Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Et_3N-Promoted Tandem Ring-Opening Reaction of *N*-Tosylaziridines with Terminal Alkynoates: A Straightforward Synthesis of Functionalized Enamines

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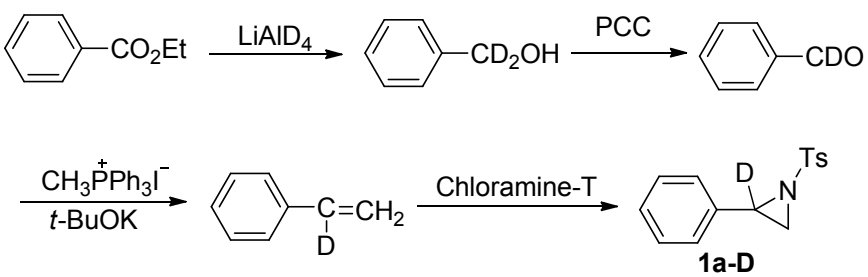
General Remarks

All reactions were conducted in oven-dried glassware with magnetic stirring. Chromatographic purification was performed on silica gel (100–200 mesh) and analytical thin layer chromatography (TLC) on silica gel 60-F_{254} (Qindao), which was detected by fluorescence. ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were measured with a Bruker AC 400 or 300 spectrometer with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet), and br (broad singlet). High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer. IR spectra were recorded as thin films or as solids in KBr pellets on a Perkin-Elmer FT210 spectrophotometer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

Preparation of the Deuterium-Labeled Aziridine 1a-D



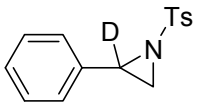
1a-D

To a solution of lithium aluminium deuteride (11.9 mmol) in THF (20 mL) were added a THF solution (15 mL) of ethyl benzoate (22.0 mmol) at room temperature, and the mixture was heated at the reflux temperature under an argon atmosphere for 3 h. The reaction was quenched by the addition of 4 *M* KOH aq. and extraction with ethyl acetate three times furnished an organic layer, which was dried and concentrated. The residue was purified by silica gel chromatography (petroleum ether/EtOAc = 10:1), which furnished benzyl-α,α-d_2 alcohol as a colorless oil.

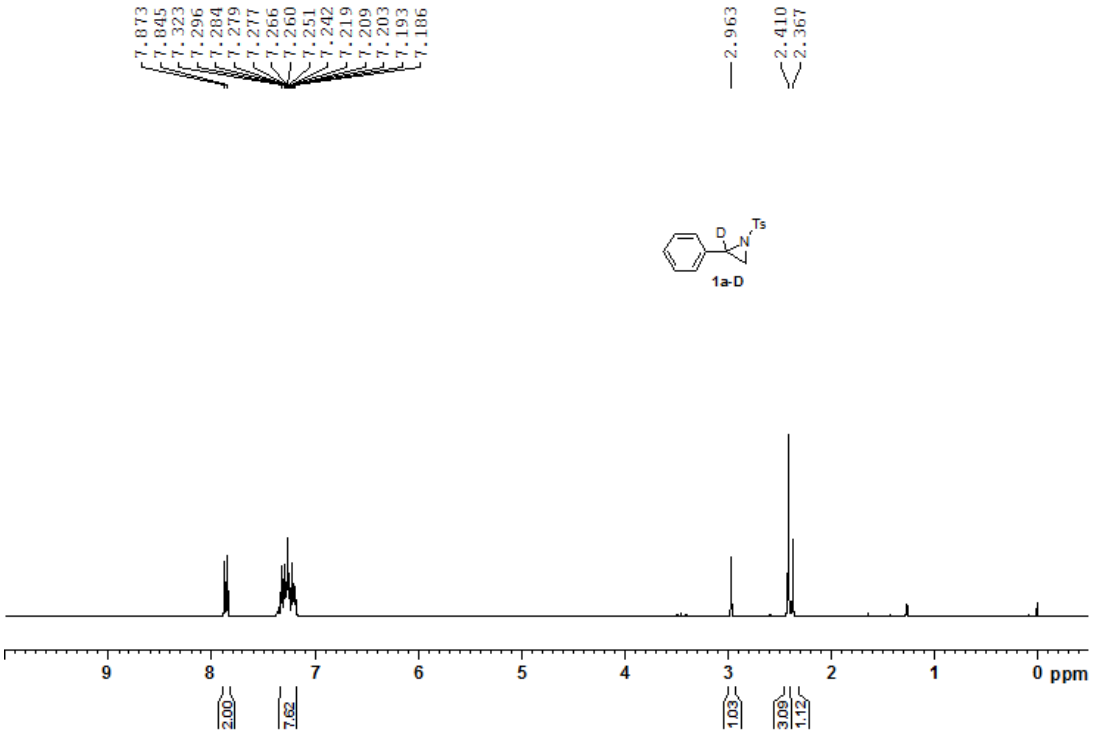
Pyridinium chlorochromate (40 mmol) was added to a stirred solution of benzyl-α,α-d_2 alcohol (19.5 mmol) in CH_2Cl_2 (100 mL), the mixture was then stirred overnight at room temperature. The resulting solution was filtered and the benz(aldehyde-*d*) was obtained as a colorless oil by silica gel chromatography (petroleum ether/EtOAc = 10:1).

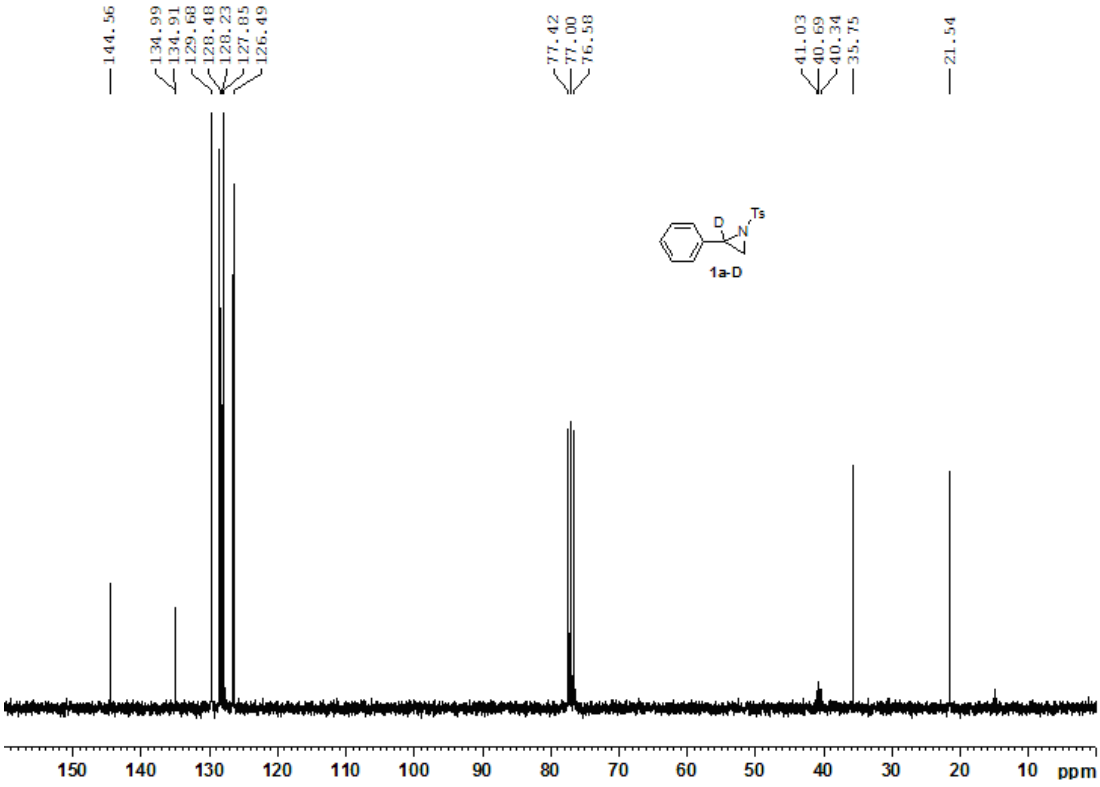
To a 100 mL round-bottomed flask contained ether solution (30 mL) of CH_3PPh_3I (10 mmol) and a magnetic stirring bar under N_2, was added *t*-BuOK (11 mmol) and the mixture was stirred for 3 h, whereupon bright-yellow precipitates formed. Then to the reaction mixture was successively added ether solution of benz(aldehyde-*d*) (10 mmol) and stirred at room temperature overnight and fluxed for 4 h. After the precipitates were filtered off, the resulting clear solution was washed with water, dried over $MgSO_4$. Then the solvent was removed in vacuo and residue was purified by column chromatography on silica gel to afford styrene-α-d_1 as colorless oil.

The styrene-α-d_1 (4.0 mmol) was added to a solution of iodine (0.2 mmol), Chloramine-T (2.0 mmol) in acetonitrile/water solution (1.5 mL/1.5 mL). The solution was stirred overnight at room temperature. Then the solution was diluted by CH_2Cl_2, dried by $MgSO_4$. Purification by flash column chromatography gave the aziridine **1a-D**.



White solid. Mp: 81–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ, 7.87 (d, *J* = 8.4 Hz, 2H), 7.32–7.18 (m, 7H), 2.96 (s, 1H), 2.41 (s, 3H), 2.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ, 144.5, 134.9, 134.9, 129.6, 128.4, 128.2, 127.8, 126.4, 41.0 (t, *J* = 26 Hz), 35.7, 21.5. IR (neat, cm^{-1}): *v* 1608; HRMS (ESI) calcd for $C_{15}H_{14}DNO_2S$ $(M+Na)^+$: 297.0778; Found: 297.0773.


7.873
7.845
7.323
7.296
7.284
7.279
7.277
7.266
7.260
7.251
7.242
7.219
7.209
7.203
7.193
7.186
2.963
2.410
2.367
D
Ts
N
1a-D
9
8
7
6
5
4
3
2
1
0 ppm
2.00
7.62
1.03
3.09
1.12


144.56
134.99
134.91
129.68
128.48
128.23
127.85
126.49
77.42
77.00
76.58
41.03
40.69
40.34
35.75
21.54
D
Ts
N
1a-D
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

Deuterium labeling experimental results, and the effect of water on the reaction by using D_2O

In order to explore the mechanism of Et_3N-promoted the reaction of *N*-tosylaziridines with terminal alkynoates, an isotopic labeling experiment was conducted. The deuterium-labeled 2-phenyl-1-tosylaziridine **1a-D** (>99% D) was subjected to the reaction with ethyl propiolate, but the isotope deuterium was lost in the desired product. So we speculated that the formation of this result was due to the presence of a few water in the reaction system. To prove our hypothesis, 1.0 equiv D_2O was added to the reaction of 2-phenyl-1-tosylaziridine **1a** with ethyl propiolate. We obtained the product enamine in yields comparable to those of the non-deuterated product enamine with 15 and 27% D at α-carbon and β-carbon atoms, respectively, and the ratio of isotope of D was further improved by increasing the amount of D_2O added to the reaction system.

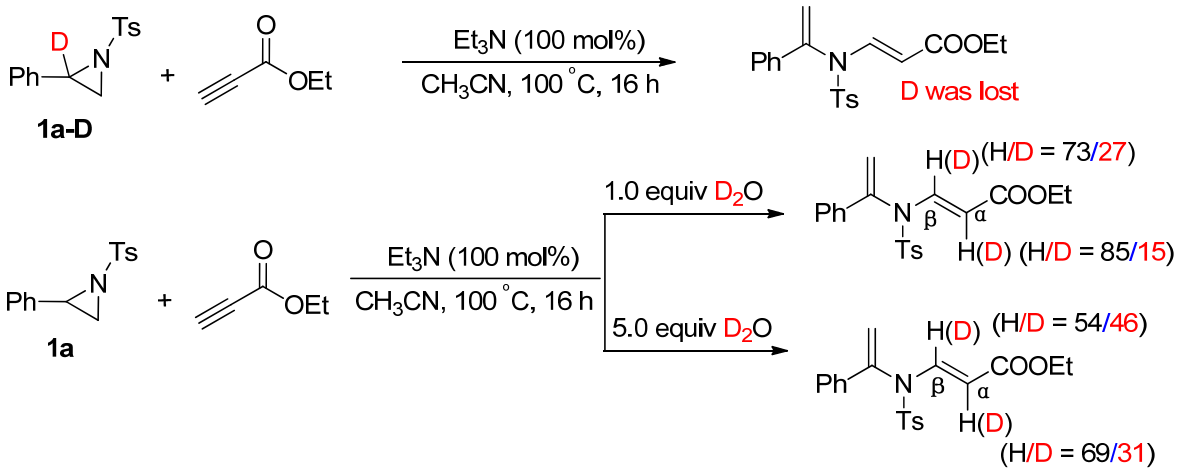
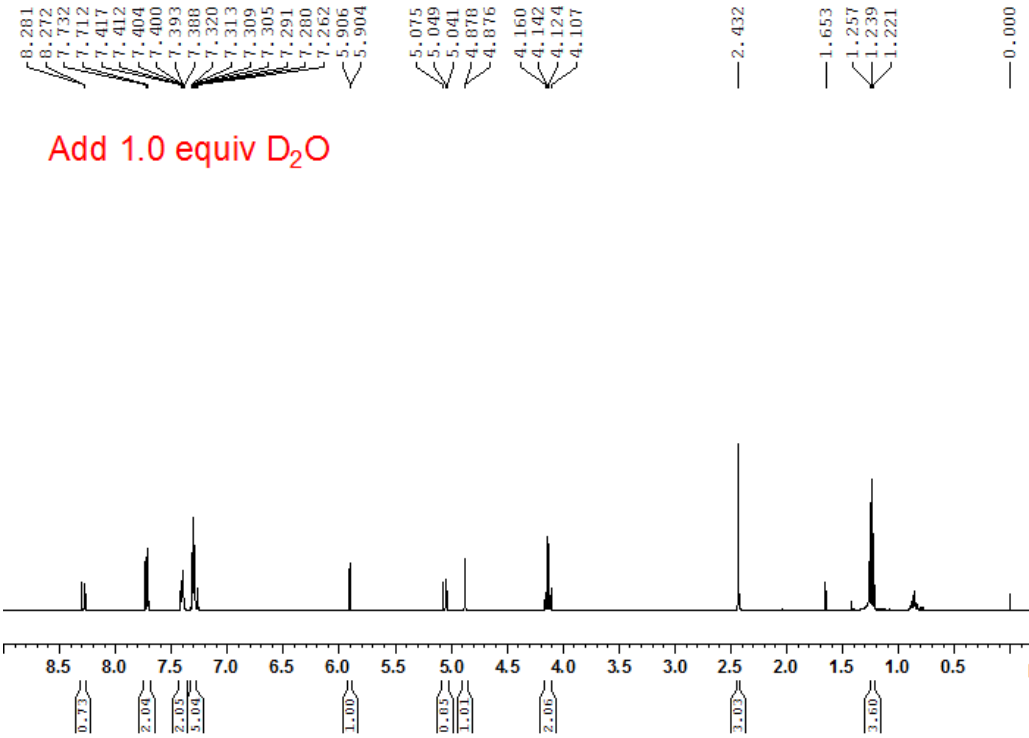
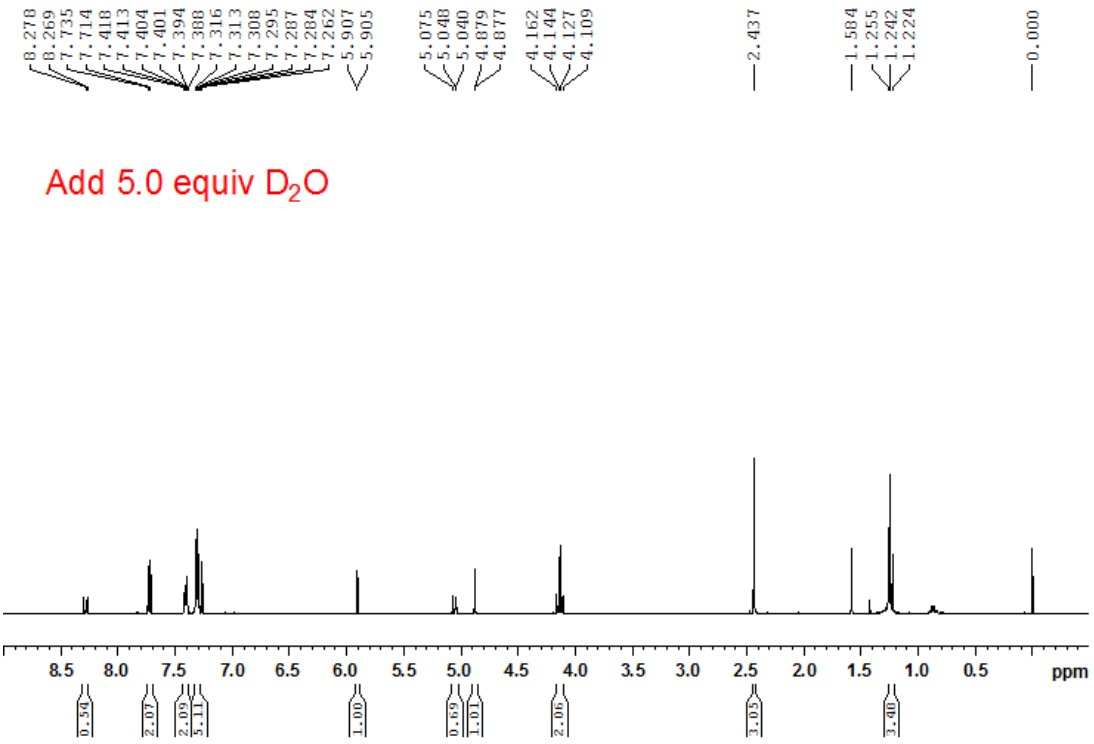


Fig. 1 Deuterium labeling experimental results, and the effect of water on the reaction

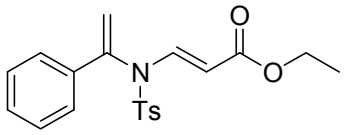

8.281
8.272
7.732
7.712
7.417
7.412
7.404
7.400
7.393
7.388
7.320
7.313
7.309
7.305
7.291
7.280
7.262
5.906
5.904
5.075
5.049
5.041
4.878
4.876
4.160
4.142
4.124
4.107
2.432
1.653
1.257
1.239
1.221
0.000
Add 1.0 equiv D2O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.73
2.04
2.05
5.04
1.00
0.65
1.01
2.06
3.03
3.60


8.278
8.269
7.735
7.714
7.418
7.413
7.404
7.401
7.394
7.388
7.316
7.313
7.308
7.295
7.287
7.284
7.262
5.907
5.905
5.075
5.048
5.040
4.879
4.877
4.162
4.144
4.127
4.109
2.437
1.584
1.255
1.242
1.224
0.000
Add 5.0 equiv D2O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.54
2.07
2.09
5.11
1.00
0.69
1.01
2.06
3.05
3.40

General Procedure for the Tandem Ring-opening Reactions of Aziridines with Terminal Alkynoates Promoted by Et_3N

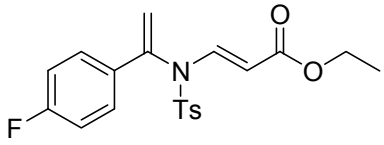
To a solution of aziridines (0.2 mmol) with terminal alkynoates (0.4 mmol) in CH_3CN (2.0 mL) was added Et_3N (28 μL, 0.2 mmol). The mixture was then stirred at 100 °C for 16 h in a reaction flask. Then the solvent was removed in vacuo and residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to give the desired product.

(*E*)-Ethyl 3-(4-methyl-*N*-(1-phenylvinyl)phenylsulfonamido)acrylate (3a)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.30 (d, *J* = 13.6 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.41–7.38 (m, 2H), 7.30–7.25 (m, 5H), 5.90 (d, *J* = 0.8 Hz, 1H), 5.07 (d, *J* = 13.6 Hz, 1H), 4.88 (d, *J* = 0.8 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 167.0, 144.8, 142.4, 141.9, 135.2, 134.0, 129.8, 129.2, 128.6, 127.8, 125.8, 117.3, 100.5, 60.0, 21.5, 14.2. IR (neat, cm^{-1}): *v* 1708, 1621; HRMS (EI) calcd for $C_{20}H_{21}NO_4S$ (M^+): 371.1190; Found: 371.1191.

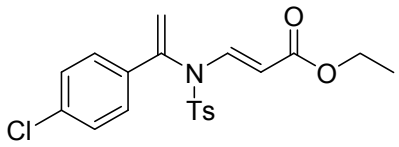
(*E*)-Ethyl 3-(*N*-(1-(4-fluorophenyl)vinyl)-4-methylphenylsulfonamido)acrylate (3b)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.28 (d, *J* = 13.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.41–7.37 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.01–6.96 (m, 2H), 5.83 (d, *J* = 0.8 Hz, 1H), 5.06 (d, *J* = 13.6 Hz, 1H), 4.85 (d, *J* = 0.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.9, 164.5 (d, *J* = 248.3 Hz), 145.0, 142.2, 141.0, 135.1, 130.3 (d, *J* = 3.6 Hz), 129.9, 127.8 (d, *J* = 8.3 Hz), 127.8, 117.1 (d, *J* = 1.7 Hz), 115.8 (d, *J* = 21.8 Hz), 100.6, 60.1, 21.6, 14.2. IR (neat, cm^{-1}): *v* 1707, 1623; HRMS (ESI) calcd

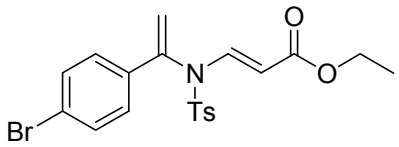
for $C_{20}H_{20}FNO_4S$ $(M+H)^+$: 390.1169; Found: 390.1173.

(*E*)-Ethyl 3-(*N*-(1-(4-chlorophenyl)vinyl)-4-methylphenylsulfonamido)acrylate (3c)



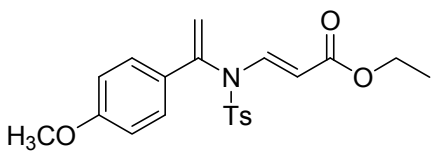
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.28 (d, *J* = 13.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.35–7.25 (m, 6H), 5.89 (d, *J* = 0.8 Hz, 1H), 5.04 (d, *J* = 13.6 Hz, 1H), 4.90 (d, *J* = 0.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.9, 145.1, 142.2, 141.0, 135.3, 135.0, 132.6, 130.0, 128.8, 127.8, 127.1, 117.8, 100.6, 60.1, 21.6, 14.2. IR (neat, cm^{-1}): *v* 1708, 1622; HRMS (ESI) calcd for $C_{20}H_{20}{}^{35}ClNO_4S$ $(M+H)^+$: 406.0874; Found: 406.0875.

(*E*)-Ethyl 3-(*N*-(1-(4-bromophenyl)vinyl)-4-methylphenylsulfonamido)acrylate (3d)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.28 (d, *J* = 13.6 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.32–7.26 (m, 4H), 5.91 (d, *J* = 0.8 Hz, 1H), 5.04 (d, *J* = 13.6 Hz, 1H), 4.90 (d, *J* = 0.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.8, 145.1, 142.2, 141.0, 135.0, 133.0, 131.8, 130.0, 127.8, 127.4, 123.5, 117.9, 100.6, 60.1, 21.6, 14.3. IR (neat, cm^{-1}) *v* 1707, 1621; HRMS (ESI) calcd for $C_{20}H_{20}{}^{79}BrNO_4S$ $(M+H)^+$: 450.0369; Found: 450.0375.

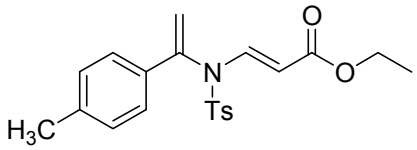
(*E*)-Ethyl 3-(*N*-(1-(4-methoxyphenyl)vinyl)-4-methylphenylsulfonamido)acrylate (3e)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.29 (d, *J* = 13.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.36–7.27 (m, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.76 (d, *J* = 0.8 Hz, 1H), 5.08 (d, *J* = 13.6 Hz,

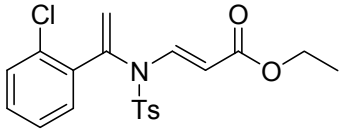
1H), 4.73 (d, *J* = 0.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 2.44 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 167.1, 160.4, 144.8, 142.4, 141.6, 135.3, 129.8, 127.8, 127.3, 126.5, 115.0, 114.0, 100.4, 60.0, 55.3, 21.5, 14.2. IR (neat, cm^{-1}) *v* 1707, 1621; HRMS (ESI) calcd for $C_{21}H_{23}NO_5S$ $(M+H)^+$: 402.1369; Found: 402.1371.

(*E*)-Ethyl 3-(4-methyl-*N*-(1-p-tolylvinyl)phenylsulfonamido)acrylate (3f)



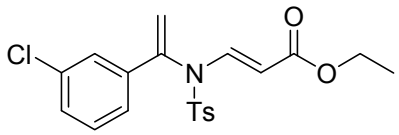
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.30 (d, *J* = 13.6 Hz, 1H), 7.74–7.72 (m, 2H), 7.33–7.29 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.85 (d, *J* = 0.8 Hz, 1H), 5.08 (d, *J* = 13.6 Hz, 1H), 4.81 (d, *J* = 0.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.33 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 167.0, 144.8, 142.4, 141.9, 139.3, 135.3, 131.1, 129.8, 129.3, 127.8, 125.7, 116.1, 100.4, 60.0, 21.5, 21.1, 14.2. IR (neat, cm^{-1}) *v* 1706, 1621; HRMS (ESI) calcd for $C_{21}H_{23}NO_4S$ $(M+H)^+$: 386.1420; Found: 386.1432.

(*E*)-Ethyl 3-(*N*-(1-(2-chlorophenyl)vinyl)-4-methylphenylsulfonamido)acrylate (3g)



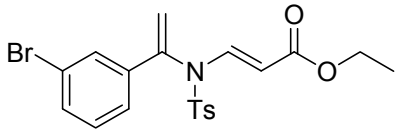
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.25 (d, *J* = 13.6 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.41–7.32 (m, 2H), 7.28–7.20 (m, 4H), 5.91 (s, 1H), 5.40 (d, *J* = 13.6 Hz, 1H), 5.28 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 167.2, 144.8, 142.7, 138.3, 135.0, 134.1, 132.6, 130.4, 130.2, 129.8, 129.7, 127.7, 126.9, 123.9, 100.7, 60.1, 21.6, 14.3. IR (neat, cm^{-1}) *v* 1708, 1621; HRMS (ESI) calcd for $C_{20}H_{20}{}^{35}ClNO_4S$ $(M+H)^+$: 406.0874; Found: 406.0880.

(*E*)-Ethyl 3-(*N*-(1-(3-chlorophenyl)vinyl)-4-methylphenylsulfonamido)acrylate (3h)



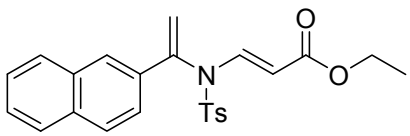
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.29 (d, *J* = 13.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.32–7.23 (m, 6H), 5.93 (d, *J* = 0.8 Hz, 1H), 5.05 (d, *J* = 13.6 Hz, 1H), 4.99 (d, *J* = 0.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ, 166.9, 145.2, 142.2, 140.7, 135.9, 134.9, 134.7, 130.0, 129.9, 129.3, 127.8, 125.8, 124.1, 118.9, 100.6, 60.2, 21.6, 14.2. IR (neat, cm^{-1}) *v* 1708, 1621; HRMS (ESI) calcd for $C_{20}H_{20}{}^{35}ClNO_4S$ $(M+H)^+$: 406.0874; Found: 406.0881.

(*E*)-Ethyl 3-(*N*-(1-(3-bromophenyl)vinyl)-4-methylphenylsulfonamido)acrylate (3i)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.28 (d, *J* = 13.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.39–7.37 (m, 2H), 7.34–7.28 (m, 3H), 7.17 (t, *J* = 8.0 Hz, 1H), 5.92 (d, *J* = 0.8 Hz, 1H), 5.04 (d, *J* = 13.6 Hz, 1H), 4.98 (d, *J* = 0.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.7, 145.1, 142.0, 140.4, 136.0, 134.7, 132.0, 130.0, 129.9, 128.5, 127.6, 124.4, 122.7, 119.0, 100.4, 60.2, 21.5, 14.1. IR (neat, cm^{-1}) *v* 1707, 1621; HRMS (ESI) calcd for $C_{20}H_{20}{}^{79}BrNO_4S$ $(M+H)^+$: 450.0369; Found: 450.0373.

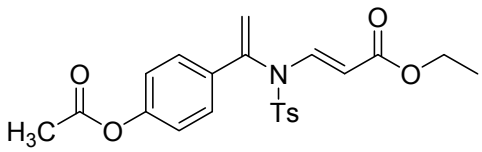
(*E*)-Ethyl 3-(4-methyl-*N*-(1-(naphthalen-2-yl)vinyl)phenylsulfonamido)acrylate (3j)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.40 (d, *J* = 13.6 Hz, 1H), 7.79–7.69 (m, 6H), 7.39–7.37 (m, 2H), 7.57 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.49–7.46 (m, 2H), 7.28–7.26 (m, 2H), 6.06 (d, *J* = 0.8 Hz, 1H), 5.13 (d, *J* = 13.6 Hz, 1H), 5.04 (d, *J* = 0.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.39

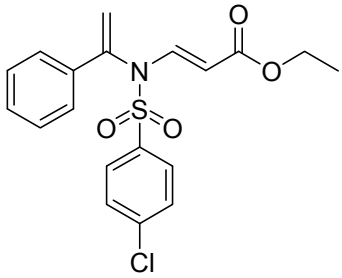
(s, 3H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 167.1, 144.9, 142.5, 141.9, 135.3, 133.5, 133.0, 131.0, 129.9, 128.6, 128.5, 127.9, 127.5, 126.8, 126.5, 125.6, 123.0, 117.9, 100.5, 60.1, 21.5, 14.2. IR (neat, cm^{-1}) v 1706, 1619; HRMS (ESI) calcd for $C_{24}H_{23}NO_4S$ $(M+H)^+$: 422.1420; Found: 422.1428.

(*E*)-Ethyl 3-(*N*-(1-(4-acetoxyphenyl)vinyl)-4-methylphenylsulfonamido)acrylate (3k)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.29 (d, J = 13.6 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 5.87 (d, J = 0.8 Hz, 1H), 5.07 (d, J = 13.6 Hz, 1H), 4.89 (d, J = 0.8 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 168.9, 166.9, 151.3, 145.0, 142.2, 135.0, 131.6, 129.9, 127.8, 127.8, 127.0, 121.7,117.5, 100.5, 60.1, 21.5, 21.0, 14.2. IR (neat, cm^{-1}) v 1763, 1708, 1621; HRMS (ESI) calcd for $C_{22}H_{23}NO_6S$ $(M+H)^+$: 430.1318; Found: 430.1322.

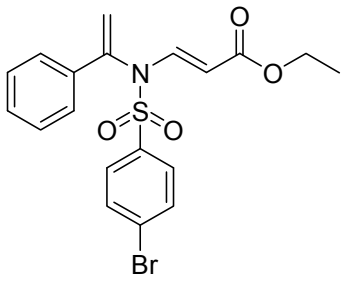
(*E*)-Ethyl 3-(4-chloro-*N*-(1-phenylvinyl)phenylsulfonamido)acrylate (3l)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.28 (d, J = 13.6 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.39–7.37 (m, 2H), 7.33–7.27 (m, 3H), 5.95 (s, 1H), 5.14 (d, J = 13.6 Hz, 1H), 4.93 (s, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.8, 141.9, 141.7, 140.4, 136.5, 133.6, 129.5, 129.3, 129.1, 128.6, 125.7, 117.6, 101.1, 60.1, 14.2. IR (neat, cm^{-1}) v 1705, 1622; HRMS (ESI) calcd for $C_{19}H_{18}{}^{35}ClNO_4S$ $(M+Na)^+$:

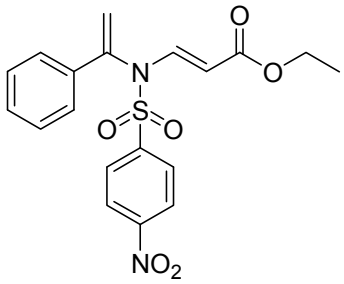
414.0537; Found: 414.0540.

(*E*)-Ethyl 3-(4-bromo-*N*-(1-phenylvinyl)phenylsulfonamido)acrylate (3m)



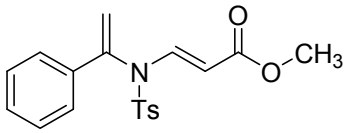
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.27 (d, *J* = 13.6 Hz, 1H), 7.69-7.62 (m, 4H), 7.38–7.28 (m, 4H), 5.94 (d, *J* = 0.8 Hz, 1H), 5.14 (d, *J* = 13.6 Hz, 1H), 4.92 (d, *J* = 0.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.7, 141.9, 141.7, 137.0, 133.6, 132.5, 129.4, 129.2, 129.0, 128.6, 125.7,117.6, 101.2, 60.1, 14.2. IR (neat, cm^{-1}) *v* 1706, 1621; HRMS (ESI) calcd for $C_{19}H_{18}{}^{79}BrNO_4S$ $(M+Na)^+$: 458.0032; Found: 458.0014.

(*E*)-Ethyl 3-(4-nitro-*N*-(1-phenylvinyl)phenylsulfonamido)acrylate (3n)



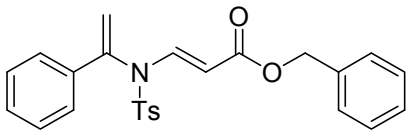
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.33 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 13.6 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.35–7.28 (m, 4H), 5.97 (d, *J* = 0.8 Hz, 1H), 5.22 (d, *J* = 13.6 Hz, 1H), 4.96 (d, *J* = 0.8 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.5, 150.5, 143.6, 141.6, 141.5, 133.4, 129.6, 129.1, 128.8, 125.8, 124.4,118.1, 102.3, 60.4, 14.2. IR (neat, cm^{-1}) *v* 1704, 1620; HRMS (ESI) calcd for $C_{19}H_{18}N_2O_6S$ $(M+Na)^+$: 425.0777; Found: 425.0760.

(*E*)-Methyl 3-(4-methyl-*N*-(1-phenylvinyl)phenylsulfonamido)acrylate (3o)



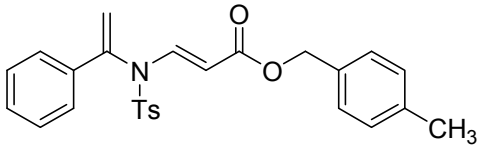
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.32 (d, J = 13.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.41–7.38 (m, 2H), 7.32–7.27 (m, 5H), 5.91 (s, 1H), 5.08 (d, J = 13.6 Hz, 1H), 4.89 (s, 1H), 3.68 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 167.4, 144.9, 142.6, 141.9, 135.2, 133.9, 129.9, 129.2, 128.6, 127.8, 125.7, 117.3, 100.0, 51.2, 21.5. IR (neat, cm^{-1}) v 1715, 1621; HRMS (ESI) calcd for $C_{19}H_{19}NO_4S$ $(M+H)^+$: 358.1107; Found: 358.1105.

(*E*)-Benzyl 3-(4-methyl-*N*-(1-phenylvinyl)phenylsulfonamido)acrylate (3p)



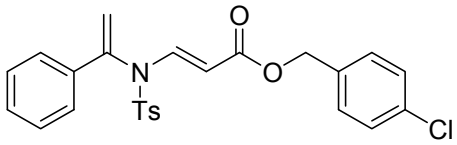
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.36 (d, J = 13.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.41–7.30 (m, 12H), 5.91 (s, 1H), 5.13 (s, 2H), 5.13 (d, J = 13.6 Hz, 1H), 4.89 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.9, 144.9, 142.9, 141.9, 136.1, 135.2, 133.9, 129.9, 129.3, 128.6, 128.5, 128.2, 128.1, 127.9, 125.8, 117.3, 100.0, 65.9, 21.6. IR (neat, cm^{-1}) v 1706, 1621; HRMS (ESI) calcd for $C_{25}H_{23}NO_4S$ $(M+H)^+$: 434.1420; Found: 434.1413.

(*E*)-4-Methylbenzyl 3-(4-methyl-*N*-(1-phenylvinyl)phenylsulfonamido)acrylate (3q)



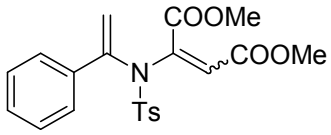
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.36 (d, J = 13.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.42–7.39 (m, 2H), 7.33–7.27 (m, 5H), 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.91 (s, 1H), 5.13 (d, J = 13.6 Hz, 1H), 5.10 (s, 2H), 4.89 (s, 1H), 2.44 (s, 3H) , 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.9, 144.9, 142.9, 138.0, 133.9, 133.1, 129.9, 129.3, 129.2, 128.6, 128.4, 127.9, 127.9, 126.5, 125.8, 117.3, 100.1, 65.9, 21.6, 21.1. IR (neat, cm^{-1}) v 1708, 1621; HRMS (ESI) calcd for $C_{26}H_{25}NO_4S$ $(M+H)^+$: 448.1577; Found: 448.1578.

(*E*)-4-Chlorobenzyl 3-(4-methyl-*N*-(1-phenylvinyl)phenylsulfonamido)acrylate (3r)

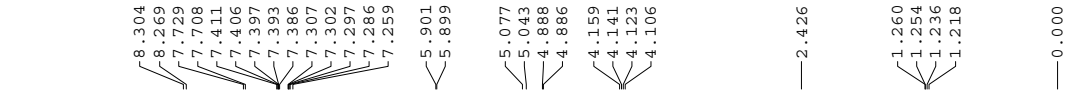


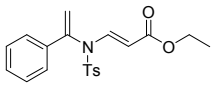
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 8.36 (d, *J* = 13.6 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.41–7.27 (m, 11H), 5.91 (s, 1H), 5.11 (d, *J* = 13.6 Hz, 1H), 5.09 (s, 2H), 4.89 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 166.8, 145.0, 143.1, 141.9, 134.7, 129.9, 129.7, 129.6, 129.3, 128.6, 128.5, 127.9, 127.9, 126.5, 125.8, 117.4, 99.6, 65.1, 21.6. IR (neat, cm^{-1}) *v* 1712, 1620; HRMS (ESI) calcd for $C_{25}H_{22}{}^{35}ClNO_4S$ $(M+H)^+$: 468.1030; Found: 468.1014.

Dimethyl 2-(4-methyl-*N*-(1-phenylvinyl)phenylsulfonamido)maleate (3s)

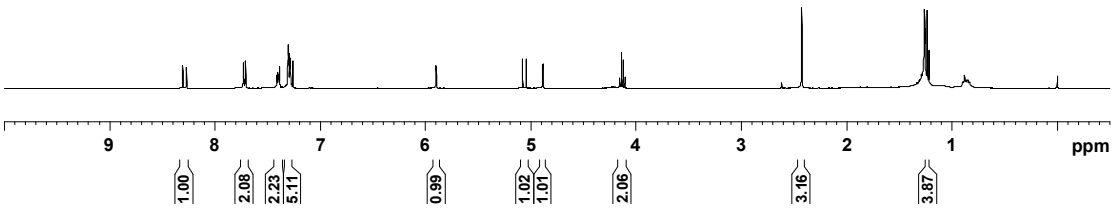


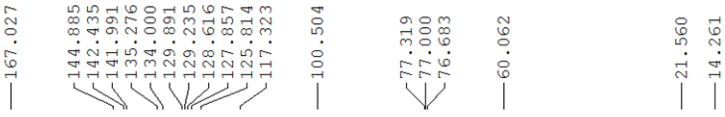
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, 7.86 (d, *J* = 13.6 Hz, 2H), 7.53–7.50 (m, 2H), 7.32–7.27 (m, 5H), 5.89 (s, 1H), 5.56 (m, 1H), 5.13 (s, 1H), 3.98 (s, 3H), 3.62 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ, 165.3, 164.2, 145.1, 145.0, 142.9, 135.1, 134.1, 129.7, 129.3, 128.6, 128.5, 126.0, 117.2, 106.9, 53.2, 51.7, 21.6. IR (neat, cm^{-1}) *v* 1746, 1717, 1602; HRMS (ESI) calcd for $C_{21}H_{21}NO_6S$ $(M+H)^+$: 416.1162; Found: 416.1167.


8.304
8.269
7.729
7.708
7.411
7.406
7.397
7.393
7.386
7.307
7.302
7.297
7.286
7.259
5.901
5.899
5.077
5.043
4.888
4.886
4.159
4.141
4.123
4.106
2.426
1.260
1.254
1.236
1.218
0.000


O
N
Ts
O

3a


9
8
7
6
5
4
3
2
1
ppm
1.00
2.08
2.23
5.11
0.99
1.02
1.01
2.06
3.16
3.87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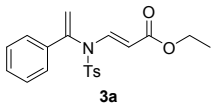
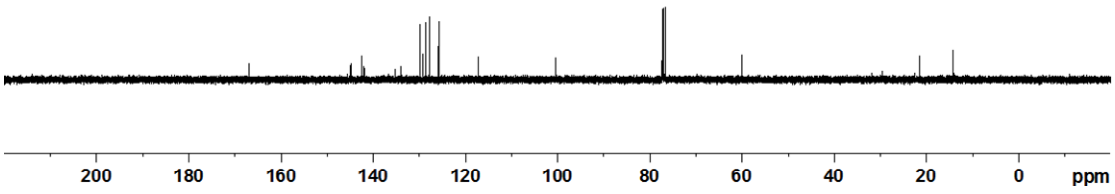
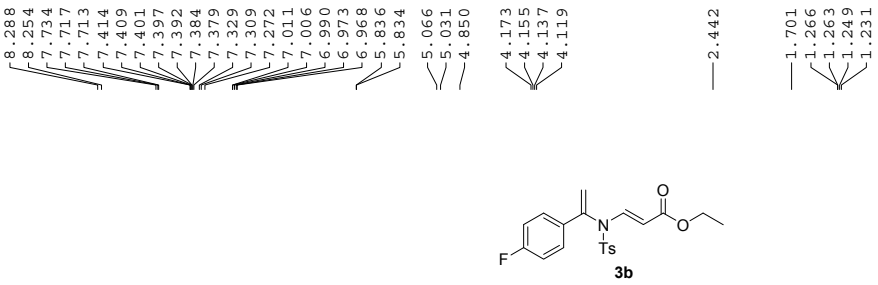
142.435
141.991
135.276
134.000
129.891
129.235
128.616
127.857
125.814
117.323
100.504
77.319
77.000
76.683
60.062
21.560
14.261


O
N
Ts
O

3a


200
180
160
140
120
100
80
60
40
20
0
ppm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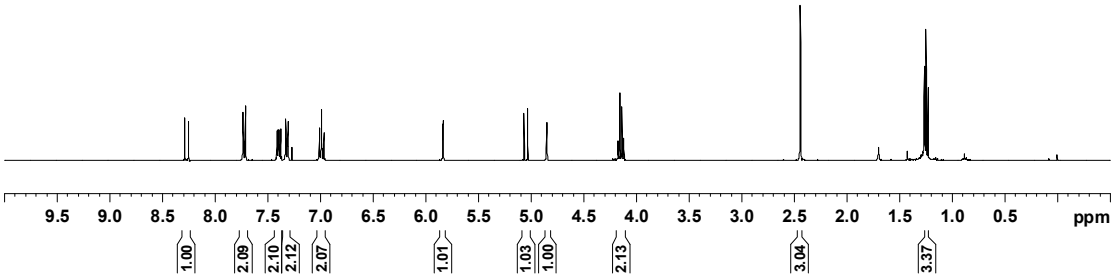
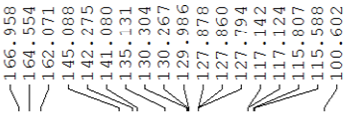
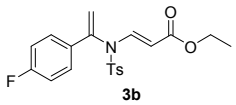
8.254
7.734
7.717
7.713
7.414
7.409
7.401
7.397
7.392
7.384
7.379
7.329
7.309
7.272
7.011
7.006
6.990
6.973
6.968
5.836
5.834
5.066
5.031
4.850
4.173
4.155
4.137
4.119
2.442
1.701
1.266
1.263
1.249
1.231

O
N
Ts
O
F

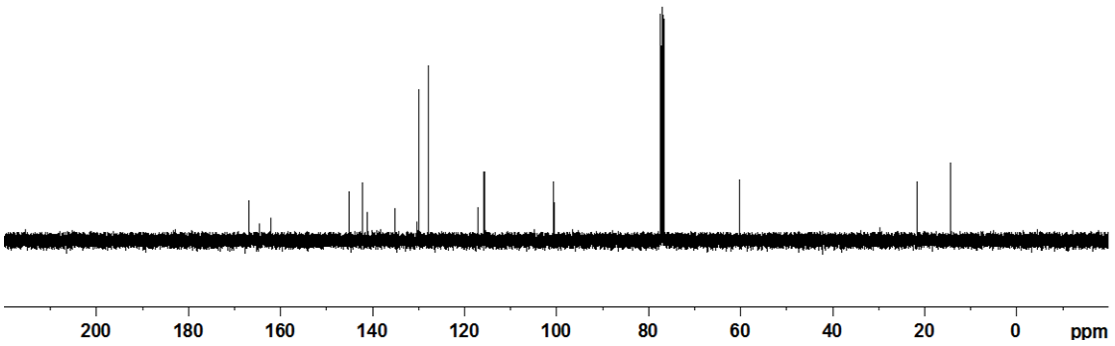
3b

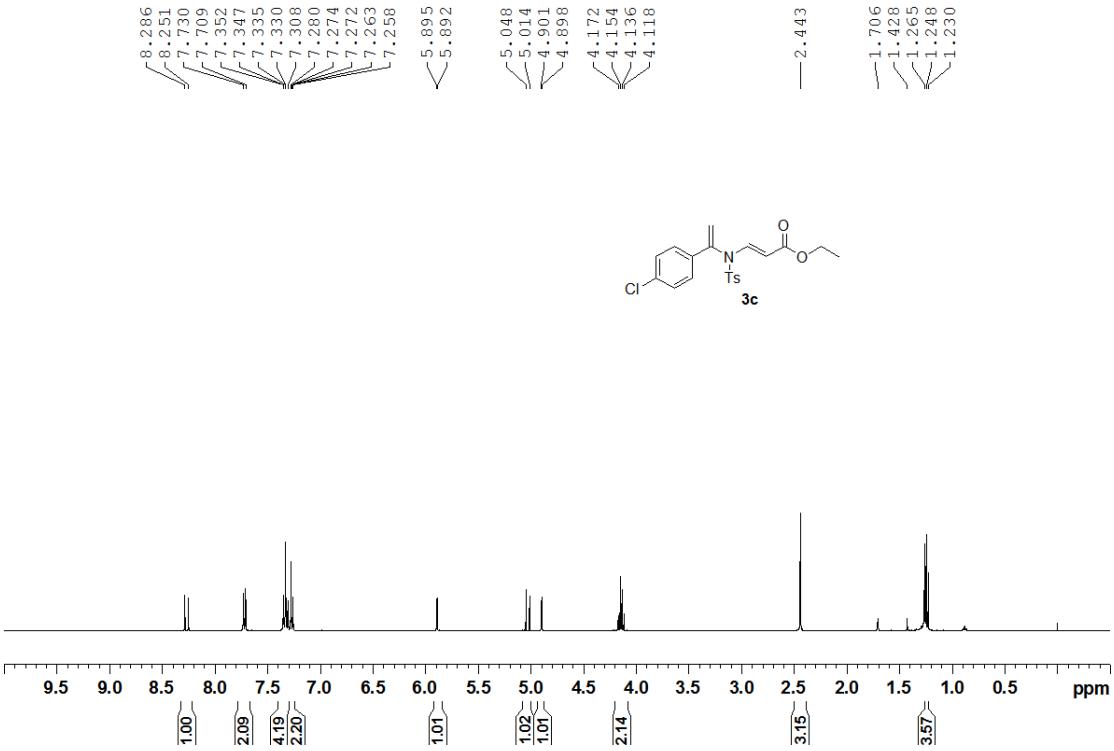

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.09
2.10
2.12
2.07
1.01
1.03
1.00
2.13
3.04
3.37

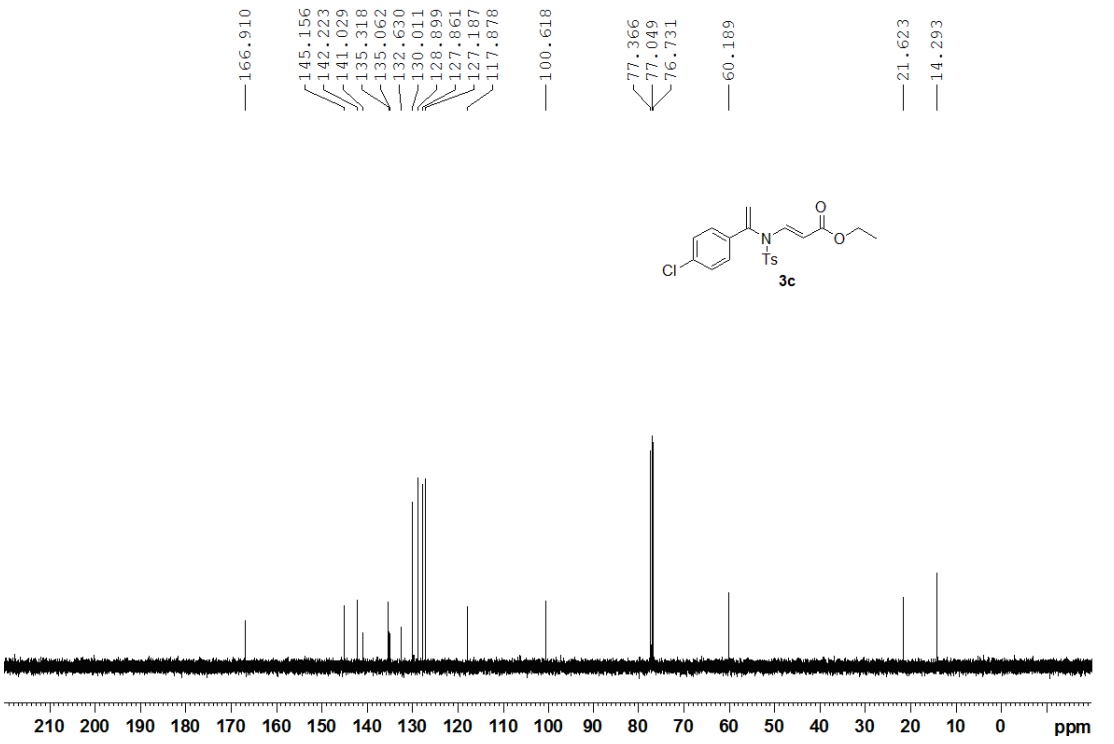

166.958
164.554
162.071
145.088
142.275
141.080
135.131
130.304
130.267
129.986
127.878
127.860
127.794
117.142
117.124
115.807
115.588
100.602
77.356
77.038
76.720
60.172
21.610
14.290


O
N
Ts
O
F

3b


200
180
160
140
120
100
80
60
40
20
0
ppm


8.286
8.251
7.730
7.709
7.352
7.347
7.335
7.330
7.308
7.280
7.274
7.272
7.263
7.258
5.895
5.892
5.048
5.014
4.901
4.898
4.172
4.154
4.136
4.118
2.443
1.706
1.428
1.265
1.248
1.230
Cl
N
Ts
O
O
3c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.09
4.19
2.20
1.01
1.02
1.01
2.14
3.15
3.57


166.910
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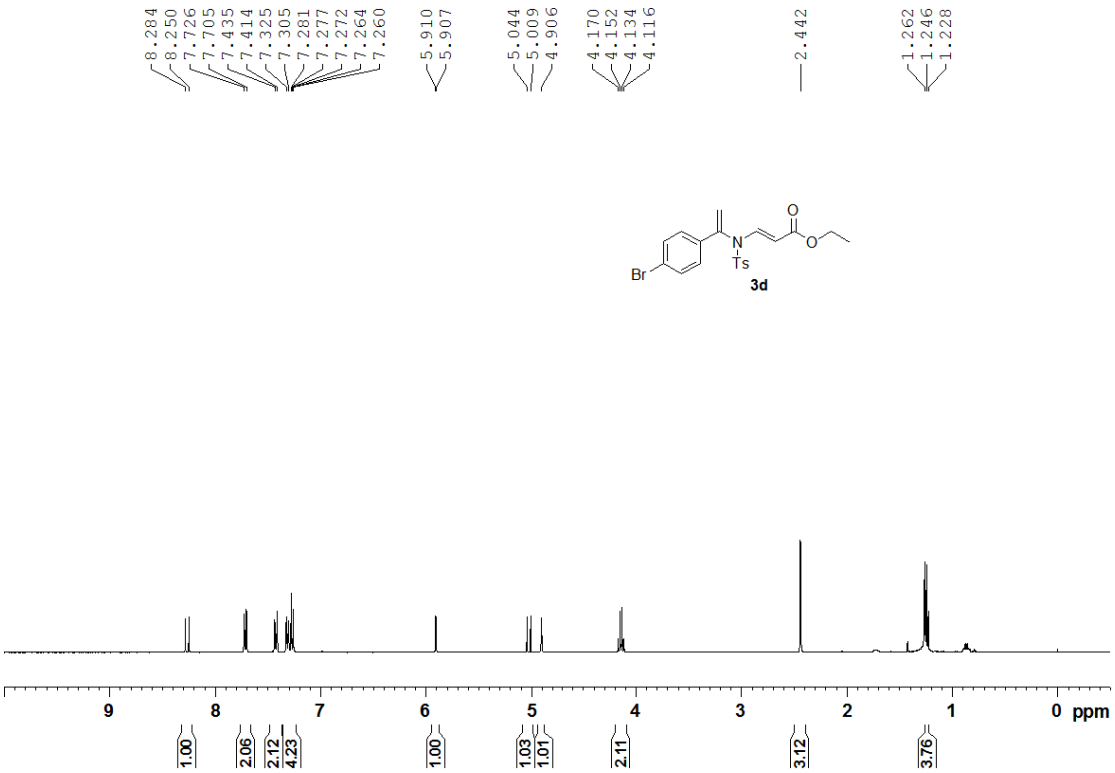
135.318
135.062
132.630
130.011
128.899
127.861
127.187
117.878
100.618
77.366
77.049
76.731
60.189
21.623
14.293
Cl
N
Ts
O
O
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.435
7.414
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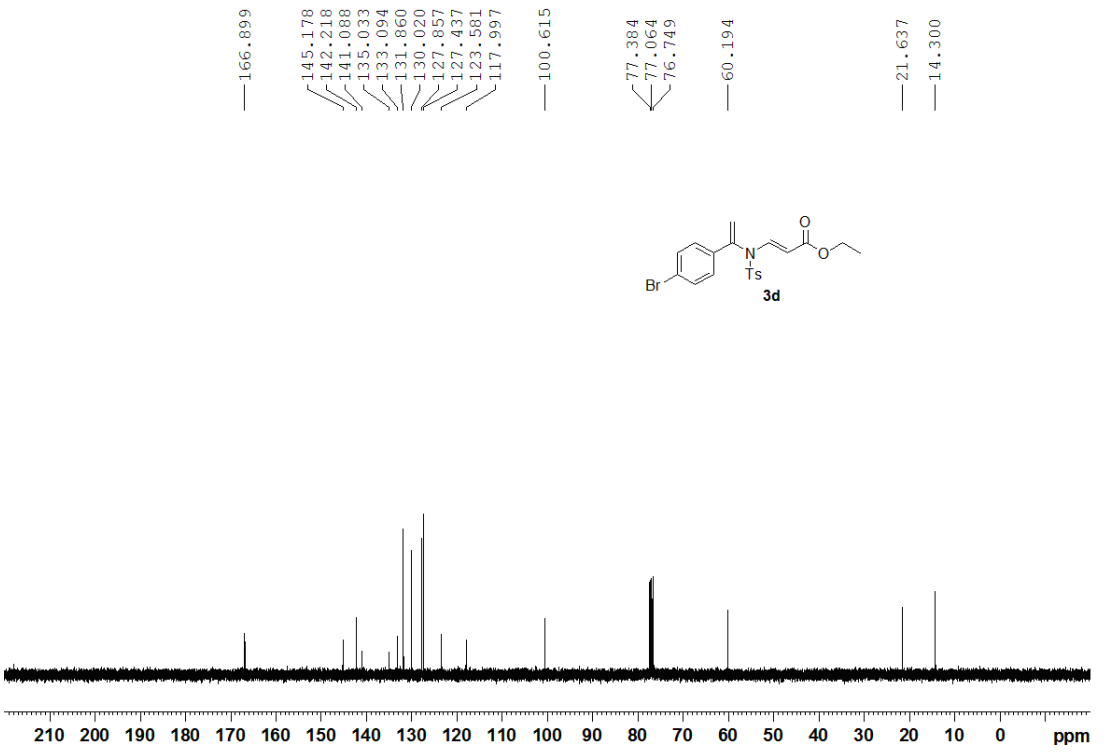
7.305
7.281
7.277
7.272
7.264
7.260
5.910
5.907
5.044
5.009
4.906
4.170
4.152
4.134
4.116
2.442
1.262
1.246
1.228
Br
N
Ts
O
O
3d
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.06
2.12
4.23
1.00
1.03
1.01
2.11
3.12
3.76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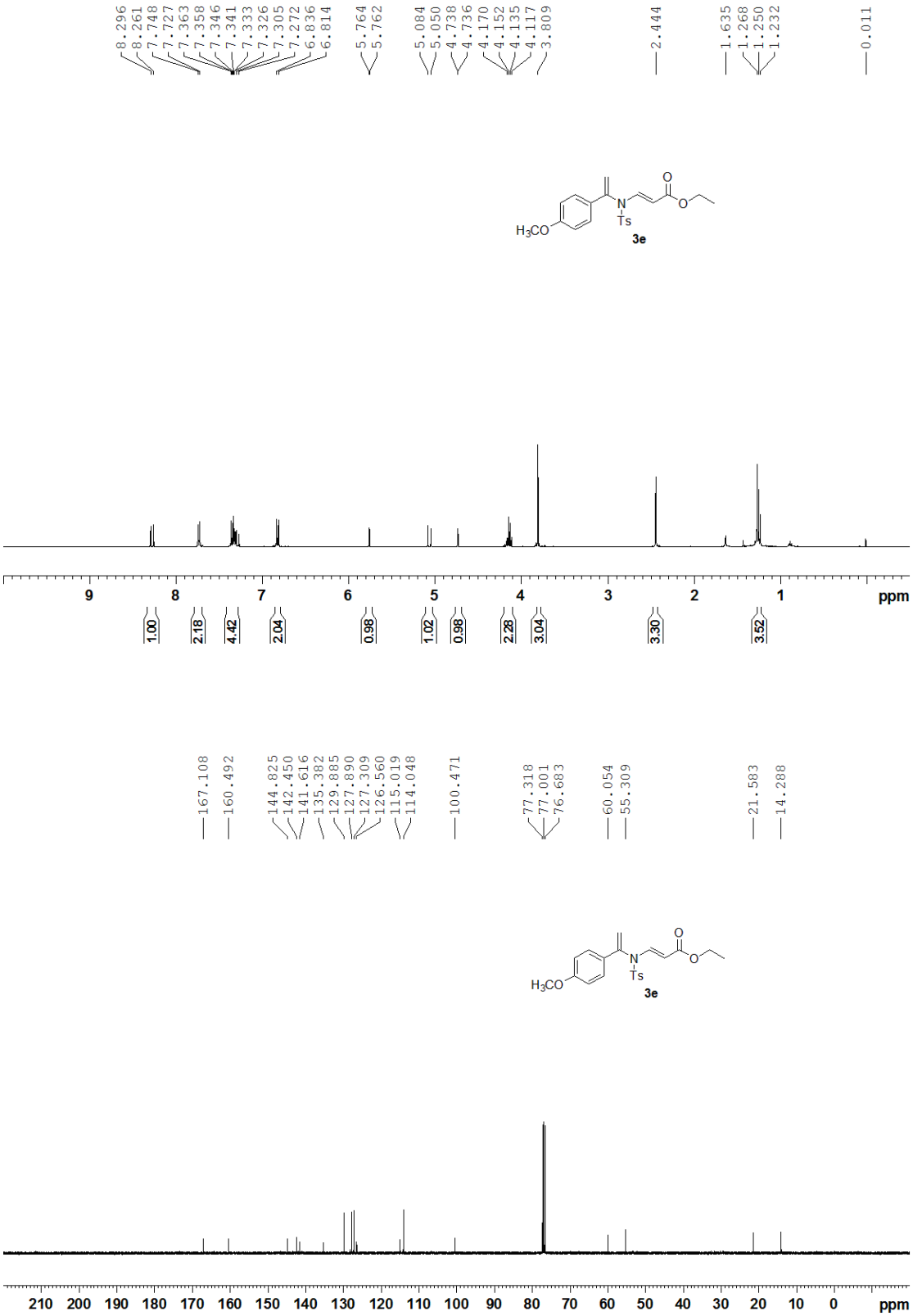
131.860
130.020
127.857
127.437
123.581
117.997
100.615
77.384
77.064
76.749
60.194
21.637
14.300
Br
N
Ts
O
O
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.727
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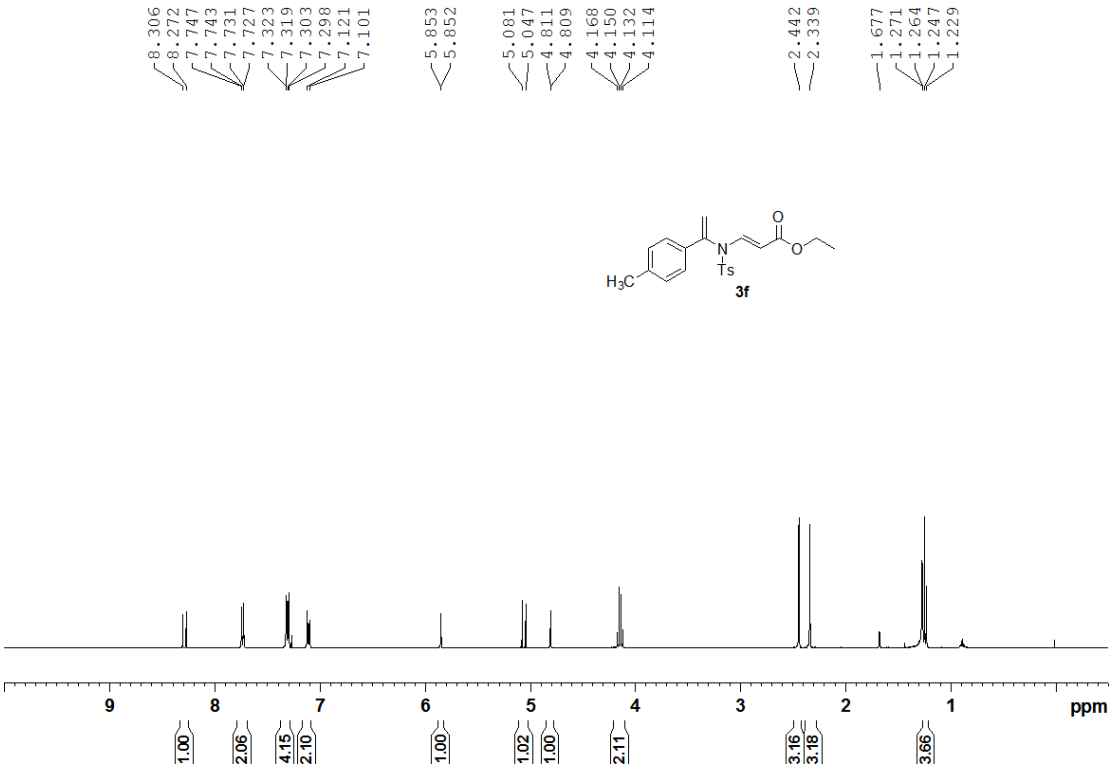
7.341
7.333
7.326
7.305
7.272
6.836
6.814
5.764
5.762
5.084
5.050
4.738
4.736
4.170
4.152
4.135
4.117
3.809
2.444
1.635
1.268
1.250
1.232
0.011
H3CO
N
Ts
O
O
3e
9
8
7
6
5
4
3
2
1
ppm
1.00
2.18
4.42
2.04
0.98
1.02
0.98
2.28
3.04
3.30
3.52
167.108
160.492
144.825
142.450
141.616
135.382
129.885
127.890
127.309
126.560
115.019
114.048
100.471
77.318
77.001
76.683
60.054
55.309
21.583
14.288
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.323
7.319
7.303
7.298
7.121
7.101
5.853
5.852
5.081
5.047
4.811
4.809
4.168
4.150
4.132
4.114
2.442
2.339
1.677
1.271
1.264
1.247
1.229
H3C
N
Ts
O
O
3f
9
8
7
6
5
4
3
2
1
ppm
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4.15
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1.00
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1.00
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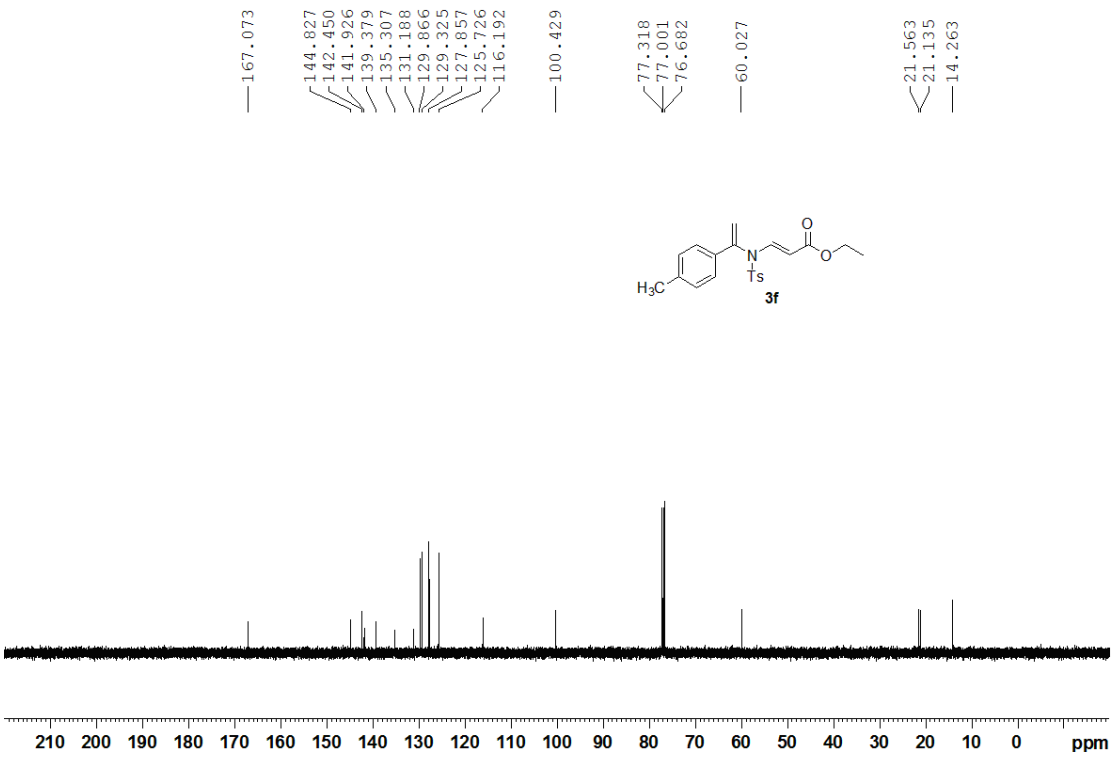
3.16
3.18
3.66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144.827
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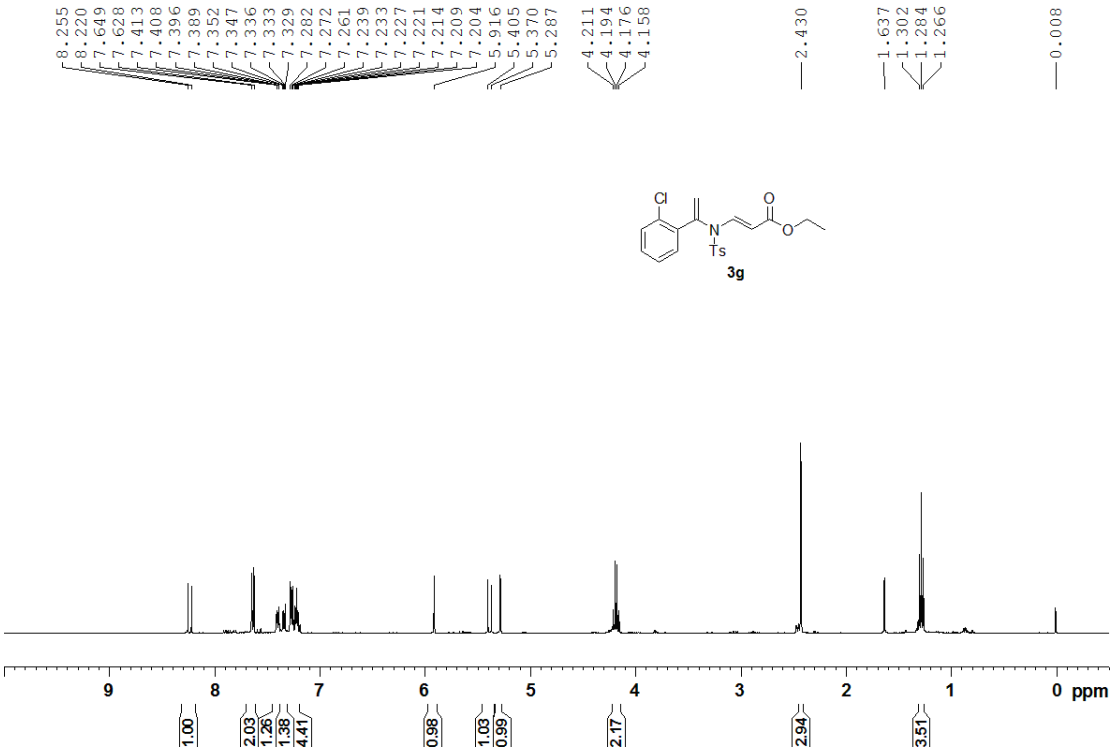
131.188
129.866
129.325
127.857
125.726
116.192
100.429
77.318
77.001
76.682
60.027
21.563
21.135
14.263
H3C
N
Ts
O
O
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.220
7.649
7.628
7.413
7.408
7.396
7.389
7.352
7.347
7.336
7.333
7.329
7.282
7.272
7.261
7.239
7.233
7.227
7.221
7.214
7.209
7.204
5.916
5.405
5.370
5.287
4.211
4.194
4.176
4.158
2.430
1.637
1.302
1.284
1.266
0.008
Cl
N
Ts
O
O
3g
9
8
7
6
5
4
3
2
1
0 ppm
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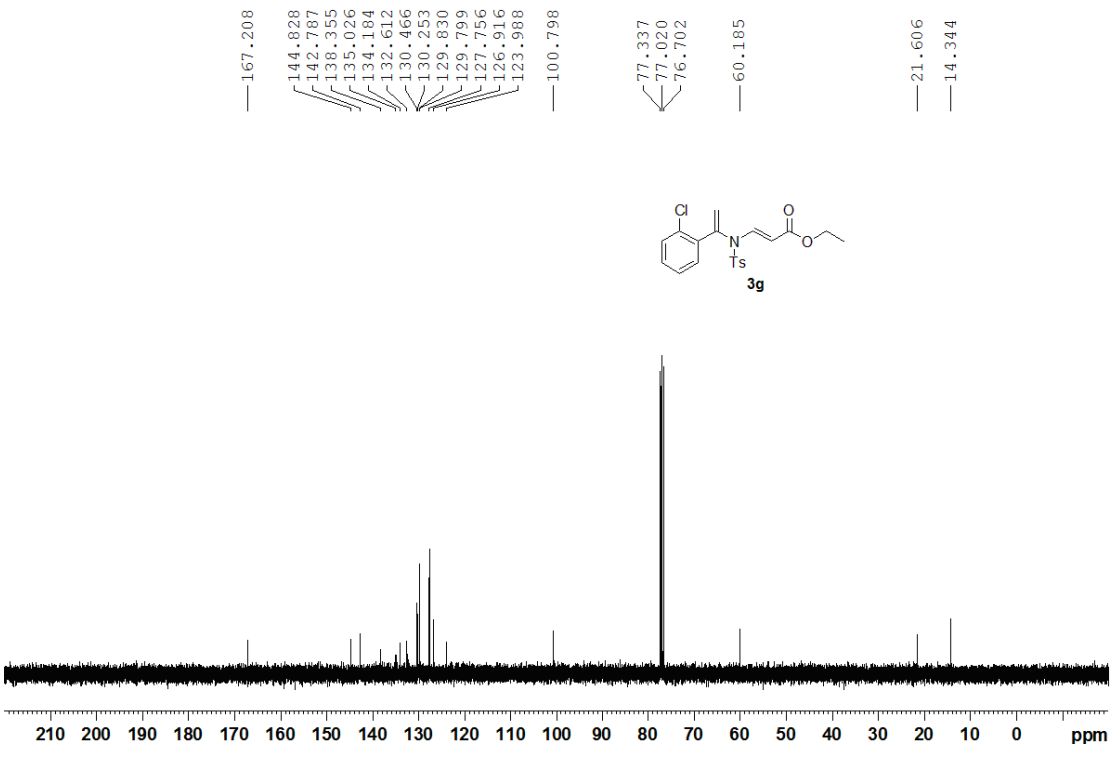
2.03
1.26
1.38
4.41
0.98
1.03
0.99
2.17
2.94
3.51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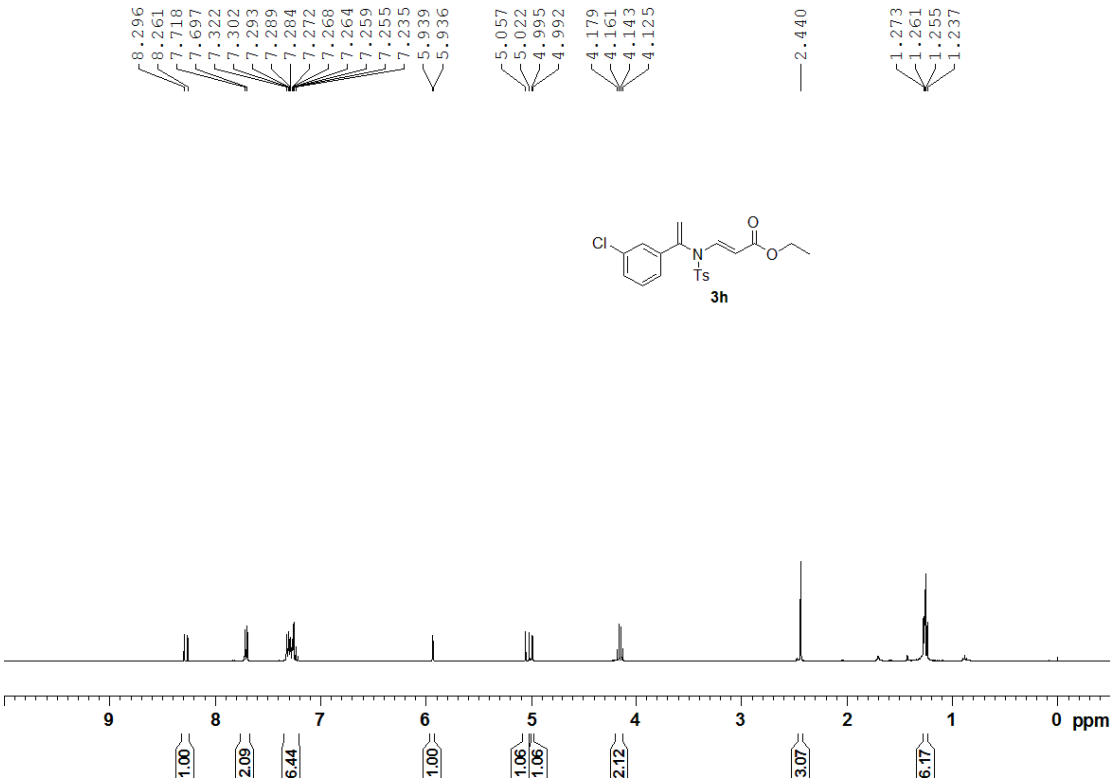
142.787
138.355
135.026
134.184
132.612
130.466
130.253
129.830
129.799
127.756
126.916
123.988
100.798
77.337
77.020
76.702
60.185
21.606
14.344
Cl
N
Ts
O
O
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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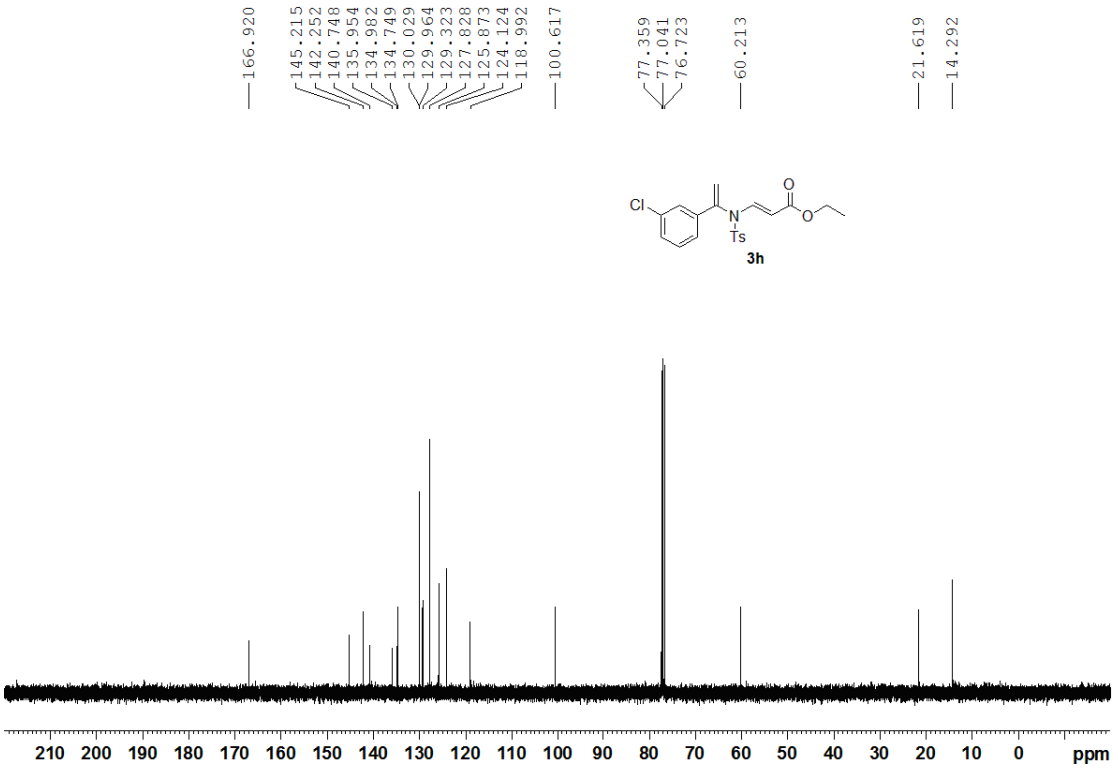
7.697
7.322
7.302
7.293
7.289
7.284
7.272
7.268
7.264
7.259
7.255
7.235
5.939
5.936
5.057
5.022
4.995
4.992
4.179
4.161
4.143
4.125
2.440
1.273
1.261
1.255
1.237
Cl
N
Ts
O
O
3h
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.09
6.44
1.00
1.06
1.06
2.12
3.07
6.17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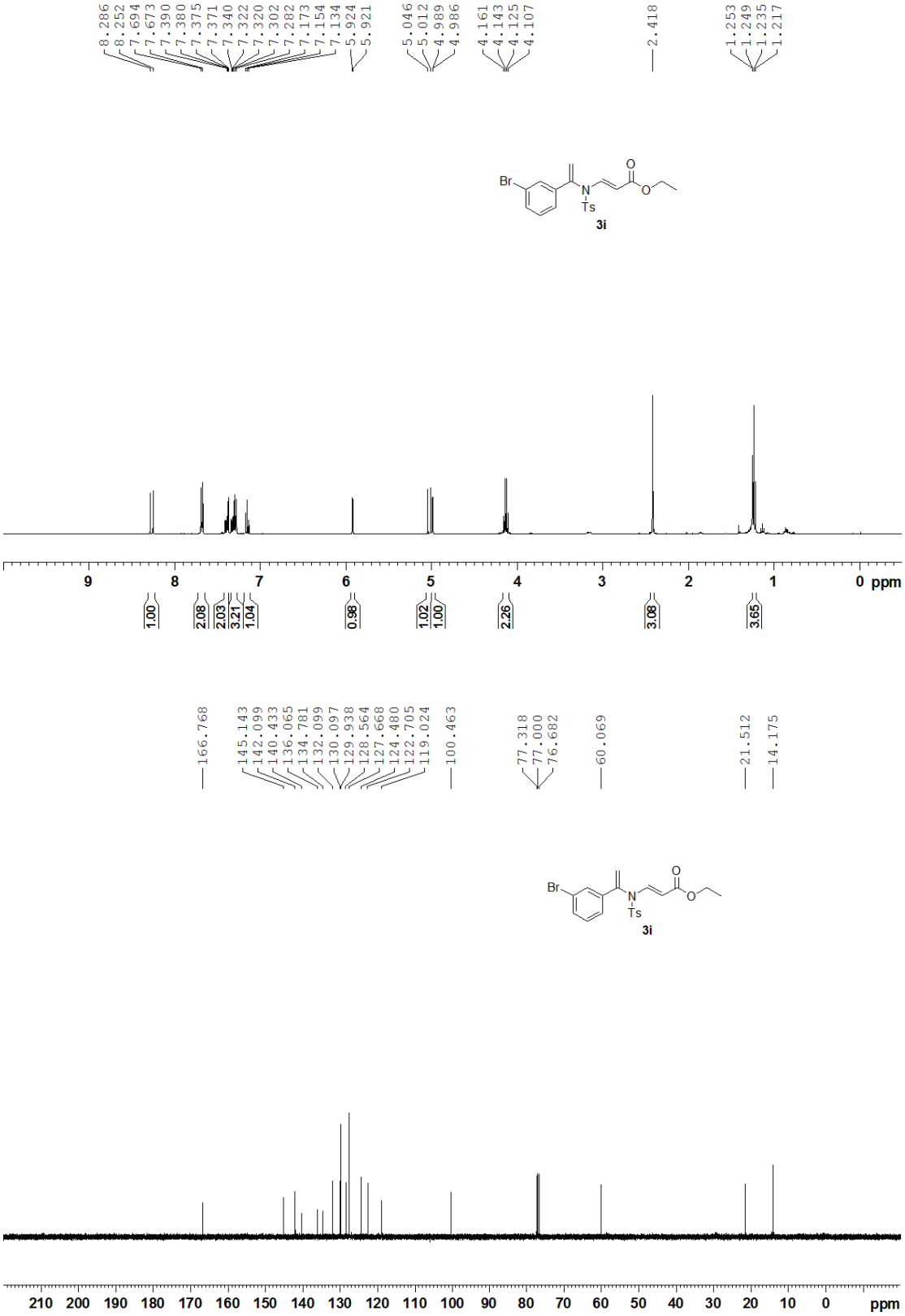
145.215
142.252
140.748
135.954
134.982
134.749
130.029
129.964
129.323
127.828
125.873
124.124
118.992
100.617
77.359
77.041
76.723
60.213
21.619
14.292
Cl
N
Ts
O
O
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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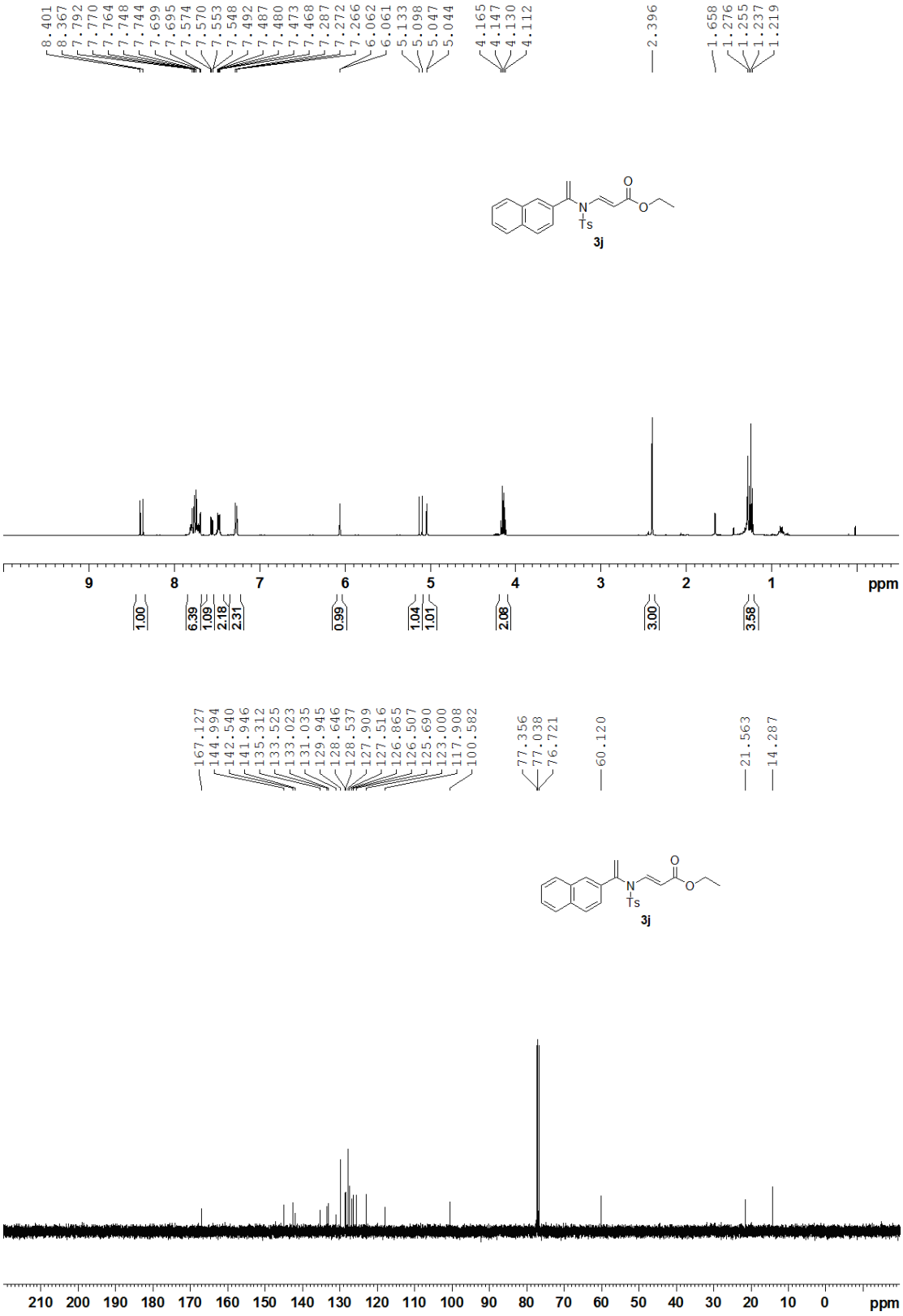
8.252
7.694
7.673
7.390
7.380
7.375
7.371
7.340
7.322
7.320
7.302
7.282
7.173
7.154
7.134
5.924
5.921
5.046
5.012
4.989
4.986
4.161
4.143
4.125
4.107
2.418
1.253
1.249
1.235
1.217
Br
N
Ts
O
O
3i
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.08
2.03
3.21
1.04
0.98
1.02
1.00
2.26
3.08
3.65
166.768
145.143
142.099
140.433
136.065
134.781
132.099
130.097
129.938
128.564
127.668
124.480
122.705
119.024
100.463
77.318
77.000
76.682
60.069
21.512
14.175
Br
N
Ts
O
O
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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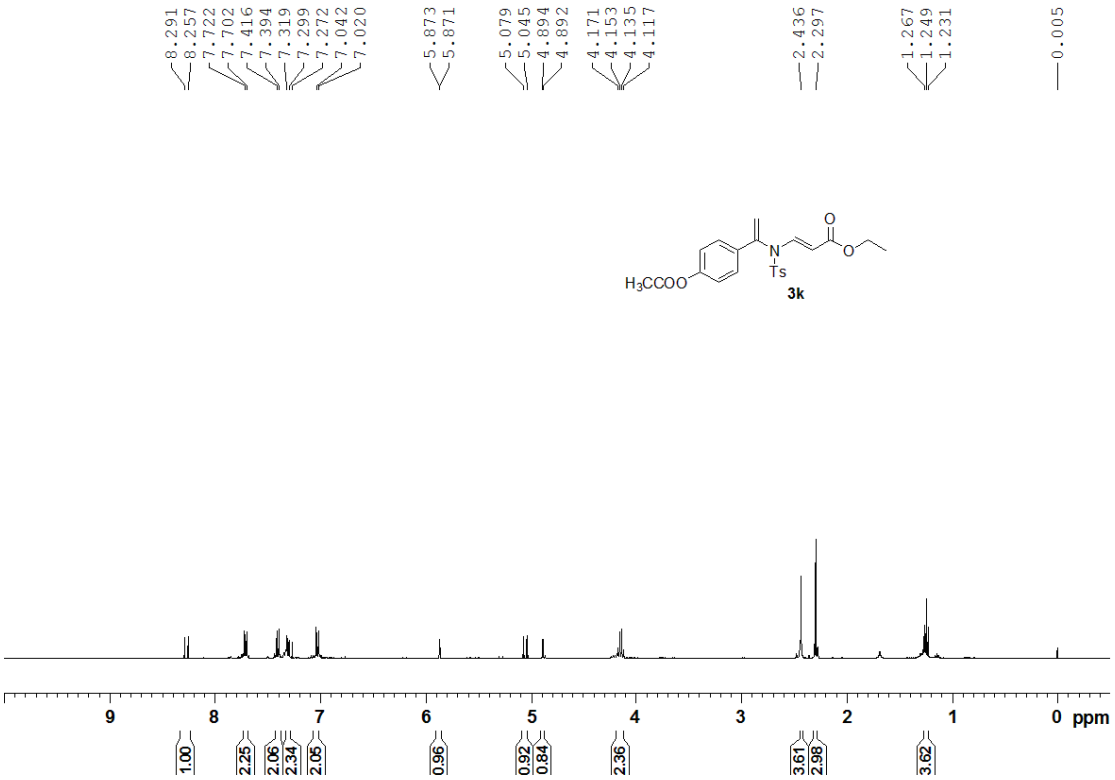
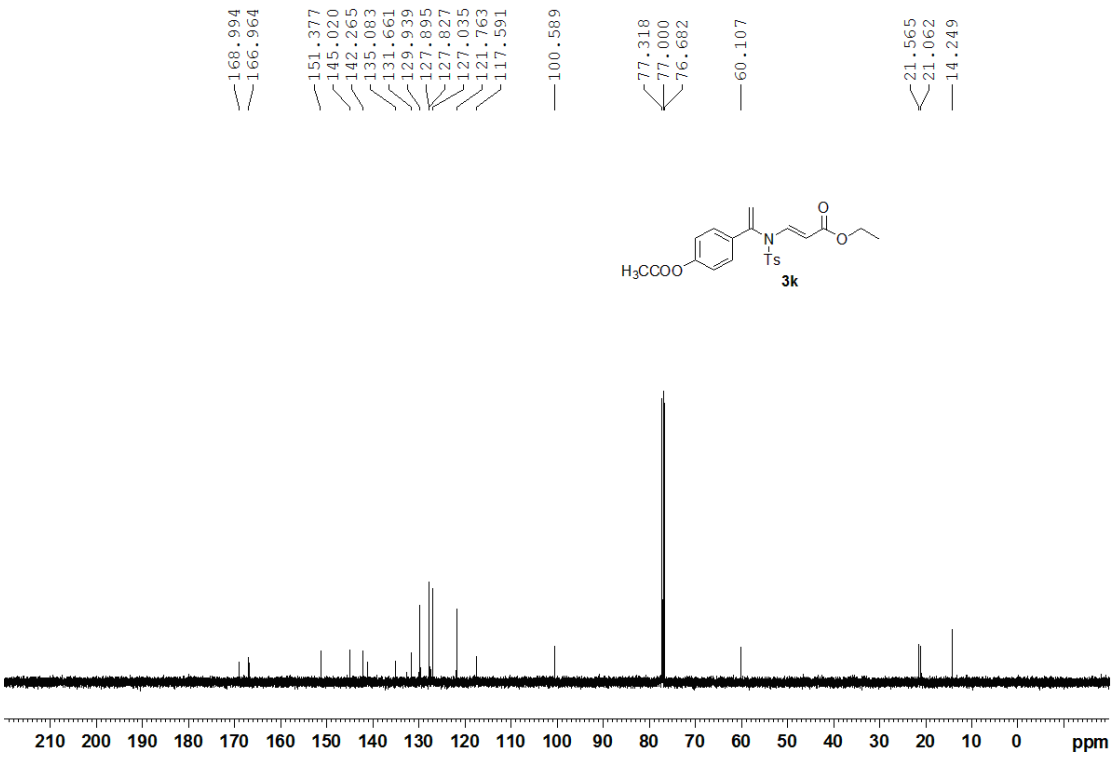
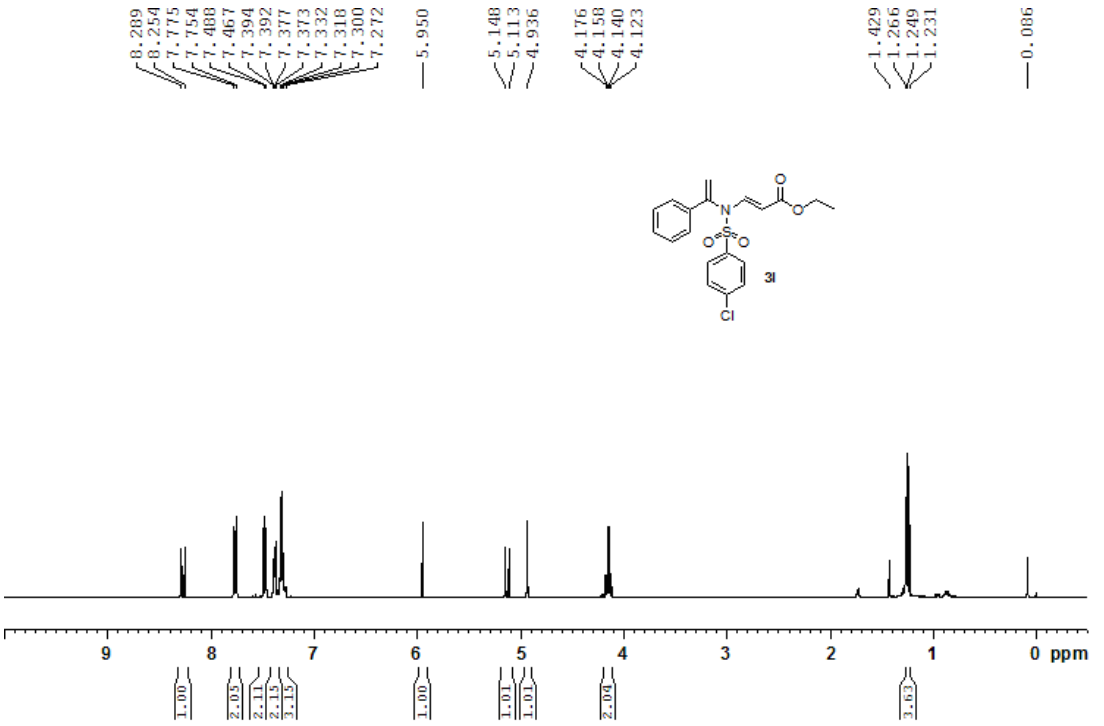
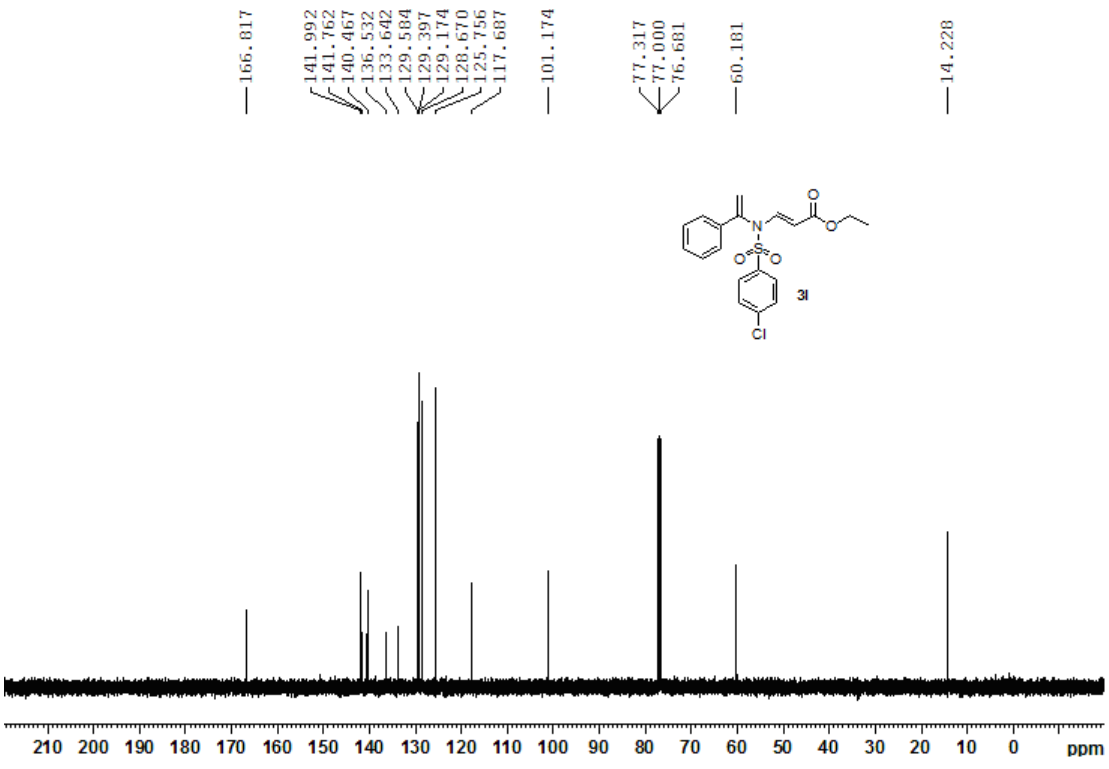
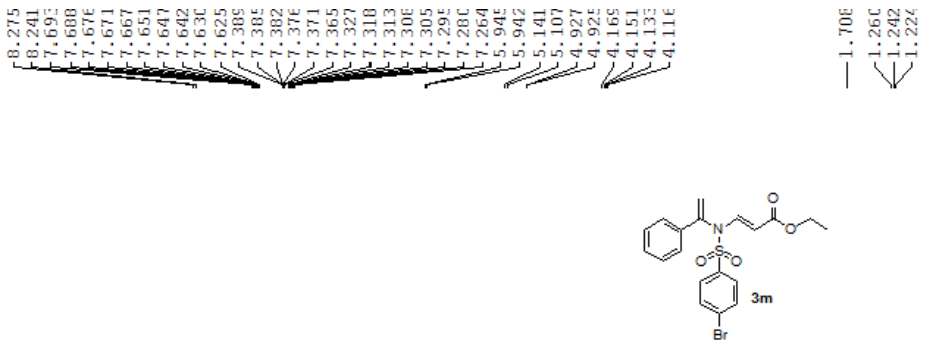
8.367
7.792
7.770
7.764
7.748
7.744
7.699
7.695
7.574
7.570
7.553
7.548
7.492
7.487
7.480
7.473
7.468
7.287
7.272
7.266
6.062
6.061
5.133
5.098
5.047
5.044
4.165
4.147
4.130
4.112
2.396
1.658
1.276
1.255
1.237
1.219
O
N
Ts
O
3j
9
8
7
6
5
4
3
2
1
ppm
1.00
6.39
1.09
2.18
2.31
0.99
1.04
1.01
2.08
3.00
3.58
167.127
144.994
142.540
141.946
135.312
133.525
133.023
131.035
129.945
128.646
128.537
127.909
127.516
126.865
126.507
125.690
123.000
117.908
100.582
77.356
77.038
76.721
60.120
21.563
14.287
O
N
Ts
O
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.291
8.257
7.722
7.702
7.416
7.394
7.319
7.299
7.272
7.042
7.020
5.873
5.871
5.079
5.045
4.894
4.892
4.171
4.153
4.135
4.117
2.436
2.297
1.267
1.249
1.231
0.005
H3CCOO
N
Ts
O
O
3k
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.25
2.06
2.34
2.05
0.96
0.92
0.84
2.36
3.61
2.98
3.62

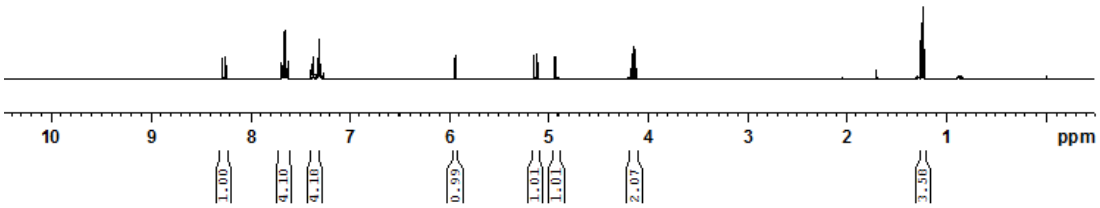

168.994
166.964
151.377
145.020
142.265
135.083
131.661
129.939
127.895
127.827
127.035
121.763
117.591
100.589
77.318
77.000
76.682
60.107
21.565
21.062
14.249
H3CCOO
N
Ts
O
O
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

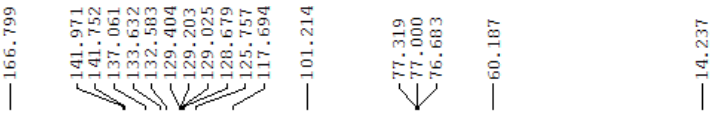

8.289
8.254
7.775
7.754
7.488
7.467
7.394
7.392
7.377
7.373
7.332
7.318
7.300
7.272
5.950
5.148
5.113
4.936
4.176
4.158
4.140
4.123
1.429
1.266
1.249
1.231
0.086
3l
Cl
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.05
2.11
2.15
3.15
1.00
1.01
1.01
2.04
3.63


166.817
141.992
141.762
140.467
136.532
133.642
129.584
129.397
129.174
128.670
125.756
117.687
101.174
77.317
77.000
76.681
60.181
14.228
3l
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.275
8.241
7.693
7.688
7.676
7.671
7.667
7.651
7.647
7.642
7.630
7.625
7.385
7.382
7.376
7.371
7.365
7.327
7.318
7.313
7.308
7.305
7.295
7.280
7.264
5.945
5.942
5.141
5.107
4.927
4.925
4.165
4.151
4.133
4.116
1.708
1.260
1.242
1.224

3m
Br


10
9
8
7
6
5
4
3
2
1
ppm
1.00
4.10
4.10
0.99
1.01
1.01
2.07
3.50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141.752
137.061
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129.203
129.025
128.679
125.757
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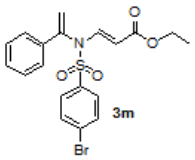
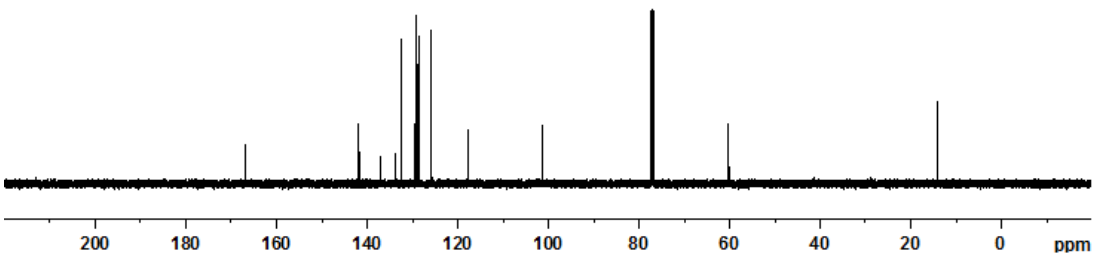
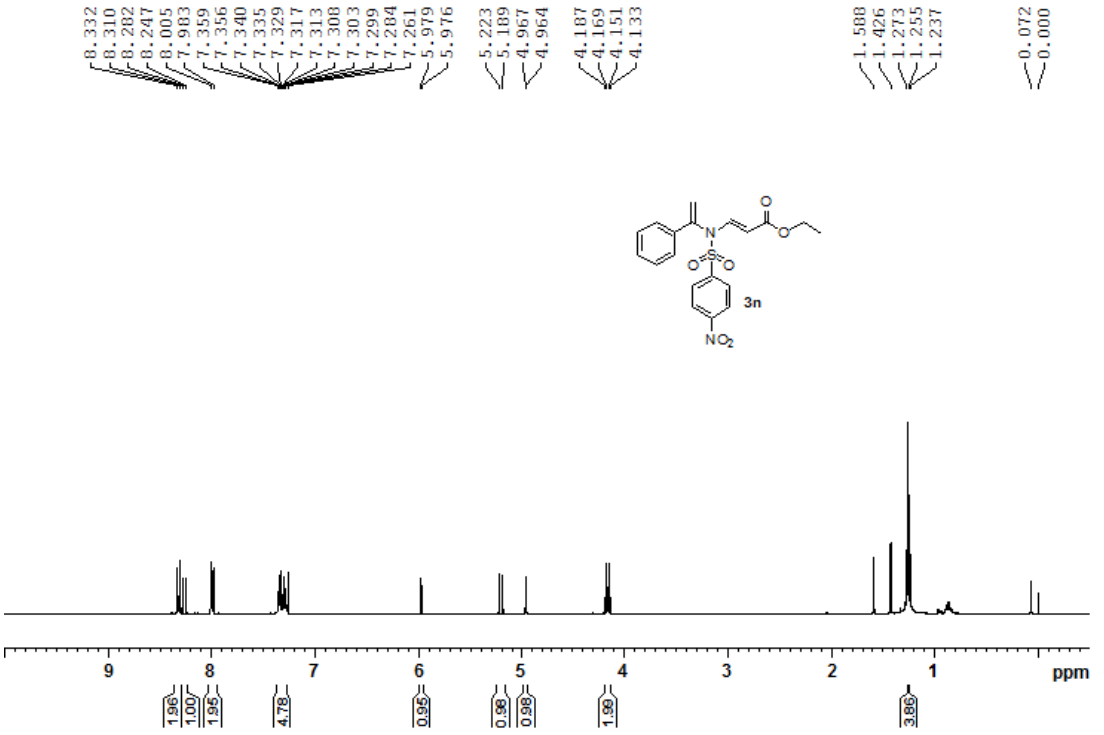
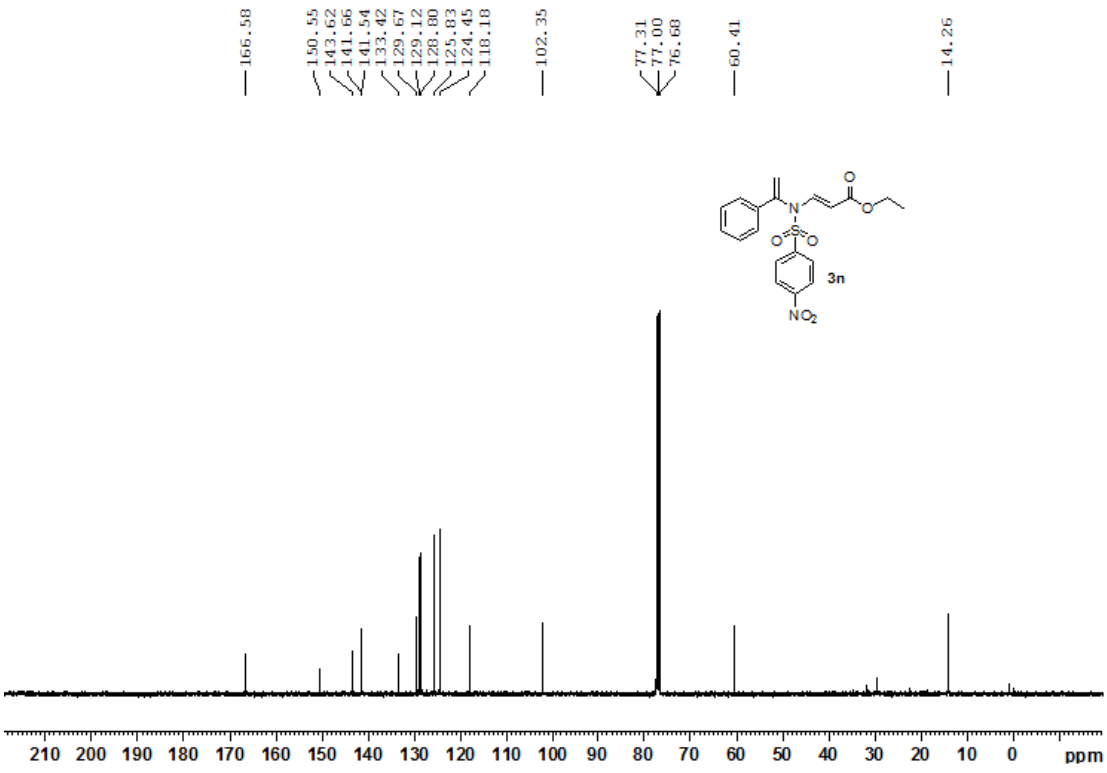
101.214
77.319
77.000
76.683
60.187
14.237


3m
Br


200
180
160
140
120
100
80
60
40
20
0
ppm


8.332
8.310
8.282
8.247
8.005
7.983
7.359
7.356
7.340
7.335
7.329
7.317
7.313
7.308
7.303
7.299
7.284
7.261
5.979
5.976
5.223
5.189
4.967
4.964
4.187
4.169
4.151
4.133
1.588
1.426
1.273
1.255
1.237
0.072
0.000
3n
NO2
9
8
7
6
5
4
3
2
1
ppm
1.96
1.00
1.96
4.78
0.95
0.98
0.98
1.99
3.86


166.58
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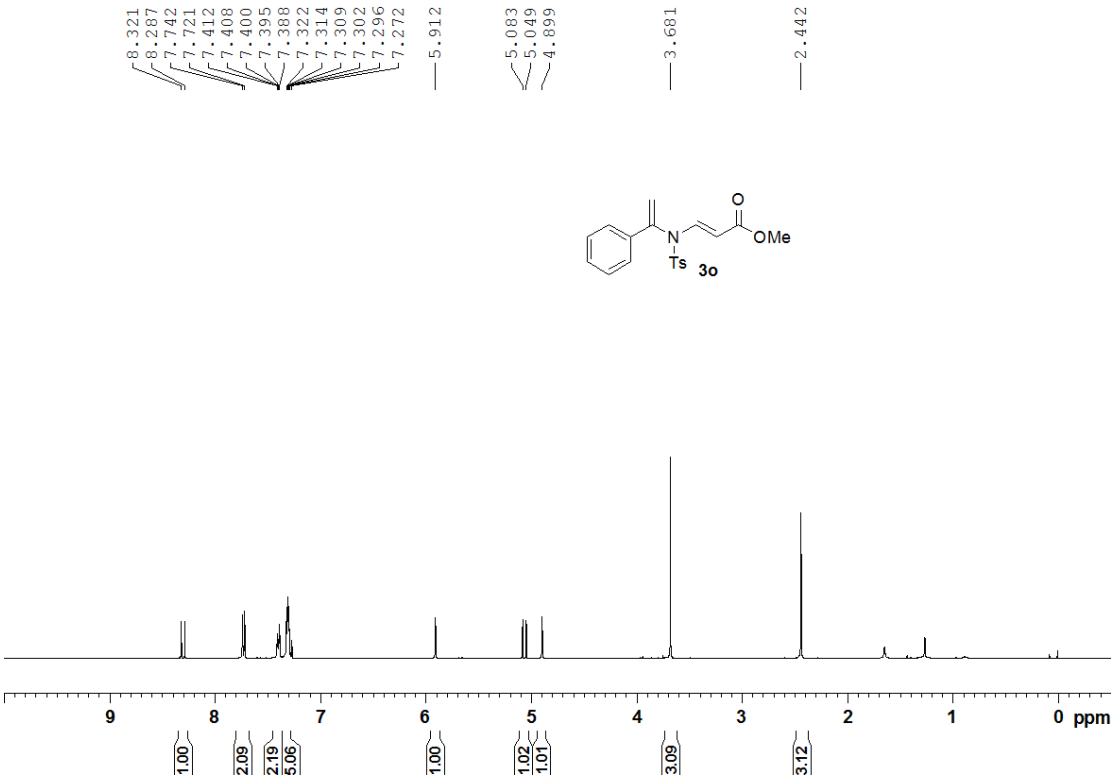
143.62
141.66
141.54
133.42
129.67
129.12
128.80
125.83
124.45
118.18
102.35
77.31
77.00
76.68
60.41
14.26
3n
NO2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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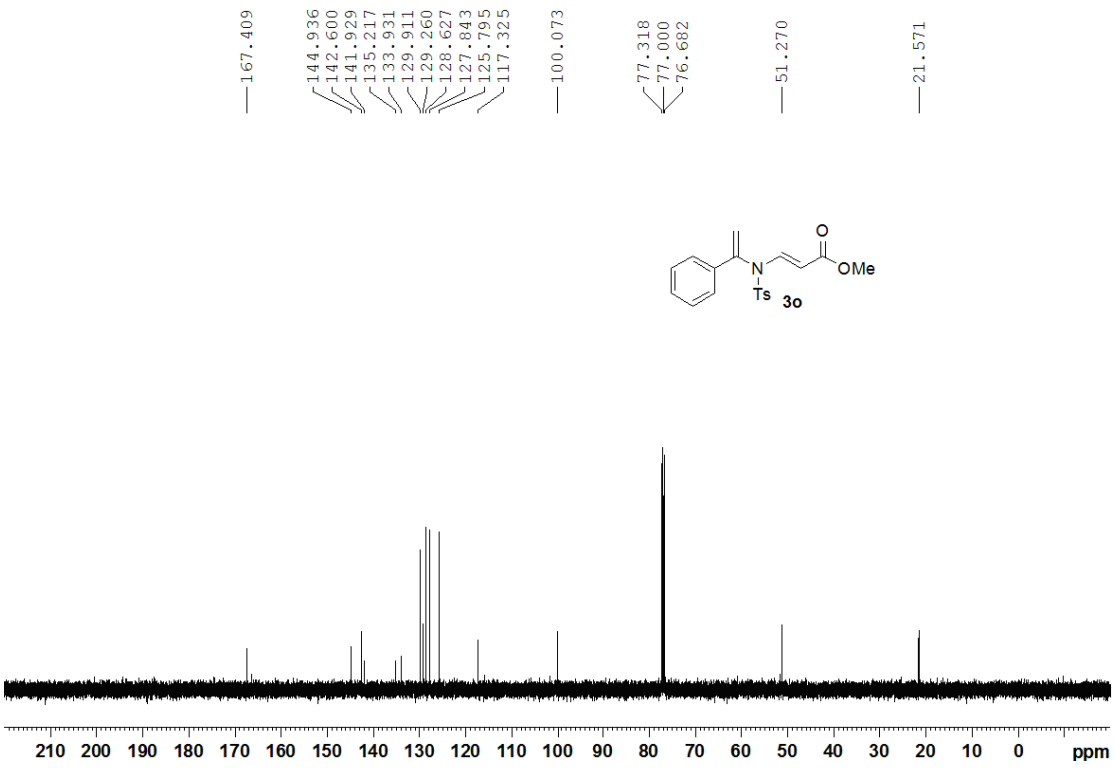
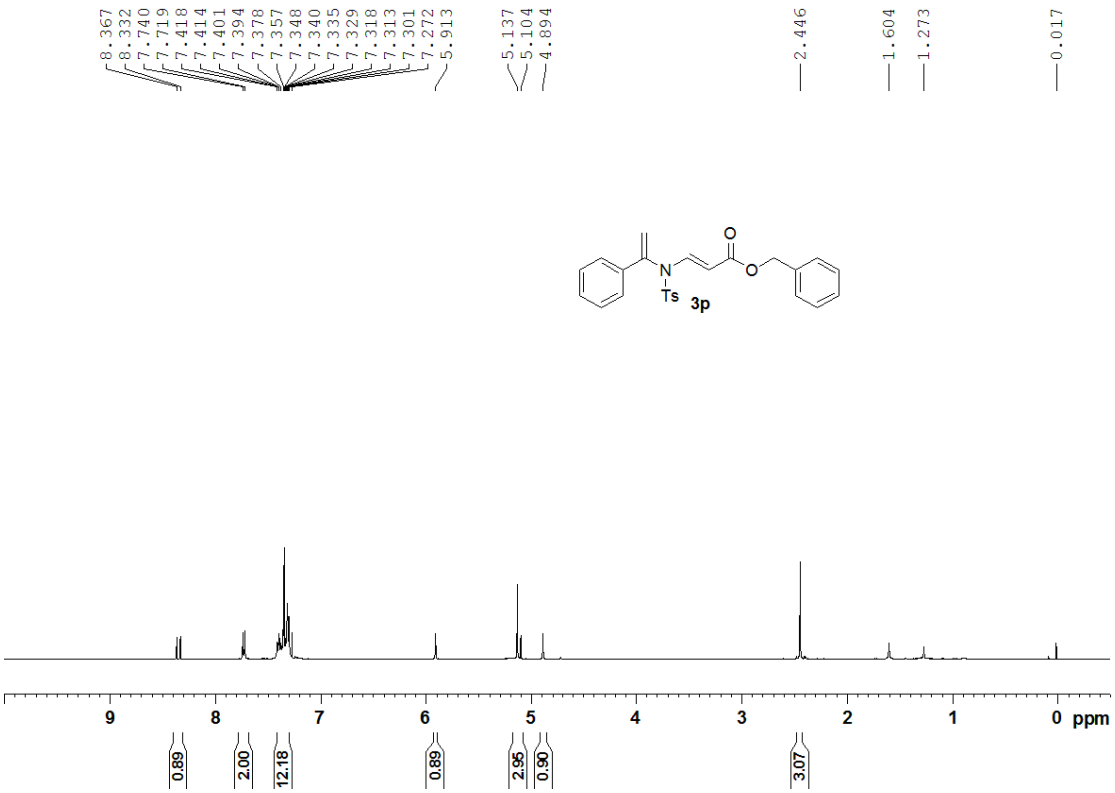
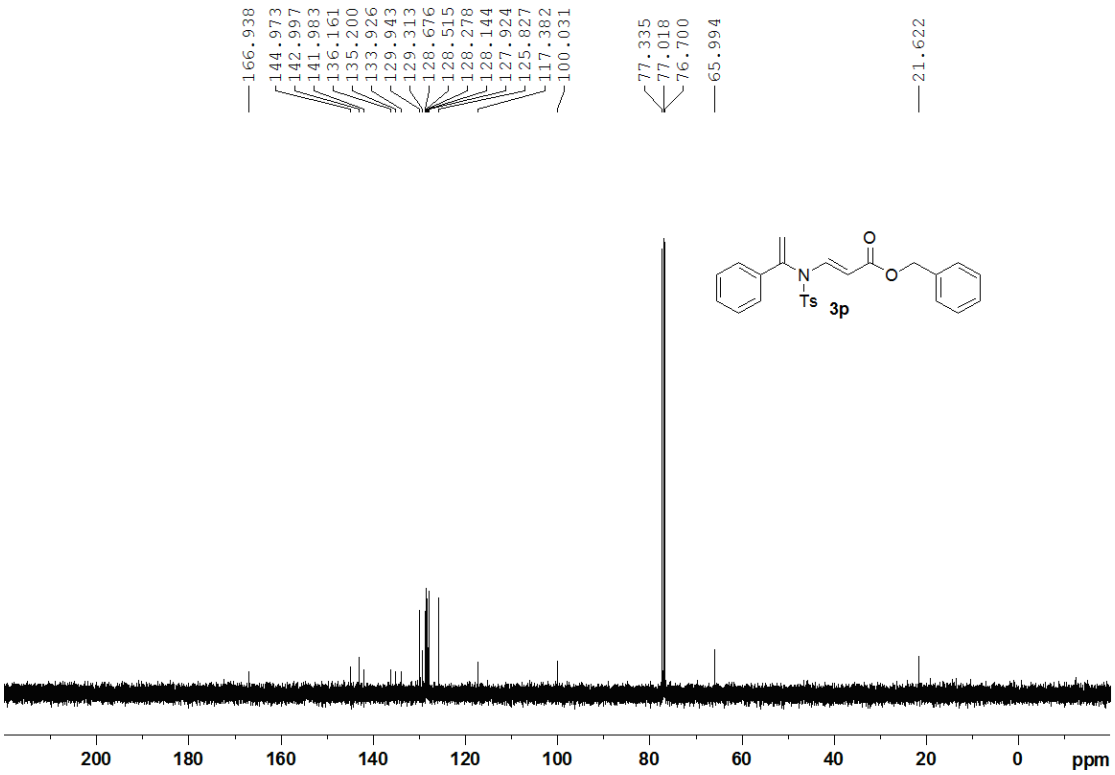
7.721
7.412
7.408
7.400
7.395
7.388
7.322
7.314
7.309
7.302
7.296
7.272
5.912
5.083
5.049
4.899
3.681
2.442
O
OMe
N
Ts
3o
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.09
2.19
5.06
1.00
1.02
1.01
3.09
3.12


167.409
144.936
142.600
141.929
135.217
133.931
129.911
129.260
128.627
127.843
125.795
117.325
100.073
77.318
77.000
76.682
51.270
21.571
O
OMe
N
Ts
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.367
8.332
7.740
7.719
7.418
7.414
7.401
7.394
7.378
7.357
7.348
7.340
7.335
7.329
7.318
7.313
7.301
7.272
5.913
5.137
5.104
4.894
2.446
1.604
1.273
0.017
3p
9
8
7
6
5
4
3
2
1
0 ppm
0.89
2.00
12.18
0.89
2.95
0.90
3.07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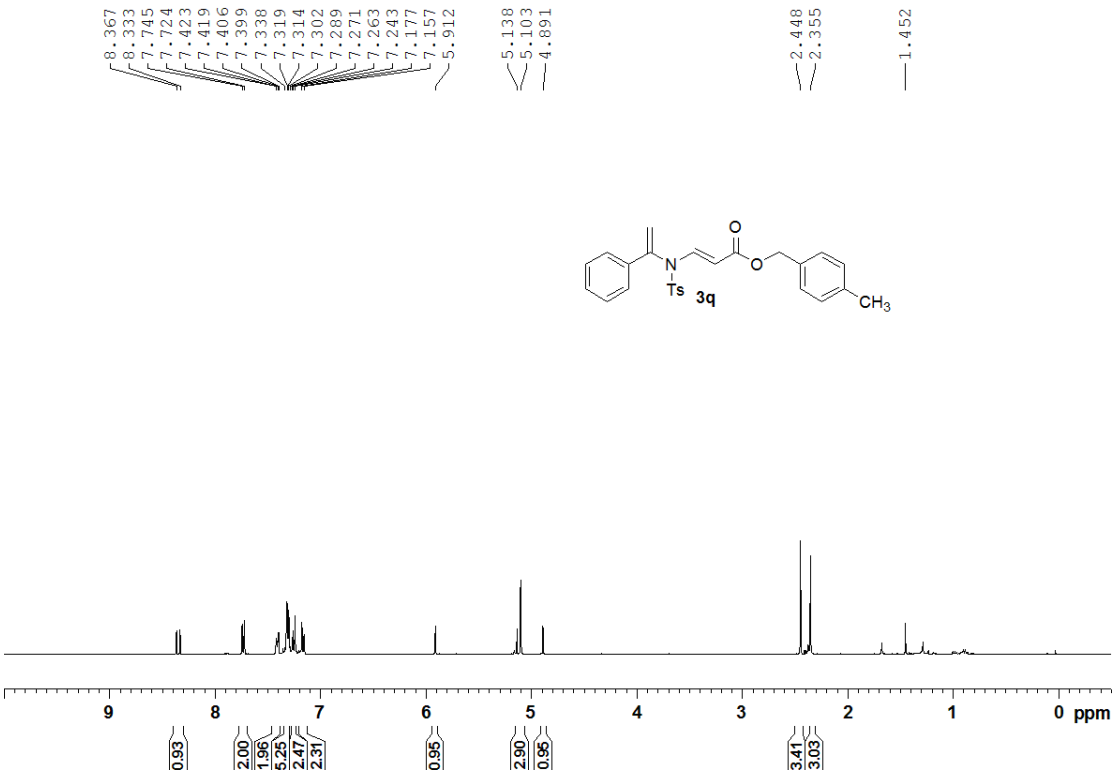
144.973
142.997
141.983
136.161
135.200
133.926
129.943
129.313
128.676
128.515
128.278
128.144
127.924
125.827
117.382
100.031
77.335
77.018
76.700
65.994
21.622
3p
200
180
160
140
120
100
80
60
40
20
0
ppm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8.333
7.745
7.724
7.423
7.419
7.406
7.399
7.338
7.319
7.314
7.302
7.289
7.271
7.263
7.243
7.177
7.157
5.912
5.138
5.103
4.891
2.448
2.355
1.452
Ts
3q
CH3
9
8
7
6
5
4
3
2
1
0 ppm
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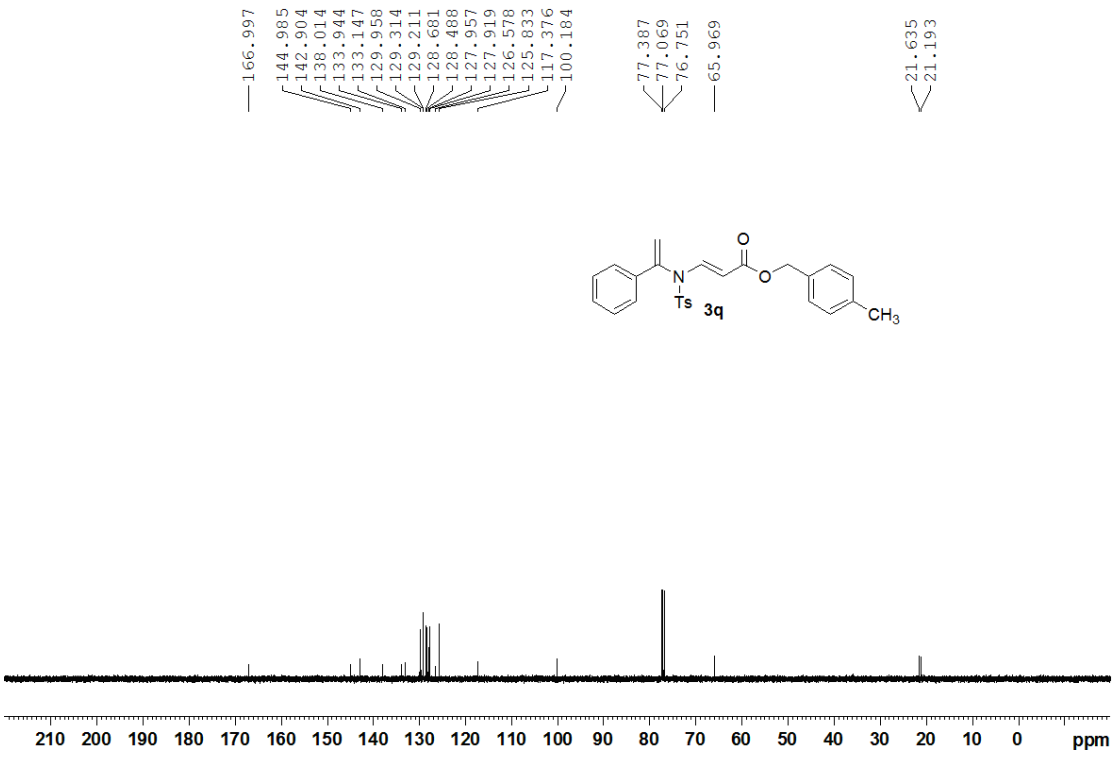
2.00
1.96
5.25
2.47
2.31
0.95
2.90
0.95
3.41
3.03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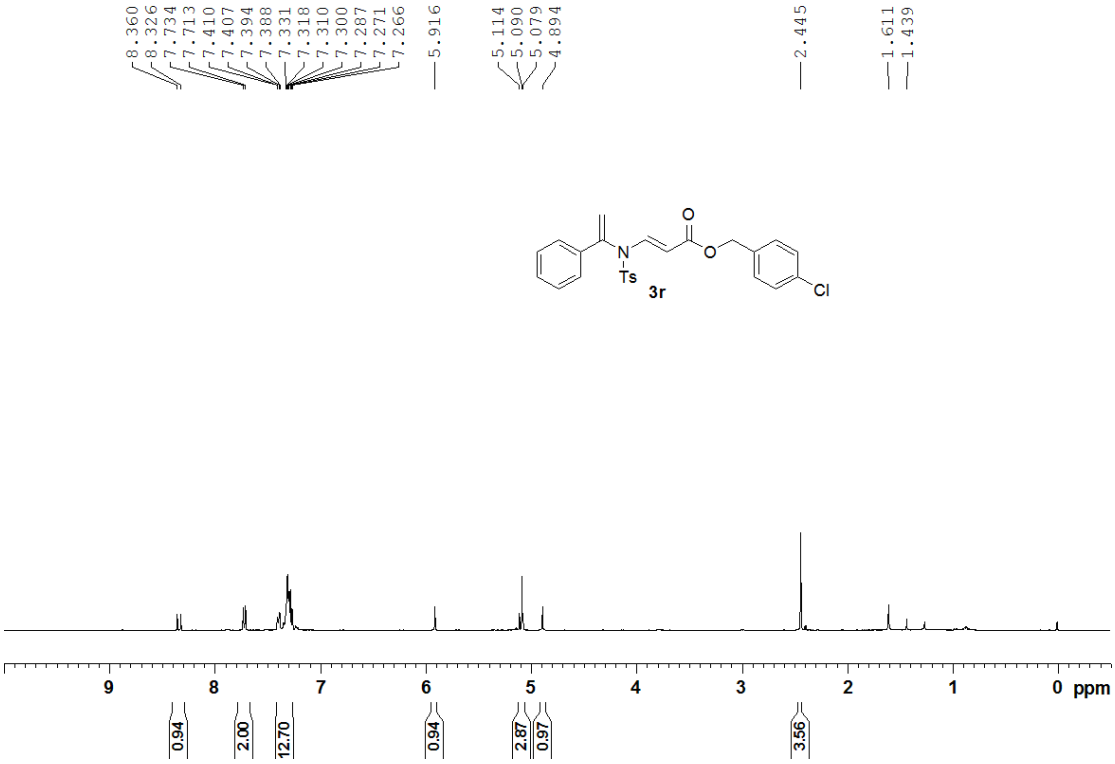
144.985
142.904
138.014
133.944
133.147
129.958
129.314
129.211
128.681
128.488
127.957
127.919
126.578
125.833
117.376
100.184
77.387
77.069
76.751
65.969
21.635
21.193
Ts
3q
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.326
7.734
7.713
7.410
7.407
7.394
7.388
7.331
7.318
7.310
7.300
7.287
7.271
7.266
5.916
5.114
5.090
5.079
4.894
2.445
1.611
1.439
O
N
Ts
O
Cl
3r
9
8
7
6
5
4
3
2
1
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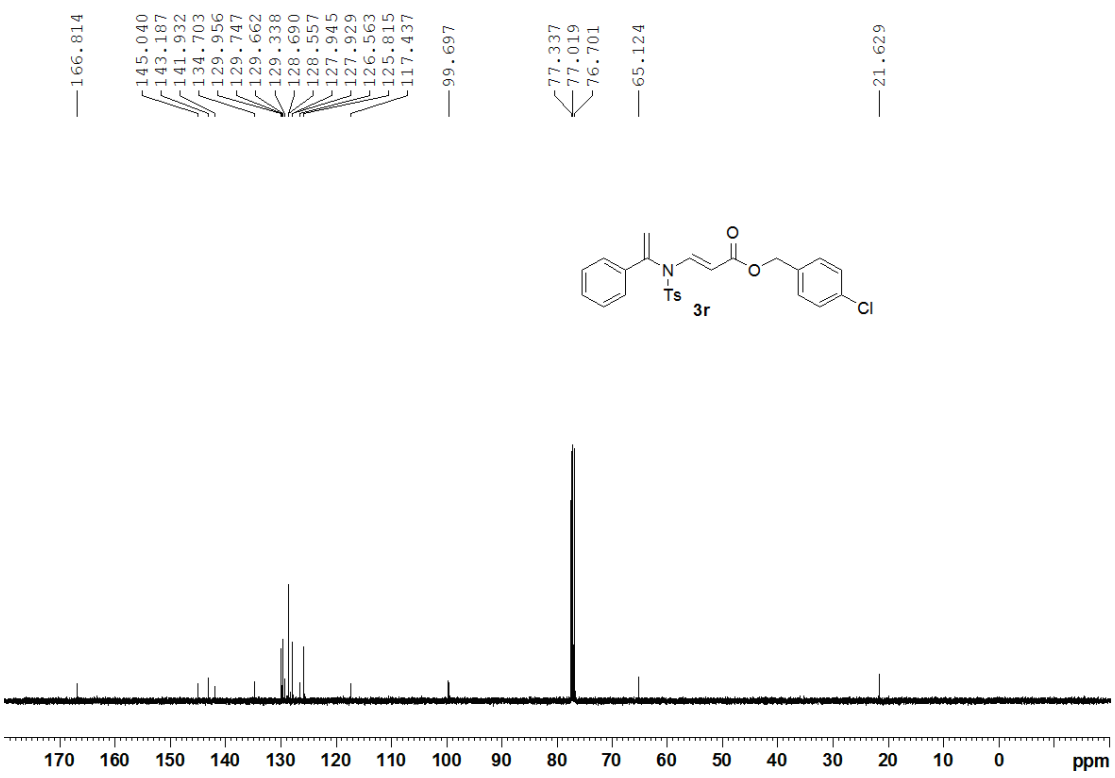
2.00
12.70
0.94
2.87
0.97
3.56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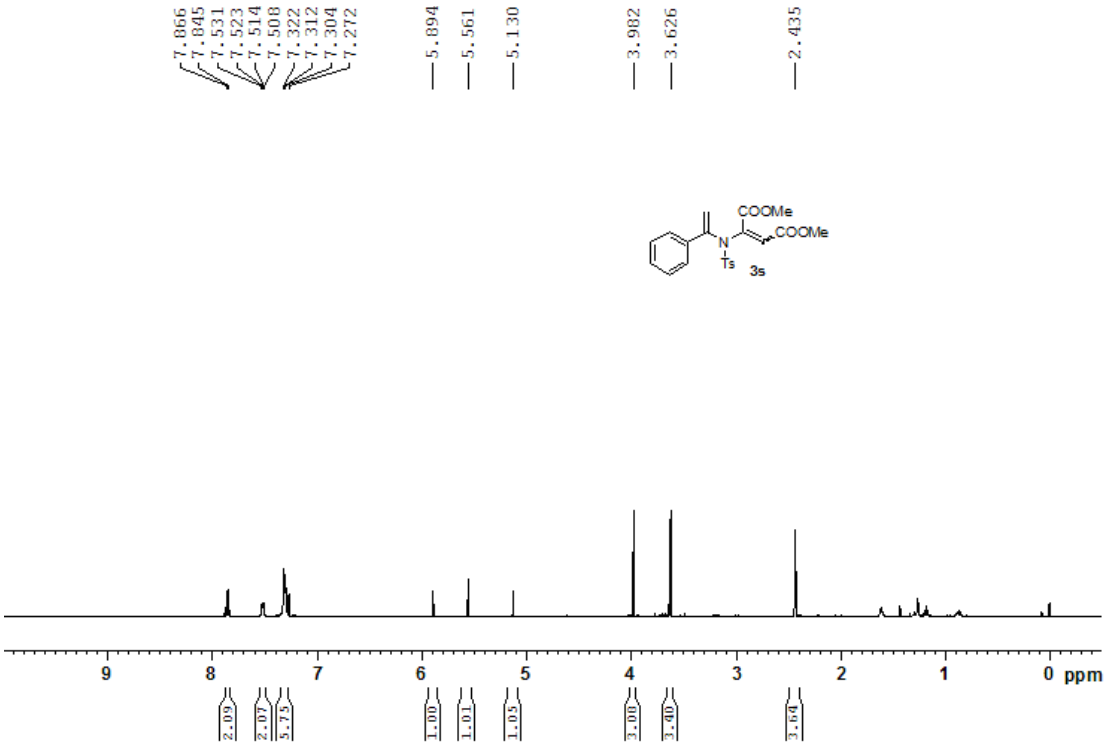
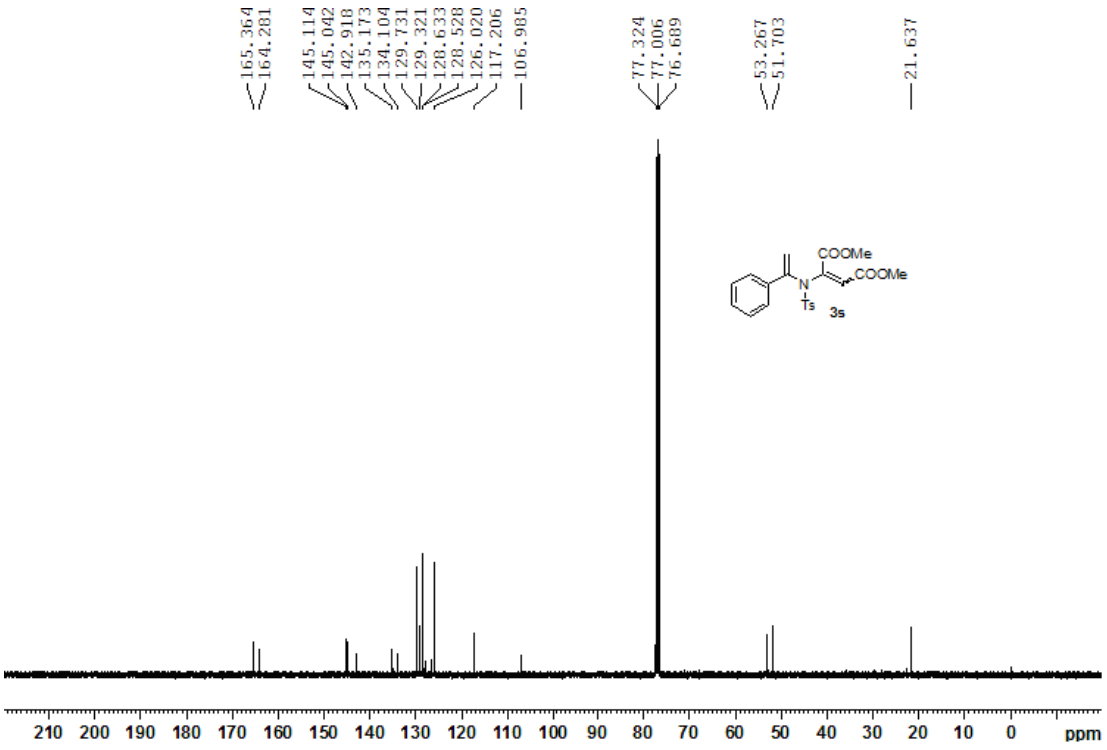
145.040
143.187
141.932
134.703
129.956
129.747
129.662
129.338
128.690
128.557
127.945
127.929
126.563
125.815
117.437
99.697
77.337
77.019
76.701
65.124
21.629
O
N
Ts
O
Cl
3r
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.866
7.845
7.531
7.523
7.514
7.508
7.322
7.312
7.304
7.272
5.894
5.561
5.130
3.982
3.626
2.435
COOMe
COOMe
N
Ts
3s
9
8
7
6
5
4
3
2
1
0 ppm
2.09
2.07
5.75
1.00
1.01
1.05
3.00
3.40
3.64


165.364
164.281
145.114
145.042
142.918
135.173
134.104
129.731
129.321
128.633
128.528
126.020
117.206
106.985
77.324
77.006
76.689
53.267
51.703
21.637
COOMe
COOMe
N
Ts
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm