DIBAL-H-mediated *N*-deacetylation of tertiary amides: synthesis of synthetically valuable secondary amines

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Experimental Section

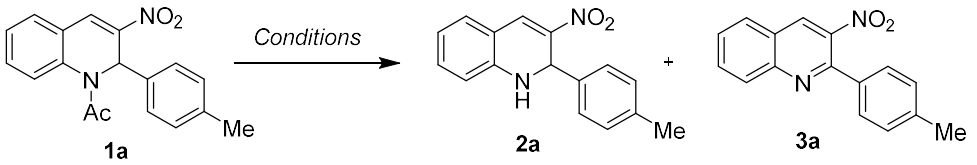
General

All reactions were conducted using oven-dried glassware under an atmosphere of Argon (Ar). Commercial AR-grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Flash column chromatography was performed in all cases using the indicated solvent system on silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on aluminum-backed plates coated with Silica gel 60 with F_{254} indicator (Merck). The ^{1}H-NMR spectra were measured with 400 & 600 MHz, and ^{13}C-NMR spectra were recorded with 400 (100 MHz) & 600 (150 MHz), using $CDCl_3$ as solvent. ^{1}H-NMR chemical shifts are expressed in parts per million (δ) downfield to $CHCl_3$ (δ = 7.26), ^{13}C-NMR chemical shifts are expressed in parts per million (δ) relative to the central $CDCl_3$ resonance (δ = 77.0). Coupling constants in ^{1}H-NMR are in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, dd = doublet of doublets, dt = doublet of triplet, td = triplet of doublet, ddd = doublet of doublet of doublet. Electro spray ionization (ESI) mass spectrometry (MS) experiments were performed on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. IR spectra were recorded using NICOLET IS5 FTIR with a KBr window. The melting point was determined by Labtronics LT-115 digital melting/boiling point apparatus (Indian make).

Substrates **6a**, **6f** and **6g** were synthesized according to the reported literature[5a-5b]

Optimization

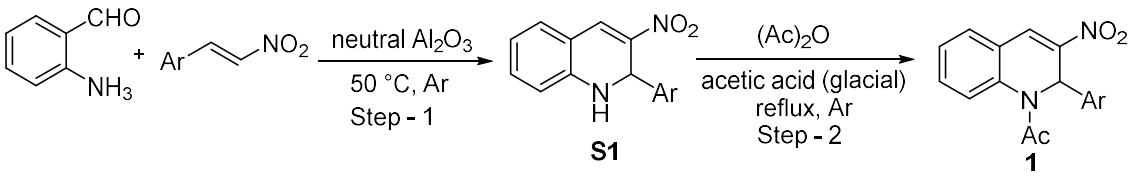
Table 1 Optimization for N-deacetylation of dihydroquinoline[a]



Entry	Conditions	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]
1	HCl and Acetic acid (1:1), 80°C, 5 h	<10	45
2	KOH (2.0 equiv.) in MeOH-THF, 50°C, 12 h	<10	51
3	DIBAL-H (1.5 equiv.), THF, -78°C, 1 h	34	-
4	DIBAL-H (1.5 equiv.), THF, 0°C or rt, 30 min	36	Trace
5	DIBAL-H (1.5 equiv.), toluene, 0°C to rt, 2 h	28	43
6	DIBAL-H (1.5 equiv.), toluene, -78°C, <5 min	68	Trace
7	DIBAL-H (1.2 equiv.), toluene, -78°C, <5 min	76	Trace
8	DIBAL-H (1.2 equiv.), toluene, 0°C, <5 min	43	23
9	DIBAL-H (1.2 equiv.), toluene, rt, <5 min	38	34
10	DIBAL-H (1.2 equiv.), DCM, -78°C to 0°C, 6 h	51	14
11	DIBAL-H (1.2 equiv.), Et2O, -78°C to 0°C, 6 h	34	17

[a] All optimized reactions were carried out in 0.5 mmol scale, solvent used in 1.0 [M]. [b] Isolated yield.

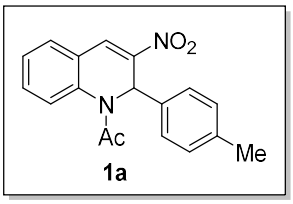
General Procedure I: *Preparation of N-acetylated 2-aryl substituted 3-nitro-1,2-dihydroquinolines*[1]**:**



Step–1: Nitroalkene[2] (1.0 equiv.) was added in one portion to a thoroughly mixed heterogeneous mixture of freshly synthesized 2-aminobenzaldehyde[3] (1.0 equiv.) and neutral alumina (g/mmol), and the reaction mixture was agitated at 50 °C for 0.5 hours. The reaction mixture turns a deep red colour after a short while, indicating the reaction's growth. The reaction mixture was then cooled to room temperature when it was completed (as shown by TLC), and it was then immediately charged on a chromatography column using silica gel (230-400 mesh) and ethyl acetate/petroleum ether (60-80 °C) as the eluent to produce the pure racemic 1,2-dihydroquinoline product **(S1)**.

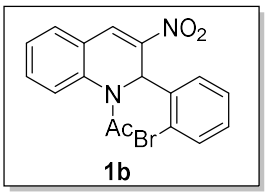
Step-2: A stirred solution of racemic 1,2-dihydroquinoline **(S1)** (1.0 equiv) in acetic acid and acetic anhydride (1:1) (2x mmol) was refluxed in a pre-heated oil bath for 3 hours while under an argon environment in an oven-dried RBF. The reaction mixture initially has a red colour that gradually fades as the reaction progresses, and once the reaction is finished, the reaction solution changes to a yellow colour. After the unprotected 1,2-dihydroquinoline had been completely consumed (as determined by TLC), the solvent was evaporated on a rotatory evaporator, and the residue was then subjected to column purification using a mixture of EtOAc and petroleum ether (60-80 °C) as an eluent to afford N-acetylated 2-aryl substituted 3-nitro-1,2-dihydroquinolines **(1)** as yellow solid.

Spectral data of *N*-Acyl-3-nitro-2-aryl-1,2-dihydroquinolines:



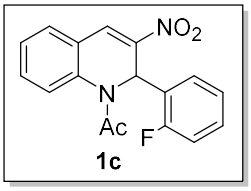
1-(3-nitro-2-(*p*-tolyl)quinolin-1(2*H*)-yl)ethan-1-one **(1a)**: Prepared according to the general reaction procedure **I** using 3-nitro-2-(*p*-tolyl)-1,2-dihydroquinoline to obtain **1a** as yellow solid; 85% yield; m.p. = 91-93 °C; R_f : 0.25 (25% ethyl acetate in petroleum-ether); **^{1}H-NMR**

($CDCl_3$, 400 MHz**):** δ 8.09 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7, 2H), 7.29-7.25 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.23 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 169.7, 138.5, 136.5, 132.9, 131.8, 130.3, 129.5, 129.1, 126.9, 126.4, 125.3, 22.8, 21.2; **HRMS** (ESI) calculated for $C_{18}H_{16}N_2O_3$, 332.10922 *m/z* $(M+Na)^+$; Found, 332.10923 *m/z*.



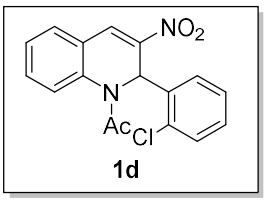
1b

1-(2-(2-bromophenyl)-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(1b)**: Prepared according to the general reaction procedure **I** using 2-(2-bromophenyl)-3-nitro-1,2-dihydroquinoline to obtain **1b** as yellow solid; 80% yield; m.p. = 141-143 °C; R_f : 0.25 (25% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 8.10 (s, 1H), 7.69 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.41 (td, *J* = 7.8, 1.2 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.06 (td, *J* = 7.6, 1.4 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.70 (dd, *J* = 7.8, 1.4 Hz, 1H), 2.22 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 169.7, 148.5, 136.9, 134.3, 134.1, 132.0, 130.4, 130.0, 129.6, 128.3, 127.5, 127.2, 126.8, 125.7, 123.7, 51.9, 22.9; **HRMS** (ESI) calculated for $C_{17}H_{13}{}^{81}BrN_2O_3$, 396.9987 *m/z* $(M+Na)^+$; Found, 396.9989 *m/z*.



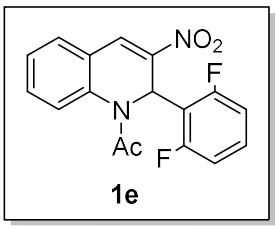
1c

1-(2-(2-fluorophenyl)-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(1c)**: Prepared according to the general reaction procedure **I** using 2-(2-fluorophenyl)-3-nitro-1,2-dihydroquinoline to obtain **1c** as yellow solid; 75% yield; m.p. = 121-123 °C; R_f : 0.20 (23% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 8.09 (s, 1H), 7.52 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.42 (td, *J* = 7.8, 1.6 Hz, 1H), 7.31 (td, *J* = 7.4, 0.8 Hz, 2H), 7.24-7.19 (m, 2H), 7.01 (t, *J* = 10.2 Hz, 1H), 6.94-6.88 (m, 2H), 2.33 (s, 3H);**^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 169.6, 131.9, 136.6, 130.8 (J_{C-F} = 8.1 Hz), 130.2, 129.7, 128.8, 126.6, 125.9, 124.9, 124.3, 122.7 (J_{C-F} = 14.1 Hz), 116.4 (J_{C-F} = 22.1 Hz), 47.9, 22.8; **HRMS** (ESI) calculated for $C_{17}H_{13}FN_2O_3$, 336.08415 *m/z* $(M+Na)^+$; Found, 336.08420 *m/z*.



1d

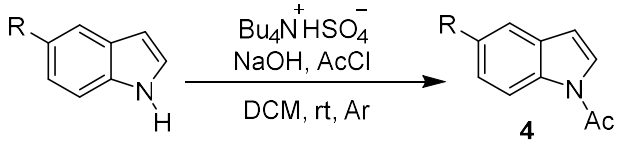
1-(2-(2-chlorophenyl)-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(1d)**: Prepared according to the general reaction procedure **I** using 2-(2-chlorophenyl)-3-nitro-1,2-dihydroquinoline to obtain **1e** as yellow solid; 78% yield; m.p. = 137-139 °C; R_f : 0.25 (25% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 8.11 (s, 1H), 7.73 (s, 1H), 7.54 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.41-7.36 (m, 2H), 7.34-7.32 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.15 (td, *J* = 7.7, 1.4 Hz, 1H), 6.95-6.91 (m, 1H), 6.73 (dd, *J* = 7.8, 1.3 Hz, 1H), 2.24 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 169.6, 148.1, 136.8, 133.8, 132.5, 131.9, 130.8, 130.2, 130.1, 129.7, 128.2, 127.1, 126.8, 126.6, 125.6, 49.8, 22.8; **HRMS** (ESI) calculated for $C_{17}H_{13}ClN_2O_3$, 353.04829 *m/z* $(M+Na)^+$; Found, 353.04830 *m/z*.



1e

1-(2-(2,6-difluorophenyl)-3-nitroquinolin-1(2*H*)-yl)ethan-1-one **(1e)**: Prepared according to the general reaction procedure **I** using 2-(2,6-difluorophenyl)-3-nitro-1,2-dihydroquinoline to obtain **1d** as yellow solid; 82% yield; m.p. = 135-137 °C; R_f : 0.25 (25% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 8.05 (s, 1H), 7.61 (s, 1H), 7.52-7.44 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.24-7.17 (m, 2H), 6.79 (td, *J* = 8.5, 1.6 Hz, 2H), 2.31 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 170.3, 161.7 (J_{C-F} = 251.7, 7.53 Hz), 144.8, 136.9, 131.9, 130.7 (J_{C-F} = 10.5 Hz), 130.3, 129.9, 126.2, 124.8, 124.5, 113.2 (J_{C-F} = 18.3 Hz), 112.0 (J_{C-F} = 25.8 Hz), 45.1, 23.1; **HRMS** (ESI) calculated for $C_{17}H_{12}F_2N_2O_3$, 331.08495 *m/z* $(M+Na)^+$; Found, 331.08496 *m/z*.

General Procedure II: *Preparation of N-acetylated Indole*[4]**:**

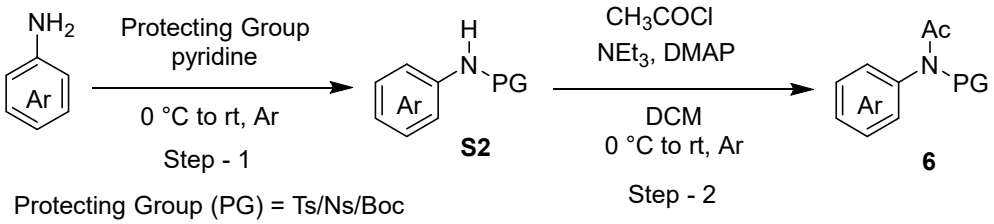


4

In DCM (0.4 M), indole (1.0 equiv) and $Bu_4N^+HSO_4^-$ (1 mol%) were dissolved. At 0 °C powdered NaOH (2.5 equiv) was added, followed by acetyl chloride (1.5 equiv.) in DCM added

dropwise to the vigorously swirling solution. TLC indicated that the initial indole was completely consumed after 1.5 hours at room temperature. The organic extract was then concentrated and purified using column chromatography with PET/ethyl acetate as the eluent to get the product **4**. All the N-acetylated indoles were synthesized by the above literature procedure.

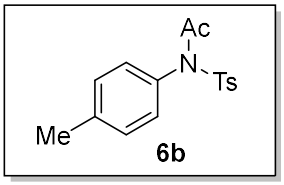
General Procedure III: *Preparation of N-acetyl and Ts/Ns/Boc substituted tertiary amide***:**



Step-1: In a 100-mL, two-necked, round-bottomed flask, aniline (1.0 equiv.) was dissolved in pyridine (0.2 M). After cooling the solution in an ice bath, the protecting group (1.2 equiv.) was progressively added to the stirring solution, and the reaction mixture was stirred at room temperature. When the aniline was totally consumed to the product (as monitored by the TLC), the resultant mixture was washed with water, extracted with ethyl acetate, and lastly the organic extract was washed with a brine solution. The organic extract was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was subsequently purified using flash column chromatography with silica gel (230-400 mesh) and an EtOAc/petroleum-ether combination as an eluent to obtain the product **S2**.

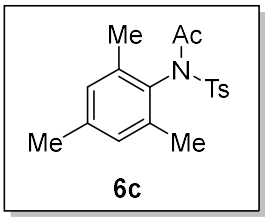
Step-2: N-protected amine **S2** (1.0 equiv.) was dissolved in dichloromethane (anhydrous) (0.3 M) in a 100-mL, two-necked, round-bottomed flask. DMAP (0.05 equiv.), triethylamine (2.0 equiv.), and acetyl chloride (1.5 equiv.) were added to the stirring solution after it had been cooled in an ice bath, and the reaction mixture was stirred at room temperature. When the N-protected amine had been completely consumed by the product (as determined by TLC), the resulting mixture was washed with water, extracted with ethyl acetate, and finally the organic extract was washed with a brine solution. The solvent was evaporated under reduced pressure after the organic extract was dried on Na_2SO_4. Following that, the residue was purified using flash column chromatography with silica gel (230-400 mesh) and an EtOAc/petroleum-ether solution as an eluent to obtain the product **6**.

Spectral data of substituted tertiary amide:



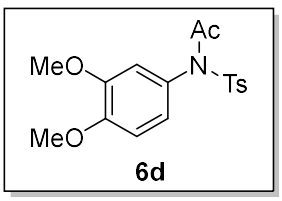
6b

N-(*p*-tolyl)-N-tosylacetamide **(6b)**: Prepared according to the general reaction procedure **III** using *p*-toluidine and PG is tosyl chloride to obtain **6b** as white solid; m.p. = 101-103 °C; 72% yield; R_f : 0.25 (8% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 8.3, 2H), 2.45 (s, 3H), 2.41 (s, 3H), 1.86 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.4, 145.0, 140.4, 136.3, 134.4, 130.6, 129.7, 129.5, 129.3, 25.2, 21.8, 21.4; **HRMS** (ESI) calculated for $C_{16}H_{17}NO_3S$, 326.08268 *m/z* $(M+Na)^+$; Found, 326.08267 *m/z*.



6c

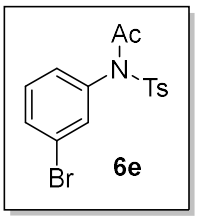
N-mesityl-N-tosylacetamide **(6c)**: Prepared according to the general reaction procedure **III** using 2,4,6-trimethylaniline and PG is tosyl chloride to obtain **6c** as white solid; m.p. = 182-184 °C; 66% yield; R_f : 0.25 (9% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.98 (s, 2H), 2.44 (s, 3H), 2.31 (s, 3H), 2.19 (s, 6H), 1.75 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.6, 145.2, 139.8, 137.9, 136.4, 132.9, 130.2, 130.1, 129.2, 24.1, 21.8, 21.2, 18.9; **HRMS** (ESI) calculated for $C_{18}H_{21}NO_3S$, 354.11398 *m/z* $(M+Na)^+$; Found, 354.11399 *m/z*.



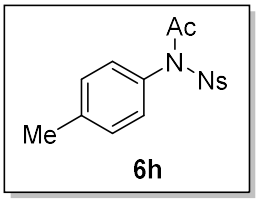
6d

N-(3,4-dimethoxyphenyl)-N-tosylacetamide **(6d)**: Prepared according to the general reaction procedure **III** using 3,4-dimethoxyaniline and PG is tosyl chloride to obtain **6d** as off-white

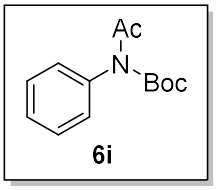
solid; m.p. = 125-127 °C; 78% yield; R_f : 0.25 (15% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 7.92 (d, *J* = 6.6 Hz, 2H), 7.34 (d, *J* = 6.5 Hz, 2H), 6.90 (d, *J* = 6.6 Hz, 1H), 6.78 (t, *J* = 1.6 Hz, 2H), 3.92 (s, 3H), 3.88 (s, 3H), 2.45 (s, 3H), 1.90 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 170.6, 150.4, 149.8, 145.1, 136.2, 129.6, 129.5, 129.4, 122.3, 113.1, 111.3, 56.3, 56.2, 25.0, 21.8; **HRMS** (ESI) calculated for $C_{17}H_{19}NO_5S$, 372.08816 *m/z* $(M+Na)^+$; Found, 372.08814 *m/z*.



N-(3-bromophenyl)-N-tosylacetamide **(6e)**: Prepared according to the general reaction procedure **III** using 3-bromoaniline and PG is tosyl chloride to obtain **6e** as white solid; m.p. = 108-110 °C; 72% yield; R_f : 0.25 (8% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.64-7.62 (m, 1H), 7.43 (t, *J* = 2.0 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 3H), 7.23-7.21 (m, 1H), 2.46 (s, 3H), 1.91 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 169.7, 145.4, 138.1, 135.9, 133.3, 133.1, 131.1, 129.7, 129.3, 128.8, 123.2, 25.2, 21.9; **HRMS** (ESI) calculated for $C_{15}H_{14}{}^{81}BrNO_3S$, 391.97550 *m/z* $(M+Na)^+$; Found, 391.97551 *m/z*.



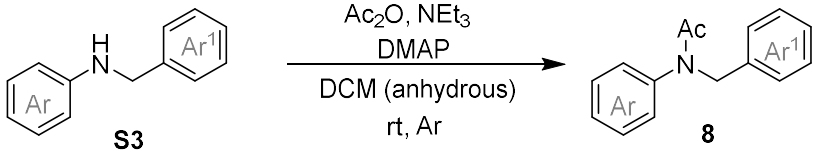
N-((4-nitrophenyl)sulfonyl)-N-(*p*-tolyl)acetamide **(6h)**: Prepared according to the general reaction procedure **III** using *p*-toluidine and PG is nosyl chloride to obtain **6h** as white solid; m.p. = 170-172 °C; 72% yield; R_f : 0.25 (7% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 8.38 (dd, *J* = 7.0, 2.0 Hz, 2H), 8.24 (dd, *J* = 7.0, 2.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H), 1.87 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.7 150.8, 144.8, 141.1, 133.6, 131.0, 130.7, 129.5, 124.0, 25.0, 21.4; **HRMS** (ESI) calculated for $C_{15}H_{14}N_2O_5S$, 357.05211 *m/z* $(M+Na)^+$; Found, 357.05212 *m/z*.



6i

tert-butyl acetyl(phenyl)carbamate **(6i)**: Prepared according to the general reaction procedure **III** using aniline and PG is Boc-anhydride to obtain **6i** as white solid; m.p. = 45-47 °C; 66% yield; R_f : 0.25 (10% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 7.40-7.37 (m, 2H), 7.33-7.31 (m, 1H), 7.08 (dd, *J* = 8.6, 1.4 Hz, 2H), 2.57 (s, 3H), 1.37 (s, 9H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 173.0 152.9, 139.0, 129.1, 128.3, 127.9, 83.3, 27.9, 26.6; **HRMS** (ESI) calculated for $C_{13}H_{17}NO_3$, 258.11061 *m/z* $(M+Na)^+$; Found, 258.11060 *m/z*.

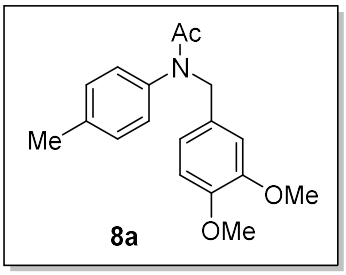
General Procedure IV: *Preparation of N-acetyl and benzyl/cinnamyl substituted tertiary amide***:**



S3 8

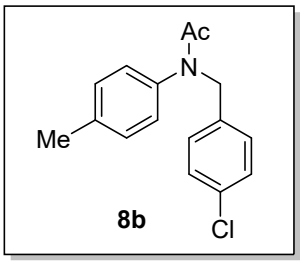
In a 100-mL, two-necked, round-bottomed flask, benzyl/cinnamyl protected amine **S3** (1.0 equiv.) was dissolved in dichloromethane (anhydrous) (0.3 M). After cooling in an ice bath, DMAP (0.05 equiv.), triethylamine (2.0 equiv.), and acetic anhydride (2.5 equiv.) were added to the stirring solution, and the reaction mixture was stirred at room temperature. When the amine was completely consumed by the product (as indicated by TLC), the resultant mixture was washed with water, extracted with ethyl acetate, and lastly washed with a brine solution. After drying the organic extract on Na_2SO_4, the solvent was evaporated under reduced pressure. The residue was then purified using flash column chromatography with silica gel (230-400 mesh) and an EtOAc/petroleum-ether solution as an eluent to obtained the products **8**.

Spectral data of N-acetyl and benzyl/cinnamyl substituted tertiary amide:



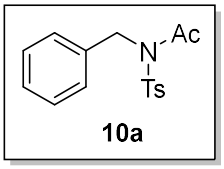
8a

N-(3,4-dimethoxybenzyl)-N-(*p*-tolyl)acetamide **(8a)**: Prepared according to the general reaction procedure **IV** using N-(3,4-dimethoxybenzyl)-4-methylaniline[5a] to obtain **8a** as light-yellow liquid; 72% yield; R_f : 0.25 (15% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 7.12 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 2.0 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.66 (dd, *J* = 8.1, 2.0 Hz, 1H), 4.78 (s, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.33 (s, 3H), 1.86 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.8, 148.8, 148.3, 140.1, 137.9, 130.2, 130.1, 128.0, 121.4, 112.3, 110.8, 55.9, 55.8, 52.6, 22.7, 21.1; **HRMS** (ESI) calculated for $C_{18}H_{21}NO_3$, 322.14191 *m/z* $(M+Na)^+$; Found, 322.14192 *m/z*.



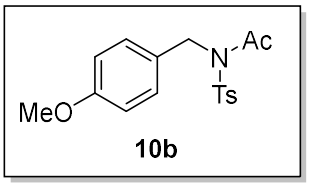
8b

N-(4-chlorobenzyl)-N-(*p*-tolyl)acetamide **(8b)**: Prepared according to the general reaction procedure **IV** using N-(4-chlorobenzyl)-4-methylaniline[5a] to obtain **8b** as light-yellow liquid; 85% yield; R_f : 0.25 (8% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 7.23-7.18 (m, 2H), 7.12-7.09 (m, 4H), 6.82 (d, *J* = 8.2 Hz, 2H), 4.79 (s, 2H), 2.31 (s, 3H), 1.84 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 170.8, 140.0, 138.1, 136.2, 133.2, 130.6, 130.3, 128.6, 128.4, 127.9, 52.2, 22.7, 21.1; **HRMS** (ESI) calculated for $C_{16}H_{16}ClNO$, 296.08181 *m/z* $(M+Na)^+$; Found, 296.08182*m/z*.



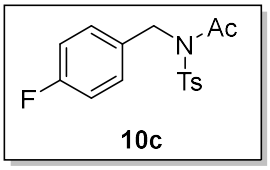
10a

N-benzyl-N-tosylacetamide **(10a)**: Prepared according to the general reaction procedure **IV** using N-benzyl-4-methylbenzenesulfonamide to obtain **10a** as white solid; m.p. = 110-112 °C; 70% yield; R_f : 0.20 (8% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 1.6 Hz, 2H), 7.34-7.32 (m, 2H), 7.30-7.29 (m, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.08 (s, 2H), 2.42 (s, 3H), 2.29 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.5, 145.0, 136.8, 136.7, 129.9, 128.7, 128.1, 127.9, 49.6, 25.0, 21.7; **HRMS** (ESI) calculated for $C_{16}H_{17}NO_3S$, 326.08268 *m/z* $(M+Na)^+$; Found, 326.08269 *m/z*.



10b

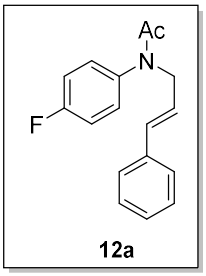
N-(4-methoxybenzyl)-N-tosylacetamide **(10b)**: Prepared according to the general reaction procedure **IV** using N-(4-methoxybenzyl)-4-methylbenzenesulfonamide to obtain **10b** as white solid; m.p. 101-102 °C; 72% yield; R_f : 0.25 (10% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.00 (s, 2H), 3.79 (s, 3H), 2.40 (s, 3H), 2.25 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 170.5, 159.3, 144.9, 136.8, 129.8, 128.9, 127.7, 114.0, 55.4, 49.0, 25.1, 21.7; **HRMS** (ESI) calculated for $C_{17}H_{19}NO_4S$, 356.09325 *m/z* $(M+Na)^+$; Found, 356.09327 *m/z*.



10c

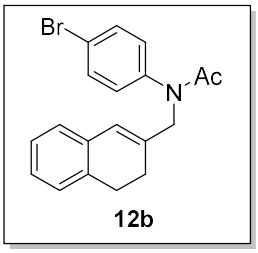
N-(4-fluorobenzyl)-N-tosylacetamide **(10c)**: Prepared according to the general reaction procedure **IV** using N-(4-fluorobenzyl)-4-methylbenzenesulfonamide to obtain **10c** as white solid; m.p. = 122-124 °C; 68% yield; R_f : 0.25 (8% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.38 (td, *J* = 5.3, 1.7 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 5.02 (s, 2H), 2.42 (s, 3H), 2.30 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.4, 163.3, 161.6, 145.2, 136.7, 132.7, 130.3 ($J_{C\text{-}F}$ = 7.8 Hz), 130.0, 127.6,

115.5 ($J_{C\text{-}F}$ = 21.2 Hz), 48.8, 25.1, 21.7; **HRMS** (ESI) calculated for $C_{16}H_{16}FNO_3S$, 344.07326 *m/z* $(M+Na)^+$; Found, 344.07327 *m/z*.



12a

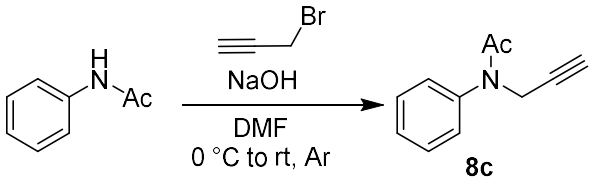
N-cinnamyl-N-(4-fluorophenyl)acetamide **(12a)**: Prepared according to the general reaction procedure **IV** using N-cinnamyl-4-fluoroaniline[6a] to obtain **12a** as white solid; m.p. = 111-112 °C; 75% yield; R_f: 0.25 (10% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 7.32-7.27 (m, 4H), 7.24-7.22 (m, 1H), 7.15-7.13 (m, 2H), 7.09-7.06 (m, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.26-6.21 (m, 1H), 4.40 (dd, *J* = 6.8, 1.0 Hz, 2H), 1.86 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.3, 162.8, 161.2, 139.0, 136.7, 133.7, 130.1 ($J_{C\text{-}F}$ = 8.5 Hz), 128.7, 127.8, 126.5, 124.2, 116.7 ($J_{C\text{-}F}$ = 22.6 Hz), 51.7, 22.8; **HRMS** (ESI) calculated for $C_{17}H_{16}FNO$, 292.11136 *m/z* $(M+Na)^+$; Found, 292.11137 *m/z*.



12b

N-(4-bromophenyl)-N-((3,4-dihydronaphthalen-2-yl)methyl)acetamide **(12b)**: Prepared according to the general reaction procedure **IV** using 4-bromo-N-((3,4-dihydronaphthalen-2-yl)methyl) aniline[6a] to obtain **12b** as white solid; m.p. = 140-142 °C; 70% yield; R_f: 0.25 (10% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 600 MHz): δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.10-7.09 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.92 (s, 1H), 6.12 (s, 1H), 4.46 (s, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.31 (t, *J* = 8.1 Hz, 2H), 1.91 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.4, 141.9, 136.2, 134.9, 133.9, 132.9, 129.8, 127.4, 127.1, 126.6, 126.2, 126.1, 121.9, 54.2, 27.9, 25.3, 22.9; **HRMS** (ESI) calculated for $C_{19}H_{18}{}^{81}BrNO$, 380.04490 *m/z* $(M+Na)^+$; Found, 380.04491 *m/z*.

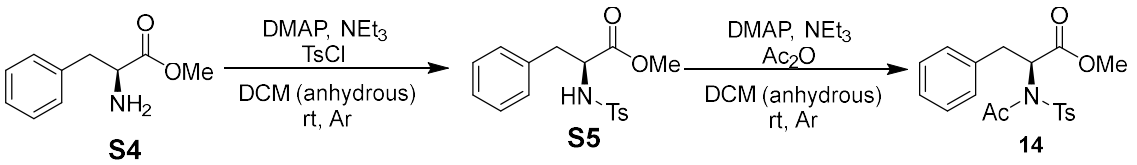
Preparation of N-phenyl-N-(prop-2-yn-1-yl)acetamide 8c:



In a 100-mL, two-necked, round-bottomed flask, acetanilide (1.0 gm, 7.398 mmol, 1.0 equiv.) was dissolved in DMF (20 mL). After chilling in an ice bath, NaOH (0.444 gm, 11.097 mmol, 1.5 equiv.) was progressively added to the stirring solution. The propargyl bromide (0.85 mL, 11.097 mmol, 1.5 equiv.) solution in DMF (5 mL) was added drop by drop to the reaction mixture, and the reaction mixture was stirred at room temperature. When the acetanilide was entirely consumed by the product (as determined by TLC), the resulting mixture was washed with water, extracted with ethyl acetate, and finally washed with a brine solution. After drying the organic extract on Na_2SO_4, the solvent was evaporated under reduced pressure. The residue was subsequently purified using flash column chromatography with silica gel (230-400 mesh) and an EtOAc/petroleum-ether (1:9, R_f : 0.25) solution as an eluent to get the brown solid product **8c** (1.0 gm, 78% yield). m.p. = 91-92 °C

^{1}H–NMR ($CDCl_3$, 600 MHz): δ 7.43 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.28-7.27 (m, 2H), 4.46 (d, *J* = 2.0 Hz, 2H), 2.18 (s, 1H), 1.85 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 150 MHz): δ 170.2, 142.4, 129.8, 128.5, 128.2, 79.3, 72.1, 38.4, 22.5; **HRMS** (ESI) calculated for $C_{11}H_{11}NO$, 196.07383 *m/z* $(M+Na)^+$; Found, 196.07384 *m/z*.

Preparation of methyl N-acetyl-N-tosyl-L-phenylalaninate 14:



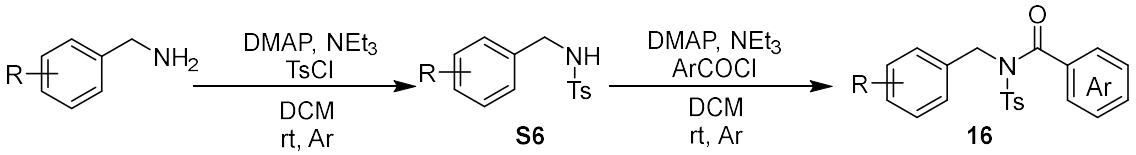
In a 100-mL, two-necked, round-bottomed flask, methyl L-phenylalaninate[6b,6c] **(S4)** (1.0 gm, 5.579 mmol, 1.0 equiv.) was dissolved in dichloromethane (anhydrous) (19 mL, 0.3 M). After cooling in an ice bath, DMAP (34 mg, 0.279 mmol, 0.05 equiv.), triethylamine (1.5 mL, 11.16 mmol, 2.0 equiv.), and tosyl chloride (1.0 gm, 5.579 mmol, 1.0 equiv.) were added to the stirring solution, and the reaction mixture was stirred at room temperature. When the methyl L-phenylalaninate was completely consumed by the product (as indicated by TLC), the

resultant mixture was washed with water, extracted with ethyl acetate, and lastly washed with a brine solution. After drying the organic extract on Na_2SO_4, the solvent was evaporated under reduced pressure to obtained the crude reaction mixture **(S5)** that was used for the next step without further purification.

The crude product (**S5**) (1.0 gm, 3.00 mmol, 1.0 equiv.) was dissolved in DCM (anhydrous) (19 mL, 0.3 M) in a 100-mL, two-necked, round-bottomed flask. After cooling in an ice bath, DMAP (18 mg, 0.150 mmol, 0.05 equiv.), triethylamine (0.8 mL, 6.00 mmol, 2.0 equiv.), and acetic anhydride (0.3 mL, 3.00 mmol, 1.0 equiv.) were added to the stirring solution, and the reaction mixture was stirred at room temperature. When the methyl tosyl-L-phenylalaninate was completely consumed by the product (as indicated by TLC), the resultant mixture was washed with water, extracted with ethyl acetate, and lastly washed with a brine solution. After drying the organic extract on Na_2SO_4, the solvent was evaporated under reduced pressure. The residue was then purified using flash column chromatography with silica gel (230-400 mesh) and 10% EtOAc/petroleum-ether (R_f = 0.25) solution as an eluent to obtained the colorless-oil product **14** (840 mg, 75 % yield).

^{1}H–NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.34-7.28 (m, 3H), 7.25-7.21 (m, 4H), 5.24 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.73 (s, 3H), 3.61 (dd, *J* = 14.2, 5.8 Hz, 1H), 3.28 (dd, *J* = 14.2, 8.8 Hz, 1H), 2.41 (s, 3H), 2.17 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 170.3, 170.0, 145.1, 137.8, 136.4, 129.9, 128.7, 128.1, 127.0, 61.8, 52.7, 36.1, 25.0, 21.7; **HRMS** (ESI) calculated for $C_{19}H_{21}NO_5S$, 398.10381 *m/z* $(M+Na)^+$; Found, 398.10379 *m/z*.

General Procedure V: *synthesis of substituted N-benzyl-N-tosylbenzamide derivatives:*

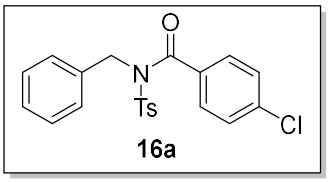


Phenylmethanamine (1.0 equiv.) was dissolved in dichloromethane (anhydrous) (0.3 M) in a 100-mL, two-necked, round-bottomed flask. DMAP (0.05 equiv.), triethylamine (2.0 equiv.), and tosyl chloride (1.0 equiv.) were added to the stirring solution after cooling in an ice bath, and the reaction mixture was stirred at room temperature. When the phenylmethanamine in the product had been consumed (as determined by TLC), the resulting mixture was washed with water, extracted with ethyl acetate, and then washed with a brine solution. The solvent was

evaporated under reduced pressure after drying the organic extract on Na_2SO_4 to get the crude reaction mixture **S6**, which was utilized for the following step without additional purification.

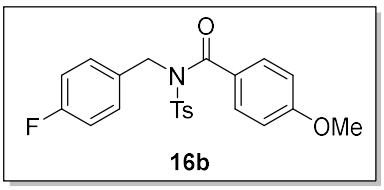
In a 100-mL, two-necked, round-bottomed flask, the crude (1.0 equiv.) was dissolved in DCM (anhydrous) (0.3 M). DMAP (0.05 equiv.), triethylamine (2.0 equiv.), and benzoyl chloride derivatives (ArCOCl, 1.3 equiv.) were added to the stirring solution after chilling in an ice bath, and the reaction mixture was stirred at room temperature. When the reaction was completed (as determined by TLC), the resulting mixture was washed with water, extracted with ethyl acetate, and finally washed with brine solution. The solvent was evaporated under reduced pressure after the organic extract was dried on Na_2SO_4. The residue was purified using flash column chromatography with silica gel (230-400 mesh) and an eluent of EtOAc/petroleum-ether solution to obtain the desired starting material **16**.

Spectral data of substituted N-benzyl-N-tosylbenzamide:



16a

N-benzyl-4-chloro-N-tosylbenzamide **(16a)**: Prepared according to the general reaction procedure **V** using phenylmethanamine and 4-chlorobenzoyl chloride to obtain **16a** as white solid; m.p. = 110-112 °C; 72% yield; R_f : 0.25 (8% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.41-7.39 (m, 2H), 7.32-7.29 (m, 2H), 7.27-7.21 (m, 7H), 4.92 (s, 2H), 2.42 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 170.7, 145.0, 138.3, 136.1, 135.8, 133.6, 132.0, 129.9, 129.7, 129.5, 128.7, 128.5, 128.4, 128.1, 128.0, 51.1, 21.7; **HRMS** (ESI) calculated for $C_{21}H_{18}ClNO_3S$, 422.05936 *m/z* $(M+Na)^+$; Found, 422.05933 *m/z*.

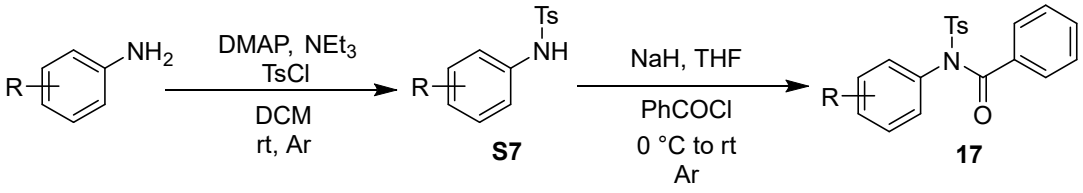


16b

N-(4-fluorobenzyl)-4-methoxy-N-tosylbenzamide **(16b)**: Prepared according to the general reaction procedure **V** using (4-fluorophenyl)methanamine and 4-methoxybenzoyl chloride to obtain **16b** as white solid; m.p. = 114-116 °C; 75% yield [16b:4-methoxybenzyl alcohol ≈ 3:1; inseparable mixture]; R_f : 0.25 (8% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400

MHz): δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.19-7.12 (m, 4H), 6.89 (t, *J* = 9.0 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.75 (s, 2H), 3.76 (s, 3H), 2.34 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 171.3, 163.2, 144.8, 135.9, 132.9, 132.1 (J_{C-F} = 3.4 Hz), 131.5, 130.1 (J_{C-F} = 8.2 Hz), 129.6, 128.3, 127.2, 115.6, 115.4, 114.2, 113.6, 55.5, 50.6, 21.7; **HRMS** (ESI) calculated for $C_{22}H_{20}FNO_4S$, 436.09948 *m/z* $(M+Na)^+$; Found, 436.09950 *m/z*.

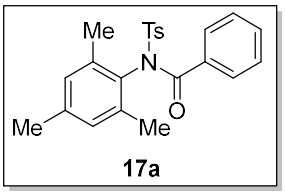
General Procedure VI: *synthesis of substituted N-phenyl-N-tosylbenzamide:*



In a 100-mL, two-necked, round-bottomed flask, substituted aniline (1.0 equiv.) was dissolved in Dichloromethane (anhydrous) (0.3 M). After cooling in an ice bath, DMAP (0.05 equiv.), triethylamine (2.0 equiv.), and tosyl chloride (1.0 equiv.) were added to the stirring solution, and the reaction mixture was stirred at room temperature. When the aniline was completely consumed by the product (as indicated by TLC), the resultant mixture was washed with water, extracted with ethyl acetate, and lastly washed with a brine solution. After drying the organic extract on Na_2SO_4, the solvent was evaporated under reduced pressure to obtained the crude reaction mixture **S7** that was used for the next step without further purification.

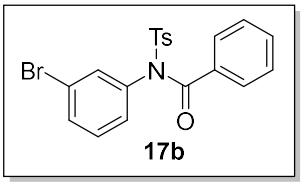
The crude **S7** (1.0 equiv.) was dissolved in THF (anhydrous) (0.06 M) in a 100-mL, two-necked, round-bottomed flask. After cooling the reaction mixture at 0 °C, NaH (1.3 equiv.) was added to the stirring solution, and the reaction mixture was stirred for 1h at the same temperature. After 1h benzoyl chloride (1.3 equiv.) was added at 0 °C and the reaction was stirred overnight at room temperature. When the reaction was completed (as indicated by TLC), the resultant mixture was quenched by the saturated solution of ammonium chloride at 0 °C by dropwise addition. The resultant mixture was extracted with ethyl acetate, and lastly washed with a brine solution. After drying the organic extract on Na_2SO_4, the solvent was evaporated under reduced pressure. The residue was then purified using flash column chromatography with silica gel (230-400 mesh) and EtOAc/petroleum-ether solution as an eluent to obtained the starting material **17**.

Spectral data of substituted N-phenyl-N-tosylbenzamide:



17a

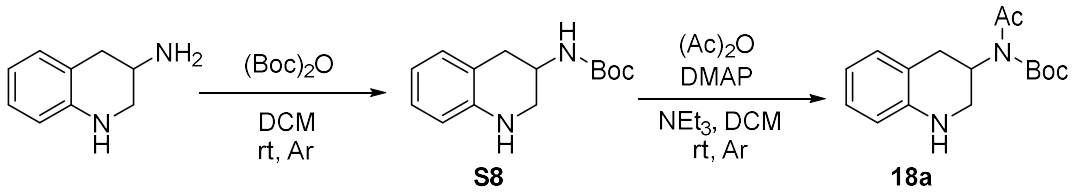
N-mesityl-N-tosylbenzamide **(17a)**: Prepared according to the general reaction procedure **VI** using 2,4,6-trimethylaniline and benzoyl chloride to obtain **17a** as white solid; m.p. = 117-119 °C; 70% yield; R_f : 0.20 (6% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29-7.27 (m, 3H), 7.12 (t, *J* = 7.2 Hz, 2H), 6.82 (s, 2H), 2.46 (s, 3H), 2.23 (s, 3H), 2.18 (s, 6H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 169.5, 145.1, 139.4, 138.1, 136.3, 134.1, 133.1, 131.4, 130.5, 129.9, 129.2, 128.2, 127.8, 21.8, 21.1, 19.3; **HRMS** (ESI) calculated for $C_{23}H_{23}NO_3S$, 416.12963 *m/z* $(M+Na)^+$; Found, 416.12960 *m/z*



17b

N-(3-bromophenyl)-N-tosylbenzamide **(17b)**: Prepared according to the general reaction procedure **VI** using 3-bromoaniline and benzoyl chloride to obtain **17b** as white solid; m.p. = 119-121 °C; 74% yield; R_f : 0.25 (6% ethyl acetate in petroleum-ether); **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.44-7.41 (m, 3H), 7.36-7.31 (m, 4H), 7.21 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.07-7.04 (m, 1H), 2.46 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 169.7, 145.3, 133.4, 132.3, 132.2, 130.3, 129.6, 129.5, 129.4, 129.1, 128.3, 122.4, 21.8; **HRMS** (ESI) calculated for $C_{20}H_{16}{}^{81}BrNO_3S$, 453.99115 *m/z* $(M+Na)^+$; Found, 453.99118 *m/z*.

***Preparation of tert-butyl acetyl(1,2,3,4-tetrahydroquinolin-3-yl)carbamate 18a**:*



S8 **18a**

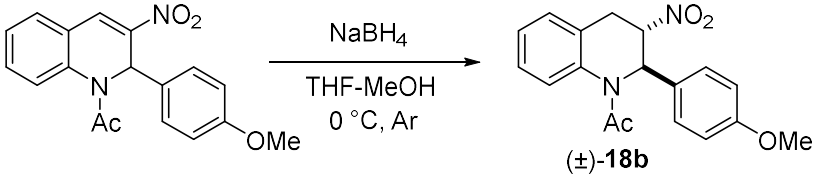
1,2,3,4-tetrahydroquinolin-3-amine (0.5 gm, 3.373 mmol, 1.0 equiv.) was dissolved in anhydrous DCM (18 mL) and added Boc anhydride (2.0 mL, 8.434 mmol, 2.5 equiv.). After

addition, reaction was continued for overnight under inert atmosphere at room temperature. After completion (checked *via* TLC) the reaction was quenched with water and solvent was evaporated under reduced pressure. Then the reaction mixture was washed with water and extracted multiple times with ethyl acetate. The combined organic layers were dried using Na_2SO_4. After removal of the combined organic layers under reduced pressure, the crude product **S8**[6d] was directly used to next step.

In a 100-mL, two-necked, round-bottomed flask, *tert*-butyl (1,2,3,4-tetrahydroquinolin-3-yl) carbamate **S8** (400 mg, 1.611 mmol, 1.0 equiv.) was dissolved in dichloromethane (anhydrous) (7 mL). After cooling in an ice bath, DMAP (10 mg, 0.08 mmol, 0.05 equiv.), triethylamine (0.35 mL, 2.416 mmol, 1.5 equiv.), and acetic anhydride (411 mg, 4.027 mmol, 2.5 equiv.) were added to the stirring solution, and the reaction mixture was stirred at room temperature. When the starting material **S8** was completely consumed (as indicated by TLC), the resultant mixture was washed with water, extracted with ethyl acetate, and lastly washed with a brine solution. After drying the organic extract on Na_2SO_4, the solvent was evaporated under reduced pressure. The residue was then purified using flash column chromatography with silica gel (230-400 mesh) and an EtOAc/petroleum-ether (1:5, R_f = 0.25) solution as an eluent to obtained the white solid product **18a** (383 mg, 82 % yield). m.p. = 104-106 °C

^{1}H–NMR ($CDCl_3$, 400 MHz): δ 7.22-7.11 (m, 4H), 4.70 (s, 1H), 4.14 (s, 1H), 3.82 (s, 2H), 3.09 (s, 1H), 2.65 (dd, *J* = 12.8, 4.2 Hz, 1H), 2.24 (s, 3H), 1.42 (s, 9H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 170.5, 159.3, 155.3, 129.3, 126.7, 125.6, 124.7, 79.9, 60.5, 33.8, 28.5, 23.1, 14.3; **HRMS** (ESI) calculated for $C_{16}H_{22}N_2O_3$, 313.15281 *m/z* $(M+Na)^+$; Found, 313.15283 *m/z*.

Preparation of 1-(2-(4-methoxyphenyl)-3-nitro-3,4-dihydroquinolin-1(2H)-yl)ethan-1-one (±)-18b[7]*:*



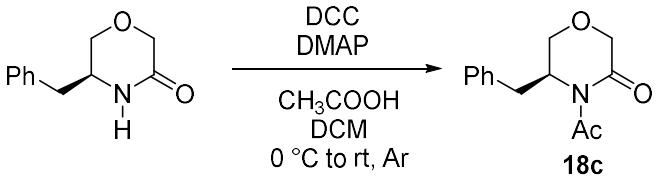
(±)-**18b**

1-(2-(4-methoxyphenyl)-3-nitroquinolin-1(2*H*)-yl)ethan-1-one (500 mg, 1.54 mmol, 1.0 equiv.) was dissolved in a mixture of THF-MeOH (10:1) (15 mL:1.5 mL) and cooled to 0 °C then added $NaBH_4$ (76 mg, 2.00 mmol, 1.3 equiv.) in portion-wise manner. After addition, reaction was continued for 30 min under inert atmosphere at 0 °C. After completion (checked

via TLC) the reaction was quenched with water and solvent was evaporated under reduced pressure. Then the resultant slurry was washed with water and extracted multiple times with ethyl acetate. The combined organic layers were dried using Na_2SO_4. After removal of the combined organic layers under reduced pressure, the crude mixture was subjected to purification by column chromatography directly using EtOAc/petroleum-ether (1:5, R_f = 0.25) as eluent to afford the yellow solid product **(±)-18b** (362 mg, 72% yield). dr ratio = 7:1; m.p. = 135-137 °C.

^{1}H–NMR ($CDCl_3$, 400 MHz): δ 7.34 (t, *J* = 5.7 Hz, 1H), 7.29-7.23 (m, 3H), 7.02 (d, *J* = 6.9 Hz, 2H), 6.77 (d, *J* = 6.9 Hz, 2H), 6.41 (s, 1H), 4.96-4.92 (m, 1H), 3.73 (s, 3H), 3.35-3.30 (m, 1H), 3.26-3.22 (m, 1H), 2.20 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 169.9, 159.4, 128.6, 128.2, 127.9, 125.7, 114.4, 88.6, 58.0, 55.3, 31.4, 22.7; **HRMS** (ESI) calculated for $C_{18}H_{18}N_2O_4$, 349.11643 *m/z* $(M+Na)^+$; Found, 349.11644 *m/z*.

***Preparation of (S)-4-acetyl-5-benzylmorpholin-3-one 18c**:*

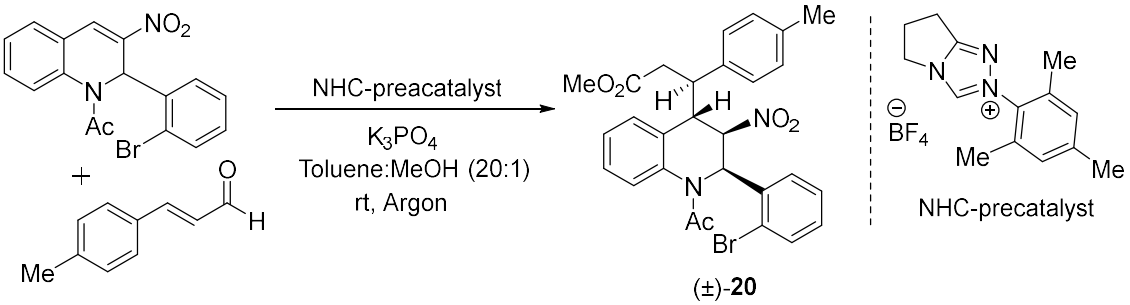


(S)-5-benzylmorpholin-3-one[8a] (500 mg, 2.62 mmol, 1.0 equiv.) was dissolved in Dichloromethane (anhydrous) (8 mL) in a 100-mL, two-necked, round-bottomed flask. Cool the reaction mixture in ice bath and DMAP (48 mg, 0.39 mmol. 0.15 equiv.) was added. N,N′-dicyclohexylcarbodiimide (809 mg, 3.92 mmol, 1.5 equiv.) and acetic acid (0.23 mL, 3.92 mmol, 1.5 equiv.) were added to the stirring solution at the same temperature and the reaction mixture was stirred at room temperature. When the (S)-5-benzylmorpholin-3-one had been completely consumed (as determined by TLC), the resulting mixture was washed with water, extracted with ethyl acetate, and finally the organic extract was washed with a brine solution. The solvent was evaporated under reduced pressure after the organic extract was dried on Na_2SO_4. Following that, the residue was purified using flash column chromatography with silica gel (230-400 mesh) and an EtOAc/petroleum-ether (3:10, R_f = 0.25) solution as an eluent to obtain the white solid product **18c** (501 mg, 82% yield). m.p. = 123-125 °C.

HPLC analysis: *ee* > 99% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane, 1.0 ml/min, 254 nm, Major: 5.00 min.]; **^{1}H–NMR** ($CDCl_3$, 400 MHz): δ 7.31-7.29 (m, 4H), 7.25

7.22 (m, 1H), 4.44-4.39 (m, 1H), 4.35 (d, *J* = 1.0 Hz, 1H), 4.20 (d, *J* = 17.6 Hz, 1H), 3.83 (d, *J* = 12.4 Hz, 1H), 3.53-3.49 (m, 1H), 2.99-2.92 (m, 2H), 2.61 (s, 3H); **^{13}C–NMR** ($CDCl_3$, 100 MHz): δ 172.4, 169.6, 137.5, 129.7, 128.8, 127.0, 68.5, 64.9, 54.6, 37.4, 28.4; **HRMS** (ESI) calculated for $C_{13}H_{15}NO_3$, 256.25677 *m/z* $(M+Na)^+$; Found, 256.25675 *m/z*.

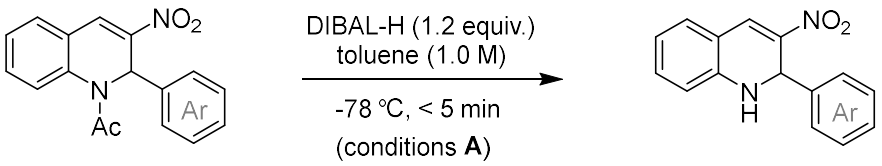
***Preparation of methyl 3-(1-acetyl-2-(2-bromophenyl)-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(p-tolyl)propanoate* (±)-20**[7]*:*



To a well-stirred solution of 1-(2-(2-bromophenyl)-3-nitroquinolin-1(2*H*)-yl)ethan-1-one (200 mg, 0.58 mmol, 1.0 equiv.) and (*E*)-3-(*p*-tolyl)acrylaldehyde[8b] (102 mg, 0.70 mmol, 1.2 equiv.) in 2.9 mL toluene-MeOH {0.1 (M) C, 20:1}, racemic NHC-precatalyst (36 mg, 0.12 mmol, 0.2 equiv.) and K_3PO_4 (36 mg, 0.17 mmol, 0.3 equiv.) were added and allowed to stir at rt under argon atmosphere. Progress of the reaction was monitored by TLC. On completion, the reaction mixture was diluted with ethyl acetate and solvent was removed under reduced pressure. Then, the crude reaction mixture was subjected to purification by flash column chromatography using silica gel (230-400 mesh) and EtOAc/petroleum-ether (3:10, R_f = 0.25) as an eluent to afford the white solid racemic product **(±)-20** (308 mg, 80% yield). m.p. = 171-173 °C.

^{1}H-NMR ($CDCl_3$, 400 MHz**):** δ 7.46 (d, *J* = 3.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31-7.24 (m, 7H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.12 (s, 1H), 5.47 (dd, *J* = 7.5, 2.2 Hz, 1H), 3.61 (dd, *J* = 11.5, 2.4 Hz, 1H), 3.36 (s, 3H), 3.27-3.20 (m, 1H), 2.76 (dd, *J* = 15.6, 5.8 Hz, 1H), 2.65 (dd, *J* = 15.6, 8.1 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 171.4, 170.5, 138.1, 136.6, 136.5, 132.7, 130.5, 130.4, 129.4, 129.0, 127.6, 127.4, 126.6, 126.1, 121.7, 87.2, 57.5, 51.7, 50.7, 42.5, 40.6, 23.1, 21.3; **HRMS** (ESI) calculated for $C_{28}H_{27}{}^{79}BrN_2O_5$, 573.1001 *m/z* $(M+Na)^+$; Found, 573.0998 *m/z*.

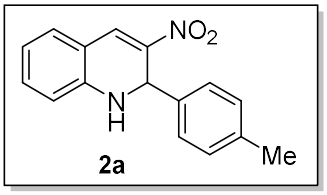
General Procedure VII: *N-Deacetylation of N-acetylated 2-aryl substituted 3-nitro-1,2-dihydroquinolines:*



1 **2**

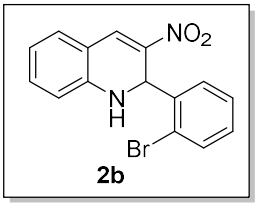
N-acetylated 2-aryl substituted 3-nitro-1,2-dihydroquinoline **1** (1.0 equiv.) was dissolved in toluene (1.0 M) under inert atmosphere and the solution was cooled to -78 °C for 20 minutes. The DIBAL-H (1.0 M in toluene) (1.2 equiv.) was then added dropwise over 1 minute. TLC was evaluated immediately after addition to confirm the completion of the reaction. After completion (as determined by TLC), the reaction was quenched with water and extracted several times with ethyl acetate. The mixed organic layers were dried with Na_2SO_4. After removing the mixed organic layers under decreased pressure, the crude product was purified by column chromatography directly utilising EtOAc/petroleum-ether as eluent to obtain product **2** with good yield.

Spectral data of 3-nitro-2-aryl substituted-1,2-dihydroquinolines:



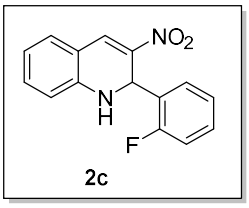
2a

3-nitro-2-(*p*-tolyl)-1,2-dihydroquinoline **(2a)**: Prepared according to the general reaction procedure **VII** using 1-(3-nitro-2-(*p*-tolyl)quinolin-1(2*H*)-yl)ethan-1-one (100 mg, 0.324 mmol, 1.0 equiv.) and DIBAL-H (0.38 mL, 0.389 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **2a** (60 mg, 70% yield) as red solid (8% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 85-87 °C; **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.96 (s, 1H), 7.27-7.25 (m, 2H), 7.18-7.15 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.69 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 5.94 (d, *J* = 1.7 Hz, 1H), 4.69 (s, 1H), 2.30 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 144.5, 141.4, 139.5, 138.7, 134.2, 131.3, 131.2, 129.7, 126.3, 118.7, 115.1, 113.5, 55.3, 21.3; **HRMS** (ESI) calculated for $C_{16}H_{14}N_2O_2$, 289.09530 *m/z* $(M+Na)^+$; Found, 289.09528 *m/z*.; **FTIR (cm^{-1}):** 3349, 1710, 1630, 1606, 1438, 1320, 1118, 750, 650.



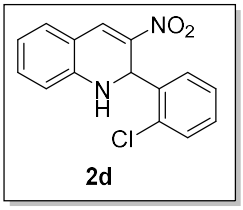
2b

2-(2-bromophenyl)-3-nitro-1,2-dihydroquinoline **(2b)**: Prepared according to the general reaction procedure **VII** using 1-(2-(2-bromophenyl)-3-nitroquinolin-1(2*H*)-yl) ethan-1-one (100 mg, 0.268 mmol, 1.0 equiv.) and DIBAL-H (0.32 mL, 0.322 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **2b** (70 mg, 79% yield) as red solid (9% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 132-134 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.19 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.24-7.21 (m, 3H), 7.17-7.12 (m, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.46-6.43 (m, 2H), 5.05 (s, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 143.9, 139.2, 139.1, 134.4, 133.6, 133.2, 131.4, 130.2, 128.5, 128.0, 121.5, 119.0, 115.3, 114.2, 53.9; **HRMS** (ESI) calculated for $C_{15}H_{11}{}^{81}BrN_2O_2$, 354.98811 *m/z* $(M+Na)^+$; Found, 354.98813 *m/z*; **FTIR (cm^{-1}):** 3395, 1730, 1645, 1615, 1455, 1330, 1120, 745, 640.



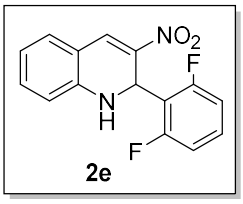
2c

2-(2-fluorophenyl)-3-nitro-1,2-dihydroquinoline **(2c)**: Prepared according to the general reaction procedure **VII** using 1-(2-(2-fluorophenyl)-3-nitroquinolin-1(2*H*)-yl) ethan-1-one (100 mg, 0.320 mmol, 1.0 equiv.) and DIBAL-H (0.38 mL, 0.384 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **2c** (68 mg, 79% yield) as red solid (8% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 113-115 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.12 (s, 1H), 7.23-7.20 (m, 2H), 7.18-7.16 (m, 1H), 7.12 (dd, *J* = 13.2, 1.6 Hz, 1H), 7.09-7.02 (m, 2H), 6.71 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 6.38 (s, 1H), 4.71 (s, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 159.3 ($J_{C\text{-}F}$ = 245.8 Hz), 144.2, 138.8, 134.3, 132.9, 131.4, 130.4 ($J_{C\text{-}F}$ = 8.2 Hz), 128.1, 124.8, 119.0, 116.2, 116.0, 115.2, 113.9, 48.8; **HRMS** (ESI) calculated for $C_{15}H_{11}FN_2O_2$, 293.07023 *m/z* $(M+Na)^+$; Found, 293.07023 *m/z*; **FTIR (cm^{-1}):** 3410, 1710, 1640, 1605, 1410, 1320, 1130, 710, 660.



2d

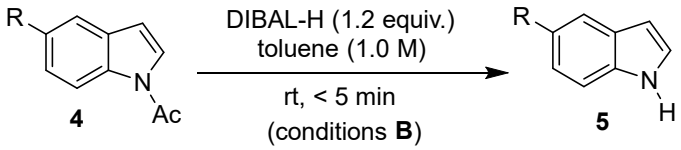
2-(2-chlorophenyl)-3-nitro-1,2-dihydroquinoline **(2d)**: Prepared according to the general reaction procedure **VII** using 1-(2-(2-chlorophenyl)-3-nitroquinolin-1(2*H*)-yl) ethan-1-one (100 mg, 0.304 mmol, 1.0 equiv.) and DIBAL-H (0.36 mL, 0.365 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **2e** (63 mg, 72% yield) as red solid (8% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 116=118 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.19 (s, 1H), 7.42 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.25-7.20 (m, 3H), 7.18-7.13 (m, 2H), 6.70 (td, *J* = 7.6, 1.0 Hz, 1H), 6.47 (s, 1H), 6.44 (d, *J* = 8.2 Hz, 1H), 5.04 (s, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 144.0, 139.0, 137.6, 134.3, 133.2, 131.4, 130.3, 129.9, 127.9, 127.8, 119.0, 115.3, 114.1, 51.5; **HRMS** (ESI) calculated for $C_{15}H_{11}ClN_2O_2$, 309.04067 *m/z* $(M+Na)^+$; Found, 309.04065 *m/z*; **FTIR (cm^{-1}):** 3345, 1715, 1630, 1604, 1485, 1320, 1140, 735, 680.



2e

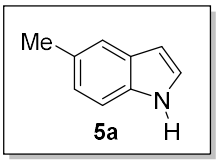
2-(2,6-difluorophenyl)-3-nitro-1,2-dihydroquinoline **(2e)**: Prepared according to the general reaction procedure **VII** using 1-(2-(2,6-difluorophenyl)-3-nitroquinolin-1(2*H*)-yl)ethan-1-one (100 mg, 0.303 mmol, 1.0 equiv.) and DIBAL-H (0.36 mL, 0.364 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **2d** (60 mg, 69% yield) as red solid (8% ethyl acetate in petroleum-ether, R_f: 0.20); m.p. = 128-130 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.99 (s, 1H), 7.24-7.15 (m, 3H), 6.86 (t, *J* = 8.3 Hz, 2H), 6.70 (td, *J* = 7.4, 0.8 Hz, 1H), 6.63 (s, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 4.54 (s, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 161.3 (J_{C-F} = 254.0 Hz), 144.4, 138.0, 134.3, 133.1, 131.5, 130.2 (J_{C-F} = 21.2, 10.6 Hz), 118.7, 115.1, 112.8, 112.1 (J_{C-F} = 25.5 Hz), 46.2; **HRMS** (ESI) calculated for $C_{15}H_{10}F_2N_2O_2$, 311.06080 *m/z* $(M+Na)^+$; Found, 311.06081 *m/z*; **FTIR (cm^{-1}):** 3338, 1725, 1635, 1599, 1450, 1321, 1135, 725, 666.

General Procedure VIII: *N-Deacetylation of N-acetylated indoles:*

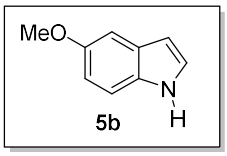


N-acetylated indole **4** (1.0 equiv.) was dissolved in toluene (1.0 M) under inert atmosphere and the solution was stirred at room temperature. The DIBAL-H (1.0 M in toluene) (1.2 equiv.) was then added dropwise over 1 minute. TLC was evaluated immediately after addition to confirm the completion of the reaction. After completion (as determined by TLC), the reaction was quenched with water and extracted several times with ethyl acetate. The mixed organic layers were dried with Na_2SO_4. After removing the mixed organic layers under decreased pressure, the crude product was purified by column chromatography directly utilising EtOAc/petroleum-ether as eluent to obtain product **5** with good yield.

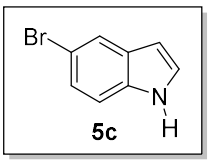
Spectral data of substituted indoles:



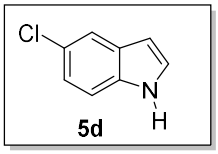
5-methyl-1*H*-indole **(5a)**[9a]: Prepared according to the general reaction procedure **VIII** using 1-(5-methyl-1*H*-indol-1-yl)ethan-1-one (100 mg, 0.577 mmol, 1.0 equiv.) and DIBAL-H (0.69 mL, 0.692 mmol, 1.2 equiv.) at rt for <5 min. to obtain **5a** (64 mg, 84% yield) as brown solid (7% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.99 (s, 1H), 7.47 (s, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.16 (s, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.50 (s, 1H), 2.49 (s, 3H).



5-methoxy-1*H*-indole **(5b)**[9a]: Prepared according to the general reaction procedure **VIII** using 1-(5-methoxy-1*H*-indol-1-yl)ethan-1-one (100 mg, 0.528 mmol, 1.0 equiv.) and DIBAL-H (0.63 mL, 0.634 mmol, 1.2 equiv.) at rt for <5 min. to obtain **5b** (47 mg, 61% yield) as brown solid (10% ethyl acetate in petroleum-ether, R_f: 0.20); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.05 (s, 1H), 7.28 (d, *J* = 12.0 Hz, 1H), 7.18 (t, *J* = 4.0 Hz, 1H), 7.12 (d, *J* = 4.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.50 (s, 1H), 3.87 (s, 3H).

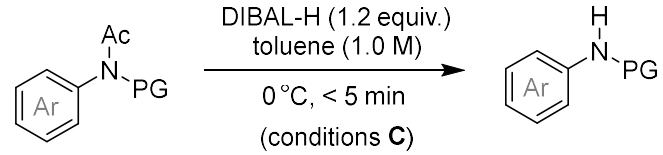


5-bromo-1*H*-indole **(5c)**[9a]: Prepared according to the general reaction procedure **VIII** using 1-(5-bromo-1*H*-indol-1-yl)ethan-1-one (100 mg, 0.420 mmol, 1.0 equiv.) and DIBAL-H (0.63 mL, 0.504 mmol, 1.2 equiv.) at rt for <5 min. to obtain **5c** (71 mg, 86% yield) as white solid (7% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.18 (s, 1H), 7.79 (s, 1H), 7.31-7.25 (m, 2H), 7.21 (t, *J* = 2.8 Hz, 1H), 6.51 (t, *J* = 2.4 Hz, 1H).



5-chloro-1*H*-indole **(5d)**[9b]: Prepared according to the general reaction procedure **VIII** using 1-(5-chloro-1*H*-indol-1-yl)ethan-1-one (100 mg, 0.516 mmol, 1.0 equiv.) and DIBAL-H (0.63 mL, 0.619 mmol, 1.2 equiv.) at rt for <5 min. to obtain **5d** (68 mg, 87% yield) as brown solid (7% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.17 (s, 1H), 7.61 (d, *J* = 1.6 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.23 (t, *J* = 2.7 Hz, 1H), 7.15 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.50 (d, *J* = 2.0 Hz, 1H).

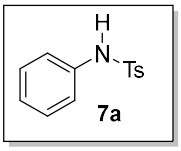
General Procedure IX: *N-Deacetylation of N-acetylated tertiary amides:*



PG = Protecting group

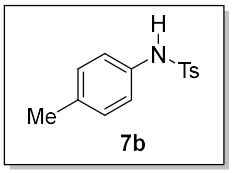
N-acetylated tertiary amide (1.0 equiv.) was dissolved in toluene (1.0 M) under inert atmosphere and the solution was cooled to 0 °C for 20 minutes. The DIBAL-H (1.0 M in toluene) (1.2 equiv.) was then added dropwise over 1 minute. TLC was evaluated immediately after addition to confirm the completion of the reaction. After completion (as determined by TLC), the reaction was quenched with water and extracted several times with ethyl acetate. The mixed organic layers were dried with Na_2SO_4. After removing the mixed organic layers under decreased pressure, the crude product was purified by column chromatography directly utilising EtOAc/petroleum-ether as eluent to obtain product with good yield.

Spectral data of deacetylated amine:



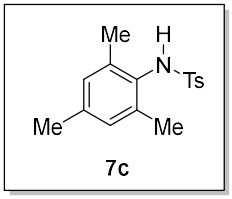
7a

4-methyl-N-phenylbenzenesulfonamide **(7a)**[5a]: Prepared according to the general reaction procedure **IX** using N-phenyl-N-tosylacetamide (100 mg, 0.346 mmol, 1.0 equiv.) and DIBAL-H (0.41 mL, 0.415 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7a** (75 mg, 88% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f: 0.20); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.69 (dd, *J* = 6.5, 1.9 Hz, 2H), 7.26-7.20 (m, 5H), 7.19-7.06 (m, 3H), 2.36 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 144.0, 136.7, 136.1, 129.8, 129.4, 125.3, 121.5, 21.6; **HRMS** (ESI) calculated for $C_{13}H_{13}NO_2S$, 270.05647 *m/z* $(M+Na)^+$; Found, 270.05649 *m/z*.



7b

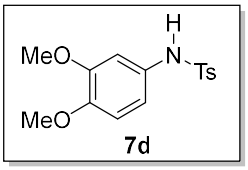
4-methyl-N-(*p*-tolyl)benzenesulfonamide **(7b)**[5a]: Prepared according to the general reaction procedure **IX** using N-(*p*-tolyl)-N-tosylacetamide (100 mg, 0.330 mmol, 1.0 equiv.) and DIBAL-H (0.39 mL, 0.396 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7b** (77 mg, 89% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.98 (q, *J* = 8.4 Hz, 4H), 2.36 (s, 3H), 2.26 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 143.8, 136.0, 135.2, 133.9, 130.0, 129.9, 129.7, 127.4, 122.1, 21.6, 20.9; **HRMS** (ESI) calculated for $C_{14}H_{15}NO_2S$, 284.07212 *m/z* $(M+Na)^+$; Found, 284.07210 *m/z*.



7c

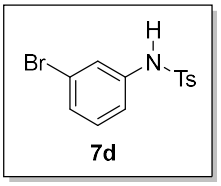
N-mesityl-4-methylbenzenesulfonamide **(7c)**: Prepared according to the general reaction procedure **IX** using N-mesityl-N-tosylacetamide (100 mg, 0.302 mmol, 1.0 equiv.) and DIBAL-H (0.36 mL, 0.362 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7c** (81 mg, 93% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 159-161 °C; **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.82 (s, 2H),

5.84 (s, 1H), 2.42 (s, 3H), 2.24 (s, 3H), 1.99 (s, 6H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 143.7, 138.0, 137.7, 137.6, 130.1, 129.7, 129.6, 127.4, 21.7, 21.0, 18.7; **HRMS** (ESI) calculated for $C_{16}H_{19}NO_2S$, 312.10342 *m/z* $(M+Na)^+$; Found, 312.10340 *m/z*; **FTIR (cm^{-1}):** 3279, 1397, 1327, 1303, 1156, 1087, 896, 856, 815, 715.



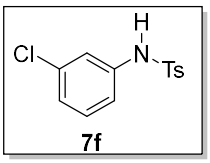
7d

N-(3,4-dimethoxyphenyl)-4-methylbenzenesulfonamide **(7d)**[5a]: Prepared according to the general reaction procedure **IX** using N-(3,4-dimethoxyphenyl)-N-tosylacetamide (dis- olve in minimum amount of DCM) (100 mg, 0.286 mmol, 1.0 equiv.) and DIBAL-H (0.34 mL, 0.343 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7d** (85 mg, 97% yield) as white solid (20% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.90-6.85 (m, 1H), 6.67-6.64 (m, 2H), 6.51 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 2.35 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 149.3, 147.4, 143.9, 136.0, 129.8, 129.5, 127.5, 115.6, 111.3, 107.9, 56.1, 56.0, 21.7; **HRMS** (ESI) calculated for $C_{15}H_{17}NO_4S$, 330.07760 *m/z* $(M+Na)^+$; Found, 330.07757 *m/z*.

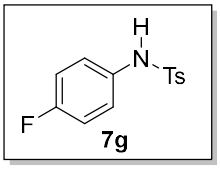


7d

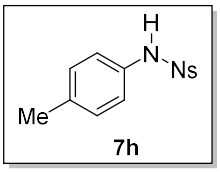
N-(3-bromophenyl)-4-methylbenzenesulfonamide **(7e)**: Prepared according to the general reaction procedure **IX** using N-(3-bromophenyl)-N-tosylacetamide (100 mg, 0.271 mmol, 1.0 equiv.) and DIBAL-H (0.32 mL, 0.325 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7e** (83 mg, 94% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 117-119 °C; **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.25-7.23 (m, 3H), 7.20-7.18 (m, 1H), 7.13 (s, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 7.02-7.01 (m, 1H), 2.37 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 144.4, 138.1, 135.8, 130.7, 129.9, 128.3, 127.4, 123.9, 122.9, 119.5, 21.7; **HRMS** (ESI) calculated for $C_{13}H_{12}{}^{81}BrNO_2S$, 349.96493 *m/z* $(M+Na)^+$; Found, 349.96491 *m/z*; **FTIR (cm^{-1}):** 3244, 1593, 1478, 1390, 1328, 1156, 1089, 918, 810, 779, 670.



N-(3-chlorophenyl)-4-methylbenzenesulfonamide **(7f)**[5a]: Prepared according to the general reaction procedure **IX** using N-(3-chlorophenyl)-N-tosylacetamide (100 mg, 0.309 mmol, 1.0 equiv.) and DIBAL-H (0.37 mL, 0.371 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7f** (79 mg, 91% yield) as white solid (2% ethyl acetate in petroleum-ether, R_f : 0.20); **^{1}H-NMR (**$CDCl_3$, 100 MHz**):** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.56 (s, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.00-6.97 (m, 1H), 2.37 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 144.5, 138.0, 135.6, 134.9, 130.4, 130.0, 127.3, 125.2, 120.8, 118.9, 21.7; **HRMS** (ESI) calculated for $C_{13}H_{12}ClNO_2S$, 304.01750 *m/z* $(M+Na)^+$; Found, 304.01753 *m/z*.

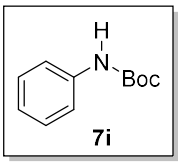


N-(4-fluorophenyl)-4-methylbenzenesulfonamide **(7g)**[5a]: Prepared according to the general reaction procedure **IX** using N-(4-fluorophenyl)-N-tosylacetamide (100 mg, 0.325 mmol, 1.0 equiv.) and DIBAL-H (0.39 mL, 0.390 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7g** (79 mg, 92% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f : 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.30 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.07-7.04 (m, 2H), 6.90 (t, *J* = 8.4 Hz, 2H), 2.37 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 161.9, 159.4, 144.2, 135.7, 132.5, 132.4, 129.8, 127.4, 124.5 (J_{C-F} = 8.3 Hz), 116.2 (J_{C-F} = 22.6 Hz), 21.7; **HRMS** (ESI) calculated for $C_{13}H_{12}FNO_2S$, 288.04705 *m/z* $(M+Na)^+$; Found, 288.04708 *m/z*.



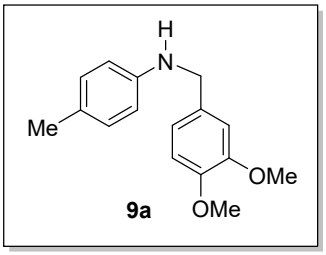
4-nitro-N-(*p*-tolyl)benzenesulfonamide **(7h)**: Prepared according to the general reaction procedure **IX** using N-((4-nitrophenyl)sulfonyl)-N-(*p*-tolyl) aceta mide (100 mg, 0.280 mmol, 1.0 equiv.) and DIBAL-H (0.33 mL, 0.336 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7h** (71 mg, 87% yield) as pale yellow solid (5% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 155-157 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.65 (s, 1H), 2.29 (s, 3H); **^{13}C-NMR**

($CDCl_3$, 100 MHz**):** δ 150.3, 144.8, 136.9, 132.6, 130.4, 128.7, 124.4, 123.3, 21.0; **HRMS** (ESI) calculated for $C_{13}H_{12}N_2O_4S$, 315.04155 *m/z* $(M+Na)^+$; Found, 315.04156 *m/z*; **FTIR (cm^{-1}):** 3244, 1526, 1508, 1349, 1300, 1160, 1085, 922, 855, 819, 734, 680.



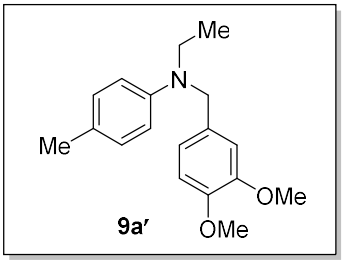
7i

tert-butyl phenylcarbamate **(7i)**[10]: Prepared according to the general reaction procedure **IX** using tert-butyl acetyl(phenyl)carbamate (100 mg, 0.425 mmol, 1.0 equiv.) and DIBAL-H (0.51 mL, 0.510 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7i** (77 mg, 94% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f: 0.20); m.p. = 110-112 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.52 (s, 1H), 1.52 (s, 9H); **HRMS** (ESI) calculated for $C_{11}H_{15}NO_2$, 216.10005 *m/z* $(M+Na)^+$; Found, 216.10002 *m/z*; **FTIR (cm^{-1}):** 3310, 1785, 1686, 1596, 1527, 1439, 1311, 1239, 1147, 1053, 744, 691.



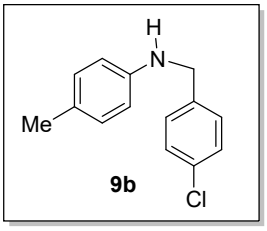
9a

N-(3,4-dimethoxybenzyl)-4-methylaniline **(9a)**: Prepared according to the general reaction procedure **IX** using N-(3,4-dimethoxybenzyl)-N-(*p*-tolyl)acetamide (100 mg, 0.334 mmol, 1.0 equiv.) and DIBAL-H (0.40 mL, 0.401 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **9a** (33 mg, 38% yield) as yellow solid (10% ethyl acetate in petroleum-ether, R_f: 0.20); m.p. = 80-82 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 6.99 (d, *J* = 8.4 Hz, 2H), 6.91-6.89 (m, 2H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.22 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 2.24 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 149.1, 148.2, 146.0, 132.2, 129.8, 126.8, 119.7, 113.1, 111.2, 110.8, 56.0, 55.9, 48.6, 20.5; **HRMS** (ESI) calculated for $C_{16}H_{19}NO_2$, 280.13135 *m/z* $(M+Na)^+$; Found, 280.13136 *m/z*; **FTIR (cm^{-1}):** 3372, 2922, 2852, 1614, 1509, 1462, 1450, 1258, 1230, 1138, 1023, 872, 796, 759.



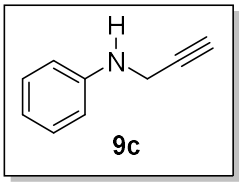
9a′

N-(3,4-dimethoxybenzyl)-N-ethyl-4-methylaniline **(9a′)**: Prepared according to the general reaction procedure **IX** using N-(3,4-dimethoxybenzyl)-N-(*p*-tolyl)acetamide (100 mg, 0.334 mmol, 1.0 equiv.) and DIBAL-H (0.40 mL, 0.401 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **9a'** (25 mg, 26% yield) as brown oil (7% ethyl acetate in petroleum-ether, R_f: 0.20); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.01 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 3H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.41 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.42 (q, *J* = 14.1 Hz, 2H), 2.26 (s, 3H), 1.17 (t, *J* = 7.0 Hz, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 149.2, 147.9, 146.7, 132.1, 129.8, 125.5, 118.7, 112.9, 111.2, 109.9, 56.0, 55.9, 54.2, 45.1, 29.8, 20.3, 12.1; **HRMS** (ESI) calculated for $C_{18}H_{23}NO_2$, 308.16265 *m/z* $(M+Na)^+$; Found, 308.16266 *m/z*; **FTIR (cm^{-1}):** 2301, 2250, 2112, 1650, 1530, 1442, 1412, 1250, 1212, 1130, 1024, 845, 780, 710.

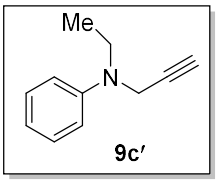


9b

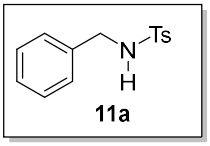
N-(4-chlorobenzyl)-4-methylaniline **(9b)**: Prepared according to the general reaction procedure **IX** using N-(4-chlorobenzyl)-N-(*p*-tolyl)acetamide (100 mg, 0.365 mmol, 1.0 equiv.) and DIBAL-H (0.44 mL, 0.438 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **9b** (65 mg, 77% yield) as yellow thick oil (4% ethyl acetate in petroleum-ether, R_f: 0.20); **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.27 (s, 4H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.51 (d, *J* = 8.3 Hz, 2H), 4.26 (s, 2H), 3.90 (s, 1H), 2.22 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 145.7, 138.4, 132.9, 129.9, 128.8, 128.80, 127.1, 113.1, 48.0, 20.5; **HRMS** (ESI) calculated for $C_{14}H_{14}ClN$, 254.07125 *m/z* $(M+Na)^+$; Found, 254.07123 *m/z*; **FTIR (cm^{-1}):** 3387, 1615, 1518, 1489, 1245, 1090, 1013, 802, 764, 666.



N-(prop-2-yn-1-yl)aniline **(9c)**: Prepared according to the general reaction procedure **IX** using N-phenyl-N-(prop-2-yn-1-yl)acetamide (100 mg, 0.577 mmol, 1.0 equiv.) and DIBAL-H (0.69 mL, 0.692 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **9c** (29 mg, 38% yield) as colourless oil (4% ethyl acetate in petroleum-ether, R_f: 0.20); **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.25-7.20 (m, 2H), 6.79-6.77 (m, 1H), 6.69-6.67 (m, 2H), 3.92 (d, *J* = 2.3 Hz, 2H), 3.85 (s, 1H), 2.20 (t, *J* = 2.3 Hz, 1H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 147.0, 129.4, 118.8, 113.6, 81.1, 71.4, 33.8; **HRMS** (ESI) calculated for C_9H_9N, 154.06327 *m/z* $(M+Na)^+$; Found, 154.06325 *m/z*; **FTIR (cm^{-1}):** 3400, 3284, 1600, 1503, 1439, 1312, 1252, 1095, 748, 690

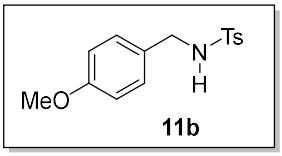


N-ethyl-N-(prop-2-yn-1-yl)aniline **(9c′)**: Prepared according to the general reaction procedure **IX** using N-phenyl-N-(prop-2-yn-1-yl)acetamide (100 mg, 0.577 mmol, 1.0 equiv.) and DIBAL-H (0.69 mL, 0.692 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **9c'** (18 mg, 20% yield) as light brown oil (2% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.27-7.24 (m, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.77 (t, *J* = 7.6 Hz, 1H), 4.02 (d, *J* = 2.3 Hz, 2H), 3.44 (q, *J* = 14.3 Hz, 2H), 2.18 (s, 1H), 1.54 (s, 1H), 1.21 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 148.0, 129.3, 117.8, 114.0, 80.5, 71.7, 45.7, 39.7, 12.6; **HRMS** (ESI) calculated for $C_{11}H_{13}N$, 182.09457 *m/z* $(M+Na)^+$; Found, 182.096455 *m/z*; **FTIR (cm^{-1}):** 3289, 2970, 1597, 1504, 1345, 1240, 1183, 746, 689.



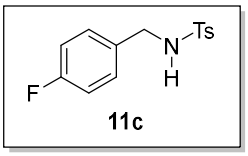
N-benzyl-4-methylbenzenesulfonamide **(11a)**[5a]: Prepared according to the general reaction procedure **IX** using N-benzyl-N-tosylacetamide (100 mg, 0.330 mmol, 1.0 equiv.) and DIBAL-H (0.40 mL, 0.396 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **11a** (80 mg, 93% yield) as white solid (5% ethyl acetate in petroleum-ether, R_f: 0.20); m.p. = 92-94 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.31-7.18 (m, 7H), 4.89 (s, 1H), 4.11 (d, *J* = 6.0 Hz,

2H), 2.43 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 143.6, 136.9, 136.4, 129.8, 128.7, 127.9, 127.3, 47.3, 21.6; **HRMS** (ESI) calculated for $C_{14}H_{15}NO_2S$, 284.07212 *m/z* $(M+Na)^+$; Found, 284.07210 *m/z*; **FTIR (cm^{-1}):** 3267, 1597, 1494, 1454, 1420, 1320, 1157, 1192, 1027, 872, 739, 697.



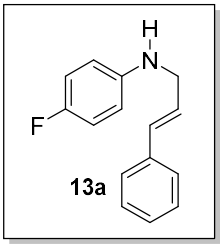
11b

N-(4-methoxybenzyl)-4-methylbenzenesulfonamide (**11b)**: Prepared according to the general reaction procedure **IX** using N-(4-methoxybenzyl)-N-tosylacetamide (100 mg, 0.300 mmol, 1.0 equiv.) and DIBAL-H (0.36 mL, 0.360 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **11b** (80 mg, 92% yield) as white solid (8% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 102-104 °C; **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 7.1 Hz, 2H), 4.63-4.55 (m, 1H), 4.05 (d, *J* = 6.2 Hz, 2H), 3.77 (s, 3H), 2.44 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 159.5, 143.6, 137.1, 129.9, 129.4, 128.4, 127.3, 114.2, 55.4, 46.9, 21.7; **HRMS** (ESI) calculated for $C_{15}H_{17}NO_3S$, 314.08268 *m/z* $(M+Na)^+$; Found, 314.08270 *m/z*; **FTIR (cm^{-1}):** 3248, 1612, 1514, 1427, 1320, 1250, 1156, 1059, 1029, 914, 815, 751, 662.

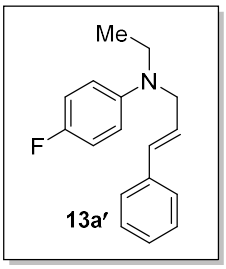


11c

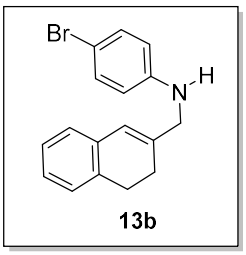
N-(4-fluorobenzyl)-4-methylbenzenesulfonamide **(11c)**[5a]: Prepared according to the general reaction procedure **IX** using N-(4-fluorobenzyl)-N-tosylacetamide (100 mg, 0.311 mmol, 1.0 equiv.) and DIBAL-H (0.37 mL, 0.373 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **11c** (75 mg, 86% yield) as white solid (5% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 79-81 °C; **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18-7.15 (m, 2H), 6.95 (t, *J* = 8.6 Hz, 2H), 4.75-4.74 (m, 1H), 4.09 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 162.5 ($J_{C\text{-}F}$ = 245.6 Hz), 143.8, 137.0, 132.2, 129.9, 129.8, 129.7, 127.3, 115.7 ($J_{C\text{-}F}$ = 21.5 Hz), 46.7, 21.7; **HRMS** (ESI) calculated for $C_{14}H_{14}FNO_2S$, 302.06270 *m/z* $(M+Na)^+$; Found, 302.06271 *m/z*; **FTIR (cm^{-1}):** 3243, 1599, 1506, 1438, 1314, 1219, 1148, 1063, 865, 830, 809, 716, 662.



N-cinnamyl-4-fluoroaniline **(13a)**: Prepared according to the general reaction procedure **IX** using N-cinnamyl-N-(4-fluorophenyl)acetamide (100 mg, 0.371 mmol, 1.0 equiv.) and DIBAL-H (0.44 mL, 0.445 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **13a** (42 mg, 50% yield) as white solid (5% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 96-98 °C; **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23-7.21 (m, 1H), 6.88 (t, *J* = 8.7 Hz, 2H), 6.61-6.57 (m, 3H), 6.32-6.27 (m, 1H), 3.88 (dd, *J* = 5.8, 1.4 Hz, 2H), 3.72 (s, 1H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 156.1 (J_{C-F} = 234.0 Hz), 144.5, 136.9, 131.8, 128.7, 127.7, 127.0, 126.4, 115.9, 115.7, 114.0 (J_{C-F} = 7.2 Hz), 46.9; **HRMS** (ESI) calculated for $C_{15}H_{14}FN$, 250.10080 *m/z* $(M+Na)^+$; Found, 250.10082 *m/z*; **FTIR (cm^{-1}):** 3350, 1601, 1560, 1485, 1360, 1230, 1149, 1064, 885, 838, 710, 650.

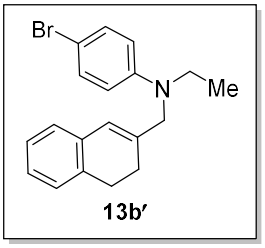


N-cinnamyl-N-ethyl-4-fluoroaniline **(13a′)**: Prepared according to the general reaction procedure **IX** using N-cinnamyl-N-(4-fluorophenyl)acetamide (100 mg, 0.371 mmol, 1.0 equiv.) and DIBAL-H (0.44 mL, 0.445 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **13a'** (23 mg, 24% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 104-106 °C; **^{1}H-NMR (**$CDCl_3$, 600 MHz**):** δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 1H), 6.93 (t, *J* = 8.9 Hz, 2H), 6.69-6.67 (m, 2H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.25-6.21 (m, 1H), 4.01 (dd, *J* = 5.3, 1.6 Hz, 2H), 3.39 (q, *J* = 14.2 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 3H); **^{13}C-NMR (**$CDCl_3$, 150 MHz**):** δ 155.4 (J_{C-F} = 233.0 Hz), 145.2, 137.0, 131.2, 128.7, 127.5, 126.5, 126.4, 115.7, 115.6, 113.9 (J_{C-F} = 7.1 Hz), 53.0, 45.4, 12.3; **HRMS** (ESI) calculated for $C_{17}H_{18}FN$, 278.13210 *m/z* $(M+Na)^+$; Found, 278.13211 *m/z*; **FTIR (cm^{-1}):** 2350, 2110, 1635, 1550, 1432, 1245, 1112, 1030, 850, 760, 705.



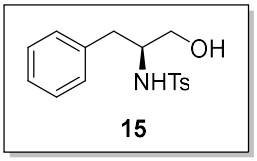
13b

4-bromo-N-((3,4-dihydronaphthalen-2-yl)methyl)aniline **(13b)**: Prepared according to the general reaction procedure **IX** using N-(4-bromophenyl)-N-((3,4-dihydronaphtha len-2-yl)methyl)acetamide (100 mg, 0.281 mmol, 1.0 equiv.) and DIBAL-H (0.34 mL, 0.337 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **13b** (60 mg, 68% yield) as pale yellow solid (5% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 135-137 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.25-7.21 (m, 2H), 7.13-7.09 (m, 3H), 6.99-6.97 (m, 1H), 6.54-6.50 (m, 2H), 6.40 (s, 1H), 4.13 (s, 1H), 3.84 (s, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.28 (t, *J* = 8.2 Hz, 2H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 147.2, 138.1, 134.8, 134.1, 132.0, 127.4, 126.9, 126.7, 126.1, 123.4, 114.7, 109.3, 49.6, 28.0, 25.5; **HRMS** (ESI) calculated for $C_{17}H_{16}{}^{81}BrN$, 338.03434 *m/z* $(M+Na)^+$; Found, 338.03436 *m/z*; **FTIR (cm^{-1}):** 3344, 1610, 1585, 1460, 1380, 1215, 1141, 1063, 885, 715, 660.



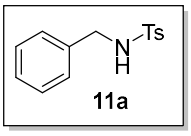
13b′

4-bromo-N-((3,4-dihydronaphthalen-2-yl)methyl)-N-ethylaniline **(13b′)**: Prepared according to the general reaction procedure **IX** using N-(4-bromophenyl)-N-((3,4-dihydronaphtha len-2-yl)methyl)acetamide (100 mg, 0.281 mmol, 1.0 equiv.) and DIBAL-H (0.34 mL, 0.337 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **13b'** (12 mg, 13% yield) as colourless oil (3% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.28-7.27 (m, 2H), 7.12-7.11 (m, 3H), 6.96 (d, *J* = 6.0 Hz, 1H), 6.58 (d, *J* = 9.0 Hz, 2H), 6.26 (s, 1H), 3.94 (s, 2H), 3.43 (q, *J* = 14.1 Hz, 2H), 2.86 (t, *J* = 8.1 Hz, 2H), 2.24 (t, *J* = 7.8 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 3H); **HRMS** (ESI) calculated for $C_{19}H_{20}{}^{81}BrN$, 366.06564 *m/z* $(M+Na)^+$; Found, 366.06562 *m/z*; **FTIR (cm^{-1}):** 2330, 2209, 2111, 1610, 1540, 1431, 1110, 1010, 840, 725.



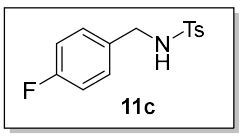
15

(S)-N-(1-hydroxy-3-phenylpropan-2-yl)-4-methylbenzenesulfonamide **(15)**: Prepared according to the general reaction procedure **IX** using methyl N-acetyl-N-tosyl-L-phenylalaninate (100 mg, 0.266 mmol, 1.0 equiv.) and DIBAL-H (0.93 mL, 0.931 mmol, 3.5 equiv.) at 0 °C for <5 min. to obtain **15** (60 mg, 82% yield) as colourless-oil (30% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.21-7.17 (m, 5H), 6.98-6.96 (m, 2H), 4.88-4.86 (m, 1H), 3.63 (dd, *J* = 11.1, 3.8 Hz, 1H), 3.52 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.47-3.42 (m, 1H), 2.78 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.68 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.41 (s, 3H), 2.17 (s, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 143.4, 137.1, 137.0, 129.8, 129.3, 128.7, 127.1, 126.7, 64.1, 56.9, 37.8, 21.6; **HRMS** (ESI) calculated for $C_{16}H_{19}NO_3S$, 328.09833 *m/z* $(M+Na)^+$; Found, 328.09835 *m/z*; **FTIR (cm^{-1}):** 3256, 3025, 1680, 1615, 1490, 1436, 1262, 1176, 1015, 810, 755.



11a

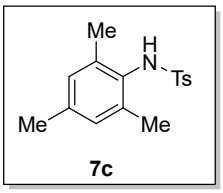
N-benzyl-4-methylbenzenesulfonamide **(11a)**[5a]: Prepared according to the general reaction procedure **IX** using N-benzyl-4-chloro-N-tosylbenzamide (100 mg, 0.250 mmol, 1.0 equiv.) and DIBAL-H (0.30 mL, 0.300 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **11a** (56 mg, 86% yield) as white solid (5% ethyl acetate in petroleum-ether, R_f: 0.20); m.p. = 92-94 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.28-7.26 (m, 2H), 7.20-7.18 (m, 2H), 4.60 (s, 1H), 4.12 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H).



11c

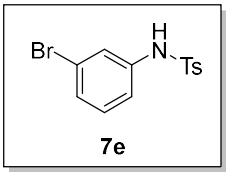
N-(4-fluorobenzyl)-4-methylbenzenesulfonamide **(11c)**[5a]: Prepared according to the general reaction procedure **IX** using N-(4-fluorobenzyl)-4-methoxy-N-tosylbenzamide (100 mg, 0.242 mmol, 1.0 equiv.) and DIBAL-H (0.30 mL, 0.290 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **11c** (47 mg, 70% yield) as white solid (5% ethyl acetate in petroleum-ether, R_f: 0.25);

m.p. = 79-81 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19-7.15 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 4.64 (m, 1H), 4.09 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H).



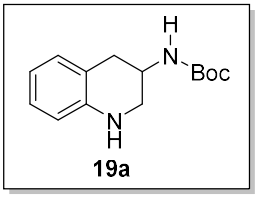
7c

N-mesityl-4-methylbenzenesulfonamide **(7c)**: Prepared according to the general reaction procedure **IX** using N-mesityl-N-tosylbenzamide (100 mg, 0.254 mmol, 1.0 equiv.) and DIBAL-H (0.30 mL, 0.305 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7c** (62 mg, 84% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 159-161 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.82 (s, 2H), 5.85 (s, 1H), 2.42 (s, 3H), 2.24 (s, 3H), 1.98 (s, 6H).



7e

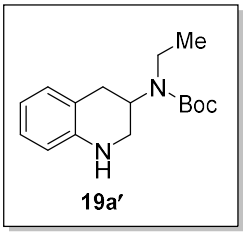
N-(3-bromophenyl)-4-methylbenzenesulfonamide **(7e)**: Prepared according to the general reaction procedure **IX** using N-(3-bromophenyl)-N-tosylbenzamide (100 mg, 0.274 mmol, 1.0 equiv.) and DIBAL-H (0.32 mL, 0.328 mmol, 1.2 equiv.) at 0 °C for <5 min. to obtain **7e** (72 mg, 80% yield) as white solid (3% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 117-119 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.25-7.21 (m, 4H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.02-6.99 (m, 1H), 6.76 (s, 1H), 2.38 (s, 3H).



19a

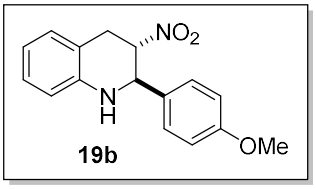
tert-butyl (1,2,3,4-tetrahydroquinolin-3-yl)carbamate **(19a)**[6b]: Prepared according to the general reaction procedure **VII** using tert-butyl acetyl(1,2,3,4-tetrahydroquinolin-3-yl) carbamate (100 mg, 0.344 mmol, 1.0 equiv.) and DIBAL-H (0.41 mL, 0.413 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **19a** (39 mg, 45% yield) as colourless liquid (6% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.02-6.95 (m, 2H), 6.66 (t, *J* =

5.9 Hz, 1H), 6.51 (d, *J* = 6.4 Hz, 1H), 5.00-4.98 (m, 1H), 4.16 (s, 1H), 4.01 (s, 1H), 3.37 (d, *J* = 8.9 Hz, 1H), 3.20 (d, *J* = 7.9 Hz, 1H), 3.04 (dd, *J* = 13.1, 3.0 Hz, 1H), 2.71 (d, *J* = 13.0 Hz, 1H), 1.42 (s, 9H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 155.5, 143.8, 130.6, 127.3, 118.5, 117.9, 114.2, 79.4, 45.9, 43.1, 33.2, 28.5; **HRMS** (ESI) calculated for $C_{14}H_{20}N_2O_2$, 271.14225 *m/z* $(M+Na)^+$; Found, 271.14228 *m/z*; **FTIR (cm^{-1}):** 3338, 1780, 1610, 1575, 1465, 1210, 1110, 850, 720.



19a′

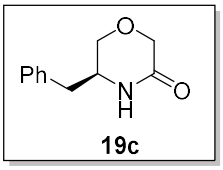
tert-butyl ethyl(1,2,3,4-tetrahydroquinolin-3-yl)carbamate **(19a′)**: Prepared according to the general reaction procedure **VII** using tert-butyl acetyl(1,2,3,4-tetrahydroquinolin-3-yl) carbamate (100 mg, 0.344 mmol, 1.0 equiv.) and DIBAL-H (0.41 mL, 0.413 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **19a'** (38 mg, 40% yield) as colourless liquid (3% ethyl acetate in petroleum-ether, R_f: 0.25); **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.09 (t, *J* = 6.2 Hz, 1H), 6.96 (d, *J* = 5.8 Hz, 1H), 6.64-6.60 (m, 2H), 4.85-4.83 (m, 1H), 4.16 (s, 1H), 3.43-3.41 (m, 2H), 3.28-3.24 (m, 1H), 3.12 (d, *J* = 8.0 Hz, 1H), 3.04 (dd, *J* = 12.4, 2.1 Hz, 1H), 2.69 (d, *J* = 12.9 Hz, 1H), 1.42 (s, 9H), 1.12 (t, *J* = 5.6 Hz, 3H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 155.5, 144.3, 130.6, 127.6, 119.2, 116.5, 110.9, 79.5, 52.3, 45.3, 43.3, 34.1, 28.5, 10.8; **HRMS** (ESI) calculated for $C_{16}H_{24}N_2O_2$, 299.17355 *m/z* $(M+Na)^+$; Found, 299.17352 *m/z*; **FTIR (cm^{-1}):** 2385, 2215, 2110, 1765, 1601, 1565, 1460, 1225, 1115, 835, 701.



19b

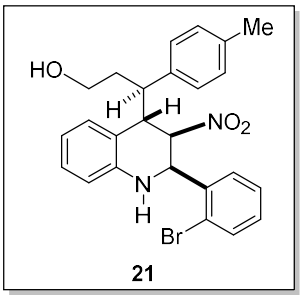
2-(4-methoxyphenyl)-3-nitro-1,2,3,4-tetrahydroquinoline **(±)-19b**: Prepared according to the general reaction procedure **VII** using 1-(2-(4-methoxyphenyl)-3-nitro-3,4-dihydroquino lin-1(2*H*)-yl)ethan-1-one (100 mg, 0.306 mmol, 1.0 equiv.) and DIBAL-H (0.36 mL, 0.367 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **(±)-19b** (65 mg, 75% yield) as yellow solid (8% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 128-130 °C; dr ratio = 10:1; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.31 (d, *J* = 6.8 Hz, 2H), 7.07 (t, *J* = 5.1 Hz, 2H), 6.89 (d, *J* = 6.9 Hz, 2H), 6.74 (t, *J* = 6.0 Hz, 1H), 6.59 (d, *J* = 6.3 Hz, 1H), 4.91-4.86 (m, 1H), 4.77 (d, *J* = 6.6 Hz,

1H), 4.08 (s, 1H), 3.80 (s, 3H), 3.60-3.54 (m, 1H), 3.27 (dd, *J* = 12.7, 4.0 Hz, 1H); **^{3}C-NMR (**$CDCl_3$, 100 MHz**):** δ 160.2, 142.9, 130.3, 129.5, 128.6, 128.1, 118.6, 118.5, 116.7, 114.5, 114.2, 85.7, 58.7, 55.4, 31.8; **HRMS** (ESI) calculated for $C_{16}H_{16}N_2O_3$, 307.10586 *m/z* $(M+Na)^+$; Found, 307.10584 *m/z*; **FTIR (cm^{-1}):** 3410, 3381, 1634, 1606, 748, 603, 588.



19c

(S)-5-benzylmorpholin-3-one **(19c)**[8a]: Prepared according to the general reaction procedure **VII** using (S)-4-acetyl-5-benzylmorpholin-3-on e (100 mg, 0.429 mmol, 1.0 equiv.) and DIBAL-H (0.51 mL, 0.515 mmol, 1.2 equiv.) at -78 °C for <5 min. to obtain **19c** (71 mg, 86% yield) as white solid (8% methanol in DCM, R_f: 0.25); m.p. = 116-118 °C; **HPLC analysis**: *ee* > 99% [Daicel CHIRALPAK IB-3 column, 20% *i*-PrOH/n-Hexane, 1.0 ml/min, 254 nm, Major: 7.65 min.]; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.34-7.24 (m, 3H), 7.18-7.16 (m, 2H), 6.11 (s, 1H), 4.16 (q, *J* = 16.7 Hz, 2H), 3.90 (dd, *J* = 11.7, 3.7 Hz, 1H), 3.78-3.72 (m, 1H), 3.55 (dd, *J* = 11.7, 6.6 Hz, 1H), 2.88 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.70 (dd, *J* = 13.5, 8.8 Hz, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 168.9, 135.9, 129.3, 129.2, 127.4, 68.0, 67.8, 53.0, 39.4; **HRMS** (ESI) calculated for $C_{11}H_{13}NO_2$, 214.08440 *m/z* $(M+Na)^+$; Found, 214.08442 *m/z*; **FTIR (cm^{-1}):** 3385, 1610, 1559, 1430, 1314, 1150, 1063, 866, 716, 650.



21

3-(2-(2-bromophenyl)-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(*p*-tolyl)propan-1-ol **(±)-21**: Prepared according to the general reaction procedure **VII** using methyl 3-(1-acetyl-2-(2-bromophenyl)-3-nitro-1,2,3,4-tetrahydroquinolin-4-yl)-3-(*p*-tolyl)propanoate (100 mg, 0.181 mmol, 1.0 equiv.) and DIBAL-H (0.63 mL, 0.633 mmol, 3.5 equiv.) at -78 °C for <5 min. to obtain **(±)-21** (63 mg, 72% yield) as white solid (20% ethyl acetate in petroleum-ether, R_f: 0.25); m.p. = 154-156 °C; **^{1}H-NMR (**$CDCl_3$, 400 MHz**):** δ 7.50-7.46 (m, 2H), 7.29-7.27 (m, 2H), 7.20-7.12 (m, 6H), 6.80-6.76 (m, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 5.23 (d, *J* = 4.3 Hz, 1H), 5.08 (dd, *J* = 4.3, 1.7 Hz, 1H), 4.12 (s, 1H), 3.58 (dd, *J* = 10.7, 1.4 Hz, 1H), 3.43-3.37 (m, 1H),

3.26-3.20 (m, 1H), 2.93 (td, *J* = 11.2, 3.7 Hz, 1H), 2.35 (s, 3H), 2.11-2.03 (m, 1H), 1.81-1.73 (m, 1H); **^{13}C-NMR (**$CDCl_3$, 100 MHz**):** δ 142.4, 137.8, 137.3, 136.8, 133.1, 130.2, 130.0, 129.1, 128.4, 128.1, 123.0, 117.6, 117.1, 114.1, 82.1, 60.8, 52.8, 47.6, 46.6, 37.7, 21.2; **HRMS** (ESI) calculated for $C_{25}H_{25}{}^{81}BrN_2O_3$, 482.10281 *m/z* $(M+Na)^+$; Found, 482.10283 *m/z*; **FTIR (cm^{-1}):** 3298, 1674, 1605, 1498, 1435, 1261, 1175, 1024, 817, 749.

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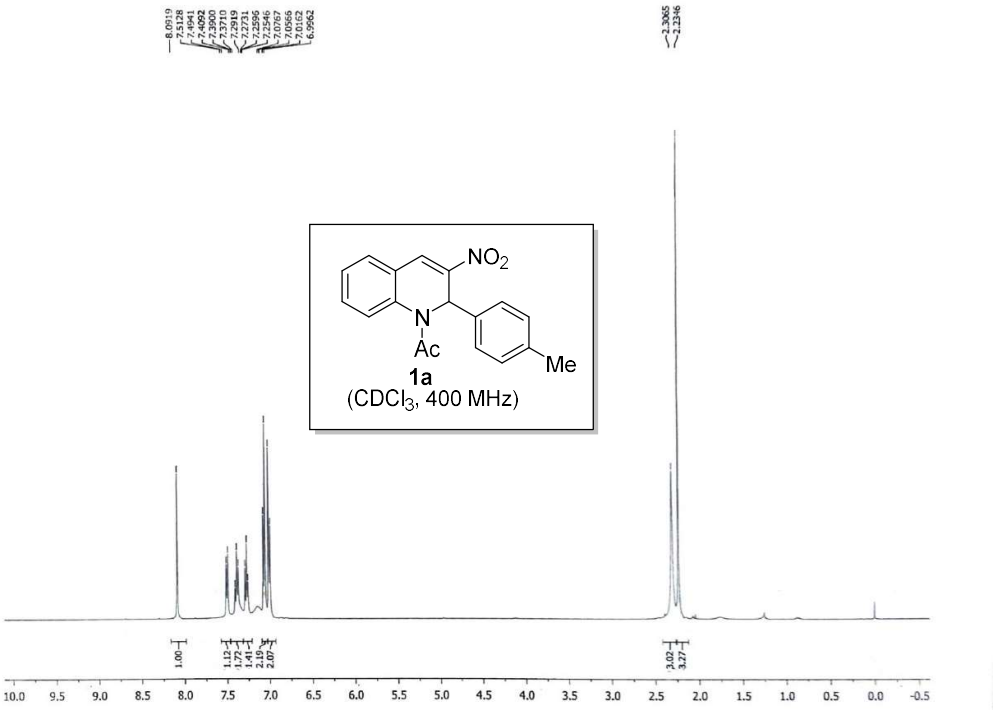
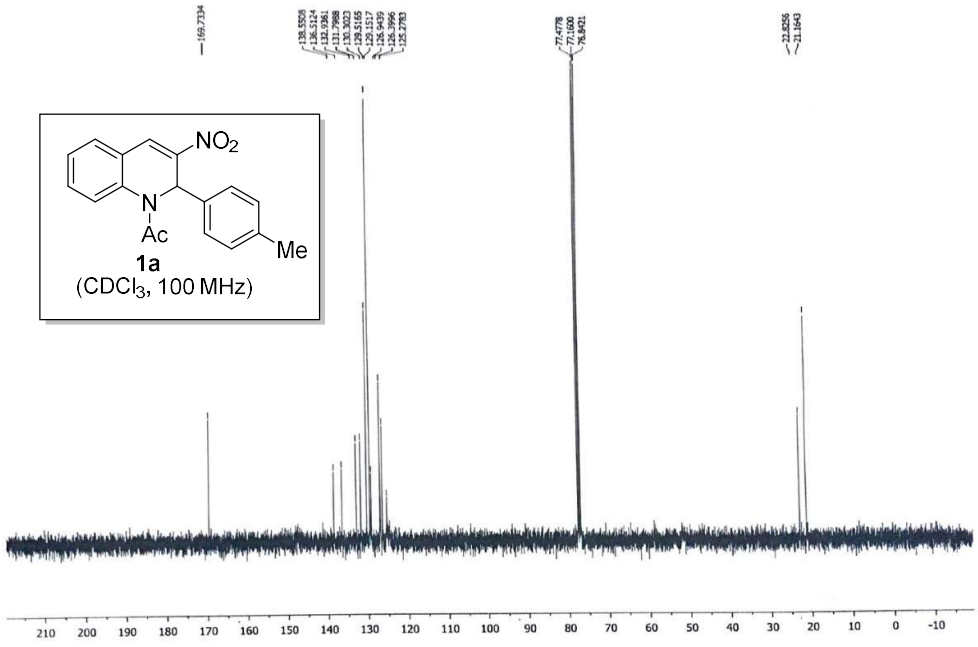
NMR Spectra of tertiary amides (Starting Materials)

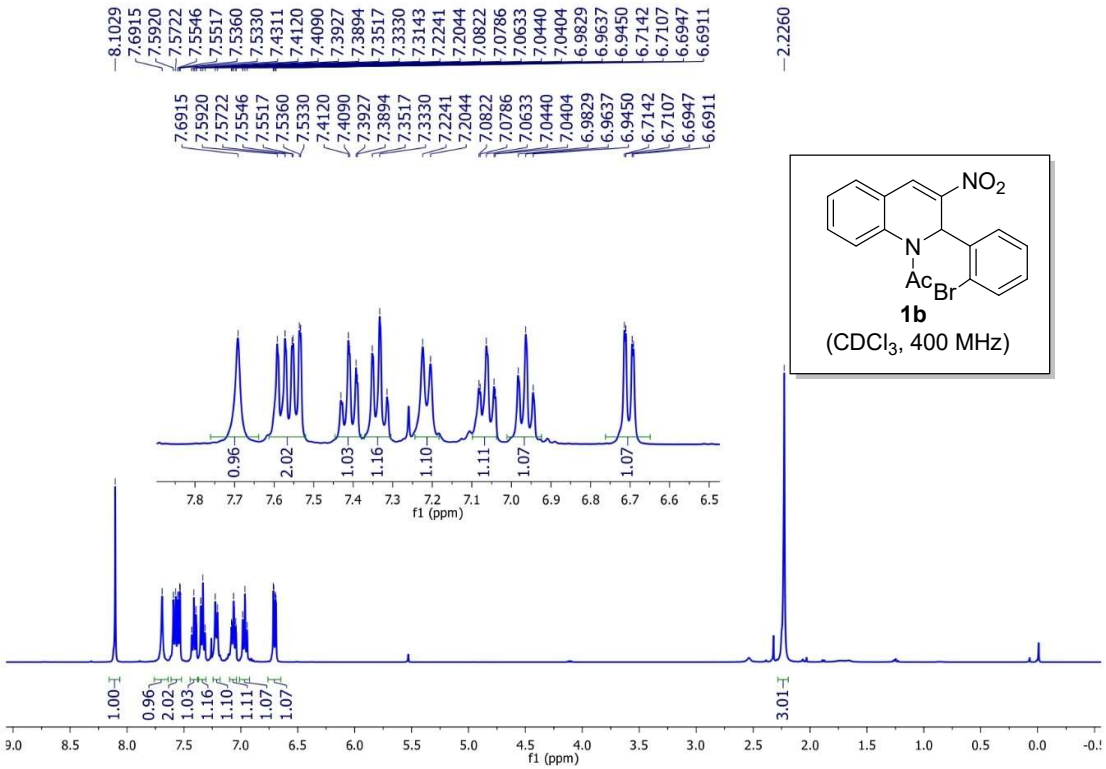
^{1}H NMR of 1a ($CDCl_3$, 400 MHz)



^{13}C NMR of 1a ($CDCl_3$, 100 MHz)



^{1}H NMR of 1b ($CDCl_3$, 400 MHz)



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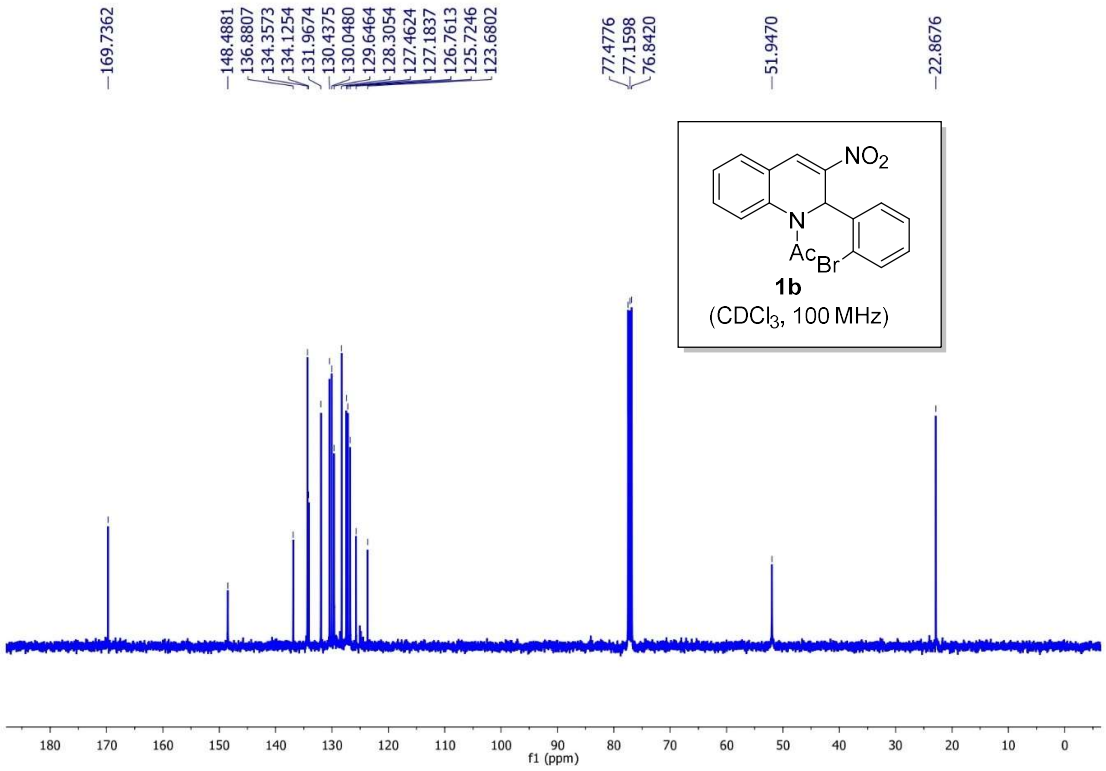
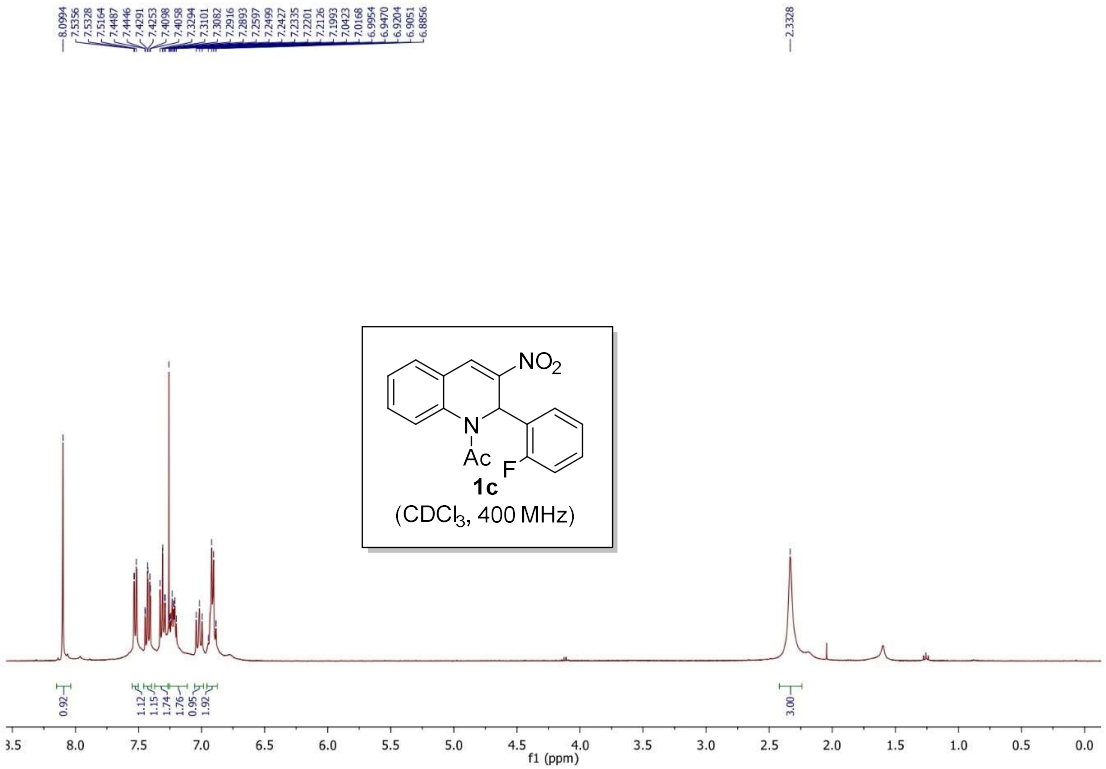


^{1}H NMR of 1c ($CDCl_3$, 400 MHz)



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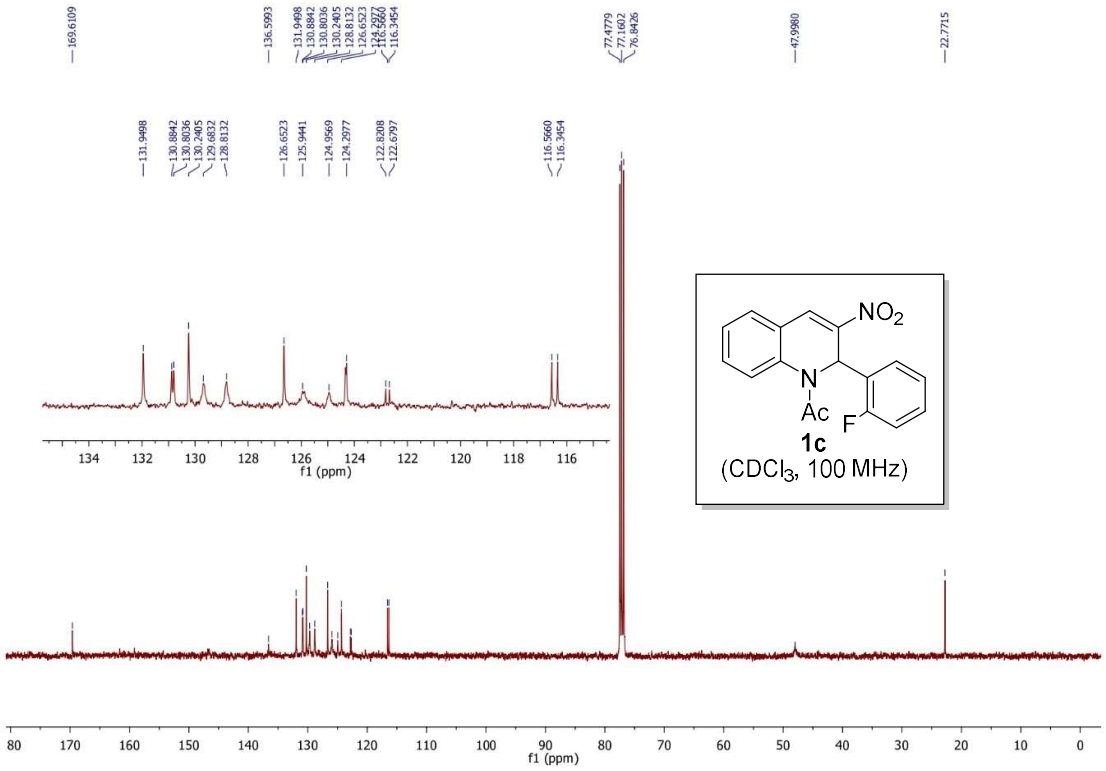

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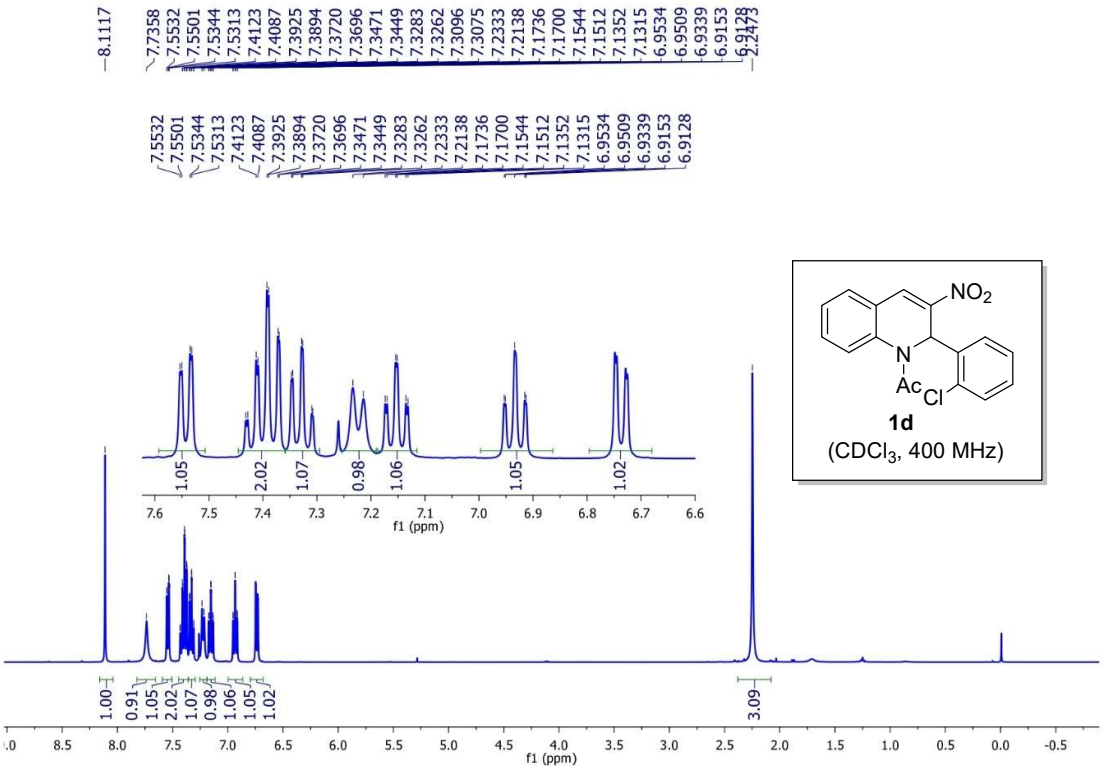

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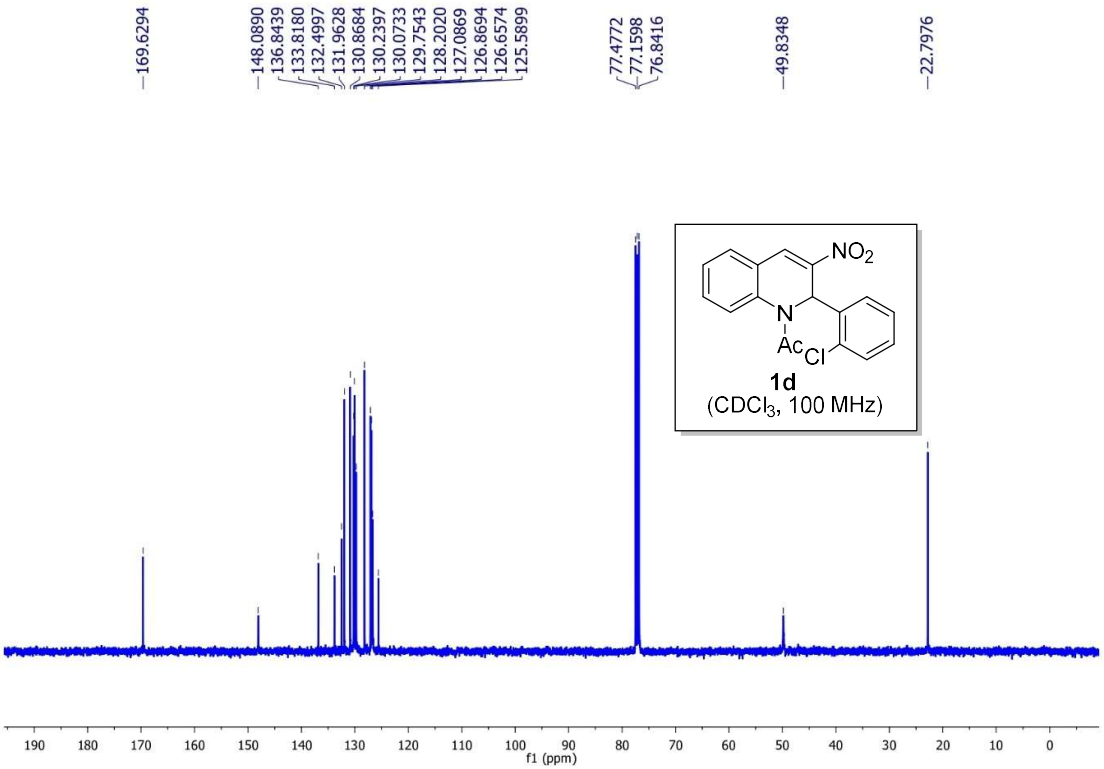

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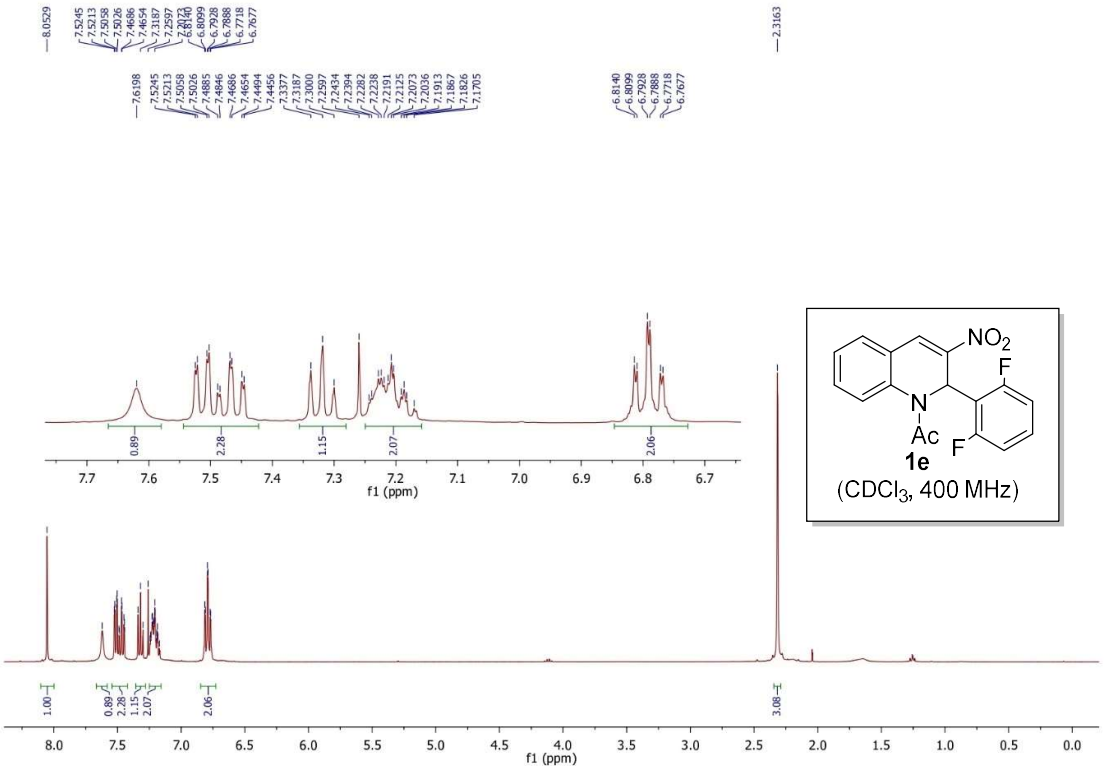

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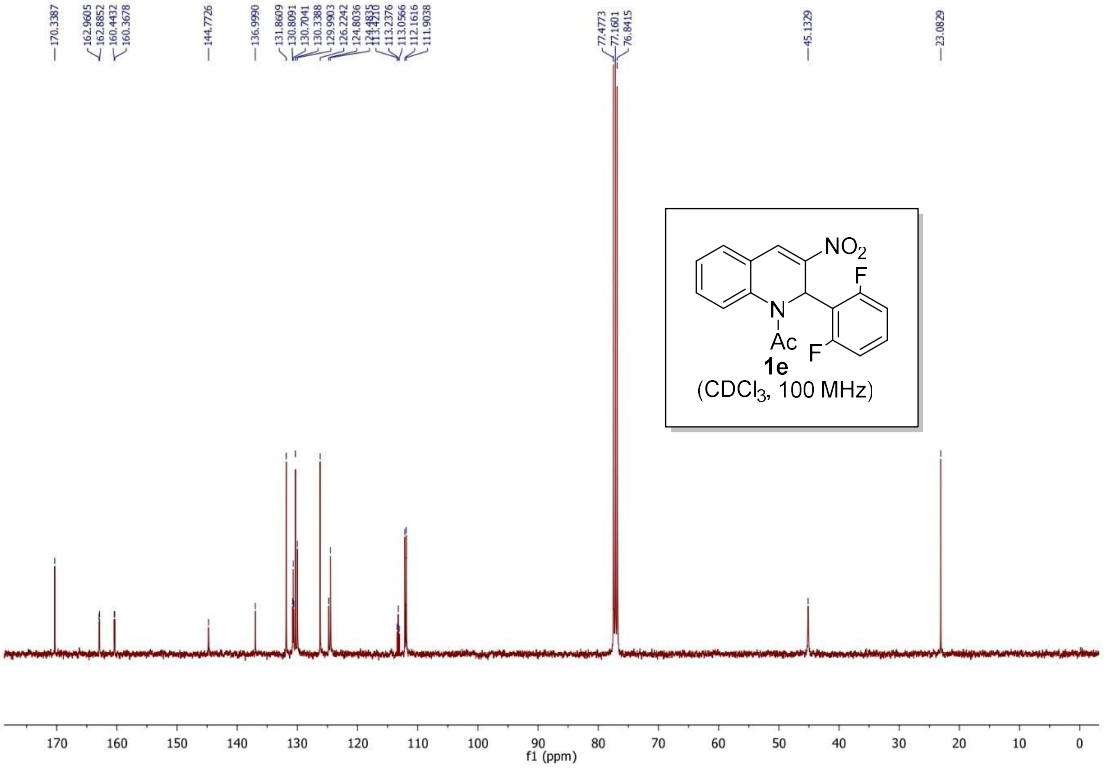
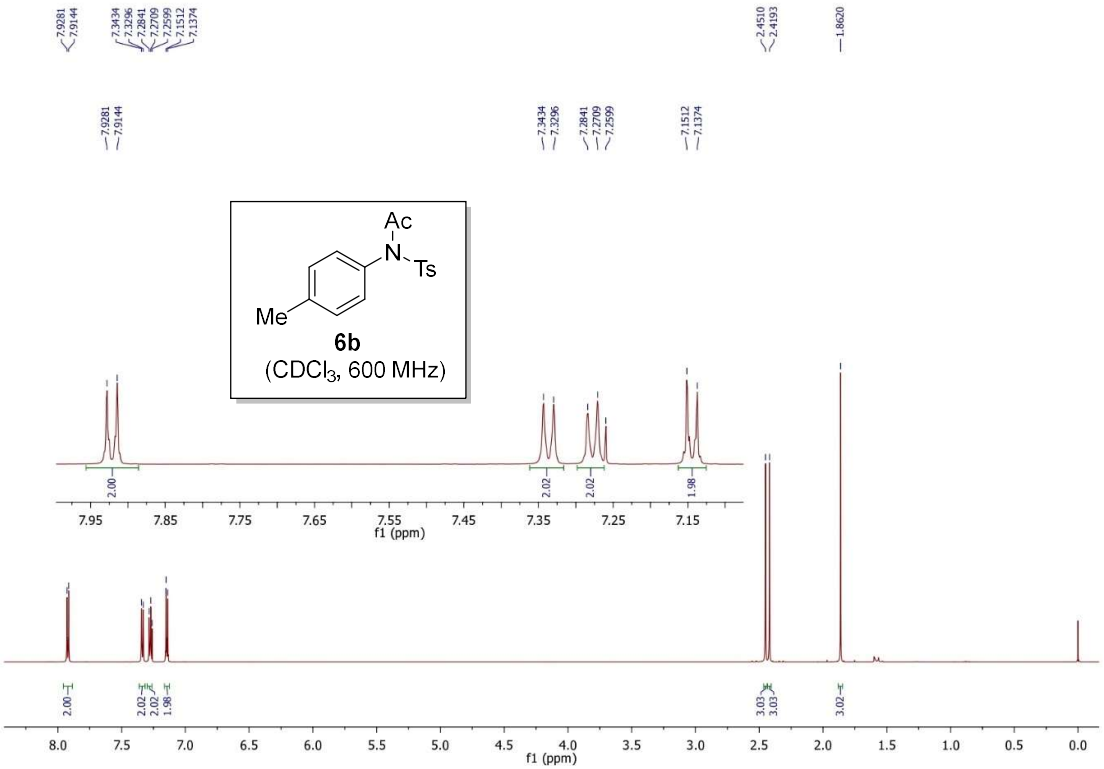
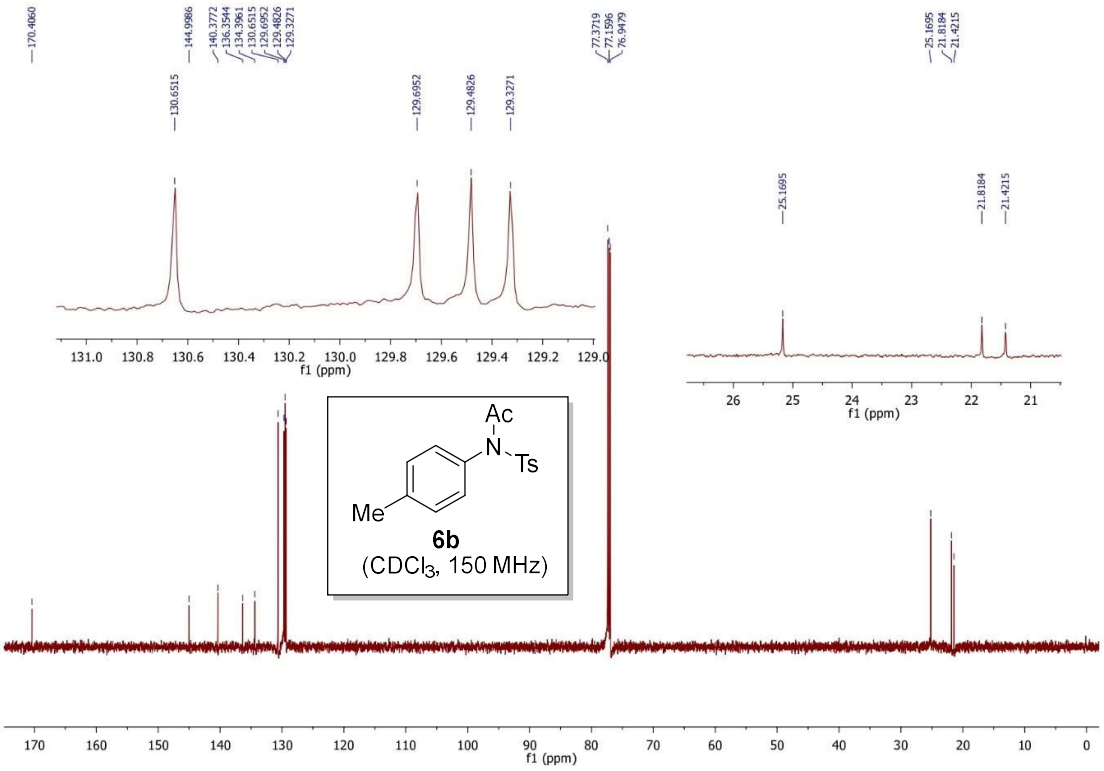


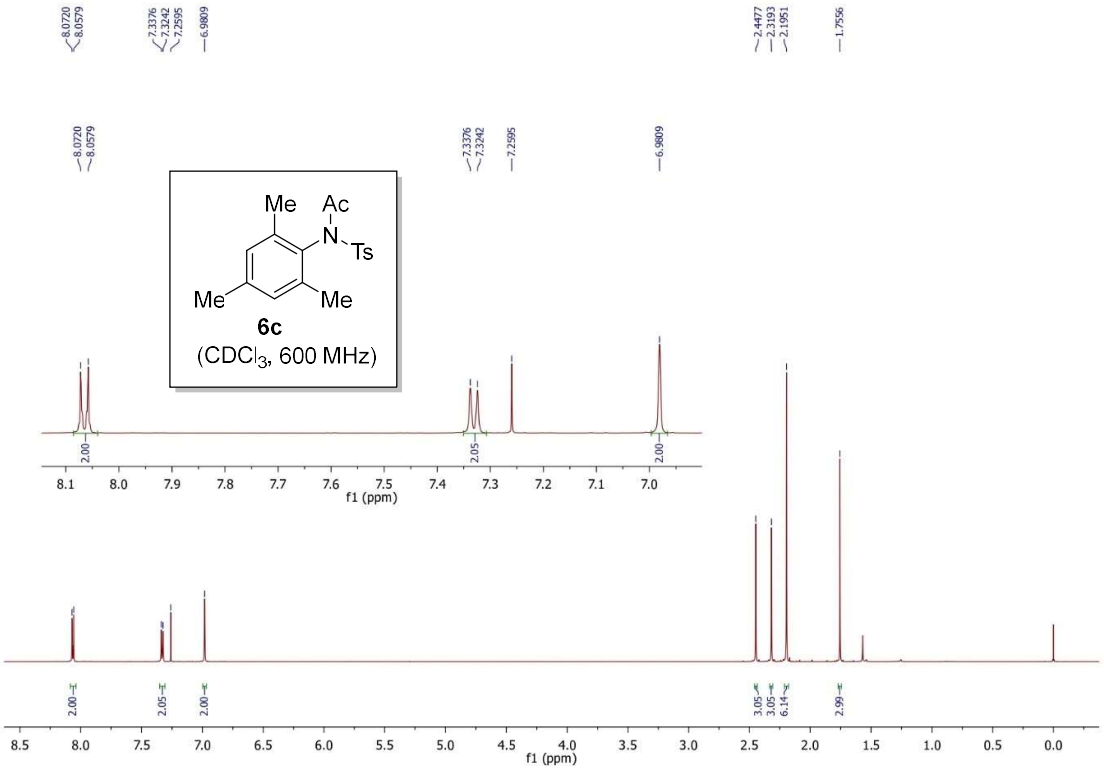
^{1}H NMR of 6b ($CDCl_3$, 600 MHz)



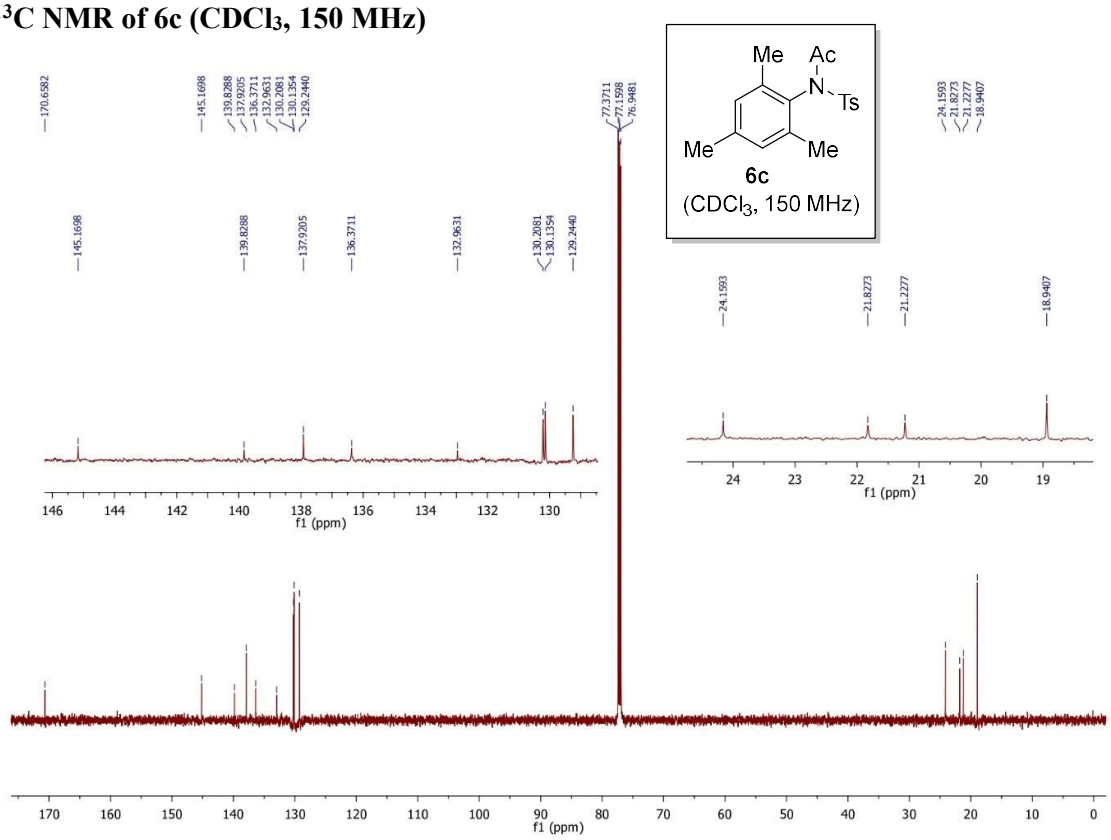
^{13}C NMR of 6b ($CDCl_3$, 150 MHz)



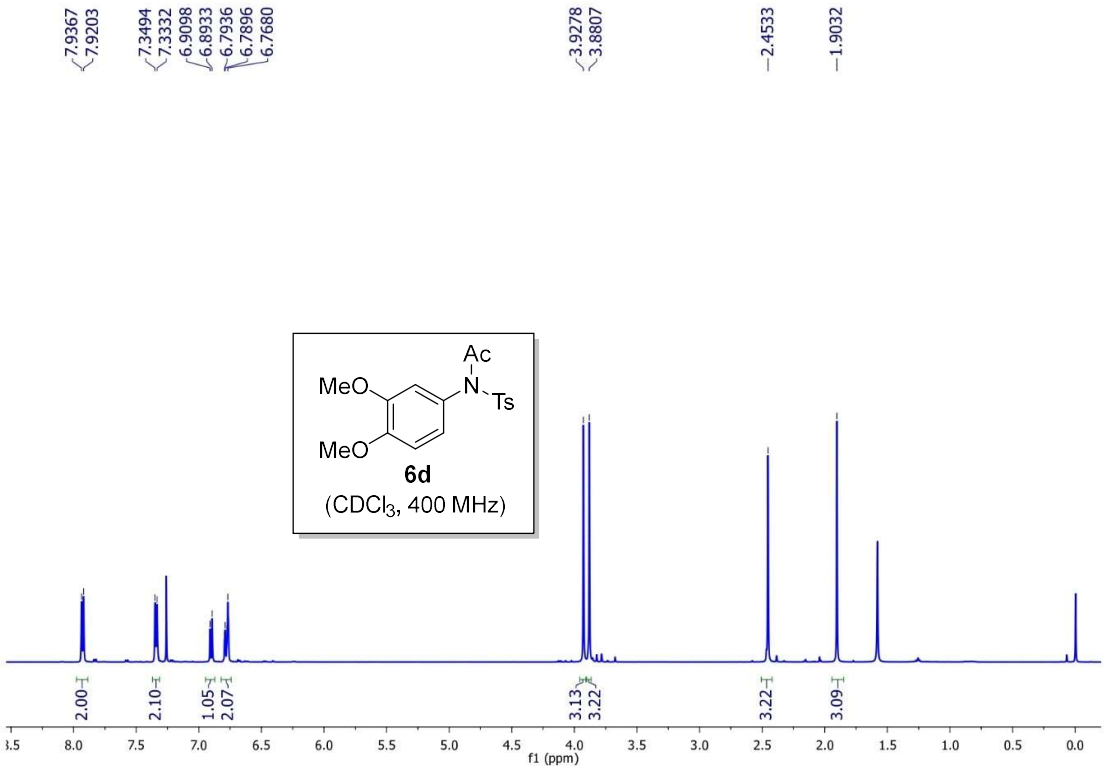
^{1}H NMR of 6c ($CDCl_3$, 600 MHz)



^{13}C NMR of 6c ($CDCl_3$, 150 MHz)



^{1}H NMR of 6d ($CDCl_3$, 400 MHz)



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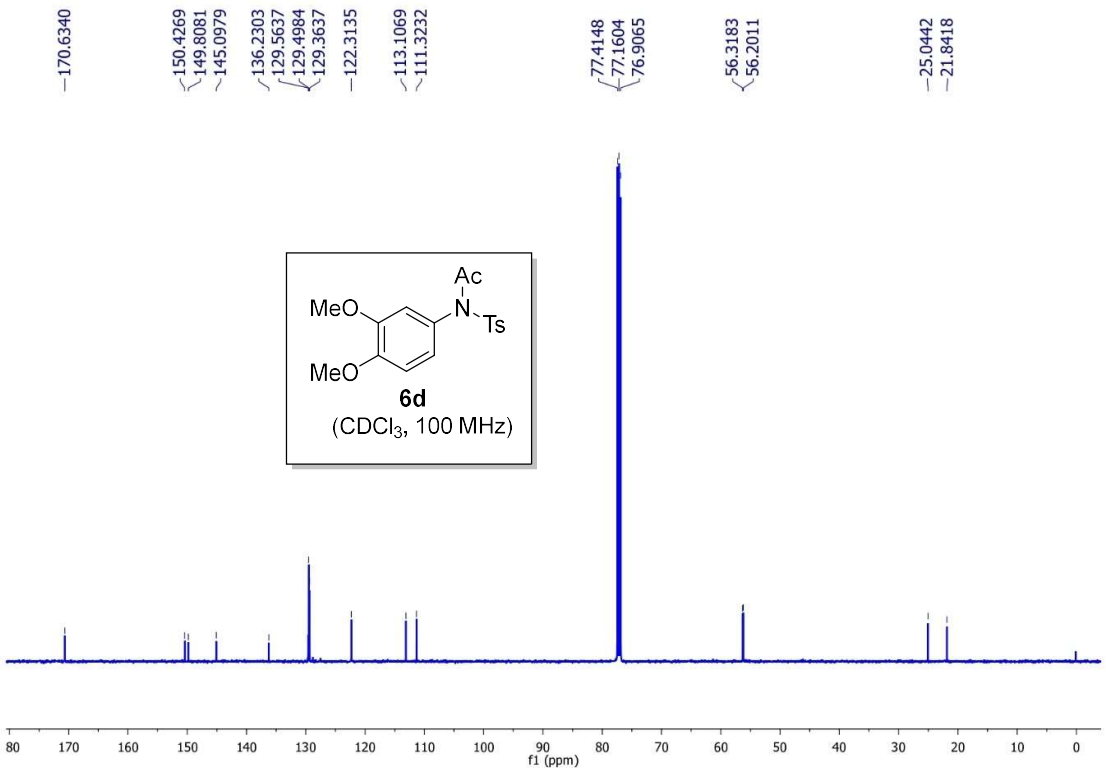

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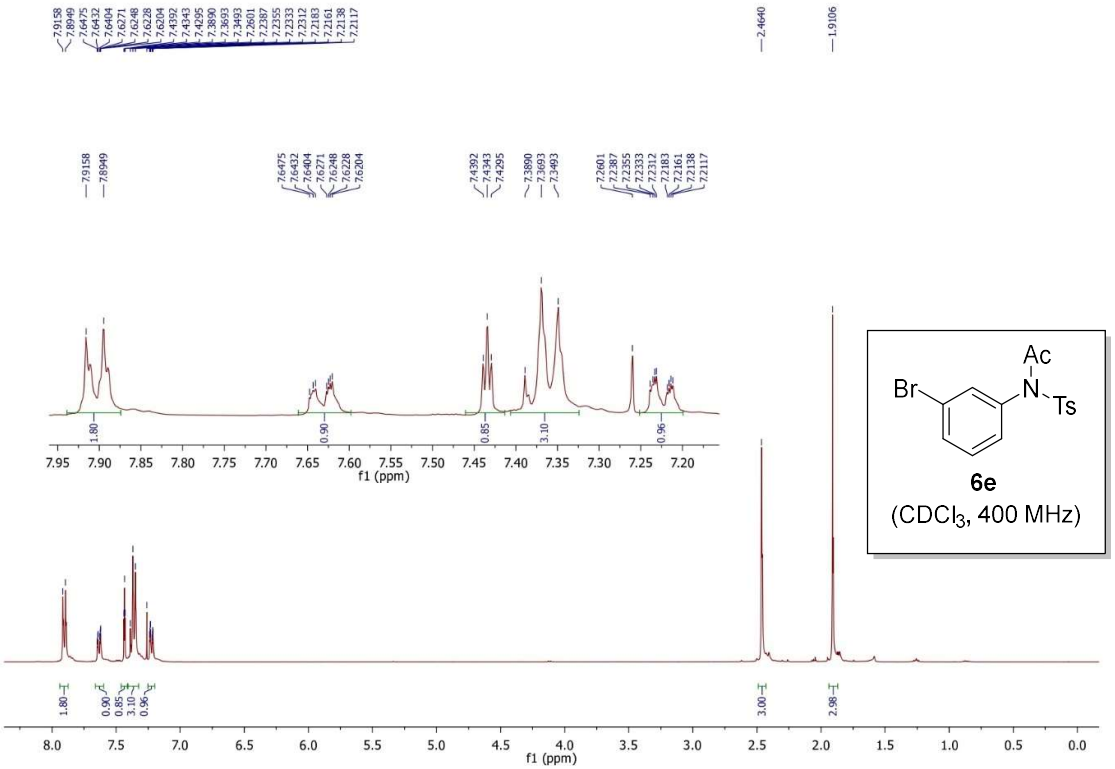

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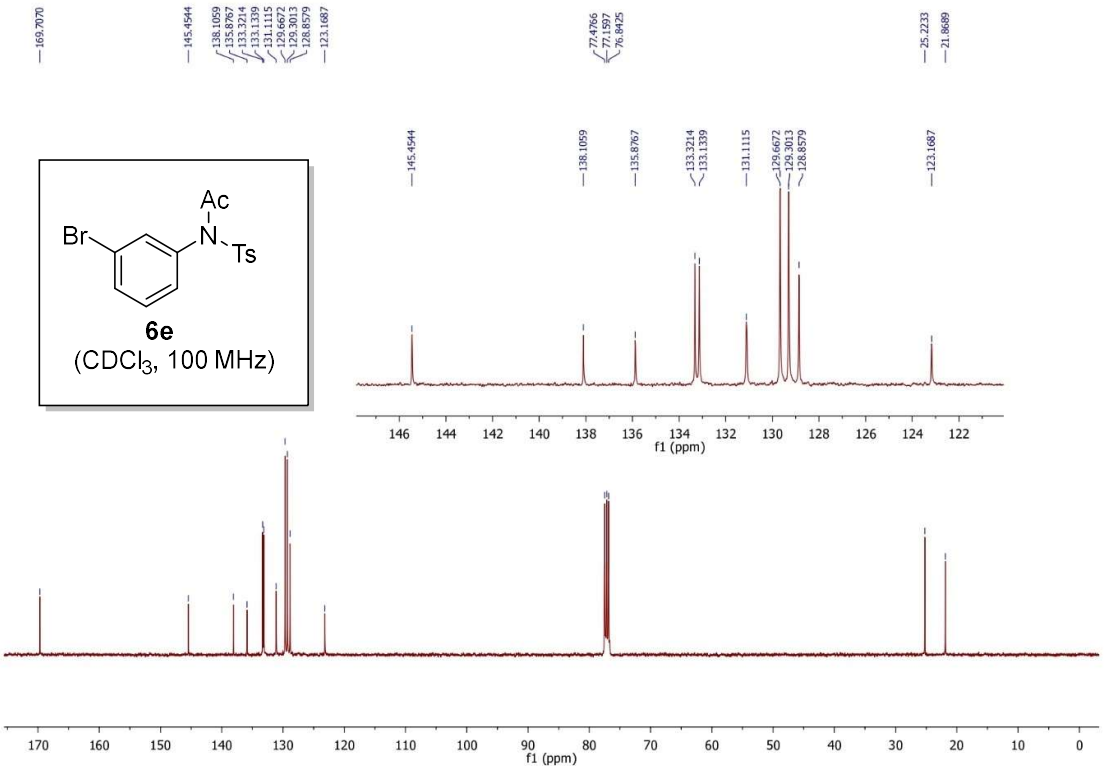
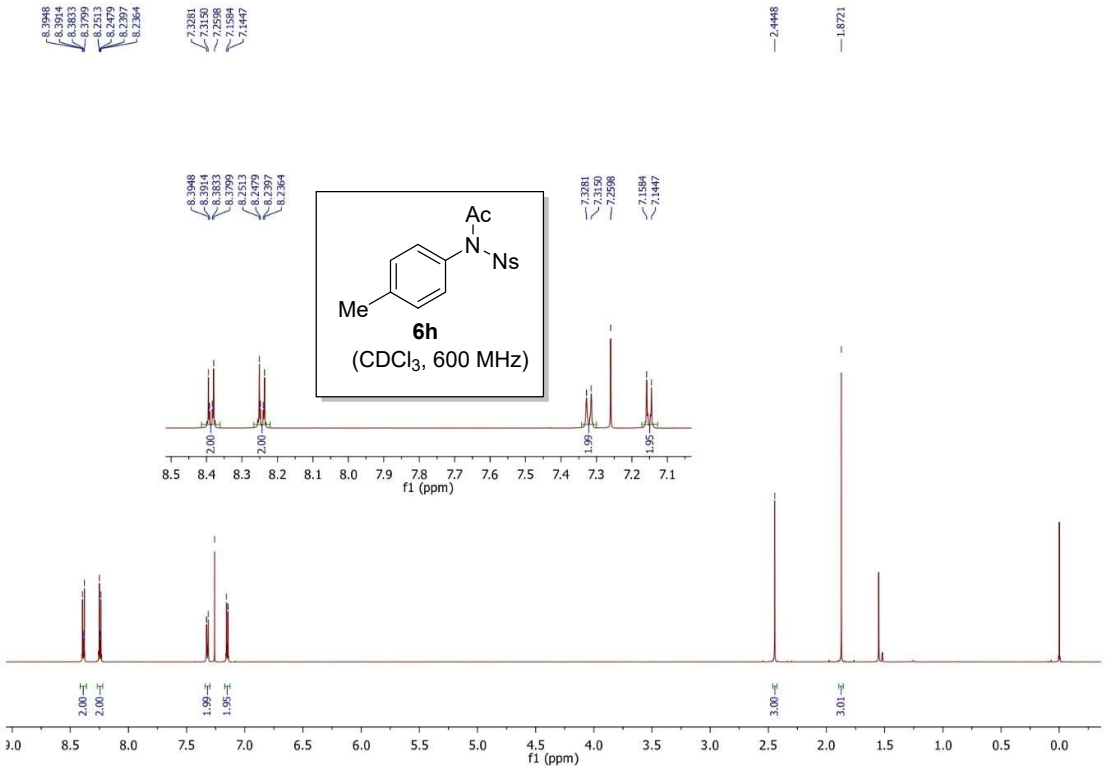


^{1}H NMR of 6h ($CDCl_3$, 600 MHz)



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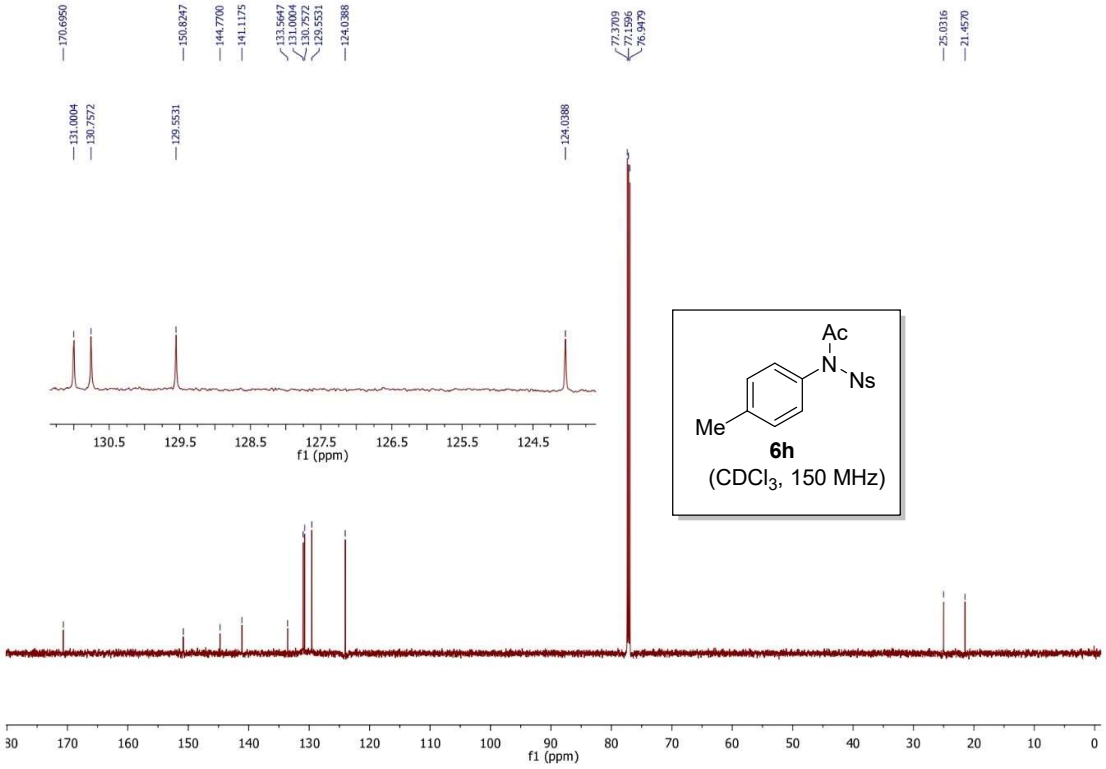
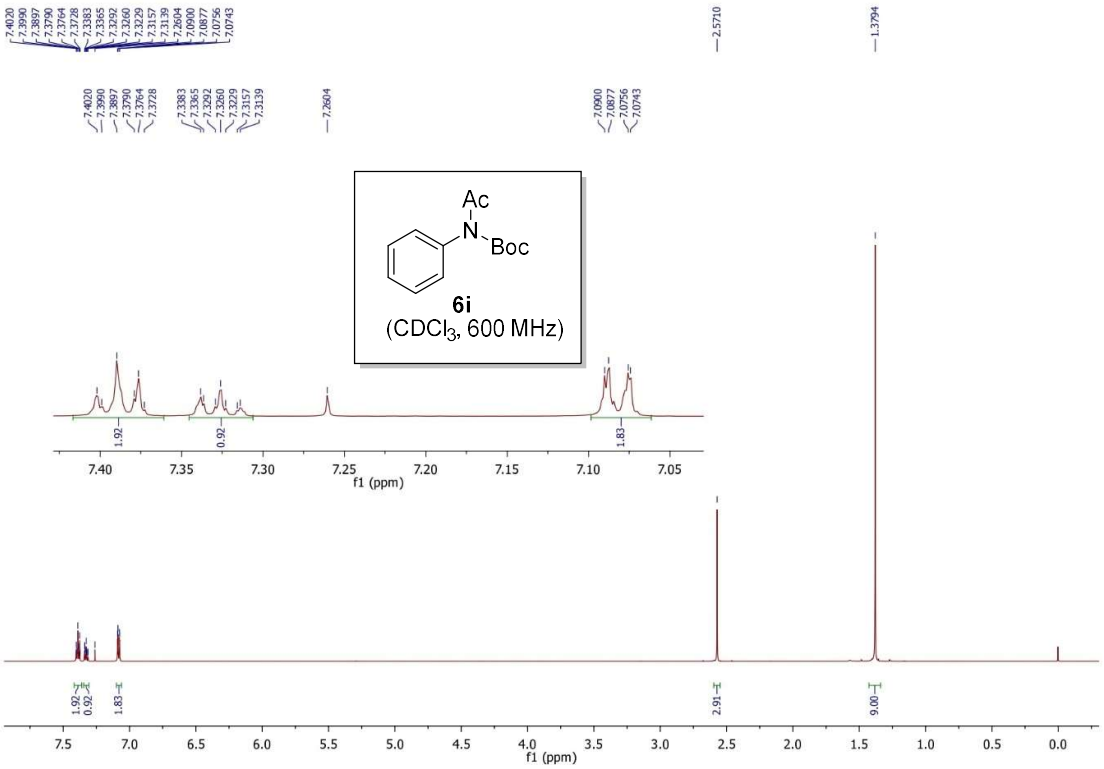


^{1}H NMR of 6i ($CDCl_3$, 600 MHz)



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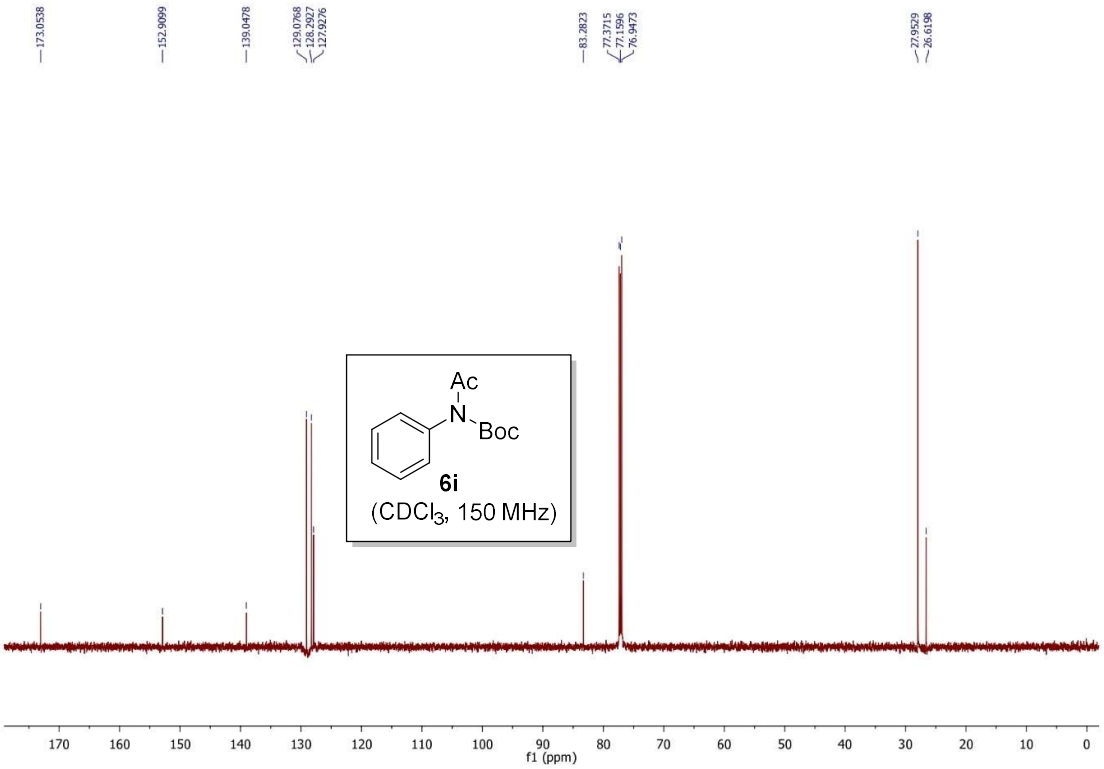
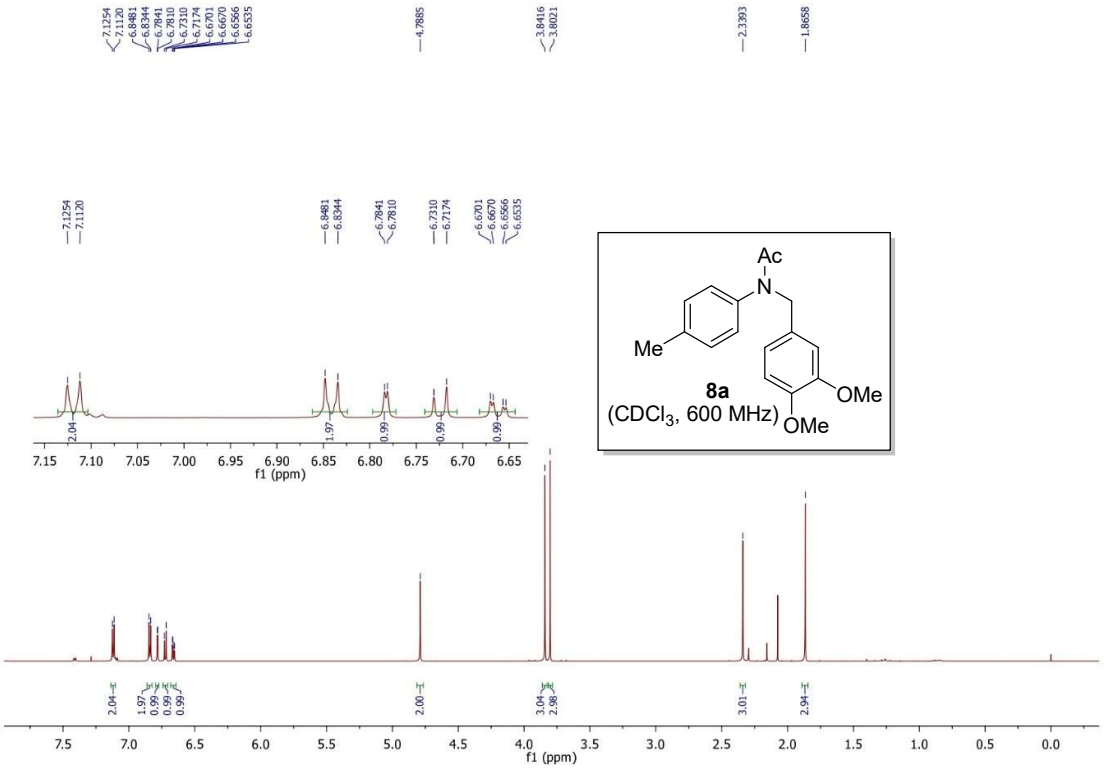


^{1}H NMR of 8a ($CDCl_3$, 600 MHz)



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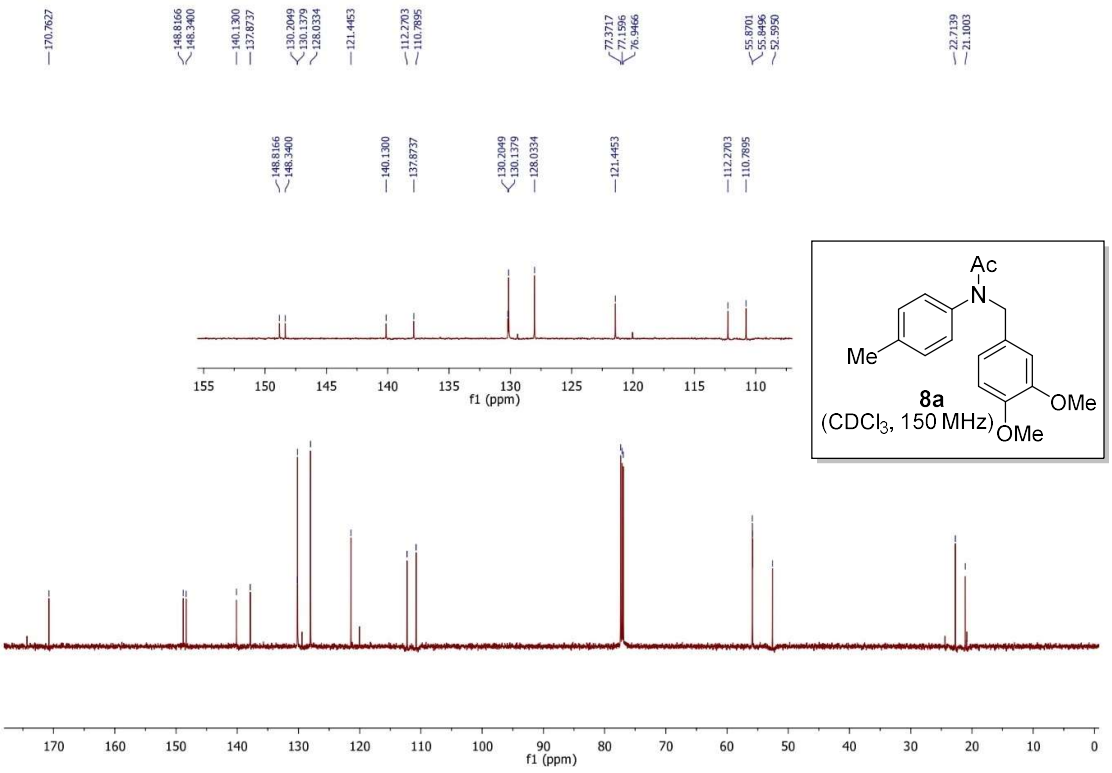
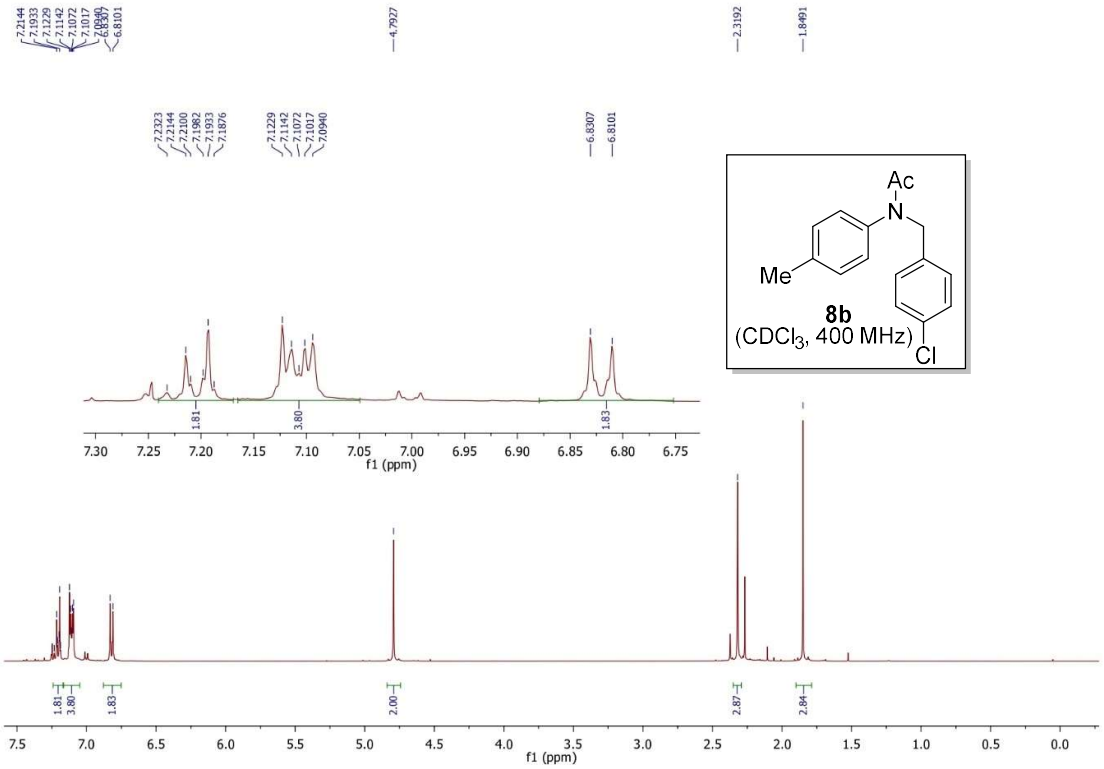
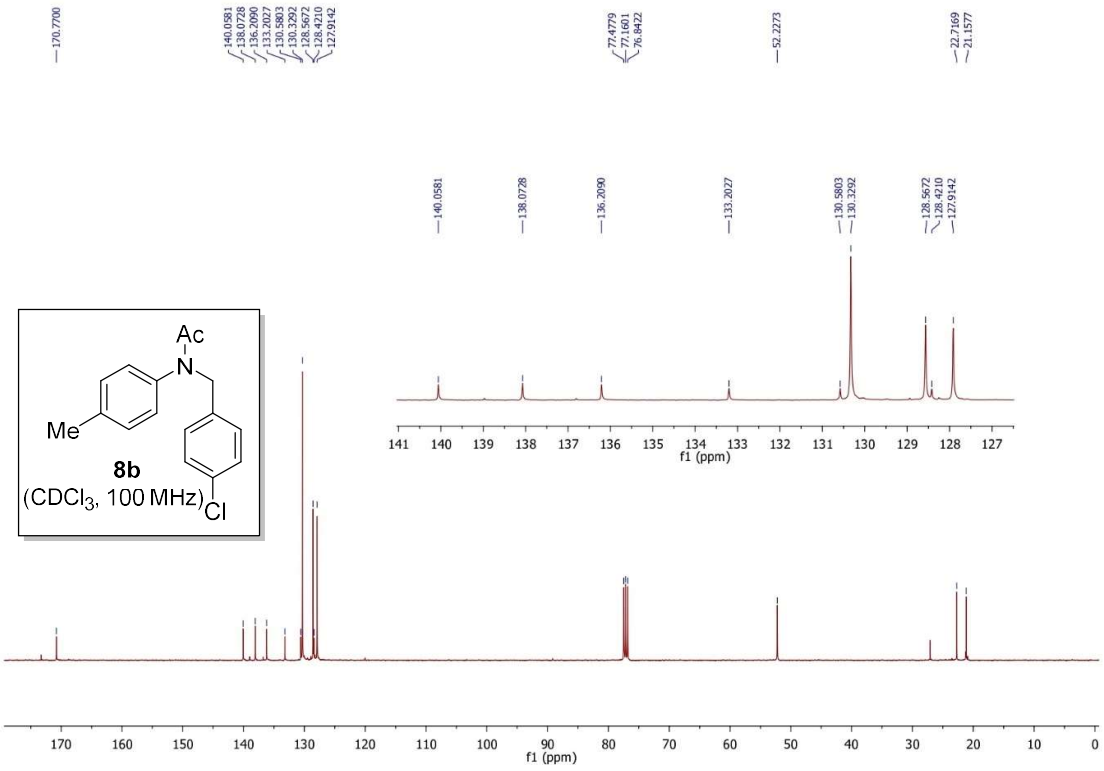


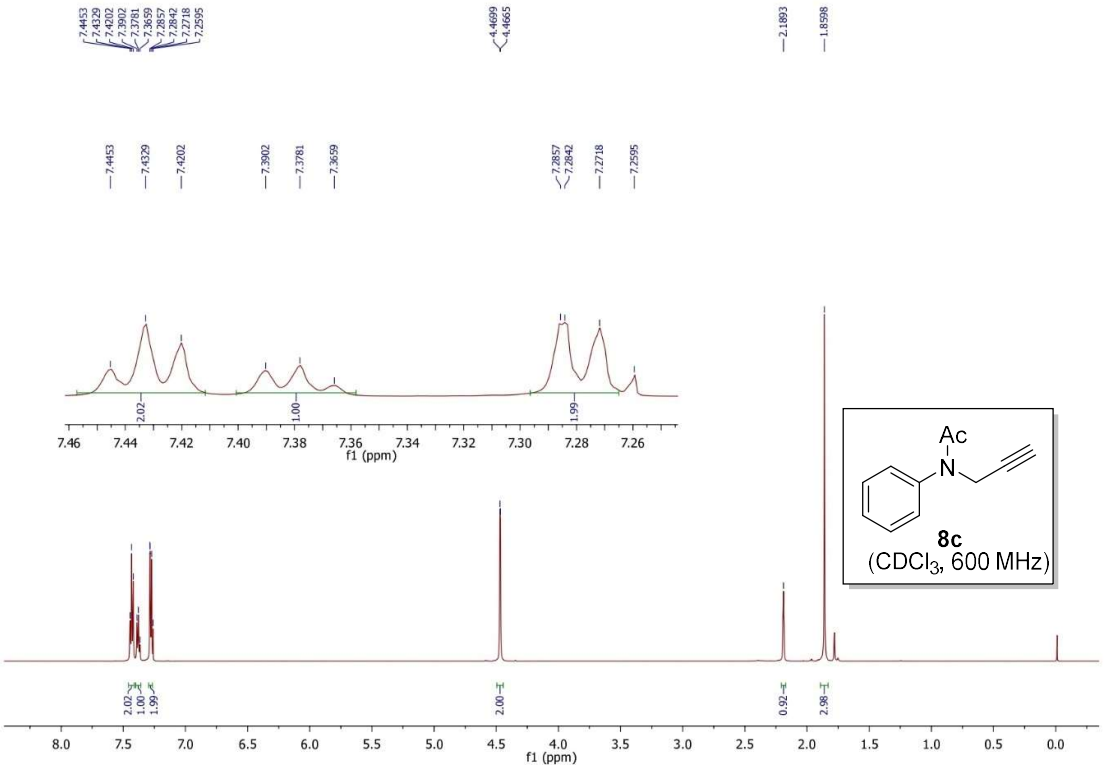
^{1}H NMR of 8b ($CDCl_3$, 400 MHz)



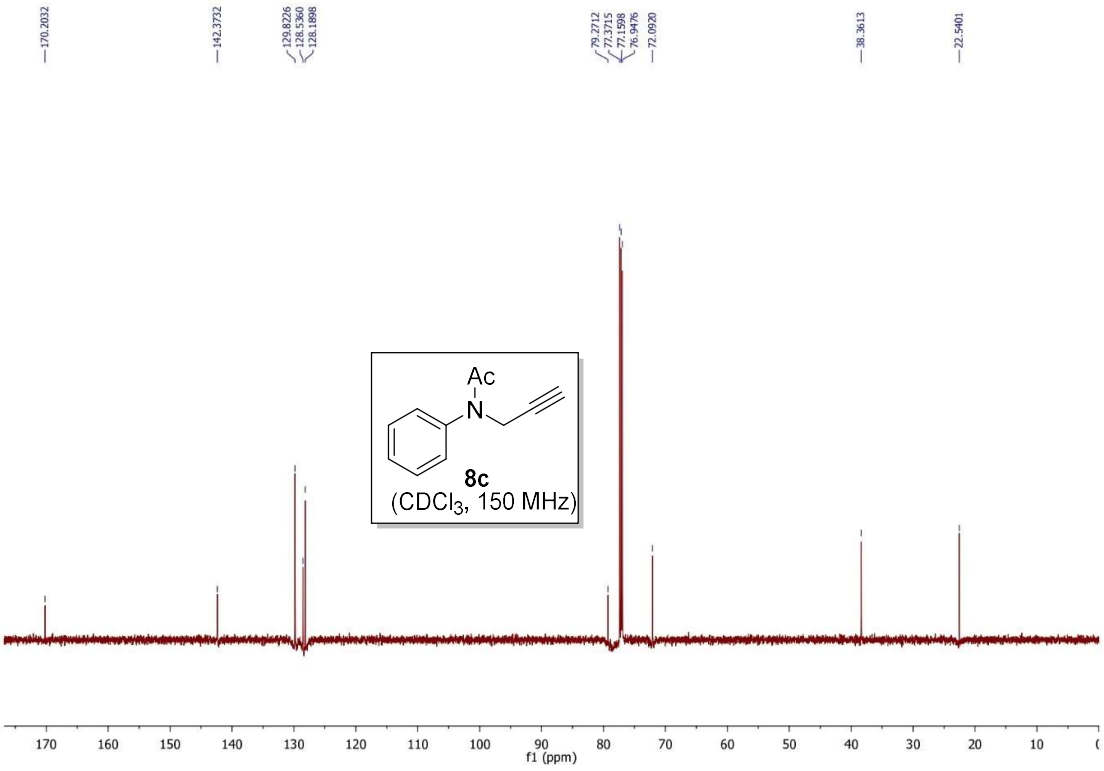
^{13}C NMR of 8b ($CDCl_3$, 100 MHz)



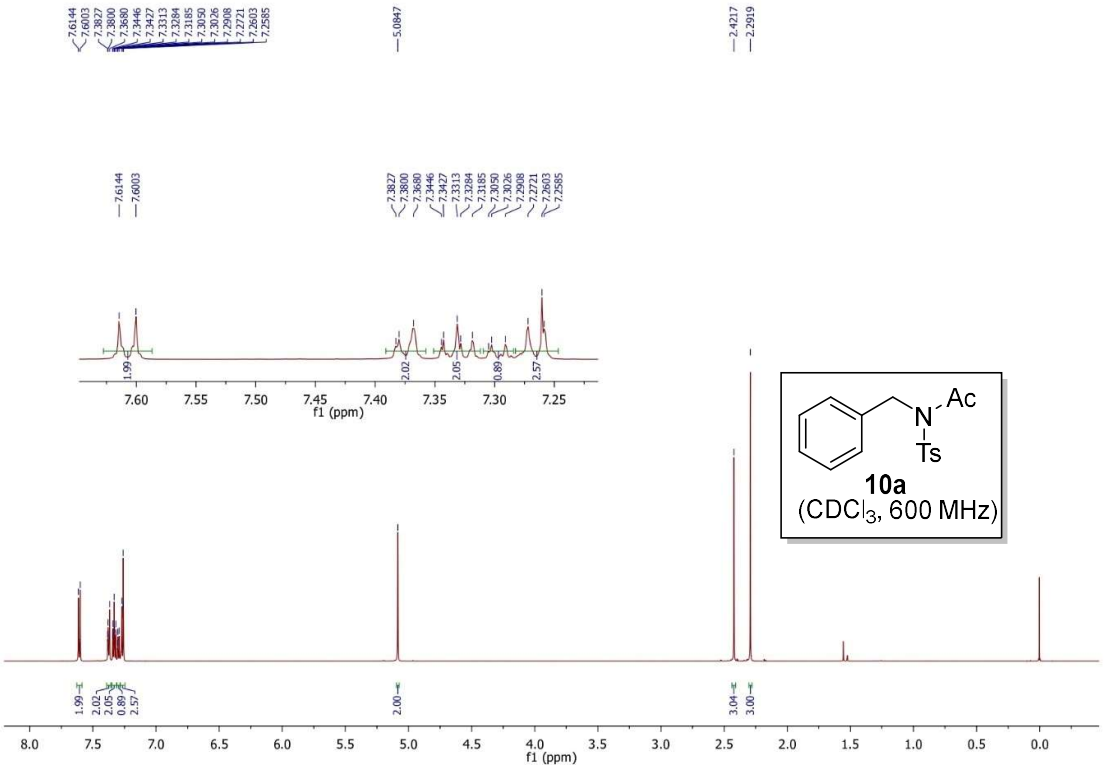
^{1}H NMR of 8c ($CDCl_3$, 600 MHz)



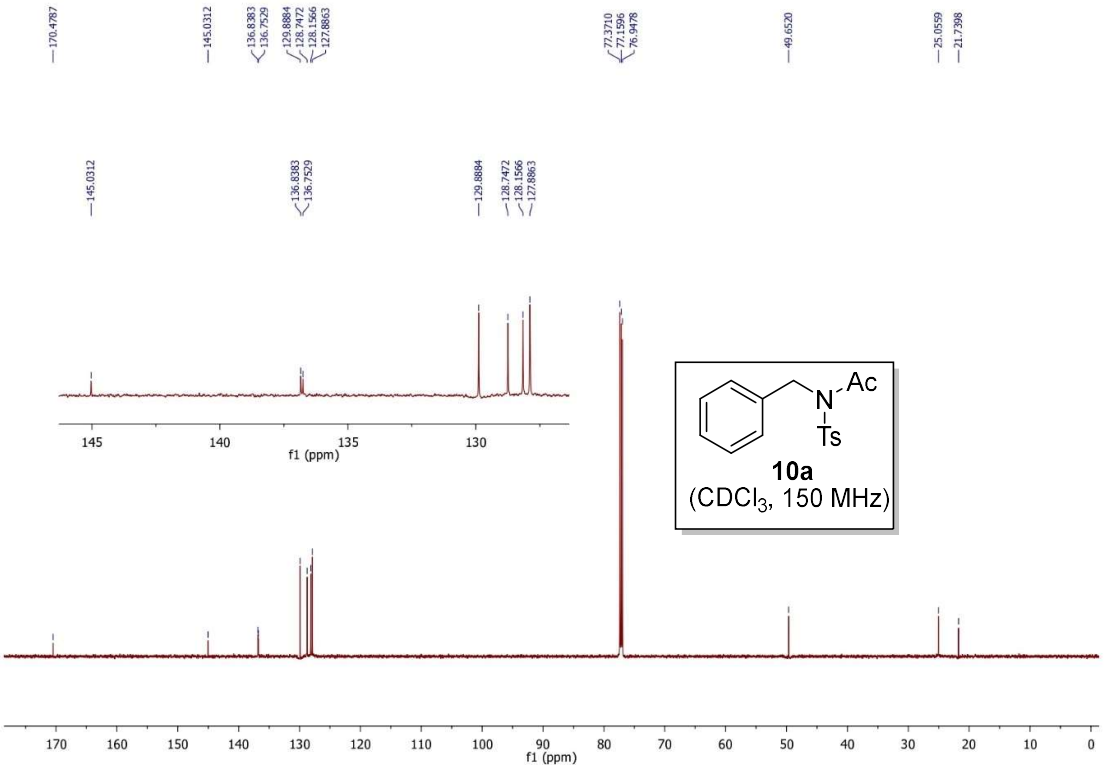
^{13}C NMR of 8c ($CDCl_3$, 150 MHz)



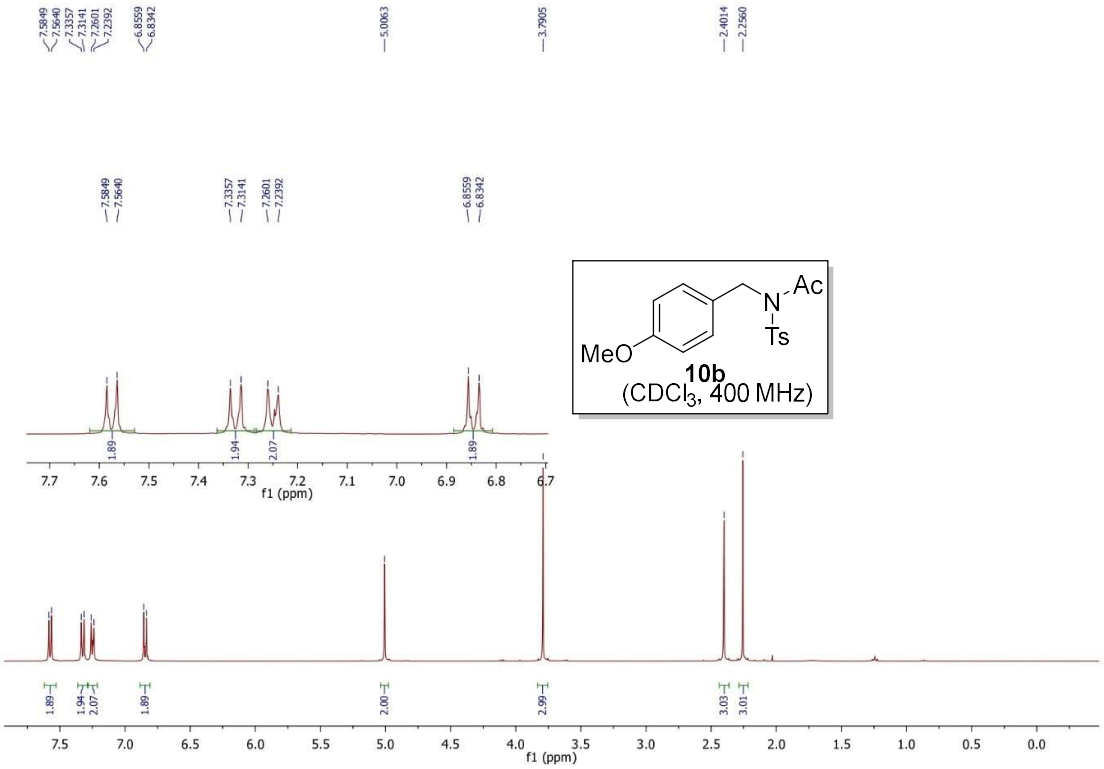
^{1}H NMR of 10a ($CDCl_3$, 600 MHz)



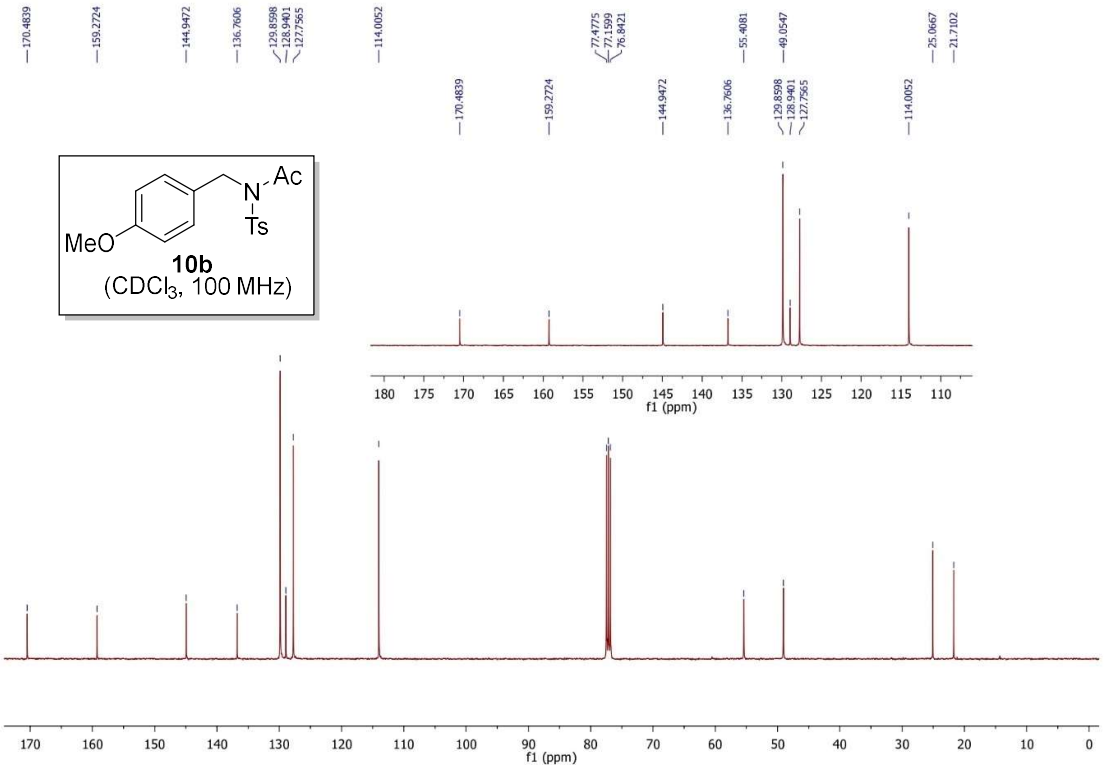
^{13}C NMR of 10a ($CDCl_3$, 150 MHz)



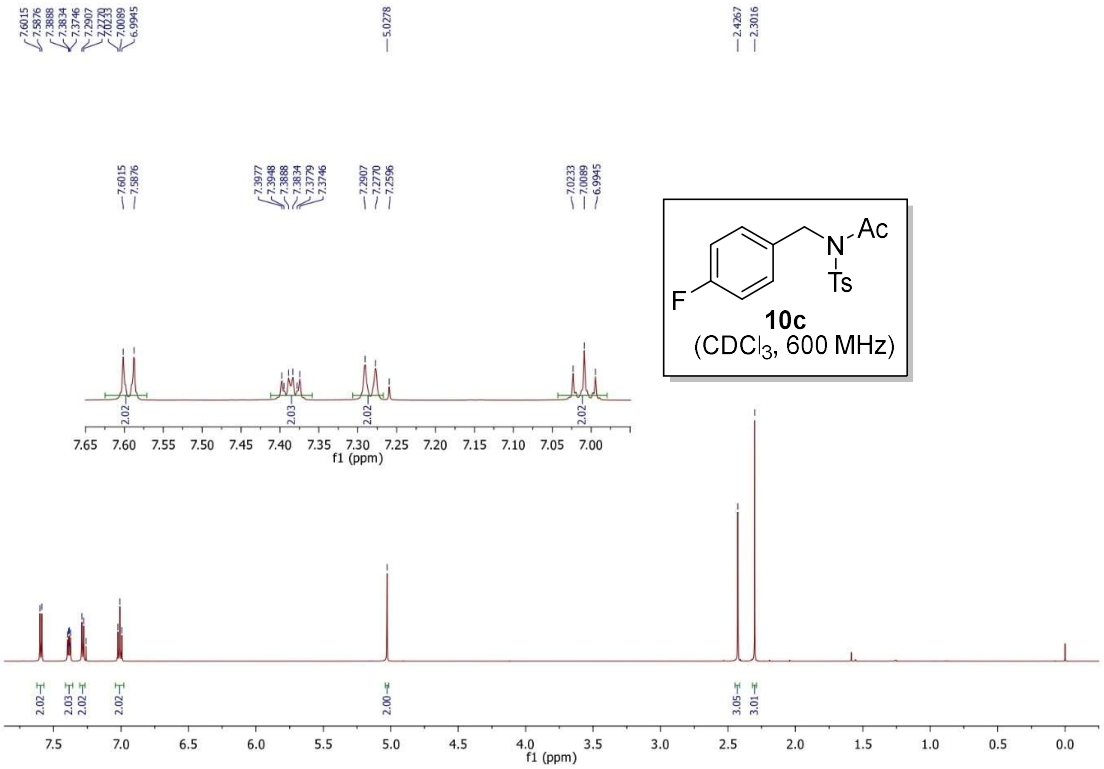
^{1}H NMR of 10b ($CDCl_3$, 400 MHz)



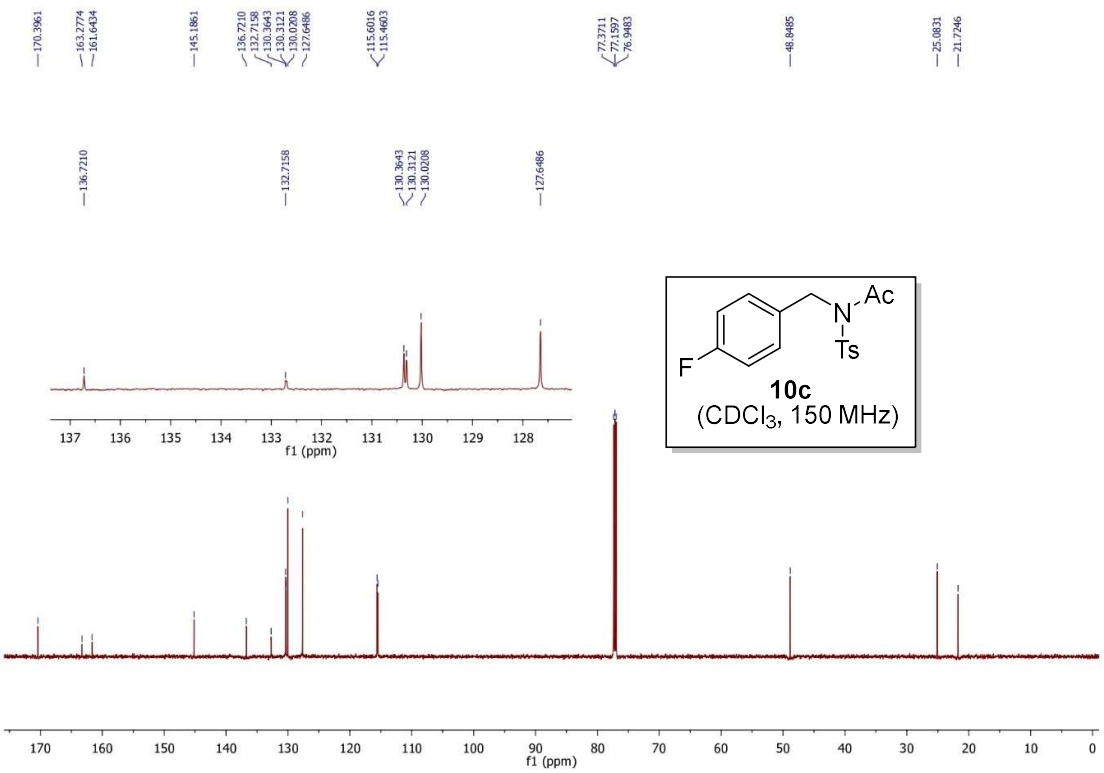
^{13}C NMR of 10b ($CDCl_3$, 100 MHz)



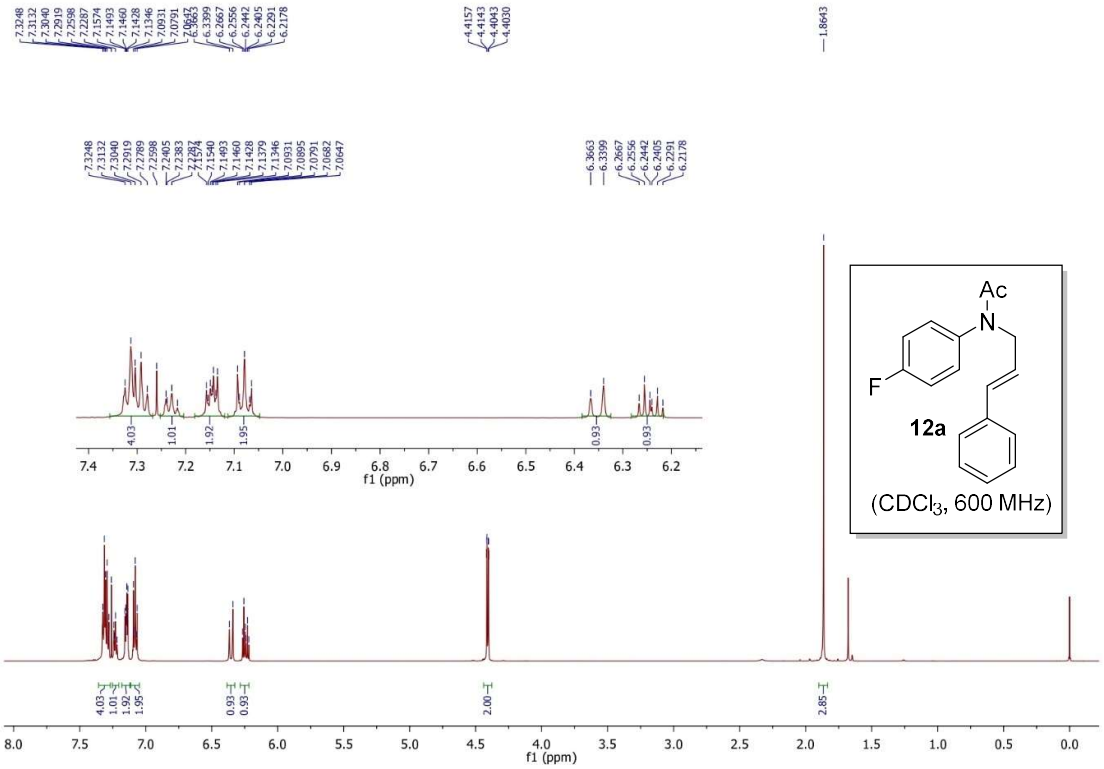
^{1}H NMR of 10c ($CDCl_3$, 600 MHz)



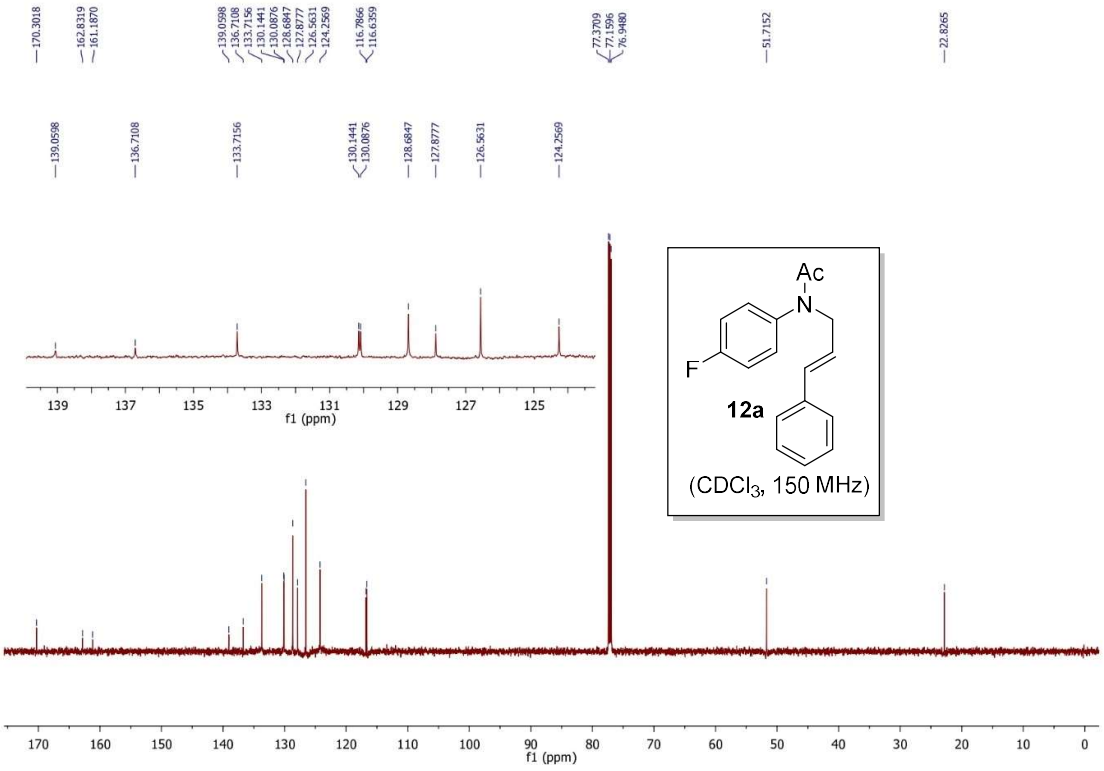
^{13}C NMR of 10c ($CDCl_3$, 150 MHz)



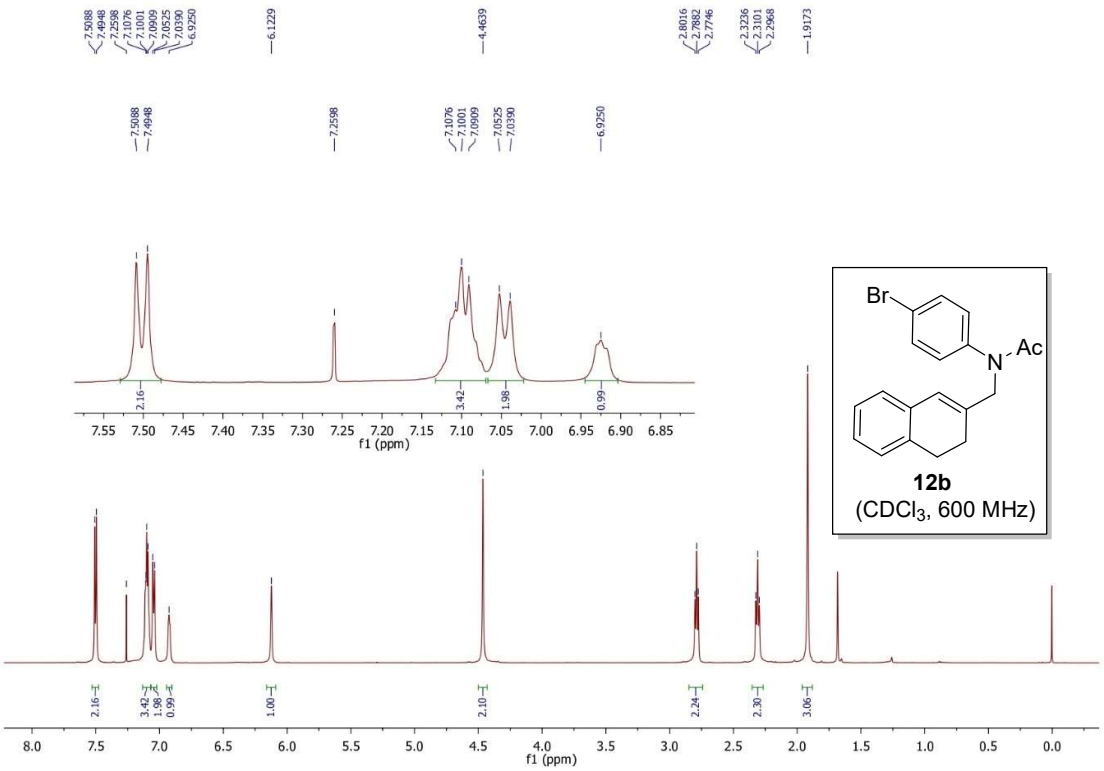
^{1}H NMR of 12a ($CDCl_3$, 600 MHz)



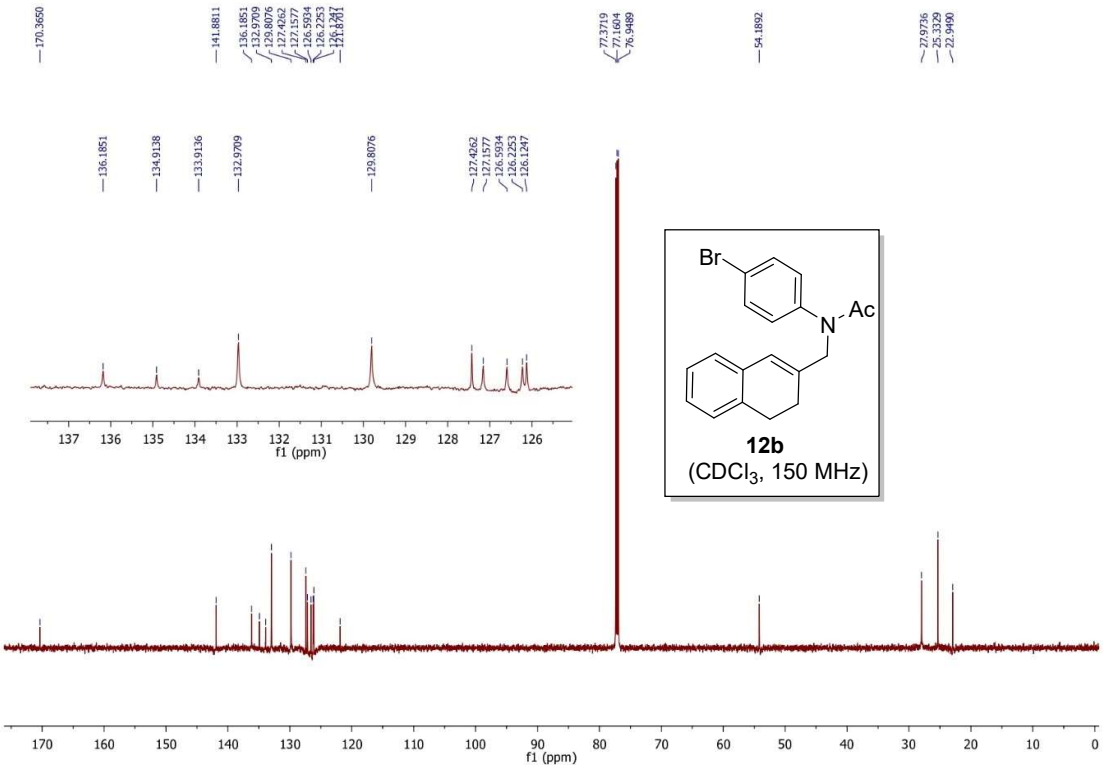
^{13}C NMR of 12a ($CDCl_3$, 150 MHz)



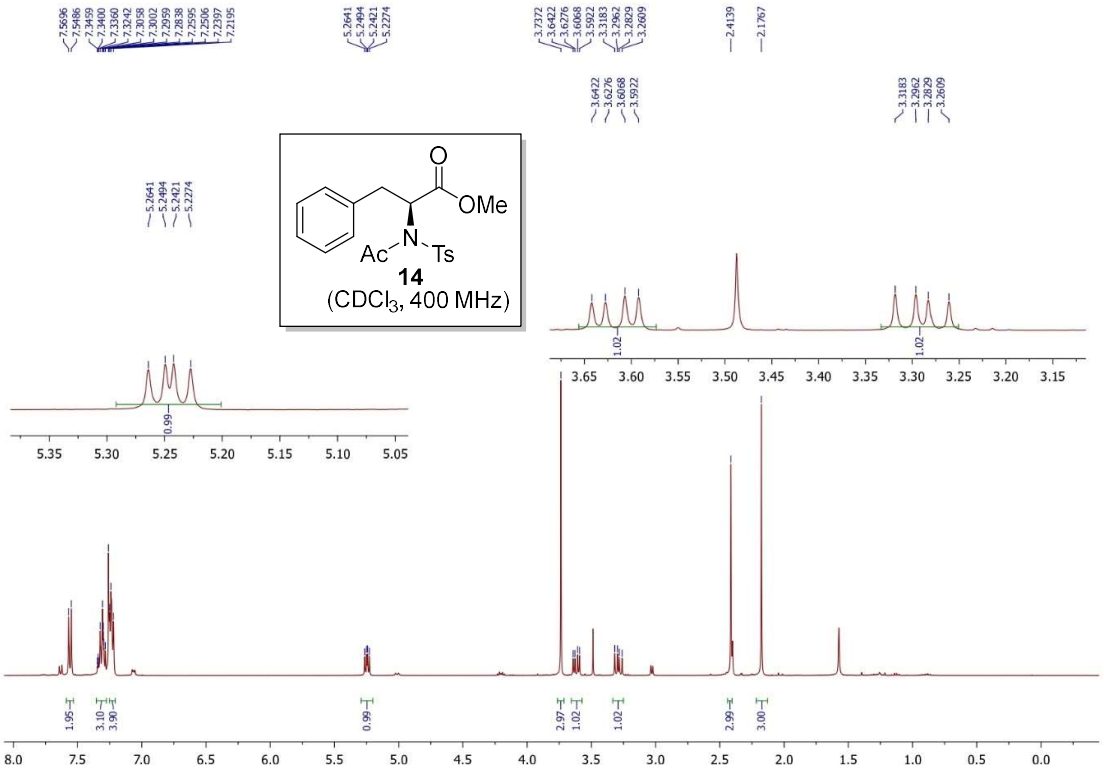
^{1}H NMR of 12b ($CDCl_3$, 600 MHz)



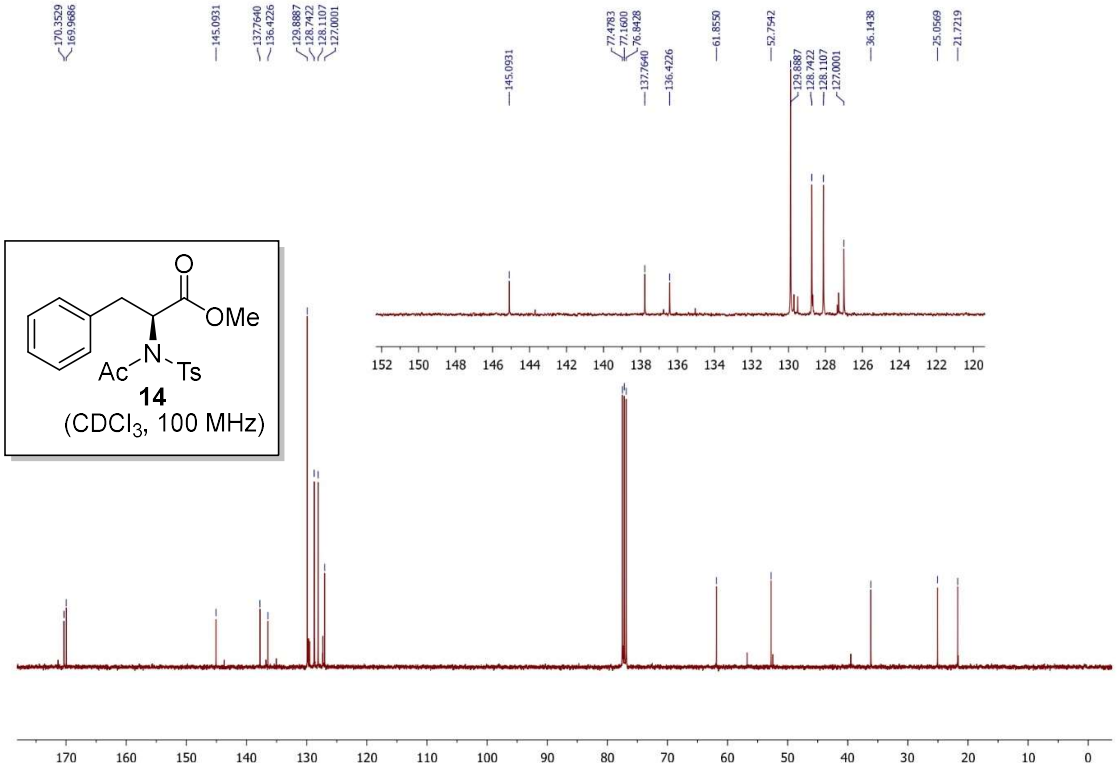
^{13}C NMR of 12b ($CDCl_3$, 150 MHz)



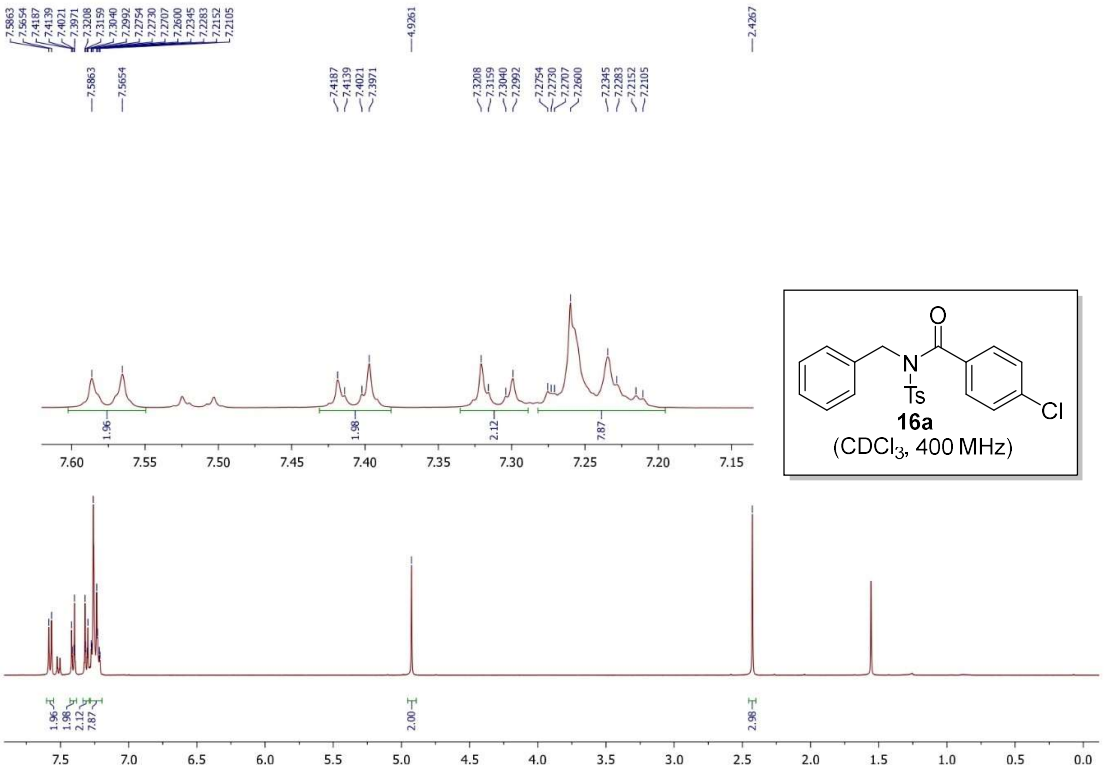
^{1}H NMR of 14 ($CDCl_3$, 400 MHz)



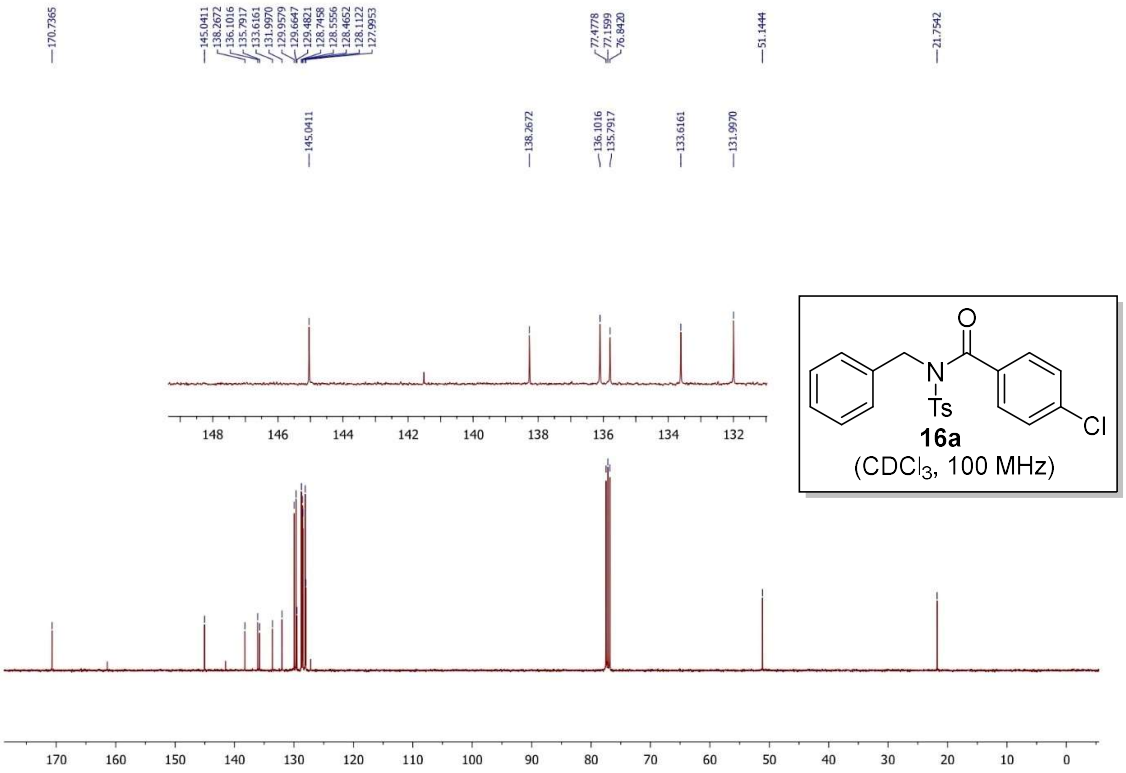
^{13}C NMR of 14 ($CDCl_3$, 100 MHz)



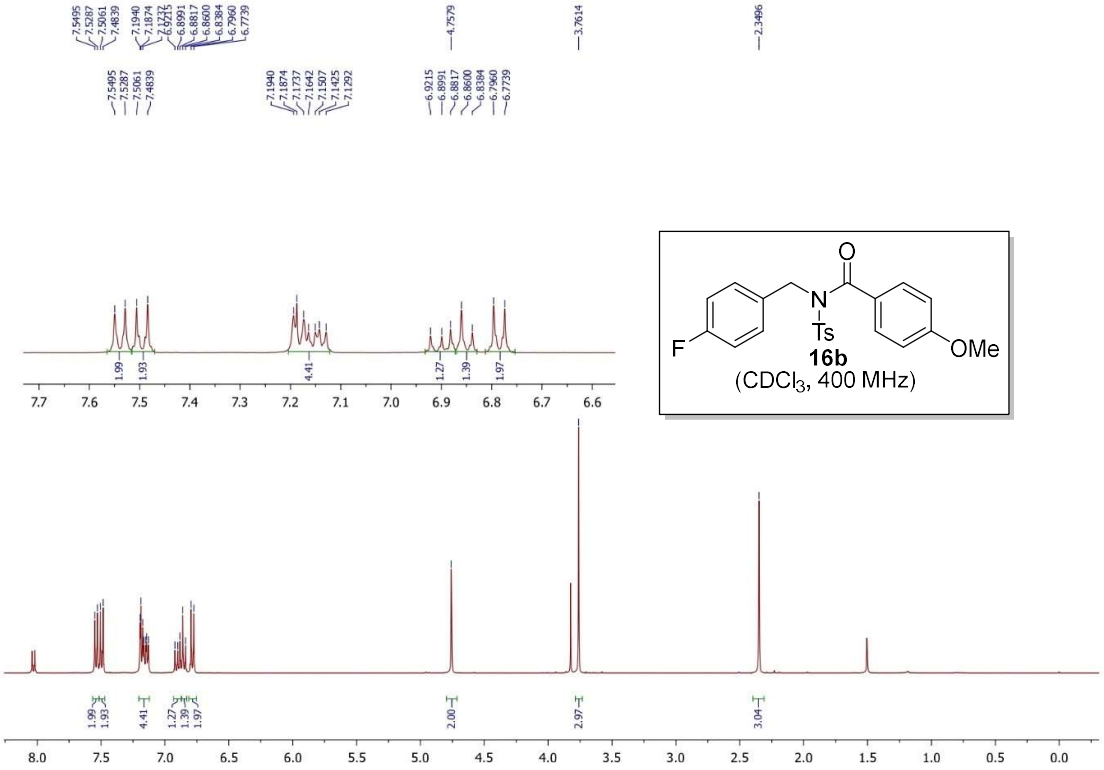
^{1}H NMR of 16a ($CDCl_3$, 400 MHz)



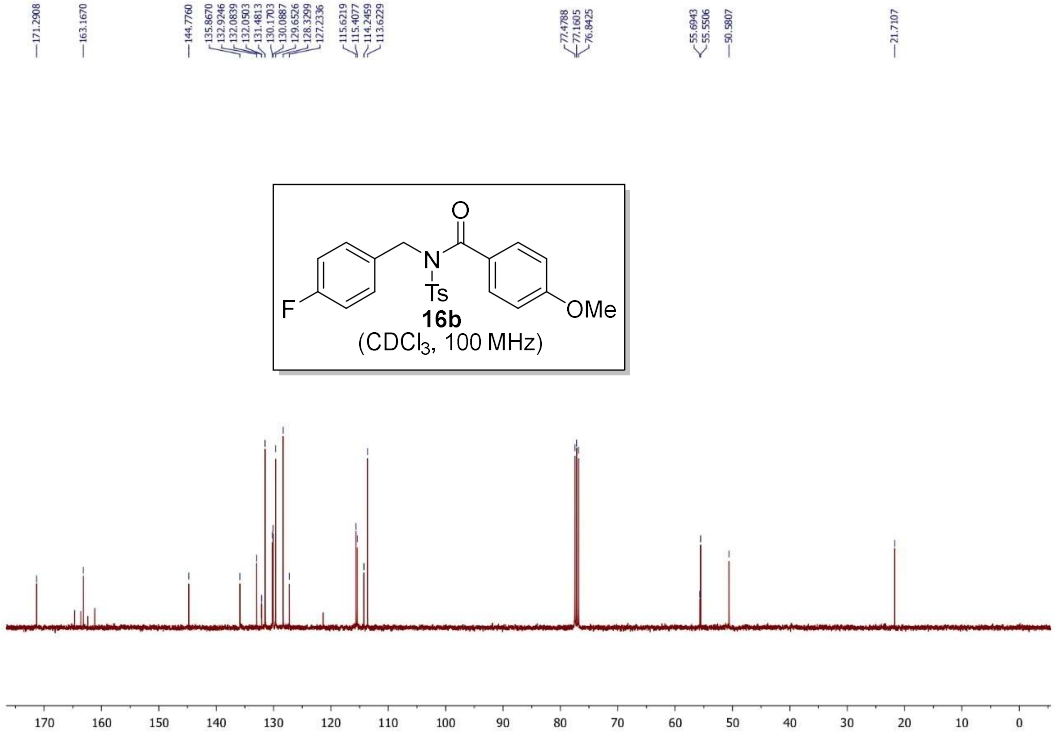
^{13}C NMR of 16a ($CDCl_3$, 100 MHz)



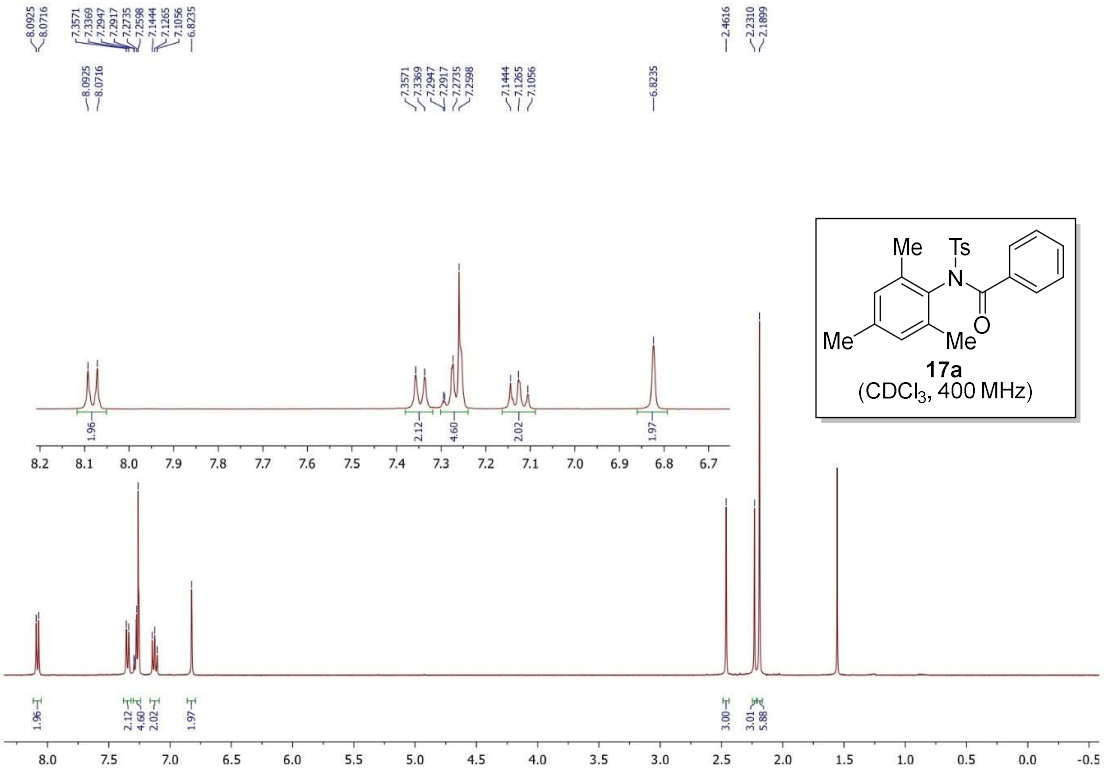
^{1}H NMR of 16b ($CDCl_3$, 400 MHz)



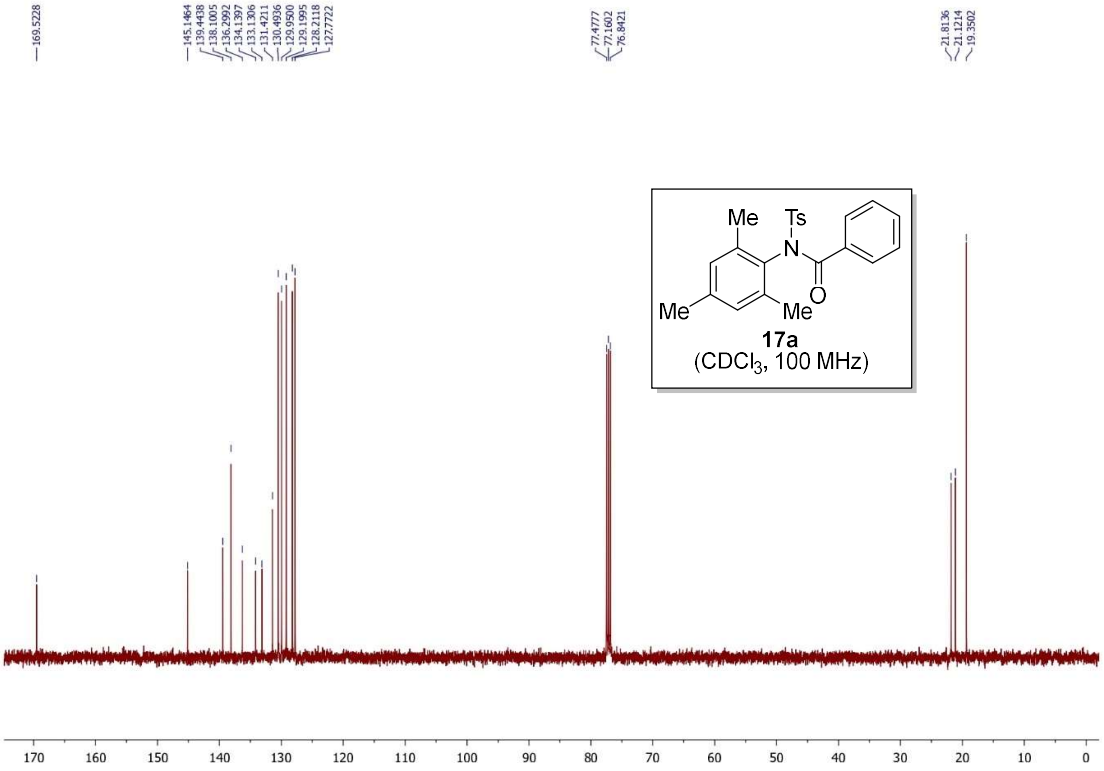
^{13}C NMR of 16b ($CDCl_3$, 100 MHz)



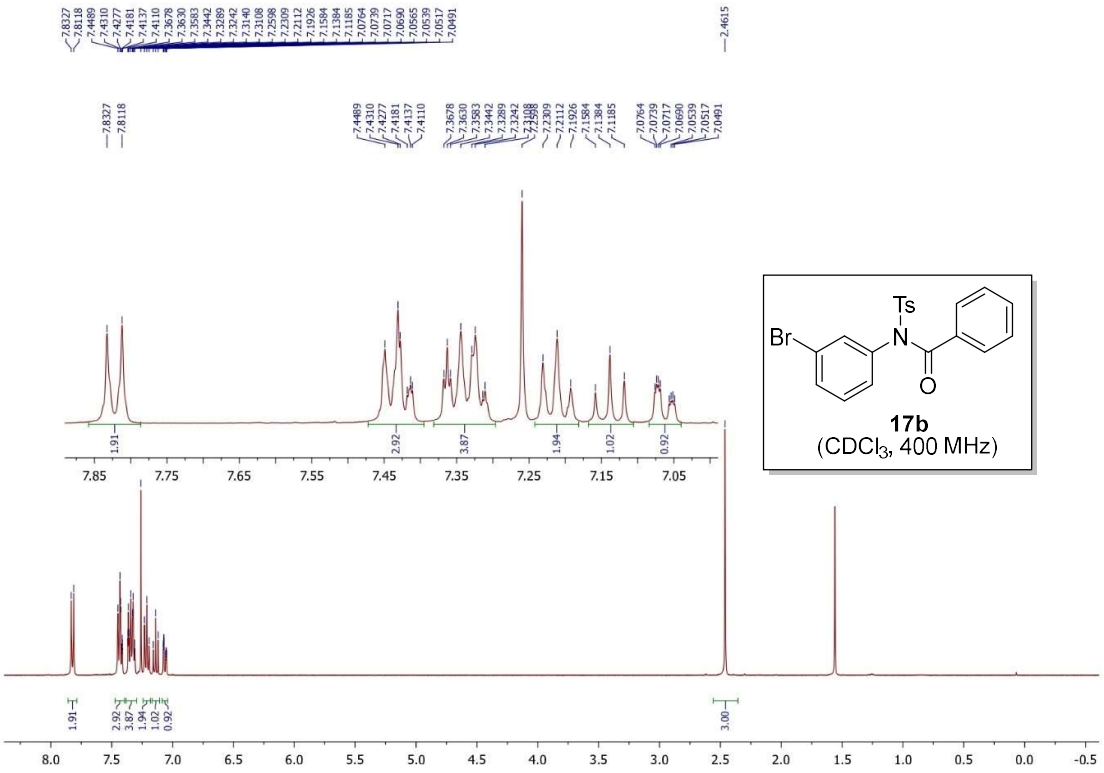
^{1}H NMR of 17a ($CDCl_3$, 400 MHz)



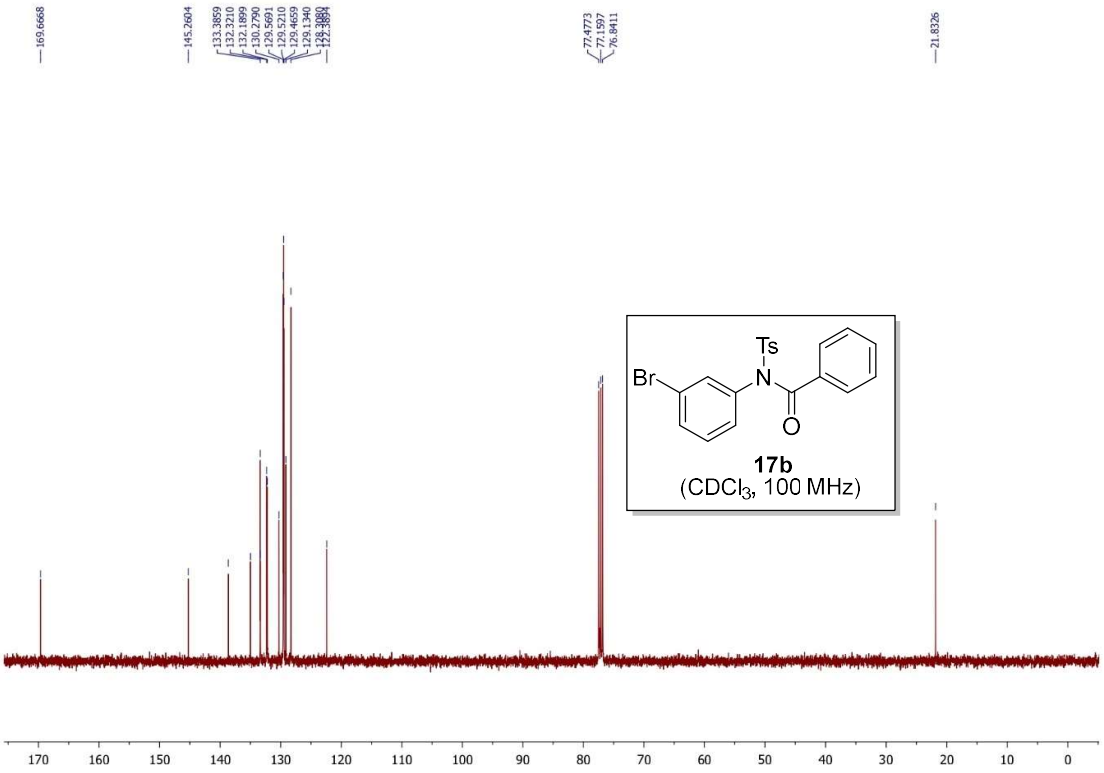
^{13}C NMR of 17a ($CDCl_3$, 100 MHz)



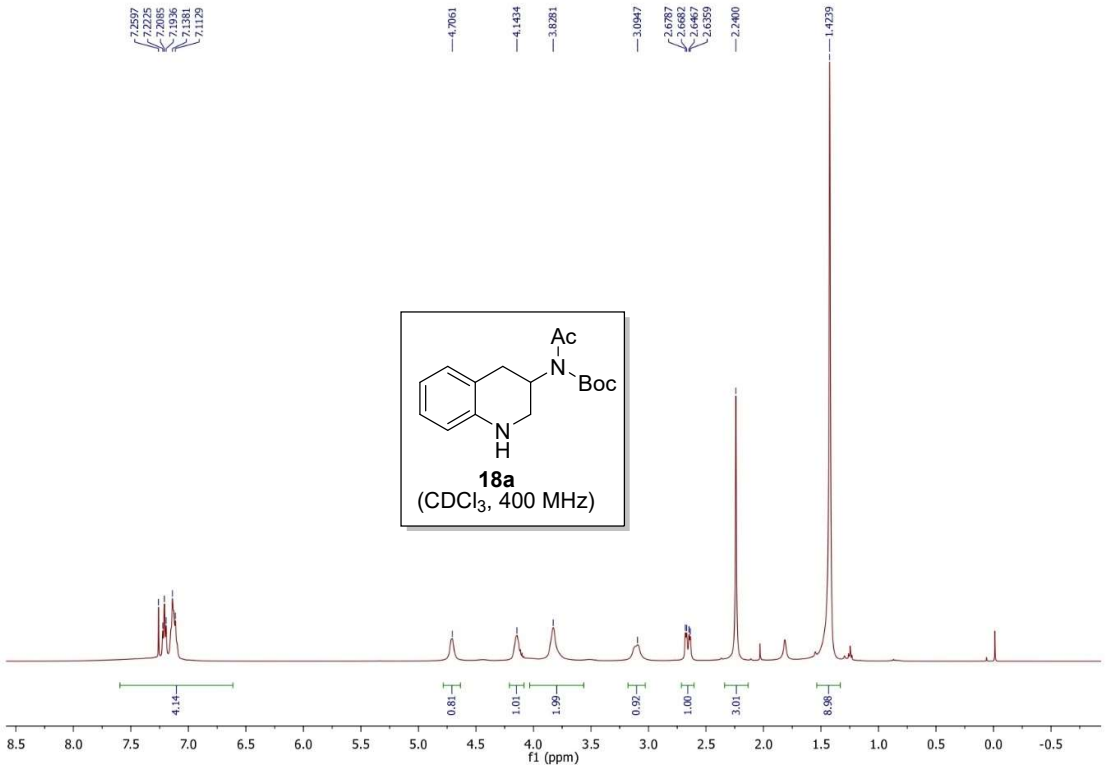
^{1}H NMR of 17b ($CDCl_3$, 400 MHz)



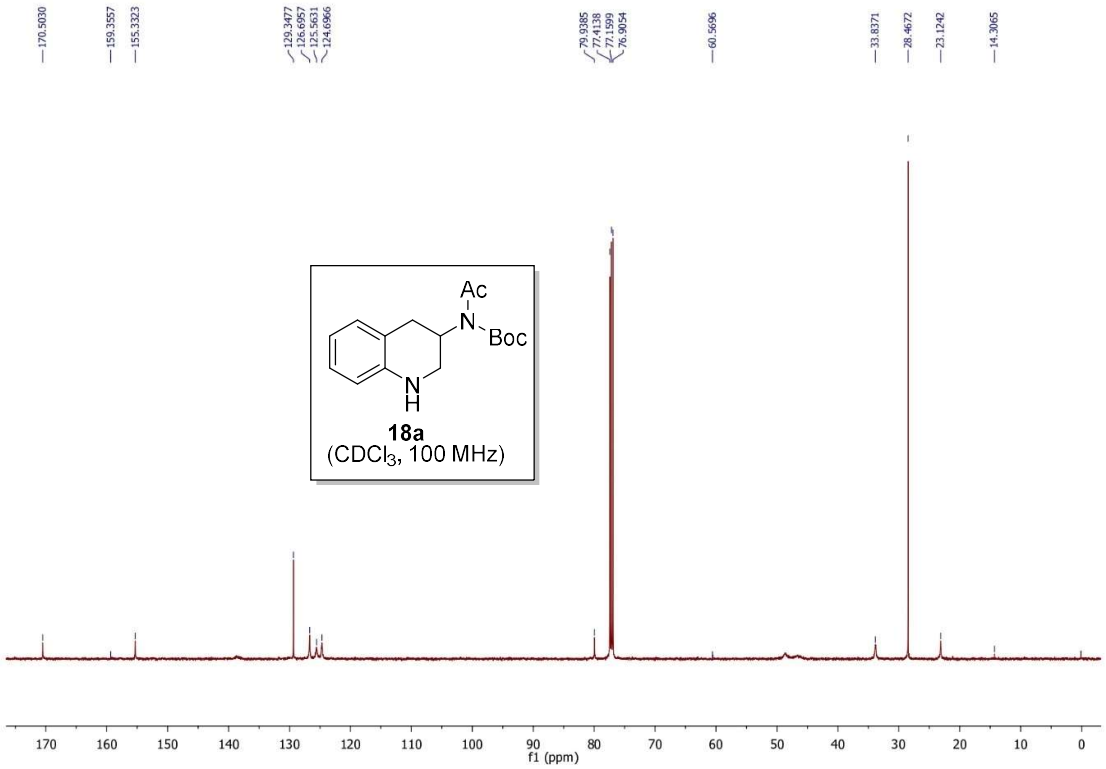
^{13}C NMR of 17b ($CDCl_3$, 100 MHz)



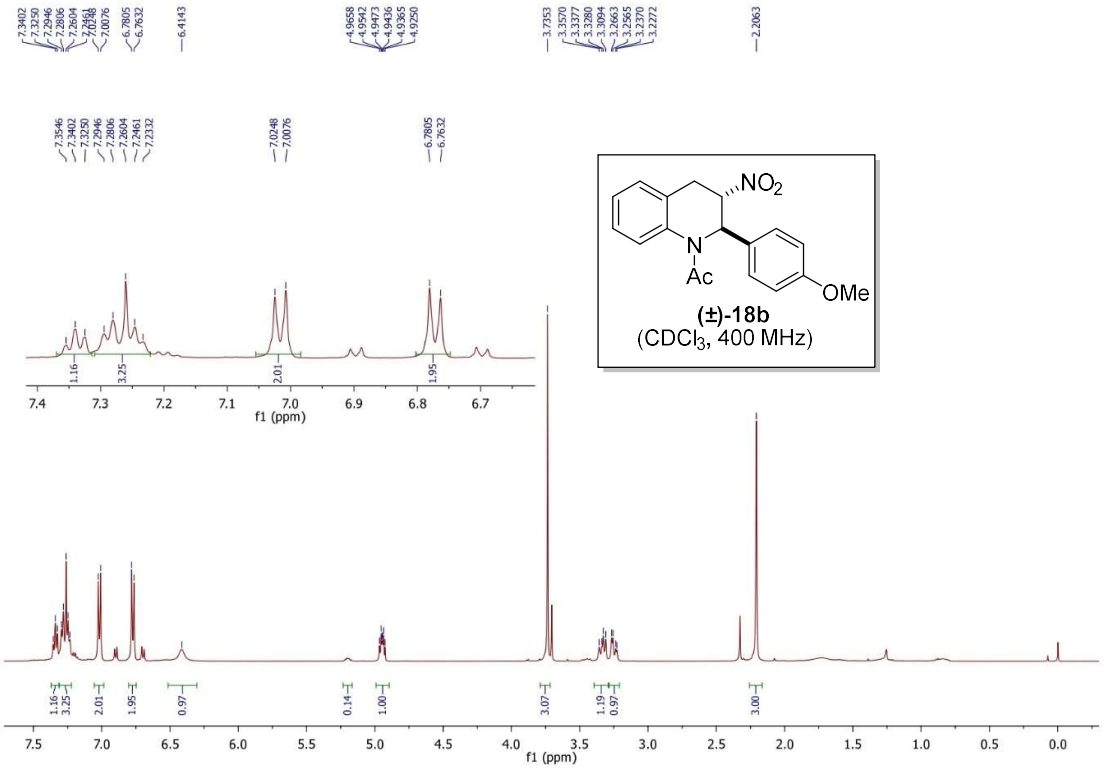
^{1}H NMR of 18a ($CDCl_3$, 400 MHz)



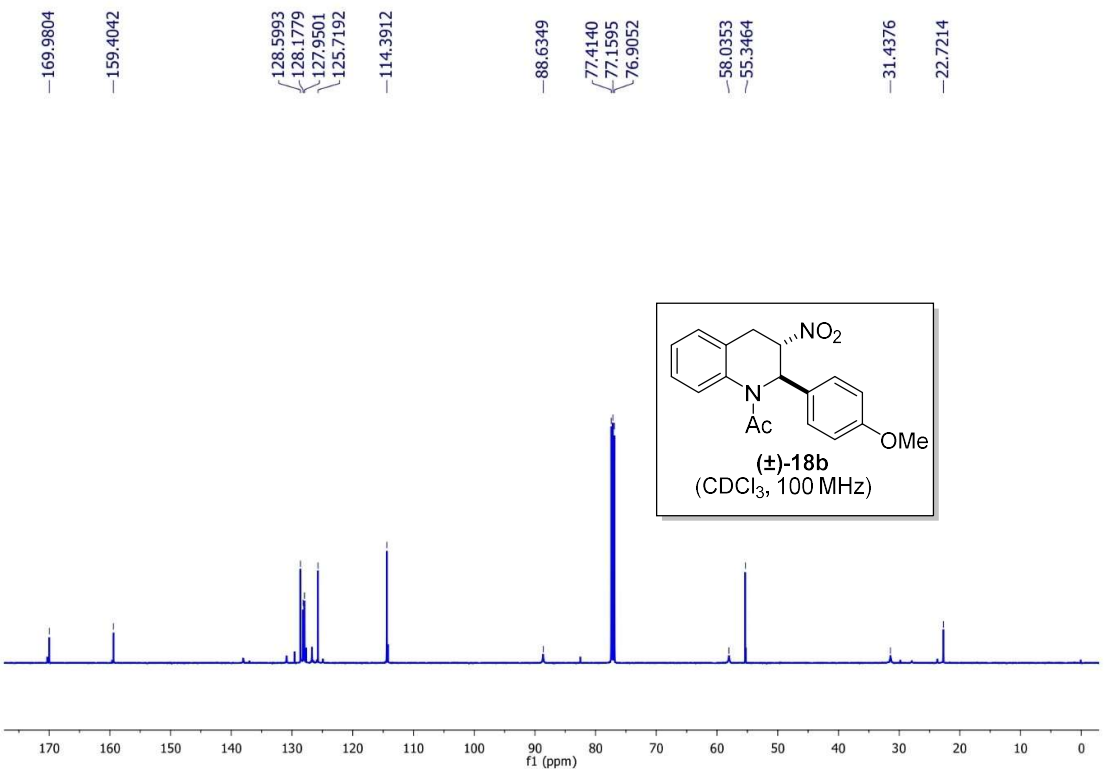
^{13}C NMR of 18a ($CDCl_3$, 100 MHz)



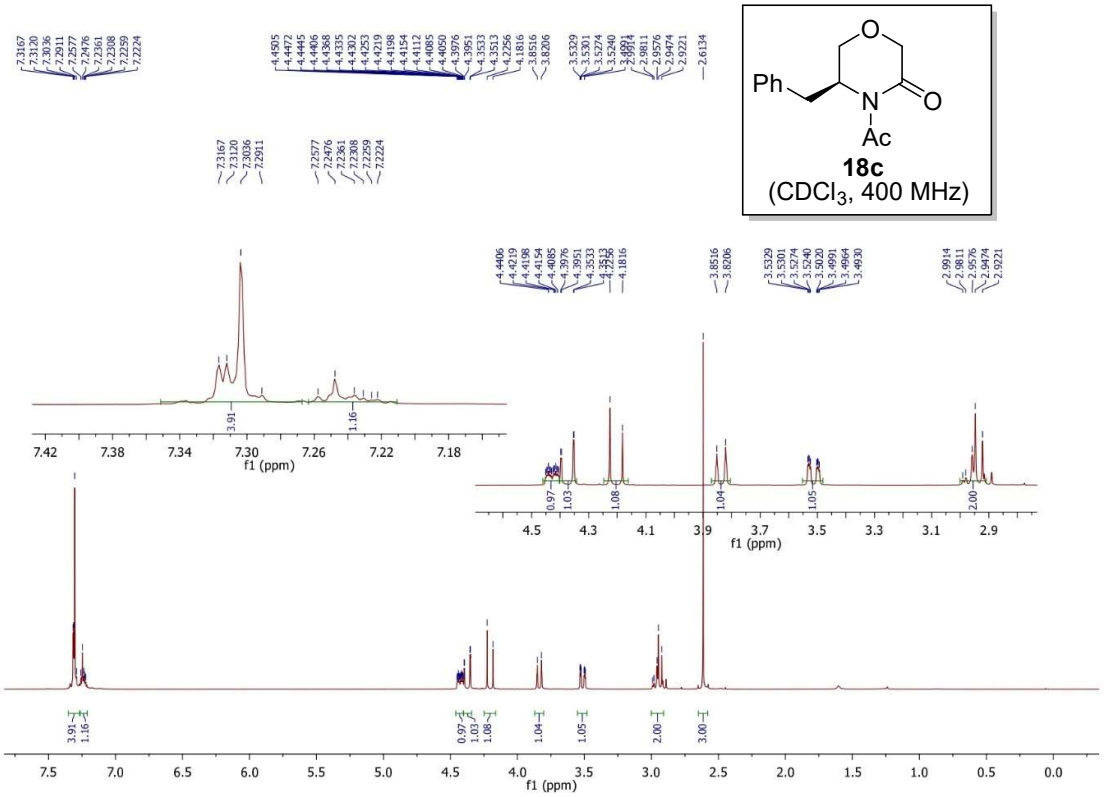
^{1}H NMR of (±)-18b ($CDCl_3$, 400 MHz)



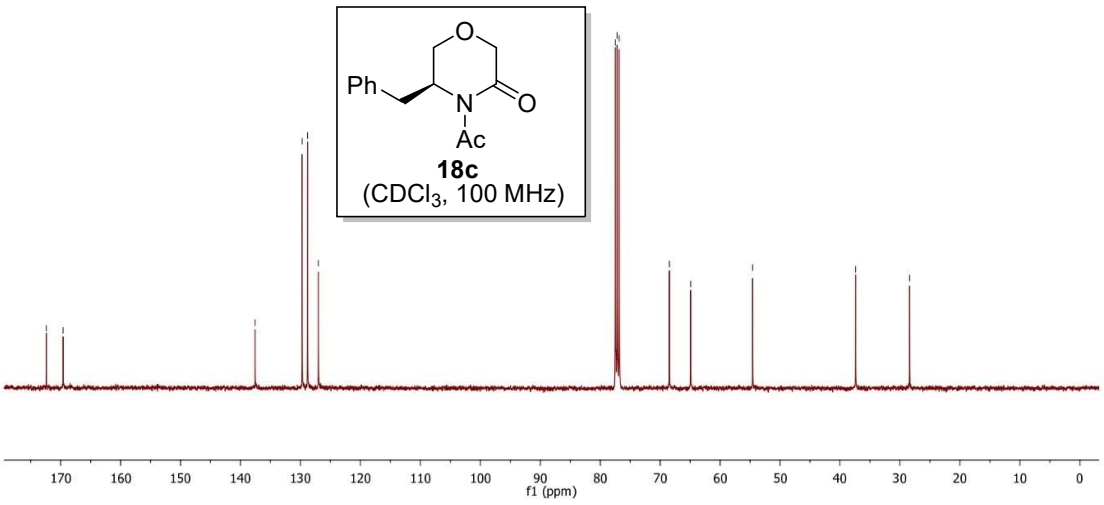
^{13}C NMR of 18b ($CDCl_3$, 100 MHz)



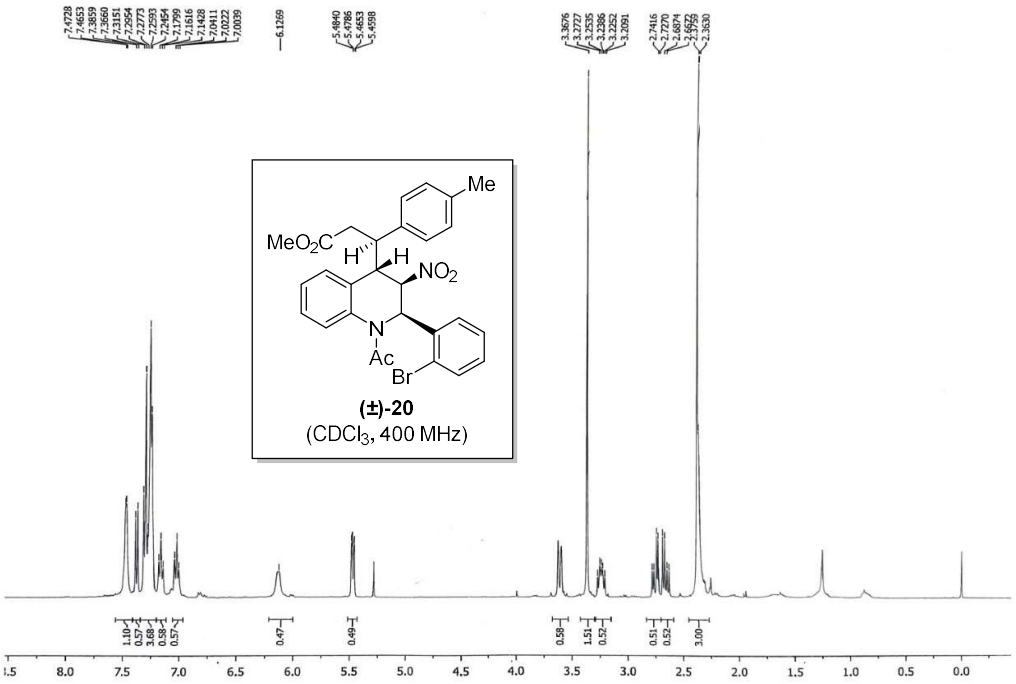
^{1}H NMR of 18c ($CDCl_3$, 400 MHz)



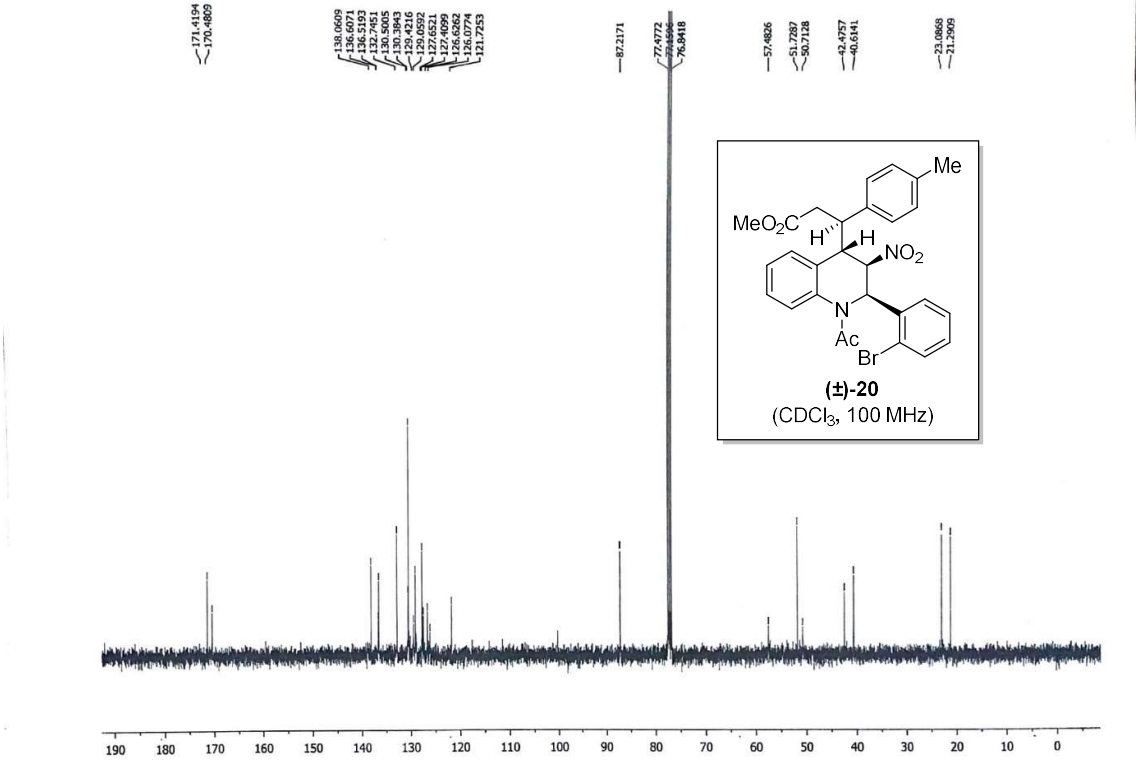
^{13}C NMR of 18c ($CDCl_3$, 100 MHz)



^{1}H NMR of (±)-20 ($CDCl_3$, 400 MHz)

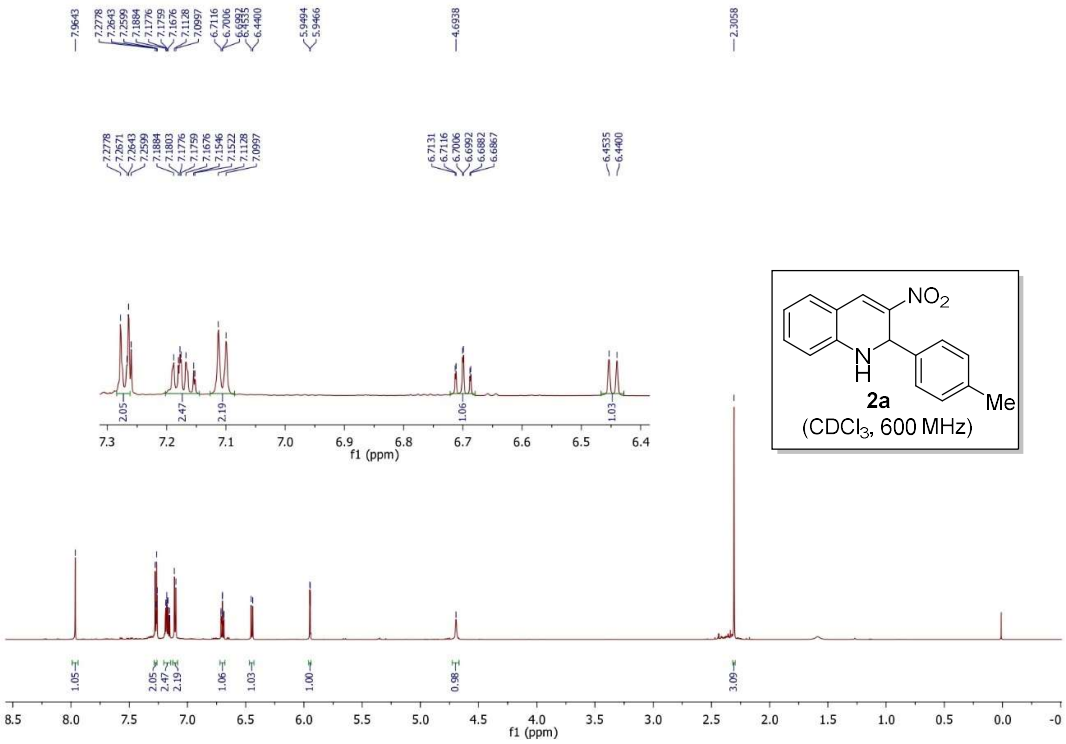


^{13}C NMR of (±)-20 ($CDCl_3$, 100 MHz)

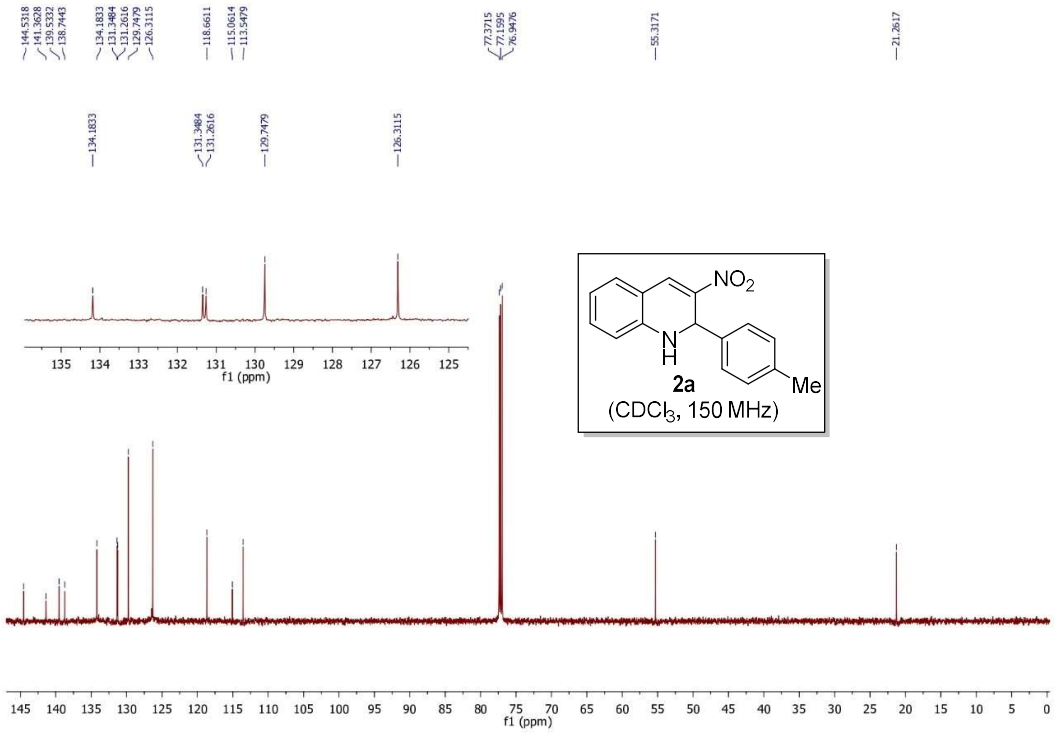


NMR spectra of N-Deacetylated product

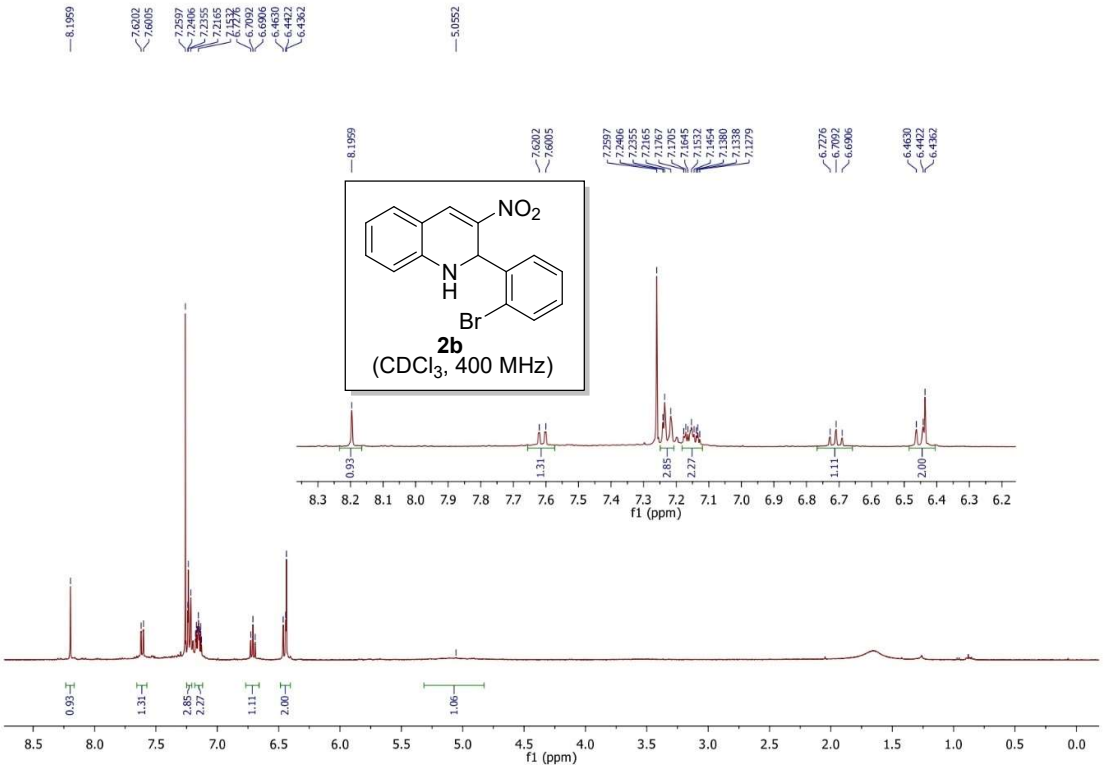
^{1}H NMR of 2a ($CDCl_3$, 600 MHz)



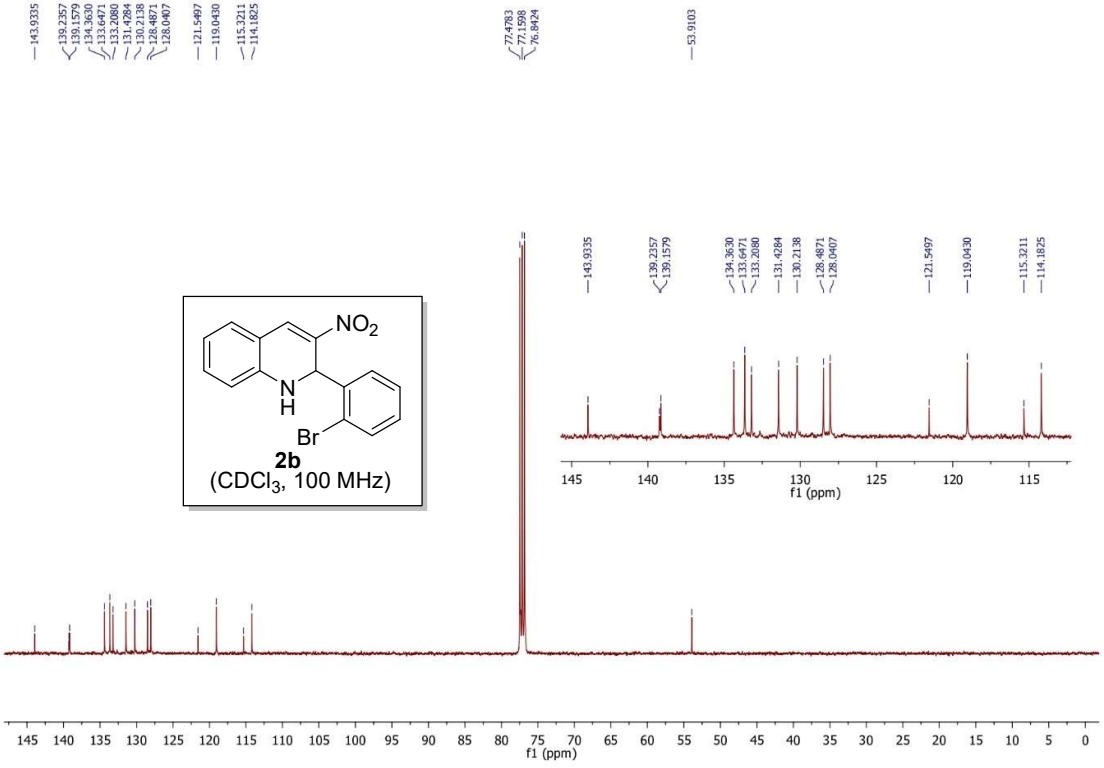
^{13}C NMR of 2a ($CDCl_3$, 150 MHz)



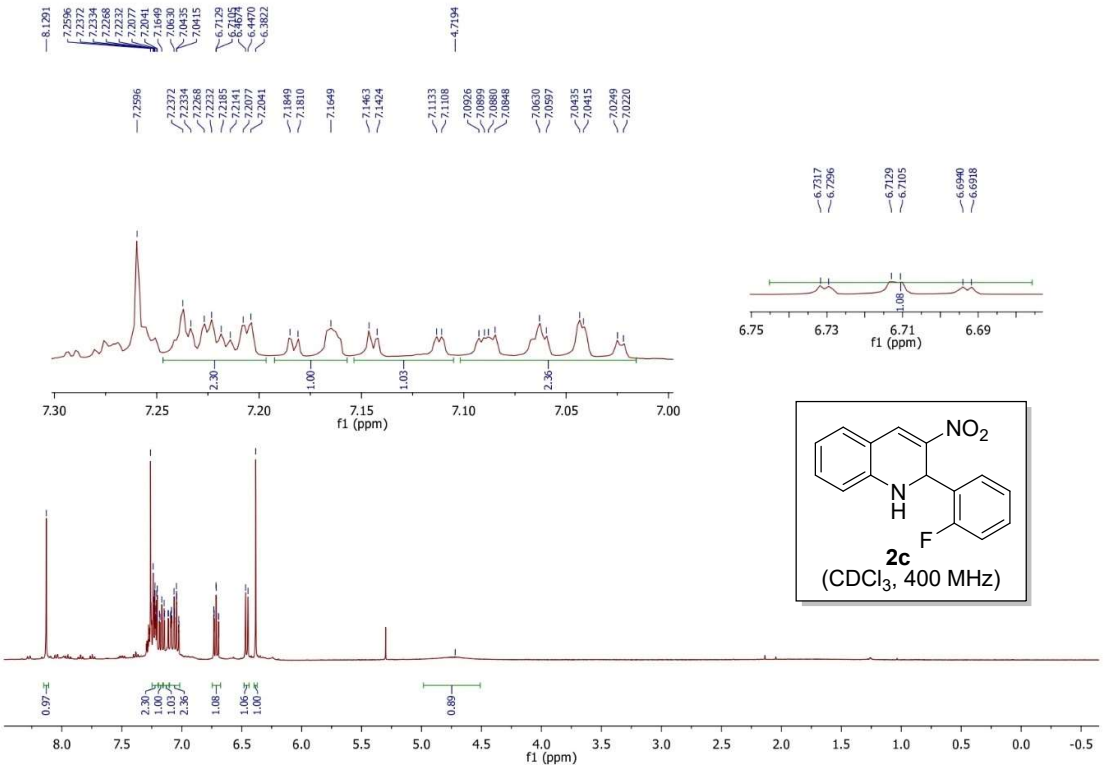
^{1}H NMR of 2b ($CDCl_3$, 400 MHz)



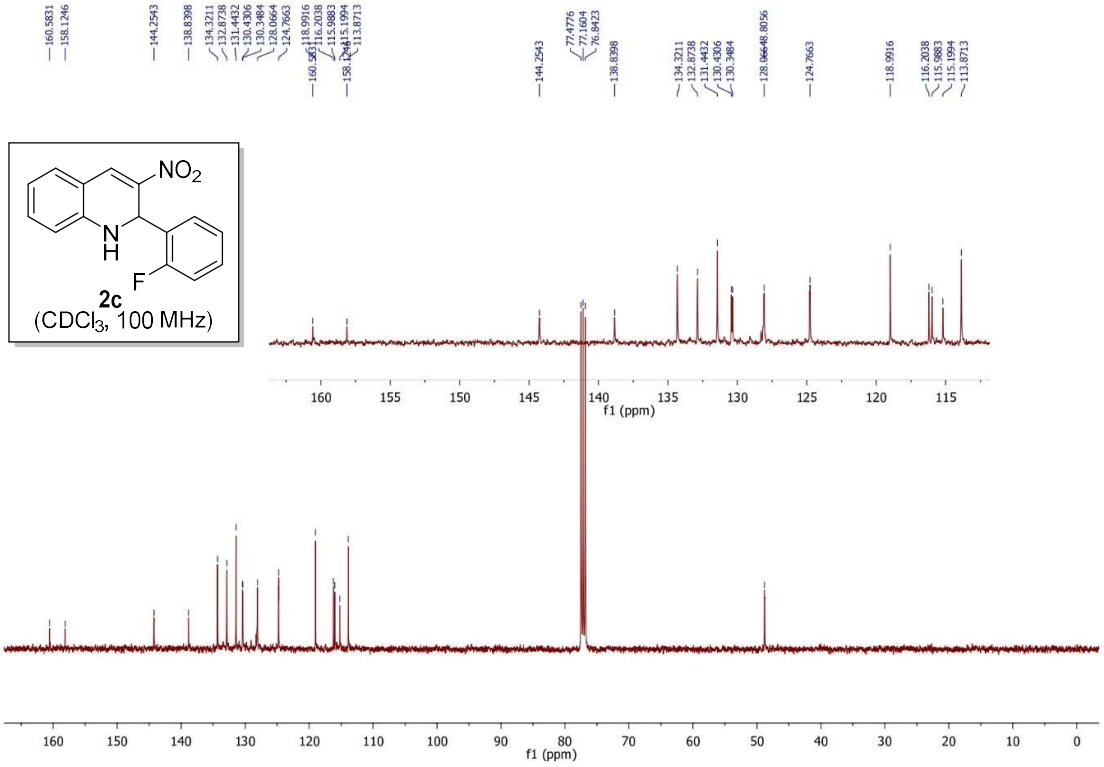
^{13}C NMR of 2b ($CDCl_3$, 100 MHz)



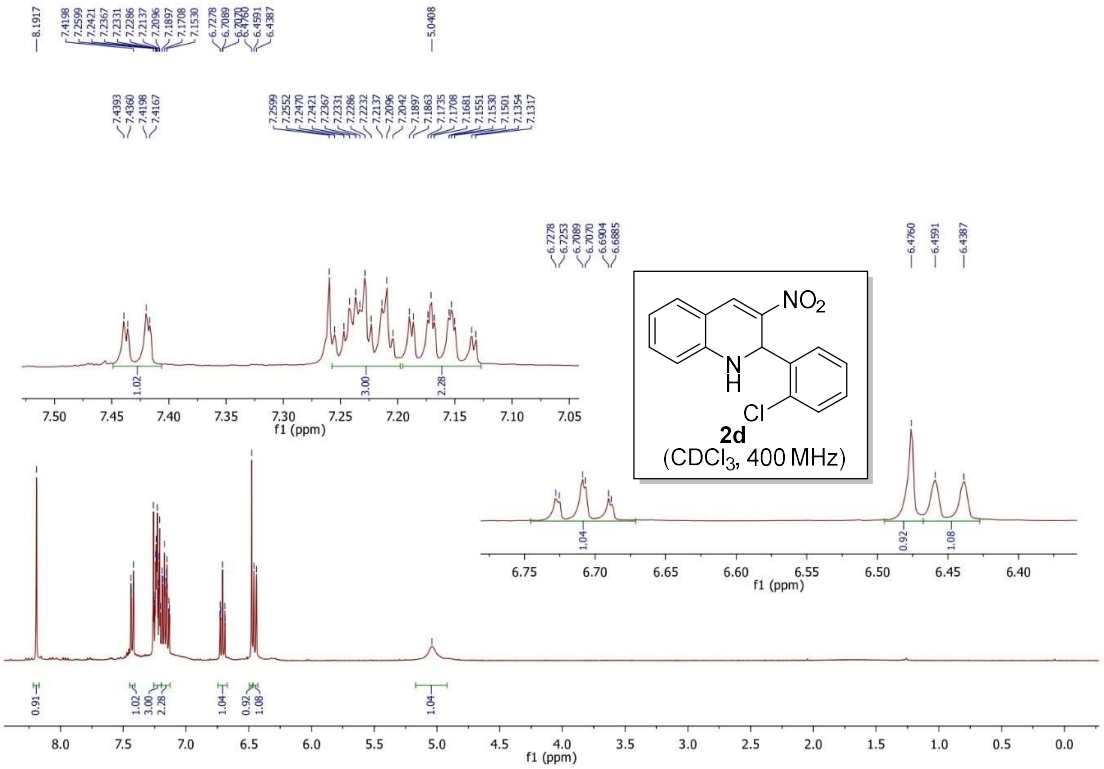
^{1}H NMR of 2c ($CDCl_3$, 400 MHz)



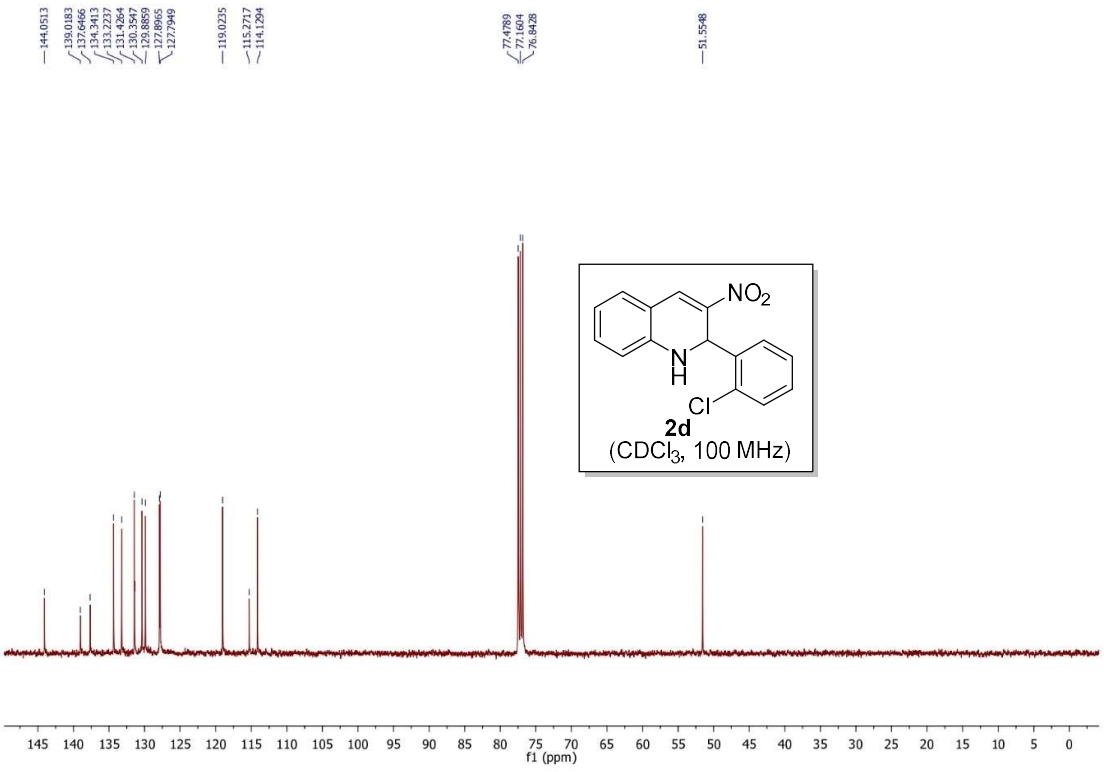
^{13}C NMR of 2c ($CDCl_3$, 100 MHz)



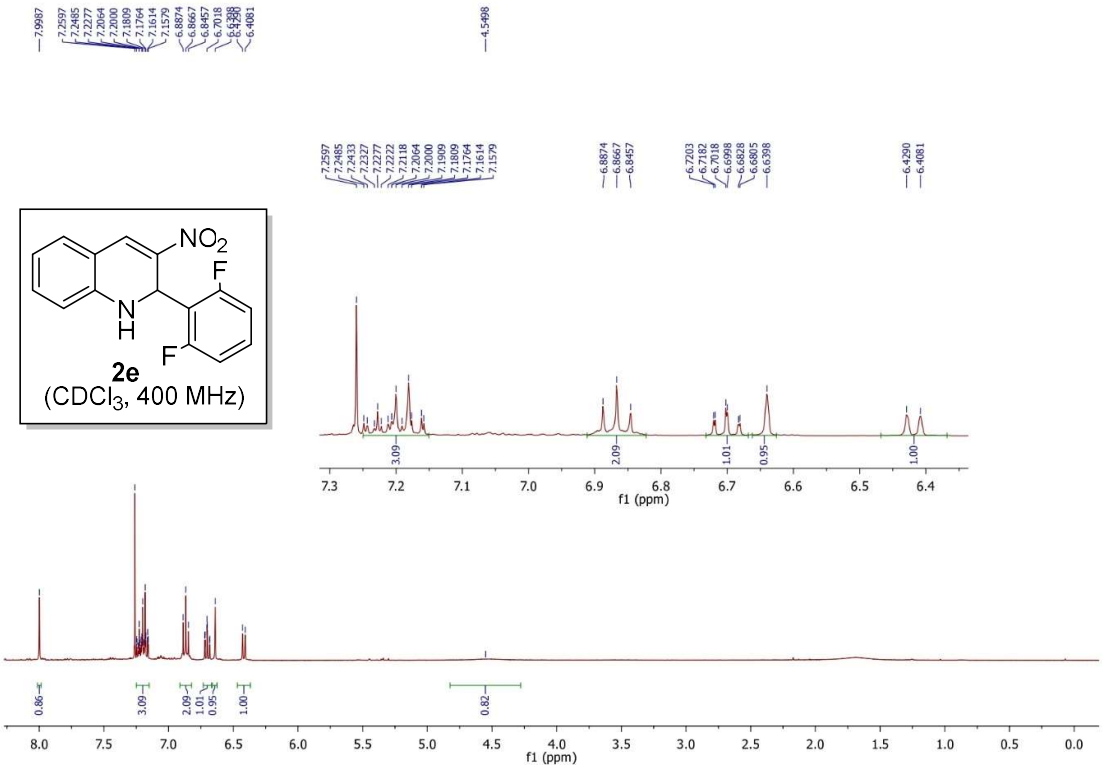
^{1}H NMR of 2d ($CDCl_3$, 400 MHz)



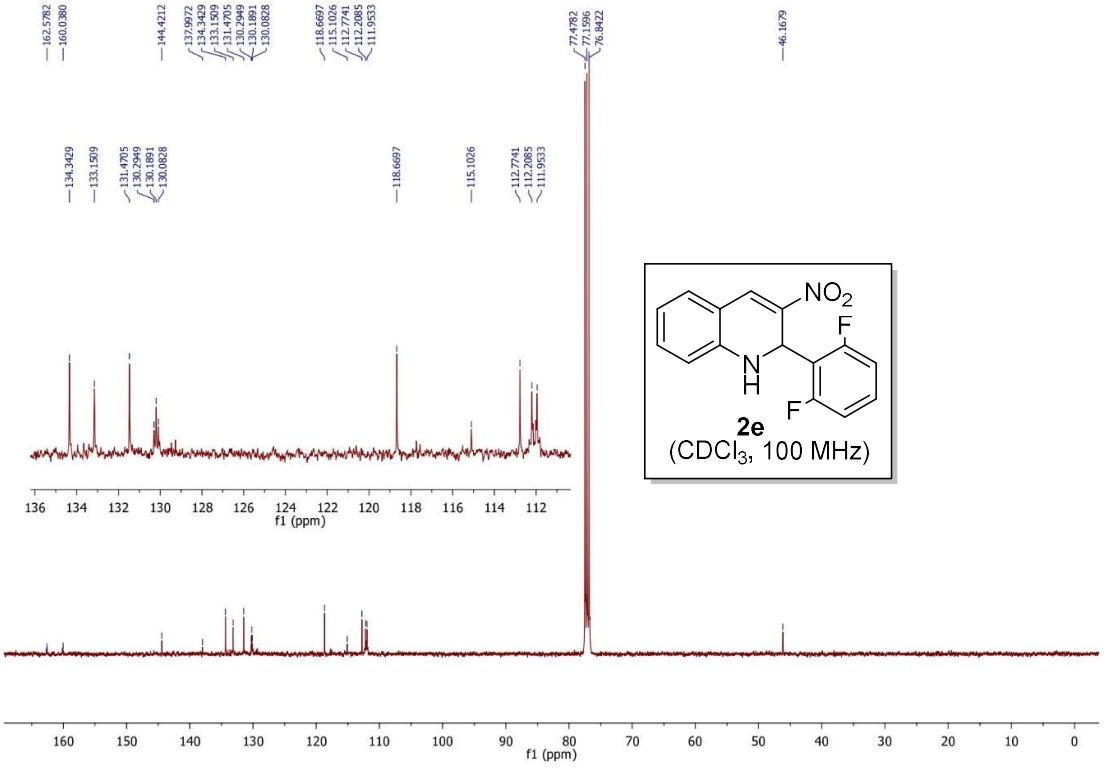
^{13}C NMR of 2d ($CDCl_3$, 100 MHz)



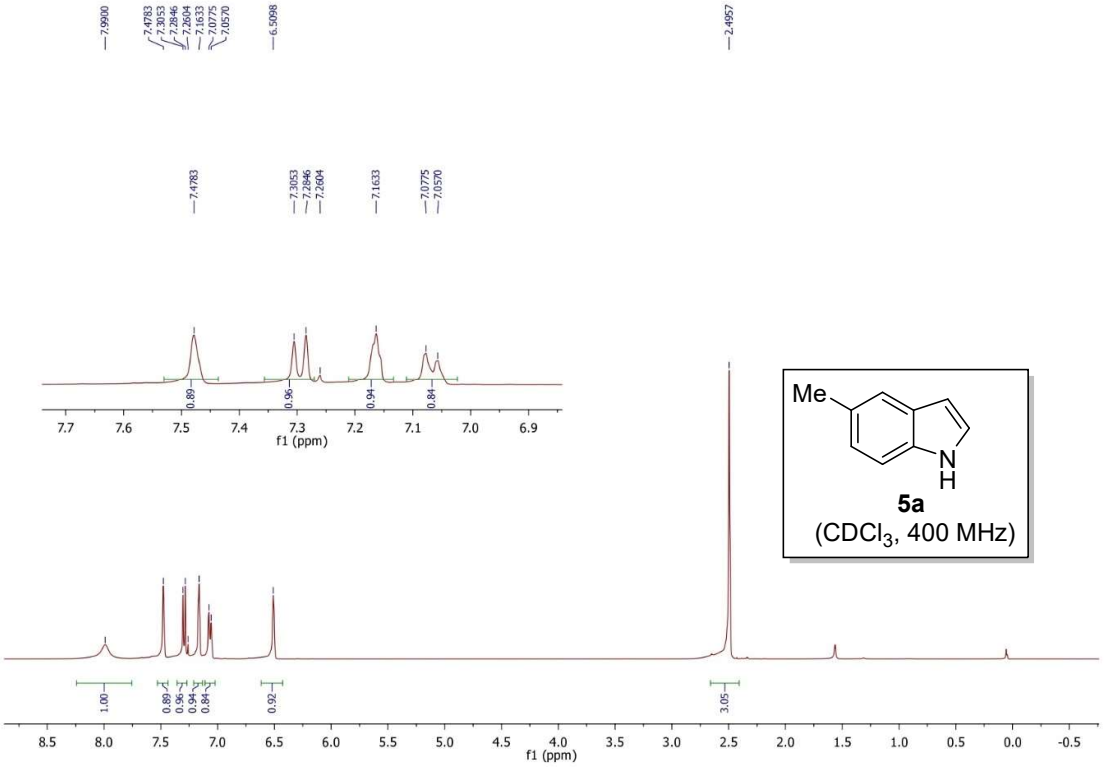
^{1}H NMR of 2e ($CDCl_3$, 400 MHz)



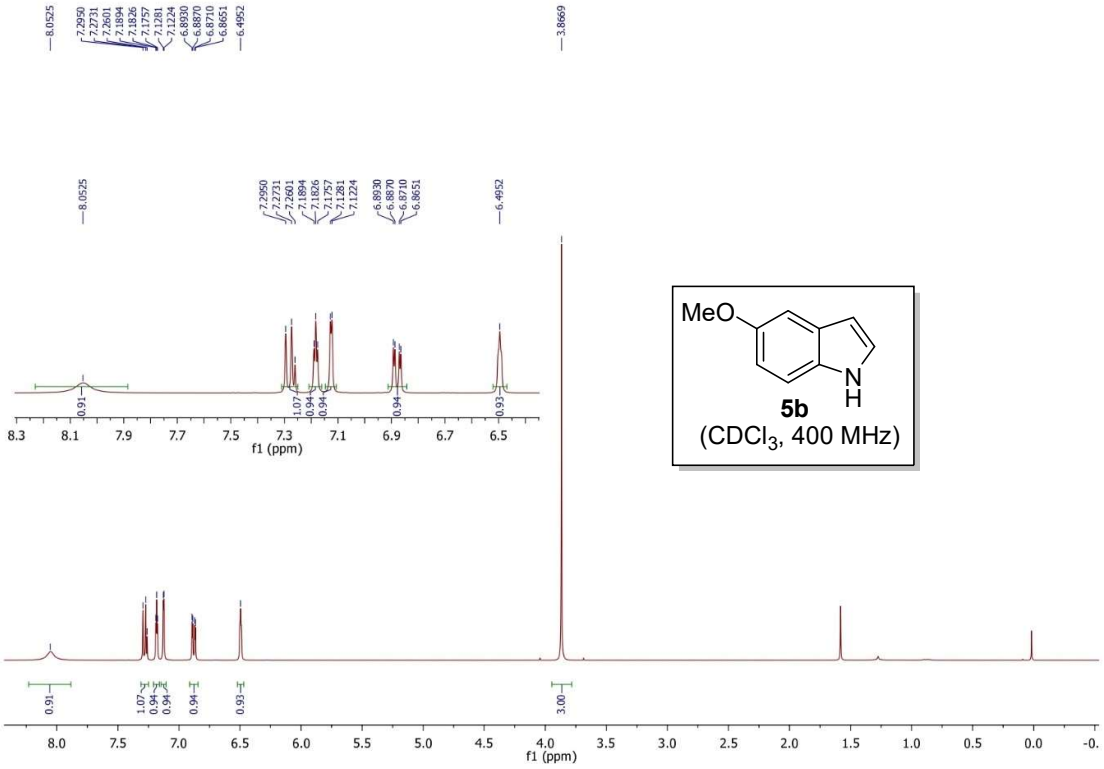
^{13}C NMR of 2e ($CDCl_3$, 100 MHz)



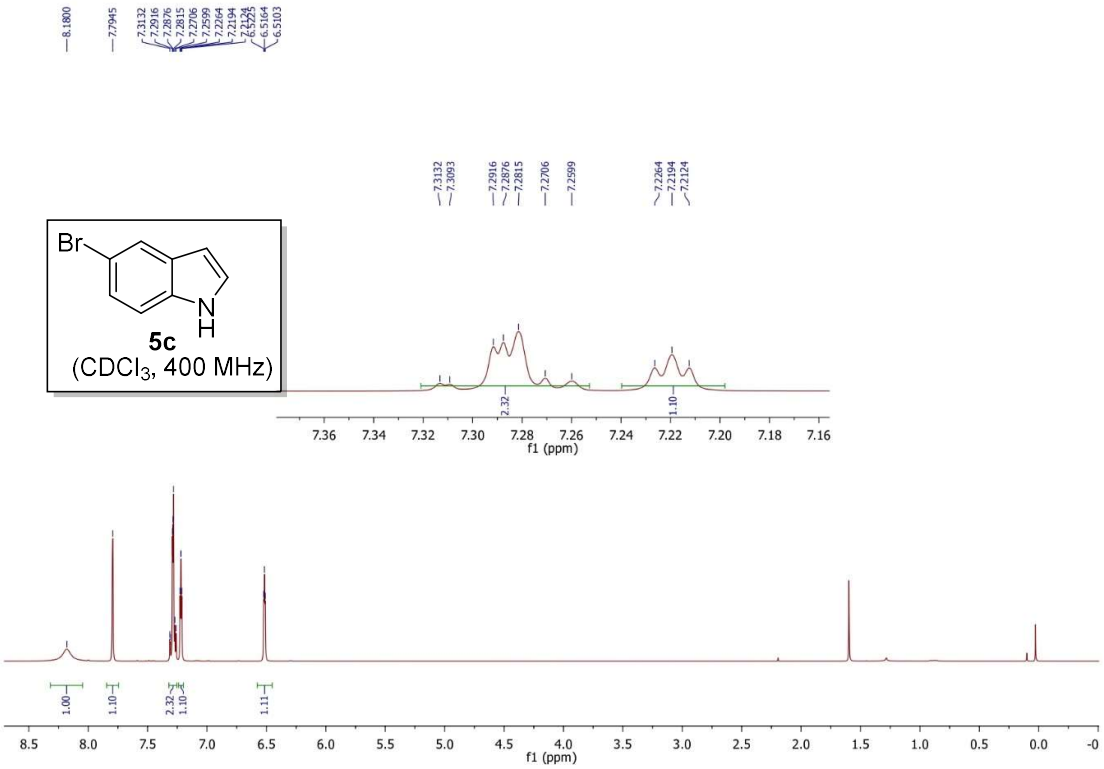
^{1}H NMR of 5a ($CDCl_3$, 400 MHz)



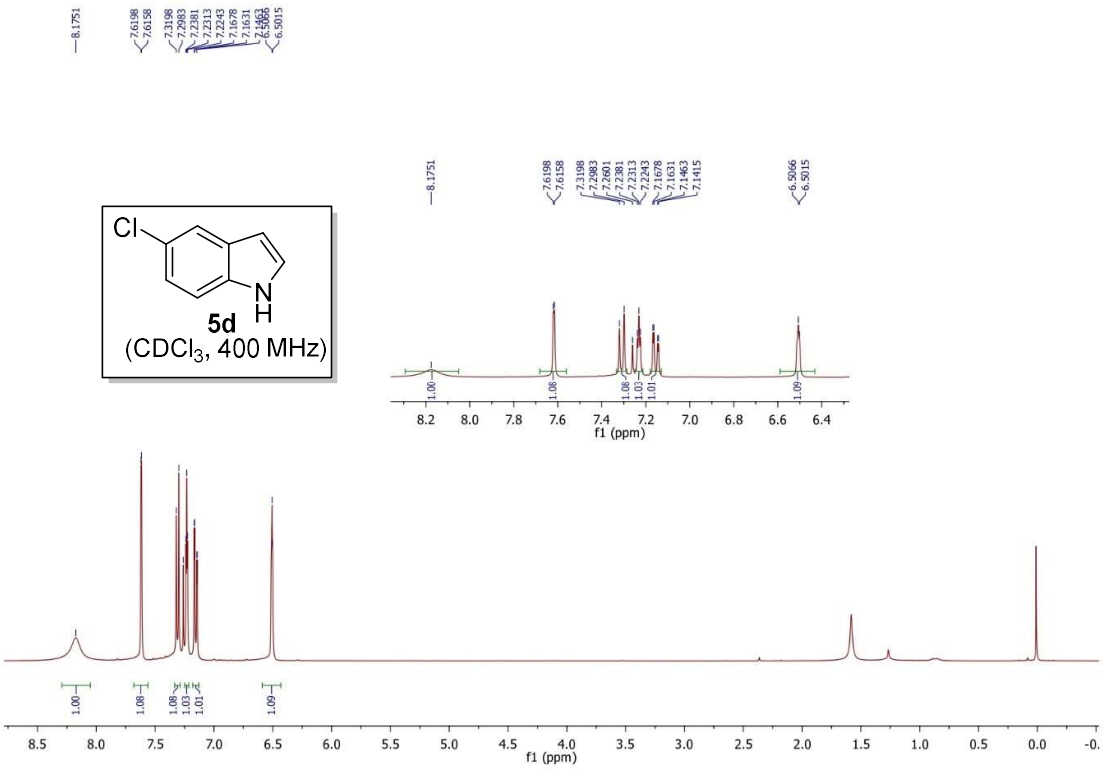
^{1}H NMR of 5b ($CDCl_3$, 400 MHz)



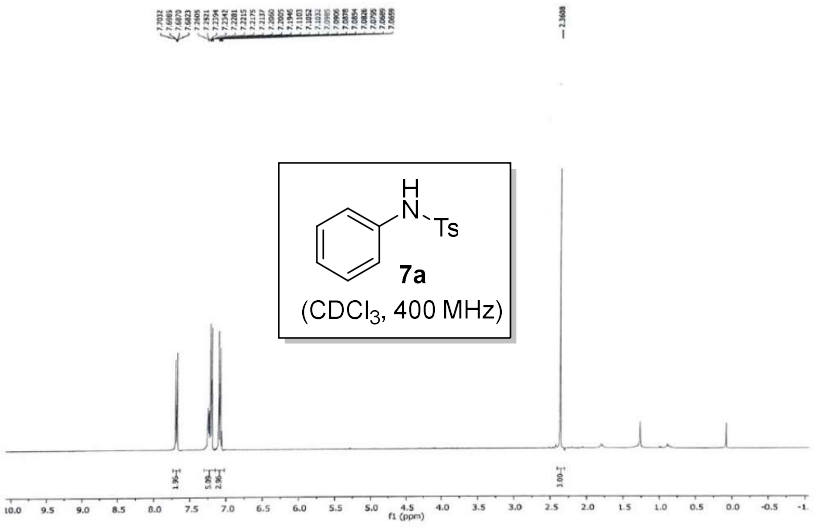
^{1}H NMR of 5c ($CDCl_3$, 400 MHz)



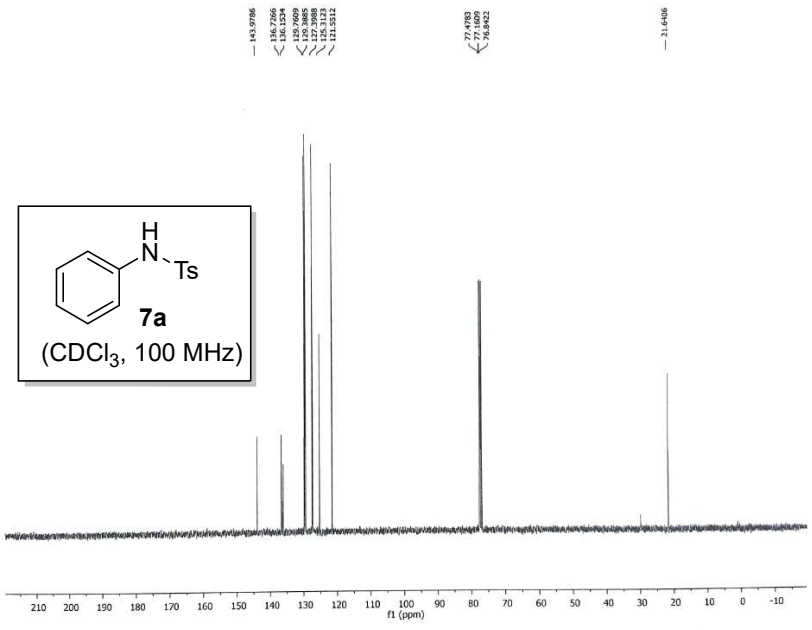
^{1}H NMR of 5d ($CDCl_3$, 400 MHz)



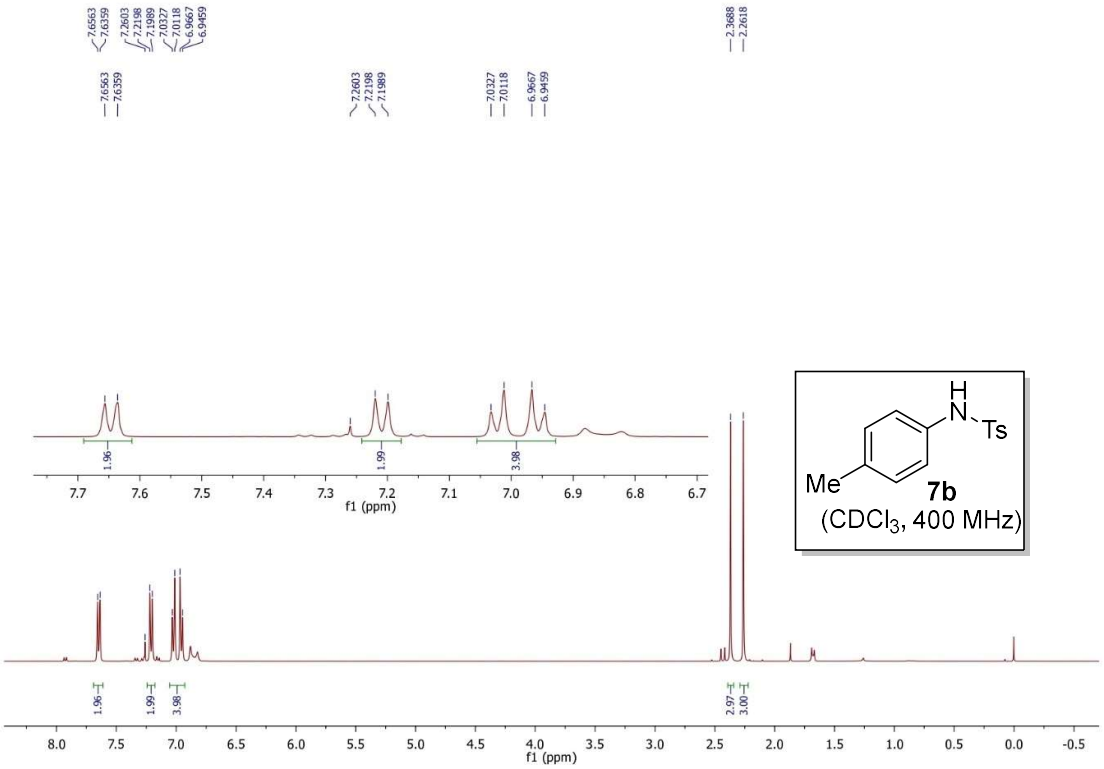
^{1}H NMR of 7a ($CDCl_3$, 400 MHz)



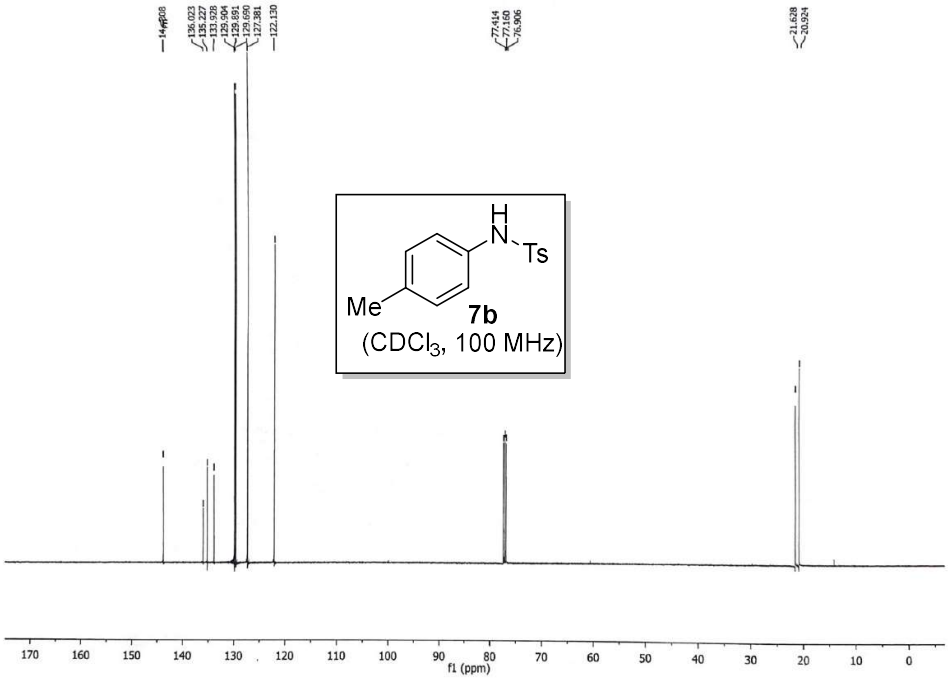
^{13}C NMR of 7a ($CDCl_3$, 100 MHz)



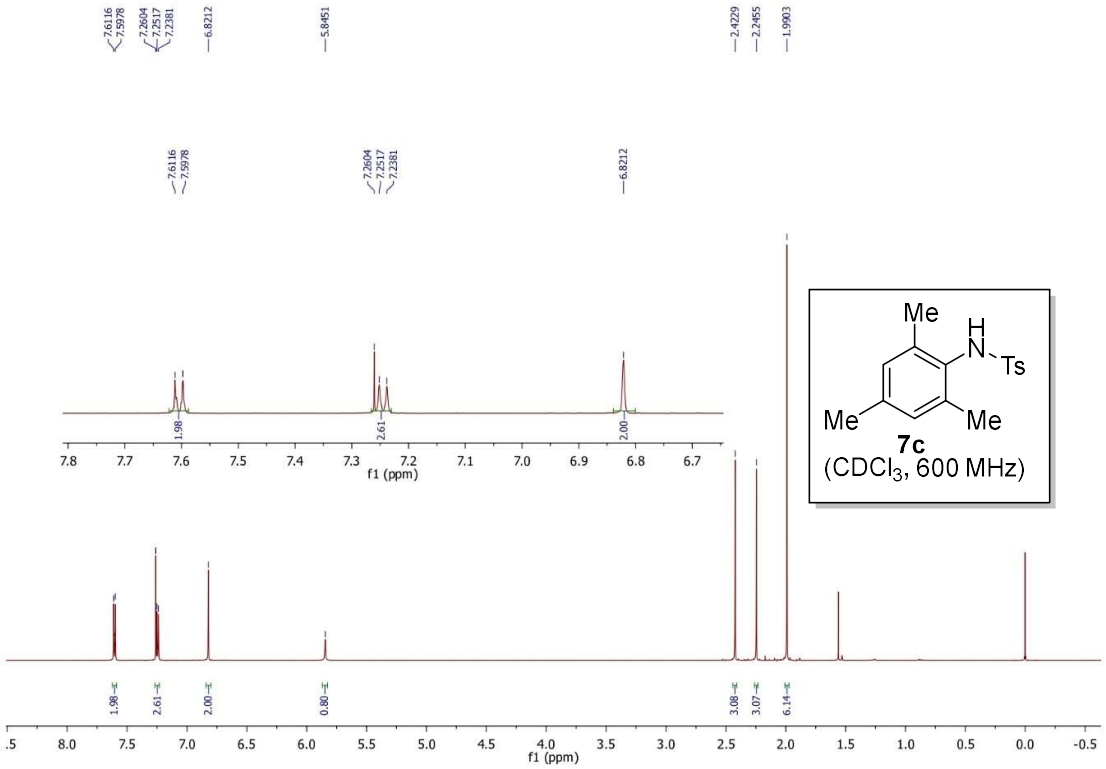
^{1}H NMR of 7b ($CDCl_3$, 400 MHz)



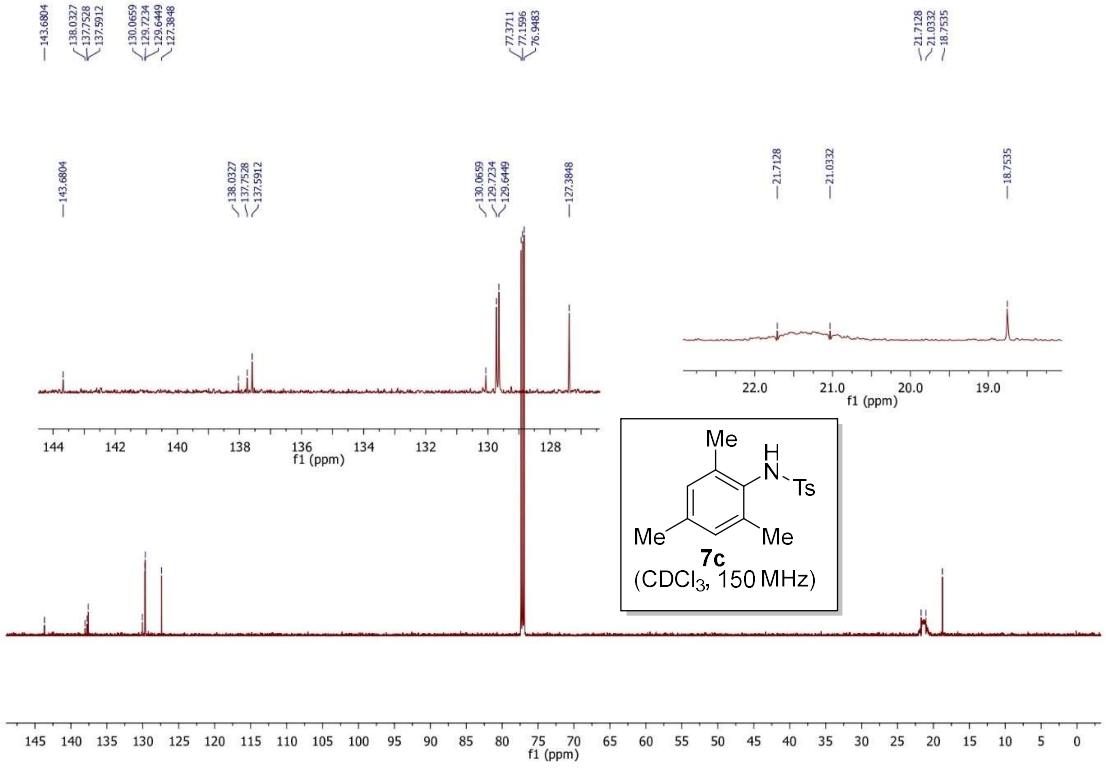
^{13}C NMR of 7b ($CDCl_3$, 100 MHz)



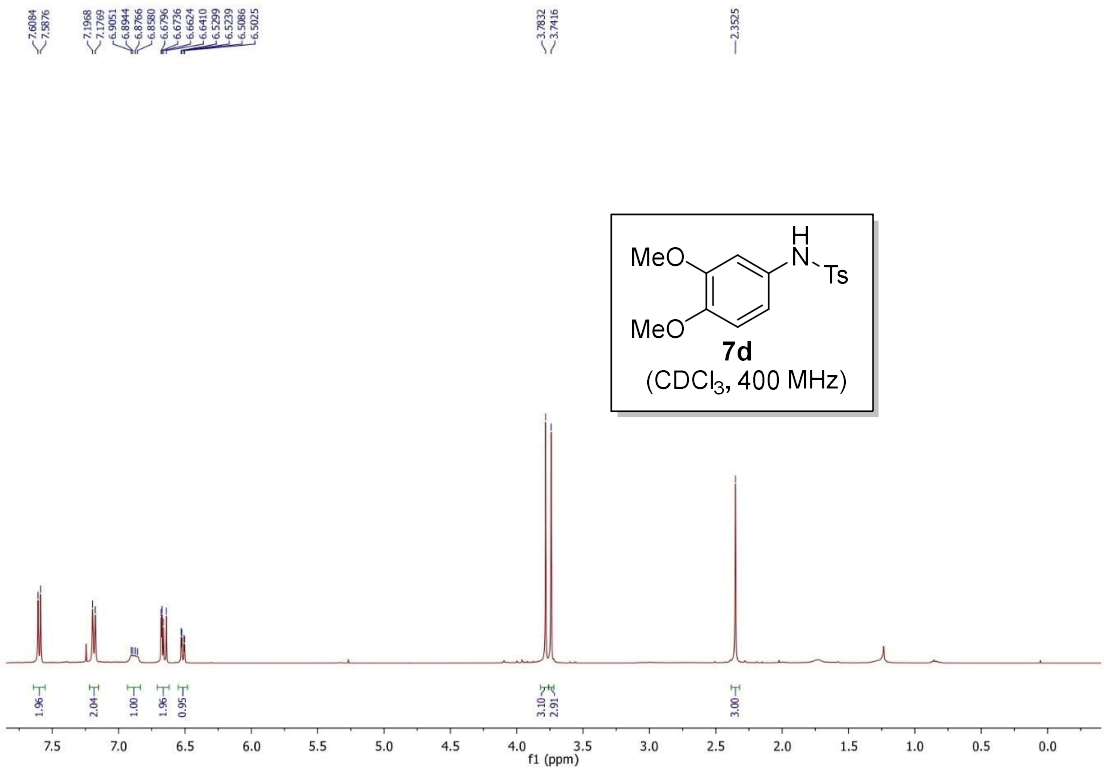
^{1}H NMR of 7c ($CDCl_3$, 600 MHz)



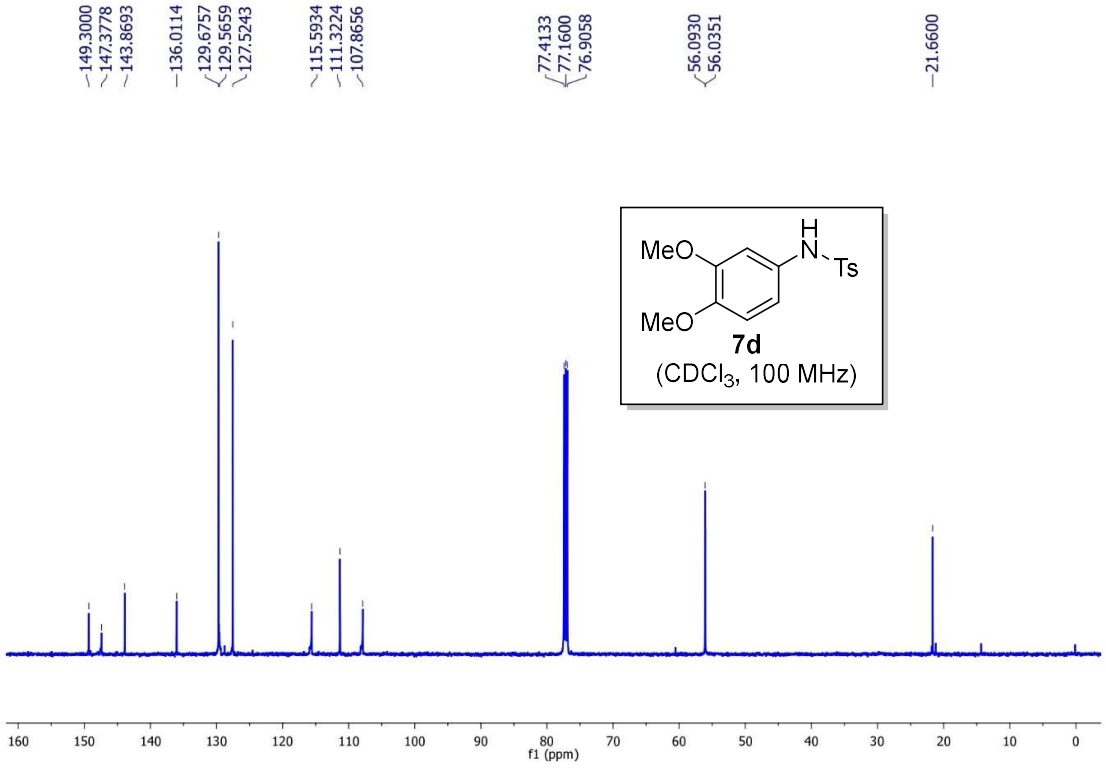
^{13}C NMR of 7c ($CDCl_3$, 150 MHz)



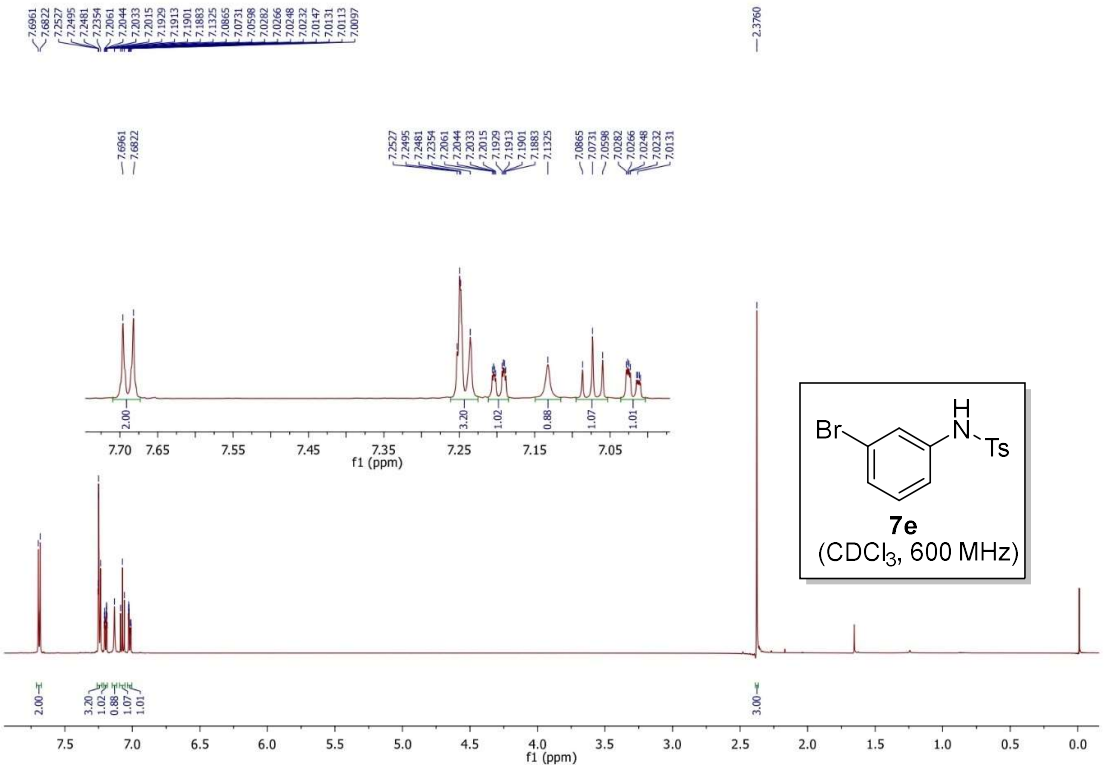
^{1}H NMR of 7d ($CDCl_3$, 400 MHz)



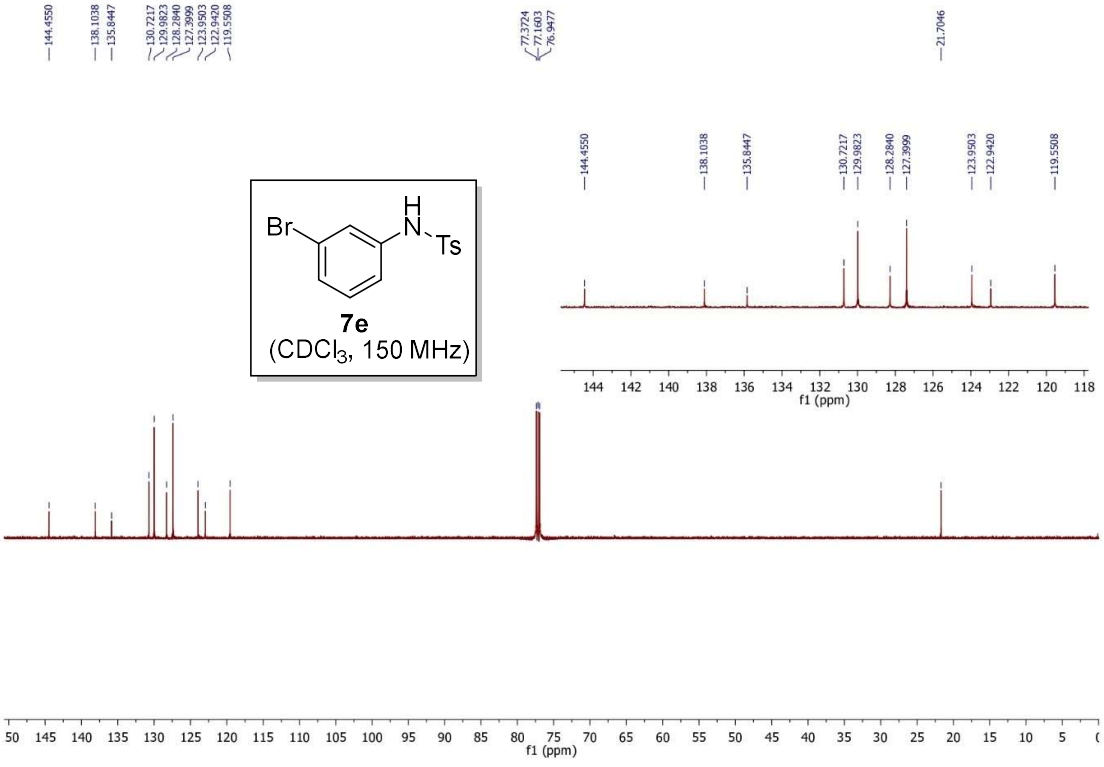
^{13}C NMR of 7d ($CDCl_3$, 100 MHz)



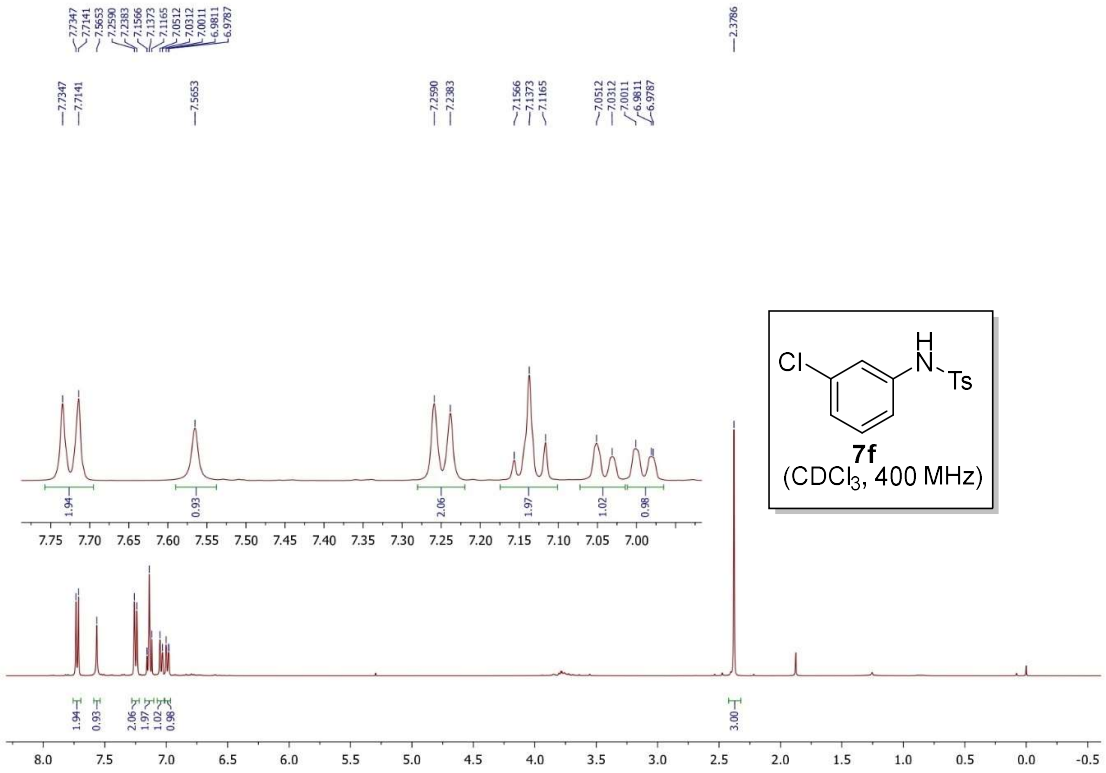
^{1}H NMR of 7e ($CDCl_3$, 600 MHz)



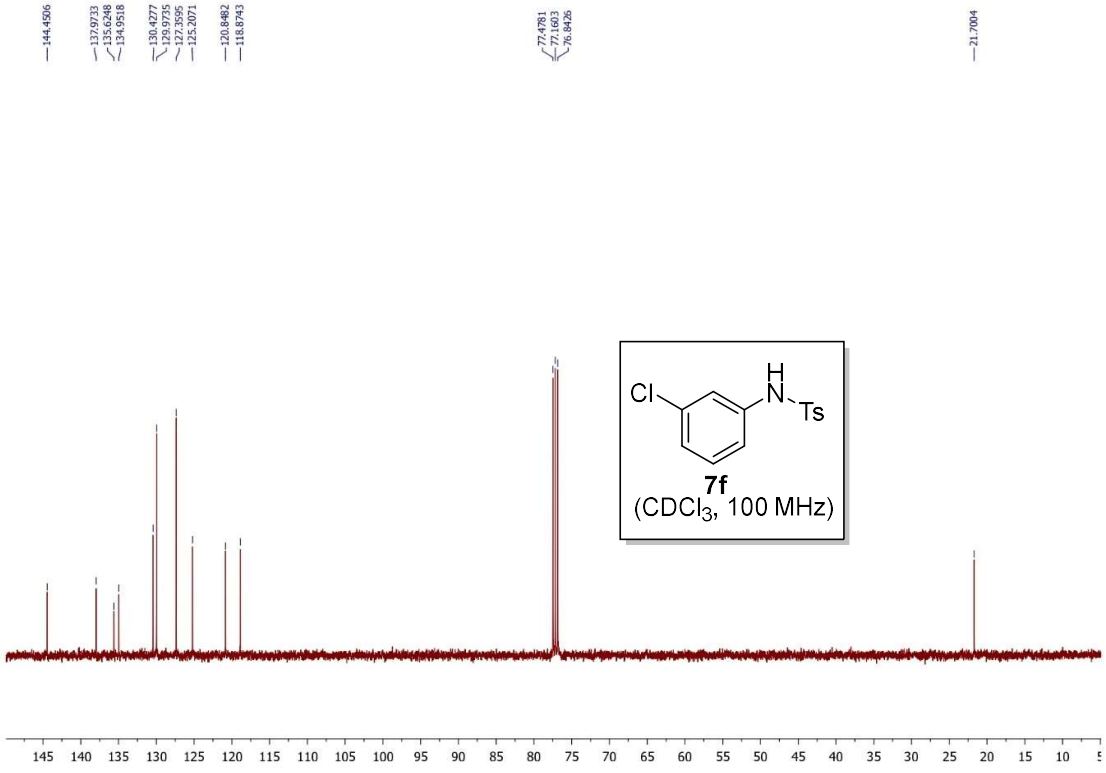
^{13}C NMR of 7e ($CDCl_3$, 150 MHz)



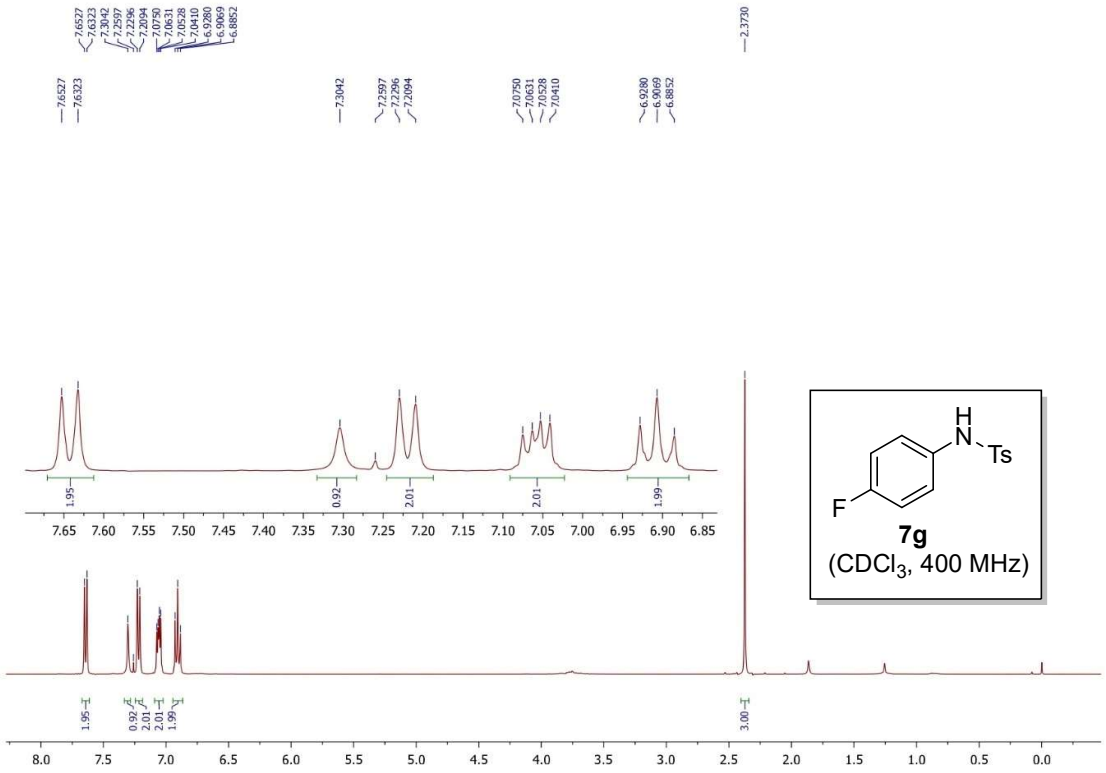
^{1}H NMR of 7f ($CDCl_3$, 400 MHz)



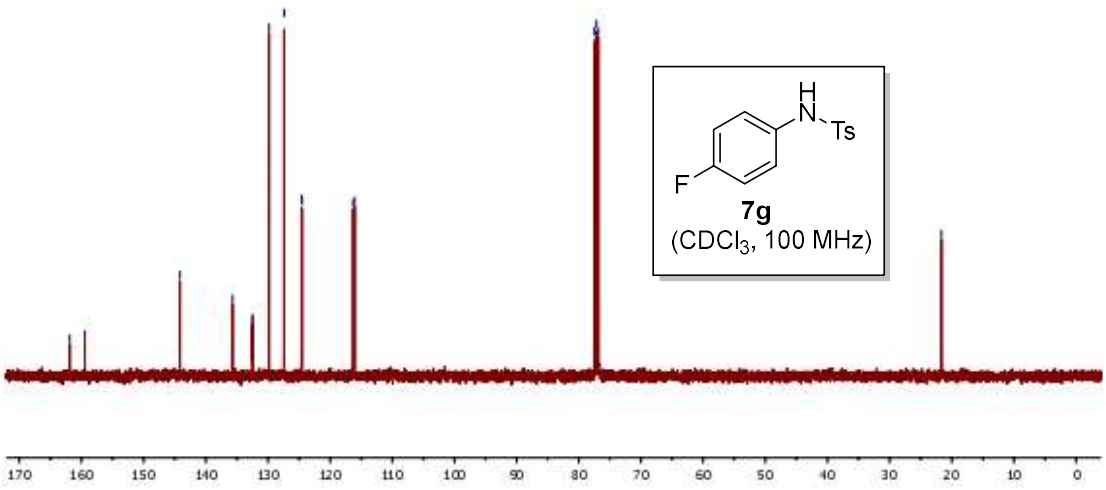
^{13}C NMR of 7f ($CDCl_3$, 100 MHz)



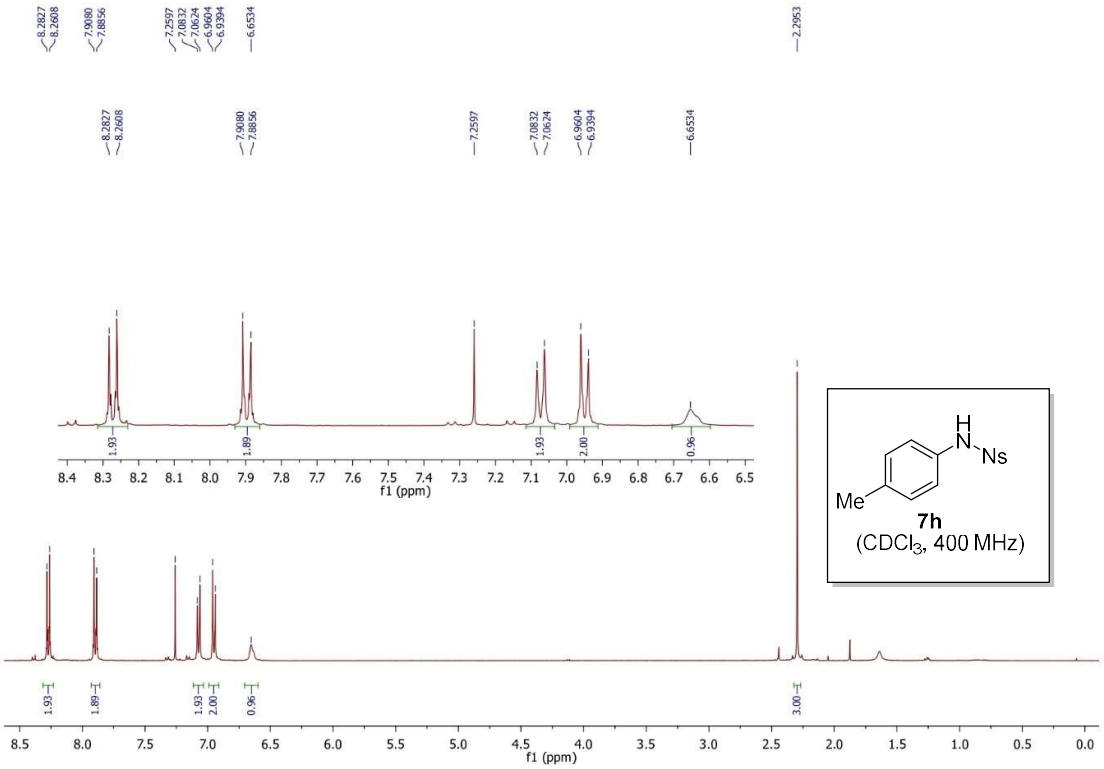
^{1}H NMR of 7g ($CDCl_3$, 400 MHz)



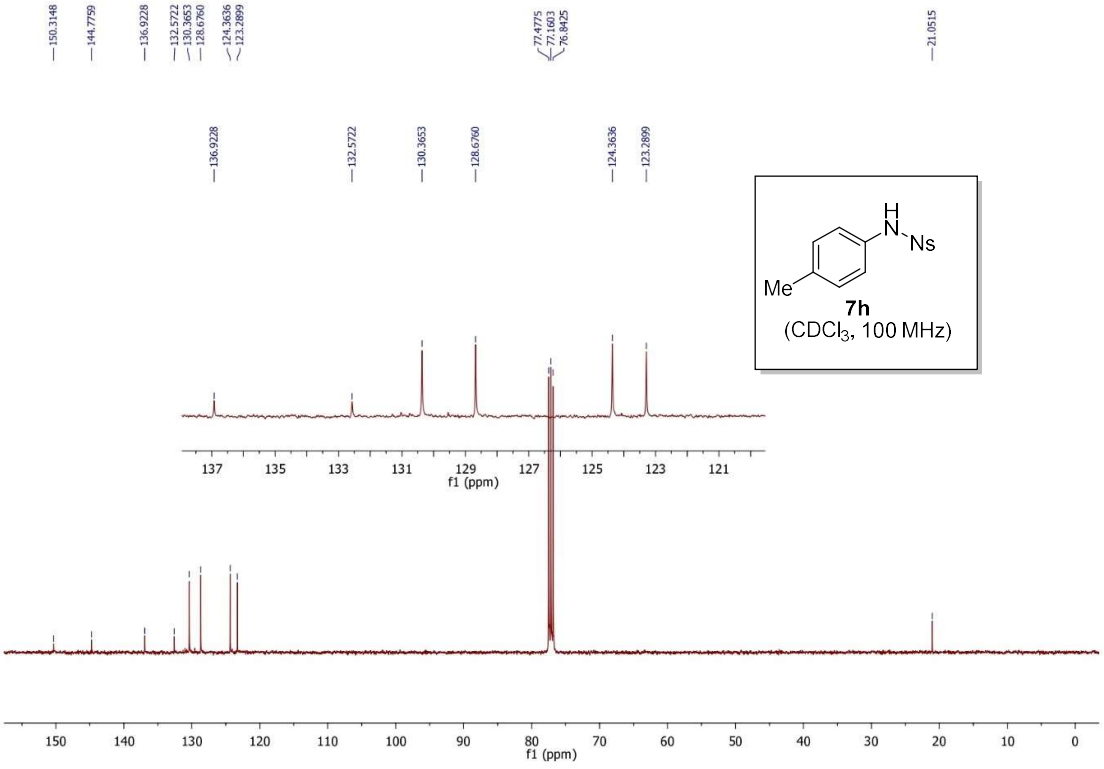
^{13}C NMR of 7g ($CDCl_3$, 100 MHz)



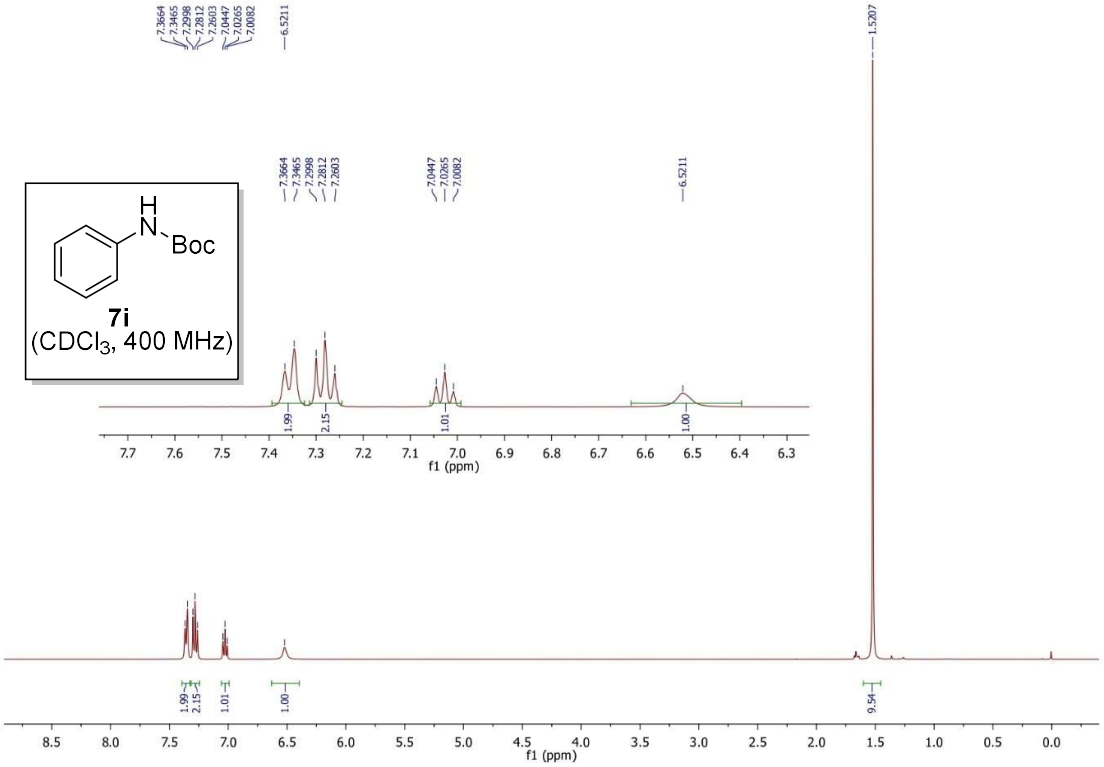
^{1}H NMR of 7h ($CDCl_3$, 400 MHz)



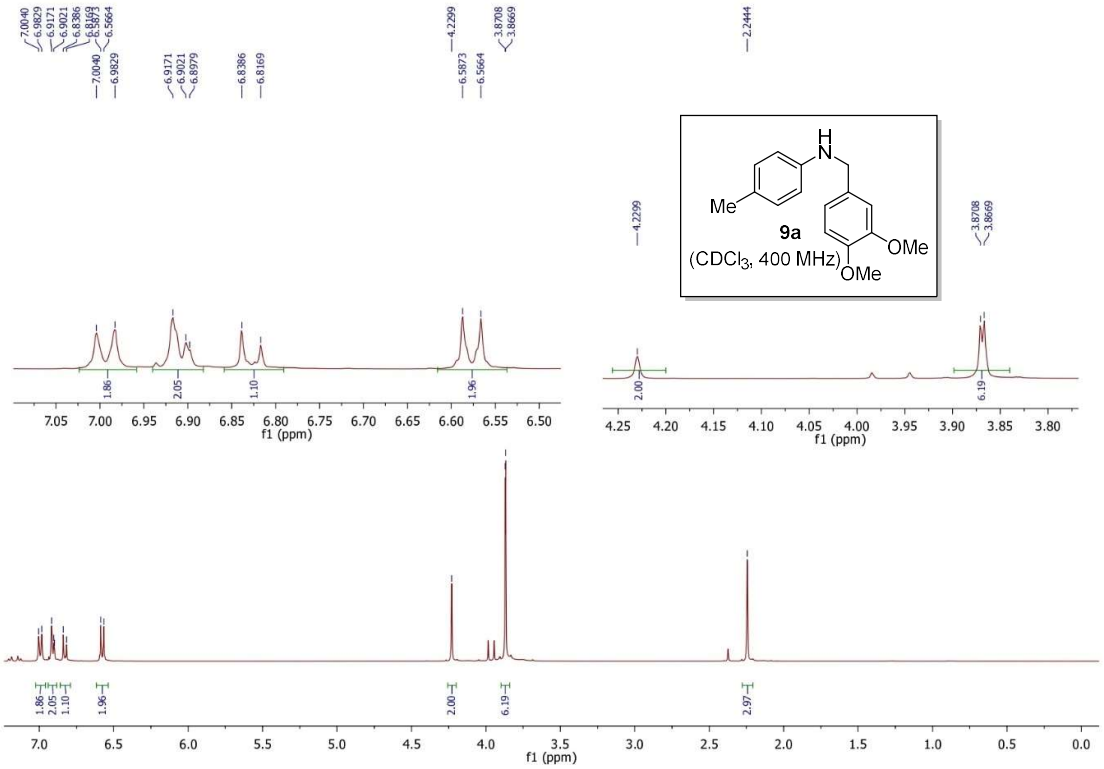
^{13}C NMR of 7h ($CDCl_3$, 100 MHz)



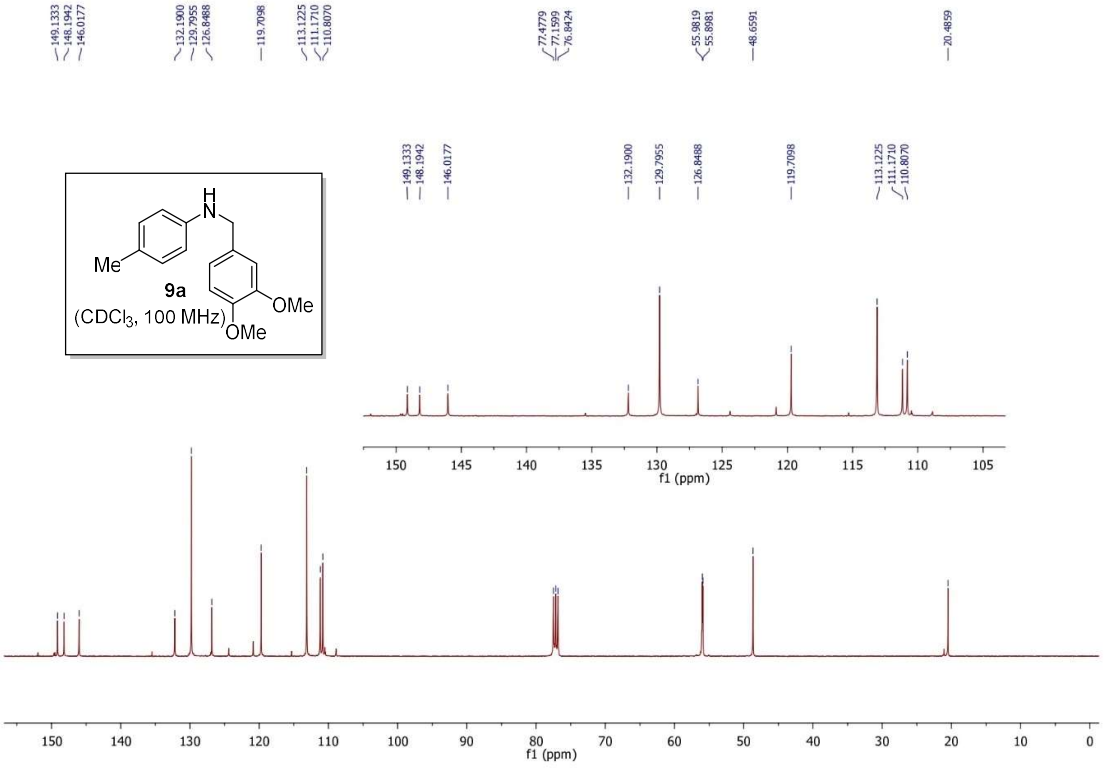
^{1}H NMR of 7i ($CDCl_3$, 400 MHz)



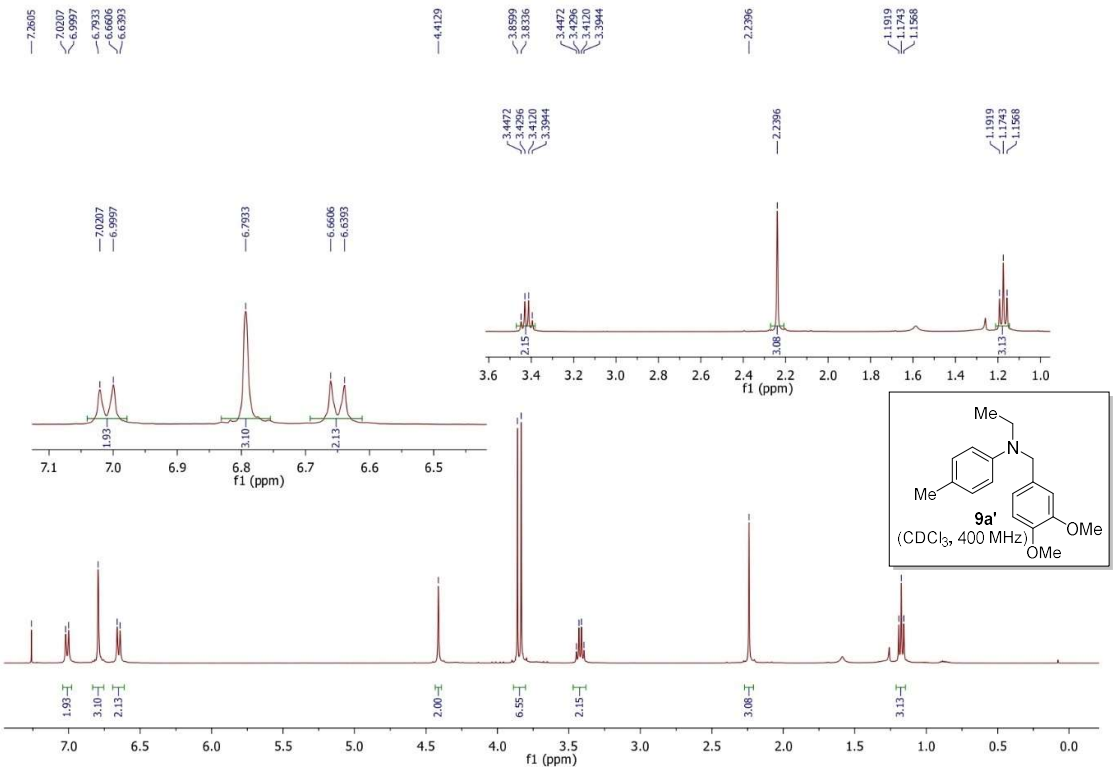
^{1}H NMR of 9a ($CDCl_3$, 400 MHz)



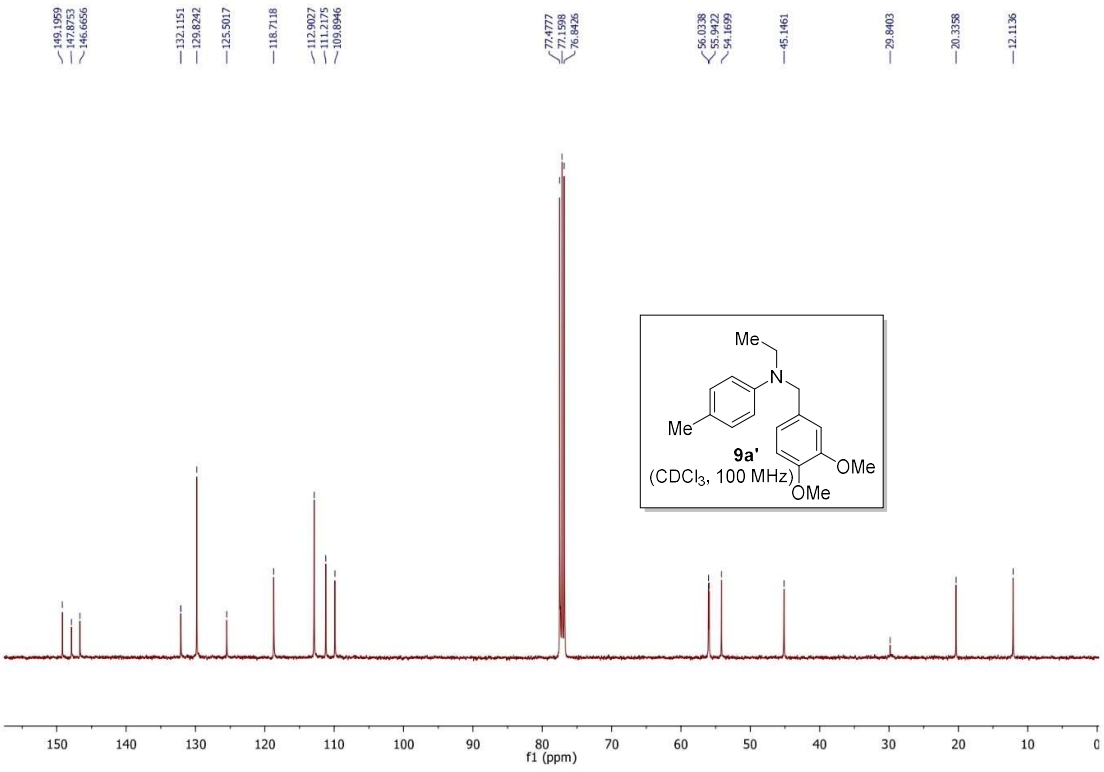
^{13}C NMR of 9a ($CDCl_3$, 100 MHz)



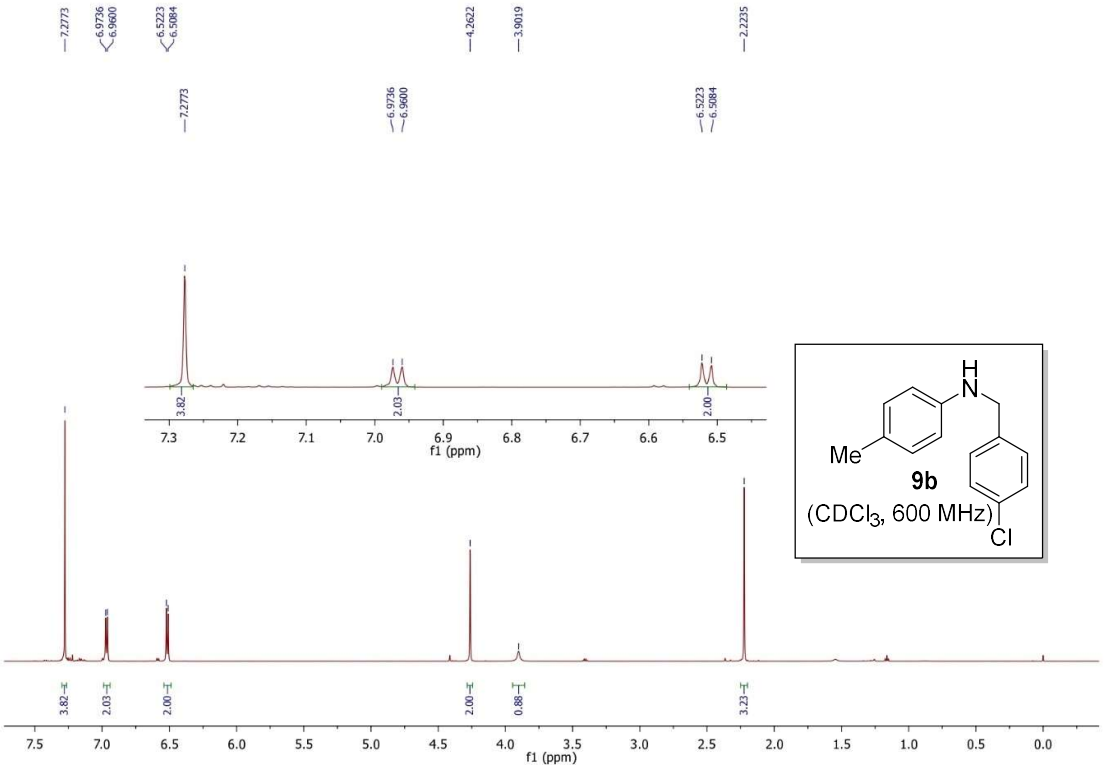
^{1}H NMR of 9a′ ($CDCl_3$, 400 MHz)



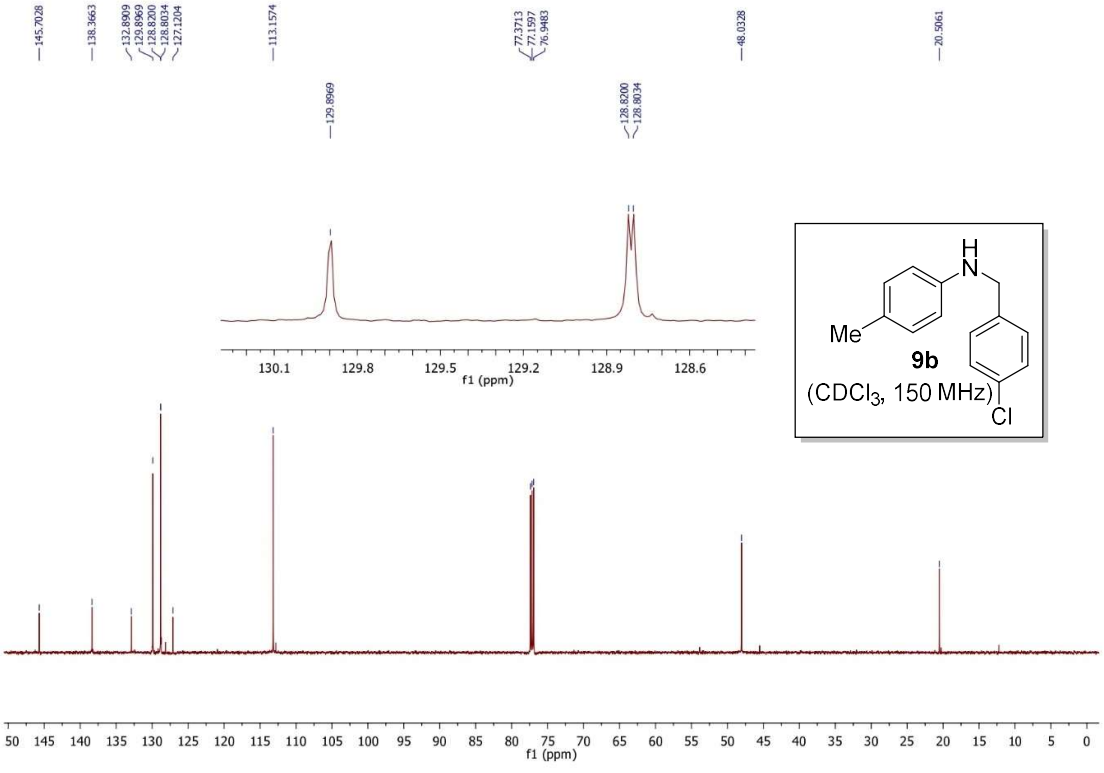
^{13}C NMR of 9a′ ($CDCl_3$, 100 MHz)



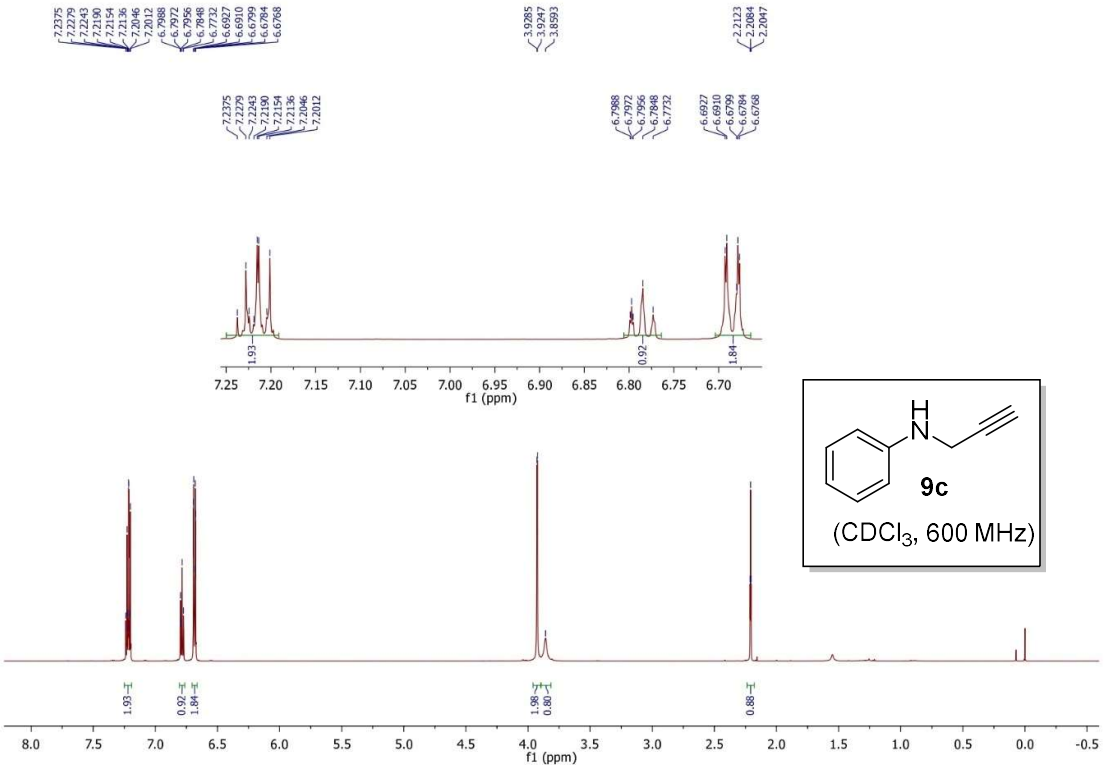
^{1}H NMR of 9b ($CDCl_3$, 600 MHz)



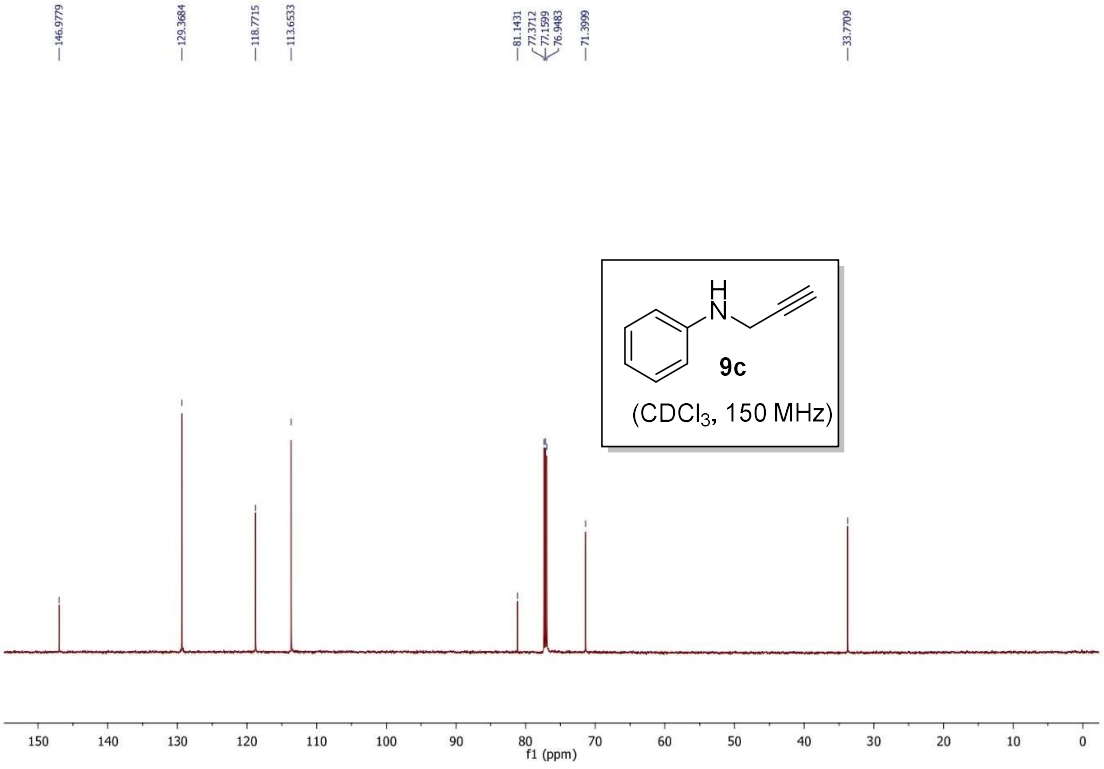
^{13}C NMR of 9b ($CDCl_3$, 150 MHz)



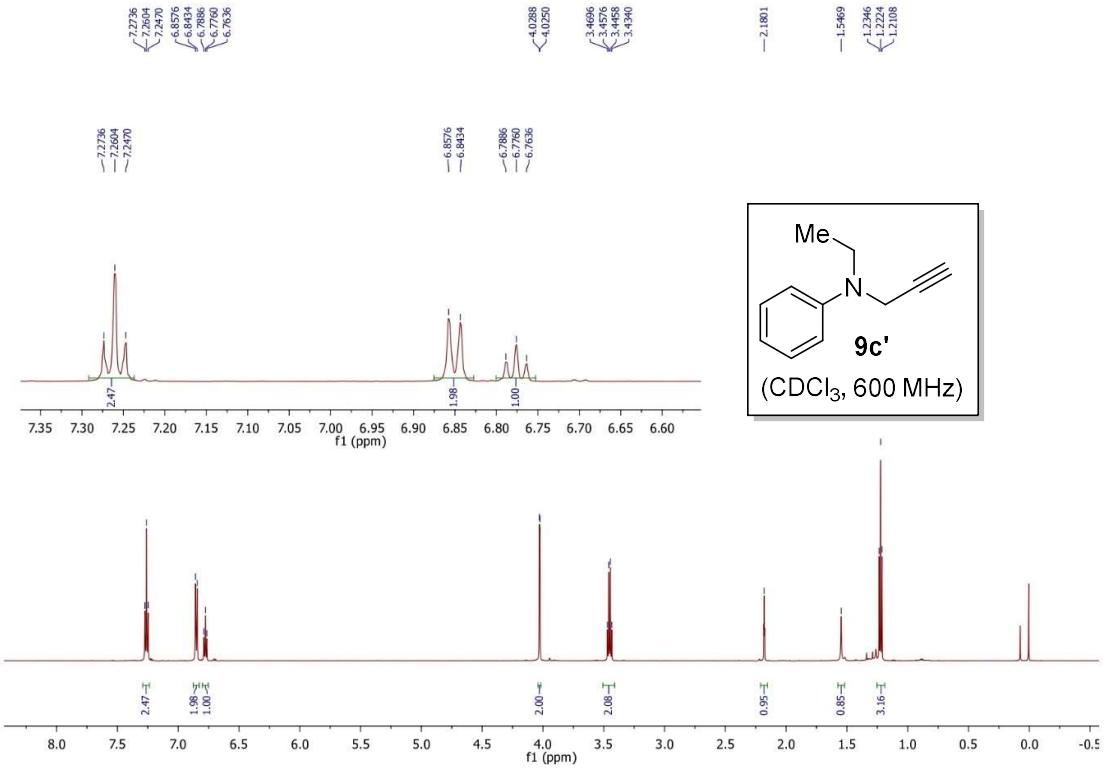
^{1}H NMR of 9c ($CDCl_3$, 600 MHz)



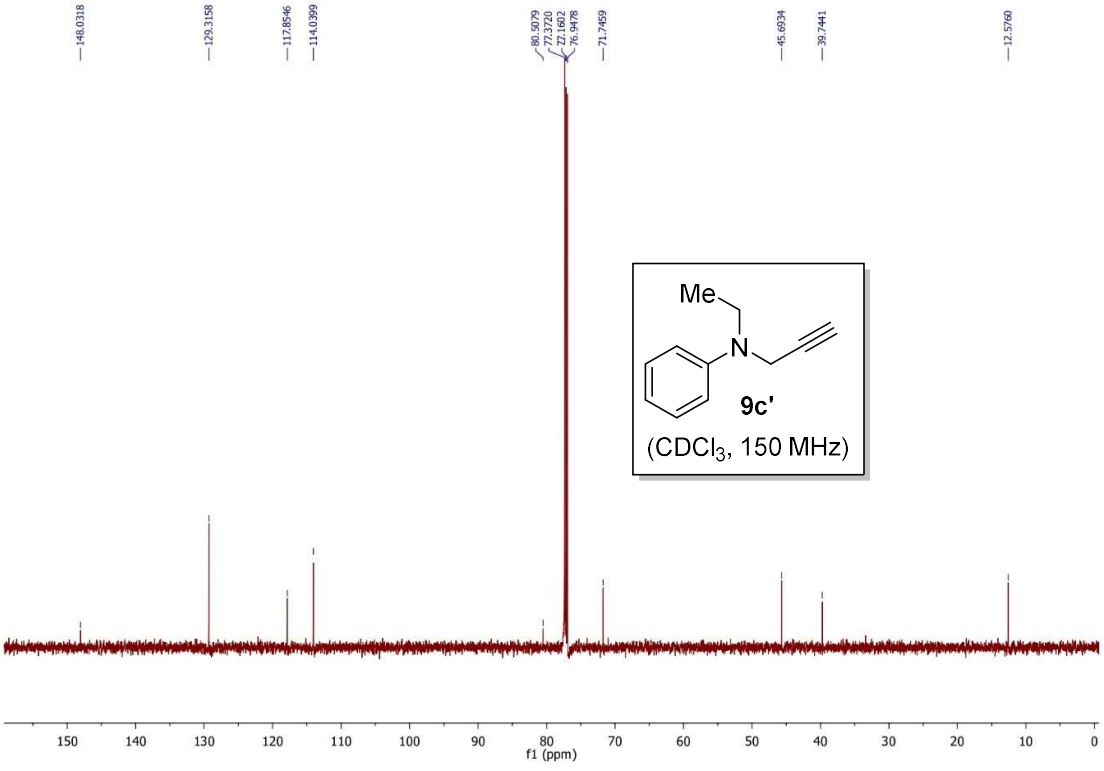
^{13}C NMR of 9c ($CDCl_3$, 150 MHz)



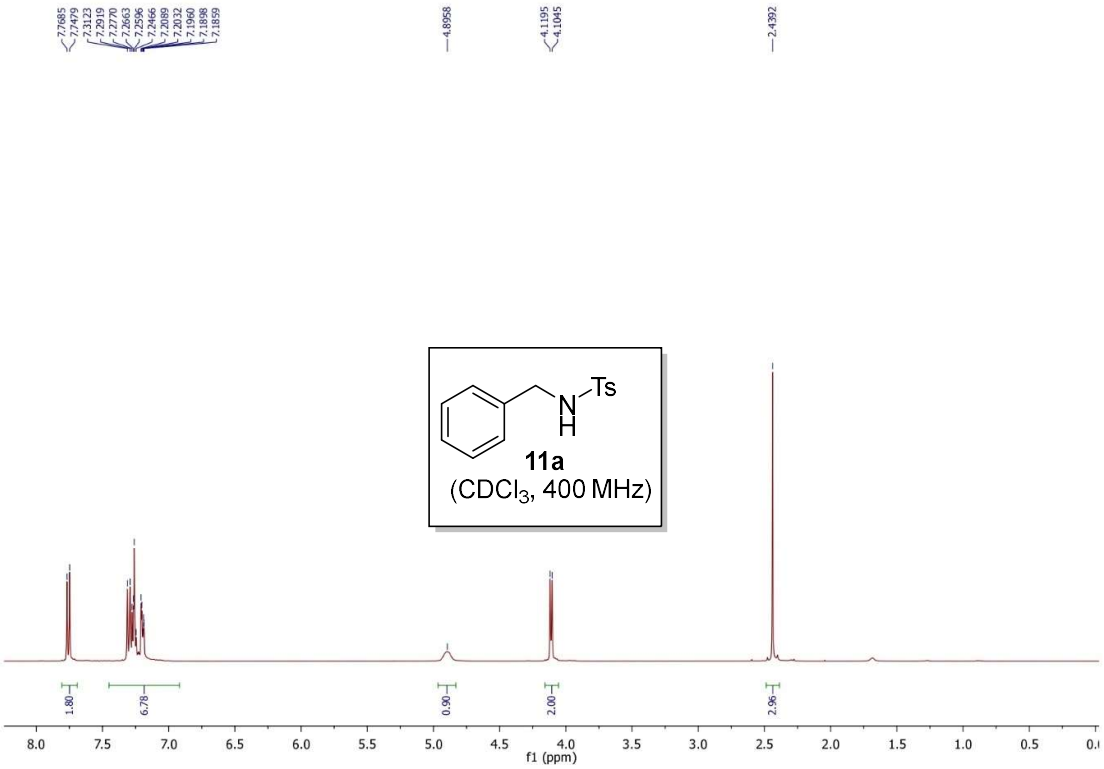
^{1}H NMR of 9c′ ($CDCl_3$, 600 MHz)



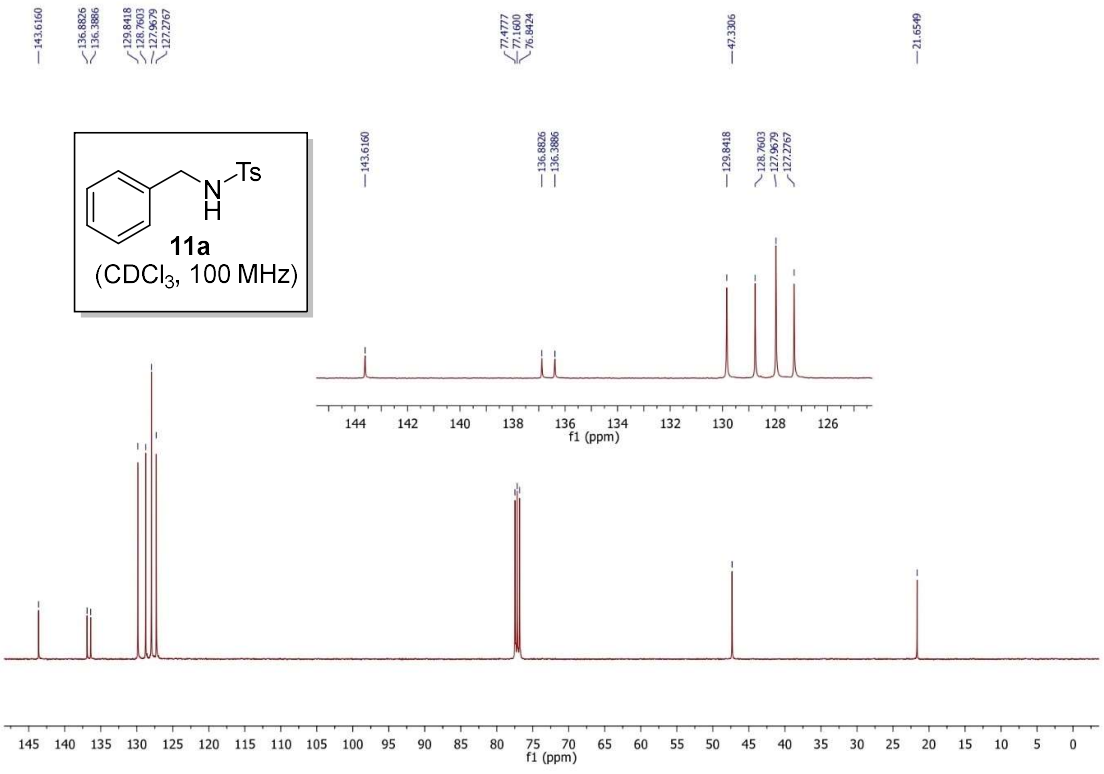
^{13}C NMR of 9c′ ($CDCl_3$, 150 MHz)



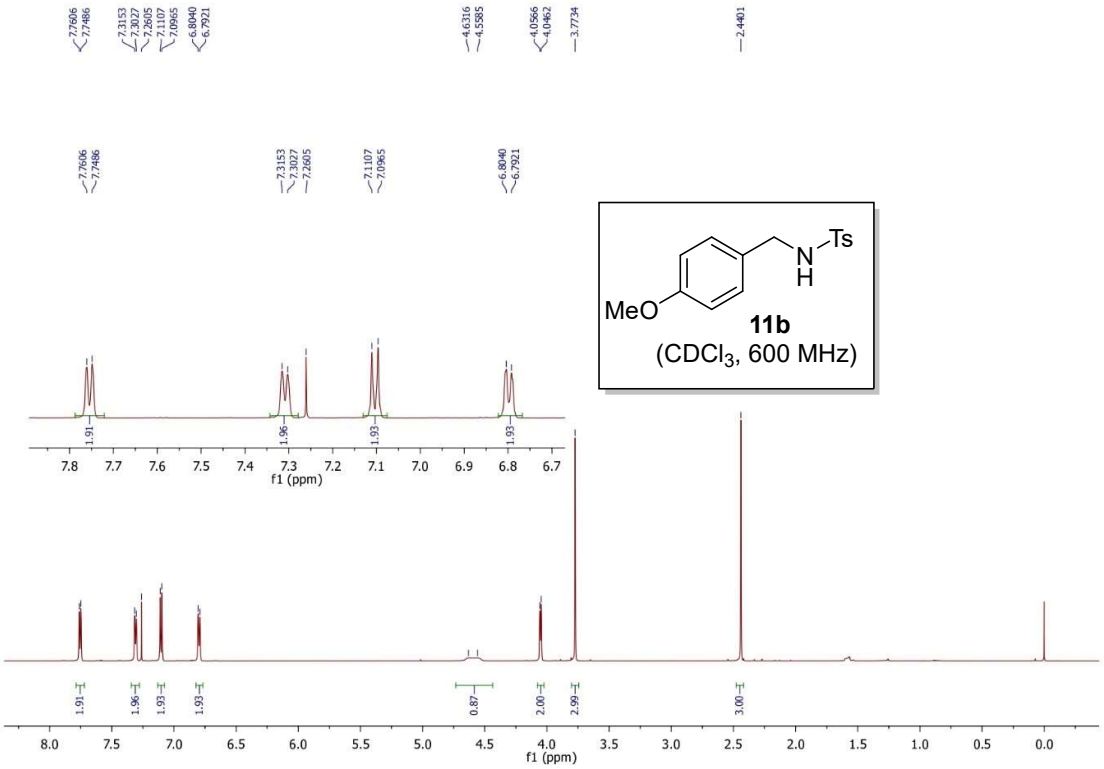
^{1}H NMR of 11a ($CDCl_3$, 400 MHz)



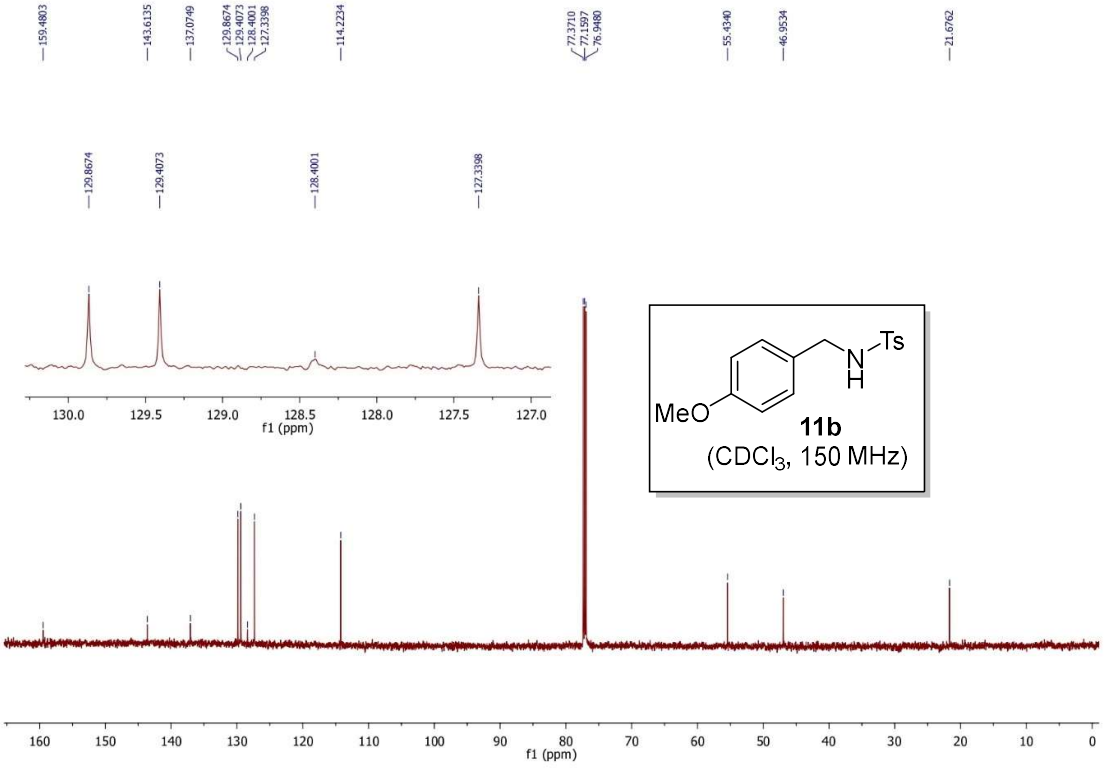
^{13}C NMR of 11a ($CDCl_3$, 100 MHz)



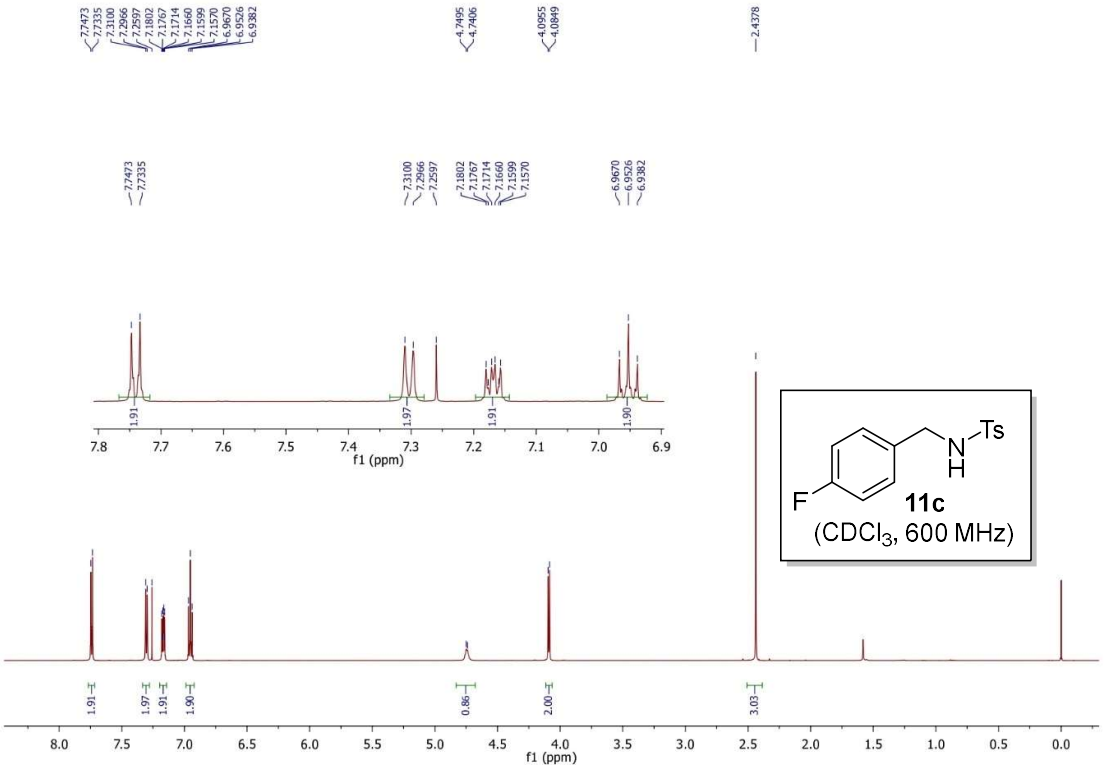
^{1}H NMR of 11b ($CDCl_3$, 600 MHz)



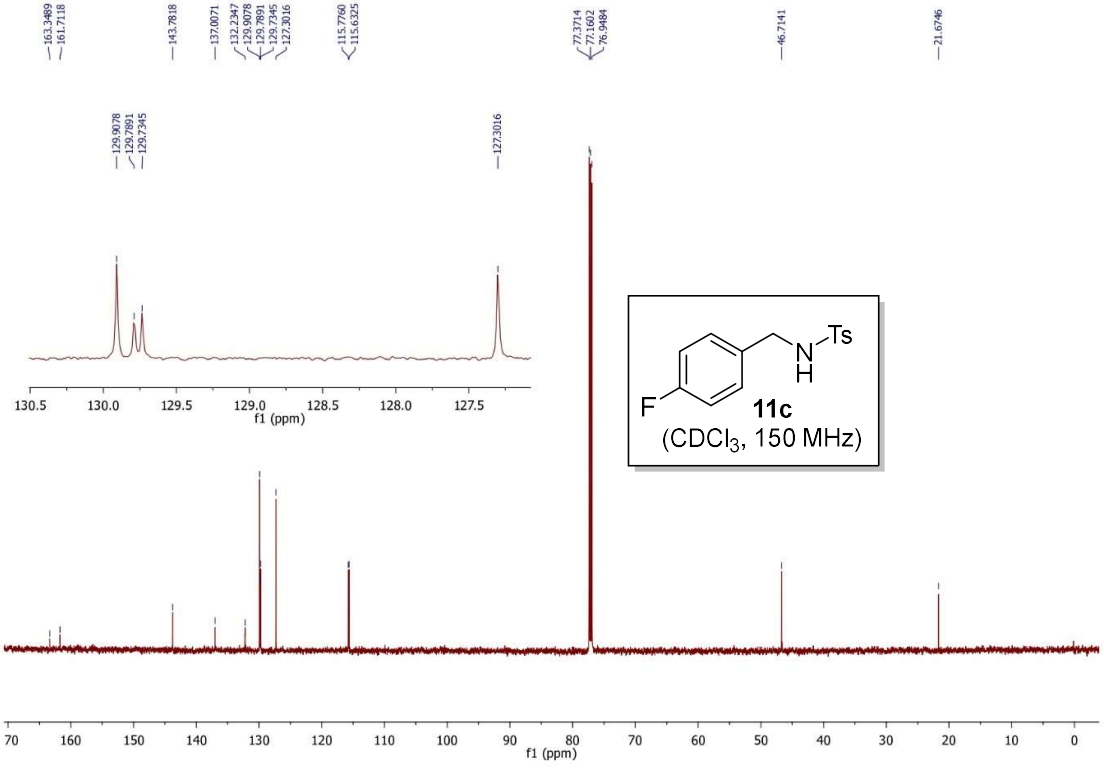
^{13}C NMR of 11b ($CDCl_3$, 150 MHz)



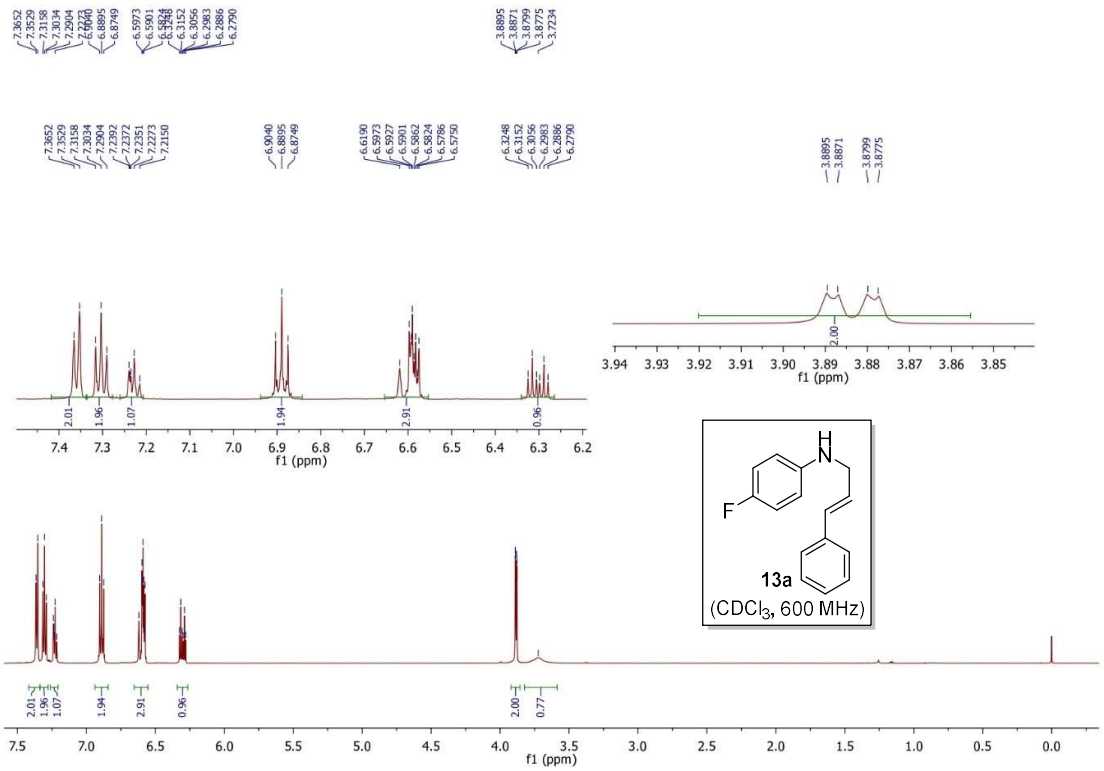
^{1}H NMR of 11c ($CDCl_3$, 600 MHz)



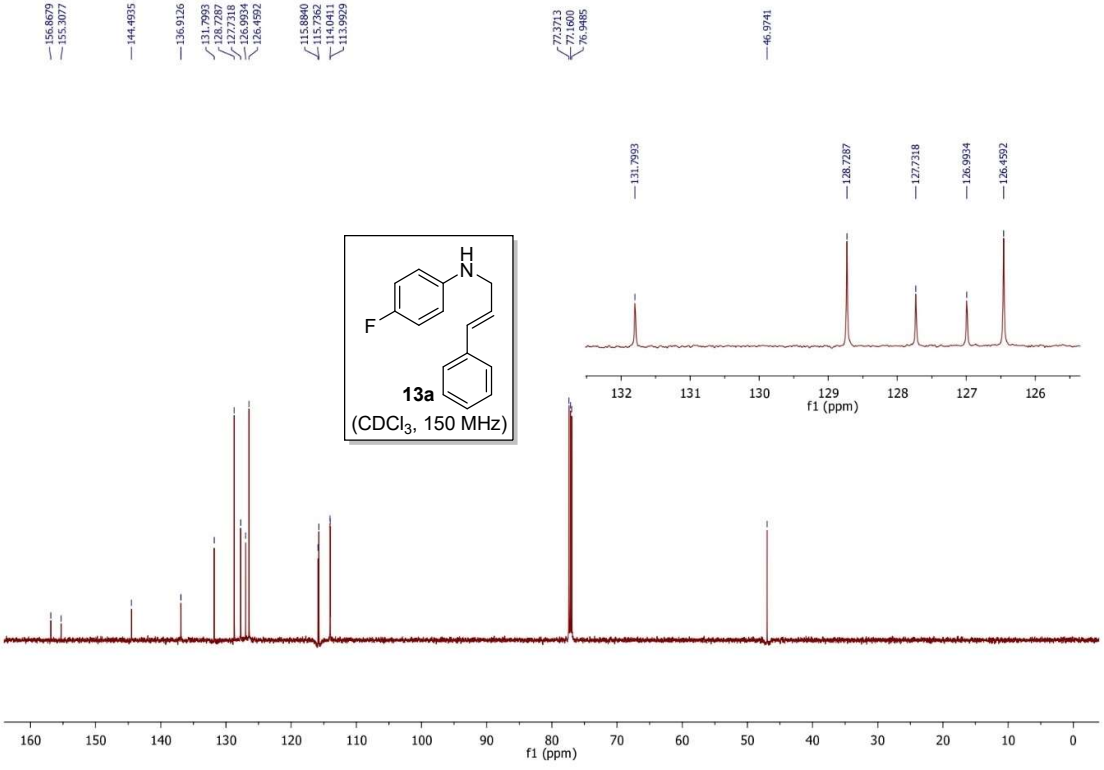
^{13}C NMR of 11c ($CDCl_3$, 150 MHz)



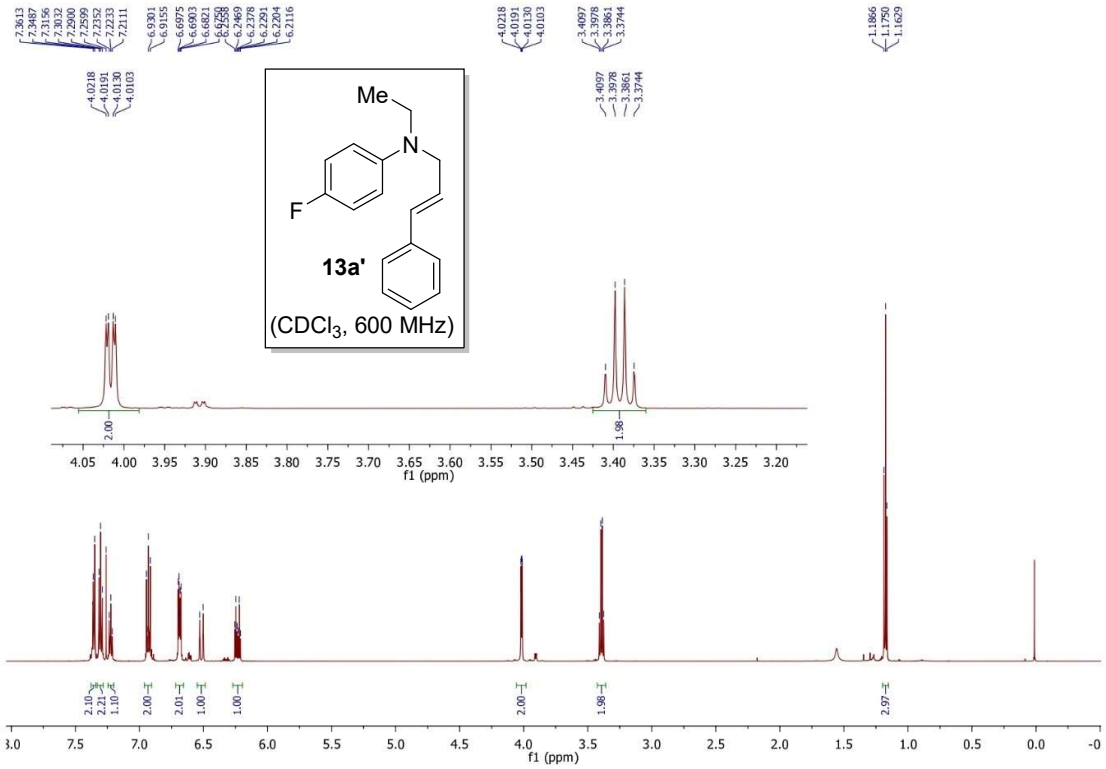
^{1}H NMR of 13a ($CDCl_3$, 600 MHz)



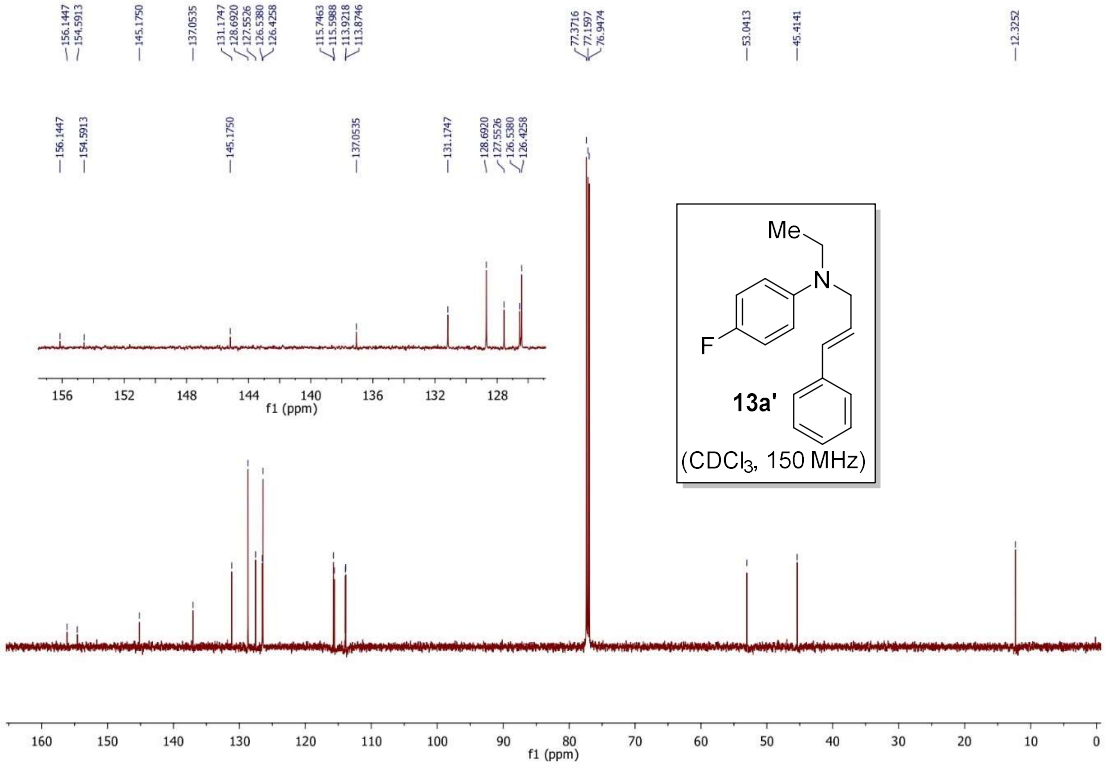
^{13}C NMR of 13a ($CDCl_3$, 150 MHz)



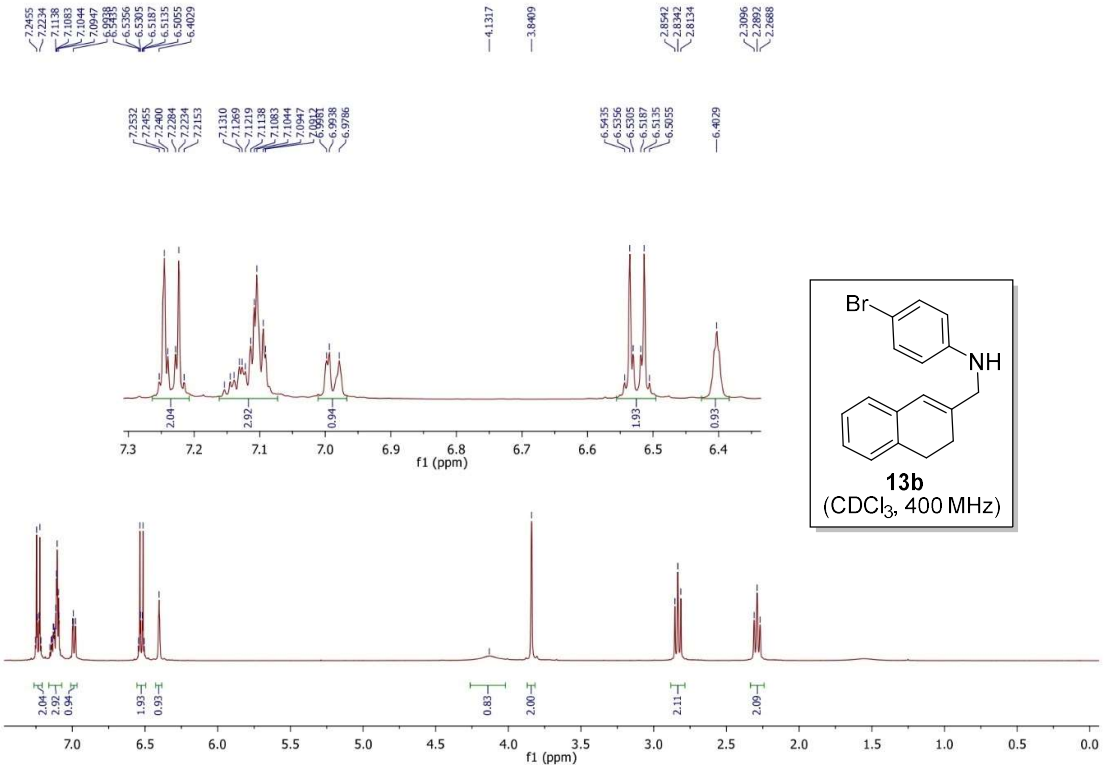
^{1}H NMR of 13a′ ($CDCl_3$, 600 MHz)



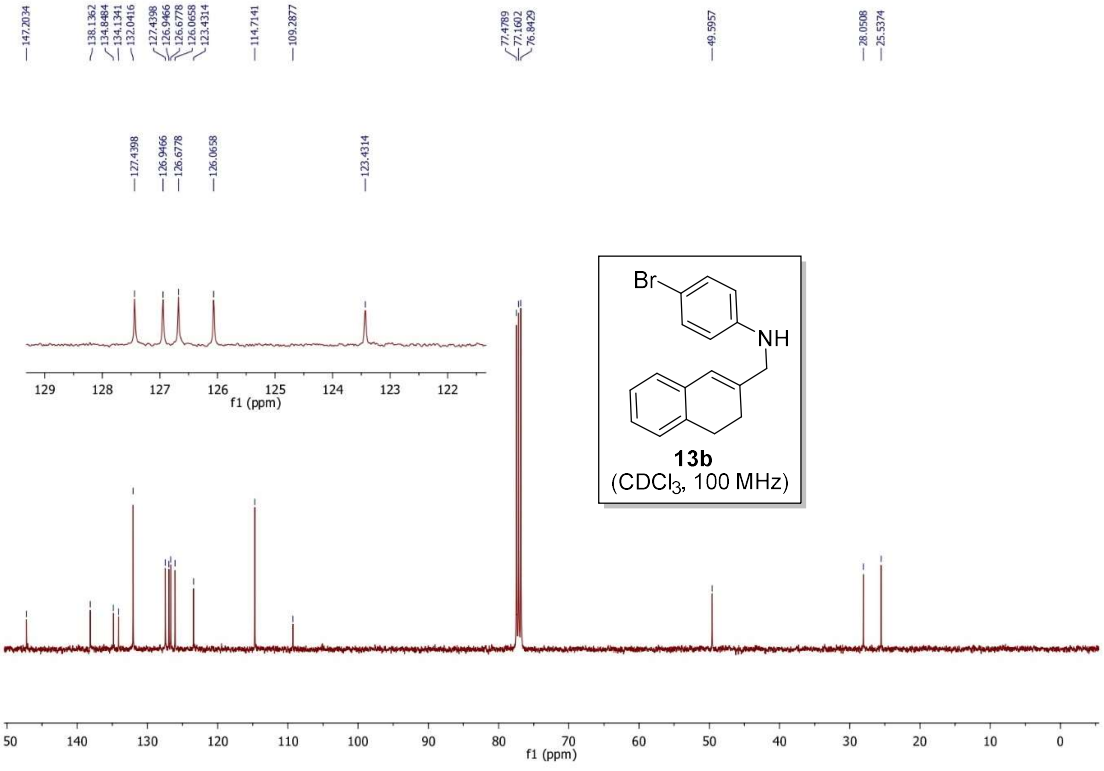
^{13}C NMR of 13a′ ($CDCl_3$, 150 MHz)



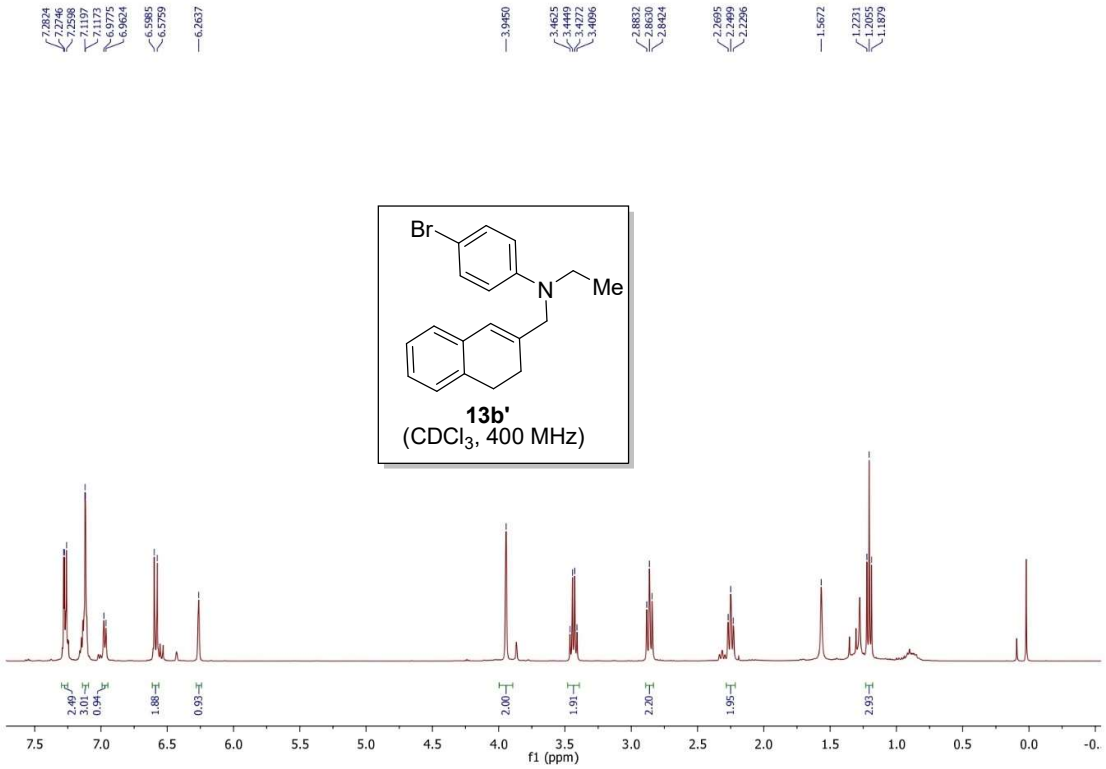
^{1}H NMR of 13b ($CDCl_3$, 400 MHz)



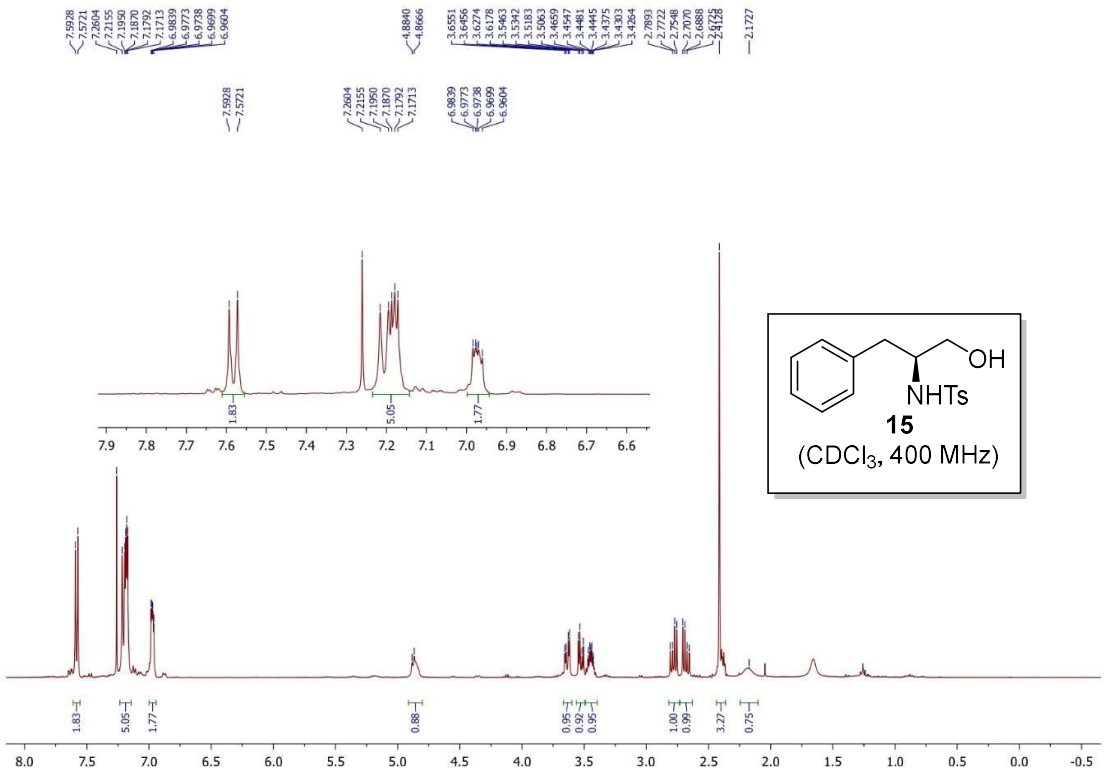
^{13}C NMR of 13b ($CDCl_3$, 100 MHz)



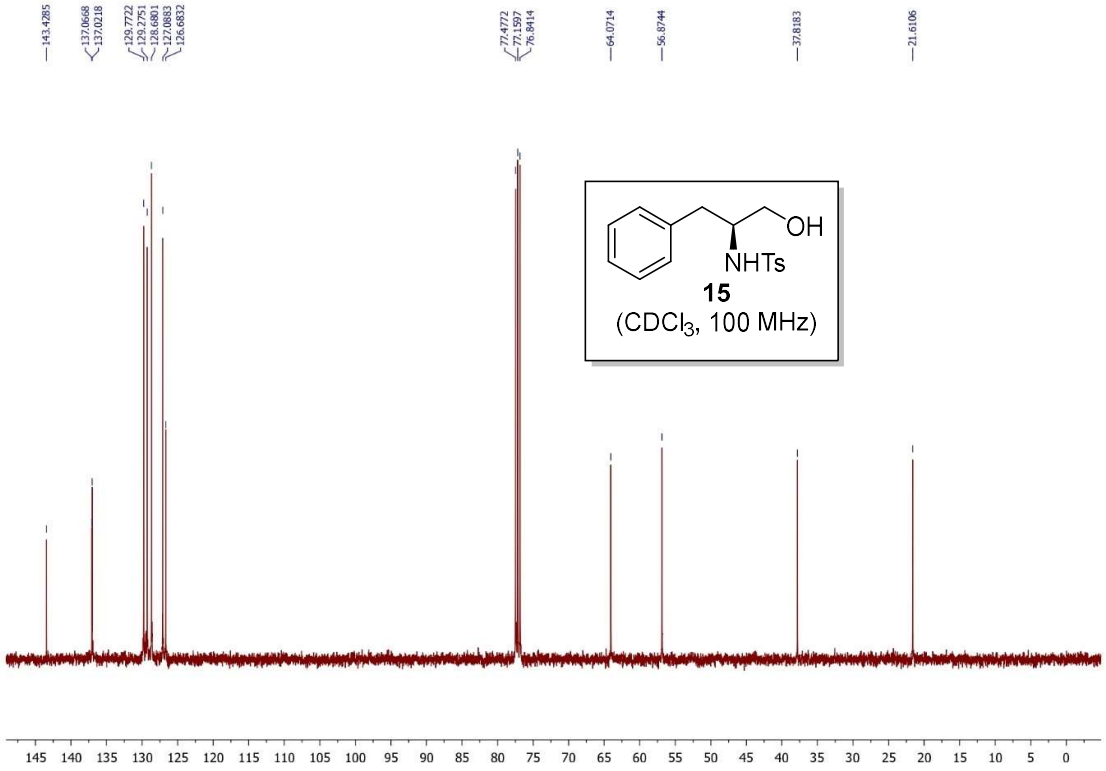
^{1}H NMR of 13b′ ($CDCl_3$, 400 MHz)



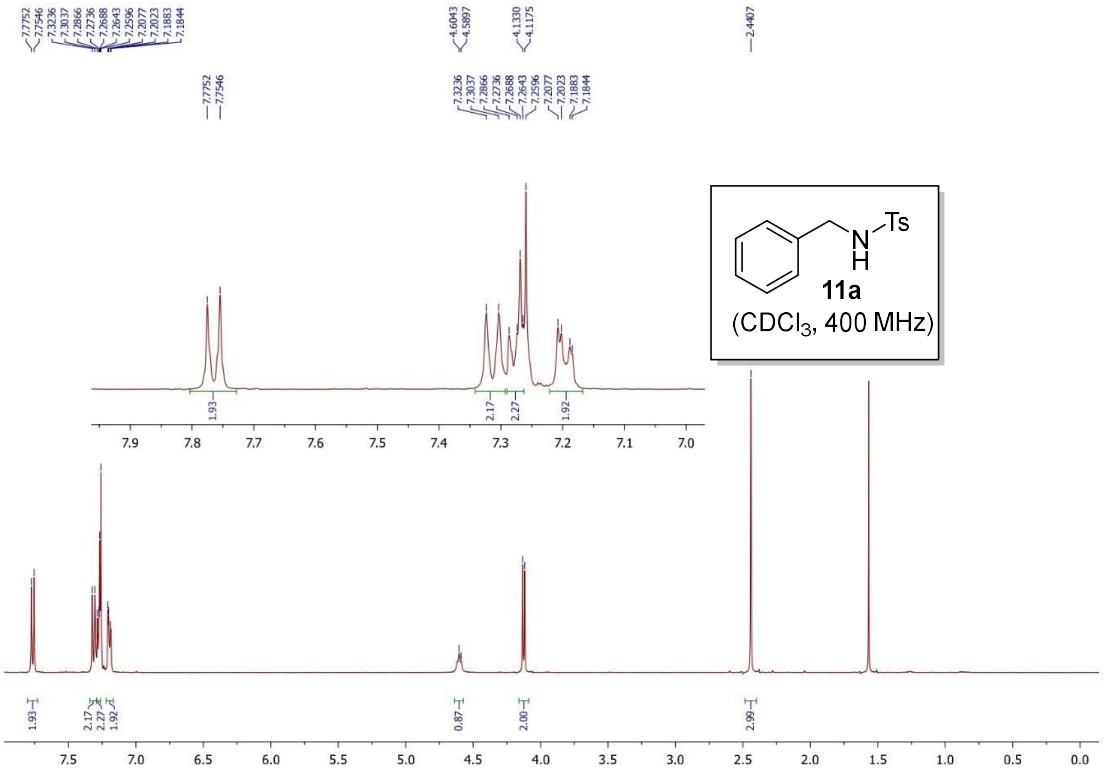
^{1}H NMR of 15 ($CDCl_3$, 400 MHz)



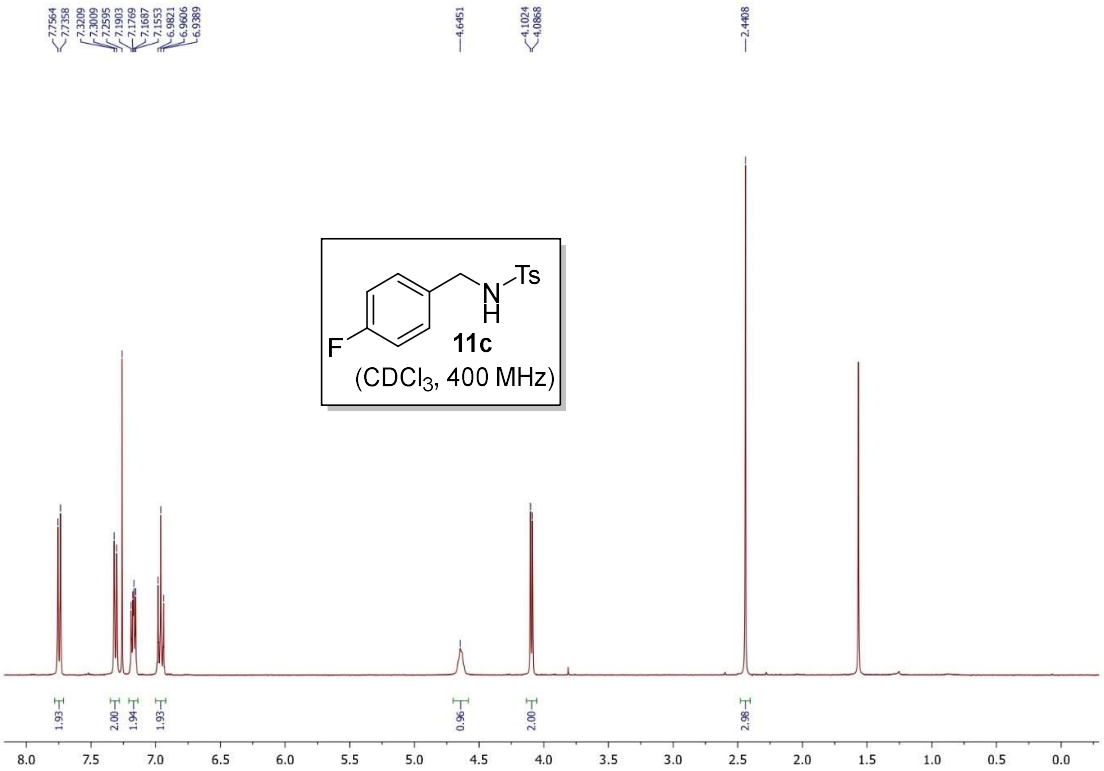
^{13}C NMR of 15 ($CDCl_3$, 100 MHz)



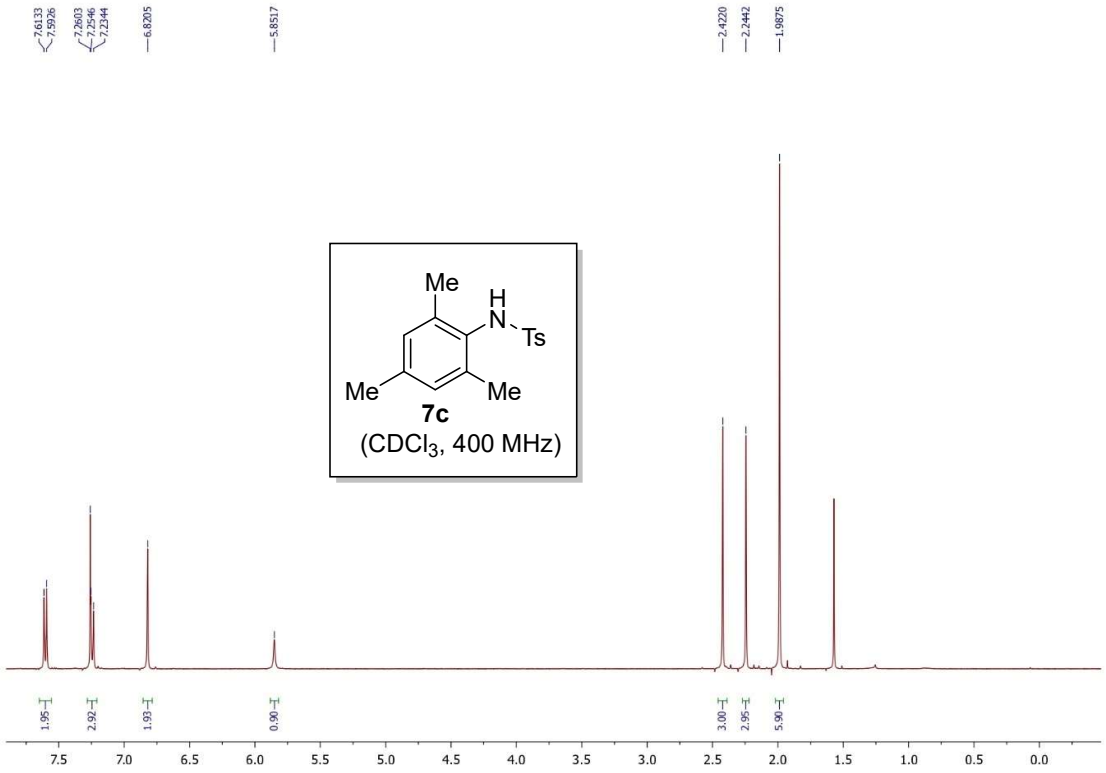
^{1}H NMR of 11a ($CDCl_3$, 400 MHz)



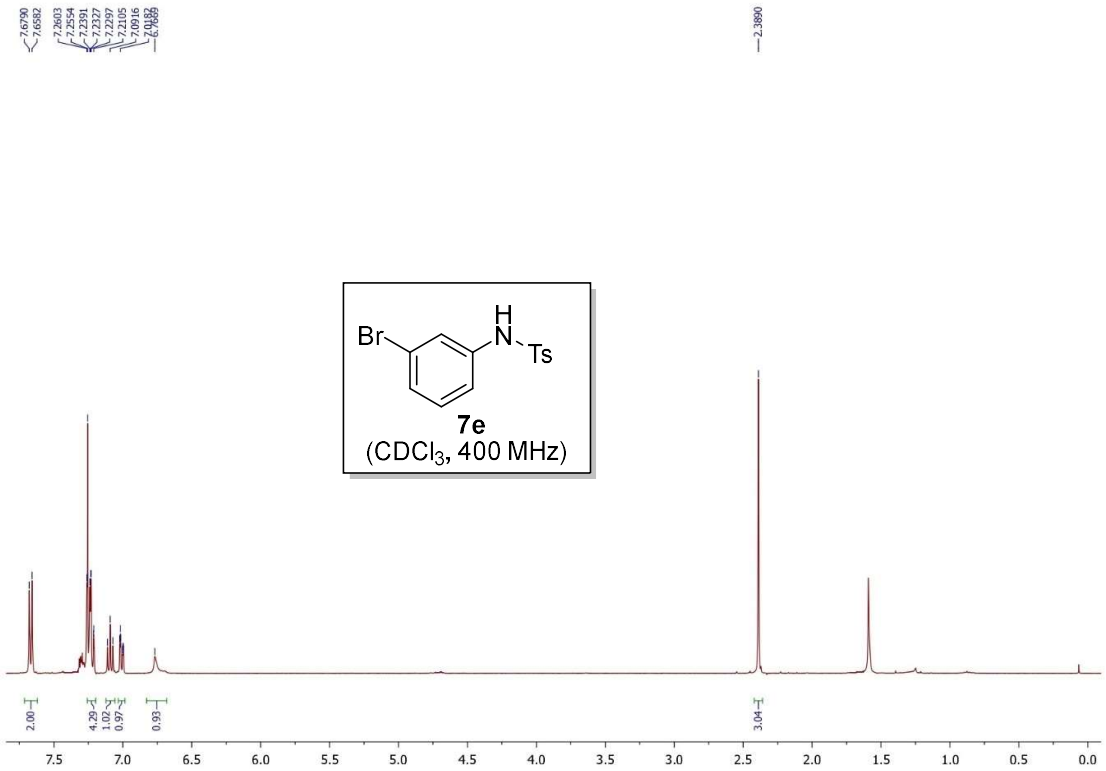
^{1}H NMR of 11c ($CDCl_3$, 400 MHz)



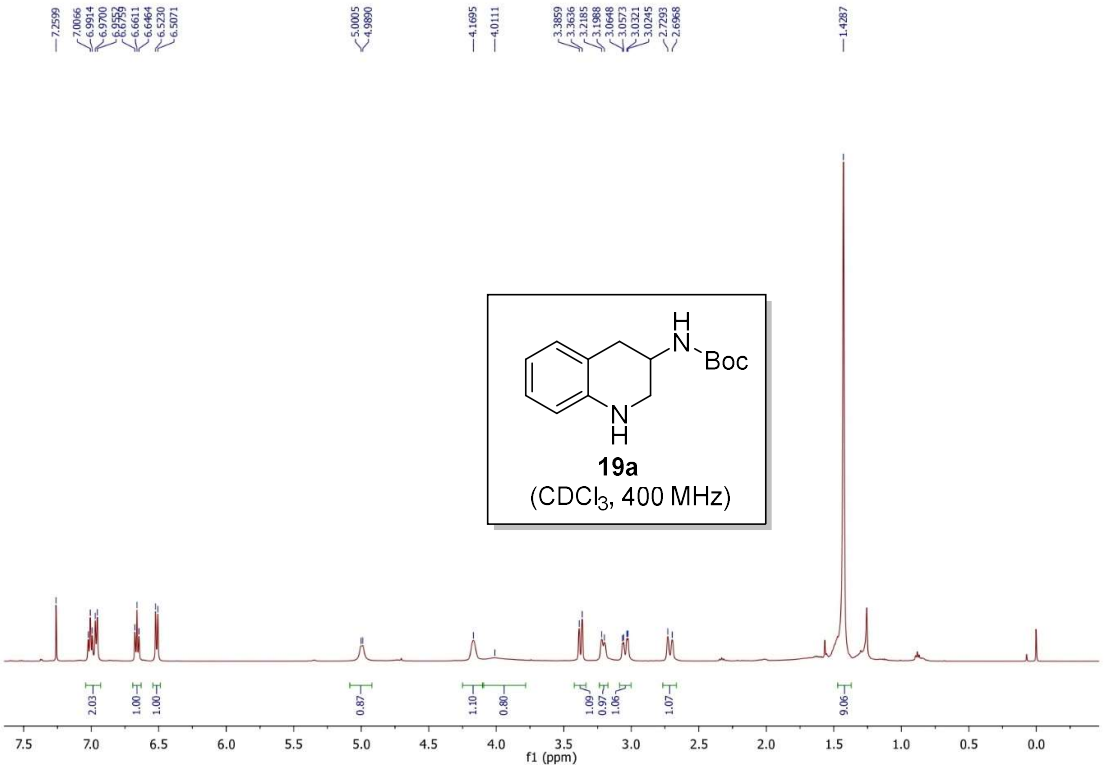
^{1}H NMR of 7c ($CDCl_3$, 400 MHz)



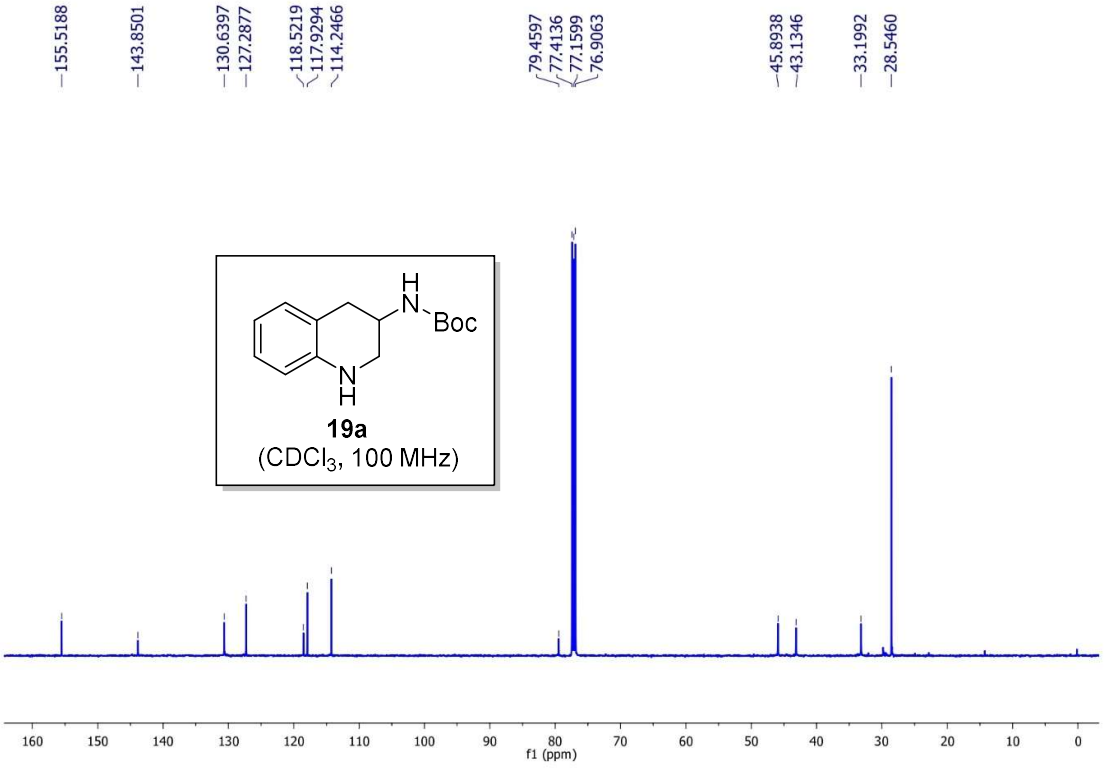
^{1}H NMR of 7e ($CDCl_3$, 400 MHz)



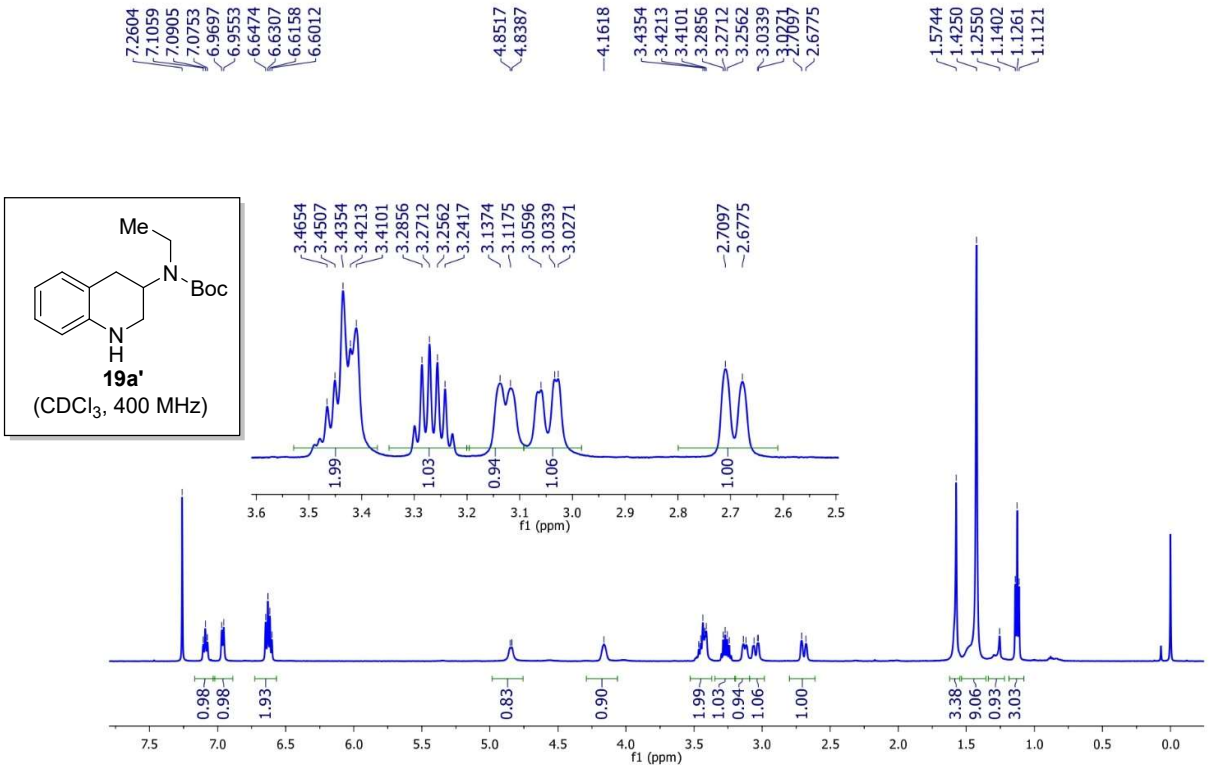
^{1}H NMR of 19a ($CDCl_3$, 400 MHz)



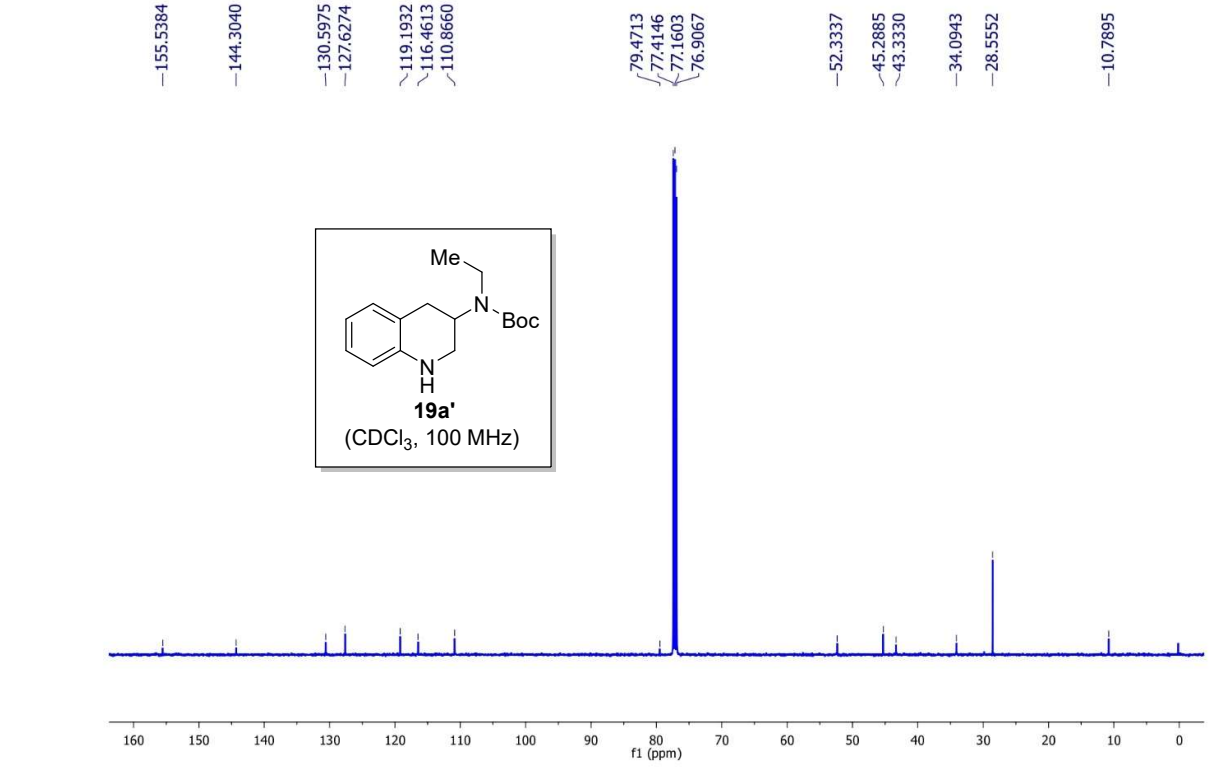
^{13}C NMR of 19a ($CDCl_3$, 100 MHz)



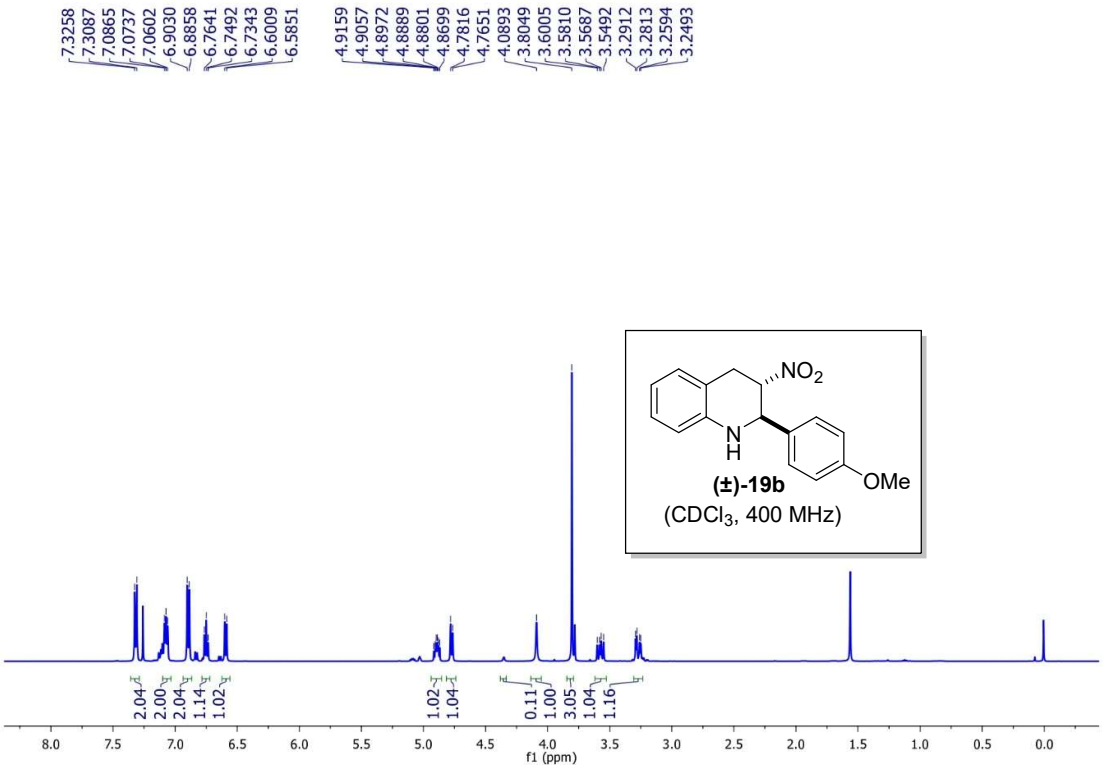
^{1}H NMR of 19a′ ($CDCl_3$, 400 MHz)



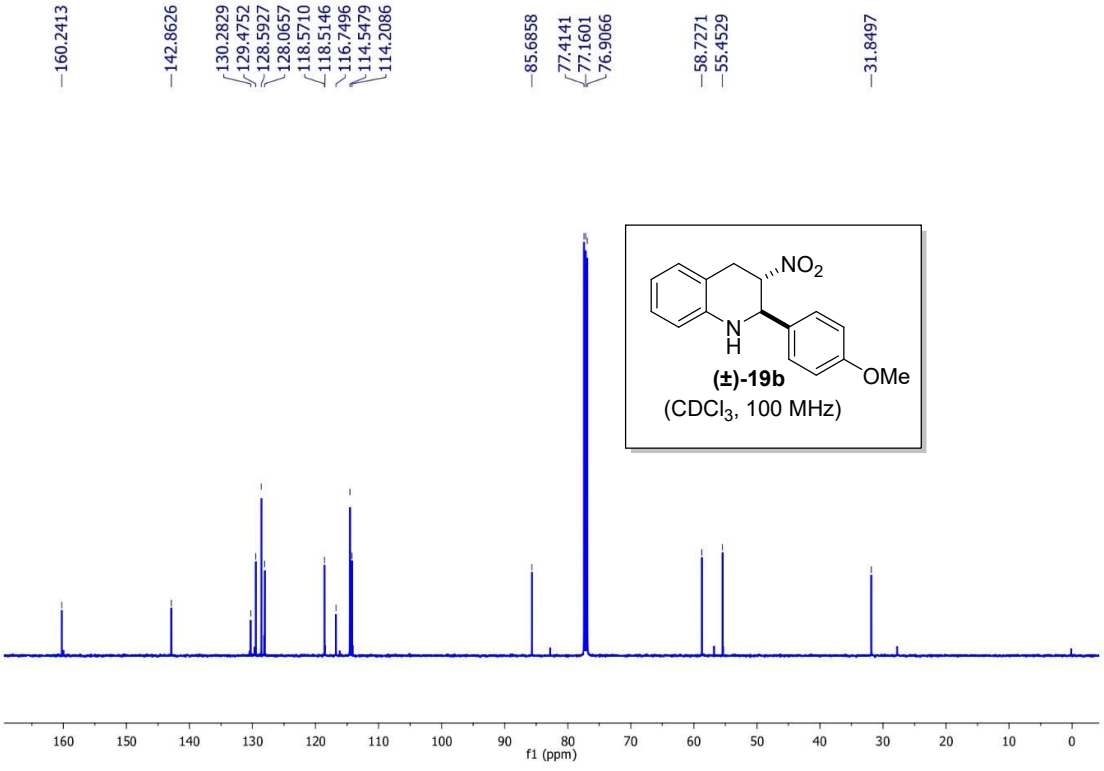
^{13}C NMR of 19a′ ($CDCl_3$, 100 MHz)



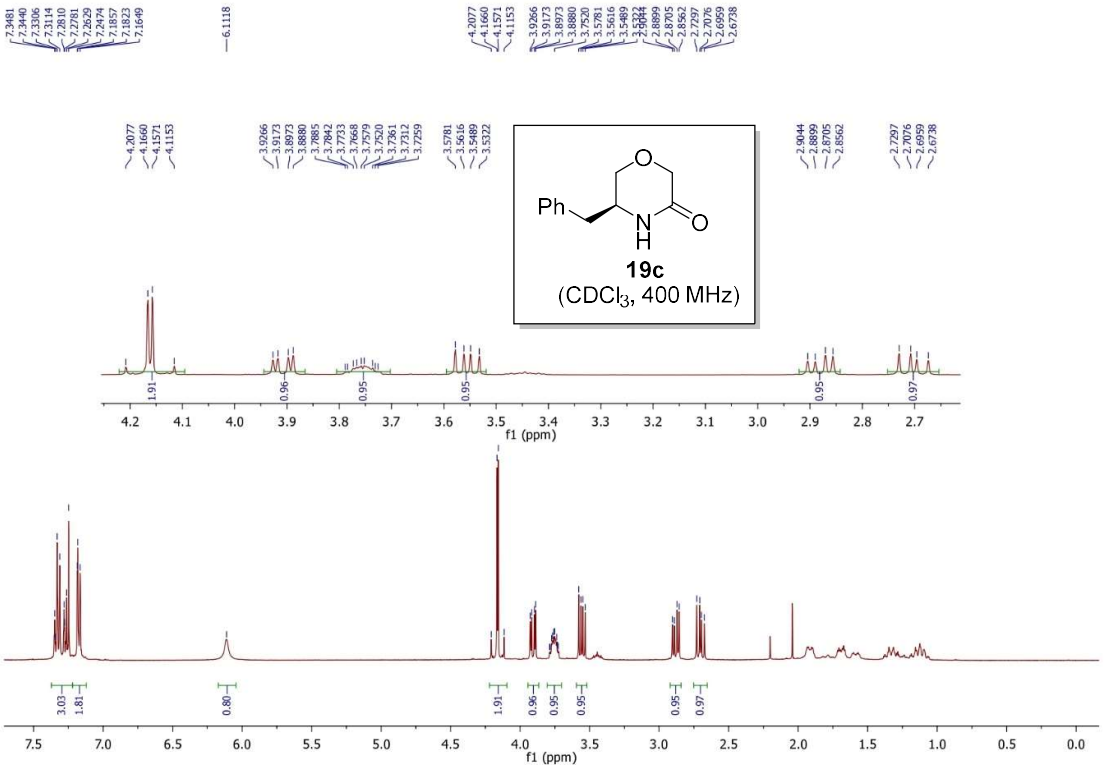
^{1}H NMR of (±)-19b ($CDCl_3$, 400 MHz)



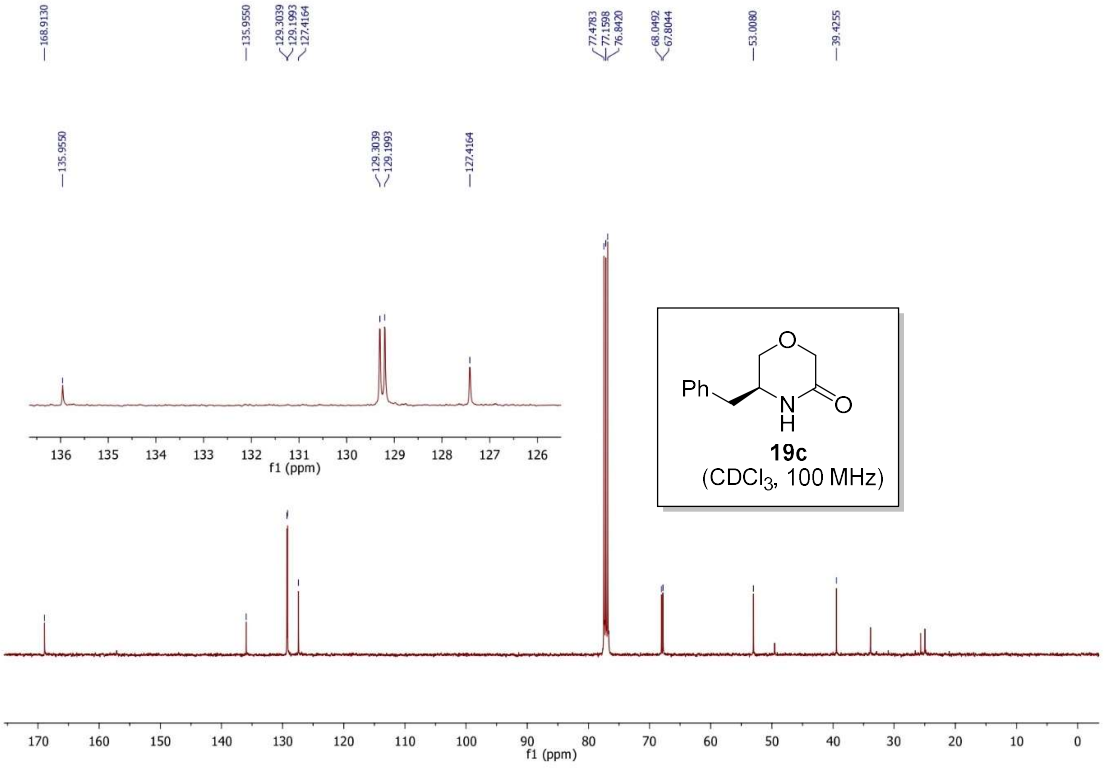
^{13}C NMR of (±)-19b ($CDCl_3$, 100 MHz)



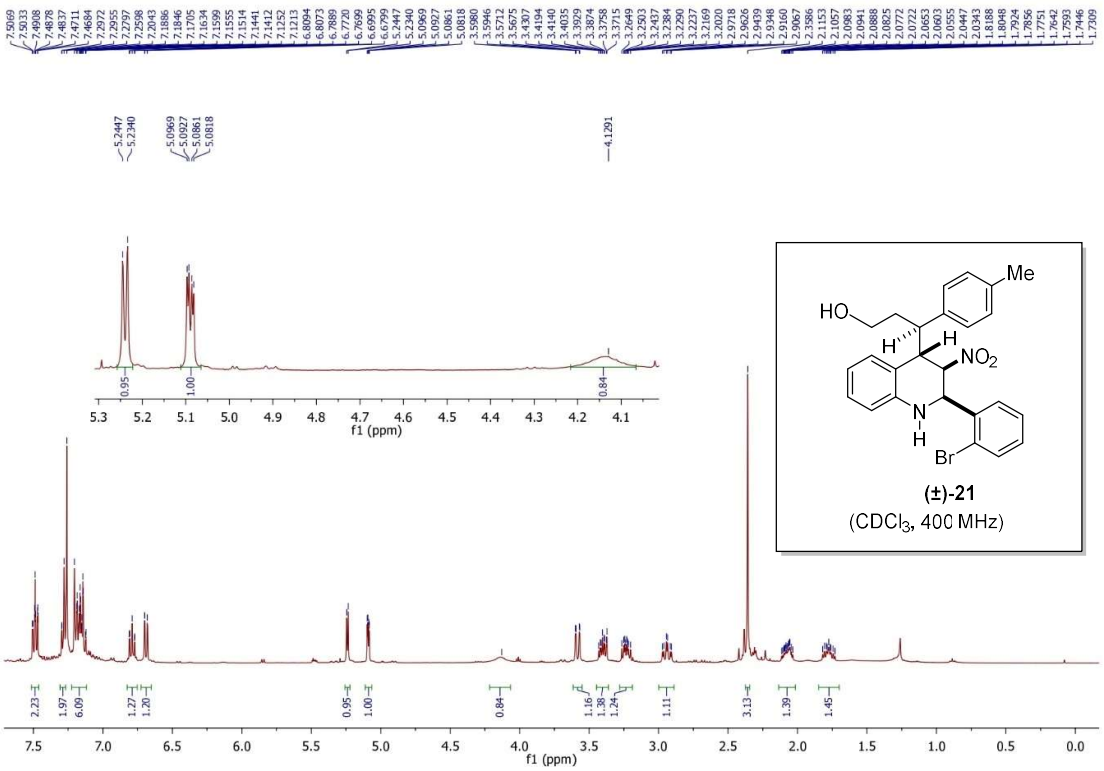
^{1}H NMR of 19c ($CDCl_3$, 400 MHz)



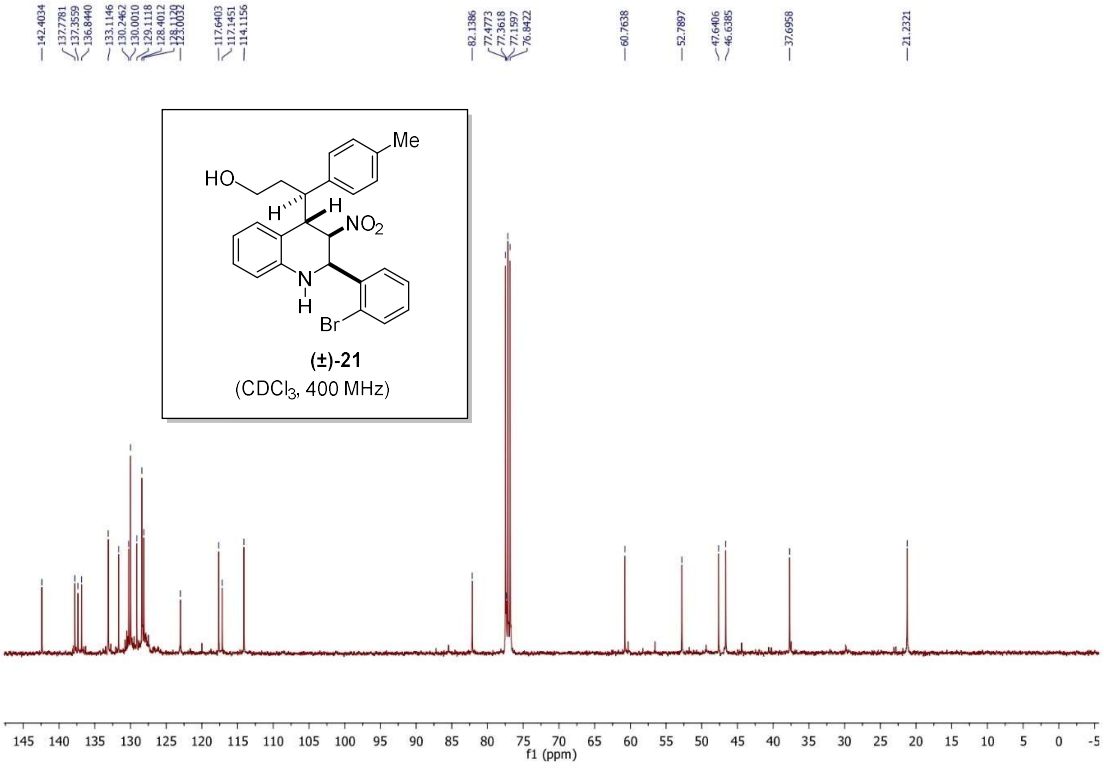
^{13}C NMR of 19c ($CDCl_3$, 100 MHz)



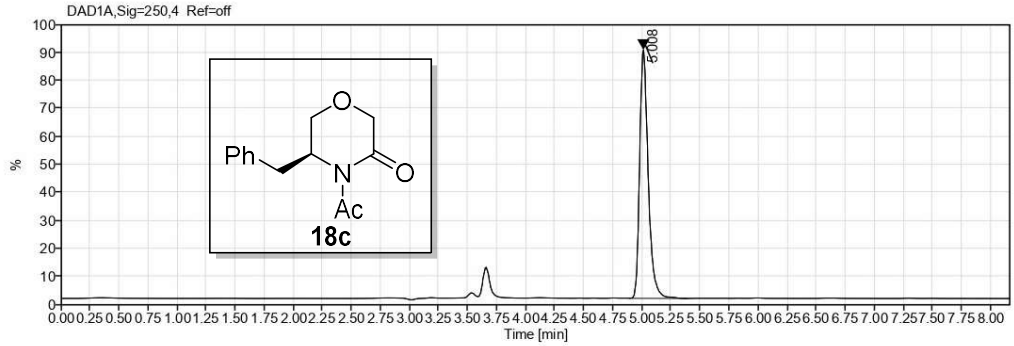
^{1}H NMR of (±)-21 ($CDCl_3$, 400 MHz)



^{13}C NMR of (±)-21 ($CDCl_3$, 100 MHz)



HPLC chromatogram of 18c



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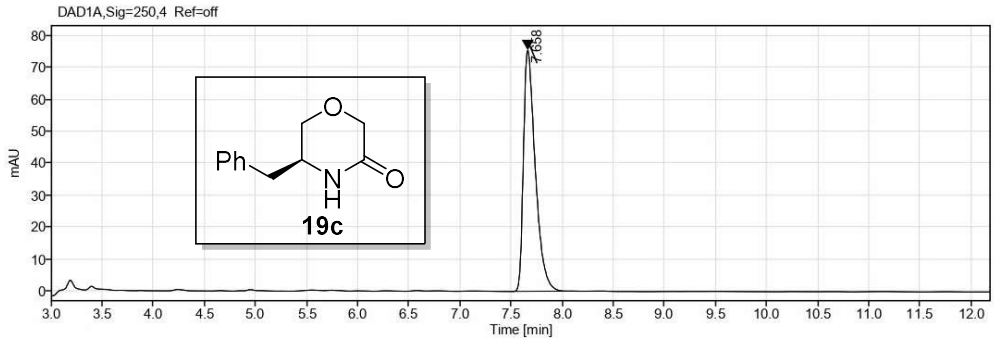
HPLC chromatogram of 19c



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		Sum	606.73			