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Supplementary Information

Multiple-Functionalizations of Terminal Alkynes with Sodium Sulfinates and *tert*-Butyl Nitrite: Facile Synthesis of 2*H*-Azirines

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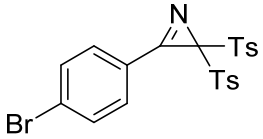
(A) General Experimental Procedures

(a) General Procedures for the Tandem Annulation of Terminal Alkynes (1) with Sodium Sulfinates (2) and *tert*-Butyl Nitrite: Facile Synthesis of 2*H*-Azirines (3):

To a Schlenk tube were added alkyne **1** (0.2 mmol), sodium sulfinate **2** (3 equiv), *t*-BuONO (3 equiv), and DCE (2 mL). Then the mixture was stirred at 50 °C (oil bath temperature) under argon atmosphere (1 atm) for 8 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 8 : 1) to afford the desired product **3**.

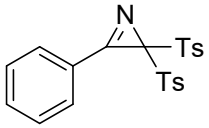
(B) Analytical data

3-(4-Bromophenyl)-2,2-ditosyl-2*H*-azirine (3aa):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73 (d, J = 4.0 Hz, 4H), 7.70 (d, J = 8.0 Hz, 4H), 7.29 (d, J = 8.0 Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.3, 146.0, 134.6, 133.2, 133.1, 131.6, 129.6, 129.5, 117.7, 69.7, 21.8; HRMS *m/z* (ESI) calcd for $C_{22}H_{19}{}^{79}BrNO_4S_2$ $(M+H)^+$ 503.9933, found 503.9941.

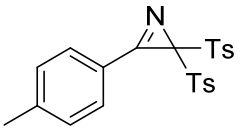
3-Phenyl-2,2-ditosyl-2*H*-azirine (3ba):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (d, J = 7.5 Hz, 2H), 7.73 (t, J = 8.0 Hz, 1H), 7.72 (d, J = 8.5 Hz, 4H), 7.59 (t, J

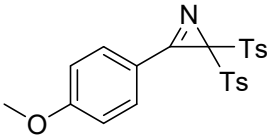
= 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 158.7, 145.8, 135.8, 134.8, 132.1, 129.6 (3C), 118.8, 69.7, 21.8; HRMS *m/z* (ESI) calcd for $C_{22}H_{20}NO_4S_2$ $(M+H)^+$ 426.0828, found 426.0836.

3-(*p*-Tolyl)-2,2-ditosyl-2*H*-azirine (3ca):



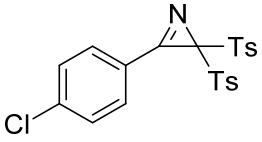
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.75 (d, *J* = 8.0Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 4H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 4H), 2.49 (s, 3H), 2.46 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 158.2, 147.6, 145.7, 134.9, 132.2, 130.4, 129.5 (2C), 115.9, 69.7, 22.2, 21.8; HRMS *m/z* (ESI) calcd for $C_{23}H_{22}NO_4S_2$ $(M+H)^+$ 440.0985, found 440.1001.

3-(4-Methoxyphenyl)-2,2-ditosyl-2*H*-azirine (3da):



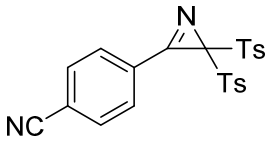
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.81 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 7.5 Hz, 2H), 3.92 (s, 3H), 2.46 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 165.6, 157.0, 145.6, 135.0, 134.5, 129.5 (2C), 115.3, 110.7, 69.8, 55.9, 21.8; HRMS *m/z* (ESI) calcd for $C_{23}H_{22}NO_5S_2$ $(M+H)^+$ 456.0934, found 456.0945.

3-(4-Chlorophenyl)-2,2-ditosyl-2*H*-azirine (3ea):



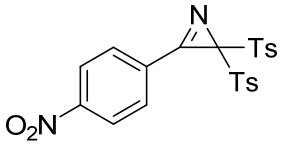
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.81 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 4H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 158.1, 146.0, 142.7, 134.6, 133.2, 130.2, 129.6, 129.5, 117.27, 69.73, 21.77; HRMS *m/z* (ESI) calcd for $C_{22}H_{19}{}^{35}ClNO_4S_2$ $(M+H)^+$ 460.0439, found 460.0445.

4-(2,2-Ditosyl-2*H*-azirin-3-yl)benzonitrile (3fa):



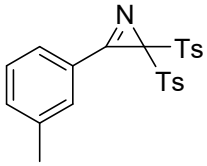
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.0 Hz, 4H), 7.30 (d, J = 8.0 Hz, 4H), 2.47 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.7, 146.2, 134.2, 133.2, 132.2, 129.7, 129.5, 122.9, 118.9, 117.1, 69.8, 21.8; HRMS *m/z* (ESI) calcd for $C_{23}H_{19}N_2O_4S_2$ $(M+H)^+$ 451.0781, found 451.0792.

3-(4-Nitrophenyl)-2,2-ditosyl-2*H*-azirine (3ga):



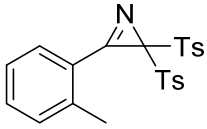
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.44 (d, J = 8.5 Hz, 2H), 8.10 (d, J = 9.0 Hz, 2H), 7.68 (d, J = 8.5 Hz, 4H), 7.31 (d, J = 8.0 Hz, 4H), 2.49 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.7, 151.6, 146.3, 134.2, 133.0, 129.8, 129.6, 124.7, 124.5, 69.9, 21.8; HRMS *m/z* (ESI) calcd for $C_{22}H_{19}N_2O_6S_2$ $(M+H)^+$ 471.0679, found 471.0693.

3-(*m*-Tolyl)-2,2-ditosyl-2*H*-azirine (3ha):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72 (d, J = 8.0 Hz, 4H), 7.69 (d, J = 7.5 Hz, 1H), 7.57 (s, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 8.5 Hz, 4H), 2.46 (s, 6H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.6, 145.7, 139.7, 136.7, 134.9, 132.5, 129.6 (2C), 129.5, 129.3, 118.5, 69.7, 21.8, 21.1; HRMS *m/z* (ESI) calcd for $C_{23}H_{22}NO_4S_2$ $(M+H)^+$ 440.0985, found 440.0994.

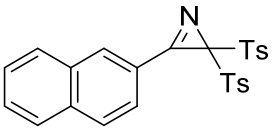
3-(*o*-Tolyl)-2,2-ditosyl-2*H*-azirine (3ia):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69 (d, J = 8.0 Hz, 4H), 7.60 (t, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.35 (t, J

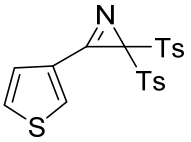
= 7.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 4H), 2.76 (s, 3H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 145.7, 143.6, 135.5, 134.8, 134.4, 131.2, 129.5, 126.7, 117.9, 68.0, 21.8, 20.3; HRMS *m/z* (ESI) calcd for $C_{23}H_{22}NO_4S_2$ $(M+H)^+$ 440.0985, found 440.0991.

3-(Naphthalen-2-yl)-2,2-ditosyl-2*H*-azirine (3ja):



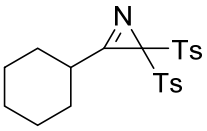
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 4H), 7.72 (t, *J* = 7.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.8, 145.9, 136.6, 135.8, 135.1, 132.5, 130.4, 129.8, 129.7 (2C), 129.6, 128.3, 127.8, 125.2, 115.9, 70.02, 21.83; HRMS *m/z* (ESI) calcd for $C_{26}H_{22}NO_4S_2$ $(M+H)^+$ 476.0985, found 476.0998.

3-(Thiophen-3-yl)-2,2-ditosyl-2*H*-azirine (3ka):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 4.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 4H), 7.70 (d, *J* = 3.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 4H), 7.28 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.7, 145.9, 139.4, 139.2, 134.7, 129.6 (2C), 129.3, 120.2, 70.2, 21.8; HRMS *m/z* (ESI) calcd for $C_{20}H_{18}NO_4S_3$ $(M+H)^+$ 432.0393, found 432.0395.

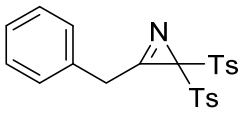
3-Cyclohexyl-2,2-ditosyl-2*H*-azirine (3la):



White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 3.12-3.07 (m, 1H), 2.44 (s, 6H), 2.18-2.13 (m, 2H), 1.90-1.86 (m, 2H), 1.75-1.67 (m, 4H), 1.47-1.34 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.0, 145.5, 134.5, 129.4, 129.2, 69.1, 35.7, 28.3, 25.3,

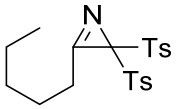
24.9, 21.7; HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_4S_2$ $(M+H)^+$ 432.1298, found 432.1305.

3-Benzyl-2,2-ditosyl-2*H*-azirine (3ma):



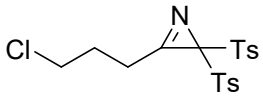
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, J = 8.5 Hz, 4H), 7.40 (s, 5H), 7.23 (d, J = 8.0 Hz, 4H), 4.38 (s, 2H), 2.44 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.5, 145.8, 134.5, 130.1, 129.6, 129.4 (2C), 129.3, 128.4, 69.0, 32.8, 21.8; HRMS *m/z* (ESI) calcd for $C_{23}H_{22}NO_4S_2$ $(M+H)^+$ 440.0985, found 440.0997.

3-Pentyl-2,2-ditosyl-2*H*-azirine (3na):



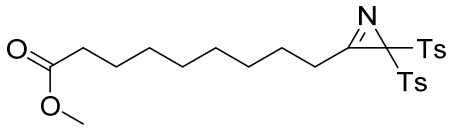
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, J = 8.5 Hz, 4H), 7.27 (d, J = 8.0 Hz, 4H), 3.01 (t, J = 7.5 Hz, 2H), 2.45 (s, 6H), 1.91-1.85 (m, 2H), 1.52-1.45 (m, 2H), 1.42-1.36 (m, 2H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.9, 145.7, 134.6, 129.6, 129.3, 68.4, 30.9, 26.2, 24.0, 22.1, 21.7, 13.8; HRMS *m/z* (ESI) calcd for $C_{21}H_{26}NO_4S_2$ $(M+H)^+$ 420.1298, found 420.1309.

3-(3-Chloropropyl)-2,2-ditosyl-2*H*-azirine (3oa):



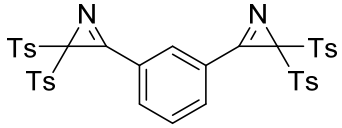
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, J = 8.0 Hz, 4H), 7.28 (d, J = 8.0 Hz, 4H), 3.73 (t, J = 6.0 Hz, 2H), 3.25 (t, J = 7.5 Hz, 2H), 2.46 (s, 6H), 2.38-2.33 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.4, 145.9, 134.4, 129.7, 129.3, 68.3, 43.0, 27.3, 23.5, 21.8; HRMS *m/z* (ESI) calcd for $C_{19}H_{21}{}^{35}ClNO_4S_2$ $(M+H)^+$ 426.0595, found 426.0603.

Methyl 9-(2,2-ditosyl-2*H*-azirin-3-yl)nonanoate (3pa):



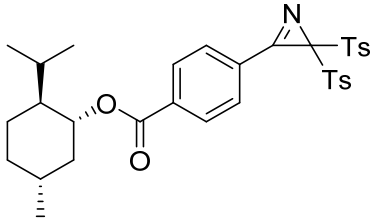
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62 (d, J = 8.5 Hz, 4H), 7.27 (d, J = 8.0 Hz, 4H), 3.67 (s, 3H), 3.02 (t, J = 7.5 Hz, 2H), 2.45 (s, 6H), 2.32 (t, J = 7.5 Hz, 2H), 1.90-1.84 (m, 2H), 1.66-1.61 (m, 4H), 1.53-1.47 (m, 2H), 1.37-1.33 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.3, 163.8, 145.7, 134.6, 129.6, 129.3, 68.4, 51.5, 34.0, 29.0, 28.9, 28.8, 28.7, 26.2, 24.8, 24.3, 21.7; HRMS *m/z* (ESI) calcd for $C_{26}H_{34}NO_6S_2$ $(M+H)^+$ 520.1822, found 520.1825.

1,3-Bis(2,2-ditosyl-2*H*-azirin-3-yl)benzene (3qa):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.21-8.20 (m, 3H), 7.87 (t, J = 8.0 Hz, 1H), 7.73 (d, J = 8.5 Hz, 8H), 7.34 (d, J = 8.0 Hz, 8H), 2.48 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.4, 146.4, 138.1, 134.3, 133.7, 131.3, 129.9, 129.6, 121.0, 69.9, 21.8; HRMS *m/z* (ESI) calcd for $C_{38}H_{33}N_2O_8S_4$ $(M+H)^+$ 773.1114, found 773.1129.

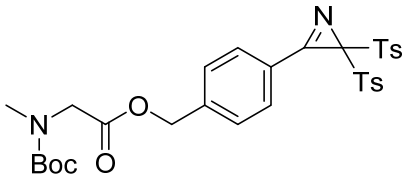
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-(2,2-ditosyl-2*H*-azirin-3-yl)benzoat e (3ra):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.23 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.0 Hz, 4H), 7.30 (d, J = 8.5 Hz, 4H), 5.01-4.96 (m, 1H), 2.47 (s, 6H), 2.16-2.12 (m, 1H), 1.96-1.90 (m, 1H), 1.78-1.73 (m, 2H), 1.62-1.56 (m, 5H), 1.19-1.12 (m, 2H), 0.96-0.93 (m, 7H), 0.81 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.3, 158.8, 146.0, 137.0, 134.6, 134.5, 131.9, 130.5, 129.7,

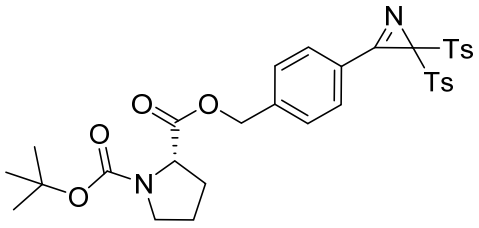
129.5, 122.3, 76.1, 69.7, 47.1, 40.8, 34.1, 31.4, 26.6, 23.6, 22.0, 21.8, 20.7, 16.5; HRMS *m/z* (ESI) calcd for $C_{33}H_{38}NO_6S_2$ $(M+H)^+$ 608.2135, found 608.2142.

4-(2,2-Ditosyl-2*H*-azirin-3-yl)benzyl-*N*-(tert-butoxycarbonyl)-*N*-methylglycinate (3sa):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.5 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.29 (s, 1H), 5.28 (s, 1H), 4.08 (s, 1H), 4.00 (s, 1H), 2.97 (s, 1.33H), 2.96 (s, 1.67H), 2.47 (s, 6H), 1.49 (s, 5H), 1.40 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.6, 158.4, 156.1, 155.3, 145.9, 144.1, 143.9, 134.7, 134.6, 132.3, 132.3, 129.6, 129.5 (2C), 128.7, 128.6, 118.7, 118.5, 80.4, 69.7, 65.4, 51.0, 50.4, 35.7, 35.6, 28.3, 28.2, 21.8; HRMS *m/z* (ESI) calcd for $C_{31}H_{35}N_2O_8S_2$ $(M+H)^+$ 627.1829, found 627.1837.

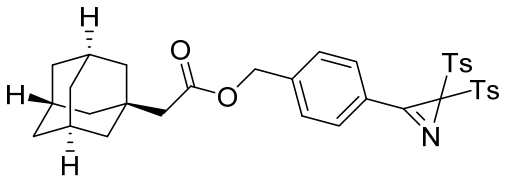
1-(*tert*-Butyl)-2-(4-(2,2-ditosyl-2H-azirin-3-yl)benzyl)-(S)-pyrrolidine-1,2-dicarboxylate (3ta):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 6.0 Hz, 1H), 7.57 (d, J = 5.5 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.36-5.21 (m, 2H), 4.43 (dd, J = 9.0 Hz, 0.5H), 4.33 (dd, J = 9.0 Hz, 0.5H), 3.61-3.40 (m, 2H), 2.47 (s, 6H), 2.34-2.21 (m, 1H), 2.02-1.88 (m, 3H), 1.48 (s, 4H), 1.37 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.8, 172.6, 158.4, 154.4,

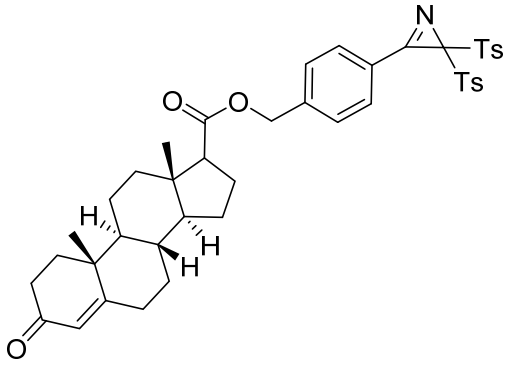
153.6, 145.8 (2C), 144.5, 144.1, 134.7, 134.6(2C), 132.4, 132.2, 129.6, 129.5 (2C), 128.7, 128.4, 118.7, 118.3, 80.1, 80.0, 69.72, 65.4, 65.3, 59.0, 58.8, 46.6, 46.3, 30.9, 29.9, 28.4, 28.3, 24.4, 23.6, 21.8; HRMS *m/z* (ESI) calcd for $C_{33}H_{37}N_2O_8S_2$ $(M+H)^+$ 653.1986, found 653.1998.

4-(2,2-Ditosyl-2*H*-azirin-3-yl)benzyl-2-((3*r*,5*r*,7*r*)-adamantan-1-yl)acetate (3ua):



White solid; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.88 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 4H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 4H), 7.57 (t, *J* = 8.5 Hz, 2H), 5.21 (s, 2H), 2.47 (s, 6H), 2.19 (s, 2H), 1.99 (t, *J* = 3.5 Hz, 3H), 1.73 (s, 1H), 1.70 (s, 2H), 1.65 (t, J = 2.5 Hz, 5H), 1.62 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 171.3, 158.4, 145.8, 144.8, 134.7, 132.3, 129.6 (2C), 128.6, 118.3, 69.8, 64.7, 48.7, 42.4, 36.6, 32.9, 28.5, 21.8; HRMS *m/z* (ESI) calcd for $C_{35}H_{38}NO_6S_2$ $(M+H)^+$ 632.2135, found 632.2147.

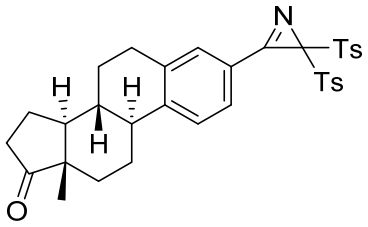
4-(2,2-Ditosyl-2*H*-azirin-3-yl)benzyl-(8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthrene-17-carboxylate (3va):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.90 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 4H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 4H), 5.73 (s, 1H), 5.27-5.19 (m, 2H), 2.47 (s, 6H), 2.42-2.35 (m, 3H), 2.34-2.26 (m, 2H), 2.21-2.17 (m, 1H), 2.06-2.01 (m, 2H), 1.90-1.86 (m, 3H),

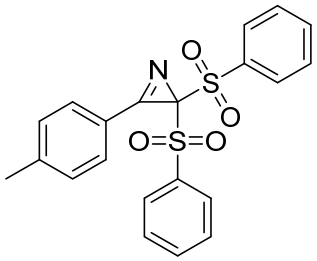
1.74-1.71 (m, 3H), 1.65-1.55 (m, 3H), 1.44-1.41 (m, 1H), 1.19 (s, 3H), 1.09-1.05(m, 1H), 1.01-0.95 (m, 1H), 0.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 199.5, 173.4, 171.0, 158.4, 145.8, 144.8, 134.6, 134.6, 132.3, 129.6, 129.5, 128.7, 123.9, 118.4, 69.7, 64.9, 55.3, 55.0, 53.6, 44.1, 38.6, 38.1, 35.6 (2C), 33.9, 32.7, 31.8, 24.4, 23.6, 21.8, 20.9, 17.3, 13.5; HRMS *m/z* (ESI) calcd for $C_{43}H_{48}NO_7S_2$ $(M+H)^+$ 754.2867, found 754.2885.

(8*S*,9*S*,13*S*,14*S*)-3-(2,2-ditosyl-2*H*-azirin-3-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (3wa):



White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.71 (d, J = 8.5 Hz, 4H), 7.67 (d, J = 7.0 Hz, 1H), 7.52 (s, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 8.0 Hz, 4H), 2.95-2.92 (m, 2H), 2.57-2.51 (m, 1H), 2.47 (s, 6H), 2.42-2.37 (m, 1H), 2.20-2.14 (m, 1H), 2.11-2.06 (m, 2H), 2.03-2.00 (m, 1H), 1.71-1.68 (m, 1H), 1.61-1.47 (m, 6H), 0.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.2, 149.1, 145.7, 138.5, 134.9, 132.7, 129.6, 129.5, 129.3, 126.8, 116.0, 69.7, 50.4, 47.8, 44.9, 37.5, 35.8, 31.4, 29.0, 25.9, 25.4, 21.8, 21.5, 13.8; HRMS *m/z* (ESI) calcd for $C_{34}H_{36}NO_5S_2$ $(M+H)^+$ 602.2029, found 602.2042.

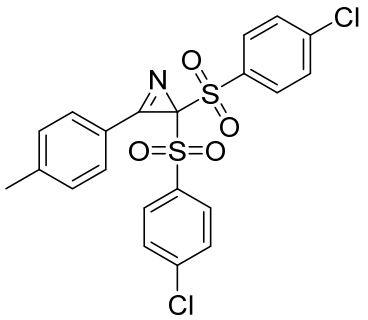
2,2-Bis(phenylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3cb):



White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, J = 7.0 Hz, 4H), 7.74 (d, J = 8.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 8.0 Hz, 4H), 7.39 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.0, 147.8, 137.8, 134.5,

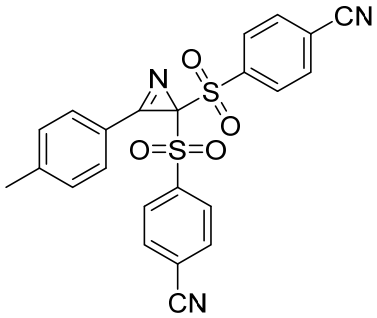
132.2, 130.5, 129.5, 129.0, 115.7, 69.6, 22.3; HRMS *m/z* (ESI) calcd for $C_{21}H_{18}NO_4S_2$ $(M+H)^+$ 412.0672, found 412.0685.

2,2-Bis((4-chlorophenyl)sulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3cc):



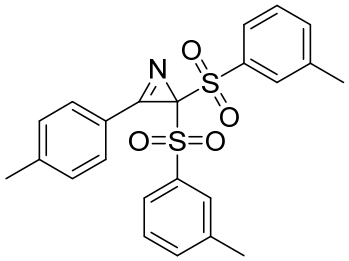
Yellow solid; ^{1}H NMR (500 MHz, CDCl3) δ: 7.79 (d, J = 8.5 Hz, 4H), 7.73 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.5 Hz, 4H), 7.42 (d, J = 7.5 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ: 157.9, 148.2, 141.7, 136.2, 132.2, 131.0, 130.6, 129.4, 115.4, 69.6, 22.3; HRMS *m/z* (ESI) calcd for $C_{21}H_{16}{}^{35}Cl_2NO_4S_2$ $(M+H)^+$ 479.9892, found 479.9901.

4,4'-(3-(*p*-Tolyl)-2*H*-azirine-2,2-disulfonyl)dibenzonitrile (3cd):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06 (d, J = 8.0 Hz, 4H), 7.87 (d, J = 8.0 Hz, 4H), 7.63 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 7.5 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.6, 148.9, 141.9, 132.8, 132.2, 130.8, 130.3, 118.5, 116.9, 114.7, 69.5, 22.4; HRMS *m/z* (ESI) calcd for $C_{23}H_{16}N_3O_4S_2$ $(M+H)^+$ 462.0577, found 462.0585.

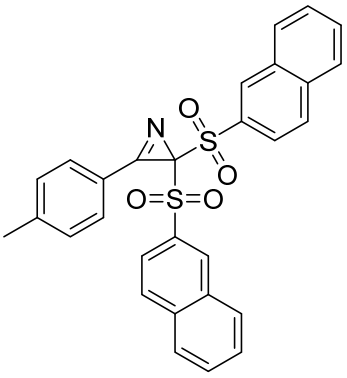
3-(*p*-Tolyl)-2,2-bis(*m*-tolylsulfonyl)-2*H*-azirine (3ce):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.79 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.55 (s, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H), 2.49 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.0, 147.6, 139.2, 137.6, 135.3, 132.3, 130.4, 129.5, 128.7,

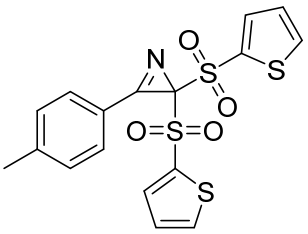
126.7, 115.8, 69.7, 22.2, 21.2; HRMS *m/z* (ESI) calcd for $C_{23}H_{22}NO_4S_2$ $(M+H)^+$ 440.0985, found 440.0993.

2,2-Bis(naphthalen-2-ylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3cf):



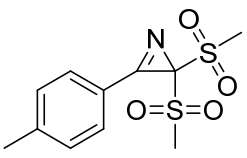
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.25 (s, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.5 Hz, 2H), 7.72-7.69 (m, 4H), 7.67 (d, J = 9.0 Hz, 2H), 7.62 (t, J = 7.0 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.1, 147.8, 135.5, 134.4, 132.4, 131.7, 131.5, 130.5, 129.5, 129.4, 128.9, 127.8, 127.5, 123.5, 116.0, 69.8, 22.2; HRMS *m/z* (ESI) calcd for $C_{29}H_{22}NO_4S_2$ $(M+H)^+$ 512.0985, found 512.0999.

2,2-Bis(thiophen-3-ylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3cg):



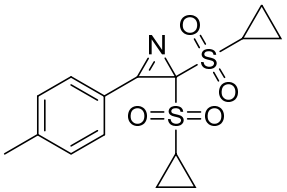
Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.80-7.77 (m, 5H), 7.76 (s, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 4 Hz, 1H), 7.17 (d, J = 4 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.9, 147.9, 137.7, 136.9, 136.0, 132.3, 130.5, 128.0, 115.5, 70.4, 22.3; HRMS *m/z* (ESI) calcd for $C_{17}H_{14}NO_4S_4$ $(M+H)^+$ 423.9800, found 423.9815.

2,2-Bis(methylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3ch):



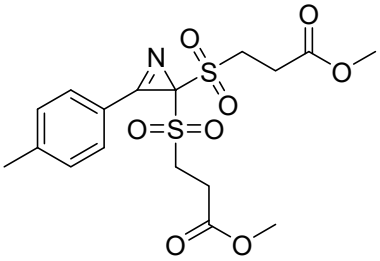
Red solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.88 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 3.35 (s, 6H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.5, 148.3, 131.9, 130.8, 115.5, 66.5, 42.1, 22.3; HRMS *m/z* (ESI) calcd for $C_{11}H_{14}NO_4S_2$ $(M+H)^+$ 288.0359, found 288.0366.

2,2-Bis(cyclopropylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3ci):



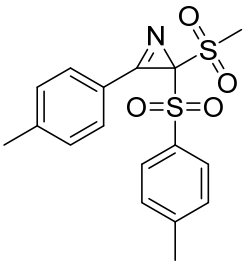
Red solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 3.19-3.14 (m, 2H), 2.51 (s, 3H), 1.42-1.36 (m, 2H), 1.22-1.17 (m, 2H), 1.14-1.08 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.2, 147.7, 131.9, 130.5, 116.3, 67.5, 31.0, 22.2, 5.8, 5.3; HRMS *m/z* (ESI) calcd for $C_{15}H_{18}NO_4S_2$ $(M+H)^+$ 340.0672, found 340.0675.

Dimethyl 3,3'-(3-(*p*-tolyl)-2*H*-azirine-2,2-disulfonyl)dipropionate (3cj):



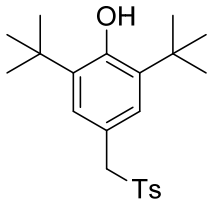
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 4.06-4.00 (m, 2H), 3.73 (s, 6H), 3.72-3.67 (m, 2H), 2.96-2.91 (m, 4H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.1, 157.2, 148.4, 132.0, 130.9, 115.4, 66.4, 52.5, 50.3, 26.3, 22.3; HRMS *m/z* (ESI) calcd for $C_{17}H_{22}NO_8S_2$ $(M+H)^+$ 432.0781, found 432.0796.

2-(Methylsulfonyl)-3-(*p*-tolyl)-2-tosyl-2*H*-azirine (3cah):



Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.26 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.8, 147.9, 146.2, 135.0, 132.1, 130.5, 129.8, 129.8, 115.7, 68.2, 41.3, 22.3, 21.8; HRMS *m/z* (ESI) calcd for $C_{17}H_{18}NO_4S_2$ $(M+H)^+$ 364.0672, found 364.0685.

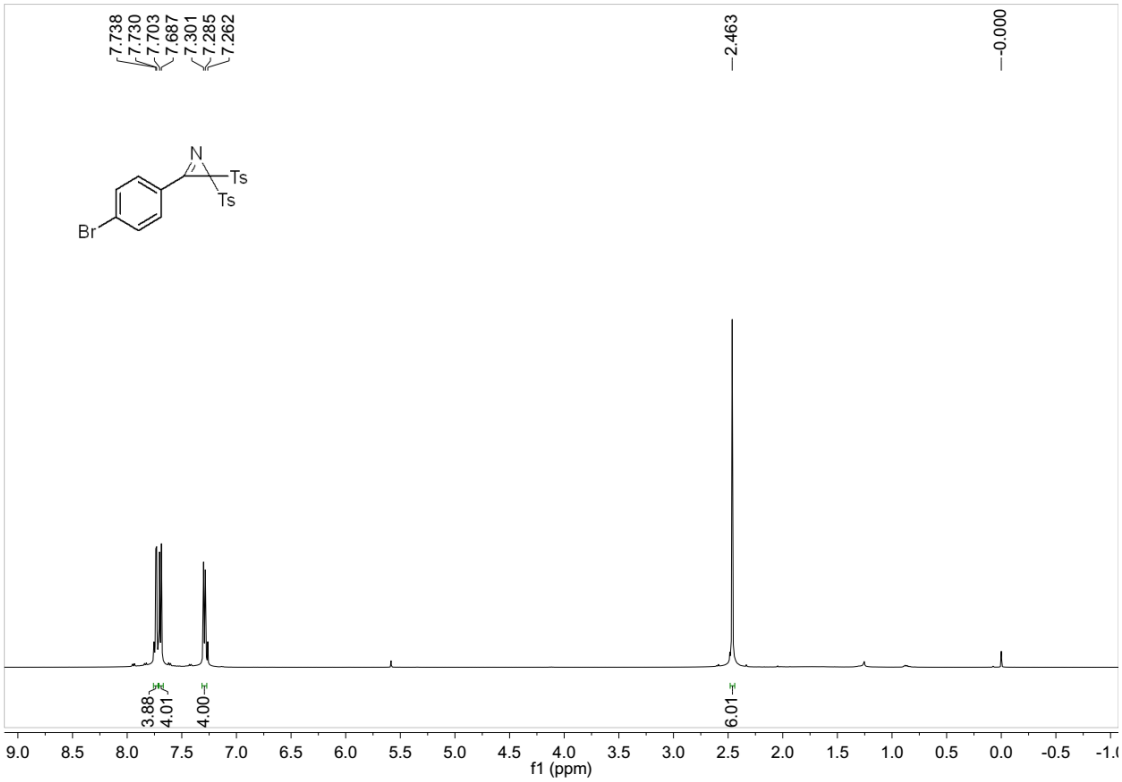
2,6-Di-*tert*-butyl-4-(tosylmethyl)phenol (4):

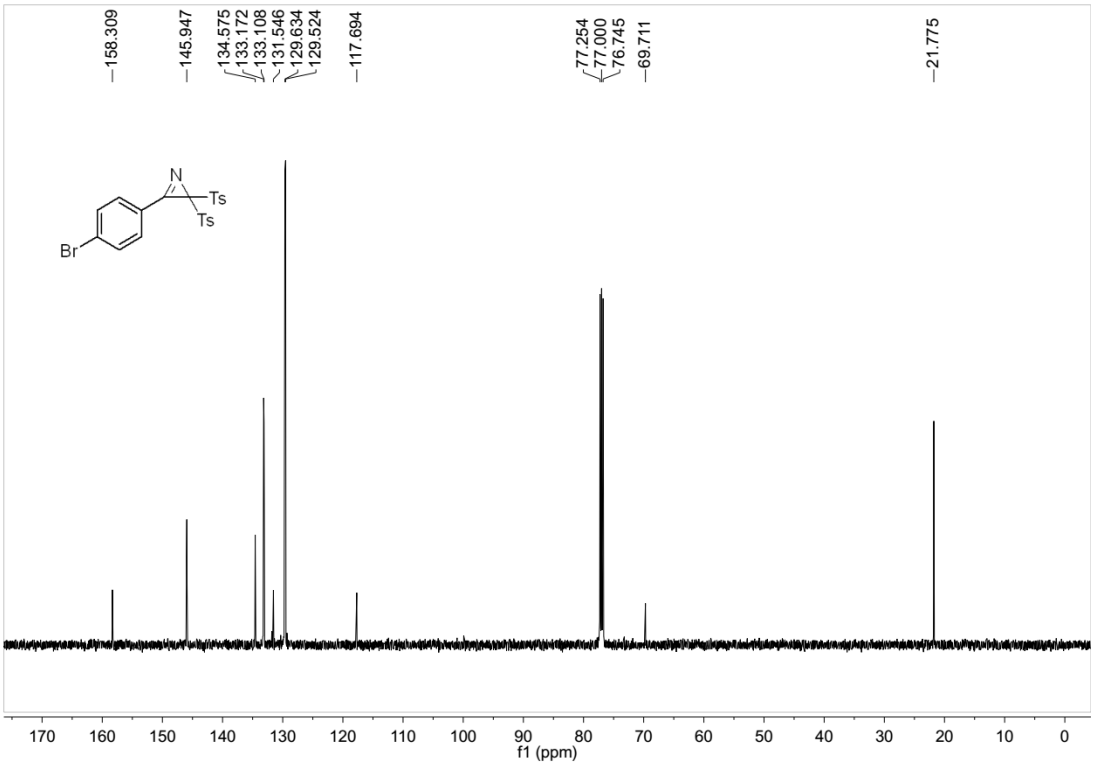


White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 7.5 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 6.73 (s, 2H), 5.25 (s, 1H), 4.19 (s, 2H), 2.41 (s, 3H), 1.32 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.1, 144.3, 135.9, 134.8, 129.3, 128.9, 127.6, 118.9, 63.2, 34.1, 30.0, 21.5; HRMS *m/z* (ESI) calcd for $C_{22}H_{31}O_3S$ $(M+H)^+$ 375.1988, found 375.1997.

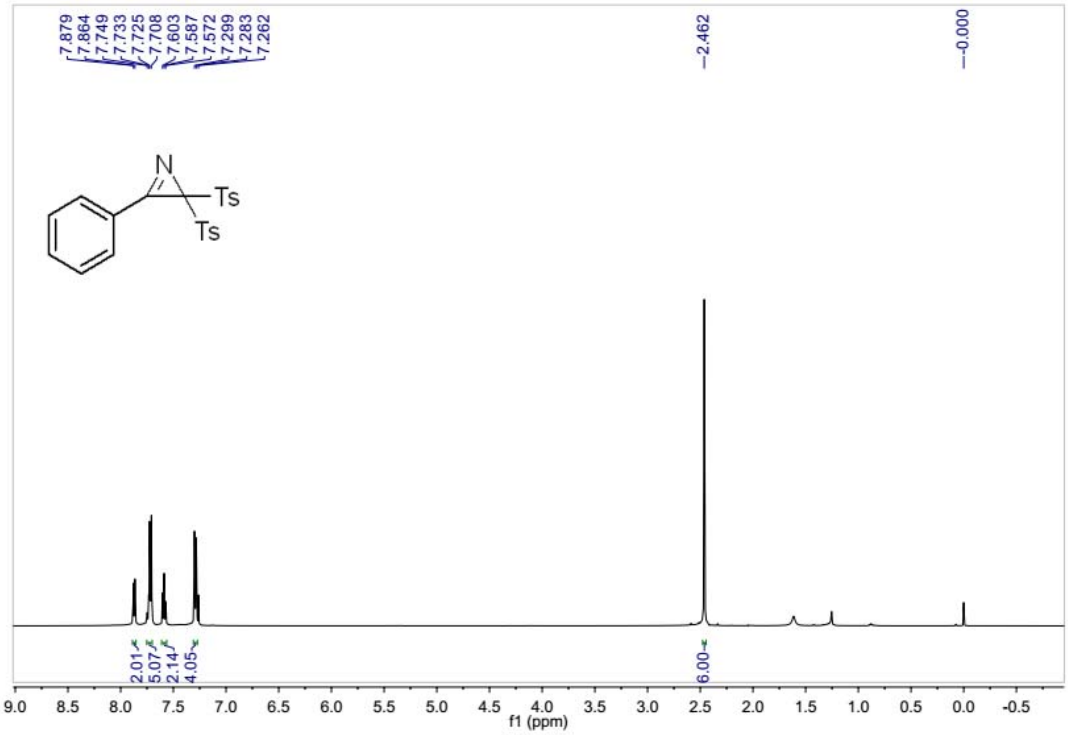
(C) Spectra

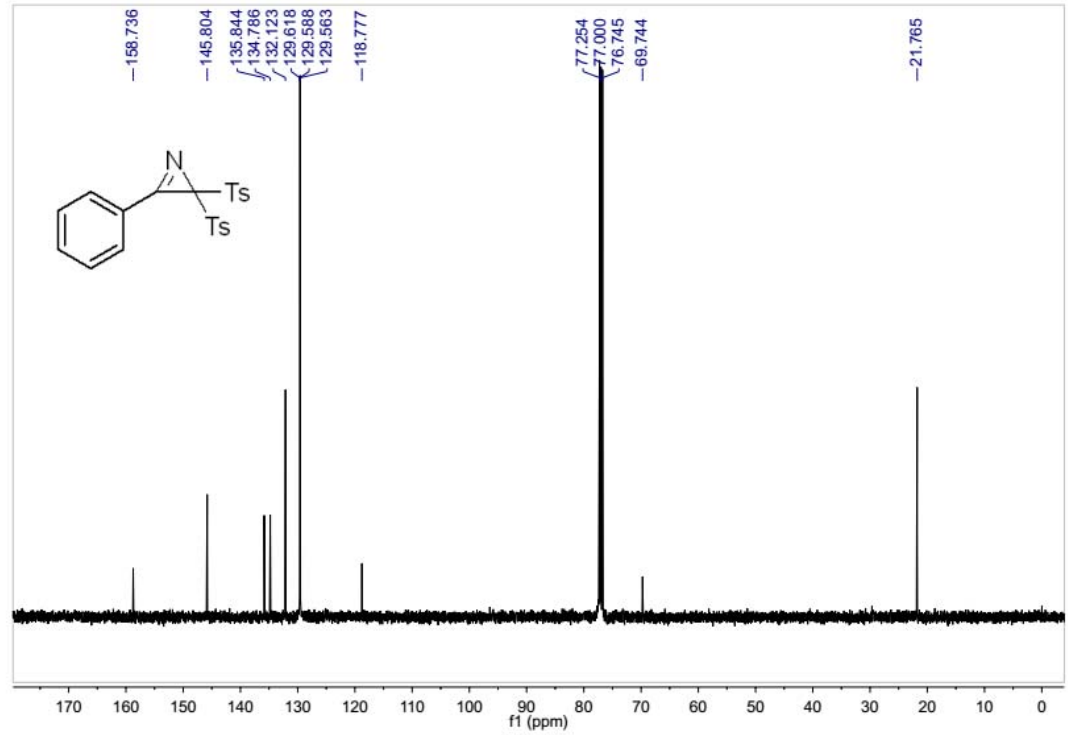
3-(4-Bromophenyl)-2,2-ditosyl-2*H*-azirine (3aa):



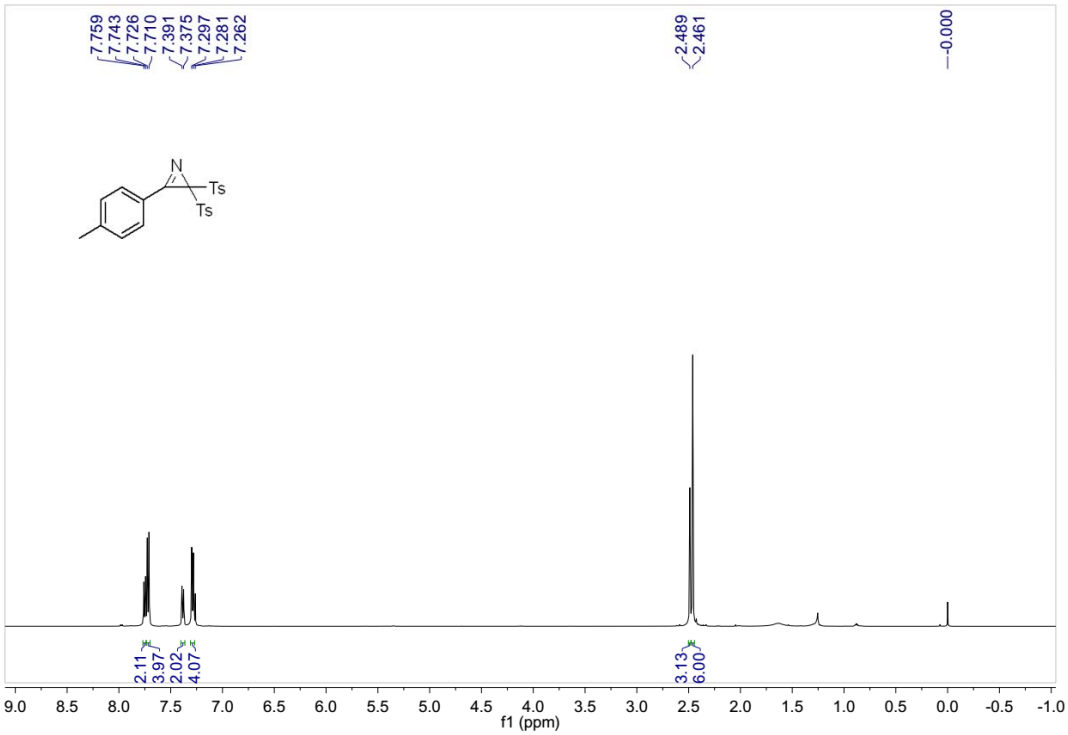


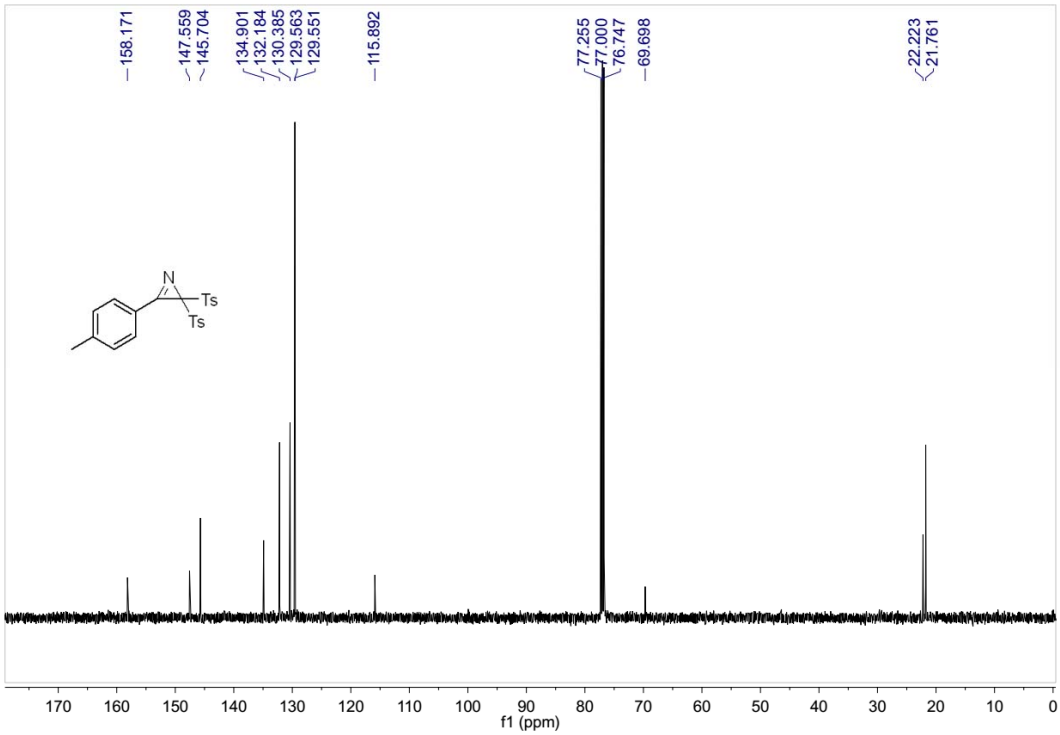
3-Phenyl-2,2-ditosyl-2*H*-azirine (3ba):



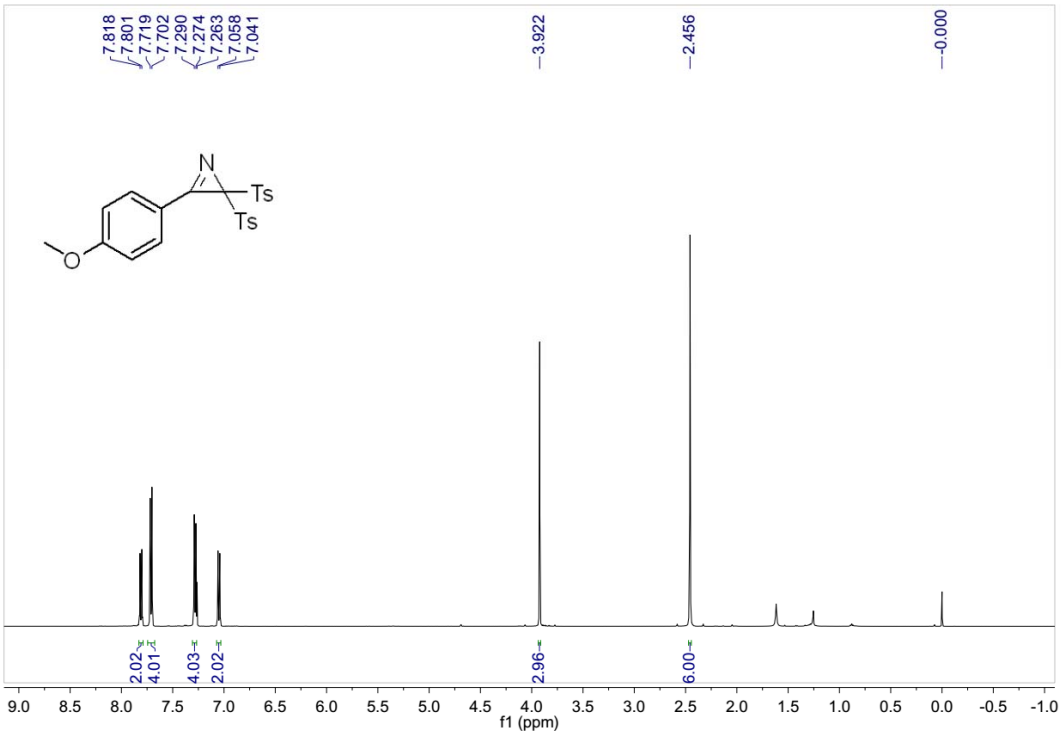


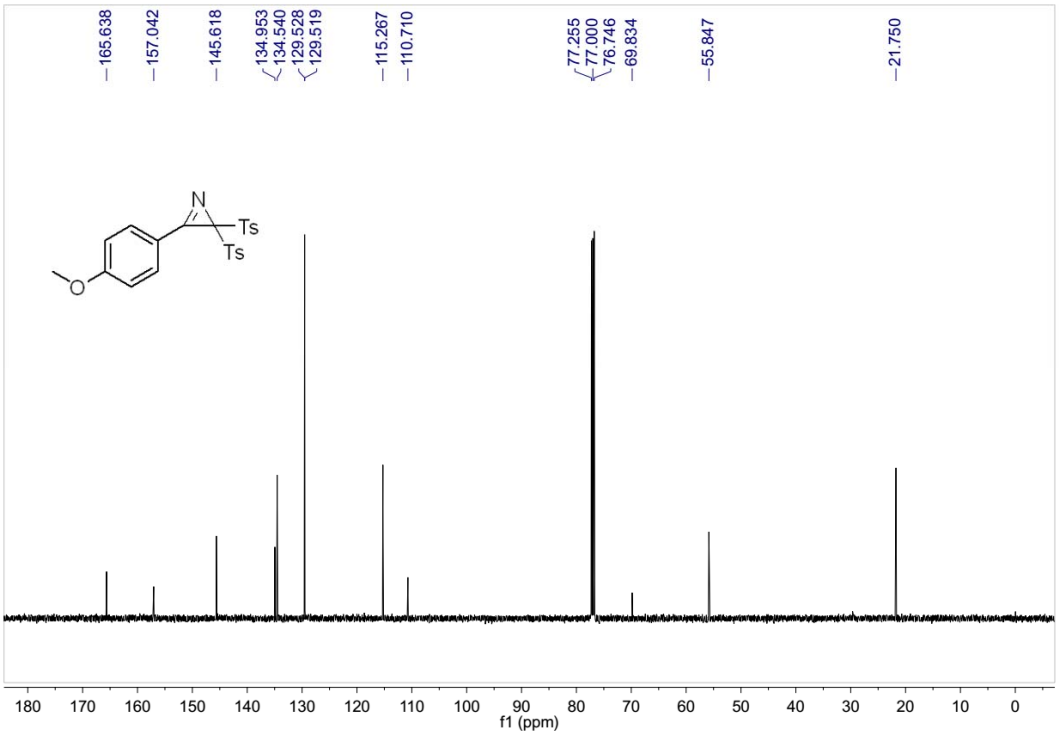
3-(*p*-Tolyl)-2,2-ditosyl-2*H*-azirine (3ca):



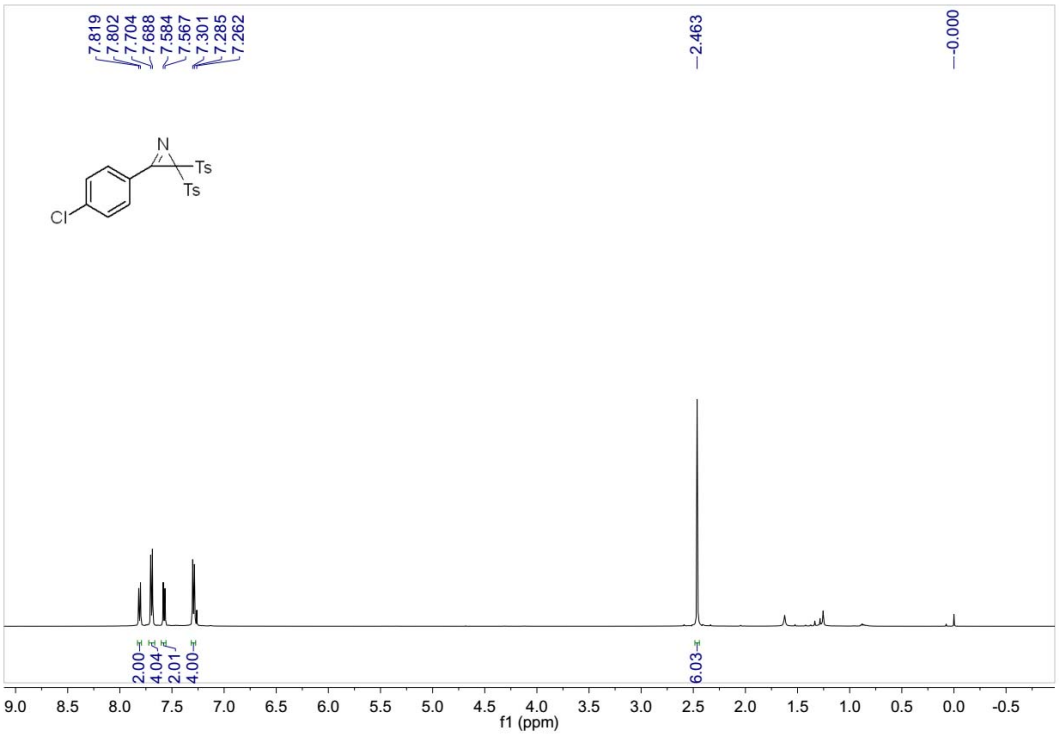


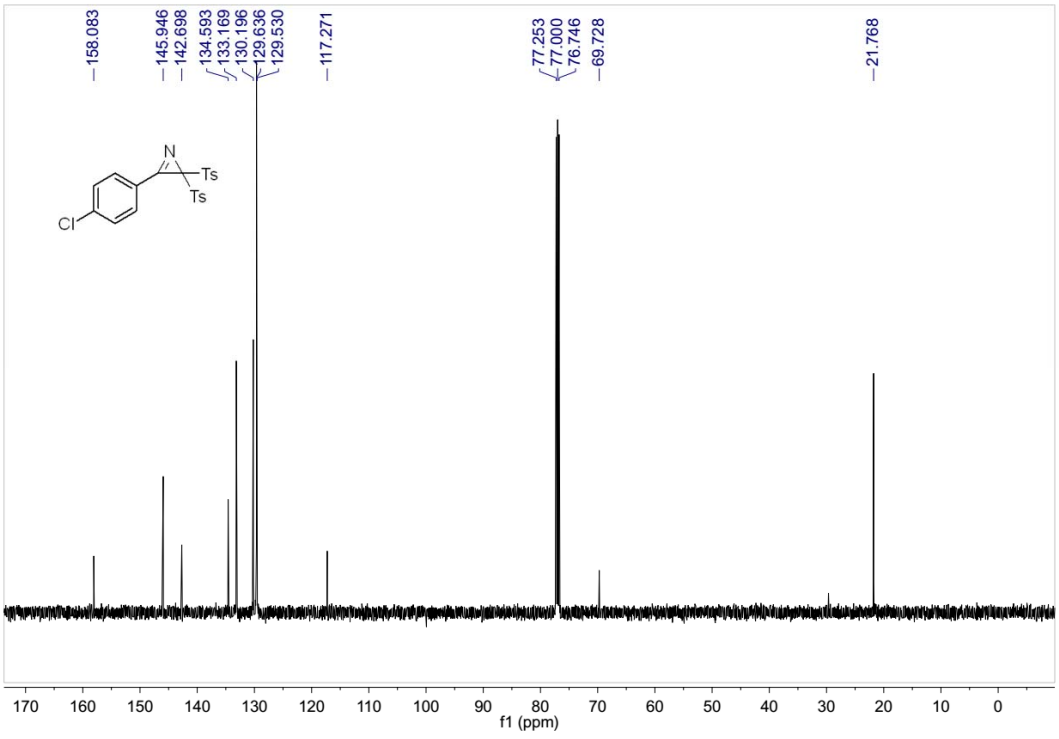
3-(4-Methoxyphenyl)-2,2-ditosyl-2*H*-azirine (3da):



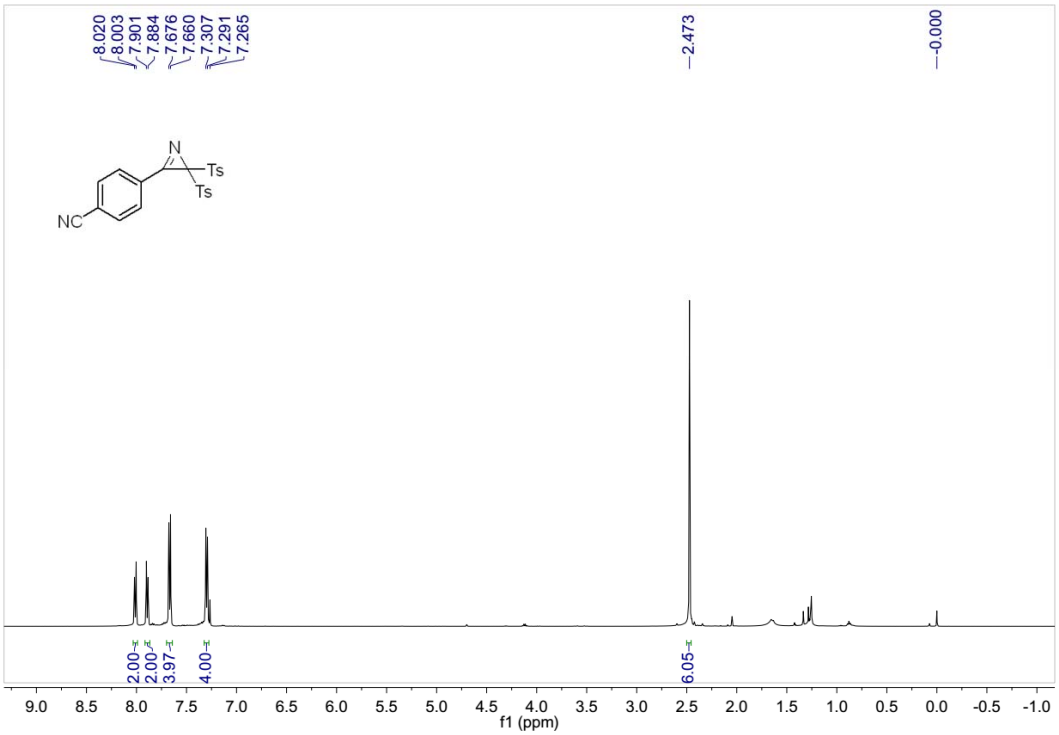


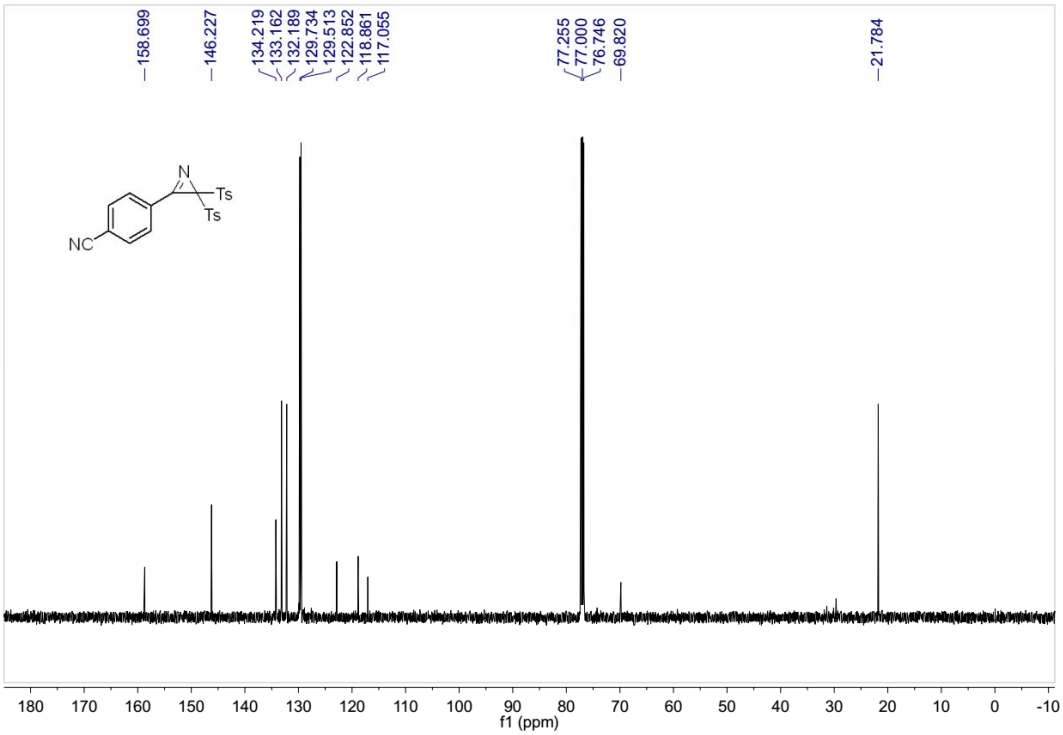
3-(4-Chlorophenyl)-2,2-ditosyl-2*H*-azirine (3ea):



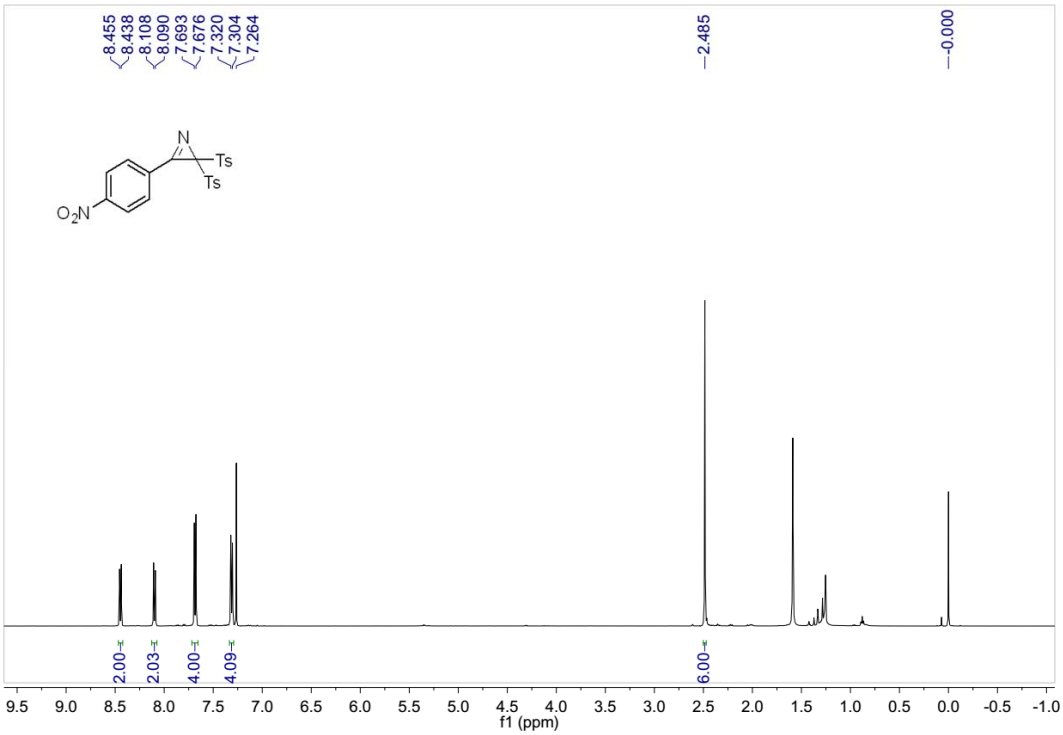


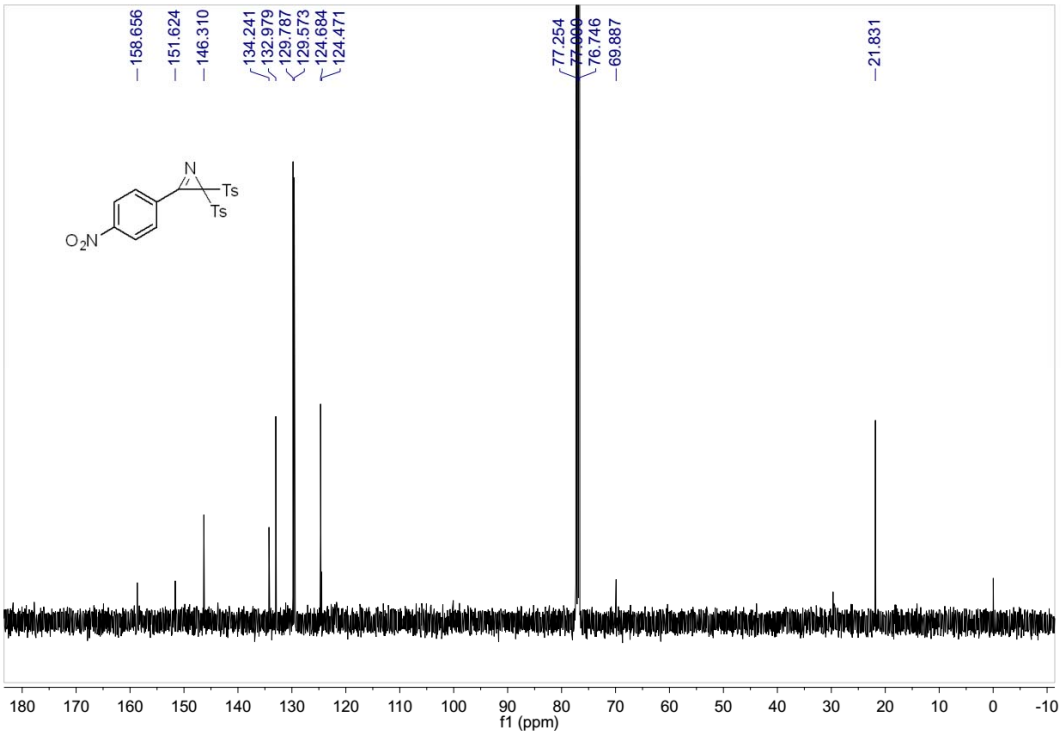
4-(2,2-Ditosyl-2*H*-azirin-3-yl)benzonitrile (3fa):



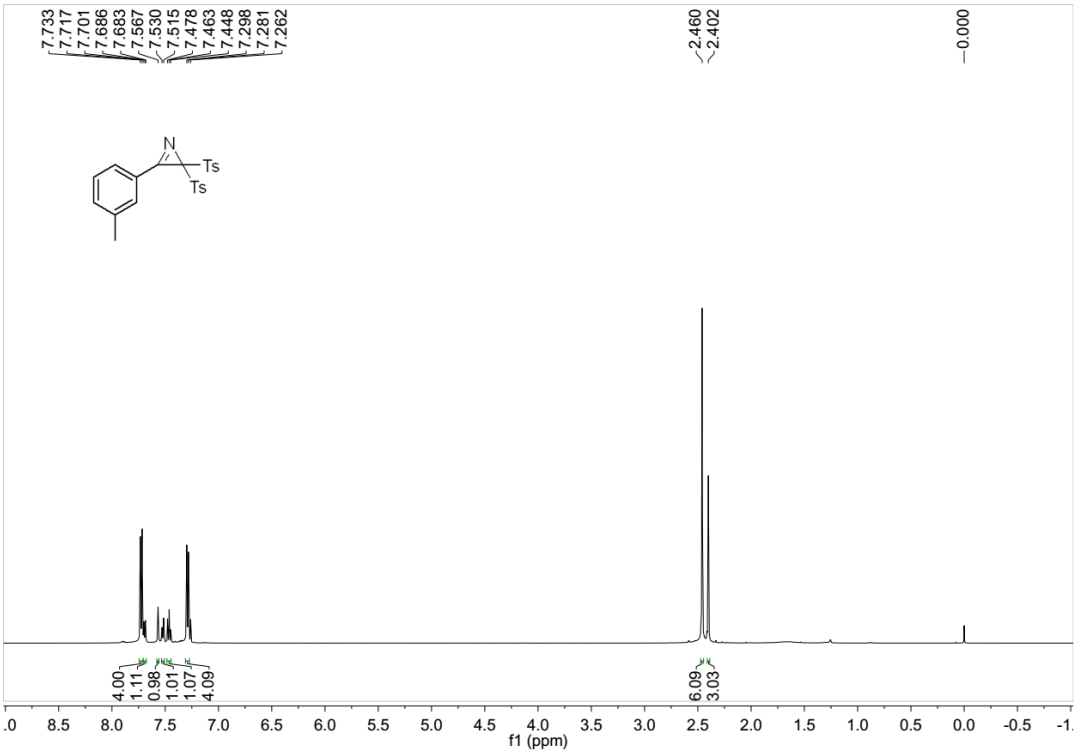


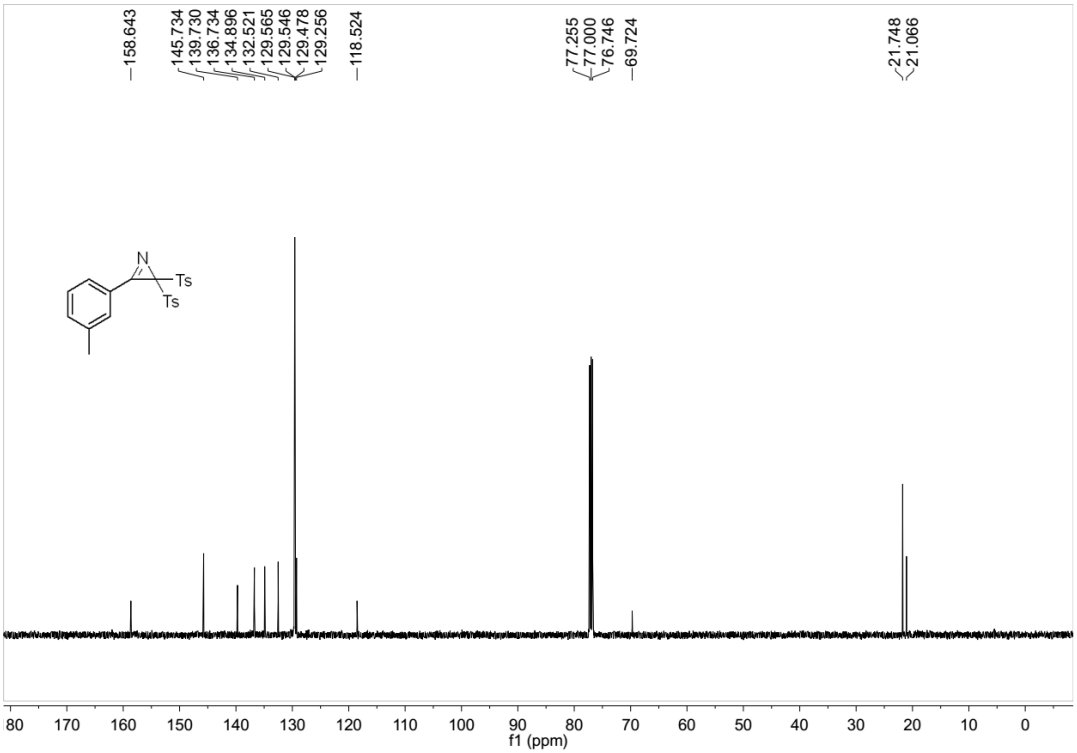
3-(4-Nitrophenyl)-2,2-ditosyl-2*H*-azirine (3ga):



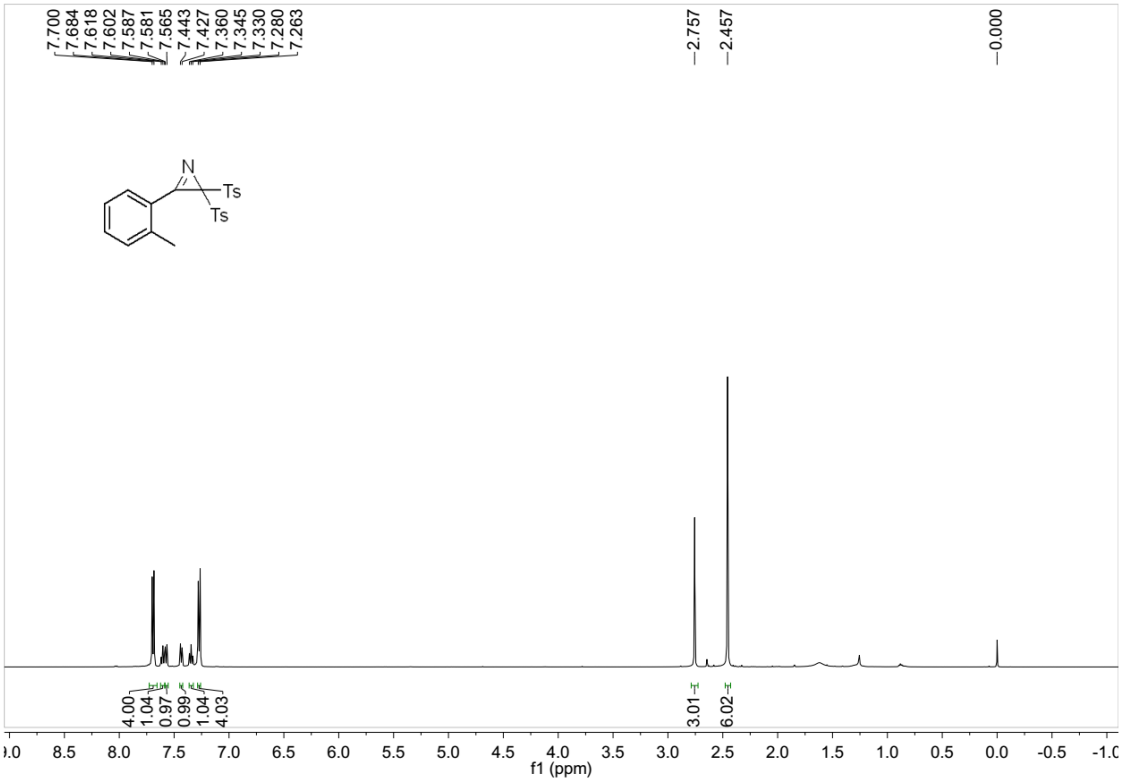


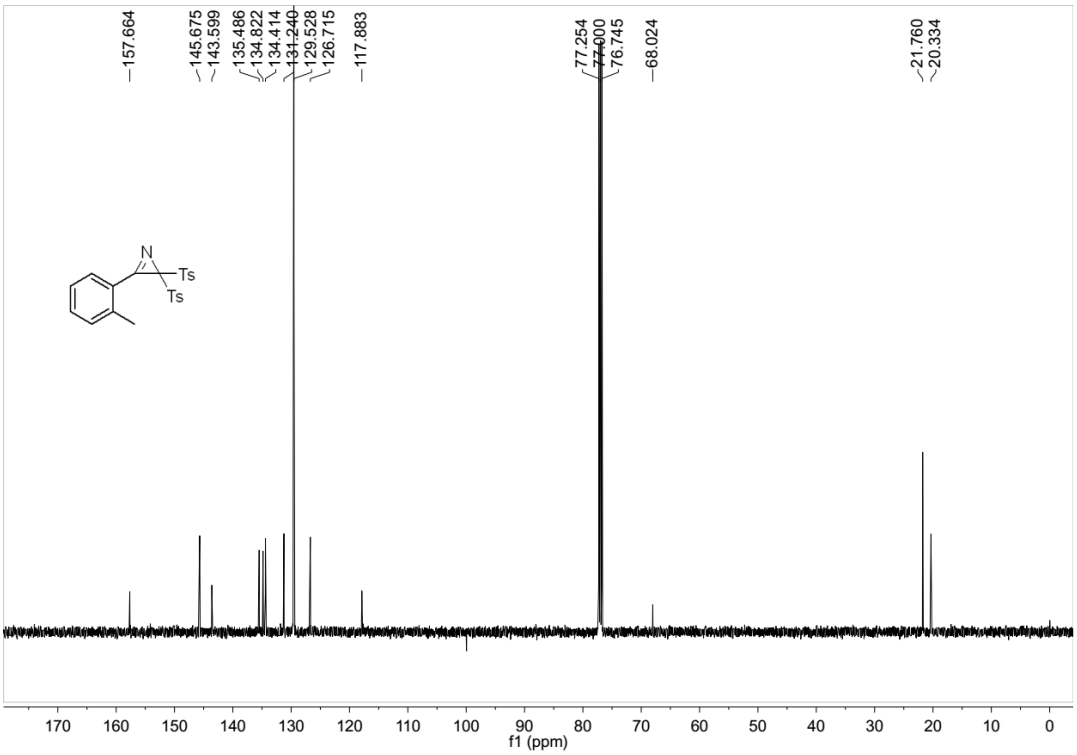
3-(*m*-Tolyl)-2,2-ditosyl-2*H*-azirine (3ha):



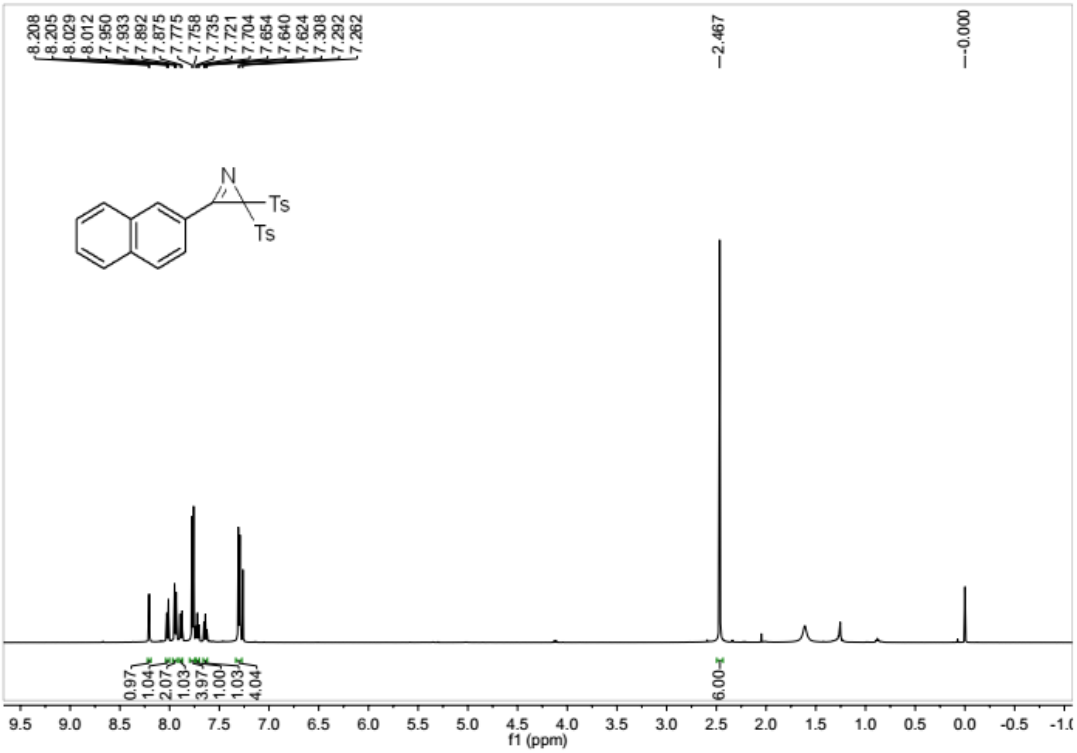


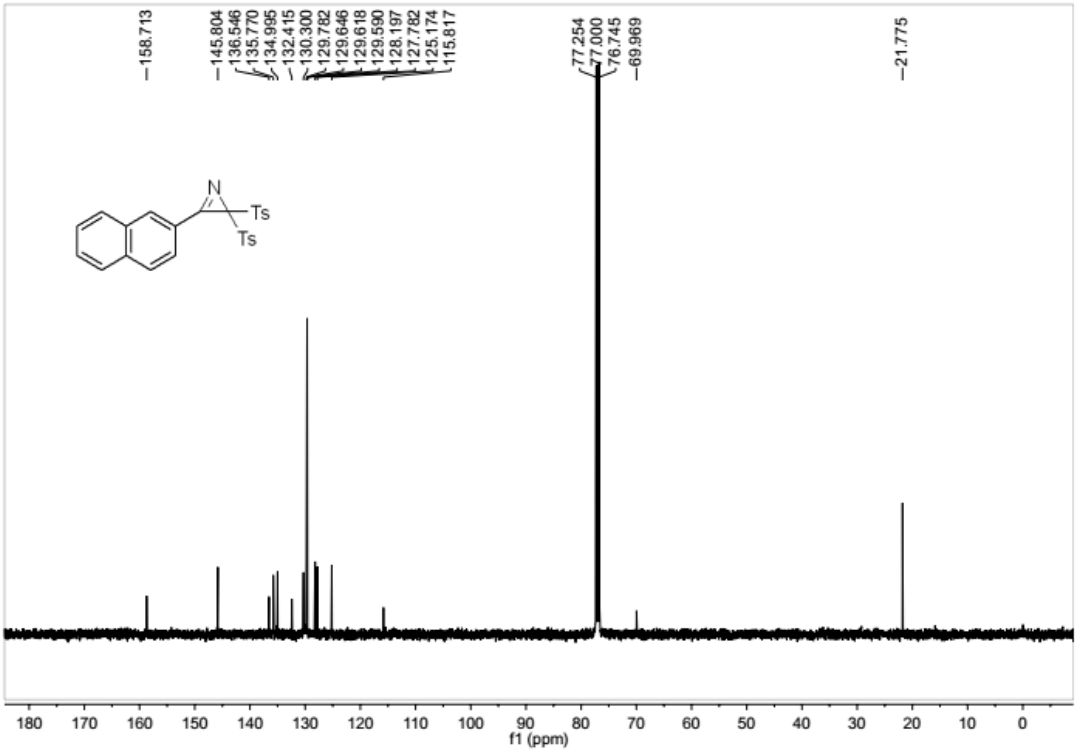
3-(*o*-Tolyl)-2,2-ditosyl-2*H*-azirine (3ia):



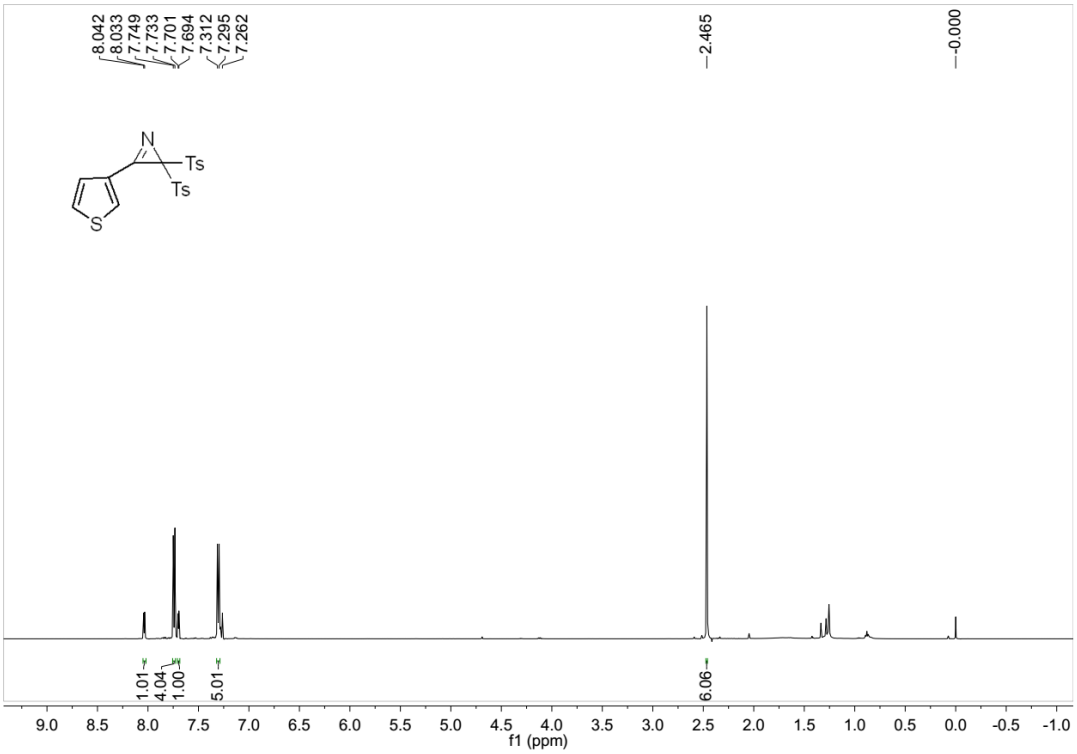


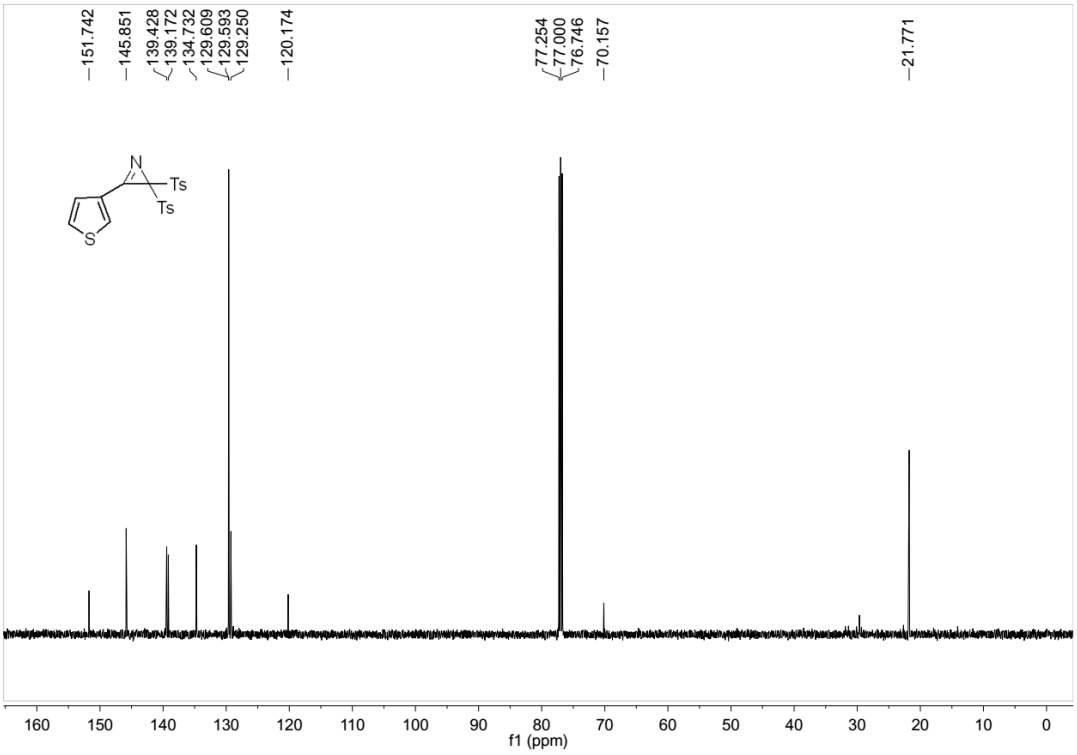
3-(Naphthalen-2-yl)-2,2-ditosyl-2*H*-azirine (3ja)：



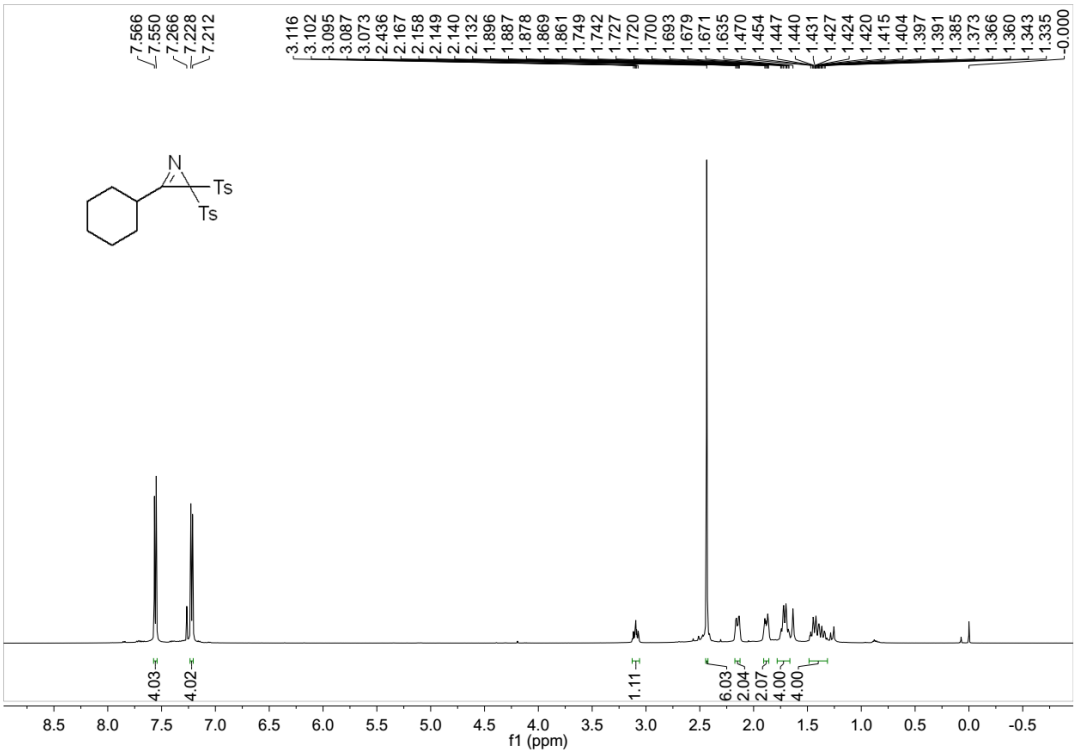


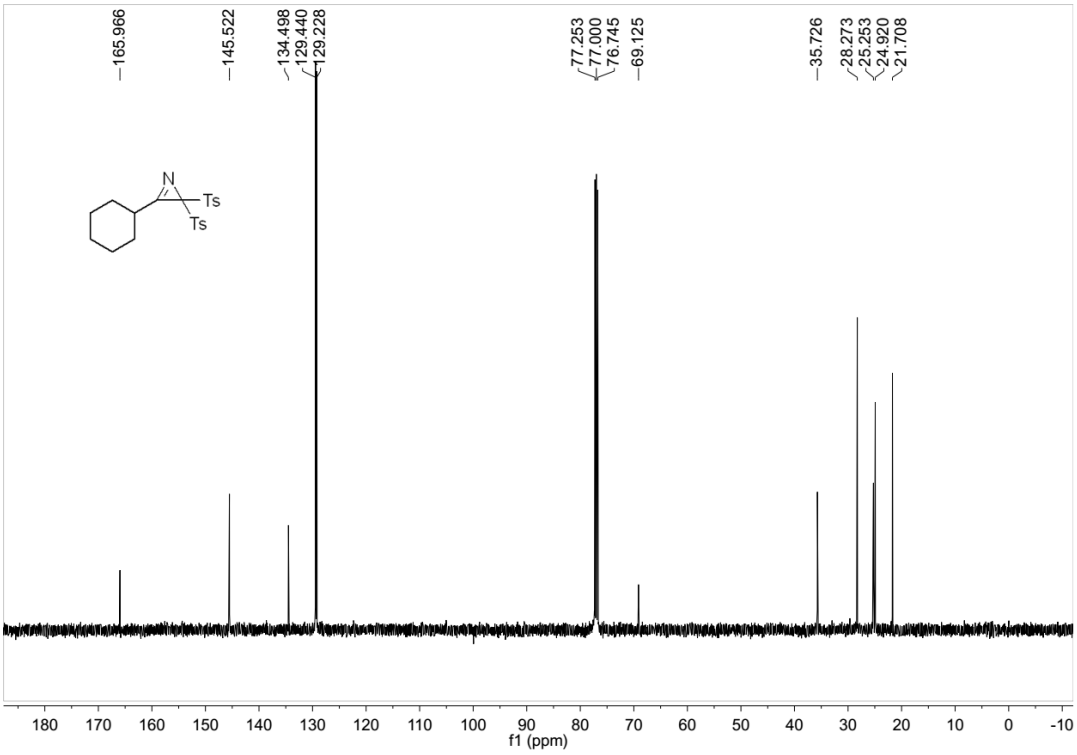
3-(Thiophen-3-yl)-2,2-ditosyl-2*H*-azirine (3ka):



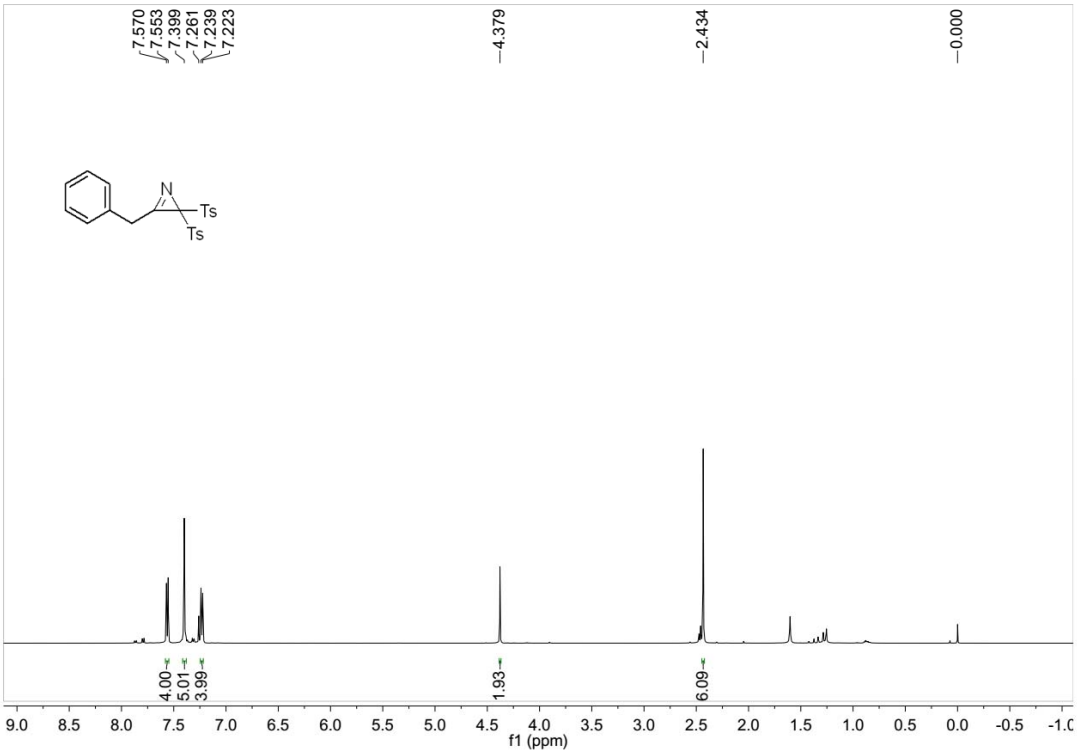


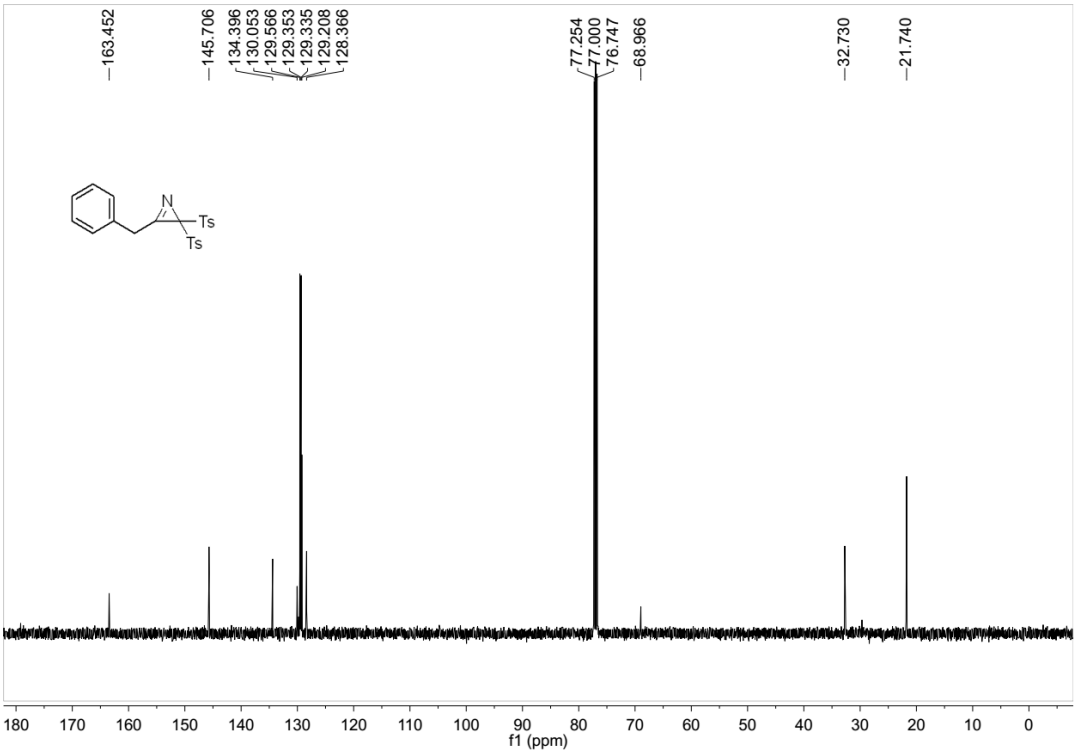
3-Cyclohexyl-2,2-ditosyl-2*H*-azirine (3la):



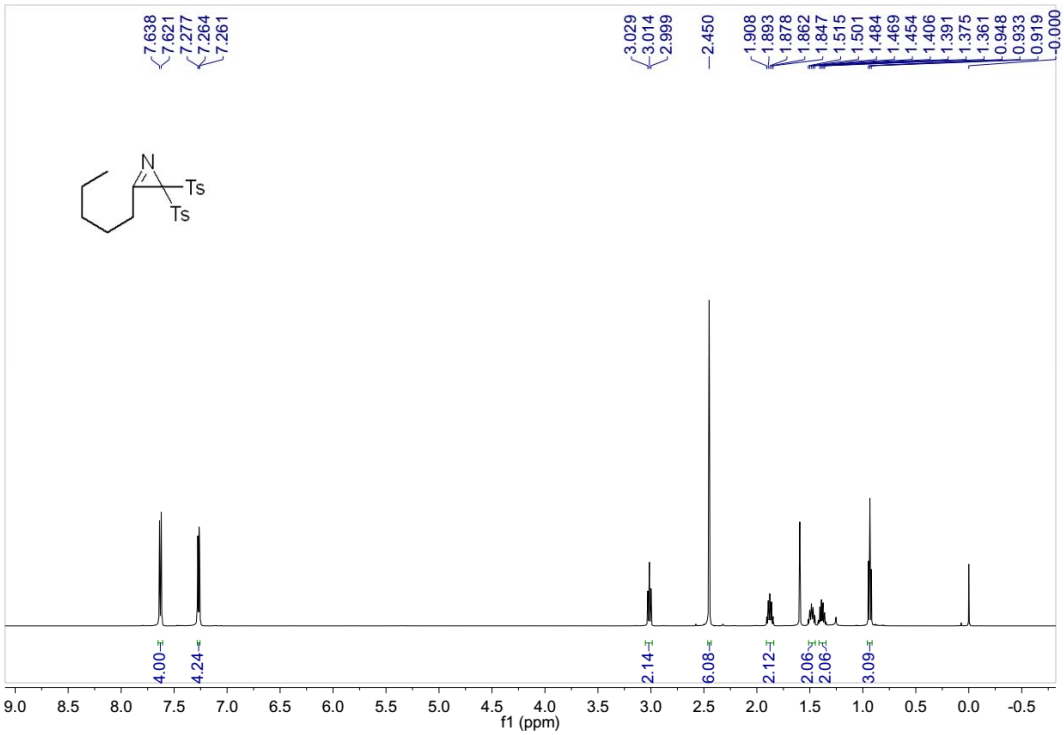


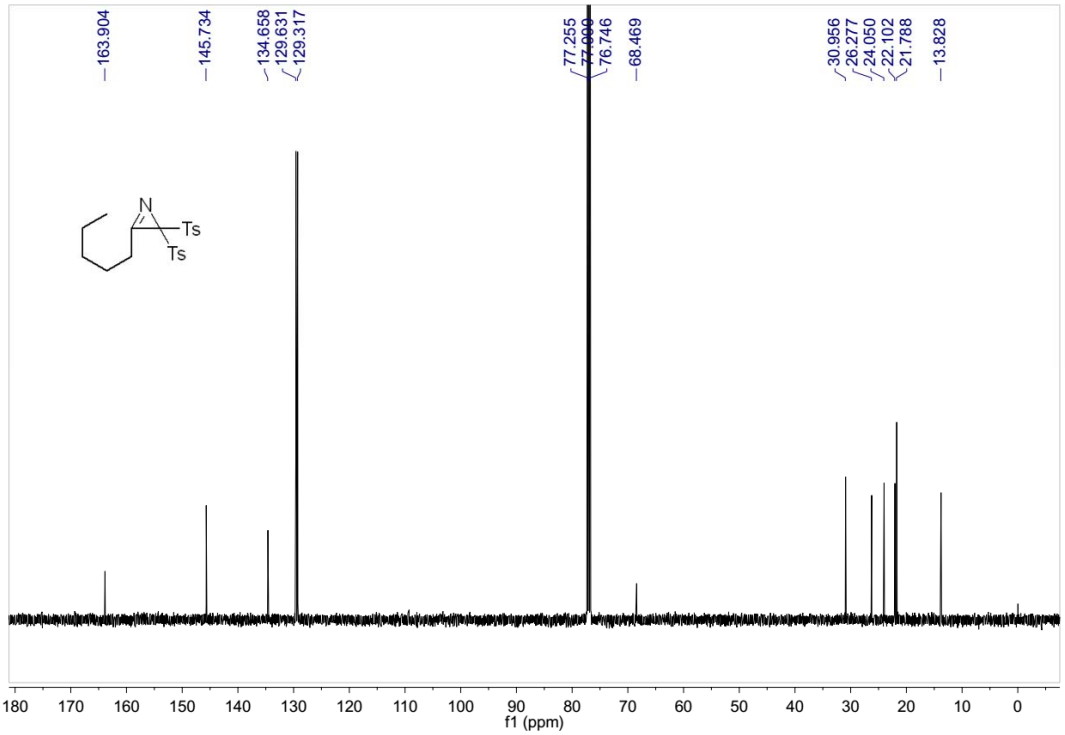
3-Benzyl-2,2-ditosyl-2*H*-azirine (3ma):



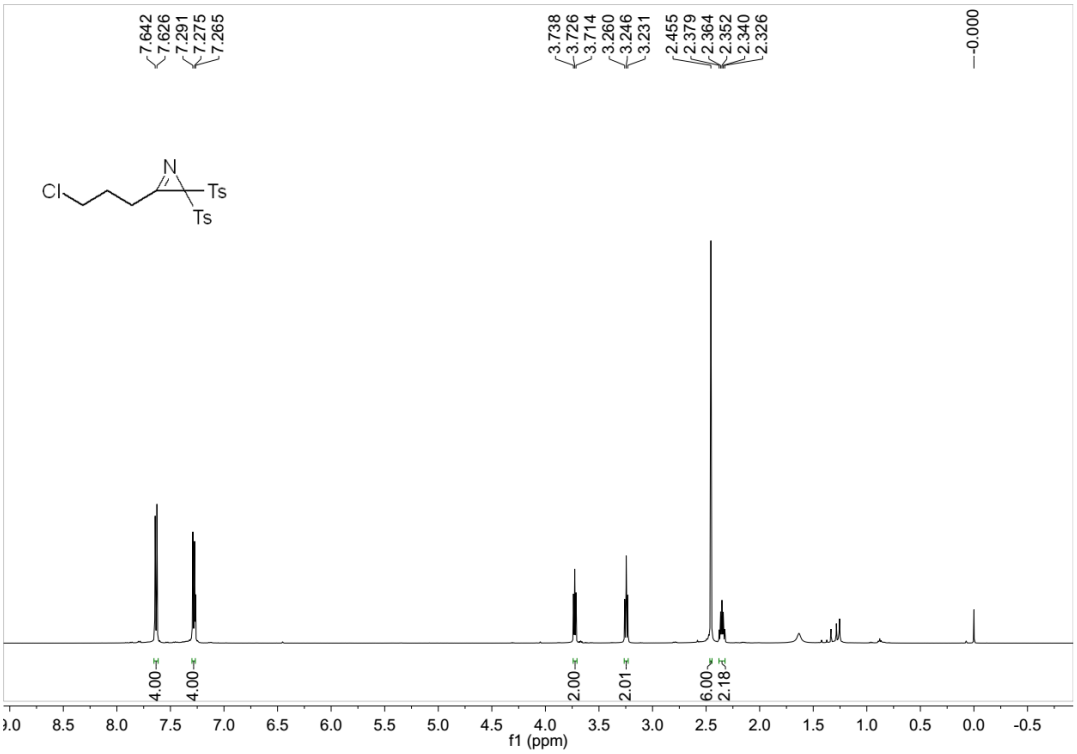


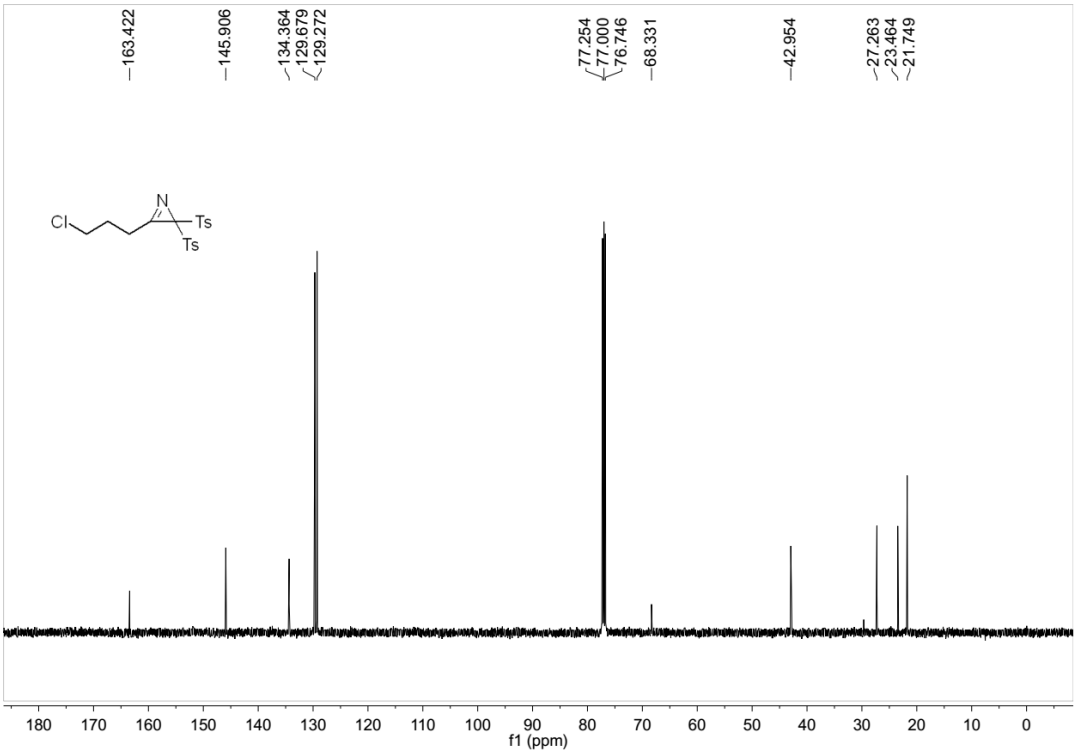
3-Pentyl-2,2-ditosyl-2*H*-azirine (3na):



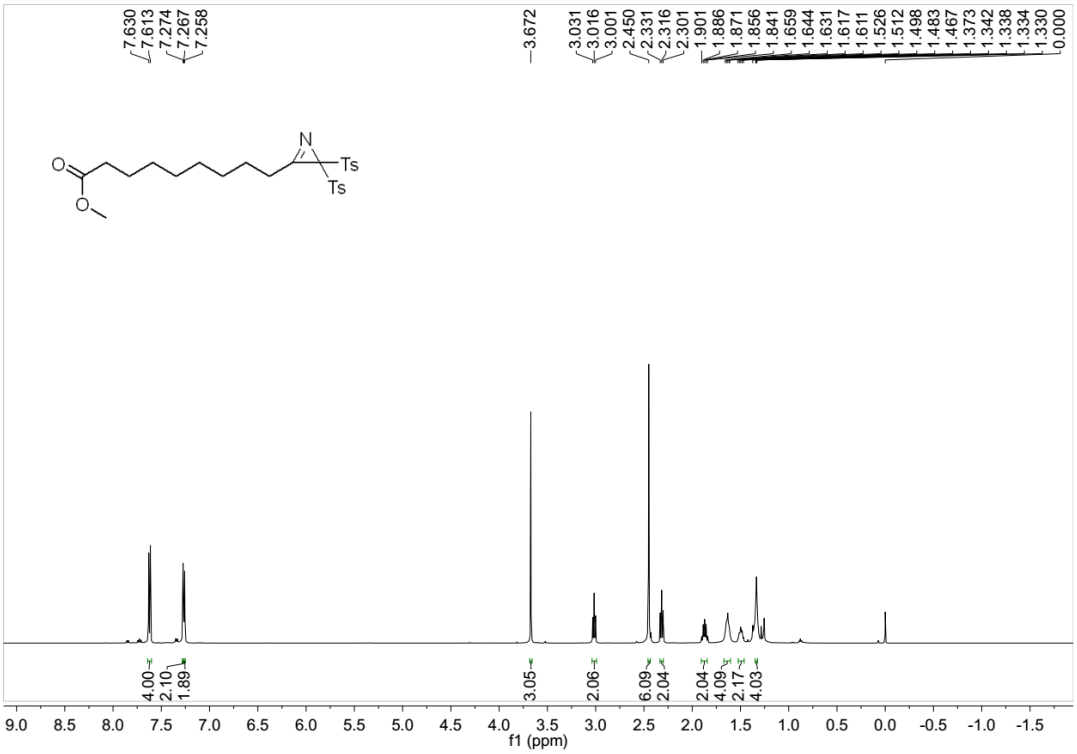


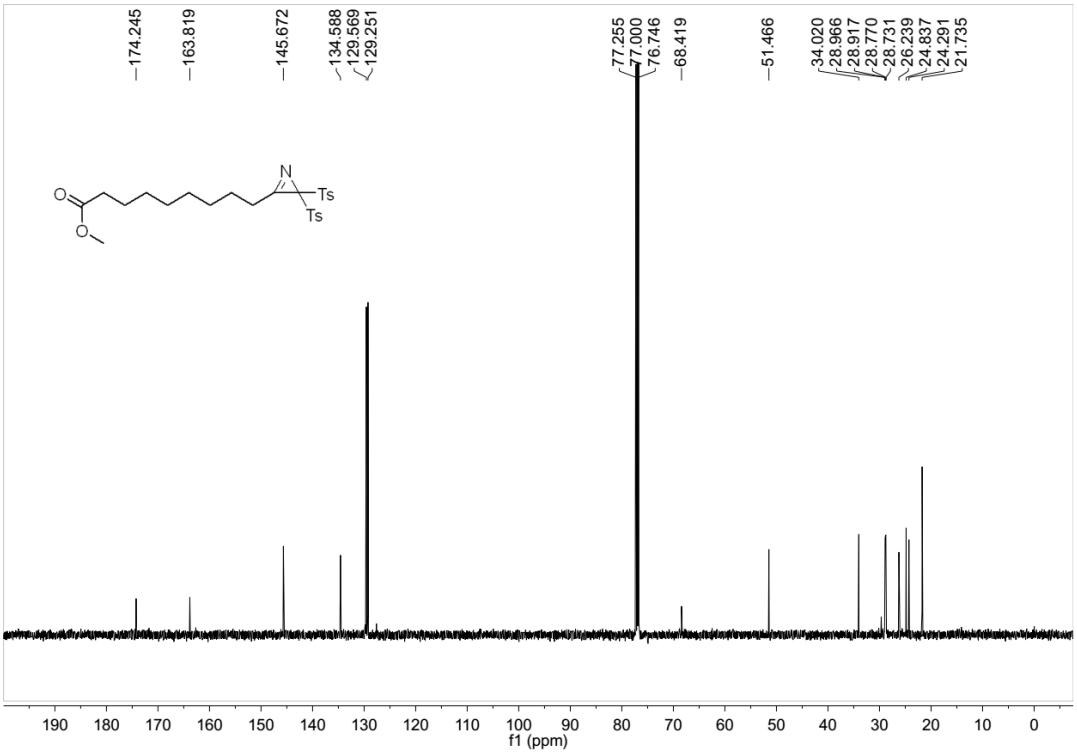
3-(3-Chloropropyl)-2,2-ditosyl-2*H*-azirine (3oa):



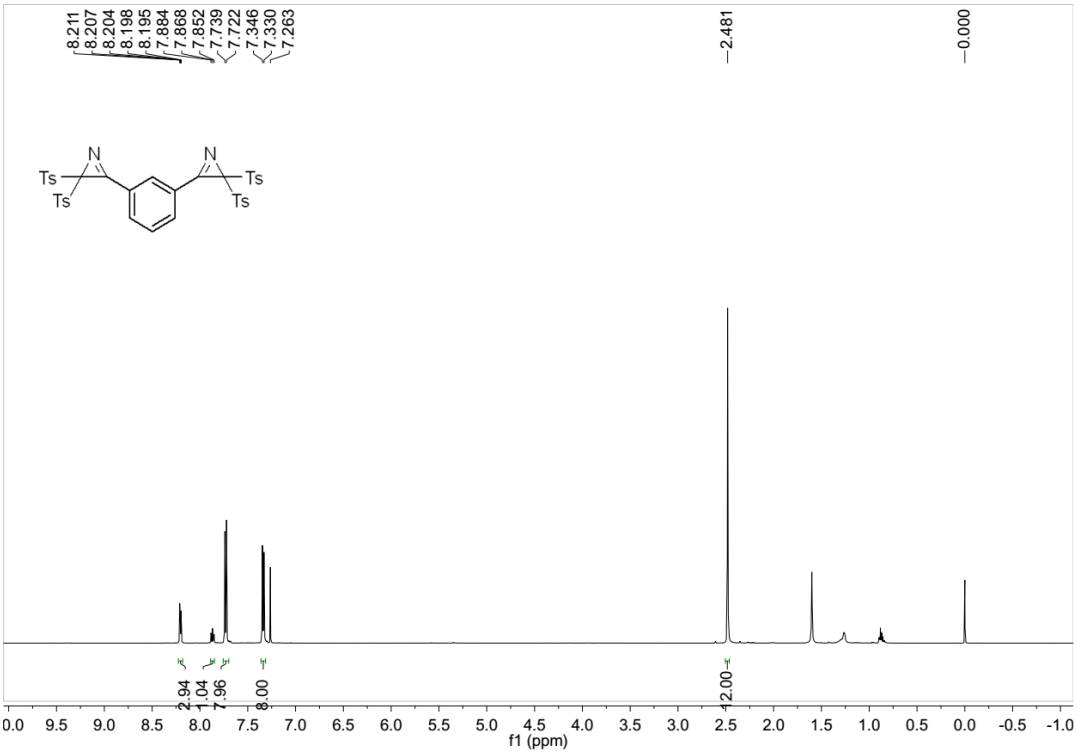


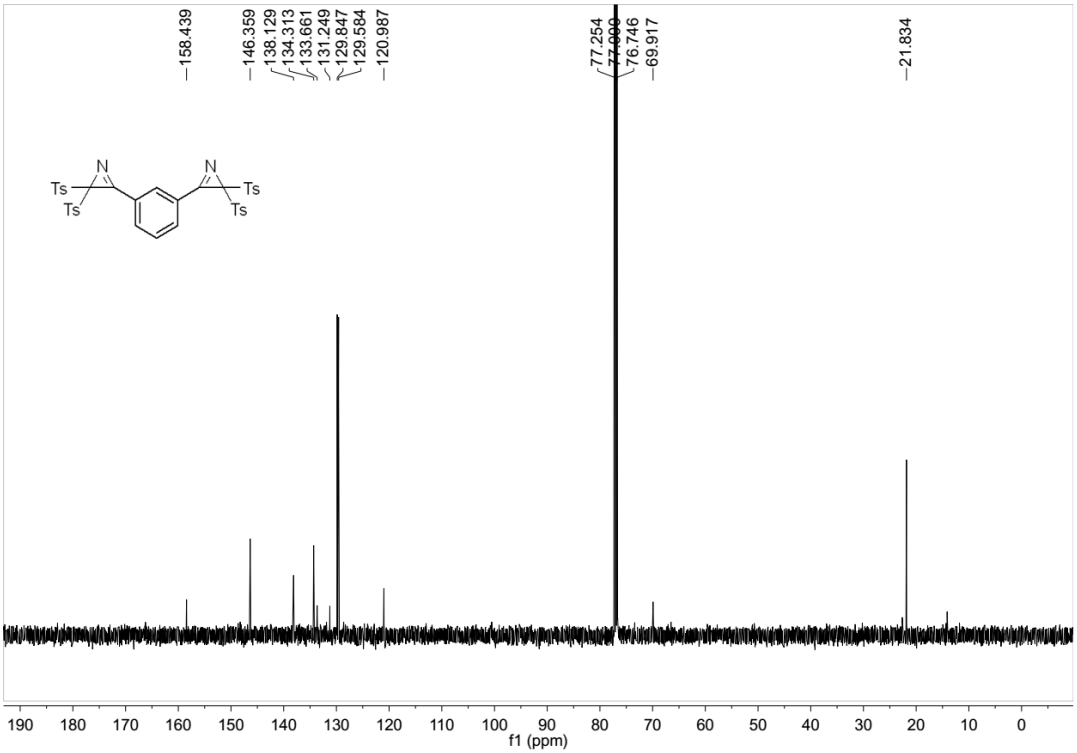
Methyl 9-(2,2-ditosyl-2*H*-azirin-3-yl)nonanoate (3pa):



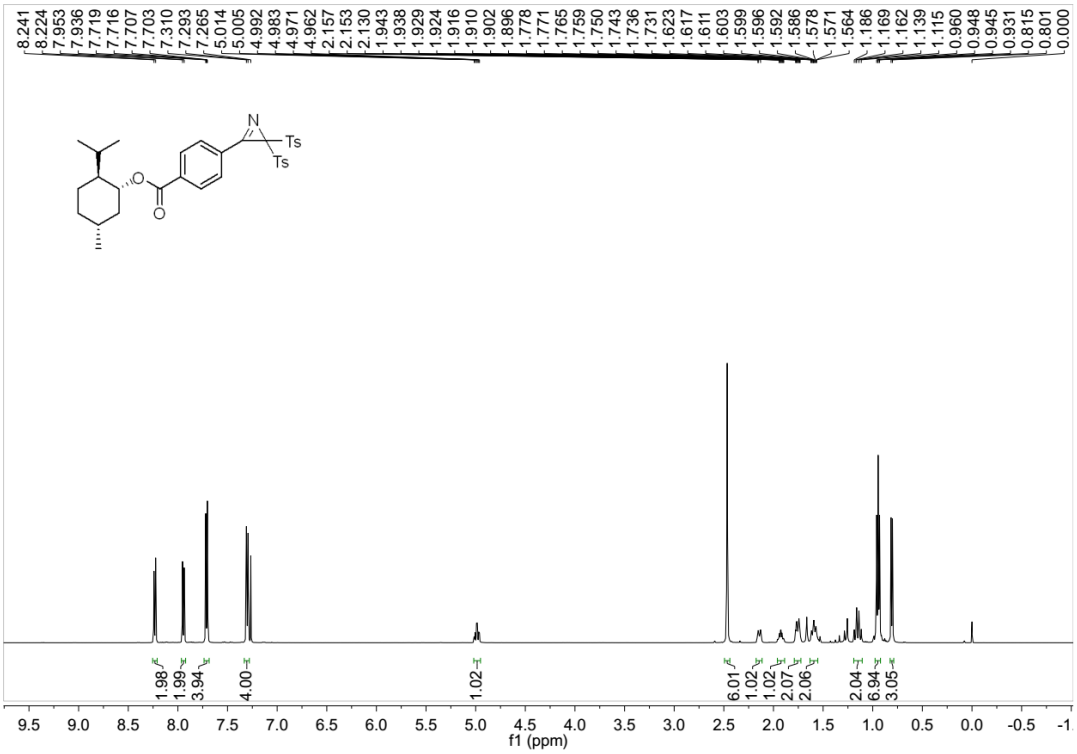


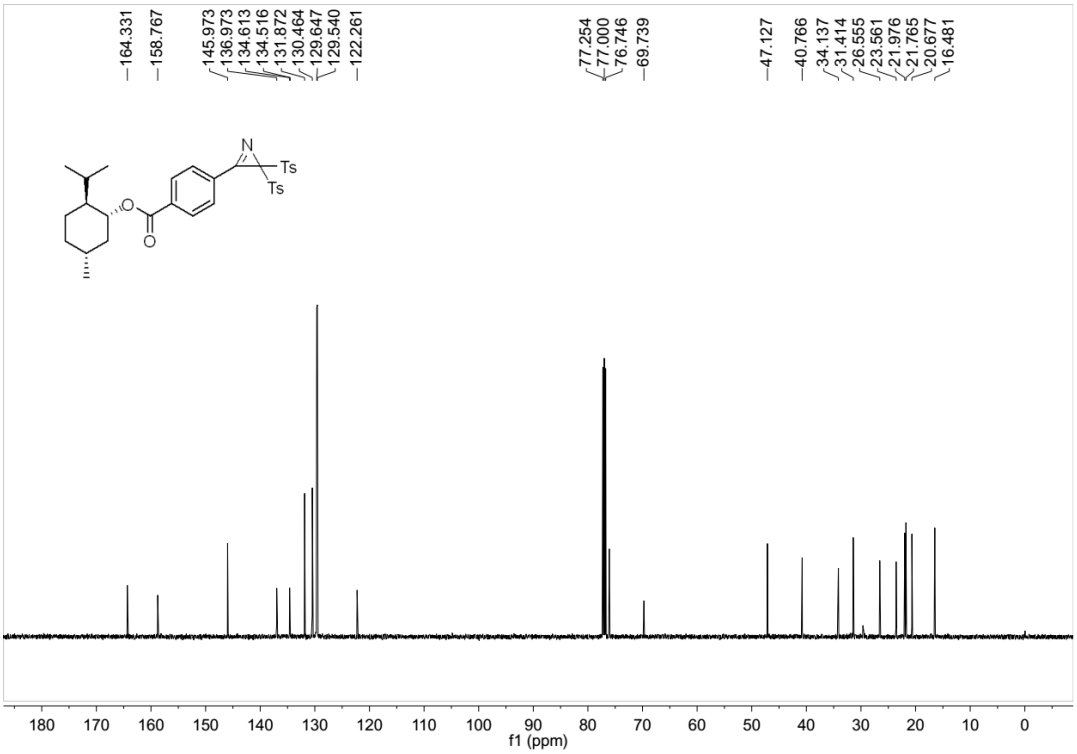
1,3-Bis(2,2-ditosyl-2*H*-azirin-3-yl)benzene (3qa):



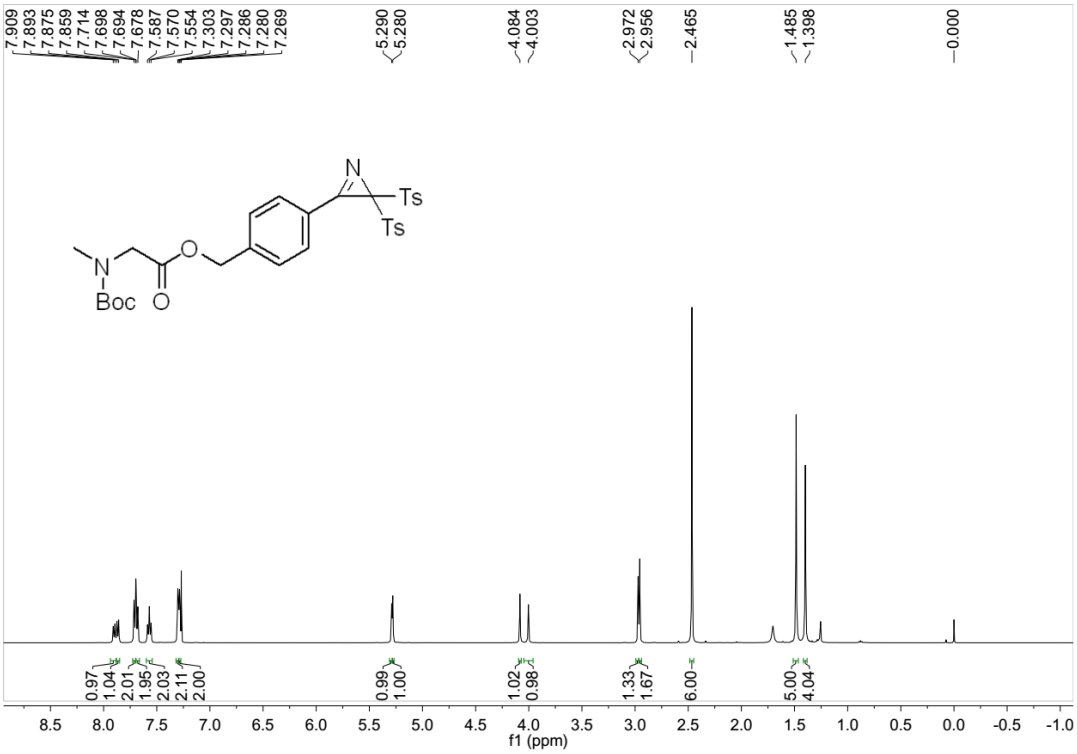


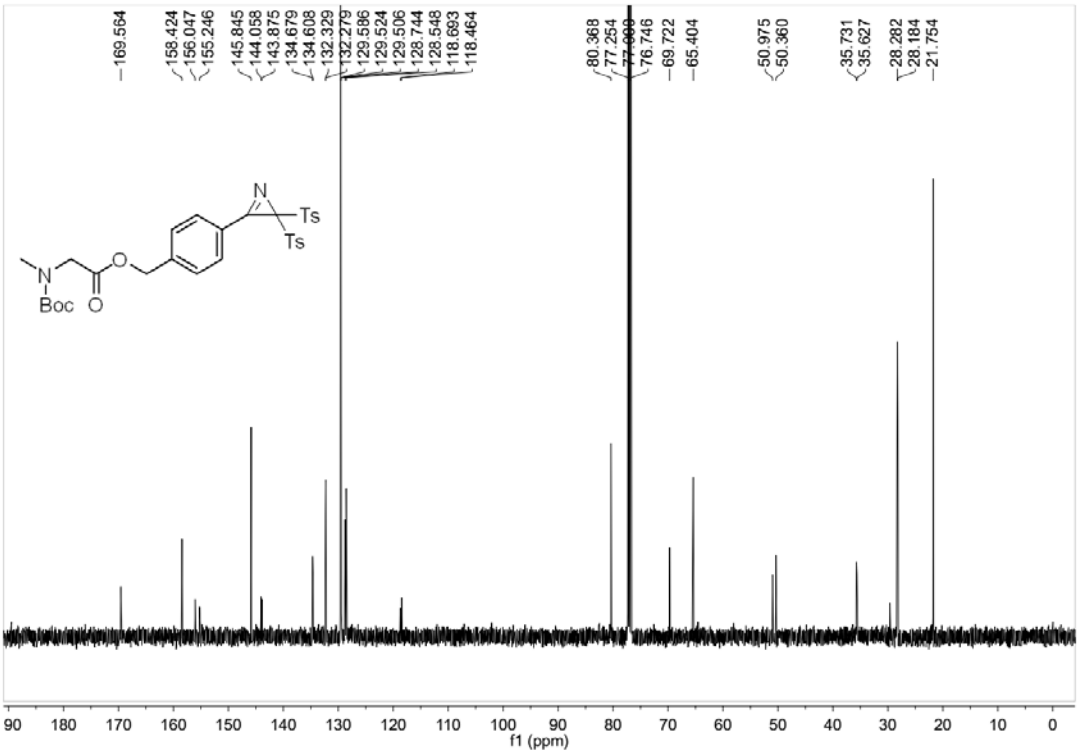
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-(2,2-ditosyl-2*H*-azirin-3-yl)benzoat e (3ra):



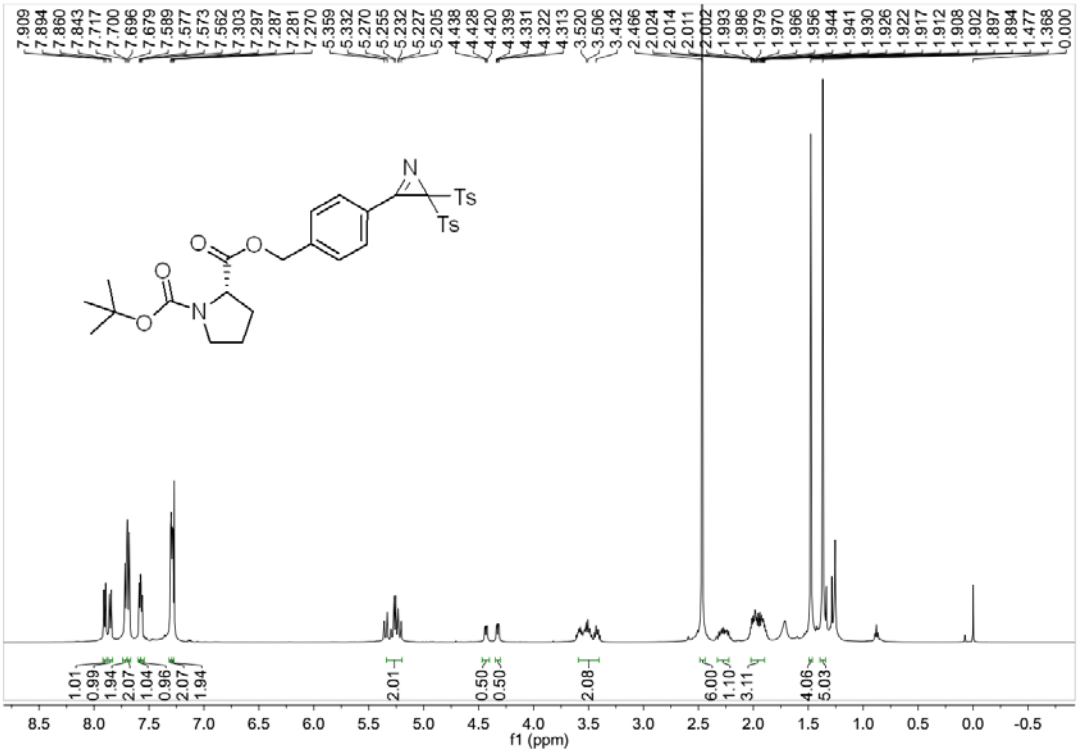


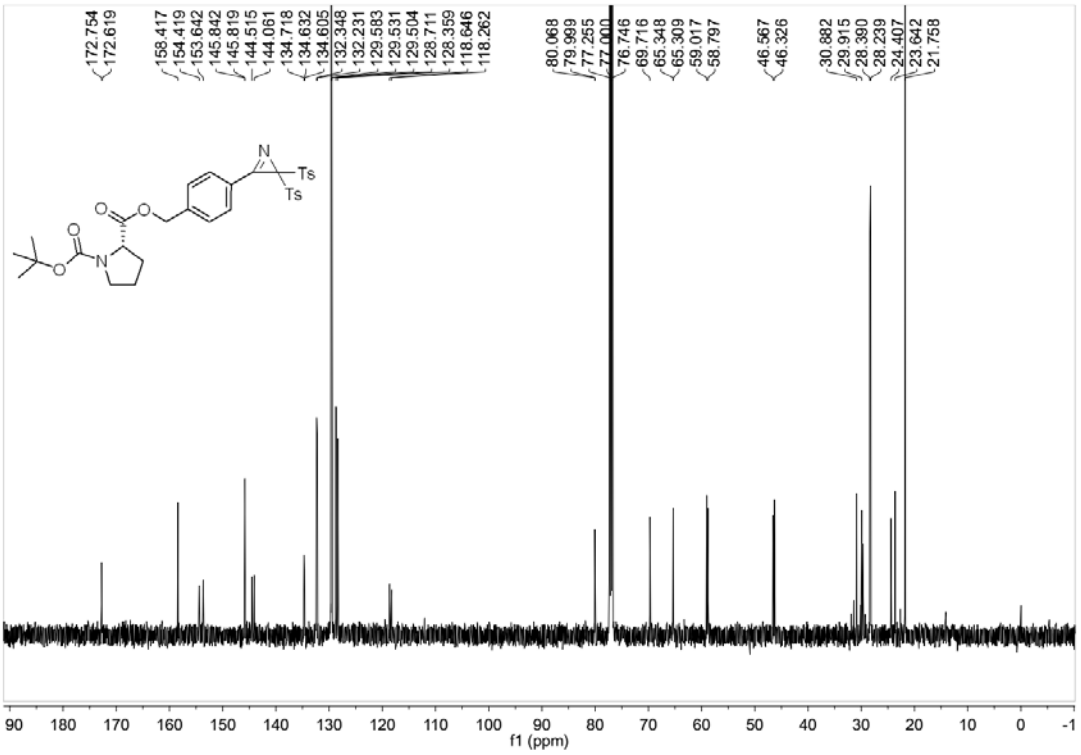
4-(2,2-Ditosyl-2*H*-azirin-3-yl)benzyl-*N*-(tert-butoxycarbonyl)-*N*-methylglycinate (3sa):



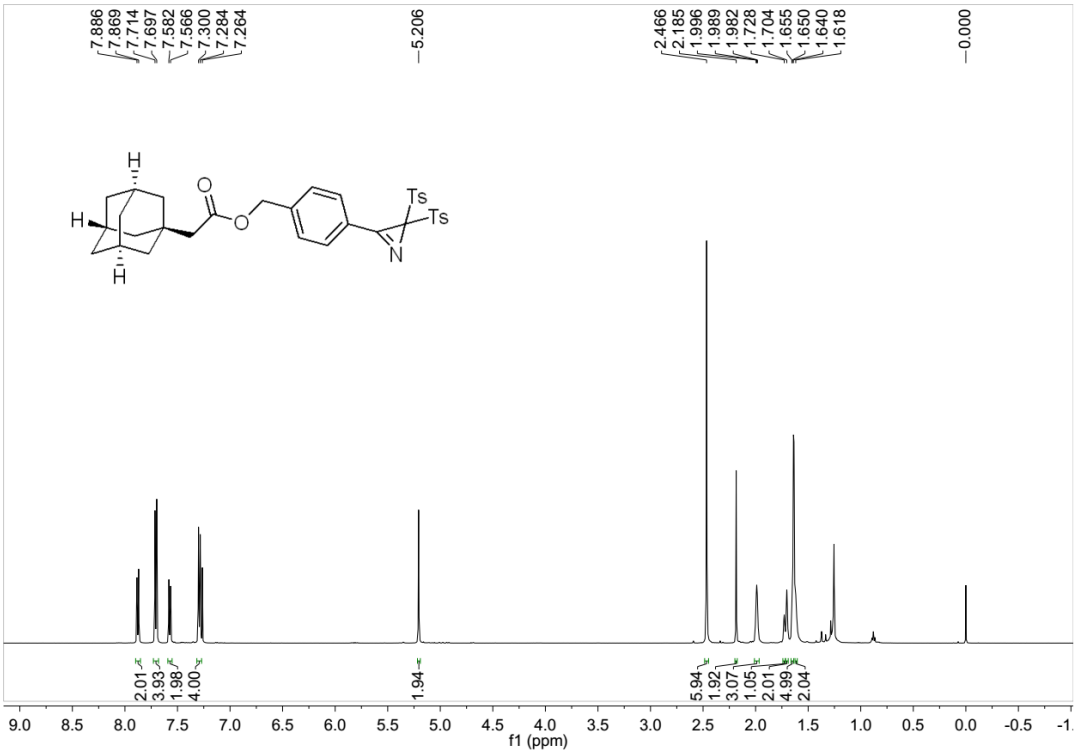


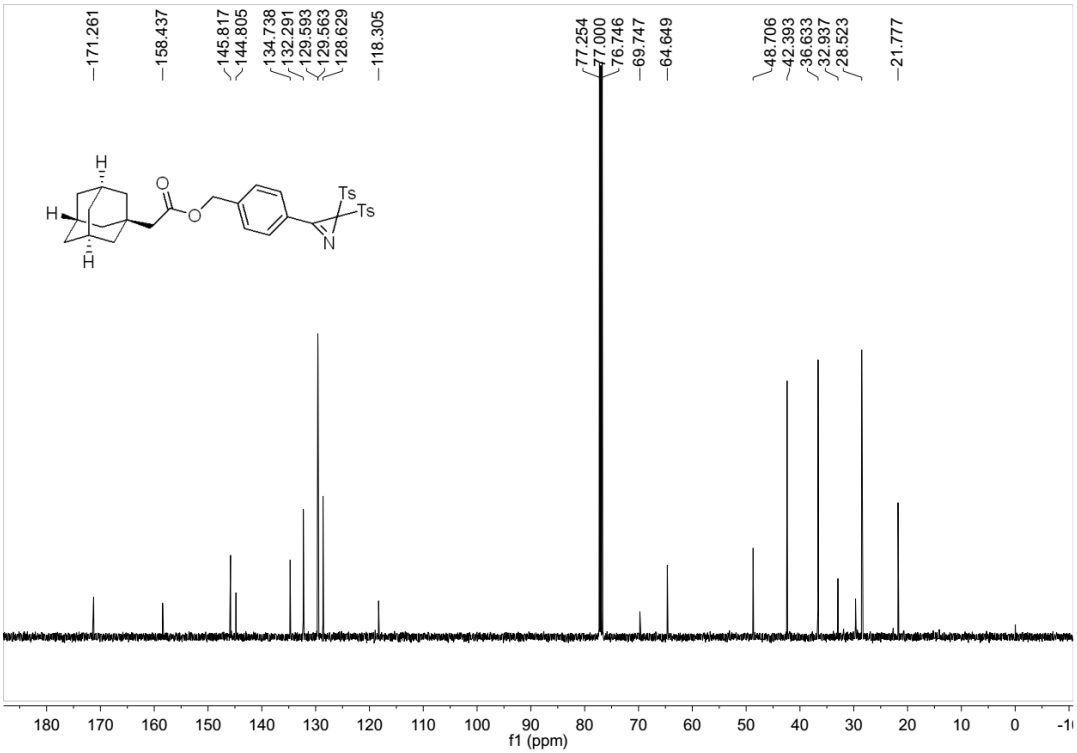
1-(*tert*-Butyl)-2-(4-(2,2-ditosyl-2*H*-azirin-3-yl)benzyl)-(*S*)-pyrrolidine-1,2-dicarboxylate (3ta):



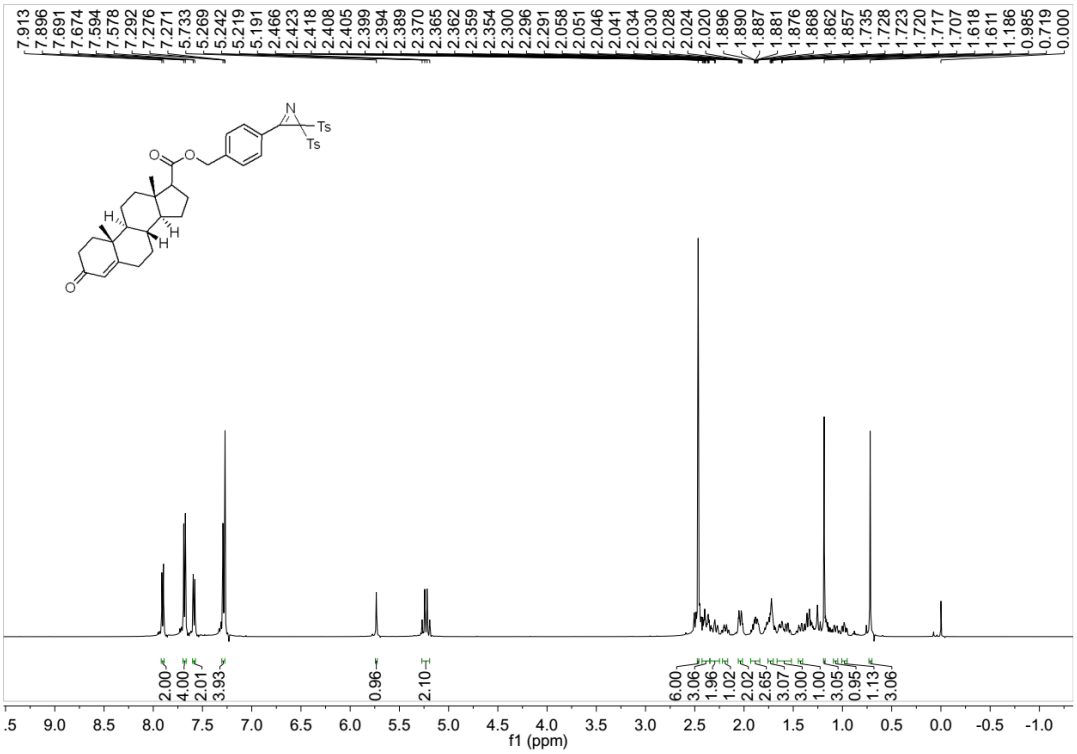


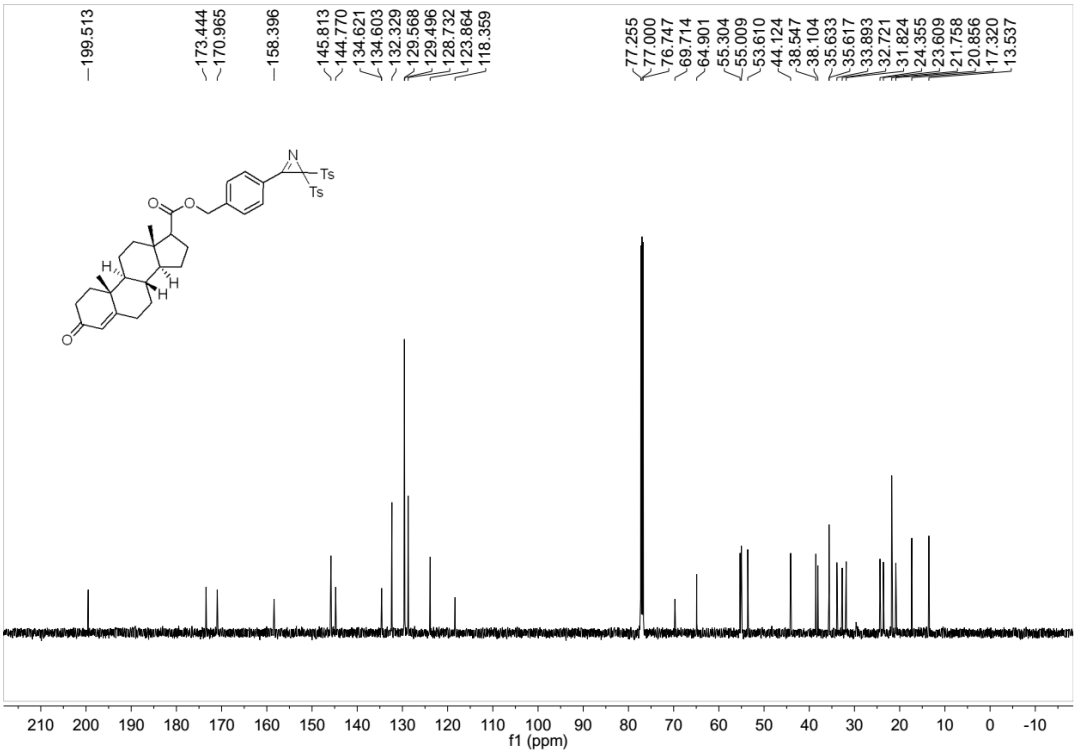
4-(2,2-Ditosyl-2*H*-azirin-3-yl)benzyl-2-((3*r*,5*r*,7*r*)-adamantan-1-yl)acetate (3ua):



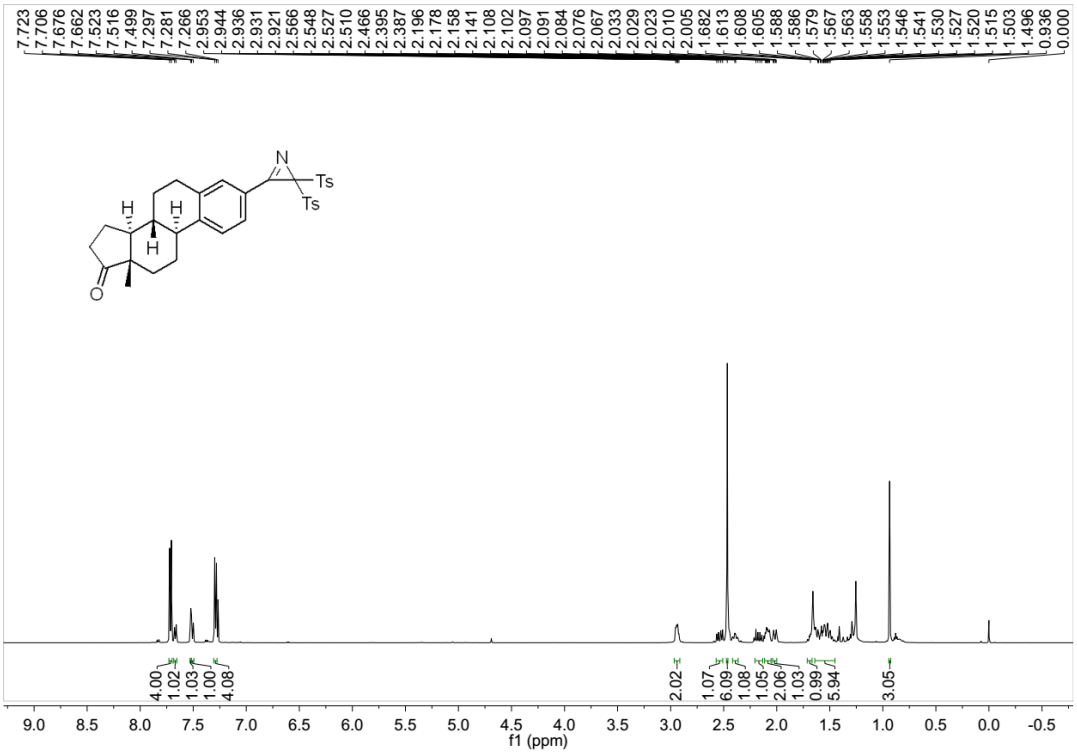


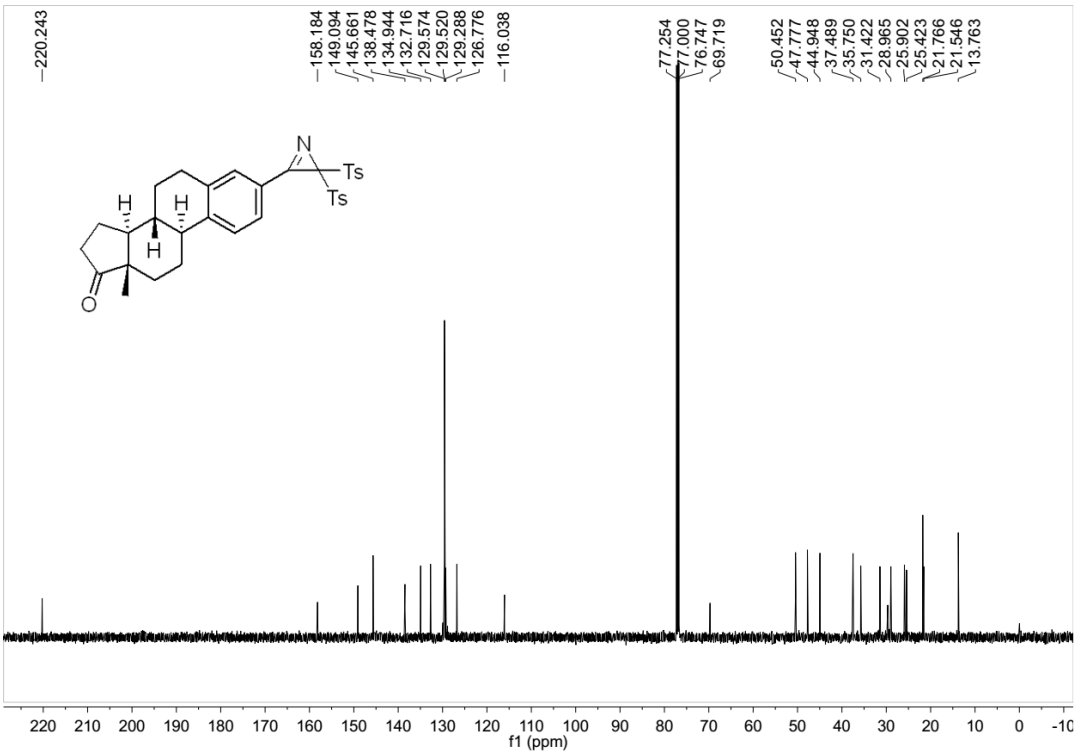
4-(2,2-Ditosyl-2*H*-azirin-3-yl)benzyl-(8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthrene-17-carboxylate (3va):



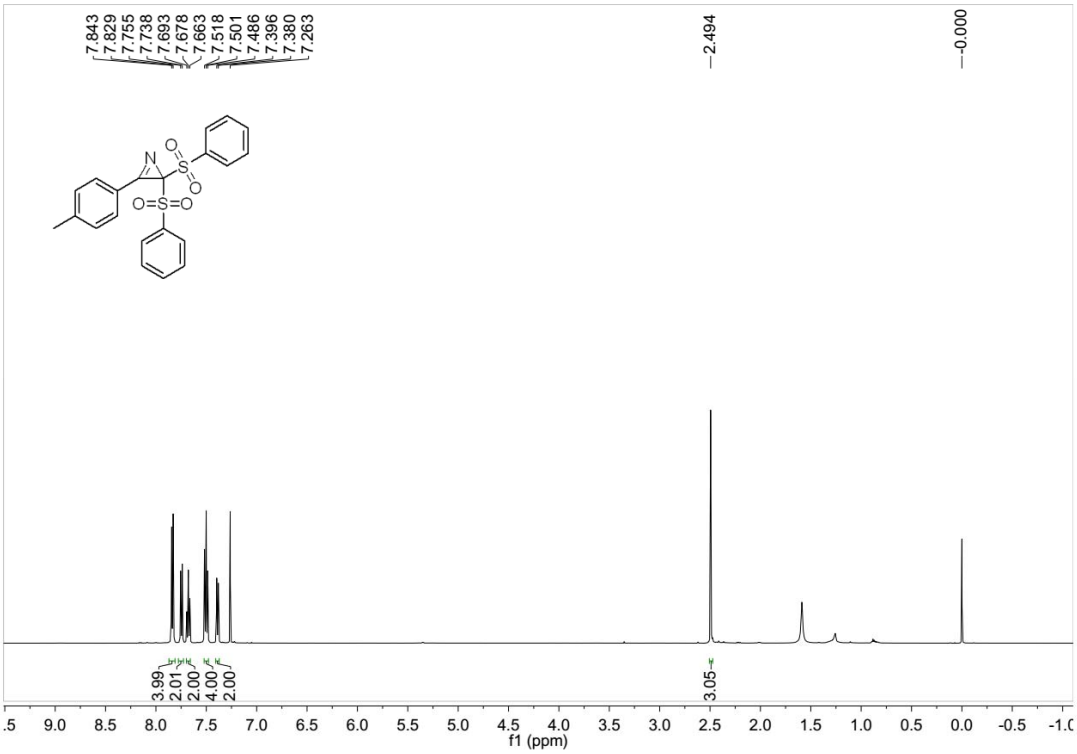


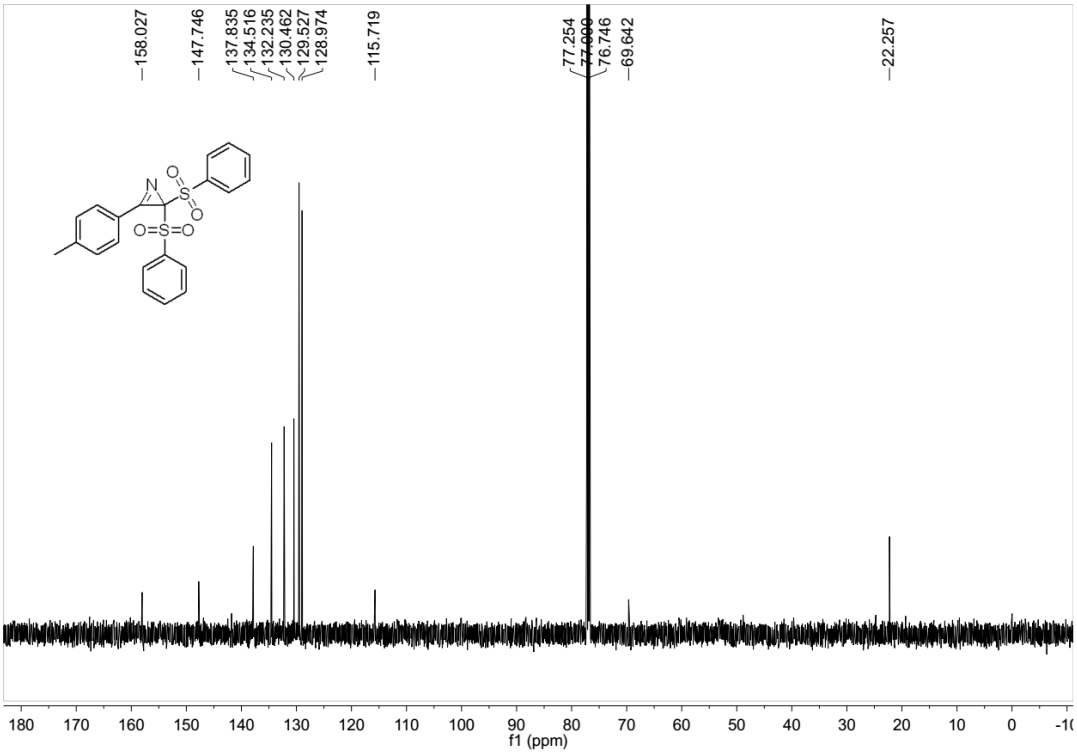
(8*S*,9*S*,13*S*,14*S*)-3-(2,2-ditosyl-2*H*-azirin-3-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (3wa):



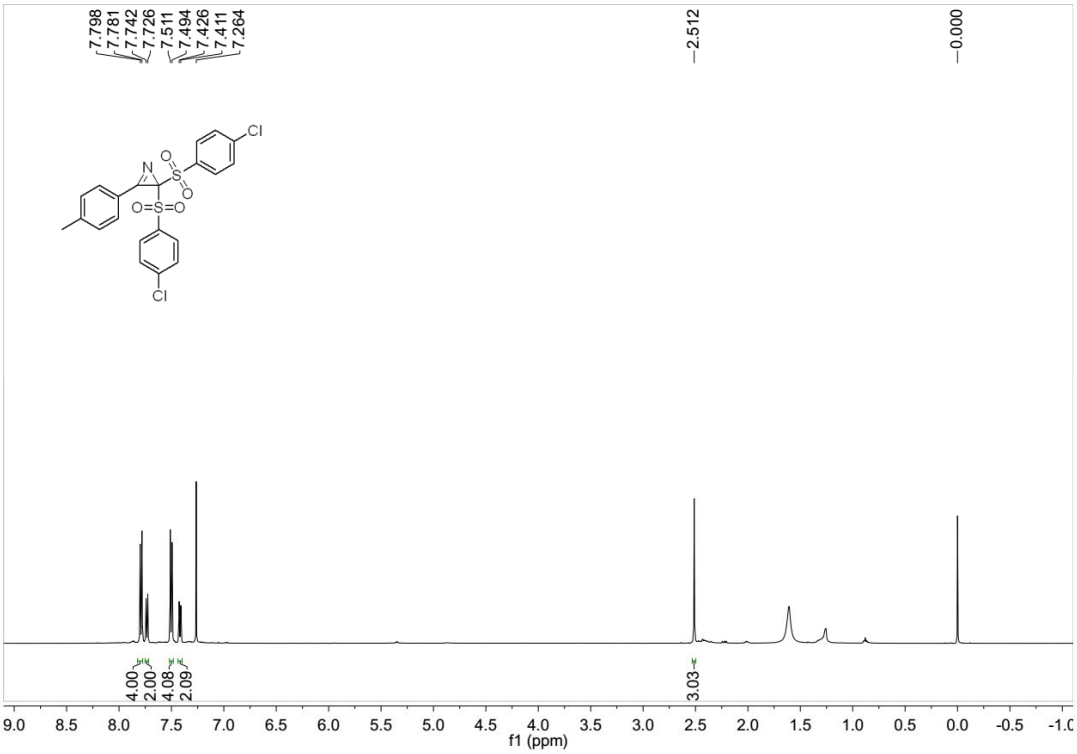


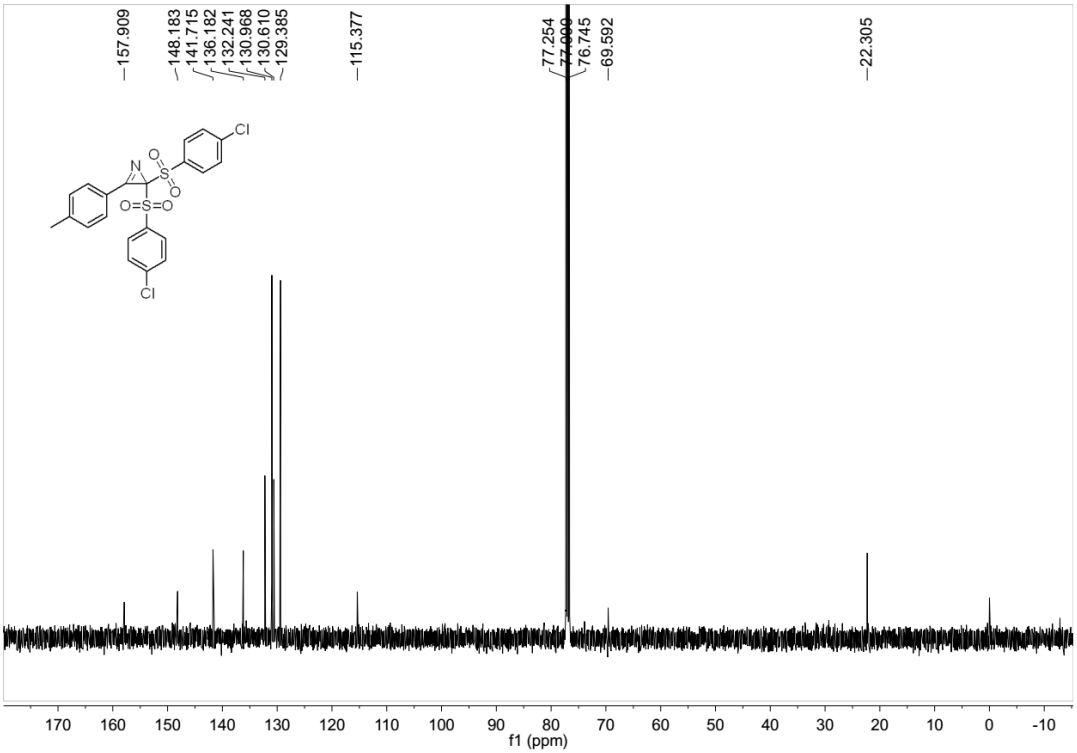
2,2-Bis(phenylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3cb):



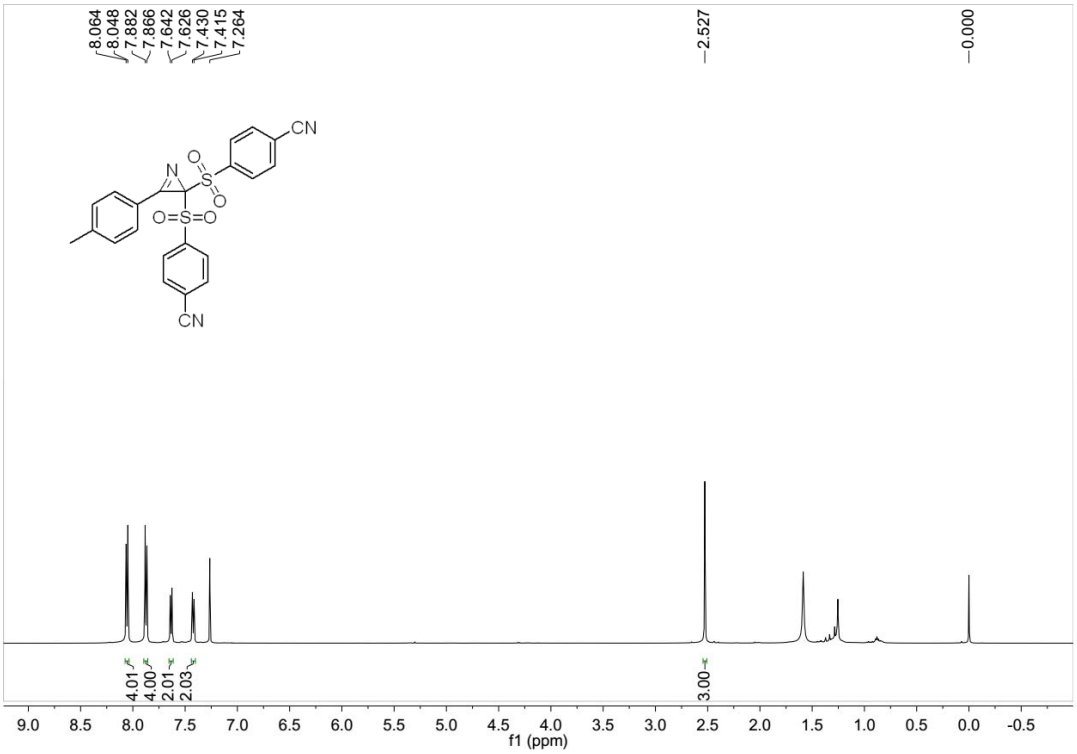


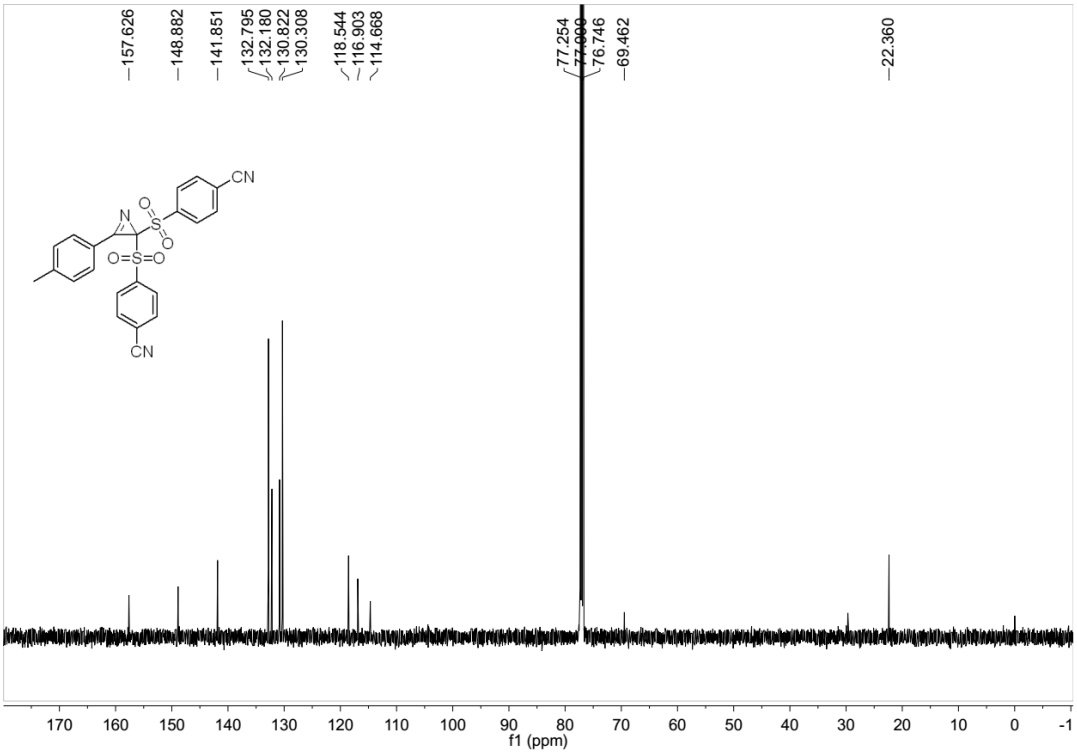
2,2-Bis((4-chlorophenyl)sulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3cc):



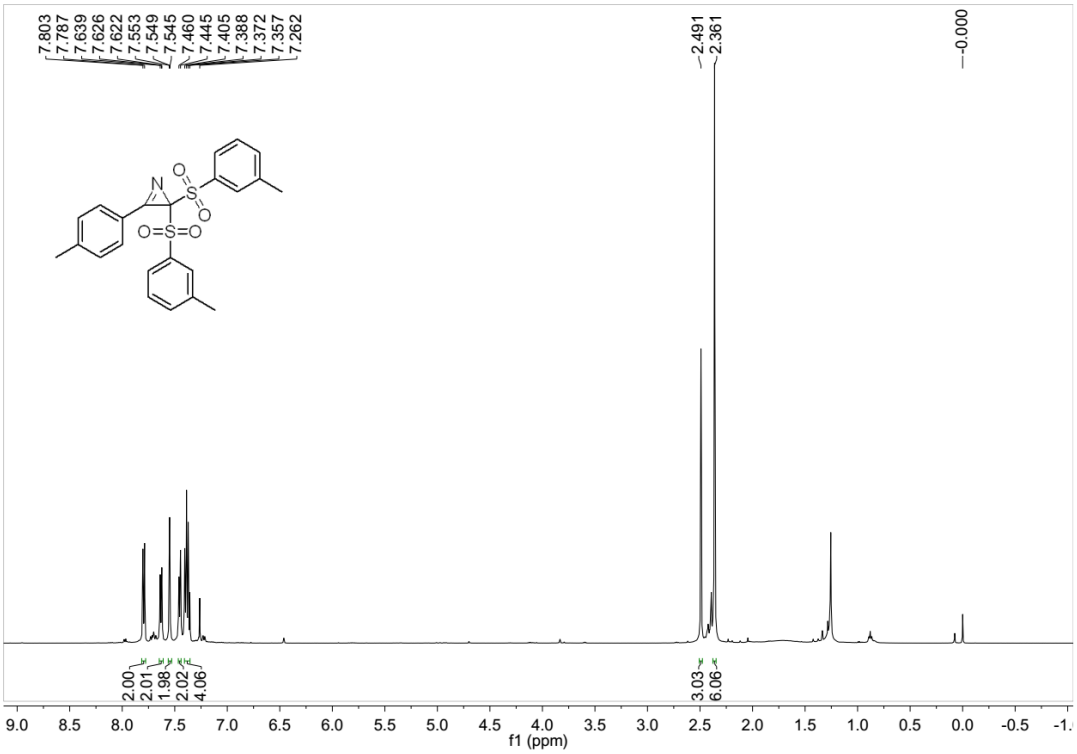


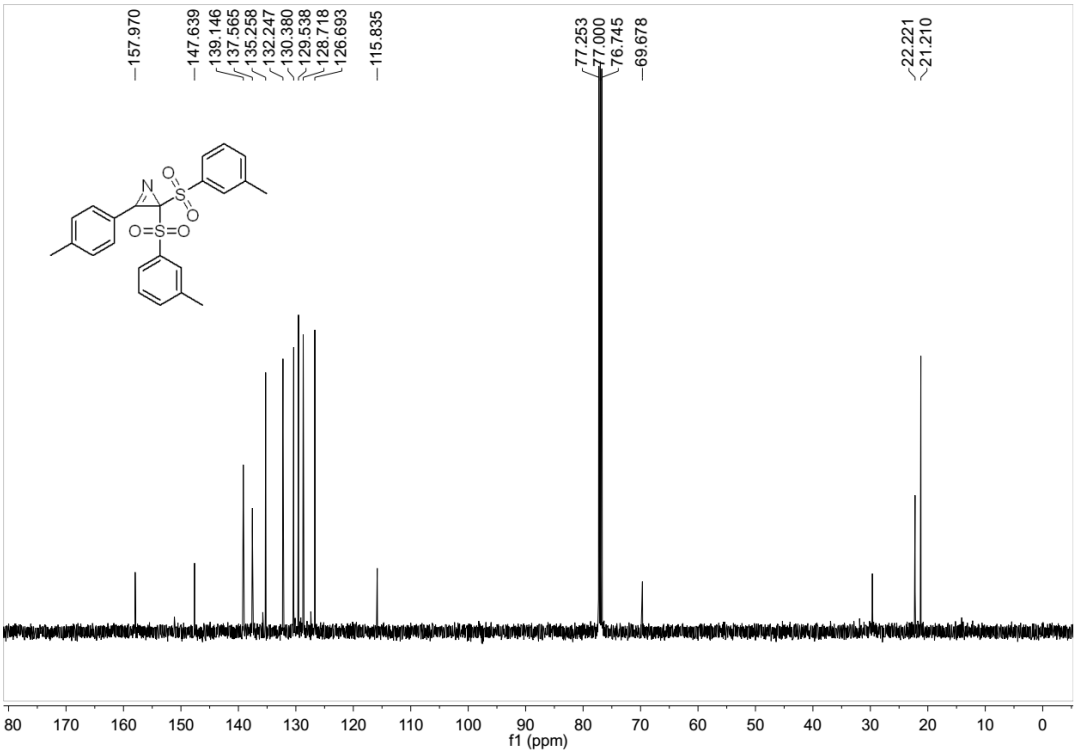
4,4'-(3-(*p*-Tolyl)-2*H*-azirine-2,2-disulfonyl)dibenzonitrile (3cd):



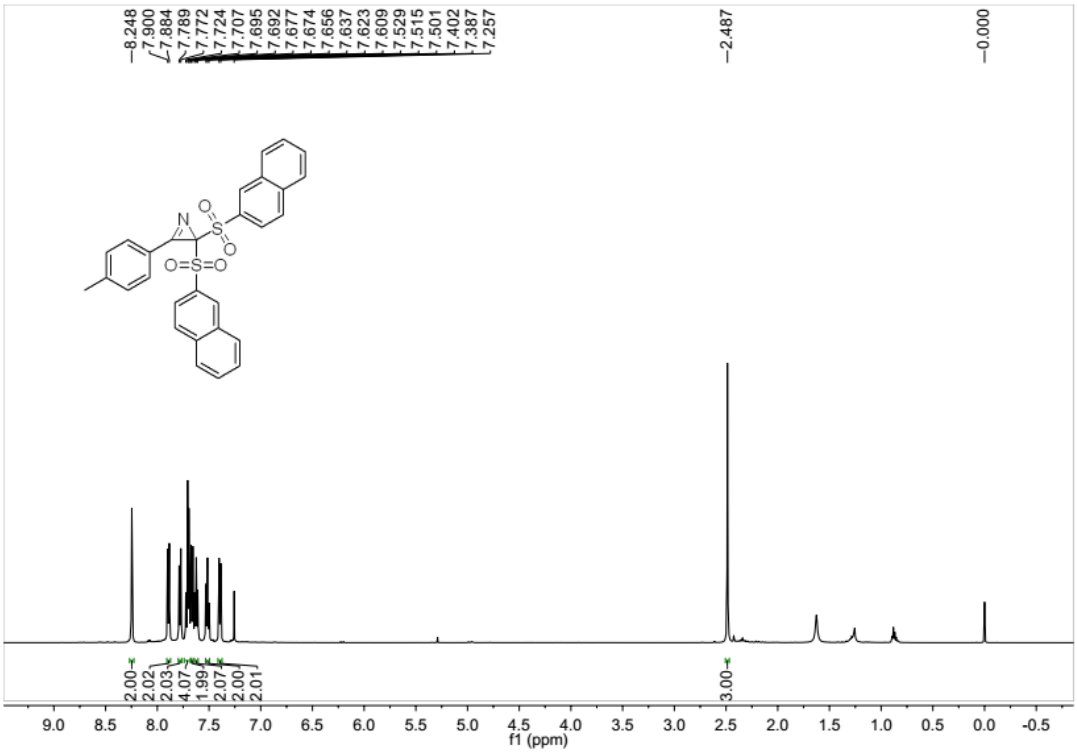


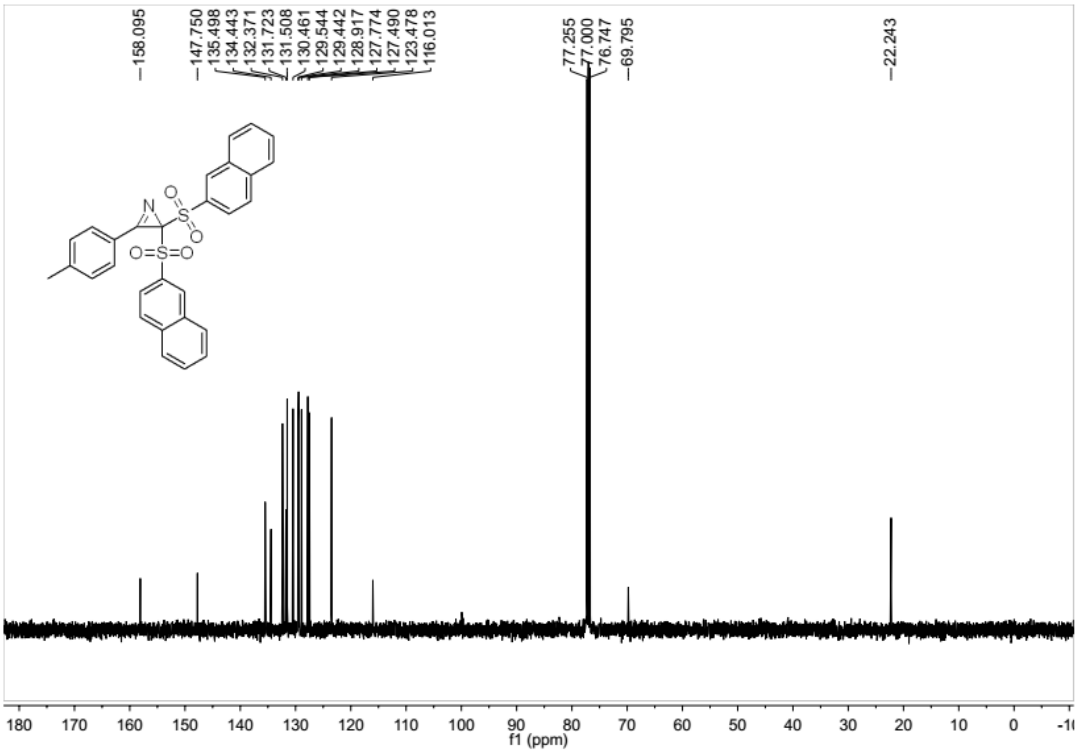
3-(*p*-Tolyl)-2,2-bis(*m*-tolylsulfonyl)-2*H*-azirine (3ce):



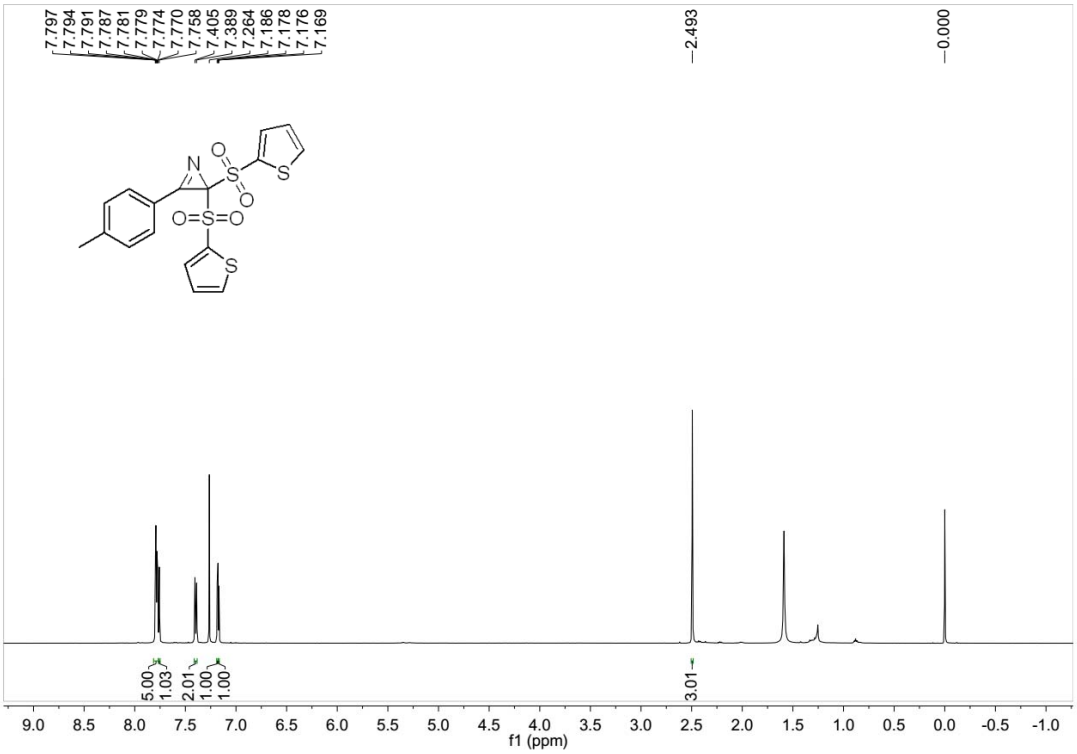


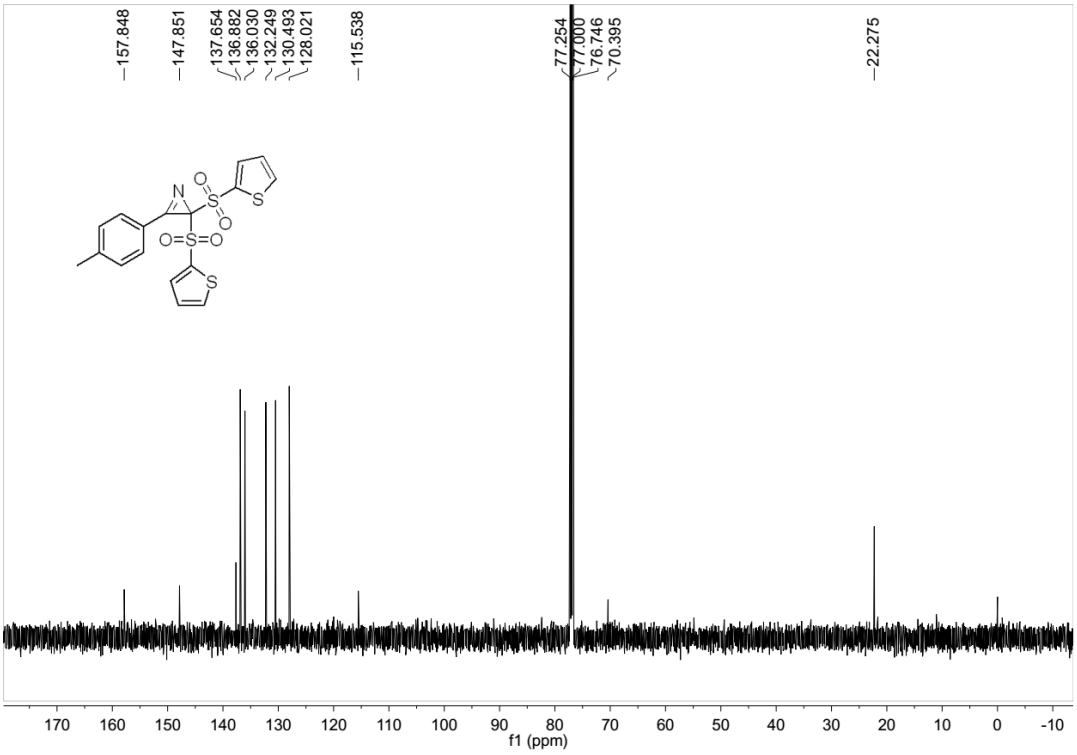
2,2-Bis(naphthalen-2-ylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3cf):



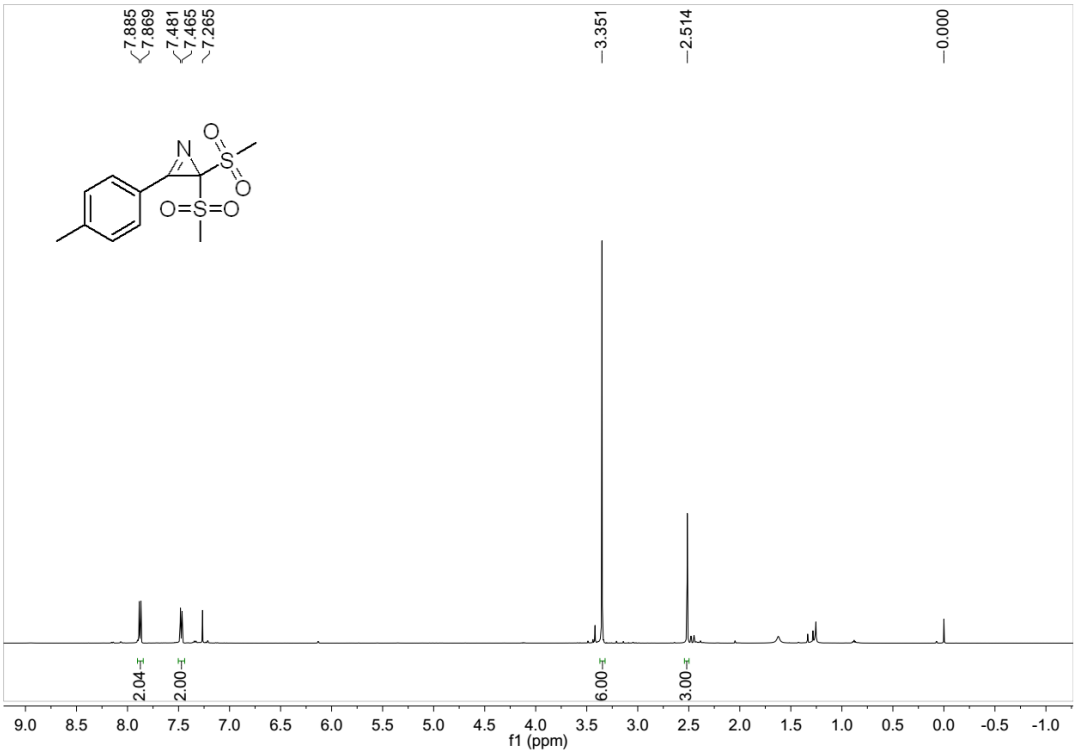


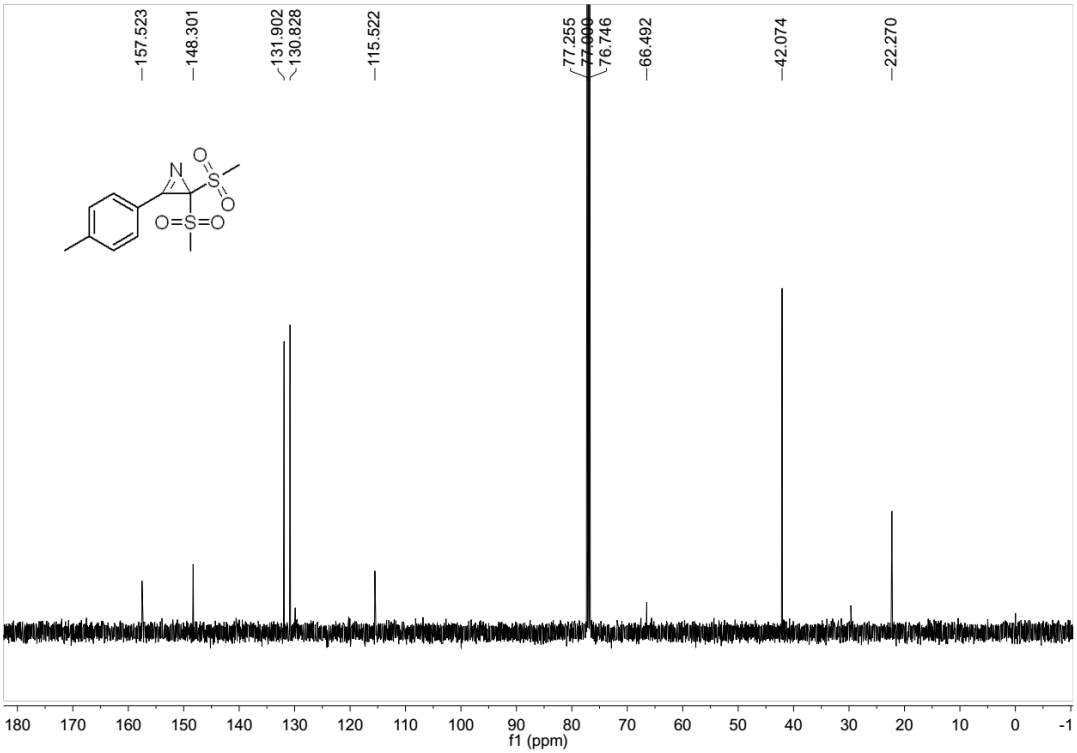
2,2-Bis(thiophen-3-ylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3cg):



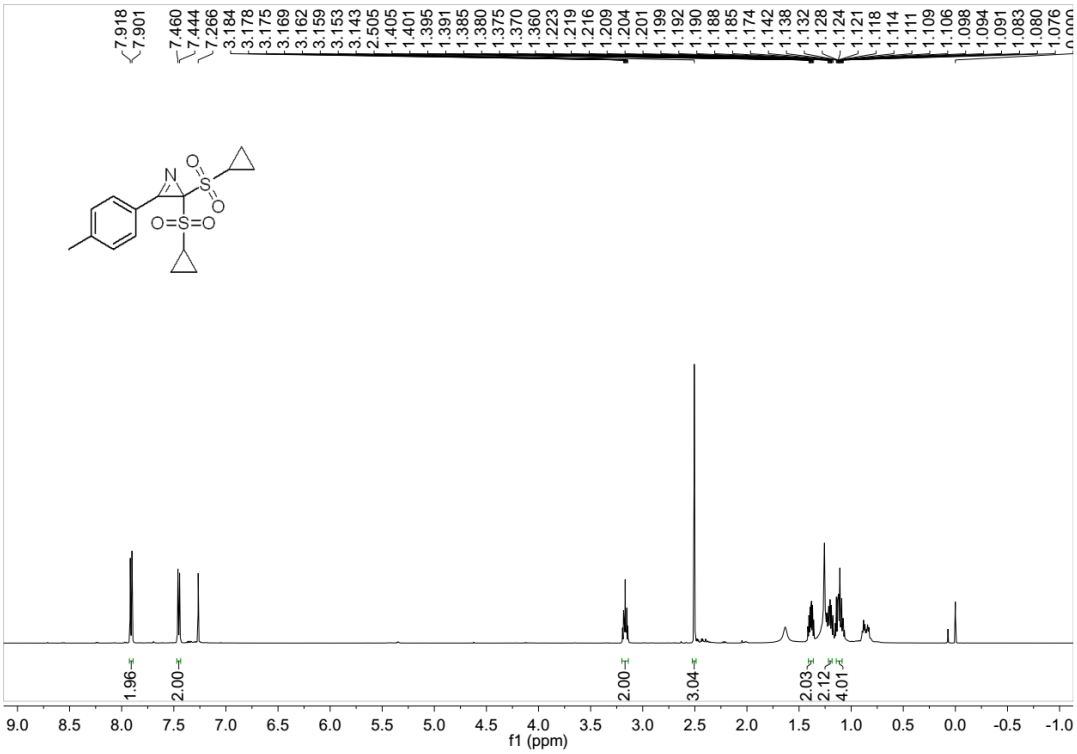


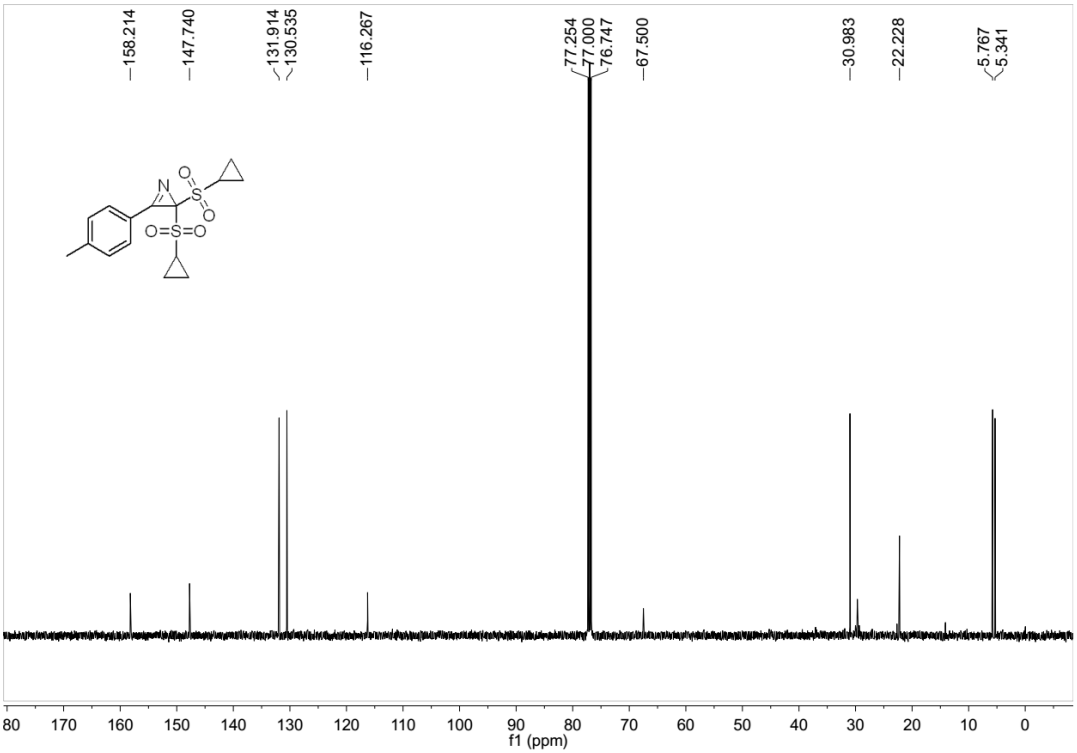
2,2-Bis(methylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3ch):



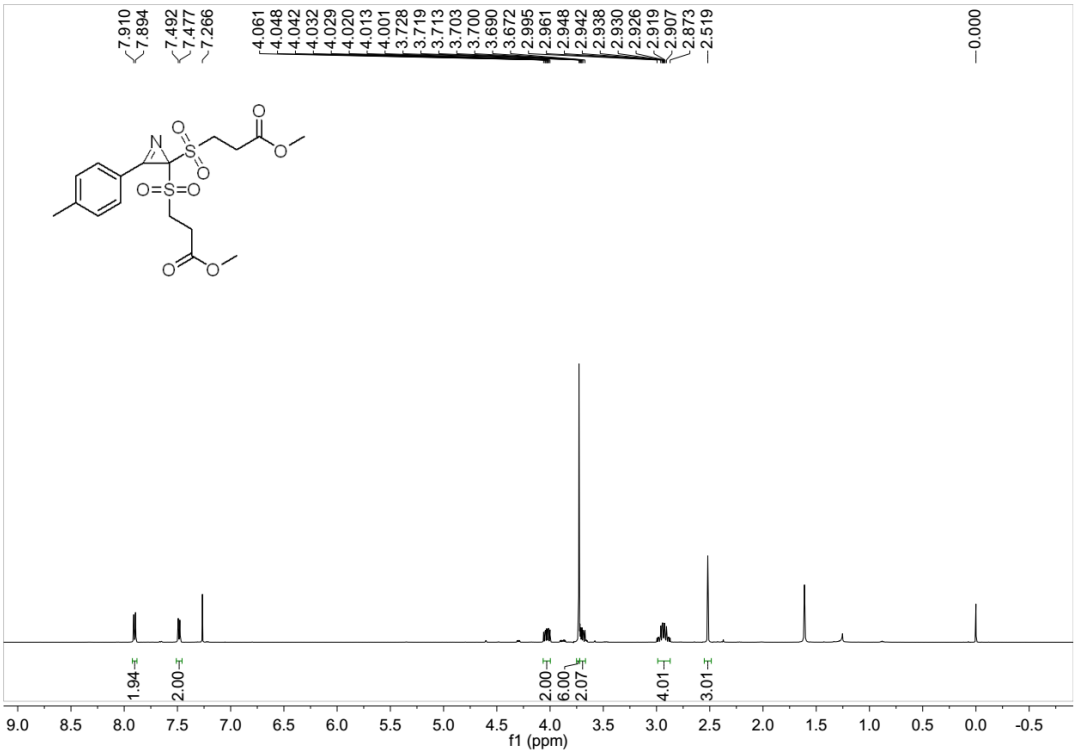


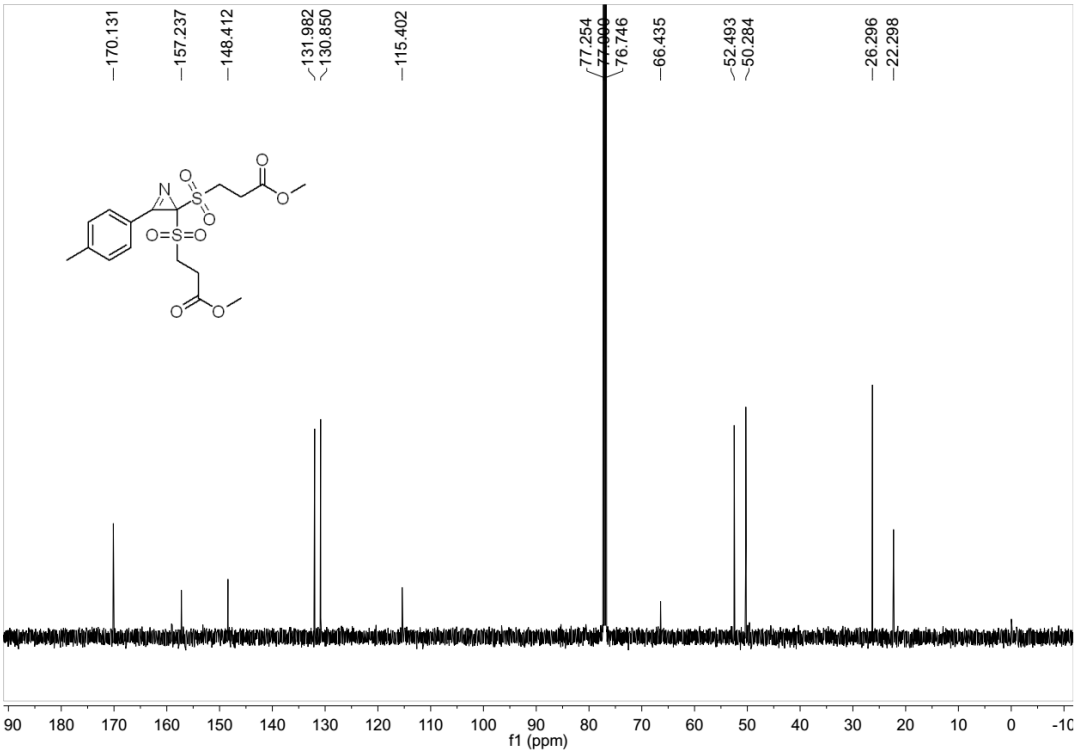
2,2-Bis(cyclopropylsulfonyl)-3-(*p*-tolyl)-2*H*-azirine (3ci):



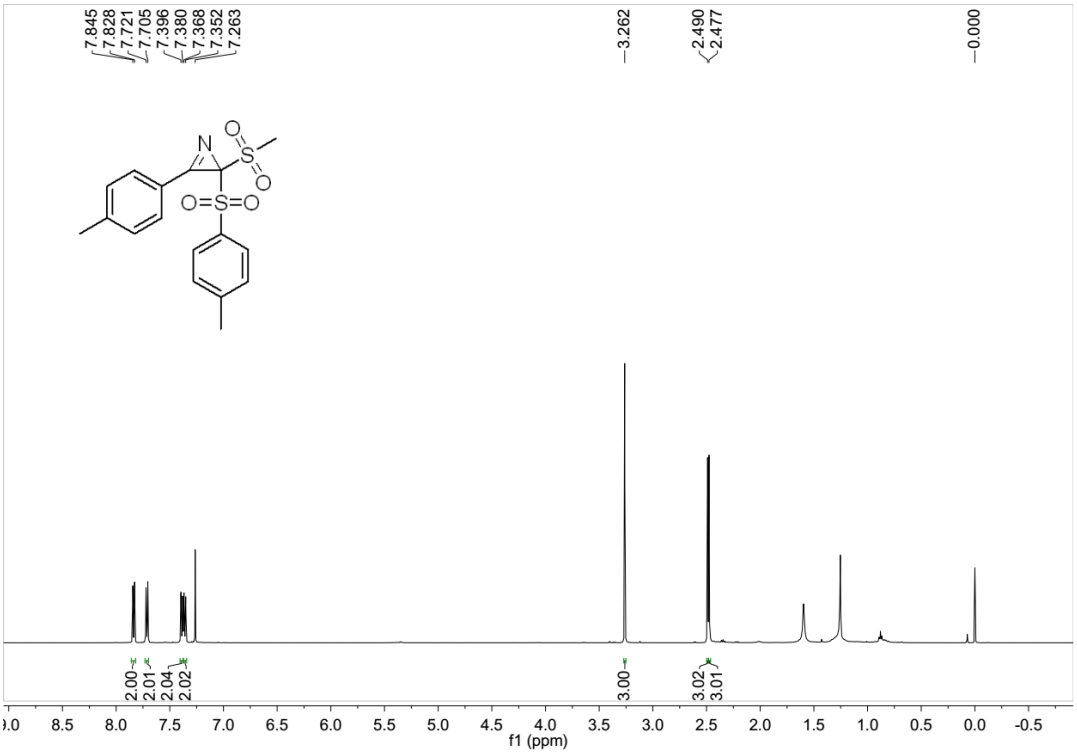


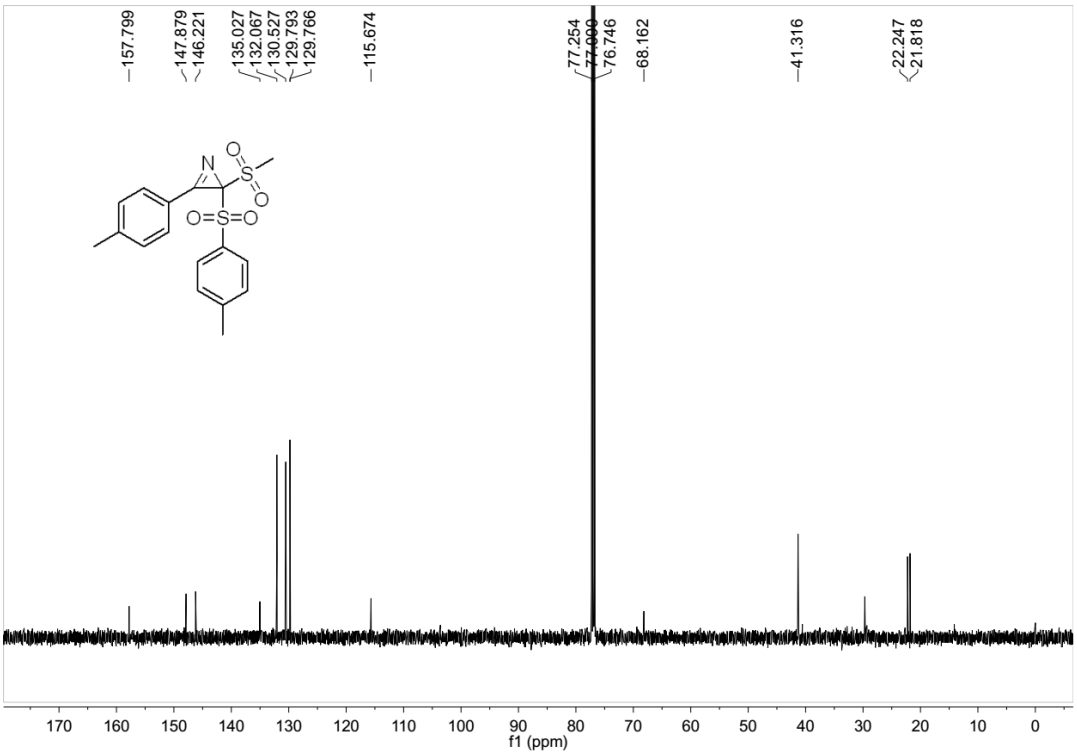
Dimethyl 3,3'-(3-(*p*-tolyl)-2*H*-azirine-2,2-disulfonyl)dipropionate (3cj):



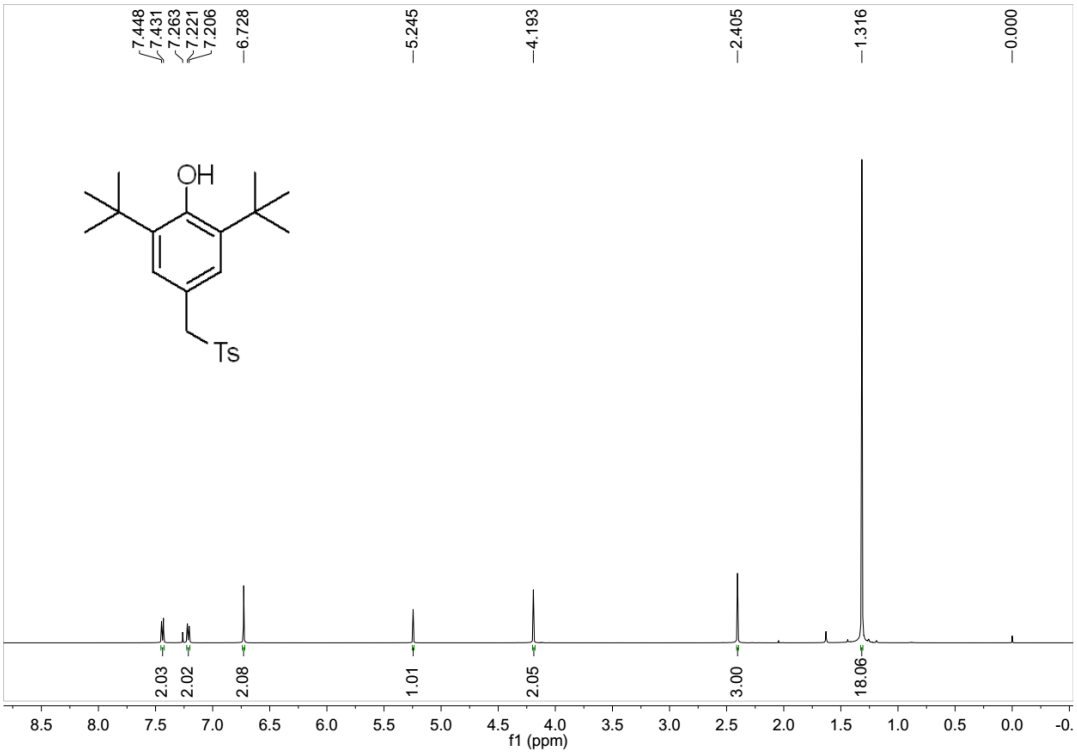


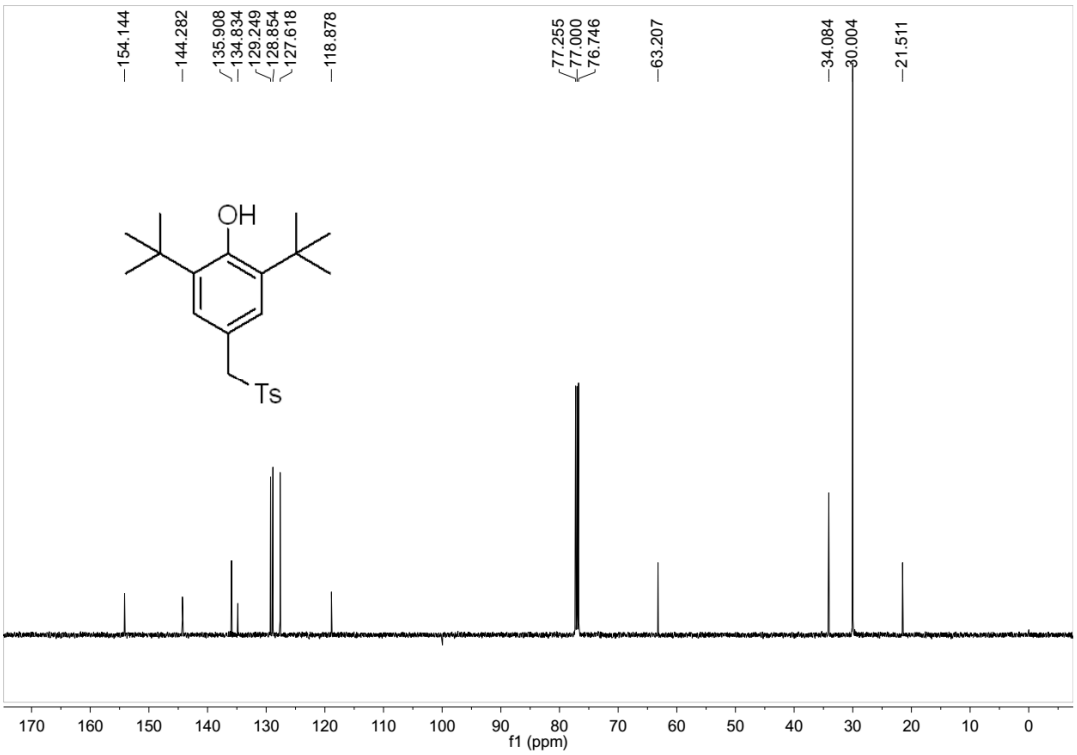
2-(Methylsulfonyl)-3-(*p*-tolyl)-2-tosyl-2*H*-azirine (3cah):



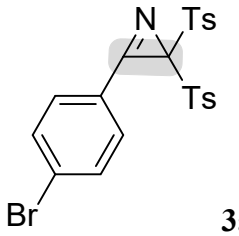


2,6-Di-*tert*-butyl-4-(tosylmethyl)phenol (4):

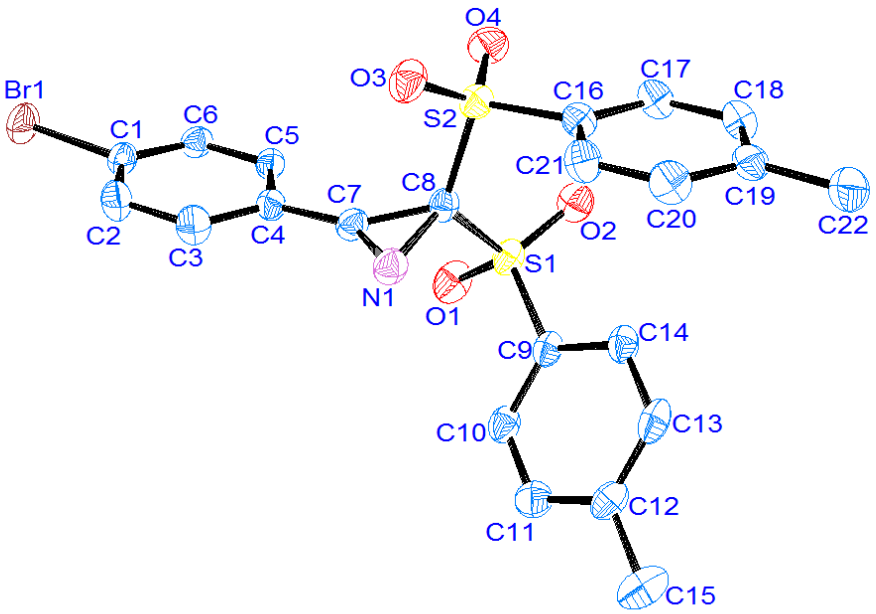




(D) The X-ray single-crystal diffraction analysis of 3aa



3aa (CCDC 1871132)



Molecular structure of 3aa with 30% probability ellipsoids

Table 1. Crystal data and structure refinement for A.

Identification code	**a**
Empirical formula	**C22 H18 Br N O4 S2**
Formula weight	**504.40**
Temperature	**296(2) K**
Wavelength	**0.71073 A**
Crystal system, space group	**Monoclinic, P2(1)/n**
Unit cell dimensions	**a = 12.9721(15) A alpha = 90 deg.**
	b = 11.6133(14) A beta = 112.6630(10) deg.

	c = 15.7313(19) A gamma = 90 deg.
Volume	2186.9(5) A^3
Z, Calculated density	4, 1.532 Mg/m^3
Absorption coefficient	2.099 mm^-1
F(000)	1024
Crystal size	0.18 x 0.14 x 0.12 mm
Theta range for data collection	2.25 to 25.50 deg.
Limiting indices	-15<=h<=15, -14<=k<=13, -17<=l<=19
Reflections collected / unique	16519 / 4060 [R(int) = 0.0447]
Completeness to theta = 25.50	99.9 %
Absorption correction	None
Max. and min. Transmission	0.777 and 0.710
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4060 / 0 / 273
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0768
R indices (all data)	R1 = 0.0732, wR2 = 0.0934
Largest diff. peak and hole	0.334 and -0.353 e.Å^3