Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary information

for

rhodium(I)-catalysed cycloisomerisation/6π electrocyclisation of 5-(ethynylamino)pent-2-yn-1-yl esters to dihydrobenzo[*f*]indoles

James Theodore Merrett,[a†] Xiaoyu Chen,[a†] Sara Helen Kyne,[a] Mandeep Harode[a] and Philip Wai Hong Chan*[a]

[a]School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

[†] These authors contributed equally to this work

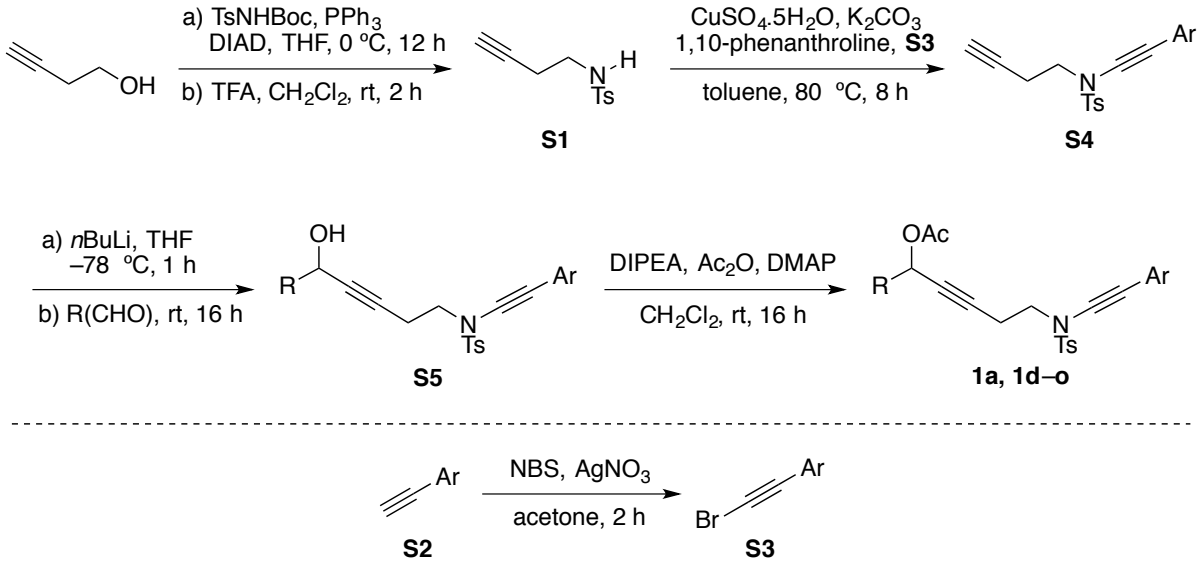
Email: phil.chan@monash.edu

Table of contents

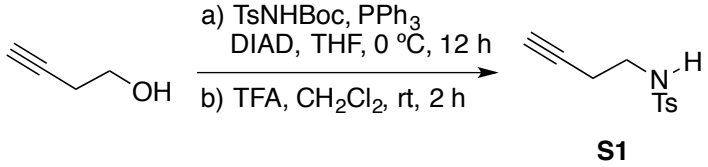
1. General information

Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. THF and toluene were dried using Na and dichloromethane was dried using CaH_2. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plates. Visualisation was achieved by UV light (254 nm) or stained with a vanillin solution. Flash column chromatography was performed using silica gel gradient solvent system (EtOAc:*n*hexane or EtOAc:petroleum benzine as eluent). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on either a 400 or 600 MHz spectrometer. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard with deuterochloroform ($CDCl_3$) as the solvent. Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hertz (Hz). Infrared spectra were recorded neat on a FT-IR spectrometer. High-resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF spectrometer using simultaneous electrospray (ESI). X-ray data was obtained on a single crystal X-ray diffractometer.

2. General procedure for the preparation of 1,6-diyne esters 1a and 1d–o



2.1 Procedure for the preparation of homopropargyl sulfonamide S1[S1]

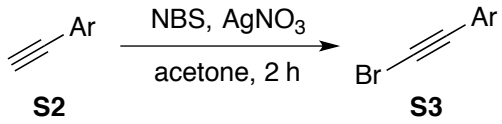


A solution of *N*-(*t*-butoxycarbonyl)-*N*-*p*-toluenesulfonamide (8.50 g, 31.2 mmol, 1.1 equiv), triphenylphosphine (8.20 g, 31.2 mmol, 1.1 equiv), and but-3-yn-1-ol (2.15 mL, 28.4 mmol, 1.0 equiv) in anhydrous THF (100 mL) was cooled to 0 °C. Diisopropyl azodicarboxylate (DIAD) (6.13 mL, 31.2 mmol, 1.1 equiv) was then added dropwise and the reaction was allowed to warm to room temperature and stir for 24 h. On completion, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (eluent: petroleum benzine:EtOAc = 9:1) to give *tert*-butyl but-3-yn-1-yl(tosyl)carbamate as a yellow solid (8.89 g, 97 % yield).

To a solution of *tert*-butyl but-3-yn-1-yl(tosyl)carbamate (27.5 mmol, 8.89 g, 1.0 equiv) in CH_2Cl_2 (90 mL) was added trifluoroacetic acid (123.8 mmol, 8.02 mL, 4.5 equiv) at room temperature and the resulting reaction mixture was stirred for 3 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (50 mL) solution until the aqueous phase was pH ~8. The

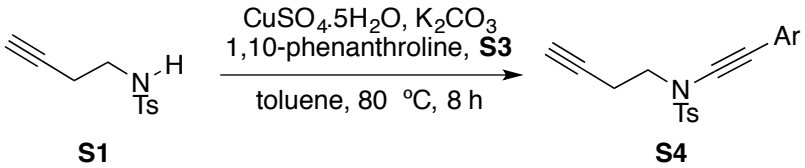
crude was extracted with CH_2Cl_2 (3 × 40 mL) and the combined organic layers were washed with brine (50 mL) and dried over anhydrous Na_2SO_4, concentrated *in vacuo* to give **S1** as a yellow solid (5.83 g, 95% yield) which was used in the next step without further purification.

2.2 General procedure for the preparation of bromoalkyne S3



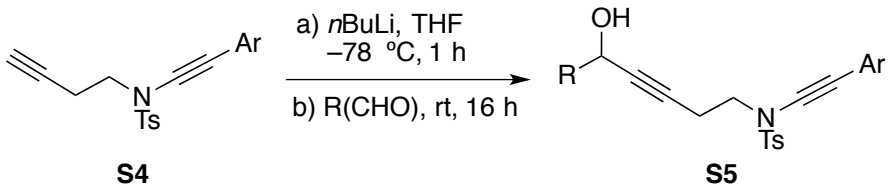
To a solution of alkyne (**S2**) (20 mmol, 1.0 equiv) in acetone (100 mL, 0.2 M) at room temperature was added *N*-bromosuccinimide (NBS, 24 mmol, 1.1 equiv) and $AgNO_3$ (2.0 mmol, 0.1 equiv) and the reaction mixture was stirred at room temperature for 2 h. On completion, the reaction mixture was concentrated and the crude product was extracted with *n*hexane (3 × 30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the bromoalkyne **S3** in 90–99% yield, which was then used for the next step without further purification.

2.3 General procedure for the preparation of diyne S4



To an oven-dried flask was added **S1** (17 mmol, 1.2 eq), $CuSO_4 \cdot 5H_2O$ (1.7 mmol, 0.1 equiv), 1,10-phenanthroline (3.4 mmol, 0.2 equiv) and K_2CO_3 (42.5 mmol, 2.5 eq), and this mixture was subsequently treated with anhydrous toluene (17 mL, 1.0 M) and **S3** (14.2 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was heated to 80 °C for 8 h. After completion, the crude reaction mixture was cooled to room temperature, filtered through Celite, and concentrated under reduced pressure. Purification of the crude residue by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc = 49:1 to 23:2) gave **S4** as a brown solid in 54–80% yield.

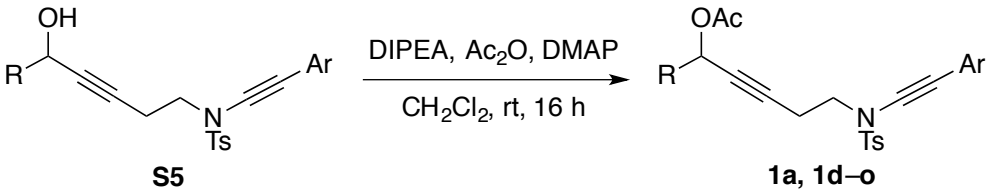
2.4 General procedure for the preparation of alcohol S5



S4 **S5**

A flame dried 50 mL round-bottom flask was charged with **S4** (3.0 mmol, 1.0 equiv) in anhydrous THF (15 mL, 0.2 M) and cooled to –78 °C under a nitrogen atmosphere. *n*BuLi (6 mmol, 2.0 equiv, 2.5 M in hexanes) was added dropwise and the reaction was stirred at –78 °C for 1 h. The corresponding aldehyde (9.0 mmol, 3.0 equiv) was added and the reaction was allowed to warm to room temperature and stirred for 16 h. Upon completion, the reaction was quenched with saturated aqueous NH_4Cl (10 mL) and the aqueous layer was extracted with EtOAc (3 × 10 mL). The organic layers were combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc = 9:1 to 4:1) to give the alcohol **S5** as an oil in 42–93% yield.

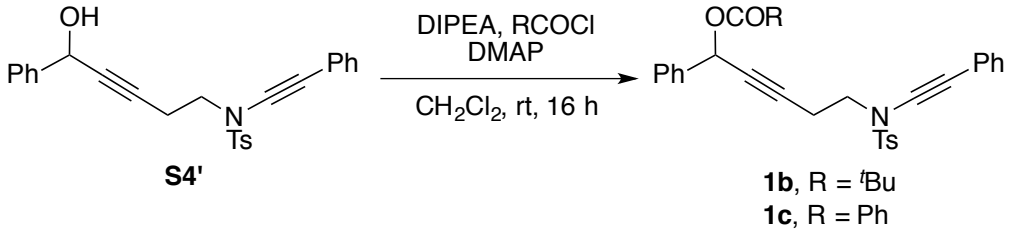
2.5 General procedure for the preparation of 1



S5 **1a, 1d–o**

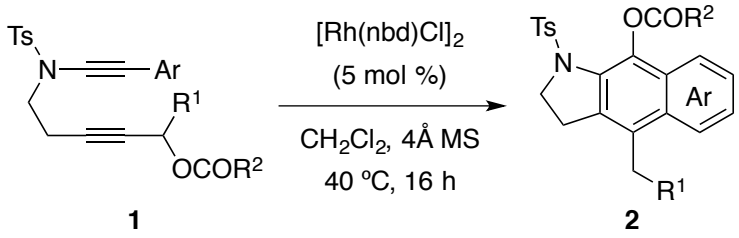
To a solution of alcohol **S4** (1.0 mmol, 1.0 eq) and DMAP (0.1 mmol, 0.1 eq) in anhydrous CH_2Cl_2 (5 mL, 0.2 M) was sequentially added DIPEA (5.0 mmol, 5.0 eq) and acetic anhydride (3.0 mmol, 3.0 eq) at room temperature. The reaction was stirred for 16 h and upon completion was quenched with NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic layers were combined and washed with brine, dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc = 20:1 to 6:1) to give **1** in 55–94% yield.

2.6 Preparation of substrates 1b and 1c



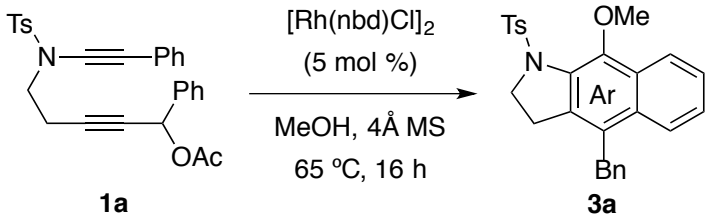
Substrates **1b** and **1c** were synthesised using the same procedure outlined in section 2.5. In lieu of the acetic anhydride, pivaloyl (**1b**) and benzoyl (**1c**) chloride were used, respectively.

3. Representative procedure for the Rh(I)-catalysed cycloisomerisation/6π electrocyclisation of 1



To a round-bottomed flask (10 mL) containing **1** (0.1 mmol), 4 Å MS (50 mg, 1:1 w/w), and $[Rh(nbd)_2Cl]_2$ (2.3 mg, 0.005 mmol, 5 mol %) was added freshly distilled dichloromethane (2 mL, 0.05 M) under a nitrogen atmosphere at room temperature. The reaction mixture was heated to 40 °C and stirred for 16 h. Upon completion, the crude reaction mixture was allowed to cool to room temperature, filtered through a pad of Celite with and washed with dichloromethane (3 × 1 mL). The filtrate was concentrated *in vacuo* and the resulting crude residue purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc = 20:1 to 9:1) to afford the desired product **2**.

4. Procedure for methoxy inserted dihydrobenzo[*f*]indole 3a

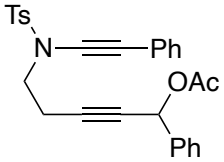


1a **3a**

To a round-bottomed flask (10 mL) containing **1a** (0.1 mmol), 4 Å MS (50 mg, 1:1 w/w), and $[Rh(nbd)_2Cl]_2$ (2.3 mg, 0.005 mmol, 5 mol %) was added methanol (2 mL, 0.05 M) under a nitrogen atmosphere at room temperature. The reaction mixture was heated to 65 °C and stirred for 16 h. Upon completion, the crude reaction mixture was allowed to cool to room temperature, filtered through a pad of Celite with and washed with dichloromethane (3 × 1 mL). The filtrate was concentrated *in vacuo* and the resulting crude residue purified by flash column chromatography on silica gel (eluent: *n*hexane:EtOAc = 10:1 to 4:1) to afford the desired product **3a**.

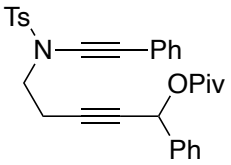
5. Analytical data

5-((4-Methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (1a)[S2]



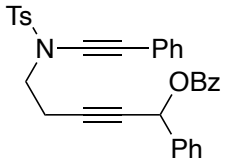
Yellow oil; 410 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 8.0 Hz, 2H), 7.50–7.48 (m, 2H), 7.35–7.28 (m, 10H), 6.40 (s, 1H), 3.61 (t, *J* = 7.7 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.9, 145.0, 137.1, 134.6, 131.6, 130.0, 129.0, 128.7, 128.4, 128.1, 127.8, 122.6, 83.3, 81.7, 79.2, 71.3, 65.9, 50.2, 21.8, 21.2, 19.0.

5-((4-Methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl pivalate (1b)



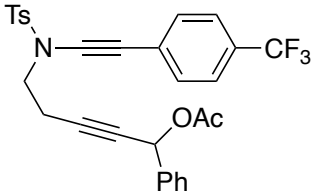
Pale yellow oil; 464 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): (ppm) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.50–7.48 (m, 2H), 7.38–7.28 (m, 10H), 6.42 (t, *J* = 1.8 Hz, 1H), 3.62 (t, *J* = 7.7 Hz, 2H), 2.71 (td, *J* = 8.1, 1.8 Hz, 2H), 2.44 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 177.2, 144.9, 137.4, 134.5, 131.5, 129.9, 128.6, 128.6, 128.3, 128.0, 127.7, 127.3, 122.6, 82.9, 81.7, 79.3, 71.2, 65.5, 50.1, 38.8, 27.0, 21.7, 19.0. IR (ATR, neat) ν (cm^{-1}): 2971, 2873, 2233, 1728, 1597, 1493, 1479, 1458, 1397, 1365, 1271, 1168, 1132, 1091, 1029, 963, 903, 813, 753, 692, 676, 656. HRMS (ESI) $[M + H]^+$ calc. for $C_{31}H_{32}NO_4S$: 514.2052, found: 514.2073.

5-((4-Methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl benzoate (1c)



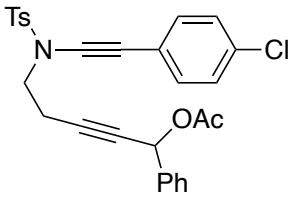
Yellow oil; 416 mg, 82% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.08 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.61–7.60 (m, 2H), 7.58–7.55 (m, 1H) 7.44–7.33 (m, 9H), 7.30–7.27 (m, 3H), 6.68 (t, *J* = 1.8 Hz, 1H), 3.65 (t, *J* = 7.7 Hz, 2H), 2.75–2.72 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 165.5, 144.9, 137.2, 134.5, 133.3, 131.5, 130.6, 130.2, 129.9, 129.8, 129.6, 129.3, 129.2, 128.9, 128.7, 128.7, 128.5, 128.4, 128.3, 128.0, 127.7, 122.6, 83.5, 81.7, 79.1, 71.2, 66.3, 50.1, 21.7, 19.0. IR (ATR, neat) ν (cm^{-1}): 3061, 2925, 2234, 1719, 1598, 1493, 1451, 1365, 1317, 1249, 1168, 1091, 1069, 1026, 964, 940, 901, 813, 754, 737, 692, 675 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{33}H_{28}NO_4S$: 534.1739, found: 534.1703.

5-((4-Methyl-*N*-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (1d)[S2]



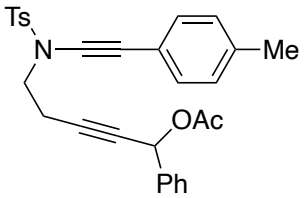
Yellow oil; 536 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 8.3 Hz, 2H), 7.52–7.48 (m, 4H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.35–7.32 (m, 5H), 6.42 (t, *J* = 1.8 Hz, 1H), 3.65 (t, *J* = 7.5 Hz, 2H), 2.72 (td, *J* = 7.4, 1.9 Hz, 2H), 2.42 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$), $CDCl_3$): δ (ppm) 169.8, 145.2, 137.0, 134.5, 131.1, 130.0, 129.4 (d, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 128.9, 128.7, 127.7, 126.7, 125.4, 125.2 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 122.7, 84.4, 83.1, 79.3, 70.5, 65.7, 50.1, 21.7, 21.0, 19.1.

5-((*N*-((4-Chlorophenyl)ethynyl)-4-methylphenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (1e)[S2]



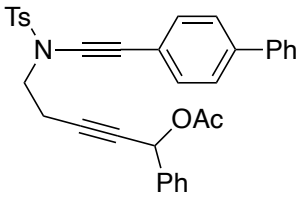
Bright orange oil; 416 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 (d, *J* = 8.3 Hz, 2H), 7.34–7.32 (m, 2H), 7.21–7.16 (m, 5H), 7.11–7.06 (m, 4H), 6.25 (s, 1H), 3.45 (t, *J* = 7.6 Hz, 2H), 2.53 (td, *J* = 7.5, 1.8 Hz, 2H), 2.27 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 145.0, 137.0, 134.5, 133.9, 132.6, 129.9, 128.9, 128.6, 128.6, 127.7, 127.6, 121.1, 83.2, 82.7, 79.2, 70.2, 65.7, 50.0, 21.7, 21.1, 19.0.

5-((4-Methyl-*N*-(*p*-tolylethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (1f)[S2]



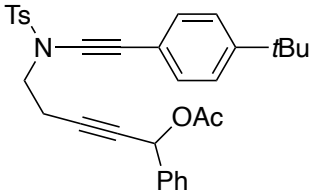
Yellow oil; 327 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, *J* = 8.0 Hz, 2H), 7.40–7.38 (m, 2H), 7.25–7.21 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.31 (s, 1H), 3.50 (t, *J* = 7.6 Hz, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 2.22 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.8, 144.8, 138.2, 137.1, 134.5, 131.6, 129.9, 129.1, 128.9, 128.6, 127.7, 127.7, 119.4, 83.3, 81.0, 79.1, 71.2, 65.7, 50.1, 21.7, 21.5, 21.1, 18.9.

5-((*N*-([1,1'-Biphenyl]-4-ylethynyl)-4-methylphenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (1g)[S2]



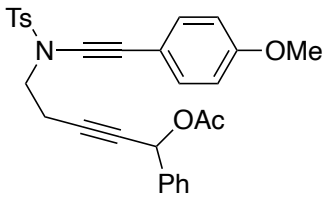
Yellow solid; 157 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.56–7.52 (m, 4H), 7.48–7.44 (m, 4H), 7.41–7.36 (m, 6H), 6.46 (s, 1H), 3.66 (t, *J* = 7.6 Hz, 2H), 2.77–2.73 (m, 2H), 2.46 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.8, 144.9, 140.7, 140.3, 137.1, 134.5, 131.9, 129.9, 128.9, 128.9, 128.7, 127.7, 127.7, 127.0, 121.5, 83.3, 82.4, 79.1, 71.1, 65.7, 50.1, 21.7, 21.1, 19.0.

5-((*N*-((4-(*tert*-Butyl)phenyl)ethynyl)-4-methylphenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (1h)[S2]



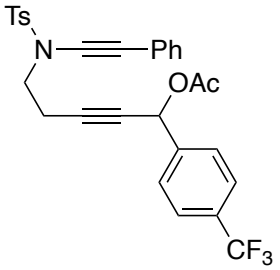
Yellow oil; 252 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (d, *J* = 8.3 Hz, 2H), 7.53–7.51 (m, 2H), 7.38–7.33 (m, 9H), 6.45 (s, 1H), 3.63 (t, *J* = 7.6 Hz, 2H), 2.72 (td, *J* = 8.5, 1.8 Hz), 2.44 (s, 3H), 2.08 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 151.3, 144.8, 137.0, 134.5, 131.4, 129.8, 128.8, 128.6, 127.7, 127.7, 125.3, 119.4, 83.3, 81.0, 79.0, 71.1, 65.6, 50.1, 34.7, 31.1, 21.6, 21.0, 18.9.

5-((*N*-((4-Methoxyphenyl)ethynyl)-4-methylphenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (1i)



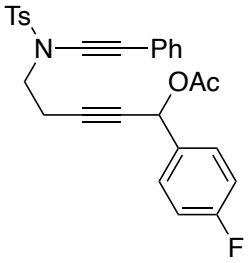
Yellow/orange oil; 376 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, J = 8.3 Hz, 2H), 7.52–7.50 (m, 2H), 7.36–7.29 (m, 7H), 6.82 (d, J = 8.8 Hz, 2H), 6.43 (s, 1H), 3.78 (s, 3H), 3.61 (t, J = 7.4 Hz, 2H), 2.73–2.68 (m, 2H), 2.43 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 159.6, 144.8, 137.0, 134.5, 133.5, 129.8, 128.8, 128.6, 127.7, 127.6, 114.3, 113.9, 83.4, 80.2, 79.0, 70.8, 65.6, 55.2, 50.1, 21.6, 21.0, 18.8. IR (ATR, neat) ν (cm^{-1}): 2935, 2838, 2235, 1737, 1605, 1512, 1457, 1364, 1288, 1247, 1223, 1167, 1091, 1017, 957, 899, 832, 812, 732, 698, 664 cm^{-1}; HRMS (ESI) $[M + H]^+$ calc. for $C_{29}H_{28}NO_5S$: 502.1688, found: 502.1677.

5-((4-Methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-(4-(trifluoromethyl)phenyl)pent-2-yn-1-yl acetate (1j)[S2]



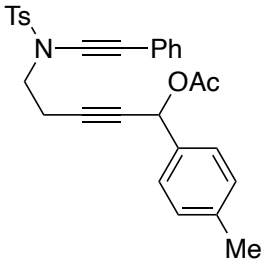
Orange oil; 318 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (d, J = 8.2 Hz, 2H), 7.63–7.58 (m, 4H), 7.36–7.27 (m, 7H), 6.45 (s, 1H), 3.62 (t, J = 7.4 Hz, 2H), 2.74–2.71 (m, 2H), 2.44 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 145.0, 141.0, 134.5, 131.5, 131.1, 130.8 (d, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 130.5, 128.4, 128.1, 128.1, 127.8, 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 122.5, 84.2, 81.8, 78.5, 71.3, 65.0, 50.1, 21.7, 21.0, 19.1.

1-(4-Fluorophenyl)-5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)pent-2-yn-1-yl acetate (1k)



Yellow oil; 383 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 8.3 Hz, 2H), 7.50–7.47 (m, 2H), 7.35–7.27 (m, 7H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.39 (s, 1H), 3.62 (t, *J* = 7.5 Hz, 2H), 2.74–2.69 (m, 2H), 2.43 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 162.9 (d $^{1}J_{C\text{-}F}$ = 247.9 Hz), 144.9, 134.5, 133.0 (d, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 131.4, 129.9, 129.8, 129.7, 128.3, 128.0, 127.7, 122.5, 115.5 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 83.6, 81.7, 78.9, 71.2, 65.0, 70.1, 21.6, 21.0, 19.0. ^{19}F NMR (376.5 MHz, $CDCl_3$) δ (ppm) -112.6. IR (ATR, neat) ν (cm^{-1}): 2926, 2233, 1737, 1599, 1508, 1441, 1420, 1364, 1219, 1166, 1119, 1090, 1013, 956, 912, 833, 813, 750, 674 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{28}H_{25}FNO_4S$: 490.1489, found: 490.1486.

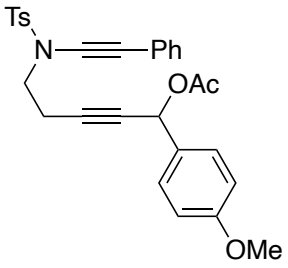
5-((4-Methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-(*p*-tolyl)pent-2-yn-1-yl acetate (1l)[S2]



Pale yellow oil; 263 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.39–7.34 (m, 4H), 7.31–7.29 (m, 3H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.42 (s, 1H), 3.64 (t, *J* = 7.6 Hz, 2H), 2.73 (td, *J* = 8.4, 1.7 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 144.9, 138.8, 134.5, 134.1, 131.4,

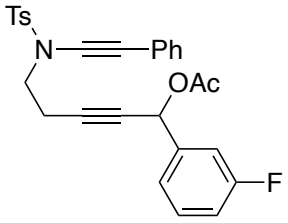
129.9, 129.3, 128.3, 128.0, 127.7, 127.6, 122.5, 83.0, 81.7, 79.2, 71.1, 65.6, 50.1, 21.6, 21.2, 21.1, 18.9.

1-(4-Methoxyphenyl)-5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)pent-2-yn-1-yl acetate (1m)[S2]



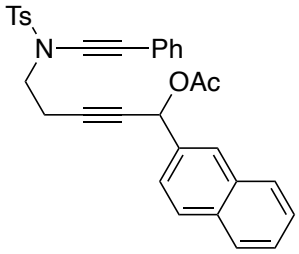
Yellow oil; 299 mg, 96% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.85 (d, J = 8.4 Hz, 2H), 7.46–7.43 (m, 2H), 7.36–7.32 (m, 4H), 7.29–7.27 (m, 3H), 6.88–6.85 (m, 2H), 6.39 (t, J = 1.9 Hz, 1H), 3.77 (s, 3H), 3.62 (t, J = 7.6 Hz, 2H), 2.73–2.70 (m, 2H), 2.43 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.8, 160.0, 144.9, 134.4, 131.1, 129.8, 129.2, 129.2, 128.2, 127.9, 127.6, 122.5, 113.9, 83.0, 81.7, 79.2, 71.1, 65.4, 55.2, 50.1, 21.6, 21.0, 18.9.

1-(3-Fluorophenyl)-5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)pent-2-yn-1-yl acetate (1n)[S2]



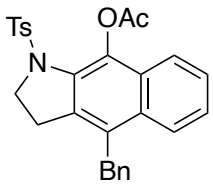
Yellow oil; 123 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (d, J = 8.2 Hz, 2H), 7.30–7.20 (m, 9H), 7.14 (d, J = 9.5 Hz, 1H), 6.96 (t, J = 7.7 Hz, 1H), 6.34 (s, 1H), 3.56 (t, J = 7.5 Hz, 2H), 2.65 (t, J = 6.8 Hz, 2H), 2.38 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.7, 162.8 (d, $^{1}J_{C\text{-}F}$ = 246.7 Hz), 145.0, 139.5 (d, $^{3}J_{C\text{-}F}$ = 7.1 Hz), 134.5, 131.5, 130.3 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 129.9, 128.3, 128.1, 127.7, 123.3 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 122.5, 115.3 (dd, $J_{C\text{-}F}$ = 120.5, 21.8 Hz), 83.7, 81.7, 78.6, 71.2, 65.0, 50.1, 21.7, 21.0, 19.0.

5-((4-Methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-(naphthalen-2-yl)pent-2-yn-1-yl acetate (1o)[S2]



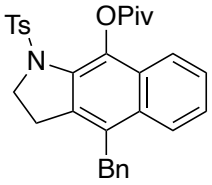
Yellow oil; 194 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (s, 1H), 7.85–7.80 (m, 5H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.49–7.47 (m, 2H), 7.35–7.25 (m, 7H), 6.60 (s, 1H), 3.65 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 6.7 Hz, 2H), 2.38 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.8, 144.9, 134.5, 134.3, 133.4, 133.0, 131.4, 129.9, 128.6, 128.3, 128.3, 128.0, 127.7, 127.1, 126.6, 126.4, 125.1, 122.5, 83.6, 81.7, 79.1, 71.2, 65.9, 50.1, 21.6, 21.1, 19.0.

4-Benzyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2a)



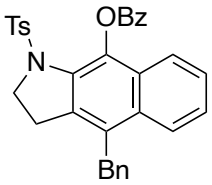
White solid; 24.1 mg, 50% yield; mp 145 – 146 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.55–7.39 (m, 3H), 7.43–7.39 (m, 1H), 7.17–7.10 (m, 5H), 6.82–6.80 (m, 2H), 4.19–4.15 (m, 4H), 2.56 (s, 3H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.3, 144.1, 139.2, 136.7, 136.3, 135.1, 132.2, 130.6, 129.7, 128.5, 128.4, 128.0, 127.5, 126.6, 126.2, 124. 3, 122.8, 53.1, 35.2, 28.4, 21.8, 21.4. IR (ATR, neat) ν (cm^{-1}): 3061, 2952, 2854, 1764, 1598, 1493, 1350, 1247, 1197, 1164, 1088, 1010, 889, 739, 698 cm^{-1}; HRMS (ESI) $[M + H]^+$ calc. for $C_{28}H_{26}NO_4S$: 472.1583, found: 472.1563.

4-Benzyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl pivalate (2b)



White solid; 24.1 mg, 47% yield; mp 228 – 230 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.89–7.87 (m, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.51–7.47 (m, 3H), 7.43–7.39 (m, 1H), 7.19–7.15 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.84–6.82 (m, 2H), 4.19–4.06 (m, 4H), 2.39–2.23 (m, 5H), 1.59 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 176.3, 144.1, 139.3, 137.8, 136.7, 135.0, 132.5, 131.2, 129.7, 129.6, 128.7, 128.5, 128.1, 127.7, 126.5, 126.2, 126.2, 124.4, 122.5, 52.9, 39.8, 35.3, 28.4, 27.7, 21.8. IR (ATR, neat) ν (cm^{-1}): 2965, 2920, 1750, 1597, 1495, 1473, 1357, 1275, 1251, 1185, 1166, 1112, 1100, 1026, 994, 977, 816, 766, 751, 675, 662 cm^{-1}; HRMS (ESI) $[M + H]^+$ calc. for $C_{31}H_{32}NO_4S$: 514.2052, found 514.2019.

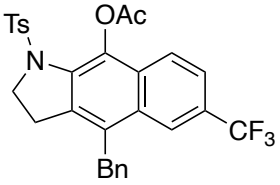
4-Benzyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl benzoate (2c)



Brown solid; 25.1 mg, 47% yield; mp 70 – 71 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.40 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.91 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.68–7.65 (m, 1H), 7.57–7.53 (m, 4H), 7.47–7.40 (m, 2H), 7.21–7.17 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.88–6.87 (m, 2H), 4.24 (br s, 2H), 4.16 (t, *J* = 7.4 Hz, 2H), 2.56–2.48 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 164.9, 144.0, 139.2, 136.9, 136.4, 135.4, 133.6, 132.3, 131.1, 130.8, 130.0, 129.7, 129.7, 128.7, 128.6, 128.6, 128.1, 127.5, 126.6, 126.3, 126.3, 124.4, 122.8, 53.0, 35.3, 28.6, 21.8. IR (ATR, neat) ν (cm^{-1}): 3070, 2950, 2855, 1732, 1599, 1509, 1495, 1453, 1355, 1243, 1174, 1164, 1107, 1087, 1057, 1022, 988, 977, 919, 813, 801, 763,

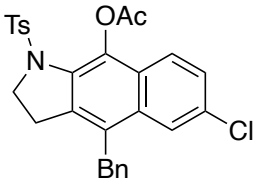
735, 717, 706, 699, 662 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{33}H_{28}NO_4S$: 534.1739, found: 534.1699.

4-Benzyl-1-tosyl-6-(trifluoromethyl)-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2d)



Yellow oil; 21.0 mg, 39% yield; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.13 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.65 (dd, *J* = 8.9, 1.5 Hz, 1H), 7.54–7.52 (m, 2H), 7.20–7.16 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.81–6.79 (m, 2H), 4.21 (s, 2H), 4.17 (br s, 2H), 2.55 (s, 3H), 2.49 (t, *J* = 7.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.2, 144.4, 138.5, 137.9, 136.3, 135.1, 132.7, 131.2, 131.1, 130.1, 129.9, 128.8, 128.3 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 128.0, 127.4, 126.6, 124.3 (q, $^1J_{C\text{-}F}$ = 272.0 Hz), 124.0, 122.0–121.9 (m), 53.1, 35.2, 28.5, 21.8, 21.4. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ (ppm) -62.4. IR (ATR, neat) ν (cm^{-1}): 2925, 2858, 1770, 1626, 1597, 1494, 1449, 1407, 1357, 1329, 1307, 1246, 1162, 1111, 1089, 1072, 1012, 908, 891, 816, 724, 698, 665 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{29}H_{25}F_3NO_4S$: 540.1457, found: 540.1455.

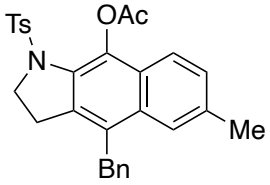
4-Benzyl-6-chloro-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2e)



White solid; 22.8 mg, 45% yield; mp 96 – 97 ℃; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 1.9 Hz), 7.52–7.51 (m, 2H), 7.20–7.16 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.80–6.78 (m, 2H), 4.13 (br s, 4H), 2.54 (s, 3H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.2, 144.3, 138.6, 137.9, 136.7, 135.0, 133.0, 132.9, 131.0, 129.8, 129.3, 128.7, 127.9, 127.5, 127.1, 126.9, 126.5, 124.6, 123.4, 53.1, 35.1, 28.5, 21.8, 21.4. IR (ATR, neat) ν (cm^{-1}): 3060, 3027, 2922, 1767, 1600, 1494, 1453, 1414,

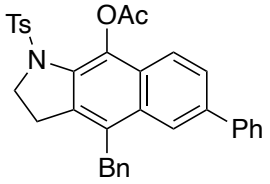
1353, 1246, 1199, 1169, 1104, 1089, 1012, 907, 868, 816, 778, 727, 699, 684, 662 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{28}H_{25}ClNO_4S$: 506.1193, found: 506.1152.

4-Benzyl-6-methyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2f)



Pale yellow solid; 19.9 mg, 41% yield; mp 176 – 177 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 8.6 Hz, 1H), 7.59 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.32 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.18–7.15 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.82–6.80 (m, 2H), 4.16–4.12 (m, 4H), 2.55 (s, 3H), 2.42 (s, 3H), 2.39 (t, *J* = 7.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 169.3, 144.0, 139.3, 136.8, 136.4, 136.4, 135.1, 132.5, 129.8, 129.7, 129.2, 128.5, 128.4, 128.0, 127.5, 126.5, 126.2, 123.5, 122.7, 53.2, 35.1, 28.4, 22.0, 21.8, 21.4. IR (ATR, neat) ν (cm^{-1}): 2924, 2861, 1767, 1619, 1600, 1493, 1453, 1436, 1420, 1352, 1247, 1201, 1171, 1110, 1092, 1023, 1011, 985, 879, 853, 816, 783, 753, 720, 696, 677, 665 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{29}H_{28}NO_4S$: 486.1739, found: 486.1724.

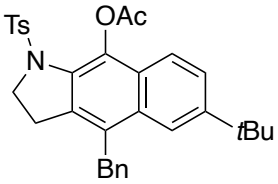
4-Benzyl-6-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2g)



Pale yellow solid; 23.0 mg, 42% yield; mp 100 – 102 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 1.4 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.74 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.56 – 7.52 (m, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.37–7.34 (m, 1H), 7.20–7.16 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.87–6.85 (m, 2H), 4.23 (s, 2H), 4.16 (br s, 2H), 2.58 (s, 3H), 2.45 (t, *J* = 7.3 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.4, 144.1, 141.0, 139.3, 139.2, 136.8, 136.7, 135.1, 132.5, 130.6, 130.3, 129.8, 129.0, 128.6, 128.1, 127.7, 127.6, 127.5, 127.5, 126.3,

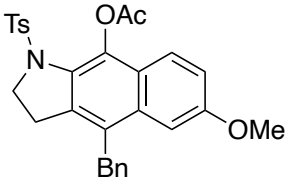
126.0, 123.5, 122.5, 53.2, 35.4, 28.5, 21.8, 21.4. IR (ATR, neat) ν (cm^{-1}): 2962, 2904, 1761, 1593, 1492, 1449, 1421, 1359, 1244, 1209, 1168, 1112, 1088, 1012, 994, 982, 888, 827, 766, 753, 732, 697, 665 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{34}H_{30}NO_4S$: 548.1896, found: 548.1835.

4-Benzyl-6-(*tert*-butyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2h)



Yellow oil; 18.5 mg, 35% yield; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.78 – 7.75 (m, 2H), 7.57 – 7.53 (m, 3H), 7.18 -7.11 (m, 5H), 6.85 – 6.84 (m, 2H), 4.16 – 4.12 (m, 4H), 2.55 (s, 3H), 2.46 – 2.42 (m, 2H), 2.35 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.5, 149.1, 144.1, 139.6, 136.8, 136.0, 135.1, 132.0, 130.2, 129.9, 129.7, 128.5, 128.2, 127.6, 126.5, 126.2, 125.0, 122.5, 119.9, 53.2, 35.6, 35.1, 31.3, 28.6, 21.8, 21.4. IR (ATR, neat) ν (cm^{-1}): 2956, 2866, 1769, 1617, 1598, 1494, 1454, 1355, 1246, 1206, 1182, 1167, 1107, 1089, 1013, 912, 879, 817, 729, 693, 669 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{32}H_{34}NO_4S$: 528.2209, found: 528.2209.

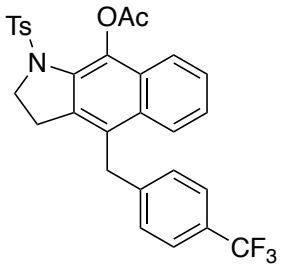
4-Benzyl-6-methoxy-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2i)



Yellow/brown solid; 21.6 mg, 43% yield; mp 140 – 141 ℃; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 9.2 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.19–7.10 (m, 6H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.83–6.82 (m, 2H), 4.13–4.12 (m, 4H), 3.74 (s, 3H), 2.54 (s, 3H), 2.42 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.3, 158.3, 144.0, 139.3, 137.1, 137.0, 135.1, 133.7, 129.7, 128.7, 128.7, 128.6, 128.0, 127.6, 126.3, 124.5, 123.5, 118.2, 103.9,

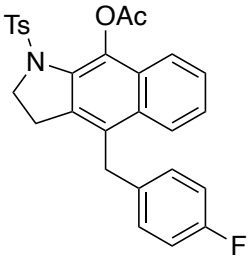
55.3, 53.2, 35.7, 28.7, 21.8, 21.4. IR (ATR, neat) ν (cm^{-1}): 3057, 2928, 2856, 1772, 1618, 1512, 1453, 1423, 1357, 1232, 1204, 1172, 1106, 1090, 981, 814, 717, 698, 666 cm^{-1}; HRMS (ESI) $[M + H]^+$ calc. for $C_{29}H_{28}NO_5S$: 502.1688, found: 502.1818.

1-Tosyl-4-(4-(trifluoromethyl)benzyl)-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2j)



Yellow oil; 21.6 mg, 40% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.90 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.55–7.50 (m, 3H), 7.44–7.40 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 4.24 (s, 2H), 4.16 (s, 2H), 2.55 (s, 3H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.2, 144.2, 143.3, 137.0, 136.6, 135.2, 132.0, 130.7, 129.8, 128.7 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 128.7, 128.5, 128.3, 127.6, 126.8, 126.5, 125.5–125.4 (m), 124.2 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 123.9, 123.0, 53.1, 34.9, 28.4, 21.6, 21.4. ^{19}F NMR (376.5 MHz, $CDCl_3$) δ (ppm) -62.5. IR (ATR, neat) ν (cm^{-1}): 2923, 2854, 1769, 1617, 1597, 1439, 1416, 1360, 1323, 1202, 1164, 1106, 1067, 1017, 910, 812, 752, 729, 679, 664 cm^{-1}; HRMS (ESI) $[M + H]^+$ calc. for $C_{29}H25F_3NO_4S$: 540.1457, found: 540.1457.

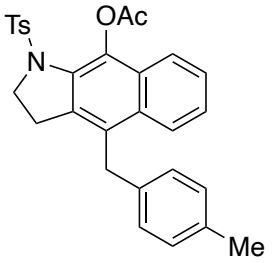
4-(4-Fluorobenzyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2k)



White solid; 20.1 mg, 41% yield; mp 86–88 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.88 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.53–7.49 (m, 3H), 7.44–7.41 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.86–6.83 (m, 2H), 6.77–6.75 (m, 2H), 4.14 (br s, 4H), 2.55 (s, 3H), 2.41

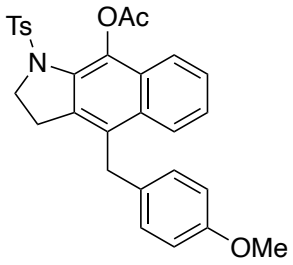
(t, J = 7.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.3, 161.4 (d, $^{1}J_{C\text{-}F}$ = 244.5 Hz), 144.1, 136.8, 136.3, 135.1, 134.8 (d, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 132.6 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 132.0, 130.7, 129.9, 129.8, 129.7, 129.4 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 128.5, 127.6, 127.5, 127.2 (d, $^{2}J_{C\text{-}F}$ = 41.1 Hz), 126.7, 126.3, 124.1, 122.9, 116.2 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 53.1, 34.3, 28.4, 21.7, 21.4. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ (ppm) -116.8. IR (ATR, neat) ν (cm^{-1}): 2922, 1765, 1597, 1508, 1438, 1413, 1356, 1292, 1200, 1165, 1104, 1089, 1011, 935, 912, 890, 815, 772, 751, 671 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{28}H_{25}FNO_4S$: 490.1489, found: 490.1472.

4-(4-Methylbenzyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2l)



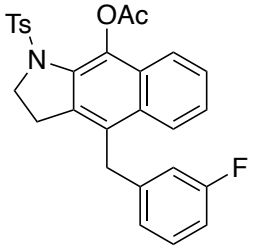
Pale brown solid; 20.9 mg, 43% yield; mp 183–184 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.86 (dd, J = 8.4, 0.6 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.54–7.53 (m, 2H), 7.49–7.47 (m, 1H), 7.42–7.39 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 7.9 Hz, 2H), 6.69 (d, J = 8.0 Hz, 2H), 4.14 (s, 4H), 2.55 (s, 3H), 2.43 (t, J = 7.5 Hz, 2H), 2.34 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.3, 144.1, 136.6, 136.2, 136.1, 135.7, 135.2, 132.2, 130.6, 130.2, 129.8, 129.3, 128.4, 127.9, 127.6, 126.5, 126.2, 124.4, 122.8, 53.2, 34.8, 28.4, 21.8, 21.4, 21.1. IR (ATR, neat) ν (cm^{-1}): 2921, 2862, 1765, 1637, 1596, 1512, 1468, 1432, 1416, 1358, 1333, 1249, 1201, 1176, 1165, 1100, 1086, 1018, 997, 890, 850, 820, 802, 766, 749, 722, 696 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{29}H_{28}NO_4S$: 486.1739, found: 486.1728.

4-(4-Methoxybenzyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2m)



Pale yellow oil; 21.6 mg, 43% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.86, (dd, *J* = 8.4, 0.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.50–7.47 (m, 1H), 7.42–7.40 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.73–6.69 (m, 4H), 4.14–4.12 (m, 4H), 3.75 (s, 3H), 2.55 (s, 3H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.3, 158.0, 144.1, 136.6, 136.1, 135.2, 132.2, 131.2, 130.6, 130.4, 129.7, 128.9, 128.4, 127.5, 126.5, 126.2, 124.4, 122.8, 114.0, 55.3, 53.2, 34.4, 28.4, 21.8, 21.4. IR (ATR, neat) ν (cm^{-1}): 2954, 2908, 1773, 1609, 1512, 1452, 1439, 1358, 1306, 1283, 1249, 1194, 1177, 1163, 1103, 1088, 1030, 1011, 992, 888, 822, 790, 775, 749, 700, 669 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{29}H_{28}NO_5S$: 502.1688, found: 502.1633.

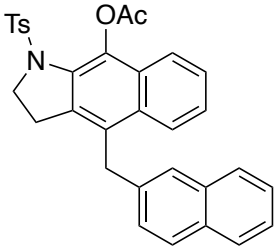
4-(3-Fluorobenzyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2n)



Yellow oil; 22.0 mg, 45% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.89 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.54–7.49 (m, 3H), 7.44–7.41 (m, 1H), 7.17–7.12 (m, 3H), 6.84 (td, *J* = 8.4, 2.1 Hz, 1H), 6.71 (dd, *J* = 7.7, 0.5 Hz, 1H), 4.18–4.15 (m, 4H), 2.56 (s, 3H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.2, 163.1 (d, $^{1}J_{C\text{-}F}$ = 246.3 Hz), 144.4, 141.9 (d, $^{3}J_{C\text{-}F}$ = 6.9 Hz), 137.0, 136.5, 135.0, 132.1, 130.7, 130.0 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 129.8, 129.1, 128.5, 127.5, 126.8, 126.4, 124.1, 123.8 (d, $^{3}J_{C\text{-}F}$ = 2.2 Hz), 122.9,

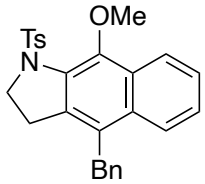
114.8 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 113.3 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 53.1, 35.0, 28.4, 21.6, 21.4. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ (ppm) -112.7. IR (ATR, neat) ν (cm^{-1}): 3076, 2920, 2954, 1771, 1611, 1588, 1486, 1451, 1434, 1353, 1264, 1246, 1192, 1164, 1100, 1089, 1009, 982, 962, 885, 817, 796, 765, 749, 721, 699, 674, 661 cm^{-1}. HRMS (ESI) $[M + H]^+$ calc. for $C_{28}H_{25}FNO_4S$: 490.1489, found: 490.1431.

4-(Naphthalen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (2o)



Pale yellow solid; 26.6 mg, 50% yield; mp 88–89 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.90–7.88 (m, 2H), 7.77–7.76 (m, 1H), 7.65–7.63 (m, 2H), 7.54–7.49 (m, 3H), 7.45–7.40 (m, 3H), 7.27 (s, 1H), 7.05 (d, 8.0 Hz, 2H), 6.98 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.35 (s, 2H), 4.14 (s, 2H), 2.56 (s, 3H), 2.46 (t, *J* = 7.5 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 169.3, 144.2, 136.7, 136.7, 136.4, 135.1, 133.5, 132.3, 132.2, 130.7, 128.8, 129.7, 128.5, 128.2, 127.7, 127.6, 127.5, 126.7, 126.6, 126.3, 126.3, 126.3, 125.7, 124.4, 122.9, 53.2, 35.5, 28.5, 21.5, 21.4. IR (ATR, neat) ν (cm^{-1}): 3063, 2962, 2859, 1765, 1597, 1509, 1431, 1352, 1201, 1165, 1087, 1013, 903, 812, 746, 698, 670 cm^{-1}; HRMS (ESI) $[M + H]^+$ calc. for $C_{32}H_{28}NO_4S$: 522.1739, found: 522.1728.

4-Benzyl-9-methoxy-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indole (3a)



Yellow oil; 16.0 mg, 36% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.41 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.49–7.40 (m, 4H), 7.19–7.15 (m, 3H), 7.07 (d, *J* = 8.0 Hz,

2H), 6.86–6.85 (m, 2H), 4.19 (s, 3H), 4.13 (s, 2H), 4.10 (t, J = 7.4 Hz, 2H), 2.36–2.33 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 147.0, 144.0, 139.7, 136.9, 135.1, 132.6, 129.6, 129.2, 128.5, 128.1, 127.8, 127.1, 126.6, 126.1, 125.9, 125.3, 124.0, 123.7, 59.7, 52.5, 35.2, 28.3, 21.8. IR (ATR, neat) ν (cm^{-1}): 3069, 2925, 2855, 1589, 1492, 1456, 1440, 1366, 1345, 1247, 1162, 1114, 1085, 1010, 950, 818, 764, 730, 699, 663 cm^{-1}; HRMS (ESI) $[M + H]^+$ calc. for $C_{27}H_{26}NO_3S$: 444.1634, found: 444.1618.

6. NMR spectra

Figure S1. ^{1}H NMR and ^{13}C NMR spectra of 5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (**1a)**

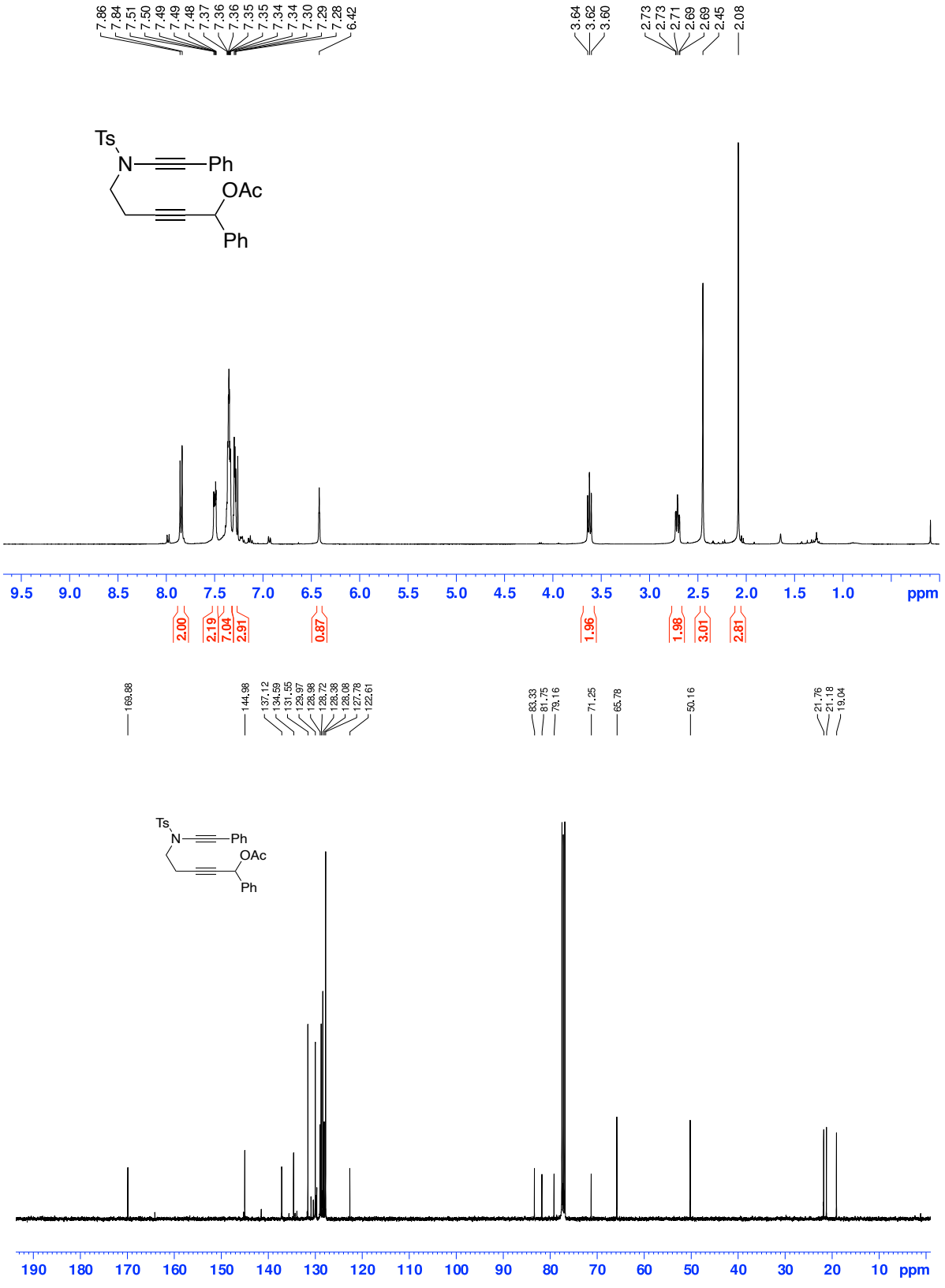


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of 5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl pivalate (**1b**)

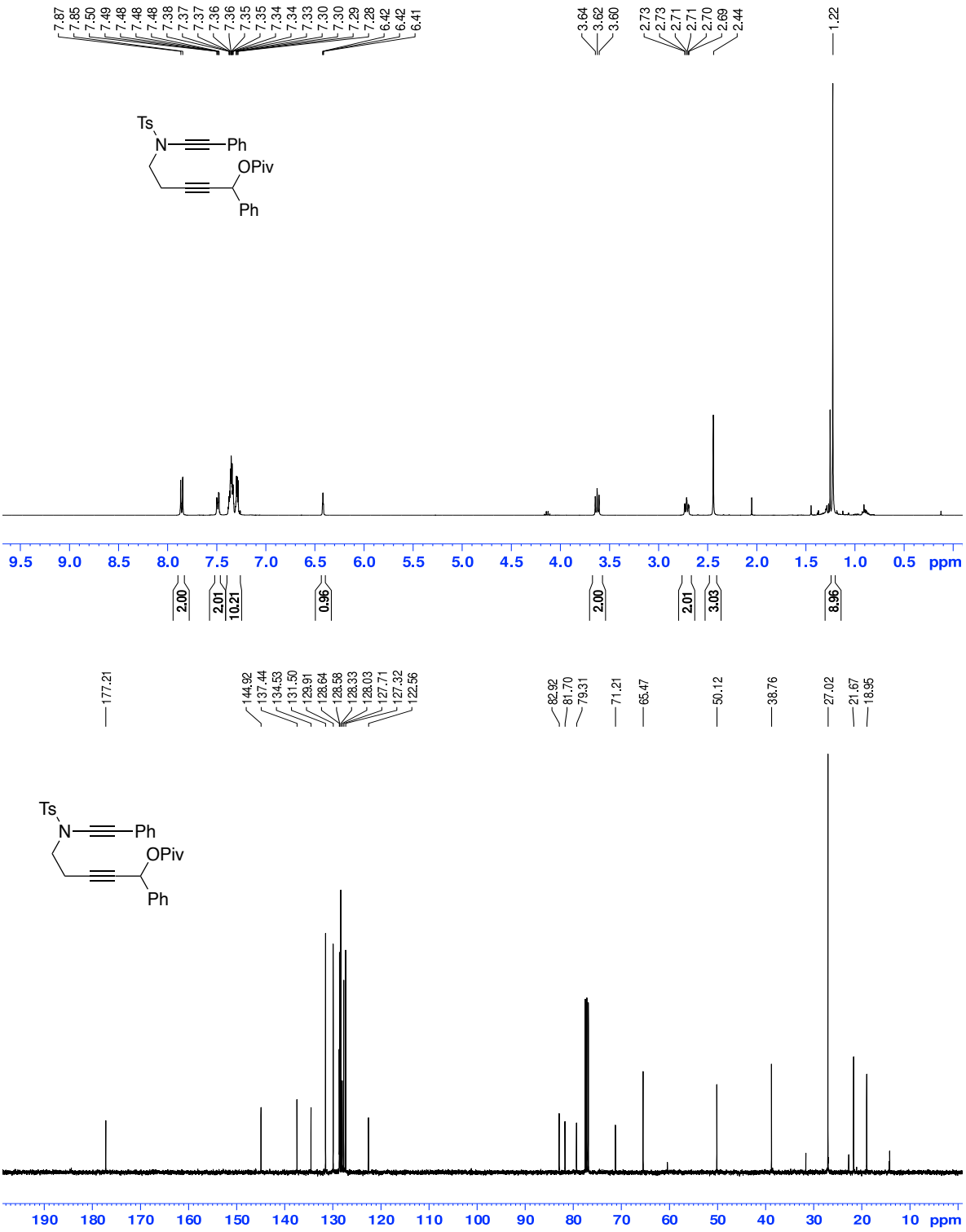


Figure S3. ^{1}H NMR and ^{13}C NMR spectra of 5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl benzoate (**1c**)

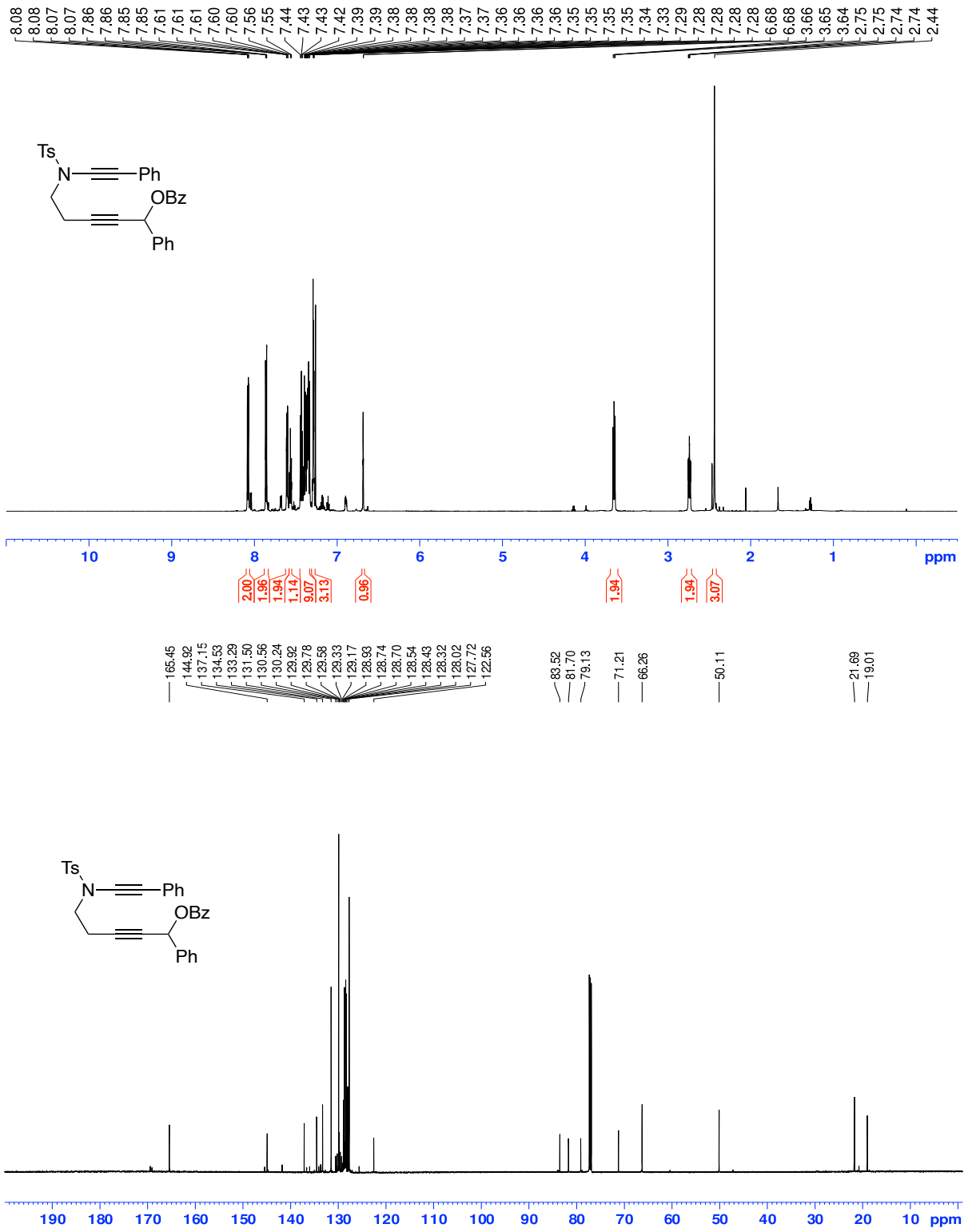


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of 5-((4-methyl-*N*-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (**1d**)

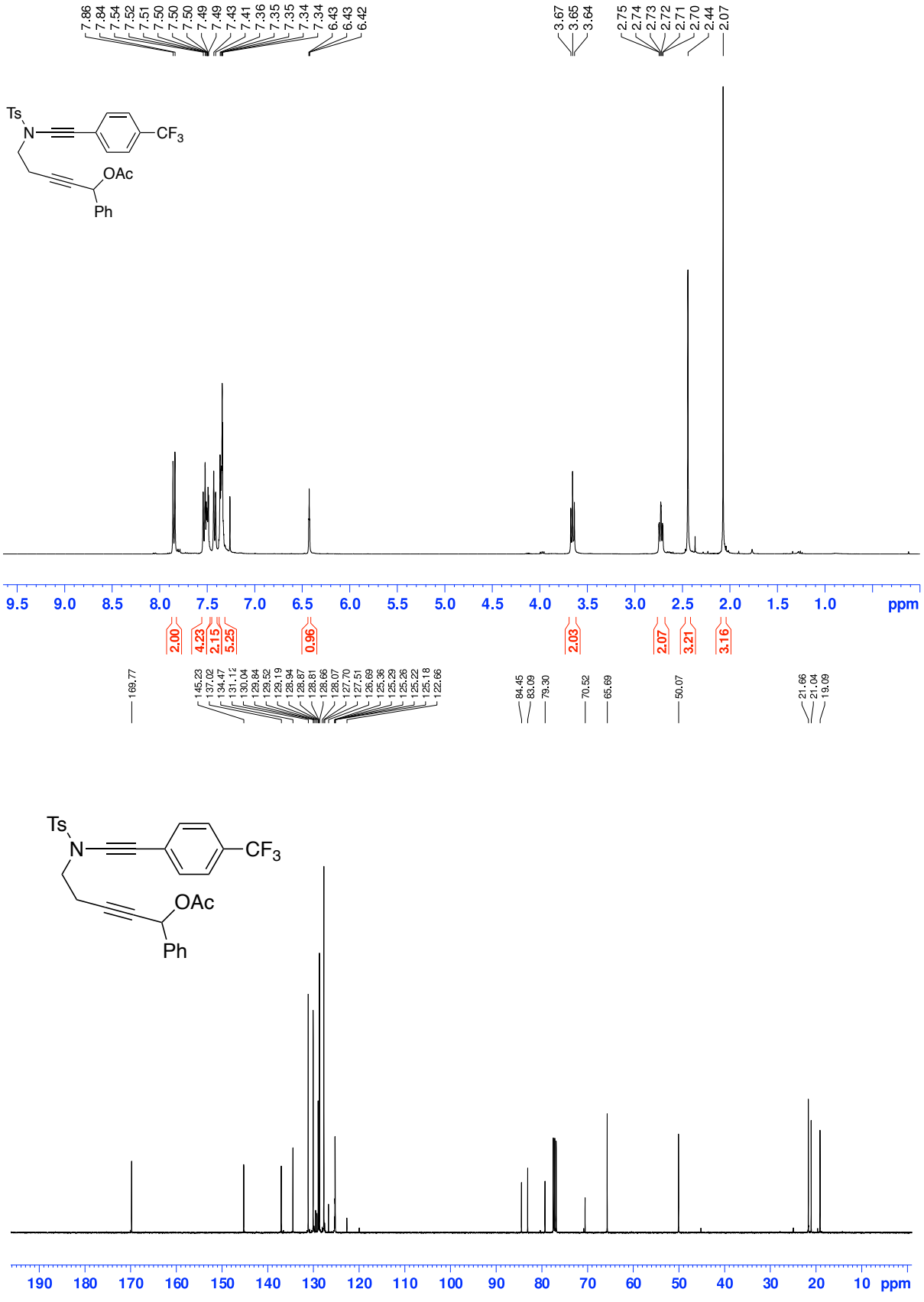


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of 5-((*N*-((4-chlorophenyl)ethynyl)-4-methylphenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (**1e**)

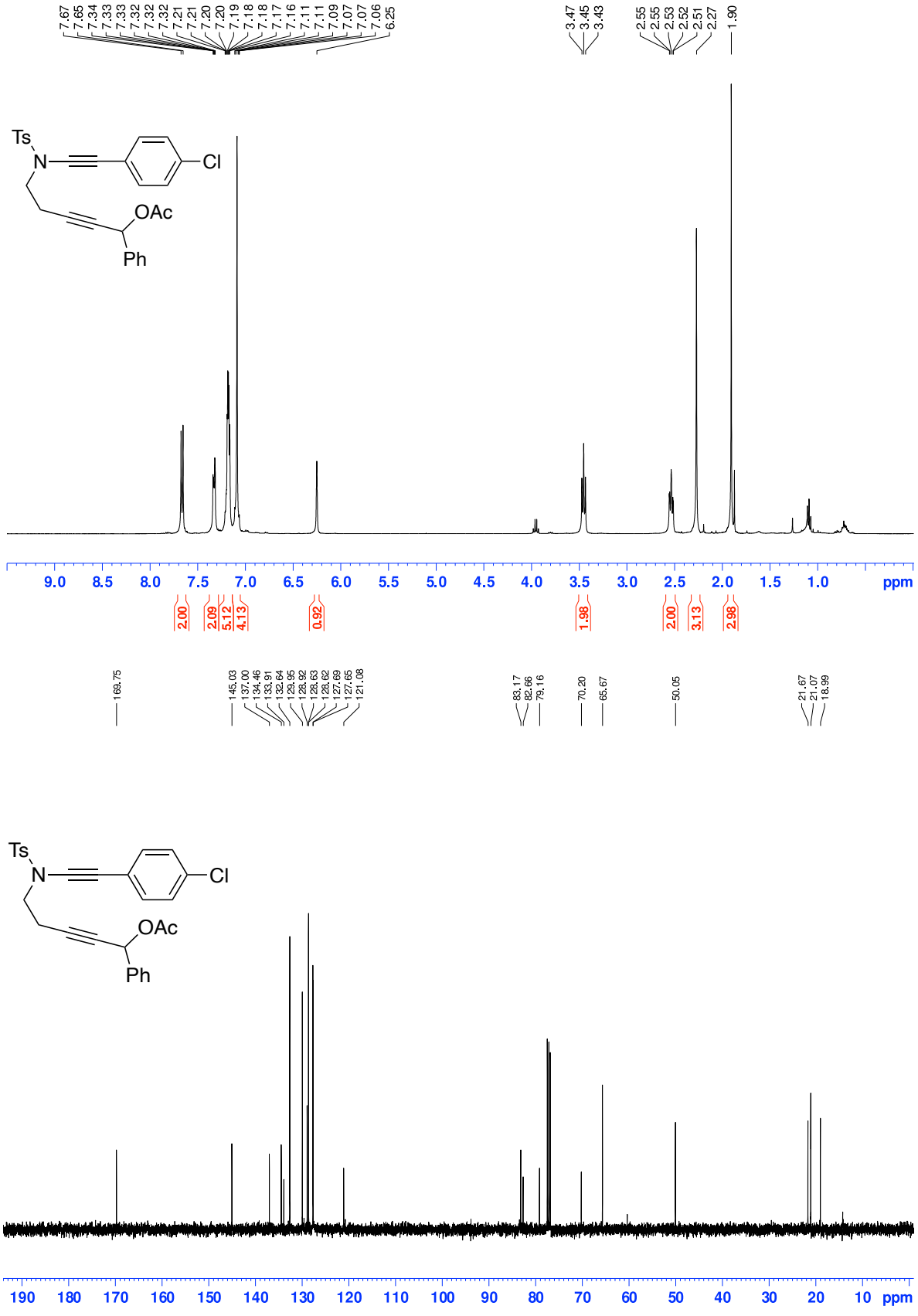


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of 5-((4-Methyl-*N*-(*p*-tolylethynyl)phenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (**1f**)

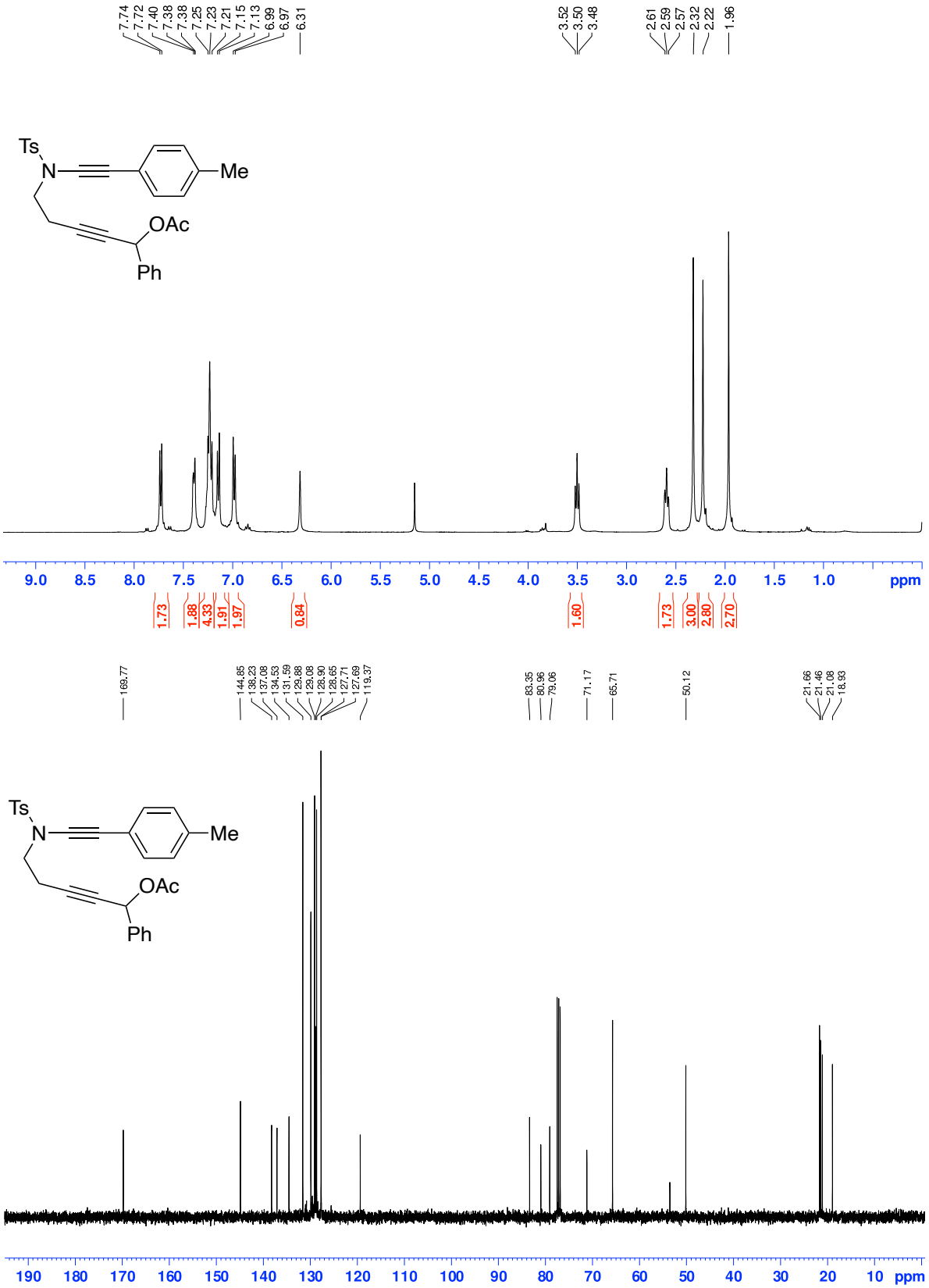


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of 5-((*N*-([1,1'-biphenyl]-4-ylethynyl)-4-methylphenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (**1g**)

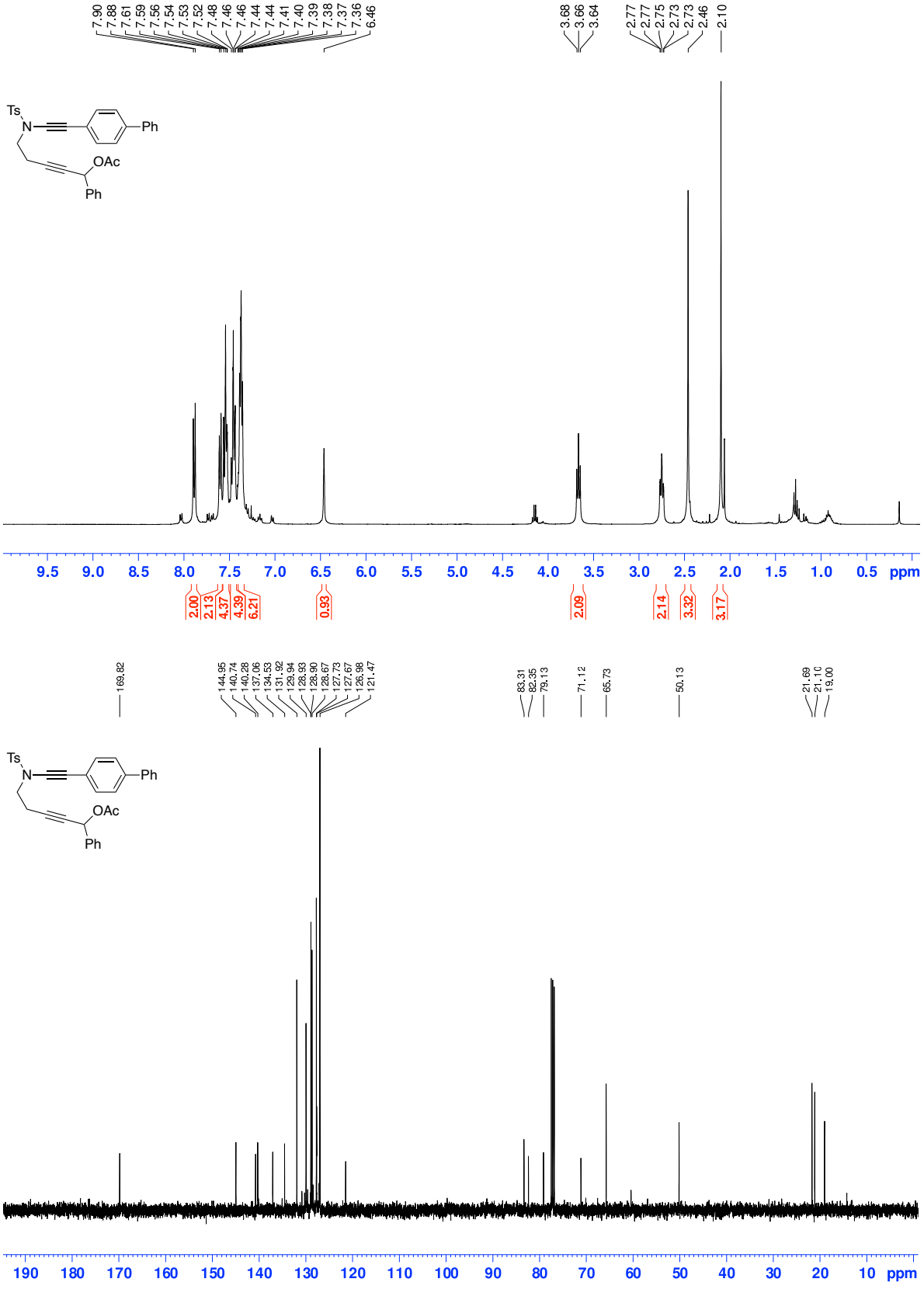


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of 5-((*N*-((4-(*tert*-butyl)phenyl)ethynyl)-4-methylphenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (**1h**)

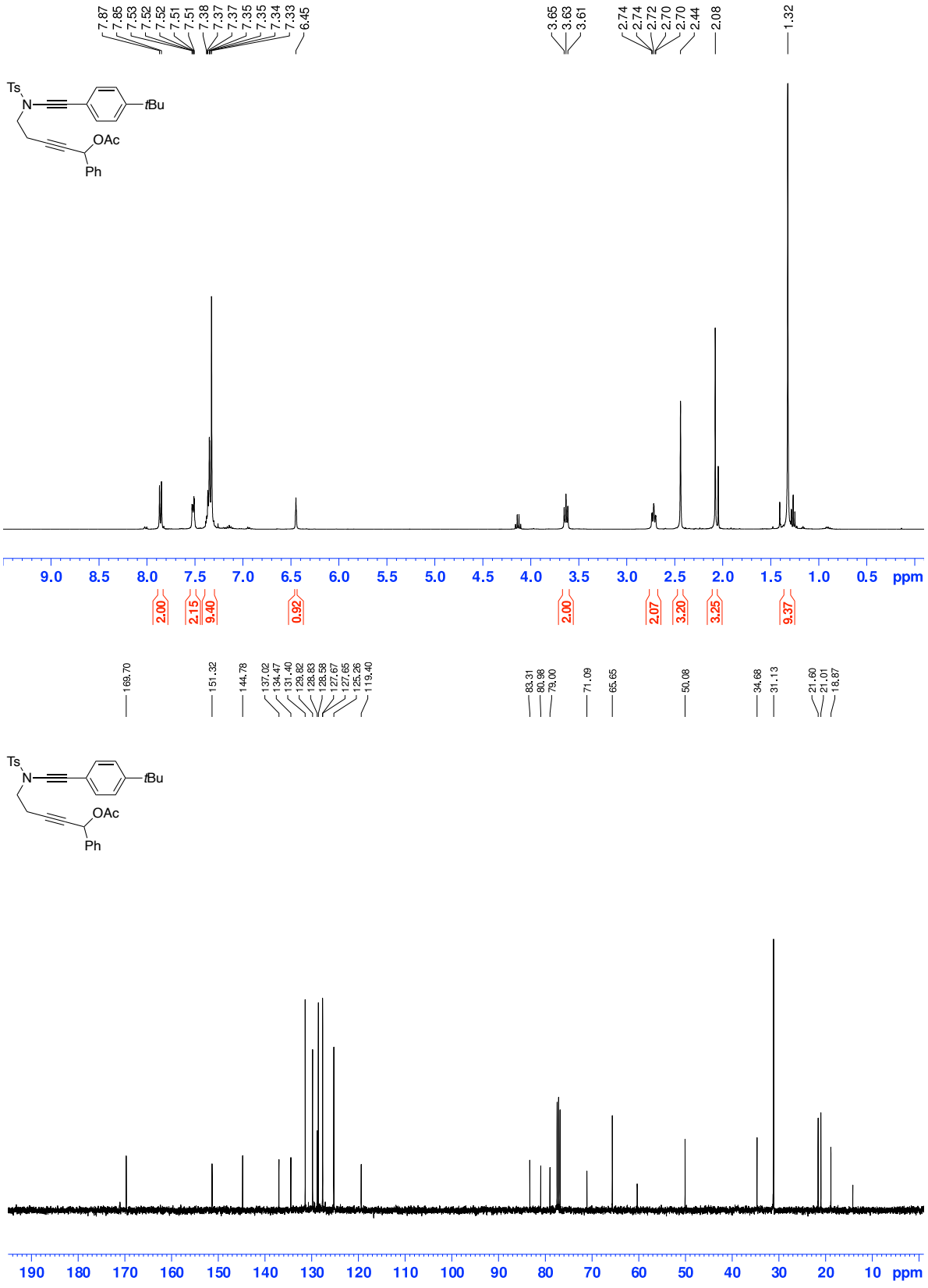
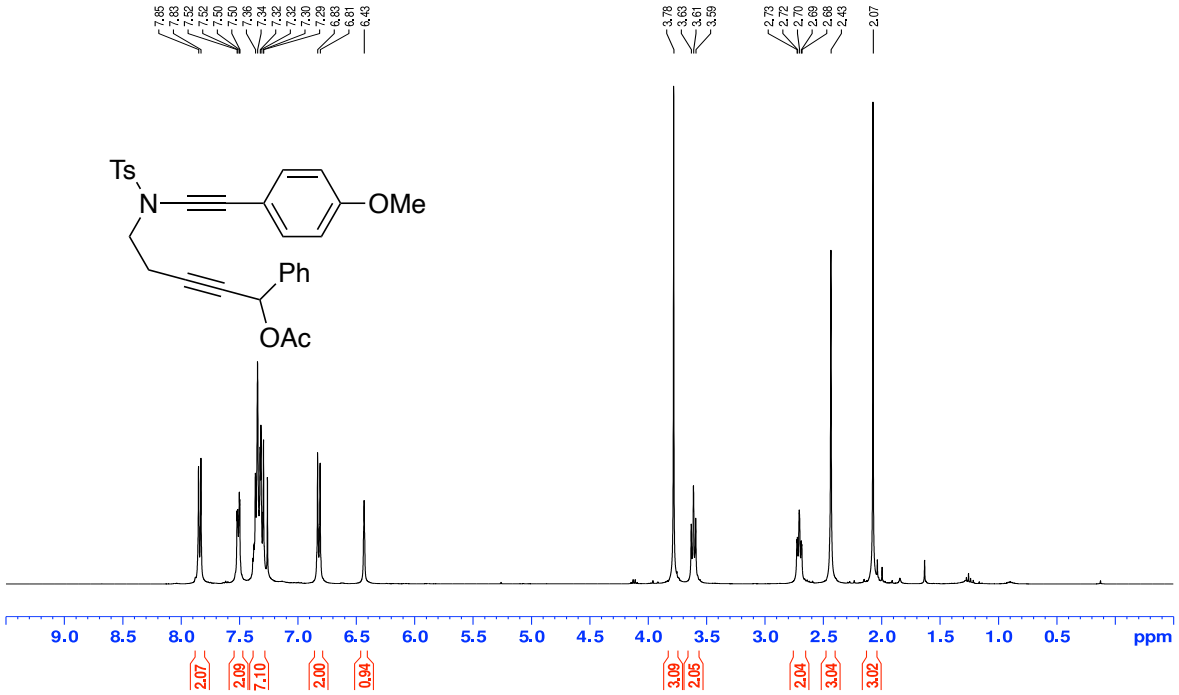


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of 5-((*N*-((4-methoxyphenyl)ethynyl)-4-methylphenyl)sulfonamido)-1-phenylpent-2-yn-1-yl acetate (**1i**)



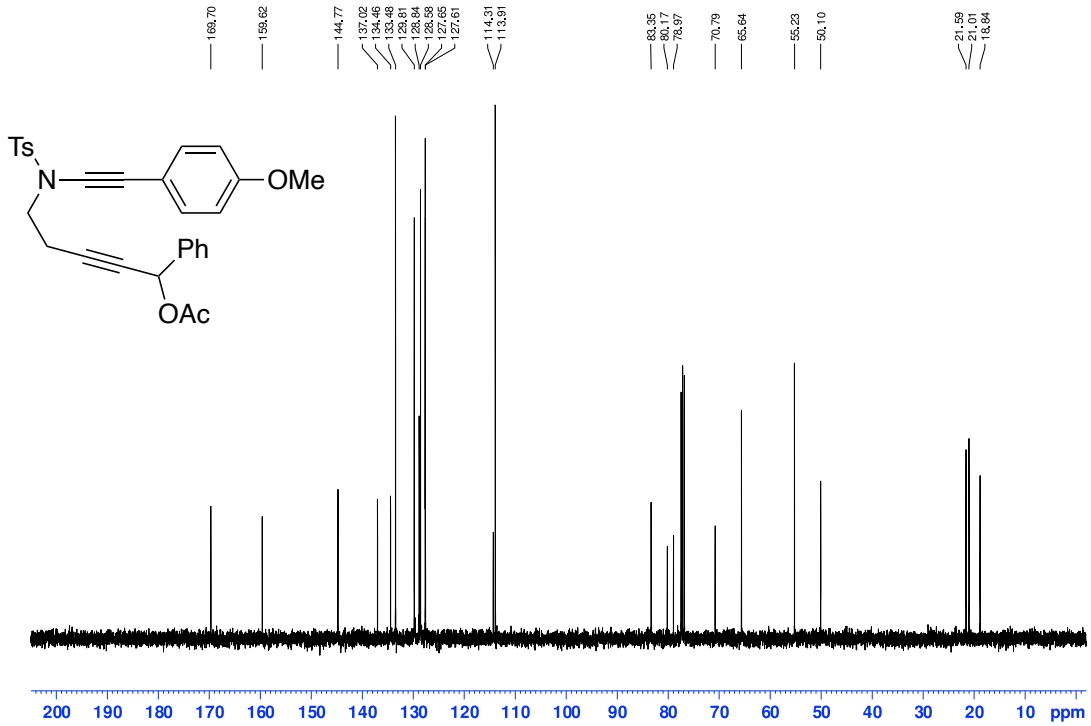


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of 5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-(4-(trifluoromethyl)phenyl)pent-2-yn-1-yl acetate (**1j**)

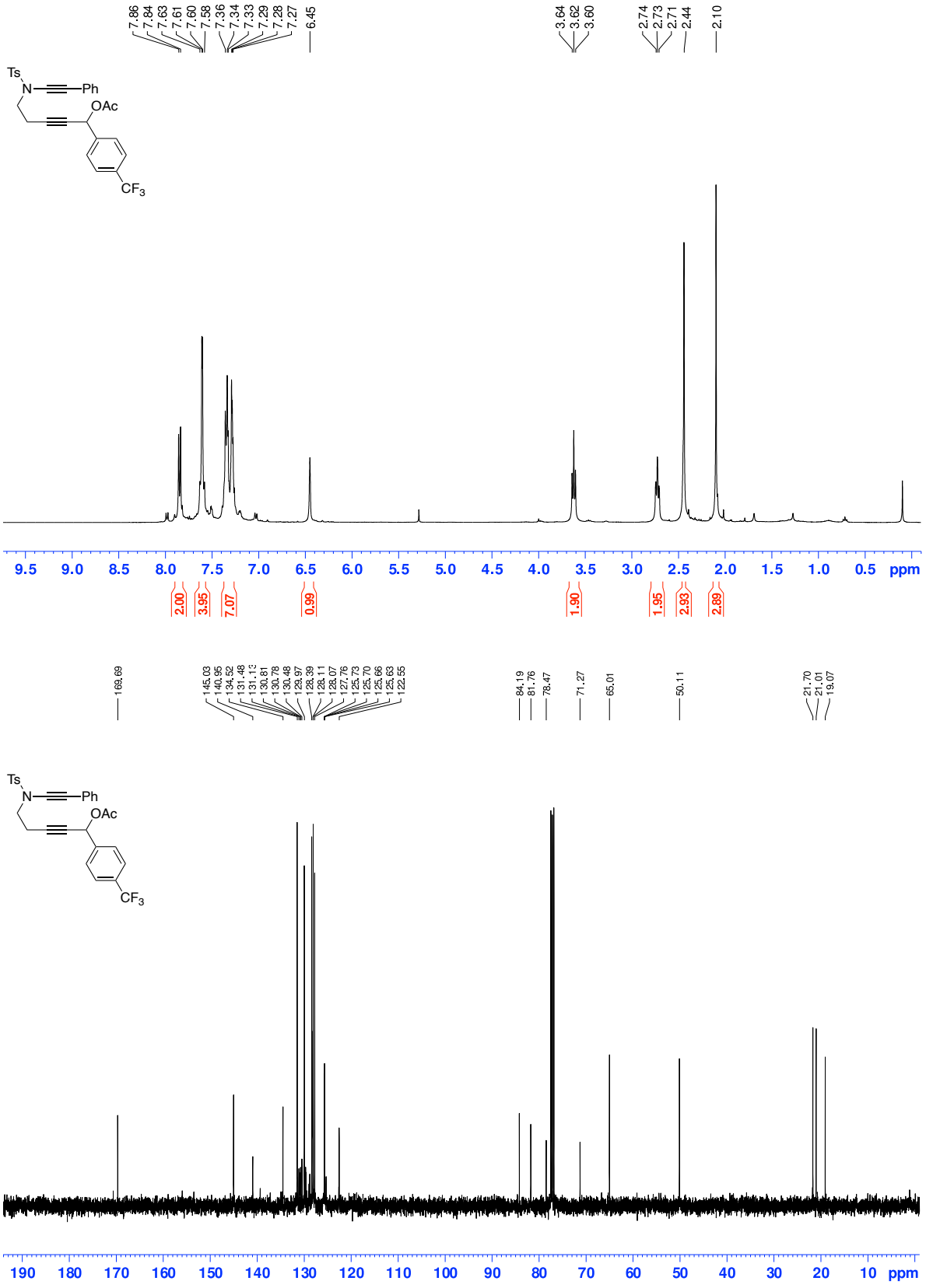
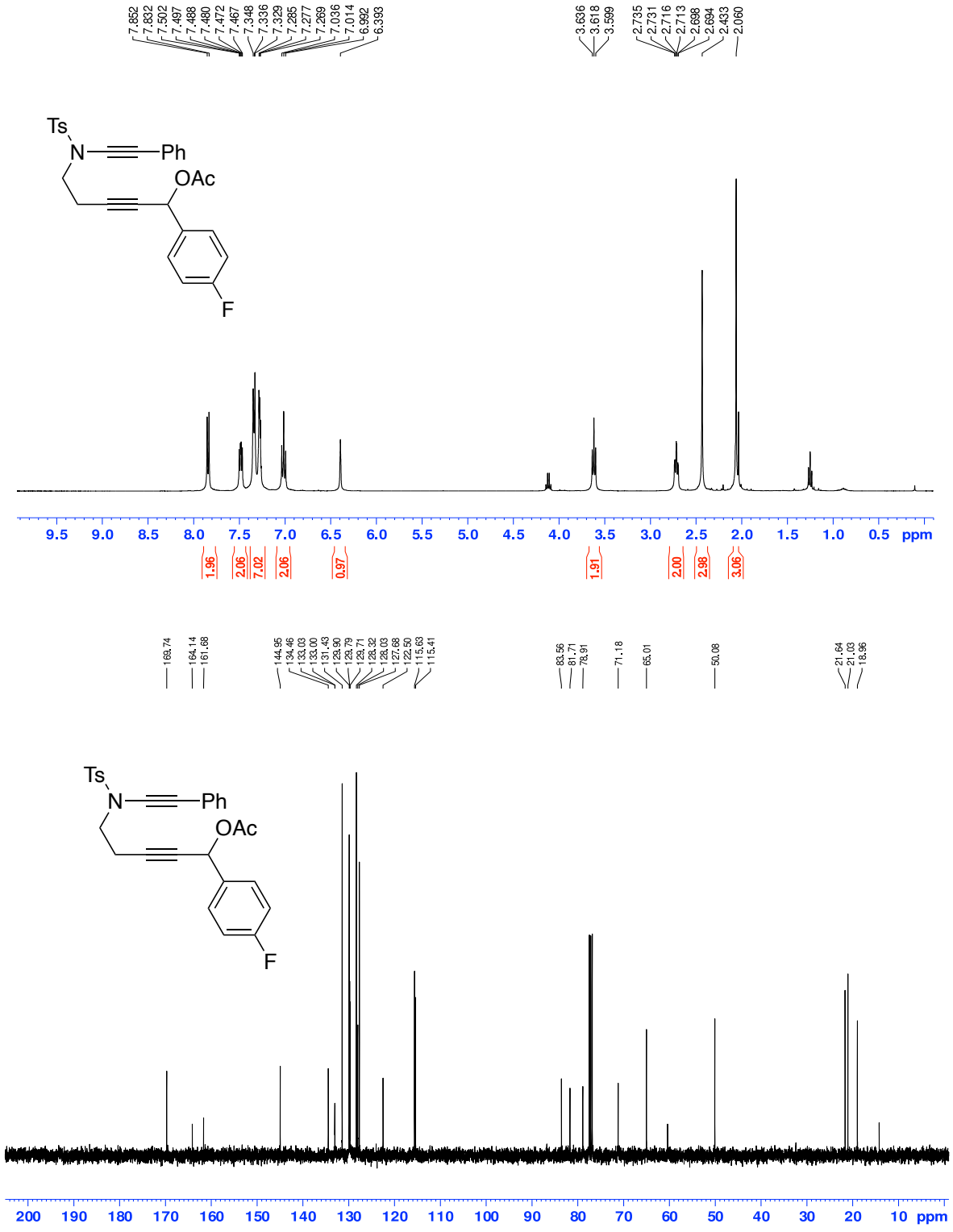


Figure S11. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of 1-(4-fluorophenyl)-5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)pent-2-yn-1-yl acetate (**1k**)



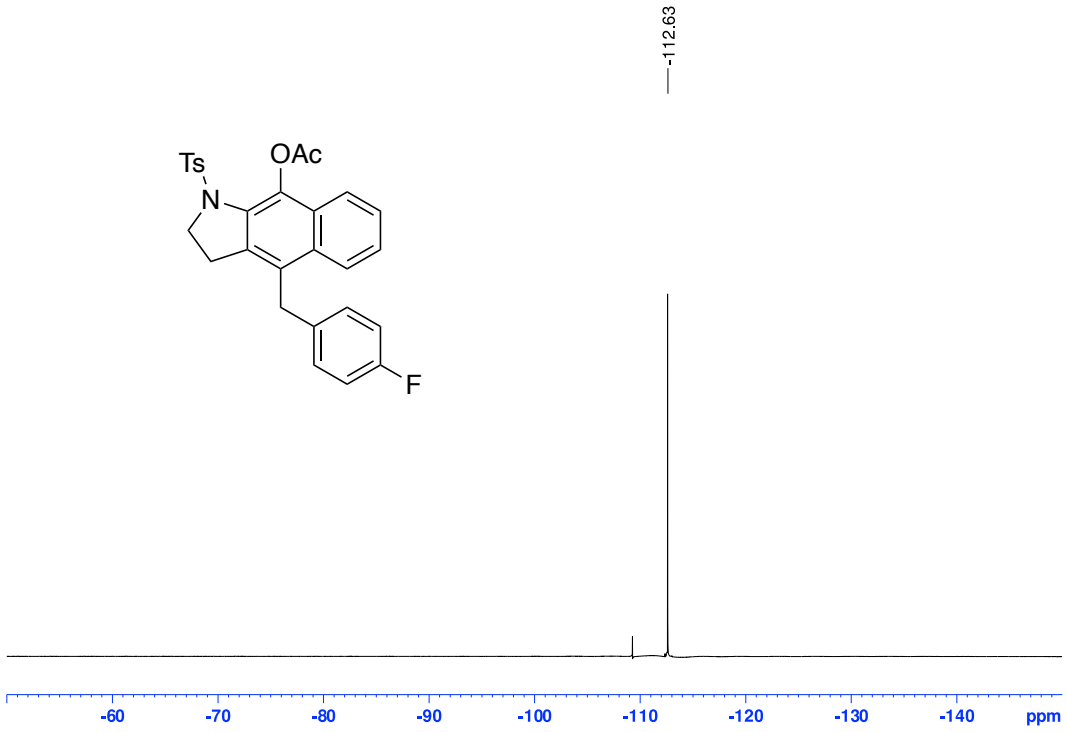

-112.63
Ts
N
OAc
F
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm

Figure S12. ^{1}H NMR and ^{13}C NMR spectra of 5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-(*p*-tolyl)pent-2-yn-1-yl acetate (**1l**)

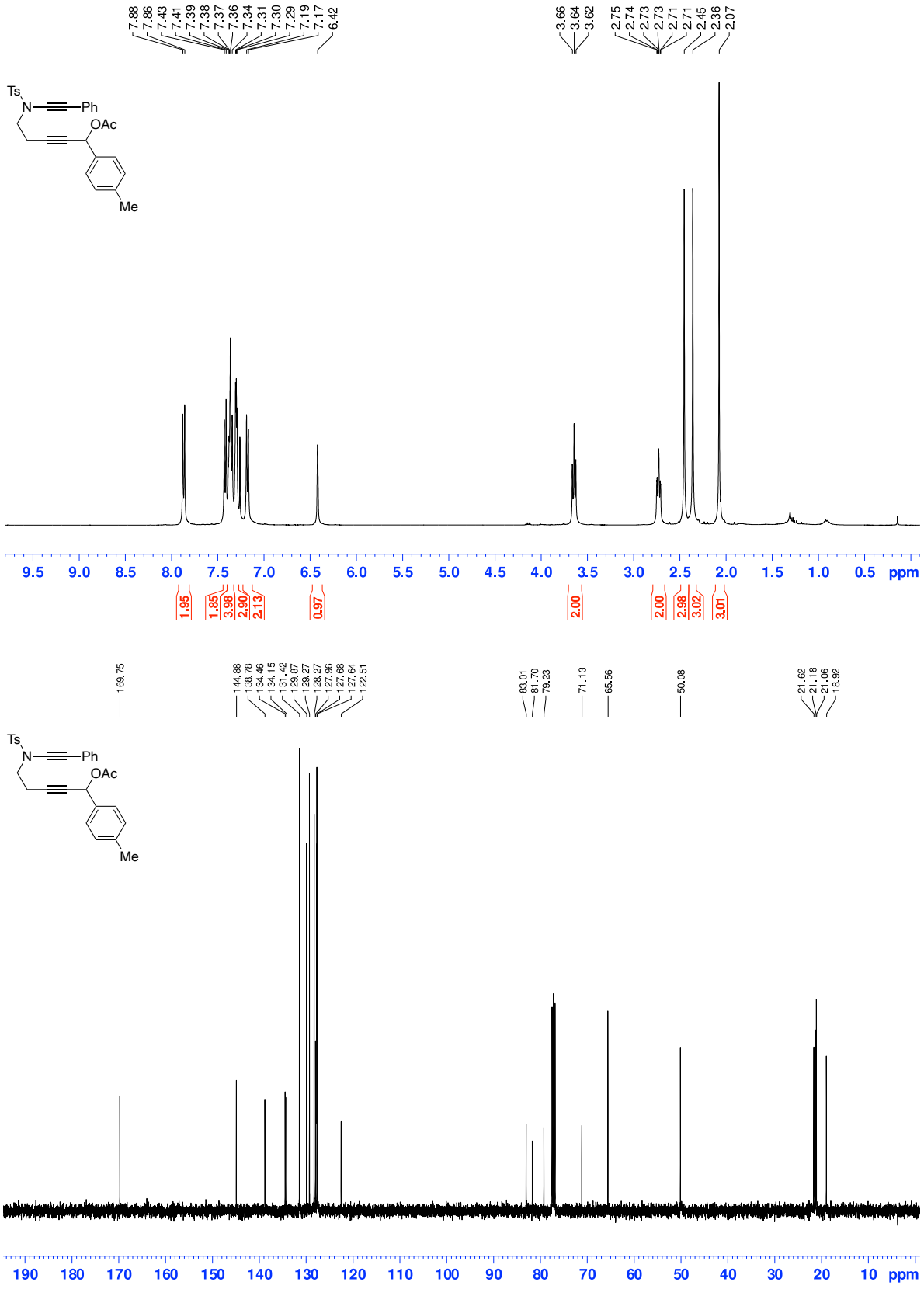


Figure S13. ^{1}H NMR and ^{13}C NMR spectra of 1-(4-methoxyphenyl)-5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)pent-2-yn-1-yl acetate (**1m**)

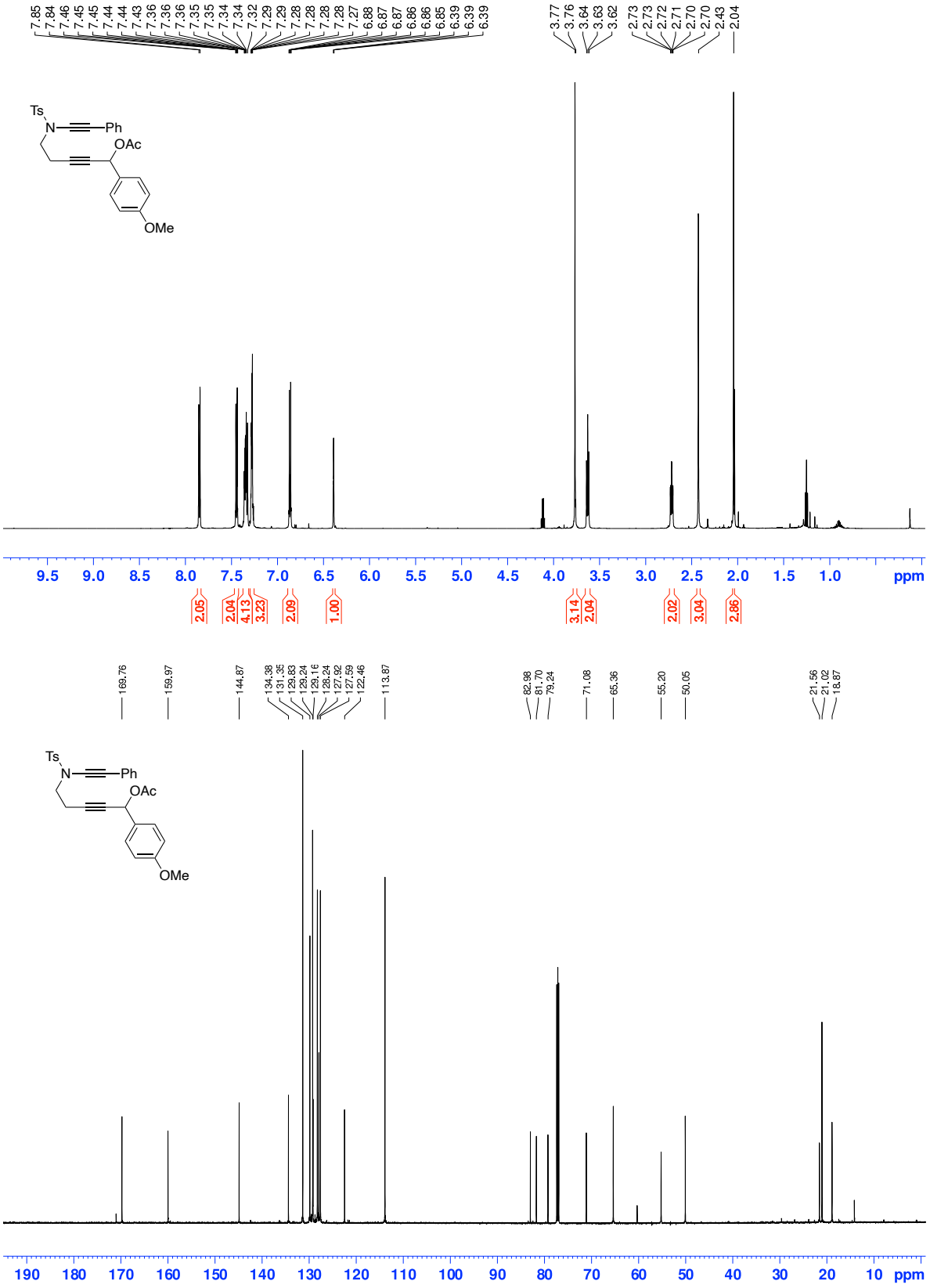


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of 1-(3-fluorophenyl)-5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)pent-2-yn-1-yl acetate (**1n**)

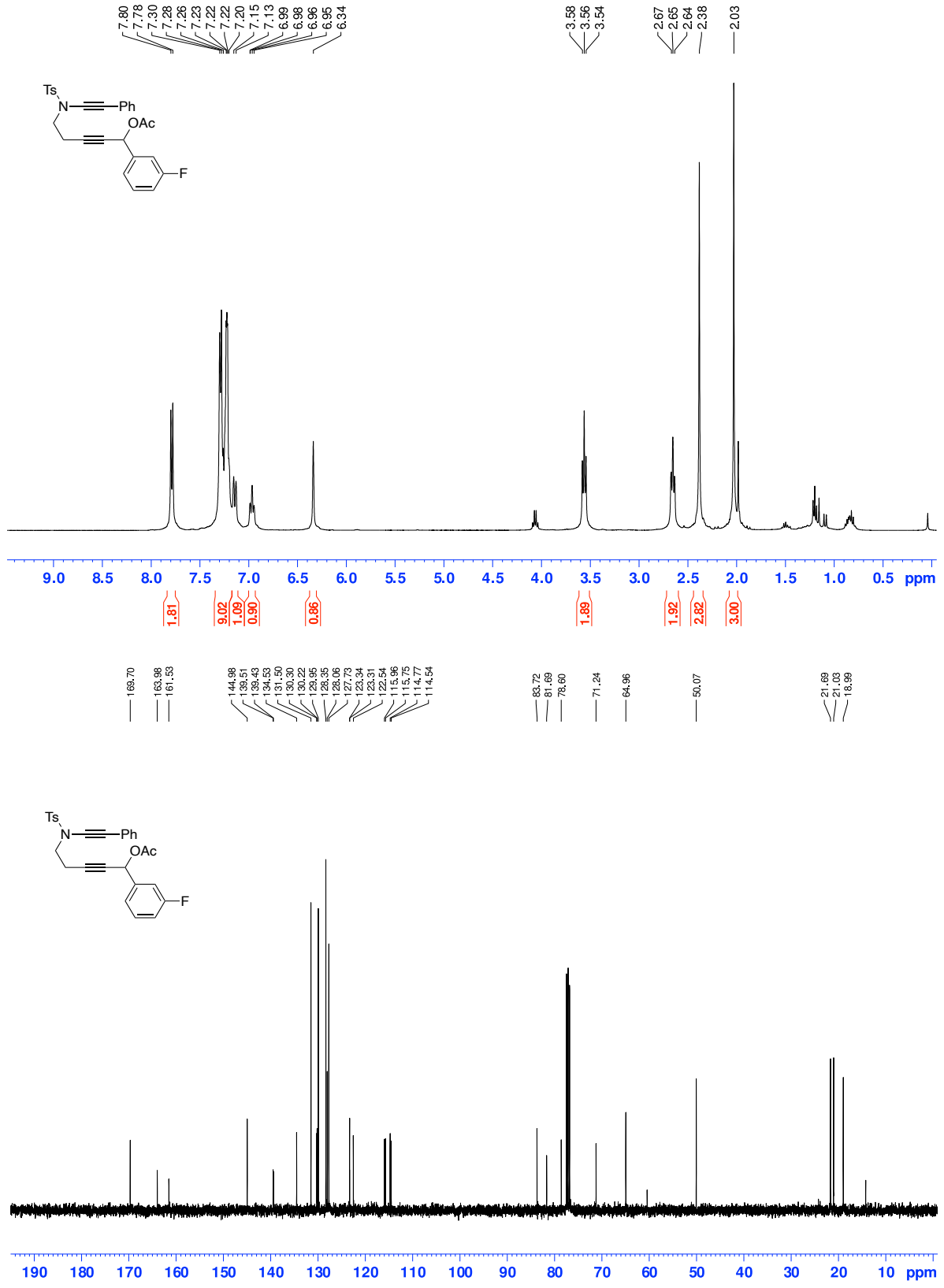


Figure S15. ^{1}H NMR and ^{13}C NMR spectra of 5-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)-1-(naphthalen-2-yl)pent-2-yn-1-yl acetate (**1o**)

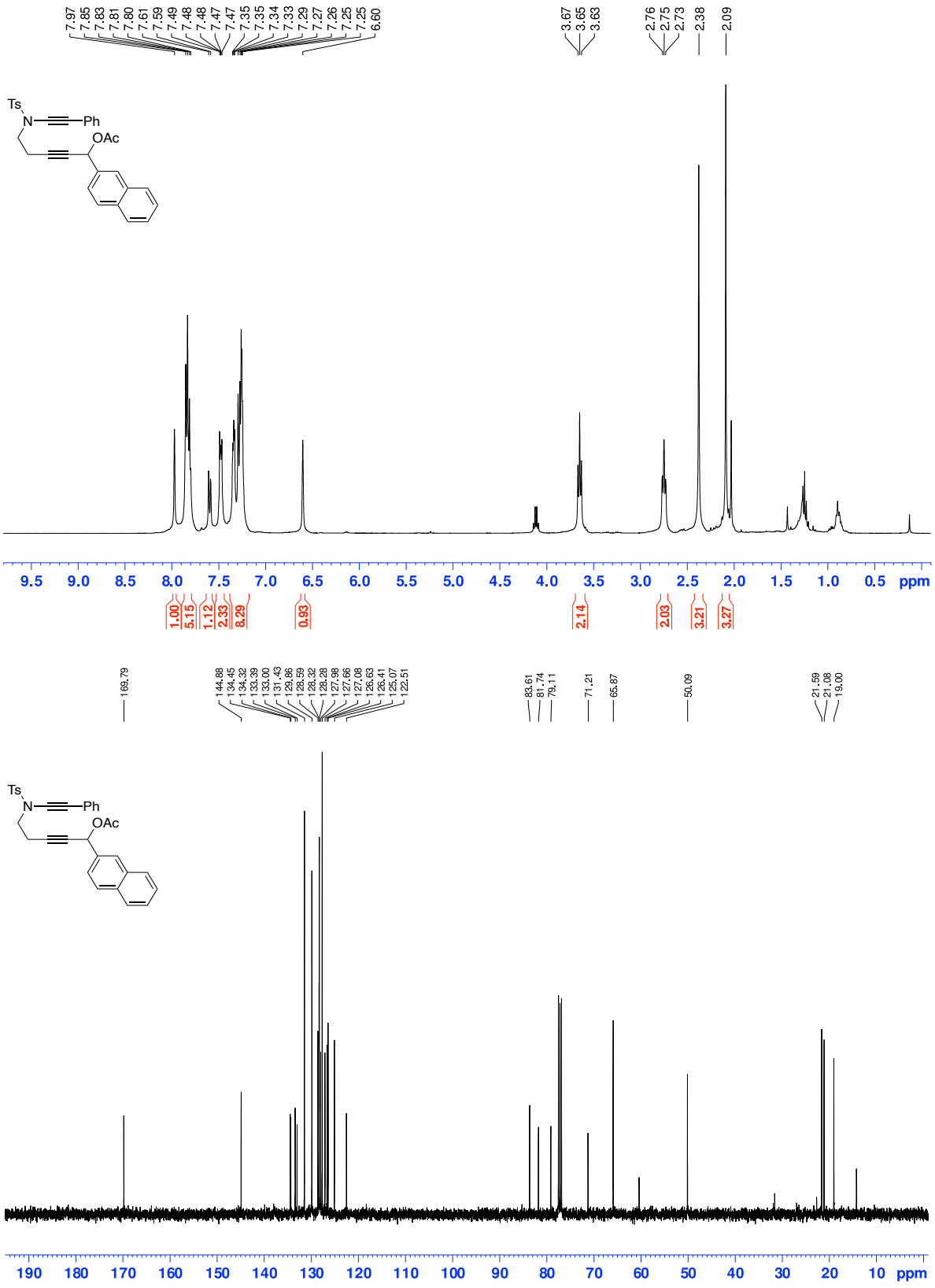


Figure S16. ^{1}H NMR and ^{13}C NMR spectra of 4-benzyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2a**)

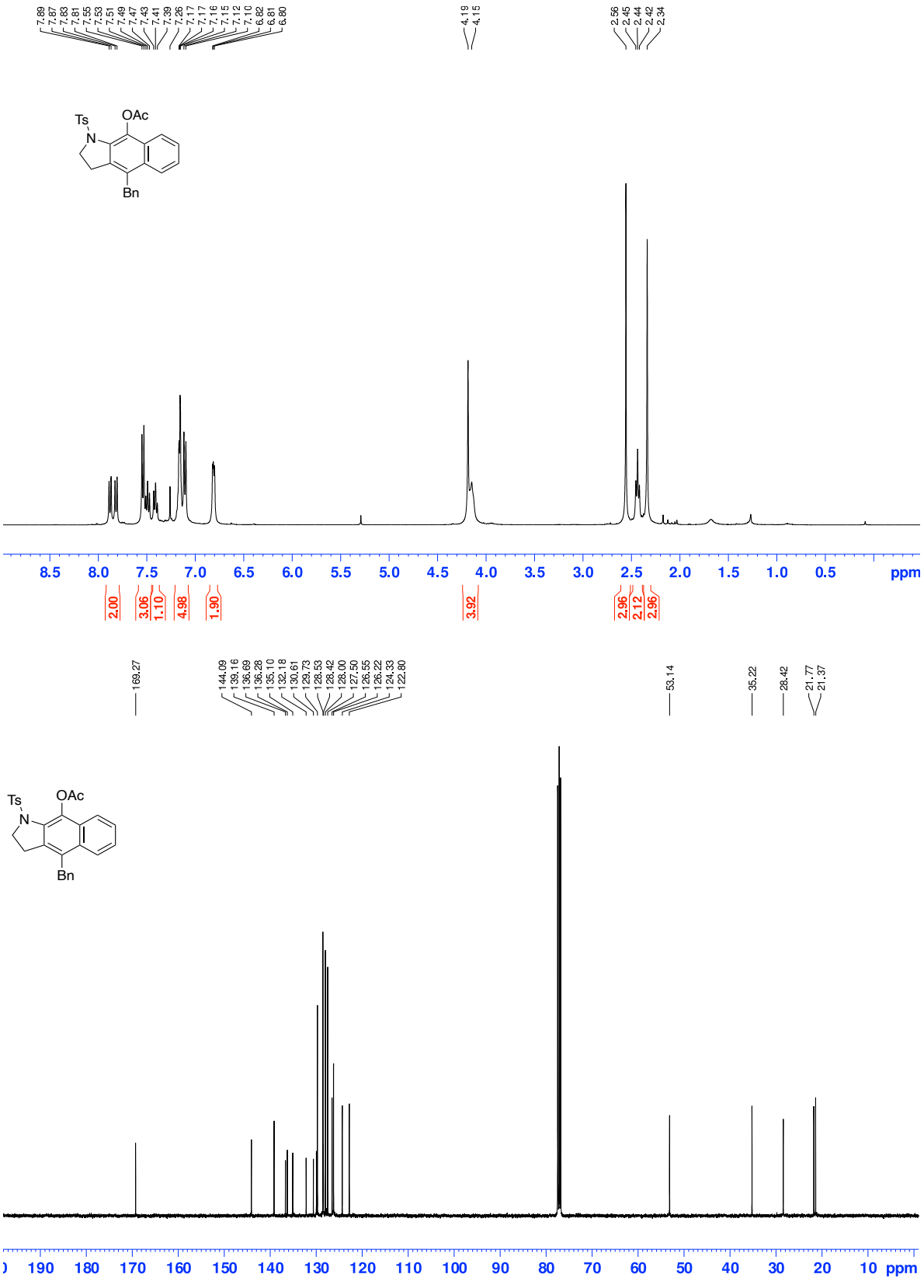


Figure S17. ^{1}H NMR and ^{13}C NMR spectra of 4-benzyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl pivalate (**2b**)

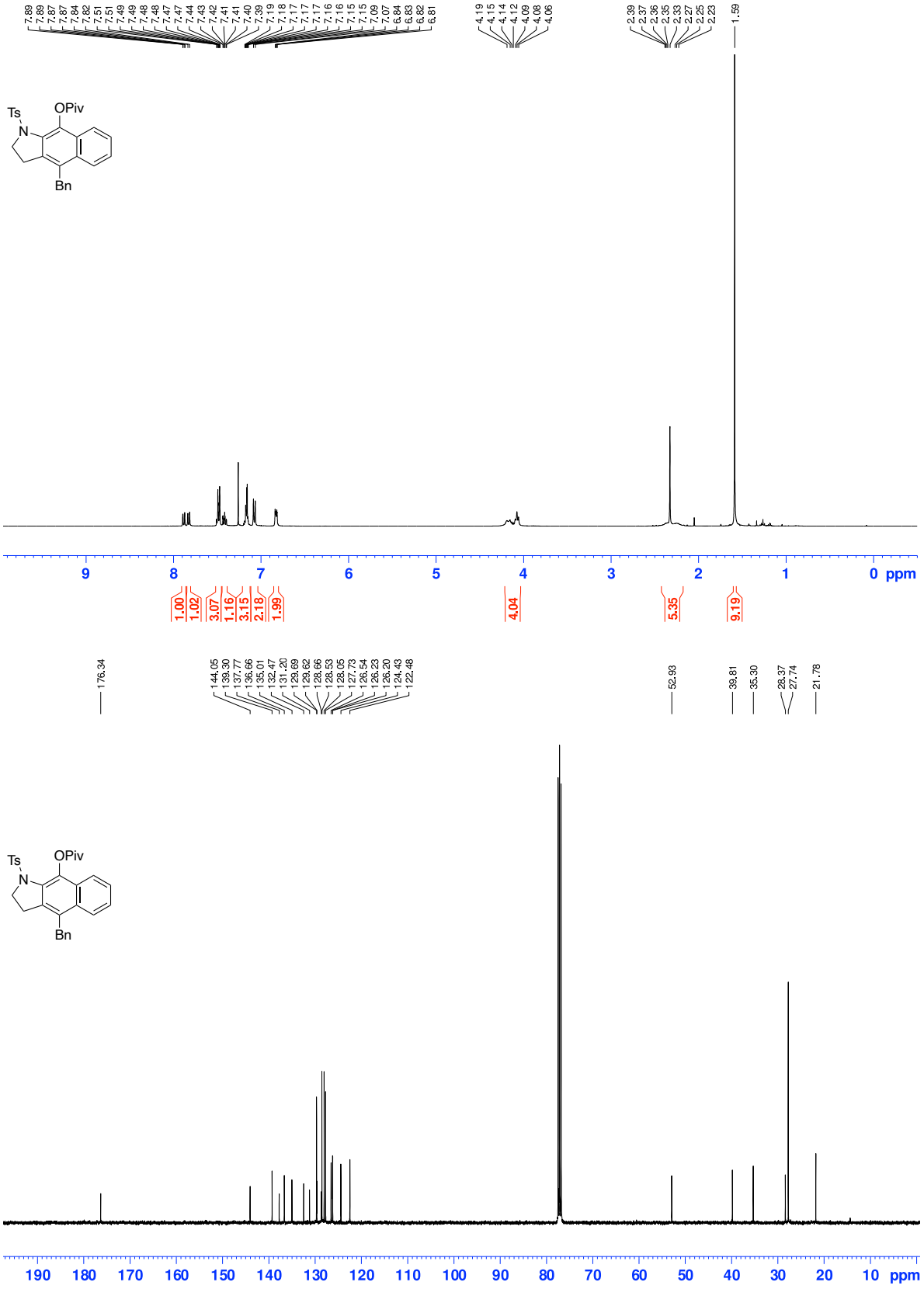


Figure S18. ^{1}H NMR and ^{13}C NMR spectra of 4-benzyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl benzoate (**2c**)

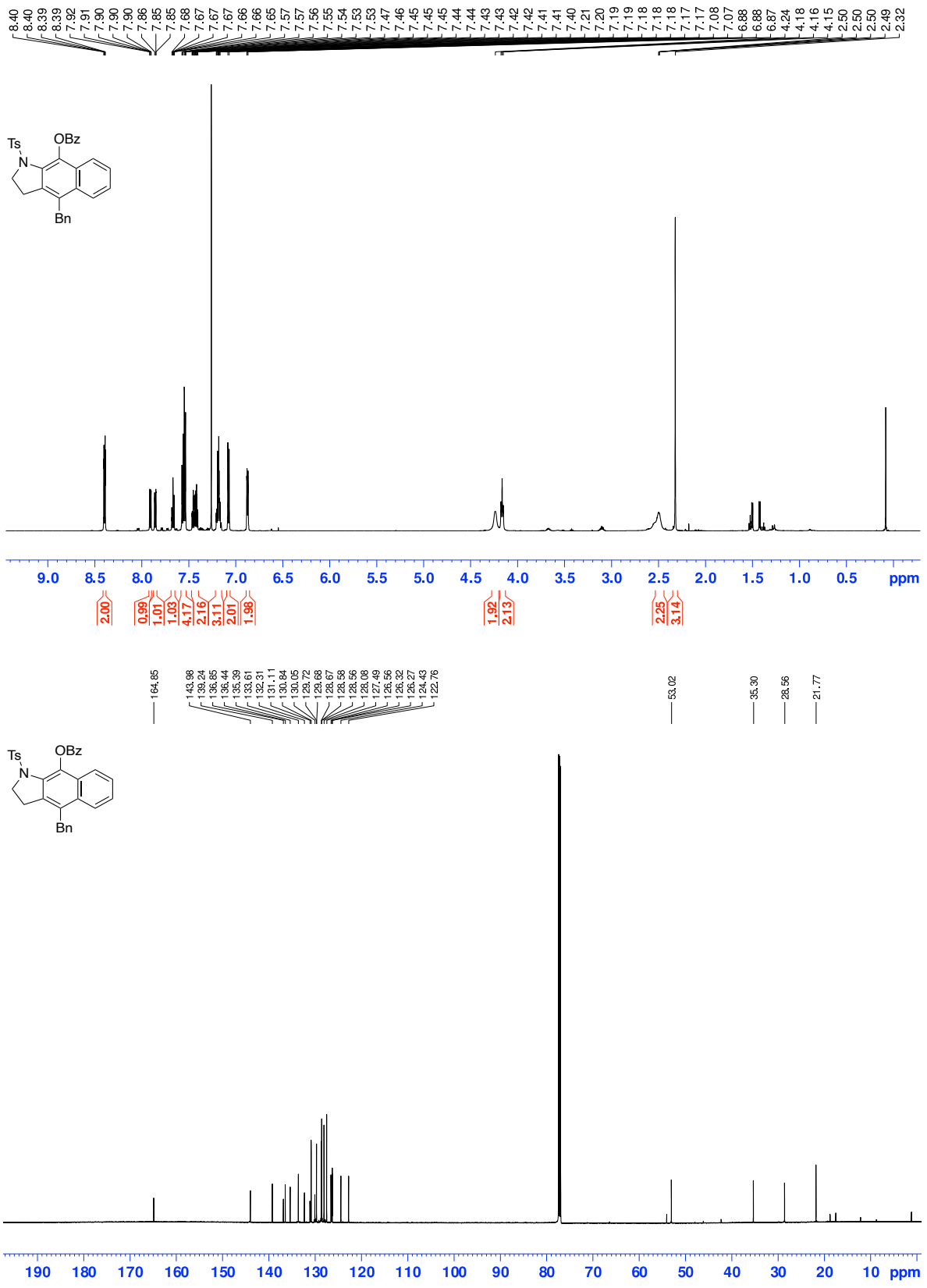
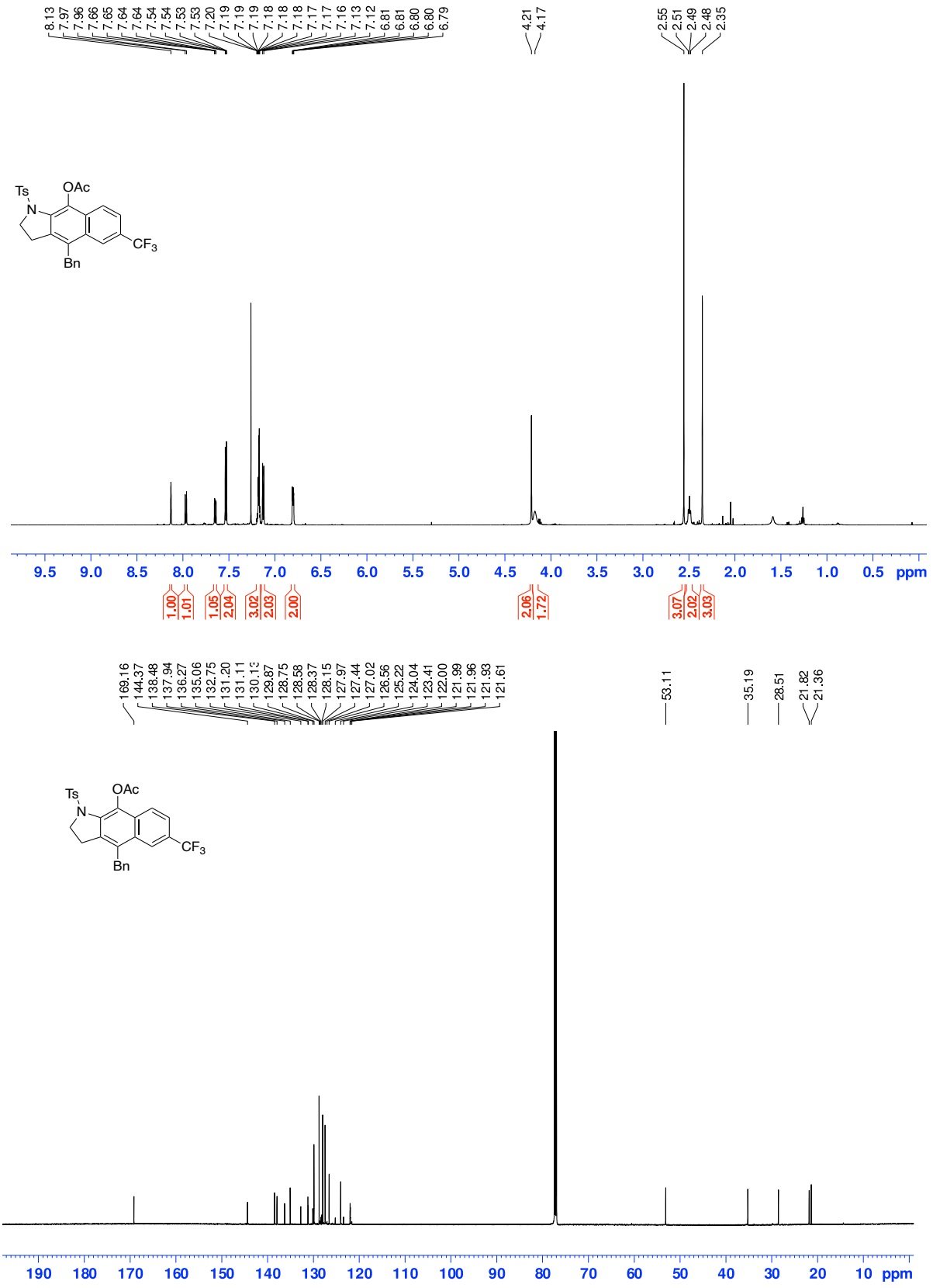


Figure S19. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of 4-benzyl-1-tosyl-6-(trifluoromethyl)-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2d**)



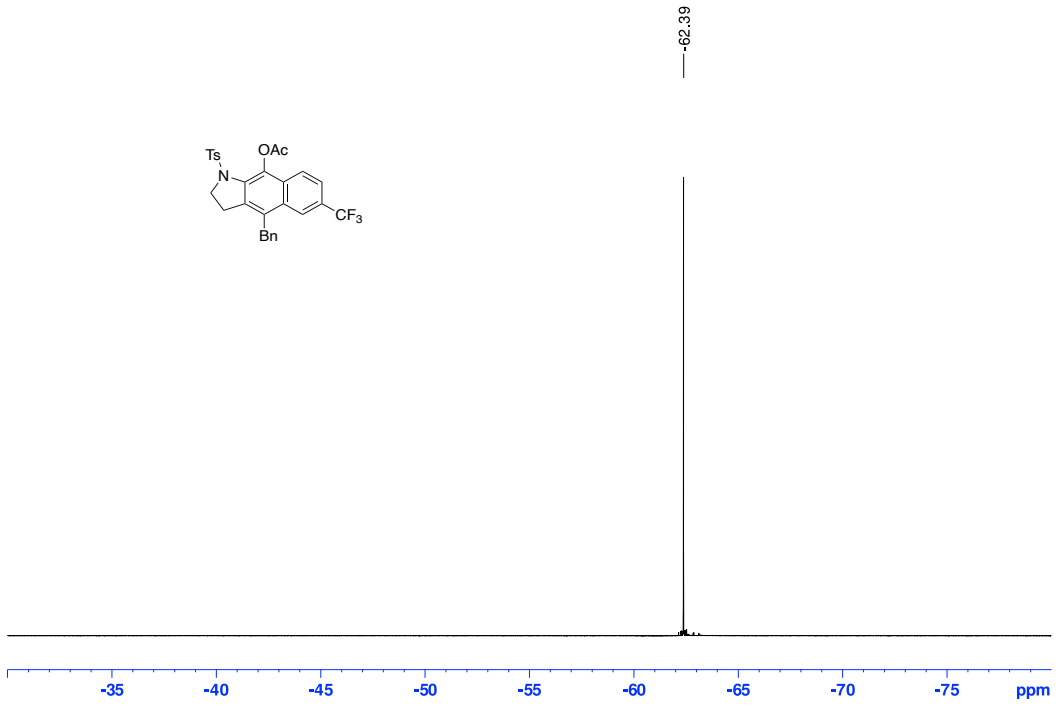

-62.39
Ts
N
OAc
Bn
CF3
-35
-40
-45
-50
-55
-60
-65
-70
-75
ppm

Figure S20. ^{1}H NMR and ^{13}C NMR spectra of 4-benzyl-6-chloro-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2e**)

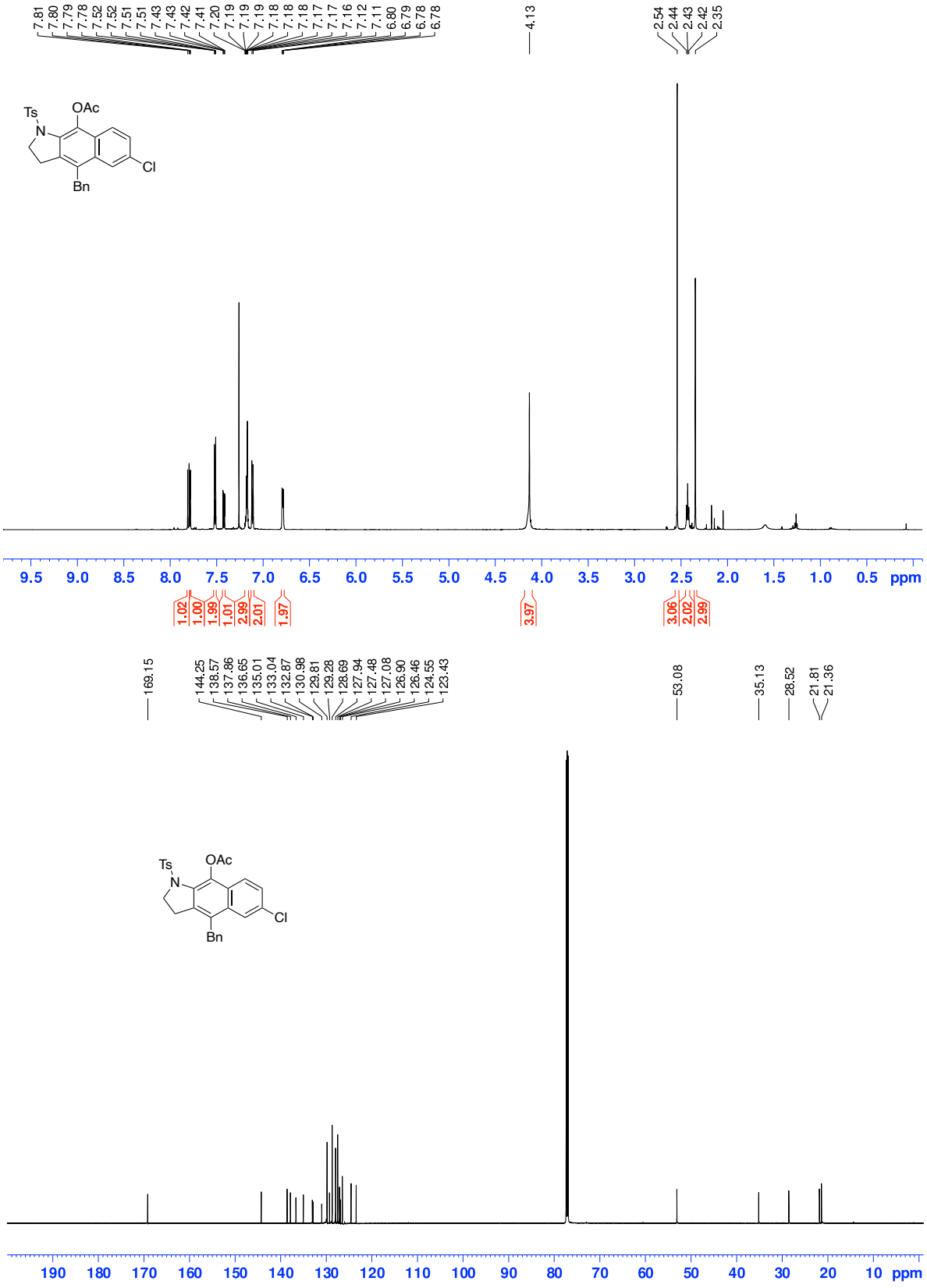


Figure S21. ^{1}H NMR and ^{13}C NMR spectra of 4-benzyl-6-methyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2f**)

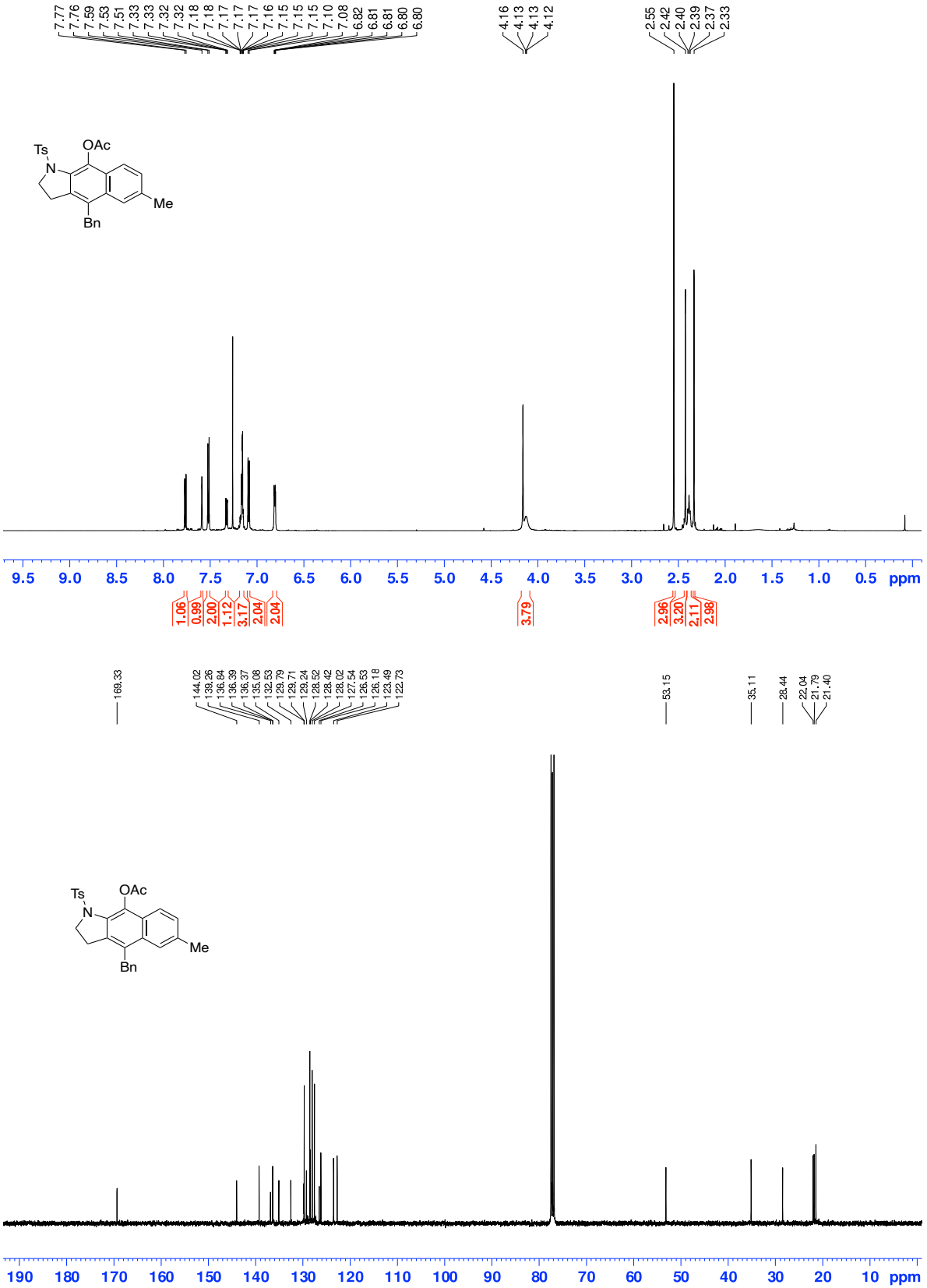


Figure S22. ^{1}H NMR and ^{13}C NMR spectra of 4-benzyl-6-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2g**)

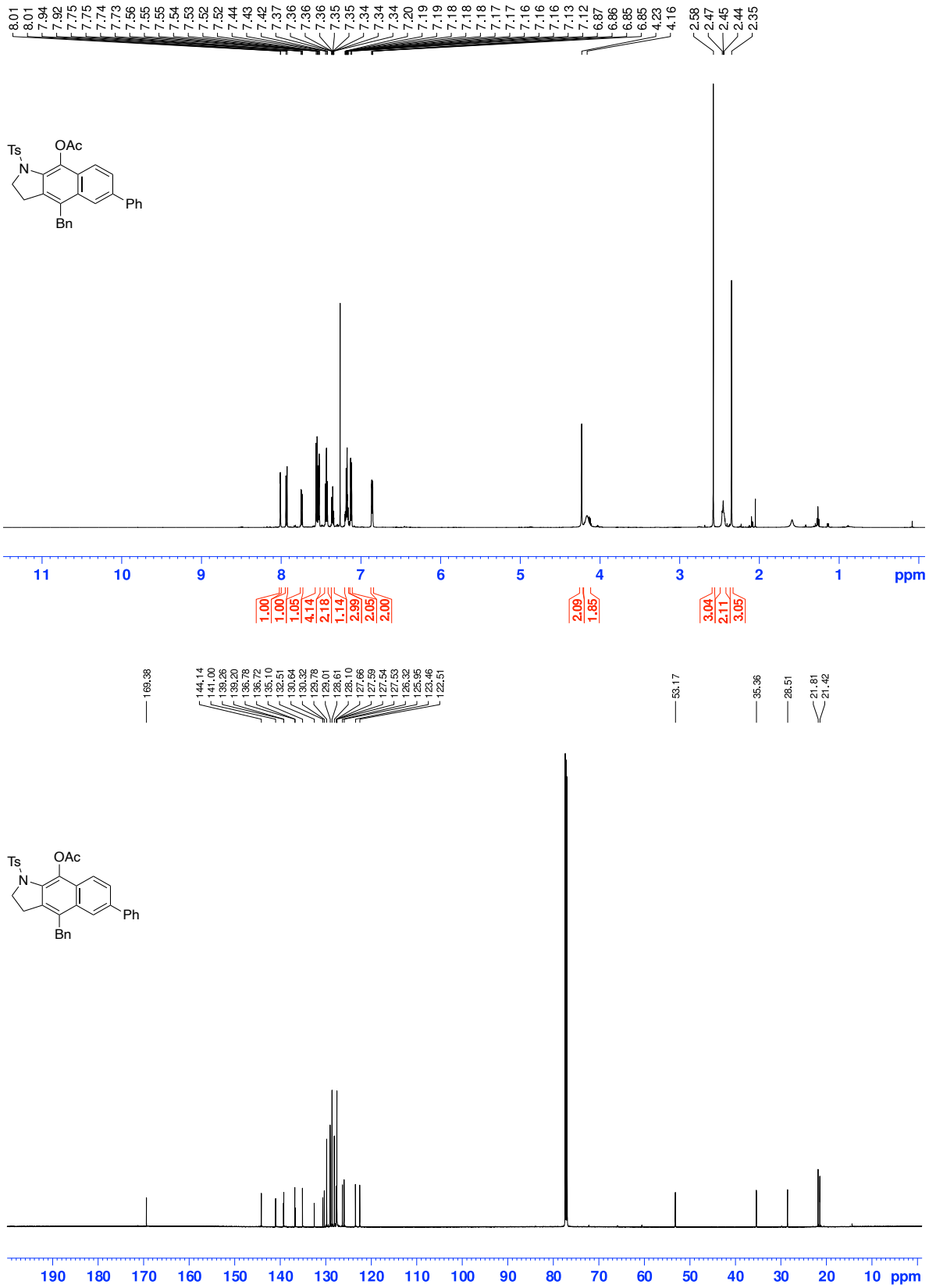


Figure S23. ^{1}H NMR and ^{13}C NMR spectra of 4-benzyl-6-(*tert*-butyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2h**)

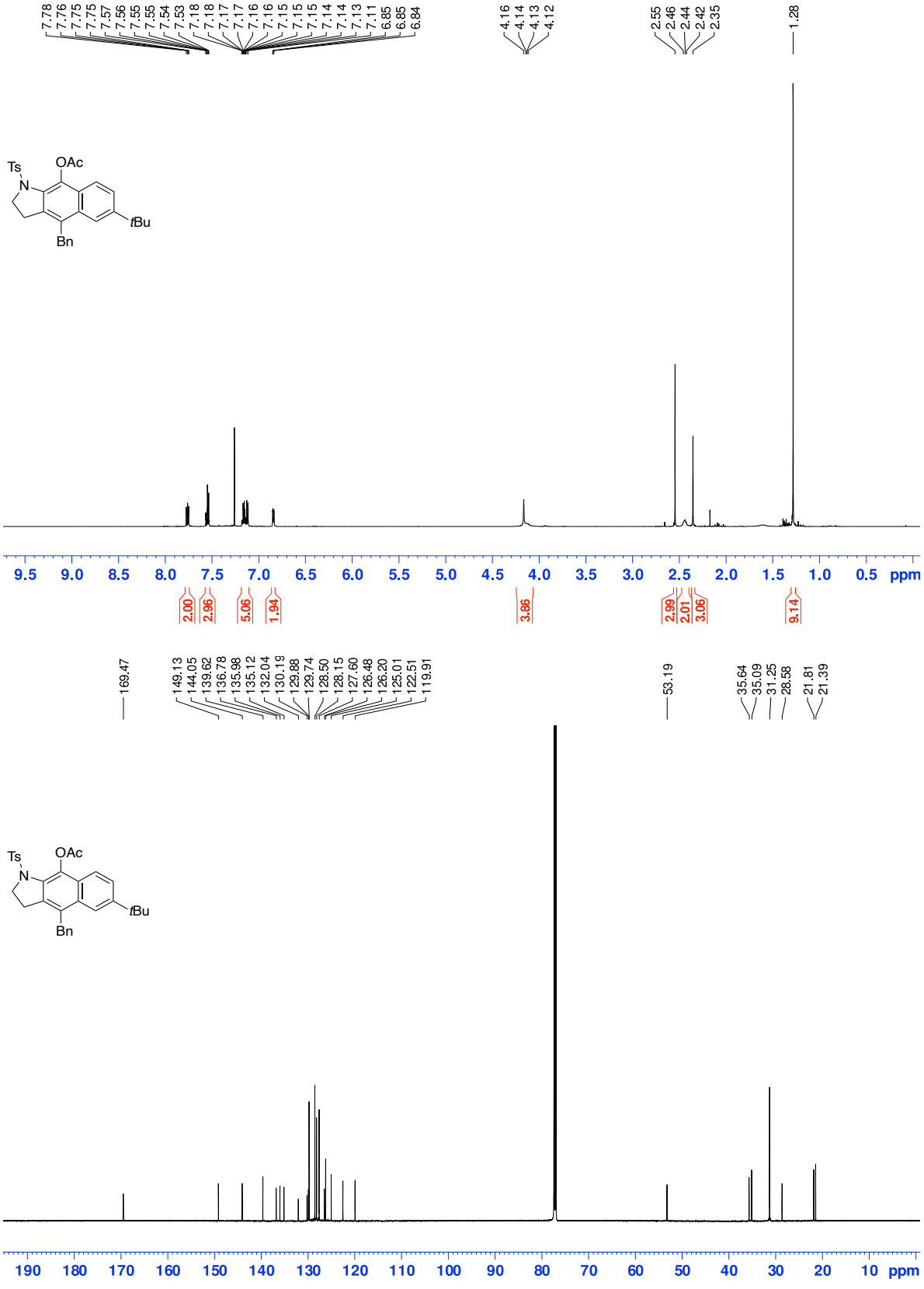


Figure S24. ^{1}H NMR and ^{13}C NMR spectra of 4-benzyl-6-methoxy-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2i**)

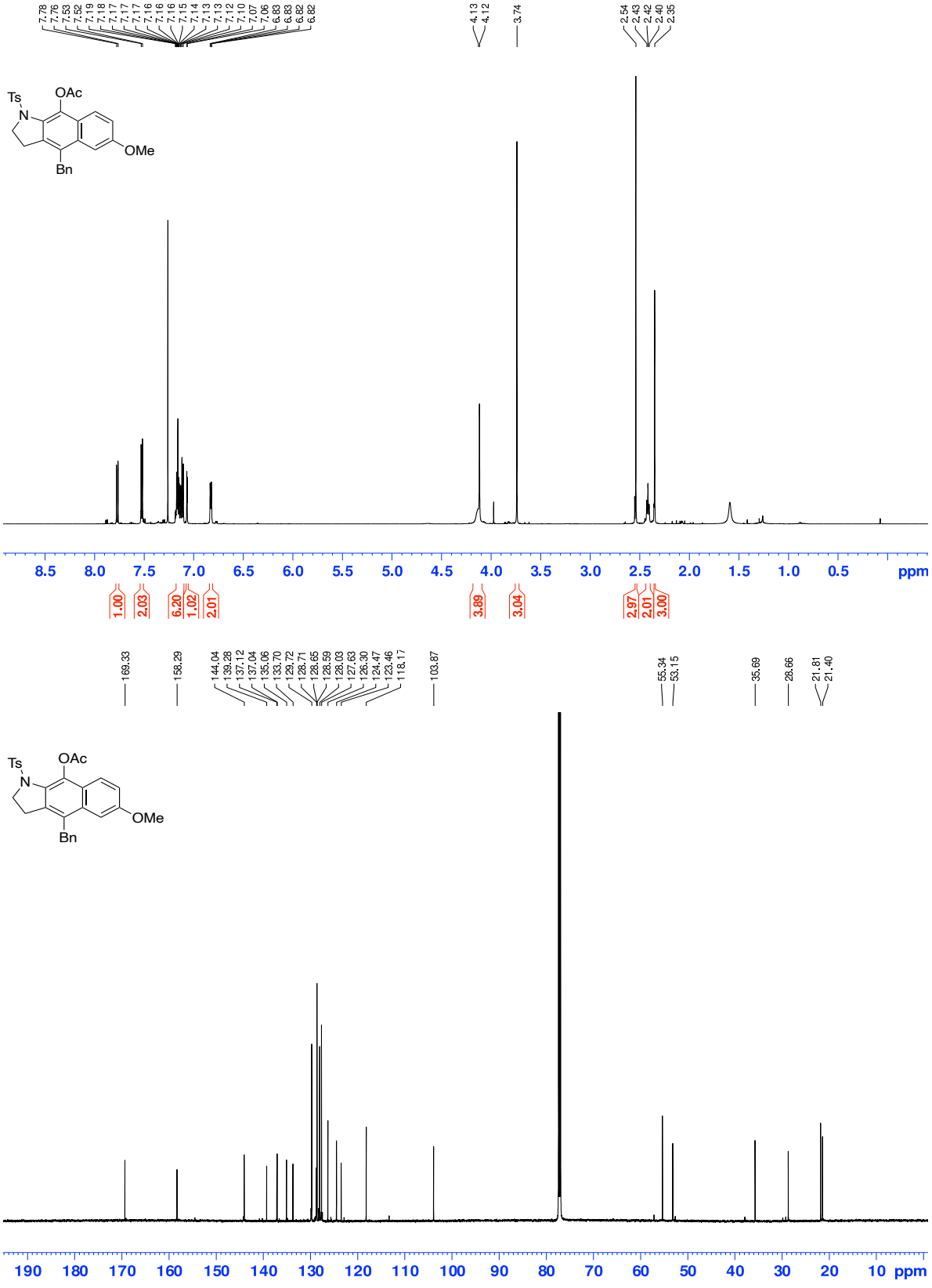
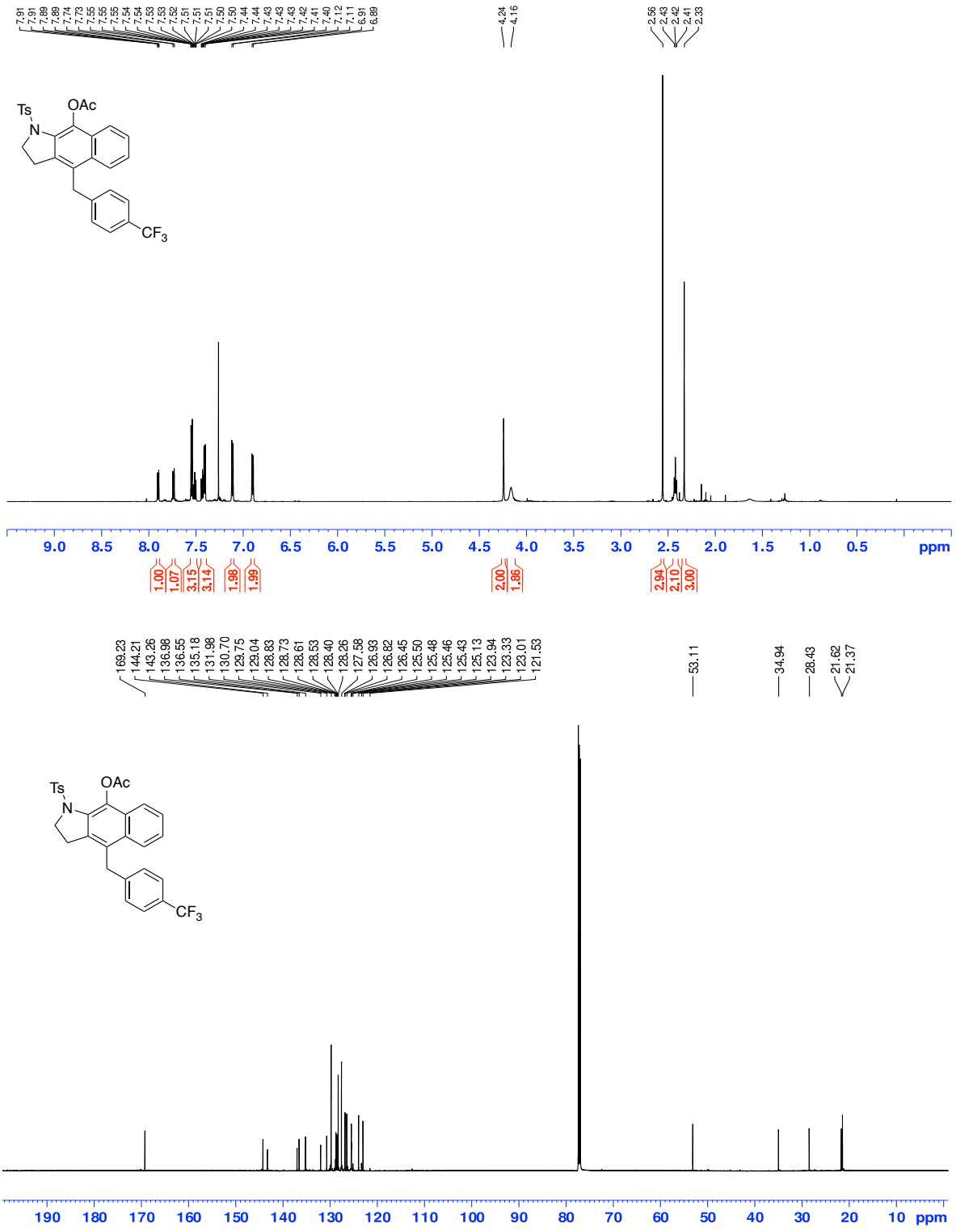
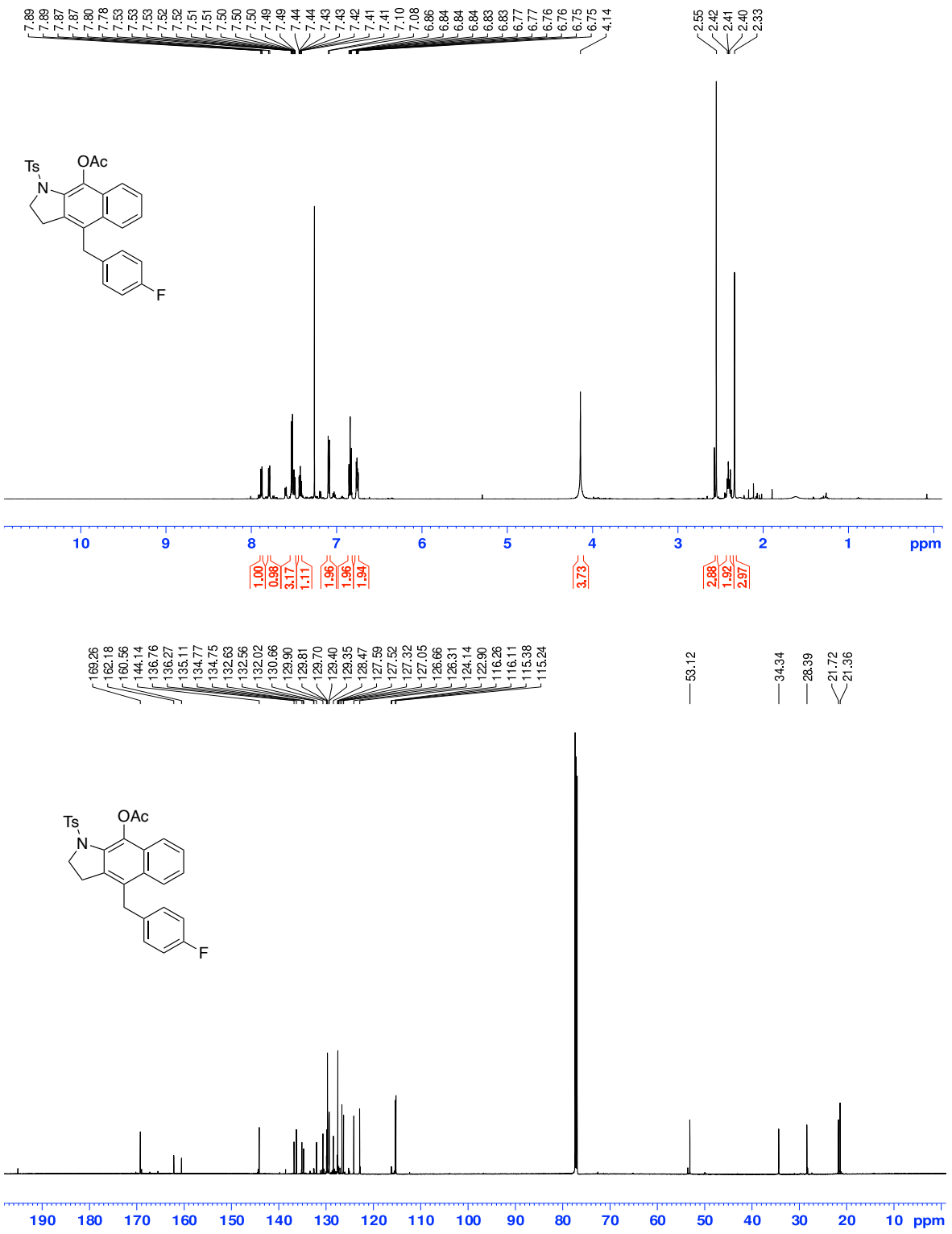


Figure S25. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of 1-tosyl-4-(4-(trifluoromethyl)benzyl)-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2j**)




-62.45
Ts
N
OAc
CF3
-35
-40
-45
-50
-55
-60
-65
-70
-75
ppm

Figure S26. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of 4-(4-fluorobenzyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2k**)



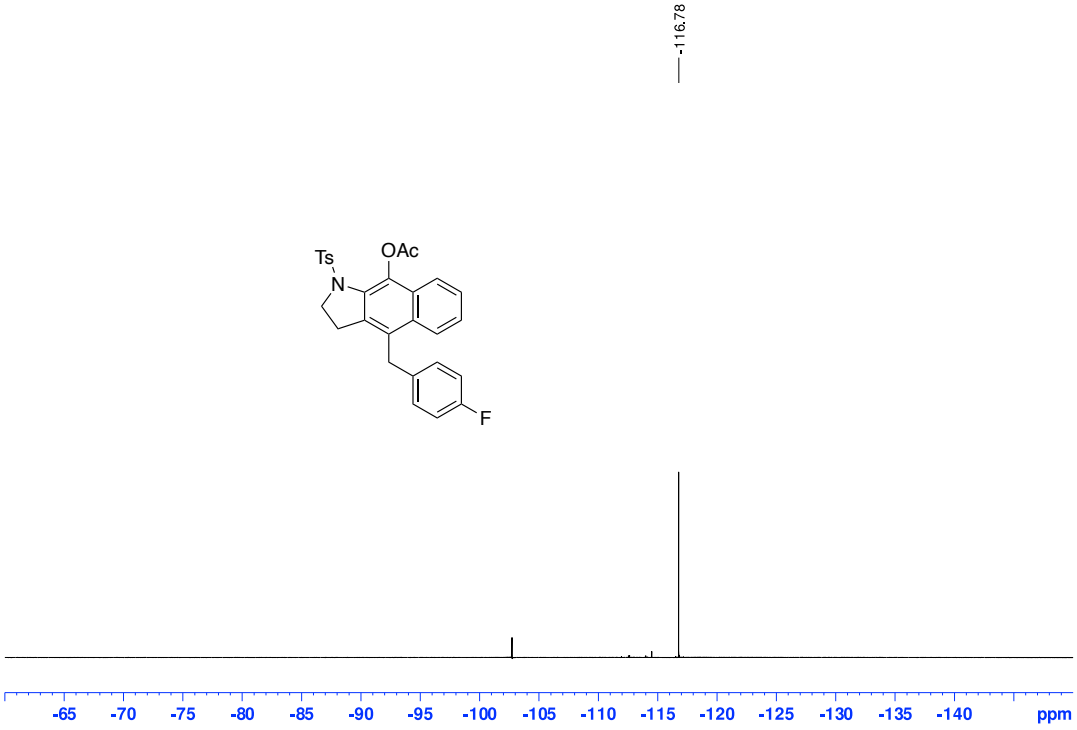

-116.78
Ts
N
OAc
F
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
ppm

Figure S27. ^{1}H NMR and ^{13}C NMR spectra of 4-(4-methylbenzyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2l**)

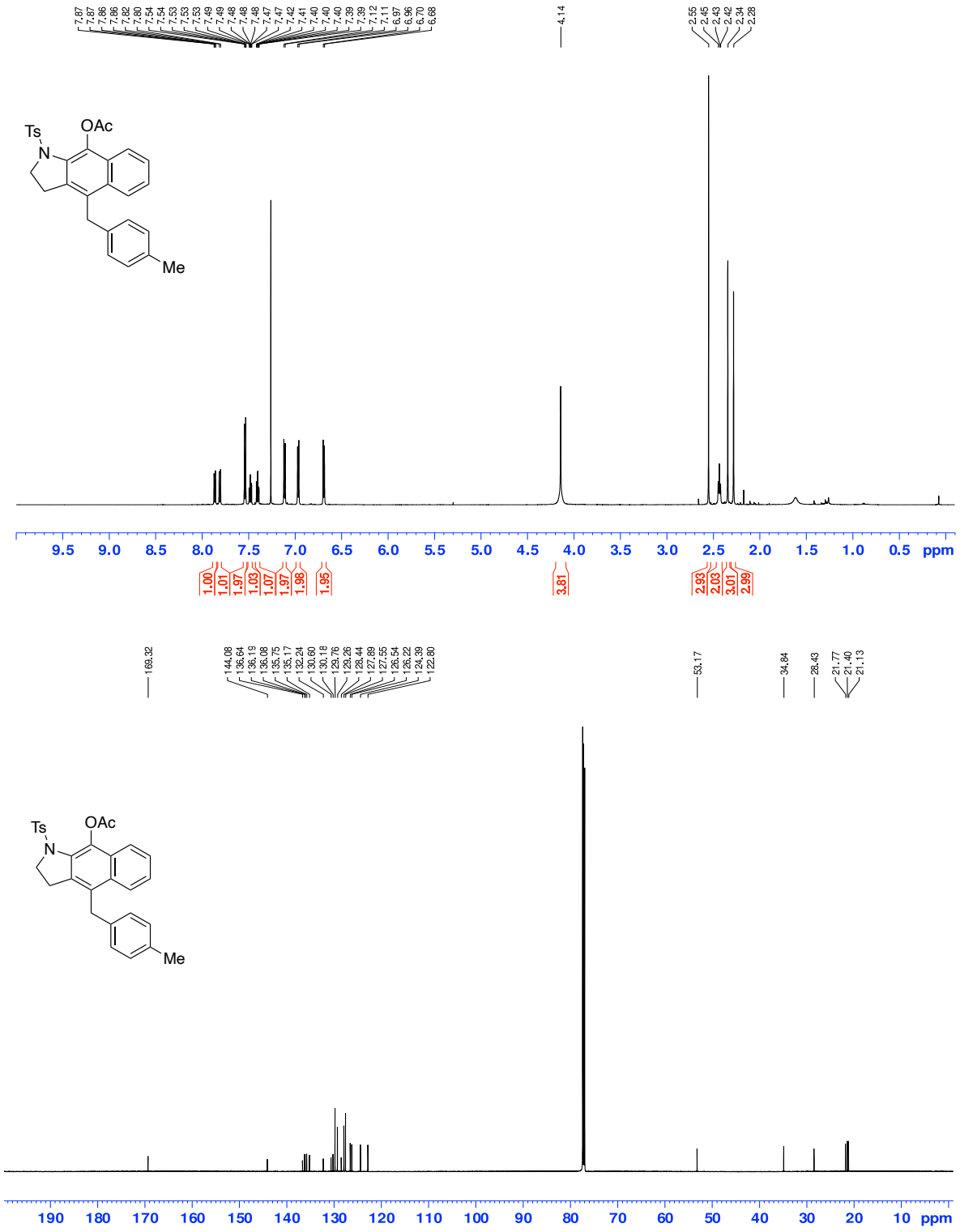


Figure S28. ^{1}H NMR and ^{13}C NMR spectra of 4-(4-methoxybenzyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2m**)

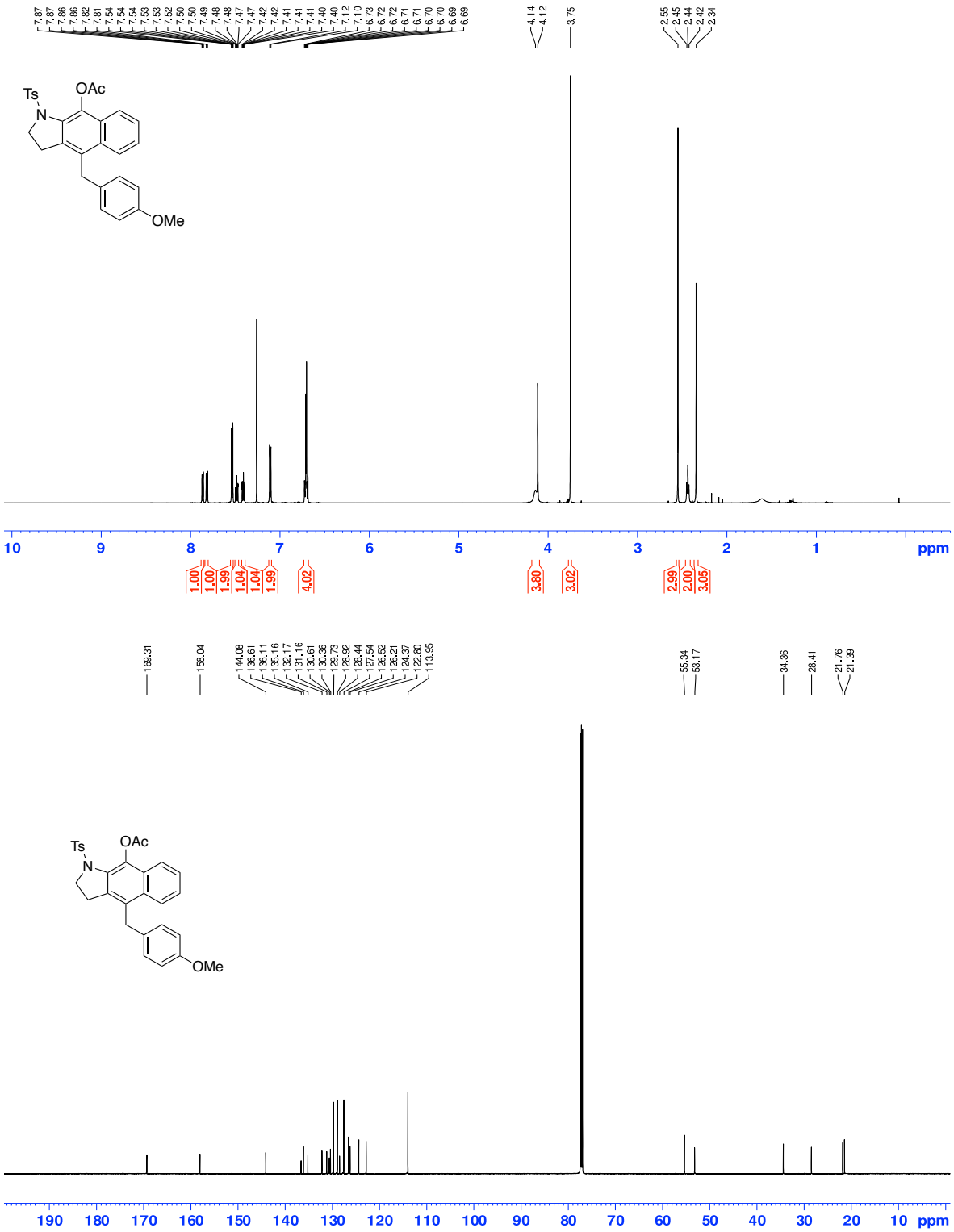
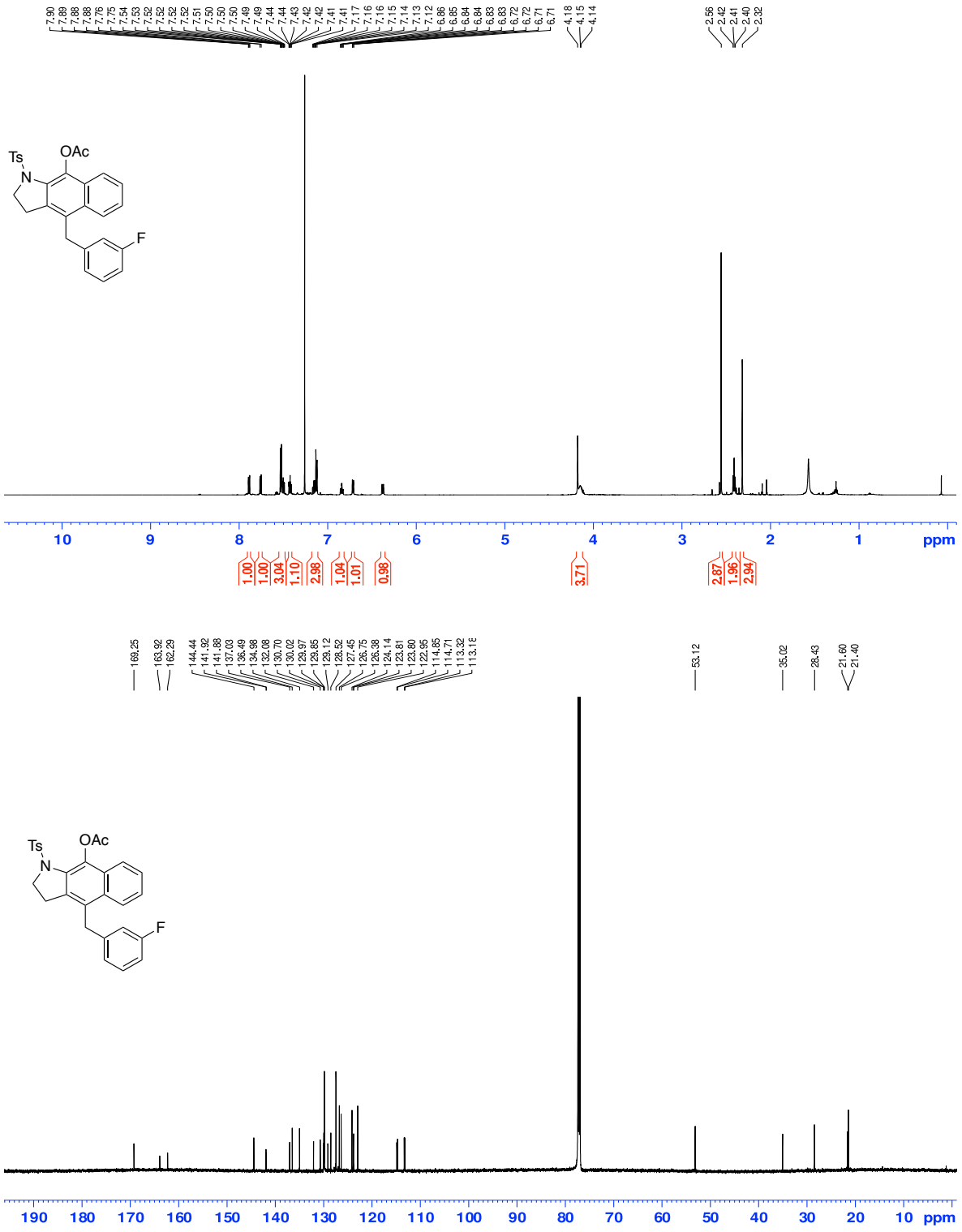


Figure S29. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of 4-(3-fluorobenzyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2n**)



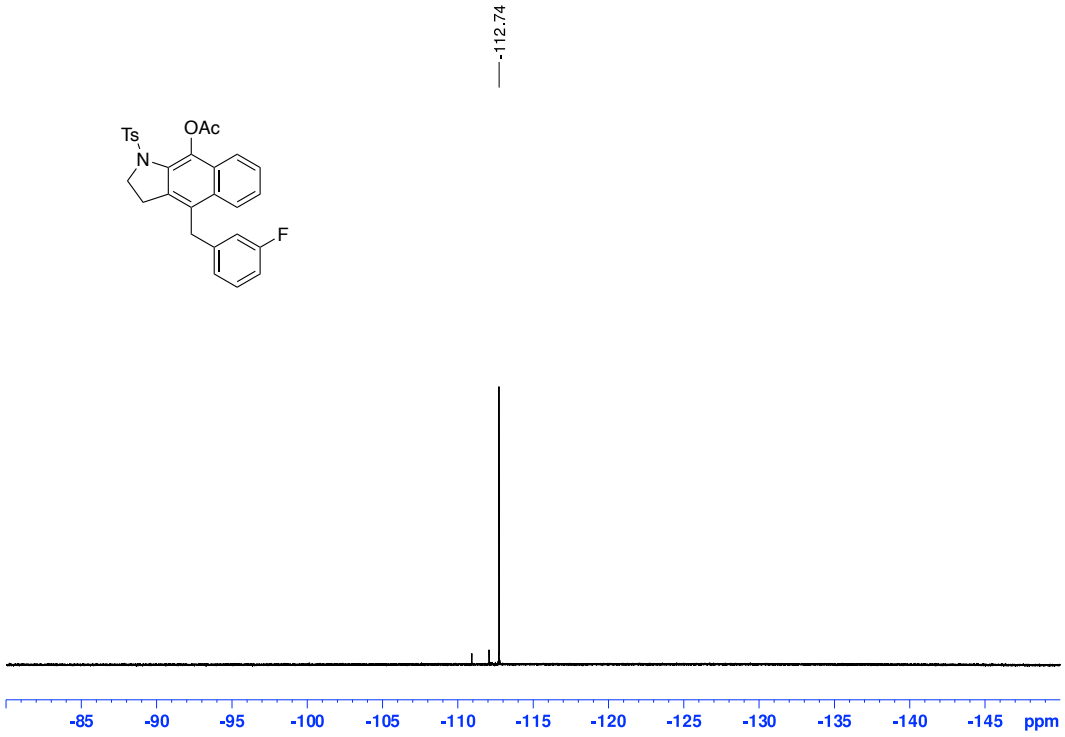

-112.74
Ts
N
OAc
F
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
ppm

Figure S30. ^{1}H NMR and ^{13}C NMR spectra of 4-(naphthalen-2-ylmethyl)-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-9-yl acetate (**2o**)

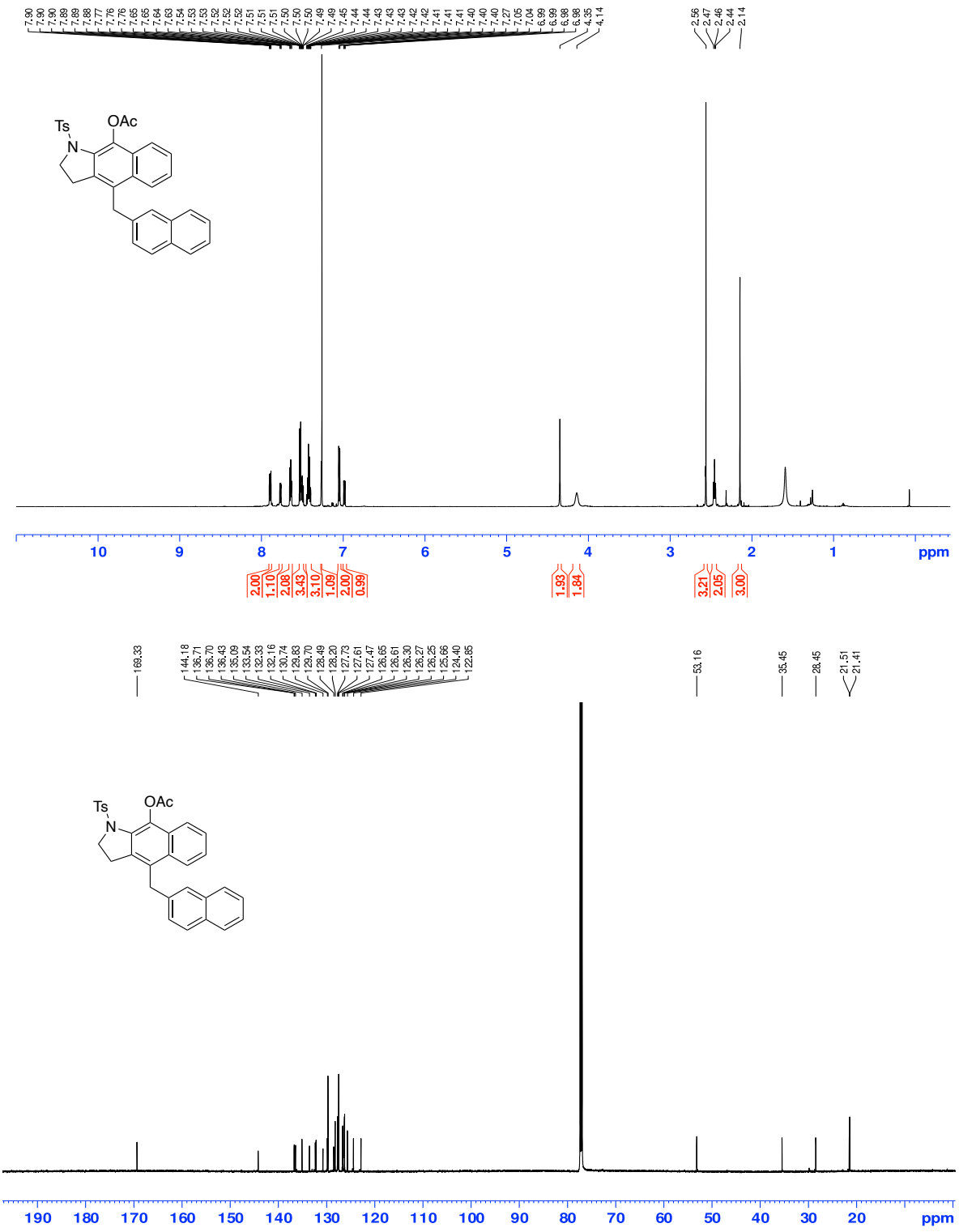
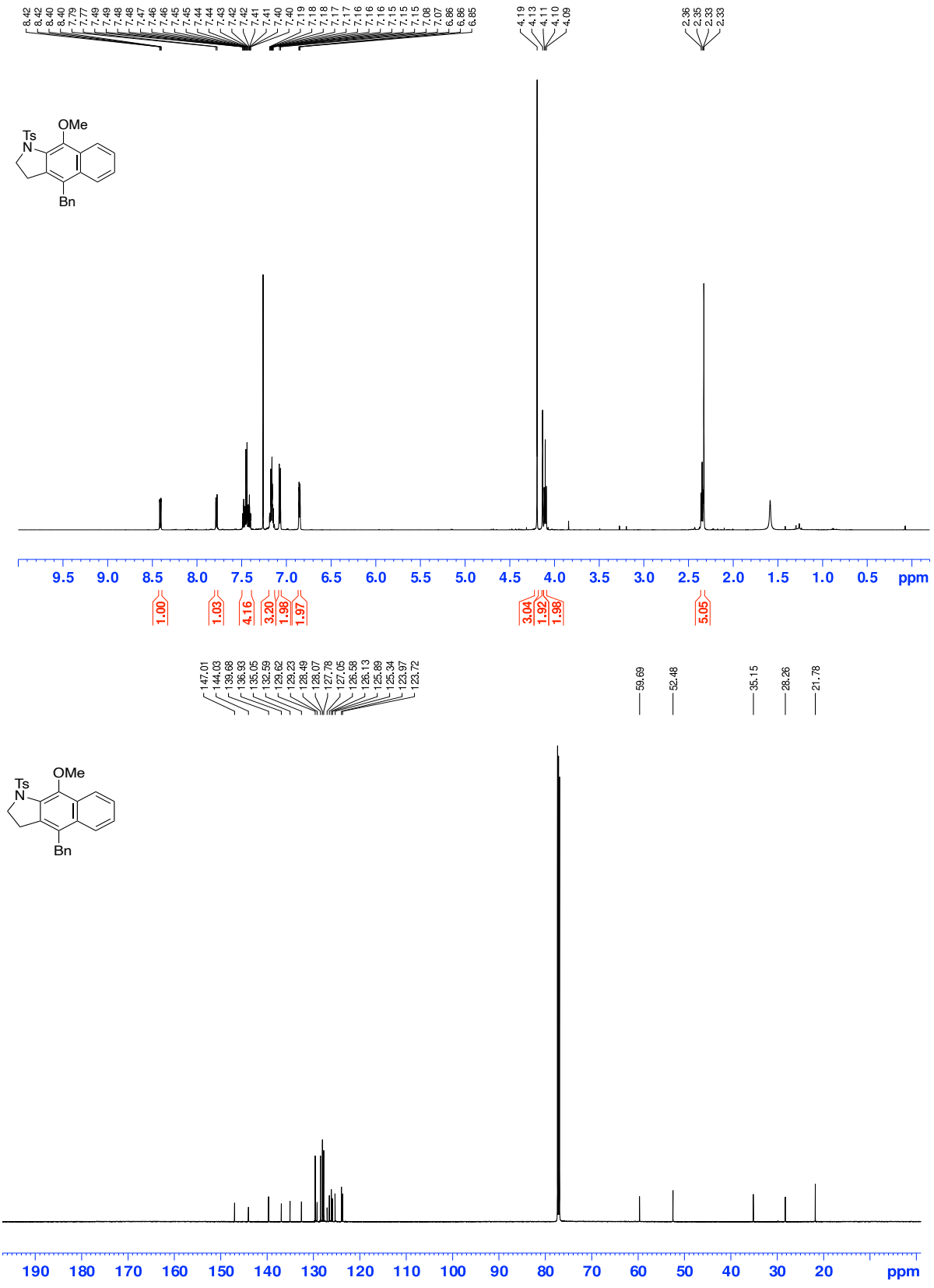
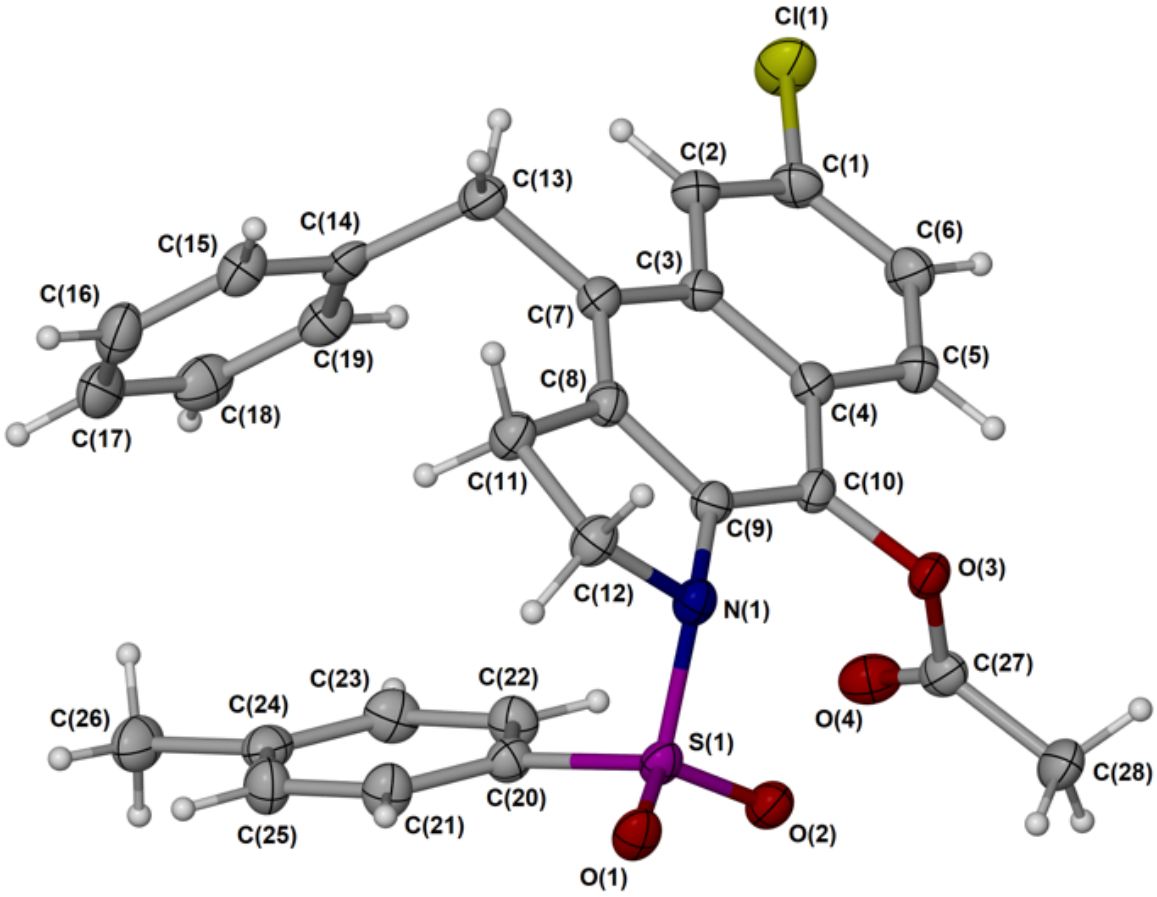


Figure S31. ^{1}H NMR and ^{13}C NMR spectra of 4-Benzyl-9-methoxy-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indole (**3a**)



7. X-Ray crystal structure drawing

Figure S32. X-Ray crystal structure drawing of **2e**



8. References

S1. Y. Liu, Y. Huang, H. Song, Y. Liu, and Q. Wang, *Chem. Eur. J.,* 2015, **21**, 5337–5340.

S2. X. Chen, J. T. Merrett and P. W. H. Chan, *Org. Lett.,* 2018, **20**, 1542–1545.