

## Supplementary Information

### Insertion of *N*-tosylacetimidates/acetimidamides onto arynes via [2+2] cycloaddition

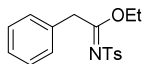
Ramagonolla Kranthikumar, Rambabu Chegondi and Srivari Chandrasekhar\*

*Division of Natural Product Chemistry, CSIR-Indian Institute of Chemical Technology,  
Hyderabad 500007, India.*

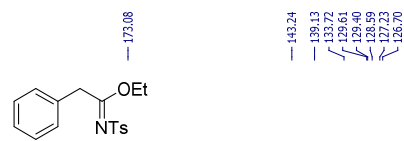
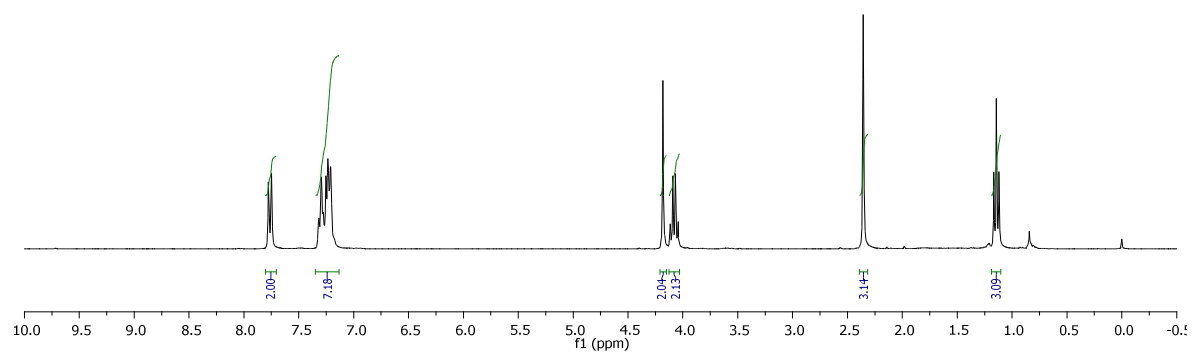
E-mail: [srivari@iict.res.in](mailto:srivari@iict.res.in)

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1. <sup>1</sup> H NMR, <sup>13</sup> C NMR spectra	S-2 to S-41
2. X-ray crystallographic data	S42 to S-44

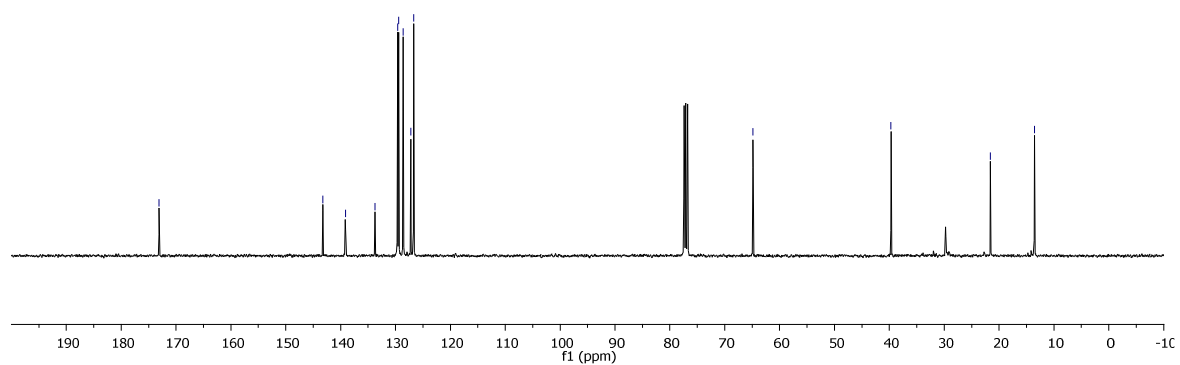
# **Ethyl (Z)-2-phenyl-N-tosylacetimidate (2a):**



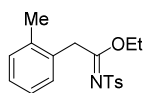
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)



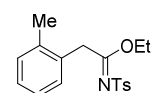
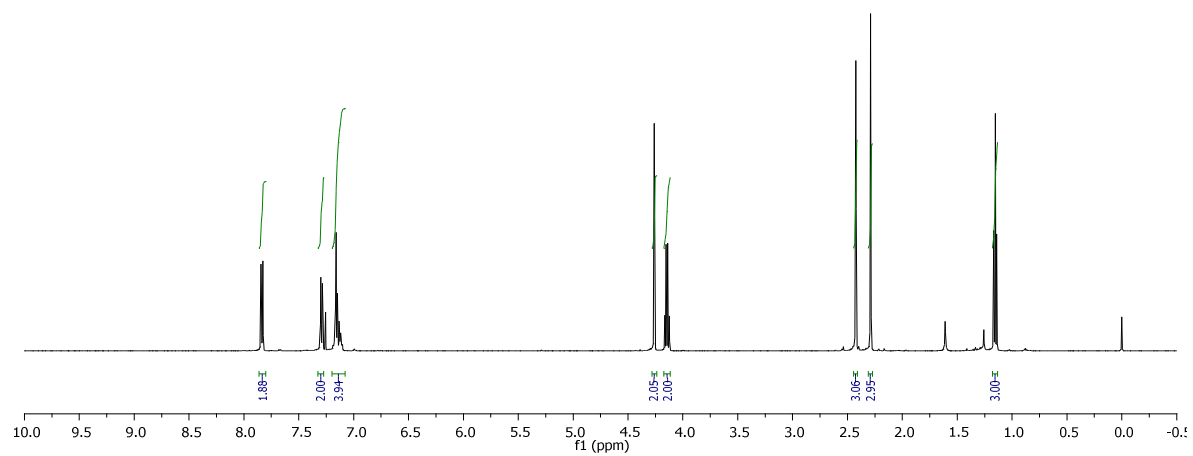
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 400 MHz)



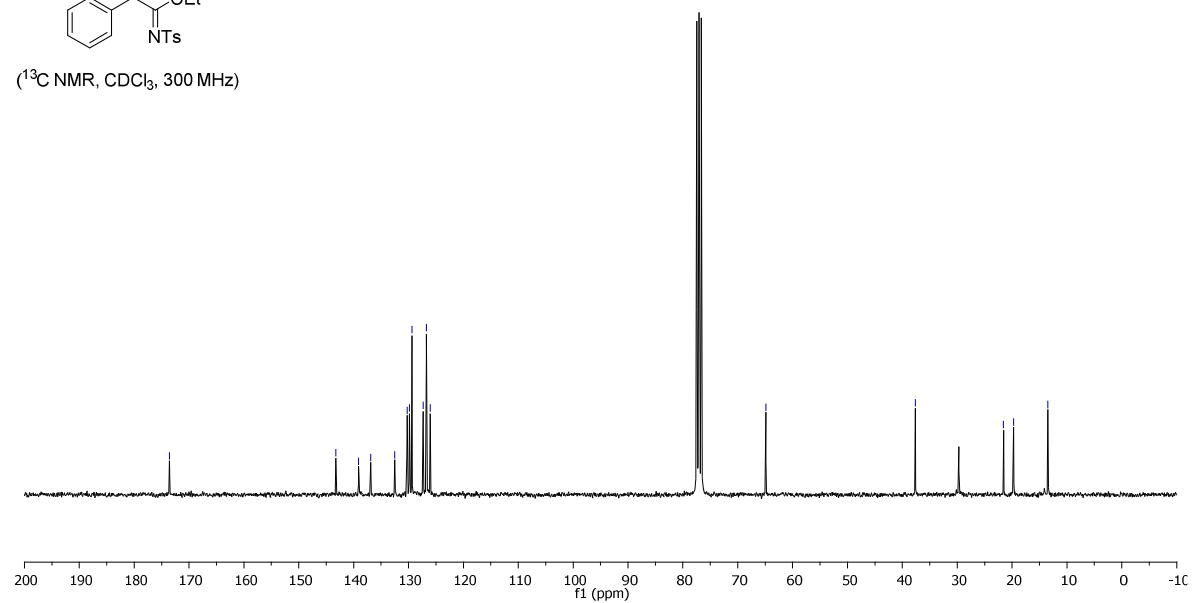
**Ethyl (*E*)-2-(*o*-tolyl)-*N*-tosylacetimidate (2b):**



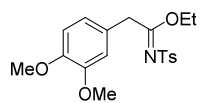
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



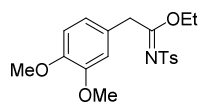
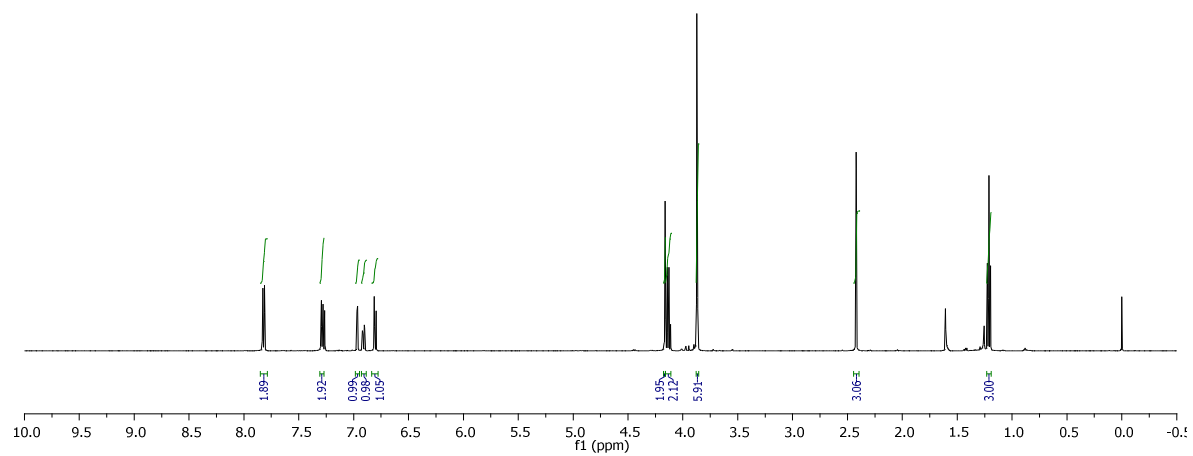
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 300 MHz)



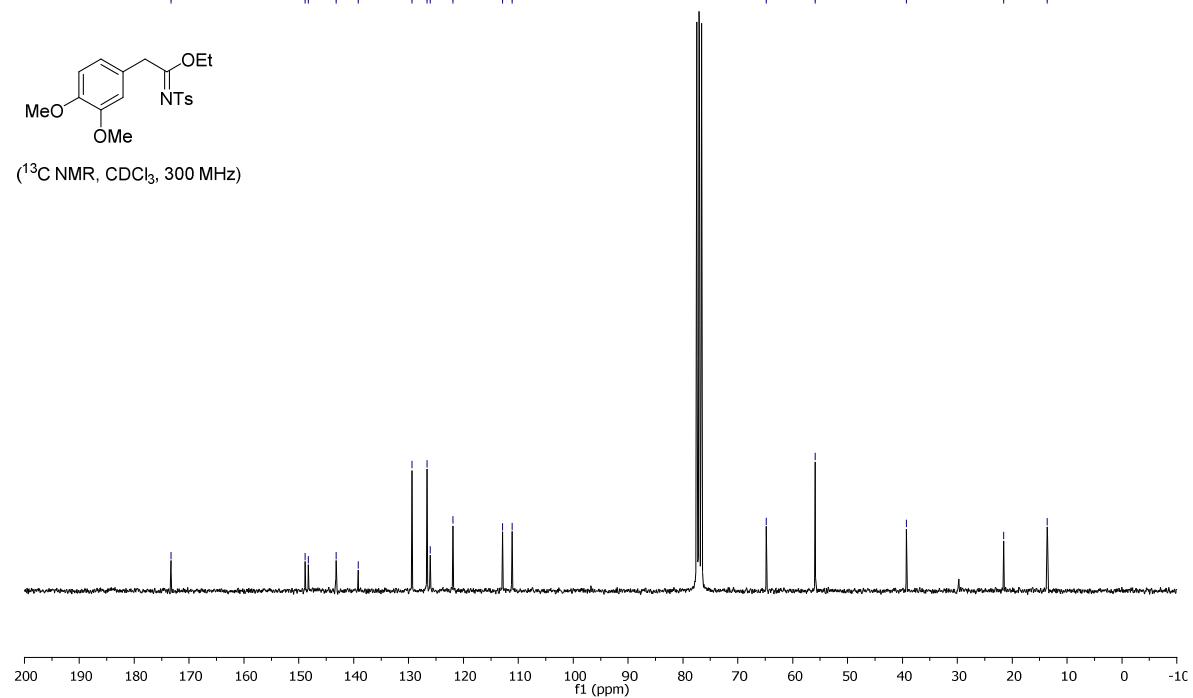
**Ethyl (*E*)-2-(3,4-dimethoxyphenyl)-*N*-tosylacetimidate (2c):**



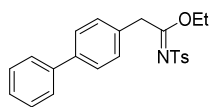
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



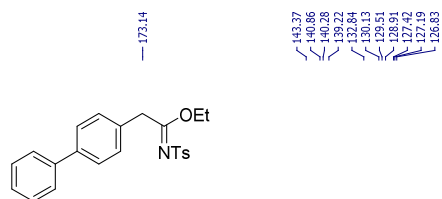
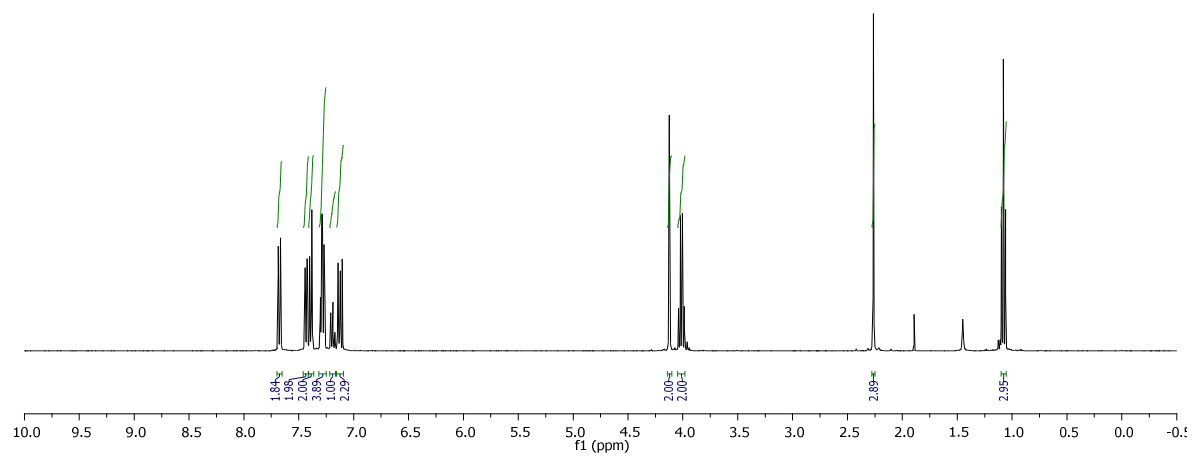
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 300 MHz)



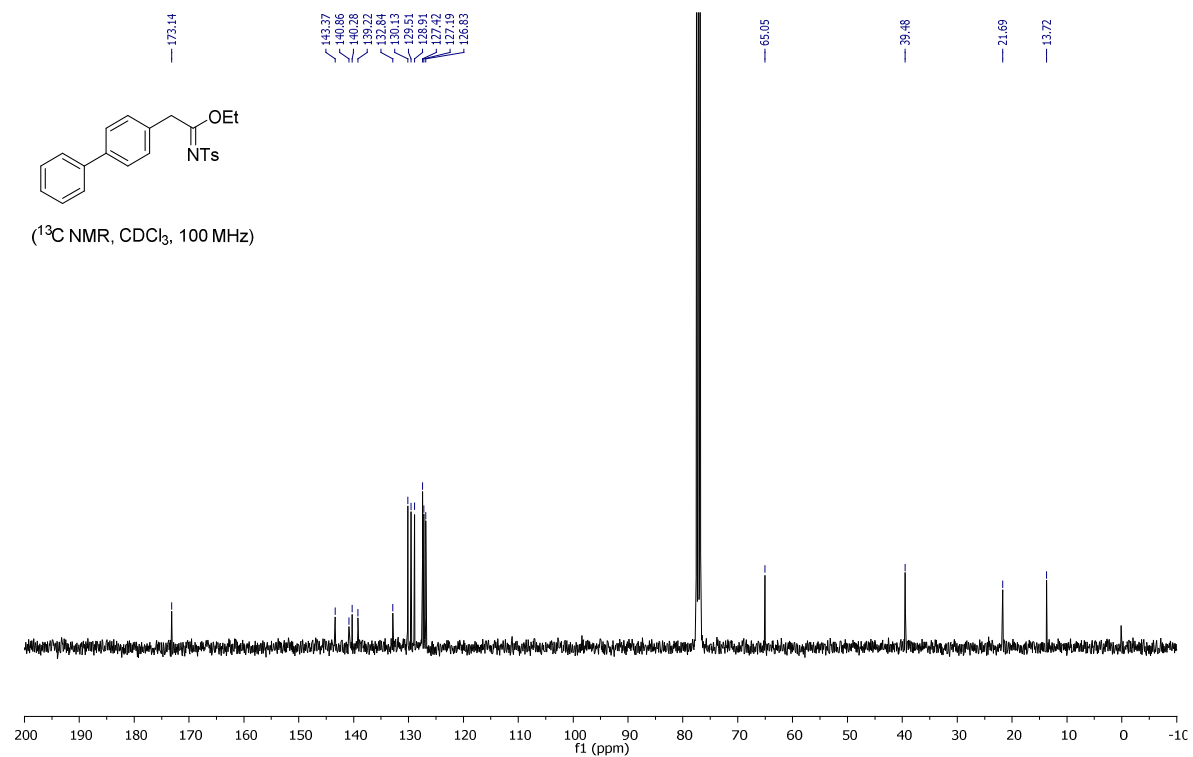
**Ethyl (*E*)-2-([1,1'-biphenyl]-4-yl)-*N*-tosylacetimidate (2d):**



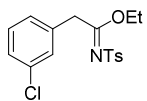
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



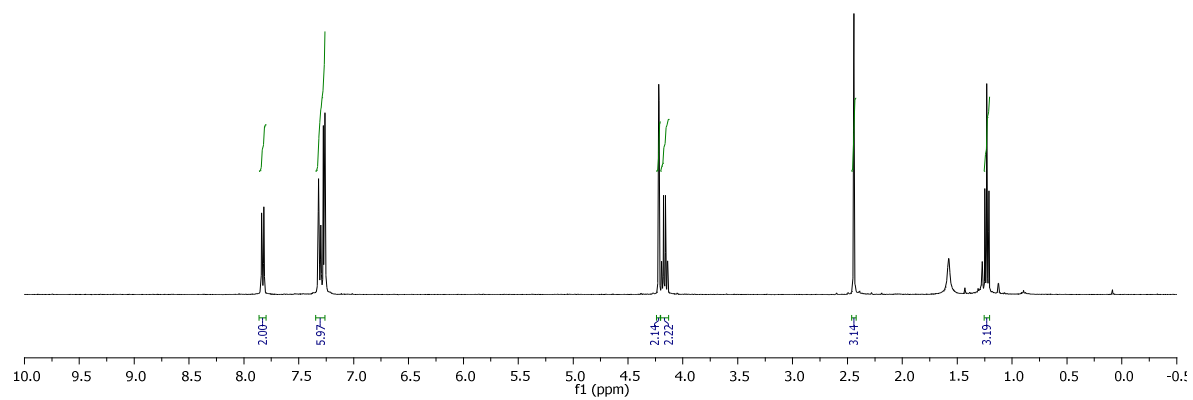
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 100 MHz)



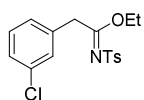
**Ethyl (*E*)-2-(3-chlorophenyl)-*N*-tosylacetimidate (2e):**



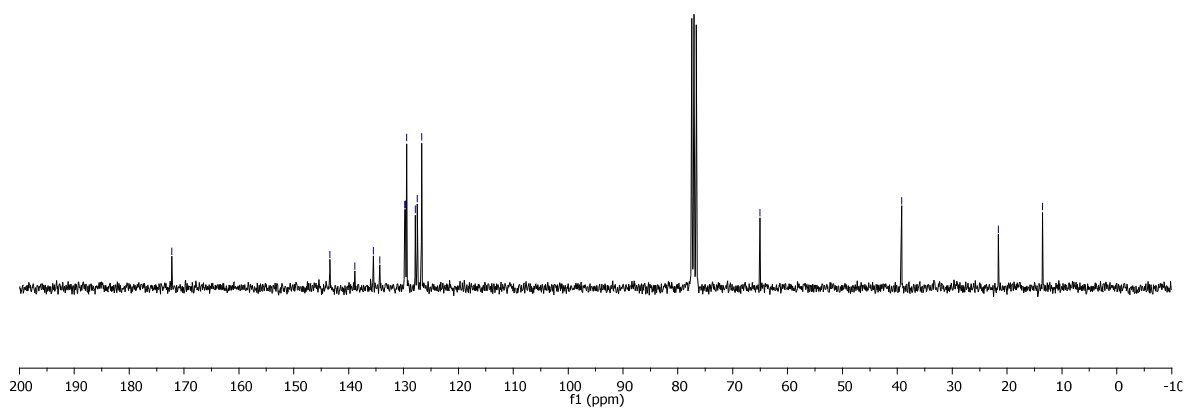
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



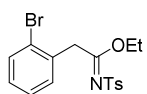
172.21, 143.41, 138.88, 135.51, 134.30, 133.80, 129.80, 129.44, 127.86, 126.70, 65.05, 39.22, 21.57, 13.55



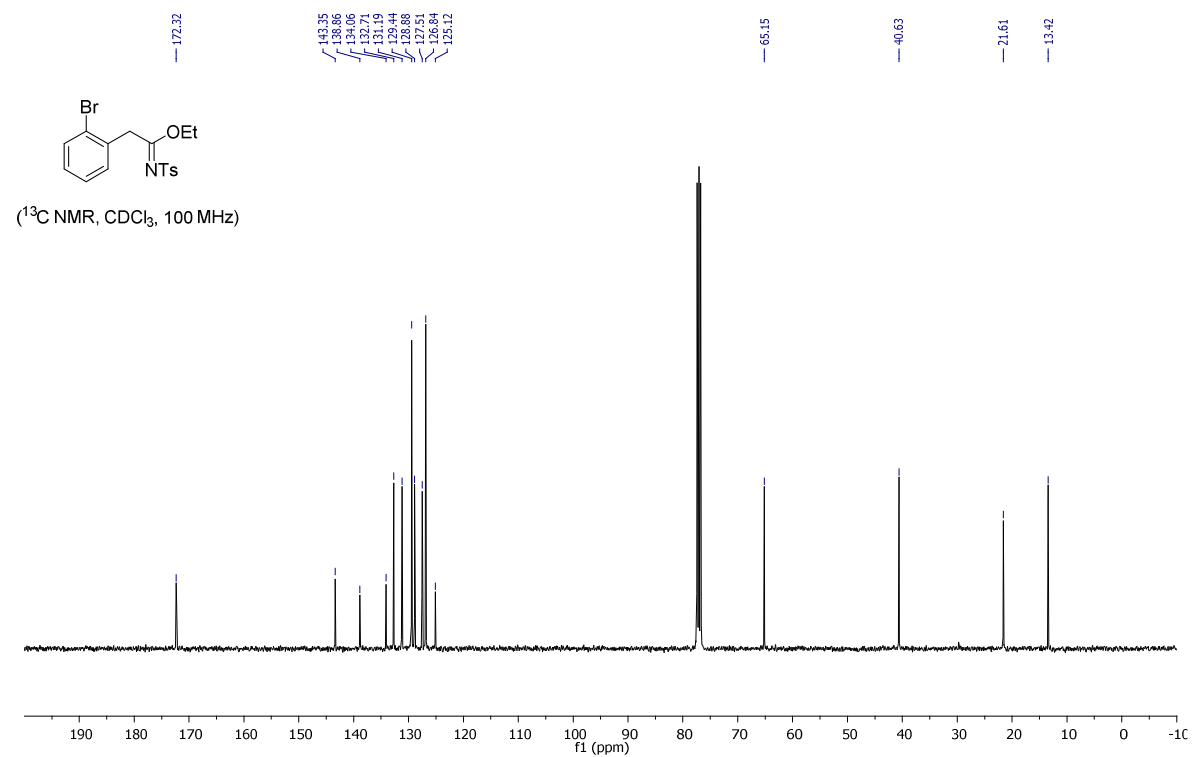
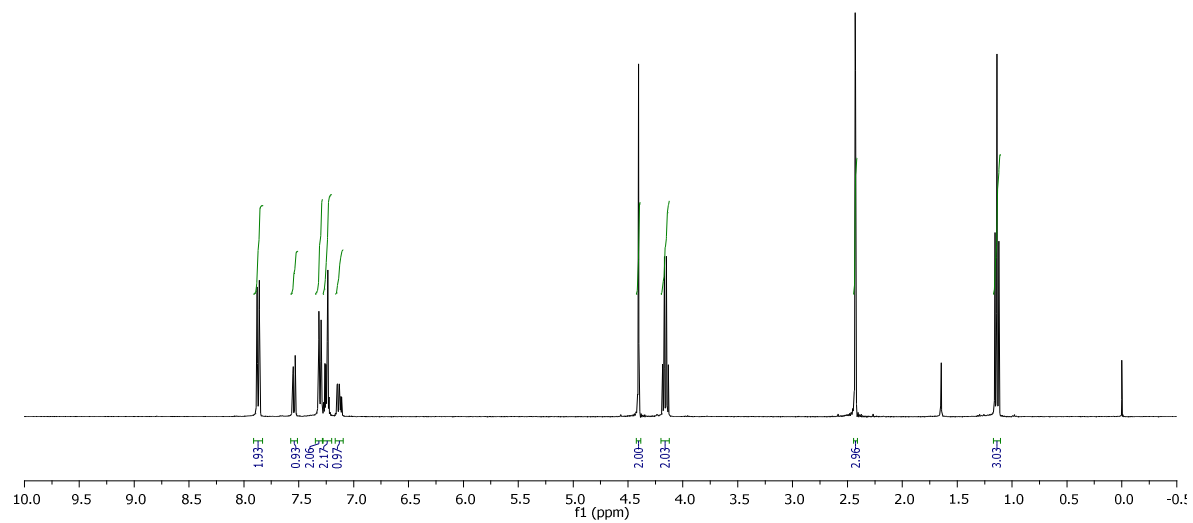
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 300 MHz)



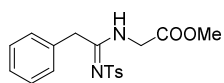
**Ethyl (*E*)-2-(2-bromophenyl)-*N*-tosylacetimidate (2f):**



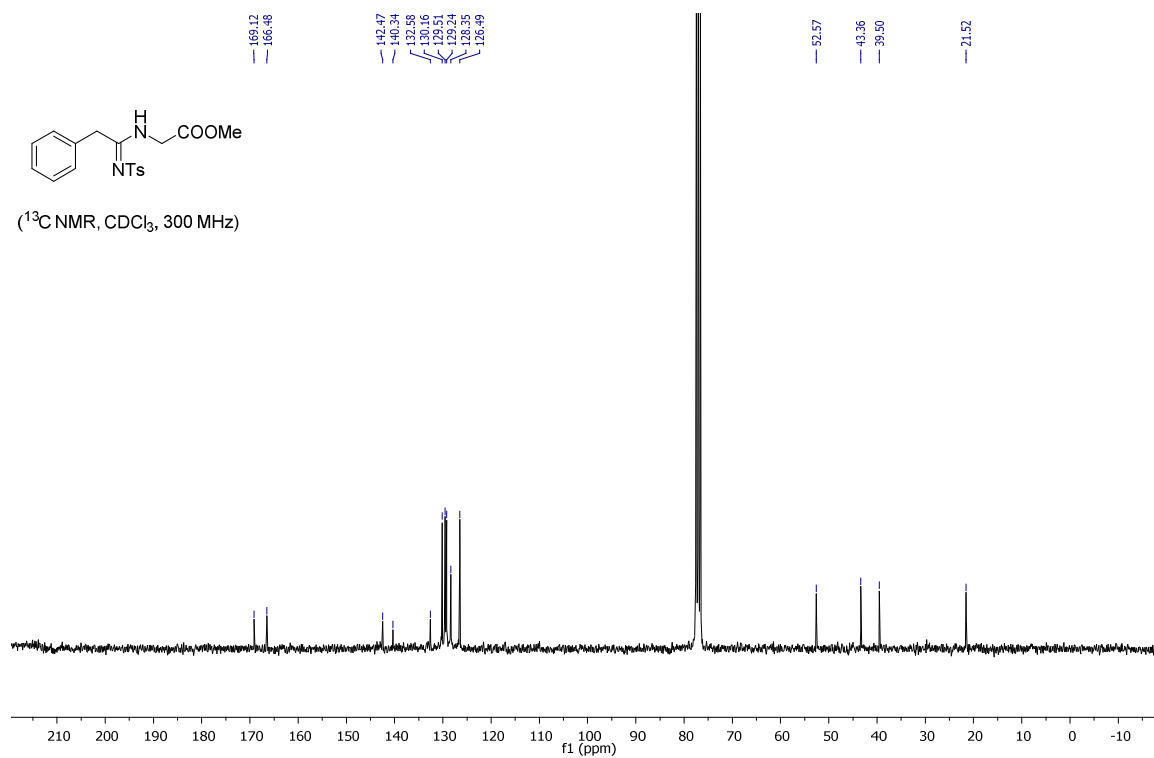
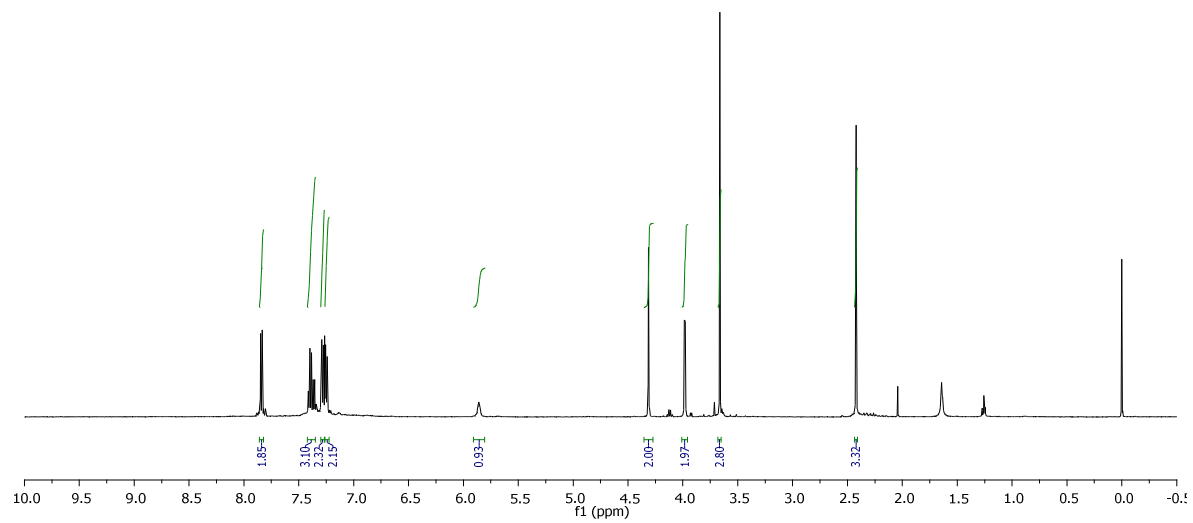
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



**Methyl (*E*)-(2-phenyl-1-(tosylimino)ethyl)glycinate (2g):**

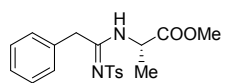


( $^1\text{H}$ NMR,  $\text{CDCl}_3$ , 500 MHz)

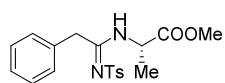
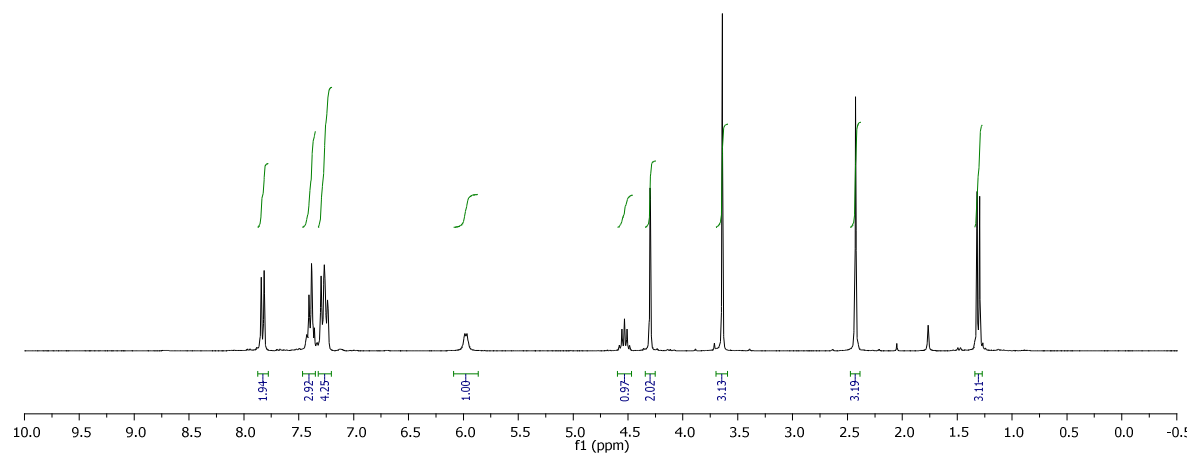




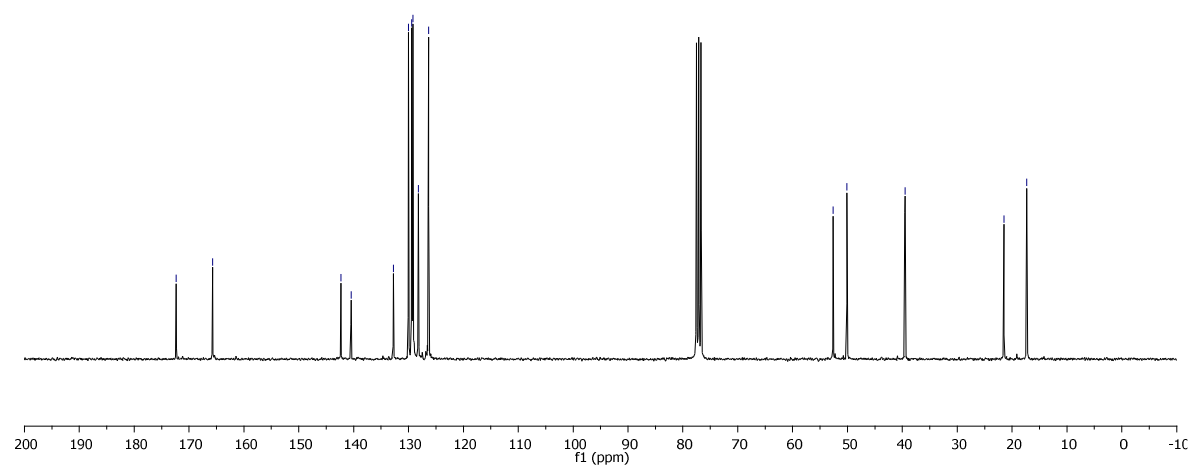
**Methyl (*E*)-(2-phenyl-1-(tosylimino)ethyl)-L-alaninate (2h):**



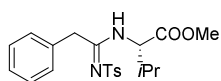
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)



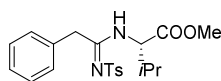
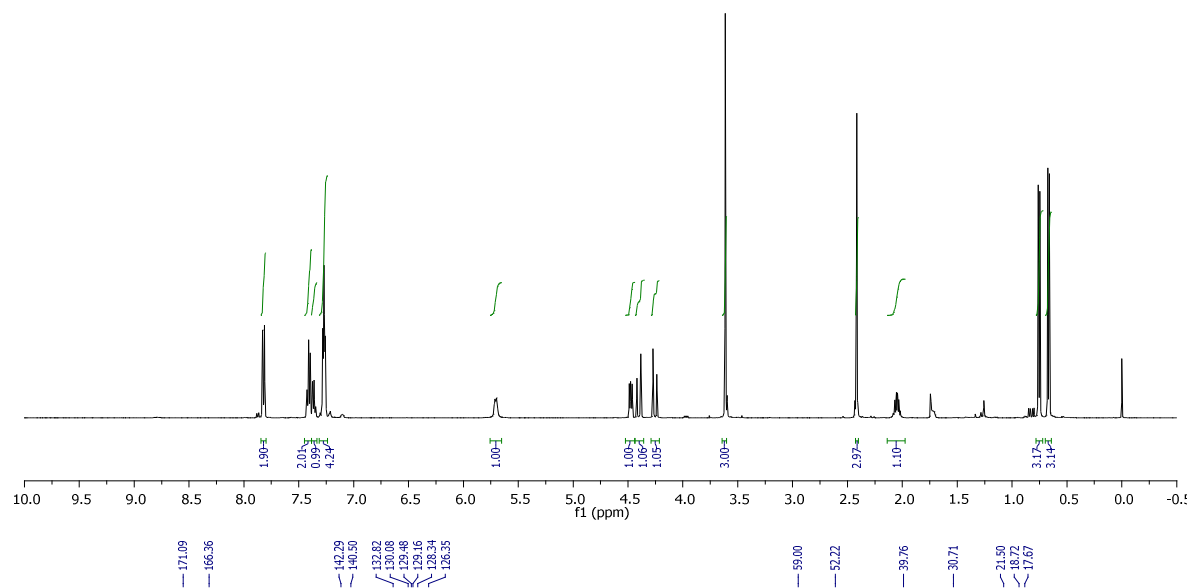
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz)



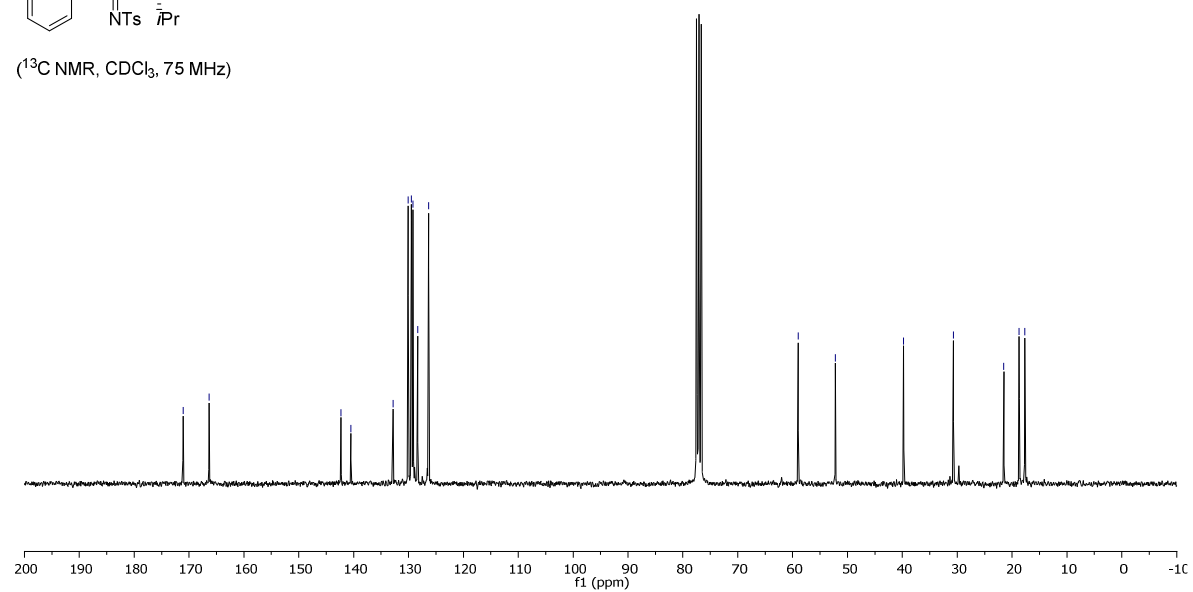
**Methyl (*E*)-(2-phenyl-1-(tosylimino)ethyl)-L-valinate (2i):**



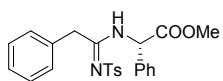
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



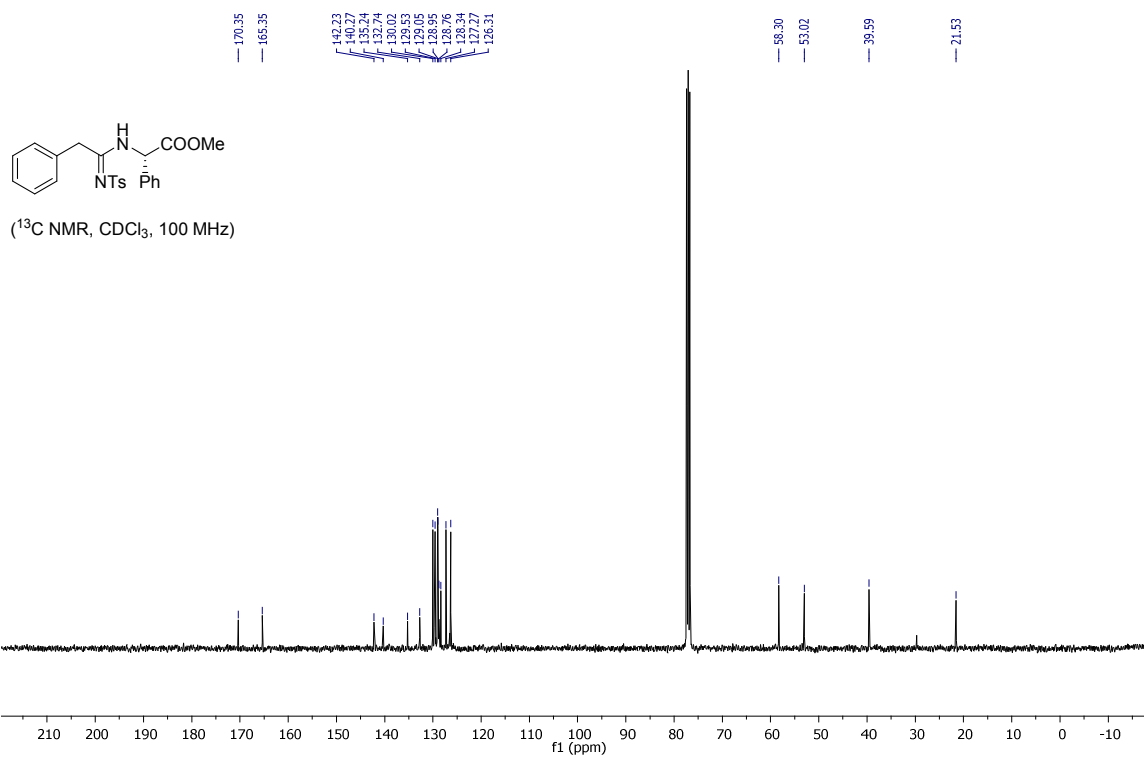
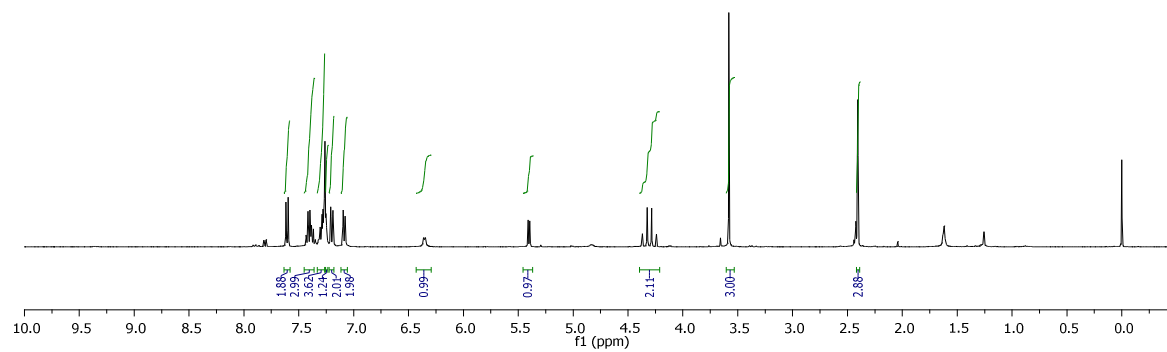
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz)



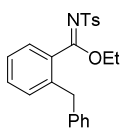
**Methyl (*S,E*)-2-phenyl-2-(2-phenyl-*N'*-tosylacetimidamido)acetate (2j):**



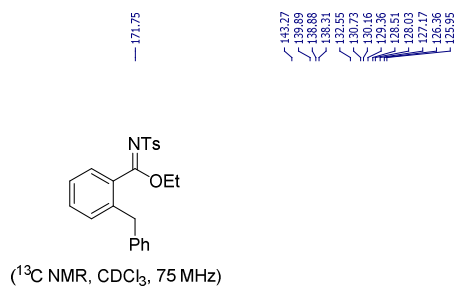
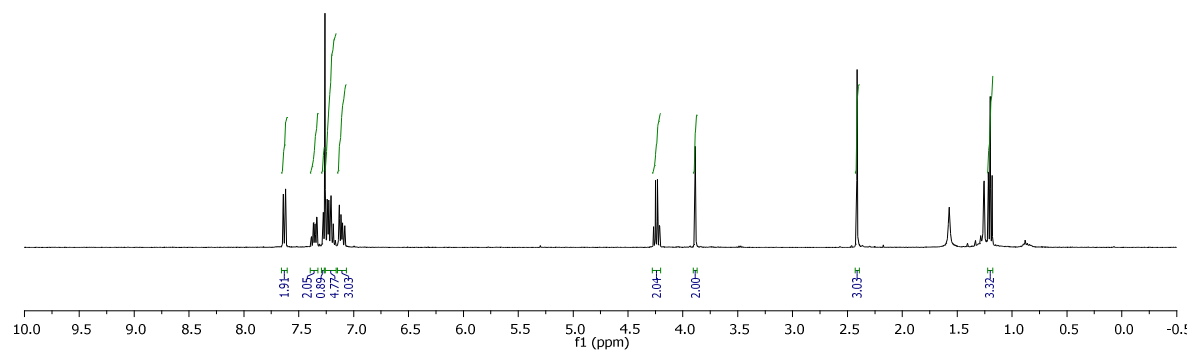
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



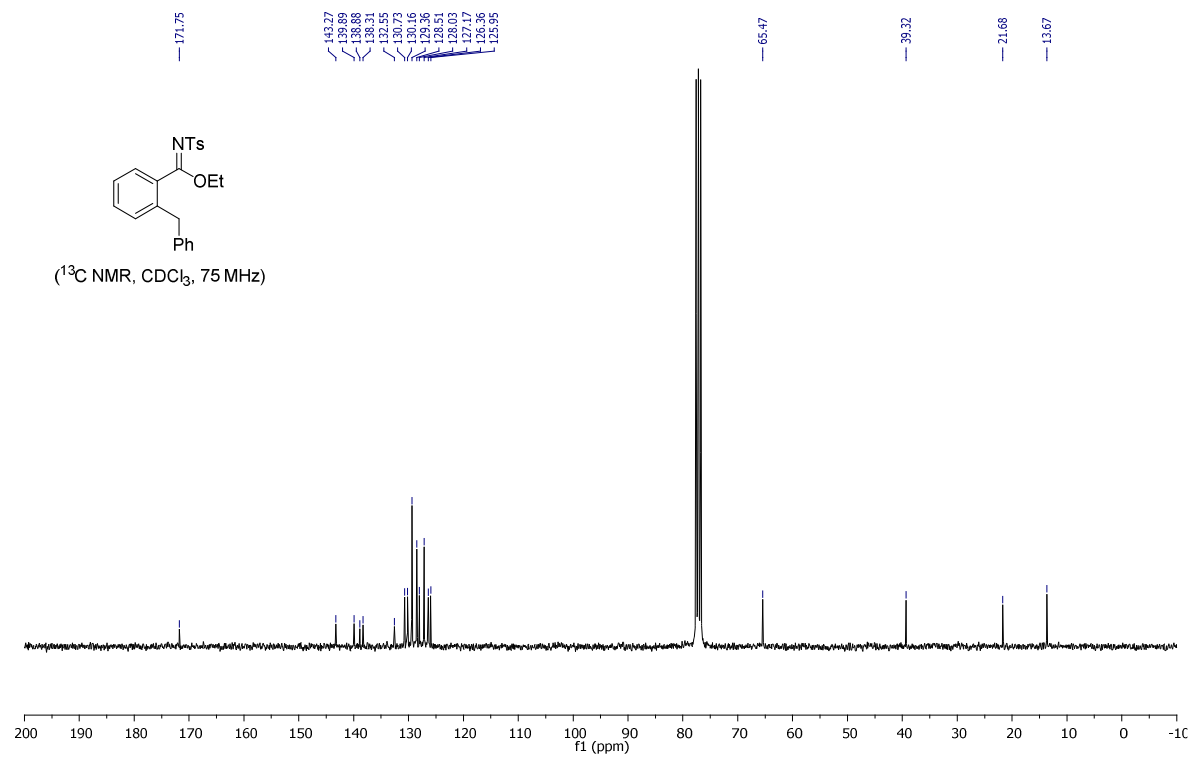
**Ethyl (Z)-2-benzyl-N-tosylbenzimidate (3a):**



( $^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz)



( $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 75 MHz)

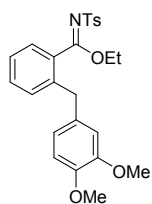


CCOC(=Nc1ccccc1)Cc2ccccc2C

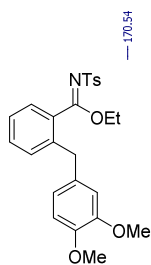
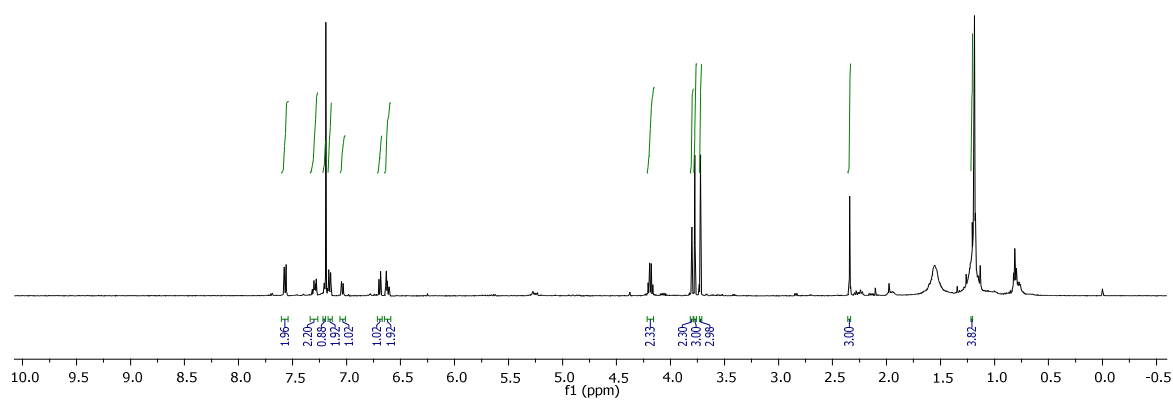
<sup>1</sup>H NMR spectrum of compound 10a in CDCl<sub>3</sub>. The spectrum shows peaks at 7.20 (d, 2H), 7.11 (d, 2H), 7.06 (d, 2H), 4.38 (s, 2H), 3.98 (s, 2H), 2.48 (s, 3H), 2.32 (s, 3H), 1.48 (s, 3H), and 1.22 (s, 3H). Integration values are shown below the peaks: 2.00, 2.76, 2.82, 3.31, 1.11, 1.06, 2.19, 2.18, 3.22, 3.08, and 3.08.



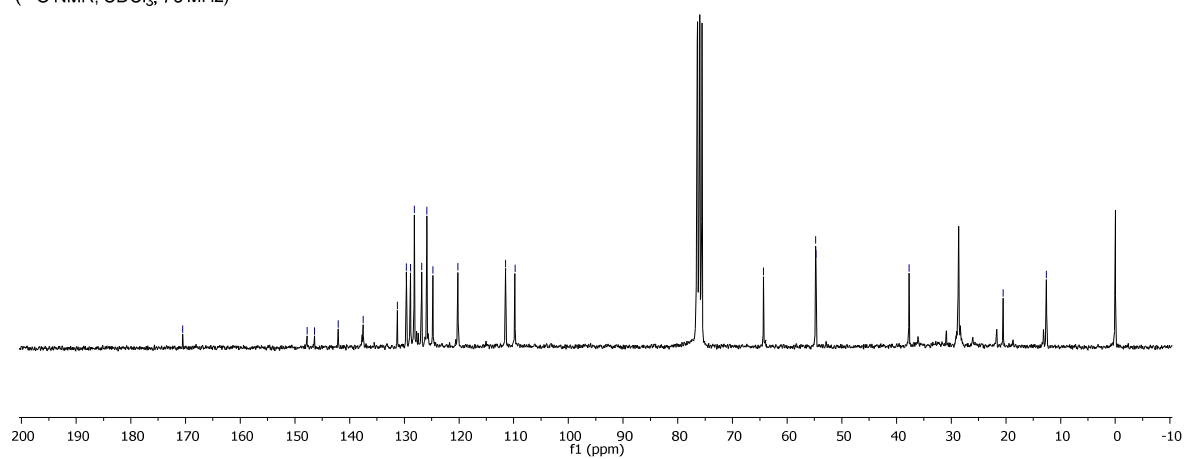
**Ethyl (Z)-2-(3,4-dimethoxybenzyl)-N-tosylbenzimidate (3c):**



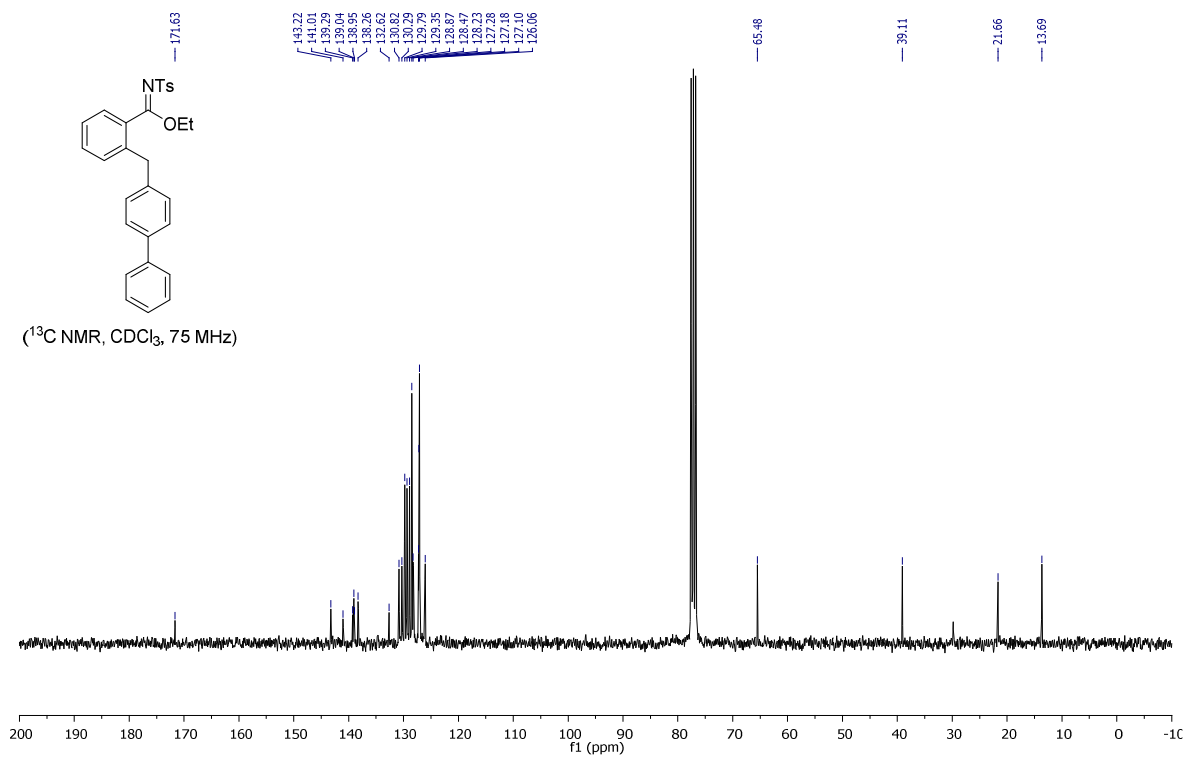
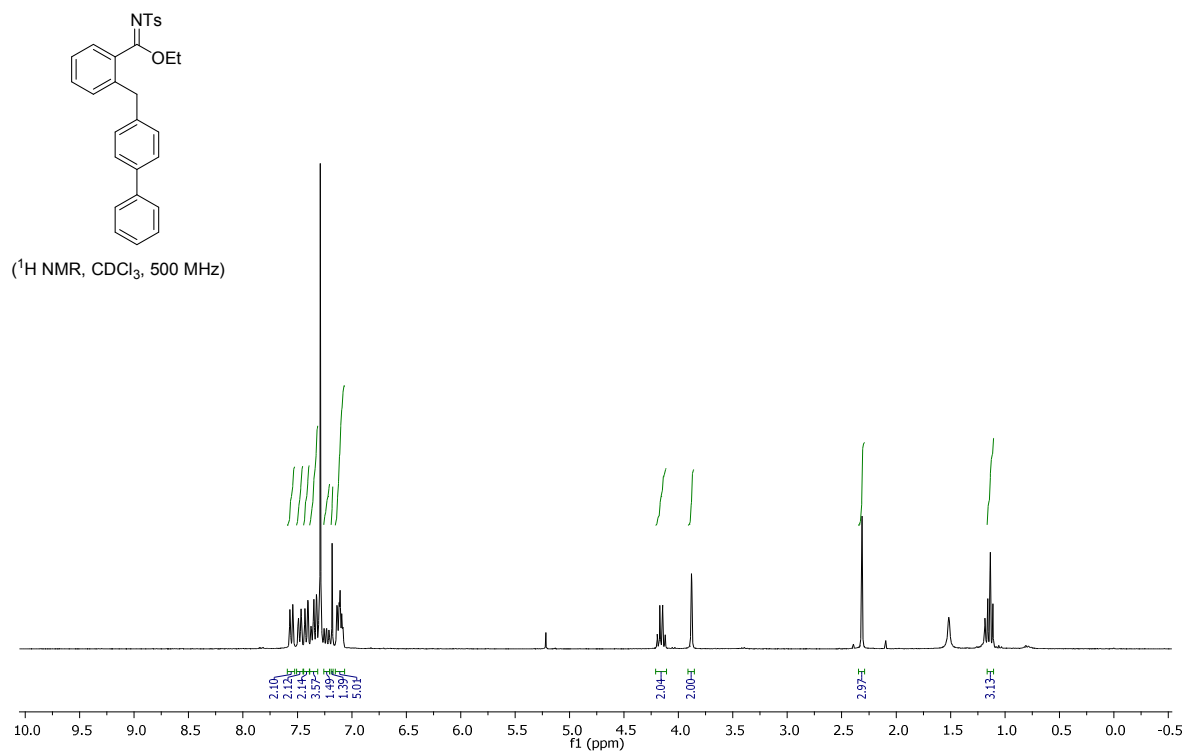
( $^1\text{H}$  NMR,  $\text{CDCl}_3$ , 500 MHz)



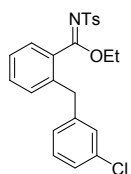
( $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 75 MHz)



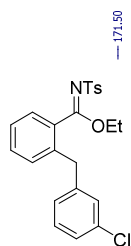
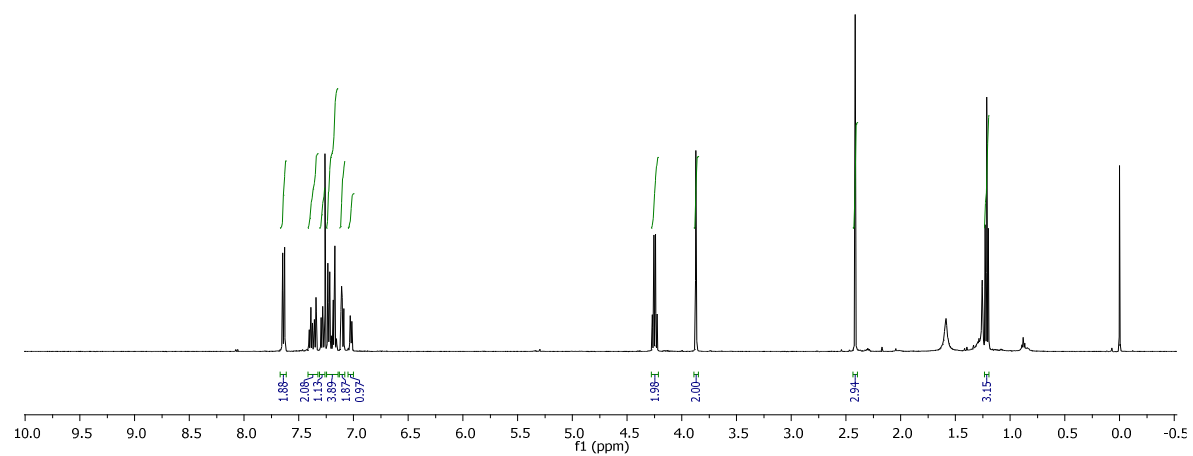
**Ethyl (Z)-2-([1,1'-biphenyl]-4-ylmethyl)-N-tosylbenzimidate (3d):**



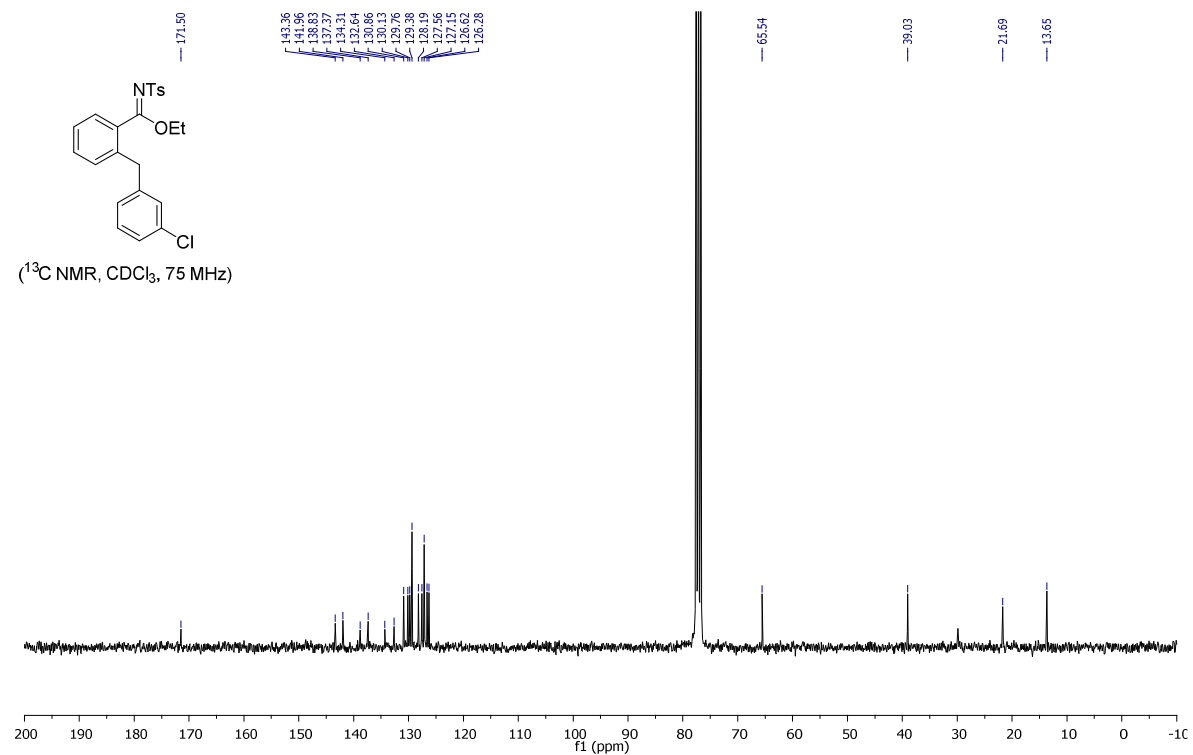
**Ethyl (Z)-2-(3-chlorobenzyl)-N-tosylbenzimidate (3e):**



(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)

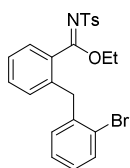


(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz)

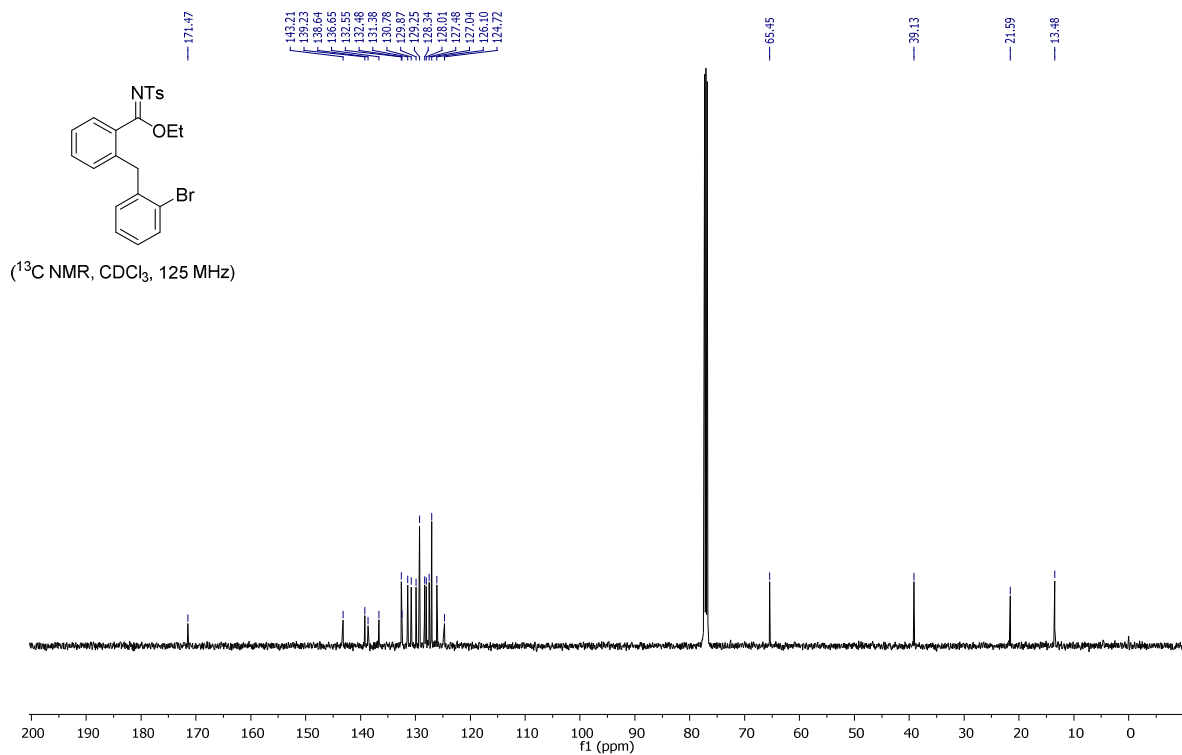
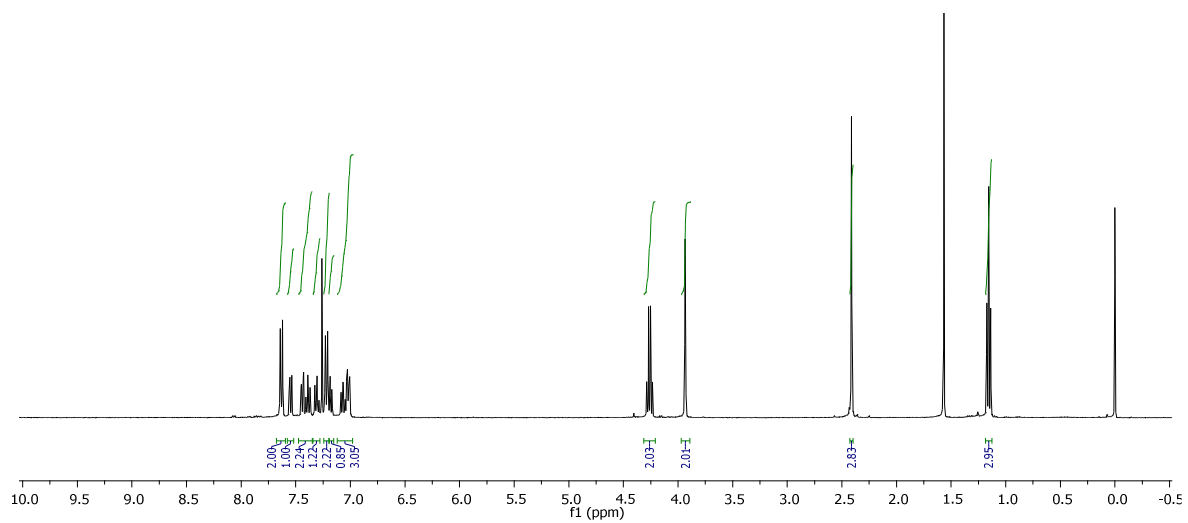




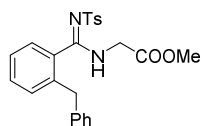
**Ethyl (Z)-2-(2-bromobenzyl)-N-tosylbenzimidate (3f):**



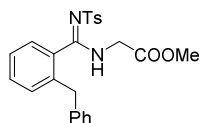
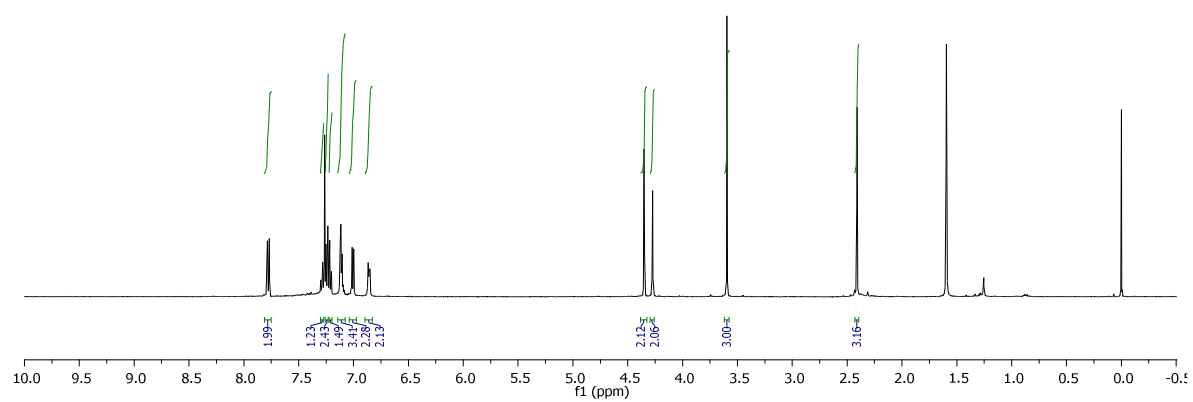
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



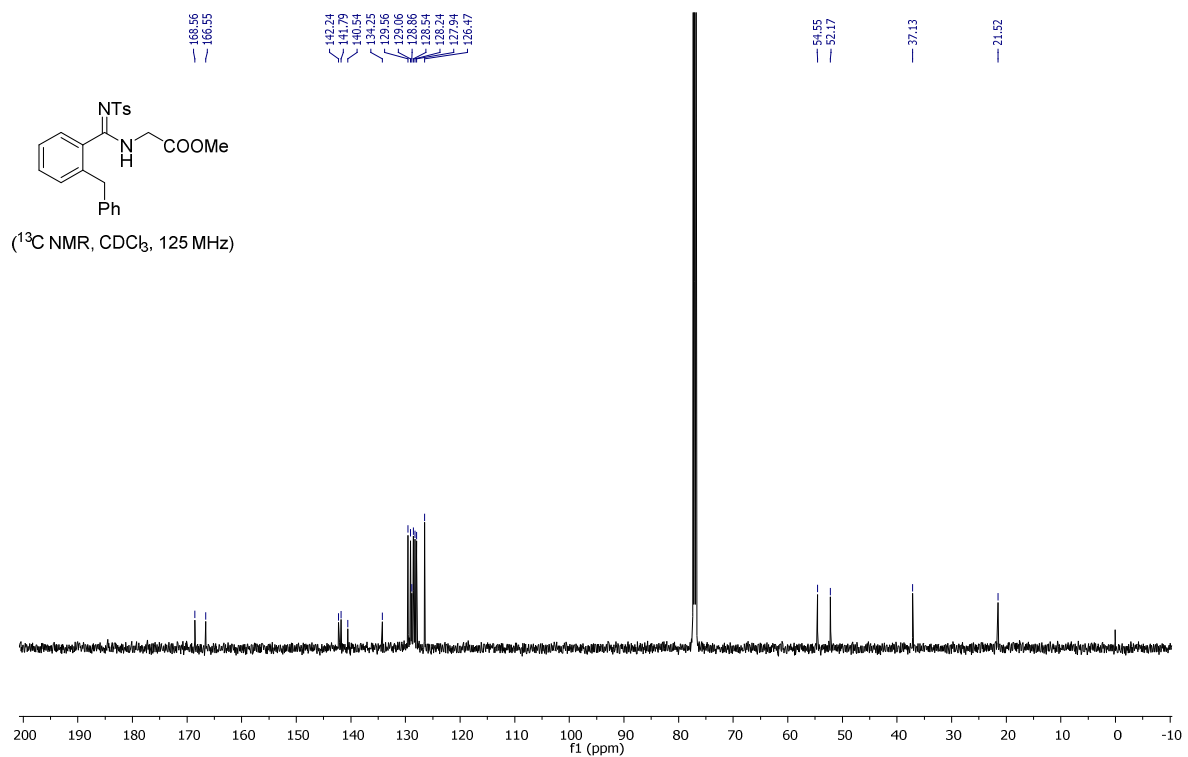
**Methyl (Z)-((2-benzylphenyl)(tosylimino)methyl)glycinate (3g):**



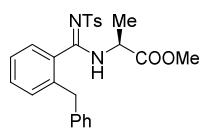
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



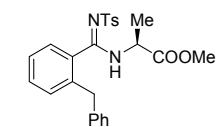
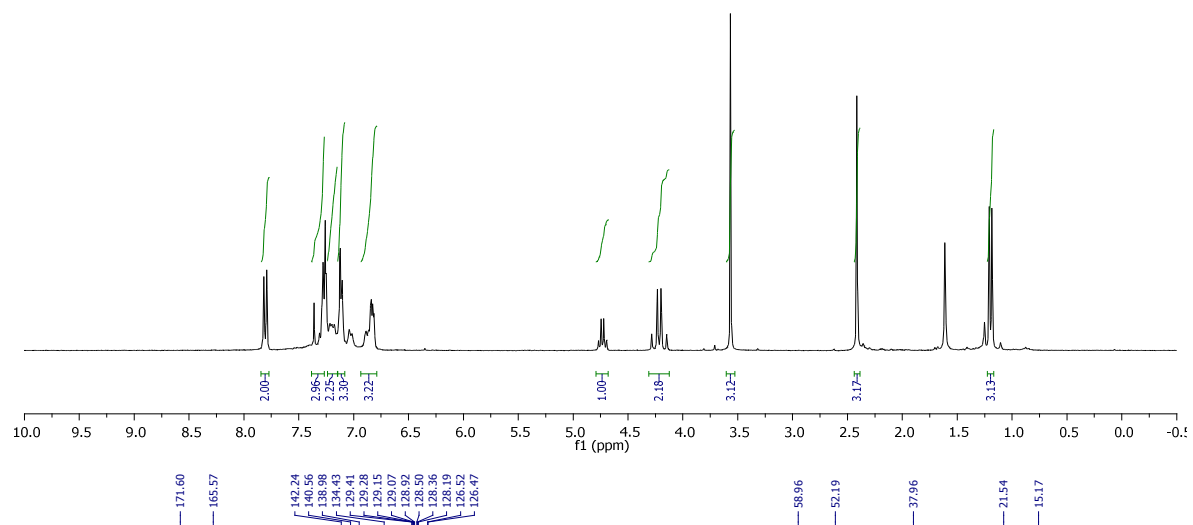
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 125 MHz)



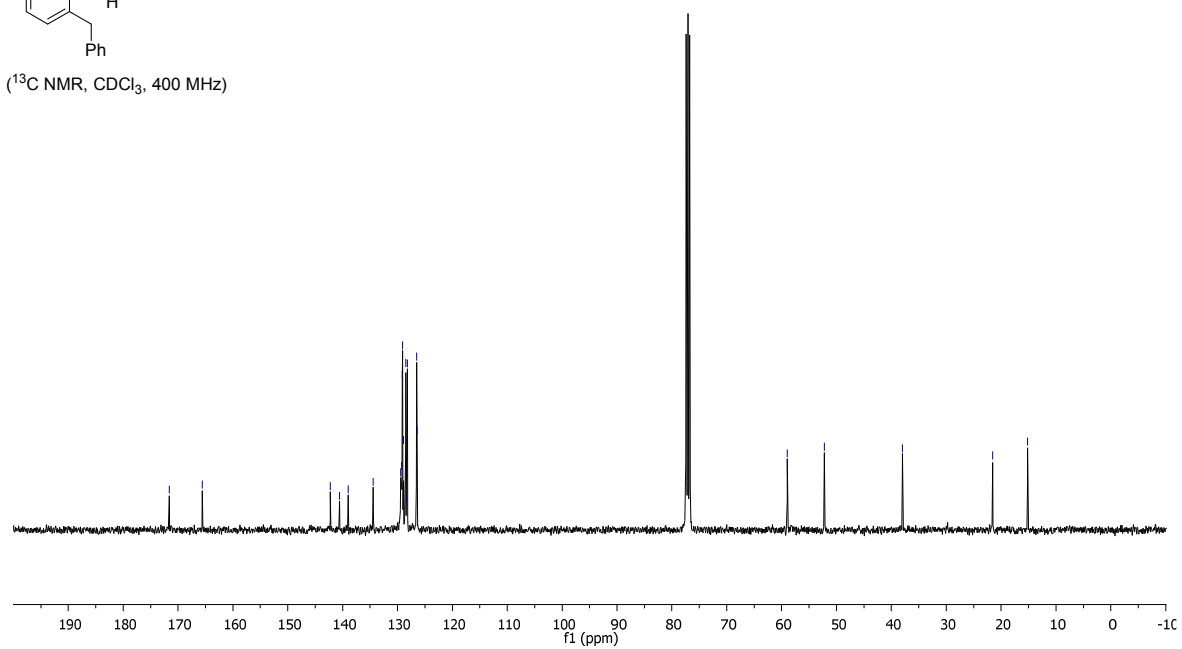
**Methyl (Z)-((2-benzylphenyl)(tosylimino)methyl)-L-alaninate (3h):**



(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)



(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 400 MHz)

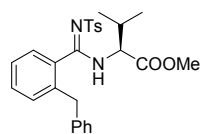


COC(=O)[C@H](C)NC(=Nc1ccccc1)Cc2ccccc2

<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)

1.87, 2.71, 2.19, 3.98, 1.01, 1.93, 2.00, 1.03, 3.00, 3.14, 1.03, 3.20, 3.16

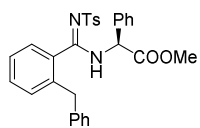
170.33, 166.01, 142.25, 141.55, 134.26, 129.09, 128.74, 128.63, 128.12, 126.54, 126.46, 70.32, 51.81, 38.07, 28.10, 21.55, 20.73



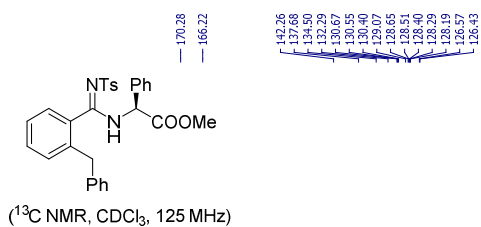
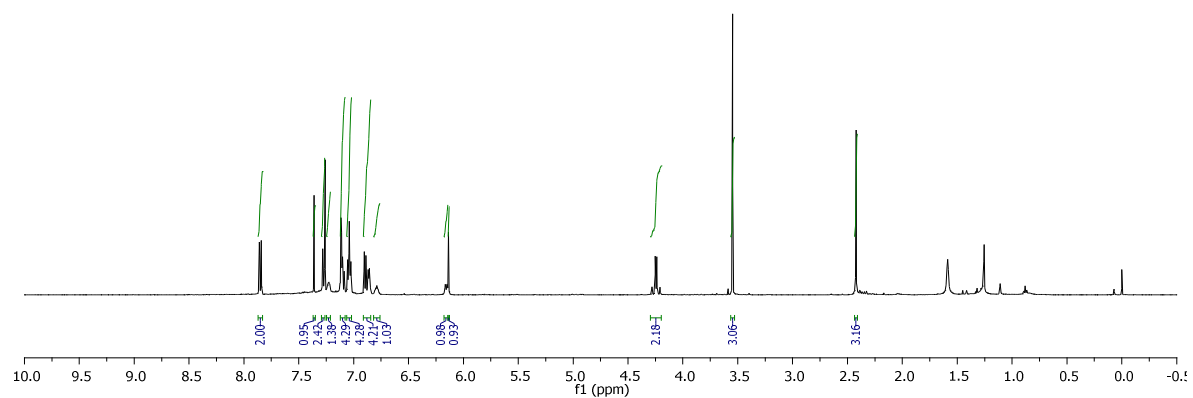
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 125 MHz)

13C NMR spectrum (CDCl<sub>3</sub>, 125 MHz) showing chemical shifts (ppm) on the x-axis (ranging from 200 to -10). The spectrum displays several peaks, including a large solvent peak at 77 ppm. Key peaks are labeled with their chemical shifts: 169.1, 132.8, 132.5, 132.2, 131.8, 131.5, 131.2, 130.8, 129.5, 129.2, 128.8, 128.5, 128.2, 127.8, 127.5, 127.2, 126.8, 126.5, 126.2, 125.8, 125.5, 125.2, 124.8, 124.5, 124.2, 123.8, 123.5, 123.2, 122.8, 122.5, 122.2, 121.8, 121.5, 121.2, 120.8, 120.5, 120.2, 119.8, 119.5, 119.2, 118.8, 118.5, 118.2, 117.8, 117.5, 117.2, 116.8, 116.5, 116.2, 115.8, 115.5, 115.2, 114.8, 114.5, 114.2, 113.8, 113.5, 113.2, 112.8, 112.5, 112.2, 111.8, 111.5, 111.2, 110.8, 110.5, 110.2, 109.8, 109.5, 109.2, 108.8, 108.5, 108.2, 107.8, 107.5, 107.2, 106.8, 106.5, 106.2, 105.8, 105.5, 105.2, 104.8, 104.5, 104.2, 103.8, 103.5, 103.2, 102.8, 102.5, 102.2, 101.8, 101.5, 101.2, 100.8, 100.5, 100.2, 99.8, 99.5, 99.2, 98.8, 98.5, 98.2, 97.8, 97.5, 97.2, 96.8, 96.5, 96.2, 95.8, 95.5, 95.2, 94.8, 94.5, 94.2, 93.8, 93.5, 93.2, 92.8, 92.5, 92.2, 91.8, 91.5, 91.2, 90.8, 90.5, 90.2, 89.8, 89.5, 89.2, 88.8, 88.5, 88.2, 87.8, 87.5, 87.2, 86.8, 86.5, 86.2, 85.8, 85.5, 85.2, 84.8, 84.5, 84.2, 83.8, 83.5, 83.2, 82.8, 82.5, 82.2, 81.8, 81.5, 81.2, 80.8, 80.5, 80.2, 79.8, 79.5, 79.2, 78.8, 78.5, 78.2, 77.8, 77.5, 77.2, 76.8, 76.5, 76.2, 75.8, 75.5, 75.2, 74.8, 74.5, 74.2, 73.8, 73.5, 73.2, 72.8, 72.5, 72.2, 71.8, 71.5, 71.2, 70.8, 70.5, 70.2, 69.8, 69.5, 69.2, 68.8, 68.5, 68.2, 67.8, 67.5, 67.2, 66.8, 66.5, 66.2, 65.8, 65.5, 65.2, 64.8, 64.5, 64.2, 63.8, 63.5, 63.2, 62.8, 62.5, 62.2, 61.8, 61.5, 61.2, 60.8, 60.5, 60.2, 59.8, 59.5, 59.2, 58.8, 58.5, 58.2, 57.8, 57.5, 57.2, 56.8, 56.5, 56.2, 55.8, 55.5, 55.2, 54.8, 54.5, 54.2, 53.8, 53.5, 53.2, 52.8, 52.5, 52.2, 51.8, 51.5, 51.2, 50.8, 50.5, 50.2, 49.8, 49.5, 49.2, 48.8, 48.5, 48.2, 47.8, 47.5, 47.2, 46.8, 46.5, 46.2, 45.8, 45.5, 45.2, 44.8, 44.5, 44.2, 43.8, 43.5, 43.2, 42.8, 42.5, 42.2, 41.8, 41.5, 41.2, 40.8, 40.5, 40.2, 39.8, 39.5, 39.2, 38.8, 38.5, 38.2, 37.8, 37.5, 37.2, 36.8, 36.5, 36.2, 35.8, 35.5, 35.2, 34.8, 34.5, 34.2, 33.8, 33.5, 33.2, 32.8, 32.5, 32.2, 31.8, 31.5, 31.2, 30.8, 30.5, 30.2, 29.8, 29.5, 29.2, 28.8, 28.5, 28.2, 27.8, 27.5, 27.2, 26.8, 26.5, 26.2, 25.8, 25.5, 25.2, 24.8, 24.5, 24.2, 23.8, 23.5, 23.2, 22.8, 22.5, 22.2, 21.8, 21.5, 21.2, 20.8, 20.5, 20.2, 19.8, 19.5, 19.2, 18.8, 18.5, 18.2, 17.8, 17.5, 17.2, 16.8, 16.5, 16.2, 15.8, 15.5, 15.2, 14.8, 14.5, 14.2, 13.8, 13.5, 13.2, 12.8, 12.5, 12.2, 11.8, 11.5, 11.2, 10.8, 10.5, 10.2, 9.8, 9.5, 9.2, 8.8, 8.5, 8.2, 7.8, 7.5, 7.2, 6.8, 6.5, 6.2, 5.8, 5.5, 5.2, 4.8, 4.5, 4.2, 3.8, 3.5, 3.2, 2.8, 2.5, 2.2, 1.8, 1.5, 1.2, 0.8, 0.5, 0.2, -0.2, -0.5, -0.8, -1.2, -1.5, -1.8, -2.2, -2.5, -2.8, -3.2, -3.5, -3.8, -4.2, -4.5, -4.8, -5.2, -5.5, -5.8, -6.2, -6.5, -6.8, -7.2, -7.5, -7.8, -8.2, -8.5, -8.8, -9.2, -9.5, -9.8, -10.2, -10.5, -10.8, -11.2, -11.5, -11.8, -12.2, -12.5, -12.8, -13.2, -13.5, -13.8, -14.2, -14.5, -14.8, -15.2, -15.5, -15.8, -16.2, -16.5, -16.8, -17.2, -17.5, -17.8, -18.2, -18.5, -18.8, -19.2, -19.5, -19.8, -20.2, -20.5, -20.8, -21.2, -21.5, -21.8, -22.2, -22.5, -22.8, -23.2, -23.5, -23.8, -24.2, -24.5, -24.8, -25.2, -25.5, -25.8, -26.2, -26.5, -26.8, -27.2, -27.5, -27.8, -28.2, -28.5, -28.8, -29.2, -29.5, -29.8, -30.2, -30.5, -30.8, -31.2, -31.5, -31.8, -32.2, -32.5, -32.8, -33.2, -33.5, -33.8, -34.2, -34.5, -34.8, -35.2, -35.5, -35.8, -36.2, -36.5, -36.8, -37.2, -37.5, -37.8, -38.2, -38.5, -38.8, -39.2, -39.5, -39.8, -40.2, -40.5, -40.8, -41.2, -41.5, -41.8, -42.2, -42.5, -42.8, -43.2, -43.5, -43.8, -44.2, -44.5, -44.8, -45.2, -45.5, -45.8, -46.2, -46.5, -46.8, -47.2, -47.5, -47.8, -48.2, -48.5, -48.8, -49.2, -49.5, -49.8, -50.2, -50.5, -50.8, -51.2, -51.5, -51.8, -52.2, -52.5, -52.8, -53.2, -53.5, -53.8, -54.2, -54.5, -54.8, -55.2, -55.5, -55.8, -56.2, -56.5, -56.8, -57.2, -57.5, -57.8, -58.2, -58.5, -58.8, -59.2, -59.5, -59.8, -60.2, -60.5, -60.8, -61.2, -61.5, -61.8, -62.2, -62.5, -62.8, -63.2, -63.5, -63.8, -64.2, -64.5, -64.8, -65.2, -65.5, -65.8, -66.2, -66.5, -66.8, -67.2, -67.5, -67.8, -68.2, -68.5, -68.8, -69.2, -69.5, -69.8, -70.2, -70.5, -70.8, -71.2, -71.5, -71.8, -72.2, -72.5, -72.8, -73.2, -73.5, -73.8, -74.2, -74.5, -74.8, -75.2, -75.5, -75.8, -76.2, -76.5, -76.8, -77.2, -77.5, -77.8, -78.2, -78.5, -78.8, -79.2, -79.5, -79.8, -80.2, -80.5, -80.8, -81.2,

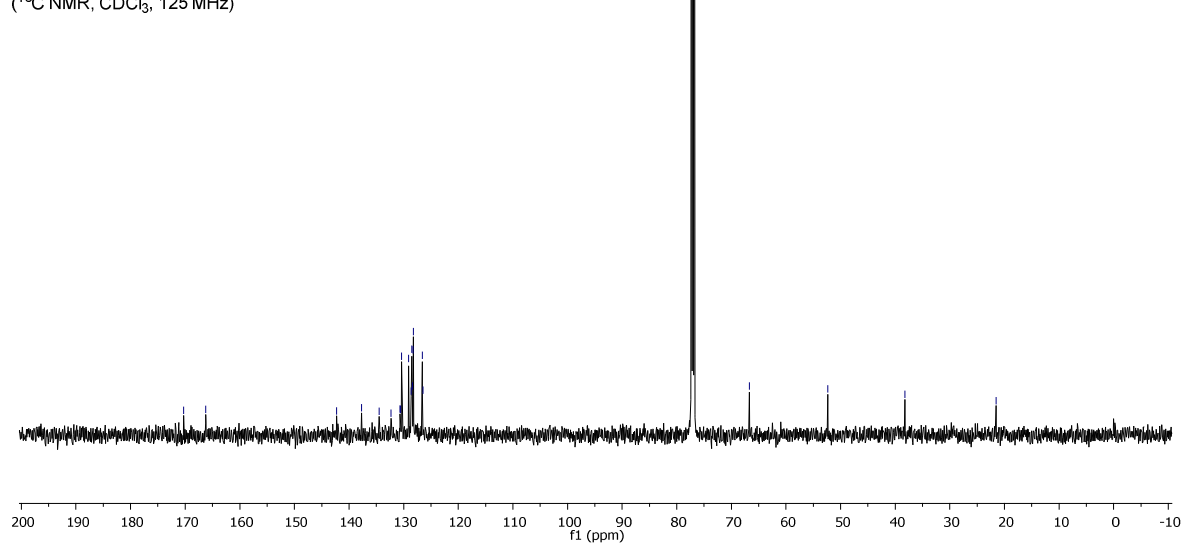
**Methyl (S,Z)-2-(2-benzyl-N'-tosylbenzimidamido)-2-phenylacetate (3j):**



(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 125 MHz)



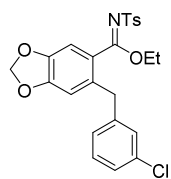
CCOC(=O)C(=Nc1ccc(cc1)-c2ccccc2)c3cc4c(cc3)OCO4

CCOC(=O)C(=O)c1ccc2c(c1)OCO2Cc3ccc(cc3)-c4ccccc4

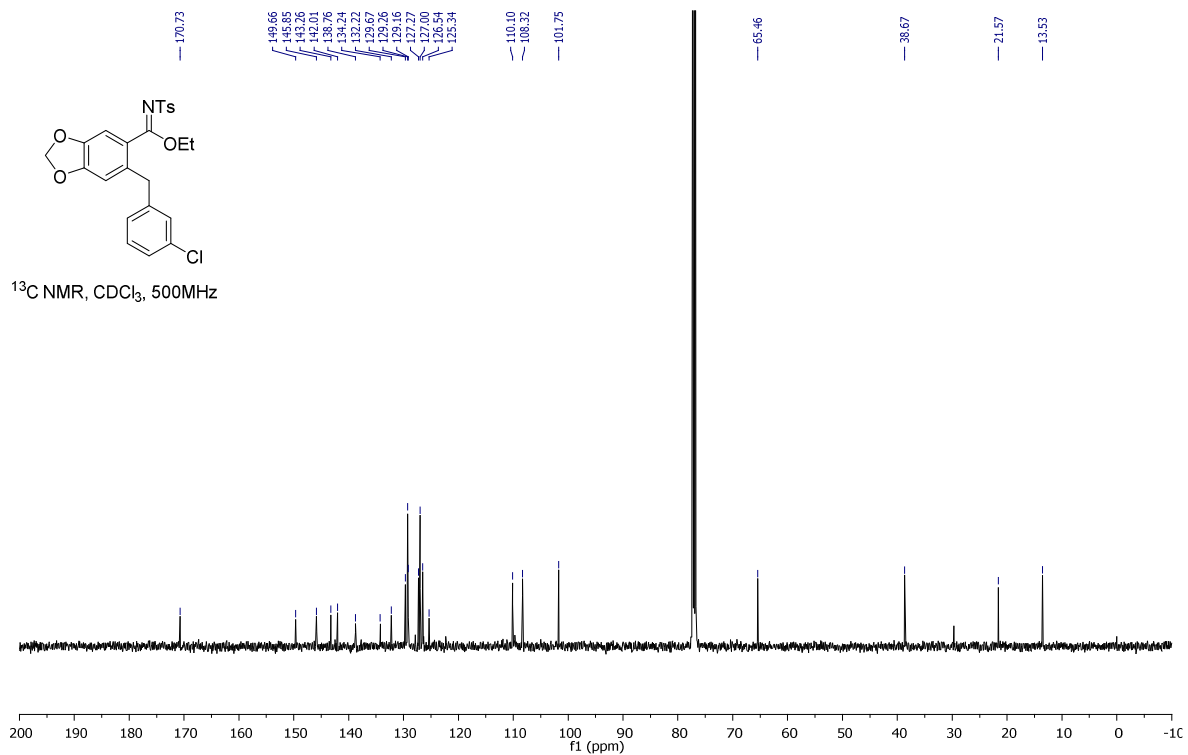
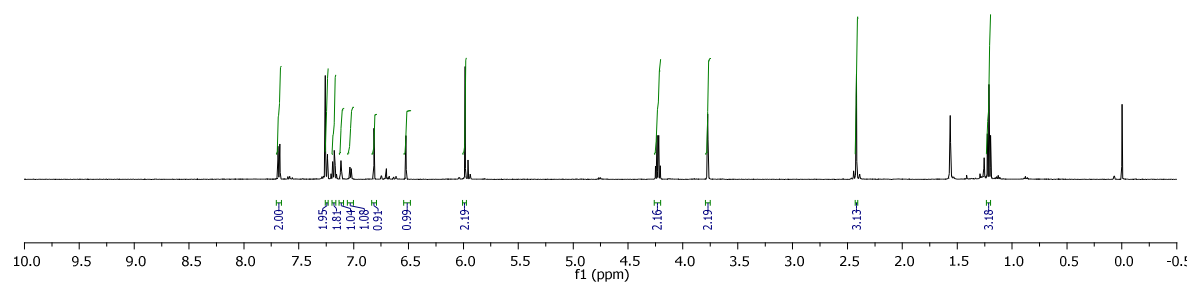
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 75 MHz

170.88  
 149.62  
 145.67  
 145.14  
 144.87  
 139.22  
 139.05  
 138.86  
 133.21  
 129.52  
 128.73  
 128.56  
 128.34  
 127.11  
 126.97  
 125.24  
 110.27  
 108.35  
 101.67  
 65.40  
 38.73  
 21.54  
 13.57

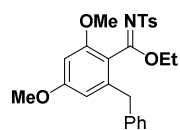
**Ethyl (Z)-6-(3-chlorobenzyl)-N-tosylbenzo[d][1,3]dioxole-5-carbimide (3l):**



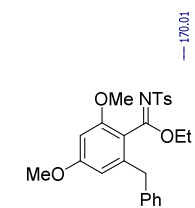
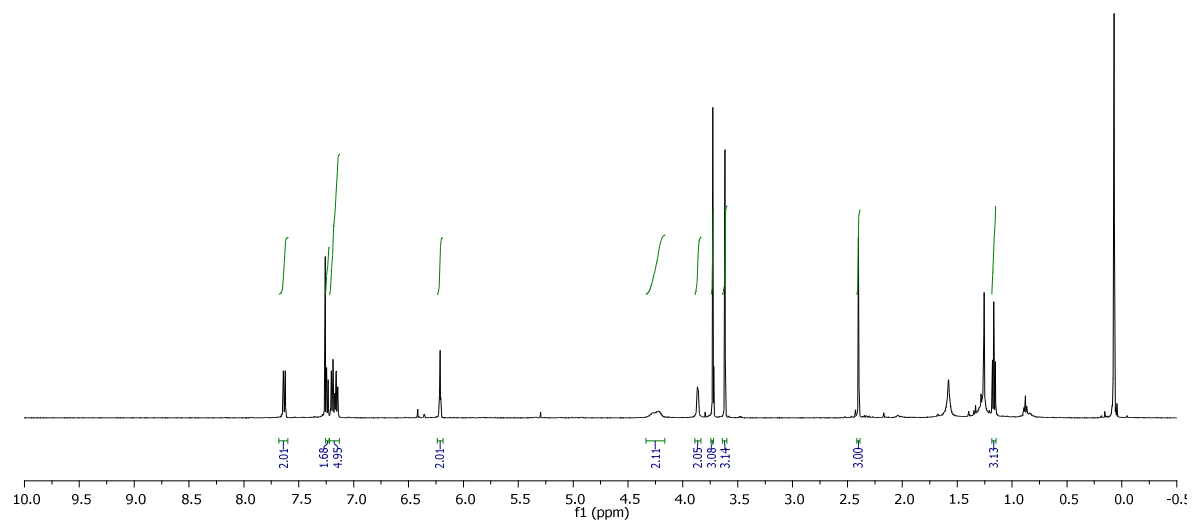
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 500MHz



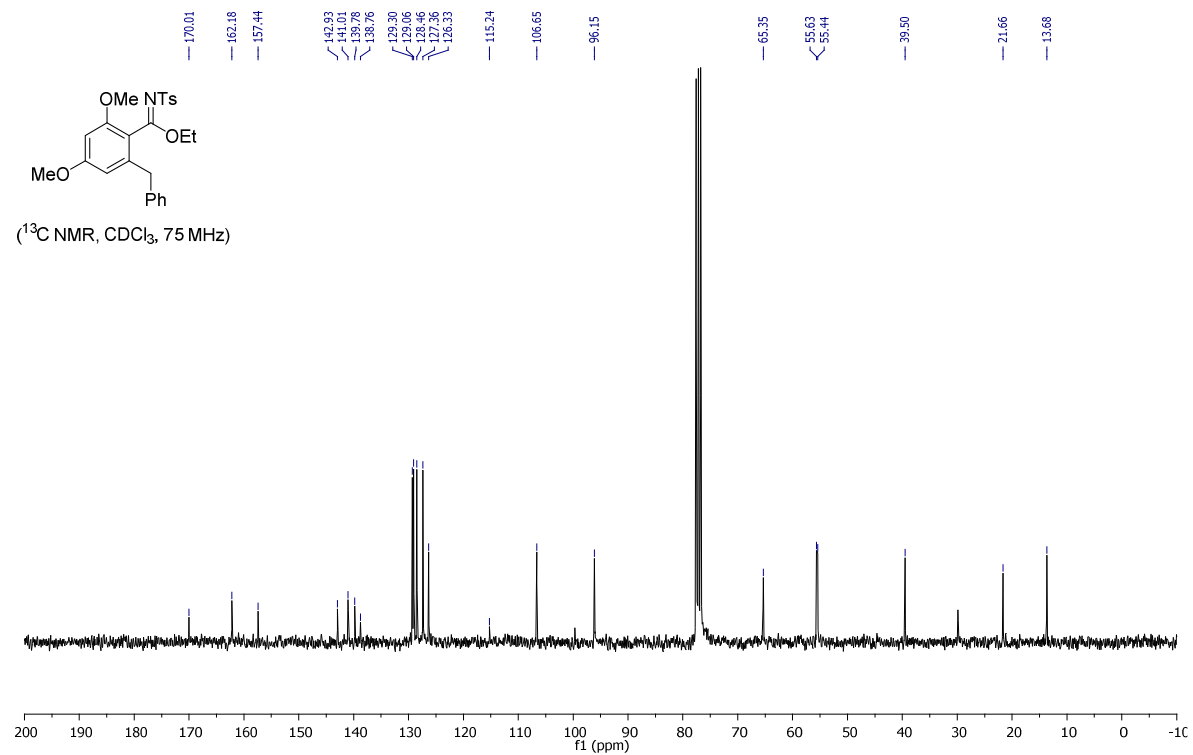
**Ethyl (Z)-2-benzyl-4,6-dimethoxy-N-tosylbenzimidate (3m):**



(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)

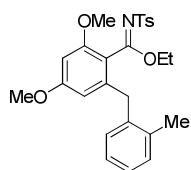


(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz)

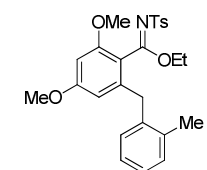
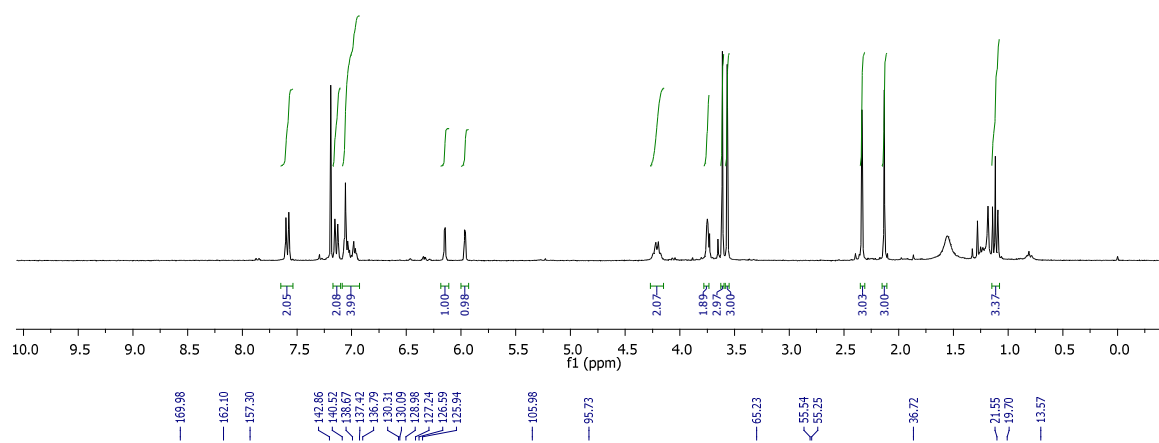




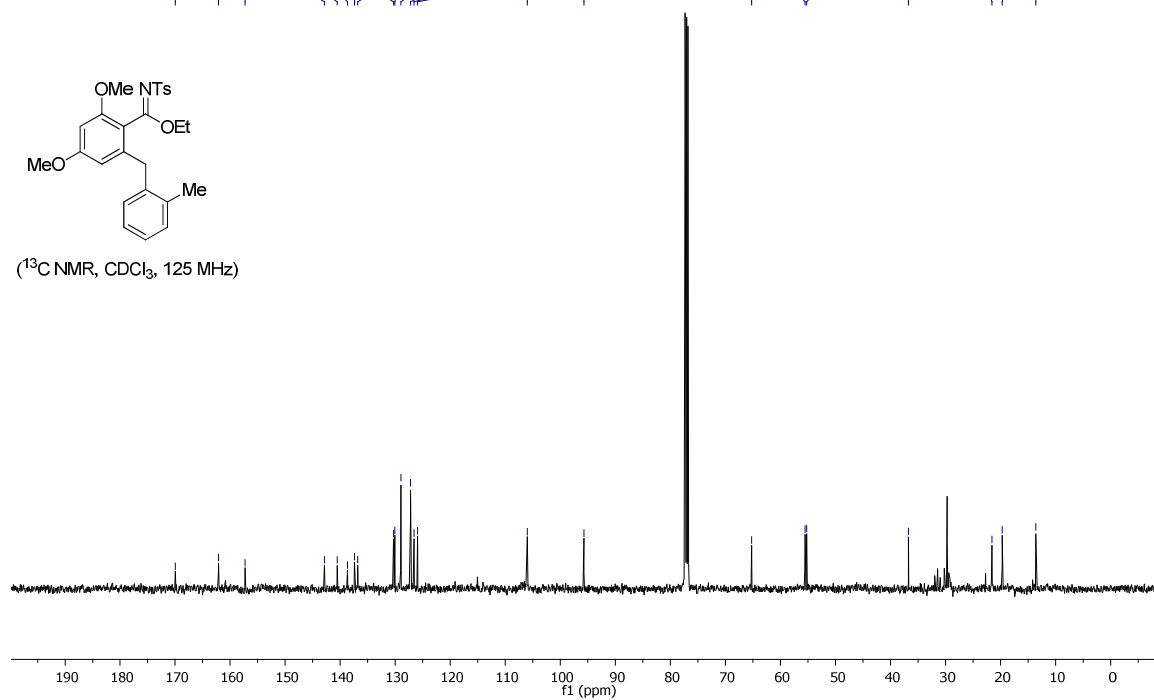
**Ethyl (Z)-2,4-dimethoxy-6-(2-methylbenzyl)-N-tosylbenzimidate (3n):**



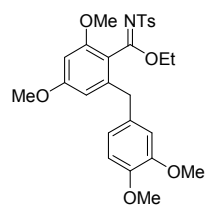
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)



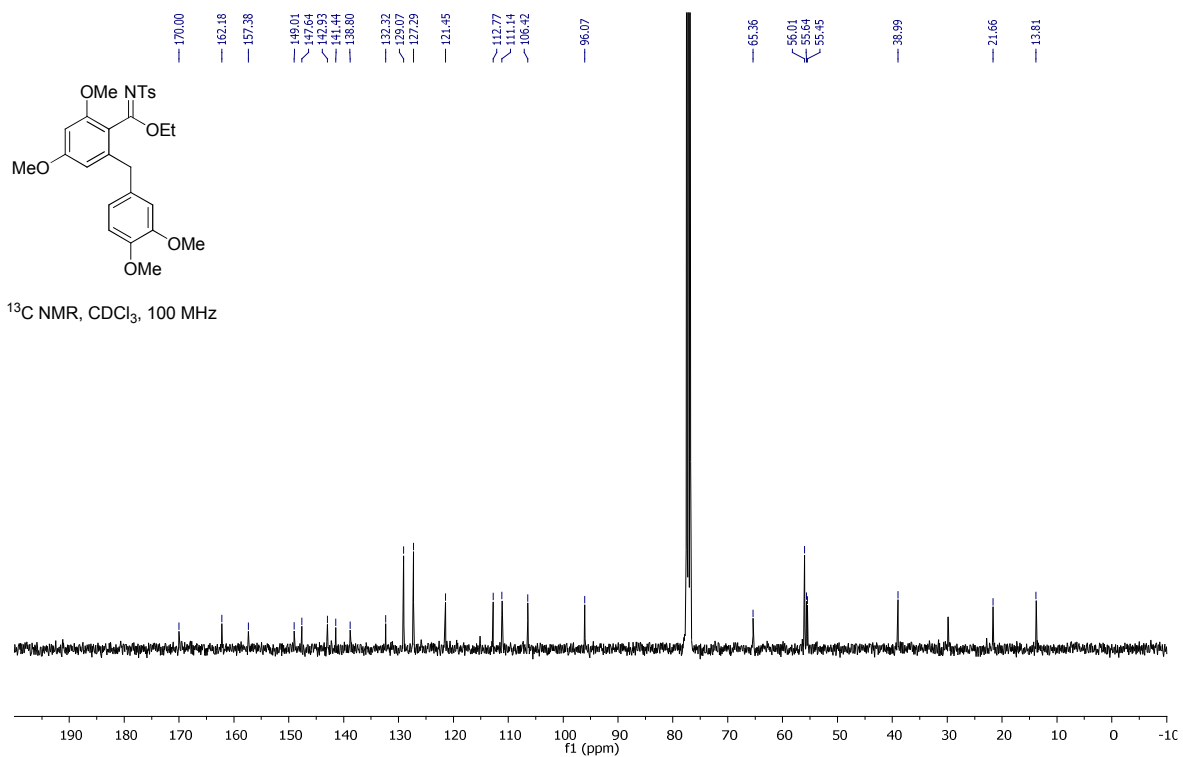
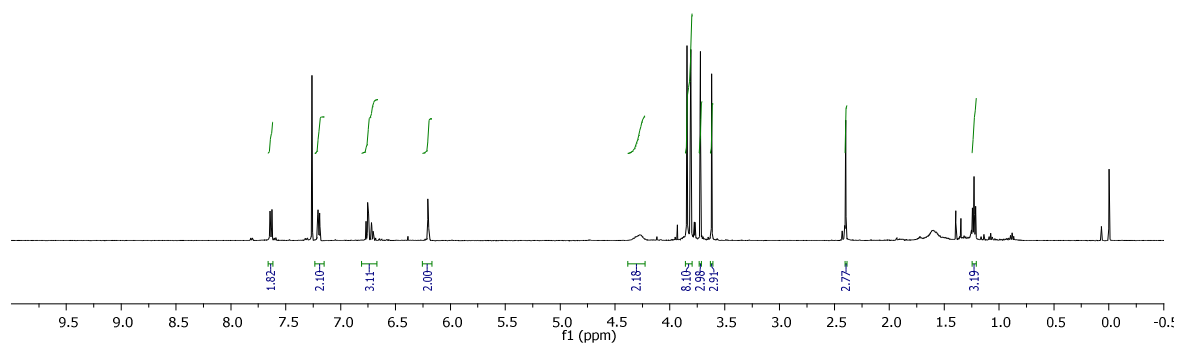
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 125 MHz)



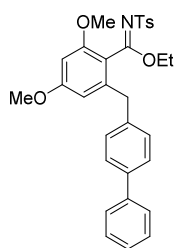
**Ethyl (Z)-2-(3,4-dimethoxybenzyl)-4,6-dimethoxy-N-tosylbenzimidate (3o):**



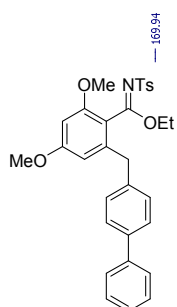
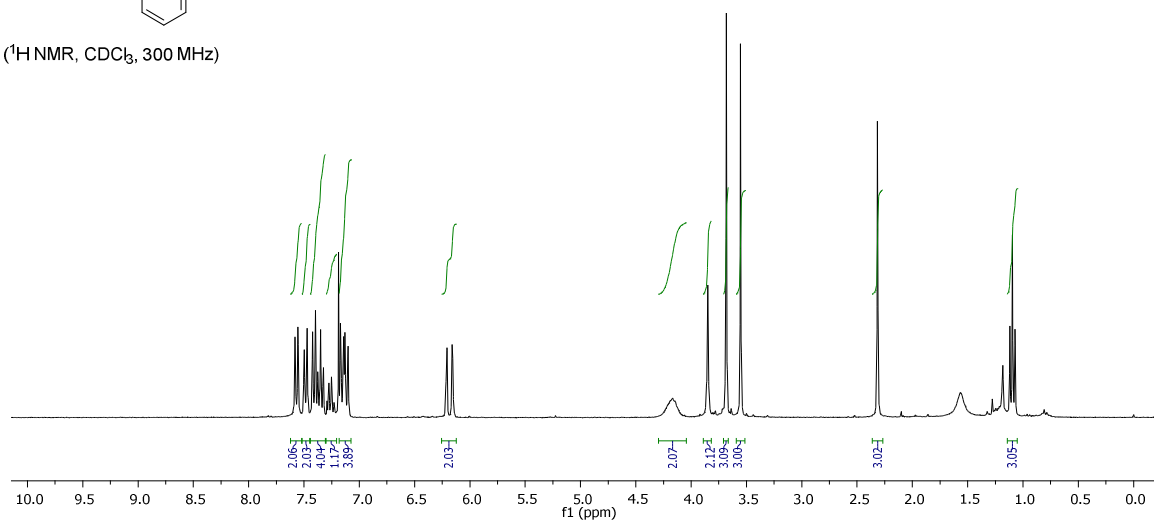
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



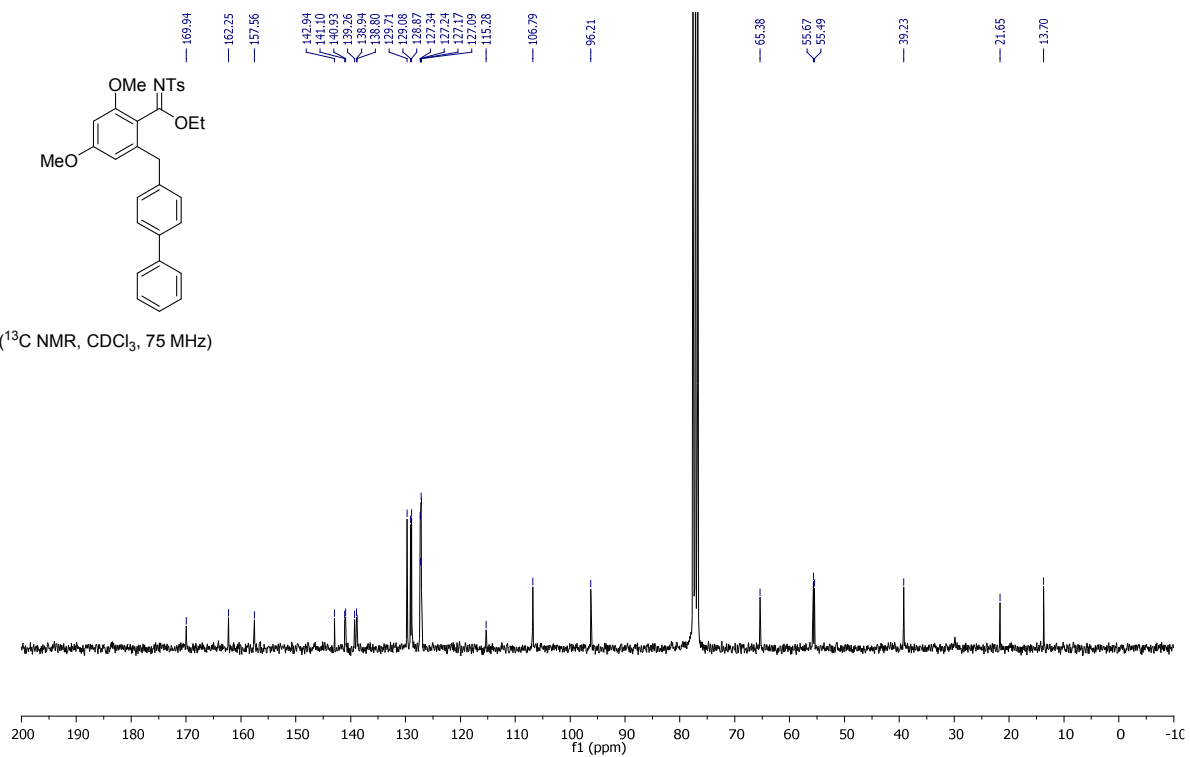
**Ethyl (Z)-2-([1,1'-biphenyl]-4-ylmethyl)-4,6-dimethoxy-*N*-tosylbenzimidate (3p):**



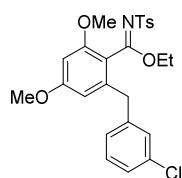
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)



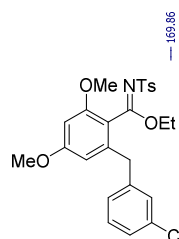
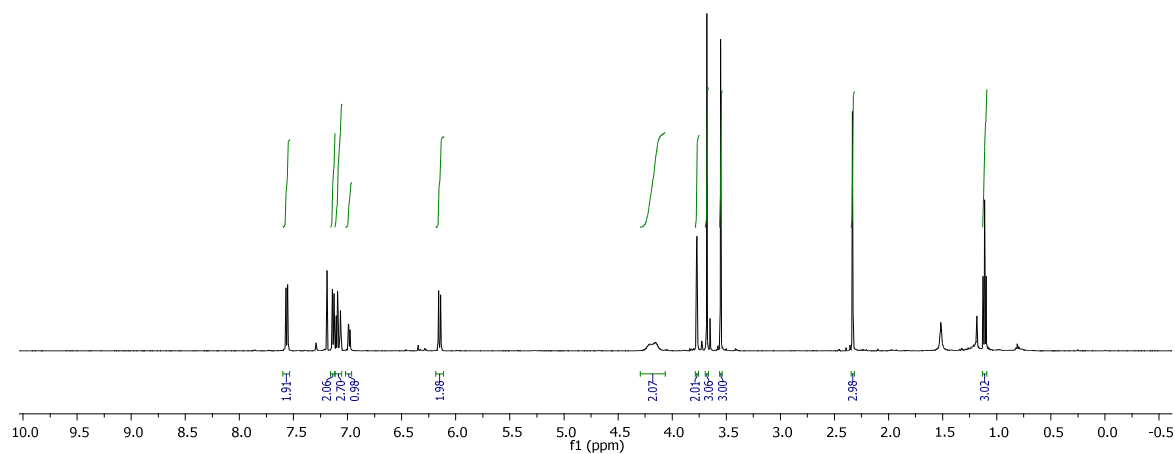
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz)



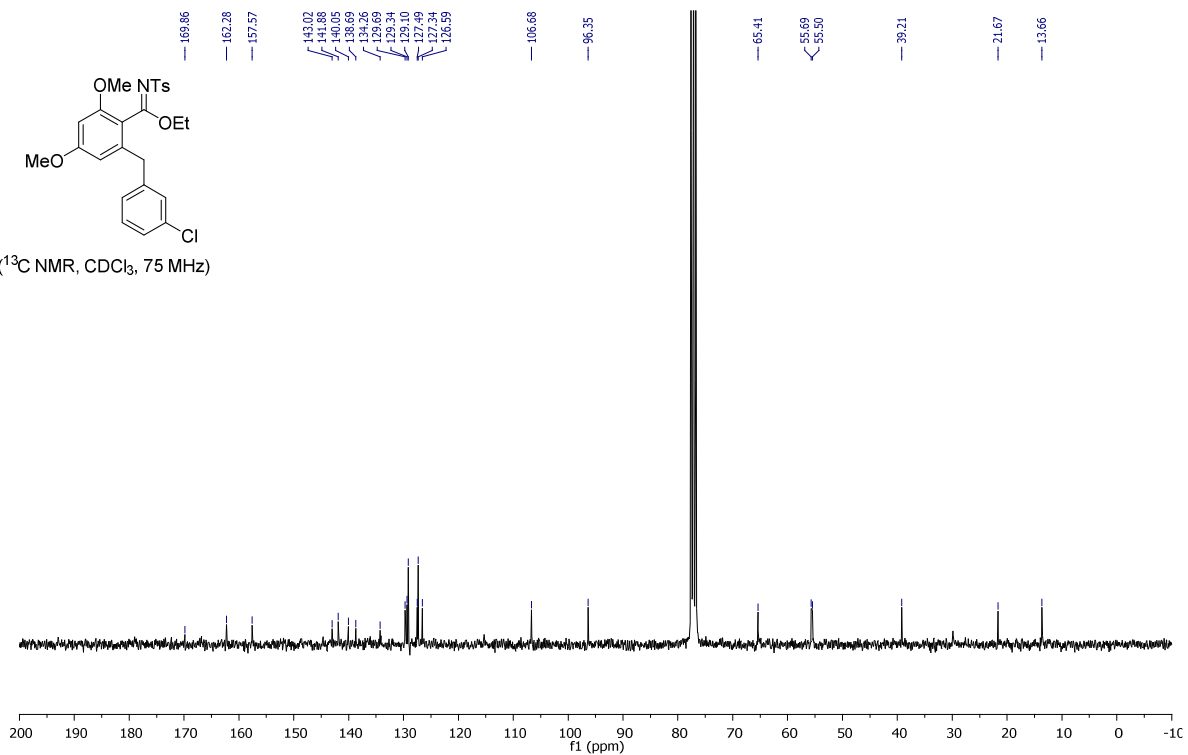
**Ethyl (Z)-2-(3-chlorobenzyl)-4,6-dimethoxy-N-tosylbenzimidate (3q):**



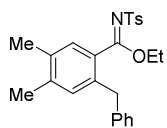
( $^1\text{H}$  NMR,  $\text{CDCl}_3$ , 500 MHz)



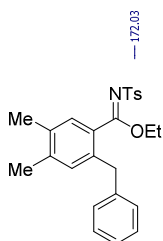
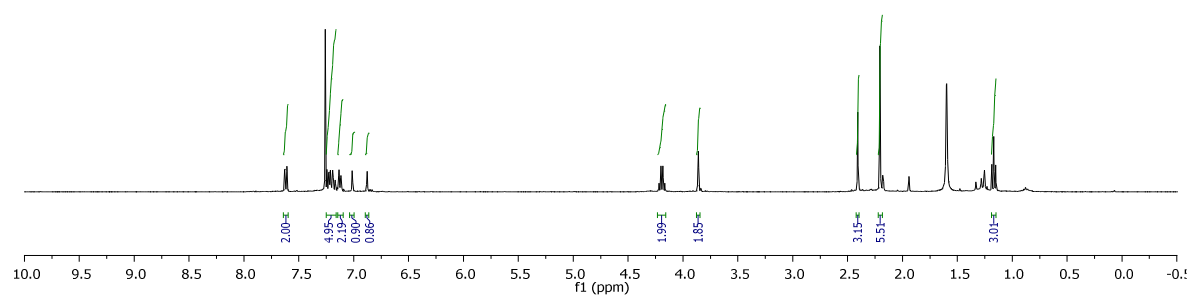
( $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 75 MHz)



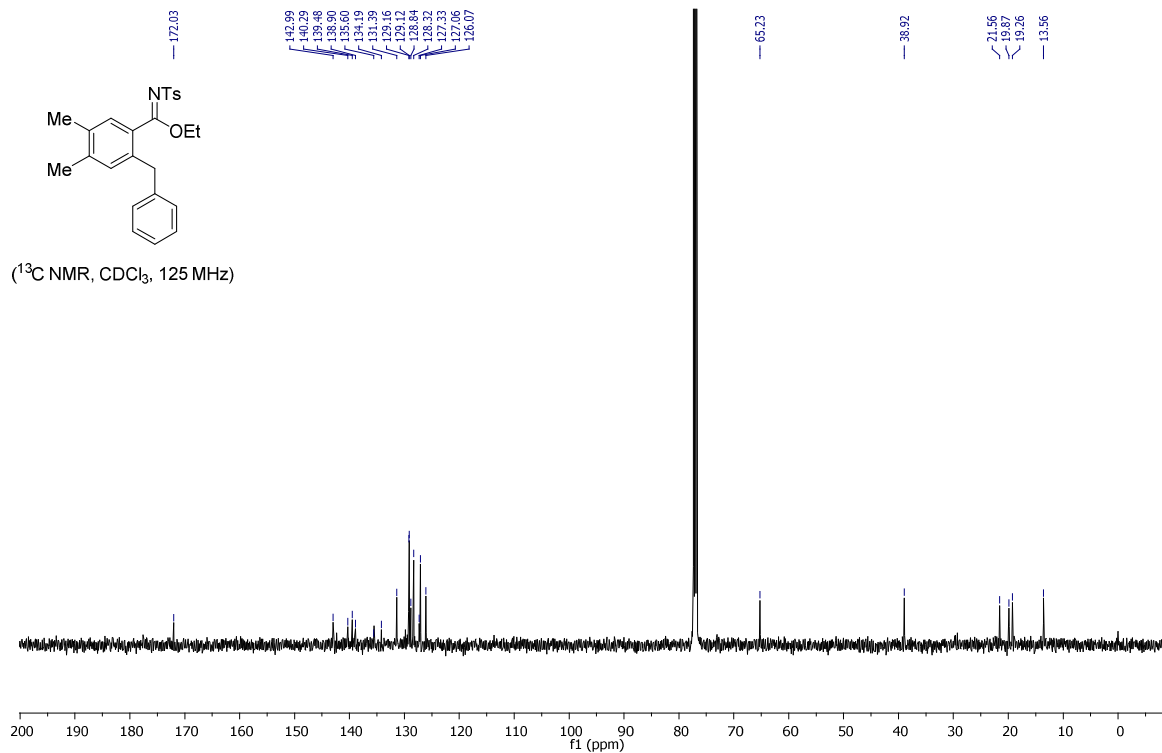
**Ethyl (Z)-2-benzyl-4,5-dimethyl-N-tosylbenzimidate (3r):**



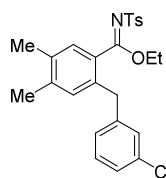
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



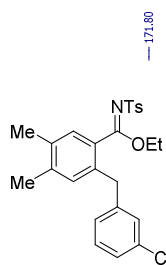
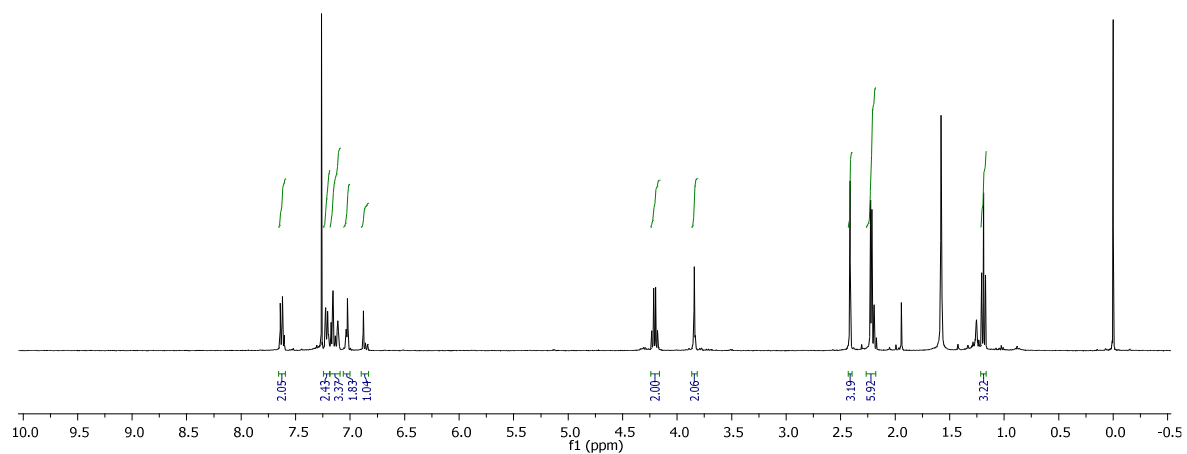
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 125 MHz)



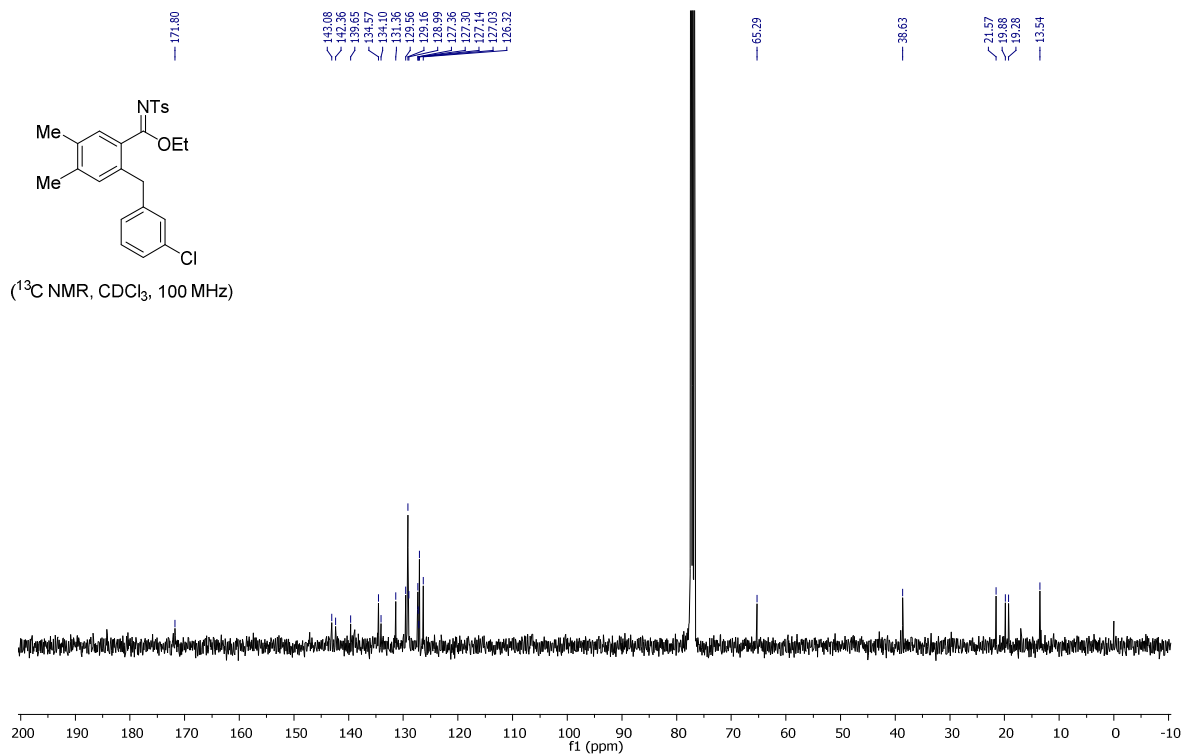
**Ethyl (Z)-2-(3-chlorobenzyl)-4,5-dimethyl-N-tosylbenzimidate (3s):**



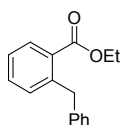
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



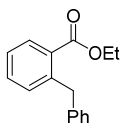
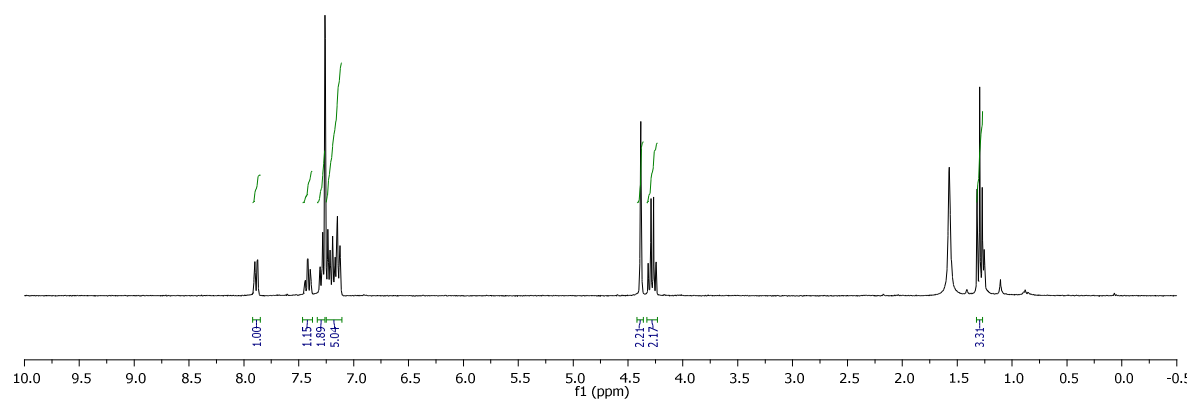
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 100 MHz)



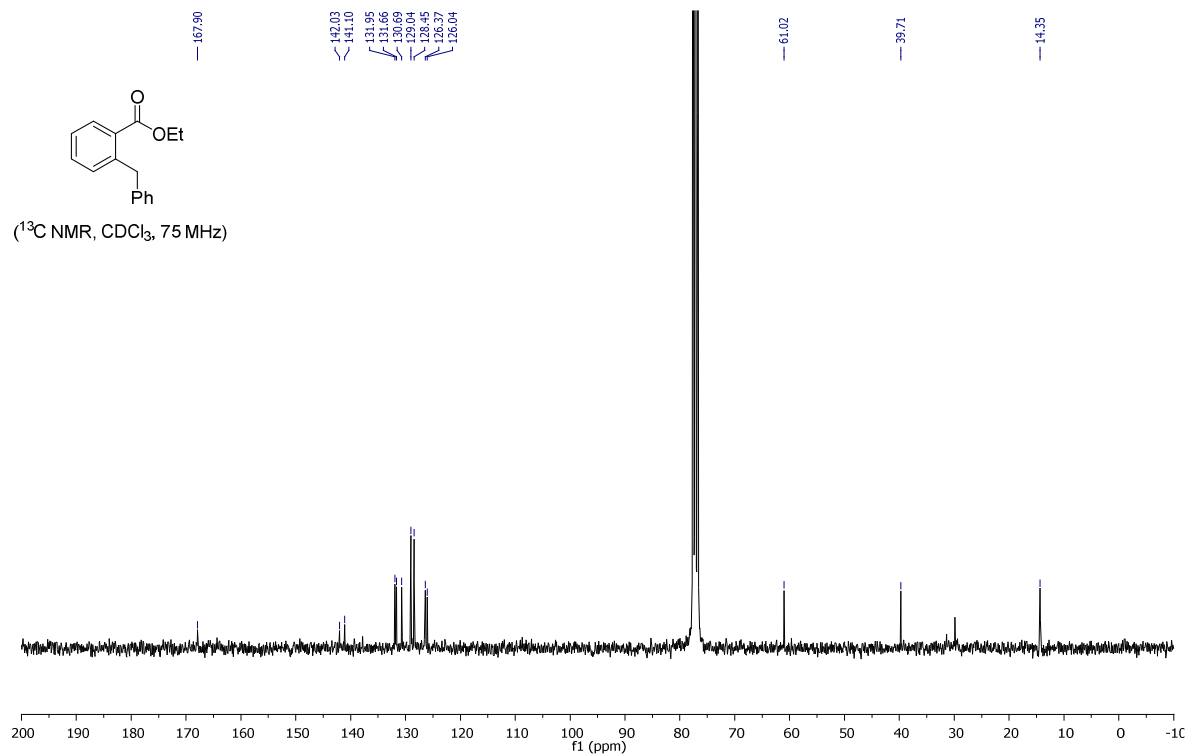
# **Ethyl 2-benzylbenzoate (4):**



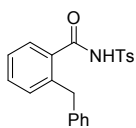
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)



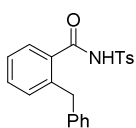
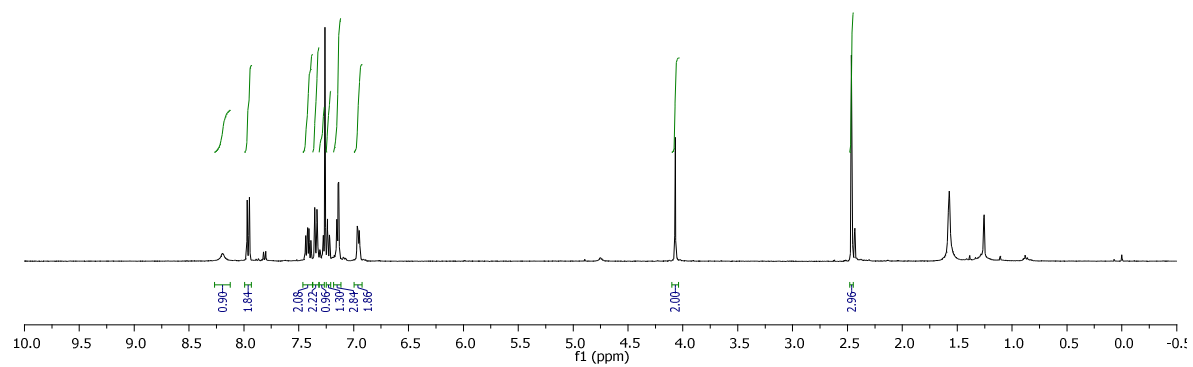
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz)



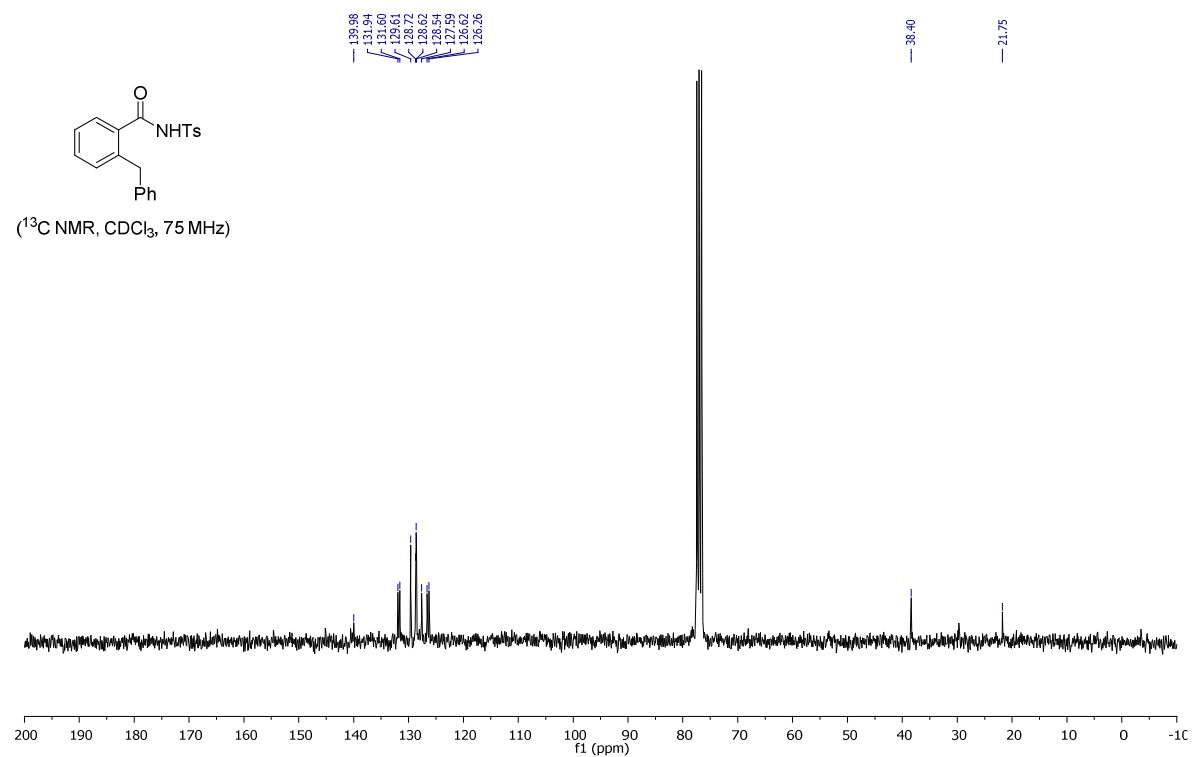
## 2-Benzyl-*N*-tosylbenzamide (5):



( $^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz)

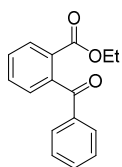


( $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 75 MHz)

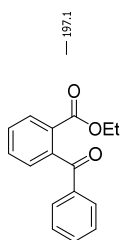
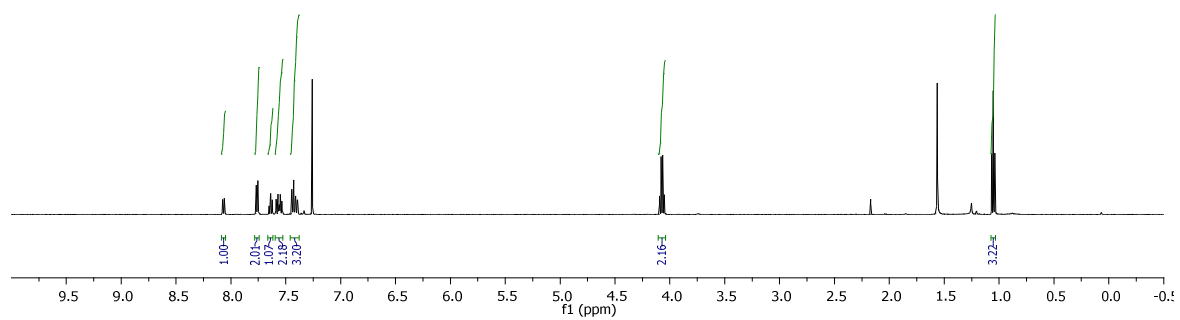




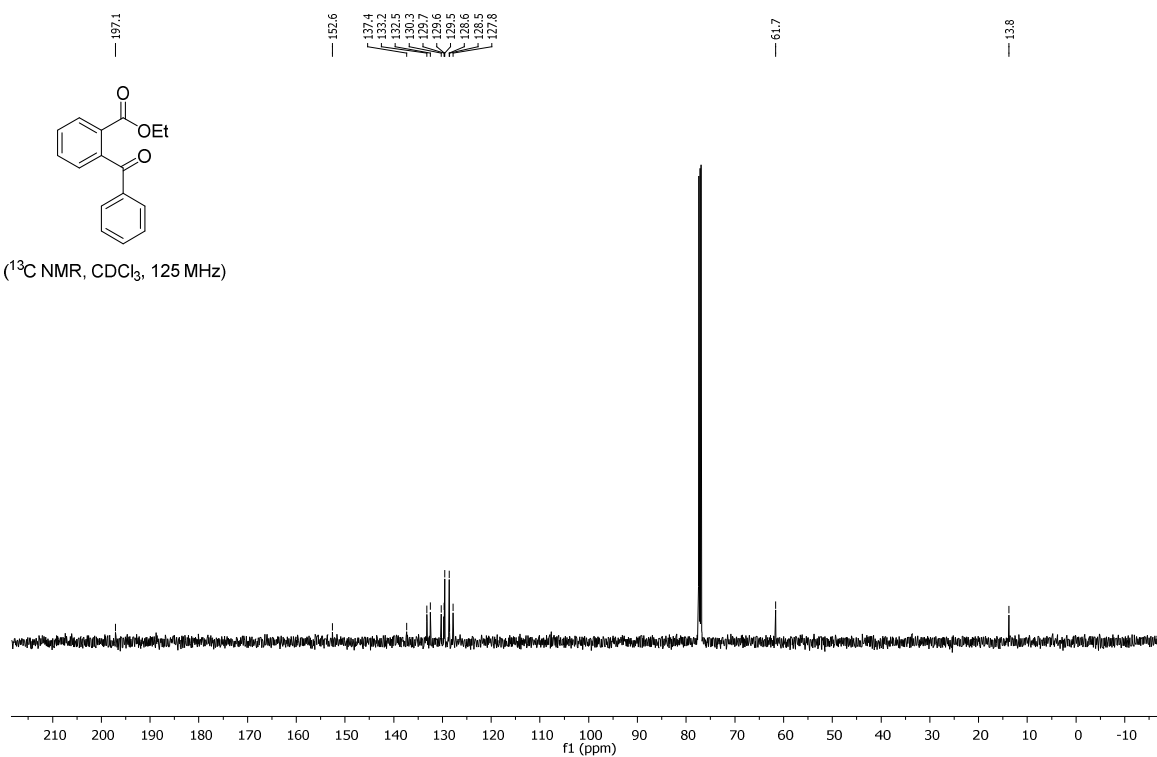
# **Ethyl 2-benzoylbenzoate (6):**



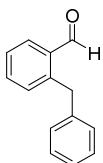
( $^1\text{H}$  NMR,  $\text{CDCl}_3$ , 500 MHz)



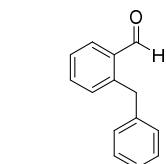
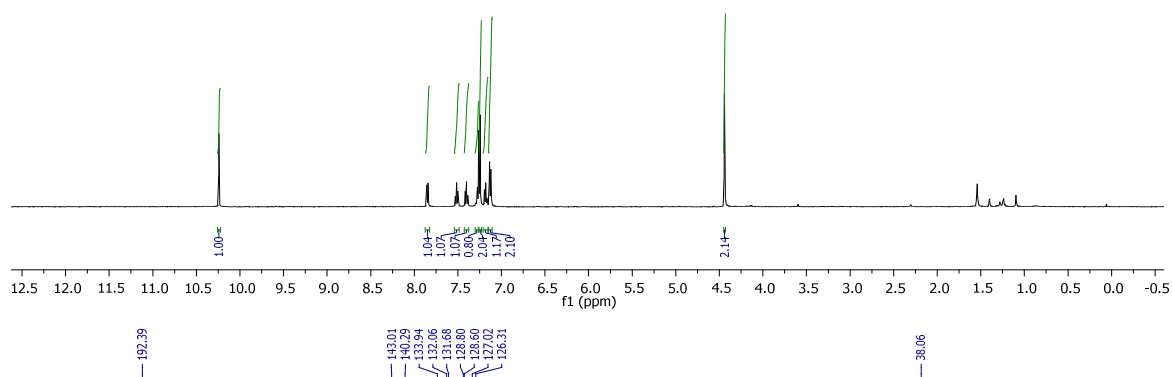
( $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 125 MHz)



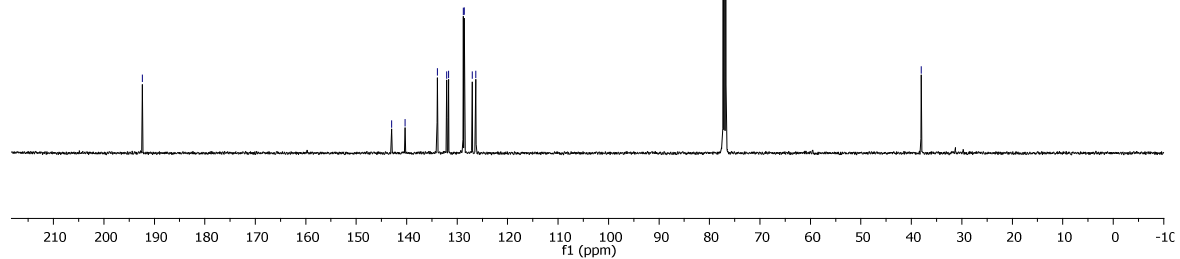
## 2-Benzylbenzaldehyde (7):



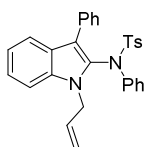
( $^1\text{H}$  NMR,  $\text{CDCl}_3$ , 500 MHz)



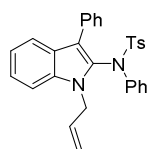
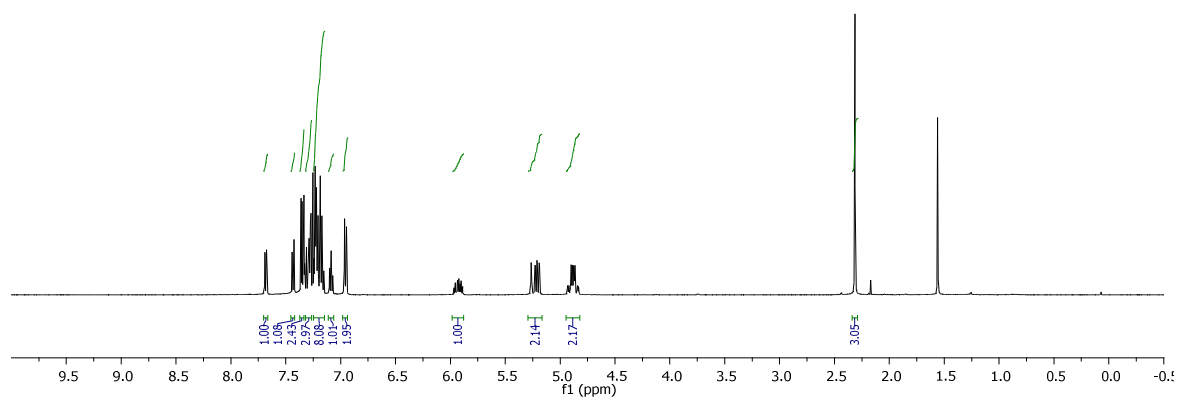
( $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 125 MHz)



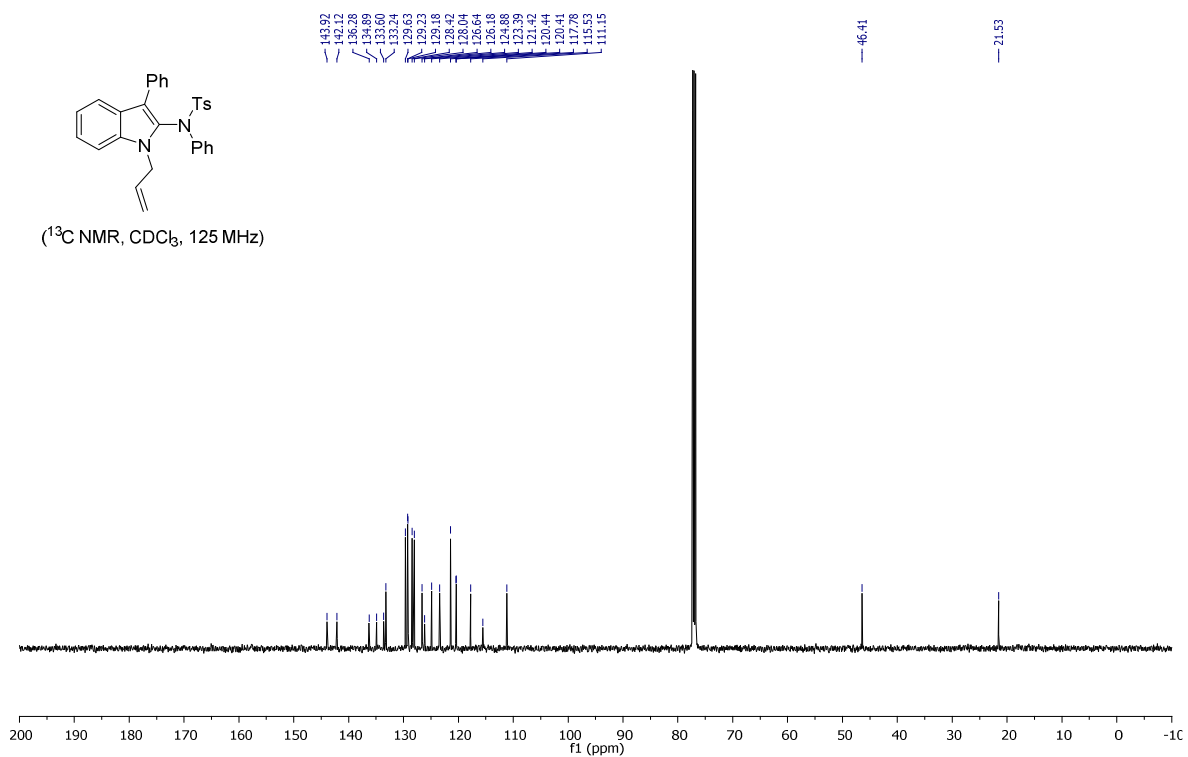
***N*-(1-Allyl-3-phenyl-1*H*-indol-2-yl)-4-methyl-*N*-phenylbenzenesulfonamide (9a):**



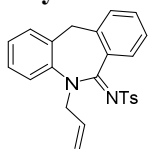
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



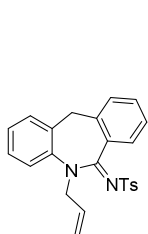
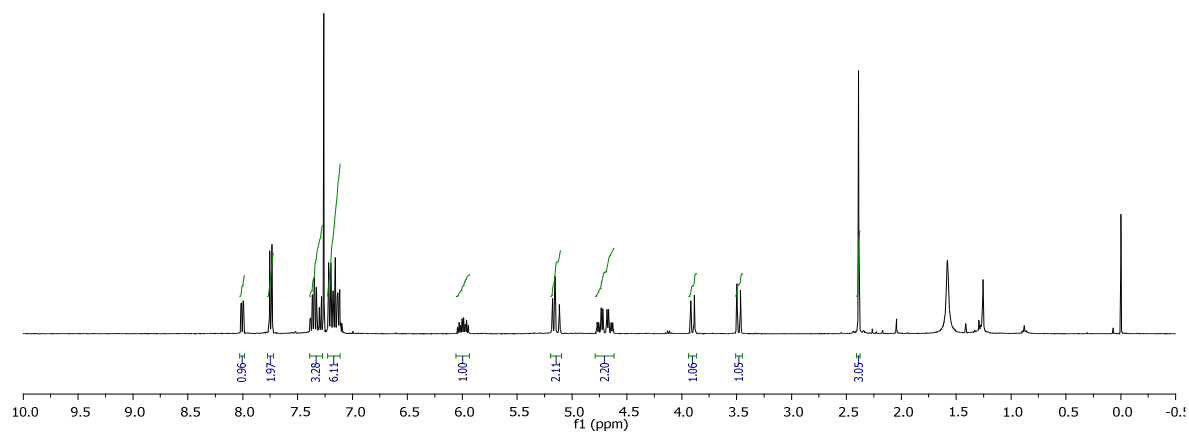
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 125 MHz)



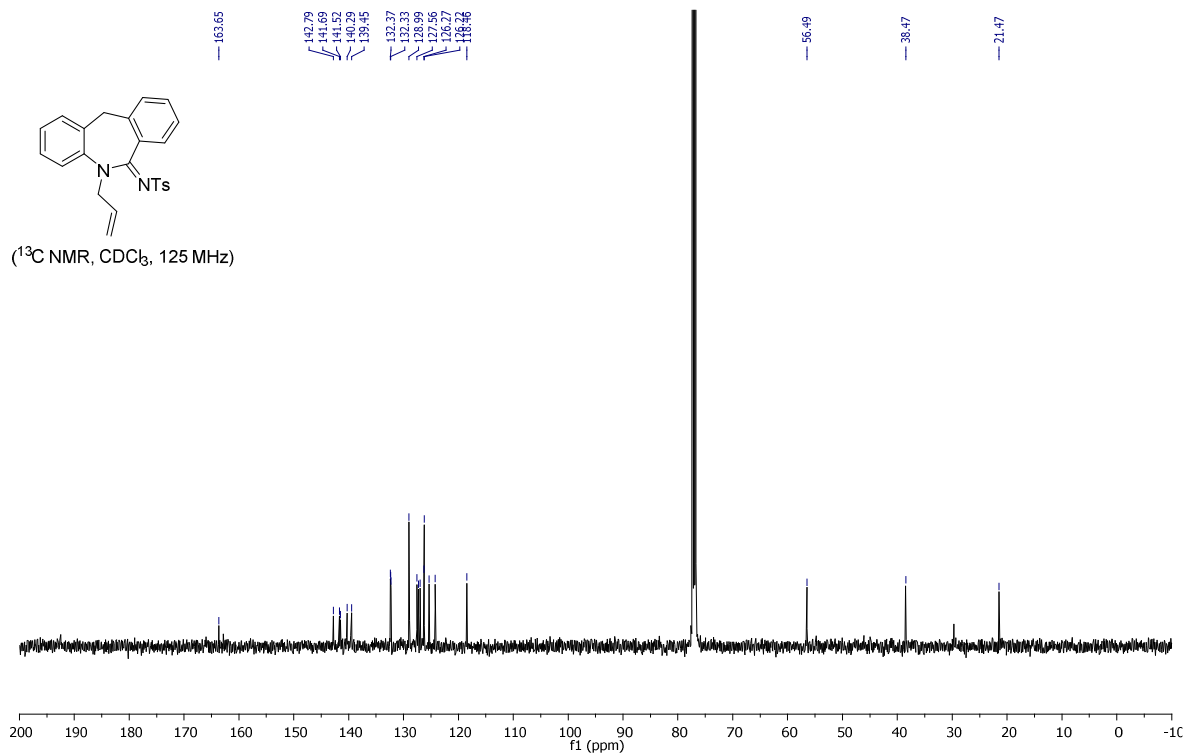
**(Z)-N-(5-Allyl-5,11-dihydro-6H-dibenzo[b,e]azepin-6-ylidene)-4-methylbenzenesulfonamide (10a):**



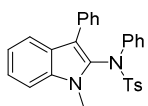
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



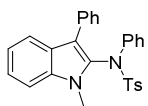
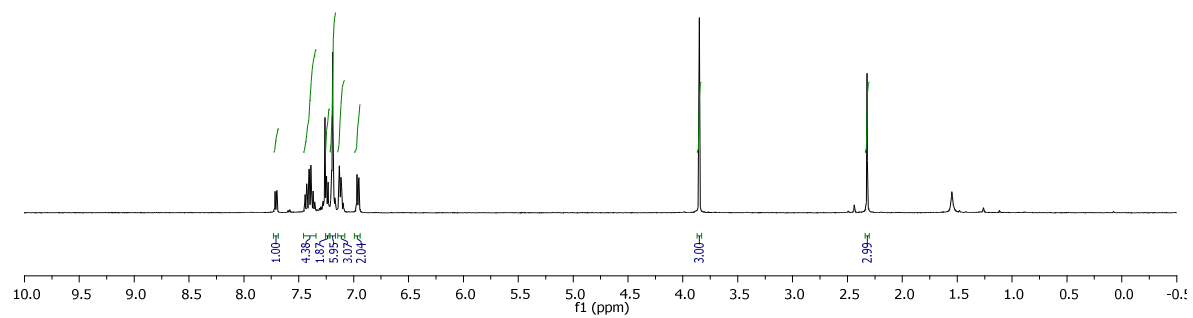
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 125 MHz)



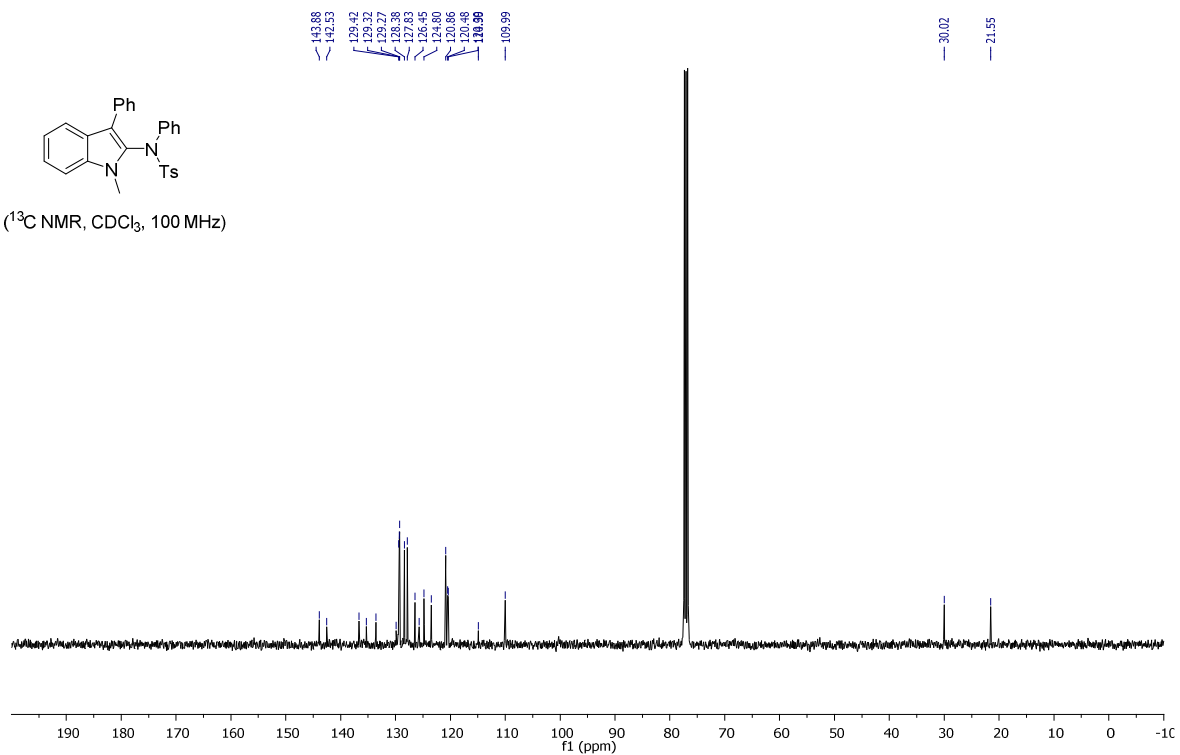
**4-Methyl-*N*-(1-methyl-3-phenyl-1H-indol-2-yl)-*N*-phenylbenzenesulfonamide (9b):**



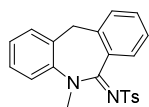
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



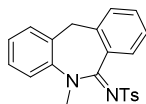
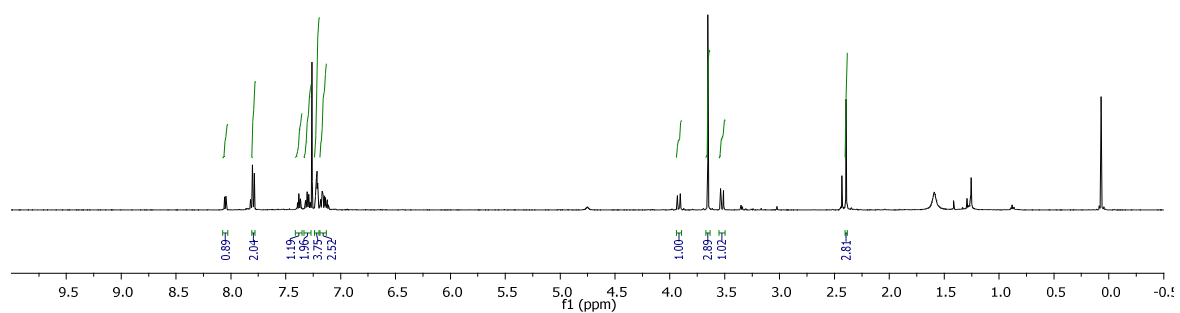
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 100 MHz)



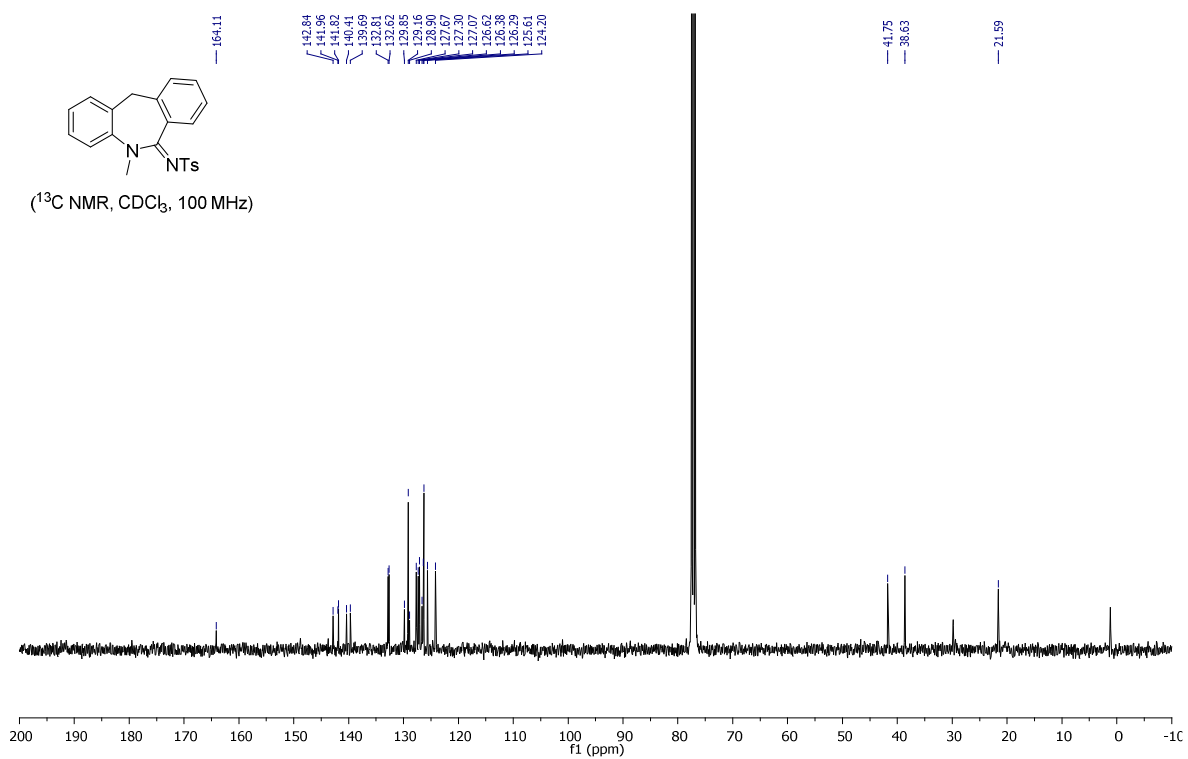
**(Z)-4-methyl-N-(5-methyl-5,11-dihydro-6H-dibenzo[b,e]azepin-6-ylidene)benzenesulfonamide (10b):**



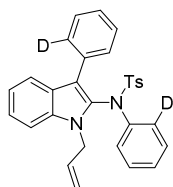
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



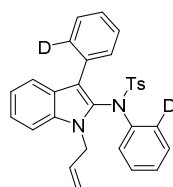
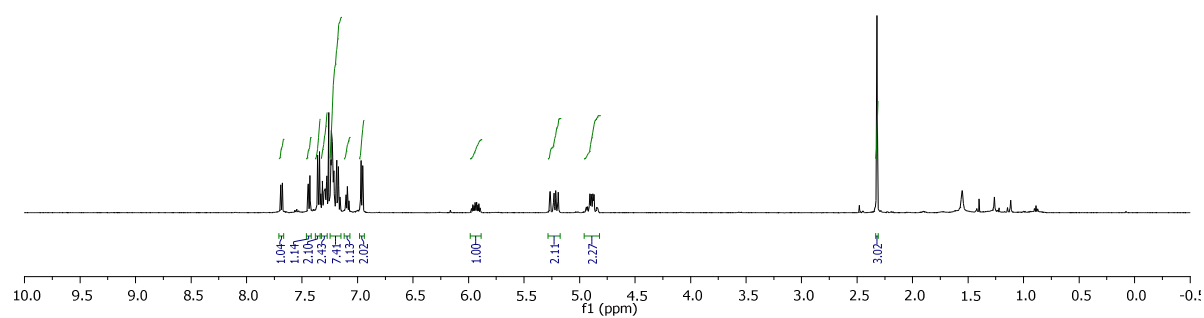
(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 100 MHz)



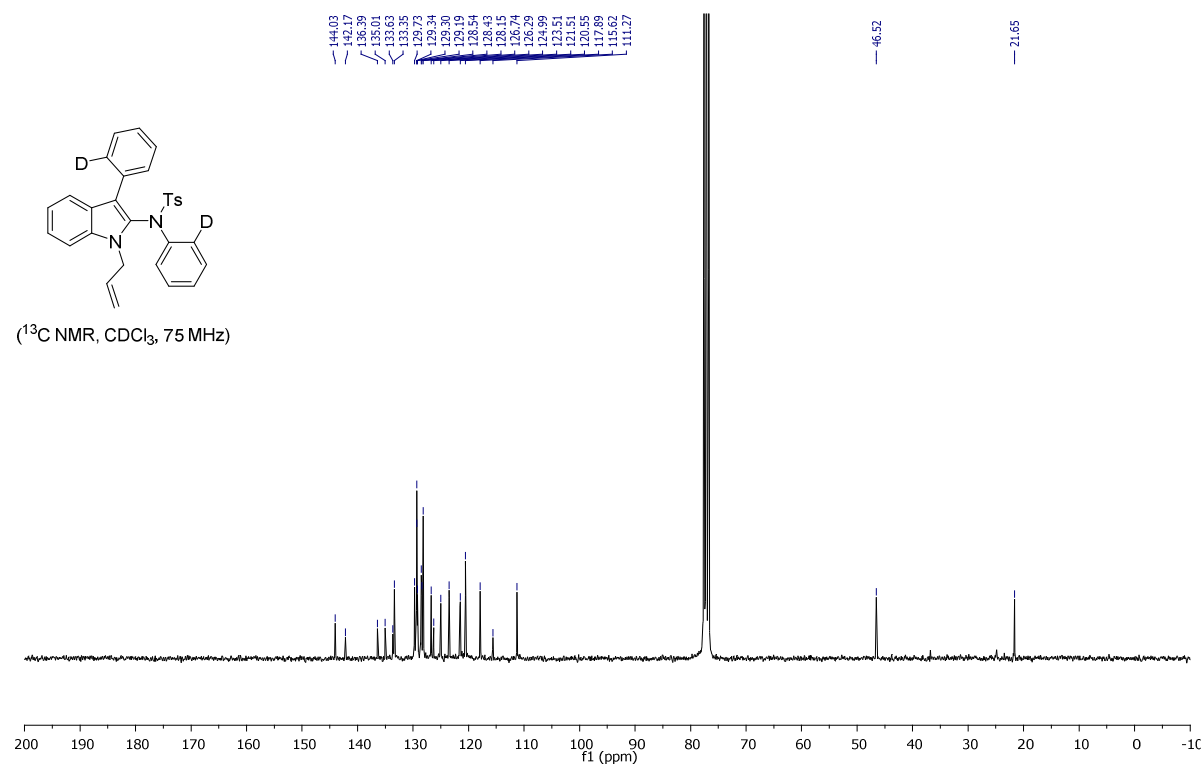
**N-(1-allyl-3-(phenyl-2-d)-1H-indol-2-yl)-4-methyl-N-(phenyl-2-d)benzenesulfonamide (11):**



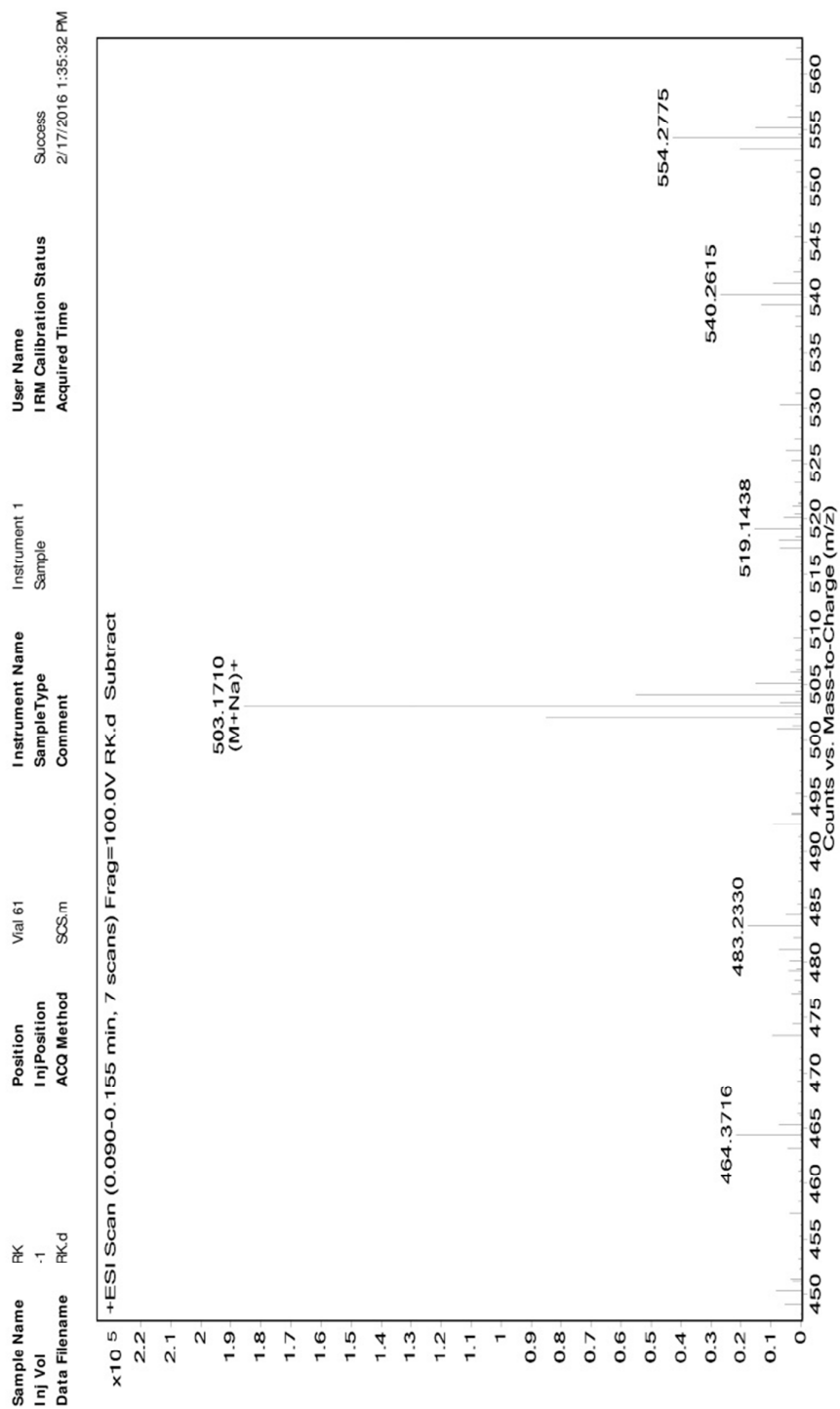
(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz)



(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz)

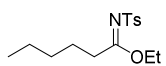


# HRMS Spectrum for compound 11:

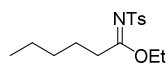
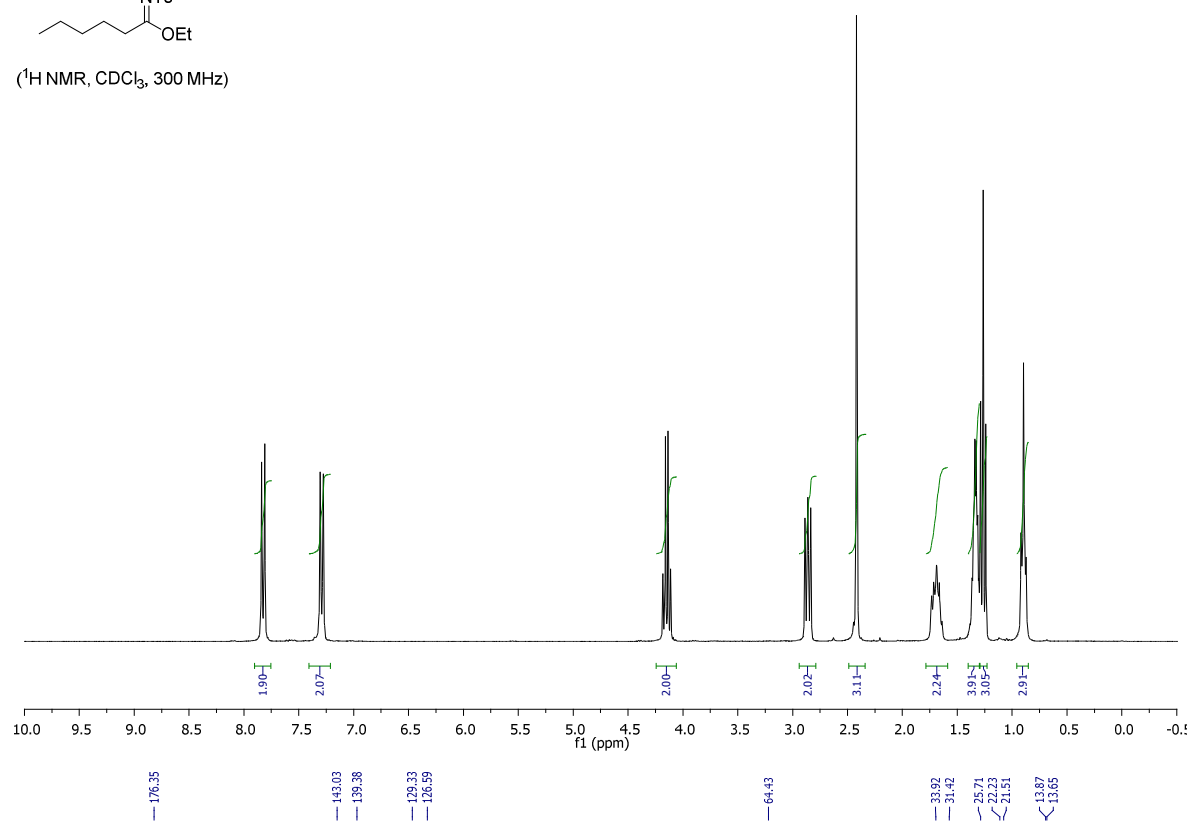




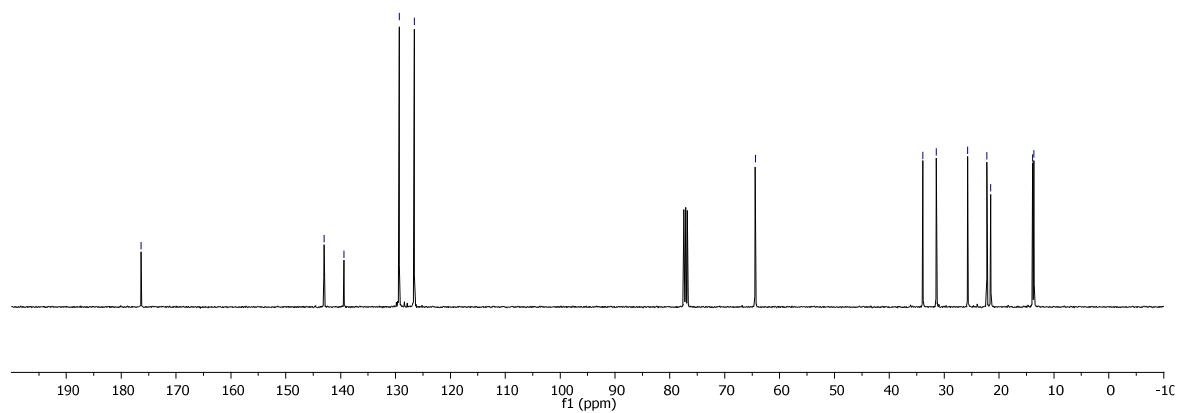
# **Ethyl (Z)-N-tosylhexanimidate (S1):**



(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 300 MHz)



(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 100 MHz)





### 3. X-ray crystallographic data

X-ray data for the compounds (BB44 and BB45) were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ) with  $\omega$ -scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data was accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms with  $U_{\text{iso}}(\text{H})\ 1.2U_{\text{eq}}(\text{C})$ . The atom C30 of BB44 shows high thermal parameter hence it was restrained with SIMU and DFIX commands (SHELXL, [2]).

#### a. Compound 3q (BB45):

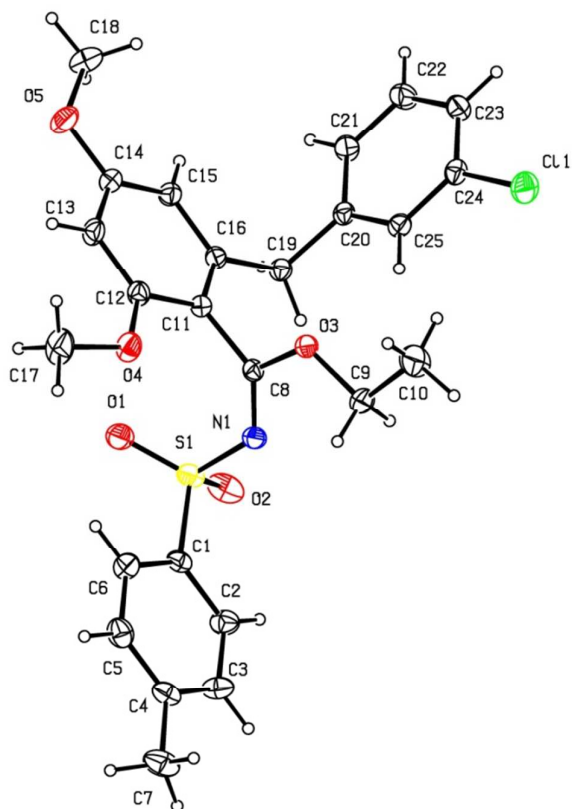
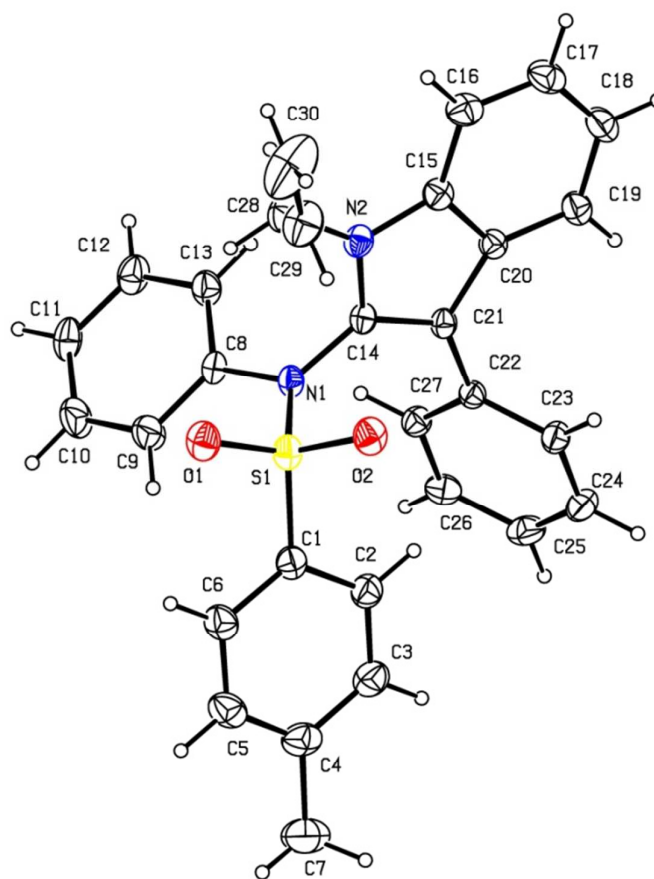


Figure 1. ORTEP of compound 3q

Figure 1. A view of BB45, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

**Crystal Data for BB45:**  $C_{25}H_{26}NO_5SCl$  ( $M=487.98$ ): monoclinic, space group  $P2_1/c$  (no. 14),  $a = 17.7060(4)$  Å,  $b = 14.3230(6)$  Å,  $c = 9.7000(8)$  Å,  $\beta = 104.923(2)^\circ$ ,  $V = 2377.0(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 294.15$  K,  $\mu(\text{MoK}\alpha) = 0.285$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.364$  g/mm<sup>3</sup>, 26482 reflections measured ( $2.38 \leq 2\theta \leq 56.65$ ), 5704 unique ( $R_{\text{int}} = 0.0289$ ) which were used in all calculations. The final  $R_1$  was 0.0552 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1463 (all data). CCDC 1435198 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

**b. Compound 9a (BB44):**



**Figure 2. ORTEP of compound 9a**

Figure 2. A view of BB44, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii

**Crystal Data for BB44:**  $C_{30}H_{26}N_2O_2S$  ( $M=478.59$ ): triclinic, space group P-1 (no. 2),  $a = 10.1720(5)$  Å,  $b = 10.4620(5)$  Å,  $c = 12.8780(6)$  Å,  $\alpha = 68.8240(10)^\circ$ ,  $\beta = 83.9450(10)^\circ$ ,  $\gamma = 83.7910(10)^\circ$ ,  $V = 1267.17(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 294.15$  K,  $\mu(\text{MoK}\alpha) = 0.157$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.254$  g/mm<sup>3</sup>, 14981 reflections measured ( $3.4 \leq 2\Theta \leq 56.554$ ), 5952 unique ( $R_{\text{int}} = 0.0199$ ) which were used in all calculations. The final  $R_1$  was 0.0504 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1424 (all data). CCDC 1435197 contains supplementary Crystallographic data for the structure.

1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.