N-Heterocyclic Carbene-Catalyzed Rearrangments of Vinyl Sulfones

Roxanne L. Atienza, Howard S. Roth, and Karl A. Scheidt*
Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208

Supporting Information

General Information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. Dichloromethane was purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and potassium permangenate stain followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker A500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl3 at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on a Bruker A500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl3 at 77.0 ppm). Mass spectral data for the isoxazolidine products and the cross-over experiment were acquired in the Electron Ionization mode (EI) on a Waters GCT Premier mass spectrometer (Beverly, MA), with an Agilent 7890 gas chromatograph (Santa Clara, CA). The spectra were analyzed in the positive ion mode on the MS using the dynamic range enhancement feature, with a scan time of 0.9 s and an interscan delay of 0.1 s. Samples were separated on a Phenomenex Zebron 5 column (Torrence, CA, 60 m, 0.25 mm OD, 0.25 μm film thickness) with a temperature ramp from 200^{o}C held for 2.0 min, 5 ^{o}C/min to 300 ^{o}C and held for 20 min. The sample (1 μl) was injected onto the column with a mobile phase of helium at 1 mL/min. and an inlet temperature of 250 ^{o}C and a split of 30:1.

All achiral nitrones were prepared according to Fu.[3] The nitrone with chiral auxiliary was prepared according to literature prep. [4]

Procedure for the Synthesis of 1,1-bis(phenylsulfonyl)ethylene 1

Following a procedure from Steinbeck[5], to a 100mL round bottom flask containing a magnetic stirring bar was added paraformaldehyde (2.6 g, 28.9 mmol) and methanol (22 mL, 1.3 M). The slurry was then heated to reflux at 80 °C. Once the solution became transparent, the flask was removed from heat and cooled to 0 °C. To the flask was added piperidine (7 mL, 6 mol) at 0 °C and stirred for 15 min. Then, the corresponding arylsulfonyl methane (2.1 g, 7.1 mmol) in 1,4-dioxane (14 mL, 0.5 M) was added dropwise at 0 °C. The reaction stirred for 15 min. Ice water was added to the flask and after 5 min, the solid was collected through vacuum filtration. The white solid (96 %) was dried over P_2O_5. The white solid was dissolved in benzene in a

---

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal*. **1996**, *15*, 1518-1520.

[2] Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals;* 3rd Ed., Pergamon Press, Oxford. 1988.

[3] Lo, M. M. C.; Fu, G. C. *J. Am. Chem. Soc*. **2002**, *124*, 4572-4573.

[4] Cicchi, S.; Marradi, M.; Corsi, M.; Faggi, C.; Goti, A. *Eur. J. Org. Chem.* **2003**, *21*, 4152-4161.

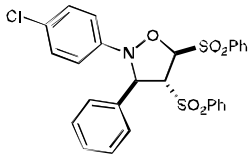
[5] Stetter, H.; Steinbeck, K. *Justus Liebigs Annalen der Chemie* **1974**, 1315-1321.

flame-dried 100 mL round bottom flask. Dry HCl gas was bubbled into the solution until the slurry becomes clear. At this point, the reaction flask was heated to reflux at 80 °C for 3 hrs. The reaction was cooled to 23 °C and the reaction mixture was filtered and concentrated. Recrystallization from benzene/hexanes or ethyl acetate/hexanes produced an off-white solid (91 %). The spectral data matches the literature data.

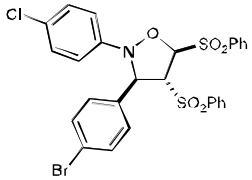
General Procedure for the formation of isoxazolidine product

To a reaction vial containing a magnetic stirring bar was added the corresponding 1,1-bissulfone (20 mg, 65 mmol), nitrone (1.05 equiv.), flame-dried 4 Å MS, and solvent (0.1 mL). Then, a solution with the corresponding solvent containing the azolium salt (13 mmol) and base (13 mmol) was added, bringing the reaction solution to 0.1 M. The reaction was then heated to reflux for 24-48 hrs. The unpurified reaction was filtered through a pad of silica, washing with EtOAc and concentrated *in vacuo*. The material was purified by column chromatography (15% EtOAc/hexanes).

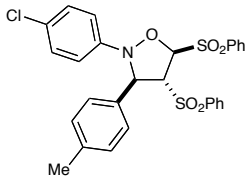
Characterization data



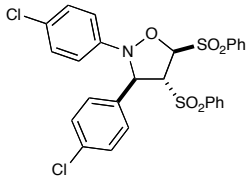
(3*R*,4*R*,5*S*)-2-(4-chlorophenyl)-3-phenyl-4,5-bis(phenylsulfonyl)isoxazolidine (4): Prepared according to the general procedure with dichloromethane, yielding 33 mg (94%) as an pale orange solid. IR: 2967, 2926, 1490, 1447, 1310, 1160, 1150 cm^{-1}; 1H-NMR (500 MHz; CDCl3): δ 7.95-7.93 (m, 1H), 7.85-7.83 (m, 1H), 7.72-7.71 (m, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.60-7.57 (m, 1H), 7.53-7.50 (m, 1H), 7.32-7.22 (m, 4H), 7.12-7.09 (m, 1H), 6.78-6.75 (m, 1H), 5.45 (dd, *J* = 3.2, 2.2 Hz), 4.89 (dd, *J* = 7.8, 3.3 Hz), 4.66 (d, *J* = 7.8 Hz); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 145.4, 137.2, 136.0, 134.9, 131.5, 129.2, 123.2, 121.4, 91.3, 74.8, 72.0; HRMS (ESI): Mass calcd for $C_{27}H_{22}ClNO_5S_2$ $[M+H]^+$, 541. Found $[M+H]^+$, 541.



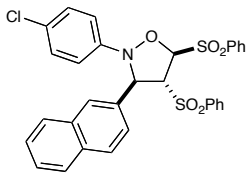
(3R,4R,5S)-3-(4-bromophenyl)-2-(4-chlorophenyl)-4,5-bis(phenylsulfonyl)isoxazolidine (5): Prepared according to the general procedure with dichloromethane, yielding 35 mg (87%) as an off-white solid. IR: 2967, 2926, 1488, 1447, 1311, 1150, 1010 $cm^{-1;}$ ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.91-7.90 (m, 2H), 7.86-7.84 (m, 2H), 7.74-7.70 (m, 2H), 7.60-7.55 (m, 5H), 7.40-7.39 (m, 2H), 7.25-7.23 (m, 3H), 7.15-7.13 (m, 2H), 6.79-6.77 (m, 2H), 5.39 (d, *J* = 3.1 Hz, 1H), 4.80 (dd, *J* = 7.6, 3.2 Hz, 1H), 4.67 (d, *J* = 7.6 Hz, 1H); [[^{13}C-NMR (125 MHz; $CDCl_3$): δ 145.4, 137.2, 136.1, 135.4, 135.2, 134.4, 132.6, 132.0, 130.5, 130.1, 129.94, 129.78, 129.3, 129.11, 128.98, 121.8, 91.6, 74.9, 71.4; HRMS (ESI): Mass calcd for $C_{27}H_{21}BrNO_5S_2$ $[M+H]^+$, 620. Found $[M+H]^+$, 620.



(3*R*,4*R*,5*S*)-2-(4-chlorophenyl)-4,5-bis(phenylsulfonyl)-3-*p*-tolylisoxazolidine (6): Prepared according to the general procedure with dichloromethane, yielding 22 mg (61%) as an off-white solid. IR: 2967, 2926, 1490, 1449, 1325, 1309, 1150, 1077 cm^{-1}; 1H-NMR (500 MHz; CDCl3): δ 7.94-7.92 (m, 2H), 7.94-7.92 (m, 2H), 7.85-7.83 (m, 2H), 7.85-7.83 (m, 2H), 7.69 (dt, *J* = 22.7, 7.5 Hz, 2H), 7.69 (dt, *J* = 22.7, 7.5 Hz, 2H), 7.59-7.51 (m, 5H), 7.59-7.51 (m, 5H), 7.18-7.17 (m, 3H), 7.18-7.17 (m, 3H), 7.11-7.09 (m, 2H), 7.11-7.09 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.77-6.75 (m, 2H), 6.77-6.75 (m, 2H), 5.42 (d, *J* = 3.3 Hz, 1H), 5.42 (d, *J* = 3.3 Hz, 1H), 4.86 (dd, *J* = 7.8, 3.3 Hz, 1H), 4.86 (dd, *J* = 7.8, 3.3 Hz, 1H), 4.64 (d, *J* = 7.8 Hz, 1H), 4.64 (d, *J* = 7.8 Hz, 1H), 2.30 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 139.1, 137.1, 136.0, 134.81, 134.67, 131.7, 131.2, 129.72, 129.64, 129.4, 128.8, 128.4, 121.3, 91.3, 74.7, 71.6, 21.3; HRMS (ESI): Mass calcd for $C_{28}H_{24}ClNO_5S_2$ $[M+H]^+$, 555. Found $[M+H]^+$, 555.

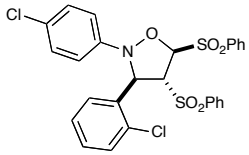


(3*R*,4*R*,5*S*)-2,3-bis(4-chlorophenyl)-4,5-bis(phenylsulfonyl)isoxazolidine (7): Prepared according to the general procedure with dichloromethane, yielding 28 mg (76%) as an off-white solid. IR: 2924, 2853, 1489, 1448, 1312, 1161, 1151, 1088 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.92-7.90 (m, 2H), 7.86-7.85 (m, 2H), 7.74-7.69 (m, 2H), 7.60-7.55 (m, 5H), 7.31-7.29 (m, 2H), 7.25-7.23 (m, 2H), 7.14-7.12 (m, 2H), 6.79-6.77 (m, 2H), 5.40 (d, *J* = 3.2 Hz, 1H), 4.81 (dd, *J* = 7.6, 3.2 Hz, 1H), 4.68 (d, *J* = 7.6 Hz, 1H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 145.1, 137.0, 135.8, 135.25, 135.14, 134.9, 133.6, 131.8, 130.00, 129.88, 129.69, 129.52, 129.40, 129.1, 128.9, 121.5, 91.4, 74.7, 71.1; HRMS (ESI): Mass calcd for $C_{27}H_{21}Cl_2NO_5S_2$ $[M+H]^+$, 576. Found $[M+H]^+$, 576.

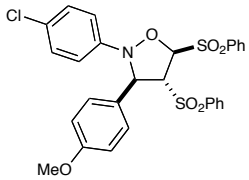


(3*R*,4*R*,5*S*)-2-(4-chlorophenyl)-3-(naphthalen-2-yl)-4,5-bis(phenylsulfonyl)isoxazolidine (8): Prepared according to the general procedure with dichloromethane, yielding 22 mg (74%) as an off-white solid. IR: 3064, 2924, 1489, 1448, 1311, 1152, 1085 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.99-7.97 (m, 2H), 7.83-7.78 (m, 5H), 7.75-7.72 (m, 1H), 7.68-7.55 (m, 7H), 7.52-7.43 (m, 6H), 7.08-7.06 (m, 2H), 6.81-6.78 (m, 2H), 5.51 (d, *J* = 3.3 Hz, 1H), 4.96 (dd, *J* = 7.8, 3.3 Hz, 1H), 4.81 (d, *J* = 7.7 Hz, 1H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 145.3, 137.0, 136.0, 134.86, 134.76, 133.5, 132.9, 132.1, 131.3, 129.68, 129.59,

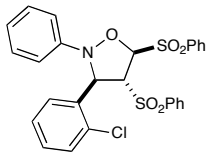
129.42, 129.28, 128.84, 128.74, 128.55, 128.1, 127.8, 126.8, 126.5, 124.9, 121.2, 91.2, 77.3, 74.5, 72.2; HRMS (ESI): Mass calcd for $C_{31}H_{24}ClNO_5S_2$ $[M+H]^+$, 591. Found $[M+H]^+$, 591.



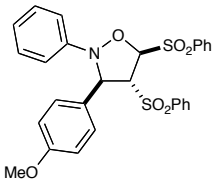
(3*R*,4*R*,5*S*)-3-(2-chlorophenyl)-2-(4-chlorophenyl)-4,5-bis(phenylsulfonyl)isoxazolidine (9): Prepared according to the general procedure with dichloromethane, yielding 28 mg (75%) as an off-white solid. IR: 3067, 2973, 1757, 1599, 1500, 1448, 1391, 1317, 1149 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.94 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.86 (ddd, *J* = 8.0, 4.8, 1.1 Hz, 3H), 7.71-7.68 (m, 1H), 7.60-7.55 (m, 3H), 7.47-7.44 (m, 2H), 7.28-7.24 (m, 2H), 7.17-7.12 (m, 4H), 6.85-6.82 (m, 2H), 5.50 (d, *J* = 3.6 Hz, 1H), 5.35 (d, *J* = 8.3 Hz, 1H), 4.99 (dd, *J* = 8.2, 3.6 Hz, 1H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 144.2, 136.9, 135.9, 134.81, 134.72, 132.5, 131.4, 130.33, 130.16, 129.8, 129.59, 129.45, 129.37, 128.9, 128.7, 127.8, 122.5, 91.0, 77.3, 74.4, 67.8 ; HRMS (ESI): Mass calcd for $C_{27}H_{21}Cl_2NO_5S_2$ $[M+H]^+$, 576. Found $[M+H]^+$, 576.



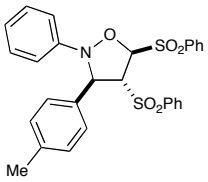
(3*R*,4*R*,5*S*)-2-(4-chlorophenyl)-3-(4-methoxyphenyl)-4,5-bis(phenylsulfonyl)isoxazolidine (10): Prepared according to the general procedure with dichloromethane, yielding 18 mg (71%) as an off-white solid. IR: 3069, 2967, 1609, 1585, 1489, 1311, 1249, 1149 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.93-7.91 (m, 2H), 7.84-7.82 (m, 2H), 7.67 (dd, *J* = 22.7, 7.5 Hz, 2H), 7.58-7.51 (m, 4H), 7.22-7.20 (m, 2H), 7.10-7.09 (m, 2H), 6.76-6.74 (m, 4H), 5.42 (d, *J* = 3.3 Hz, 1H), 4.84 (dd, *J* = 7.8, 3.3 Hz, 1H), 4.60 (d, *J* = 7.8 Hz, 1H), 3.77 (s, 2H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 160.0, 145.3, 137.1, 135.9, 134.81, 134.68, 131.3, 129.79, 129.64, 129.4, 128.76, 128.73, 126.4, 121.3, 114.4, 91.2, 77.3, 74.5, 71.6, 55.3 ; HRMS (ESI): Mass calcd for $C_{28}H_{24}ClNO_6S_2$ $[M+H]^+$, 571. Found $[M+H]^+$, 571.



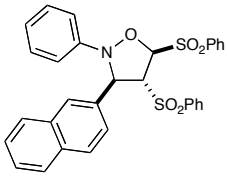
(3*R*,4*R*,5*S*)-3-(2-chlorophenyl)-2-phenyl-4,5-bis(phenylsulfonyl)isoxazolidine (11): Prepared according to the general procedure with dichloromethane, yielding 17 mg (81%) as an off-white solid. IR: 2926, 2855, 1698, 1596, 1489, 1479, 1311, 1151 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.97-7.95 (m, 2H), 7.89-7.87 (m, 3H), 7.71-7.68 (m, 1H), 7.61-7.55 (m, 4H), 7.48-7.45 (m, 2H), 7.27-7.24 (m, 2H), 7.19-7.11 (m, 6H), 6.92-6.90 (m, 2H), 5.51 (d, *J* = 3.7 Hz, 1H), 5.42 (d, *J* = 8.2 Hz, 1H), 5.00 (dd, *J* = 8.2, 3.7 Hz, 1H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 145.7, 137.0, 136.0, 134.78, 134.65, 131.9, 130.23, 130.13, 129.73, 129.65, 129.42, 129.33, 128.77, 128.69, 127.7, 127.0, 121.1, 91.2, 77.3, 74.6, 67.6 ; HRMS (ESI): Mass calcd for $C_{27}H_{22}ClNO_5S_2$ $[M+H]^+$, 541. Found $[M+H]^+$, 541.



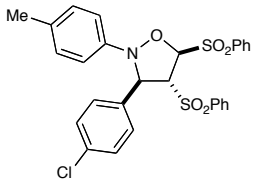
(3*R*,4*R*,5*S*)-3-(4-methoxyphenyl)-2-phenyl-4,5-bis(phenylsulfonyl)isoxazolidine (12): Prepared according to the general procedure with dichloromethane, yielding 10 mg (63%) as an off-white solid. IR: 2932, 1613, 1586, 1491, 1324, 1252, 1178, 1151 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.98 (dd, *J* = 8.2, 0.9 Hz, 3H), 7.88 (dd, *J* = 8.3, 0.9 Hz, 3H), 7.73-7.68 (m, 3H), 7.58 (dt, *J* = 21.0, 7.9 Hz, 6H), 7.29-7.25 (m, 4H), 7.17 (t, *J* = 7.8 Hz, 3H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.87-6.86 (m, 3H), 6.78 (d, *J* = 8.7 Hz, 3H), 5.47 (d, *J* = 3.2 Hz, 1H), 4.88 (dd, *J* = 7.7, 3.2 Hz, 1H), 4.72 (d, *J* = 7.7 Hz, 1H), 3.80 (s, 3H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 159.9, 146.8, 137.2, 136.0, 134.7, 129.7, 129.3, 128.7, 127.0, 125.8, 120.0, 114.3, 91.3, 74.7, 71.2, 55.3 ; HRMS (ESI): Mass calcd for $C_{28}H_{25}NO_6S_2$ $[M+H]^+$, 537. Found $[M+H]^+$, 537.



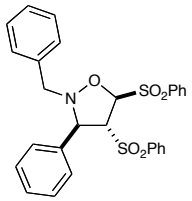
(3*R*,4*R*,5*S*)-2-phenyl-4,5-bis(phenylsulfonyl)-3-*p*-tolylisoxazolidine (13): Prepared according to the general procedure with 1,2-dichloroethane, yielding 17 mg (70%) as an off-white solid. IR: 3067, 1599, 1491, 1448, 1325, 1311, 1151, 1084 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.98-7.96 (m, 2H), 7.88-7.86 (m, 2H), 7.70 (dd, *J* = 20.2, 7.5 Hz, 3H), 7.61-7.53 (m;, 6H), 7.22-7.20 (m, 3H), 7.17-7.14 (m, 3H), 7.09-7.04 (m, 4H), 6.87-6.85 (m, 2H), 5.44 (d, *J* = 3.3 Hz, 1H), 4.87 (dd, *J* = 7.7, 3.2 Hz, 1H), 4.75 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 146.8, 138.8, 137.2, 136.1, 134.74, 134.58, 132.2, 129.72, 129.61, 129.3, 128.80, 128.65, 128.3, 125.8, 119.9, 91.4, 77.26, 77.21, 77.18, 74.9, 71.2, 21.3 ; HRMS (ESI): Mass calcd for $C_{28}H_{25}NO_5S_2$ $[M+H]^+$, 521. Found $[M+H]^+$, 521.



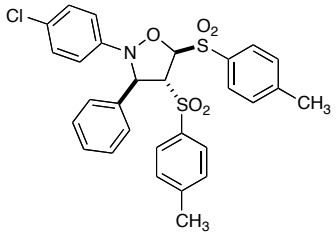
(3*R*,4*R*,5*S*)-3-(naphthalen-2-yl)-2-phenyl-4,5-bis(phenylsulfonyl)isoxazolidine (14): Prepared according to the general procedure with 1,2-dichloroethane, yielding 19 mg (77%) as an off-white solid. IR: 3064, 2929, 1733, 1599, 1586, 1490, 1448, 1323, 1312, 1245 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 8.01-7.99 (m, 2H), 7.84-7.83 (m, 2H), 7.77 (ddd, *J* = 23.8, 14.2, 8.6 Hz, 4H), 7.68-7.54 (m, 7H), 7.50-7.43 (m, 5H), 7.13-7.10 (m, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.88-6.87 (m, 2H), 5.52 (d, *J* = 3.2 Hz, 1H), 4.96 (dd, *J* = 7.7, 3.2 Hz, 1H), 4.90 (d, *J* = 7.7 Hz, 1H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 146.8, 137.1, 136.0, 134.80, 134.67, 133.4, 133.0, 132.7, 129.75, 129.56, 129.37, 129.1, 128.77, 128.72, 128.4, 128.2, 127.7, 126.7, 126.3, 125.8, 125.1, 119.9, 91.3, 77.31, 77.26, 74.6, 71.8 ; HRMS (ESI): Mass calcd for $C_{31}H_{25}NO_5S_2$ $[M+H]^+$, 557. Found $[M+H]^+$, 557.



(3*R*,4*R*,5*S*)-3-(4-chlorophenyl)-4,5-bis(phenylsulfonyl)-2-*p*-tolylisoxazolidine (15): Prepared according to the general procedure with dichloromethane, yielding 24 mg (67%) as an off-white solid. IR: 3073, 2924, 1585, 1508, 1492, 1448, 1310, 1152 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.93 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.86 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.70-7.68 (m, 2H), 7.56 (td, *J* = 7.9, 4.7 Hz, 5H), 7.29-7.26 (m, 10H), 7.21-7.19 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.40 (d, *J* = 3.1 Hz, 1H), 4.81 (dd, *J* = 7.8, 3.2 Hz, 1H), 4.73 (d, *J* = 7.8 Hz, 1H), 2.24 (s, 3H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 143.7, 137.1, 136.6, 134.91, 134.82, 134.63, 133.7, 130.0, 129.71, 129.70, 129.42, 129.32, 129.1, 128.8, 120.9, 91.5, 77.5, 77.26, 77.15, 76.95, 76.91, 74.6, 70.9, 21.0; HRMS (ESI): Mass calcd for $C_{28}H_{24}ClNO_5S_2$ $[M+H]^+$, 555. Found $[M+H]^+$, 555.

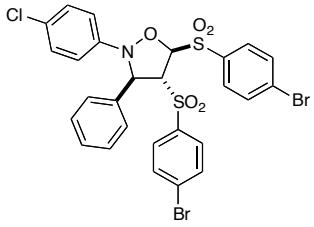


(3*R*,4*R*,5*S*)-2-benzyl-3-phenyl-4,5-bis(phenylsulfonyl)isoxazolidine (16): Prepared according to the general procedure with dichloromethane with vinyl sulfone (2 equiv.) and nitrone (1 equiv.) for 24 hrs, yielding 29 mg (86%) as an off-white solid. IR: 3065, 1497, 1448, 1326, 1311, 1293, 1178, 1147, 1108, 1087, 1075, 1064 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.83-7.81 (m, 1H), 7.63 (s, 1H), 7.52-7.44 (m, 8H), 7.32-7.22 (m, 10H), 5.22 (d, *J* = 3.5 Hz, 1H), 4.80 (dd, *J* = 8.2, 3.5 Hz, 1H), 4.32 (d, *J* = 8.2 Hz, 1H), 3.88 (d, *J* = 14.2 Hz, 1H), 3.66 (d, *J* = 14.2 Hz, 1H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 137.3, 136.5, 135.4, 134.64, 134.55, 134.1, 131.6, 131.3, 129.50, 129.30, 129.22, 129.18, 129.16, 129.15, 129.07, 128.96, 128.85, 128.79, 128.66, 128.55, 128.52, 128.25, 128.21, 128.12, 127.95, 127.65, 127.54, 91.1, 77.31, 77.26, 77.1, 76.8, 73.7, 72.1, 59.4 ; HRMS (ESI): Mass calcd for $C_{28}H_{25}NO_5S_2$ $[M+H]^+$, 521. Found $[M+H]^+$, 521.

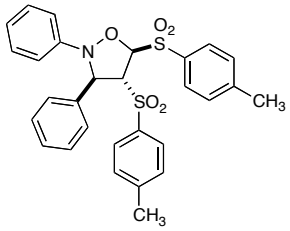


(3*R*,4*R*,5*S*)-2-(4-chlorophenyl)-3-phenyl-4,5-ditosylisoxazolidine (17): Prepared according to the general procedure with 1,2-dichloroethane at 40 °C, yielding 122 mg (72%) as an off-white solid. IR: 3066, 2952, 1597, 1490, 1324, 1304, 1151, 1121 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.81 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.32-7.23 (m, 7H), 7.10 (d, J = 8.9 Hz, 2H), 6.77 (d, J = 8.9 Hz, 2H), 5.41 (d, J = 3.2, 1H), 4.85 (dd, J = 7.7, 3.2 Hz, 1H), 4.66 (d, J = 7.7 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 146.07,

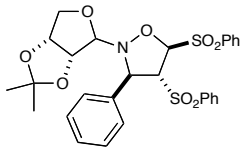
145.90, 145.4, 135.0, 134.1, 132.9, 131.1, 130.2, 130.0, 129.6, 129.00, 128.92, 128.75, 128.5, 121.1, 91.3, 74.9, 71.8, 21.8; HRMS (ESI): Mass calcd for $C_{29}H_{26}ClNO_5S_2$ $[M+H]^+$, 569. Found $[M+H]^+$, 569.



(3*R*,4*R*,5*S*)-4,5-bis((4-bromophenyl)sulfonyl)-2-(4-chlorophenyl)-3-phenylisoxazolidine (18): Prepared according to the general procedure with 1,2-dichloroethane at 40 °C, yielding 90 mg (60%) as an off-white solid. IR: 2963, 2933, 2875, 1766, 1574, 1491, 1329, 1150 , 1069 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.0 Hz, 4H), 7.29 (m, J = 3.5 Hz, 5H), 7.15 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 5.46 (d, J = 3.3 Hz, 1H), 4.90 (dd, J = 7.9, 3.4 Hz, 1H), 4.62 (s, 1H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 145.0, 136.0, 134.7, 134.2, 132.94, 132.88, 132.76, 131.8, 131.1, 130.5, 130.1, 129.4, 129.12, 128.93, 128.91, 128.88, 128.5, 121.5, 97.1, 91.0, 74.6, 72.4 ; HRMS (ESI): Mass calcd for $C_{27}H_{20}Br_2ClNO_5S_2$ $[M+H]^+$, 699. Found $[M+H]^+$, 699.

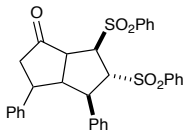


(3*R*,4*R*,5*S*)-2,3-diphenyl-4,5-ditosylisoxazolidine (19): Prepared according to the general procedure with 1,2-dichloroethane at 40 °C, yielding 61 mg (77%) as an off-white solid. IR: 2959, 2874, 1597, 1491, 1455, 1324, 1183, 1151, 1085 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.36-7.19 (m, 9H), 7.15-7.11 (m, 2H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.84-6.82 (m, 2H), 5.40 (d, *J* = 3.2 Hz, 1H), 4.83 (dd, *J* = 7.6, 3.2 Hz, 1H), 4.73 (d, *J* = 7.6 Hz, 1H), 2.46 (s, 4H), 2.42 (s, 3H); ^{13}C-NMR (125 MHz; $CDCl_3$): 13-C NMR (126 MHz; CDCl3): δ 146.9, 145.97, 145.78, 135.5, 133.0, 130.2, 130.0, 129.7, 128.82, 128.78, 128.65, 128.52, 125.7, 119.8, 91.4, 75.0, 71.4, 21.84, 21.81; HRMS (ESI): Mass calcd for $C_{29}H_{27}NO_5S_2$ $[M+H]^+$, 535. Found $[M+H]^+$, 535.



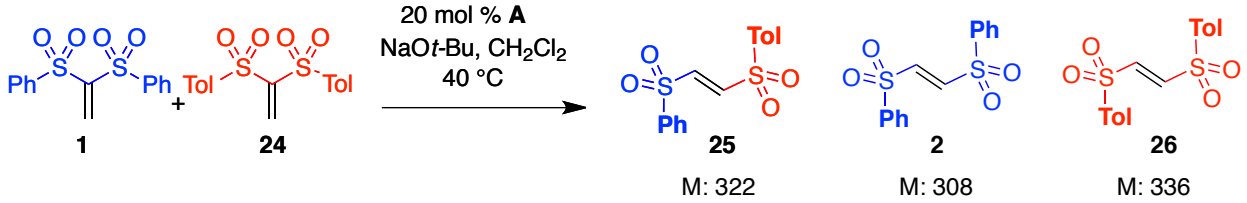
(3*R*,4*R*,5*S*)-2-((3a*R*,6a*R*)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3-phenyl-4,5-bis(phenylsulfonyl)isoxazolidine (21): Prepared according to the general procedure with 1,2-dichloroethane, yielding 22 mg (65%) as an off-white solid. IR: 2926, 2854. 1697, 1448, 1373, 1312, 1152, 1100 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.94 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.82 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.65-7.59 (m, 5H), 7.53-7.49 (m, 2H), 7.30-7.28

(m, 2H), 7.23-7.20 (m, 4H), 5.36 (d, *J* = 3.3 Hz, 1H), 4.75 (dd, *J* = 7.5, 3.3 Hz, 1H), 4.71 (d, *J* = 6.0 Hz, 1H), 4.62 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.56 (s, 1H), 4.49 (d, *J* = 7.5 Hz, 1H), 3.62 (d, *J* = 10.2 Hz, 1H), 3.28 (dd, *J* = 10.3, 3.9 Hz, 1H), 3.06 (s,), 1.38 (s, 4H), 1.28 (s, 4H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 137.0, 135.9, 134.81, 134.68, 129.70, 129.63, 129.3, 128.71, 128.69, 128.3, 112.4, 98.9, 92.0, 81.6, 80.6, 77.26, 77.21, 76.96, 76.95, 76.91, 76.7, 74.4, 74.1, 68.8, 26.3, 24.9 ; HRMS (ESI): Mass calcd for $C_{28}H_{29}NO_8S_2$ $[M+H]^+$, 573. Found $[M+H]^+$, 573.



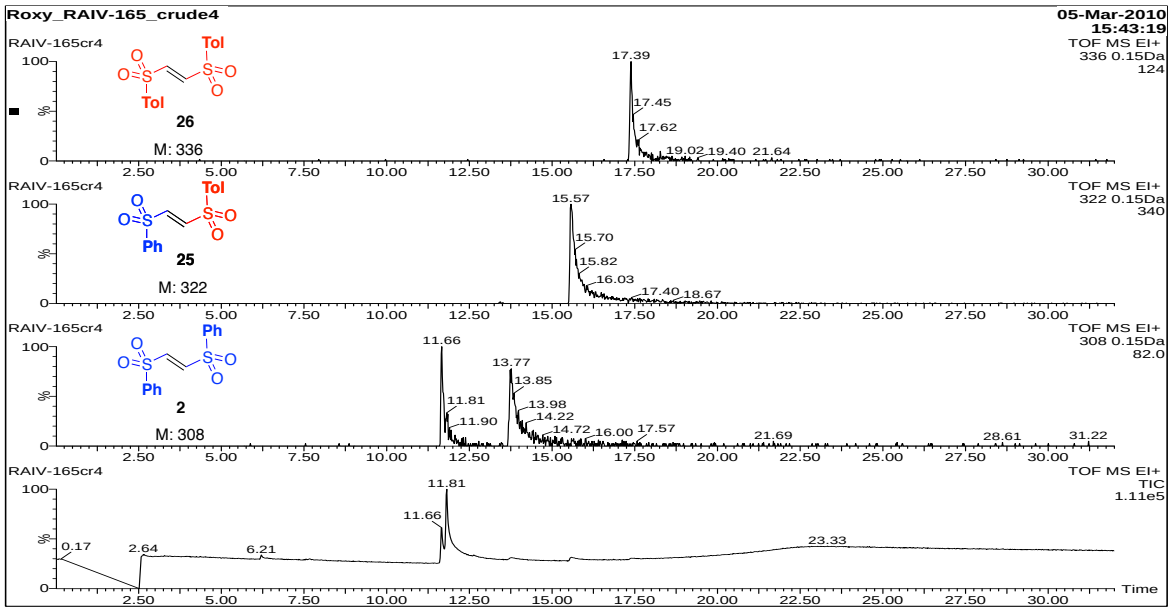
(5*R*,6*R*,7*S*)-3,5-diphenyl-6,7-bis(phenylsulfonyl)tetrahydropyrazolo[1,2-*a*]pyrazol-1(5*H*)-one (22): Prepared according to the general procedure with 1,2-dichloroethane, yielding 32 mg (88%) as an off-white solid. IR: 2958, 2926, 1715, 1584, 1495, 1448, 1328, 1149, 1083 cm^{-1}; ^{1}H-NMR (500 MHz; $CDCl_3$): (major) δ 7.90 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.63-7.61 (m, 4H), 7.49 (t, *J* = 7.9 Hz, 3H), 7.42-7.40 (m, 3H), 7.30-7.22 (m, 4H), 7.12-7.10 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 5.76 (d, *J* = 6.3 Hz, 1H), 5.34 (dd, *J* = 7.0, 6.4 Hz, 1H), 4.45 (d, *J* = 7.1 Hz, 1H), 4.01 (dd, *J* = 9.4, 5.6 Hz, 1H), 2.27 (qd, *J* = 15.6, 7.5 Hz, 2H); ^{13}C-NMR (125 MHz; $CDCl_3$): δ 174.0, 168.3, 139.0, 137.7, 135.6, 133.7, 133.2, 129.7, 129.2, 128.5, 128.22, 128.06, 127.76, 127.71, 127.67, 127.0, 125.5, 125.1, 71.3, 69.0, 67.2, 56.0, 40.2 ; HRMS (ESI): Mass calcd for $C_{30}H_{26}N_2O_5S_2$ $[M+H]^+$, 559. Found $[M+H]^+$, 560.

Procedure for the Formation of Cross-over Product 25 from Combination of 1 and 24



To a reaction vial containing a magnetic stirring bar was added the corresponding 1,1-bis(phenylsulfonyl)ethylene (20 mg, 0.07 mmol), 1,1-bis(tosyl)ethylene[6] (22 mg, 0.07 mmol), and dichloromethane (0.55 mL). Then, a DCM solution containing the azolium salt **A** (0.01 mmol) and NaO*t*-Bu (0.01 mmol) was added, bringing the reaction solution to 0.1 M. The reaction was then heated to reflux for 24-48 hrs. The unpurified reaction was concentrated *in vacuo*. The material was analyzed by GC-TOF. Mass spectral data for the cross-over experiment were acquired in the Electron Ionization mode (EI) on a Waters GCT Premier mass spectrometer (Beverly, MA), with an Agilent 7890 gas chromatograph (Santa Clara, CA). The spectra were analyzed in the positive ion mode on the MS using the dynamic range enhancement feature, with a scan time of 0.9 s and an interscan delay of 0.1 s. Samples were separated on a Phenomenex Zebron 5 column (Torrence, CA, 60 m, 0.25 mm OD, 0.25 μm film thickness) with a temperature ramp from 200 °C held for 2.0 min, 5 °C/min to 300 °C and held for 20 min. The sample (1 μl) was injected onto the column with a mobile phase of helium at 1 mL/min. and an inlet temperature of 250 °C and a split of 30:1.

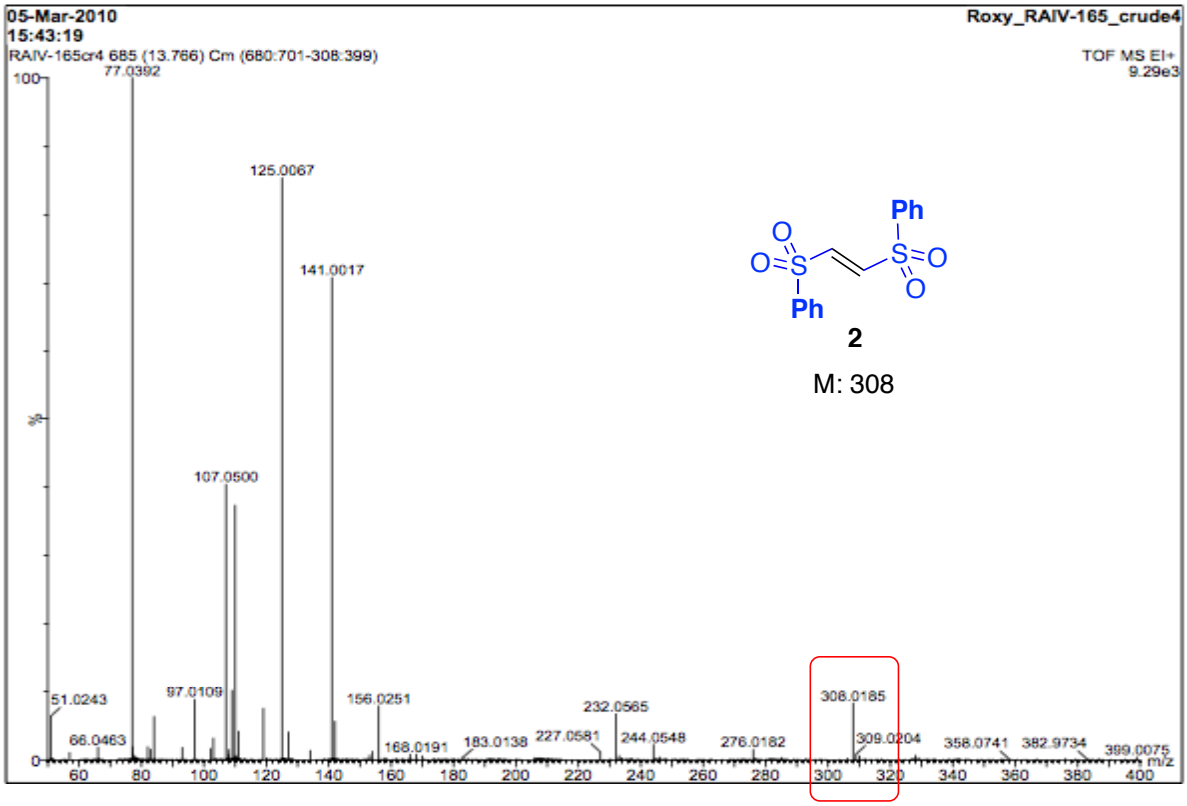
Mass Spectral Trace Data (single injection of reaction above)



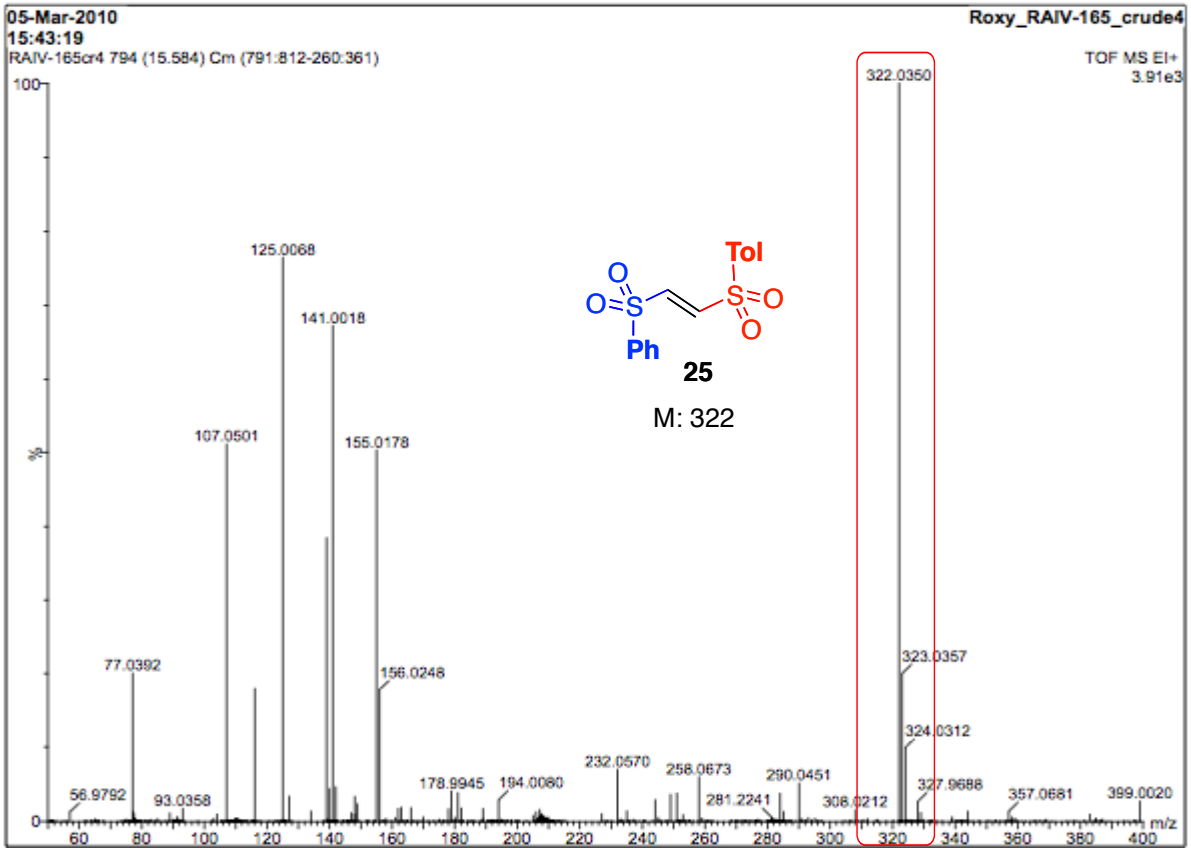
---

[6] Carpino, L. A. *J. Org. Chem.* **1973**, *38*, 2600-2603.

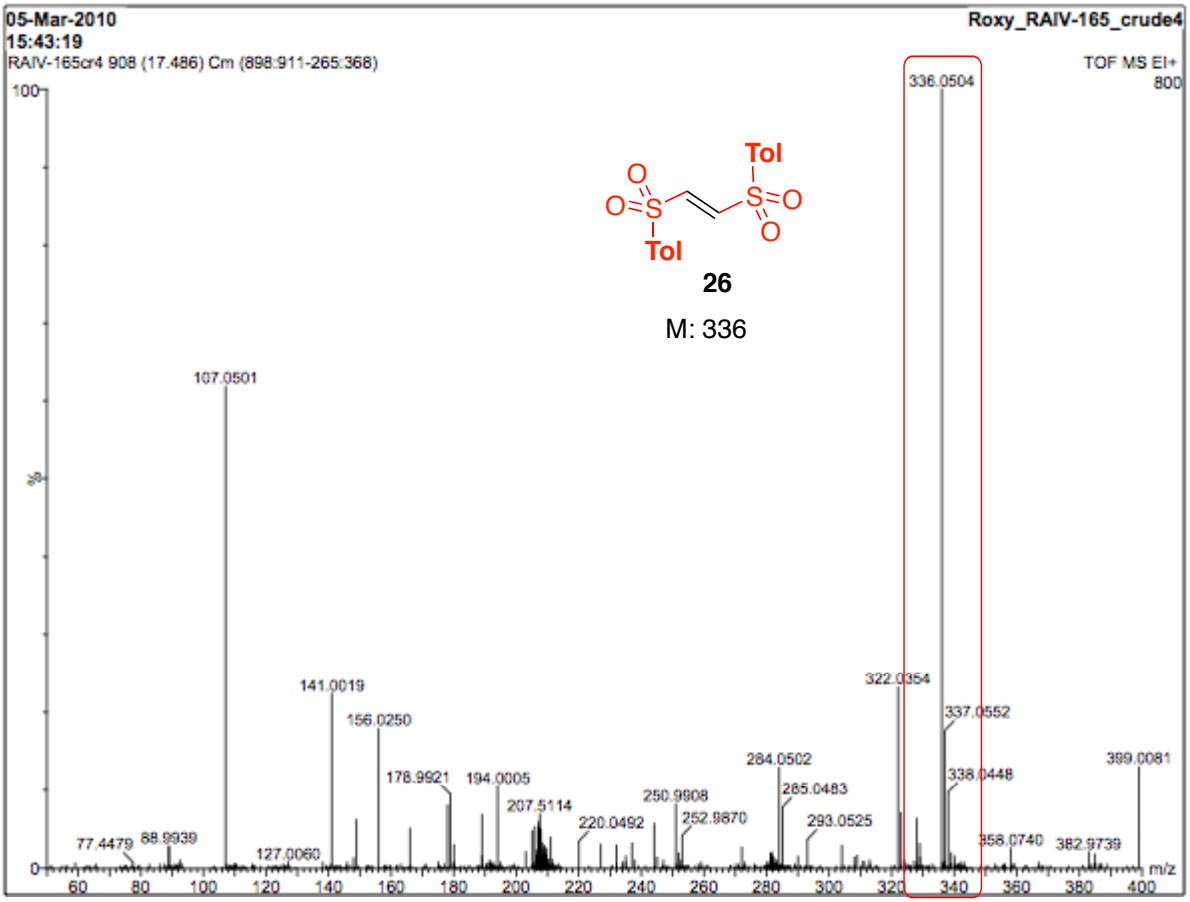
Mass Spectral Data for 2



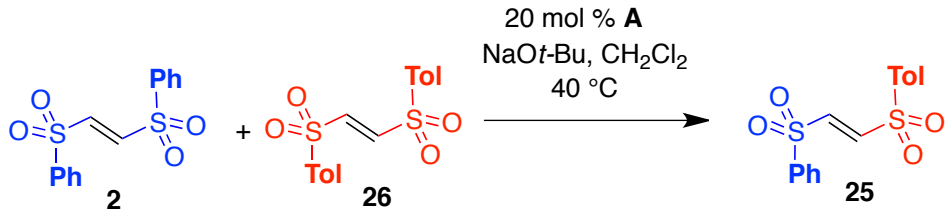
Mass Spectral Data for 25



Mass Spectral Data for 26

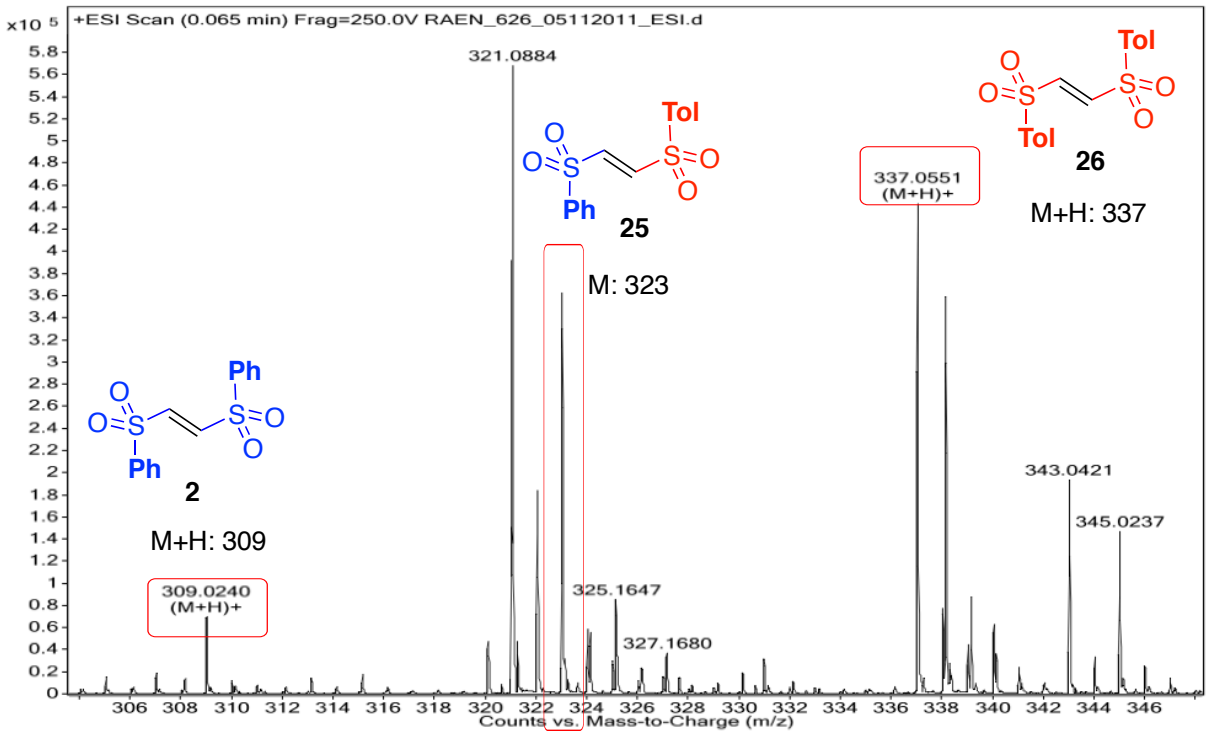


Procedure for the Formation of Cross-over Product 25 from Combination of 2 and 26

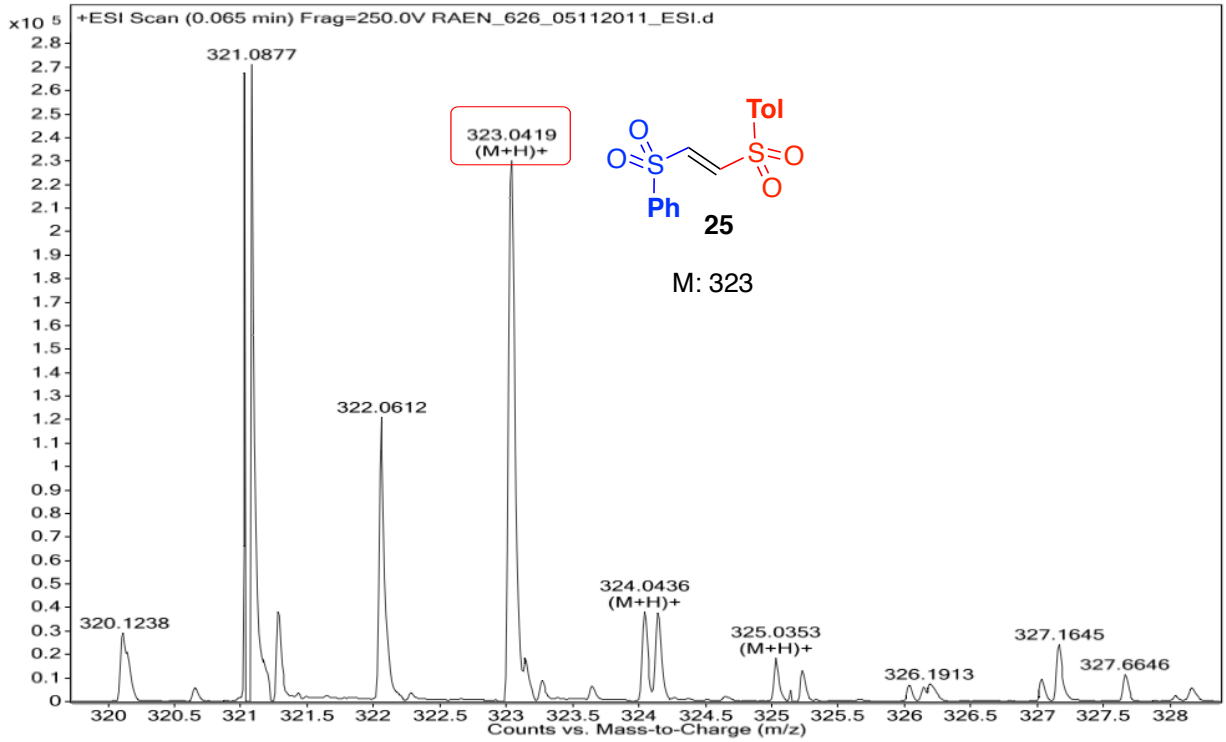


To a reaction vial containing a magnetic stirring bar was added the corresponding trans-1,2-bis(phenylsulfonyl)ethylene (10 mg, 0.03 mmol), 1,2-bis(tosyl)ethylene (11 mg, 0.03 mmol), and dichloromethane (0.220 mL). At this time, a DCM solution containing the azolium salt **A** (0.01 mmol) and NaO*t*-Bu (0.01 mmol) was added, bringing the reaction solution to 0.1 M. The reaction was then heated to reflux for 24-48 hrs. The unpurified reaction was concentrated *in vacuo*. The material was analyzed by mass spectrometry (ESI). Mass spectral data for the cross-over experiment were acquired in the Electrospray Ionization mode (ESI) on an Agilent 6210 Time of Flight LC/MS. The spectra were analyzed in the positive ion mode on the MS using 80% MeOH/ 20% Dichloromethane as the carrier solvent with a flow rate of 0.6 mL/min and direct injection (no column).

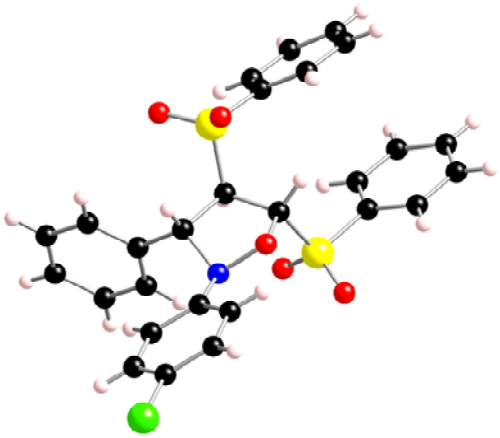
Mass Spectral Data [M+H] for 2, 25, and 26



Mass Spectral Data Expansion for 25



X-ray Crystal Structure of 4



X-ray diffraction was performed at –120 °C and raw frame data were processed using SAINT. Molecular structure was solved using direct methods and refined by F2 by full-matrix least-squares techniques. The GOF = 0.90 for 325 variables refined to R1 = 0.043 for 5341 reflections with I>2 (I). There was no absorption correction of Flack parameters. Further information is contained in the CIF file.

Selected Spectra