Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Direct and Modular Access to Allylic Amines via Nickel-Catalyzed Three-Component coupling

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I. General Information

Unless otherwise stated, all experiments were carried out in oven-dried glassware using nitrogen manifolds or in a glovebox. Reactions were monitored by thin-layer chromatography (TLC). TLC was performed using Huanghai 8 ± 0.2 μm precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, $KMnO_4$, *p*-anisaldehyde, or phosphomolybdic acid staining. Huanghai silica gel (particle size 300 − 400 or 200 − 300 mesh) was used for chromatography. The NMR spectra were taken with Bruker Avance 400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR). All ^{1}H NMR experiments were measured in relative to the signals of $CDCl_3$ (7.26 ppm), ^{13}C NMR experiments were measured relative to the signal of $CDCl_3$ (77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Most of the High-resolution mass spectrometry (HRMS) was performed on either a SCIEX X500R LC-Q-TOF, ESI ion Source. Infrared (IR) spectra were recorded on a Bruker ALPHA II FT-IR Spectrometer, max in cm^{-1}. Enantiomeric excess (ee) was determined by an Agilent 1260 Series HPLC utilizing DAICEL Chiralpak AD-H (Size: 250 × 4.6 mm).

II. Catalysts, Reagents, and Solvents

$Ni(cod)_2$ was purchased from Bidepharm and used as received.

PCy_3 was purchased from Energy Chemical and used as received.

PPh_3 was purchased from Energy Chemical and used as received.

PBu_3 was purchased from Energy Chemical and used as received.

$P(4\text{-}FC_6H_4)_3$ was purchased from Bidepharm and used as received.

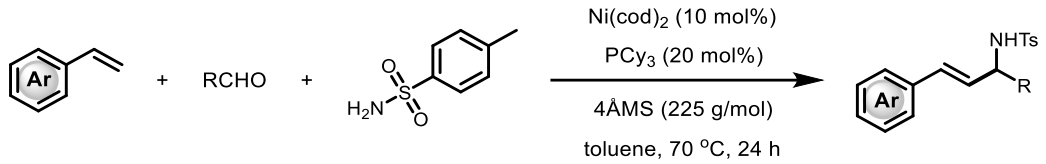
Cy-JohnPhos was purchased from Energy Chemical and used as received.

DMF, THF, 1,4-dioxane, and **$PhCF_3$** (99.8%, Extra Dry, with molecular sieve Water ≤ 50 ppm) were purchased from J&K and used as received.

Toluene was distilled over sodium and stored in the glovebox.

■ Unless noted, all other reagents were purchased from Bidepharm, Accela, Adamas, Energy Chemical, Heowns, and Innochem, and all liquid substrates were distilled before use.

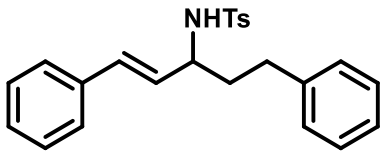
III. General Procedure for the Synthesis of Allylamine.



In an N_2-filled glovebox, $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv), $Ni(cod)_2$ (11.0 mg, 0.04 mmol, 10 mol%), PCy_3 (22.4 mg, 0.08 mmol, 20 mol%), aldehydes (0.4 mol, 1.0 equiv), olefins (0.8 mol, 2.0 equiv), toluene (2.0 mL) and 4Å Molecular sieves (90 mg) was added to a 100 × 16 mm screw-capped vial. The vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction mixture was stirred at 70 °C for 24-50 h. After being cooled to room temperature, 5.0 mL EtOAc was added to the mixture and then filtered through a short plug of silica gel (EtOAc eluent). The filtrate was concentrated in vacuo, and the residue was purified by silica gel column chromatography to afford the corresponding product.

IV. Characterization Data for New Compounds:

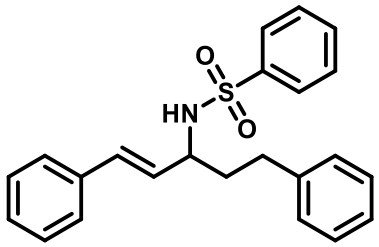
In ^{13}C NMR spectra, signals of carbons directly bonded to boron were not detected because of quadrupolar relaxation.



(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (4a)[1]:

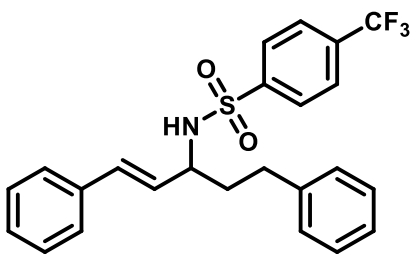
The title compound **4a** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **2a** (26.8 mg, 0.2 mmol, 1.0 equiv), and $TsNH_2$ (37.6 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (59.5 mg, 76 % yield). **M.P.**: 128-129 °C. **IR (neat):** 3254, 3026, 2359, 1493, 1434, 1299, 1150, 1092, 972, 807, 745, 700, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, J = 8.2 Hz, 2H), 7.29-7.17 (m, 8H), 7.11 (m, 4H),

6.20 (d, J = 15.9 Hz, 1H), 5.74 (dd, J = 15.9, 7.5 Hz, 1H), 4.67 (t, J = 9.6 Hz, 1H), 4.03 – 3.90 (m, 1H), 2.67-2.62 (m, 2H), 2.30 (s, 3H), 1.92-1.85 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.45, 141.08, 138.13, 136.24, 132.01, 129.69, 128.61, 128.55, 128.54, 128.49, 127.93, 127.43, 126.48, 126.20, 56.10, 37.62, 31.85, 21.54. **HRMS (ESI):** Calcd for $C_{24}H_{29}N_2O_2S$ $[M+NH_4]^+$: 409.1944; Found: 409.1943.



(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)benzenesulfonamide (4b):

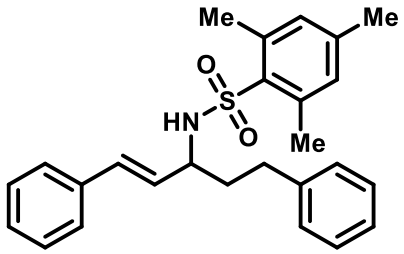
The title compound **4b** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **2a** (26.8 mg, 0.2 mmol, 1.0 equiv), and **3b** (34.6 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (41.5mg, 56% NMR yield, 54 % isolated yield). **M.P.**: 81-82 ℃. **IR (neat):** 3290, 3056, 2924, 1446, 1319, 1157, 1091, 963, 718, 744, 687. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 – 7.77 (m, 2H), 7.50 – 7.37 (m, 3H), 7.29 – 7.18 (m, 6H), 7.14 – 7.06 (m, 4H), 6.24 (d, J = 15.9 Hz, 1H), 5.78 (dd, J = 15.9, 7.5 Hz, 1H), 4.85 (d, J = 7.9 Hz, 1H), 4.06 – 3.94 (m, 1H), 2.70 – 2.59 (m, 2H), 1.96 – 1.83 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 141.18, 141.04, 136.19, 132.59, 132.14, 129.09, 128.62, 128.60, 128.53, 127.99, 127.34, 126.50, 126.22, 53.95, 37.60, 31.85. **HRMS (ESI):** Calcd for $C_{23}H_{27}N_2O_2S$ $[M+NH_4]^+$: 395.1788; Found: 395.1787.



(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)-4-(trifluoromethyl)benzenesulfonamide (4c):

The title compound **4c** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **2a**

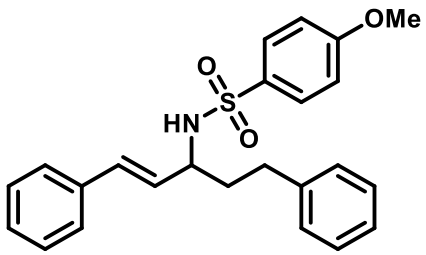
(26.8 mg, 0.2 mmol, 1.0 equiv), and **3c** (49.5 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.15) to give a white solid (25.8 mg, 29% NMR yield, 29 % isolated yield). **M.P.**: 96-98 ℃. **IR (neat):** 3263, 2924, 1403, 1319, 1155, 1127, 1106, 1093, 1017, 968, 836, 748, 710, 695. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.17 (m, 4H), 7.14 – 7.09 (m, 2H), 7.09 – 7.03 (m, 2H), 6.23 (d, *J* = 15.8 Hz, 1H), 5.67 (dd, *J* = 15.8, 7.8 Hz, 1H), 4.70 (d, *J* = 7.7 Hz, 1H), 4.09 – 3.98 (m, 1H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.99 – 1.88 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.86, 140.74, 135.72, 134.38, 133.70, 132.78, 128.70, 128.51, 128.28, 127.93, 127.91, 126.36, 126.19(q, *J* = 3.7 Hz), 123.27 (q, *J* = 273.0 Hz), 56.48, 37.45, 31.81. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -63.19. **HRMS (ESI):** Calcd for $C_{24}H_{26}F_3N_2O_2S$ $[M+NH_4]^+$: 463.1662; Found: 463.1665.



(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)-2,4,6-trimethylbenzenesulfonamide (4d):

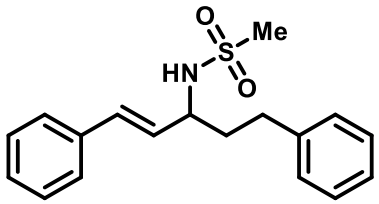
The title compound **4d** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **2a** (26.8 mg, 0.2 mmol, 1.0 equiv), and **3d** (43.8 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (69.6 mg, 85% NMR yield, 83 % isolated yield). **M.P.**: 98-100 ℃. **IR (neat):** 3303, 2914, 1410, 1313, 1143, 1054, 970, 751, 691, 657. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.29 – 7.18 (m, 6H), 7.12 – 7.04 (m, 4H), 6.83 (s, 2H), 6.15 (d, *J* = 15.8 Hz, 1H), 5.72 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.74 (d, *J* = 7.6 Hz, 1H), 3.94 – 3.85 (m, 1H), 2.67 – 2.62 (m, 2H), 2.60 (s, 6H), 2.18 (s, 3H), 1.99 – 1.81 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.20, 141.05, 138.85, 136.24, 135.04, 132.06, 132.00, 128.58, 128.52, 128.47, 128.20, 127.88, 126.44, 126.18, 55.94, 37.45, 31.81, 23.15, 20.90. **HRMS (ESI):** Calcd for $C_{26}H_{33}N_2O_2S$ $[M+NH_4]^+$: 437.2257; Found:

437.2252.



(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)-4-methoxybenzenesulfonamide (4e):

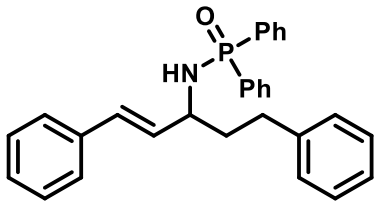
The title compound **4e** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **2a** (26.8 mg, 0.2 mmol, 1.0 equiv), and **3e** (41.2 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (47.3 mg, 59% NMR yield, 57 % isolated yield). **M.P.**: 97-99 ℃. **IR (neat):** 3265, 2923, 1494, 1432, 1261, 1151, 1044, 1026, 828, 750, 690. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 – 7.70 (m, 2H), 7.28 – 7.24 (m, 4H), 7.24 – 7.16 (m, 2H), 7.15 – 7.07 (m, 4H), 6.87 – 6.80 (m, 2H), 6.22 (d, *J* = 15.9 Hz, 1H), 5.75 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.56 (d, *J* = 7.8 Hz, 1H), 3.99 – 3.90 (m, 1H), 3.74 (s, 3H), 2.71 – 2.60 (m, 2H), 1.95 – 1.85 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.82, 141.13, 136.31, 132.71, 132.00, 129.56, 128.64, 128.59, 128.56, 128.55, 127.90, 126.49, 126.17, 114.19, 57.55, 55.59, 38.04, 32.32. **HRMS (ESI):** Calcd for $C_{24}H_{29}N_2O_3S$ $[M+NH_4]^+$: 425.1893; Found: 425.1891.



(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)methanesulfonamide (4f):

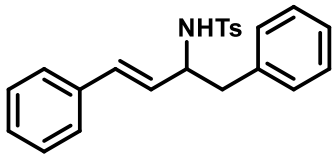
The title compound **4f** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **2a** (26.8 mg, 0.2 mmol, 1.0 equiv), and **3f** (20.9 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (20.8 mg, 33 % NMR yield, 33% isolated yield). **M.P.**:

108-109 ℃. **IR (neat):** 3240, 2923, 1453, 1311, 1138, 1058, 985, 967, 755, 746, 698, 691. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 – 7.26 (m, 7H), 7.24 – 7.16 (m, 3H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.08 (dd, *J* = 15.9, 8.0 Hz, 1H), 4.58 (d, *J* = 7.8 Hz, 1H), 4.18 – 4.06 (m, 1H), 2.94 (s, 3H), 2.80 – 2.70 (m, 2H), 2.06 – 1.92 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.92, 136.03, 132.68, 129.09, 128.89, 128.70, 128.55, 128.35, 126.66, 126.34, 56.36, 42.49, 37.86, 32.09. **HRMS (ESI):** Calcd for $C_{18}H_{21}NNaO_2S$ $[M+Na]^+$: 338.1185; Found: 338.1190.



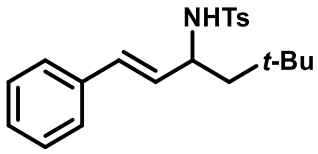
(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)-*P*,*P*-diphenylphosphinic amide (4g):

The title compound **4g** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **2a** (26.8 mg, 0.2 mmol, 1.0 equiv), and **3g** (47.8 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 3:1, R_f = 0.2) to give a white solid (42.0 mg, 49% NMR yield, 48 % isolated yield). **M.P.**: 137-138 ℃. **IR (neat):** 3135, 2921, 1437, 1193, 1180, 1107, 966, 744, 722, 690. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 – 7.84 (m, 4H), 7.52 – 7.38 (m, 6H), 7.34 – 7.28 (m, 4H), 7.26 – 7.20 (m, 3H), 7.18 – 7.11 (m, 3H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.9, 7.0 Hz, 1H), 3.92 – 3.80 (m, 1H), 3.07 – 2.92 (m, 1H), 2.71 (t, J = 8.0 Hz, 2H), 2.18 – 2.06 (m, 1H), 2.05 – 1.96 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 141.60, 136.83, 132.60 (d, *J* = 9.6 Hz), 132.05 (d, *J* = 7.6 Hz), 131.98, 131.96, 131.94, 131.68 (d, *J* = 5.4 Hz), 130.84, 128.71, 128.64, 128.58, 128.53, 128.50, 127.73, 126.58, 126.00, 53.77, 39.57 (d, *J* = 4.5 Hz), 32.53. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 22.41. **HRMS (ESI):** Calcd for $C_{29}H_{29}NOP$ $[M+H]^+$: 438.1981; Found: 4383.1977.



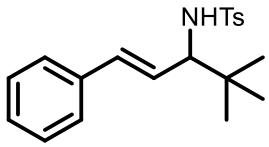
(*E*)-*N*-(1,4-Diphenylbut-3-en-2-yl)-4-methylbenzenesulfonamide (5):

The title compound **5** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S5** (36.1 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (66.5 mg, 59 % yield). **M.P.**: 110-111 ℃. **IR (neat):** 3254, 2918, 2359, 1455, 1492, 1434, 1299, 1150, 1092, 972, 744, 701, 674. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.27 (s, 1H), 7.26 – 7.18 (m, 5H), 7.17 – 7.07 (m, 6H), 6.24 (d, *J* = 15.9 Hz, 1H), 5.85 (dd, *J* = 15.9, 7.1 Hz, 1H), 4.60 (t, *J* = 7.9 Hz, 1H), 4.19 (m, 1H), 2.87 (m, 2H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.38, 137.72, 136.34, 136.16, 131.75, 129.70, 129.65, 128.78, 128.56, 128.46, 127.87, 127.38, 127.07, 126.53, 56.88, 42.45, 21.57. **HRMS (ESI):** Calcd for $C_{23}H_{27}N_2O_2S$ $[M+NH_4]^+$: 395.1787; Found: 395.1786.



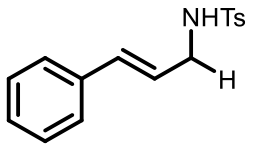
(*E*)-*N*-(5,5-Dimethyl-1-phenylhex-1-en-3-yl)-4-methylbenzenesulfonamide (6):

The title compound **6** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S6** (30.1 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (84.4 mg, 79 % yield). **M.P.**: 105-106 ℃. **IR (neat):** 3317, 2956, 2360, 1313, 1149, 1089, 971, 815, 755, 698, 663. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.03 – 7.01 (m, 2H), 6.07 (d, *J* = 15.8 Hz, 1H), 5.63 (dd, *J* = 15.8, 8.5 Hz, 1H), 5.21 (d, *J* = 8.1 Hz, 1H), 4.14 – 4.02 (m, 1H), 2.20 (s, 3H), 1.56 (dd, *J* = 14.2, 6.6 Hz, 1H), 1.47 (dd, *J* = 14.2, 6.5 Hz, 1H), 0.94 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.10, 138.41, 136.44, 130.76, 130.18, 129.45, 128.32, 127.54, 127.42, 126.31, 54.56, 49.79, 30.65, 30.13, 21.36. **HRMS (ESI):** Calcd for $C_{21}H_{31}N_2O_2S$ $[M+NH_4]^+$: 375.2100; Found: 375.2103.

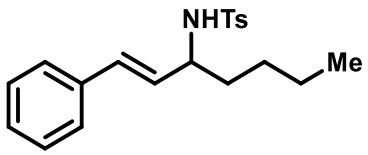


(*E*)-*N*-(4,4-Dimethyl-1-phenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (7):

The title compound **7** was prepared using styrene (20.9 mg, 0.2 mmol, 2.0 equiv), **S7** (8.6 mg, 0.1 mmol, 1.0 equiv) and $TsNH_2$ (18.8 mg, 0.11 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (9.6 mg, 28 % yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.14 – 7.08 (m, 2H), 7.01 (m, 2H), 5.95 (d, *J* = 15.9 Hz, 1H), 5.68 (dd, *J* = 15.8, 8.5 Hz, 1H), 4.68 (d, *J* = 9.3 Hz, 1H), 3.57 (t, *J* = 8.9 Hz, 1H), 2.20 (s, 3H), 0.93 (s, 9H). All other spectra data were in accordance with reported in the literature.[2]



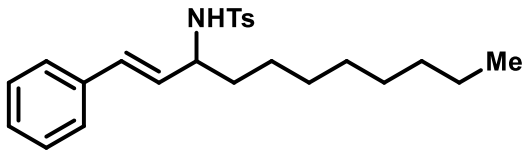
***(E)-N*-Cinnamyl-4-methylbenzenesulfonamide (8):** The title compound **8** was prepared using styrene (20.9 mg, 0.2 mmol, 2.0 equiv), **S8** (3.0 mg, 0.1 mmol, 1.0 equiv) and $TsNH_2$ (18.8 mg, 0.11 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, Rf = 0.15) to give a white solid (26.4 mg, 92 % yield). **^{1}H NMR (400 MHz, CDCl3):** δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.22 (m, 7H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.01 (dt, *J* = 15.8, 6.4 Hz, 1H), 4.68 (t, *J* = 6.3 Hz, 1H), 3.75 (td, *J* = 6.3, 1.5 Hz, 2H), 2.41 (s, 3H). All other spectra data were in accordance with reported in the literature.[2]



(*E*)-4-Methyl-*N*-(1-phenylhept-1-en-3-yl)benzenesulfonamide (9):

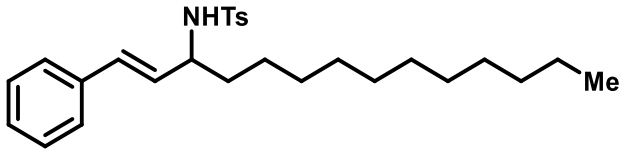
The title compound **9** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **S9** (17.2 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ºC

for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (51.4 mg, 75 % yield). **M.P.**: 96-97 ℃. **IR (neat):** 3297, 2928, 1320, 1149, 1089, 970, 815, 754, 696, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.16 (m, 5H), 7.11 (d, *J* = 6.9 Hz, 2H), 6.20 (d, *J* = 15.9 Hz, 1H), 5.71 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.40 (d, *J* = 7.6 Hz, 1H), 3.96 – 3.87 (m, 1H), 2.31 (s, 3H), 1.54 (m, 2H), 1.26 (m, , 4H), 0.84 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.27, 138.28, 136.41, 131.41, 129.57, 129.08, 128.45, 127.69, 127.40, 126.42, 56.53, 35.74, 27.67, 22.40, 21.48, 14.01. **HRMS (ESI):** Calcd for $C_{20}H_{29}N_2O_2S$ $[M+NH_4]^+$: 361.1944; Found: 391.1940.



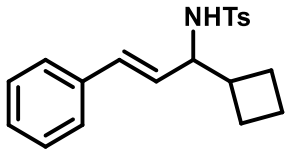
(*E*)-4-Methyl-*N*-(1-phenylundec-1-en-3-yl)benzenesulfonamide (10):

The title compound **10** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S10** (42.7 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (96.7 mg, 81 % yield). **M.P.**: 75-77 ℃. **IR (neat):** 3282, 2919, 2359, 1421, 1317, 1148, 1086, 971, 817, 753, 696, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.20 (d, *J* = 15.9 Hz, 1H), 5.71 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.67 (dd, *J* = 28.6, 7.8 Hz, 1H), 3.92 (m, 1H), 2.30 (s, 3H), 1.58 – 1.49 (m, 2H), 1.28 – 1.18 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.32, 138.28, 136.42, 131.47, 129.61, 129.12, 128.50, 127.76, 127.43, 126.45, 56.49, 36.08, 31.96, 29.53, 29.33, 25.55, 22.78, 21.52, 14.25. **HRMS (ESI):** Calcd for $C_{24}H_{37}N_2O_2S$ $[M+NH_4]^+$: 417.2570; Found: 417.2574.



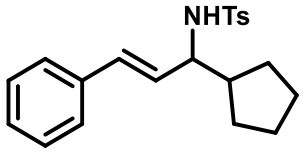
(*E*)-4-Methyl-*N*-(1-phenyltetradec-1-en-3-yl)benzenesulfonamide (11):

The title compound **11** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S11** (55.3 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (116.4 mg, 88 % yield). **M.P.**: 88-89 ℃ **IR (neat):** 3279, 2916, 2847, 2359, 1421, 1318, 1148, 1088, 970, 818, 754, 695, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.16 (m, 5H), 7.13 – 7.08 (m, 2H), 6.20 (d, *J* = 15.9 Hz, 1H), 5.71 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.58 (dd, *J* = 16.6, 7.6 Hz, 1H), 3.91 (m, 1H), 2.30 (s, 3H), 1.53 (m, 2H), 1.30 – 1. 21 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.33, 138.28, 136.41, 131.48, 129.61, 129.11, 128.51, 127.77, 127.44, 126.45, 56.49, 36.09, 32.05, 29.77, 29.75, 29.68, 29.58, 29.49, 29.34, 25.55, 22.83, 21.53, 14.28. **HRMS (ESI):** Calcd for $C_{27}H_{43}N_2O_2S$ $[M+NH_4]^+$: 459.3040; Found: 459.3049.



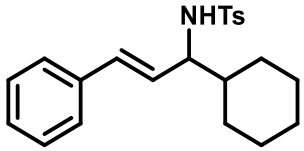
(*E*)-*N*-(1-Cyclobutyl-3-phenylallyl)-4-methylbenzenesulfonamide (12):

The title compound **12** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S12** (25.2 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (57.2 mg, 56 % yield). **M.P.**: 175-176 ℃ **IR (neat):** 3225, 2931, 2359, 1317, 1152, 1091, 1028, 966, 815, 747, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.15 (m, 5H), 7.12 – 7.04 (m, 2H), 6.19 (d, *J* = 15.9 Hz, 1H), 5.62 (dd, *J* = 15.9, 7.6 Hz, 1H), 4.65 (d, *J* = 7.6 Hz, 1H), 3.81 (q, *J* = 8.0 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.29 (s, 3H), 2.03 – 1.71 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.33, 138.25, 136.46, 131.95, 129.58, 128.48, 127.73, 127.48, 127.05, 126.46, 61.30, 39.56, 25.15, 24.88, 21.53, 17.58. **HRMS (ESI):** Calcd for $C_{20}H_{27}N_2O_2S$ $[M+NH_4]^+$: 359.1787; Found: 359.1786.



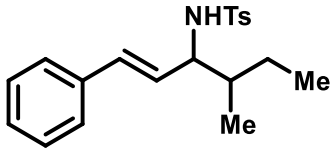
(*E*)-*N*-(1-Cyclopentyl-3-phenylallyl)-4-methylbenzenesulfonamide (13):

The title compound **13** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S13** (29.5 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (81.4 mg, 76 % yield). **M.P.**: 119-121 ℃. **IR (neat):** 3297, 2952, 2360, 1321, 1148, 1089, 971, 816, 753, 696, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.11 (m, 5H), 7.05 (d, *J* = 6.8 Hz, 2H), 6.11 (d, *J* = 15.8 Hz, 1H), 5.66 (dd, *J* = 15.8, 8.1 Hz, 1H), 4.76 – 4.62 (m, 1H), 3.75 (q, *J* = 8.0 Hz, 1H), 2.26 (s, 3H), 1.98 (m, 1H), 1.77 (m, 1H), 1.59 – 1.48 (m, 4H), 1.36 – 1.23 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.26, 138.29, 136.48, 131.93, 129.55, 128.45, 128.11, 127.69, 127.47, 126.42, 60.93, 44.99, 29.40, 29.25, 25.57, 25.41, 21.50. **HRMS (ESI):** Calcd for $C_{21}H_{29}N_2O_2S$ $[M+NH_4]^+$: 373.1944; Found: 373.1948.

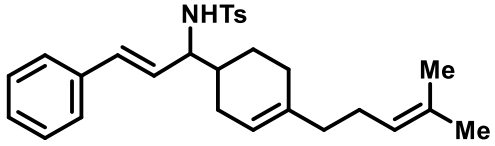


(*E*)-*N*-(1-Cyclohexyl-3-phenylallyl)-4-methylbenzenesulfonamide (14):

The title compound **14** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S14** (44.9 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 40 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (90.3 mg, 61 % yield). **M.P.**: 156-157 ℃. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.11 (m, 5H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.06 (d, *J* = 15.8 Hz, 1H), 5.69 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.57 (d, *J* = 8.0 Hz, 1H), 3.73 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.27 (s, 3H), 1.84 – 1.61 (m, 5H), 1.49 – 1.42 (m, 1H), 1.22 – 1.07 (m, 3H), 1.05- 0.93 (m, 2H). All other spectra data were in accordance with reported in the literature.[3]

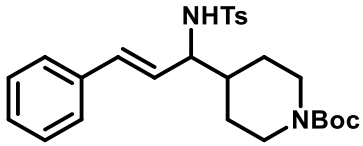


(*E*)-4-Methyl-*N*-(5-methyl-1-phenylhept-1-en-3-yl)benzenesulfonamide (15): The title compound **15** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S15** (25.8 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 °C for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (87.6 mg, 85 % yield, 1:1 dr). **M.P.**: 95-96 °C. **IR (neat):** 3291, 2946, 1320, 1153, 1096, 962, 823, 732, 699, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.26 – 7.13 (m, 5H), 7.09 – 7.03 (m, 2H), 6.10 (d, *J* = 10.9 Hz, 1H), 5.73 (dd, J = 7.7 Hz, 5.5 Hz, 1H), 4.84 (d, *J* = 8.4 Hz, 1H), 3.88 – 3.80 (m, 1H), 2.26 (s, 3H), 1.62 – 1.53 (m, 1H), 1.52 – 1.42 (m, 1H), 1.18 – 1.06 (m, 1H), 0.90 – 0.84 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.30, 138.19, 138.12, 136.43, 132.41, 131.88, 129.58, 128.46, 127.71, 127.67, 127.64, 127.40, 126.48, 126.40, 126.37, 60.58, 60.45, 40.14, 40.01, 25.66, 25.61, 21.50, 14.97, 14.94, 11.68, 11.62. **HRMS (ESI):** Calcd for $C_{20}H_{29}N_2O_2S$ $[M+NH_4]^+$: 361.1944; Found: 361.1938.

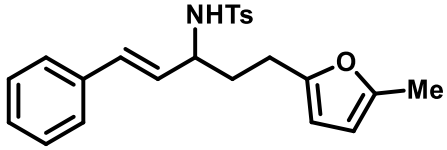


(*E*)-4-Methyl-*N*-(1-(4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)-3-phenylallyl)-benzenesulfonamide (16): The title compound **16** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S16** (76.9 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 °C for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (108.8 mg, 60 % yield, 3:1 dr). **M.P.**: 107-108 °C. **IR (neat):** 3238, 2925, 2359, 1321, 1158, 1091, 967, 756, 696, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.17 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.09 – 7.02 (m, 2H), 6.13 – 6.00 (m, 1H), 5.75 – 5.64 (m, 1H), 5.39 – 5.26 (m, 1H), 5.13 – 4.98 (m, 1H), 4.89 – 4.76 (m, 1H), 3.84 – 3.69 (m, 1H), 2.25 (d, *J* = 4.8 Hz, 3H), 2.10 – 1.87 (m, 7H), 1.85 – 1.72 (m, 2H), 1.71 – 1.64 (m, 4H), 1.59 (s, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.21, 143.18, 138.13, 137.87,

137.64, 136.46, 136.25, 132.61, 132.54, 132.20, 132.13, 131.47, 129.47, 128.37, 127.67, 127.63, 127.34, 127.32, 127.16, 127.11, 126.31, 126.28, 124.24, 120.44, 119.31, 119.19, 61.00, 60.83, 60.54, 39.42, 39.01, 38.99, 37.70, 37.49, 31.29, 28.10, 28.06, 26.42, 26.40, 25.72, 25.33, 25.26, 24.91, 21.35, 17.76, 17.71. **HRMS (ESI):** Calcd for $C_{28}H_{39}N_2O_2S$ $[M+NH_4]^+$: 467.2727. Found: 467.2735.

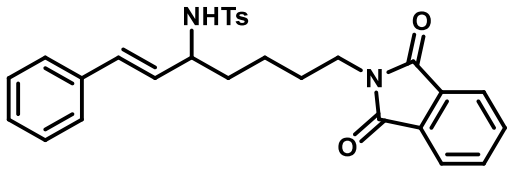


***Tert*-butyl (*E*)-4-(1-((4-methylphenyl)sulfonamido)-3-phenylallyl)piperidine-1-carboxylate (17)**[2]**:** The title compound **17** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S17** (64.0 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.1) to give a white solid (127.1 mg, 90 % yield). **M.P.**: 130-131 ℃. **IR (neat):** 3207, 2920, 2359, 1668, 1431, 1327, 1161, 1091, 970, 814, 692, 674. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.13 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 6.8 Hz, 2H), 5.95 (d, *J* = 15.8 Hz, 1H), 5.75 (d, *J* = 8.8 Hz, 1H), 5.69 – 5.57 (m, 1H), 4.05 (s, 2H), 3.64 (d, *J* = 7.0 Hz, 1H), 2.58 (s, 2H), 2.24 (s, 3H), 1.79 (m, 1H), 1.58 (m, 2H), 1.41 (s, 9H), 1.21 – 1.05 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.66, 143.20, 137.95, 136.01, 132.66, 129.57, 129.43, 128.29, 127.66, 127.23, 126.29, 126.26, 126.21, 79.36, 61.08, 43.89, 43.21, 41.12, 28.42, 21.29. **HRMS (ESI):** Calcd for $C_{26}H_{34}N_2NaO_4S$ $[M+Na]^+$: 493.2131; Found: 493.2135.

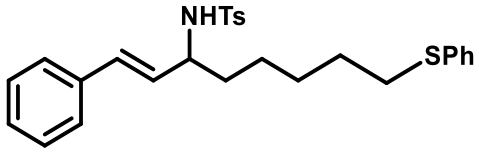


(*E*)-4-Methyl-*N*-(5-(5-methylfuran-2-yl)-1-phenylpent-1-en-3-yl)benzenesulfonamide (18): The title compound **18** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S18** (55.3 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv)

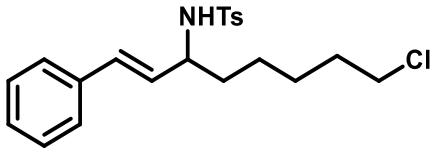
at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (110.6 mg, 70 % yield). **M.P.**: 83-84 ℃. **IR (neat):** 3242, 2921, 2360, 1319, 1155, 1092, 964, 794, 755, 696, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.15 (m, 5H), 7.12 – 7.04 (m, 2H), 6.20 (d, *J* = 15.9 Hz, 1H), 5.83 (s, 2H), 5.72 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.90 – 4.77 (m, 1H),4.01 – 3.94 (m, 1H), 2.67 – 2.55 (m, 2H), 2.30 (s, 3H), 2.23 (s, 3H), 1.98 – 1.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.79, 150.67, 143.40, 138.14, 136.24, 131.98, 129.65, 128.51, 128.33, 127.87, 127.41, 126.47, 106.17, 106.03, 55.98, 34.34, 24.32, 21.53, 13.63. **HRMS (ESI):** Calcd for $C_{23}H_{29}N_2O_3S$ $[M+NH_4]^+$: 413.1893; Found: 413.1895.



(*E*)-*N*-(7-(1,3-Dioxoisoindolin-2-yl)-1-phenylhept-1-en-3-yl)-4-methylbenzenesulfonamide (19): The title compound **19** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S19** (92.5 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (162.5 mg, 83 % yield). **M.P.**: 142-143 ℃. **IR (neat):** 3257, 2941, 1697, 1402, 1322, 1154, 978, 753, 720, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.86 – 7.78 (m, 2H), 7.70 (d, *J* = 6.9 Hz, 4H), 7.26 – 7.13 (m, 5H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.20 (d, *J* = 15.8 Hz, 1H), 5.72 (dd, *J* = 15.8, 7.4 Hz, 1H), 4.66 (d, *J* = 7.7 Hz, 1H), 3.97 – 3.82 (m, 1H), 3.63 (t, *J* = 6.9 Hz, 2H), 2.29 (s, 3H), 1.72 – 1.63 (m, 2H), 1.62 – 1.54 (m, 2H), 1.37 – 1.26 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 168.61, 143.34, 138.30, 136.34, 134.06, 132.20, 131.69, 129.62, 128.87, 128.50, 127.80, 127.41, 126.49, 123.36, 56.27, 37.40, 35.21, 28.10, 22.55, 21.52. **HRMS (ESI):** Calcd for $C_{28}H_{32}N_3O_4S$ $[M+NH_4]^+$: 506.2108; Found: 506.2112.

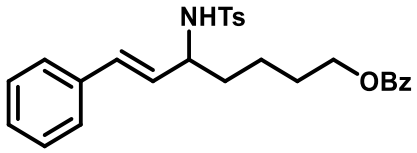


(*E*)-4-Methyl-*N*-(1-phenyl-8-(phenylthio)oct-1-en-3-yl)benzenesulfonamide (20): The title compound **20** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S20** (83.3 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (123.6 mg, 66 % yield). **M.P.**: 93-94 ℃. **IR (neat):** 3303, 2923, 1319, 1150, 1088, 971, 816, 754, 733, 665. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.14 (m, 10H), 7.12 – 7.07 (m, 2H), 6.18 (d, *J* = 15.9 Hz, 1H), 5.69 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.67 (d, *J* = 5.6 Hz, 1H), 3.98 – 3.83 (m, 1H), 2.86 (t, J = 7.3 Hz, 2H), 2.29 (s, 3H), 1.63 – 1.48 (m, 4H), 1.37 (d, *J* = 6.1 Hz, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.41, 138.18, 136.85, 136.28, 131.60, 129.64, 129.04, 128.98, 128.83, 128.52, 127.83, 127.40, 126.44, 125.87, 56.38, 35.89, 33.50, 28.98, 28.41, 25.12, 21.53. **HRMS (ESI):** Calcd for $C_{27}H_{31}NNaO_2S_2$ $[M+Na]^+$: 488.1688; Found: 488.1693.

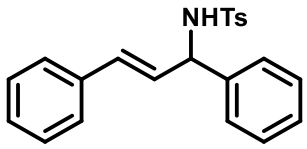


(*E*)-*N*-(7-Chloro-1-phenylhept-1-en-3-yl)-4-methylbenzenesulfonamide (21): The title compound **21** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S21** (48.2 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.3) to give a white solid (97.2 mg, 62 % yield). **M.P.**: 104-105 ℃. **IR (neat):** 3298, 2941, 2360, 1421, 1319, 1150, 1088, 968, 816, 755, 697, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.16 (m, 5H), 7.13 – 7.07 (m, 2H), 6.19 (d, *J* = 15.9 Hz, 1H), 5.70 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.70 (d, *J* = 7.6 Hz, 1H), 3.98 – 3.86 (m, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.30 (s, 3H), 1.74 – 1.66 (m, 2H), 1.57 (m, 2H), 1.42 – 1.27 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.39, 138.19, 136.29,

131.57, 129.62, 128.77, 128.48, 127.79, 127.38, 126.43, 56.38, 45.00, 35.81, 32.45, 26.51, 24.84, 21.49. **HRMS (ESI):** Calcd for $C_{21}H_{27}ClNO_2S$ $[M+H]^+$: 392.1446; Found: 392.1455.

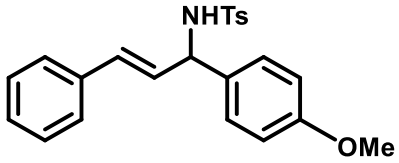


(*E*)-5-((4-Methylphenyl)sulfonamido)-7-phenylhept-6-en-1-yl benzoate (22): The title compound **22** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S22** (82.5 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a colorless oil (84.0 mg, 45 % yield). **IR (neat):** 3272, 2924, 1714, 1450, 1314, 1272, 1155, 1114, 1092, 813, 711, 693, 664. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.21 (m,3H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 2H), 6.21 (d, *J* = 16.0 Hz, 1H), 5.71 (dd, *J* = 15.8, 7.3 Hz, 1H), 4.53 (d, *J* = 7.8 Hz, 1H), 4.26 (t, *J* = 6.2 Hz, 2H), 3.99 – 3.91 (m, 1H), 2.28 (s, 3H), 1.77 – 1.70 (m, 2H), 1.67 – 1.60 (m, 2H), 1.51 – 1..41 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.77, 143.49, 138.24, 137.14, 133.04, 131.89, 130.45, 129.68, 128.68, 128.57, 128.51, 127.93, 127.43, 126.49, 64.61, 56.29, 35.62, 28.43, 22.17, 21.52. **HRMS (ESI):** Calcd for $C_{27}H_{33}N_2O_4S$ $[M+NH_4]^+$: 481.2155; Found: 481.2152.

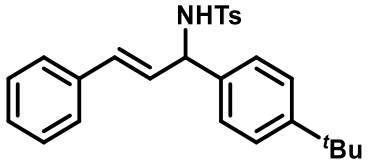


(*E*)-*N*-(1,3-Diphenylallyl)-4-methylbenzenesulfonamide (23): The title compound **23** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **S23** (21.2 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (70.0 mg, 96 % yield). **M.P.**: 129-130 ℃. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.20 (m, 8H), 7.21 – 7.09 (m, 4H), 6.34 (d,

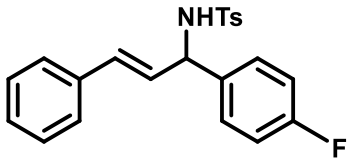
J = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.43 (d, *J* = 7.5 Hz, 1H), 5.12 (t, *J* = 6.9 Hz, 1H), 2.31 (s, 3H). All other spectra data were in accordance with reported in the literature.[3]



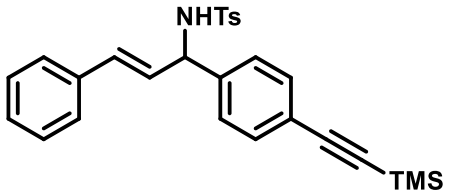
(*E*)-*N*-(1-(4-Methoxyphenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (24): The title compound **24** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S24** (54.5 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 °C for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (101.1 mg, 64 % yield). **M.P.**: 130-131 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.20 (m, 3H), 7.20 – 7.09 (m, 6H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.07 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.33 – 5.22 (m, 1H), 5.07 (t, *J* = 6.9 Hz, 1H), 3.76 (s, 3H), 2.32 (s, 3H). All other spectra data were in accordance with reported in the literature.[3]



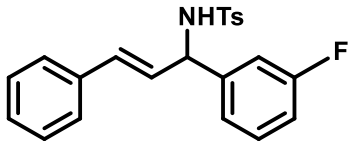
(*E*)-*N*-(1-(4-(Tert-butyl)phenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (25): The title compound **25** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **S25** (32.5mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (62.0 mg, 74 % yield). **M.P.**: 148-149 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.18 (m, 7H), 7.15 – 7.10 (m, 4H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.09 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.10 (t, *J* = 6.7 Hz, 1H), 4.96 (d, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 1.28 (s, 9H). All other spectra data were in accordance with reported in the literature.[3]



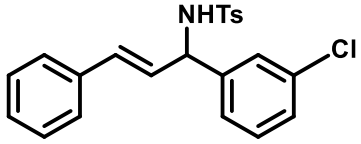
(*E*)-*N*-(1-(4-Fluorophenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (26): The title compound **26** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S26** (49.6 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 °C for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (135.8 mg, 89 % yield). **M.P.**: 122-123 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.09 (m, 9H), 6.92 – 6.88 (m, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.80 (d, *J* = 6.8 Hz, 1H), 5.11 (t, *J* = 7.3 Hz, 1H), 2.30 (s, 3H). All other spectra data were in accordance with reported in the literature.[4]



(*E*)-4-Methyl-*N*-(3-phenyl-1-(4-((trimethylsilyl)ethynyl)phenyl)allyl)benzenesulfonamide (27): The title compound **27** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S27** (80.9 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 °C for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (100.4 mg, 55 % yield). **M.P.**: 124-125 °C. **IR (neat):** 3270, 2958, 2360, 1419, 1326, 1153, 862, 809, 829, 746, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.22 (m, 3H), 7.17 – 7.14 (m, 6H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.38 (d, *J* = 7.6 Hz, 1H), 5.09 (t, *J* = 7.1 Hz, 1H), 2.32 (s, 3H), 0.25 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.51, 139.92, 137.63, 135.99, 132.58, 132.28, 129.57, 128.58, 128.09, 127.64, 127.33, 127.09, 126.64, 122.69, 104.67, 94.72, 59.57, 21.51, 0.07. **HRMS (ESI):** Calcd for $C_{27}H_{29}NNaO_2SSi$ $[M+Na]^+$: 482.1580; Found:482.1578.

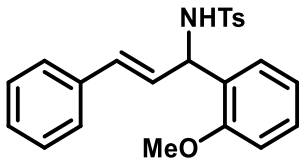


(*E*)-*N*-(1-(3-Fluorophenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (28): The title compound **28** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S28** (49.6 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (134.6 mg, 88 % yield). **M.P.**: 113-115 ℃. **IR (neat):** 3275, 1591, 1447, 1318, 1160, 1047, 975, 890, 815, 738, 691, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.09 (m, 8H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.91 (m, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 7.0 Hz, 1H), 5.79 (d, *J* = 7.9 Hz, 1H), 5.11 (t, *J* = 7.4 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.81 (d, *J* = 246.7 Hz), 143.48, 142.33 (d, *J* = 6.8 Hz), 136.72 (d, *J* = 165.4 Hz), 132.54, 130.24 (d, *J* = 8.2 Hz), 129.52, 128.51, 128.06, 127.41, 127.30, 126.62, 122.80, 122.77, 114.62 (d, *J* = 21.1 Hz), 114.15 (d, *J* = 22.3 Hz), 59.37 (d, *J* = 1.7 Hz), 21.43. **^{19}F NMR (376 MHz, $CDCl_3$):** δ-112.38. **HRMS (ESI):** Calcd for $C_{22}H_{20}FNNaO_2S$ $[M+Na]^+$: 404.1091; Found: 404.1095.

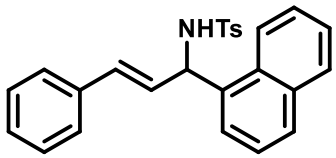


(*E*)-*N*-(1-(3-Chlorophenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (29): The title compound **29** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S29** (56.2 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (127.0 mg, 80 % yield). **M.P.**: 108-110 ℃. **IR (neat):** 3275, 1438, 1323, 1151, 1090, 965, 925, 814, 754, 692, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.19 – 7.10 (m, 8H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 6.8 Hz, 1H), 5.66 (d, *J* = 7.7 Hz, 1H), 5.08

(t, J = 7.2 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.55, 141.70, 137.48, 135.87, 134.48, 132.65, 130.00, 129.56, 128.56, 128.13, 127.89, 127.37, 127.34, 127.29, 126.66, 125.40, 59.39, 21.49. **HRMS (ESI):** Calcd for $C_{22}H_{24}ClN_2O_2S$ $[M+NH_4]^+$: 415.1241; Found: 415.1233.

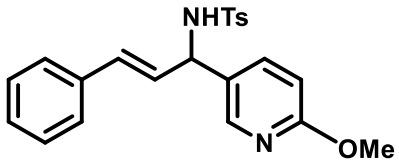


(*E*)-*N*-(1-(2-Methoxyphenyl)-3-phenylallyl)-4-methylbenzenesulfonamide (30): The title compound **30** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S30** (54.5 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (90.3 mg, 57 % yield). **M.P.**: 126-127 ℃. **IR (neat):** 3269, 2960, 2360, 1325, 1151, 1029, 956, 816, 748, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, J = 8.2 Hz, 2H), 7.28 – 7.13 (m, 6H), 7.06 – 7.02 (m, 3H), 6.84 – 6.76 (m, 1H), 6.69 (d, J = 8.2 Hz, 1H), 6.33 (d, J = 16.1 Hz, 1H), 6.22 (dd, J = 15.9, 6.0 Hz, 1H), 5.78 (d, J = 9.3 Hz, 1H), 5.19 (dd, J = 8.7, 6.2 Hz, 1H), 3.72 (s, 3H), 2.28 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.44, 142.89, 137.90, 136.59, 131.07, 129.18, 129.13, 129.08, 128.48, 127.68, 127.21, 127.11, 126.57, 120.91, 110.98, 58.44, 55.38, 21.47. **HRMS (ESI):** Calcd for $C_{23}H_{27}N_2O_3S$ $[M+NH_4]^+$: 411.1737; Found: 411.1739.

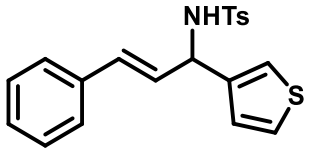


(*E*)-4-Methyl-*N*-(1-(naphthalen-1-yl)-3-phenylallyl)benzenesulfonamide (31): The title compound **31** was prepared using styrene (62.5 mg, 0.6 mmol, 2.0 equiv), **S31** (46.9 mg, 0.3 mmol, 1.0 equiv) and $TsNH_2$ (56.5 mg, 0.33 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (84.1 mg, 68 % yield). **M.P.**: 163-165 ℃. **IR**

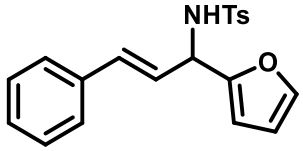
(neat): 3236, 2921, 2359, 1312, 1152, 1091, 1047, 970, 809, 791, 768, 735, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.15 – 8.05 (m, 1H), 7.87 – 7.80 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.38 (d, *J* = 6.9 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 9.4, 7.2 Hz, 3H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 15.9, 5.8 Hz, 1H), 5.91 (t, *J* = 6.5 Hz, 1H), 5.46 (d, *J* = 7.3 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.15, 137.62, 136.18, 135.17, 134.00, 132.26, 130.50, 129.30, 128.87, 128.79, 128.48, 128.18, 127.89, 127.24, 126.66, 126.60, 125.88, 125.57, 125.25, 123.41, 56.53, 21.43. **HRMS (ESI):** Calcd for $C_{26}H_{27}N_2O_2S$ $[M+NH_4]^+$: 431.1787; Found: 431.1795.



(*E*)-*N*-(1-(6-Methoxypyridin-3-yl)-3-phenylallyl)-4-methylbenzenesulfonamide (32): The title compound **32** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S32** (55.3 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 °C for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (137.9 mg, 87 % yield). **M.P.**: 120-122 °C. **IR (neat):** 3263, 1608, 1492, 1396, 1314, 1288, 1162, 1023, 832, 743, 689, 670. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.94 (d, *J* = 2.1 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.42 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.17 – 7.08 (m, 4H), 6.57 (d, *J* = 8.6 Hz, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 6.6 Hz, 1H), 5.82 (d, *J* = 7.6 Hz, 1H), 5.06 (t, *J* = 7.1 Hz, 1H), 3.87 (s, 3H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.71, 145.64, 143.44, 137.66, 137.52, 135.88, 132.38, 129.56, 128.52, 128.16, 128.05, 127.55, 127.29, 126.59, 110.98, 57.19, 53.57, 21.46. **HRMS (ESI):** Calcd for $C_{22}H_{22}N_2NaO_3S$ $[M+Na]^+$: 417.1243; Found: 417.1243.

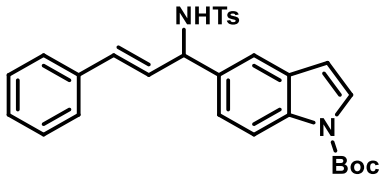


(*E*)-4-Methyl-*N*-(3-phenyl-1-(thiophen-2-yl)allyl)benzenesulfonamide (33): The title compound **33** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **S33** (22.4 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (59.6 mg, 81 % yield). **M.P.**: 113-114 ℃. **IR (neat):** 3264, 2923, 1439, 1316, 1154, 1092, 1022, 873, 763, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.30 (m, 1H), 7.30 – 7.24 (m, 1H), 7.26 – 7.20 (m, 3H), 7.20 – 7.13 (m, 4H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.23 (d, *J* = 1.9 Hz, 1H), 6.01 (dd, *J* = 15.8, 6.9 Hz, 1H), 5.25 (d, *J* = 8.0 Hz, 1H), 5.08 (t, *J* = 7.5 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.71, 143.51, 139.92, 137.92, 136.07, 132.28, 129.62, 128.56, 128.05, 127.39, 127.28, 126.64, 125.16, 109.28, 52.28, 21.51. **HRMS (ESI):** Calcd for $C_{20}H_{19}NNaO_2S_2$ $[M+Na]^+$: 392.0749; Found: 392.0748.

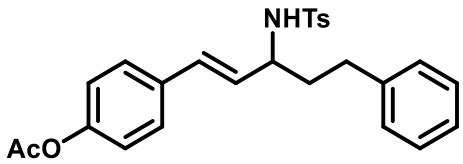


(*E*)-*N*-(1-(Furan-2-yl)-3-phenylallyl)-4-methylbenzenesulfonamide (34): The title compound **34** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S34** (38.4 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (124.1 mg, 88 % yield). **M.P.**: 117-118 ℃. **IR (neat):** 3282, 2972, 2359, 1423, 1317, 1158, 1146, 1042, 965, 917, 812, 736, 691, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.11 (m, 8H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.16 – 6.06 (m, 2H), 5.58 (d, *J* = 8.1 Hz, 1H), 5.22 (t, *J* = 7.4 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.80, 143.25, 142.45, 137.72, 135.94, 132.72, 129.46, 128.47, 128.01, 127.22, 126.64, 125.52, 110.33, 107.50, 53.69, 21.44. **HRMS (ESI):** Calcd for $C_{20}H_{23}N_2O_3S$

$[M+NH_4]^+$: 371.1424; Found: 371.1430.

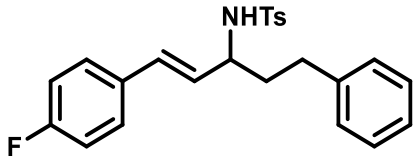


(*E*)-4-Methyl-*N*-(3-phenyl-1-(1-tosyl-1H-indol-5-yl)allyl)benzenesulfonamide (35): The title compound **35** was prepared using styrene (41.7 mg, 0.4 mmol, 2.0 equiv), **S35** (49.1 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (79.6 mg, 79 % yield). **M.P.**: 64-65 °C. **IR (neat):** 3268, 2978, 2360, 1729, 1371, 1325, 1257, 1155, 1130, 1081, 1022, 765, 749, 668. **^{1}H NMR (400 MHz, Acetone-*d6*):** δ 8.01 (d, *J* = 8.6 Hz, 1H), 7.65 (m, 3H), 7.51 (s, 1H), 7.29 – 7.22 (m, 5H), 7.14 (dd, *J* = 17.3, 8.3 Hz, 3H), 6.59 (d, *J* = 3.6 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.27 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.22 (t, *J* = 7.4 Hz, 1H), 2.24 (s, 3H), 1.67 (s, 9H). **^{13}C NMR (100 MHz, Acetone-*d6*):** δ 150.20, 143.40, 140.00, 137.49, 136.05, 135.22, 131.75, 131.46, 130.12, 129.99, 129.27, 128.38, 127.94, 127.21, 127.18, 124.37, 120.44, 115.70, 108.08, 84.41, 60.70, 28.17, 21.25. **HRMS (ESI):** Calcd for $C_{29}H_{30}N_2NaO_4S$ $[M+Na]^+$: 525.1818; Found: 525.1818.

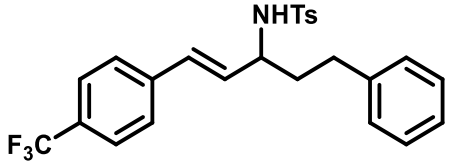


(*E*)-4-(3-((4-Methylphenyl)sulfonamido)-5-phenylpent-1-en-1-yl)phenyl acetate (36): The title compound **36** was prepared using **S36** (129.8 mg, 0.8 mmol, 2.0 equiv), 3-phenylpropanal (53.7 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 °C for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (107.7 mg, 60% yield). **M.P.**: 68-69 °C. **IR (neat):** 3251, 2923, 2360, 1755, 1305, 1194, 1155, 909, 811, 751, 701, 663. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 7.7 Hz, 2H), 7.29 – 7.22 (m, 2H),

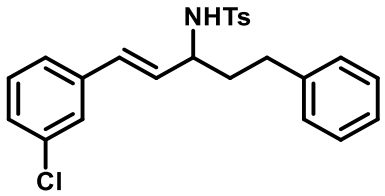
7.20 – 7.17 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 4H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.18 (d, *J* = 15.9 Hz, 1H), 5.68 (dd, J = 15.7, 7.4 Hz, 1H), 4.69 (d, *J* = 7.9 Hz, 1H), 4.00 – 3.90 (m, 1H), 2.63 (t, *J* = 9.4 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 3H), 1.93 – 1.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.56, 150.29, 143.51, 141.01, 138.14, 134.05, 130.99, 129.70, 128.83, 128.62, 128.53, 127.42, 126.22, 121.71, 56.03, 37.58, 31.84, 21.54, 21.27. **HRMS (ESI):** Calcd for $C_{26}H_{31}N_2O_4S$ $[M+NH_4]^+$: 467.1999; Found: 467.2006.



(*E*)-*N*-(1-(4-Fluorophenyl)-5-phenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (37): The title compound **37** was prepared using **S37** (97.7 mg, 0.8 mmol, 2.0 equiv), 3-phenylpropanal (53.7 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (107.4 mg, 66 % yield). **M.P.**: 114-115 ℃. **IR (neat):** 3231, 2925, 2360, 1508, 1320, 1224, 1149, 1061, 967, 811, 753, 700, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 2H), 7.23 – 7.13 (m, 3H), 7.12 – 7.03 (m, 4H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.17 (d, *J* = 15.9 Hz, 1H), 5.70 (dd, *J* = 15.9, 7.8 Hz, 1H), 5.60 (d, *J* = 8.2 Hz, 1H), 4.04 – 3.88 (m, 1H), 2.72 – 2.59 (m, 2H), 2.28 (s, 3H), 1.98 – 1.83 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.30 (d, *J* = 246.9 Hz), 143.25, 141.08, 138.17, 132.48 (d, *J* = 3.3 Hz), 130.51, 129.56, 128.46, 128.39 (d, *J* = 2.2 Hz), 127.93 (d, *J* = 8.0 Hz), 127.35, 126.02, 115.27 (d, *J* = 21.6 Hz), 56.10, 37.39, 31.76, 21.40. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -113.97. **HRMS (ESI):** Calcd for $C_{24}H_{24}FNNaO_2S$ $[M+Na]^+$: 432.1404; Found: 432.1400.

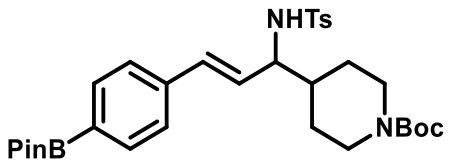


(*E*)-4-Methyl-*N*-(5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-1-en-3-yl)benzenesulfonamide (38): The title compound **38** was prepared using **S38** (137.7 mg, 0.8 mmol, 2.0 equiv), 3-phenylpropanal (53.7 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (138.0 mg, 75% yield). **M.P.**: 135-136 ℃. **IR (neat):** 3306, 2925, 2360, 1323, 1153, 1108, 1065, 969, 810, 748, 698, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.24-7.28 (m, 2H), 7.21 – 7.16 (m, 5H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 5.85 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.99 (d, *J* = 8.0 Hz, 1H), 4.02 – 3.95 (m, 1H), 2.71 – 2.58 (m, 2H), 2.28 (s, 3H), 1.98 – 1.83 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.47, 140.92, 139.79, 138.10, 131.41, 130.31, 129.65, 128.54, 128.48, 127.37, 126.58, 126.15, (125.41,125.38, 125.34, 125.30, q, *J* = 3.7 Hz), (128.26, 125.56, 122.86, 120.15, q, *J* = 271.9 Hz), 55.98, 37.26, 31.76, 21.36. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.53. **HRMS (ESI):** Calcd for $C_{25}H_{28}F_3N_2O_2S$ $[M+NH_4]^+$: 477.1818; Found: 477.1823.

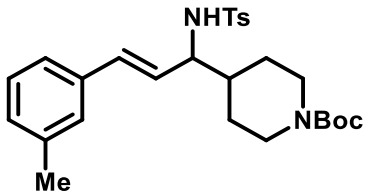


(*E*)-*N*-(1-(3-Chlorophenyl)-5-phenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (39): The title compound **39** was prepared using **S39** (110.0 mg, 0.8 mmol, 2.0 equiv), 3-phenylpropanal (53.7 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (140.8 mg, 83% yield). **M.P.**: 117-119 ℃. **IR (neat):** 3255, 2943, 1435, 1306, 1159, 1093, 978, 782, 750, 702, 682. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.15 (m, 7H), 7.10 (d, *J* = 7.0 Hz, 2H), 7.04 – 6.91 (m, 2H), 6.12 (d, *J* = 15.9 Hz, 1H), 5.74 (dd, *J* = 15.9, 7.8 Hz, 1H), 5.61 (d, *J* = 8.2 Hz, 1H), 4.00 – 3.93 (m, 1H), 2.71 – 2.59 (m, 2H), 2.30 (s, 3H), 1.99 – 1.78 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.49, 140.96, 138.15, 138.09, 134.29, 130.39, 130.15, 129.67, 129.65, 128.50, 128.48, 127.63,

127.34, 126.21, 126.10, 124.73, 55.98, 37.29, 31.74, 21.46. **HRMS (ESI):** Calcd for $C_{24}H_{28}ClN_2O_2S$ $[M+NH_4]^+$: 443.1555; Found: 443.1545.

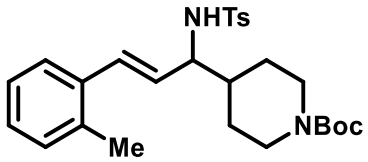


***Tert*-butyl (*E*)-4-(1-((4-methylphenyl)sulfonamido)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)allyl)piperidine-1-carboxylate (40):** The title compound **40** was prepared using **S40** (92.0 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 3:1, R_f = 0.1) to give a white solid (72.6 mg, 61% yield). **M.P.**: 83-84 ℃. **IR (neat):** 2977, 2360, 1667, 1358, 1321, 1274, 1158, 1142, 1088, 858, 813, 730, 655. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68 (dd, *J* = 8.1, 2.7 Hz, 4H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.00 (d, *J* = 15.8 Hz, 1H), 5.73 (dd, *J* = 15.7, 8.0 Hz, 1H), 4.56 (d, *J* = 8.6 Hz, 1H), 4.20 – 4.03 (s, 2H), 3.79 – 3.68 (s, 1H), 2.68 – 2.52 (s, 2H), 2.27 (s, 3H), 1.80 (d, *J* = 12.1 Hz, 1H), 1.59 – 1.54 (m, 2H), 1.43 (s, 9H), 1.34 (s, 12H), 1.21 – 1.15 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.80, 143.52, 138.74, 138.03, 134.99, 132.95, 129.64, 127.37, 125.69, 83.95, 79.58, 60.95, 43.79, 43.62, 41.48, 28.56, 24.98, 21.49. **HRMS (ESI):** Calcd for $C_{32}H_{46}BN_2O_6S$ $[M+H]^+$: 597.3164; Found: 597.3149.

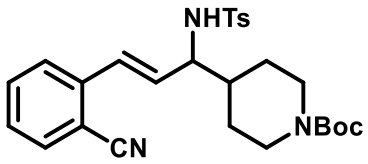


***Tert*-butyl (*E*)-4-(1-((4-methylphenyl)sulfonamido)-3-(m-tolyl)allyl)piperidine-1-carboxylate (41):** The title compound **41** was prepared using **S41** (46.5 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column

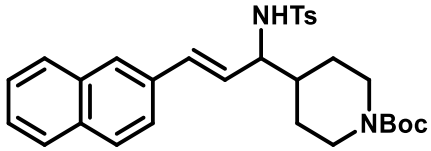
chromatography (PE:EA = 3:1, R_f = 0.2) to give a white solid (52.1 mg, 54 % yield). **M.P.**: 140-141 ℃. **IR (neat):** 3195, 2923, 2360, 1670, 1431, 1331, 1235, 1162, 1138, 1090, 961, 815, 766, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.10 (m, 3H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 2H), 5.96 (d, *J* = 15.8 Hz, 1H), 5.64 (dd, *J* = 15.7, 8.2 Hz, 1H), 5.02 (d, *J* = 7.7 Hz, 1H), 4.09 (s, 2H), 3.69 (d, *J* = 5.6 Hz, 1H), 2.59 (s, 2H), 2.29 (s, 3H), 2.27 (s, 3H), 1.80 (m, 1H), 1.59 (m, 2H), 1.43 (s, 9H), 1.22 – 1.11 (m, 2H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.79, 143.43, 138.04, 138.02, 136.01, 133.08, 129.64, 128.72, 128.40, 127.40, 127.06, 126.02, 123.63, 79.57, 61.01, 43.87, 43.29, 41.48, 28.55, 21.49, 21.45. **HRMS (ESI):** Calcd for $C_{27}H_{36}N_2NaO_4S$ $[M+Na]^+$: 507.2288; Found: 507.2288.



***Tert*-butyl (*E*)-4-(1-((4-methylphenyl)sulfonamido)-3-(o-tolyl)allyl)piperidine-1-carboxylate (42):** The title compound **42** was prepared using **S42** (46.5 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ℃ for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 3:1, R_f = 0.2) to give a white solid (53.4 mg, 55% yield). **M.P.**: 53-55 ℃. **IR (neat):** 3261, 2923, 2360, 1666, 1423, 1326, 1277, 1156, 1091, 966, 750, 664. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.04 (m, 3H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 5.58 (dd, *J* = 15.6, 8.1 Hz, 1H), 4.92 (d, *J* = 8.3 Hz, 1H), 4.21 – 4.01 (s, 2H), 3.75 (d, *J* = 6.8 Hz, 1H), 2.71 – 2.53 (s, 2H), 2.28 (s, 3H), 2.13 (s, 3H), 1.81 (d, *J* = 9.8 Hz, 1H), 1.65 – 1.57(d, *J* = 10.9 Hz, 2H), 1.44 (s, 9H), 1.24 – 1.12 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.79, 143.42, 138.18, 135.34, 135.21, 130.80, 130.23, 129.63, 127.82, 127.78, 127.27, 125.98, 125.65, 79.56, 61.17, 43.91, 43.44, 41.50, 28.54, 21.45, 19.66. **HRMS (ESI):** Calcd for $C_{27}H_{36}N_2NaO_4S$ $[M+Na]^+$: 507.2288; Found: 507.2297.

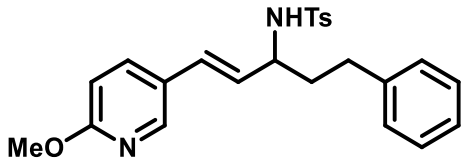


***Tert*-butyl (*E*)-4-(3-(2-cyanophenyl)-1-((4-methylphenyl)sulfonamido)allyl)piperidine-1-carboxylate (43):** The title compound **43** was prepared using **S43** (50.8 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 2:1, R_f = 0.2) to give a yellow solid (64.9 mg, 65% yield). **M.P.**: 66-68 ℃. **IR (neat):** 3255, 2923, 2360, 1661, 1424, 1156, 1037, 966, 760, 665. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.97 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.03 (d, *J* = 8.4 Hz, 1H), 4.20 – 4.04 (s, 2H), 3.78 – 3.68 (m, 1H), 2.70 – 2.53 (s, 2H), 2.24 (s, 3H), 1.80 (d, *J* = 12.6 Hz, 1H), 1.64 – 1.55 (m, 2H), 1.43 (s, 9H), 1.23 – 1.14 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.74, 143.61, 139.13, 137.60, 133.00, 132.71, 131.81, 129.77, 128.29, 128.04, 127.39, 125.78, 117.68, 110.87, 79.61, 60.85, 43.86, 43.30, 41.27, 28.51, 21.44. **HRMS (ESI):** Calcd for $C_{27}H_{33}N_3NaO_4S$ $[M+Na]^+$: 518.2084; Found: 518.2092.

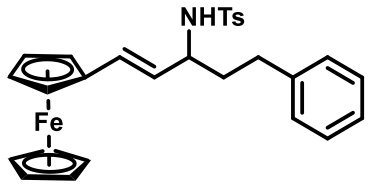


***Tert*-butyl (*E*)-4-(1-((4-methylphenyl)sulfonamido)-3-(naphthalen-2-yl)allyl)piperidine-1-carboxylate (44)**[2]**:** The title compound **44** was prepared using **S44** (154.2 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 40 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (88.2 mg, 85% yield). **M.P.**: 148-149 ℃. **IR (neat):** 3217, 2947, 2360, 1668, 1429, 1330, 1161, 1135, 966, 812, 749, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 – 7.71 (m, 4H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.15 (d, *J* = 15.7 Hz, 1H), 5.79 (dd, *J* = 15.7, 8.3 Hz, 1H), 5.52 (d, *J* = 7.9 Hz, 1H),

4.22 - 3.98 (s, 2H), 3.74 (m, 1H), 2.61 (s, 2H), 2.12 (s, 3H), 1.85 (m, 1H), 1.63 (m, 2H), 1.43 (s, 9H), 1.21 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.76, 143.36, 138.10, 138.07, 133.56, 133.42, 133.04, 132.94, 129.56, 128.03, 127.93, 127.68, 127.36, 126.71, 126.40, 126.07, 123.41, 79.48, 61.08, 43.85, 43.44, 41.35, 28.51, 21.33. **HRMS (ESI):** Calcd for $C_{30}H_{37}N_2O_4S$ $[M+H]^+$: 521.2469; Found: 521.2469.

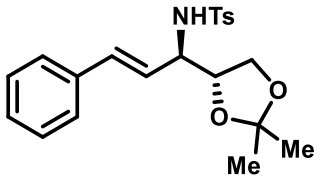


(*E*)-*N*-(1-(6-Methoxypyridin-3-yl)-5-phenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (45): The title compound **45** was prepared using **S45** (108.1 mg, 0.8 mmol, 2.0 equiv), 3-phenylpropanal (53.7 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (101.8 mg, 60% yield). **M.P.**: 95-96 ℃. **IR (neat):** 3292, 2941, 2360, 1600, 1489, 1320, 1278, 1148, 1022, 959, 812, 756, 701, 674. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 2.3 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.32 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.26-7.22 (m, 2H), 7.19 – 7.15 (m, 3H), 7.07 (d, *J* = 7.0 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 1H), 6.10 (d, *J* = 15.9 Hz, 1H), 5.62 (dd, *J* = 15.9, 7.8 Hz, 1H), 5.40 (d, *J* = 8.1 Hz, 1H), 3.96-3.89 (m, 1H), 3.91 (s, 3H), 2.69 – 2.56 (m, 2H), 2.28 (s, 3H), 1.92 – 1.79 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.67, 145.62, 143.36, 141.01, 138.12, 135.45, 129.59, 128.50, 128.48, 127.91, 127.36, 126.09, 125.45, 110.75, 56.16, 53.64, 37.42, 31.80, 21.47. **HRMS (ESI):** Calcd for $C_{24}H_{27}N_2O_3S$ $[M+H]^+$: 423.1737; Found: 423.1737.

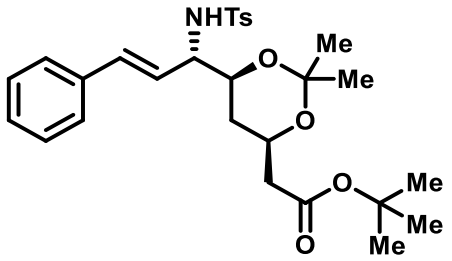


(*E*)-*N*-(1-Ferrocene-5-phenylpent-1-en-3-yl)-4-methylbenzenesulfonamide (46): The title compound **46** was prepared using **S46** (169.7 mg, 0.8 mmol, 2.0 equiv), 3-

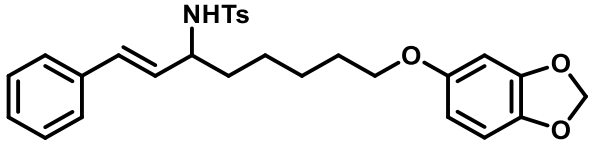
phenylpropanal (53.7 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a brown solid (126.0 mg, 63% yield). **M.P.**: 117-119 ℃. **IR (neat):** 3251, 2360, 1418, 1319, 1095, 969, 811, 744, 699, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.25-7.29 (m, 4H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.03 (d, *J* = 15.6 Hz, 1H), 5.45 (dd, *J* = 15.6, 7.0 Hz, 1H), 4.61 (d, *J* = 7.4 Hz, 1H), 4.19 (s, 4H), 4.06 (s, 5H), 3.89 – 3.78 (m, 1H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 1.93 – 1.76 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.41, 141.23, 138.20, 129.75, 128.59, 128.49, 127.30, 126.15, 125.88, 69.36, 69.03, 67.20, 66.65, 56.02, 37.73, 31.88, 21.68. **HRMS (ESI):** Calcd for $C_{28}H_{29}FeNNaO_2S$ $[M+Na]^+$: 522.1161; Found: 522.1165.



***N*-((*R*,*E*)-1-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-3-phenylallyl)-4-methylbenzenes-ulfonamide (47):** The title compound **47** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S47** (52.0 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (102.1 mg, 66 % yield, 1.25:1 dr). **M.P.**: 99-100 ℃. **IR (neat):** 3238, 2966, 2360, 1326, 1152, 1028, 840, 816, 747, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.07 (m, 7H), 6.23 (m, 1H), 5.85 – 5.74 (m, 1H), 5.29 – 5.19 (m, 1H), 4.21– 4.08 (m, 1H), 4.03 – 3.81 (m, 3H), 2.27 (s, 3H), 1.41 – 1.34 (m, 3H), 1.32 – 1.26 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.56, 137.84, 136.03, 134.02, 129.66, 128.50, 128.04, 127.43, 126.56, 123.80, 110.02, 77.66, 66.01, 58.13, 26.37, 25.00, 21.50. **HRMS (ESI):** Calcd for $C_{21}H_{25}NNaO_4S$ $[M+Na]^+$: 410.1396; Found: 410.1391.

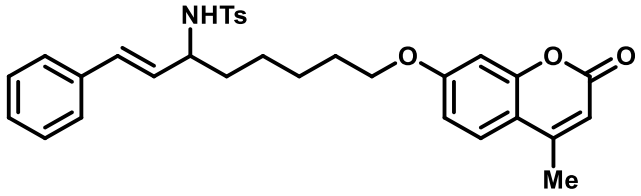


***Tert*-butyl 2-((4*R*,6*S*)-2,2-dimethyl-6-((*S*,*E*)-1-((4-methylphenyl)sulfonamido)-3-phenylallyl)-1,3-dioxan-4-yl)acetate (48):** The title compound **48** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S48** (103.2 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 50 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a colorless oil (100.5 mg, 49 % yield, 1.7:1 dr). **IR (neat):** 3274, 2980, 1726, 1324, 1152, 1092, 751, 706, 693, 671. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 – 7.64 (m, 2H), 7.27 – 7.18 (m, 3H), 7.16 – 7.06 (m, 4H), 6.18 (m, 1H), 5.76 (m, 1H), 5.31 – 5.15 (m, 1H), 4.26 – 4.15 (m, 1H), 4.04 (m, 0.62H), 3.92 – 3.83 (m, 1H), 3.78 – 3.71 (m, 0.38H), 2.46 – 2.31 (m, 2H), 2.28 (s, 1.17H), 2.23 (s, 1.88H), 1.46 – 1.43 (m, 2H), 1.40 (s, 9H), 1.39 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.09, 170.07, 143.29, 138.03, 137.86, 136.10, 136.08, 134.15, 133.44, 129.52, 129.48, 128.43, 128.39, 127.90, 127.51, 127.36, 126.51, 125.57, 123.84, 99.31, 99.25, 80.78, 71.37, 70.94, 65.83, 65.79, 60.46, 59.75, 42.50, 32.55, 32.12, 29.84, 29.82, 28.11, 21.46, 21.41, 19.72, 19.61. **HRMS (ESI):** Calcd for $C_{28}H_{41}N_2O_6S$ $[M+NH_4]^+$: 533.2680; Found: 533.2677.

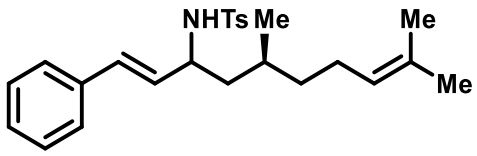


(*E*)-*N*-(8-(Benzo[d][1,3]dioxol-5-yloxy)-1-phenyloct-1-en-3-yl)-4-methylbenzenesulfonamide (49): The title compound **49** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S49** (94.5 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 40 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.3) to give a white solid (141.8 mg, 72 % yield). **M.P.**: 103-104 ℃. **IR (neat):** 3300, 2945, 2362, 1725, 1623, 1359, 1319, 1289, 1159,

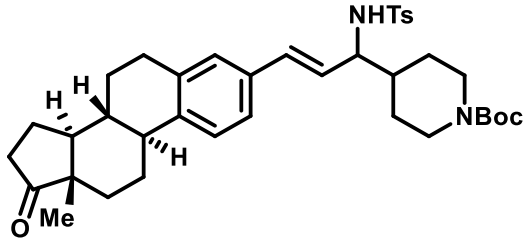
1071, 851, 691, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.15 (m, 5H), 7.09 (d, *J* = 7.0 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 6.32 – 6.25 (m, 1H), 6.19 (d, *J* = 15.9 Hz, 1H), 5.90 (s, 2H), 5.70 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.66 (m, 1H), 3.97 – 3.87 (m, 1H), 3.82 (t, *J* = 6.4 Hz, 2H), 2.29 (s, 3H), 1.68 – 1.55 (m, 4H), 1.43 – 1.31 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.65, 148.31, 143.39, 141.58, 138.23, 136.31, 131.61, 129.63, 128.87, 128.52, 127.82, 127.42, 126.45, 108.05, 105.72, 101.19, 98.13, 68.73, 56.41, 35.97, 29.20, 25.79, 25.33, 21.51. **HRMS (ESI):** Calcd for $C_{28}H_{35}N_2O_5S$ $[M+NH_4]^+$: 511.2261; Found: 511.2265.



(*E*)-4-Methyl-*N*-(8-((4-methyl-1-oxo-1H-isochromen-7-yl)oxy)-1-phenyloct-1-en-3-yl)benzenesulfonamide (50): The title compound **50** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S50** (109.7 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 °C for 24 h. The pure product was isolated by silica gel column chromatography (PE:EA = 5:1, R_f = 0.2) to give a white solid (98.2 mg, 46 % yield). **M.P.**: 87-88 °C. **IR (neat):** 3303, 2931, 2360, 1716, 1614, 1386, 1320, 1291, 1149, 1067, 816, 695, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.24 – 7.10 (m, 5H), 7.05 (d, *J* = 7.0 Hz, 2H), 6.79 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.72 (d, *J* = 1.9 Hz, 1H), 6.21 – 6.05 (m, 2H), 5.71 (dd, *J* = 15.8, 7.7 Hz, 1H), 5.41 (d, *J* = 8.0 Hz, 1H), 3.91 (t, *J* = 6.1 Hz, 3H), 2.35 (s, 3H), 2.23 (s, 3H), 1.75 – 1.67 (m, 2H), 1.64 – 1.51 (m, 2H), 1.43 – 1.33 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.09, 161.49, 155.14, 152.84, 143.11, 138.23, 136.25, 131.29, 129.45, 128.82, 128.32, 127.56, 127.26, 126.29, 125.54, 113.37, 112.58, 111.67, 101.27, 68.30, 56.41, 35.71, 28.74, 25.55, 25.18, 21.34, 18.67. **HRMS (ESI):** Calcd for $C_{31}H_{33}NNaO_5S$ $[M+Na]^+$: 554.1971; Found: 554.1971.

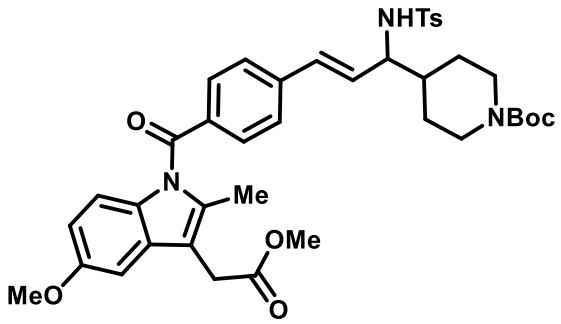


***N*-((5*S*,*E*)-5,9-Dimethyl-1-phenyldeca-1,8-dien-3-yl)-4-methylbenzenesulfonamid-e (51):** The title compound **51** was prepared using styrene (83.3 mg, 0.8 mmol, 2.0 equiv), **S51** (61.7 mg, 0.4 mmol, 1.0 equiv) and $TsNH_2$ (75.3 mg, 0.44 mmol, 1.1 equiv) at 70 ºC for 40 h. The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give a white solid (132.1 mg, 80 % yield, 1.25:1 dr). **M.P.**: 69-70 ℃. **IR (neat):** 3330, 2936, 2364, 1319, 1161, 1098, 978, 886, 757, 698, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 7.4 Hz, 2H), 7.26 – 7.12 (m, 5H), 7.08 (t, *J* = 6.8 Hz, 2H), 6.21 (m, 1H), 5.68 (m, 1H), 5.04 (m, 1H), 4.85 – 4.52 (m, 1H), 4.04 – 3.95 (m, 1H), 2.27 (s, 3H), 1.97 – 1.83 (m, 2H), 1.67 – 1.67 (m, 3H), 1.59 – 1.56 (m, 3H), 1.51 – 1.37 (m, 2H), 1.33 – 1.26 (m, 2H), 1.19 – 1.08 (m, 1H). 0.88 – 0.84 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.18, 138.20, 136.32, 136.29, 131.59, 131.44, 131.35, 131.01, 129.46, 129.41, 128.79, 128.35, 127.64, 127.59, 127.33, 126.34, 126.31, 124.50, 54.80, 54.48, 43.37, 43.28, 36.92, 36.77, 28.90, 28.66, 25.73, 25.70, 25.23, 21.38, 19.33, 19.27, 17.70, 17.67. **HRMS (ESI):** Calcd for $C_{25}H_{37}N_2O_2S$ $[M+NH_4]^+$: 429.2570; Found: 425.2569.



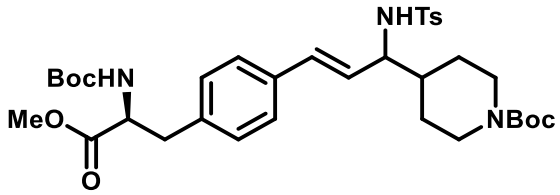
***Tert*-butyl 4-((*E*)-3-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-1-((4-methylphenyl)sulfonamide-o)allyl)piperidine-1-carboxylate (52):** The title compound **52** was prepared using **S52** (112.2 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 2:1, R_f = 0.2) to give a white solid (119.7 mg,

93 % yield, 1:1 dr). **M.P.**: 114-115 ℃. **IR (neat):** 2927, 2360, 1736, 1688, 1423, 1157, 1091, 966, 907, 813, 727, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.06 (m, 3H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.77 (s, 1H), 5.93 (d, *J* = 15.7 Hz, 1H), 5.64 (dd, *J* = 15.7, 8.3 Hz, 1H), 5.50 (d, *J* = 7.8 Hz, 1H), 4.06 (s, 2H), 3.65 (d, *J* = 6.0 Hz, 1H), 2.82 (d, *J* = 3.7 Hz, 2H), 2.63 – 2.44 (m, 3H), 2.37 (m, 1H), 2.27 (s, 3H), 2.25 – 2.19 (m, 1H), 2.19 – 1.86 (m, 5H), 1.78 (m, 1H), 1.60 (m, 2H), 1.56 – 1.44 (m, 5H), 1.41 (s, 9H), 1.21 – 1.07 (m, 2H), 0.88 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.70, 143.19, 143.17, 139.54, 138.03, 136.47, 136.45, 133.66, 132.55, 129.55, 127.30, 127.04, 126.82, 125.65, 125.42, 123.94, 123.73, 79.45, 60.95, 50.45, 48.01, 44.42, 43.78, 43.27, 41.38, 38.14, 35.90, 31.58, 29.38, 28.48, 26.47, 25.73, 21.61, 21.48, 13.87. **HRMS (ESI):** Calcd for $C_{38}H_{51}N_2O_5S$ $[M+H]^+$: 647.3513; Found: 647.3517.

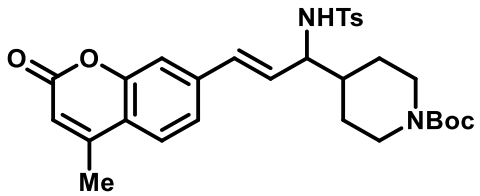


***Tert*-butyl (*E*)-4-(3-(4-(5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1H-indole-1-carbonyl)phenyl)-1-((4-methylphenyl)sulfonamido)allyl)piperidine-1-carboxylate (53):** The title compound **53** was prepared using **S53** (145.4 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 1:1, R_f = 0.3) to give a yellow solid (111.0 mg, 76 % yield). **M.P.**: 83-84 ℃. **IR (neat):** 2928, 2360, 1737, 1674, 1477, 1433, 1362, 1316, 1261, 1224, 1158, 1066, 812, 758, 722, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 8.2 Hz, 4H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.12 (d, *J* = 15.8 Hz, 1H), 5.86 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.31 (brs, 1H), 4.10 (s, 2H), 3.83 (s, 3H), 3.74 (m, 1H), 3.70 (s, 3H), 3.67 (s, 2H), 2.59 (s, 2H), 2.37 (s, 3H), 2.27 (s, 3H), 1.85 – 1.74 (m, 1H), 1.59 (m, 2H), 1.43 (s, 9H), 1.22 – 1.10 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.51, 168.98, 155.99,

154.73, 143.49, 140.53, 137.96, 136.07, 134.49, 131.56, 130.93, 130.62, 130.13, 129.74, 129.60, 127.33, 126.54, 115.01, 112.29, 111.58, 101.21, 79.59, 60.81, 55.78, 52.25, 43.82, 43.26, 41.24, 30.20, 28.49, 21.52, 13.42. **HRMS (ESI):** Calcd for $C_{40}H_{48}N_3O_8S$ $[M+H]^+$: 730.3157; Found: 730.3164.

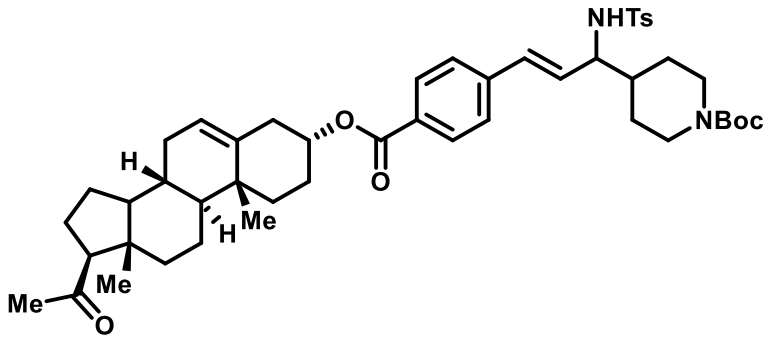


***Tert*-butyl (*E*)-4-(3-(4-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl)-1-((4-methylphenyl)sulfonamido)allyl)piperidine-1-carboxylate (54):** The title compound **54** was prepared using **S54** (121.7 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 2:1, R_f = 0.1) to give a white solid (119.6 mg, 89 % yield, 1:1 dr). **M.P.**: 69-70 °C. **IR (neat):** 2976, 2360, 1688, 1365, 1276, 1156, 967, 764, 729, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.01 – 6.88 (m, 4H), 5.95 (d, *J* = 15.6 Hz, 1H), 5.62 (dd, *J* = 15.6, 8.2 Hz, 1H), 5.45 (brs, 1H), 4.98 (d, *J* = 7.3 Hz, 1H), 4.53 (q, *J* = 6.6 Hz, 1H), 4.09 (s, 2H), 3.69 (s, 3H), 3.66 – 3.59 (m, 1H), 3.11 – 2.93 (m, 2H), 2.56 (s, 2H), 2.23 (s, 3H), 1.84 – 1.71 (m, 1H), 1.61 – 1.50 (m, 2H), 1.40 (s, 18H), 1.18 – 1.06 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 172.32, 155.13, 154.73, 143.32, 138.00, 135.72, 134.88, 132.37, 129.54, 129.39, 127.32, 126.52, 126.20, 80.04, 79.50, 60.96, 54.42, 52.33, 43.84, 43.34, 41.35, 37.96, 28.49, 28.36, 21.45. **HRMS (ESI):** Calcd for $C_{35}H_{50}N_3O_8S$ $[M+H]^+$: 672.3313; Found: 672.3316.



***Tert*-butyl (*E*)-4-(3-(4-methyl-2-oxo-2H-chromen-7-yl)-1-((4-methylphenyl)sulfonamido)allyl)piperidine-1-carboxylate (55):** The title compound **55** was prepared

using **S55** (74.5 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 2:1, R_f = 0.1) to give a white solid (101.5 mg, 92% yield). **M.P.**: 179-180 °C. **IR (neat):** 3177, 2922, 2359, 1731, 1665, 1611, 1434, 1160, 1143, 1090, 960, 852, 751, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.93 (s, 1H), 6.26 (s, 1H), 6.10 (d, *J* = 15.9 Hz, 1H), 5.86 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.17 (brs, 1H), 4.10 (s, 2H), 3.82 – 3.69 (m, 1H), 2.60 (s, 2H), 2.41 (s, 3H), 2.27 (s, 3H), 1.85 – 1.74 (m, 1H), 1.73 – 1.58 (m, 2H), 1.42 (s, 9H), 1.22 – 1.08 (m, 2H).**^{13}C NMR (100 MHz, Acetone-D6):** δ 160.58, 154.98, 154.61, 153.26, 143.56, 141.35, 140.22, 131.67, 131.36, 130.21, 128.04, 125.91, 123.13, 119.89, 115.06, 114.45, 79.31, 61.71, 44.61, 44.11, 41.86, 28.62, 21.29, 18.48. **HRMS (ESI):** Calcd for $C_{30}H_{40}N_3O_6S$ $[M+NH_4]^+$: 570.2632; Found: 570.2636.



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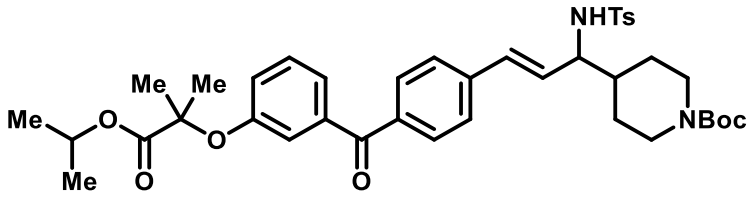
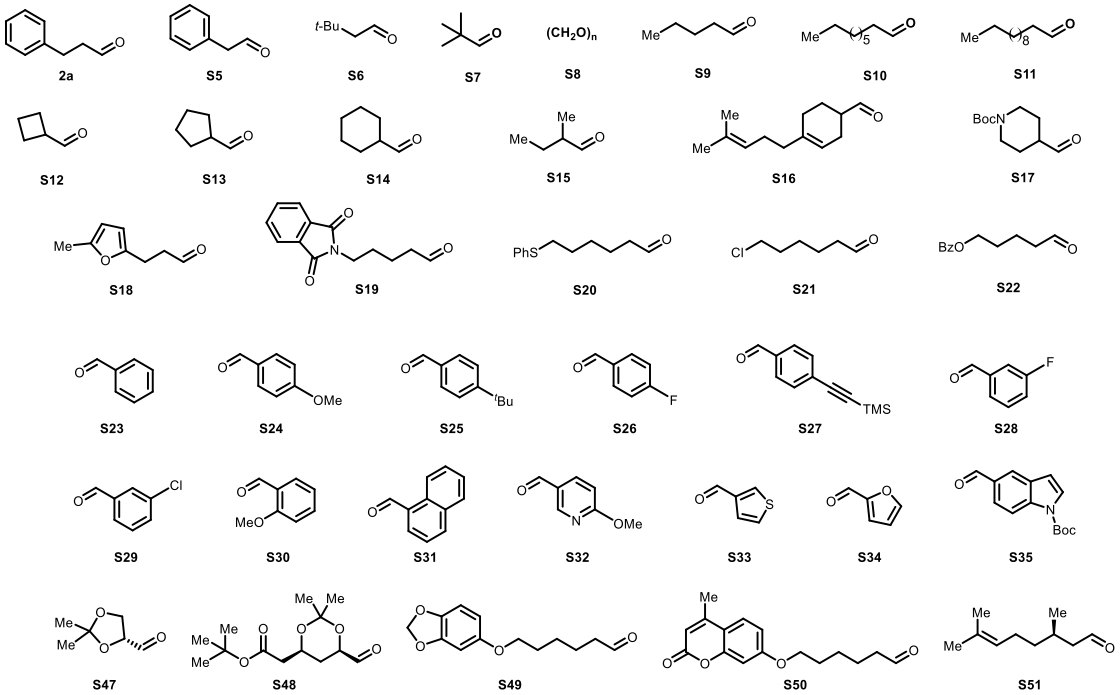
***Tert*-butyl 4-((*E*)-3-(4-((((*3R,8S,9S,10R,13S,17S*)-17-acetyl-10,13-dimethyl-2,3,-4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)carbonyl)phenyl)-1-((4-methylphenyl)sulfonamido)allyl)piperidine-1-carboxylate (56):** The title compound **56** was prepared using **S56** (178.7 mg, 0.4 mmol, 2.0 equiv), **S17** (42.8 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 °C for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 2:1, R_f = 0.2) to give a white solid (89.4 mg, 55% yield, 1:1 dr). **M.P.**: 123-124 °C. **IR (neat):** 2937, 2360, 1693, 1427, 1274, 1159, 1091, 964, 667. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.06 (d, *J* = 15.8 Hz, 1H), 5.79 (dd, *J* =

15.7, 8.1 Hz, 1H), 5.41 (d, *J* = 3.7 Hz, 1H), 5.13 (d, *J* = 8.3 Hz, 1H), 4.89 – 4.78 (m, 1H), 4.10 (s, 2H), 3.72 (d, *J* = 6.7 Hz, 1H), 2.66 – 2.50 (m, 3H), 2.45 (d, *J* = 7.7 Hz, 2H), 2.24 (s, 3H), 2.20 – 2.15 (m, 1H), 2.13 (s, 3H), 2.06 – 1.96 (m, 3H), 1.95 – 1.89 (m, 1H), 1.70 – 1.53 (m, 7H), 1.53 – 1.44 (m, 3H), 1.42 (s, 9H), 1.28 – 1.10 (m, 6H), 1.06 (s, 4H), 0.63 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 209.80, 165.75, 154.77, 143.57, 140.34, 139.71, 137.97, 131.99, 129.97, 129.82, 129.66, 129.05, 127.36, 126.21, 122.64, 79.65, 74.64, 63.79, 60.84, 56.94, 49.99, 44.12, 43.82, 43.40, 41.37, 38.89, 38.28, 37.14, 36.78, 31.94, 31.91, 31.72, 28.54, 27.96, 24.61, 22.94, 21.53, 21.17, 19.51, 13.37. **HRMS (ESI):** Calcd for $C_{48}H_{65}N_2O_7S$ $[M+H]^+$: 813.4507; Found: 813.4502.



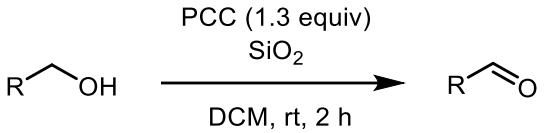
***Tert*-butyl (*E*)-4-(3-(4-(3-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)-phenyl)-1-((4-methylphenyl)sulfonamido)allyl)piperidine-1-carboxylate (57):** The title compound **57** was prepared using **S57** (141.0 mg, 0.4 mmol, 2.0 equiv), **S17** (42.7 mg, 0.2 mmol, 1.0 equiv) and $TsNH_2$ (37.7 mg, 0.22 mmol, 1.1 equiv) at 70 ºC for 48 h. The pure product was isolated by silica gel column chromatography (PE:EA = 2:1, R_f = 0.2) to give a white solid (136.2 mg, 95% yield). **M.P.**: 80-81 ℃. **IR (neat):** 2984, 2360, 1658, 1597, 1276, 1158, 1099, 929, 764, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 – 7.67 (m, 4H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.08 (m, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.08 (d, *J* = 15.8 Hz, 1H), 5.81 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.39 (d, *J* = 8.6 Hz, 1H), 5.13 – 5.02 (m, 1H), 4.08 (s, 2H), 3.72 (d, *J* = 6.9 Hz, 1H), 2.58 (s, 2H), 2.24 (s, 3H), 1.83 – 1.75 (m, 1H), 1.65 (s, 6H), 1.61 – 1.58 (m, 2H), 1.41 (s, 9H), 1.19 (d, *J* = 6.3 Hz, 6H), 1.16 – 1.12 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 194.96, 173.24, 159.65, 154.75, 143.51, 139.69, 137.98, 137.22, 132.03, 131.90, 130.61, 130.17, 129.64, 129.05, 127.36, 126.11, 117.26, 79.60, 79.46, 69.44, 60.89, 43.89, 43.43, 41.33, 28.52, 25.46, 21.63, 21.52. **HRMS (ESI):** Calcd for $C_{40}H_{51}N_2O_8S$ $[M+H]^+$: 719.3361; Found: 719.3352.

V. Synthesis of substrates



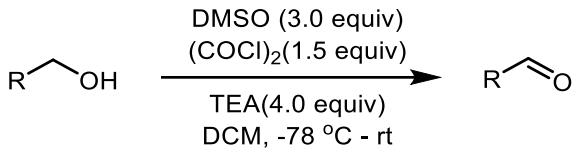
Aldehyde substrates **2a - S18, S23 - 34, S47 - 48, S51** were purchased from commercial sources. **S19 – S22, S35, S49 - 50** were prepared according to the literature.

1. Method A for the Synthesis of Aldehydes[5]

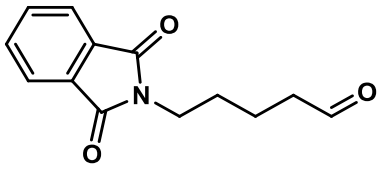


To a solution of pyridinium chlorochromate (PCC, 1.3 equiv) and an equivalent amount of SiO_2 in CH_2Cl_2 (0.3 M), alcohol (1.0 equiv) was added slowly. The reaction mixture was stirred at room temperature for 2 h, and then the resulting solution was filtered through a pad of silica gel, eluting with DCM. The solvent was removed under reduced pressure, and the remaining crude residue was purified by flash column chromatography (SiO_2, petroleum ether/ethyl acetate) to afford the corresponding aldehydes.

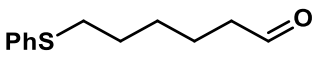
2. Method B for the Synthesis of Aldehydes[6]



To a solution of oxalyl chloride (1.5 equiv) in DCM, a solution of dimethyl sulfoxide (DMSO) (3.0 equiv) in DCM was added at –78 °C. The mixture was stirred for 5 min at –78 °C, and a solution of alcohol (1.0 equiv) in DCM (2.5 mL) was added dropwise. After stirring for 15 min, TEA (4.0 equiv) was added to the reaction mixture within 5 min and then allowed to warm to 0 °C. When completed (monitored by TLC), aqueous $NaHCO_3$ was added to the reaction mixture, and the mixture was then extracted with DCM three times and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate) to afford the corresponding aldehydes.

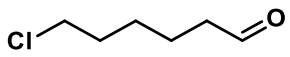


5-(1,3-Dioxoisoindolin-2-yl)pentanal (S19)[7]**:** Accordng to *Method B*, The title compound **S19** was prepared from 2-(5-hydroxypentyl)isoindoline-1,3-dione which was synthesized according to the literature.[8] Purification by silica gel column chromatography (PE:EA = 5:1, R_f = 0.3) gave the title compound (353.8 mg, 51 %) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.76 (t, *J* = 1.4 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.73 – 7.68 (m, 2H), 3.70 (t, *J* = 6.7 Hz, 2H), 2.56 – 2.44 (m, 2H), 1.78 – 1.64 (m, 4H).

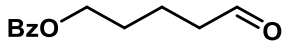


6-(Phenylthio)hexanal (S20)[8]**:** According to *Method A*, the title compound **S20** was prepared from 6-(phenylthio)hexan-1-ol which was synthesized according to the literature[7] using 6-Chlorohexanol and sodium thiophenolate. Purification by silica gel

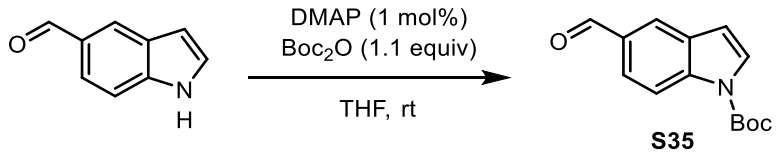
column chromatography (PE, R_f = 0.6) gave the title compound (729.0 mg, 70 %) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.75 (t, *J* = 1.6 Hz, 1H), 7.34 – 7.26 (m, 4H), 7.21 – 7.13 (m, 1H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.43 (td, *J* = 7.3, 1.6 Hz, 2H), 1.68 – 1.62 (m, 4H), 1.51 – 1.45 (m, 2H).



6-Chlorohexanal (S21)[9]**:** According to *Method A*, the title compound **S21** was prepared from 6-Chlorohexanol. Purification by silica gel column chromatography (PE:EA = 10:1, R_f = 0.8) gave the title compound (417.5 mg, 62 %) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.77 (s, 1H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.46 (td, *J* = 7.3 Hz, 1.4 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.69 – 1.62 (m, 2H), 1.51 – 1.44 (m, 2H).



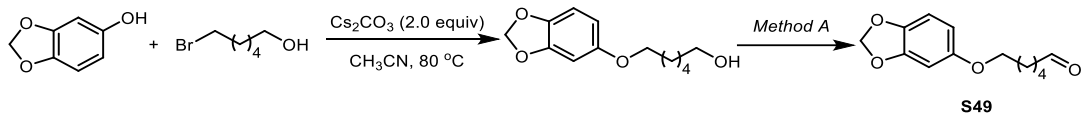
5-Oxopentyl benzoate (S22)[10]**:** According to *Method B*, The title compound **S22** was prepared from 5-hydroxypentyl benzoate, which was synthesized according to the literature[11] using benzoic acid and 5-bromopentan-1-ol. Purification by silica gel column chromatography (PE:EA = 5:1, R_f = 0.3) gave the title compound (501.2 mg, 81 %) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.80 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.34 (t, *J* = 5.6 Hz, 2H), 2.54 (t, *J* = 6.0 Hz, 2H), 1.87 – 1.72 (m, 4H).



S35

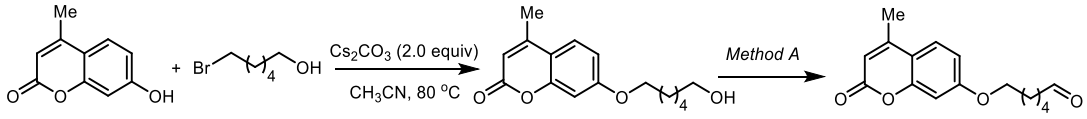
***Tert*-butyl 5-formyl-1H-indole-1-carboxylate (S35)**[12]**:** The title compound **S35** was synthesized according to the following procedure.[13] To a stirred solution of 1H-indole-5-carbaldehyde (1.0 equiv) and DMAP (1.0 mol%.) in THF (0.3 M), Boc_2O (1.1 equiv) was added and the mixture was stirred at room temperature for 2 h. Evaporation followed by column chromatography (PE:EA = 10:1, R_f = 0.3) afforded the title

compound **S35** as white solid in quantitative yield(740.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.05 (s, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 0.9 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.68 (d, *J* = 3.7 Hz, 1H), 6.68 (d, *J* = 3.7 Hz, 1H), 1.68 (s, 9H).



S49

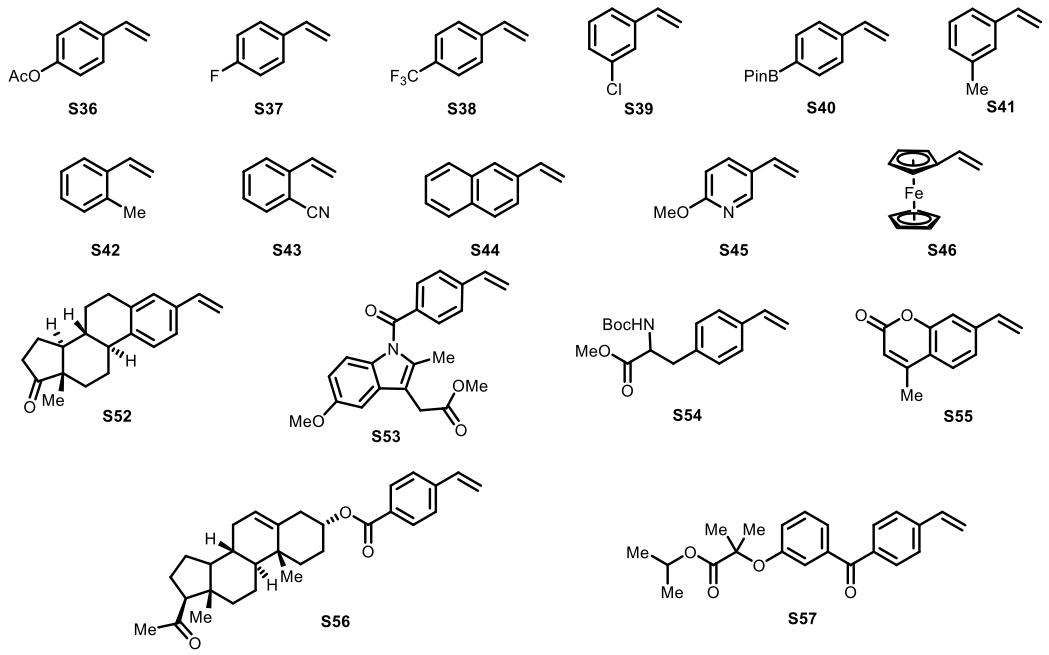
6-(Benzo[*d*][1,3]dioxol-5-yloxy)hexanal (S49): The title compound **S49** was synthesized according to the above procedure. To a solution of sesamol (1.0 equiv) in acetonitrile (0.25 M) was added cesium carbonate (2.0 equiv) 6-bromo-1-hexanol (1.2 equiv). The reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, water was added, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to yield the 6-(benzo[*d*][1,3]dioxol-5-yloxy)hexan-1-ol. It was used in the next step without further purification. Then according to *Method A,* the title compound **S49** was prepared from the above alcohol. Purification by silica gel column chromatography (PE, R_f = 0.7) gave the title compound (673.3 mg, 57 % over two steps) as a light yellow oil. **IR (neat):** 3025, 2923, 2360, 1492, 1452, 1183, 1028, 966, 745, 692. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.77 (s, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 2.2 Hz, 1H), 6.29 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.89 (s, 2H), 3.87 (t, *J* = 6.3 Hz, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 1.81 – 1.64 (m, 4H), 1.53 – 1.45 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.56, 154.63, 148.33, 141.64, 108.03, 105.74, 101.18, 98.14, 68.62, 43.90, 29.18, 25.81, 21.91. **HRMS (ESI):** Calcd for $C_{13}H_{17}O_4$ $[M+H]^+$: 237.1122; Found: 237.1115.



S50

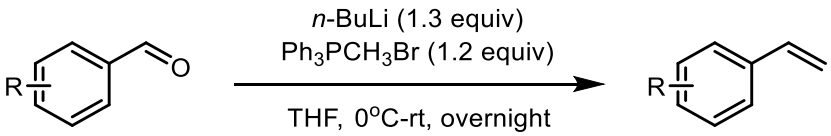
6-((4-Methyl-1-oxo-1H-isochromen-7-yl)oxy)hexanal (S50): The title compound **S50** was synthesized according to the above procedure. To a solution of 4-methylumbelliferone (1.0 equiv) in acetonitrile (0.25 M) was added cesium carbonate (2.0 equiv), 6-bromo-1-hexanol (1.2 equiv). The reaction mixture was stirred at 80 °C

for 12 h. After cooling to room temperature, water was added and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to yield the 7-((6-hydroxyhexyl)oxy)-4-methyl-2H-chromen-2-one. It was used in the next step without further purification. Then according to *Method A,* the title compound **S50** was prepared from the above alcohol. Purification by silica gel column chromatography (PE:EA = 2:1, R_f = 0.3) gave the title compound (833.5 mg, 61 % over two steps) as a white solid. **IR (neat):** 2942, 2360, 1717, 1612, 1388, 1293, 1280, 1264, 1146, 1070, 847, 749. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.79 (s, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 6.13 (s, 1H), 4.02 (t, *J* = 6.3 Hz, 2H), 2.49 (t, *J* = 6.6 Hz, 2H), 2.39 (s, 3H), 1.90 – 1.80 (m, 2H), 1.76 – 1.68 (m, 2H), 1.57 – 1.49 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.46, 162.18, 161.48, 155.40, 152.71, 125.63, 113.63, 112.73, 112.01, 101.46, 68.29, 43.87, 28.93, 25.75, 21.87, 18.80. **HRMS (ESI):** Calcd for $C_{16}H_{19}O_4$ $[M+H]^+$: 275.1278; Found: 275.1274.

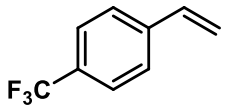


Olefin substrates **S36 - 37, S44** were purchased from commercial sources. **S38 - 43, S45 – 46, S52 – 57** were prepared according to the literature.

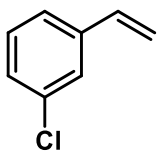
3. Method C for the Synthesis of Olefins[14]



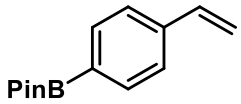
In an oven-dried 100 mL flask, Ph_3PCH_3Br (1.2 equiv) was suspended in THF (20 mL) under N_2 and cooled to 0 °C. n-BuLi (2.4 M in hexane, 1.3 equiv) was added dropwise, and the solution was stirred for 1 h at this temperature. Then aldehyde (1.0 equiv) was added dropwise, and the mixture was stirred overnight at room temperature. The mixture was quenched with NH_4Cl saturated solution, extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo. The crude product was purified by silica gel column chromatography to afford the corresponding alkene.



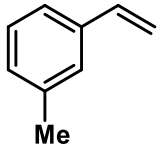
1-(Trifluoromethyl)-4-vinylbenzene (S38)[15]**:** According to *Method C,* the title compound **S38** was prepared from 4-(trifluoromethyl)benzaldehyde. Purification by silica gel column chromatography (PE, R_f = 0.7) gave the title compound (382.2 mg, 74 %) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.39 (d, *J* = 10.9 Hz, 1H).



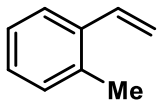
1-Chloro-3-vinylbenzene (S39)[16]**:** According to *Method C,* the title compound **S39** was prepared from 3-chlorobenzaldehyde. Purification by silica gel column chromatography (PE, R_f = 0.8) gave the title compound (450.5 mg, 65 %) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 (s, 1H), 7.31 – 7.21 (m, 3H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H).



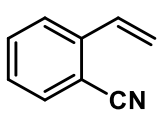
4,4,5,5-Tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (S40)[17]**:** According to *Method C,* the title compound **S40** was prepared from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde. Purification by silica gel column chromatography (PE:EA = 50:1, R_f = 0.5) gave the title compound (925.8 mg, 80 %) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.82 (d, *J* = 17.6 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 1.35 (s, 12H).



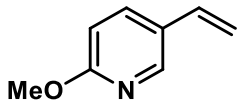
1-Methyl-3-vinylbenzene (S41)[15]**:** According to *Method C,* the title compound **S41** was prepared from 3-methylbenzaldehyde. Purification by silica gel column chromatography (PE, R_f = 0.8) gave the title compound (267.8 mg, 45 %) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.24 (m, 3H), 7.10 (s, 1H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 2.37 (s, 3H).



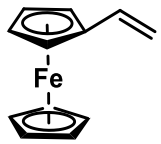
1-Methyl-2-vinylbenzene (S42)[18]**:** According to *Method C,* the title compound **S42** was prepared from 2-methylbenzaldehyde. Purification by silica gel column chromatography (PE, R_f = 0.9) gave the title compound (334.6 mg, 56 %) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 – 7.42 (m, 1H), 7.23 – 7.08 (m, 3H), 6.96 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.65 (d, *J* = 17.4 Hz, 1H), 5.30 (d, *J* = 11.0 Hz, 1H), 2.37 (s, 3H).



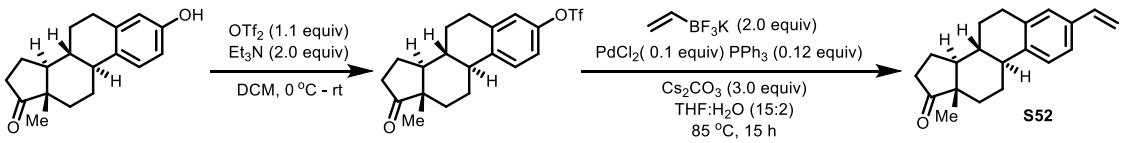
2-Vinylbenzonitrile (S43)[19]**:** According to *Method C,* the title compound **S43** was prepared from 2-formylbenzonitrile. Purification by silica gel column chromatography (PE, R_f = 0.5) gave the title compound (345.8 mg, 54 %) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.08 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.95 (d, *J* = 17.4 Hz, 1H), 5.54 (d, *J* = 11.0 Hz, 1H).



2-Methoxy-5-vinylpyridine (S45)[20]**:** According to *Method C,* the title compound **S45** was prepared from 6-methoxynicotinaldehyde. Purification by silica gel column chromatography (PE, R_f = 0.4) gave the title compound (1.13g, 84 %) as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.10 (d, *J* = 2.3 Hz, 1H), 7.66 (d, *J* = 2.4 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 6.63 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.62 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 11.0 Hz, 1H), 3.92 (s, 3H).



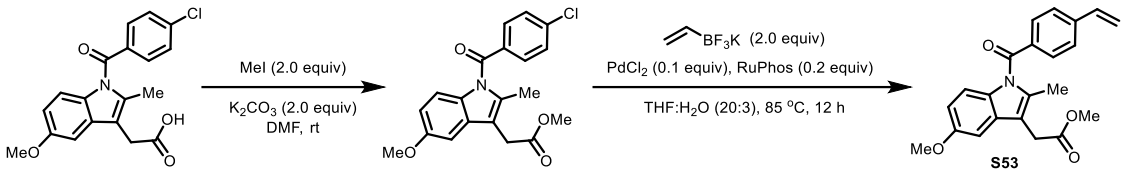
Vinylferrocene (S46)[21]**:** According to *Method C,* the title compound **S46** was prepared from ferrocene carboxaldehyde. Purification by silica gel column chromatography (PE, R_f = 0.7) gave the title compound (394.3 mg, 62 %) as a red-brown solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.47 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.36 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.04 (dd, *J* = 10.7, 1.4 Hz, 1H), 4.37 (t, *J* = 1.7 Hz, 2H), 4.22 (t, *J* = 1.7 Hz, 2H), 4.12 (s, 5H).



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cycl-

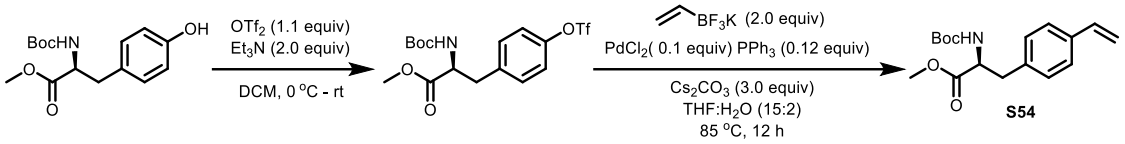
openta[a]phenanthren-17-one (S52)[22]**:** The title compound **S52** was prepared according to the reported procedure.[22] A dry round-bottomed flask equipped with a magnetic stirring bar was charged with estrone (1.35 g, 5.0 mmol, 1.0 equiv) and it was dissolved in anhydrous DCM (20 mL). The mixture was cooled down to 0 ºC and then Et_3N (1.4 mL, 10 mmol, 2.0 equiv) and subsequently Tf_2O (0.93 mL, 5.5 mmol, 1.1 equiv) were added dropwise. The resulting brown mixture was allowed to warm to room temperature and further stirred for 5 h. A saturated aqueous solution of $NaHCO_3$ was added and the mixture was extracted three times with DCM. Combined organic phases were dried over anhydrous Na_2SO_4, concentrated in vacuum and the crude product was purified by column chromatography (PE:EA = 10:1, R_f = 0.3) to afford the (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate (1.21 g, 60 %) as a pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 (d, *J* = 8.6 Hz, 1H), 7.08 – 6.94 (m, 2H), 2.94 (m, 2H), 2.52 (dd, *J* = 18.9, 8.7 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.34 – 2.23 (m, 1H), 2.21 – 1.94 (m, 4H), 1.68 – 1.44 (m, 6H), 0.92 (s, 3H).

A dry round-bottomed flask equipped with a magnetic stirring bar was charged with estrone-triflate (603.6 mg, 1.5 mmol), potassium vinyl trifluoroborate (401.8 mg, 3.0 mmol, 2.0 equiv), $PdCl_2$ (26.6 mg, 0.15 mmol, 0.1 equiv), PPh_3 (47.2 mg, 0.18 mmol, 0.12 equiv) and Cs_2CO_3 (1.47 g, 4.5 mmol, 3.0 equiv). Anhydrous THF (15 mL) and distilled water (2.0 mL) were added. Then the resulting dark brown mixture was stirred at 85 ºC for 15 h. More water was added, and the mixture was extracted three times with DCM. The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated in a vacuum. The crude product was purified by column chromatography (PE:EA = 8:1, R_f = 0.2) to afford the title compound **S52** (294.4 mg, 70 %) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.27 – 7.21 (m, 2H), 7.15 (s, 1H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 5.20 (d, *J* = 10.9 Hz, 1H), 2.95 – 2.90 (m 2H), 2.51 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.34 – 2.27 (m, 1H), 2.20 – 1.95 (m, 4H), 1.69 – 1.59 (m, 2H), 1.57 – 1.40 (m, 4H), 0.91 (s, 3H).



Methyl 2-(5-methoxy-2-methyl-1-(4-vinylbenzoyl)-1*H*-indol-3-yl)acetate (S53)[22]**:** The title compound **S53** was prepared according the reported procedure.[22] In a dried flask, MeI (1.42 g, 10 mmol, 2.0 equiv) was added to a suspension of indomethacin (1.79 g, 5.0 mmol) and K_2CO_3 (1.38 g, 10 mmol, 2.0 equiv) in dry DMF (20 mL) at room temperature. After 12 h, water (30 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (PE:EA = 10:1, R_f = 0.3) to afford methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate as a yellow solid (1.62 g, 89 % yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.67 (s, 2H), 2.39 (s, 3H).

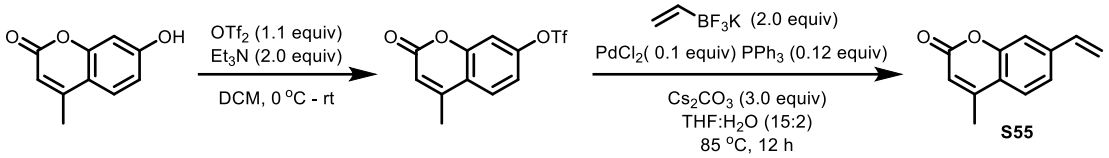
A dry round-bottomed flask equipped with a magnetic stirring bar was charged with methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (1.12 g, 3 mmol), potassium vinyltrifluoroborate (803.6 mg, 6.0 mmol, 2.0 equiv), $PdCl_2$ (53.2 mg, 0.3 mmol, 0.1 equiv), RuPhos (280.0 mg, 0.6 mmol, 0.2 equiv) and Cs_2CO_3 (2.93 g, 9.0 mmol, 3.0 equiv). Anhydrous THF (20 mL) and distilled water (3.0 mL) were added. Then the resulting dark brown mixture was stirred at 85 °C for 12 h. More water was added and the mixture was extracted three times with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated in vacuum, and the crude product was purified by column chromatography on silica gel (PE:EA = 10:1, R_f = 0.25) to afford the title compound **S53** as a yellow solid (838.3 mg, 77 % yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.79 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.91 (d, *J* = 17.6 Hz, 1H), 5.44 (d, *J* = 10.9 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.68 (s, 2H), 2.40 (s, 3H).



Methyl (*S*)-2-((tert-butoxycarbonyl)amino)-3-(4-vinylphenyl)propanoate (S54)[23]: The title compound **S54** was prepared according the reported procedure.[22] A dry round-bottomed flask equipped with a magnetic stirring bar was charged with Boc-L-Tyrosine methyl ester (1.48 g, 5.0 mmol, 1.0 equiv) and it was dissolved in anhydrous DCM (15 mL). The mixture was cooled to 0 ºC and then Et_3N (1.4 mL, 10 mmol, 2.0 equiv) and subsequently Tf_2O (0.93 mL, 5.5 mmol, 1.1 equiv) were added dropwise. The resulting brown mixture was allowed to warm to room temperature and further stirred for 5 h. A saturated aqueous solution of $NaHCO_3$ was added and the mixture was extracted three times with DCM. Combined organic phases were dried over anhydrous Na_2SO_4, concentrated in vacuum and the crude product was purified by column chromatography (PE:EA = 5:1, R_f = 0.3) to afford the methyl (*S*)-2-((tert-butoxycarbonyl)amino)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate (1.97 g, 92 %) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.24 – 7.17 (m, 4H), 5.03 (d, *J* = 6.3 Hz, 1H), 4.60 (d, *J* = 6.6 Hz, 1H), 3.71 (s, 3H), 3.17 (dd, *J* = 13.8, 5.5 Hz, 1H), 3.03 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.40 (s, 9H).

A dry round-bottomed flask equipped with a magnetic stirring bar was charged with (*S*)-2-((tert-butoxycarbonyl)amino)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate (1.28 g, 3.0 mmol), potassium vinyltrifluoroborate (803.6 mg, 6.0 mmol, 2.0 equiv), $PdCl_2$ (53.2 mg, 0.3 mmol, 0.1 equiv), PPh_3 (94.2 mg, 0.36 mmol, 0.12 equiv) and Cs_2CO_3 (2.94 g, 9.0 mmol, 3.0 equiv). Anhydrous THF (15 mL) and distilled water (2.0 mL) were added. Then the resulting solution was stirred at 85 ºC for 15 h. More water was added and the mixture was extracted three times with DCM. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated in vacuum, and the crude product was purified by column chromatography (PE:EA = 10:1, R_f = 0.3) to afford the title compound **S54** (603.6 mg, 66 %) as a white solid. **^{1}H NMR (400 MHz,**

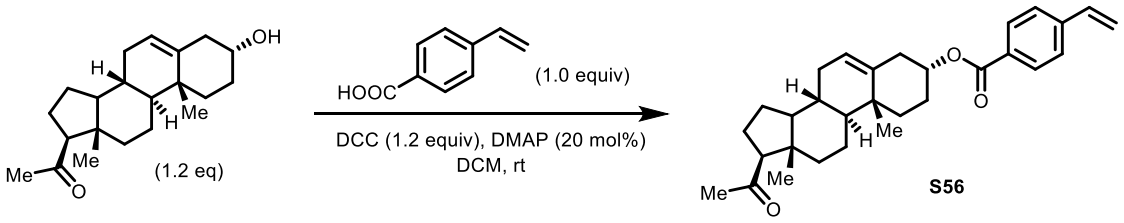
$CDCl_3$): δ 7.34 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 4.97 (d, *J* = 7.4 Hz, 1H), 4.64 – 4.50 (m, 1H), 3.71 (s, 3H), 3.15 – 2.98 (m, 2H), 1.42 (s, 9H).



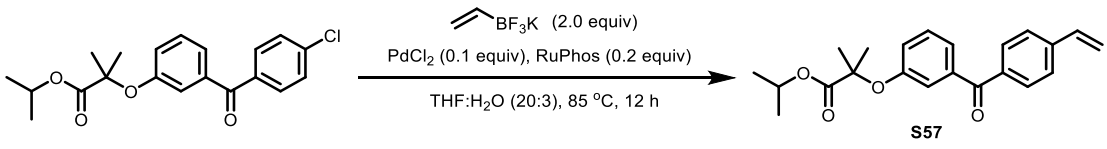
4-Methyl-7-vinyl-2*H*-chromen-2-one (S55)[22]**:** The title compound **S55** was prepared according the reported procedure.[22] A dry round-bottomed flask equipped with a magnetic stirring bar was charged with hymecromone (881.0 mg, 5.0 mmol, 1.0 equiv) and it was dissolved in anhydrous DCM (15 mL). The mixture was cooled down to 0 °C and then Et_3N (1.4 mL, 10 mmol, 2.0 equiv) and Tf_2O (0.93 mL, 5.5 mmol, 1.1 equiv) were added dropwise. The resulting brown mixture was allowed to warm to room temperature and further stirred for 5 h. A saturated aqueous solution of $NaHCO_3$ was added and the mixture was extracted three times with DCM. Combined organic phases were dried over anhydrous Na_2SO_4, concentrated in vacuum and the crude product was purified by column chromatography (PE:EA = 5:1, R_f = 0.4) to afford the 4-methyl-2-oxo-2*H*-chromen-7-yl trifluoromethane sulfonate (1.42 g, 90 %) as a pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 8.7 Hz, 1H), 7.29 – 7.22 (m, 2H), 6.35 (s, 1H), 2.46 (s, 3H).

A dry round-bottomed flask equipped with a magnetic stirring bar was charged with 4-methyl-2-oxo-2*H*-chromen-7-yl trifluoromethane sulfonate (462.3 mg, 1.5 mmol), potassium vinyl trifluoroborate (401.8 mg, 3.0 mmol, 2.0 equiv), $PdCl_2$ (26.6 mg, 0.15 mmol, 0.1 equiv), PPh_3 (47.2 mg, 0.18 mmol, 0.12 equiv) and Cs_2CO_3 (1.47 g, 4.5 mmol, 3.0 equiv). Anhydrous THF (15 mL) and distilled water (2.0 mL) were added. Then the resulting dark brown mixture was stirred at 85 °C for 15 h. More water was added and the mixture was extracted three times with DCM. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated in vacuum, and the crude product was purified by column chromatography (PE:EA = 10:1, R_f = 0.5) to afford the

title compound **S55** (183 mg, 66 %) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.27 (m, 2H), 6.74 (dd, *J* = 17.5, 10.9 Hz, 1H), 6.25 (s, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.42 (d, *J* = 10.9 Hz, 1H), 2.42 (s, 3H).



(3*R*,8*S*,9*S*,10*R*,13*S*,17*S*)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,1-6,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 4-vinylbenzoate (S56)[24]: The title compound **S56** was prepared according the reported procedure.[25] A dried round flask equipped with a magnetic stirring bar was charged with pregnenolone (759.6 mg, 2.4 mmol, 1.2 equiv), 4-Vinylbenzoic acid (292.3 mg, 2.0 mmol, 1.0 equiv), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 495.2 mg, 2.4 mmol, 2.4 equiv), 4-dimethylaminopyridine (DMAP, 48.1 mg, 0.4 mmol, 20 mol%.) and DCM (15 mL). The reaction mixture was stirred at room temperature overnight. The reaction mixture was washed with water (20 mL) and extracted three times with DCM. The organic phase was dried with anhydrous Na_2SO_4, then concentrated under vacuum and purified by column chromatography on silica gel (PE:EA = 10:1, R_f = 0.3) to afford the title compound **S56** as a white solid (679.4 mg, 76 % yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.42 (d, *J* = 4.1 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H), 4.91 – 4.79 (m, 1H), 2.55 (t, *J* = 8.9 Hz, 1H), 2.47 (d, *J* = 7.8 Hz, 2H), 2.23 – 2.16 (m, 1H), 2.13 (s, 3H), 2.08 – 1.97 (m, 3H), 1.96 – 1.89 (m, 1H), 1.79 – 1.60 (m, 5H), 1.56 – 1.42 (m, 4H), 1.29 – 1.16 (m, 3H), 1.07 (s, 3H), 0.64 (s, 3H).

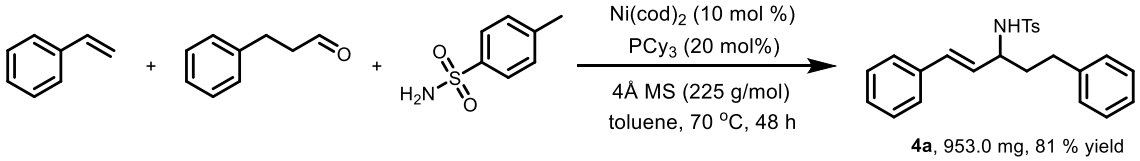


Isopropyl 2-methyl-2-(3-(4-vinylbenzoyl)phenoxy)propanoate (S57)[22]: The title

compound **S57** was prepared according to the literature.[22] A dry round-bottomed flask equipped with a magnetic stirring bar was charged with fenofibrate (721.7 mg, 2 mmol), potassium vinyl trifluoroborate (535.8 mg, 4.0 mmol, 2.0 equiv), $PdCl_2$ (35.5 mg, 0.2 mmol, 0.1 equiv), RuPhos (186.7 mg, 0.4 mmol, 0.2 equiv) and Cs_2CO_3 (1.95 g, 6.0 mmol, 3.0 equiv). Anhydrous THF (20 mL) and distilled water (3.0 mL) were added. Then the resulting dark brown mixture was stirred at 85 °C for 12 h. More water was added, and the mixture was extracted three times with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated in vacuum, and the crude product was purified by column chromatography (PE:EA = 20:1, R_f = 0.1) to afford the title compound **S57** (599.0 mg, 85 %) as a yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (t, *J* = 8.7 Hz, 4H), 7.49 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.78 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.39 (d, *J* = 10.9 Hz, 1H), 5.14 – 5.03 (m, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H).

VI Preparative-Scale Reaction and Diversification

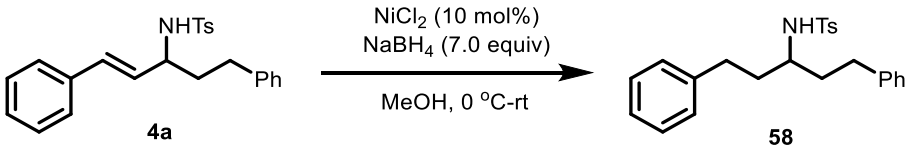
1. Preparative-Scale Reaction.



4a, 953.0 mg, 81 % yield

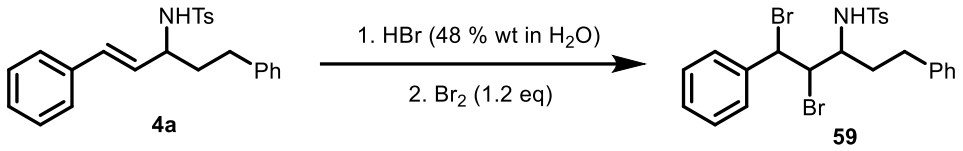
(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)-4-methyl benzenesulfonamide (4a): The title compound **4a** was prepared according to the general procedure for the synthesis of allylamine (using 3.0 mmol of aldehyde). The pure product was isolated by silica gel column chromatography (PE:EA = 10:1, R_f = 0.1) to give a white solid (953.0 mg, 81 % yield).

2. Diversification.



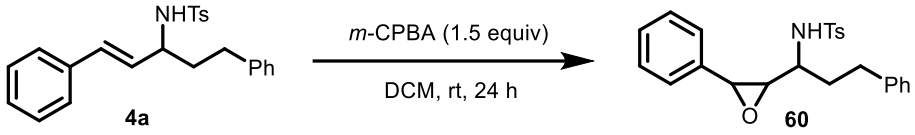
4a **58**

***N*-(1,5-Diphenylpentan-3-yl)-4-methylbenzenesulfonamide (58):** According to the literature.[26] To a stirred solution of **4a** (39.2 mg, 0.1 mmol, 1.0 equiv) in methanol (2.0 mL) was added anhydrous nickel(II) chloride (1.3 mg, 0.01 mmol, 0.01 equiv) at rt. Then, sodium borohydride (26.5 mg, 0.7 mmol, 7.0 equiv) was added at 0 °C, and then the reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with dichloromethane. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give product **58** as a white solid (33.9 mg, 86 %). **M.P.**: 102-103 ℃. **IR (neat)**: 3292, 2928, 2360, 1424, 1320, 1151, 1086, 815, 749, 698, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.16 (m, 8H), 6.99 (d, *J* = 6.9 Hz, 4H), 4.86 (d, *J* = 8.6 Hz, 1H), 3.39 – 3.20 (m, 1H), 2.62 – 2.46 (m, 4H), 2.45 (s, 3H), 1.83 – 1.72 (m, 2H), 1.71 – 1.61 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.37, 141.38, 138.30, 129.82, 128.50, 128.45, 127.19, 126.03, 53.42, 36.85, 31.70, 21.64. **HRMS (ESI):** Calcd for $C_{24}H_{28}NO_2S$ $[M+H]^+$: 394.1835. Found: 394.1833.



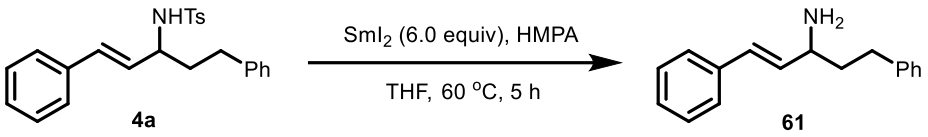
***N*-(1,2-Dibromo-1,5-diphenylpentan-3-yl)-4-methylbenzenesulfonamide (59):** According to the literature.[27] A mixture of HBr (48 % wt in H_2O, 1.5 mL, 1.0 equiv) and **4a** (39.2 mg, 0.1 mmol, 1.0 equiv) was stirred for 10 min. Next, the water was evaporated under reduced pressure, and the residue was dissolved in 2.0 mL DCM, dried over Na_2SO_4, and filtered into a 5.0 mL flask. The flask was cooled to 0 °C, and a solution of Br_2 (6.5 μL, 0.2 mmol, 1.2 equiv) in DCM (1.0 mL) was added dropwise at 0 °C and allowed to warm to room temperature. The reaction flask was covered in foil and stirred overnight. The reaction mixture was quenched with aqueous $NaHSO_3$ and basified with 20 % KOH until pH = 9. The aqueous layer was extracted with DCM

and the organic and aqueous layers were separated, dried with Na_2SO_4, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (PE:EA = 10:1, R_f = 0.2) to give product **59** as a white solid (42.7 mg, 77 %, 1:2:3.6 dr.). **M.P.**: 107-108 ℃. **IR (neat):** 3258, 2922, 2360, 1323, 1155, 1089, 1065, 814, 765, 748, 694, 662**. ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 – 7.82 (m, 1.57H), 7.65 – 7.52 (m, 0.68H), 7.46 – 7.40 (m, 0.72H), 7.38 – 7.27 (m, 6H), 7.24 – 7.10 (m, 5H), 7.07 – 7.01 (m, 0.72H), 6.86 (d, *J* = 6.0 Hz, 0.44H), 6.80 – 6.73 (m, 0.18H), 5.24 – 5.18 (m, 0.19H), 5.08 – 4.97 (m, 0.41H), 4.94 – 4.85 (m, 1.05H), 4.84 – 4.78 (m, 0.31H), 4.78 – 4.66 (m, 0.52H), 4.59 – 4.52 (m, 0.48H), 4.31 – 4.15 (m, 1.10H), 3.28 – 3.16 (m, 0.20H), 2.92 – 2.79 (m, 0.42H), 2.67 – 2.59 (m, 1H), 2.52 (s, 0.91H), 2.48 – 2.42 (m, 2.25H), 2.35 – 2.24 (m, 0.31H), 2.04 – 1.75 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.07, 143.86, 143.72, 141.09, 140.19, 140.07, 139.59, 139.48, 138.41, 138.13, 137.85, 130.12, 129.88, 129.82, 129.35, 129.24, 129.11, 129.09, 129.01, 128.87, 128.78, 128.66, 128.57, 128.55, 128.52, 128.42, 128.16, 127.89, 127.85, 127.48, 127.44, 127.35, 126.95, 126.32, 126.19, 116.89, 63.25, 62.63, 60.98, 56.57, 55.95, 54.87, 54.21, 53.53, 52.76, 37.05, 36.21, 32.17, 31.74, 31.71, 31.67, 21.63, 21.57. **HRMS (ESI):** Calcd for $C_{24}H_{26}Br_2NO_2S$ $[M+H]^+$: 550.0046. Found: 550.0056.

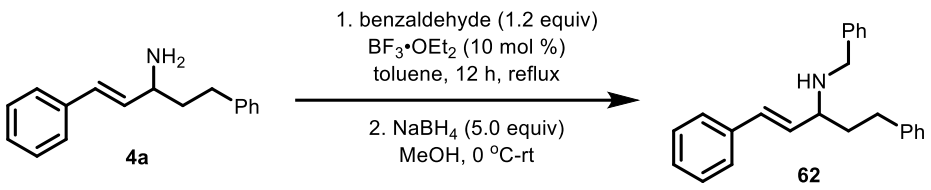


4-Methyl-*N*-(3-phenyl-1-(3-phenyloxiran-2-yl)propyl)benzenesulfonamide (60): According to the literature.[26] To a stirred solution of **4a** (39.2 mg, 0.1 mmol, 1.0 equiv) in DCM (2.0 mL), *m*-CPBA (85% content, 31 mg, 0.15 mmol, 1.5 equiv) was added at rt. After being stirred for 24 h, the reaction mixture was poured into saturated $NaHCO_3$ with DCM. The aqueous layer was extracted with DCM. The combined extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE:EA = 10:1, R_f = 0.3) to give product **60** (31.1 mg, 76 %, 7:3 dr.) as a white solid. **M.P.**: 116-117 ℃. **IR (neat):** 2922, 2360,

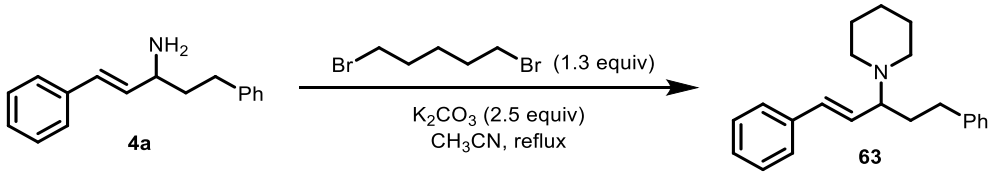
1330, 1275, 1152, 1088, 749, 696, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 – 7.73 (m, 2H), 7.33 – 7.18 (m, 8H), 7.13 – 7.04 (m, 4H), 5.24 (d, *J* = 7.5 Hz, 0.3H), 5.01 (d, *J* = 8.9 Hz, 0.7H), 3.79 – 3.71 (m, 0.67H), 3.70 (d, *J* = 1.8 Hz, 0.32H), 3.61 (d, *J* = 1.8 Hz, 0.72H), 3.26 – 3.13 (m, 0.33H), 3.01 (t, *J* = 2.1 Hz, 0.68H), 2.89 (dd, *J* = 7.0, 1.9 Hz, 0.32H), 2.73 – 2.53 (m, 2H), 2.44 (s, 2.13H), 2.38 (s, 0.87H), 2.07 – 1.79 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.67, 143.59, 140.89, 138.23, 137.81, 136.38, 136.21, 133.48, 133.37, 130.50, 130.37, 129.96, 129.85, 128.57, 128.55, 128.47, 128.42, 128.39, 128.35, 127.12, 127.08, 126.20, 126.16, 125.82, 125.71, 63.81, 63.64, 58.49, 55.76, 55.05, 52.31, 35.27, 34.25, 31.64, 31.40, 21.65, 21.64. **HRMS (ESI):** Calcd for $C_{24}H_{26}NO_3S$ $[M+H]^+$: 408.1628. Found: 408.1629.



(*E*)-1,5-Diphenylpent-1-en-3-amine (61): According to the literature.[28] **4a** (39.2 mg, 0.1 mmol, 1.0 equiv) in dry THF was added to a 0.1 M THF solution of SmI_2 (6 mL, 0.6 mmol, 6.0 equiv) and HMPA (0.5 mL) at rt. The solution was heated at 60 ºC for 5 h until the purple color of the solution disappeared. The reaction was cooled to rt and quenched with saturated aqueous NaCl (10 mL) and extracted with ethyl acetate (3 ×15 mL). The organic layer was washed with brine (3 × 10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE:EA = 2:1 (with drops of Et_3N), R_f = 0.1) to give product **61** (16.6 mg, 70 %) as a colorless oil. **IR (neat):** 3024, 2922, 2853, 2360, 1494, 1452, 964, 746, 691**. ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.17 (m, 4H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.8, 7.4 Hz, 1H), 3.51 (q, *J* = 13.5, 6.7 Hz, 1H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.78 (brs, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.08, 137.18, 134.59, 129.70, 128.70, 128.54, 128.52, 127.54, 126.42, 125.96, 53.87, 39.47, 32.62. **HRMS (ESI):** Calcd for $C_{17}H_{20}N$ $[M+H]^+$: 238.1590. Found: 238.1589.

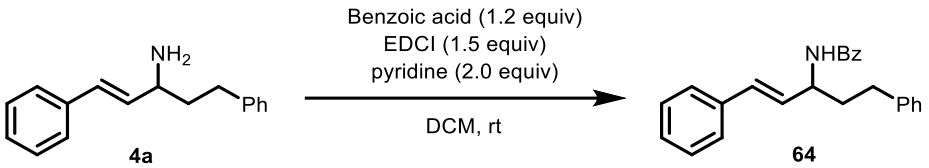


(*E*)-*N*-Benzyl-1,5-diphenylpent-1-en-3-amine (62): According to the literature[29] To a mixture of **61** (17.5 mg, 0.073 mmol, 1.0 equiv) and benzaldehyde (9.3 mg, 0.088 mmol, 1.2 equiv) in toluene (2.0 mL) was slowly added boron trifluoride diethyl ether complex (1 μL, 0.0073 mmol, 10 mol%), the mixture was stirred at 110 °C for 12 h. After cooling to room temperature, the mixture was quenched with 1.0 M aq. NaOH and extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Then the residue was diluted with MeOH, and $NaBH_4$ (13.8 mg, 0.36 mmol, 5.0 equiv) was added at 0 °C. The mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with DCM (3 ×15 mL). The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 5:1, R_f = 0.2) to afford the product **62** (9.1 mg, 38 %) as a colorless oil. **IR (neat):** 3024, 2922, 2360, 1493, 1452, 1260, 966, 744, 692. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.31 (m, 5H), 7.30 – 7.23 (m, 5H), 7.21 – 7.16 (m, 3H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.09 (dd, *J* = 15.9, 8.4 Hz, 1H), 3.87 (d, *J* = 13.2 Hz, 1H), 3.70 (d, *J* = 13.2 Hz, 1H), 3.33 – 3.22 (m, 1H), 2.75 – 2.63 (m, 2H), 1.98 – 1.83 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.22, 140.70, 137.16, 132.85, 131.91, 128.73, 128.54, 128.48, 128.33, 127.58, 127.02, 126.47, 125.90, 60.32, 51.49, 37.77, 32.45. **HRMS (ESI):** Calcd for $C_{24}H_{26}N$ $[M+H]^+$: 328.2060. Found: 328.2058.



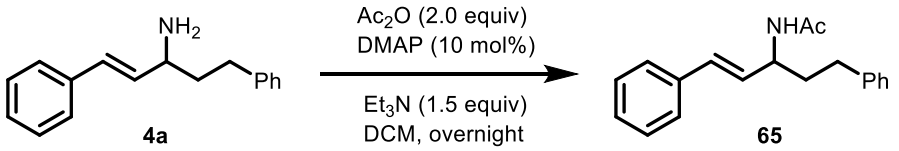
(*E*)-1-(1,5-Diphenylpent-1-en-3-yl)piperidine (63): According to the literature[30] A mixture of **61** (17.9 mg, 0.075 mmol, 1.0 equiv), 1,5-dibromopentane (13.3 μL, 0.098

mmol, 1.3 equiv) and K_2CO_3 (26.1 mg, 0.189 mmol, 2.5 equiv) in acetonitrile (2.0 mL) was reflux for 24 h, and then it was cooled to room temperature. Most of the acetonitrile was removed by rotary evaporation. The residue was diluted with ethyl acetate and then washed with 1.0 M aq. NaOH. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash column chromatography (PE:EA = 10:1, R_f = 0.3) to afford the product **63** (16.7 mg, 73 %) as a yellow oil. **IR (neat):** 2929, 2360, 1600, 1494, 1451, 968, 745, 692, 668. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.26 (m, 4 H), 7.25 – 7.12 (m, 4 H), 6.45 (d, *J* = 15.9 Hz, 1 H), 6.22 (dd, *J* = 15.9, 9.0 Hz, 1 H), 3.00 – 2.91 (m, 1 H), 2.75 – 2.55 (m, 4 H), 2.53 – 2.39 (m, 2 H), 2.14 – 2.03 (m, 1 H), 1.90 – 1.79 (m, 1 H), 1.65 – 1.52 (m, 4 H), 1.47 – 1.38 (m, 2 H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.57, 137.19, 132.83, 129.76, 128.70, 128.60, 128.40, 127.48, 126.42, 125.79, 67.79, 50.88, 34.34, 32.97, 26.54, 24.91. **HRMS (ESI):** Calcd for $C_{22}H_{28}N$ $[M+H]^+$: 306.2216. Found: 306.2212.



(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)benzamide (64): According to the literature[31] To a solution of **61** (16.4 mg, 0.069 mmol, 1.0 equiv) in DCM (2.0 mL), benzoic acid (10.2 mg, 0.083 mmol, 1.2 equiv), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 19.9 mg, 0.10 mmol, 1.5 equiv) and pyridine (11 μL, 0.14 mmol, 2.0 equiv) was added. The reaction mixture was stirred at room temperature for 6 h. Water (10 mL) was added and the aqueous phase was extracted with DCM (3 ×15 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (PE:EA = 2:1 (with drops of Et_3N), R_f = 0.3) to afford the product **64** (18.1 mg, 77 %) as a white solid. **M.P.**: 190-191 °C. **IR (neat):** 3243, 2921, 2360, 1628, 1532, 1488, 1313, 958, 747, 695, 668**. ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.45 – 7.27 (m, 8H), 7.25 – 7.14 (m, 4H), 6.60 (d, *J* =

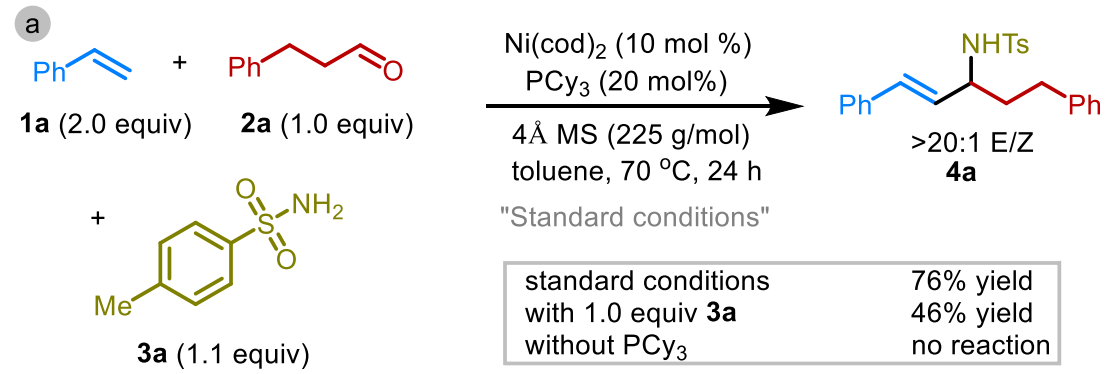
15.9 Hz, 1H), 6.31 – 6.11 (m, 2H), 5.09 – 4.77 (m, 1H), 2.86 – 2.71 (m, 2H), 2.09 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.81, 141.61, 136.68, 134.65, 131.63, 131.20, 129.54, 128.71, 128.69, 128.56, 127.84, 127.03, 126.56, 126.19, 51.54, 36.87, 32.45. **HRMS (ESI):** Calcd for $C_{24}H_{24}NO$ $[M+H]^+$: 342.1852. Found: 342.1853.

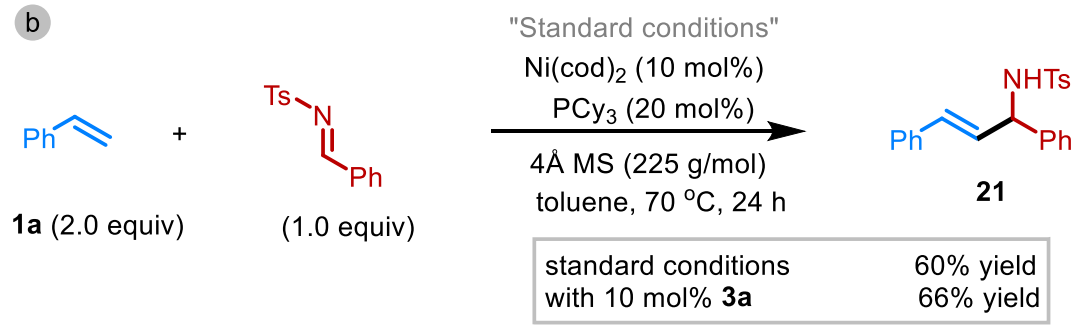


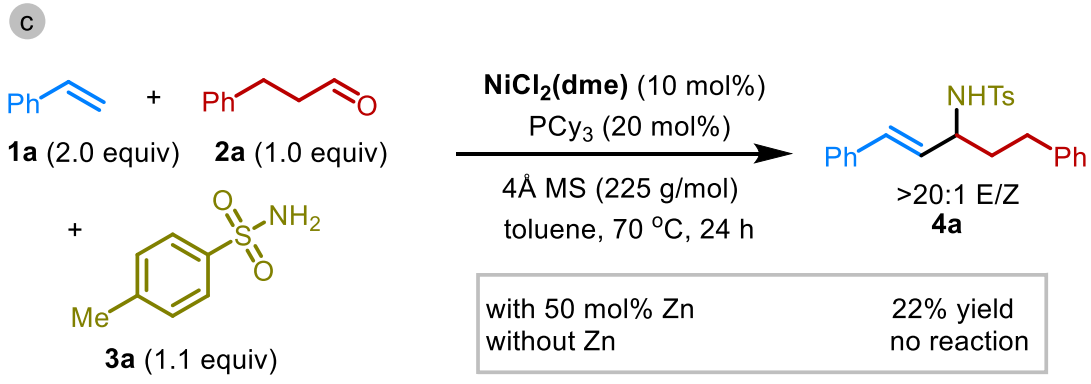
(*E*)-*N*-(1,5-Diphenylpent-1-en-3-yl)acetamide (65): According to the literature.[32] To a solution of **61** (16.6 mg, 0.07 mmol, 1.0 equiv) in DCM, DMAP (0.9 mg, 0.007 mmol, 10 mol%), Et_3N (15 μL, 0.11 mmol, 1.5 equiv) and Ac_2O (13 μL, 0.14 mmol, 2.0 equiv) was added. The resulting mixture was stirred overnight and then was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (PE:EA = 2:1, R_f = 0.2) to give product **65** (14.1 mg, 72 %) as a white solid. **M.P.**: 120-122 ℃. **IR (neat):** 3245, 2360, 1635, 1547, 1494, 1453, 1374, 1305, 959, 746, 696**. ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 – 7.23 (m, 7H), 7.22 – 7.17 (m, 3H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.12 (dd, *J* = 15.9, 6.5 Hz, 1H), 5.59 (d, *J* = 8.5 Hz, 1H), 4.77 – 4.62 (m, 1H), 2.71 (t, J = 7.9 Hz, 2H), 1.99 (s, 3H), 1.98 – 1.91 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.44, 141.58, 136.68, 130.94, 129.63, 128.68, 128.60, 128.47, 127.79, 126.49, 126.13, 51.11, 36.87, 32.42, 23.63. **HRMS (ESI):** Calcd for $C_{19}H_{22}NO$ $[M+H]^+$: 280.1696. Found: 280.1693.

VII Control experiments

Some mechanism experiments were conducted to enhance the mechanistic understanding of the transformation. The results demonstrate that the reaction undergoes a process of oxidative cyclization of nickel(0) with olefins and in situ formed imines. And the excess trace amount of $TsNH_2$ can effectively promote the reaction.

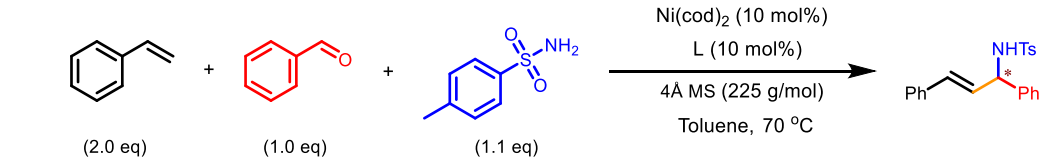






VIII. Exploration of asymmetric reactions

An array of chiral ligands were tested, only phosphoramidite ligands gave products, and very low yields and moderate enantioselectivity were obtained.



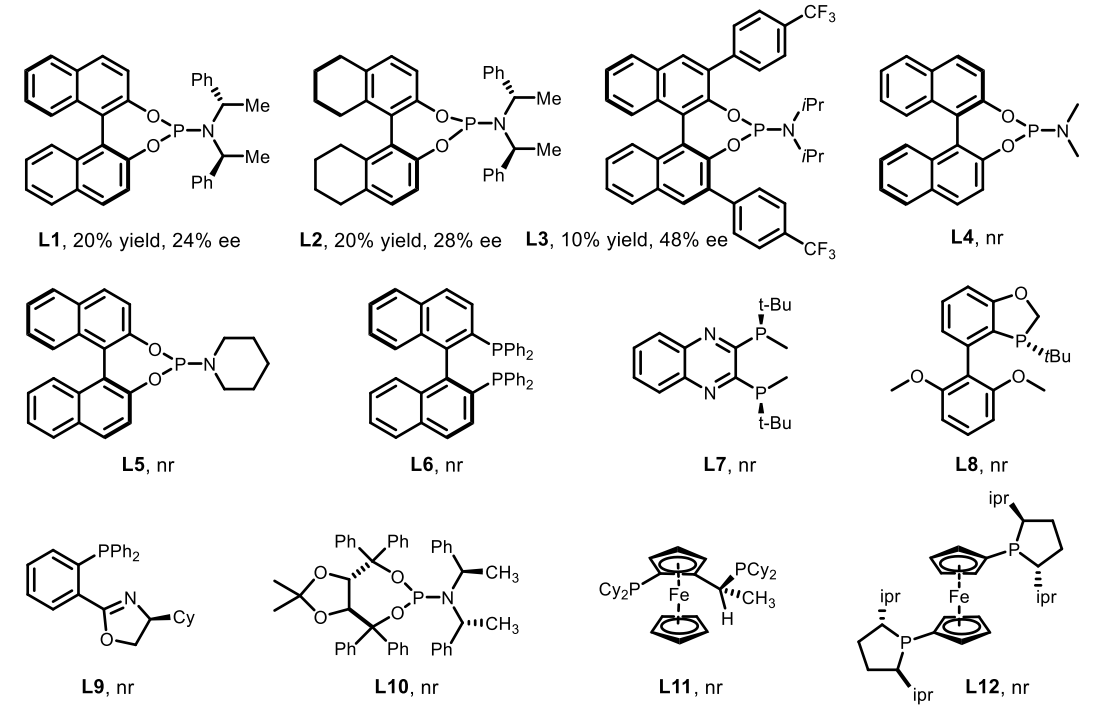


Figure S1. Initial attempt on Ni-catalyzed asymmetric three-component reaction. Reactions were performed with styrene (0.2 mmol, 2.0 equiv), benzaldehyde (0.1 mmol, 1.0 equiv), $TsNH_2$ (0.11 mmol, 1.1 equiv), $Ni(cod)_2$ (0.01 mmol, 10 mol%), Ligand (0.01 mmol, 10 mol%), and 4Å MS (22.5 mg, 225 g/mol) in toluene (0.5 mL) at 70 °C for 24 h. Enantiomeric excess (ee) was determined by HPLC on a chiral stationary phase. nr = no reaction.

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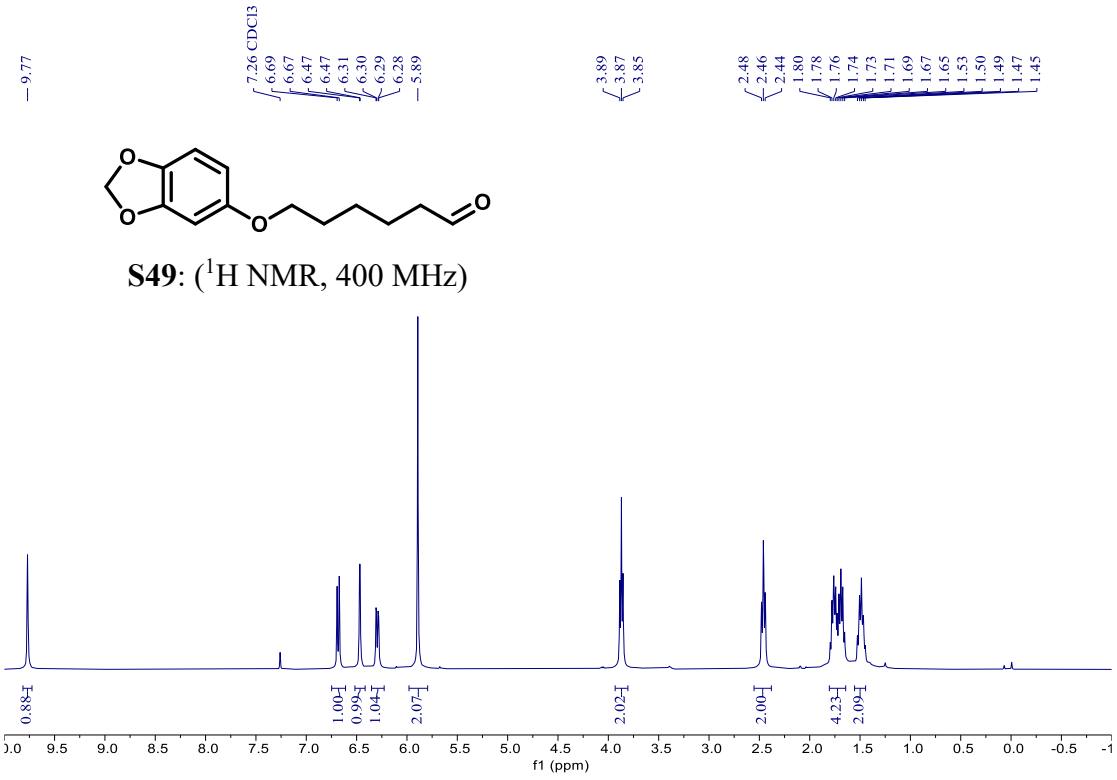
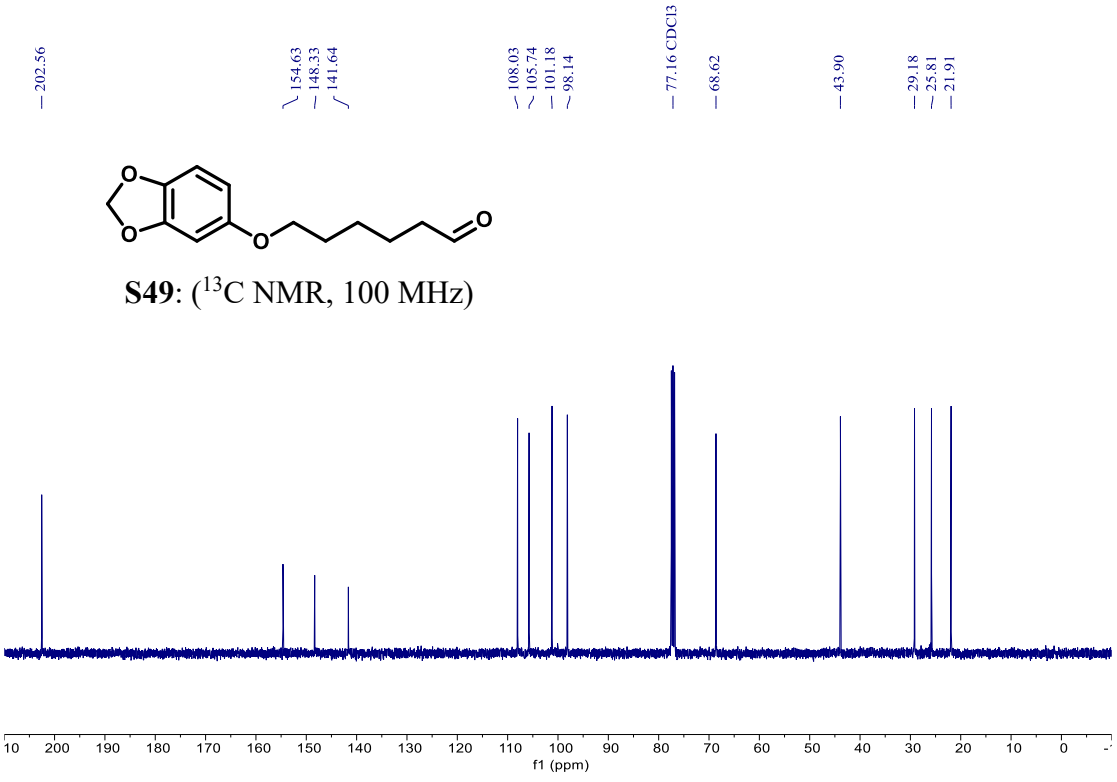
X NMR Spectra of New Compounds



S49: (^{1}H NMR, 400 MHz)



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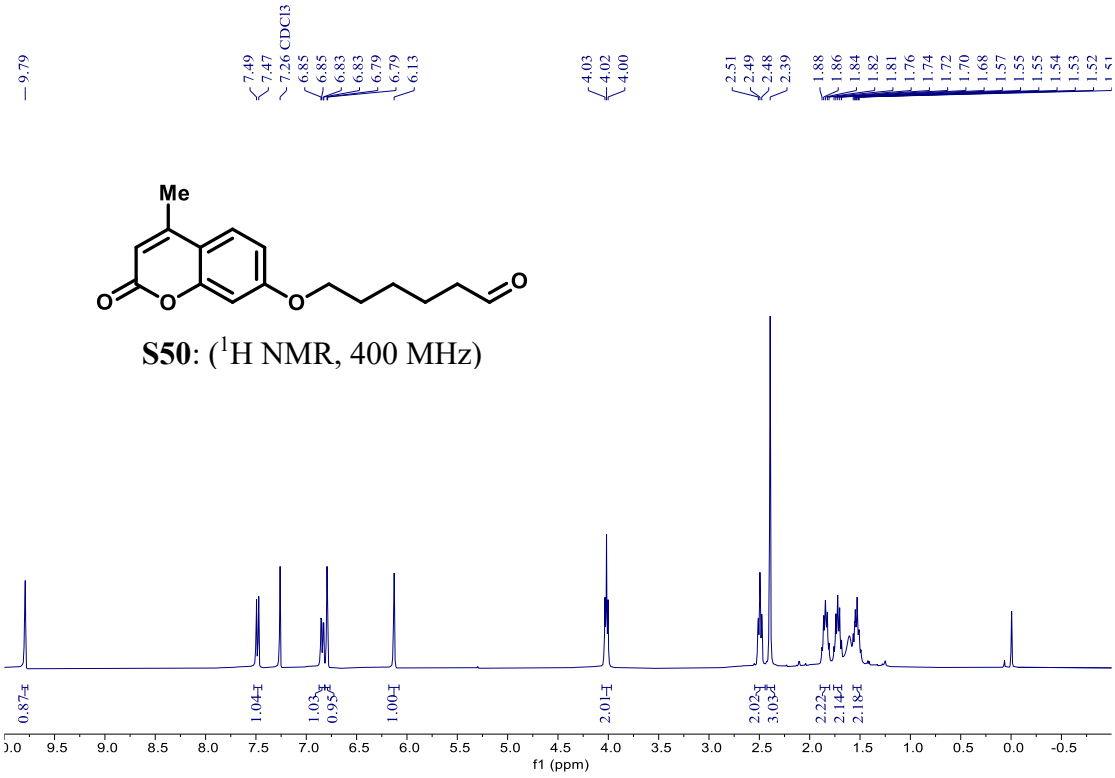

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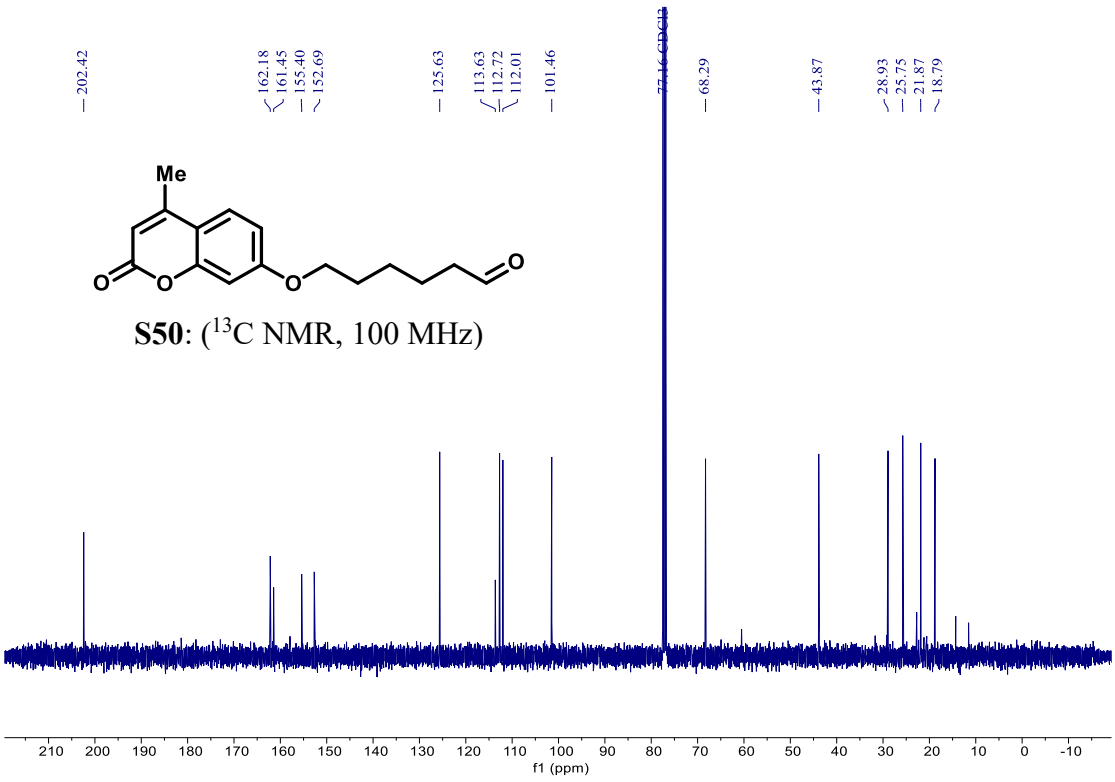

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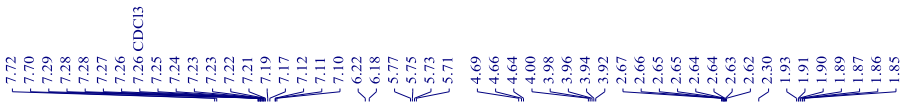

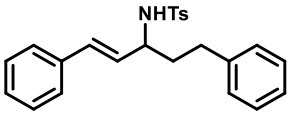

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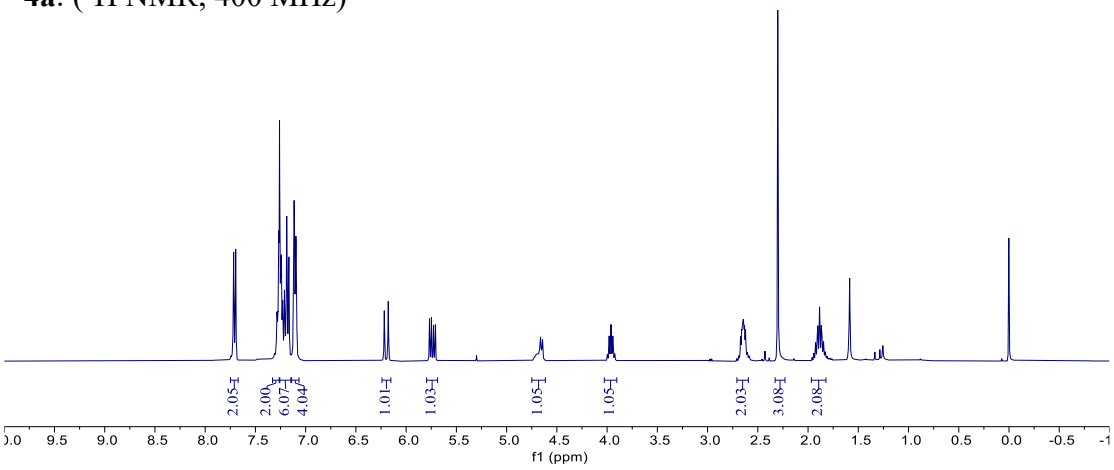

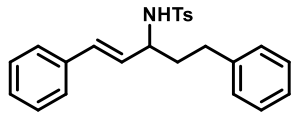

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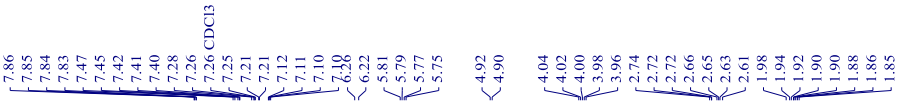

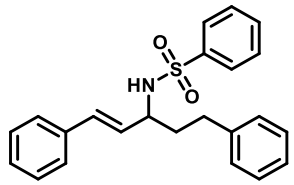

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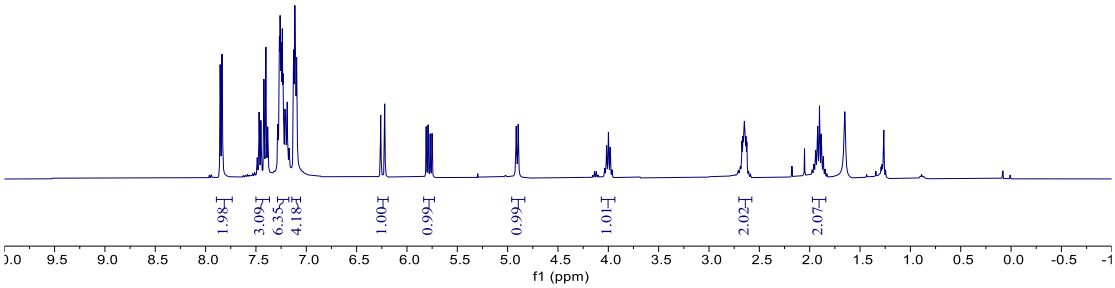
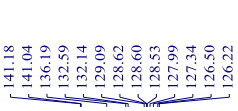
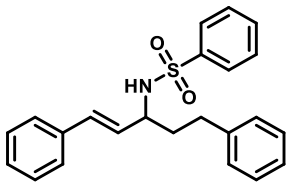
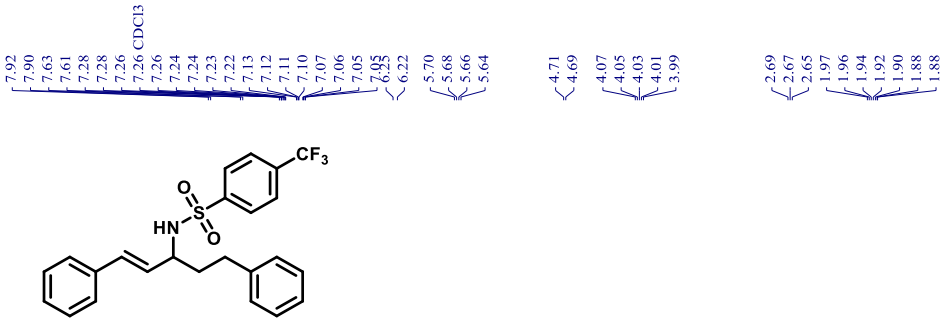


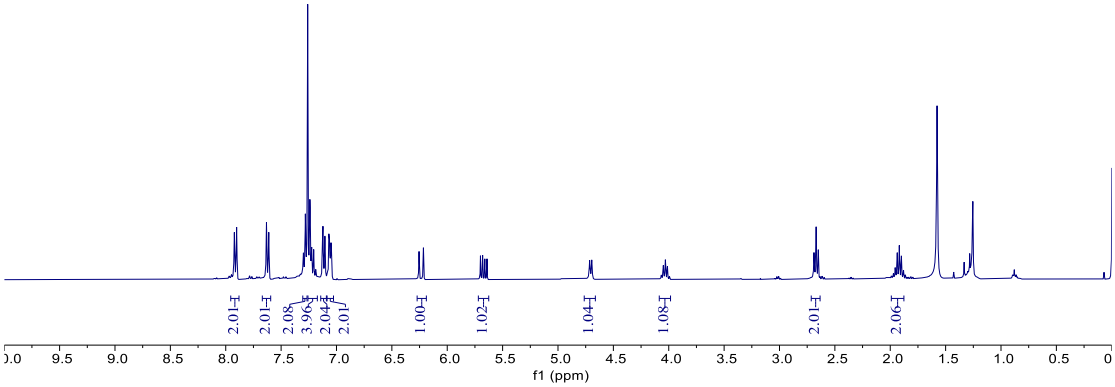


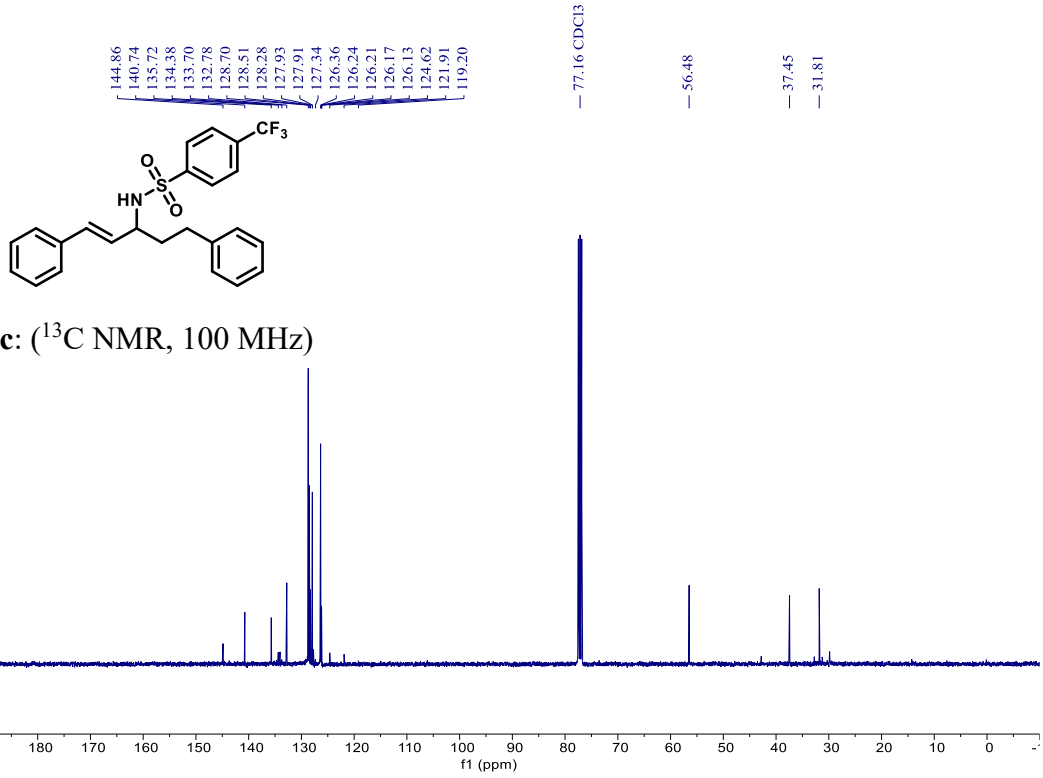


4b: (^{13}C NMR, 100 MHz)

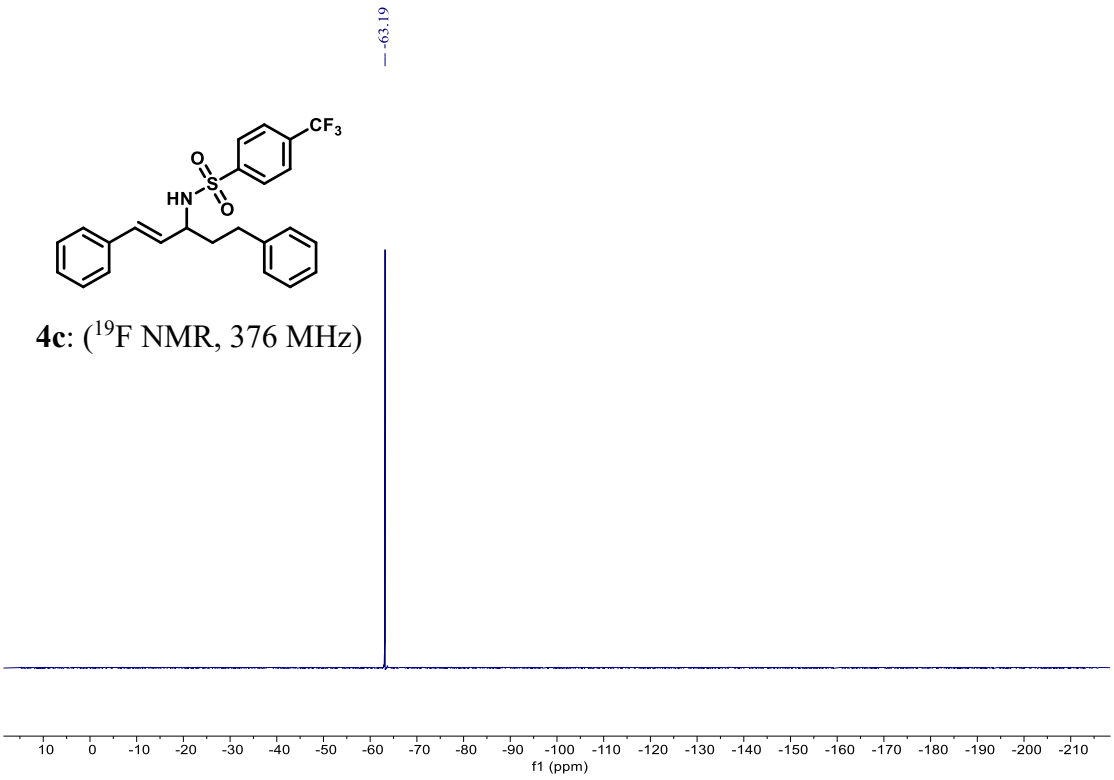


4c: (^{1}H NMR, 400 MHz)

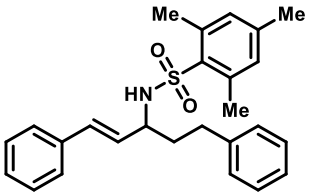




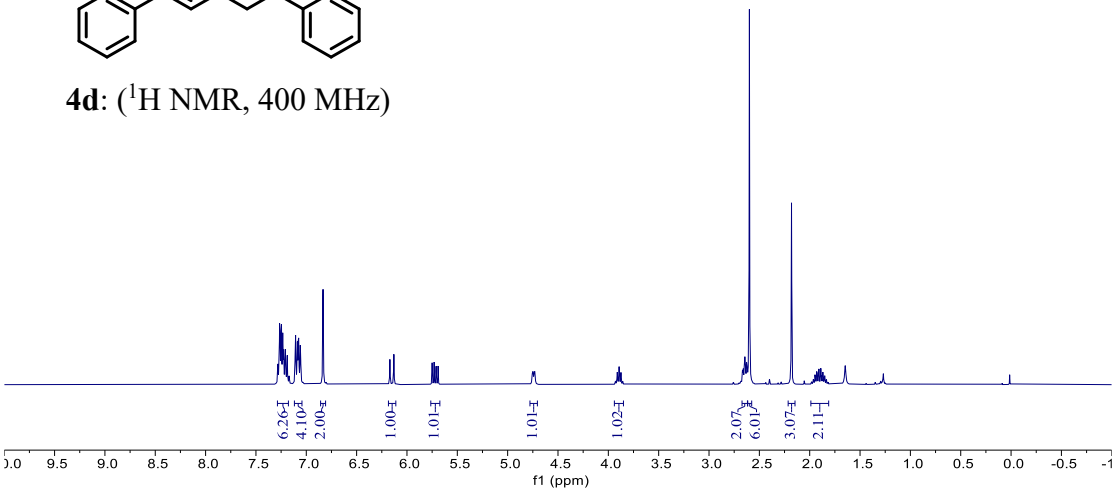
4c: (^{13}C NMR, 100 MHz)

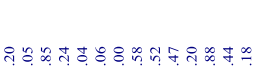


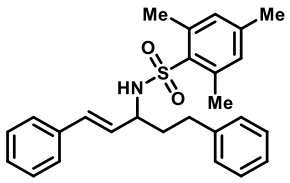
4c: (^{19}F NMR, 376 MHz)



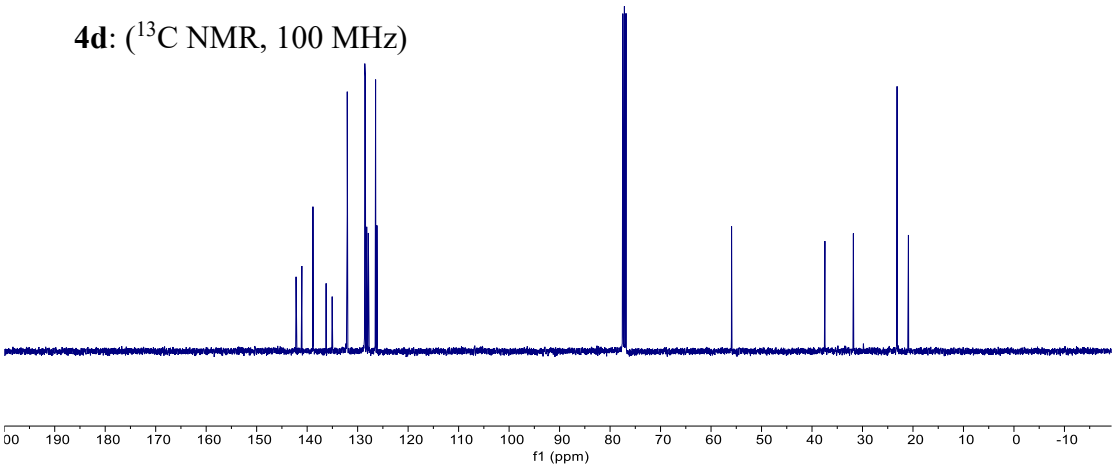
4d: (^{1}H NMR, 400 MHz)

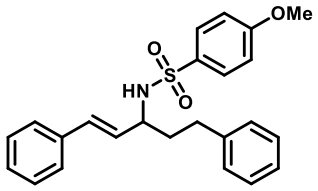




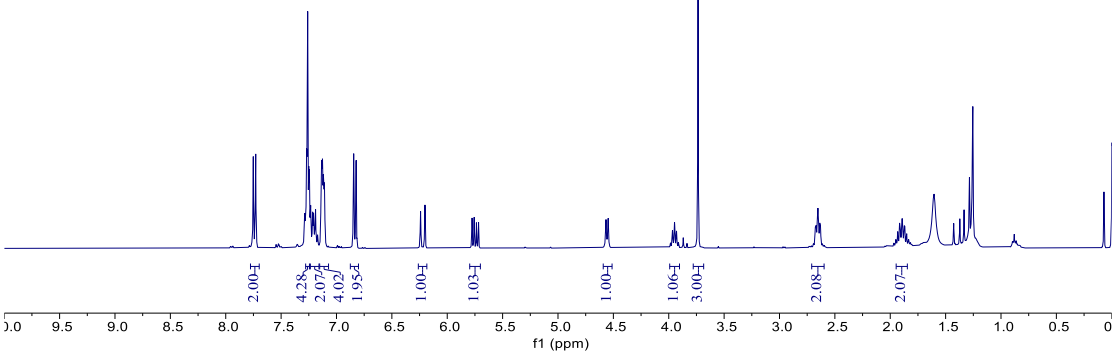


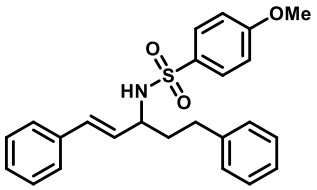
4d: (^{13}C NMR, 100 MHz)



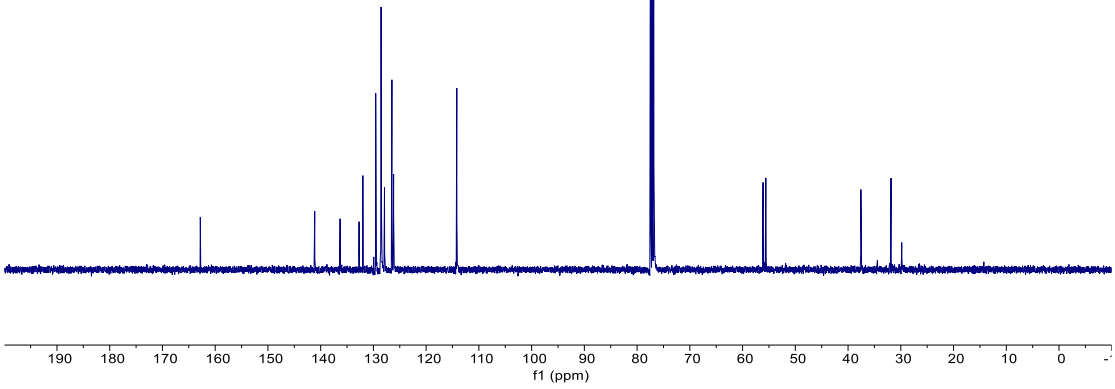


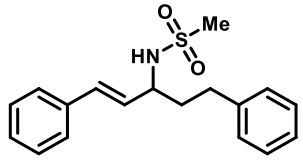
4e: (^{1}H NMR, 400 MHz)



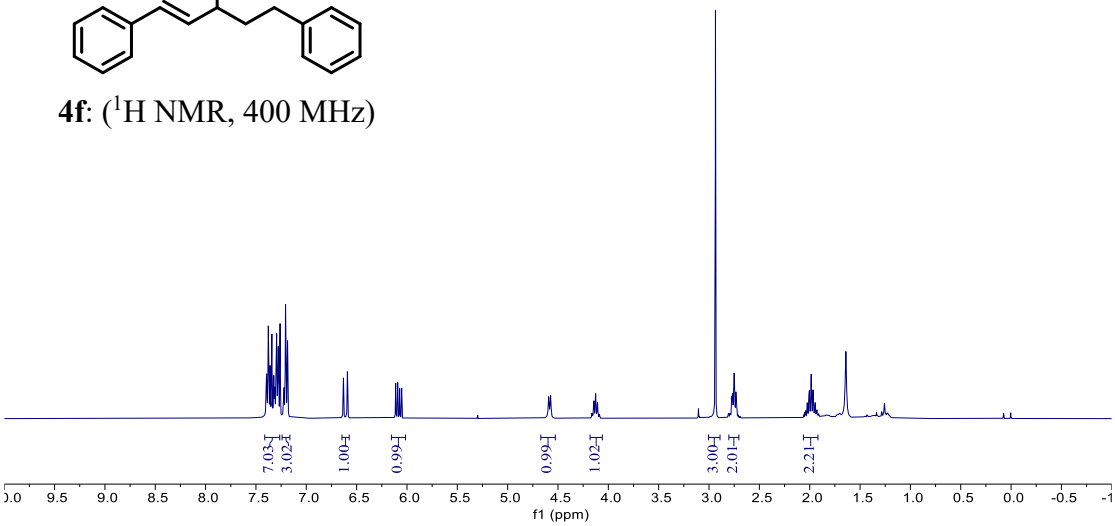


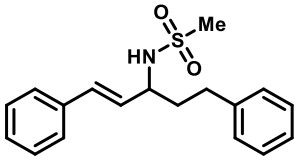
4e: (^{13}C NMR, 100 MHz)



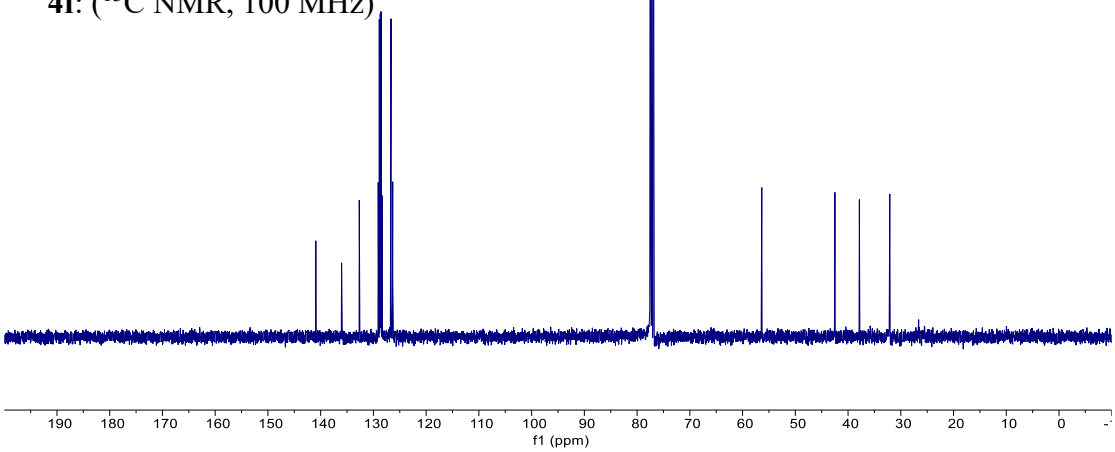


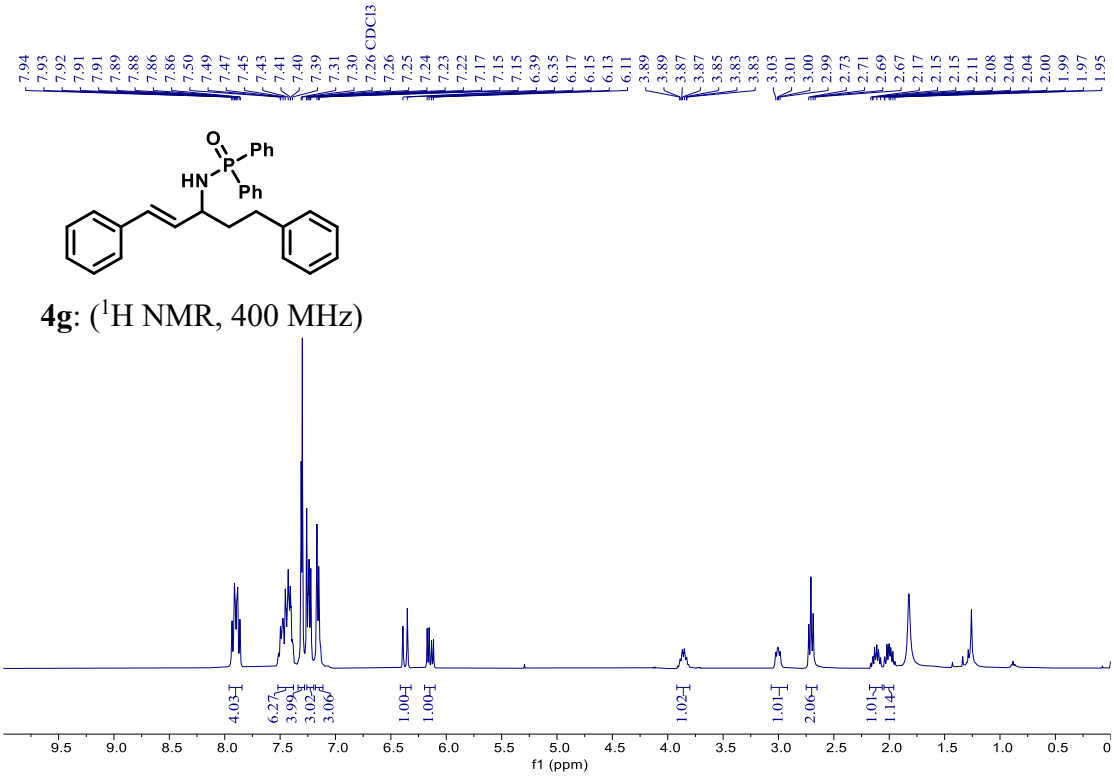
4f: (^{1}H NMR, 400 MHz)



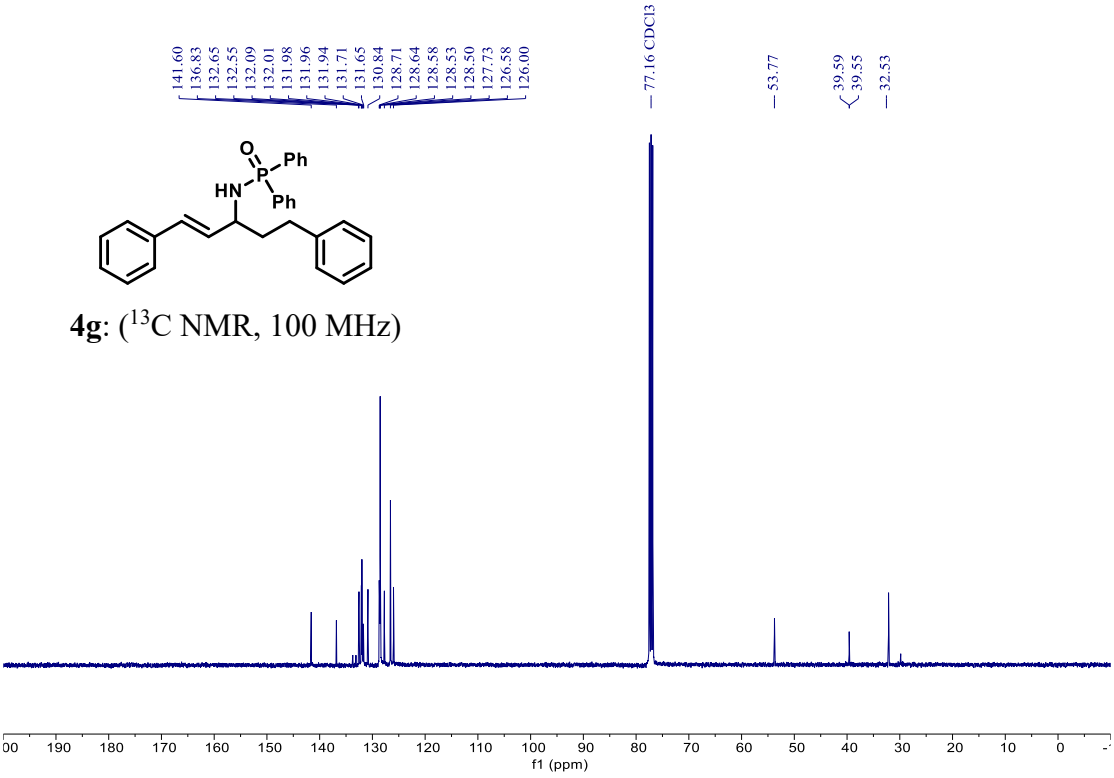


4f: (^{13}C NMR, 100 MHz)

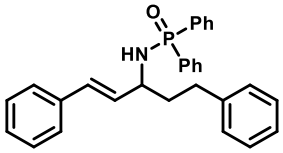




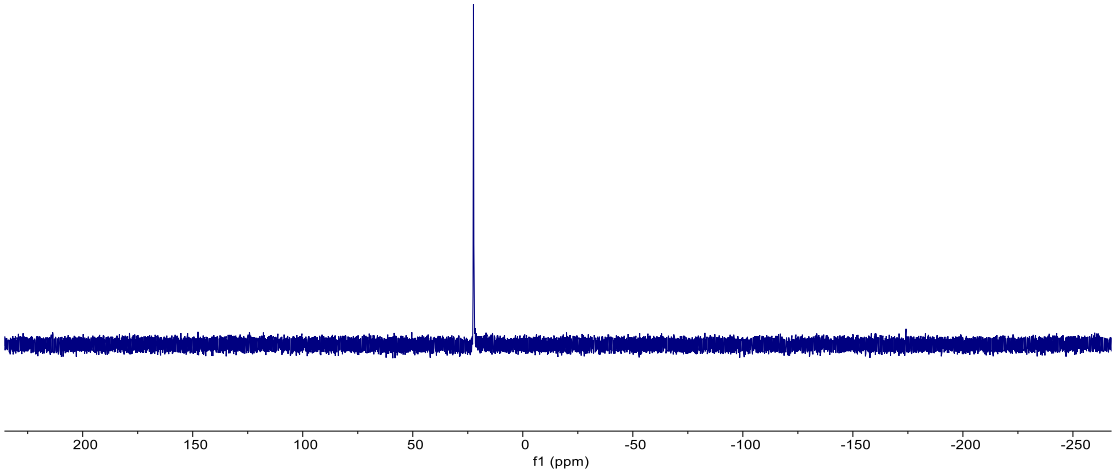
4g: (^{1}H NMR, 400 MHz)

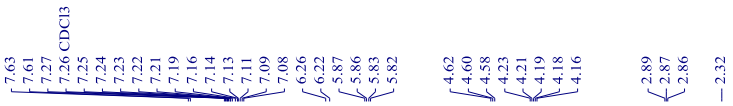


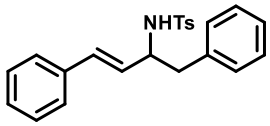
4g: (^{13}C NMR, 100 MHz)



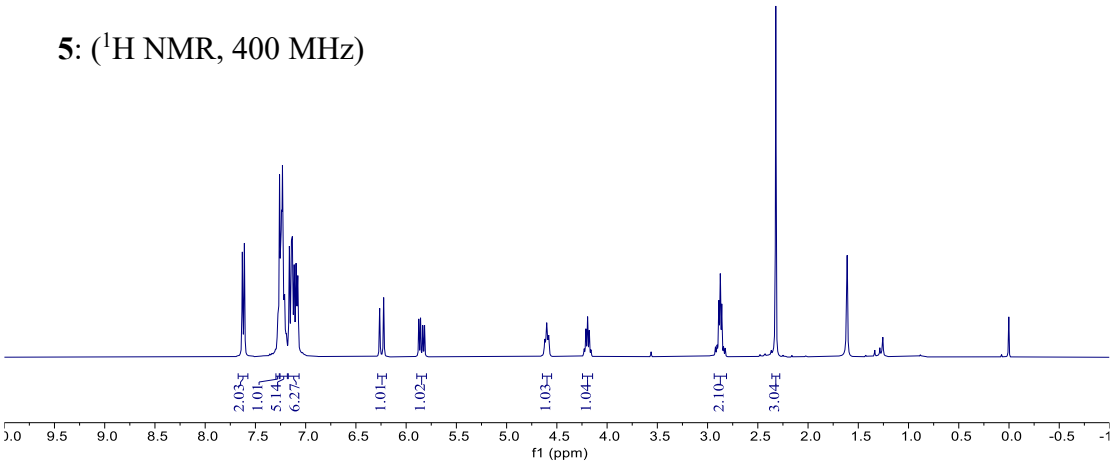
4g: (^{31}P NMR, 162 MHz)

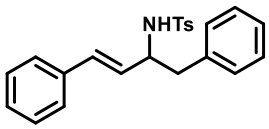




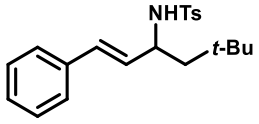


5: (^{1}H NMR, 400 MHz)

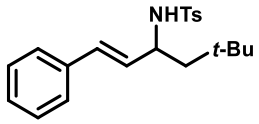




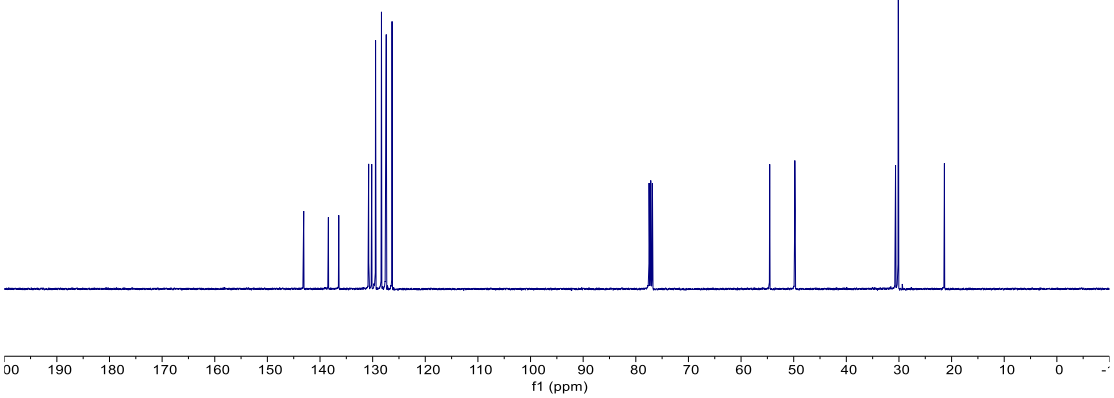
5: (^{13}C NMR, 100 MHz)

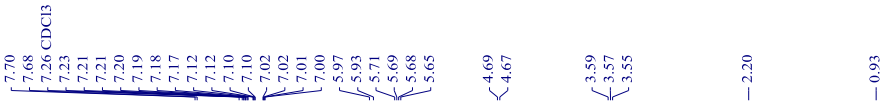


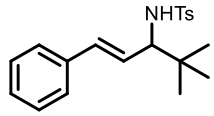
6: (^{1}H NMR, 400 MHz)



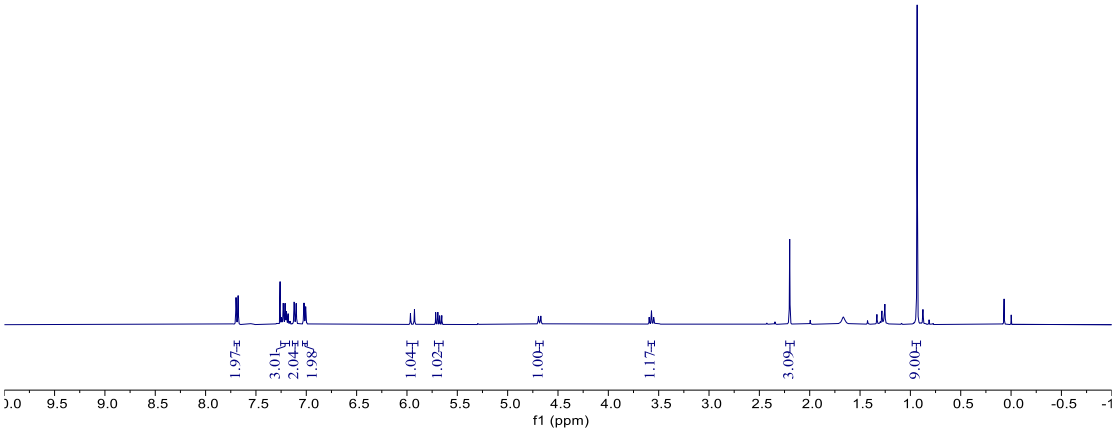
6: (^{13}C NMR, 100 MHz)

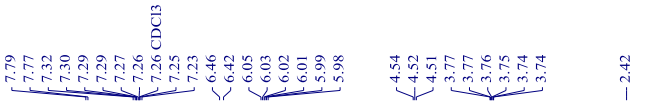


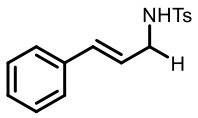




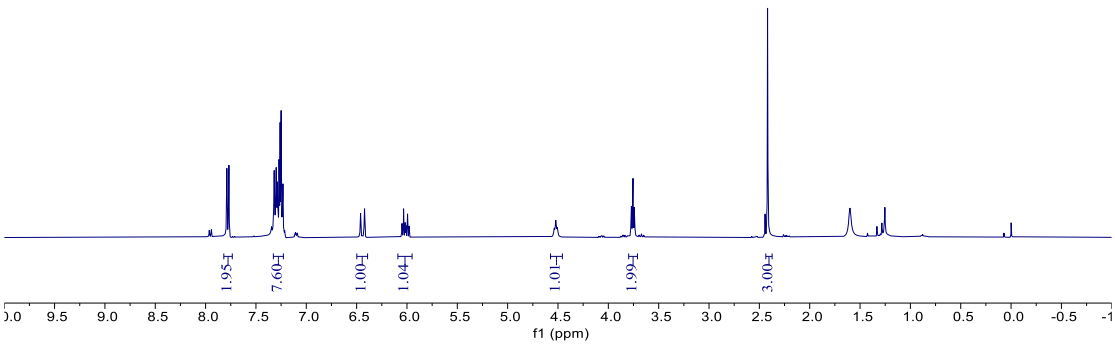
7: (^{1}H NMR, 400 MHz)

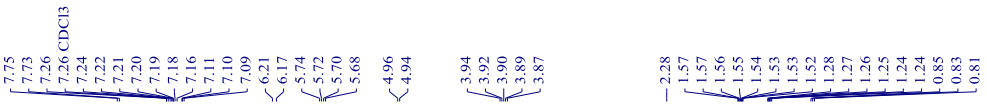


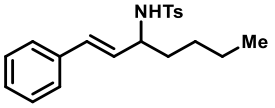




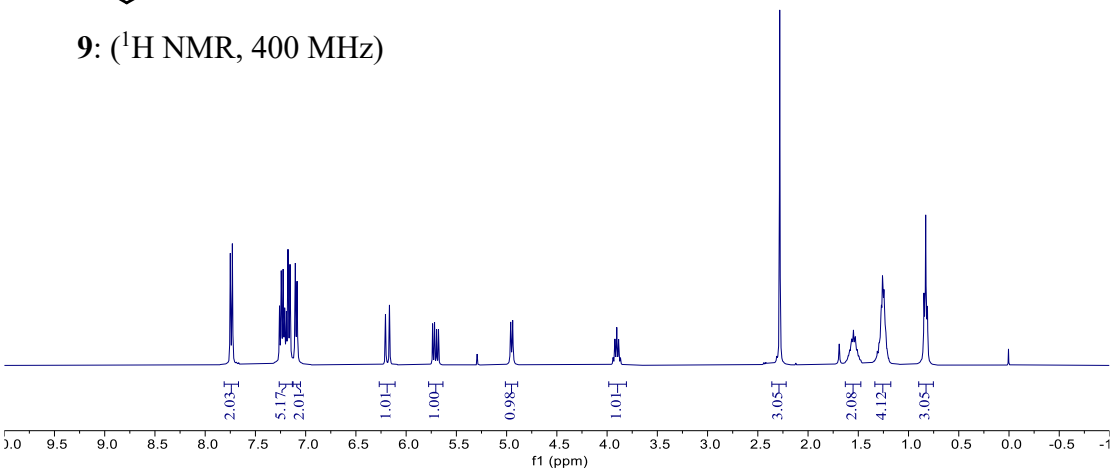
8: (^{1}H NMR, 400 MHz)

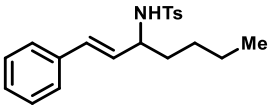




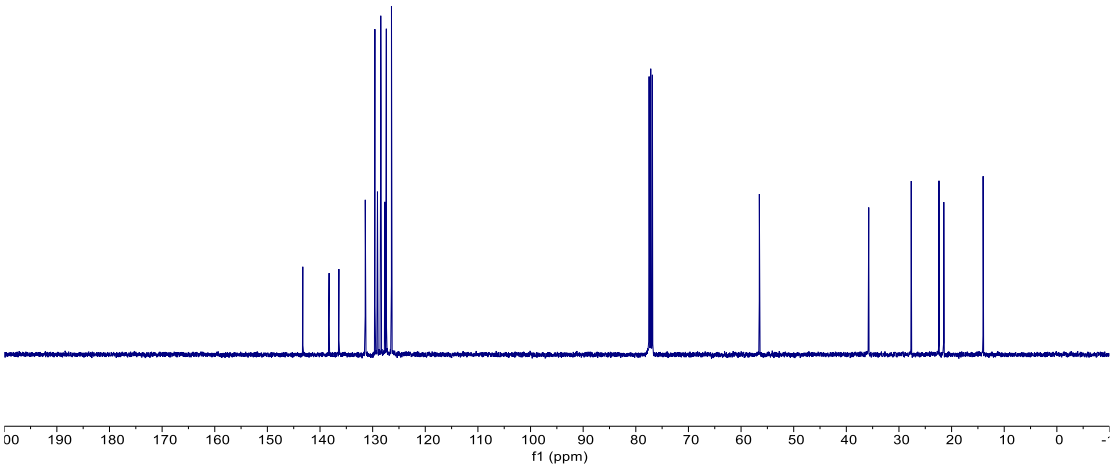


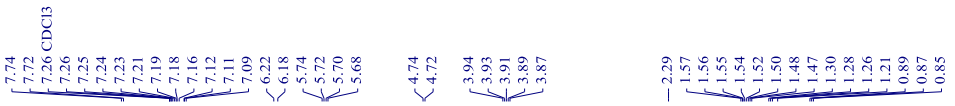
9: (^{1}H NMR, 400 MHz)

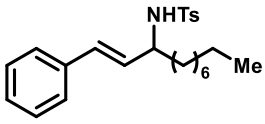




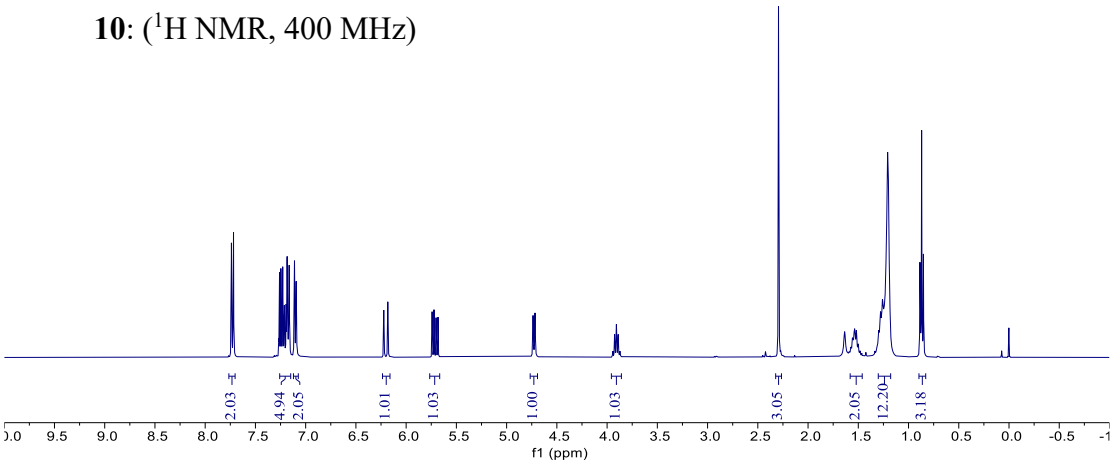
9: (^{13}C NMR, 100 MHz)

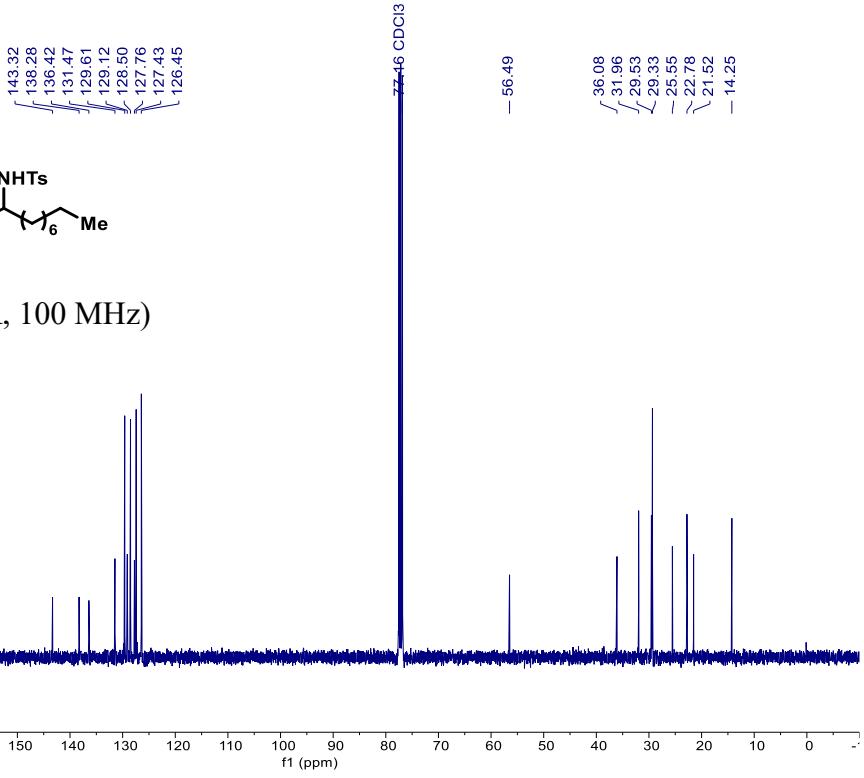


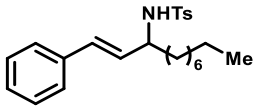




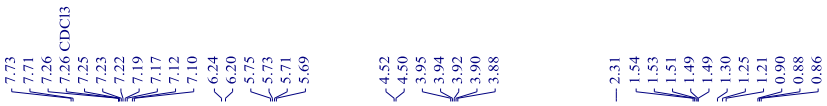
10: (^{1}H NMR, 400 MHz)

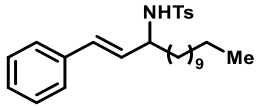




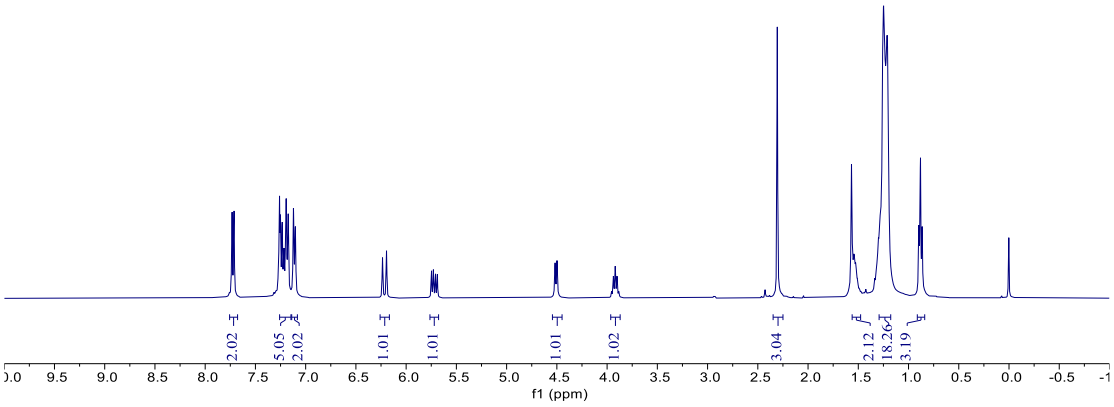


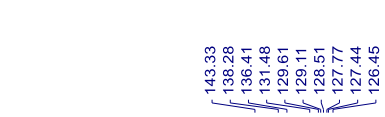
10: (^{13}C NMR, 100 MHz)



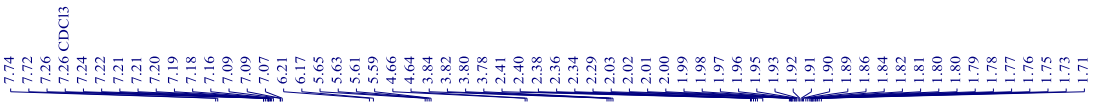


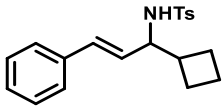
11: (^{1}H NMR, 400 MHz)



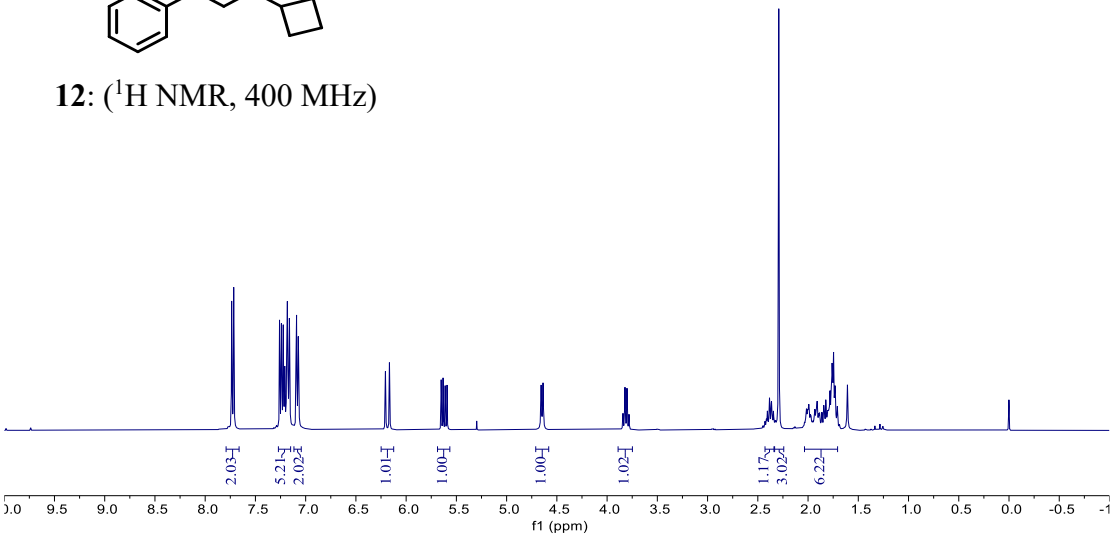


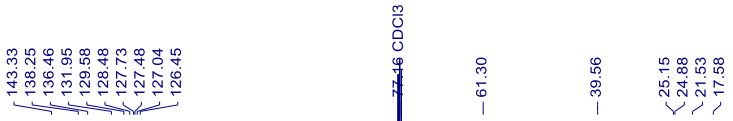
11: (^{13}C NMR, 100 MHz)

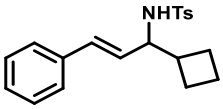




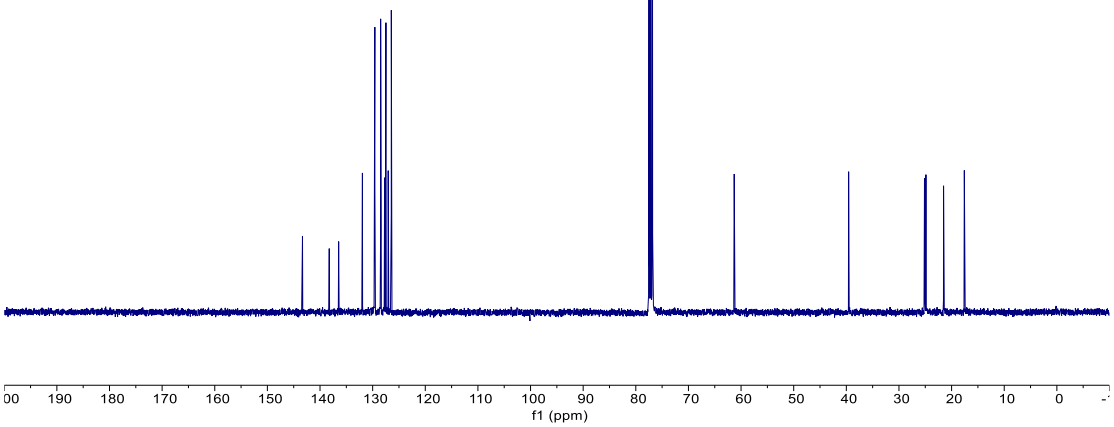
12: (^{1}H NMR, 400 MHz)

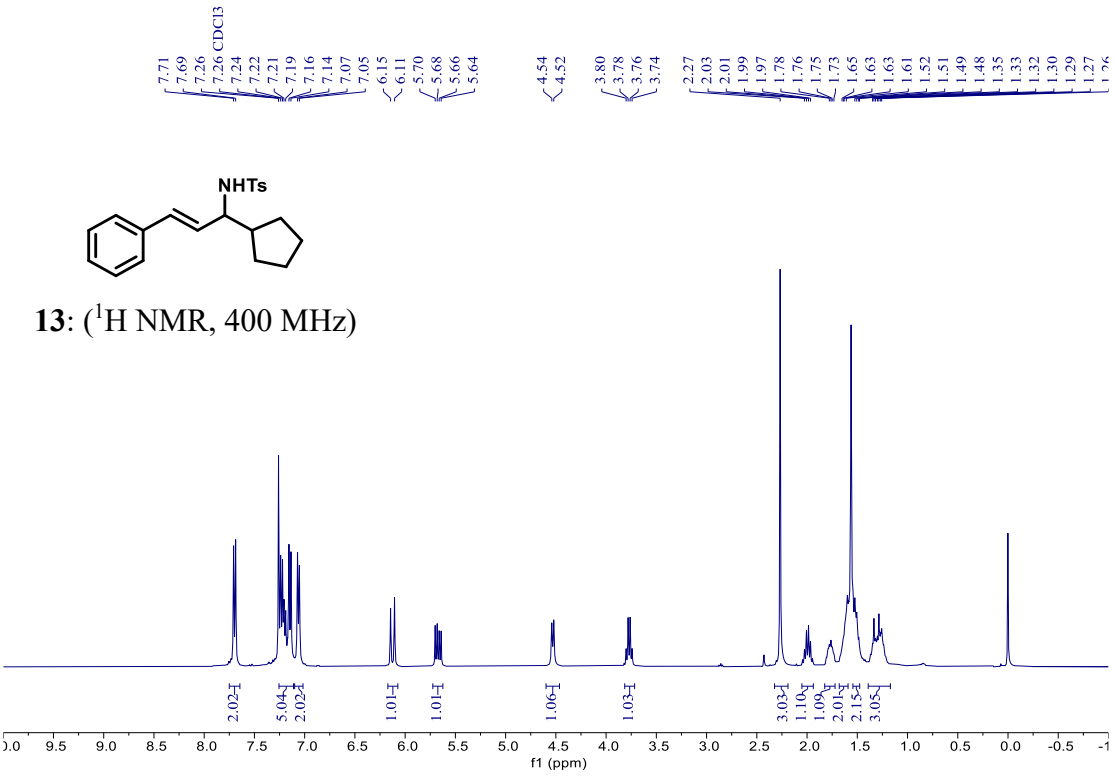




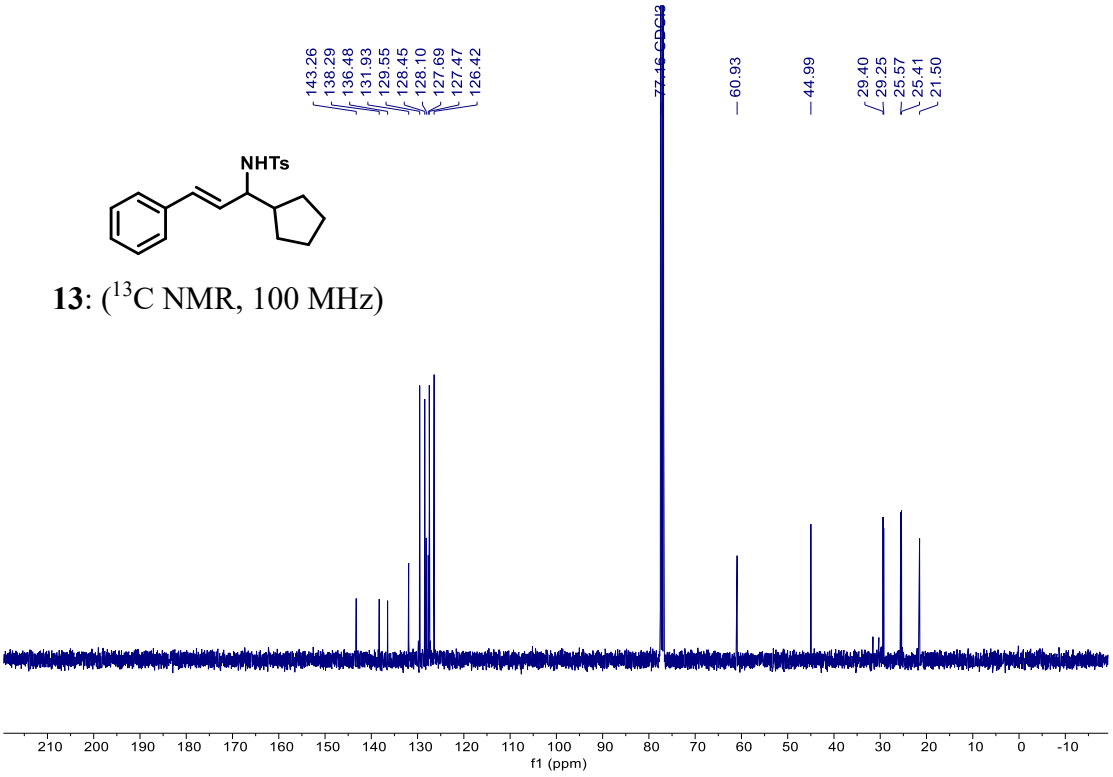


12: (^{13}C NMR, 100 MHz)

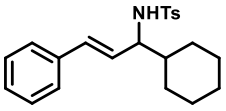




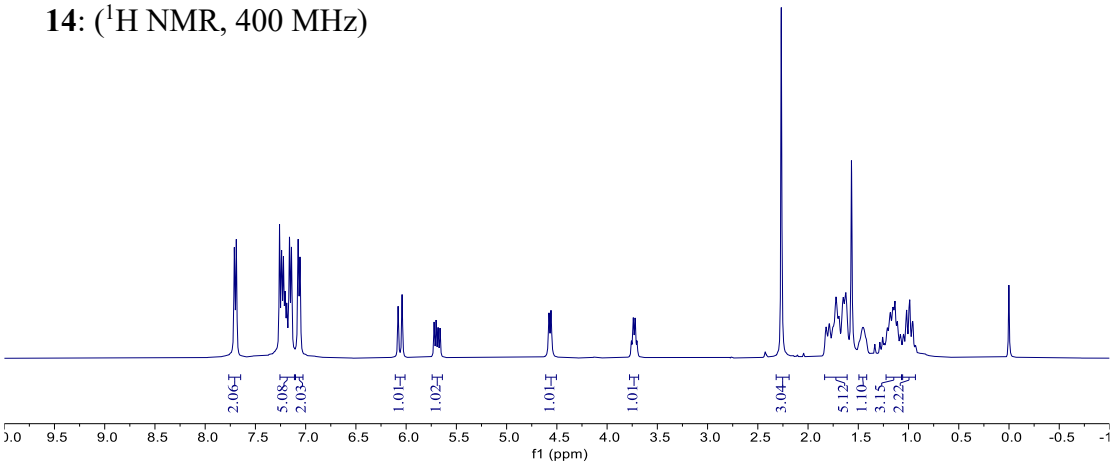
13: (^{1}H NMR, 400 MHz)

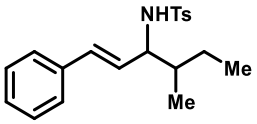


13: (^{13}C NMR, 100 MHz)



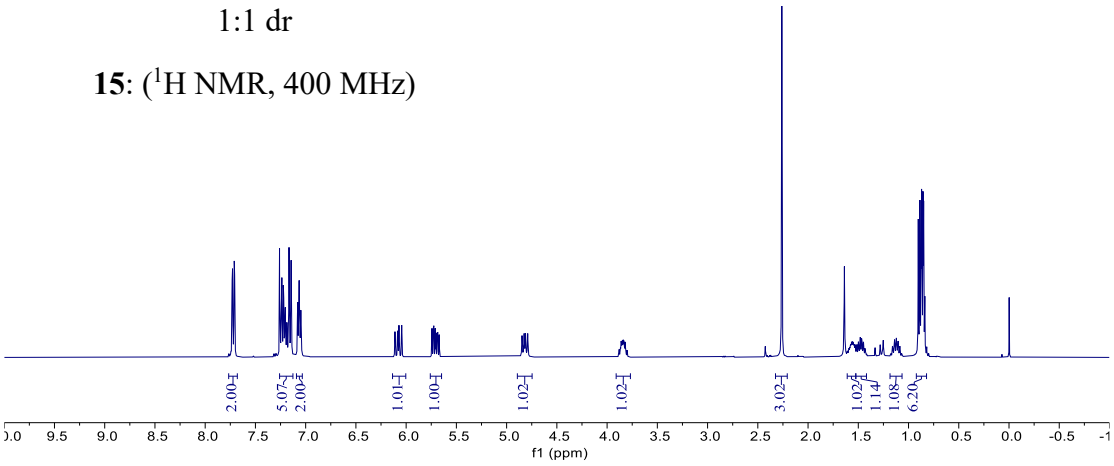
14: (^{1}H NMR, 400 MHz)

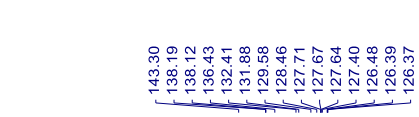


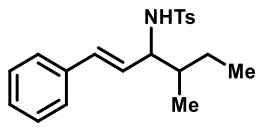


1:1 dr

15: (^{1}H NMR, 400 MHz)

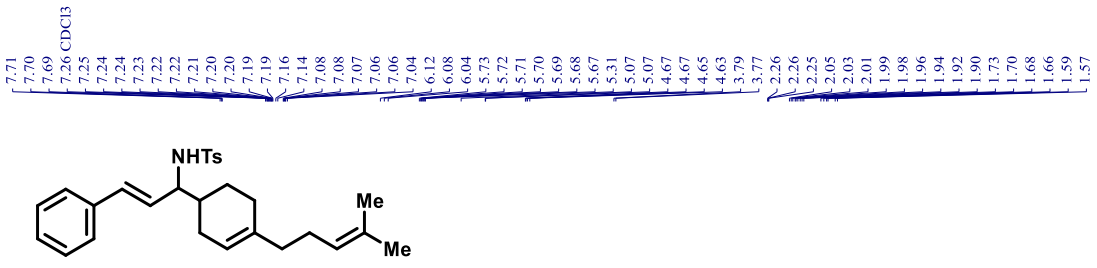






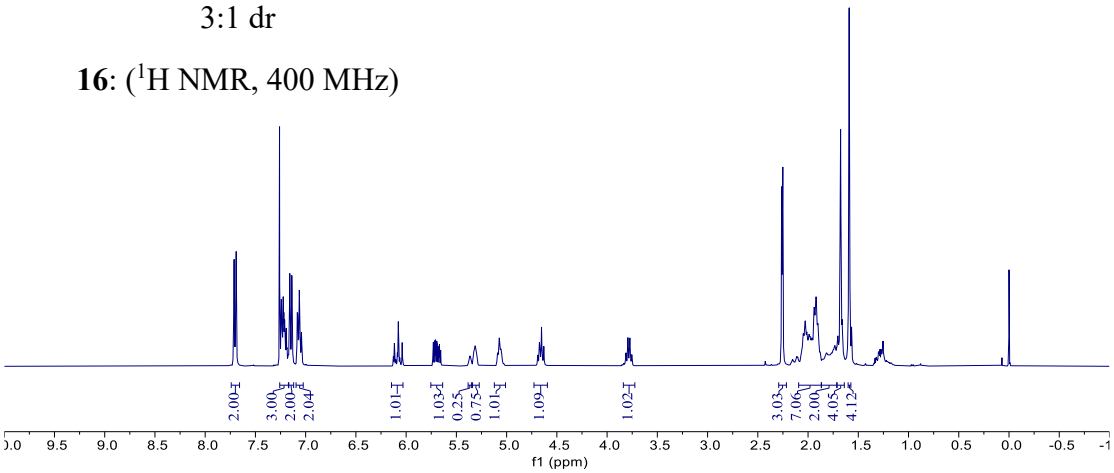
1:1 dr

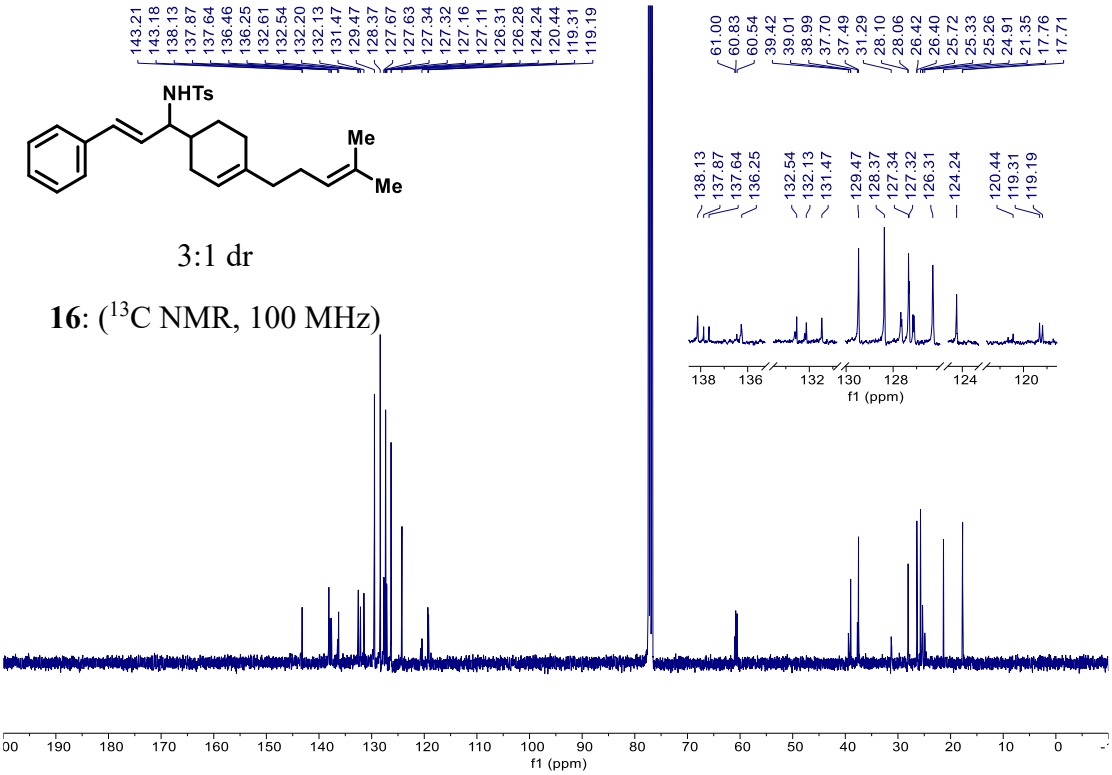
15: (^{13}C NMR, 100 MHz)



3:1 dr

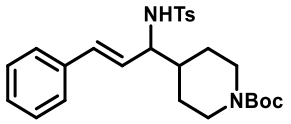
16: (^{1}H NMR, 400 MHz)



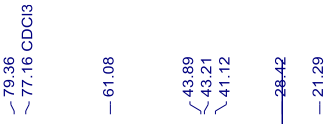


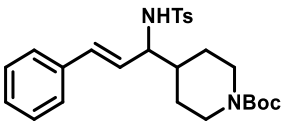
3:1 dr

16: (^{13}C NMR, 100 MHz)

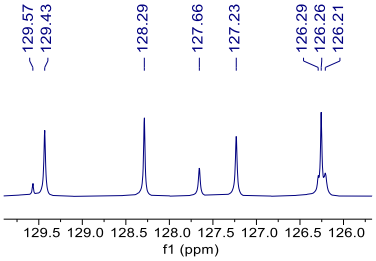


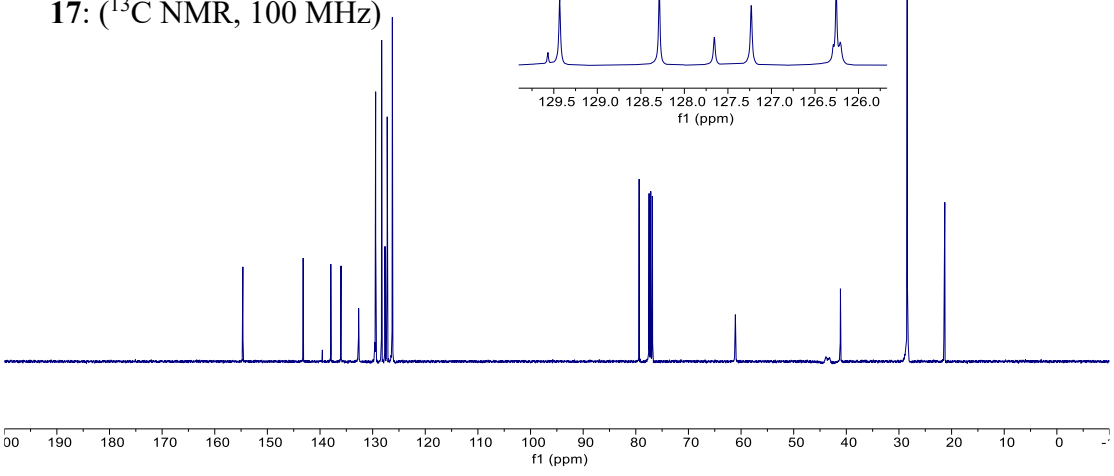
17: (^{1}H NMR, 400 MHz)

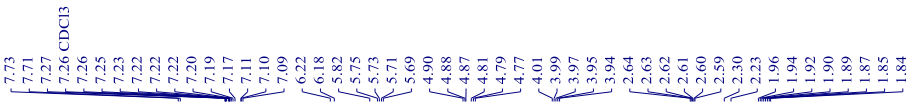


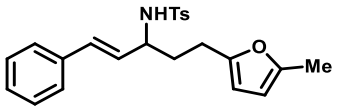


17: (^{13}C NMR, 100 MHz)

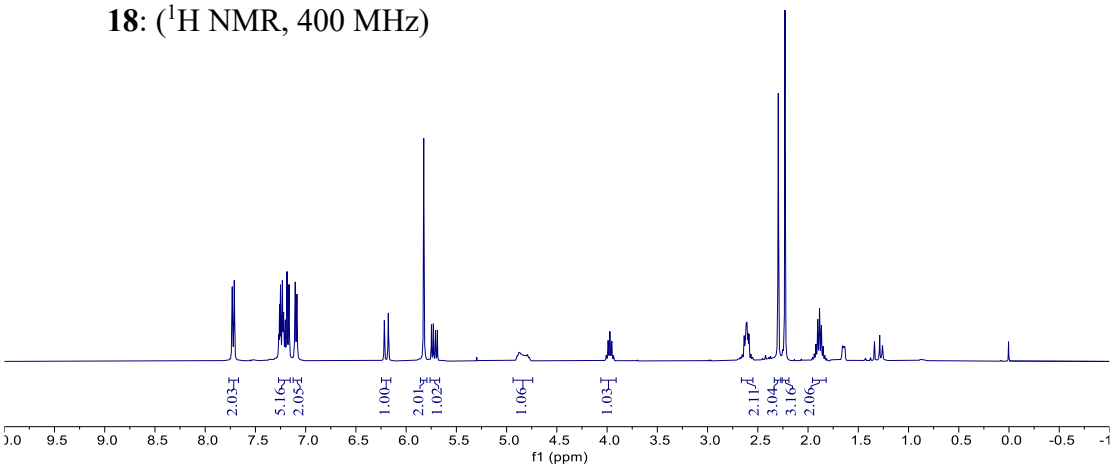


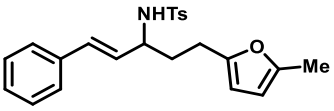




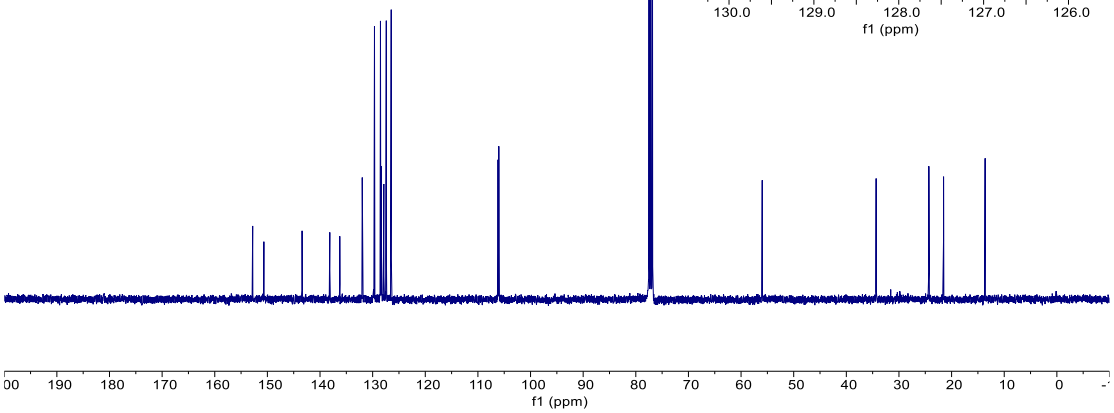


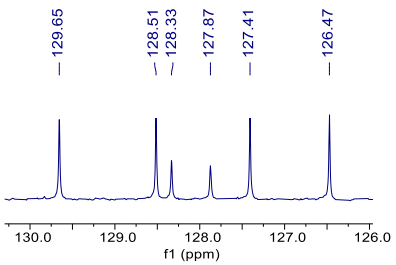
18: (^{1}H NMR, 400 MHz)

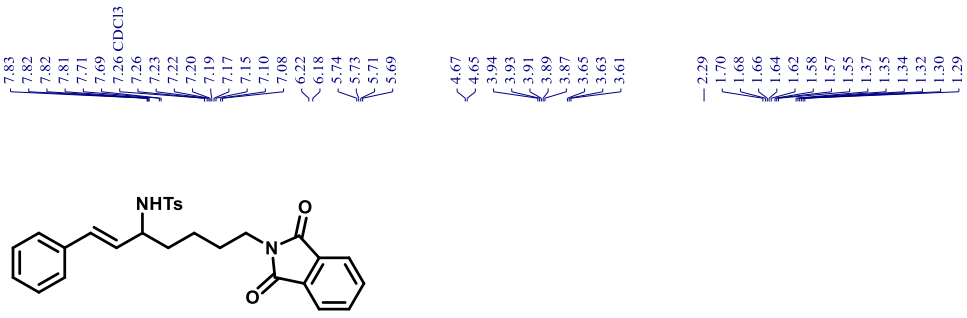




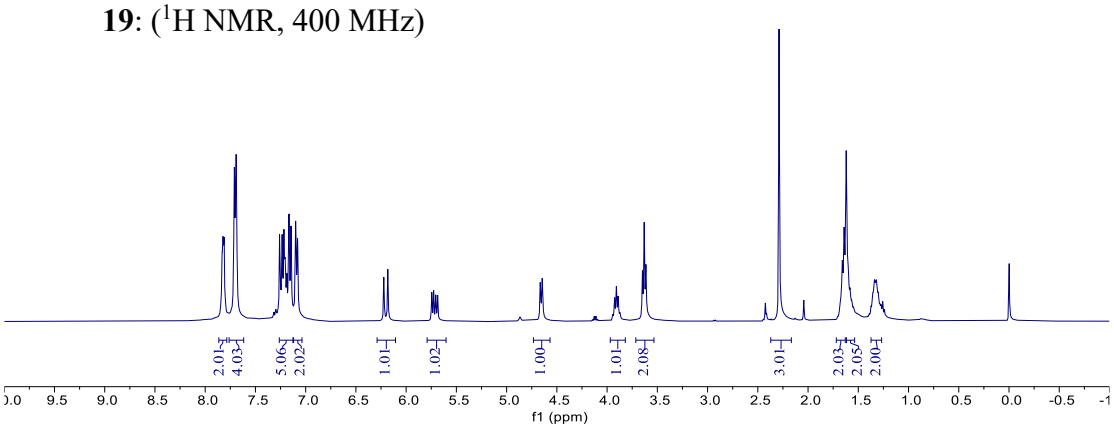
18: (^{13}C NMR, 100 MHz)

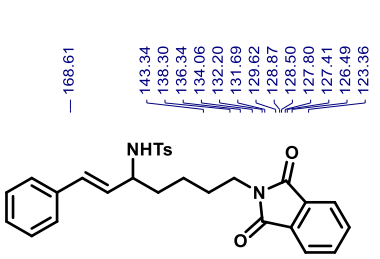




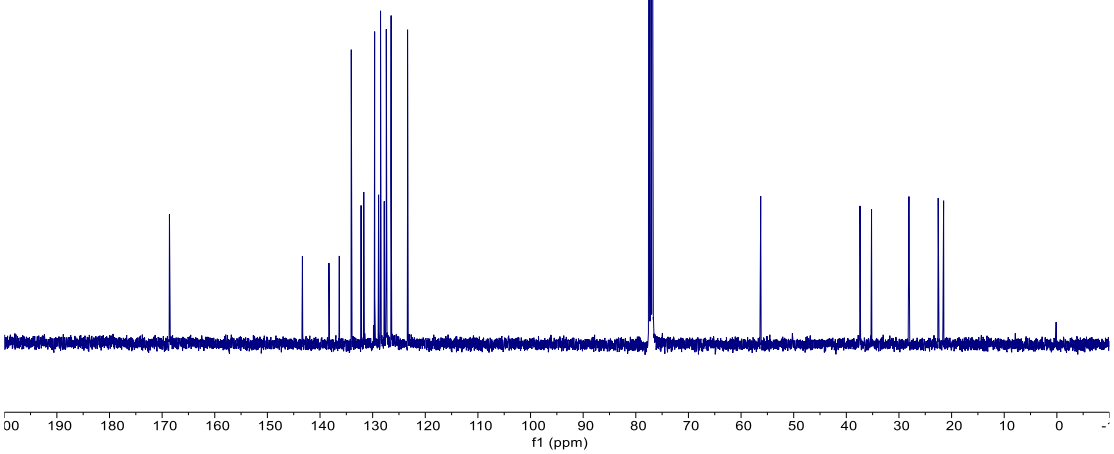


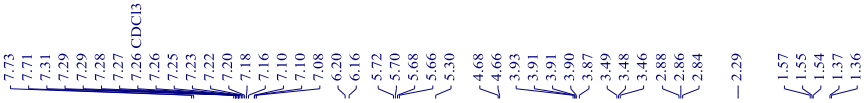
19: (^{1}H NMR, 400 MHz)

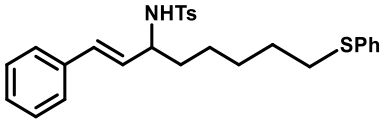




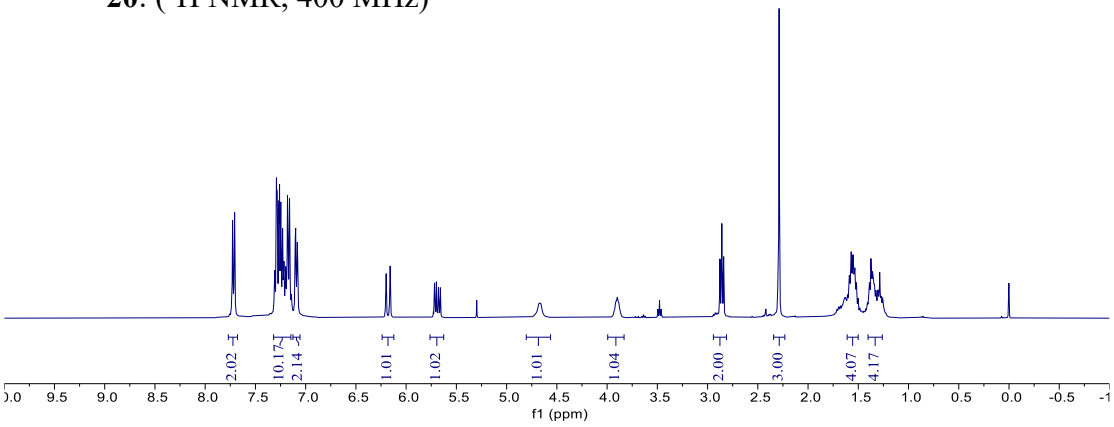
19: (^{13}C NMR, 100 MHz)

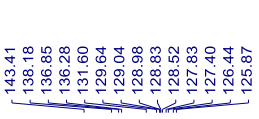


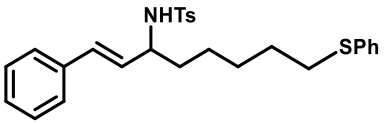




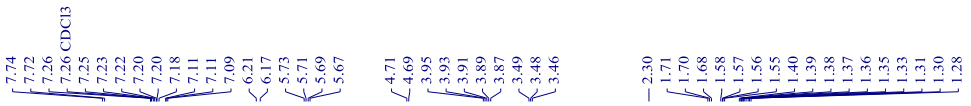
20: (^{1}H NMR, 400 MHz)

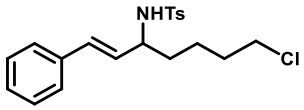




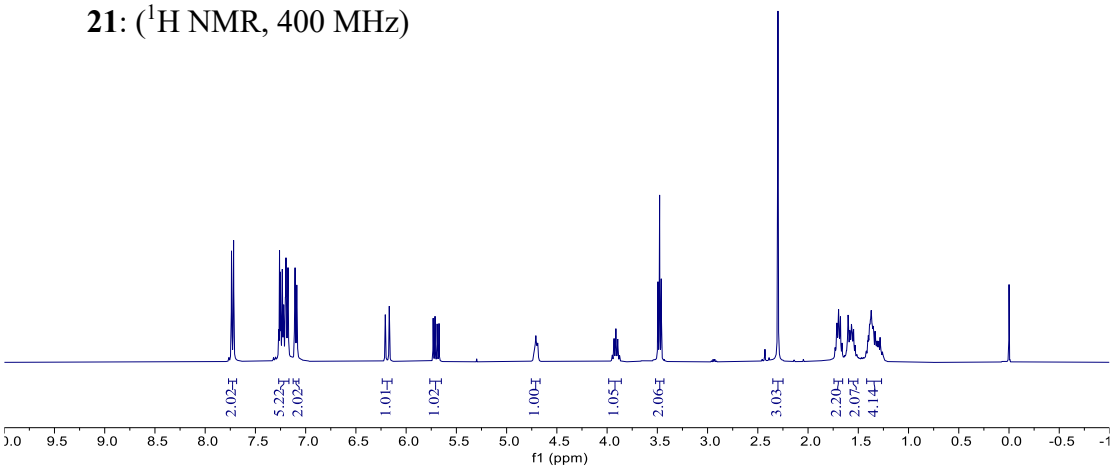


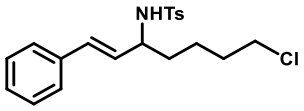
20: (^{13}C NMR, 100 MHz)



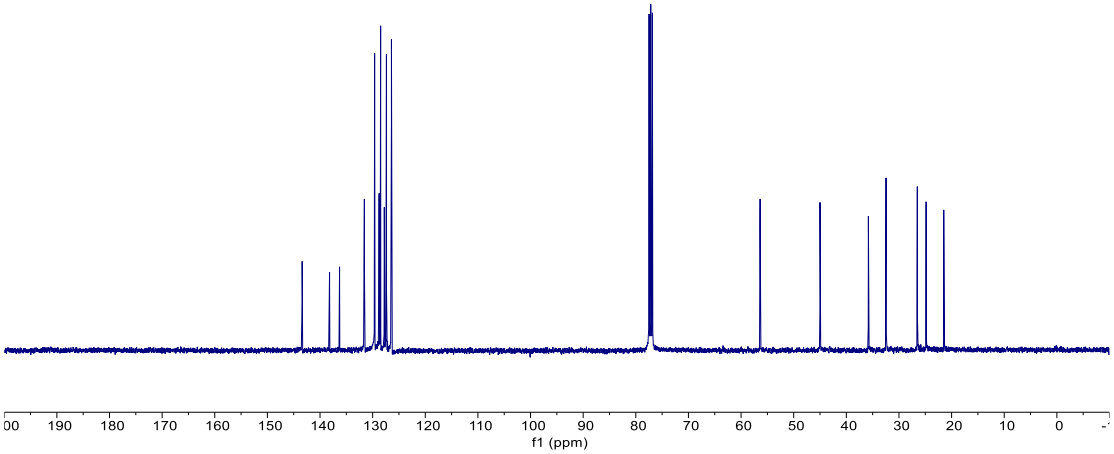


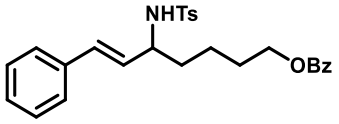
21: (^{1}H NMR, 400 MHz)



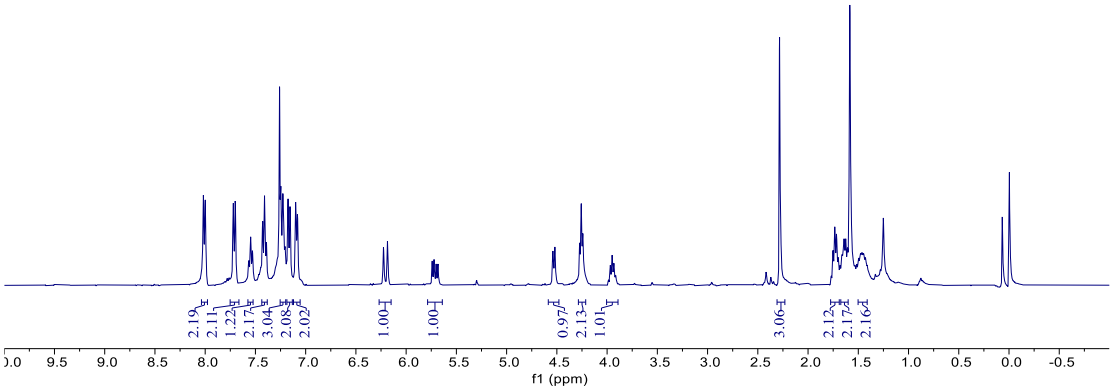


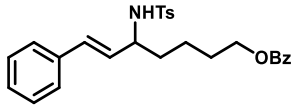
21: (^{13}C NMR, 100 MHz)



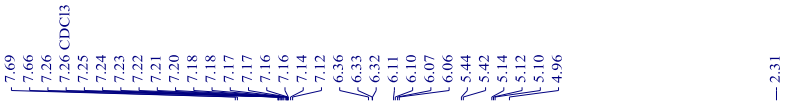


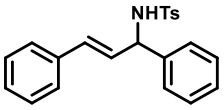
22: (^{1}H NMR, 400 MHz)



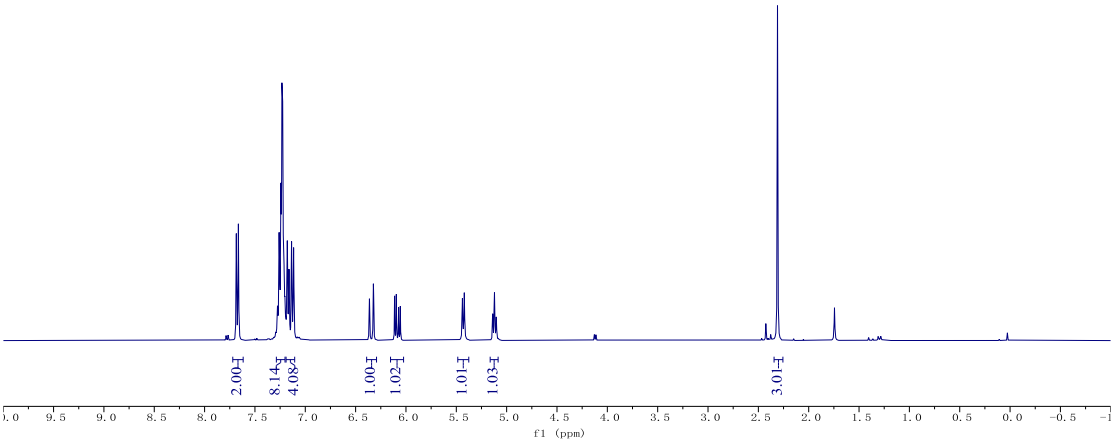


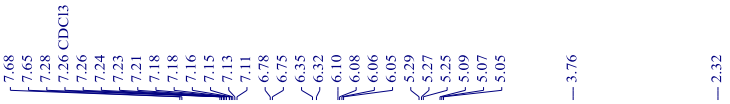
22: (^{13}C NMR, 100 MHz)

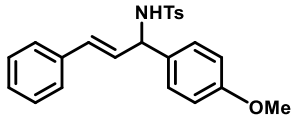




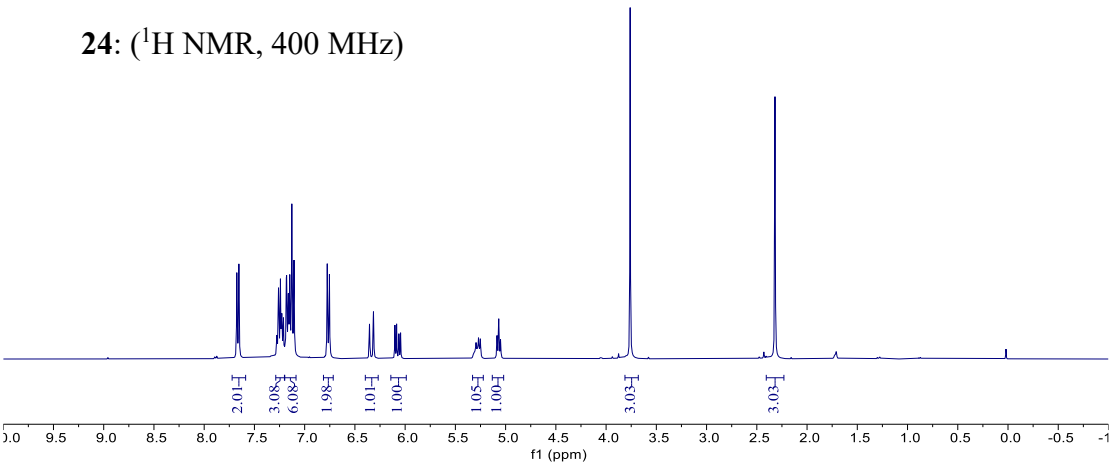
23: (^{1}H NMR, 400 MHz)

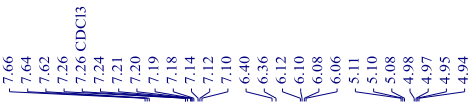


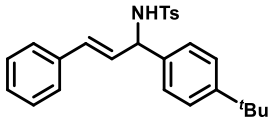




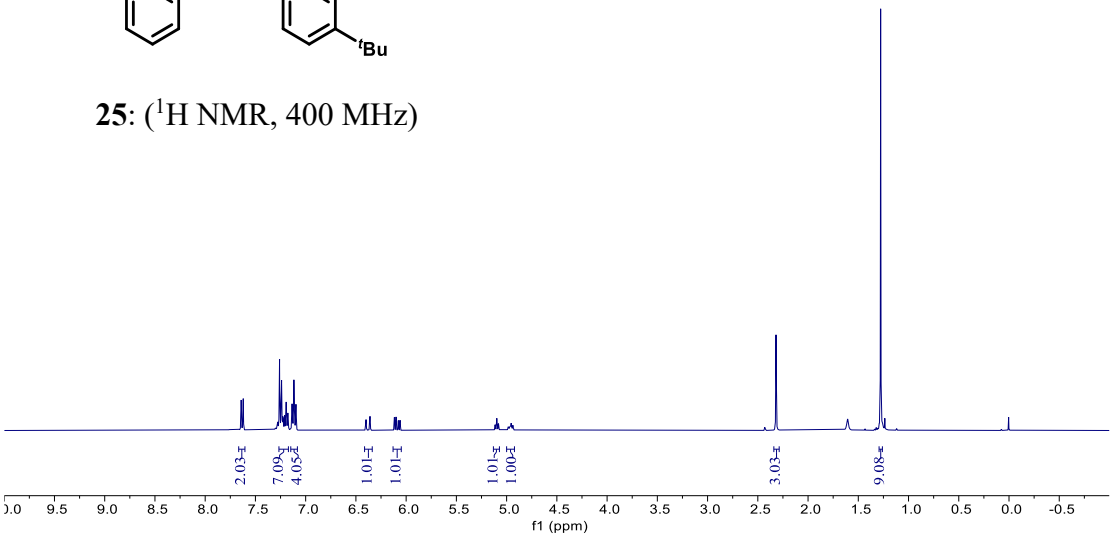
24: (^{1}H NMR, 400 MHz)

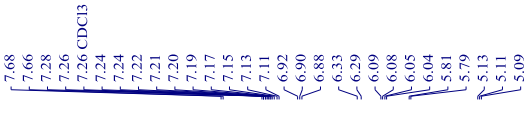


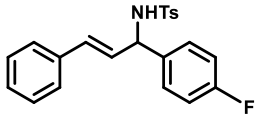




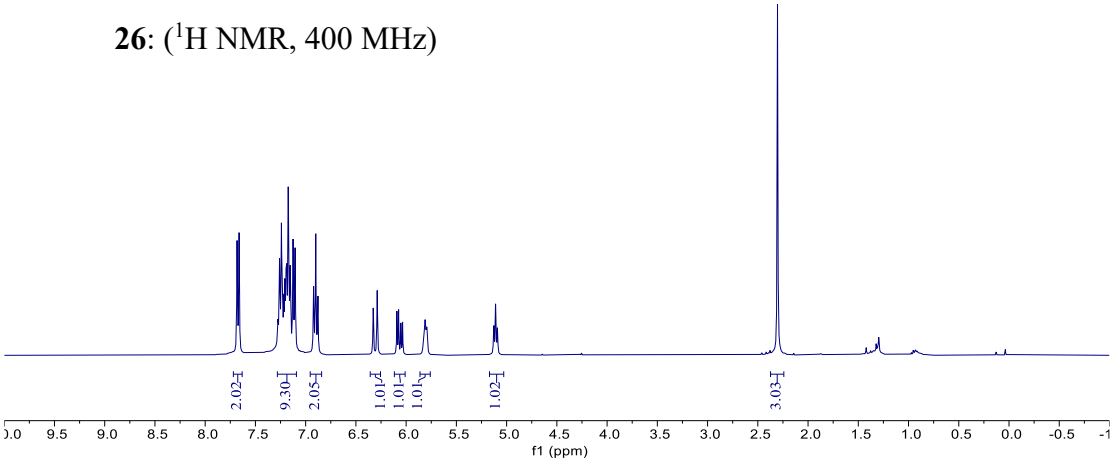
25: (^{1}H NMR, 400 MHz)

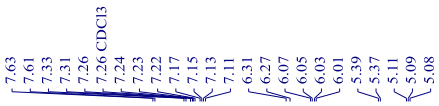


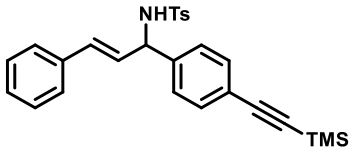




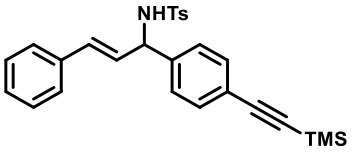
26: (^{1}H NMR, 400 MHz)



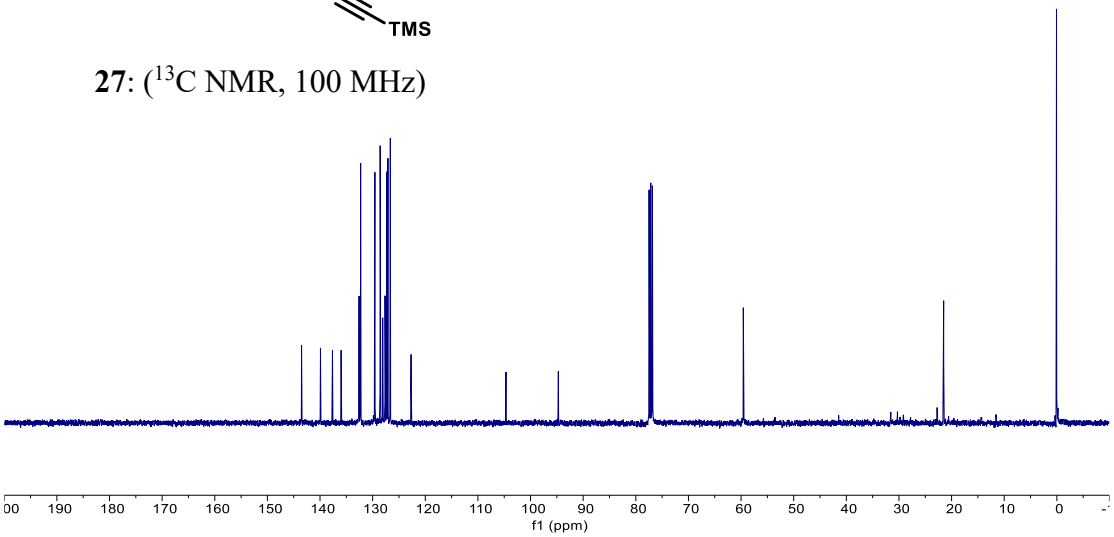


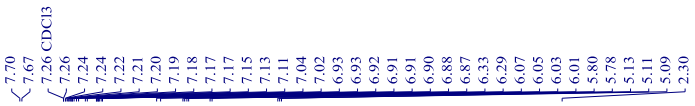


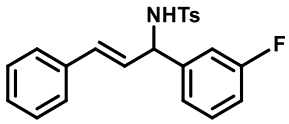
27: (^{1}H NMR, 400 MHz)



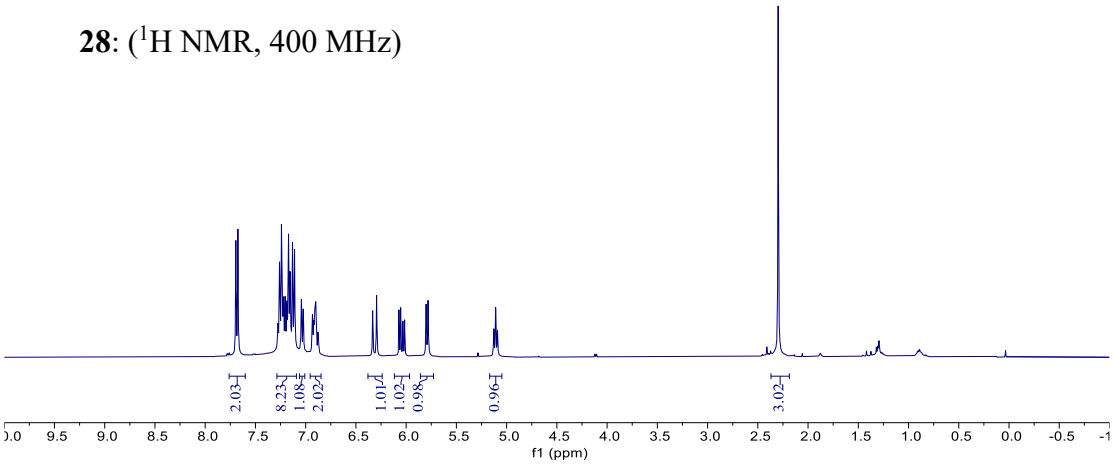
27: (^{13}C NMR, 100 MHz)

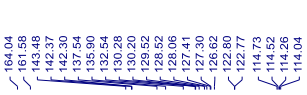


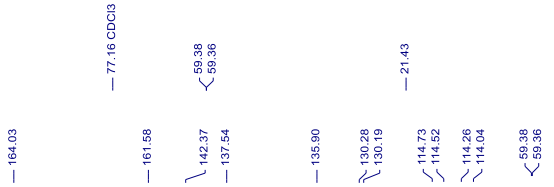


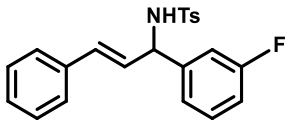


28: (^{1}H NMR, 400 MHz)

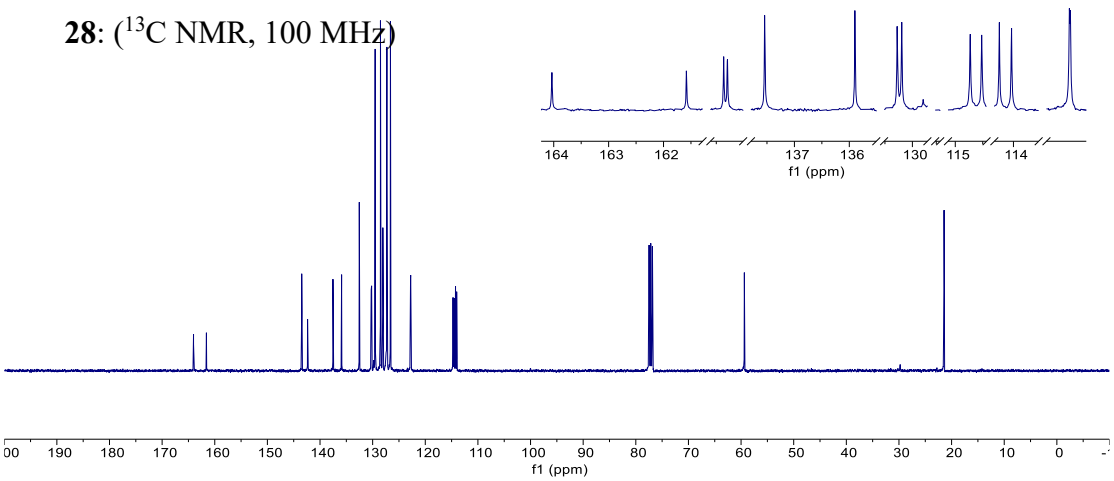


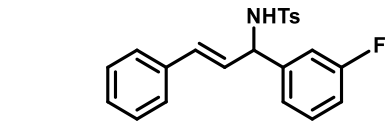




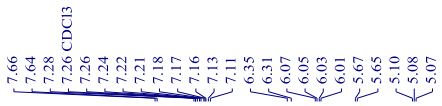


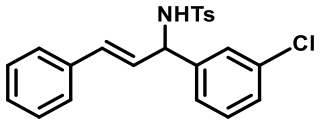
28: (^{13}C NMR, 100 MHz)



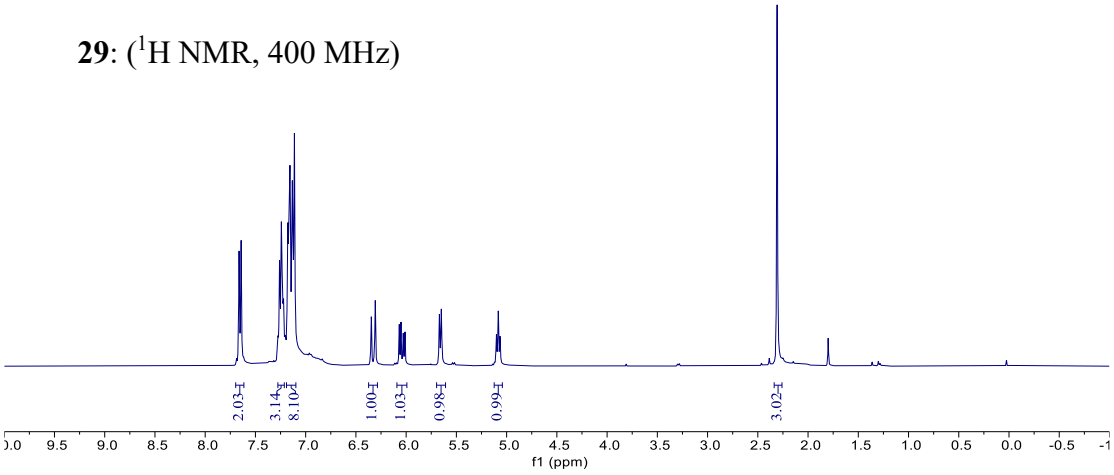


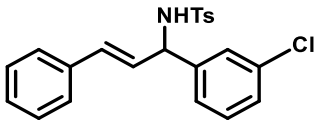
28: (^{19}F NMR, 376 MHz)



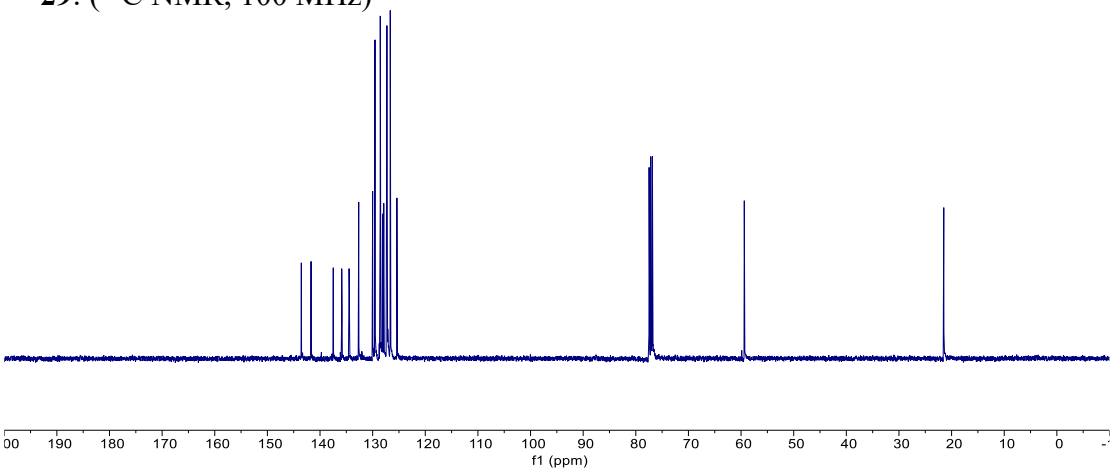


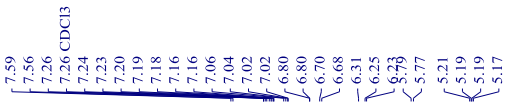
29: (^{1}H NMR, 400 MHz)

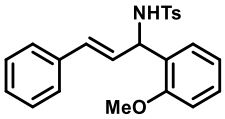




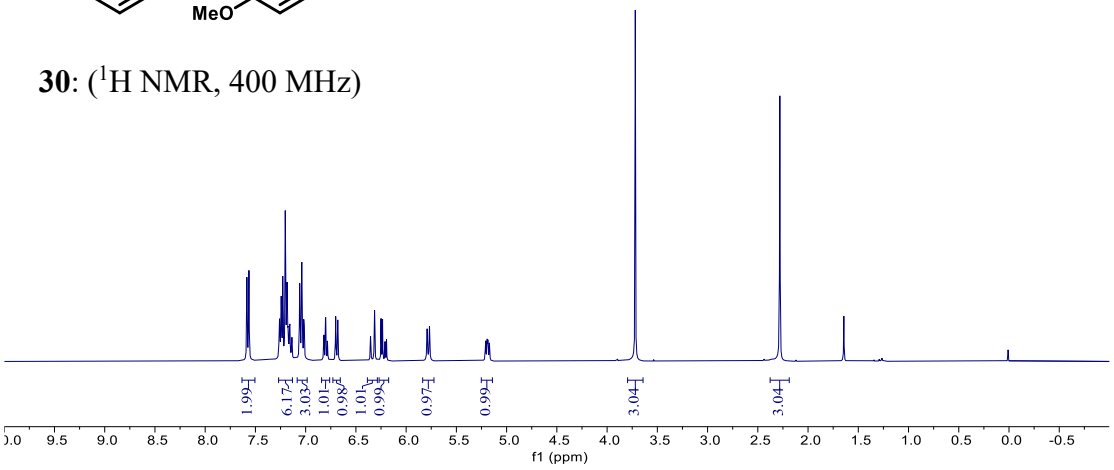
29: (^{13}C NMR, 100 MHz)



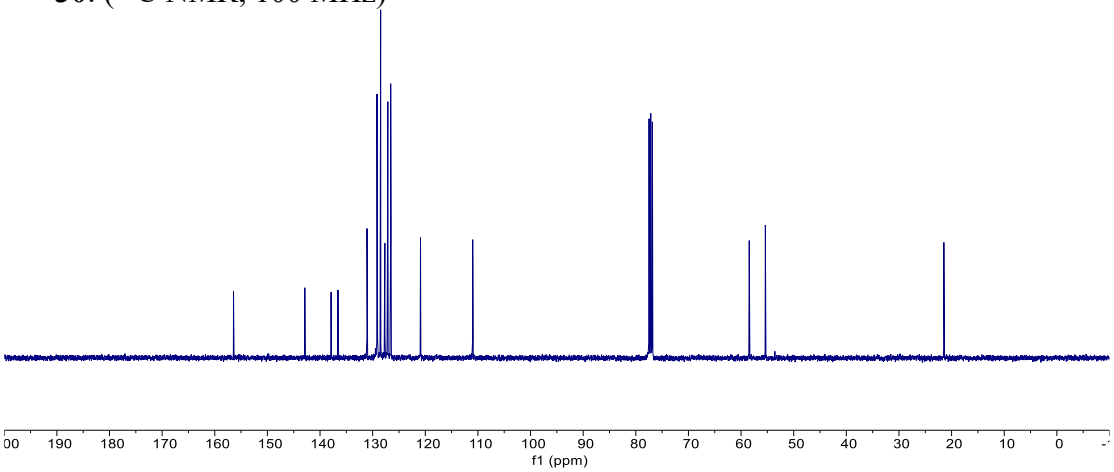


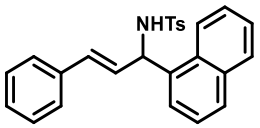


30: (^{1}H NMR, 400 MHz)

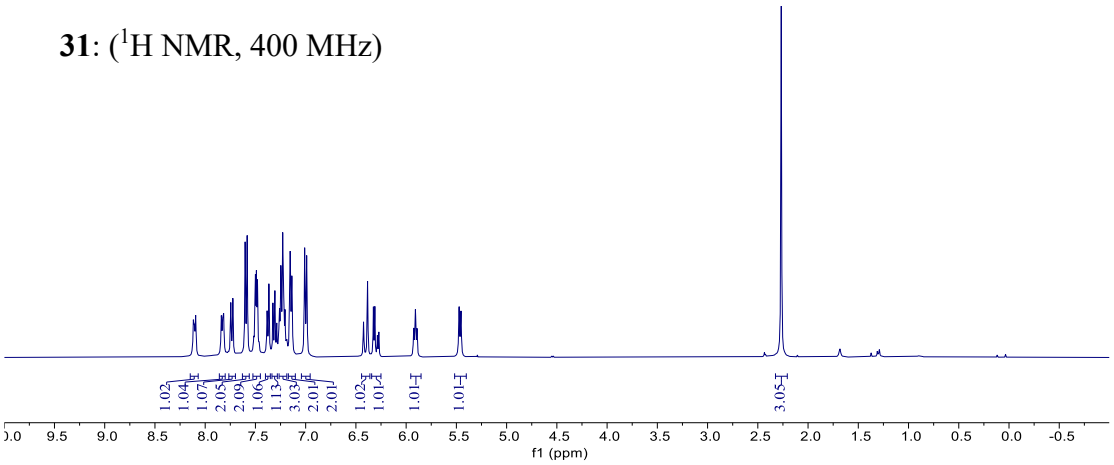


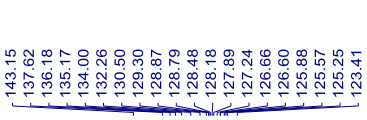
30: (^{13}C NMR, 100 MHz)

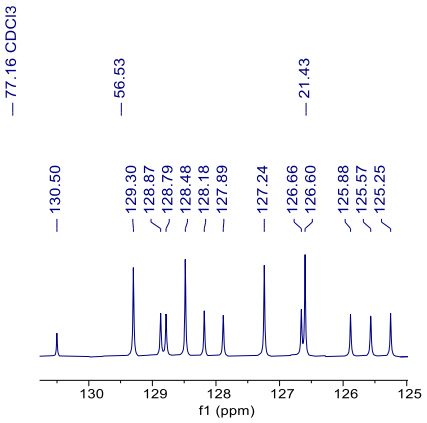


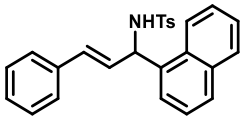


31: (^{1}H NMR, 400 MHz)

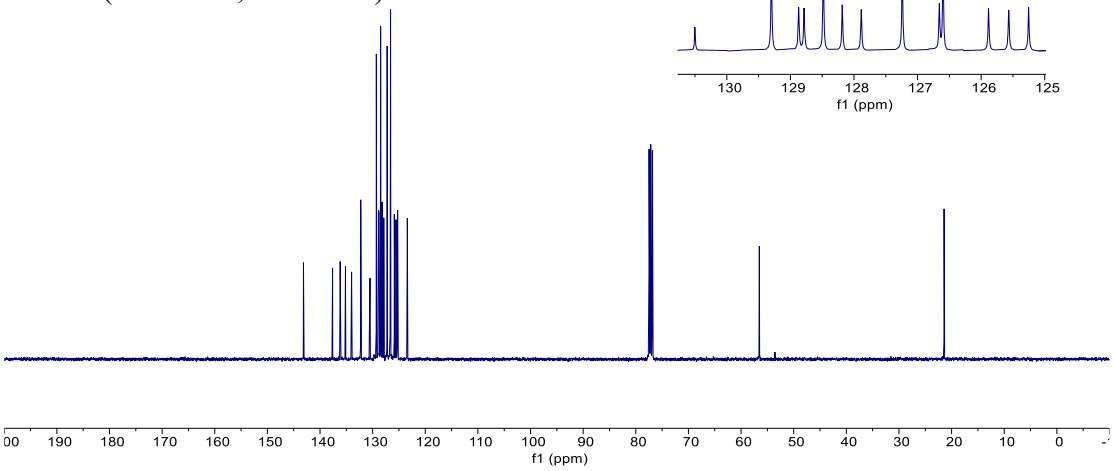


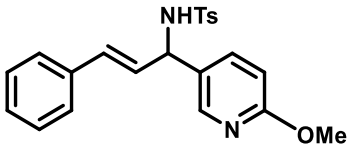




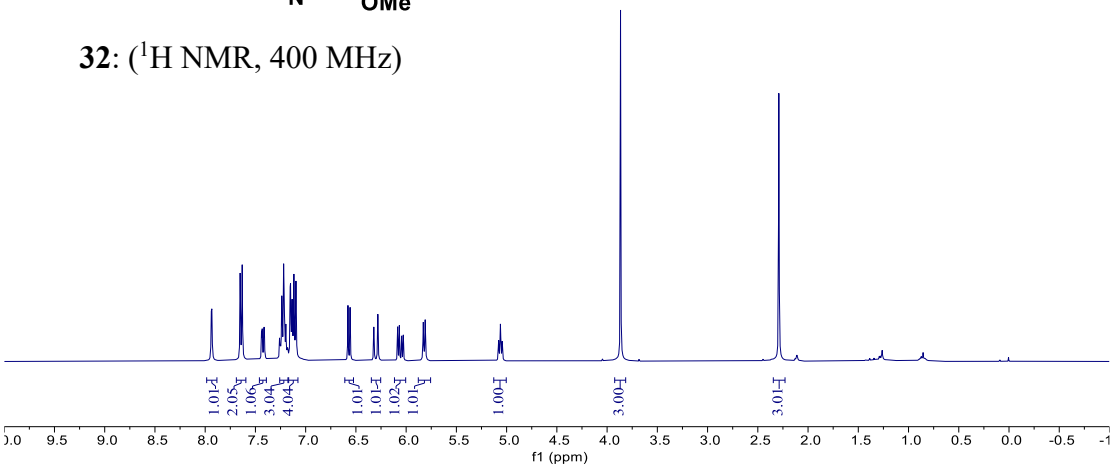


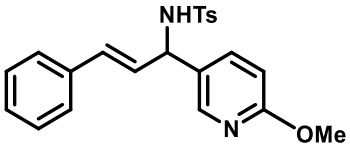
31: (^{13}C NMR, 100 MHz)



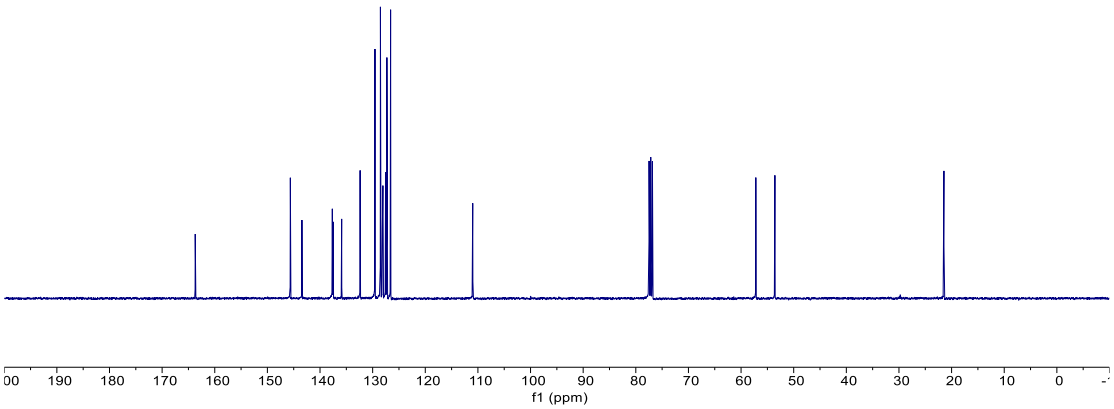


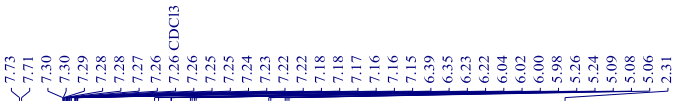
32: (^{1}H NMR, 400 MHz)

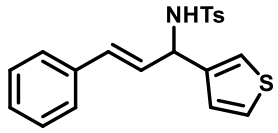




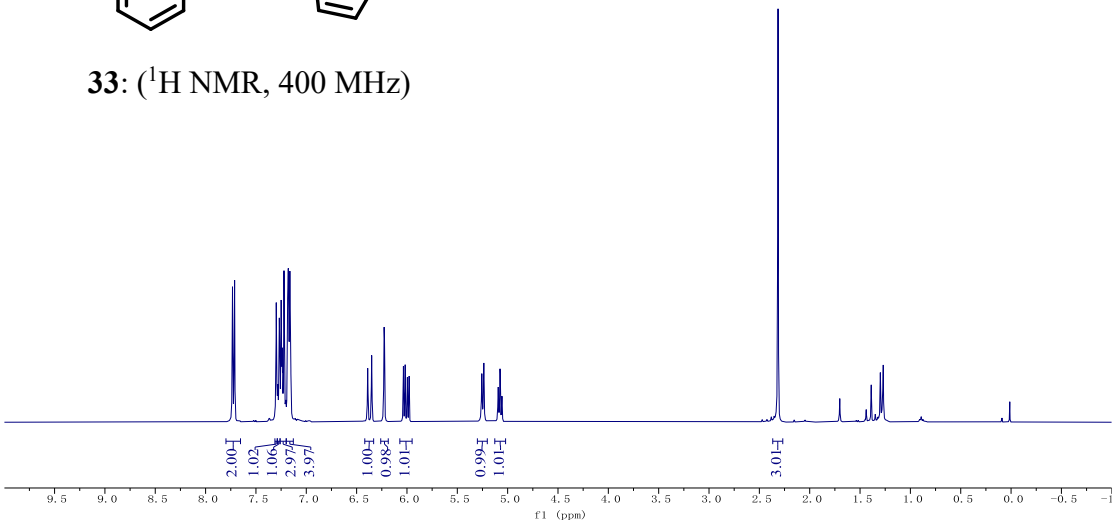
32: (^{13}C NMR, 100 MHz)

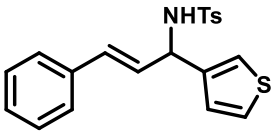




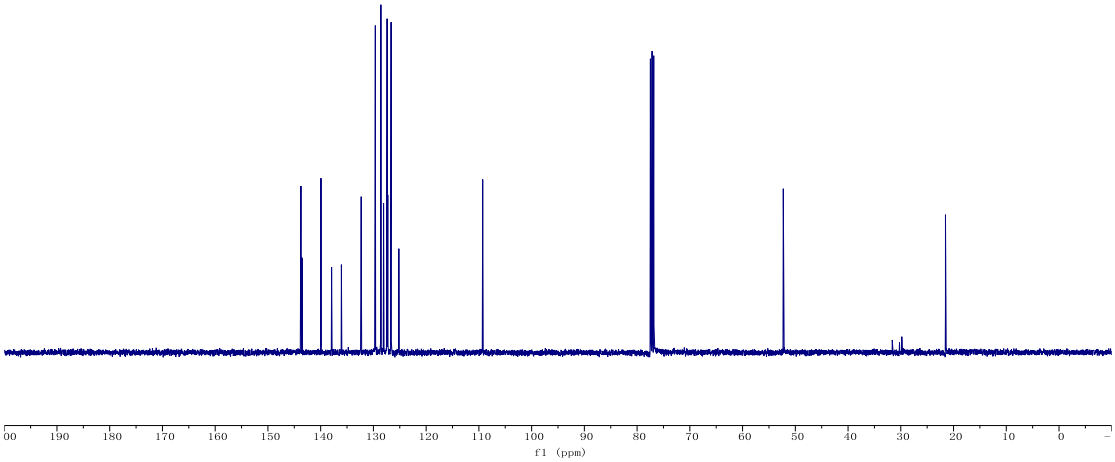


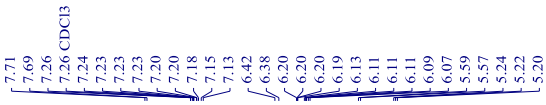
33: (^{1}H NMR, 400 MHz)

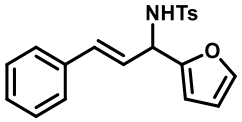




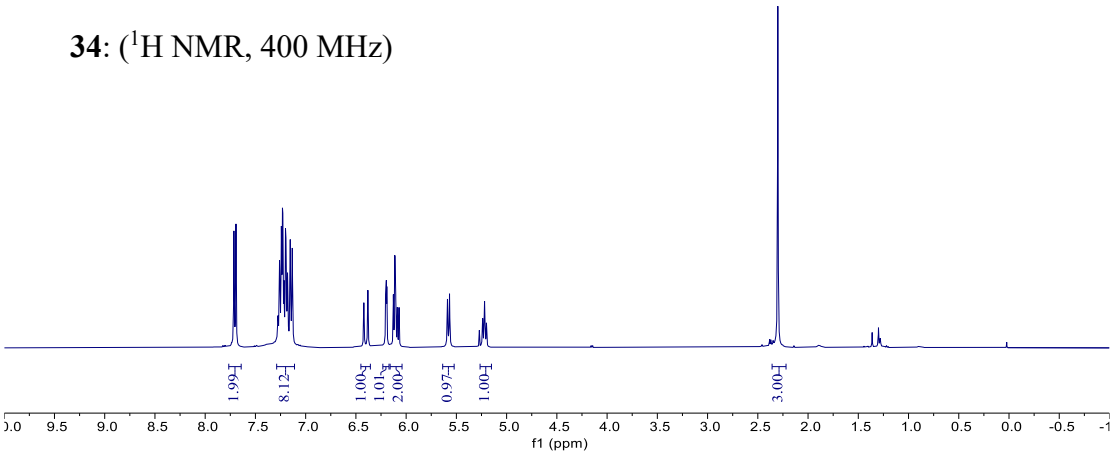
33: (^{13}C NMR, 100 MHz)

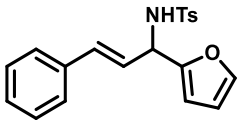




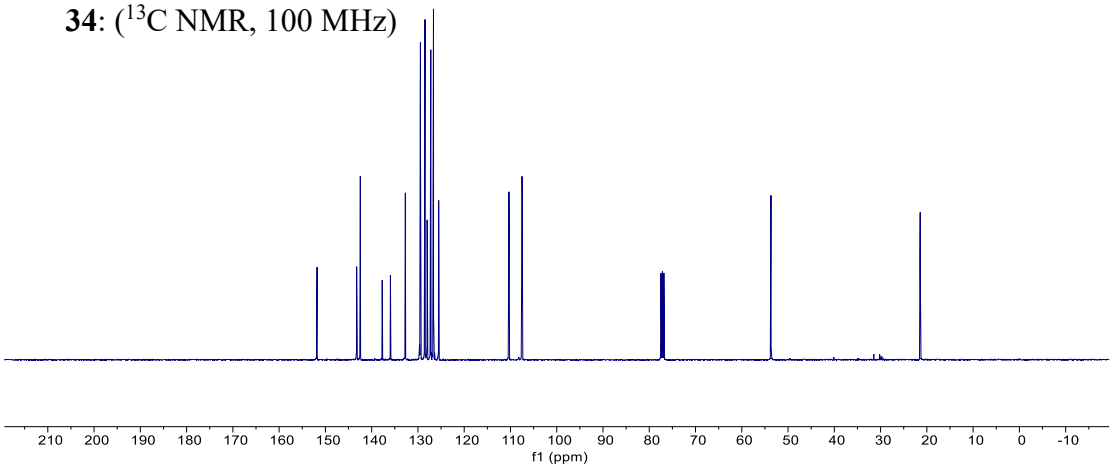


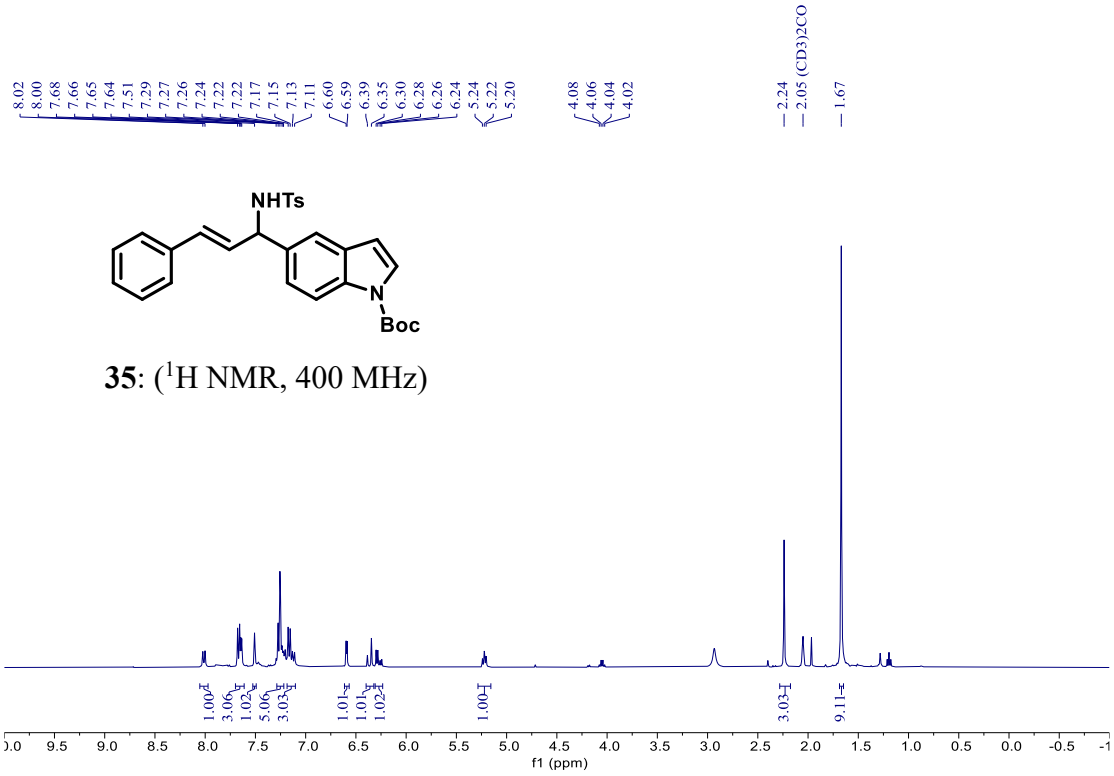
34: (^{1}H NMR, 400 MHz)



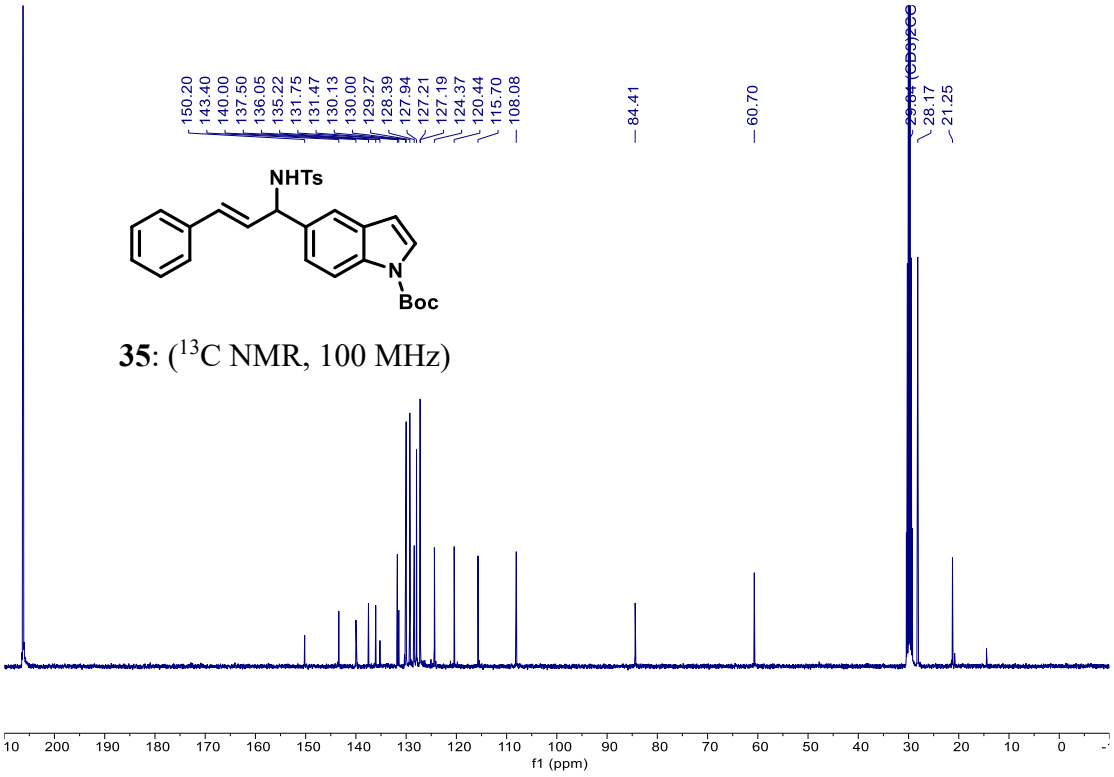


34: (^{13}C NMR, 100 MHz)

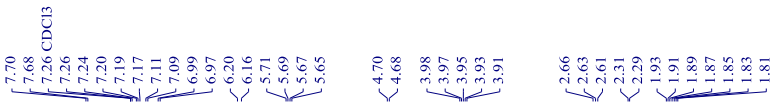


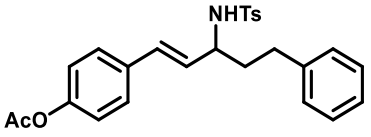


35: (^{1}H NMR, 400 MHz)

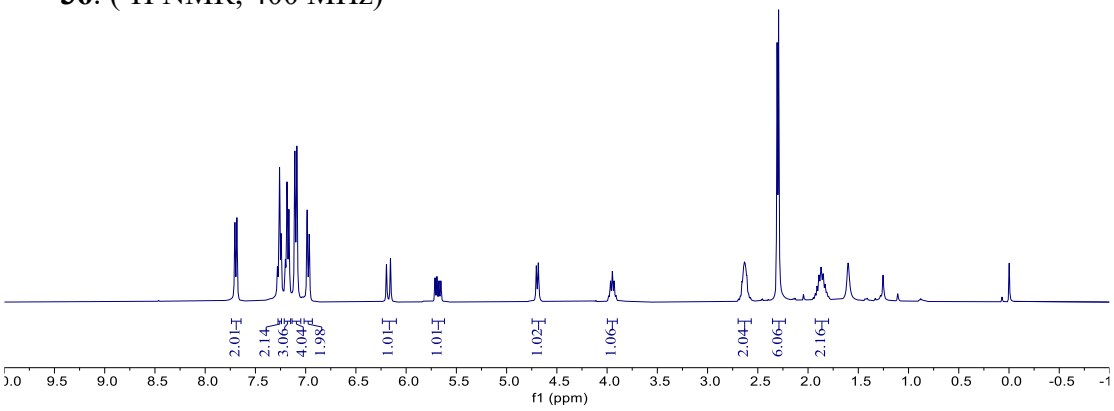


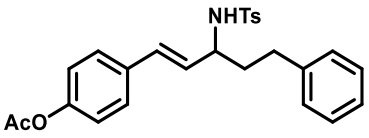
35: (^{13}C NMR, 100 MHz)



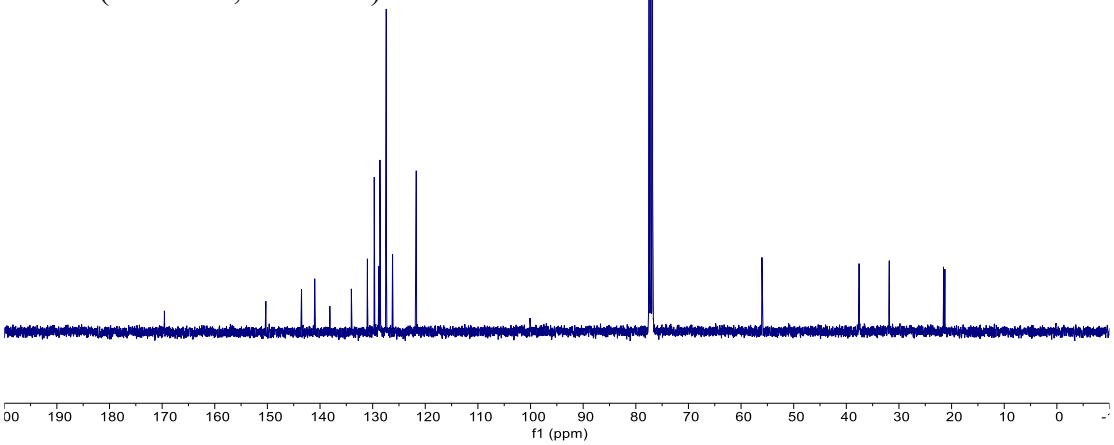


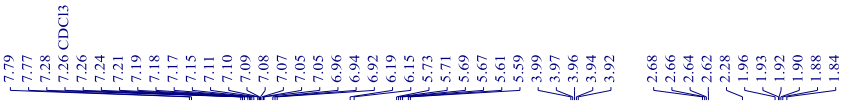
36: (^{1}H NMR, 400 MHz)

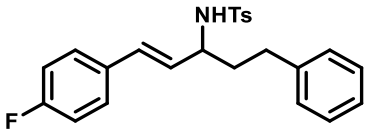




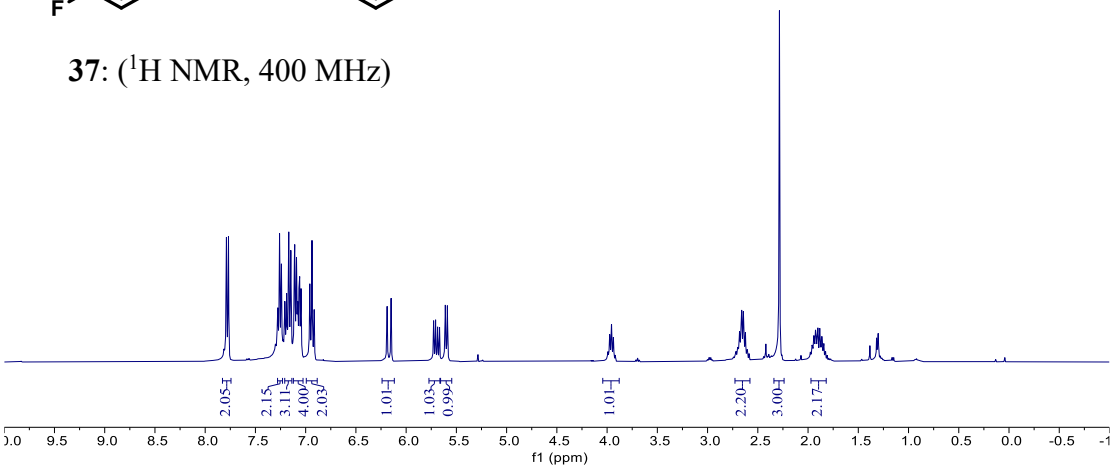
36: (^{13}C NMR, 100 MHz)

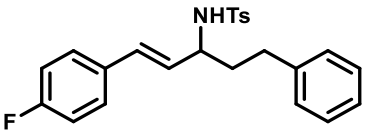




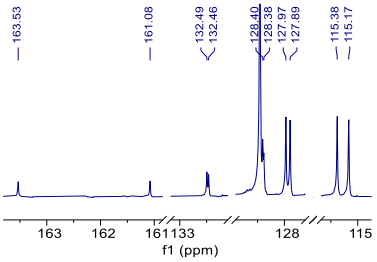


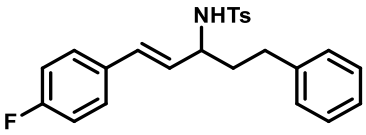
37: (^{1}H NMR, 400 MHz)



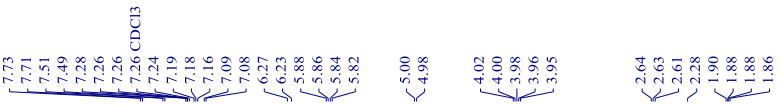


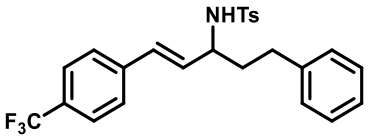
37: (^{13}C NMR, 100 MHz)



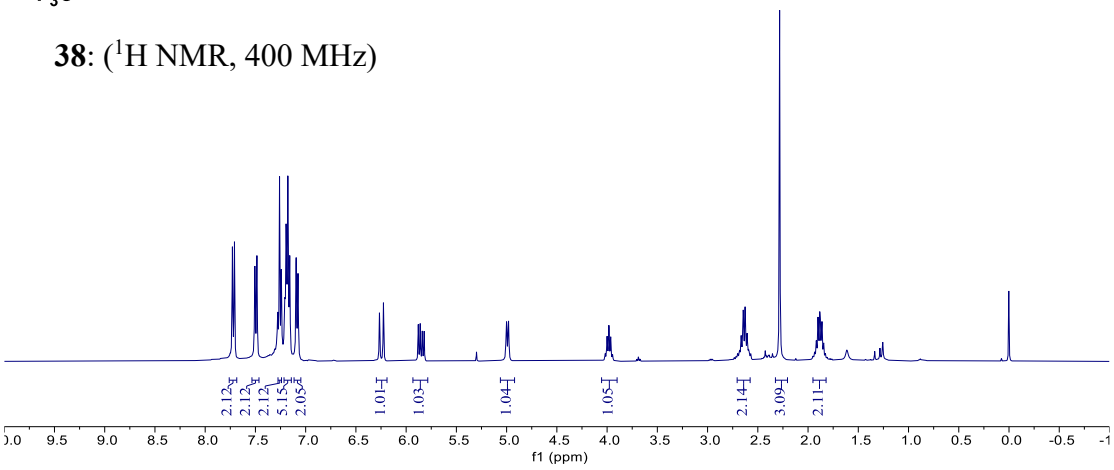


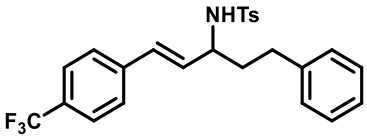
37: (^{19}F NMR, 376 MHz)



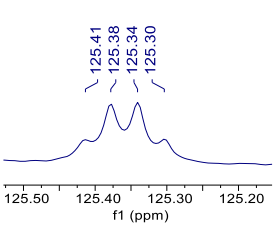


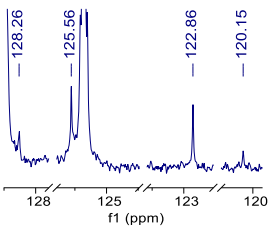
38: (^{1}H NMR, 400 MHz)

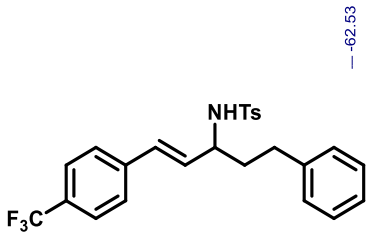




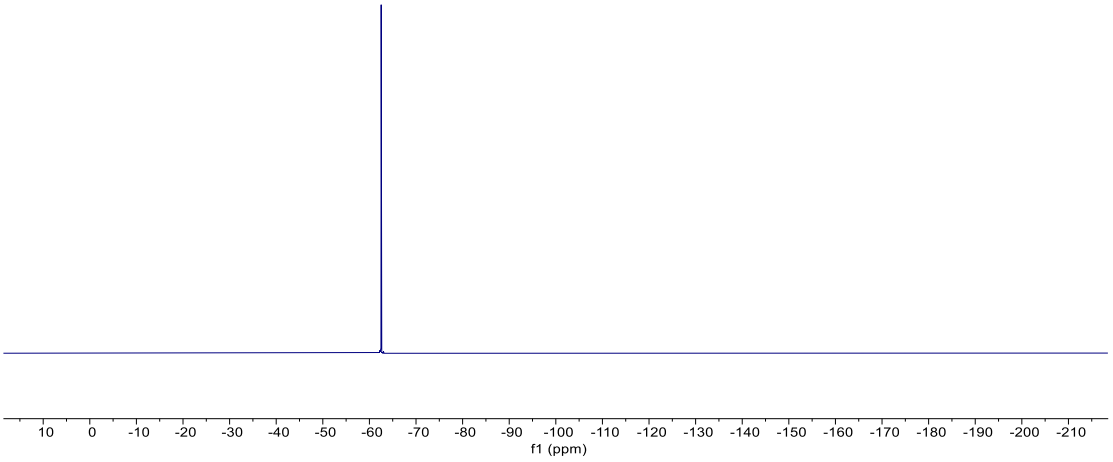
38: (^{13}C NMR, 100 MHz)

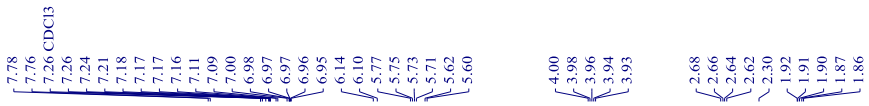


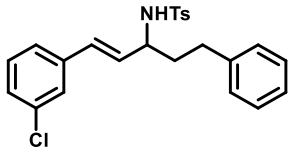




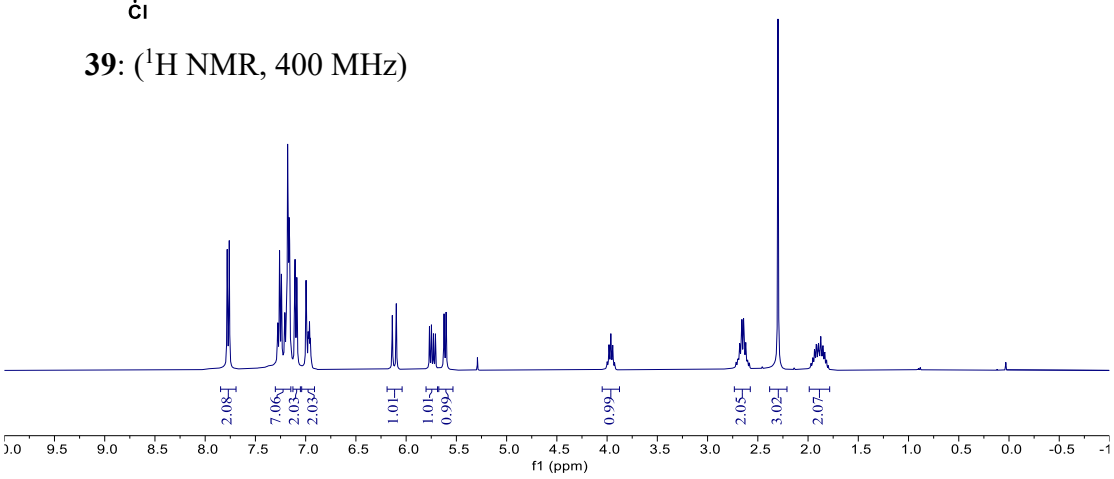
38: (^{19}F NMR, 376 MHz)

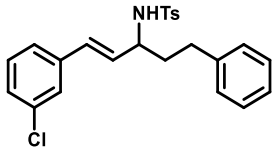




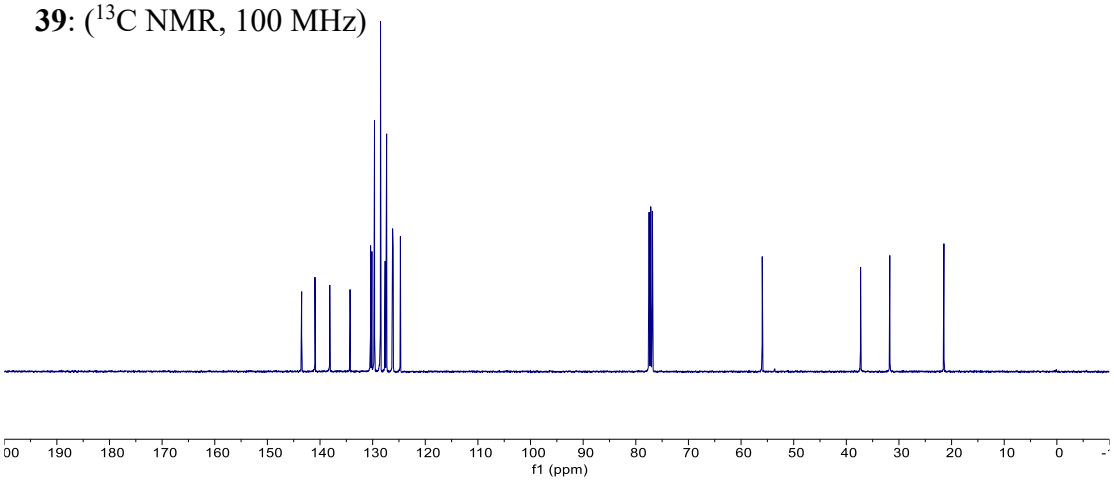


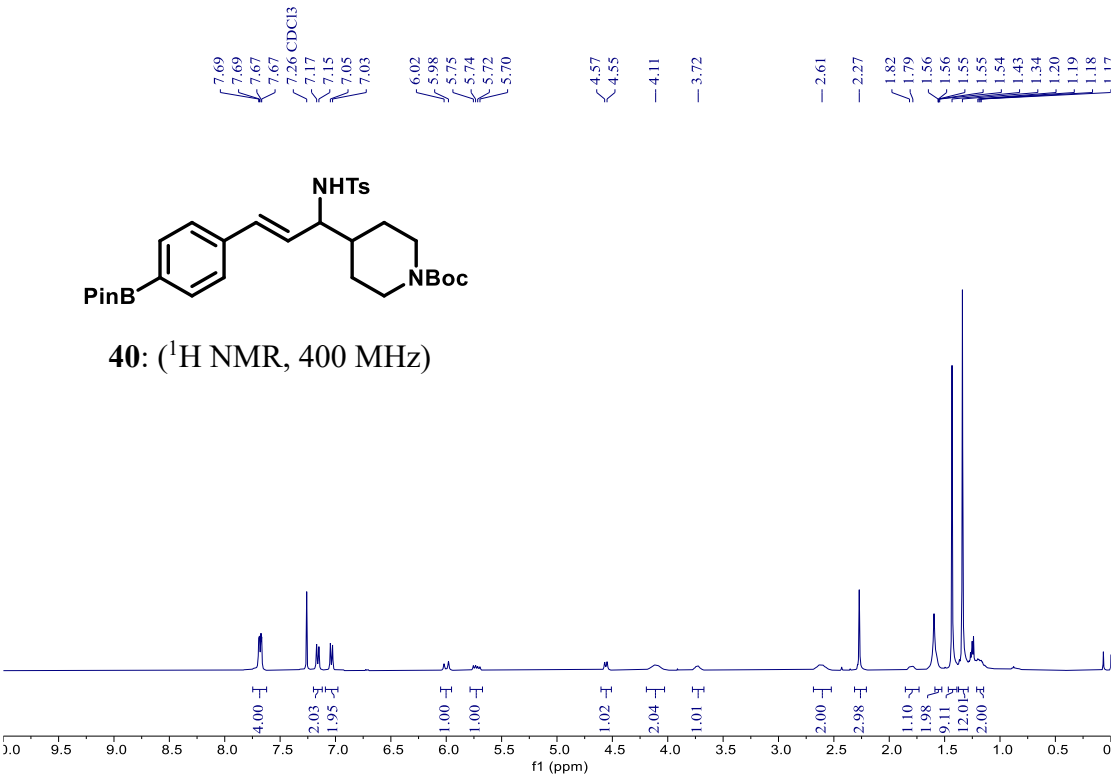
39: (^{1}H NMR, 400 MHz)



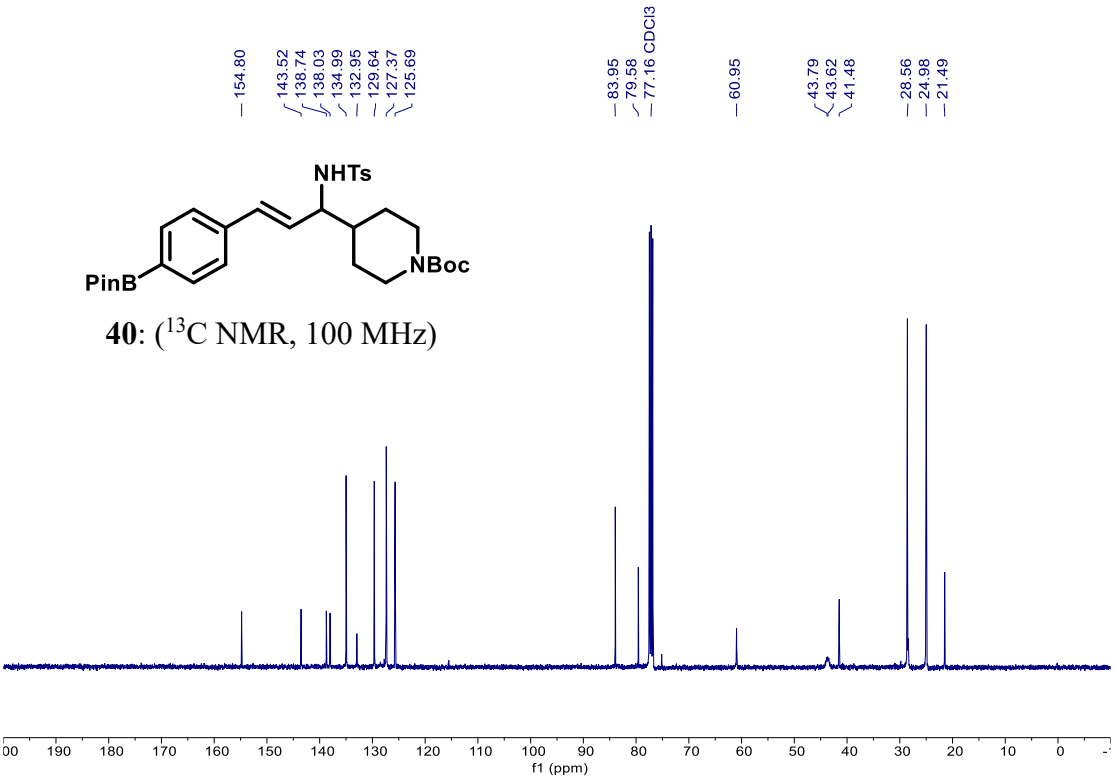


39: (^{13}C NMR, 100 MHz)

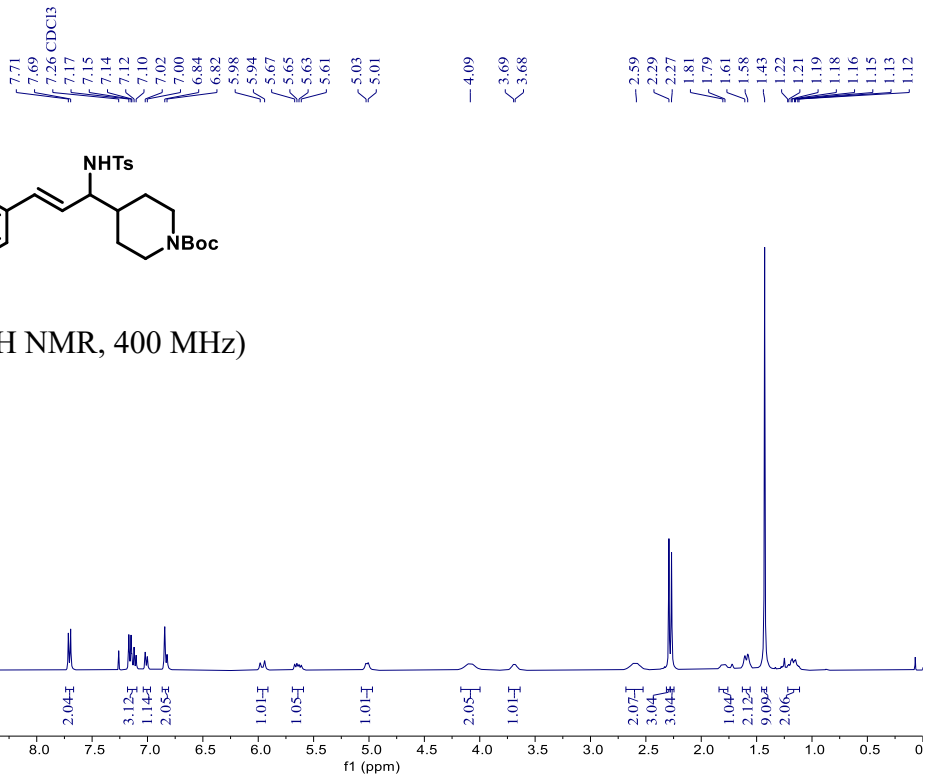




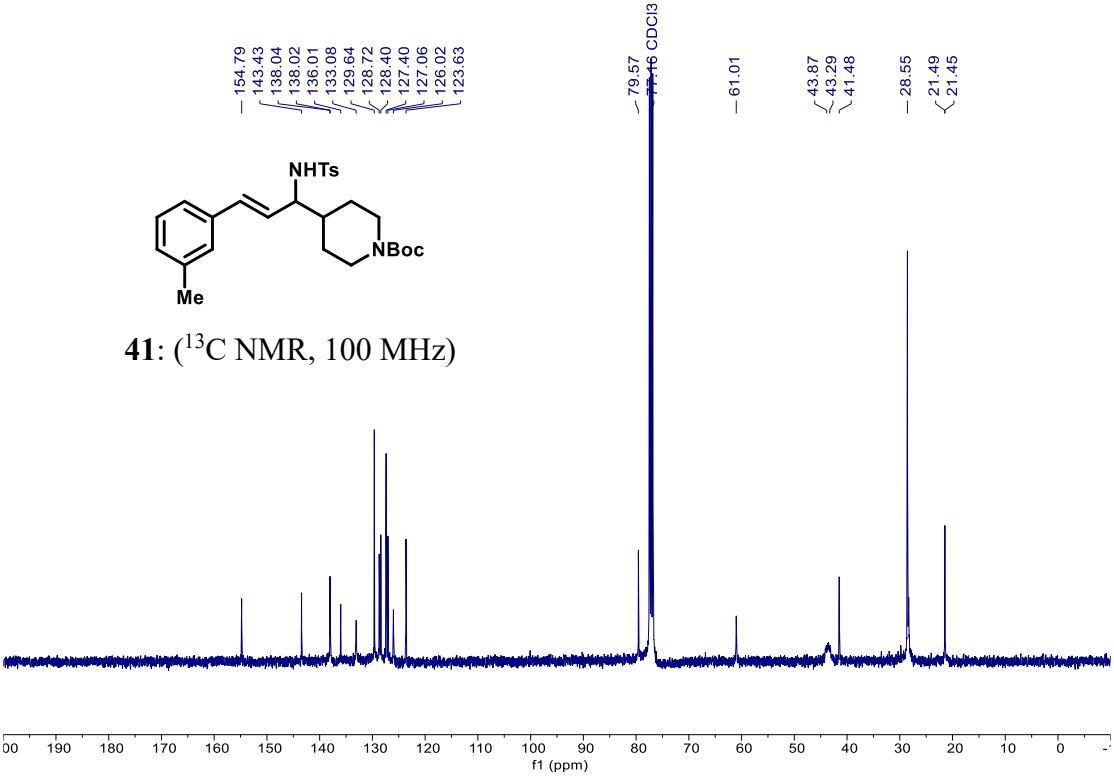
40: (^{1}H NMR, 400 MHz)



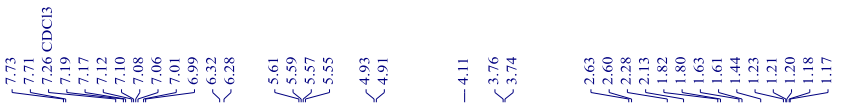
40: (^{13}C NMR, 100 MHz)

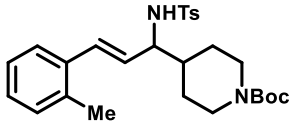


41: (^{1}H NMR, 400 MHz)

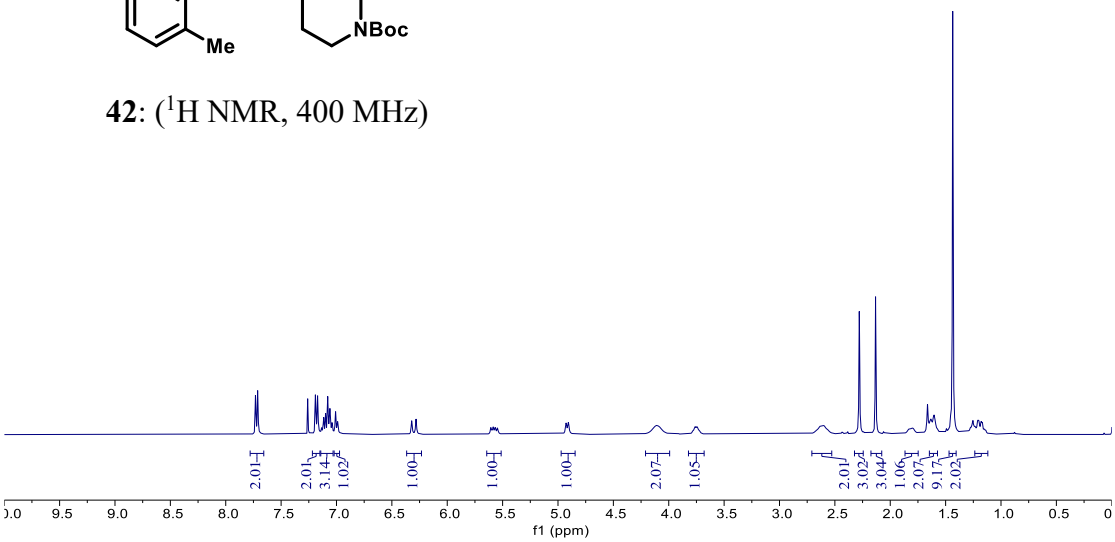


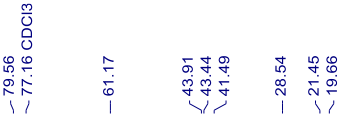
41: (^{13}C NMR, 100 MHz)

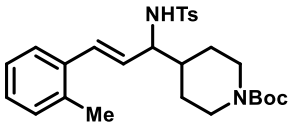




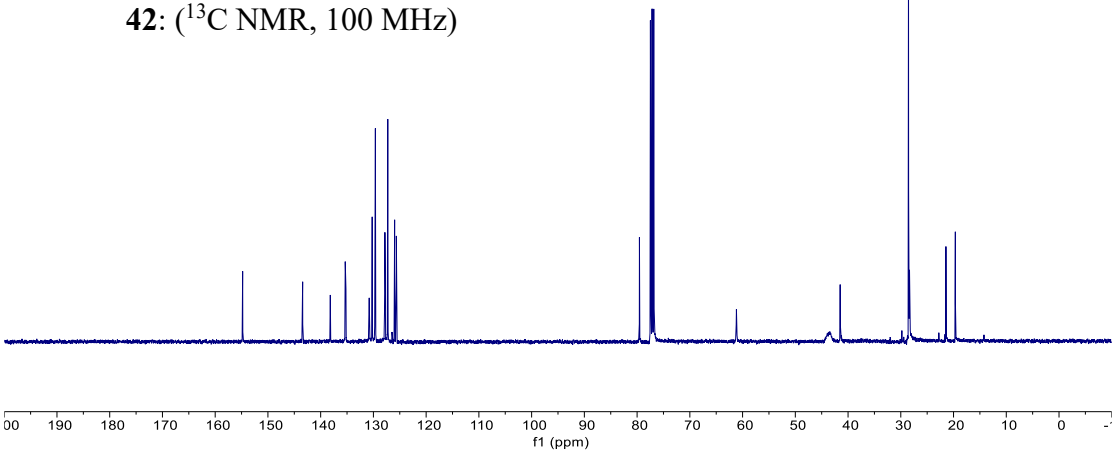
42: (^{1}H NMR, 400 MHz)

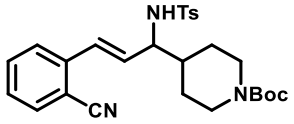




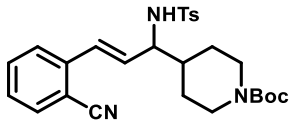


42: (^{13}C NMR, 100 MHz)

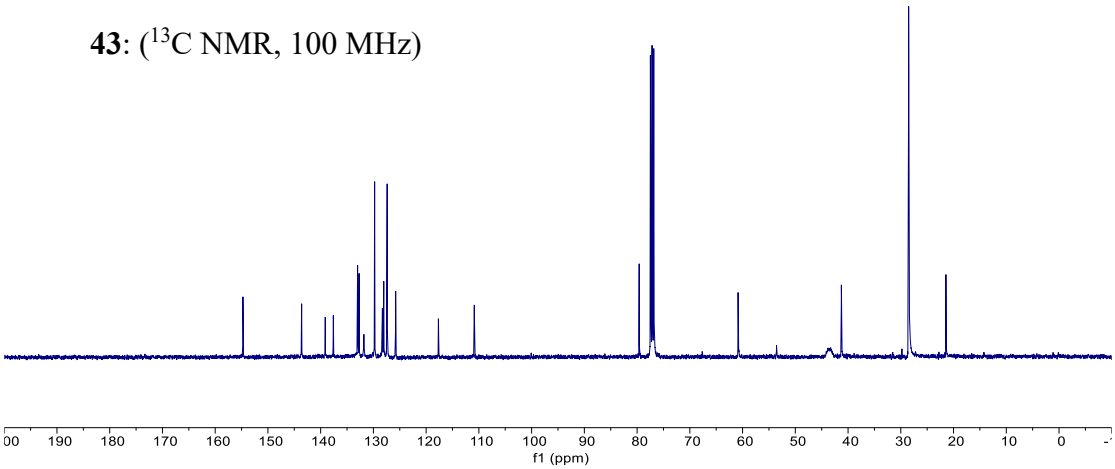


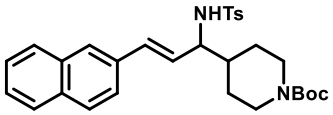


43: (^{1}H NMR, 400 MHz)

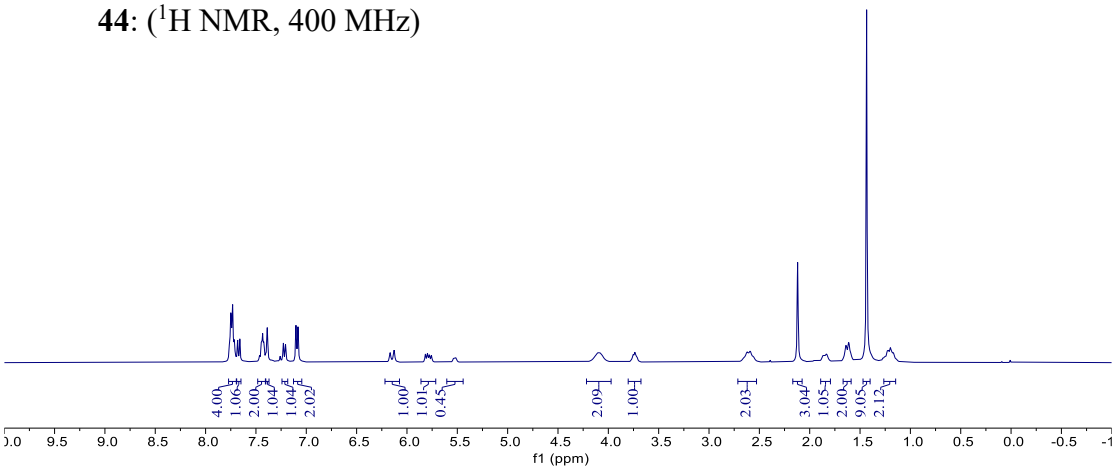


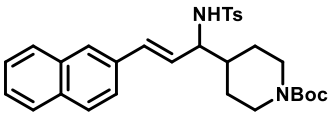
43: (^{13}C NMR, 100 MHz)



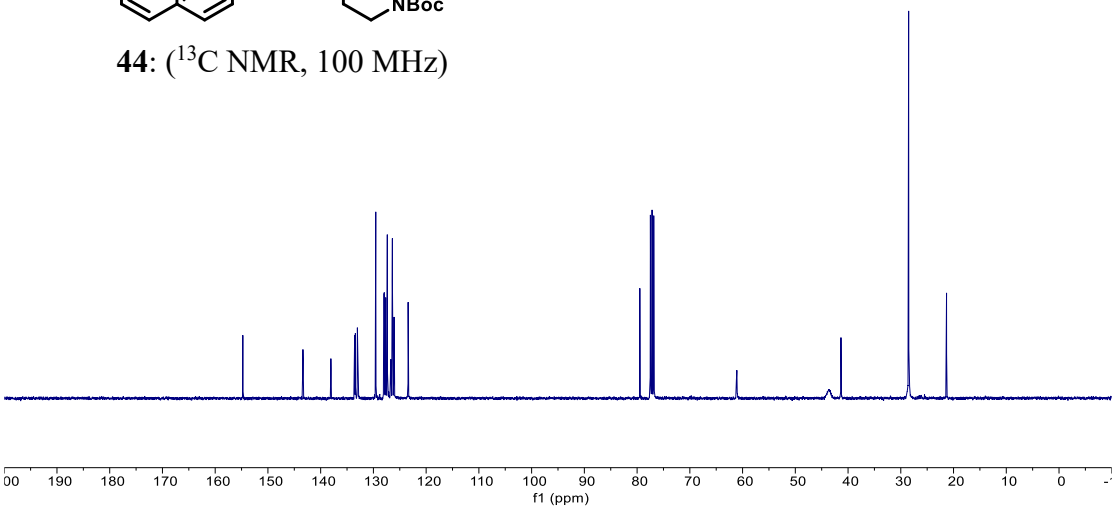


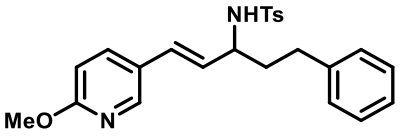
44: (^{1}H NMR, 400 MHz)



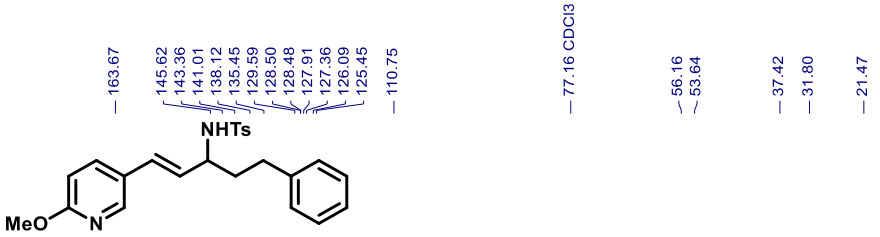


44: (^{13}C NMR, 100 MHz)

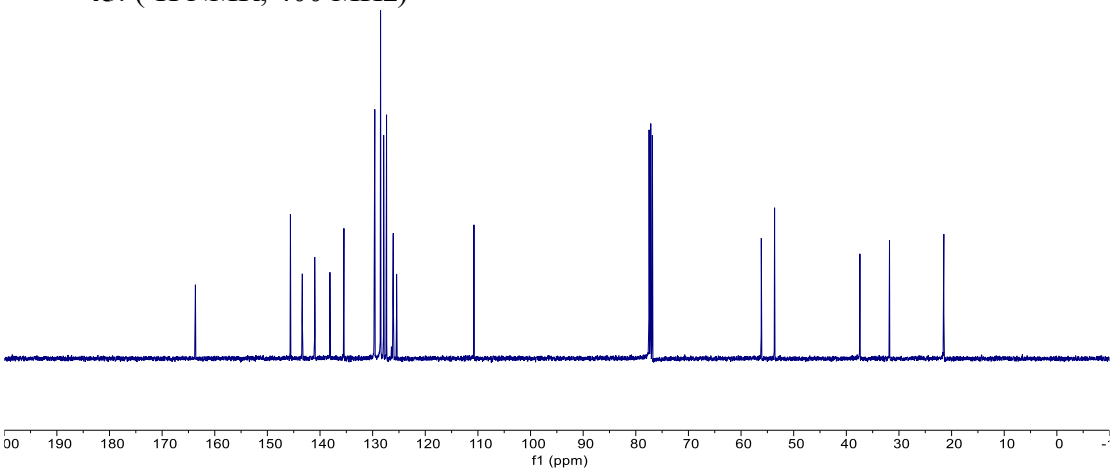


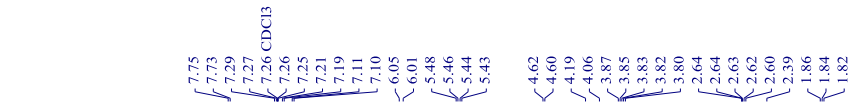


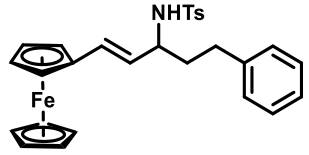
45: (^{1}H NMR, 400 MHz)



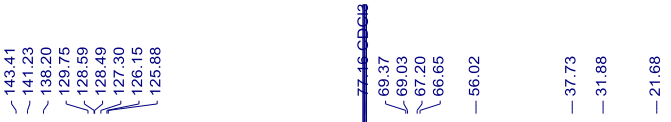
45: (^{1}H NMR, 400 MHz)

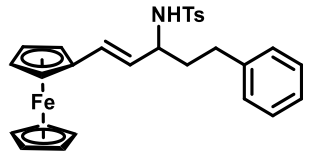




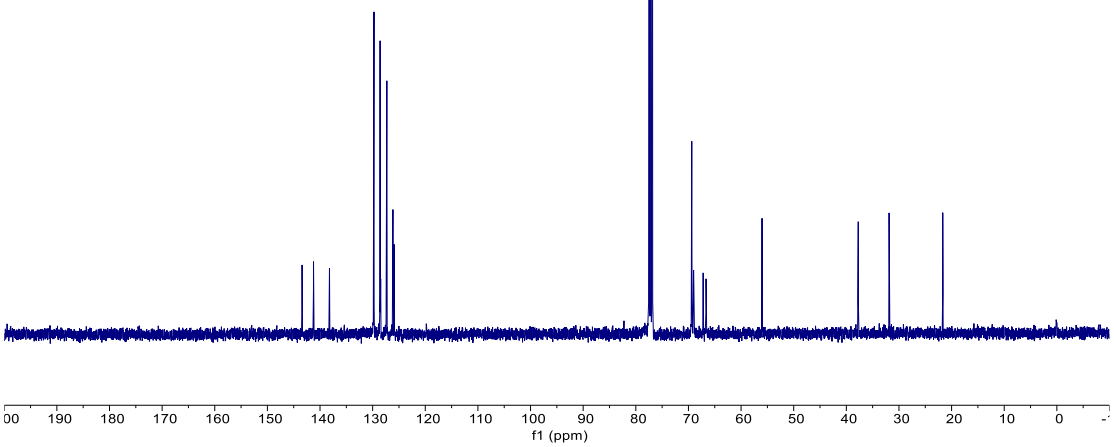


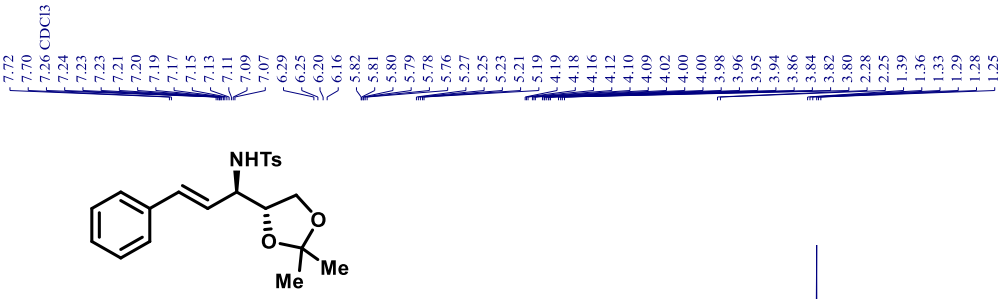
46: (^{1}H NMR, 400 MHz)





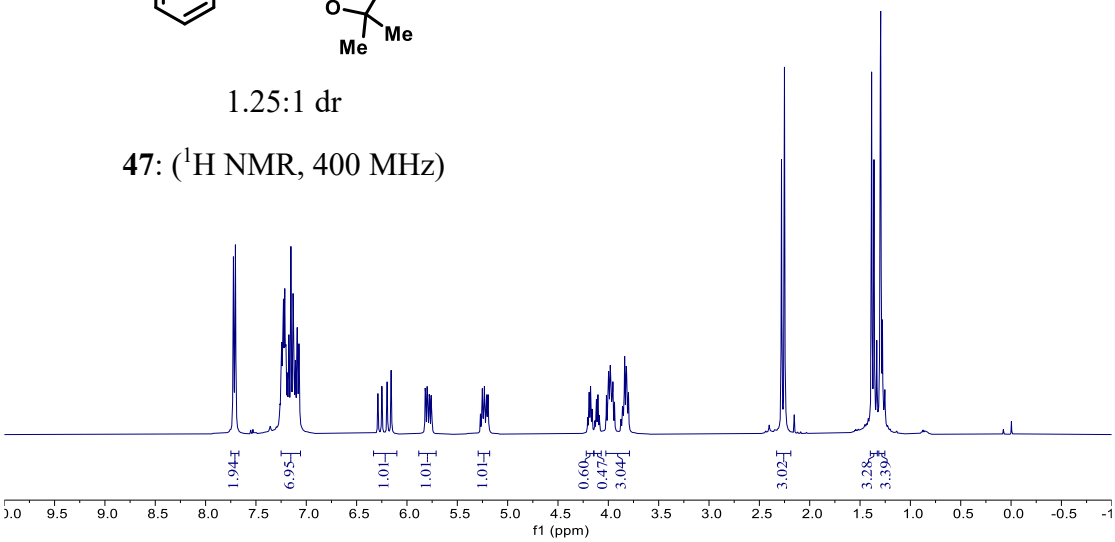
46: (^{13}C NMR, 100 MHz)

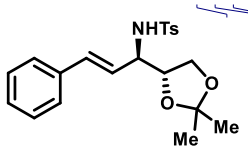




1.25:1 dr

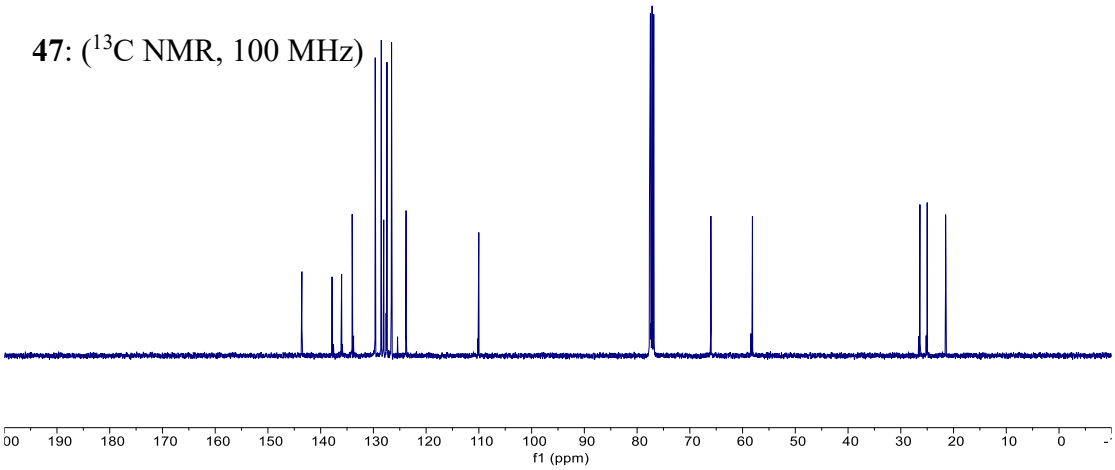
47: (^{1}H NMR, 400 MHz)

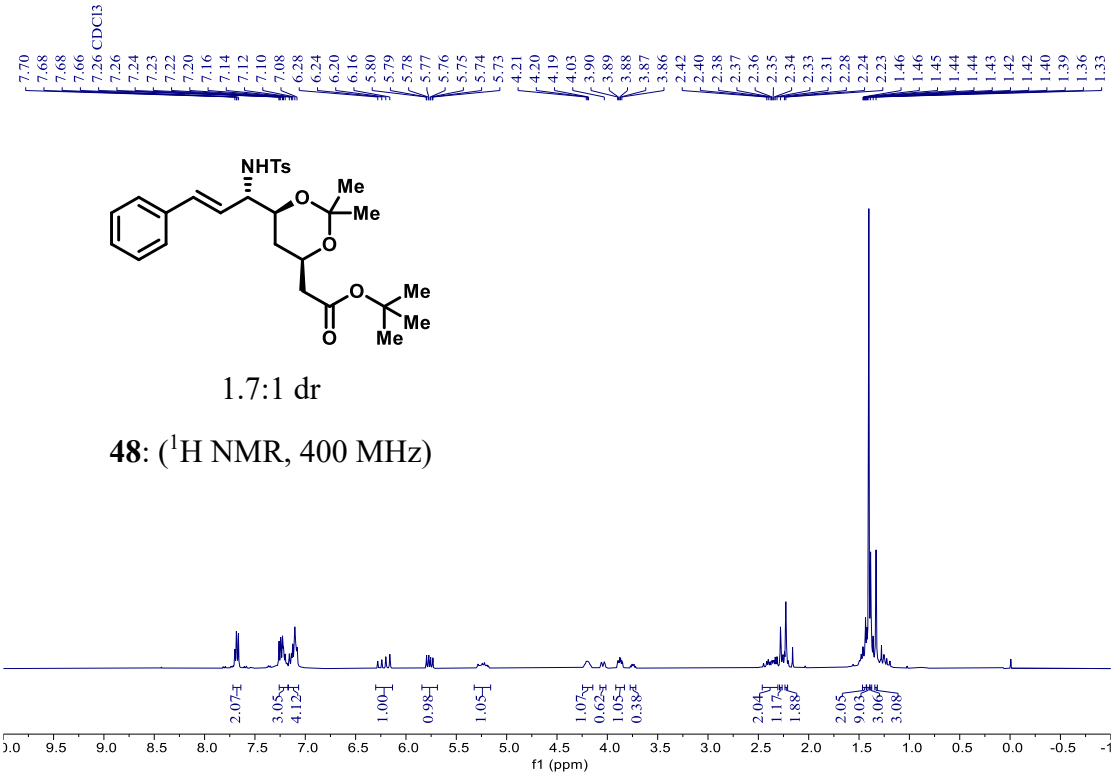




1.25:1 dr

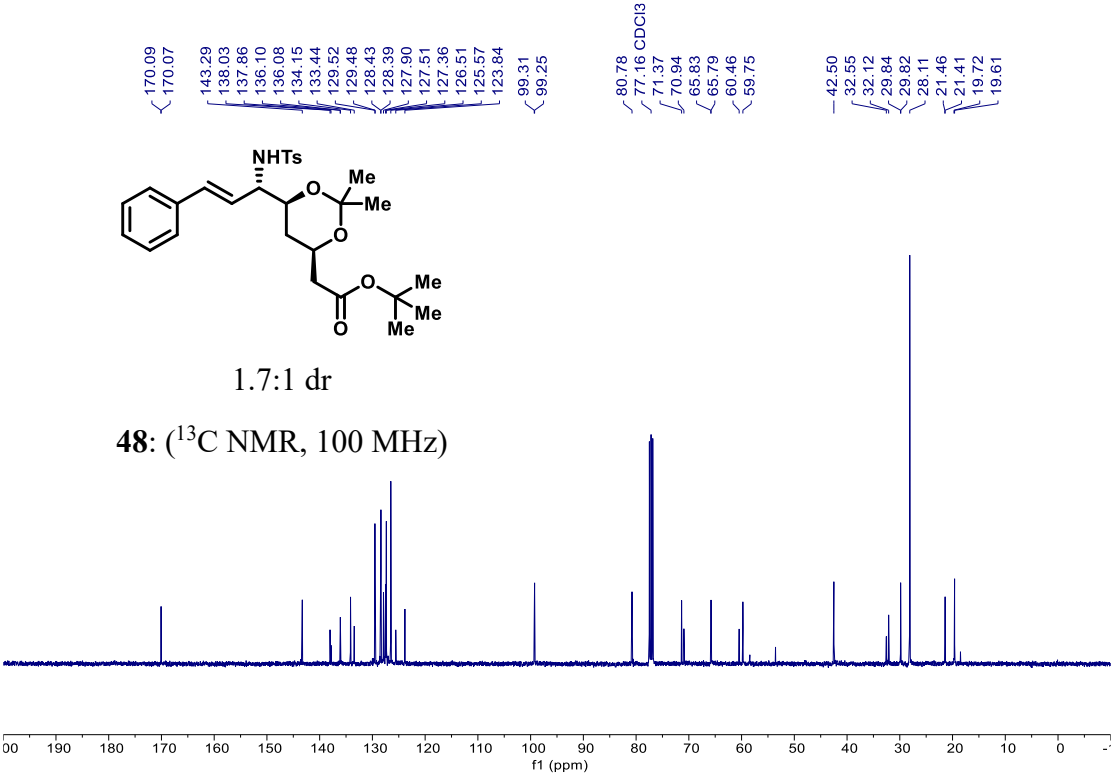
47: (^{13}C NMR, 100 MHz)





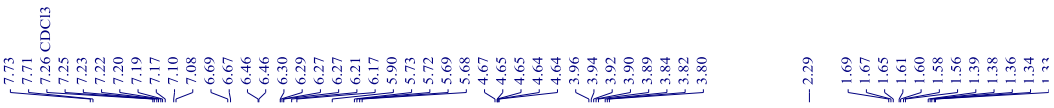
1.7:1 dr

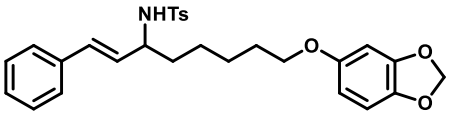
48: (^{1}H NMR, 400 MHz)



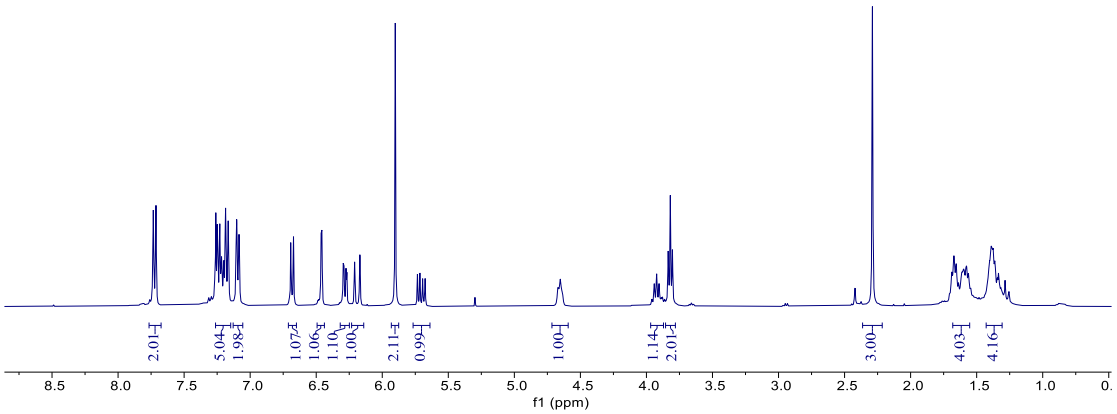
1.7:1 dr

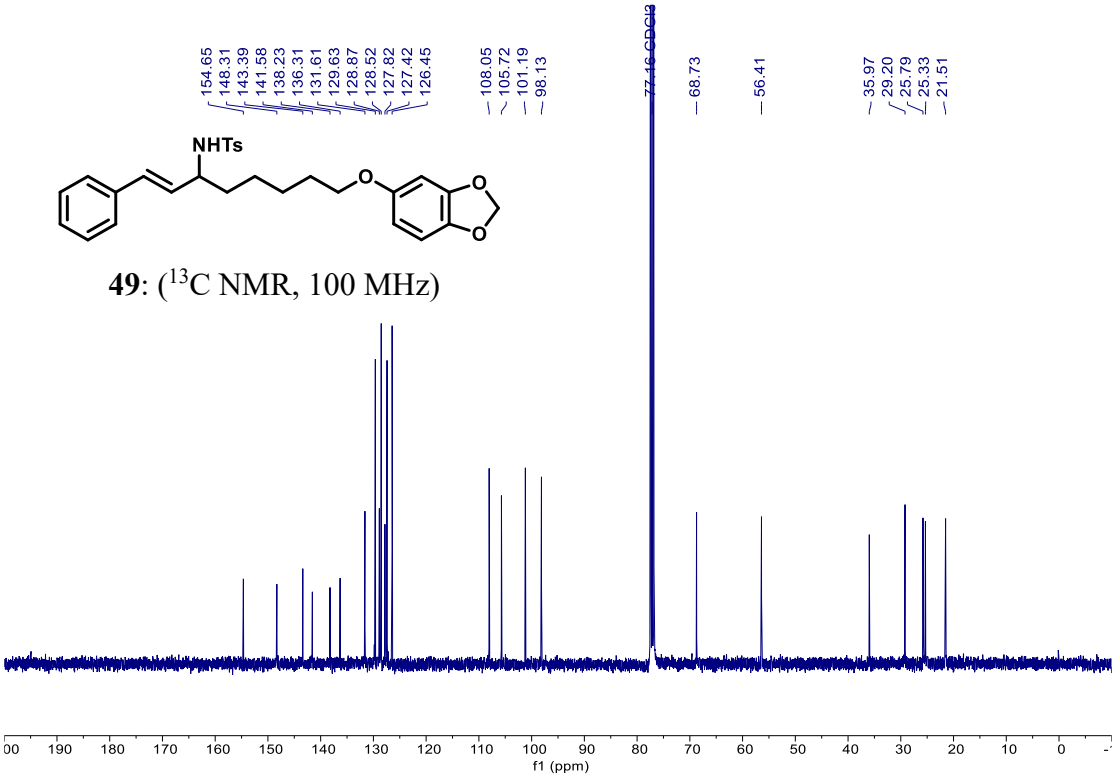
48: (^{13}C NMR, 100 MHz)



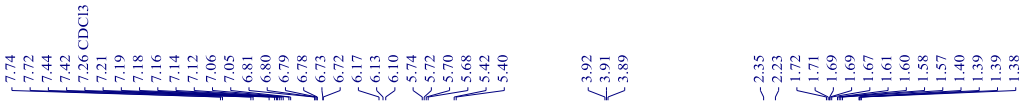


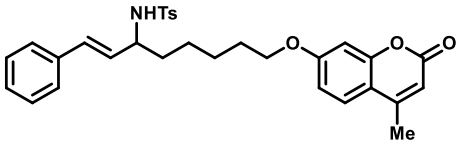
49: (^{1}H NMR, 400 MHz)



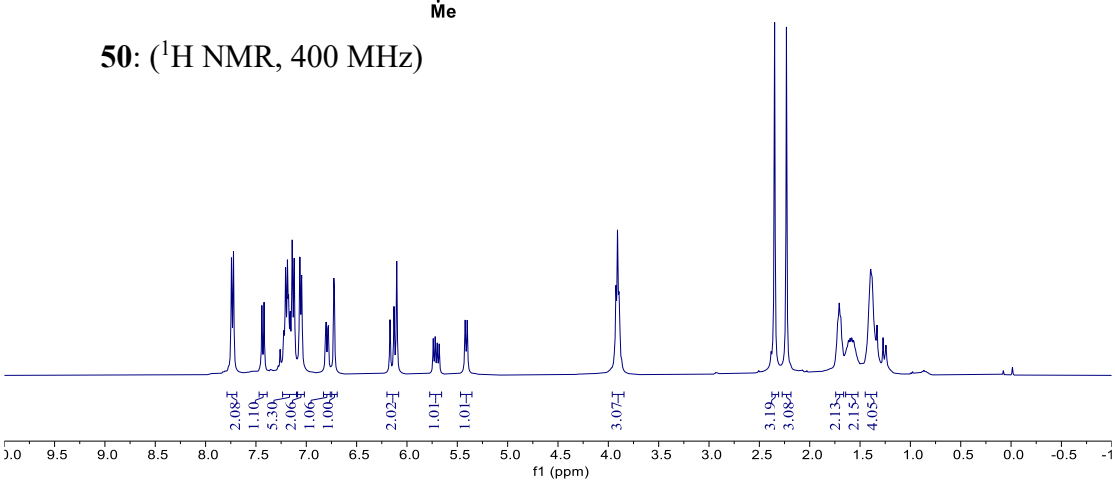


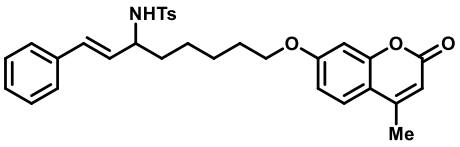
49: (^{13}C NMR, 100 MHz)



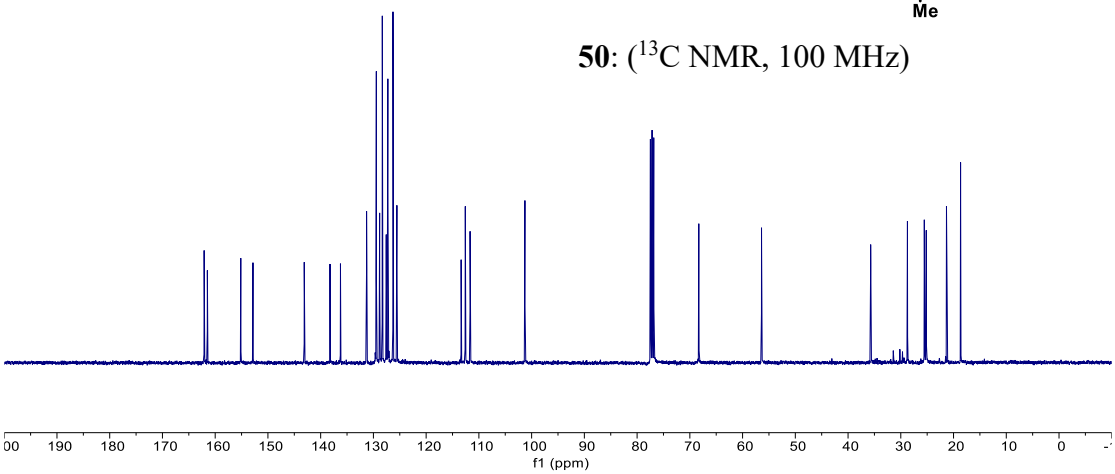


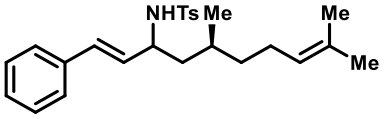
50: (^{1}H NMR, 400 MHz)





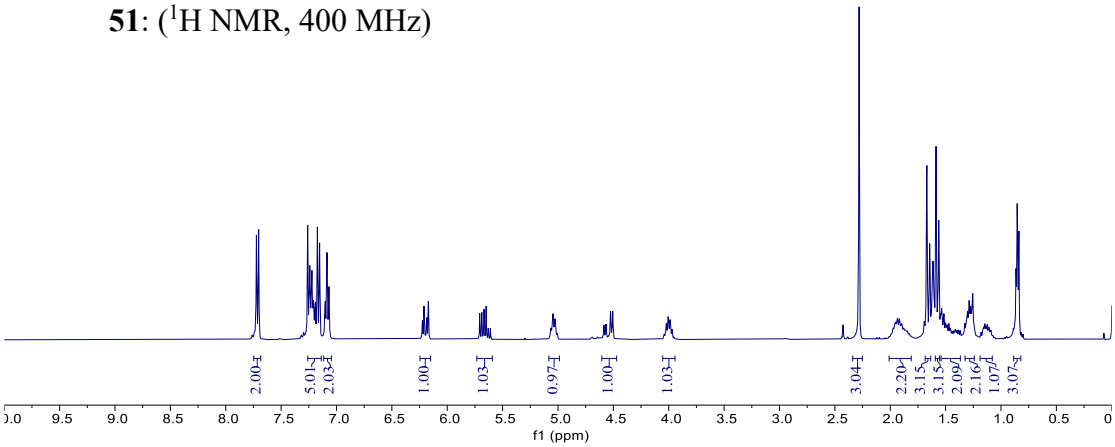
50: (^{13}C NMR, 100 MHz)

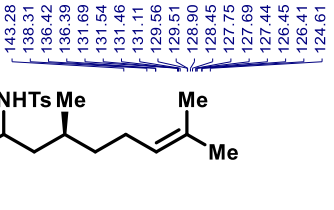




1.25:1 dr

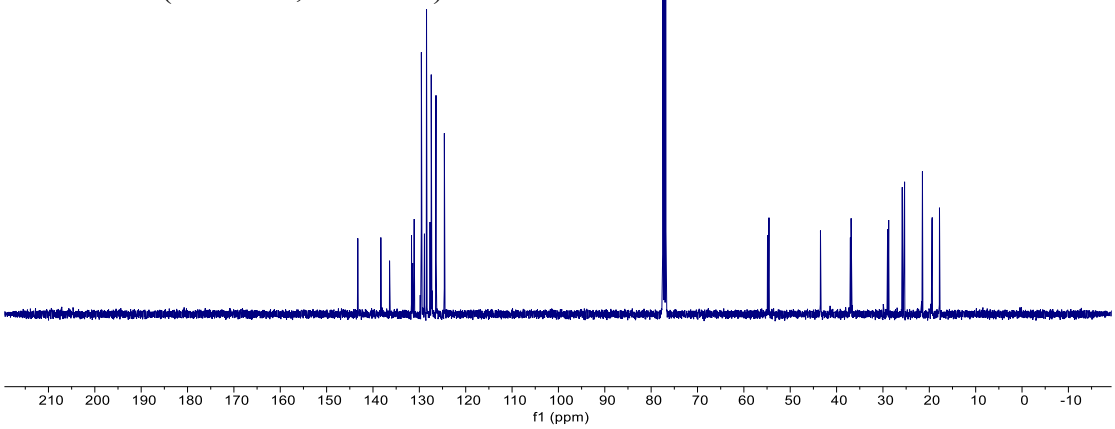
51: (^{1}H NMR, 400 MHz)

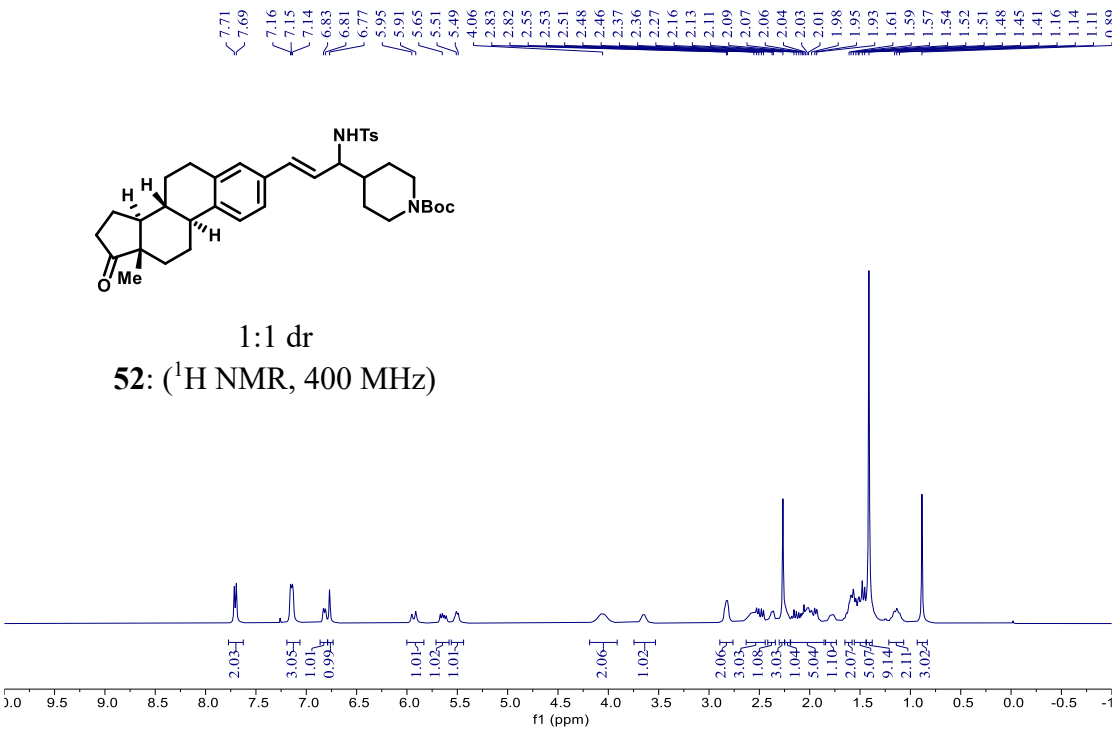




1.25:1 dr

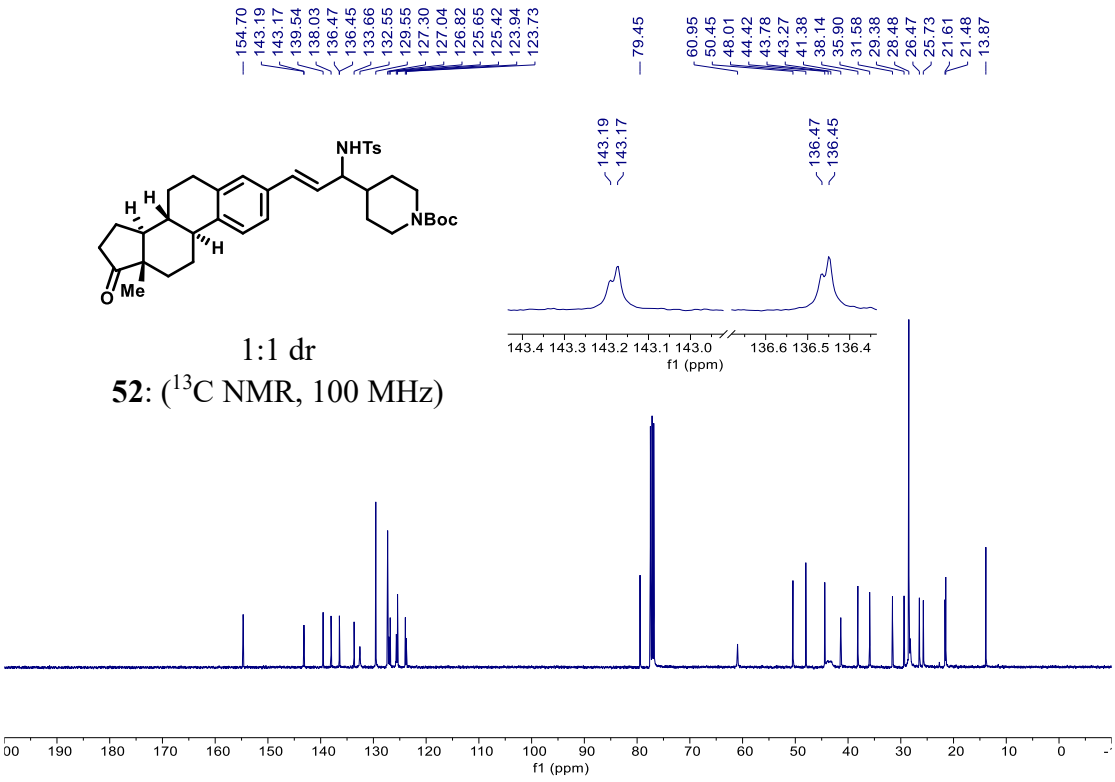
51: (^{13}C NMR, 100 MHz)





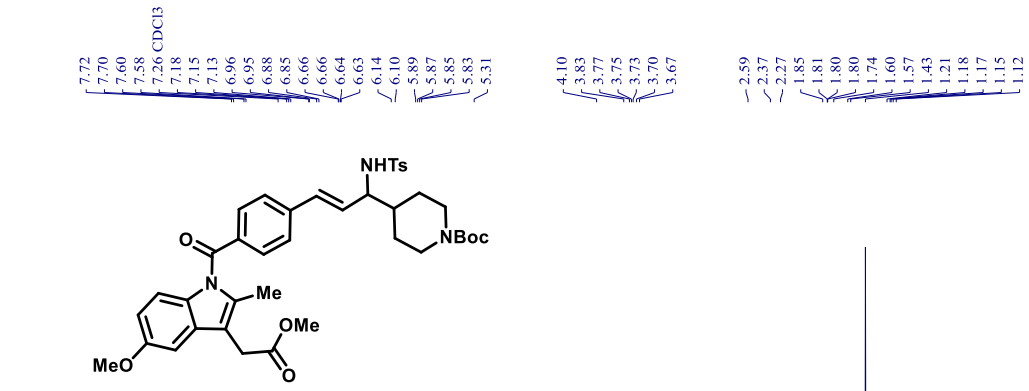
1:1 dr

52: (^{1}H NMR, 400 MHz)

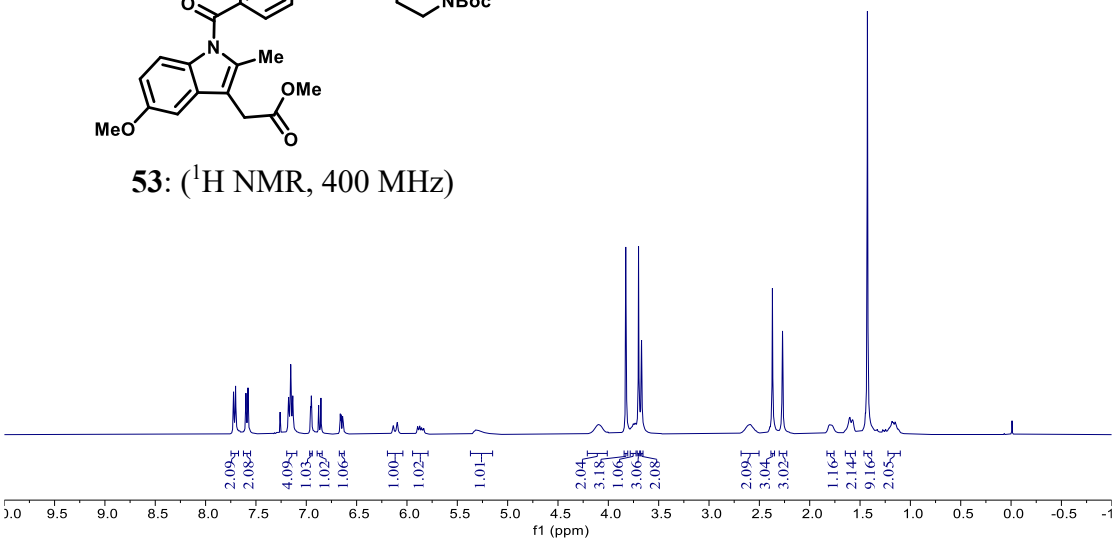


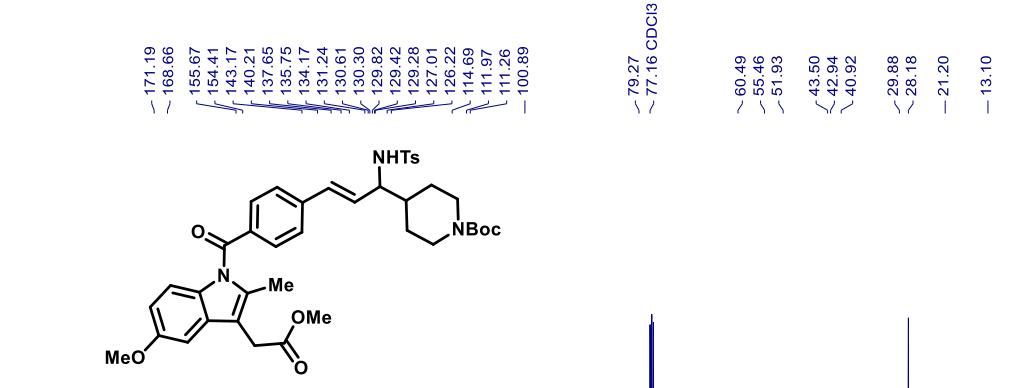
1:1 dr

52: (^{13}C NMR, 100 MHz)

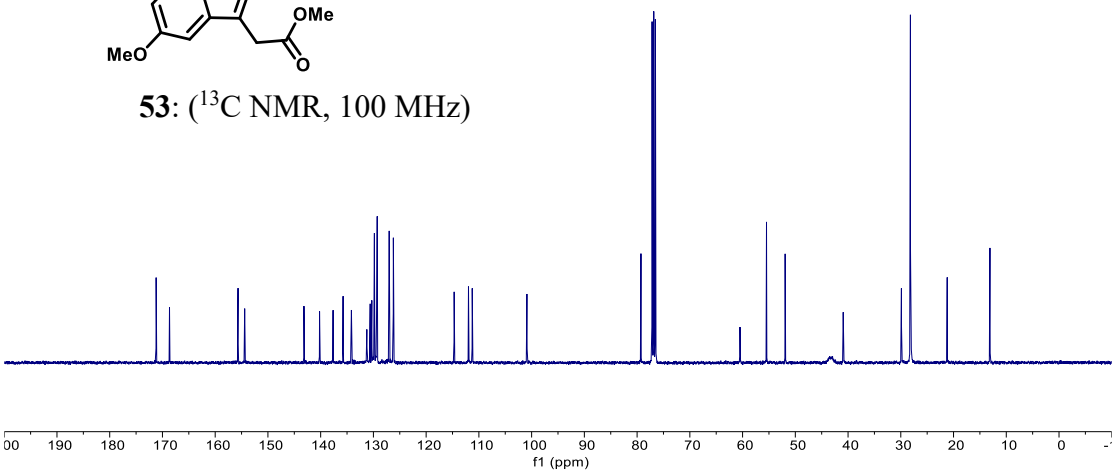


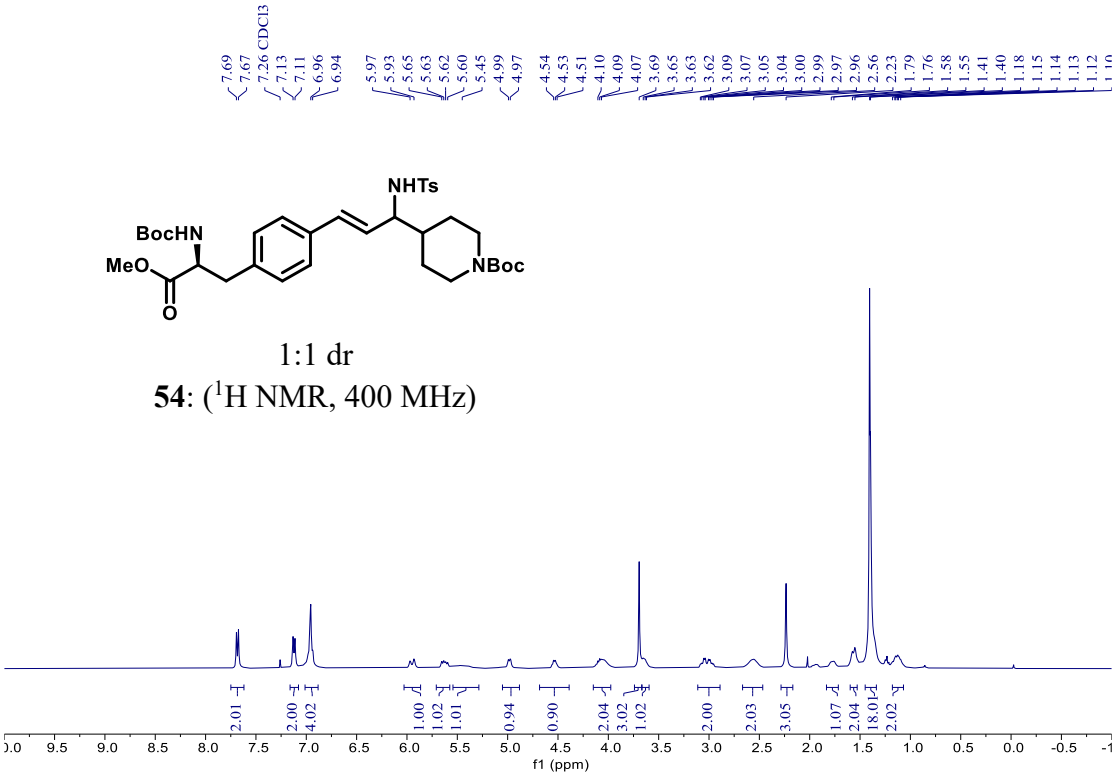
53: (^{1}H NMR, 400 MHz)





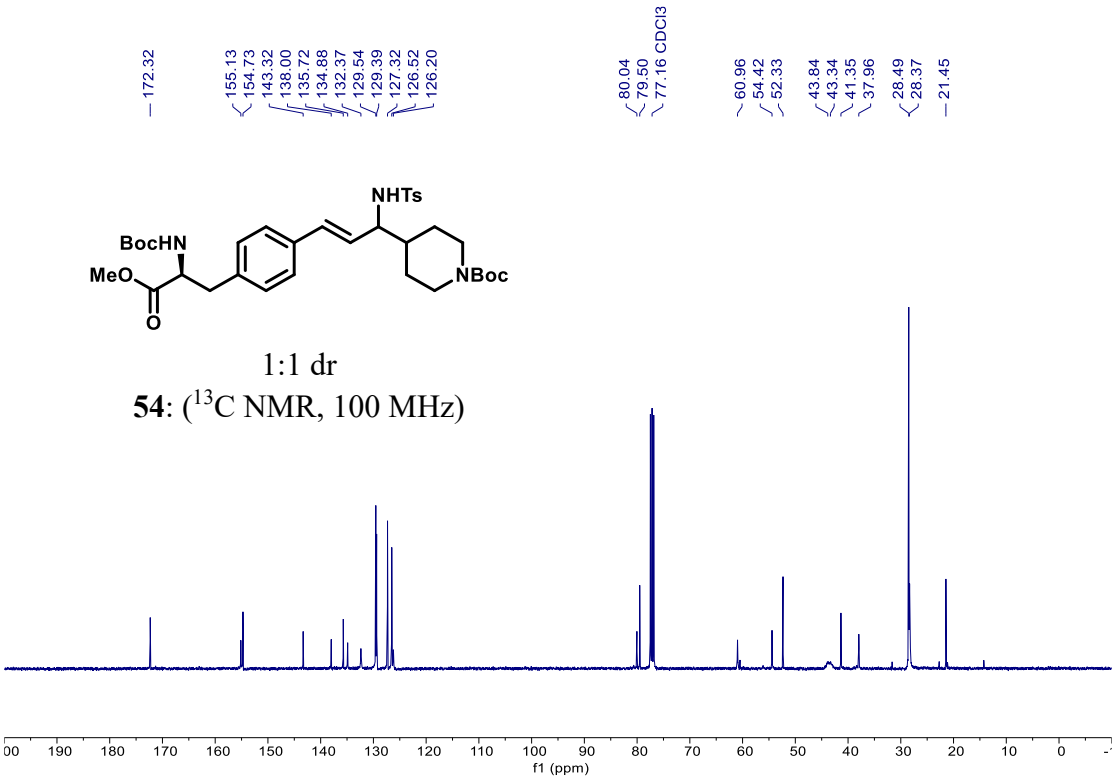
53: (^{13}C NMR, 100 MHz)





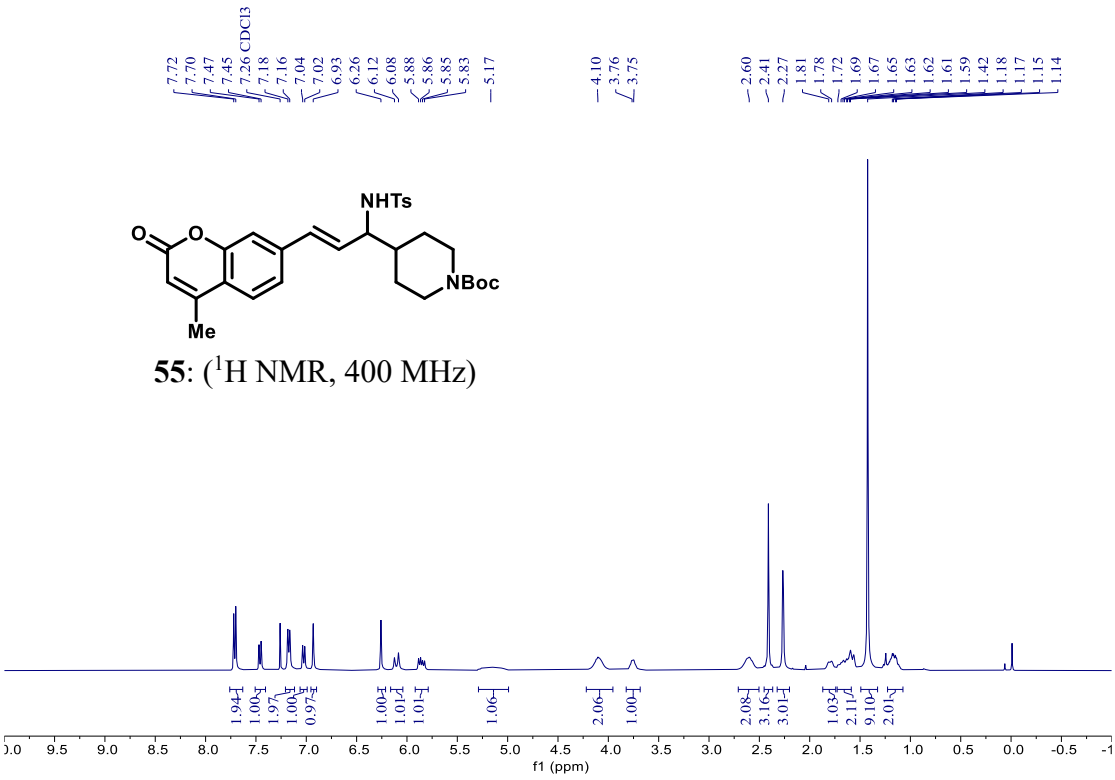
1:1 dr

54: (^{1}H NMR, 400 MHz)

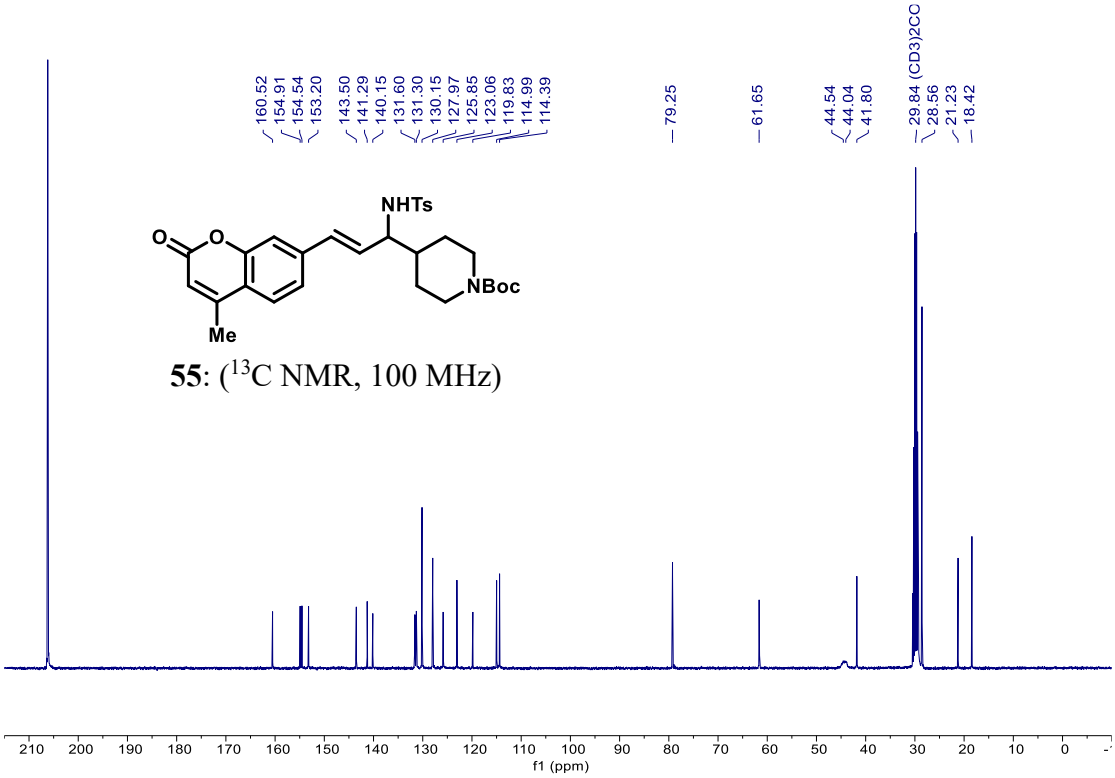


1:1 dr

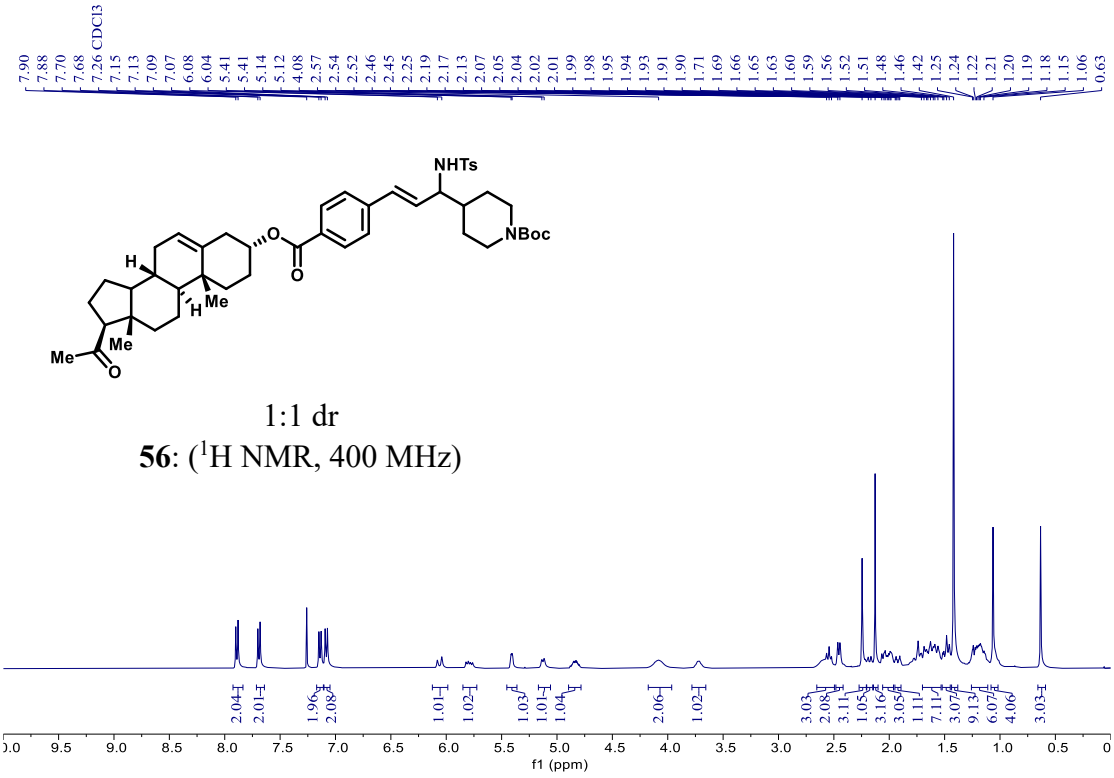
54: (^{13}C NMR, 100 MHz)



55: (^{1}H NMR, 400 MHz)

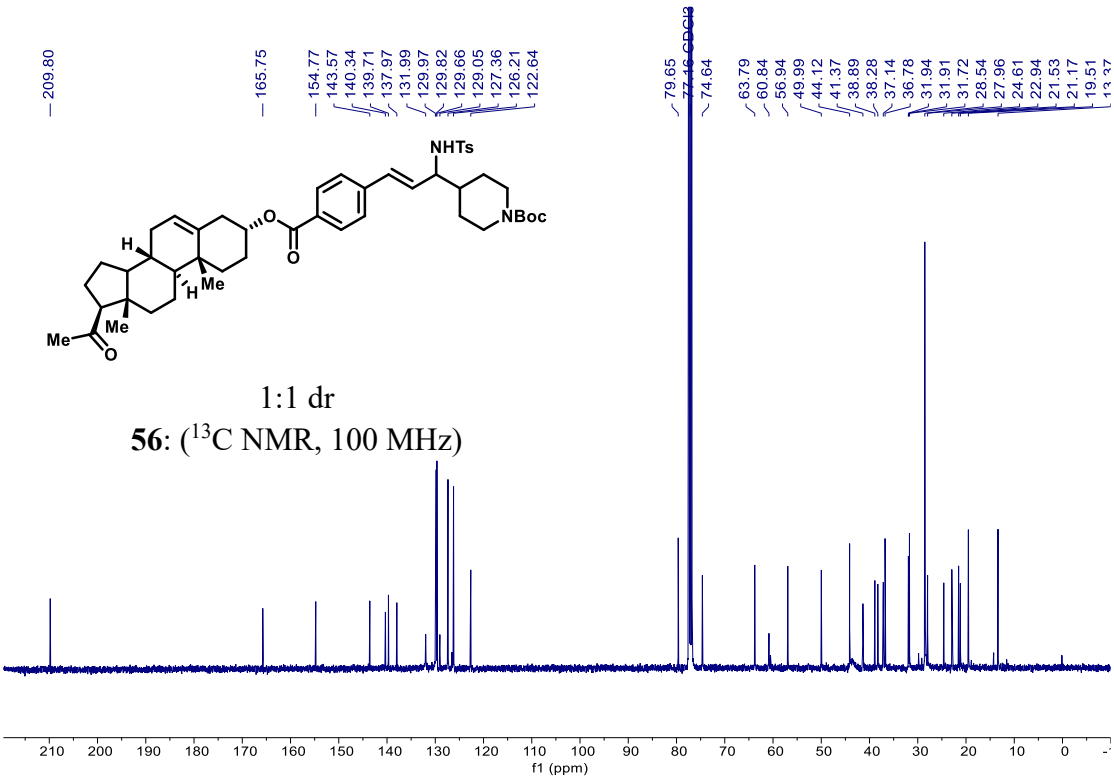


55: (^{13}C NMR, 100 MHz)



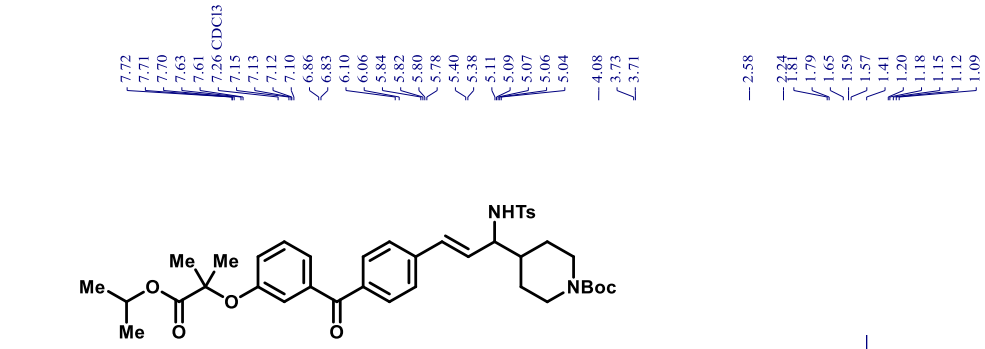
1:1 dr

56: (^{1}H NMR, 400 MHz)

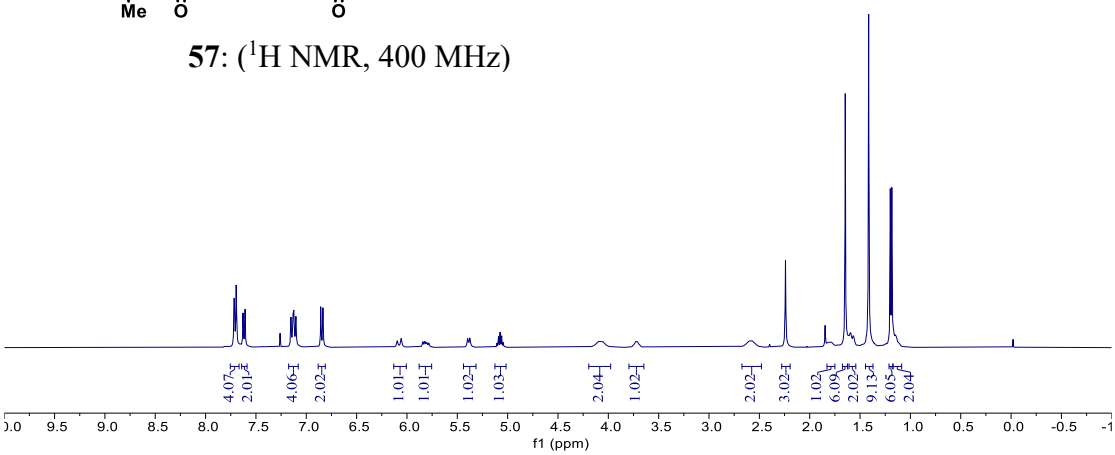


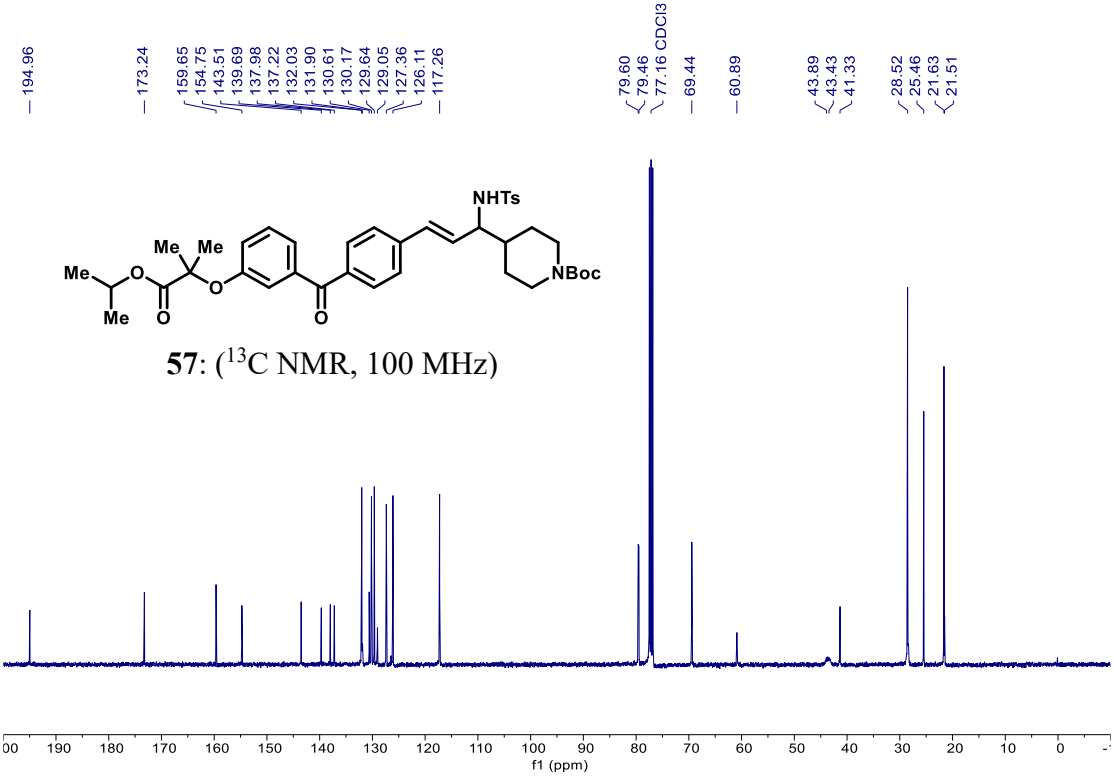
1:1 dr

56: (^{13}C NMR, 100 MHz)

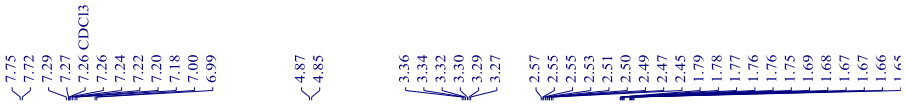


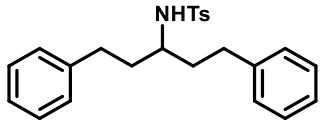
57: (^{1}H NMR, 400 MHz)



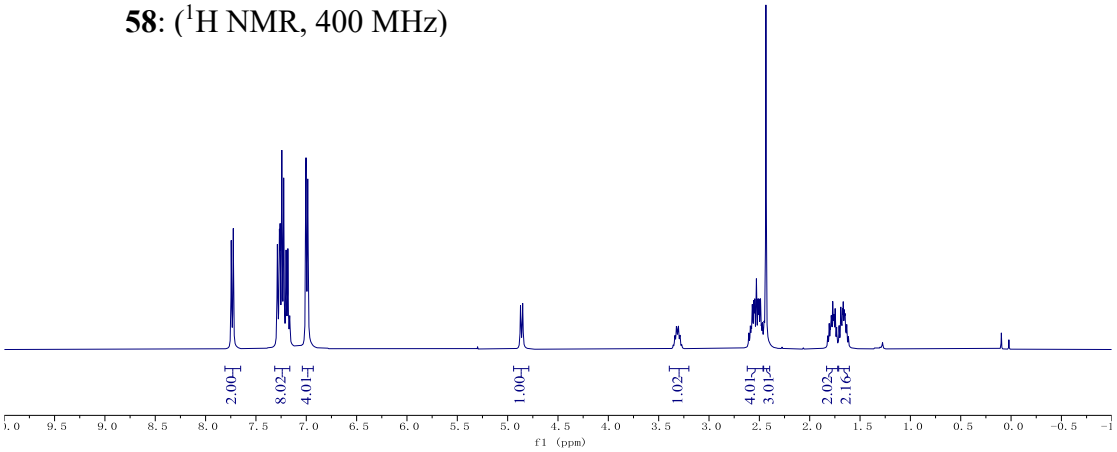


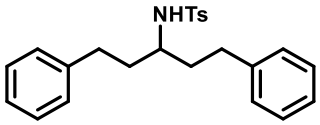
57: (^{13}C NMR, 100 MHz)



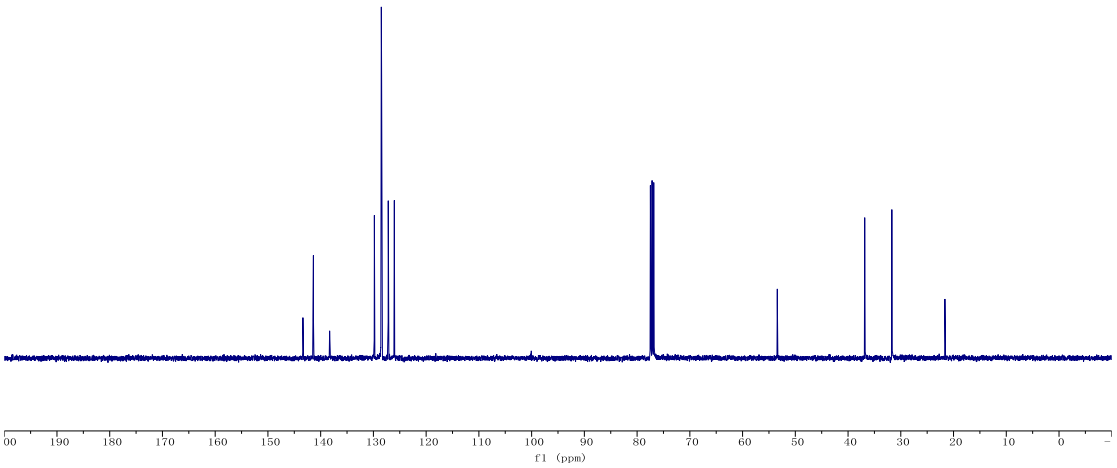


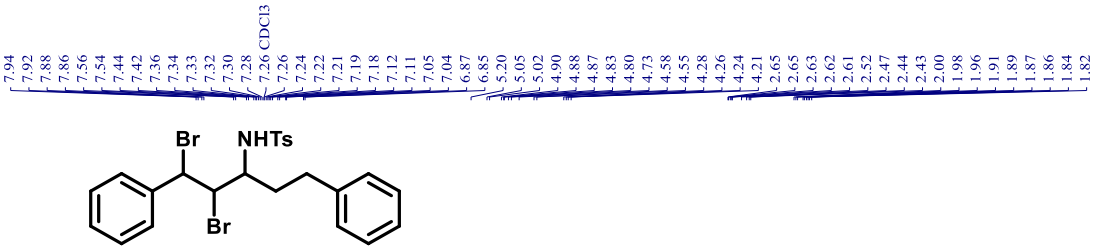
58: (^{1}H NMR, 400 MHz)





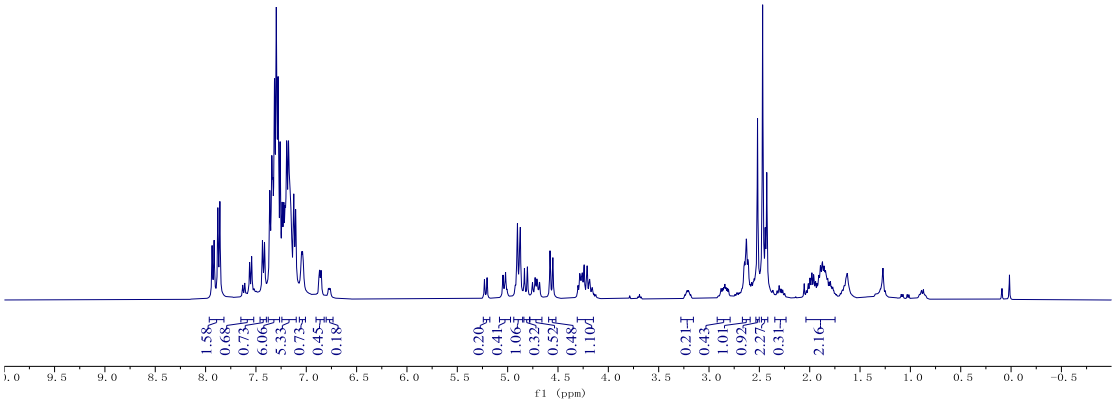
58: (^{13}C NMR, 100 MHz)

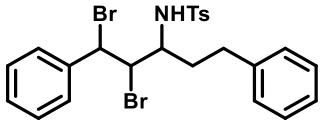




1:2.3:6 dr

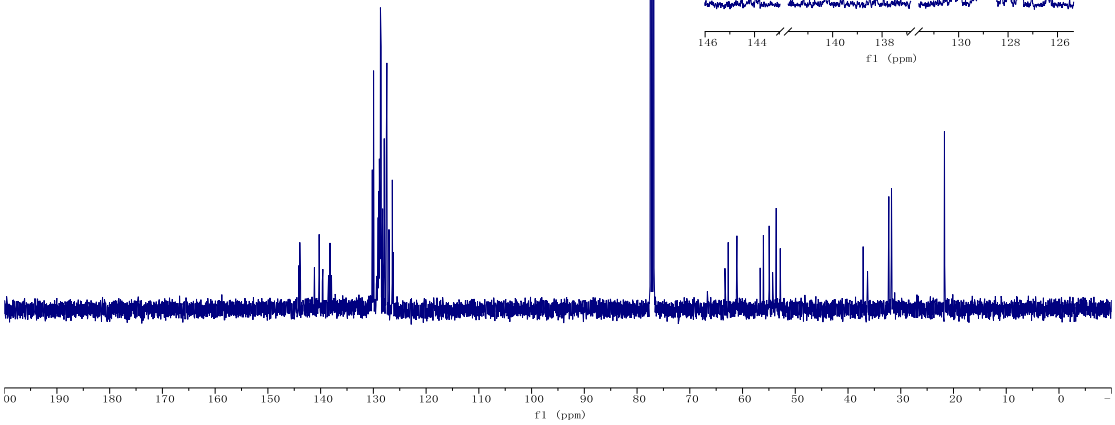
59: (^{1}H NMR, 400 MHz)

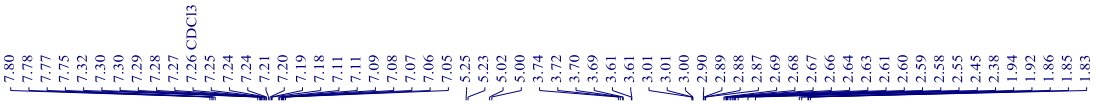


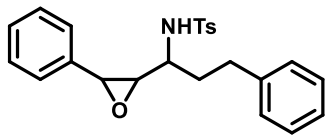


1:2.3:6 dr

59: (^{13}C NMR, 100 MHz)

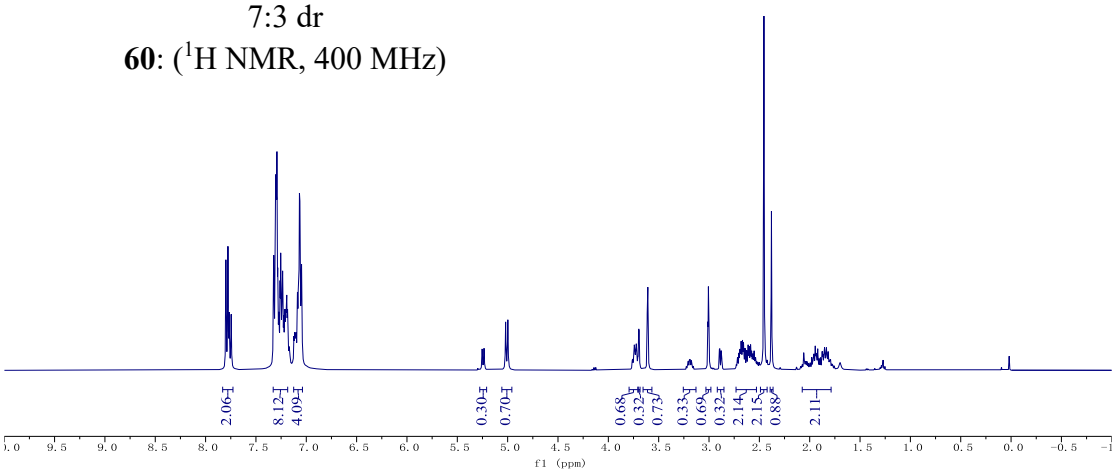


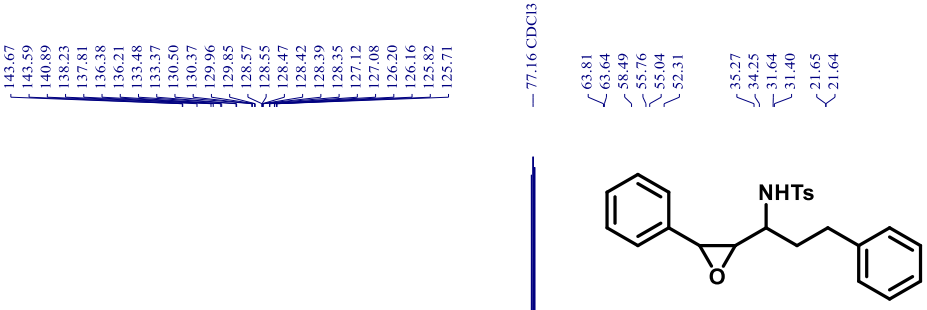




7:3 dr

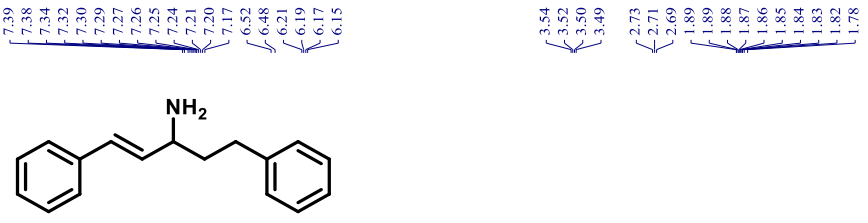
60: (^{1}H NMR, 400 MHz)



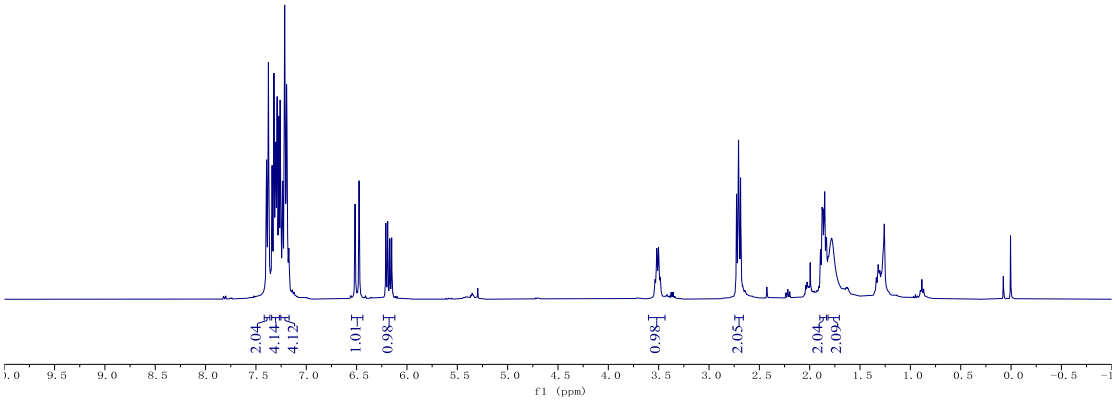


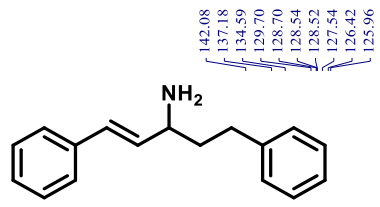
7:3 dr

60: (^{13}C NMR, 100 MHz)

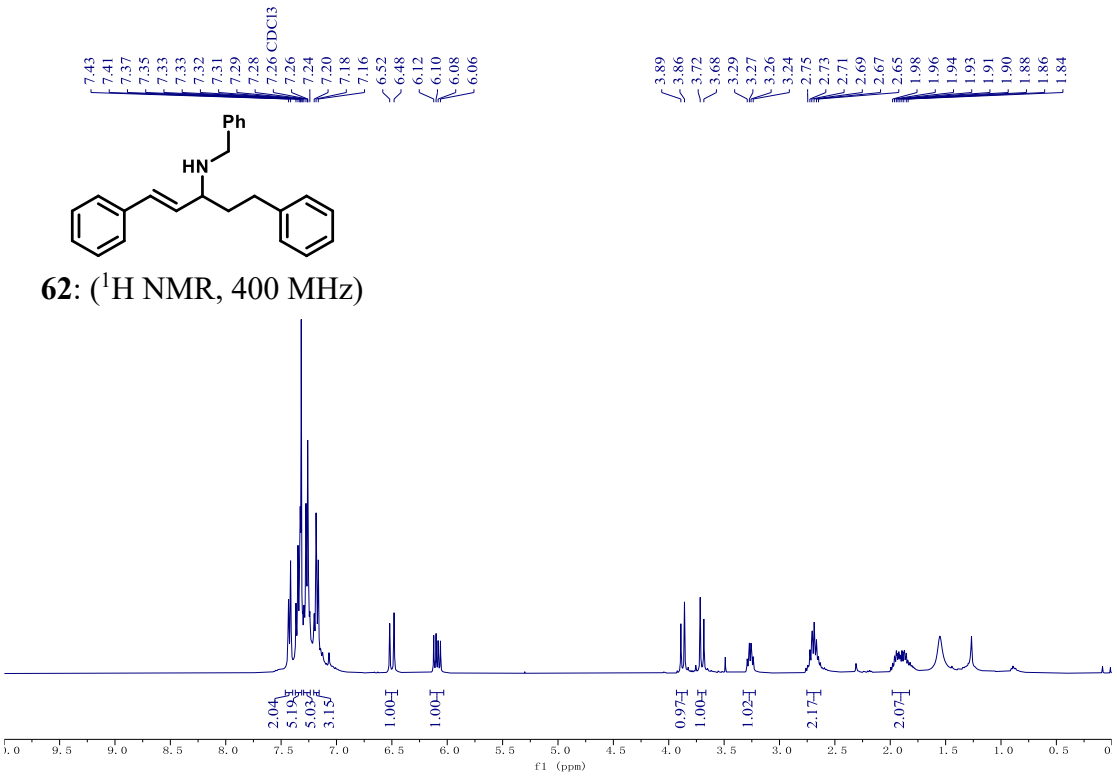


61: (^{1}H NMR, 400 MHz)

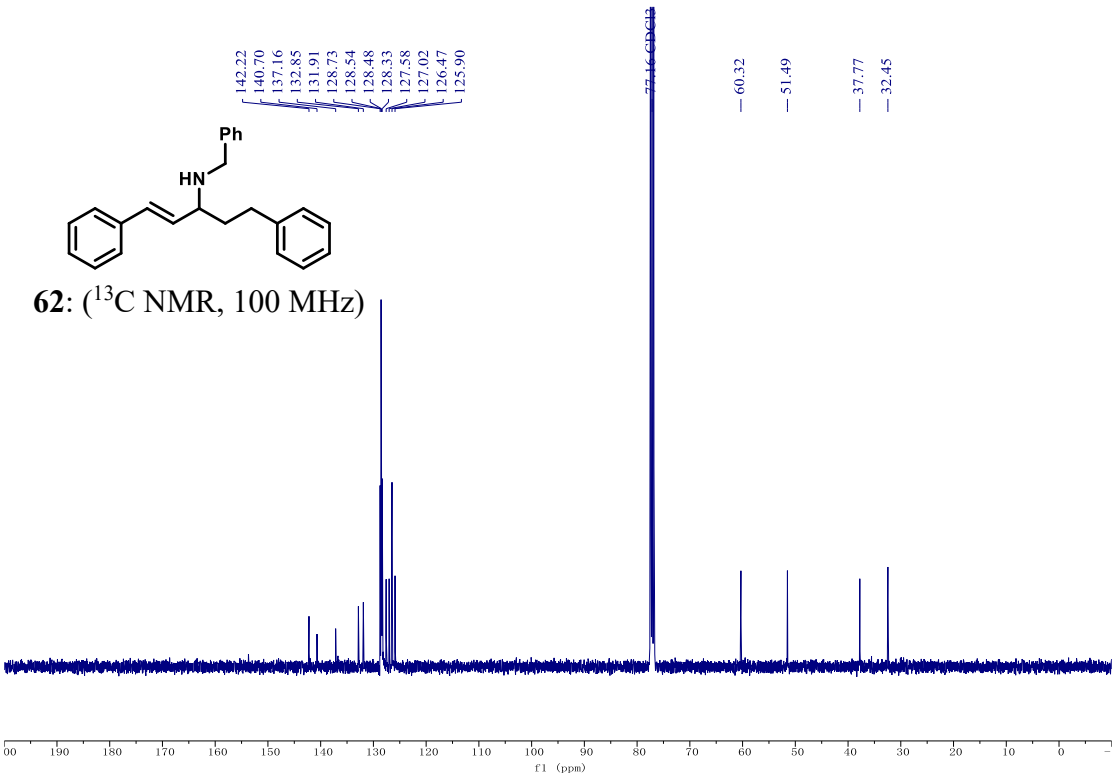




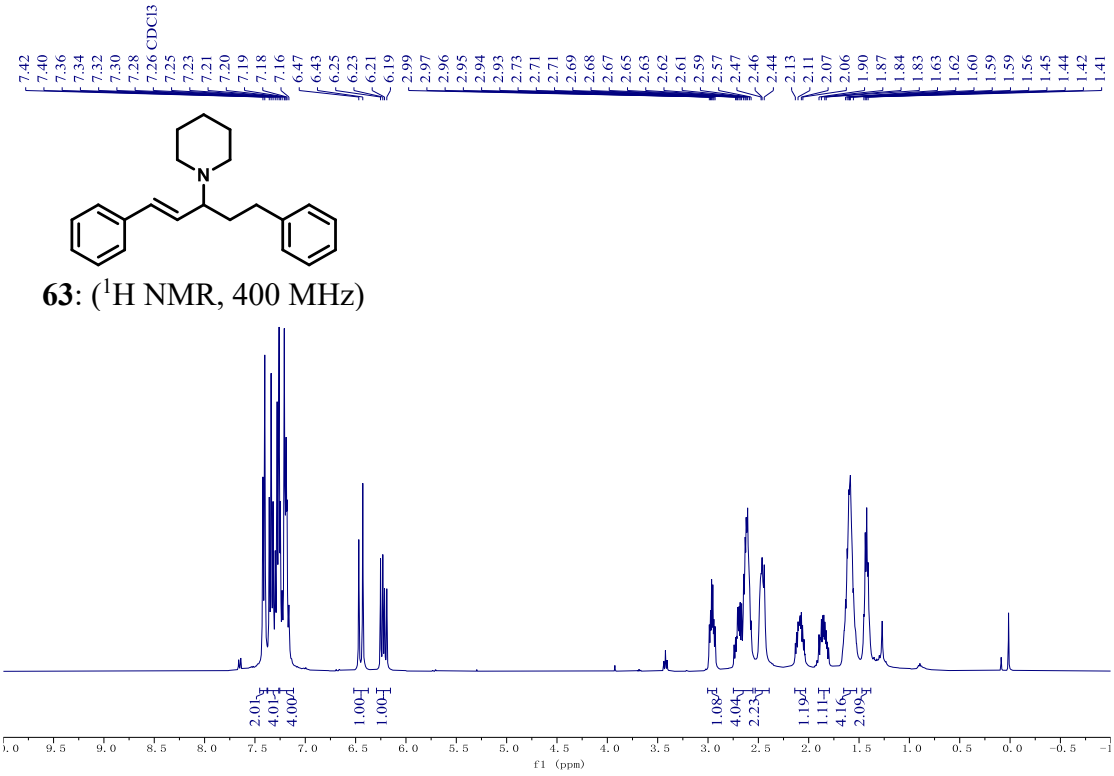
61: (^{13}C NMR, 100 MHz)



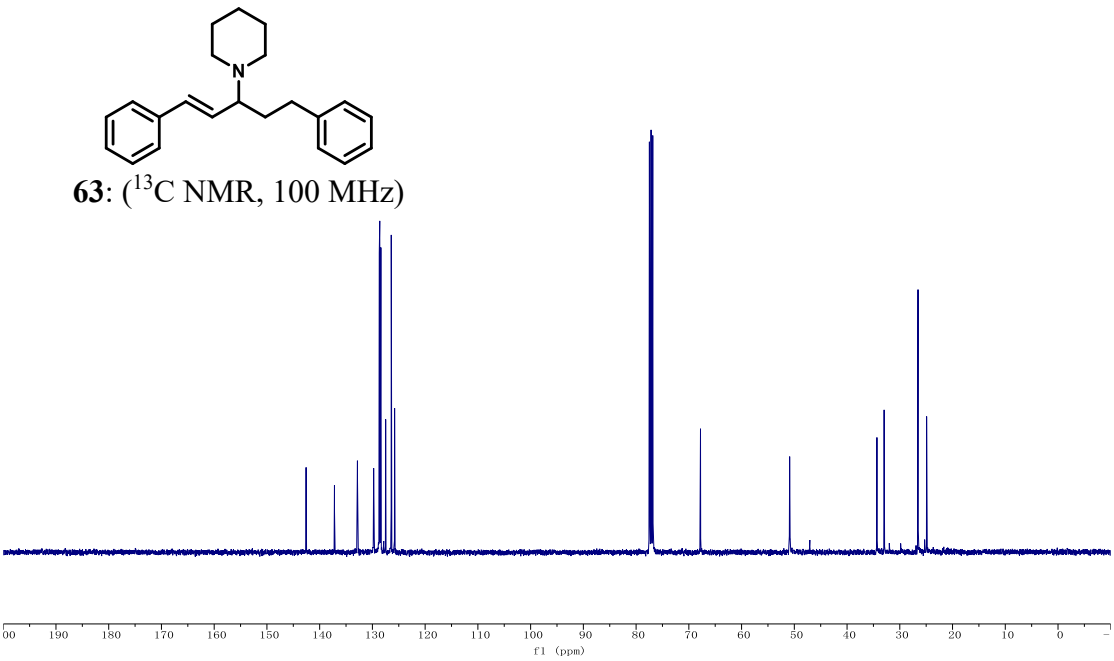
62: (^{1}H NMR, 400 MHz)



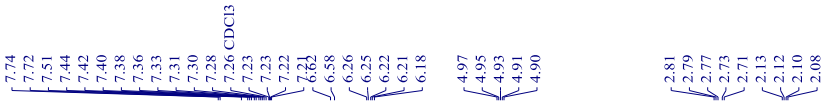
62: (^{13}C NMR, 100 MHz)

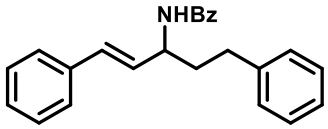


63: (^{1}H NMR, 400 MHz)

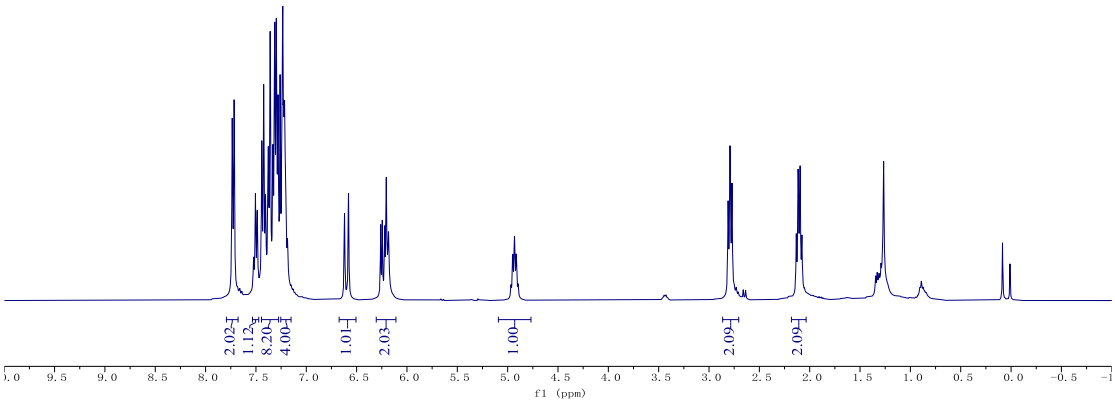


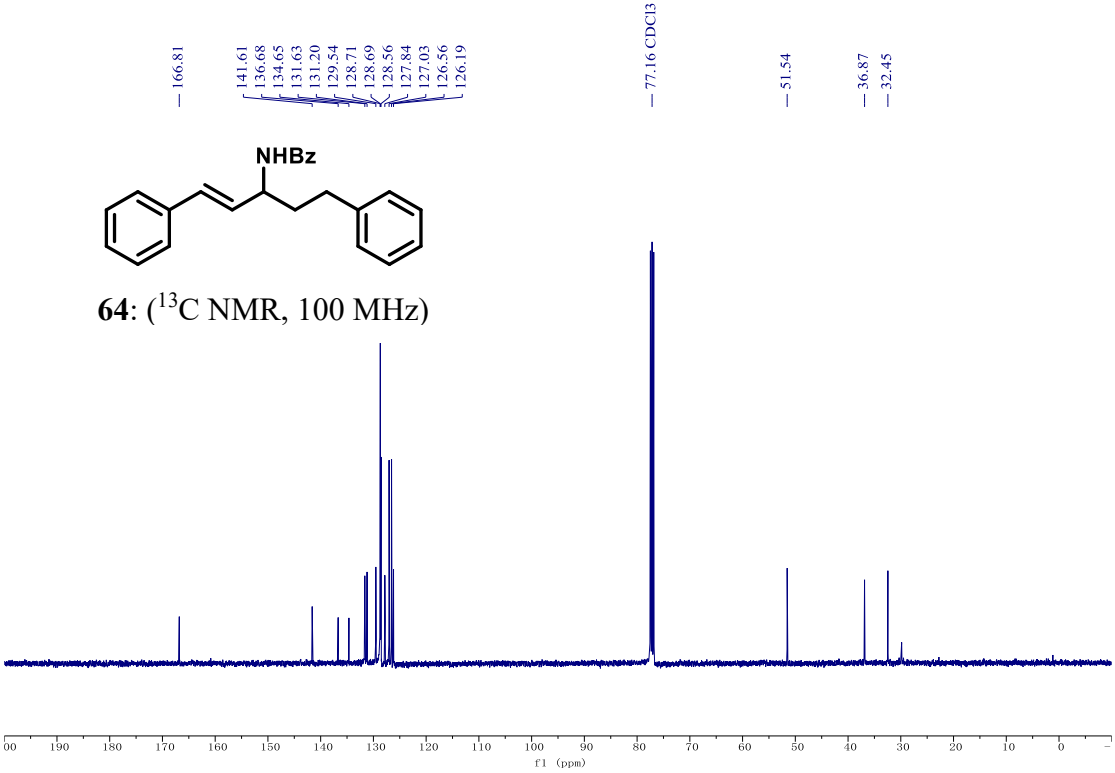
63: (^{13}C NMR, 100 MHz)



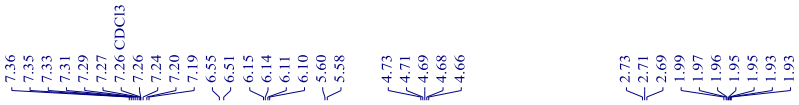


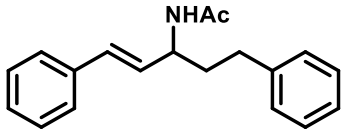
64: (^{1}H NMR, 400 MHz)



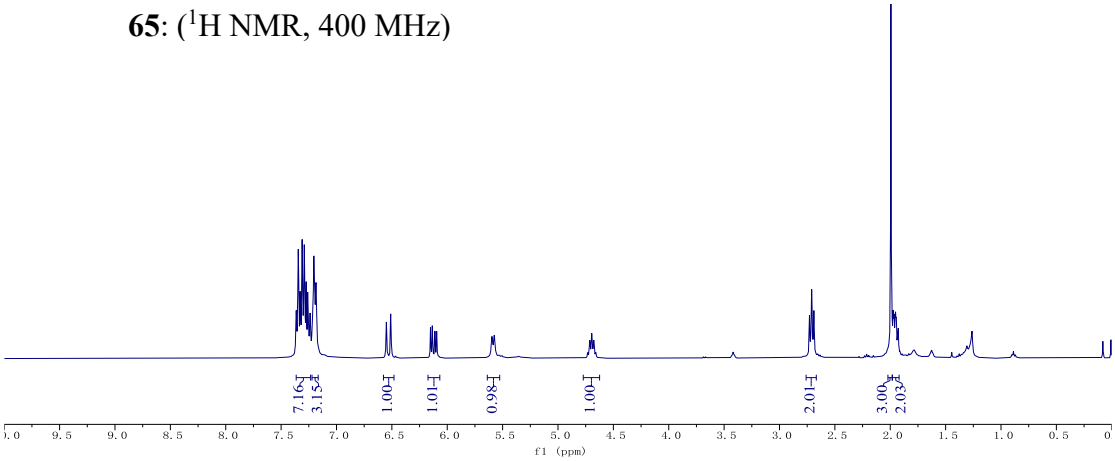


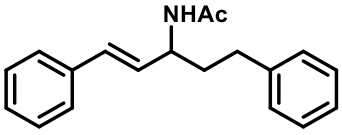
64: (^{13}C NMR, 100 MHz)



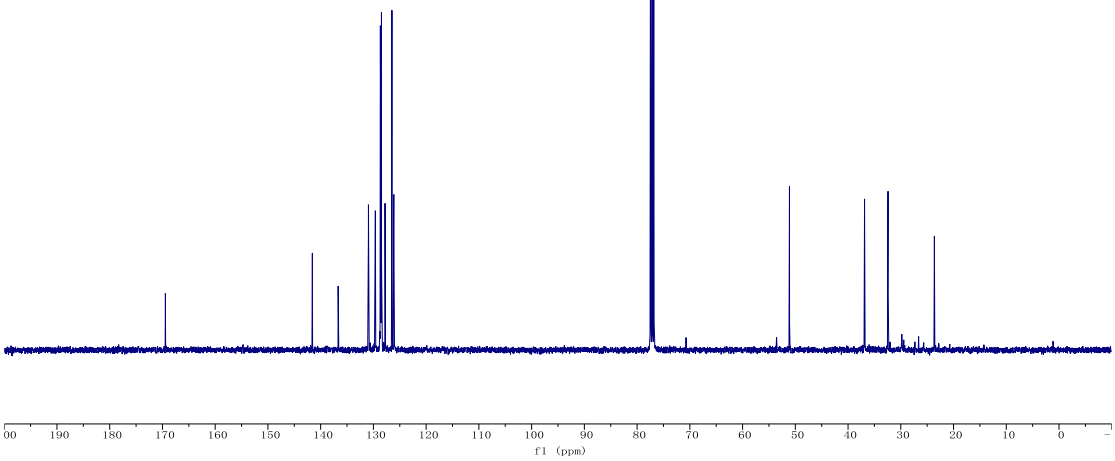


65: (^{1}H NMR, 400 MHz)





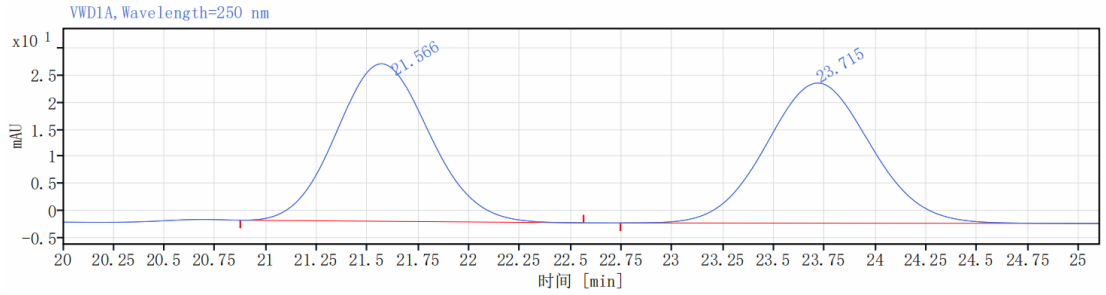
65: (^{13}C NMR, 100 MHz)



X. HPLC Charts

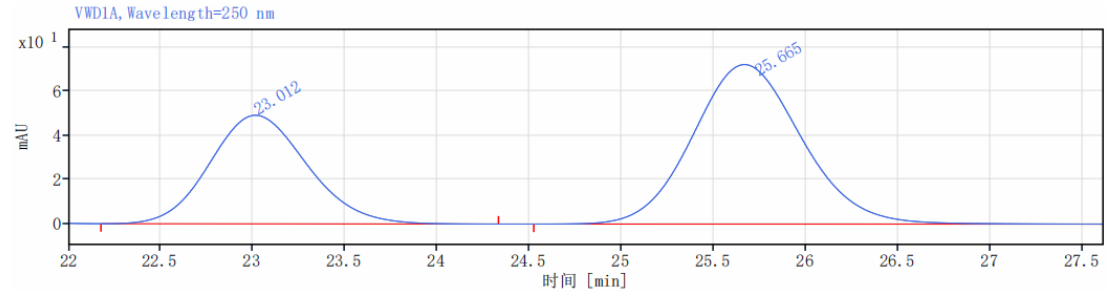
Condition: Chiralpak AD-H column, n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min.

HPLC Chart of Racemic Product **21**



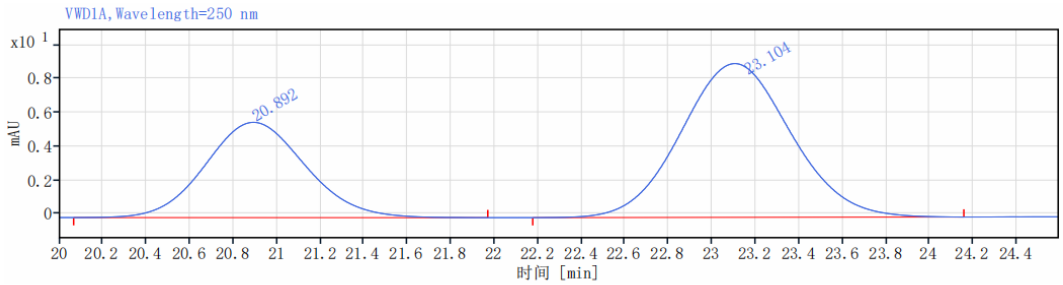
Resolution Time (min)	Width (min)	Area	Height	Area %
21.566	1.690	926.9	28.9	49.94
23.715	2.525	929.0	25.7	50.06

HPLC Chart of Product **21** using **L1**



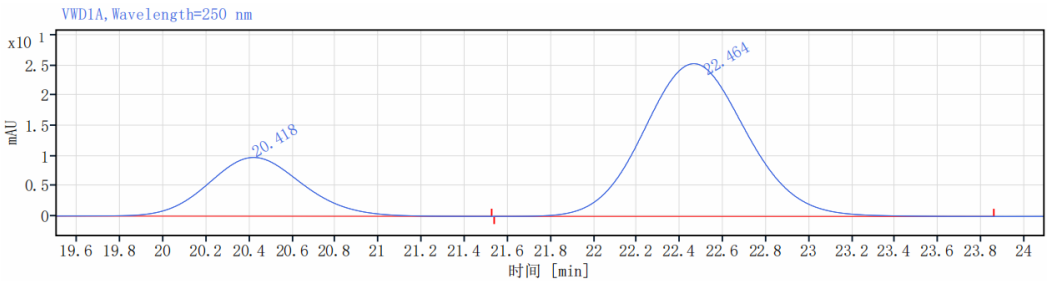
Resolution Time (min)	Width (min)	Area	Height	Area %
23.012	2.157	1817.3	49.3	37.81
25.665	3.655	2989.0	72.5	62.19

HPLC Chart of Product **21** using **L2**



Resolution Time (min)	Width (min)	Area	Height	Area %
20.892	1.903	180.6	5.6	36.08
23.104	1.981	319.9	9.1	63.92

HPLC Chart of Product **21** using **L3**



Resolution Time (min)	Width (min)	Area	Height	Area %
20.418	2.142	299.9	9.8	26.09
22.464	2.322	849.3	25.4	73.91