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


# Visible-Light Induced Sulfonylation of Baylis-Hillman Acetates under Metal- and Oxidant-free Conditions

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## 1. Experimental section

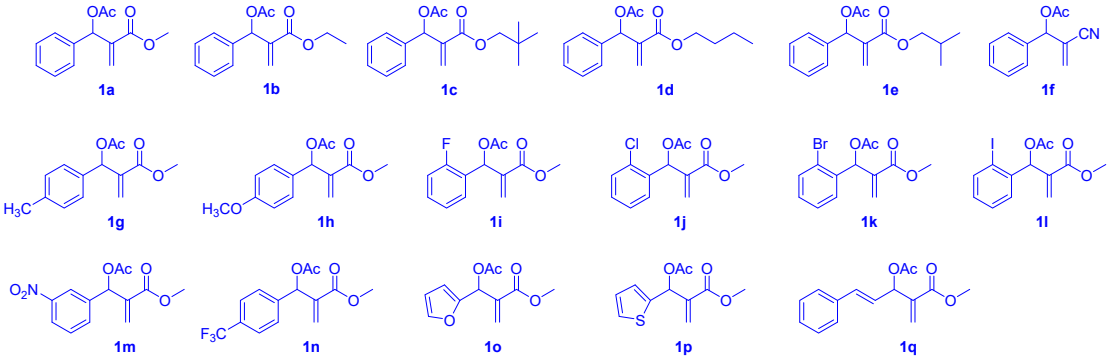
All chemicals were purchased from the Wencai New Material Technology and Merck in high purityand were used directly without any purification. Solvents were freshly distilled prior to use. All reactions were carried out under air atmosphere unless noted. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded with a Bruker Avance III 500 MHz spectrometer in $CDCl_3$ or DMSO-*d6* solution. Highresolution mass (HRMS) spectra were measured with a VG Auto Spec-3000 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25mm layer of Merck silica gel 60 F254. Silica gel (200-300 mesh) was used for column chromatography.

## 2. Experimental procedures

### A. General procedure for preparation of Baylis-Hillman acetates (1a-q)

The Morita-Baylis-Hillman (MBH) adducts was synthesized by literature[1,2]. To a stirred solution of MBH products (1 equiv.) in dichloromethane was added acetic anhydride (1.5 equiv.) and *N*,*N*-dimethylaminopyridine (0.2 equiv.) at room temperature. After stirring at the same temperature for 1 hour, the reaction mixture was treated with water and extracted with dichlorormethane. The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure and purified by silica gel column chromatography.

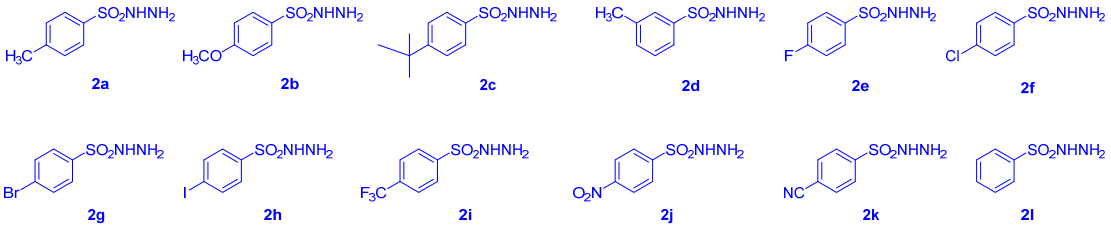
**Baylis-Hillman acetates (1a-q) were synthesized using the above method:**




### B. General procedure for preparation of Aryl Sulfonylhydrazide (2a-l)

To a stirred solution of arylsulfonyl chloride (1.0 equiv.) in tetrahydrofuran was added hydrazine hydrate (2.1 equiv.) at 0 °C. After stirring at the same temperature for 30 min, the reaction mixture was treated with water and extracted with ethyl acetate. The combined organic layer was washed with saturated sodium chloride and dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure and purified by silica gel column chromatography.

**Aryl Sulfonylhydrazide (2a-l) were synthesized using the above method:**




### C. General experimental procedure for Allyl ArylSulfone Derivatives with aryl sulfonylhydrazides

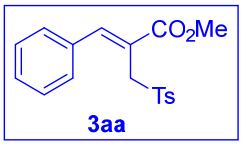
To a mixture of Baylis-Hillman acetates **1** (0.2 mmol), aryl sulfonylhydrazides **2** (0.4 mmol, 2.0 equiv.), tetramethylammonium iodide (TMAI) (0.3 mmol, 1.5 equiv.), $Na_2$-esoin Y (0.004mmol, 2 mol%), $NaHCO_3$ (0.4 mmol, 2 equiv.) was added 2 mL DMF/$H_2O$ (v/v = 5:1) under air atmosphere. The solution was placed in a distance of ~3 cm from 2×9 W blue LED (450-455 nm) at room temperature for 18 h. The reaction mixture was quenched with water (3 mL), extracted with EtOAc (8 mL×3), washed with brine (6 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. Column chromatography on silica gel afford the desired product.

## Reference:

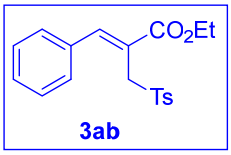

[1] W.-X. Wang, Q.-Z. Zhang, T.-Q. Zhang, Z.-S. Li, W. Zhang, W. Yu, *Adv. Synth. Catal.* **2015**, *357*, 221-226.

[2] Z. He, B. Wibbeling, A. Studer, *Adv. Synth. Catal.* **2013**, *355*, 3639-3647.

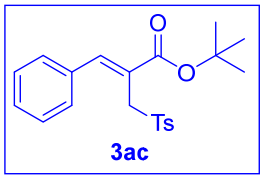
## 3. $^{1}H$ and $^{13}C$ NMR data of Allyl Aryl Sulfone Derivatives (3aa-3aq, 4aa-4ak)



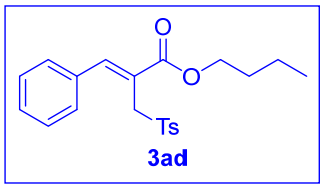

**(*Z*)-methyl-3-phenyl-2-(tosylmethyl)acrylate (3aa)**[1]: Brown solid. $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.38-7.34 (m, 3H), 7.27 (s, 1H), 7.26 (s, 1H), 4.47 (s, 2H), 3.61 (s, 3H), 2.42 (s, 3H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 167.1, 146.3, 144.9, 136.4, 133.8, 129.8, 129.8, 129.3, 128.8, 128.7, 121.1, 55.2, 52.5, 21.8.



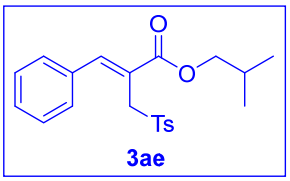

**(*Z*)-ethyl-3-phenyl-2-(tosylmethyl)acrylate (3ab)**[1]: Yellow liquid. $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.45 (dd, *J* = 6.8, 2.8 Hz, 2H), 7.38-7.33 (m, 3H), 7.27-7.22 (m, 2H), 4.47 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 166.3, 145.7, 144.6, 136.1, 133.6, 129.5, 129.4, 129.0, 128.5, 128.4, 121.2, 61.4, 54.9, 21.4, 13.9.



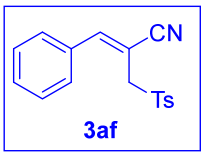

**(*Z*)-tert-butyl-3-phenyl-2-(tosylmethyl)acrylate (3ac):** White solid, Mp: 99-100 °C. $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.41 (dd, *J* = 6.9, 2.7 Hz, 2H), 7.37-7.31 (m, 3H), 7.24 (d, *J* = 7.9 Hz, 2H), 4.45 (s, 2H), 2.40 (s, 3H), 1.44 (s, 9H).$^{13}C$ NMR (126 MHz, $CDCl_3$) δ 165.9, 145.5, 145.0, 136.7, 134.4, 130.1, 129.7, 129.4, 129.0, 128.9, 123.1, 82.3, 55.3, 28.3, 22.0. HRMS (ESI) [M+$H^+$] Calcd For $C_{21}H_{24}O_4S$: 372.1395, Found: 372.1397.



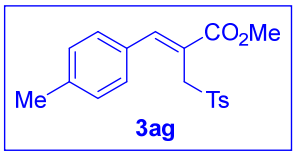

**(*Z*)-butyl-3-phenyl-2-(tosylmethyl)acrylate (3ad)**[1]: Yellow liquid. $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 6.7, 2.6 Hz, 2H), 7.39-7.33 (m, 3H), 7.25 (d, *J* = 7.6 Hz, 2H), 4.48 (s, 2H), 4.00 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 1.62-1.56 (m, 2H), 1.39 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).$^{13}C$ NMR (126 MHz, $CDCl_3$) δ 166.7, 146.0, 144.8, 136.4, 133.9, 129.8, 129.7, 129.3, 128.8, 128.7, 121.5, 65.6, 55.2, 30.6, 21.8, 19.3, 13.9.



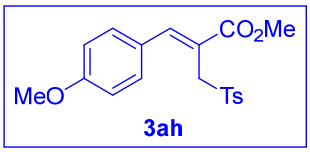

**(*Z*)-isobutyl-3-phenyl-2-(tosylmethyl)acrylate (3ae):** Yellow liquid. $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.45 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.38-7.32 (m, 3H), 7.27-7.22 (m, 2H), 4.48 (s, 2H), 3.80 (d, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 1.92 (dp, *J* = 13.4, 6.7 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 6H).$^{13}C$ NMR (126 MHz, $CDCl_3$) δ 166.7, 145.8, 144.8, 136.3, 133.8, 129.7, 129.7, 129.3, 128.8, 128.6, 121.5, 71.7, 55.2, 27.8, 21.7, 19.3. HRMS (ESI) [M+$H^+$] Calcd For $C_{21}H_{24}O_4S$: 372.1395, Found: 372.1400.



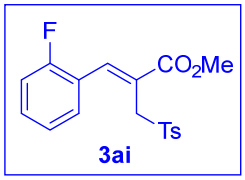

**(*Z*)-3-phenyl-2-(tosylmethyl)acrylonitrile (3af)**[1]: Yellow solid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.70 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.46-7.42 (m, 3H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.12 (s, 1H), 4.02 (s, 2H), 2.47 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 151.7, 145.8, 134.5, 132.4, 131.5, 130.1, 129.2, 128.9, 128.7, 117.0, 98.0, 61.3, 21.7.



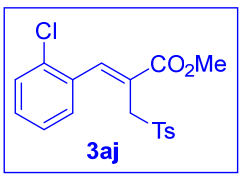

**(*Z*)-methyl-3-(p-tolyl)-2-(tosylmethyl)acrylate (3ag):** White solid, Mp: 93-95 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.28-7.24 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.48 (s, 2H), 3.57 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.2, 146.4, 144.8, 140.3, 136.5, 130.9, 129.7, 129.5, 129.5, 128.6, 119.9, 55.3, 52.4, 21.7, 21.5. HRMS (ESI) [M+H$^+$] Calcd For $C_{19}H_{21}O_4S$: 345.1155, Found: 345.1156.



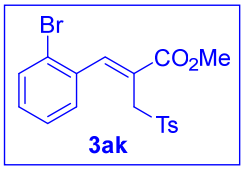

**(*Z*)-methyl-3-(4-methoxyphenyl)-2-(tosylmethyl)acrylate (3ah)**[2]: White solid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.27-7.23 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 3.50 (s, 3H), 2.38 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.1, 160.9, 146.0, 144.6, 136.3, 131.4, 129.4, 128.4, 126.0, 118.0, 114.0, 55.3, 52.1, 21.5.



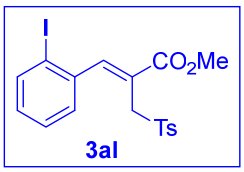

**(*Z*)-methyl-3-(2-fluorophenyl)-2-(tosylmethyl)acrylate (3ai):** Yellow solid, Mp: 115-117 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.37-7.32 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.06-7.00 (m, 1H), 4.43 (s, 2H), 3.65 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.6, 144.9, 138.9 (d, $J_{CF}$ = 4.0 Hz), 136.1, 131.6 (d, $J_{CF}$ = 8.5 Hz), 130.2 (d, $J_{CF}$ = 1.9 Hz), 129.8, 128.6, 124.5 (d, $J_{CF}$ = 3.6 Hz), 123.4, 121.9 (d, $J_{CF}$ = 13.2 Hz), 115.8 (d, $J_{CF}$ = 21.6 Hz), 55.3, 52.7, 21.8. $^{19}$F NMR (471 MHz, $CDCl_3$) δ 111.2. $^{19}$F NMR (471 MHz, $CDCl_3$) δ 111.2. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{18}FO_4S$: 349.0904, Found: 349.0905.



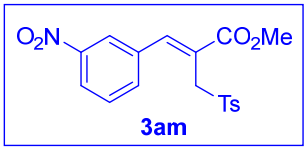

**(*Z*)-methyl-3-(2-chlorophenyl)-2-(tosylmethyl)acrylate (3aj)**[1]: Yellow solid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.66-7.60 (m, 1H), 7.38-7.33 (m, 1H), 7.32-7.25 (m, 4H), 4.37 (s, 2H), 3.64 (s, 3H), 2.42 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.6, 144.9, 143.1, 136.3, 134.2, 132.4, 130.7, 130.2, 129.8, 129.8, 128.6, 127.1, 123.3, 55.1, 52.7, 21.8.



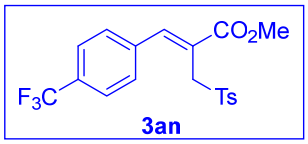

**(*Z*)-methyl-3-(2-bromophenyl)-2-(tosylmethyl)acrylate (3ak)**[1]: White solid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 6.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 7.26 (d, *J* = 3.3 Hz, 1H), 7.22 (td, *J* = 7.7, 1.5 Hz, 1H), 4.35 (s, 2H), 3.64 (s, 3H), 2.42 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.5, 145.2, 144.9, 136.4, 134.2, 133.0, 130.8, 130.3, 129.9, 128.6, 127.7, 124.2, 123.0, 55.1, 52.7, 21.8.



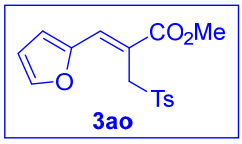

**(*Z*)-methyl-3-(2-iodophenyl)-2-(tosylmethyl)acrylate (3al):** Yellow solid, Mp: 116-118 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.91-7.81 (m, 2H), 7.71 (dd, *J* = 7.2, 3.6 Hz, 2H), 7.62-7.53 (m, 1H), 7.39 (t, *J* = 5.8 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.10-7.01 (m, 1H), 4.32 (s, 2H), 3.64 (s, 3H), 2.43 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.5, 149.0, 144.9, 139.4, 137.7, 136.5, 130.7, 129.9, 129.7, 128.6, 128.5, 122.6, 99.5, 55.0, 52.7, 21.8. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{18}IO_4S$: 456.9965, Found: 456.9969.




**(*Z*)-methyl-3-(3-nitrophenyl)-2-(tosylmethyl)acrylate (3am)**[3]: Yellow liquid. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.27-8.19 (m, 2H), 7.94 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 8.3 Hz, 1H), 7.30-7.25 (m, 2H), 4.41 (s, 2H), 3.69 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.3, 148.4, 145.4, 143.2, 136.0, 135.4, 134.8, 130.0, 129.9, 128.7, 124.1, 124.1, 123.9, 54.8, 52.9, 21.7.

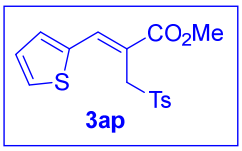



**(*Z*)-methyl-2-(tosylmethyl)-3-(4-(trifluoromethyl)phenyl)acrylate (3an):** White solid, Mp: 95-97 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.28-7.24 (m, 2H), 4.42 (s, 2H), 3.65 (s, 3H), 2.42 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.6, 145.2, 144.3, 137.3, 136.2, 129.9, 129.3, 128.6, 125.8, 125.7 (q, $J_{CF}$ = 3.7 Hz), 123.4, 54.9, 52.8, 21.7. $^{19}$F NMR (471 MHz, $CDCl_3$) δ 62.9. HRMS (ESI) [M+H$^+$] Calcd For $C_{19}H_{18}F_3O_4S$: 399.0872, Found: 399.0875.

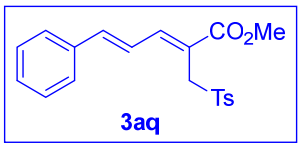



**(*Z*)-methyl-3-(furan-2-yl)-2-(tosylmethyl)acrylate (3ao):** Brown solid, Mp: 90-92 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.52 (s, 1H), 7.39 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 3.3 Hz, 1H), 6.40 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.76 (s, 2H), 3.60 (s, 3H), 2.35 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ

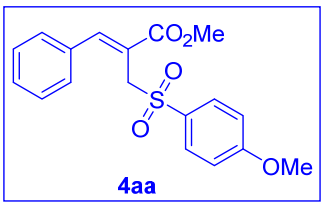
167.0, 150.2, 145.8, 144.6, 136.4, 130.7, 129.3, 128.8, 119.0, 115.6, 112.2, 55.5, 52.5, 21.6. HRMS (ESI) [M+H$^+$] Calcd For $C_{16}H_{17}O_5S$: 321.0791, Found: 321.0796.



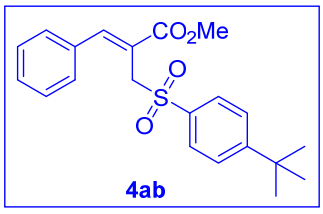

**(*Z*)-methyl-3-(thiophen-2-yl)-2-(tosylmethyl)acrylate (3ap)**[1]: White solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.52 (dd, *J* = 6.8, 4.4 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.61 (s, 2H), 3.53 (s, 3H), 2.41 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.0, 144.9, 138.4, 136.9, 136.5, 134.3, 131.0, 129.7, 128.9, 127.9, 116.4, 56.2, 52.5, 21.8.



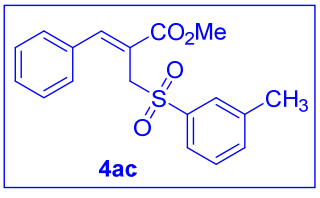

**(2*Z*,4*E*)-methyl-5-phenyl-2-(tosylmethyl)penta-2,4-dienoate (3aq)**[1]: White solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 11.6 Hz, 1H), 7.42-7.32 (m, 5H), 7.27 (s, 1H), 7.25 (s, 1H), 6.90 (d, *J* = 15.3 Hz, 1H), 6.76 (dd, *J* = 15.3, 11.6 Hz, 1H), 4.40 (s, 2H), 3.59 (s, 3H), 2.24 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.4, 145.2, 144.9, 143.2, 135.5, 135.3, 129.6, 129.5, 128.7, 128.7, 127.5, 122.5, 118.2, 54.5, 52.1, 21.3.




**(*Z*)-methyl-2-(((4-methoxyphenyl)sulfonyl)methyl)-3-phenyl acrylate (4aa):** Yellow solid, Mp: 83-85 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.47-7.42 (m, 2H), 7.35 (dd, *J* = 4.9, 1.7 Hz, 3H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.47 (s, 2H), 3.84 (s, 3H), 3.62 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.3, 164.1, 146.4, 134.0, 131.0, 130.9, 130.0, 129.5, 129.1, 121.5, 114.5, 56.0, 55.5, 52.8. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{19}O_5S$: 347.0948, Found: 347.0951.

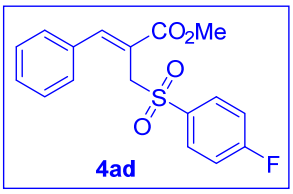



**(*Z*)-methyl-2-(((4-(tert-butyl)phenyl)sulfonyl)methyl)-3-phenyl acrylate (4ab)**[4]: White solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.78-7.74 (m, 2H), 7.52-7.48 (m, 2H), 7.46 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.38-7.34 (m, 3H), 4.48 (s, 2H), 3.57 (s, 3H), 1.33 (s, 9H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.1, 157.8, 146.4, 136.3, 133.8, 129.8, 129.3, 128.9, 128.6, 126.3, 121.1, 55.2, 52.5, 35.4, 31.2.

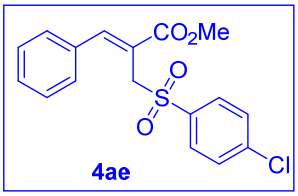



**(*Z*)-methyl-3-phenyl-2-((m-tolylsulfonyl)methyl)acrylate (4ac):** White solid, Mp: 74-76 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.67-7.60 (m, 2H), 7.49-7.43 (m, 2H), 7.40-7.34 (m, 5H), 4.47

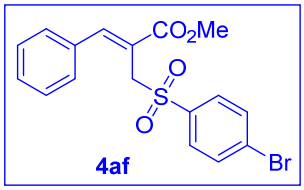
(s, 2H), 3.61 (s, 3H), 2.38 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.0, 146.3, 139.5, 139.2, 134.6, 133.7, 129.7, 129.2, 129.0, 128.8, 128.8, 125.8, 121.1, 55.1, 52.5, 21.4. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{19}O_4S$: 331.0999, Found: 331.1004.



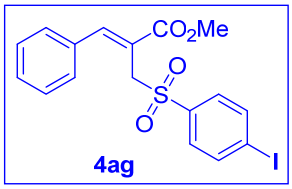

**(*Z*)-methyl-2-(((4-fluorophenyl)sulfonyl)methyl)-3-phenylacrylate (4ad)**[4]: Colorless oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.88-7.78 (m, 2H), 7.43 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.37 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.12 (t, *J* = 8.6 Hz, 2H), 4.50 (s, 2H), 3.65 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.9 (d, $J_{CF}$ = 9.2 Hz), 165.0, 146.5, 135.2 (d, $J_{CF}$ = 3.1 Hz), 133.6, 131.5 (d, $J_{CF}$ = 9.7 Hz), 129.9, 129.2, 128.9, 120.8, 116.4 (d, $J_{CF}$ = 22.6 Hz), 55.1, 52.6. $^{19}$F NMR (471 MHz, $CDCl_3$) δ 103.4.



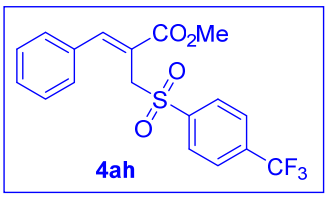

**(*Z*)-methyl-2-(((4-chlorophenyl)sulfonyl)methyl)-3-phenylacrylate (4ae)**[4]: White solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.39 (m, 7H), 4.51 (s, 2H), 3.66 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.9, 146.6, 140.7, 137.5, 133.6, 130.1, 129.9, 129.4, 129.1, 128.9, 120.8, 55.0, 52.7.




**(*Z*)-methyl-2-(((4-bromophenyl)sulfonyl)methyl)-3-phenylacrylate (4af)**[4]: White solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.37 (s, 5H), 4.51 (s, 2H), 3.66 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.9, 146.6, 138.0, 133.6, 132.4, 130.2, 129.8, 129.3, 129.1, 129.0, 120.8, 54.9, 52.7.

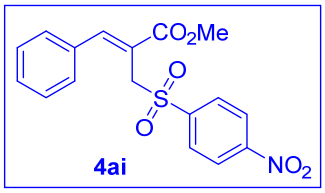



**(*Z*)-methyl-2-(((4-iodophenyl)sulfonyl)methyl)-3-phenylacrylate (4ag):** White solid, Mp: 138-140 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.38 (s, 5H), 4.51 (s, 2H), 3.67 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.7, 146.3, 138.4, 138.1, 133.4, 129.7, 129.6, 128.9, 128.7, 120.6, 101.9, 54.7, 52.5. HRMS (ESI) [M+H$^+$] Calcd For $C_{17}H_{16}IO_4S$: 442.9808, Found: 442.9812.

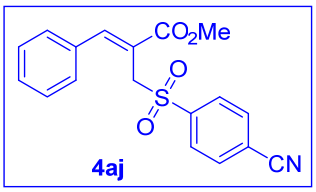



**(*Z*)-methyl-3-phenyl-2-(((4-(trifluoromethyl)phenyl)sulfonyl) methyl)acrylate (4ah):** White solid, Mp: 63-65 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.96-7.89 (m, 3H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.35

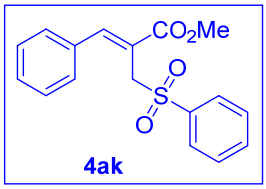
(s, 5H), 4.56 (s, 2H), 3.65 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.8, 146.7, 142.5, 133.5, 129.9, 129.3, 129.0, 126.2 (q, $J_{CF}$ = 3.6 Hz), 120.6, 54.8, 52.7. $^{19}$F NMR (471 MHz, $CDCl_3$) δ 63.2. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{16}F_3O_4S$: 385.0716, Found: 385.0719.




**(*Z*)-methyl-2-(((4-nitrophenyl)sulfonyl)methyl)-3-phenylacrylate (4ai):** Yellow solid, Mp: 131-133 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.28-8.23 (m, 2H), 8.01-7.95 (m, 3H), 7.39-7.34 (m, 5H), 4.59 (s, 2H), 3.70 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.0, 147.2, 145.0, 133.7, 130.4, 129.4, 129.3, 124.4, 120.6, 55.2, 53.1. HRMS (ESI) [M+H$^+$] Calcd For $C_{17}H_{16}NO_6S$: 362.0693, Found: 362.0695.




**(*Z*)-methyl-2-(((4-cyanophenyl)sulfonyl)methyl)-3-phenylacrylate (4aj):** White solid, Mp: 118-120 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.38 (s, 5H), 4.56 (s, 2H), 3.69 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.5, 146.7, 143.1, 133.2, 132.5, 129.8, 129.1, 128.9, 128.8, 120.1, 117.3, 117.0, 54.6, 52.5.




**(*Z*)-methyl-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (4ak)**[4]: Yellow solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52-7.45 (m, 4H), 7.41-7.34 (m, 3H), 4.49 (s, 2H), 3.58 (s, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.0, 146.6, 139.4, 133.9, 133.7, 129.9, 129.3, 129.2, 128.9, 128.6, 120.9, 55.2, 52.5. HRMS (ESI) [M+H$^+$] Calcd For $C_{18}H_{16}NO_4S$: 342.0795, Found: 342.0800.

## Reference:


[1] X. Li, X. Xu, Y. Tang, *Org. Biomol. Chem.* **2013**, *11*, 1739-1742.

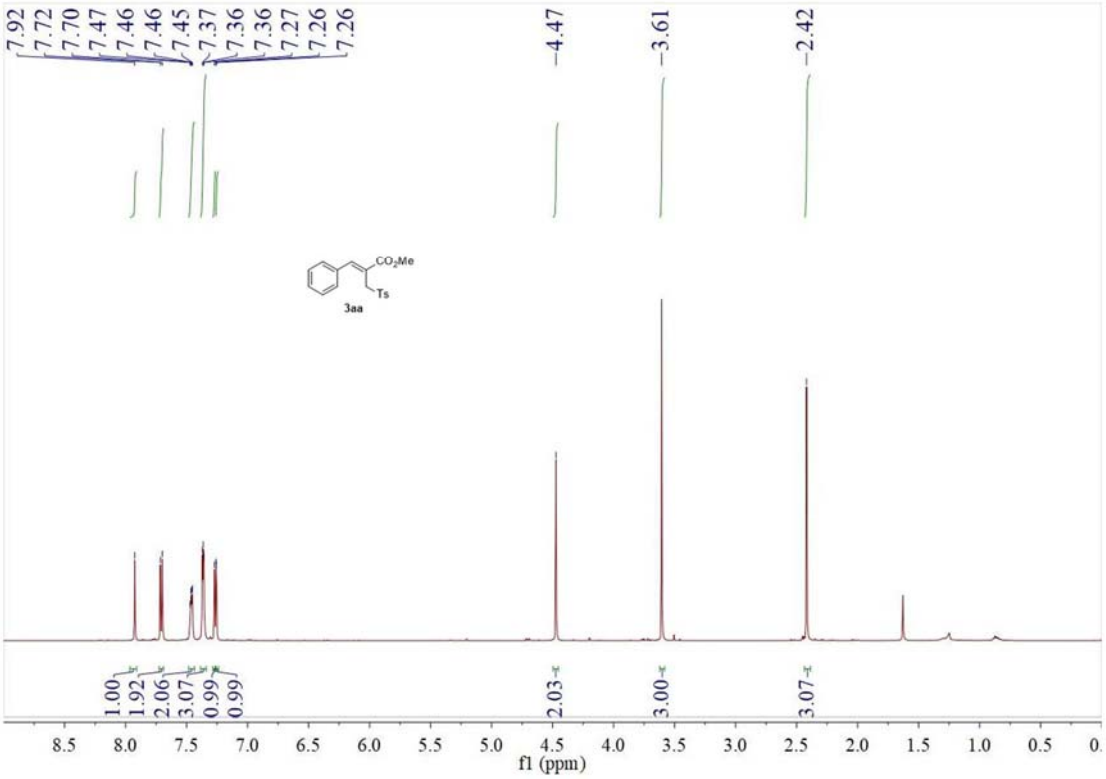
[2] Garima, V. P. Srivastava, L. D. S. Yadav, *Tetrahedron Lett.* **2011**, *52*, 4622-4626.

[3] K. Karnakar, J. Shankar, S. Narayana Murthy, Y. V. D. Nageswar, *Helv. Chim. Acta* **2011**, *94*, 875-880.

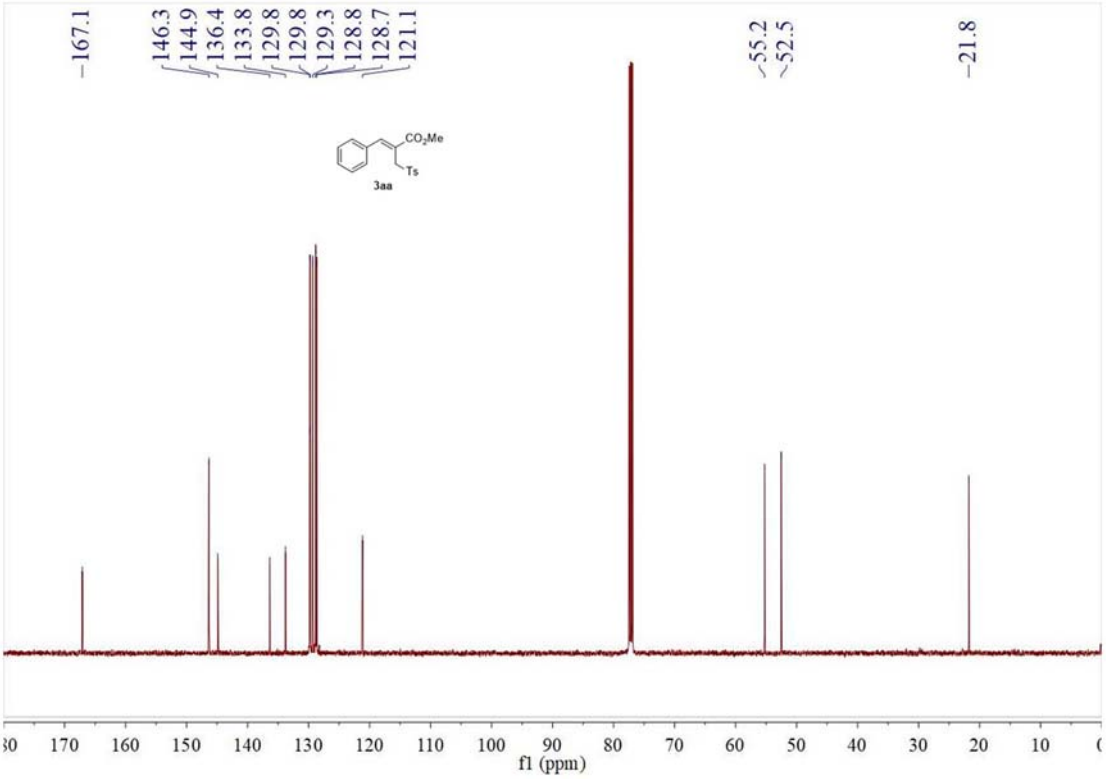
[4] R. J. Reddy, A. Shankar, M. Waheed, *SynOpen* **2021**, *05*, 91-99.

## 4. $^{1}$H and $^{13}$C NMR spectra of Allyl Aryl Sulfone Derivatives (3aa-3aq, 4aa-4ak)

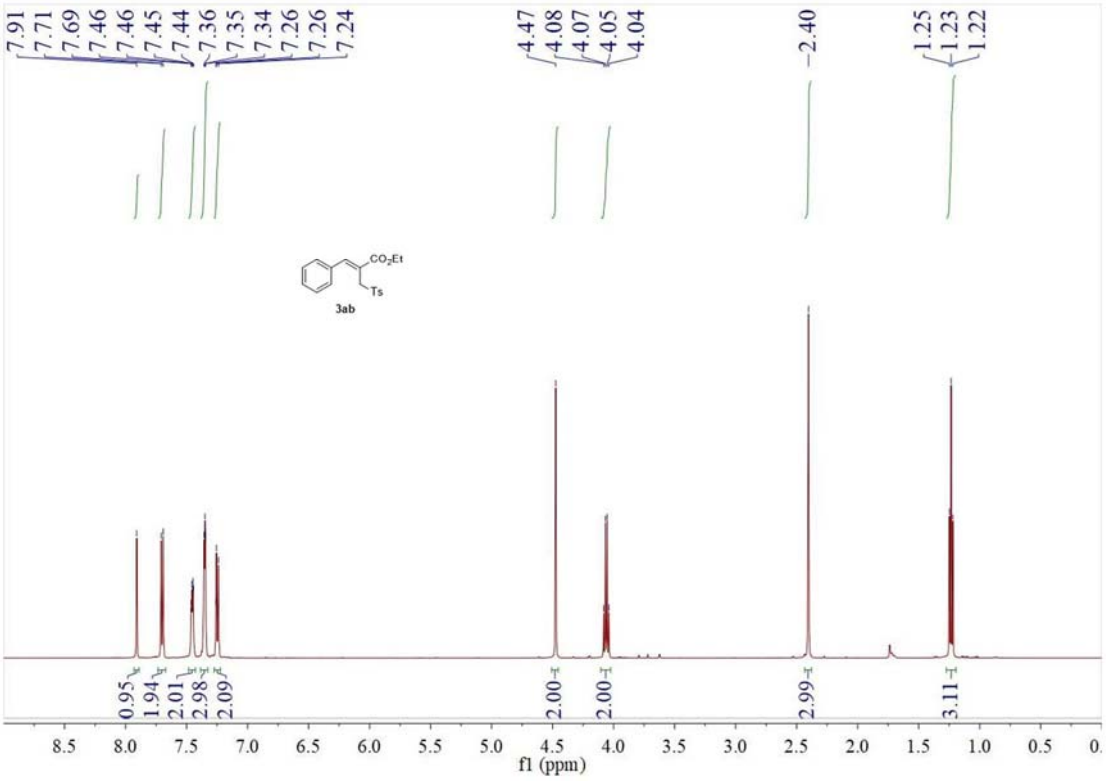
$^{1}$H NMR of **3aa** in $CDCl_3$



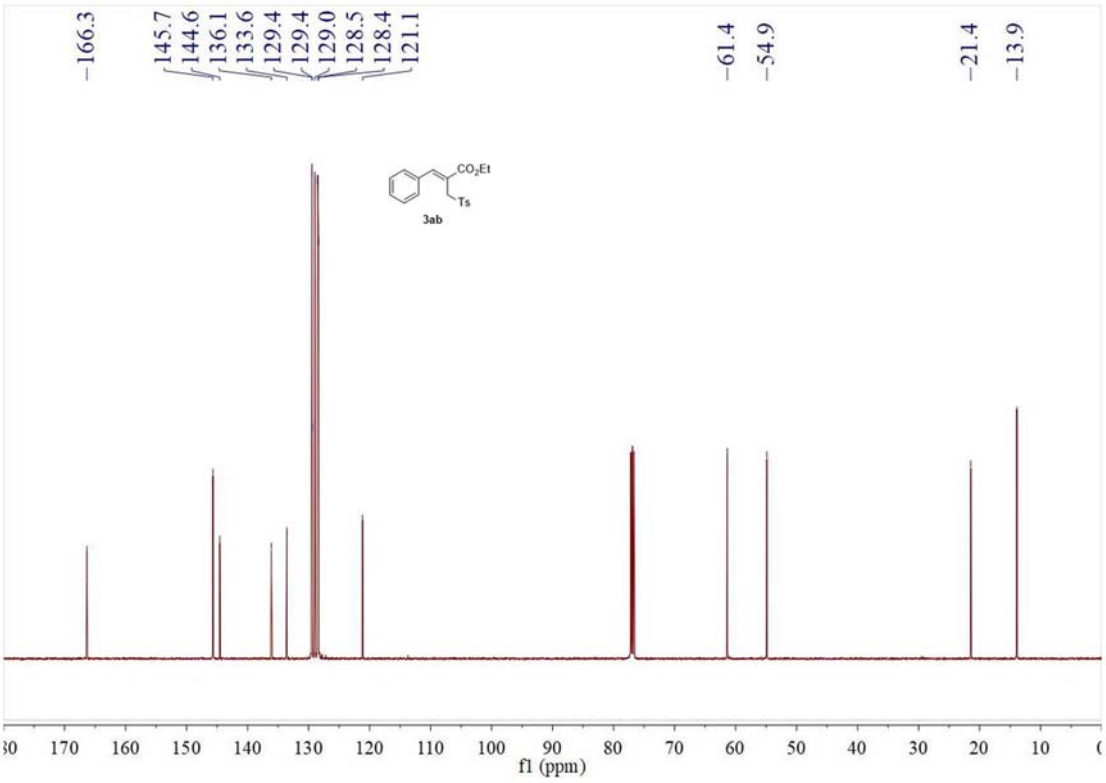

$^{13}$C NMR of **3aa** in $CDCl_3$



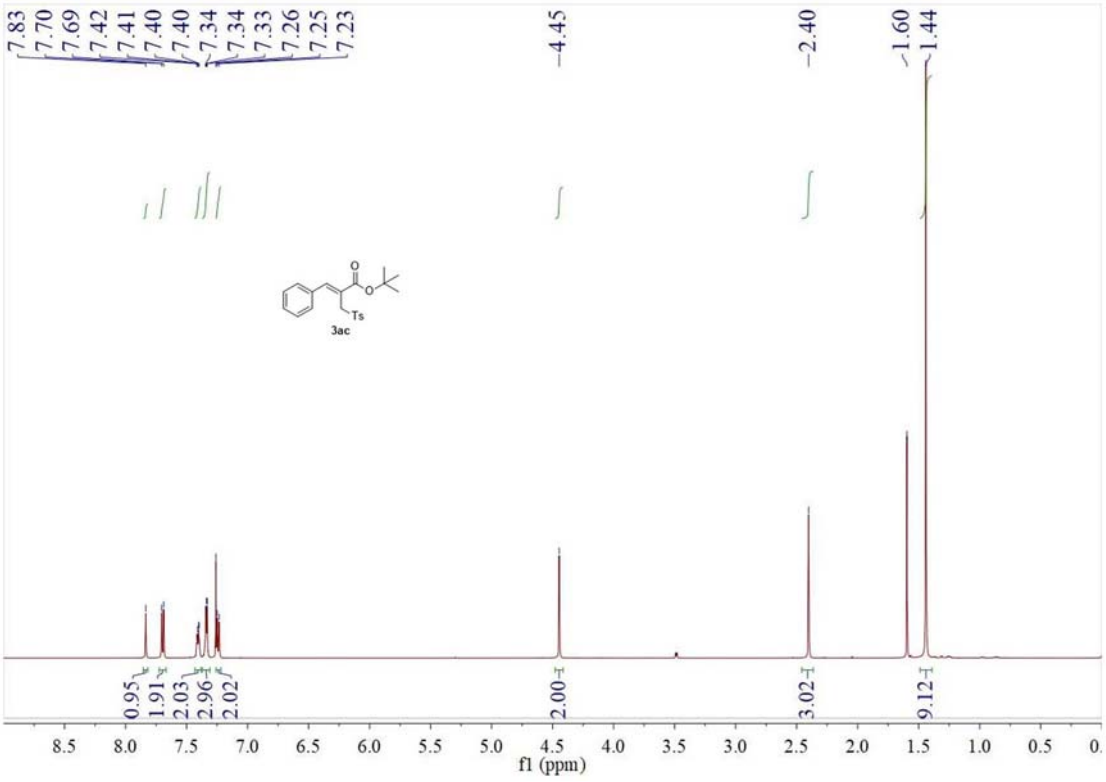
$^{1}$H NMR of **3ab** in $CDCl_3$



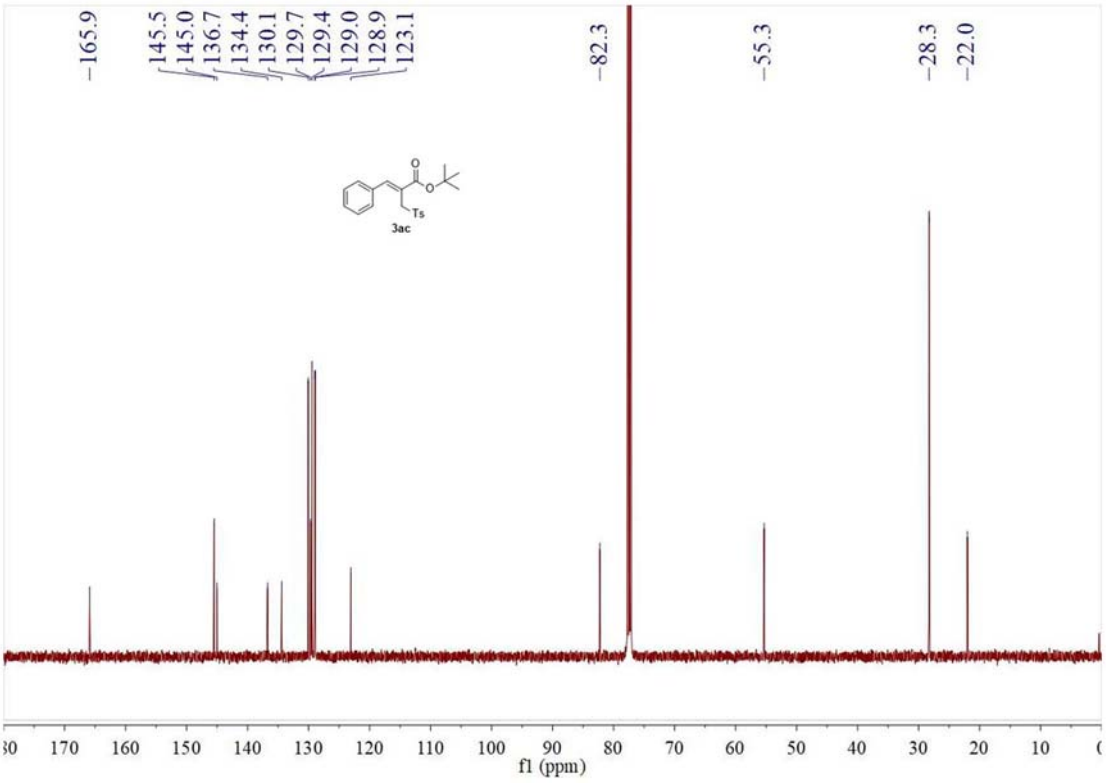

$^{13}$C NMR of **3ab** in $CDCl_3$



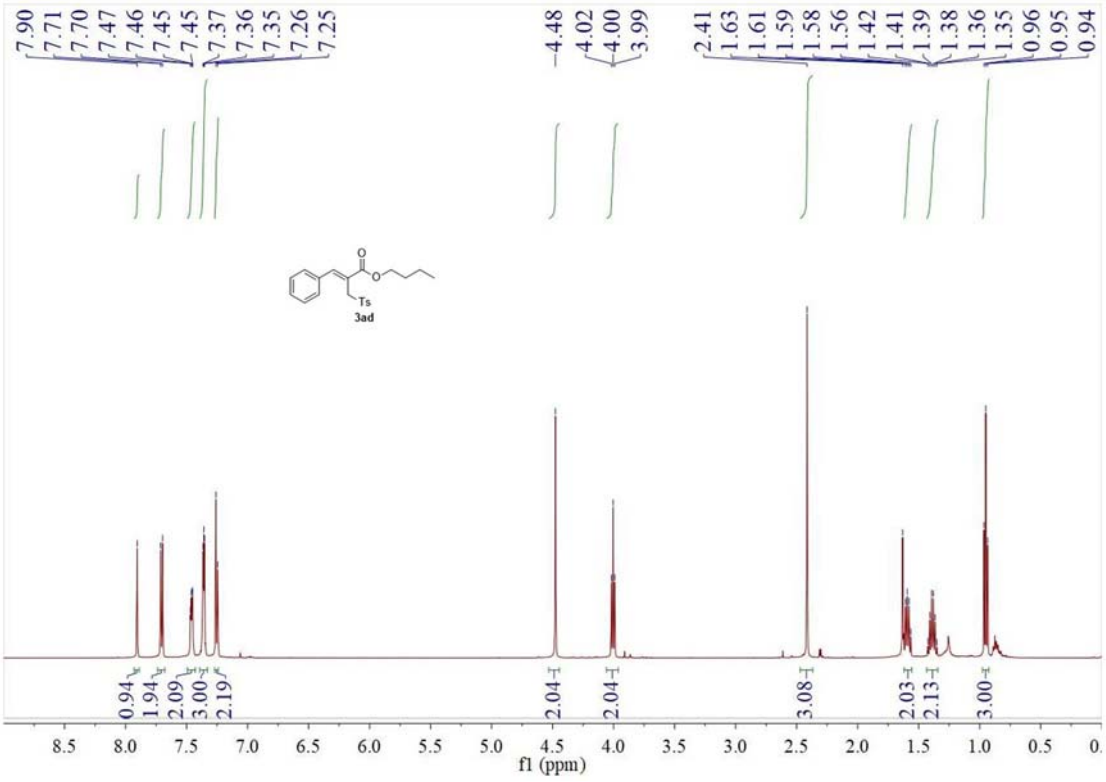
$^{1}$H NMR of **3ac** in $CDCl_3$



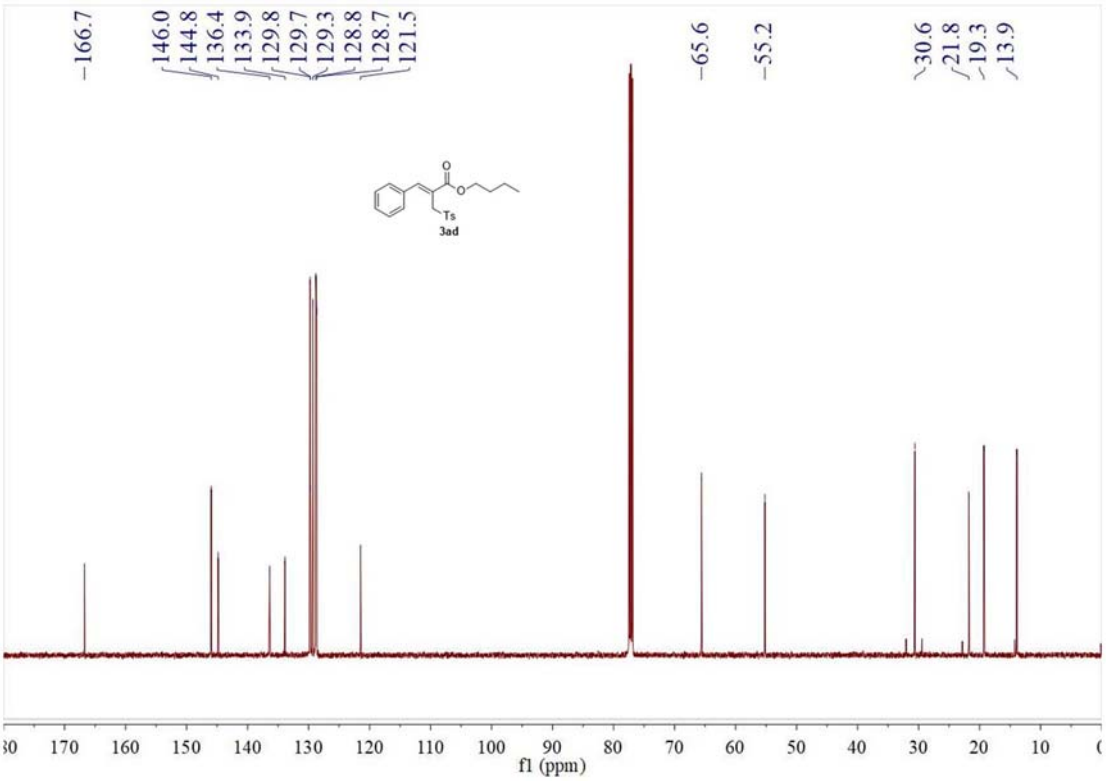

$^{13}$C NMR of **3ac** in $CDCl_3$



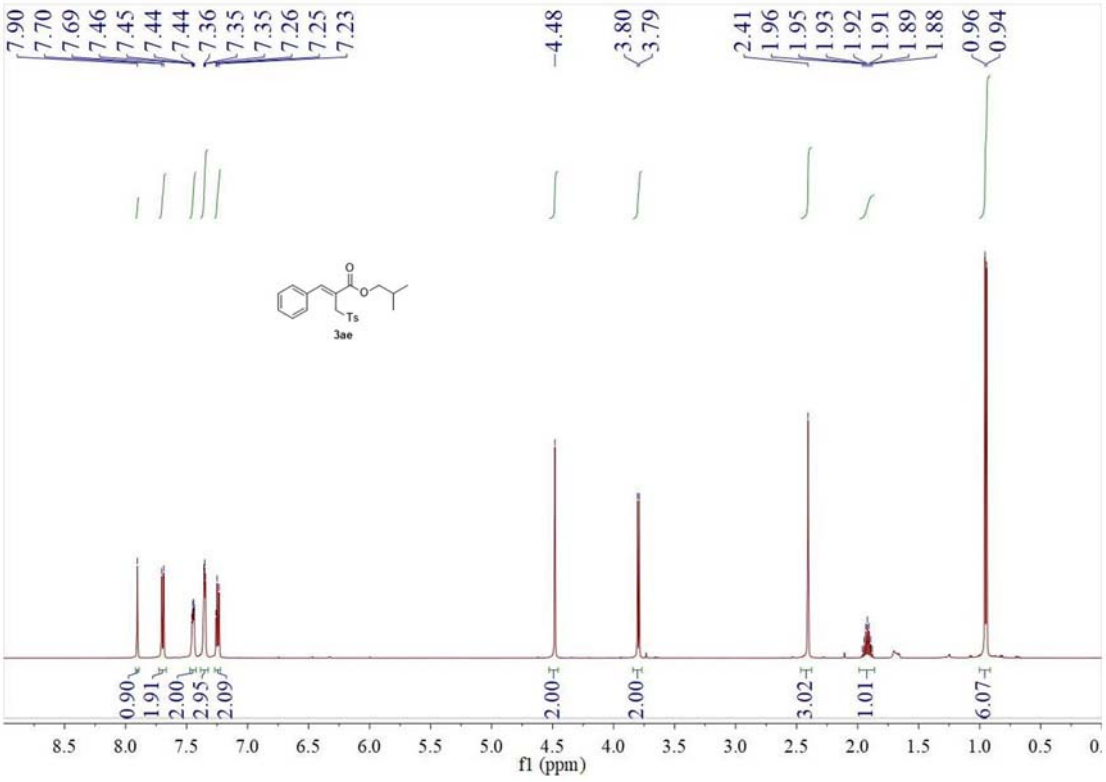
$^{1}$H NMR of **3ad** in $CDCl_3$



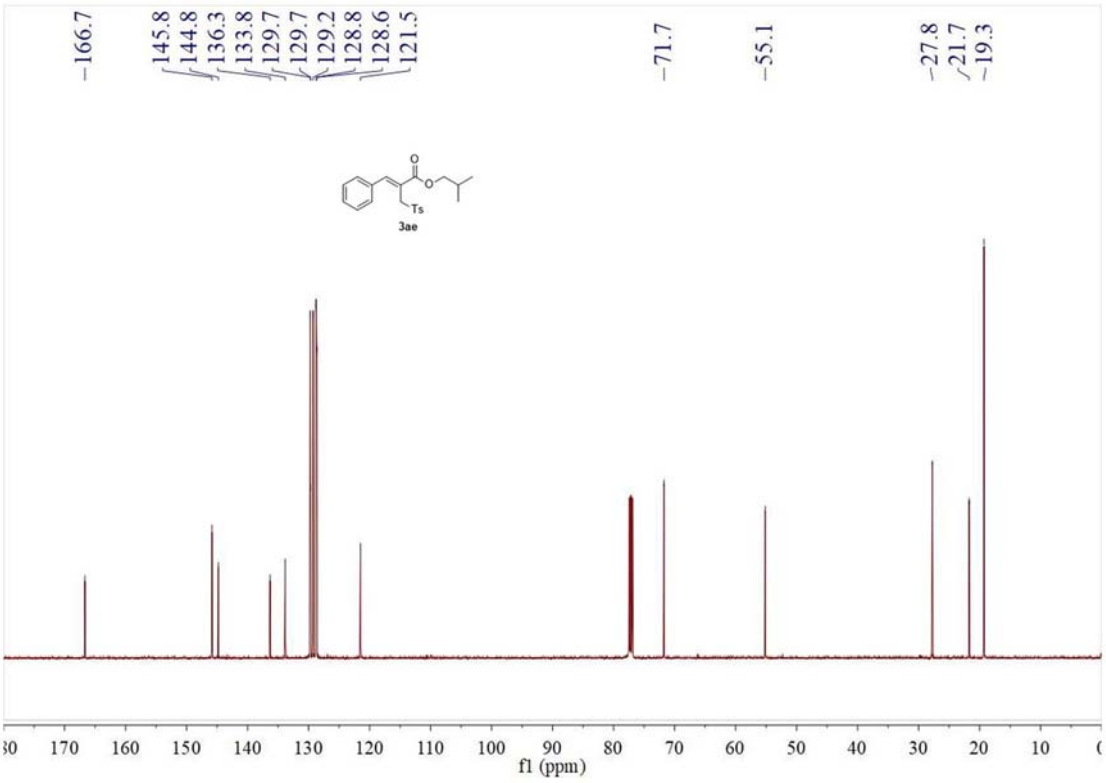

$^{13}$C NMR of **3ad** in $CDCl_3$



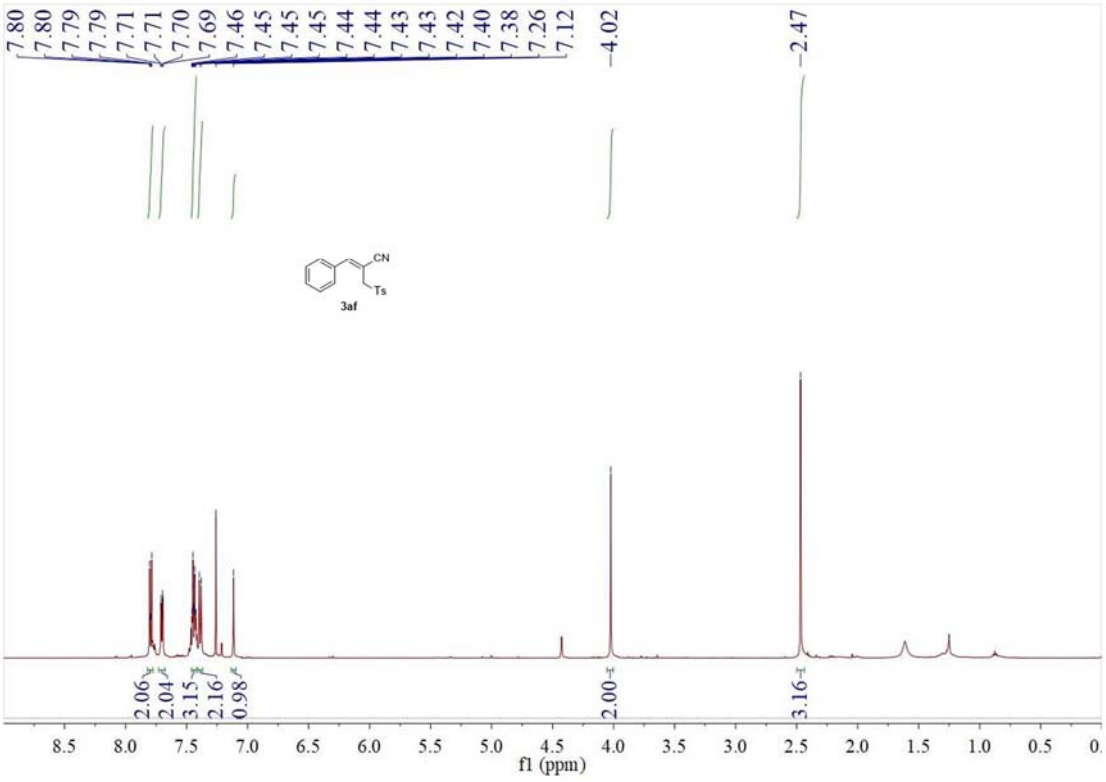
$^{1}$H NMR of **3ae** in $CDCl_3$



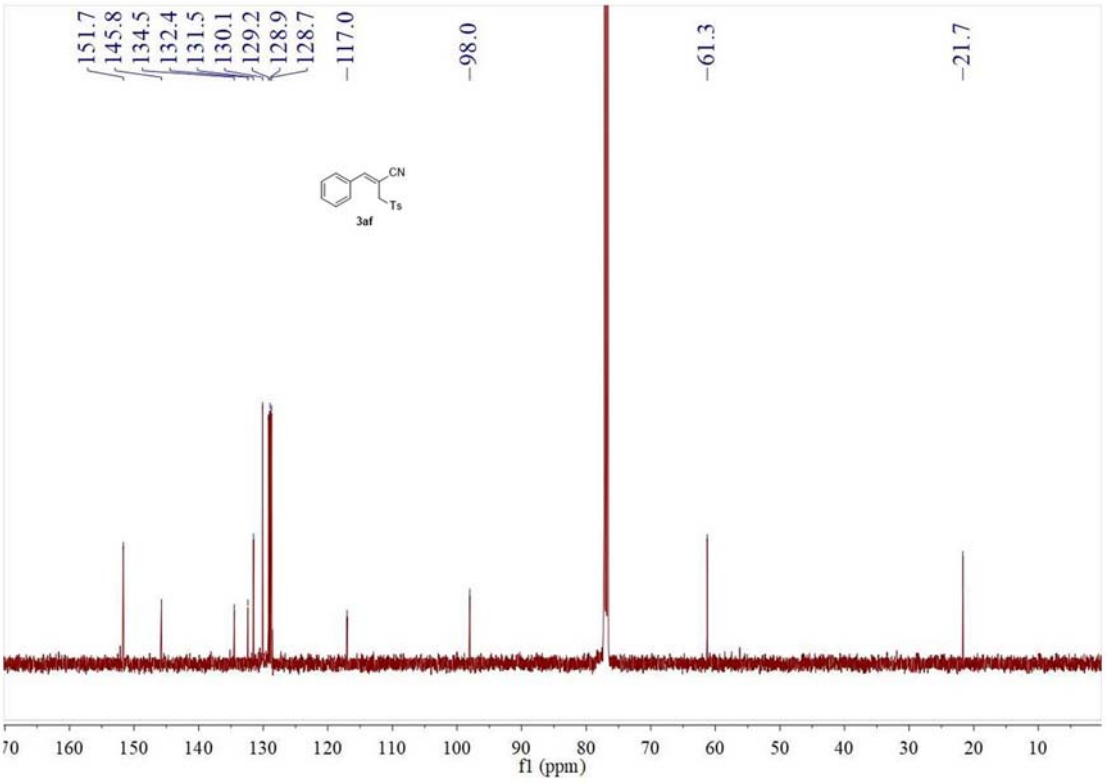

$^{13}$C NMR of **3ae** in $CDCl_3$



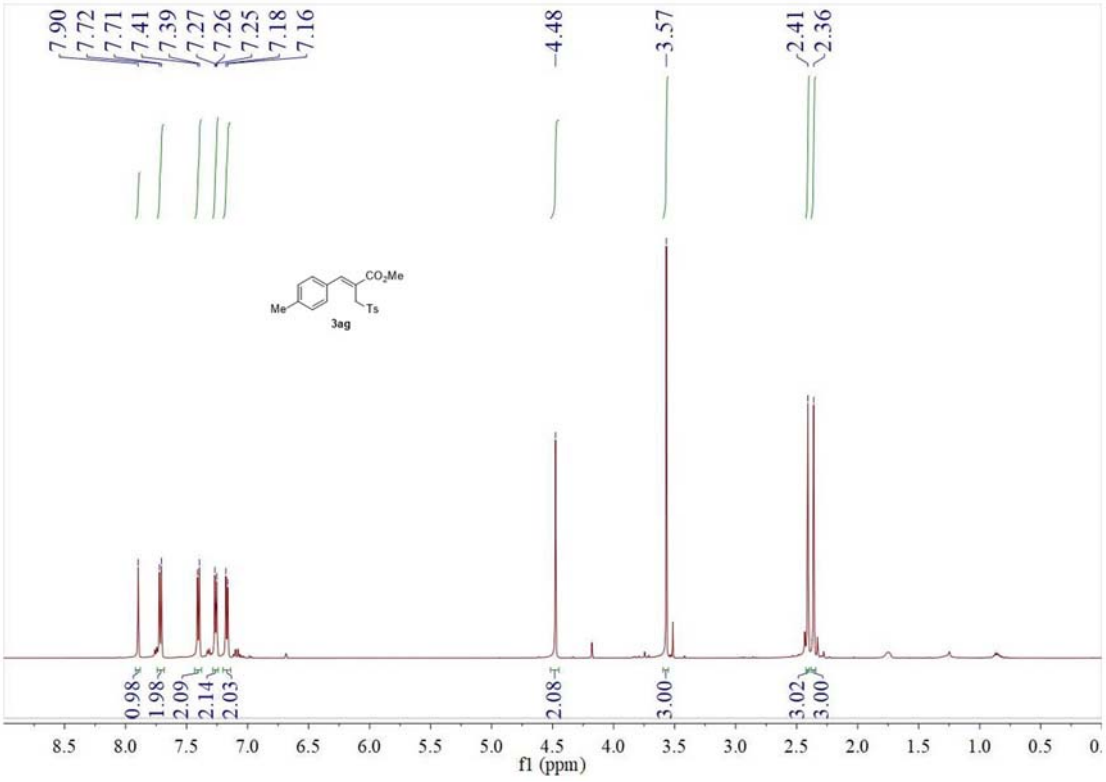
$^{1}$H NMR of **3af** in $CDCl_3$



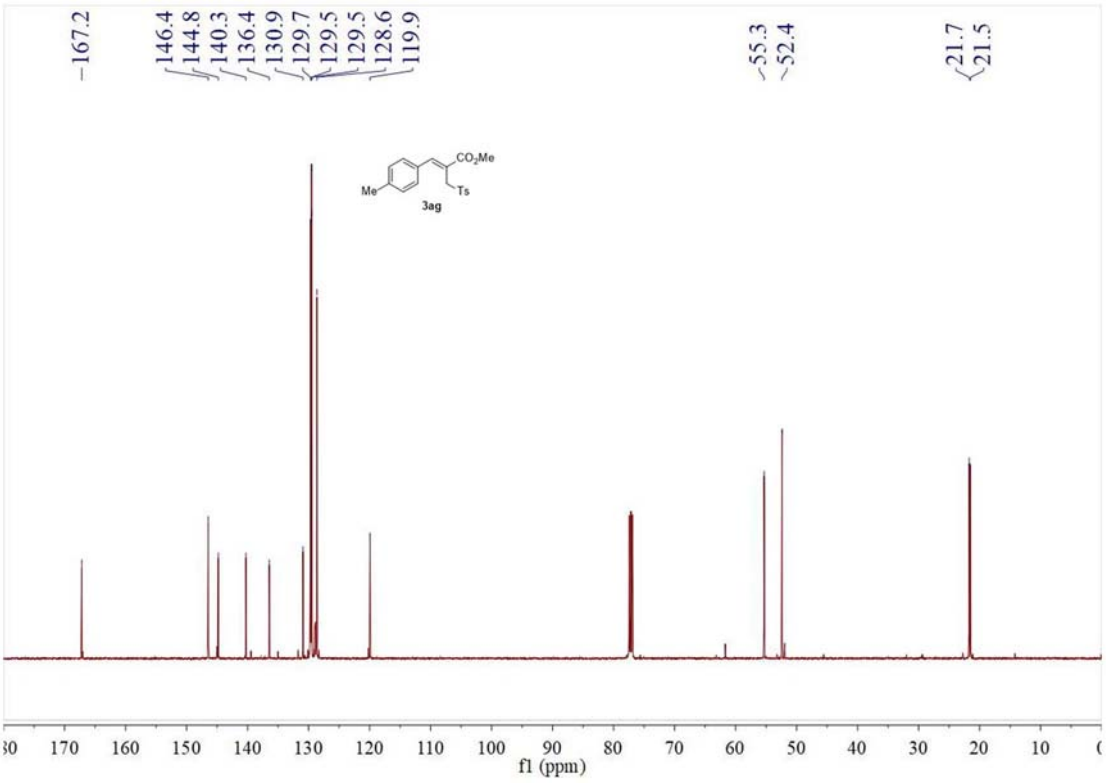

$^{13}$C NMR of **3af** in $CDCl_3$



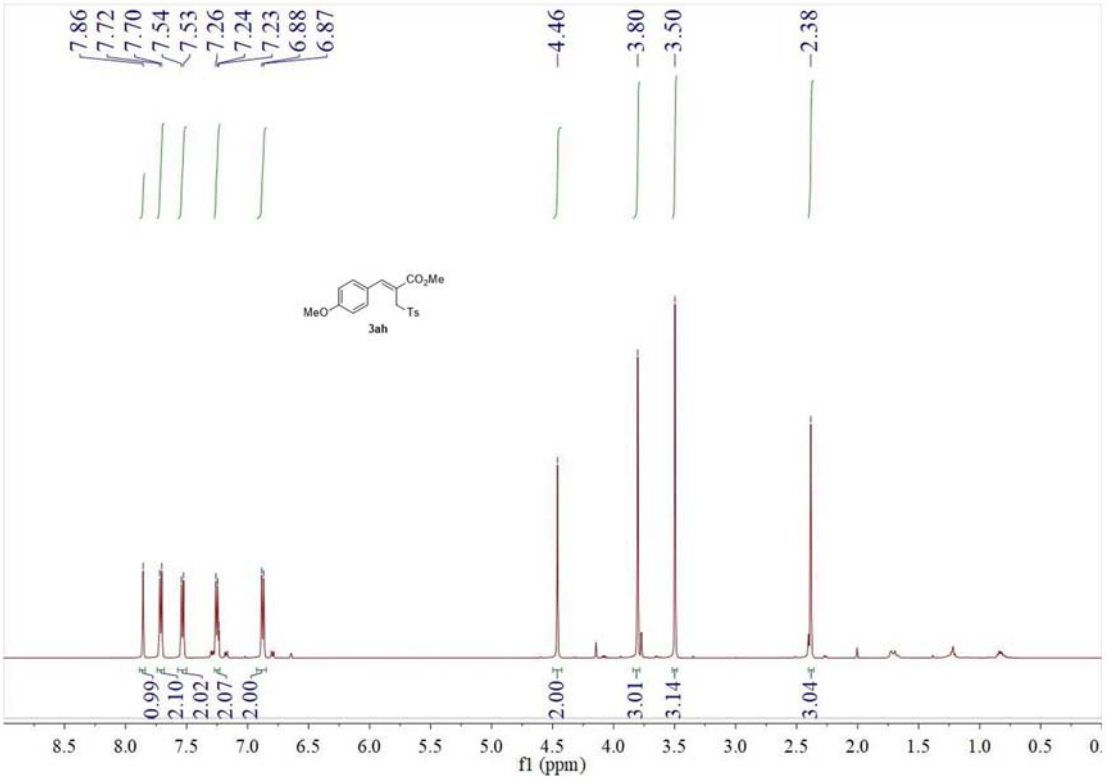
$^{1}$H NMR of **3ag** in $CDCl_3$



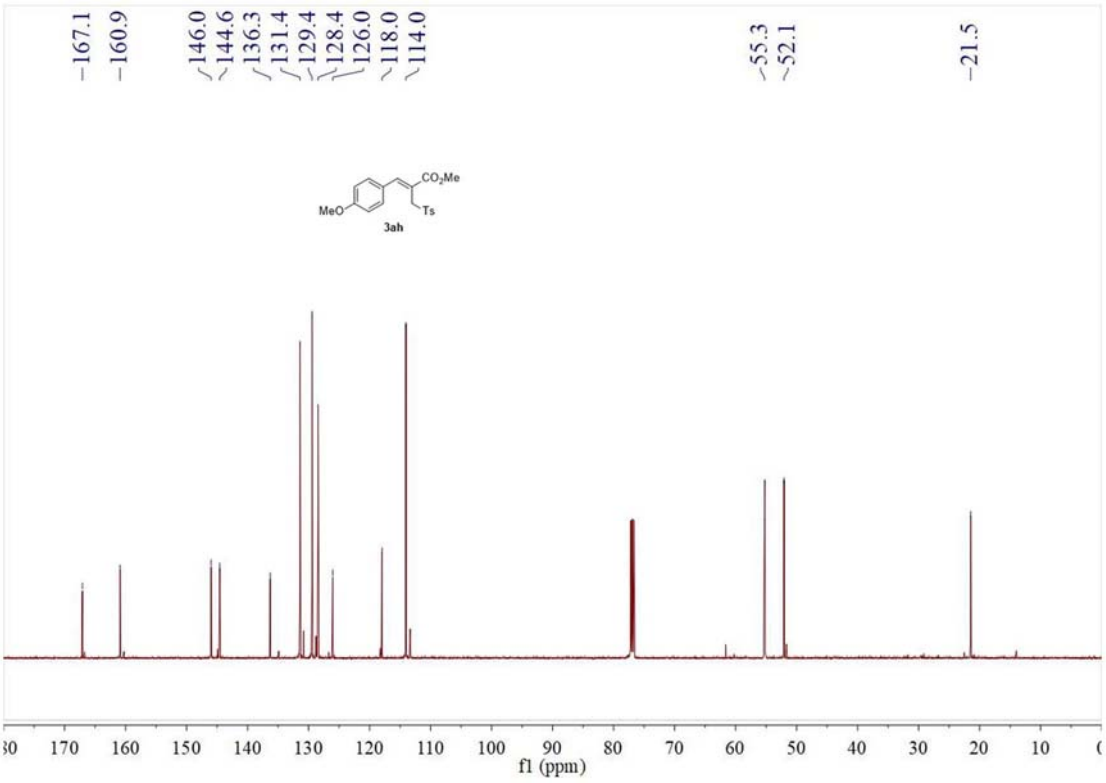

$^{13}$C NMR of **3ag** in $CDCl_3$



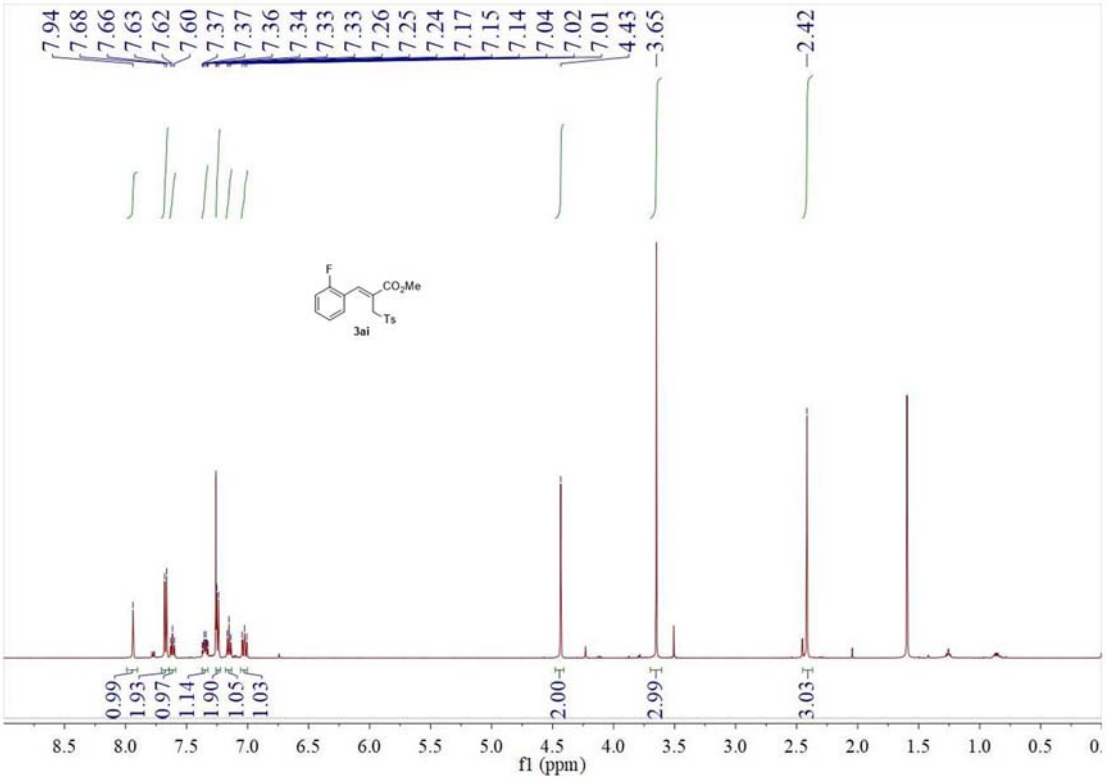
$^{1}$H NMR of **3ah** in $CDCl_3$



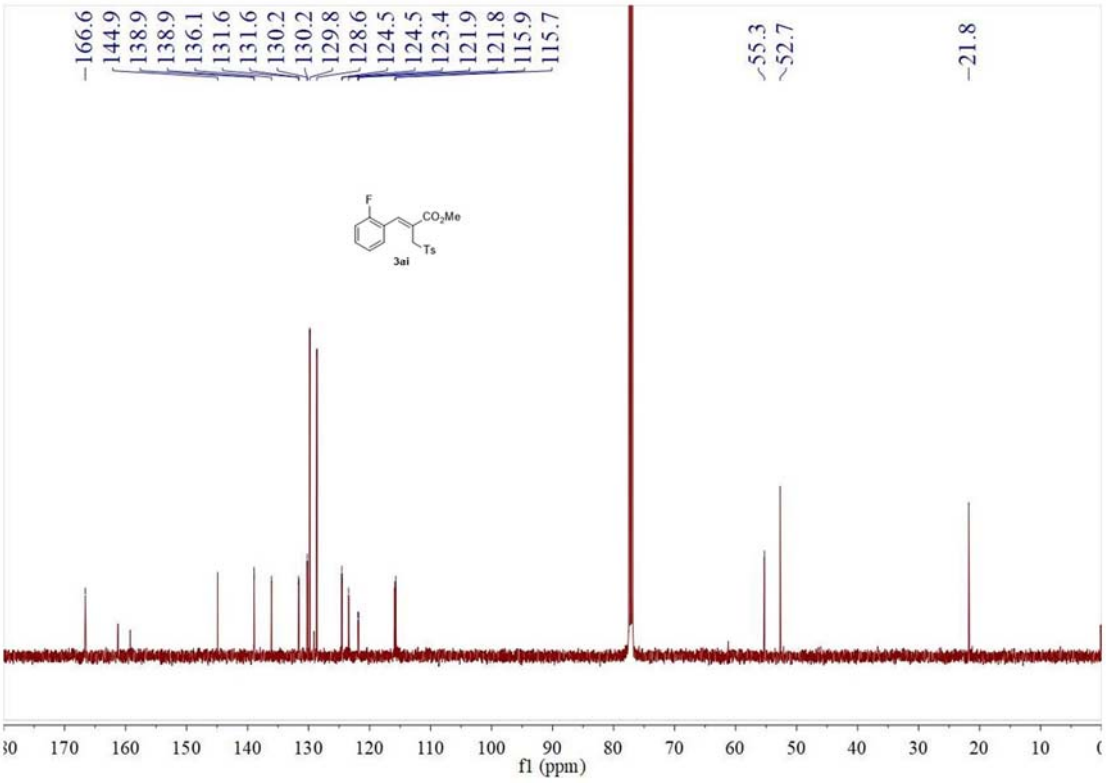

$^{13}$C NMR of **3ah** in $CDCl_3$



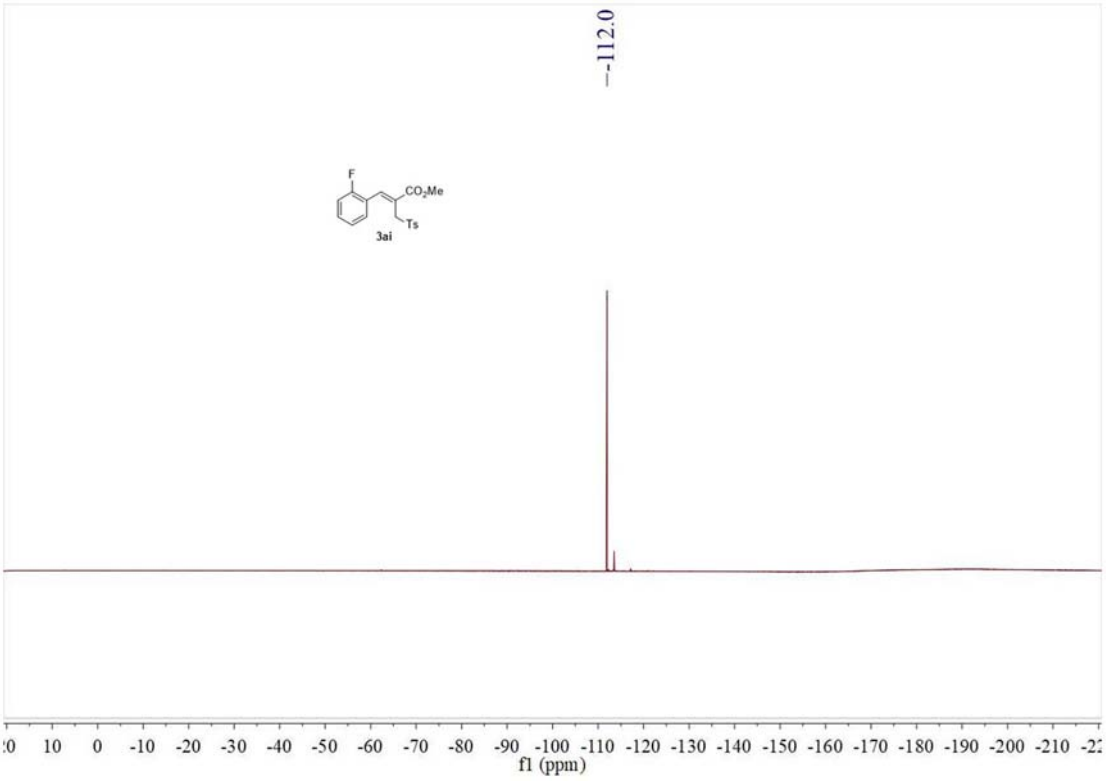
$^{1}$H NMR of **3ai** in $CDCl_3$



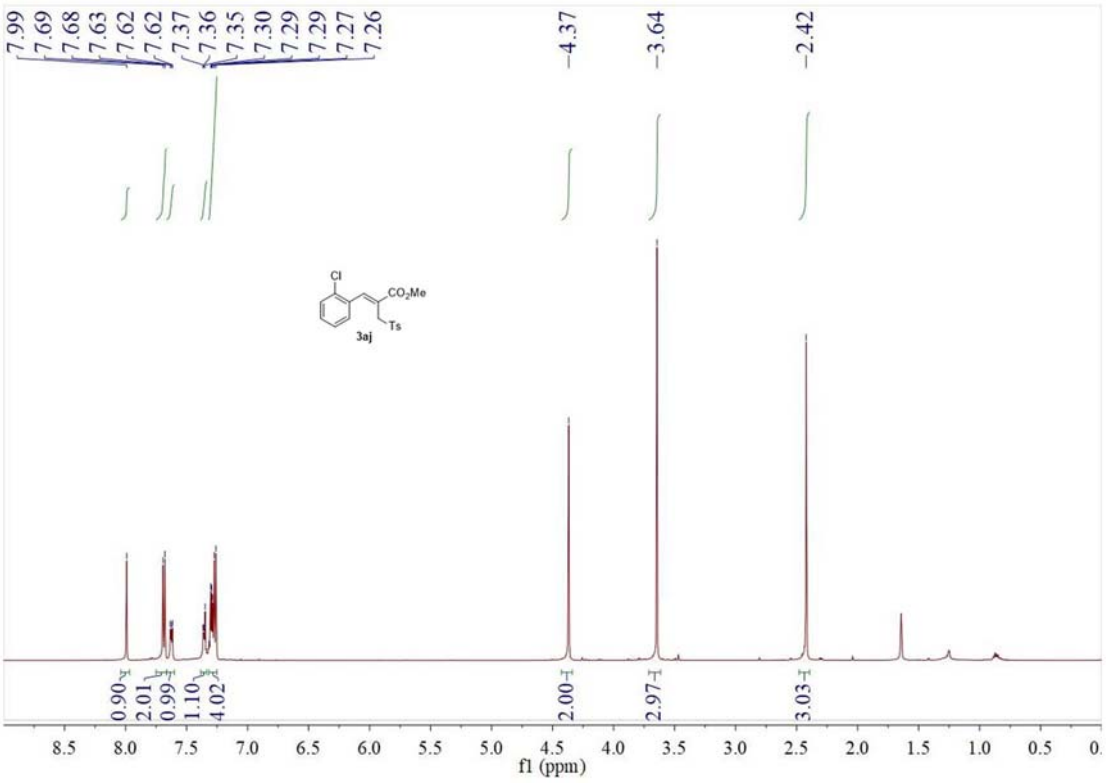

$^{13}$C NMR of **3ai** in $CDCl_3$



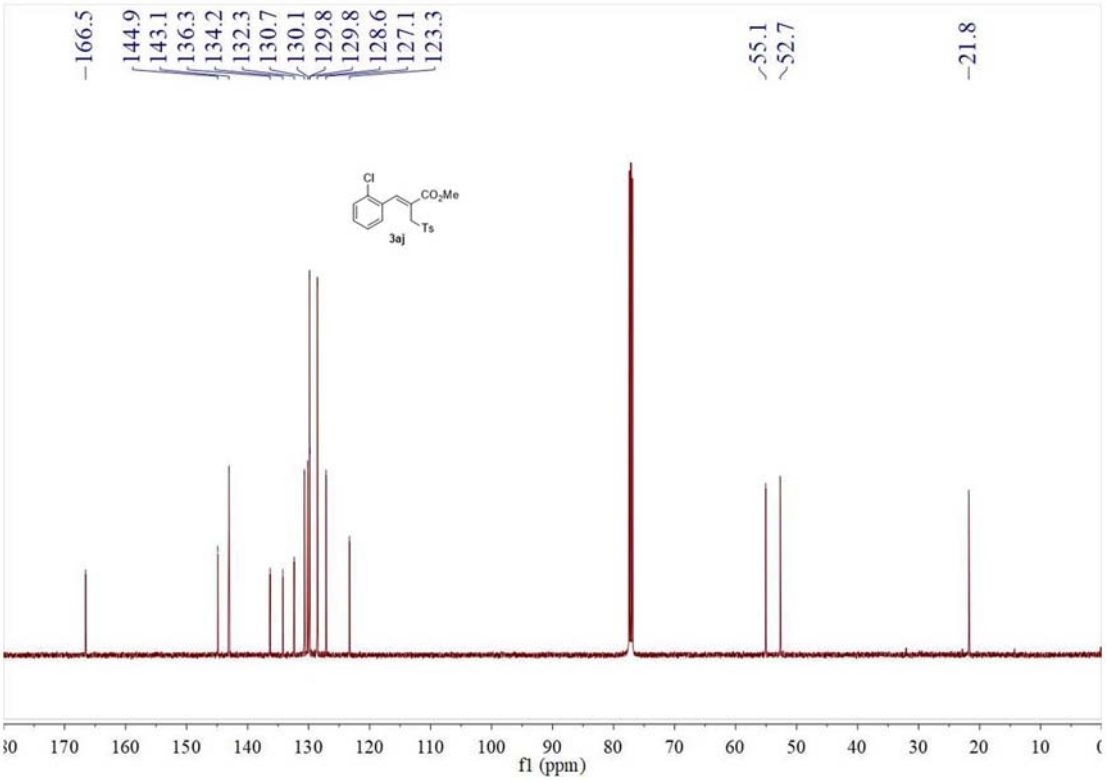
$^{19}$FNMR of **3ai** in $CDCl_3$



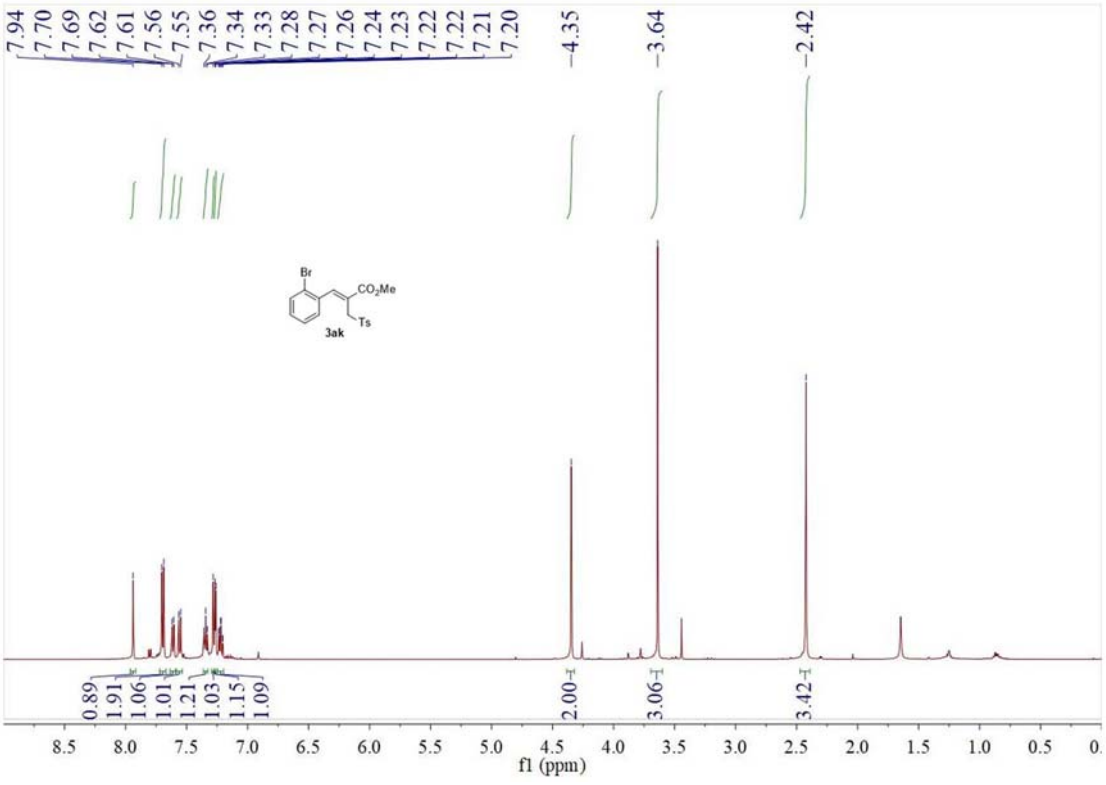

$^{1}$H NMR of **3aj** in $CDCl_3$



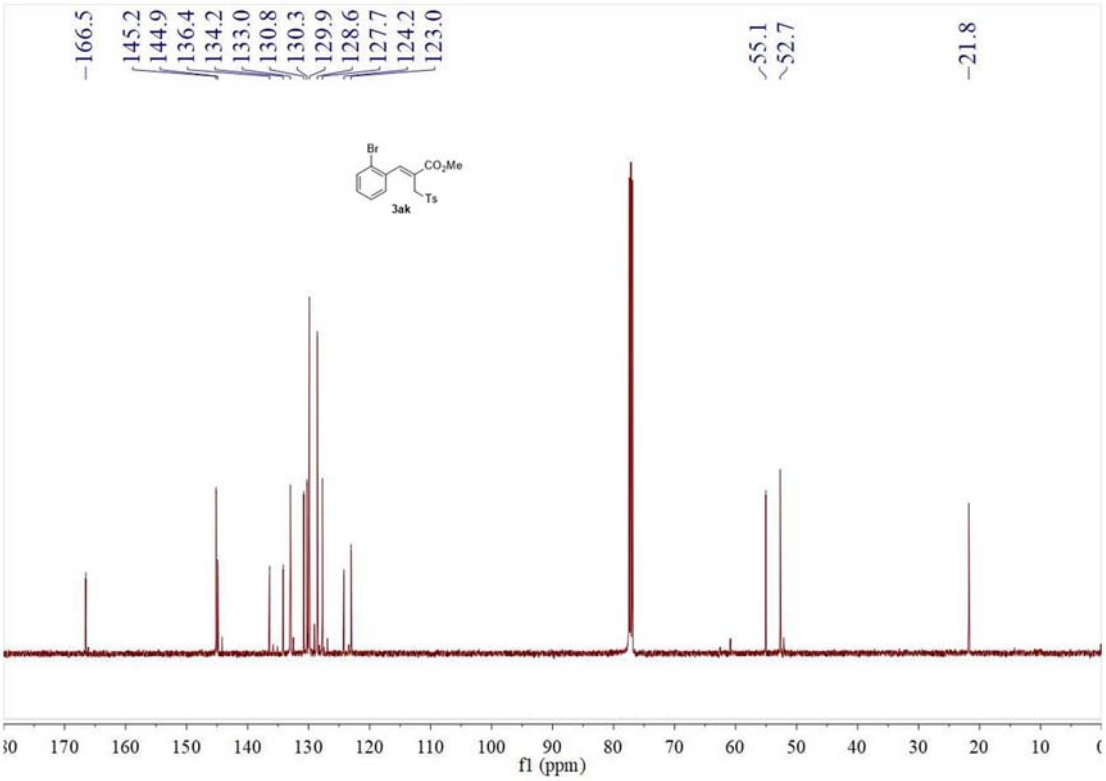
$^{13}$C NMR of **3aj** in $CDCl_3$



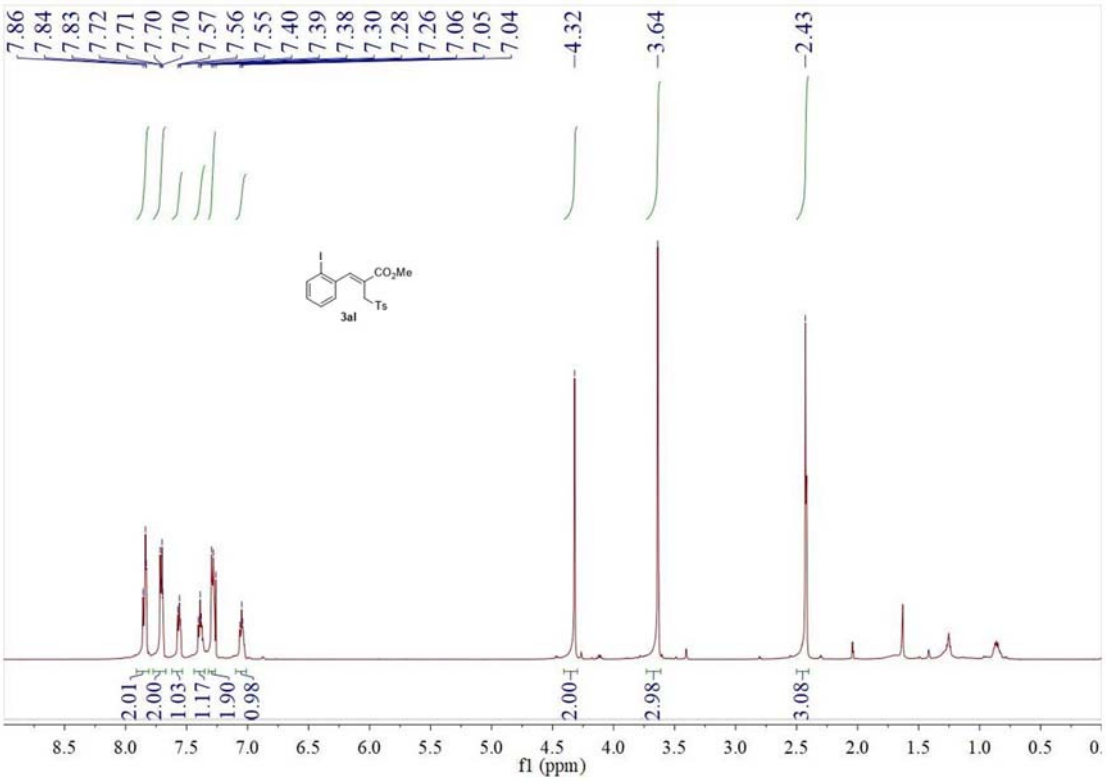

$^{1}$H NMR of **3ak** in $CDCl_3$



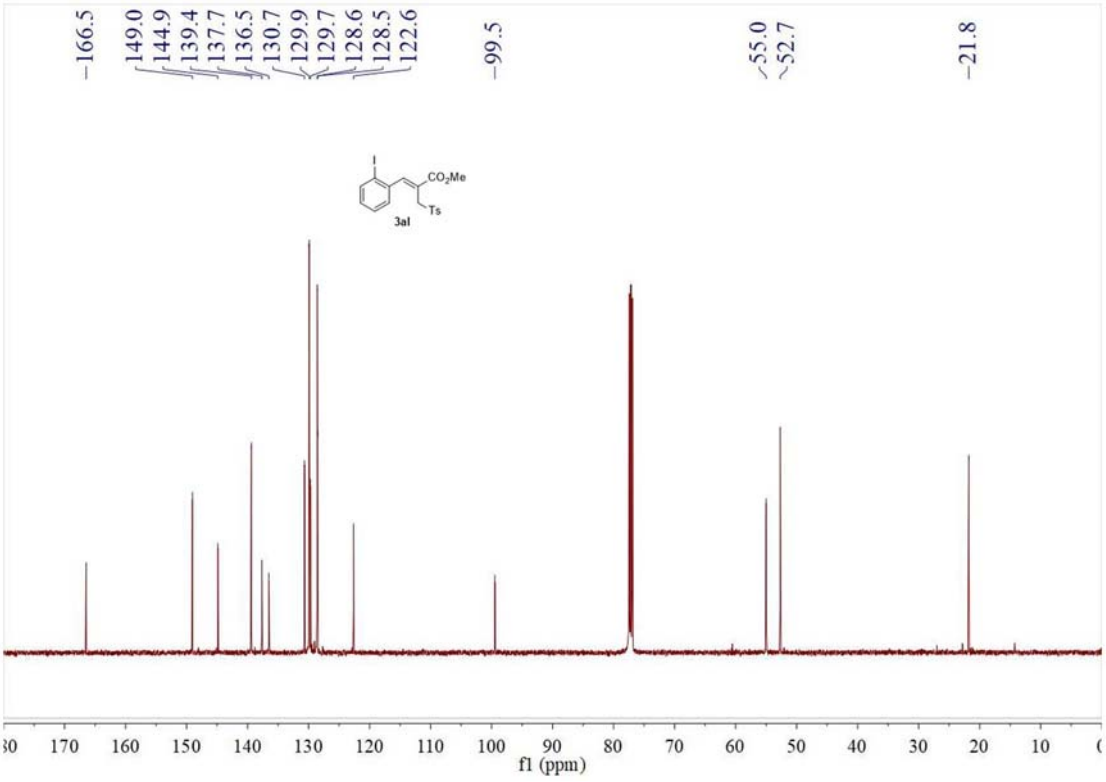
$^{13}$C NMR of **3ak** in $CDCl_3$



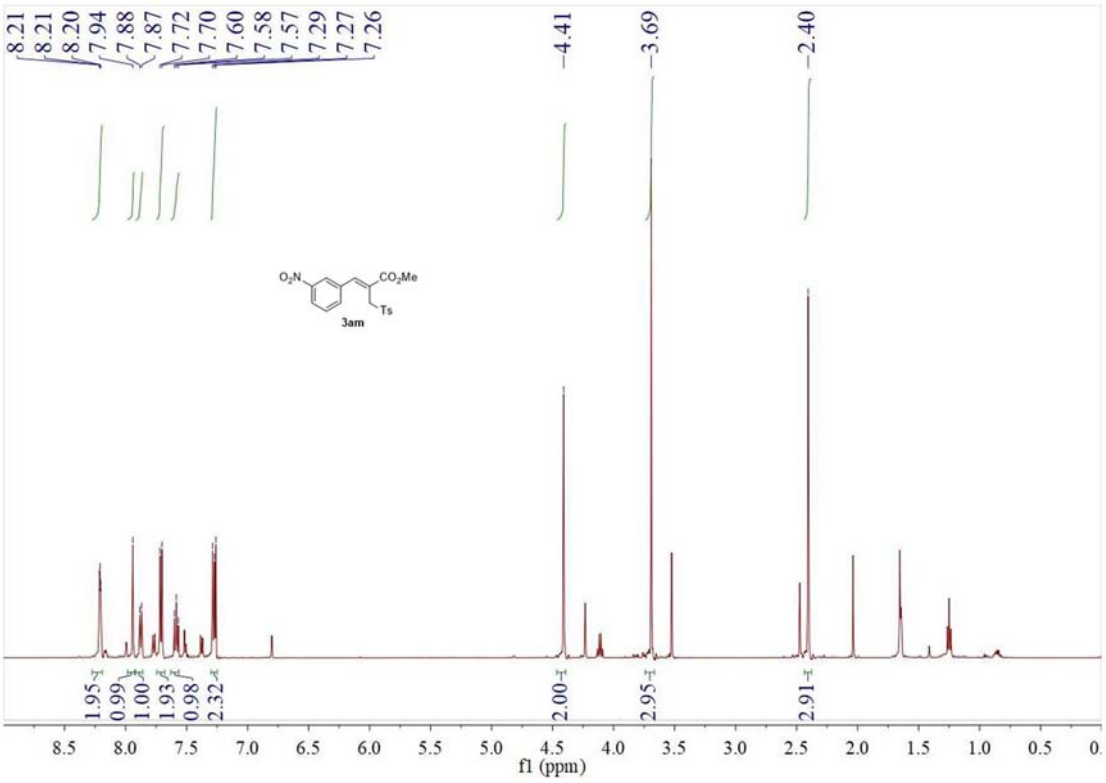

$^{1}$H NMR of **3al** in $CDCl_3$



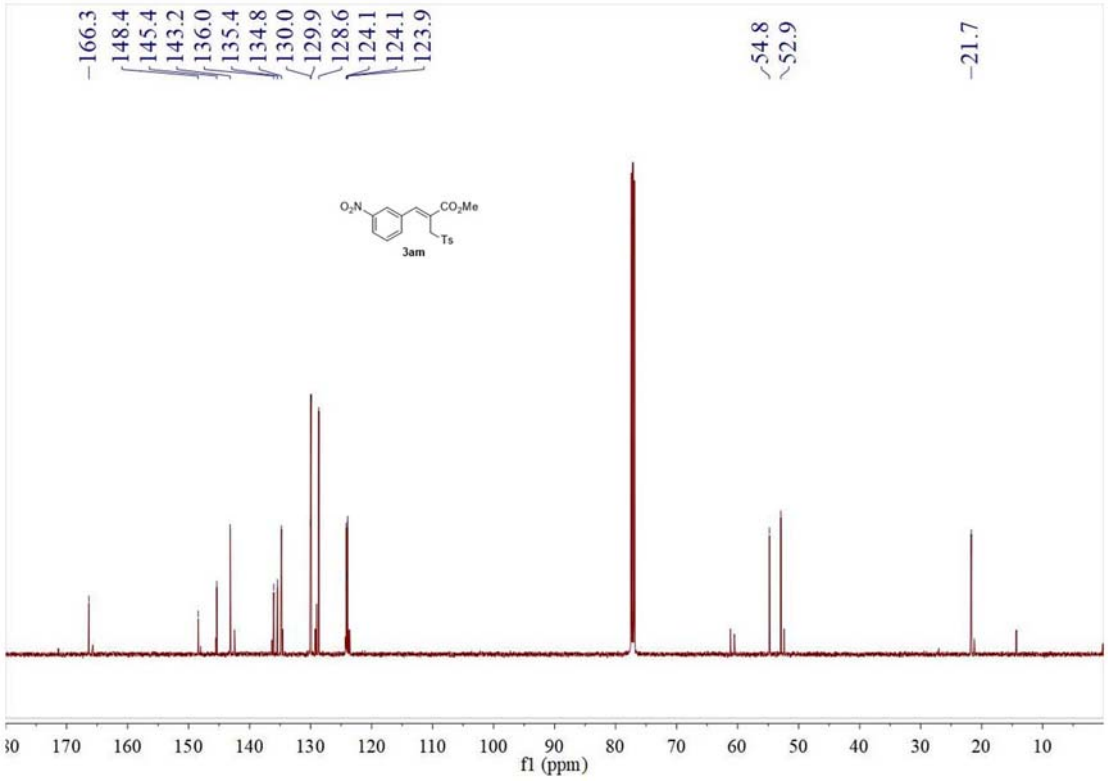
$^{13}C$ NMR of **3al** in $CDCl_3$



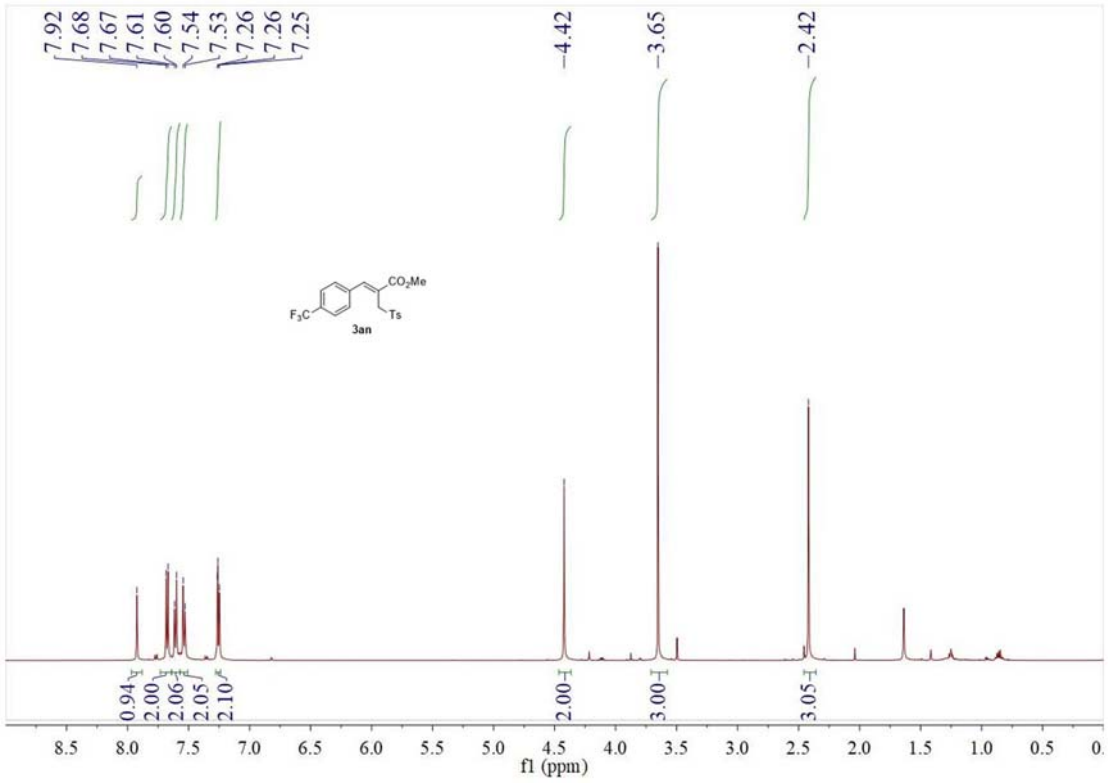

$^{1}H$ NMR of **3am** in $CDCl_3$



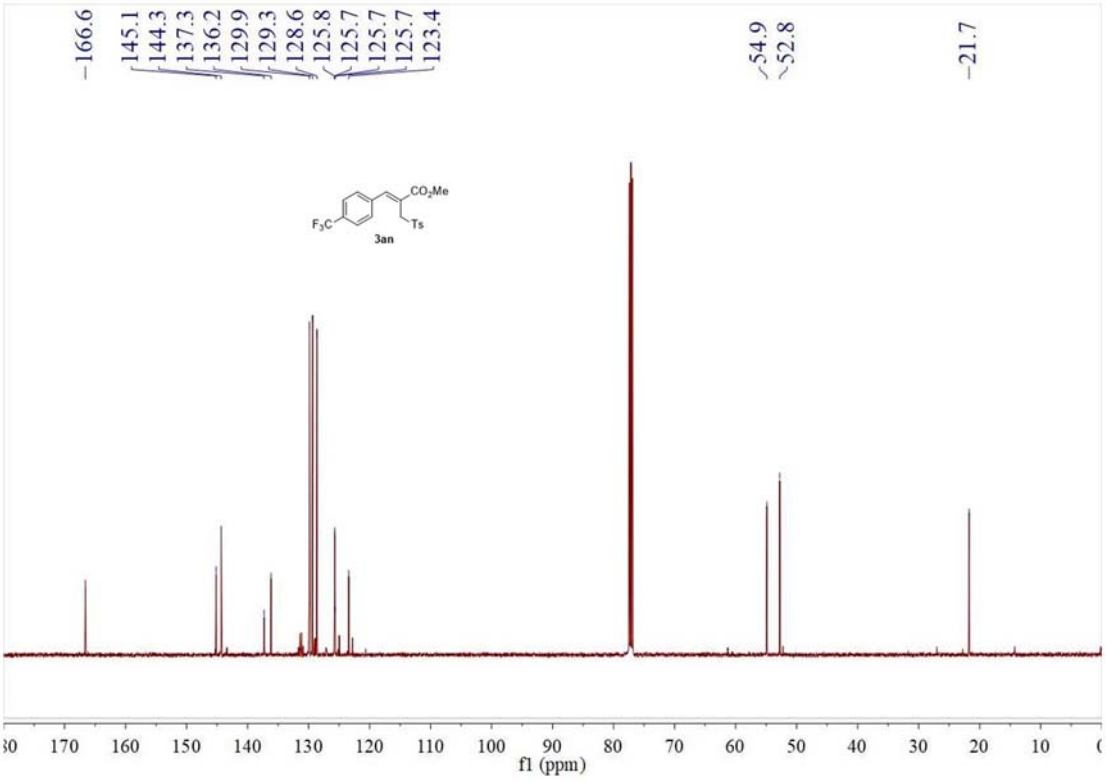
$^{13}$C NMR of **3am** in $CDCl_3$



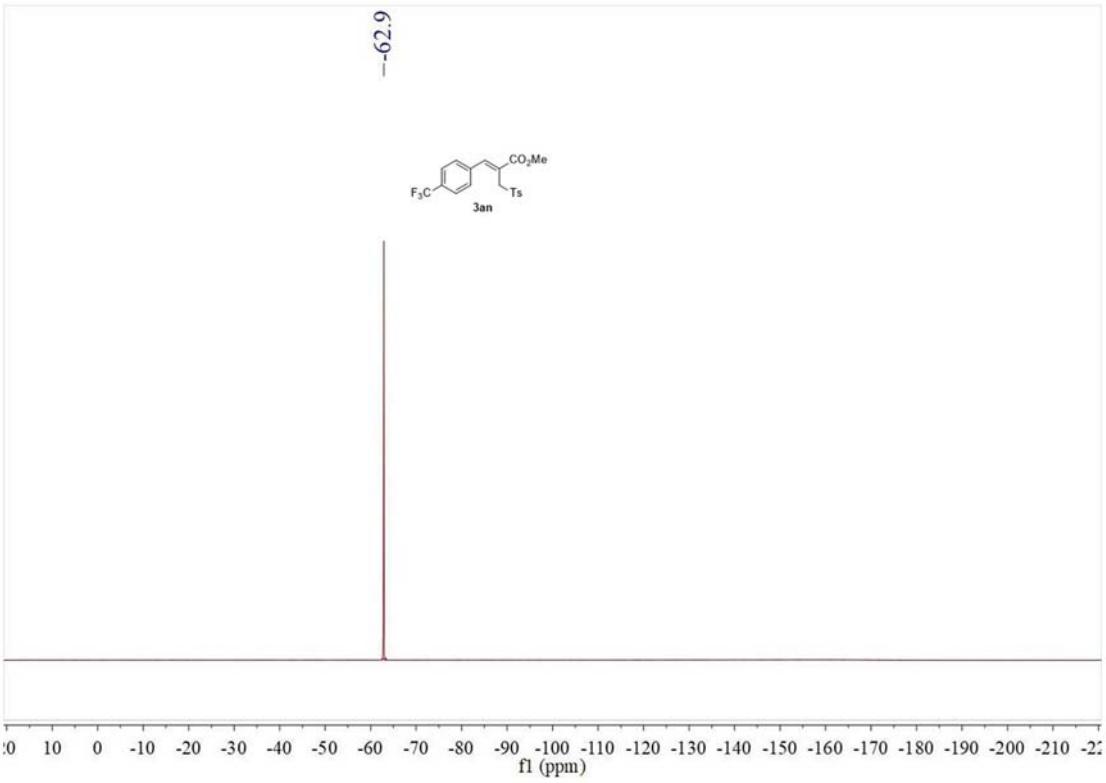

$^{1}$H NMR of **3an** in $CDCl_3$



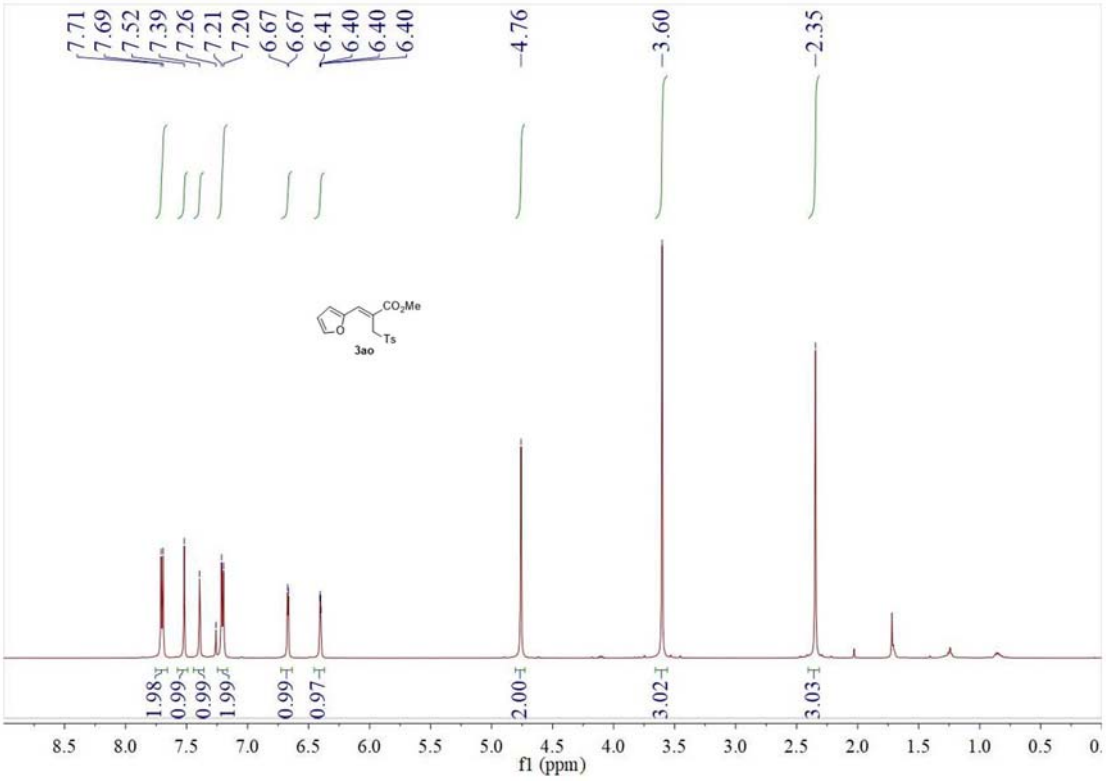
$^{13}$C NMR of **3an** in $CDCl_3$



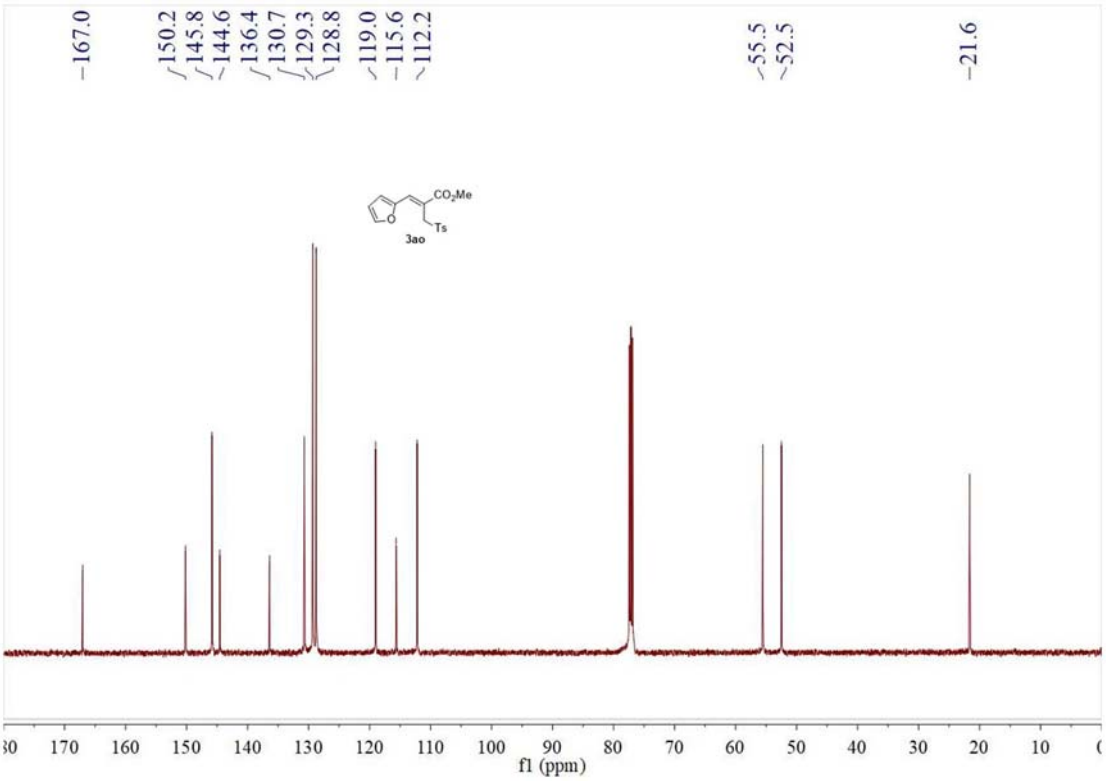

$^{19}$FNMR of **3an** in $CDCl_3$



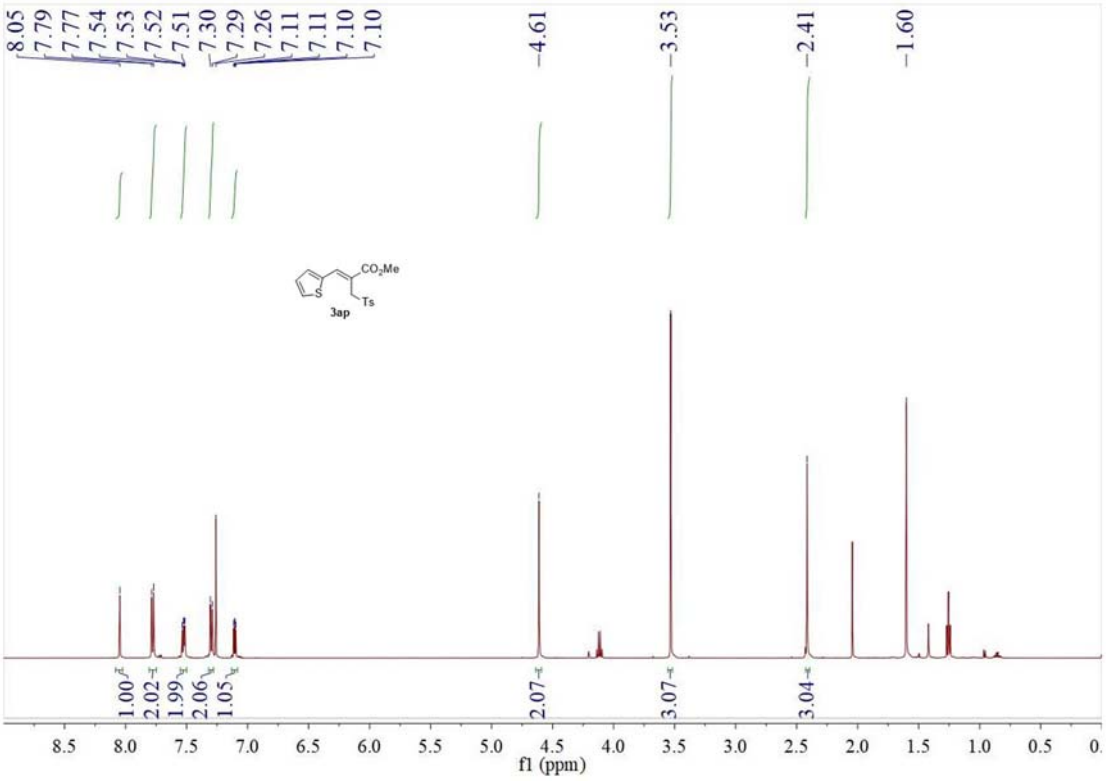
$^{1}$H NMR of **3ao** in $CDCl_3$



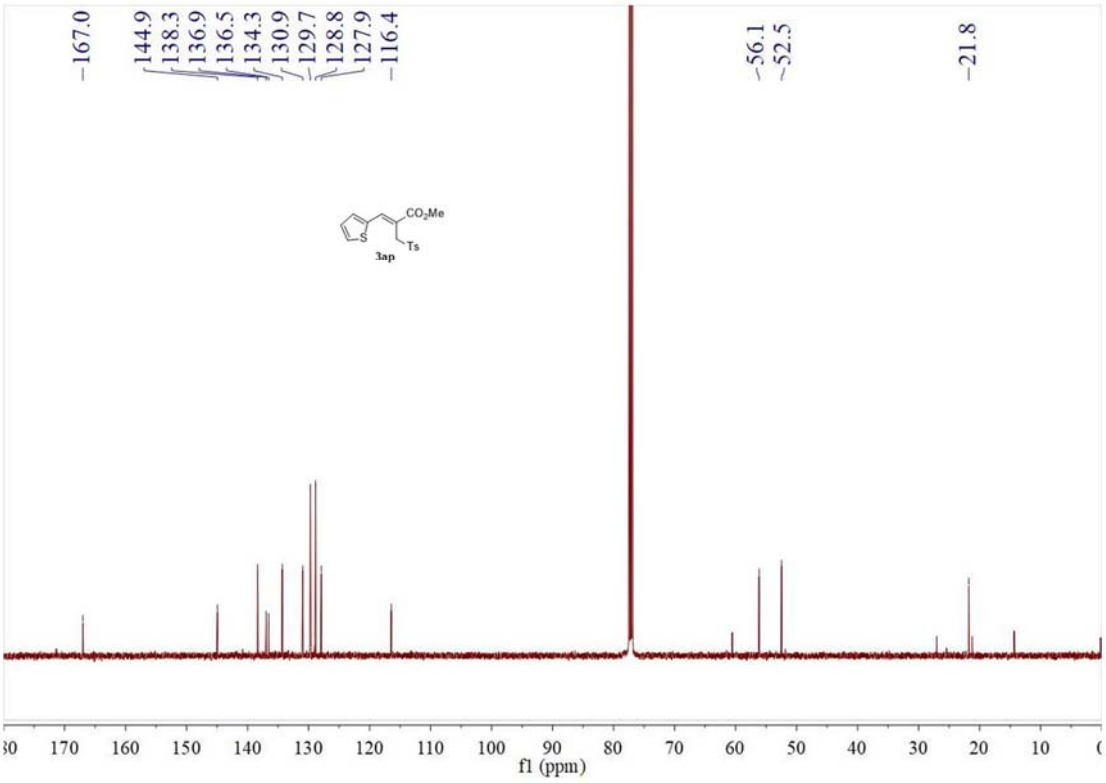

$^{13}$C NMR of **3ao** in $CDCl_3$



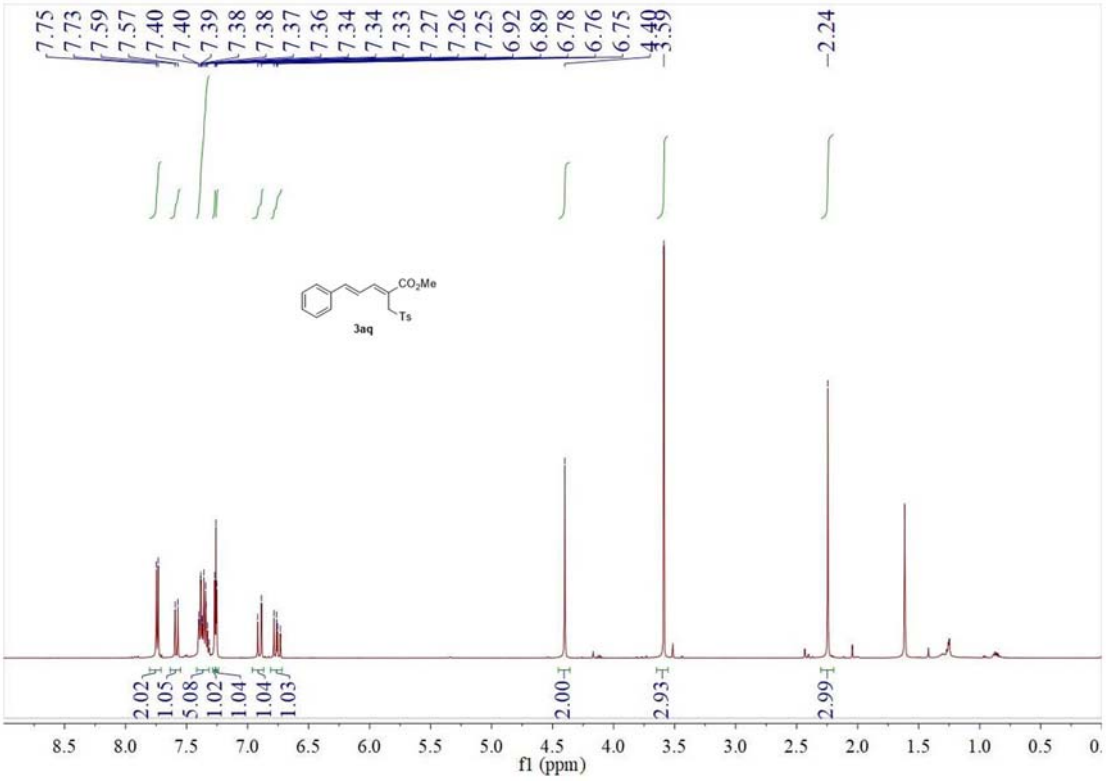
$^{1}$H NMR of **3ap** in $CDCl_3$



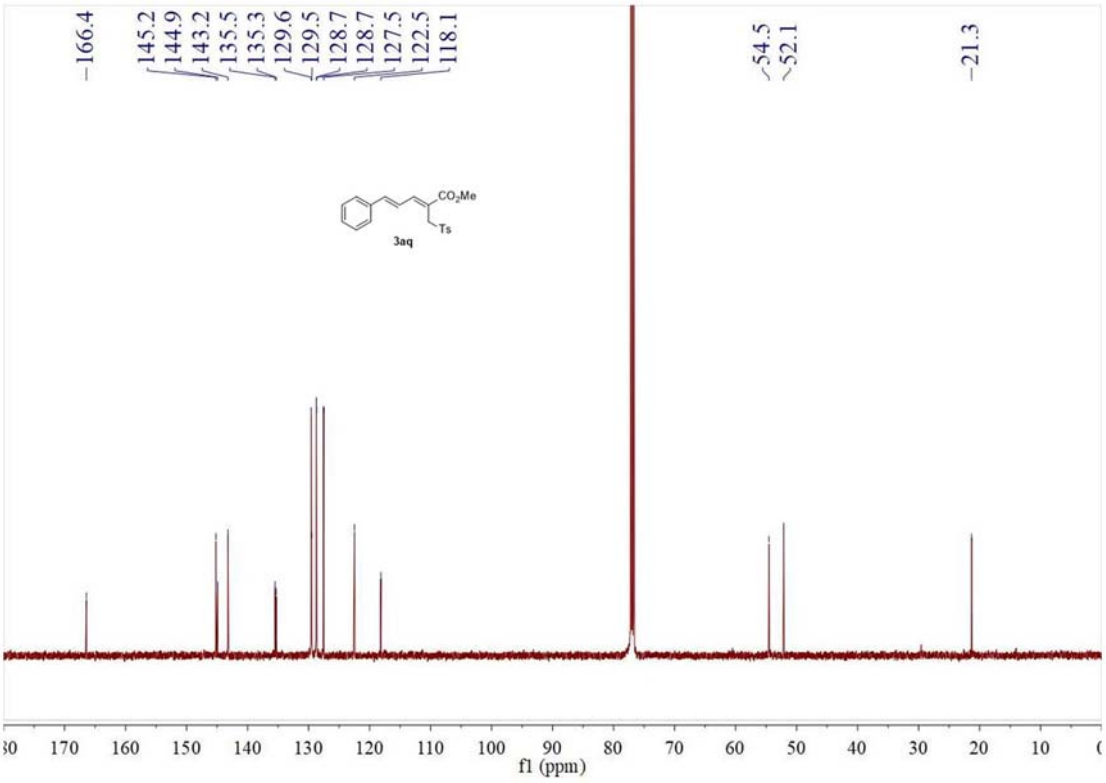

$^{13}$C NMR of **3ap** in $CDCl_3$



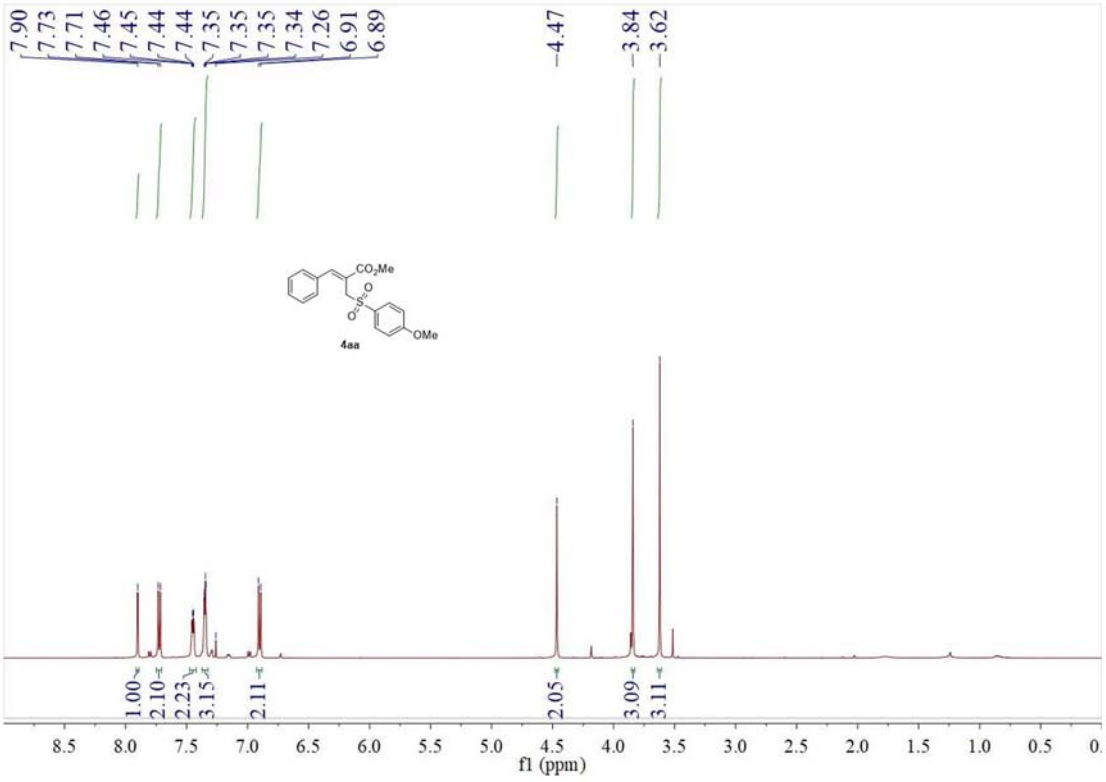
$^{1}$H NMR of **3aq** in $CDCl_3$



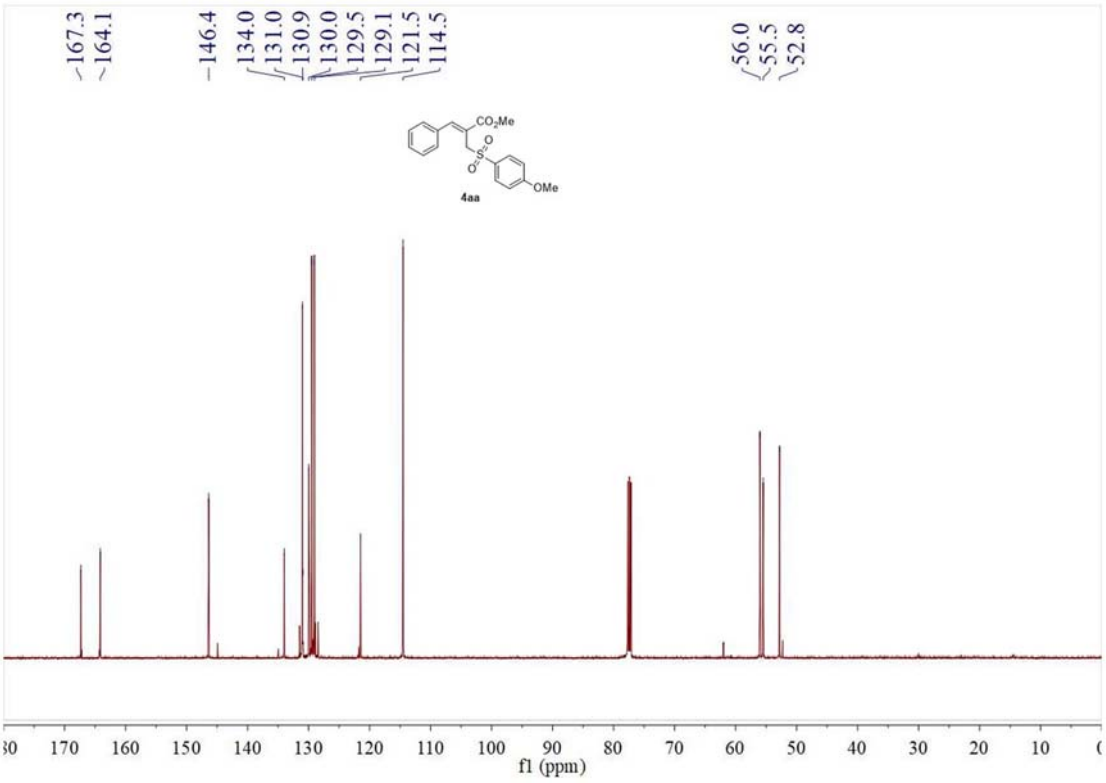

$^{13}$C NMR of **3aq** in $CDCl_3$



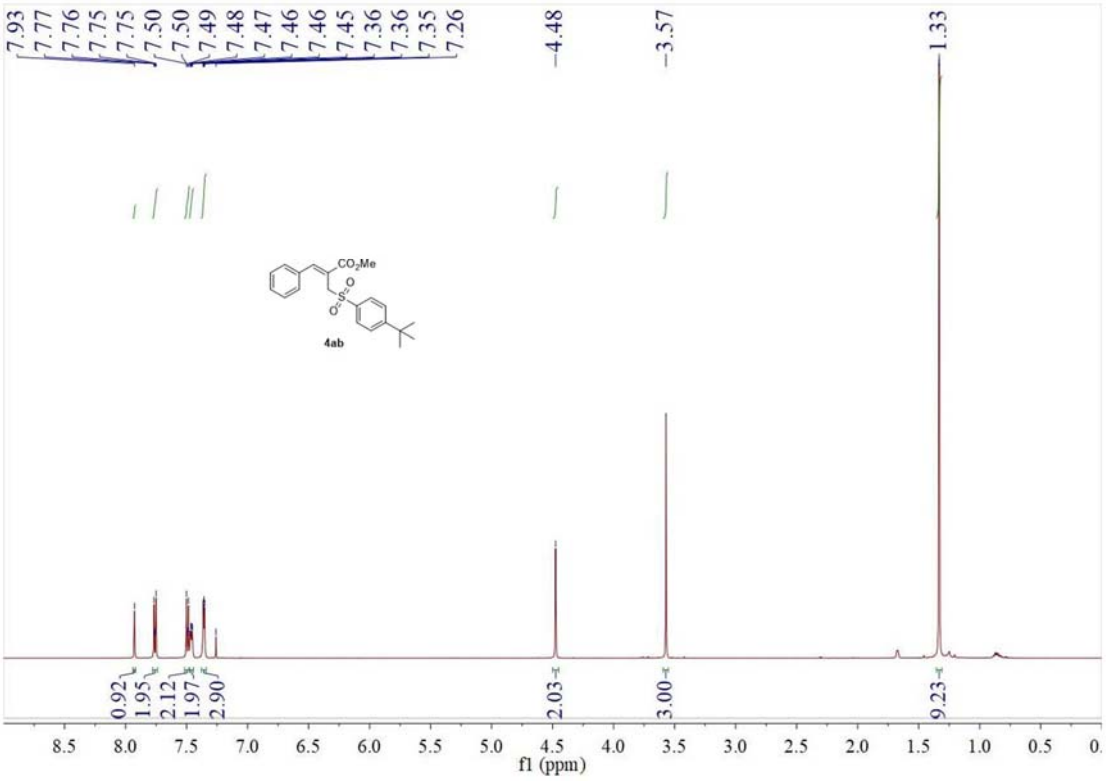
$^{1}$H NMR of **4aa** in $CDCl_3$



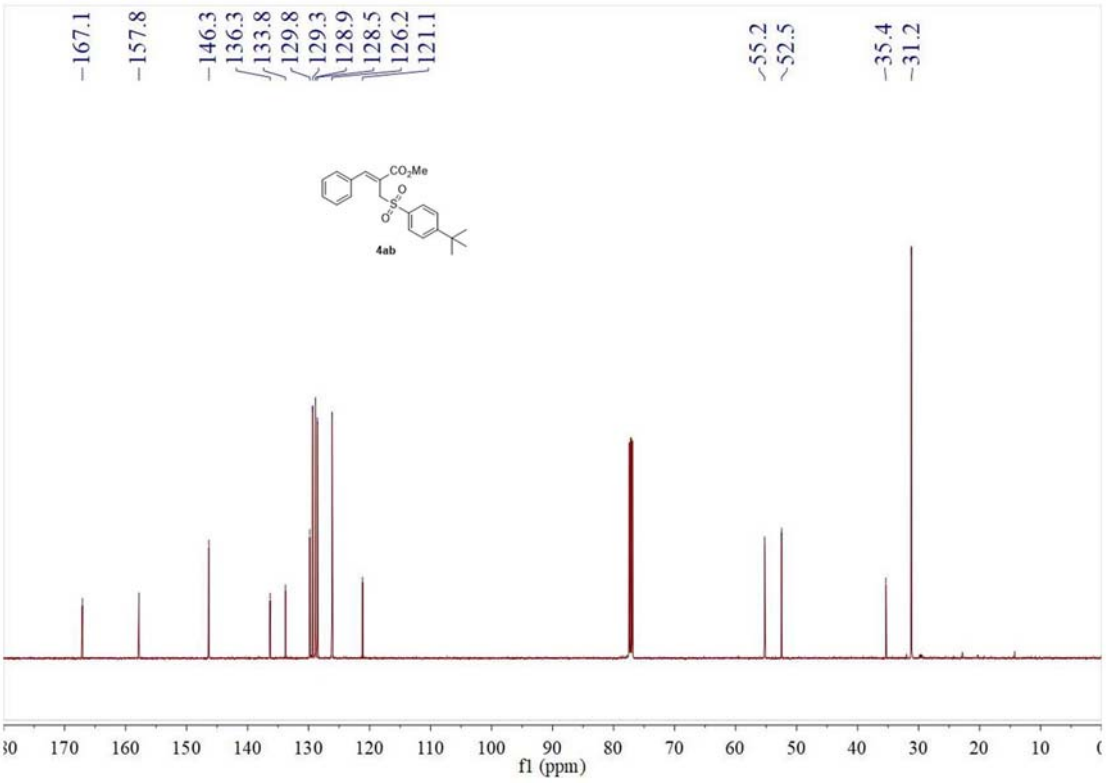

$^{13}$C NMR of **4aa** in $CDCl_3$



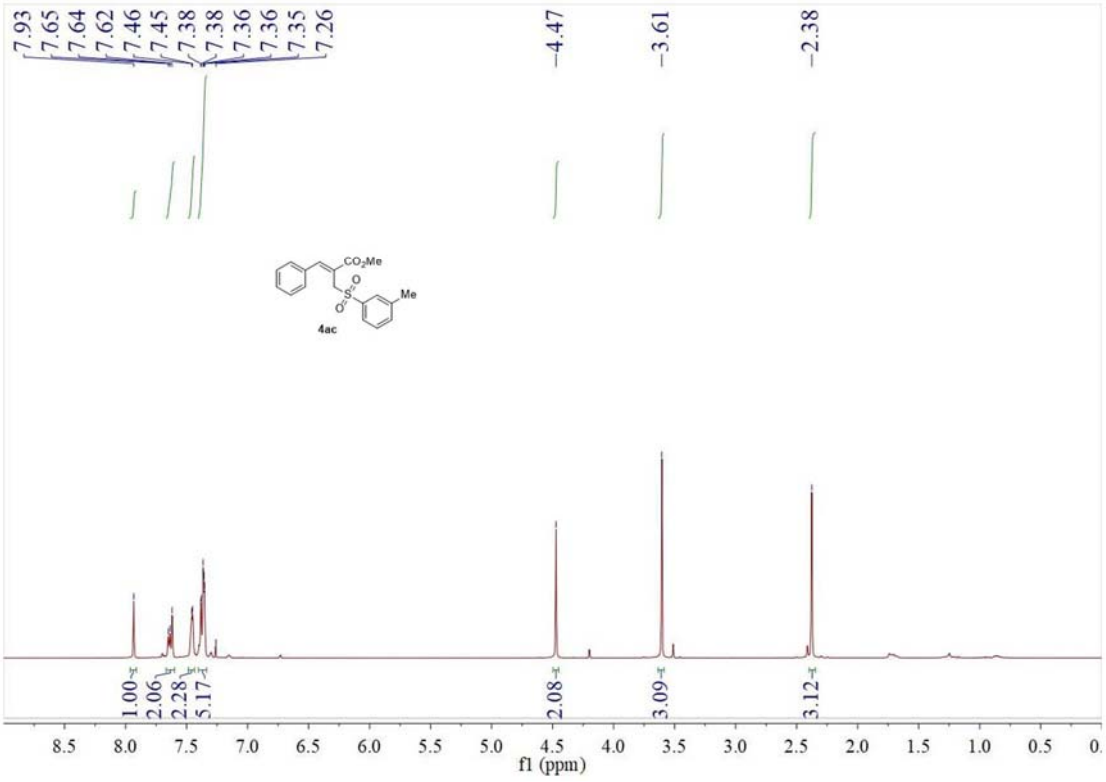
$^{1}$H NMR of **4ab** in $CDCl_3$



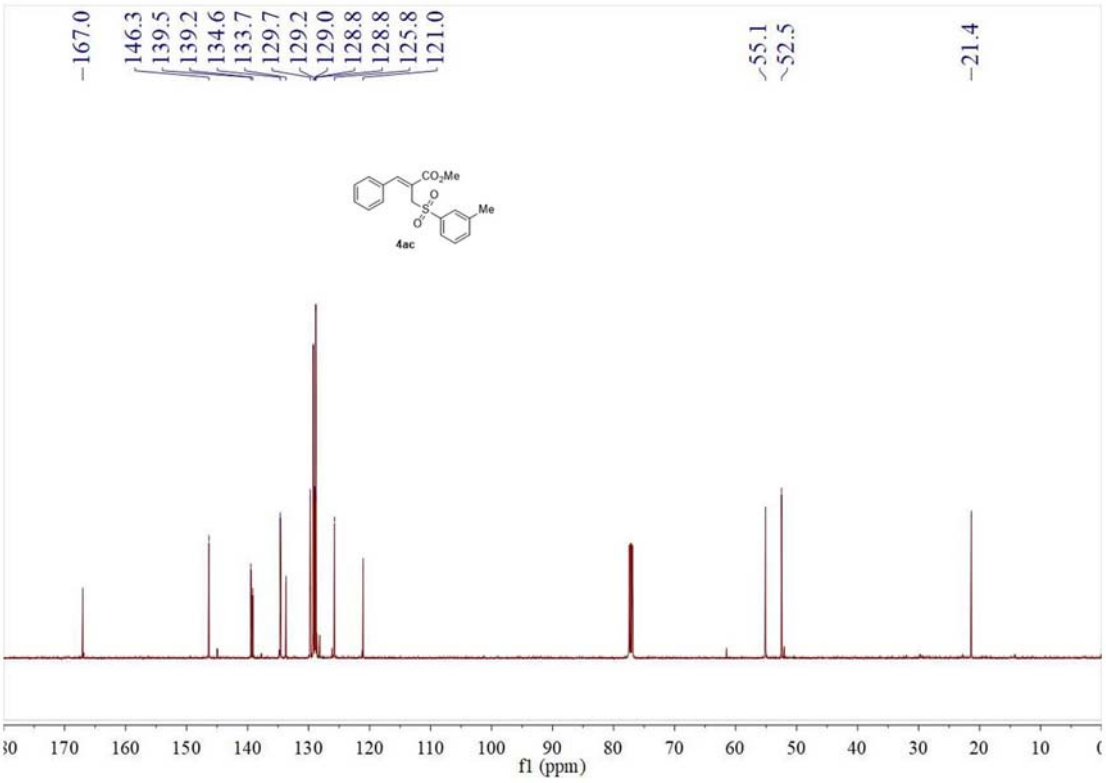

$^{13}$C NMR of **4ab** in $CDCl_3$



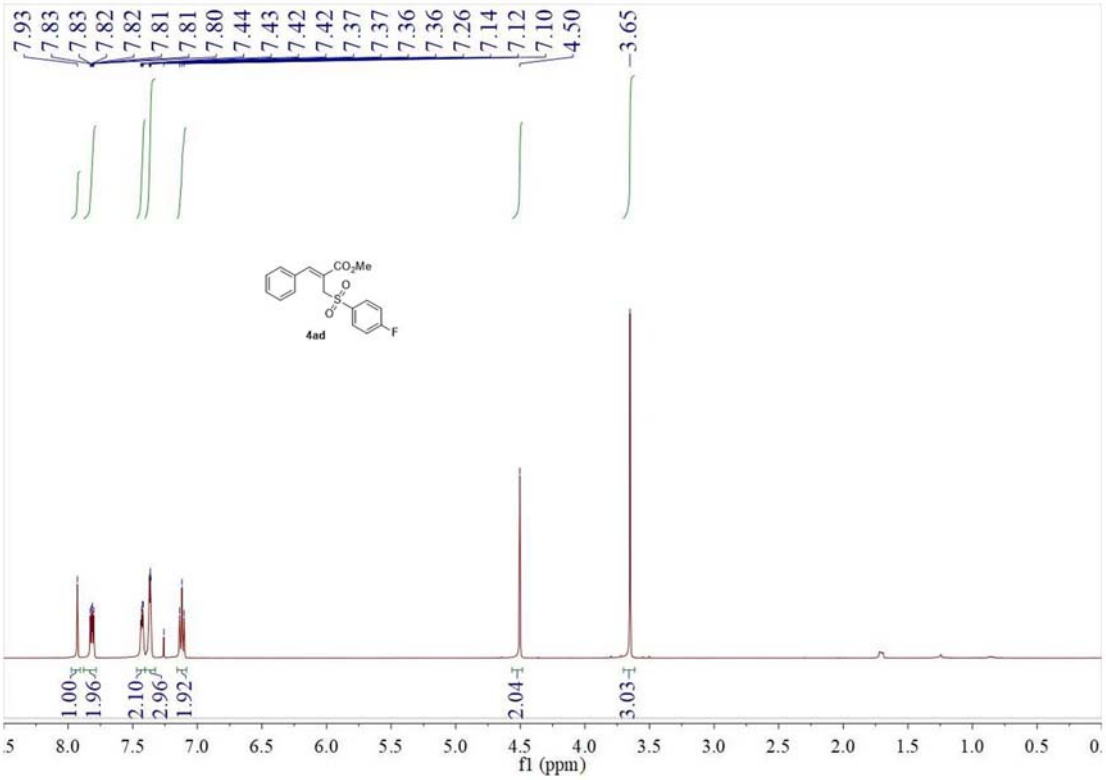
$^{1}$H NMR of **4ac** in $CDCl_3$



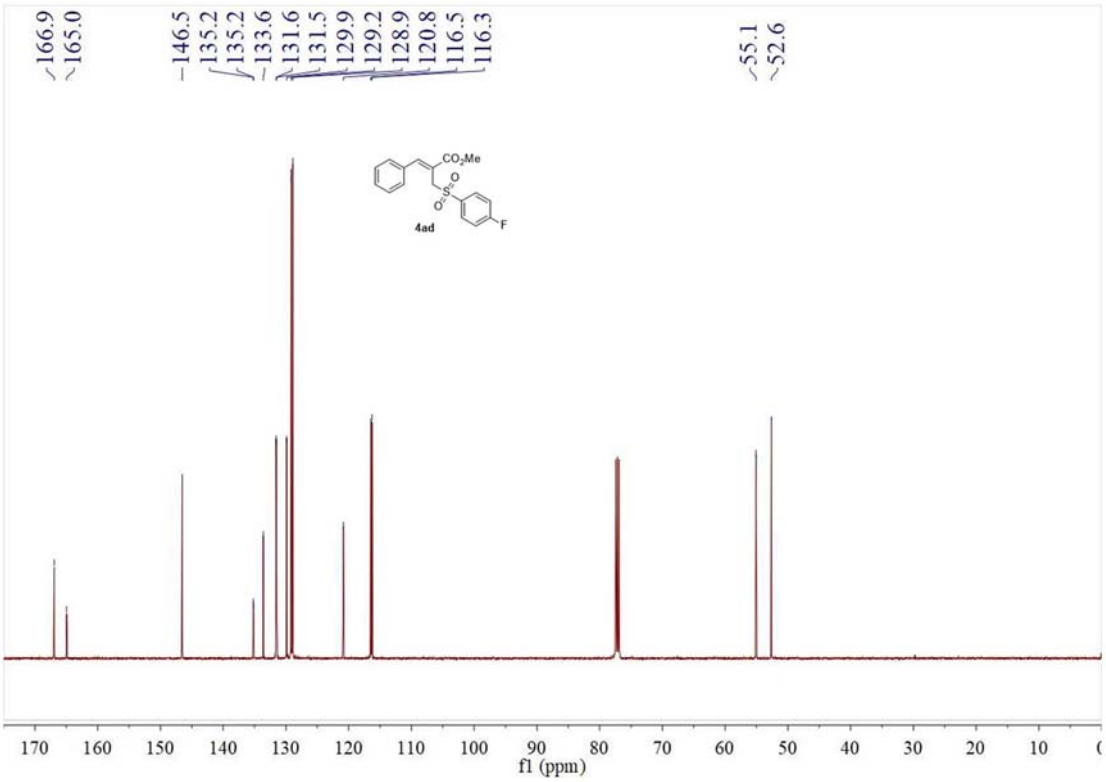

$^{13}$C NMR of **4ac** in $CDCl_3$



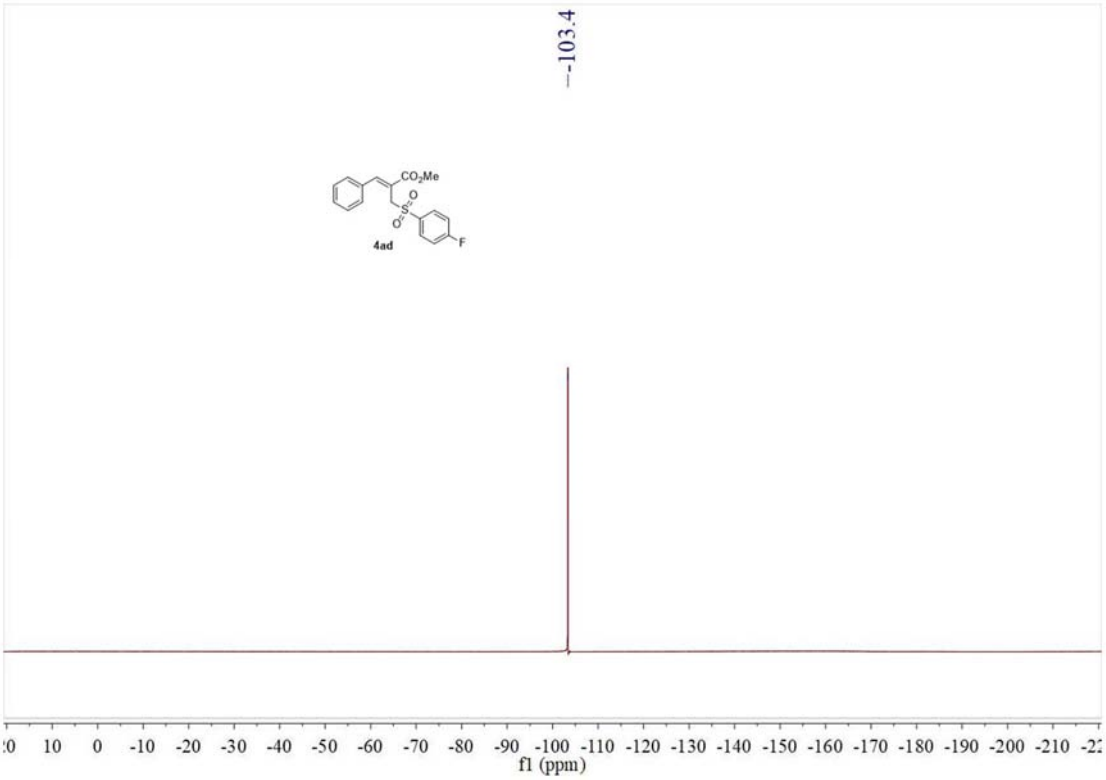
$^{1}$H NMR of **4ad** in $CDCl_3$



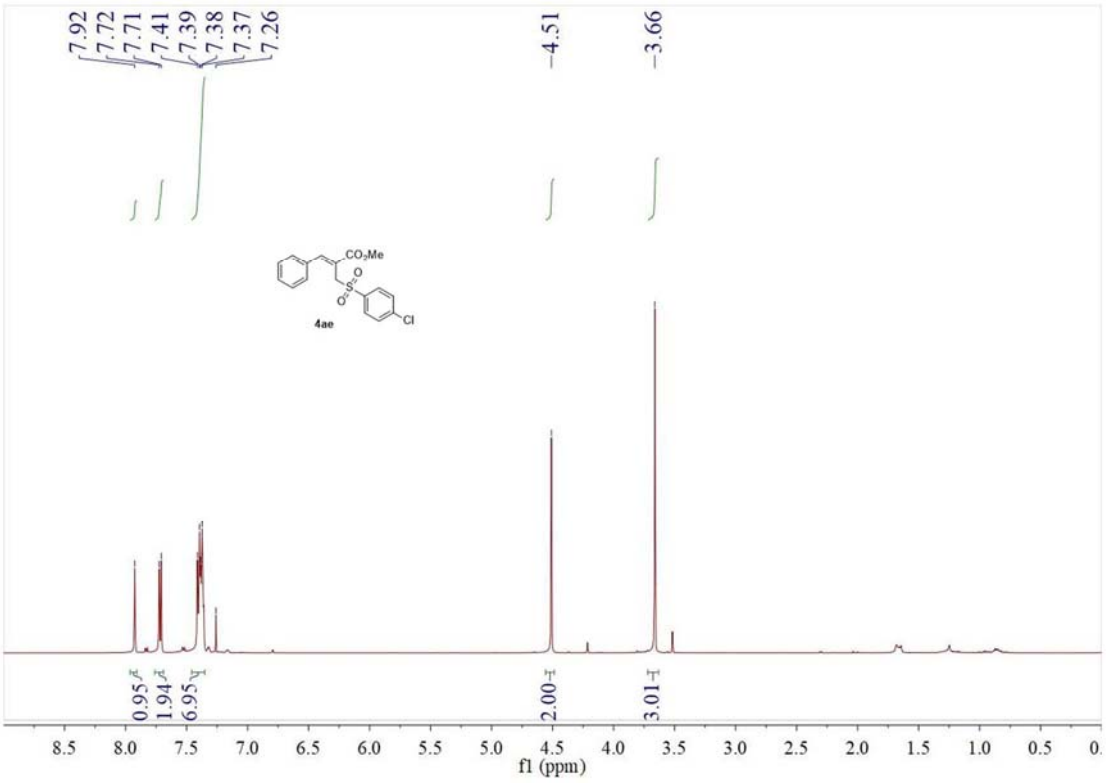

$^{13}$C NMR of **4ad** in $CDCl_3$



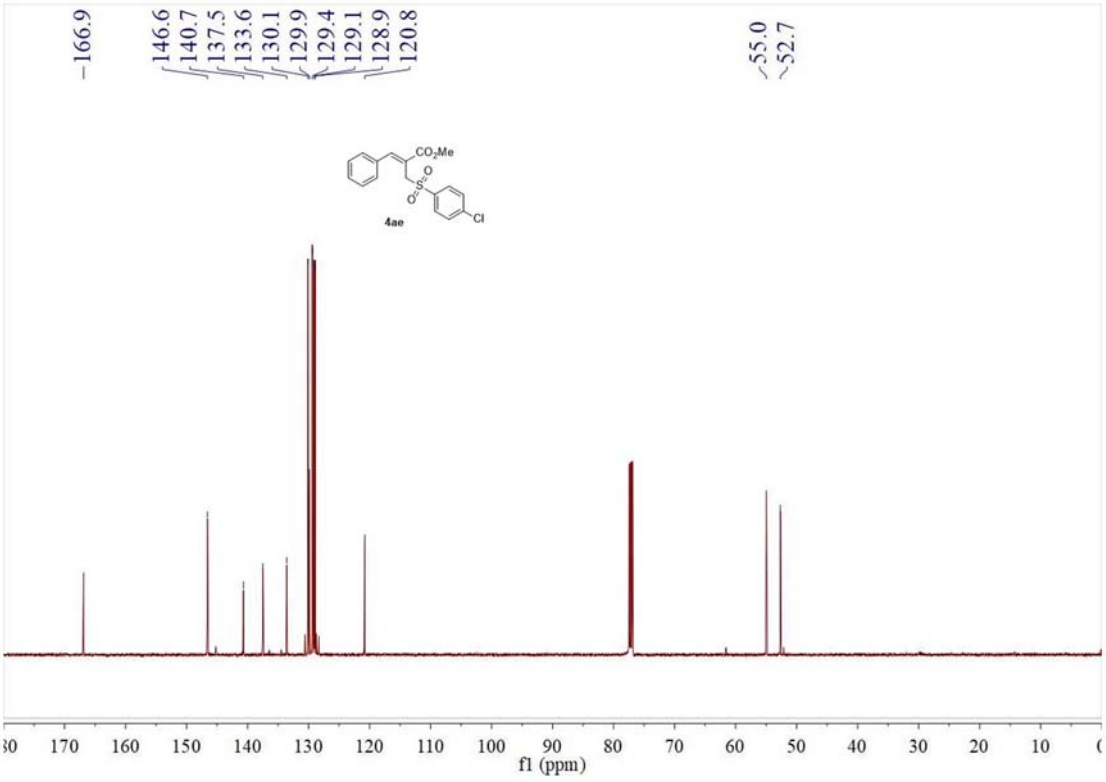
$^{19}$FNMR of **4ad** in $CDCl_3$



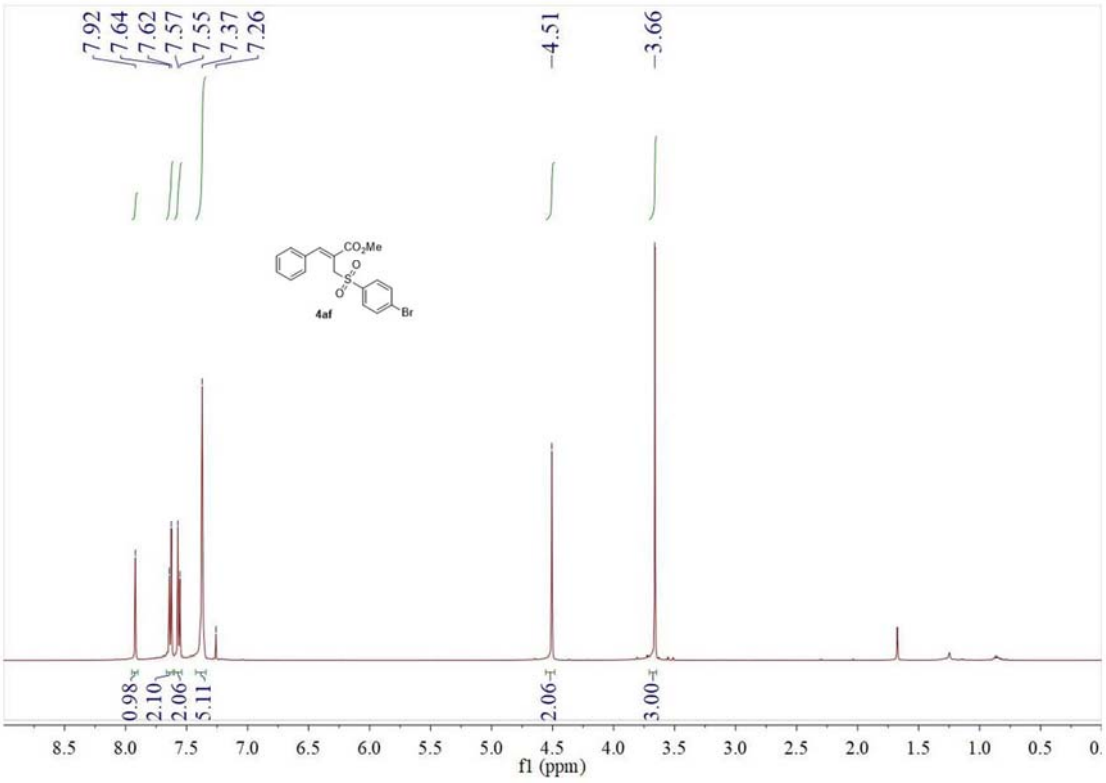

$^{1}$H NMR of **4ae** in $CDCl_3$



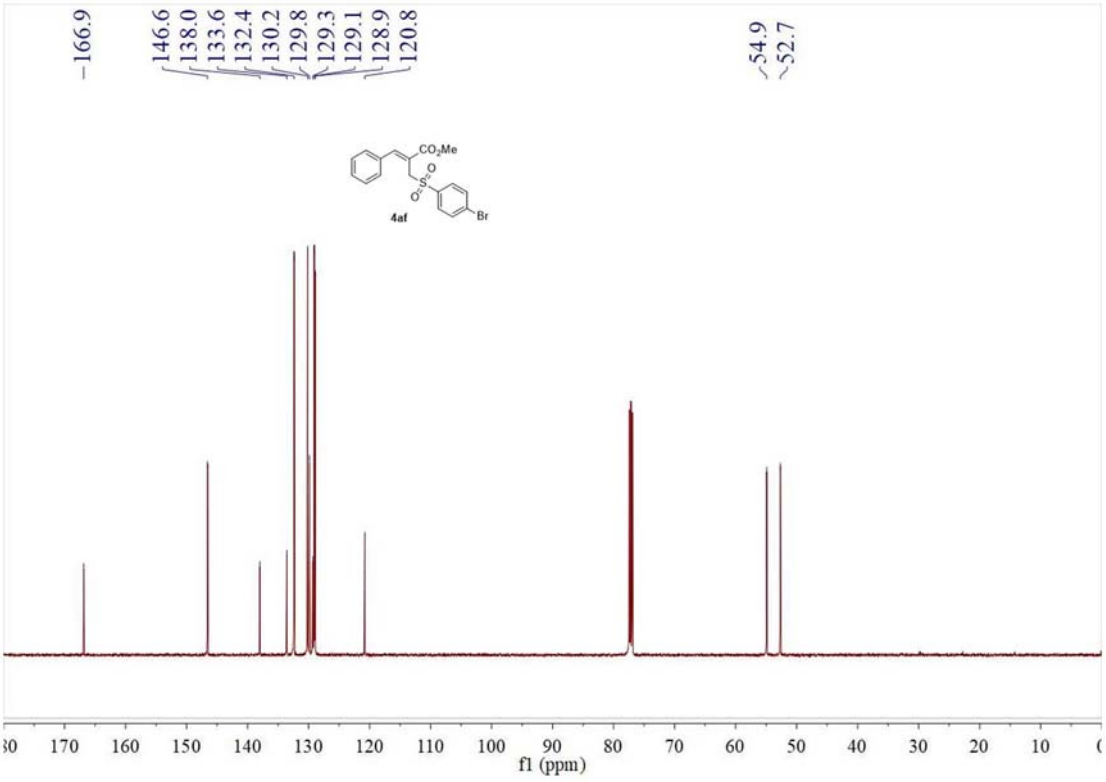
$^{13}C$ NMR of **4ae** in $CDCl_3$



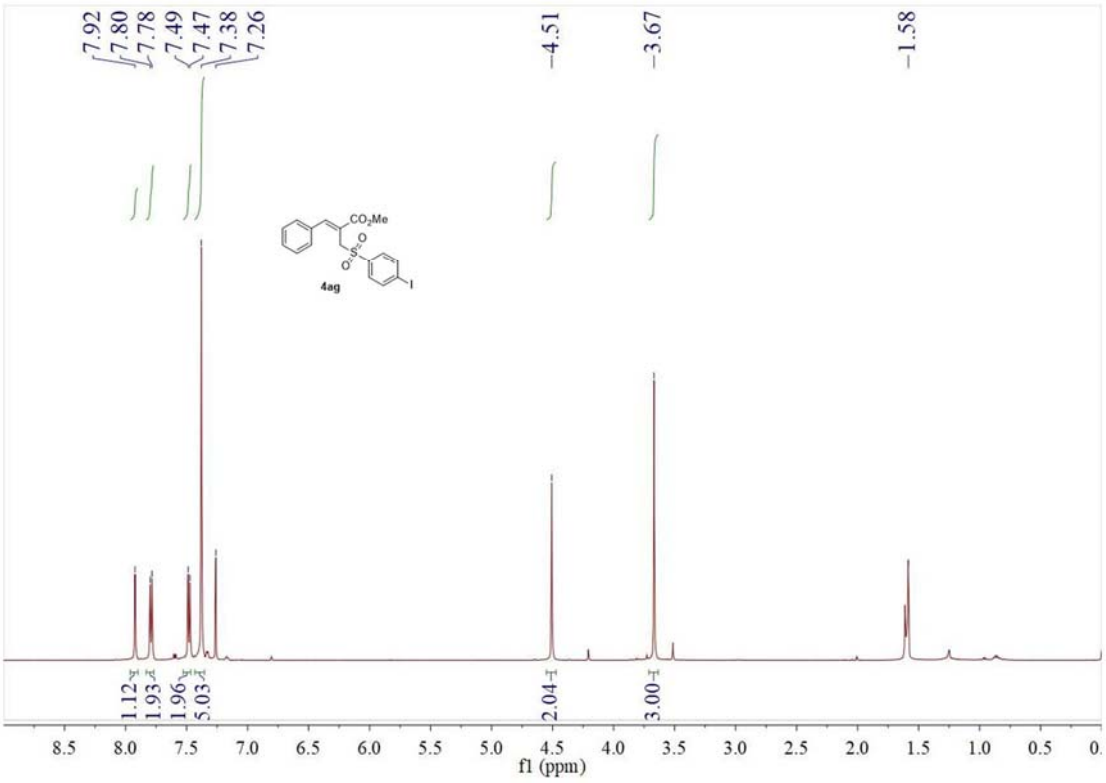

$^{1}H$ NMR of **4af** in $CDCl_3$



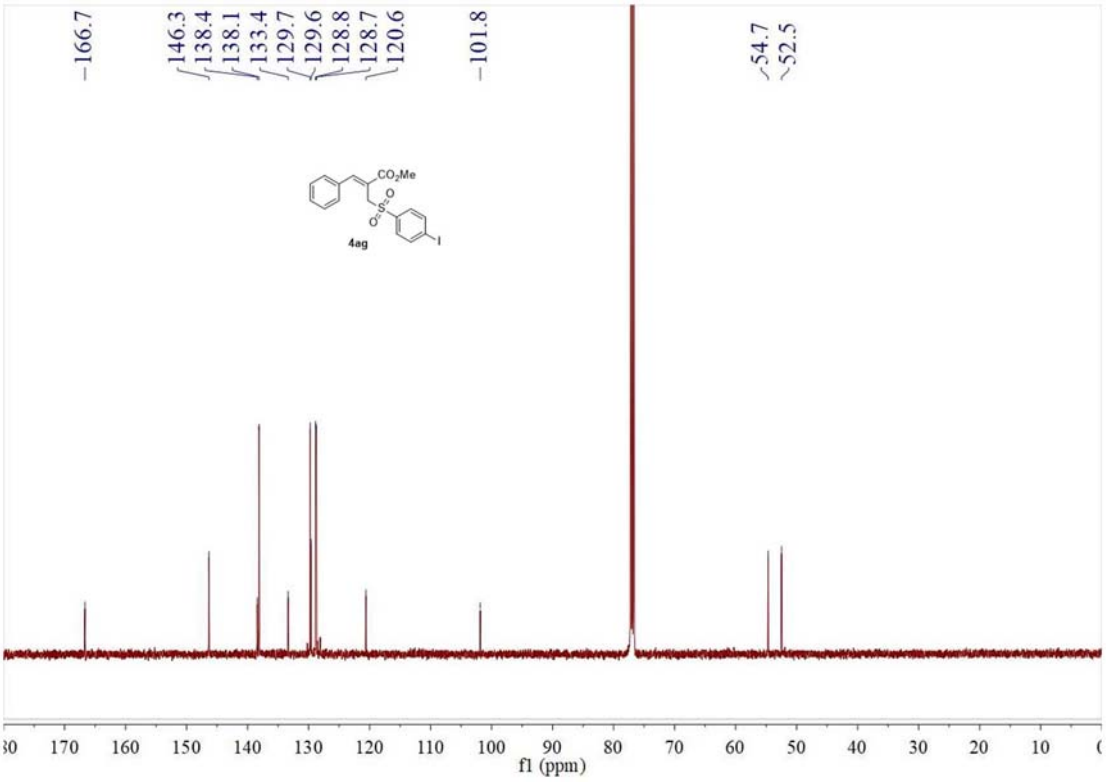
$^{13}$C NMR of **4af** in $CDCl_3$



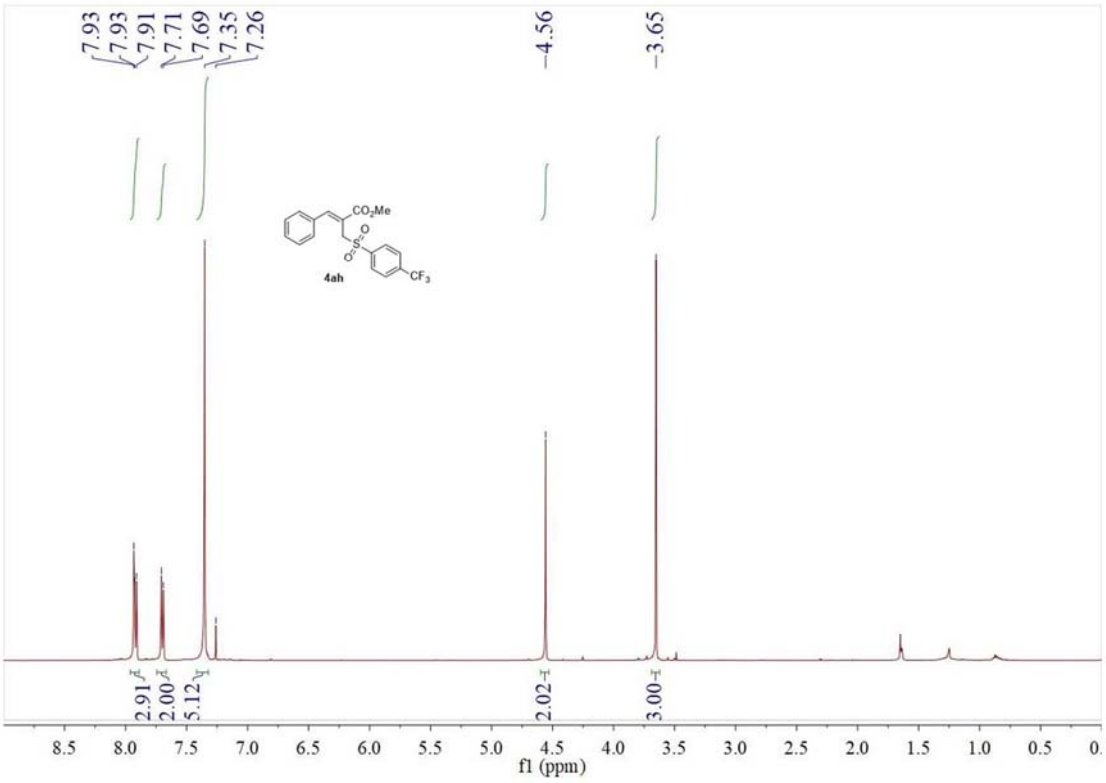

$^{1}$H NMR of **4ag** in $CDCl_3$



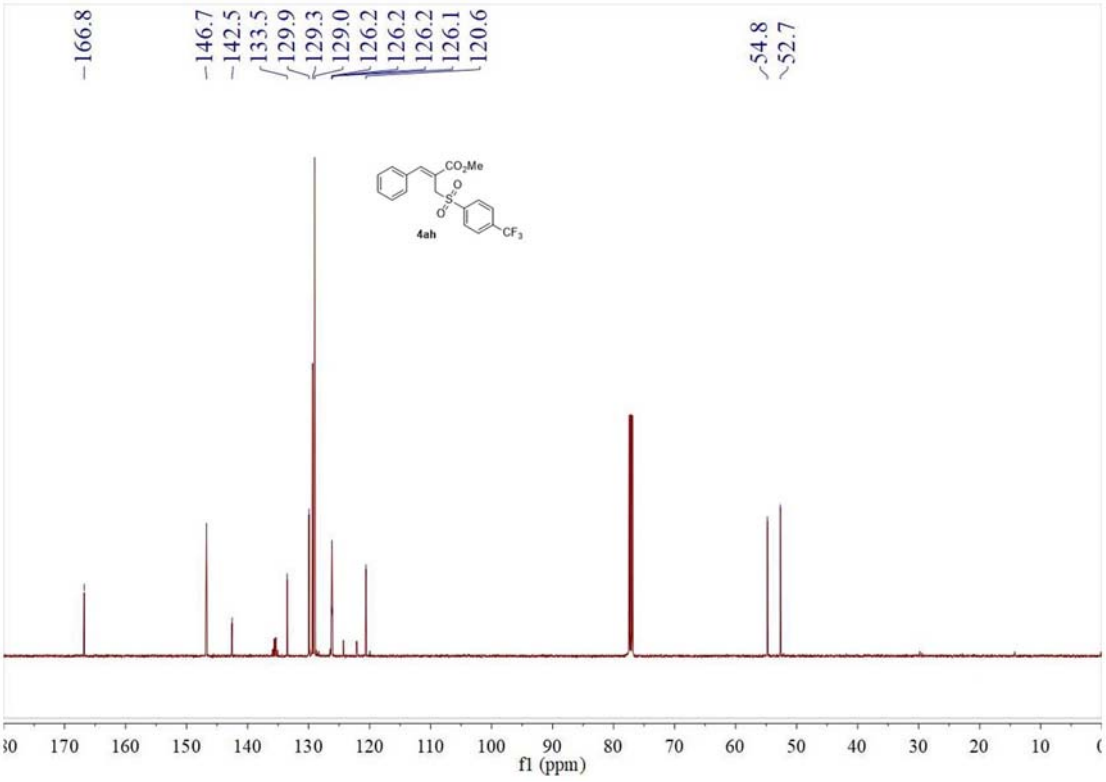
$^{13}C$ NMR of **4ag** in $CDCl_3$



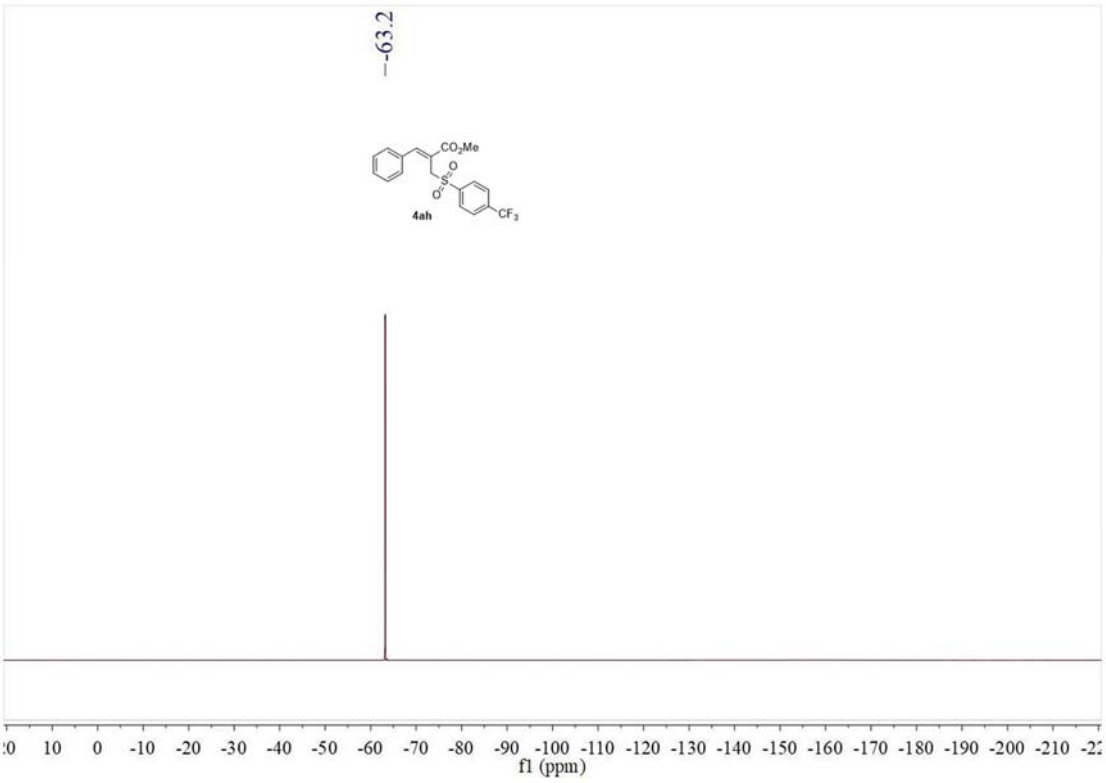

$^{1}H$ NMR of **4ah** in $CDCl_3$



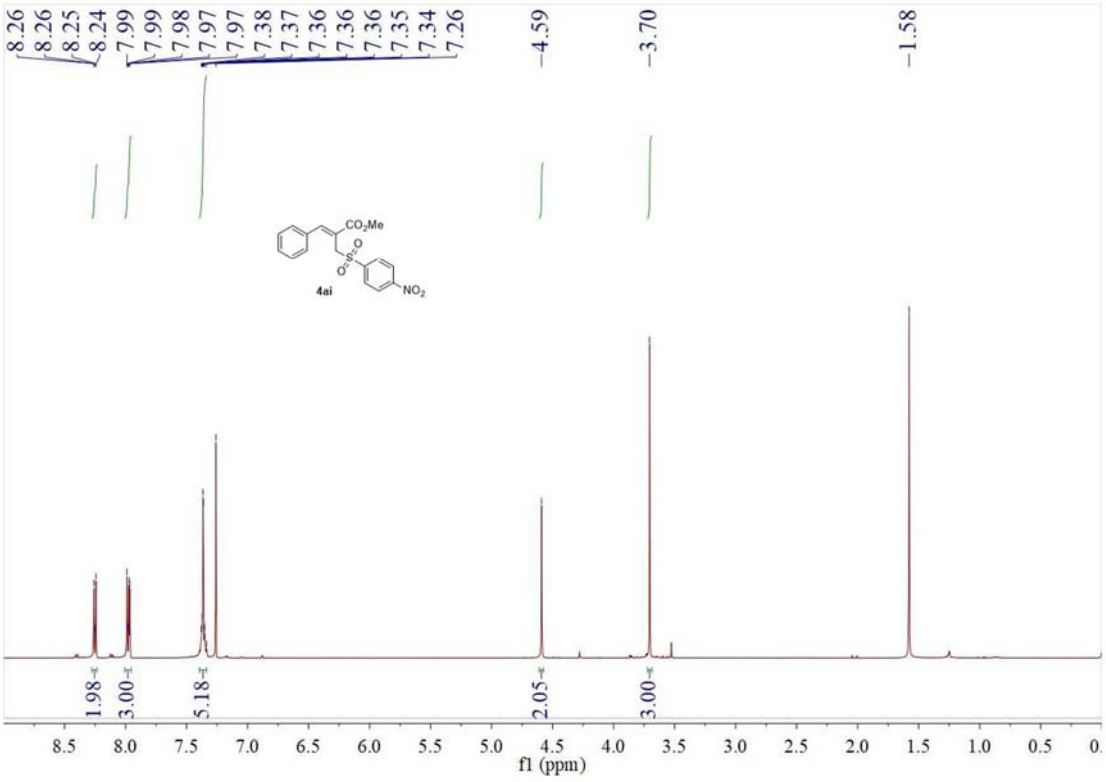
$^{13}$C NMR of **4ah** in $CDCl_3$



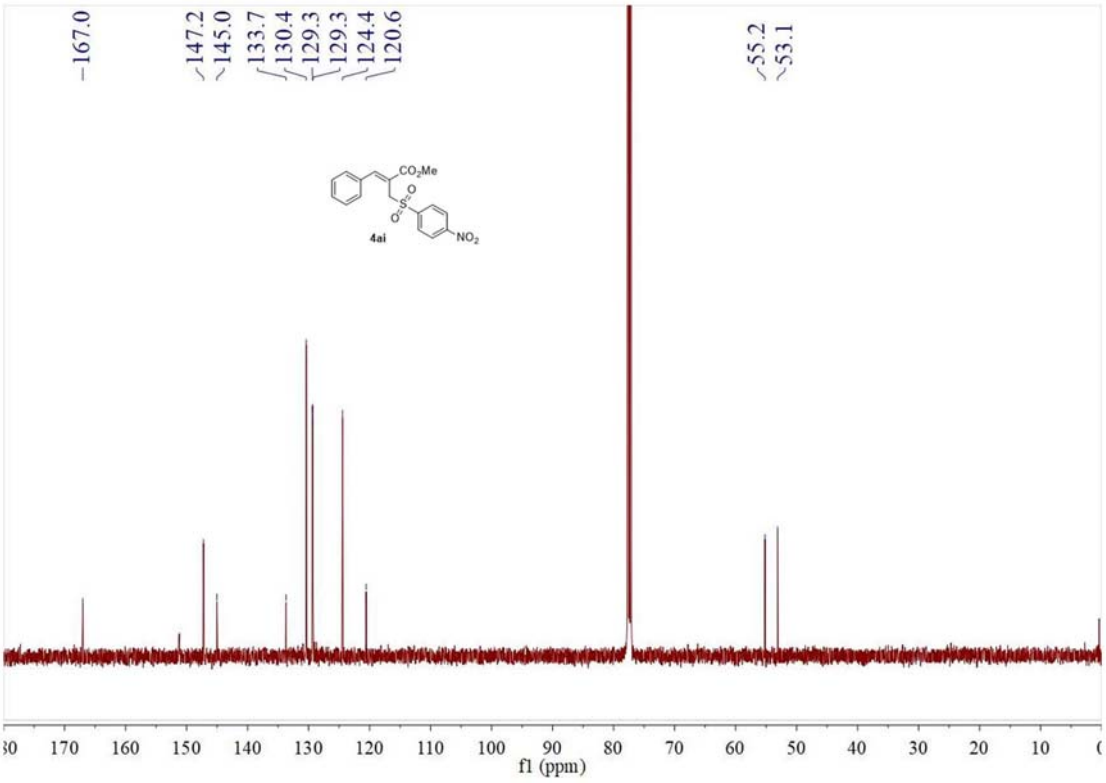

$^{19}$FNMR of **4ah** in $CDCl_3$



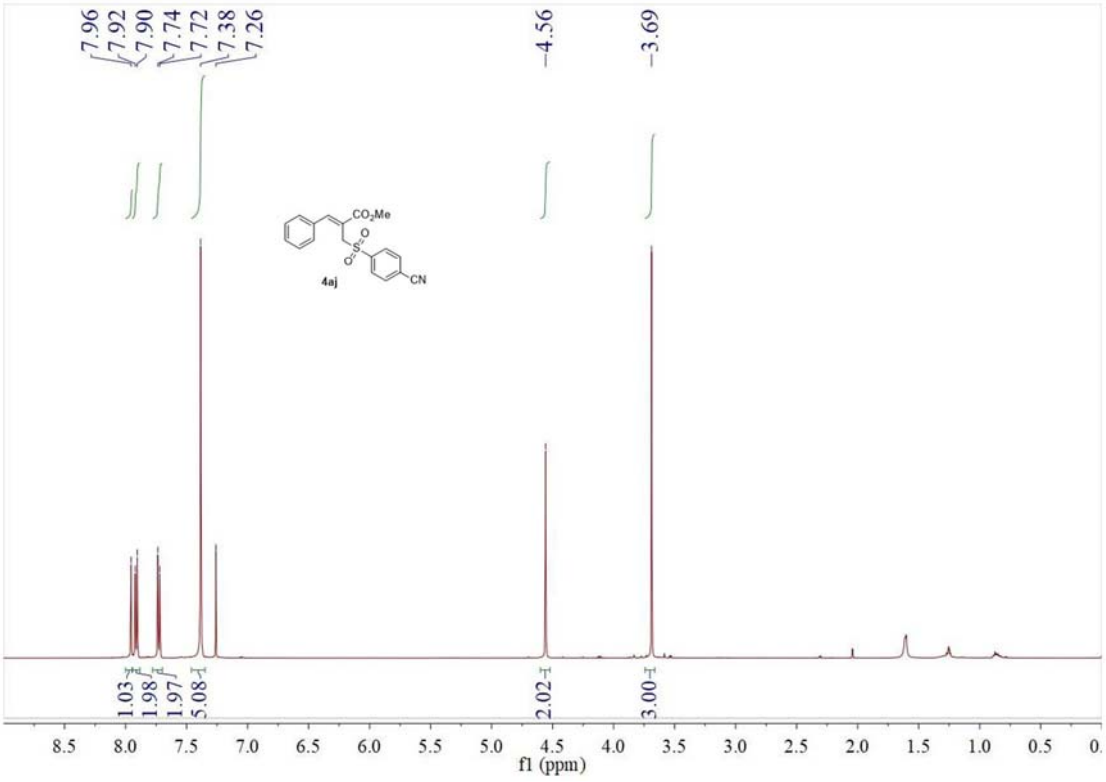
$^{1}$H NMR of **4ai** in $CDCl_3$



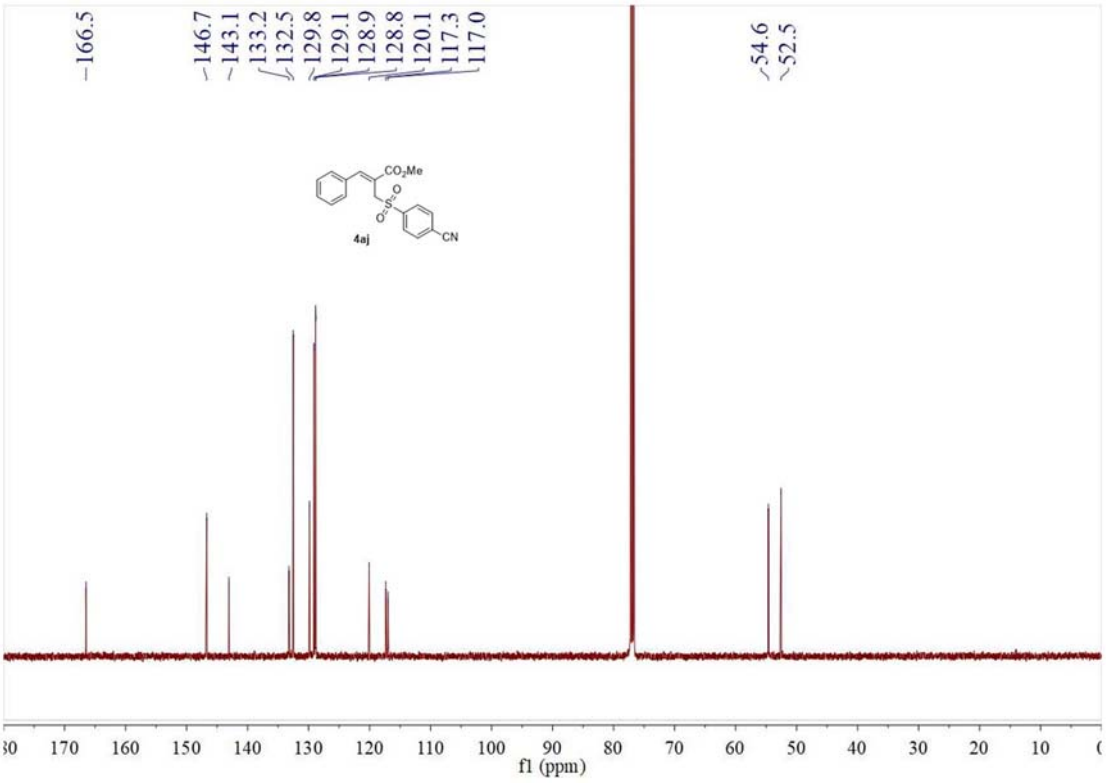

$^{13}$C NMR of **4ai** in $CDCl_3$



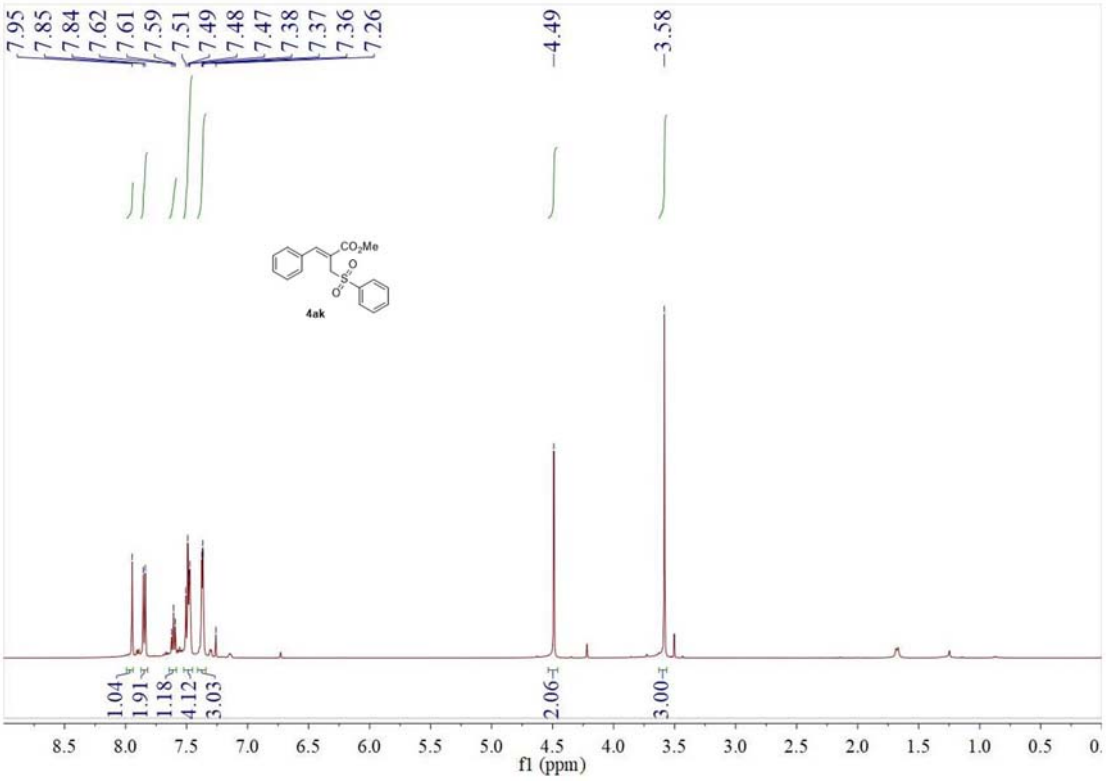
$^{1}$H NMR of **4aj** in $CDCl_3$




$^{13}$C NMR of **4aj** in $CDCl_3$



$^{1}$H NMR of **4ak** in $CDCl_3$




$^{13}$C NMR of **4ak** in $CDCl_3$