Supplementary Information

Water-Mediated Radical C–H Tosylation of Alkenes with Tosyl Cyanides

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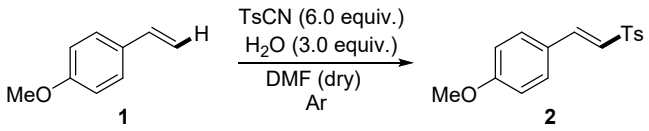
Table of Contents

1. General information

All reactions were performed under argon using flame-dried glassware unless otherwise noted. DMF was distilled over CaH_2 and rigorously degassed by freeze/pump/thaw. All reagents and starting materials were commercially available and used without further purification unless indicated otherwise. Thin layer chromatographies were carried out on GF254 plates (0.25 mm layer thickness). Flash chromatographies were performed with 200–300 mesh silica gels. Reactions were monitored by TLC and visualized by $KMnO_4$ stain. Yields reported were for isolated, spectroscopically pure compounds.

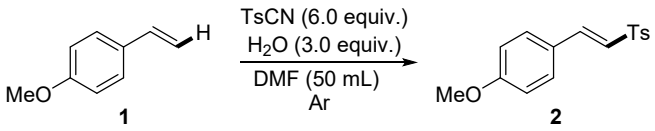
^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker Avance 400, 500, and 600 MHz spectrophotometers. Chemical shifts (δ) were expressed in ppm and *J*-values are given in Hz. Chemical shifts in ^1H NMR spectrawere reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.26 ppm). Data for ^{13}C NMR spectra were presented in terms of chemical shift in ppm from the central peak of CDCl3 (77.16 ppm). ^1H NMR data were presented as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, br s = broad singlet), coupling constant in Herts (Hz) and integration. HR-ESI-MS were taken on Agilent 6540 Q-TOF spectrometer. EPR spectra were recorded by an ADANI SPINSCAN X spectrometer. Melting points were measured on a Hanon MP 430 auto melting-point system and values are uncorrected.

2. General procedure for the tosylation of alkenes with tosyl cyanide



To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (1.8 mmol, 6.0 equiv.) under argon. Then DMF (3.0 mL), alkenes (0.3 mmol, 1.0 equiv.), and H_2O (0.9 mmol, 3.0 equiv.) were added. After stirring at room temperature for 48 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford **2**.[1] The spectral properties were consistent with the reported values. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.81 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 15.3 Hz, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 15.3 Hz, 1H), 3.83 (s, 3H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 162.0, 144.1, 141.7, 138.2, 130.3, 129.9, 127.6, 125.1, 124.9, 114.5, 55.4, 21.6.

3. Reaction setup for the geam-scale experiment

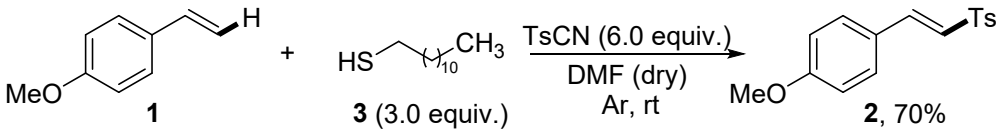


1 **2**

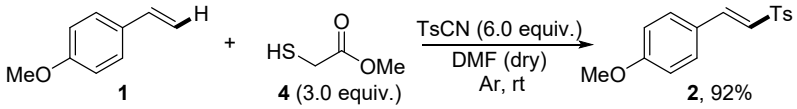
10.0 mmol Y= 89 %

To an oven dried 100mL round-bottom flask with a magnetic stirring bar was added TsCN (10.9 g, 60 mmol) under argon. Then DMF (50 mL), *p*-methoxystyrene **1** (1.34 g, 10 mmol), and H_2O (540 μL, 30 mmol) were added. After stirred at room temperature for 56 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (45 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford **2** (2.5 g, 89% yield).

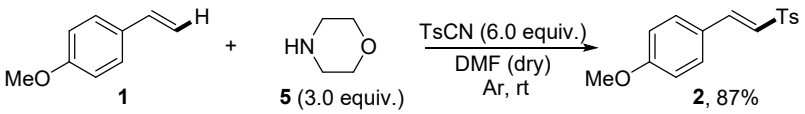
4. Controlled experiments for water-mediated tosylation



To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (326.2 mg, 1.8 mmol) under argon. Then DMF (3.0 mL), *p*-methoxystyrene **1** (40 μL, 0.3 mmol), and dodecanethiol **3** (216 μL, 0.9 mmol) were added. After stirred at room temperature for 48 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether =1:10) on silica gel to afford **2** (60.7 mg, 70% yield).

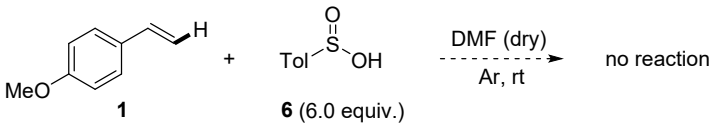


To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (326.2 mg, 1.8 mmol) under argon. Then DMF (3.0 mL), *p*-methoxystyrene **1** (40 μL, 0.30 mmol), and methyl thioglycolate **4** (80 μL, 0.9 mmol) were added. After stirred at room temperature for 48 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford **2** (79.2 mg, 92% yield).

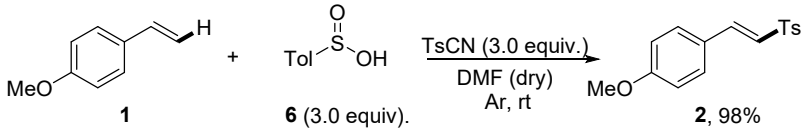


To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (326.2 mg, 1.8 mmol) under argon. Then DMF (3.0 mL), *p*-methoxystyrene **1** (40 μL, 0.3 mmol), and morpholine **5** (79 μL, 0.9 mmol) were added. After stirred at room

temperature for 48 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford **2** (75.1 mg, 87% yield).

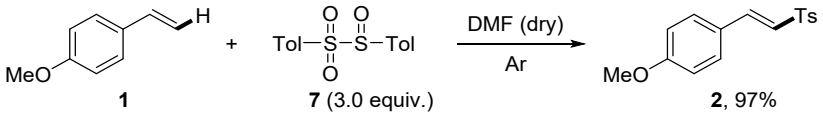


To an oven dried 10 mL glass tube with a magnetic stirring bar was added *p*-toluenesulfinic acid **6**. (281.2 mg, 1.8 mmol) under argon. Then DMF (3.0 mL) and *p*-methoxystyrene **1** (40 μL, 0.3 mmol) were added. The reaction mixture was stirred at room temperature for 48 h and monitored by TLC. The TLC showed that there was no target product generated.

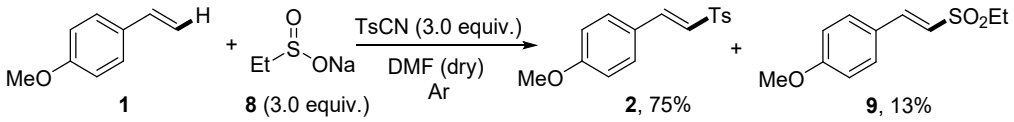


To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (163.1 mg, 0.9 mmol) under argon. Then DMF (3.0 mL), *p*-methoxystyrene **1** (40 μL, 0.3 mmol), and *p*-toluenesulfinic acid **6** (140.1 mg, 0.9 mmol) were added. After stirred at room temperature for 48 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford **2** (84.7 mg, 98% yield).

5. Experiments for radical pathway investigation

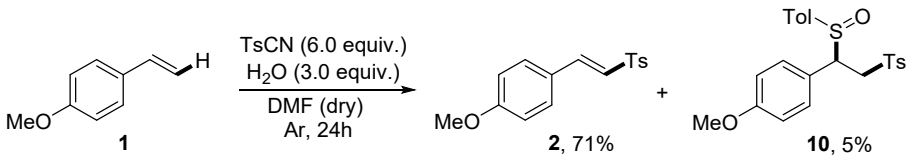


To an oven dried 10 mL glass tube with a magnetic stirring bar was added sulfinyl sulfone **7** (264.6 mg, 0.9 mmol) under argon. Then DMF (3.0 mL) and *p*-methoxystyrene **1** (40 μL, 0.3 mmol) were added. After stirred at room temperature for 24 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford **2** (83.6 mg, 97% yield). Sulfinyl sulfone **7** was prepared according to the known procedures.[2] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.33–7.28 (m, 4H), 2.45 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ 146.9, 144.6, 134.8, 130.3, 129.9, 129.8, 129.7, 125.8, 21.9, 21.8.

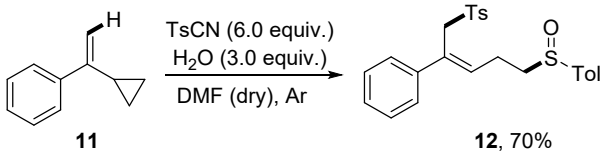


To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (163.1 mg, 0.9 mmol) under argon. Then DMF (3.0 mL), *p*-methoxystyrene **1** (40 μL, 0.3 mmol), and sodium ethylsulfinate **8** (104.5 mg, 0.9 mmol) were added. After stirred at room temperature for 48 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford **2** (65.1mg, 75% yield) and **9** as a white powder (8.9 mg, 13% yield). The spectral properties of **9** were consistent with the reported values.[3] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (d, *J* = 15.4 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 15.4 Hz, 1H), 3.85 (s, 3H), 3.08 (q, *J* = 7.4 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 3H). ^{13}C

{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 162.2, 144.9, 130.4, 124.9, 121.1, 114.6, 55.5, 49.6, 7.4.



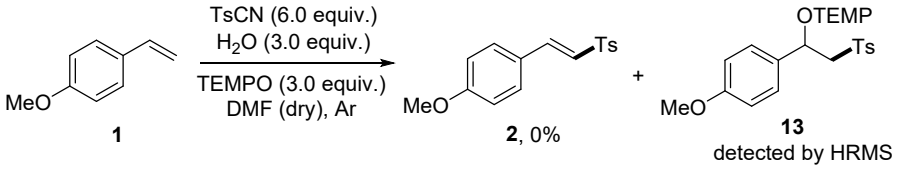
To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (326.2 mg, 1.8 mmol) under argon. Then DMF (3.0 mL), *p*-methoxystyrene **1** (40 μL, 0.3 mmol), and H_2O (16 μL 0.9 mmol) were added. After stirred at room temperature for 24 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford **2** (61.3 mg, 71% yield) and **10** as a white powder (6.4 mg, 5% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.17–7.10 (m, 4H), 6.81 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 4.09 (dd, J = 11.8, 3.0 Hz, 1H), 3.89 (dd, J = 14.3, 3.0 Hz, 1H), 3.81 (dd, J=14.0, 2.3 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 160.0, 144.5, 142.2, 137.8, 136.6, 130.4, 129.7, 129.6, 127.9, 124.9, 123.1, 114.0, 66.0, 55.3, 55.0, 21.6, 21.5. HR-ESI-MS (m/z): calcd. for $C_{23}H_{25}O_4S_2$ $[M + H]^+$, 429.1189, found 429.1185.



Compound **11** was prepared according to the known procedures.[4] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62–7.57 (m, 2H), 7.36–7.30 (m, 2H), 7.29–7.23 (m, 1H), 5.27 (d, J = 1.1 Hz, 1H), 4.92 (d, J = 1.1 Hz, 1H), 1.71–1.58 (m, 1H), 0.86–0.76 (m, 2H), 0.61–0.53 (m, 2H).

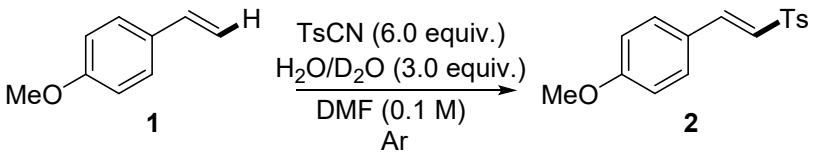
To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (326.2 mg, 1.8mmol) under argon. Then DMF (3.0 mL), α-cyclopropylstyrene **11** (43.3

mg, 0.3 mmol), and H_2O (16 μL 0.9 mmol) were added. After stirred at room temperature for 24 h, the reaction mixture was diluted with ethyl acetate. The mixture was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford **12** as a colorless oil (92.3 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.20–7.14 (m, 7H), 5.96 (t, *J* = 7.7 Hz, 1H), 4.36–4.22 (m, 2H), 2.95–2.82 (m, 2H), 2.68–2.59 (m, 1H), 2.46–2.41 (m, 1H), 2.41 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 144.6, 141.5, 140.5, 140.3, 136.2, 134.1, 130.4, 130.0, 129.6, 128.35, 128.32, 127.4, 126.5, 124.1, 57.7, 55.6, 22.4, 21.6, 21.4. HR-ESI-MS (m/z): calcd. for $C_{25}H_{27}O_3S_2$ $[M + H]^+$, 439.1396, found 439.1391.



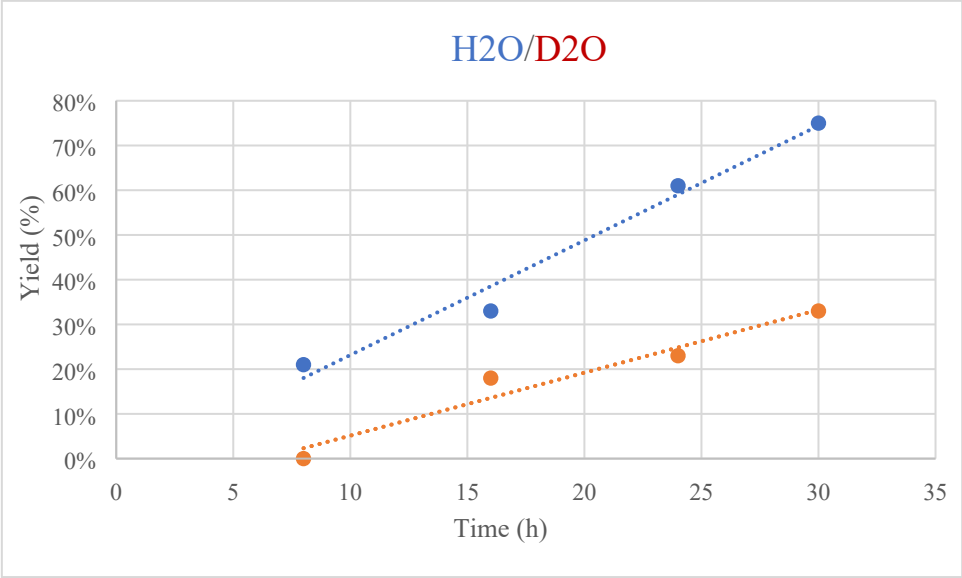
To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (326.2 mg, 1.8mmol) under argon. Then DMF (3.0 mL),), *p*-methoxystyrene **1** (40 μL, 0.3 mmol), TEMPO (140.4 mg, 0.9 mmol), and H_2O (16 μL 0.9 mmol) were added. The reaction mixture was stirred at room temperature for 48 h. Compound **13** was detected by HRMS. HR-ESI-MS (m/z): calcd. for $C_{25}H_{36}NO_4S$ $[M + H]^+$, 4446.2360, found 446.2356.

6. Parallel KIE experiments



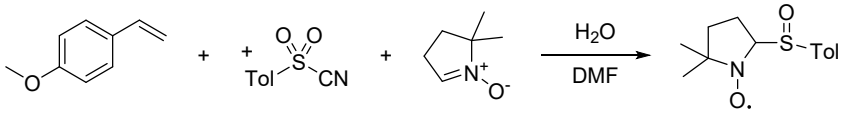
0.1 mmol

To an oven dried 10 mL glass tube with a magnetic stirring bar was added TsCN (108.6 mg, 0.6 mmol) under argon. Then DMF (1.0 mL), *p*-methoxystyrene **1** (13μL, 0.1 mmol), and H_2O (5.4 μL, 0.3 mmol) or D_2O (5.7 μL, 0.3 mmol) were added. The mixture was stirring at room temperature for corresponding time, and the product yield was analyzed by NMR with diphenylacetonitrile as internal standard.



$KIE = K_H/K_D = 1.82$

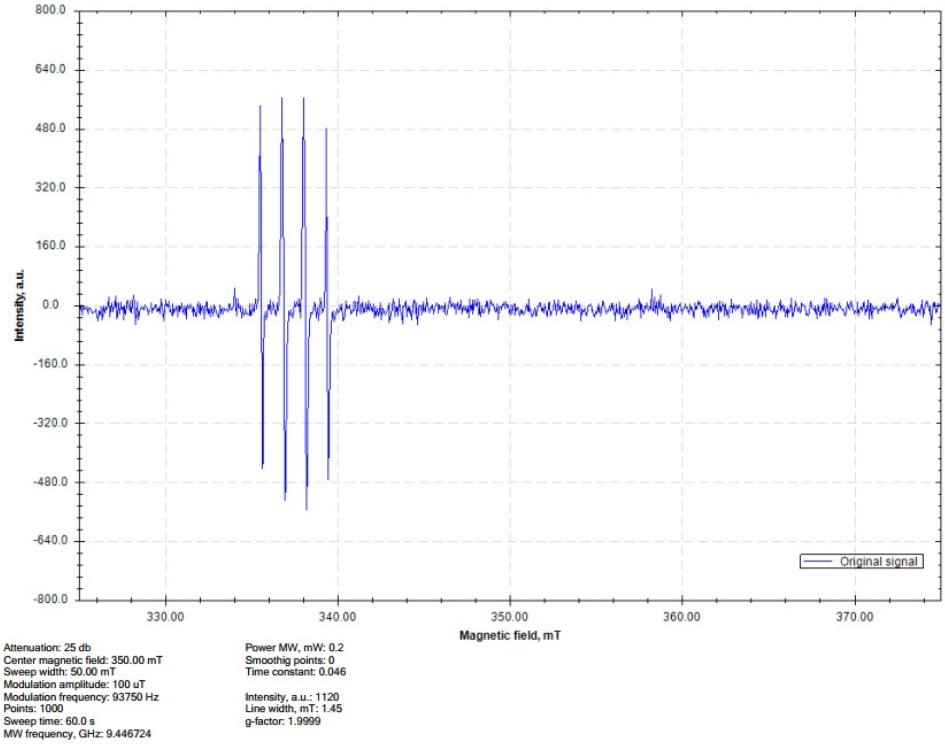
7. EPR experiments



EPR spectra were recorded at room temperature on an ANANI SPINSCAN X spectrometer.

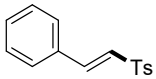
EPR spectrometer was operated at 9.446724 GHz. Typical spectrometer parameters are shown as following: scan range: 50 100 μT; modulation frequency: 93750 Hz; power attenuation: 25 dB; g-factor:1.9999

A mixture of *p*-methoxystyrene **1** (13 μL, 0.1 mmol) and TsCN (108.7 mg, 0.6 mmol) in degassed dry DMF (1.0 mL) was added H_2O (5.4 μL, 0.3 mmol). After stirred under an argon atmosphere for 5h, DMPO (67.9 mg, 0.6 mmol) was added into the reaction. Afterwards, 20 μL of the mixture was quickly taken out into a small tube and analyzed by EPR.[5] A_N= 13.5 G, $A_{H\beta}$ = 12.5 G.



8. Identification of compounds

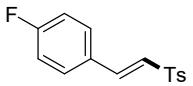
(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (14)[6]



14

Prepared according to the general procedure using styrene (34 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **14** as a colorless solid (69.8 mg, 90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 15.4 Hz, 1H), 7.48 (dd, J = 7.5, 2.1 Hz, 2H), 7.43–7.32 (m, 5H), 6.85 (d, J = 15.4 Hz, 1H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.4, 142.0, 137.7, 132.5, 131.1, 130.0, 129.1, 128.5, 127.7, 127.6, 21.6.

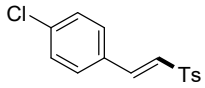
(*E*)-1-Fluoro-4-(2-tosylvinyl)benzene (15)[7]



15

Prepared according to the general procedure using 1-fluoro-4-vinylbenzene (36 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **15** as a colorless solid (70.1 mg, 85% yield). ^{1}H NMR ($CDCl_3$,600 MHz) δ 7.82 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 15.3 Hz, 1H), 7.50–7.44 (m, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H), 6.78 (d, J = 15.3 Hz, 1H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 165.2 (d, $^1J_{C–F}$ = 251.4 Hz), 144.5, 140.6, 137.7, 130.6 (d, $^3J_{C–F}$ = 10.3 Hz), 130.0, 128.7, 127.7, 127.4, 116.4 (d, $^2J_{C–F}$ = 22.0 Hz), 21.6. ^{19}F NMR ($CDCl_3$, 565 MHz) δ –107.91 (s, 1F).

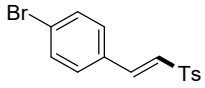
(*E*)-1-Chloro-4-(2-tosylvinyl)benzene (16)[7]



16

Prepared according to the general procedure using 1-chloro-4-vinylbenzene (36 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **16** as a colorless solid (68.8 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 15.4 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.36–7.32 (m, 4H), 6.83 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 144.6, 140.4, 137.5, 137.1, 131.0, 130.1, 129.7, 129.4, 128.3, 127.8, 21.7.

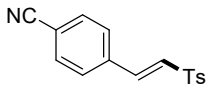
(*E*)-1-Bromo-4-(2-tosylvinyl)benzene (17)[7]



17

Prepared according to the general procedure using 1-bromo-4-vinylbenzene (39 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **17** as a colorless solid (90.2 mg, 90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 15.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.37–7.31 (m, 4H), 6.84 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.6, 140.5, 137.4, 132.4, 131.4, 130.1, 129.9, 128.3, 127.8, 125.5, 21.6.

(*E*)-4-(2-Tosylvinyl)benzonitrile (18)[1]

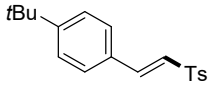


18

Prepared according to the general procedure using 4-vinylbenzonitrile (36 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **18** as

a colorless solid (69.3 mg, 82% yield). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 15.4 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 145.0, 139.2, 136.9, 136.8, 132.8, 131.4, 130.2, 128.9, 128.0, 118.0, 114.3, 21.7.

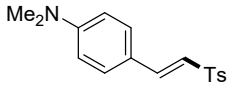
(*E*)-1-(*tert*-Butyl)-4-(2-tosylvinyl)benzene (19)[8]



19

Prepared according to the general procedure using 1-(*ter*t-butyl)-4-vinylbenzene (55 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **19** as a colorless solid (78.9 mg, 84% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 15.4 Hz, 1H), 7.44–7.38 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz,) δ 154.9, 144.3, 142.0, 138.0, 130.0, 129.7, 128.4, 127.7, 126.6, 126.1, 35.0, 31.1, 21.6.

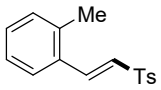
(*E*)-*N*,*N*-Dimethyl-4-(2-tosylvinyl)aniline (20)[9]



20

Prepared according to the general procedure using *N*,*N*-dimethyl-4-vinylaniline (42 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:5) on silica gel to afford product **20** as a colorless solid (85.0 mg, 71% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 15.2 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 15.2 Hz, 1H), 3.01 (s, 6H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 152.2, 143.7, 142.8, 139.0, 130.3, 129.8, 127.4, 121.2, 120.0, 111.7, 40.1 21.6.

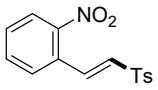
(*E*)-1-Methyl-2-(2-tosylvinyl)benzene (21)[10]



21

Prepared according to the general procedure using 1-methyl-2-vinylbenzene (40 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **21** as a colorless solid (67.8 mg, 83% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, *J* = 15.3 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.8Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.32–7.25 (m, 1H), 7.23–7.15 (m, 2H), 6.77 (d, *J* = 15.3 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 144.4, 139.6, 138.2, 137.8, 131.4, 131.0, 130.9, 130.0, 128.6, 127.7, 126.9, 126.8, 21.6, 19.8.

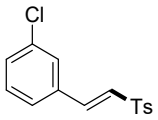
(*E*)-1-Nitro-2-(2-tosylvinyl)benzene (22)[11]



22

Prepared according to the general procedure using 1-nitro-2-vinylbenzene (42 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:5) on silica gel to afford product **22** as a colorless solid (69.5 mg, 76% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.32–(m, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 15.4 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 148.7, 145.0, 138.8, 136.9, 134.3, 134.2, 131.1, 130.3, 130.2, 128.0, 125.3, 122.8, 21.7.

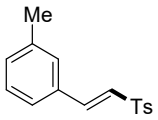
(*E*)-1-Chloro-3-(2-tosylvinyl)benzene (23)[1]



23

Prepared according to the general procedure using 1-chloro-3-vinylbenzene (38 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **23** as a colorless solid (69.7 mg, 80% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.48 (s, 1H), 7.43–7.32 (m, 5H), 6.89 (d, *J* = 15.4 Hz, 1H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 144.7, 140.2, 137.4, 135.1, 134.3, 131.0, 130.3, 130.1, 129.3, 128.2, 127.8, 126.8, 21.6.

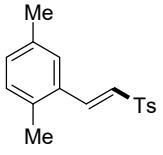
(*E*)-1-Methyl-3-(2-tosylvinyl)benzene (24)[10]



24

Prepared according to the general procedure using 1-methyl-3-vinylbenzene (39 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **24** as a colorless solid (68.2 mg, 84% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 15.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34–7.29 (m, 3H), 7.25 (s, 1H), 6.88 (d, *J* = 15.3 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.4, 142.1, 138.8, 137.8, 132.4, 132.0, 130.0, 129.1, 129.0, 127.7, 127.4, 125.8, 21.6, 21.3.

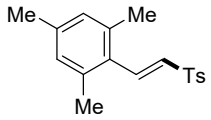
(*E*)-1,4-Dimethyl-2-(2-tosylvinyl)benzene (25)[12]



25

Prepared according to the general procedure using 1,4-dimethyl-2-vinylbenzene (44 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **25** as a colorless solid (66.3 mg, 77% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 15.3 Hz, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.24 (s, 1H), 7.10 (d, J = 1.1 Hz, 2H), 6.76 (d, J = 15.3 Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.3, 139.8, 137.9, 136.0, 135.2, 131.7, 131.1, 131.0, 130.0, 128.2, 127.7, 127.3, 21.6, 20.9, 19.3.

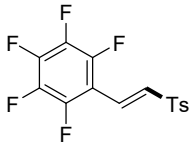
(*E*)-1,3,5-Trimethyl-2-(2-tosylvinyl)benzene (26)[8]



26

Prepared according to the general procedure using 1,3,5-trimethyl-2-vinylbenzene (48 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:25) on silica gel to afford product **26** as a colorless solid (85.0 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.87–7.79 (m, 3H), 7.35 (d, J = 8.0 Hz, 2H), 6.87 (s, 2H), 6.52 (d, J = 15.7 Hz, 1H), 2.44 (s, 3H), 2.27 (d, J = 6.7 Hz, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 144.4, 140.4, 139.4, 138.1, 137.6, 135.8, 132.2, 130.1, 129.9, 129.5, 128.7, 127.7, 29.8, 21.7, 21.2 21.1.

(*E*)-1,2,3,4,5-Pentafluoro-6-(2-tosylvinyl)benzene (27)[13]

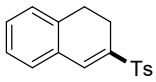


27

Prepared according to the general procedure using 1,2,3,4,5-pentafluoro-6-vinylbenzene (42 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol) and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified

by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **27** as a colorless solid (93.3 mg, 89% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 15.8 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 15.8 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 146.7(dm, $^{1}J_{C\text{-}F}$ = 257.0 Hz), 145.2(s), 143.4(dm, $^{1}J_{C\text{-}F}$ = 258.5 Hz), 138.8(dm, $^{1}J_{C\text{-}F}$ = 252.4 Hz), 136.5(s), 135.7(tm, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 130.2(s), 128.1(s), 125.3(s), 108.2(dt, $^{2}J_{C\text{-}F}$ = 16.3 Hz, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 21.7(s). ^{19}F NMR ($CDCl_3$, 471 MHz) δ -138.19 – -138.35 (m, 2F), -148.86 – -149.03 (m, 1F), -160.75 (td, *J* = 19.5, 6.1 Hz, 2F).

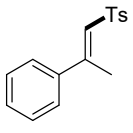
3-Tosyl-1,2,4a,8a-tetrahydronaphthalene (28)[14]



28

Prepared according to the general procedure using 1,2-dihydronaphthalene (35 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **28** as a colorless solid (58.1 mg, 68% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.56 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28–7.22 (m, 3H), 7.12 (d, *J* = 7.0 Hz, 1H), 2.86 (t, *J* = 8.3 Hz, 2H), 2.49 (t, *J* = 8.3 Hz, 2H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.3, 138.5, 136.6, 135.6, 134.8, 131.1, 130.4, 129.9, 129.0, 128.0, 127.8, 127.2, 27.6, 21.7, 21.6.

(*E*)-1-Methyl-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (29)[15]

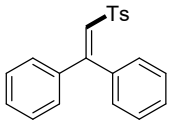


29

Prepared according to the general procedure using prop-1-en-2-ylbenzene (39 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 72 h and purified by column chromatography (acetone/petroleum ether = 1:45) on silica gel to afford product **29** as

a colorless solid (60.4 mg, 74% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.40–7.33 (m, 7H), 6.60 (q, *J* = 1.3 Hz, 1H), 2.52 (d, *J* = 1.3 Hz, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 153.0, 144.2, 140.2, 139.3, 129.9, 129.8, 128.7, 127.8, 127.3, 126.3, 21.6, 17.2.

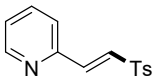
(2-Tosylethene-1,1-diyl)dibenzene (30)[15]



30

Prepared according to the general procedure using ethene-1,1-diyldibenzene (53 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 72 h and purified by column chromatography (acetone/petroleum ether = 1:45) on silica gel to afford product **30** as a colorless solid (79.3 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.40–7.34 (m, 2H), 7.33–7.27 (m, 4H), 7.23–7.18 (m, 2H), 7.17–7.13 (m, 2H), 7.12–7.07 (m, 2H), 6.99 (s, 1H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 154.7, 143.8, 139.2, 138.6, 135.6, 130.2, 129.8, 129.3, 129.0, 128.9, 128.6, 128.2, 127.8, 127.7 21.6.

(*E*)-2-(2-Tosylvinyl)pyridine (31)[11]

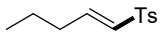


31

Prepared according to the general procedure using 2-vinylpyridine (32 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:5) on silica gel to afford product **31** as a colorless solid (50.6 mg, 65% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.60 (d, *J* = 4.7 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 14.9 Hz, 1H), 7.46–7.37 (m, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.31–7.26 (m, 1H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125

MHz) δ 151.2, 150.3, 144.6, 140.0, 137.3, 137.0, 132.2, 130.0, 128.0, 125.4, 124.9, 21.6.

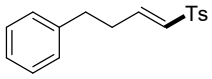
(*E*)-1-Methyl-4-(pent-1-en-1-ylsulfonyl)benzene (32)[16]



32

Prepared according to the general procedure using pent-1-ene (33 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **32** as a colorless solid (38.5 mg, 57% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.94 (dt, *J* = 15.1, 6.8 Hz, 1H), 6.29 (dt, *J* = 15.1, 1.6 Hz, 1H), 2.42 (s, 3H), 2.19 (qd, *J* = 7.3, 1.6 Hz, 2H), 1.55–1.41 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 146.4, 144.2, 137.8, 130.7, 129.9, 127.6, 33.4, 21.6, 20.9, 13.6.

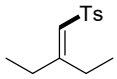
(*E*)-1-Methyl-4-((4-phenylbut-1-en-1-yl)sulfonyl)benzene (33)[17]



33

Prepared according to the general procedure using but-3-en-1-ylbenzene (42 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **33** as a colorless solid (61.9 mg, 72% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.29–7.22 (m, 2H), 7.22–7.16 (m, 1H), 7.14–7.09 (m, 2H), 6.97 (dt, *J* = 15.1, 6.8 Hz, 1H), 6.28 (d, *J* = 15.1 Hz, 1H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.60–2.49 (m, 2H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 145.3, 144.2, 140.0, 137.6, 131.3, 129.9, 128.6, 128.3, 127.6, 126.4, 33.9, 33.1, 21.6.

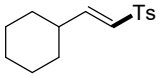
1-((2-Ethylbut-1-en-1-yl)sulfonyl)-4-methylbenzene) (34)[16]



34

Prepared according to the general procedure using 3-methylenepentane (37 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 72 h and purified by column chromatography (acetone/petroleum ether = 1:45) on silica gel to afford product **34** as a colorless solid (44.6 mg, 62% yield). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.09 (s, 1H), 2.60 (q, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 2.18 (qd, *J* = 7.4, 1.5 Hz, 2H), 1.02 (t, *J* = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 163.8, 143.8, 139.8, 129.7, 127.2, 124.8, 29.9, 24.5, 21.6, 12.8, 11.6.

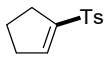
(*E*)-1-((2-Cyclohexylvinyl)sulfonyl)-4-methylbenzene (35)[18]



35

Prepared according to the general procedure using vinylcyclohexane (41 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:45) on silica gel to afford product **35** as a colorless solid (50.2 mg, 63% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.92 (dd, *J* = 15.2, 6.4 Hz, 1H), 6.23 (dd, *J* = 15.2, 1.5 Hz, 1H), 2.43 (s, 3H), 2.22-2.21 (m, 1H), 1.81–1.70 (m, 4H), 1.33–1.18 (m, 3H), 1.18–1.06 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 151.2, 144.1, 137.9, 129.9, 128.6, 127.6, 39.8, 31.3, 25.7, 25.6, 21.6.

1-(Cyclopent-1-en-1-ylsulfonyl)-4-methylbenzene (36)[14]

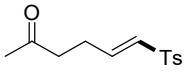


36

Prepared according to the general procedure using cyclopentene (27 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography

(acetone/petroleum ether = 1:20) on silica gel to afford product **36** as a colorless solid (50.7mg, 76% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.71 (q, *J* = 2.2, 1.6 Hz, 1H), 2.55–2.49 (m, 4H), 2.43 (s, 3H), 2.06–1.97 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.9, 144.3, 142.8, 136.7, 129.8, 128.0, 32.9, 30.8, 23.6, 21.6.

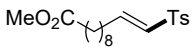
(*E*)-6-Tosylhex-5-en-2-one (37)



37

Prepared according to the general procedure using hex-5-en-2-one (33 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **37** as a colorless oil (53.8 mg, 71% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 6.92 (dt, *J* = 15.1, 6.7 Hz, 1H), 6.32 (dt, *J* = 15.1, 1.5 Hz, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.49 (q, *J* = 7.0, 6.5 Hz, 2H), 2.44 (s, 3H), 2.15 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 206.2, 144.5, 144.4, 137.4, 131.5, 129.9, 127.7, 41.0, 29.9, 25.2, 21.6. HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{17}O_3S$ $[M + H]^+$, 253.0893, found 253.0896.

Methyl (*E*)-2-(2-tosylvinyl)nonanoate (38)

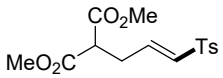


38

Prepared according to the general procedure using methyl 2-vinylnonanoate (67 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **38** as a colorless solid (74.5 mg, 70% yield), m.p.: 86–88 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 6.93 (dt, *J* = 15.1, 6.8 Hz, 1H), 6.27 (dt, *J* = 15.1, 1.6 Hz, 1H), 3.65 (s, 3H), 2.42 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.23–2.16 (m, 2H), 1.63–1.54 (m, 2H), 1.48–1.36 (m, 2H), 1.30–1.22 (m, 8H). ^{13}C{^{1}H} NMR

($CDCl_3$, 100 MHz) δ 174.3, 146.6, 144.2, 137.8, 130.6, 129.9, 127.6, 51.5, 34.0, 31.4, 29.04, 29.01, 28.9, 27.5, 24.9, 21.6. HR-ESI-MS (m/z): calcd. for $C_{19}H_{29}O_4S$ $[M + H]^+$, 353.1781, found 353.1786.

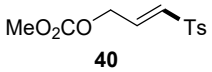
Dimethyl (*E*)-2-(3-tosylallyl)malonate (39)



39

Prepared according to the general procedure using dimethyl 2-allylmalonate (48 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **39** as a colorless oil (92.0 mg, 94% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.86 (dt, *J* = 15.1, 7.2 Hz, 1H), 6.38 (dt, *J* = 15.1, 1.4 Hz, 1H), 3.69 (s, 6H), 3.51 (t, *J* = 7.4 Hz, 1H), 2.79 (td, *J* = 7.3, 1.5 Hz, 2H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.3, 144.5, 141.0, 137.1, 133.5, 129.9, 127.7, 52.9, 49.9, 30.3, 21.6. HR-ESI-MS (m/z): calcd. for $C_{15}H_{19}O_6S$ $[M + H]^+$ 327.0897, found 327.0897.

Methyl (*E*)-(3-tosylallyl) carbonate (40)

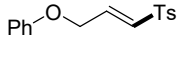


40

Prepared according to the general procedure using allyl methyl carbonate (34 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **40** as a colorless solid (49.6 mg, 61% yield), m.p.: 88–90 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.93 (dt, *J* = 15.1, 3.9 Hz, 1H), 6.58 (dt, *J* = 15.1, 2.1 Hz, 1H), 4.82 (dd, *J* = 3.9, 2.1 Hz, 2H), 3.79 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 154.9, 144.8, 137.9, 136.8, 131.9, 130.0, 127.9,

64.7, 55.3, 21.6. HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{15}O_5S$ $[M + H]^+$, 271.0635, found 271.0632.

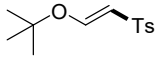
(*E*)-1-Methyl-4-((3-phenoxyprop-1-en-1-yl)sulfonyl)benzene (41)[19]



41

Prepared according to the general procedure using (allyloxy)benzene (40 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 56 h and purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **41** as a colorless solid (68.5 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.31–7.24 (m, 2H), 7.09 (dt, *J* = 15.0, 3.4 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 15.0 Hz, 1H), 4.71 (d, *J* = 2.7 Hz, 2H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 157.6, 144.6, 140.1, 137.2, 131.5, 130.0, 129.7, 127.8, 121.7, 114.6, 65.5, 21.6.

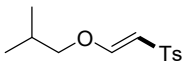
(*E*)-1-((2-(*tert*-Butoxy)vinyl)sulfonyl)-4-methylbenzene (42)



42

Prepared according to the general procedure using 2-methyl-2-(vinyloxy)propane (39 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **42** as a colorless oil (59.1 mg, 78% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 11.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.75 (d, *J* = 11.6 Hz, 1H), 2.41 (s, 3H), 1.37 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 156.3, 143.4, 139.9, 129.7, 126.8, 108.4, 81.3, 28.1, 21.5. HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{19}O_3S$ $[M + H]^+$, 255.1049, found 255.1050.

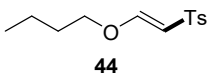
(*E*)-1-((2-Isobutoxyvinyl)sulfonyl)-4-methylbenzene (43)



43

Prepared according to the general procedure using 2-methyl-1-(vinyloxy)propane (39 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **43** as a colorless oil (54.6 mg, 72% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 12.2 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 5.66 (d, J = 12.2 Hz, 1H), 3.57 (d, J = 6.5 Hz, 2H), 2.42 (s, 3H), 2.03–1.92 (m, 1H), 0.93 (d, J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 160.7, 143.6, 139.8, 129.8, 130.0, 106.7, 78.1, 28.0, 21.6, 18.8. HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{19}O_3S$ $[M + H]^+$, 255.1049, found 255.1047.

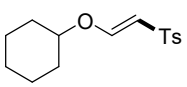
(*E*)-1-((2-Butoxyvinyl)sulfonyl)-4-methylbenzene (44)[20]



44

Prepared according to the general procedure using 1-(vinyloxy)butane (39 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **44** as a colorless solid (50.8 mg, 67% yield). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.76 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 12.2 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 5.67 (d, J = 12.2 Hz, 1H), 3.81 (t, J = 6.5 Hz, 2H), 2.43 (s, 3H), 1.73–1.62 (m, 2H), 1.43–1.35 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 160.6, 143.6, 139.8, 129.7, 127.0, 106.8, 71.7, 30.7, 21.6, 18.9, 13.6.

(*E*)-1-((2-(Cyclohexyloxy)vinyl)sulfonyl)-4-methylbenzene (45)

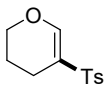


45

Prepared according to the general procedure using (vinyloxy)cyclohexane (44 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The

mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **45** as a colorless solid (66.5 mg, 79% yield), m.p.: 110–112 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 12.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.71 (d, *J* = 12.0 Hz, 1H), 3.97–3.90 (m, 1H), 2.42 (s, 3H), 1.94–1.85 (m, 2H), 1.77–1.69 (m, 2H), 1.56–1.43 (m, 3H), 1.37–1.21 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 159.7, 143.4, 139.9, 129.7, 126.9, 107.2, 82.1, 31.7, 25.1, 23.4, 21.5. HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{21}O_3S$ $[M + H]^+$, 281.1206, found 281.1206.

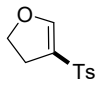
5-Tosyl-3,4-dihydro-2*H*-pyran (46)



46

Prepared according to the general procedure using 5-tosyl-3,4-dihydro-2H-pyran (27 μL, 0.30 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **46** as a colorless solid (50.2 mg, 70% yield), m.p.: 125–127 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.60 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.03–3.98 (m, 2H), 2.43 (s, 3H), 2.17–2.15 (m, 2H), 1.90–1.82 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 153.4, 143.7, 137.7, 129.7, 127.5, 115.5, 66.5, 21.5, 20.8, 18.9. HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{15}O_3S$ $[M + H]^+$, 239.0736 found 239.0732.

4-Tosyl-2,3-dihydrofuran (47)[21]

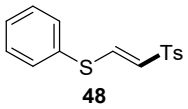


47

Prepared according to the general procedure using 2,3-dihydrofuran (23 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **47** as a colorless solid

(42.5 mg, 63% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.20 (s, 1H), 4.61 (t, *J* = 9.8 Hz, 2H), 2.79 (td, *J* = 9.8, 1.8 Hz, 2H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz,) δ 156.4, 144.0, 137.8, 129.8, 127.3, 117.6, 74.0, 28.1, 21.6.

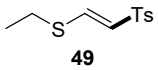
(*E*)-Phenyl(2-tosylvinyl)sulfane (48)[22]



48

Prepared according to the general procedure using phenyl(vinyl)sulfane (39 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **48** as a colorless solid (63.7 mg, 73% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79 (d, *J* = 14.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.47–7.39 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.98 (d, *J* = 14.5 Hz, 1H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 145.6, 144.1, 138.0, 133.4, 130.0, 129.9, 129.8, 129.2, 127.4, 123.5, 21.6.

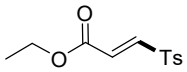
(*E*)-Ethyl(2-tosylvinyl)sulfane (49)



49

Prepared according to the general procedure using ethyl(vinyl)sulfane (30 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **49** as white foam (51.6 mg, 71% yield). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 14.6 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.12 (d, *J* = 14.6 Hz, 1H), 2.79 (q, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.35–1.30 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz,) δ 145.0, 144.0, 138.4, 129.9, 127.4, 122.0, 26.4, 21.6, 13.5. HR-ESI-MS (*m/z*): calcd. for $C_{11}H_{15}O_2S_2$ $[M + H]^+$, 243.0508, found 243.0507.

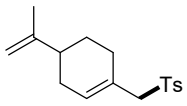
Ethyl (*E*)-3-tosylacrylate (50)[23]



50

Prepared according to the general procedure using ethyl acrylate (33 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 48 h and purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **50** as a colorless solid (47.3 mg, 62% yield). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 15.1 Hz, 1H), 6.79 (d, *J* = 15.1 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 163.5, 145.6, 143.5, 135.6, 130.5, 130.3, 128.4, 62.0, 21.7, 14.0.

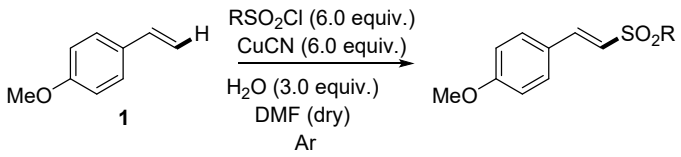
1-Methyl-4-(((4-(prop-1-en-2-yl) cyclohex-1-en-1-yl) methyl) sulfonyl) benzene (51)



51

Prepared according to the general procedure using (1*S*,5*S*)-6,6-dimethyl-2-methylenebicyclo [3.1.1] heptane (47 μL, 0.3 mmol), TsCN (326.2 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at 80 °C for 56 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **51** as a colorless solid (81.1 mg, 93% yield), m.p.: 178–180 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.44 (dd, *J* = 4.8, 2.4 Hz, 1H), 4.73 (d, *J* = 1.7 Hz, 2H), 3.68 (s, 2H), 2.45 (s, 3H), 2.23–2.13 (m, 2H), 2.13–1.99 (m, 2H), 1.94–1.75 (m, 2H), 1.71 (s, 3H), 1.49–1.34 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 149.1, 144.5, 135.7, 132.2, 129.5, 128.5, 125.9, 108.9, 64.5, 40.1, 31.0, 29.1, 27.5, 21.7, 20.8. HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{22}O_2SNa$ $[M + Na]^+$, 313.1233 found 313.1233.

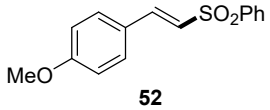
General procedure for the arylsulfonylation of alkenes



1

To an oven dried 10 mL glass tube with a magnetic stirring bar was added CuCN (1.8 mmol, 6.0 equiv.) and sulfonyl chloride (1.8 mmol, 6.0 equiv.) in DMF (3.0 mL) under argon. After the mixture was stirred for 30 min at room temperature, *p*-methoxystyrene **1** (40 μL, 0.3 mmol) and H_2O (0.9 mmol, 3.0 equiv.) were added. The mixture was stirred for 24 h at room temperature. Then the reaction mixture was diluted with ethyl acetate followed by addition of water and filtered. The filter liquor was washed with water (15 mL × 3), followed by $NaHCO_3$ aq. and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude product was subjected to column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford desired product.

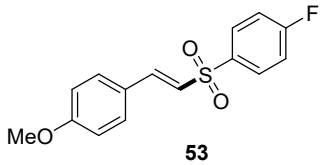
(*E*)-1-Methoxy-4-(2-(phenylsulfonyl)vinyl)benzene[24]



52

Prepared according to the general procedure using *p*-methoxystyrene **1** (40 μL, 0.3 mmol), CuCN (161.2 mg, 1.8 mmol), benzenesulfonyl chloride (0.23mL, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 24 h and purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **52** as a colorless solid (60.1 mg, 73% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.66 – 7.57 (m, 2H), 7.56 – 7.50 (m, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 15.3 Hz, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 162.1, 142.3, 141.1, 133.2, 130.4, 129.3, 127.5, 125.0, 124.4, 114.5, 55.5.

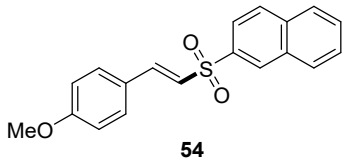
(*E*)-1-Fluoro-4-((4-methoxystyryl)sulfonyl)benzene[25]



53

Prepared according to the general procedure using *p*-methoxystyrene **1** (40 μL, 0.3 mmol), CuCN (161.2 mg, 1.8 mmol), 4-fluorobenzenesulfonyl chloride (350.3 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 24 h and purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **53** as a colorless solid (67.6 mg, 77% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 – 7.90 (m, 2H), 7.63 (d, *J* = 15.3 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.17 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 15.3 Hz, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 166.8, 164.2, 162.2, 142.5, 137.2 (d, *J* = 3.0 Hz), 130.6 – 130.2 (m), 124.8, 124.2, 116.7, 116.5, 114.6, 55.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –104.4.

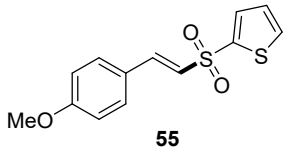
(*E*)-2-((4-Methoxystyryl)sulfonyl)naphthalene



54

Prepared according to the general procedure using *p*-methoxystyrene **1** (40 μL, 0.3 mmol), CuCN (161.2 mg, 1.8 mmol), naphthalene-2-sulfonyl chloride (408.0 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 24 h and purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **54** as a colorless solid (74.9 mg, 77% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (s, 1H), 7.99 (dd, *J* = 8.6, 6.1 Hz, 2H), 7.94 – 7.85 (m, 2H), 7.71 – 7.60 (m, 3H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 15.4 Hz, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 162.1, 142.4, 137.9, 135.1, 132.3, 130.4, 129.6, 129.4, 129.1, 129.0, 128.0, 127.6, 125.0, 124.5, 122.6, 114.6, 114.5, 55.5. HR-ESI-MS (m/z): calcd. for $C_{19}H_{16}O_3S$ $[M + H]^+$, 325.0893, found 325.0890.

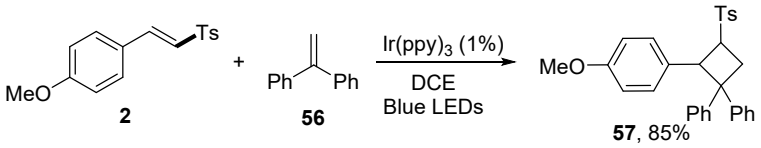
(*E*)-2-((4-Methoxystyryl)sulfonyl)thiophene[3]



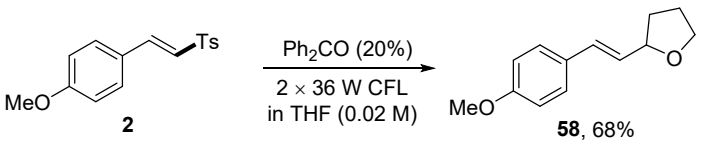
55

Prepared according to the general procedure using *p*-methoxystyrene **1** (40 μL, 0.3 mmol), CuCN (161.2 mg, 1.8 mmol), thiophene-2-sulfonyl chloride (328.8 mg, 1.8 mmol), H_2O (16 μL, 0.9 mmol), and DMF (3.0 mL). The mixture was stirred at room temperature for 24 h and purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **55** as a colorless solid (78.3 mg, 93% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.67 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.63 (d, *J* = 15.3 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.13 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 15.3 Hz, 1H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 162.2, 142.8, 142.0, 133.6, 133.1, 130.5, 128.0, 125.0, 124.8, 114.6, 55.5.

9. Transformations of alkenyl sulfone



Prepared according to the known procedures.[26] A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with **2** (57.8 mg, 0.2 mmol), 1,1-diphenylethylene **56** (176 μL, 1.0 mmol), $Ir(ppy)_3$ (1.3 mg, 1 mmol%) and 2 mL $ClCH_2CH_2Cl$. This system was bubbled with argon for 10 minutes, then sealed and irradiated at room temperature by blue LED for 5 h. Then, the mixture was evaporated to remove the solvent and the residue was purified by column chromatography (ethyl acetate/hexane = 1:30) on silica gel to afford product **57** as colorless powder (79.7 mg, 85%). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.22 (m, 4H), 7.20 – 7.15 (m, 1H), 7.12 – 7.04 (m, 5H), 6.89 (d, *J* = 9.8 Hz, 2H), 6.47 (s, 4H), 4.59 (d, *J* = 10.5 Hz, 1H), 4.06 – 3.94 (m, 1H), 3.68 (s, 3H), 3.34 (dd, *J* = 11.8, 7.8 Hz, 1H), 2.93 (dd, *J* = 11.9, 10.5 Hz, 1H), 2.28 (s, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz) δ 158.5, 149.6, 144.3, 140.3, 135.4, 129.8, 129.5, 128.7, 128.5, 128.4, 128.2, 127.9, 126.5, 126.3, 126.0, 113.1, 59.0, 55.1, 53.5, 51.2, 31.4, 21.5. HR-ESI-MS (m/z): calcd. for $C_{30}H_{29}O_3S$ $[M + H]^+$, 469.1832, found 469.1834.

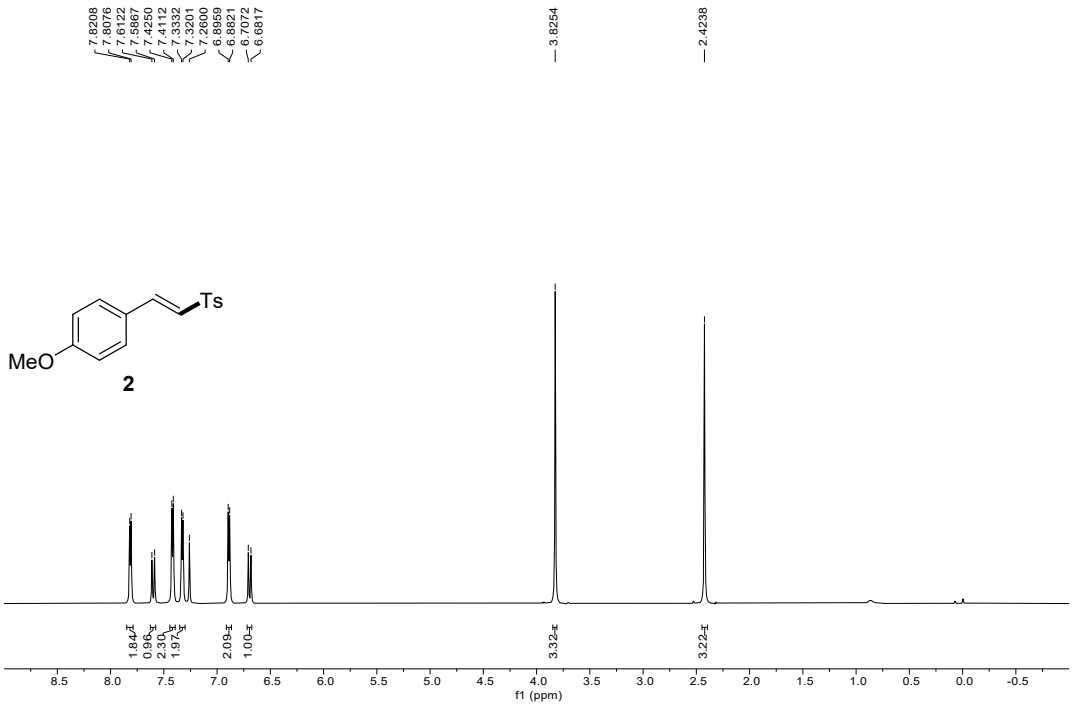


Prepared according to the known procedures.[27] To an oven dried screw cap tube (10 mL) equipped with a magnetic stir bar, charged with **2** (57.8 mg, 0.2 mmol), and benzophenone (7.3 mg, 20 mmol%), followed by tetrahydrofuran (10.0 mL, 0.02 M). The resultant reaction mixture was placed in front of two 36 W household CFL bulb and allowed to stir at room temperature for 80 h. Then, the reaction mixture was neutralized with saturated aqueous solution of $NaHCO_3$ and diluted with distilled water followed by extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The

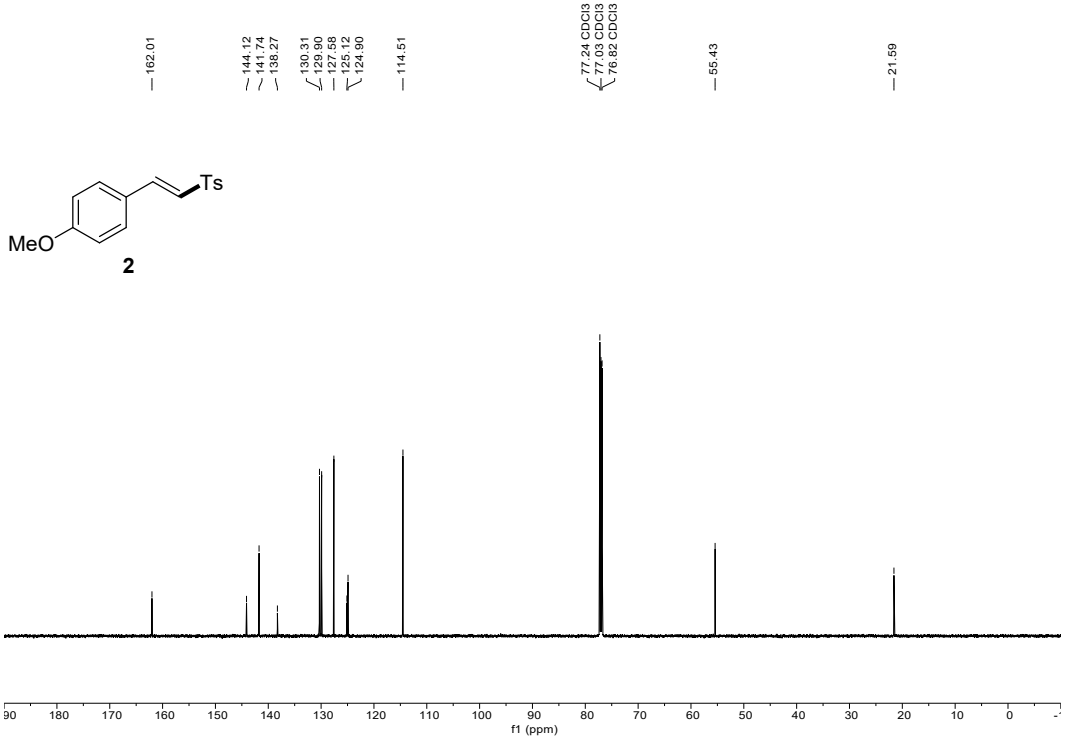
crude material was purified by column chromatography (acetone/petroleum ether = 1:50) on silica gel to afford product **58** as a colorless oil (27.3 mg, 68%).[28] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 15.8, 1H), 6.07 (dd, *J* = 15.8, 6.8 Hz, 1H), 4.49 – 4.39 (m, 1H), 4.02 – 3.91 (m, 1H), 3.88 – 3.78 (m, 4H), 3.80 (s, 3H), 2.17 – 2.05 (m, 1H), 2.04 – 1.88 (m, 2H), 1.77 – 1.62 (m, 1H).

10. Copies of NMR spectra

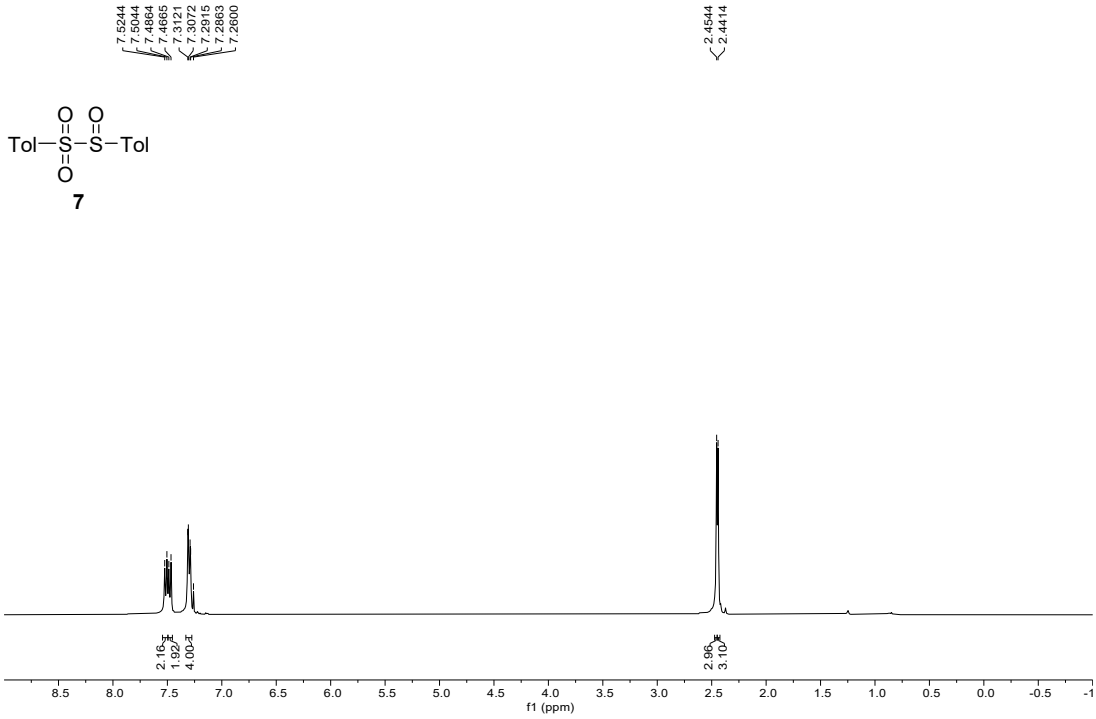
^{1}H NMR ($CDCl_3$, 600 MHz) of **2**



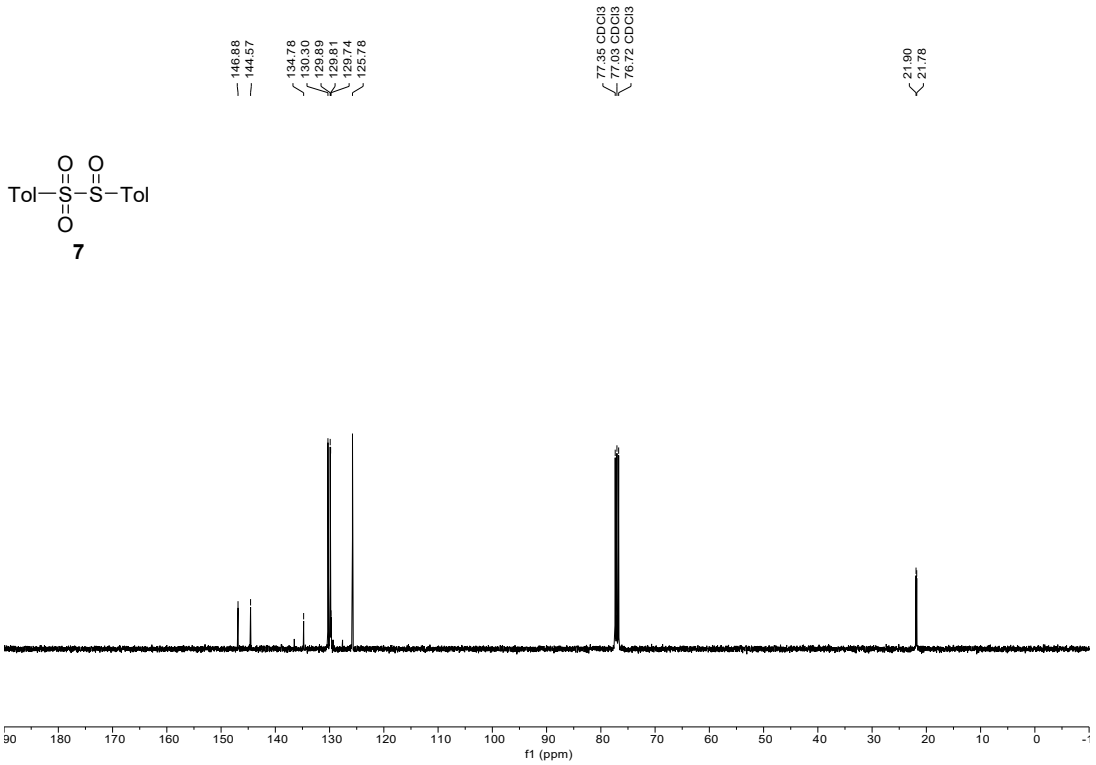
^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) of **2**



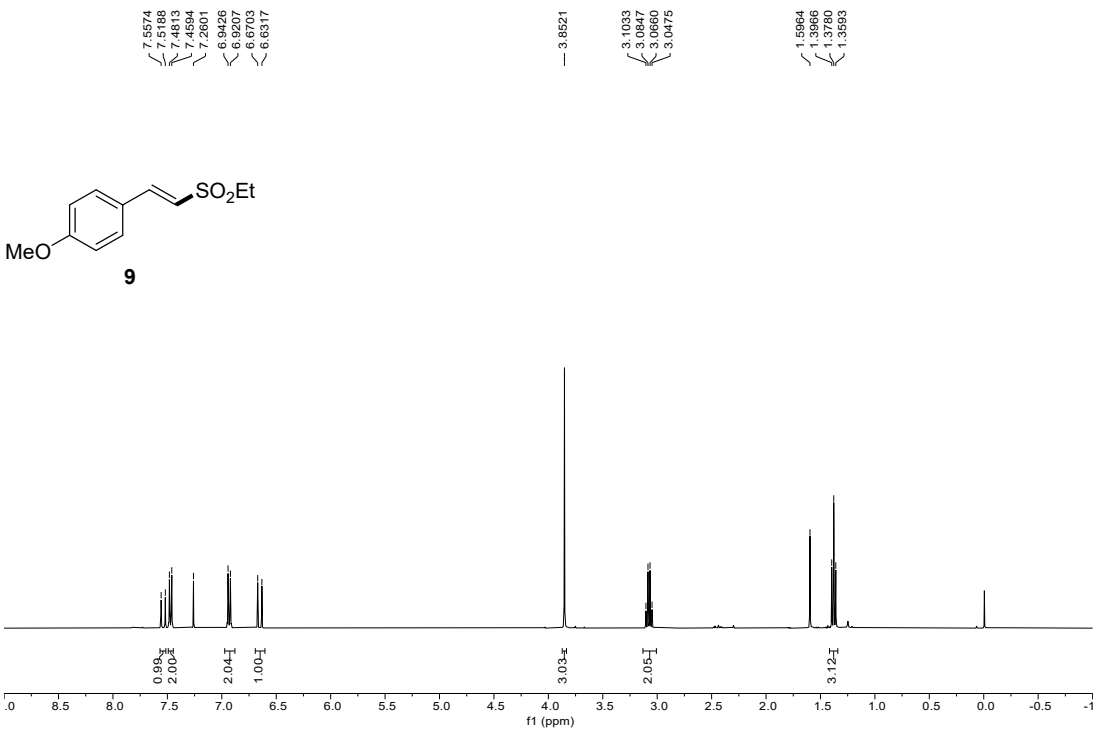
^{1}H NMR ($CDCl_3$, $CDCl_3$) of **7**



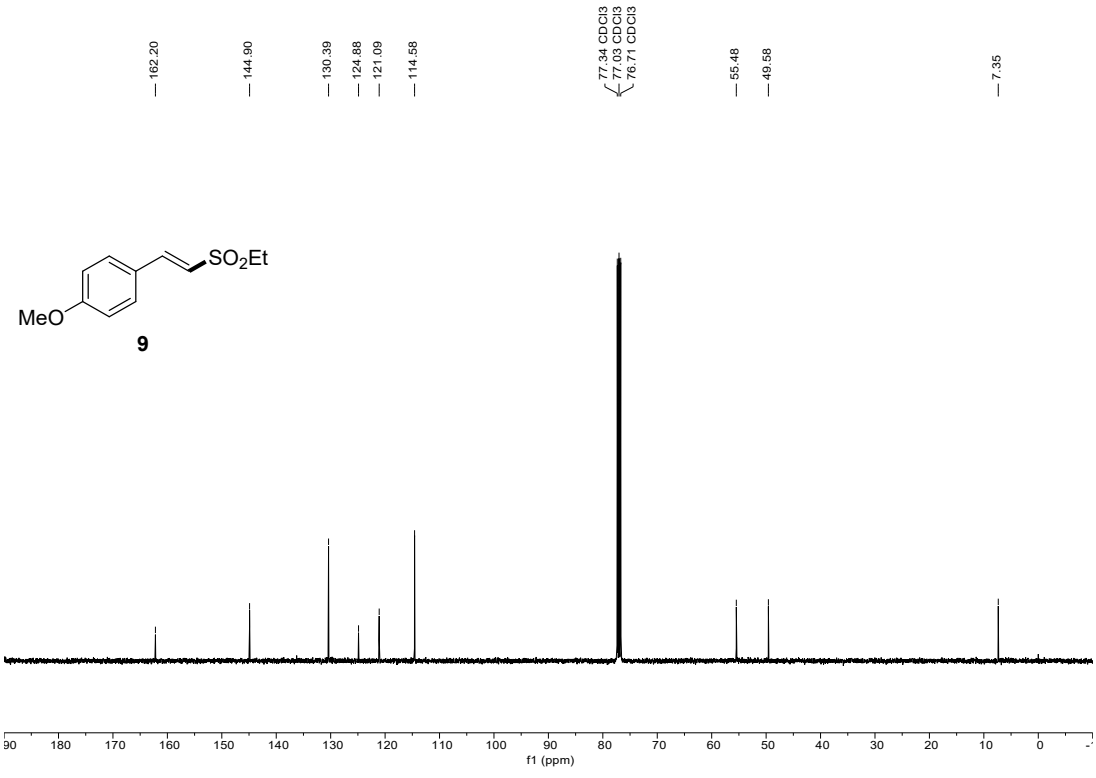
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, $CDCl_3$) of **7**



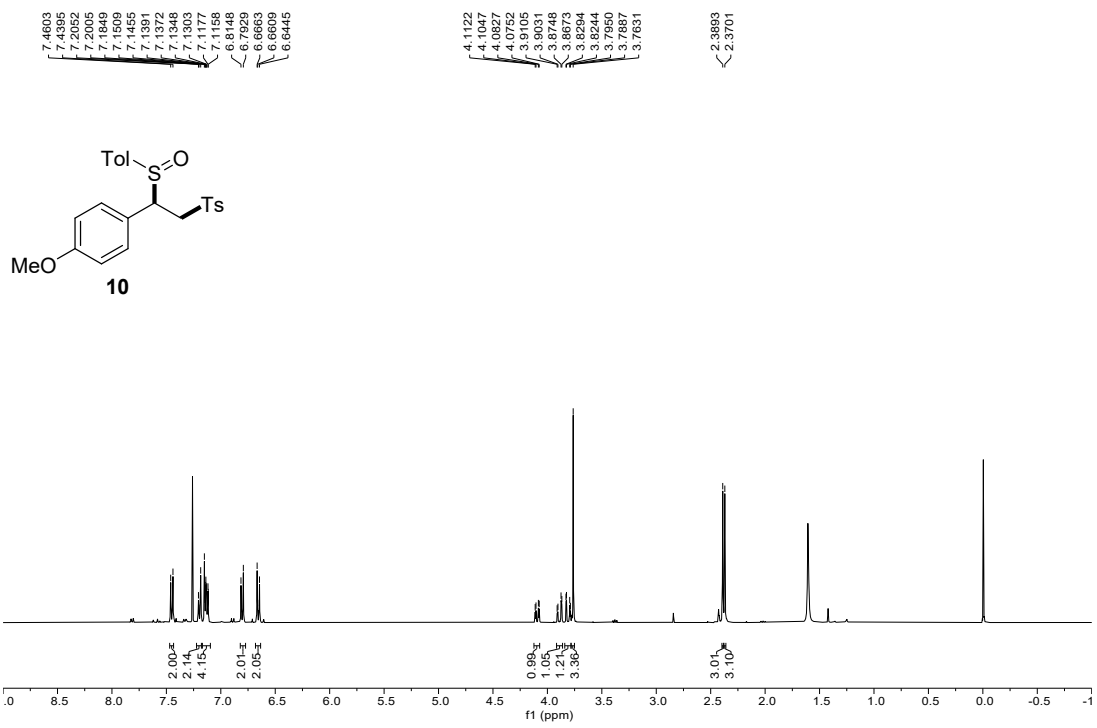
^{1}H NMR ($CDCl_3$, 400 MHz) of **9**



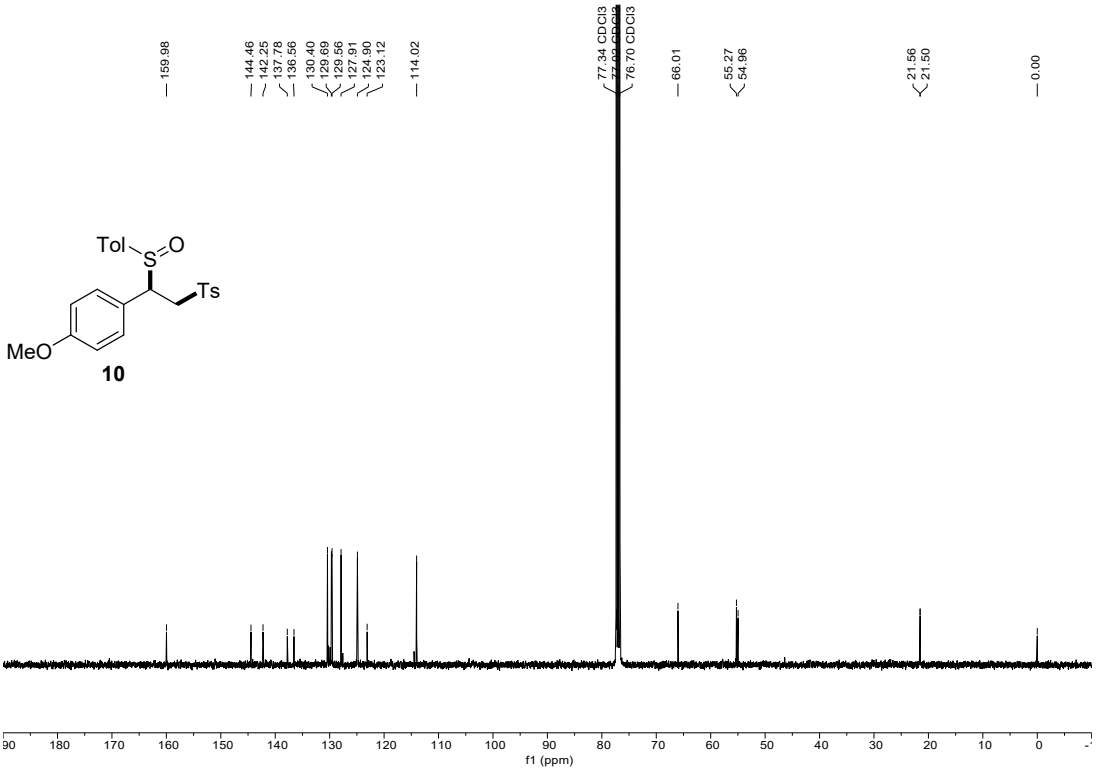
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **9**



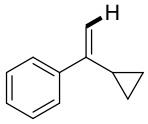
^{1}H NMR ($CDCl_3$, 400 MHz) of **10**



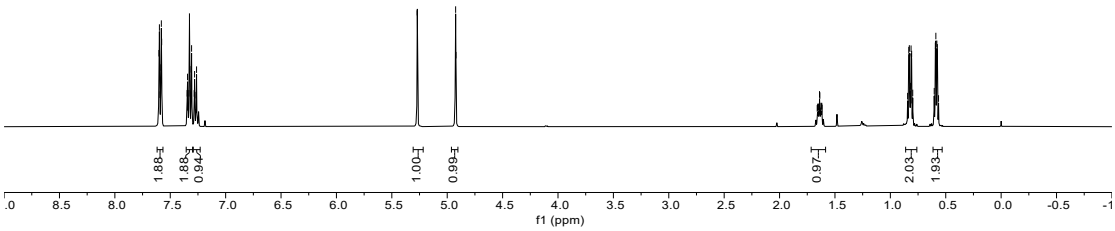
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **10**



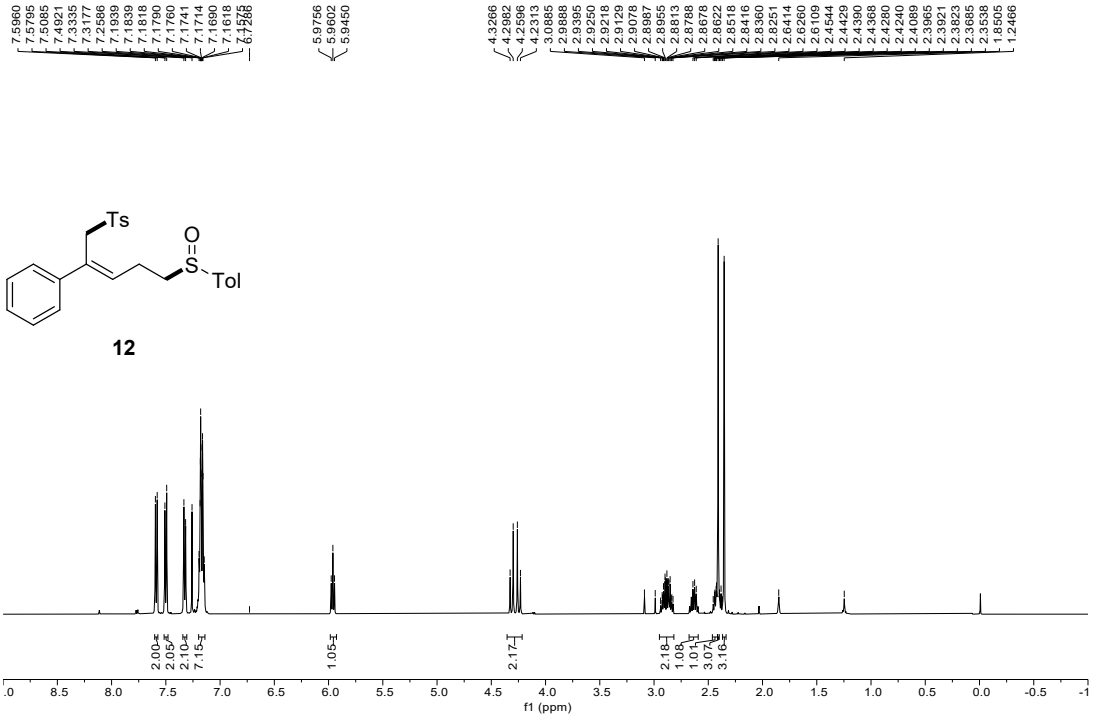
^{1}H NMR ($CDCl_3$, 400 MHz) of **11**



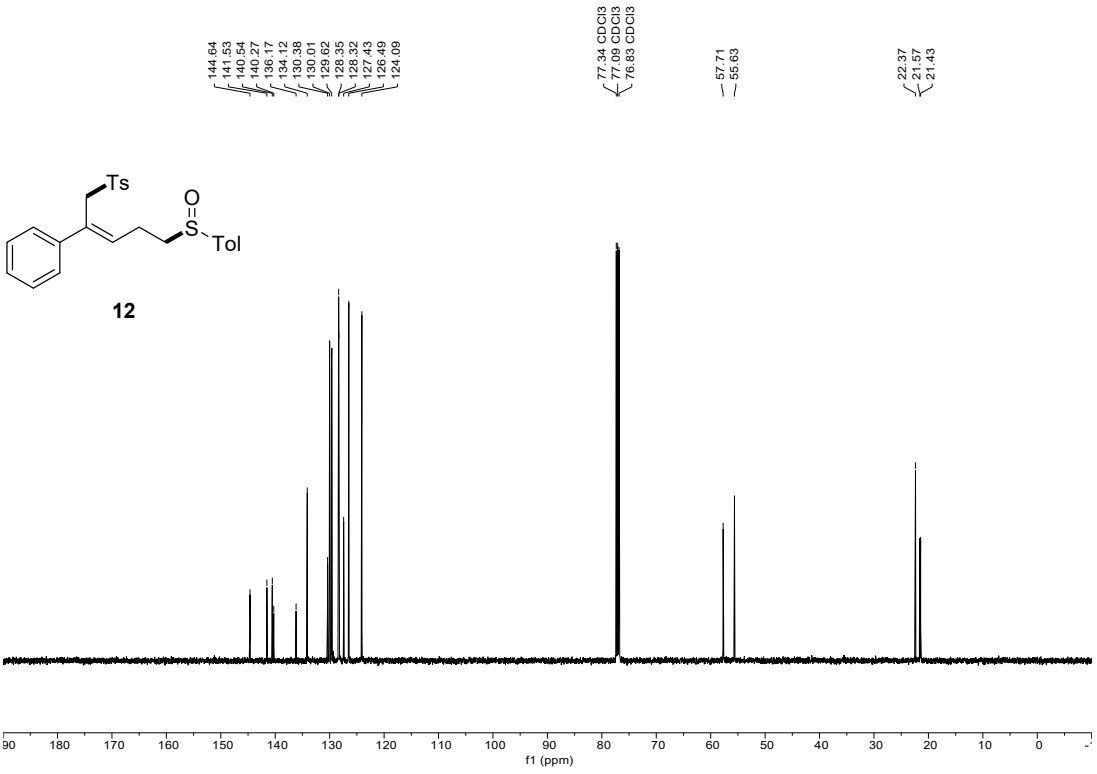
11



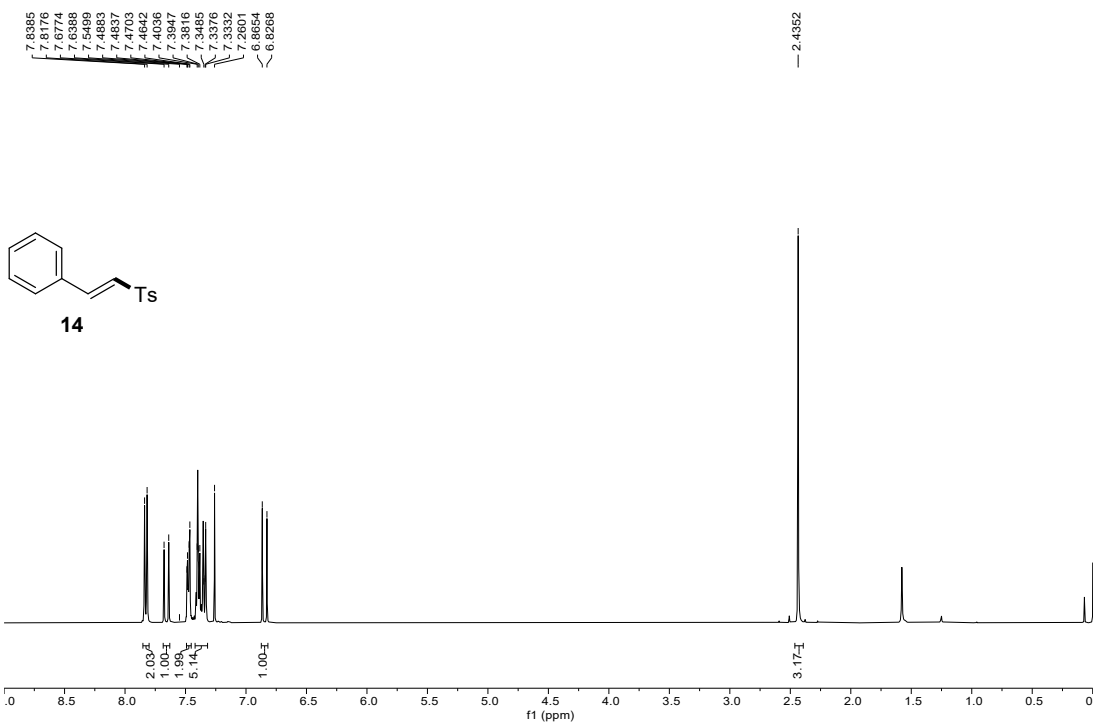
^{1}H NMR ($CDCl_3$, 500 MHz) of **12**



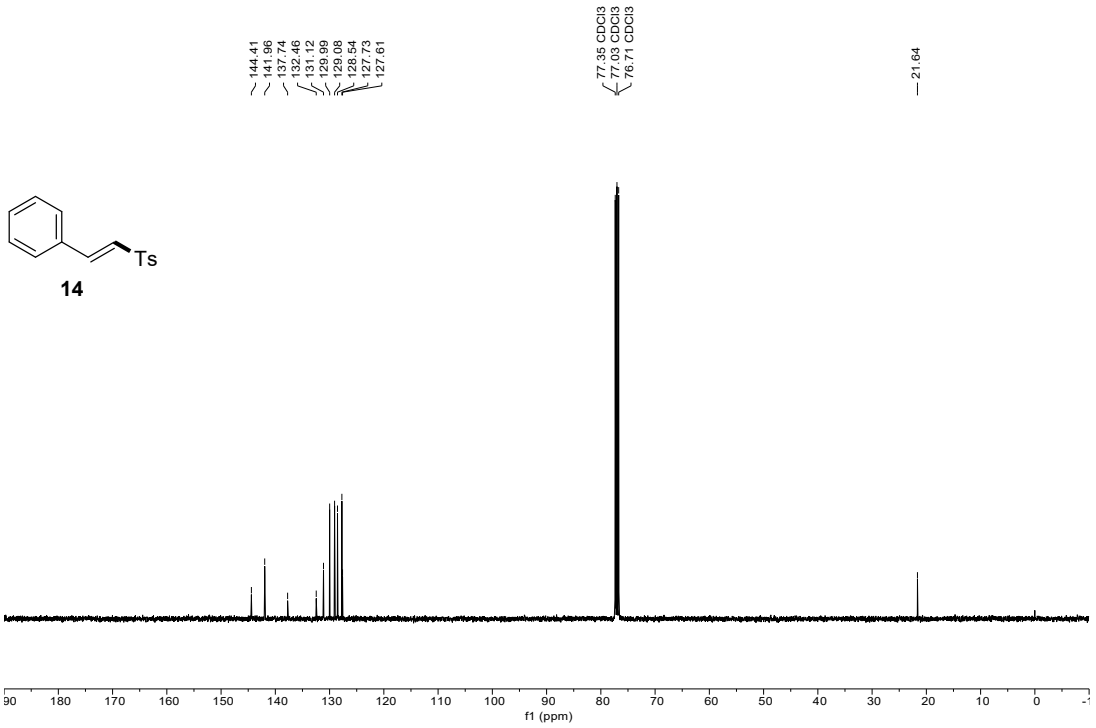
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **12**



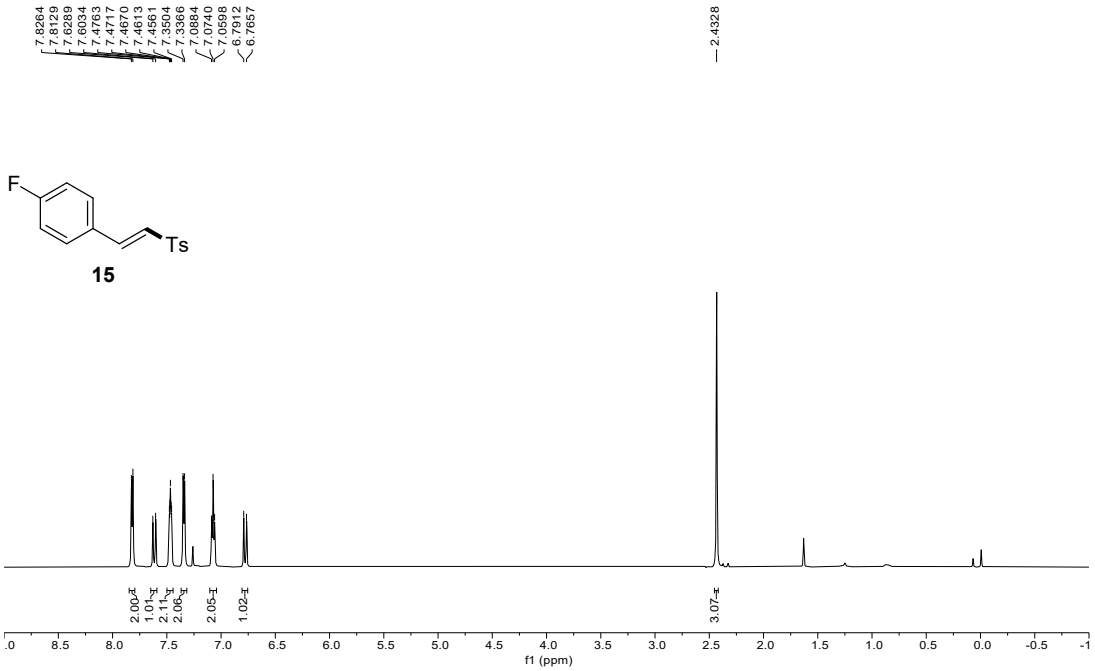
^{1}H NMR ($CDCl_3$, 400 MHz) of **14**



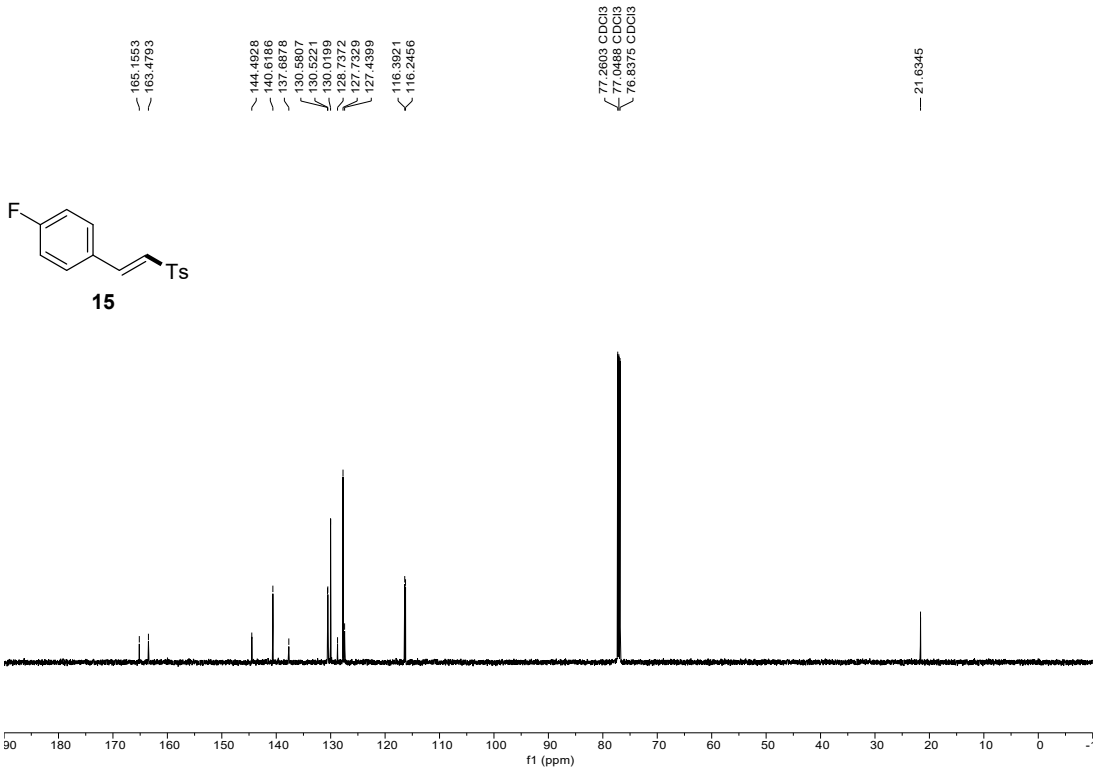
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **14**



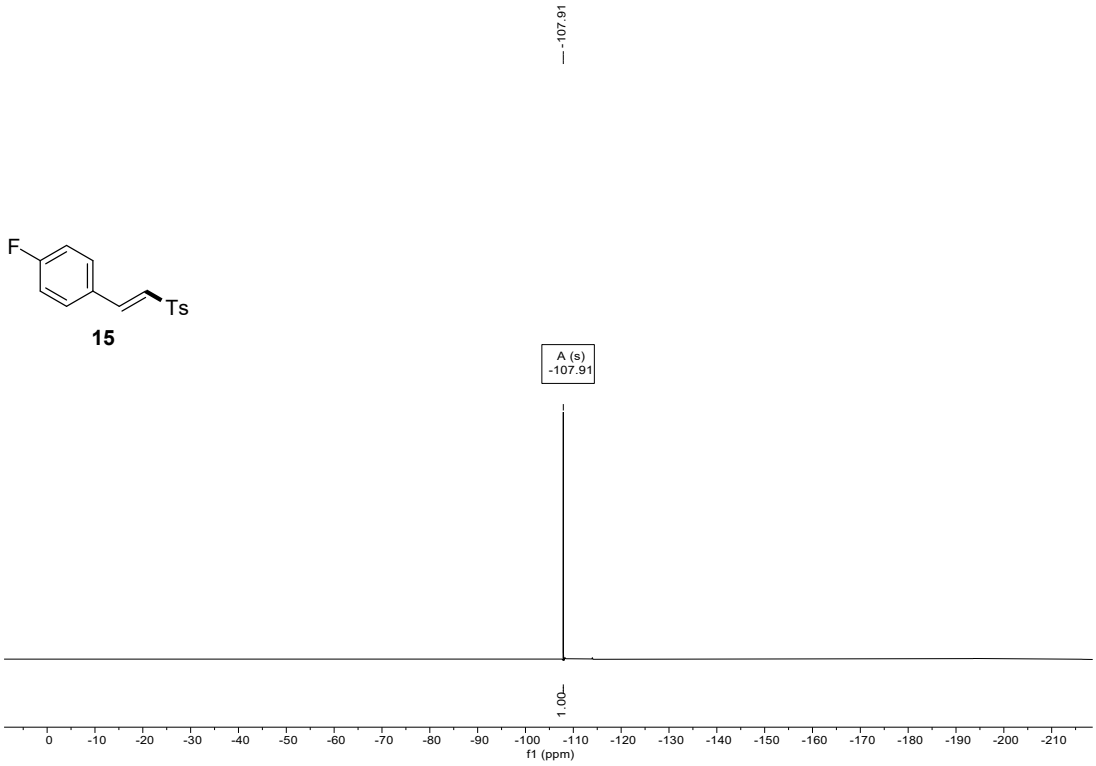
^{1}H NMR ($CDCl_3$, 600 MHz) of **15**



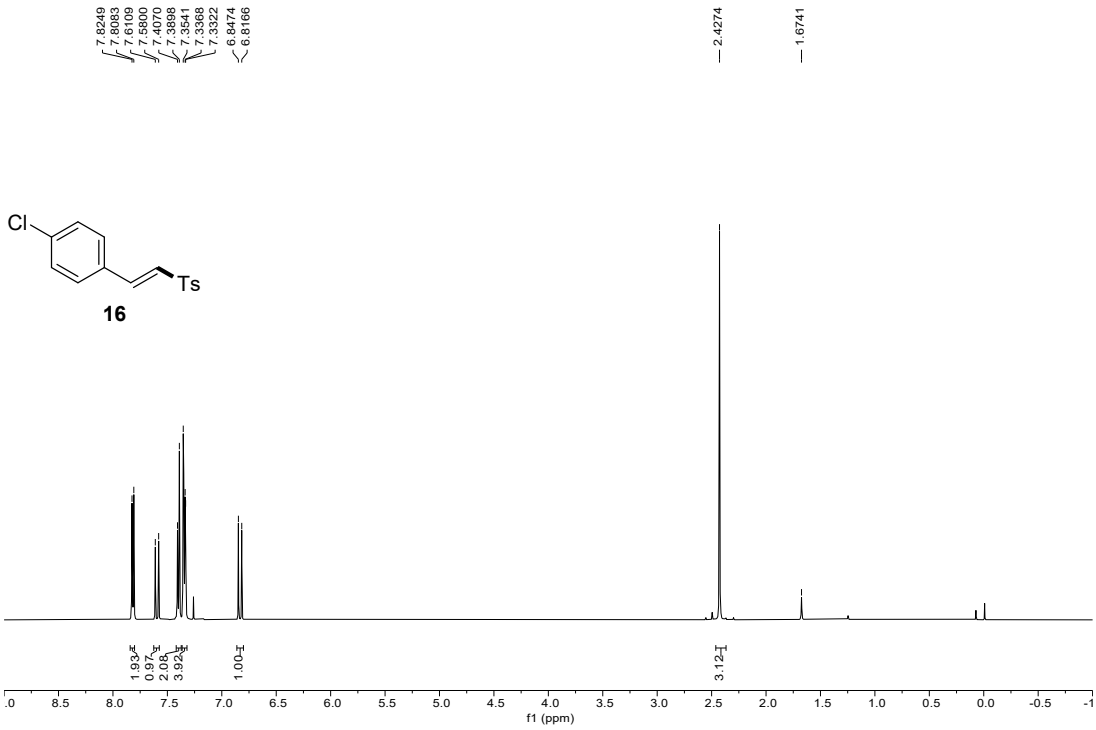
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) of **15**



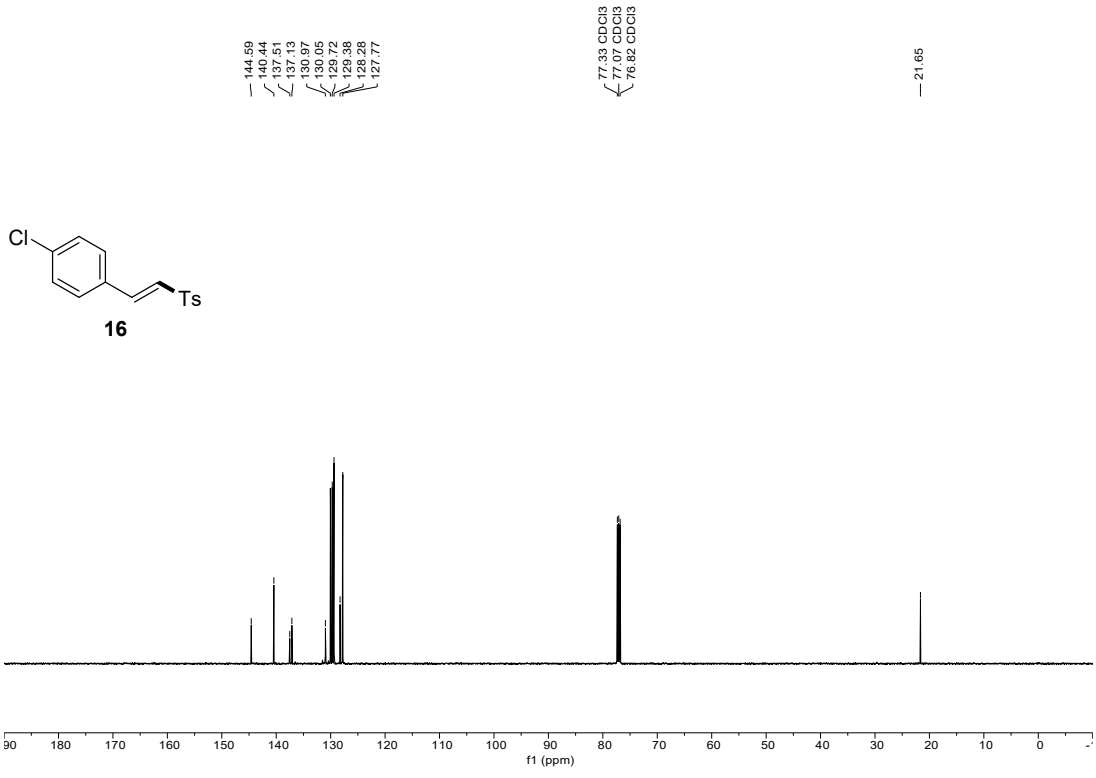
^{19}F NMR (565 MHz, $CDCl_3$) of **15**



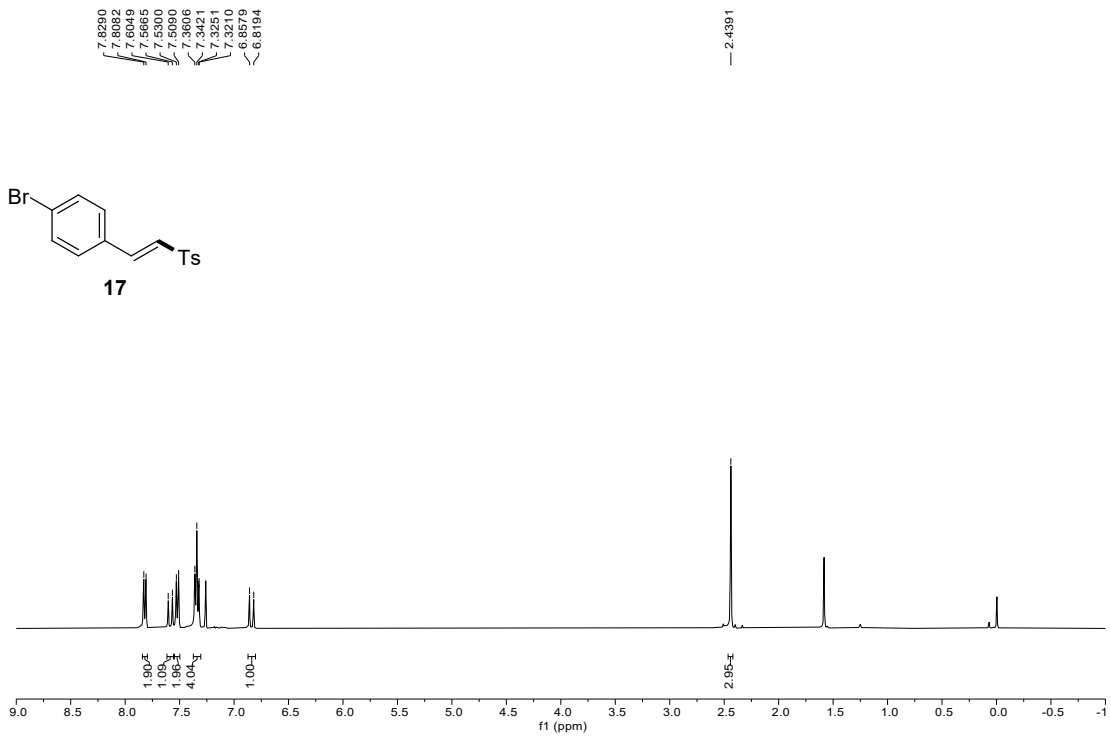
^{1}H NMR ($CDCl_3$, 500 MHz) of **16**



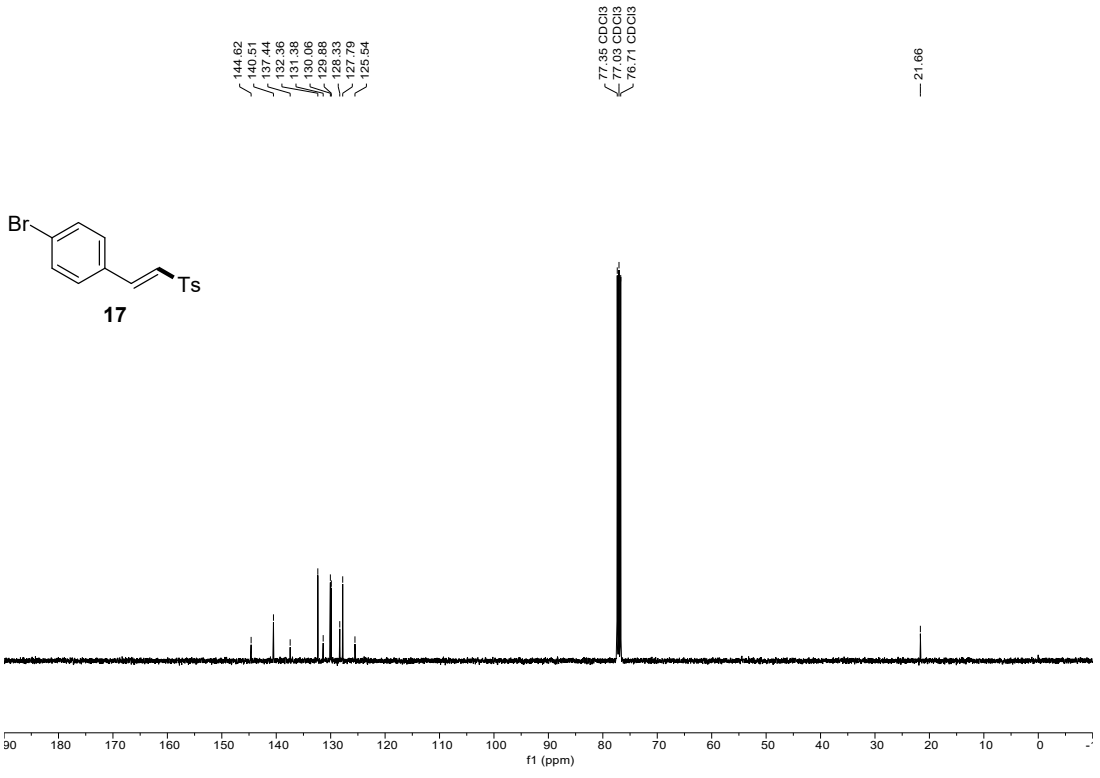
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **16**



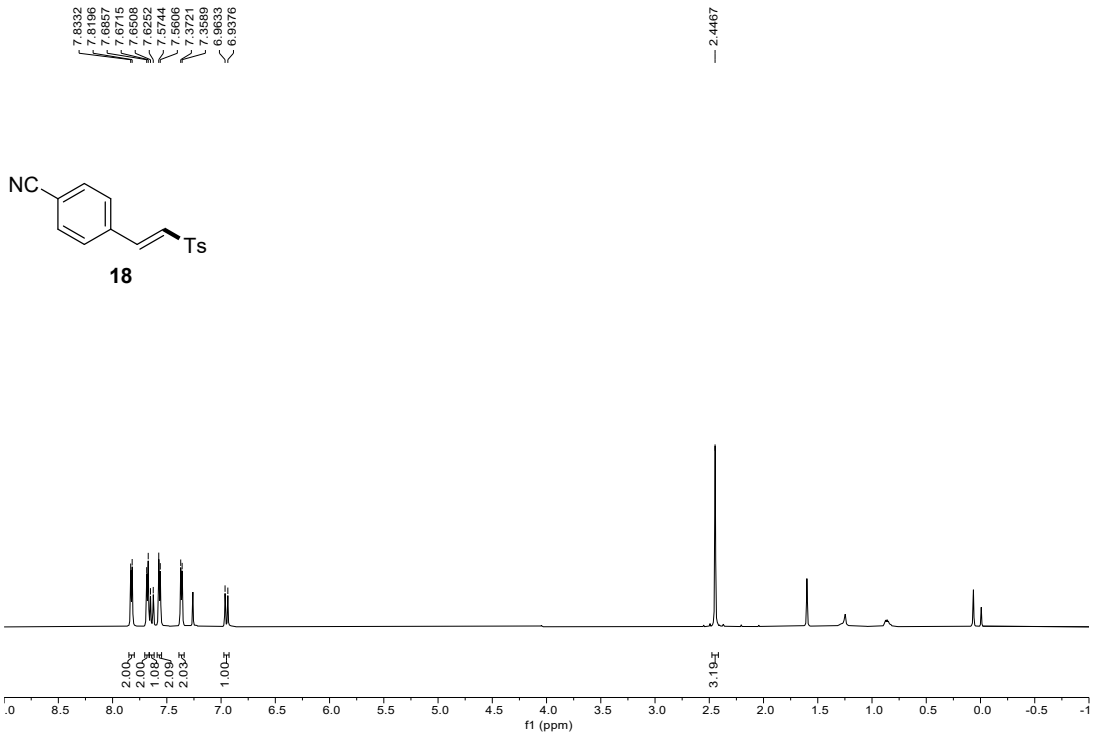
^{1}H NMR ($CDCl_3$, 400 MHz) of **17**



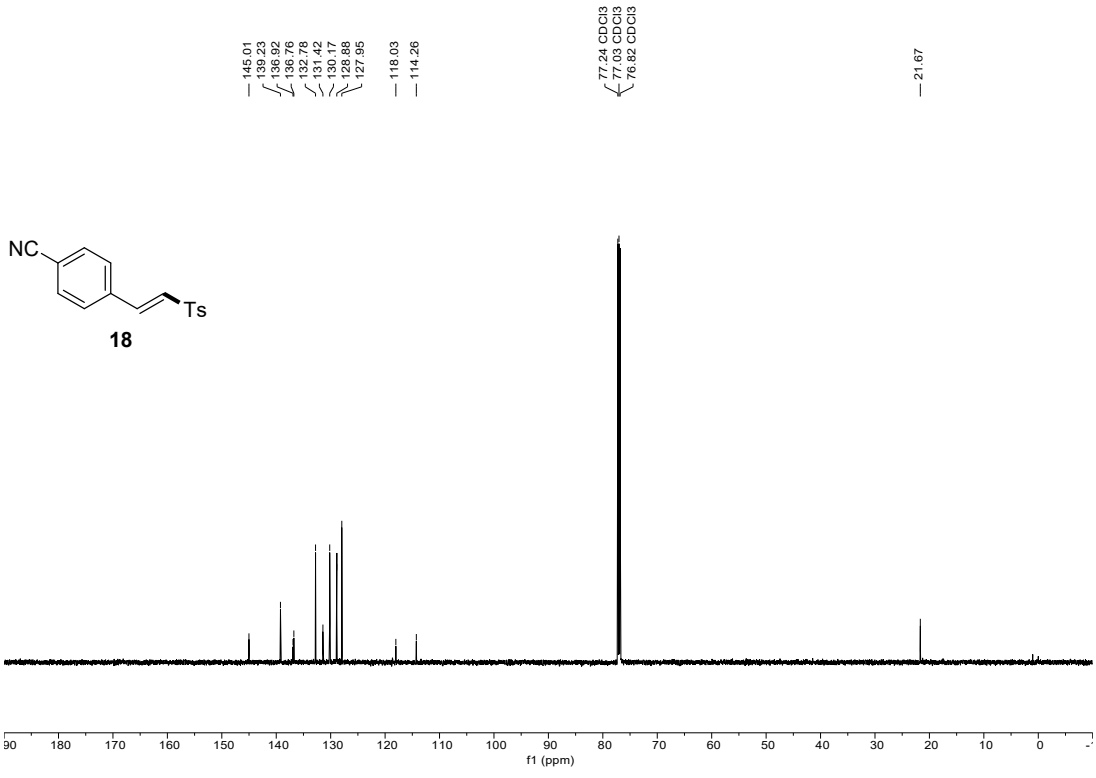
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **17**



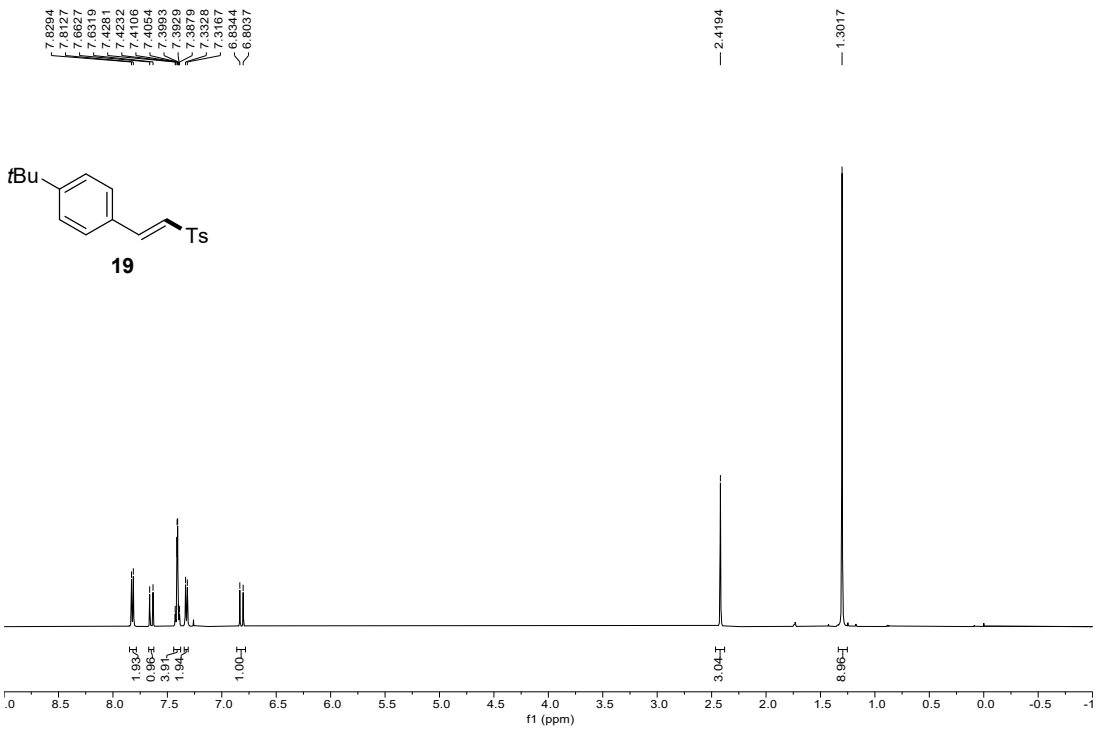
^{1}H NMR ($CDCl_3$, 600 MHz) of **18**



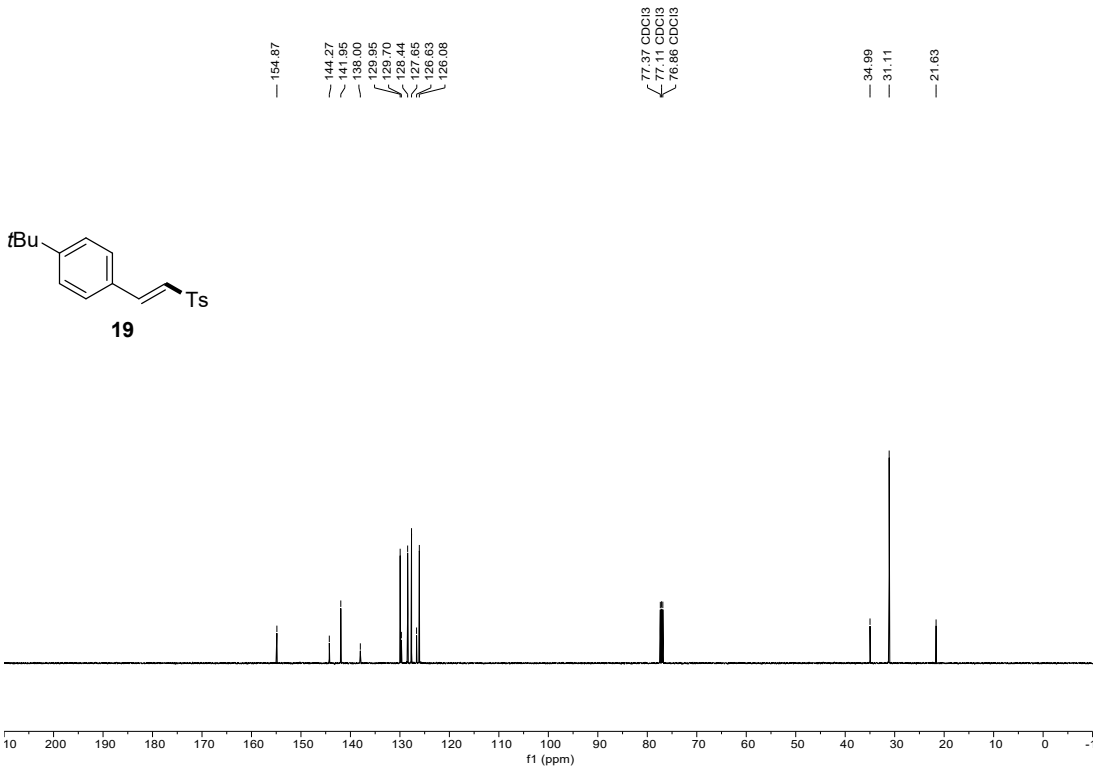
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) of **18**



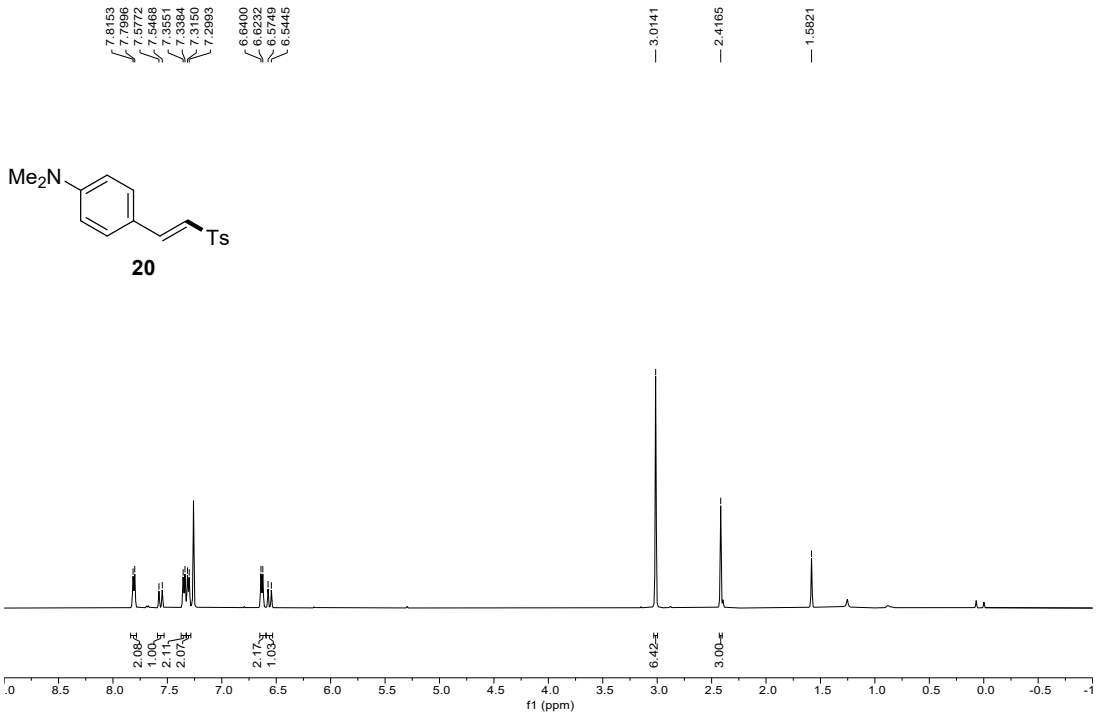
^{1}H NMR ($CDCl_3$, 500 MHz) of **19**



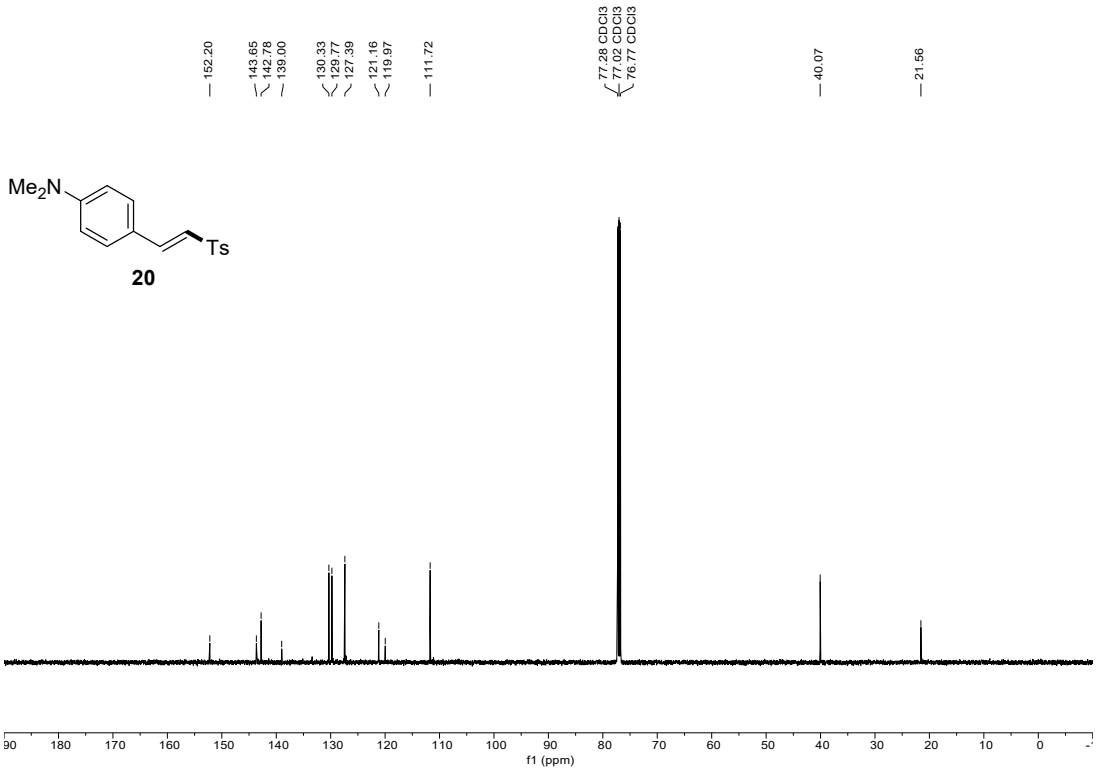
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **19**



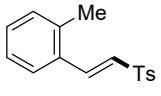
^{1}H NMR ($CDCl_3$, 500 MHz) of **20**



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **20**



^{1}H NMR ($CDCl_3$, 500 MHz) of **21**



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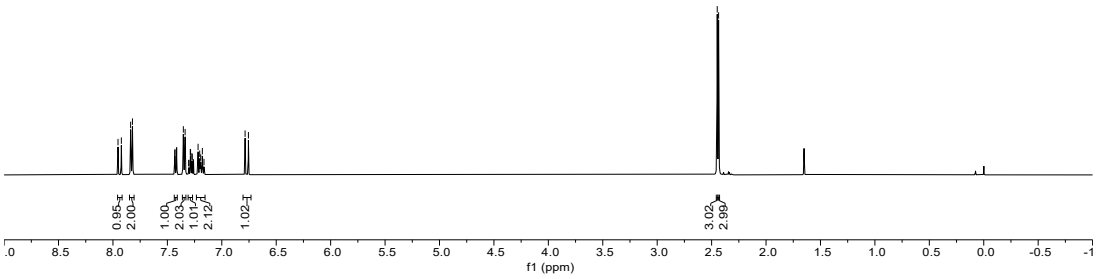
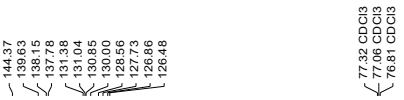
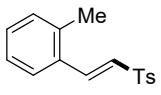


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125MHz) of **21**





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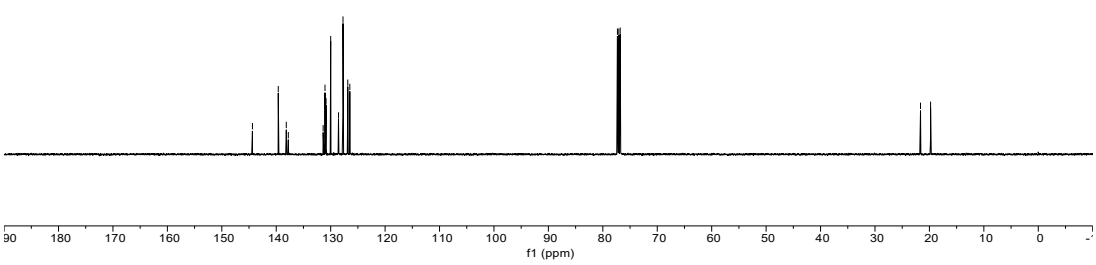
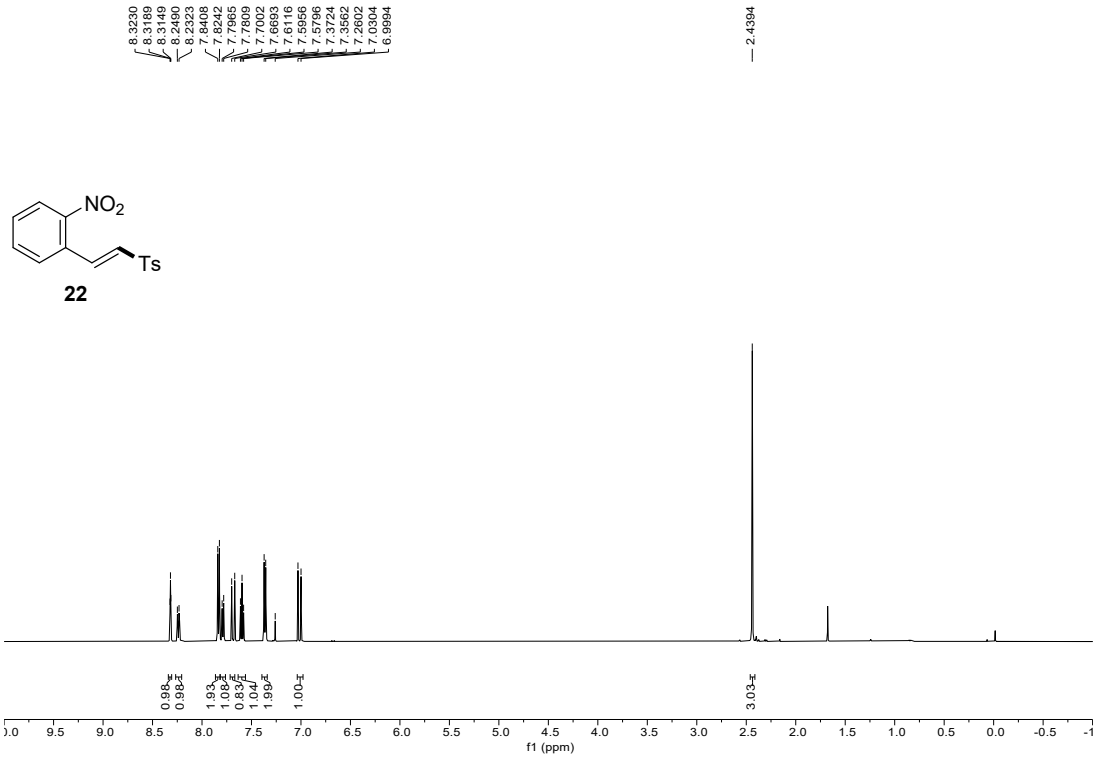
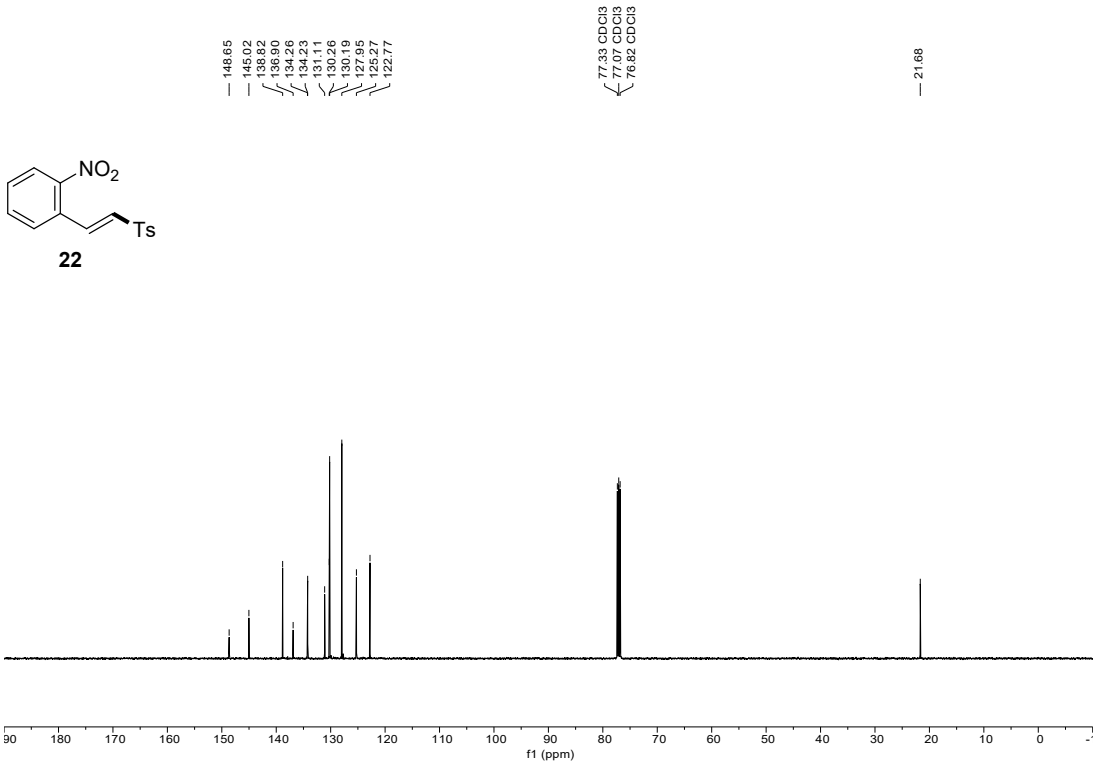


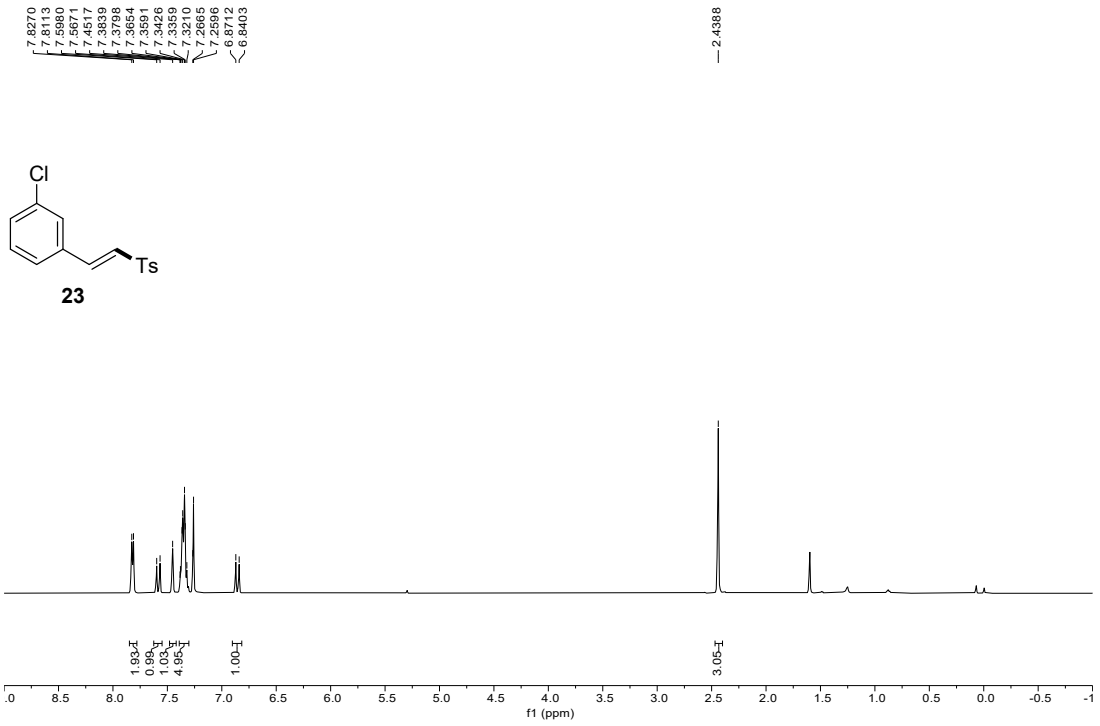
^{1}H NMR ($CDCl_3$, 500 MHz) of **22**



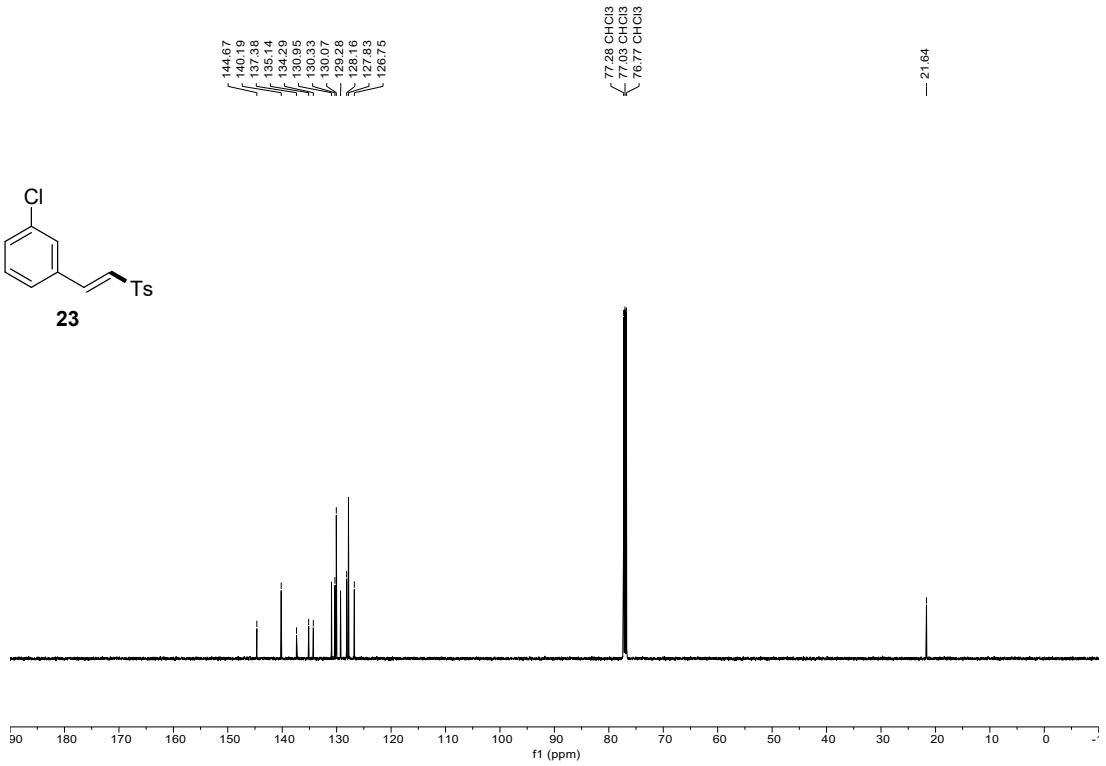
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **22**



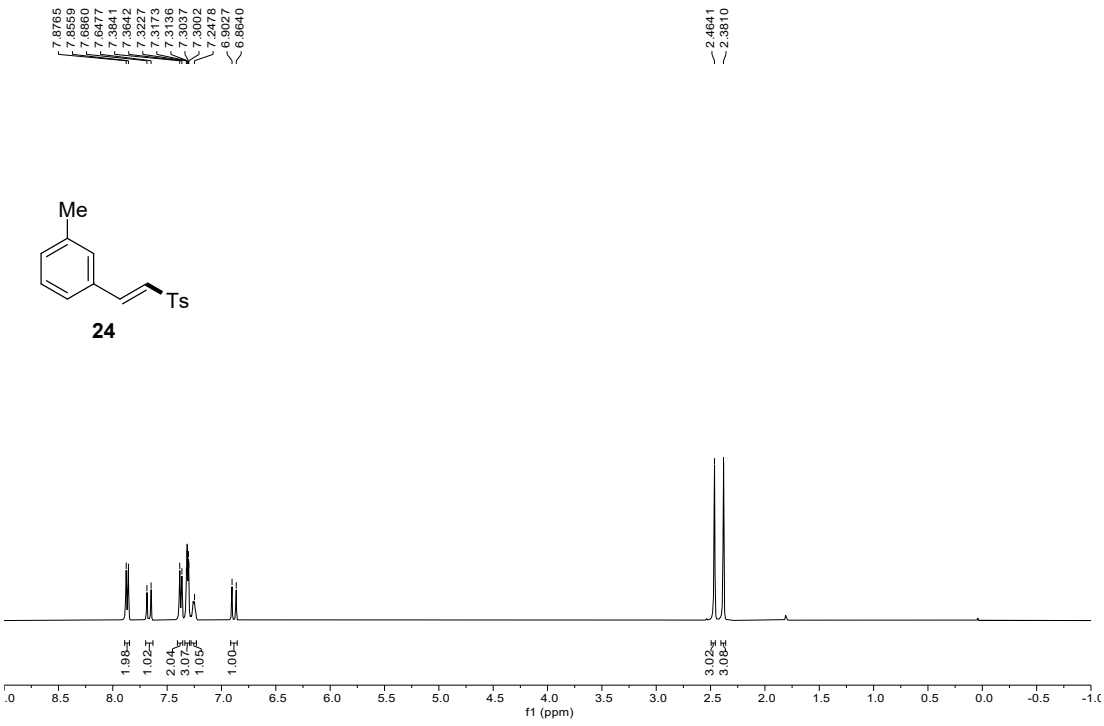
^{1}H NMR ($CDCl_3$, 500 MHz) of **23**



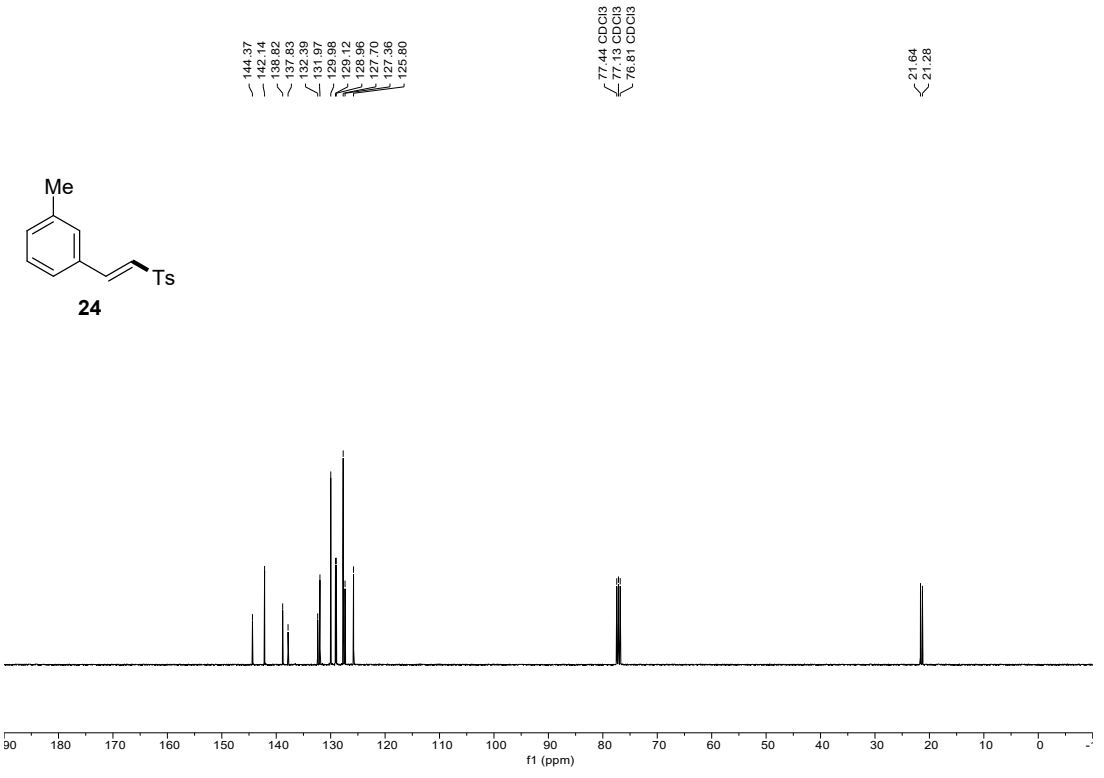
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **23**



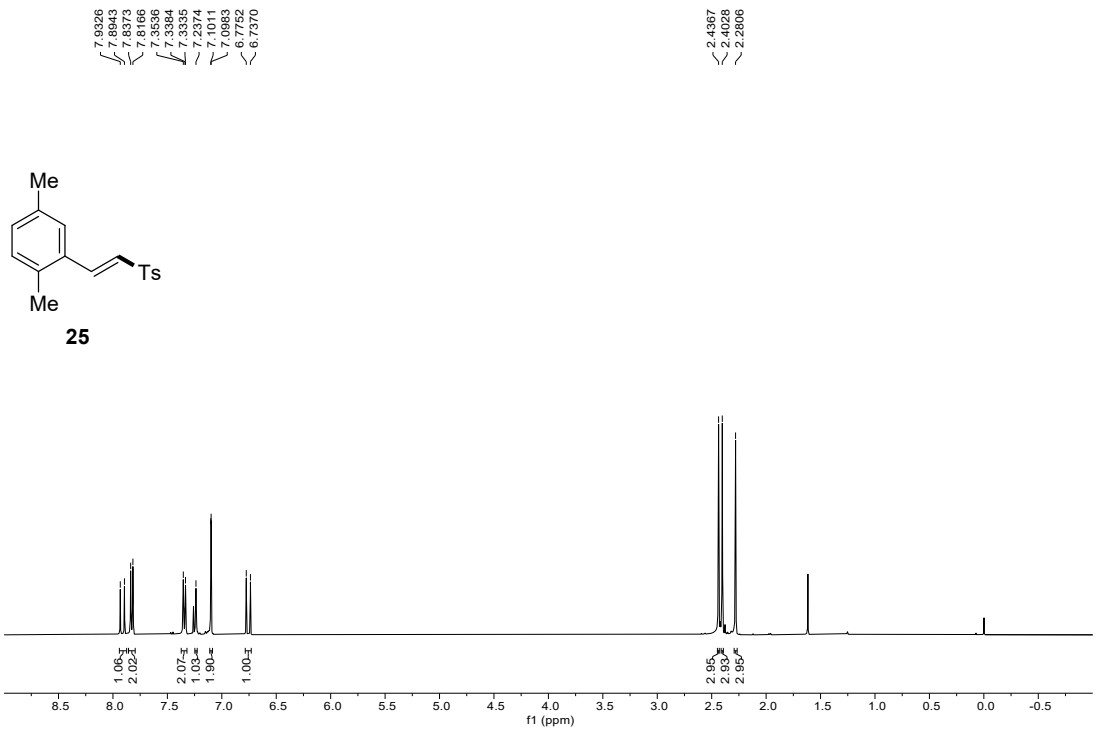
^{1}H NMR ($CDCl_3$, 400 MHz) of **24**



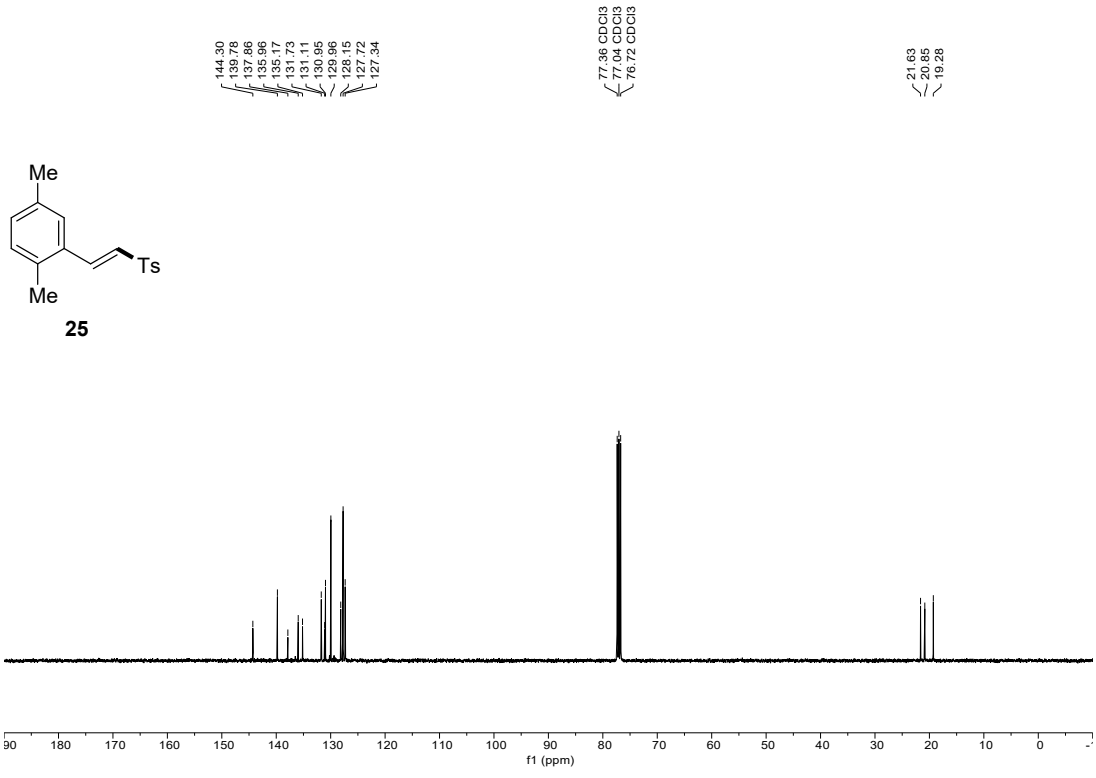
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **24**



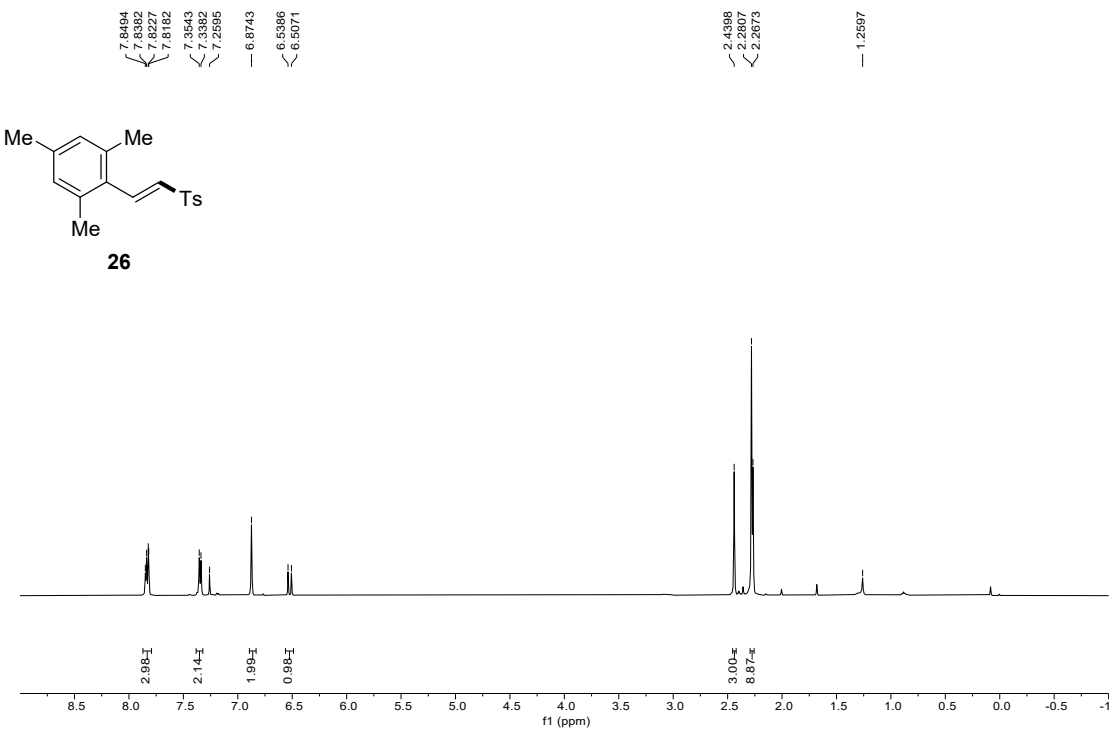
^{1}H NMR ($CDCl_3$, 400 MHz) of **25**



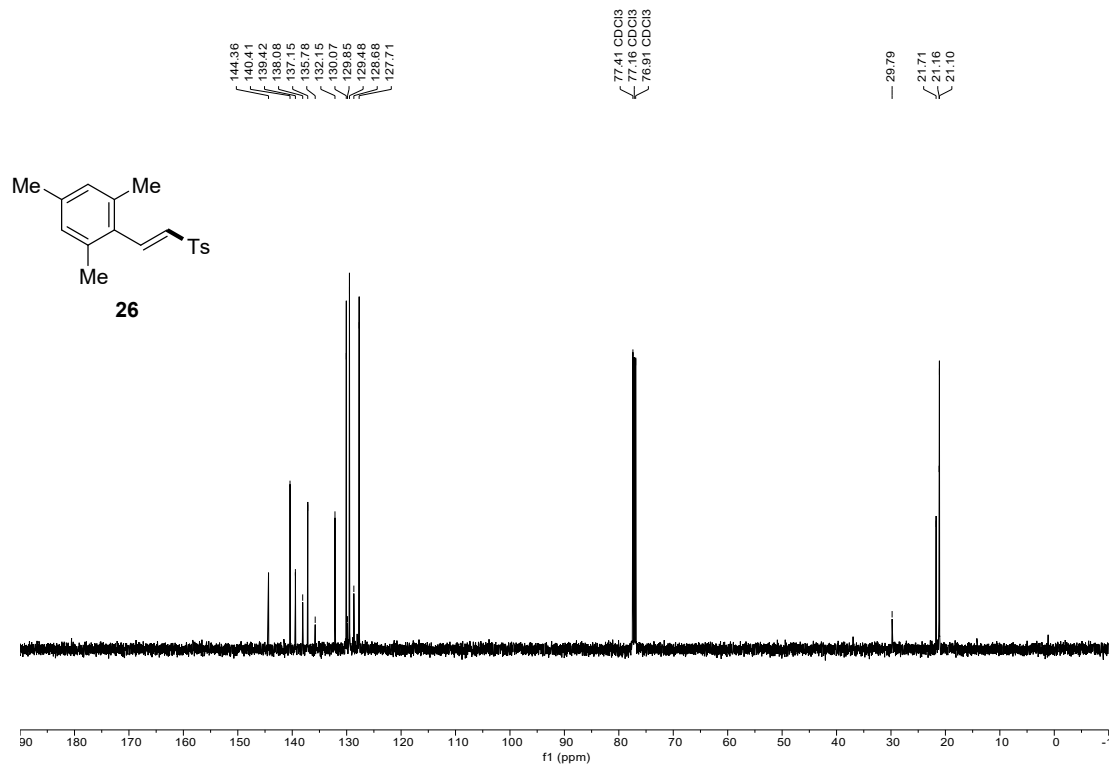
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **25**



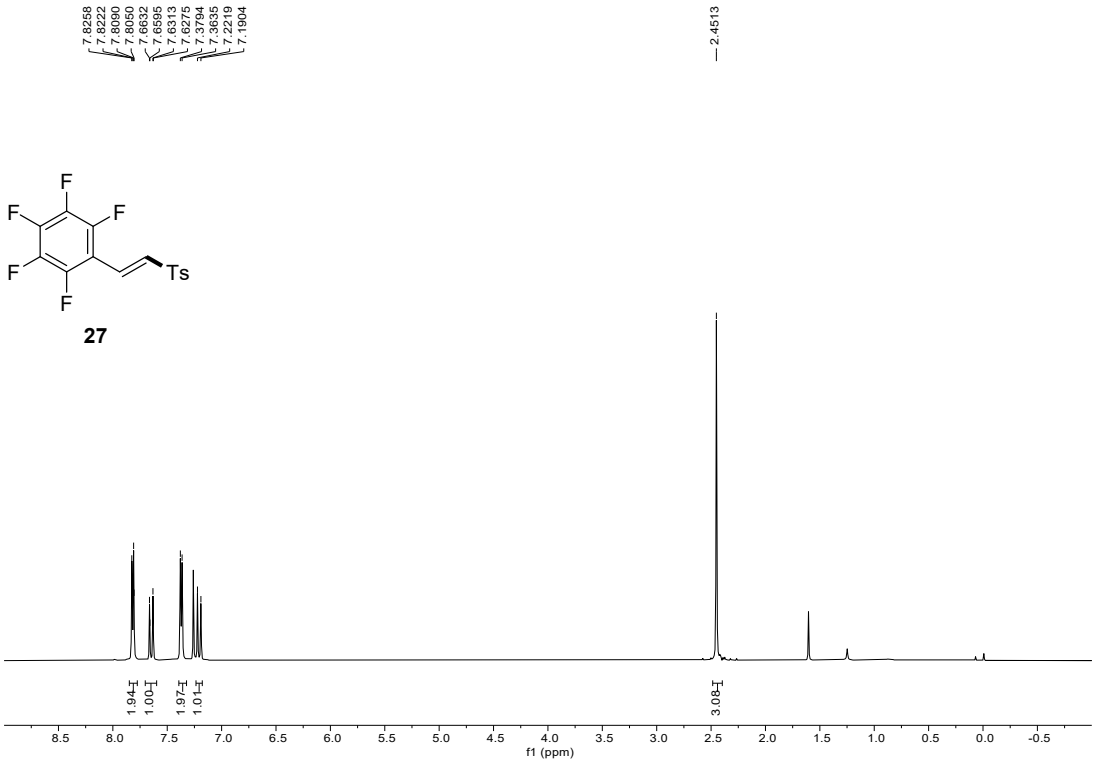
^{1}H NMR ($CDCl_3$, 500 MHz) of **26**



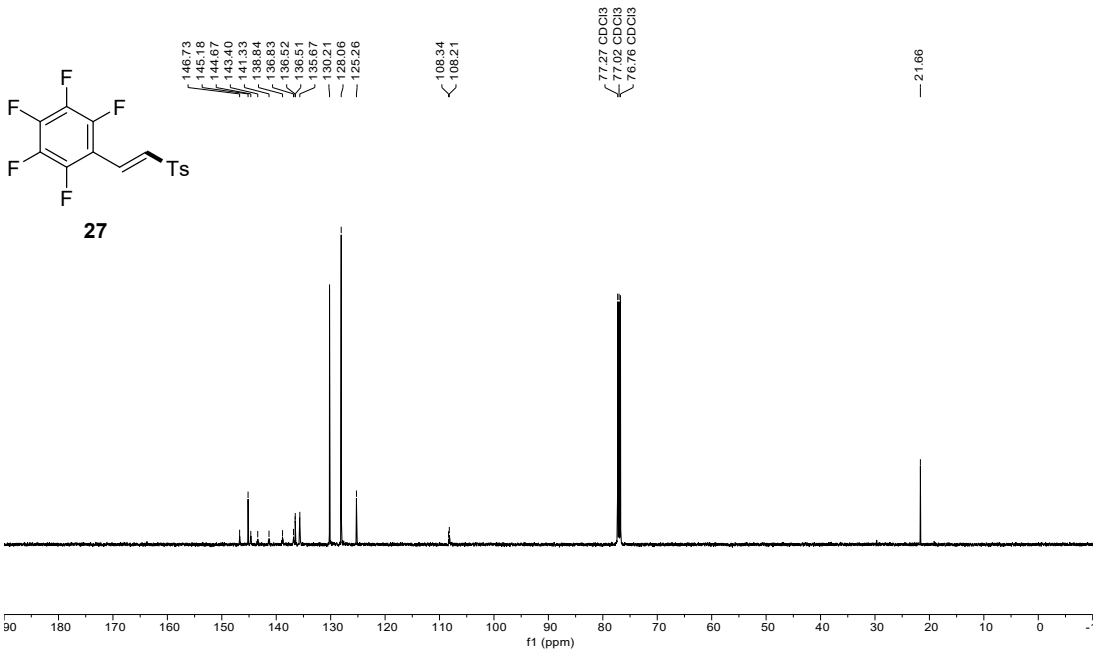
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **26**



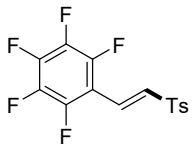
^{1}H NMR ($CDCl_3$, 500 MHz) of **27**



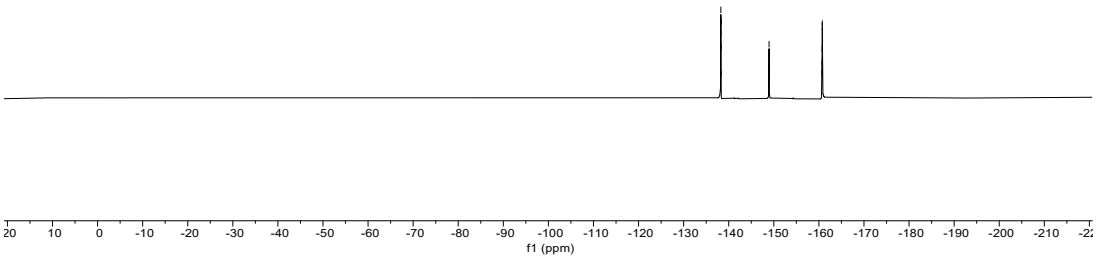
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) of **27**



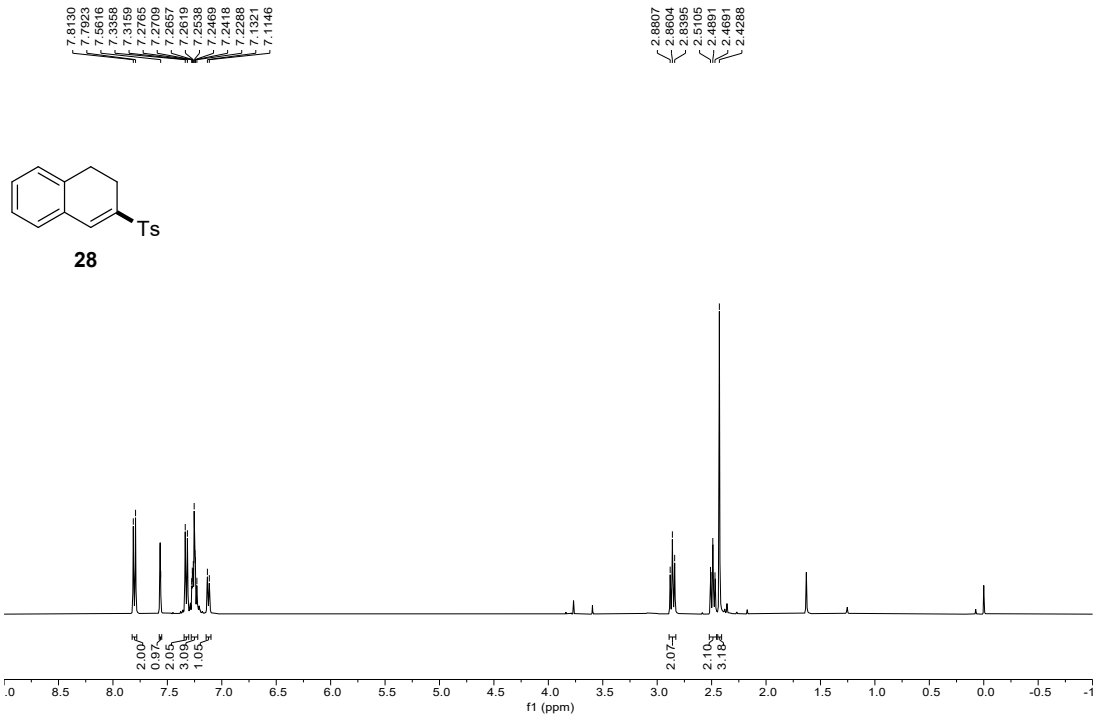
^{19}F NMR ($CDCl_3$, 471 MHz) of **27**



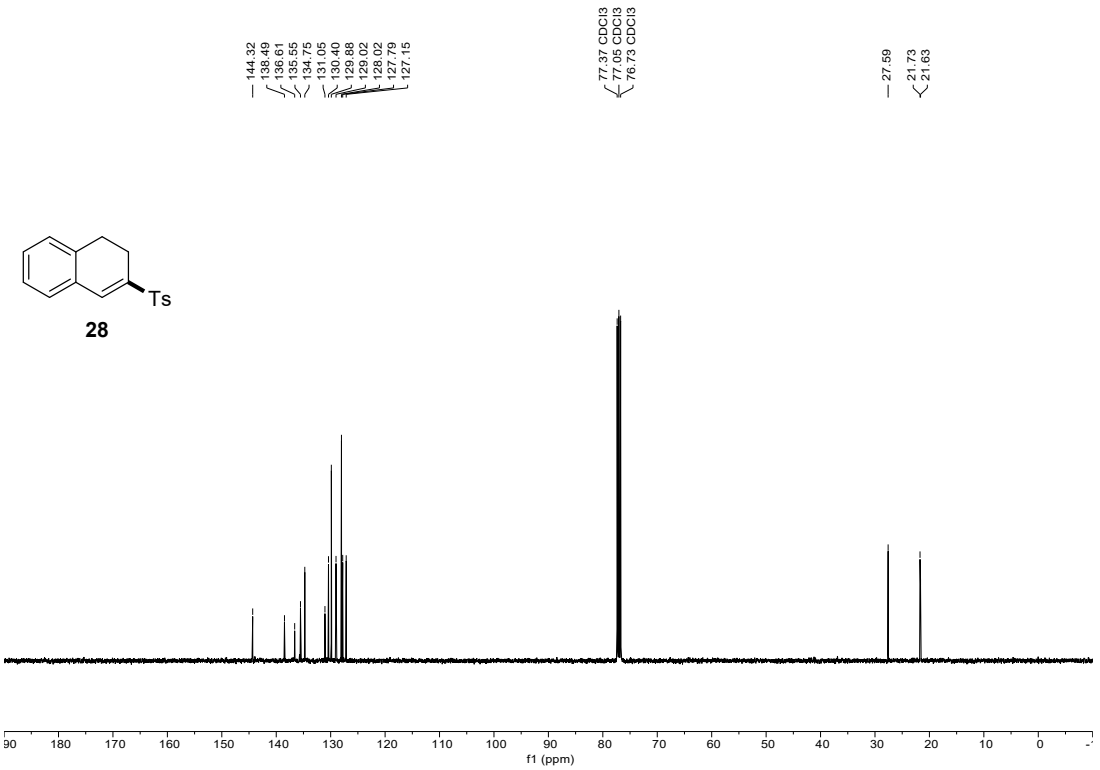
27



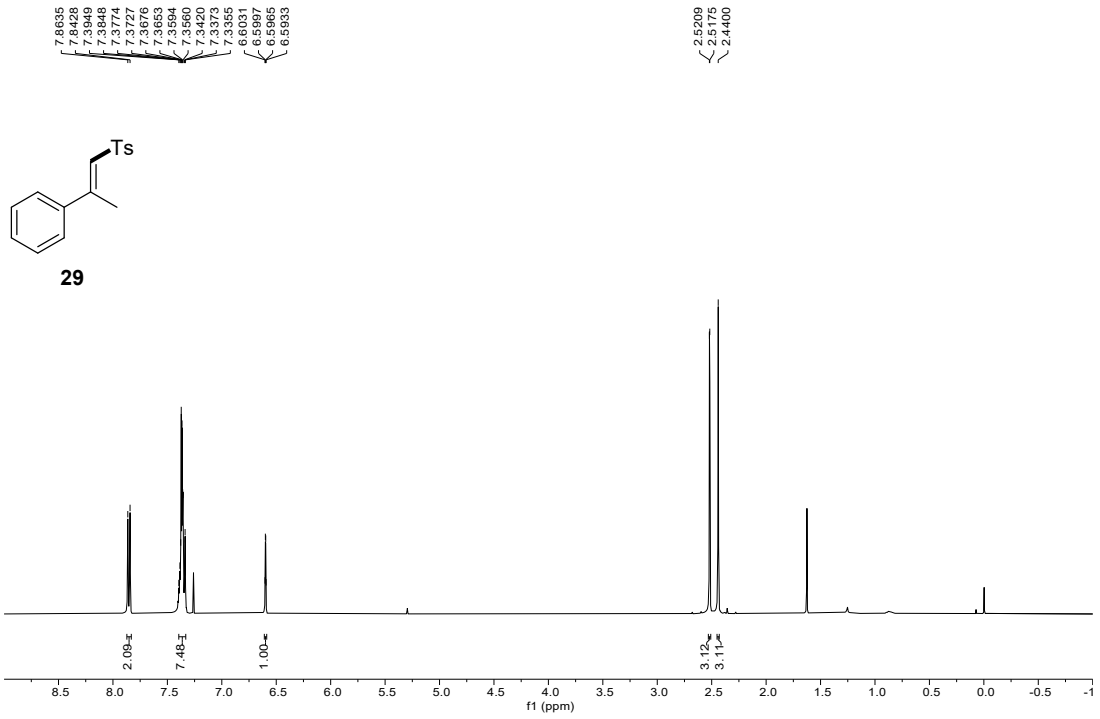
^{1}H NMR ($CDCl_3$, 400 MHz) of **28**



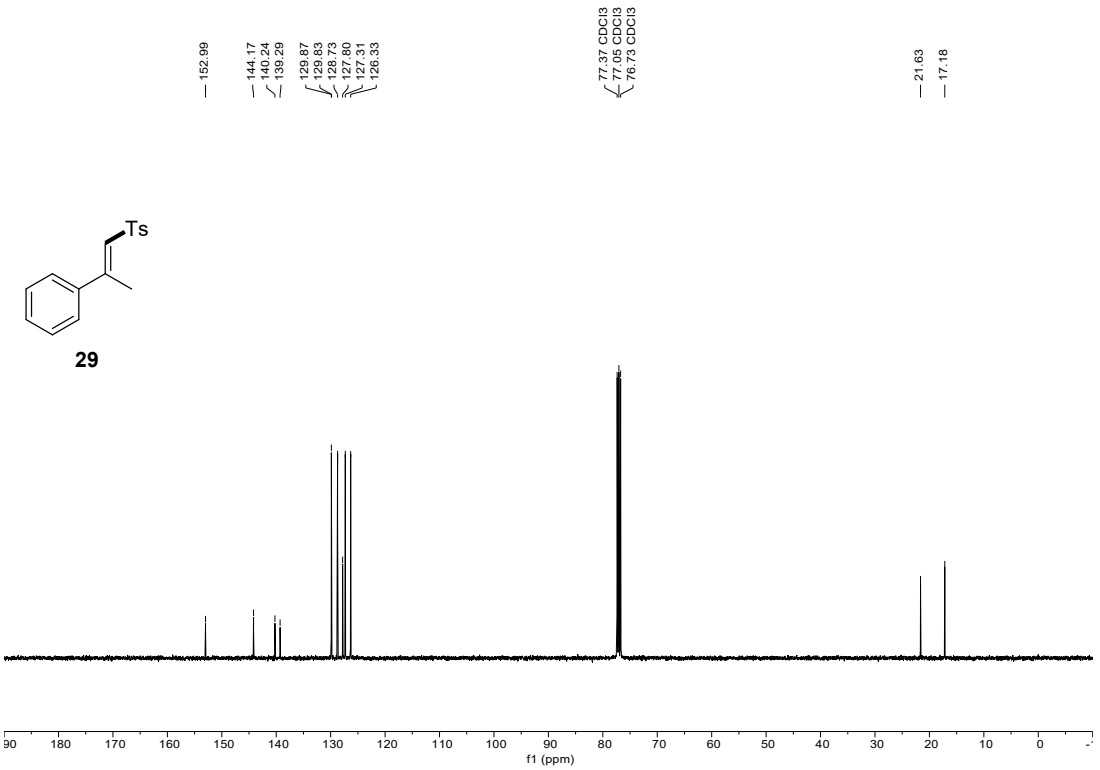
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **28**



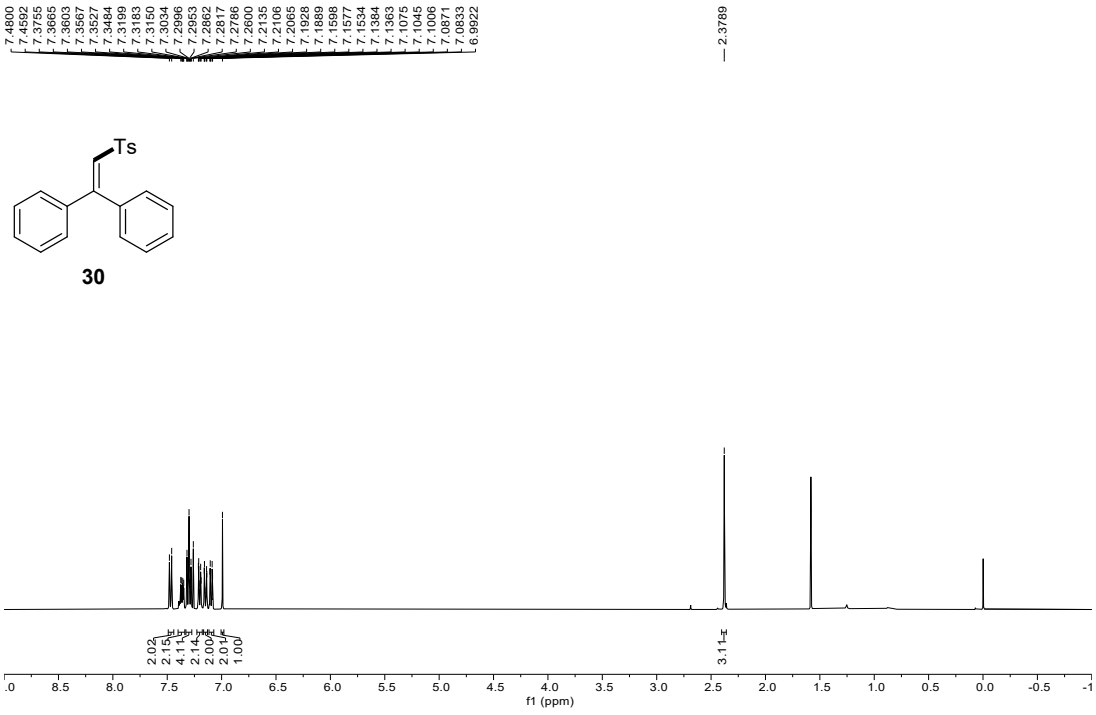
^{1}H NMR ($CDCl_3$, 400 MHz) of **29**



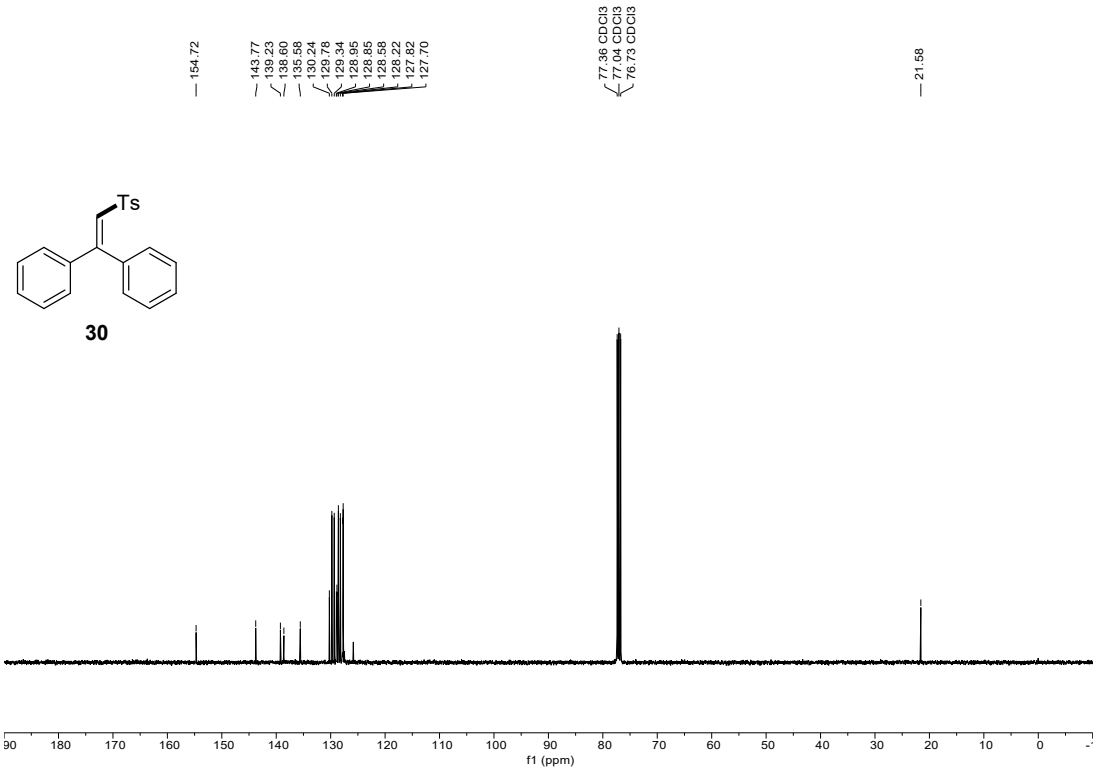
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **29**



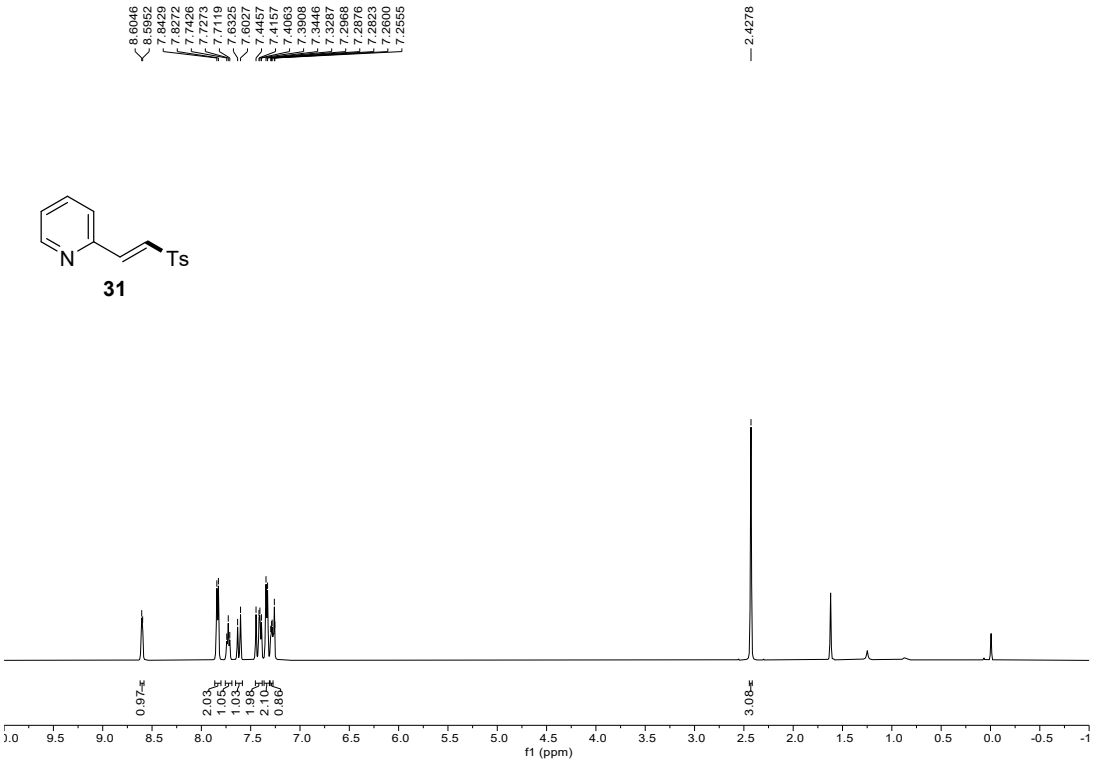
^{1}H NMR ($CDCl_3$, 400 MHz) of **30**



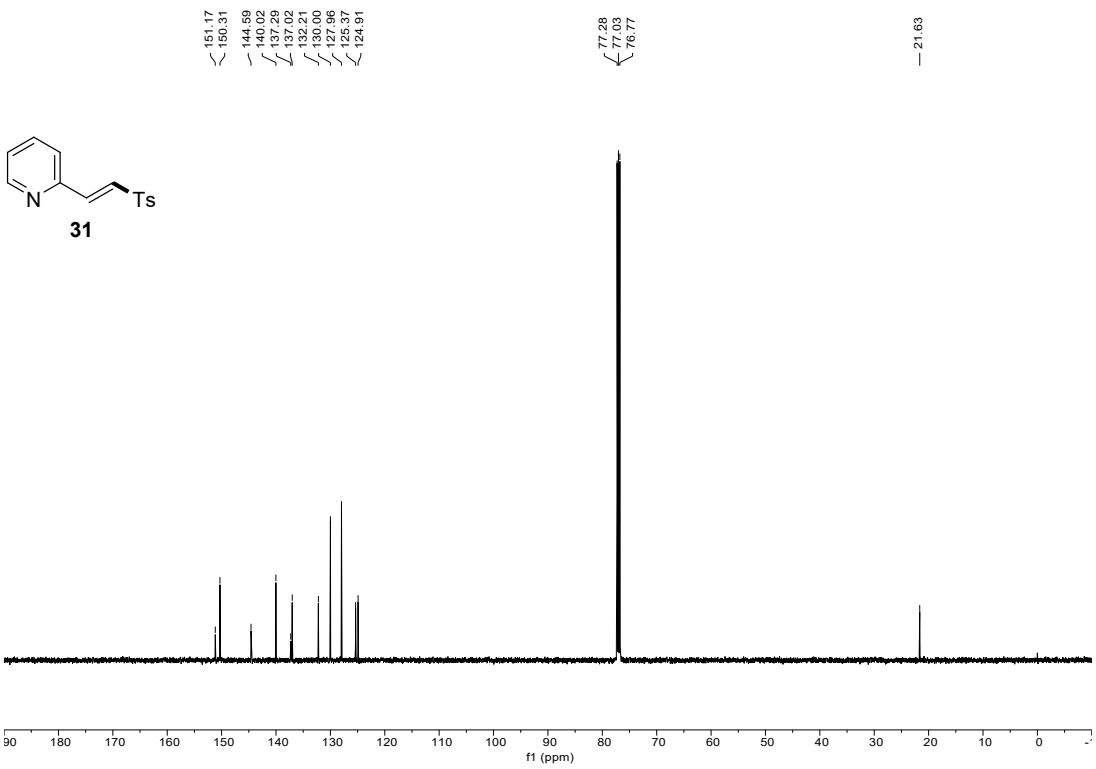
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **30**



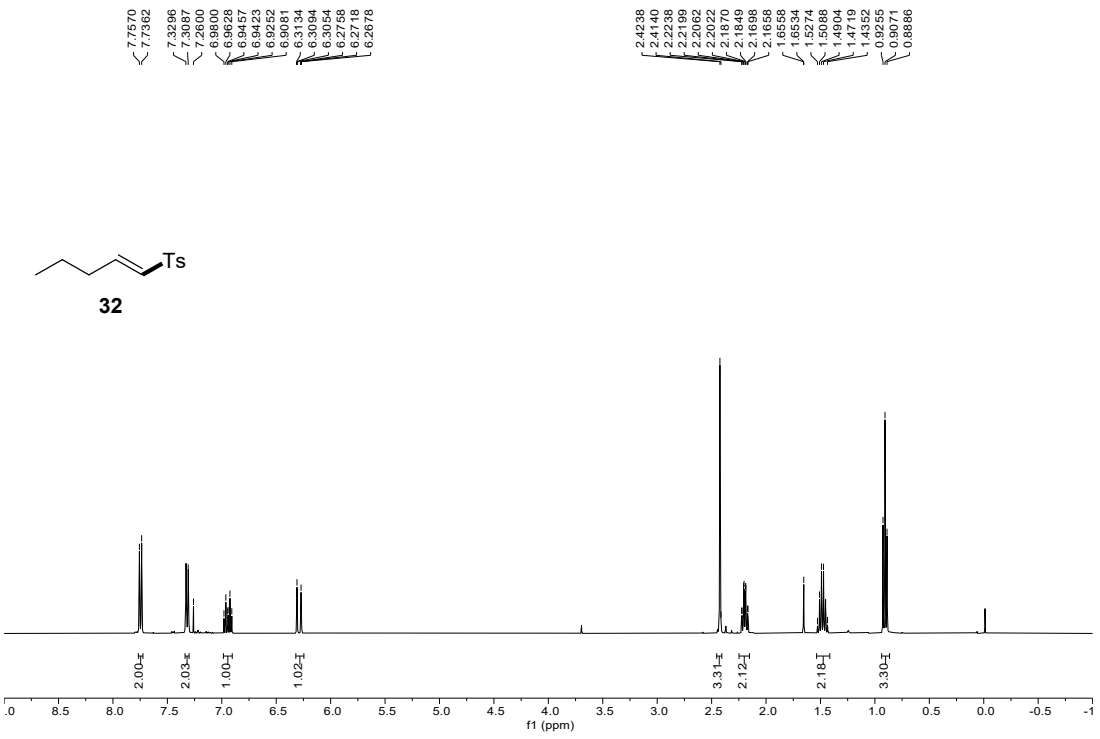
^{1}H NMR ($CDCl_3$, 500 MHz) of **31**



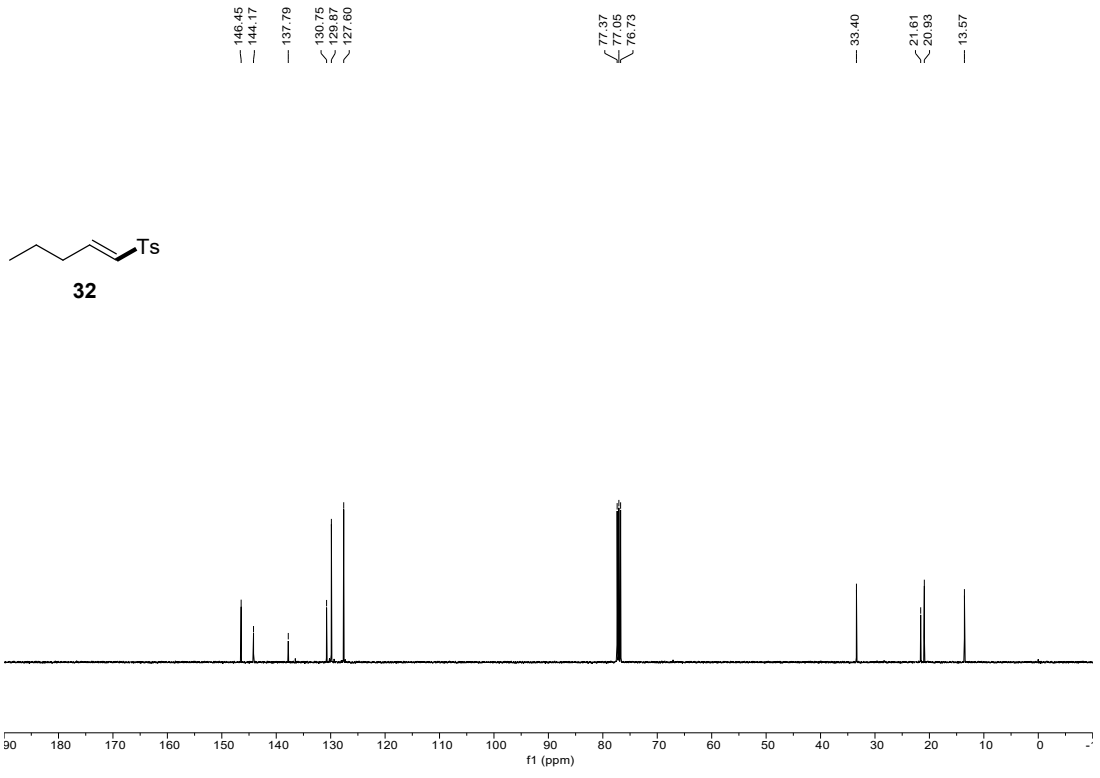
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) of **31**



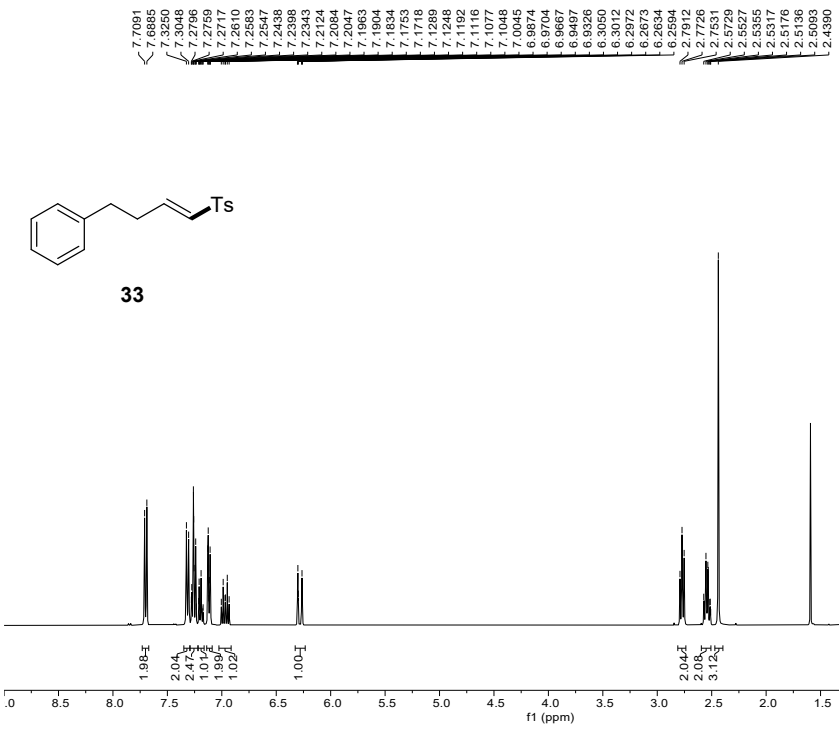
^{1}H NMR ($CDCl_3$, 400 MHz) of **32**



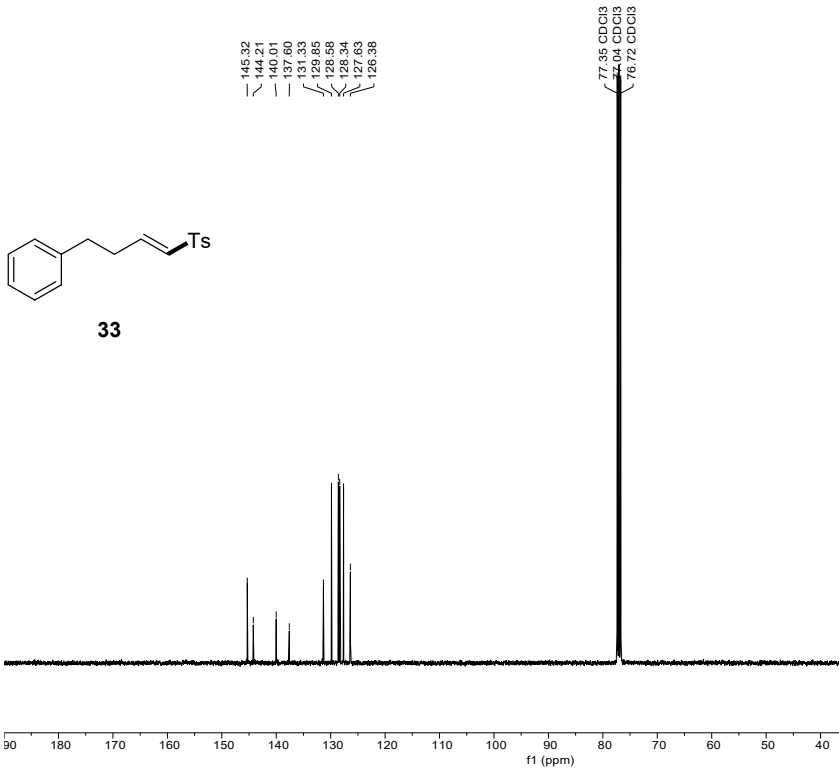
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **32**



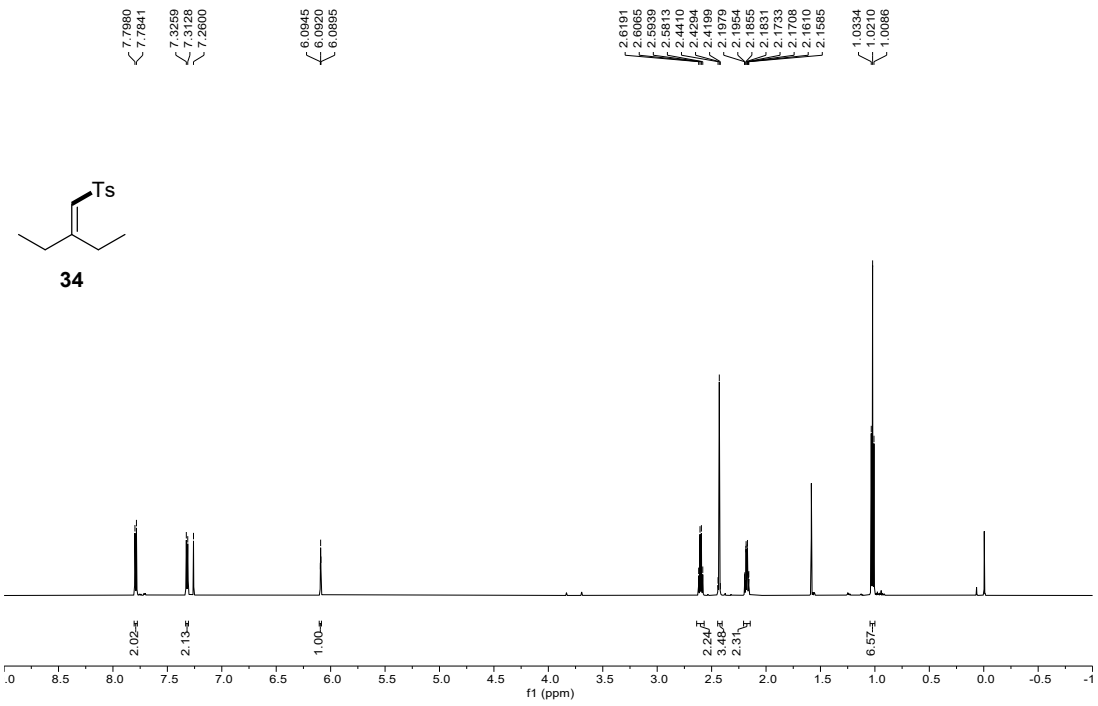
^{1}H NMR ($CDCl_3$, 400 MHz) of **33**



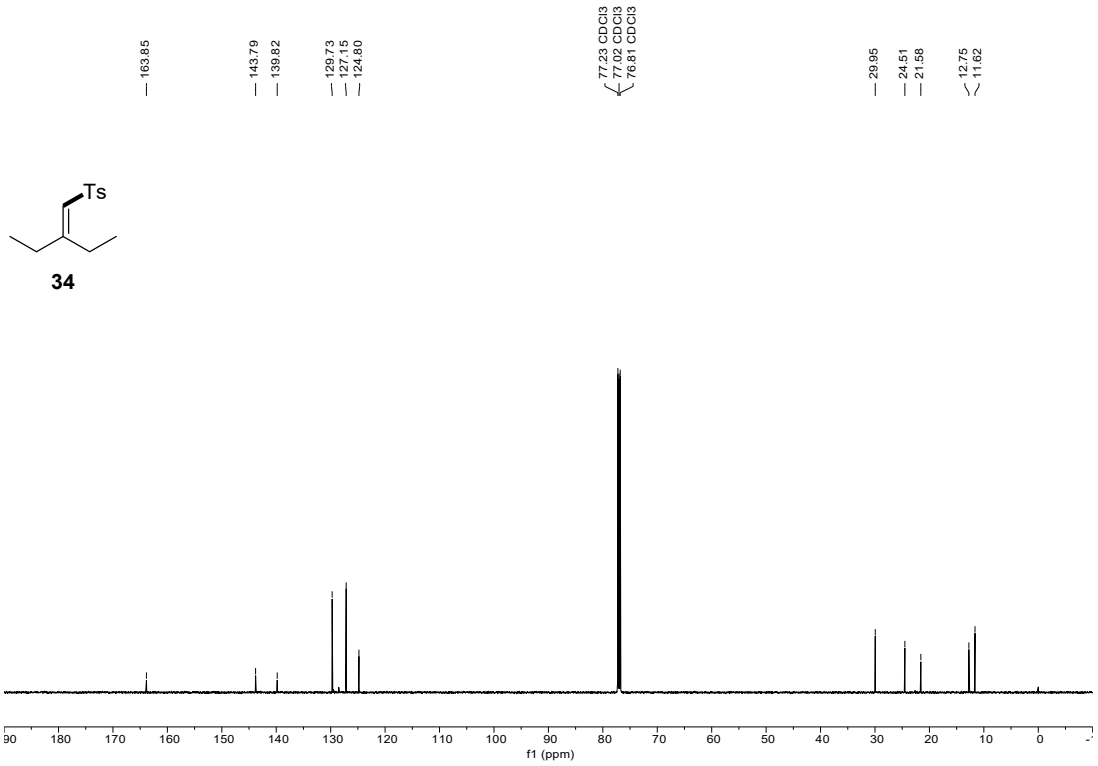
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **33**



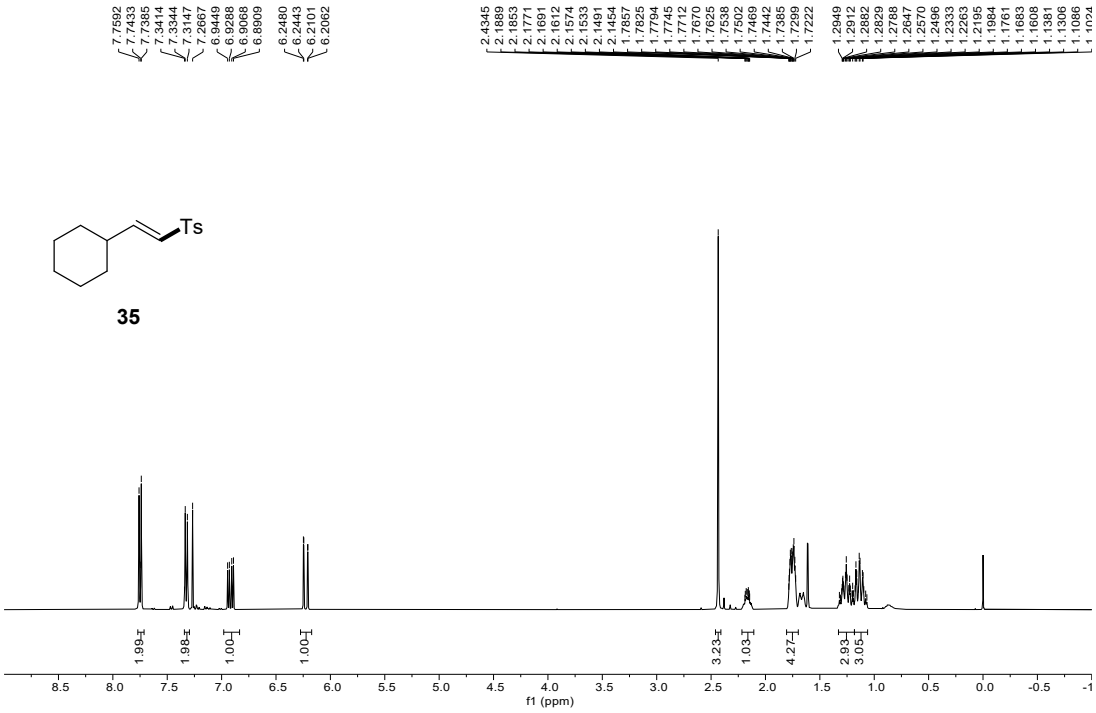
^{1}H NMR ($CDCl_3$, 600 MHz) of **34**



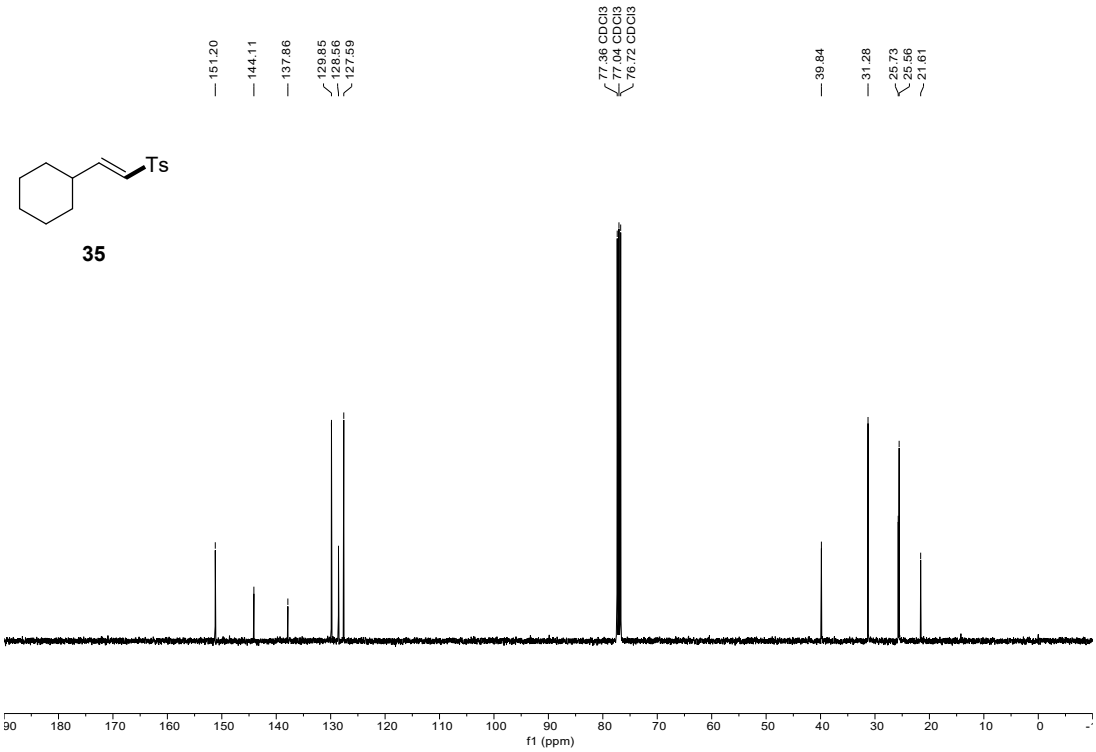
^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) of **34**



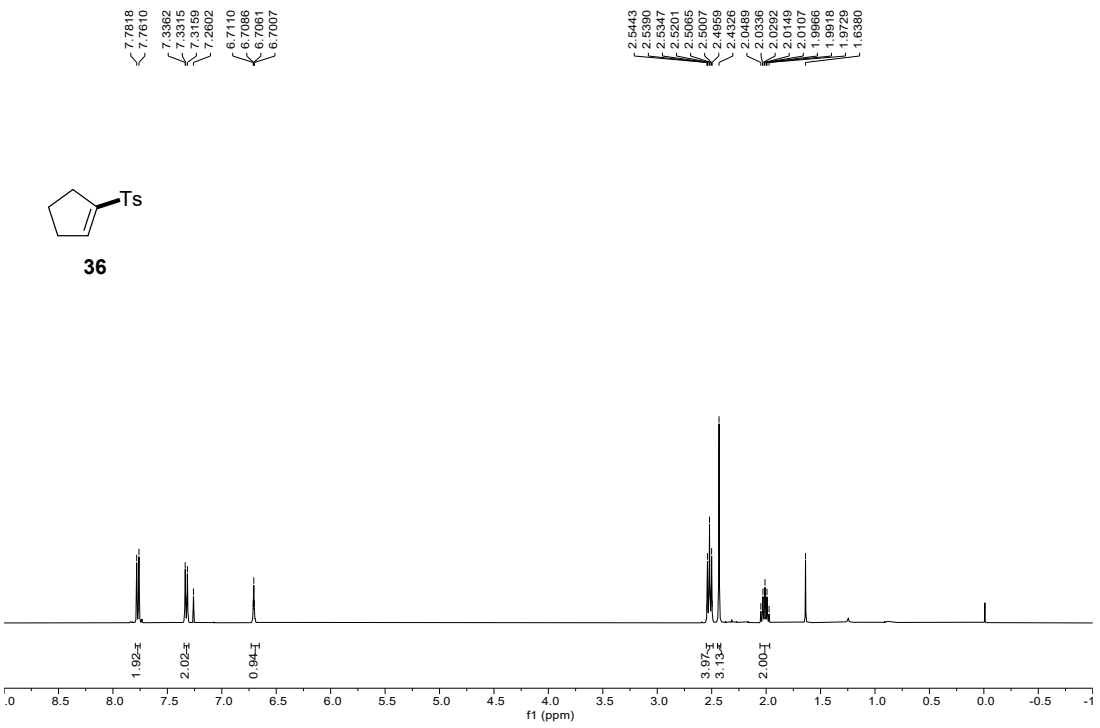
^{1}H NMR ($CDCl_3$, 400 MHz) of **35**



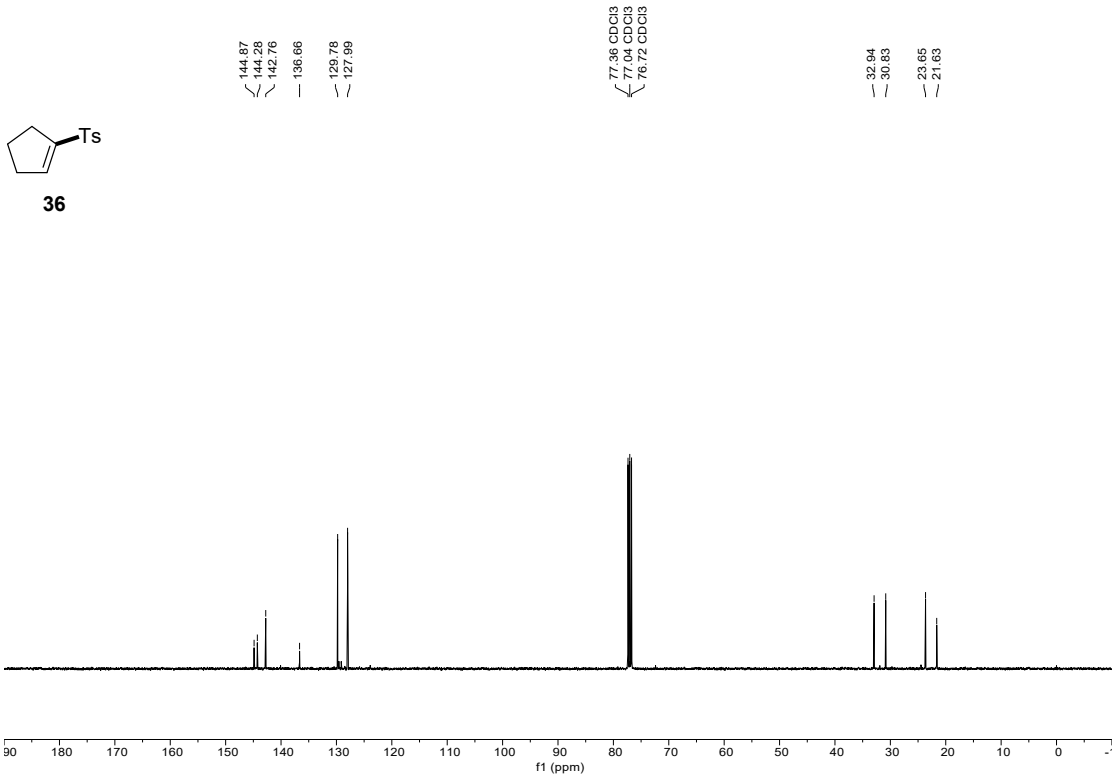
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **35**



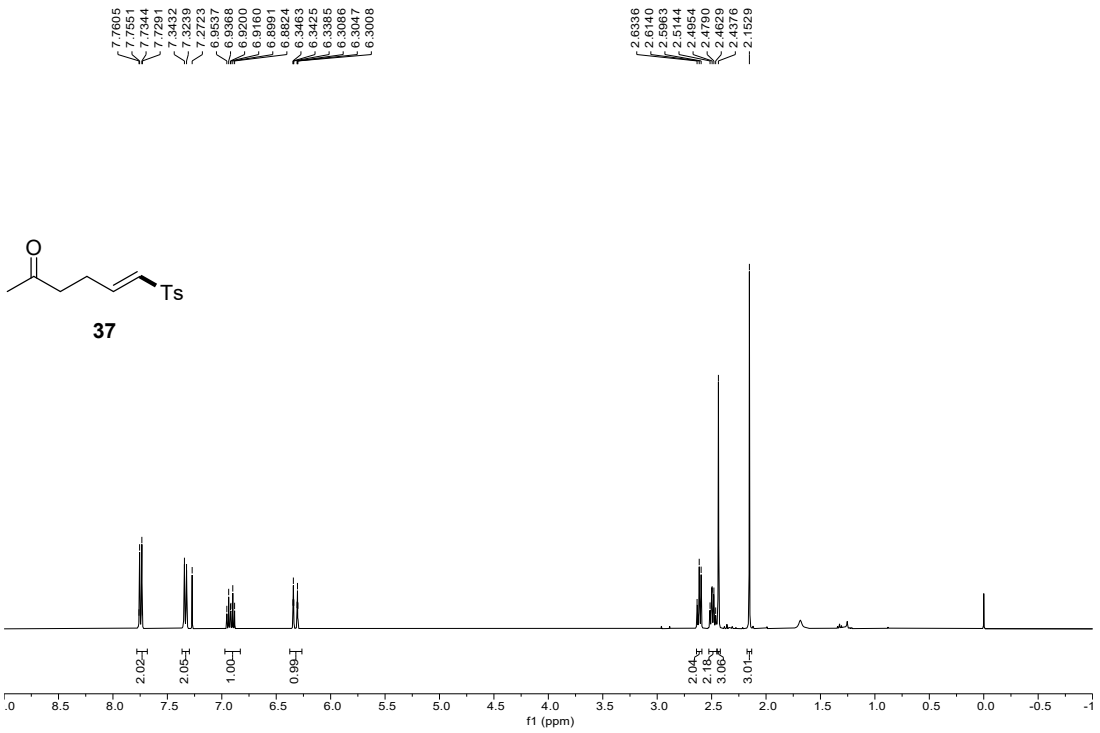
^{1}H NMR ($CDCl_3$, 400 MHz) of **36**



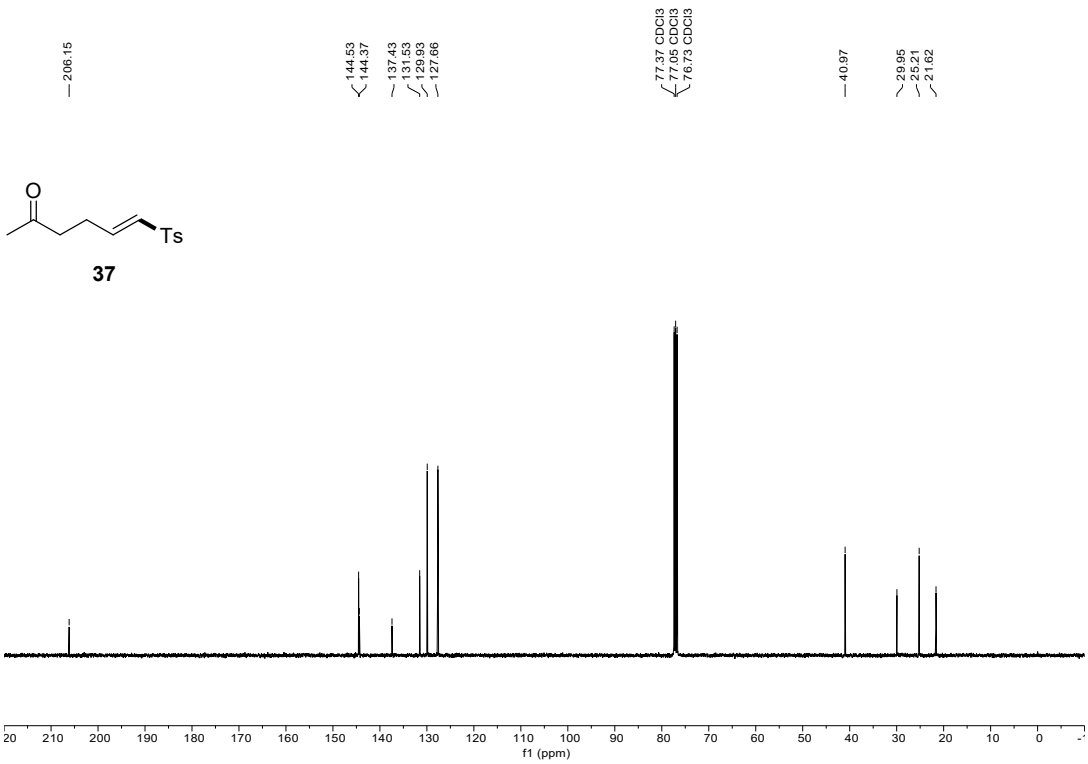
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **36**



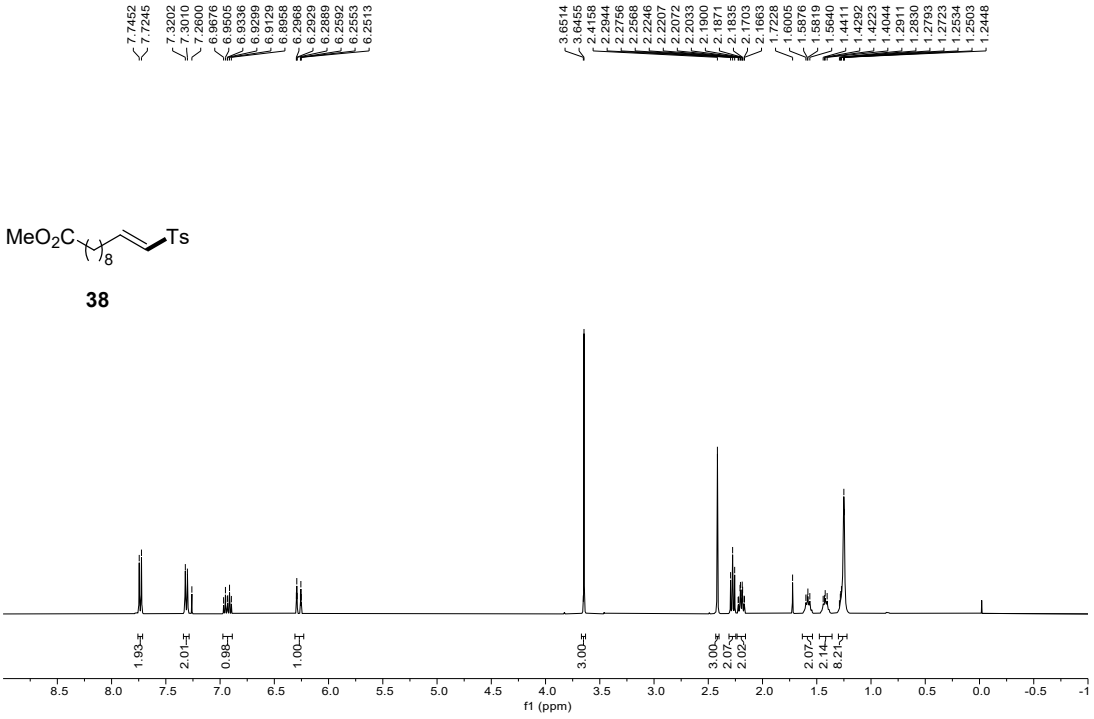
^{1}H NMR ($CDCl_3$, 400 MHz) of **37**



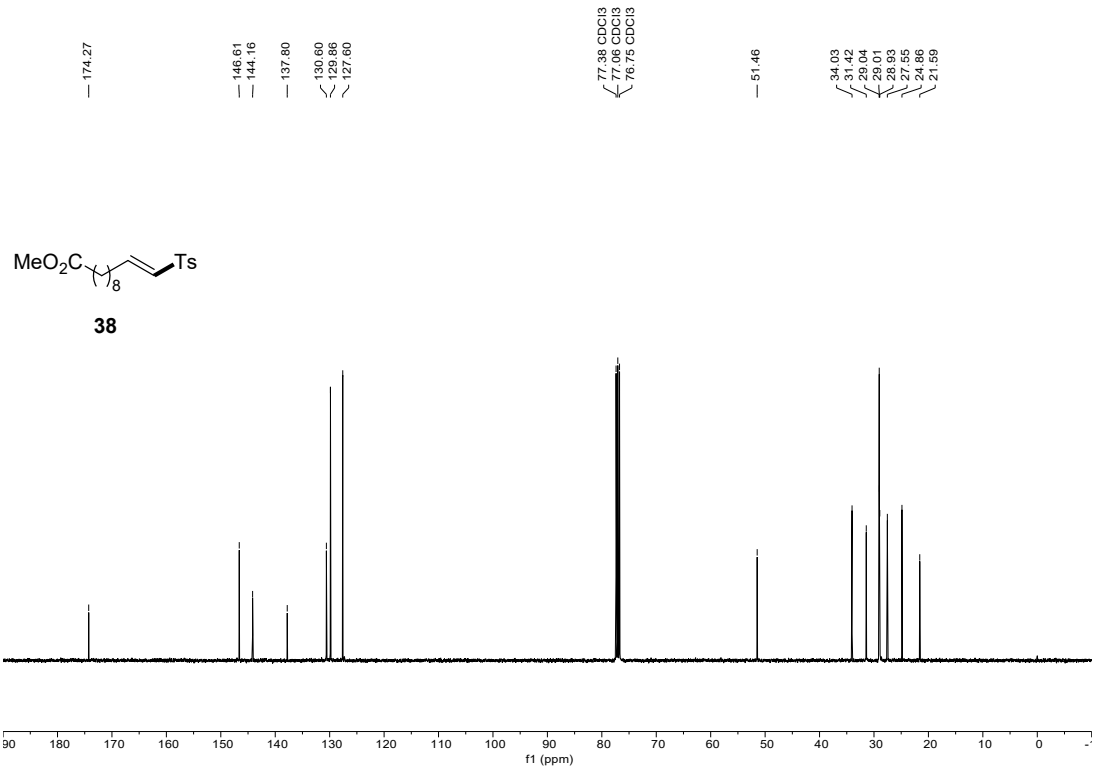
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **37**



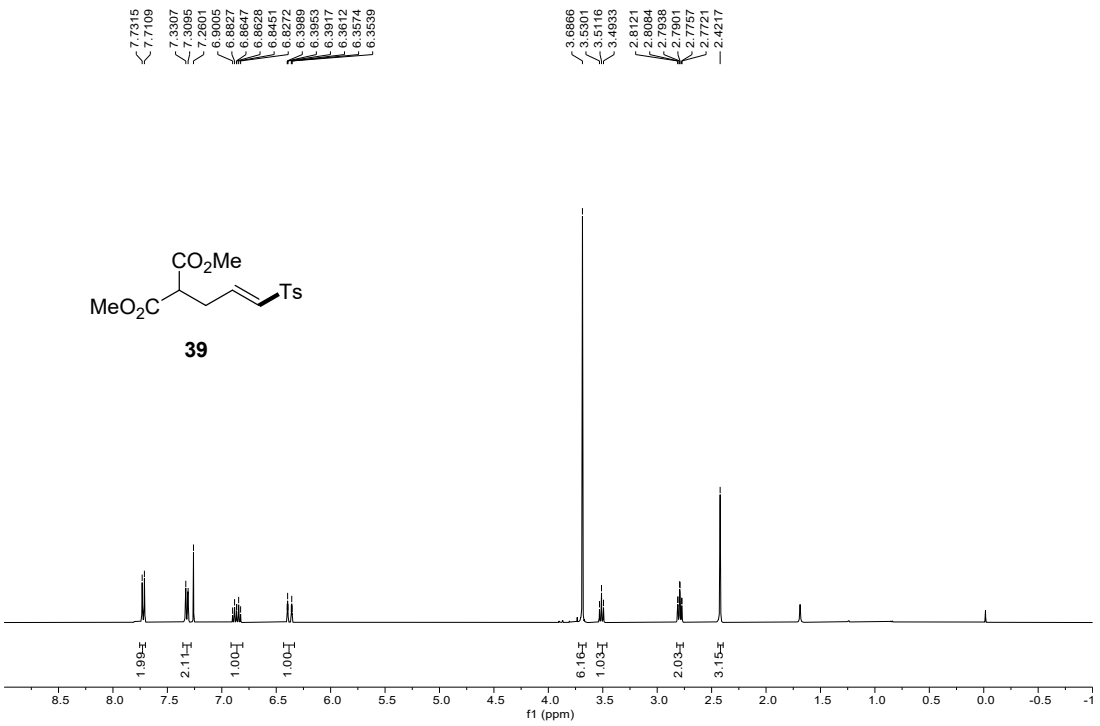
^{1}H NMR ($CDCl_3$, 400 MHz) of **38**



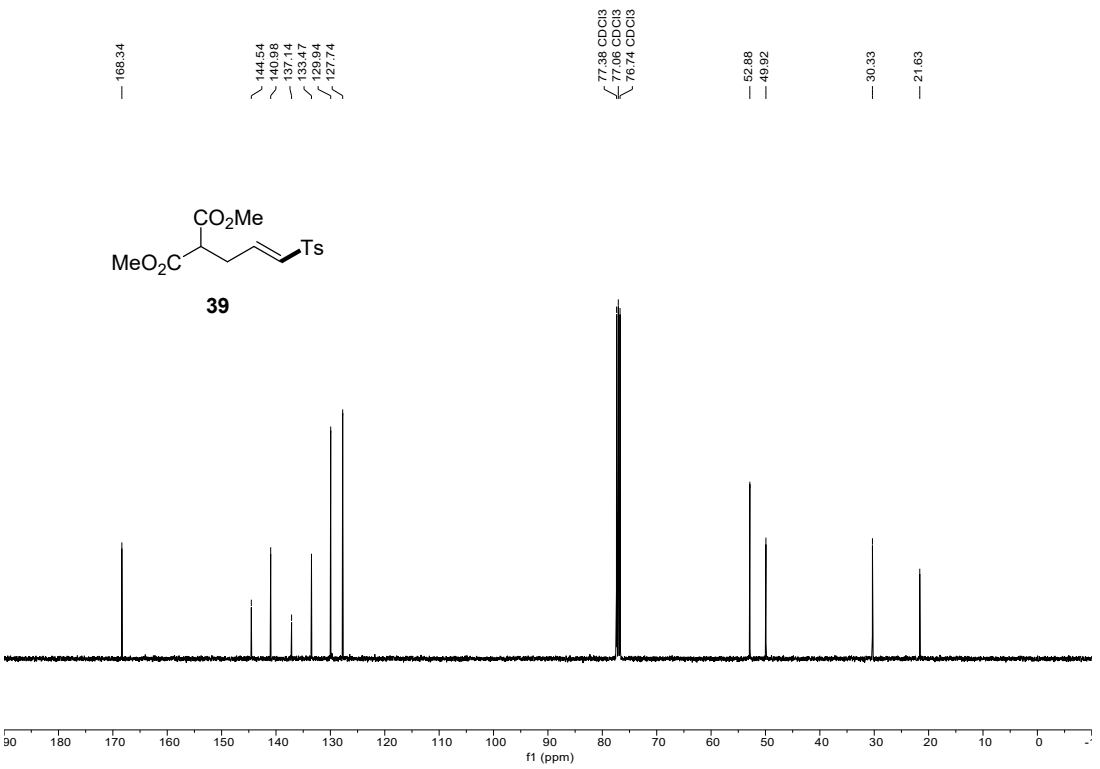
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **38**



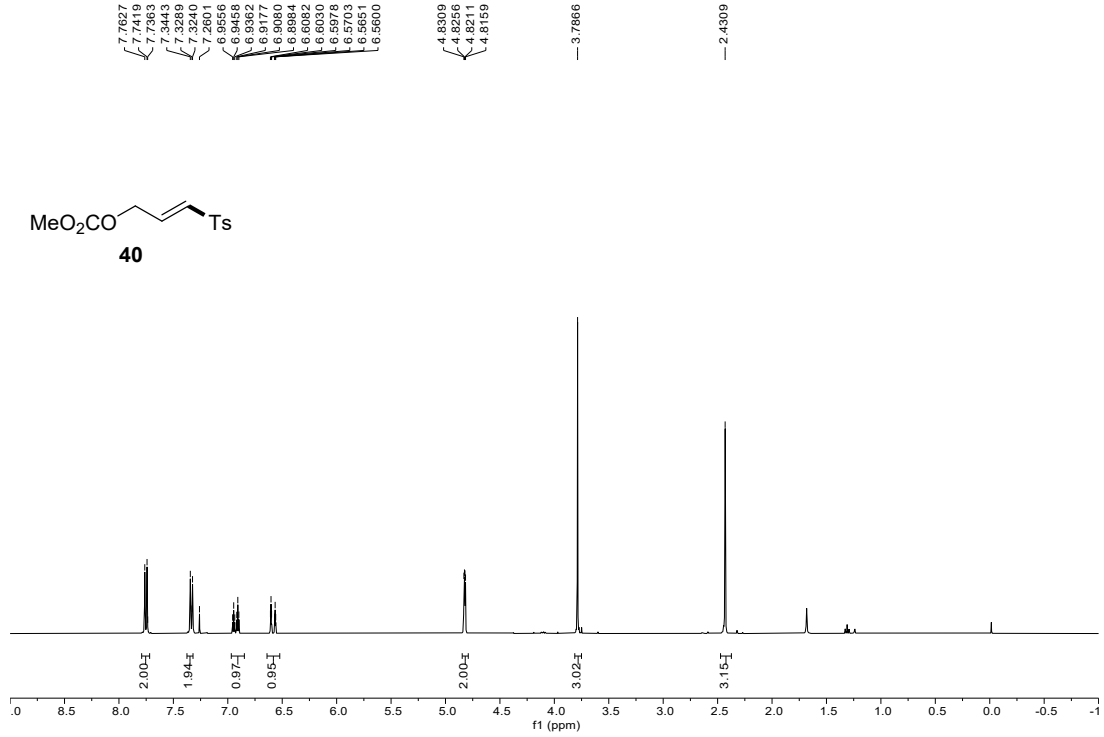
^{1}H NMR ($CDCl_3$, 400 MHz) of **39**



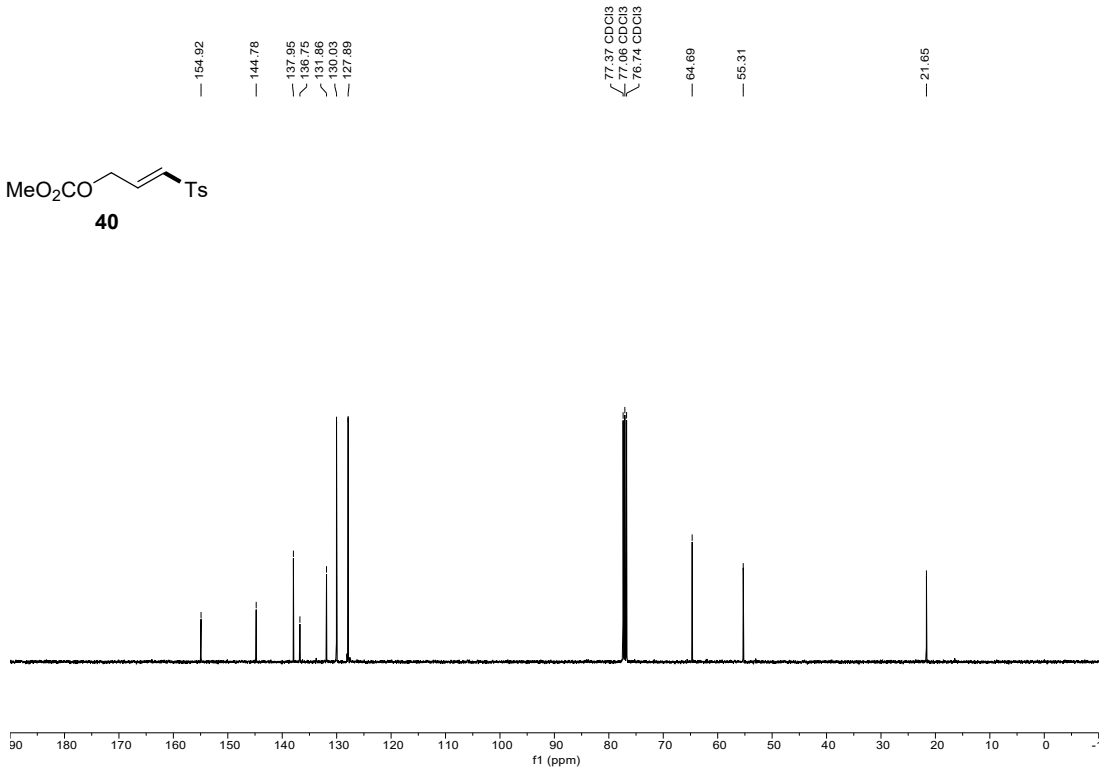
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **39**



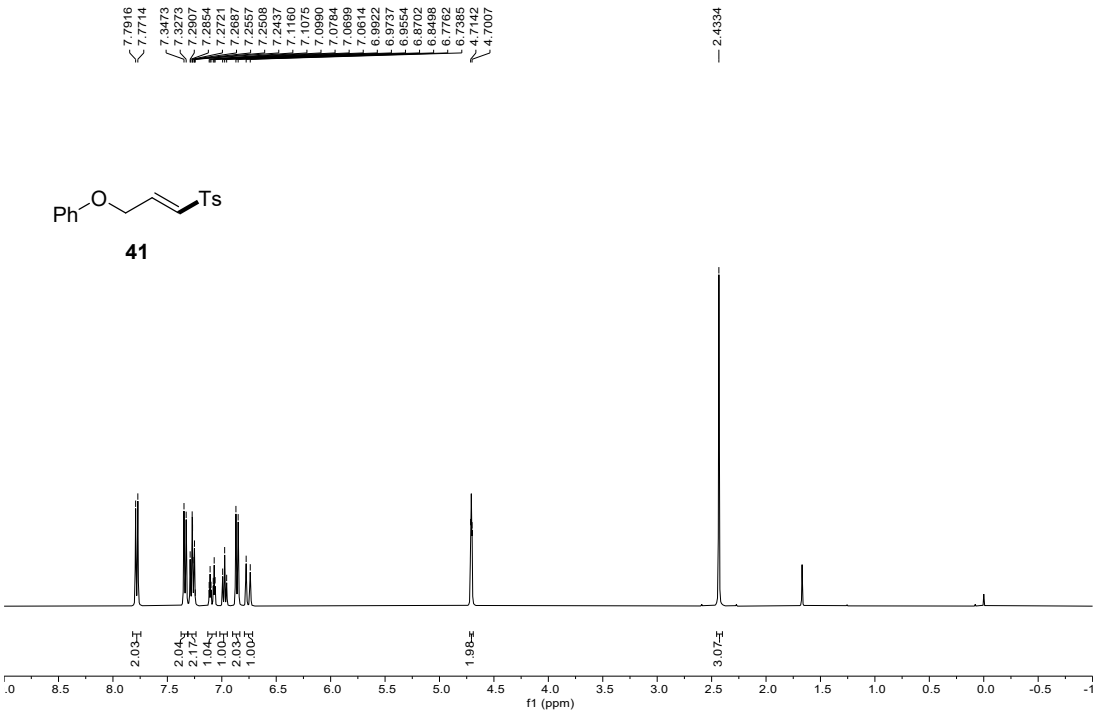
^{1}H NMR ($CDCl_3$, 400 MHz) of **40**



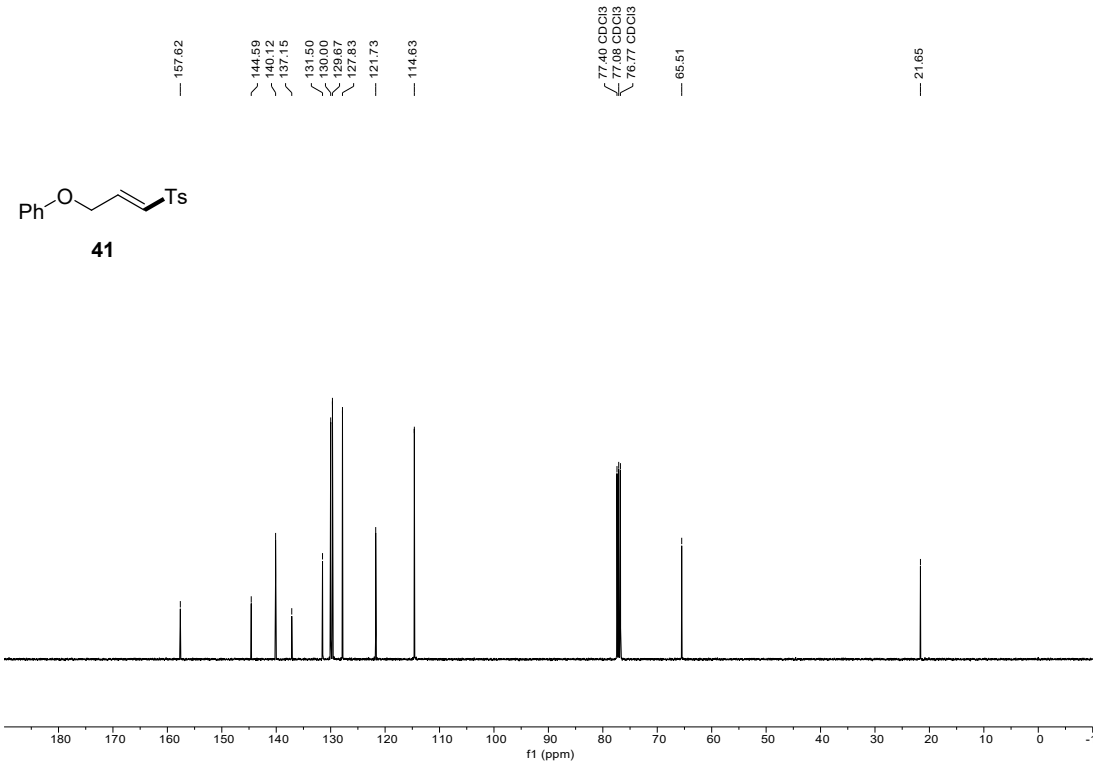
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **40**



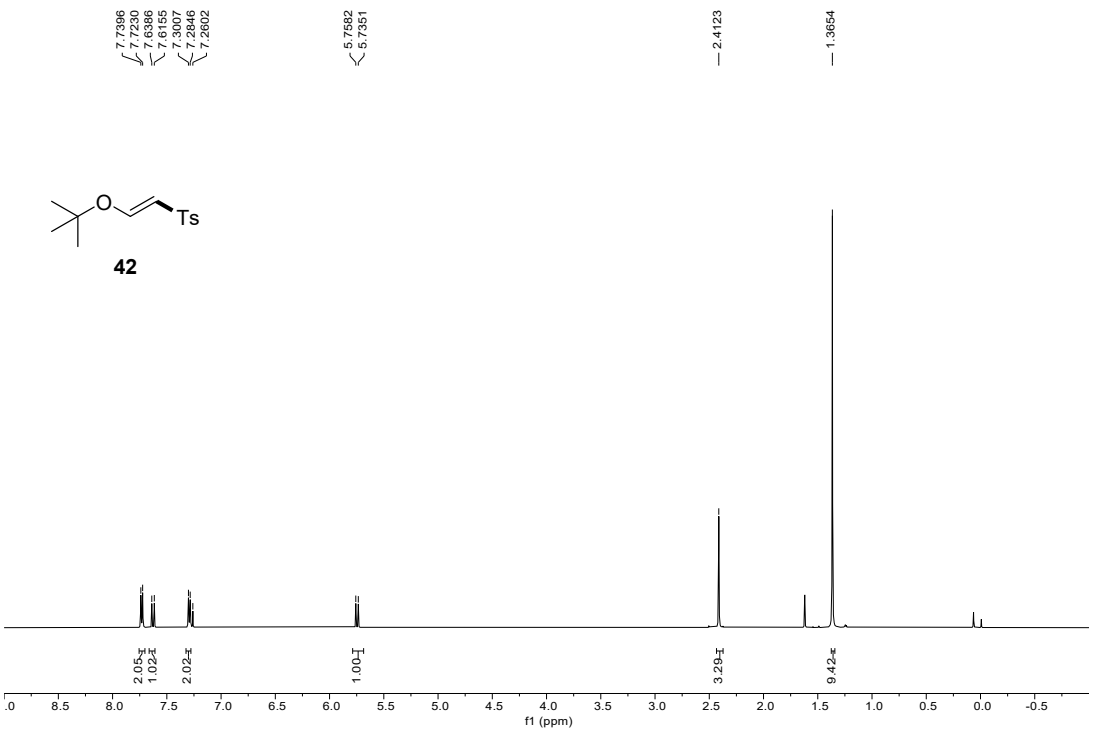
^{1}H NMR ($CDCl_3$, 400 MHz) of **41**



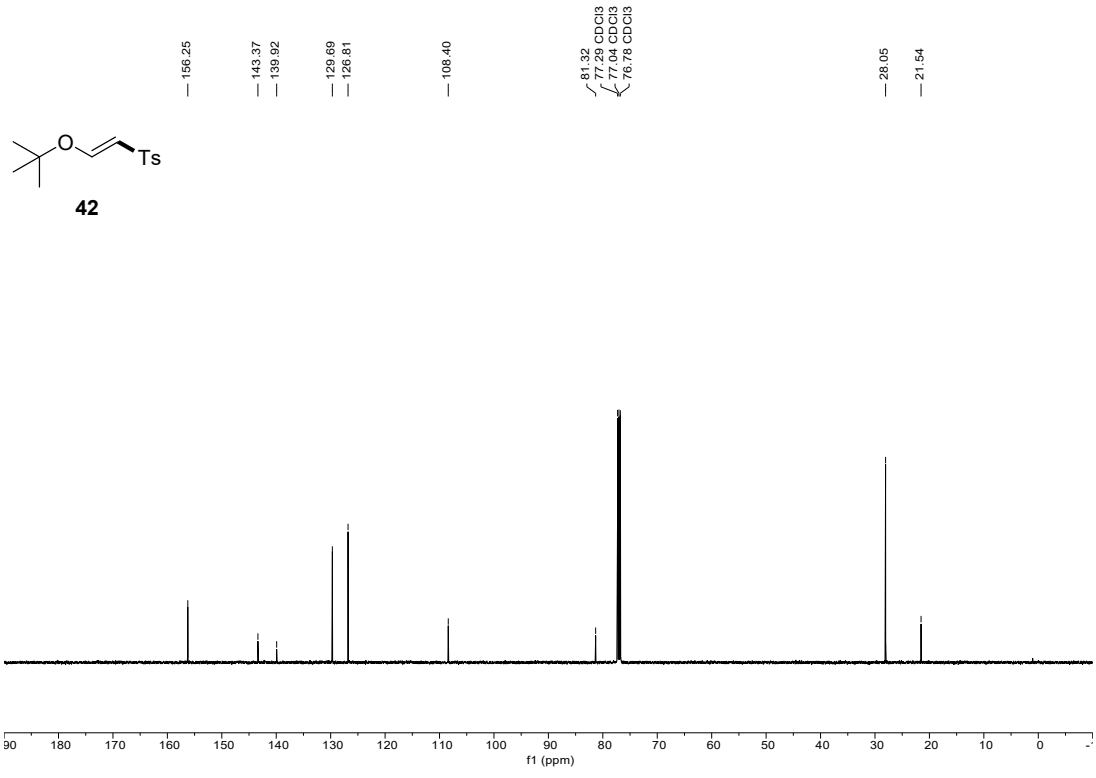
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **41**



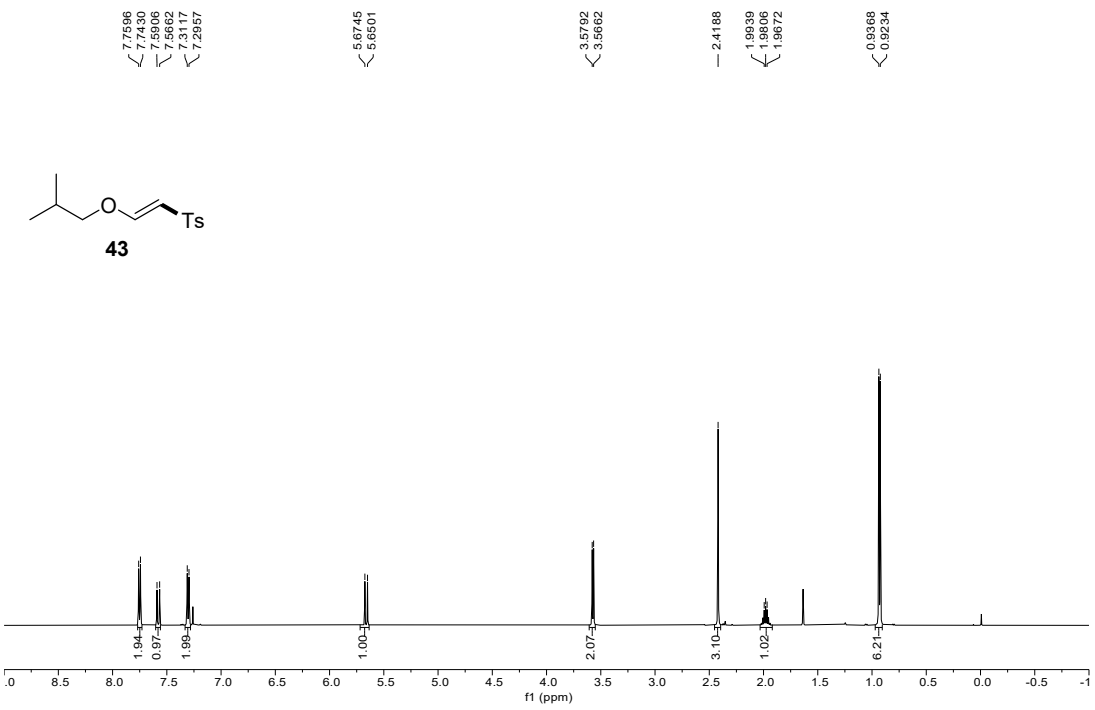
^{1}H NMR ($CDCl_3$, 500 MHz) of **42**



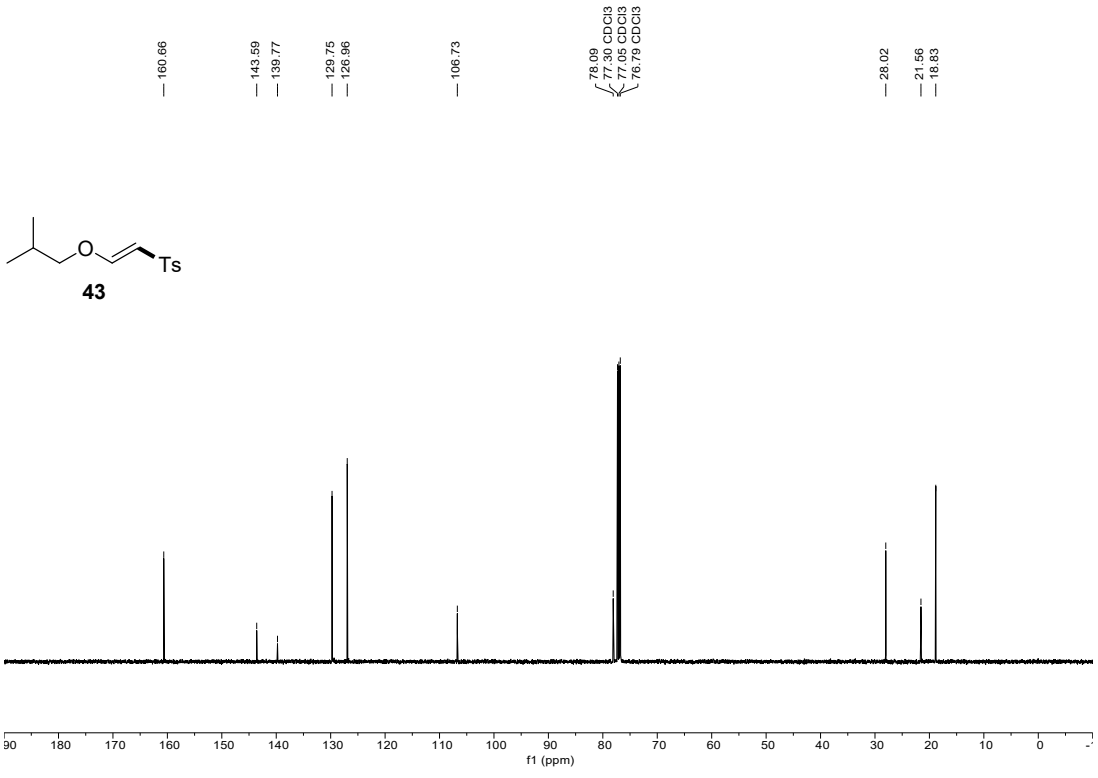
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) of **42**



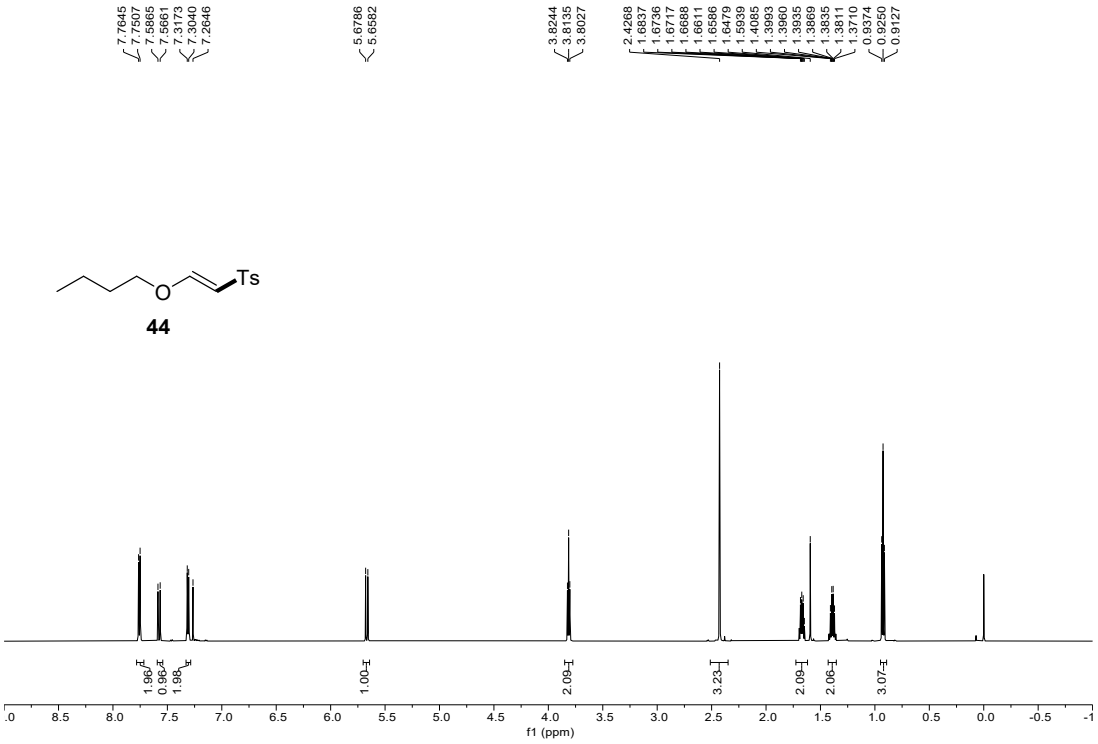
^{1}H NMR ($CDCl_3$, 500 MHz) of **43**



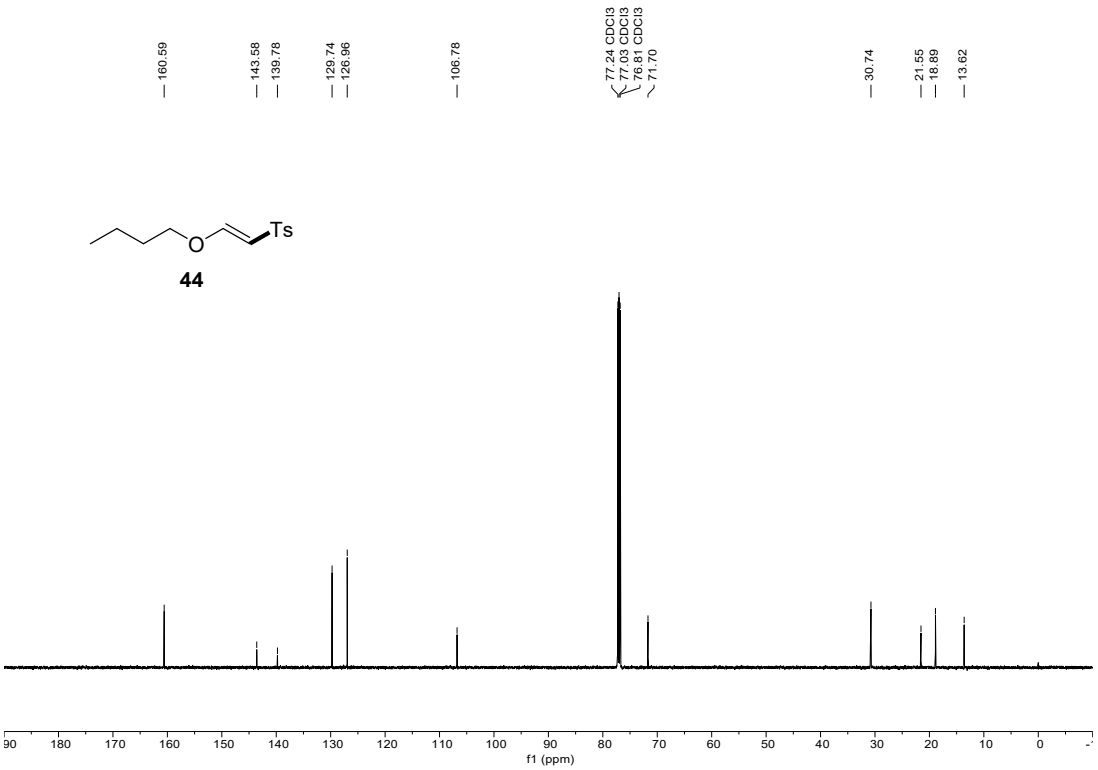
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **43**



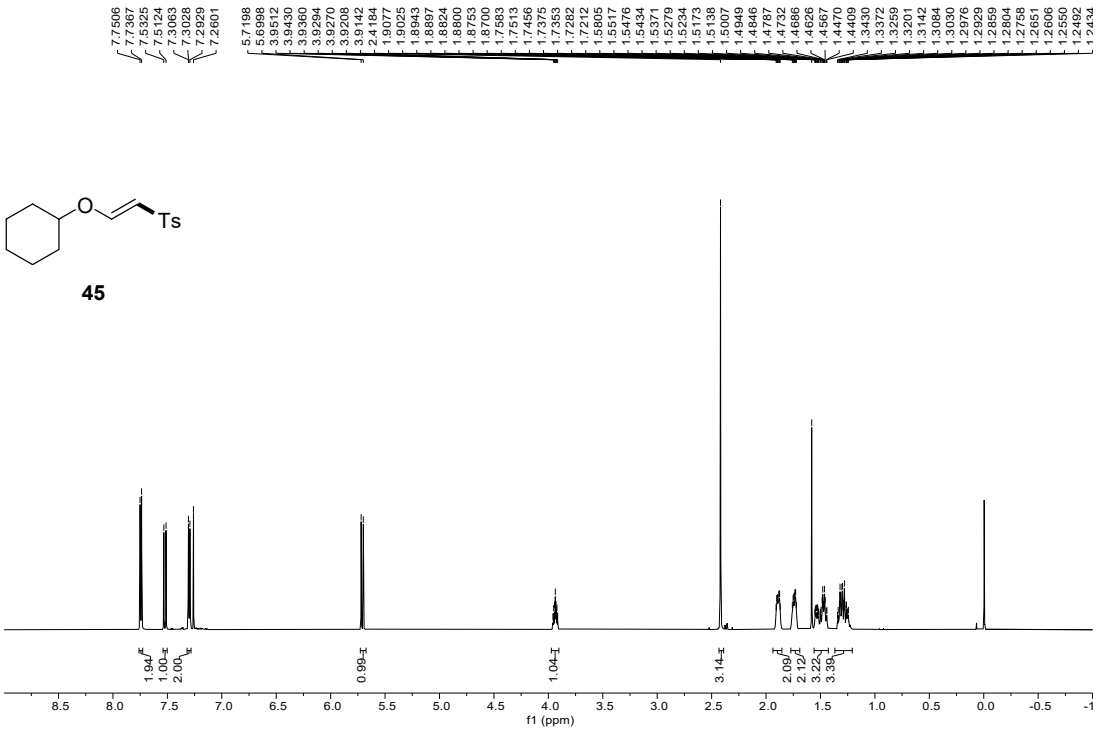
^{1}H NMR ($CDCl_3$, 600 MHz) of **44**



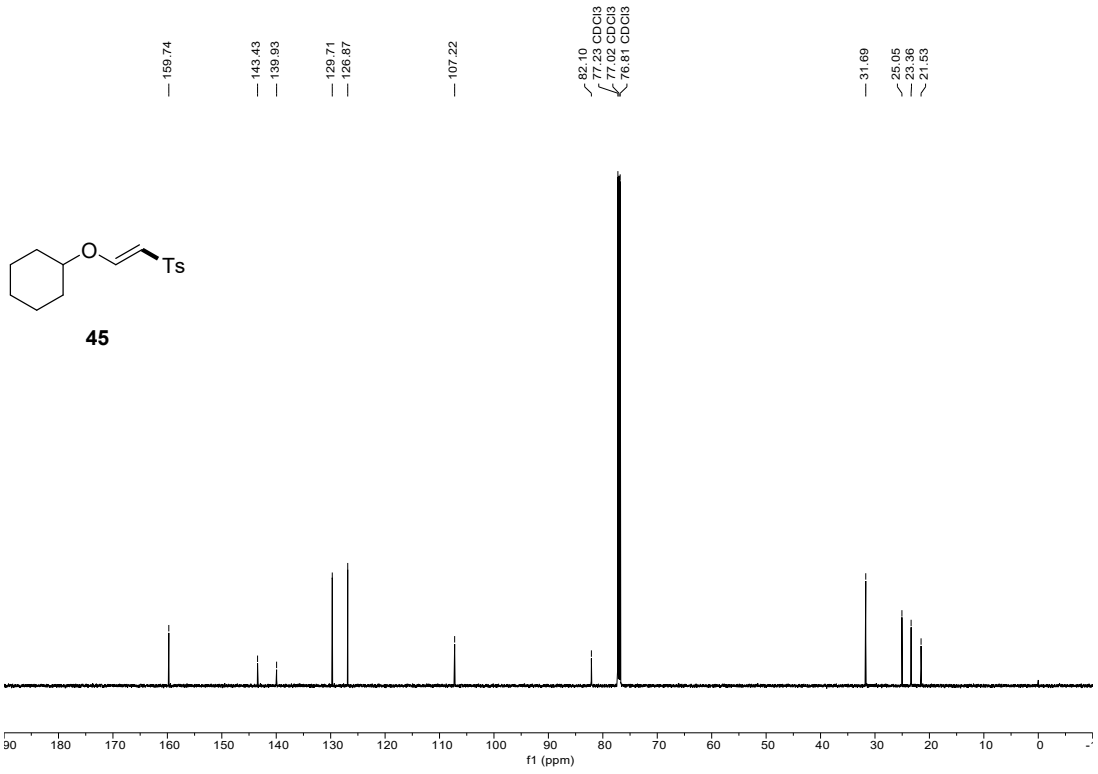
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) of **44**



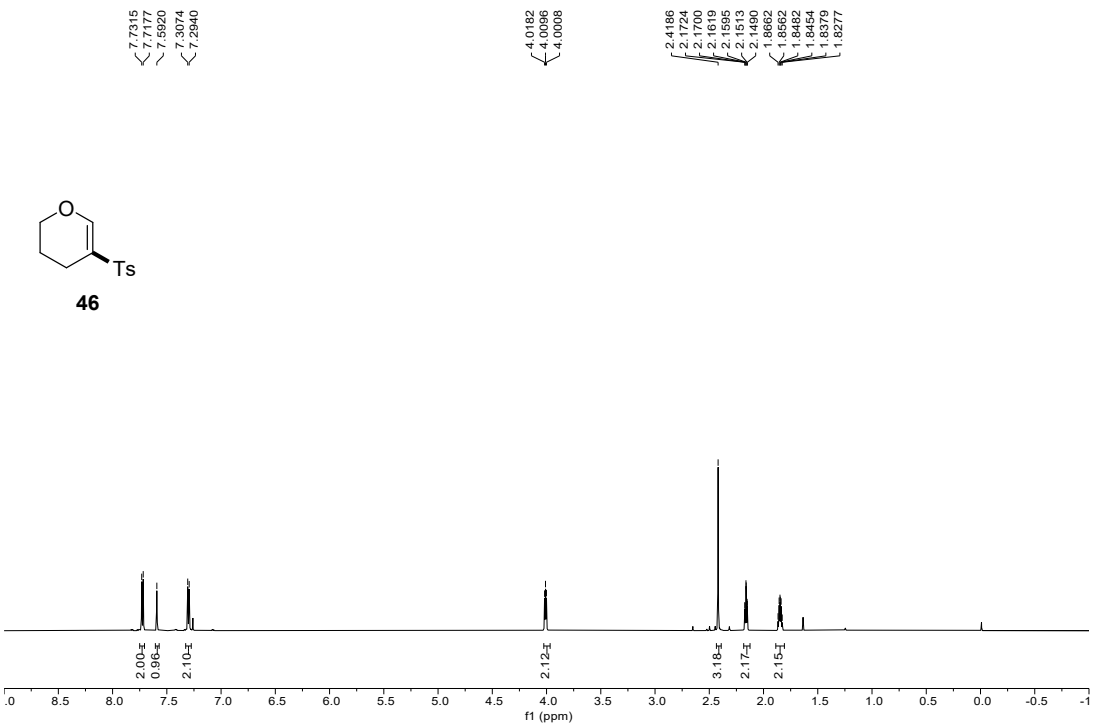
^{1}H NMR ($CDCl_3$, 600 MHz) of **45**



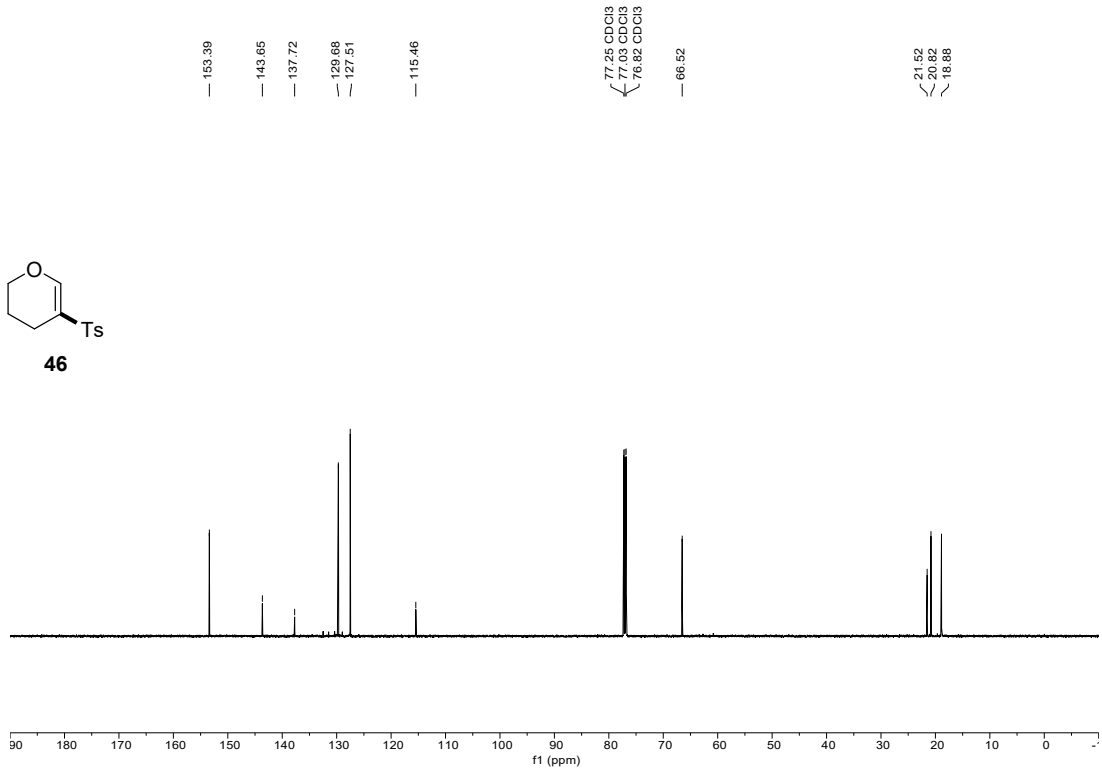
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) of **45**



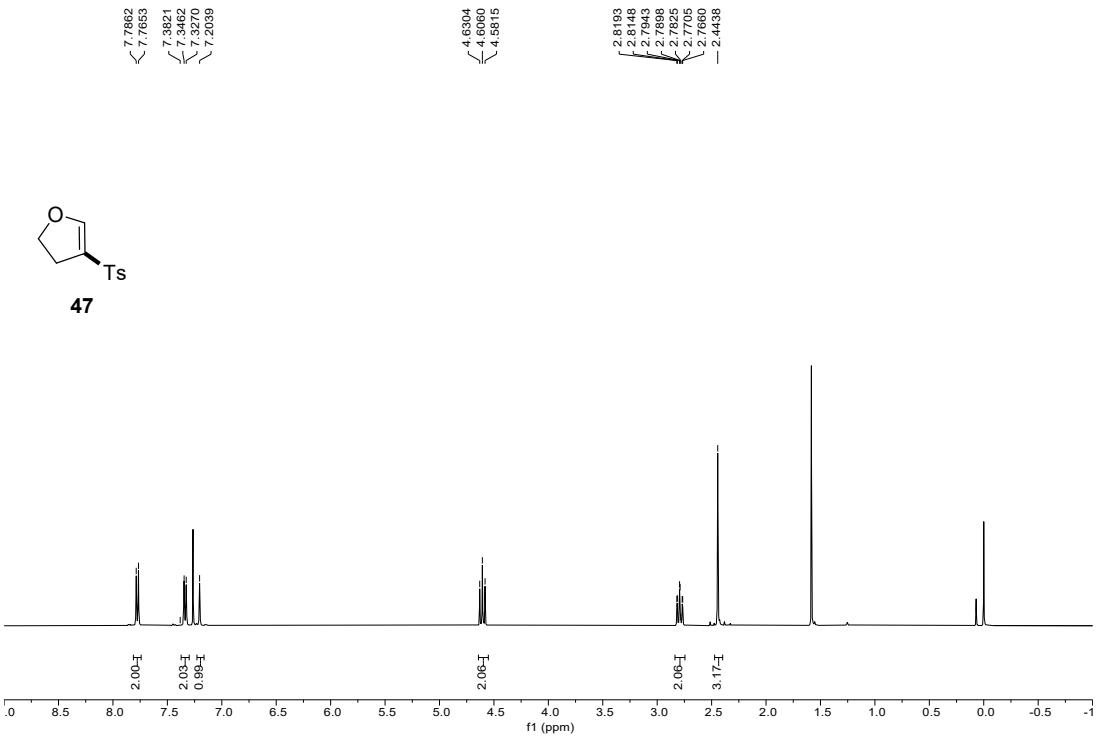
^{1}H NMR ($CDCl_3$, 600 MHz) of **46**



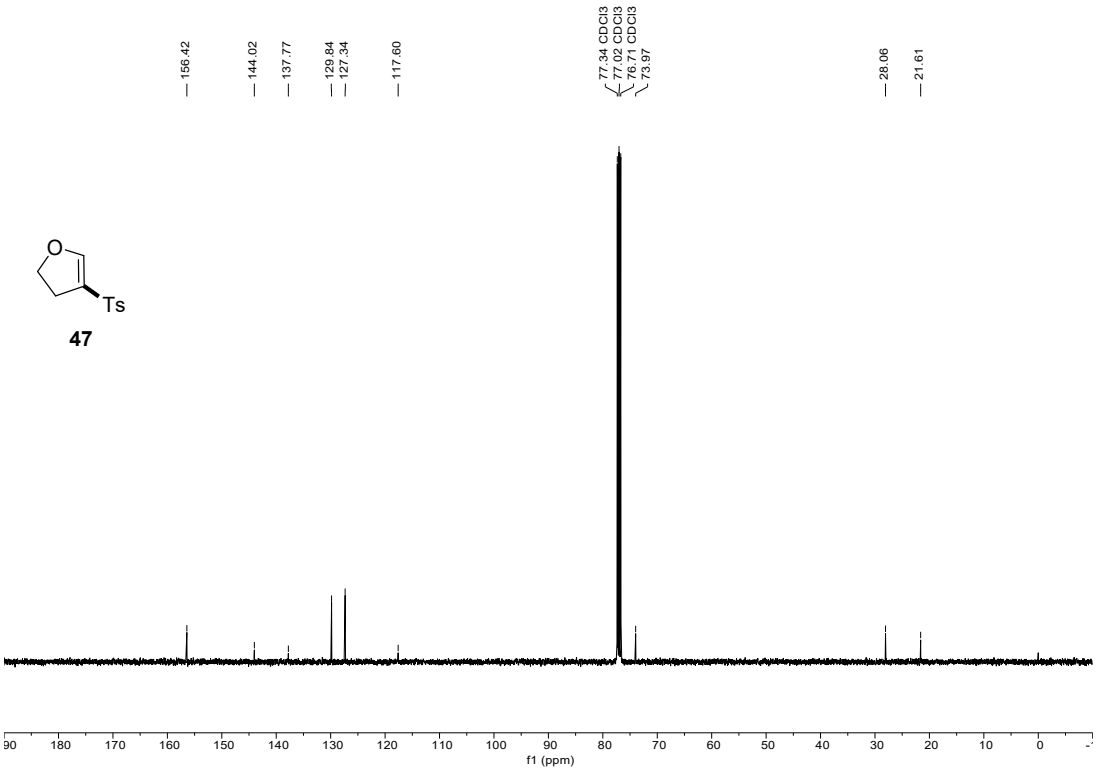
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) of **46**



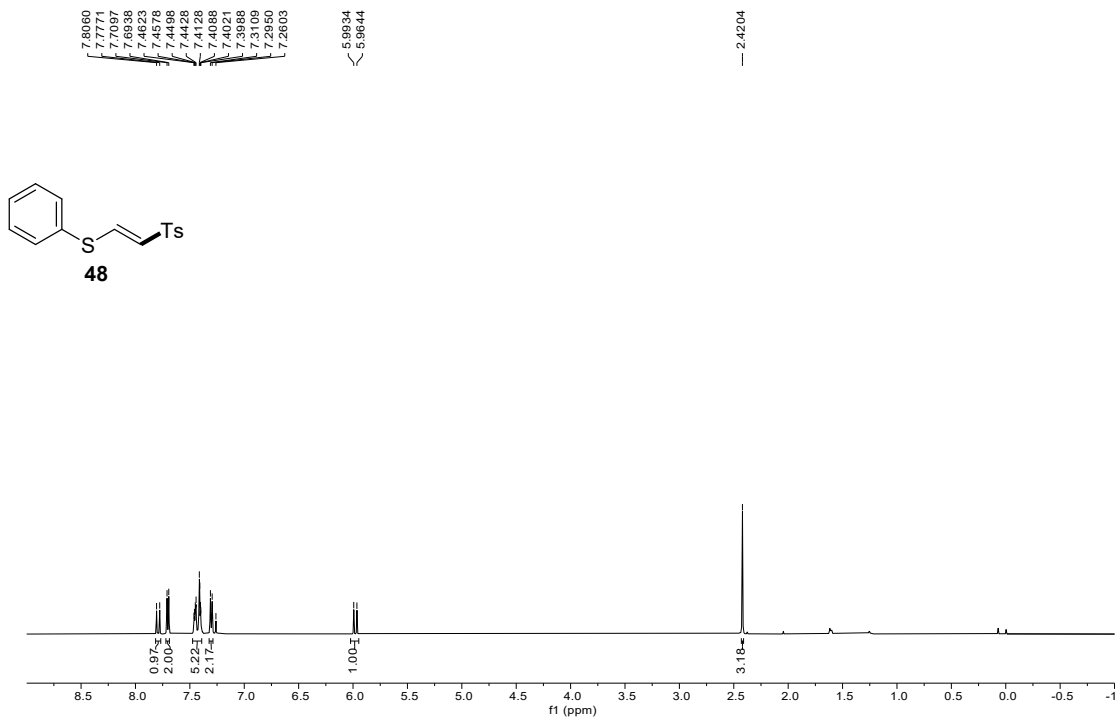
^{1}H NMR ($CDCl_3$, 400 MHz) of **47**



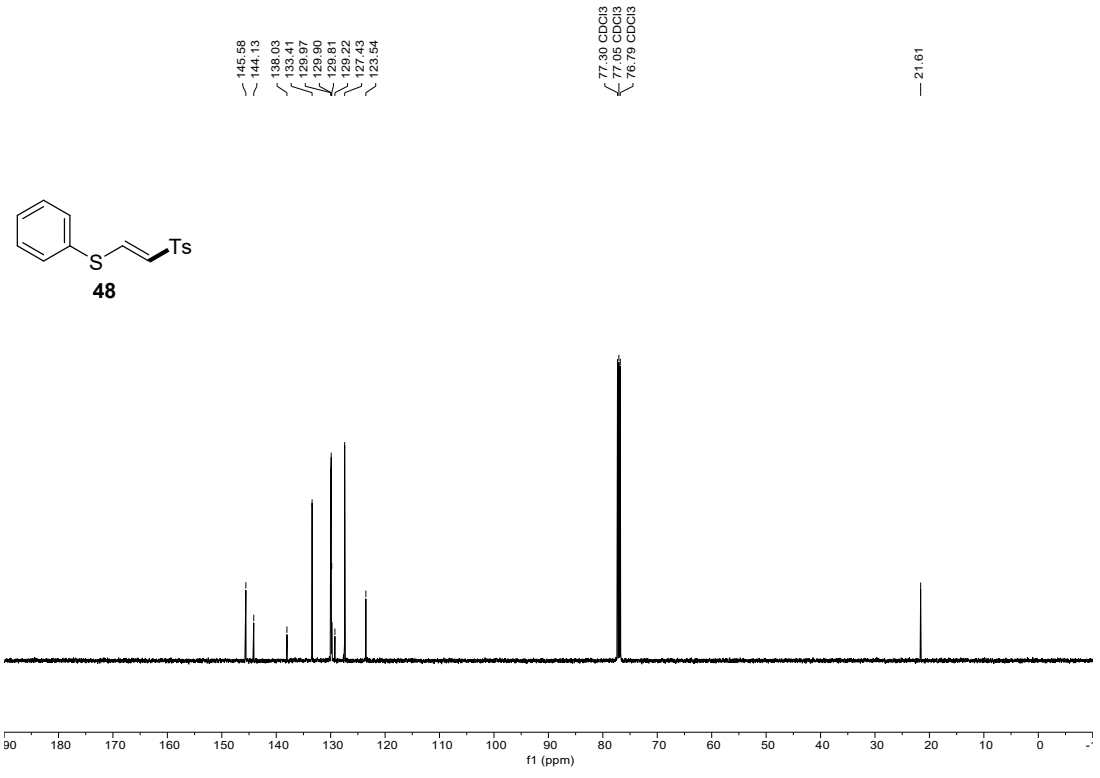
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **47**



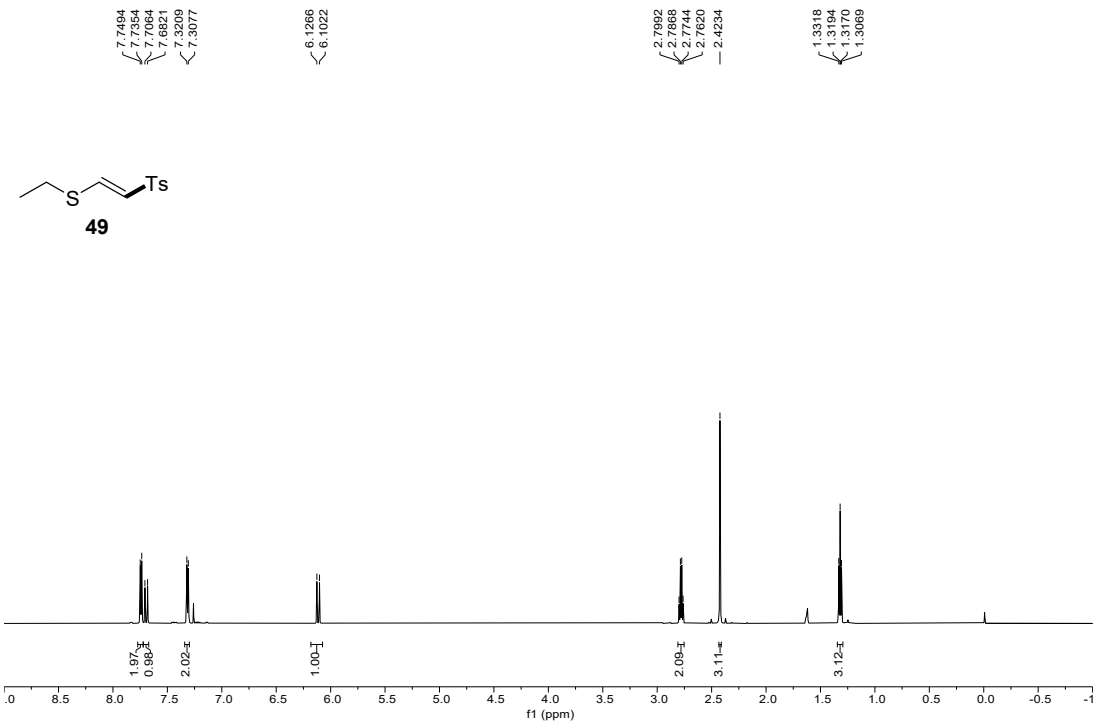
^{1}H NMR ($CDCl_3$, 500 MHz) of **48**



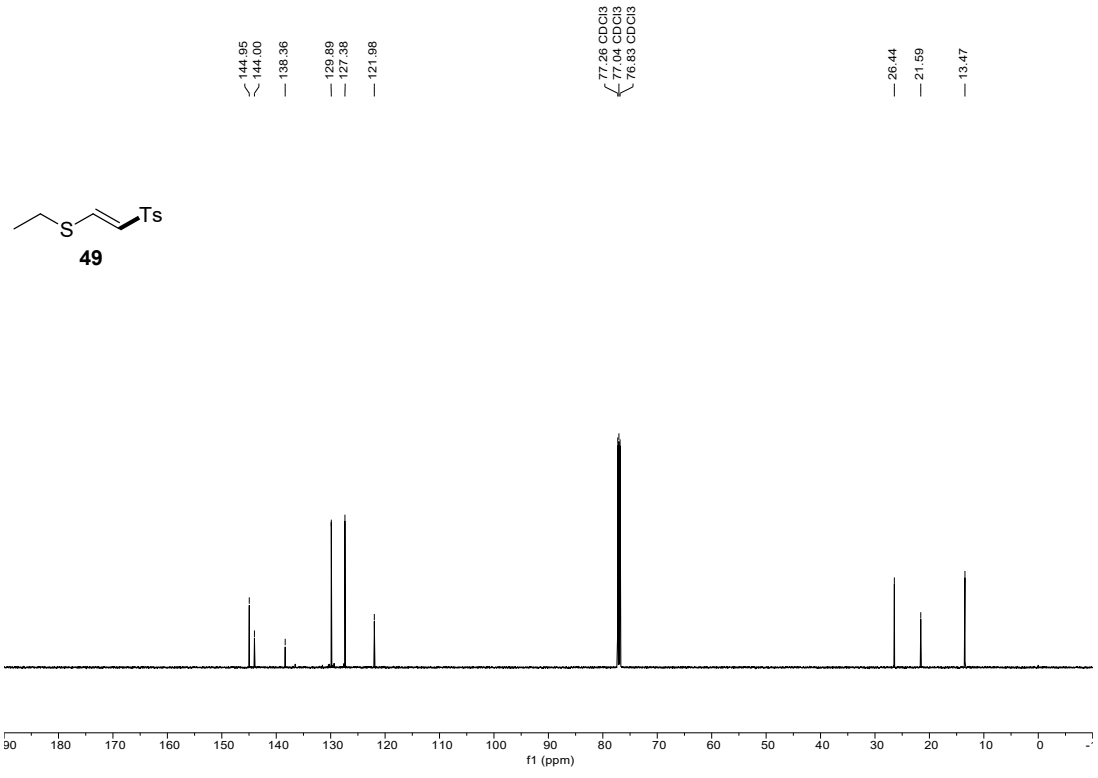
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **48**



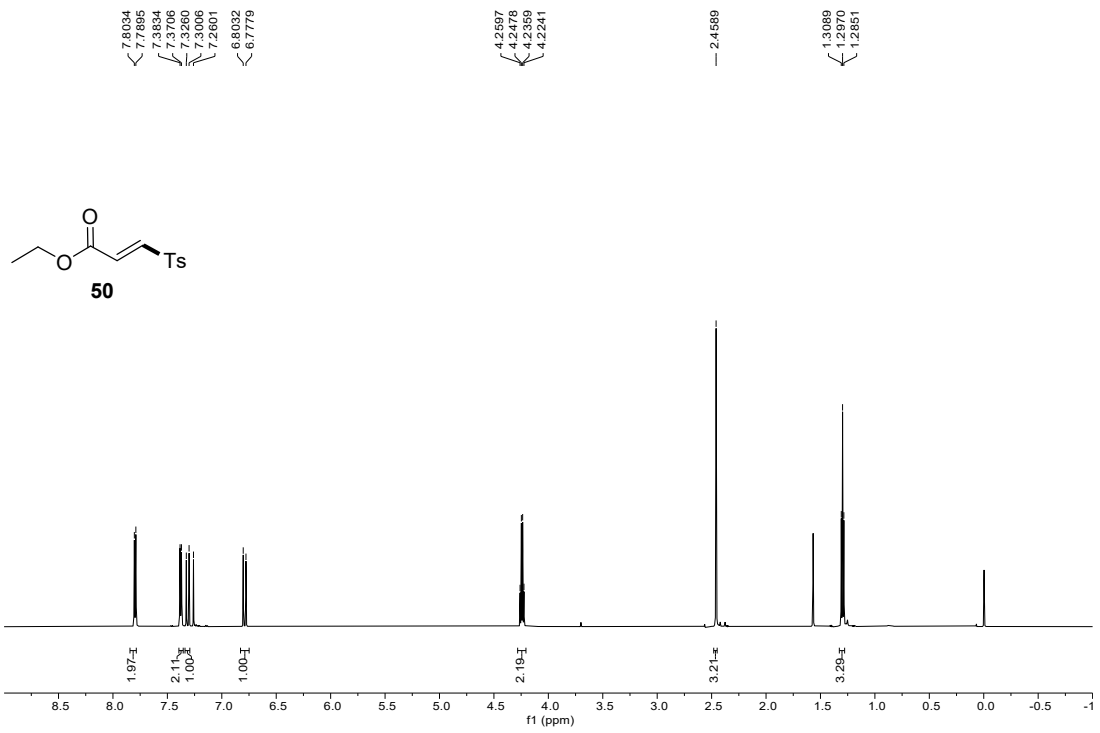
^{1}H NMR ($CDCl_3$, 600 MHz) of **49**



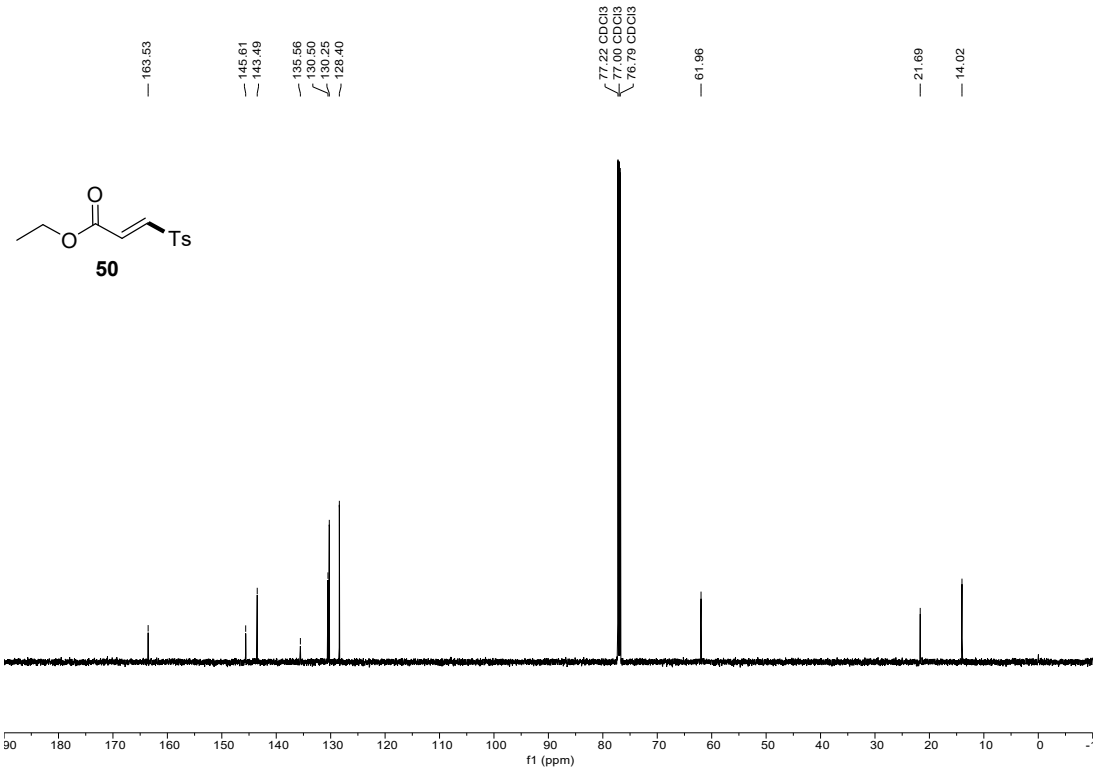
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) of **49**



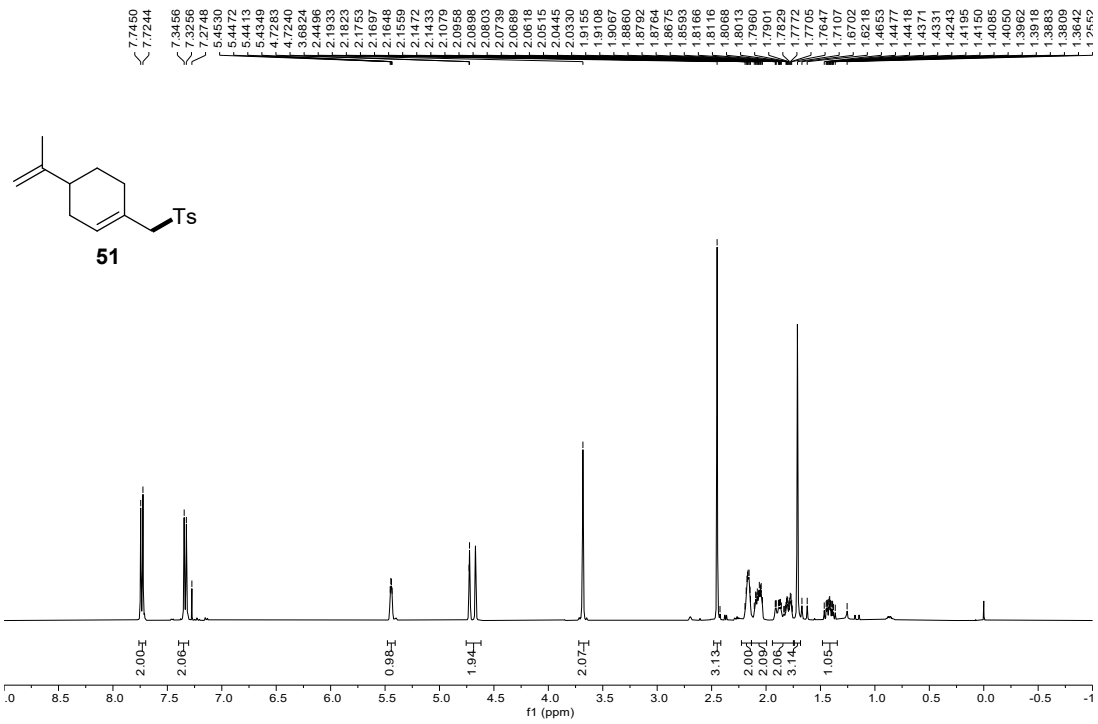
^{1}H NMR ($CDCl_3$, 600 MHz) of **50**



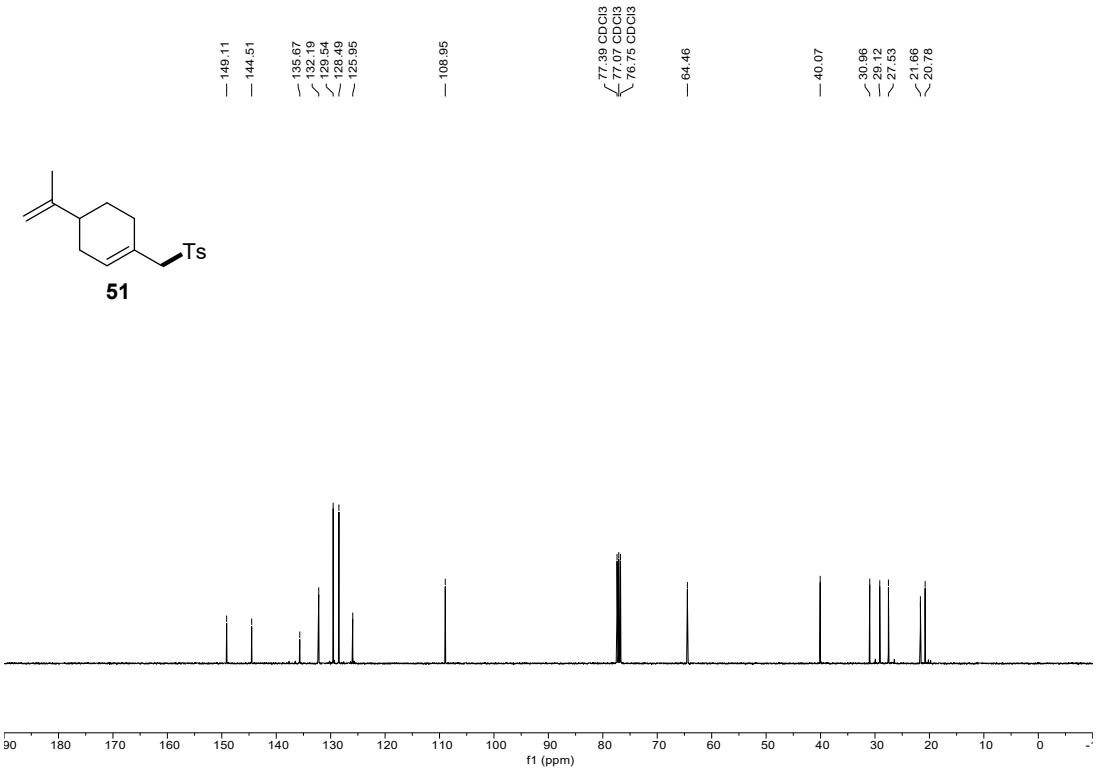
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) of **50**



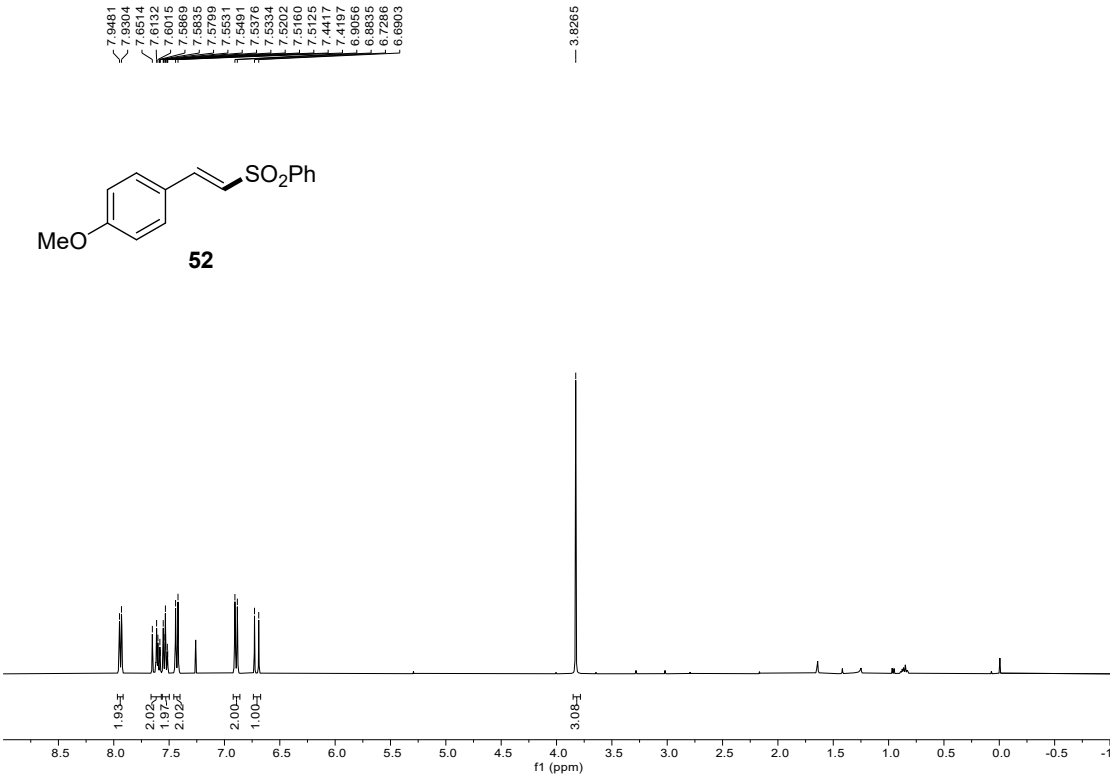
^{1}H NMR ($CDCl_3$, 400 MHz) of **51**



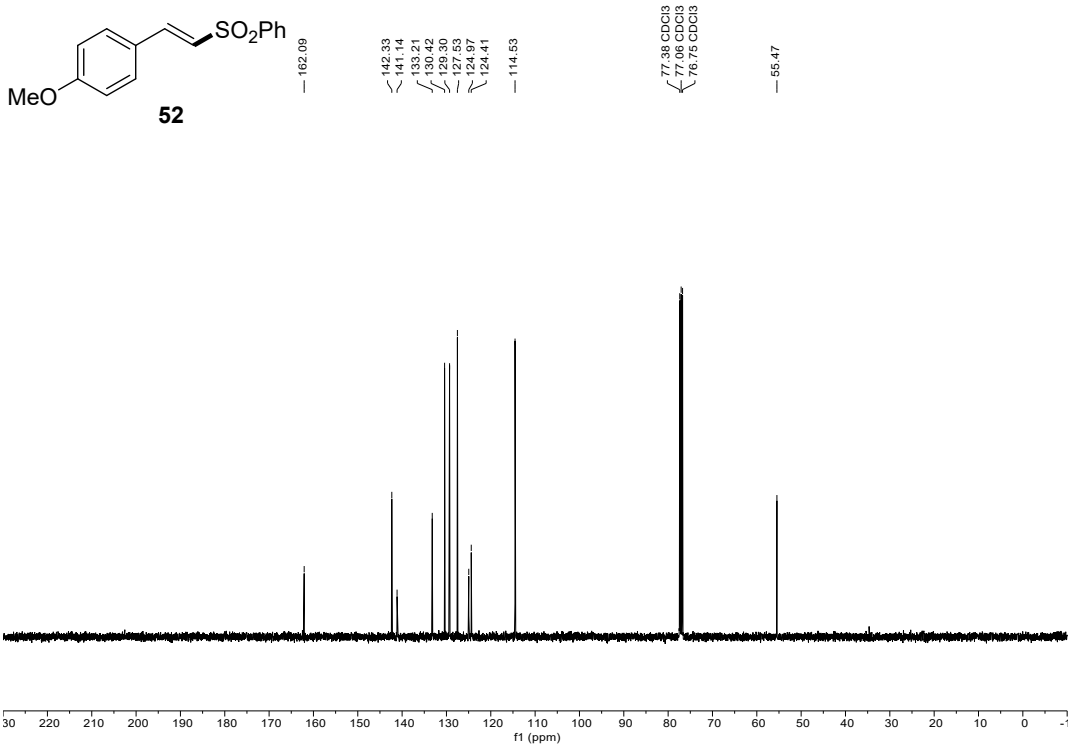
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **51**



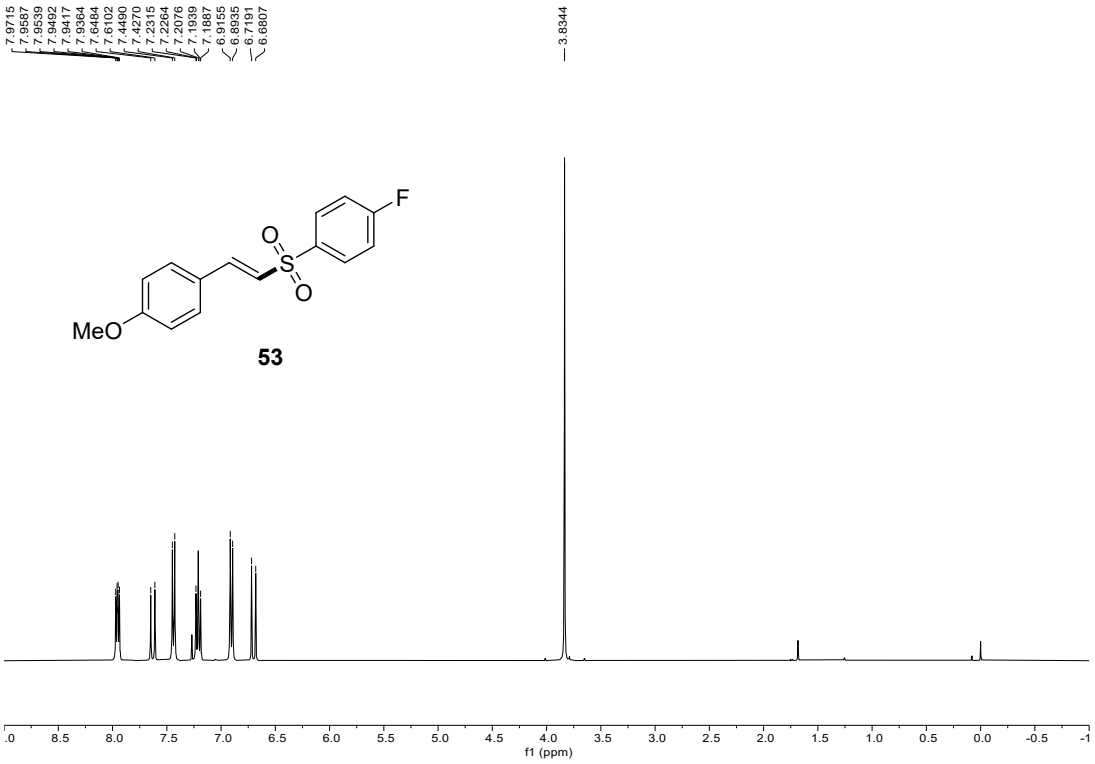
^{1}H NMR ($CDCl_3$, 400 MHz) of **52**



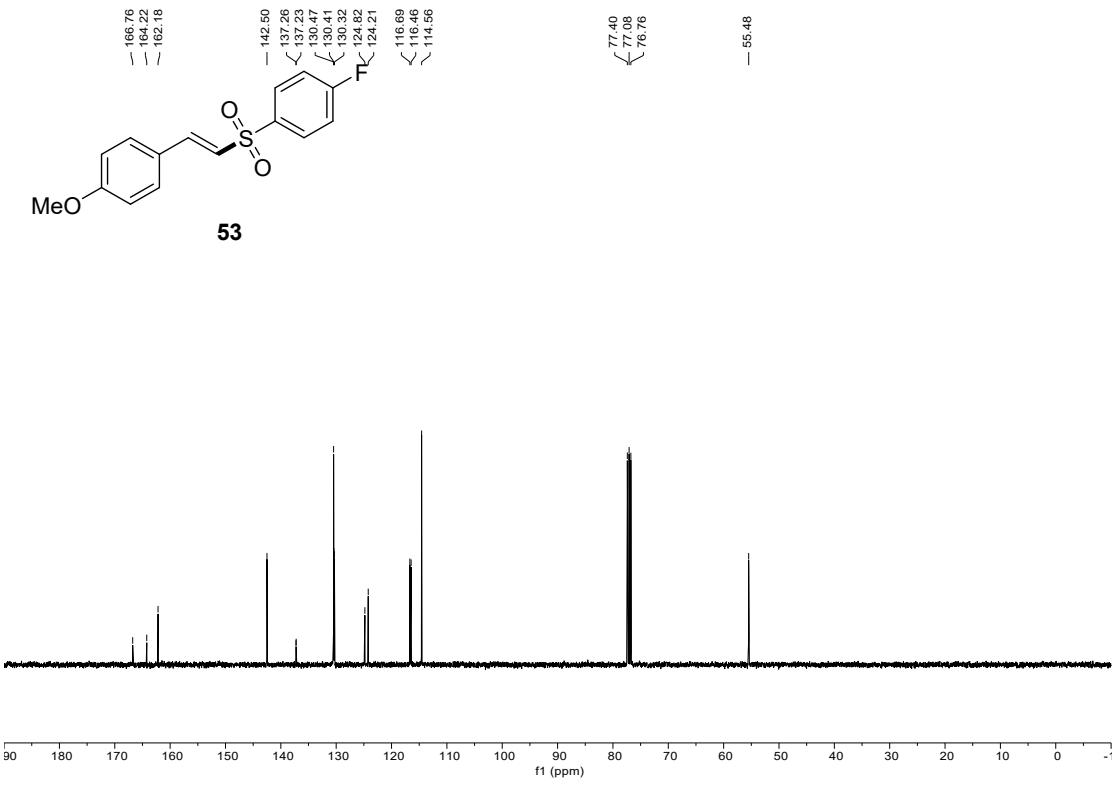
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **52**



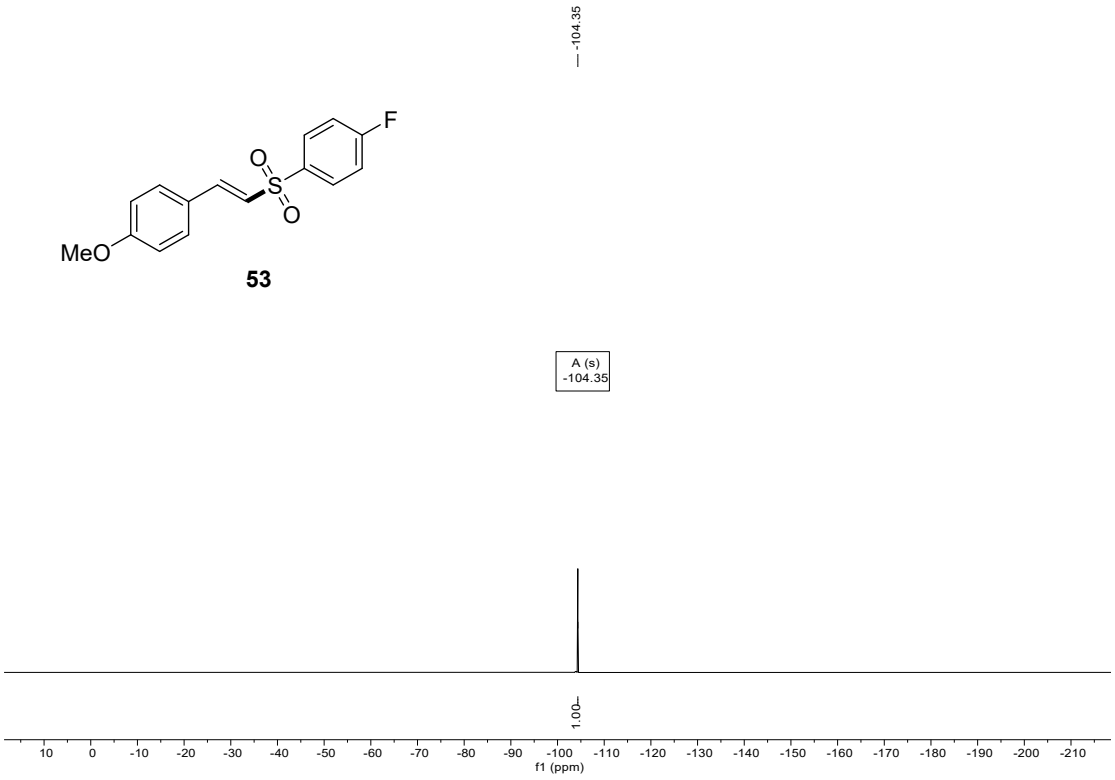
^{1}H NMR ($CDCl_3$, 400 MHz) of **53**



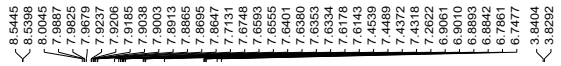
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **53**

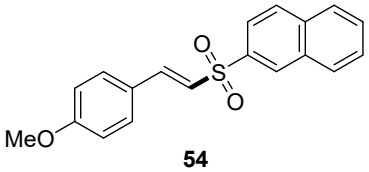


^{19}F NMR ($CDCl_3$, 471 MHz) of **53**



^{1}H NMR ($CDCl_3$, 400 MHz) of **54**





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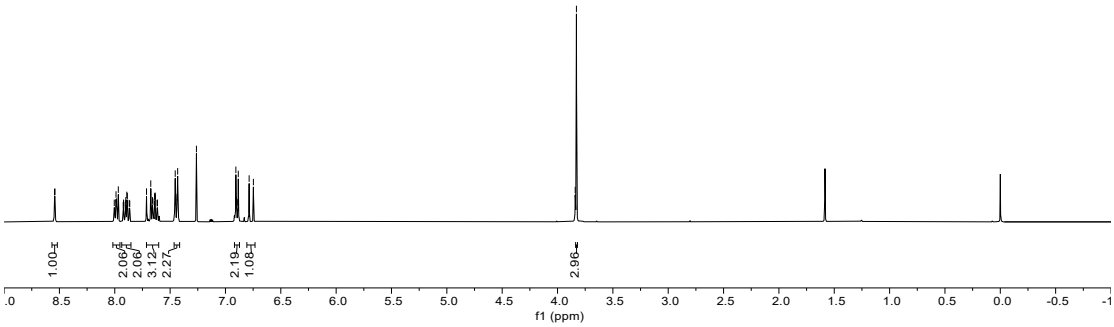
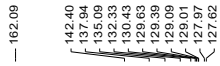
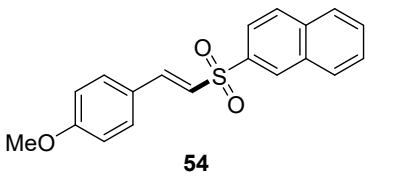


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **54**





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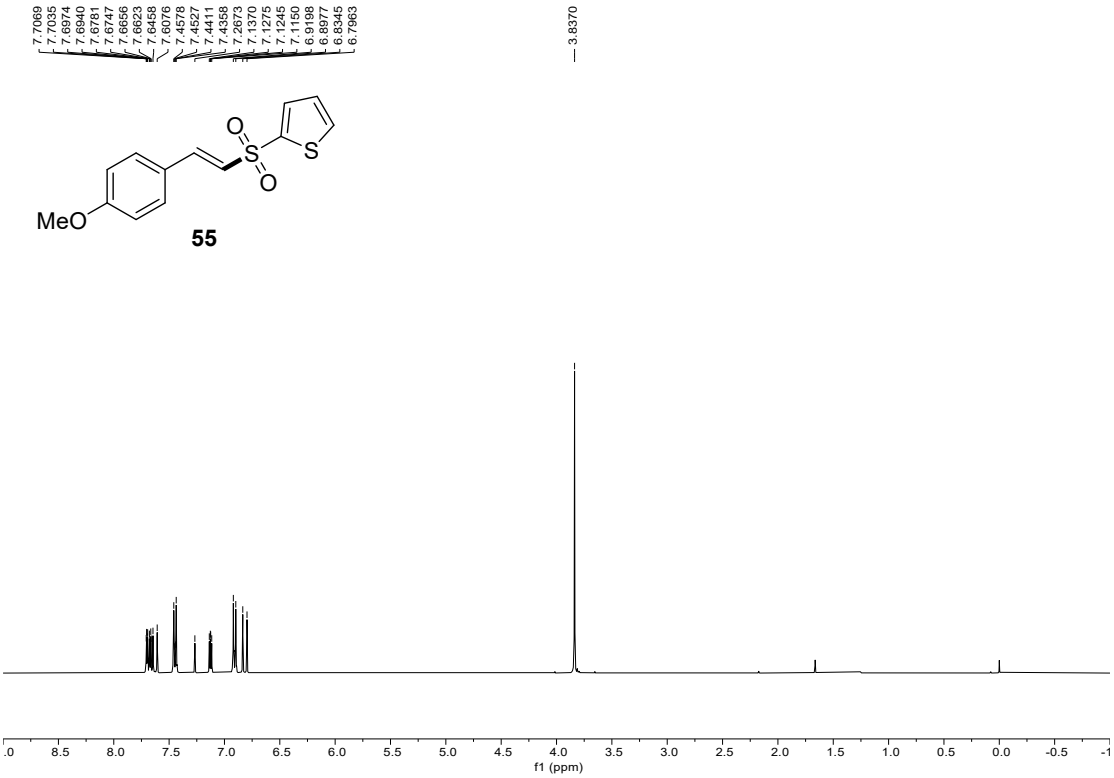
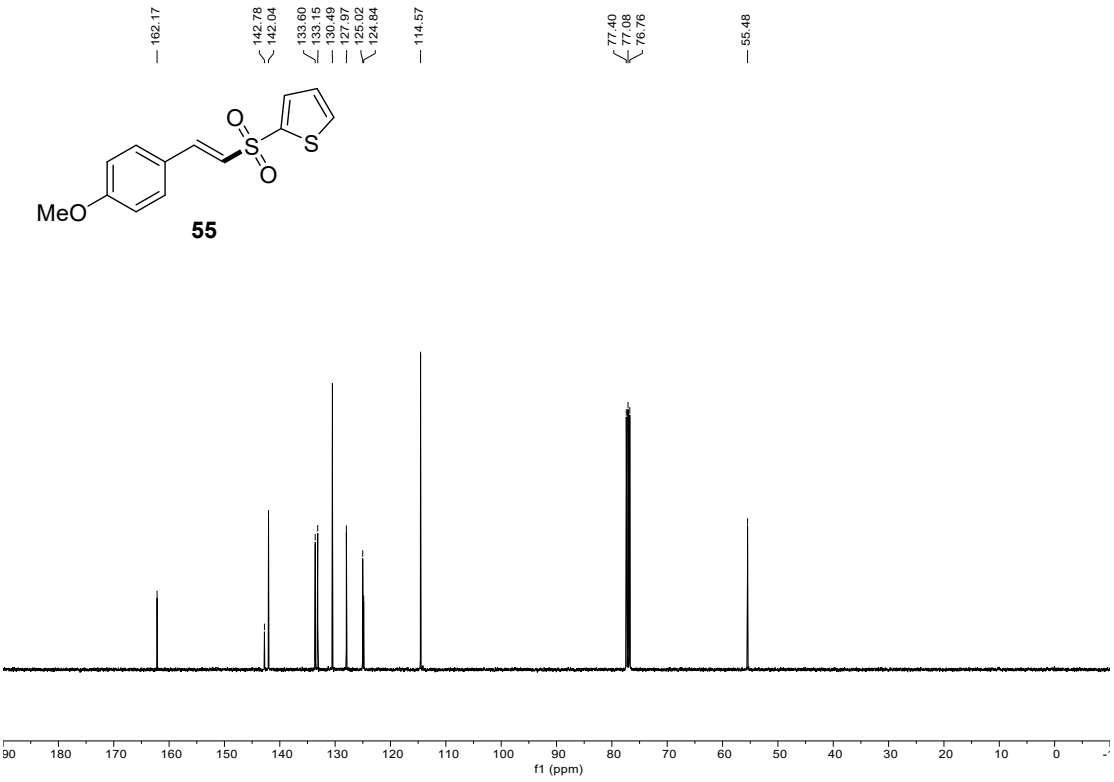
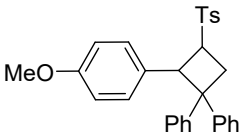
^{1}H NMR ($CDCl_3$, 400 MHz) of **55**



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **55**



^{1}H NMR ($CDCl_3$, 400 MHz) of **57**



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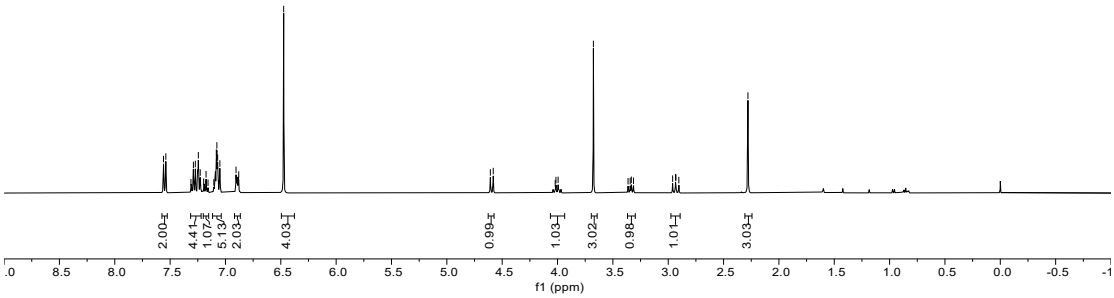
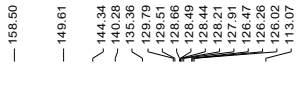
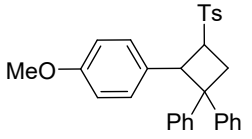


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of **57**





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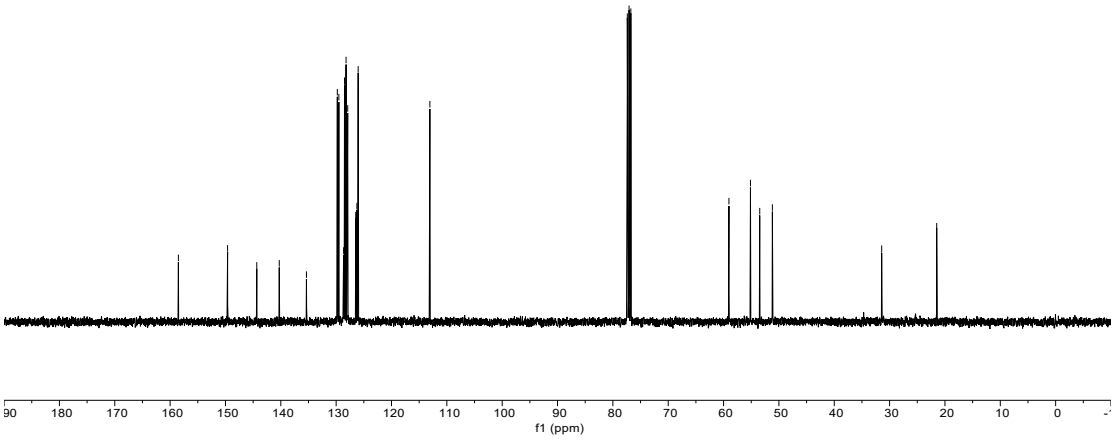
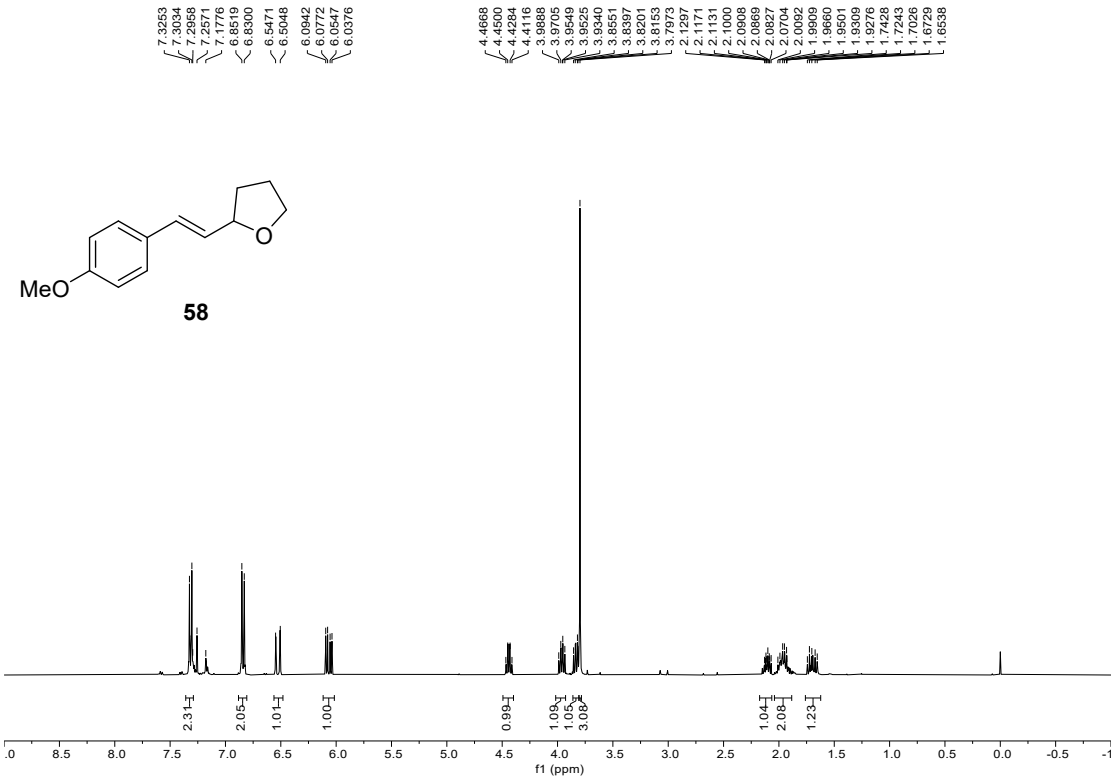


^{1}H NMR ($CDCl_3$, 400 MHz) of **58**



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