Supporting Information for

Construction of Polycyclic γ-Lactams and Related Heterocycles via Electron Catalysis

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1. General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. THF was freshly distilled from K under argon. All other solvents and reagents were purified according to standard procedures or were used as received from Alfa Aesar, TCI, Aldrich, Fluka, Acros or ABCR. The starting materials were synthesized according to literature procedures.

TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light or dipping into a solution of $KMnO_4$ (1.5 g in 400mL H_2O, 5 g $NaHCO_3$), followed by heating.

Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 µm) applying a pressure of about 0.2 bar.

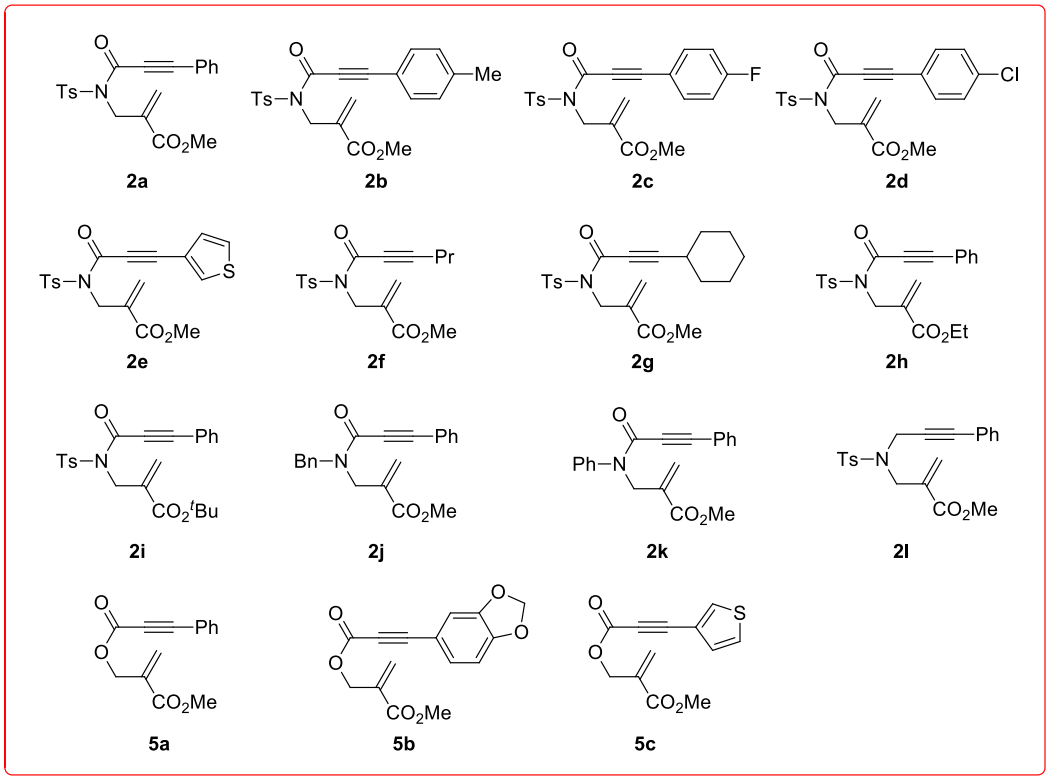
^{1}H NMR and **^{13}C NMR** spectra were recorded on a *DPX 300*, *AV 400* or *DD2 600* at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR).

Mass spectra were recorded on a Finnigan MAT 4200S, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quatro LCZ* (ESI); peaks are given in m/z (% of basis peak).

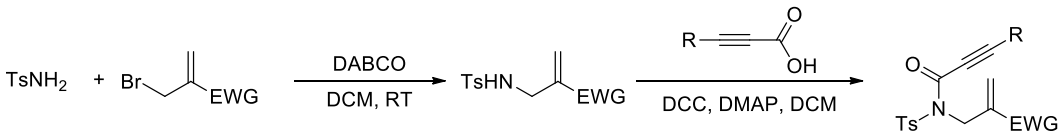
IR spectra were recorded on a *Digilab FTS 4000* with a Specac MKII Golden Gate Single Refelxtion ART System.IR signals are described as *w* (weak), *m* (middle), *s* (strong).

Melting points (MP) were determined by *Stuart SMP10* and are uncorrected.

2. Preparation and Spectral Data of starting materials [1-4]



Substrates **2a-i** were prepared according to the following steps (***GP1***).

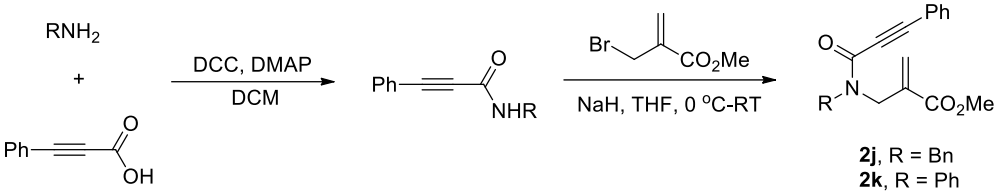


2a-i

Step I: Under the protection of argon, DABCO (1.3 equiv.) was added to a solution of toluene sulphonamide (5.0 equiv.) in DCM (0.1 M). Then, the corresponding allyl bromide derivative (1.0 equiv.) was added in a solution of DCM (0.5 M) dropwise over 2 hours. The resulting mixture was then stirred at room temperature overnight. After that, the mixture was poured into a separatory funnel and water was added. The aqueous phase was extracted with DCM three times and the combined organic phases were washed with brine. The organic solution was dried with Na_2SO_4 and collected by vacuum into a round bottom flask. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the corresponding product.

Step II: Under the protection of argon, a solution of amide (1.0 equiv.) and the corresponding propynoic acid (1.1 equiv.) in CH_2Cl_2 (2.0 M) was cooled to 0 °C. Then, DMAP (0.1 equiv.) and DCC (1.1 equiv.) in CH_2Cl_2 (1.0 M) were added dropwise. The mixture was then stirred at room temperature until full consumption of the starting material as monitored by TLC. The crude mixture was filtered and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by a silica gel column chromatography to afford the product **2a-i**.

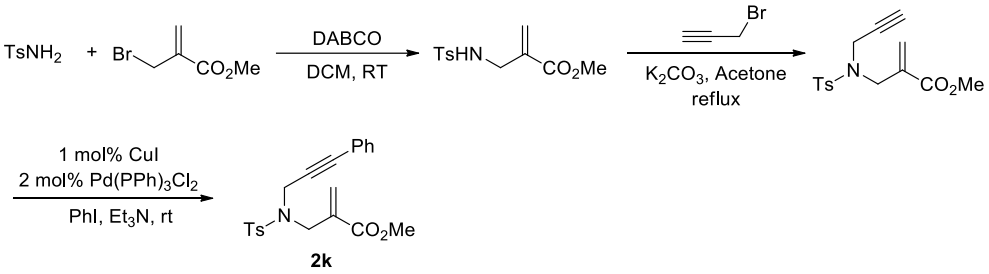
Substrates **2j, 2k** were prepared according to the following steps (***GP2***).



Step I: Under the protection of argon, a solution of amine (1.0 equiv.) and 3-phenylpropiolic acid (1.1 equiv.) in CH_2Cl_2 (2.0 M) was cooled to 0 °C. Then, DMAP (0.1 equiv.) and DCC (1.1 equiv.) in CH_2Cl_2 (1.0 M) were added drop-wise. The mixture was then stirred at room temperature until full consumption of the starting material as monitored by TLC. The crude mixture was filtered and washed with CH_2Cl_2. The filtrate was concentrated and the residue was purified by silica gel column chromatography to afford the amide product.

Step II: Under the protection of argon, NaH (60% in mineral oil, 2.0 equiv.) was added to a solution of the above amide (1.0 equiv.) in THF (0.4 M) at 0 °C in portions. After stirring for 20 min at 0 °C, methyl 2-(bromomethyl)acrylate (1.2 equiv) was added drop-wise and the reaction mixture was allowed to warm to room temperature and stirred for another 2 h. After quenching with water, the residue was extracted with ethyl acetate twice. The combined organic layer was washed with brine, dried with Na_2SO_4, filtrated and concentrated. The residue was purified by silica gel column chromatography to afford the product **2j-k**.

Substrates **2l** were prepared according to the following steps (***GP3***).



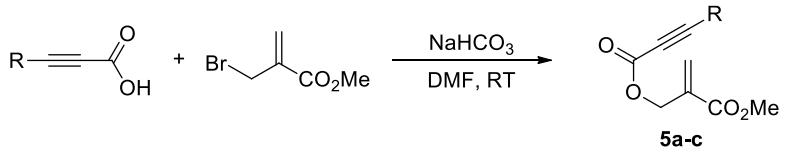
Step I: Under the protection of argon, DABCO (1.3 equiv.) was added to a solution of toluene sulphonamide (5.0 equiv.) in DCM (0.1 M). Then, 2-(bromomethyl)acrylate (1.0 equiv.) was added in a solution of DCM (0.5 M) dropwise over 2 hours. The resulting mixture was then stirred at room temperature overnight. The mixture was poured into a separatory funnel and water was added. The aqueous phase was extracted with DCM three times and the combined organic phases were washed with water and brine. The organic solution was dried with Na_2SO_4 and collected by vacuum into a round bottom flask. The solvent was removed under reduced pressure and the residue was purified by flash chromatographyon silica gel to afford the corresponding product.

Step II: A mixture of the above obtained amide (1.0 equiv.), 3-bromo-1-propyne (3.0 equiv) and K_2CO_3 (3.0 equiv.) in acetone (0.1 M) was heated to reflux for 2 h. After cooling to room temperature, the crude mixture was filtered and the solid was washed with acetone. The filtrate was concentrated and the residue was purified by silica gel column chromatography to afford the propargylated product.

Step III: Under the protection of argon, $Pd(PPh_3)_2Cl_2$ (0.02 equiv.) was added to a solution of

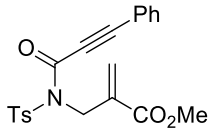
iodobenzene (1.5 equiv.), alkyne (1.0 equiv.) in Et_3N (0.25 M). The mixture was stirred for 5 min and then CuI (0.01 equiv.) was added. The resulting system was then stirred at room temperature until full consumption of the alkyne as monitored by ^1H NMR. The formed ammonium salt was removed by filtration and washed with Et_2O several times. The filtrate was then washed with brine and the aqueous layer was extracted with Et_2O for 3 times. The combined organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the corresponding coupling product **2l**.

Substrates **5a-c** were prepared according to the following steps (***GP4***).



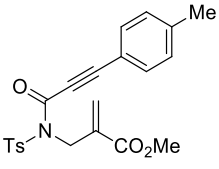
$NaHCO_3$ (2.0 equiv.) was added to a stirred solution of substituted propiolic acid (1.0 equiv.) in dry DMF (1.0 M) at room temperature. After stirring for 1 h, the allyl bromide derivatives (1.1 equiv.), was added and the resulting mixture was then stirred at room temperature overnight. The mixture was poured into a separatory funnel and water was added. The aqueous phase was extracted with Et_2O three times and the combined organic phases were washed with brine. The organic solution was dried with Na_2SO_4 and collected by vacuum into a round bottom flask. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the corresponding product **5a-c**.

Methyl 2-((3-phenyl-N-tosylpropiolamido)methyl)acrylate (**2a**)



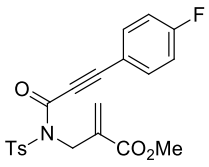
The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.41 (m, 3H), 7.40 – 7.27 (m, 4H), 6.43 (t, *J* = 1.5 Hz, 1H), 5.87 (t, *J* = 1.8 Hz, 1H), 4.95 (s, 2H), 3.78 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.7, 152.6, 145.3, 135.6, 135.4, 132.8, 131.0, 129.5, 128.7, 128.6, 126.1, 119.1, 92.9, 81.2, 52.0, 47.6, 21.6; **HRMS** (ESI) exact mass calculated for $C_{21}H_{19}NO_5S$: 420.0882, found: 420:0876 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2952*w*, 2214*s*, 1716*s*, 1668*s*, 1596*w*, 1491*w*, 1444*w*, 1358*m*, 1269*m*, 1169*s*, 1145*s*, 1088*s*, 996*w*, 875*w*, 813*w*, 757*m*, 669*s*, 635*w*.

Methyl 2-((3-(p-tolyl)-N-tosylpropiolamido)methyl)acrylate (**2b**)



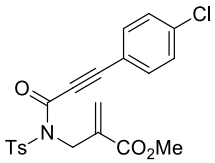
The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.43 (t, *J* = 1.7 Hz, 1H), 5.86 (t, *J* = 1.7 Hz, 1H), 4.94 (s, 2H), 3.79 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.7, 152.7, 145.3, 141.9, 135.7, 135.5, 132.8, 129.4, 128.7, 126.0, 116.0, 93.6, 81.0, 52.0, 47.6, 21.7, 21.6; **HRMS** (ESI) exact mass calculated for $C_{22}H_{21}NO_5S$: 434.1038, found: 434.1030 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2954*w*, 2210*s*, 1717*s*, 1668*s*, 1509*w*, 1359*m*, 1271*w*, 1188*w*, 1168*s*, 1089*s*, 951*w*, 815*m*, 667*s*, 587*s*.

Methyl 2-((3-(4-fluorophenyl)-N-tosylpropiolamido)methyl)acrylate (**2c**)



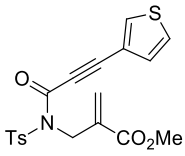
The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.91 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.43 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 6.42 (t, *J* = 1.6 Hz, 1H), 5.86 (t, *J* = 1.9 Hz, 1H), 4.92 (s, 2H), 3.78 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.7, 164.1 (d, *J* = 252.8), 152.5, 145.4, 135.6, 135.4, 135.2 (d, *J* = 9.0), 129.5, 128.6, 126.1, 116.2 (d, *J* = 22.5), 115.3, (d, *J* = 3.0), 91.9, 81.1 (d, *J* = 1.5), 52.1, 47.5, 21.6; **HRMS** (ESI) exact mass calculated for $C_{21}H_{18}FNO_5S$: 438.0787, found: 438.0780 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2957*w*, 2216*m*, 1717*s*, 1669*s*, 1599*m*, 1507*s*, 1403*w*, 1360*m*, 1271*w*, 1169*s*, 1120*m*, 1070*m*, 952*w*, 880*w*, 840*w*, 667*s*, 587*s*, 558*w*.

Methyl 2-((3-(4-chlorophenyl)-N-tosylpropiolamido)methyl)acrylate (**2d**)



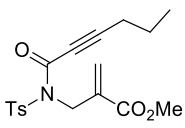
The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.21 (m, 6H), 6.36 (t, *J* = 1.6 Hz, 1H), 5.79 (t, *J* = 1.9 Hz, 1H), 4.85 (s, 2H), 3.72 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.7, 152.4, 145.5, 137.6, 135.6, 135.3, 134.0, 129.6, 129.2, 128.7, 126.2, 117.7, 91.7, 82.0, 52.1, 47.5, 21.7; **HRMS** (ESI) exact mass calculated for $C_{21}H_{18}ClNO_5S$: 454.0492, found: 454.0490 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2950*w*, 2217*s*, 1717*s*, 1671*s*, 1592*w*, 1490*m*, 1361*s*, 1272*m*, 1168*s*, 1121*m*, 1089*s*, 1015*w*, 876*w*, 822*w*, 679*w*, 662*m*, 584*s*.

Methyl 2-((3-(thiophen-3-yl)-N-tosylpropiolamido)methyl)acrylate (**2e**)



The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.91 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.65 (m, 1H), 7.31 (dd, *J* = 7.2, 1.9 Hz, 3H), 7.22 – 7.05 (m, 1H), 6.42 (t, *J* = 1.6 Hz, 1H), 5.86 (t, *J* = 1.9 Hz, 1H), 4.93 (s, 2H), 3.78 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.7, 152.6, 145.3, 135.6, 135.4, 134.2, 129.8, 129.5, 128.7, 126.3, 126.1, 118.4, 88.6, 81.3, 52.1, 47.5, 21.6; **HRMS** (ESI) exact mass calculated for $C_{19}H_{17}NO_5S_2$: 426.0446, found: 426.0441 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2955*w*, 2211*s*, 1716*s*, 1666*s*, 1596*w*, 1437*w*, 1360*s*, 1274*m*, 1169*s*, 1143*m*, 1088*m*, 952*w*, 882*w*, 804*m*, 664*s*, 580*s*.

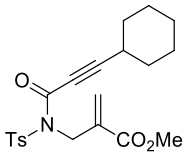
Methyl 2-((N-tosylhex-2-ynamido)methyl)acrylate (**2f**)



The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 8.5 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.44 (t, *J* = 1.7 Hz, 1H), 5.83 (t, *J* = 1.9 Hz, 1H), 4.90 (s, 2H), 3.82 (s, 3H), 2.47 (s, 3H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.56 (h, *J* = 7.3 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.7, 152.6, 145.3, 135.7, 135.6, 129.4, 128.8, 125.9, 96.6, 73.9, 52.0, 47.7, 21.6, 20.9, 20.8, 13.3; **HRMS** (ESI) exact mass calculated for $C_{18}H_{21}NO_5S$: 386.1038, found: 386.1033 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2966*w*, 2222*m*, 1719*s*, 1673*s*, 1597*w*, 1358*s*, 1326*m*, 1302*m*, 1270*m*, 1168*s*, 1089*m*, 1063*w*, 957*w*, 814*w*,

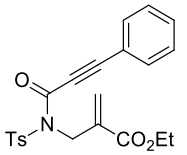
669s, 587s.

Methyl 2-((3-cyclohexyl-N-tosylpropiolamido)methyl)acrylate (**2g**)



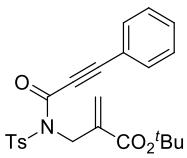
The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.91 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.43 (t, *J* = 1.6 Hz, 1H), 5.82 (t, *J* = 1.8 Hz, 1H), 4.89 (s, 2H), 3.80 (s, 3H), 2.63 – 2.47 (m, 1H), 2.45 (s, 3H), 1.78 – 1.56 (m, 4H), 1.52 – 1.26 (m, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.6, 152.7, 145.2, 135.6, 135.5, 129.3, 128.7, 125.8, 99.8, 73.7, 52.0, 47.8, 31.0, 28.9, 25.4, 24.3, 21.6; **HRMS** (ESI) exact mass calculated for $C_{21}H_{25}NO_5S$: 426.1351, found: 426.1350 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2932*w*, 2221*m*, 1717*m*, 1674*s*, 1495*w*, 1358*m*, 1269*m*, 1227*m*, 1165*s*, 1132*s*, 991*w*, 952*m*, 851*w*, 813*m*, 731*m*, 663*m*, 578*s*.

Ethyl 2-((3-phenyl-N-tosylpropiolamido)methyl)acrylate (**2h**)



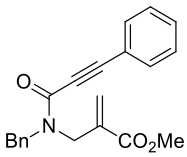
The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.96 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.45 (m, 3H), 7.44 – 7.31 (m, 4H), 6.46 (d, *J* = 1.7 Hz, 1H), 5.89 (t, *J* = 1.9 Hz, 1H), 4.98 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.3, 152.7, 145.4, 135.7, 135.7, 132.9, 131.1, 129.5, 128.8, 128.7, 126.0, 119.2, 92.9, 81.3, 61.1, 47.7, 21.7, 14.2; **HRMS** (ESI) exact mass calculated for $C_{22}H_{21}NO_5S$: 434.1038, found: 434.1033 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2981*w*, 2231*s*, 1710*s*, 1670*s*, 1491*w*, 1325*s*, 1267*m*, 1169*s*, 1146*m*, 1088*s*, 1070*m*, 995*w*, 878*w*, 813*w*, 703*w*, 669*s*, 577*s*.

***tert*-Butyl 2-((3-phenyl-N-tosylpropiolamido)methyl)acrylate** (**2i**)



The title compound was prepared according to general procedure ***GP1***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.97 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.44 (m, 3H), 7.43 – 7.31 (m, 4H), 6.37 (t, *J* = 1.7 Hz, 1H), 5.81 (t, *J* = 1.9 Hz, 1H), 4.95 (s, 2H), 2.46 (s, 3H), 1.52 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 164.5, 152.7, 145.3, 137.0, 135.7, 132.9, 131.1, 129.5, 128.8, 128.6, 125.1, 119.2, 92.7, 81.7, 81.3, 47.9, 28.0, 21.6; **HRMS** (ESI) exact mass calculated for $C_{24}H_{25}NO_5S$: 462.1351, found: 462.1346 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2980*w*, 2215*m*, 1704*m*, 1673*s*, 1596*w*, 1366*s*, 1309*s*, 1170*s*, 1145*s*, 1119*s*, 1089*m*, 1070*w*, 951*w*, 814*w*, 689*m*, 669*s*.

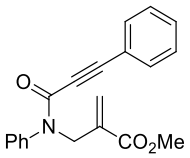
Methyl 2-((N-benzyl-3-phenylpropiolamido)methyl)acrylate (**2j**)



The title compound was prepared according to general procedure ***GP2,*** isomer ratio = 1:0.9. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 – 7.21 (m, 19H), 6.42 (t, *J* = 1.5 Hz, 0.9H), 6.39 (t, *J* = 1.1 Hz, 1H), 5.82 – 5.69 (m, 1.9H), 4.93 (s, 2H), 4.69 (s, 1.8H), 4.49 (s, 1.8H), 4.26 (d, *J* = 1.4 Hz, 2H), 3.80 (s, 2.7H), 3.78 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.4, 166.0, 155.4, 154.9, 136.2, 136.2, 135.4, 134.3, 132.4, 130.1, 130.1, 128.8, 128.7, 128.5, 128.4, 128.3, 127.9, 127.7, 127.6, 127.1, 126.5, 120.3, 120.2, 90.6, 90.3, 81.5, 81.3, 52.6, 52.0, 51.9, 48.4,

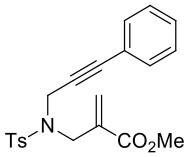
47.4, 44.3; **HRMS** (ESI) exact mass calculated for $C_{21}H_{19}NO_3$: 356.1263, found: 356.1257 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2951*w*, 2216*m*, 1715*s*, 1624*s*, 1490*m*, 1443*m*, 1415*s*, 1300*m*, 1269*m*, 1196*s*, 1138*s*, 1080*w*, 955*w*, 815*w*, 757*s*, 733*m*, 690*s*, 613*w*, 586*w*.

Methyl 2-((N,3-diphenylpropiolamido)methyl)acrylate (**2k**)



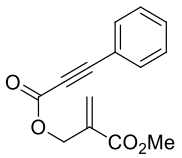
The title compound was prepared according to general procedure ***GP2***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.45 – 7.31 (m, 6H), 7.30 – 7.22 (m, 2H), 7.21 – 7.10 (m, 2H), 6.43 – 6.35 (m, 1H), 5.85 (t, *J* = 2.4 Hz, 1H), 4.75 (s, 2H), 3.73 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.1, 154.3, 141.9, 134.8, 132.5, 130.0, 129.1, 128.3, 128.1, 127.2, 120.3, 91.4, 82.5, 51.9, 49.1; **HRMS** (ESI) exact mass calculated for $C_{21}H_{17}NO_3$: 342.1106, found: 342.1101 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2952*w*, 2218*m*, 1719*s*, 1637*s*, 1594*m*, 1491*s*, 1444*w*, 1387*s*, 1310*s*, 1270*w*, 1145*m*, 1072*w*, 994*w*, 954*w*, 817*w*, 760*m*, 690*m*, 605*w*.

Methyl 2-((4-methyl-N-(3-phenylprop-2-yn-1-yl)phenylsulfonamido)methyl)acrylate (**2l**)



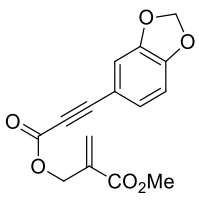
The title compound was prepared according to general procedure ***GP3***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.73 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.11 (m, 5H), 7.05 – 6.94 (m, 2H), 6.36 (td, $J_1 = J_2$ = 1.1 Hz, 1H), 5.93 (td, $J_1 = J_2$ = 1.5 Hz, 1H), 4.24 (s, 2H), 4.08 (s, 2H), 3.70 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.2, 143.6, 135.9, 134.9, 131.5, 129.6, 128.4, 128.1, 127.8, 127.7, 122.0, 85.9, 81.7, 52.1, 47.0, 37.8, 21.4; **HRMS** (ESI) exact mass calculated for $C_{21}H_{21}NO_4S$: 406.1089, found: 406.1083 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2953*w*, 1716*s*, 1598*w*, 1491*w*, 1442*w*, 1350*s*, 1304*w*, 1162*s*, 1093*m*, 966*w*, 896*w*, 814*w*, 759*s*, 692*w*, 658*m*, 587*w*.

Methyl 2-(((3-phenylpropioloyl)oxy)methyl)acrylate (**5a**)



The title compound was prepared according to general procedure ***GP4***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.74 – 7.55 (m, 2H), 7.53 – 7.31 (m, 3H), 6.45 (td, $J_1 = J_2$ = 1.0 Hz, 1H), 5.98 (td, $J_1 = J_2$ = 1.4 Hz, 1H), 4.99 (s, 2H), 3.82 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.4, 153.4, 134.5, 133.0, 130.8, 128.6, 128.4, 119.5, 87.0, 80.3, 63.7, 52.1; **HRMS** (ESI) exact mass calculated for $C_{14}H_{12}O_4$: 267.0633, found: 267.0628 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2954*w*, 2226*s*, 1710*s*, 1643*w*, 1491*w*, 1444*w*, 1283*s*, 1185*s*, 1151*s*, 1031*w*, 976*w*, 924*w*, 758*s*, 689*m*, 603*w*.

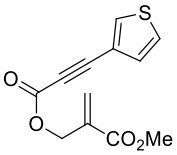
Methyl 2-(((3-(benzo[d][1,3]dioxol-5-yl)propioloyl)oxy)methyl)acrylate (**5b**)



The title compound was prepared according to general procedure ***GP4***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.45 (d, *J* = 1.0 Hz, 1H), 6.04 (s, 2H), 5.97 (td, $J_1 = J_2$ = 1.3 Hz, 1H), 4.97 (s, 2H), 3.82 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.4, 153.5, 150.1, 147.7, 134.5, 129.0, 128.4, 112.5, 112.4, 108.8, 101.8, 87.6, 79.3, 63.6, 52.1; **HRMS** (ESI)

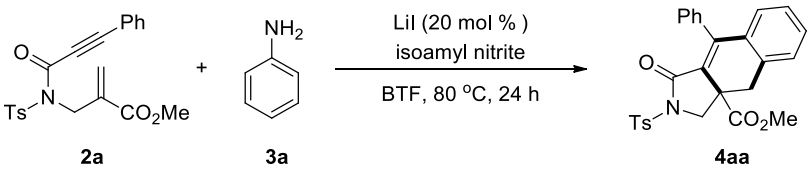
exact mass calculated for $C_{15}H_{12}O_6$: 311.0532, found: 311.0526 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2955*w*, 2210*s*, 1708*s*, 1616*w*, 1489*m*, 1444*w*, 1401*w*, 1275*w*, 1228*s*, 1183*m*, 1155*w*, 1100*m*, 1037*m*, 928*w*, 862*w*, 815*w*, 744*w*, 615*w*.

Methyl 2-(((3-(thiophen-3-yl)propioloyl)oxy)methyl)acrylate (**5c**)



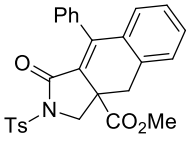
The title compound was prepared according to general procedure ***GP4***. **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.34 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.24 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.44 (td, $J_1 = J_2$ = 1.0 Hz, 1H), 5.96 (td, $J_1 = J_2$ = 1.3 Hz, 1H), 4.97 (s, 2H), 3.81 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.4, 153.4, 134.4, 134.0, 130.2, 128.5, 126.2, 118.7, 82.5, 80.3, 63.6, 52.1; **HRMS** (ESI) exact mass calculated for $C_{12}H_{10}O_4S$: 273.0197, found: 273.0191 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2953*w*, 2220*s*, 1709*s*, 1439*w*, 1361*w*, 1267*s*, 1208*s*, 1145*s*, 996*w*, 948*w*, 790*m*, 745*w*, 700*w*, 626*w*.

3. General Procedure and Spectral Data of Products



General procedure (*GP5*): A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **2a** (1.0 equiv., 0.2 mmol), **3a** (2.0 equiv., 0.4 mmol) and LiI (0.2 equiv., 0.04 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times). Then, BTF (2.0 mL) and isoamyl nitrite (2.5 equiv., 0.5 mmol) were added successively under a flow of argon. The reaction mixture was then stirred at 80 °C for 10 h. After cooling to room temperature, an additional portionof **3a** (2.0 equiv., 0.4 mmol) and isoamyl nitrite (2.5 equiv., 0.5 mmol) were added to the reaction system under a flow of argon and the resulting mixture was stirred at 80 °C for 14h. The solvent was then removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford pure product **4aa** as a light brown solid in 64% yield.

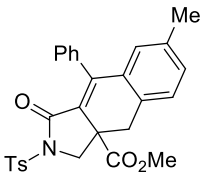
Methyl 1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (**4aa**)



According to ***GP5*** with **2a** (76.7 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4aa** as a light brown solid in 64% yield (60.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.34 – 7.11 (m, 7H), 6.87 (d, *J* = 7.7 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 3.76 (d, *J* = 10.4 Hz, 1H), 3.64 (d, *J* = 15.4 Hz, 1H), 3.52 (s, 3H), 3.08 (d, *J* = 15.3 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.5, 163.0, 147.9, 144.9, 135.3, 134.5, 134.1, 133.9, 130.2, 129.6, 129.4, 128.6, 128.1, 128.1, 127.7, 127.4, 124.1, 54.4, 52.9, 45.2, 36.5, 21.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{23}NO_5S$: 496.1195, found: 496.1189 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2953*w*, 1723*s*, 1629*w*, 1597*w*, 1480*w*, 1357*m*, 1318*w*, 1215*m*, 1168*s*, 1132*m*, 1080*s*, 969*w*, 909*m*, 814*w*, 759*m*, 727*s*, 701*s*, 588*w*, 564*s*; **Mp**: 167 °C.

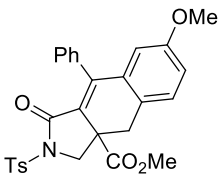
Methyl 7-methyl-1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ab)



According to ***GP5*** with **2a** (76.7 mg, 0.200 mmol, 1.0 equiv.), *p*-toluidine **3b** (42.9 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3b** (42.9 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ab** as a light brown solid in 47% yield (45.7 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.21 – 6.98 (m, 6H), 6.54 (s, 1H), 4.31 (d, *J* = 10.4 Hz, 1H), 3.63 (d, *J* = 10.5 Hz, 1H), 3.49 (d, *J* = 15.3 Hz, 1H), 3.41 (s, 3H), 2.91 (d, *J* = 15.3 Hz, 1H), 2.33 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.6, 163.1, 148.1, 144.8, 137.1, 135.4, 134.4, 134.0, 131.1, 131.0, 130.0, 129.8, 129.6, 128.6, 128.1, 128.0, 127.7, 124.0, 54.4, 52.9, 45.3, 36.3, 21.6, 21.1; **HRMS** (ESI) exact mass calculated for $C_{28}H_{25}NO_5S$: 510.1351, found: 510.1346 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2954*w*, 1725*s*, 1633*w*, 1570*w*, 1493*w*, 1358*m*, 1321*w*, 1213*m*, 1170*s*, 1132*s*, 1081*s*, 910*m*, 815*w*, 730*s*, 701*w*, 660*s*, 575*s*; **Mp**: 216 °C.

Methyl 7-methoxy-1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ac)

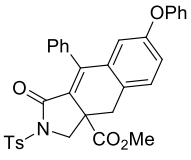


According to ***GP5*** with **2a** (76.7 mg, 0.200 mmol, 1.0 equiv.), *p*-anisidine **3c** (51.0 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3c** (51.0 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ac** as a light brown solid in 43% yield (43.7 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.23 – 7.06 (m, 5H), 6.74 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.30 (d, *J* = 2.7 Hz, 1H), 4.31 (d, *J* = 10.4 Hz, 1H), 3.63 (d, *J* = 10.5 Hz, 1H), 3.53 (s, 3H), 3.47 (d, *J* = 15.4 Hz, 1H), 3.42 (s, 3H), 2.89 (d, *J* = 15.0 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.7, 163.0, 158.7, 147.9, 144.9, 135.7, 135.4, 133.8, 129.7, 129.6, 128.9, 128.7, 128.1, 127.7, 126.1, 124.6, 115.6, 115.1, 55.2, 54.3, 53.0, 45.6, 35.9, 21.7; **HRMS** (ESI) exact mass calculated for $C_{28}H_{25}NO_6S$: 526.1300, found: 526.1295 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2956*w*, 1727*s*, 1631*w*, 1606*w*, 1571*w*,

1493*w*, 1360*w*, 1215*w*, 1167*s*, 1084*m*, 1037*w*, 972*w*, 911*w*, 662*m*, 578*m*; **Mp**: 208 °C.

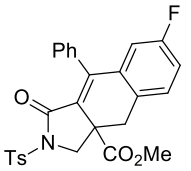
Methyl 1-oxo-7-phenoxy-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ad)



According to ***GP5*** with **2a** (76.7 mg, 0.200 mmol, 1.0 equiv.), 4-phenoxyaniline **3d** (74.1 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3d** (74.1 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ad** as a yellow oil in 52% yield (58.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.25 (m, 4H), 7.21 – 7.10 (m, 6H), 7.01 – 6.93 (m, 2H), 6.83 – 6.77 (m, 2H), 6.48 (d, J = 2.5 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 3.64 (d, *J* = 10.3 Hz, 1H), 3.51 (d, *J* = 15.5 Hz, 1H), 3.44 (s, 3H), 2.91 (d, *J* = 15.3 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.5, 162.9, 156.5, 156.4, 147.4, 144.9, 136.1, 135.3, 133.5, 129.7, 129.7, 129.6, 129.6, 129.1, 128.7, 128.6, 128.1, 127.7, 124.7, 123.5, 120.1, 119.7, 118.7, 54.3, 53.0, 45.5, 35.9, 21.6; **HRMS** (ESI) exact mass calculated for $C_{33}H_{27}NO_6S$: 588.1457, found: 588.1462 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2954*w*, 1725*s*, 1589*w*, 1567*w*, 1485*s*, 1435*w*, 1359*w*, 1211*s*, 1166*s*, 1133*m*, 1080*s*, 909*w*, 814*w*, 757*m*, 730*s*, 661*s*, 575*m*.

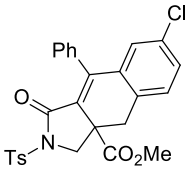
Methyl 7-fluoro-1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ae)



According to ***GP5*** with **2a** (76.7 mg, 0.200 mmol, 1.0 equiv.), 4-fluoroaniline **3e** (44.5 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3e** (44.5 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ae** as a light brown solid in 50% yield (49.3 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.85 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.32 (m, 3H), 7.26 – 7.02 (m, 5H), 6.98 – 6.89 (m, 1H), 6.51 (dd, *J* = 9.8, 2.7 Hz, 1H), 4.37 (d, *J* = 10.5 Hz, 1H), 3.69 (d, *J* = 10.6 Hz, 1H), 3.56 (d, *J* = 15.4 Hz, 1H), 3.46 (s, 3H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.3, 162.7, 161.9 (d, *J* = 244.5), 146.8, 146.7, 145.0, 136.4 (d, *J* = 7.5), 135.2, 133.3, 129.6, 129.5 (d, *J* = 8.6), 129.3, 128.9, 128.1, 127.9, 125.3, 116.8 (d, *J* = 21.8), 116.2 (d, *J* = 23.3), 54.3, 53.0, 45.4, 35.8, 21.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{22}FNO_5S$: 514.1100, found: 514.1106 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2958*w*, 1726*s*, 1597*w*, 1579*w*, 1485*w*, 1358*m*, 1257*w*, 1214*m*, 1162*s*, 1082*s*, 911*w*, 862*s*, 759*s*, 730*m*, 660*s*, 574*s*; **Mp**: 235 °C.

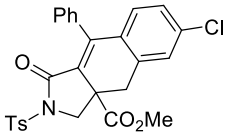
Methyl 7-chloro-1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4af)



According to ***GP5*** with **2a** (76.7 mg, 0.200 mmol, 1.0 equiv.), 4-chloroaniline **3f** (51.0 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3f** (51.0 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4af** as a light brown solid in 52% yield (53.0 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, J = 8.4 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.23 – 7.02 (m, 6H), 6.72 (d, *J* = 1.8 Hz, 1H), 4.32 (d, *J* = 10.5 Hz, 1H), 3.64 (d, *J* = 10.4 Hz, 1H), 3.51 (d, *J* = 15.5 Hz, 1H), 3.42 (s, 3H), 2.92 (d, *J* = 15.4 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.2, 162.7, 146.6, 145.0, 136.2, 135.2, 133.3, 133.1, 132.4, 130.0, 129.6, 129.3, 129.1, 129.0, 128.1, 127.9, 125.4, 54.2, 53.1, 45.2, 35.9, 21.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{22}ClNO_5S$: 530.0805, found: 530.0799 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2955*w*, 1729*s*, 1635*w*, 1558*w*, 1477*w*, 1360*m*, 1217*m*, 1170*s*, 1136*m*, 1085*s*, 972*w*, 761*w*, 730*w*, 663*s*, 572*s*; **Mp**: 189 °C.

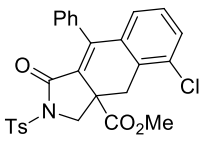
Methyl 6-chloro-1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ag)



According to ***GP5*** with **2a** (76.7 mg, 0.200 mmol, 1.0 equiv.), 3-chloroaniline **3g** (51.0 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3g** (51.0 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ag** as a light brown solid in 34% yield (34.2 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.39 – 7.32 (m, 3H), 7.31 – 7.11 (m, 3H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.46 (d, *J* = 10.5 Hz, 1H), 3.76 (d, *J* = 10.5 Hz, 1H), 3.62 (d, *J* = 15.5 Hz, 1H), 3.57 (s, 3H), 3.08 (d, *J* = 15.5 Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.2, 162.8, 146.9, 145.0, 136.2, 136.0, 135.3, 133.5, 133.1, 130.6, 129.6, 128.9, 128.3, 128.1, 127.9, 127.6, 124.3, 54.3, 53.1, 45.1, 36.2, 21.7; **HRMS** (ESI) exact mass calculated for $C_{27}H_{22}ClNO_5S$: 530.0805, found: 530.0800 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2956*w*,1725*s*, 1633*w*, 1595*w*, 1359*m*, 1307*w*, 1217*m*, 1170*s*, 1081*s*, 911*m*, 814*w*, 759*w*, 731*s*, 661*m*, 579*s*; **Mp**: 258 °C.

Methyl 5-chloro-1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ah)

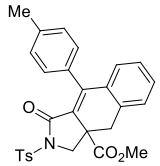


According to ***GP5*** with **2a** (76.7 mg, 0.200 mmol, 1.0 equiv.), 2-chloroaniline **3h** (51.0 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3h** (51.0 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ah** as a light brown

solid in 32% yield (31.5 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.07 (m, 8H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 10.5 Hz, 1H), 4.08 (d, *J* = 16.1 Hz, 1H), 3.69 (d, *J* = 10.5 Hz, 1H), 3.43 (s, 3H), 2.71 (d, *J* = 16.2 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.0, 162.7, 147.0, 145.0, 136.4, 135.2, 133.6, 133.5, 132.1, 131.1, 129.6, 128.8, 128.1, 128.1, 128.0, 127.8, 127.8, 124.8, 54.3, 53.0, 44.9, 33.0, 21.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{22}ClNO_5S$: 530.0805, found: 530.0800 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2955*w*, 1726*s*, 1637*w*, 1559*w*, 1444*w*, 1358*m*, 1215*w*, 1169*s*, 1138*m*, 1084*s*, 909*m*, 813*w*, 729*s*, 704*w*, 659*s*, 628*w*, 591*w*; **Mp**: 201 °C.

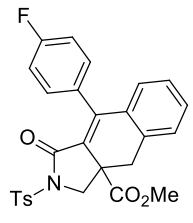
Methyl 1-oxo-9-(p-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ba)



According to ***GP5*** with **2b** (82.3 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ba** as a light brown solid in 62% yield (60.2 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.82 (d, *J* = 8.3 Hz, 2H), 7.22 – 6.99 (m, 9H), 6.78 (d, *J* = 7.8 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 3.63 (d, *J* = 10.4 Hz, 1H), 3.51 (d, *J* = 15.3 Hz, 1H), 3.40 (s, 3H), 2.95 (d, *J* = 15.4 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.6, 163.1, 148.2, 144.8, 138.5, 135.4, 134.6, 134.1, 130.9, 130.2, 129.8, 129.5, 129.5, 128.4, 128.1, 128.1, 127.3, 123.7, 54.4, 52.9, 45.2, 36.6, 21.6, 21.4; **HRMS** (ESI) exact mass calculated for $C_{28}H_{25}NO_5S$: 510.1351, found: 510.1346 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2955*w*, 1723*s*, 1624*w*, 1598*w*, 1434*w*, 1357*m*, 1294*w*, 1259*w*, 1214*m*, 1169*s*, 1133*m*, 1709*s*, 1021*w*, 910*m*, 814*m*, 729*s*, 659*s*, 566*s*; **Mp**: 225 °C.

Methyl 9-(4-fluorophenyl)-1-oxo-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ca)

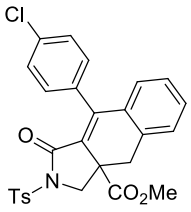


According to ***GP5*** with **2c** (83.1 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ca** as a light brown solid in 54% yield (53.4 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.88 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.01 (m, 9H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.40 (d, *J* = 10.4 Hz, 1H), 3.71 (d, *J* = 10.5 Hz, 1H), 3.59 (d, *J* = 15.4 Hz, 1H), 3.48 (s, 3H), 3.03 (d, *J* = 15.4 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.4, 163.1, 162.9 (d, *J* = 246.8), 146.9, 145.0, 135.2, 134.3, 134.1, 131.8, 130.4, 129.6, 129.6, 129.3, 128.2, 128.1, 127.5, 124.4, 114.8 (d, *J* = 21.8), 54.4, 53.0, 45.2, 36.5, 21.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{22}FNO_5S$: 514.1100, found: 514.1095 ($[M+Na]^+$); **IR** (neat,

cm^{-1}): 2956*w*, 1724*s*, 1603*w*, 1508*m*, 1359*m*, 1318*w*, 1217*s*, 1188*w*, 1171*s*, 1134*m*, 1082*s*, 911*w*, 832*w*, 734*m*, 660*s*; **Mp**: 201 °C.

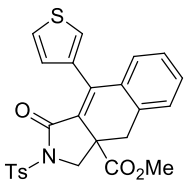
Methyl 9-(4-chlorophenyl)-1-oxo-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4da)



According to ***GP5*** with **2d** (86.4 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4da** as a light brown solid in 53% yield (54.0 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.03 (m, 9H), 6.74 (d, *J* = 7.5 Hz, 1H), 4.33 (d, *J* = 10.4 Hz, 1H), 3.65 (d, *J* = 10.5 Hz, 1H), 3.53 (d, *J* = 15.4 Hz, 1H), 3.41 (s, 3H), 2.96 (d, *J* = 15.3 Hz, 1H), 2.35 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.3, 163.0, 146.6, 145.0, 135.2, 134.7, 134.1, 132.2, 130.5, 129.6, 129.2, 128.3, 128.1, 128.0, 127.5, 124.5, 54.4, 53.0, 45.2, 36.5, 21.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{22}ClNO_5S$: 530.0805, found: 530.0799 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2955*w*, 1724*s*, 1632*w*, 1596*w*, 1489*w*, 1318*m*, 1215*m*, 1169*s*, 1134*m*, 1083*s*, 972*w*, 911*m*, 828*w*, 815*w*, 729*s*, 659*s*, 563*s*; **Mp**: 213 °C.

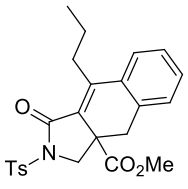
Methyl 1-oxo-9-(thiophen-3-yl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ea)



According to ***GP5*** with **2e** (80.7 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ea** as a light brown solid in 60% yield (57.7 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 (d, J = 8.4 Hz, 2H), 7.37 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.26 – 7.19 (m, 5H), 7.13 – 7.06 (m, 1H), 6.96 – 6.89 (m, 2H), 4.32 (d, *J* = 10.4 Hz, 1H), 3.64 (d, *J* = 10.5 Hz, 1H), 3.49 (d, *J* = 15.3 Hz, 1H), 3.38 (s, 3H), 2.94 (d, *J* = 15.3 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.4, 163.1, 144.9, 142.9, 135.3, 134.4, 134.1, 133.2, 130.3, 129.7, 129.6, 129.3, 128.1, 128.1, 127.8, 127.4, 124.4, 124.2, 54.4, 52.9, 45.4, 36.5, 21.6; **HRMS** (ESI) exact mass calculated for $C_{25}H_{21}NO_5S_2$: 502.0759, found: 502.0753 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2956*w*, 1723*s*, 1597*w*, 1621*w*, 1359*m*, 1303*w*, 1215*m*, 1169*s*, 1133*m*, 1079*s*, 911*m*, 730*s*, 660*s*; **Mp**: 201 °C.

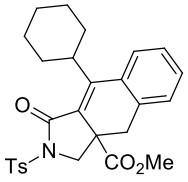
Methyl 1-oxo-9-propyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4fa)



According to ***GP5*** with **2f** (72.7 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4fa** as a light brown solid in 45% yield (39.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.47 (m, 1H), 7.39 – 7.23 (m, 5H), 4.35 (d, *J* = 10.5 Hz, 1H), 3.71 (d, *J* = 10.5 Hz, 1H), 3.53 (d, *J* = 15.3 Hz, 1H), 3.38 (s, 3H), 3.35 – 3.23 (m, 1H), 3.03 – 2.75 (m, 2H), 2.47 (s, 3H), 1.67 – 1.42 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.5, 164.9, 149.9, 144.9, 135.5, 134.4, 133.0, 130.0, 129.5, 128.5, 128.1, 127.5, 125.9, 123.7, 54.4, 52.6, 44.8, 36.6, 28.1, 22.9, 21.6, 13.9; **HRMS** (ESI) exact mass calculated for $C_{24}H_{25}NO_5S$: 462.1351, found: 462.1346 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2960*w*, 1716*s*, 1636*w*, 1597*w*, 1453*w*, 1361*m*, 1253*w*, 1216*m*, 1171*s*, 1133*m*, 1080*m*, 770*w*, 729*w*, 662m; **Mp**: 175 °C.

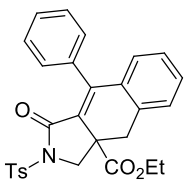
Methyl 9-cyclohexyl-1-oxo-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ga)



According to ***GP5*** with **2g** (80.7 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ga** as a light brown solid in 50% yield (48.3 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.95 (d, *J* = 8.3 Hz, 2H), 7.77 (td, *J* = 4.0, 1.7 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.24 (d, *J* = 3.3 Hz, 3H), 4.26 (d, *J* = 10.5 Hz, 1H), 3.94 – 3.78 (m, 1H), 3.70 (d, J = 10.5 Hz, 1H), 3.40 (d, *J* = 14.9 Hz, 1H), 3.28 (s, 3H), 2.81 (d, *J* = 14.9 Hz, 1H), 2.44 (s, 3H), 1.96 – 1.69 (m, 6H), 1.52 – 1.25 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.5, 164.7, 154.7, 144.9, 135.6, 134.8, 133.2, 129.6, 129.5, 128.6, 128.0, 127.7, 126.8, 125.1, 54.2, 52.6, 45.6, 38.8, 36.9, 31.7, 29.9, 26.9, 26.5, 26.0, 21.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{29}NO_5S$: 502.1664, found: 502.1659 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2928*w*, 1737*s*, 1714*s*, 1620*w*, 1480*w*, 1359*m*, 1266*w*, 1215*m*, 1171*s*, 1132*m*, 1081*s*, 912*w*, 731*m*, 661*m*, 582*w*; **Mp**: 198 °C.

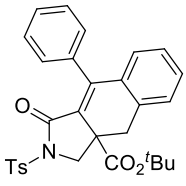
Ethyl 1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ha)



According to ***GP5*** with **2h** (82.2 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ha** as a light brown solid in 53% yield (51.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.82 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.22 – 7.10 (m, 5H), 7.09 – 7.00 (m, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 4.35 (d, *J* = 10.4 Hz, 1H), 3.98 – 3.79 (m, 2H), 3.64 (d, *J* = 10.4 Hz, 1H), 3.50 (d, *J* = 15.3 Hz, 1H), 2.98 (d, *J* = 15.4 Hz, 1H), 2.33 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.1, 163.0, 147.8, 144.8, 135.4, 134.7, 134.1, 134.0, 130.1, 129.7, 129.6, 129.3, 128.6, 128.1, 127.7, 127.3, 124.3, 61.8, 54.2, 45.2, 36.6, 21.6, 13.7; **HRMS** (ESI) exact mass calculated for $C_{28}H_{25}NO_5S$: 510.1351, found: 510.1346 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2982*w*, 1723*s*, 1630*w*, 1568*w*, 1479*w*, 1357*w*, 1256*w*, 1212*m*, 1169*s*, 1082*s*, 909*m*, 759*w*, 728*m*, 664*m*, 564*s*; **Mp**: 171 °C.

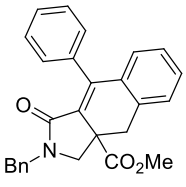
tert-Butyl 1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ia)



According to ***GP5*** with **2i** (87.9 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ia** as a light brown solid in 60% yield (61.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.20 – 7.09 (m, 5H), 7.07 – 7.01 (m, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 4.36 (d, *J* = 10.3 Hz, 1H), 3.60 (d, *J* = 10.3 Hz, 1H), 3.42 (d, *J* = 15.3 Hz, 1H), 2.95 (d, *J* = 15.3 Hz, 1H), 2.32 (s, 3H), 1.07 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.2, 163.1, 147.3, 144.8, 135.5, 135.0, 134.3, 134.1, 129.9, 129.7, 129.7, 129.6, 129.1, 128.5, 128.1, 128.0, 127.7, 127.2, 125.1, 82.4, 54.1, 46.0, 36.9, 27.4, 21.6; **HRMS** (ESI) exact mass calculated for $C_{30}H_{29}NO_5S$: 538.1664, found: 538.1665 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2980*w*, 1723*s*, 1632*w*, 1598*w*, 1478*w*, 1367*m*, 1254*w*, 1170*s*, 1154*s*, 1083*s*, 910*w*, 815*w*, 765*w*, 729*m*, 664*m*, 564*s*; **Mp**: 166 °C.

Methyl 2-benzyl-1-oxo-9-phenyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4ja)

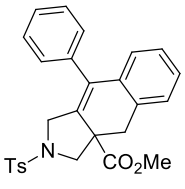


According to ***GP5*** with **2j** (66.7 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4ja** as a light yellow oil in 44% yield (36.8 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.43 – 7.25 (m, 7H), 7.21 – 7.05 (m, 6H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.74 (d, *J* = 14.8 Hz, 1H), 4.17 (d, *J* = 14.8 Hz, 1H), 3.53 (dd, *J* = 9.9, 8.4 Hz, 2H), 3.48 (s, 3H), 3.20 (d, *J* = 10.3 Hz, 1H), 2.96 (d, *J* = 15.3 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 173.5, 165.9, 142.6, 136.1, 135.3, 135.1, 134.0, 130.3, 129.5, 129.1, 128.6, 128.6, 128.2, 128.1, 128.0, 127.6, 127.2, 127.0, 54.5, 52.6, 46.6, 45.3, 36.9; **HRMS** (ESI) exact mass calculated for $C_{27}H_{23}NO_3$: 432.1576, found: 432.1570 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2955*w*, 1732*s*, 1684*s*, 1485*w*, 1433*m*, 1420*m*, 1287*m*, 1227*m*, 1202*m*, 1170*m*, 1079*w*, 975*w*, 911*w*,

765*m*, 731*s*, 700*s*, 605*w*.

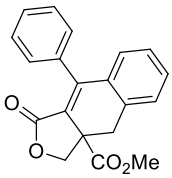
Methyl 9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (4la)



According to ***GP5*** with **2l** (76.7 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **4la** as a light brown solid in 57% yield (52.4 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.71 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.40 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.04 (m, 5H), 6.78 (d, *J* = 7.4 Hz, 1H), 4.37 (d, *J* = 14.7 Hz, 1H), 4.03 (d, *J* = 10.4 Hz, 1H), 3.87 (d, *J* = 14.7 Hz, 1H), 3.44 (d, *J* = 15.1 Hz, 1H), 3.43 (s, 3H), 3.35 (d, *J* = 10.5 Hz, 1H), 2.92 (d, *J* = 15.1 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 173.2, 143.6, 137.1, 134.5, 134.1, 133.9, 133.4, 132.6, 129.7, 128.5, 128.0, 127.8, 127.7, 127.6, 127.0, 126.2, 58.5, 52.6, 52.4, 51.0, 36.5, 21.5; **HRMS** (ESI) exact mass calculated for $C_{27}H_{25}NO_4S$: 482.1402, found: 482.1397 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2952*w*, 1733*s*, 1598*w*, 1494*w*, 1346*s*, 1208*w*, 1160*s*, 1093*s*, 1036*w*, 911*w*, 815*w*, 731*s*, 703*m*, 663*s*, 590*m*; **Mp**: 148 °C.

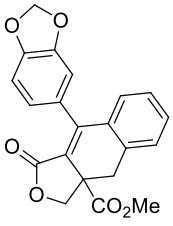
Methyl 1-oxo-9-phenyl-1,3,3a,4-tetrahydronaphtho[2,3-c]furan-3a-carboxylate (6a)



According to ***GP5*** with **5a** (48.8 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **6a** as a light brown solid in 62% yield (39.7 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.43 – 7.32 (m, 3H), 7.31 – 7.18 (m, 4H), 7.14 – 7.04 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.63 (d, *J* = 9.4 Hz, 1H), 4.11 (d, *J* = 9.4 Hz, 1H), 3.57 (s, 3H), 3.55 (d, *J* = 15.4 Hz, 1H), 3.04 (d, *J* = 15.3 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.8, 167.1, 148.7, 134.6, 134.0, 133.7, 130.4, 129.8, 129.5, 128.8, 128.3, 127.8, 127.5, 120.3, 74.1, 53.1, 48.7, 36.0; **HRMS** (ESI) exact mass calculated for $C_{20}H_{16}O_4$: 343.0946, found: 343.0941 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2957*w*, 1756*s*, 1736*s*, 1637*w*, 1569*w*, 1477*w*, 1372*w*, 1214*s*, 1188*w*, 1135*m*, 1037*s*, 1006*m*, 973*w*, 912*w*, 768*m*, 732*s*, 699*s*, 604*w*; **Mp**: 199 °C.

Methyl 9-(benzo[d][1,3]dioxol-5-yl)-1-oxo-1,3,3a,4-tetrahydronaphtho[2,3-c]furan-3a-carboxylate (6b)

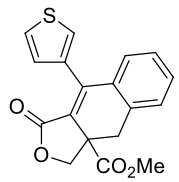


According to ***GP5*** with **5b** (57.7 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred

at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **6b** as a light brown solid in 57% yield (41.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.40 – 7.32 (m, 2H), 7.28 – 7.20 (m, 1H), 7.07 (d, J = 7.7 Hz, 1H), 6.98 – 6.76 (m, 3H), 6.11 – 6.00 (m, 2H), 4.75 (d, *J* = 9.3 Hz, 1H), 4.23 (d, *J* = 9.4 Hz, 1H), 3.69 (s, 3H), 3.65 (d, *J* = 15.4 Hz, 1H), 3.14 (d, *J* = 15.4 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.8, 167.2, 148.5, 148.2, 147.2, 134.7, 134.1, 130.5, 129.6, 128.3, 127.5, 127.1, 124.1, 120.1, 110.5, 107.9, 101.3, 74.0, 53.1, 48.8, 36.1; **HRMS** (ESI) exact mass calculated for $C_{21}H_{16}O_6$: 387.0845, found: 387.0839 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2952*w*, 1755*s*, 1737*s*, 1568*w*, 1503*m*, 1489*m*, 1341*w*, 1251*w*, 1215*m*, 1132*w*, 1077*m*, 1035*s*, 931*w*, 816*w*, 768*w*, 734*w*, 572*w*; **Mp**: 171 °C.

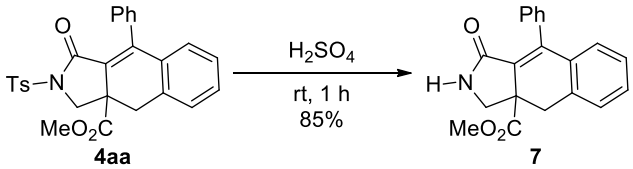
Methyl 1-oxo-9-(thiophen-3-yl)-1,3,3a,4-tetrahydronaphtho[2,3-c]furan-3a-carboxylate (6c)



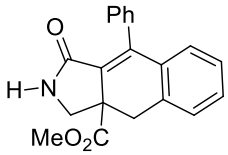
According to ***GP5*** with **5c** (50.1 mg, 0.200 mmol, 1.0 equiv.), aniline **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.), LiI (5.35 mg, 0.040 mmol, 20 mol %) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) in 2 mL BTF at 80 °C for 10 h. Then an additional portion of **3a** (37.3 mg, 0.400 mmol, 2.0 equiv.) and isoamyl nitrite (58.6 mg, 0.500 mmol, 2.5 equiv.) were added and the mixture was stirred at 80 °C for 14 h. Purification by silica gel chromatography afforded the desired **6c** as a light brown solid in 58% yield (37.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.58 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.38 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.25 – 7.18 (m, 1H), 7.15 – 7.08 (m, 2H), 4.71 (d, *J* = 9.3 Hz, 1H), 4.18 (d, *J* = 9.3 Hz, 1H), 3.63 (s, 3H), 3.59 (d, *J* = 15.3 Hz, 1H), 3.08 (d, *J* = 15.3 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.8, 167.2, 143.7, 134.5, 134.0, 133.1, 130.5, 129.7, 129.4, 128.2, 128.1, 127.5, 124.4, 120.5, 74.1, 53.1, 49.0, 36.0; **HRMS** (ESI) exact mass calculated for $C_{18}H_{14}O_4S$: 349.0510, found: 349.0505 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 2958*w*, 1753*s*, 1735*s*, 1625*w*, 1568*w*, 1477*w*, 1371*w*, 1253*w*, 1215*m*, 1183*m*, 1134*m*, 1078*m*, 1038*m*, 913*w*, 848*w*, 770*m*, 734*m*, 664*w*; **Mp**: 150 °C.

4. Follow-up Chemistry



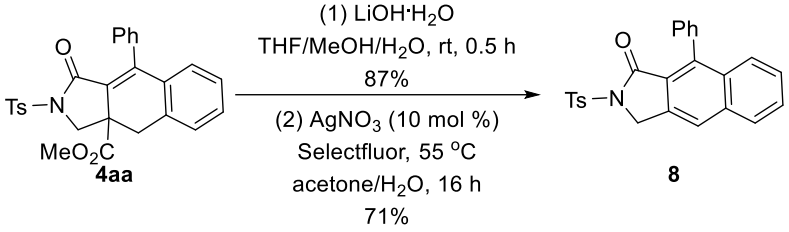
Methyl 1-oxo-9-phenyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (7)



H_2SO_4 (96%, 2.25 mL) was added to a flame dried *Schlenk*-flask containing **4aa** (0.050 mmol, 23.7 mg) and the formed mixture was stirred at rt for 1 h. The solution was diluted with 10 mL EtOAc and neutralized with saturated Na_2CO_3 at 0 °C. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the corresponding product **7** as a light yellow oil in 85%

yield. (13.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.35 (dd, *J* = 5.4, 2.0 Hz, 3H), 7.30 – 7.12 (m, 4H), 7.12 – 7.00 (m, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.32 (s, 1H), 3.73 (d, *J* = 9.8 Hz, 1H), 3.52 (s, 3H), 3.50 (d, *J* = 12.8 Hz, 1H), 3.32 (d, *J* = 10.1 Hz, 1H), 3.02 (d, *J* = 15.3 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 173.9, 168.9, 143.2, 135.4, 135.0, 134.0, 130.0, 129.2, 128.7, 128.1, 128.0, 127.6, 127.2, 126.2, 52.8, 50.6, 48.0, 37.4; **HRMS** (ESI) exact mass calculated for $C_{20}H_{17}O_3$: 342.1106, found: 342.1106 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2954*w*, 1731*m*, 1690*s*, 1643*w*, 1485*w*, 1434*w*, 1361*w*, 1279*w*, 1226*w*, 1203*m*, 1116*w*, 1046*w*, 909*m*, 767*m*, 731*s*, 698*m*, 570*w*.



1-oxo-9-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylic acid (8)

Step I: LiOH·H_2O (21.0 mg, 0.500 mmol, 10 equiv.) in 0.5 mL H_2O was added dropwise to a solution of **4aa** (23.7 mg, 0.005 mmol) in 0.5 mL MeOH and 0.5 mL THF. The resulting mixture was then stirred at room temperature for 1 h. After that, the mixture was acidified with 2 N HCl solution and extracted with DCM. The combined organic phase was dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (dichloromethane/MeOH) to afford the corresponding carboxylic acid as a light yellow solid in 87% yield. (20.0 mg).

Step II: The carboxylic acid (32.2 mg, 0.070 mmol, 1.0 equiv.), $AgNO_3$ (1.19 mg, 0.04 mmol, 0.1 equiv.) and Selectfluor (49.6 mg, 0.140 mmol, 2.0 equiv.) were placed in a Schlenk-tube. The reaction vessel was evacuated and filled with Argon. Acetone (0.7 mL) and water (0.7 mL) were then added. The reaction mixture was stirred at 55 °C for 16 h. Upon completion of the reaction, the resulting mixture was cooled down to room temperature and extracted with dichloromethane. The combined organic phase was dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by flash chromatography on silica gel (pentane/ethyl acetate) to afford product **8** as a white solid in 71% yield. (20.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.90 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 10.5 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.43 – 7.33 (m, 4H), 7.24 – 7.18 (m, 4H), 4.97 (s, 2H), 2.31 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 164.9, 144.9, 141.6, 135.9, 135.5, 134.9, 134.5, 132.7, 130.0, 129.7, 128.5, 128.1, 128.1, 127.9, 127.9, 127.9, 126.7, 124.0, 121.8, 48.5, 21.6; **HRMS** (ESI) exact mass calculated for $C_{25}H_{19}NO_3S$: 436.0983, found: 436.0978 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 2294*w*, 1731*s*, 1629*w*, 1457*w*, 1362*m*, 1320*m*, 1172*s*, 1121*s*, 1089*s*, 1065*m*, 907*m*, 765*m*, 671*s*, 602*m*, 566*s*. **Mp**: 259 °C.

5. X-ray Crystallographic Data

X-Ray diffraction: Data sets for the compound **4af** were collected with a D8 Venture CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0;[5] cell refinement: SAINT V8.34A;[5] data reduction: SAINT V8.34A;[5] absorption correction, SADABS V2014/2;[5] structure solution SHELXT-2014;[6] structure refinement SHELXL-2014.[6] *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections.

Exceptions and special features: Compound **4af** crystallized with two molecule in the asymmetric unit. For both molecules the methoxy carbonyl groups were found disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

X-ray crystal structure analysis of 4af: A pale yellow prism-like specimen of $C_{27}H_{22}ClNO_5S$, approximate dimensions 0.142 mm x 0.222 mm x 0.356 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 4183 frames were collected. The total exposure time was 20.91 hours. The frames were integrated with the Bruker SAINT Software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 62096 reflections to a maximum θ angle of 68.33° (0.83 Å resolution), of which 8390 were independent (average redundancy 7.401, completeness = 99.5%, R_{int} = 3.17%, R_{sig} = 1.81%) and 7608 (90.68%) were greater than 2σ(F^2). The final cell constants of a = 10.9967(3) Å, b = 16.5944(4) Å, c = 25.1871(5) Å, β = 91.5930(10)°, volume = 4594.46(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 9310 reflections above 20 σ(I) with 6.379° < 2θ < 136.5°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.840. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4500 and 0.7030. The final anisotropic full-matrix least-squares refinement on F^2 with 711 variables converged at R1 = 4.29%, for the observed data and wR2 = 11.97% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.971 $e^-/Å^3$ and the largest hole was -0.410 $e^-/Å^3$ with an RMS deviation of 0.063 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.469 g/cm^3 and F(000), 2112 e^-

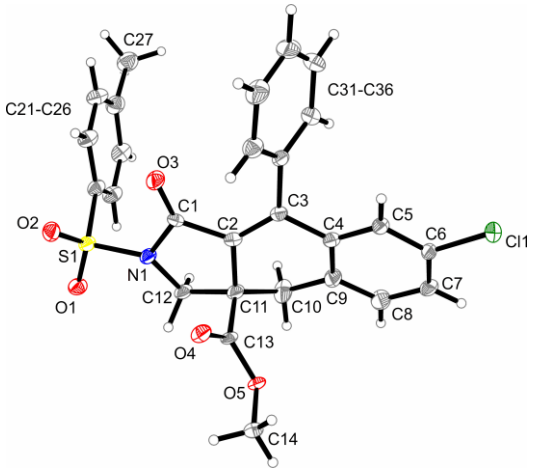


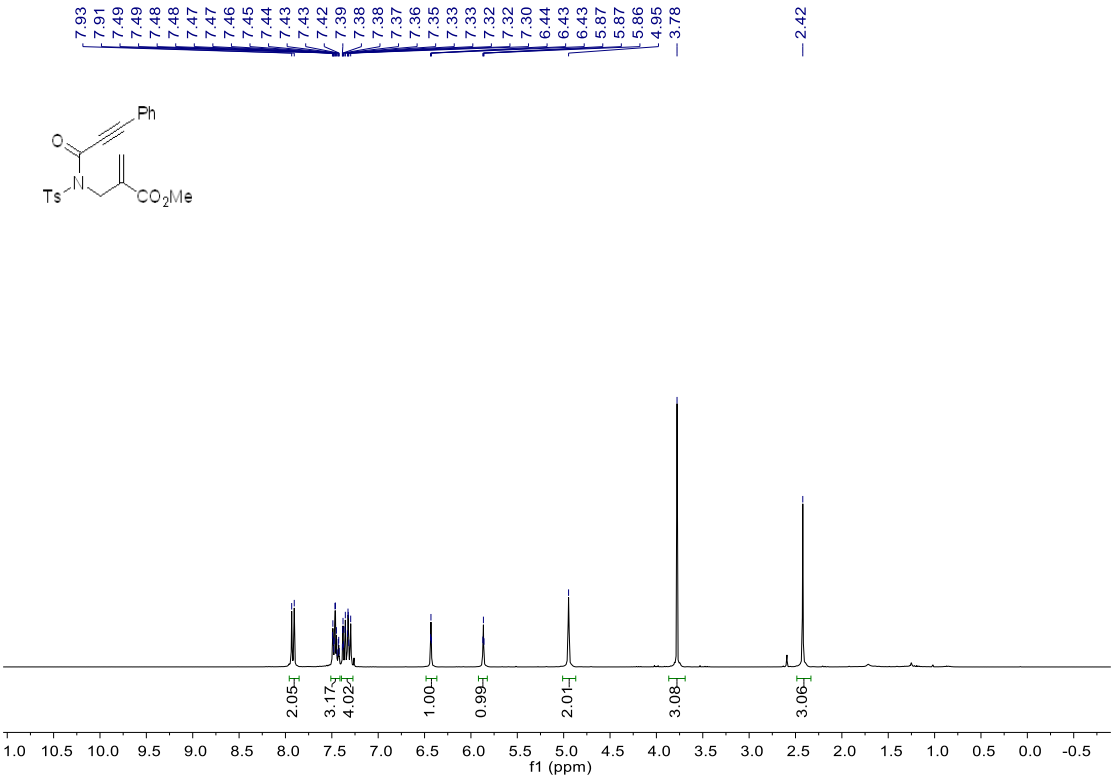
***Figure 1. Crystal structure of compound* 4af**.

Only one molecule of two found in the asymmetric unit is shown.

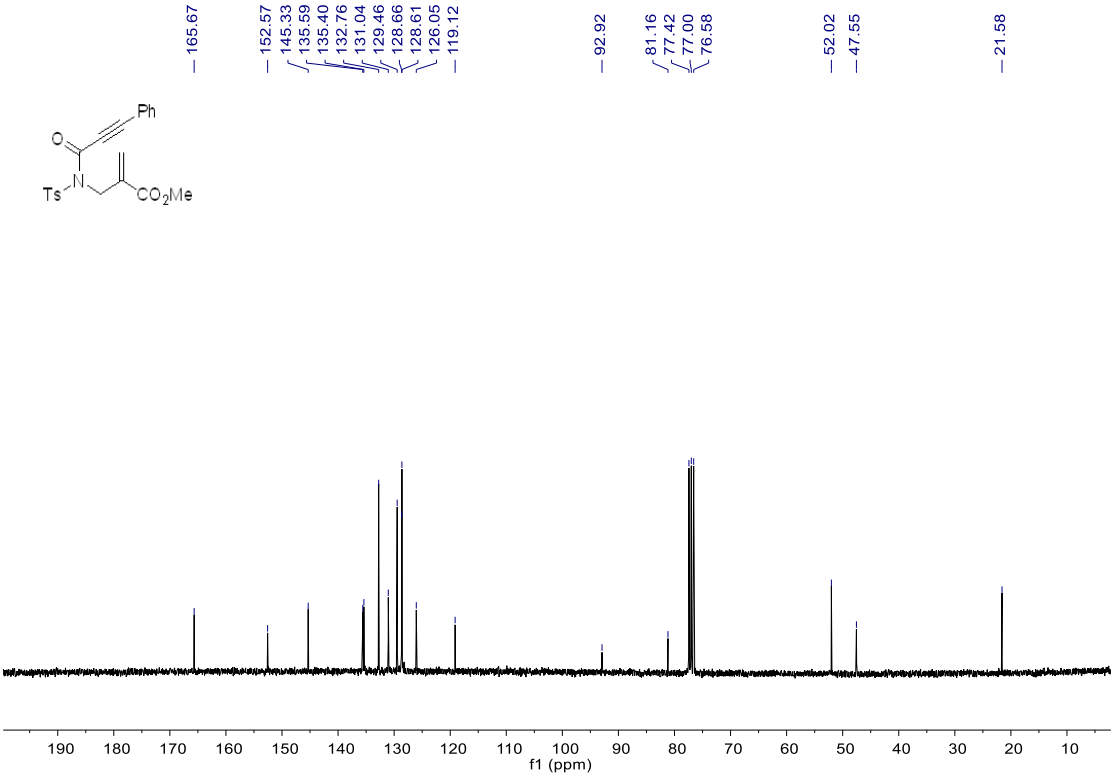
(Thermal ellipsoids are shown with 50% probability.)

6. Copies of ^{1}H NMR and ^{13}C NMR Spectrums

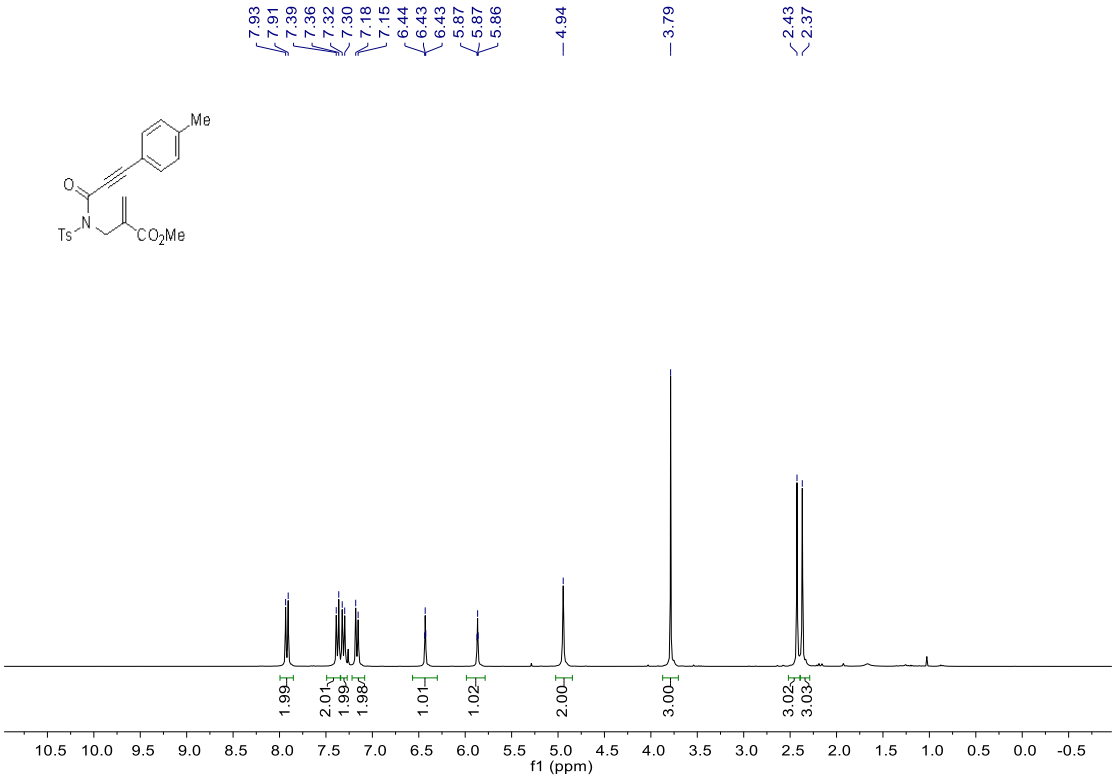
^{1}H NMR Spectrum of 2a



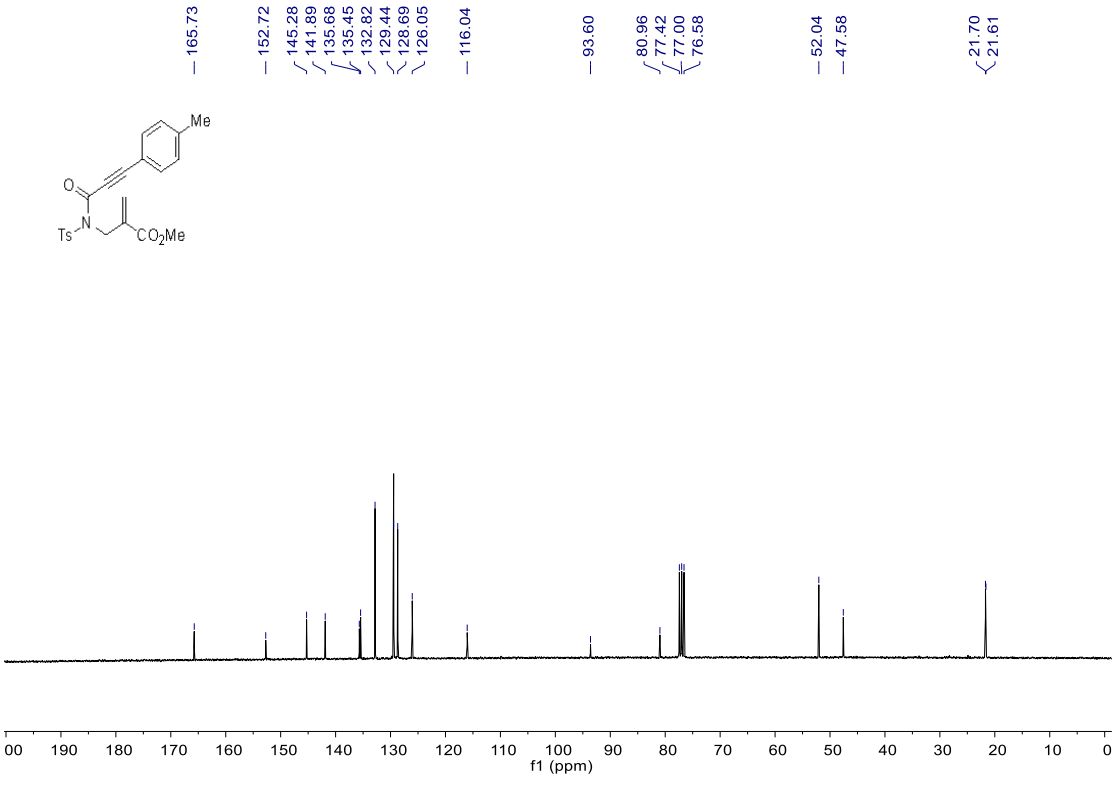
^{13}C NMR Spectrum of 2a



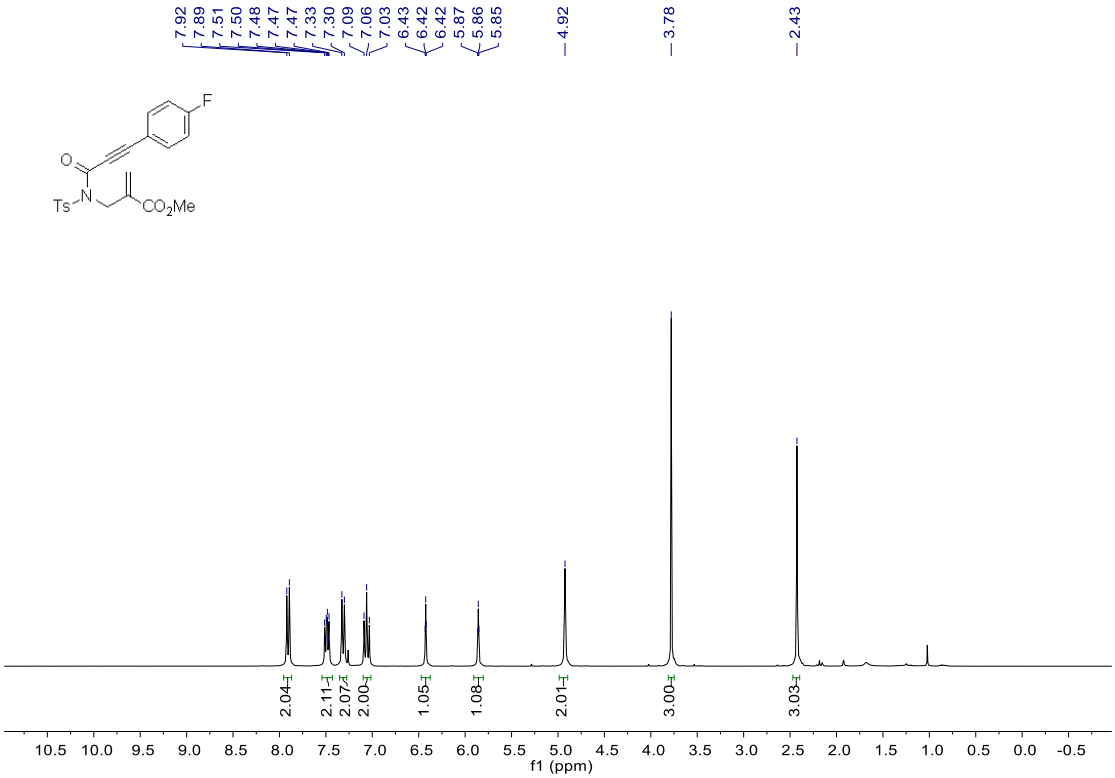
^{1}H NMR Spectrum of 2b



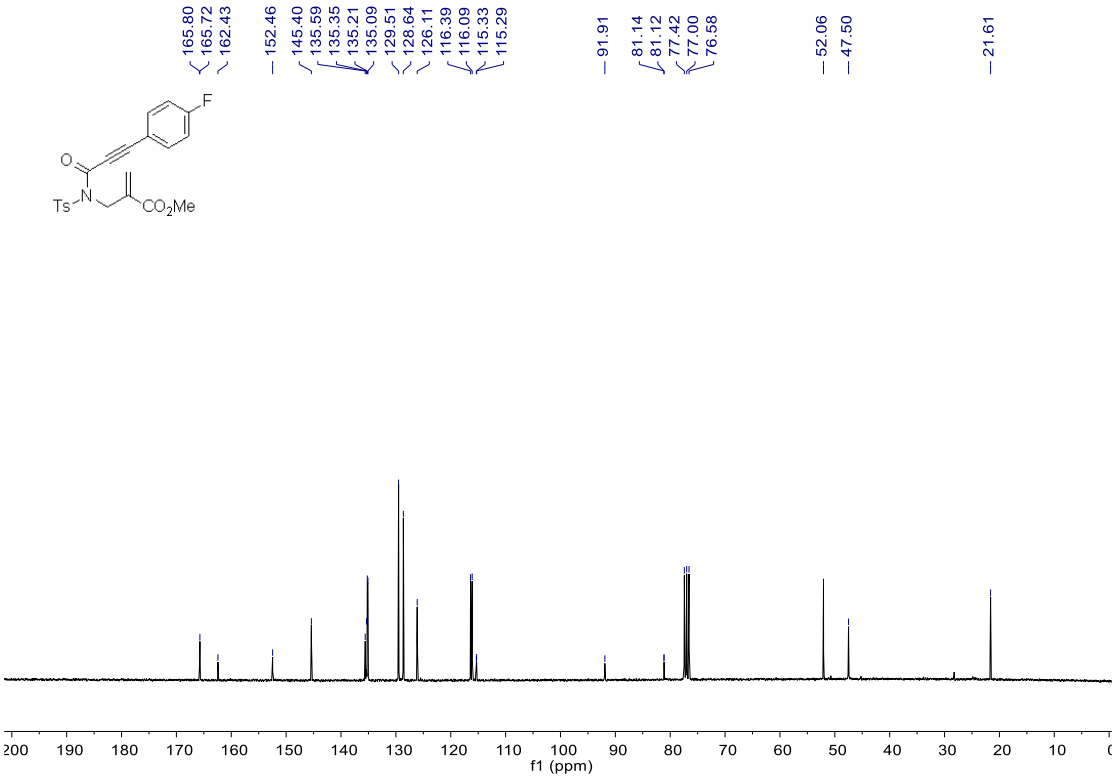
^{13}C NMR Spectrum of 2b



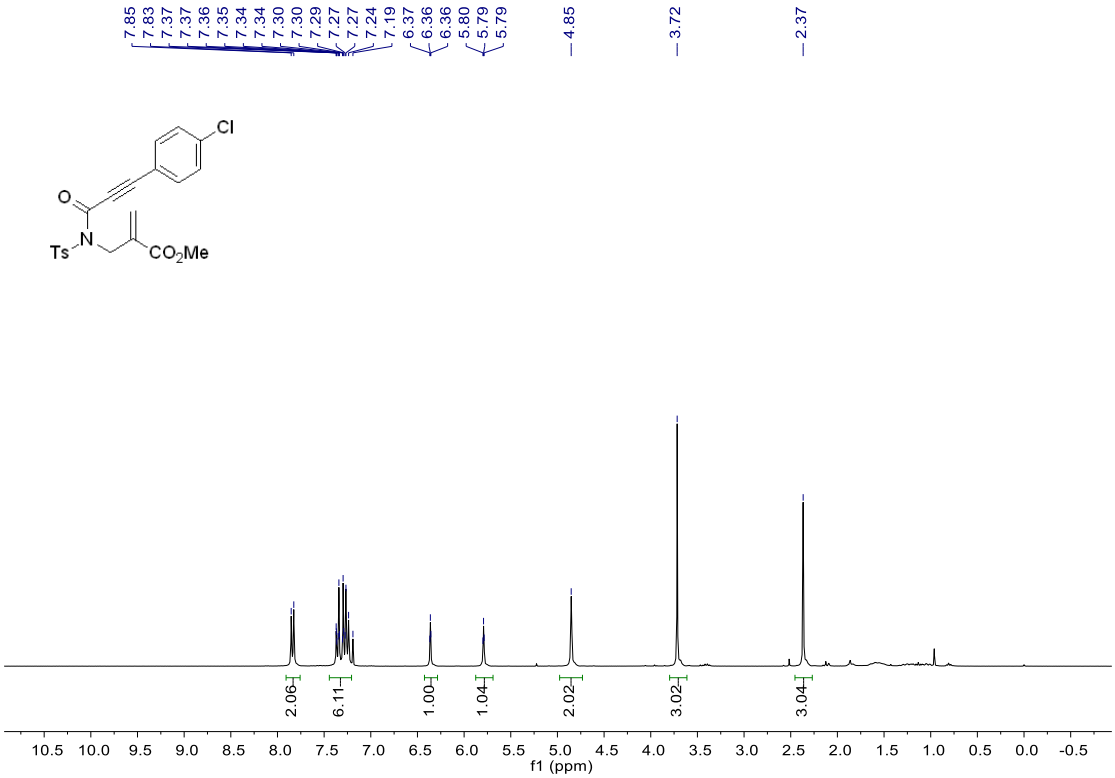
^{1}H NMR Spectrum of 2c



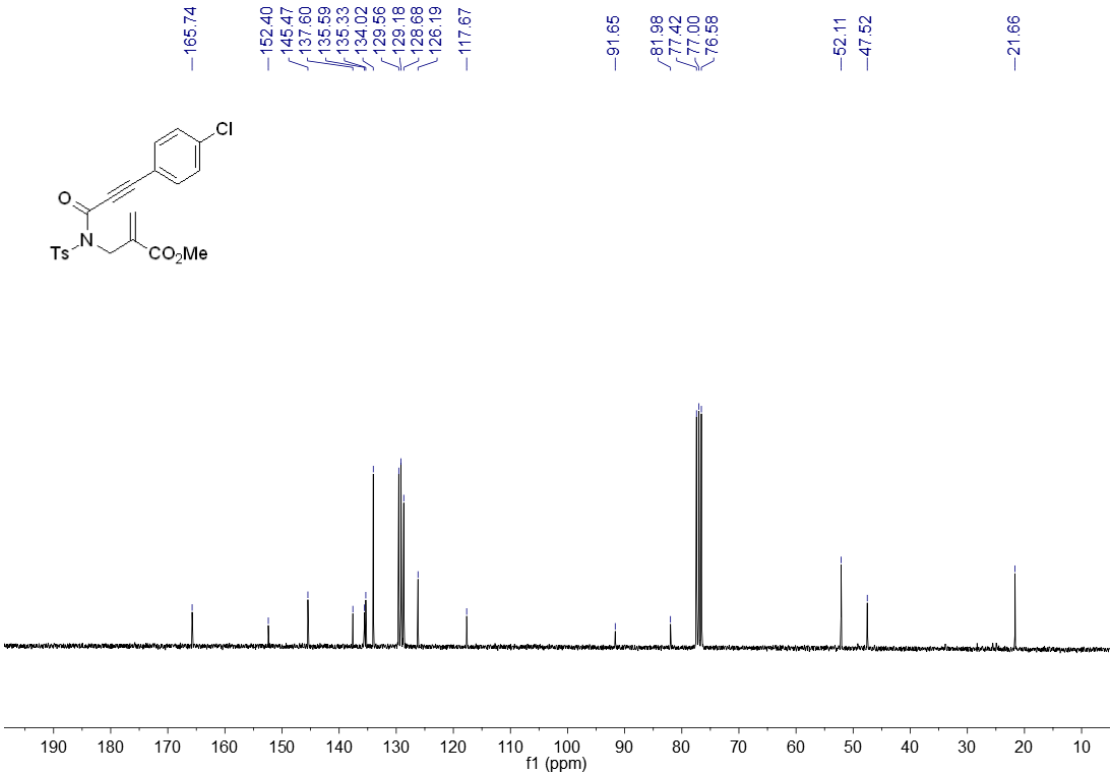
^{13}C NMR Spectrum of 2c



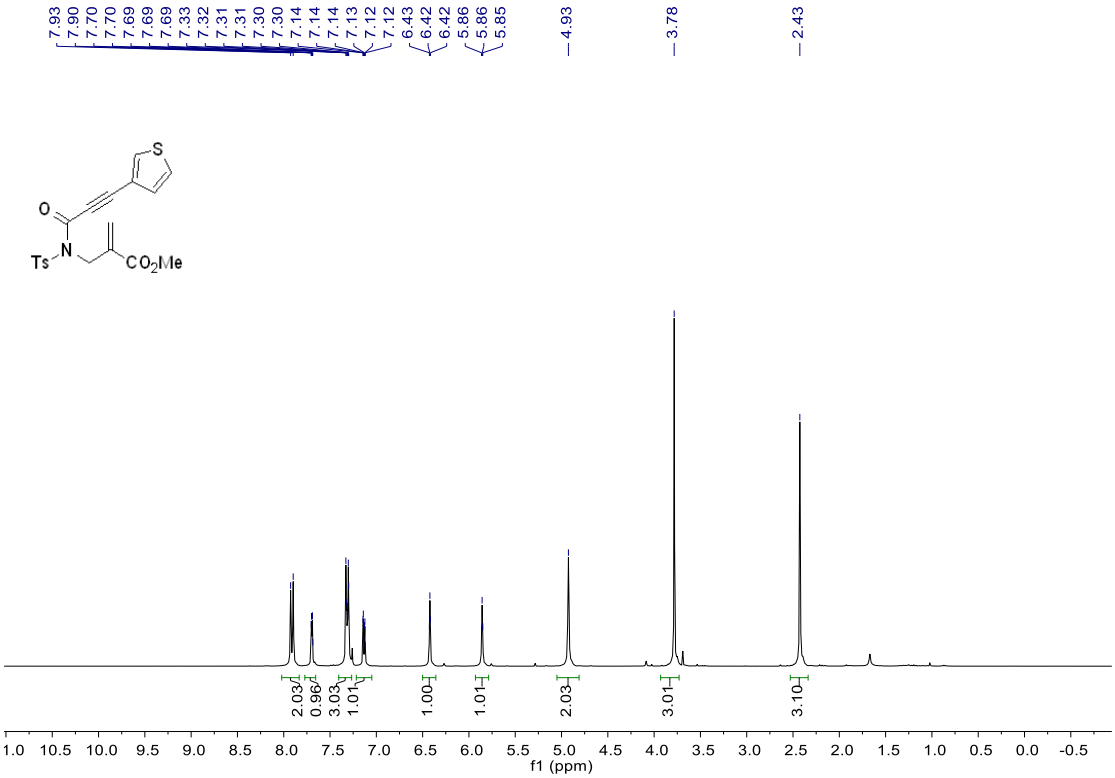
^{1}H NMR Spectrum of 2d



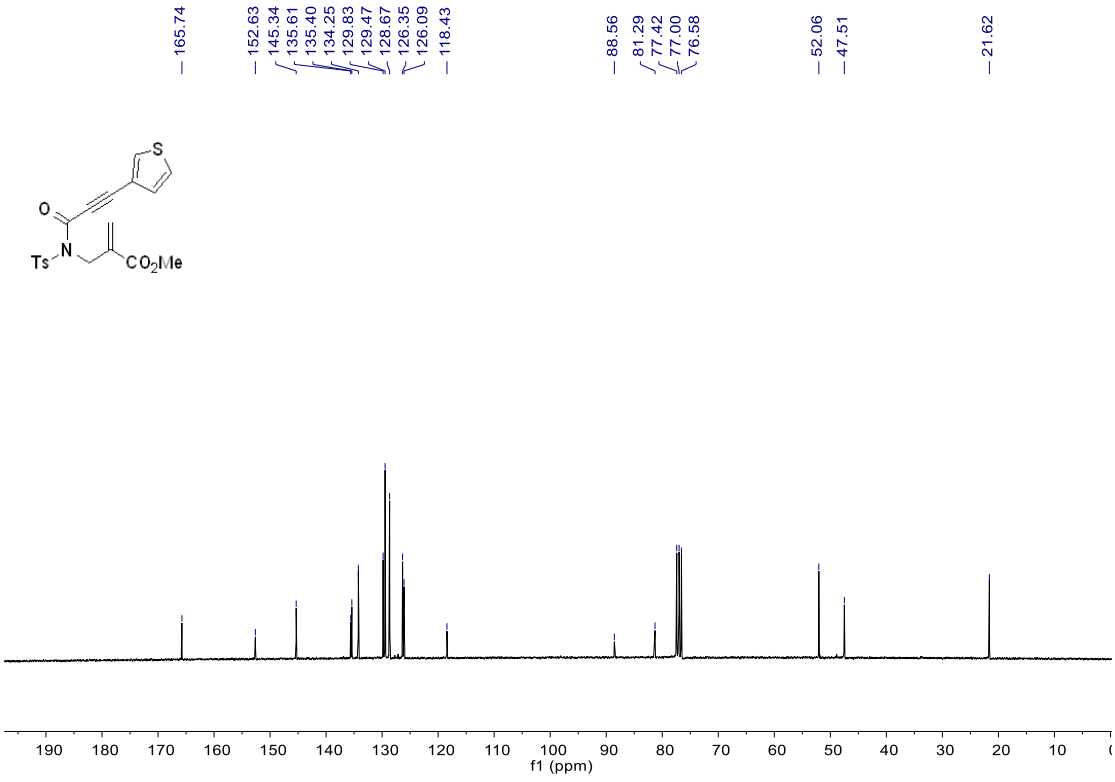
^{13}C NMR Spectrum of 2d



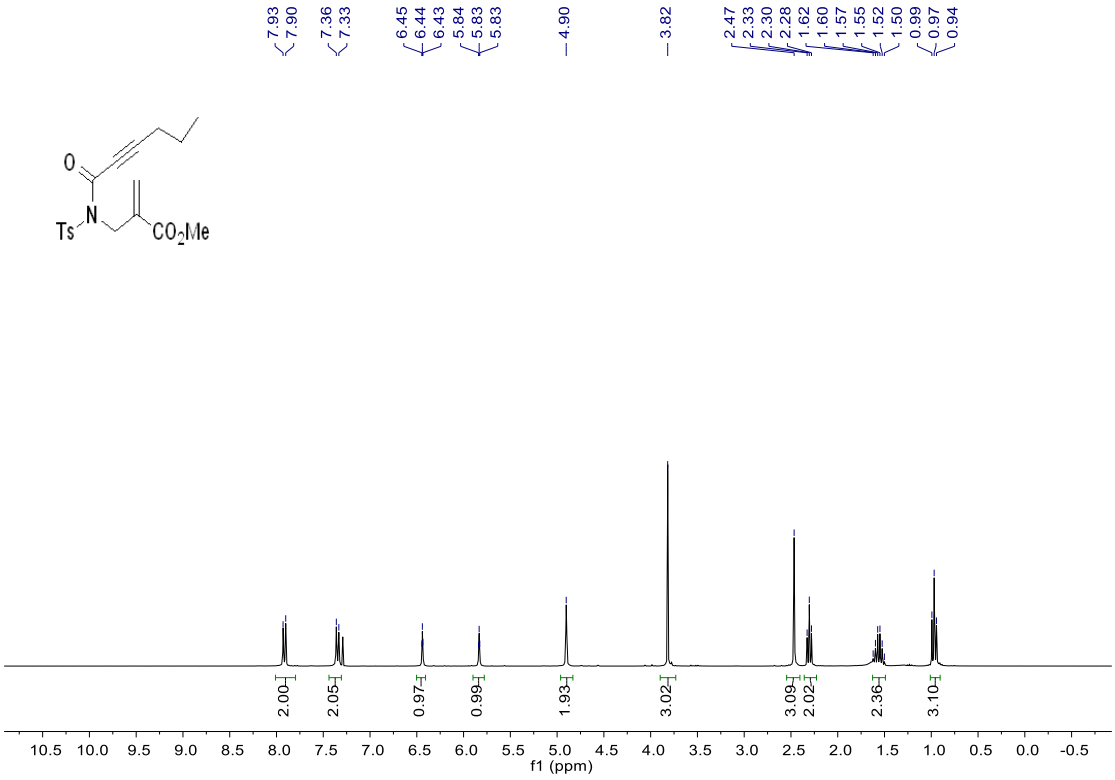
^{1}H NMR Spectrum of 2e



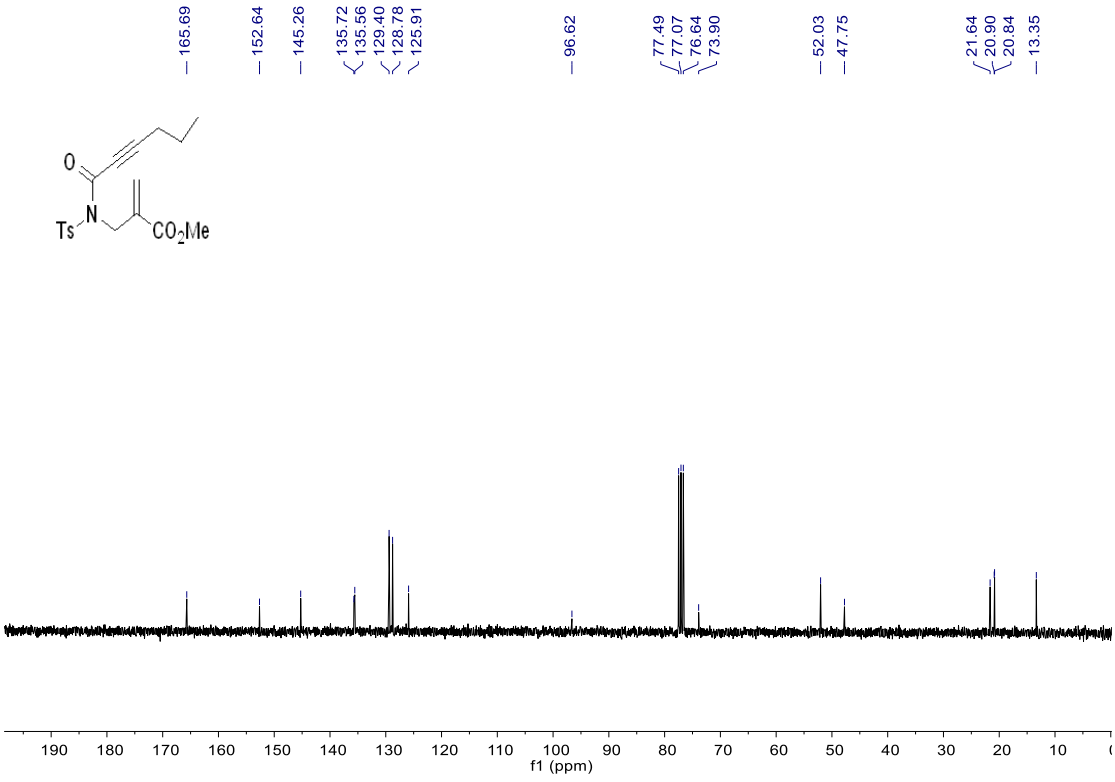
^{13}C NMR Spectrum of 2e



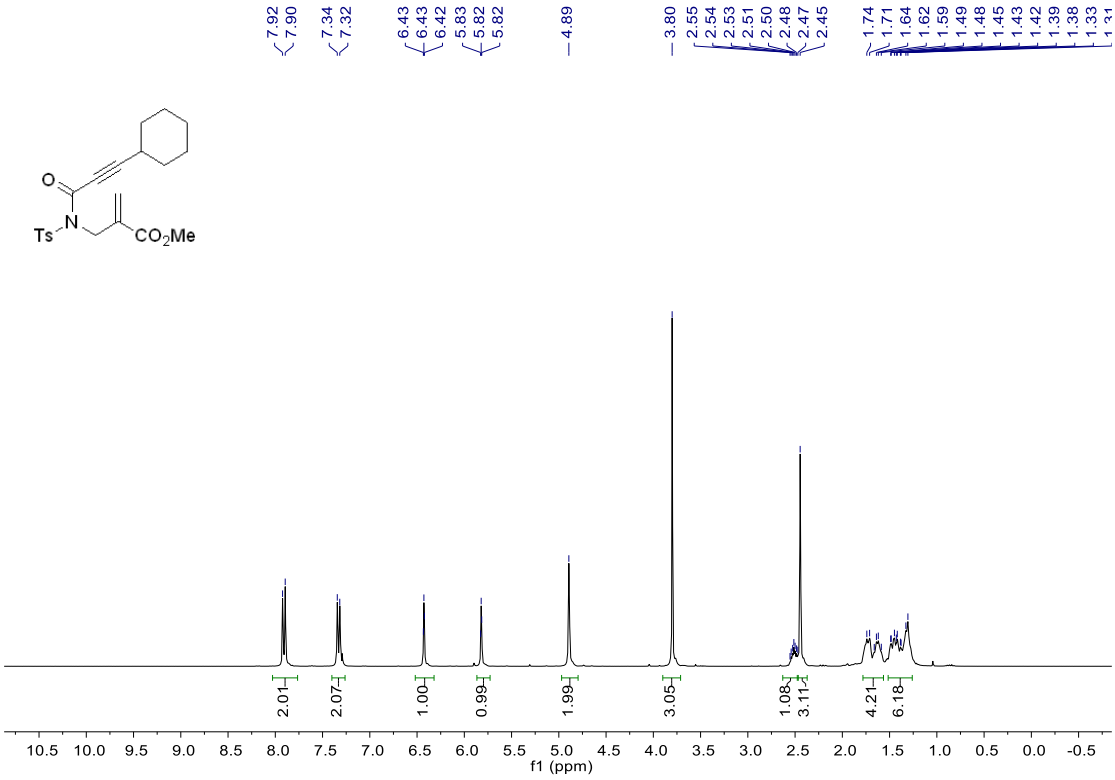
^{1}H NMR Spectrum of 2f



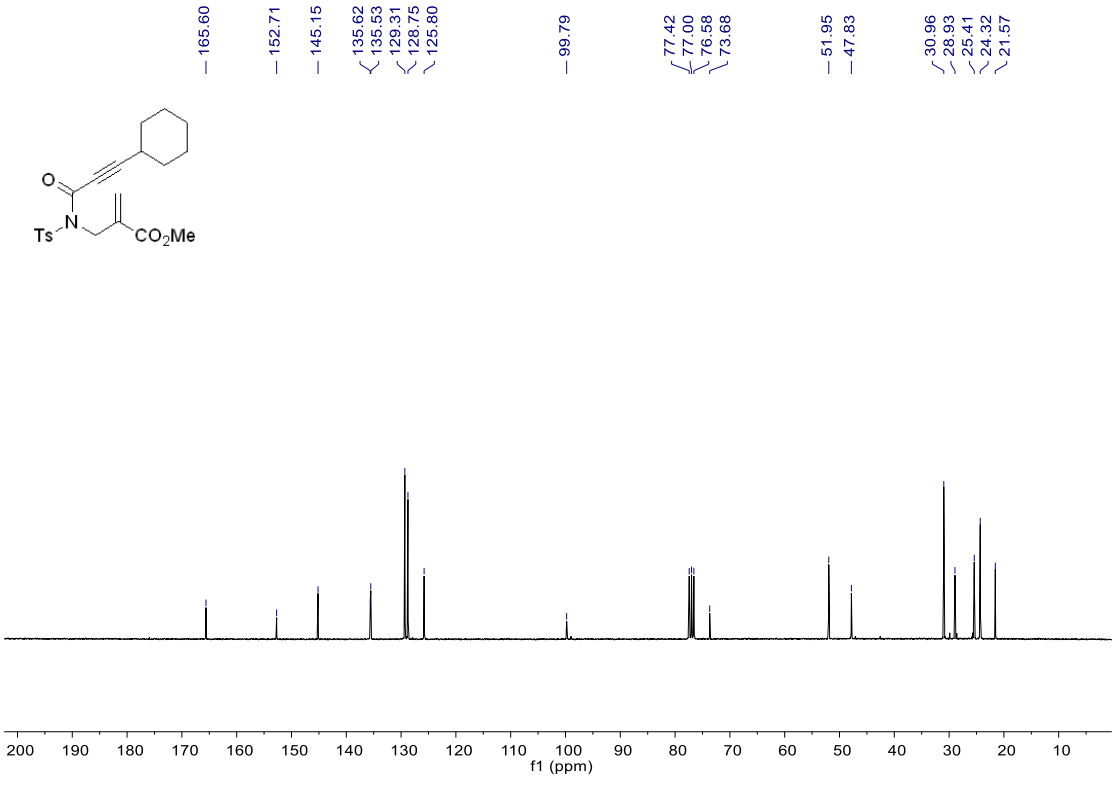
^{13}C NMR Spectrum of 2f



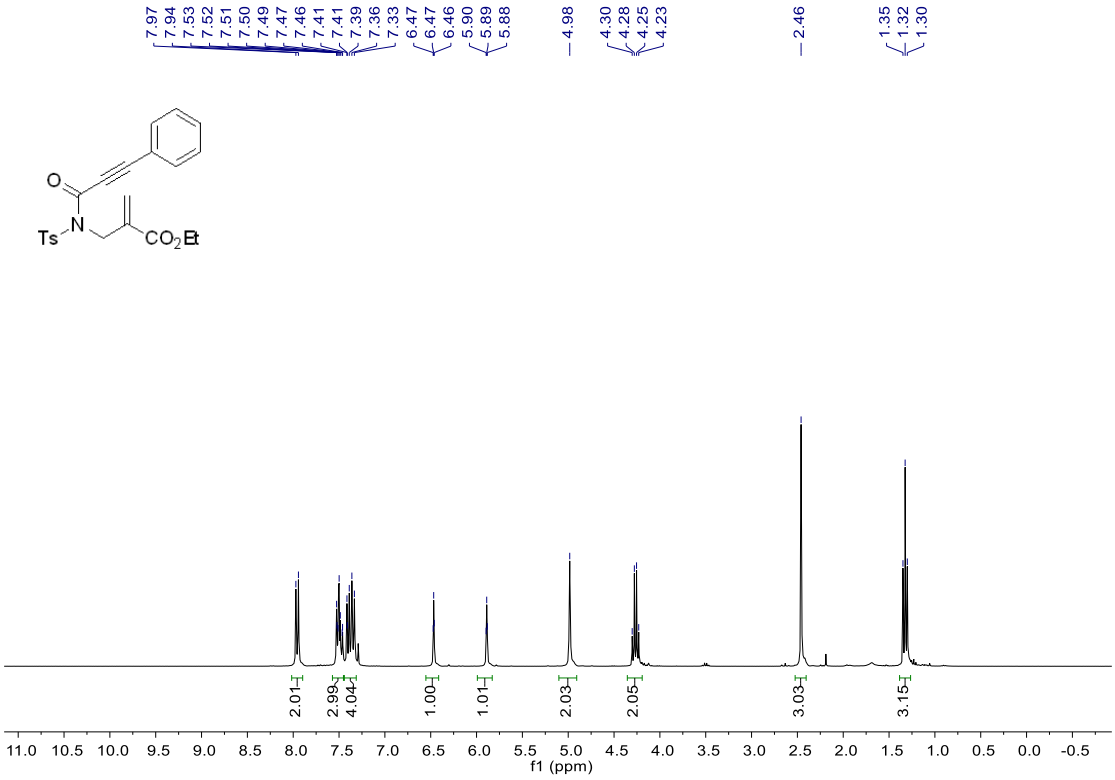
^{1}H NMR Spectrum of 2g



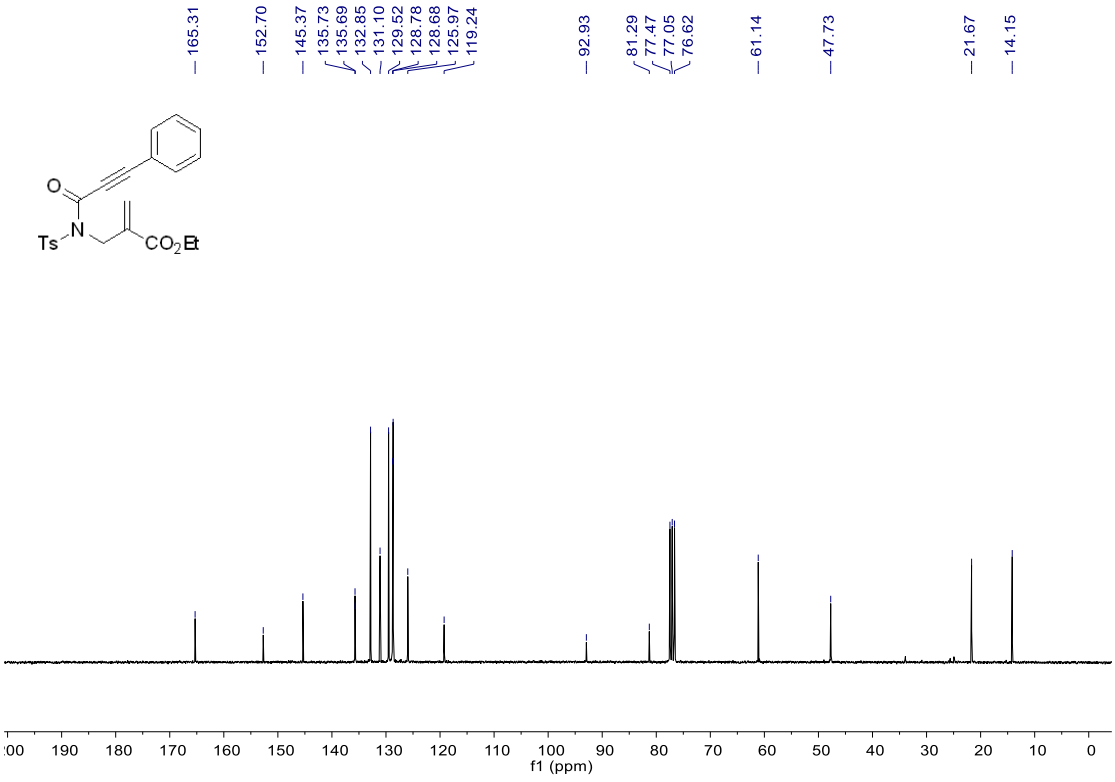
^{13}C NMR Spectrum of 2g



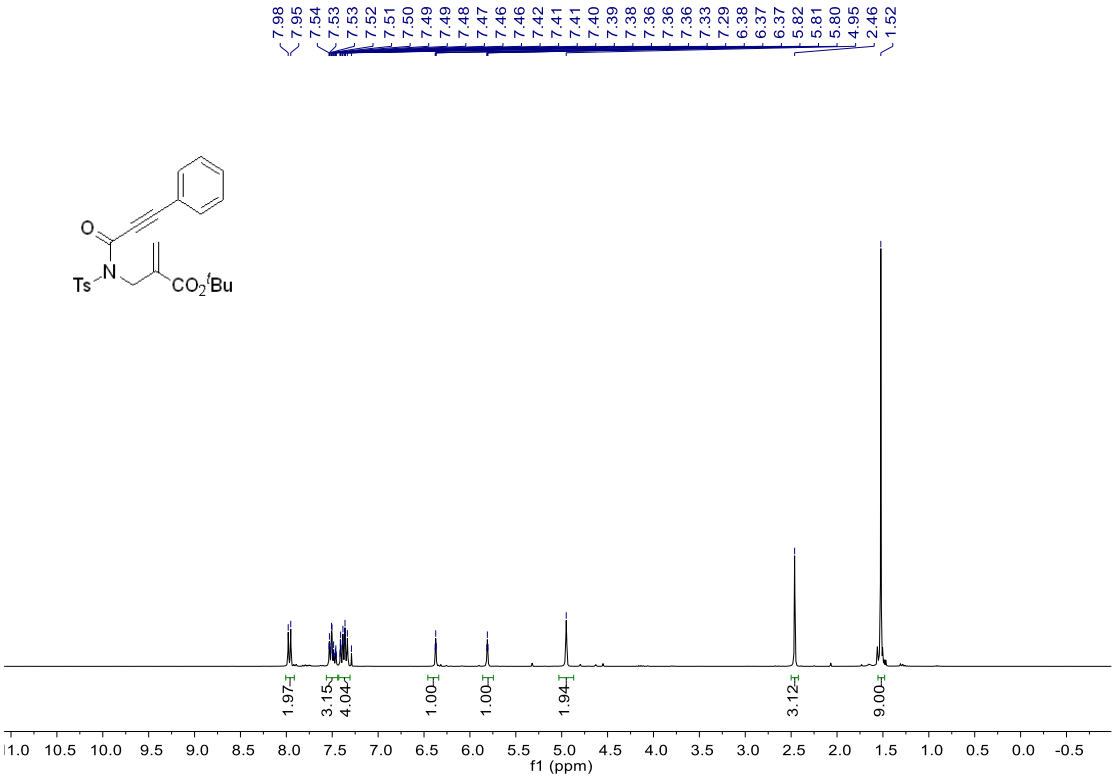
^{1}H NMR Spectrum of 2h



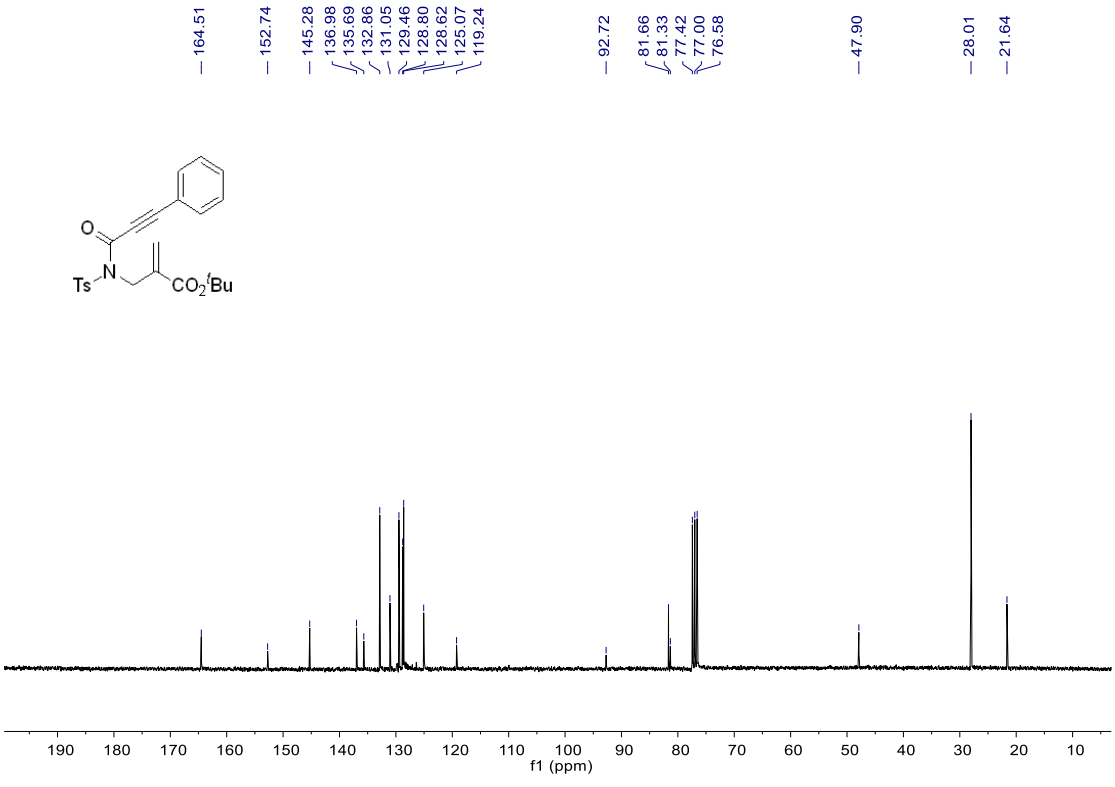
^{13}C NMR Spectrum of 2h



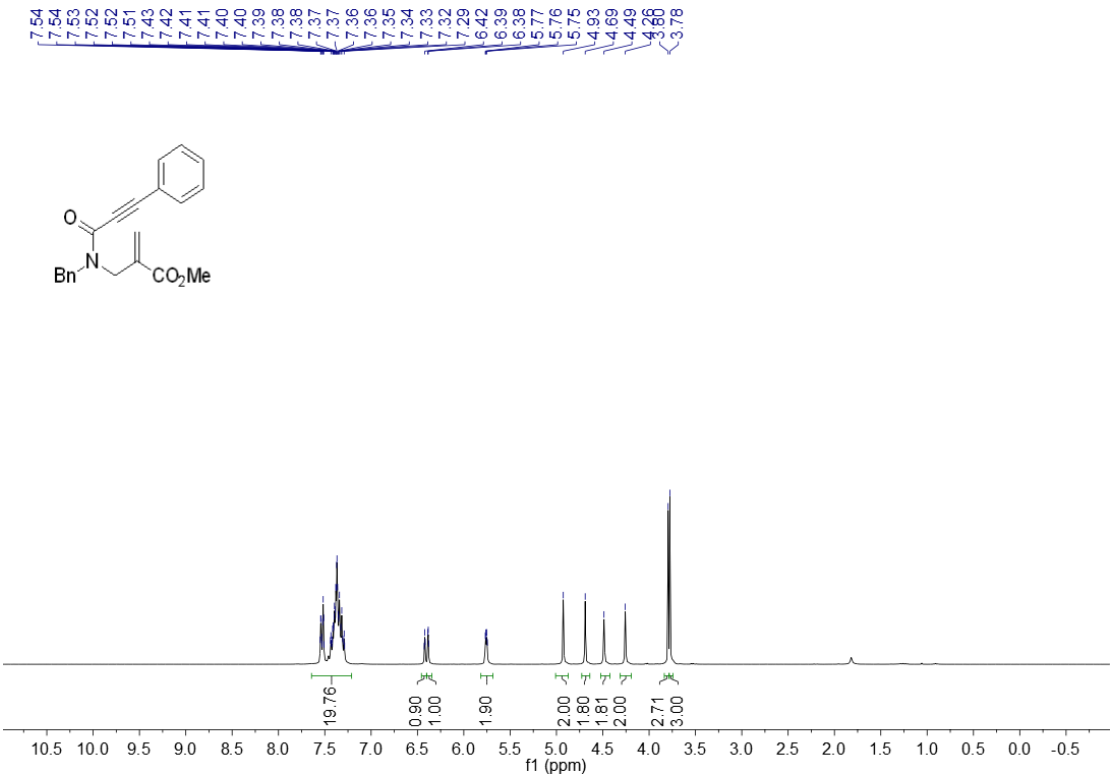
^{1}H NMR Spectrum of 2i



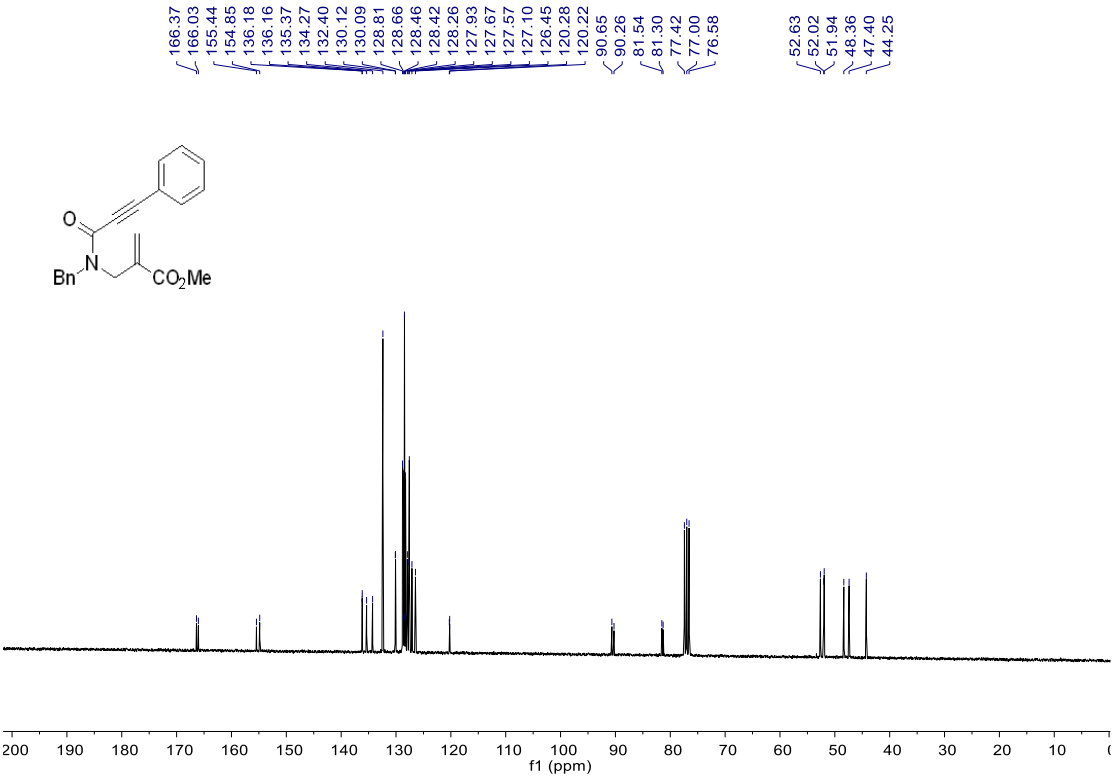
^{13}C NMR Spectrum of 2i



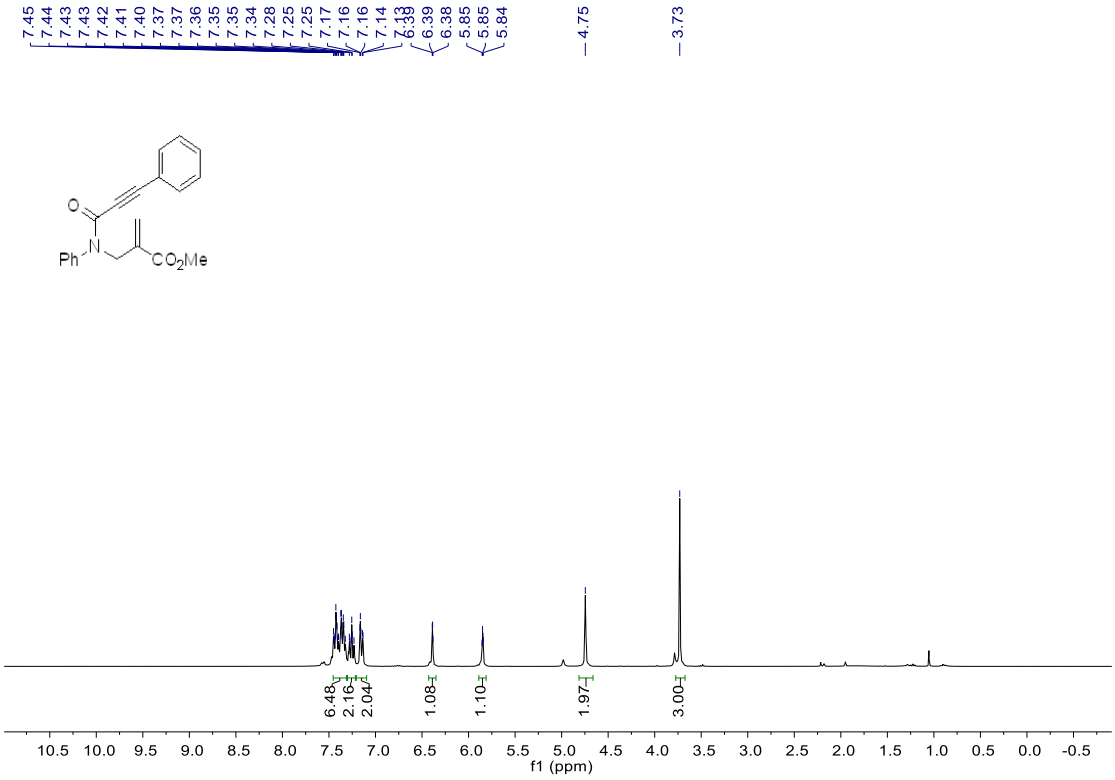
^{1}H NMR Spectrum of 2j (isomer ratio 1:0.9)



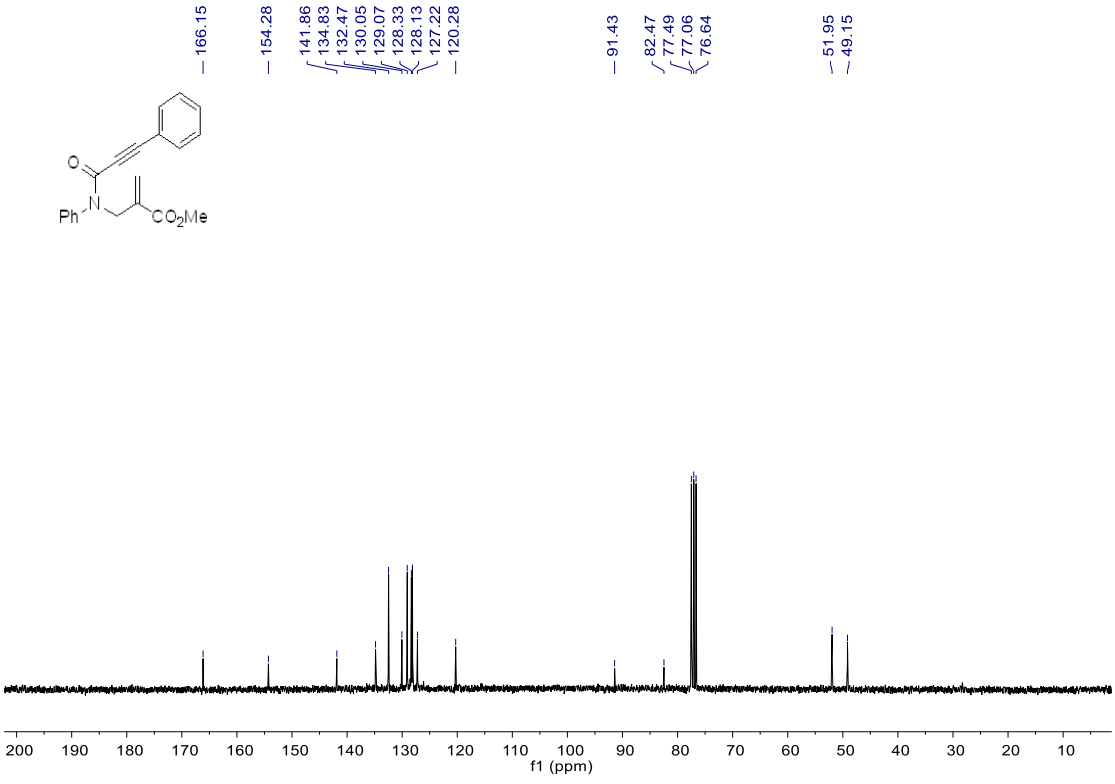
^{13}C NMR Spectrum of 2j (isomer ratio 1:0.9)



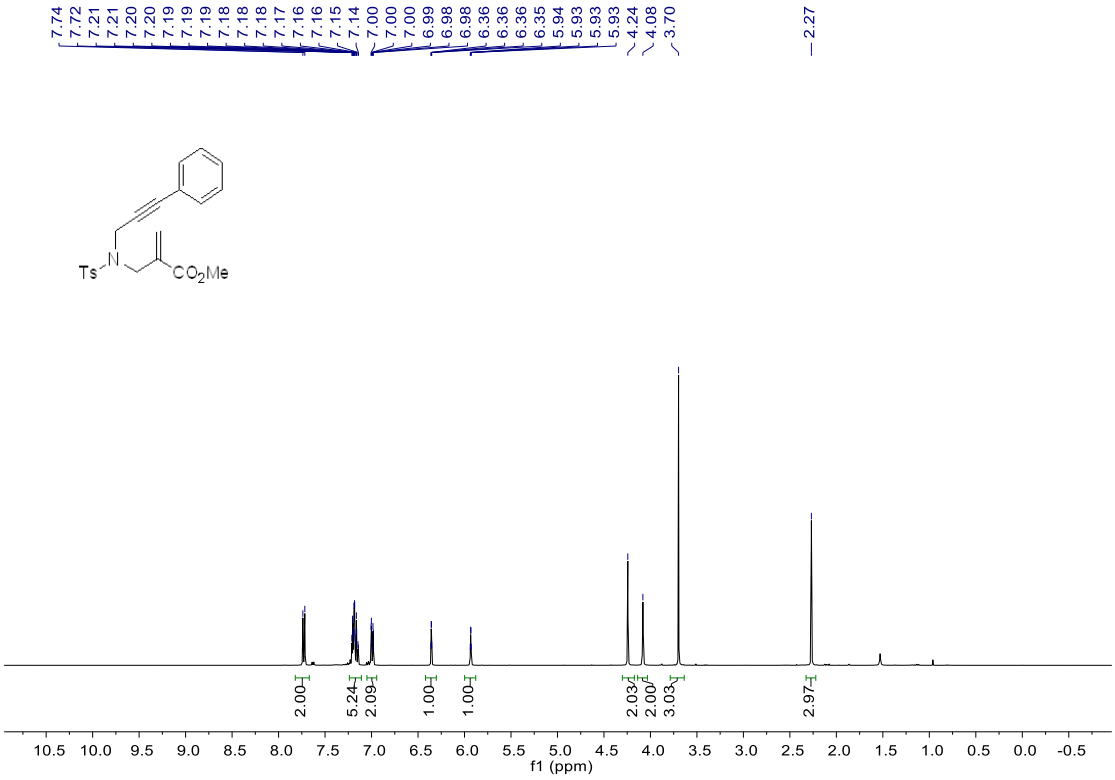
^{1}H NMR Spectrum of 2k



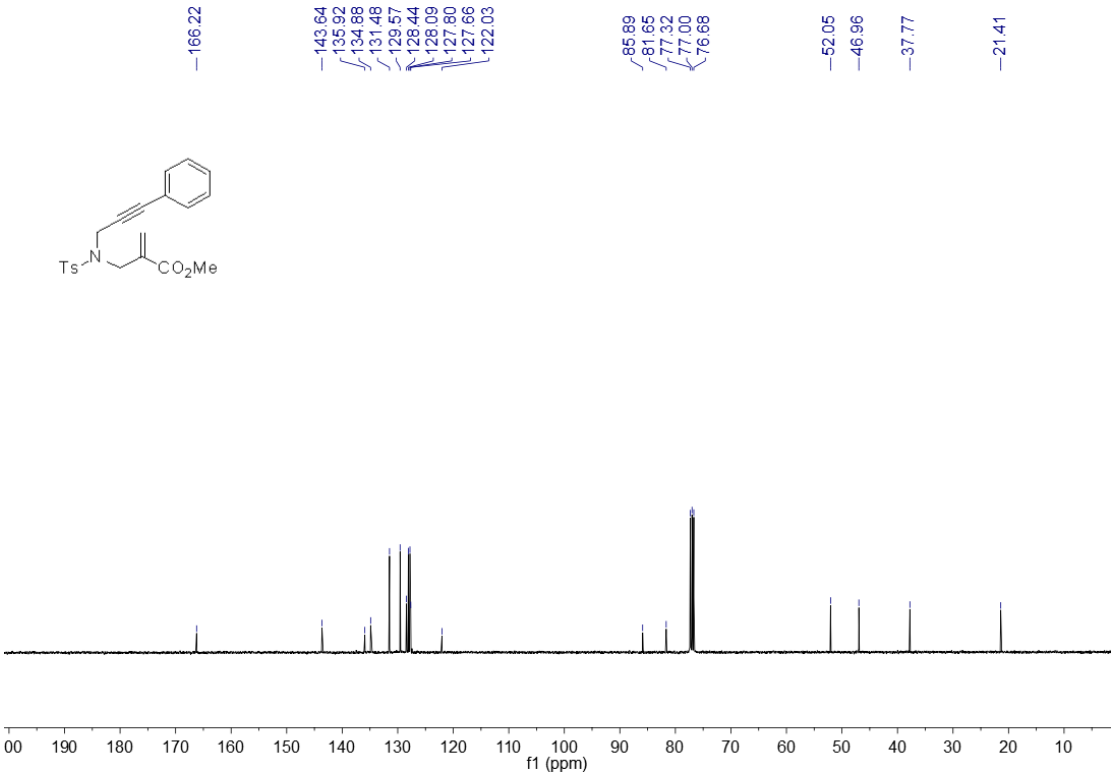
^{13}C NMR Spectrum of 2k



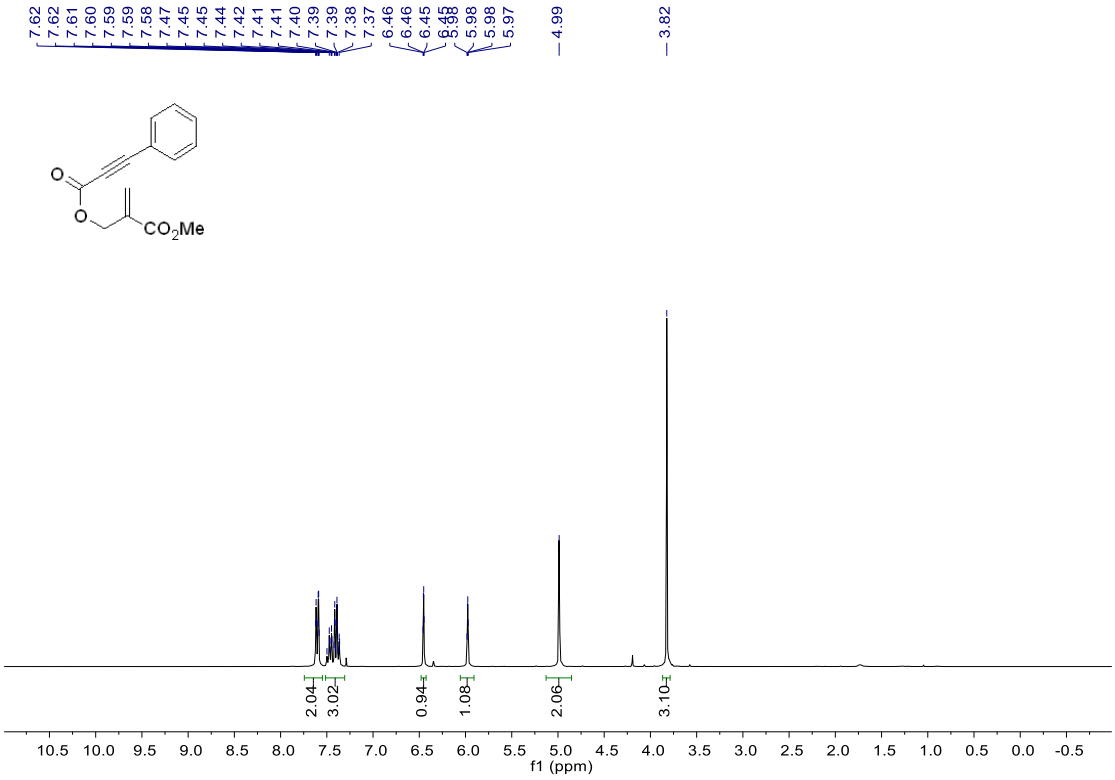
^{1}H NMR Spectrum of 2l



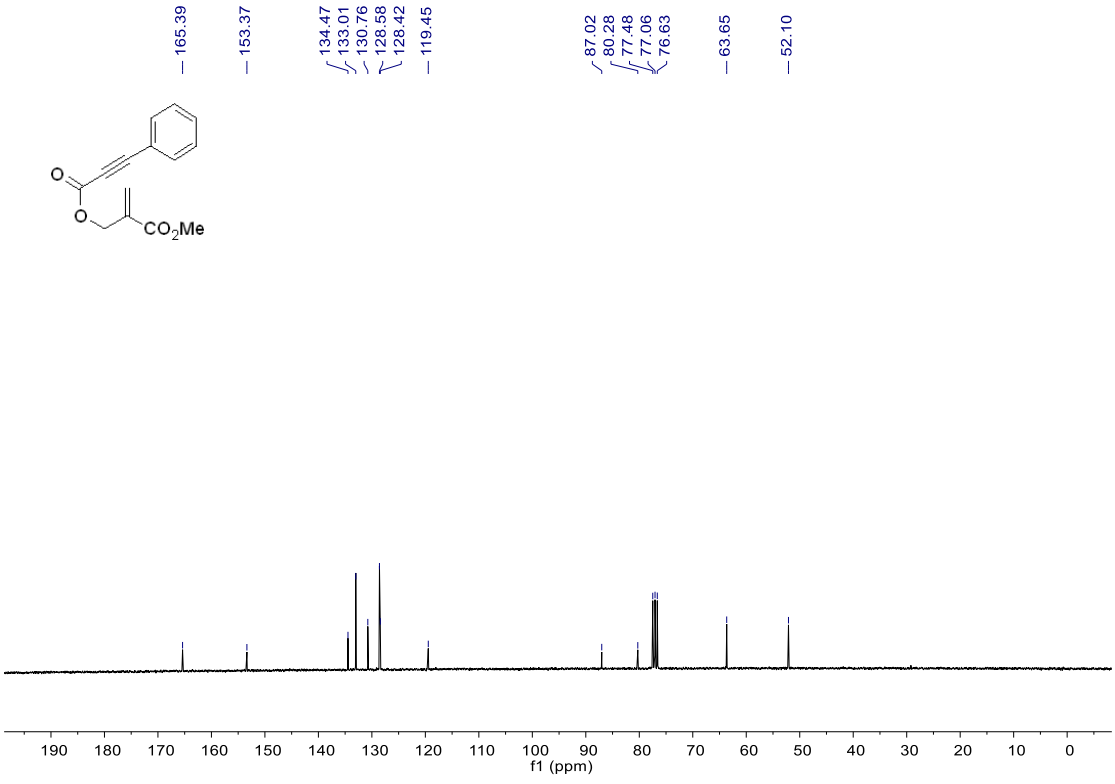
^{13}C NMR Spectrum of 2l



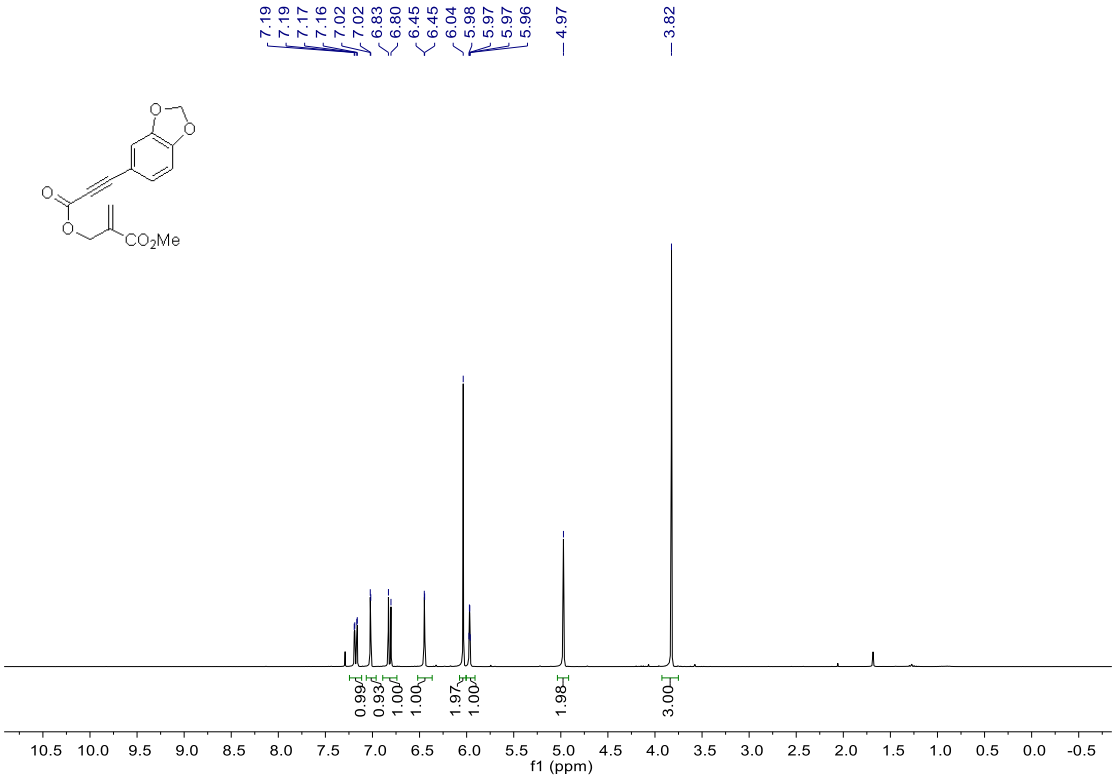
^{1}H NMR Spectrum of 5a



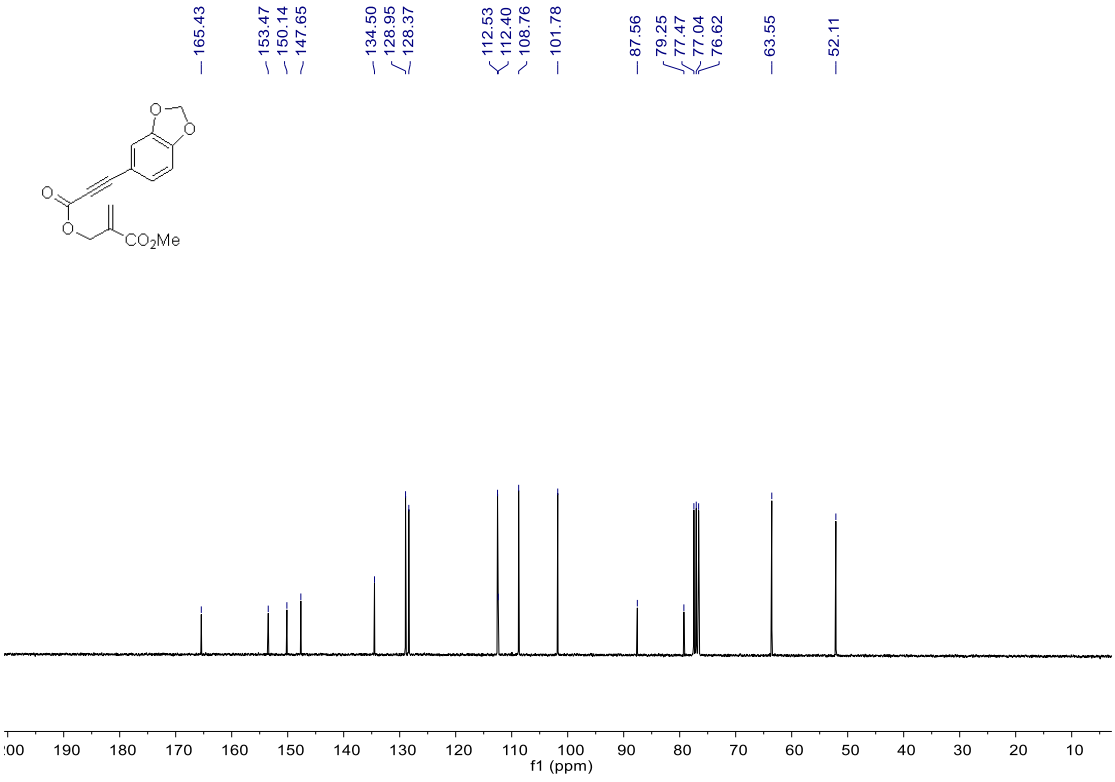
^{13}C NMR Spectrum of 5a



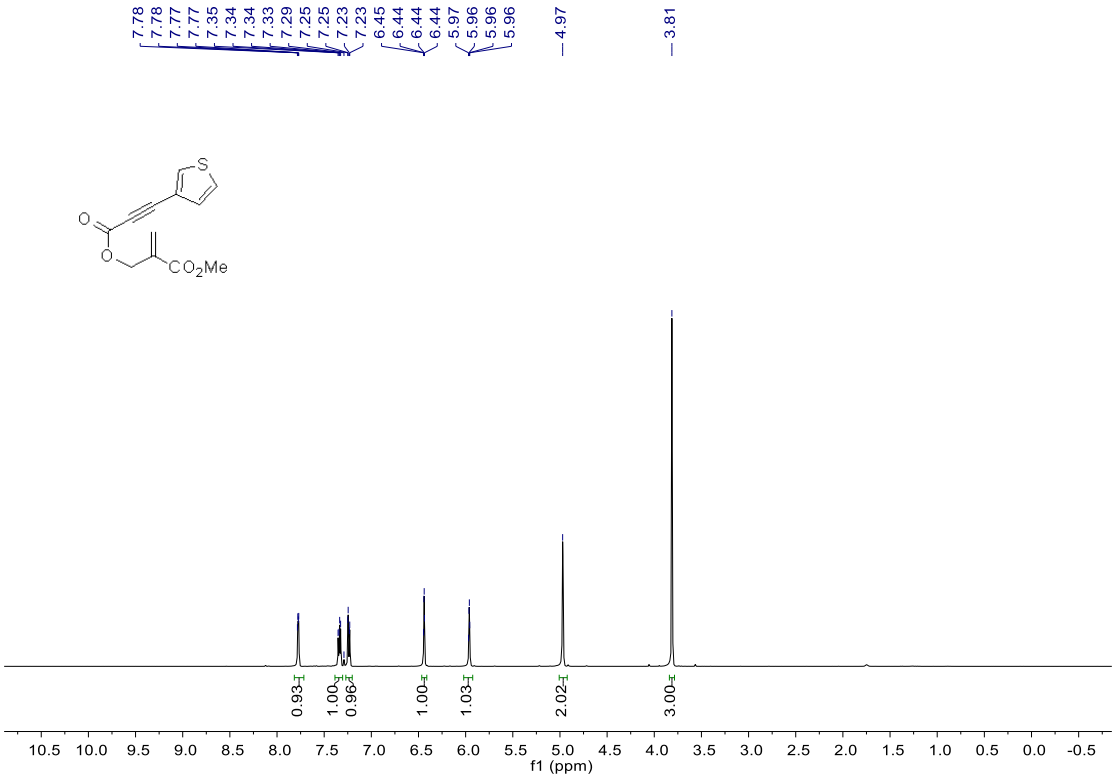
^{1}H NMR Spectrum of 5b



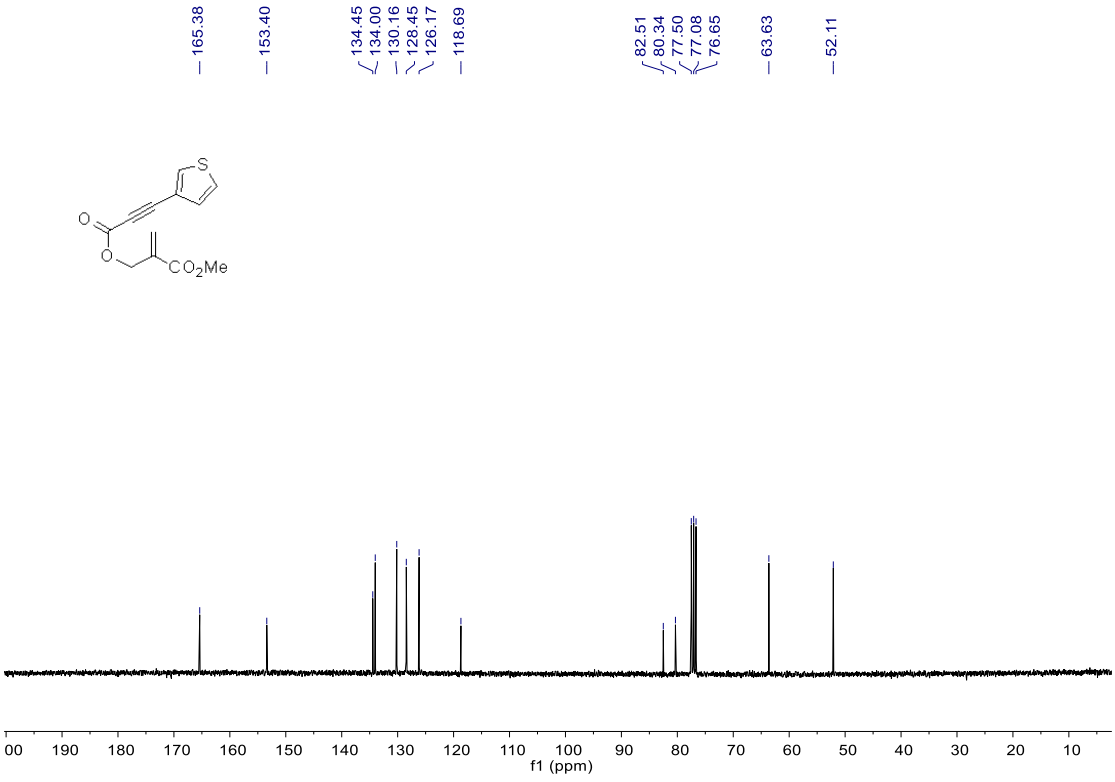
^{13}C NMR Spectrum of 5b



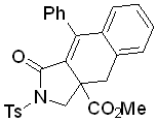
^{1}H NMR Spectrum of 5c

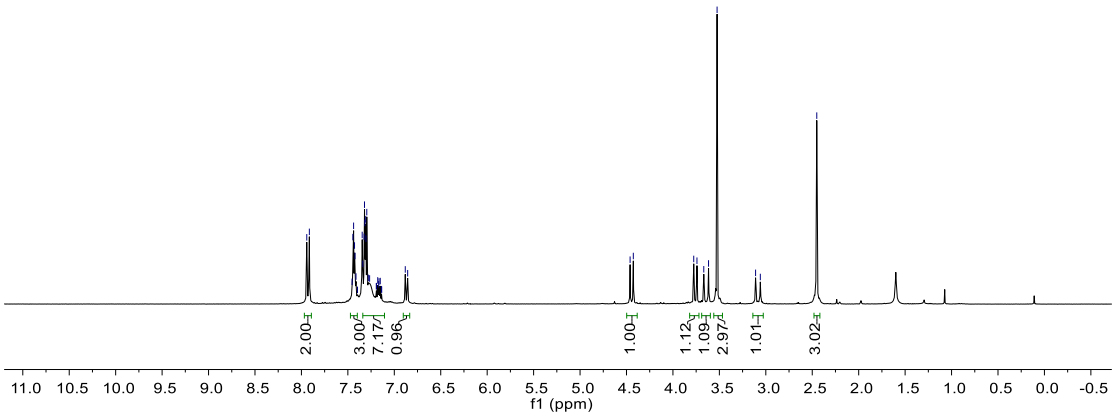


^{13}C NMR Spectrum of 5c

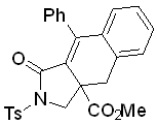


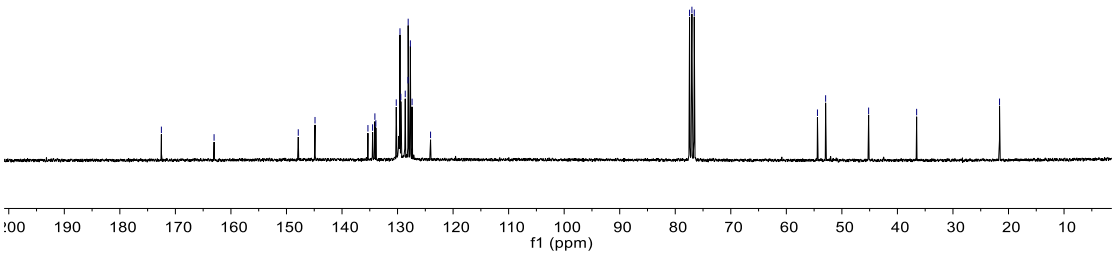
^{1}H NMR Spectrum of 4aa



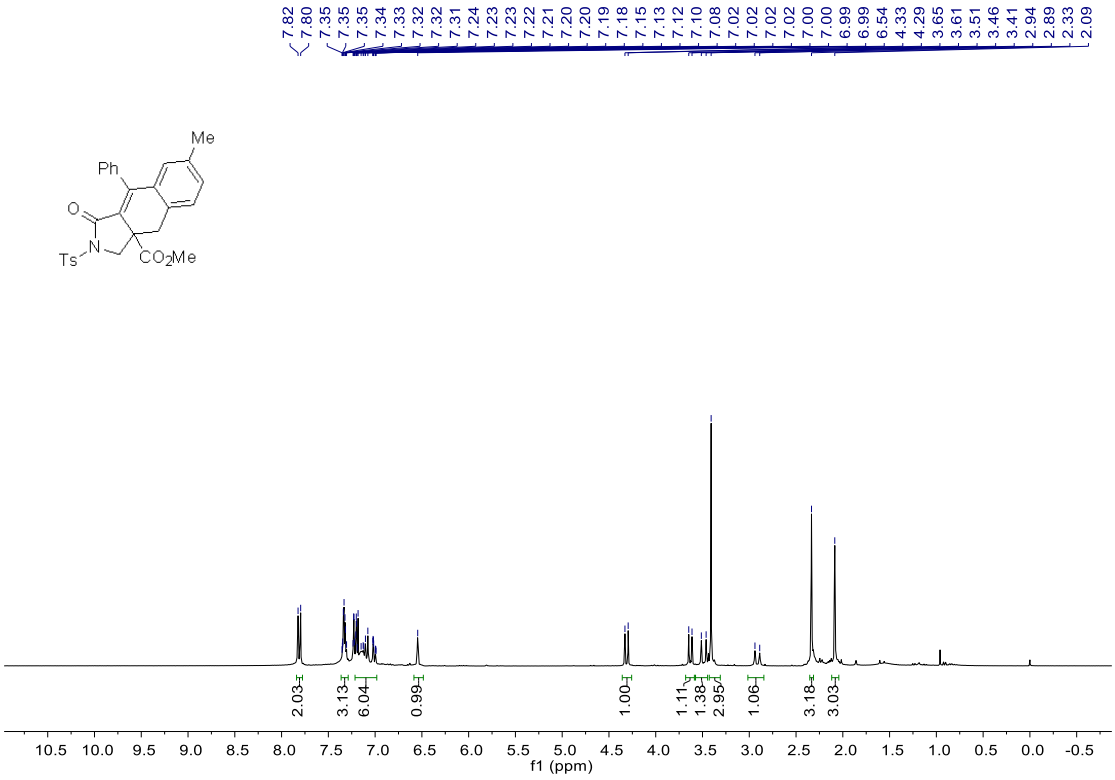


^{13}C NMR Spectrum of 4aa

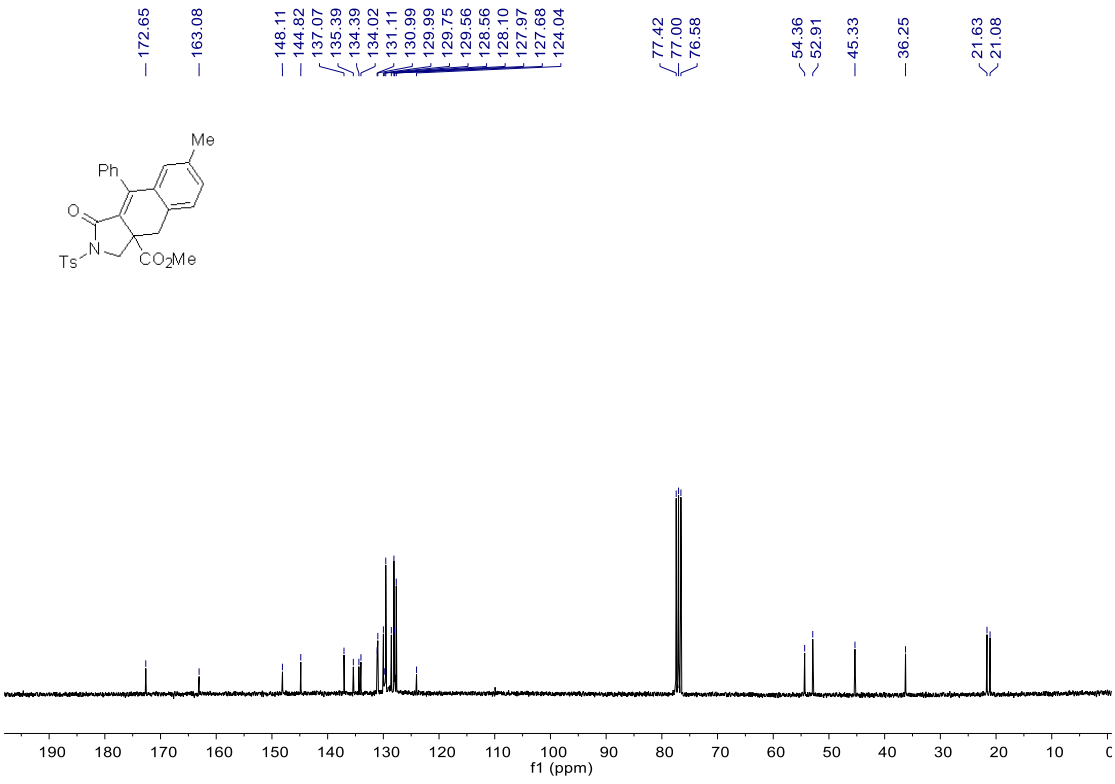




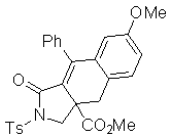
^{1}H NMR Spectrum of 4ab

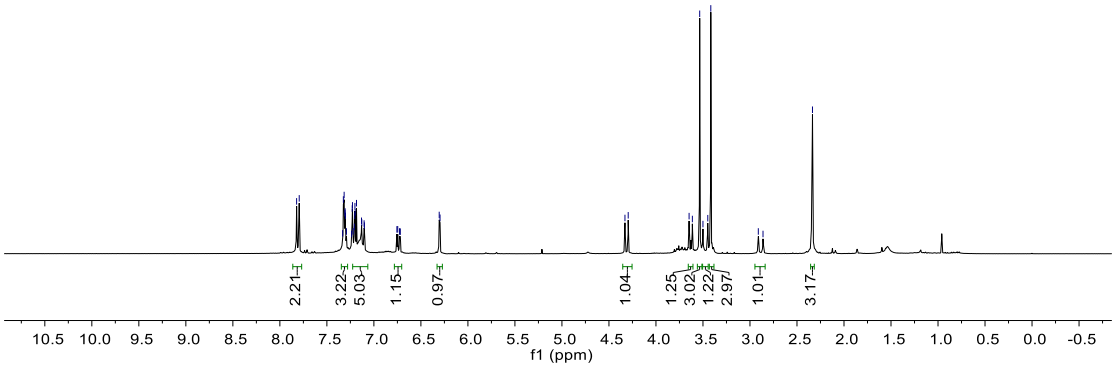


^{13}C NMR Spectrum of 4ab

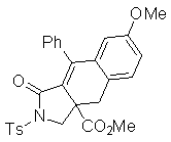


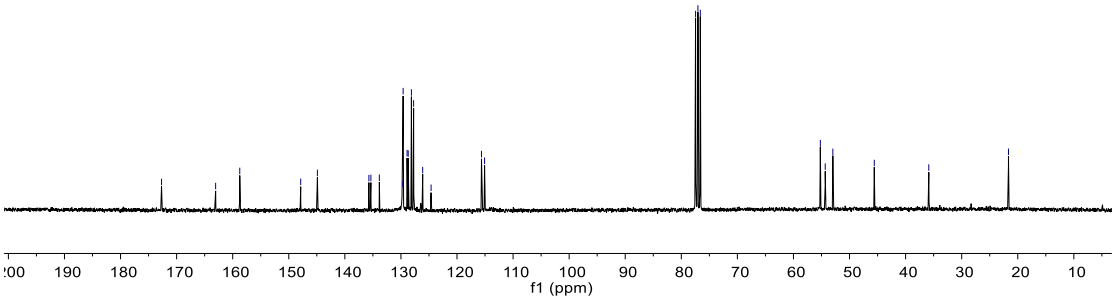
^{1}H NMR Spectrum of 4ac



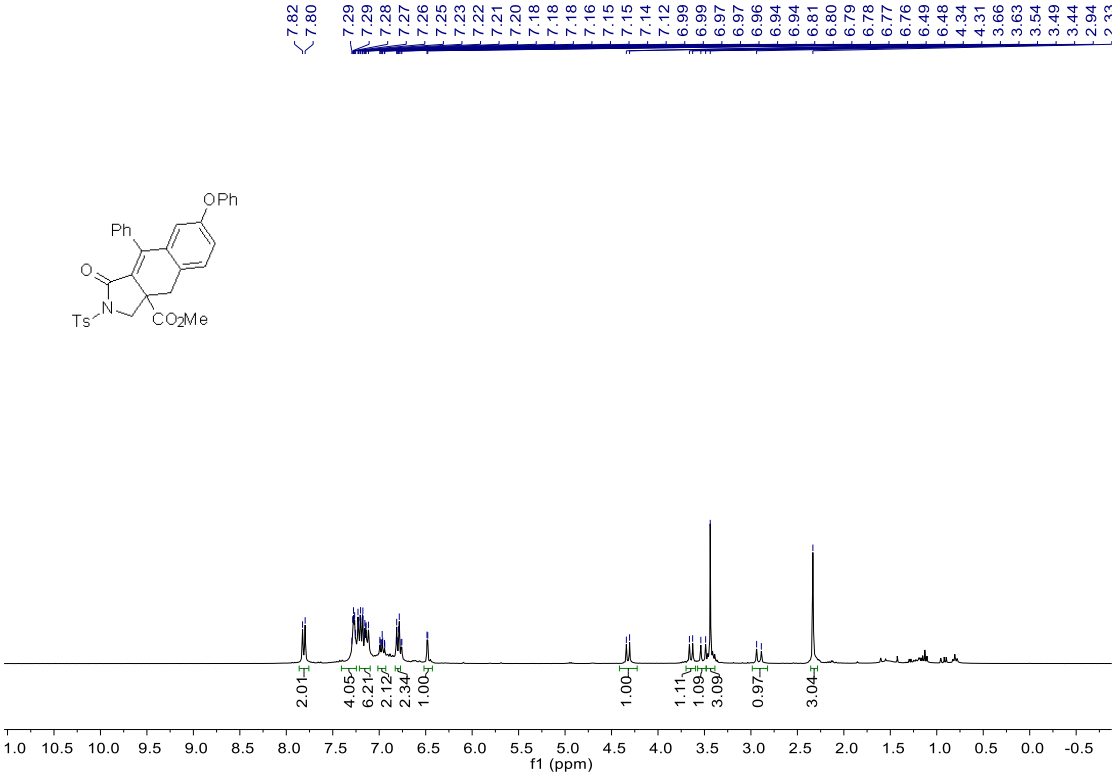


^{13}C NMR Spectrum of 4ac

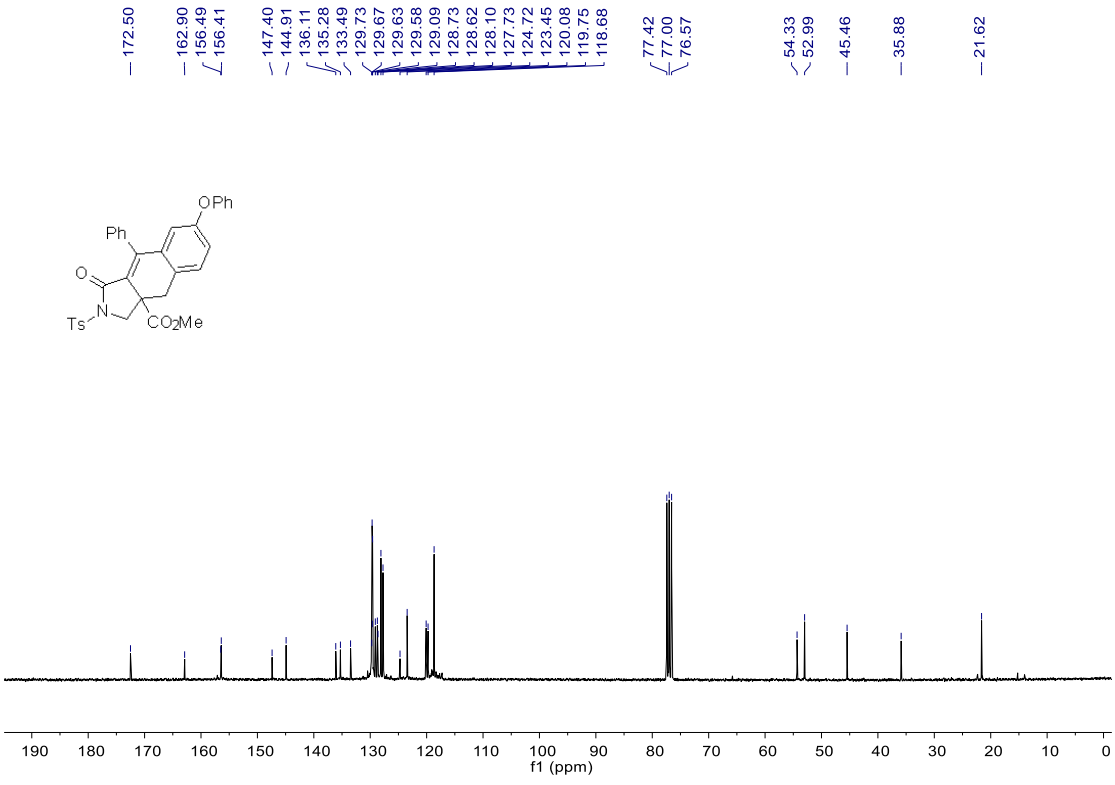




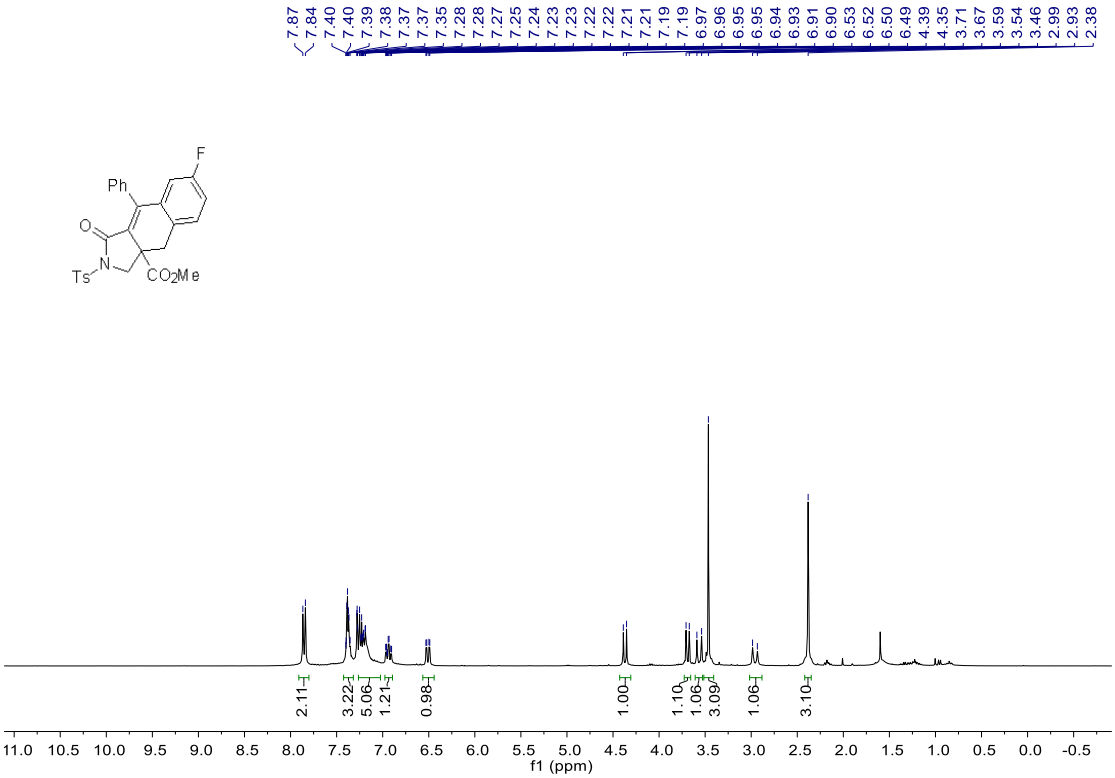
^{1}H NMR Spectrum of 4ad



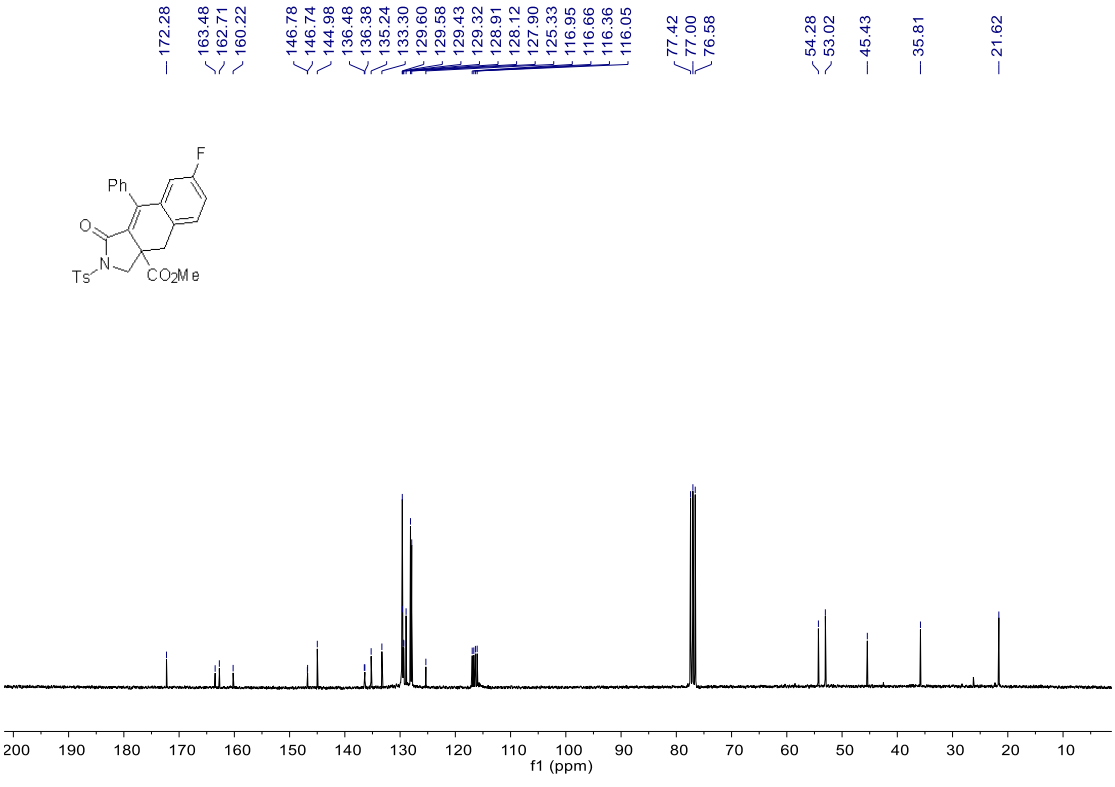
^{13}C NMR Spectrum of 4ad



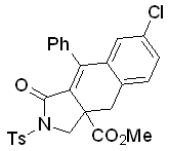
^{1}H NMR Spectrum of 4ae

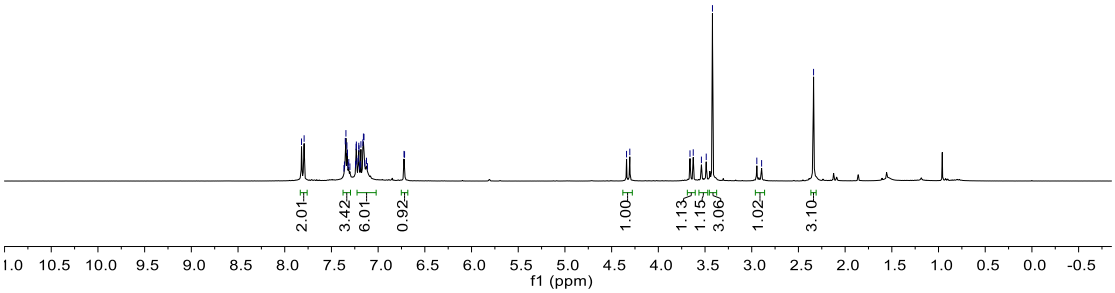


^{13}C NMR Spectrum of 4ae

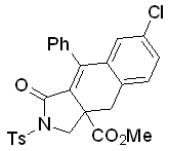


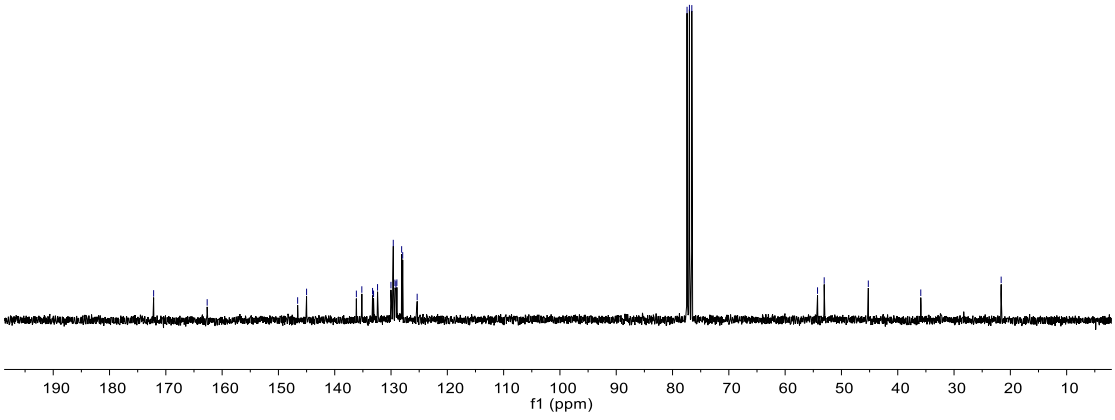
^{1}H NMR Spectrum of 4af



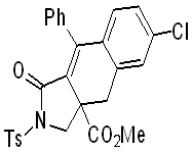


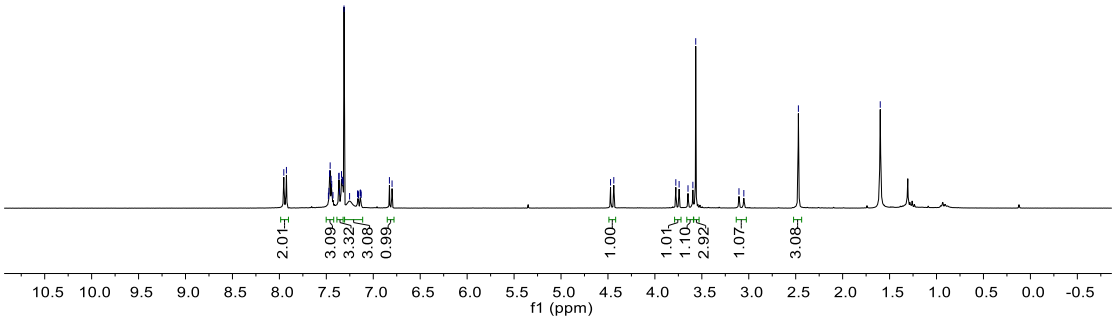
^{13}C NMR Spectrum of 4af



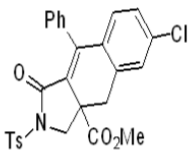


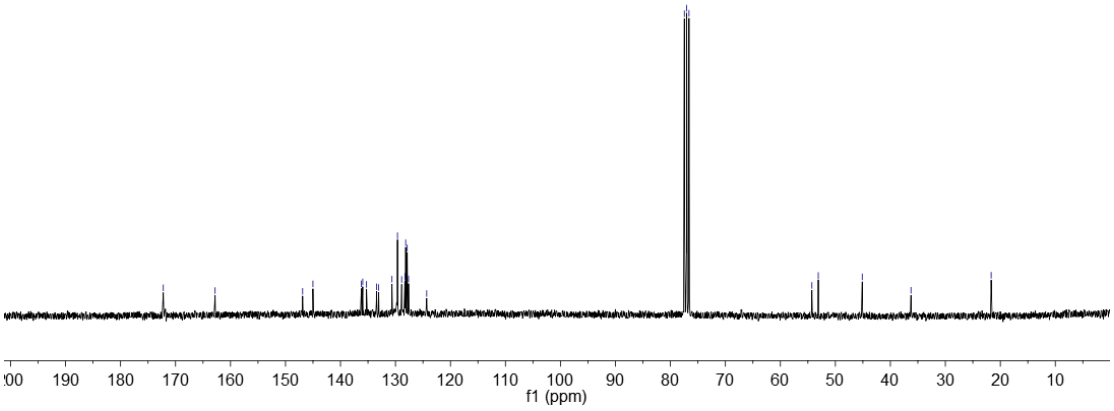
^{1}H NMR Spectrum of 4ag



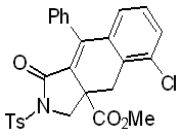


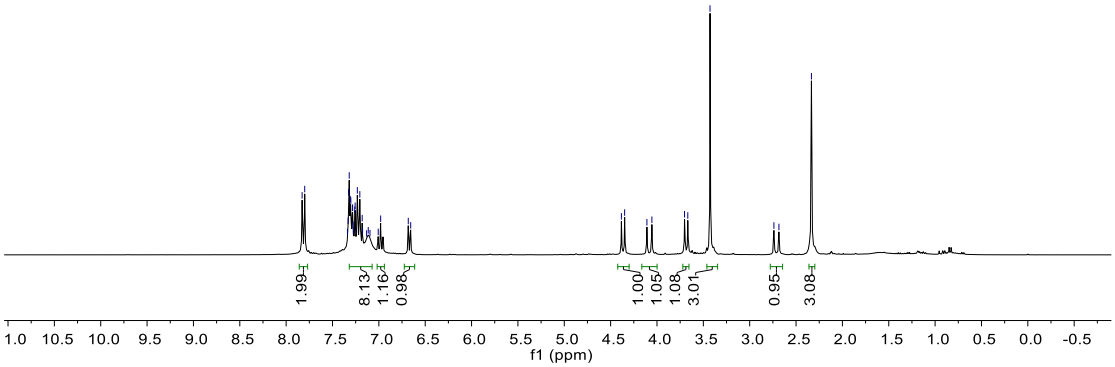
^{13}C NMR Spectrum of 4ag



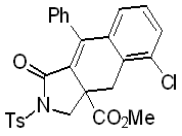


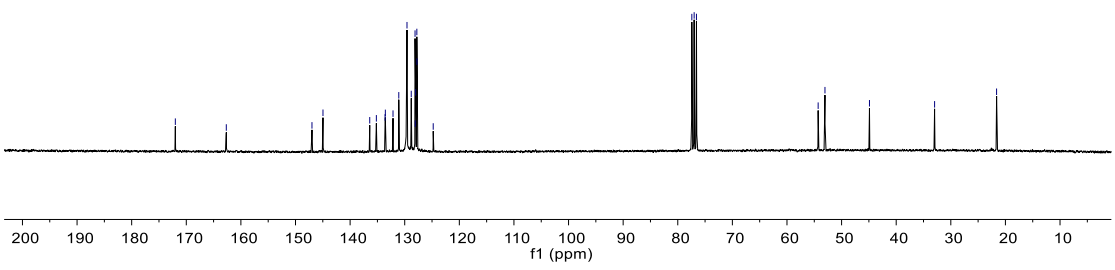
^{1}H NMR Spectrum of 4ah



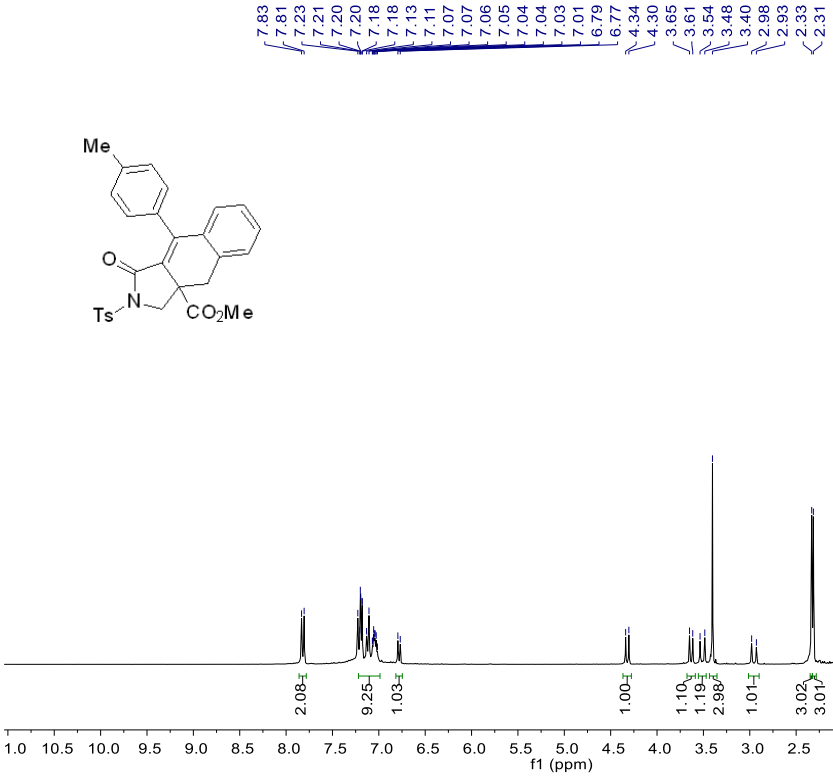


^{13}C NMR Spectrum of 4ah

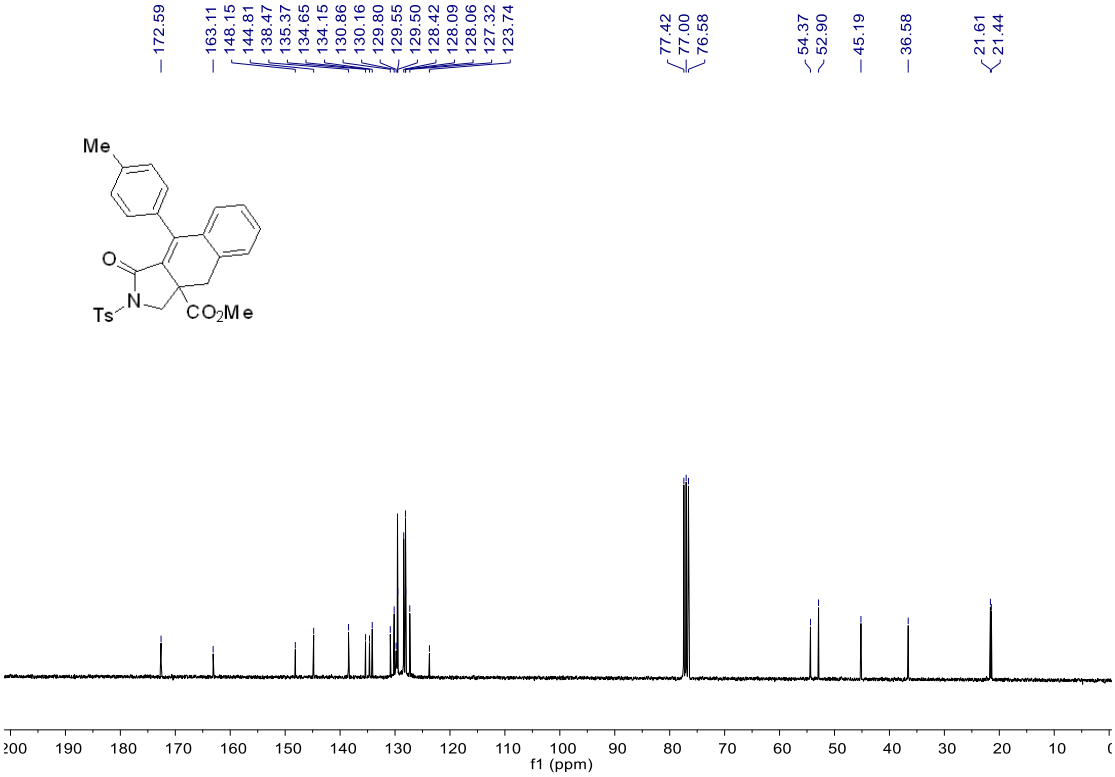




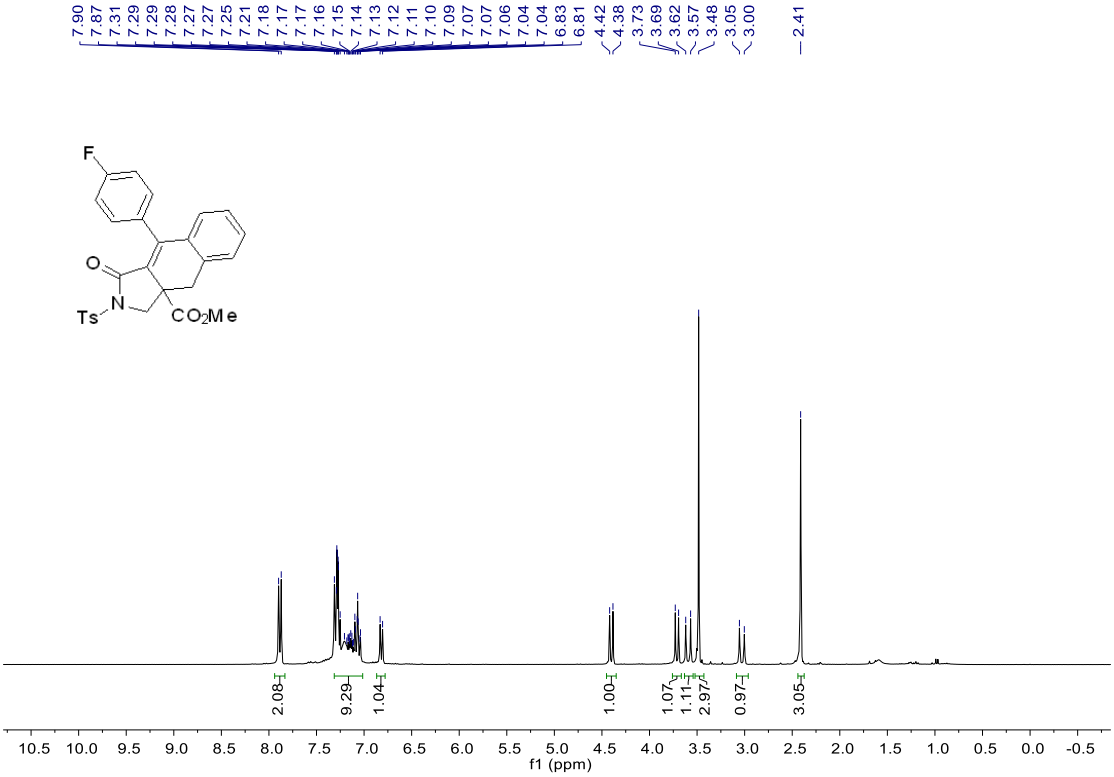
^{1}H NMR Spectrum of 4ba



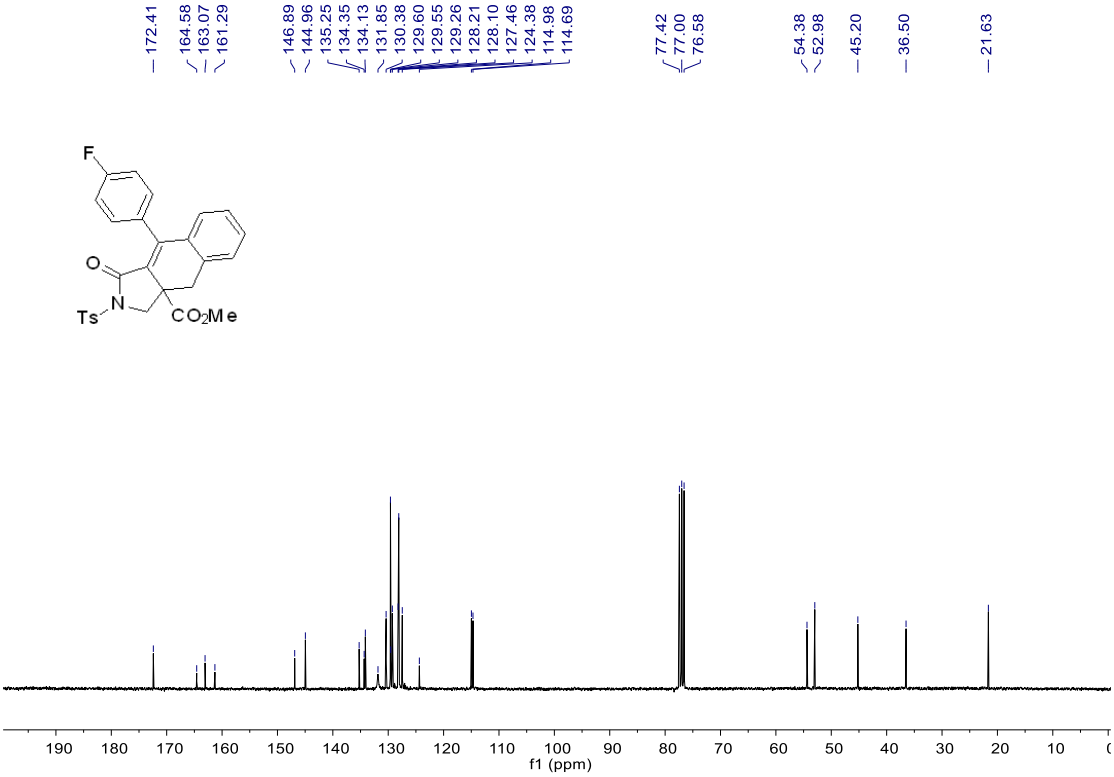
^{13}C NMR Spectrum of 4ba



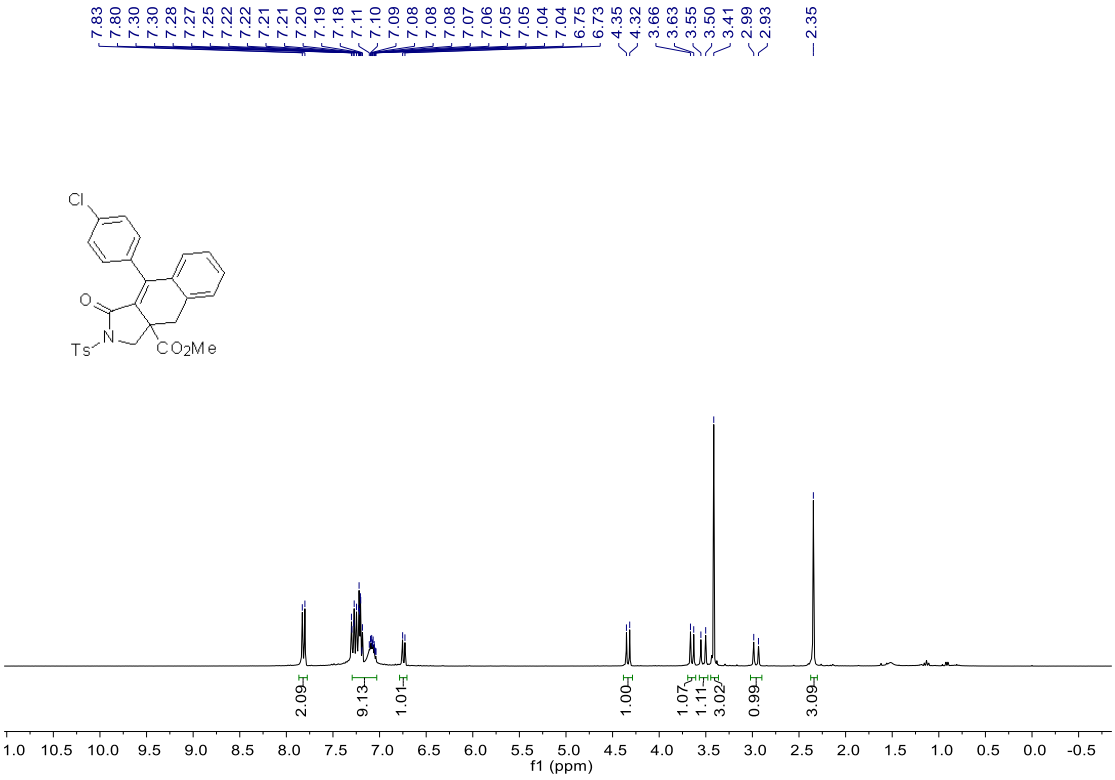
^{1}H NMR Spectrum of 4ca



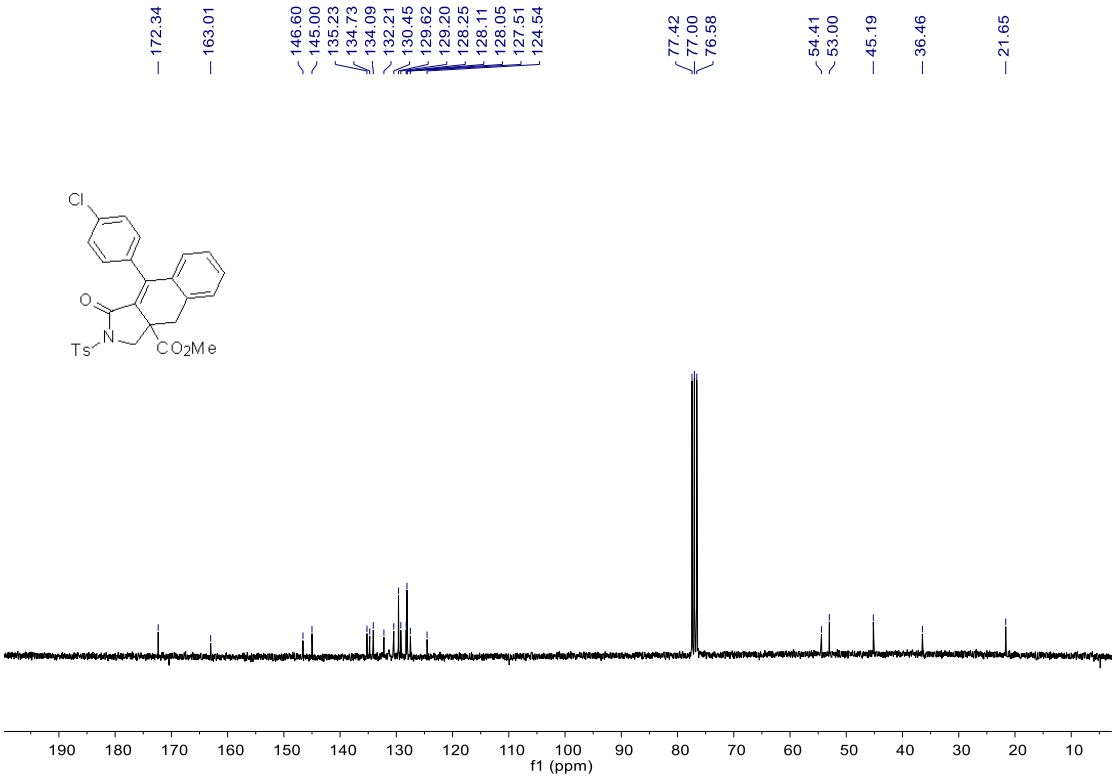
^{13}C NMR Spectrum of 4ca



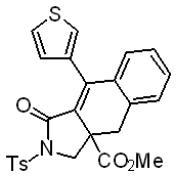
^{1}H NMR Spectrum of 4da

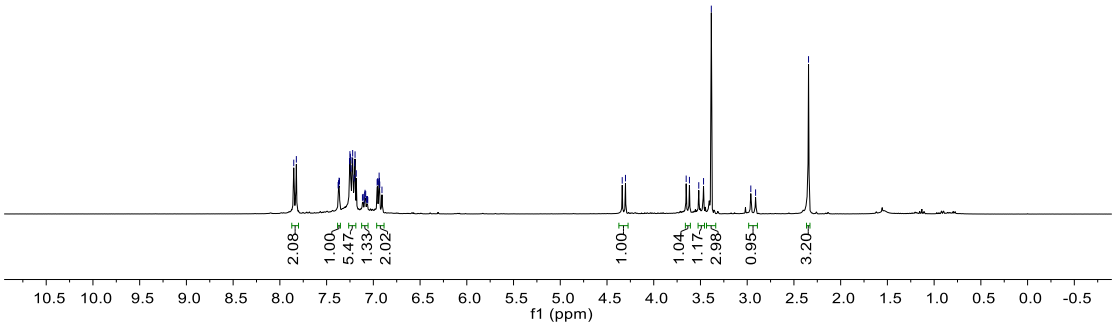


^{13}C NMR Spectrum of 4da

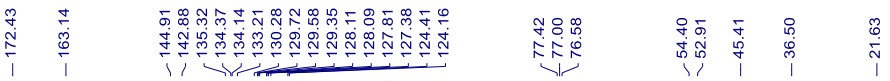


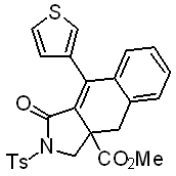
^{1}H NMR Spectrum of 4ea

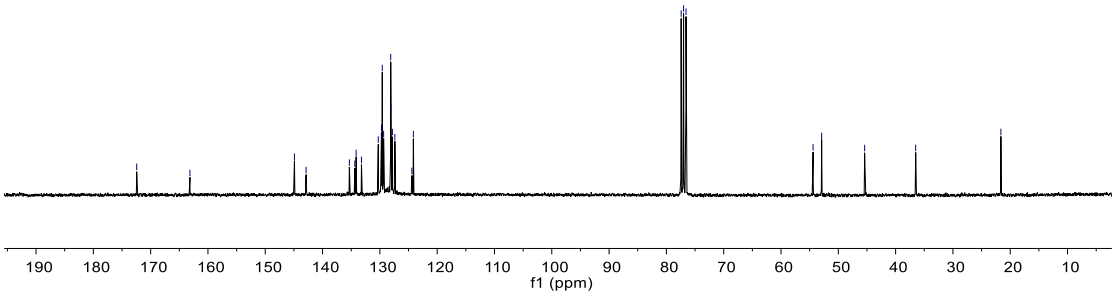




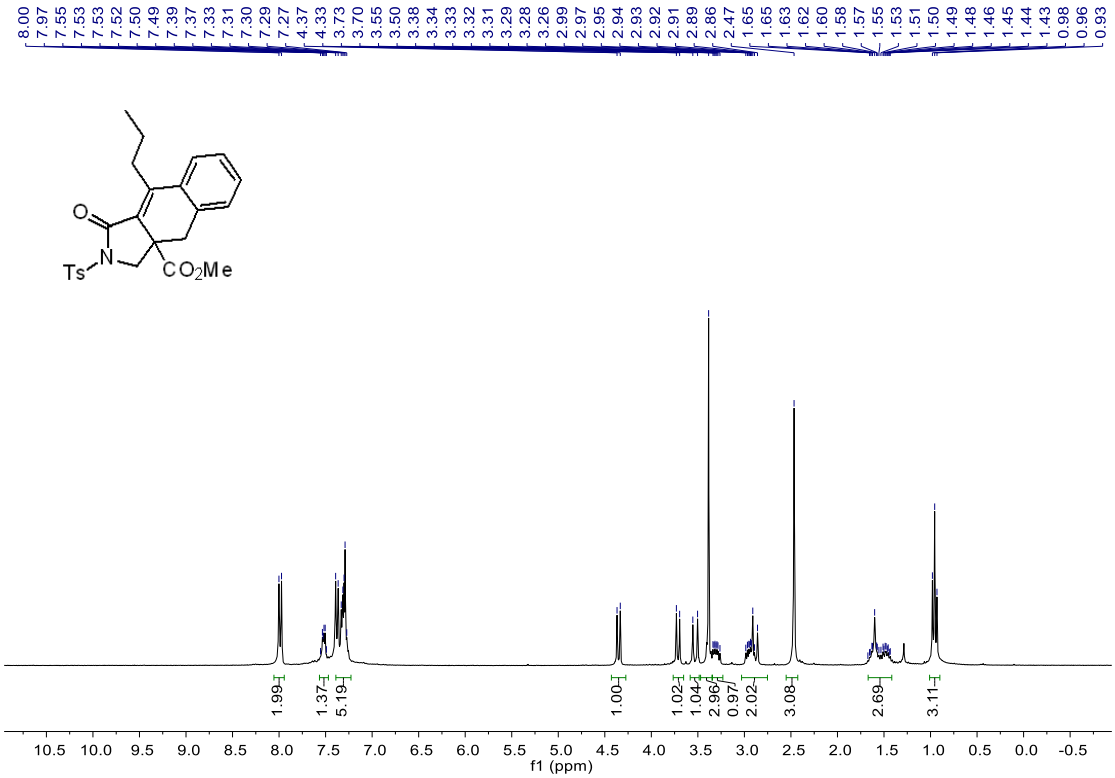
^{13}C NMR Spectrum of 4ea



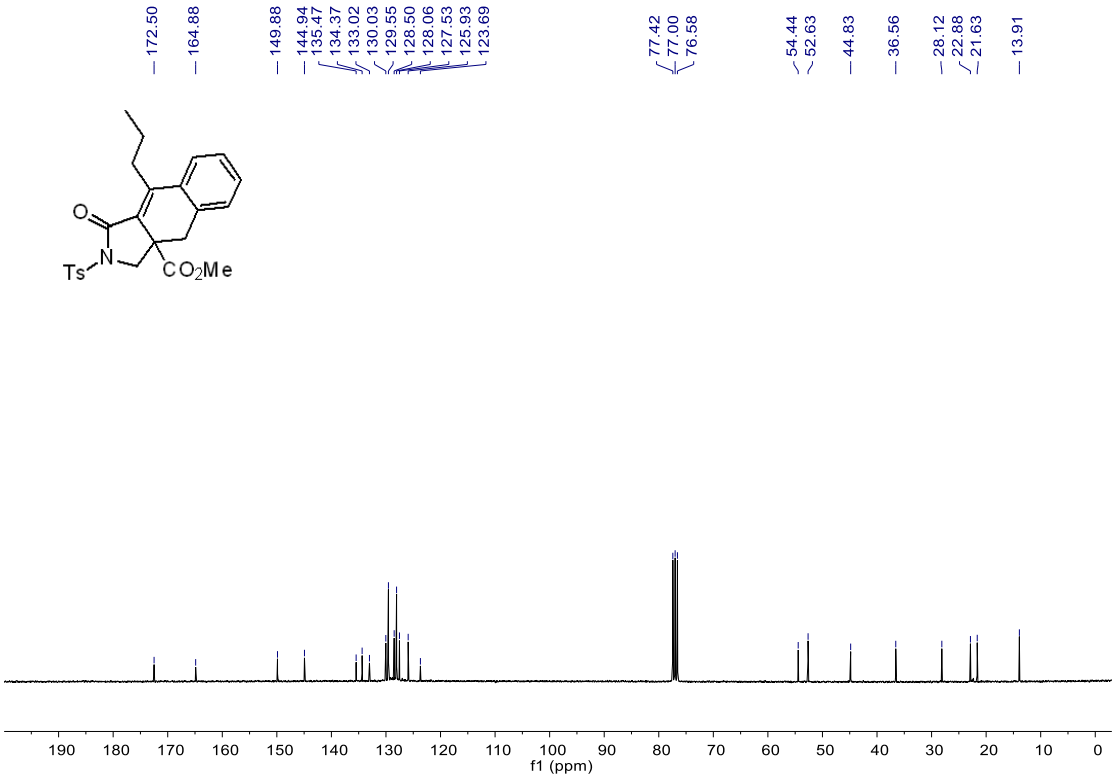




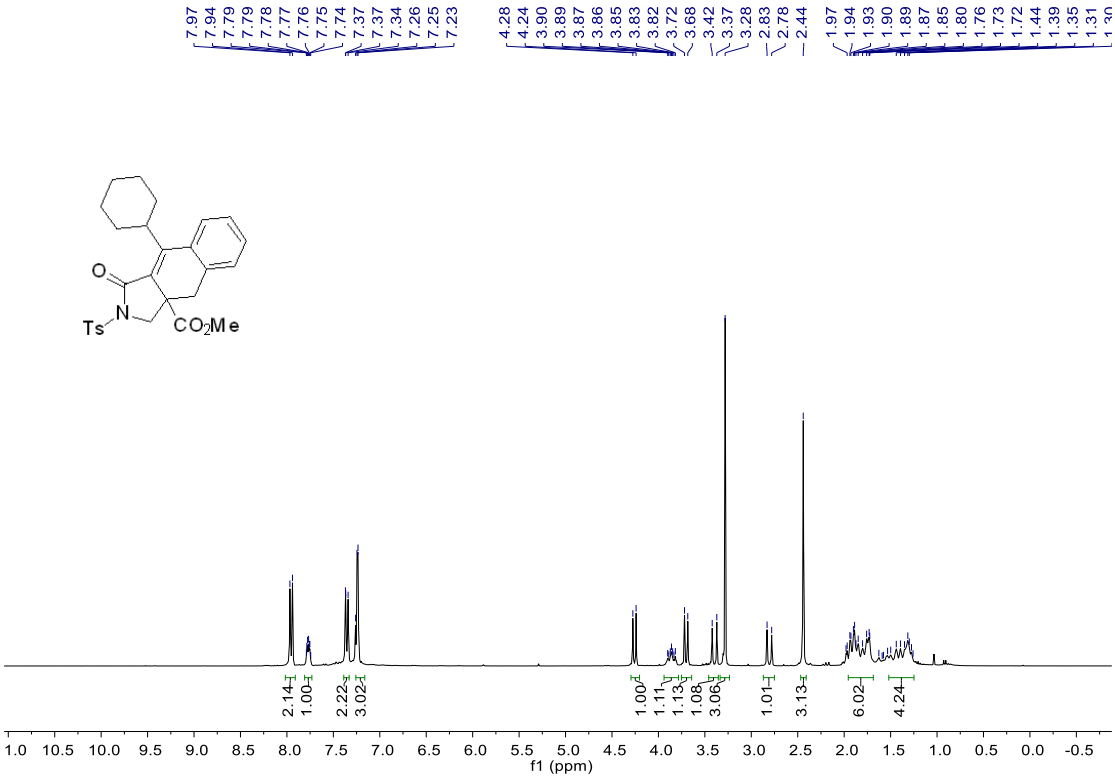
^{1}H NMR Spectrum of 4fa



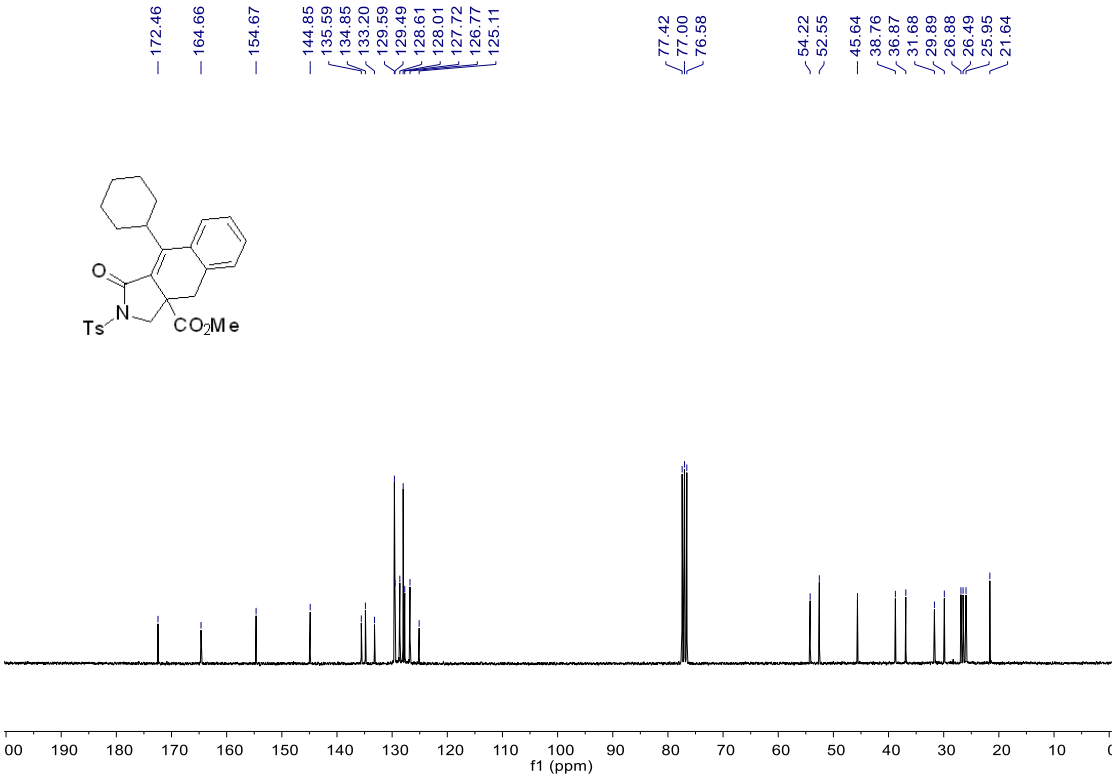
^{13}C NMR Spectrum of 4fa



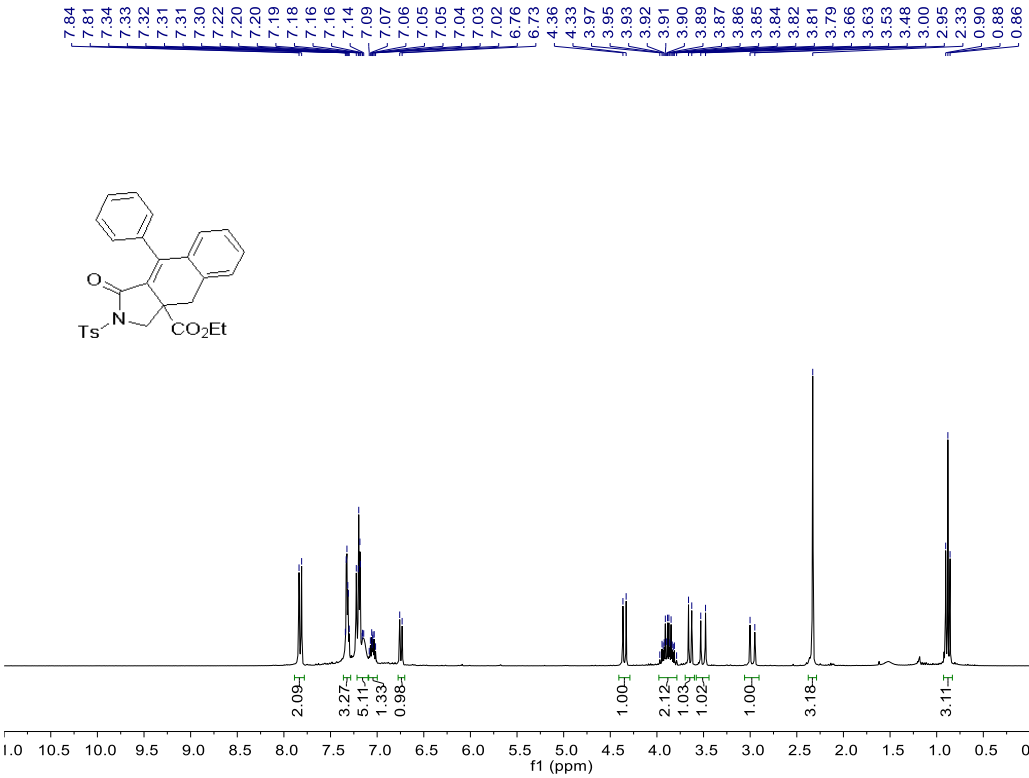
^{1}H NMR Spectrum of 4ga



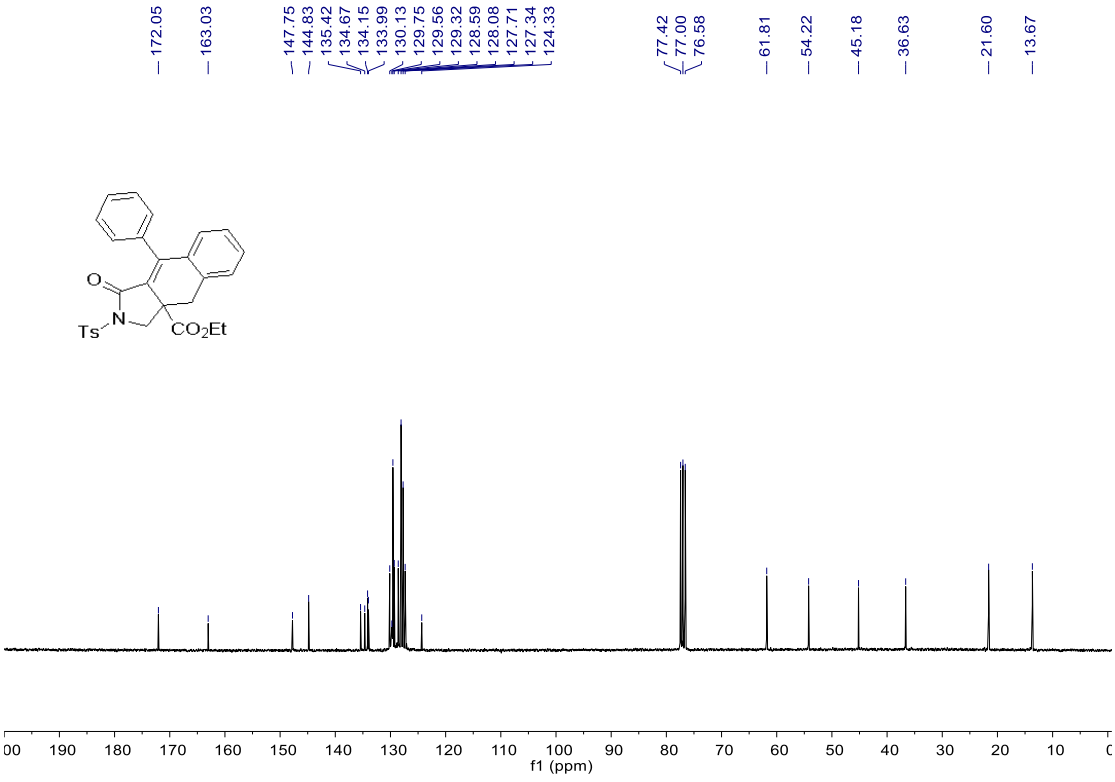
^{13}C NMR Spectrum of 4ga



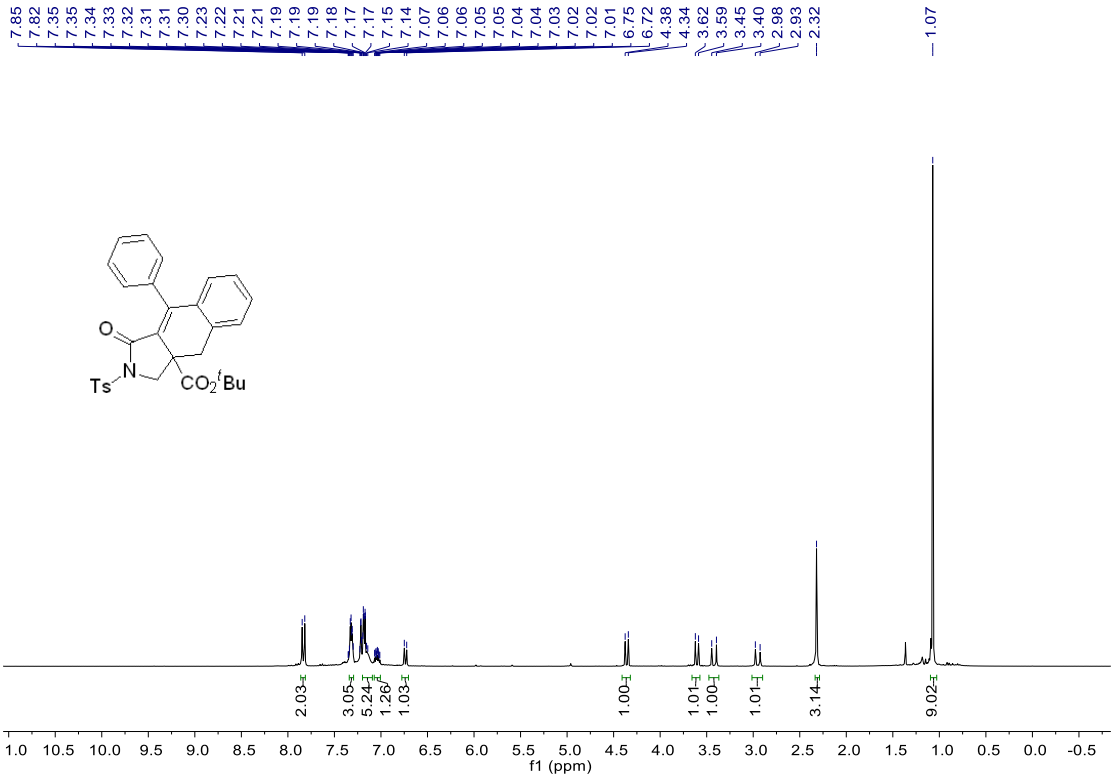
^{1}H NMR Spectrum of 4ha



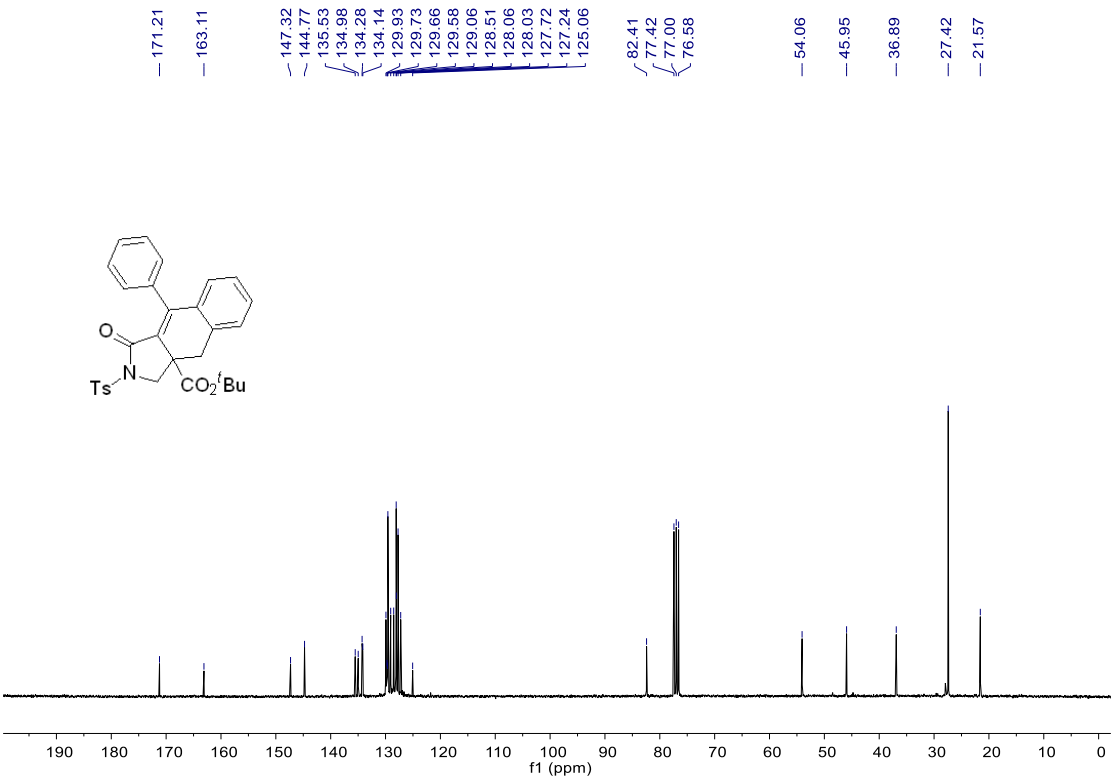
^{13}C NMR Spectrum of 4ha



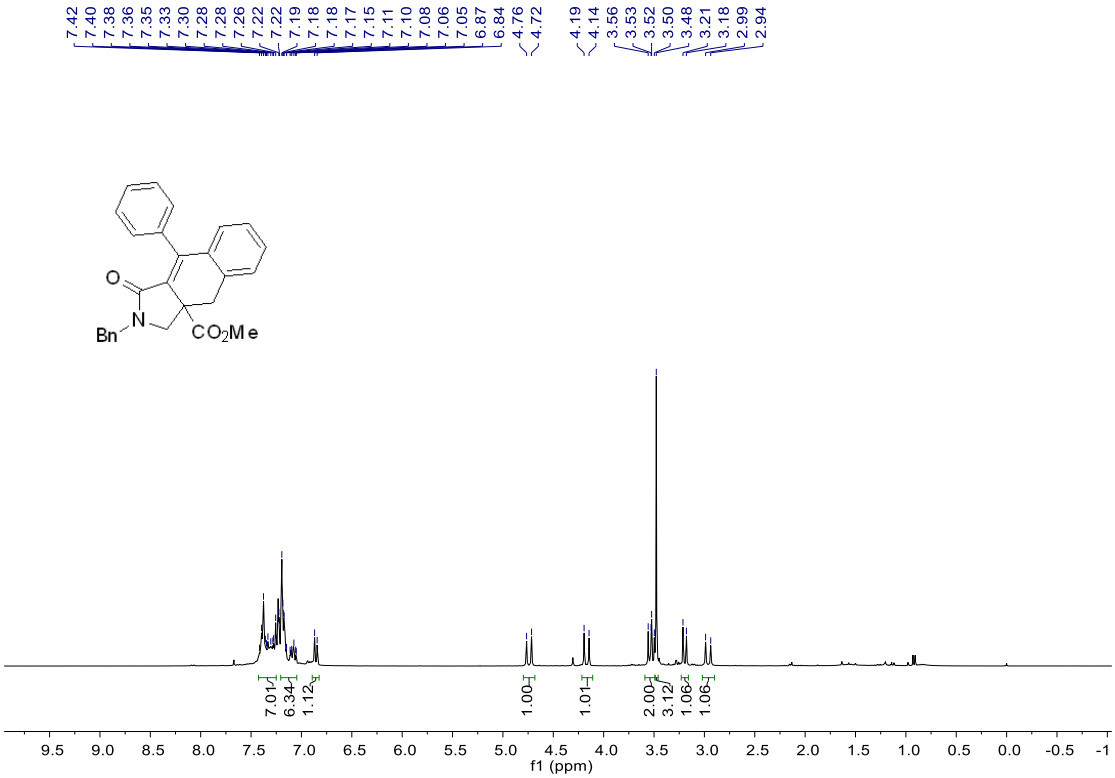
^{1}H NMR Spectrum of 4ia



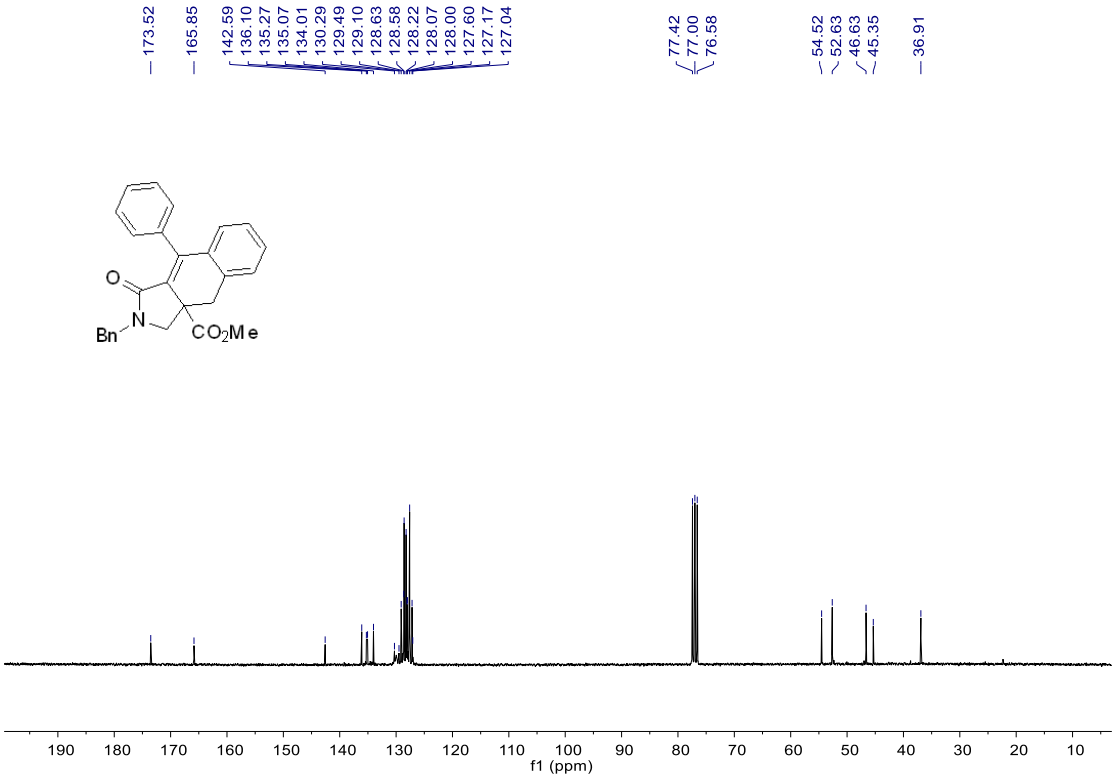
^{13}C NMR Spectrum of 4ia



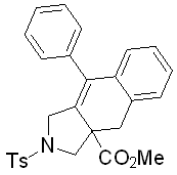
^{1}H NMR Spectrum of 4ja

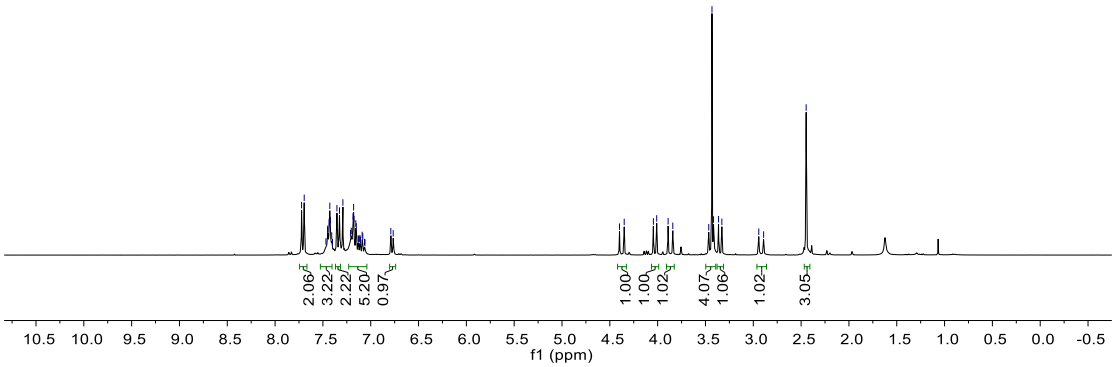


^{13}C NMR Spectrum of 4ja

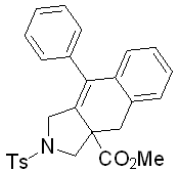


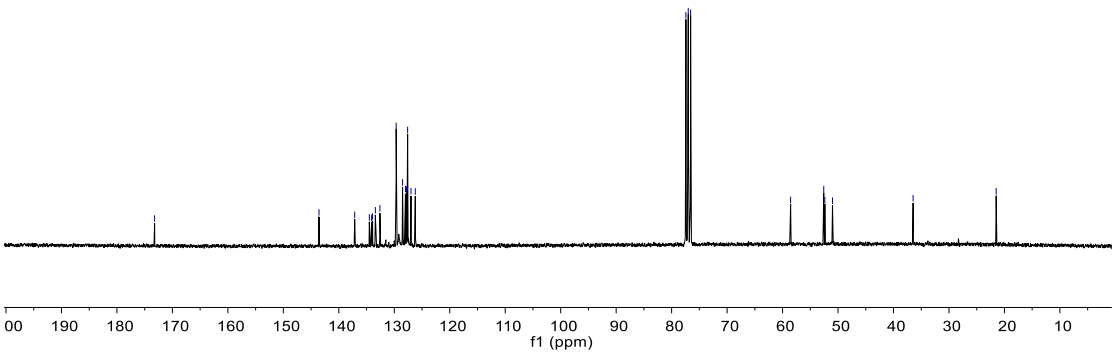
^{1}H NMR Spectrum of 4la



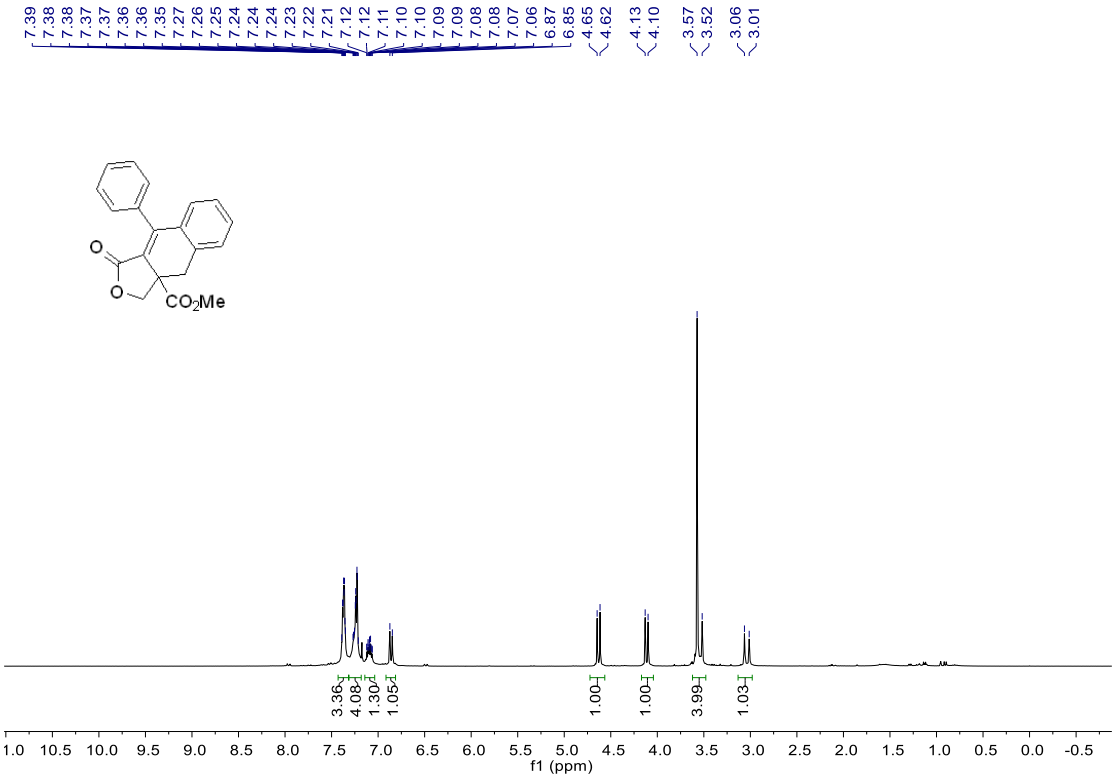


^{13}C NMR Spectrum of 4la

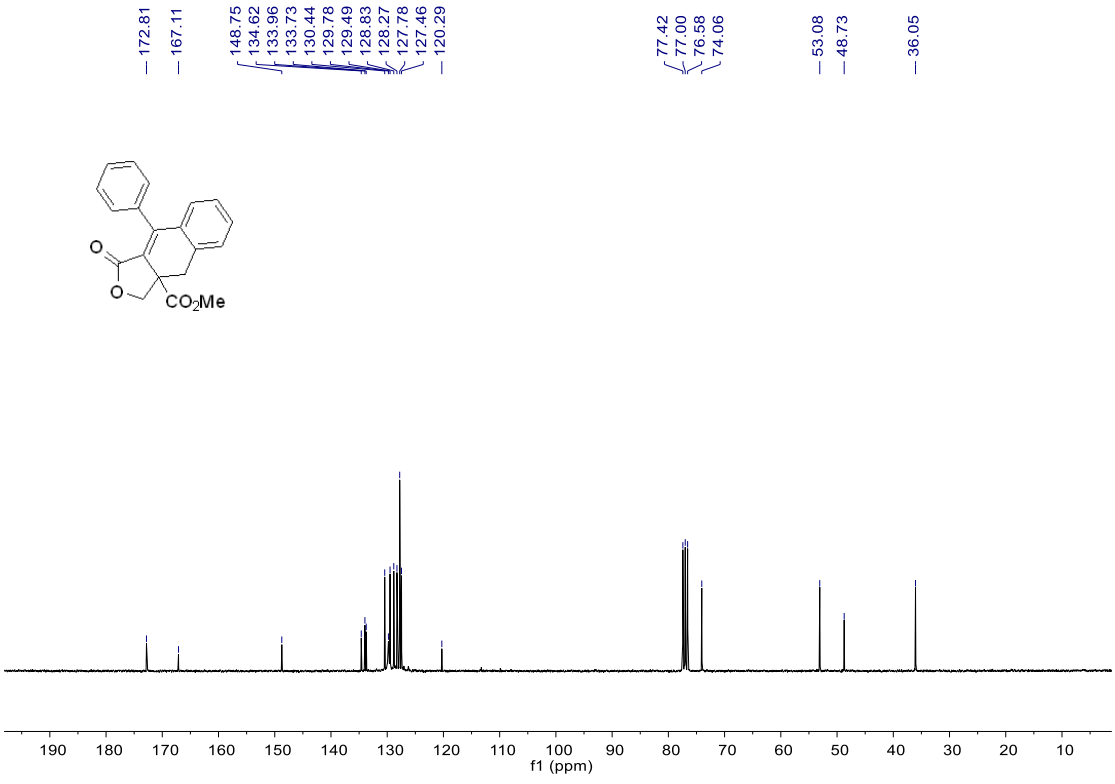




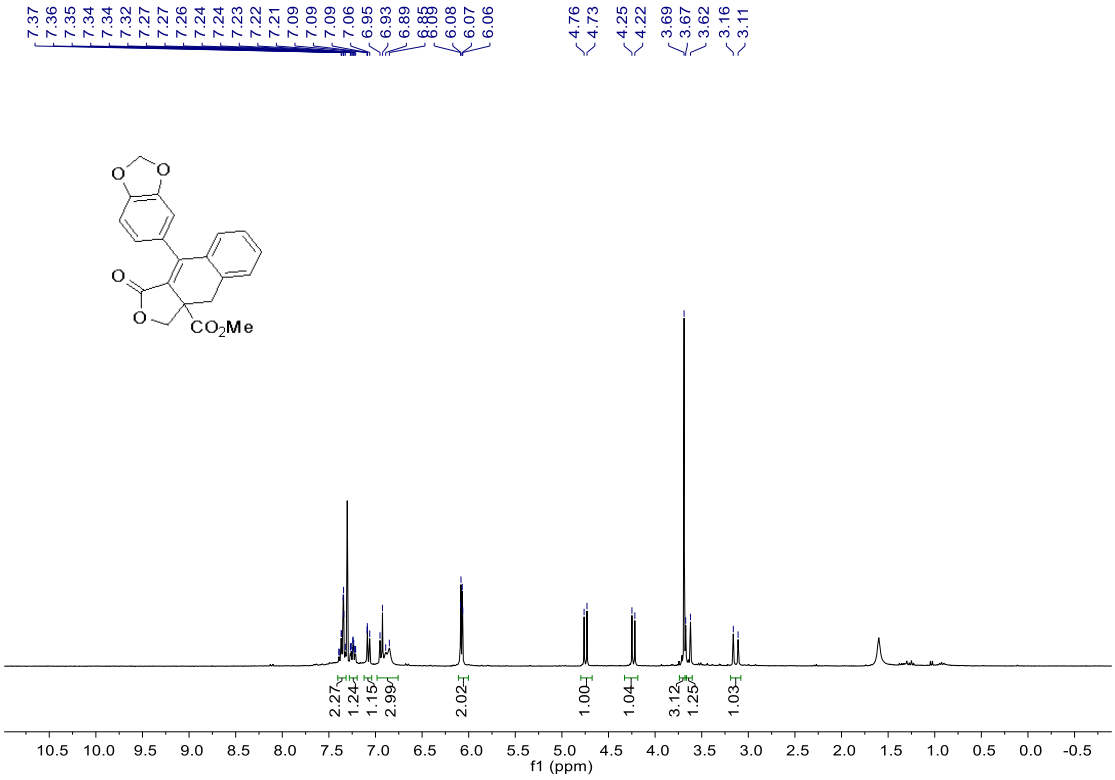
^{1}H NMR Spectrum of 6a



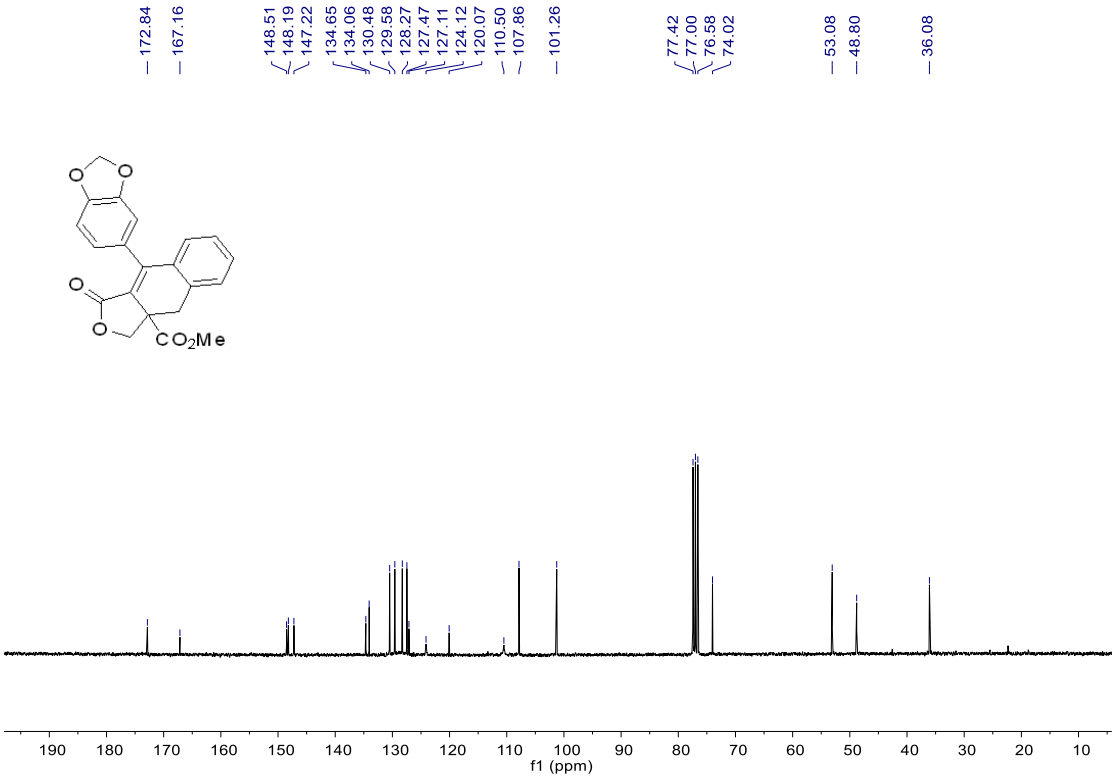
^{13}C NMR Spectrum of 6a



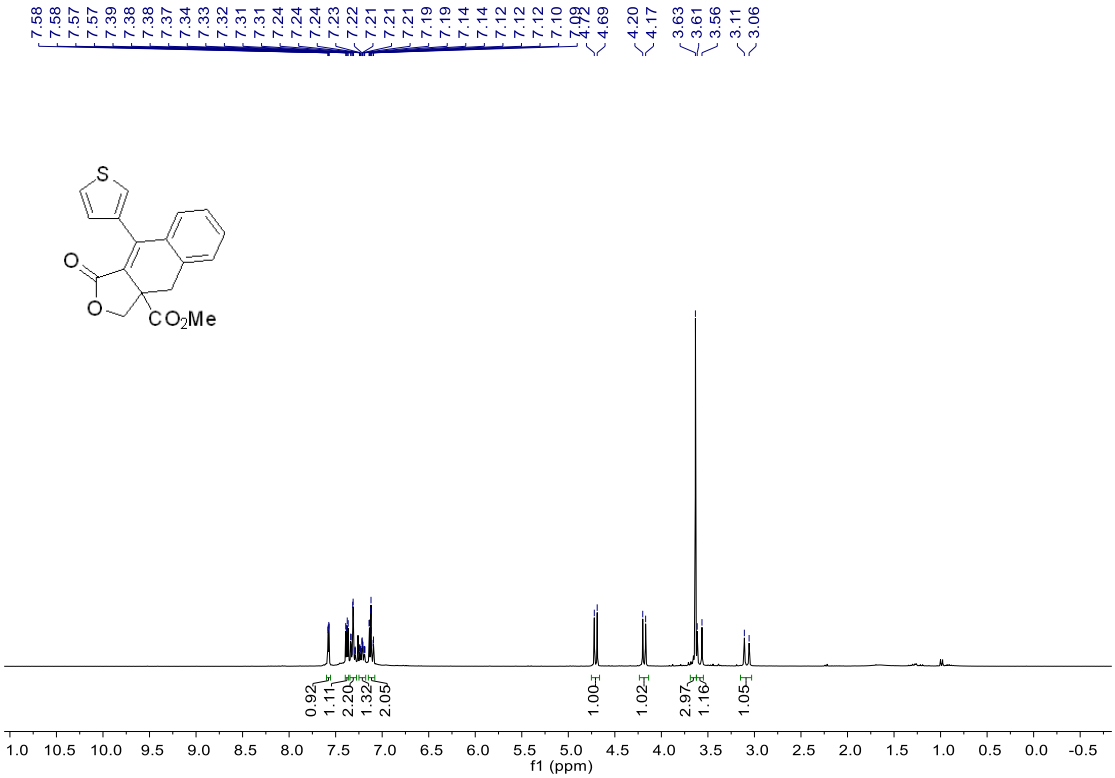
^{1}H NMR Spectrum of 6b



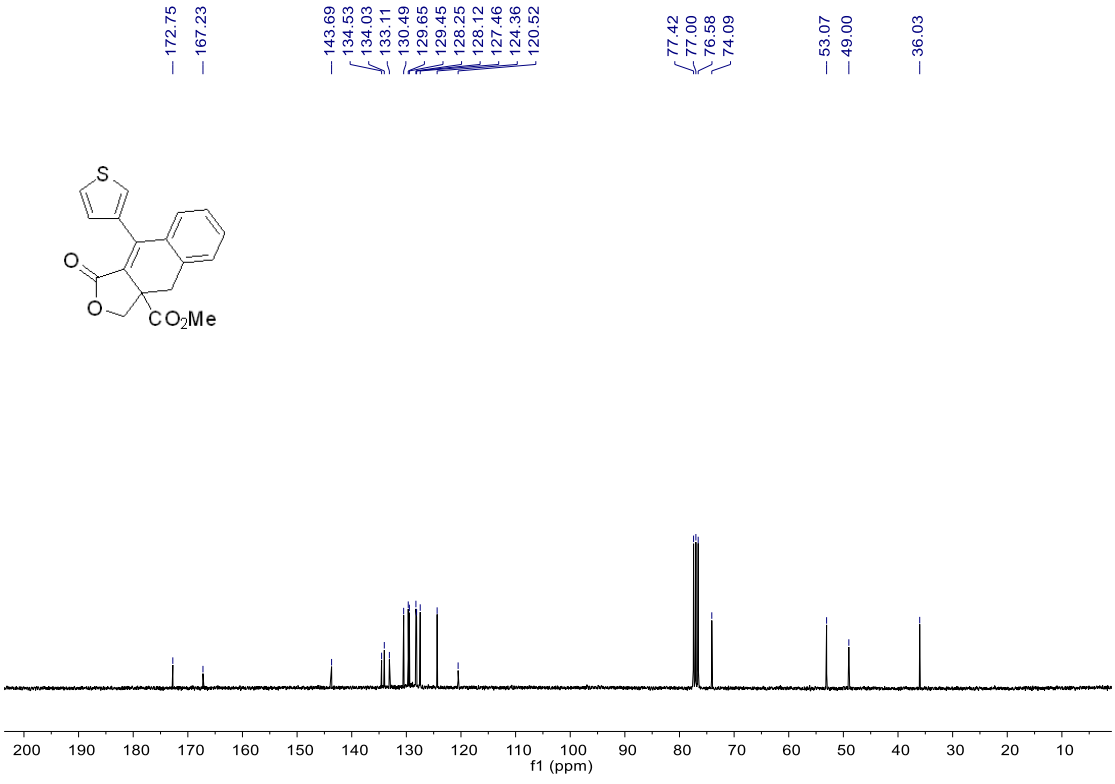
^{13}C NMR Spectrum of 6b



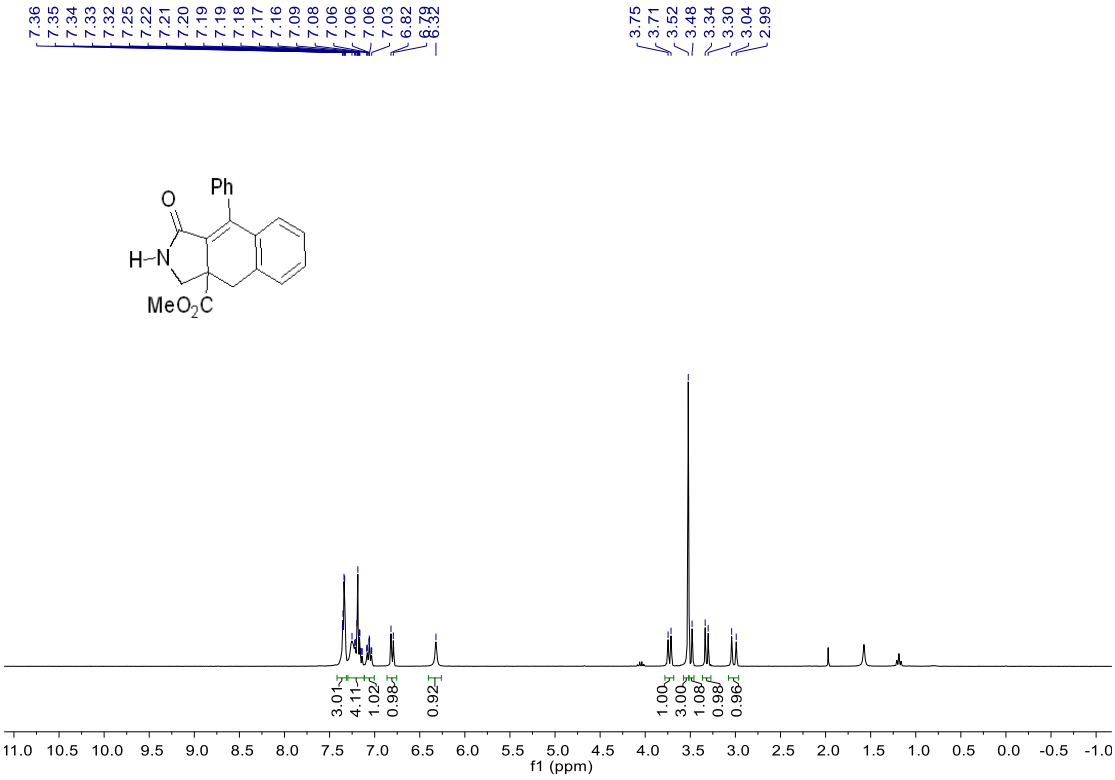
^{1}H NMR Spectrum of 6c



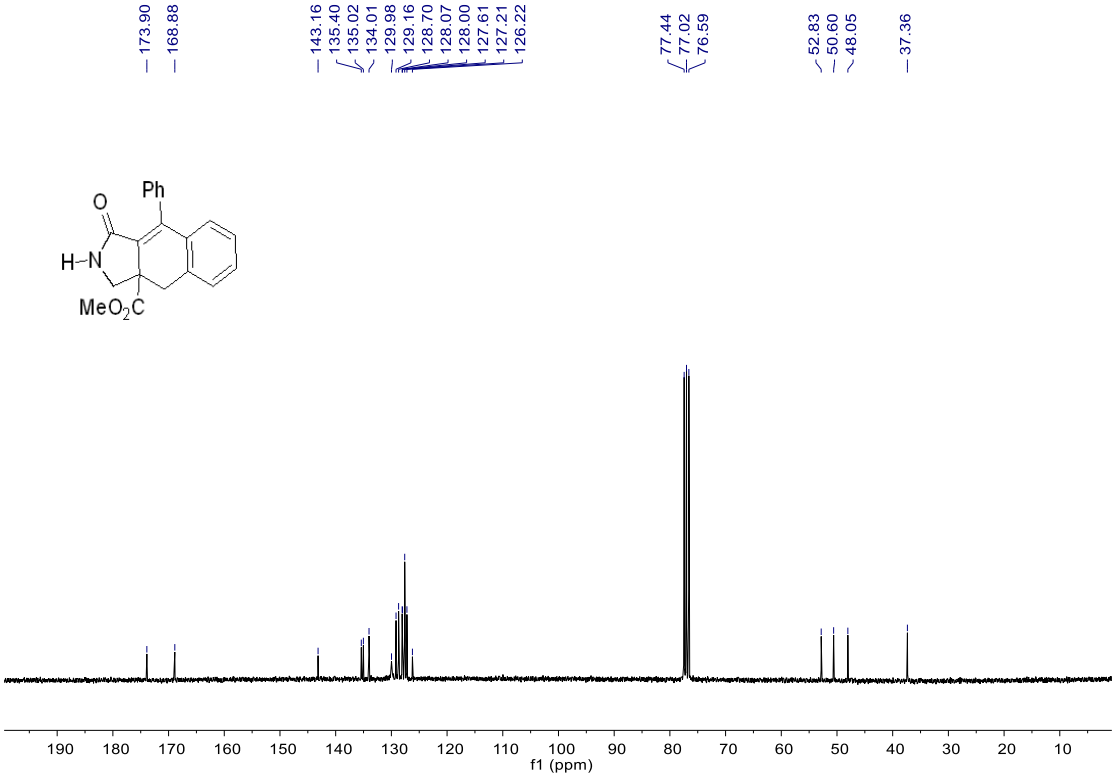
^{13}C NMR Spectrum of 6c



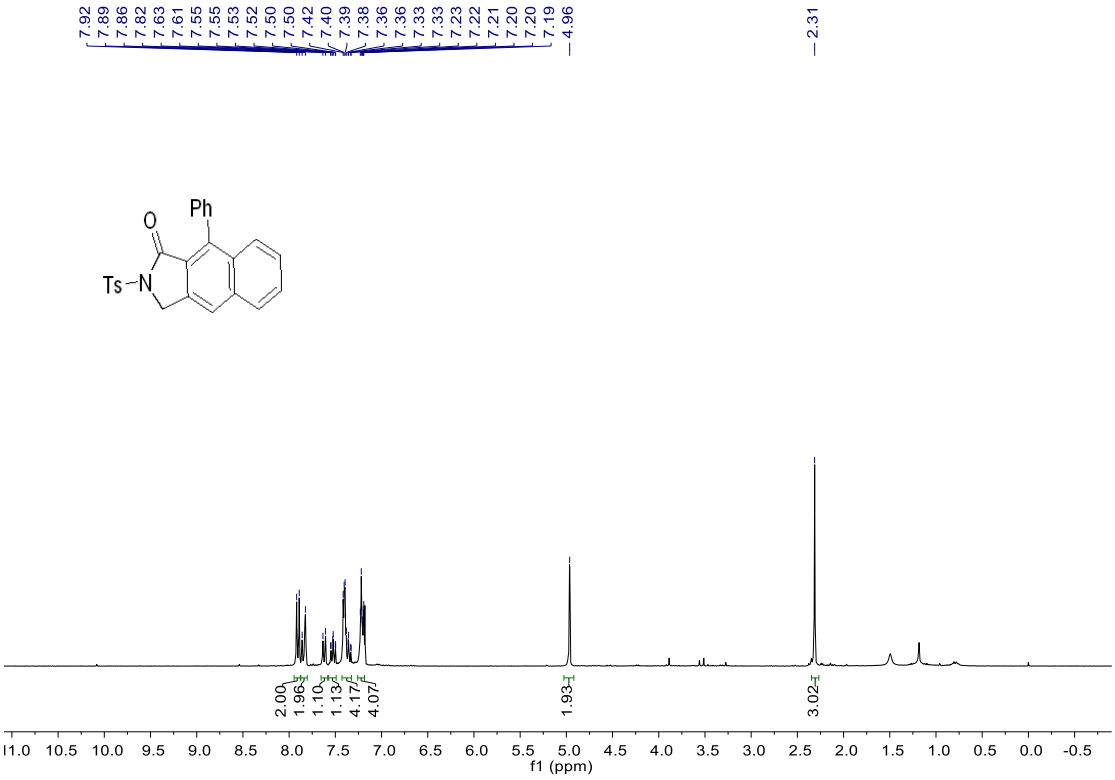
^{1}H NMR Spectrum of 7



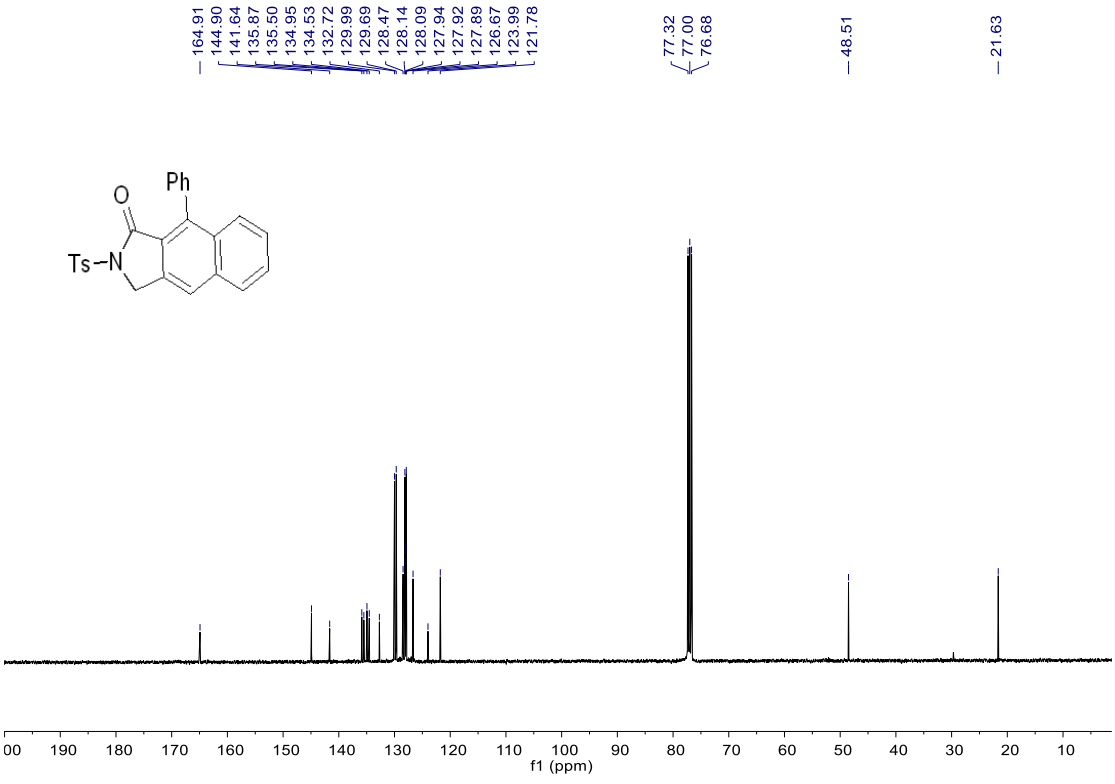
^{13}C NMR Spectrum of 7



^{1}H NMR Spectrum of 8



^{13}C NMR Spectrum of 8



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