Electronic supplementary information

Ortho-allylation of anilines with vinylaziridines in hexafluoroisopropanol

Jing-Jing Nie and Zhong-Xia Wang

CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: zxwang@ustc.edu.cn

Contents

1. General Information

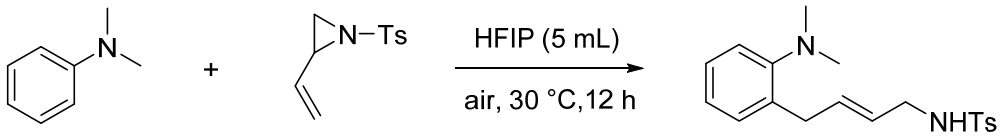
Unless otherwise noted, all reactions were performed in air. Solvents TFE, HFIP, MeOH, THF and DCE were purchased from commercial vendors and degassed prior to use in the process of screening reaction conditions. In the stage of the substrate expansion the purchased HFIP was directly used. The anilines used were purchased from commercial vendors or prepared according to literature.[1] *N*-Allyl-*N*,*N*-dimethylbenzenaminium bromide[2] and vinylaziridines[3] were prepared according to the reported methods. All other chemicals were purchased from commercial vendors and used as received. NMR spectra were recorded on a Bruker ARX400 or Bruker AV500 spectrometer. The chemical shifts of the ^{1}H NMR spectra were referenced to TMS or residual protiated solvent and the chemical shifts of the ^{13}C{^{1}H} NMR spectra were referenced to internal solvent resonances. High resolution mass spectra (HRMS) were performed on Waters XEVO G2 Q-TOF mass spectrometer.

2. Reaction of anilines with 2-vinylaziridines in HFIP

2.1 General procedure

Aniline **1** (0.2 mmol), 2-vinylaziridine **2** (0.3 mmol) and HFIP (1.5 mL) were successively added into a Schlenk tube. The mixture was stirred at 30 °C (oil bath) for 12 hours and then concentrated by rotatory evaporation. The residue was purified by column chromatography to afford the desired product.

2.2 Gram-scale preparation

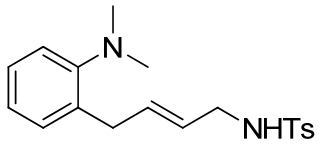


1a (3 mmol) **2a** (4.5 mmol) **3a** 0.884 g, 86%

N,N-Dimethylaniline **1a** (3.0 mmol), 1-tosyl-2-vinylaziridine **2a** (4.5 mmol) and HFIP (5.0 mL) were successively added into a Schlenk tube. The mixture was stirred at 30 °C (oil bath) for 12 hours and then concentrated by rotatory evaporation. The residue was purified by column chromatography (eluent: petroleum ether/ethyl acetate 5:1) to afford the product **3a**, yield 0.884 g (86%).

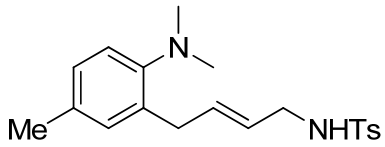
2.3 Characterization data

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3a**)



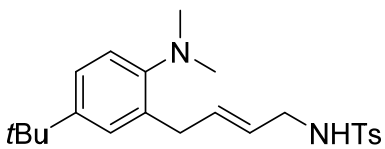
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 58.5 mg (85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13–7.06 (m, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 5.67 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.33 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.40 (t, *J* = 6.2 Hz, 1H), 3.49 (t, *J* = 6.3 Hz, 2H), 3.31 (d, *J* = 6.6 Hz, 2H), 2.56 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.6, 143.5, 137.2, 134.12, 134.09, 130.2, 129.8, 127.3, 127.2, 125.8, 123.4, 119.5, 45.5, 45.2, 33.4, 21.7. HRMS (ESI): calcd. for $C_{19}H_{25}N_2O_2S$ $[M+H]^+$ 345.1631, found 345.1648.

(E)-N-(4-(2-(dimethylamino)-5-methylphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3b**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 65.2 mg (91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 2H), 6.79 (s, 1H), 5.67 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.33 (dt, *J* = 15.2, 6.5 Hz, 1H), 4.33 (s, 1H), 3.49 (t, *J* = 6.3 Hz, 2H), 3.28 (d, *J* = 6.6 Hz, 2H), 2.53 (s, 6H), 2.35 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.5, 137.1, 134.3, 134.2, 133.0, 130.8, 129.8, 127.78, 127.3, 125.6, 119.5, 45.5, 45.4, 33.4, 21.7, 20.9. HRMS (ESI): calcd. for $C_{20}H_{26}N_2O_2S$ $[M+H]^+$ 359.1788, found 359.1797.

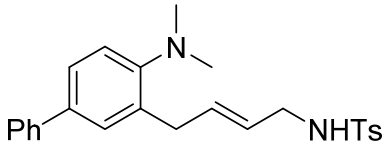
(E)-N-(4-(5-(*tert*-butyl)-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3c**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 76.0 mg (95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.69 (dt, *J* = 15.3, 6.6 Hz,

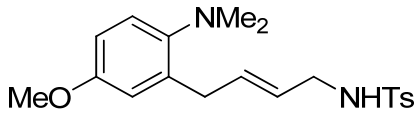
1H), 5.33 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.45 (t, *J* = 6.1 Hz, 1H), 3.48 (t, *J* = 6.2 Hz, 2H), 3.30 (d, *J* = 6.2 Hz, 2H), 2.53 (s, 6H), 2.33 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.0, 146.0, 143.5, 137.1, 134.4, 133.5, 129.8, 127.3, 127.2, 125.4, 123.9, 119.0, 45.5, 45.3, 34.3, 33.8, 31.6, 21.6. HRMS (ESI): calcd. for $C_{23}H_{33}N_2O_2S$ $[M+H]^+$ 401.2257, found 401.2259.

(E)-N-(4-(4-(dimethylamino)-[1,1'-biphenyl]-3-yl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3d**)



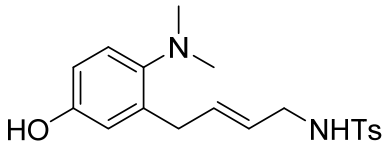
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 75.6 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.48–7.41 (m, 2H), 7.37–7.29 (m, 3H), 7.26–7.19 (m, 2H), 7.05 (d, *J* = 8.3 Hz, 1H), 5.70 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.38 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.44 (s, 1H), 3.49 (t, *J* = 5.4 Hz, 2H), 3.36 (d, *J* = 6.5 Hz, 2H), 2.59 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.0, 143.5, 141.1, 137.1, 136.1, 134.3, 134.0, 129.8, 129.0, 128.8, 127.3, 126.99, 126.96, 125.9, 125.8, 119.7, 45.5, 45.1, 33.7, 21.6. HRMS (ESI): calcd. for $C_{25}H_{28}N_2O_2S$ $[M+Na]^+$ 443.1764, found 443.1776.

(E)-N-(4-(2-(dimethylamino)-5-methoxyphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3e**)



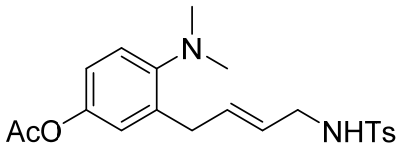
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 64.4 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.65 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.55 (d, *J* = 3.0 Hz, 1H), 5.65 (dt, *J* = 15.2, 6.4 Hz, 1H), 5.33 (dt, *J* = 15.4, 6.3 Hz, 1H), 4.42 (t, *J* = 5.8 Hz, 1H), 3.68 (s, 3H), 3.52–3.44 (m, 2H), 3.30 (d, *J* = 6.4 Hz, 2H), 2.51 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.8, 145.9, 143.6, 137.0, 136.1, 133.9, 129.8, 127.3, 125.8, 120.7, 115.8, 111.7, 55.5, 45.8, 45.5, 33.4, 21.7. HRMS (ESI): calcd. for $C_{20}H_{27}N_2O_3S$ $[M+H]^+$ 375.1737, found 375.1753.

(E)-N-(4-(2-(dimethylamino)-5-hydroxyphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3f**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 51.5 mg (72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.67–6.57 (m, 2H), 5.61 (dt, *J* = 15.3, 6.8 Hz, 1H), 5.32 (dt, *J* = 15.2, 6.4 Hz, 1H), 5.26 (s, 1H), 3.49–3.39 (m, 2H), 3.28 (d, *J* = 6.4 Hz, 2H), 2.55 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.7, 136.8, 135.8, 133.5, 129.9, 129.86, 127.3, 126.3, 120.8, 116.9, 114.0, 45.9, 45.4, 33.0, 21.7. HRMS (ESI): calcd. for $C_{19}H_{24}N_2O_3S$ $[M+Na]^+$ 383.1400, found 383.1403.

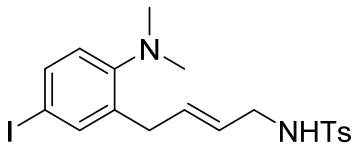
(E)-4-(dimethylamino)-3-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phenyl acetate (**3g**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 25.5 mg (32%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.69 (d, *J* = 2.8 Hz, 1H), 5.62 (dt, *J* = 15.3, 6.7 Hz, 1H), 5.35 (dt, *J* = 15.3, 6.4, 1.5 Hz, 1H), 4.48 (s, 1H), 3.53–3.44 (m, 2H), 3.29 (d, *J* = 6.7 Hz, 2H), 2.54 (s, 6H), 2.34 (s, 3H), 2.20 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.0, 146.4, 143.54, 137.1, 135.7, 133.3, 129.8, 127.3, 127.2, 126.4, 122.8, 120.3, 119.9, 45.4, 45.2, 33.3, 21.6, 21.3. HRMS (ESI): calcd. for $C_{21}H_{27}N_2O_4S$ $[M+H]^+$ 403.1686, found 403.1685.

This reaction also produced **3f** in 48% yield which can be separated from **3g** by column chromatography.

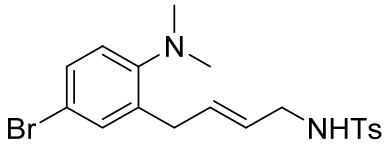
(E)-N-(4-(2-(dimethylamino)-5-iodophenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3h**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), yellow oil, yield 34.2 mg (36%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.38 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.28–7.20 (m, 3H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.61 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.34 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.36 (t, *J* = 6.3 Hz, 1H), 3.57–3.45 (m, 2H), 3.24 (d, *J* = 6.3 Hz, 2H), 2.54 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.6, 138.8, 137.1, 136.8, 136.1, 133.1, 129.9,

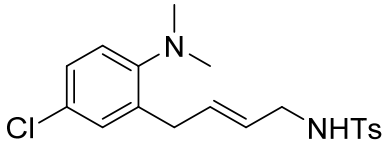
127.3, 126.0, 121.7, 45.4, 44.9, 33.2, 21.7. HRMS (ESI): calcd. for $C_{19}H_{23}IN_2O_2S$ $[M+Na]^+$ 493.0417, found 493.0454.

(E)-N-(4-(5-bromo-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3i**)



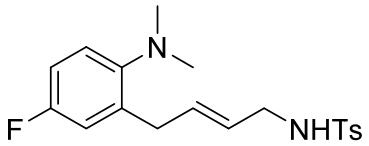
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 75.1 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.18 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 5.61 (dtt, *J* = 15.3, 6.6, 1.3 Hz, 1H), 5.33 (dtt, *J* = 15.3, 6.3, 1.5 Hz, 1H), 4.51 (t, *J* = 6.2 Hz, 1H), 3.51 (tq, *J* = 6.3, 1.5 Hz, 2H), 3.25 (d, *J* = 6.5 Hz, 2H), 2.53 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.7, 143.6, 137.0, 136.4, 132.9, 132.8, 130.0, 129.8, 127.3, 126.5, 121.2, 116.1, 45.3, 45.0, 33.2, 21.7. HRMS (ESI): calcd. for $C_{19}H_{24}BrN_2O_2S$ $[M+H]^+$ 423.0736, found 423.0750.

(E)-N-(4-(5-chloro-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3j**)



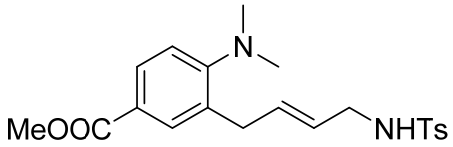
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 60.0 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.94–6.86 (m, 2H), 5.61 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.33 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.55 (t, *J* = 6.1 Hz, 1H), 3.50 (dt, *J* = 6.2, 1.4 Hz, 2H), 3.25 (d, *J* = 6.6 Hz, 2H), 2.52 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.2, 143.5, 137.1, 136.1, 132.9, 129.9, 129.8, 128.3, 127.3, 127.0, 126.5, 120.8, 45.3, 45.1, 33.2, 21.6. HRMS (ESI): calcd. for $C_{19}H_{24}ClN_2O_2S$ $[M+H]^+$ 379.1242, found 379.1247.

(E)-N-(4-(2-(dimethylamino)-5-fluorophenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3k**)



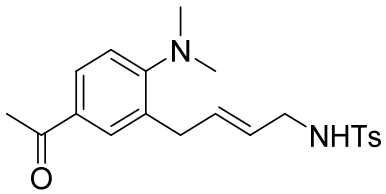
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 53.6 mg (74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.96 (dd, *J* = 8.8, 5.3 Hz, 1H), 6.76 (dt, *J* = 8.4, 3.1 Hz, 1H), 6.64 (dd, *J* = 9.5, 3.1 Hz, 1H), 5.62 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.33 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.64–4.40 (m, 1H), 3.50 (t, *J* = 6.3 Hz, 2H), 3.28 (d, *J* = 6.6 Hz, 2H), 2.51 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1 (d, *J* = 241.7 Hz), 148.7, 143.6, 137.2, 136.8 (d, *J* = 7.2 Hz), 133.1 (d, *J* = 3.0 Hz), 129.8, 127.3, 126.4, 120.9 (d, *J* = 8.3 Hz), 116.4 (d, *J* = 22.0 Hz), 113.4 (d, *J* = 21.8 Hz), 45.5, 45.3, 33.3, 21.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ –119.90. HRMS (ESI): calcd. for $C_{19}H_{24}FN_2O_2S$ $[M+H]^+$ 363.1537, found 363.1543.

methyl (E)-4-(dimethylamino)-3-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)benzoate (**3l**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 71.6 mg (89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.70–7.58 (m, 3H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 5.65 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.36 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.64 (t, *J* = 6.3 Hz, 1H), 3.79 (s, 3H), 3.53–3.46 (m, 2H), 3.29 (d, *J* = 6.5 Hz, 2H), 2.63 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.2, 156.8, 143.5, 137.1, 133.0, 132.6, 131.9, 129.8, 128.8, 127.3, 126.5, 123.7, 118.3, 52.0, 45.3, 44.3, 33.9, 21.6. HRMS (ESI): calcd. for $C_{21}H_{26}N_2O_4S$ $[M+Na]^+$ 425.1505, found 425.1545.

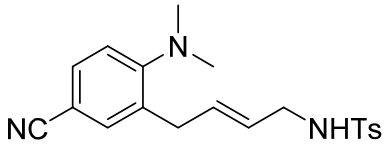
(E)-N-(4-(5-acetyl-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3m**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 62.6 mg (81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71–7.64 (m, 3H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.67 (dt, *J* = 15.3, 6.4 Hz, 1H), 5.38 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.67 (t, *J* = 6.2 Hz, 1H), 3.50 (t, *J* = 6.2 Hz, 2H), 3.29 (d, *J* = 6.5 Hz, 2H), 2.65 (s, 6H), 2.44 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.4, 157.1, 143.5, 137.1, 132.9, 132.5,

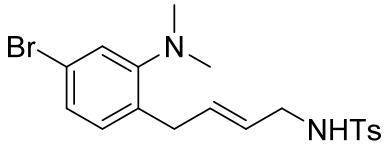
131.2, 130.9, 129.8, 128.0, 127.2, 126.7, 118.0, 45.3, 44.2, 34.1, 26.5, 21.6. HRMS (ESI): calcd. for $C_{21}H_{27}N_2O_3S$ $[M+H]^+$ 387.1737, found 387.1746.

(E)-N-(4-(5-cyano-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3n**)



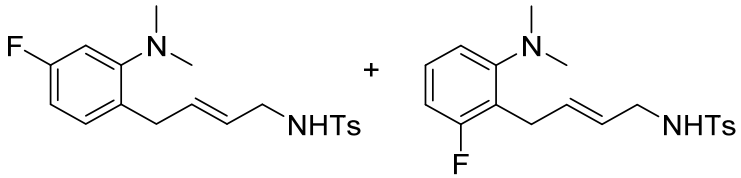
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 47.1 mg (64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.60 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.38 (dt, *J* = 15.3, 6.2 Hz, 1H), 4.76 (t, *J* = 6.2 Hz, 1H), 3.56–3.47 (m, 2H), 3.26 (d, *J* = 6.5 Hz, 2H), 2.65 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.4, 143.6, 137.1, 134.1, 133.6, 131.9, 131.2, 129.8, 127.4, 127.2, 119.7, 118.9, 104.8, 45.2, 44.0, 33.7, 21.6. HRMS (ESI): calcd. for $C_{20}H_{23}N_3O_2S$ $[M+Na]^+$ 392.1403, found 392.1412.

(E)-N-(4-(4-bromo-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3o**)



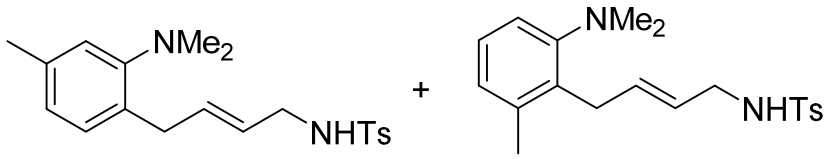
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 43.1 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 5.62 (dtt, *J* = 15.3, 6.5, 1.3 Hz, 1H), 5.33 (dtt, *J* = 15.3, 6.3, 1.5 Hz, 1H), 4.41 (t, *J* = 6.2 Hz, 1H), 3.55–3.44 (m, 2H), 3.23 (d, *J* = 6.3 Hz, 2H), 2.55 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 143.6, 137.1, 133.3, 132.9, 131.6, 129.8, 127.3, 126.3, 126.1, 122.8, 120.4, 45.3, 44.9, 33.1, 21.7. HRMS (ESI): calcd. for $C_{19}H_{23}BrN_2O_2S$ $[M+Na]^+$ 445.0556, found: 445.0579.

(E)-N-(4-(2-(dimethylamino)-4-fluorophenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3p**) and (E)-N-(4-(2-(dimethylamino)-6-fluorophenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3p′**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 58.2 mg (80%) as a mixture of **3p** and **3p′** (about 2.8:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 0.7H), 7.24–7.15 (m, 2.7H), 7.09–7.01 (m, 0.4H), 6.88 (dd, *J* = 8.3, 7.0 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 0.37H), 6.70–6.61 (m, 1.36H), 6.57 (dt, *J* = 8.1, 2.6 Hz, 1H), 5.74–5.57 (m, 1.4H), 5.37–5.20 (m, 1.4H), 4.47 (t, *J* = 6.2 Hz, 1H), 4.34 (t, *J* = 6.1 Hz, 0.37H), 3.53–3.47 (m, 2H), 3.47–3.42 (m, 0.74H), 3.31 (d, *J* = 5.9 Hz, 0.72H), 3.24 (d, *J* = 6.4 Hz, 2H), 2.55, 2.54 (s, s, 6H), 2.35, 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.3 (d, *J* = 244.7 Hz), 162.0 (d, *J* = 245.1 Hz), 154.7 (d, *J* = 7.4 Hz), 154.2 (d, *J* = 7.4 Hz), 143.6, 143.5, 137.2, 137.1, 133.8, 131.1 (d, *J* = 9.2 Hz), 129.82, 129.8, 129.2 (d, *J* = 3.2 Hz), 127.7 (d, *J* = 10.5 Hz), 127.27, 127.25, 126.0, 125.1, 121.2 (d, *J* = 15.8 Hz), 115.1 (d, *J* = 2.6 Hz), 110.2 (d, *J* = 23.3 Hz), 109.5 (d, *J* = 21.1 Hz), 106.6 (d, *J* = 21.9 Hz), 45.37, 45.35, 44.8, 32.9, 27.6, 27.5, 21.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ −114.64, −115.22. HRMS (ESI): calcd. for $C_{19}H_{23}FN_2O_2S$ $[M+Na]^+$ 385.1356, found 385.1378.

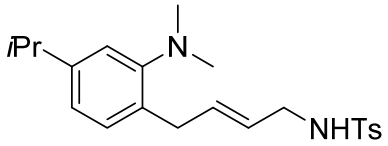
(E)-N-(4-(2-(dimethylamino)-4-methylphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3q**) and (E)-N-(4-(2-(dimethylamino)-6-methylphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3q′**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 57.4 mg (80%) as a mixture of **3q** and **3q′** (about 5:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.2 Hz, 1.27H), 7.69 (d, *J* = 8.2 Hz, 0.72H), 7.31–7.21 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 0.42H), 6.98 (d, *J* = 8.1 Hz, 0.42H), 6.91 (d, *J* = 7.6 Hz, 0.64H), 6.89–6.83 (m, 1H), 6.78 (d, *J* = 7.6 Hz, 0.63H), 5.76–5.63 (m, 1H), 5.38 (dt, *J* = 15.3, 6.4 Hz, 0.65H), 5.12 (dt, *J* = 15.3, 6.4 Hz, 0.39H), 4.65–4.43 (m, 1H), δ 3.53 (t, *J* = 6.2 Hz, 1.26H), 3.49 (t, *J* = 6.2 Hz, 0.76H), 3.44 (d, *J* = 5.7 Hz, 0.77H), 3.31 (d, *J* = 6.5 Hz, 1.30H), 2.60 (s, 3.67H), 2.57 (s, 2.31H), 2.404, 2.396 (s, s, 3H), 2.29 (s, 1.90H), 2.16 (s, 1.11H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.3, 152.4, 143.5, 138.2, 137.1, 137.0, 136.7, 134.3, 133.4, 133.0, 130.9, 130.0, 129.8, 127.3, 127.2, 126.9,

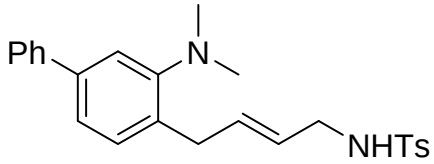
126.0, 125.5, 124.6, 124.0, 120.1, 117.8, 45.9, 45.5, 45.4, 45.1, 33.1, 30.5, 21.6, 21.3, 20.0. HRMS (ESI): calcd. for $C_{19}H_{22}F_2N_2O_2S$ $[M+Na]^+$ 403.1262, found 403.1262.

(E)-N-(4-(2-(dimethylamino)-4-isopropylphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3r**)



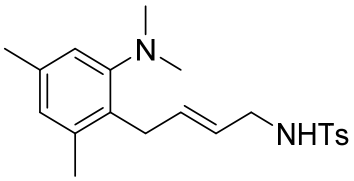
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 39.1 mg (53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.25–7.19 (m, 2H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.86 (s, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.67 (dt, *J* = 15.2, 6.6 Hz, 1H), 5.35 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.33 (s, 1H), 3.54–3.41 (m, 2H), 3.28 (d, *J* = 5.7 Hz, 2H), 2.84–2.72 (m, 1H), 2.57 (s, 6H), 2.35 (s, 3H), 1.16 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.0, 143.6, 137.1, 134.4, 131.3, 130.0, 129.8, 127.3, 125.6, 121.2, 117.6, 45.5, 45.2, 34.1, 33.2, 24.2, 21.7. HRMS (ESI): calcd. for $C_{22}H_{30}N_2O_2S$ $[M+Na]^+$ 493.0417, found 493.0454.

(E)-N-(4-(3-(dimethylamino)-[1,1'-biphenyl]-4-yl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3s**)



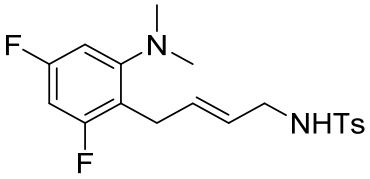
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 33.8 mg (40%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.51–7.45 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.29–7.18 (m, 4H), 7.13 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 5.69 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.38 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.52–4.39 (m, 1H), 3.54–3.45 (m, 2H), 3.34 (d, *J* = 6.6 Hz, 2H), 2.62 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 141.4, 140.3, 137.1, 134.0, 133.1, 130.6, 129.8, 128.9, 127.3, 127.2, 125.9, 122.1, 118.4, 45.5, 45.2, 33.3, 21.7. HRMS (ESI): calcd. for $C_{25}H_{28}N_2O_2S$ $[M+Na]^+$ 443.1764, found: 443.1776.

(E)-N-(4-(2-(dimethylamino)-4,6-dimethylphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3t**)



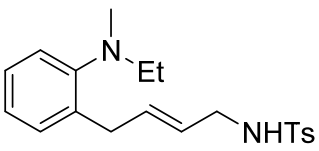
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 56.0 mg (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.73 (s, 1H), 6.64 (s, 1H), 5.61 (dt, *J* = 15.3, 5.5 Hz, 1H), 5.15 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.31 (s, 1H), 3.42 (t, *J* = 6.3 Hz, 2H), 3.33 (d, *J* = 5.7 Hz, 2H), 2.50 (s, 6H), 2.34 (s, 3H), 2.20 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.2, 143.5, 138.0, 137.1, 136.4, 133.7, 129.9, 129.8, 127.2, 126.9, 124.5, 118.5, 45.9, 45.5, 30.2, 21.6, 21.3, 20.0. HRMS (ESI): calcd for $C_{21}H_{29}N_2O_2S$ $[M+H]^+$ 373.1944, found 373.1953.

(E)-N-(4-(2-(dimethylamino)-4,6-difluorophenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3u**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 61.4 mg (81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.46 (d, *J* = 10.8 Hz, 1H), 6.40–6.31 (m, 1H), 5.65 (dt, *J* = 15.3, 6.1 Hz, 1H), 5.22 (dt, *J* = 15.3, 6.1 Hz, 1H), 4.56 (t, *J* = 6.3 Hz, 1H), 3.50–3.38 (m, 2H), 3.22 (d, *J* = 5.4 Hz, 2H), 2.53 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.3 (dd, *J* = 245.5, 14.7 Hz), 161.9 (dd, *J* = 245.8, 16.0 Hz), 155.4, 143.5, 137.0, 132.2, 129.8, 127.2, 125.3, 116.3 (dd, *J* = 16.5, 4.1 Hz), 102.4 (dd, *J* = 22.2, 3.2 Hz), 98.1 (t, *J* = 26.4 Hz), 45.2, 44.9, 27.34, 27.32, 21.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ −111.46, −112.66. HRMS (ESI): calcd. for $C_{19}H_{22}F_2N_2O_2S$ $[M+Na]^+$ 403.1262, found 403.1262.

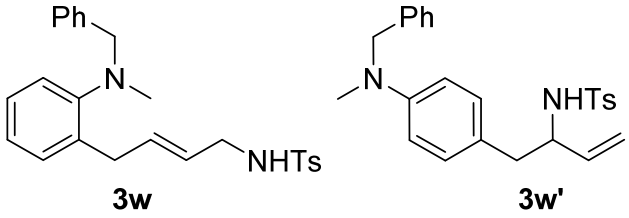
(E)-N-(4-(2-(ethyl(methyl)amino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3v**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 50.9 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.13–7.06 (m,

1H), 7.04–6.95 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 5.66 (dt, *J* = 15.2, 6.5 Hz, 1H), 5.32 (dt, *J* = 15.2, 6.4 Hz, 1H), 4.33 (t, *J* = 6.2 Hz, 1H), 3.49 (t, *J* = 6.3 Hz, 2H), 3.29 (d, *J* = 6.7 Hz, 2H), 2.77 (q, *J* = 7.1 Hz, 2H), 2.53 (s, 3H), 2.35 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.0, 143.6, 137.0, 135.2, 134.2, 130.0, 129.8, 127.3, 127.0, 125.5, 123.5, 120.9, 51.3, 45.5, 42.0, 33.4, 21.7, 13.1. HRMS (ESI): calcd. for $C_{20}H_{27}N_2O_2S$ $[M+H]^+$ 359.1788, found 359.1786.

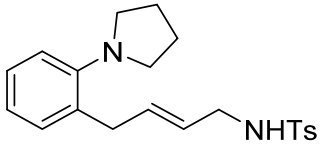
(E)-N-(4-(2-(benzyl(methyl)amino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3w**)
N-(1-(4-(benzyl(methyl)amino)phenyl)but-3-en-2-yl)-4-methylbenzenesulfonamide (**3w′**)



3w **3w'**

Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 68.6 mg as a mixture of **3w** (~74%) and **3w′** (~8%). ^{1}H NMR of **3w** (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.27–7.22 (m, 2H), 7.21–7.16 (m, 3H), 7.14–7.09 (m, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.03–6.97 (m, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 5.67 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.30 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.28 (t, *J* = 5.7 Hz, 1H), 3.89 (s, 2H), 3.51–3.43 (m, 2H), 3.40 (d, *J* = 6.5 Hz, 2H), 2.45 (s, 3H), 2.33 (s, 3H). ^{13}C NMR of **3w** (126 MHz, $CDCl_3$): δ 152.2, 143.5, 139.0, 137.1, 134.9, 134.1, 130.2, 129.8, 128.5, 128.4, 127.3, 127.2, 127.18, 125.7, 123.9, 121.2, 61.7, 45.4, 41.9, 33.4, 21.7. HRMS (ESI): calcd. for $C_{19}H_{22}F_2N_2O_2S$ $[M+Na]^+$ 443.1764, found 443.1772.

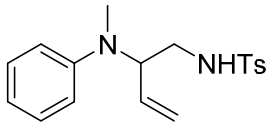
(E)-4-methyl-N-(4-(2-(pyrrolidin-1-yl)phenyl)but-2-en-1-yl)benzenesulfonamide (**3x**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 44.4 mg (60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.09–7.01 (m, 1H), 6.93–6.89 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 5.67 (dt, *J* = 15.3, 6.4 Hz, 1H), 5.32 (d, *J* = 15.3, 6.4 Hz, 1H), 4.49 (s, 1H), 3.53–3.44 (m, 2H), 3.26 (d, *J* = 6.5 Hz, 2H), 3.01 (s, 4H), 2.34 (s, 3H), 1.88–1.77 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.0, 143.5, 137.1, 133.9, 131.1, 130.6, 129.8, 127.3, 127.0, 125.8, 121.1, 117.1, 51.9, 45.4, 35.1,

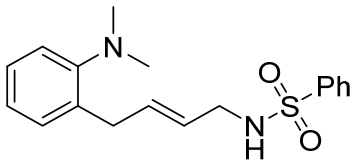
25.0, 21.6. HRMS (ESI): calcd. for $C_{21}H_{27}N_2O_2S$ $[M+H]^+$ 371.1788, found 371.1795.

4-methyl-N-(2-(methyl(phenyl)amino)but-3-en-1-yl)benzenesulfonamide (**3y**)



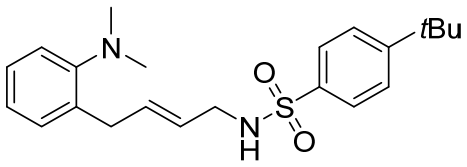
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 58 mg (88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16–7.09 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 2H), 5.59 (ddd, *J* = 17.4, 10.7, 5.4 Hz, 1H), 5.12 (dt, *J* = 10.7, 1.3 Hz, 1H), 5.00 (dt, *J* = 17.6, 1.4 Hz, 1H), 4.69 (d, *J* = 6.2 Hz, 1H), 4.25–4.16 (m, 1H), 3.21 (ddd, *J* = 12.9, 8.3, 5.4 Hz, 1H), 3.05 (ddd, *J* = 12.9, 10.1, 3.1 Hz, 1H), 2.51 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.2, 143.7, 136.8, 133.2, 129.9, 129.3, 127.3, 118.9, 118.4, 115.0, 60.6, 43.4, 31.7, 21.7. HRMS (ESI): calcd. for $C_{18}H_{22}N_2NaO_2S$ M+Na]$^+$ 353.1294, found 353.1294.

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)benzenesulfonamide (**3aa**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 58.7 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.76 (m, 2H), 7.53–7.46 (m, 1H), 7.46–7.39 (m, 2H), 7.15–7.07 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.92 (t, *J* = 7.1 Hz, 1H), 5.68 (dt, *J* = 15.2, 6.6 Hz, 1H), 5.33 (dtt, *J* = 15.3, 6.4, 1.6 Hz, 1H), 4.43 (s, 1H), 3.52 (dt, *J* = 6.3, 1.2 Hz, 2H), 3.32 (d, *J* = 6.5 Hz, 2H), 2.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.1, 134.2, 134.0, 132.8, 130.2, 129.2, 127.2, 125.7, 119.5, 45.5, 45.2, 33.4. HRMS (ESI): calcd. for $C_{18}H_{23}N_2O_2S$ $[M+H]^+$ 331.1475, found 331.1487.

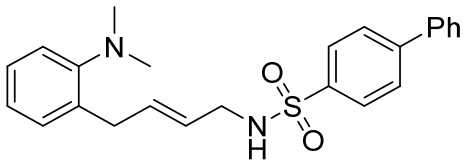
(E)-4-(*tert*-butyl)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)benzenesulfonamide (**3ab**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 58.7 mg (76%). ^{1}H

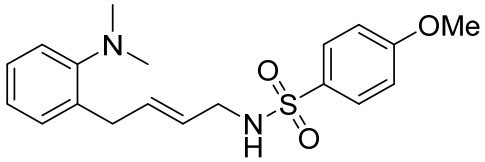
NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.08 (dt, *J* = 7.6, 1.8 Hz, 1H), 6.98 (dt, *J* = 7.9, 1.5 Hz, 2H), 6.89 (dt, *J* = 7.4, 1.5 Hz, 1H), 5.67 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.35 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.57 (t, *J* = 6.1 Hz, 1H), 3.50 (t, *J* = 6.1 Hz, 2H), 3.30 (d, *J* = 6.3 Hz, 2H), 2.55 (s, 6H), 1.26 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.5, 152.5, 137.0, 134.1, 134.0, 130.1, 127.12, 127.1, 126.2, 125.8, 123.3, 119.4, 45.4, 45.1, 35.2, 33.4, 31.2. HRMS (ESI): calcd. for $C_{22}H_{31}N_2O_2S$ $[M+H]^+$ 387.2101, found 387.2115.

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-[1,1'-biphenyl]-4-sulfonamide (**3ac**)



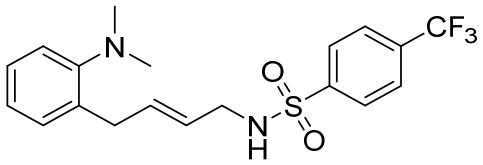
Elution with petroleum ether/ethyl acetate 5:1 (v/v), white solid, mp 100.7–101 °C, yield 78.0 mg (96%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.56–7.49 (m, 2H), 7.45–7.37 (m, 2H), 7.37–7.31 (m, 1H), 7.12–7.04 (m, 1H), 7.03–6.95 (m, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 5.71 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.36 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.52 (s, 1H), 3.55 (dt, *J* = 6.2, 1.2 Hz, 2H), 3.33 (d, *J* = 6.5 Hz, 2H) 2.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.7, 139.4, 138.7, 134.2, 134.0, 130.2, 129.2, 128.6, 127.84, 127.78, 127.5, 127.2, 125.7, 123.4, 119.5, 45.5, 45.2, 33.4. HRMS (ESI): calcd. for $C_{27}H_{40}N_2O_2S$ $[M+Na]^+$ 407.1793, found 407.1789.

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methoxybenzenesulfonamide (**3ad**)



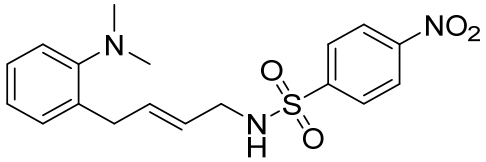
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 44.6 mg (62%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 9.0, Hz, 2H), 7.13–7.06 (m, 1H), 6.99 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.93–6.89 (m, 1H), 6.87 (d, *J* = 9.0, Hz, 2H), 5.66 (dtt, *J* = 15.3, 6.6, 1.3 Hz, 1H), 5.33 (dtt, *J* = 15.3, 6.4, 1.5 Hz, 1H), 4.50 (t, *J* = 5.6 Hz, 1H), 3.78 (s, 3H), 3.48 (dt, *J* = 6.3, 1.1 Hz, 2H), 3.30 (d, *J* = 6.4 Hz, 2H), 2.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.9, 152.5, 134.1, 134.0, 131.6, 130.1, 129.4, 127.1, 125.8, 123.3, 119.4, 114.3, 55.7, 45.4, 45.1, 33.4. HRMS (ESI): calcd. for $C_{19}H_{25}N_2O_3S$ $[M+H]^+$ 361.1580, found 361.1588.

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (**3ae**)



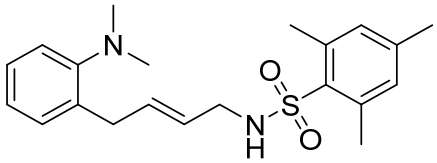
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 67.7 mg (85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.14–7.06 (m, 1H), 7.01 (dd, *J* = 8.1 Hz, 1H), 6.95 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 5.70 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.31 (dtt, *J* = 15.3, 6.4, 1.5 Hz, 1H), 4.66 (t, *J* = 6.0 Hz, 1H), 3.55 (dt, *J* = 6.3, 0.9 Hz, 2H), 3.30 (d, *J* = 6.5 Hz, 2H), 2.55 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.6, 144.0, 134.6, 134.5 (q, *J* = 33.1 Hz), 134.0, 130.1, 127.8, 127.3, 126.4 (q, *J* = 3.7 Hz), 125.3, 123.4, 123.36 (q, *J* = 273.4 Hz), 119.6, 45.5, 45.2, 33.4. ^{19}F NMR (471 MHz, $CDCl_3$): δ –63.06. HRMS (ESI): calcd. for $C_{19}H_{22}F_3N_2O_2S$ $[M+H]^+$ 399.1349, found 399.1360.

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-4-nitrobenzenesulfonamide (**3af**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 53.3 mg (71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.13–7.06 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.95–6.86 (m, 2H), 5.69 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.28 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.66 (s, 1H), 3.61 (t, *J* = 6.0 Hz, 2H), 3.30 (d, *J* = 6.3 Hz, 2H), 2.55 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.3, 150.1, 146.3, 134.8, 133.8, 130.1, 128.4, 127.4, 125.0, 124.5, 123.4, 119.6. 45.5, 45.2, 33.4. HRMS (ESI): calcd. for $C_{18}H_{22}N_3O_4S$ $[M+H]^+$ 376.1326, found 376.1331.

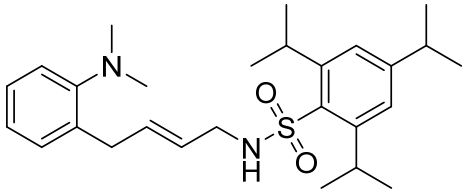
(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (**3ag**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 65.2 mg (91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (t, *J* = 7.1 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 6.7

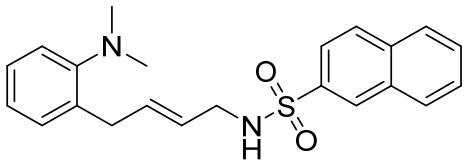
Hz, 1H), 6.91 (t, *J* = 7.1 Hz, 1H), 6.87 (s, 2H), 5.67 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.39 (dt, *J* = 15.3, 6.5 Hz, 1H), 4.41 (s, 1H), 3.45 (t, *J* = 6.4 Hz, 2H), 3.30 (d, *J* = 6.5 Hz, 2H), 2.57 (s, 6H), 2.55 (s, 6H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.6, 142.3, 139.2, 134.1, 134.0, 133.9, 132.1, 130.2, 127.2, 125.9, 123.4, 119.5, 45.2, 44.9, 33.5, 23.1, 21.1. HRMS (ESI): calcd. for $C_{21}H_{28}N_2NaO_2S$ $[M+Na]^+$ 395.1764, found 395.1767.

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-2,4,6-triisopropylbenzenesulfonamide (**3ah**)



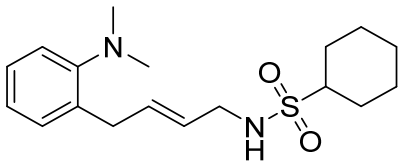
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 51.1 mg (56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13–7.05 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 5.71 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.39 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.22 (t, *J* = 6.4 Hz, 1H), 4.09 (hept, *J* = 6.7 Hz, 2H), 3.50 (t, *J* = 6.3 Hz, 2H), 3.32 (d, *J* = 6.6 Hz, 2H), 2.83 (hept, *J* = 6.7 Hz, 1H), 2.56 (s, 6H), 1.18 (d, *J* = 6.7 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.9, 152.6, 150.4, 134.2, 134.15, 132.4, 130.1, 127.2, 126.0, 123.9, 123.3, 119.5, 45.1, 34.3, 33.5, 29.7, 25.0, 23.7. HRMS (ESI): calcd. for $C_{27}H_{40}N_2NaO_2S$ $[M+Na]^+$ 479.2703, found 479.2715.

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)naphthalene-2-sulfonamide (**3ai**)



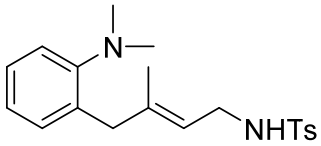
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 57.0 mg (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.89–7.83 (m, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.59–7.48 (m, 2H), 7.09–7.02 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.89 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.83 (dt, *J* = 7.4, 1.3 Hz, 1H), 5.65 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.31 (dt, *J* = 15.3, 6.3 Hz, 1H), 4.61 (t, *J* = 5.8 Hz, 1H), 3.54 (t, *J* = 5.9 Hz, 2H), 3.24 (d, *J* = 6.5 Hz, 2H), 2.50 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.6, 137.0, 134.9, 134.2, 134.0, 132.3, 130.1, 129.6, 129.4, 128.9, 128.6, 128.0, 127.7, 127.1, 125.6, 123.3, 122.5, 119.4, 45.5, 45.1, 33.4. HRMS (ESI): calcd. for $C_{22}H_{25}N_2O_2S$ $[M+H]^+$ 381.1631, found 381.1641.

(E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)cyclohexanesulfonamide (**3aj**)



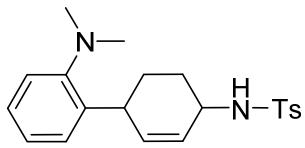
Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 49.3 mg (73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (dt, *J* = 7.6, 1.8 Hz, 1H), 7.08–7.05 (m, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 5.80 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.47 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.07 (t, *J* = 6.0 Hz, 1H), 3.65 (t, *J* = 6.3 Hz, 2H), 3.40 (d, *J* = 6.6 Hz, 2H), 2.76 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.60 (s, 6H), 2.13–2.04 (m, 2H), 1.85–1.76 (m, 2H), 1.66–1.58 (m, 1H), 1.42 (dq, *J* = 12.5, 3.0 Hz, 2H), 1.23–1.05 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.7, 134.2, 133.8, 130.2, 127.2, 126.9, 123.4, 119.5, 61.8, 45.6, 45.2, 33.5, 26.6, 25.28, 25.25. HRMS (ESI): calcd. for $C_{18}H_{29}N_2O_2S$ $[M+H]^+$ 337.1944, found 337.1950.

(E)-N-(4-(2-(dimethylamino)phenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (**3ak**)



Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 59.6 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.13–7.04 (m, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.91–6.83 (m, 2H), 5.00 (tq, *J* = 7.1, 1.3 Hz, 1H), 4.47 (t, *J* = 5.8 Hz, 1H), 3.57–3.47 (m, 2H), 3.25 (s, 2H), 2.53 (s, 6H), 2.34 (s, 3H), 1.43 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.0, 143.4, 141.0, 137.1, 133.3, 130.3, 129.8, 127.3, 127.1, 123.2, 120.3, 119.3, 45.1, 41.1, 39.9, 21.6, 16.6. HRMS (ESI): calcd. for $C_{20}H_{27}N_2O_2S$ $[M+H]^+$ 359.1788, found: 359.1804.

N-(2'-(dimethylamino)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (**3am**)

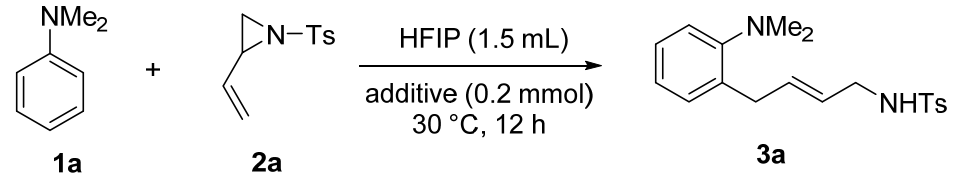


Elution with petroleum ether/ethyl acetate 5:1 (v/v), colorless oil, yield 37.1 mg (50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.12–7.02 (m,

2H), 6.98–6.90 (m, 2H), 5.57 (d, *J* = 10.2 Hz, 1H), 5.44 (d, *J* = 10.1 Hz, 1H), 4.66 (d, *J* = 8.3 Hz, 1H), 3.98–3.87 (m, 2H), 2.55 (s, 6H), 2.36 (s, 3H), 1.96–1.88 (m, 2H), 1.52–1.35 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.6, 143.4, 140.5, 138.6, 135.4, 129.9, 128.5, 128.4, 127.18, 127.16, 124.2, 120.3, 50.4, 46.1, 35.2, 31.1, 30.8, 21.7. HRMS (ESI): calcd. for $C_{21}H_{26}N_2O_2S$ $[M+H]^+$ 371.1788, found 371.1798.

3. Mechanistic studies

3.1 Free radical scavenger effect

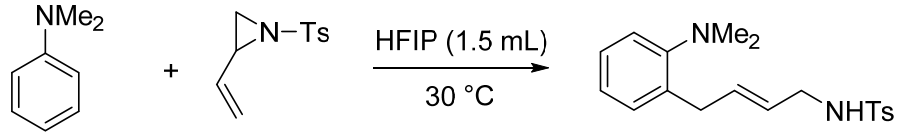


1a (0.2 mmol) + **2a** (0.3 mmol) → **3a**

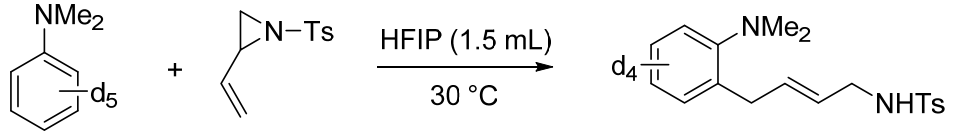
additive	yield
$Ph_2C=CH_2$	85%
BHT	90%

Aniline **1a** (24.2 mg, 0.2 mmol), 2-vinylaziridine **2a** (66.9 mg, 0.3 mmol), 1,1-diphenylethylene (36 mg, 0.2 mmol) or BHT (22 mg, 0.2 mmol) and HFIP (1.5 mL) were successively added into a Schlenk tube. The mixture was stirred in air at 30 °C for 12 hours. Solvent was removed under vacuum and the residue was purified by column chromatography with petroleum ether/ethyl acetate (5:1) as eluent to give the product **3a**. When 1,1-diphenylethylene was used as additive, the yield of **3a** was 85%. When BHT was used as additive, the yield of **3a** was 90%.

3.2 Kinetic isotope effect (KIE) experiment



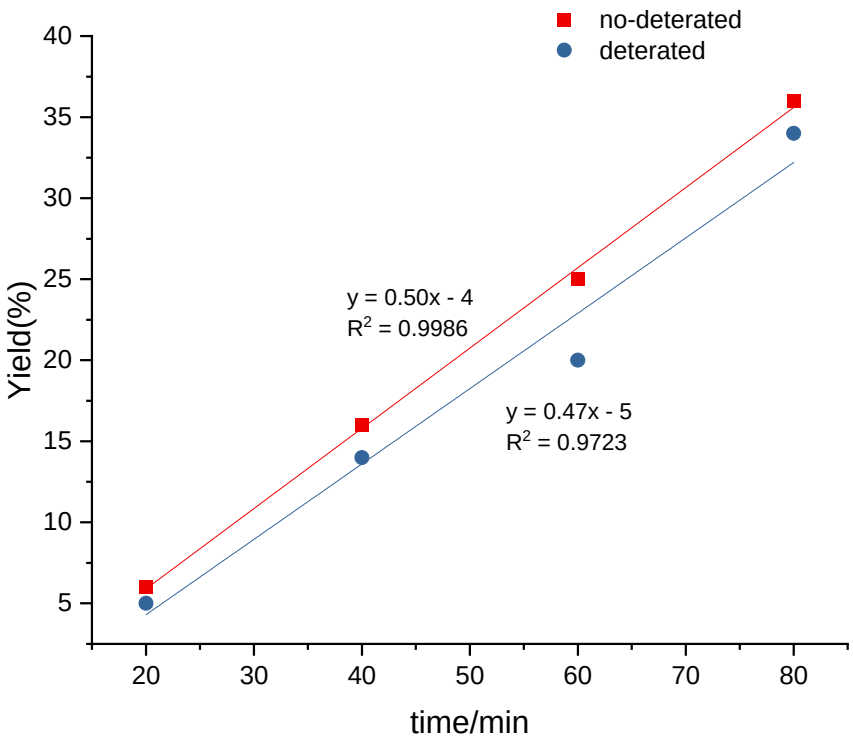
0.2 mmol + 0.24 mmol



0.2 mmol + 0.24 mmol

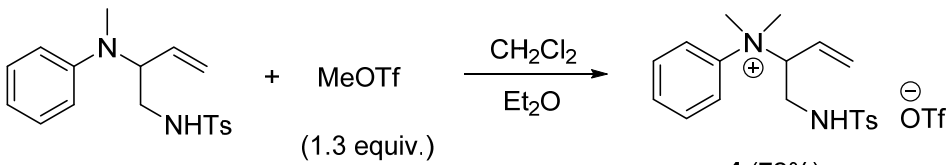
N,N-dimethylaniline (0.2 mmol), 2-vinylaziridine **2a** (0.24 mmol) and HFIP (1.5 mL) were

successively added into a Schlenk tube. In another Schlenk tube, N,N-dimethylaniline-d_5 (0.2 mmol) was used instead of N,N-dimethylaniline. The two reactions were allowed to stir at 30 °C. An aliquot of each reaction mixture was taken at the time of 20, 40, 60, and 80 min. The relative yield of each product was determined by ^{1}H NMR spectroscopy (1,1,2,2-tetrachloro-ethane as an internal standard). A kinetic isotope effect value (k_H/k_D) of 1.06 was observed.



3.3 Preparation and transformation of ammonium salt **4**

(i) Preparation of ammonium salt **4**

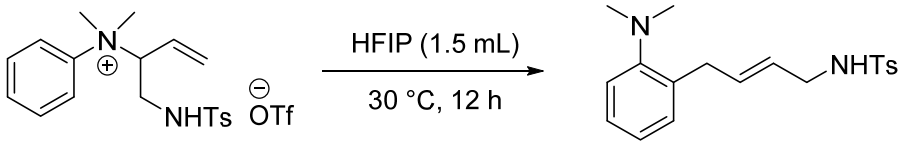


3y (0.56 mmol) **4** (72%)

To a solution of **3y** (0.1863 g, 0.56 mmol) in dry Et_2O (5 mL) and CH_2Cl_2 (0.5 mL), MeOTf (0.1198 g, 0.73 mmol) was added under N_2 at 25 °C. The solution was stirred overnight. Solvents was removed by rotary evaporation. The residue was washed using Et_2O (3 × 3 mL) and dried under vacuum for 3 h to afford a white solid, yield 0.1983 g (72%), mp

95.4-96.1 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.10–7.99 (m, 2H), 7.79–7.68 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.87 (t, *J* = 6.3 Hz, 1H). 6.14 (dt, *J* = 16.7, 9.7 Hz, 1H), 5.91 (dd, *J* = 16.7, 1.3 Hz, 1H), 5.83 (dd, *J* = 10.1, 1.3 Hz, 1H), 4.84 (td, *J* = 9.4, 3.5 Hz, 1H), 3.79 (s, 6H), 3.40–3.28 (m, 1H), 3.08–2.98 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 145.04, 143.08, 136.35, 130.30, 130.08, 129.96, 129.60, 127.72, 126.43, 121.75, 78.20, 54.65, 46.65, 40.51, 20.92. HRMS (ESI): calcd. for $C_{19}H_{25}N_2O_2S$ $[M–OTf]^+$ 345.1631, found 345.1641.

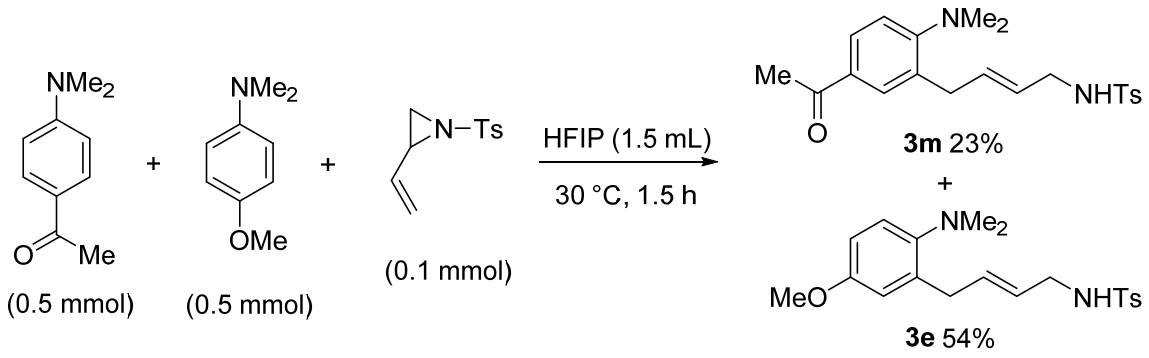
(ii) Transformation of ammonium salt **4**



4 (0.2 mmol) **3a** (90%)

A solution of **4** (98.8 mg, 0.2 mmol) in HFIP (1.5 mL) was stirred at 30 °C for 12 hours. Solvent was removed under vacuum and the resulting mixture was purified by column chromatography (eluent: petroleum ether/ethylacetate 5:1) to give **3a** (62.3 mg, 90%).

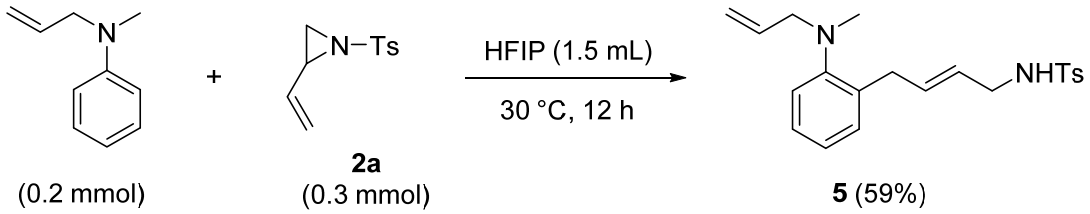
3.4 Competition experiment



(0.5 mmol) (0.5 mmol) (0.1 mmol)

1-(4-(Dimethylamino)phenyl)ethan-1-one (81.5 mg, 0.5 mmol), 4-methoxy-N,N-dimethyl-aniline (75.5 mg, 0.5 mmol), 2-vinylaziridine **2a** (22.3 mg, 0.1 mmol) and HFIP (1.5 mL) were successively added to a Schlenk tube. The mixture was stirred at 30 °C for 1.5 hours. Solvent was removed under vacuum and the residue was purified by column chromatography with petroleum ether/ethylacetate (5:1) as eluent to give the products **3m** in 23% yield and **3e** in 54% yield.

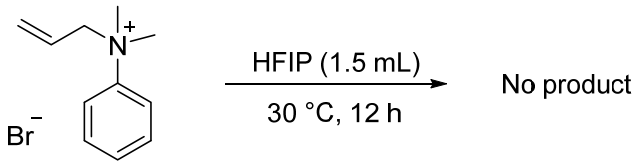
3.5 Reaction of *N*-allyl-*N*-methylaniline with 1-tosyl-2-vinylaziridine



(0.2 mmol) **2a** (0.3 mmol) **5** (59%)

N-allyl-N-dimethylaniline (29.4 mg, 0.2 mmol), 1-tosyl-2-vinylaziridine (66.9 mg, 0.3 mmol) and HFIP (1.5 mL) were added into a Schlenk tube. The solution was stirred at 30 °C for 12 hours. Solvent was removed under vacuum and the residue was purified by silica gel column chromatography (elution with 5:1 petroleum ether/ethyl acetate) to give product **5** (43.7 mg, 59%) as a white solid, mp 65–65.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13–7.06 (m, 1H), 7.04–6.94 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 5.80–5.70 (m, 1H), 5.66 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.32 (dt, *J* = 15.3, 6.4 Hz, 1H), 5.15 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.07 (dq, *J* = 10.2, 1.2 Hz, 1H), 4.33 (t, *J* = 6.0 Hz, 1H), 3.49 (dt, *J* = 6.2, 0.8 Hz, 2H), 3.37–3.26 (m, 4H), 2.52 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.96, 143.55, 137.08, 135.59, 134.65, 134.11, 130.16, 129.83, 127.28, 127.04, 125.64, 123.53, 120.77, 117.19, 77.41, 77.16, 76.91, 60.41, 45.46, 41.49, 33.44, 21.68. HRMS (ESI): calcd. for $C_{21}H_{26}N_2O_2S$ $[M+Na]^+$ 393.1607, found 393.1611.

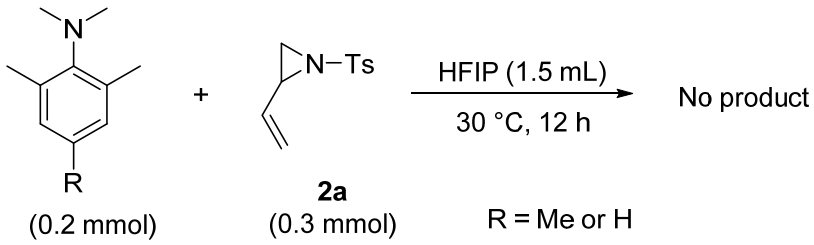
3.6 Conversion of *N*-allyl-*N*,*N*-dimethylbenzenaminium bromide (**6**) in HFIP



6 (0.2 mmol)

N-Allyl-*N*,*N*-dimethylbenzenaminium bromide (48.5 mg, 0.2 mmol) and HFIP (1.5 mL) were added into a Schlenk tube. The mixture was stirred at 30 °C (oil bath) for 12 hours. Solvent was removed in vacuo and the residue was determined by ^{1}H NMR spectroscopy. No rearrangement product was observed.

3.7 Reaction of *N*,*N*,2,4,6-pentamethylaniline or *N*,*N*,2,6-tetramethylaniline with **2a**



N,*N*,2,4,6-pentamethylaniline (32.6 mg, 0.2 mmol) or *N*,*N*,2,6-tetramethylaniline (30 mg, 0.2 mmol), 1-tosyl-2-vinylaziridine **2a** (67 mg, 0.3 mmol) and HFIP (1.5 mL) were successively added into a Schlenk tube. The mixture was stirred at 30 °C (oil bath) for 12 hours. Solvent was removed in vacuo and the residue was determined by ^{1}H NMR spectroscopy. No ammonium salt product was observed.

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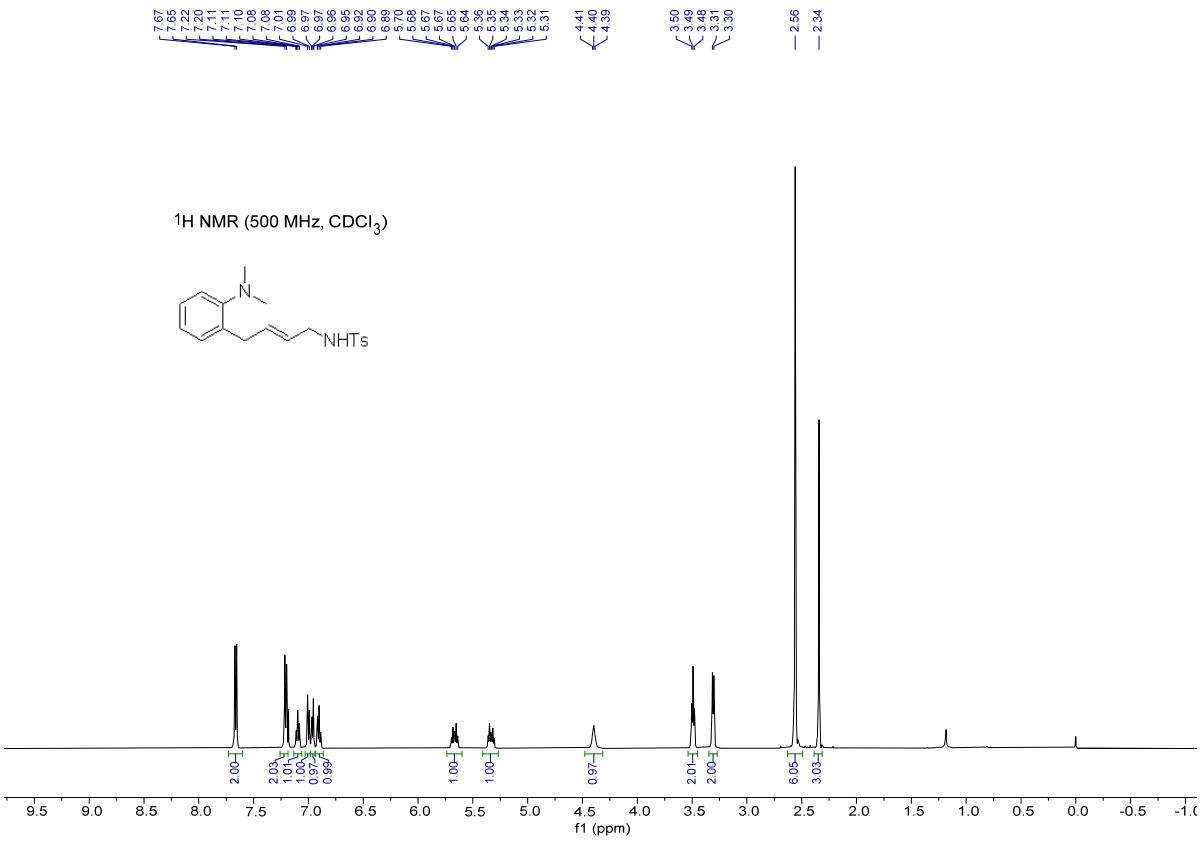
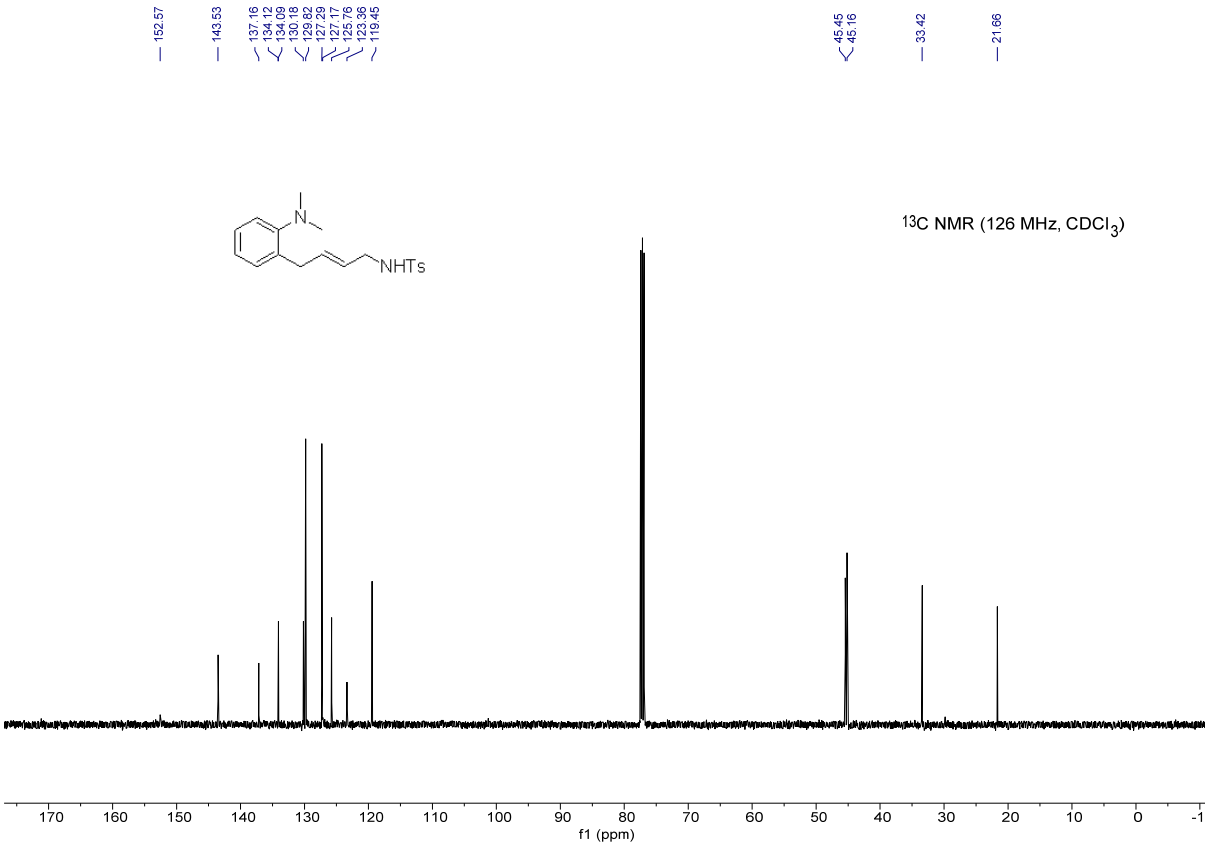
3 (a) H. Aghahosseini, A. Ramazani, N. S. Jalayer, Z. Ranjdoost, A. Souldozi, K. Ślepokura and T. Lis, *Org. Lett.*, 2019, **21**, 9247–9250; (b) L. Kong, B. Biletskyi, D. Nuel and H. Clavier, *Org. Chem. Front.*, 2018, **5**, 1600–1603.

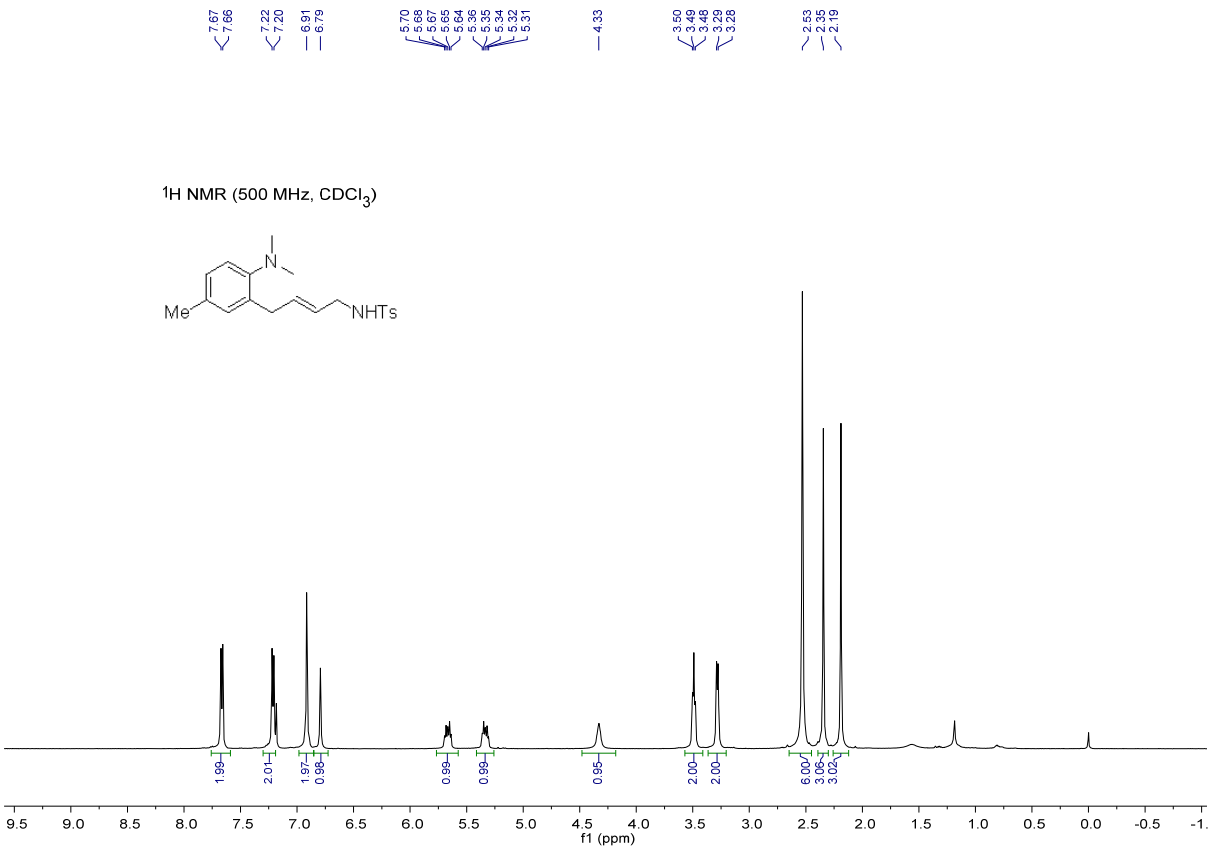
4. Spectral copies

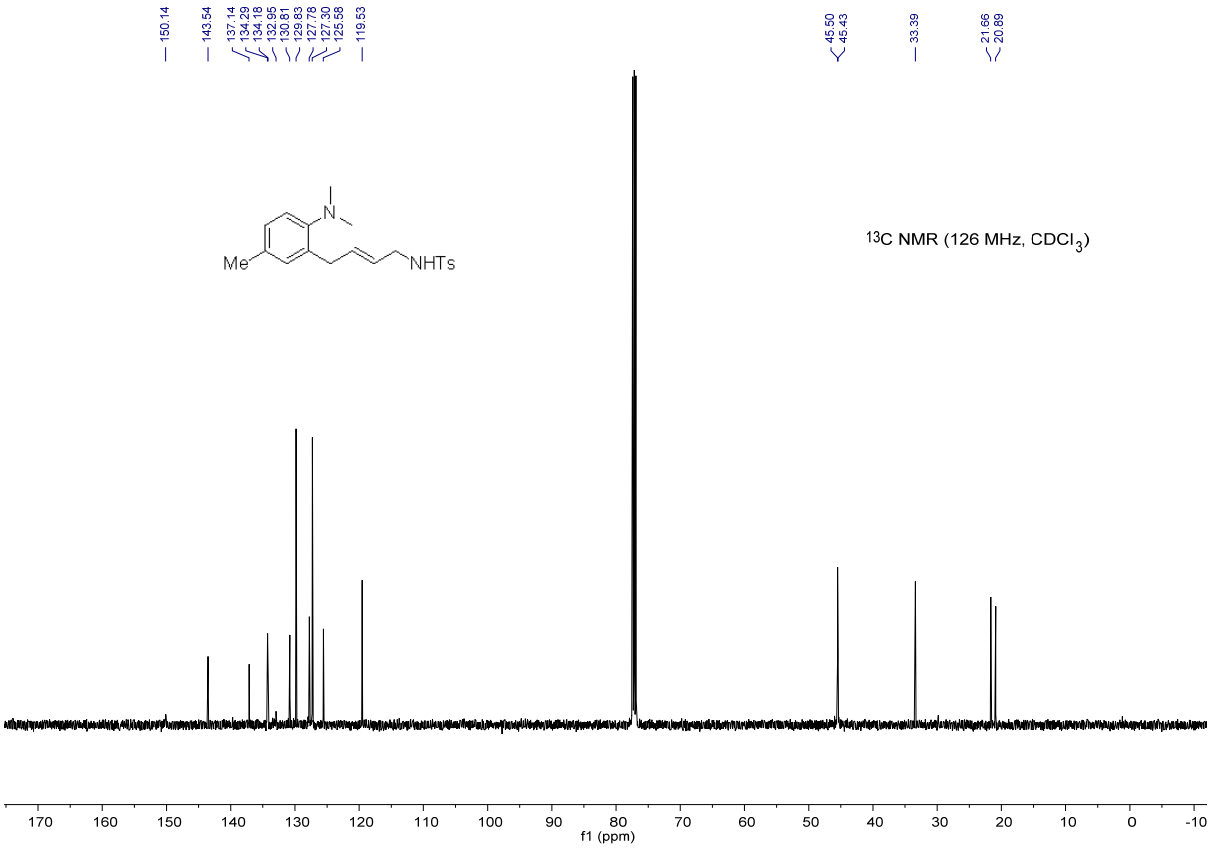
(1) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3a**)



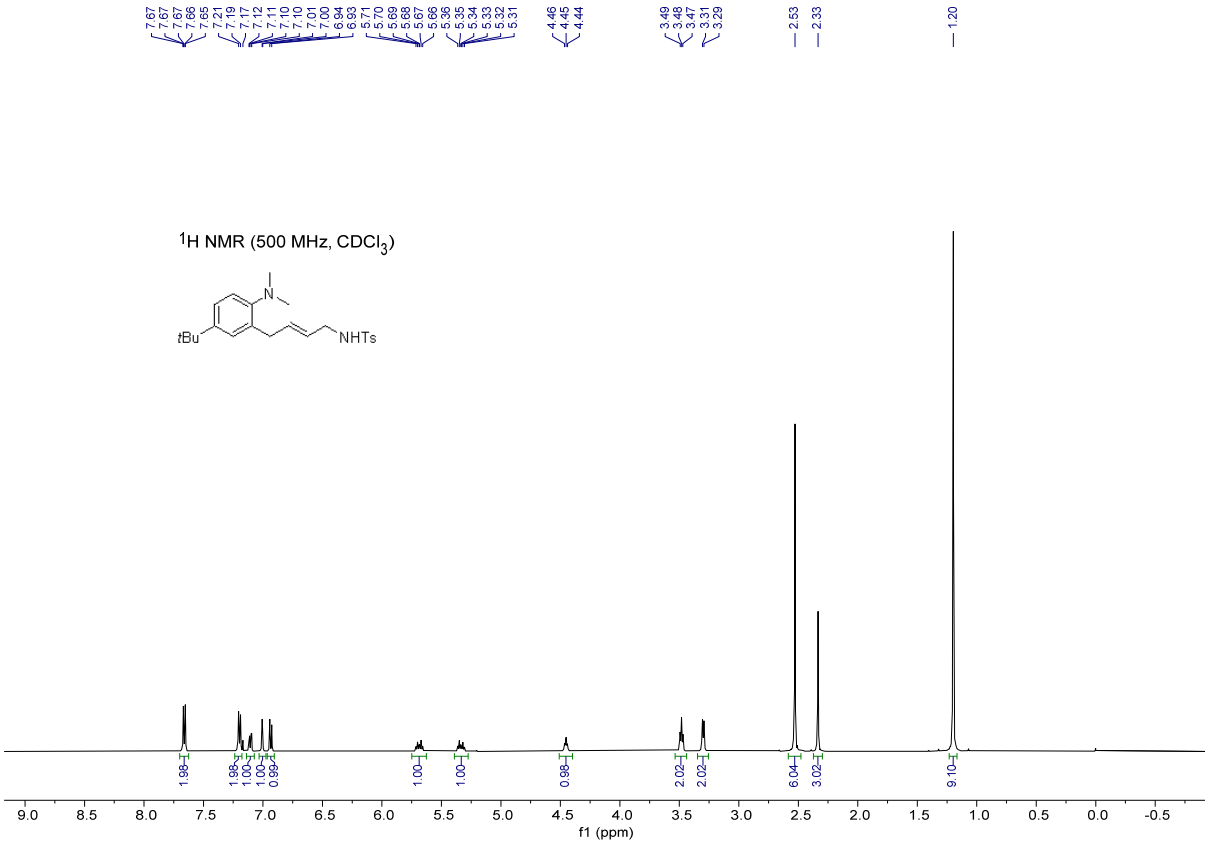


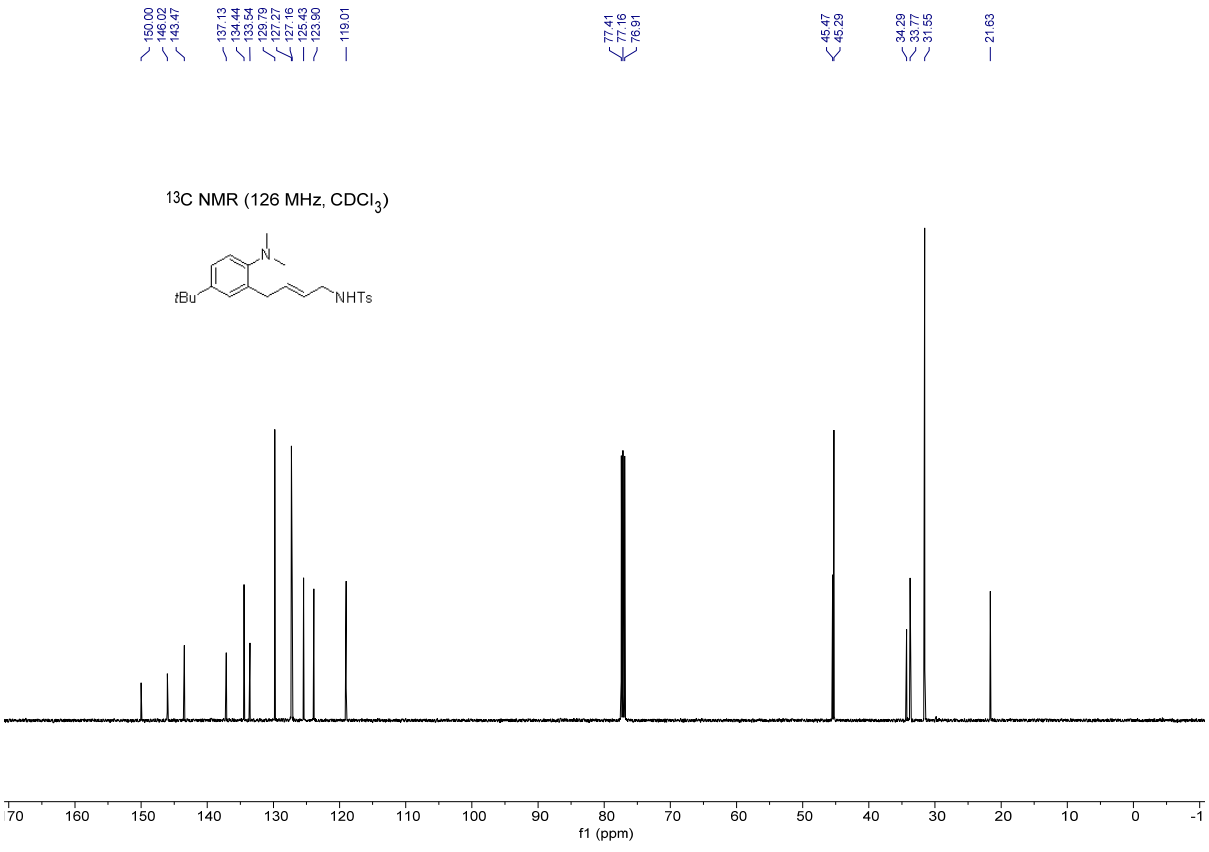
(2) (E)-N-(4-(2-(dimethylamino)-5-methylphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3b**)



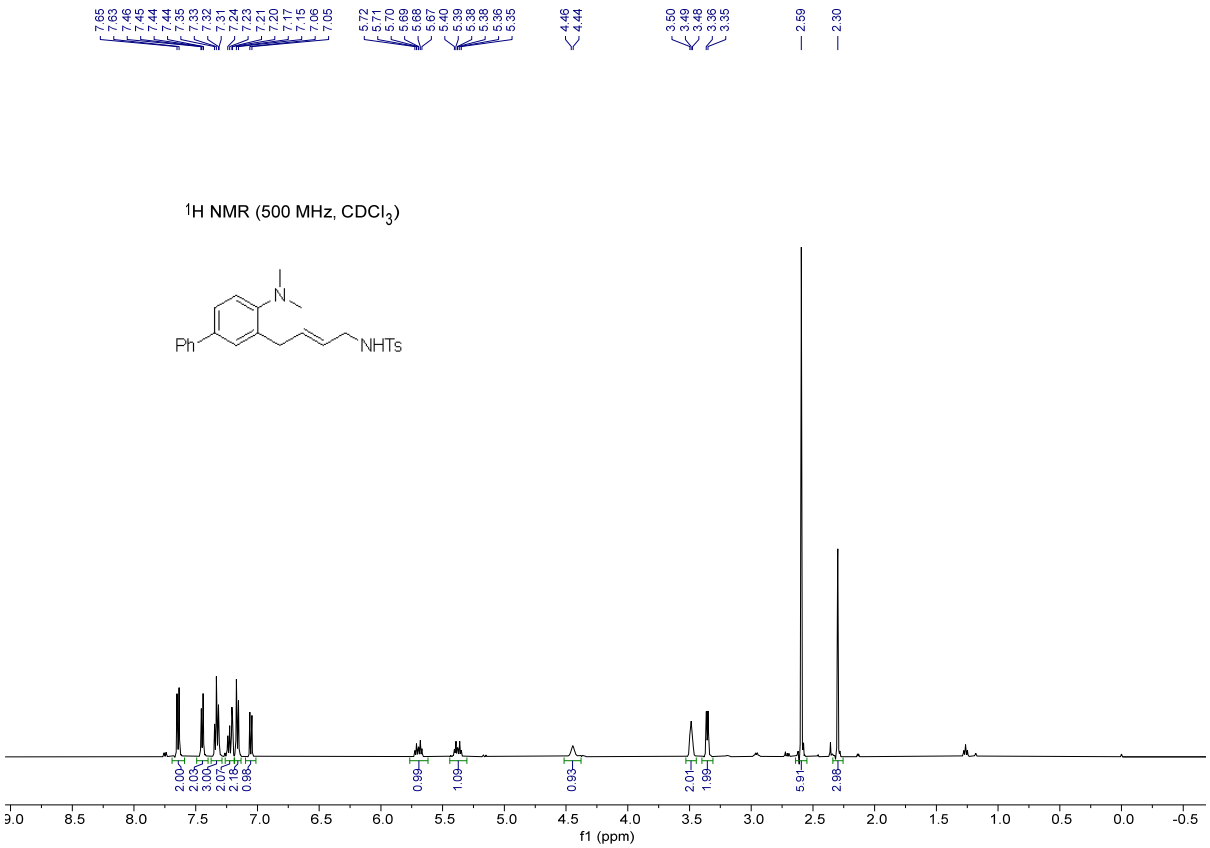


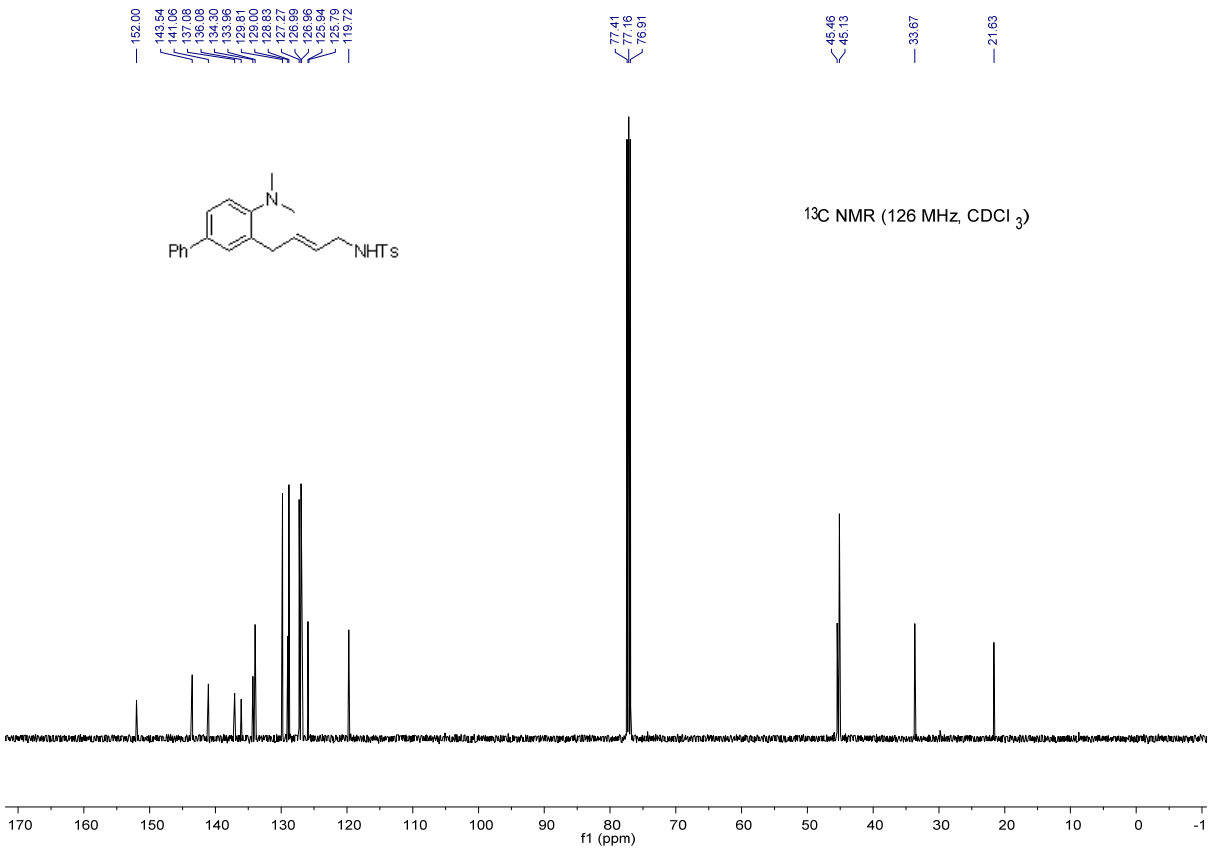
(3) (E)-N-(4-(5-(tert-butyl)-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3c**)



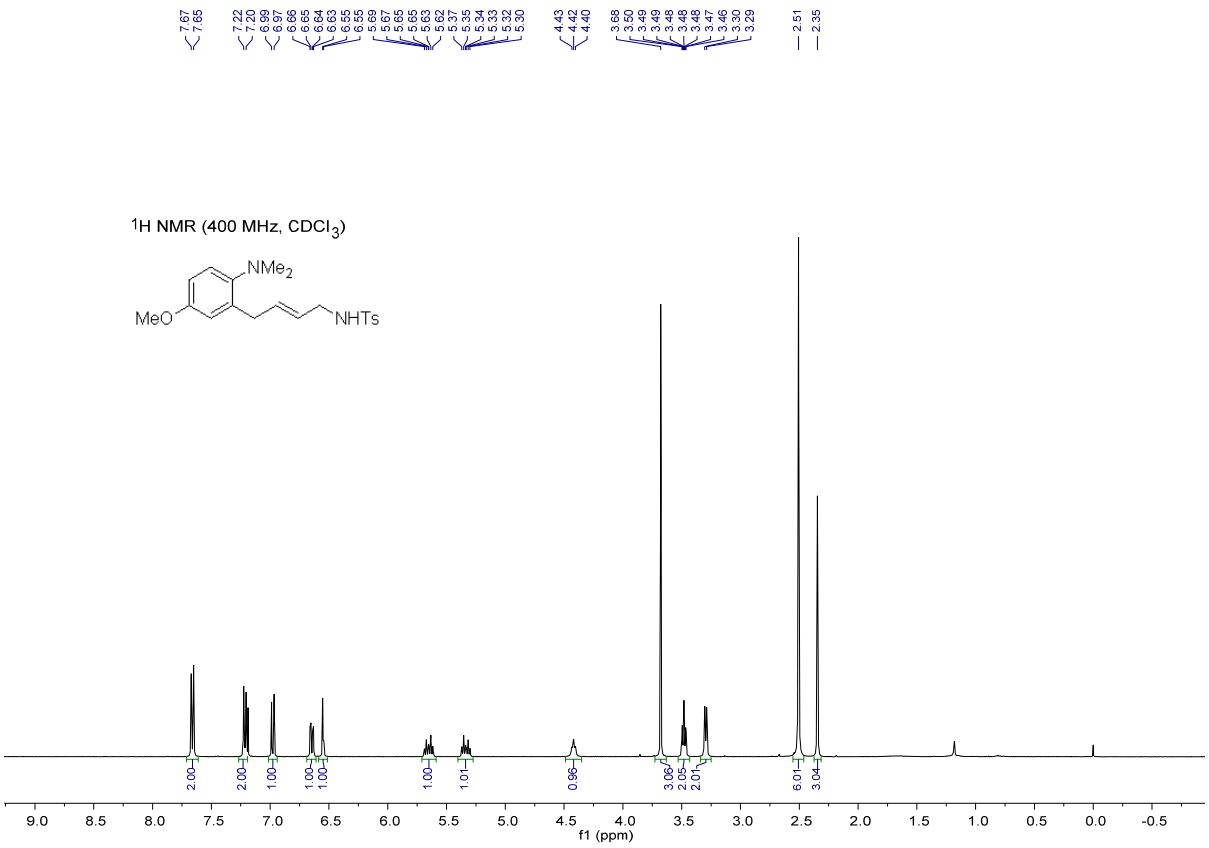


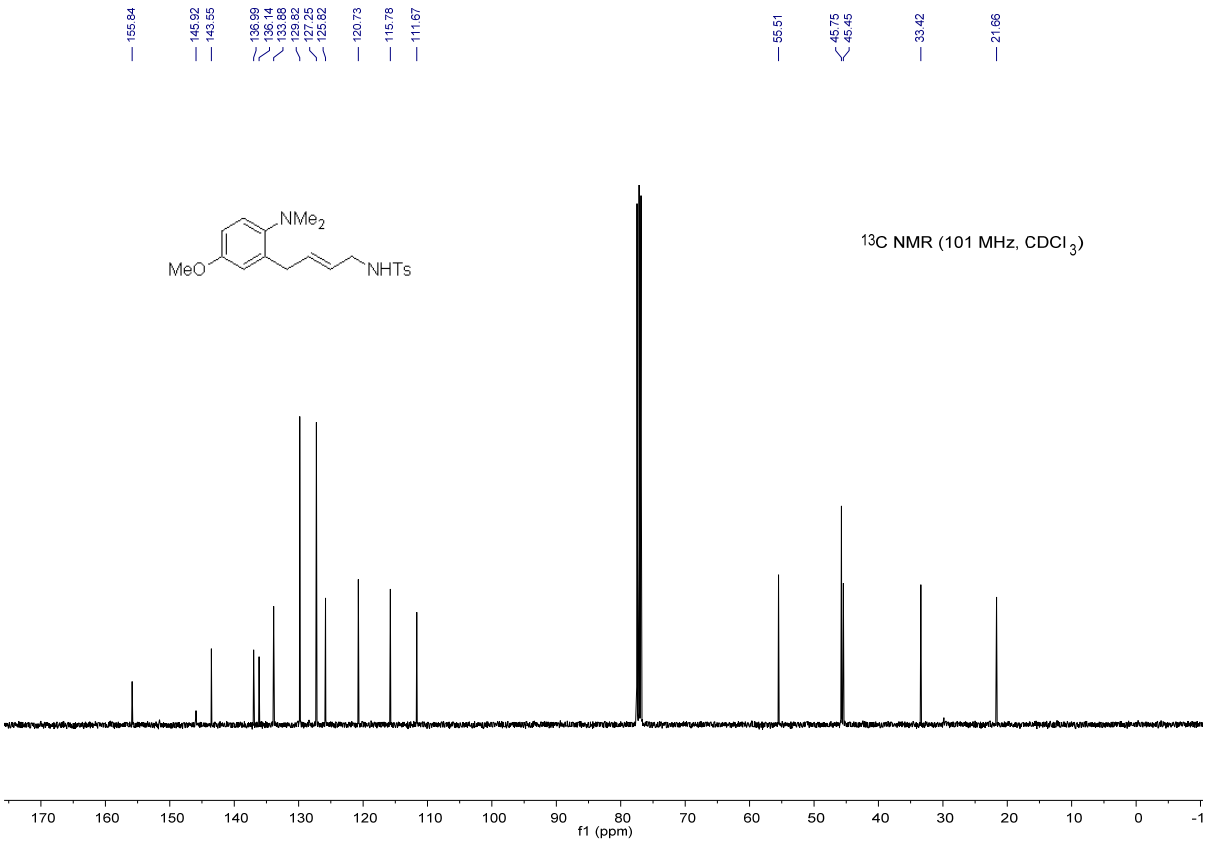
(4) (E)-N-(4-(4-(dimethylamino)-[1,1'-biphenyl]-3-yl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3d**)



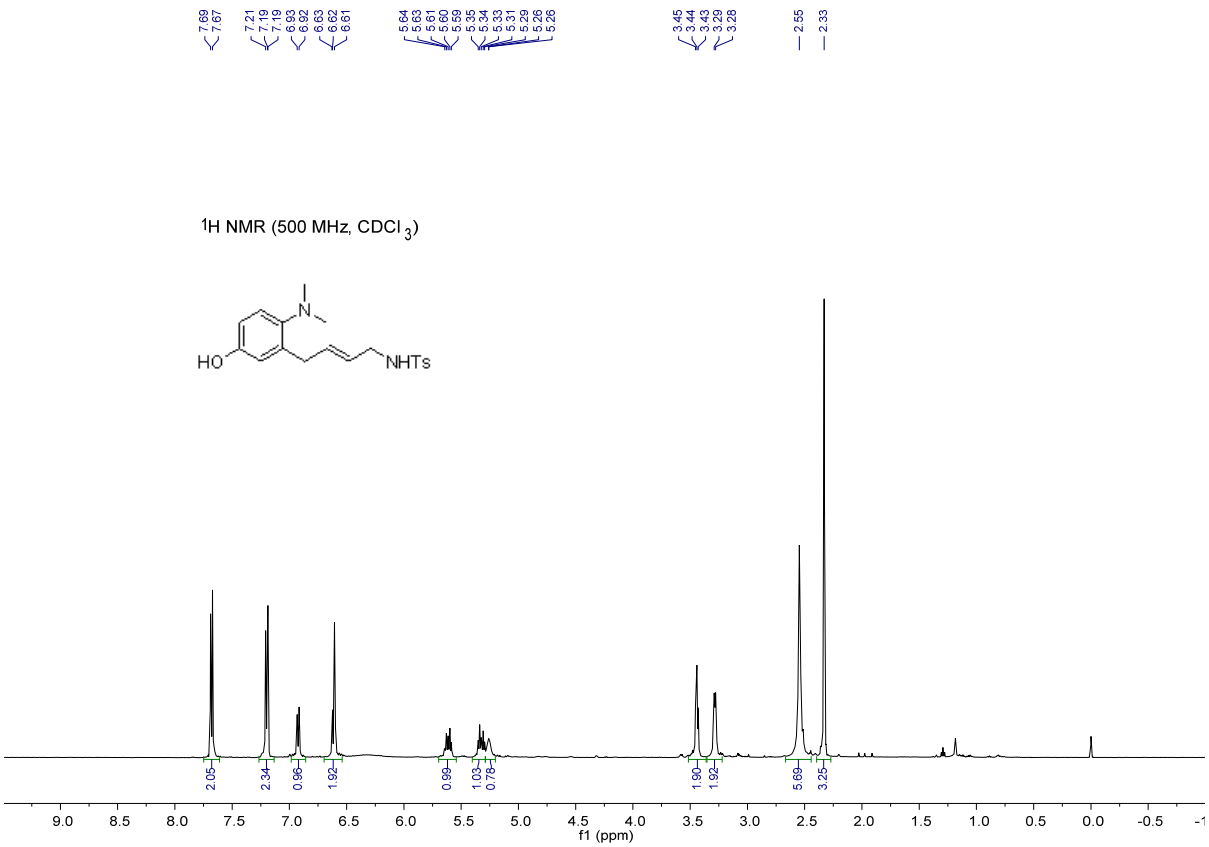


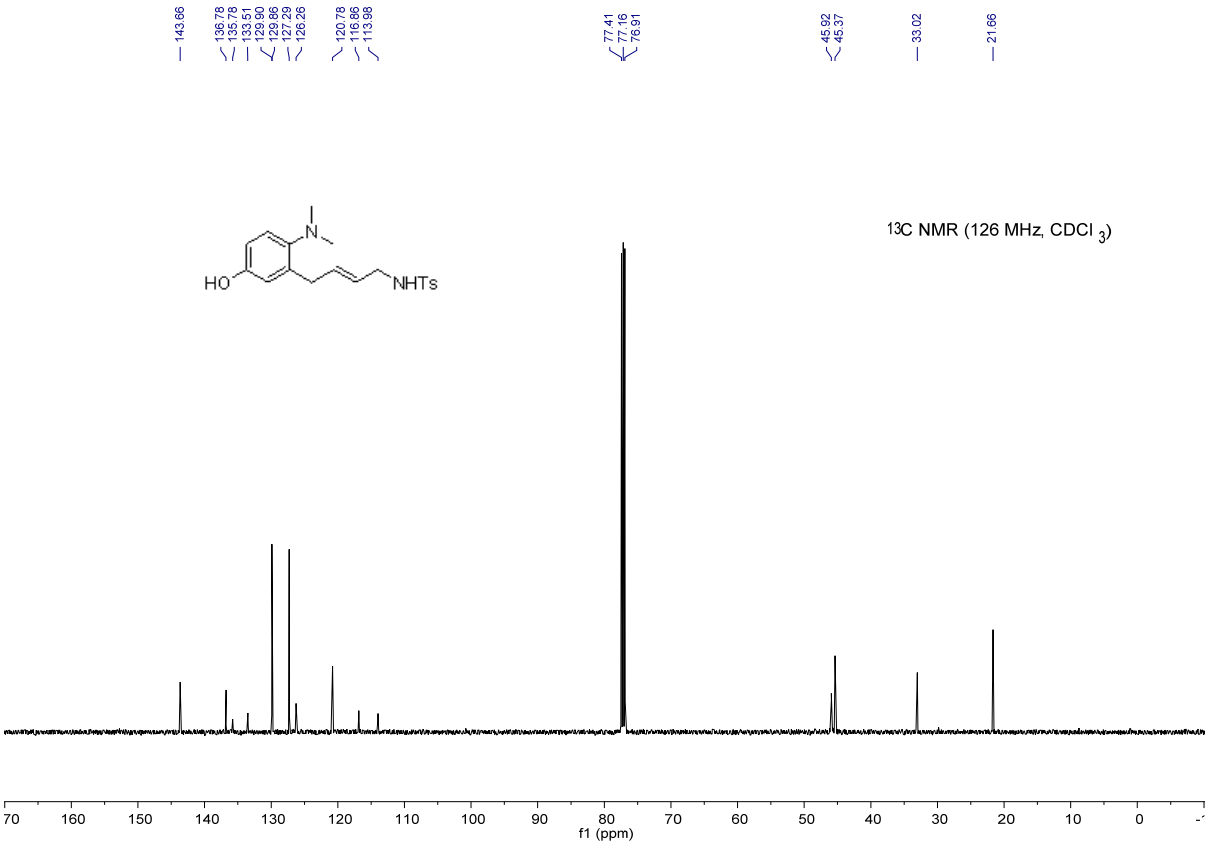
(5) (E)-N-(4-(2-(dimethylamino)-5-methoxyphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3e**)



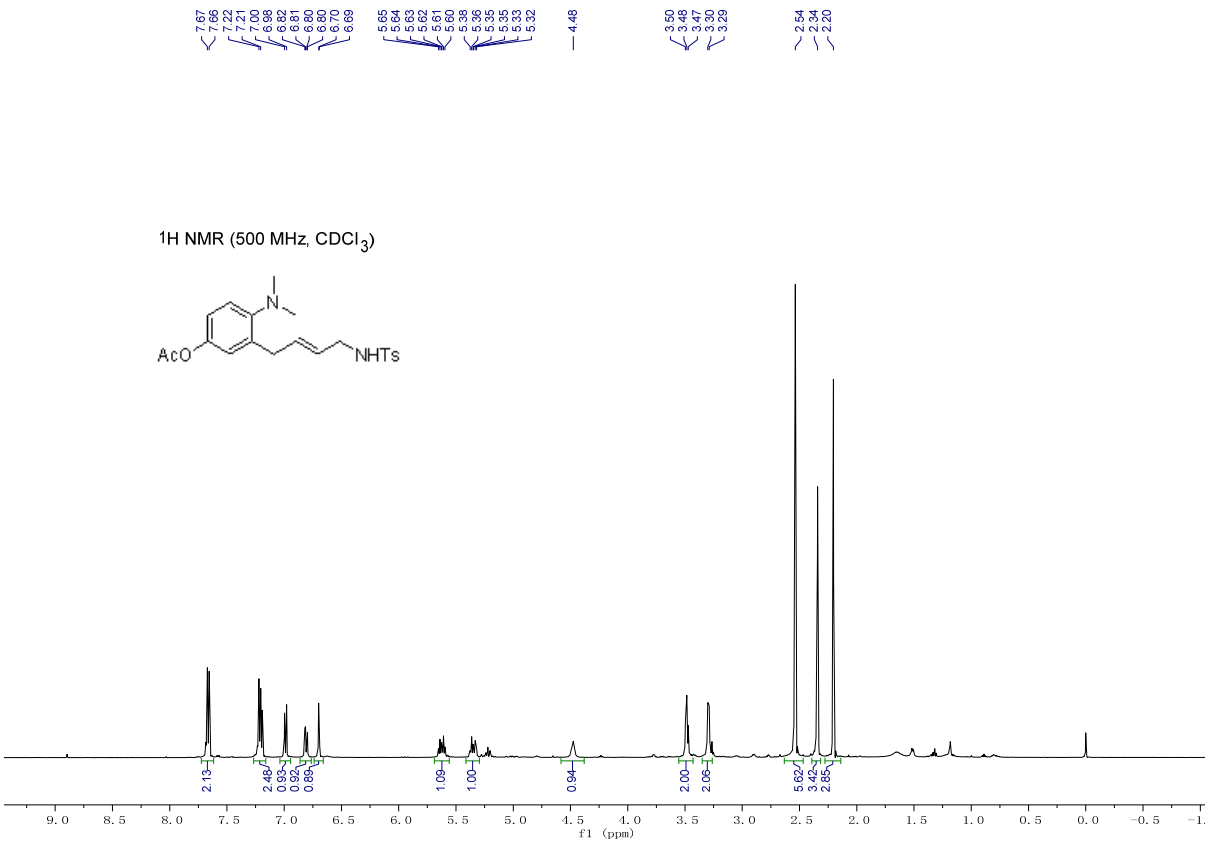


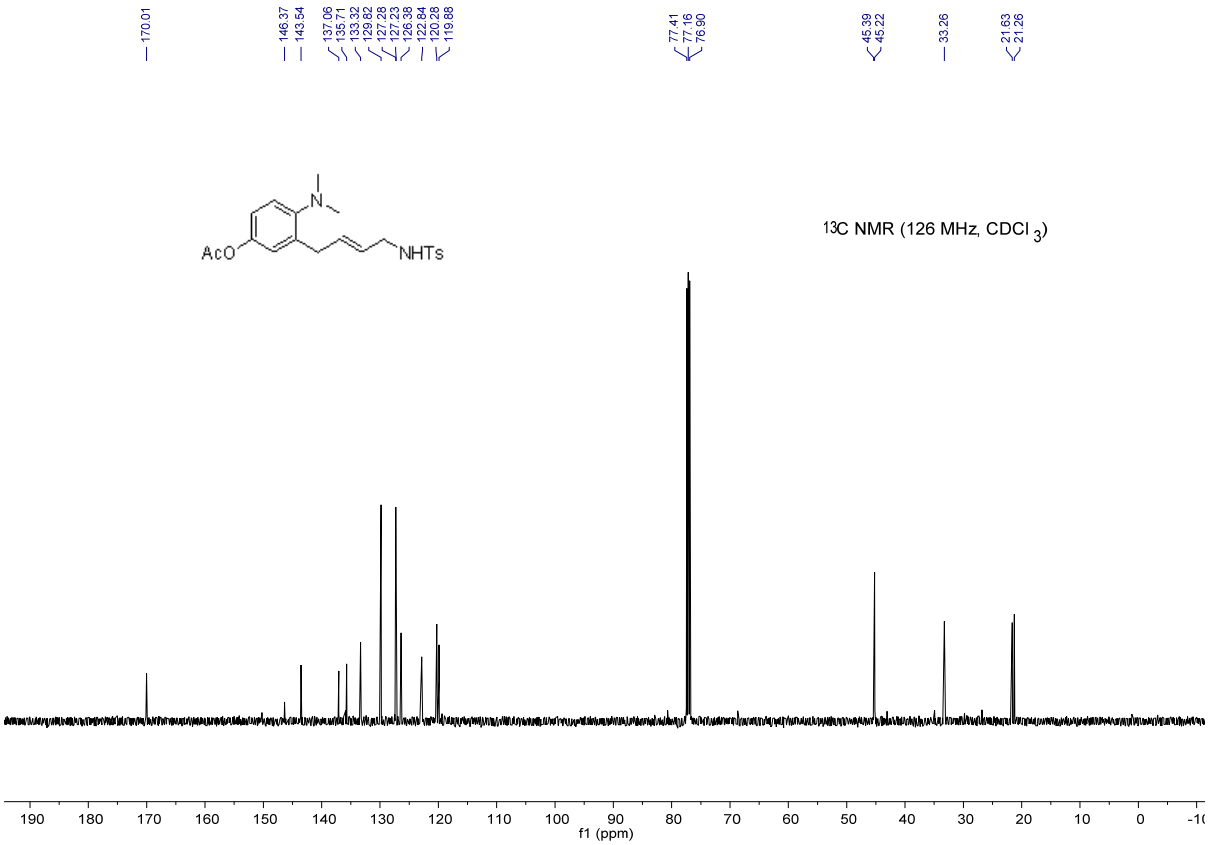
(6) (E)-N-(4-(2-(dimethylamino)-5-hydroxyphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3f**)



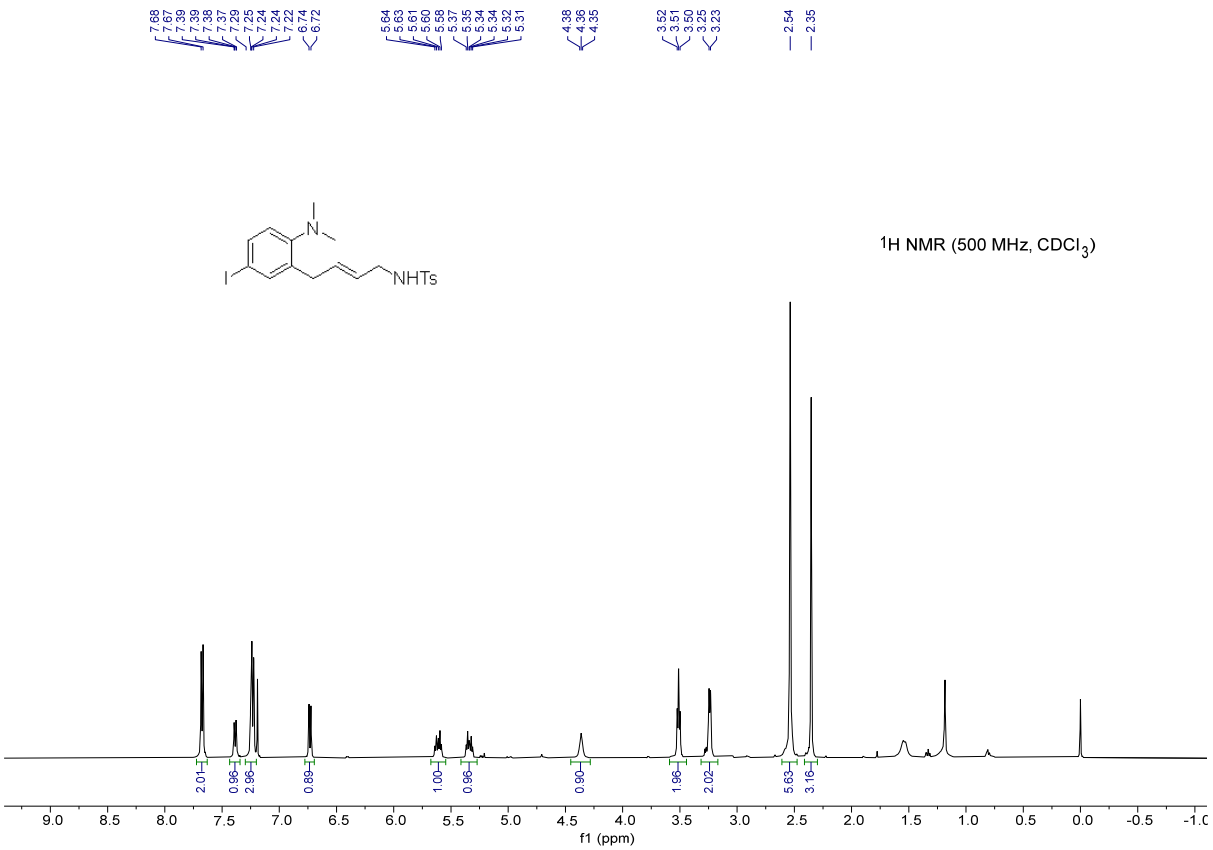


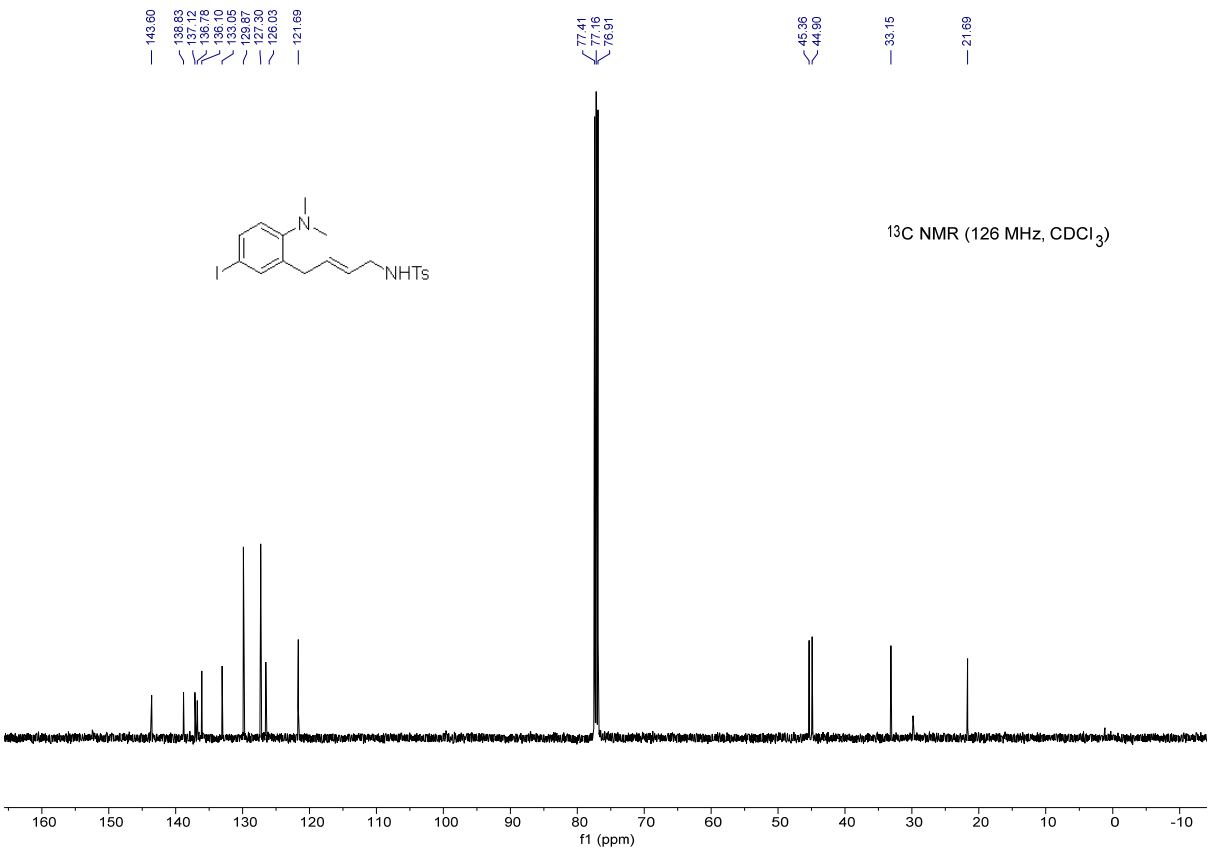
(7) (E)-4-(dimethylamino)-3-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phenyl acetate (**3g**)



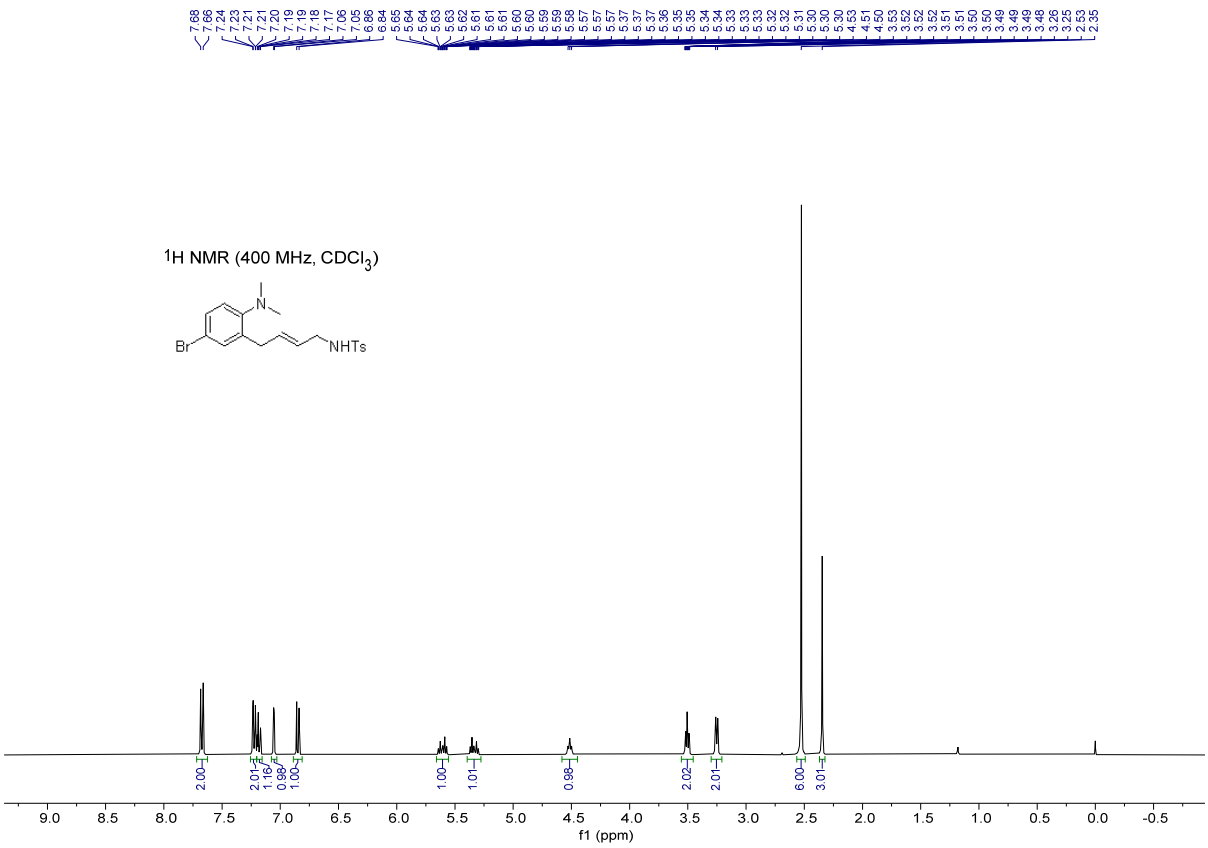


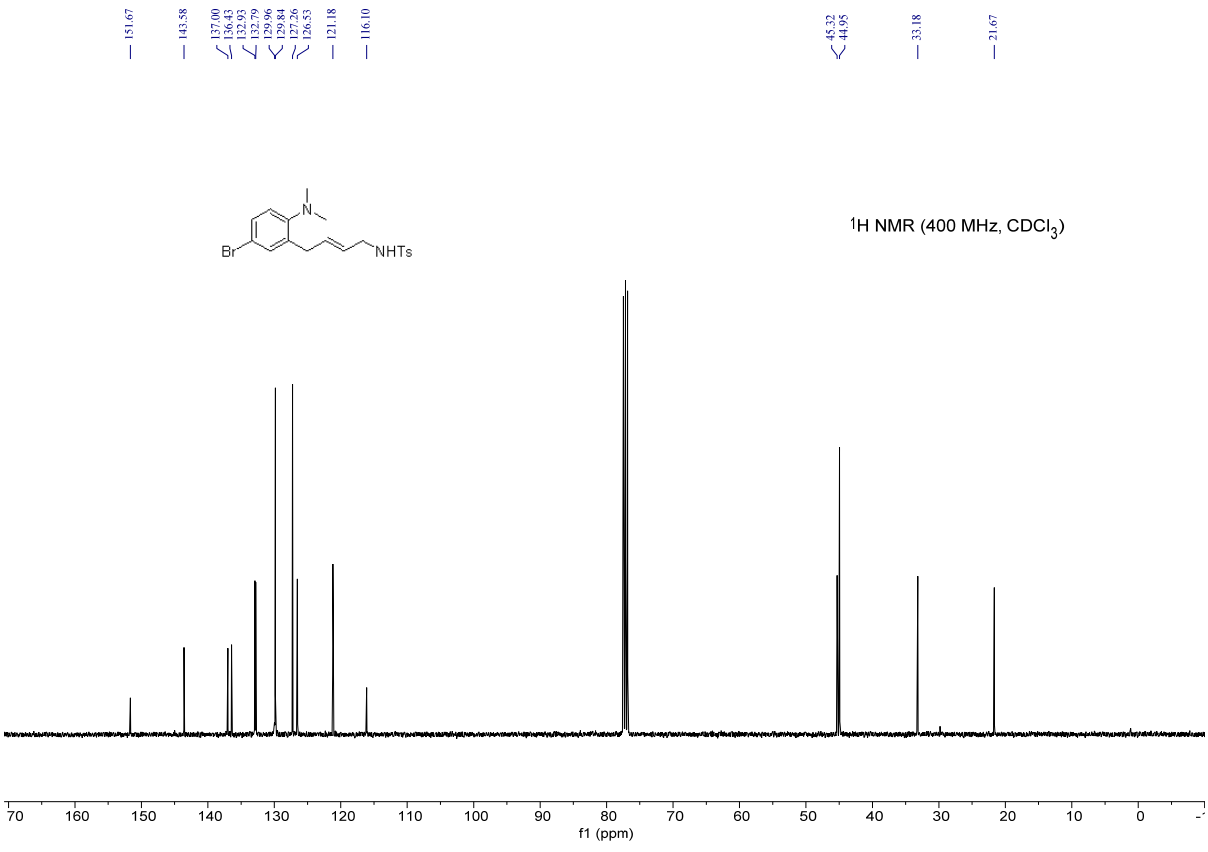
(8) (E)-N-(4-(2-(dimethylamino)-5-iodophenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3h**)



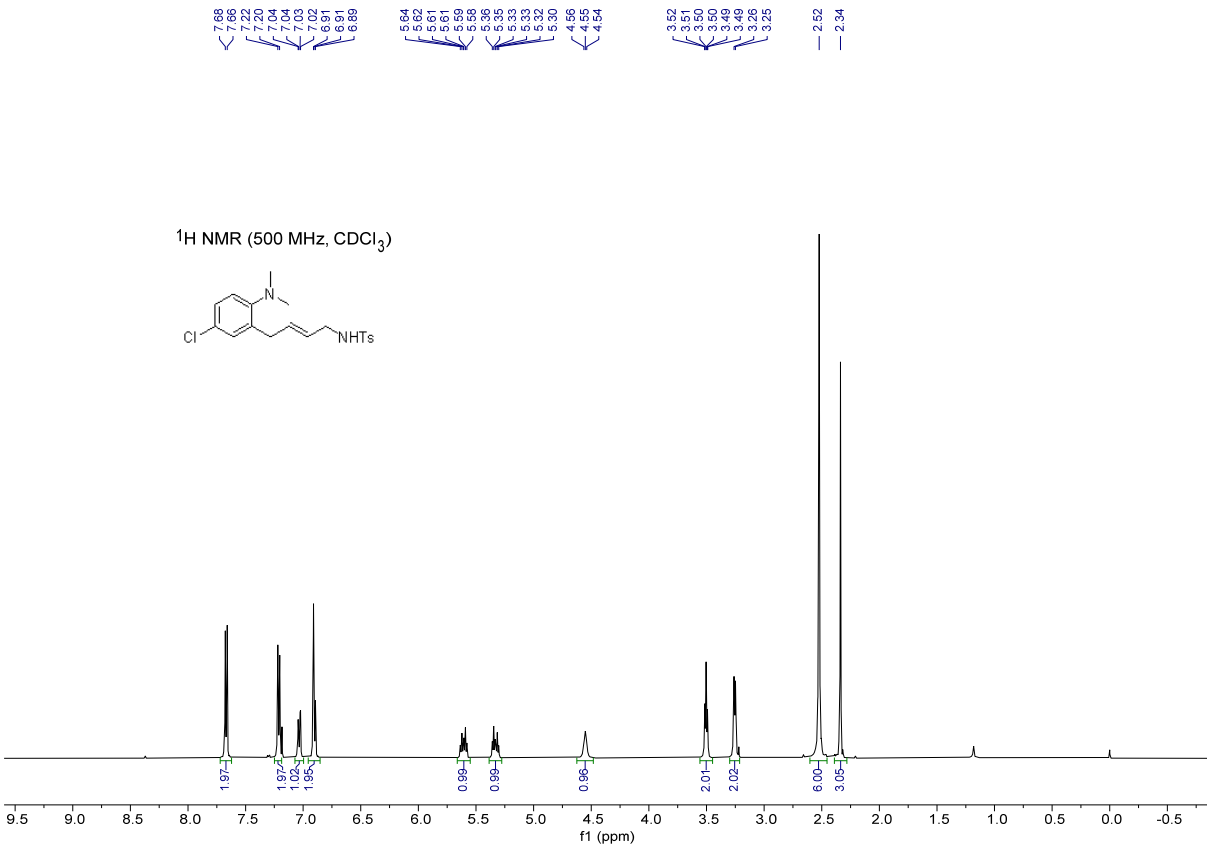


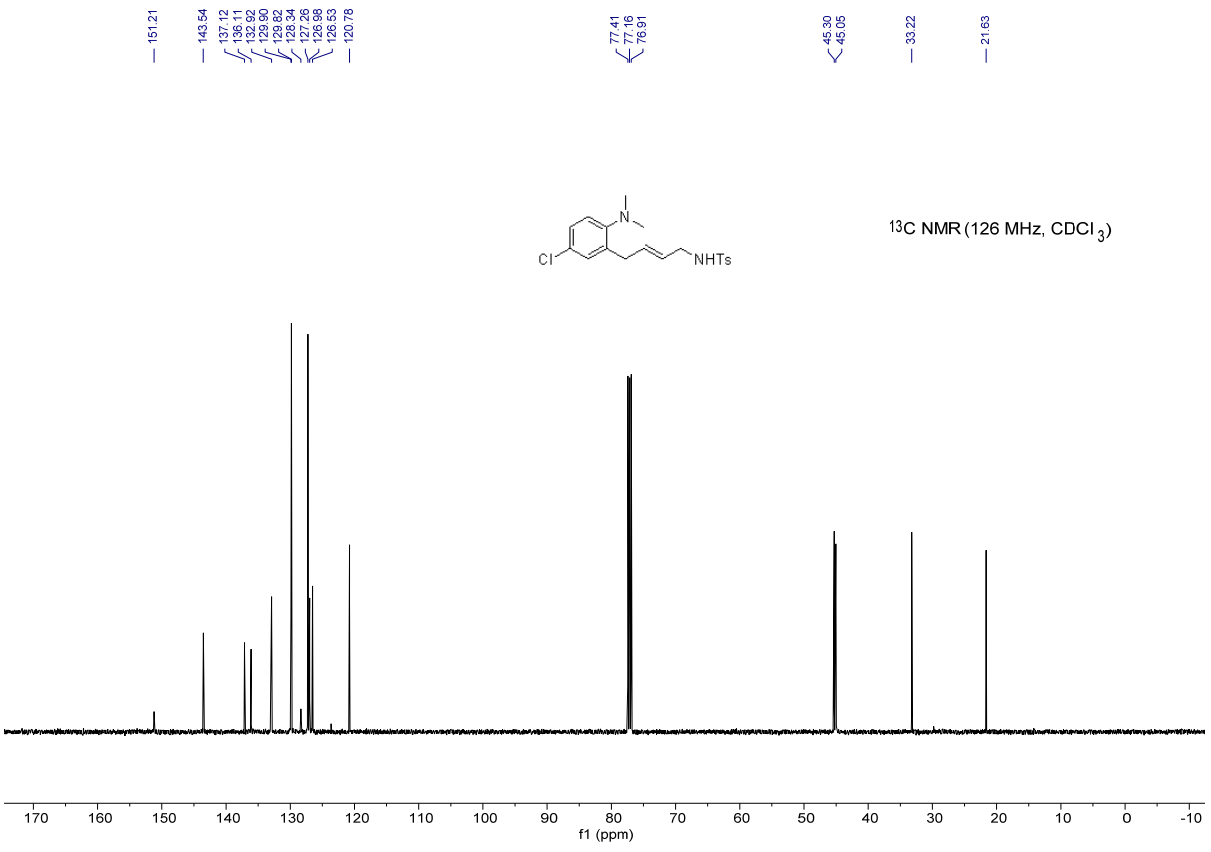
(9) (E)-N-(4-(5-bromo-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3i**)



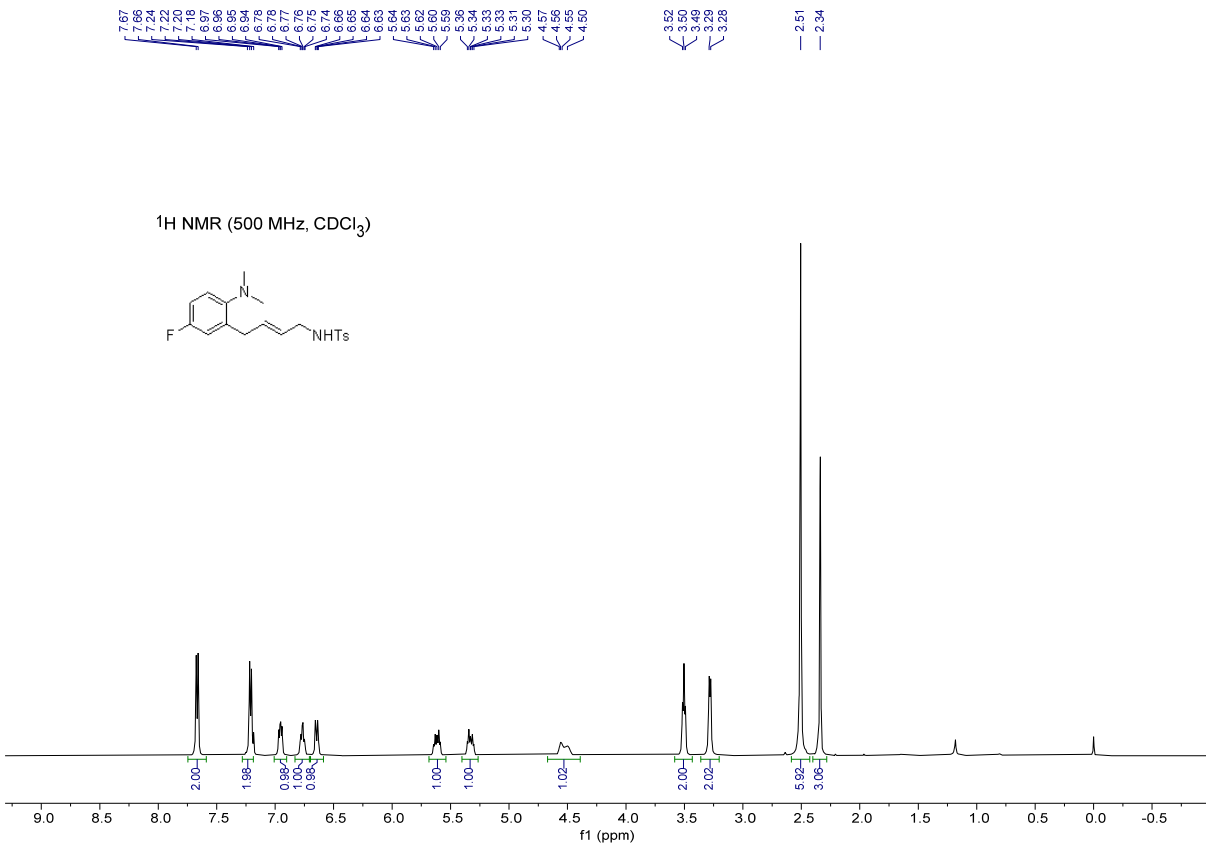


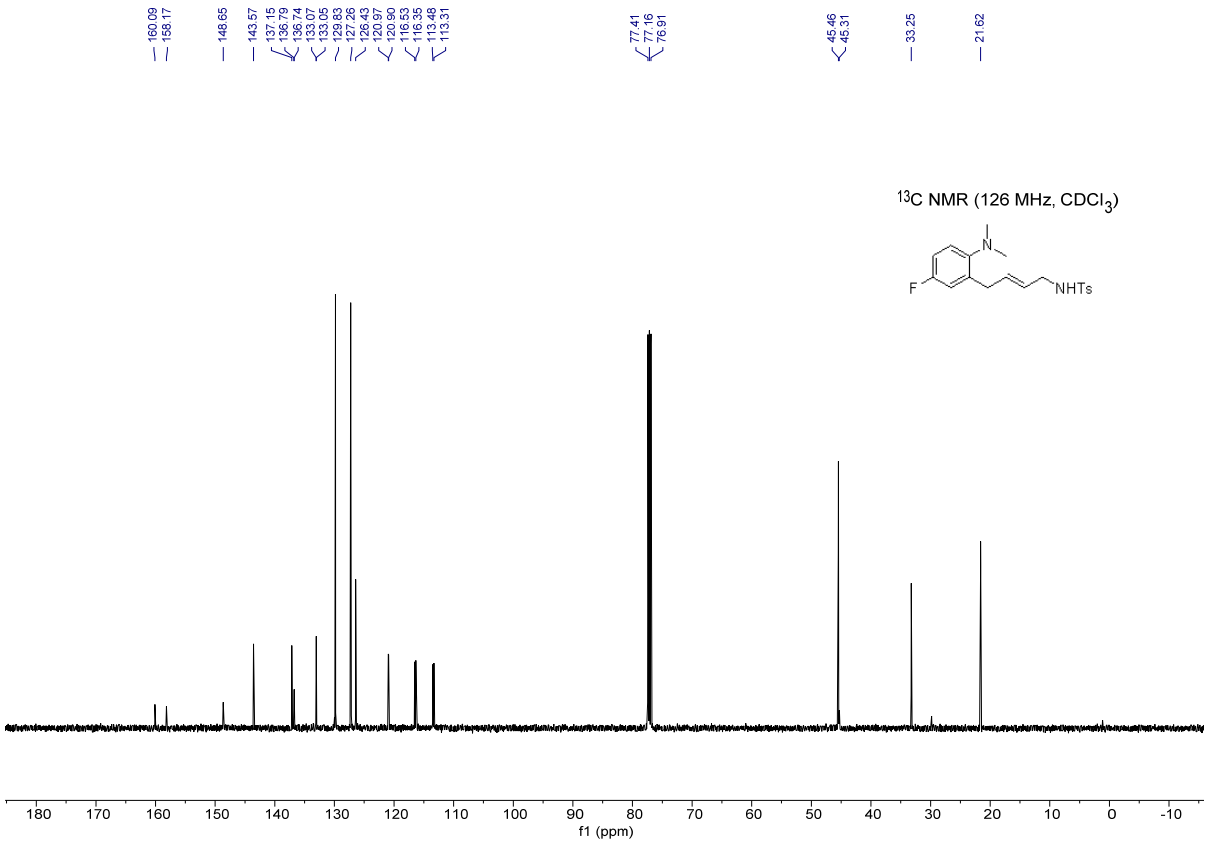
(10) (E)-N-(4-(5-chloro-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3j**)

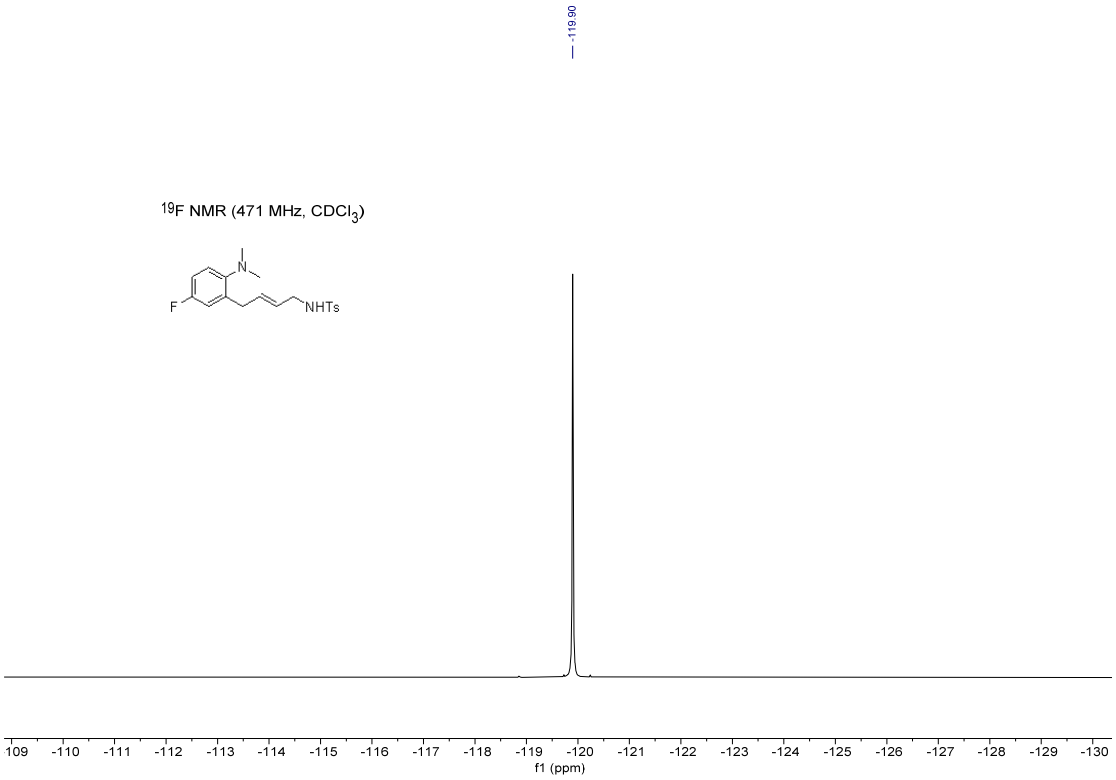




(11) (E)-N-(4-(2-(dimethylamino)-5-fluorophenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3k**)



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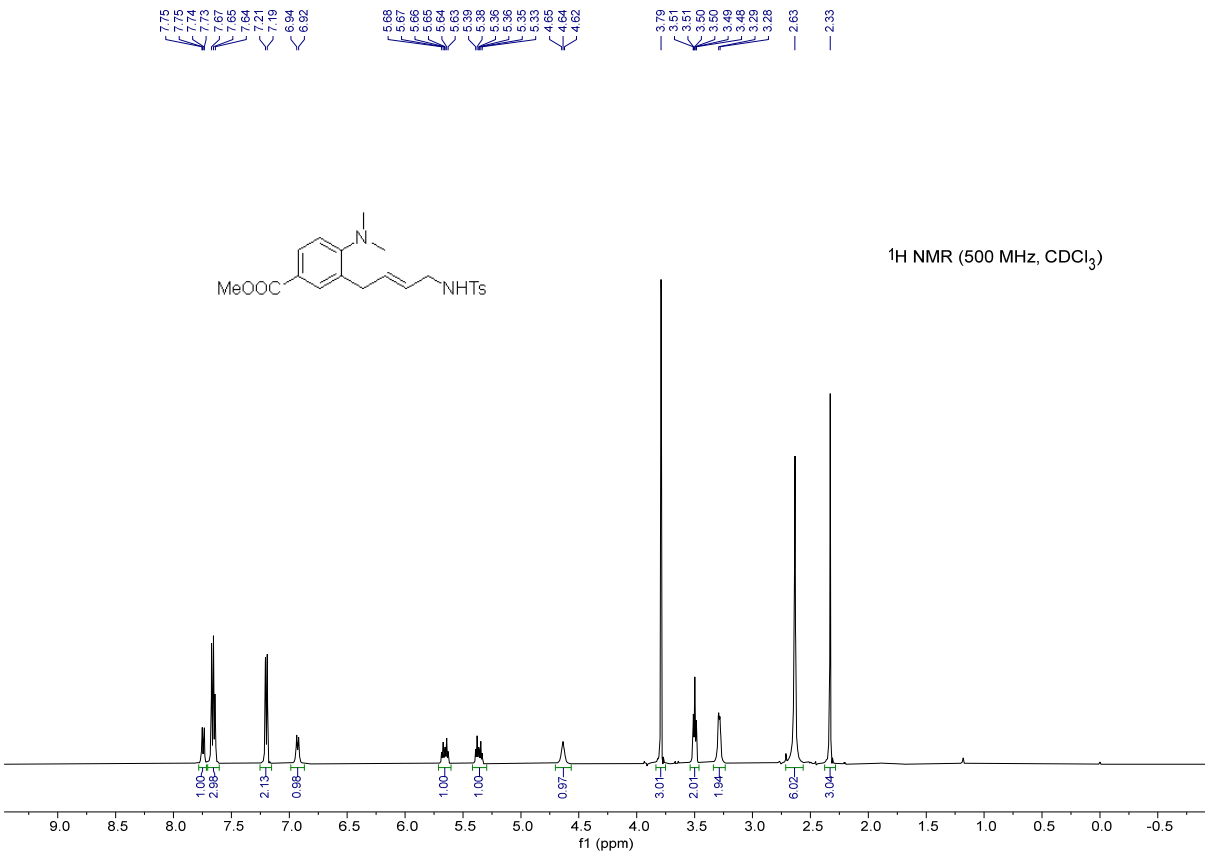
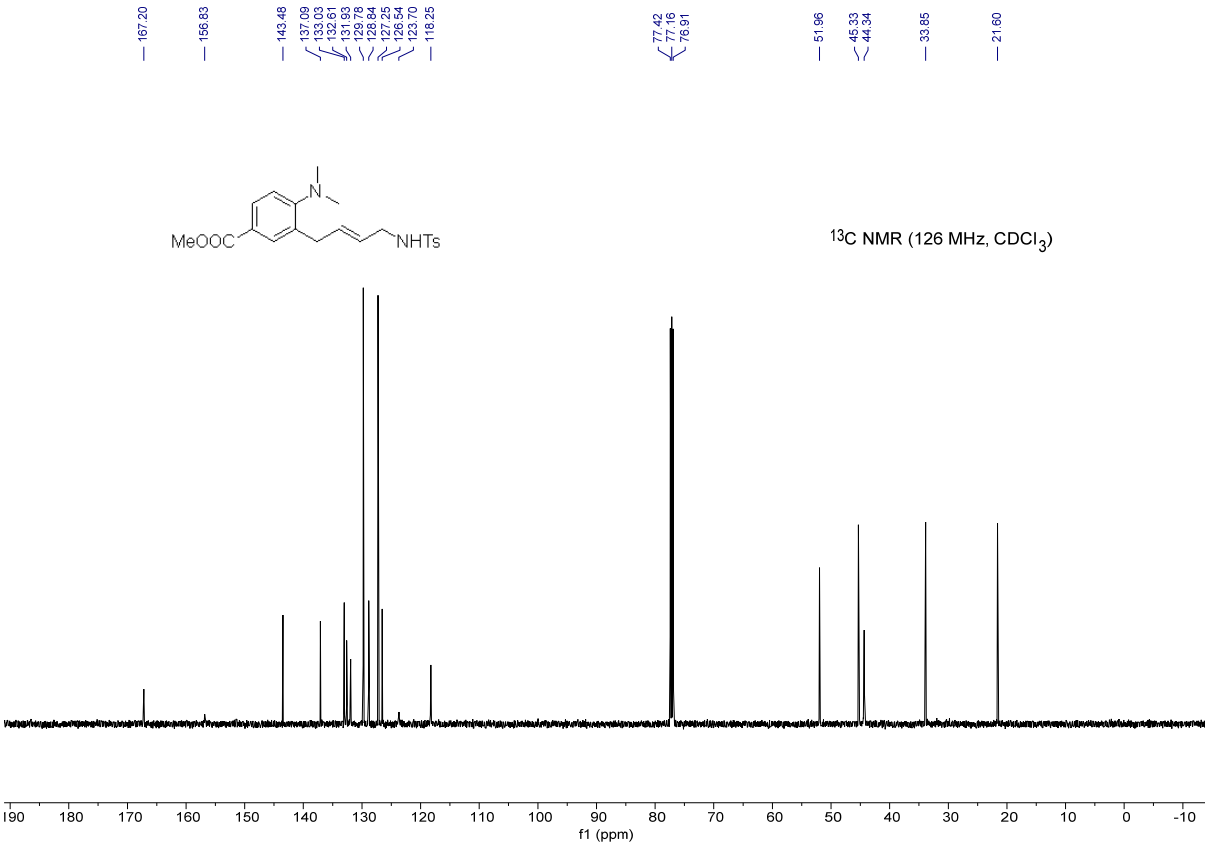
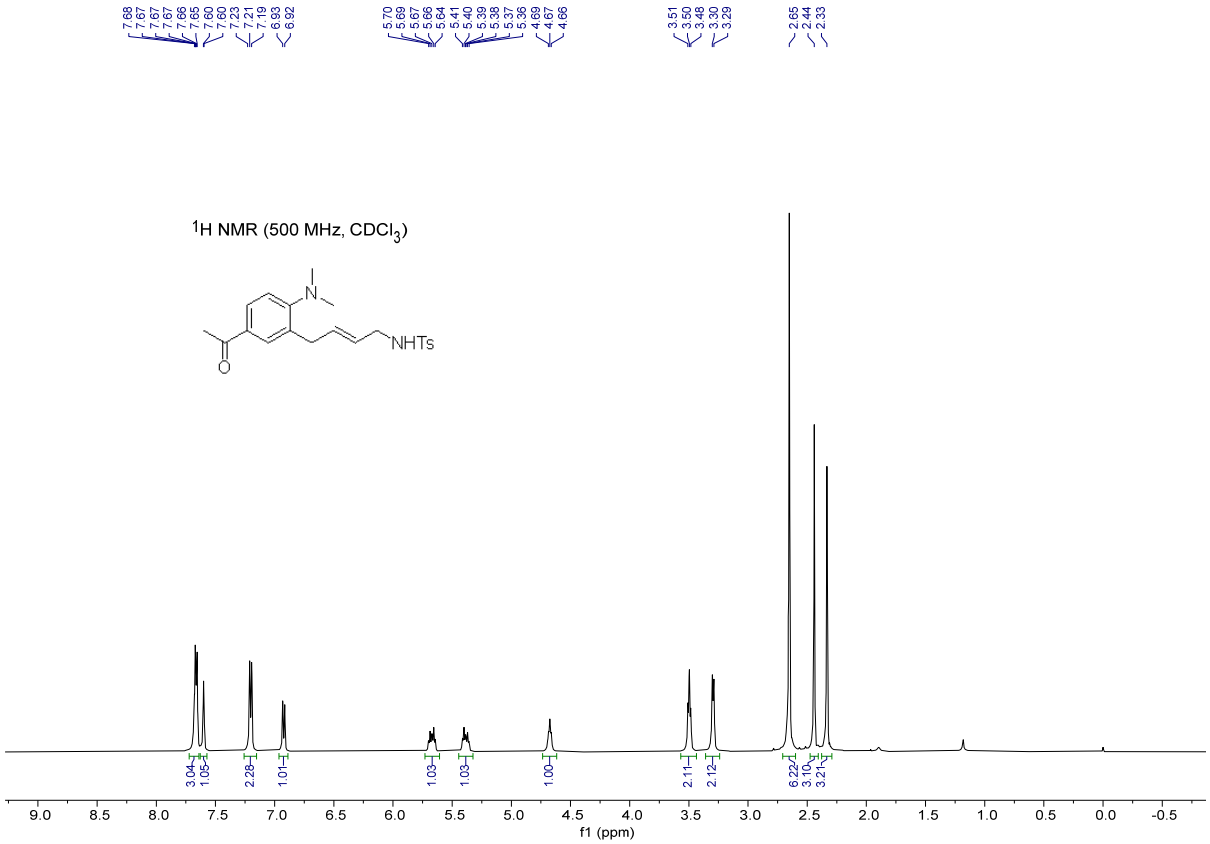
19F NMR (471 MHz, CDCl3)
N
F
NHTs
-109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127 -128 -129 -130
f1 (ppm)

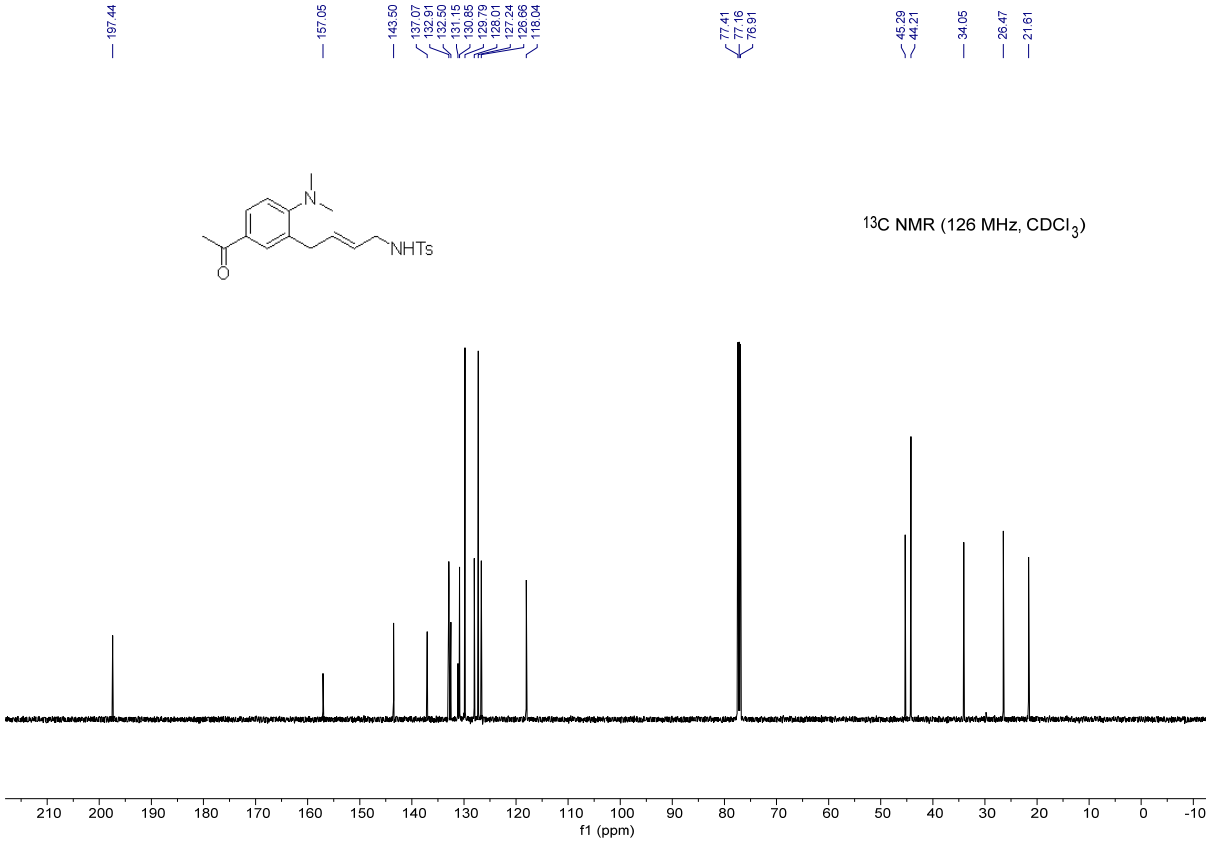
(12) methyl (E)-4-(dimethylamino)-3-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)benzoate (**3l**)



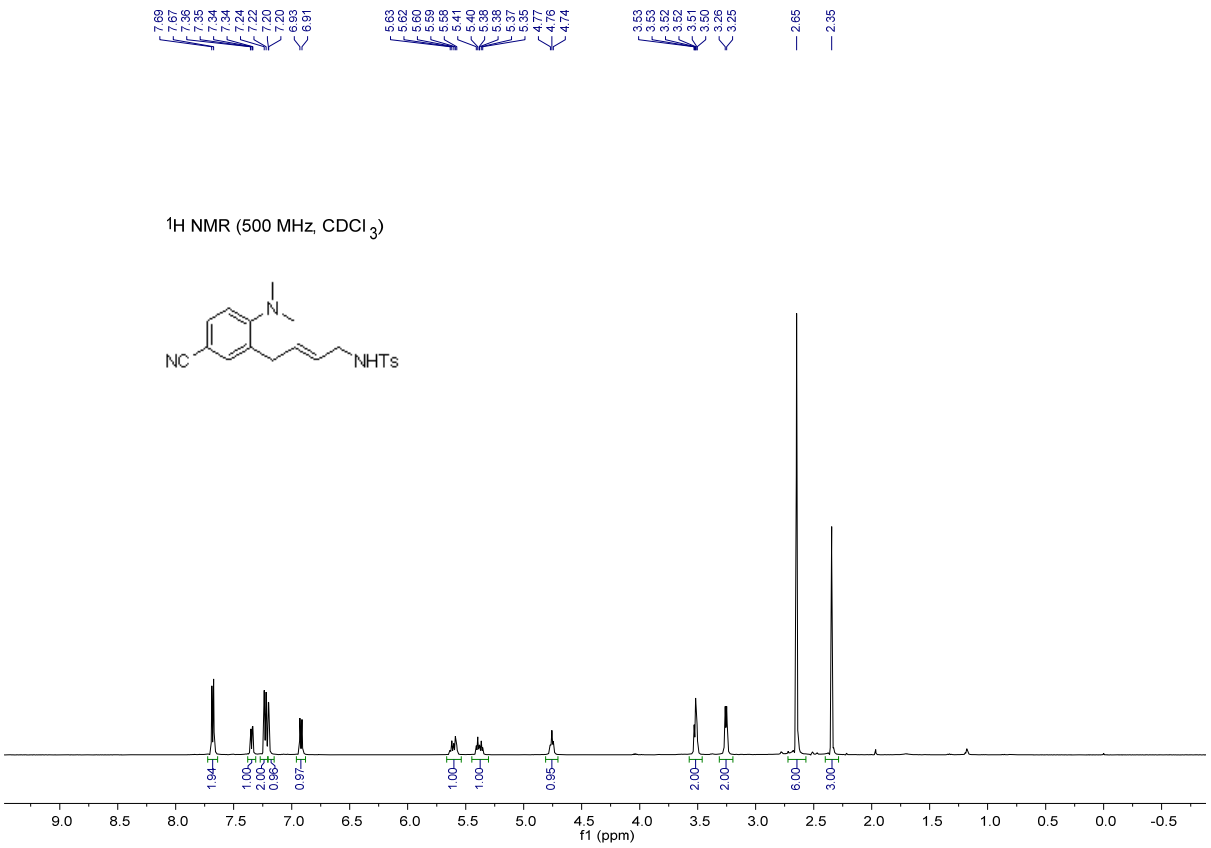


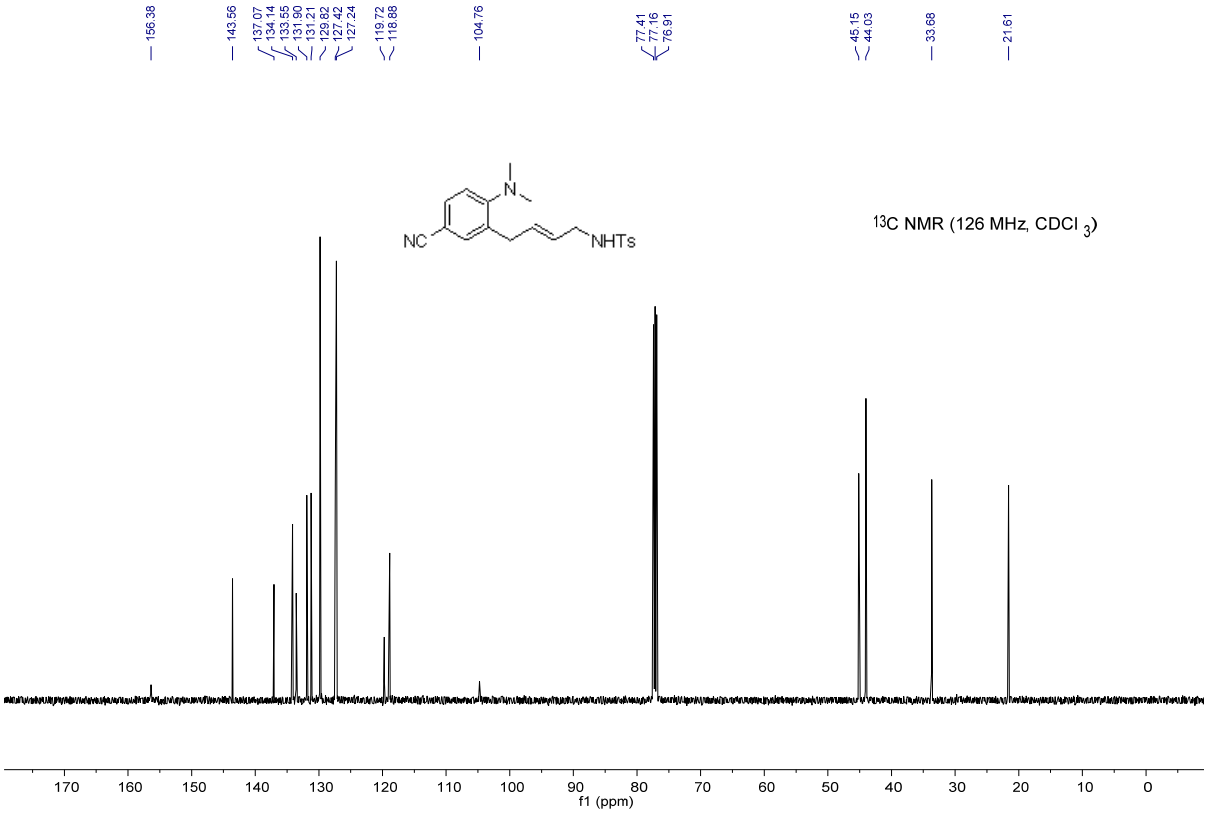
(13) (E)-N-(4-(5-acetyl-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3m**)



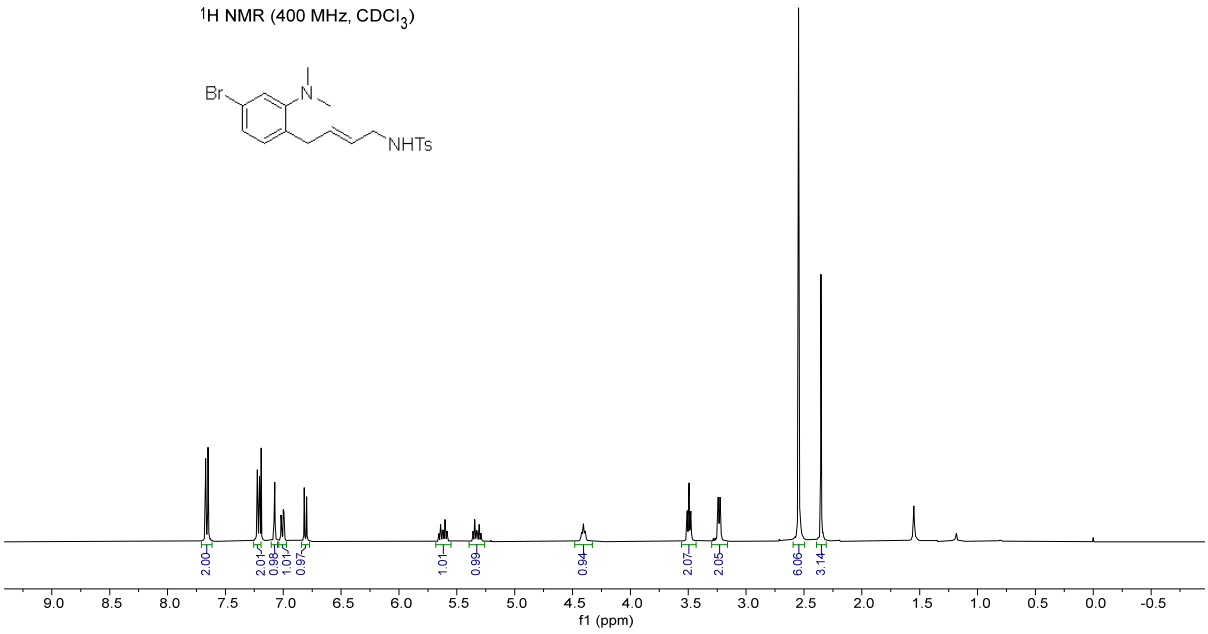


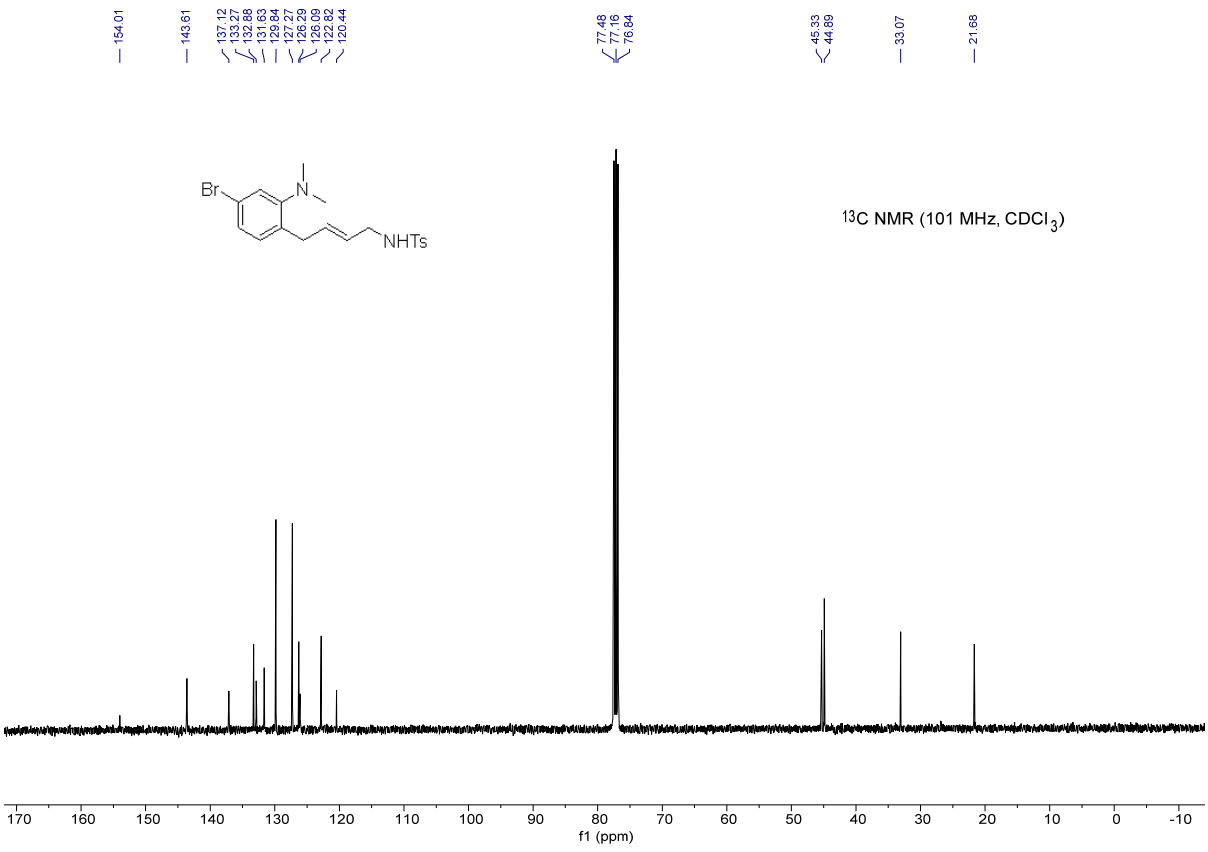
(14) (E)-N-(4-(5-cyano-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3n**)



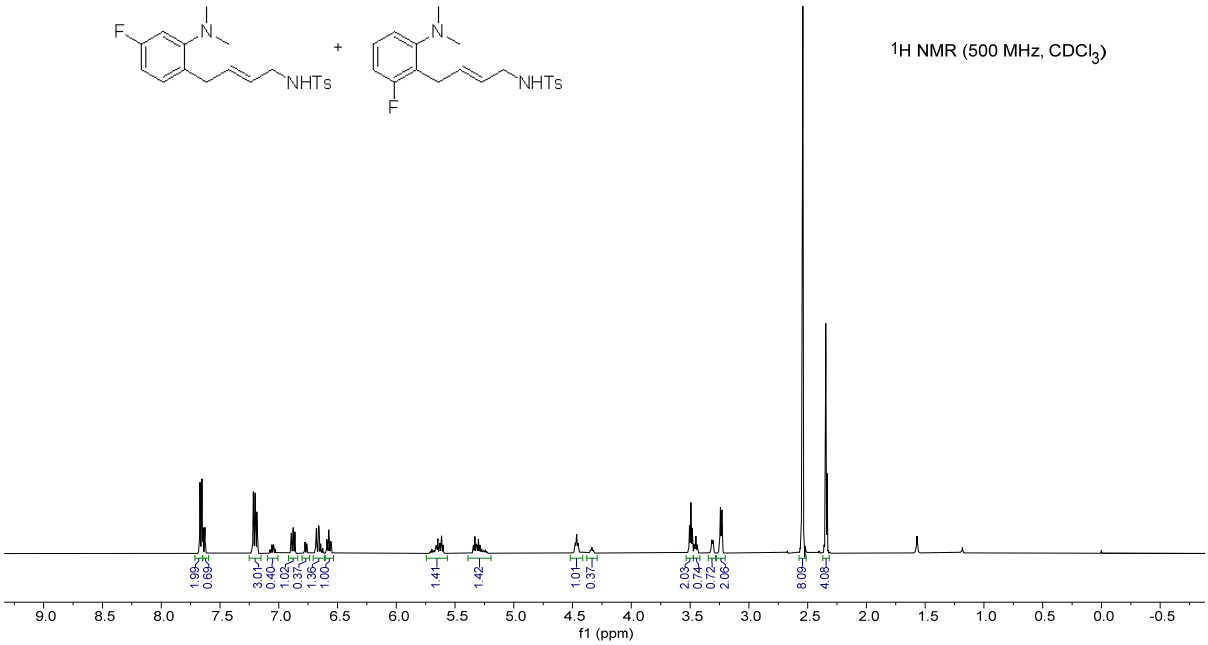


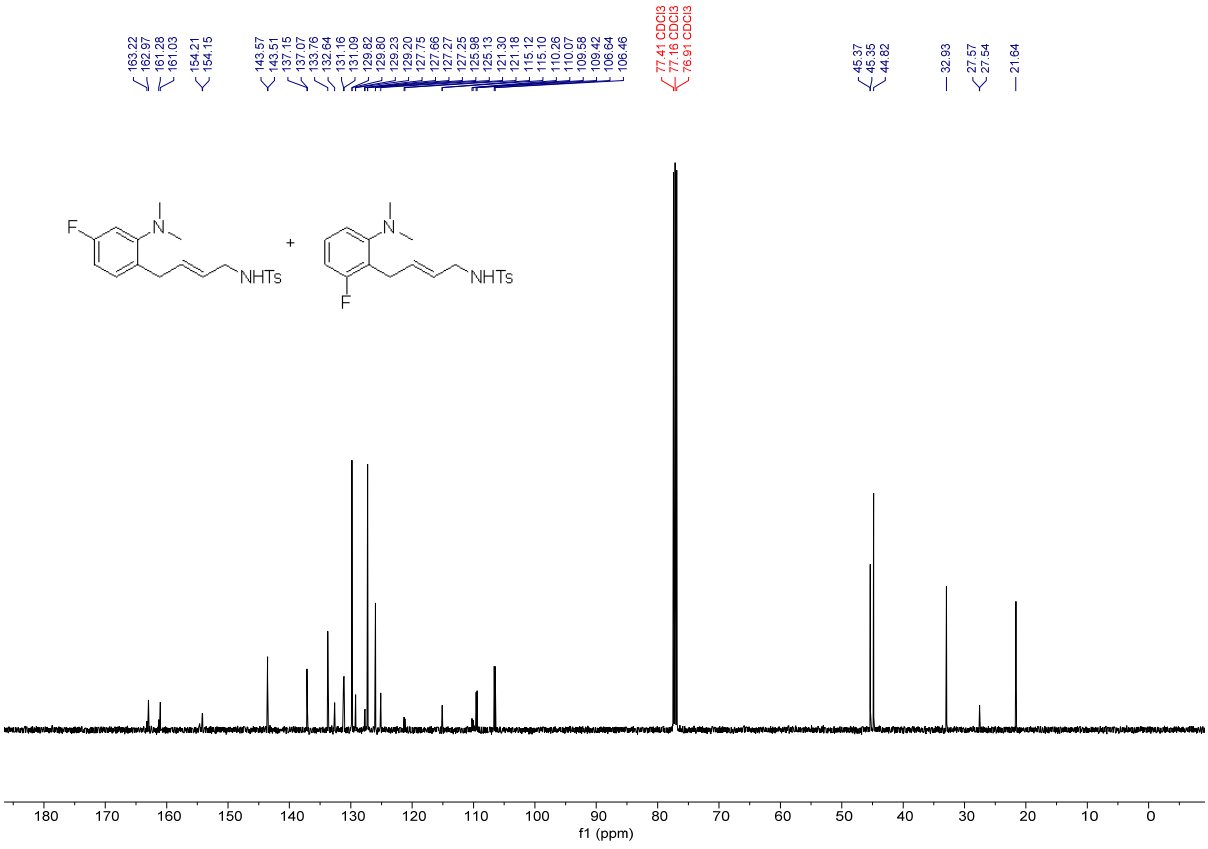
(15) (E)-N-(4-(4-bromo-2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3o**)

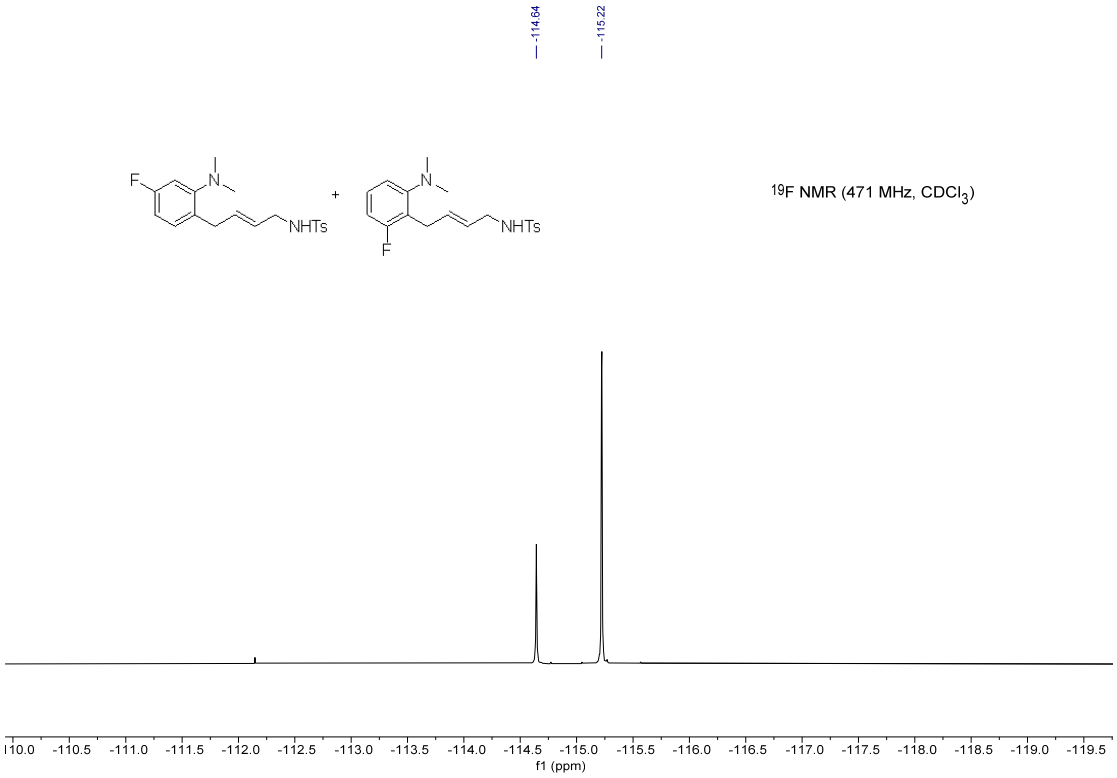




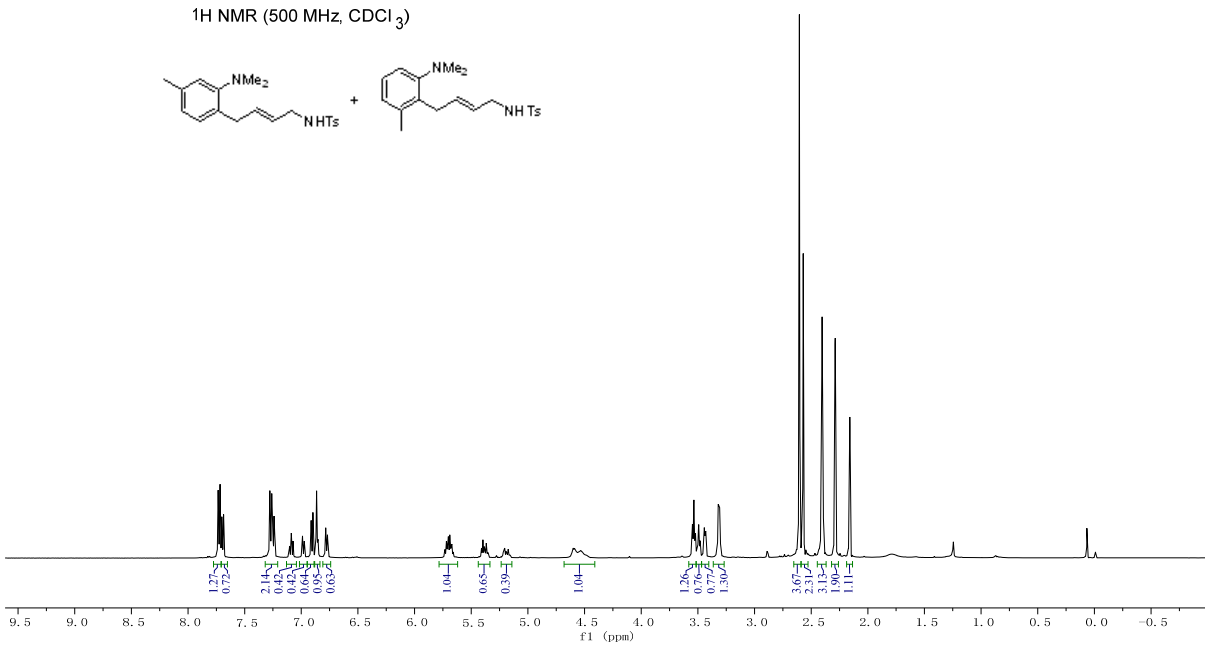
(16) (E)-N-(4-(2-(dimethylamino)-4-fluorophenyl)but-2-en-1-yl)-4-methylbenzenesulfon- amide (**3p**) and (E)-N-(4-(2-(dimethylamino)-6-fluorophenyl)but-2-en-1-yl)-4-methylbenz- enesulfonamide (**3p′**)

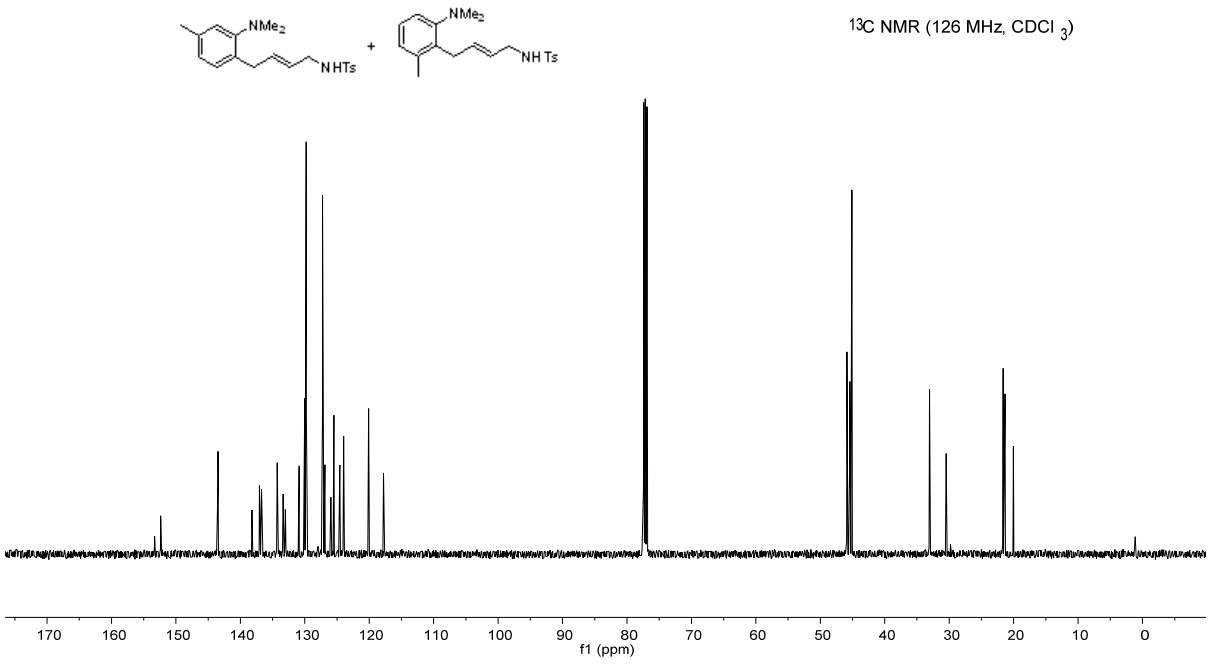




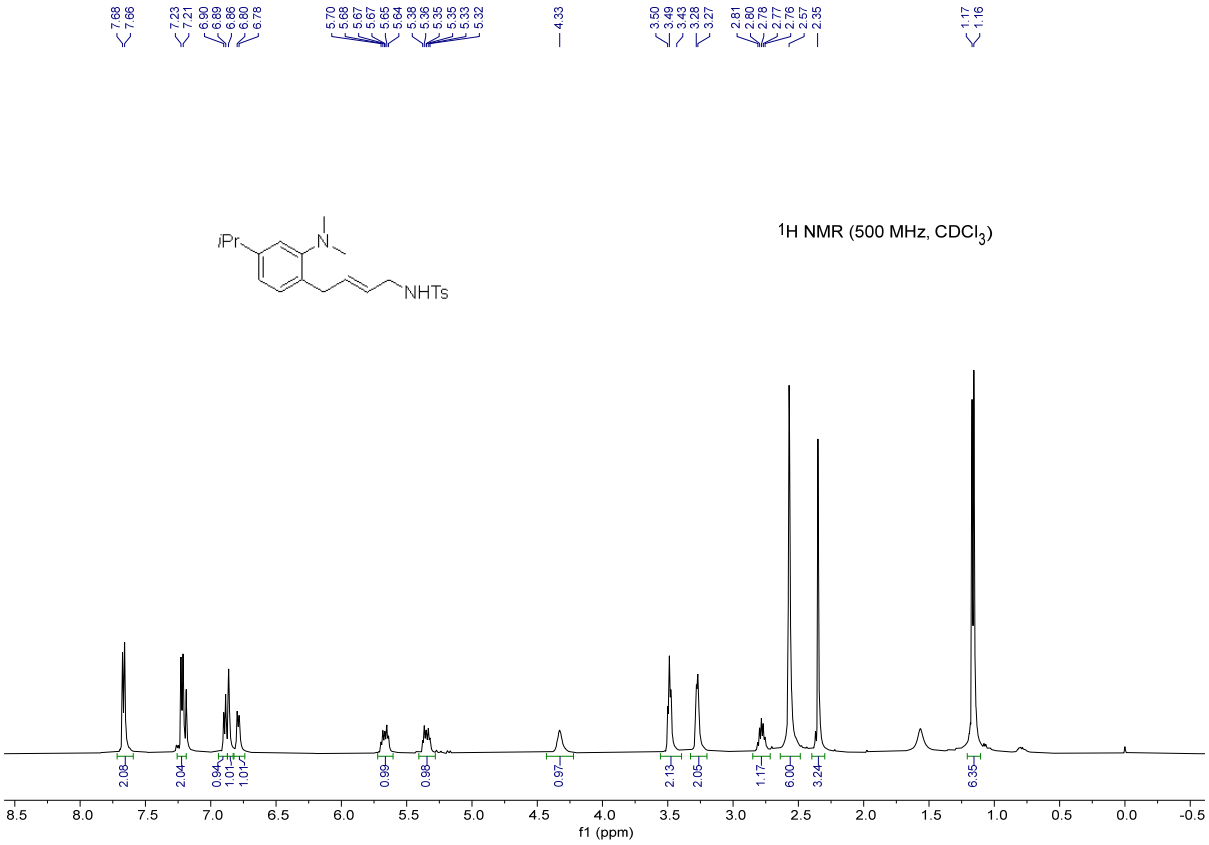

-114.64
-115.22
F
N
NHTs
+
N
NHTs
F
^{19}F NMR (471 MHz, $CDCl_3$)
-110.0 -110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5
f1 (ppm)

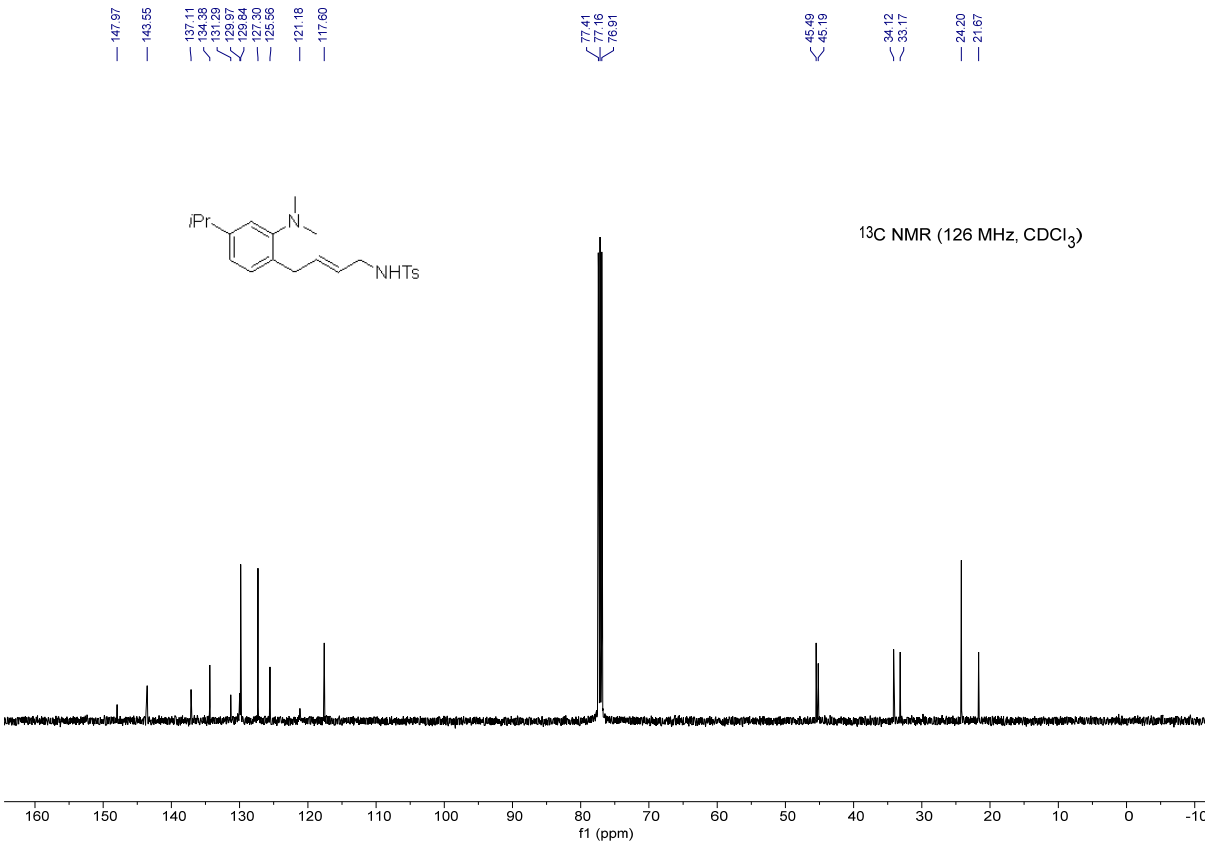
(17) (E)-N-(4-(2-(dimethylamino)-4-methylphenyl)but-2-en-1-yl)-4-methylbenzenesulfon- amide (**3q**) and (E)-N-(4-(2-(dimethylamino)-6-methylphenyl)but-2-en-1-yl)-4-methyl- benzenesulfonamide (**3q′**)



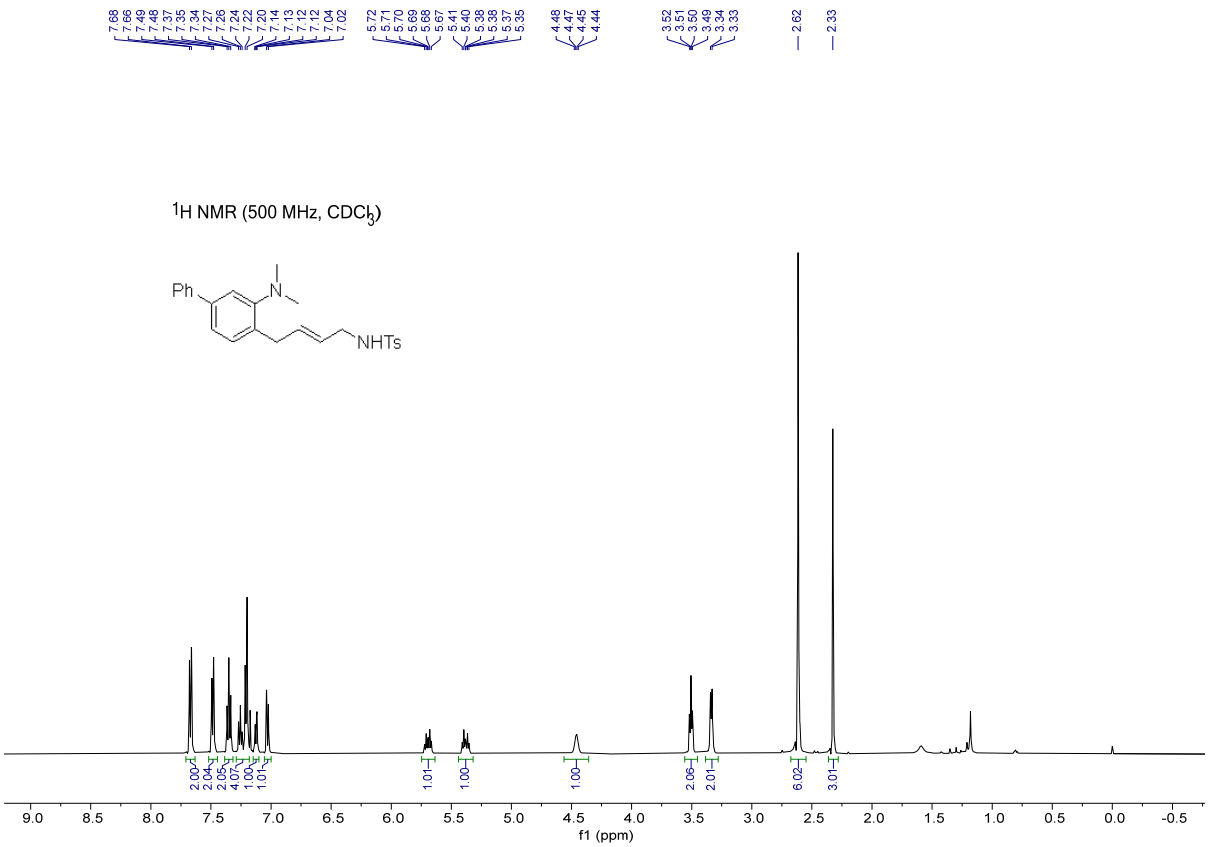


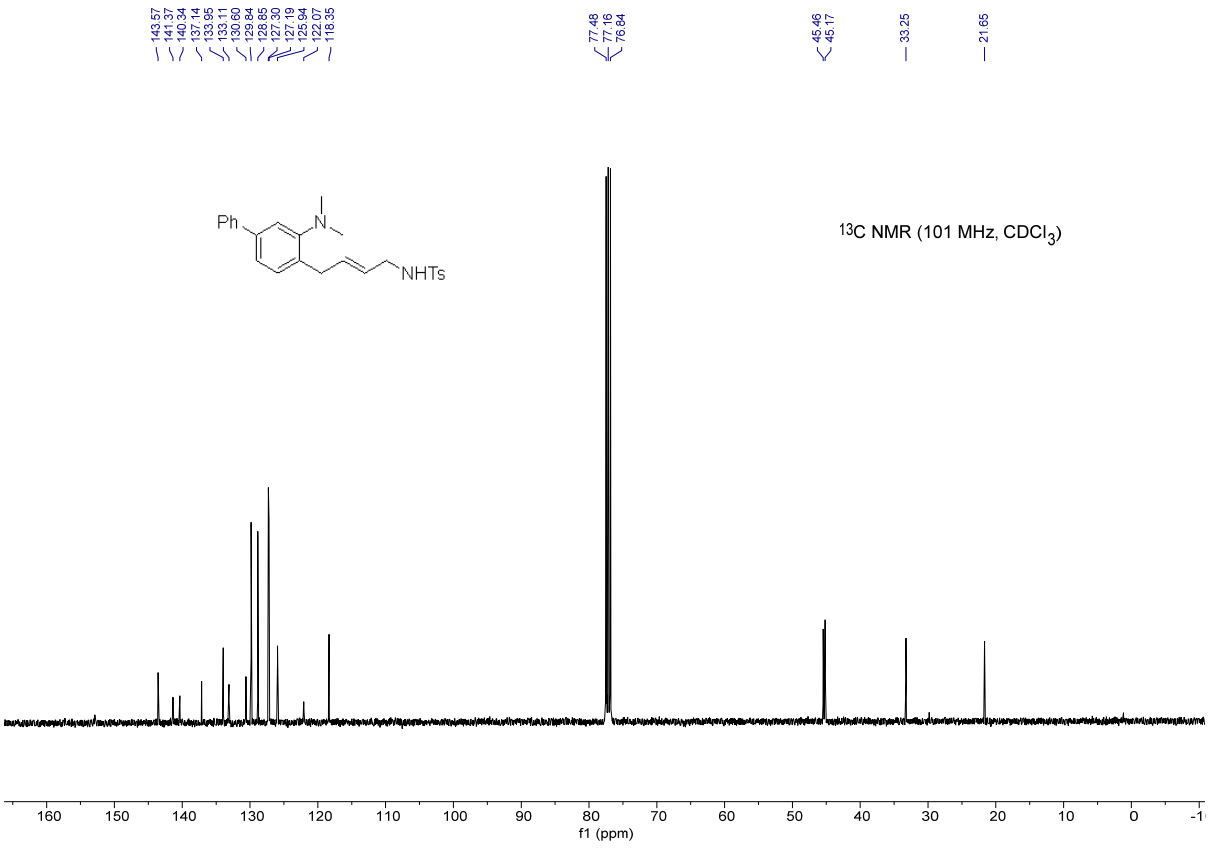
(18) (E)-N-(4-(2-(dimethylamino)-4-isopropylphenyl)but-2-en-1-yl)-4-methylbenzenesulfon- amide (**3r**)



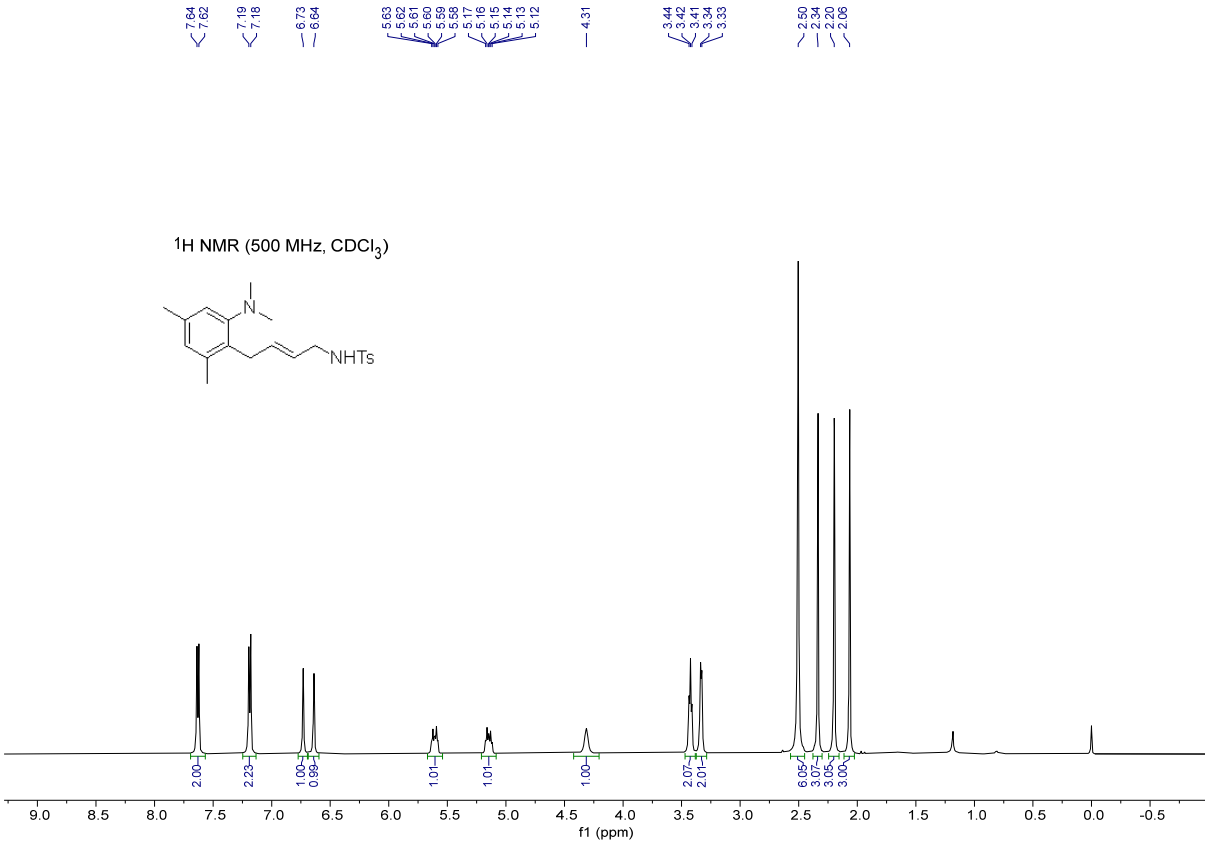


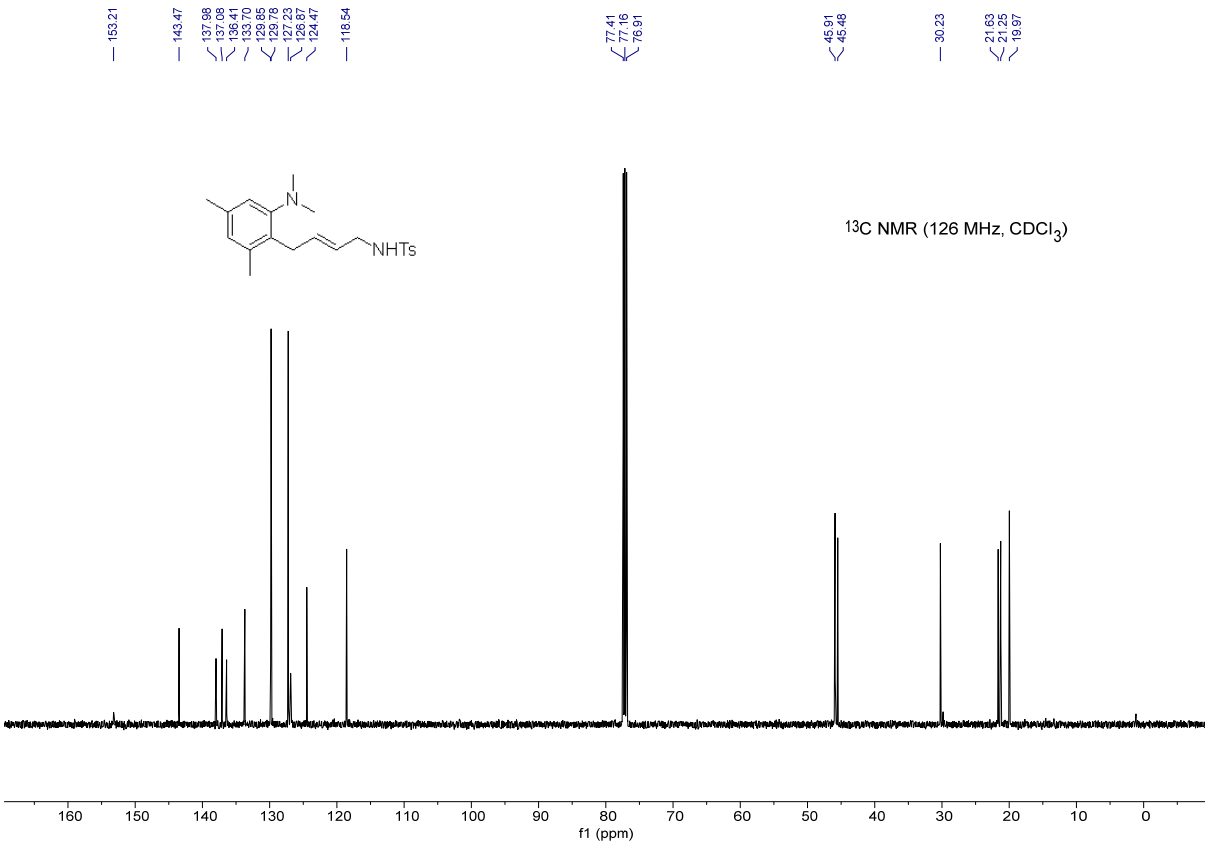
(19) (E)-N-(4-(3-(dimethylamino)-[1,1'-biphenyl]-4-yl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3s**)



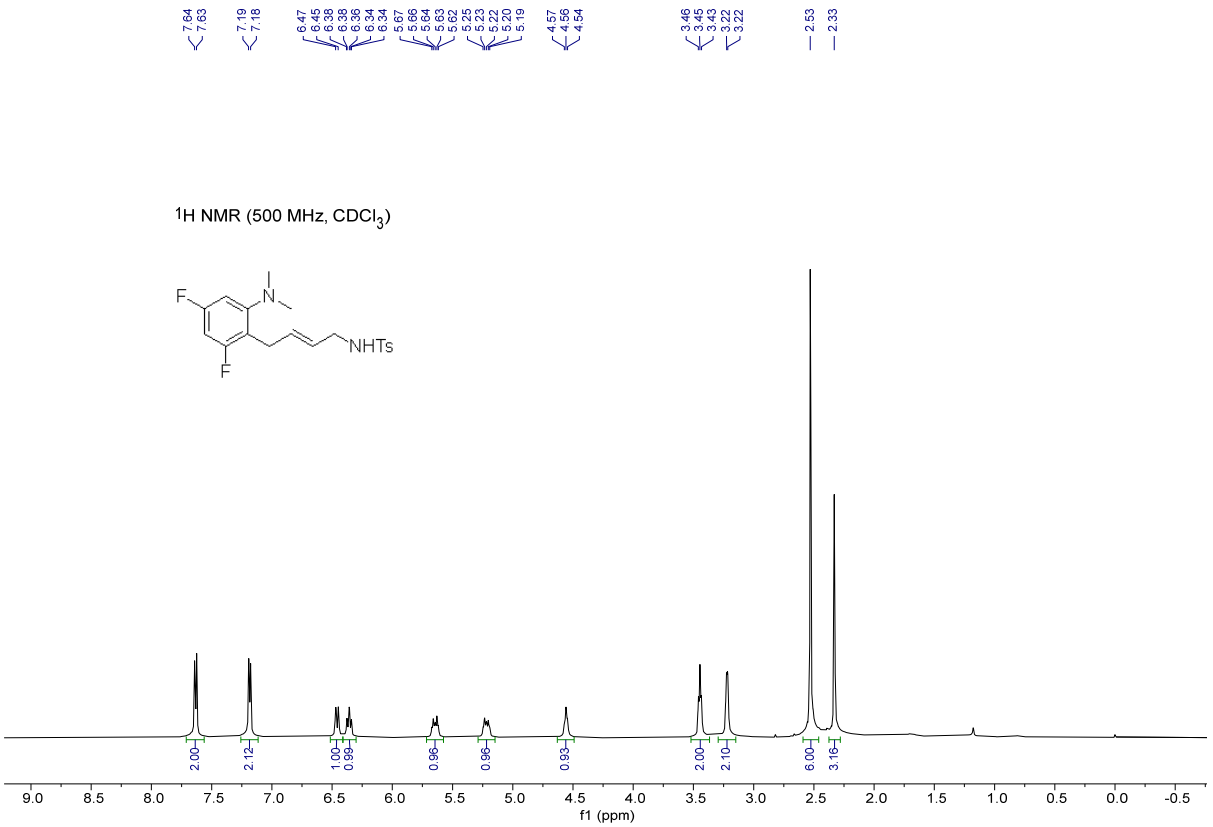


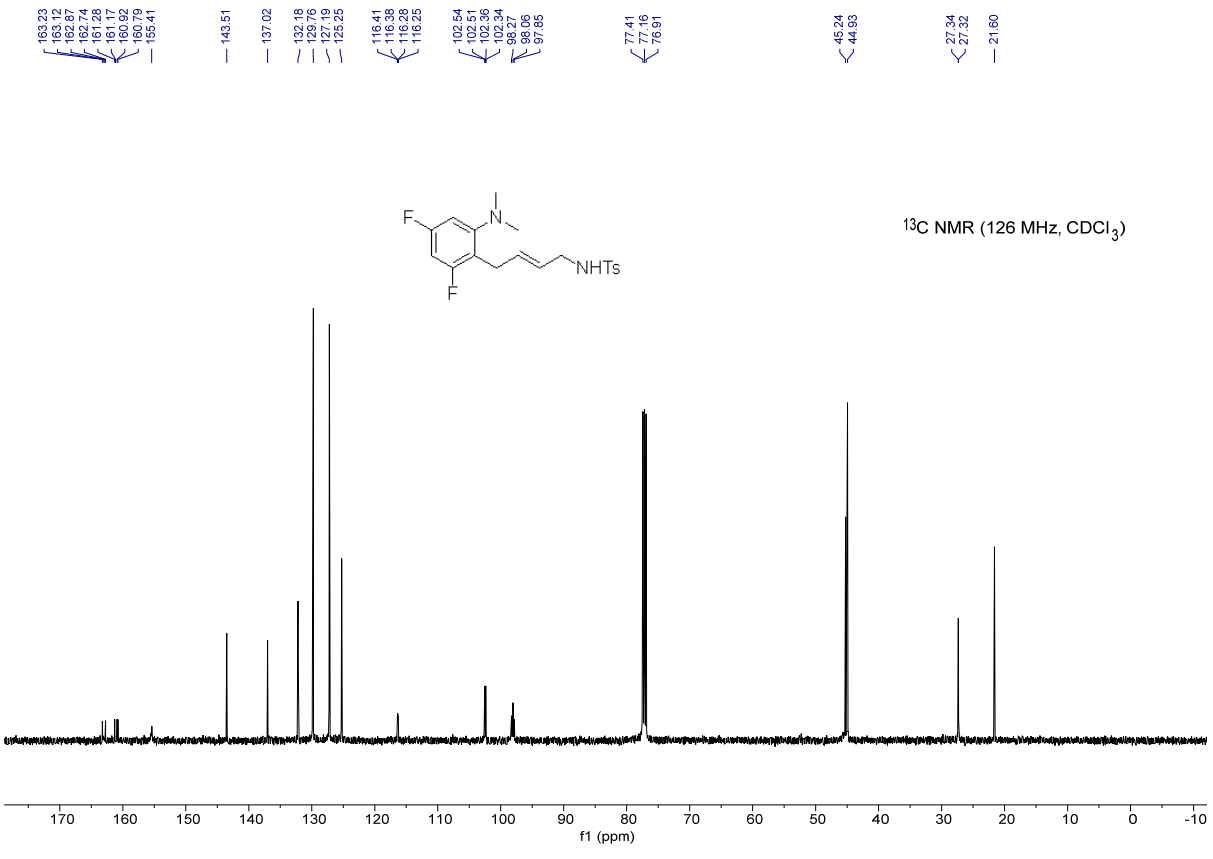
(20) (E)-N-(4-(2-(dimethylamino)-4,6-dimethylphenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3t**)

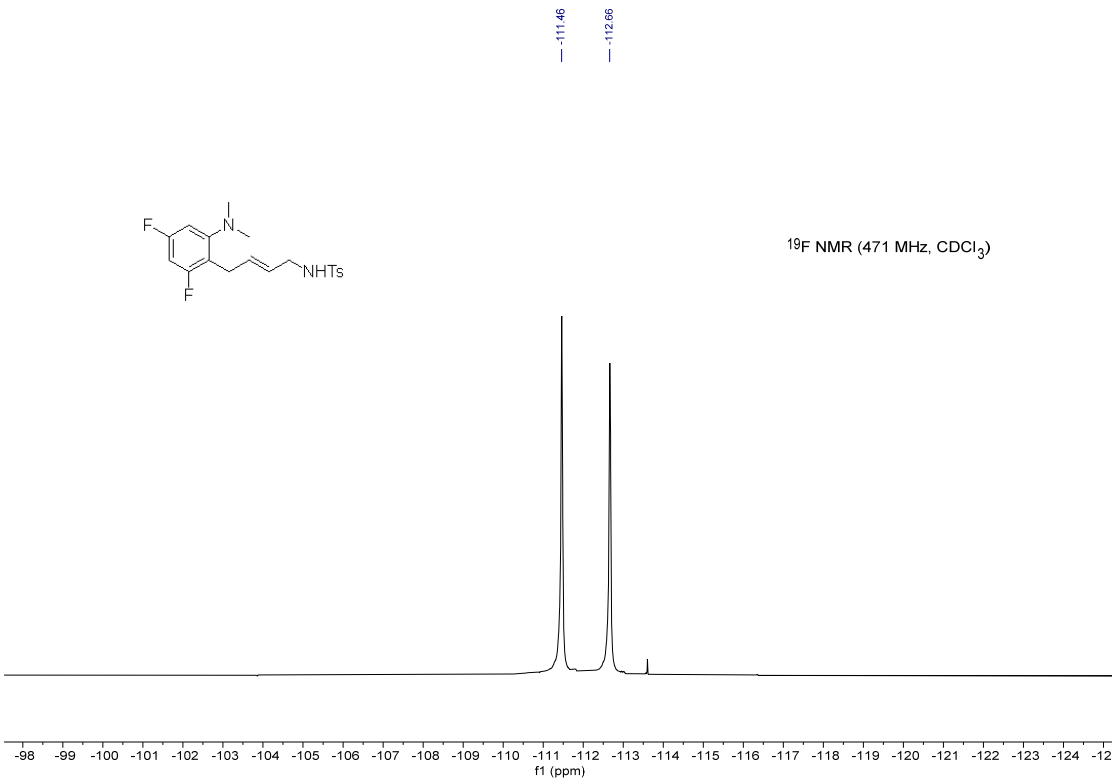




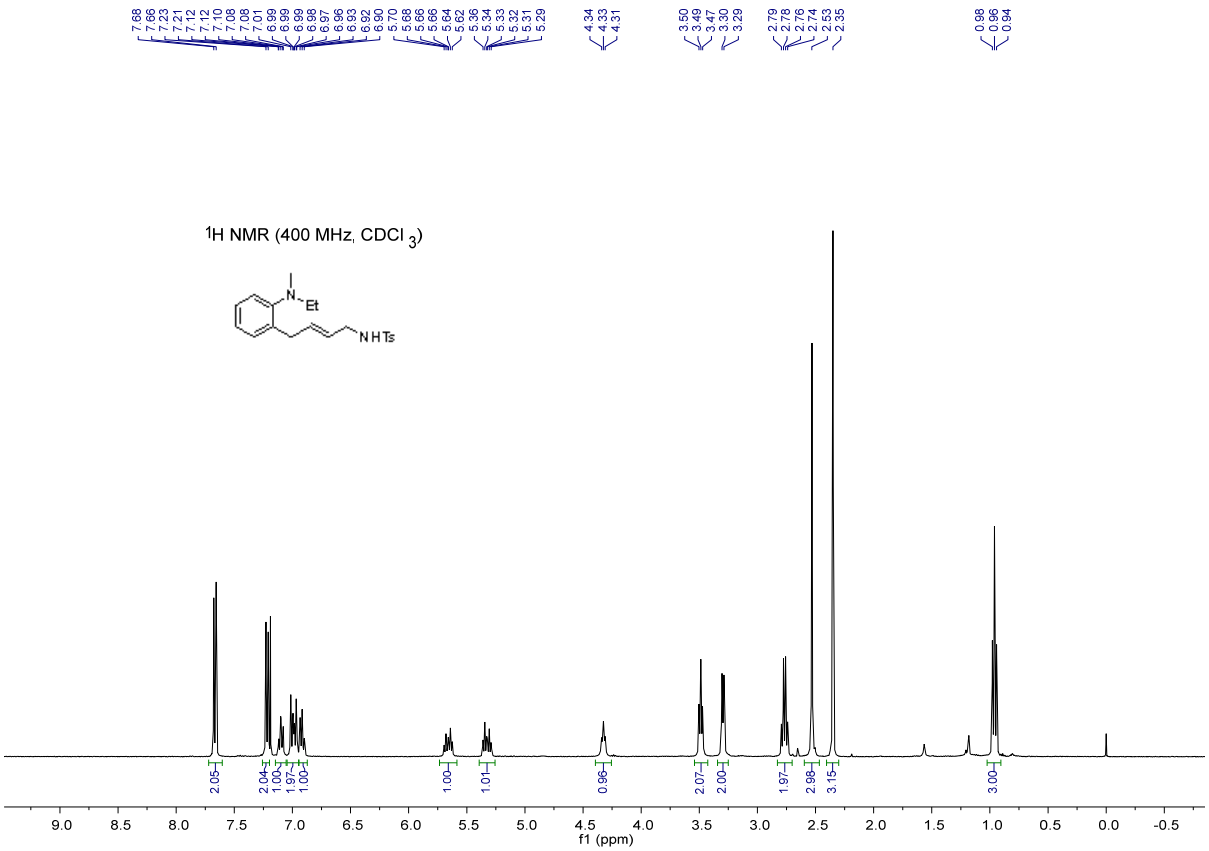
(21) (E)-N-(4-(2-(dimethylamino)-4,6-difluorophenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3u**)

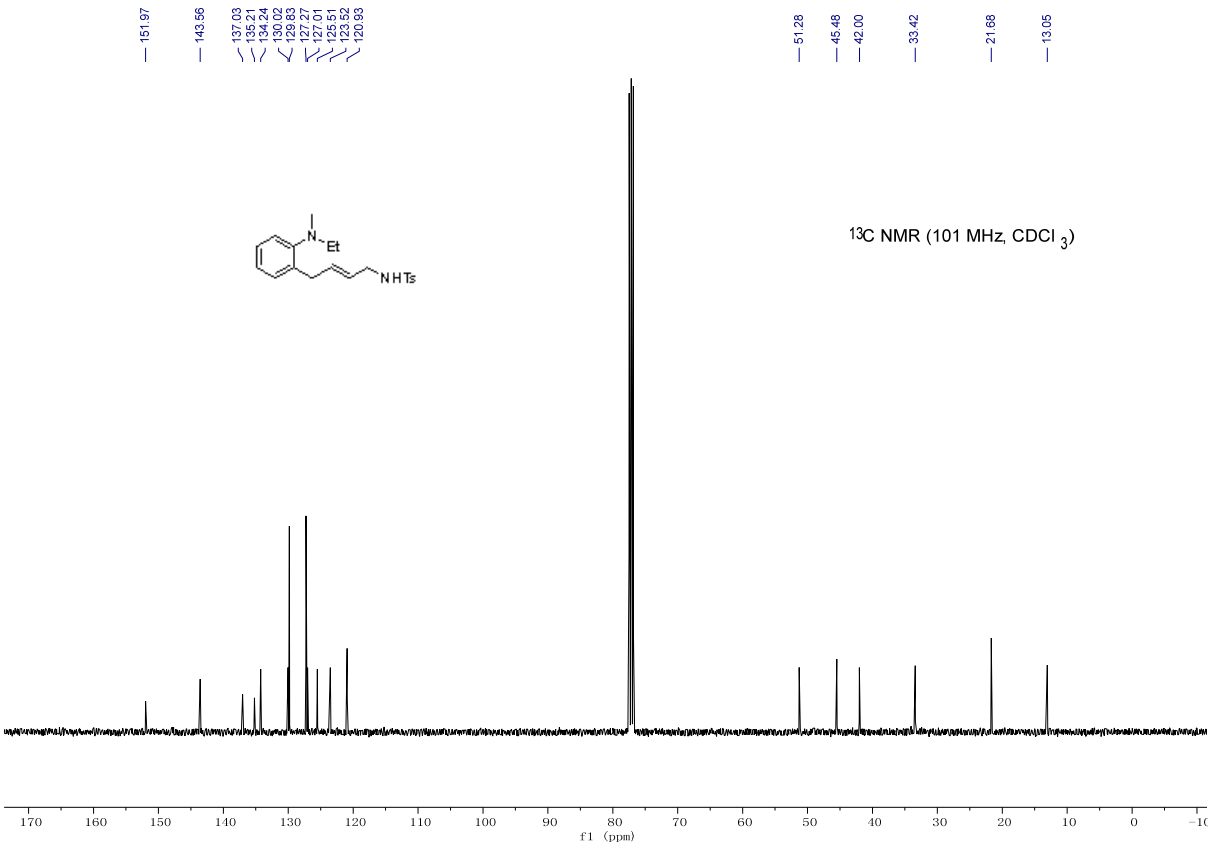




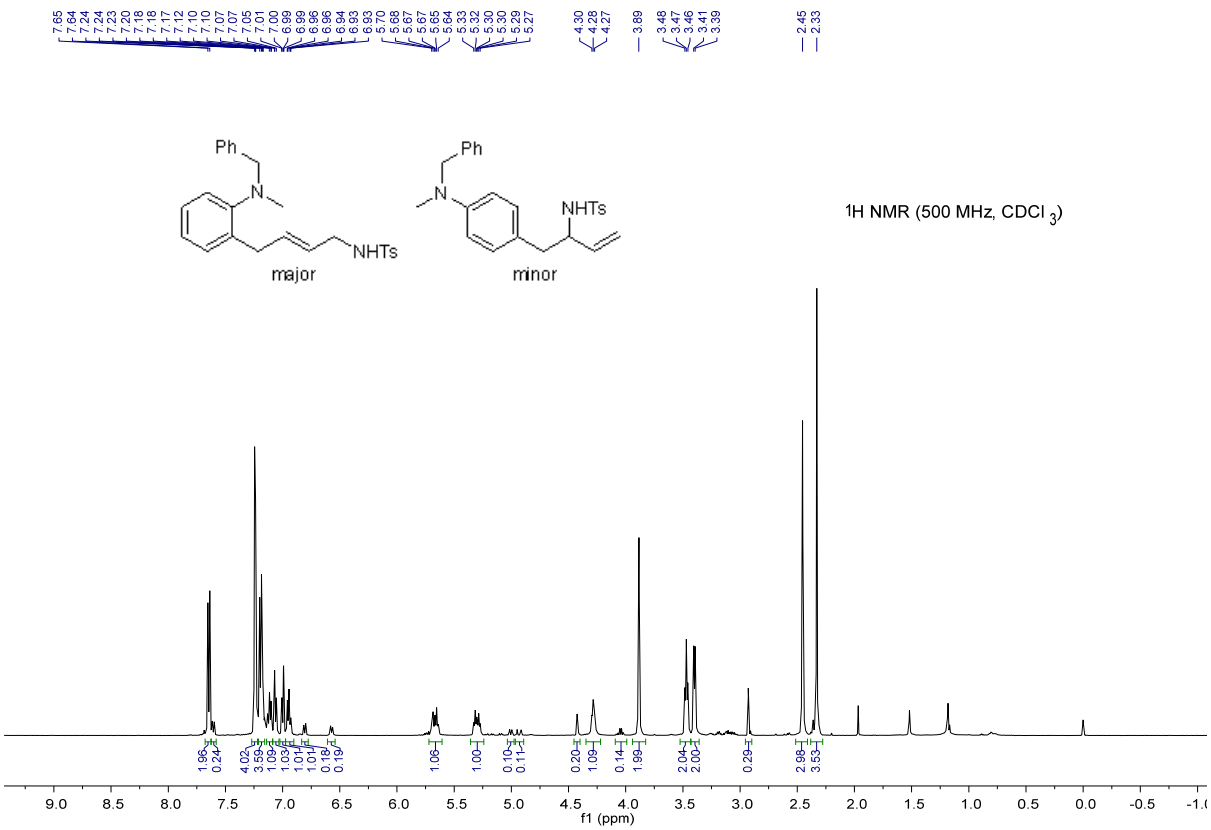

-111.46
-112.66
F
N
NHTs
F
^{19}F NMR (471 MHz, $CDCl_3$)
-98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -12
f1 (ppm)

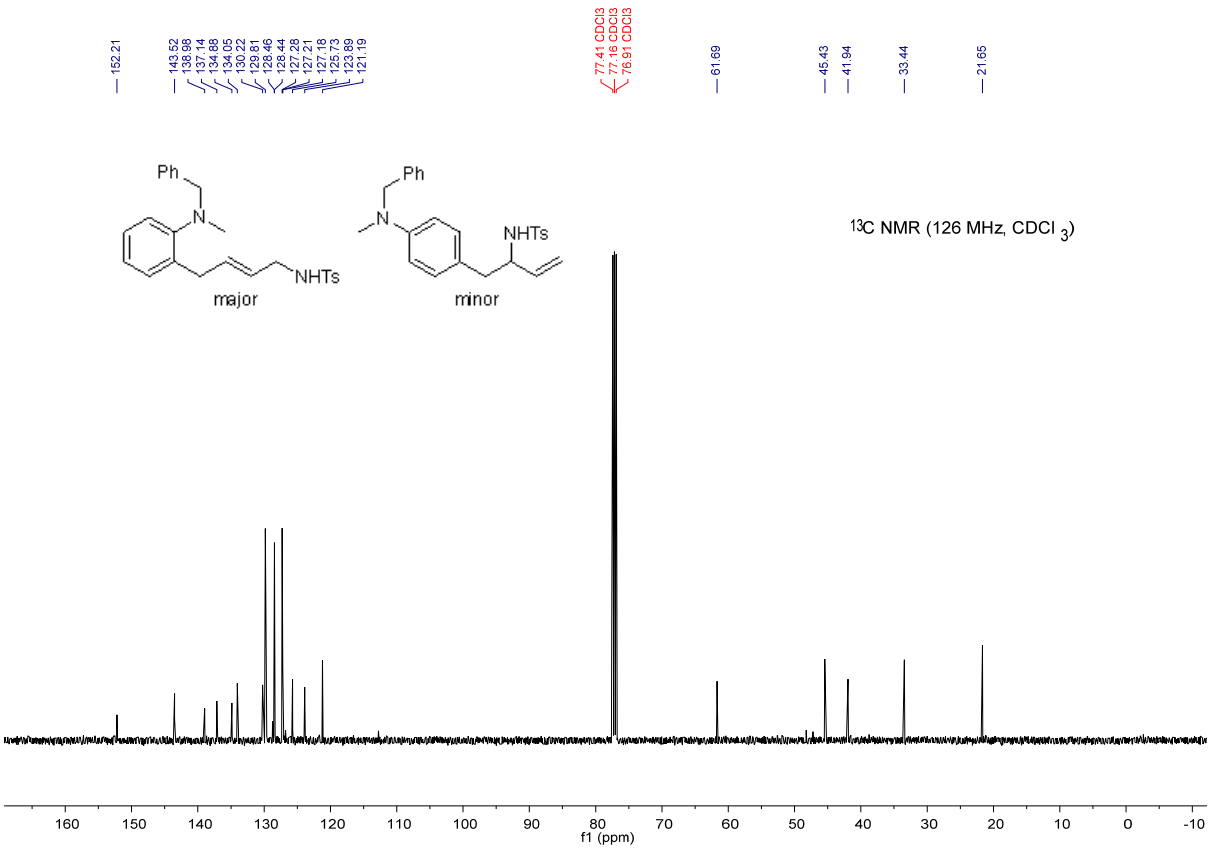
(22) (E)-N-(4-(2-(ethyl(methyl)amino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3v**)





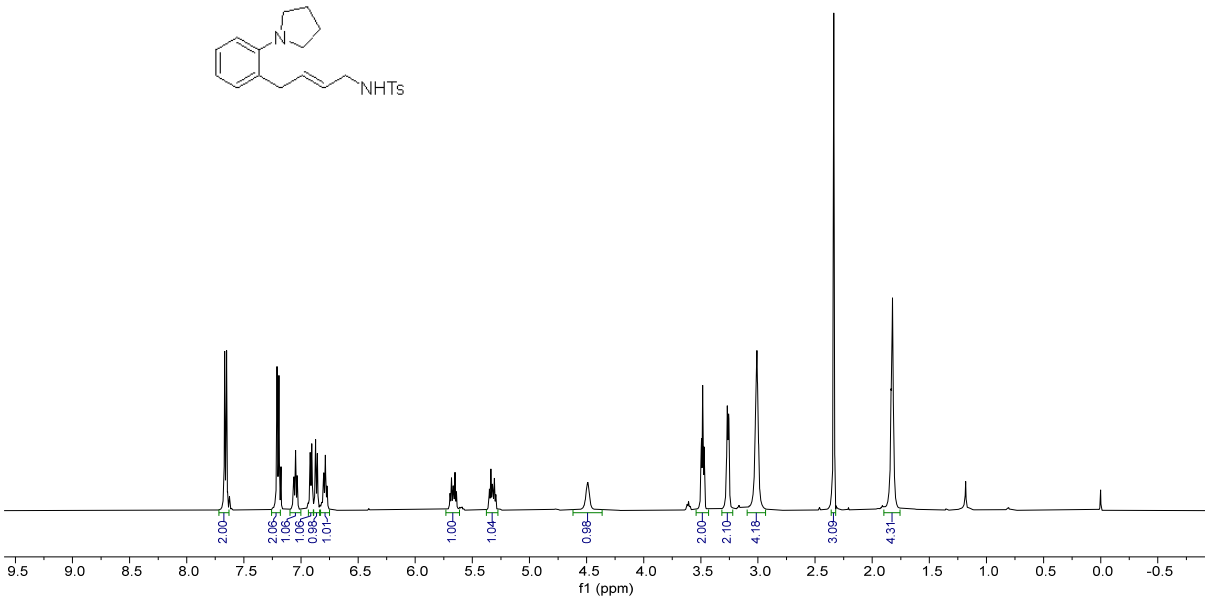
(23) (E)-N-(4-(2-(benzyl(methyl)amino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3w**)



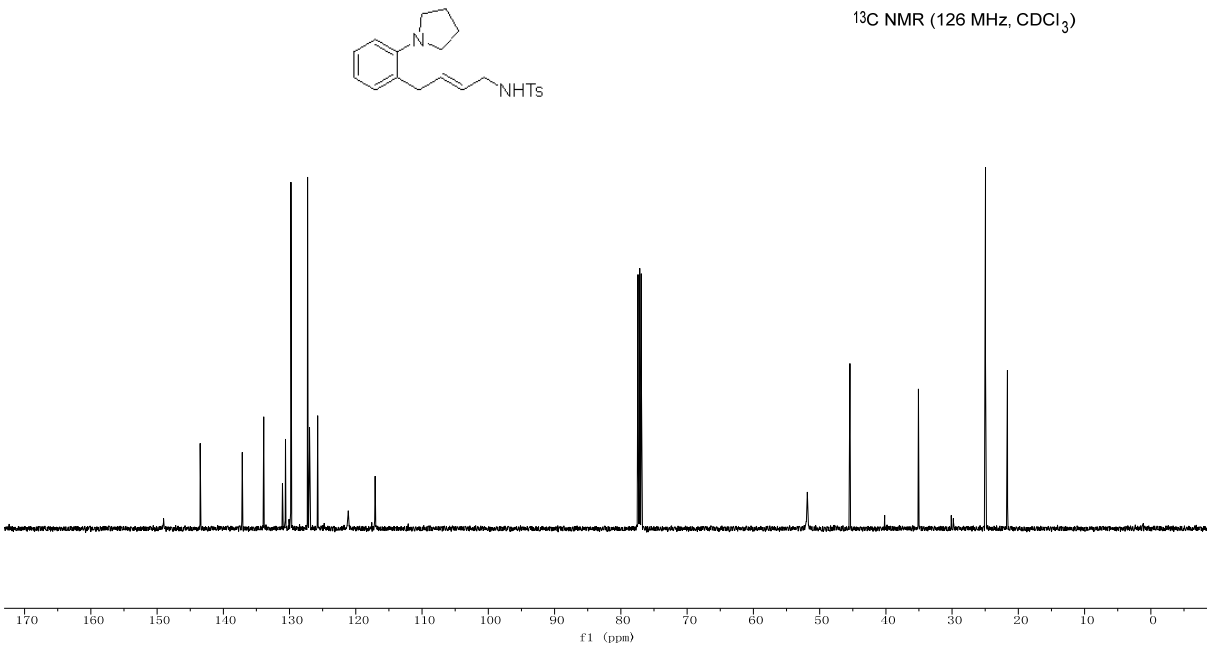


(24) (E)-4-methyl-N-(4-(2-(pyrrolidin-1-yl)phenyl)but-2-en-1-yl)benzenesulfonamide (**3x**)

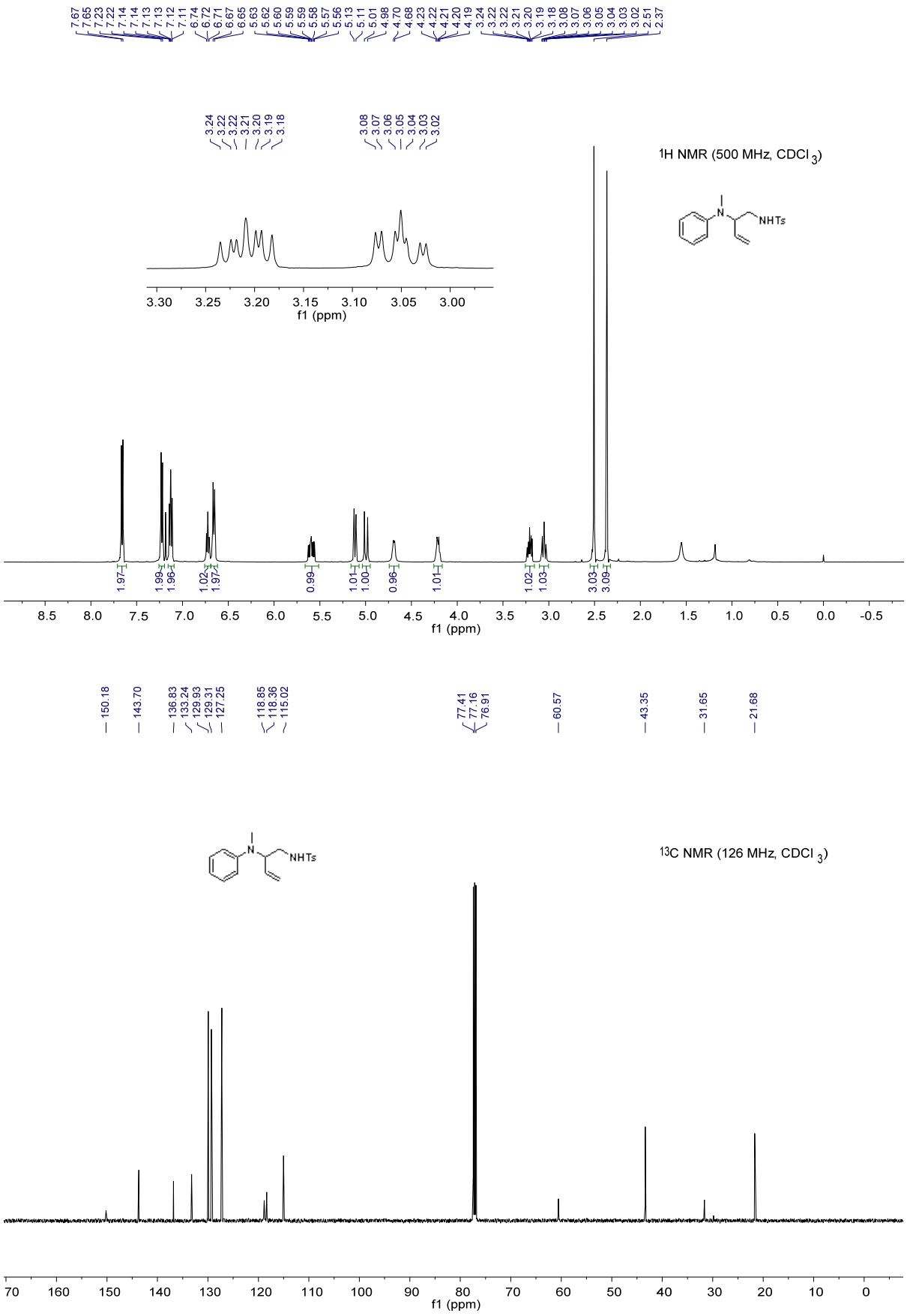
^{1}H NMR (500 MHz, $CDCl_3$):

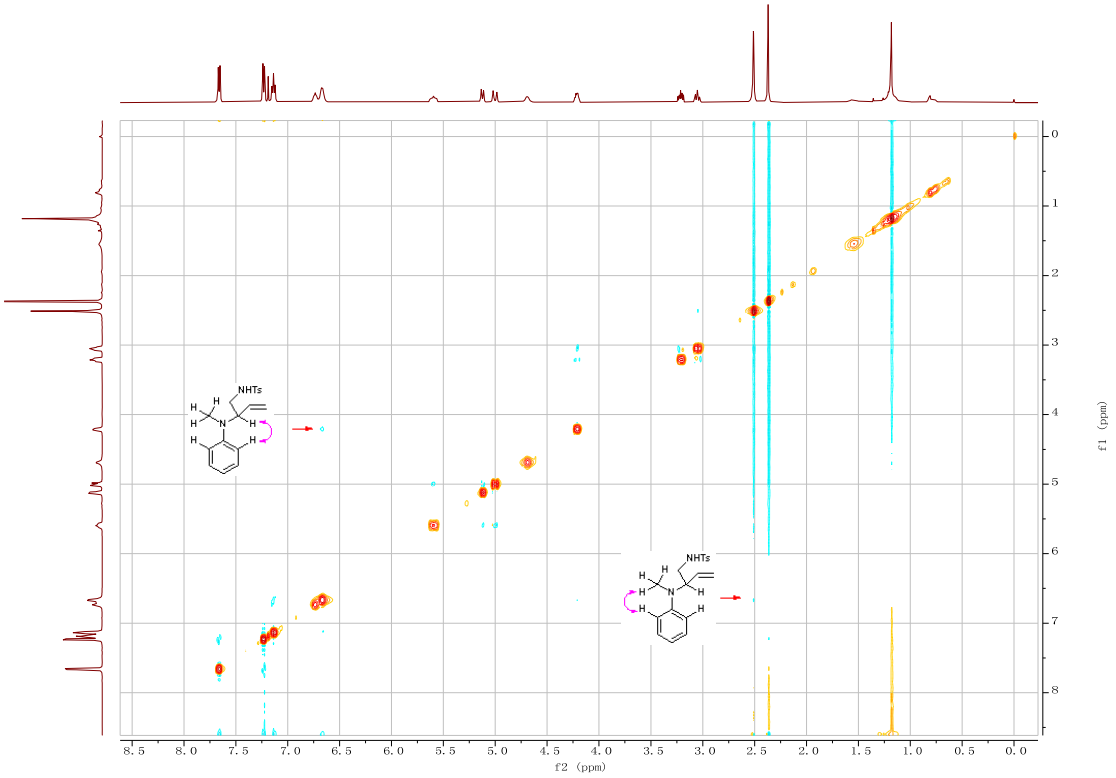


^{13}C NMR (126 MHz, $CDCl_3$)



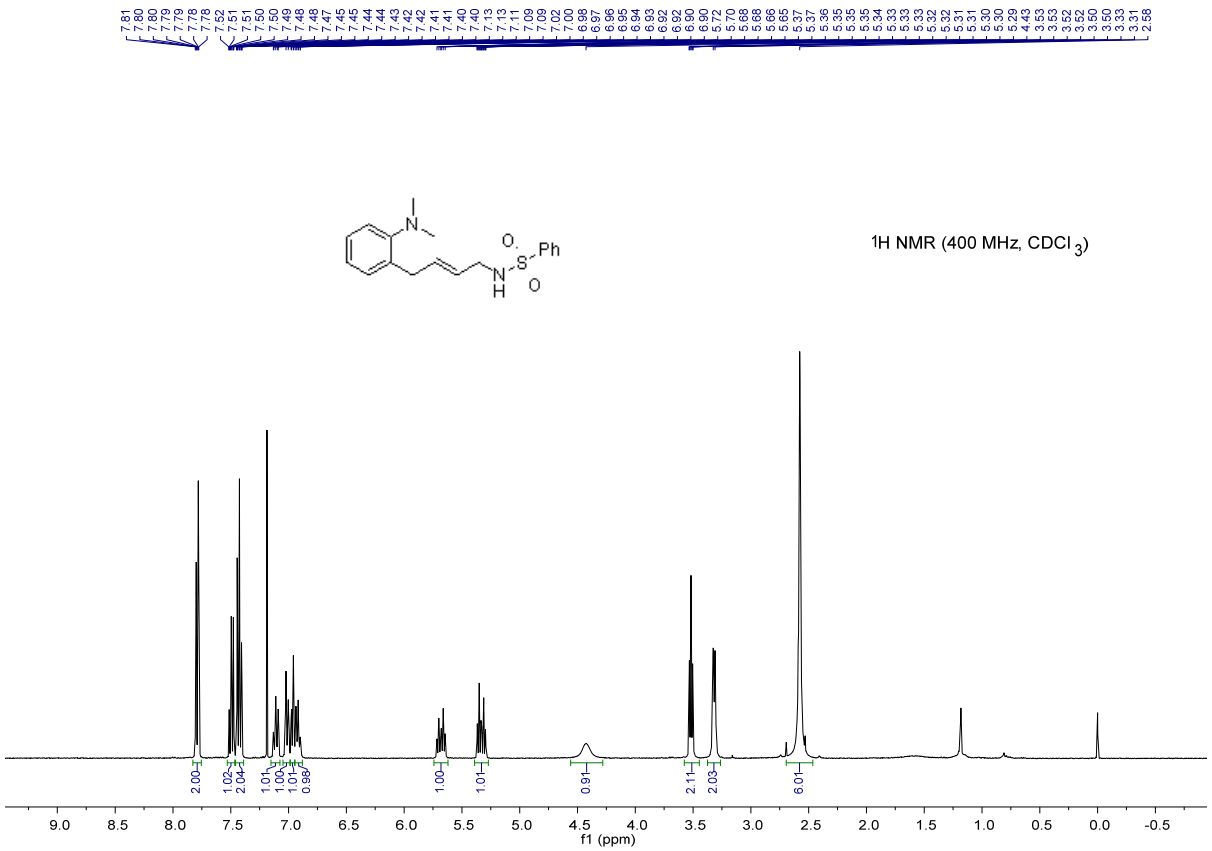
(25) 4-methyl-N-(2-(methyl(phenyl)amino)but-3-en-1-yl)benzenesulfonamide (**3y**)

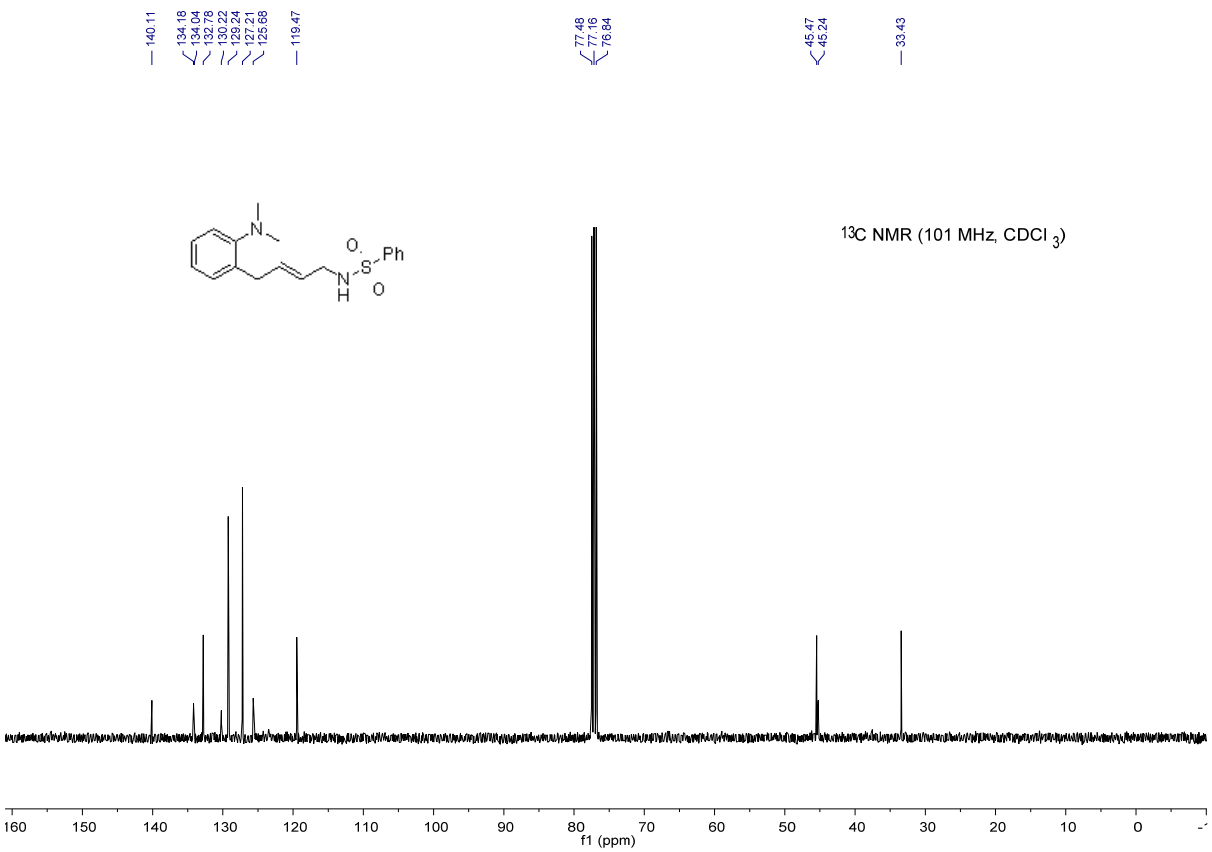




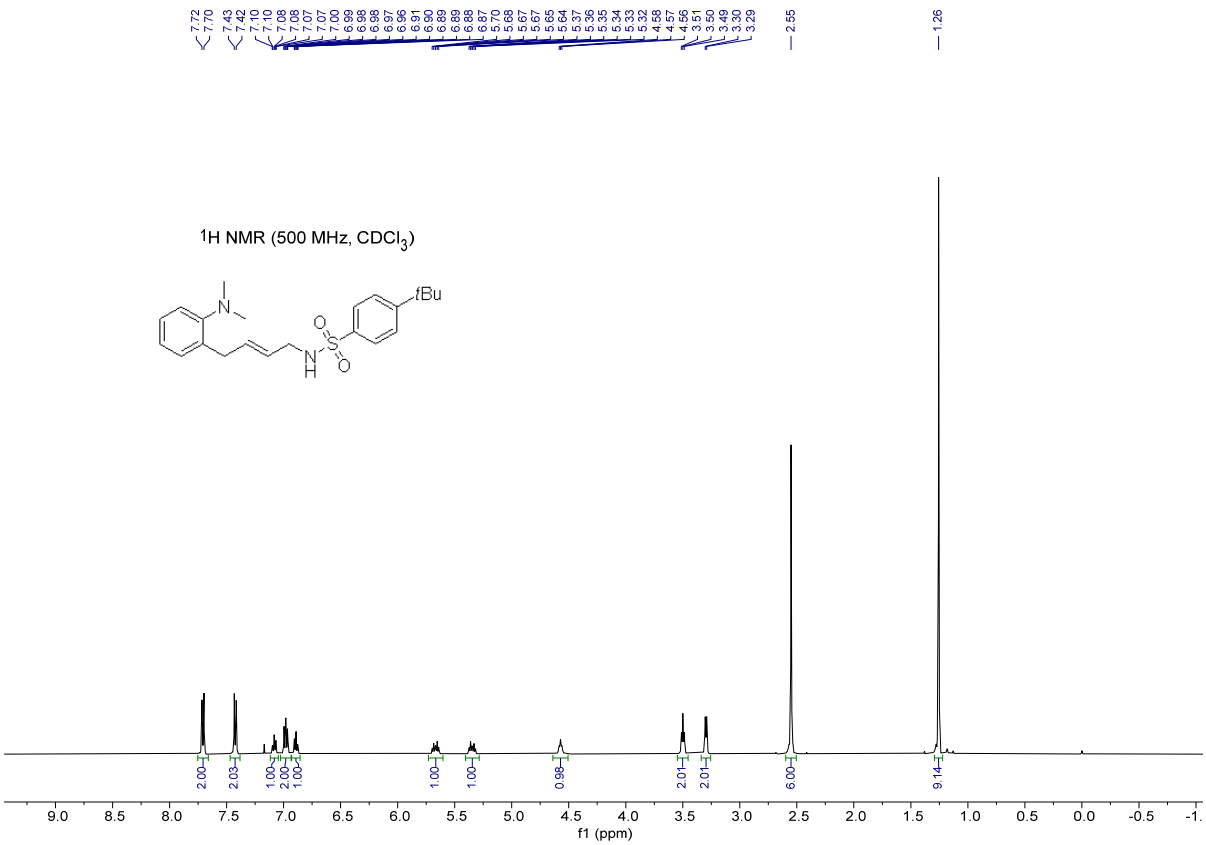
^{1}H-^{1}H NOESY of **3y** (500 MHz, $CDCl_3$)

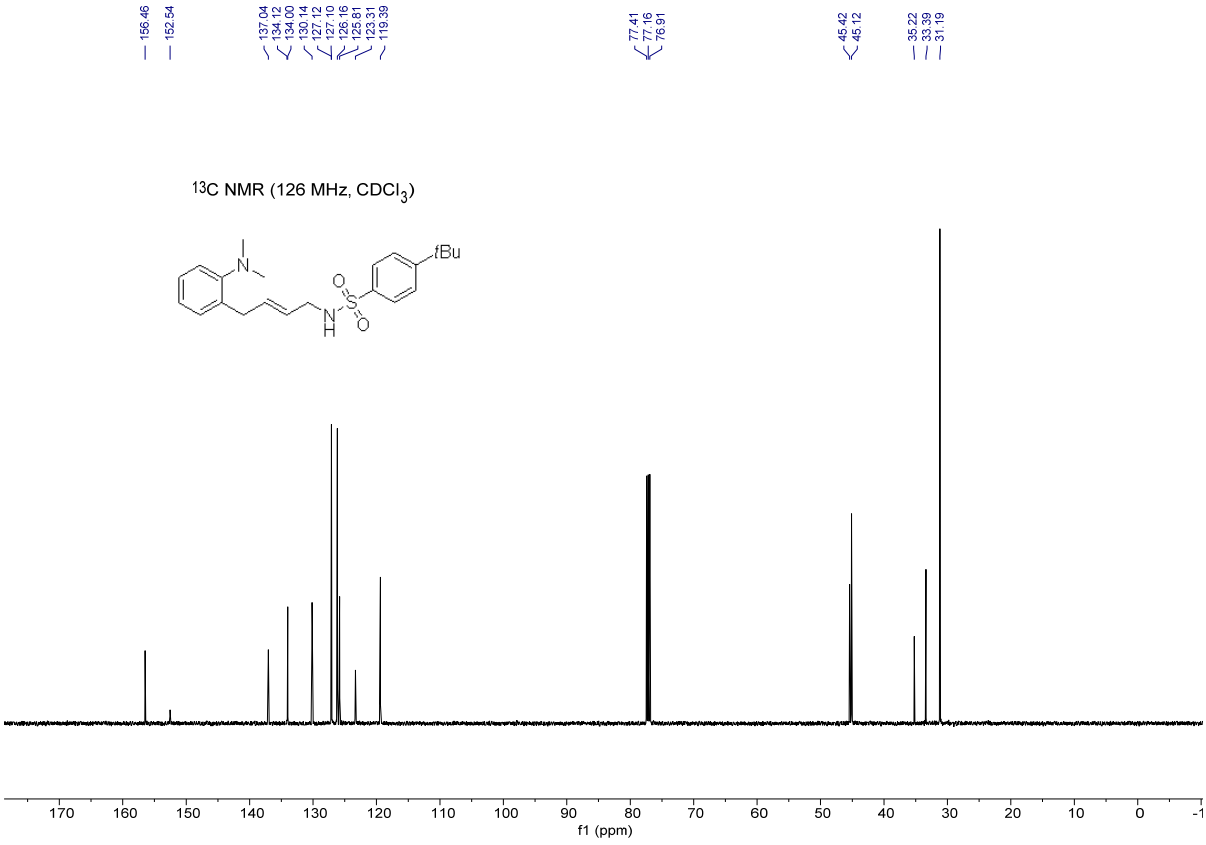
(26) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)benzenesulfonamide (**3aa**)



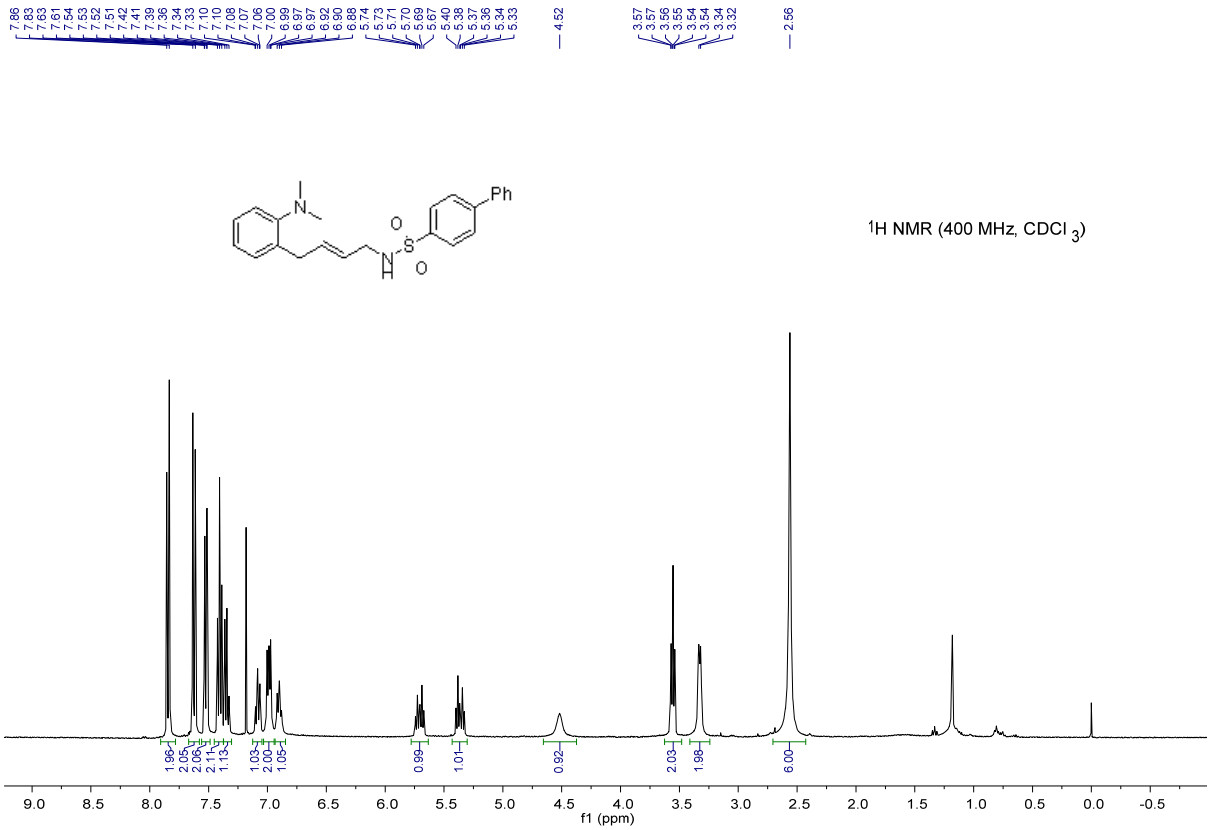


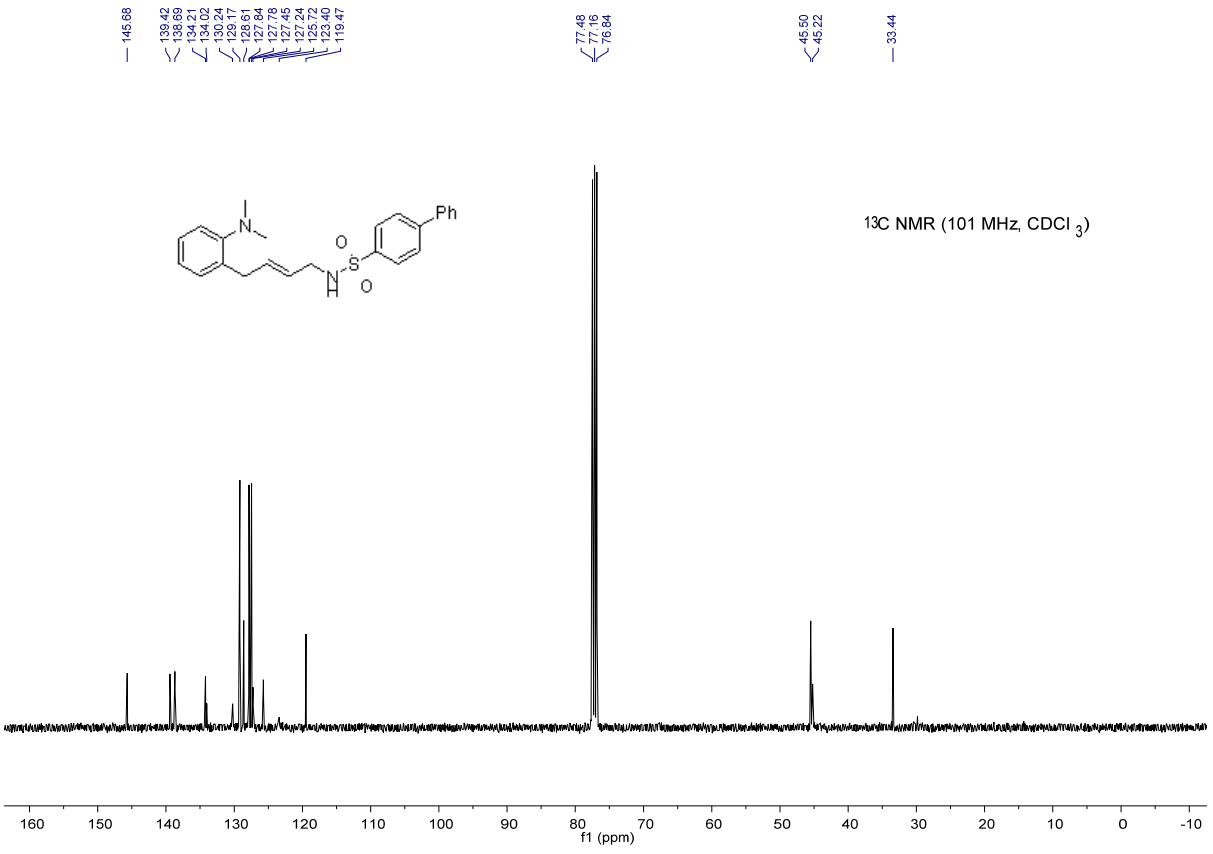
(27) (E)-4-(tert-butyl)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)benzenesulfonamide (**3ab**)



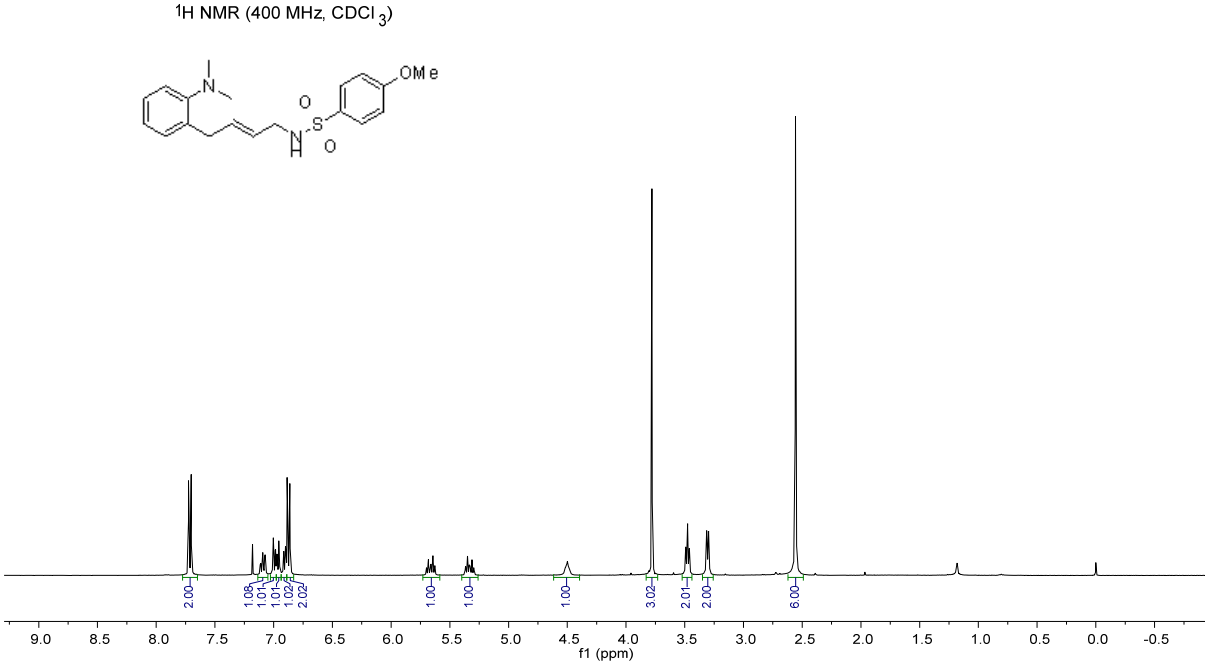


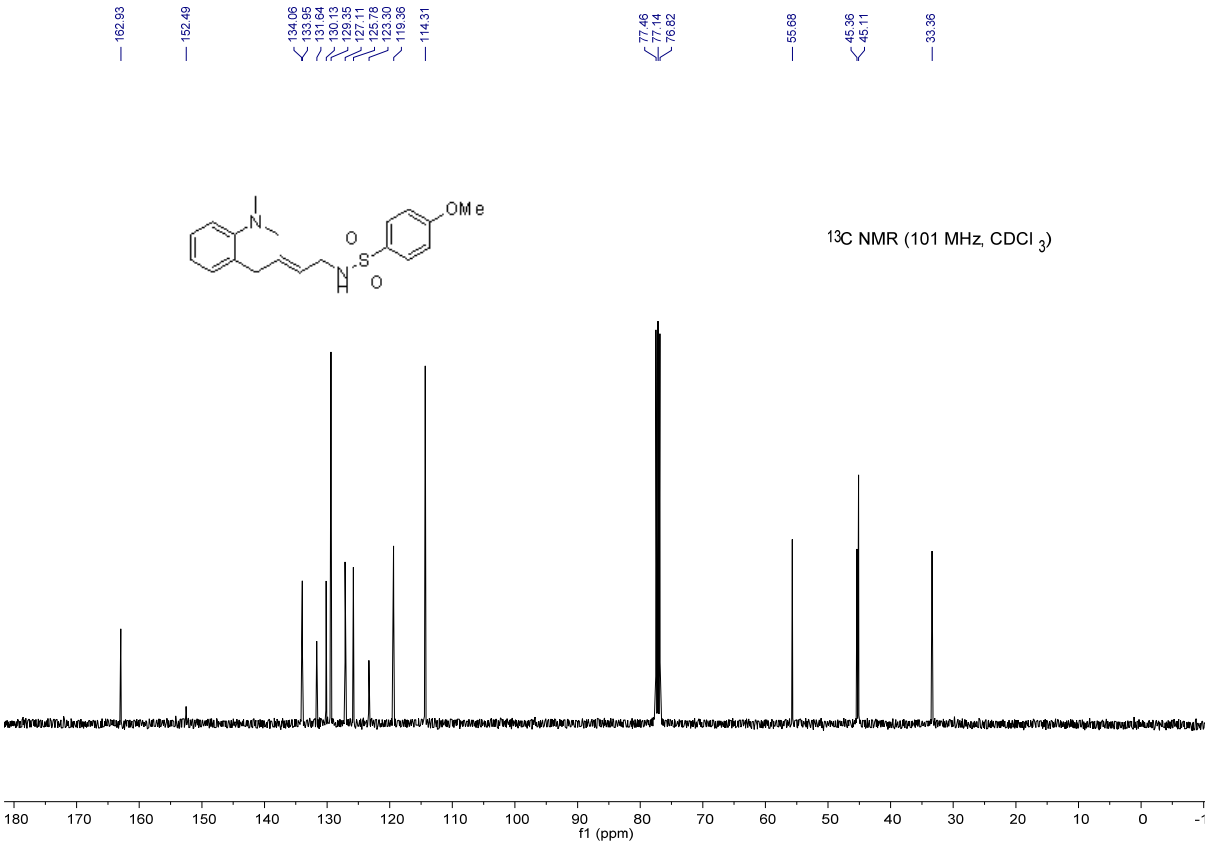
(28) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-[1,1'-biphenyl]-4-sulfonamide (**3ac**)



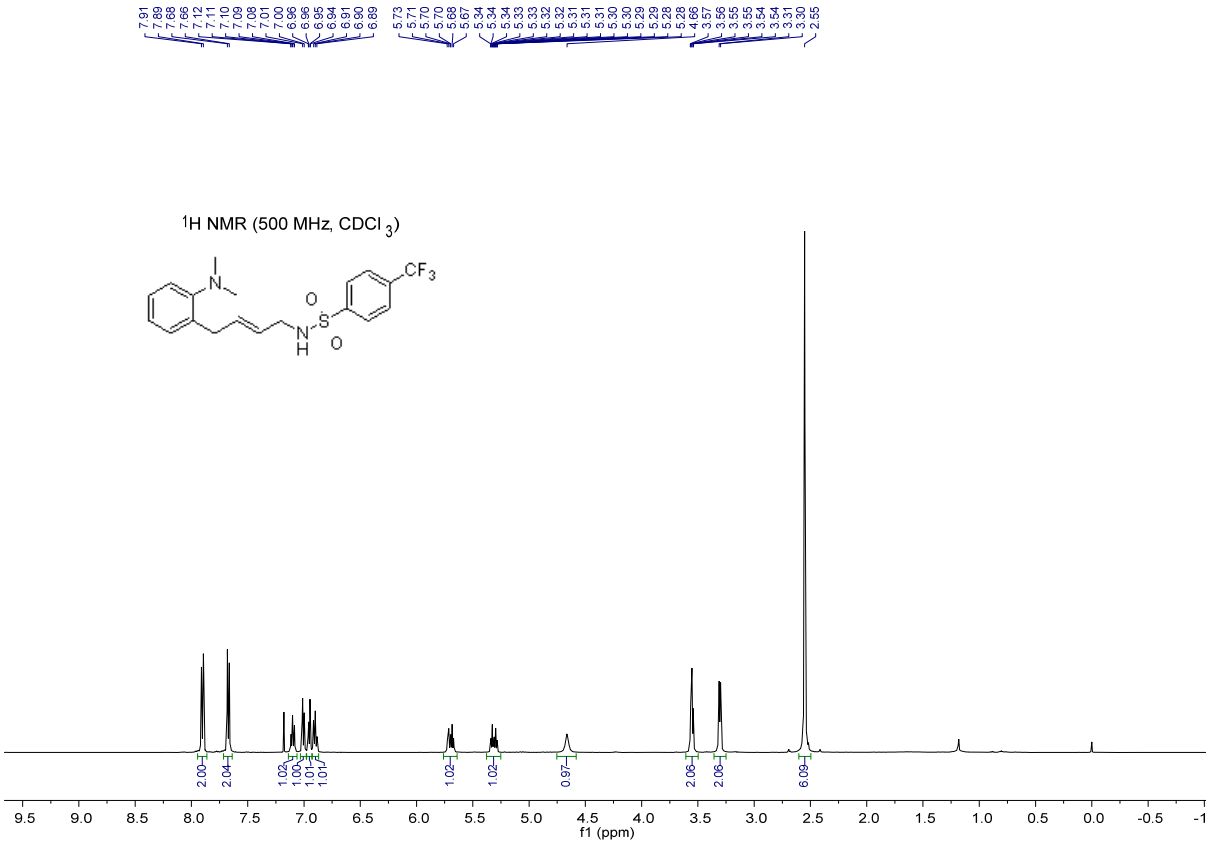


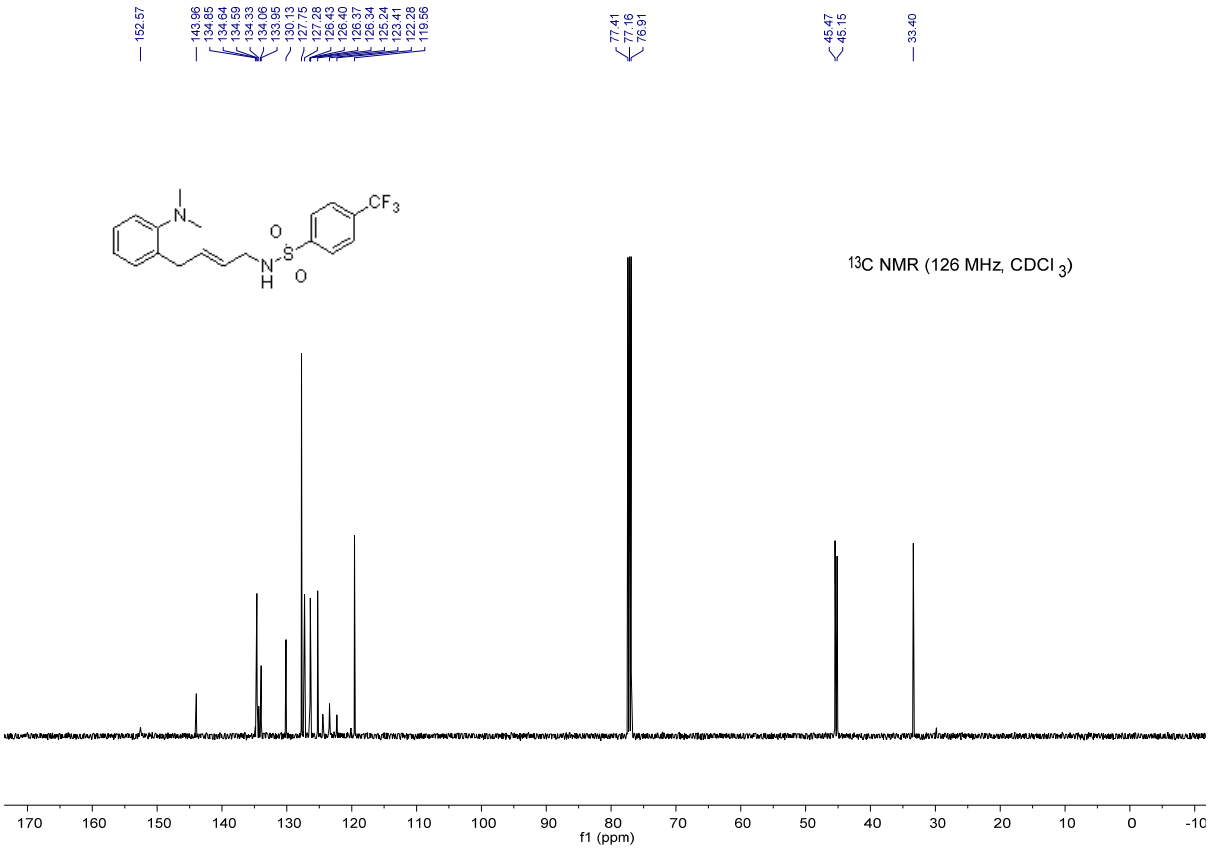
(29) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-4-methoxybenzenesulfonamide (**3ad**)

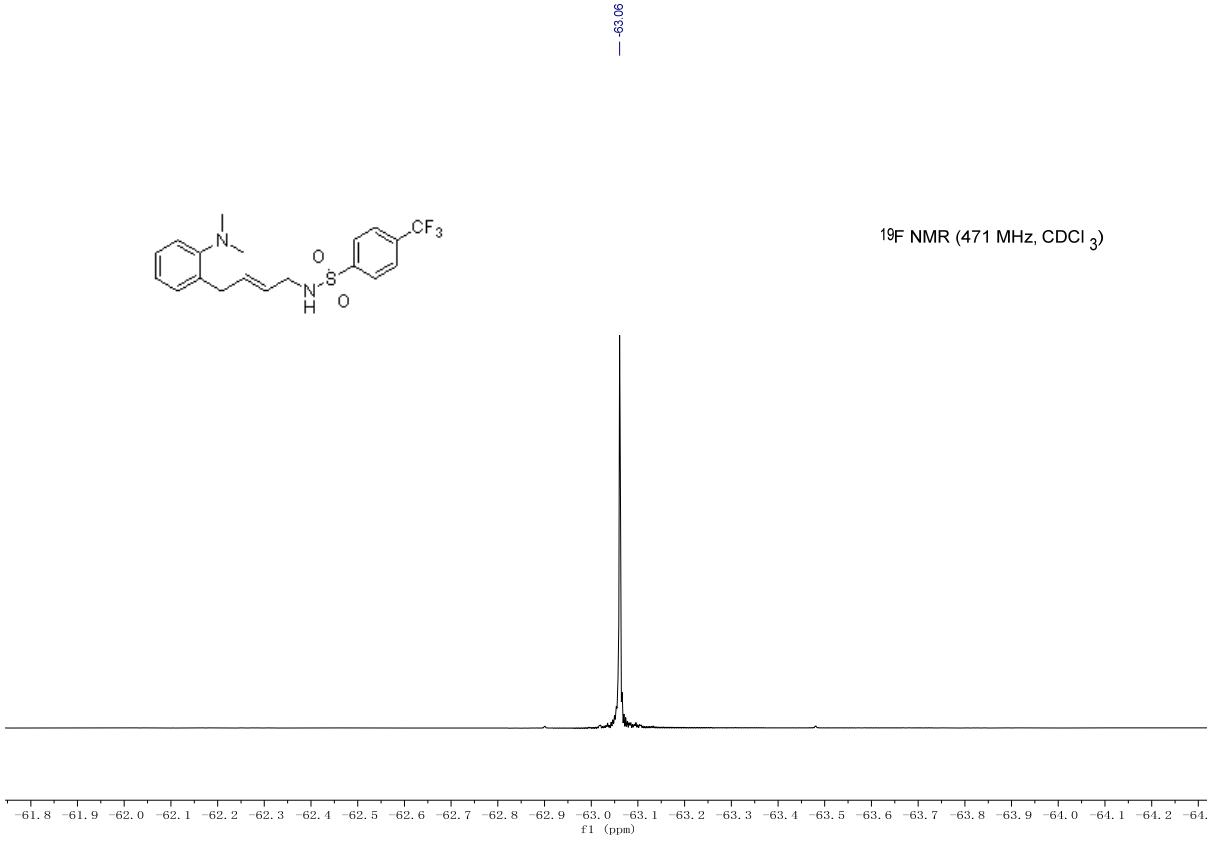




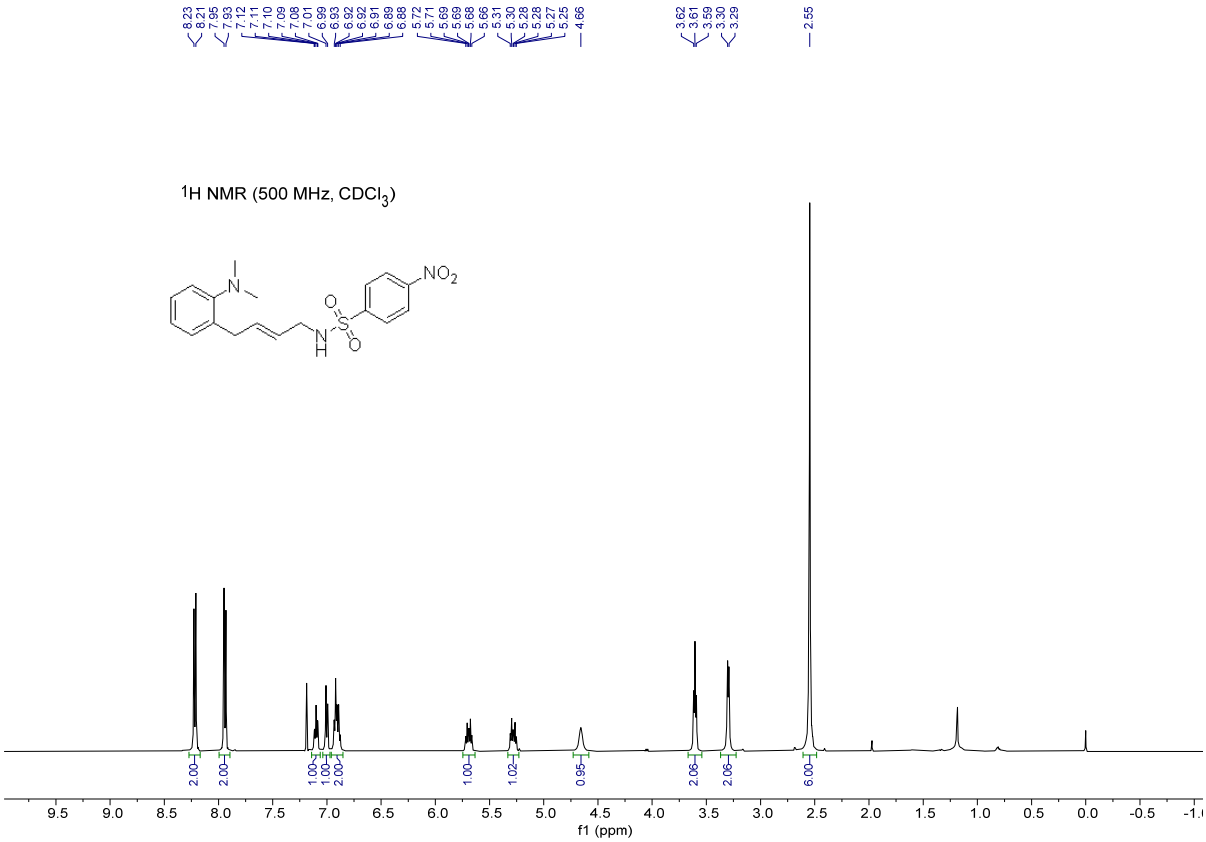
(30) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (**3ae**)

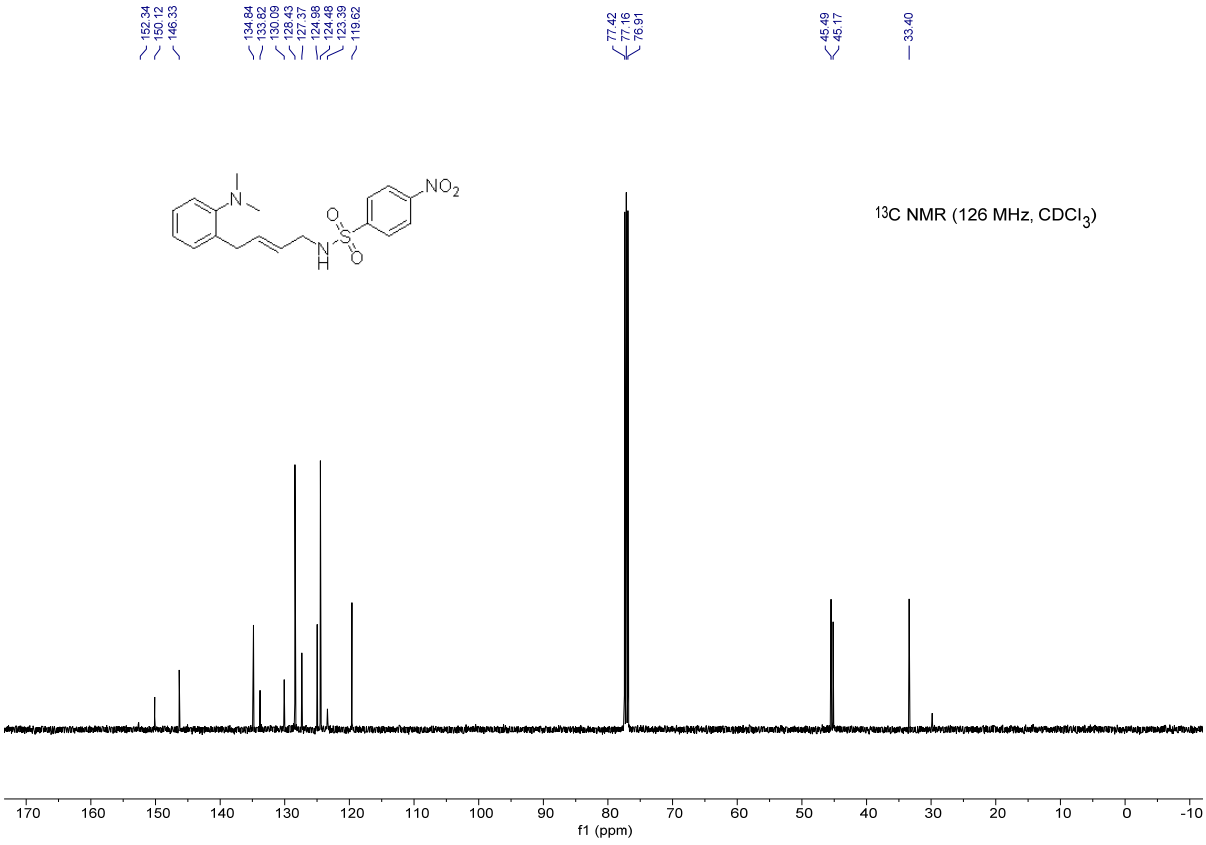




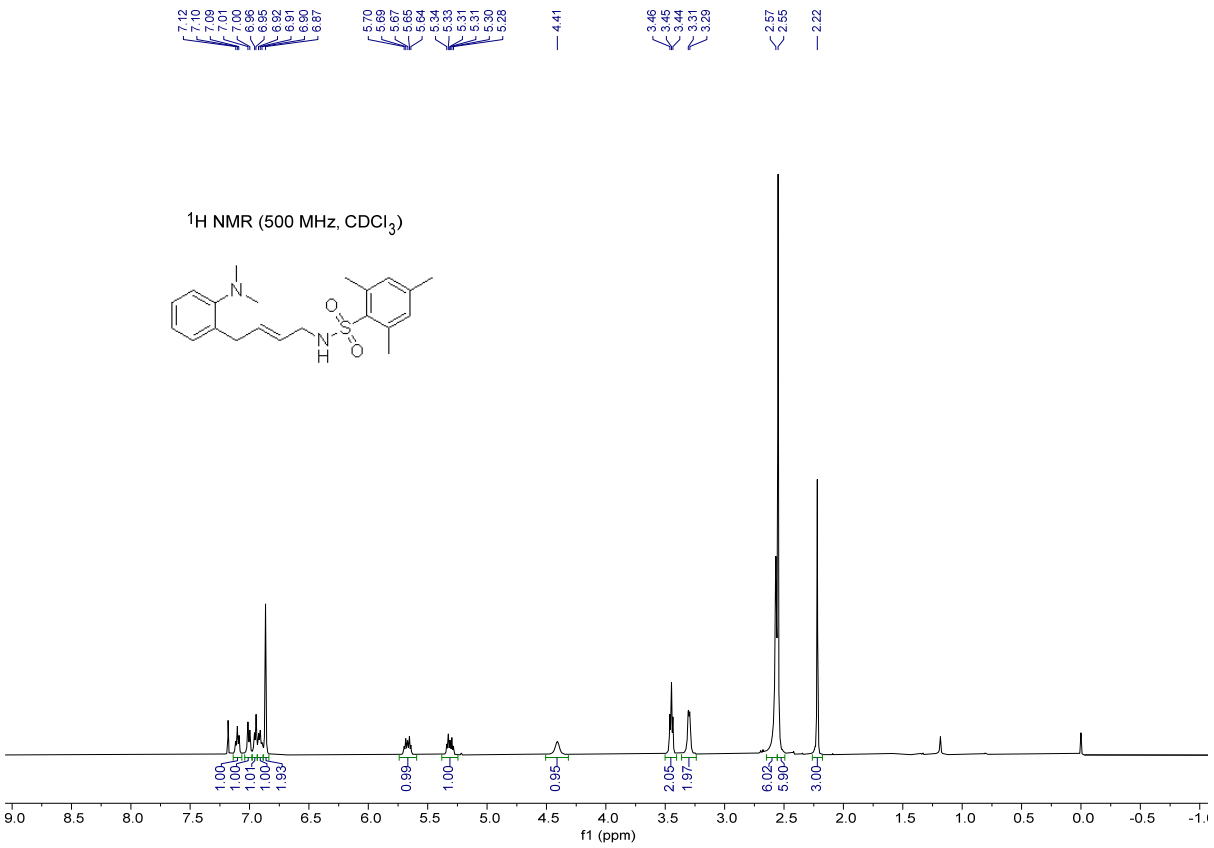

-63.06
CF3
O
S
N
H
O
19F NMR (471 MHz, CDCl 3)
-61.8 -61.9 -62.0 -62.1 -62.2 -62.3 -62.4 -62.5 -62.6 -62.7 -62.8 -62.9 -63.0 -63.1 -63.2 -63.3 -63.4 -63.5 -63.6 -63.7 -63.8 -63.9 -64.0 -64.1 -64.2 -64.
f1 (ppm)

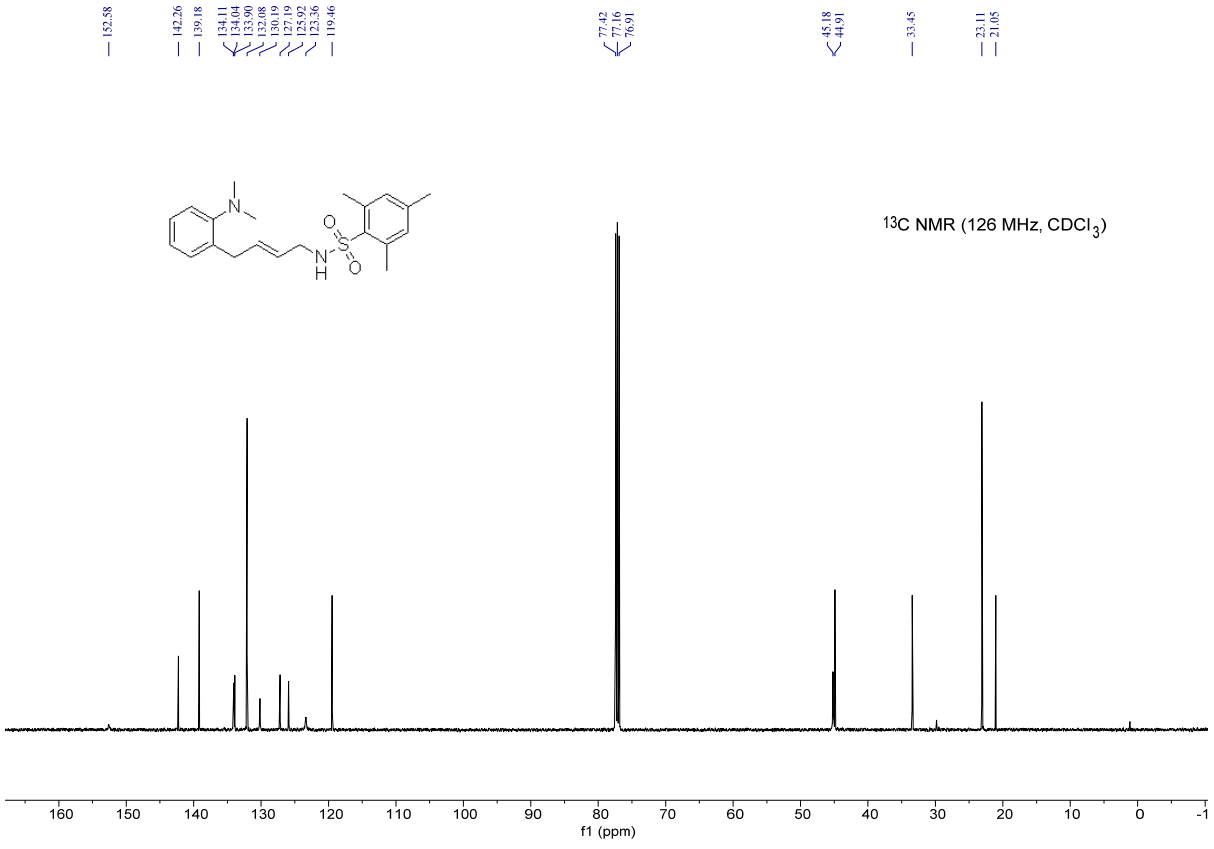
(31) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-4-nitrobenzenesulfonamide (**3af**)



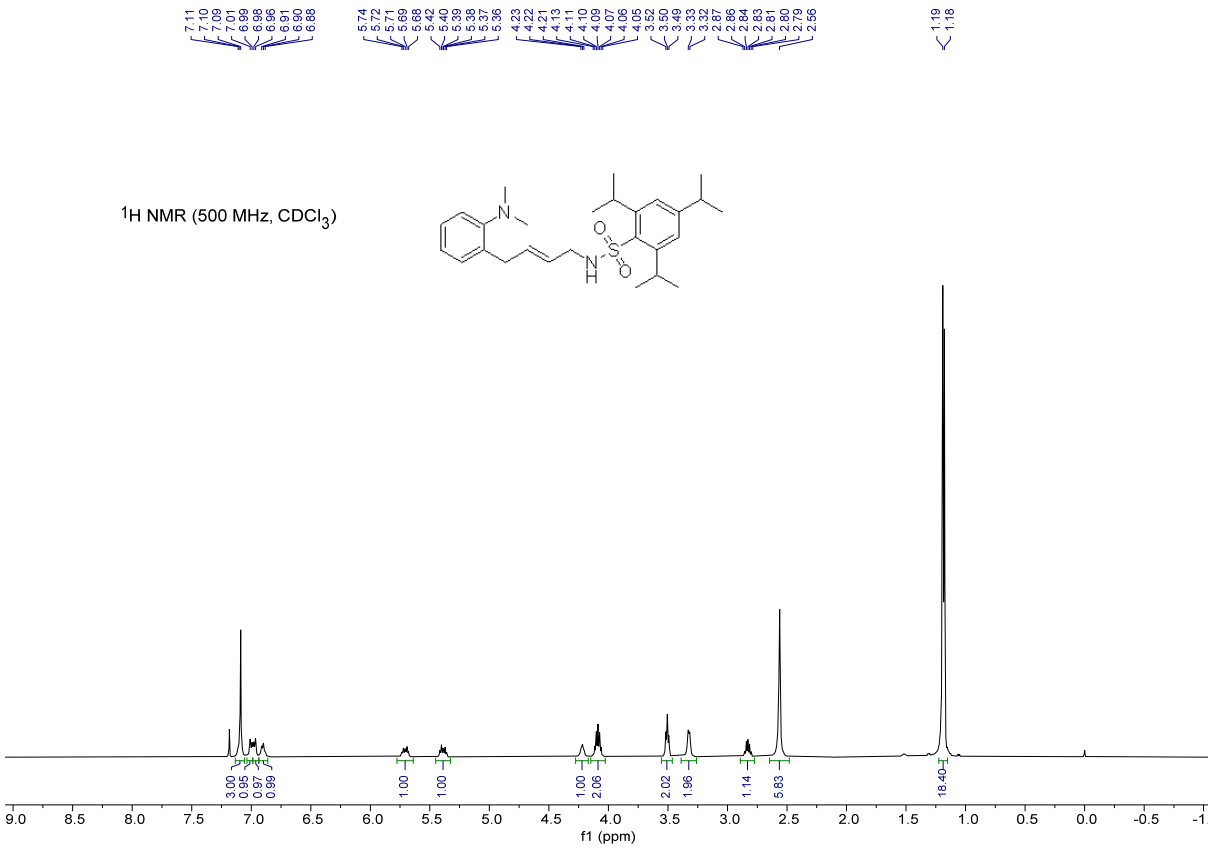


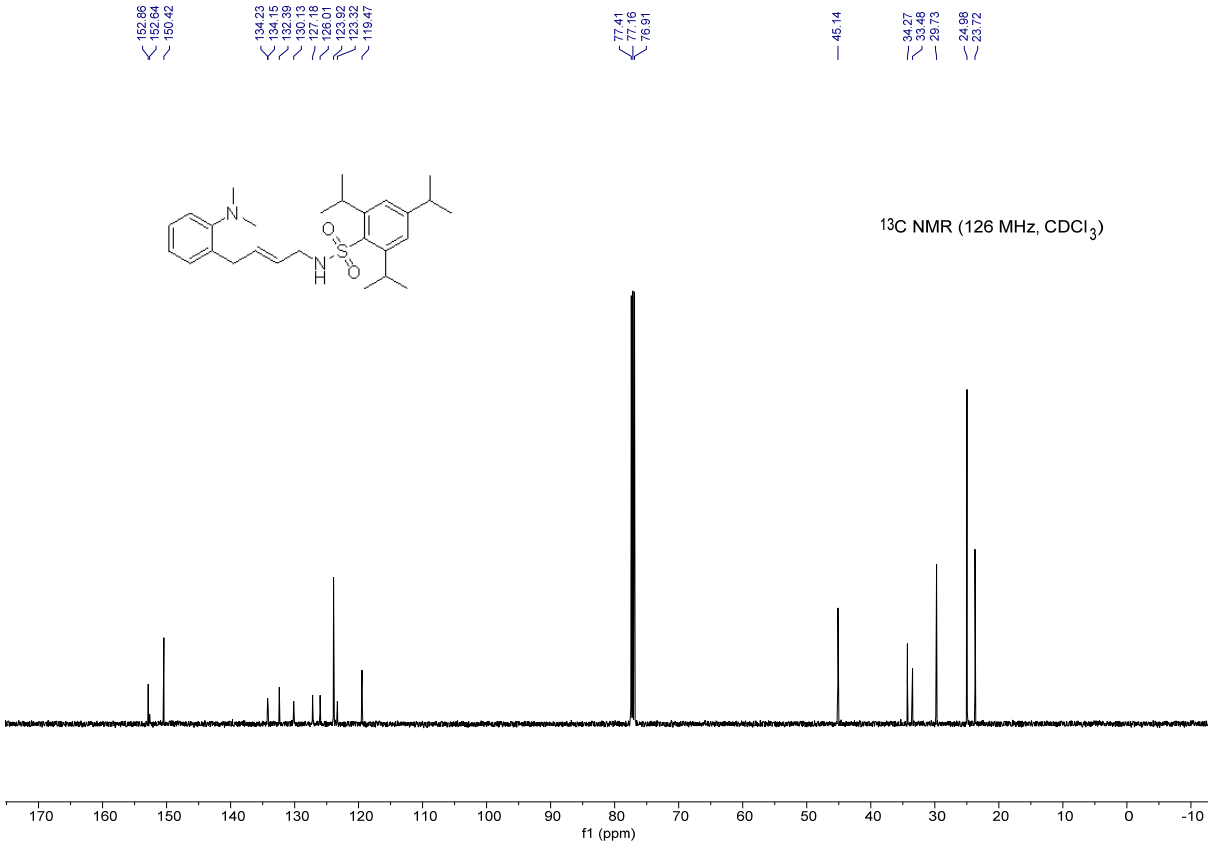
(32) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (**3ag**)



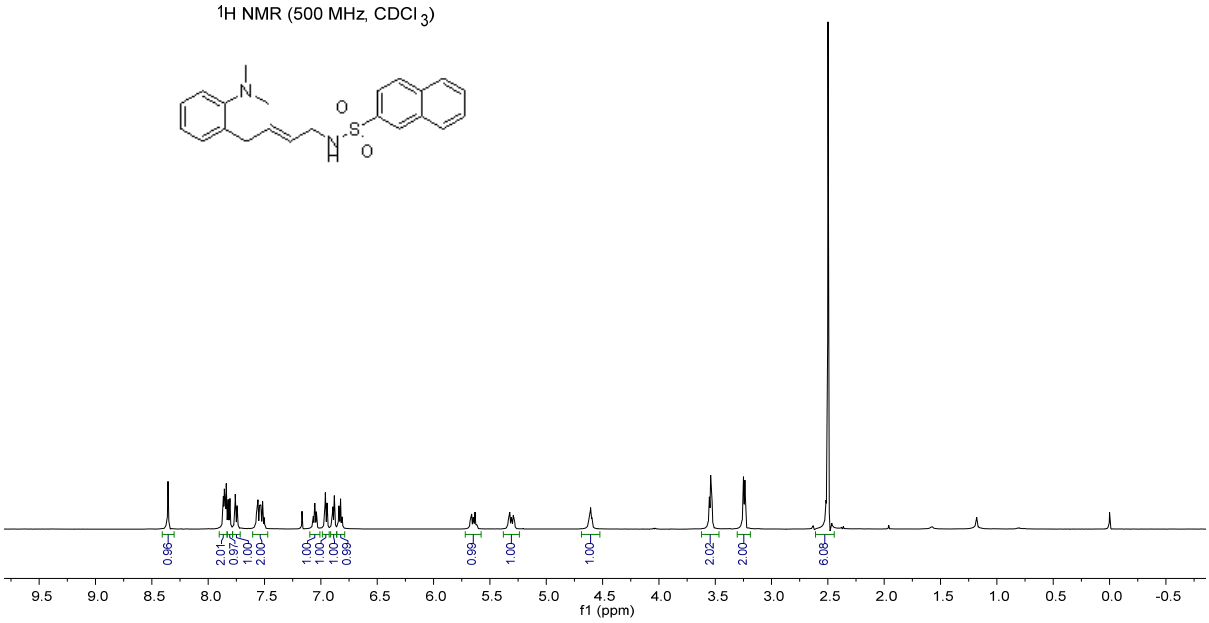


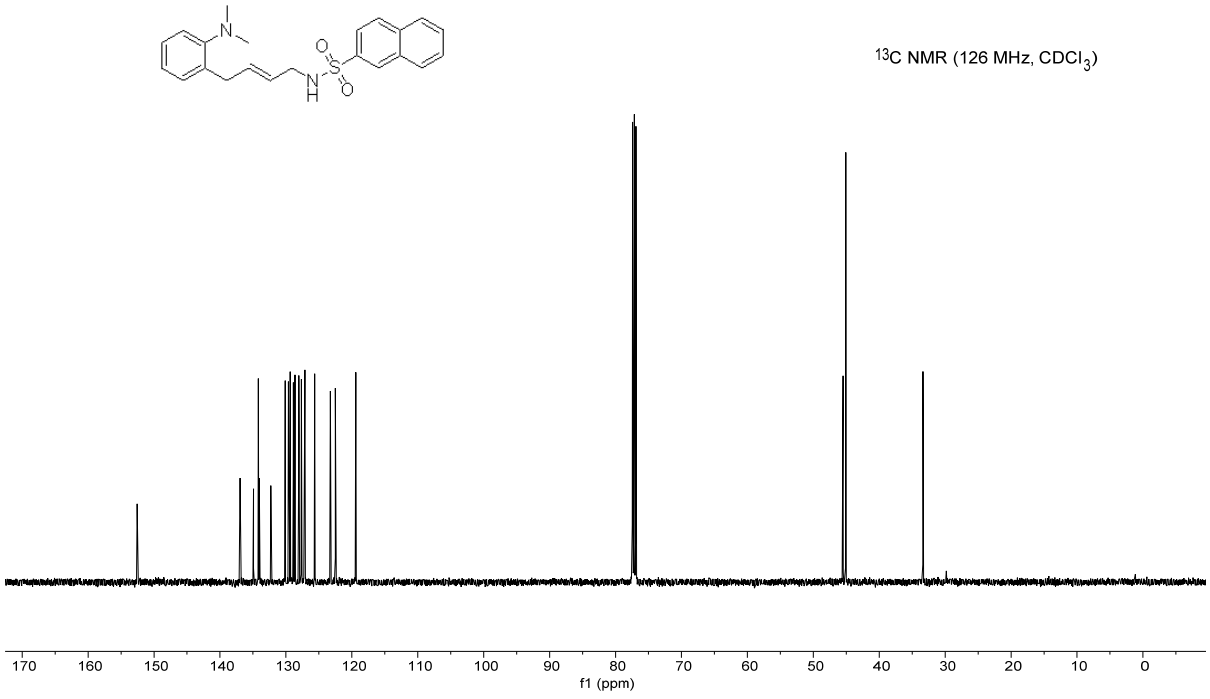
(33) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)-2,4,6-triisopropylbenzenesulfonamide (**3ah**)



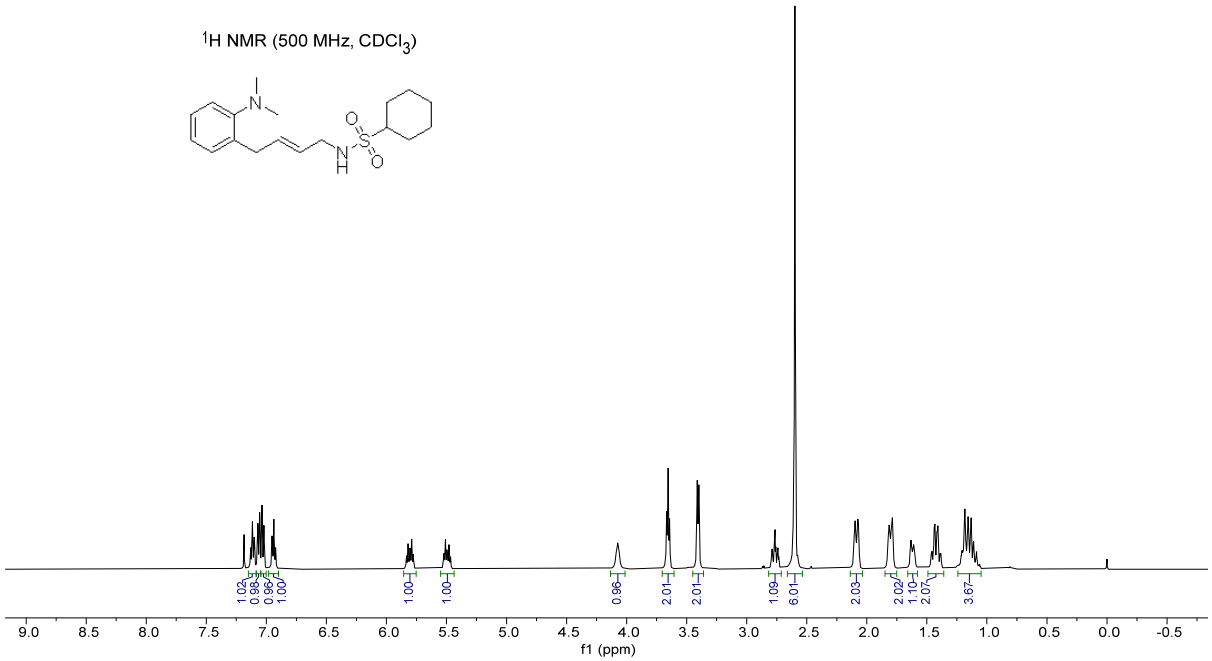


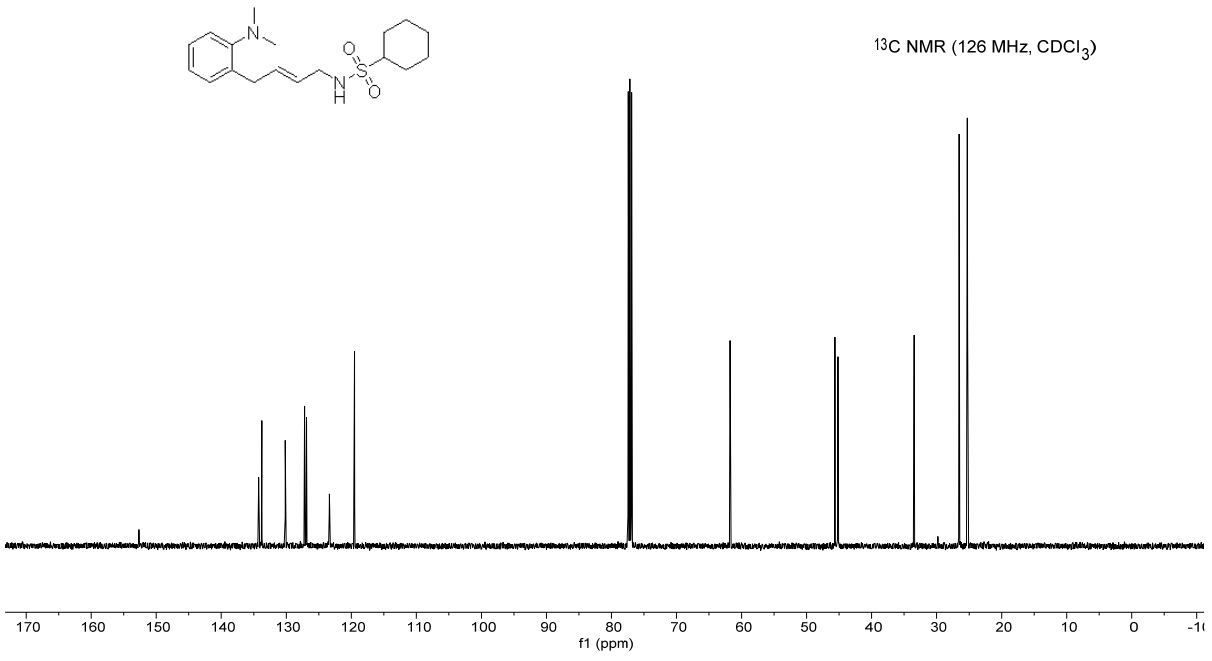
(34) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)naphthalene-2-sulfonamide (**3ai**)



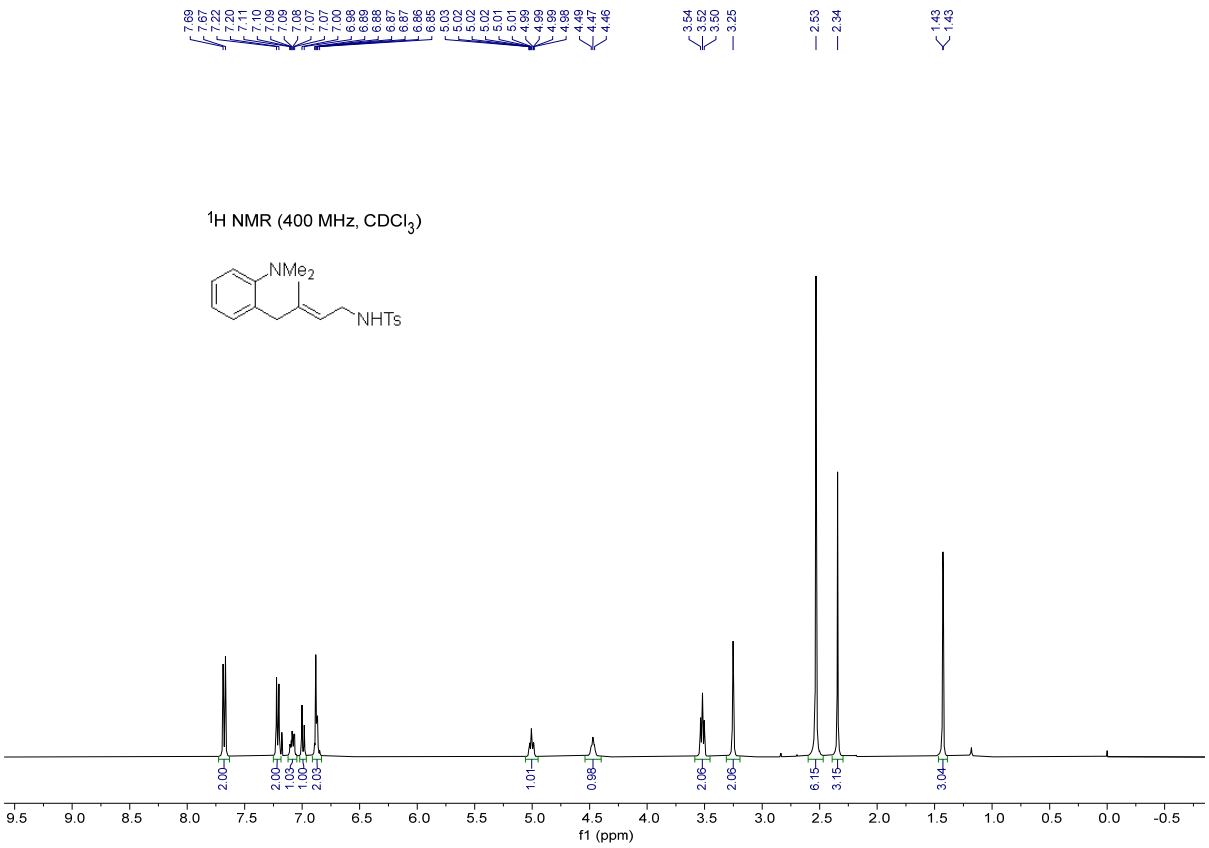


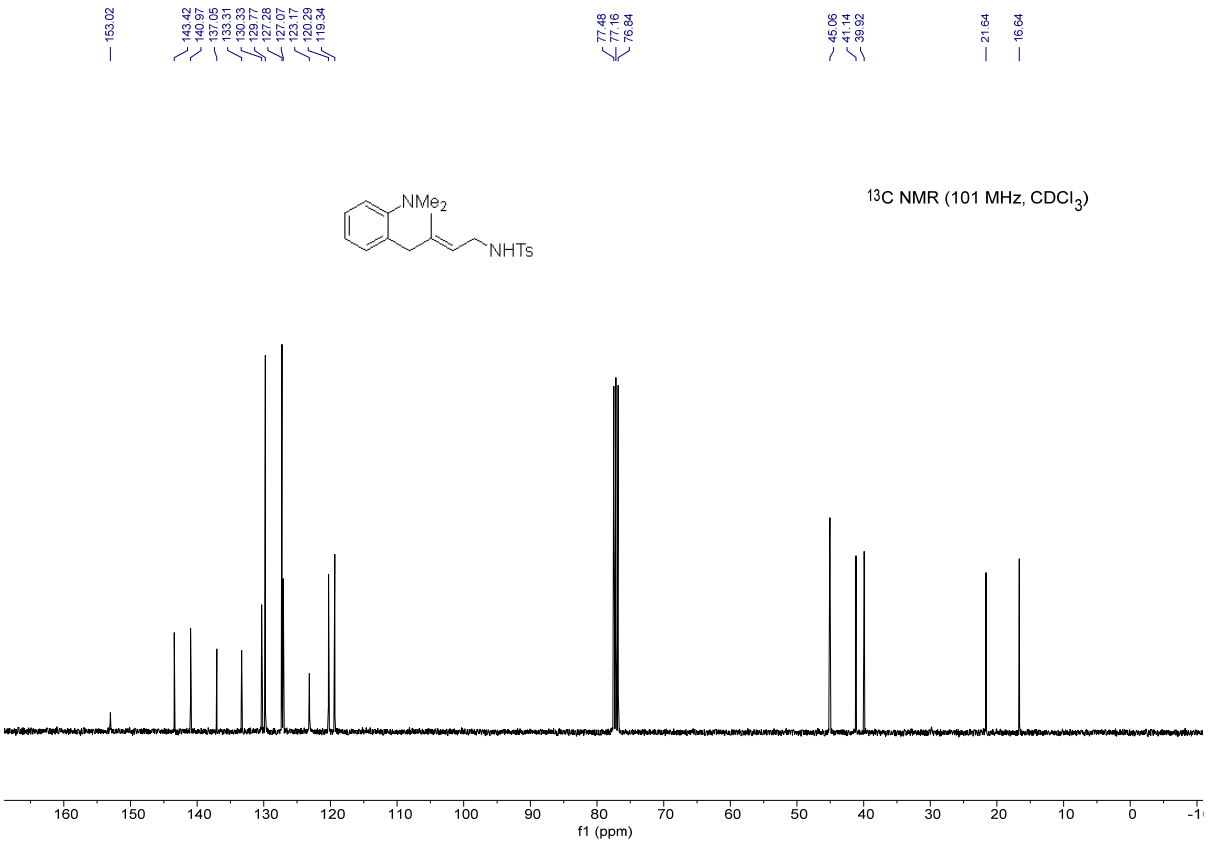
(35) (E)-N-(4-(2-(dimethylamino)phenyl)but-2-en-1-yl)cyclohexanesulfonamide (**3aj**)



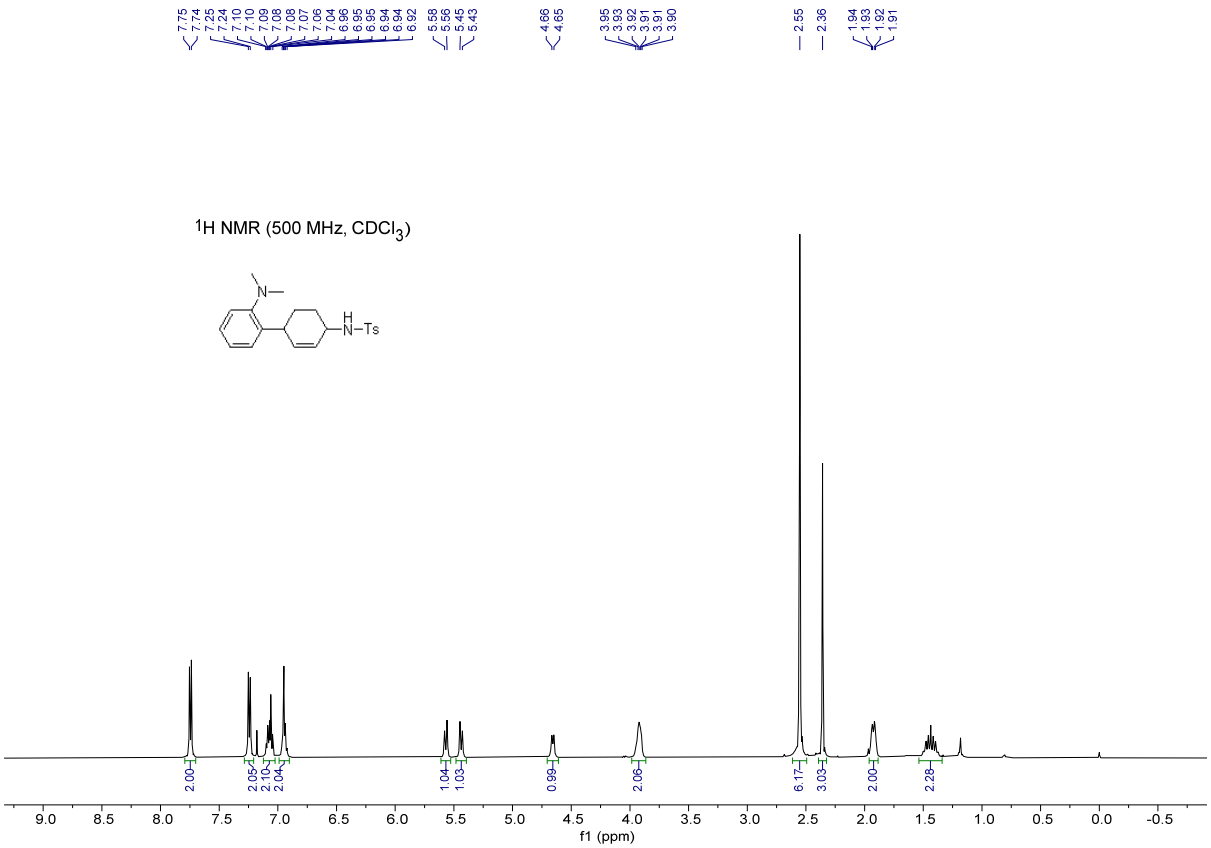


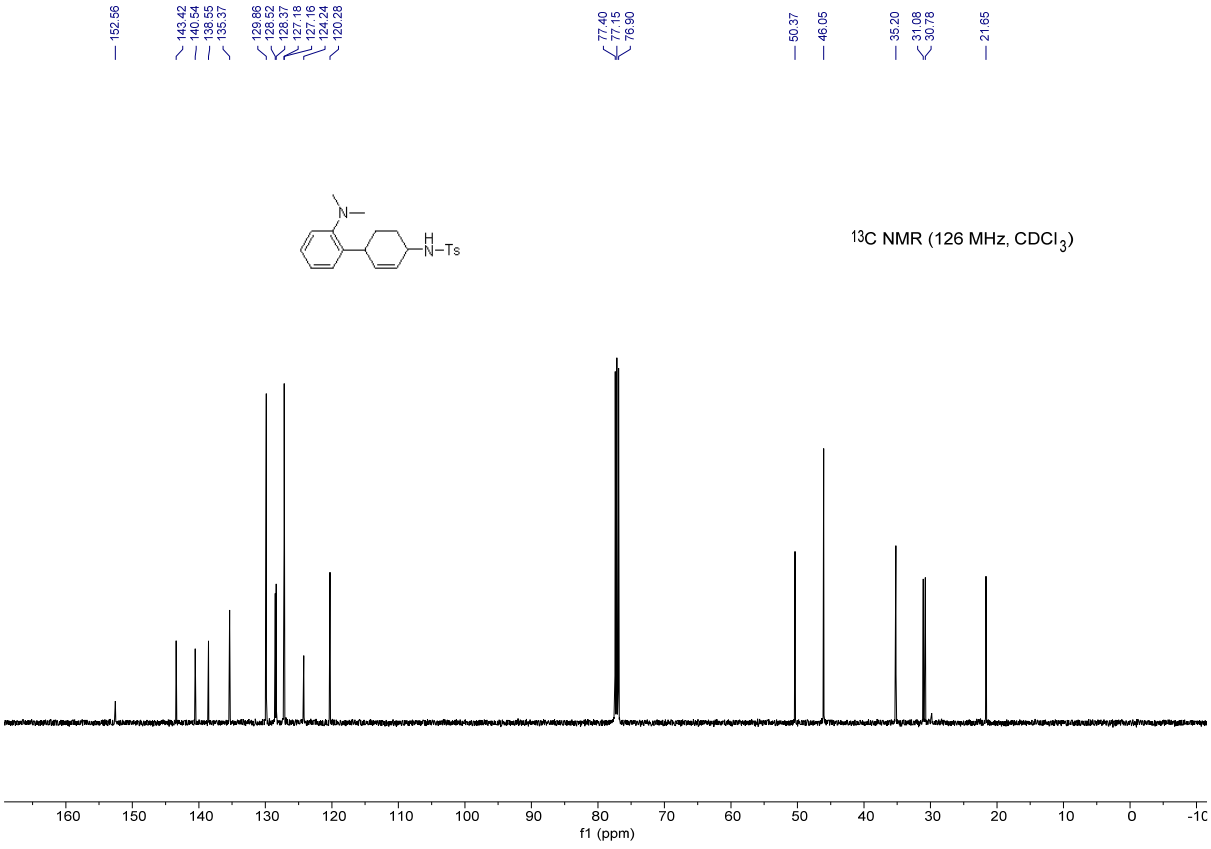
(36) (E)-N-(4-(2-(dimethylamino)phenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (**3ak**)



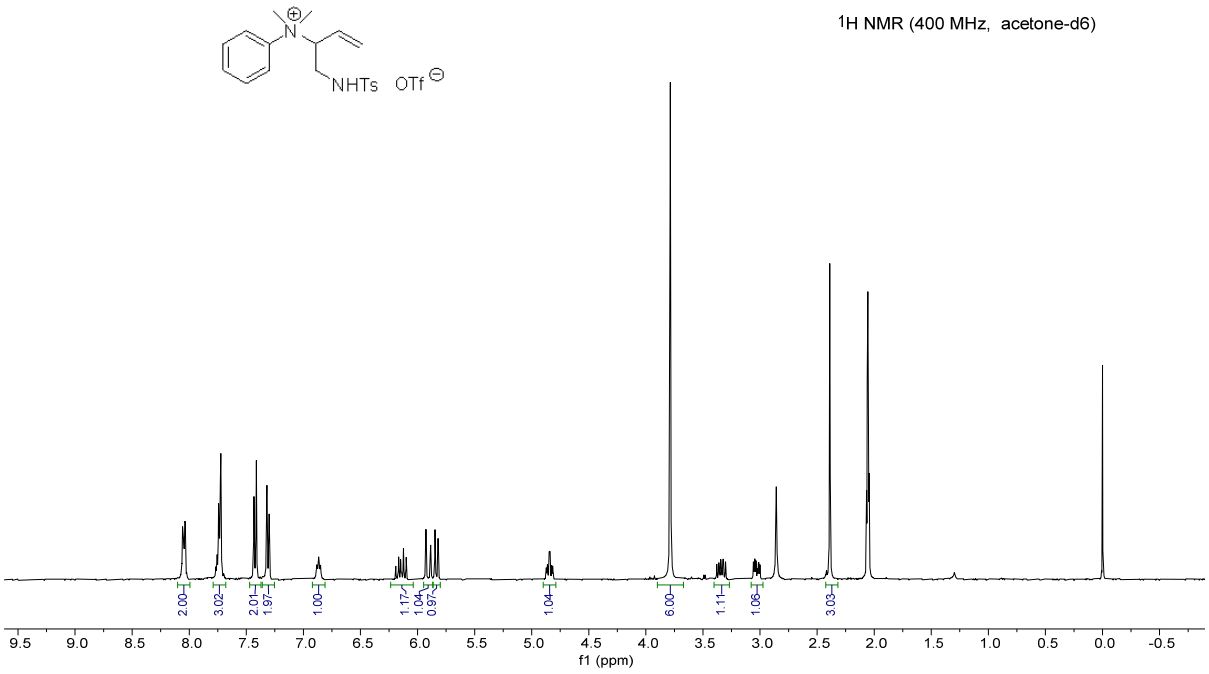


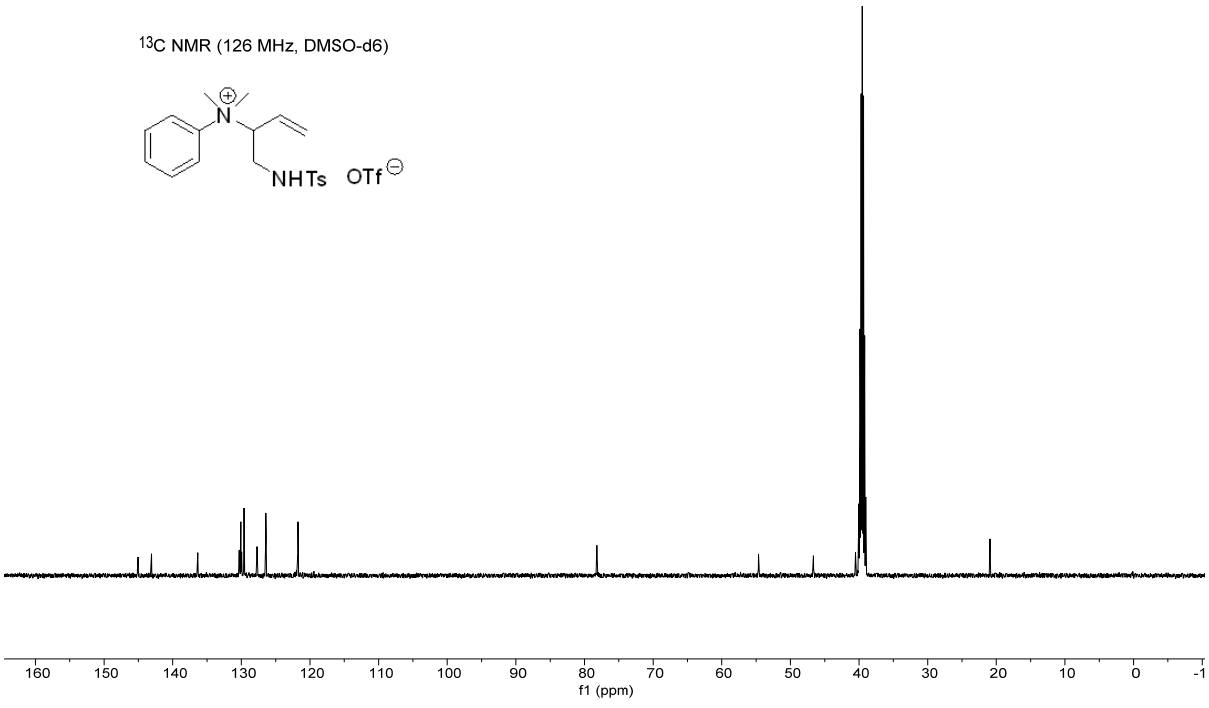
(37) N-(2'-(dimethylamino)-1,2,3,4-tetrahydro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (**3am**)





(38) *N*,*N*-dimethyl-*N*-(1-((4-methylphenyl)sulfonamido) but-3-en-2-yl)benzenaminium triflate (**4**)





(39) (E)-N-(4-(2-(allyl(methyl)amino)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**5**)