Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Contents

General Information

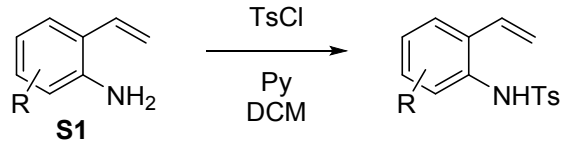
Unless otherwise indicated, all commercial reagents were used without additional purification. Toluene and THF was distilled form sodium/ benzophenone. CH_2Cl_2 was distilled form P_2O_5. ^1H NMR and ^{13}C NMR were recorded on a Bruker-400MHz Spectrometer (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. HRMS (ESI) were recorded on a Water ™ Q-TOF Premier Mass Spectrometer.

Preparation of Substances

Synthesis of Substances

1a, **1l** - **1n** were known compounds and synthesized according to the literature.[1]

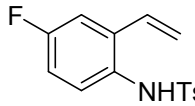
1b - **1k** were synthesized according to the following process.



Synthesis of 1b - 1k

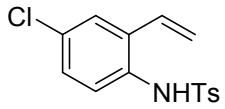
To a 25 mL round-bottomed flask was added **S1** [2] (2 mmol, 1 equiv) and pyridine 0.5 mL. TsCl (3 mmol, 1.5 equiv) in 5 mL DCM was added dropwise at 0 °C. Then the mixture was stirred at room temperature for 1 hour following by treated with 10 mL 1 N HCl. The water phase was extracted with DCM (10 mL × 3). The combine organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (EtOAc : PE) to afford **1**.

Characterization Data for the substances



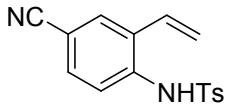
***N*-(4-fluoro-2-vinylphenyl)-4-methylbenzenesulfonamide (1b)**

White solid. m.p. 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 6.8 Hz, 2H), 7.25 – 7.18 (m, 3H), 7.09 (dd, *J* = 9.5, 2.9 Hz, 1H), 6.95 – 6.86 (m, 1H), 6.59 – 6.45 (m, 2H), 5.52 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 11.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, *J* = 246.5 Hz), 144.0, 136.1, 136.0, 130.7 (d, *J* = 1.9 Hz), 129.7, 128.8 (d, *J* = 2.8 Hz), 128.5 (d, *J* = 8.8 Hz), 127.2, 118.7, 115.4 (d, *J* = 22.8 Hz), 112.9 (d, *J* = 23.2 Hz), 21.5. HRMS (ESI) m/z calcd for. $C_{15}H_{14}FNO_2SNa$ $[M+Na]^+$ 314.0627, found 314.0620.



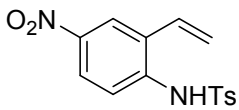
***N*-(4-chloro-2-vinylphenyl)-4-methylbenzenesulfonamide (1c)**

White solid. m.p. 123-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.17 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.52 – 6.41 (m, 2H), 5.51 (d, *J* = 17.3 Hz, 1H), 5.36 – 5.20 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 136.1, 134.5, 132.3, 131.7, 130.4, 129.8, 128.6, 127.2, 126.8, 126.5, 119.5, 21.6. HRMS (ESI) m/z calcd for. $C_{15}H_{14}ClNO_2SNa$ $[M+Na]^+$ 330.0326, found 330.0328.



***N*-(4-cyano-2-vinylphenyl)-4-methylbenzenesulfonamide (1d)**

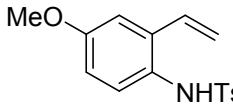
White solid. m.p. 159-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 1.7 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.48 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.33 – 7.23 (m, 2H), 7.06 (s, 1H), 6.53 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.58 (d, *J* = 17.3 Hz, 1H), 5.48 (d, *J* = 11.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 137.6 135.8, 132.1, 131.5, 131.2, 130.0, 129.6, 127.1, 121.7, 121.6, 118.3, 108.7, 21.6.



4-methyl-*N*-(4-nitro-2-vinylphenyl)benzenesulfonamide (1e)

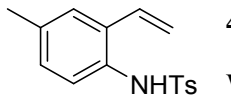
Yellow solid. m.p. 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.6 Hz, 1H), 8.07 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.60

(d, J = 9.0 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.13 (s, 1H), 6.58 (dd, J = 17.3, 11.0 Hz, 1H), 5.68 (d, J = 17.3 Hz, 1H), 5.55 (d, J = 11.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.4, 139.3, 135.6, 130.0, 129.6, 127.2, 125.0, 123.8, 122.2, 120.7, 114.4, 21.6. HRMS (ESI) m/z calcd for. $C_{15}H_{14}N_2O_4SNa$ $[M+Na]^+$ 341.0566, found 341.0567.



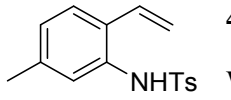
N-(4-methoxy-2-vinylphenyl)-4-methylbenzenesulfonamide (1f)

White solid. m.p. 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.8 Hz, 1H), 6.91 (d, J = 2.9 Hz, 1H), 6.74 (dd, J = 8.8, 2.9 Hz, 1H), 6.53 (dd, J = 17.4, 11.0 Hz, 1H), 6.30 (s, 1H), 5.50 (dd, J = 17.4, 0.7 Hz, 1H), 5.19 (dd, J = 11.0, 0.7 Hz, 1H), 3.79 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 143.7, 136.4, 135.9, 131.7, 129.6, 128.7, 127.3, 125.8, 117.5, 114.1, 111.2, 55.4, 21.6. HRMS (ESI) m/z calcd for. $C_{16}H_{17}NO_3SNa$ $[M+Na]^+$ 326.0821, found 326.0822.



4-methyl-N-(4-methyl-2-vinylphenyl)benzenesulfonamide (1g)

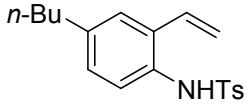
White solid. m.p. 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.14 (d, J = 8.2 Hz, 1H), 7.00 (dd, J = 8.2, 1.4 Hz, 1H), 6.62 – 6.46 (m, 2H), 5.49 (dd, J = 17.4, 0.9 Hz, 1H), 5.20 (dd, J = 11.0, 0.9 Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 136.5, 136.4, 133.1, 131.6, 130.4, 129.5, 129.3, 127.2, 127.1, 125.7, 117.5, 21.5, 21.0. HRMS (ESI) m/z calcd for. $C_{16}H_{17}NO_2SNa$ $[M+Na]^+$ 310.0872, found 310.0887.



4-methyl-N-(5-methyl-2-vinylphenyl)benzenesulfonamide (1h)

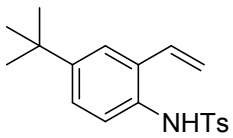
White solid. m.p. 117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.20 – 7.08 (m, 4H), 6.89 (d, J = 7.8 Hz, 1H), 6.43 – 6.31 (m, 2H), 5.37 (dd, J = 17.4, 0.9 Hz, 1H), 5.11 (dd, J = 11.0, 0.9 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 137.8, 135.4, 131.9, 130.2, 128.7, 128.6, 126.3, 126.2, 125.6, 124.5, 116.4, 20.5, 20.2. HRMS (ESI) m/z calcd for. $C_{16}H_{17}NO_2SNa$

[M+Na]$^+$ 310.0872, found 310.0886.



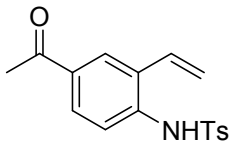
_N_-(4-butyl-2-vinylphenyl)-4-methylbenzenesulfonamide (1i)

White solid. m.p. 89 - 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.12 (m, 4H), 7.01 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.59 - 6.52 (m, 2H), 5.50 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.20 (dd, *J* = 11.0, 0.9 Hz, 1H), 2.55 (t, *J* = 7.76 Hz, 2H), 2.38 (s, 3H), 1.63 – 1.49 (m, 2H), 1.41 – 1.27 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 140.5, 135.4, 132.1, 130.7, 129.6, 128.5, 127.6, 126.2, 125.5, 124.6, 116.4, 34.1, 32.4, 21.3, 20.5, 12.9. HRMS (ESI) m/z calcd for. $C_{19}H_{23}NO_2SNa$ [M+Na]$^+$352.1342, found 352.1336.



_N_-(4-(*tert*-butyl)-2-vinylphenyl)-4-methylbenzenesulfonamide (1j)

White solid. m.p. 86 - 87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.22 – 7.06 (m, 4H), 6.51 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.43 (s, 1H), 5.44 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.16 (dd, *J* = 11.0, 1.1 Hz, 1H), 2.32 (s, 3H), 1.20 (d, *J* = 11.1 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 143.8, 136.7, 132.5, 132.2, 130.5, 129.6, 127.3, 125.8, 124.9, 123.6, 117.6, 34.5, 31.3, 21.6. HRMS (ESI) m/z calcd for. $C_{19}H_{23}NO_2SNa$ [M+Na]$^+$352.1342, found 352.1345.



_N_-(4-acetyl-2-vinylphenyl)-4-methylbenzenesulfonamide (1k)

White solid. m.p. 146 - 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.0 Hz, 1H), 7.79 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.06 (s, 1H), 6.58 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.60 (dd, *J* = 17.3, 0.5 Hz, 1H), 5.48 – 5.36 (m, 1H), 2.54 (d, *J* = 14.2 Hz, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 144.4, 137.8, 136.1, 133.9, 130.8, 130.6, 129.9, 128.9, 127.7, 127.2, 121.4, 120.5, 26.5, 21.6. HRMS (ESI) m/z calcd for. $C_{17}H_{18}NO_3SNa$ [M+H]$^+$ 316.1002, found 316.1001.

Examination of the Reaction Conditions for Different Carboxylic Acid [a]

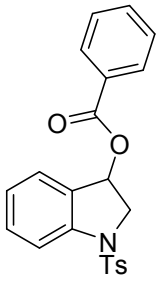
Entry	Carboxylic	Yield (%) [b]
1	4-chlorobenzoic acid	trace
2	4-bromobenzoic acid	26
3	4-formylbenzoic acid	40
4	4-methoxybenzoic acid	35
5	4-methylbenzoic acid	28
6	4-cyanobenzoic acid	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), water (2 mL), TBHP (0.6 mmol, 70% in water), TBAI (20% mol).[b] isolated yield.

General Procedure for the Synthesis of Indoline

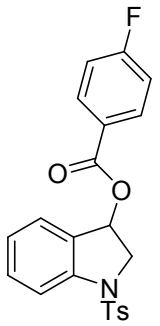
To a 10 mL tube was added **1** (0.2 mmol, 1 equiv), **2** (0.3 mmol, 1.5equiv), TMDAI (20% mol, 0.04 mmol), then added water 2 mL and TBHP (0.6 mmol, 3equiv). The mixture was stirred at 45 °C for 12 hours and then extracted with CH_2Cl_2 (2 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by chromatography to afford **3**.

Characterization Data for the Products



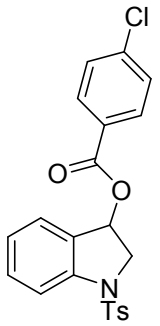
1-tosylindolin-3-yl benzoate (3aa)

White solid. m.p. 125 °C (from CDCl3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.33 (m, 4H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.16 (dd, *J* = 5.8, 2.8 Hz, 1H), 4.25 – 4.05 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 144.2, 143.0, 133.7, 133.2, 131.0, 129.7, 129.6, 129.2, 129.0, 128.2, 127.2, 127.0, 124.2, 115.5, 71.9, 55.7, 21.5. HRMS (ESI) m/z calcd for. $C_{22}H_{19}NO_4FNaS$ $[M+Na]^+$ 416.0932, found 416.0940.



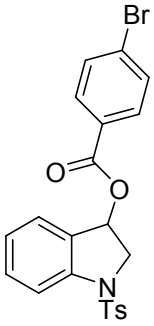
1-tosylindolin-3-yl 4-fluorobenzoate (3ab)

White solid. m.p.133 - 134 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 3H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.43-7.39 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.07 (m, 1H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.16 (t, *J* = 4.4 Hz, 1H), 4.14-4.13 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, *J* = 254.8 Hz), 165.0, 144.3, 143.1, 133.8, 132.3(d, *J* = 9.4 Hz), 131.1, 129.8, 128.9, 127.4, 127.1, 125.6 (d, *J* = 3.0 Hz), 124.3, 115.6 (d, *J* = 6.2 Hz), 115.4, 72.1, 55.8, 21.6. HRMS (ESI) m/z calcd for. $C_{22}H_{18}NO_4FNaS$ $[M+Na]^+$ 434.0838, found 434.0832.



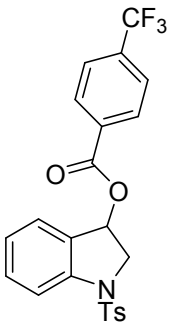
1-tosylindolin-3-yl 4-chlorobenzoate (3ac)

White solid. m.p. 159 - 161 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 1H), 7.74 – 7.62 (m, 4H), 7.42 (t, *J* = 6.4 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.15 (t, *J* = 4.3 Hz, 1H), 4.17 – 4.10 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 144.3, 143.2, 139.8, 133.8, 131.2, 131.1, 129.7, 128.8, 128.7, 127.8, 127.4, 127.0, 124.3, 115.6, 72.2, 55.7, 21.6. HRMS (ESI) m/z calcd for. $C_{22}H_{18}NO_4ClNaS$ $[M+Na]^+$ 450.0543, found 450.0541.



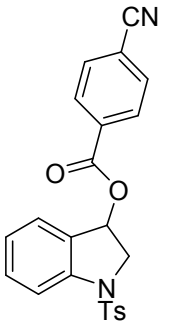
1-tosylindolin-3-yl 4-bromobenzoate (3ad)

White solid. m.p. 157 - 158 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.55 – 7.48 (m, 2H), 7.44-7.40 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (td, *J* = 7.6, 0.9 Hz, 1H), 6.15 (t, *J* = 4.4 Hz, 1H), 4.22 – 4.01 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 144.2, 143.1, 133.8, 131.6, 131.2, 129.7, 128.7, 128.5, 128.2, 127.3, 127.0, 124.3, 115.5, 72.2, 55.7, 21.5. HRMS (ESI) m/z calcd for. $C_{22}H_{18}NO_4BrNaS$ $[M+Na]^+$ 494.0038, found 494.0048.



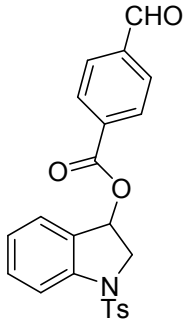
1-tosylindolin-3-yl 4-(trifluoromethyl)benzoate (3ae)

White solid. m.p. 127 – 129 °C (from $CDCl_3$). ^1H NMR (400 MHz, CDCl3) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.39 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.19 (t, *J* = 4.2 Hz, 1H), 4.15 (d, *J* = 4.4 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 144.3, 143.2, 134.7 (q, *J* = 32.7 Hz), 133.7, 132.5, 131.3, 130.1, 129.7, 128.6, 127.3, 127.0, 125.3 (q, *J* = 3.7 Hz), 124.8, 124.3, 122.1, 72.6, 55.6, 21.5. HRMS (ESI) m/z calcd for. $C_{23}H_{18}NO_4NaF_3S$ $[M+Na]^+$ 484.0806, found 484.0809.



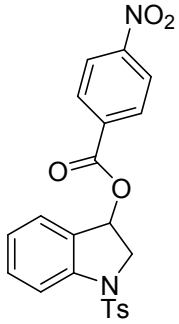
1-tosylindolin-3-yl 4-cyanobenzoate (3af)

White solid. m.p. 154 - 156 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 4H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 6.0 Hz, 1H), 4.23 – 3.99 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 144.4, 143.2, 133.7, 133.2, 132.1, 131.4, 130.2, 129.8, 128.3, 127.4, 127.1, 124.3, 117.8, 116.7, 115.5, 72.8, 55.6, 21.6. HRMS (ESI) m/z calcd for. $C_{23}H_{18}NO_4NaS$ $[M+Na]^+$ 441.0885, found 441.0884.



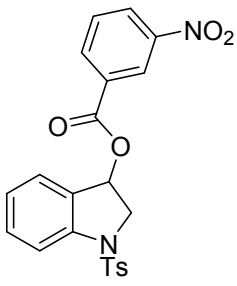
1-tosylindolin-3-yl 4-formylbenzoate (3ag)

White solid. m.p. 111-113 °C (from $CDCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.82 – 7.78 (m, 2H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.28 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.02 (td, *J* = 7.5, 0.7 Hz, 1H), 6.13-6.11 (m, 1H), 4.20 – 3.87 (m, 2H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 164.8, 144.3, 143.1, 139.2, 134.1, 133.6, 131.2, 130.2, 129.7, 129.3, 128.5, 127.2, 127.0, 124.2, 115.4, 72.5, 55.6, 21.5. HRMS (ESI) m/z calcd for. $C_{23}H_{19}NO_5NaS$ $[M+Na]^+$ 444.0882, found 444.0881.



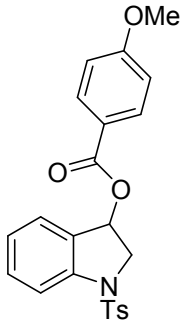
1-tosylindolin-3-yl 4-nitrobenzoate (3ah)

White solid. m.p. 124 - 126 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.44 (t, *J* = 6.4 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.22 (d, *J* = 6.1 Hz, 1H), 4.30 – 4.04 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 150.7, 144.4, 143.2, 134.7, 133.8, 131.4, 130.9, 129.8, 128.3, 127.4, 127.1, 124.3, 123.4, 115.5, 73.0, 55.6, 21.6. HRMS (ESI) m/z calcd for. $C_{22}H_{18}N2O_6NaS$ $[M+Na]^+$ 461.0783, found 461.0781.



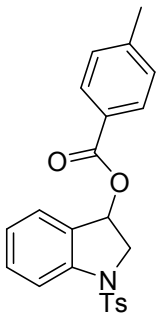
1-tosylindolin-3-yl 3-nitrobenzoate (3ai)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.25-6.23 (m, 1H), 4.26 – 4.06 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 148.2, 144.5, 143.2, 135.4, 133.7, 131.4, 131.1, 129.8, 129.7, 128.3, 127.8, 127.3, 127.2, 124.6, 124.4, 115.4, 73.0, 55.6, 21.5. HRMS (ESI) m/z calcd for. $C_{22}H_{18}N2O_6NaS$ $[M+Na]^+$ 461.0783, found 461.0786.



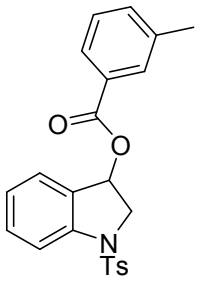
1-tosylindolin-3-yl 4-methoxybenzoate (3aj)

White solid. m.p. 123 - 124 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.14 (d, *J* = 4.0 Hz, 1H), 4.22 – 4.07 (m, 2H), 3.85 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 163.7, 144.3, 143.2, 133.9, 131.9, 131.1, 129.9, 129.4, 127.4, 127.1, 124.4, 121.8, 115.6, 113.6, 71.7, 56.0, 55.6, 21.7. HRMS (ESI) m/z calcd for. $C_{22}H_{21}NO_5NaS$ $[M+Na]^+$ 446.1038, found 446.1037.



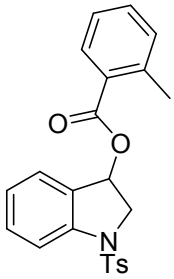
1-tosylindolin-3-yl 4-methylbenzoate (3ak)

White solid. m.p.146 - 147 (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.68-7.64 (m, 4H), 7.40 (t, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.15 (dd, *J* = 6.2, 2.7 Hz, 1H), 4.25 – 4.06 (m, 2H), 2.39 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 144.2, 144.1, 143.1, 133.8, 131.0, 129.8, 129.7, 129.2, 129.0, 127.3, 127.1, 126.6, 124.3, 115.5, 71.8, 55.9, 21.7, 21.6. HRMS (ESI) m/z calcd for. $C_{23}H_{21}NO_4NaS$ $[M+Na]^+$ 430.1089, found 430.1088.



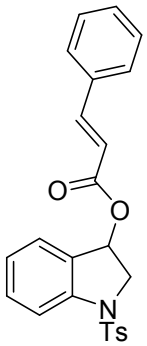
1-tosylindolin-3-yl 3-methylbenzoate (3al)

White solid. m.p. 124 – 125 (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.68-7.66 (m, 3H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.43-7.37 (m, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.16 (t, *J* = 4.2 Hz, 1H), 4.14 (d, *J* = 4.4 Hz, 2H), 2.36 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 144.2, 143.0, 138.0, 134.0, 133.6, 130.9, 130.1, 129.6, 129.1, 128.9, 128.0, 127.2, 127.0, 126.7, 124.1, 115.3, 71.8, 55.7, 21.4, 21.1. HRMS (ESI) m/z calcd for. $C_{23}H_{21}NO_4NaS$ $[M+Na]^+$ 430.1089, found 430.1079.



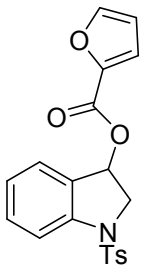
1-tosylindolin-3-yl 2-methylbenzoate (3am)

White solid. m.p. 121 - 123 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.07 (m, 4H), 6.13 (dd, *J* = 6.7, 2.3 Hz, 1H), 4.19-4.09 (m, 2H), 2.47 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 144.3, 143.1, 140.6, 133.7, 132.4, 131.7, 131.0, 130.7, 129.7, 129.2, 128.5, 127.3, 126.9, 125.6, 124.3, 115.7, 71.7, 55.9, 21.8, 21.5. HRMS (ESI) m/z calcd for. $C_{23}H_{21}NO_4NaS$ $[M+Na]^+$ 430.1089, found 430.1086.



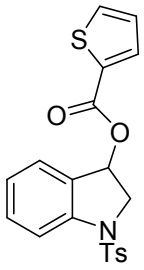
1-tosylindolin-3-yl cinnamate (3an)

Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 16.0 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.40 (d, *J* = 8.8 Hz, 5H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.15 (d, *J* = 16.0 Hz, 1H), 6.05 (t, *J* = 4.2 Hz, 1H), 4.07 (d, *J* = 4.3 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 145.6, 144.1, 143.0, 134.0, 133.6, 130.9, 130.5, 129.6, 129.1, 128.9, 128.0m 127.3, 126.9, 124.2, 117.1, 115.4, 71.4, 55.8, 21.4. HRMS (ESI) m/z calcd for. $C_{24}H_{17}NO_4NaS$ $[M+Na]^+$ 442.1089, found 442.1089.



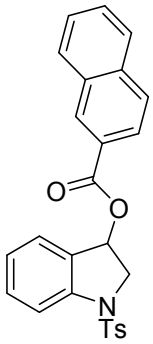
1-tosylindolin-3-yl furan-2-carboxylate (3ao)

White solid. m.p. 117 – 118 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 1H), 7.43-7.38 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 2.9 Hz, 1H), 6.46 (s, 1H), 6.16 (d, *J* = 2.9 Hz, 1H), 4.37 – 3.92 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 146.7, 144.2, 143.7, 143.0, 133.6, 131.1, 129.7, 128.5, 127.3, 127.1, 124.2, 118.5, 115.2, 111.8, 71.8, 55.6, 21.5. HRMS (ESI) m/z calcd for. $C_{20}H_{17}NO_5NaS$ $[M+Na]^+$ 406.0725, found 406.0727.



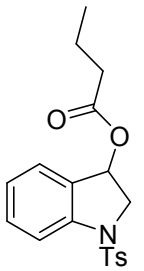
1-tosylindolin-3-yl thiophene-2-carboxylate (3ap)

White solid. m.p. 119 - 120 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.43-7.38 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 4.3 Hz, 1H), 6.14 (t, *J* = 4.4 Hz, 1H), 4.13 (d, *J* = 4.6 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 144.2, 143.0, 133.8, 133.6, 133.0, 132.8, 131.0, 129.7, 128.7, 127.6, 127.2, 127.0, 124.2, 115.3, 72.1, 55.6, 21.5. HRMS (ESI) m/z calcd for. $C_{20}H_{17}NO_4NaS_2$ $[M+Na]^+$ 422.0497, found 422.0486.



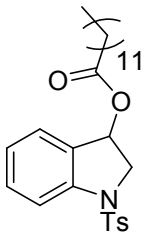
1-tosylindolin-3-yl 2-naphthoate (3aq)

White solid. m.p. 124 -125 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 9.8 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.15-7.10 (m, 3H), 6.22 (dd, *J* = 4.5, 3.1 Hz, 1H), 4.32 – 4.11 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 144.3, 143.2, 135.6, 133.7, 132.3, 131.3, 131.0, 129.7, 129.3, 129.0, 128.5, 128.0, 127.7, 127.3, 127.1, 126.7, 126.5, 125.0, 124.2, 115.5, 72.1, 55.9, 21.4. HRMS (ESI) m/z calcd for. $C_{26}H_{21}NO_4NaS$ $[M+Na]^+$ 466.1089, found 466.1097.



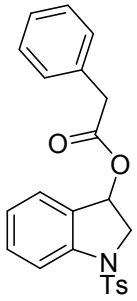
1-tosylindolin-3-yl butyrate (3ar)

Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.95 (d, *J* = 6.6 Hz, 1H), 4.02 (dd, *J* = 12.9, 6.9 Hz, 1H), 3.95 (d, *J* = 12.9 Hz, 1H), 2.36 (s, 3H), 2.07 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.42 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 144.2, 142.9, 133.7, 130.8, 129.6, 129.2, 127.3, 126.8, 124.2, 115.4, 71.0. 55.7. 35.8. 21.5. 18.2. 13.5. HRMS (ESI) m/z calcd for. $C_{19}H_{21}NO_4NaS$ $[M+Na]^+$ 382.1089, found 382.1081.



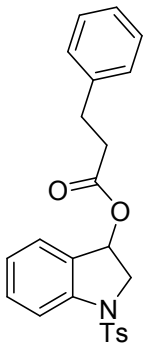
1-tosylindolin-3-yl dodecanoate (3as)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.94 (d, *J* = 6.4 Hz, 1H), 4.02 (dd, *J* = 13.0, 6.8 Hz, 1H), 3.95 (d, *J* = 12.9 Hz, 1H), 2.36 (s, 3H), 2.07 (t, *J* = 7.6 Hz, 2H), 1.57 – 1.44 (m, 2H), 1.26 (t, *J* = 12.5 Hz, 16H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 144.2, 142.9, 133.7, 130.8, 129.6, 129.2, 127.3, 126.8, 124.1, 115.4, 71.0, 55.7, 34.0, 31.8, 29.6, 29.5, 29.4, 29.3, 29.1, 29.0, 24.7, 22.6, 21.5, 14.1. HRMS (ESI) m/z calcd for. $C_{27}H_{37}NO_4NaS$ $[M+Na]^+$ 494.2341, found 494.2343.



1-tosylindolin-3-yl 2-phenylacetate (3at)

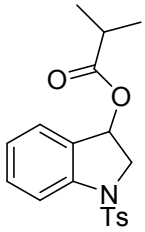
White solid. m.p. 123-124 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.35 (m, 1H), 7.34 – 7.26 (m, 4H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 5.95 (dd, *J* = 6.1, 2.9 Hz, 1H), 4.10 – 3.92 (m, 2H), 3.39 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 144.2, 142.9, 133.6, 133.2, 130.9, 129.6, 129.0, 128.9, 128.5, 127.3, 127.2, 126.8, 124.2, 115.3, 71.7, 55.6, 40.8, 21.5. HRMS (ESI) m/z calcd for. $C_{23}H_{21}NO_4NaS$ $[M+Na]^+$ 430.1083, found 430.1082.



1-tosylindolin-3-yl 3-phenylpropanoate (3au)

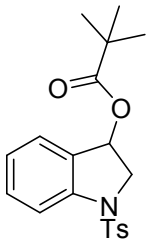
White solid. m.p. 117-118 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.21-7.17 (m, 3H), 7.09 (d, *J* = 7.3 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.92 (d, *J* = 5.8 Hz, 1H), 3.99 (dd, *J* = 13.1, 6.8 Hz, 1H), 3.91 (d, *J* = 13.0 Hz, 1H), 2.81 (t, *J* = 7.7 Hz, 2H), 2.39 (t, *J* = 7.7 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 144.2, 142.9, 140.0, 133.6, 130.8, 129.6, 129.0, 128.5, 128.1, 127.3, 126.8, 126.3, 124.2,

115.4, 71.3, 55.6, 35.5, 30.6, 21.4. HRMS (ESI) m/z calcd for. $C_{20}H_{17}NO_4NaS$ $[M+Na]^+$ 406.0725, found 406.0727.



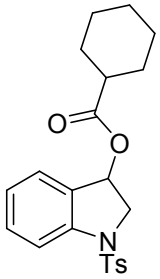
1-tosylindolin-3-yl isobutyrate (3av)

Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.95 (dd, *J* = 7.0, 1.6 Hz, 1H), 4.04 (dd, *J* = 13.0, 7.1 Hz, 1H), 3.92 (dd, *J* = 13.0, 2.0 Hz, 1H), 2.36 (s, 3H), 2.29 (dq, *J* = 13.9, 7.0 Hz, 1H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 144.3, 142.9, 133.7, 130.9, 129.7, 129.3, 127.3, 126.8, 124.2, 115.3, 71.0, 55.8, 33.7, 21.5, 18.7, 18.6. HRMS (ESI) m/z calcd for. $C_{19}H_{21}NO_4NaS$ $[M+Na]^+$ 382.1089, found 382.1081.



1-tosylindolin-3-yl pivalate (3aw)

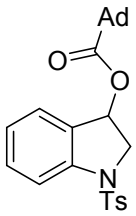
Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.97 (d, *J* = 7.0 Hz, 1H), 4.08 (dd, *J* = 13.0, 7.5 Hz, 1H), 3.88 (dd, *J* = 13.0, 1.2 Hz, 1H), 2.35 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 144.2, 142.7, 133.7, 130.7, 129.7, 129.1, 127.2, 126.6, 124.0, 115.0, 70.9, 55.5, 38.4, 26.7, 21.4. HRMS (ESI) m/z calcd for. $C_{20}H_{23}NO_4NaS$ $[M+Na]^+$ 396.1245, found 396.1258.



1-tosylindolin-3-yl cyclohexanecarboxylate (3ax)

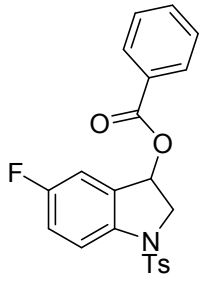
White solid. m.p. 105 – 106 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.86 (d, *J* = 6.7 Hz, 1H), 3.97 (dd, *J* = 13.1, 7.1 Hz, 1H), 3.83 (d, *J* = 13.1 Hz, 1H), 2.29 (s, 3H), 1.95 (t, *J* = 10.9 Hz, 1H), 1.64-1.53 (m, 5H), 1.28-1.02 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 144.1, 142.8, 133.7, 130.7, 129.6, 129.2, 127.3, 126.6, 124.1, 115.3, 70.8, 55.7, 42.6, 28.6, 28.6, 25.5, 25.2,

21.5. HRMS (ESI) m/z calcd for. $C_{22}H_{25}NO_4NaS$ [M+Na] $^+$ 422.1402, found 422.1431.



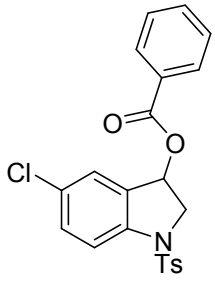
1-tosylindolin-3-yl (3r,5r,7r)-adamantane-1-carboxylate (3ay)

White solid. m.p. 149 - 150 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.97 (d, *J* = 7.2 Hz, 1H), 4.08 (dd, *J* = 13.0, 7.4 Hz, 1H), 3.87 (d, *J* = 13.0 Hz, 1H), 2.36 (s, 3H), 1.95 (s, 3H), 1.76 – 1.57 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 144.2, 142.8, 133.9, 130.8, 129.7, 129.2, 127.3, 126.7, 124.0, 115.0, 70.7, 55.7, 40.4, 38.4, 36.3, 27.7, 21.5. HRMS (ESI) m/z calcd for. $C_{26}H_{29}NO_4NaS$ [M+Na] $^+$ 474.1715, found 474.1716.



5-fluoro-1-tosylindolin-3-yl benzoate (3ba)

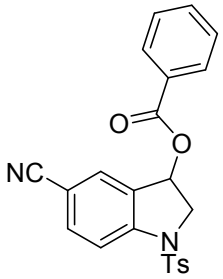
White solid. m.p. 125-127 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 3H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.07 (m, 4H), 6.09 (d, *J* = 6.6 Hz, 1H), 4.21 (dd, *J* = 13.4, 6.8 Hz, 1H), 4.14 (d, *J* = 13.3 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 159.6 (d, J = 243.9), 144.4, 139.2 (d, *J* = 2.0 Hz), 133.4, 130.9 (d, *J* = 8.5 Hz), 129.8, 129.7, 129.0, 128.3, 127.3, 118.0 (d, *J* = 23.7 Hz), 117.0 (d, *J* = 8.3 Hz), 113.9 (d, *J* = 24.3 Hz), 71.5 (d, *J* = 1.4 Hz), 56.1, 21.5. HRMS (ESI) m/z calcd for. $C_{22}H_{18}NO_4NaSF$ [M+Na] $^+$ 434.0838, found 434.0827.



5-chloro-1-tosylindolin-3-yl benzoate (3ca)

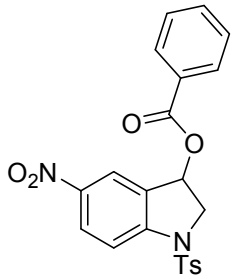
White solid. m.p. 145-146 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6-7.72 (m, 3H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.40-7.36 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 5.9 Hz, 1H), 4.18 (dd, *J* = 13.4, 6.7 Hz, 1H), 4.13 (d, *J* = 13.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 144.5, 141.7, 133.4, 131.0,

130.8, 129.8, 129.6, 129.4, 128.9, 128.2, 127.2, 127.1, 116.6, 71.3, 55.9, 21.5. HRMS (ESI) m/z calcd for. $C_{22}H_{18}NO_4NaSCl$ $[M+Na]^+$ 450.0543, found 450.0531.



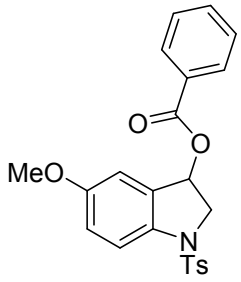
5-cyano-1-tosylindolin-3-yl benzoate (3da)

White solid. m.p. 152 – 153 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.81-7.7.78 (m, 2H), 7.76-7.75 (m, 1H), 7.73 – 7.66 (m, 3H), 7.60 – 7.54 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.20 (dd, *J* = 5.3, 4.0 Hz, 1H), 4.28 – 4.14 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 146.5, 145.1, 135.3, 133.6, 133.4, 131.3, 130.0, 129.9, 129.7, 128.7, 128.3, 127.1, 118.3, 115.2, 107.1, 70.6, 55.8, 21.5. HRMS (ESI) m/z calcd for. $C_{23}H_{18}N_2O_4NaS$ $[M+Na]^+$ 441.0885, found 441.0891.



5-nitro-1-tosylindolin-3-yl benzoate (3ea)

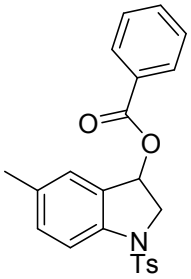
White solid. m.p. 124 – 126 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.87 (d, *J* = 9.6 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 6.25 (d, *J* = 5.1 Hz, 1H), 4.34 – 4.19 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 148.2, 145.3, 144.0, 133.7, 133.4, 130.1, 129.8, 129.8, 128.7, 128.4, 127.4, 127.1, 123.3, 114.4, 70.4, 56.5, 21.6. HRMS (ESI) m/z calcd for. $C_{22}H_{18}N_2O_6NaS$ $[M+Na]^+$ 461.0783, found 461.0787.



5-methoxy-1-tosylindolin-3-yl benzoate (3fa)

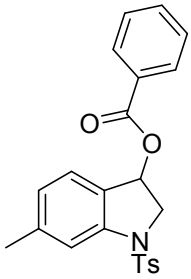
White solid. m.p.149 – 150 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 3H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.00 – 6.92 (m, 2H), 6.07 (dd, *J* = 6.8, 1.8 Hz, 1H), 4.18 (dd, *J* = 13.6, 6.9 Hz, 1H), 4.10 (dd, *J* = 13.6, 2.1 Hz, 1H), 3.77 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 156.9, 144.0, 136.5, 133.5, 133.2, 130.5, 129.6,

129.5, 129.2, 128.2, 127.3, 117.1, 117.0, 111.4, 72.2, 56.0, 55.6, 21.5. HRMS (ESI) m/z calcd for. $C_{23}H_{21}NO_5NaS$ $[M+Na]^+$ 446.1038, found 446.1042.



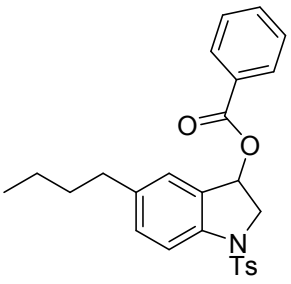
5-methyl-1-tosylindolin-3-yl benzoate (3ga)

White solid. m.p. 131 – 133 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.71 – 7.67 (m, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.48 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.22-7.20 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.12 (dd, *J* = 6.4, 2.4 Hz, 1H), 4.15 (dd, *J* = 13.4, 6.4 Hz, 1H), 4.10 (dd, *J* = 13.4, 2.5 Hz, 1H), 2.30 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 144.0, 140.7, 134.2, 133.6, 133.2, 131.7, 130.1, 129.6, 129.3, 129.2, 128.4, 128.2, 127.3, 115.4, 72.0, 55.9, 21.5, 20.8. HRMS (ESI) m/z calcd for. $C_{23}H_{21}NO_4NaS$ $[M+Na]^+$ 430.1089, found 430.1092.



6-methyl-1-tosylindolin-3-yl benzoate (3ha)

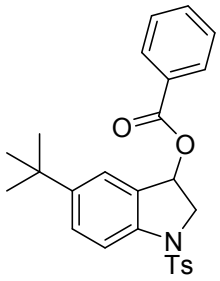
White solid. m.p. 122 - 123 °C (from $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.63 (s, 1H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.12 (s, 1H), 4.21 – 4.06 (m, 2H), 2.43 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 144.1, 143.3, 141.6, 133.9, 133.2, 129.7, 129.6, 129.4, 128.2, 127.2, 126.6, 126.3, 125.2, 116.0, 71.9, 56.1, 21.9, 21.5. HRMS (ESI) m/z calcd for. $C_{23}H_{21}NO_4NaS$ $[M+Na]^+$ 430.1089, found 430.1092.



5-butyl-1-tosylindolin-3-yl benzoate (3ia)

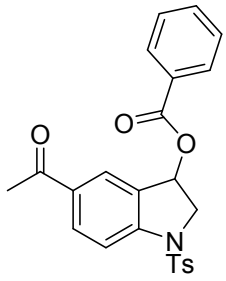
White solid. m.p. 110 – 111 °C (from $CDCl_3$). ^1H NMR (400 MHz, CDCl3) δ 7.70 – 7.65 (m, 2H), 7.64 – 7.60 (m, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 6.7 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.06 (dd, *J* = 6.5, 2.3 Hz, 1H), 4.08 (dd, *J* = 13.3, 6.6 Hz, 1H), 4.02 (dd, *J* = 13.3, 2.4 Hz, 1H), 2.48 (t, *J* = 7.8 Hz, 2H), 2.22 (s, 3H), 1.55 – 1.41 (m, 2H), 1.25 (dq, *J* = 14.6,

7.3 Hz, 2H), 0.82 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ165.9, 144.0, 140.9, 139.3, 133.8, 133.2, 131.1, 29.7, 129.6, 129.3, 129.1, 128.2, 127.3, 126.6, 115.4, 72.1, 55.9, 35.0, 33.6, 22.3, 21.5, HRMS (ESI) m/z calcd for. $C_{26}H_{27}NO_4NaS$ $[M+Na]^+$ 472.1558, found 472.1552.



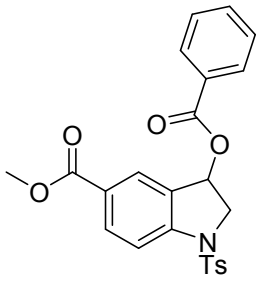
5-(*tert*-butyl)-1-tosylindolin-3-yl benzoate (3ja)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.70 (d, J = 9.7 Hz, 2H), 7.67 (s, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 6.16 (dd, J = 6.4, 2.3 Hz, 1H), 4.15 (dd, J = 13.2, 6.5 Hz, 1H), 4.10 (dd, J = 13.2, 2.5 Hz, 1H), 2.30 (s, 3H), 1.27 (d, J = 9.8 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 147.5, 144.0, 140.6, 133.8, 133.2, 129.8, 129.7, 129.4, 128.6, 128.2, 127.3, 126.8, 123.6, 114.9, 72.2, 56.0, 34.5, 31.4, 21.5. HRMS (ESI) m/z calcd for. $C_{26}H_{27}NO_4NaS$ $[M+Na]^+$ 472.1558, found 472.1566.



5-acetyl-1-tosylindolin-3-yl benzoate (3ka)

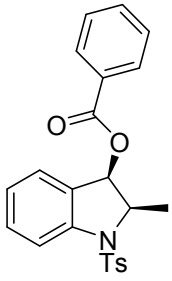
White solid. m.p.145 – 146 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 6.23 (d, J = 5.4 Hz, 1H), 4.28 – 4.13 (m, 2H), 2.56 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 165.8, 146.9, 144.8, 133.6, 133.5, 133.3, 132.0, 129.9, 129.7, 129.2, 129.0, 128.3, 127.6, 127.1, 114.5, 71.1, 56.3, 26.5, 21.5. HRMS (ESI) m/z calcd for. $C_{24}H_{21}NO_5NaS$ $[M+Na]^+$ 458.1038, found 458.1035.



methyl 3-(benzoyloxy)-1-tosylindoline-5-carboxylate (3la)

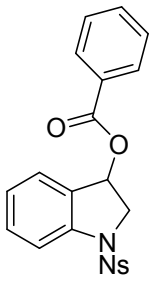
White solid. m.p.158 – 160 °C (from $CDCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 1H), 8.09 (s, 1H), 7.83 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.20 (d, J =

7.9 Hz, 2H), 6.21 (d, *J* = 6.1 Hz, 1H), 4.29 – 4.11 (m, 2H), 3.88 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.8, 146.9, 144.8, 133.7, 133.5, 133.1, 129.9, 129.8, 129.1, 129.1, 128.7, 128.3, 127.2, 126.1, 114.6, 71.1, 56.3, 52.2, 21.6. HRMS (ESI) m/z calcd for. $C_{24}H_{21}NO_6NaS$ $[M+Na]^+$ 474.0987, found 474.0987.



2-methyl-1-tosylindolin-3-yl benzoate (3ma)

White solid. m.p. 121 – 122 °C (from $CDCl_3$). dr: > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 6.5 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.20 (d, *J* = 8.1 Hz, 1H), 4.50-4.43 (m, 1H), 2.37 (s, 3H), 1.52 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 144.4, 141.7, 134.2, 133.6, 130.5, 129.9, 129.8, 129.7, 129.2, 128.6, 127.2, 126.0, 124.9, 117.0, 74.6, 61.4, 21.6, 15.8. HRMS (ESI) m/z calcd for. $C_{23}H_{21}NO_4NaS$ $[M+Na]^+$ 430.1089, found 430.1087.

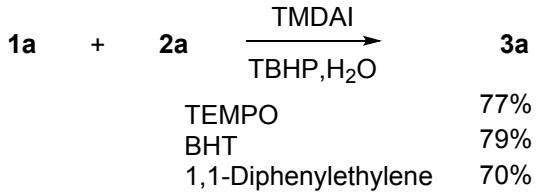


1-((4-nitrophenyl)sulfonyl)indolin-3-yl benzoate (3na)

Brown solid. m.p. 129 -131 °C (from $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.87 – 7.78 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.24 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.01 (d, *J* = 5.5 Hz, 1H), 4.18 (dd, *J* = 13.8, 6.6 Hz, 1H), 4.07 (dd, *J* = 13.8, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 150.2, 142.3, 142.2, 133.7, 131.3, 129.3, 129.3, 128.7, 128.3, 127.3, 125.4, 124.2, 116.1, 71.8, 56.1. $C_{21}H_{16}N_2O_6NaS$ $[M+Na]^+$ 447.0627, found 447.0634.

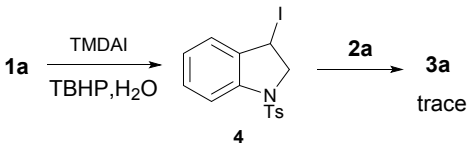
Mechanistic Studies

1. Radial Trapping Experiments



Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), TBHP (0.6 mmol, 70% in water), TMDAI (20% mol), radial scavenger (0.6 mmol), water (2 mL).

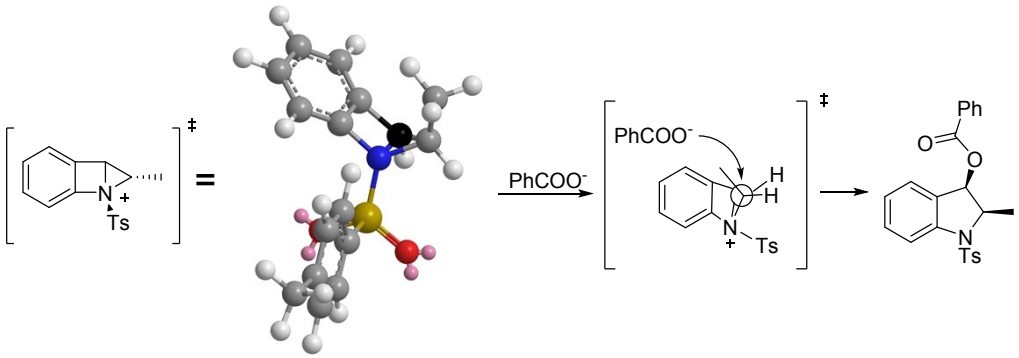
2. Intermediate Experiments



detected by GC-MS

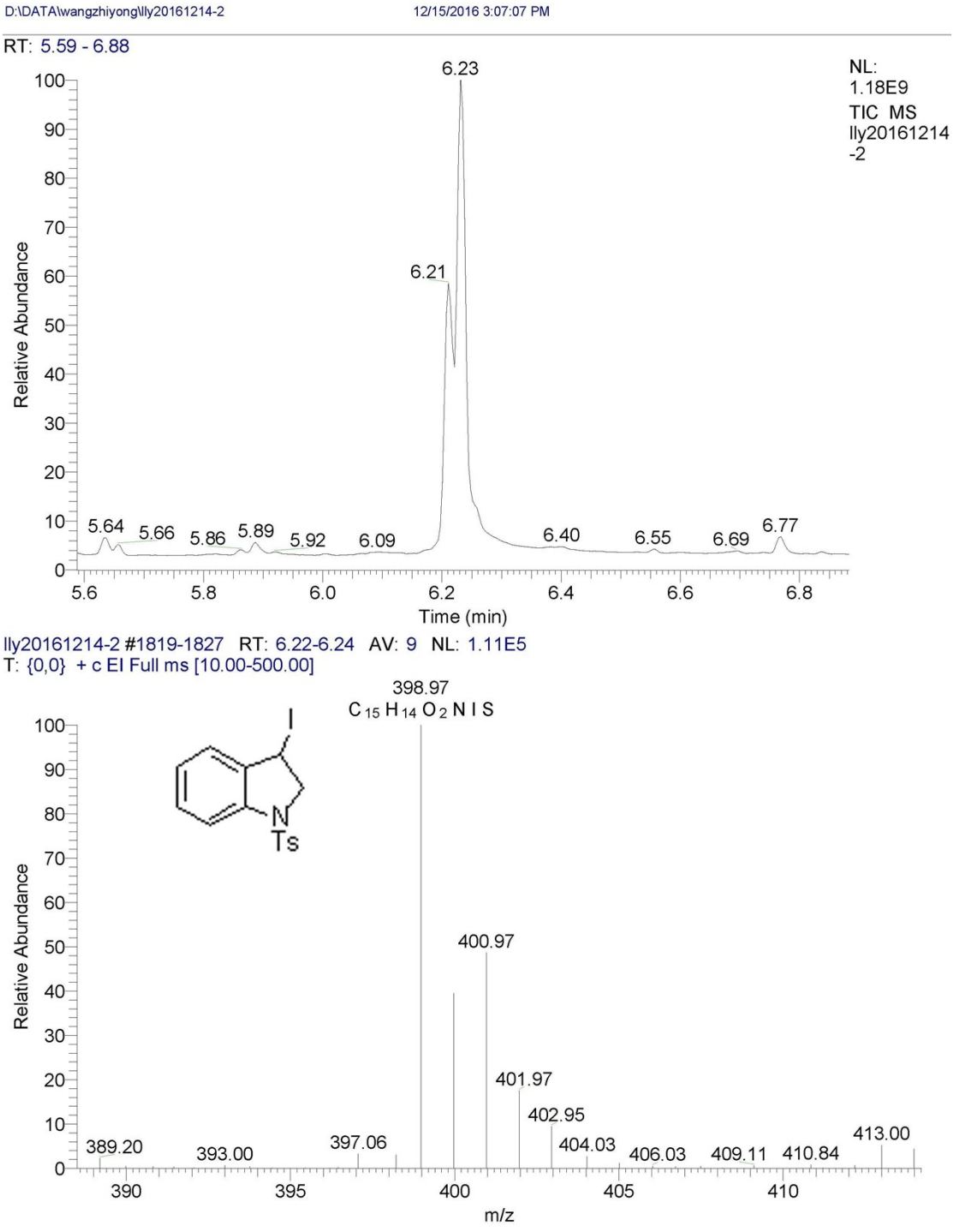
To a 10 mL tube was added **1a** (0.2 mmol), TBHP (0.6 mmol, 70% in water), TMDAI (20% mol) and water (2 mL). This mixture was stirred at 45 °C for 12 h and analyzed by GC-MS before adding **2a** (0.3 mmol). Then the mixture was stirred at 45 °C for another 12 h. After treated according to standing process, only trace of **3a** was obtained**.**

3. Plausible transition state



The carboxylic acid attacks the carbon atom (the black one in the 3D picture) from the backside of the carbon-nitrogen bond to breaking the carbon-nitrogen bond, giving the *syn*-product. Also the steric hindrance of this pathway is relatively small due to the Ts group exists in the front side.

The Result of GC-MS Analysis



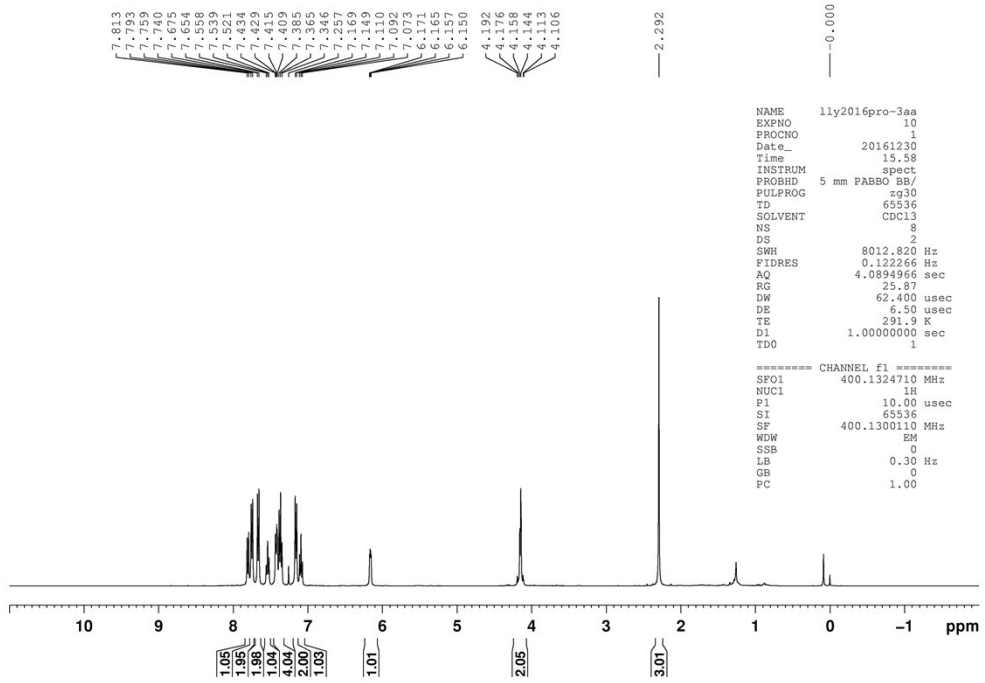
References

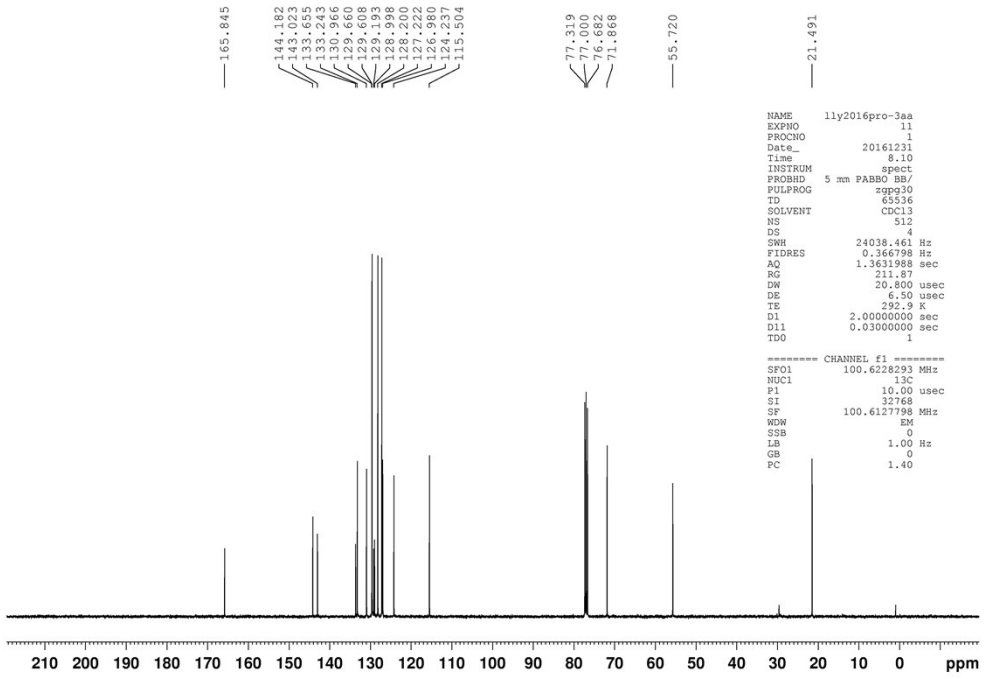
1. X. Zhang, R. Guo and X. Zhao, *Org. Chem. Front.*, 2015, **2**, 1334-1337.

2. A. Aoyama, K. Endo-Umeda, K. Kishida, K. Ohgane, T. Noguchi-Yachide, H. Aoyama, M. Ishikawa, H. Miyachi, M. Makishima and Y. Hashimoto, *J Med Chem*, 2012, **55**, 7360-7377.

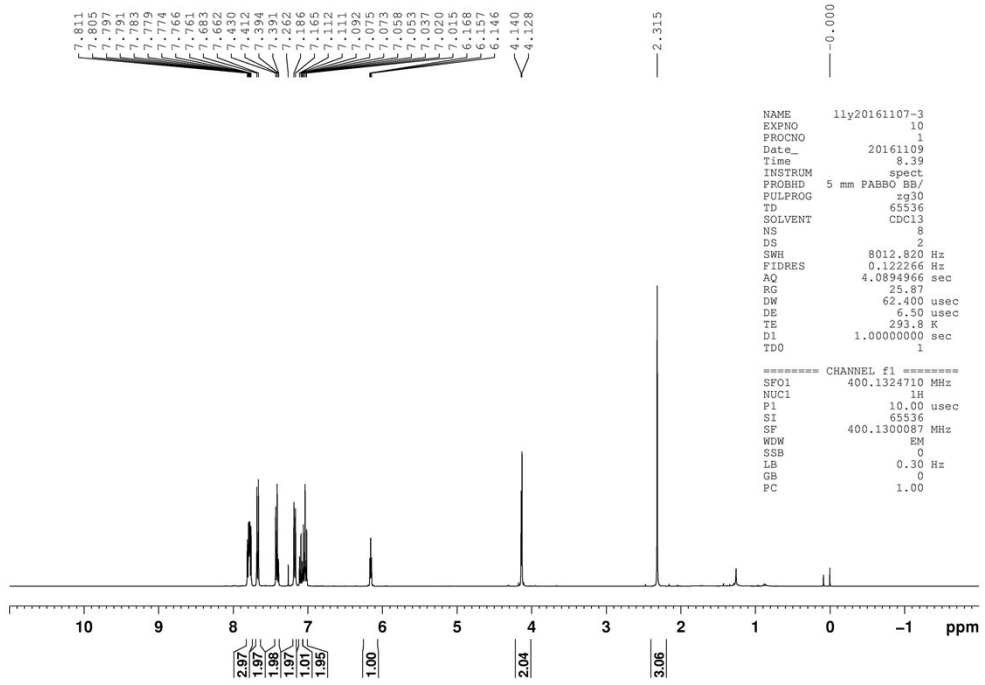
^{1}H NMR and ^{13}C NMR spectra

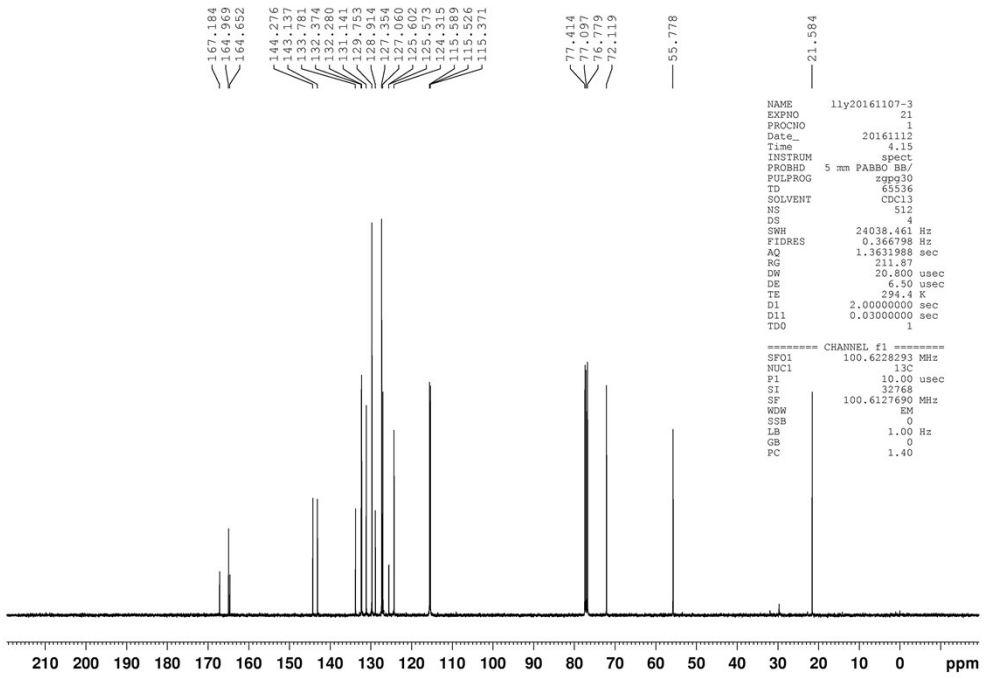
1-tosylindolin-3-yl benzoate (3aa)



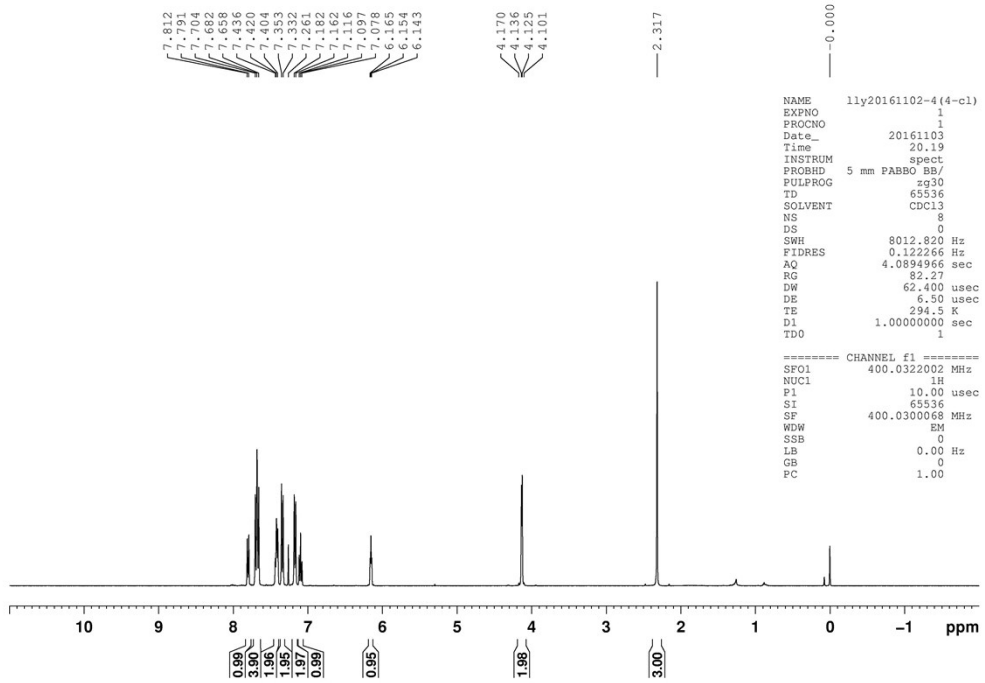


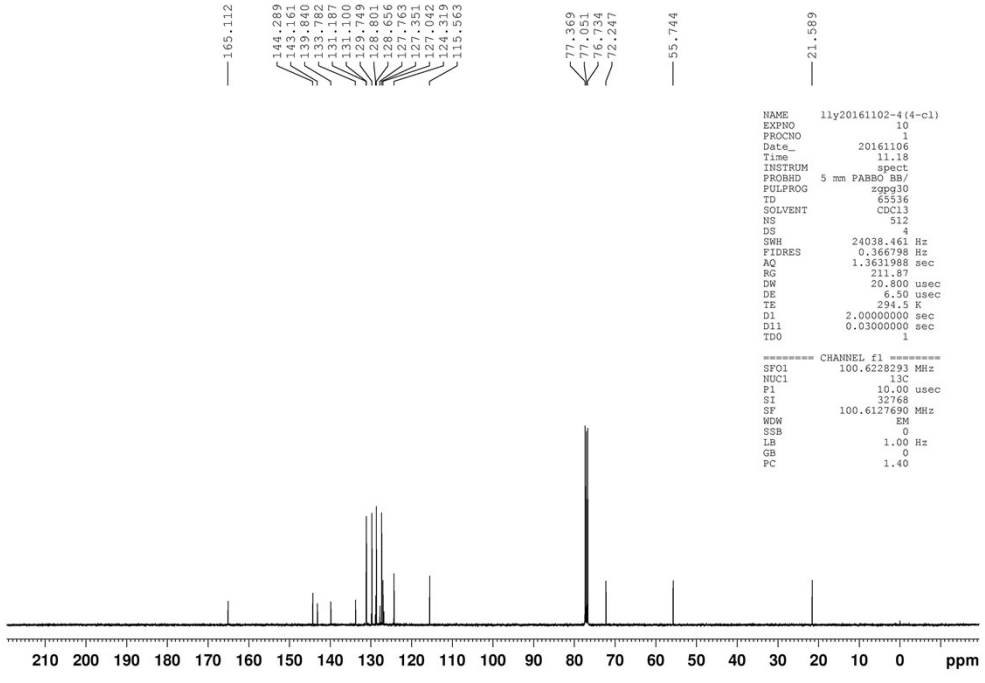
1-tosylindolin-3-yl 4-fluorobenzoate (3ab)



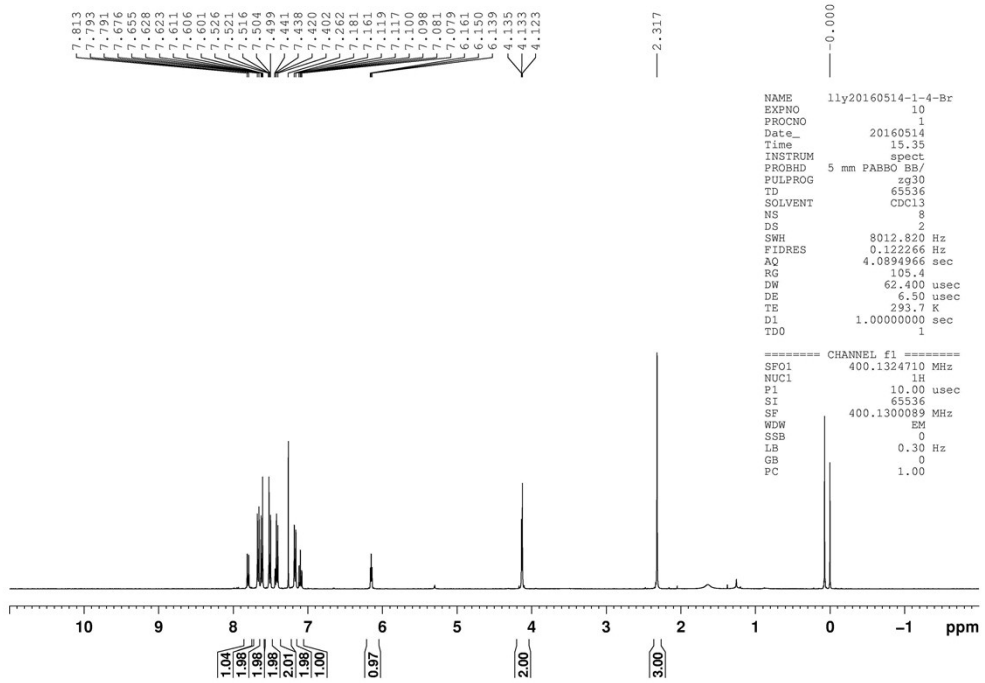


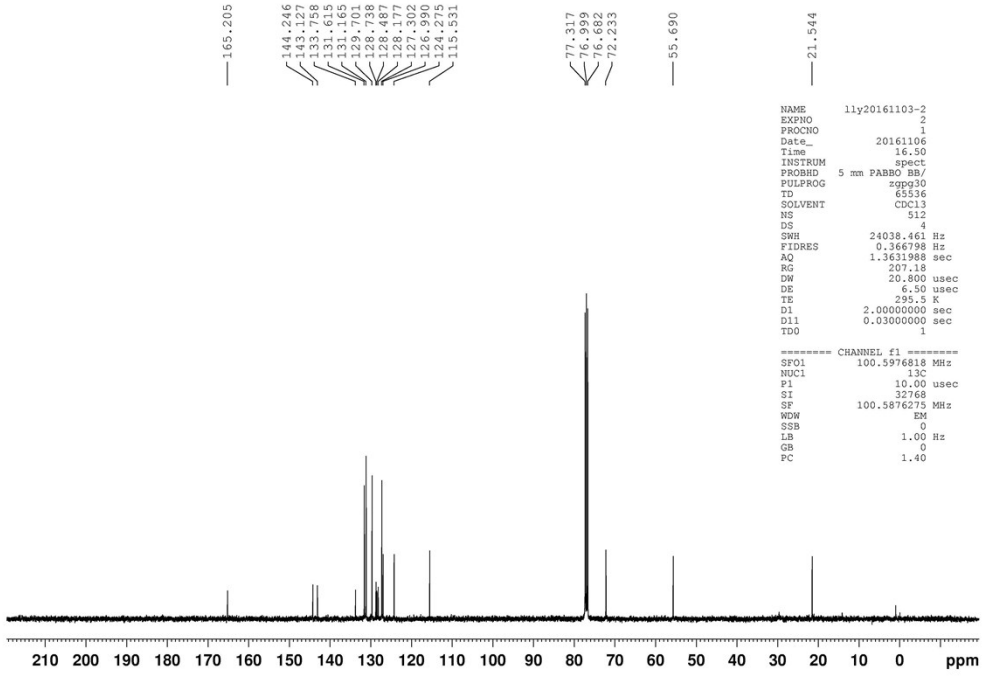
1-tosylindolin-3-yl 4-chlorobenzoate (3ac)



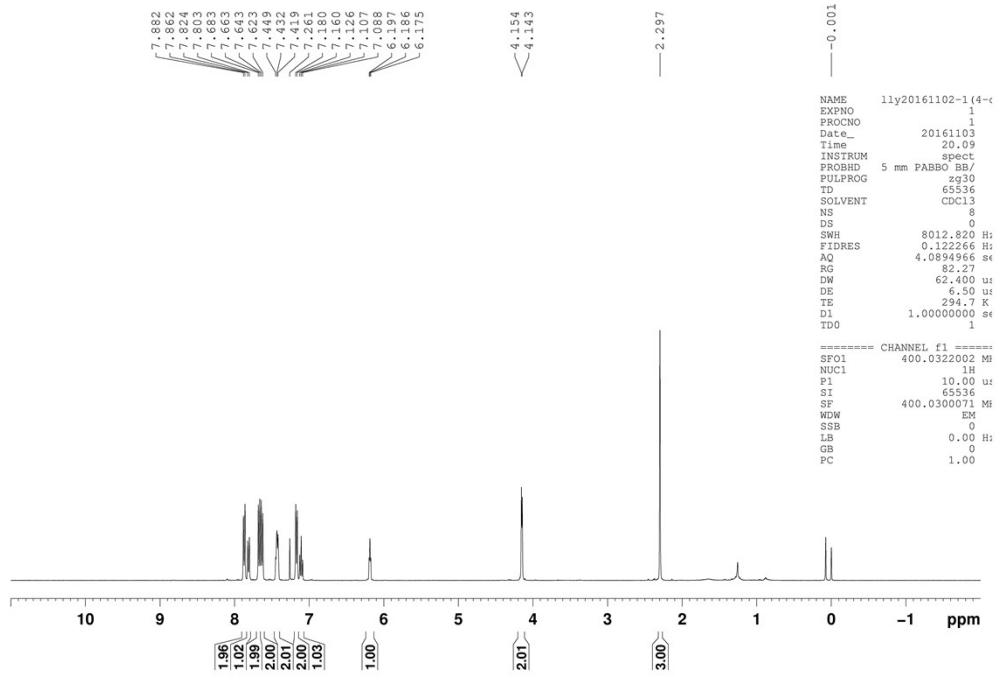


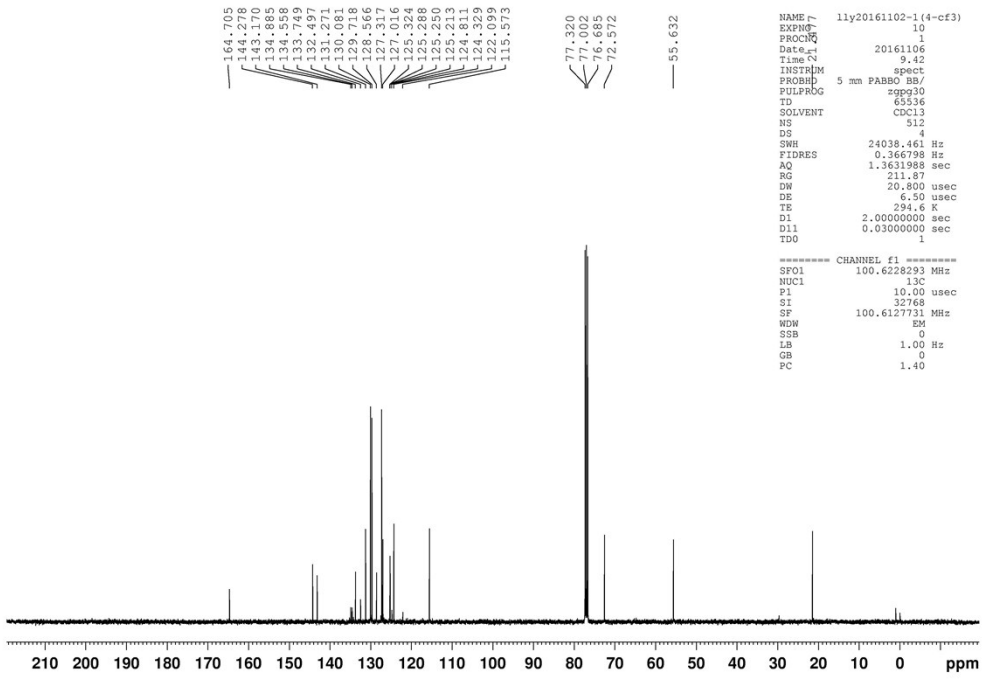
1-tosylindolin-3-yl 4-bromobenzoate (3ad)



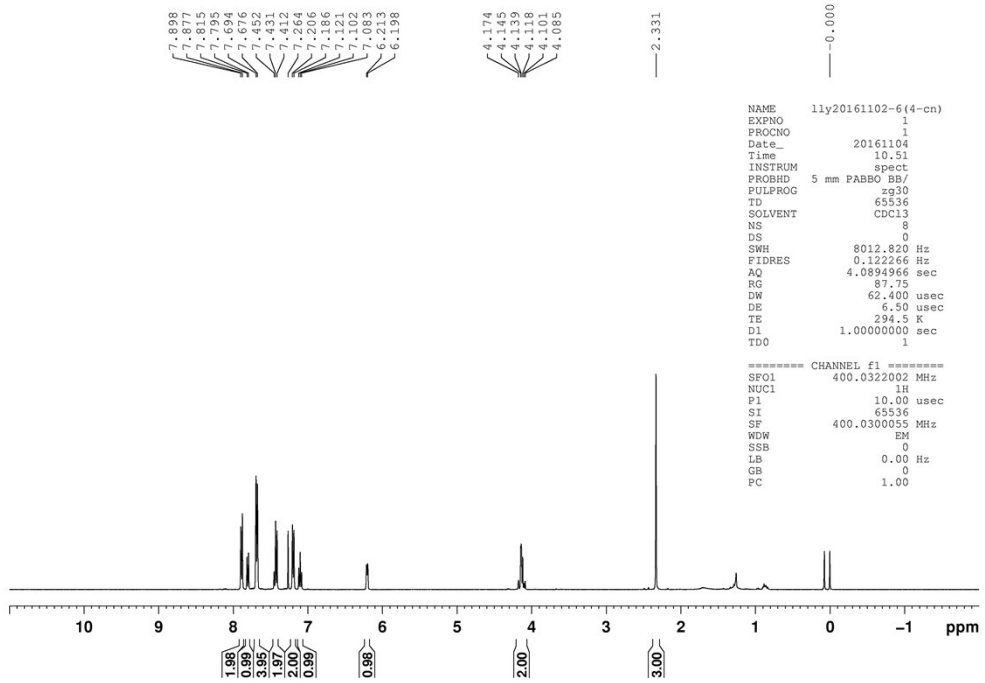


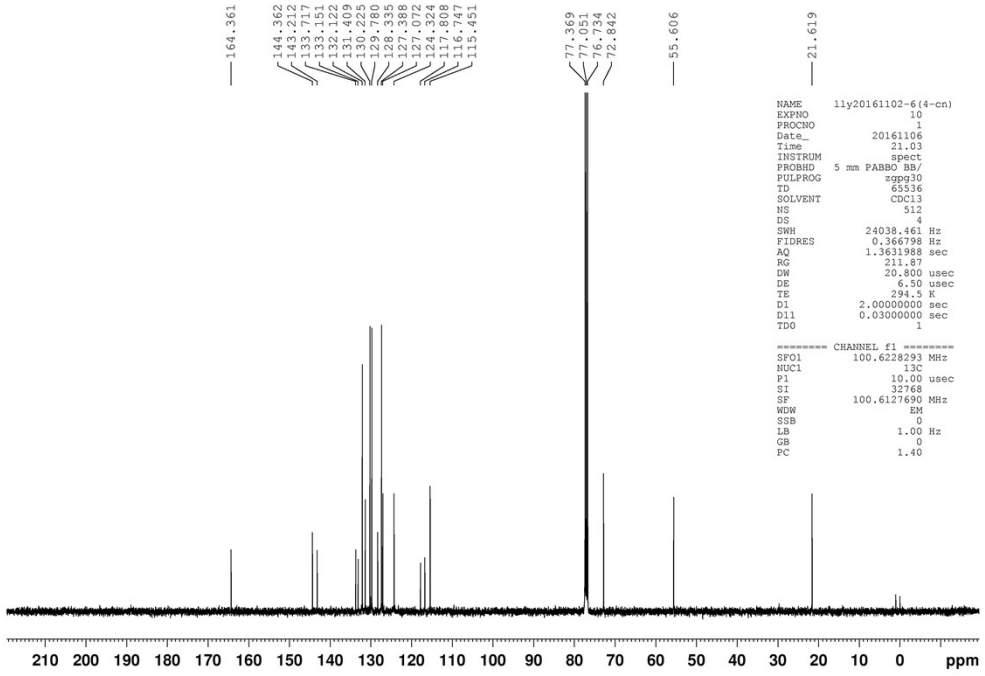
1-tosylindolin-3-yl 4-(trifluoromethyl)benzoate (3ae)



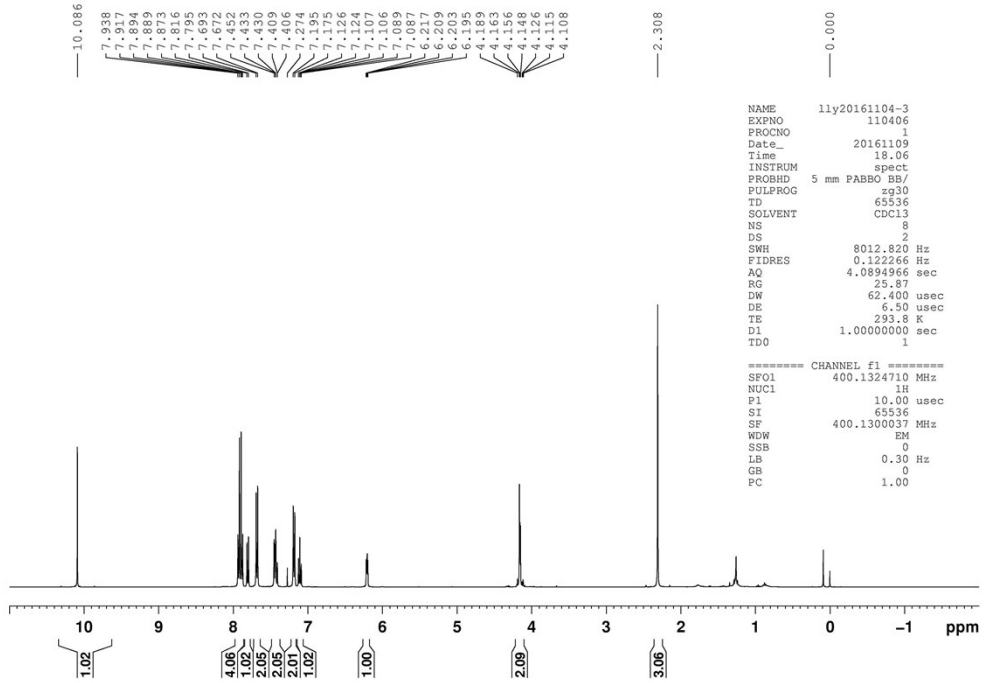


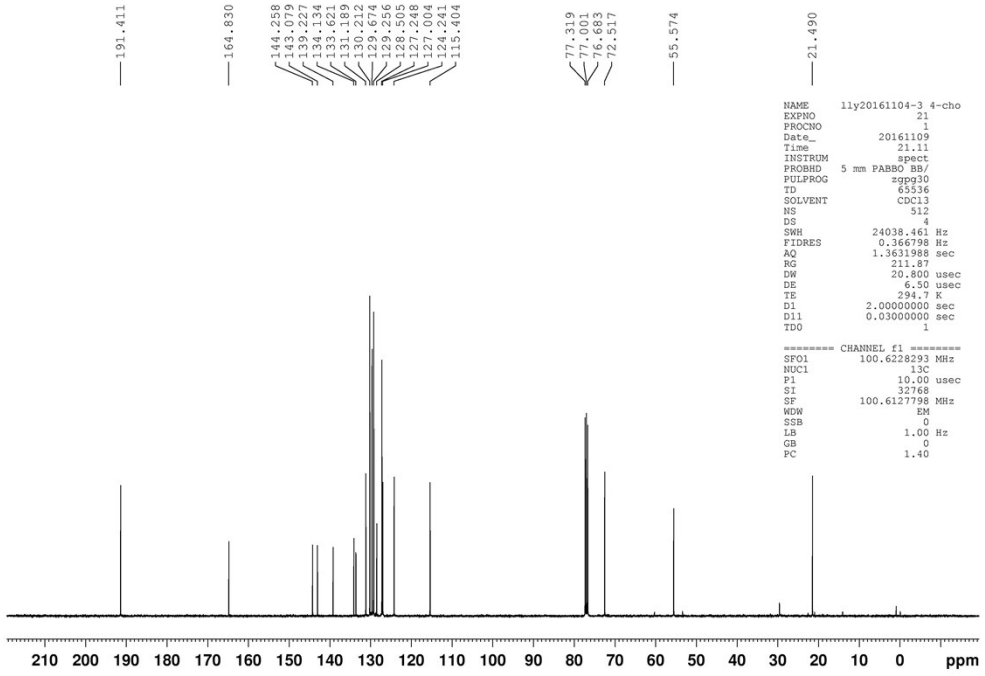
1-tosylindolin-3-yl 4-cyanobenzoate (3af)



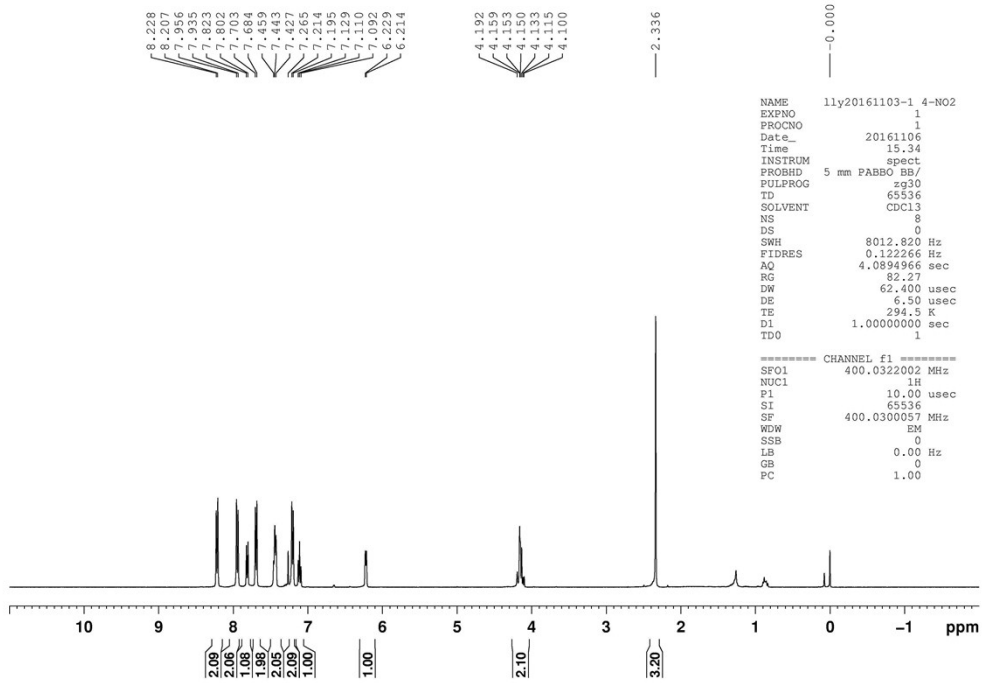


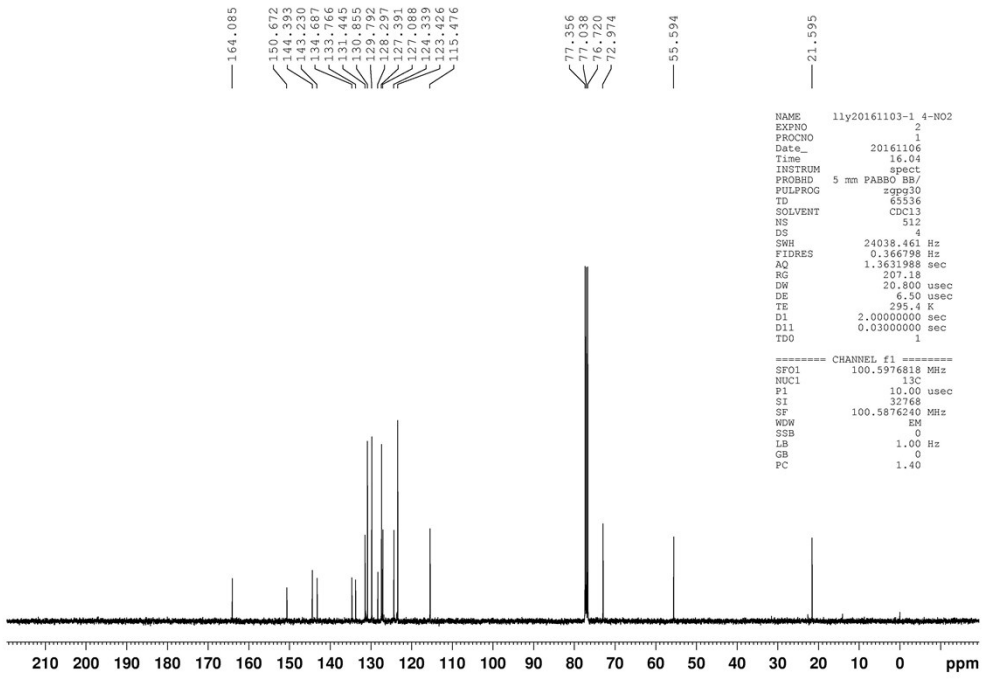
1-tosylindolin-3-yl 4-formylbenzoate (3ag)



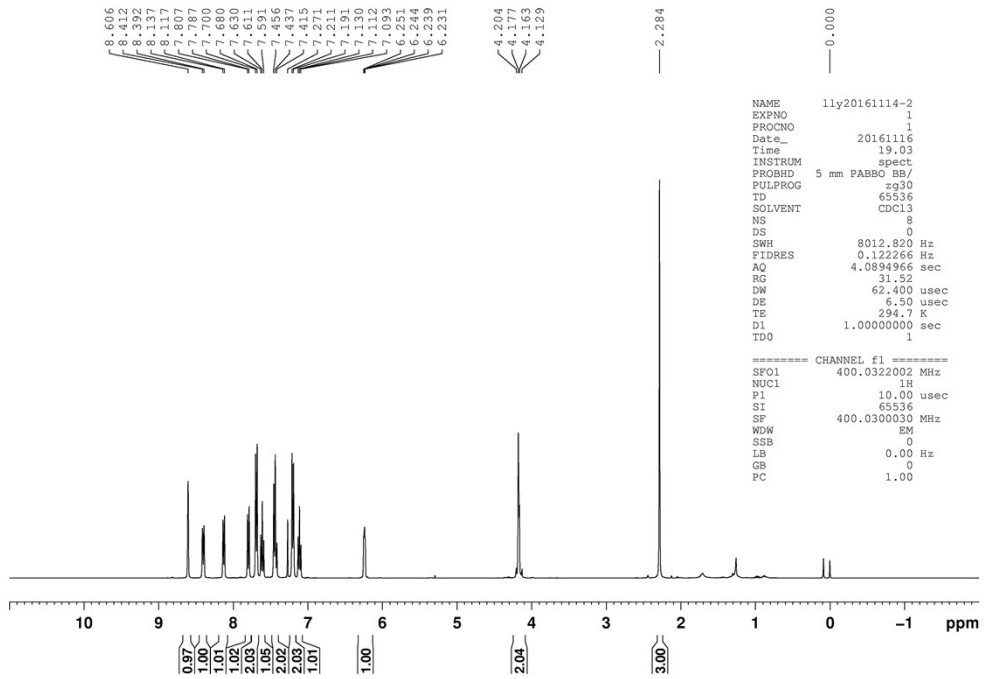


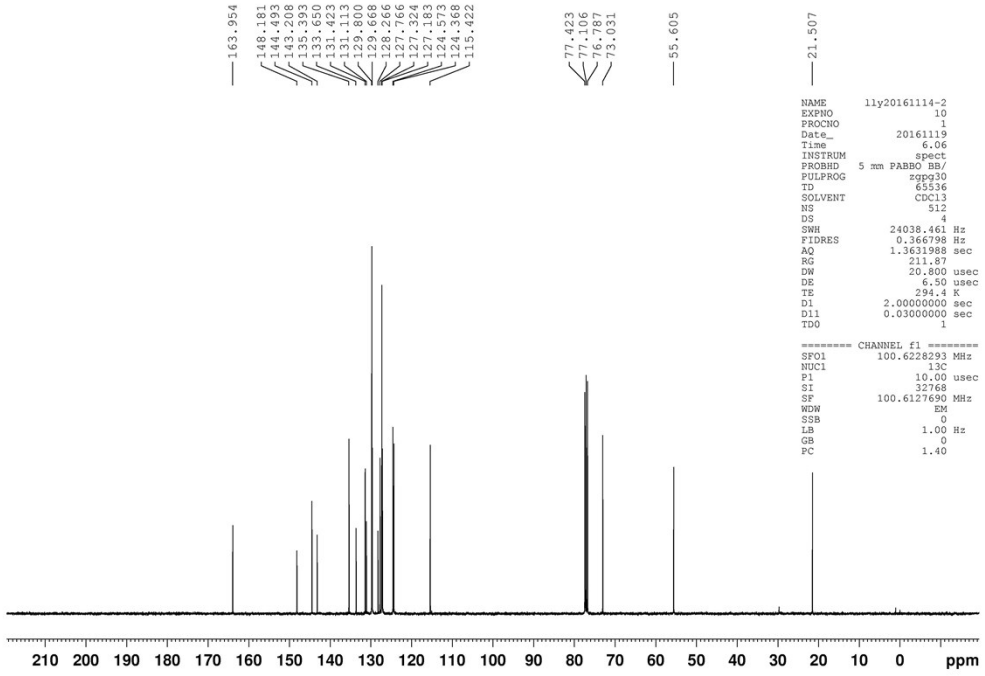
1-tosylindolin-3-yl 4-nitrobenzoate (3ah)



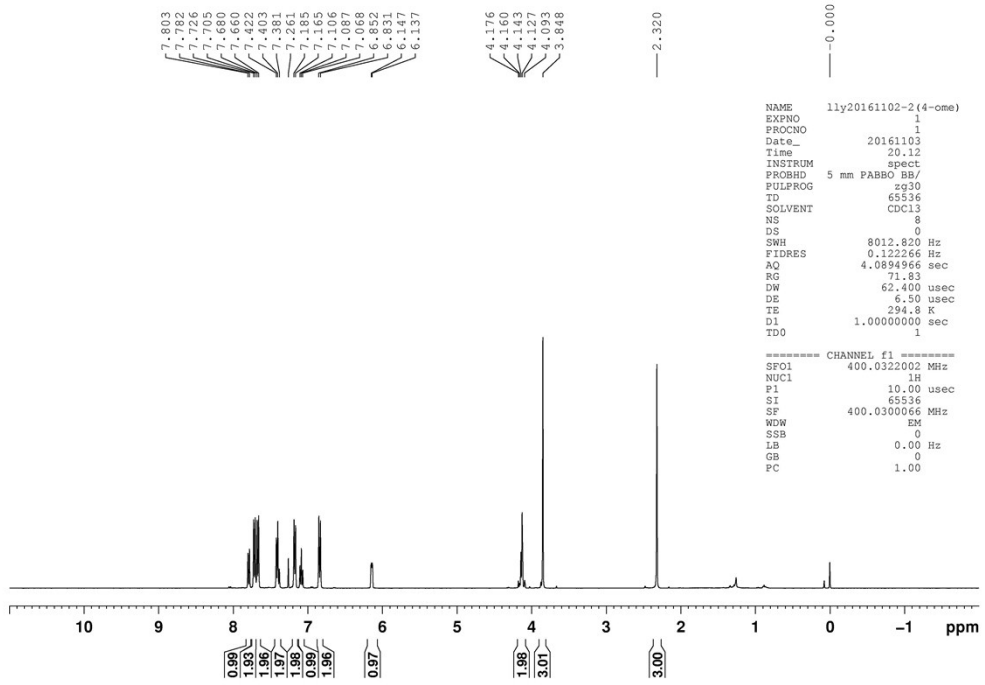


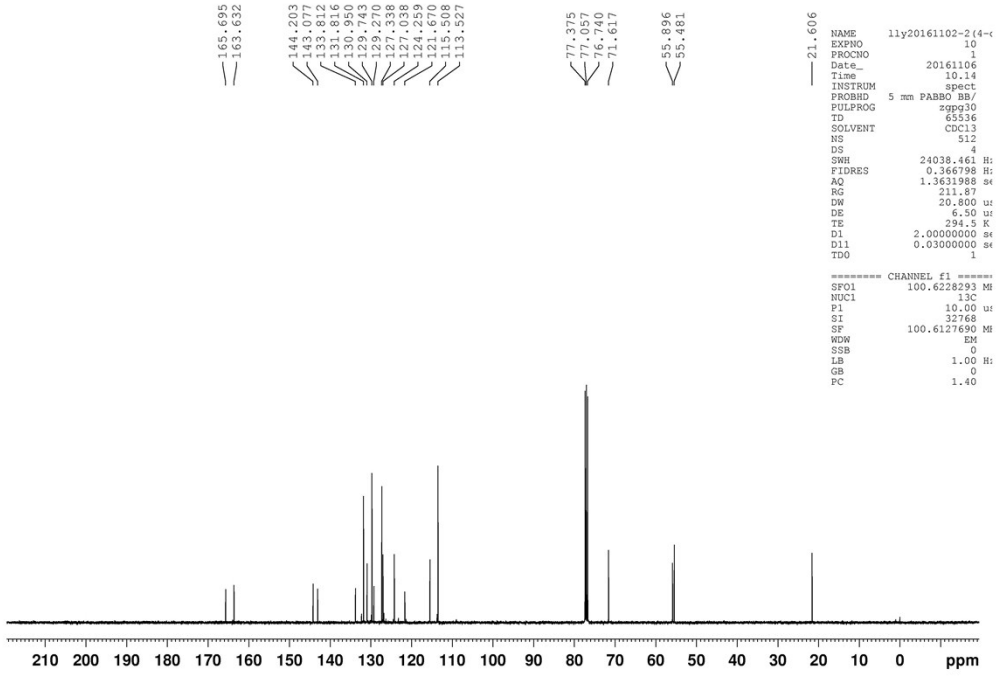
1-tosylindolin-3-yl 3-nitrobenzoate (3ai)



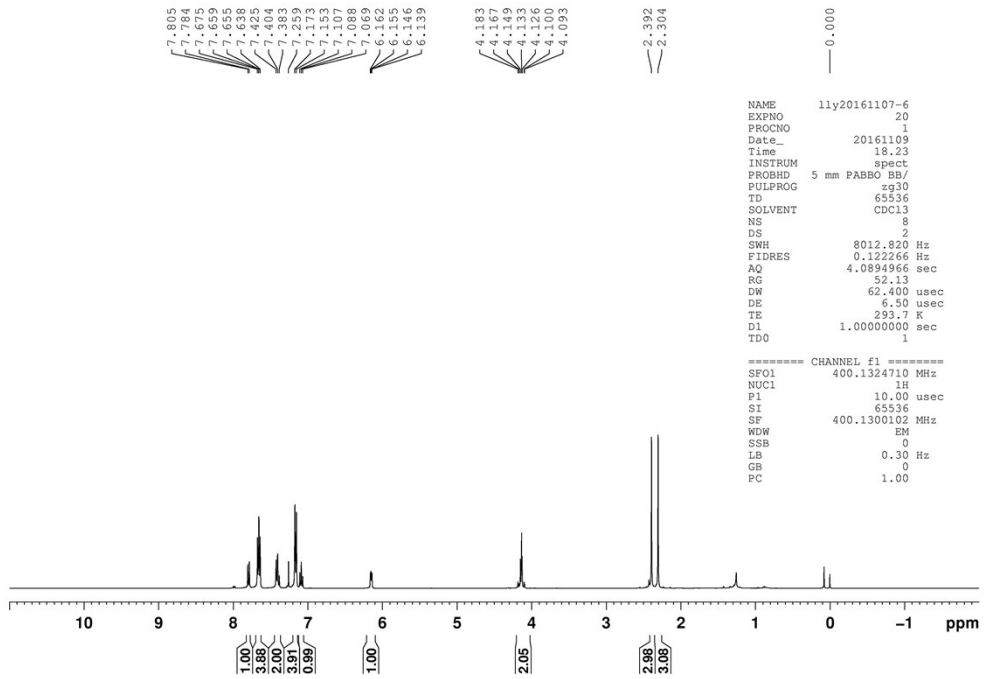


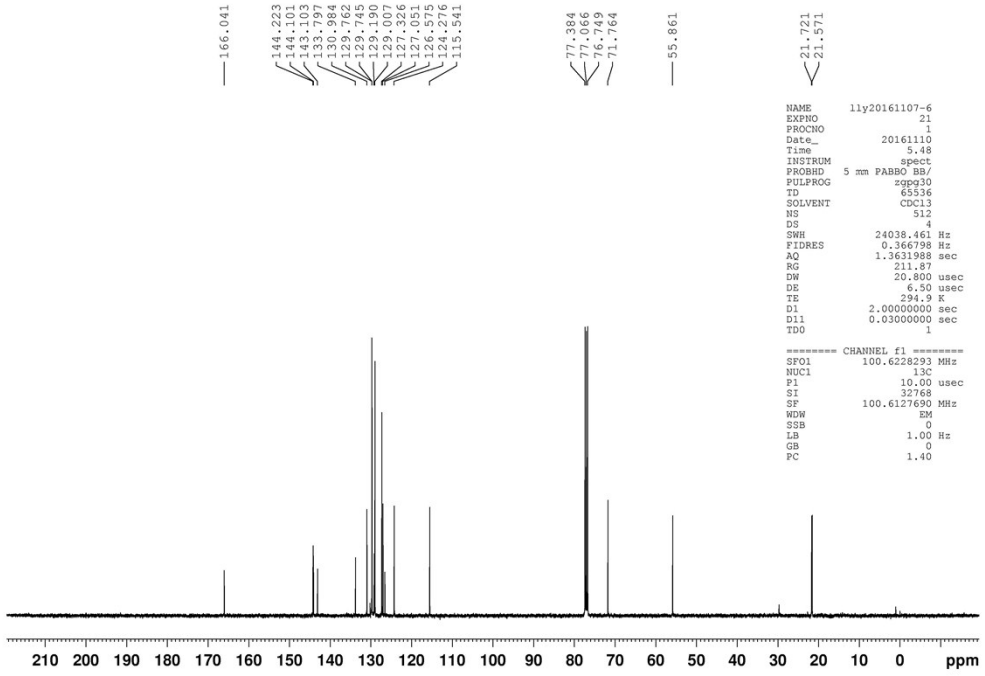
1-tosylindolin-3-yl 4-methoxybenzoate (3aj)



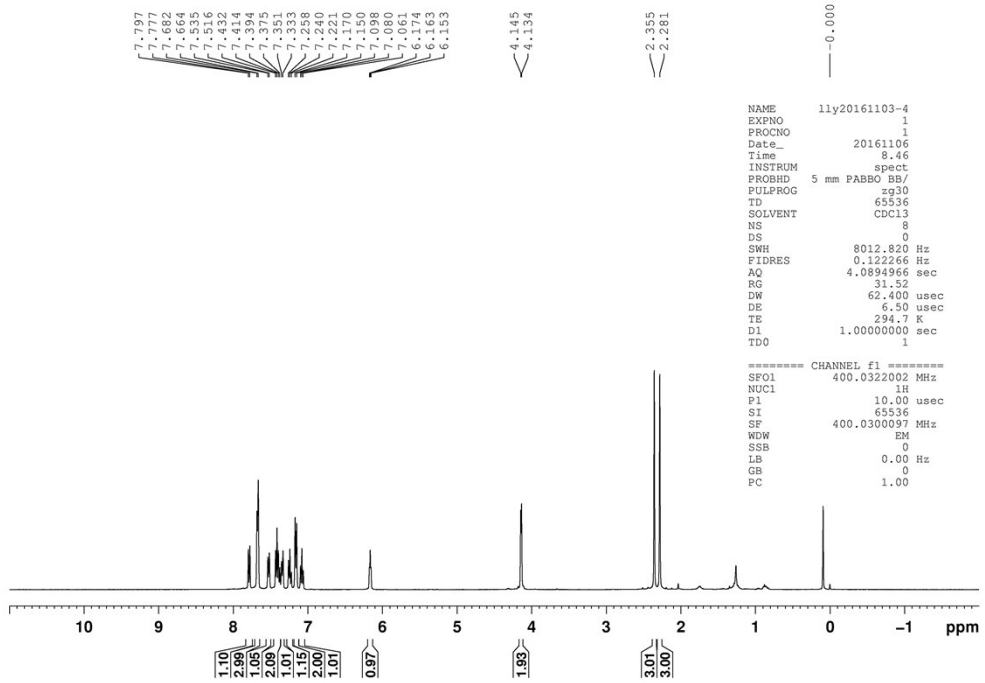


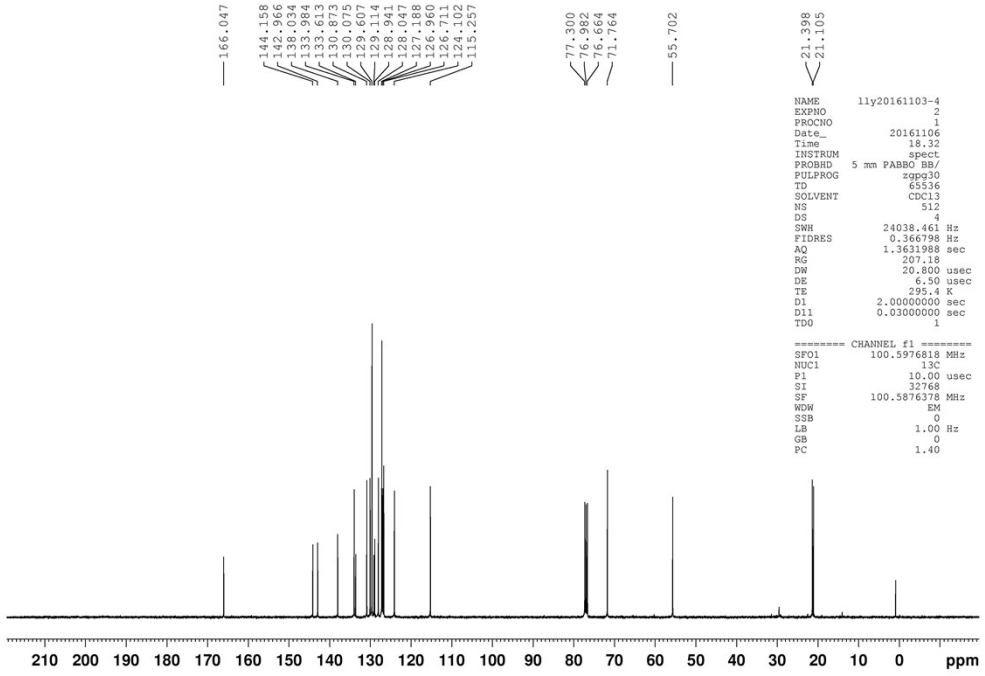
1-tosylindolin-3-yl 4-methylbenzoate (3ak)



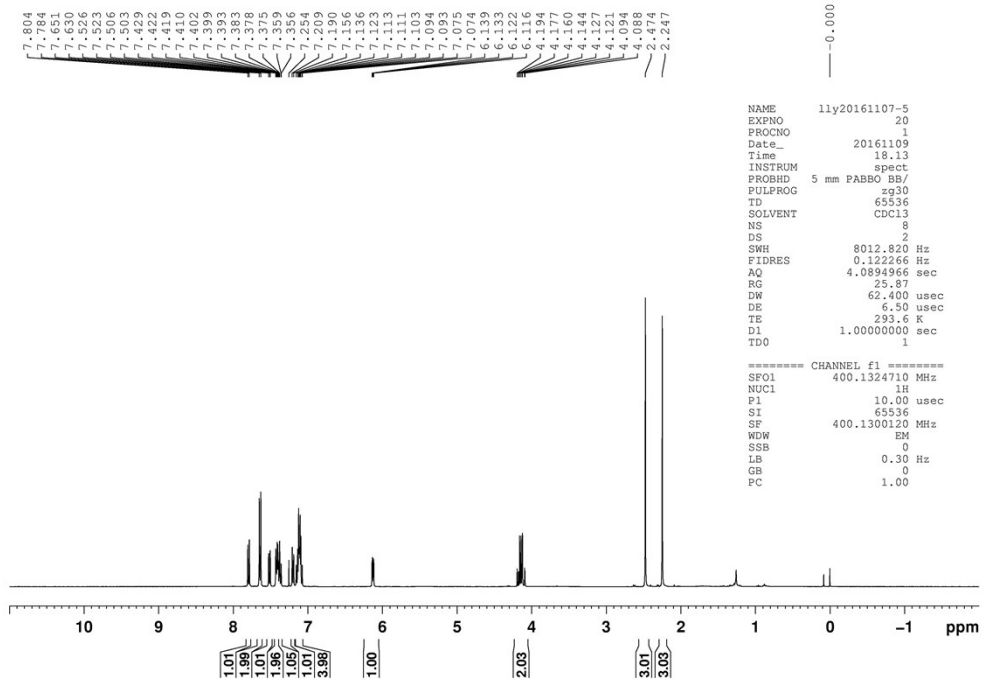


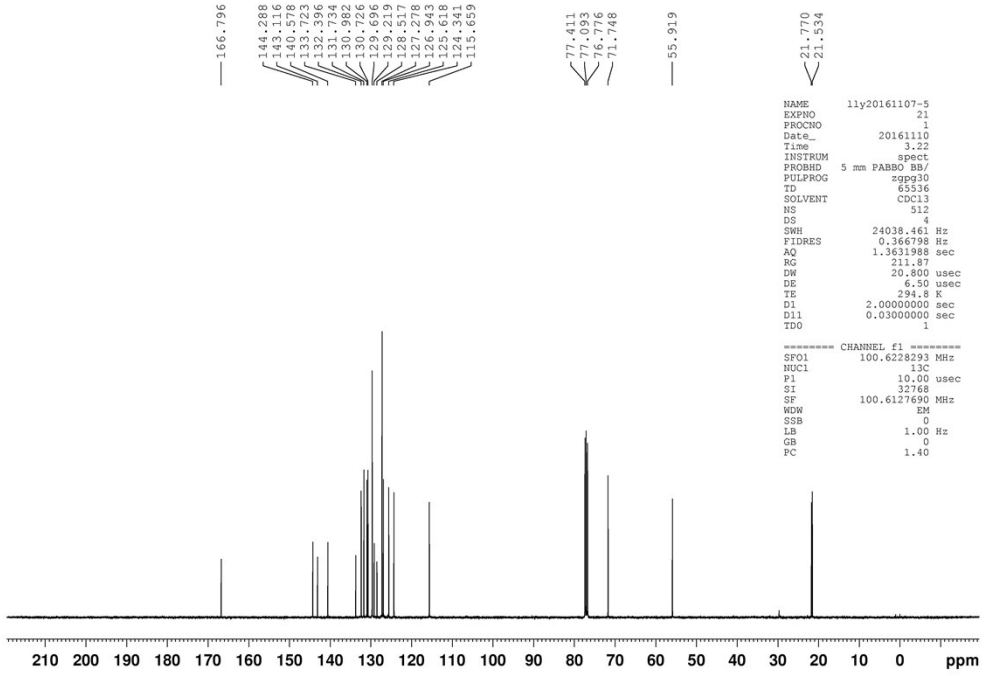
1-tosylindolin-3-yl 3-methylbenzoate (3al)



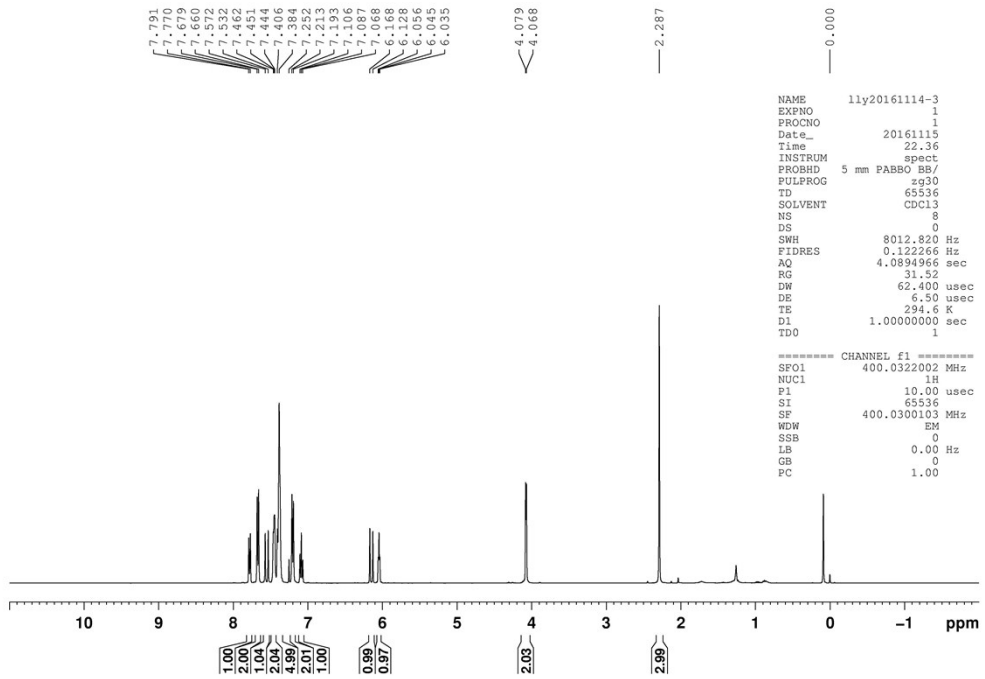


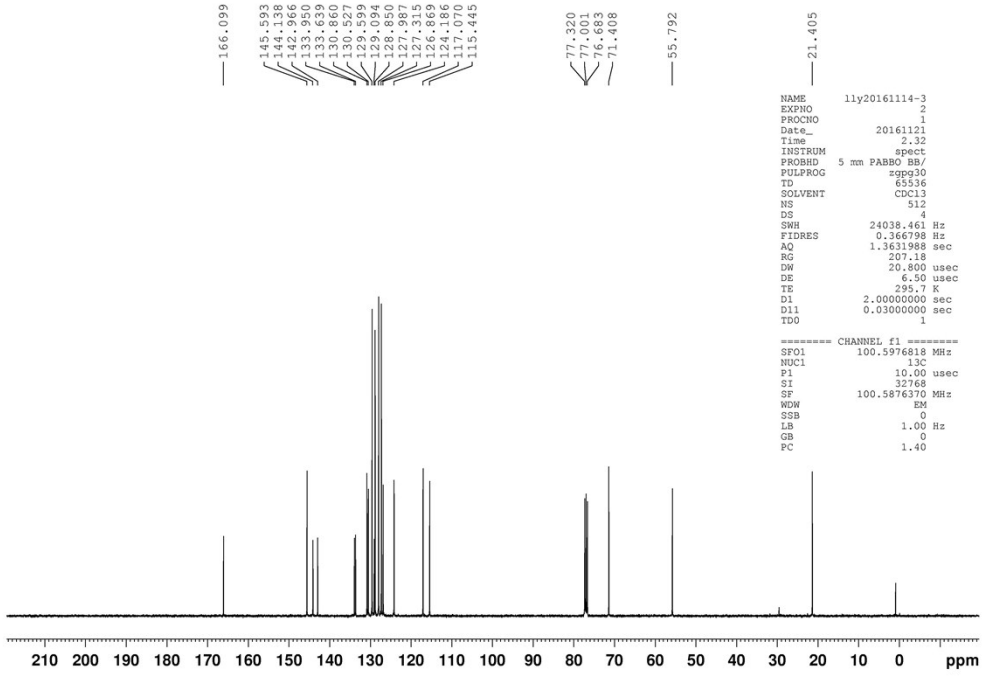
1-tosylindolin-3-yl 2-methylbenzoate (3am)



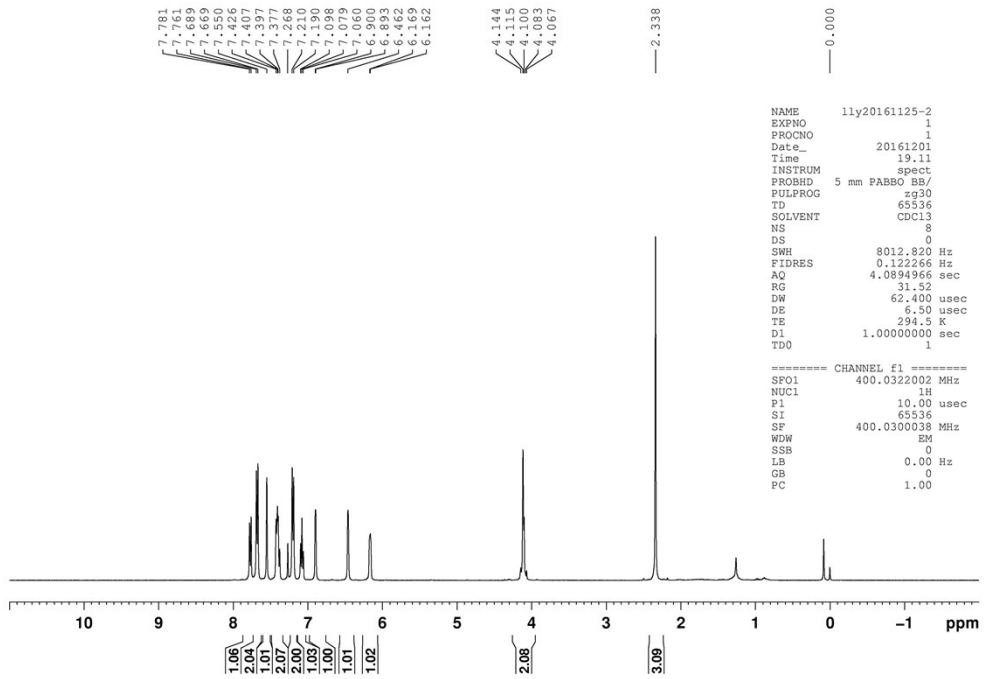


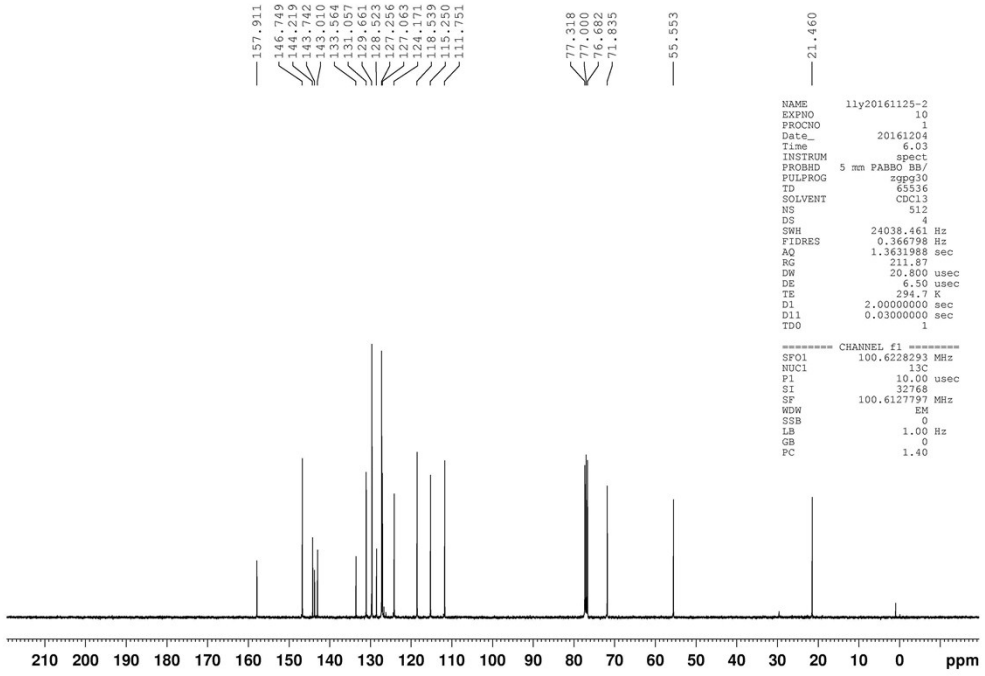
1-tosylindolin-3-yl cinnamate (3an)



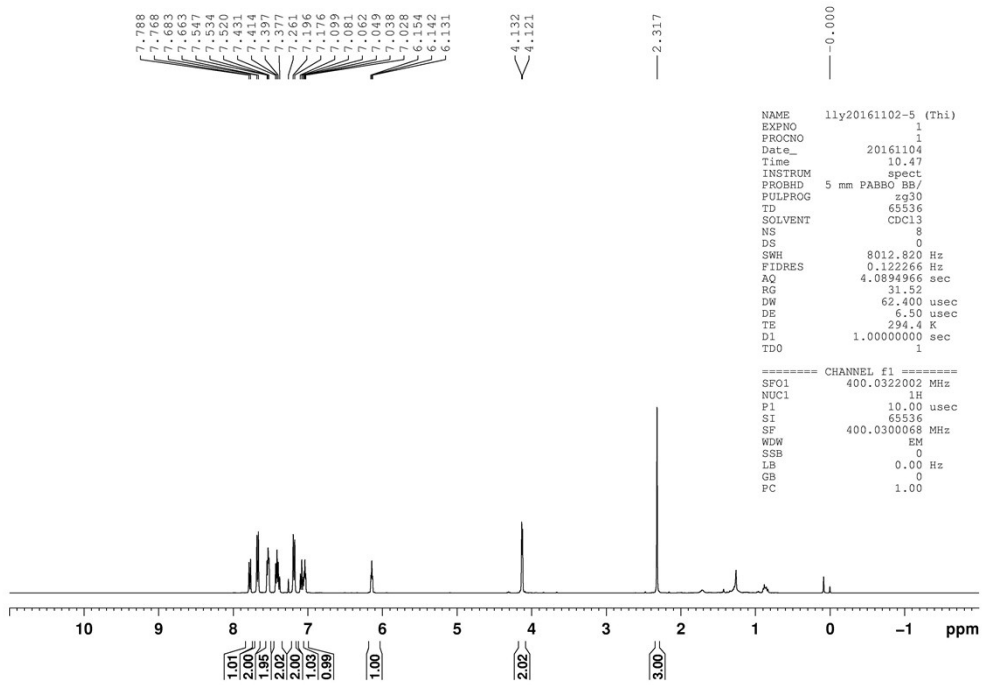


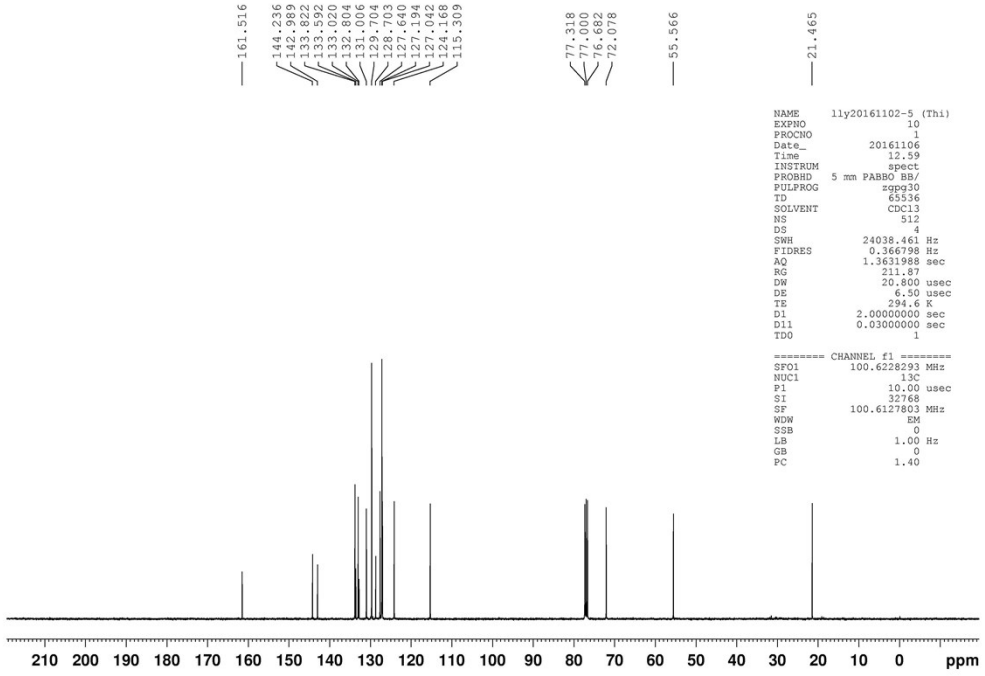
1-tosylindolin-3-yl furan-2-carboxylate (3ao)



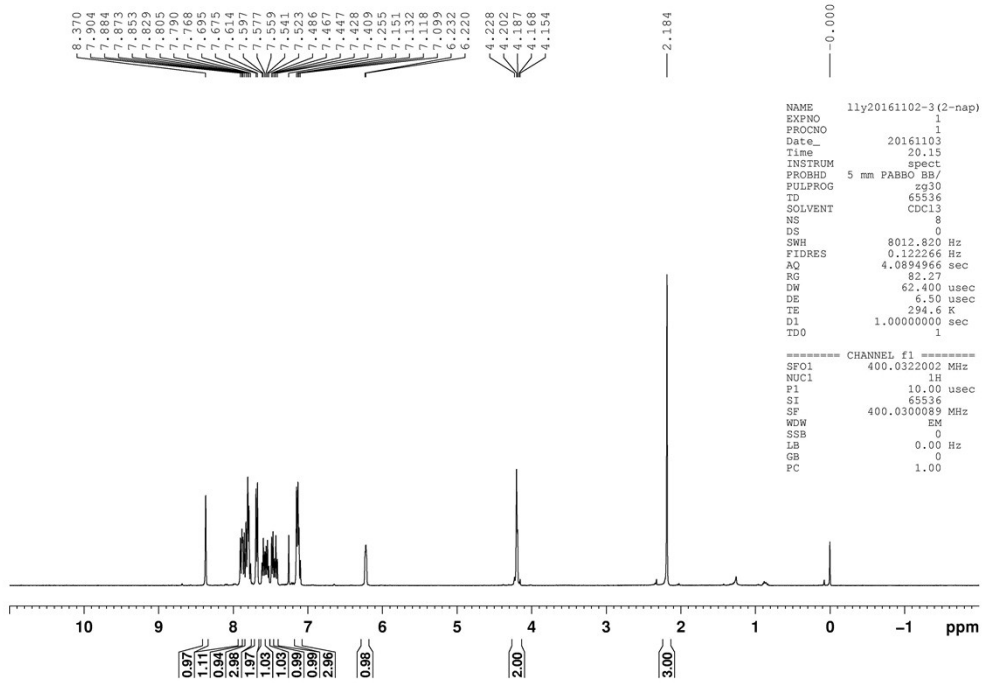


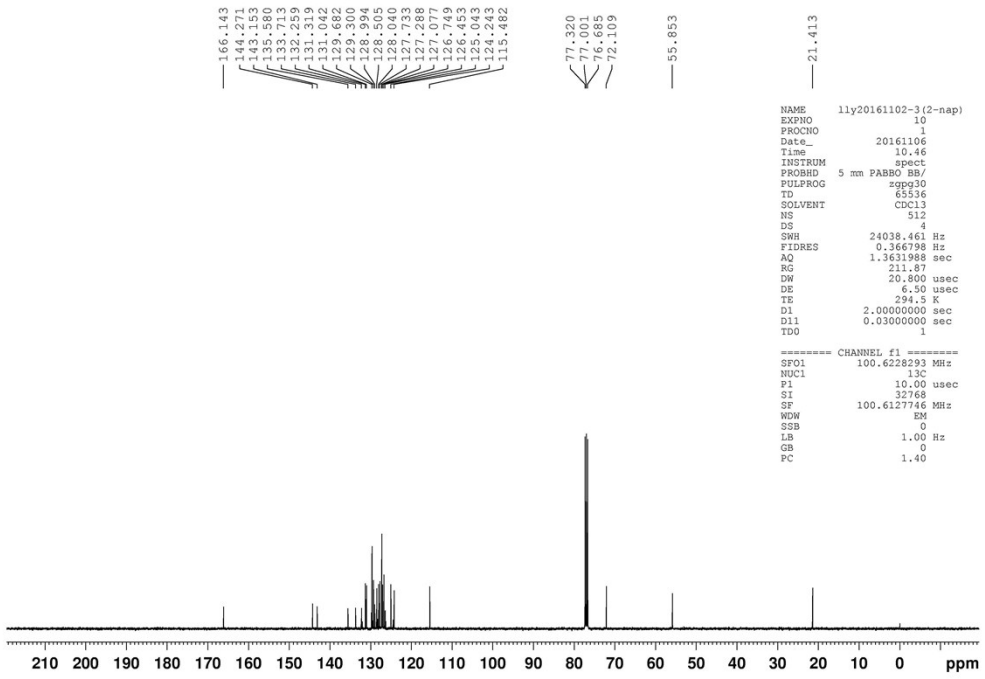
1-tosylindolin-3-yl thiophene-2-carboxylate (3ap)



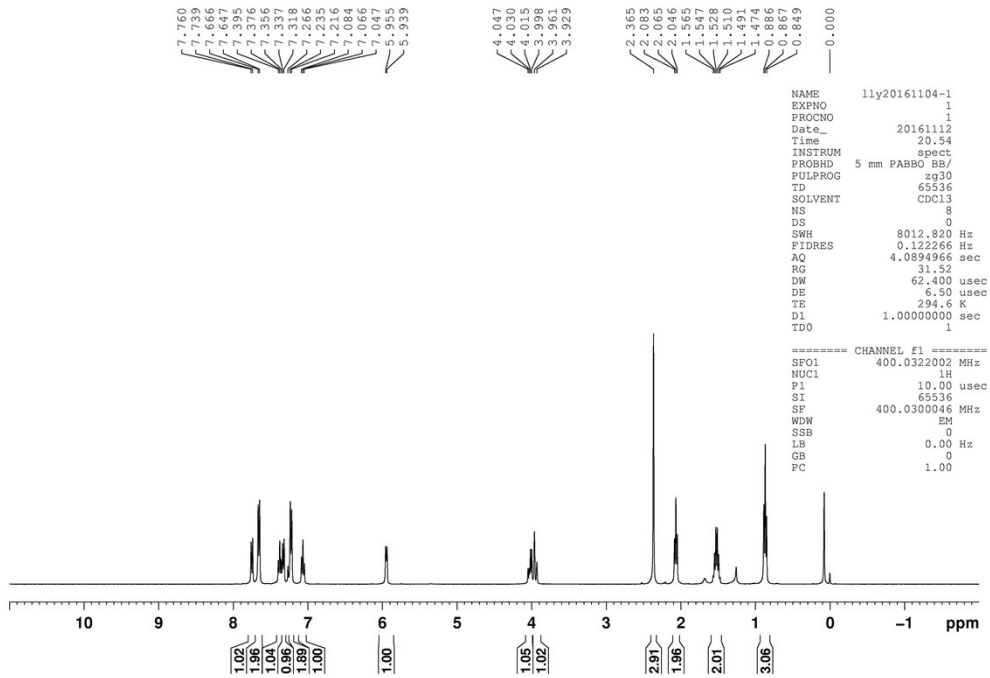


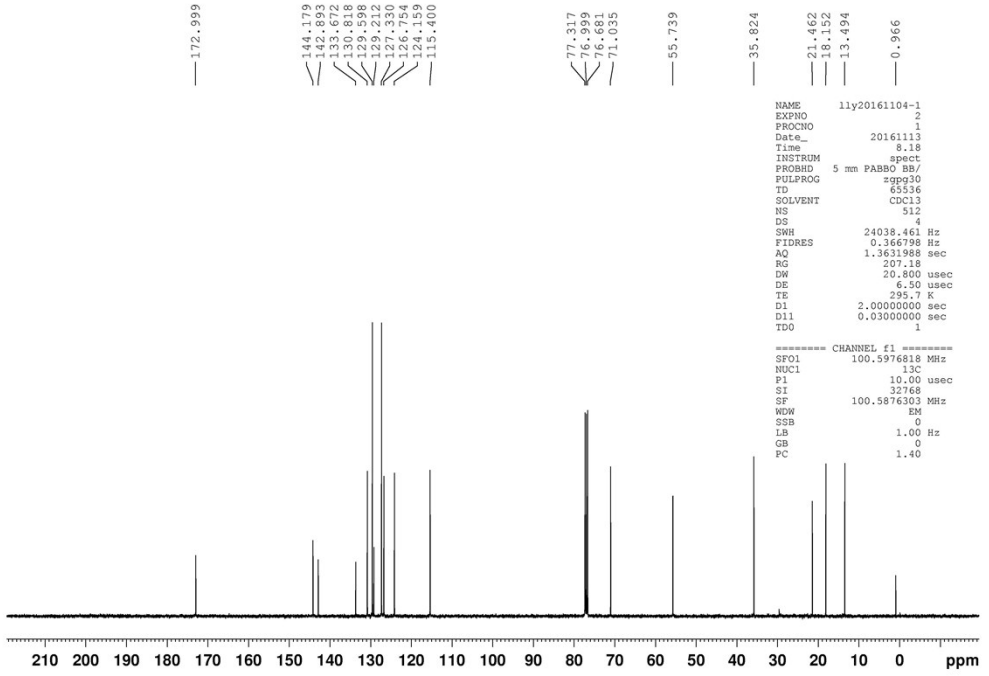
1-tosylindolin-3-yl 2-naphthoate (3aq)



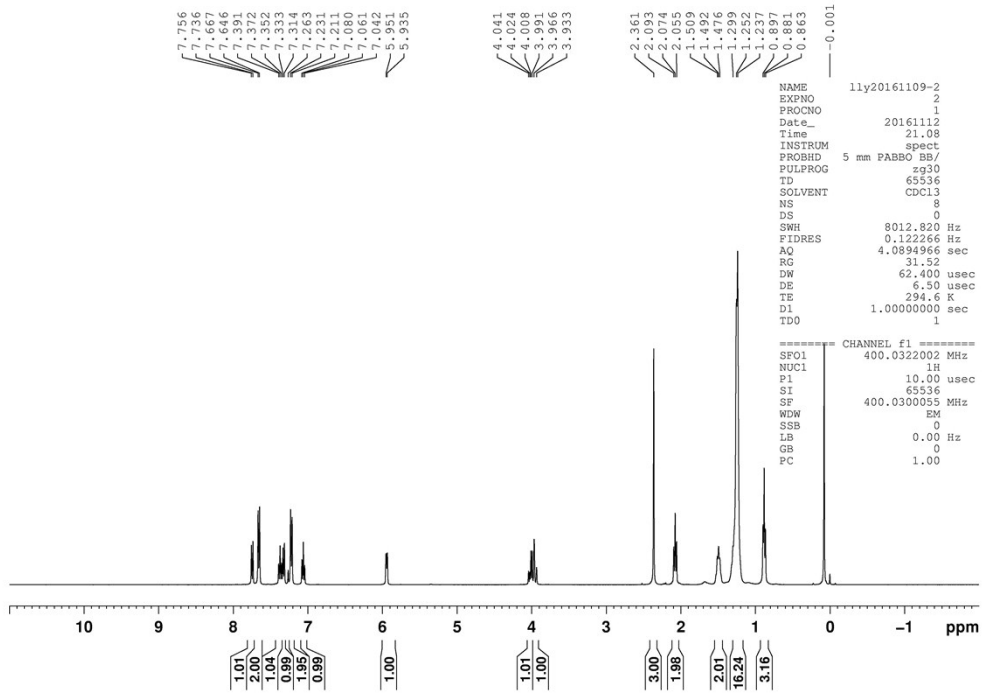


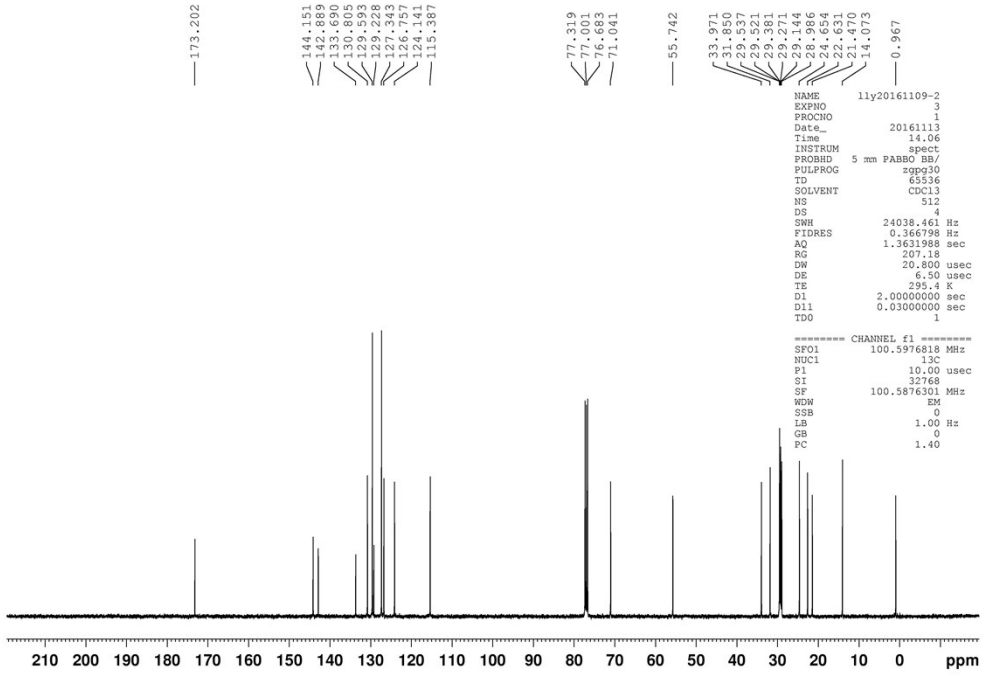
1-tosylindolin-3-yl butyrate (3ar)



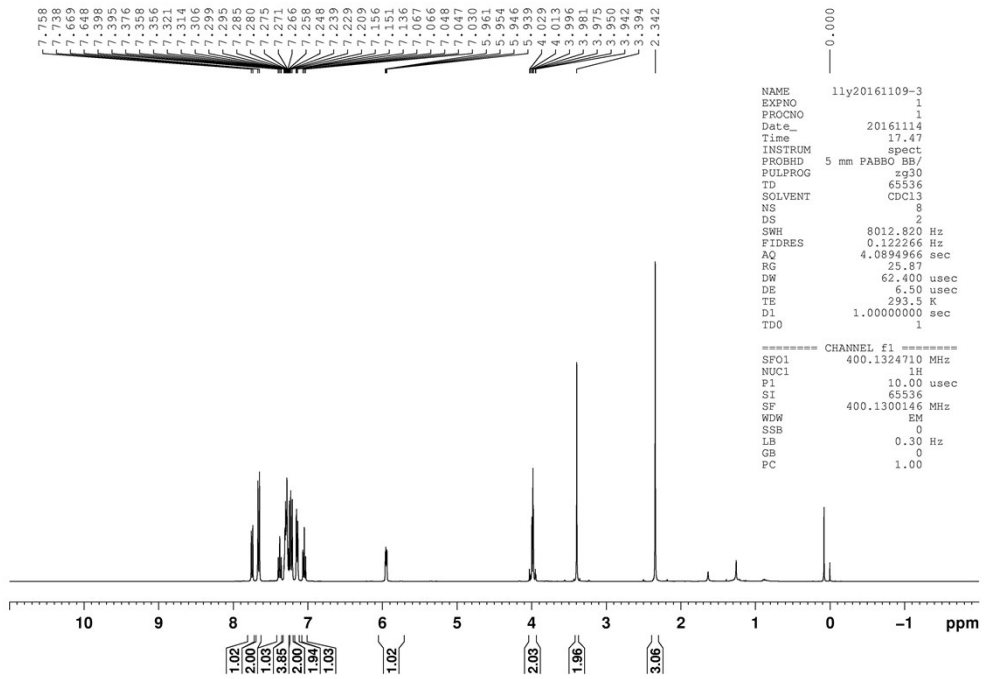


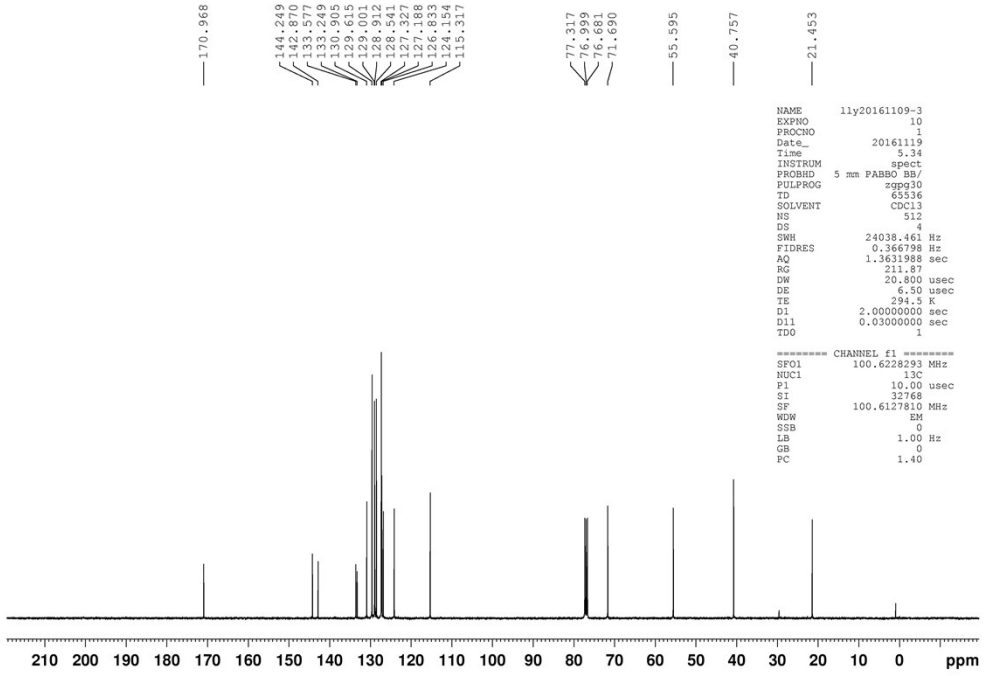
1-tosylindolin-3-yl dodecanoate (3as)



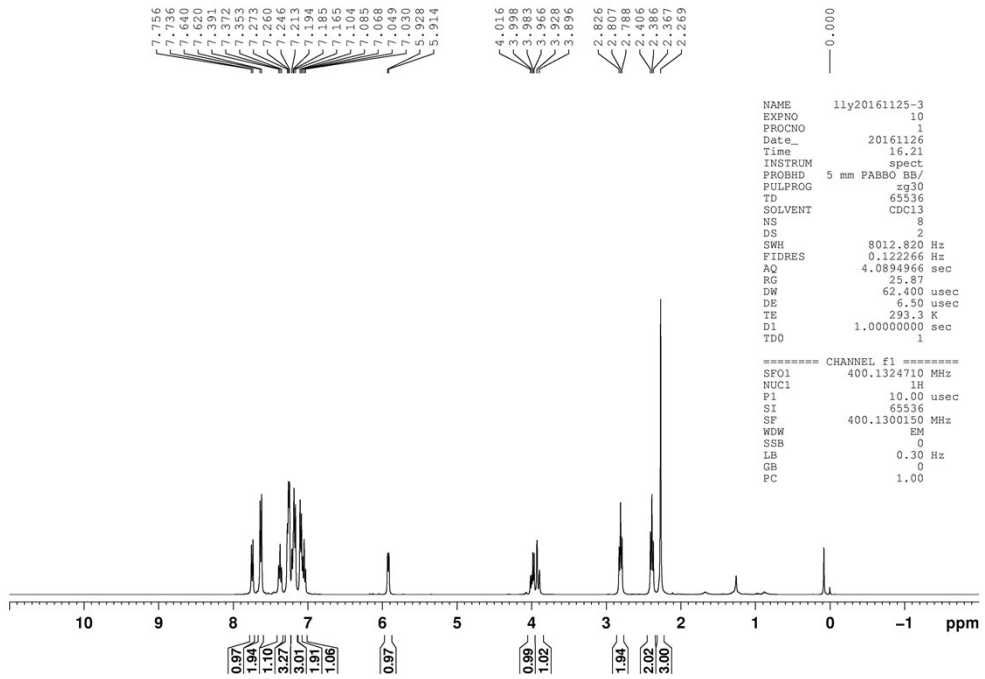


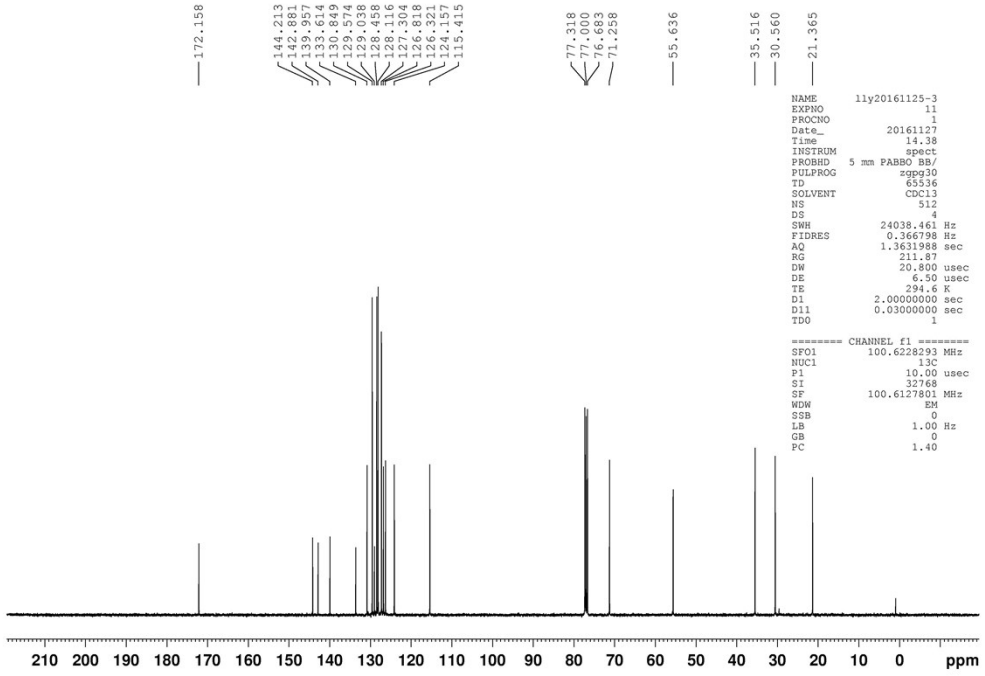
1-tosylindolin-3-yl 2-phenylacetate (3at)



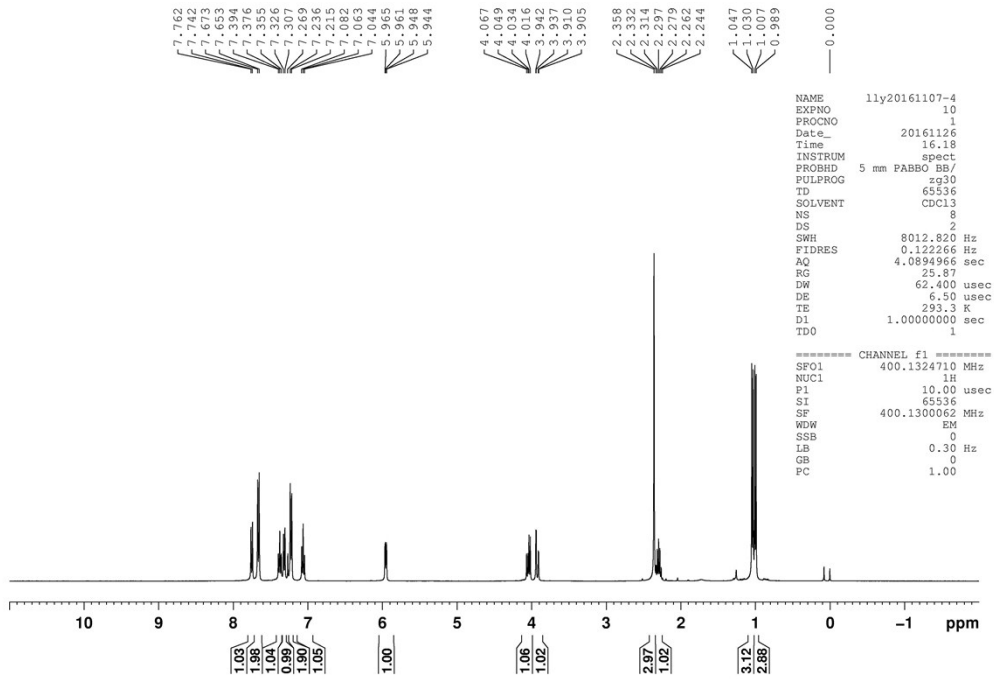


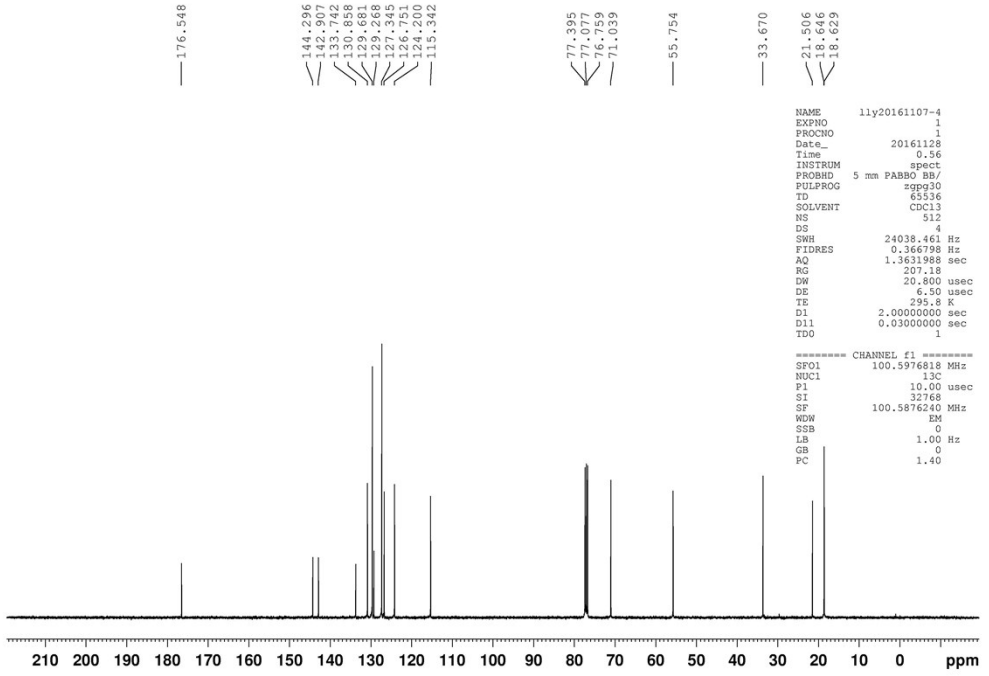
1-tosylindolin-3-yl 3-phenylpropanoate (3au)



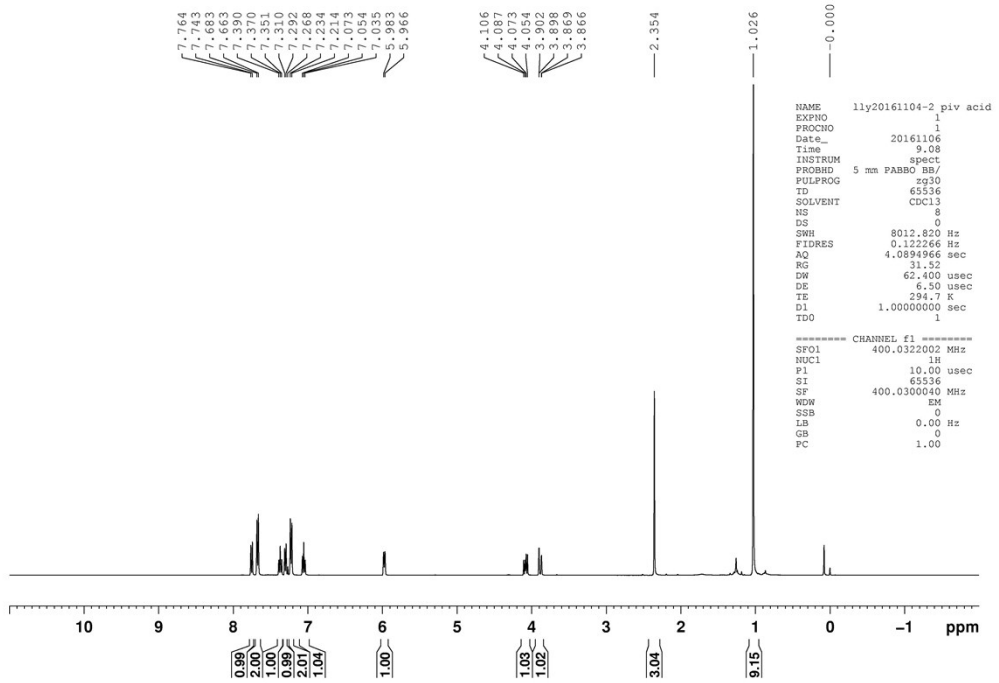


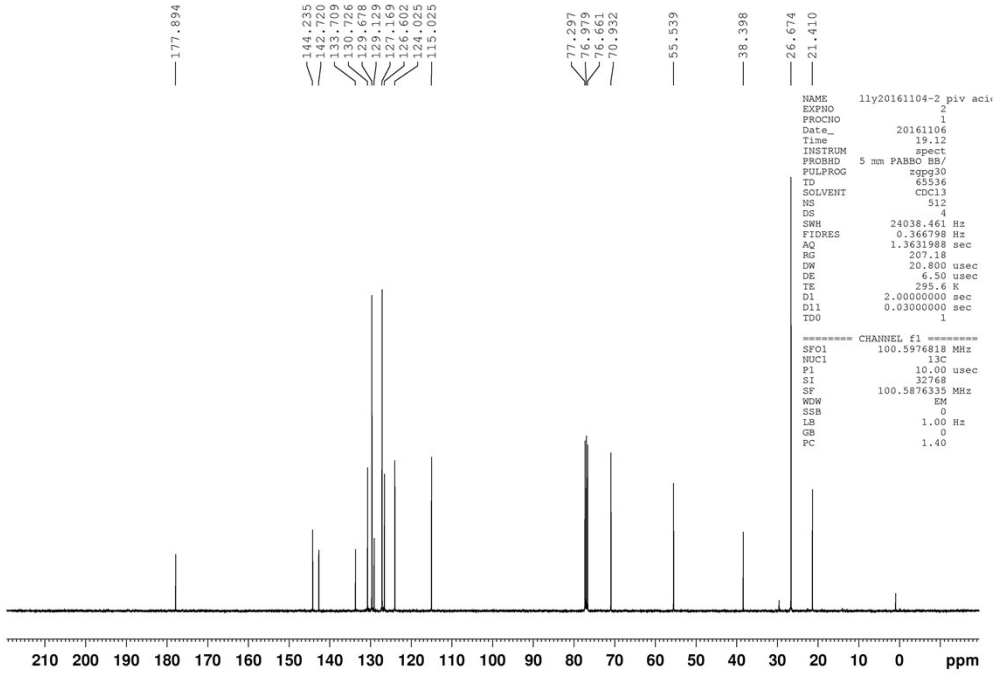
1-tosylindolin-3-yl isobutyrate (3av)



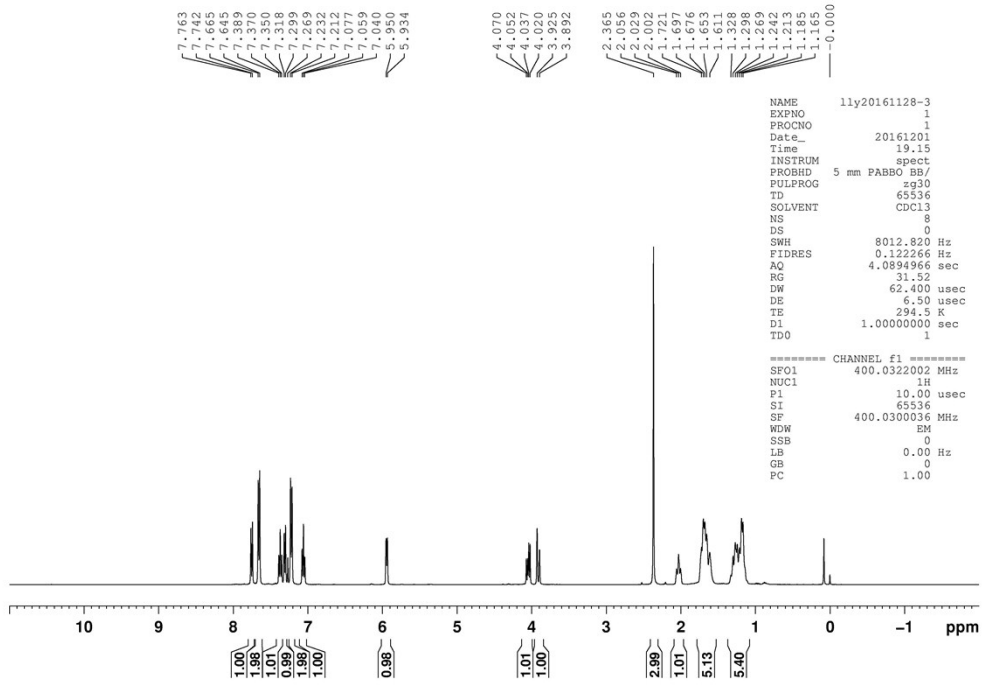


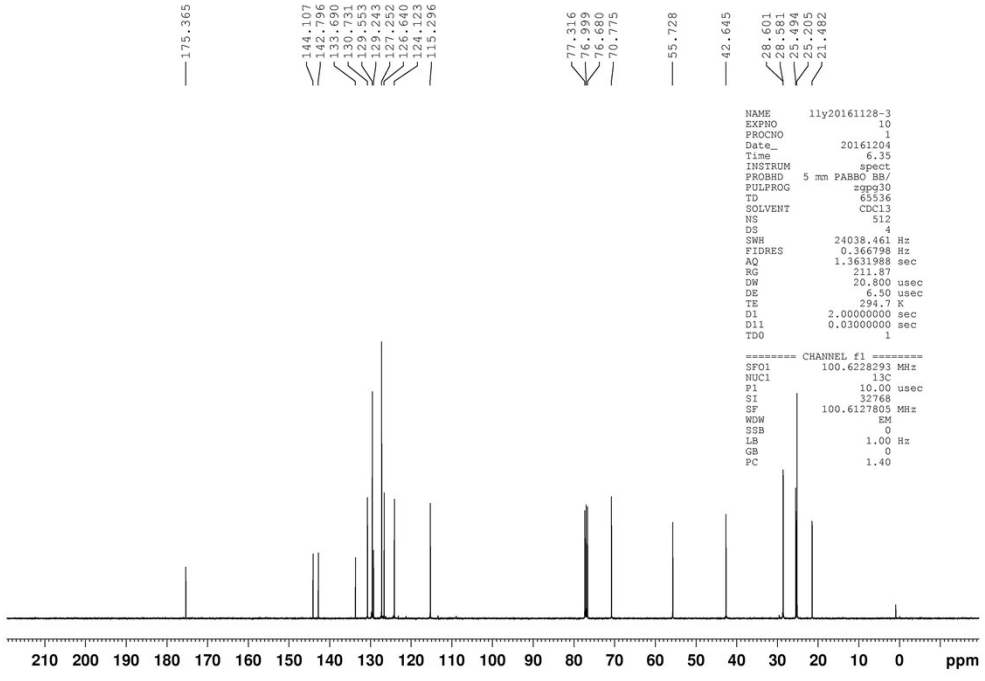
1-tosylindolin-3-yl pivalate (3aw)



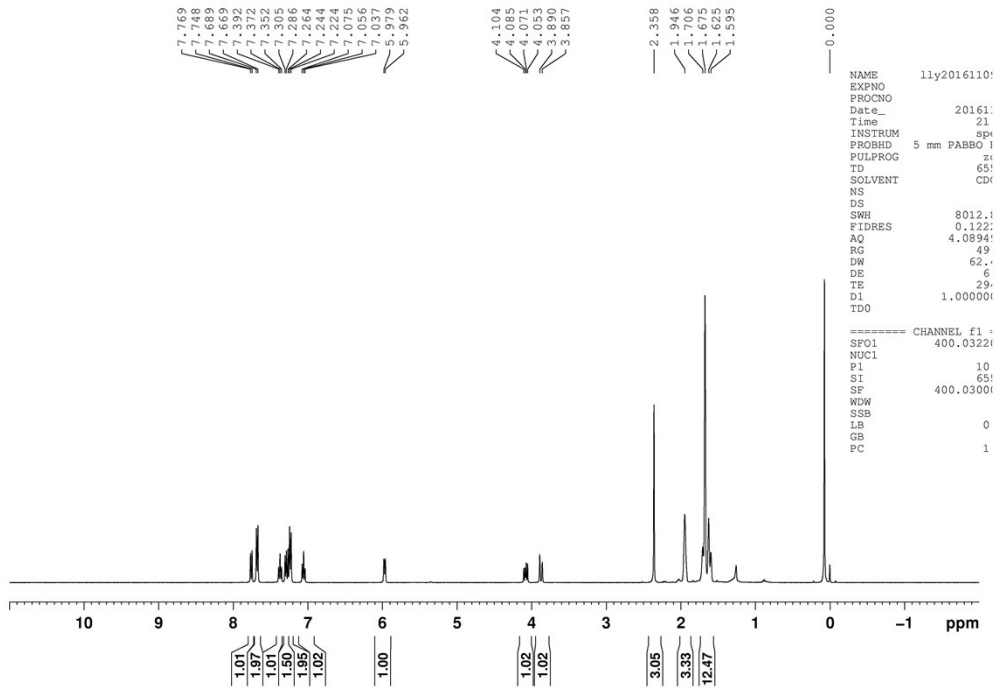


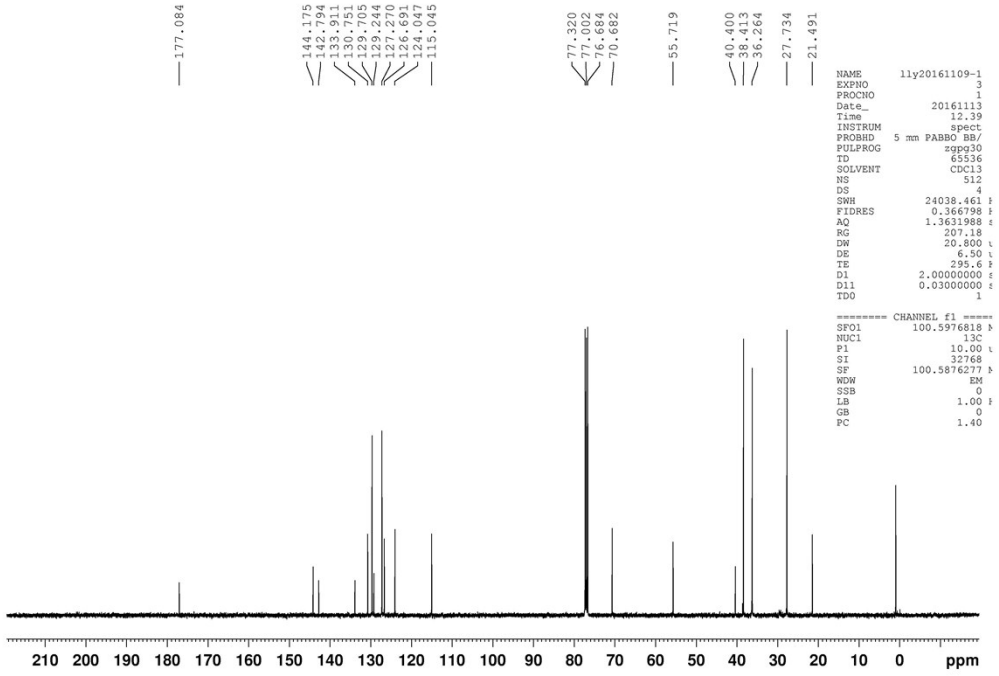
1-tosylindolin-3-yl cyclohexanecarboxylate (3ax)



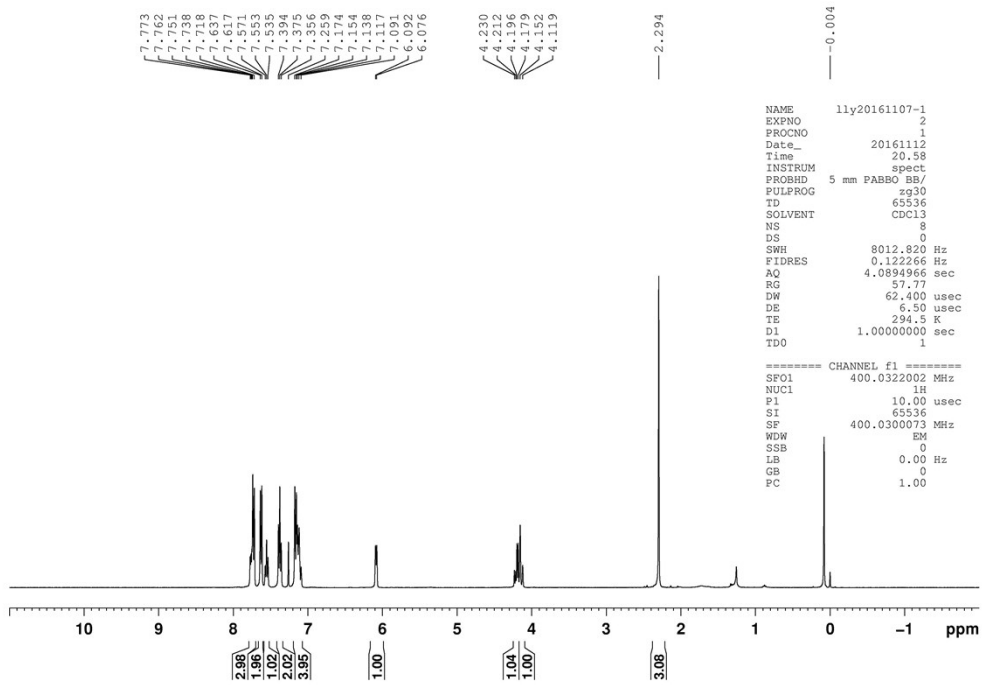


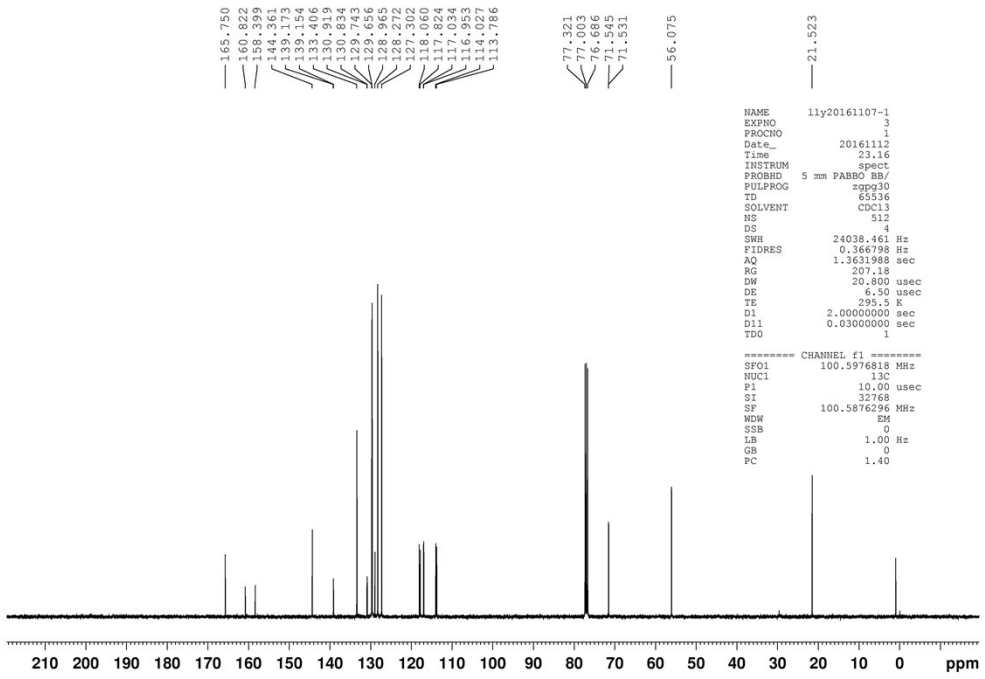
1-tosylindolin-3-yl (3r,5r,7r)-adamantane-1-carboxylate (3ay)



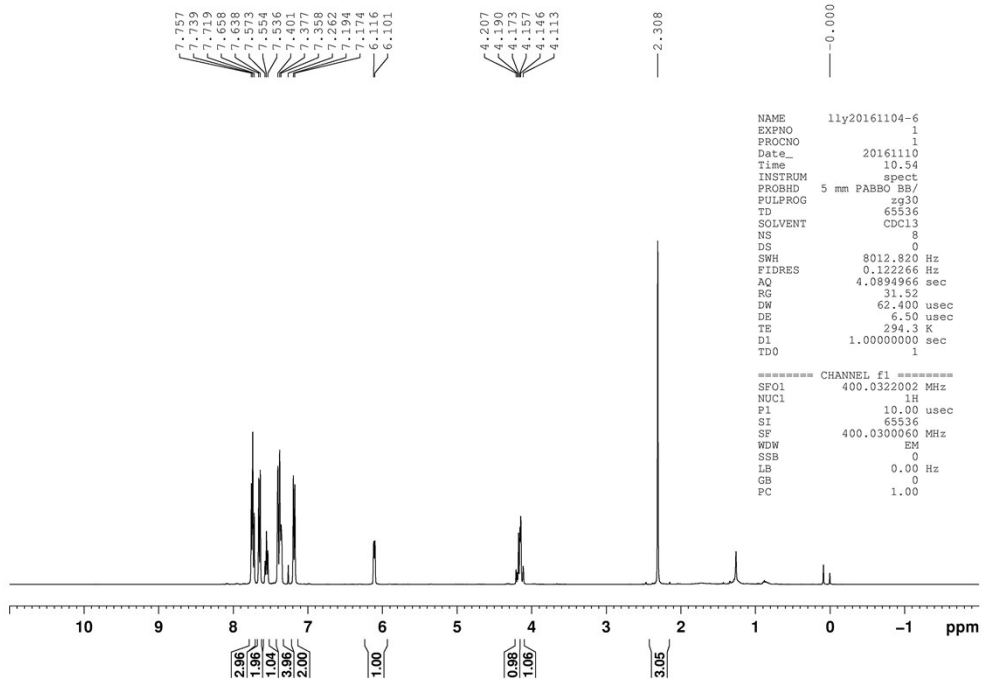


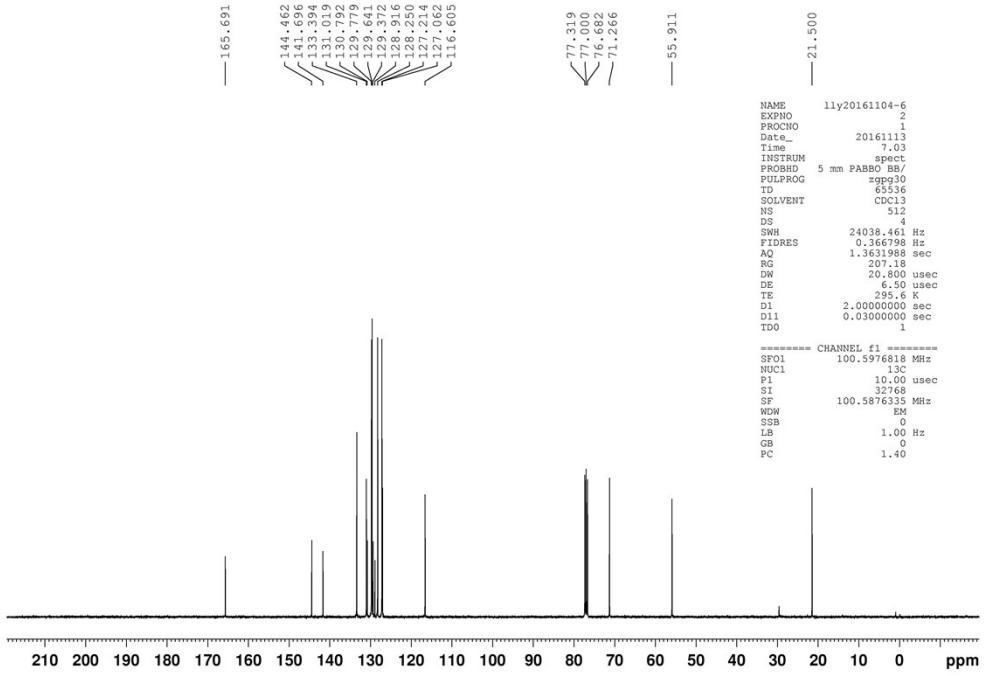
5-fluoro-1-tosylindolin-3-yl benzoate (3ba)



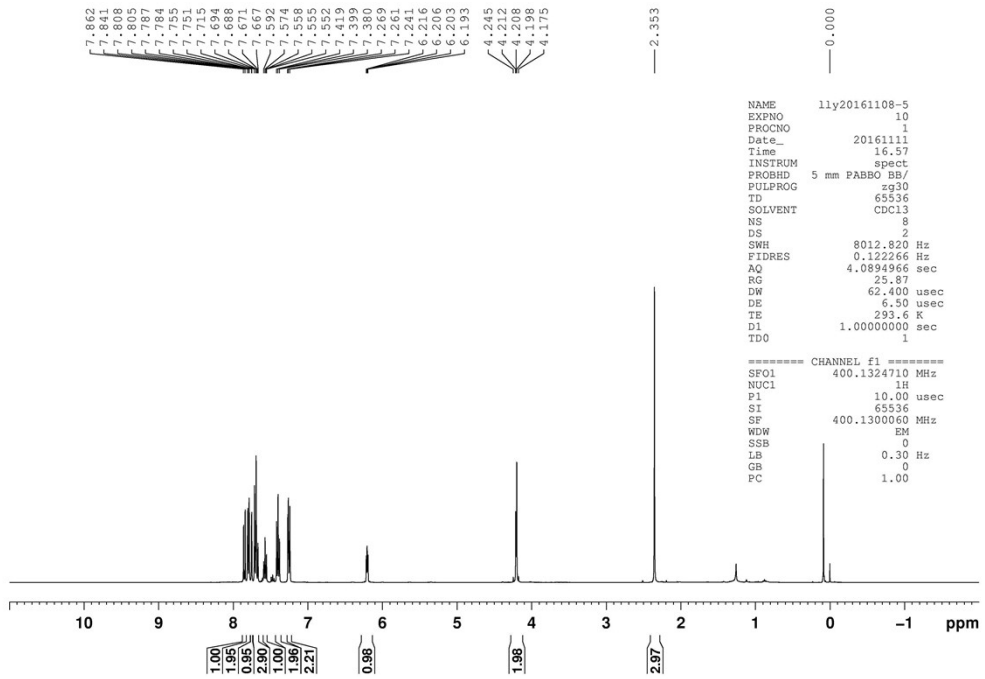


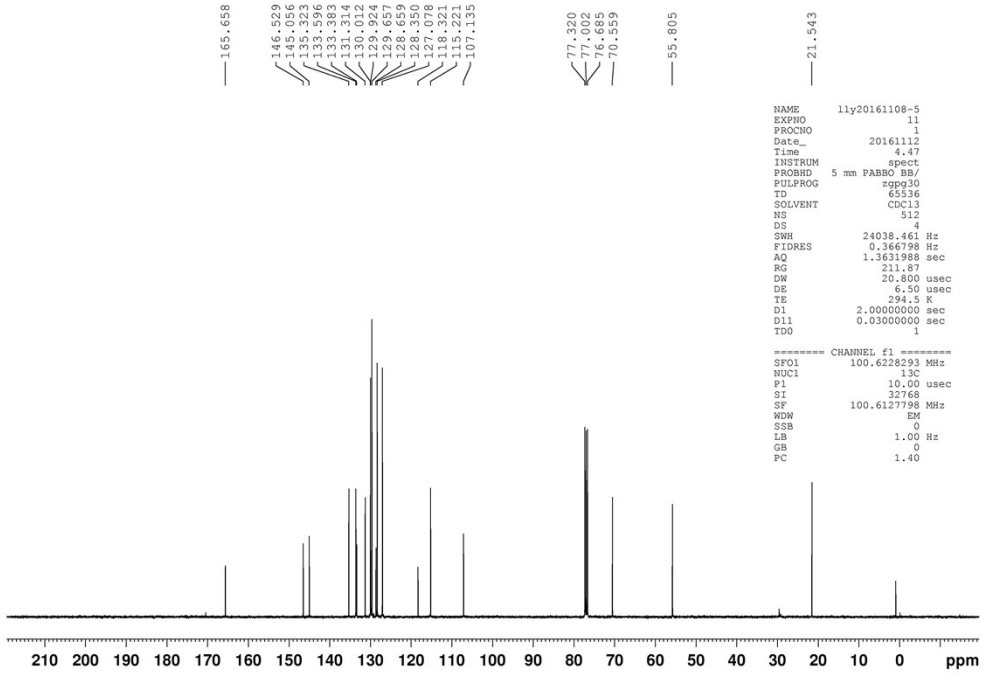
5-chloro-1-tosylindolin-3-yl benzoate (3ca)



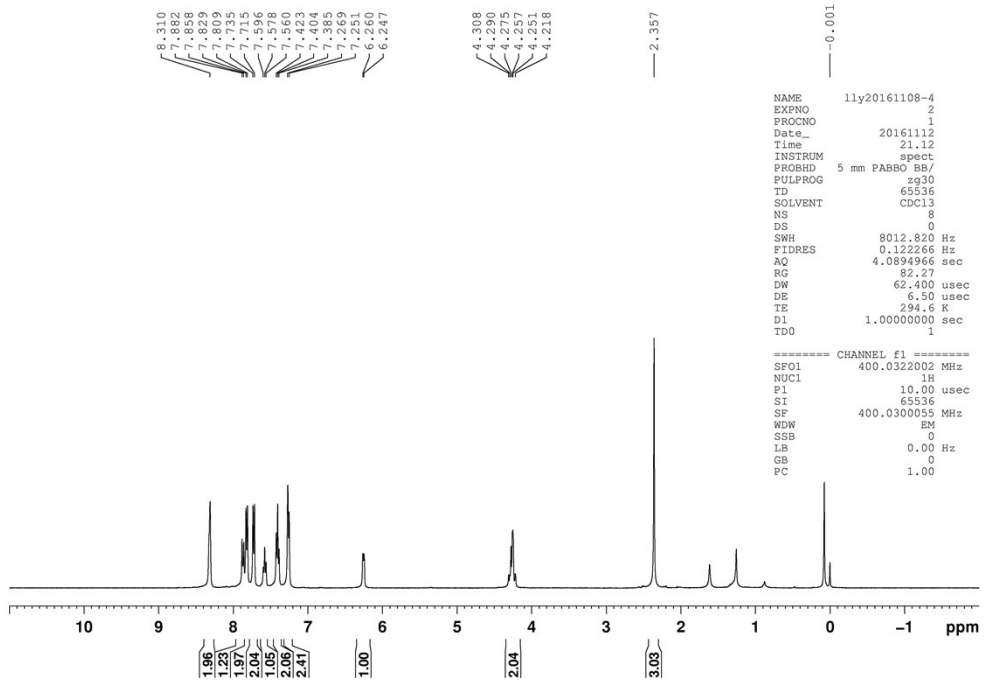


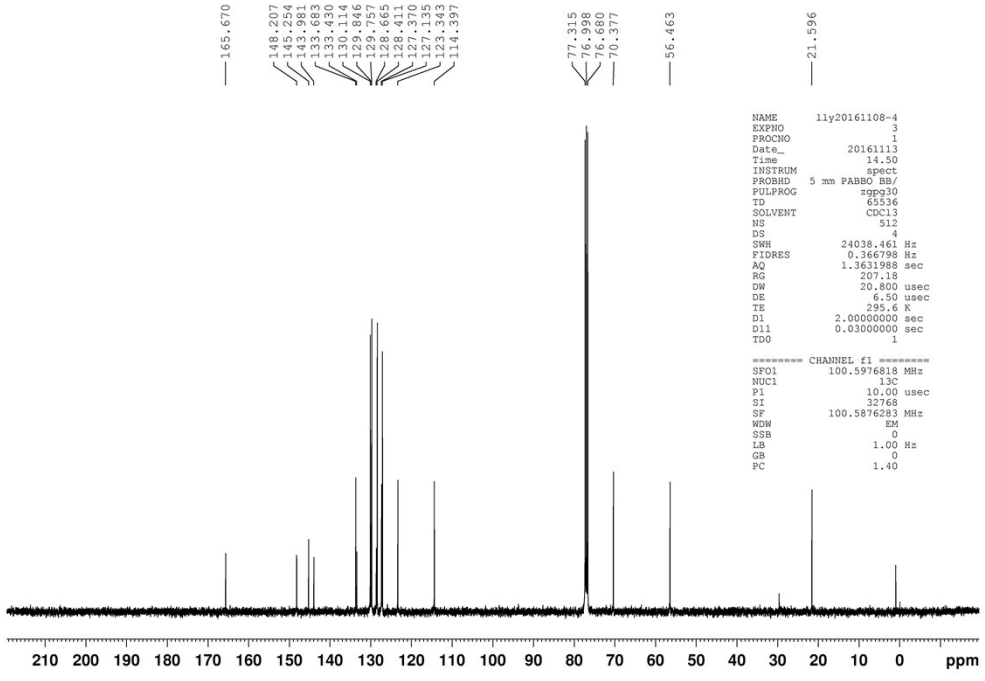
5-cyano-1-tosylindolin-3-yl benzoate (3da)



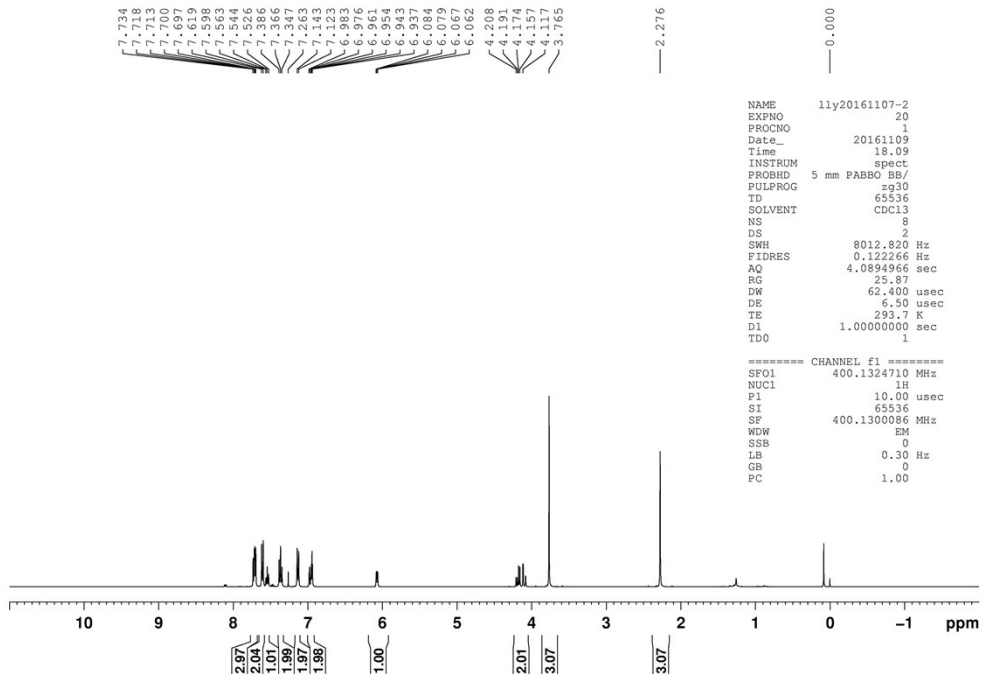


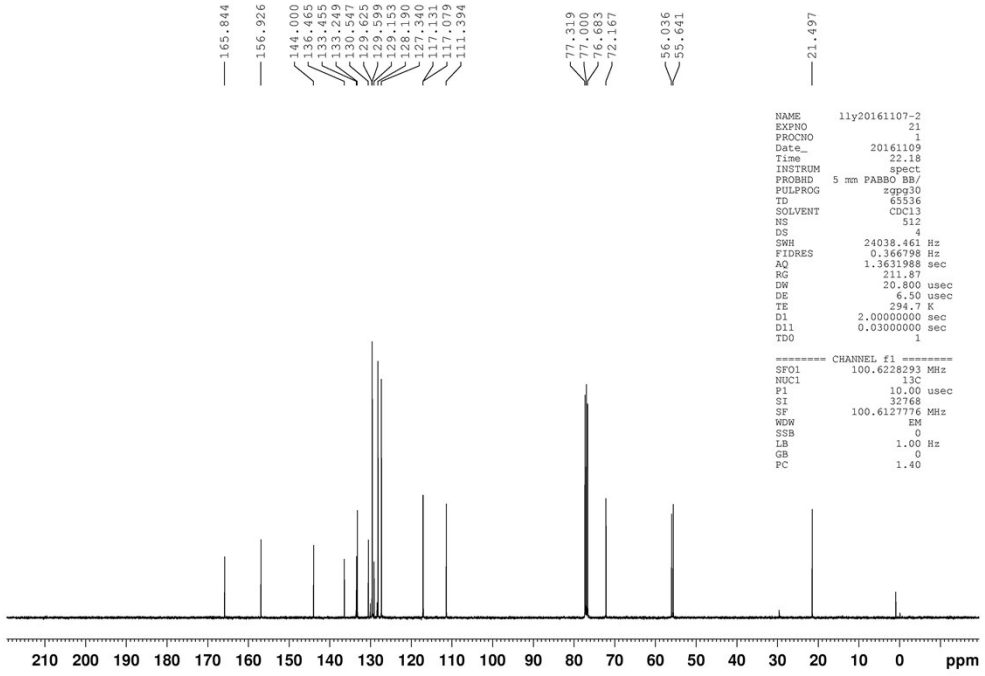
5-nitro-1-tosylindolin-3-yl benzoate (3ea)



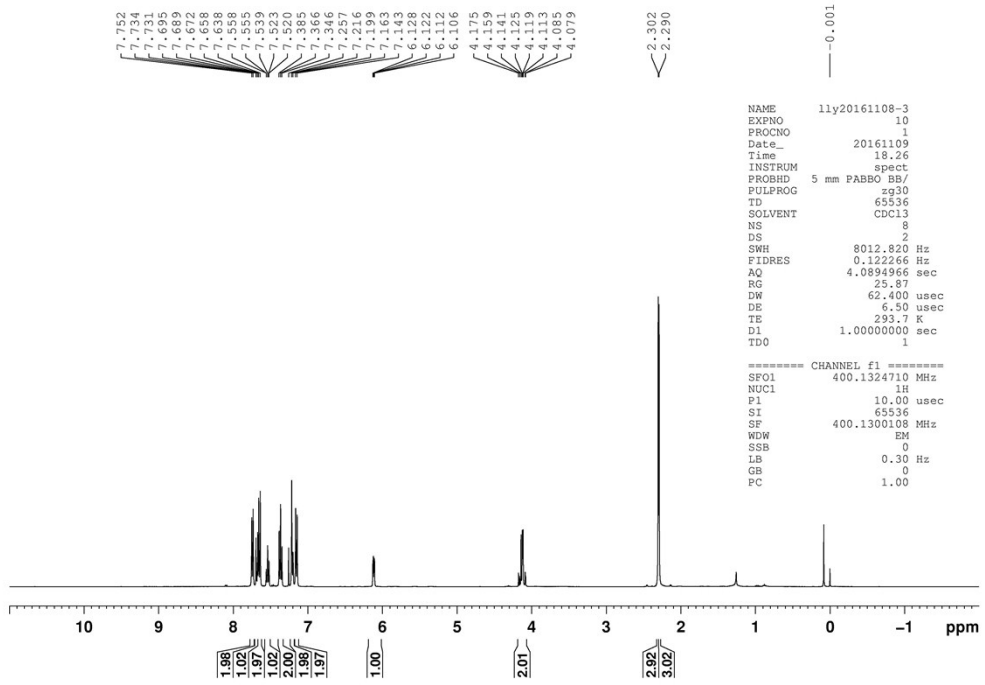


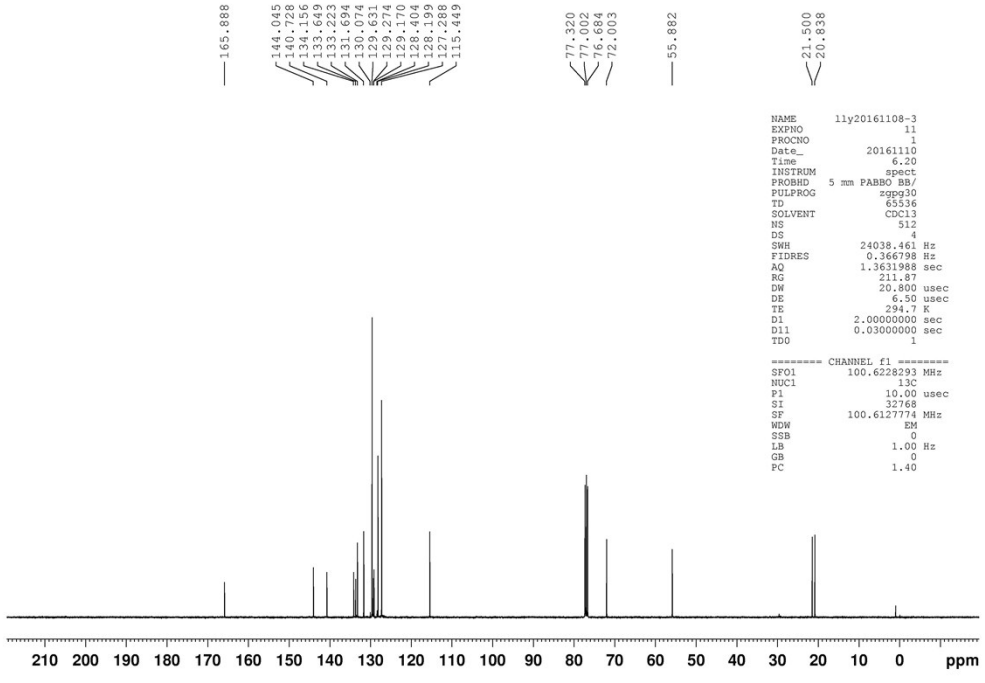
5-methoxy-1-tosylindolin-3-yl benzoate (3fa)



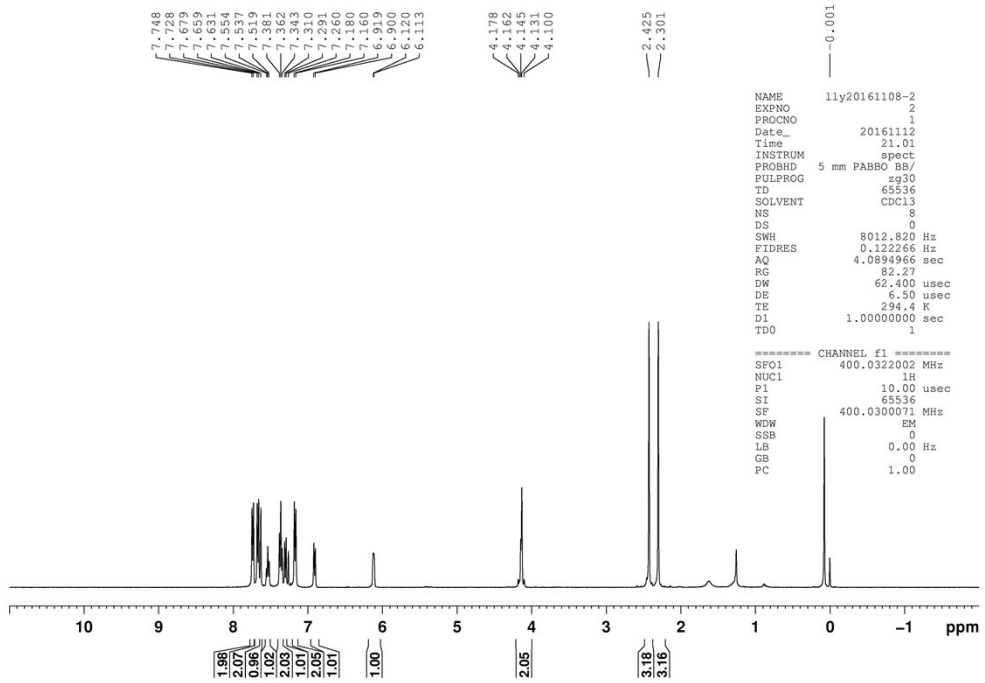


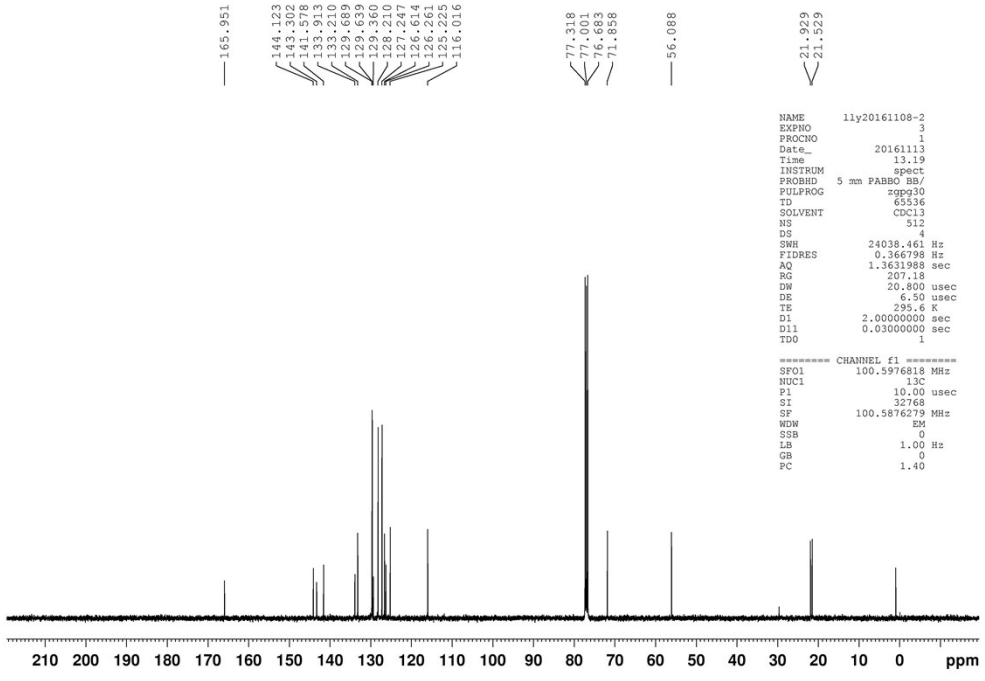
5-methyl-1-tosylindolin-3-yl benzoate (3ga)



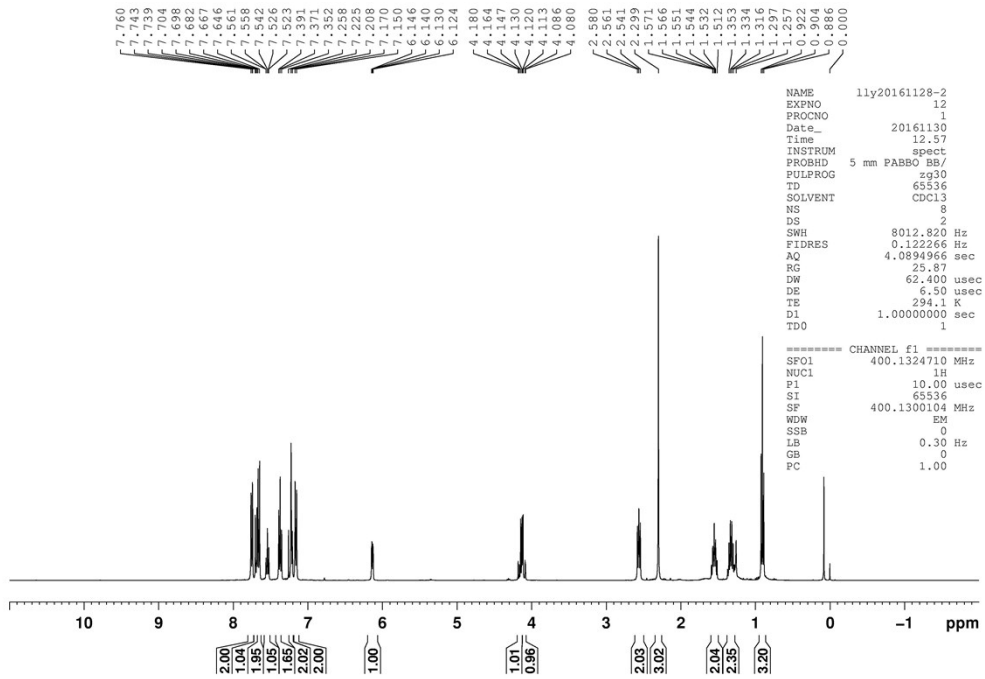


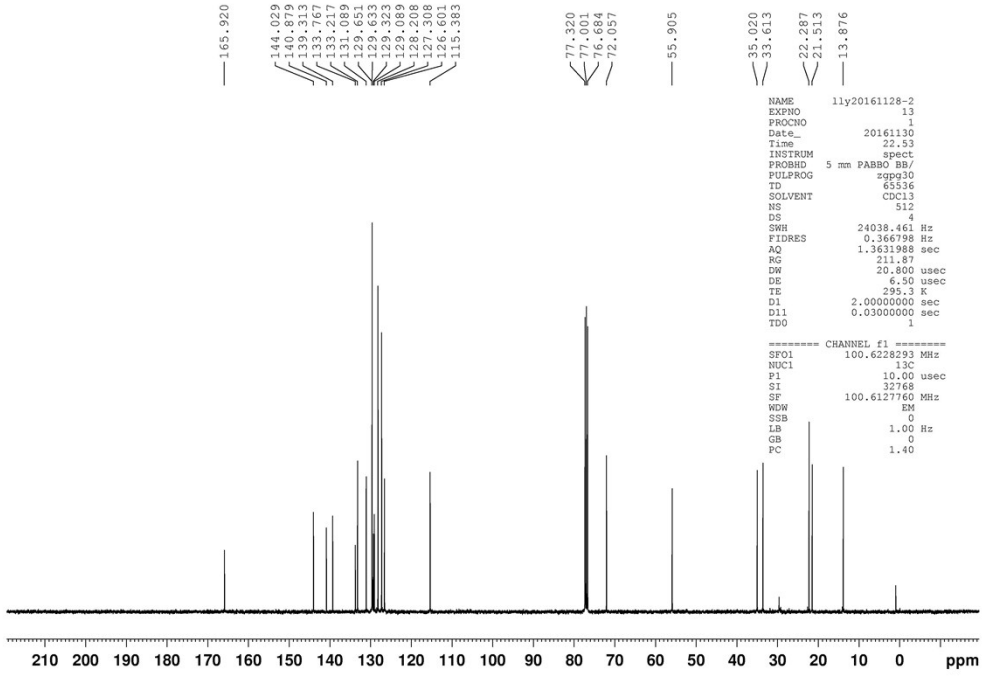
6-methyl-1-tosylindolin-3-yl benzoate (3ha)



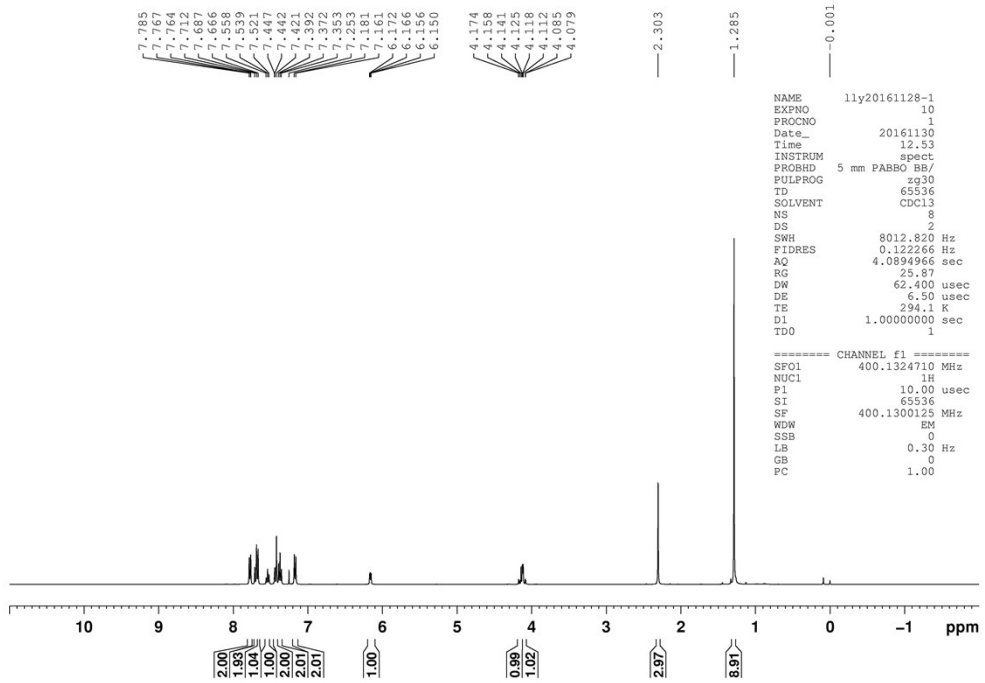


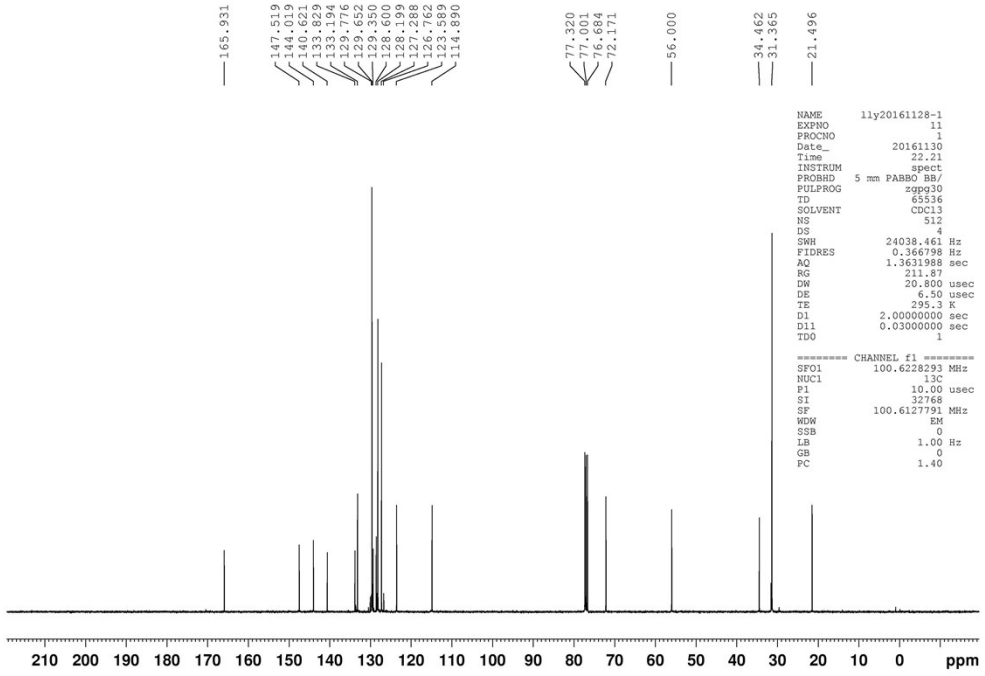
5-butyl-1-tosylindolin-3-yl benzoate (3ia)



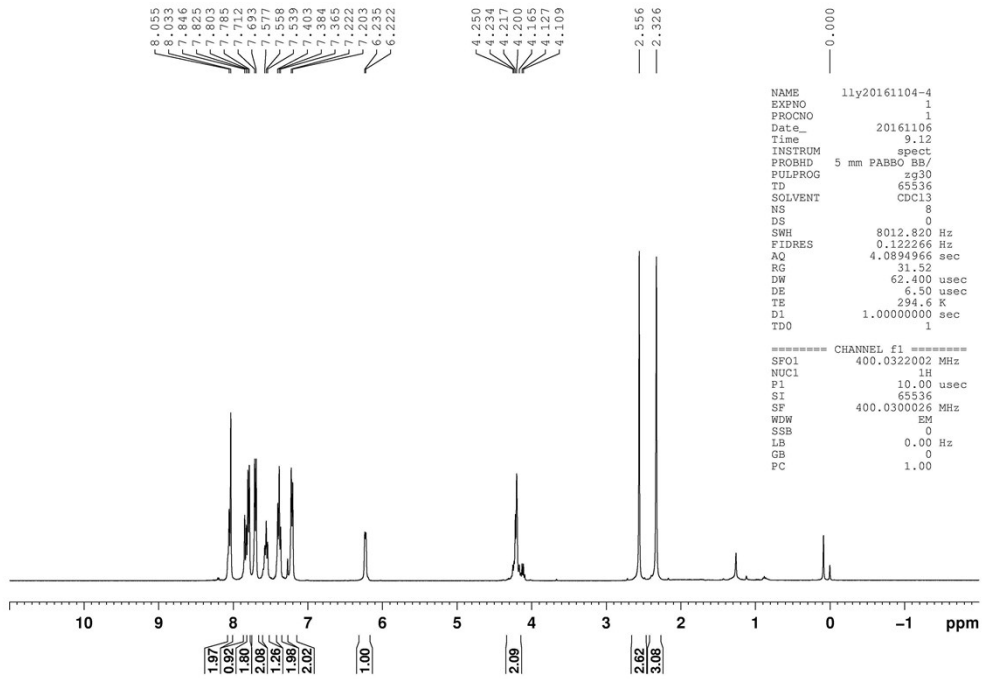


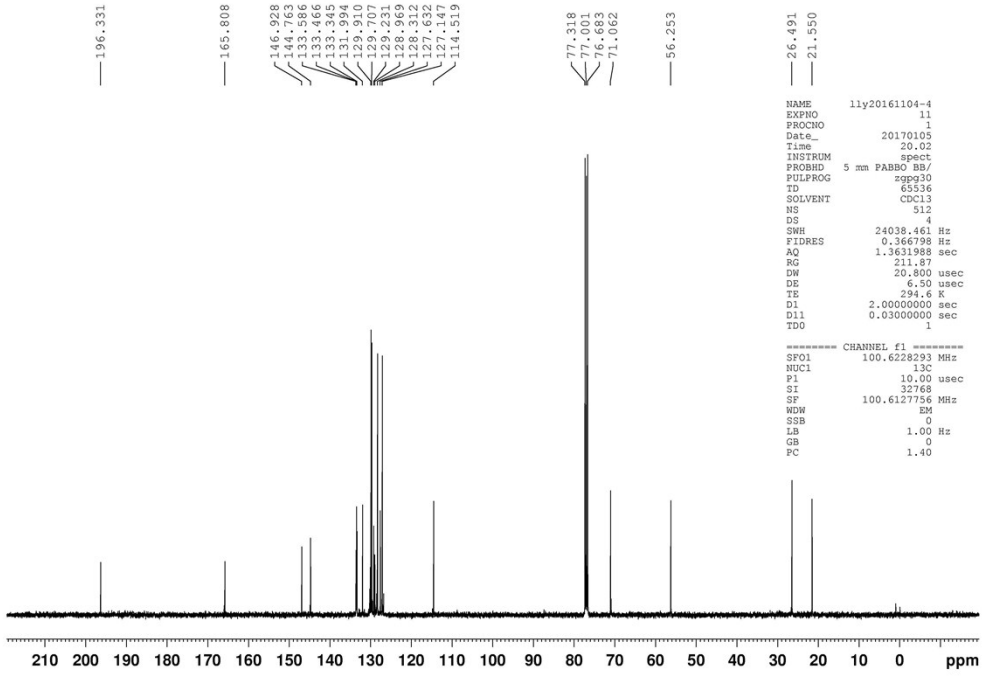
5-(*tert*-butyl)-1-tosylindolin-3-yl benzoate (3ja)



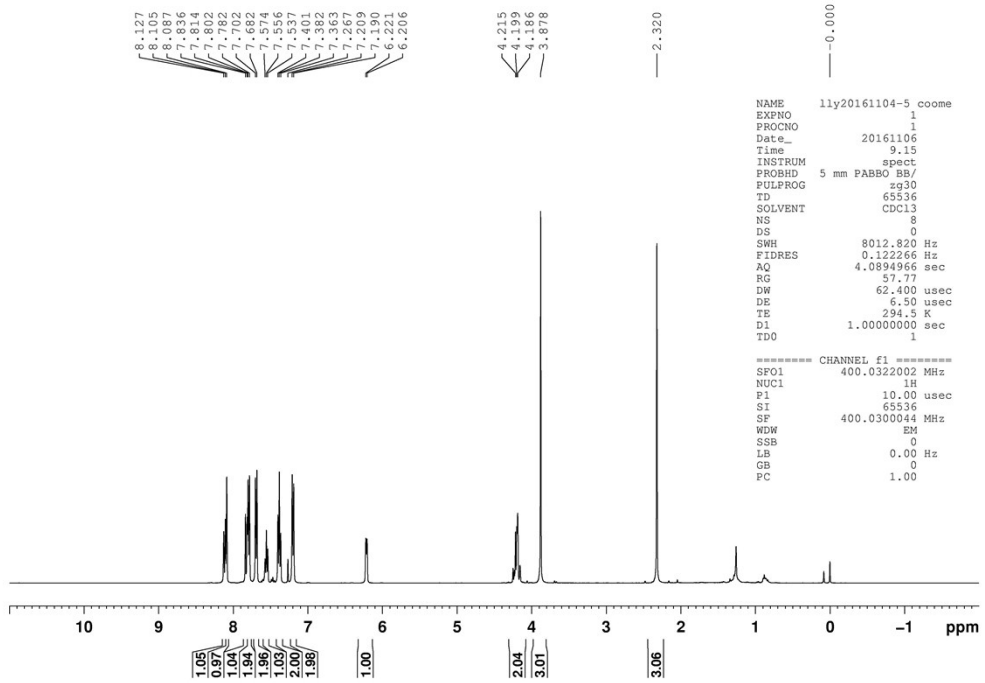


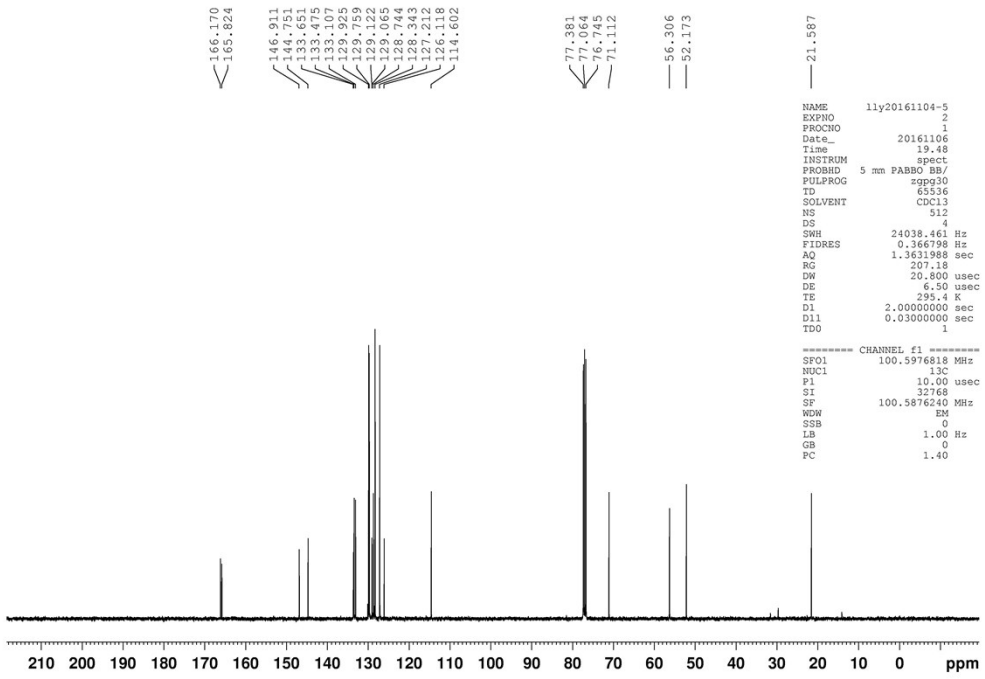
5-acetyl-1-tosylindolin-3-yl benzoate (3ka)



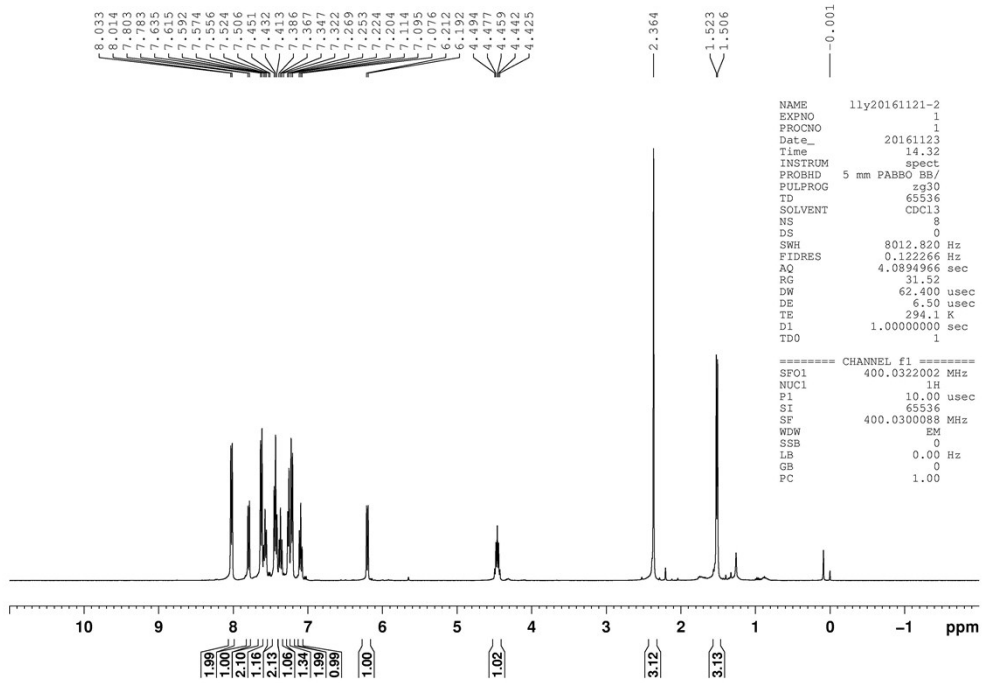


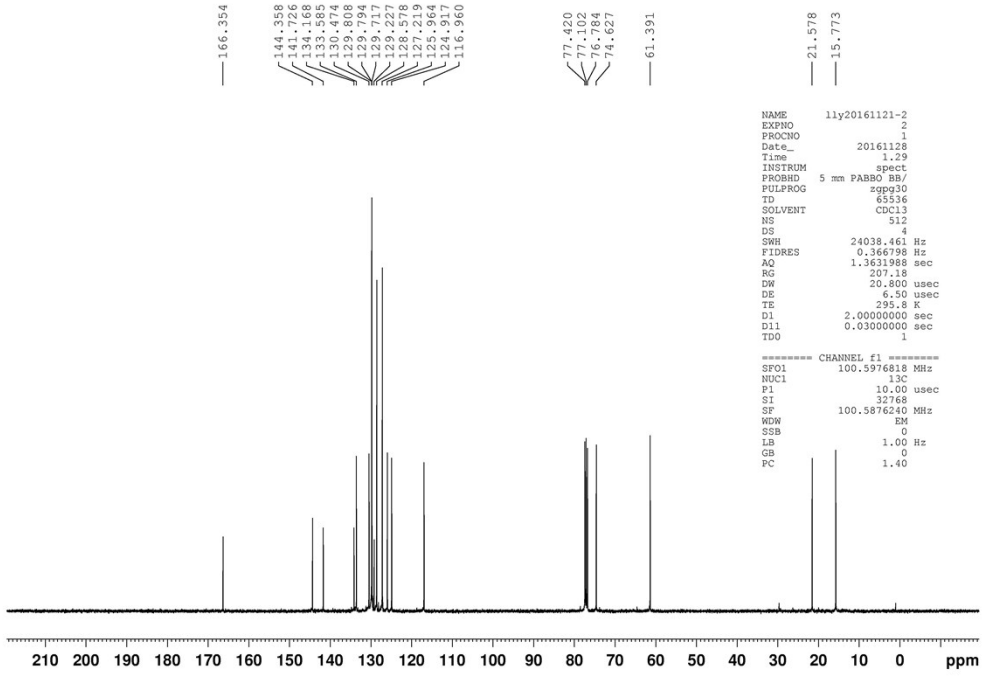
methyl 3-(benzoyloxy)-1-tosylindoline-5-carboxylate (3la)



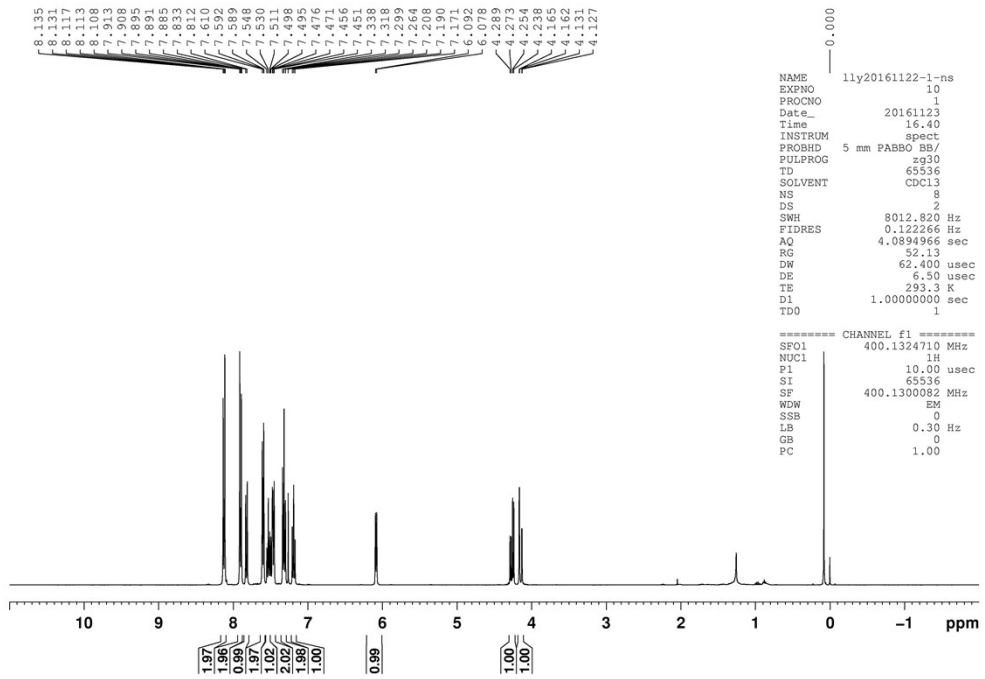


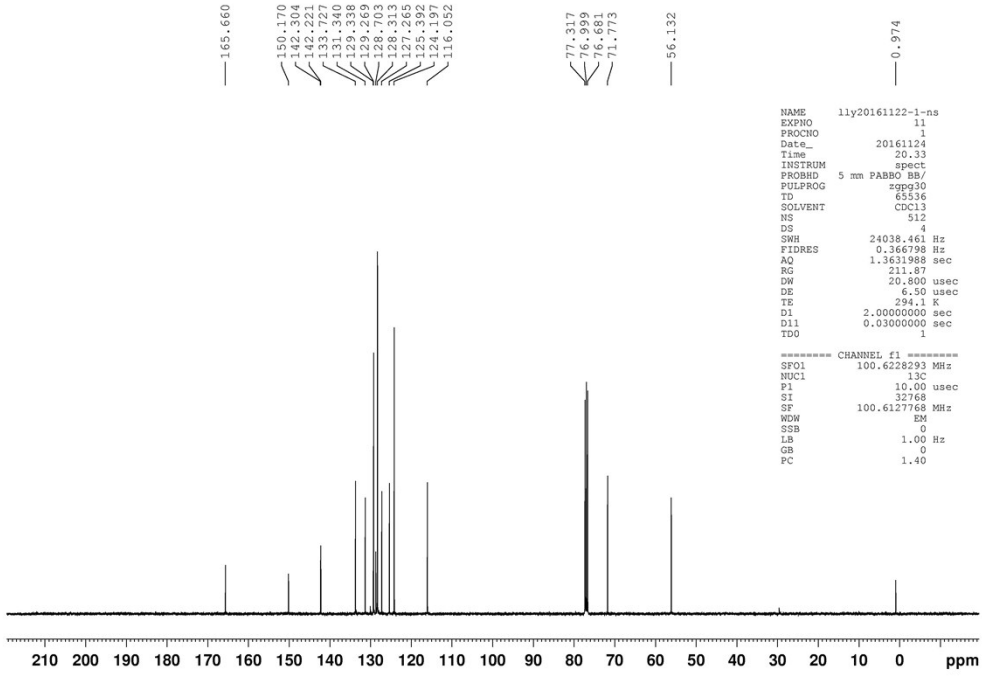
2-methyl-1-tosylindolin-3-yl benzoate (3ma)





1-((4-nitrophenyl)sulfonyl)indolin-3-yl benzoate (3na)





NOE spectra of 3ma