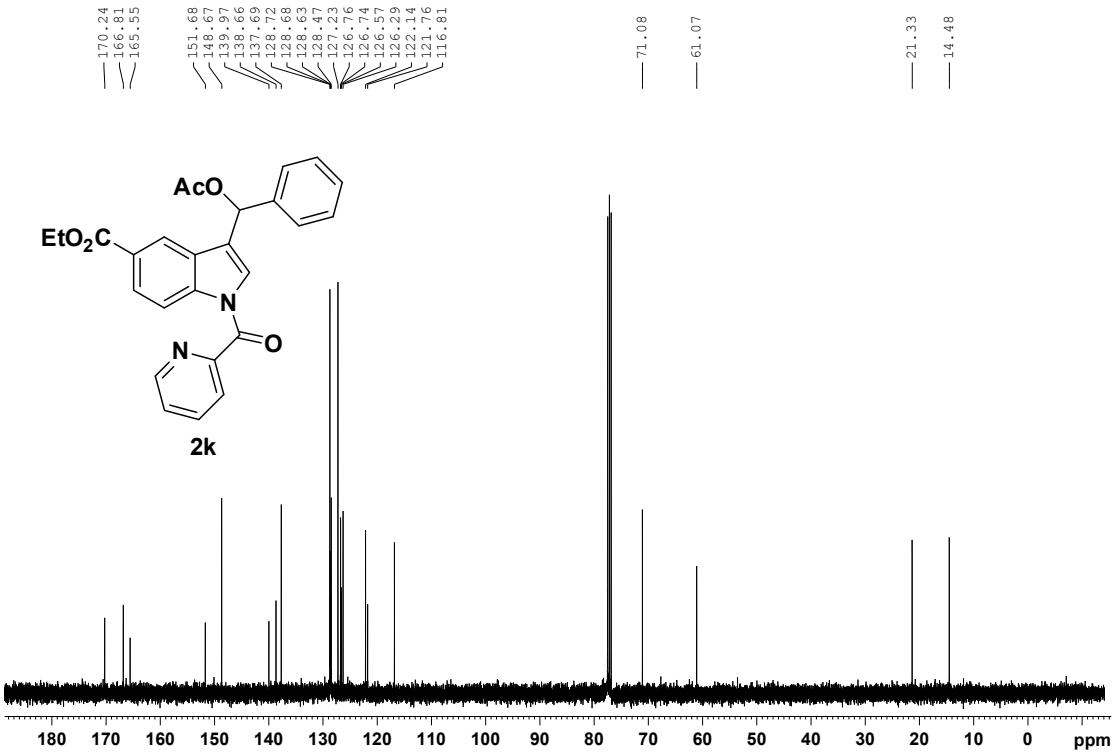
8.125
8.114
8.082
8.078
8.060
8.056
7.970
7.966
7.951
7.947
7.931
7.928
7.551
7.539
7.537
7.532
7.520
7.480
7.463
7.377
7.373
7.356
7.337
7.322
7.304
7.166
4.400
4.383
4.365
4.347
2.159
1.415
1.397
1.379
AcO
EtO2C
N
N
O
2k
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
1.03
2.01
1.09
1.15
1.14
2.33
3.31
1.09
2.31
3.13
3.46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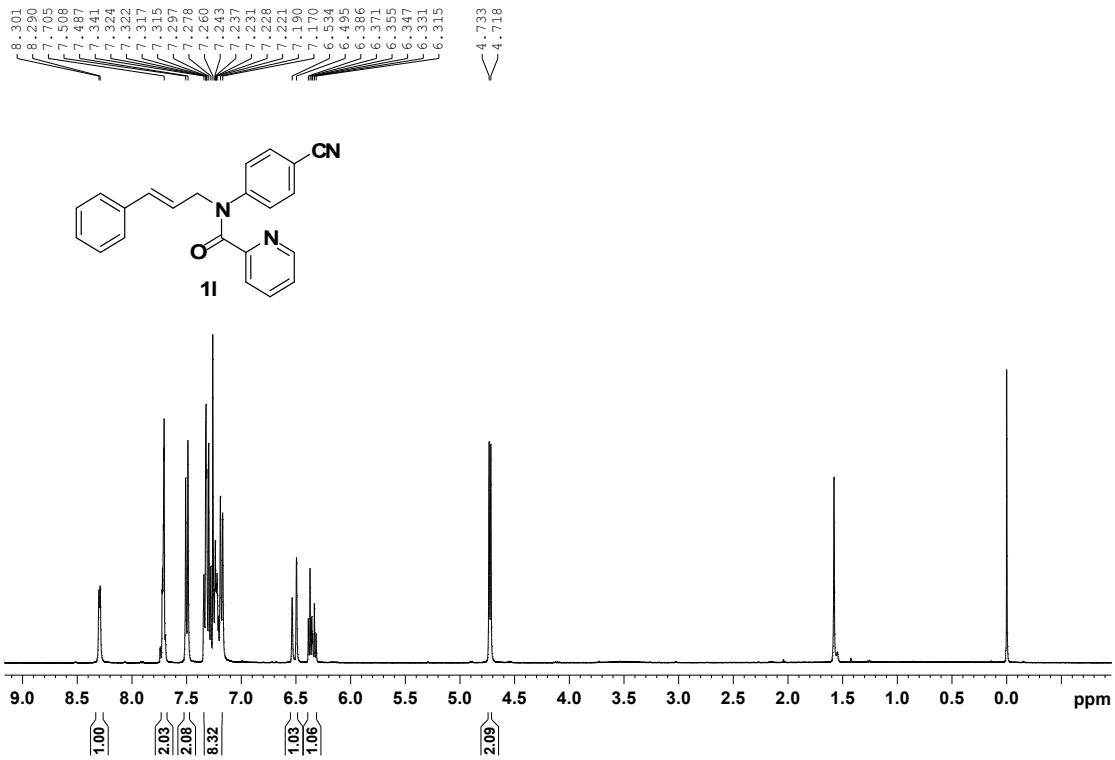
166.81
165.55
151.68
148.67
139.97
138.66
137.69
128.72
128.68
128.63
128.47
127.23
126.76
126.74
126.57
126.29
122.14
121.76
116.81
71.08
61.07
21.33
14.48
AcO
EtO2C
N
O
N
2k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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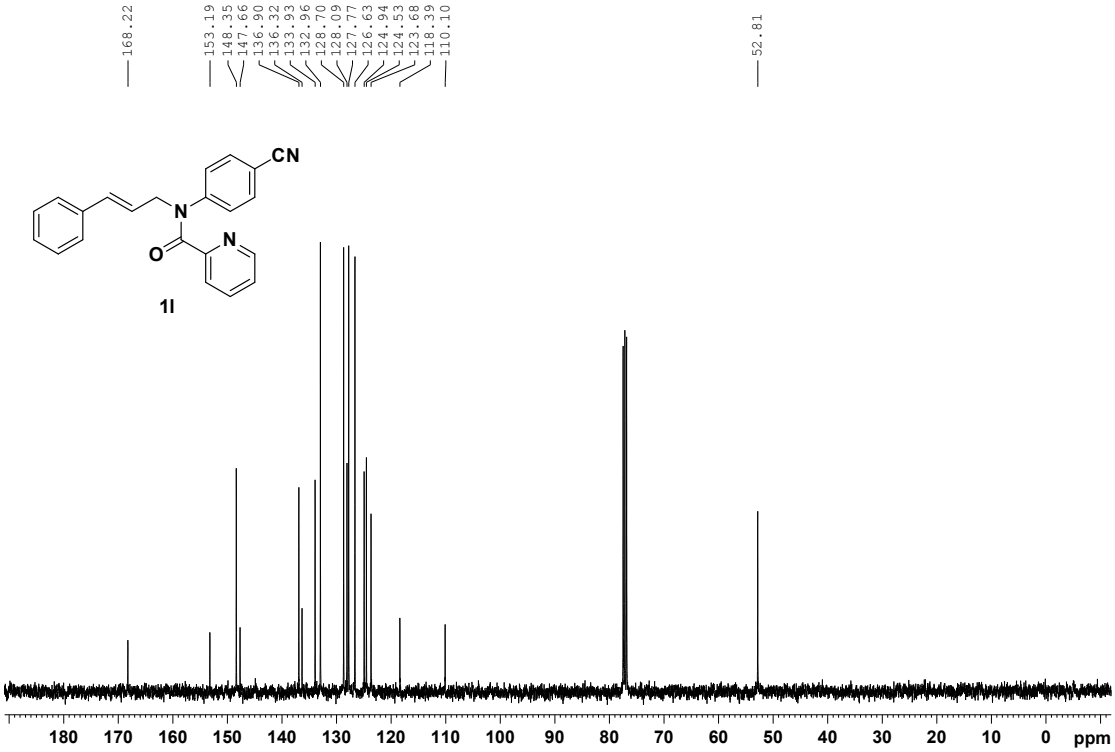
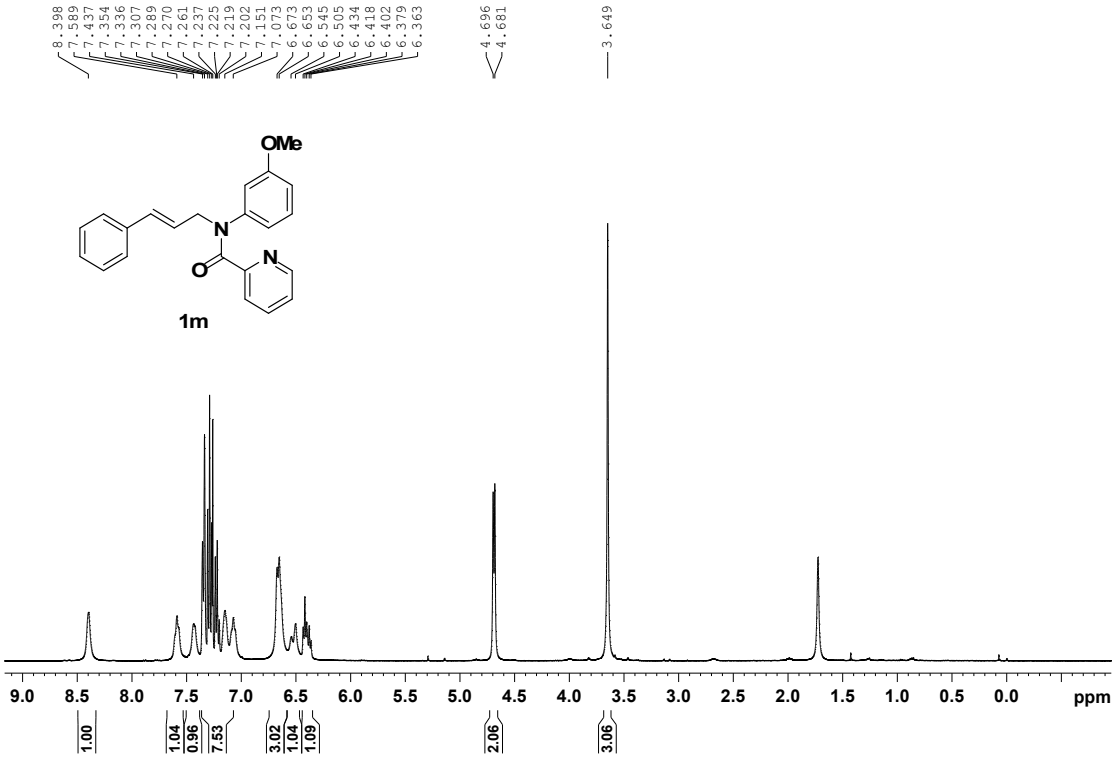
8.290
7.705
7.508
7.487
7.341
7.324
7.322
7.317
7.315
7.297
7.278
7.260
7.243
7.237
7.231
7.228
7.221
7.190
7.170
6.534
6.495
6.386
6.371
6.355
6.347
6.331
6.315
4.733
4.718
CN
N
O
N
1l
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.03
2.08
8.32
1.03
1.06
2.09


168.22
153.19
148.35
147.66
136.90
136.32
133.93
132.96
128.70
128.09
127.77
126.63
124.94
124.53
123.68
118.39
110.10
52.81
CN
N
O
N
1l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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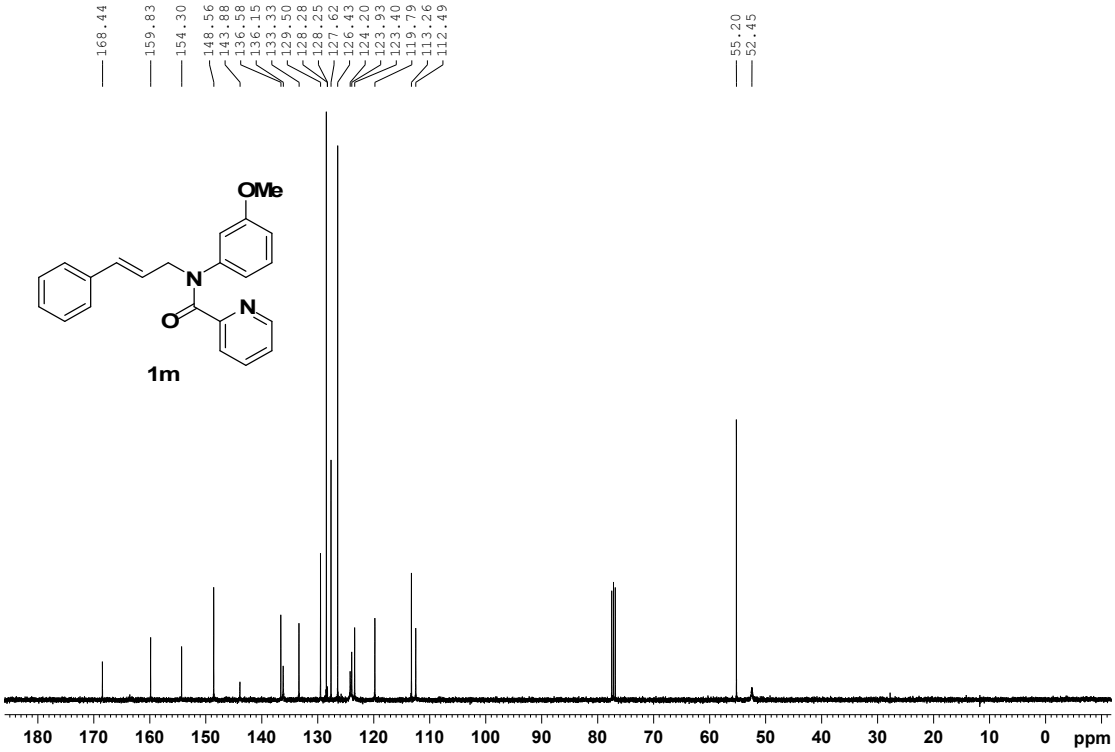
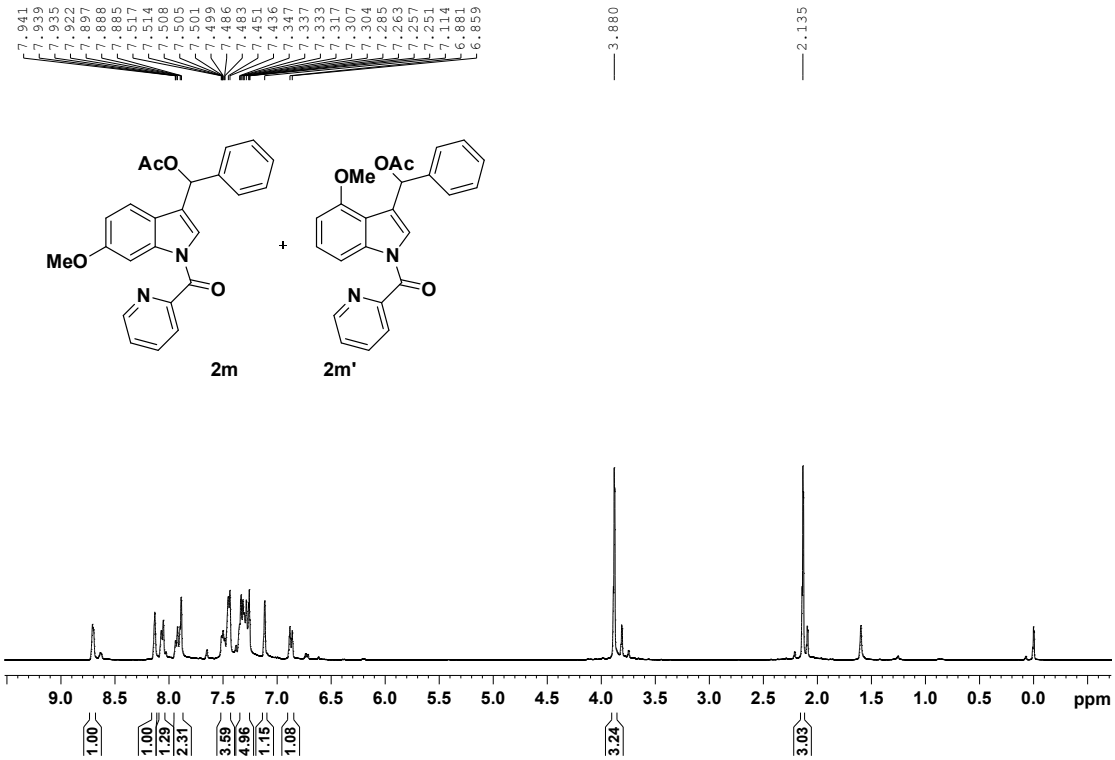
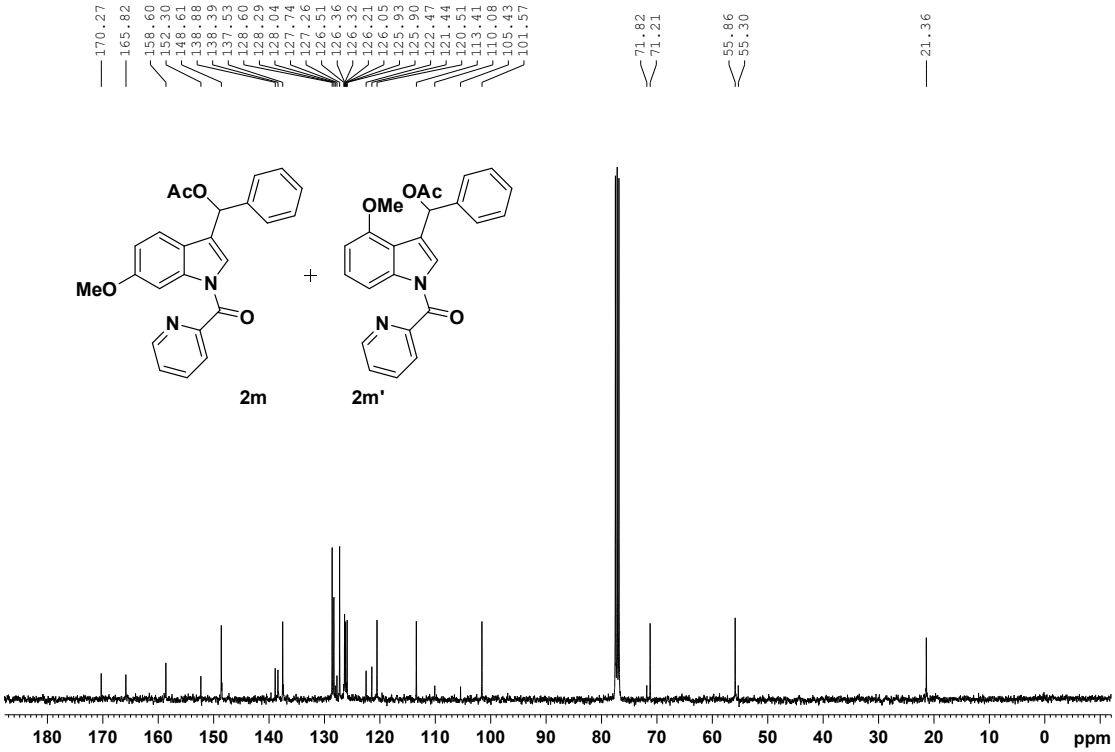
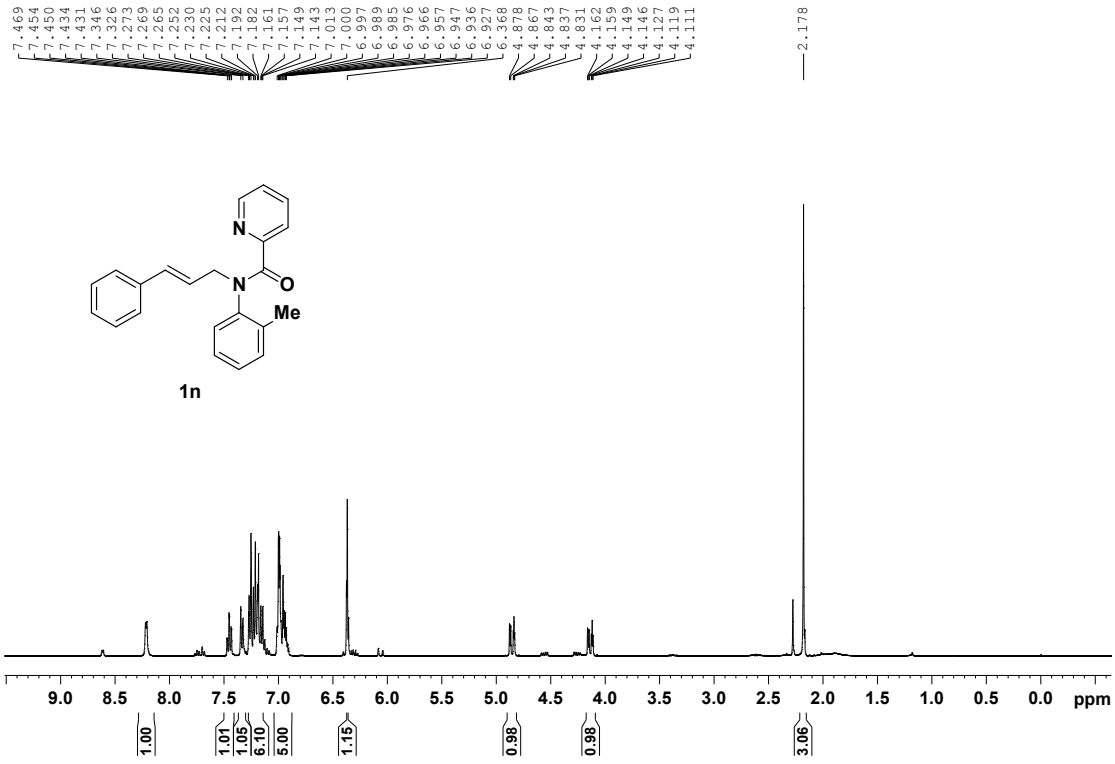
7.589
7.437
7.354
7.336
7.307
7.289
7.270
7.261
7.237
7.225
7.219
7.202
7.151
7.073
6.673
6.653
6.545
6.505
6.434
6.418
6.402
6.379
6.363
4.696
4.681
3.649
OMe
N
O
N
1m
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.04
0.96
7.53
3.02
1.04
1.09
2.06
3.06


168.44
159.83
154.30
148.56
143.88
136.58
136.15
133.33
129.50
128.28
128.25
127.62
126.43
124.20
123.93
123.40
119.79
113.26
112.49
55.20
52.45
OMe
N
O
N
1m
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.941
7.939
7.935
7.922
7.897
7.888
7.885
7.517
7.514
7.508
7.505
7.501
7.499
7.486
7.483
7.451
7.436
7.347
7.337
7.333
7.317
7.307
7.304
7.285
7.263
7.257
7.251
7.114
6.881
6.859
3.880
2.135
AcO
MeO
N
O
N
2m
+
OMe
OAc
N
O
N
2m'
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
1.29
2.31
3.59
4.36
1.15
1.08
3.24
3.03


170.27
165.82
158.60
152.30
148.61
138.88
138.39
137.53
128.60
128.29
128.04
127.74
127.26
126.51
126.36
126.32
126.21
126.05
125.93
125.90
122.47
121.44
120.51
113.41
110.08
105.43
101.57
71.82
71.21
55.86
55.30
21.36
AcO
MeO
N
O
N
OMe
OAc
2m
2m'
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.450
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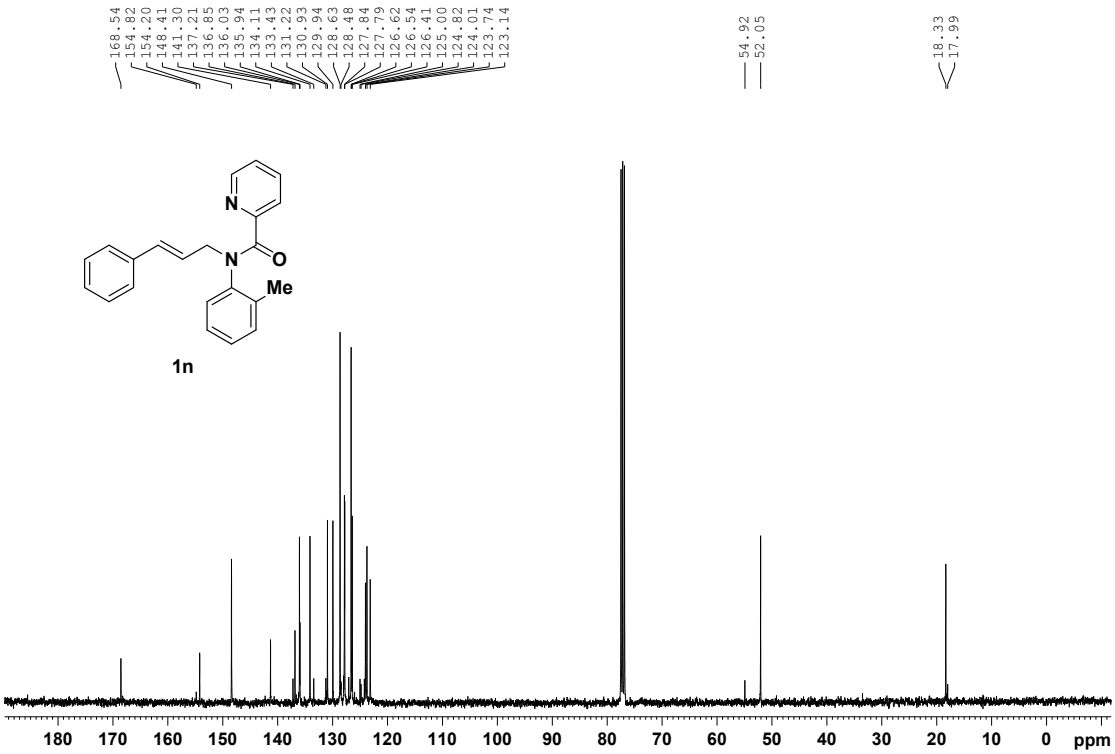
7.431
7.346
7.326
7.273
7.269
7.265
7.252
7.230
7.225
7.212
7.192
7.182
7.161
7.157
7.149
7.143
7.013
7.000
6.997
6.989
6.985
6.976
6.966
6.957
6.947
6.936
6.927
6.368
4.878
4.867
4.843
4.837
4.831
4.162
4.159
4.149
4.146
4.127
4.119
4.111
2.178
N
N
O
Me
1n
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.01
1.05
6.10
5.00
1.15
0.98
0.98
3.06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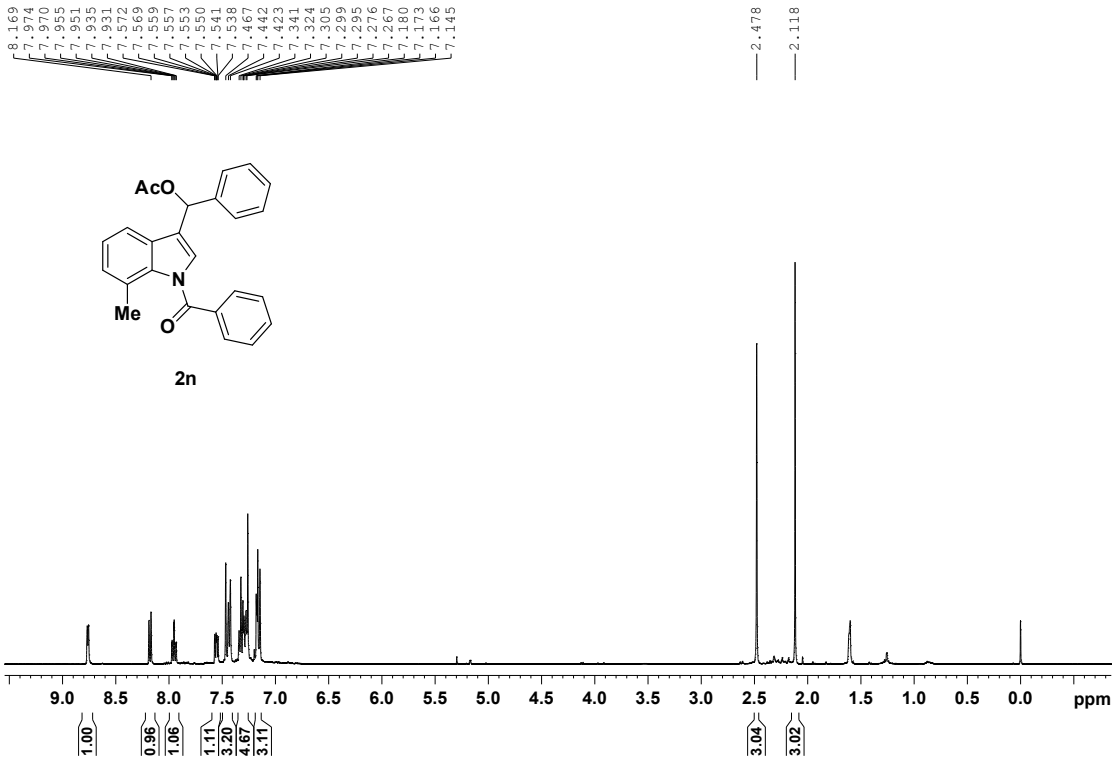
154.82
154.20
148.41
141.30
137.21
136.85
136.03
135.94
134.11
133.43
131.22
130.93
129.94
128.63
128.48
127.84
127.79
126.62
126.54
126.41
125.00
124.82
124.01
123.74
123.14
54.92
52.05
18.33
17.99
N
N
O
Me
1n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.970
7.955
7.951
7.935
7.931
7.572
7.569
7.559
7.557
7.553
7.550
7.541
7.538
7.467
7.442
7.423
7.341
7.324
7.305
7.299
7.295
7.276
7.267
7.180
7.173
7.166
7.145
2.478
2.118
AcO
N
Me
O
2n
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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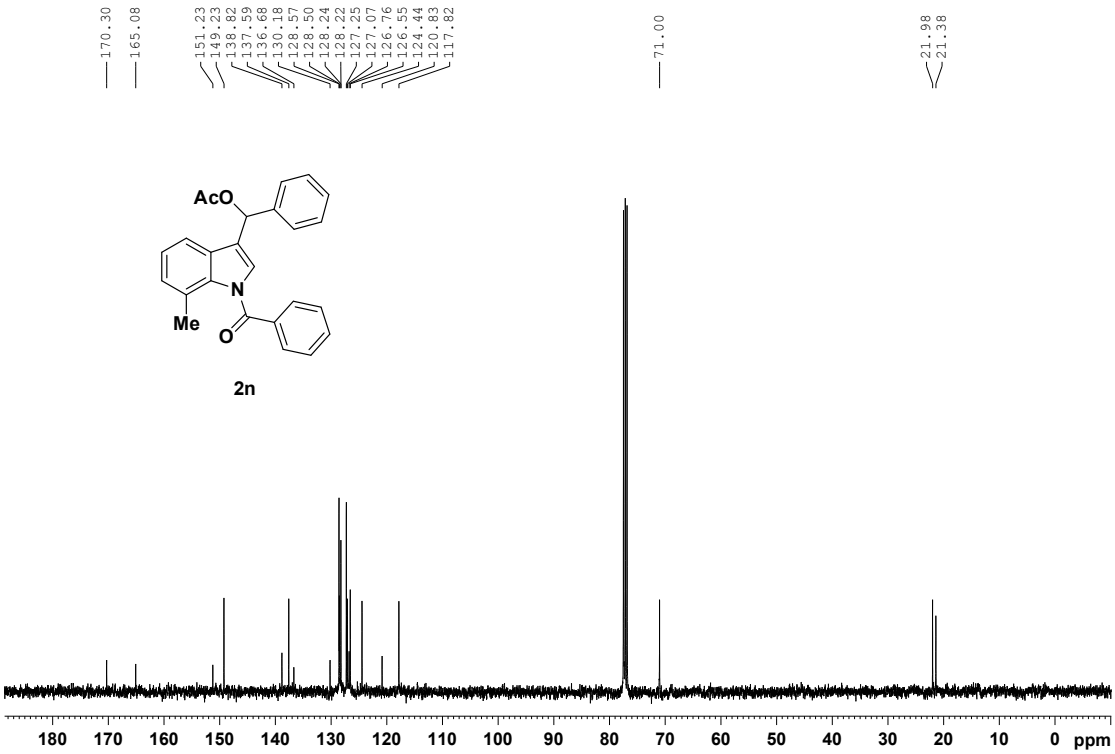
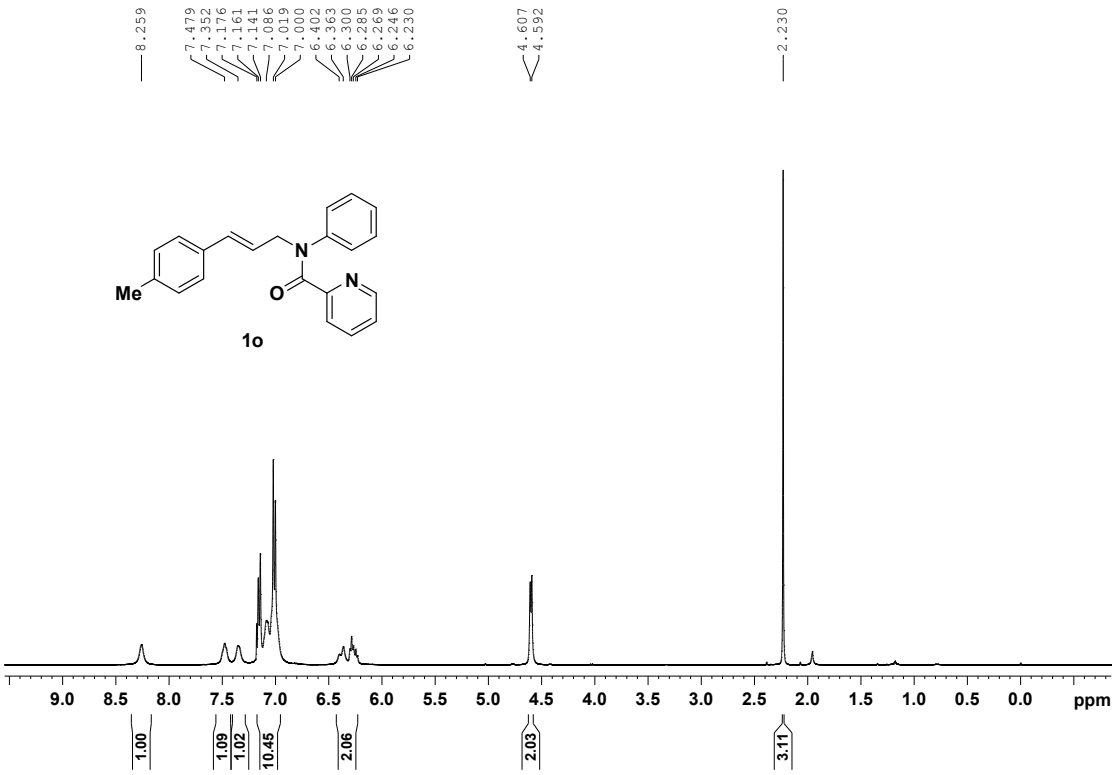
0.96
1.06
1.11
3.20
4.67
3.11
3.04
3.02


170.30
165.08
151.23
149.23
138.82
137.59
136.68
130.18
128.57
128.50
128.24
128.22
127.25
127.07
126.76
126.55
124.44
120.83
117.82
71.00
21.98
21.38
AcO
N
Me
O
2n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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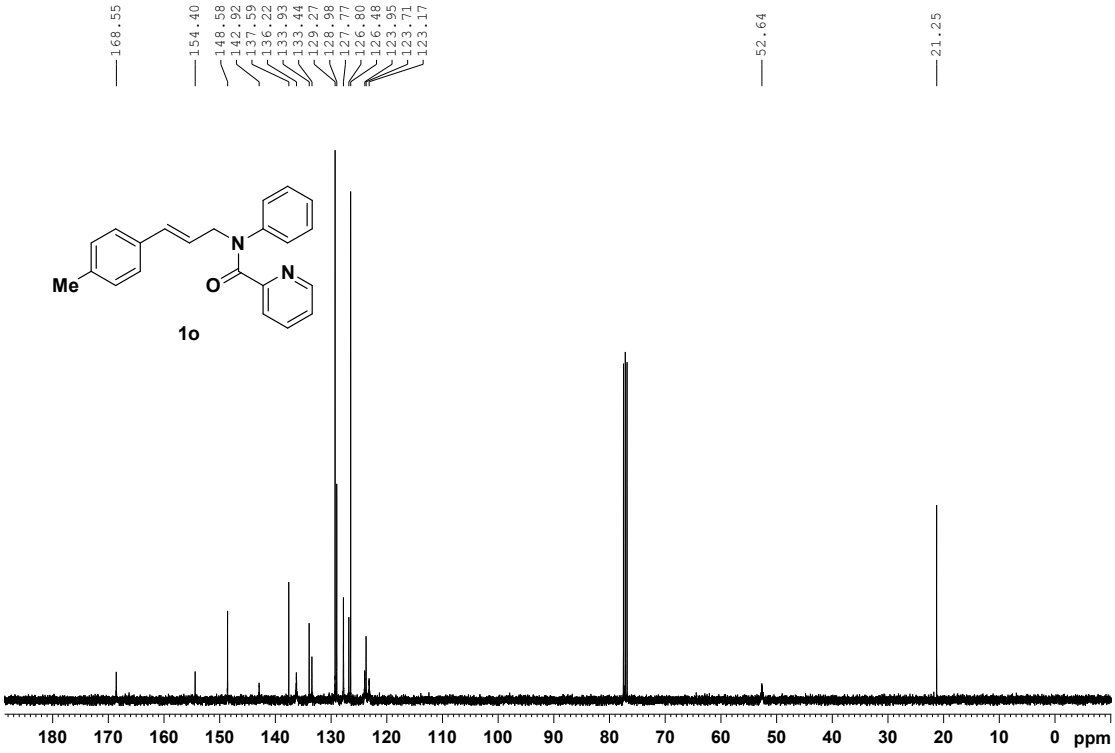
7.352
7.176
7.161
7.141
7.086
7.019
7.000
6.402
6.363
6.300
6.285
6.269
6.246
6.230
4.607
4.592
2.230
N
Me
O
N
1o
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.09
1.02
10.45
2.06
2.03
3.11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154.40
148.58
142.92
137.59
136.22
133.93
133.44
129.27
128.98
127.77
126.80
126.48
123.95
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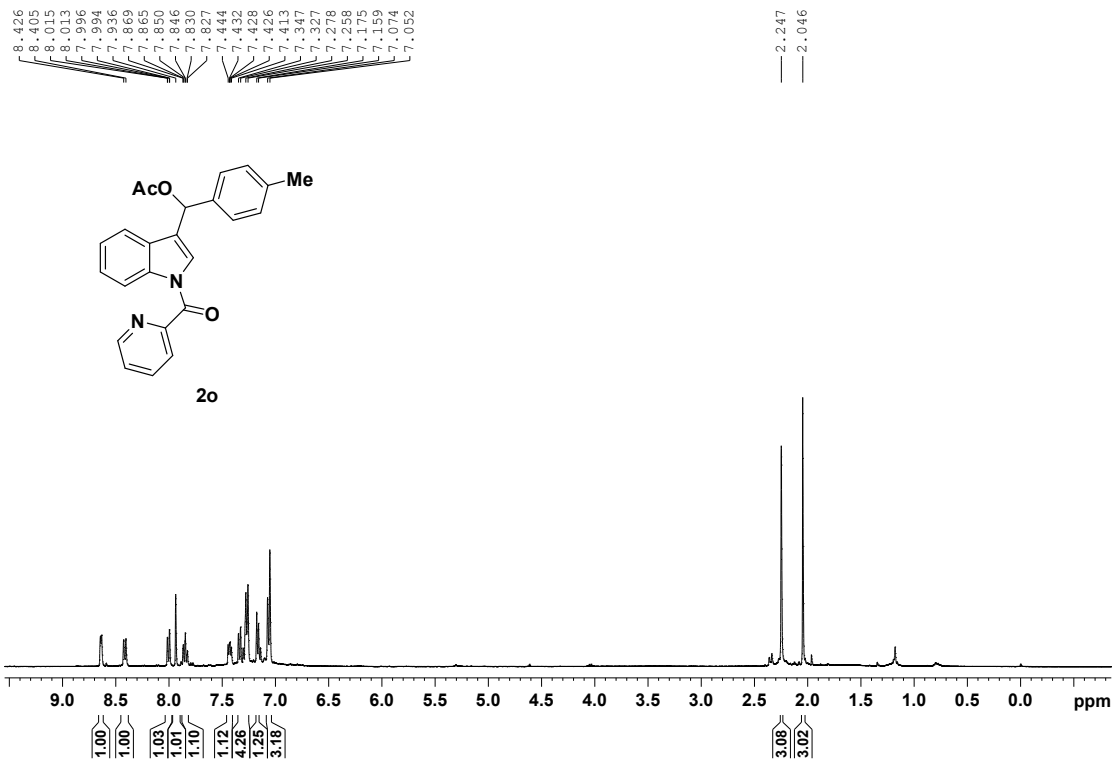
Me
N
O
N
1o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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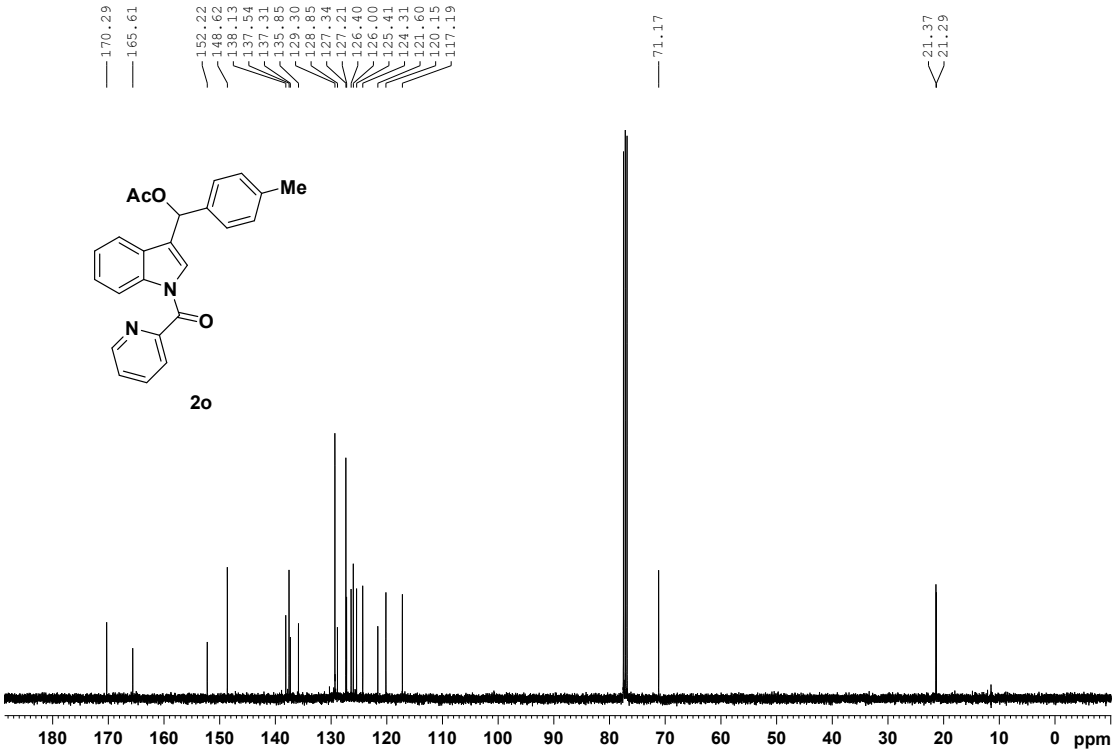
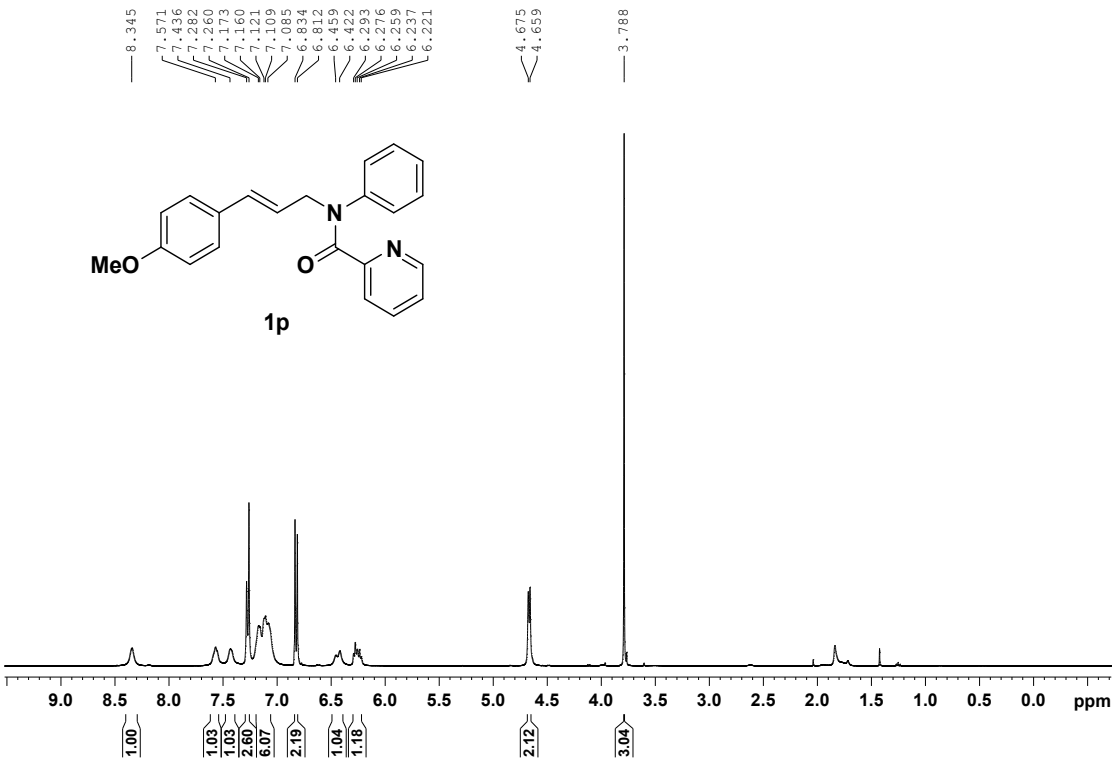
8.405
8.015
8.013
7.996
7.994
7.936
7.869
7.865
7.850
7.846
7.830
7.827
7.444
7.432
7.428
7.426
7.413
7.347
7.327
7.278
7.258
7.175
7.159
7.074
7.052
2.247
2.046
AcO
Me
N
N
O
2o
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
1.03
1.01
1.10
1.12
4.26
1.25
3.18
3.08
3.02


170.29
165.61
152.22
148.62
138.13
137.54
137.31
135.85
129.30
128.85
127.34
127.21
126.40
126.00
125.41
124.31
121.60
120.15
117.19
71.17
21.37
21.29
AcO
Me
N
O
N
2o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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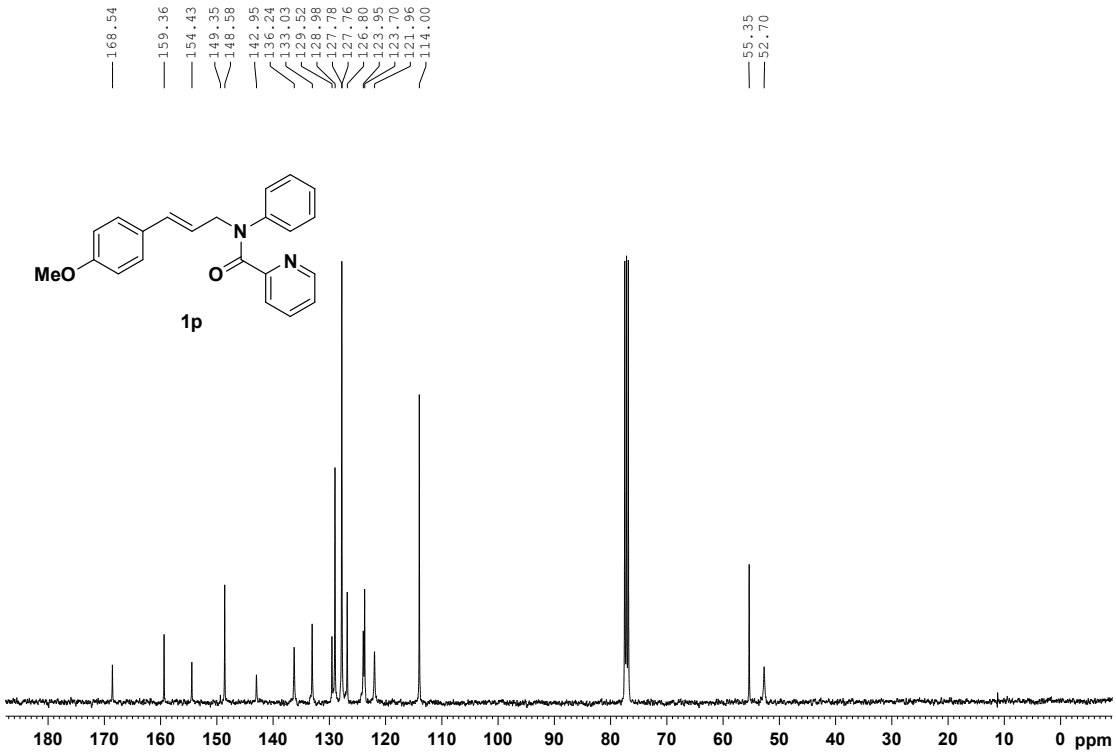
7.436
7.282
7.260
7.173
7.160
7.121
7.109
7.085
6.834
6.812
6.459
6.422
6.293
6.276
6.259
6.237
6.221
4.675
4.659
3.788
MeO
N
O
N
1p
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.03
1.03
2.60
6.07
2.19
1.04
1.18
2.12
3.04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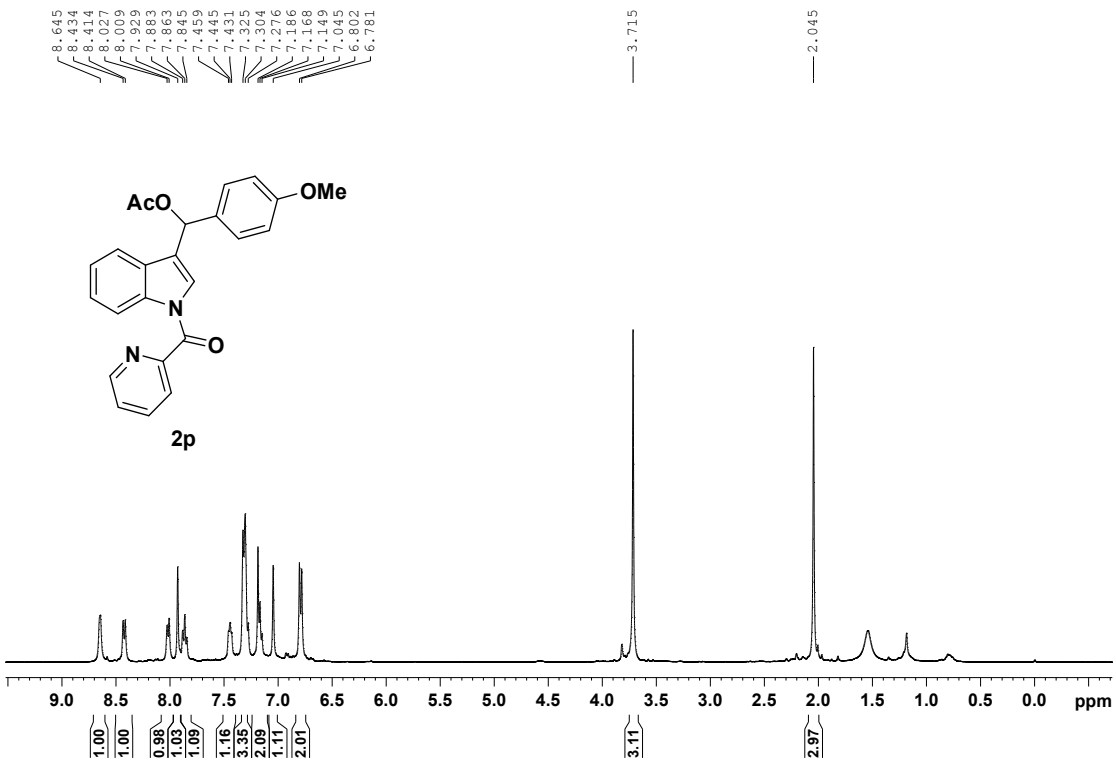
159.36
154.43
149.35
148.58
142.95
136.24
133.03
129.52
128.98
127.78
127.76
126.80
123.95
123.70
121.96
114.00
55.35
52.70
MeO
N
O
N
1p
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.434
8.414
8.027
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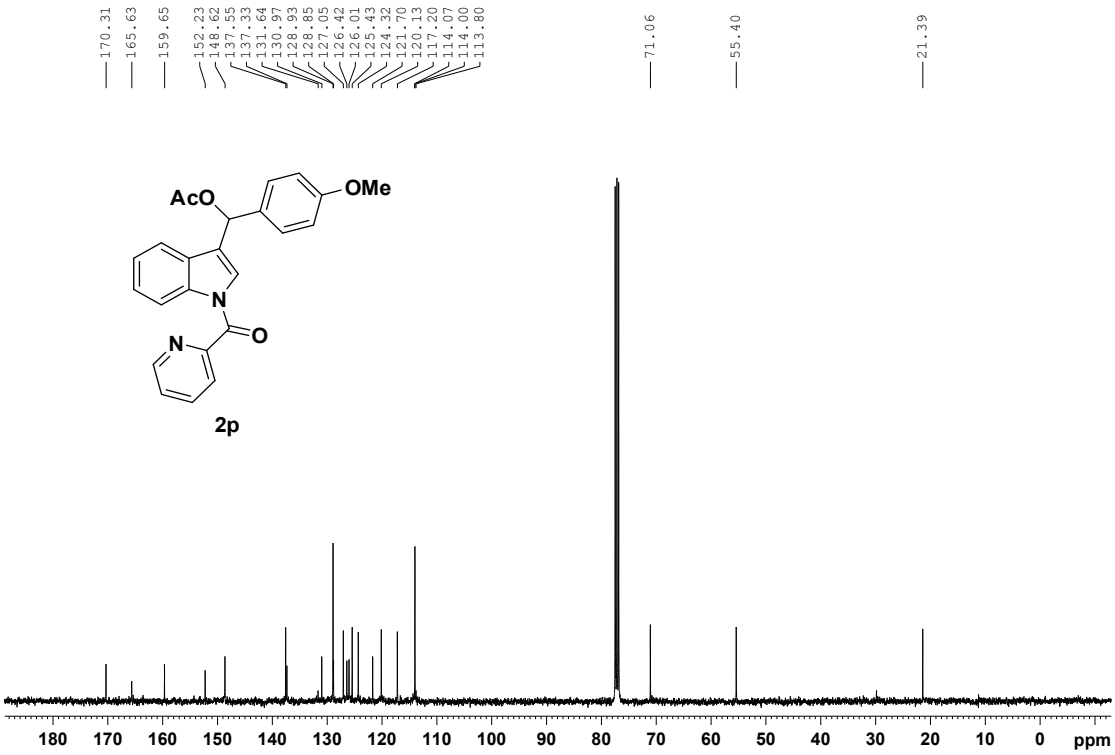
7.929
7.883
7.863
7.845
7.459
7.445
7.431
7.325
7.304
7.276
7.186
7.168
7.149
7.045
6.802
6.781
3.715
2.045
AcO
OMe
N
O
N
2p
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
0.98
1.03
1.09
1.16
3.35
2.09
1.11
2.01
3.11
2.97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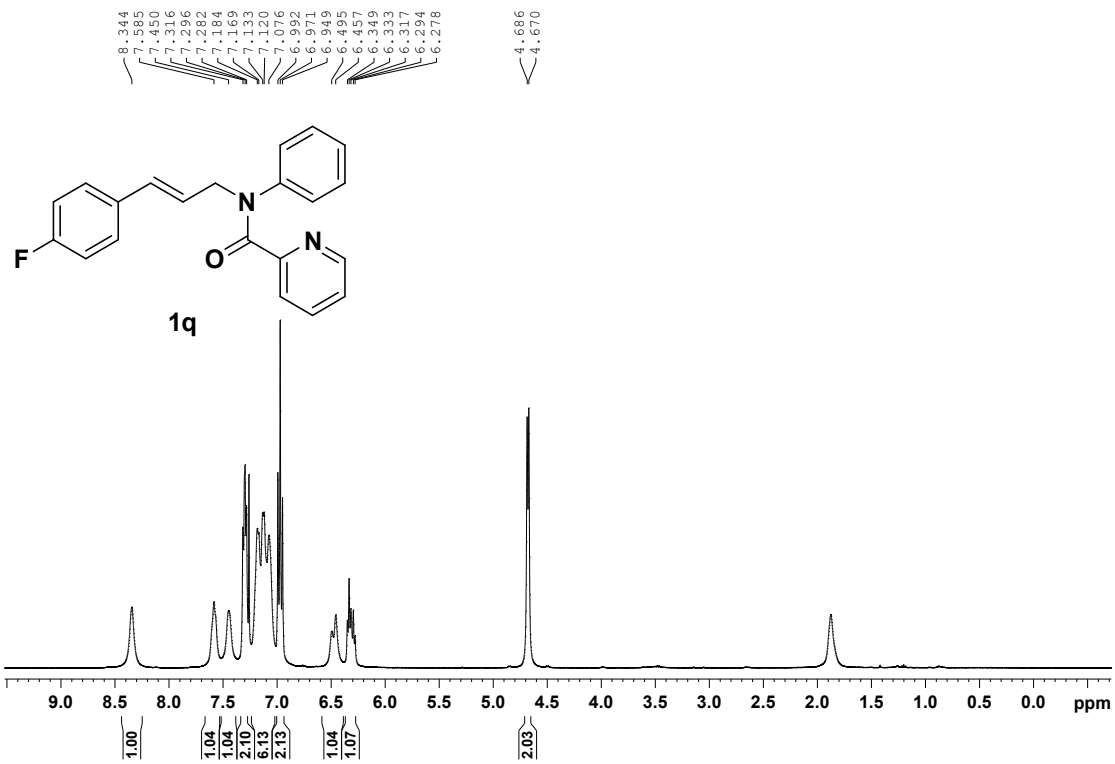
165.63
159.65
152.23
148.62
137.55
137.33
131.64
130.97
128.93
128.85
127.05
126.42
126.01
125.43
124.32
121.70
120.13
117.20
114.07
114.00
113.80
71.06
55.40
21.39
AcO
OMe
N
O
N
2p
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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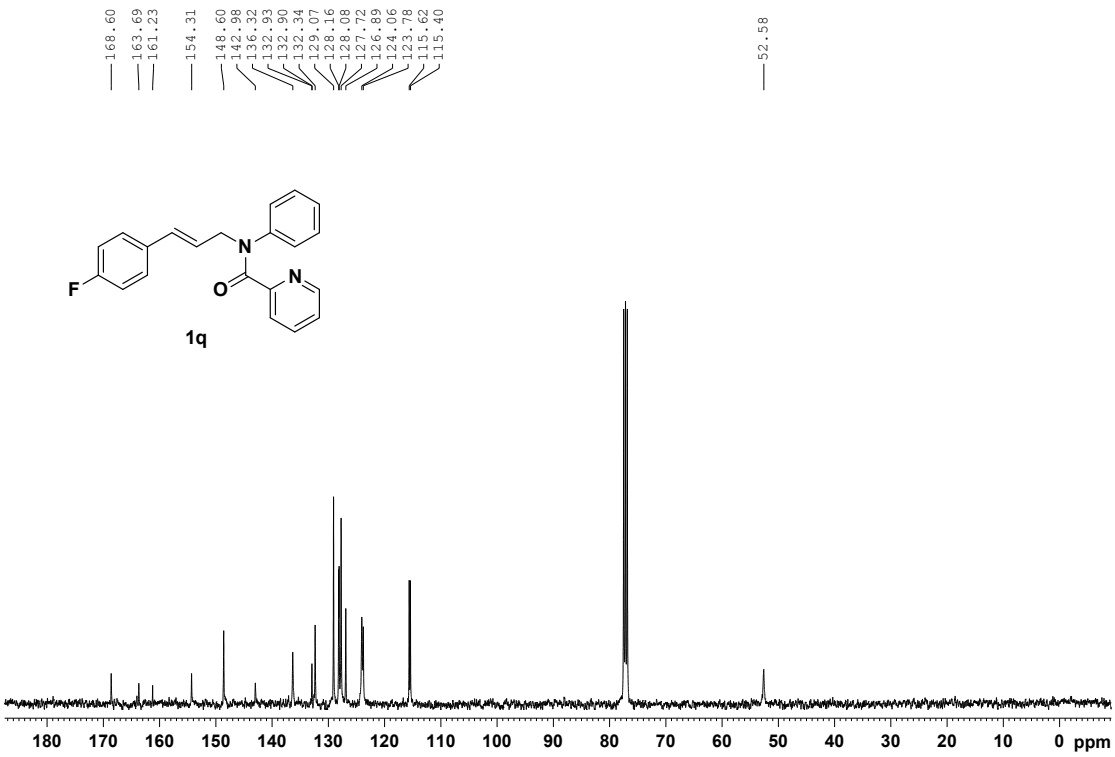
7.585
7.450
7.316
7.296
7.282
7.184
7.169
7.133
7.120
7.076
6.992
6.971
6.949
6.495
6.457
6.349
6.333
6.317
6.294
6.278
4.686
4.670
N
O
N
F
1q
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.04
1.04
2.10
6.13
2.13
1.04
1.07
2.03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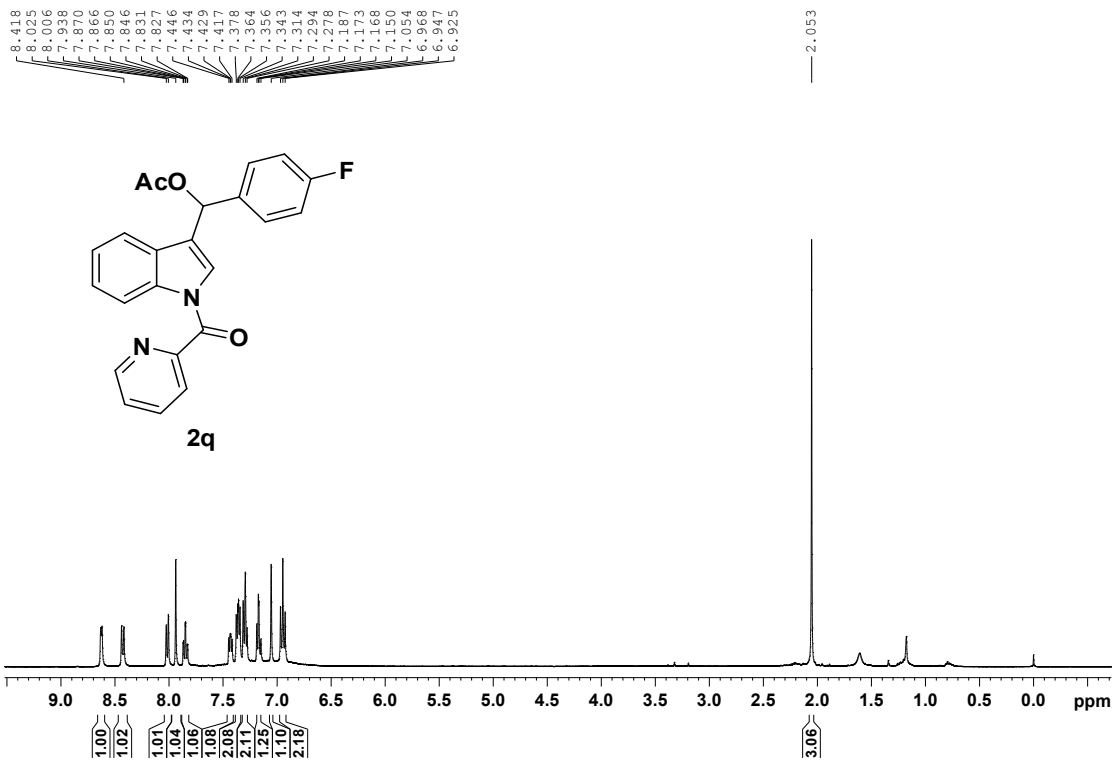
163.69
161.23
154.31
148.60
142.98
136.32
132.93
132.90
132.34
129.07
128.16
128.08
127.72
126.89
124.06
123.78
115.62
115.40
52.58
F
O
N
N
1q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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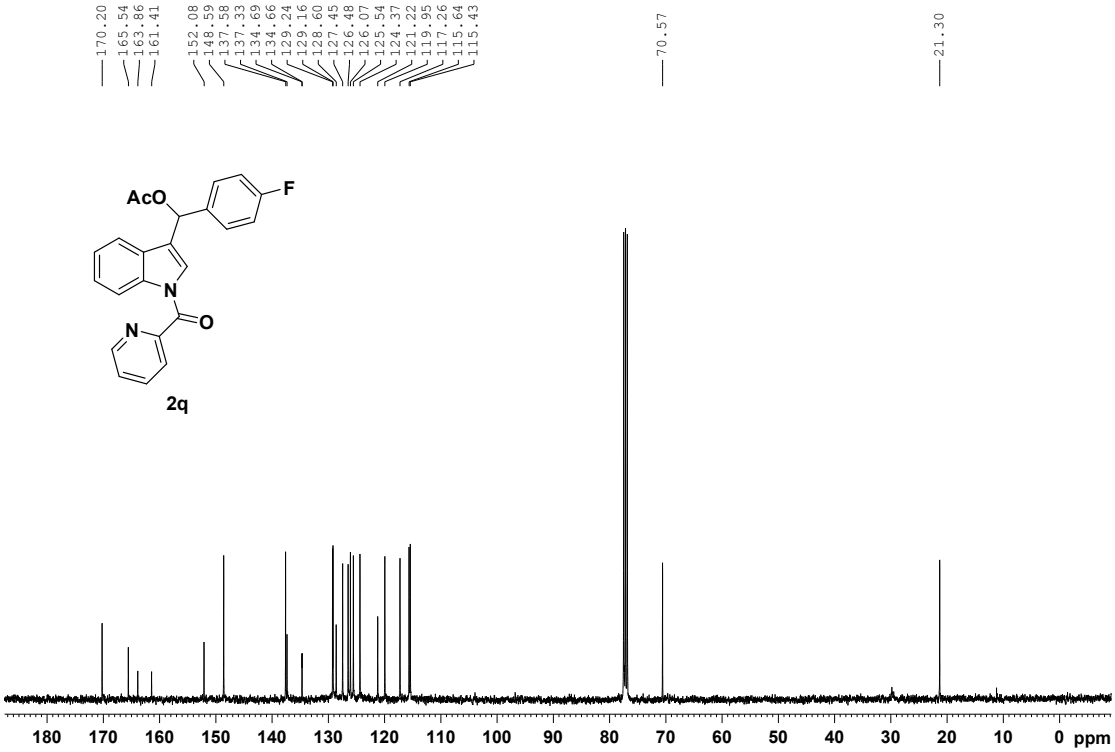
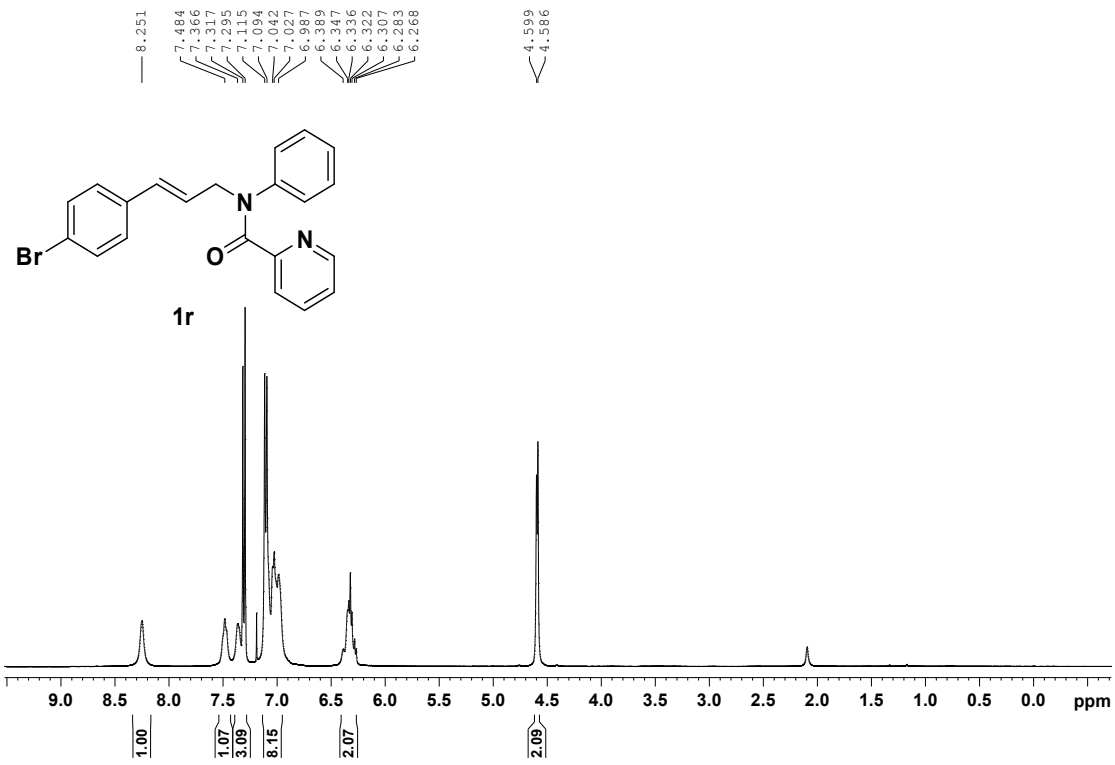
8.025
8.006
7.938
7.870
7.866
7.850
7.846
7.831
7.827
7.446
7.434
7.429
7.417
7.378
7.364
7.356
7.343
7.314
7.294
7.278
7.187
7.173
7.168
7.150
7.054
6.968
6.947
6.925
2.053
AcO
F
N
N
O
2q
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
1.01
1.04
1.06
1.08
2.08
2.11
1.25
1.10
2.18
3.06


170.20
165.54
163.86
161.41
152.08
148.59
137.58
137.33
134.69
134.66
129.24
129.16
128.60
127.45
126.48
126.07
125.54
124.37
121.22
119.95
117.26
115.64
115.43
70.57
21.30
AcO
F
N
O
N
2q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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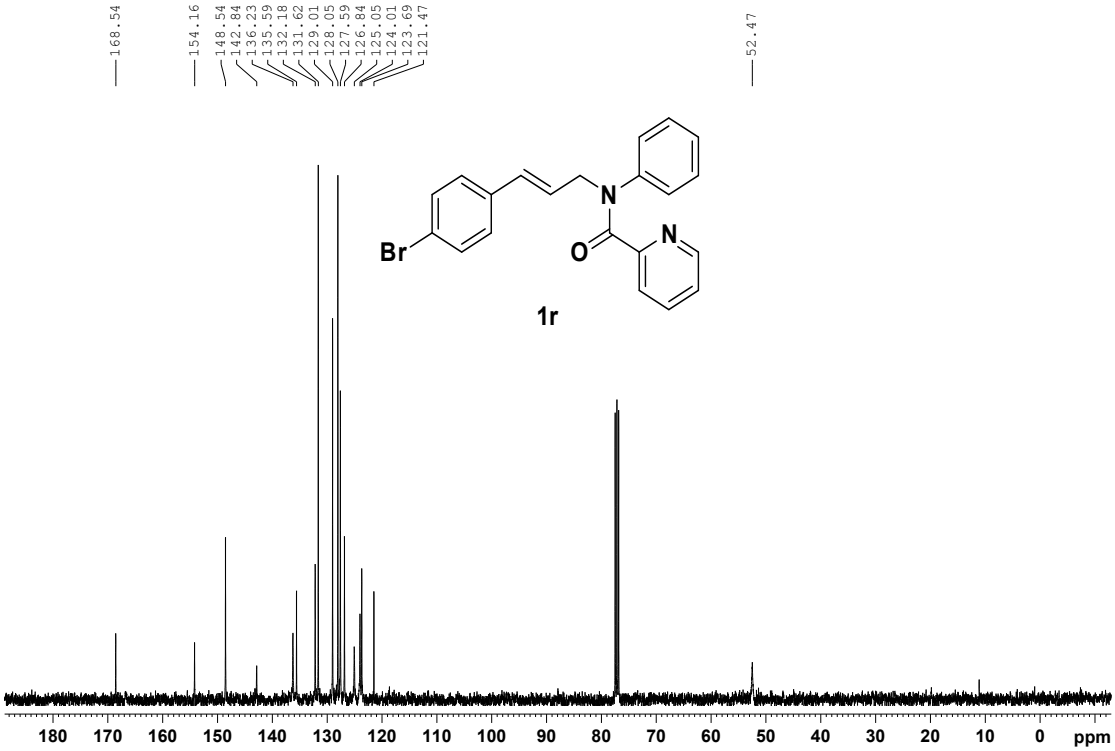
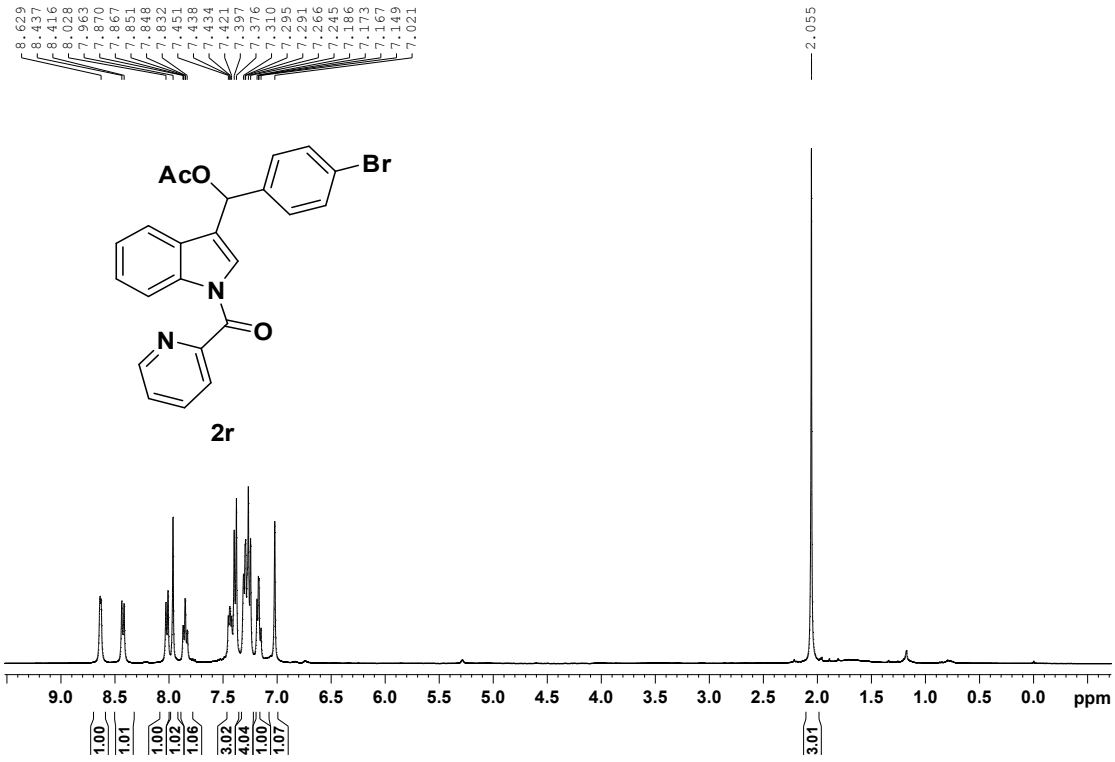
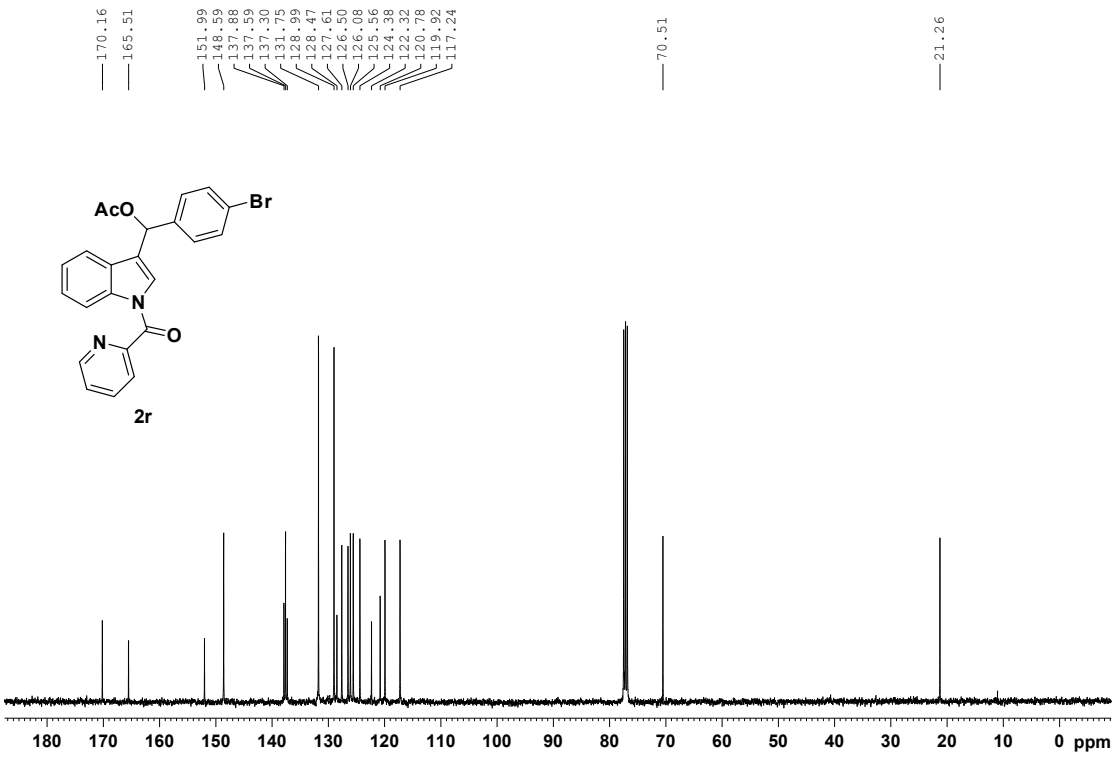
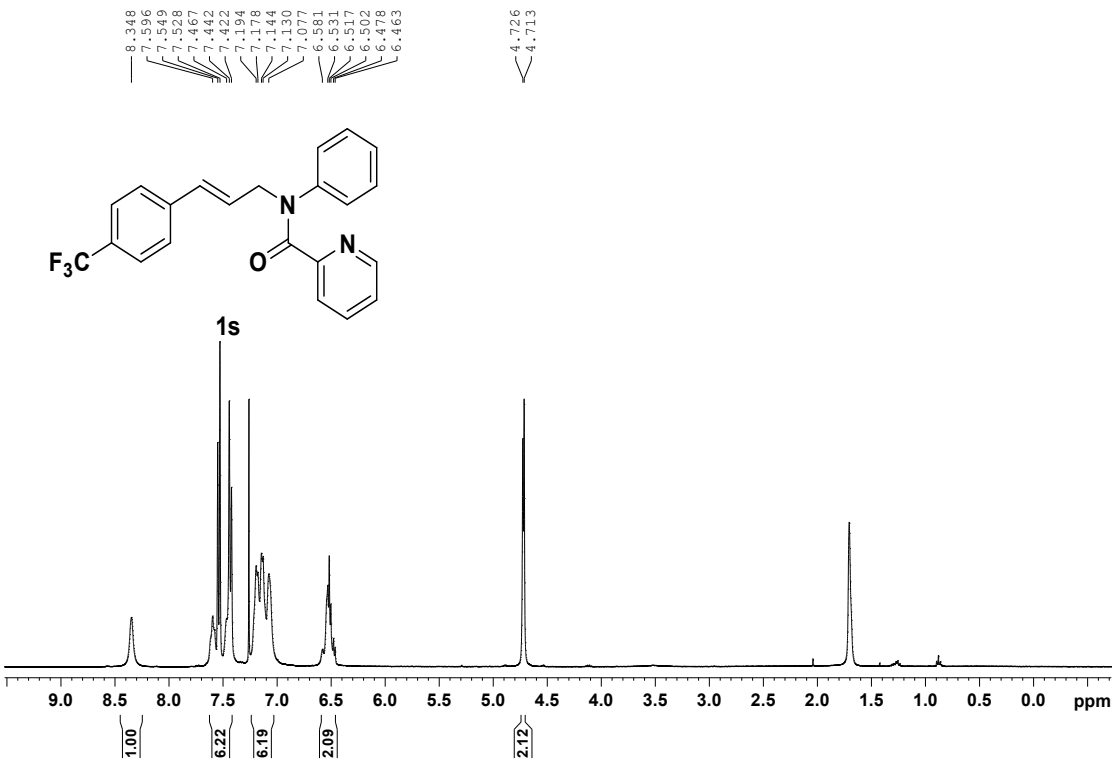
7.484
7.366
7.317
7.295
7.115
7.094
7.042
7.027
6.987
6.389
6.347
6.336
6.322
6.307
6.283
6.268
4.599
4.586
N
Br
O
N
1r
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.07
3.09
8.15
2.07
2.09


168.54
154.16
148.54
142.84
136.23
135.59
132.18
131.62
129.01
128.05
127.59
126.84
125.05
124.01
123.69
121.47
52.47
Br
N
O
N
1r
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.629
8.437
8.416
8.028
7.963
7.870
7.867
7.851
7.848
7.832
7.451
7.438
7.434
7.421
7.397
7.376
7.310
7.295
7.291
7.266
7.245
7.186
7.173
7.167
7.149
7.021
2.055
AcO
Br
N
N
O
2r
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.01 1.00 1.02 1.06 3.02 4.04 1.00 1.07
3.01


170.16
165.51
151.99
148.59
137.88
137.59
137.30
131.75
128.99
128.47
127.61
126.50
126.08
125.56
124.38
122.32
120.78
119.92
117.24
70.51
21.26
AcO
Br
N
O
N
2r
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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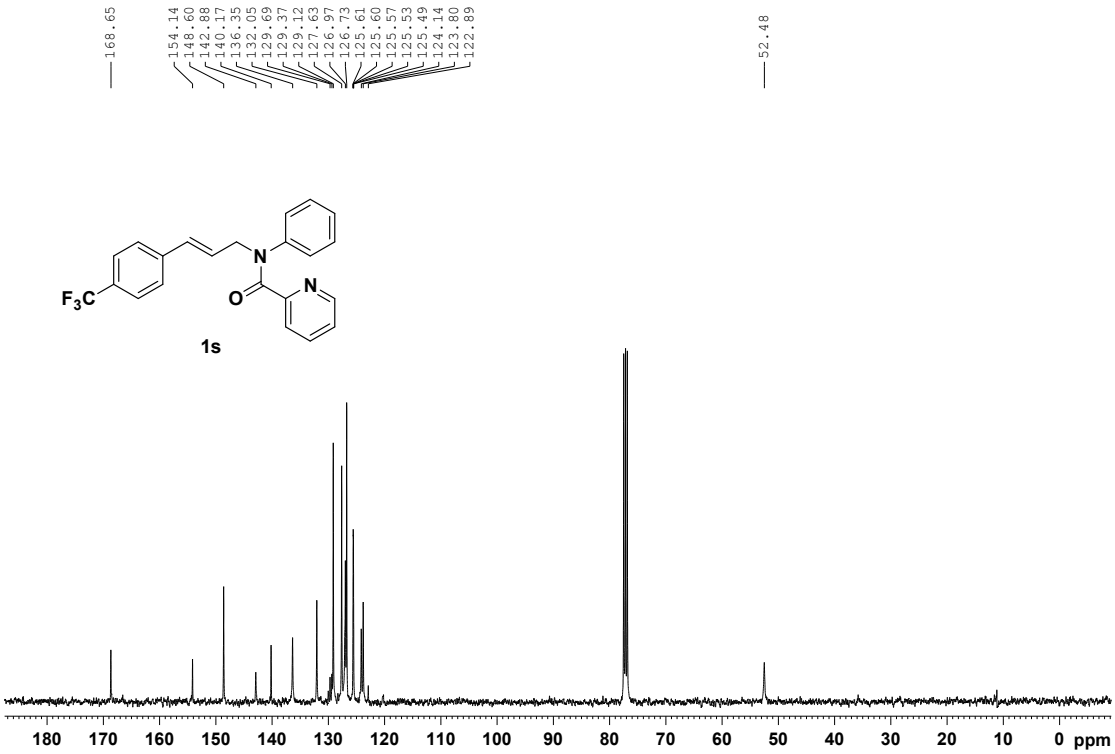
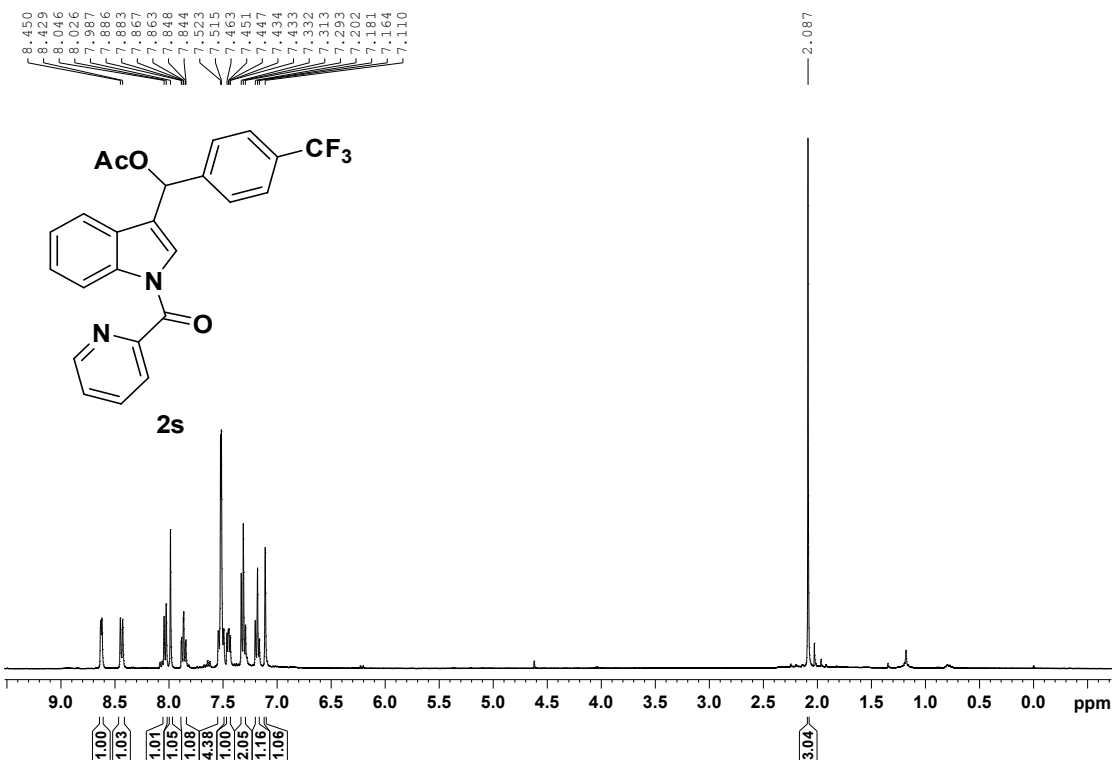
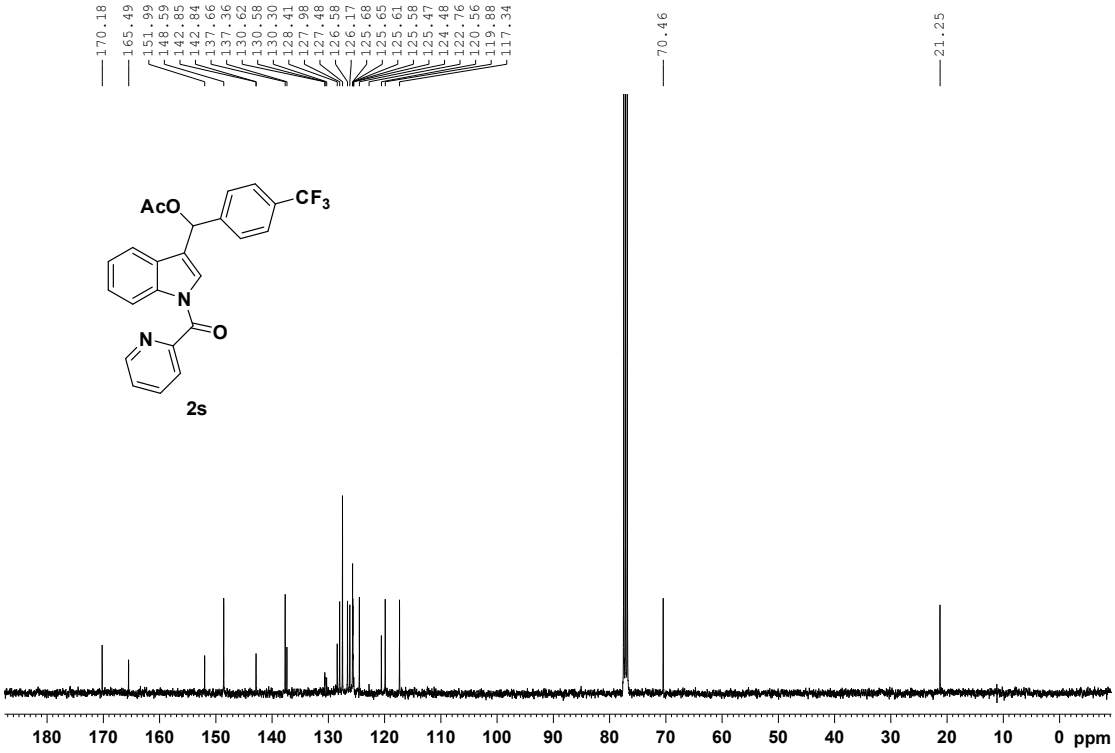
7.596
7.549
7.528
7.467
7.442
7.422
7.194
7.178
7.144
7.130
7.077
6.581
6.531
6.517
6.502
6.478
6.463
4.726
4.713
N
O
N
F3C
1s
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
6.22
6.19
2.09
2.12


168.65
154.14
148.60
142.88
140.17
136.35
132.05
129.69
129.37
129.12
127.63
126.97
126.73
125.61
125.60
125.57
125.53
125.49
124.14
123.80
122.89
52.48
F3C
N
O
N
1s
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.450
8.429
8.046
8.026
7.987
7.886
7.883
7.867
7.863
7.848
7.844
7.523
7.515
7.463
7.451
7.447
7.434
7.433
7.332
7.313
7.293
7.202
7.181
7.164
7.110
2.087
AcO
CF3
N
O
N
2s
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.03
1.01
1.05
1.08
4.38
1.00
2.05
1.16
1.06
3.04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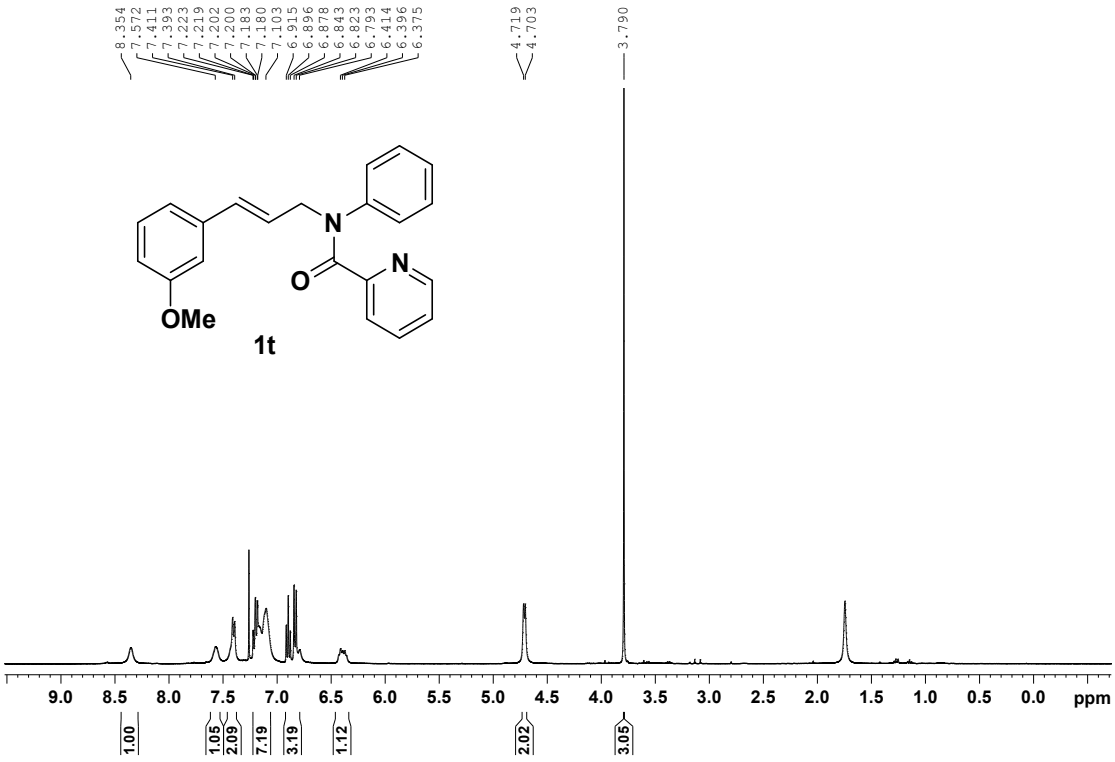
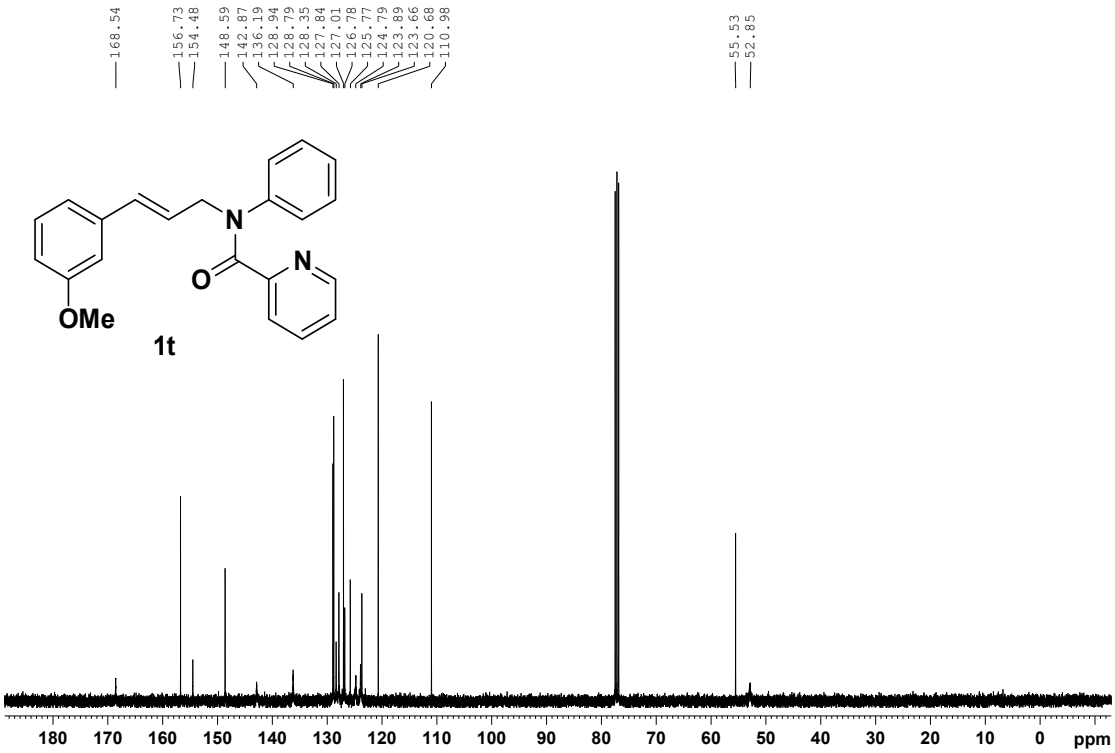
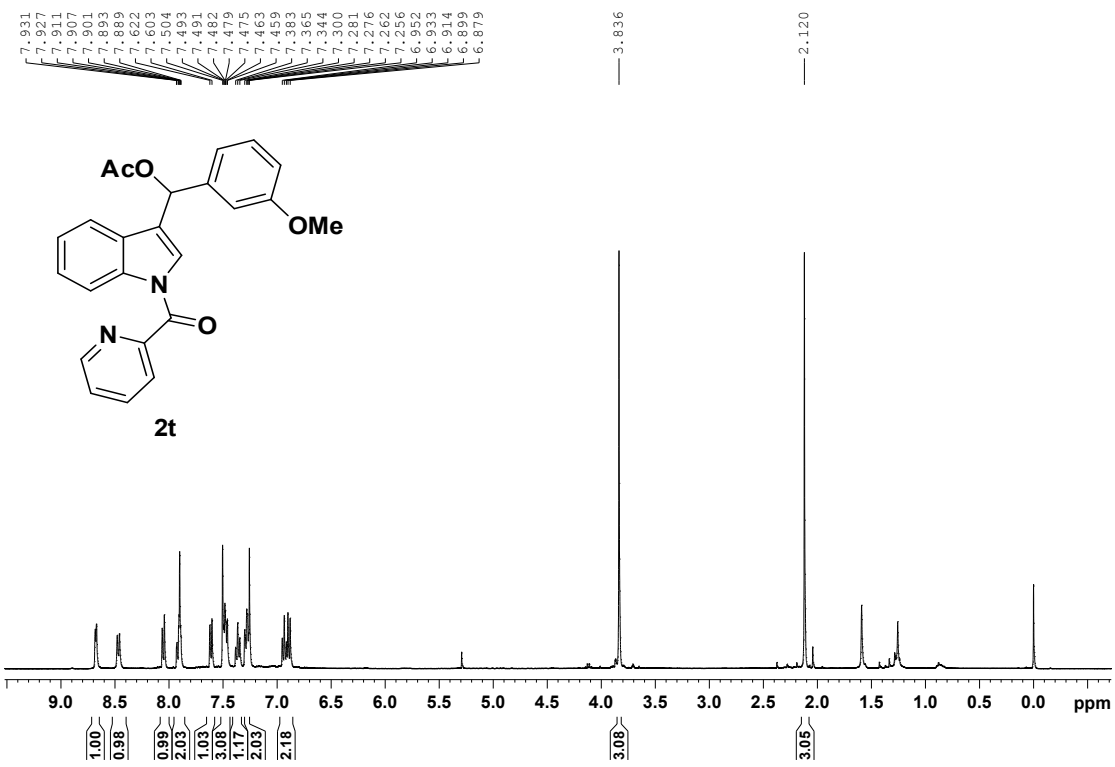
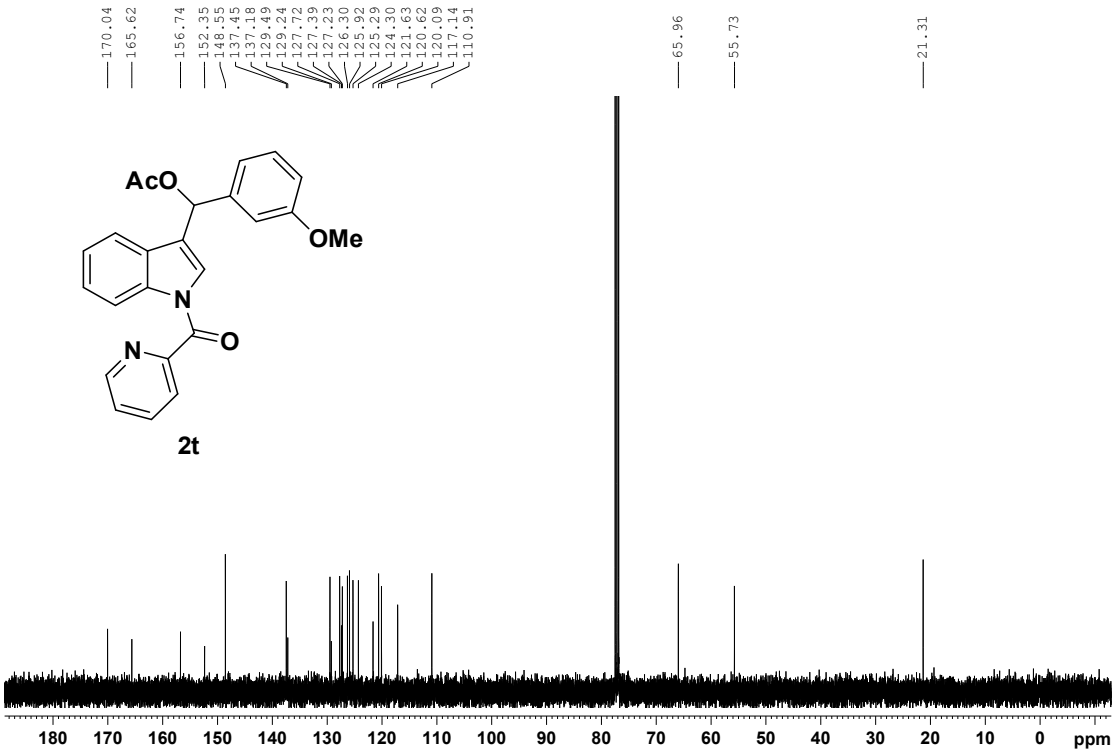
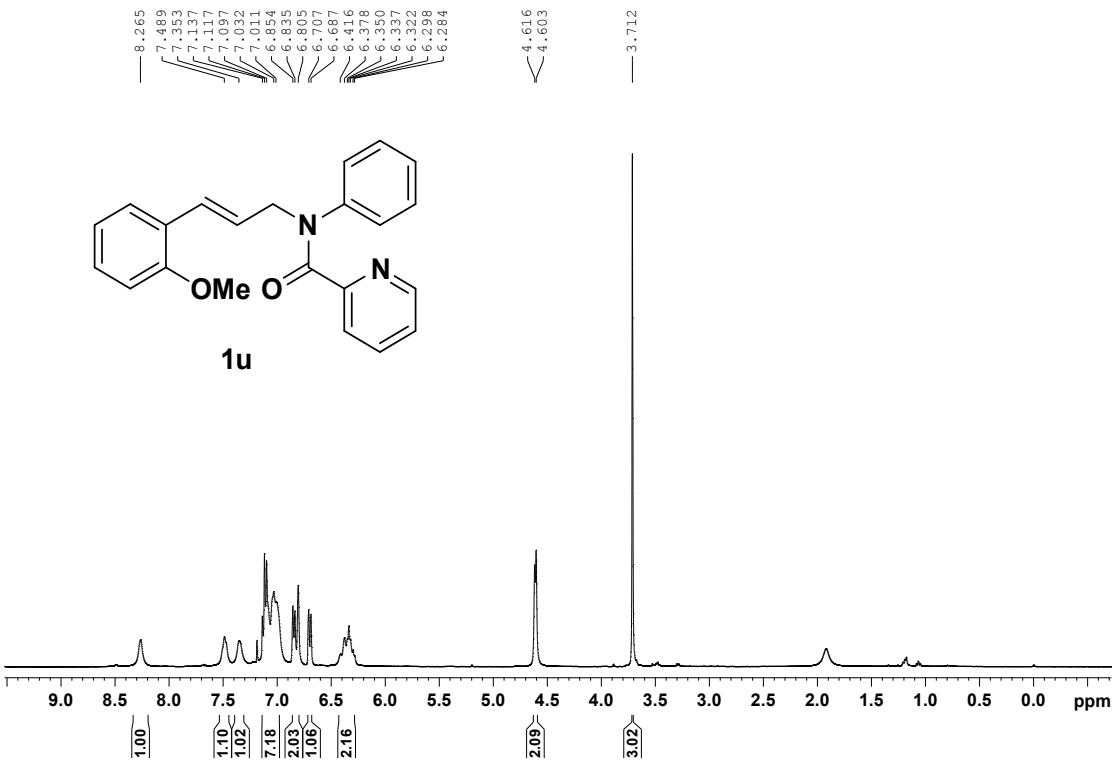
165.49
151.99
148.59
142.85
142.84
137.66
137.36
130.62
130.58
130.30
128.41
127.98
127.48
126.58
126.17
125.68
125.65
125.61
125.58
125.47
124.48
122.76
120.56
119.88
117.34
70.46
21.25
AcO
CF3
N
O
N
2s
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

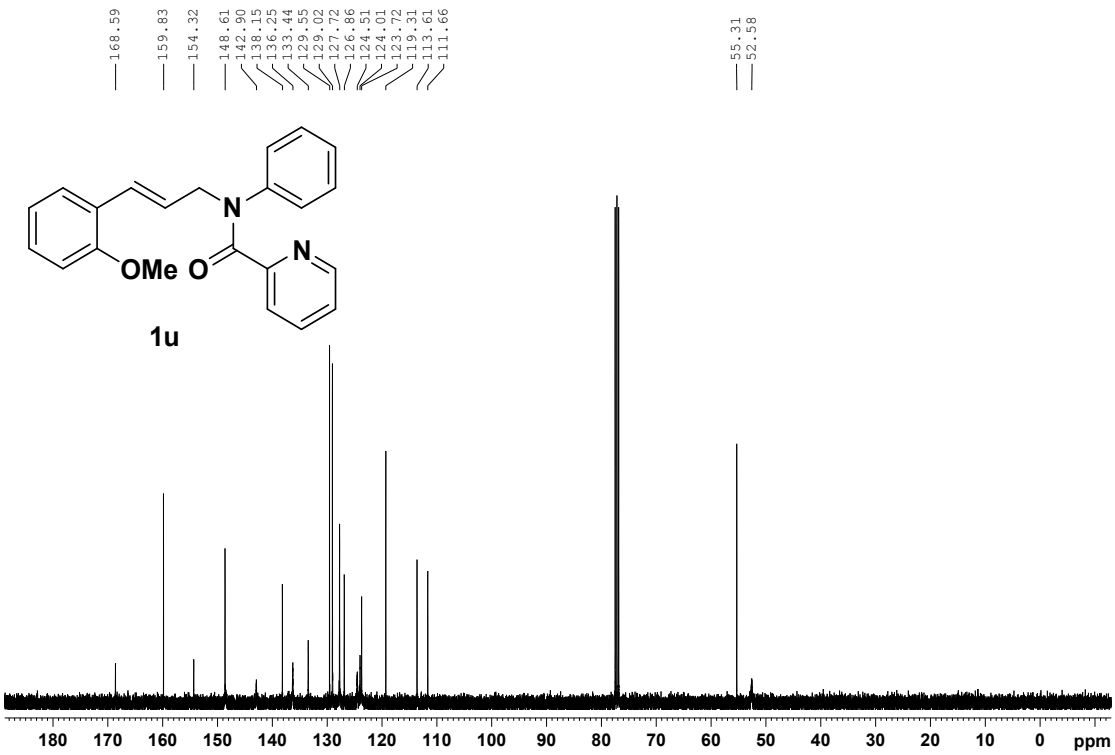

8.354
7.572
7.411
7.393
7.223
7.219
7.202
7.200
7.183
7.180
7.103
6.915
6.896
6.878
6.843
6.823
6.793
6.414
6.396
6.375
4.719
4.703
3.790
N
O
N
OMe
1t
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.05
2.09
7.19
3.19
1.12
2.02
3.05

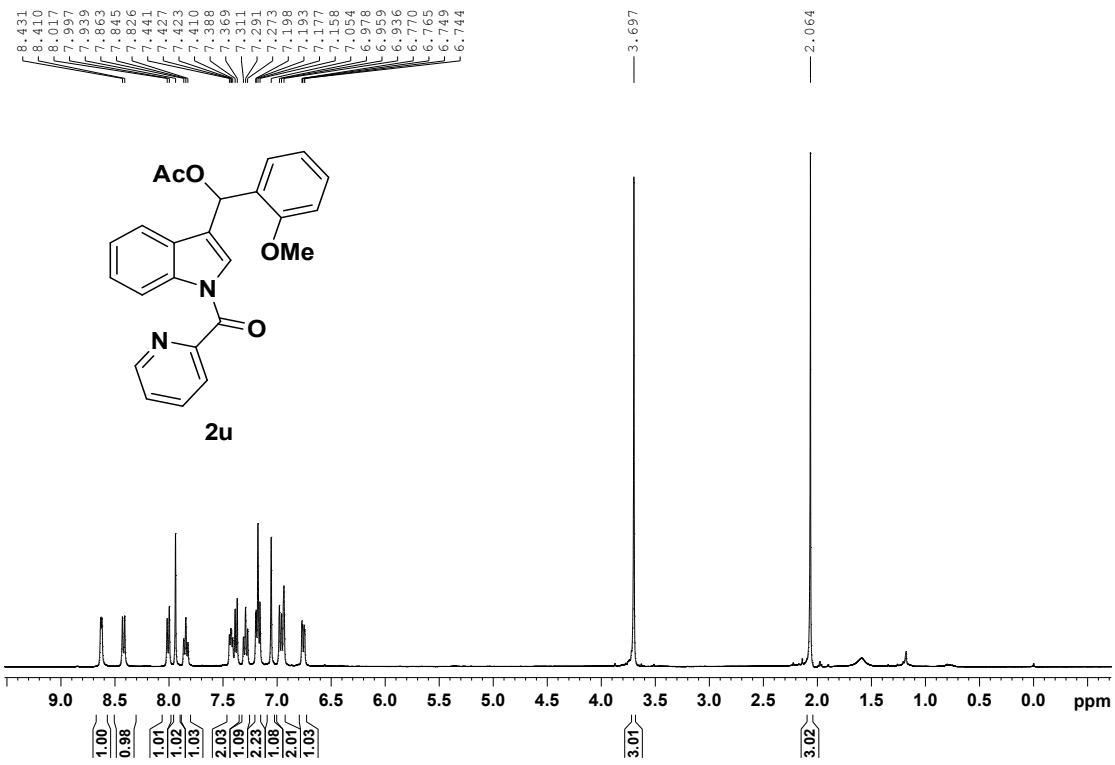

168.54
156.73
154.48
148.59
142.87
136.19
128.94
128.79
128.35
127.84
127.01
126.78
125.77
124.79
123.89
123.66
120.68
110.98
55.53
52.85
N
O
N
OMe
1t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

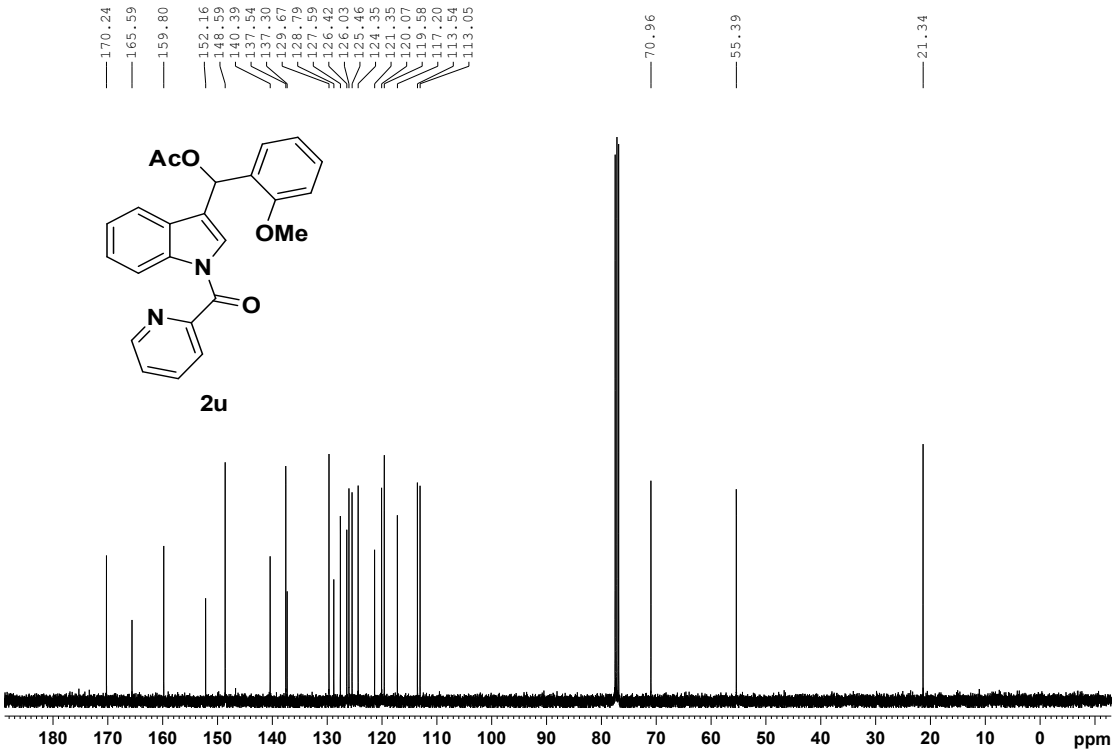

7.931
7.927
7.911
7.907
7.901
7.893
7.889
7.622
7.603
7.504
7.493
7.491
7.482
7.479
7.475
7.463
7.459
7.383
7.365
7.344
7.300
7.281
7.276
7.262
7.256
6.952
6.933
6.914
6.899
6.879
3.836
2.120
AcO
OMe
N
O
N
2t
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.98
0.99
2.03
1.03
3.08
1.17
2.03
2.18
3.08
3.05

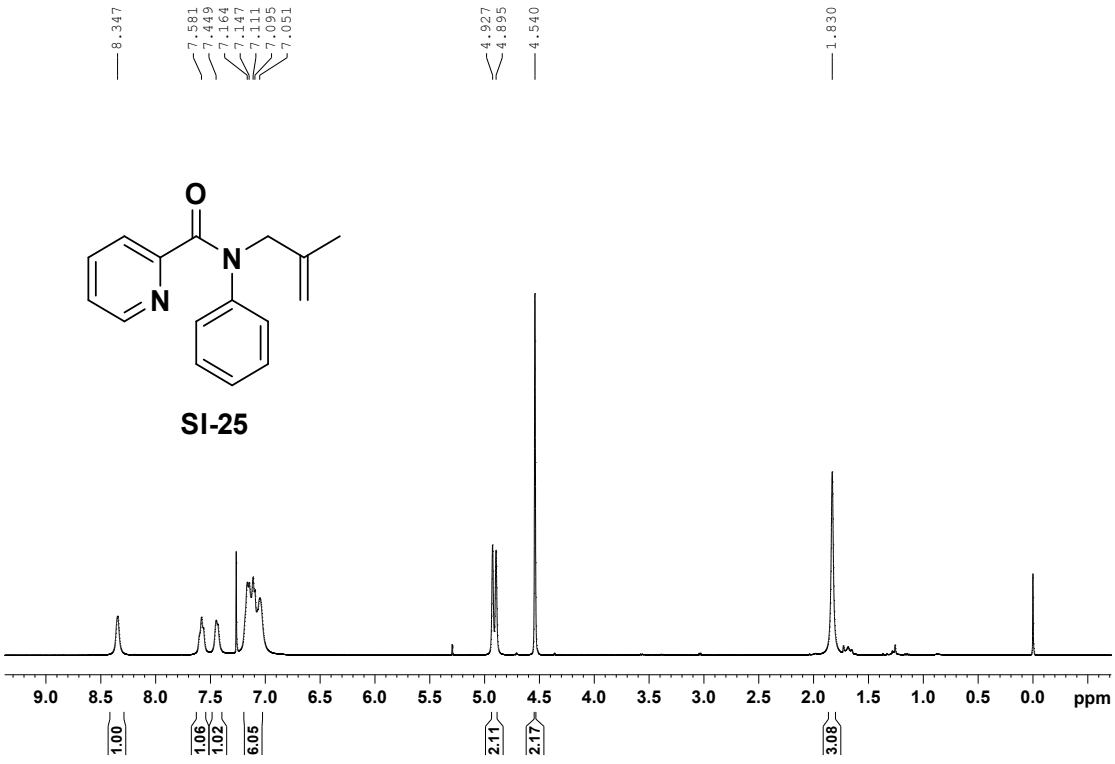

170.04
165.62
156.74
152.35
148.55
137.45
137.18
129.49
129.24
127.72
127.39
127.23
126.30
125.92
125.29
124.30
121.63
120.62
120.09
117.14
110.91
65.96
55.73
21.31
AcO
OMe
N
O
N
2t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

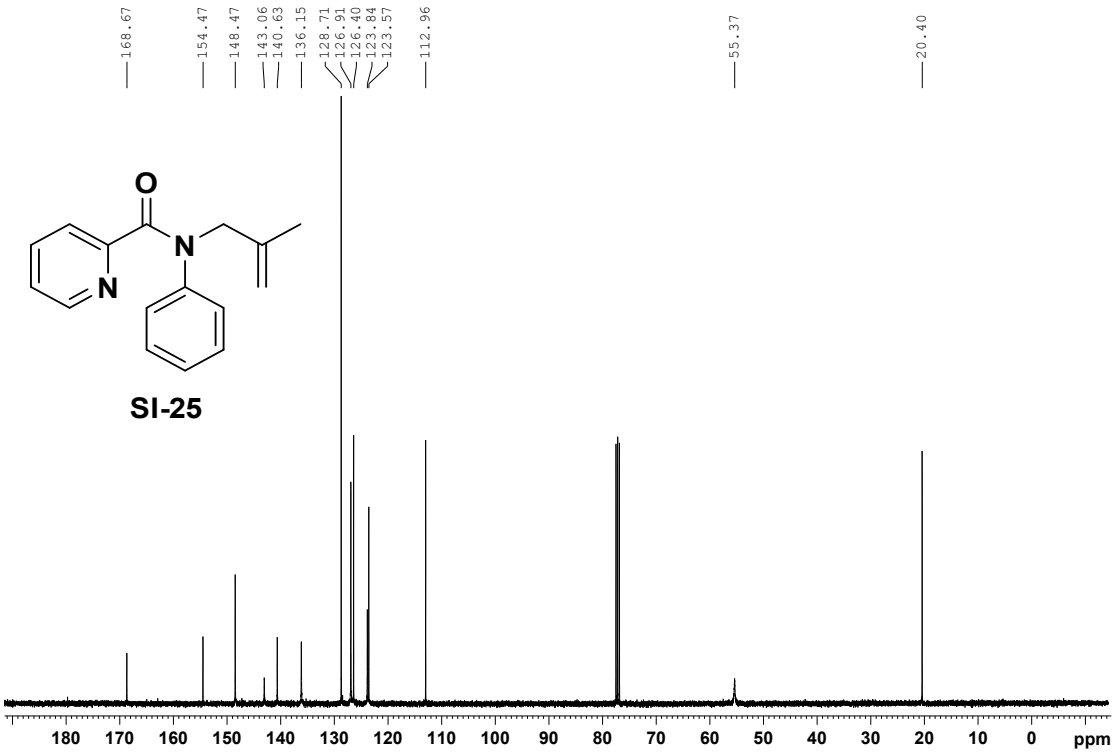

8.265
7.489
7.353
7.137
7.117
7.097
7.032
7.011
6.854
6.835
6.805
6.707
6.687
6.416
6.378
6.350
6.337
6.322
6.298
6.284
4.616
4.603
3.712
N
OMe O
N
1u
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.10
1.02
7.18
2.03
1.06
2.16
2.09
3.02

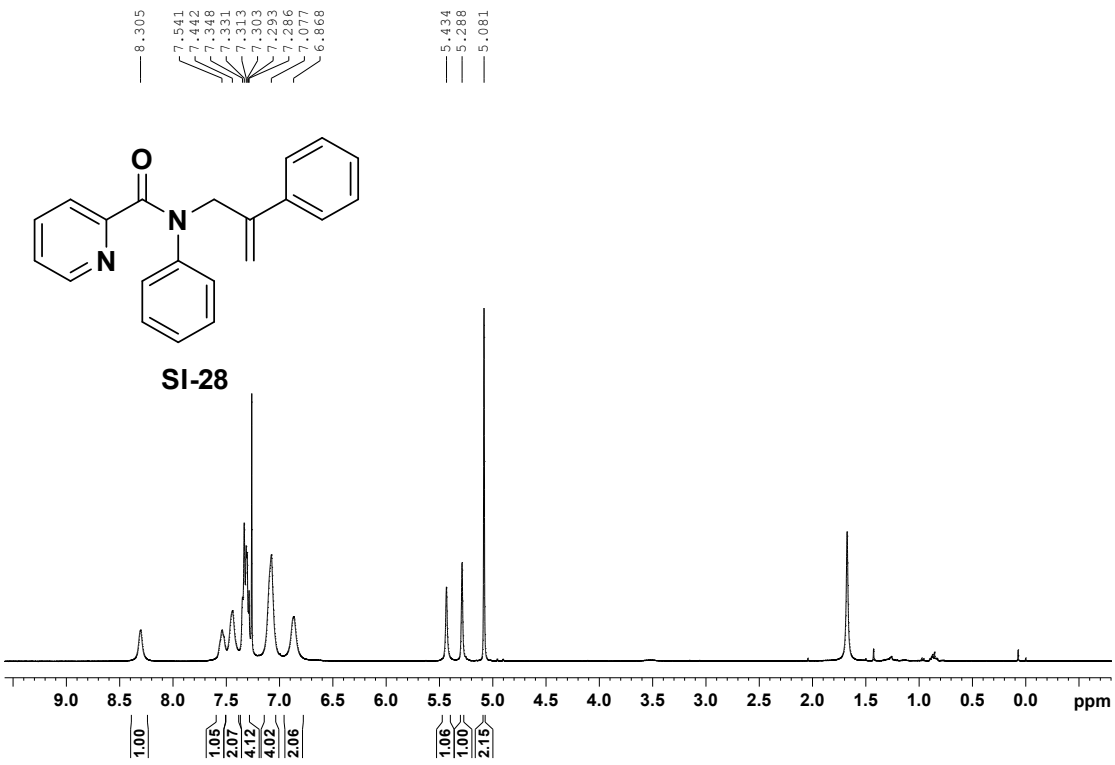

168.59
159.83
154.32
148.61
142.90
138.15
136.25
133.44
129.55
129.02
127.72
126.86
124.51
124.01
123.72
119.31
113.61
111.66
55.31
52.58
N
OMe O
N
1u
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

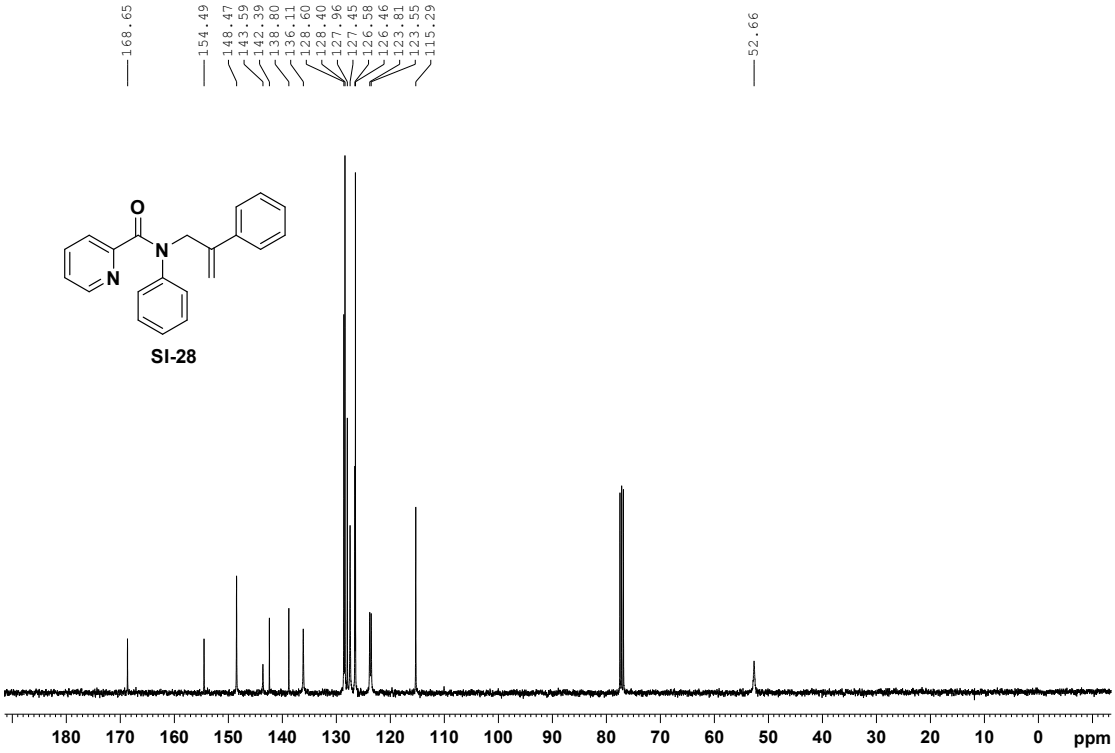

8.431
8.410
8.017
7.997
7.939
7.863
7.845
7.826
7.441
7.427
7.423
7.410
7.388
7.369
7.311
7.291
7.273
7.198
7.193
7.177
7.158
7.054
6.978
6.959
6.936
6.770
6.765
6.749
6.744
3.697
2.064
AcO
OMe
N
O
N
2u
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.98
1.01
1.02
1.03
2.03
1.09
2.23
1.06
2.01
1.03
3.01
3.02

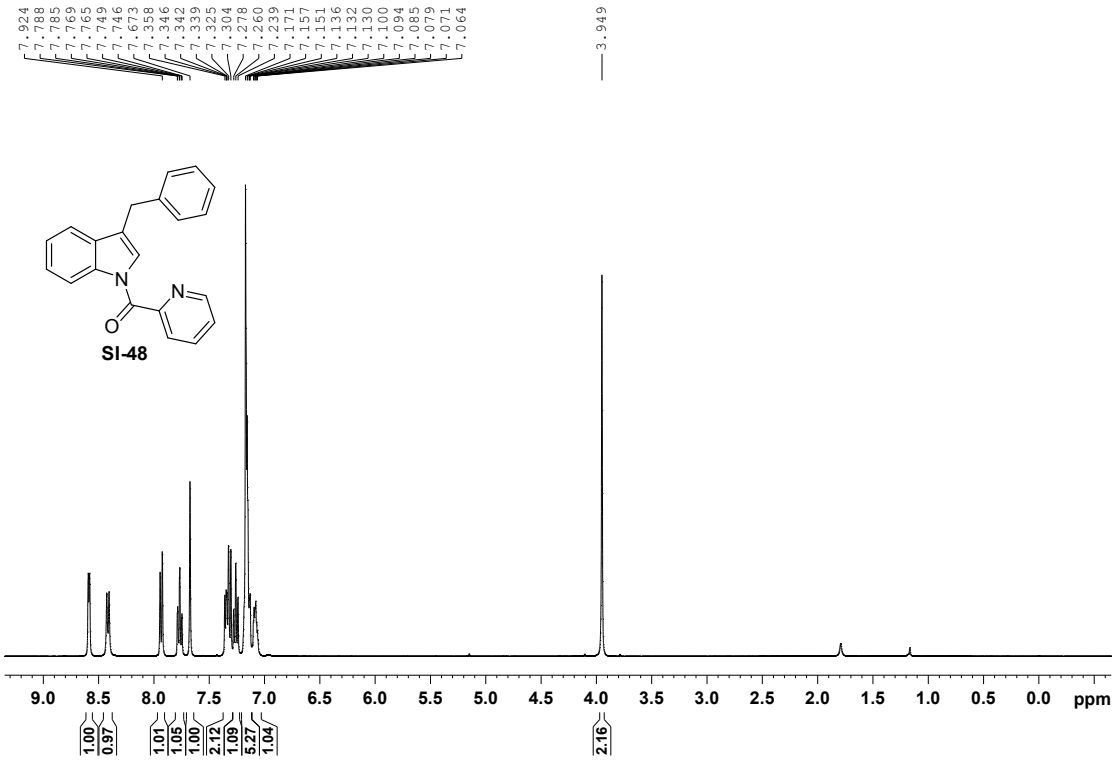

170.24
165.59
159.80
152.16
148.59
140.39
137.54
137.30
129.67
128.79
127.59
126.42
126.03
125.46
124.35
121.35
120.07
119.58
117.20
113.54
113.05
70.96
55.39
21.34
AcO
OMe
N
O
N
2u
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.347
7.581
7.449
7.164
7.147
7.111
7.095
7.051
4.927
4.895
4.540
1.830
O
N
N
SI-25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.06
1.02
6.05
2.11
2.17
3.08


168.67
154.47
148.47
143.06
140.63
136.15
128.71
126.91
126.40
123.84
123.57
112.96
55.37
20.40
O
N
N
SI-25
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.305
7.541
7.442
7.348
7.331
7.313
7.303
7.293
7.286
7.077
6.868
5.434
5.288
5.081
O
N
N
SI-28
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.05
2.07
4.12
4.02
2.06
1.06
1.00
2.15


168.65
154.49
148.47
143.59
142.39
138.80
136.11
128.60
128.40
127.96
127.45
126.58
126.46
123.81
123.55
115.29
52.66
O
N
N
SI-28
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.924
7.788
7.785
7.769
7.765
7.749
7.746
7.673
7.358
7.346
7.342
7.339
7.325
7.304
7.278
7.260
7.239
7.171
7.157
7.151
7.136
7.132
7.130
7.100
7.094
7.085
7.079
7.071
7.064
3.949
N
N
O
SI-48
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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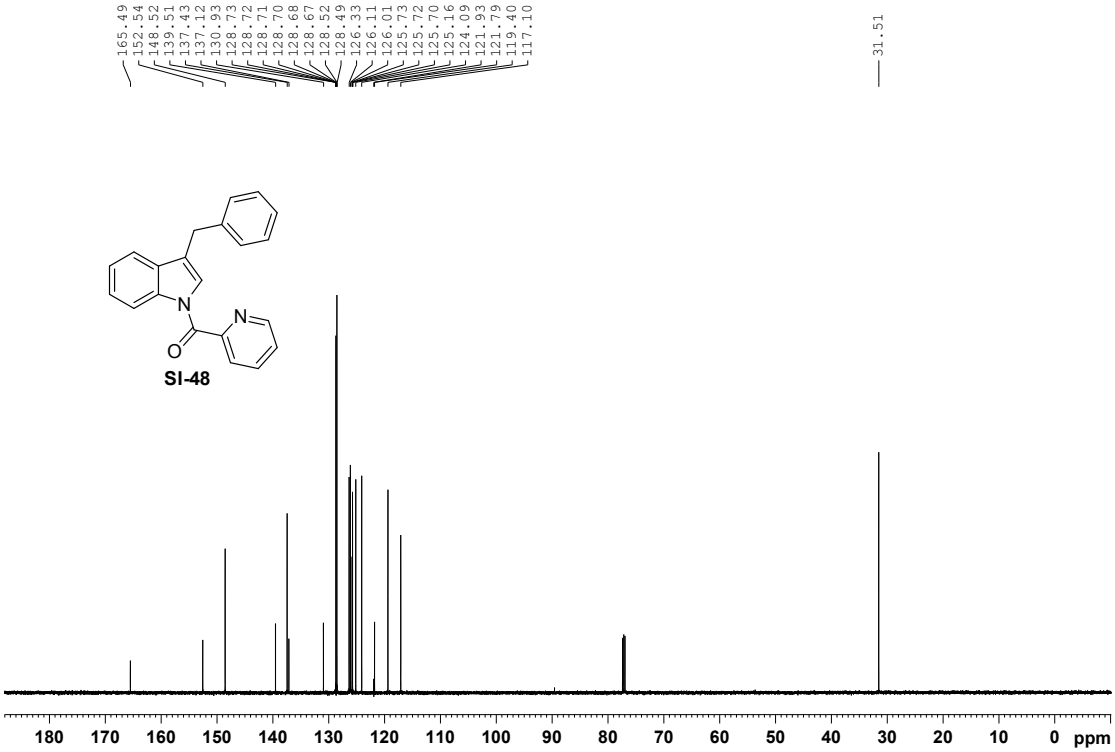
0.97
1.01
1.05
1.00
2.12
1.09
5.27
1.04
2.16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152.54
148.52
139.51
137.43
137.12
130.93
128.73
128.72
128.71
128.70
128.68
128.67
128.52
128.49
126.33
126.11
126.01
125.73
125.72
125.70
125.16
124.09
121.93
121.79
119.40
117.10
31.51
SI-48
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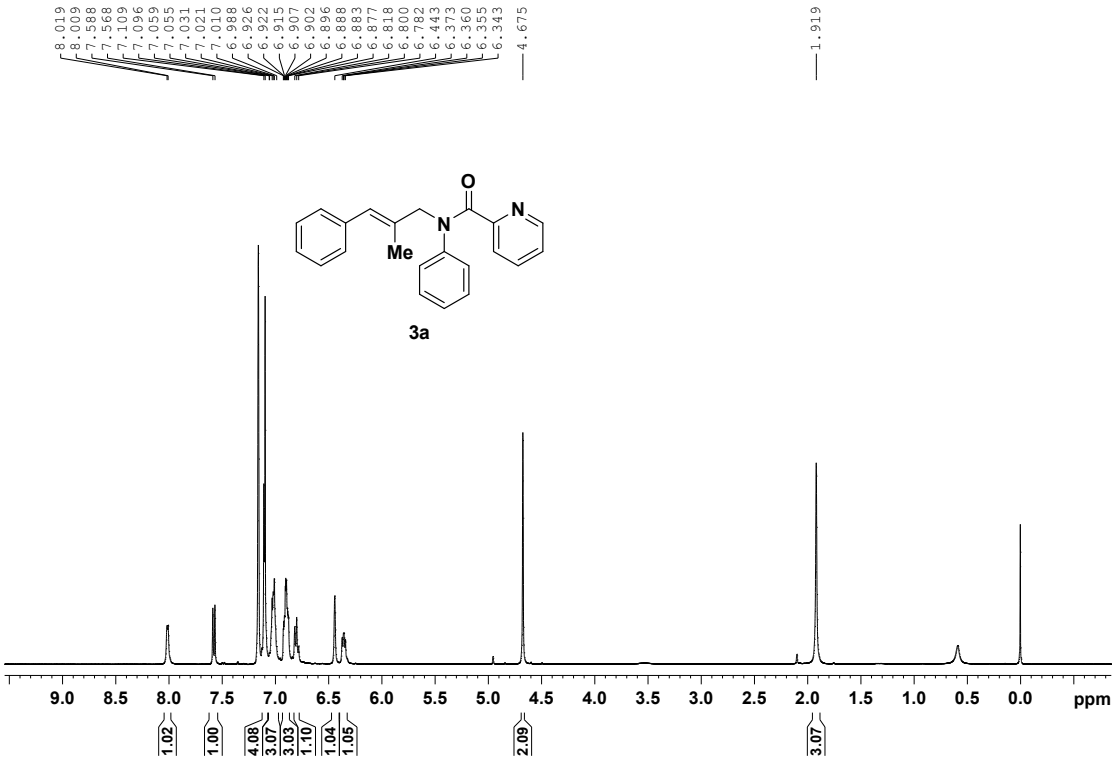
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7.096
7.059
7.055
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7.021
7.010
6.988
6.926
6.922
6.915
6.907
6.902
6.896
6.888
6.883
6.877
6.818
6.800
6.782
6.443
6.373
6.360
6.355
6.343
4.675
1.919
Me
3a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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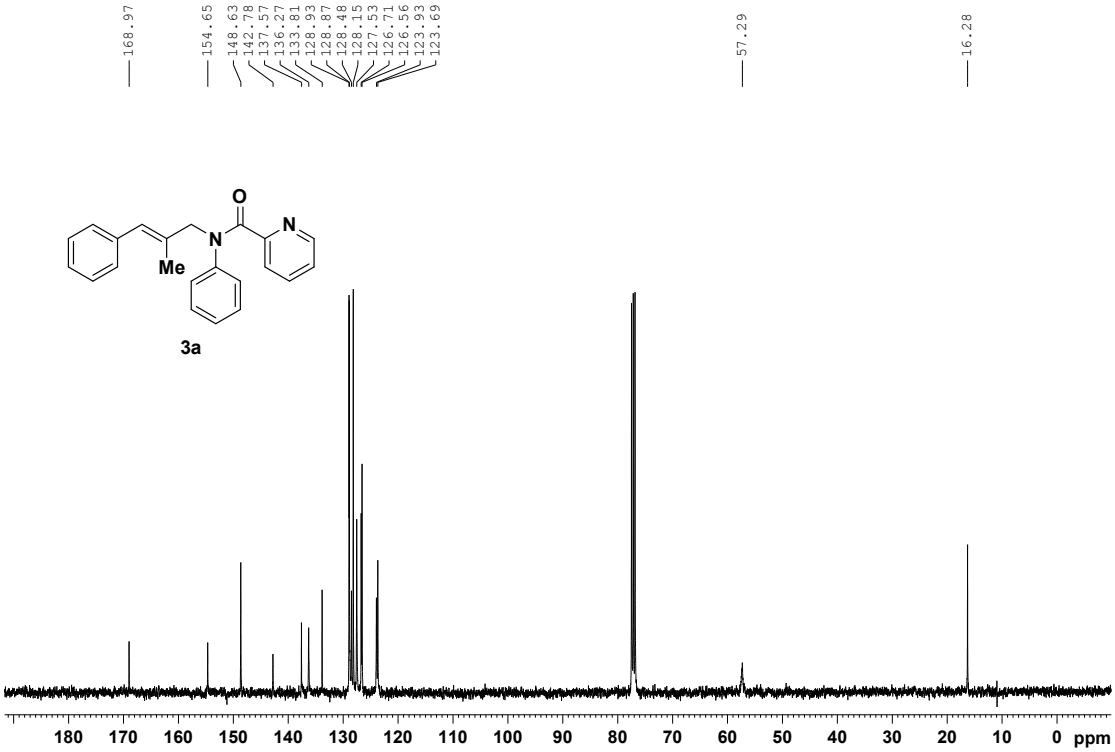
1.00
4.08
3.07
3.03
1.10
1.04
1.05
2.09
3.07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154.65
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142.78
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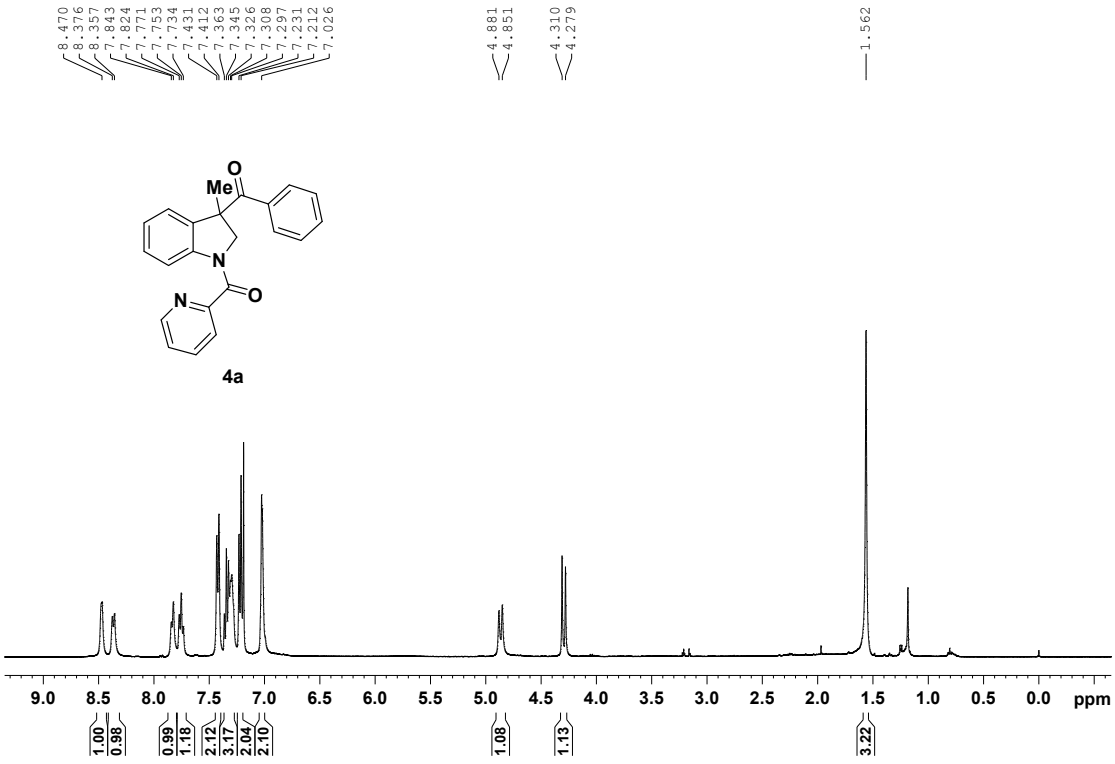
136.27
133.81
128.93
128.87
128.48
128.15
127.53
126.71
126.56
123.93
123.69
57.29
16.28
O
N
N
Me
3a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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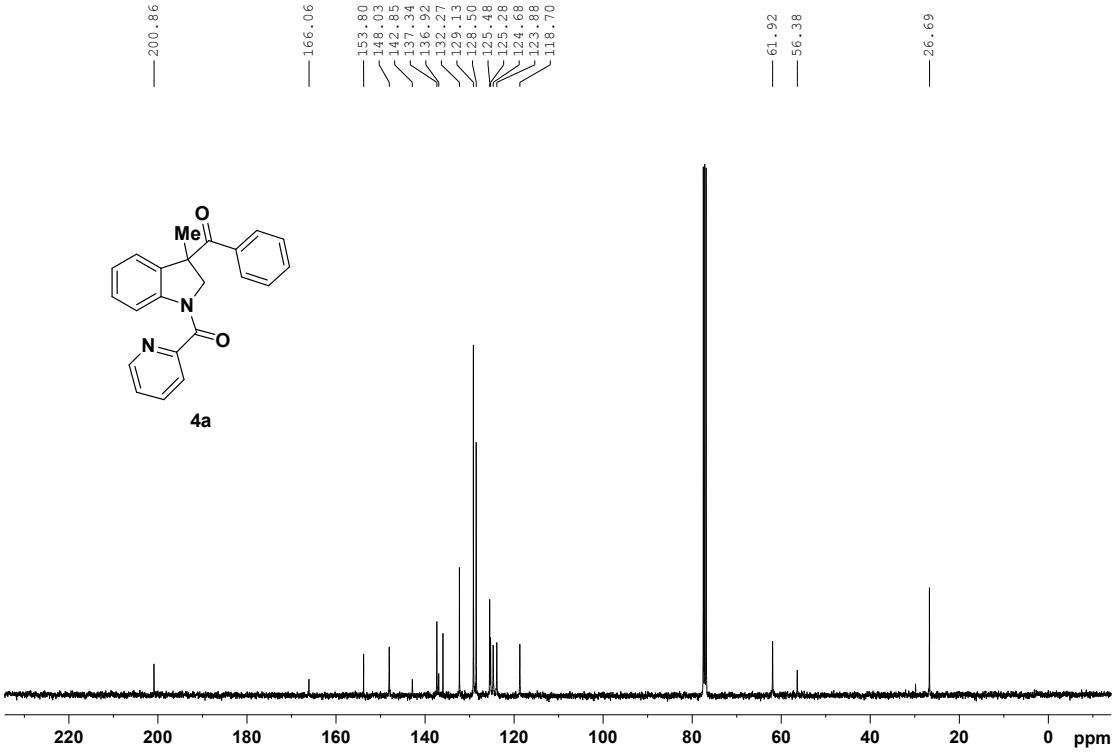
8.376
8.357
7.843
7.824
7.771
7.753
7.734
7.431
7.412
7.363
7.345
7.326
7.308
7.297
7.231
7.212
7.026
4.881
4.851
4.310
4.279
1.562
O
Me
N
O
N
4a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.98
0.99
1.18
2.12
3.17
2.04
2.10
1.08
1.13
3.22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153.80
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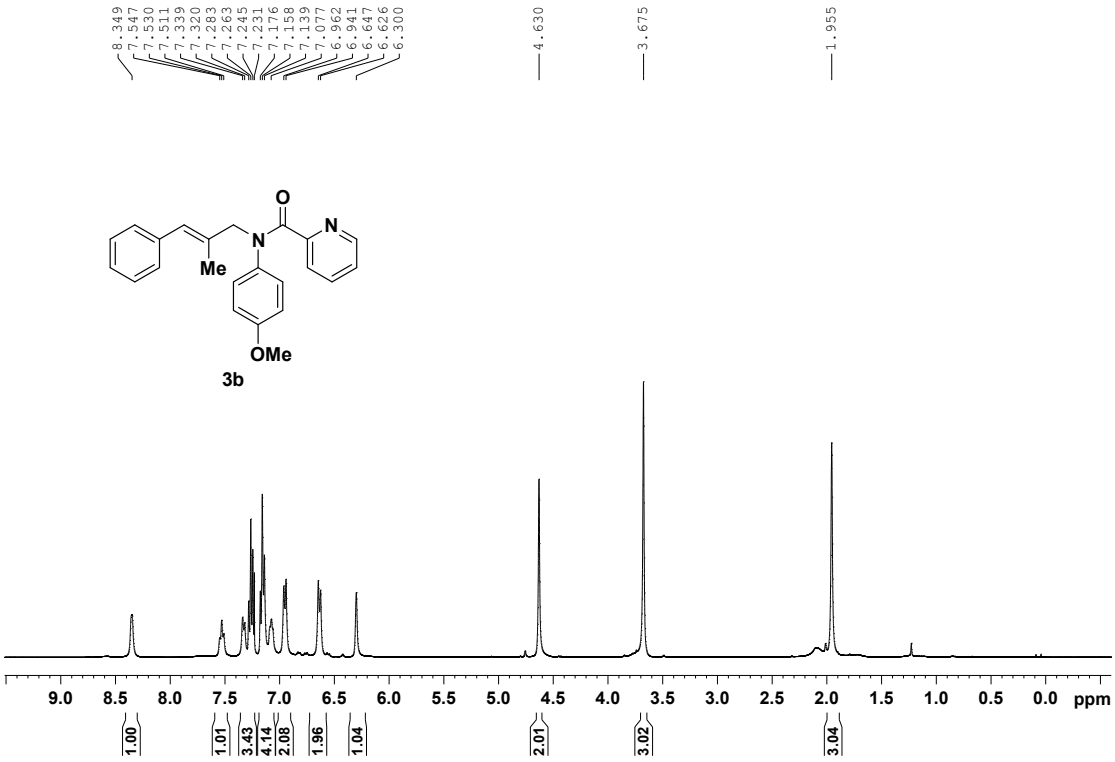
142.85
137.34
136.92
132.27
129.13
128.50
125.48
125.28
124.68
123.88
118.70
61.92
56.38
26.69
Me
O
N
O
N
4a
220
200
180
160
140
120
100
80
60
40
20
0
ppm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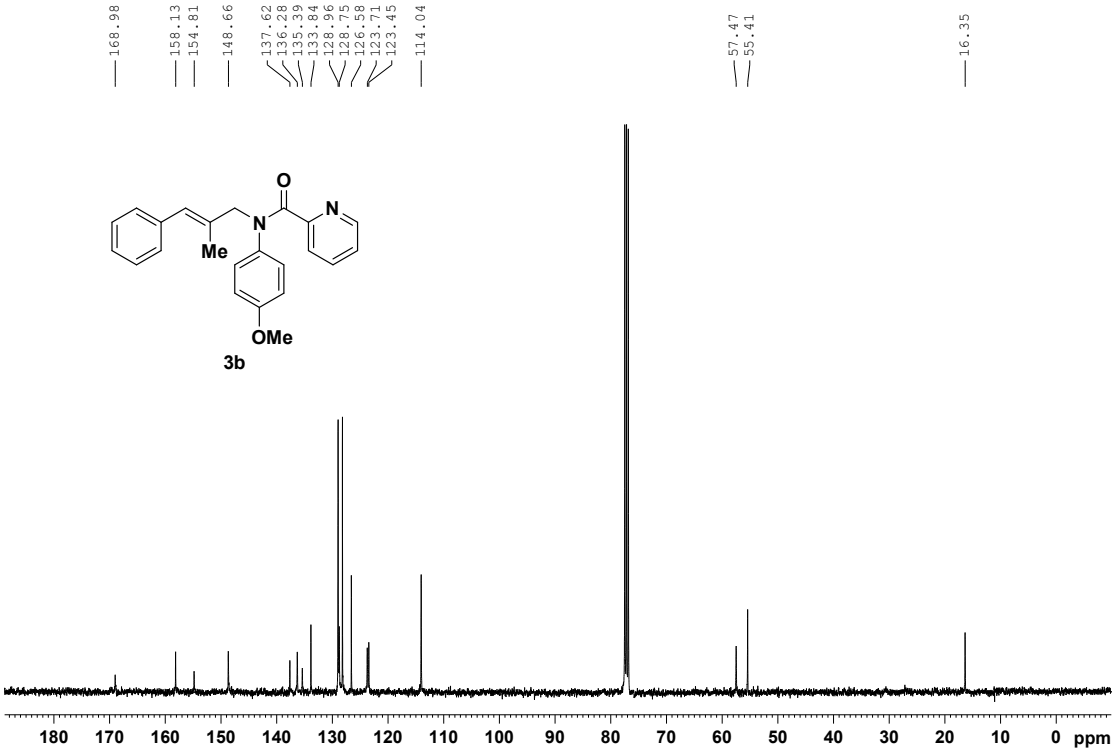
7.530
7.511
7.339
7.320
7.283
7.263
7.245
7.231
7.176
7.158
7.139
7.077
6.962
6.941
6.647
6.626
6.300
4.630
3.675
1.955
O
N
N
Me
OMe
3b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.01
3.43
4.14
2.08
1.96
1.04
2.01
3.02
3.04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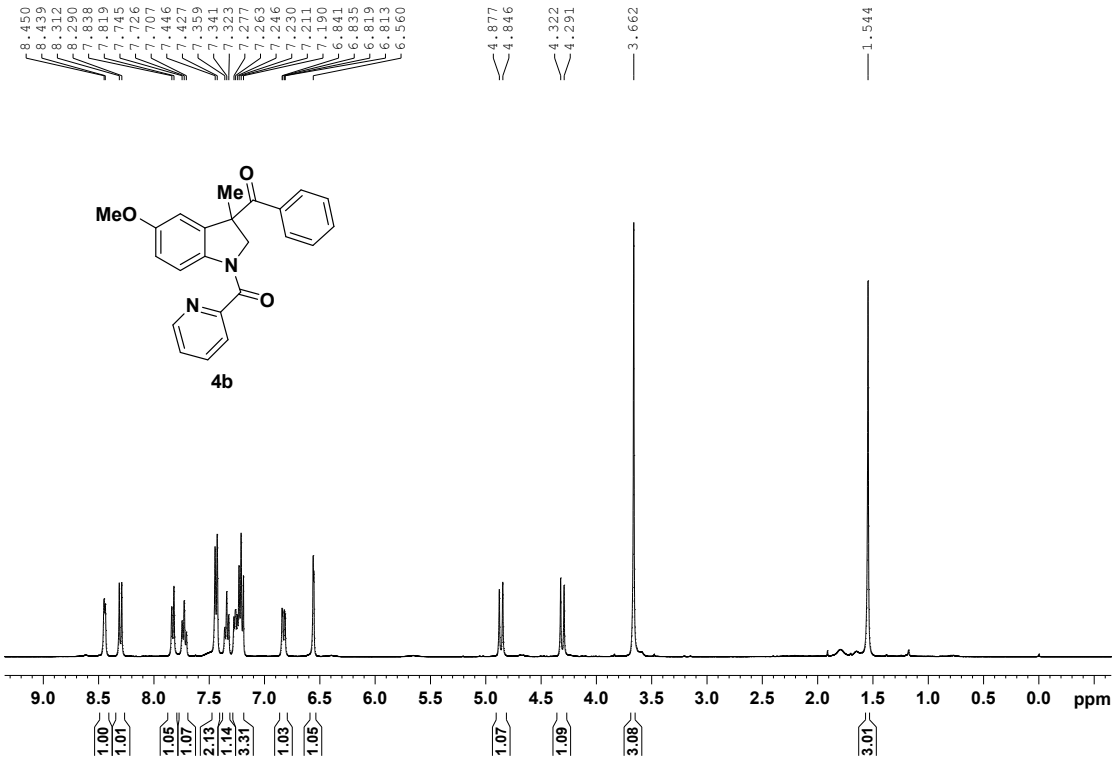
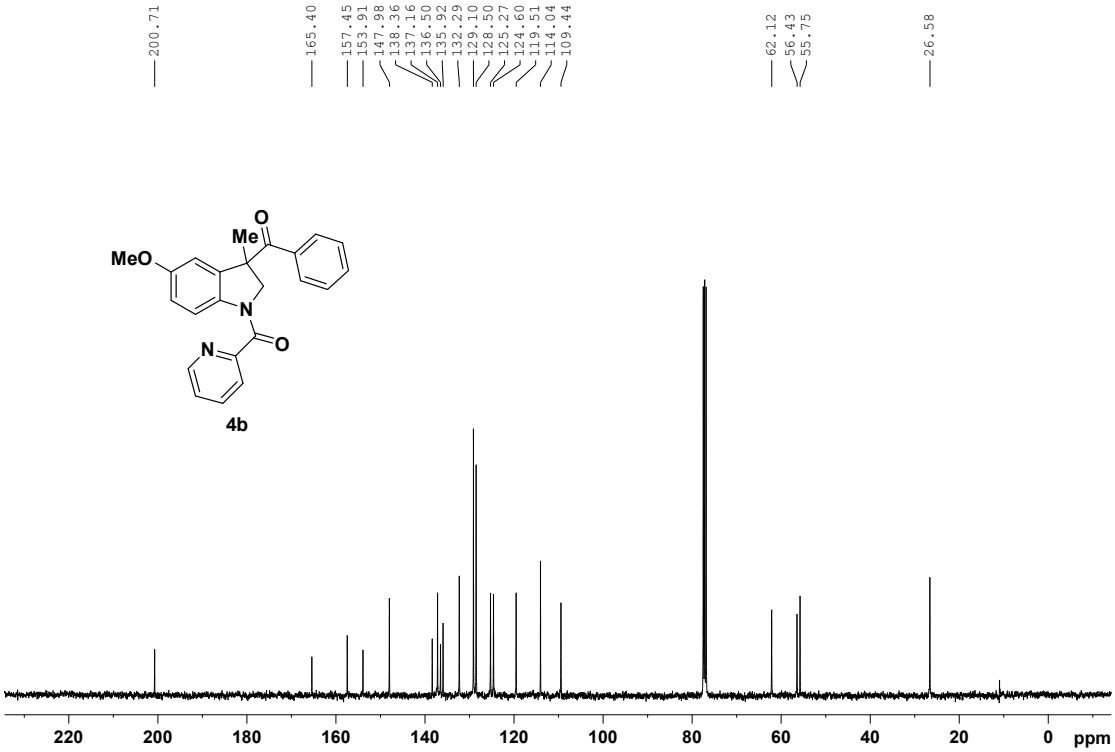
158.13
154.81
148.66
137.62
136.28
135.39
133.84
128.96
128.75
126.58
123.71
123.45
114.04
57.47
55.41
16.35
O
N
N
Me
OMe
3b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.450
8.439
8.312
8.290
7.838
7.819
7.745
7.726
7.707
7.446
7.427
7.359
7.341
7.323
7.277
7.263
7.246
7.230
7.211
7.190
6.841
6.835
6.819
6.813
6.560
4.877
4.846
4.322
4.291
3.662
1.544
O
Me
MeO
N
N
O
4b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.01
1.05
1.07
2.13
1.14
3.31
1.03
1.05
1.07
1.09
3.08
3.01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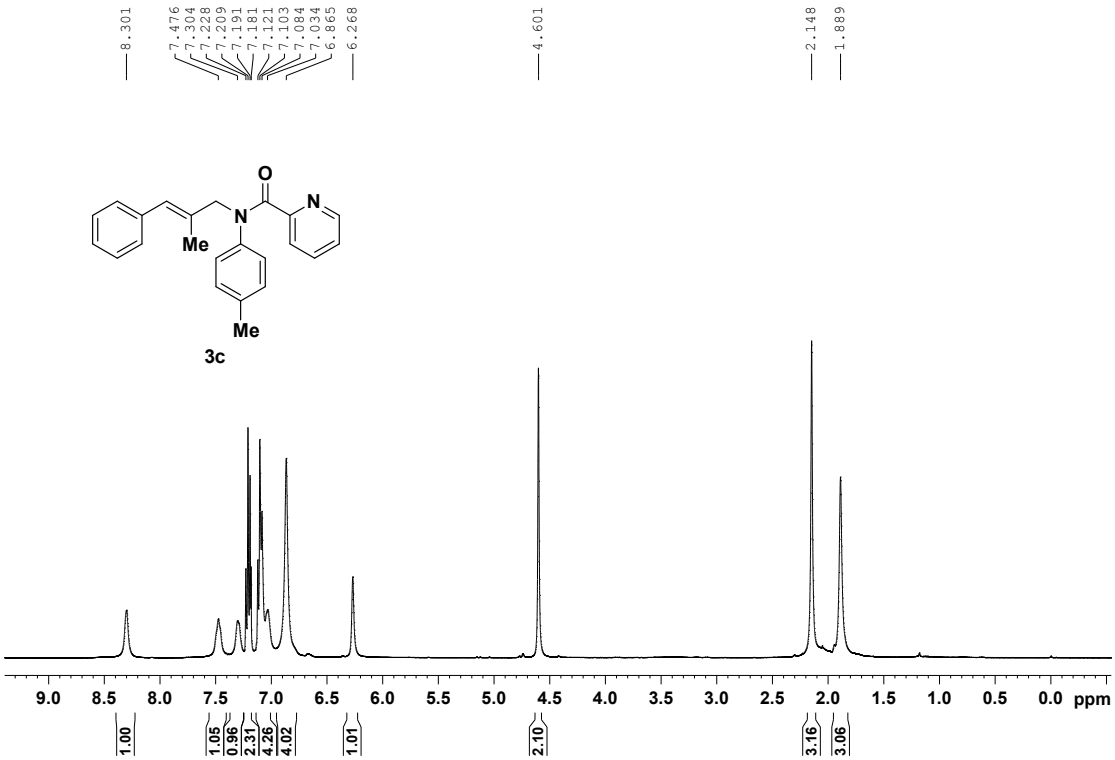
165.40
157.45
153.91
147.98
138.36
137.16
136.50
135.92
132.29
129.10
128.50
125.27
124.60
119.51
114.04
109.44
62.12
56.43
55.75
26.58
O
Me
MeO
N
N
O
4b
220
200
180
160
140
120
100
80
60
40
20
0
ppm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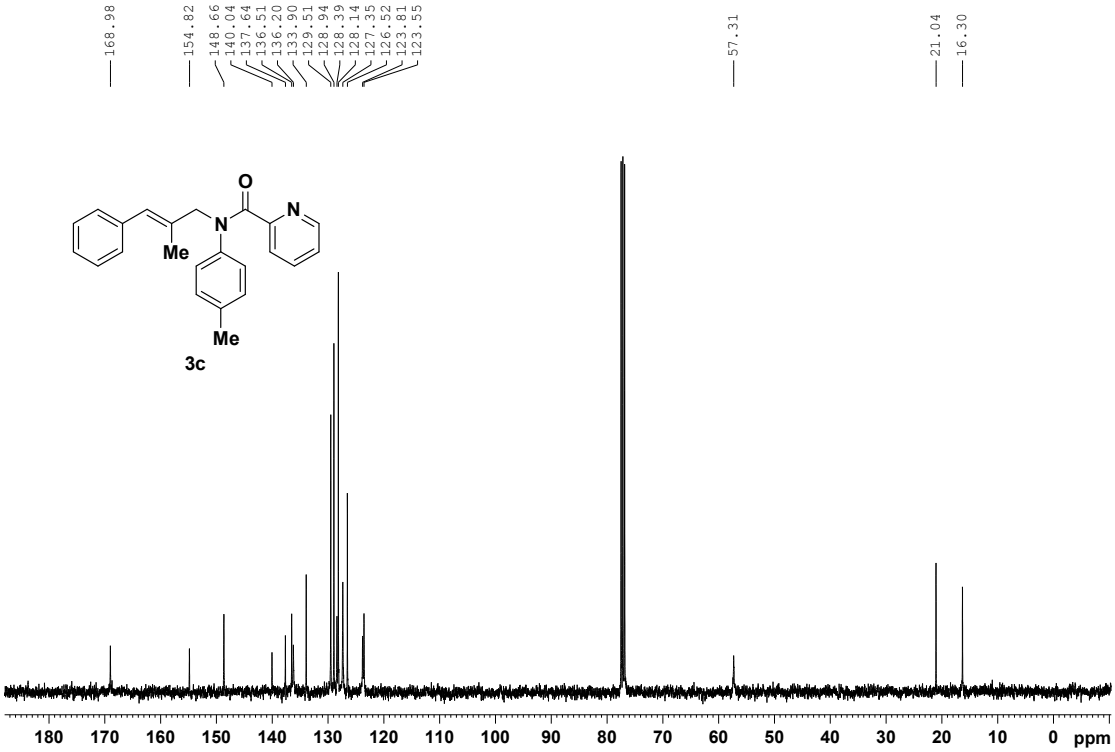
7.476
7.304
7.228
7.209
7.191
7.181
7.121
7.103
7.084
7.034
6.865
6.268
4.601
2.148
1.889
O
N
N
Me
Me
3c
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.05
0.96
2.31
4.26
4.02
1.01
2.10
3.16
3.06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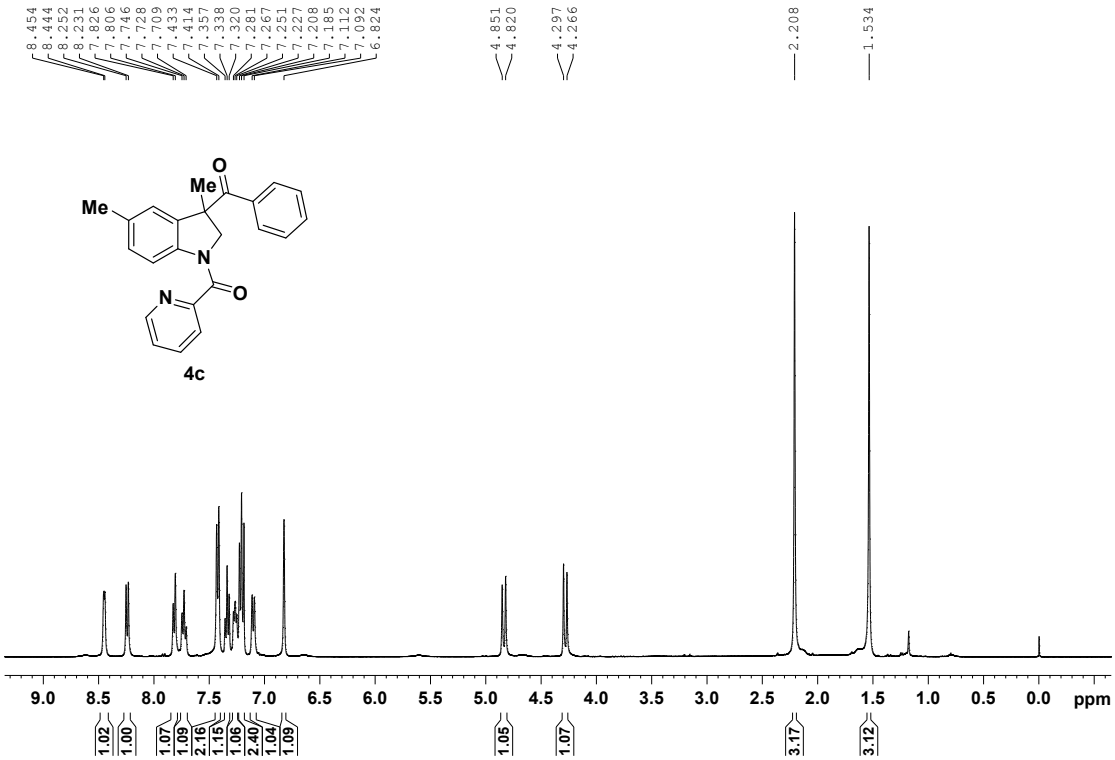
154.82
148.66
140.04
137.64
136.51
136.20
133.90
129.51
128.94
128.39
128.14
127.35
126.52
123.81
123.55
57.31
21.04
16.30
O
N
N
Me
Me
3c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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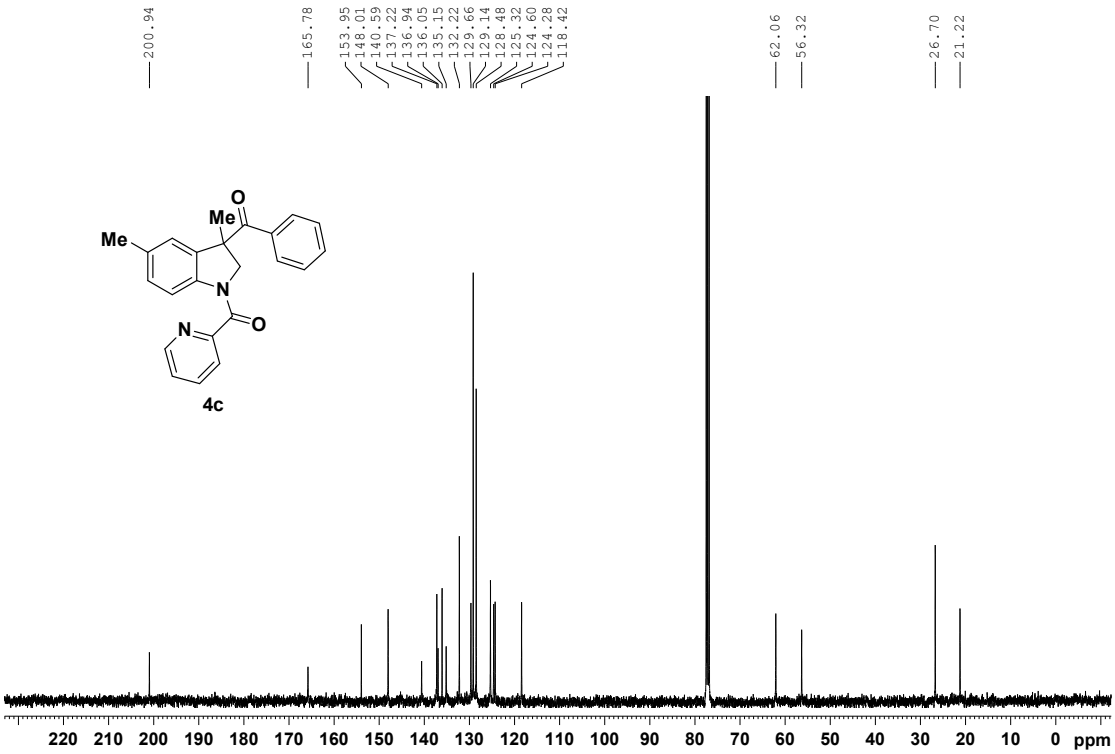
8.444
8.252
8.231
7.826
7.806
7.746
7.728
7.709
7.433
7.414
7.357
7.338
7.320
7.281
7.267
7.251
7.227
7.208
7.185
7.112
7.092
6.824
4.851
4.820
4.297
4.266
2.208
1.534
O
Me
Me
N
N
O
4c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.02
1.00
1.07
1.09
2.16
1.15
1.06
2.40
1.04
1.09
1.05
1.07
3.17
3.12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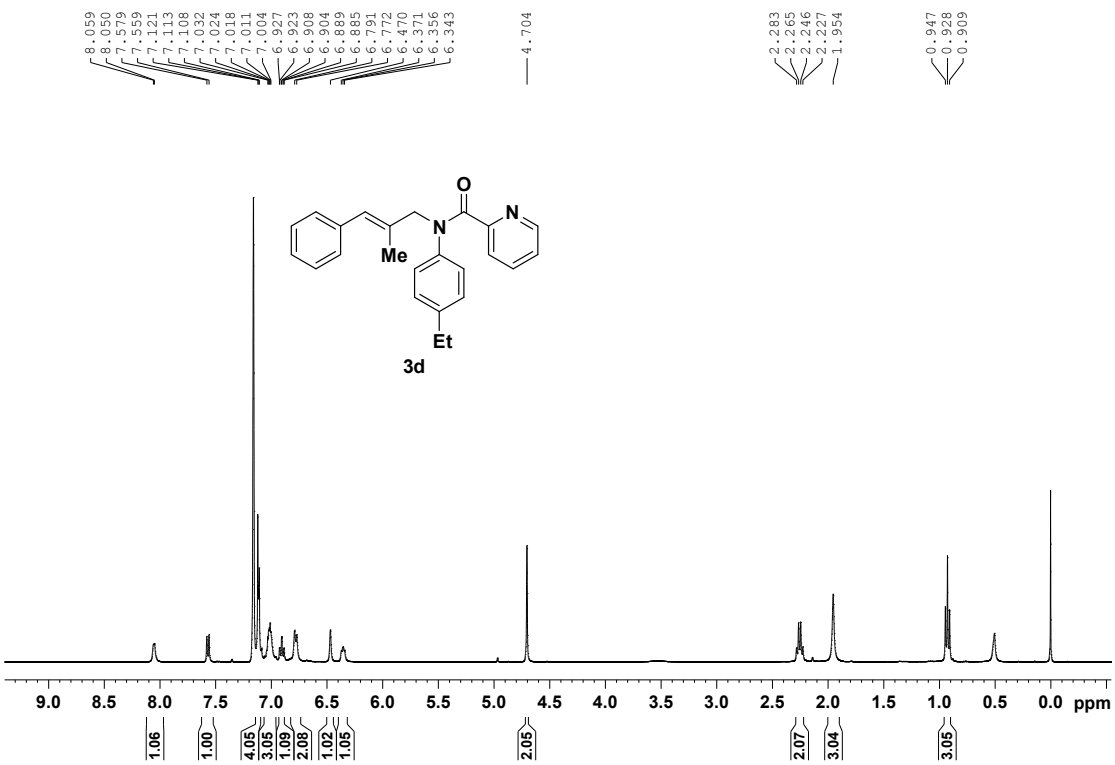
153.95
148.01
140.59
137.22
136.94
136.05
135.15
132.22
129.66
129.14
128.48
125.32
124.60
124.28
118.42
62.06
56.32
26.70
21.22
O
Me
Me
N
N
O
4c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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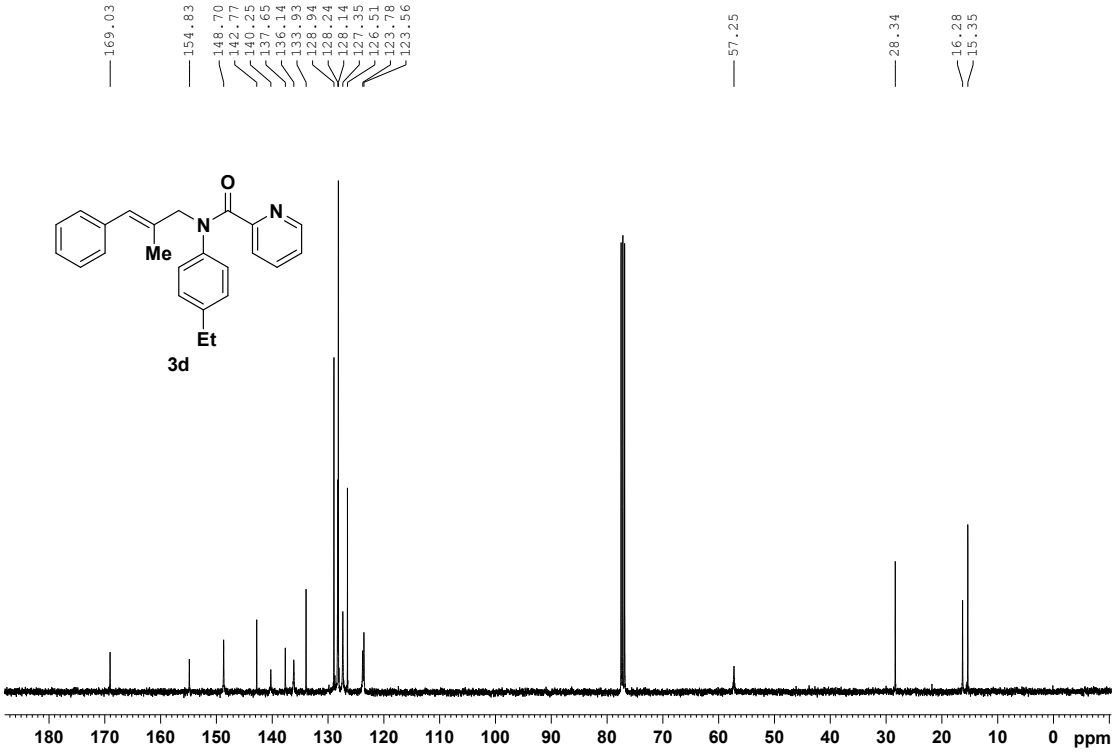
8.050
7.579
7.559
7.121
7.113
7.108
7.032
7.024
7.018
7.011
7.004
6.927
6.923
6.908
6.904
6.889
6.885
6.791
6.772
6.470
6.371
6.356
6.343
4.704
2.283
2.265
2.246
2.227
1.954
0.947
0.928
0.909
O
N
N
Me
Et
3d
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.06
1.00
4.05
3.05
1.09
2.08
1.02
1.05
2.05
2.07
3.04
3.05


169.03
154.83
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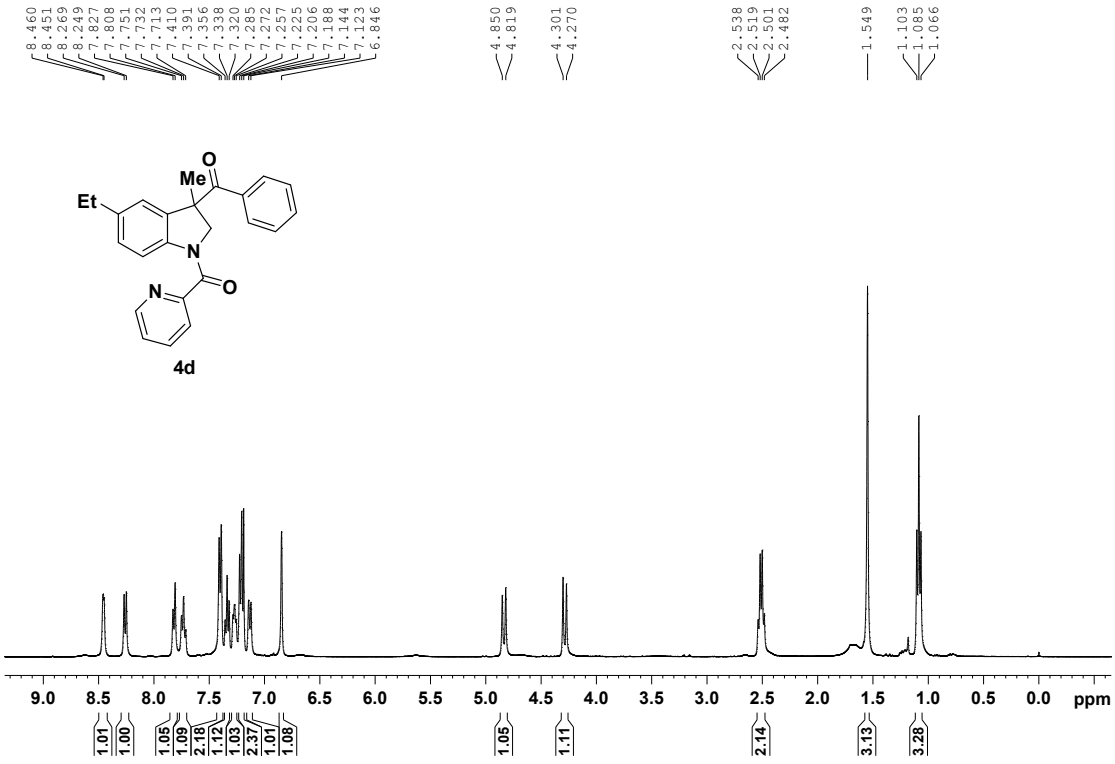
142.77
140.25
137.65
136.14
133.93
128.94
128.24
128.14
127.35
126.51
123.78
123.56
57.25
28.34
16.28
15.35
O
N
N
Me
Et
3d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.269
8.249
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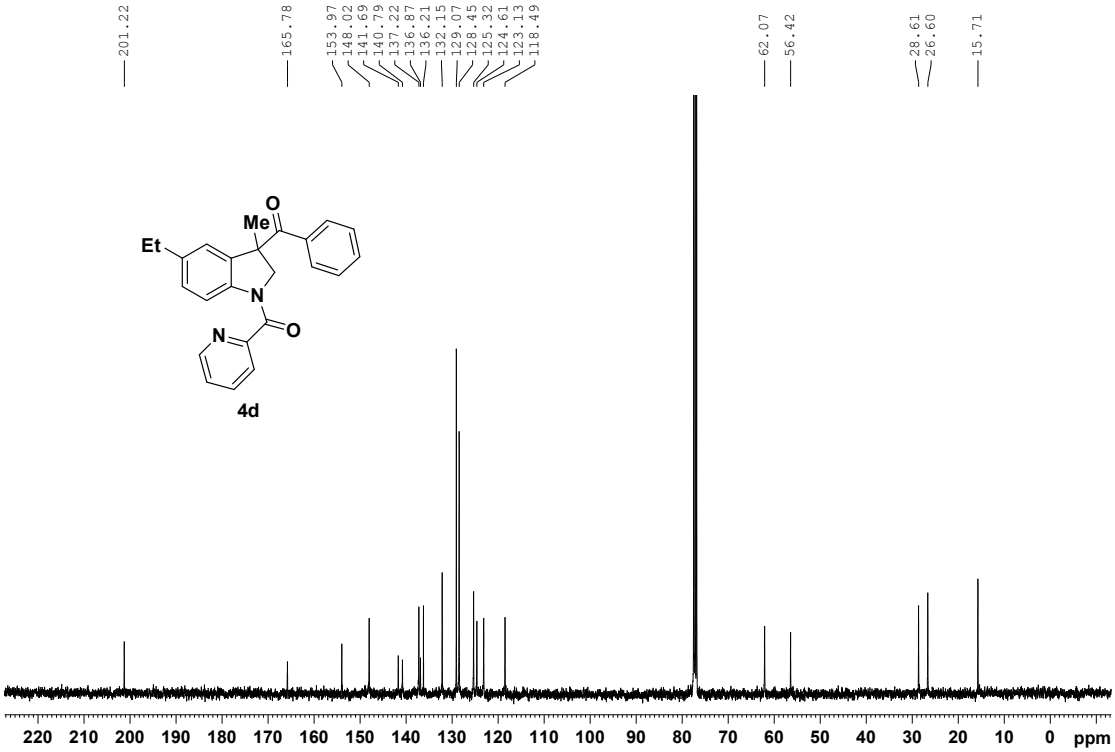
7.808
7.751
7.732
7.713
7.410
7.391
7.356
7.338
7.320
7.285
7.272
7.257
7.225
7.206
7.188
7.144
7.123
6.846
4.850
4.819
4.301
4.270
2.538
2.519
2.501
2.482
1.549
1.103
1.085
1.066
O
Me
Et
N
N
O
4d
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.01
1.00
1.05
1.09
2.18
1.12
1.03
2.37
1.01
1.08
1.05
1.11
2.14
3.13
3.28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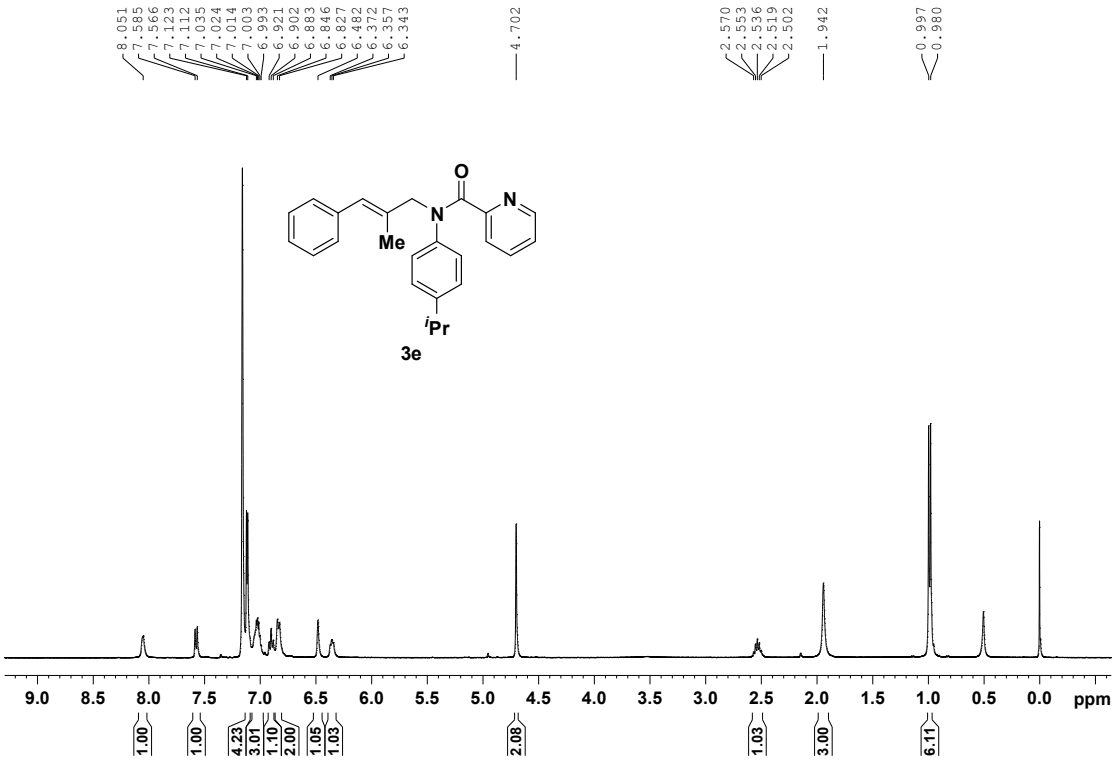
153.97
148.02
141.69
140.79
137.22
136.87
136.21
132.15
129.07
128.45
125.32
124.61
123.13
118.49
62.07
56.42
28.61
26.60
15.71
Et
Me
O
N
O
N
4d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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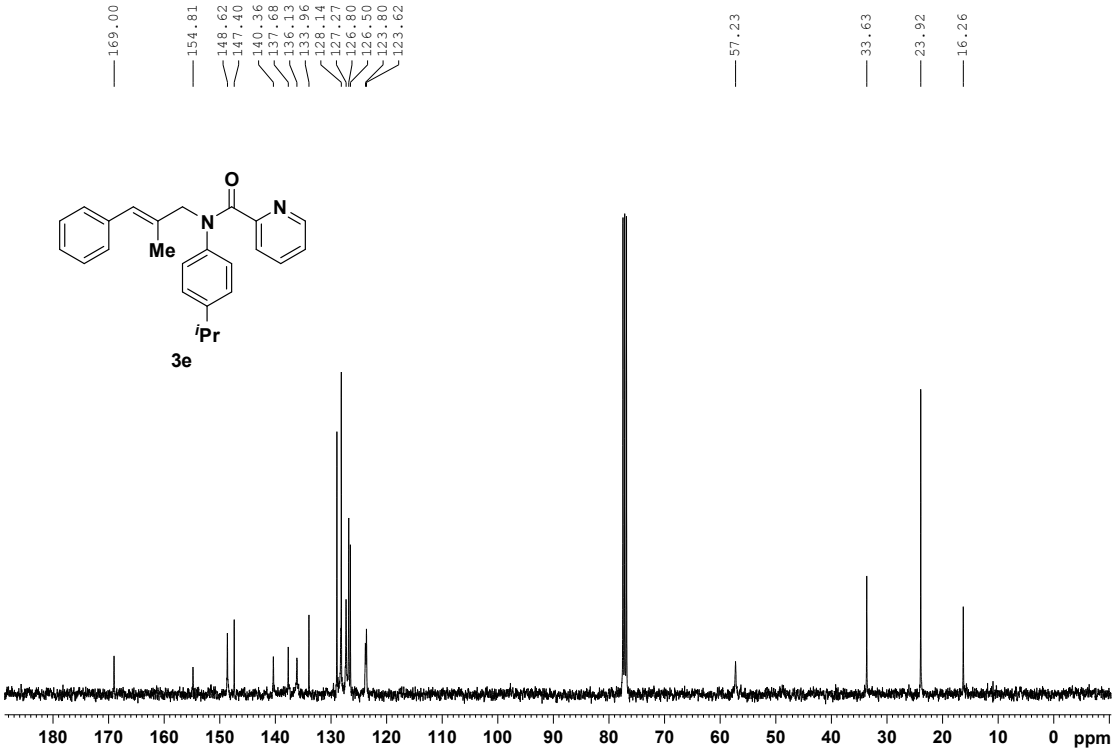
7.566
7.123
7.112
7.035
7.024
7.014
7.003
6.993
6.921
6.902
6.883
6.846
6.827
6.482
6.372
6.357
6.343
4.702
2.570
2.553
2.536
2.519
2.502
1.942
0.997
0.980
O
N
N
Me
iPr
3e
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
4.23
3.01
1.10
2.00
1.05
1.03
2.08
1.03
3.00
6.11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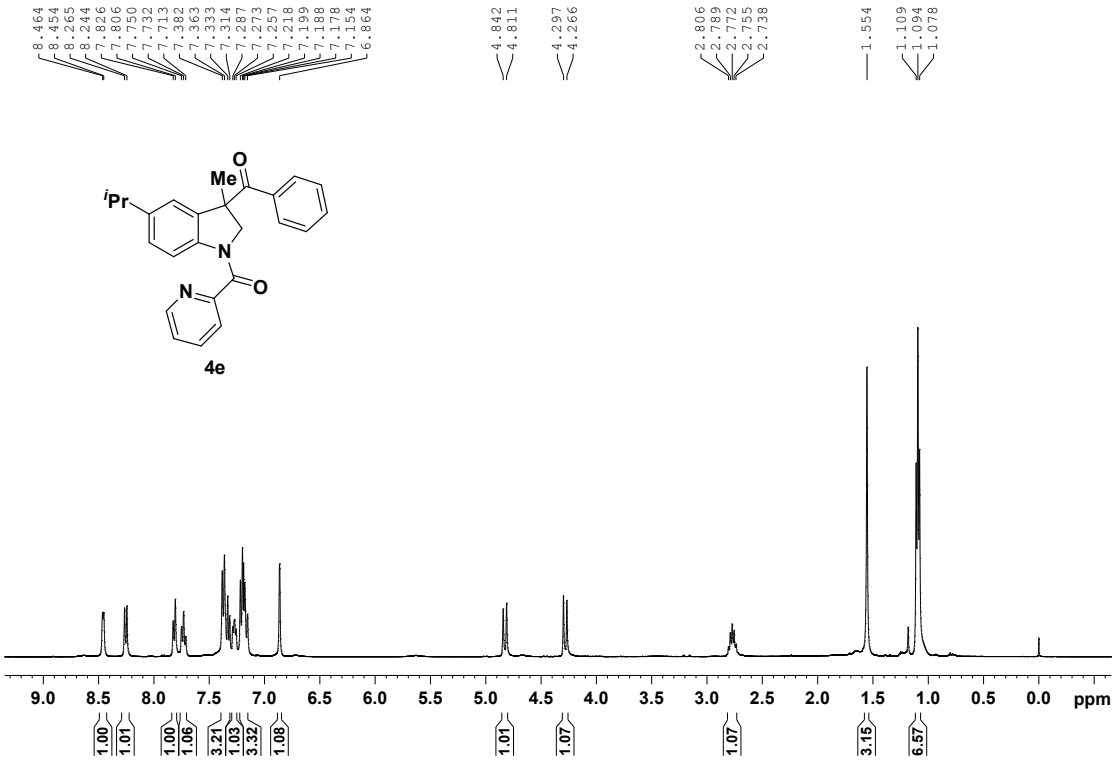
148.62
147.40
140.36
137.68
136.13
133.96
128.14
127.27
126.80
126.50
123.80
123.62
57.23
33.63
23.92
16.26
O
N
N
Me
iPr
3e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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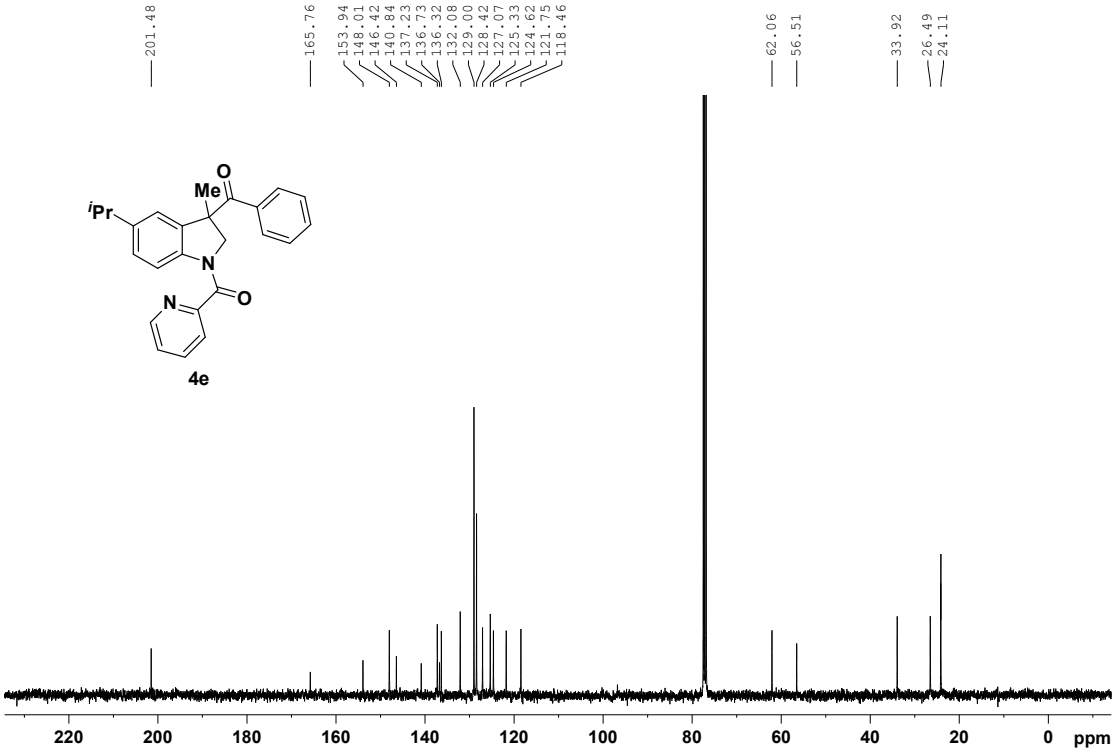
8.454
8.265
8.244
7.826
7.806
7.750
7.732
7.713
7.382
7.363
7.333
7.314
7.287
7.273
7.257
7.218
7.199
7.188
7.178
7.154
6.864
4.842
4.811
4.297
4.266
2.806
2.789
2.772
2.755
2.738
1.554
1.109
1.094
1.078
O
Me
iPr
N
N
O
4e
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.01
1.00
1.06
3.21
1.03
3.32
1.08
1.01
1.07
1.07
3.15
6.57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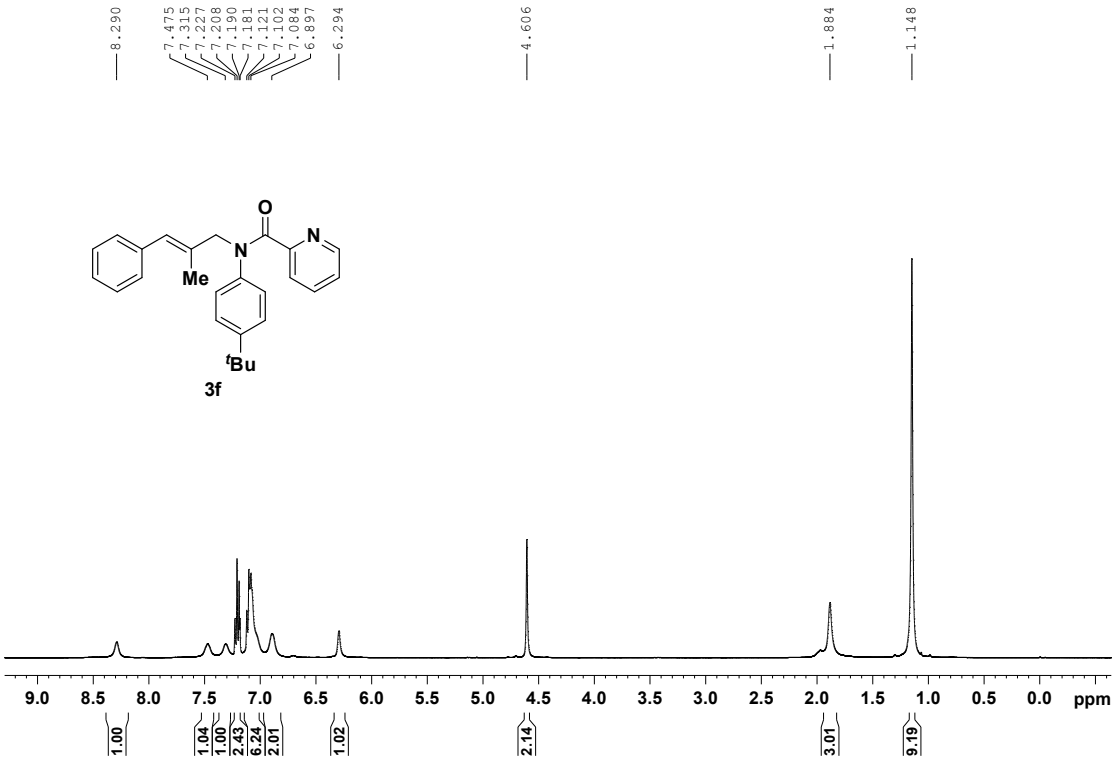
148.01
146.42
140.84
137.23
136.73
136.32
132.08
129.00
128.42
127.07
125.33
124.62
121.75
118.46
62.06
56.51
33.92
26.49
24.11
O
Me
iPr
N
O
N
4e
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.315
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7.208
7.190
7.181
7.121
7.102
7.084
6.897
6.294
4.606
1.884
1.148
O
N
N
Me
tBu
3f
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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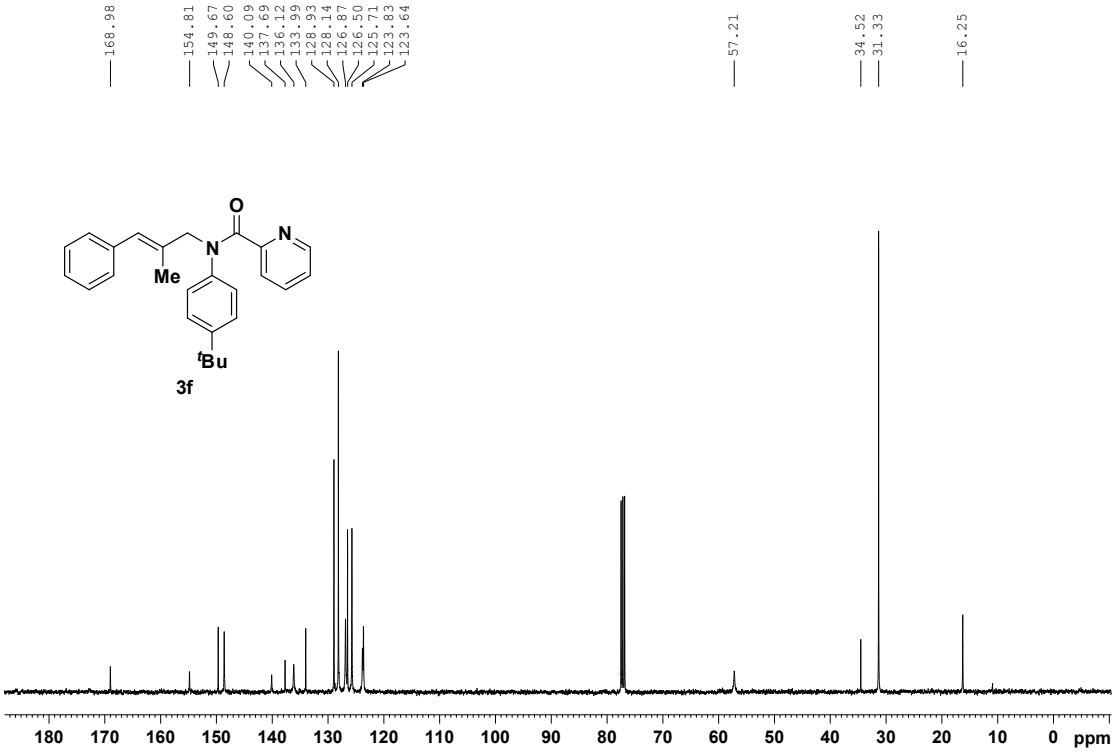
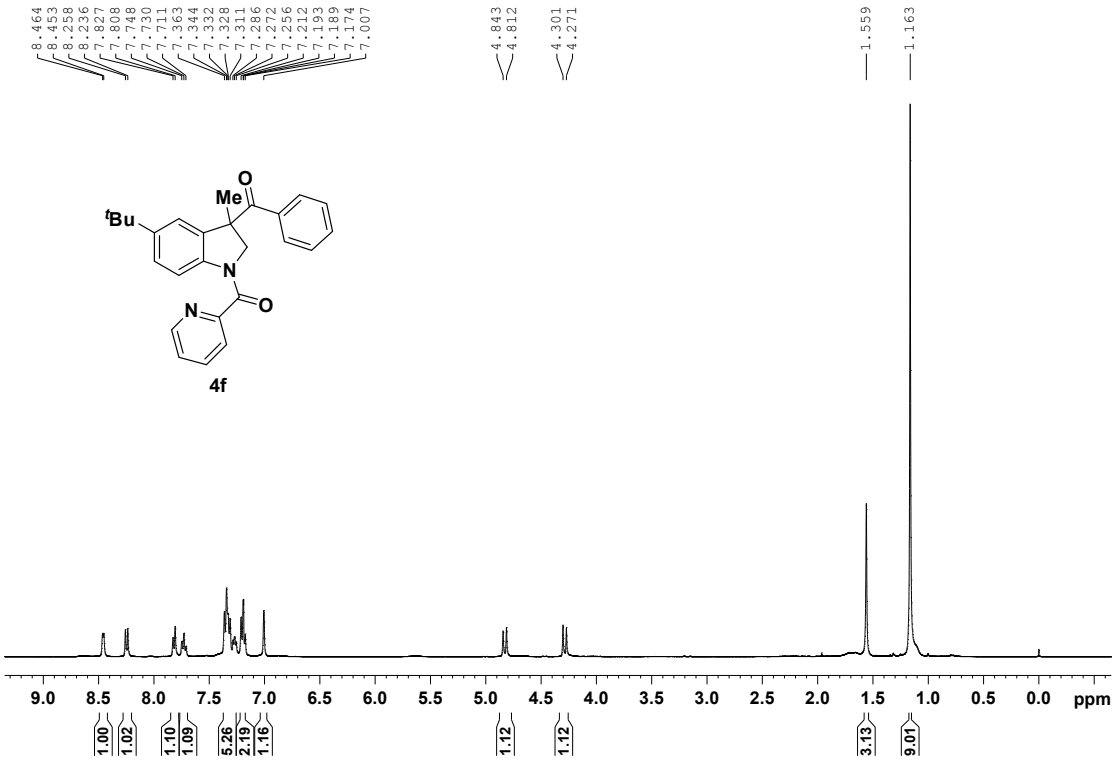
1.04
1.00
2.43
6.24
2.01
1.02
2.14
3.01
9.19


168.98
154.81
149.67
148.60
140.09
137.69
136.12
133.99
128.93
128.14
126.87
126.50
125.71
123.83
123.64
57.21
34.52
31.33
16.25
O
N
N
Me
tBu
3f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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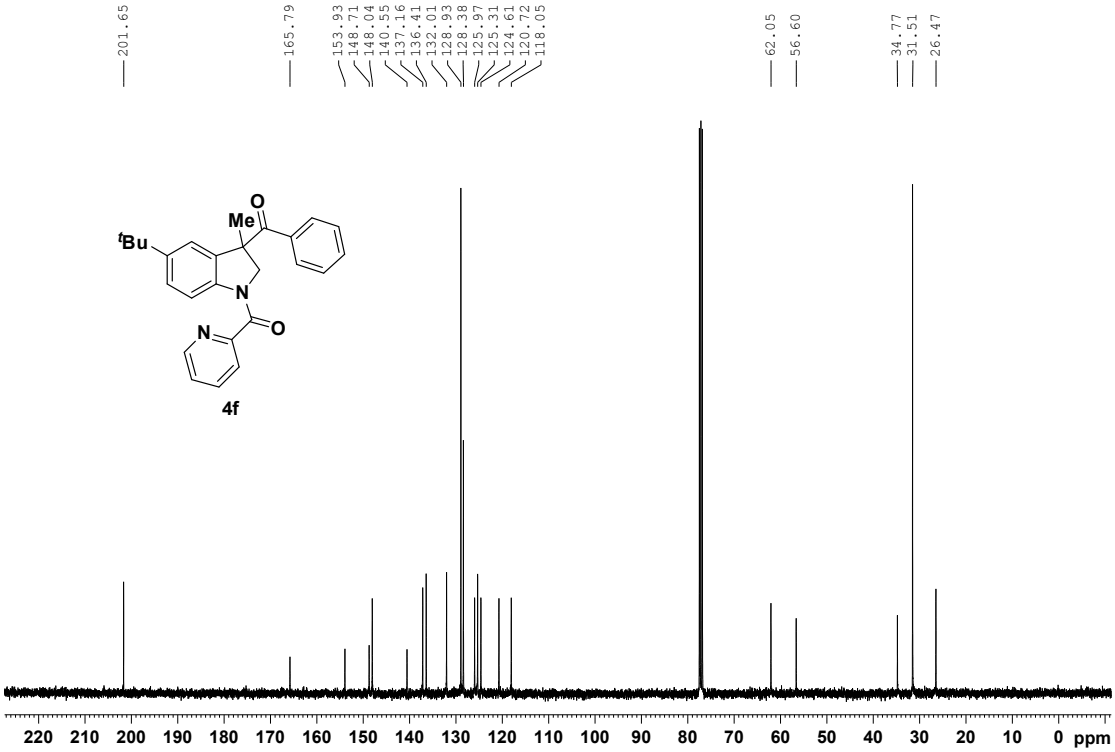
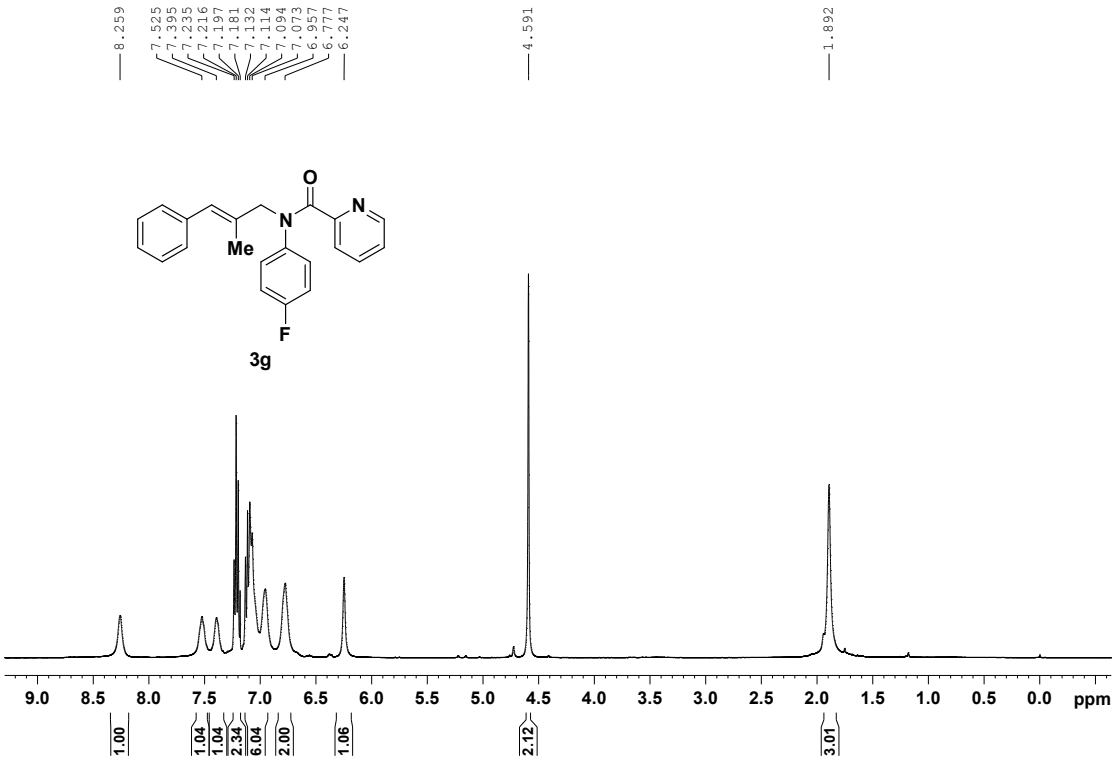
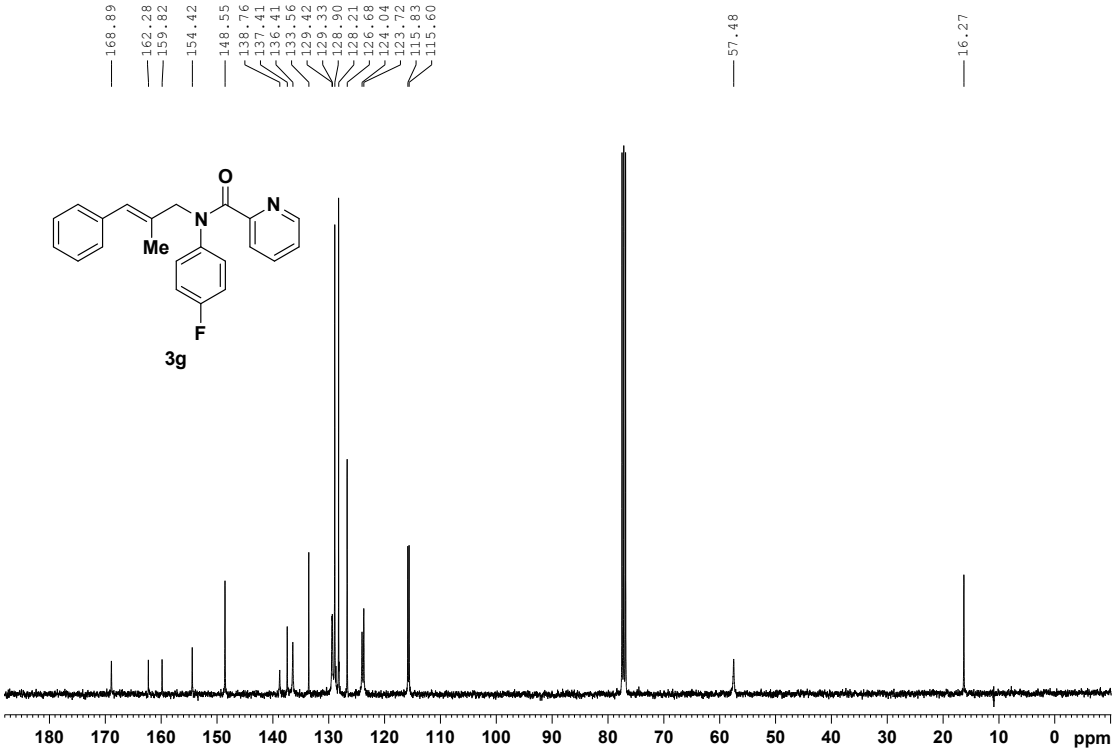
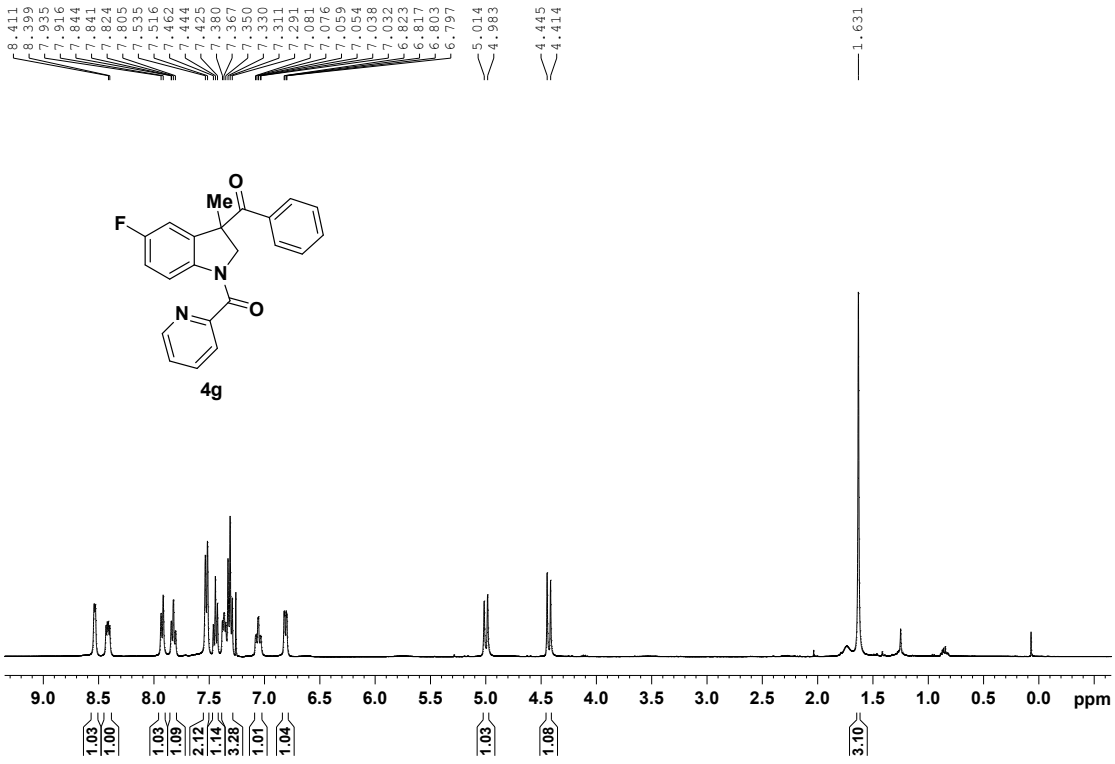
8.453
8.258
8.236
7.827
7.808
7.748
7.730
7.711
7.363
7.344
7.332
7.328
7.311
7.286
7.272
7.256
7.212
7.193
7.189
7.174
7.007
4.843
4.812
4.301
4.271
1.559
1.163
O
Me
tBu
N
N
O
4f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
1.10
1.09
5.26
2.19
1.16
1.12
1.12
3.13
9.01


201.65
165.79
153.93
148.71
148.04
140.55
137.16
136.41
132.01
128.93
128.38
125.97
125.31
124.61
120.72
118.05
62.05
56.60
34.77
31.51
26.47
O
Me
tBu
N
N
O
4f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.259
7.525
7.395
7.235
7.216
7.197
7.181
7.132
7.114
7.094
7.073
6.957
6.777
6.247
4.591
1.892
O
N
N
Me
F
3g
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.04
1.04
2.34
6.04
2.00
1.06
2.12
3.01


168.89
162.28
159.82
154.42
148.55
138.76
137.41
136.41
133.56
129.42
129.33
128.90
128.21
126.68
124.04
123.72
115.83
115.60
57.48
16.27
O
N
N
Me
F
3g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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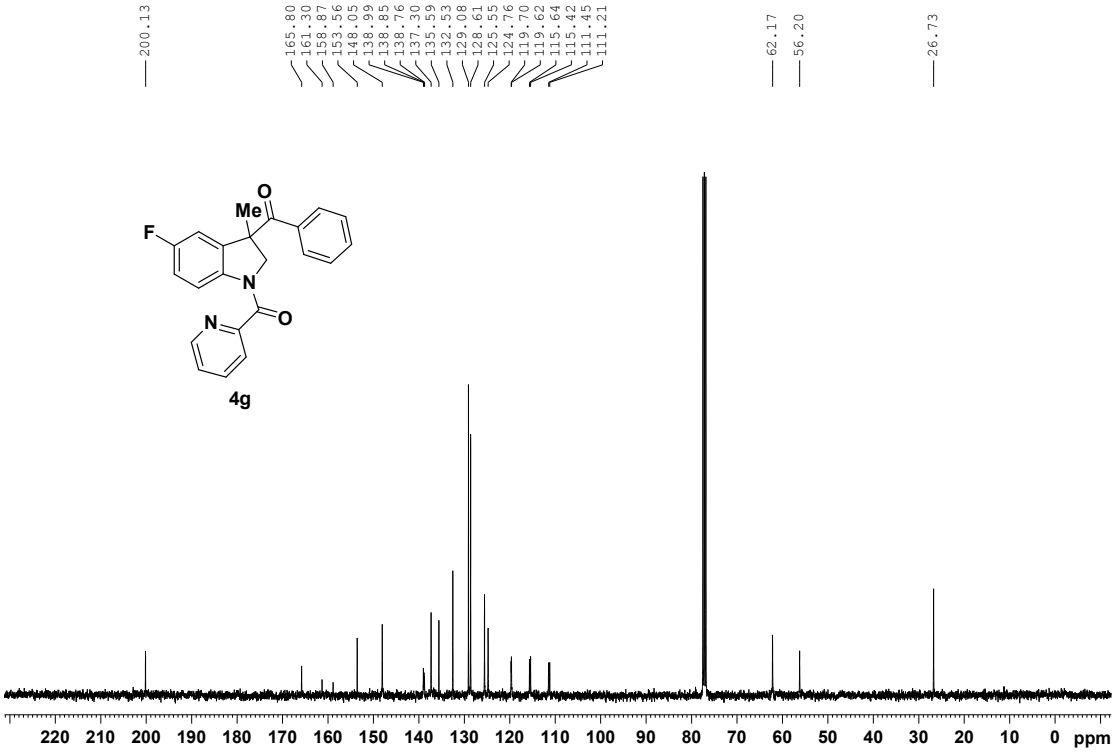
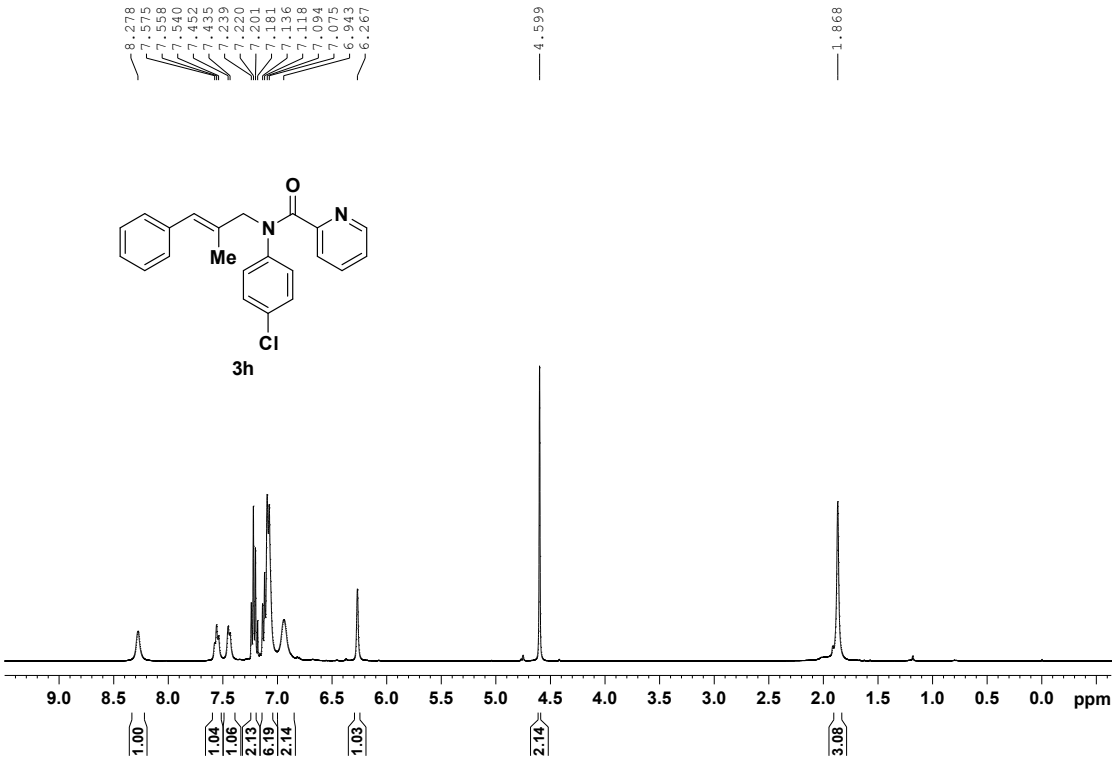
8.399
7.935
7.916
7.844
7.841
7.824
7.805
7.535
7.516
7.462
7.444
7.425
7.380
7.367
7.350
7.330
7.311
7.291
7.081
7.076
7.059
7.054
7.038
7.032
6.823
6.817
6.803
6.797
5.014
4.983
4.445
4.414
1.631
O
Me
F
N
N
O
4g
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.03
1.00
1.03
1.09
2.12
1.14
3.28
1.01
1.04
1.03
1.08
3.10


200.13
165.80
161.30
158.87
153.56
148.05
138.99
138.85
138.76
137.30
135.59
132.53
129.08
128.61
125.55
124.76
119.70
119.62
115.64
115.42
111.45
111.21
62.17
56.20
26.73
O
Me
F
N
N
O
4g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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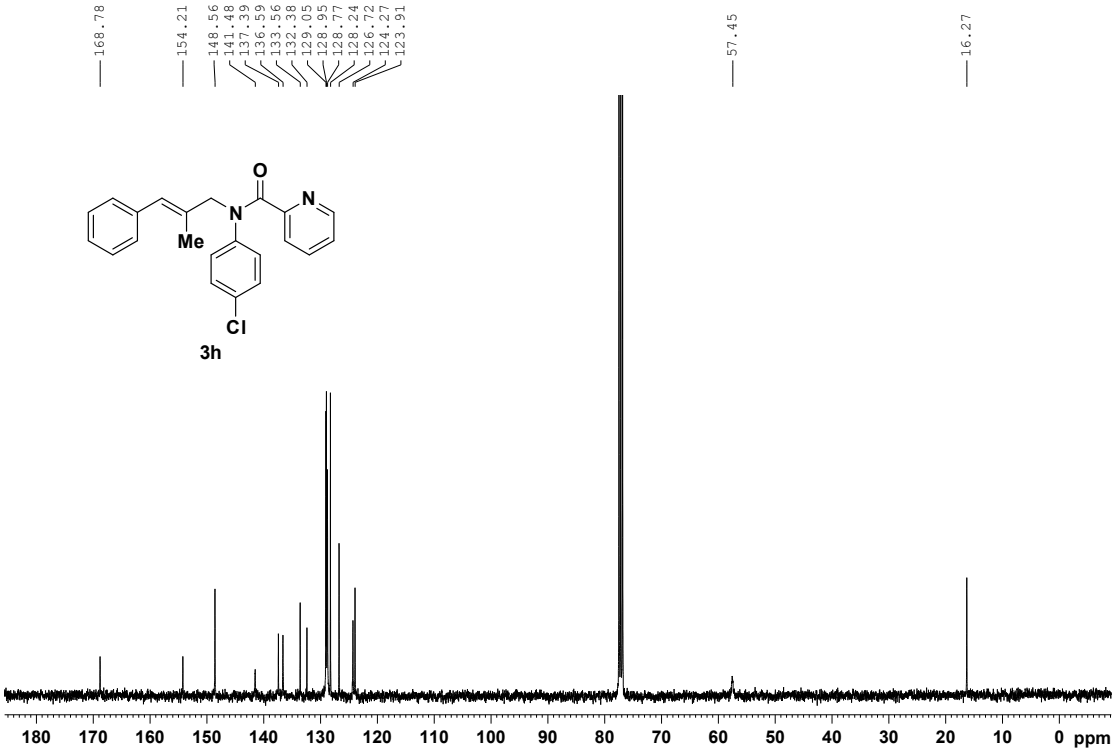
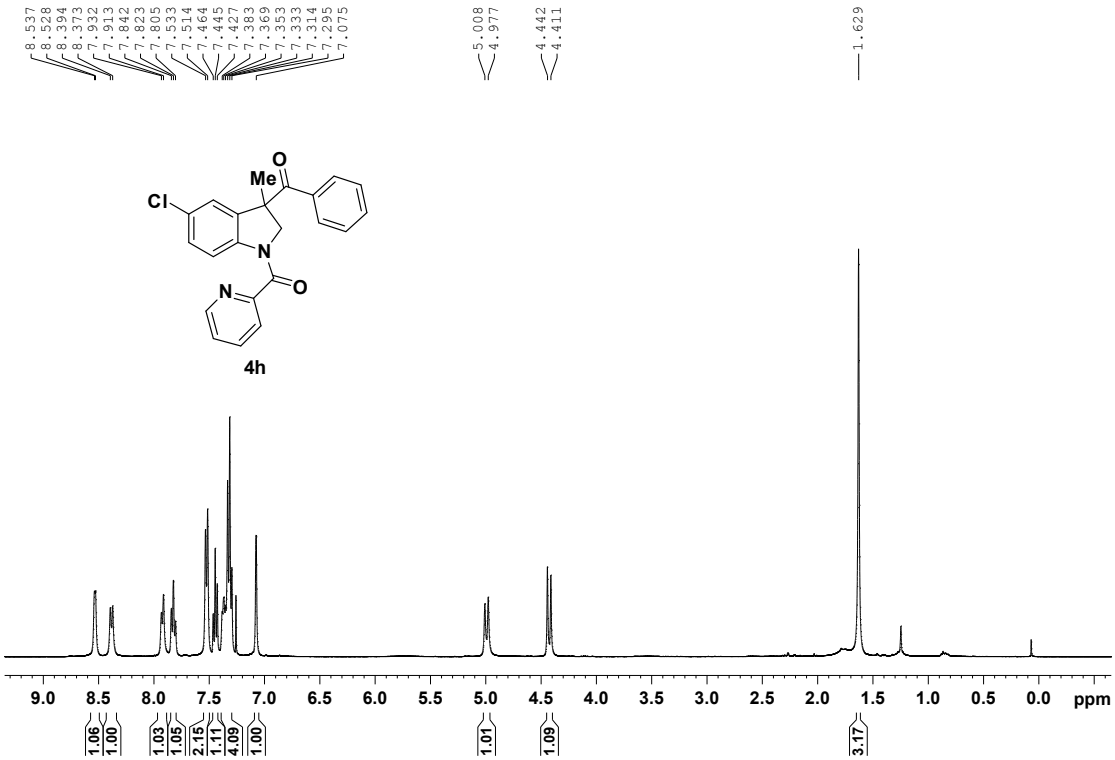
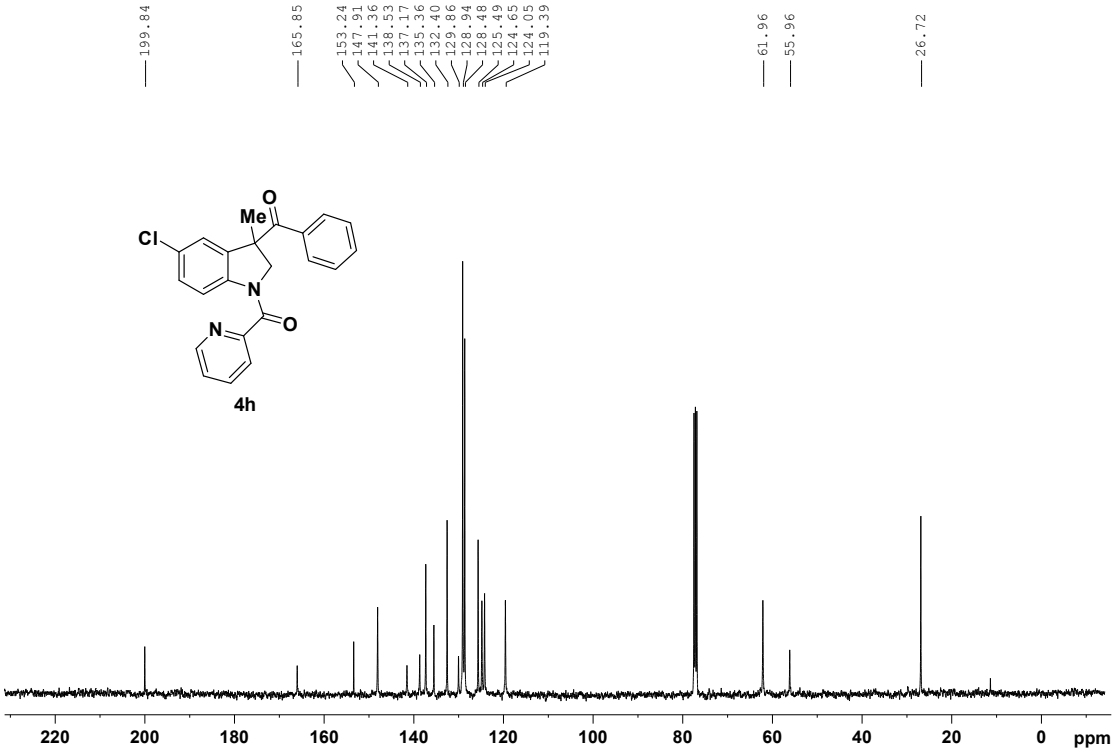
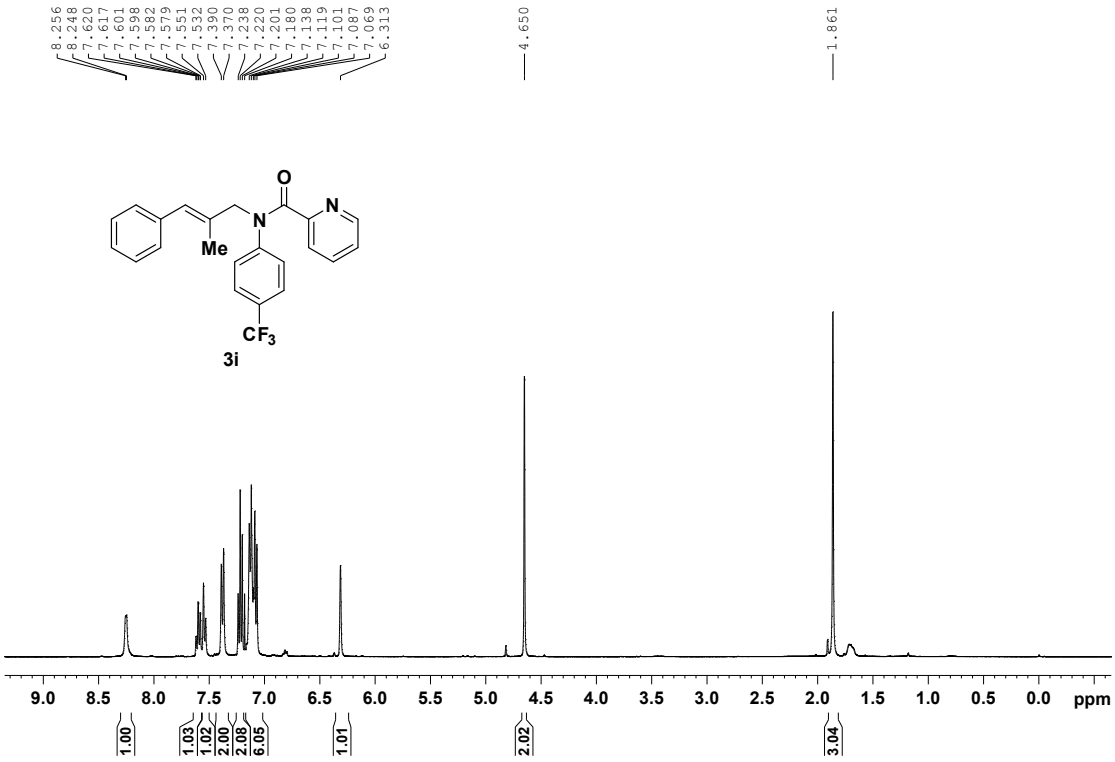
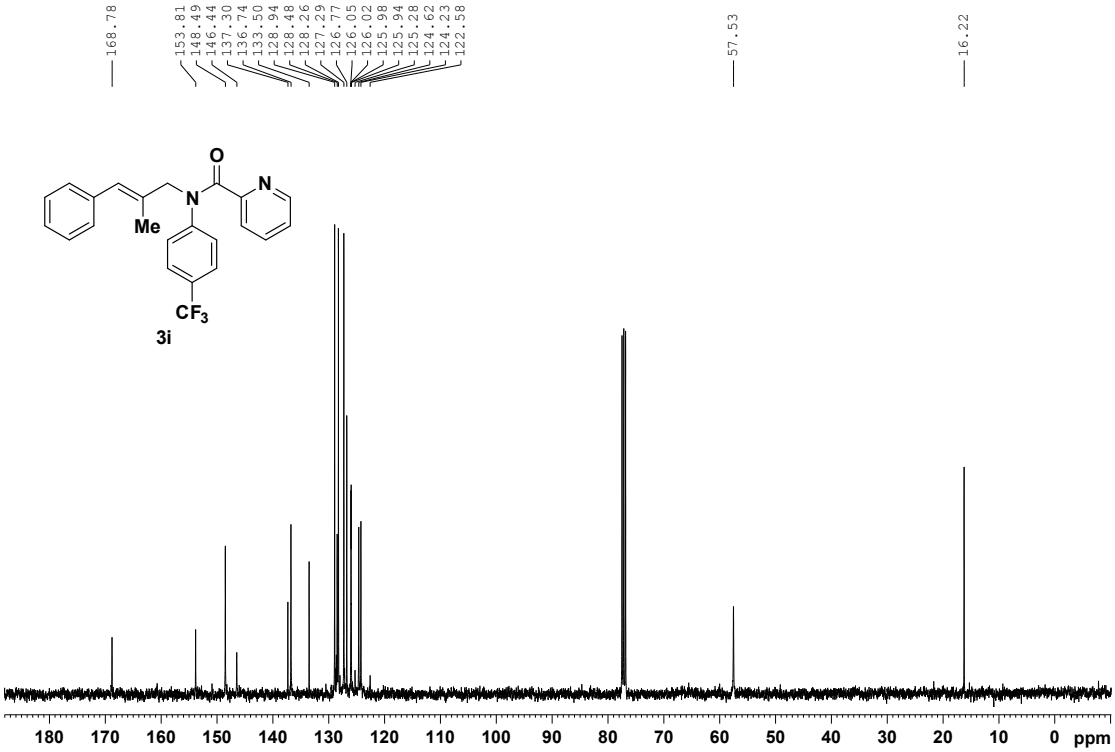
7.575
7.558
7.540
7.452
7.435
7.239
7.220
7.201
7.181
7.136
7.118
7.094
7.075
6.943
6.267
4.599
1.868
O
N
N
Me
Cl
3h
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.04
1.06
2.13
6.19
2.14
1.03
2.14
3.08

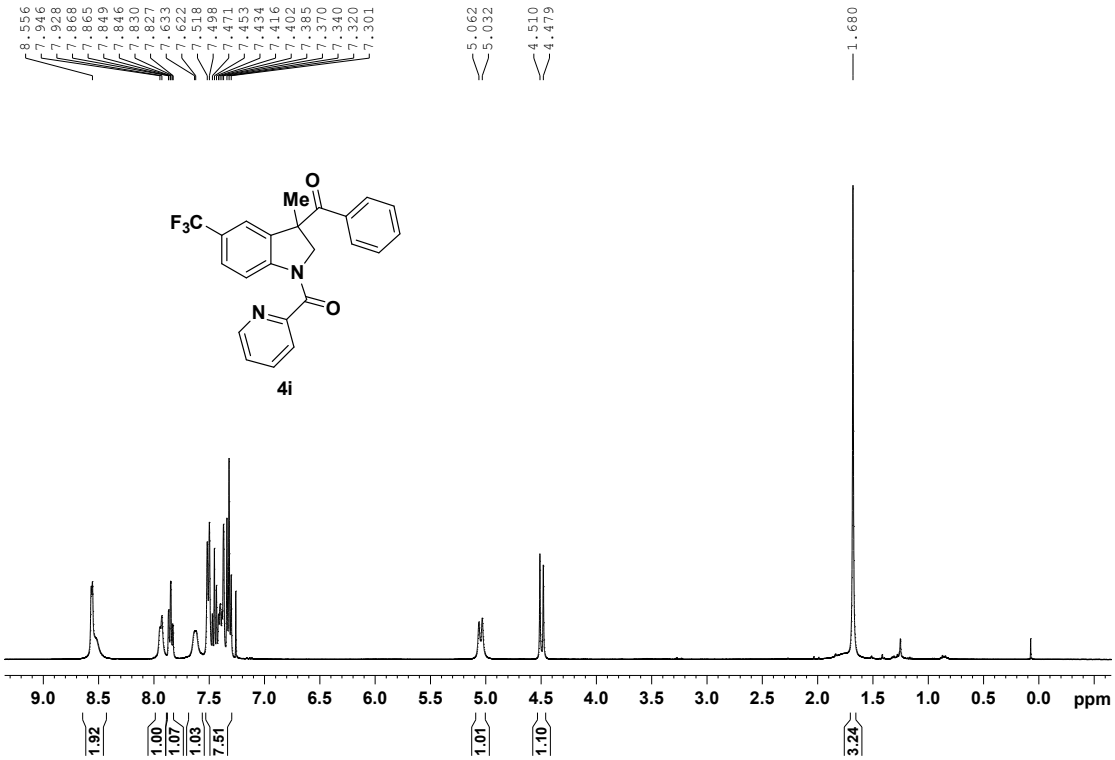

168.78
154.21
148.56
141.48
137.39
136.59
133.56
132.38
129.05
128.95
128.77
128.24
126.72
124.27
123.91
57.45
16.27
O
N
N
Me
Cl
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.537
8.528
8.394
8.373
7.932
7.913
7.842
7.823
7.805
7.533
7.514
7.464
7.445
7.427
7.383
7.369
7.353
7.333
7.314
7.295
7.075
5.008
4.977
4.442
4.411
1.629
O
Me
Cl
N
N
O
4h
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.06
1.00
1.03
1.05
2.15
1.11
4.09
1.00
1.01
1.09
3.17


199.84
165.85
153.24
147.91
141.36
138.53
137.17
135.36
132.40
129.86
128.94
128.48
125.49
124.65
124.05
119.39
61.96
55.96
26.72
O
Me
Cl
N
N
O
4h
220
200
180
160
140
120
100
80
60
40
20
0
ppm


8.256
8.248
7.620
7.617
7.601
7.598
7.582
7.579
7.551
7.532
7.390
7.370
7.238
7.220
7.201
7.180
7.138
7.119
7.101
7.087
7.069
6.313
4.650
1.861
O
N
N
Me
CF3
3i
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.03
1.02
2.00
2.08
6.05
1.01
2.02
3.04


168.78
153.81
148.49
146.44
137.30
136.74
133.50
128.94
128.48
128.26
127.29
126.77
126.05
126.02
125.98
125.94
125.28
124.62
124.23
122.58
57.53
16.22
O
N
N
Me
CF3
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.928
7.868
7.865
7.849
7.846
7.830
7.827
7.633
7.622
7.518
7.498
7.471
7.453
7.434
7.416
7.402
7.385
7.370
7.340
7.320
7.301
5.062
5.032
4.510
4.479
1.680
O
Me
F3C
N
N
O
4i
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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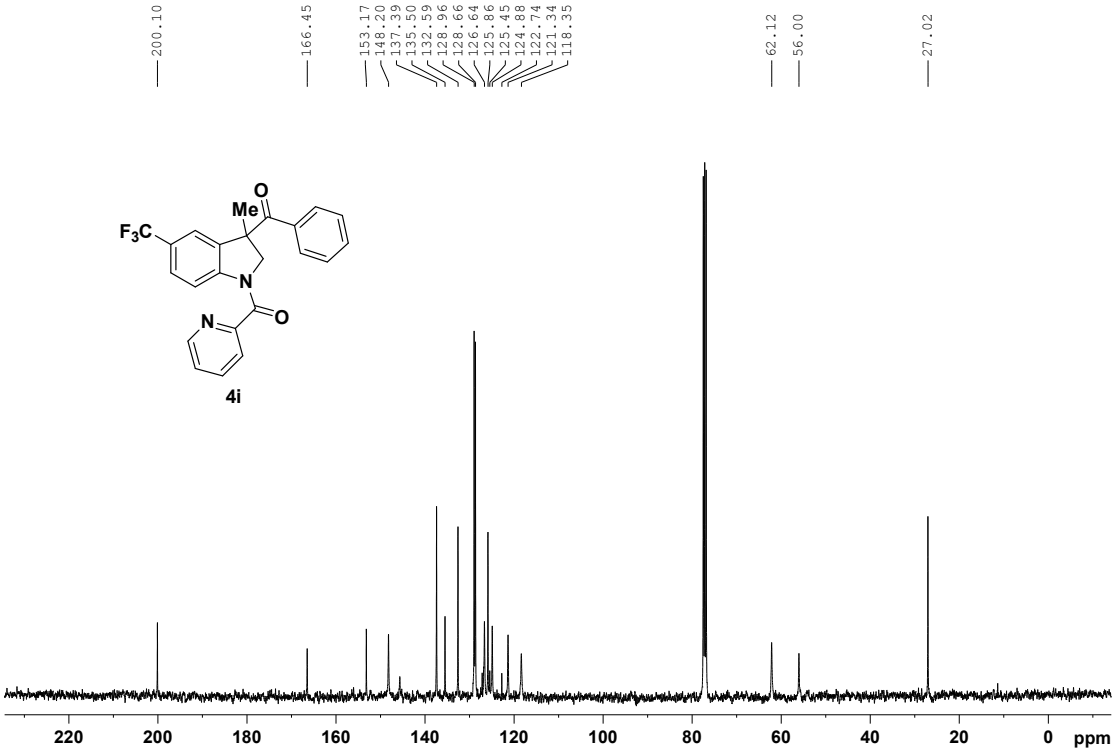
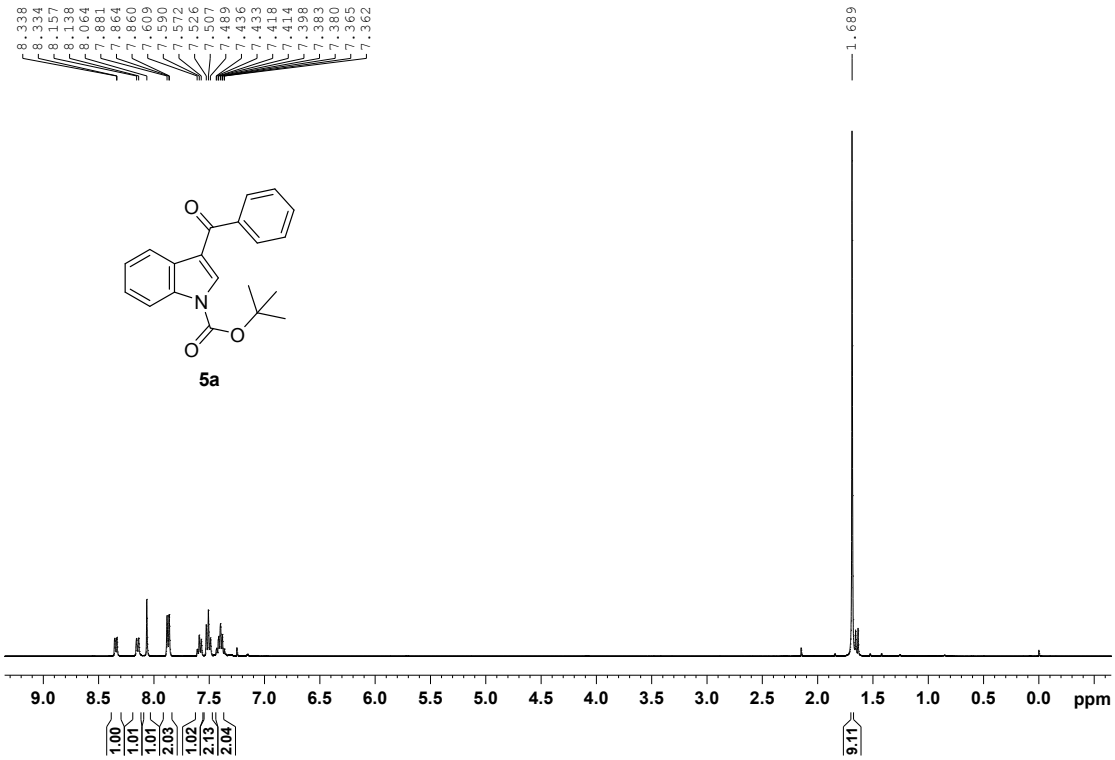
1.00
1.07
1.03
7.51
1.01
1.10
3.24


200.10
166.45
153.17
148.20
137.39
135.50
132.59
128.96
128.66
126.64
125.86
125.45
124.98
122.74
121.34
118.35
62.12
56.00
27.02
O
Me
F3C
N
N
O
4i
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.864
7.860
7.609
7.590
7.572
7.526
7.507
7.489
7.436
7.433
7.418
7.414
7.398
7.383
7.380
7.365
7.362
1.689
O
N
O
O
5a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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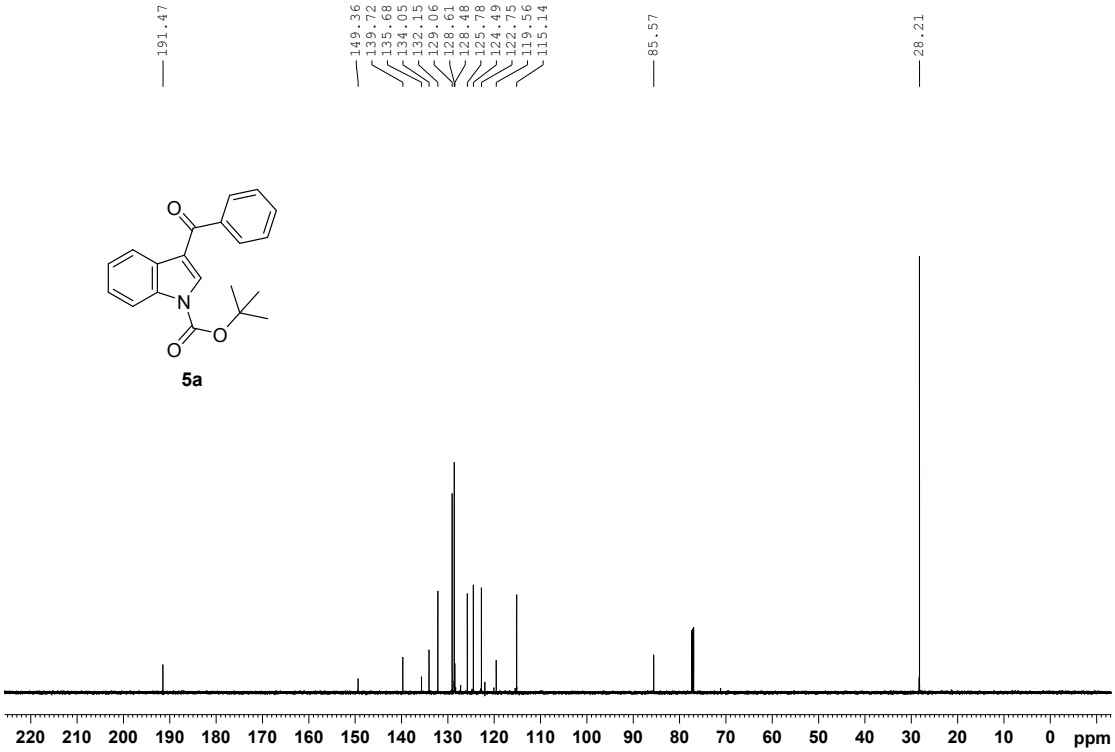
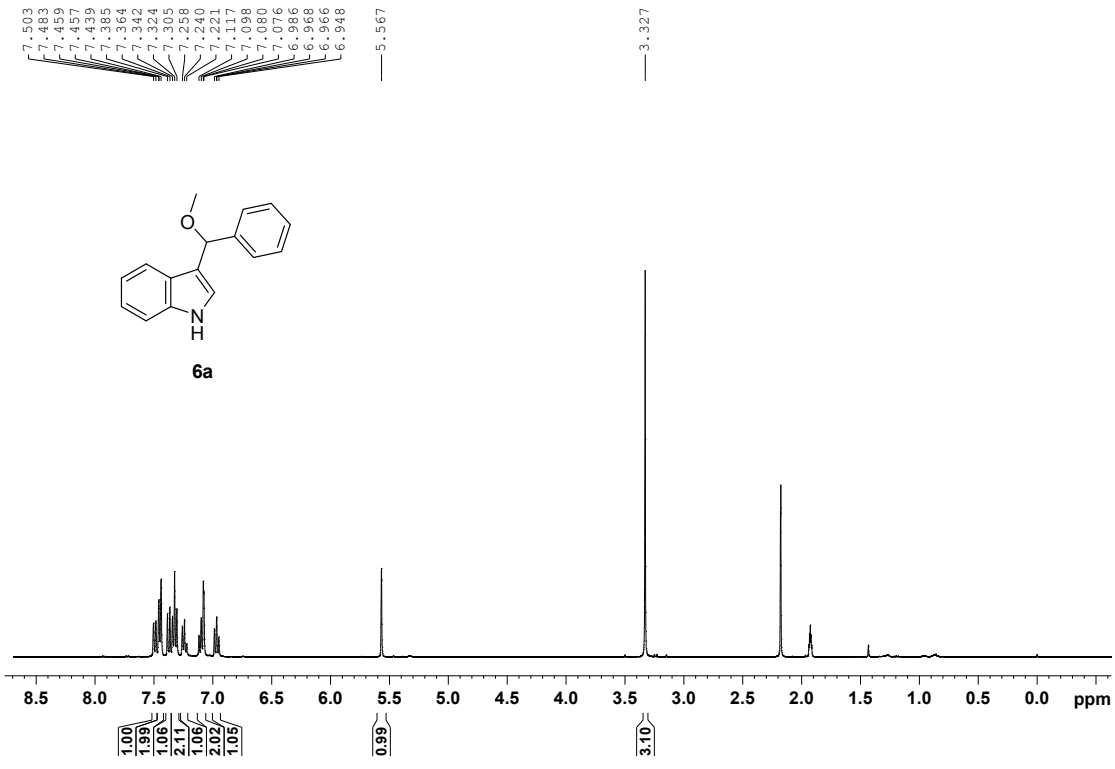
1.01
1.01
2.03
1.02
2.13
2.04
9.11


191.47
149.36
139.72
135.68
134.05
132.15
129.06
128.61
128.48
125.78
124.49
122.75
119.56
115.14
85.57
28.21
O
N
O
O
5a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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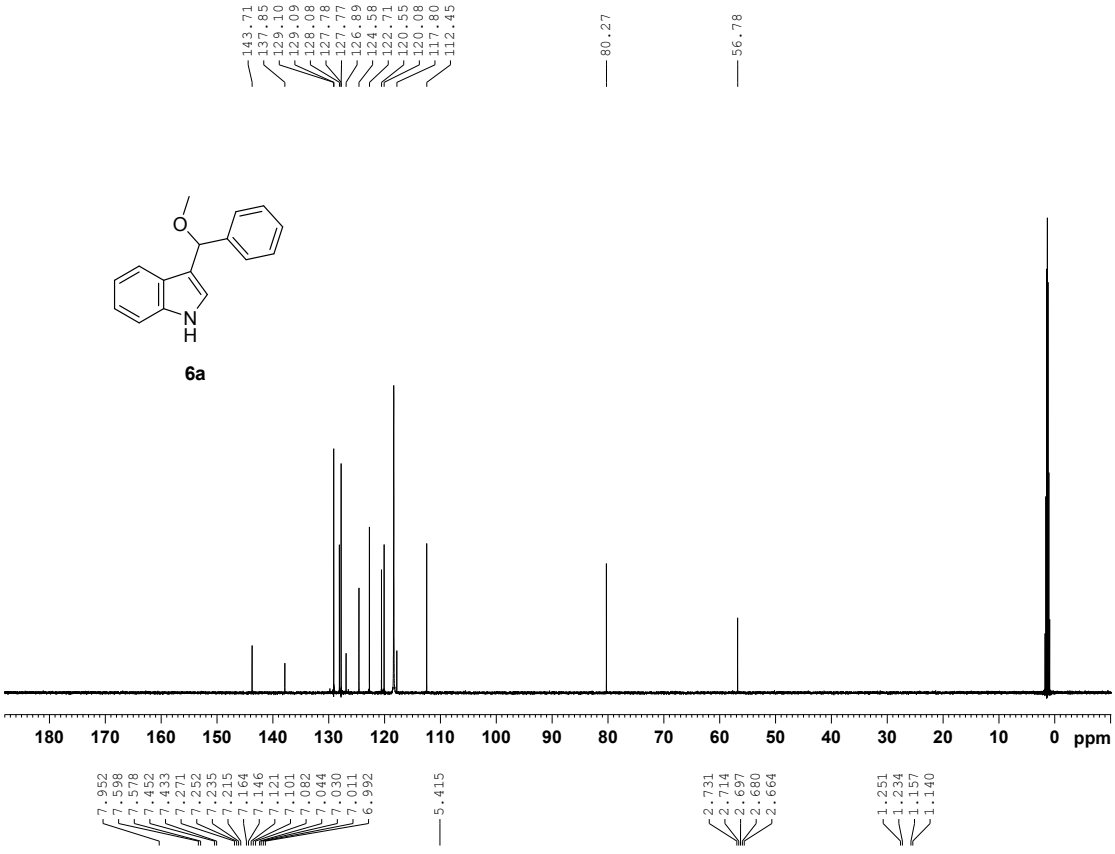
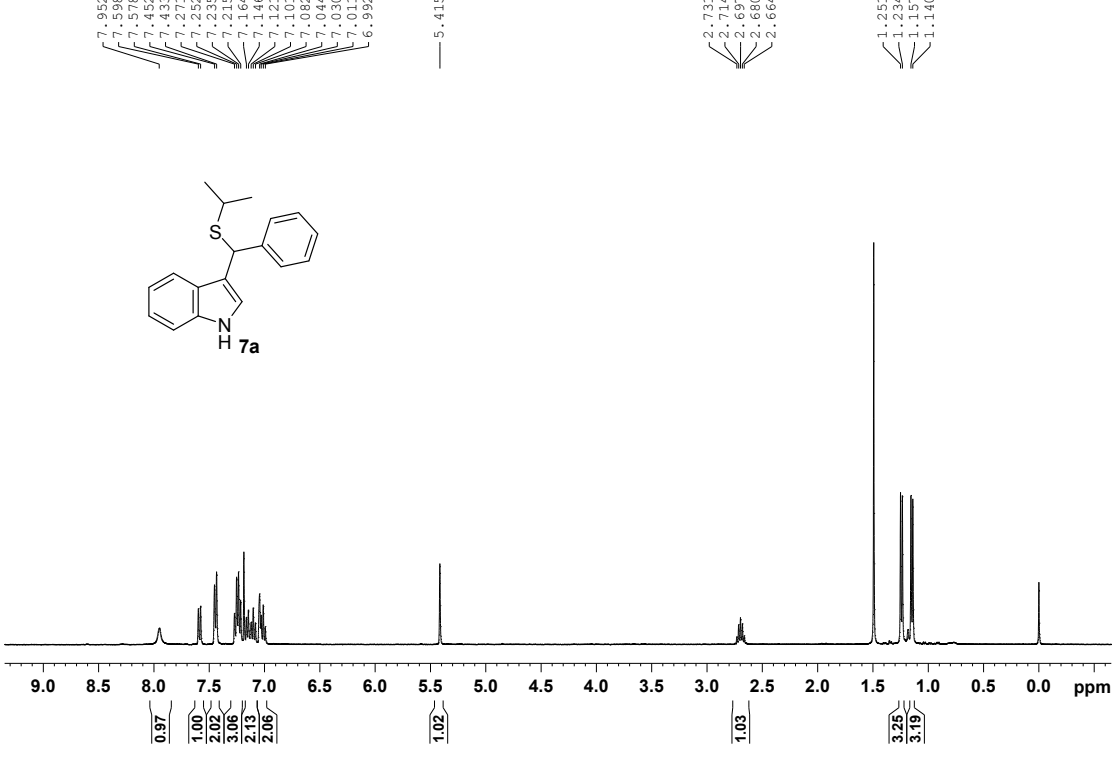
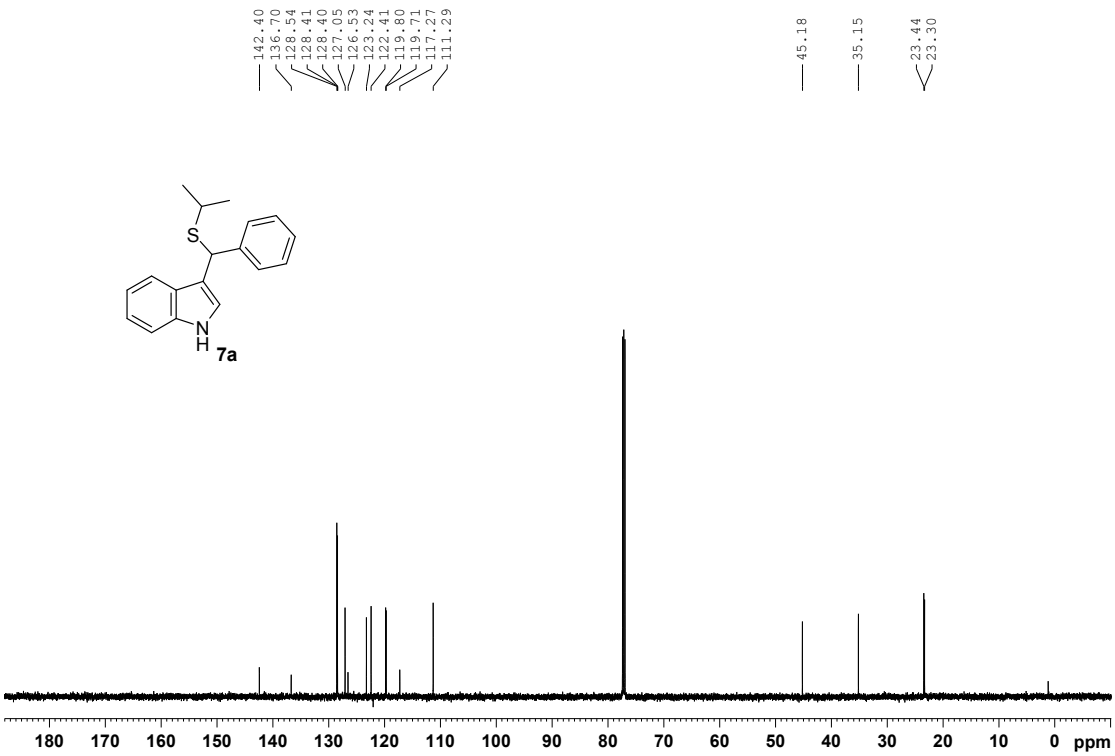
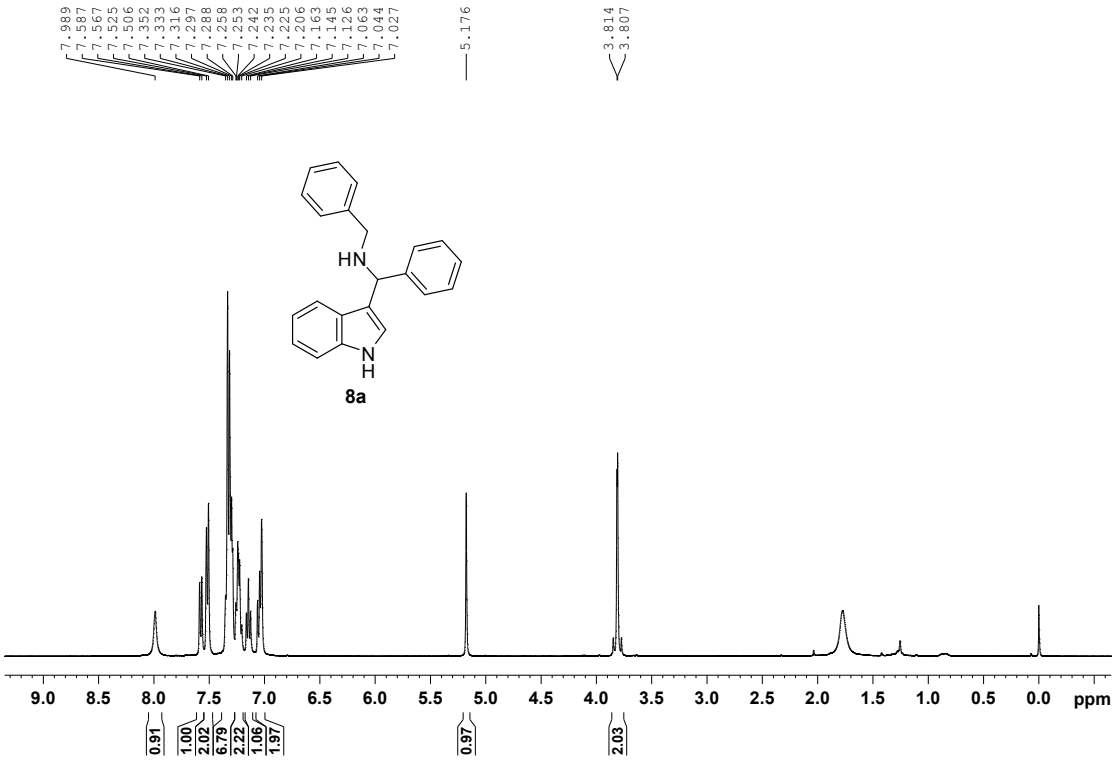
7.457
7.439
7.385
7.364
7.342
7.324
7.305
7.258
7.240
7.221
7.117
7.098
7.080
7.076
6.986
6.968
6.966
6.948
5.567
3.327
O
N
H
6a
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.99
1.06
2.11
1.06
2.02
1.05
0.99
3.10


143.71
137.85
129.10
129.09
128.08
127.78
127.77
126.89
124.58
122.71
120.55
120.08
117.80
112.45
80.27
56.78
O
N
H
6a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.952
7.598
7.578
7.452
7.433
7.271
7.252
7.235
7.215
7.164
7.146
7.121
7.101
7.082
7.044
7.030
7.011
6.992
5.415
2.731
2.714
2.697
2.680
2.664
1.251
1.234
1.157
1.140
S
N
H
7a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.97
1.00
2.02
3.06
2.13
2.06
1.02
1.03
3.25
3.19


142.40
136.70
128.54
128.41
128.40
127.05
126.53
123.24
122.41
119.80
119.71
117.27
111.29
45.18
35.15
23.44
23.30
S
N
H
7a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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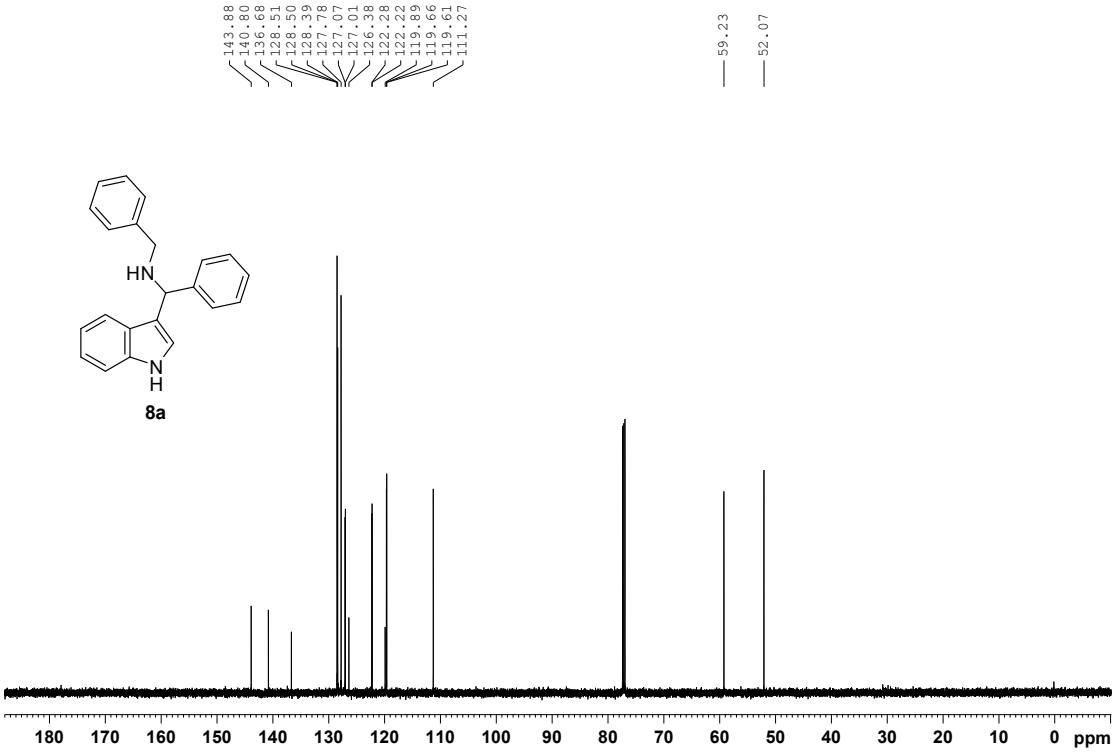
7.587
7.567
7.525
7.506
7.352
7.333
7.316
7.297
7.288
7.258
7.253
7.242
7.235
7.225
7.206
7.163
7.145
7.126
7.063
7.044
7.027
5.176
3.814
3.807
HN
N
H
8a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.91
1.00
2.02
6.79
2.22
1.06
1.97
0.97
2.03


143.88
140.80
136.68
128.51
128.50
128.39
127.78
127.07
127.01
126.38
122.28
122.22
119.89
119.66
119.61
111.27
59.23
52.07
HN
N
H
8a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm