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Metal-Ligand Bifunctional Activation and Transfer of N-H Bonds

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General remarks

All organic reagents if not noted otherwise were purchased from Acros. Dichloromethane was dried over $CaCl_2$ and distilled from CaH_2. Toluene, THF and Et_2O were distilled from Na/benzophenone. Column chromatography was performed with silica gel (Merck, type 60, 0.063-0.2mm). Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and 10% ethanolic phosphomolybdic acid or ninhydrin solution and heat as developing agents. NMR spectra were recorded on Bruker Avance 400 MHz, Bruker DPX 300 MHz and Bruker DRX 500 MHz spectrometers. All chemical shifts in NMR experiments are reported as ppm downfield from TMS. The following calibrations were used: $CDCl_3$ d = 7.26 and 77.00ppm. HRMS experiments for analysis of **2a–f** were performed on a FC-ITR spectrometer within the service centers at the Kekulé-Department, Bonn University or on a MALDI-TOFTOF spectrometer available at ICIQ Tarragona.

General Experimental Procedures

Formation of the Activated 16e⁻-Species. The active 16e⁻-complexes **1a–c** were synthesized by a modified literature procedure:[S1] generally, 0.1 mmol of the chloride-complex was dissolved in 2 mL of dichloromethane. While the solution was stirred, an excess of potassium hydroxide was added to cause a color change of the solution to deep purple. Washing with water and quick drying over CaH_2 under argon atmosphere gave a solution of the activated complex. The mixture was filtered under argon atmosphere and washed with abs. dichloromethane. This solution containing the pure complex was concentrated to 5 mL and used immediately.

General procedure for the N-H activation and resulting formation of the discussed N-[M] complexes. A solution of 0.1 mmol 16e⁻-species in 5 ml abs. dichloromethane was kept under Argon atmosphere and stirred at room temperature. A solution of the desired amide (0.1 mmol in 1 ml CH_2Cl_2, 1 equiv) was added dropwise until the solution changed its color to bright yellow. The resulting complex was isolated by removal of solvent under reduced pressure in excellent purity.

Alternatively, the activated 16e⁻-species was titrated with a solution of the N-H source and monitored by ^{1}H NMR until the conversion was complete. Evaporation of solvent yielded the pure complex.

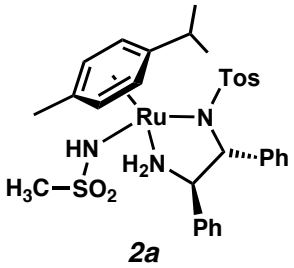
General Procedure for the Cyclization of 3 to 4 with *in situ* Preparation of the Ru Catalysts 1a–c

To a mixture of KH (10 mg, 0.25 mmol, 1.9 eq) and free ligand (0.13 mmol, 1 eq) was added toluene (11 ml). The suspension was stirred for 30 min (until all hydrogen formation had ceased) and (hexamethylbenzene)ruthenium(II) dichloride dimer (43mg, 0.065 mmol, 0.5 eq) was added. The mixture was stirred at room temperature overnight and then at 50 ºC for 1h. The purple solution of prepared catalyst with known concentration (0.01 M) was subsequently used for catalysis.

[S1] K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya and R. Noyori, *Angew. Chem. Int Ed. Engl.* 1997, **36**, 285.

To the solution of starting material (0.05 mmol) in toluene (2 ml) at –15 ºC was added a solution with known concentration of activated catalyst (0.5 ml of the solution per reaction, 0.005 mmol, 10 mol%). The reaction was stirred at this temperature for 1 day, quenched with saturated solution of NH_4Cl (5 ml) and extracted with $CHCl_3$ (15 ml). The organic layer was dried over $MgSO_4$ and concentrated to provide the crude product mixture. Purification for the HPLC analysis was carried out by column chromatography as described for the racemic products below.

Characterization Data of Complexes 2a–f

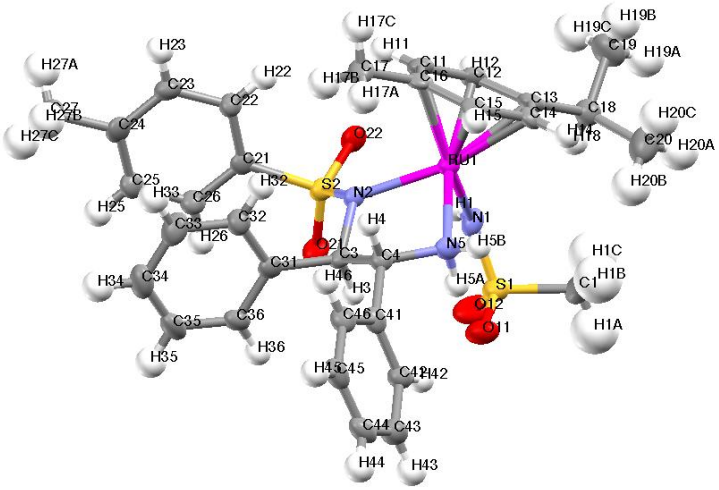


2a

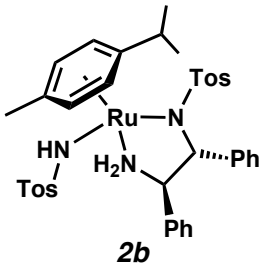
Synthesized according to the general procedure for N-H activation. Isolated after evaporation of the solvent as yellow solid in 99% yield. Crystallized from dichloromethane. $[\alpha_D]^{25}$ = +10 (c = 0,15 g/100 ml, MeOH). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.37 (d, *J* = 6.80 Hz, 3H), 1.45 (d, *J* = 6.80 Hz, 3H), 2.22 (s, 3H), 2.33 (s, 3H), 2.63 (s, 1H), 2.91 (s, 1H), 3.02 (hep, *J* = 6.80 Hz, 1H), 3.04 (s, 3H), 3.58 (t, *J* = 11.15 Hz, 1H), 3.96 (d, *J* = 11.15 Hz, 1H), 5.03 (d, *J* = 8.68 Hz, 1H), 5.32 (m, 2H), 5.61 (m, 4H), 6.54 (d, *J* = 7.18 Hz, 2H), 6.63 (t, *J* = 7.55 Hz, 2H), 6.76 (m, 5H), 7.07 (m, 5H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 18.56, 21.13, 22.32, 23.22, 30.42, 43.11, 44.86, 68.77, 72.60, 81.34, 82.05, 82.50, 83.67, 98.26, 103.64, 126.22, 126.58, 127.05, 128.07, 128.41, 128.70, 138.39, 139.10, 139.38, 142.49. HRMS (FT-ICR neg.,MeOH): [M(^{102}Ru)+Cl^-] 730.1109 calcd: 730.1129, [M-H^+] 694.1364 calcd: 694.1369, [M+HCl+Cl^- -$H_3CSO_2NH_2$] 671.1, [M +Cl^- -$H_3CSO_2NH_2$] 635.1, [M-$H_3CSO_2NH_2$ -H^+] 599.1. IR (KBr): ν [cm^{-1}] = 3336, 3257, 3134, 3020, 2964, 2906, 1581, 1416, 1333, 1261, 1097, 1022, 877, 800, 698, 532, 492.

Structure Determination of 2a via X-Ray Analysis:

Deposition Number: CCDC-772672



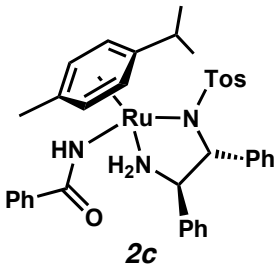
Empirical formula	C32 H39 N3 O4 Ru S2
Formula weight	694.85
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1) (No.19)
Unit cell dimensions	a = 9.0303(2) A alpha = 90 deg.
	b = 13.7496(3) A beta = 90 deg.
	c = 25.4242(6) A gamma = 90 deg.
Volume	3156.75(12) A^3
Z, Calculated density	4, 1.462 Mg/m^3
Absorption coefficient	0.670 mm^-1
F(000)	1440
Crystal size	0.30 x 0.20 x 0.10 mm
Diffractometer	Nonius KappaCCD
Theta range for data collection	2.96 to 25.03 deg.
Limiting indices	-10<=h<=10, -14<=k<=16, -30<=l<=29
Reflections collected / unique	17169 / 5556 [R(int) = 0.0469]
Completeness to theta = 25.03	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.91692 and 0.85560
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5556 / 3 / 391
Goodness-of-fit on F^2	0.975
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0666
R indices (all data)	R1 = 0.0422, wR2 = 0.0689
Absolute structure parameter	-0.11(3)
Largest diff. peak and hole	0.913 and -0.410 e.A^-3



2b

Synthesized according to the general procedure for N-H activation. Isolated after evaporation of the solvent as yellow solid in 98% yield.

$[\alpha_D]^{25}$ = +25 (c = 0.088 g/100 ml, MeOH). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.23 (d, *J* = 6.99 Hz, 3H), 1.32 (d, *J* = 6.80 Hz, 3H), 2.12 (s, 3H), 2.29 (s, 1H), 2.33 (s, 3H), 2.61 (s, 1H), 2.85 (dq, *J* = 6.99 Hz, 6.80 Hz, 1H), 3.50 (t, *J* = 11.90 Hz, 1H), 3.91 (d, *J* = 10.96 Hz, 1H), 4.90 (d, *J* = 8.12 Hz, 1H), 5.05 (t, *J* = 11.90 Hz, 1H), 5.34 (s, 1H), 5.42 (d, *J* = 5.86 Hz, 1H), 5.51 (d, *J* = 6.04 Hz, 1H), 5.54 (d, *J* = 6.04 Hz, 1H), 5.60 (d, *J* = 5.86 Hz, 1H), 6.48 (d, *J* = 6.99 Hz, 2H), 6.55-6.63 (m, 4H), 6.68 (d, *J* = 8.12 Hz, 2H), 6.85-6.95 (m, 3H), 7.02 (d, *J* = 8.30 Hz, 2H), 7.09 (d, *J* = 8.12 Hz, 1H), 7.18 (d, *J* = 8.88 Hz, 2H), 7.57 (d, *J* = 8.12 Hz, 1H), 7.79 (d, *J* = 8.12 Hz, 2H). ^{13}C-NMR (CDCl3, 75 MHz): δ = 18.48, 21.11, 21.38, 22.34, 23.17, 30.33, 68.79, 72.54, 80.96, 82.16, 82.24, 84.13, 98.40, 103.46, 126.10, 126.17, 126.24, 126.54, 126.99, 127.88, 128.06, 128.34, 128.35, 128.70, 129.15, 129.46, 138.69, 139.15, 139.30, 140.89, 142.41, 143.66. HRMS (MALDI-TOFTOF) calcd for $C_{38}H_{44}N_3O_4{}^{102}RuS_2^+$: 772.1805, found: 772.1833. IR (KBr): ν [cm^{-1}] = 3336, 3257, 3228, 3135, 3063, 3027, 2966, 2930, 2868, 1265, 1102, 1030, 810, 707, 579.

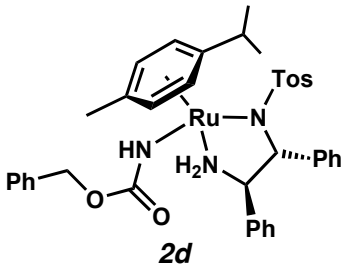


2c

Synthesized according to the general procedure for N-H activation. Isolated after evaporation of the solvent as yellow solid in 99% yield.

$[\alpha_D]^{25}$ = +63 (c = 0,051 g/100 ml, MeOH). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.33 (d, *J* = 6.80 Hz, 3H), 1.37 (d, *J* = 6.80 Hz, 3H), 2.21 (s, 3H), 2.32 (s, 3H), 2.89 (hep, *J* = 6.80 Hz,

1H), 3.58 (dt, *J* = 11.33 Hz, 3.28 Hz, 1H), 3.92 (d, *J* = 11.33 Hz, 1H), 4.54 (d, *J* = 7.05 Hz, 1H), 5.33 (d, *J* = 6.04 Hz, 1H), 5.35 (d, *J* = 6.04 Hz, 1H), 5.52 (d, *J* = 5.54 Hz, 1H), 5.61 (d, *J* = 5.54 Hz, 1H), 6.13 (s, 1H), 6.51 (d, *J* = 7.05 Hz, 2H), 6.60 (t, *J* = 7.81 Hz, 2H), 6.73 (d, *J* = 8.31 Hz, 2H), 6.79 (d, *J* = 6.80 Hz, 2H), 6.98 (m, 2H), 7.07 (d, *J* = 8.06 Hz, 3H), 7.39 (m, 3H), 7.78 (d, *J* = 7.55 Hz, 1H), 7.93 (dd, *J* = 8.06 Hz, 1.51 Hz, 2H), 9.12 (t, *J* = 11.34 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.63, 21.13, 21.79, 23.32, 30.83, 53.40, 69.57, 73.16, 80.06, 82.90, 83,69. 84.89, 96.85, 105.23, 126.06, 126.48, 126.64, 126.89, 127.18, 127.35, 127.60, 127.90, 128.13, 128.19, 128.52, 128.92, 129.02, 138.59, 139.00, 139.63, 140.53, 143.20, 178.03. HRMS (FT-ICR neg.,MeOH): [M(^{102}Ru)+Cl^-] 756.1621 calcd: 756.1606, [M+HCl+Cl^- -PhC(O)NH_2] 671.1, [M+Cl^- -PhC(O)NH_2] 635.1, 599.1 [M-H^+-PhC(O)NH_2]. IR (KBr): ν [cm^{-1}] = 3421, 3390, 3259, 3059, 3030, 2964, 1591, 1552, 1448, 1280, 1086, 1026, 912, 807, 698, 575.

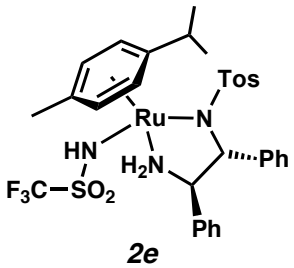


2d

Synthesized according to the general procedure for N-H activation. Isolated after evaporation of the solvent as yellow solid in 96% yield.

$[\alpha_D]^{25}$ = +91 (c = 0,056 g/100 ml, MeOH). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.30 (d, *J* = 4.03 Hz, 3H), 1.31 (d, *J* = 4.03 Hz, 3H), 2.21 (s, 3H), 2.27 (s, 3H), 2.85 (hep, *J* = 7.05 Hz, 1H), 3.51 (td, *J* = 11.33 Hz, 3.52 Hz, 1H), 3.80 (d, *J* = 11.33 Hz, 1H), 4.12 (s, 1H), 4.48 (dd, *J* = 10.07 Hz, 2.52 Hz, 1H), 4.77 (s, 1H), 5.06 (s, 1H), 5.10 (d, *J* = 2.77 Hz, 2H), 5.26 (t, *J* = 5.79 Hz, 2H), 5.43 (d, *J* = 5.54 Hz, 1H), 5.51 (d, *J* = 5.79 Hz, 1H), 6.53 (dd, *J* = 8.31 Hz, 1.26, 2H), 6.64 (m, 4H), 6.75 (m, 2H), 6.93 (t, *J* = 7.30 Hz, 2H), 7.01 (t, *J* = 7.30 Hz, 1H), 7.07 (d, *J* = 8.31 Hz, 2H), 7.26 (t, *J* = 7.30 Hz, 1H), 7.37 (m, 3H), 7.48 (dd, *J* = 8.31 Hz, 1.26 Hz, 2H), 7.86 (t, *J* = 11.33 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 18.51, 21.12, 21.66, 23.27, 30.61, 65.78, 66.79, 69.27, 73.29, 79.91, 82.70, 83.15, 84.85, 96.76, 104.73, 126.04, 126.59, 126.86, 126.95, 127.08, 127.12, 127.56, 127.89, 128.05, 128.15, 128.50, 128.85, 136.26, 138.84, 138.98, 139.52, 142.93, 163.32. IR (KBr): ν [cm^{-1}] = 3421,

3271, 3205, 3062, 3030, 2962, 2924, 2868, 1691, 1645, 1446, 1402, 1346, 1261, 1182, 1084, 1039, 1026, 914, 806, 698, 577.

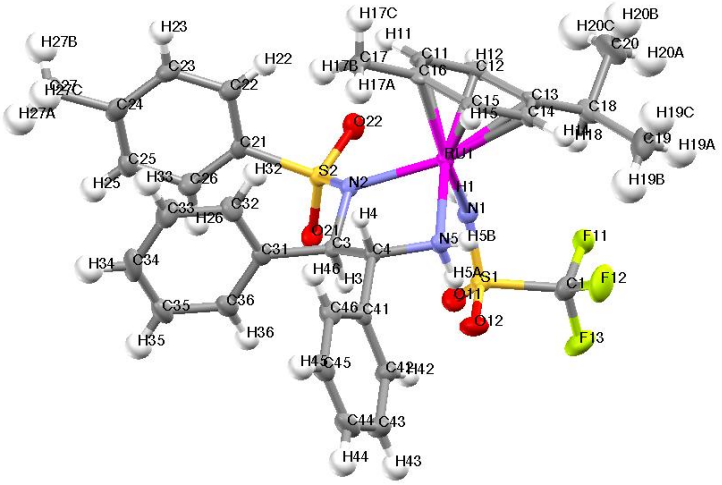


2e

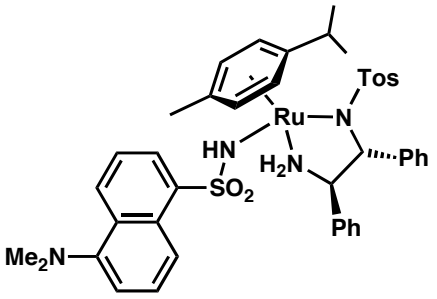
Synthesized according to the general procedure for N-H activation. Isolated after evaporation of the solvent as orange solid in 93% yield. Crystallized from DMSO.
$[\alpha_D]^{25}$ = +19 (c = 0,03 g/100 ml, DMSO). ^{1}H-NMR (300 MHz, DMSO): δ = 1.29 (d, *J* = 6.8 Hz, 3H), 1.33 (d, *J* = 7.0 Hz, 3H), 2.20 (s, 3H), 2.21 (s, 3H), 3.00 (hep, *J* = 6.8 Hz, 1H) 3.58 (t, *J* = 11.3 Hz, 1H), 3.66 (s, 1H), 3.95 (d, *J* = 11.3 Hz, 1H), 4.23 (t, *J* = 11.9 Hz, 1H), 5.58 (d, *J* = 5.9 Hz, 1H), 5.73 (m, 2H), 5.82 (d, *J* = 5.9 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 2H), 6.69 (t, *J* = 7.6 Hz, 2H), 6.82 (m, 5H), 7.01 (d, *J* = 8.3 Hz, 2H), 7.16 (m, 3H), 7.46 (d, *J* = 9.8 Hz, 1H), 8.69 (br, 1H). ^{13}C-NMR (75 MHz, DMSO): δ = 17.75, 20.71, 21.69, 22.38, 29.08, 54.87, 67.82, 71.60, 81.36, 82.07, 82.51, 96.88, 103.26, 126.10, 126.86, 126.90, 127.79, 128.35, 128.58, 138.68, 139.50, 143.06. ^{19}F-NMR (300 MHz, DMSO): −77.84 ppm; δ($CF_3SO_2NH_2$) = −79.47. IR (KBr): ν [cm^{-1}] = 3442, 3314, 3268, 3237, 3160, 2971, 2879, 1639, 1619, 1317, 1260, 1180, 1178, 1076, 994, 933, 805, 702, 610, 579.

Structure Determination of 2e via X-Ray Analysis:

Deposition Number: CCDC-772673



Empirical formula	C32 H36 F3 N3 O4 Ru S2
Formula weight	748.83
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1) (No.19)
Unit cell dimensions	a = 9.0451(1) A alpha = 90 deg.
	b = 13.9640(1) A beta = 90 deg.
	c = 25.3405(3) A gamma = 90 deg.
Volume	3200.65(6) A^3
Z, Calculated density	4, 1.554 Mg/m^3
Absorption coefficient	0.680 mm^-1
F(000)	1536
Crystal size	0.20 x 0.15 x 0.10 mm
Diffractometer	Nonius KappaCCD
Theta range for data collection	2.92 to 25.03 deg.
Limiting indices	-10<=h<=10, -15<=k<=16, -30<=l<=30
Reflections collected / unique	37931 / 5626 [R(int) = 0.0903]
Completeness to theta = 25.03	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99074 and 0.86345
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5626 / 3 / 417
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)] R1 =	0.0299, wR2 = 0.0645
R indices (all data) R1 =	0.0330, wR2 = 0.0656
Absolute structure parameter	-0.04(2)
Largest diff. peak and hole	0.858 and -0.504 e.A^-3



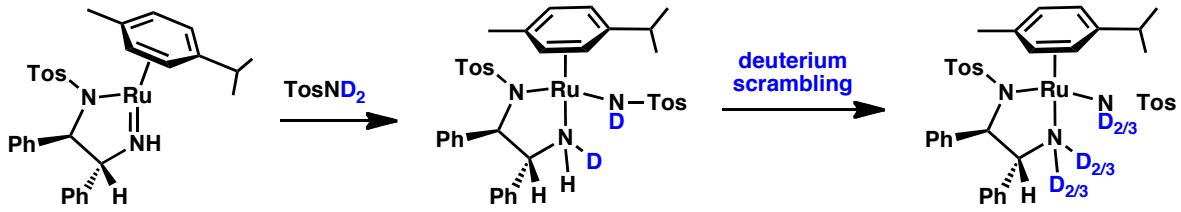
2f

Synthesized according to the general procedure for N-H activation. Isolated after evaporation of the solvent as yellow solid in 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, *J* = 6.8 Hz, 3H), 1.-27 (d, *J* = 6.8 Hz, 3H), 2.09 (s, 3H), 2.19 (s, 3H), 2.75 (hep, *J* = 6.8 Hz, 1H), 2.86 (s, 1H), 2.90 (s, 6H), 3.02 (s, 1H), 3.60 (dt, *J* = 2.4, 12.4 Hz, 1NH), 4.04 (d, *J* = 10.8 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1NH), 5.21 (t, *J* = 12.4 Hz, 1NH), 5.33 (d, *J* = 5.6 Hz, 1H), 5.44 (d, *J* = 5.6 Hz, 1H), 5.49 (d, *J* = 5.6 Hz, 1H), 5.63 (d, *J* = 5.6 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 6.66-6.74 (m, 7H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.51 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.55 (dd, *J* = 8.0, 8.4 Hz, 1H), 8.33 (d, *J* = 6.8 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 8.8 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 18.20, 21.14, 22.29, 23.05, 30.36, 45.47, 68.75, 72.90, 80.31, 81.37, 83.04, 84.48, 97.62, 104.08, 114.77, 115.12, 118.68, 121.00, 123.52, 126.13, 126.29, 126.65, 126.96, 127.07, 127.15, 127.36, 127.75, 128.08, 128.46, 128.68, 129.90, 130.05, 130.22, 138.85, 138.91, 139.41, 142.14, 142.22, 151.37.

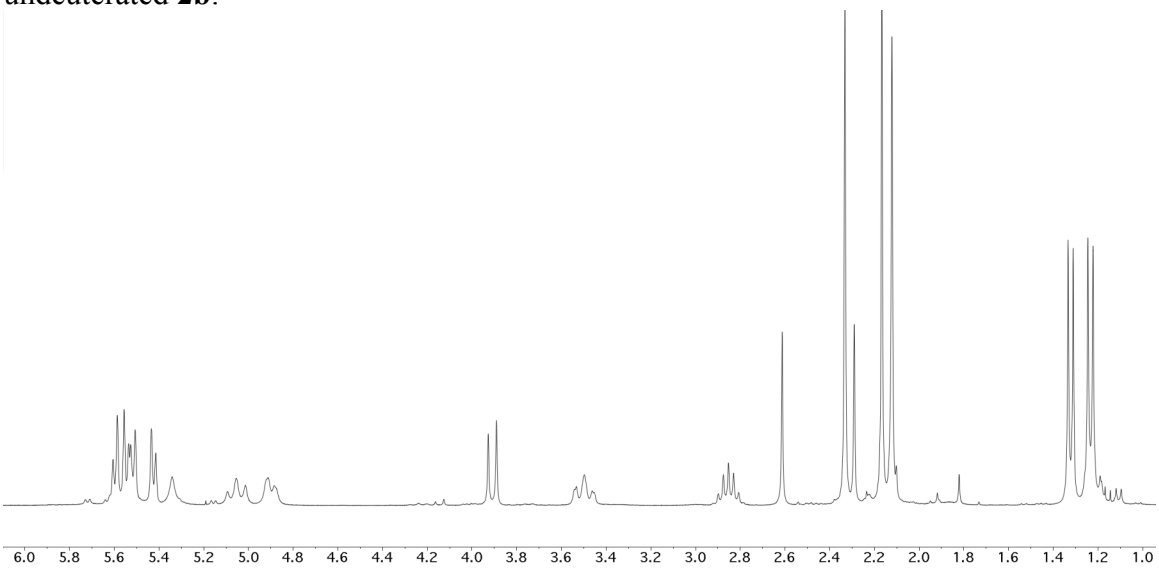
Deuterium Labeling Experiment

Fully *N*-deuterated tosylamide was prepared by stirring a solution of tosylamide in methanol-d_4 for 5 days at room temperature. An equimolar amount of $TosND_2$ was then reacted with **1a** as described for the undeuterated substrate. The product was analyzed by ^{1}H-nmr and a clear loss in signal intensity of the N-H hydrogens at 2.6, 4.9 and 5.1 ppm was observed as well as a shift of the latter two signals to 4.7 and 5.2 ppm. This suggests that the initially formed product **2b-d_2** undergoes deuterium scrambling to arrive at **2b'-d_2** with a statistical deuteration grade of 2/3 for all three N-H bonds. As a result, related acidity is assumed for the three N-H bonds of **2b**.

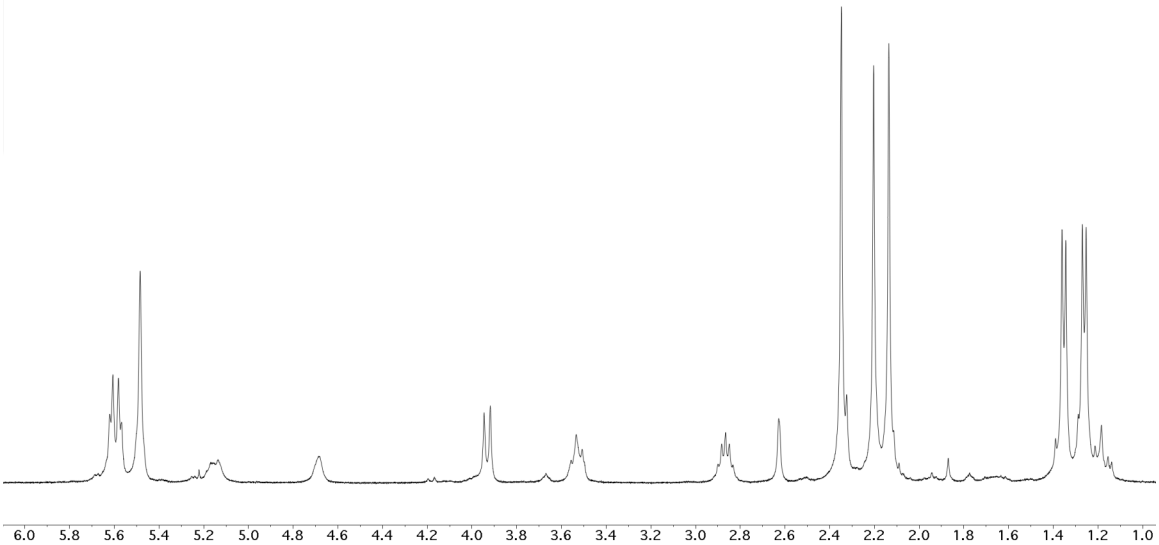


1a ***2b-d$_2$*** ***2b'-d$_2$***

undeuterated **2b**:



partially deuterated **2b'**:



Fluorescence Spectrum of 2f at 340 nm

The photophysical investigation of N-H activation was carried out using dansyl amide. Formation of the corresponding ruthenium amidato complex **2f** proceeds with complete quench of fluorescence. This reaction is instantaneous and irreversible as could be observed at various wave lengths. Figure S1 shows the different extinction coefficients for dansyl amide and complex **2f** at different wave lengths. Attempts to measure kinetics for the formation of ruthenium complex **2f** were not possible due to rapid and irreversible N-H activation.

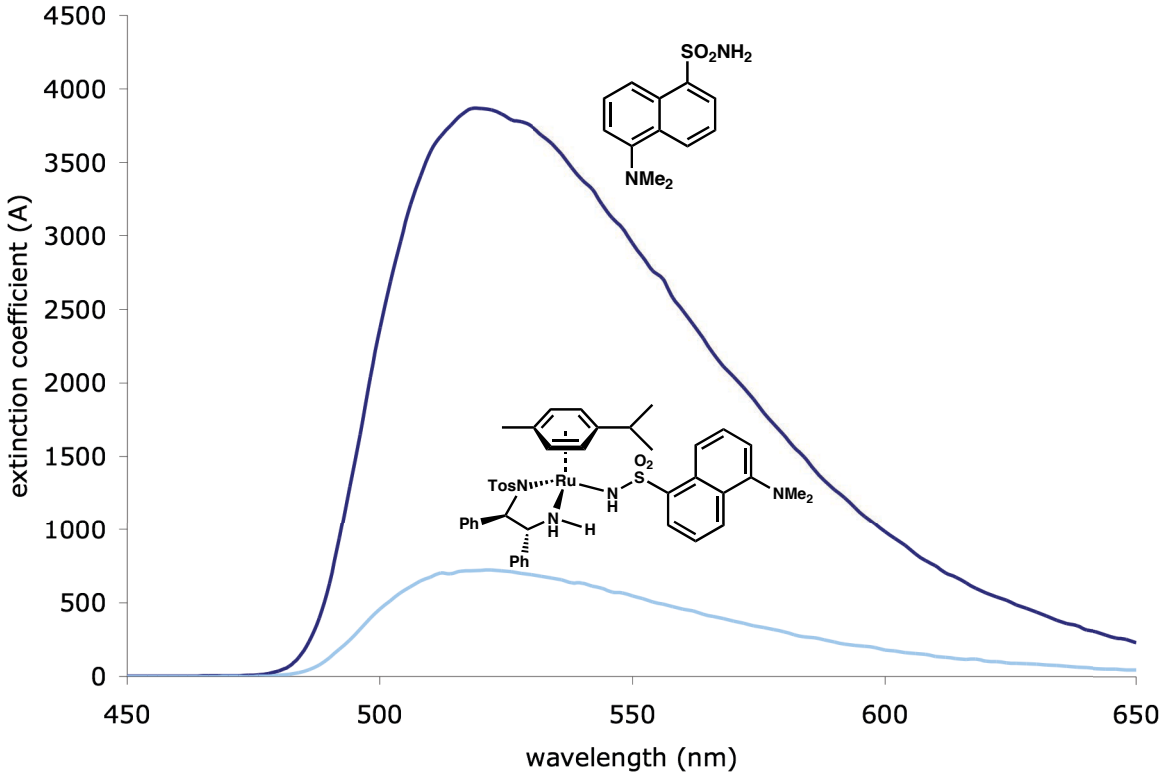
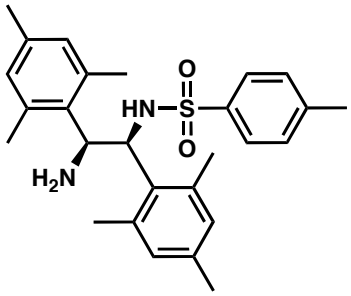


Figure S1. Fluorescence spectrum for dansyl amide (dark blue) and Ru complex **2f** (light blue) at UV-light (340 nm).

Preparation of Ligands

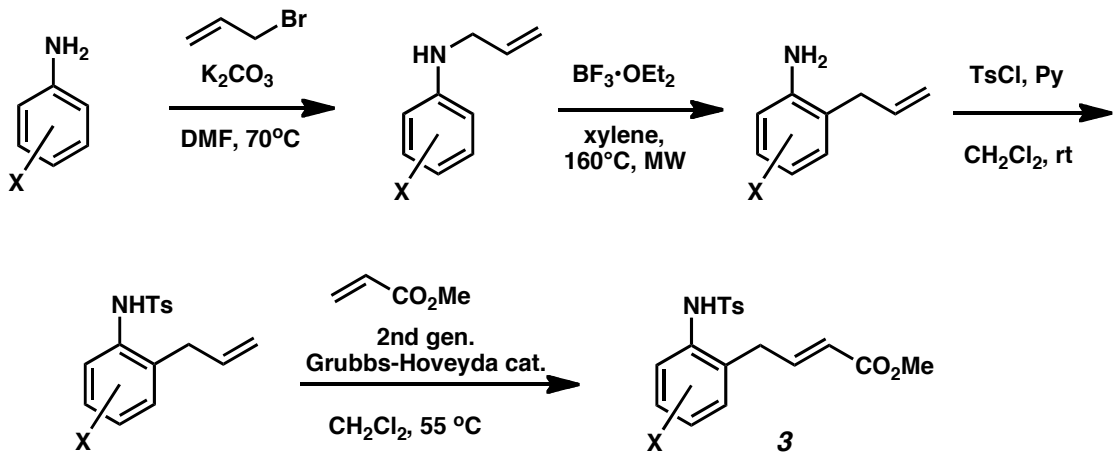
***N*-((1*S*,2*S*)-2-Amino-1,2-dimesitylethyl)-4-methylbenzenesulfonamide**



To a suspension of (*S,S*)-TPEN dihydrochloride (369 mg, 1 mmol) in 15 ml of dichloromethane at 0ºC was added triethylamine (0.43 ml, 3.1 mmol). After dissolving of dihydrochloride a solution of tosyl chloride (191 mg, 1 mmol) in 5 ml of dichloromethane was added dropwise. The mixture was then stirred overnight at rt, washed with 15 ml of water, dried with $MgSO_4$ and evaporated under reduced pressure to afford the crude product which was purified by silica gel column chromatography (ethyl acetate/hexane, 1:1, v/v) to afford the product as a white solid (401 mg, 89%). $[\alpha]_D^{27}$ = –57.7 ± 0.8 (*c* 0.125, CH_2Cl_2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.52 (s, 3H), 1.54 (s, 3H), 2.12 (s, 3H), 2.17 (s, 3H), 2.26 (s, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 4.43 (d, *J* = 9.9 Hz, 1H), 4.87 (d, *J* = 9.9 Hz, 1H), 6.45 (s, 1H), 6.50 (s, 1H), 6.54 (s, 1H), 6.79 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 19.8, 20.2, 20.4, 20.8, 20.9, 21.5, 52.1, 55.1, 127.3, 128.8, 128.9, 129.1, 130.9, 131.3, 132.1, 135.4, 136.5, 136.6, 136.7, 136.8, 137.4, 137.5, 142.7. ATR-FTIR: ν_{max}(cm^{-1}) = 3345, 3166, 3010, 2963, 2920, 2866, 1611, 1599, 1481, 1451, 1377, 1356, 1322, 1302, 1220, 1151, 1093, 1057, 1029, 966, 936, 851, 813, 755, 707, 662, 587. HRMS: m/z (ESI) calcd for $C_{27}H_{35}N_2O_2S$ $[M + H]^+$ 451.2419, found 451.2410.

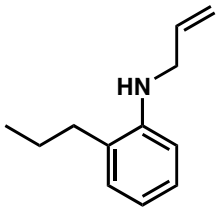
Synthesis of Starting Materials and Racemic Cyclic Products

All reactions were conducted following the following sequence of *N*-allylation, Claisen rearrangement, *N*-tosylation, metathesis with acrylates and C-N bond formaton:



Representative Procedure for *N*-Allylation of Anilines

***N*-Allyl-2-propylaniline**



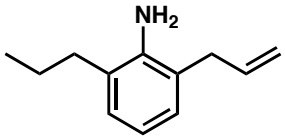
Following a modified procedure[S2] allyl bromide (1.3 mL, 15 mmol) was added to a solution of 2-propylaniline (2.1 mL, 15 mmol) and K_2CO_3 (5.0 g, 36 mmol) in DMF (30 mL). The solution was heated to 70 ºC and stirred at this temperature overnight. The mixture was allowed to cool down to room temperature and washed with water (30 ml). The aqueous phase was extracted with diethyl ether (2×30 ml). The combined organic layers were washed with brine, dried over MgSO4 and concentrated to provide the crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane, 1:40, v/v) to afford *N*-allyl-2-propylaniline (1.8 g, 68%) as a yellowish oil. ^{1}H-NMR (400 MHz,

(S2) A. Correa, I. Tellitu, E. Domínguez, and R. SanMartin, *J. Org. Chem*. **2006**, *71*, 8316.

$CDCl_3$): δ = 1.14 (t, J = 7.3 Hz, 3H), 1.71-1.89 (m, 2H), 2.59 (pst, J_1 = 7.6, J_2 = 7.9 Hz, 2H), 3.84 (s, 1H), 3.94 (dt, J_1 = 5.3, J_2 = 1.6 Hz, 2H), 5.36 (ddd, J_1 = 13.7, J_2 = 11.7, J_3 = 1.5 Hz, 2H), 6.12 (ddt, J_1 = 17.1, J_2 = 10.4, J_3 = 5.2 Hz, 1H), 6.76 (dd, J_1 = 8.1, J_2 = 0.7 Hz, 1H), 6.83 (td, J_1 = 7.4, J_2 = 1.1 Hz, 1H), 7.18 (dd, J_1 = 7.4, J_2 = 1.2 Hz, 1H), 7.25 (td, J_1 = 7.9, J_2 = 1.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.3, 21.8, 33.4, 46.6, 110.6, 116.1, 117.2, 126.3, 127.1, 129.1, 135.7, 145.5. ATR-FTIR: ν_{max}(cm^{-1}) = 3440, 3073, 3040, 3010, 2957, 2928, 2869, 1644, 1603, 1584, 1506, 1453, 1416, 1377, 1308, 1253, 1161, 1138, 1060, 992, 915, 743. HRMS: m/z (ESI) calcd for $C_{12}H_{18}N$ $[M + H]^+$ 176.1439, found 176.1436.

Representative Procedure for the Claisen Rearrangement of *N*-Allylanilines to 2-Allylanilines

2-Allyl-6-propylaniline



Following a modified procedure[S3] BF_3•OEt_2 (0.7 ml, 5.5 mmol) was added dropwise to a stirred solution of *N*-allyl-2-propylaniline (876 mg, 5 mmol) in xylene (3 mL) under an argon atmosphere. The solution was irradiated at 160 °C in a microwave oven for 6h. After cooling, the reaction mixture was poured into sat. aqueous K_2CO_3 solution (10 ml) and extracted with EtOAc (2×20 mL). The combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$ and concentrated to provide the crude product. Purification was carried out by silica gel column chromatography (ethyl acetate/hexane, 1:15, v/v) to afford 2-allyl-6-propylaniline (683 mg, 78%) as a yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, J = 7.3 Hz, 3H), 1.66-1.77 (m, 2H), 2.54 (pst, J_1 = 7.6, J_2 = 7.9 Hz, 2H), 3.38 (d, J = 6.2 Hz, 2H), 3.71 (s, 2H), 5.12-5.27 (m, 2H), 6.02 (ddt, J_1 = 14.1, J_2 = 10.8, J_3 = 6.2 Hz, 1H), 6.76 (t, J = 7.5 Hz, 1H), 7.01 (dd, J_1 = 13.9, J_2 = 7.5 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.0, 33.7, 37.0, 116.2, 118.3, 123.9, 126.8, 128.0, 128.0, 136.3, 142.6. ATR-FTIR: ν_{max}(cm^{-1}) = 3475, 3389, 3076, 3039, 3004, 2957, 2928, 2869, 1737, 1620,

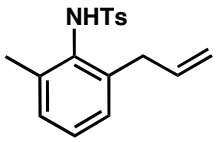
(S3) J. J. Neumann, S. Rakshit, T. Dröge, and F. Glorius, *Angew. Chem. Int. Ed*. **2009**, *48*, 6892.

1460, 1377, 1268, 1166, 1091, 996, 912, 745, 678, 574. HRMS: m/z (ESI) calcd for $C_{12}H_{18}N$ $[M + H]^+$ 176.1439, found 176.1439.

All other 2-allylaniline substrates were prepared in an identical fashion and were subsequently transformed into the required tosylamides without further characterization. In particular, non-substituted aniline was prepared starting from the commercially available *N*-allylaniline.

Representative Procedure for the Tosylation of 2-Allylanilines[S4]

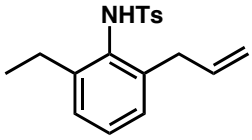
***N*-(2-Allyl-6-methylphenyl)-4-methylbenzenesulfonamide**



2-Allyl-6-methylaniline (294 mg, 2 mmol) was dissolved in 15 mL of dry methylene chloride, and the solution was treated with *p*-toluenesulfonyl chloride (400 mg, 2.1 mmol) and pyridine (0.49 ml, 6 mmol). The reaction mixture was stirred at room temperature for 24 h and then washed with 1N HCl solution (20 ml) and water (20 ml). The aqueous phase was extracted with diethyl ether (2×20 ml). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to provide the crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane, 1:9, v/v) to afford the product (549 mg, 91%) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.84 (s, 3H), 2.15 (s, 3H), 2.83 (d, J = 6.4 Hz, 2H), 4.65 (dq, J_1 = 17.1, J_2 = 1.7 Hz, 1H), 4.77 (ddd, J_1 = 10.1, J_2 = 3.1, J_3 = 1.4 Hz, 1H), 5.48 (ddt, J_1 = 16.6, J_2 = 10.1, J_3 = 6.4 Hz, 1H), 6.11 (s, 1H), 6.74 (dd, J_1 = 7.4, J_2 = 1.1 Hz, 1H), 6.80 (d, J = 6.6 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 19.0, 21.6, 36.5, 116.3, 127.2, 128.0, 128.1, 129.6, 129.7, 132.8, 136.7, 137.8, 138.3, 138.8, 143.8. ATR-FTIR: ν_{max}(cm^{-1}) = 3243, 3061, 2958, 2925, 2853, 1639, 1595, 1461, 1403, 1385, 1326, 1304, 1289, 1247, 1184, 1154, 1089, 1036, 1018, 992, 913, 810, 787, 772, 705, 664, 580. HRMS: m/z (ESI) calcd for $C_{17}H_{19}NO_2SNa$ $[M + Na]^+$ 324.1034, found 324.1023.

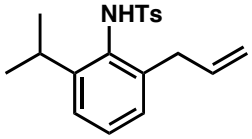
(S4) P. H. Fuller, J.-W. Kim and S. R. Chemler, *J. Am. Chem. Soc.* **2008**, *130*, 17638.

_N_-(2-Allyl-6-ethylphenyl)-4-methylbenzenesulfonamide



Prepared by the same procedure using 2-allyl-6-ethylaniline (322 mg, 2 mmol), *p*-toluenesulfonyl chloride (400 mg, 2.1 mmol) and pyridine (0.49 ml, 6 mmol), but the reaction mixture was stirred at 40 ºC for 24h. The crude product was purified by silica gel chromatography (ethyl acetate/hexane, 1:9, v/v) to afford the product as a white solid (536 mg, 85%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, J = 7.5 Hz, 3H), 2.47 (s, 3H), 2.61 (q, J = 7.5 Hz, 2H), 3.10 (d, J = 6.3 Hz, 2H), 5.02 (ddd, J_1 = 18.5, J_2 = 13.6, J_3 = 1.2 Hz, 2H), 5.80 (ddt, J_1 = 16.6, J_2 = 10.1, J_3 = 6.4 Hz, 1H), 6.24 (s, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.21 (dd, J_1 = 17.2, J_2 = 7.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.7, 21.7, 24.6, 36.7, 116.4, 127.2, 127.8, 128.1, 128.4, 129.7, 132.1, 136.7, 137.8, 138.6, 143.8, 144.3. ATR-FTIR: ν_{max}(cm^{-1}) = 3246, 3066, 3034, 3002, 2959, 2926, 2893, 2866, 1640, 1595, 1494, 1470, 1450, 1398, 1331, 1288, 1276, 1262, 1186, 1153, 1121, 1090, 995, 915, 905, 814, 790, 704, 674, 590. HRMS: m/z (ESI) calcd for $C_{18}H_{21}NO_2SNa$ $[M + Na]^+$ 338.1191, found 338.1176.

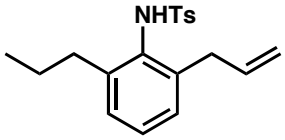
_N_-(2-Allyl-6-isopropylphenyl)-4-methylbenzenesulfonamide



Prepared by the same procedure using 2-allyl-6-isopropylaniline (351 mg, 2 mmol), *p*-toluenesulfonyl chloride (400 mg, 2.1 mmol) and pyridine (0.49 ml, 6 mmol), but the reaction mixture was stirred at 40 ºC for 24h. The crude product was purified by silica gel chromatography (ethyl acetate/hexane, 1:10, v/v) to afford the product as a yellowish solid (573 mg, 87%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.08 (d, J = 6.8 Hz, 6H), 2.47 (s, 3H), 3.12 (d, J = 6.3 Hz, 2H), 3.20-3.47 (m, 1H), 4.95 (dd, J_1 = 17.1, J_2 = 1.6 Hz, 1H), 5.09 (dd, J_1 = 10.1, J_2 = 1.3 Hz, 1H), 5.81 (ddt, J_1 = 16.7, J_2 = 10.1, J_3 = 6.3 Hz, 1H), 6.21 (s, 1H), 7.04 (dd, J_1 = 7.1, J_2 = 1.8 Hz, 1H), 7.21-7.28 (m, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 23.9, 28.3, 36.9, 116.4, 125.1,

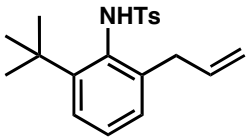
127.3, 127.9, 128.6, 129.7, 131.2, 136.8, 137.7, 138.6, 143.8, 149.0. ATR-FTIR: $\nu_{max}(cm^{-1})$ = 3260, 3062, 2963, 2923, 2867, 1594, 1472, 1446, 1396, 1383, 1363, 1327, 1307, 1289, 1185, 1151, 1091, 1046, 993, 921, 815, 789, 665, 608, 555. HRMS: m/z (ESI) calcd for $C_{19}H_{23}NO_2SNa$ $[M + Na]^+$ 352.1347, found 352.1329.

_N_-(2-Allyl-6-propylphenyl)-4-methylbenzenesulfonamide



Prepared by the same procedure using 2-allyl-6-propylaniline (351 mg, 2 mmol), *p*-toluenesulfonyl chloride (400 mg, 2.1 mmol) and pyridine (0.49 ml, 6 mmol), but the reaction mixture was stirred at 40 ºC for 24h. The crude product was purified by silica gel chromatography (ethyl acetate/hexane, 1:10, v/v) to afford the product as a light yellowish solid (580 mg, 88%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, J = 7.3 Hz, 3H), 1.36-1.60 (m, 2H), 2.36-2.54 (m, 5H), 3.13 (d, J = 6.3 Hz, 2H), 4.93 (ddd, J_1 = 17.1, J_2 = 3.3, J_3 = 1.6 Hz, 1H), 5.07 (dd, J_1 = 10.1, J_2 = 1.6 Hz, 1H), 5.80 (ddt, J_1 = 16.5, J_2 = 10.1, J_3 = 6.3 Hz, 1H), 6.21 (s, 1H), 7.03 (dd, J_1 = 7.4, J_2 = 1.3 Hz, 1H), 7.12 (dd, J_1 = 7.6, J_2 = 1.3 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 13.1, 20.6, 22.7, 32.6, 35.7, 115.3, 126.2, 127.1, 127.2, 127.4, 128.7, 131.3, 135.7, 136.9, 137.8, 141.7, 142.8. ATR-FTIR: $\nu_{max}(cm^{-1})$ = 3283, 2960, 2928, 2870, 1595, 1448, 1429, 1393, 1327, 1304, 1289, 1184, 1156, 1088, 995, 927, 894, 813, 801, 782, 671, 568. HRMS: m/z (ESI) calcd for $C_{19}H_{23}NO_2SNa$ $[M + Na]^+$ 352.1347, found 352.1330.

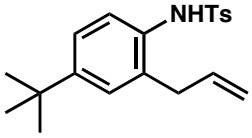
_N_-(2-Allyl-6-(*tert*-butyl)phenyl)-4-methylbenzenesulfonamide



2-Allyl-6-(*tert*-butyl)aniline (379 mg, 2 mmol) was dissolved in 10 mL of pyridine, and the solution was treated with *p*-toluenesulfonyl chloride (400 mg, 2.1 mmol). The reaction mixture was stirred at 80 ºC for 24 h, then poured into 1N HCl solution (50 ml), and

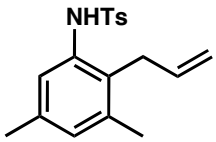
extracted with EtOAc (3×25 ml). The aqueous phase was extracted with diethyl ether (2×20 ml). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to provide the crude product, which was purified by silica gel column chromatography (ethyl acetate/hexane, 1:15, v/v) to afford the product (543 mg, 79%) as a yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.47 (s, 9H), 2.47 (s, 3H), 2.99 (d, J = 6.4 Hz, 2H), 4.86 (dd, J_1 = 17.1, J_2 = 1.7 Hz, 1H), 5.04 (dd, J_1 = 10.1, J_2 = 1.5 Hz, 1H), 5.73 (ddt, J_1 = 16.6, J_2 = 10.1, J_3 = 6.3 Hz, 1H), 6.28 (s, 1H), 7.05 (d, J = 7.4 Hz, 1H), 7.23 (t, J = 7.7 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.45 (dd, J_1 = 8.1, J_2 = 1.2 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 32.8, 36.7, 37.2, 116.1, 127.2, 127.7, 127.9, 128.3, 129.6, 131.9, 137.0, 138.6, 140.2, 143.6, 149.7. ATR-FTIR: ν_{max}(cm^{-1}) = 3279, 3073, 2959, 2922, 2870, 1638, 1598, 1482, 1429, 1398, 1381, 1321, 1305, 1261, 1209, 1154, 1091, 996, 911, 812, 785, 746, 705, 664, 580. HRMS: m/z (ESI) calcd for $C_{20}H_{25}NO_2SNa$ $[M + Na]^+$ 366.1504, found 366.1512.

_N_-(2-Allyl-4-(*tert*-butyl)phenyl)-4-methylbenzenesulfonamide



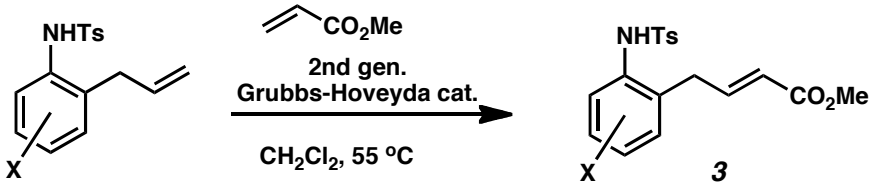
Prepared by the same procedure using 2-allyl-4-(*tert*-butyl)aniline (379 mg, 2 mmol), *p*-toluenesulfonyl chloride (400 mg, 2.1 mmol) and pyridine (0.49 ml, 6 mmol). The crude product was purified by silica gel chromatography (ethyl acetate/hexane, 1:9, v/v) to afford the product as a yellowish solid (660 mg, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 9H), 2.38 (s, 3H), 3.06 (d, J = 6.1 Hz, 2H), 4.95 (dq, J_1 = 17.2, J_2 = 1.6 Hz, 1H), 5.07 (dq, J_1 = 10.1, J_2 = 1.4 Hz, 1H), 5.78 (ddt, J_1 = 16.3, J_2 = 10.1, J_3 = 6.2 Hz, 1H), 6.62 (s, 1H), 7.08 (d, J = 2.3 Hz, 1H), 7.18 (dd, J_1 = 8.4, J_2 = 2.3 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 31.4, 34.5, 36.5, 116.8, 124.5, 124.6, 127.2, 127.4, 129.6, 132.1, 132.2, 136.1, 137.2, 143.7, 149.5. ATR-FTIR: ν_{max}(cm^{-1}) = 3272, 2963, 2932, 2904, 2867, 1639, 1596, 1496, 1461, 1407, 1384, 1363, 1334, 1287, 1263, 1186, 1162, 1123, 1089, 988, 911, 888, 876, 838, 811, 707, 671, 603, 583. HRMS: m/z (ESI) calcd for $C_{20}H_{25}NO_2SNa$ $[M + Na]^+$ 366.1504, found 366.1514.

_N_-(2-Allyl-3,5-dimethylphenyl)-4-methylbenzenesulfonamide

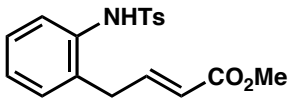


Prepared by the same procedure using 2-allyl-3,5-dimethylaniline (322 mg, 2 mmol), *p*-toluenesulfonyl chloride (400 mg, 2.1 mmol) and pyridine (0.49 ml, 6 mmol). The crude product was purified by silica gel chromatography (ethyl acetate/hexane, 1:9, v/v) to afford the product as a white solid (600 mg, 95%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3H), 2.24 (s, 3H), 2.38 (s, 3H), 3.03 (dt, J_1 = 5.2, J_2 = 1.8 Hz, 2H), 4.77 (dd, J_1 = 17.2, J_2 = 1.6 Hz, 1H), 5.00 (dd, J_1 = 10.2, J_2 = 1.6 Hz, 1H), 5.76 (ddt, J_1 = 17.1, J_2 = 10.4, J_3 = 5.4 Hz, 1H), 6.53 (s, 1H), 6.82 (s, 1H), 7.08 (s, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.0, 21.0, 21.6, 31.3, 115.9, 122.9, 127.2, 127.4, 129.1, 129.6, 134.9, 135.0, 136.7, 137.0, 137.4, 143.7. ATR-FTIR: ν_{max}(cm^{-1}) = 3252, 3081, 2997, 2975, 2918, 2857, 1638, 1596, 1491, 1448, 1414, 1386, 1322, 1302, 1287, 1198, 1156, 1136, 1086, 1049, 997, 894, 809, 798, 730, 697, 663, 613, 600, 575. HRMS: m/z (ESI) calcd for $C_{18}H_{21}NO_2SNa$ $[M + Na]^+$ 338.1191, found 338.1184.

Metathesis Reactions of 2-Allyl Anilines with Methyl Acrylate



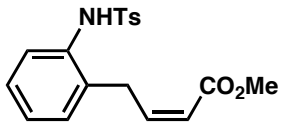
(*E*)-Methyl 4-(2-(4-methylphenylsulfonamido)phenyl)but-2-enoate



3a

Prepared by the same procedure using *N*-(2-allylphenyl)-4-methylbenzenesulfonamide (287 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a white solid (262 mg, 76%). R_f = 0.2. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 3.34 (dd, J_1 =1.4 Hz, J_2 =6.4 Hz, 2H), 3.69 (s, 3H), 5.60 (d, J =15.8 Hz, 1H), 6.70 (s, 1H), 6.85-6.93 (m, 1H), 7.06-7.09 (m, 1H), 7.14-7.23 (m, 5H), 7.58 (d, J =8.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.8, 34.0, 51.9, 122.7, 126.5, 127.4, 127.5, 128.2, 130.0, 130.8, 133.1, 134.5, 136.7, 144.3, 146.4, 166.9. ATR-FTIR: ν_{max}(cm^{-1}) = 3176, 1711, 1644, 1415, 1322, 1270, 1149, 1094, 1017, 924, 813, 767, 668. HRMS: m/z (ESI) calcd for $C_{18}H_{19}NO_4SNa$ $[M + Na]^+$ 368.0932, found 368.0931.

(*Z*)-Methyl 4-(2-(4-methylphenylsulfonamido)phenyl)but-2-enoate

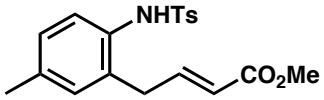


(Z)-3a

Prepared by the same procedure using *N*-(2-allylphenyl)-4-methylbenzenesulfonamide (287 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a white solid (52 mg, 15%). R_f = 0.3.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 3.60 (dd, J_1 =0.9 Hz, J_2 =8.5 Hz, 2H), 3.85 (s, 3H), 5.76 (dt, J_1 =1.5 Hz, J_2 =11.1 Hz, 1H), 6.05 (m, 1H), 7.02-7.12 (m, 2H), 7.15-7.20 (m, 3H), 7.55 (d, J =8.2 Hz, 1H), 7.64 (d, J =8.5 Hz, 2H), 8.25 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 21.8, 31.4, 52.3, 119.6, 123.3, 125.6, 127.5, 128.1, 129.1, 129.6, 130.9, 136.0, 137.3, 143.7, 146.4, 168.3. ATR-FTIR: ν_{max}(cm^{-1}) = 3185, 1693, 1641, 1597, 1493, 1438, 1400, 1336, 1290, 1251, 1230, 1186, 1161, 1087, 985, 909, 811, 767, 734, 706, 694, 665, 649, 577. HRMS: m/z (ESI) calcd for $C_{18}H_{19}NO_4SNa$ $[M + Na]^+$ 368.0932, found 368.0940.

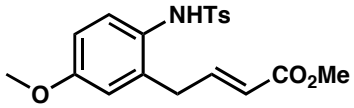
(*E*)-Methyl 4-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate



3b

Prepared by the same procedure using *N*-(2-allyl-4-methylphenyl)-4-methylbenzenesulfonamide (301 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a white solid (295 mg, 82%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 2.40 (s, 3H), 3.29 (dd, J_1 = 1.6 Hz, J_2 = 6.3 Hz, 2H), 3.71 (s, 3H), 5.61 (dt, J_1 = 1.7 Hz, J_2 = 15.7 Hz, 1H), 6.30 (s, 1H), 6.83-7.05 (m, 4H), 7.23 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.1, 21.7, 33.9, 51.7, 122.5, 127.0, 127.4, 128.7, 129.8, 131.3, 131.5, 133.5, 136.7, 137.6, 144.0, 146.4, 166.7. ATR-FTIR: ν_{max}(cm^{-1}) = 3278, 2949, 2920, 2854, 1723, 1649, 1595, 1496, 1443, 1431, 1396, 1334, 1302, 1269, 1214, 1185, 1161, 1120, 1104, 1087, 1025, 989, 924, 881, 815, 675, 590. HRMS: m/z (ESI) calcd for $C_{37}H_{43}N_2O_2S$ $[M + H]^+$ 579.3045, found 579.3043.

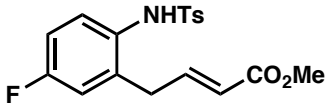
(*E*)-Methyl 4-(5-methoxy-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate



3c

Prepared by the same procedure using *N*-(2-allyl-4-methoxyphenyl)-4-methylbenzenesulfonamide (317 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:3, v/v) as a yellowish oil (319 mg, 85%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 3.32 (dd, J_1 = 1.5 Hz, J_2 = 6.8 Hz, 2H), 3.65 (s, 3H), 3.71 (s, 3H), 5.62 (d, J = 15.8 Hz, 1H), 6.58-6.63 (m, 2H), 6.80-6.93 (m, 3H), 7.19 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 34.1, 51.7, 55.6, 112.8, 115.8, 122.4, 126.7, 127.5, 129.7, 129.8, 136.7, 137.0, 144.0, 146.7, 159.0, 167.0. ATR-FTIR: ν_{max}(cm^{-1}) = 3247, 2950, 1717, 1653, 1600, 1496, 1434, 1327, 1277, 1206, 1155, 1091, 1035, 985, 894, 814, 752, 664. HRMS: m/z (ESI) calcd for $C_{19}H_{21}NO_5SNa$ $[M + Na]^+$ 398.1038, found 398.1049.

(*E*)-Methyl 4-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate

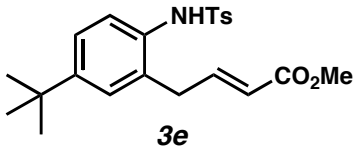


3d

Prepared by the same procedure using *N*-(2-allyl-4-fluorophenyl)-4-methylbenzenesulfonamide (305 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a white solid (287 mg, 79%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 3.32 (dd, J_1 = 1.5 Hz, J_2 = 6.4 Hz, 2H), 3.71 (s, 3H), 5.63 (dt, J_1 = 1.6 Hz, J_2 =15.7 Hz, 1H), 6.40 (s, 1H), 6.77-6.91 (m, 3H), 7.06 (dd, J_1 = 5.3 Hz, J_2 = 8.7 Hz, 1H), 7.24 (d, J = 8.9 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 33.9, 51.8, 114.7, 114.9, 117.1, 117.4, 123.1, 127.4, 129.4, 129.5, 129.9, 136.3, 137.0, 137.0, 144.3, 145.3, 160.4, 162.9, 166.5. ATR-FTIR: ν_{max}(cm^{-1}) = 2956, 2921, 2851, 1709, 1658, 1598, 1501, 1452, 1439, 1375, 1345, 1328, 1312, 1289, 1260, 1229, 1200, 1180, 1162, 1149, 1089, 1062, 1020, 1000, 977,

875, 851, 813, 712, 674, 641, 578. HRMS: m/z (ESI) calcd for $C_{19}H_{21}NO_4SNa$ $[M + Na]^+$ 382.1089, found 382.1106.

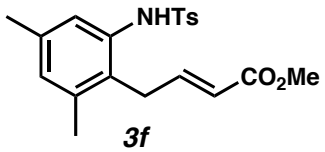
(*E*)-Methyl 4-(5-(*tert*-butyl)-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate



3e

Prepared by the same procedure using *N*-(2-allyl-4-(*tert*-butyl)phenyl)-4-methylbenzenesulfonamide (343 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a white solid (337 mg, 84%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 9H), 2.41 (s, 3H), 3.33 (dd, J_1 = 6.2, J_2 = 1.5 Hz, 2H), 3.71 (s, 3H), 5.61 (dt, J_1 = 15.7, J_2 = 1.6 Hz, 1H), 6.33 (s, 1H), 6.92 (dt, J_1 = 15.6, J_2 = 6.2 Hz, 1H), 7.06 (dd, J_1 = 10.3, J_2 = 5.3 Hz, 2H), 7.17 (dd, J_1 = 8.4, J_2 = 2.3 Hz, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 31.4, 34.4, 34.6, 51.7, 122.3, 125.1, 126.3, 127.4, 127.6, 129.8, 131.5, 132.6, 136.9, 143.9, 146.6, 150.6, 166.7. ATR-FTIR: ν_{max}(cm^{-1}) = 3296, 2966, 2902, 2871, 1725, 1647, 1596, 1502, 1459, 1441, 1431, 1393, 1362, 1329, 1305, 1266, 1186, 1158, 1126, 1088, 1019, 989, 936, 917, 881, 835, 808, 668, 593. HRMS: m/z (ESI) calcd for $C_{22}H_{27}NO_4SNa$ $[M + Na]^+$ 424.1559, found 424.1550.

(*E*)-Methyl 4-(2,4-dimethyl-6-(4-methylphenylsulfonamido)phenyl)but-2-enoate

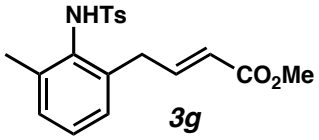


3f

Prepared by the same procedure using *N*-(2-allyl-3,5-dimethylphenyl)-4-methylbenzenesulfonamide (315 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a white solid (321 mg, 86%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3H), 2.20 (s, 3H), 2.40 (s, 3H), 3.32 (dd, J_1 = 5.4, J_2 = 1.9 Hz, 2H), 3.67 (s, 3H), 5.40 (dt, J_1 = 15.7, J_2 = 1.9 Hz, 1H),

6.30 (s, 1H), 6.86 (s, 2H), 6.97-6.87 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.0, 21.0, 21.7, 30.1, 51.6, 121.6, 124.6, 127.4, 127.9, 129.7, 130.1, 134.4, 136.8, 137.3, 137.9, 143.9, 146.0, 166.7. ATR-FTIR: ν_{max}(cm^{-1}) = 3184, 2949, 1713, 1649, 1432, 1421, 1401, 1337, 1321, 1303, 1270, 1186, 1168, 1151, 1138, 1092, 1054, 1019, 983, 970, 918, 885, 817, 736, 665, 597. HRMS: m/z (ESI) calcd for $C_{20}H_{23}NO_4SNa$ $[M + Na]^+$ 396.1245, found 396.1258.

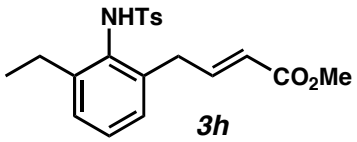
(*E*)-Methyl 4-(3-methyl-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate



3g

Prepared by the same procedure using *N*-(2-allyl-6-methylphenyl)-4-methylbenzenesulfonamide (301 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:3, v/v) as a yellowish oil (320 mg, 89%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 3H), 2.47 (s, 3H), 3.51 (dd, J_1 = 6.6, J_2 = 1.3 Hz, 2H), 3.74 (s, 3H), 5.72 (dt, J_1 = 15.6, J_2 = 1.6 Hz, 1H), 6.26 (s, 1H), 6.96 (dt, J_1 = 15.6, J_2 = 6.6 Hz, 1H), 7.07 (dd, J_1 = 14.1, J_2 = 7.5 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 18.6, 21.7, 34.9, 51.6, 122.1, 127.3, 128.4, 128.5, 129.8, 130.0, 132.5, 137.6, 137.9, 138.2, 144.0, 147.3, 167.0. ATR-FTIR: ν_{max}(cm^{-1}) = 3255, 2951, 2924, 2853, 1718, 1701, 1653, 1596, 1463, 1435, 1402, 1327, 1304, 1273, 1193, 1153, 1090, 1036, 1018, 984, 905, 813, 786, 662, 573. HRMS: m/z (ESI) calcd for $C_{19}H_{21}NO_4SNa$ $[M + Na]^+$ 382.1089, found 382.1099.

(*E*)-Methyl 4-(3-ethyl-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate

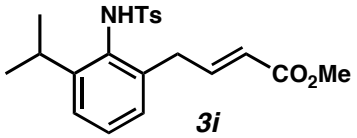


3h

Prepared by the same procedure using *N*-(2-allyl-6-ethylphenyl)-4-methylbenzenesulfonamide (315 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03

mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a light yellowish oil (332 mg, 89%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.5 Hz, 3H), 2.32 (q, J = 7.5 Hz, 2H), 2.41 (s, 3H), 3.44 (d, J = 6.6 Hz, 2H), 3.69 (s, 3H), 5.67 (dt, J_1 = 15.5, J_2 = 1.5 Hz, 1H), 6.31 (s, 1H), 6.90 (dt, J_1 = 15.6, J_2 = 6.7 Hz, 1H), 7.00 (d, J = 7.4 Hz, 1H), 7.10 (d, J = 6.9 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.5, 21.7, 24.2, 34.9, 51.6, 122.1, 127.3, 127.9, 128.3, 128.6, 129.8, 131.7, 137.5, 137.9, 143.9, 144.1, 147.4, 167.00. ATR-FTIR: ν_{max}(cm^{-1}) = 3258, 3027, 2962, 2875, 1719, 1702, 1651, 1597, 1494, 1453, 1436, 1402, 1327, 1304, 1272, 1208, 1183, 1153, 1091, 1037, 1018, 985, 909, 812, 732, 664, 556. HRMS: m/z (ESI) calcd for $C_{20}H_{23}NO_4SNa$ $[M + Na]^+$ 396.1245, found 396.1255.

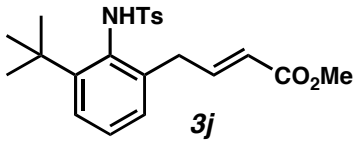
(*E*)-Methyl 4-(3-isopropyl-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate



3i

Prepared by the same procedure using *N*-(2-allyl-6-isopropylphenyl)-4-methylbenzenesulfonamide (329 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:5, v/v) as a white solid (341 mg, 88%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.94 (d, J = 6.9 Hz, 6H), 2.41 (s, 3H), 2.96 (hept, J = 6.8 Hz, 1H), 3.50 (d, J = 6.0 Hz, 2H), 3.70 (s, 3H), 5.71 (dt, J_1 = 15.6, J_2 = 1.3 Hz, 1H), 6.63 (s, 1H), 6.94 (dt, J_1 = 15.6, J_2 = 6.7 Hz, 1H), 7.01 (dd, J_1 = 7.4, J_2 = 1.3 Hz, 1H), 7.16 (dd, J_1 = 7.8, J_2 = 1.4 Hz, 1H), 7.20-7.29 (m, 3H), 7.60 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 23.7, 28.3, 35.1, 51.5, 122.0, 125.2, 127.3, 128.1, 128.8, 129.7, 130.7, 137.4, 137.9, 143.8, 147.5, 148.8, 167.0. ATR-FTIR: ν_{max}(cm^{-1}) = 3252, 2962, 2950, 2927, 1719, 1655, 1596, 1445, 1433, 1395, 1348, 1329, 1308, 1271, 1247, 1213, 1187, 1153, 1089, 1032, 983, 904, 818, 780, 707, 692, 677, 560. HRMS: m/z (ESI) calcd for $C_{21}H_{25}NO_4SNa$ $[M + Na]^+$ 410.1402, found 410.1409.

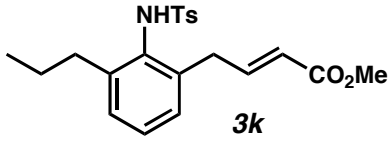
(*E*)-Methyl 4-(3-(*tert*-butyl)-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate



3j

Into a flame-dried Schlenk-flask were introduced *N*-(2-allyl-6-(*tert*-butyl)phenyl)-4-methylbenzenesulfonamide (343 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The flask was equipped with a stopper and the reaction mixture heated to 55 ºC overnight. The mixture was concentrated and the product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a yellowish oil (341 mg, 85%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.38 (s, 9H), 2.42 (s, 3H), 3.25 (dd, J_1 = 6.6, J_2 = 1.4 Hz, 2H), 3.69 (s, 3H), 5.56 (dt, J_1 = 15.6, J_2 = 1.6 Hz, 1H), 6.30 (s, 1H), 6.79 (dt, J_1 = 15.6, J_2 = 6.6 Hz, 1H), 6.98 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 7.6 Hz, 2H), 7.39 (dd, J_1 = 8.1, J_2 = 1.5 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 32.6, 35.6, 36.5, 51.6, 122.0, 127.2, 127.8, 128.1, 128.6, 129.7, 132.0, 138.6, 138.7, 143.8, 147.5, 149.4, 166.9. ATR-FTIR: ν_{max}(cm^{-1}) = 3267, 2953, 2923, 2871, 1720, 1702, 1650, 1597, 1433, 1400, 1365, 1323, 1305, 1273, 1210, 1152, 1090, 1036, 1018, 985, 909, 813, 788, 659, 587, 543. HRMS: m/z (ESI) calcd for $C_{22}H_{27}NO_4SNa$ $[M + Na]^+$ 424.1559, found 424.1565.

(*E*)-Methyl 4-(2-(4-methylphenylsulfonamido)-3-propylphenyl)but-2-enoate

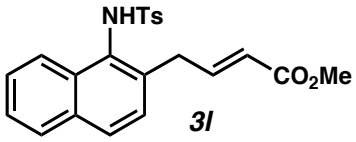


3k

Prepared by the same procedure using *N*-(2-allyl-6-propylphenyl)-4-methylbenzenesulfonamide (329 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and methyl acrylate (0.8 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:5, v/v) as a light brown solid (349 mg, 90%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.76 (t, J = 7.3 Hz, 3H), 1.38 (dq, J_1 = 14.9, J_2 = 7.3 Hz, 2H), 2.19 (pst, J_1 = 8.1, J_2 = 7.7 Hz, 2H), 2.41 (s, 3H), 3.49 (d, J = 6.4 Hz, 2H), 3.70 (s, 3H), 5.69 (d, J = 15.6 Hz, 1H), 6.25 (s, 1H), 6.93 (dt, J_1 = 15.5, J_2 =

6.7 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.6, 23.6, 33.3, 35.0, 51.6, 122.1, 127.3, 128.4, 128.5, 128.6, 129.8, 132.0, 137.6, 138.0, 142.5, 143.9, 147.4, 167.0. ATR-FTIR: $\nu_{max}(cm^{-1})$ = 3282, 2959, 2928, 2870, 1716, 1653, 1596, 1450, 1433, 1383, 1324, 1304, 1278, 1258, 1208, 1183, 1152, 1107, 1088, 1050, 986, 891, 812, 785, 669, 569. HRMS: m/z (ESI) calcd for $C_{21}H_{25}NO_4SNa$ $[M + Na]^+$ 410.1402, found 410.1414.

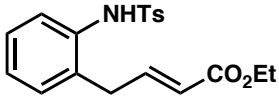
(*E*)-Methyl 4-(1-(4-methylphenylsulfonamido)naphthalen-2-yl)but-2-enoate



3l

Prepared by the same procedure using *N*-(2-allylnaphthalen-1-yl)-4-methylbenzenesulfonamide (1.69 g, 5 mmol), Grubbs-Hoveyda catalyst (94 mg, 0.03 mmol), dichloromethane (15 ml) and methyl acrylate (4.1 ml, 45 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) as a light brown solid (1.74 g, 88%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 3.64 (dd, J_1 = 6.6, J_2 = 1.2 Hz, 2H), 3.69 (s, 3H), 5.71 (dt, J_1 = 15.6, J_2 = 1.5 Hz, 1H), 6.89 (s, 1H), 6.95 (dt, J_1 = 15.6, J_2 = 6.6 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.22 (ddd, J_1 = 8.2, J_2 = 6.9, J_3 = 1.0 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.37 (ddd, J_1 = 7.9, J_2 = 6.8, J_3 = 0.7 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.75 (dd, J_1 = 8.2, J_2 = 3.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 34.9, 51.6, 122.4, 123.5, 126.0, 126.6, 127.4, 127.8, 128.0, 129.0, 129.1, 129.7, 132.0, 133.5, 135.6, 137.2, 143.9, 146.9, 166.9. ATR-FTIR: $\nu_{max}(cm^{-1})$ = 3234, 2950, 2922, 2852, 1713, 1648, 1596, 1435, 1395, 1335, 1320, 1301, 1273, 1239, 1212, 1151, 1092, 1078, 1014, 987, 921, 899, 832, 810, 785, 759, 652, 567. HRMS: m/z (ESI) calcd for $C_{22}H_{21}NO_4SNa$ $[M + Na]^+$ 418.1089, found 418.1089.

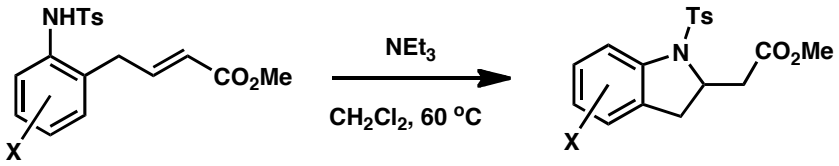
(*E*)-Ethyl 4-(2-(4-methylphenylsulfonamido)phenyl)but-2-enoate



Prepared by the same procedure using *N*-(2-allylphenyl)-4-methylbenzenesulfonamide (287 mg, 1 mmol), Grubbs-Hoveyda catalyst (19 mg, 0.03 mmol), dichloromethane (3 ml) and ethyl acrylate (1.0 ml, 9 mmol). The product was separated by silica gel column chromatography (ethyl acetate/hexane, 1:5, v/v) as a light brown oil (298 mg, 83%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.1 Hz, 3H), 2.38 (s, 3H), 3.33 (dd, J_1 = 6.3, J_2 = 1.6 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 5.59 (dt, J_1 = 15.6, J_2 = 1.6 Hz, 1H), 6.78 (s, 1H), 6.89 (dt, J_1 = 15.7, J_2 = 6.3 Hz, 1H), 7.03-7.24 (m, 6H), 7.58 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.3, 21.6, 33.7, 60.5, 122.9, 126.3, 127.2, 127.3, 127.9, 129.7, 130.6, 133.0, 134.3, 136.5, 144.0, 145.9, 166.3. ATR-FTIR: ν_{max}(cm^{-1}) = 3260, 2981, 2927, 1715, 1651, 1598, 1493, 1455, 1399, 1368, 1331, 1306, 1270, 1234, 1157, 1091, 1039, 984, 917, 813, 756, 707, 663, 565. HRMS: m/z (ESI) calcd for $C_{19}H_{21}NO_4SNa$ $[M + Na]^+$ 382.1089, found 382.1086.

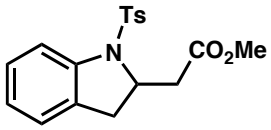
Synthesis and Characterization of Racemic N-C Coupling Products

The racemic products were synthesized according to the following general procedure:



A Pyrex tube equipped with a stirrer bar was charged with the substrate (40 mg, 0.1 mmol), CH_2Cl_2 (5 ml) and Et_3N (0.14 ml, 1 mmol), sealed and heated to 60 ºC overnight. The mixture was evaporated and purified by flash silica gel column chromatography to afford the racemic product.

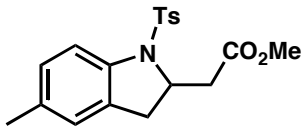
Methyl 2-(1-tosylindolin-2-yl)acetate



4a

Prepared by the same procedure using (*E*)-methyl 4-(2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (35 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:4, v/v) to afford the racemic product (33 mg, 94%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.55-2.68 (m, 2H), 2.94 (dd, J_1 = 9.4 Hz, J_2 = 16.4 Hz, 1H), 3.06 (dd, J_1 = 3.8 Hz, J_2 = 16.1 Hz, 1H), 3.68 (s, 3H), 4.53-4.60 (m, 1H), 6.98-7.02 (m, 2H), 7.14-7.20 (m, 3H), 7.54 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 7.9 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.8, 35.0, 41.6, 52.1, 59.0, 117.5, 125.1, 125.6, 127.4, 128.2, 130.0, 131.5, 135.0, 141.3, 144.4, 171.6. ATR-FTIR: ν_{max}(cm^{-1}) = 2951, 2360, 1732, 1597, 1478, 14.60, 1437, 1352, 1241, 1198, 1164, 1090, 1016, 968, 899, 813, 753, 709, 664. HRMS: m/z (ESI) calcd for $C_{18}H_{19}NO_4SNa$ $[M + Na]^+$ 368.0932, found 368.0933. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 17.95 min (*R*-enantiomer), tR_2 = 24.18 min (*S*-enantiomer).

Methyl 2-(5-methyl-1-tosylindolin-2-yl)acetate

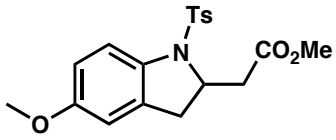


4b

Prepared by the same procedure using (*E*)-methyl 4-(5-methyl-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (36 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:4, v/v) to afford the racemic product (33 mg, 92%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 2.35 (s, 3H), 2.53 (dd, J_1 = 16.5, J_2 = 2.7 Hz, 1H), 2.64 (dd, J_1 = 16.2, J_2 = 10.1 Hz, 1H), 2.89 (dd, J_1 = 16.5, J_2 = 9.3 Hz, 1H), 3.05 (dd, J_1 = 16.2, J_2 = 4.1 Hz, 1H), 3.69 (s, 3H), 4.48-4.62 (m, 1H), 6.84 (s, 1H), 7.02 (d, J = 8.2 Hz, 1H), 7.16 (t, J = 8.2 Hz, 2H), 7.54 (dd, J_1 = 8.3, J_2 = 2.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.1, 21.7,

34.8, 41.4, 51.9, 58.9, 117.2, 126.0, 127.3, 128.6, 129.8, 131.4, 134.7, 134.8, 138.8, 144.0, 171.5. ATR-FTIR: $\nu_{max}(cm^{-1})$ = 2951, 2861, 2362, 1733, 1597, 1486, 1436, 1352, 1317, 1292, 1246, 1197, 1162, 1111, 1090, 1044, 1018, 970, 895, 814, 751, 707, 665. HRMS: m/z (ESI) calcd for $C_{19}H_{21}NO_4SNa$ $[M + Na]^+$ 382.1089, found 382.1073. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 25.22 min (*R*-enantiomer), tR_2 = 29.68 min (*S*-enantiomer).

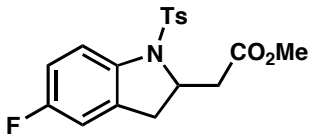
Methyl 2-(5-methoxy-1-tosylindolin-2-yl)acetate



4c

Prepared by the same procedure using (*E*)-methyl 4-(5-methoxy-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (38 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:3, v/v) to afford the racemic product (34 mg, 89%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 2.49 (dd, J_1 = 2.4 Hz, J_2 = 16.6 Hz, 1H), 2.61 (dd, J_1 = 10.1 Hz, J_2 = 16.1 Hz, 1H), 2.80 (dd, J_1 = 9.1 Hz, J_2 = 16.5 Hz, 1H), 2.99 (dd, J_1 = 4.4 Hz, J_2 = 16.1 Hz, 1H), 3.68 (s, 3H), 3.74 (s, 3H), 4.49-2.59 (m, 1H), 6.57 (d, J = 2.5 Hz, 1H), 6.75 (dd, J_1 = 2.5 Hz, J_2 = 8.8 Hz, 1H), 7.15 (d, J = 8.3 Hz, 2H), 7.53 (psc, J_1 = 8.8 Hz, J_2 = 8.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.8, 35.1, 41.4, 52.1, 55.9, 59.3, 111.2, 113.3, 118.9, 127.4, 129.9, 133.5, 134.6, 134.7, 144.2, 157.8, 171.6. ATR-FTIR: $\nu_{max}(cm^{-1})$ = 2951, 2837, 2360, 1732, 1597, 1485, 1435, 1350, 1309, 1261, 1195, 1162, 1088, 1029, 969, 843, 813, 749, 706, 666. HRMS: m/z (ESI) calcd for $C_{19}H_{21}NO_5SNa$ $[M + Na]^+$ 398.1038, found 398.1039. HPLC: Chiralcel-OD, 0.5 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 27.47 min (*R*-enantiomer), tR_2 = 29.78 min (*S*-enantiomer).

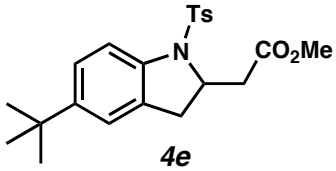
Methyl 2-(5-fluoro-1-tosylindolin-2-yl)acetate



4d

Prepared by the same procedure using (*E*)-methyl 4-(5-fluoro-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (36 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:4, v/v) to afford the racemic product (34 mg, 94%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 2.56 (dd, J_1 = 16.8, J_2 = 2.6 Hz, 1H), 2.66 (dd, J_1 = 16.3, J_2 = 10.0 Hz, 1H), 2.88 (dd, J_1 = 16.9, J_2 = 9.5 Hz, 1H), 3.04 (dd, J_1 = 16.3, J_2 = 4.2 Hz, 1H), 3.70 (s, 3H), 4.49-4.68 (m, 1H), 6.74 (dd, J_1 = 8.0, J_2 = 2.5 Hz, 1H), 6.92 (td, J_1 = 8.8, J_2 = 2.6 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.61 (dd, J_1 = 8.8, J_2 = 4.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 34.8, 41.2, 52.0, 59.3, 112.4, 112.7, 114.6, 114.8, 118.6, 118.7, 127.3, 129.9, 133.6, 133.7, 134.4, 137.2, 144.4, 159.4, 161.8, 171.3. ATR-FTIR: ν_{max}(cm^{-1}) = 2923, 2360, 1734, 1598, 1480, 1438, 1354, 1259, 1164, 1089, 1017, 938, 857, 813, 754, 707, 666. HRMS: m/z (ESI) calcd for $C_{18}H_{18}NO_4FSNa$ $[M + Na]^+$ 386.0838, found 386.0824. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 20.23 min (*R*-enantiomer), tR_2 = 27.22 min (*S*-enantiomer).

Methyl 2-(5-(*tert*-butyl)-1-tosylindolin-2-yl)acetate

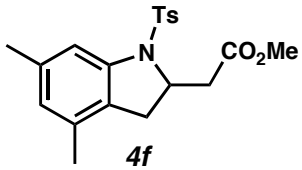


4e

Prepared by the same procedure using (*E*)-methyl 4-(5-(*tert*-butyl)-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (40 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:4, v/v) to afford the racemic product (37 mg, 93%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 9H), 2.35 (s, 3H), 2.57 (dd, J_1 = 16.4, J_2 = 2.8 Hz, 1H), 2.66 (dd, J_1 = 16.2, J_2 = 10.2 Hz, 1H), 2.95 (dd, J_1 = 16.4, J_2 = 9.4 Hz, 1H), 3.08 (dd, J_1 = 16.2, J_2 = 4.1 Hz, 1H), 3.69 (s, 3H), 4.63-4.48 (m, 1H), 7.04 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.22 (dd, J_1 = 8.5, J_2

= 1.9 Hz, 1H), 7.56 (dd, J = 8.4, 3.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 31.6, 34.6, 35.1, 41.4, 51.9, 58.9, 116.6, 122.3, 125.0, 127.3, 129.7, 130.8, 135.0, 138.6, 144.0, 148.2, 171.5. ATR-FTIR: ν_{max}(cm^{-1}) = 2955, 2867, 1733, 1597, 1488, 1460, 1437, 1395, 1353, 1318, 1304, 1251, 1197, 1163, 1123, 1090, 1045, 1017, 971, 892, 813, 714, 664, 603, 583. HRMS: m/z (ESI) calcd for $C_{22}H_{27}NO_4SNa$ $[M + Na]^+$ 424.1559, found 424.1573. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 12.57 min (*S*-enantiomer), tR_2 = 19.42 min (*R*-enantiomer).

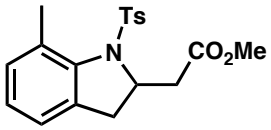
Methyl 2-(4,6-dimethyl-1-tosylindolin-2-yl)acetate



4f

Prepared by the same procedure using (*E*)-methyl 4-(2,4-dimethyl-6-(4-methylphenylsulfonamido)phenyl)but-2-enoate (37 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:4, v/v) to afford the racemic product (35 mg, 95%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 3H), 2.32 (s, 3H), 2.35 (s, 3H), 2.47 (dd, J_1 = 16.4, J_2 = 2.8 Hz, 1H), 2.65 (dd, J_1 = 16.3, J_2 = 10.2 Hz, 1H), 2.84 (dd, J_1 = 16.3, J_2 = 9.5 Hz, 1H), 3.10 (dd, J_1 = 16.3, J_2 = 4.0 Hz, 1H), 3.69 (s, 3H), 4.57 (tt, J_1 = 9.8, J_2 = 3.5 Hz, 1H), 6.66 (s, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.33 (s, 1H), 7.57 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 18.7, 21.6, 33.6, 41.7, 51.8, 58.9, 100.1, 115.0, 126.7, 126.8, 127.2, 129.7, 134.4, 134.9, 138.0, 140.9, 144.0, 171.5. ATR-FTIR: ν_{max}(cm^{-1}) = 2951, 2922, 2856, 1733, 1596, 1492, 1437, 1415, 1352, 1291, 1264, 1198, 1163, 1090, 1045, 954, 849, 813, 666, 581. HRMS: m/z (ESI) calcd for $C_{20}H_{23}NO_4SNa$ $[M + Na]^+$ 396.1245, found 396.1256. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 12.03 min (*R*-enantiomer), tR_2 = 13.37 min (*S*-enantiomer).

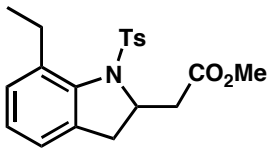
Methyl 2-(7-methyl-1-tosylindolin-2-yl)acetate



4g

Prepared by the same procedure using (*E*)-methyl 4-(3-methyl-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (36mg, 0.1 mmol), CH_2Cl_2 (5 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:3, v/v) to afford the racemic product (32 mg, 89%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.15 (d, J = 16.1 Hz, 1H), 2.22 (dd, J_1 = 16.2, J_2 = 7.1 Hz, 1H), 2.44-2.34 (m, 4H), 2.65 (dd, J_1 = 15.5, J_2 = 5.7 Hz, 1H), 2.56 (s, 3H), 3.64 (s, 3H), 4.66 (dtd, J_1 = 8.6, J_2 = 7.0, J_3 = 1.3 Hz, 1H), 6.85 (d, J = 7.2 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.0, 21.7, 34.3, 39.7, 51.9, 60.7, 122.6, 126.9, 127.8, 129.6, 130.6, 133.4, 134.6, 135.9, 140.2, 144.2, 171.1. ATR-FTIR: ν_{max}(cm^{-1}) = 2955, 2923, 2853, 1737, 1595, 1432, 1418, 1348, 1332, 1304, 1280, 1240, 1226, 1197, 1185, 1166, 1154, 1087, 1060, 1027, 1018, 962, 899, 843, 815, 789, 772, 737, 673, 641, 580. HRMS: m/z (ESI) calcd for $C_{19}H_{21}NO_4SNa$ $[M + Na]^+$ 382.1089, found 382.1102. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 12.12 min (*S*-enantiomer), tR_2 = 14.37 min (*R*-enantiomer).

Methyl 2-(7-ethyl-1-tosylindolin-2-yl)acetate

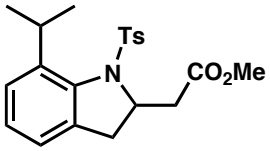


4h

Prepared by the same procedure using (*E*)-methyl 4-(3-ethyl-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (37 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:4, v/v) to afford the racemic product (30 mg, 81%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.5 Hz, 3H), 2.12 (d, J = 15.9 Hz, 1H), 2.19 (dd, J_1 = 16.2, J_2 = 6.8 Hz, 1H), 2.31-2.49 (m, 4H), 2.66 (dd, J_1 = 15.6, J_2 = 5.8 Hz, 1H), 2.90 (dq, J_1 = 15.0, J_2 = 7.5 Hz, 1H), 3.22 (dq, J_1 = 15.1, J_2 = 7.5 Hz, 1H), 3.65 (s, 3H), 4.67 (dddd, J_1 = 8.5, J_2 = 7.0, J_3 =

5.8, J_4 = 1.4 Hz, 1H), 6.85 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.5, 21.7, 25.6, 34.2, 39.6, 51.9, 60.8, 122.6, 127.3, 127.9, 128.7, 129.6, 134.5, 136.0, 139.5, 139.6, 144.2, 171.1. ATR-FTIR: $\nu_{max}(cm^{-1})$ = 2954, 2929, 2874, 1736, 1597, 1435, 1353, 1326, 1305, 1286, 1248, 1164, 1089, 1030, 1017, 986, 957, 814, 707, 676, 574. HRMS: m/z (ESI) calcd for $C_{20}H_{23}NO_4SNa$ $[M + Na]^+$ 396.1245, found 396.1265. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 10.85 min (*S*-enantiomer), tR_2 = 12.80 min (*R*-enantiomer).

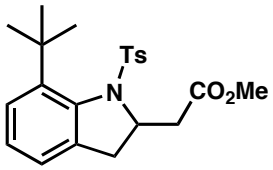
Methyl 2-(7-isopropyl-1-tosylindolin-2-yl)acetate



4i

Prepared by the same procedure using (*E*)-methyl 4-(3-isopropyl-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (39 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:5, v/v) to afford the racemic product (30 mg, 77%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.9 Hz, 3H), 1.43 (d, J = 6.8 Hz, 3H), 2.06-2.22 (m, 2H), 2.32-2.43 (m, 4H), 2.66 (dd, J_1 = 15.6, J_2 = 5.9 Hz, 1H), 3.65 (s, 3H), 3.82-3.95 (m, 1H), 4.68 (dtd, J_1 = 7.9, J_2 = 6.3, J_3 = 1.7 Hz, 1H), 6.83 (dd, J_1 = 7.2, J_2 = 0.7 Hz, 1H), 7.10-7.17 (m, 3H), 7.26 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 22.3, 25.5, 29.0, 34.3, 39.5, 51.9, 60.7, 122.5, 125.8, 127.7, 127.9, 129.5, 134.4, 135.9 138.6, 144.2, 144.5, 171.0. ATR-FTIR: $\nu_{max}(cm^{-1})$ = 2952, 2926, 2868, 1736, 1597, 1478, 1435, 1353, 1327, 1304, 1284, 1244, 1164, 1088, 1028, 1006, 949, 814, 801, 785, 754, 707, 678, 581. HRMS: m/z (ESI) calcd for $C_{21}H_{25}NO_4SNa$ $[M + Na]^+$ 410.1402, found 410.1409. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 9.53 min (*S*-enantiomer), tR_2 = 10.95 min (*R*-enantiomer).

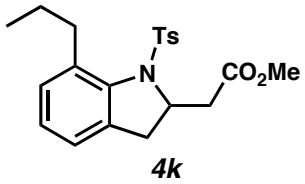
Methyl 2-(7-(*tert*-butyl)-1-tosylindolin-2-yl)acetate



4j

A Pyrex tube equipped with a stirrer bar was charged with (*E*)-methyl 4-(3-(*tert*-butyl)-2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (40 mg, 0.1 mmol), CH_2Cl_2 (5 ml) and Et_3N (0.14 ml, 1 mmol), sealed and heated to 60 ºC overnight. The mixture was evaporated and purified by flash silica gel column chromatography (ethyl acetate/hexane, 1:4, v/v) to afford racemic product (37 mg, 92%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 9H), 1.94 (dd, J_1 = 16.4, J_2 = 6.6 Hz, 1H), 2.00 (d, J = 15.9 Hz, 1H), 2.33-2.47 (m, 4H), 2.71 (dd, J_1 = 15.7, J_2 = 6.2 Hz, 1H), 3.67 (s, 3H), 4.63 (dtd, J_1 = 8.0, J_2 = 6.5, J_3 = 1.4 Hz, 1H), 6.78 (d, J = 7.1 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.8, 32.5, 33.6, 37.1, 39.4, 51.9, 59.9, 122.1, 127.2, 128.4, 129.3, 129.4, 134.1, 137.6, 137.8, 144.2, 146.8, 171.1. ATR-FTIR: ν_{max}(cm^{-1}) = 2954, 2926, 2855, 1741, 1483, 1433, 1418, 1349, 1334, 1279, 1251, 1220, 1192, 1165, 1144, 1086, 1068, 1025, 987, 953, 869, 811, 782, 754, 678, 577. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 8.90 min (*S*-enantiomer), tR_2 = 10.40 min (*R*-enantiomer).

Methyl 2-(7-propyl-1-tosylindolin-2-yl)acetate



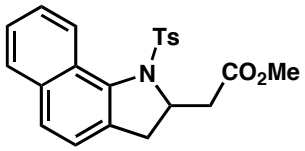
4k

Prepared by the same procedure using (*E*)-methyl 4-(2-(4-methylphenylsulfonamido)-3-propylphenyl)but-2-enoate (39 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:5, v/v) to afford the racemic product (31 mg, 79%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.3 Hz, 3H), 1.60-1.81 (m, 2H), 2.08-2.22 (m, 2H), 2.31-2.45 (m, 4H), 2.67 (dd, J_1 = 15.7, J_2 = 5.7 Hz, 1H), 2.77 (ddd, J_1 = 14.7, J_2 = 9.1, J_3 = 5.9 Hz, 1H), 3.28 (ddd, J_1 = 14.8, J_2 = 9.1, J_3 =

6.8 Hz, 1H), 3.66 (s, 3H), 4.67 (dddd, J_1 = 8.8, J_2 = 7.0, J_3 = 5.8, J_4 = 1.4 Hz, 1H), 6.85 (d, J = 7.1 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.2, 21.7, 23.4, 34.2, 34.5, 39.5, 51.9, 60.7, 122.6, 127.2, 127.9, 129.4, 129.5, 134.5, 136.0, 138.1, 139.8, 144.2, 171.1. ATR-FTIR: ν_{max}(cm^{-1}) = 2956, 2927, 2870, 1736, 1597, 1436, 1354, 1305, 1286, 1244, 1165, 1090, 1029, 1009, 953, 813, 773, 707, 678, 574. HRMS: m/z (ESI) calcd for $C_{21}H_{25}NO_4SNa$ $[M + Na]^+$ 410.1402, found 410.1414.

HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 11.25 min (*S*-enantiomer), tR_2 = 12.13 min (*R*-enantiomer).

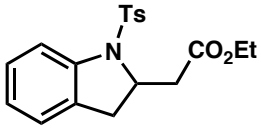
Methyl 2-(1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-2-yl)acetate



4l

Prepared by the same procedure using (*E*)-methyl 4-(1-(4-methylphenylsulfonamido)naphthalen-2-yl)but-2-enoate (1.19 g, 3 mmol), toluene (25 ml) and Et_3N (4.2 ml, 30 mmol). Heated to 100 ºC overnight. Purified by flash column chromatography (ethyl acetate/hexane, 1:4, v/v) to afford the racemic product (1.13 mg, 95%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.27-2.41 (m, 5H), 2.46 (dd, J_1 = 15.7, J_2 = 9.2 Hz, 1H), 2.77 (dd, J_1 = 15.7, J_2 = 5.4 Hz, 1H), 3.63 (s, 3H), 4.80-4.91 (m, 1H), 7.08 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 1H), 7.24 (d, J = 8.3 Hz, 2H), 7.49 (ddd, J_1 = 8.0, J_2 = 6.8, J_3 = 0.9 Hz, 1H), 7.57 (ddd, J_1 = 8.3, J_2 = 6.9, J_3 = 1.1 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 8.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.7, 34.9, 39.8, 51.9, 61.5, 122.5, 125.9, 126.0, 126.3, 127.7, 127.8, 128.1, 129.5, 132.5, 133.8, 134.1, 137.0, 144.3, 171.1. ATR-FTIR: ν_{max}(cm^{-1}) = 2923, 2852, 2361, 1736, 1596, 1437, 1355, 1292, 1261, 1168, 1089, 1034, 949, 893, 813, 750, 699, 661. HRMS: m/z (ESI) calcd for $C_{22}H_{21}NO_4SNa$ $[M + Na]^+$ 418.1089, found 418.1093. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 21.18 min (*R*-enantiomer), tR_2 = 22.38 min (*S*-enantiomer).

Ethyl 2-(1-tosylindolin-2-yl)acetate

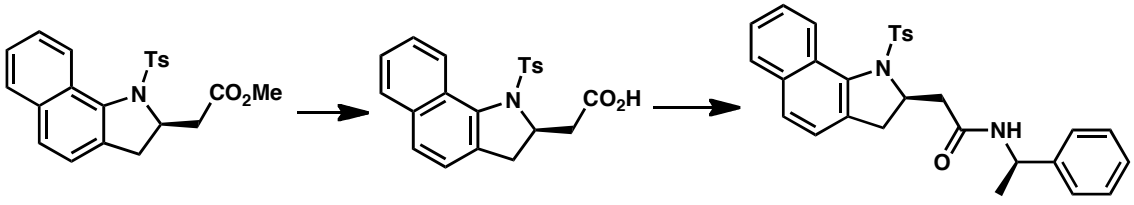


Prepared by the same procedure using (*E*)-ethyl 4-(2-(4-methylphenylsulfonamido)phenyl)but-2-enoate (36 mg, 0.1 mmol), CH_2Cl_2 (10 ml) and Et_3N (0.14 ml, 1 mmol). Purified by flash column chromatography (ethyl acetate/hexane, 1:5, v/v) to afford the racemic product (32 mg, 89%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.1 Hz, 3H), 2.35 (s, 3H), 2.56-2.71 (m, 2H), 2.96 (dd, J_1 = 16.5, J_2 = 9.4 Hz, 1H), 3.06 (dd, J_1 = 16.2, J_2 = 4.0 Hz, 1H), 4.00-4.34 (m, 2H), 4.49-4.72 (m, 1H), 6.99-7.07 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.19-7.24 (m, 1H), 7.56 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.1 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.3, 21.7, 34.9, 41.6, 58.8, 60.9, 117.3, 124.9, 125.4, 127.2, 128.0, 129.8, 131.3, 134.9, 141.2, 144.2, 171.0. ATR-FTIR: ν_{max}(cm^{-1}) = 2980, 2360, 1727, 1597, 1478, 1460, 1353, 1311, 1240, 1185, 1164, 1090, 1026, 969, 814, 753, 709, 664. HRMS: m/z (ESI) calcd for $C_{19}H_{21}NO_4SNa$ $[M + Na]^+$ 382.1089, found 382.1073. HPLC: Chiralpak-AD, 0.7 mL/min, 2-PrOH/hexane, 10/90, v/v, tR_1 = 17.33 min (*R*-enantiomer), tR_2 = 20.50 min (*S*-enantiomer).

Determination of the Absolute Configuration of 4l

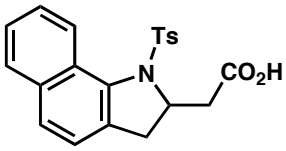
Chemical Correlation

The absolute configuration of the catalysis products was determined for the product ***ent*-4l** from the respective catalysis (Table 2, entry 11b). This product was submitted to ester hydrolysis to provide the free acid. This carboxylic acid was converted into a single diastereomeric amide upon standard coupling with (*R*)-phenylethylamine of known configuration:



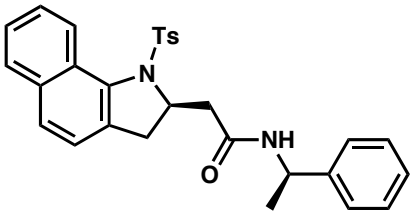
X-Ray analysis of this amide revealed an absolute (*R*,*R*)-configuration (see below). Based on this outcome, the absolute configuration of **4l** must be (*S*).

2-(1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-2-yl)acetic acid



Methyl 2-(1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-2-yl)acetate (1.07 g, 2.7 mmol) was hydrolyzed by stirring in the methanol/water solution (50 ml, 3:1, v/v) of KOH (224 mg, 4 mmol) at 50 ºC for 1h. The methanol was partially evaporated and HCl 1N solution (10 ml) was added. The mixture was extracted with dichloromethane (3×30 mL), the organic layers were combined, dried over $MgSO_4$, and evaporated under reduced pressure to afford the product as a white solid (978 mg, 95%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.27-2.57 (m, 6H), 2.85 (dd, J_1 = 5.1 Hz, J_2 = 16.2 Hz, 1H), 4.77-4.95 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.2 Hz, 1H), 7.25 (d, J = 7.1 Hz, 2H), 7.47-7.54 (m, 1H), 7.55-7.64 (m, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.7, 34.0, 38.7, 60.2, 121.5, 125.0, 125.1, 125.4, 126.8, 126.9, 127.3, 128.6, 131.4, 132.7, 133.2, 136.0, 143.4, 175.4. ATR-FTIR: ν_{max}(cm^{-1}) = 3054, 2922, 2853, 1708, 1595, 1438, 1404, 1347, 1304, 1290, 1262, 1219, 1185, 1162, 1088, 1057, 948, 908, 888, 810, 776, 730, 701, 677, 656, 599. HRMS: m/z (ESI) calcd for $C_{21}H_{19}NO_4SNa$ [M + Na]$^+$ 404.0932, found 404.0949.

***N*-((*R*)-1-phenylethyl)-2-((*R*)-1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-2-yl)acetamide**



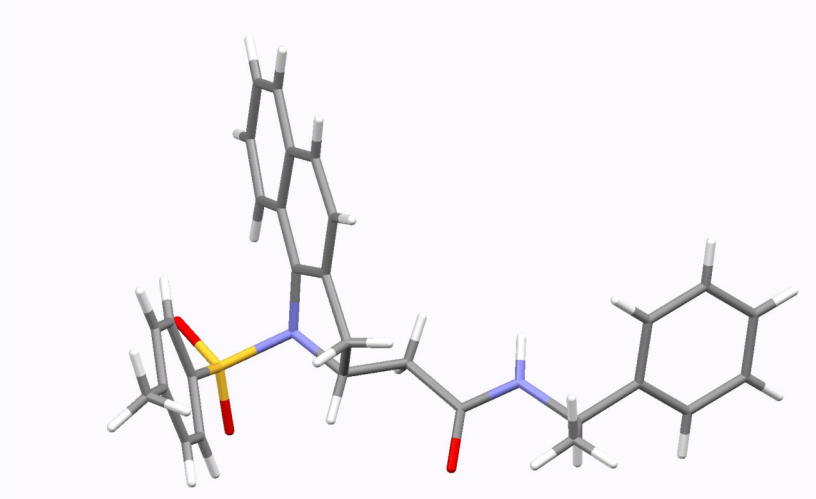
Following a modified procedure[S5] 2-(1-tosyl-2,3-dihydro-1*H*-benzo[*g*]indol-2-yl)acetic acid (763 mg, 2 mmol) and hydroxybenzotriazole (68 mg, 0.5 mmol) were dissolved in 50

(S5) Arnott, G.; Hunter, R.; Su, H.*Tetrahedron* **2006**, *62*, 977-991.

ml dichloromethane and cooled to 0°C. Dicyclohexylcarbodiimide (867 mg, 4.2 mmol) was added, followed by addition of (*R*)-α-methylbenzylamine (0.27 mL, 2.1 mmol). The reaction was allowed to warm to room temperature slowly overnight. On completion, *N*,*N*'-dicyclohexylurea (DCU) was filtered off, the solution was washed with aqueous sodium carbonate (50 mL), organic phase was separated and aqueous phase was extracted with dichloromethane (3×25 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated under reduced pressure to yield a crude product, which was purified by silica gel chromatography (ethyl acetate/hexane, 1:1, v/v) to afford the mixture of two diastereoisomers as a white solid (940 mg, 97%). Crystallization from the mixture EtOAc/hexane, 5:1, v/v afforded the pure product (107 mg, 11%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.30 (d, J = 6.9 Hz, 3H), 2.25-2.43 (m, 6H), 2.51 (dd, J_1 = 15.3, J_2 = 7.7 Hz, 1H), 4.80 (q, J = 6.2 Hz, 1H), 5.04 (p, J = 7.0 Hz, 1H), 6.42 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.27-7.41 (m, 5H), 7.51 (ddd, J_1 = 15.0, J_2 = 13.9, J_3 = 6.9 Hz, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 8.45 (d, J = 8.3 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.4, 21.7, 34.9, 42.1, 49.2, 61.9, 122.6, 125.8, 126.1, 126.5, 126.6, 127.5, 127.9, 128.0, 128.3, 128.8, 129.5, 133.2, 133.4, 134.2, 136.8, 143.3, 144.5, 168.5. ATR-FTIR: ν_{max}(cm^{-1}) = 3241, 3069, 3028, 2971, 2930, 1657, 1650, 1630, 1594, 1561, 1557, 1537, 1513, 1493, 1447, 1433, 1425, 1376, 1351, 1305, 1286, 1166, 1088, 1063, 948, 814, 771, 762, 747, 700, 656, 623, 598. HRMS: m/z (ESI) calcd for $C_{29}H_{28}N_2O_3SNa$ $[M + Na]^+$ 507.1718, found 507.1733.

Structure Determination of *ent*-4l via X-Ray Analysis:

Deposition Number: CCDC- 780370

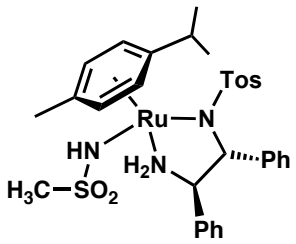


The structure was solved using the programme Sir2007 (Caliandro, R.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Siliqi D. *J. Appl. Cryst*. **2007**, *40*, 883-890)

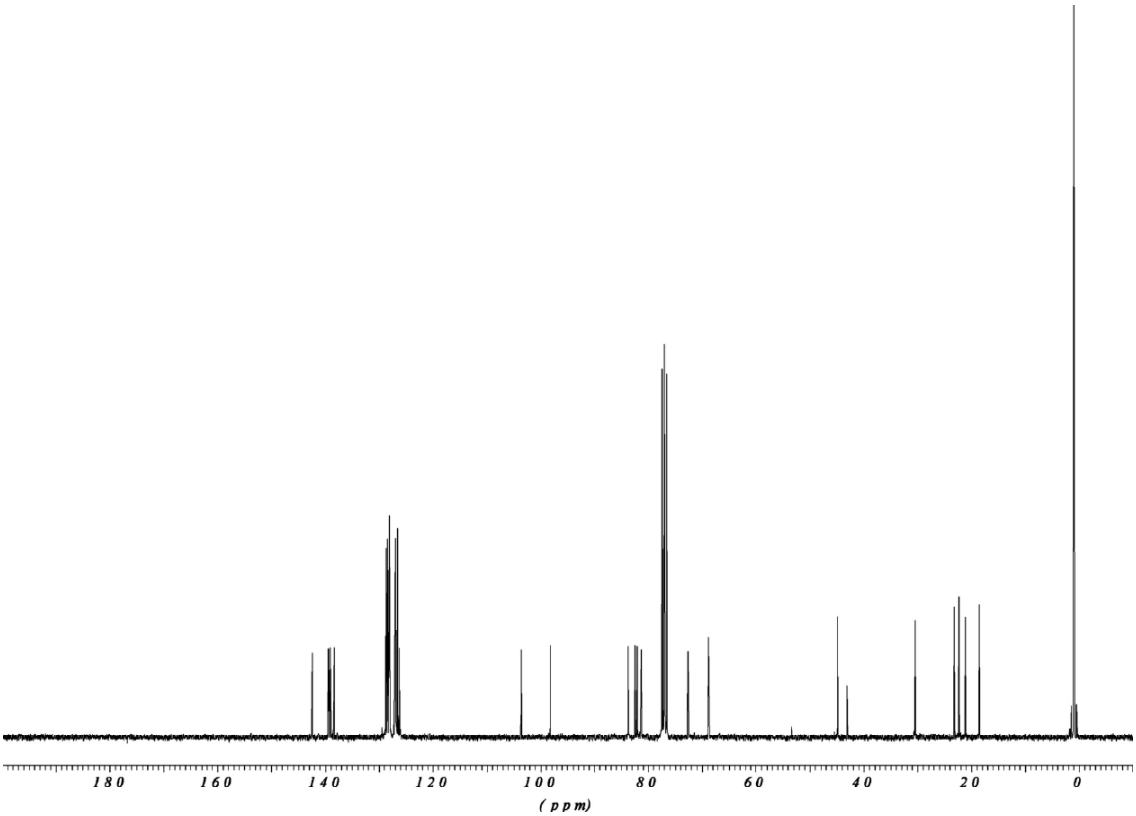
Flack parameter = -0.01(4) ('Flack, H. D., *Acta Cryst*. **1983**, *A39*, 876-881)

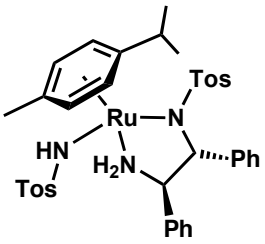
Empirical formula	C29 H28 N2 O3 S
Formula weight	484.59
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 12.47700(10) A alpha = 90 deg.
	b = 17.6950(2) A beta = 112.7570(2) deg.
	c = 12.67200(10) A gamma = 90 deg.
Volume	2579.94(4) A^3
Z, Calculated density	4, 1.248 Mg/m^3
Absorption coefficient	0.158 mm^-1
F(000)	1024
Crystal size	0.4 x 0.1 x 0.06 mm
Diffractometer	Nonius FR 591
Theta range for data collection	1.74 to 33.45 deg.
Limiting indices	-19<=h<=18, -27<=k<=26, -19<=l<=19
Reflections collected / unique	40781 / 17828 [R(int) = 0.0340]
Absorption correction	Empirical
Max. and min. transmission	0.99074 and 0.86345
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17828 / 1 / 659
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)] R1 =	0.0458, wR2 = 0.1105
R indices (all data) R1 =	0.0572, wR2 = 0.1181
Absolute structure parameter	-0.01(4)

Spectral Characterization



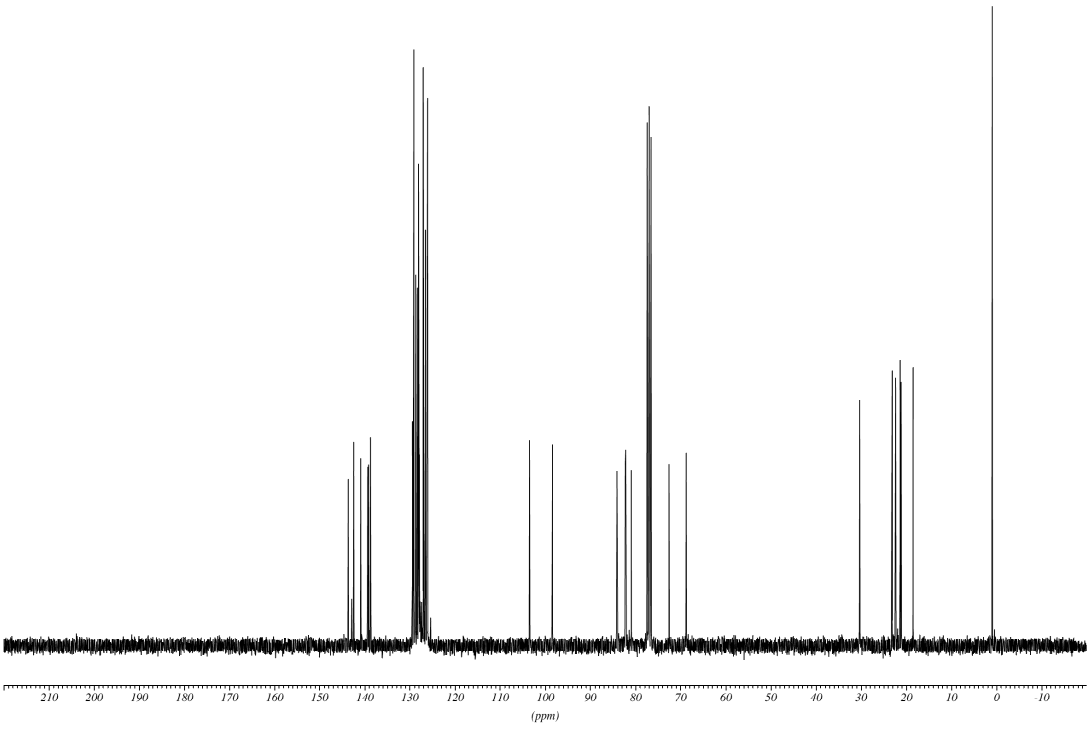
2a

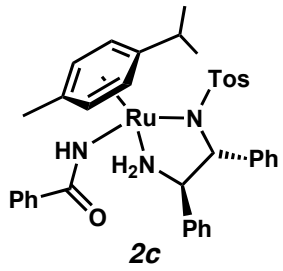



Tos
Ru
N
HN
H2N
Ph
Tos
Ph

2b

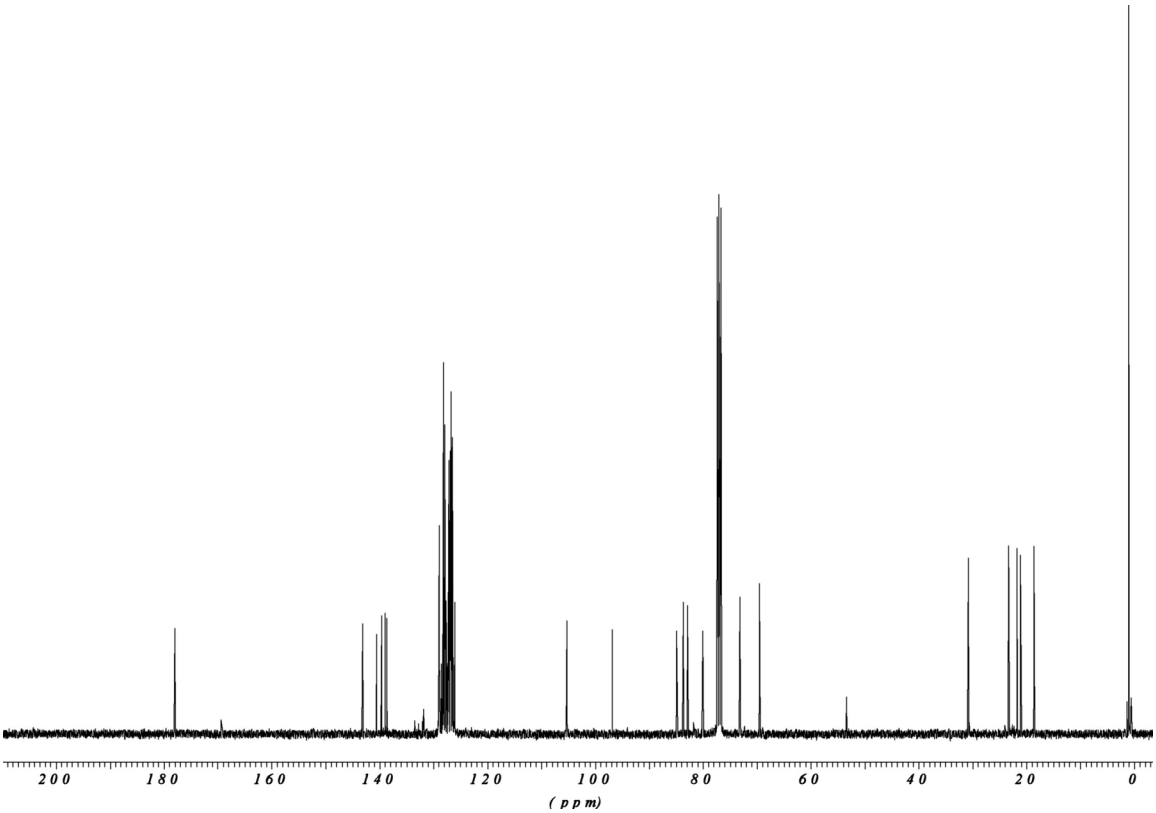
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

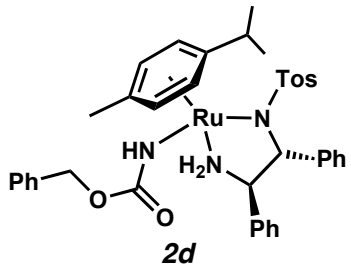

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


Tos
Ru
N
HN
H2N
Ph
Ph
O
Ph

2c

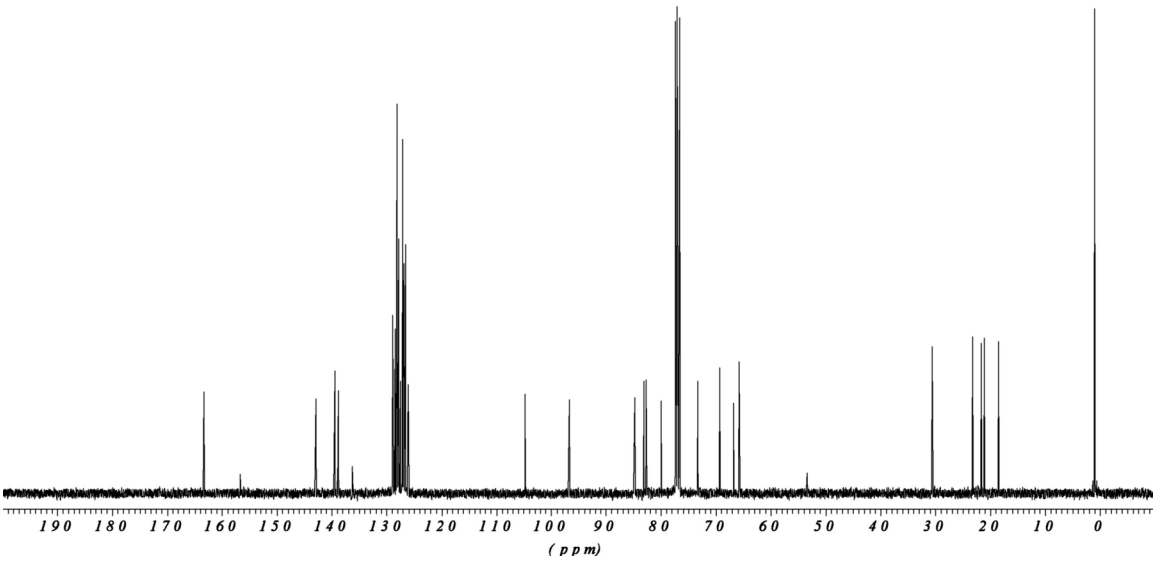
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

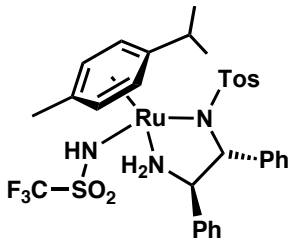

200
180
160
140
120
100
80
60
40
20
0
(ppm)


Tos
Ru
N
HN
H2N
Ph
Ph
O
O
Ph

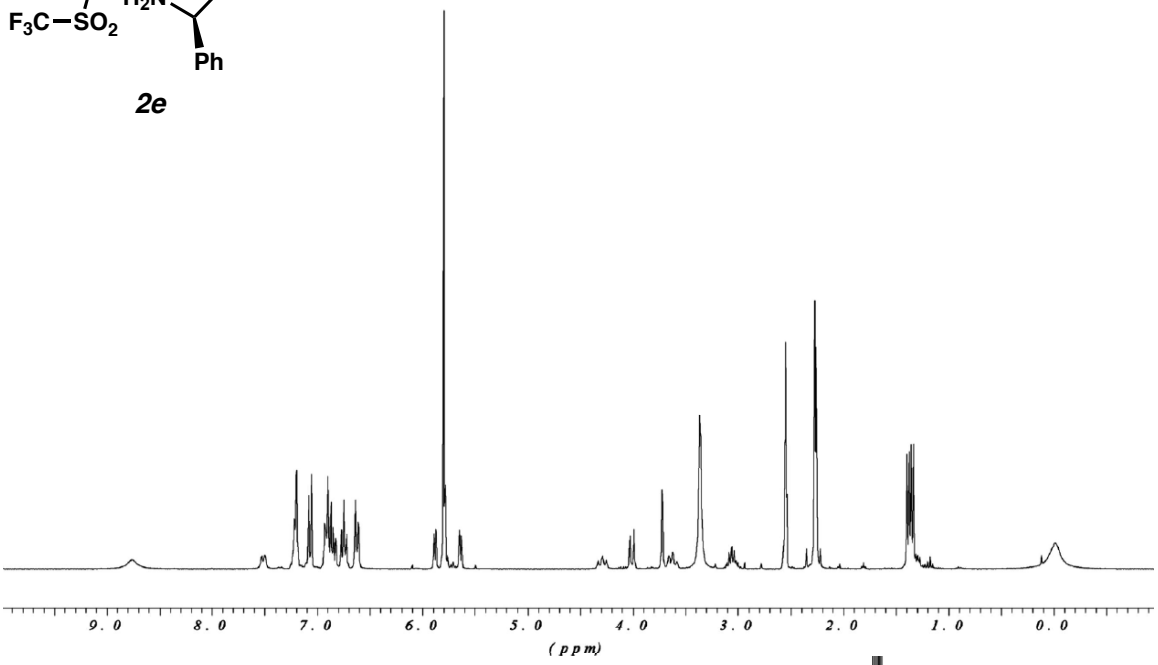
2d

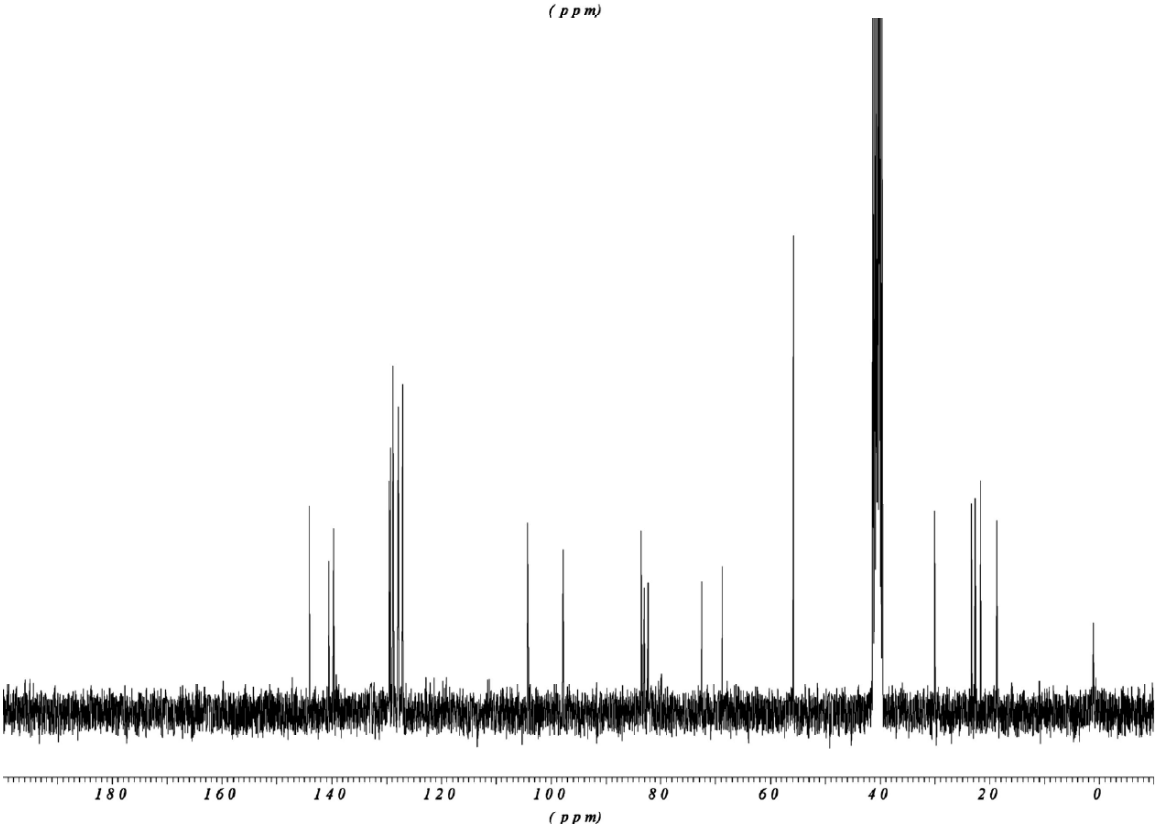
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

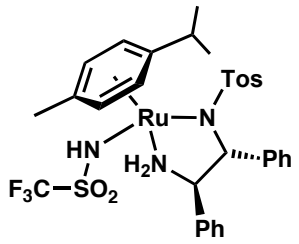

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


Tos
Ru
N
HN
H2N
Ph
F3C
SO2
Ph

2e

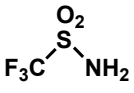

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

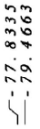

180
160
140
120
100
80
60
40
20
0
(ppm)

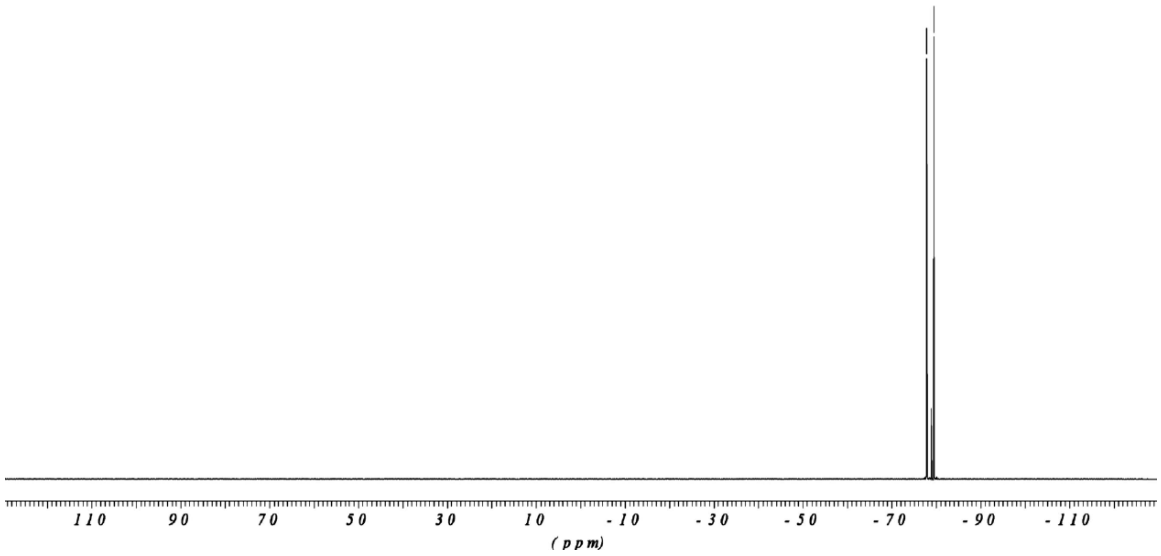

Tos
Ru
N
HN
H2N
Ph
F3C–SO2
Ph

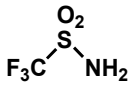
2e

+

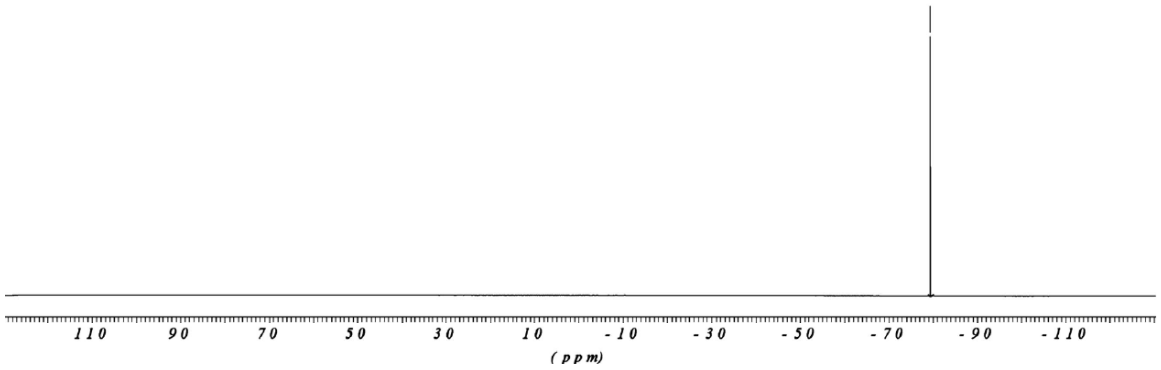

O2
S
F3C
NH2

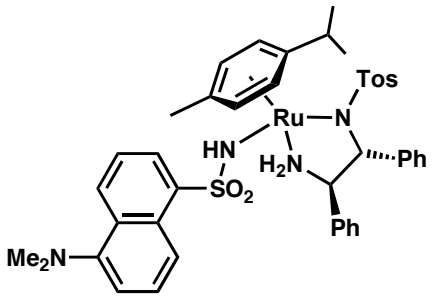

-77.8335
-79.4663


110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
(ppm)


O2
S
F3C
NH2

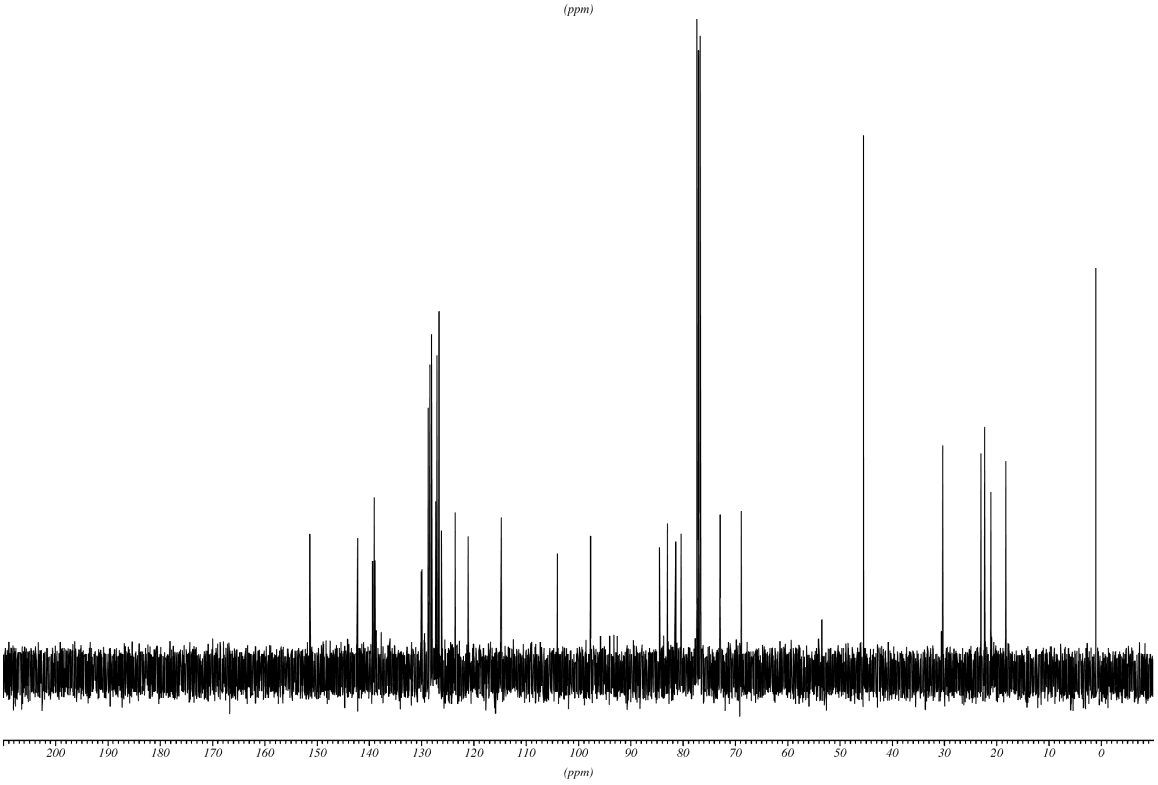

-79.3432

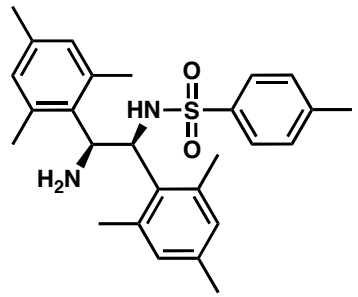

110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
(ppm)

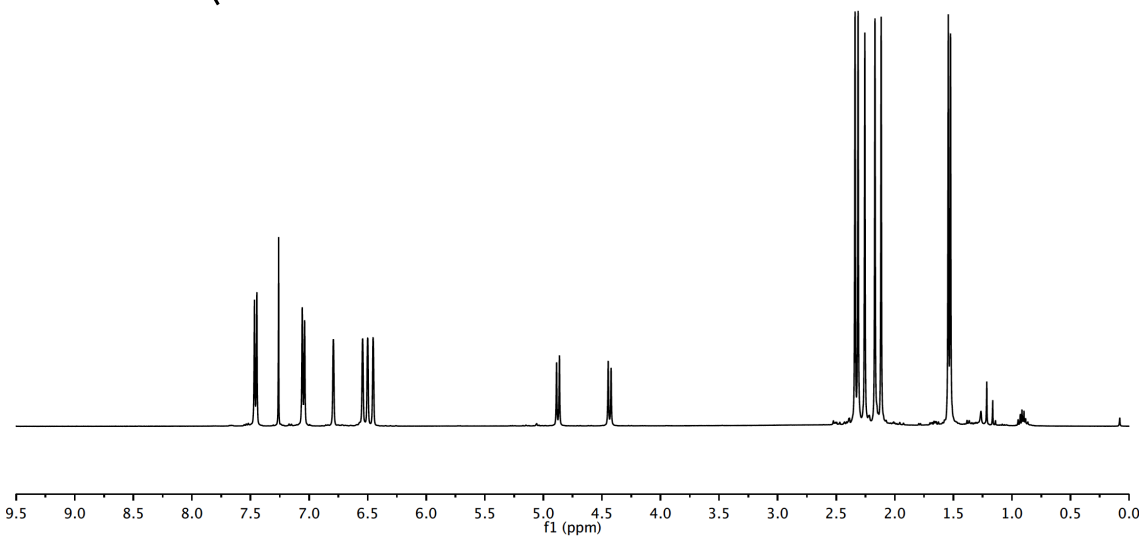

Tos
Ru
N
HN
H2N
Ph
SO2
Ph
Me2N

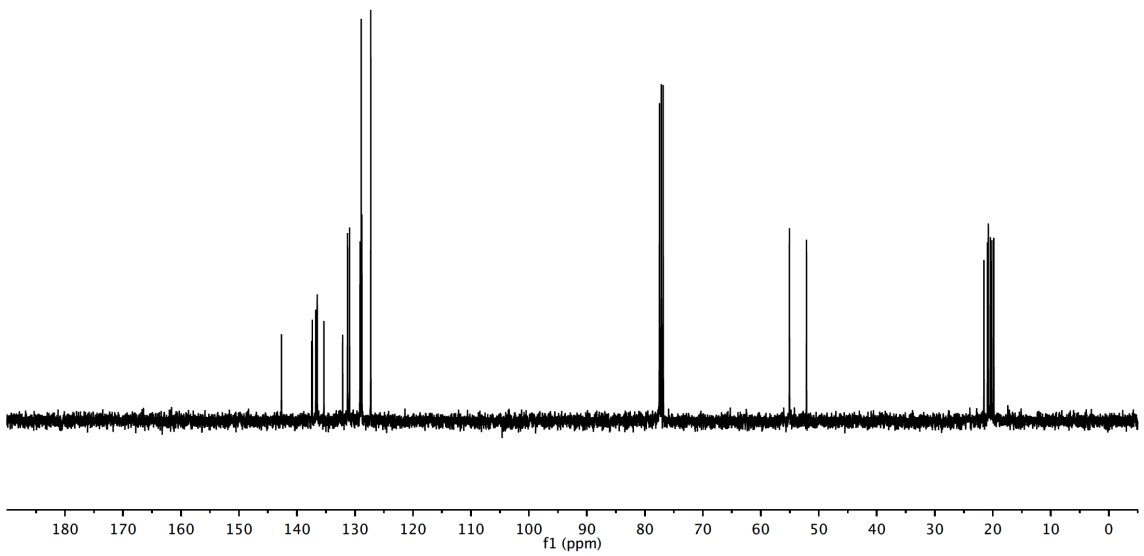
2f

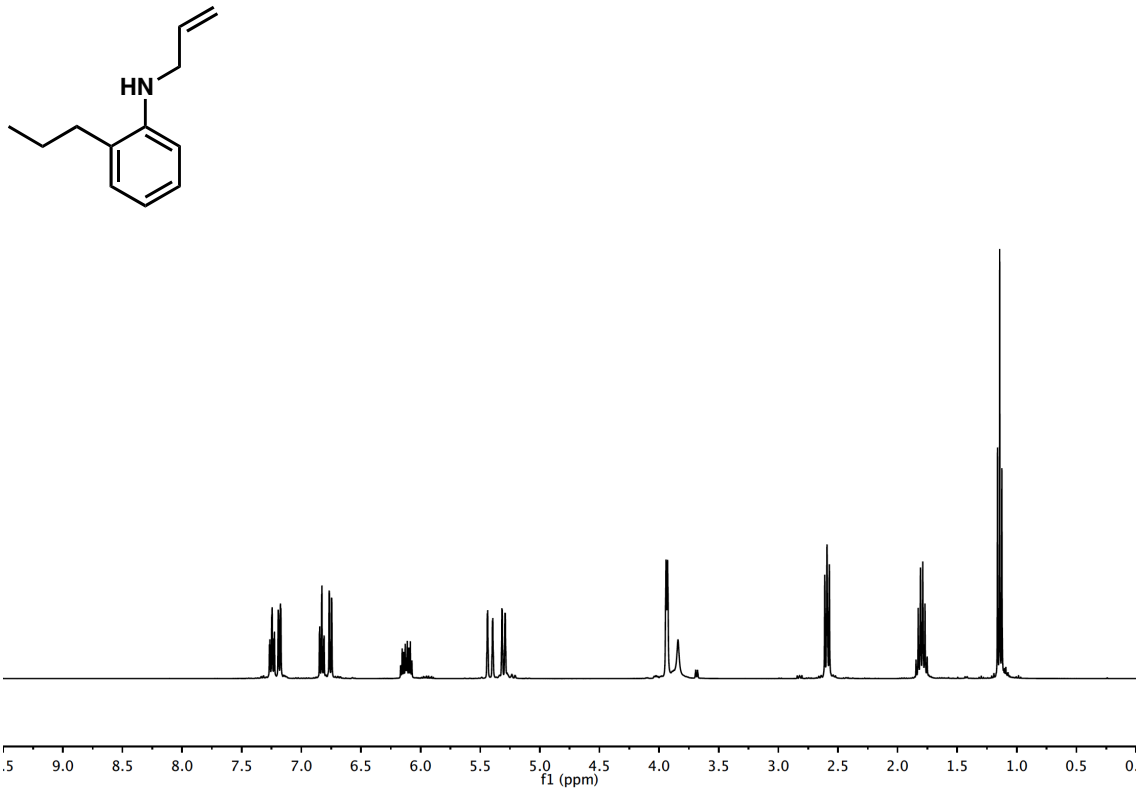
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

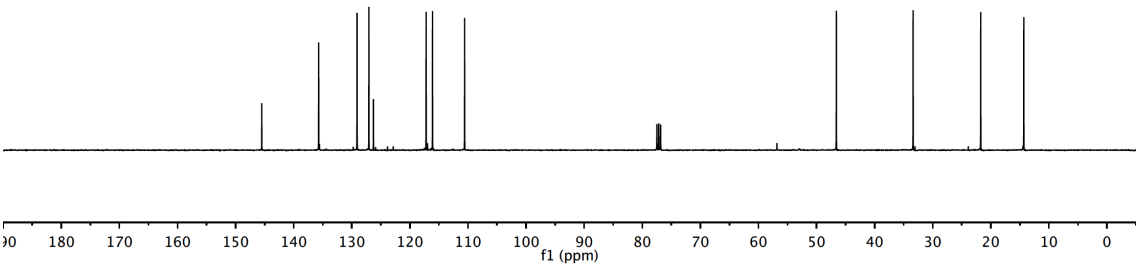

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

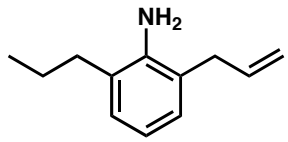

O
HN
S
O
H2N

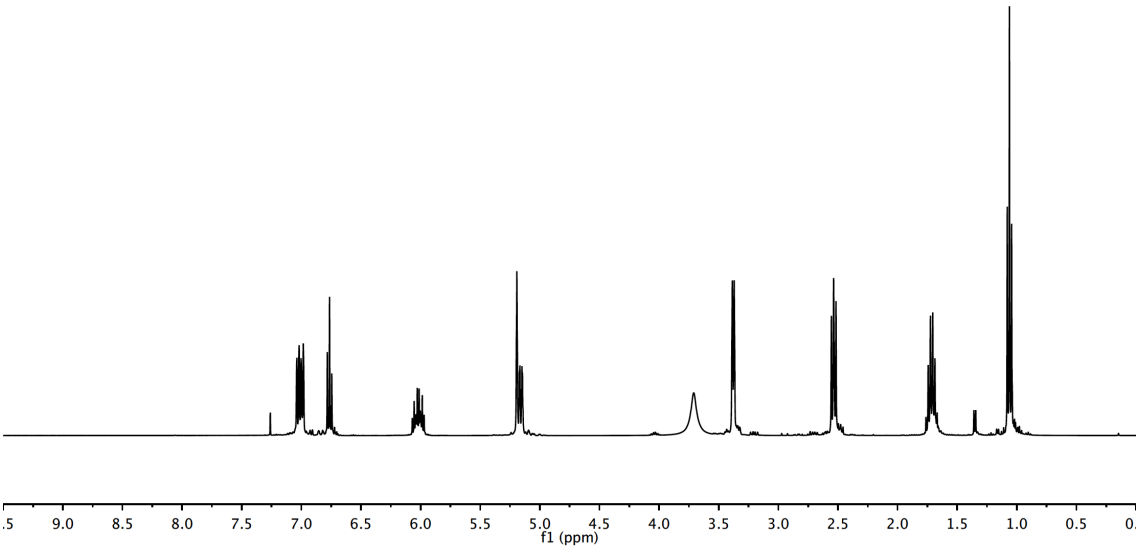

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

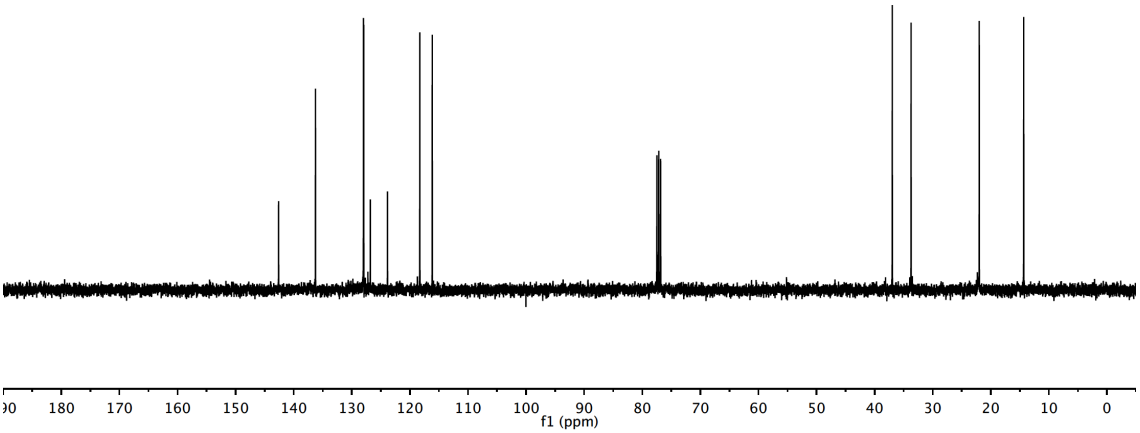

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


HN
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NH2


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
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160
150
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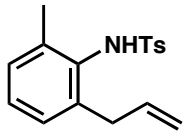
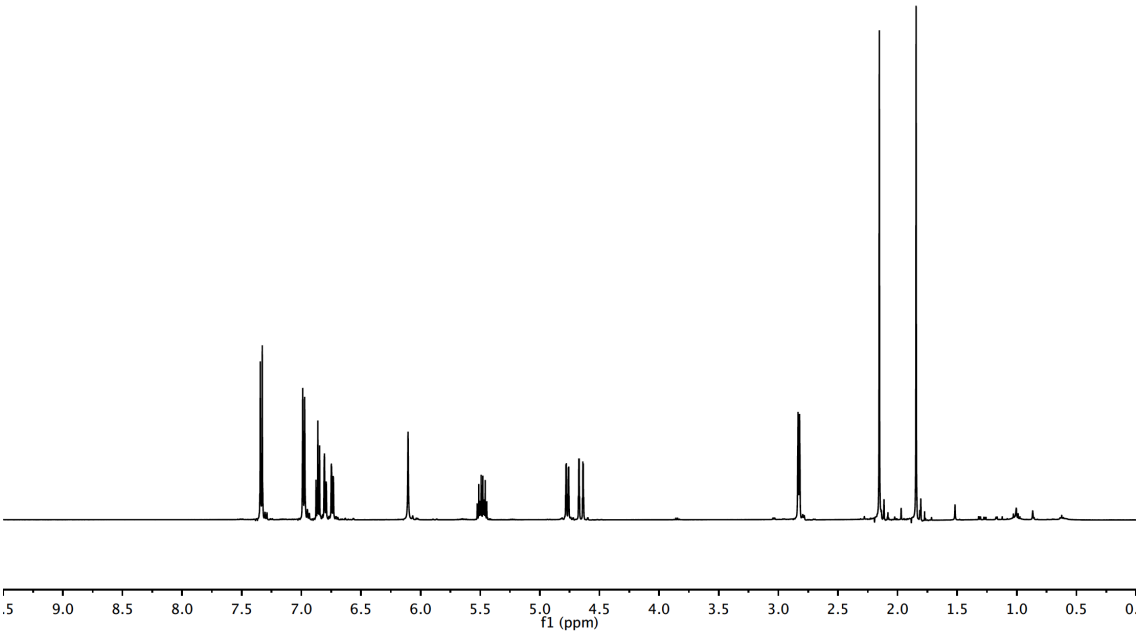
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NHTs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7.5
7.0
6.5
6.0
5.5
5.0
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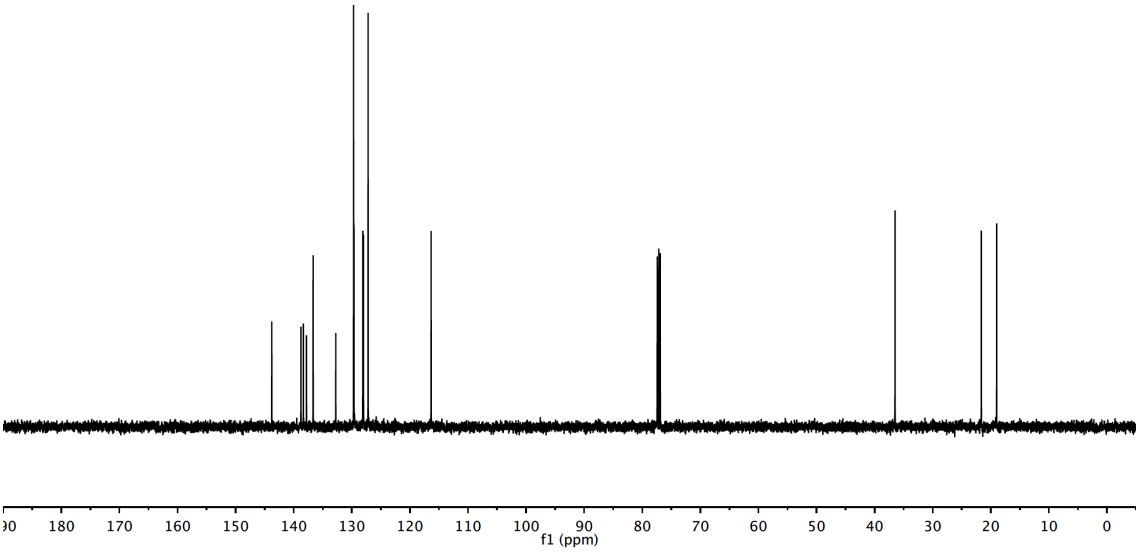
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
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120
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100
90
80
70
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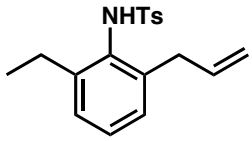
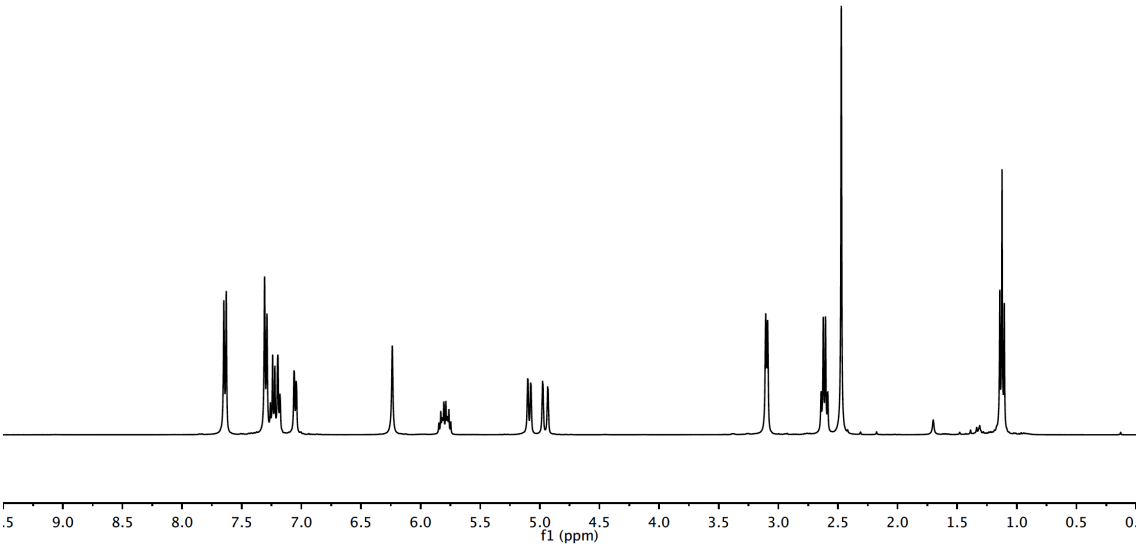
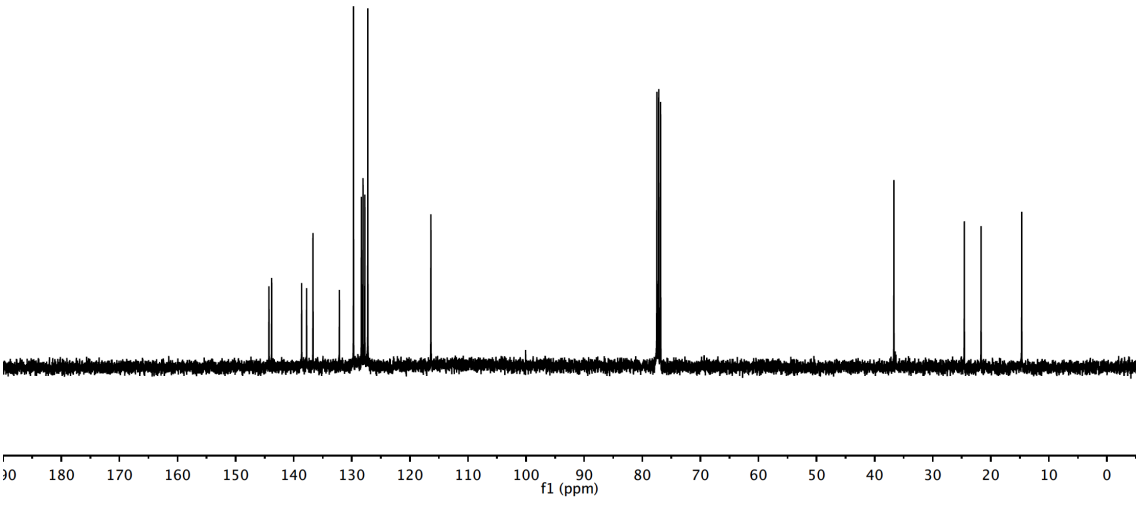
50
40
30
20
10
0
f1 (ppm)


NHTs


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
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150
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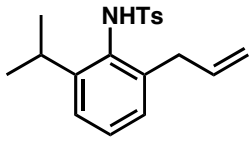
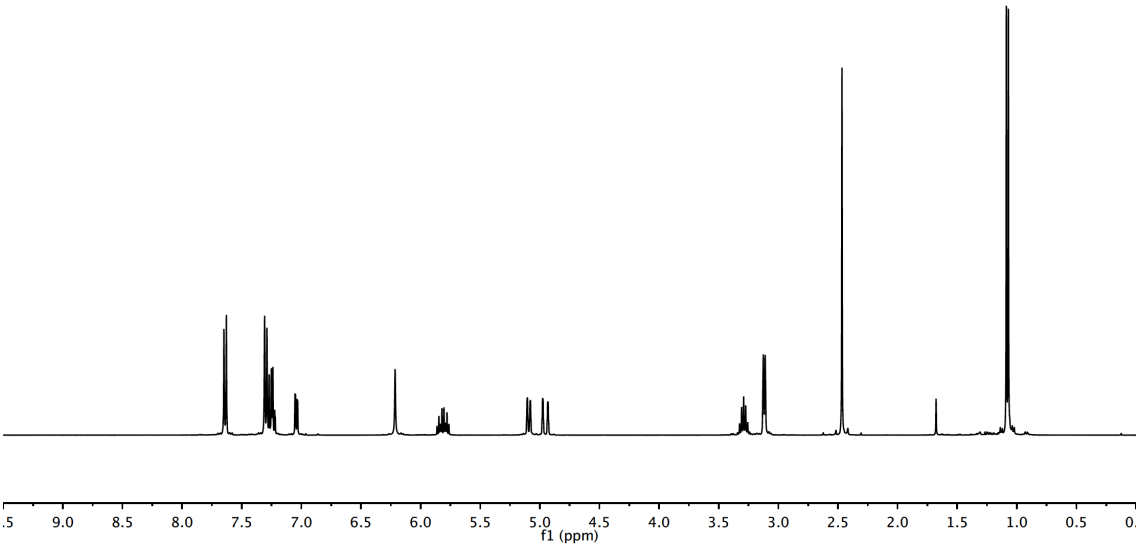
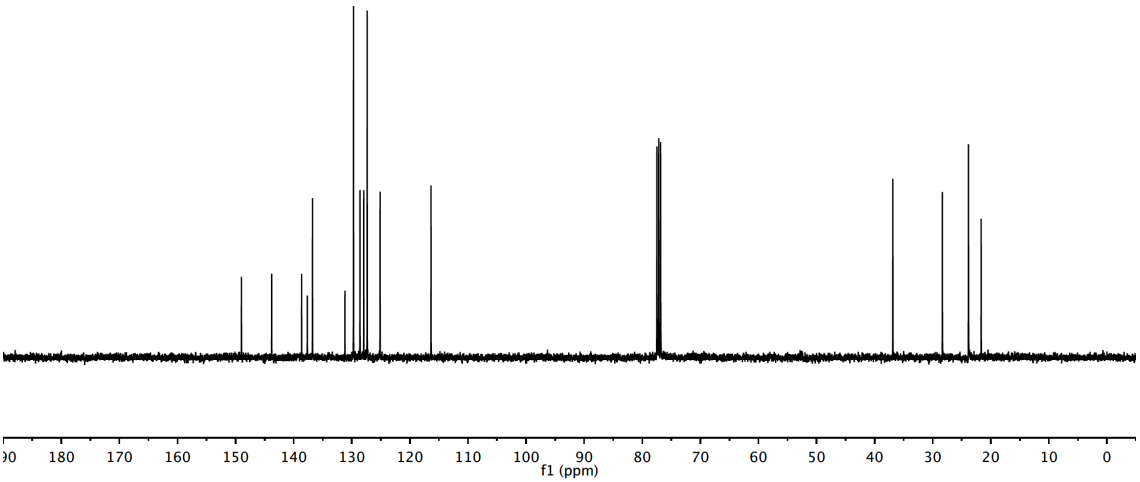
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NHTs


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
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160
150
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130
120
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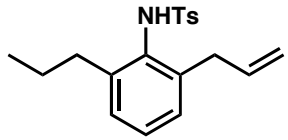
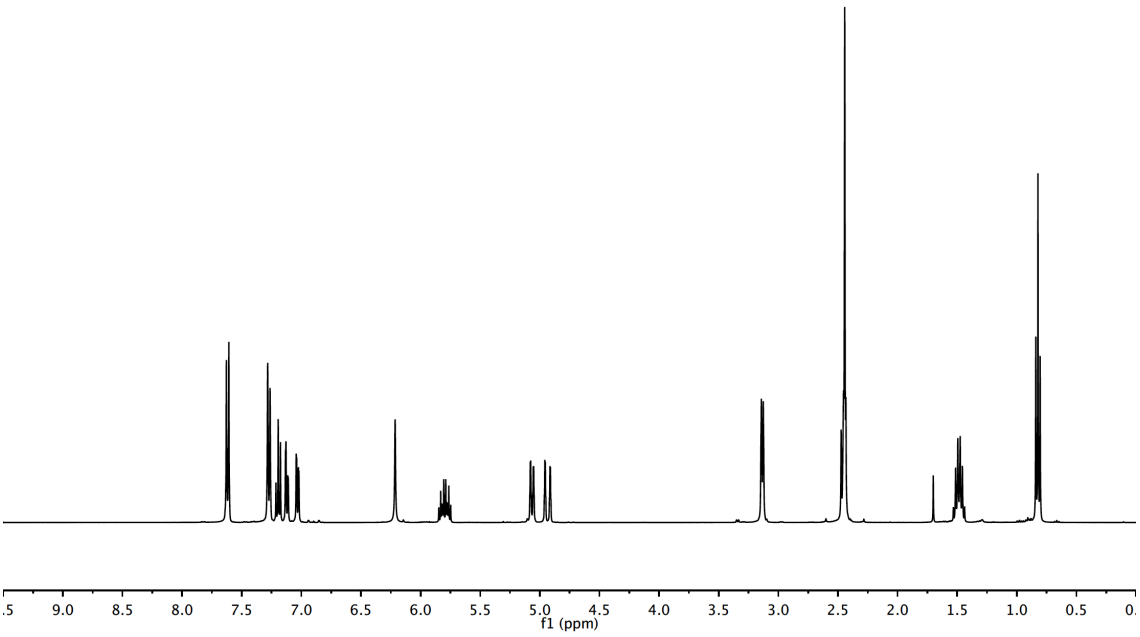
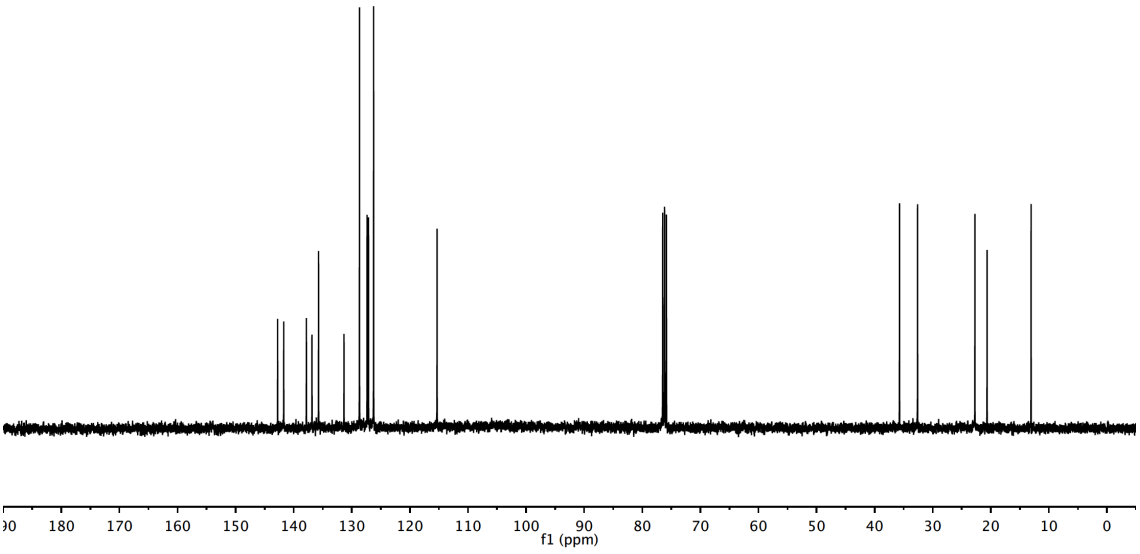
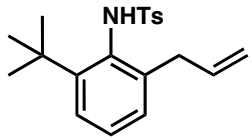
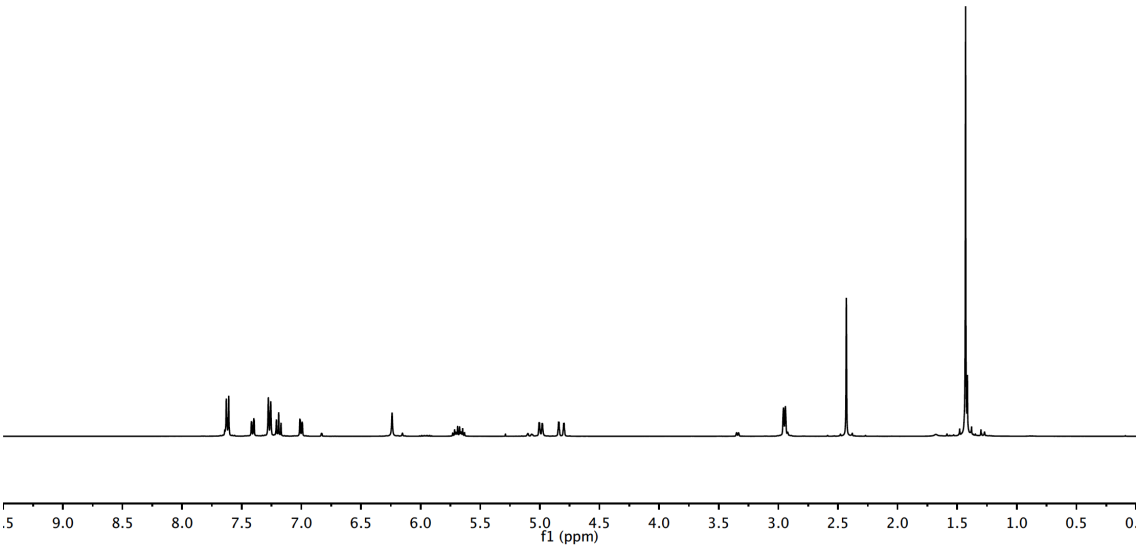
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

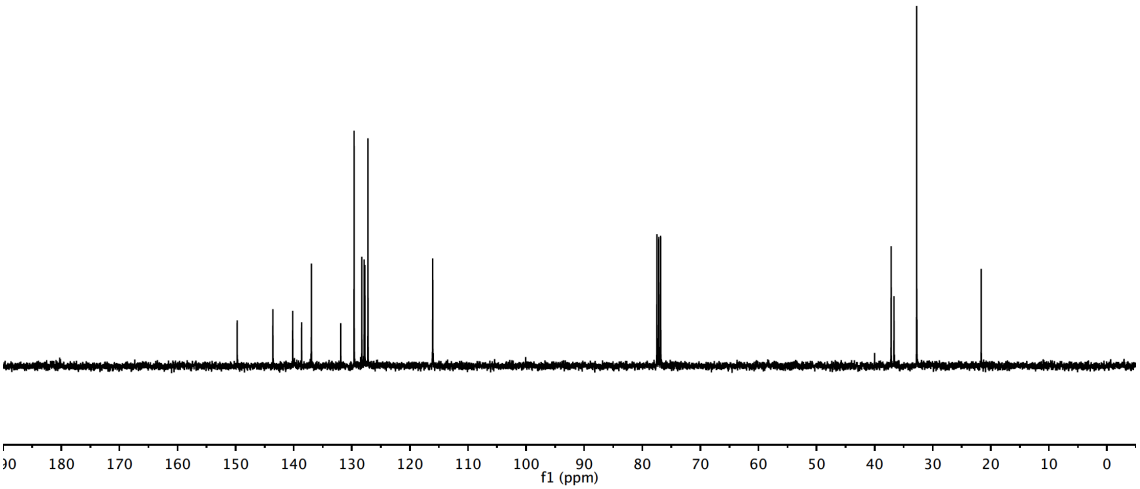

NHTs


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NHTs


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
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160
150
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130
120
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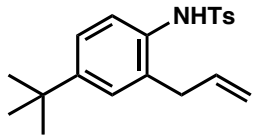
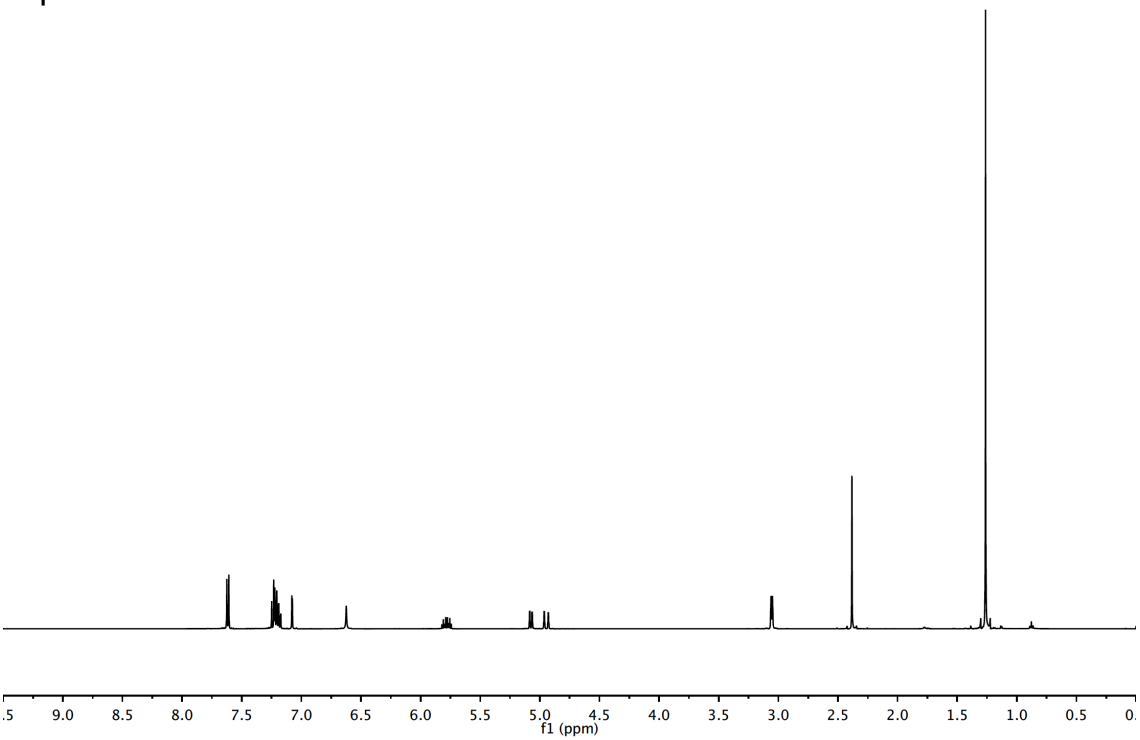
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NHTs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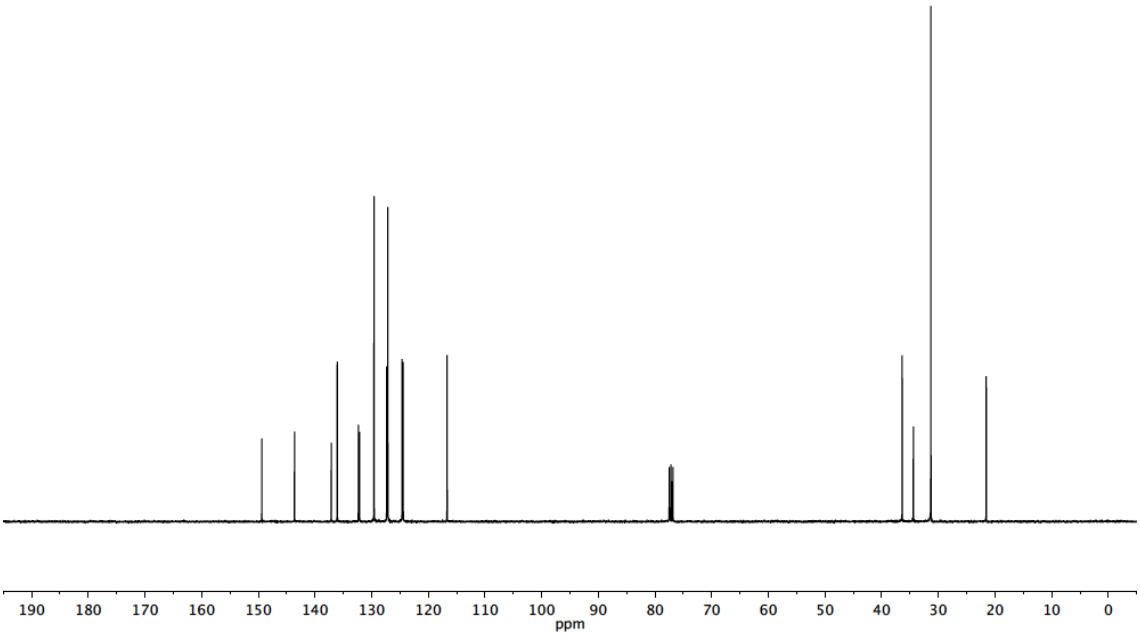
f1 (ppm)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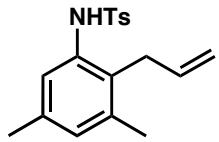
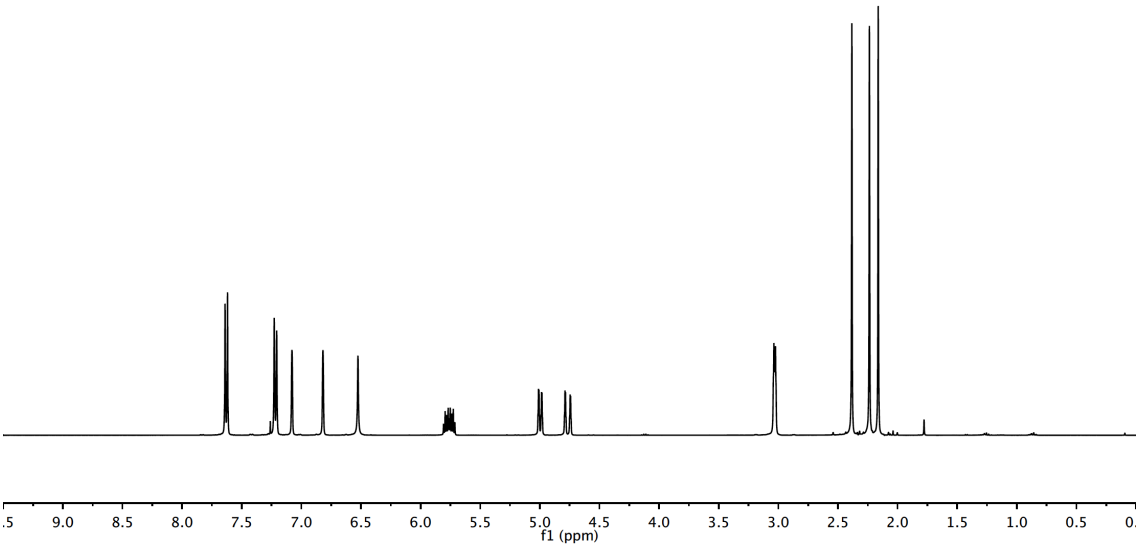

NHTs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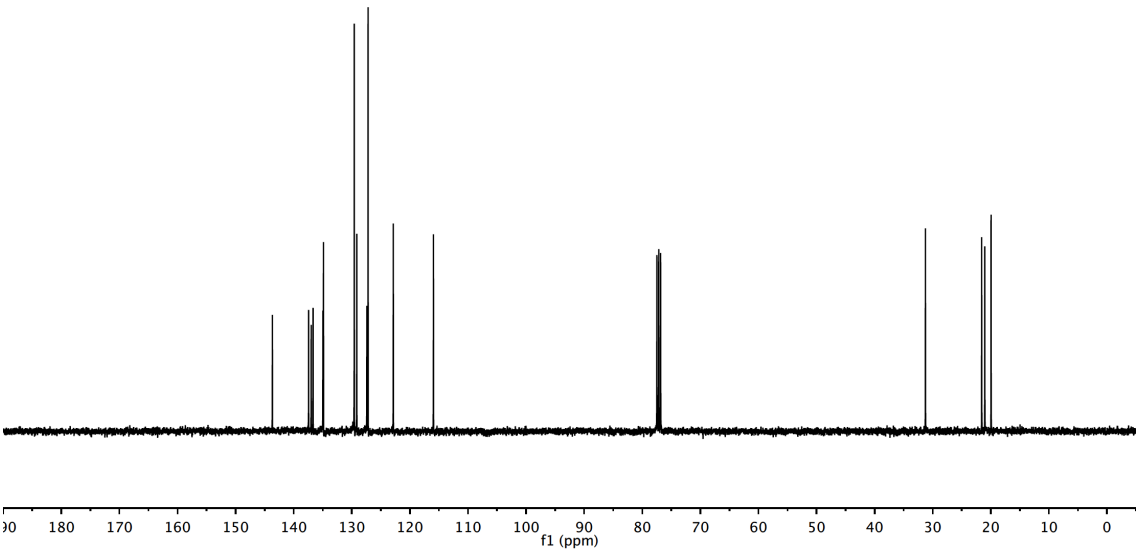
0.5
f1 (ppm)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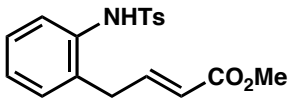
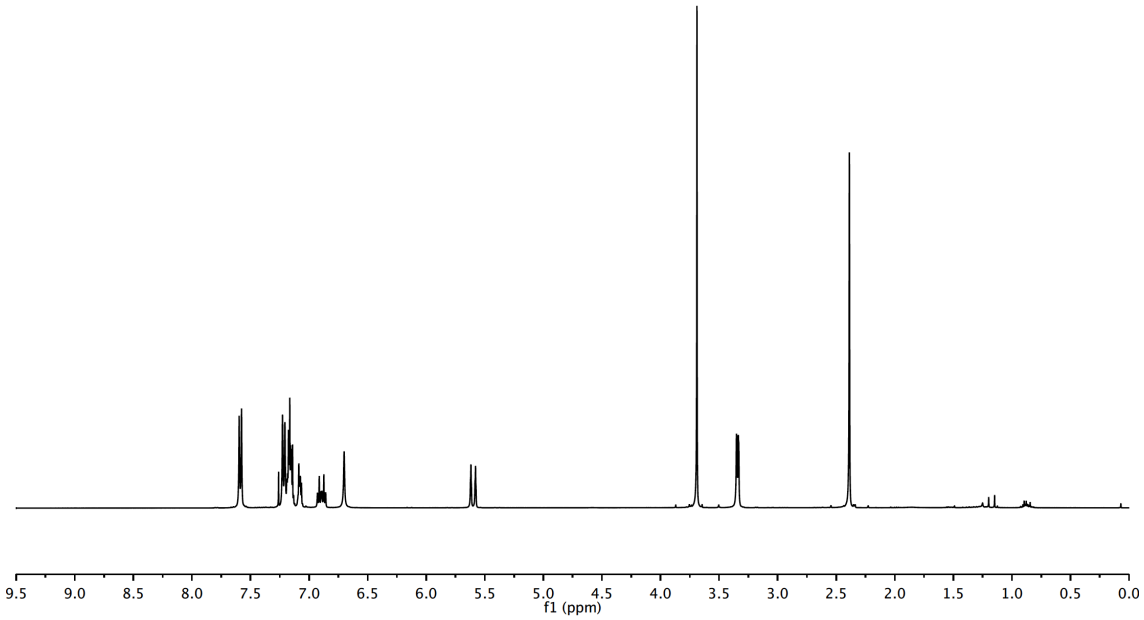
f1 (ppm)


NHTs
CO2Me

3a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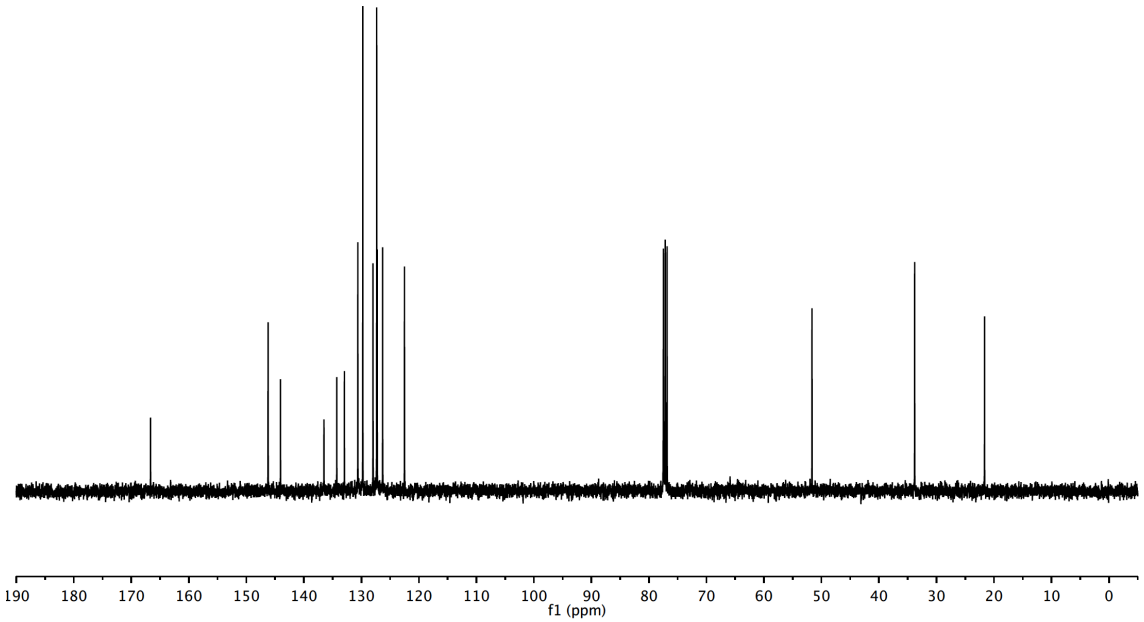
f1 (ppm)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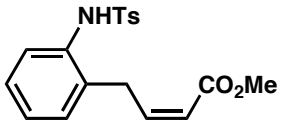
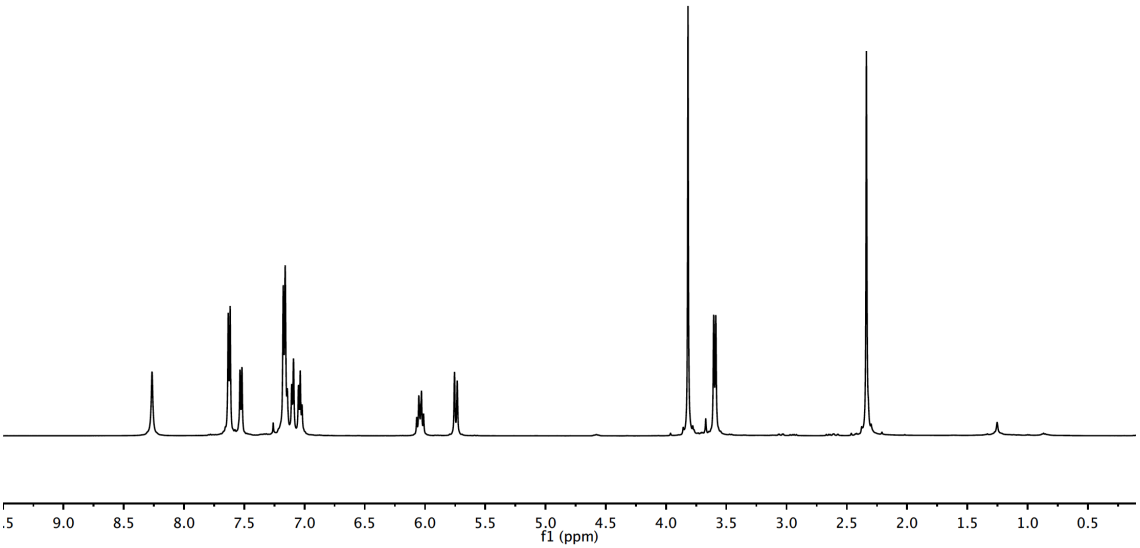
f1 (ppm)


NHTs
CO2Me

(Z)-3a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1.5
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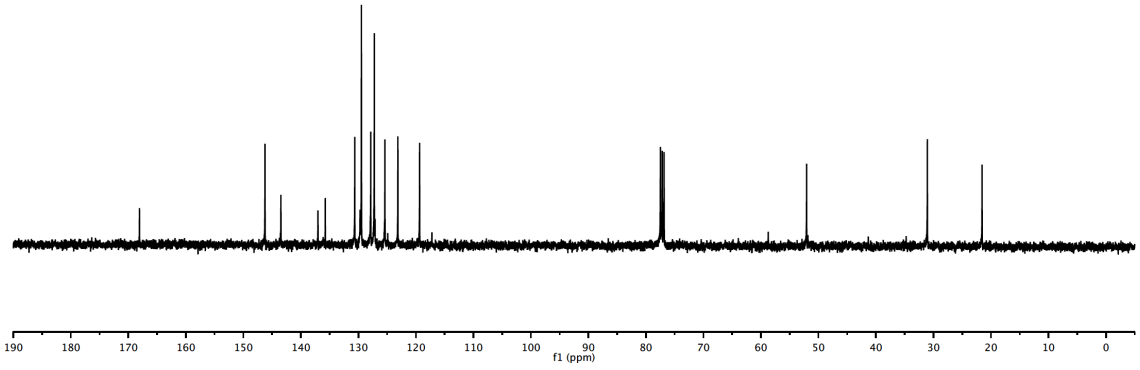
0.5
f1 (ppm)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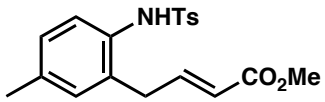
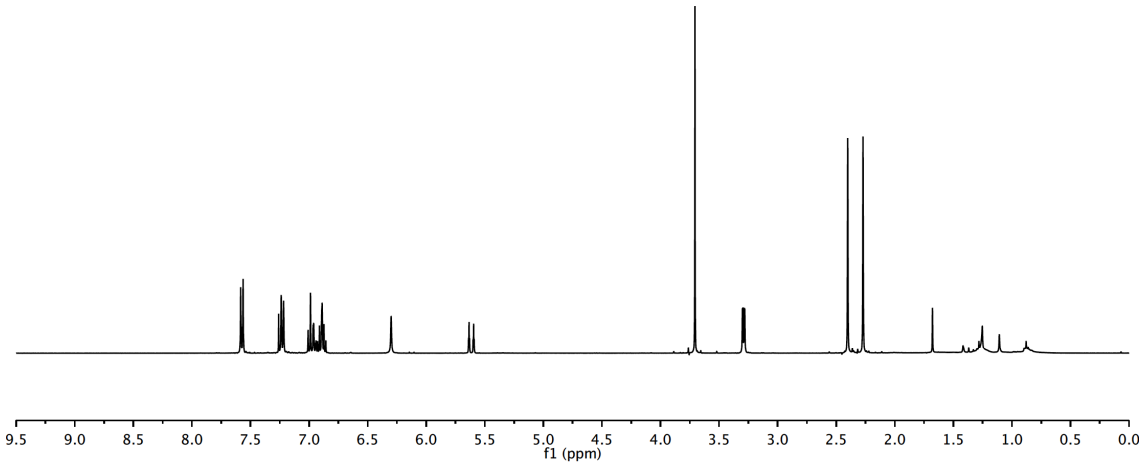
10
0
f1 (ppm)


NHTs
CO2Me

3b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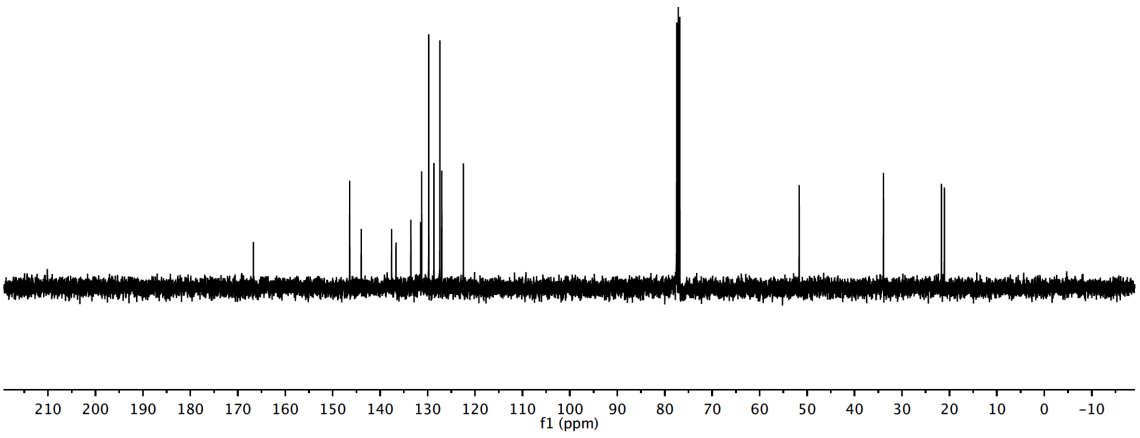
f1 (ppm)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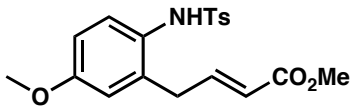
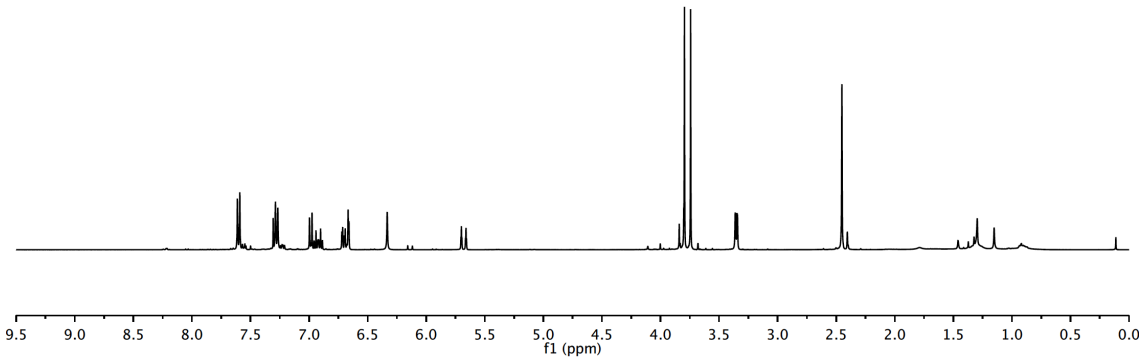
f1 (ppm)


NHTs
CO2Me
O

3c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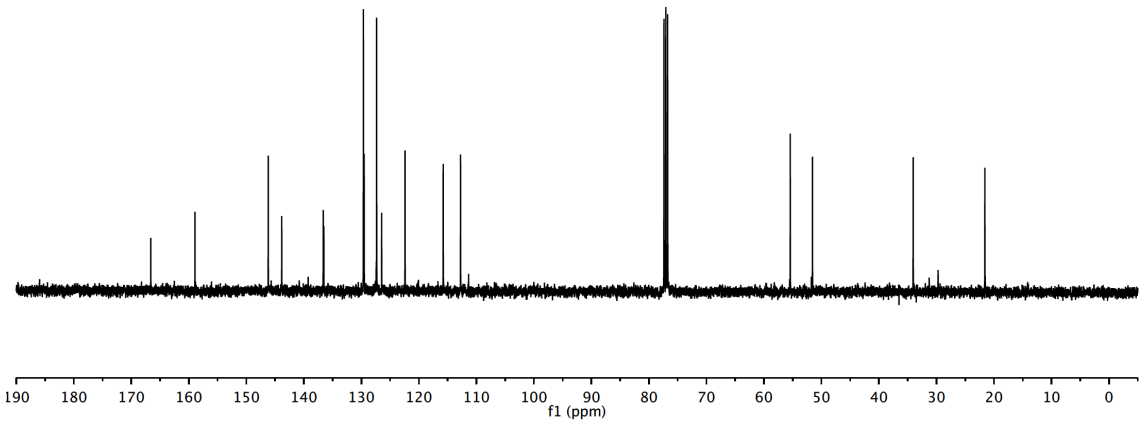
f1 (ppm)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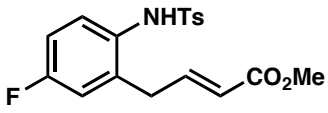
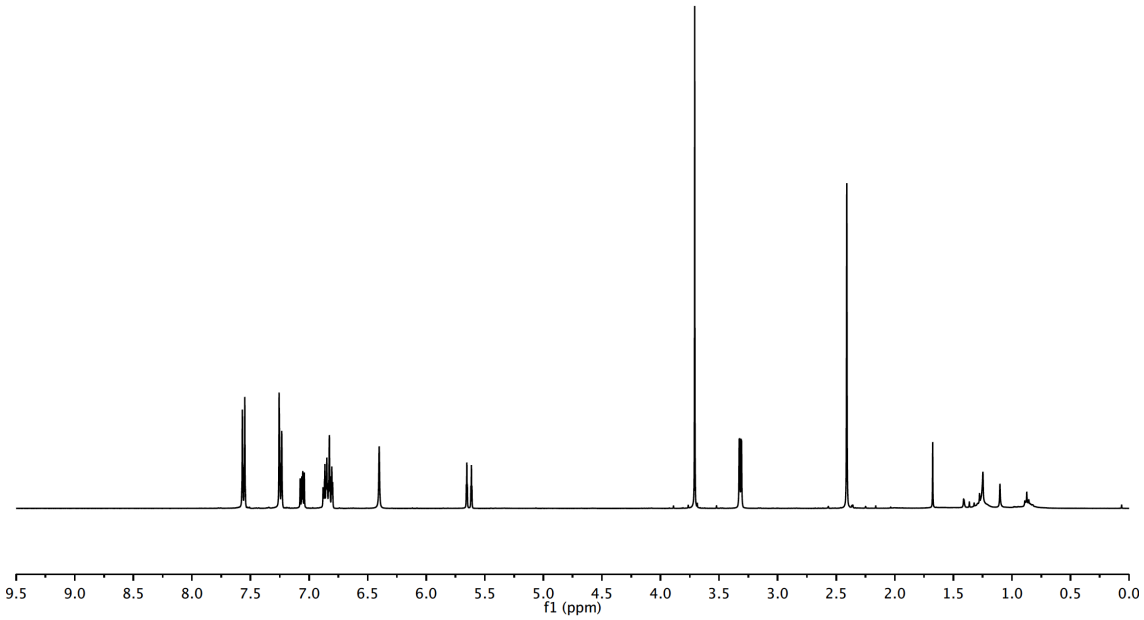
f1 (ppm)


NHTs
F
CO2Me

3d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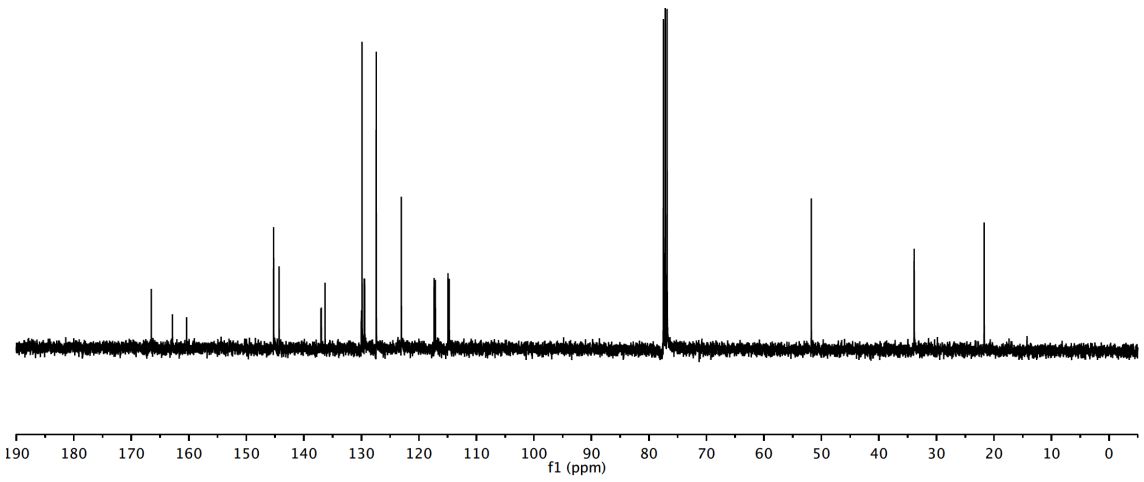
f1 (ppm)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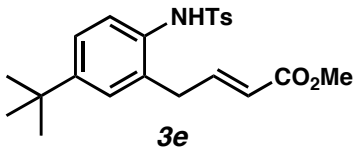

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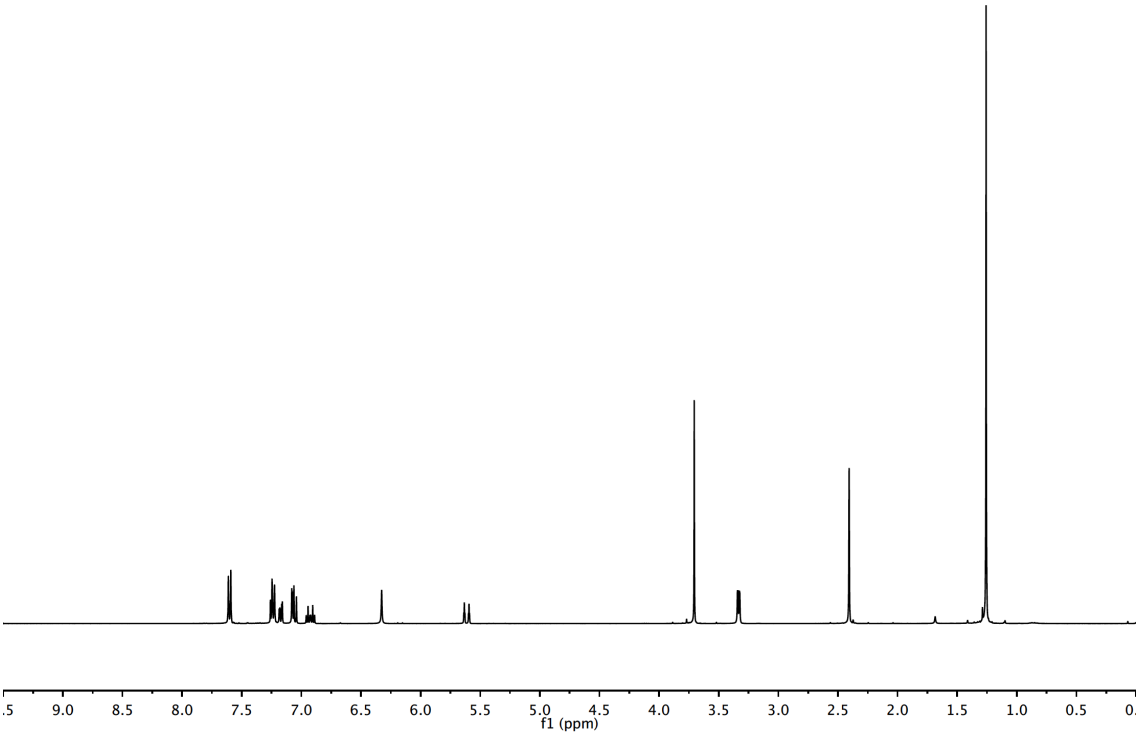
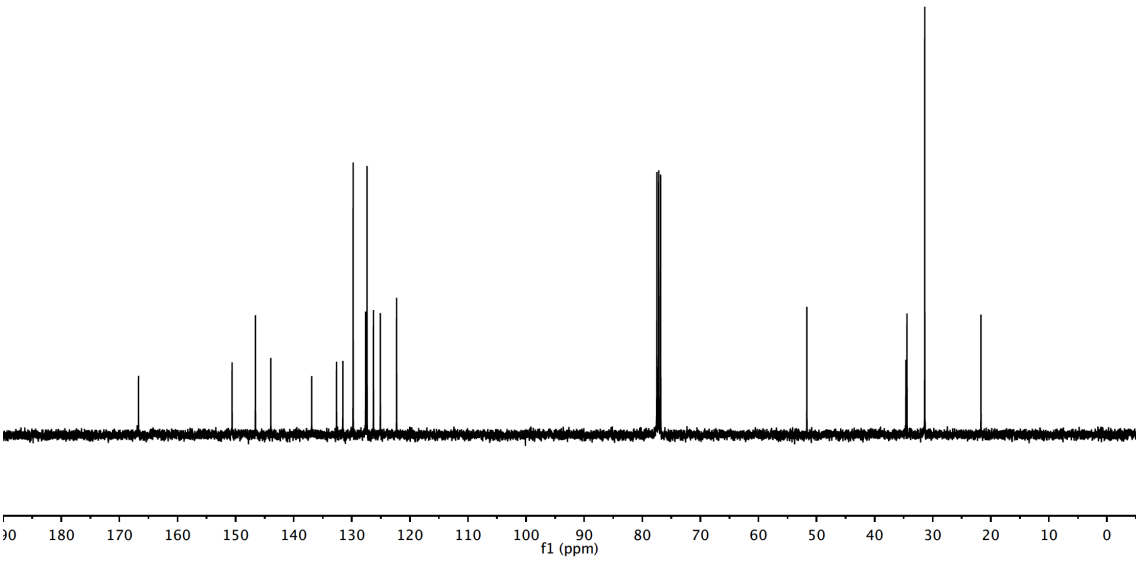
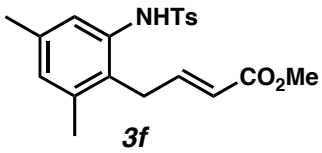
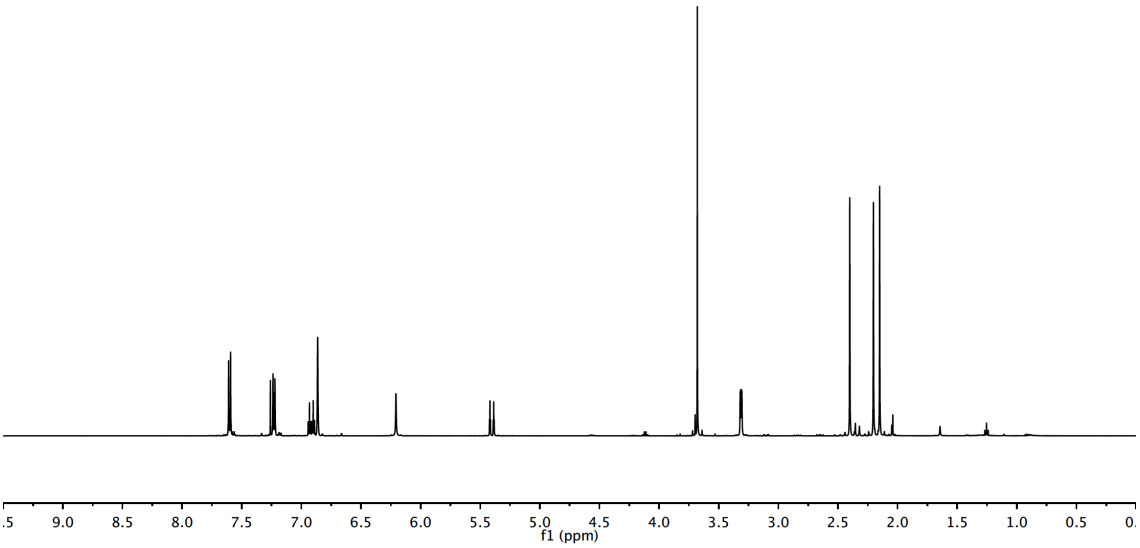





NHTs
CO2Me

3f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3.0
2.5
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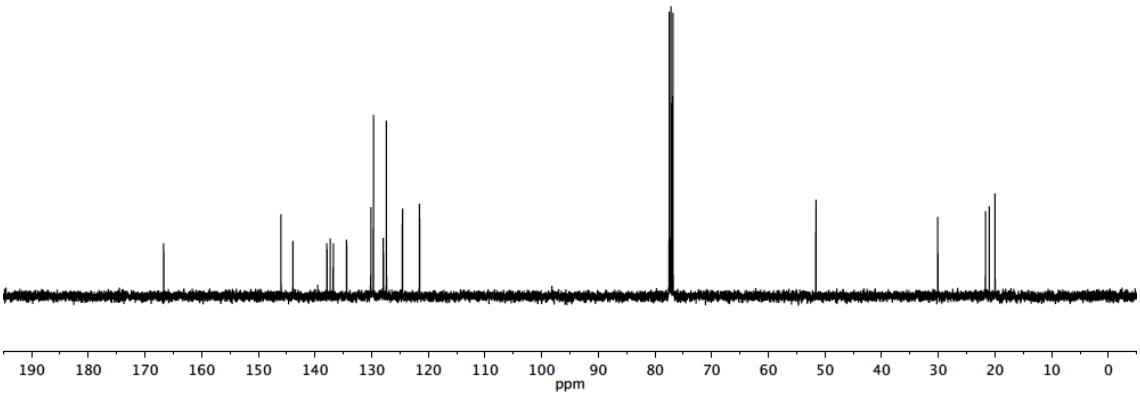
1.0
0.5
f1 (ppm)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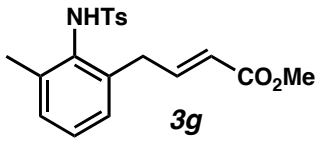
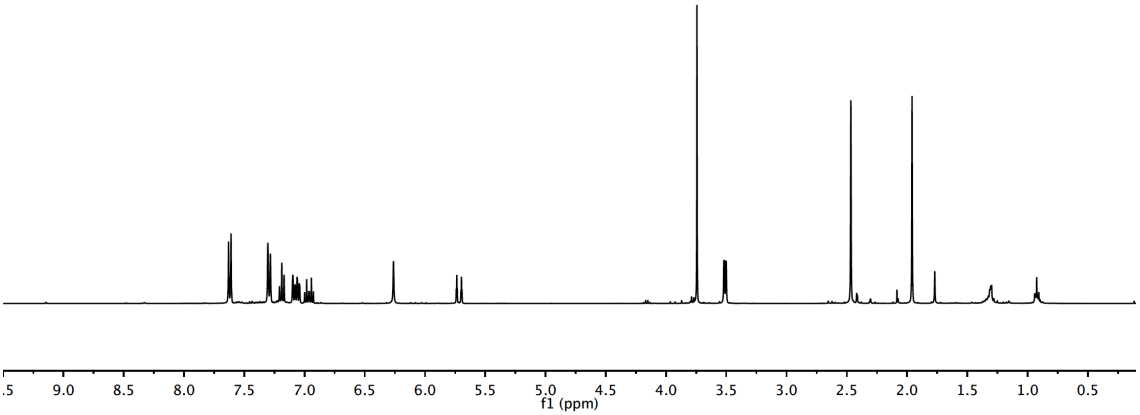
0
ppm


NHTs
CO2Me

3g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3.0
2.5
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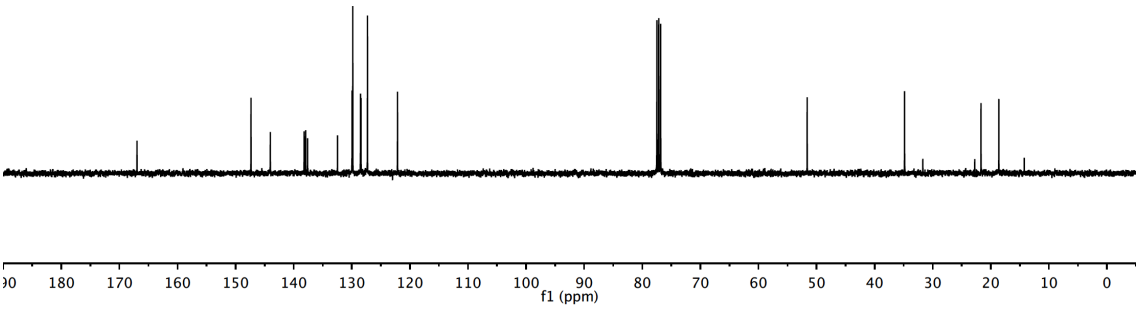
1.5
1.0
0.5
f1 (ppm)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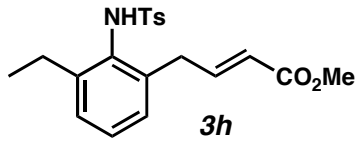
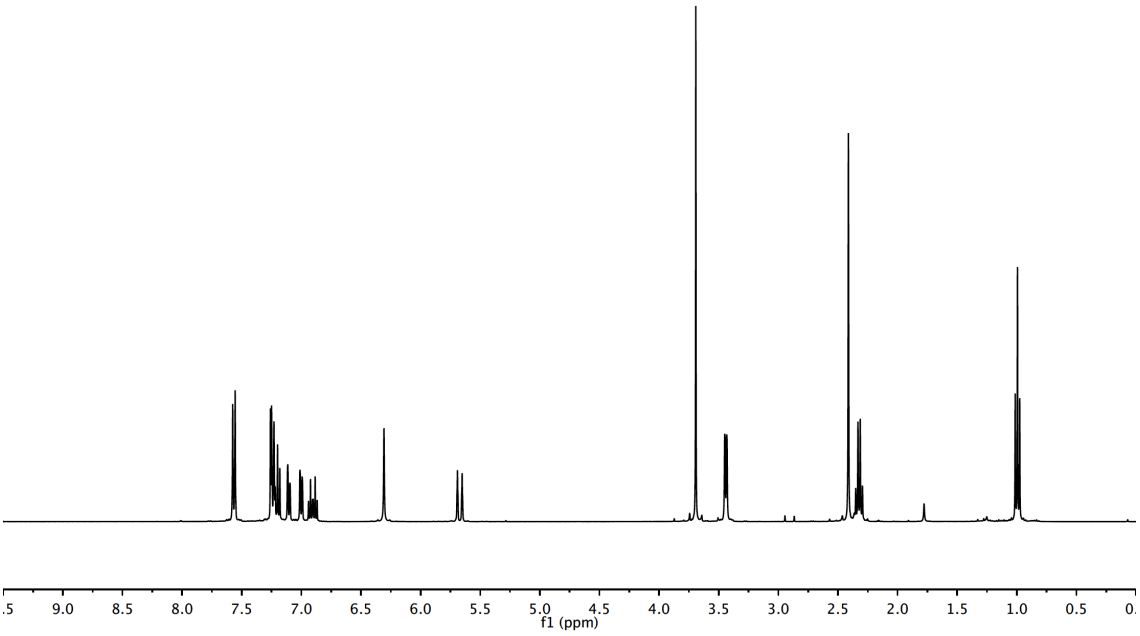
f1 (ppm)


NHTs
CO2Me

3h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3.0
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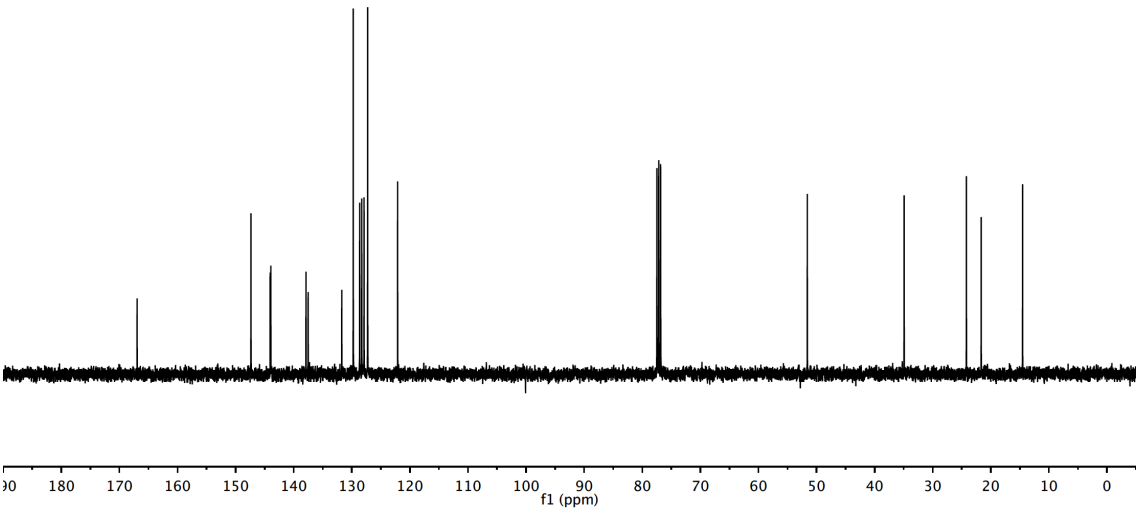
1.5
1.0
0.5
f1 (ppm)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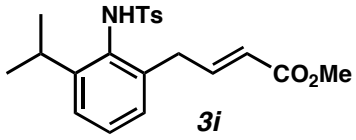
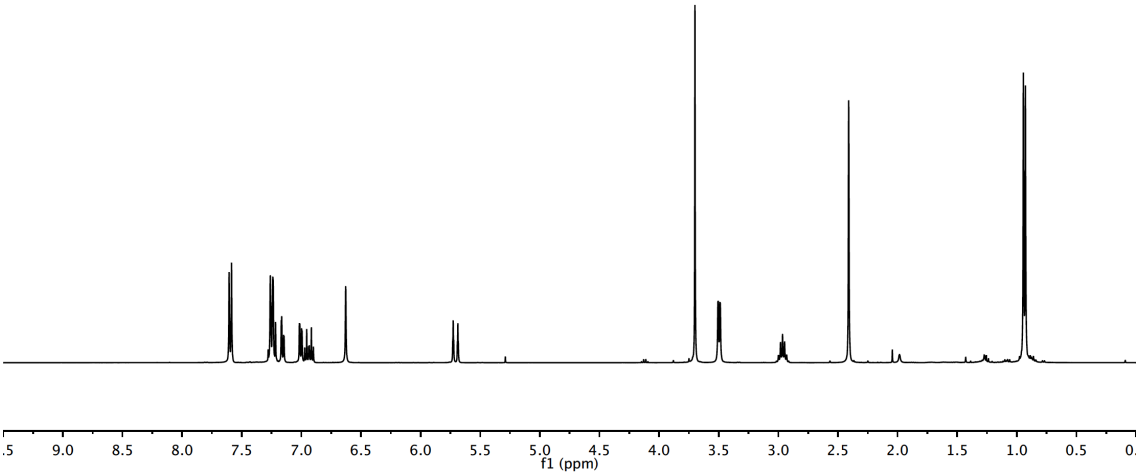
f1 (ppm)


NHTs
CO2Me

3i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6.0
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5.0
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4.0
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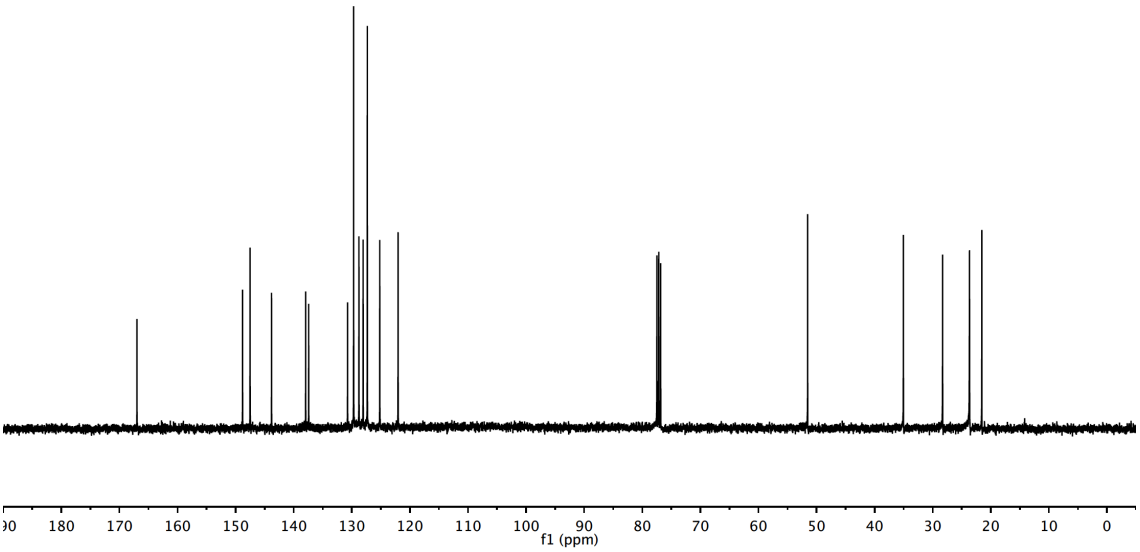
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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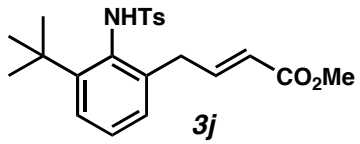
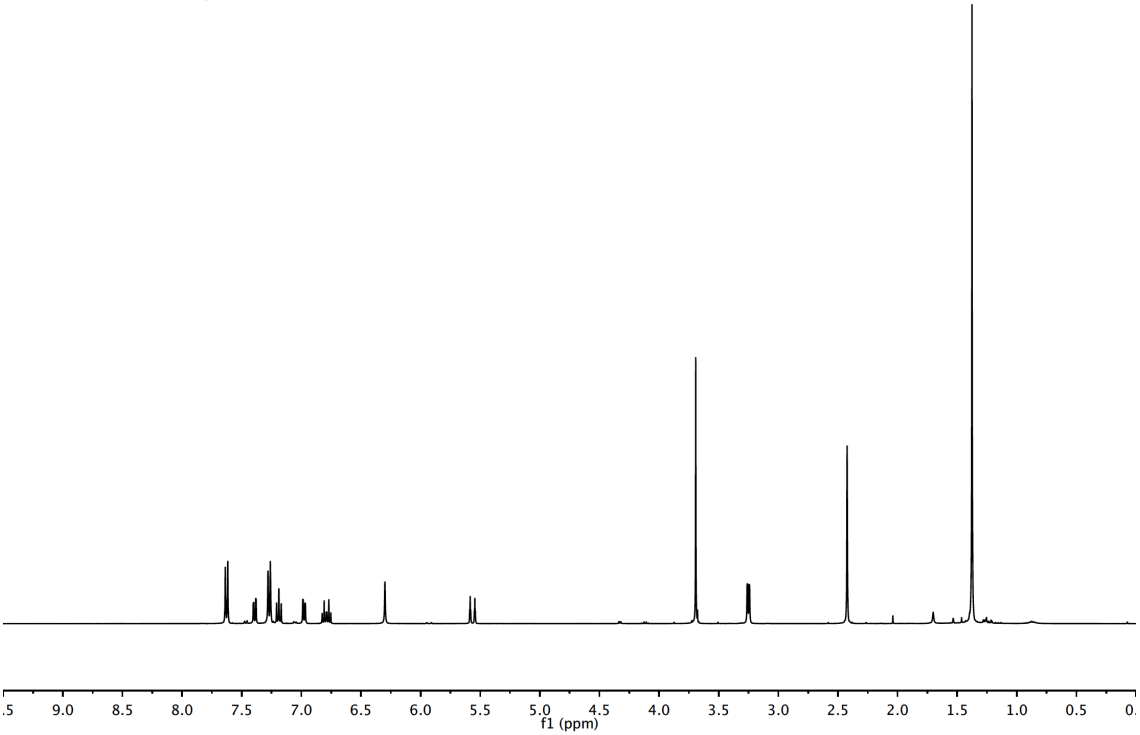
f1 (ppm)


NHTs
CO2Me

3j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1.5
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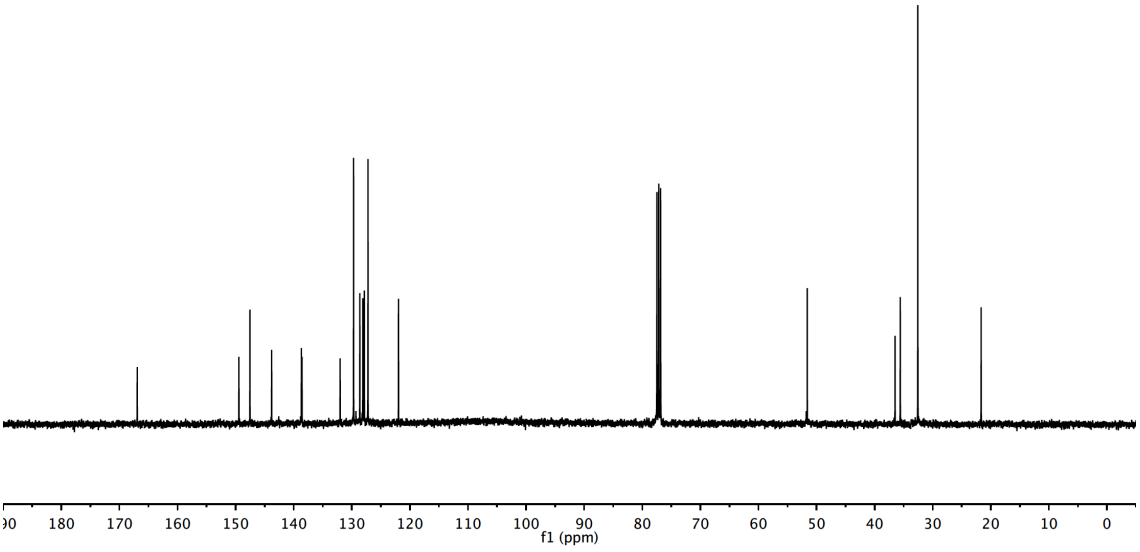
0.5
f1 (ppm)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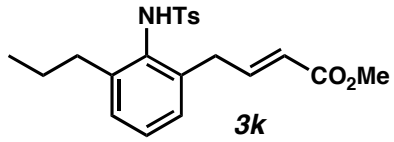
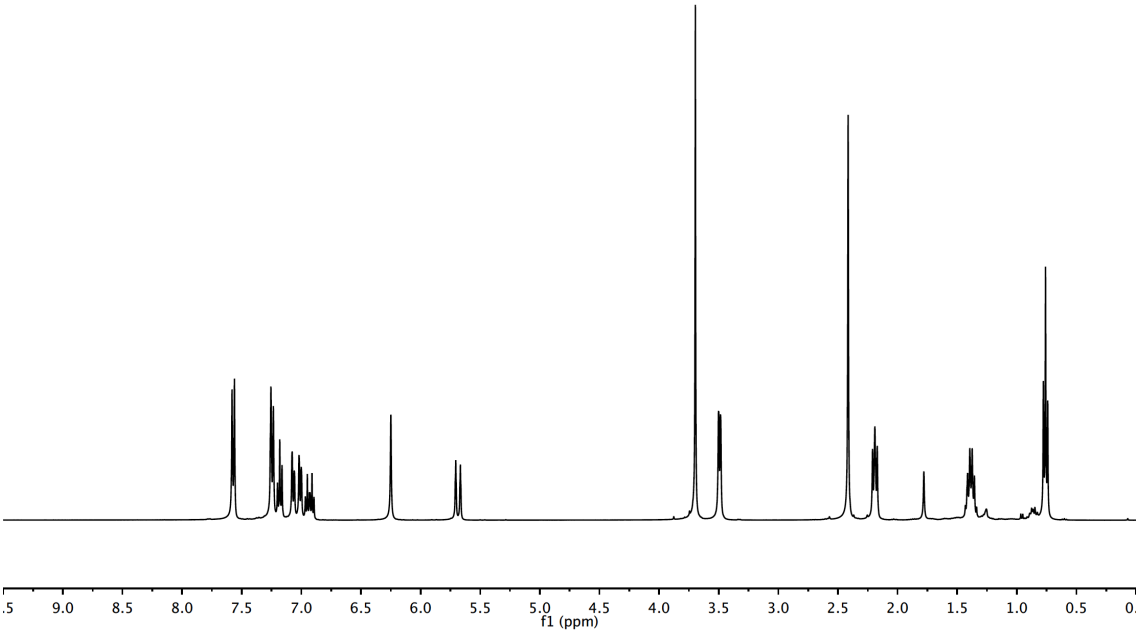
0
f1 (ppm)


NHTs
CO2Me

3k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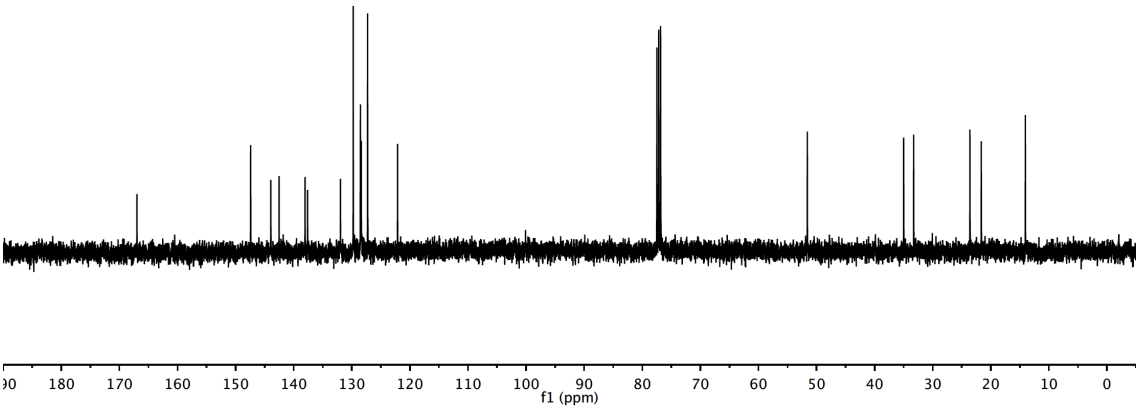
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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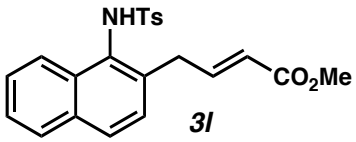
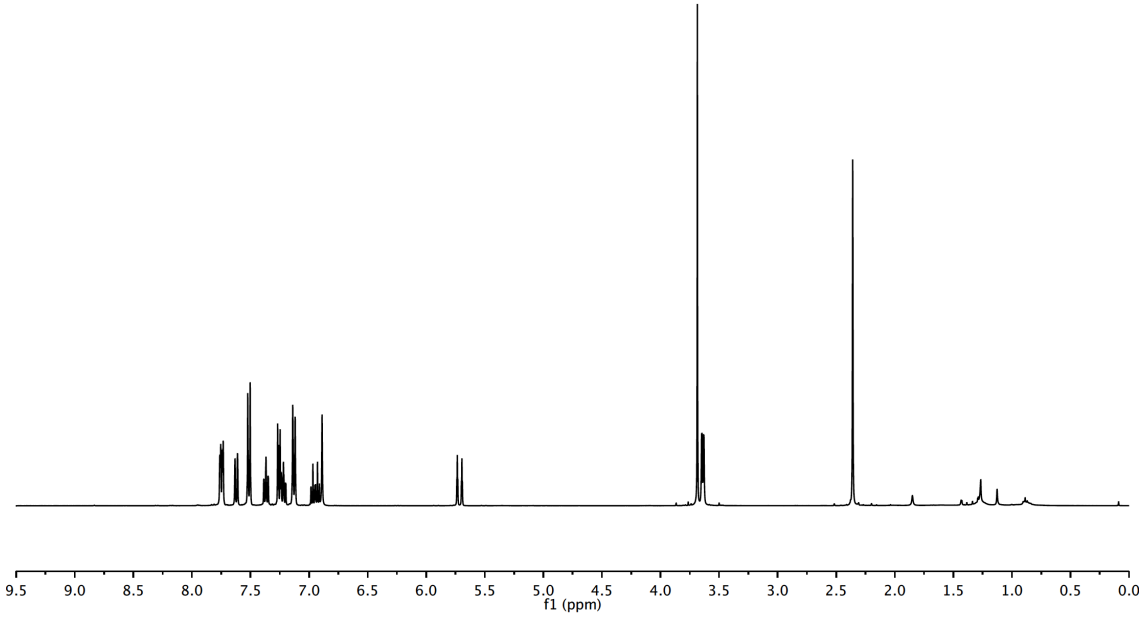
0
f1 (ppm)


NHTs
CO2Me

3l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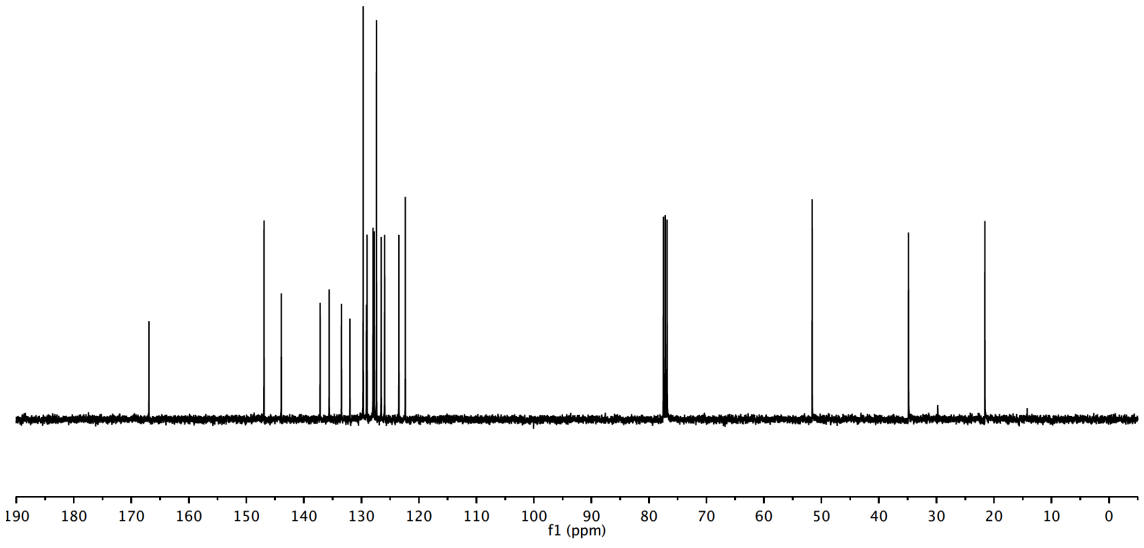
f1 (ppm)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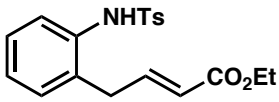
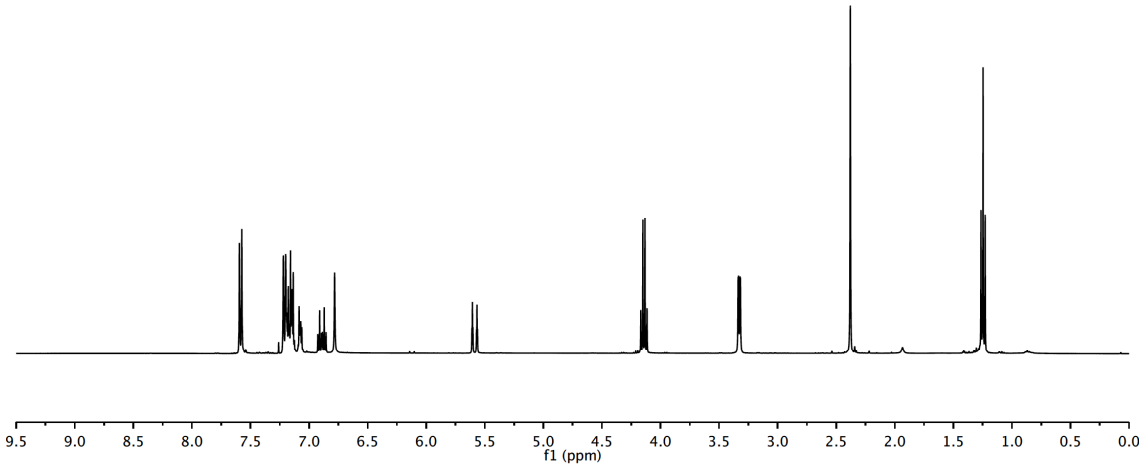
f1 (ppm)


NHTs
CO2Et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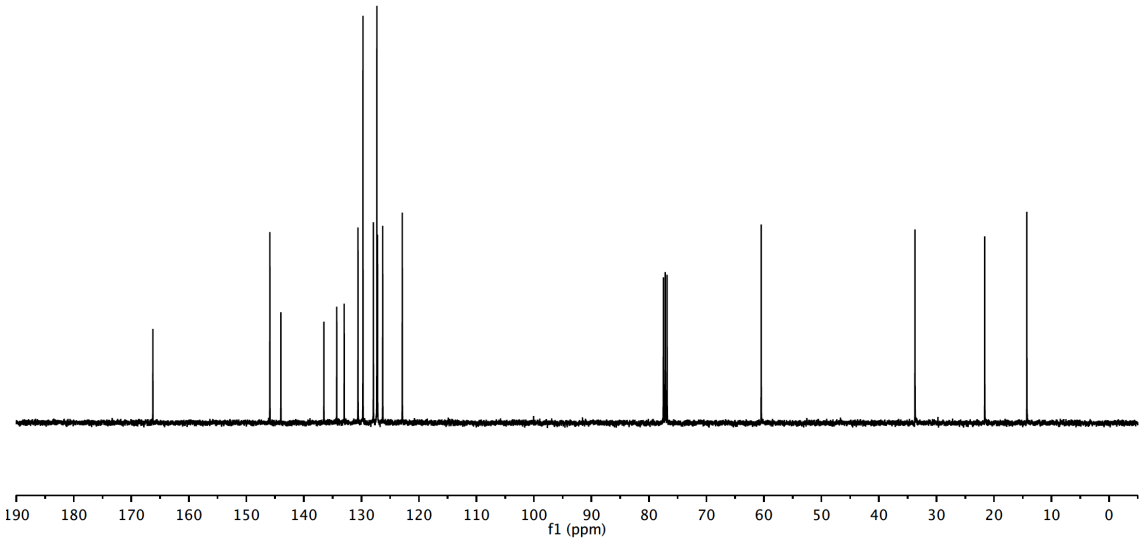
f1 (ppm)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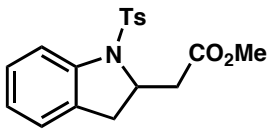
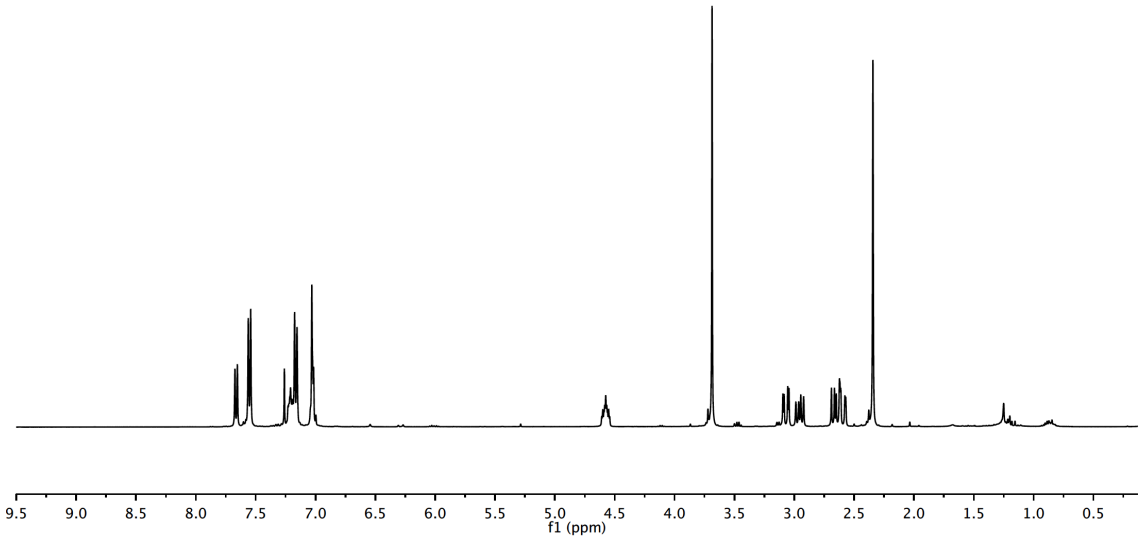
f1 (ppm)


Ts
N
CO2Me

4a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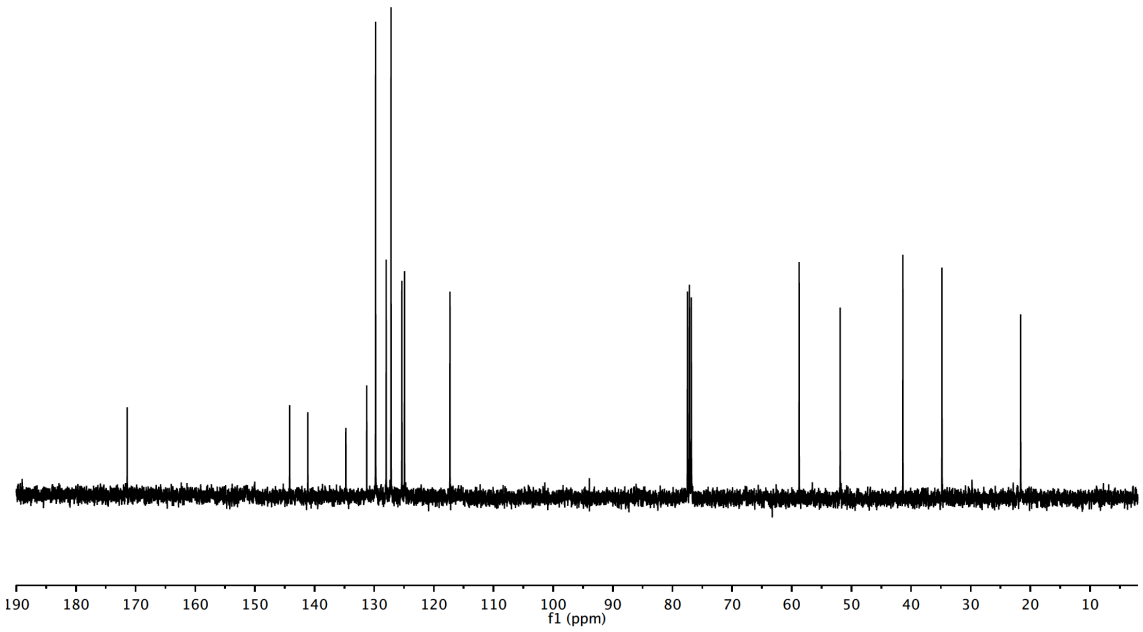
f1 (ppm)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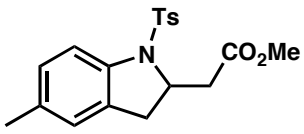
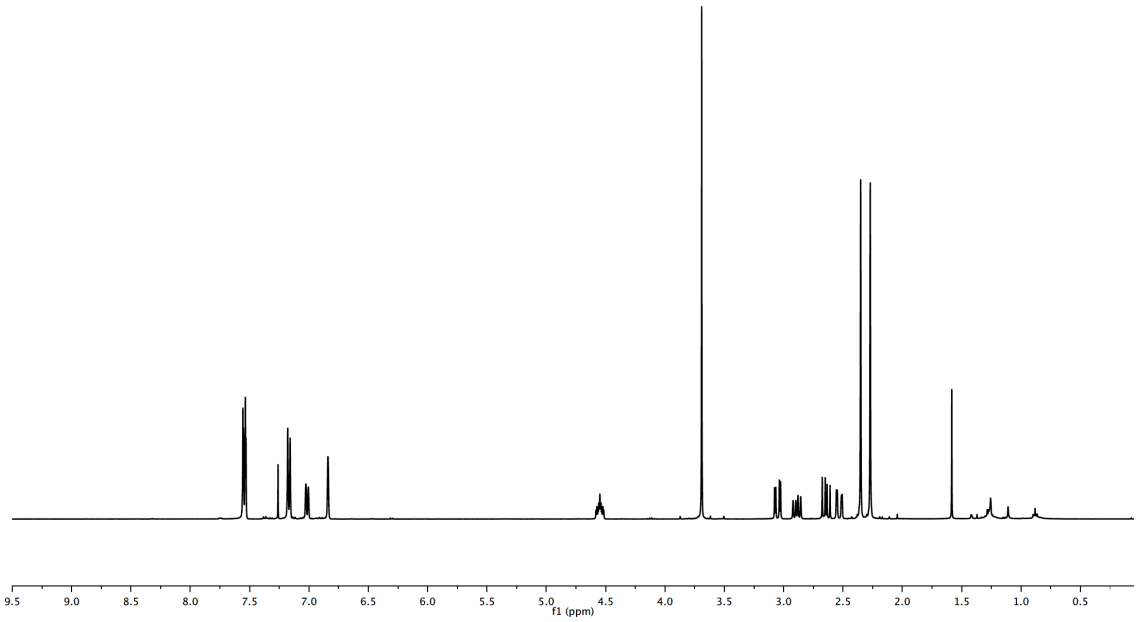
f1 (ppm)


Ts
N
CO2Me

4b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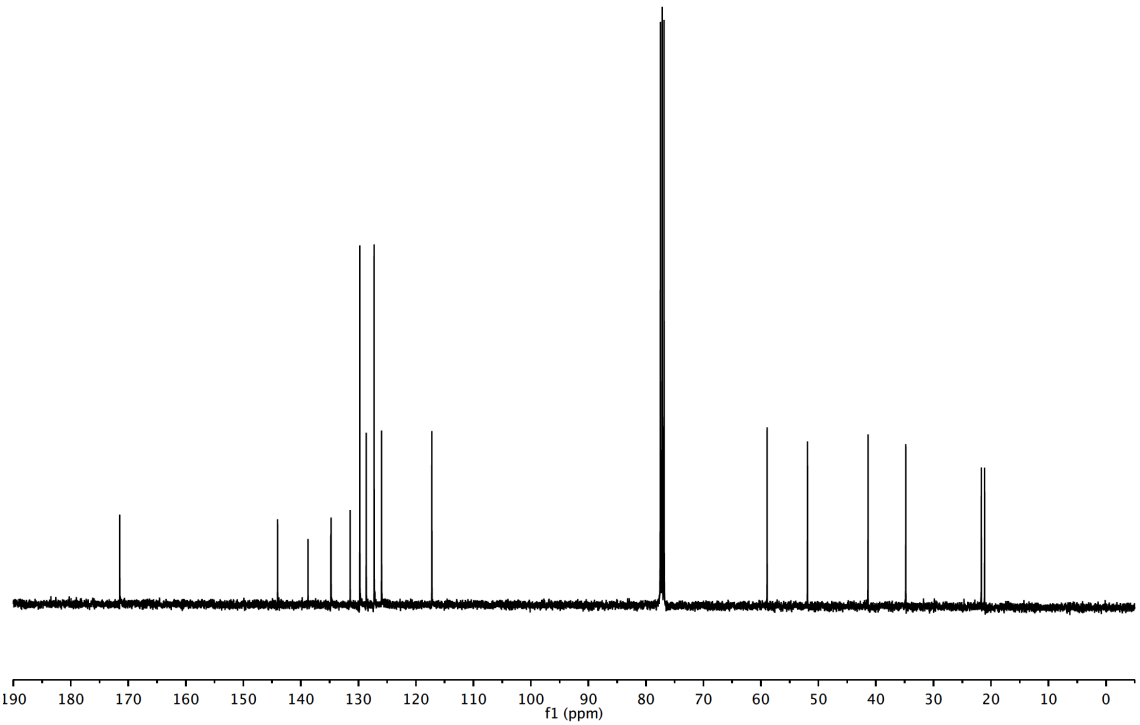
f1 (ppm)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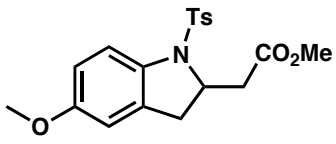
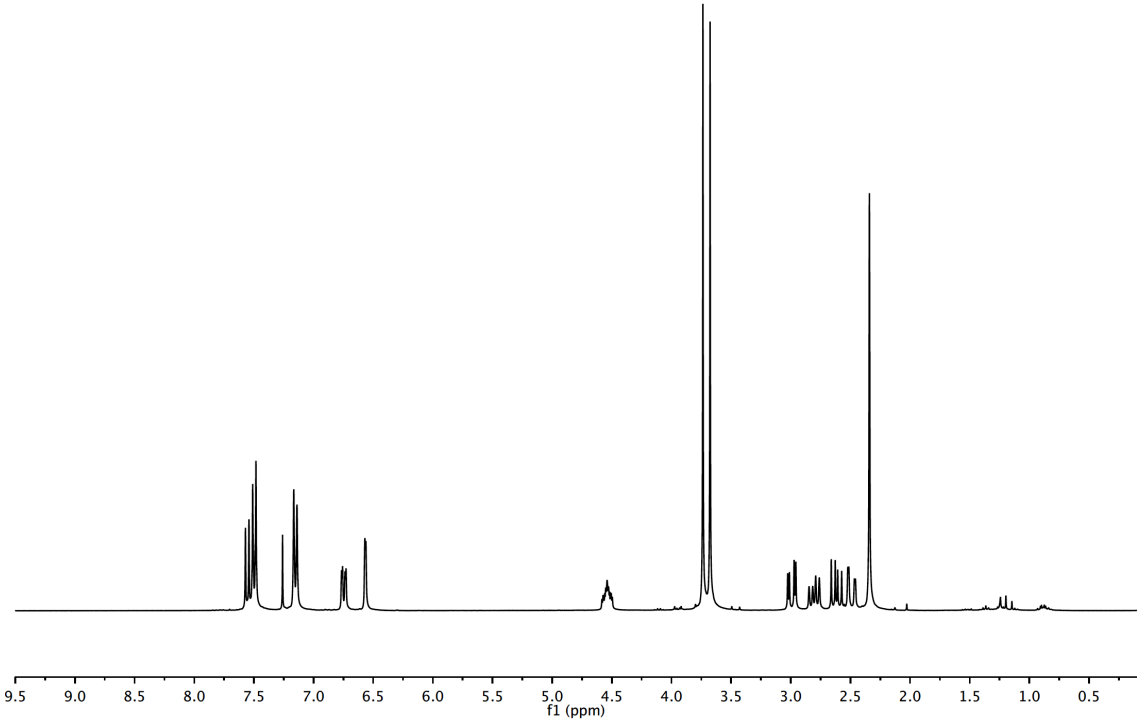
f1 (ppm)


Ts
N
CO2Me
O

4c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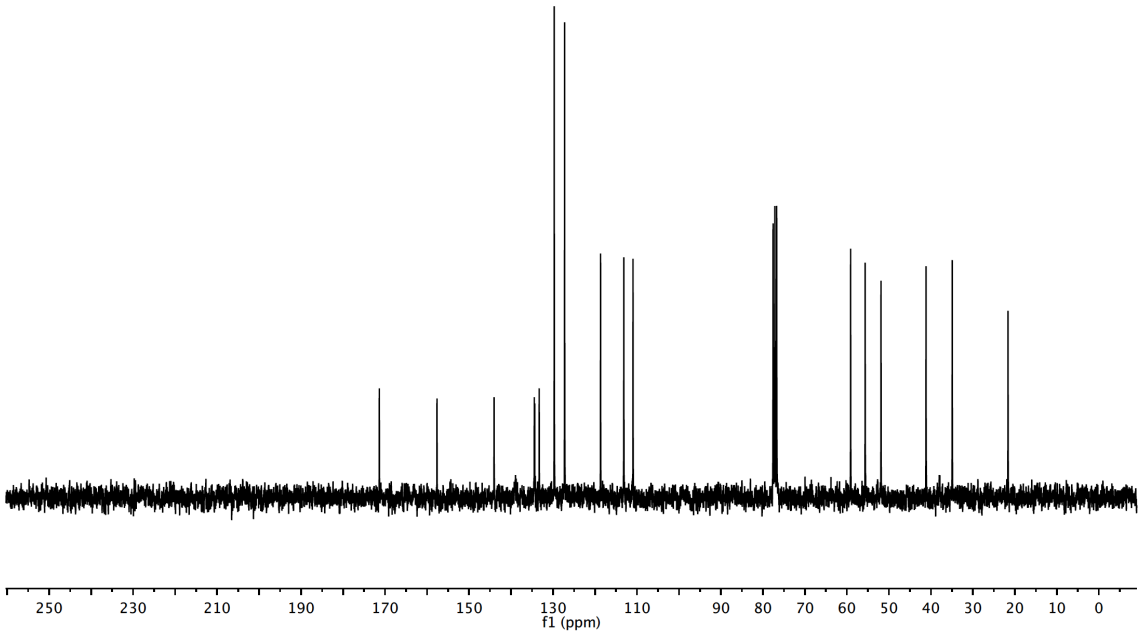
f1 (ppm)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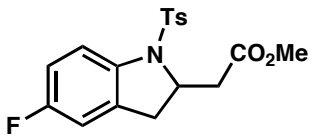
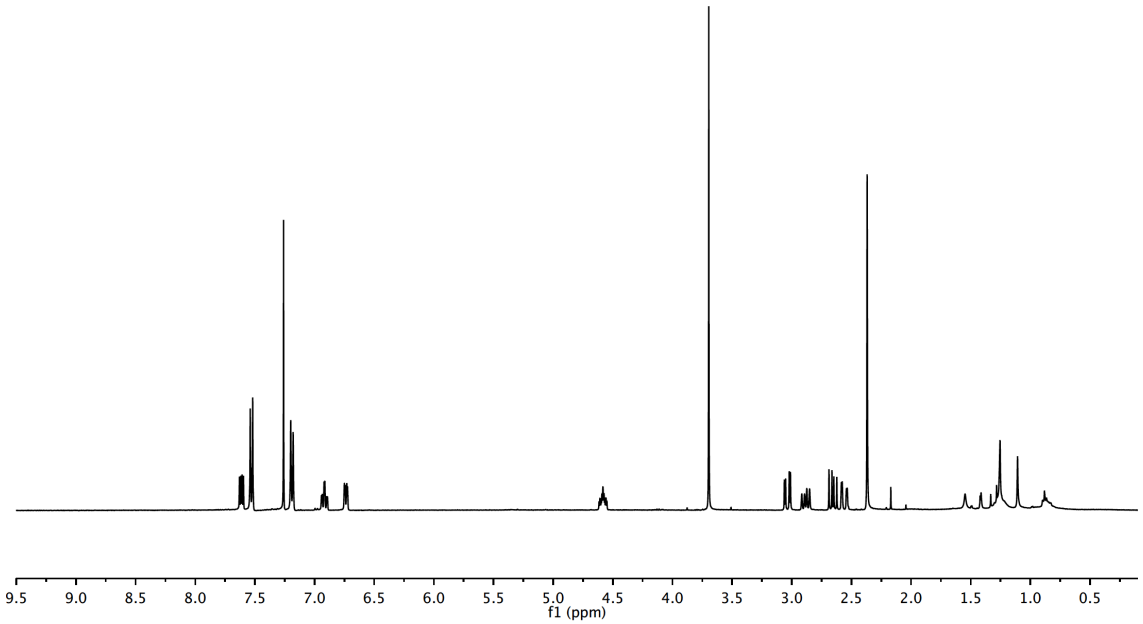
f1 (ppm)


Ts
N
CO2Me
F

4d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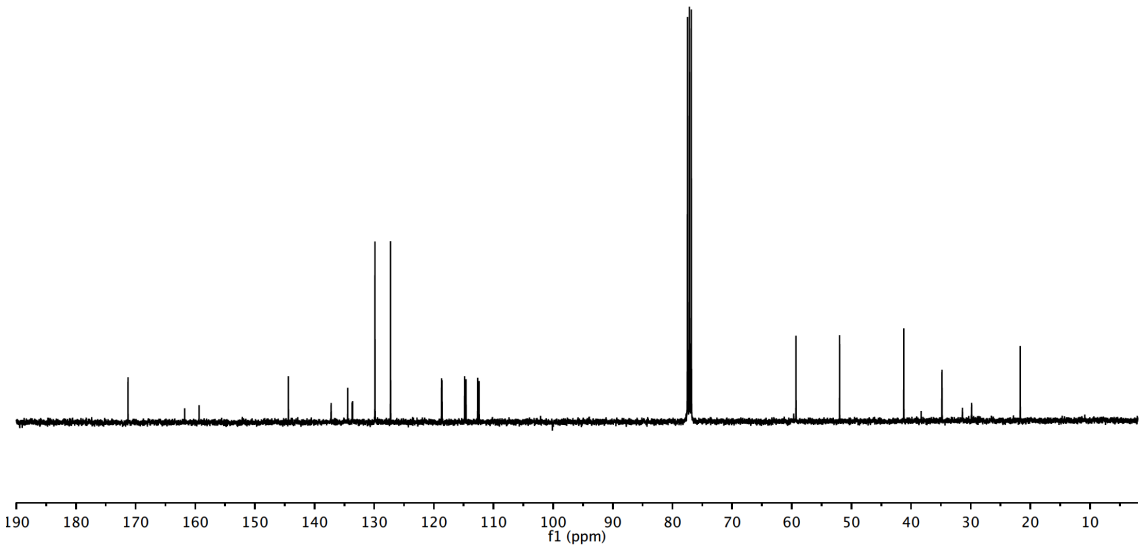
f1 (ppm)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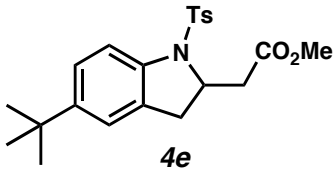
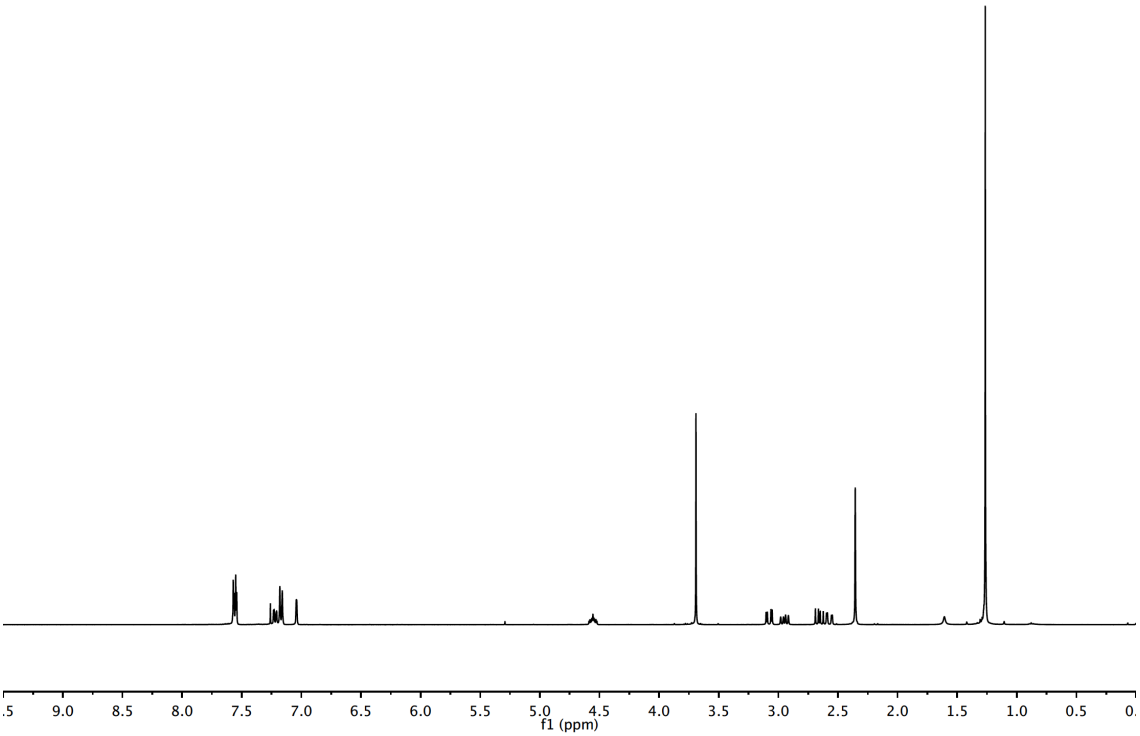

Ts
N
CO2Me

4e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6.5
6.0
5.5
5.0
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4.0
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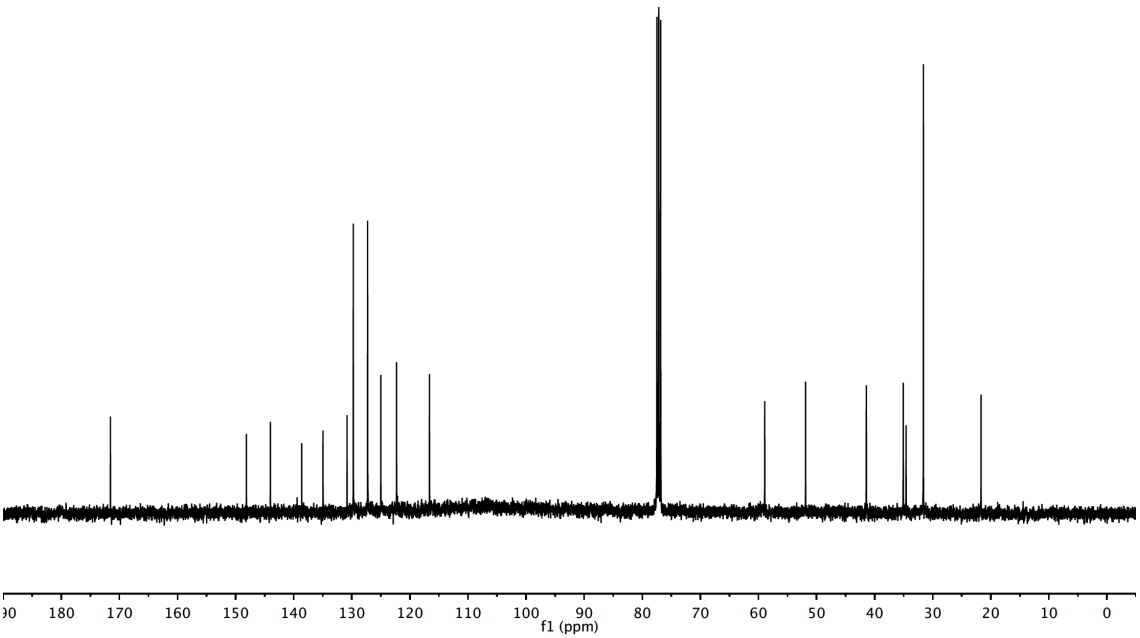
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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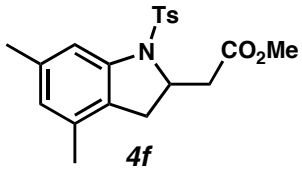
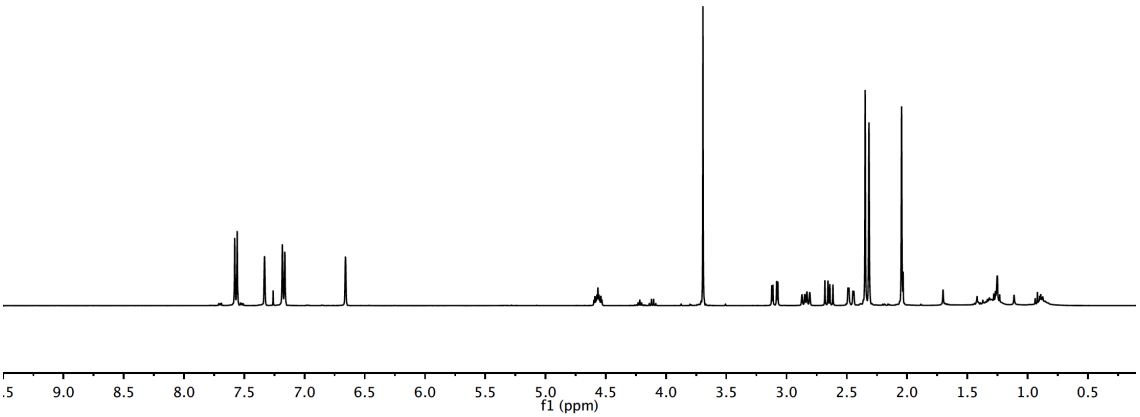
f1 (ppm)


Ts
N
CO2Me

4f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6.0
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3.0
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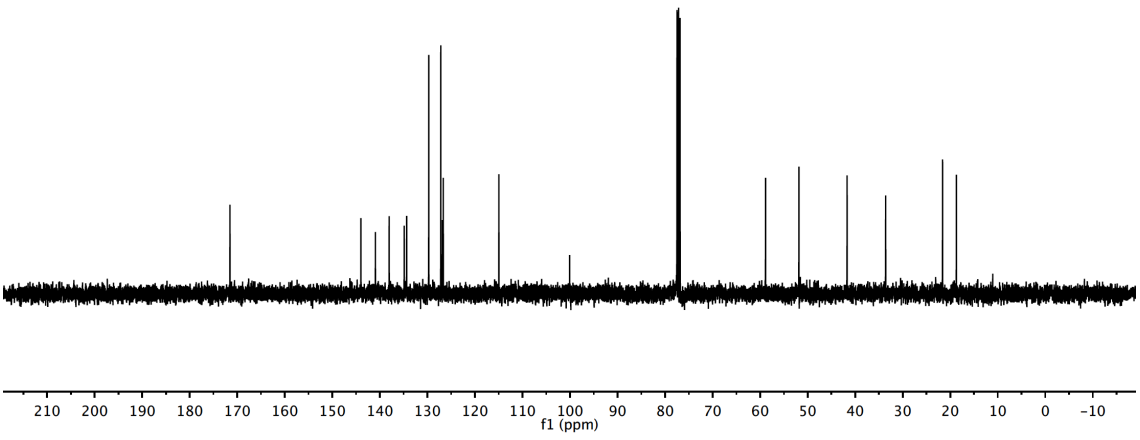
2.0
1.5
1.0
0.5
f1 (ppm)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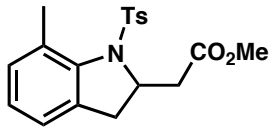
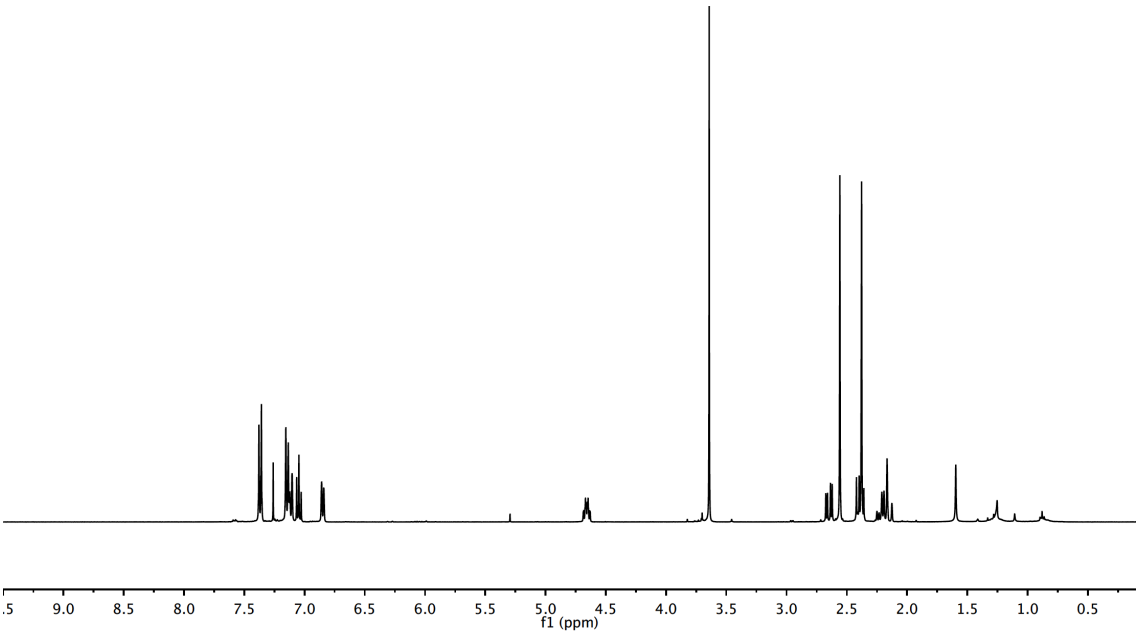
-10
f1 (ppm)


Ts
N
CO2Me

4g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5.5
5.0
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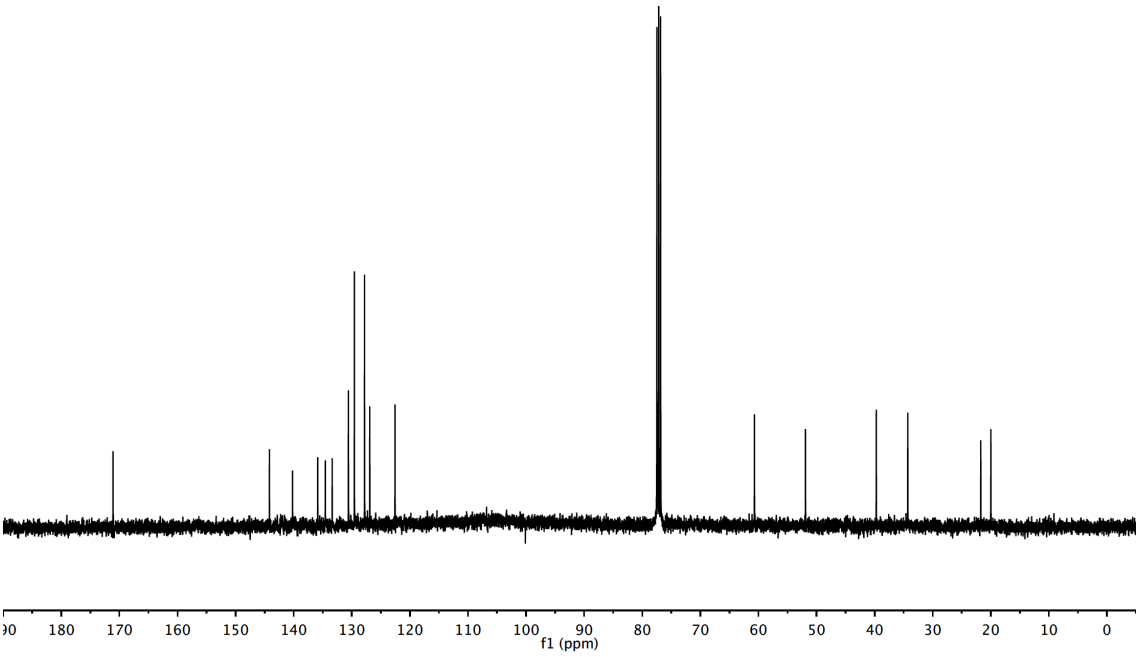
0.5
f1 (ppm)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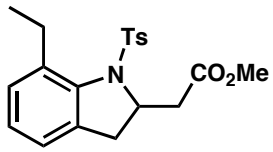
Ts
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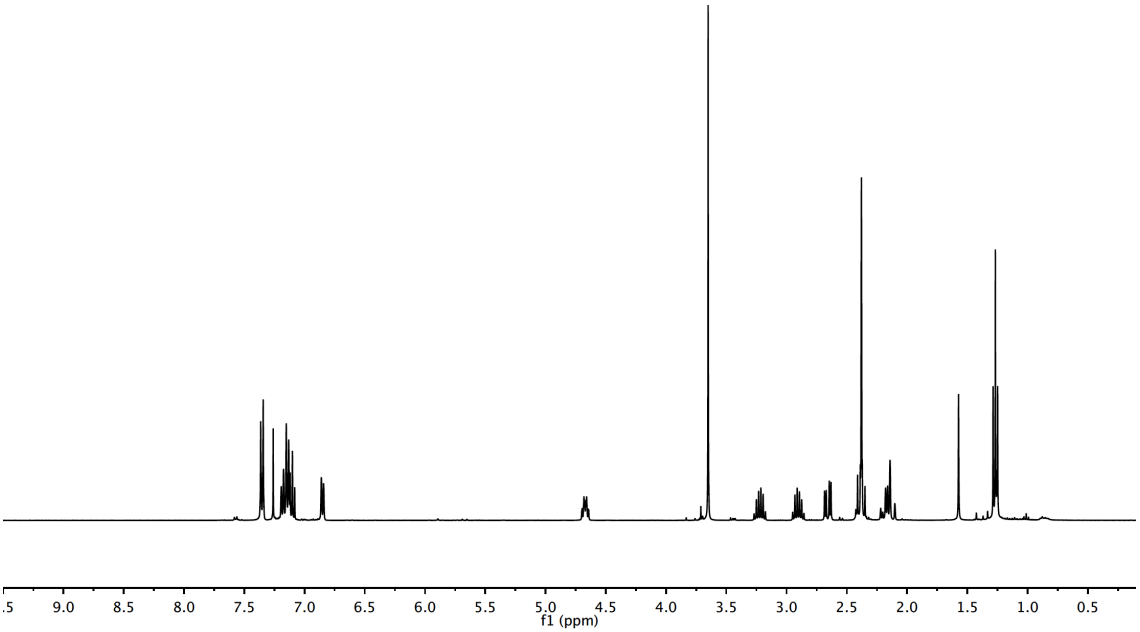
CO2Me

4h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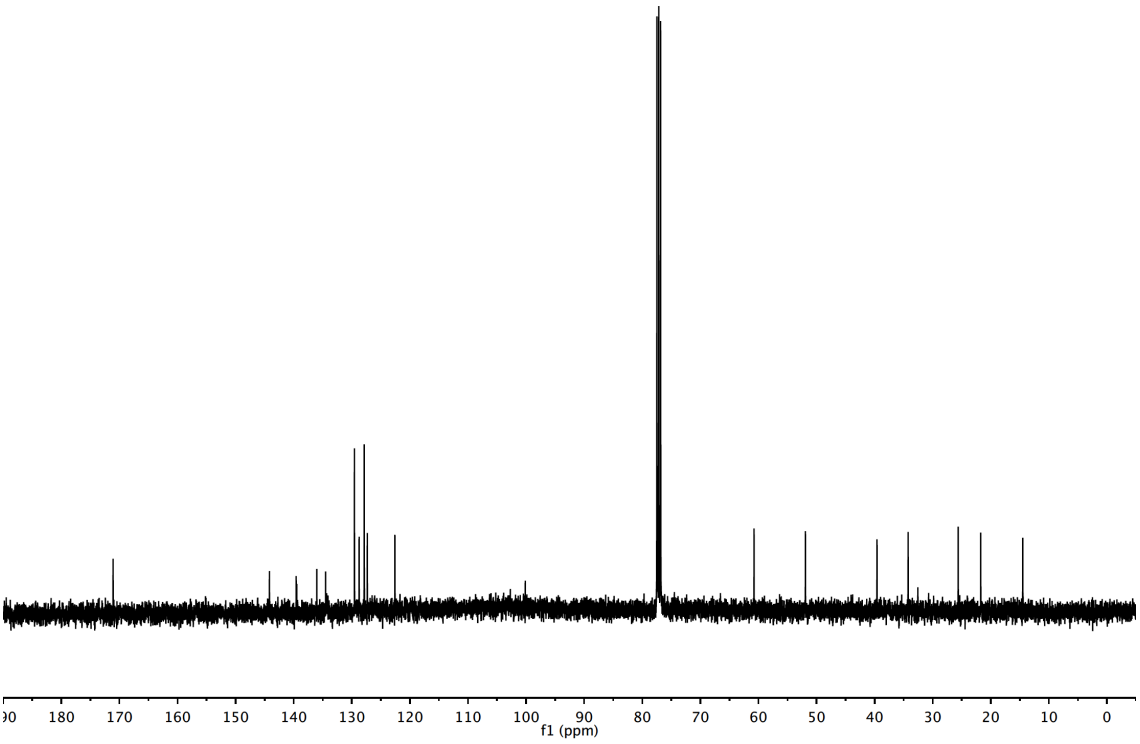
0.5
f1 (ppm)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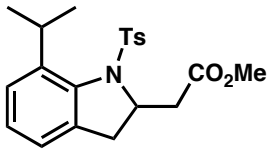
Ts
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CO2Me

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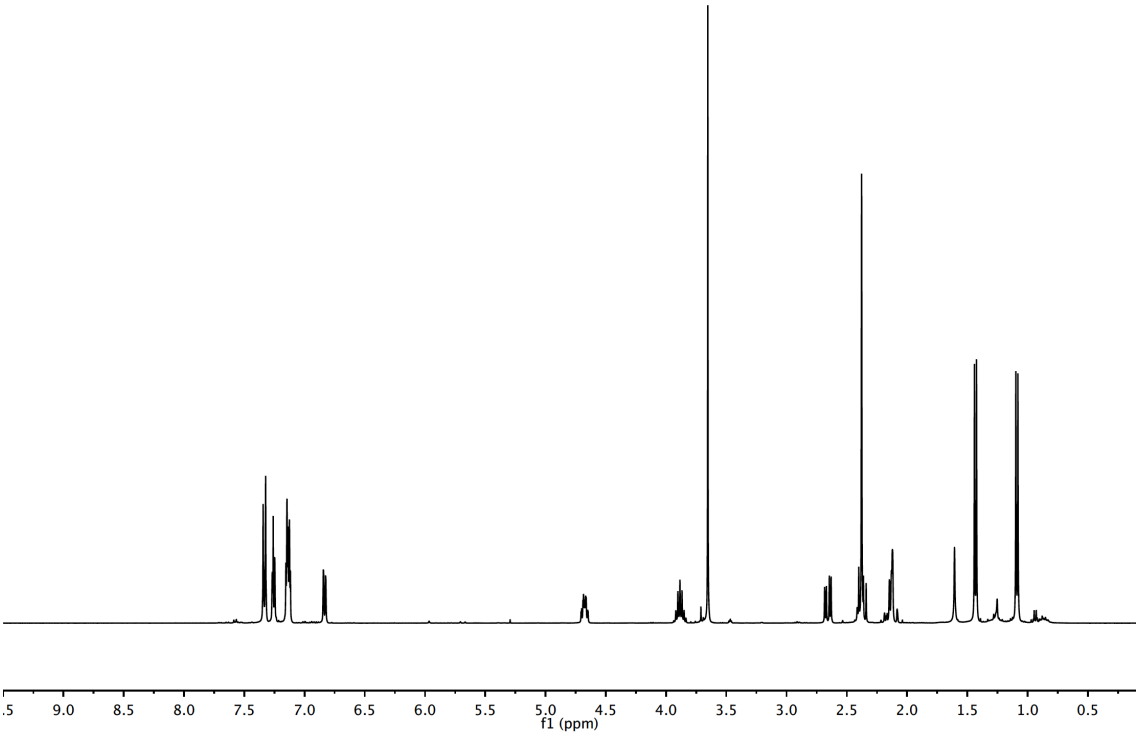
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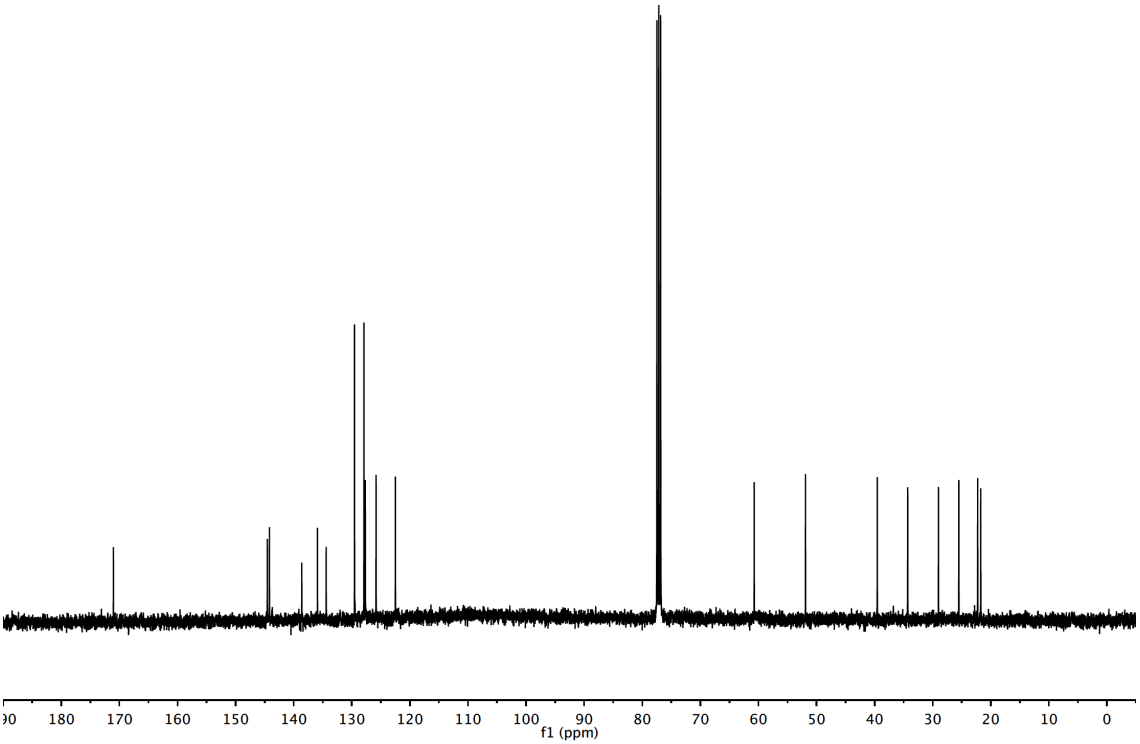
0.5
f1 (ppm)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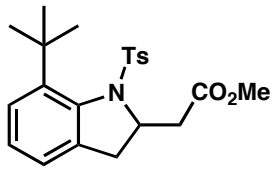
Ts
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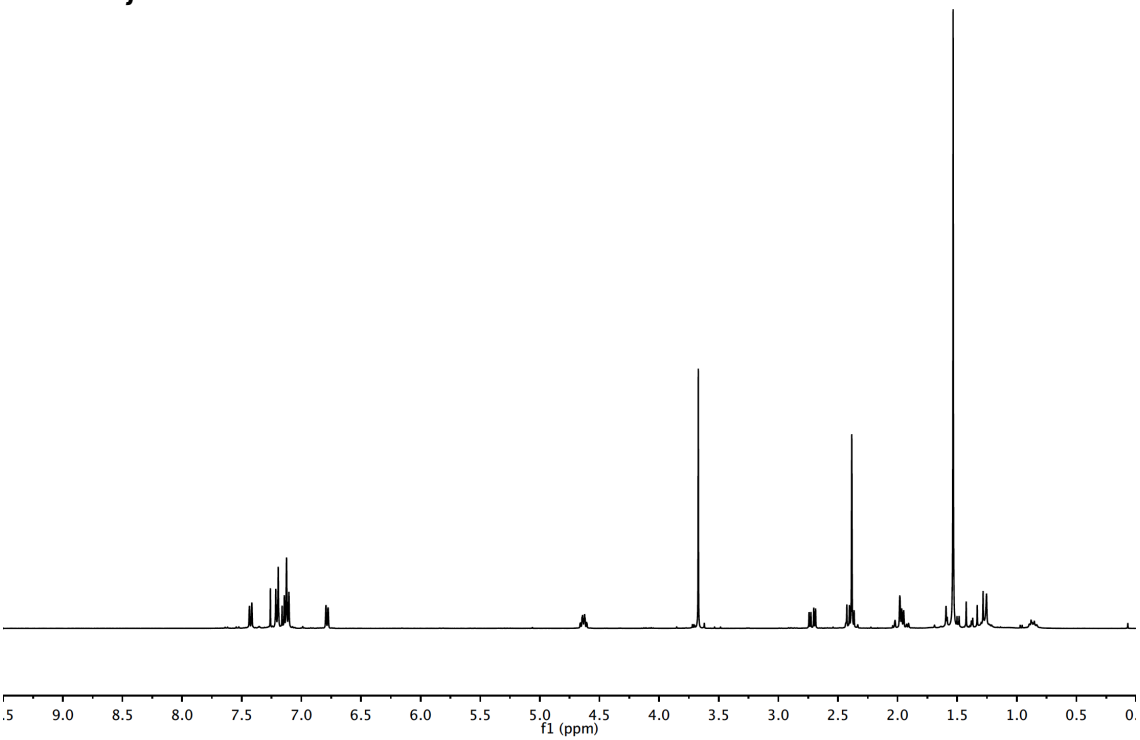
CO2Me

4j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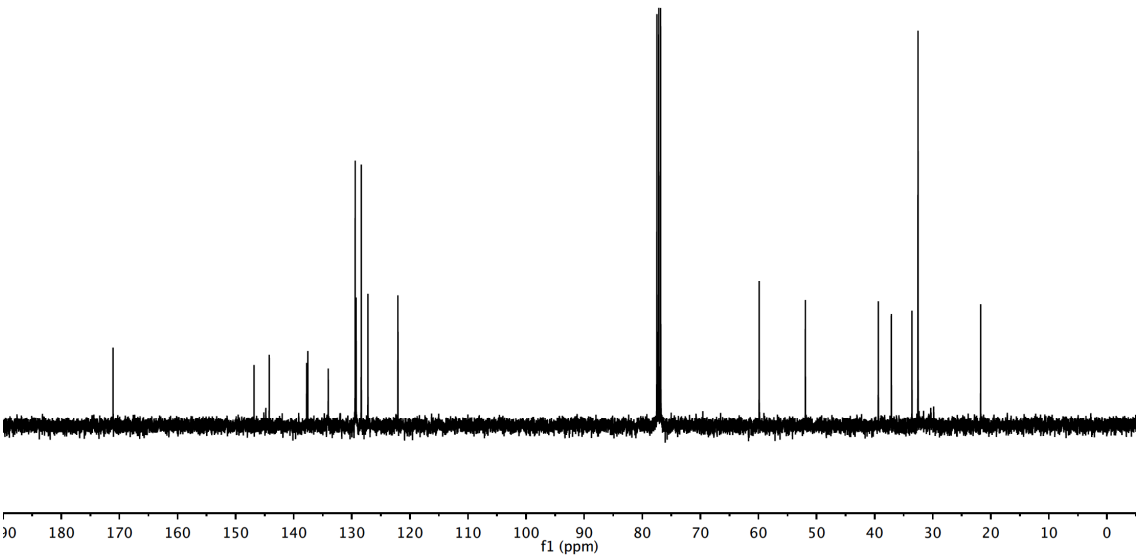
0.5
f1 (ppm)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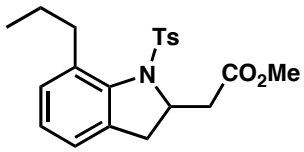
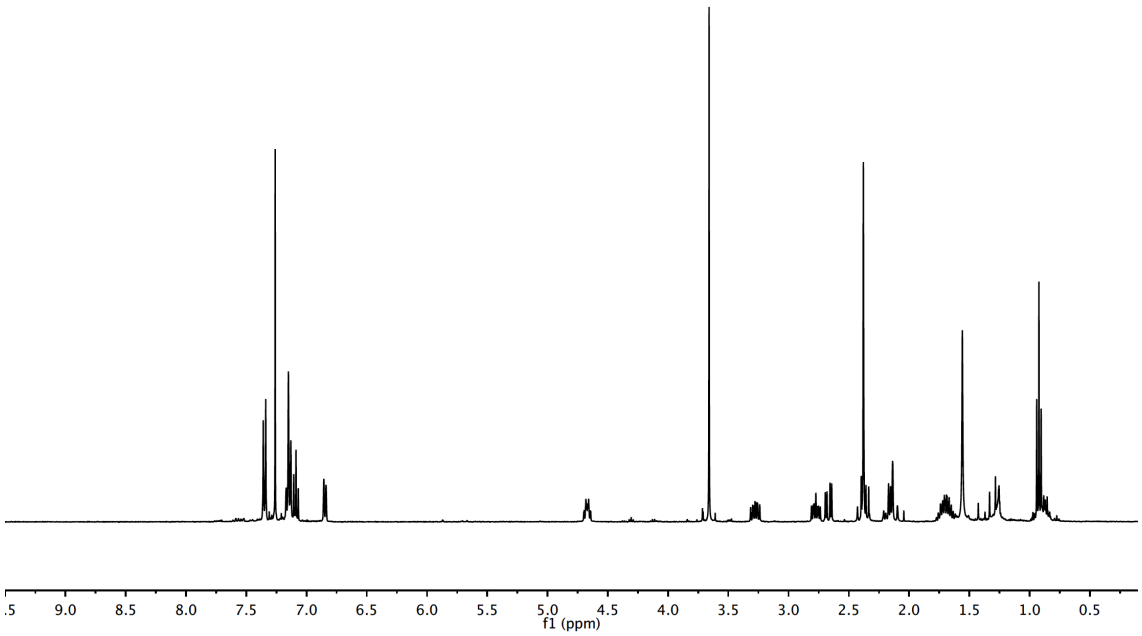

Ts
N
CO2Me

4k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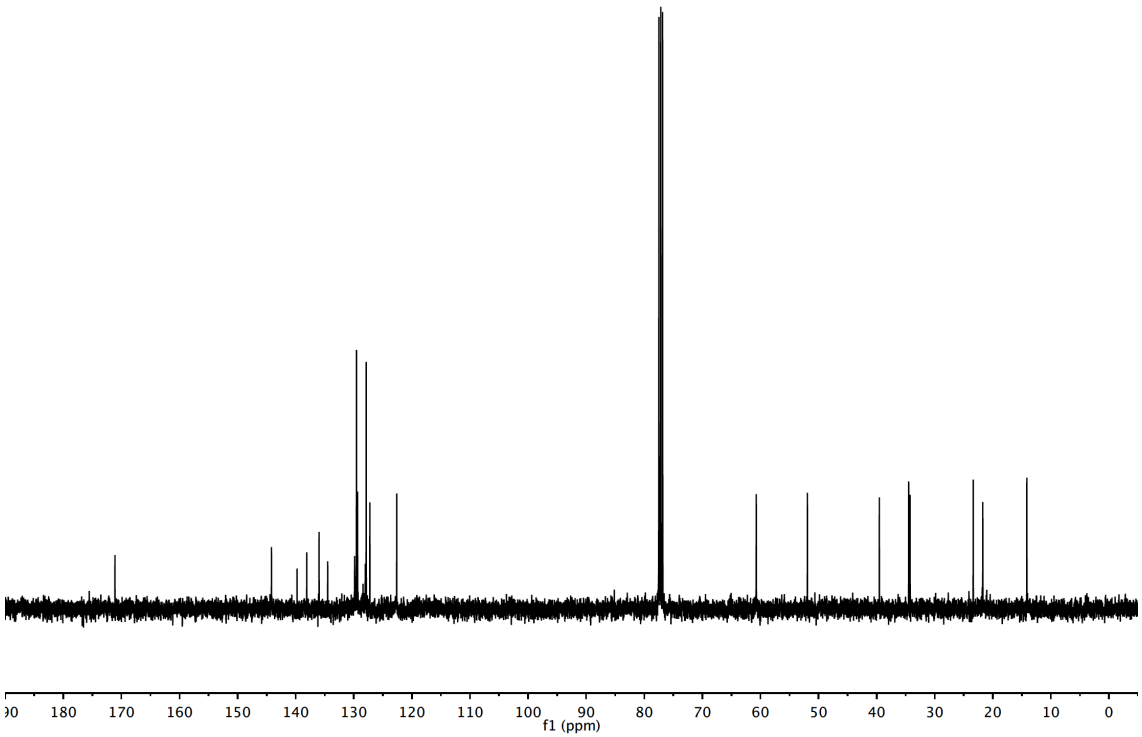
0.5
f1 (ppm)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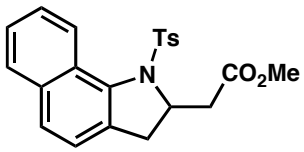
0
f1 (ppm)


Ts
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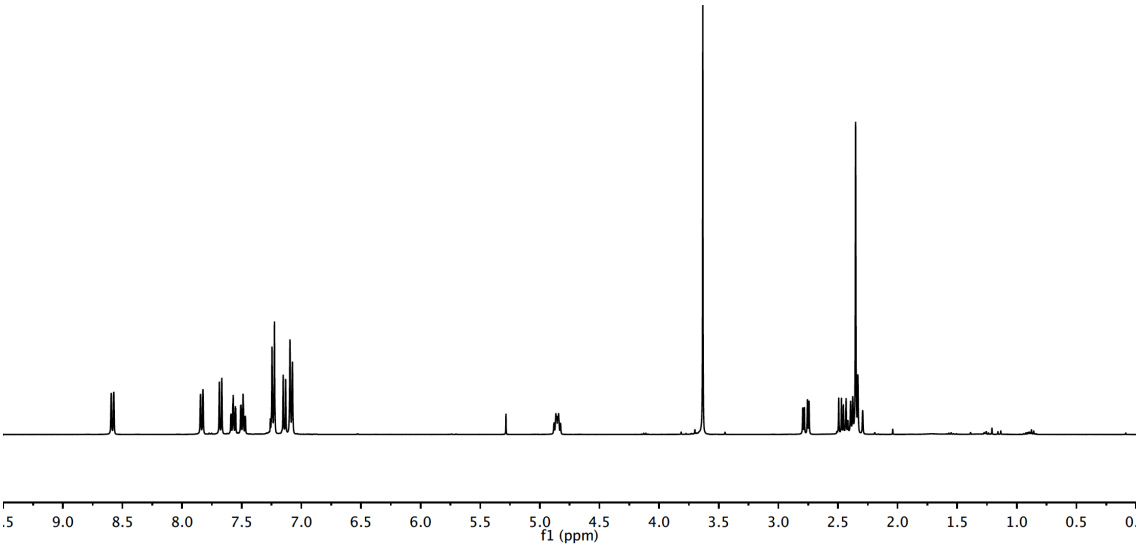
CO2Me

4l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2.5
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1.5
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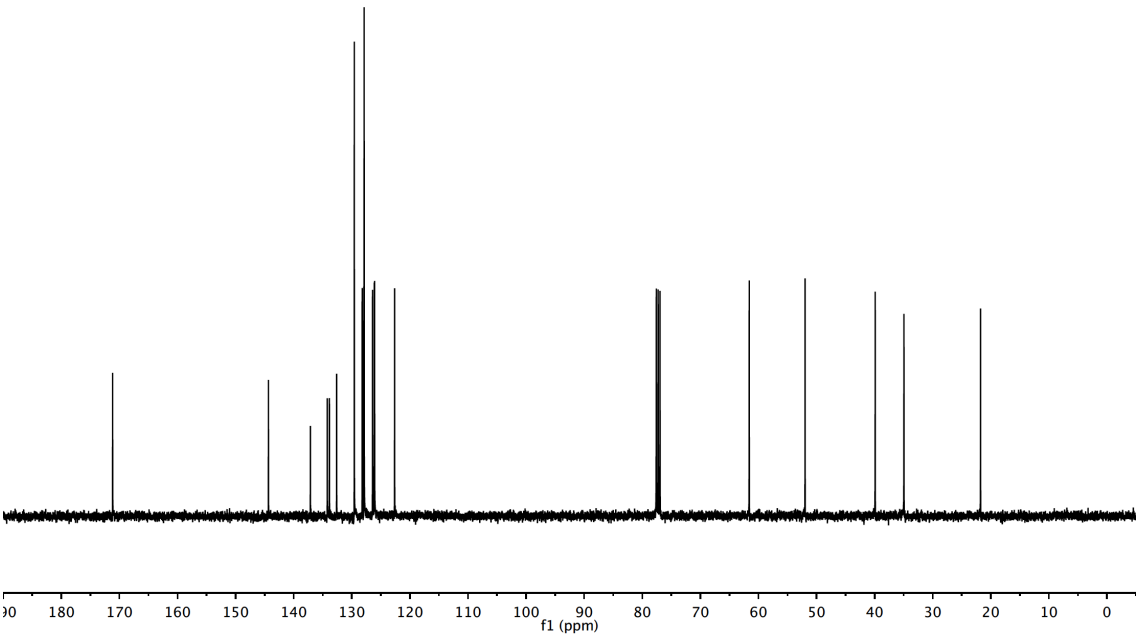
0.5
f1 (ppm)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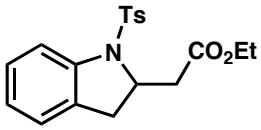
f1 (ppm)


Ts
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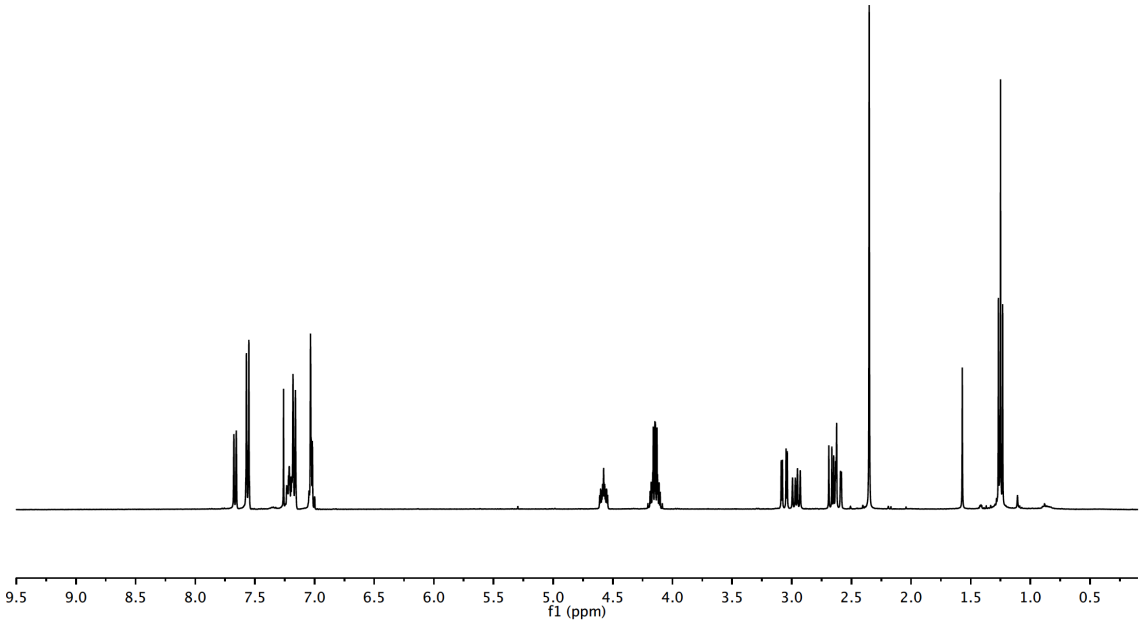
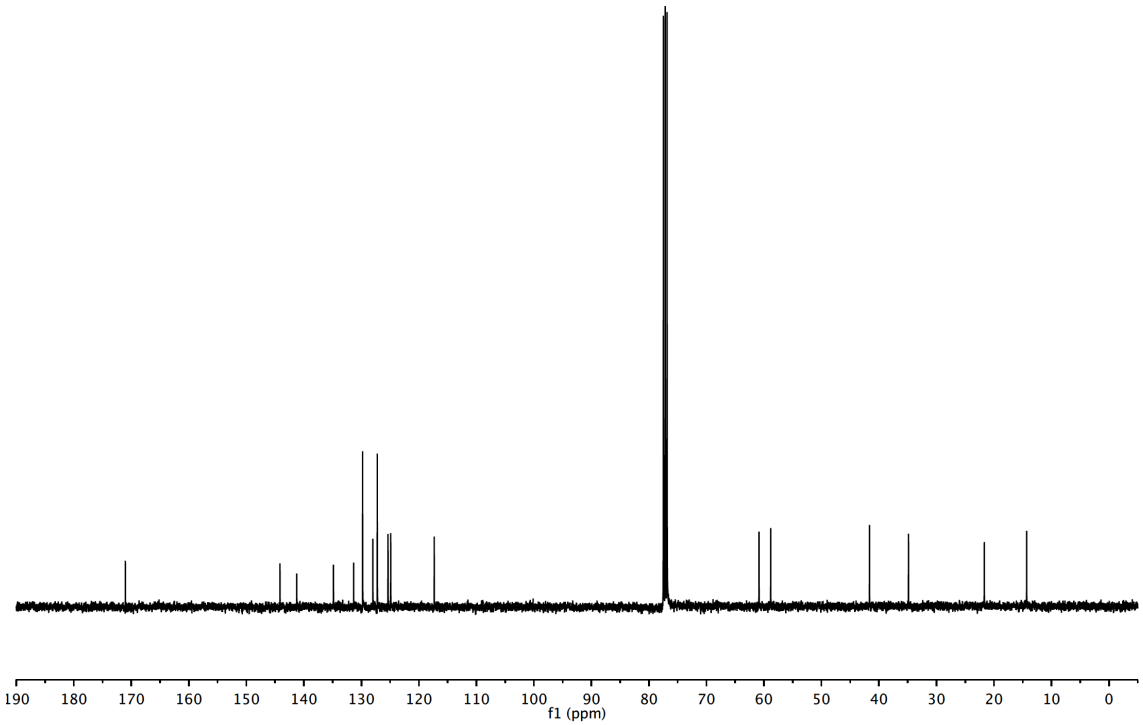
CO2Et


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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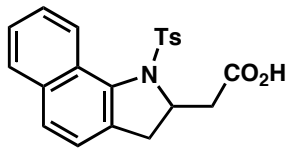
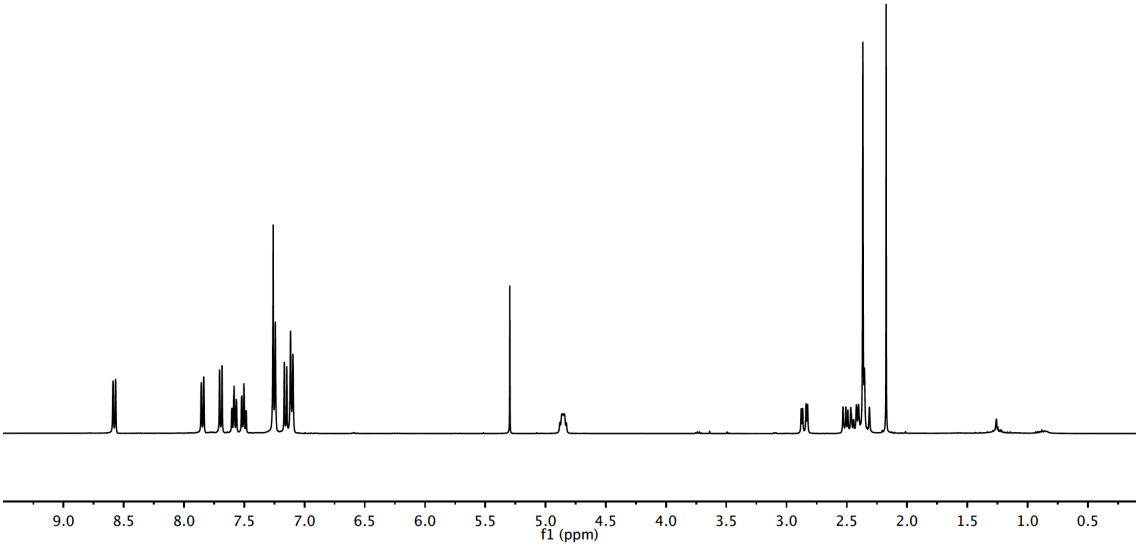
f1 (ppm)


Ts
N
CO2H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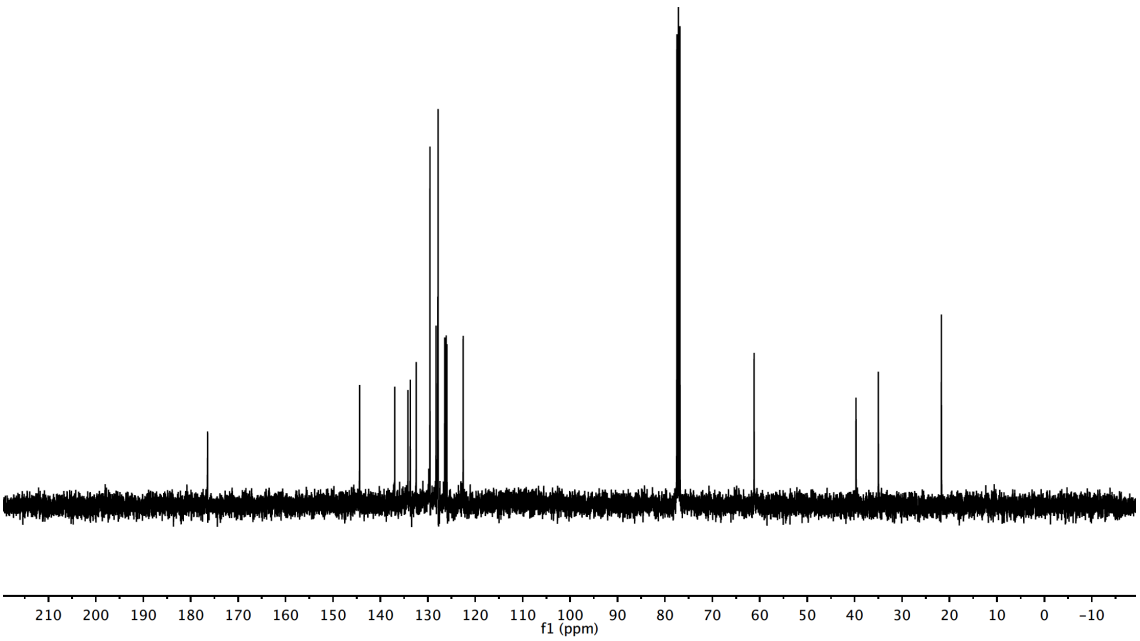
f1 (ppm)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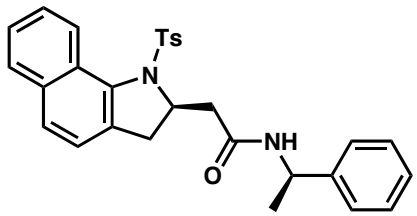
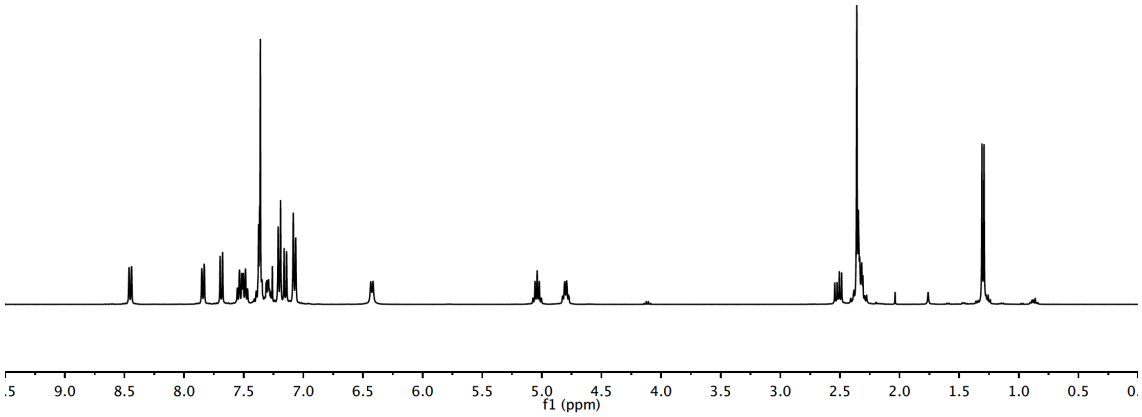
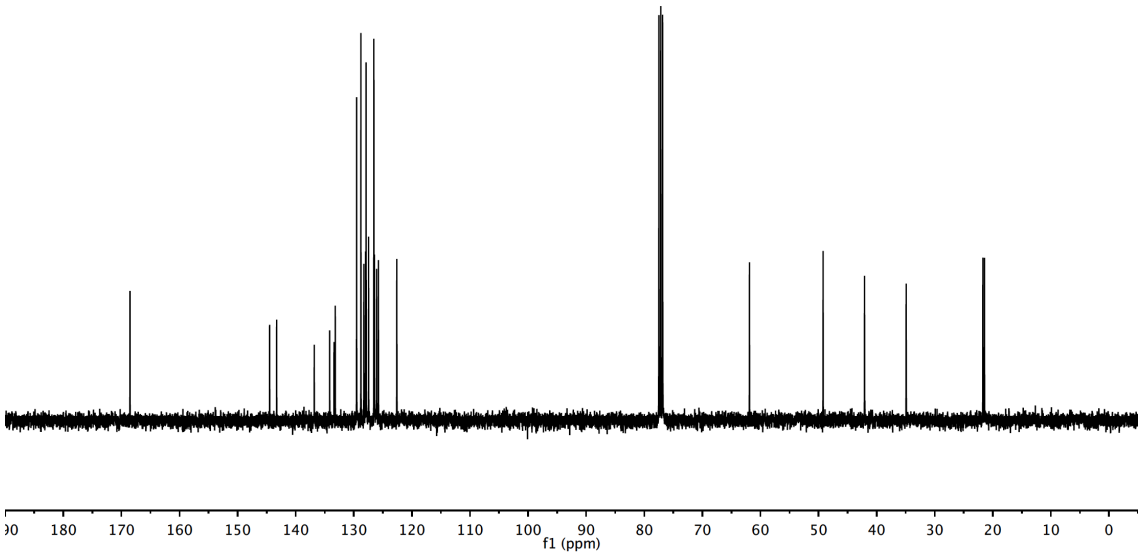
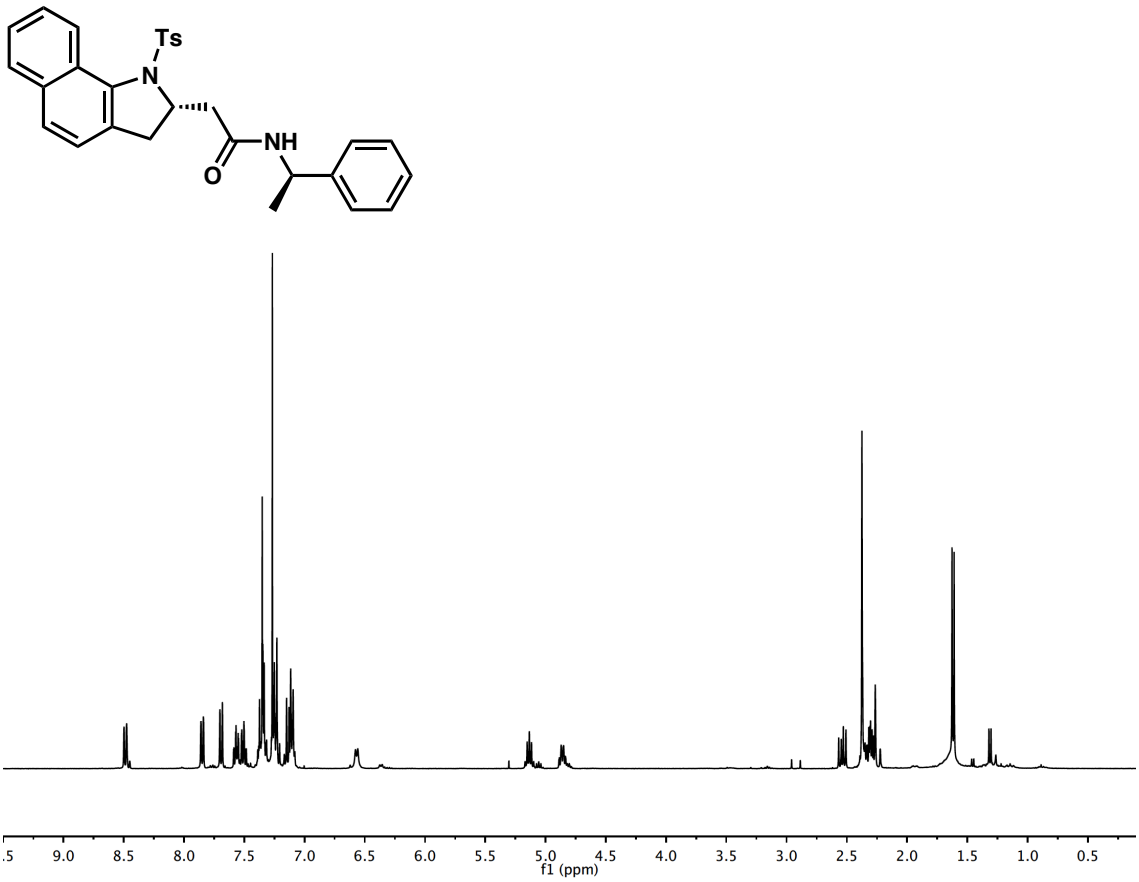
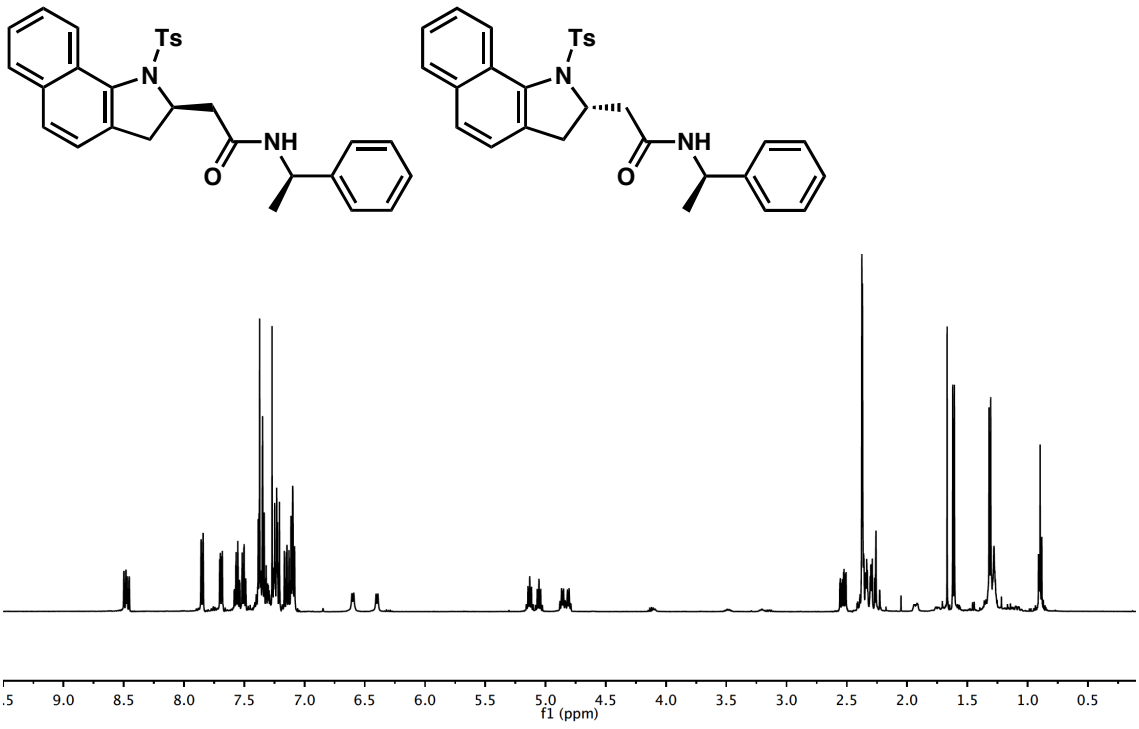
f1 (ppm)


Ts
N
NH
O


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
NH
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Ts
N
NH
O
Ts
N
NH
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)