

Supporting Information
for
Regio- and Stereoselective Synthesis of Ensulfonamides/Enamides via
Catalyst-Free Intermolecular addition of Indoles/Pyrroles/Imidazole to
Allenamides

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1. General considerations

All reactions were performed using Schlenk-tubes, septa, and syringes under nitrogen atmosphere. THF and DCE were obtained by fresh distilled over sodium/benzophenone or Calciumhydride respectively. Commercial reagents were used as supplied or purified by standard techniques where necessary. Column chromatography was performed using 200-300 mesh silica with the proper solvent system according to TLC analysis using KMnO_4 stain and UV light to visualize the reaction components. Unless otherwise noted, nuclear magnetic resonance spectra were recorded on a Agilent 400 MHz spectrometer using CDCl_3 with TMS as internal reference at room temperature. NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and bs = broad singlet), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuteriochloroform (77.0 ppm) as the internal standard. Melting points were determined on a WRS-1B digital melting point instrument. IR spectra were obtained on Nicoletisso FTIR using KBr disks. HR-MS spectral were determined on a Bruker Daltonics Bio TOF mass spectrometer.

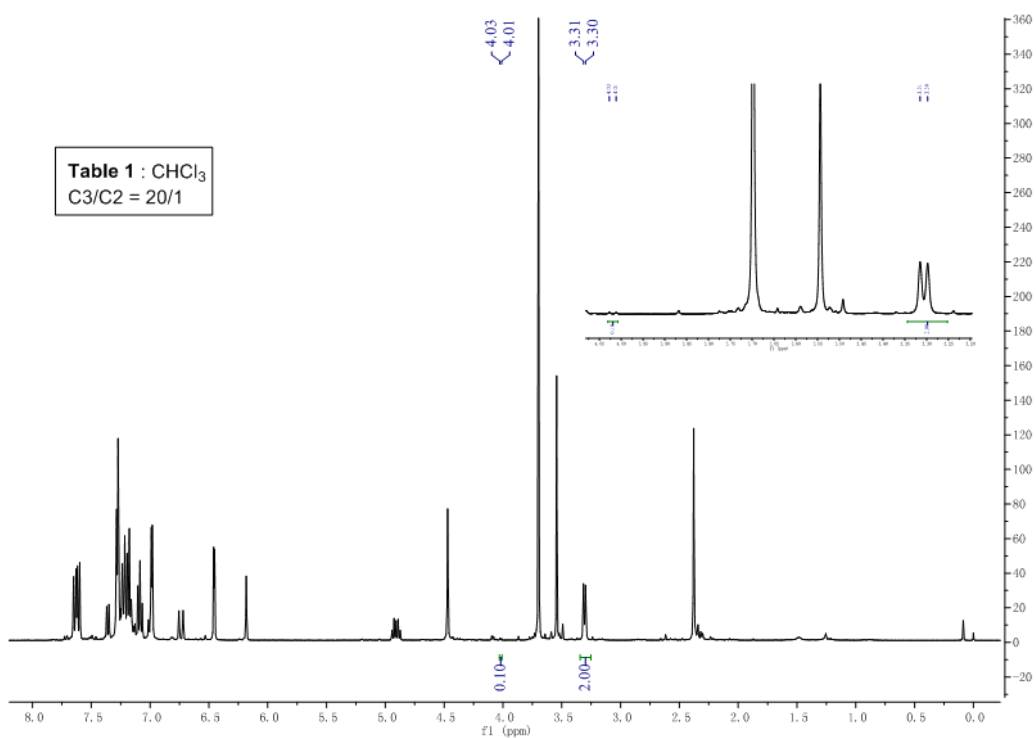
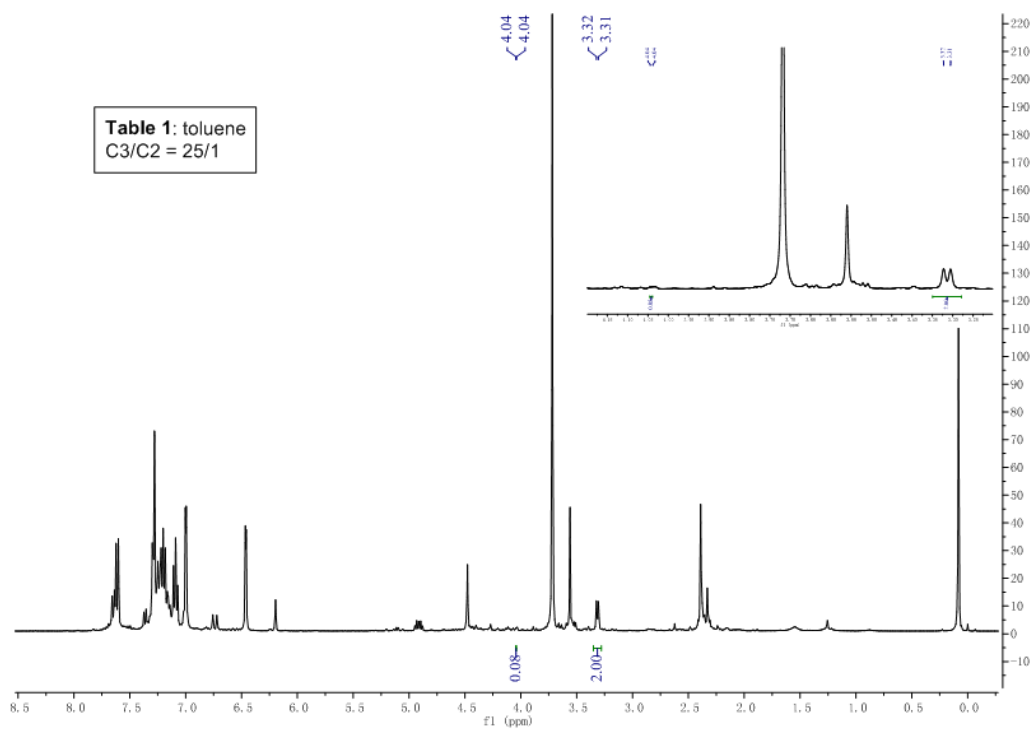
Allenamides **1-11** were prepared according to the published methods.^{1, 2, 3} Indoles pyrroles, and imidazole were obtained commercially and used without further purification. The data of enamide **3k** was referred to the published report.⁴

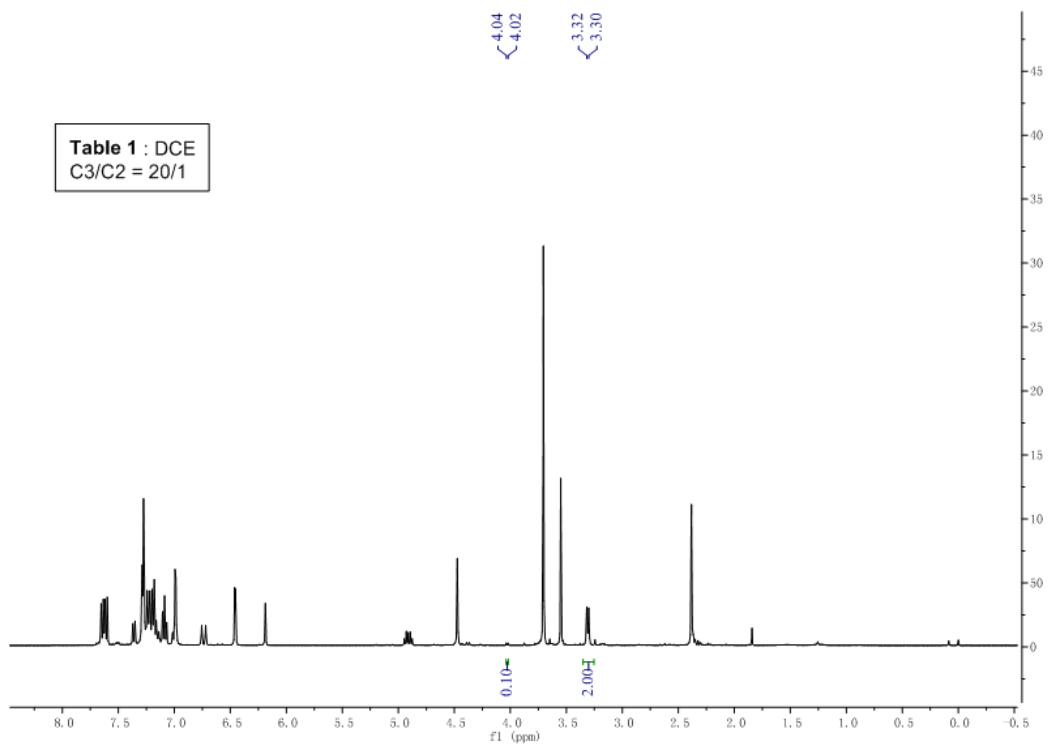
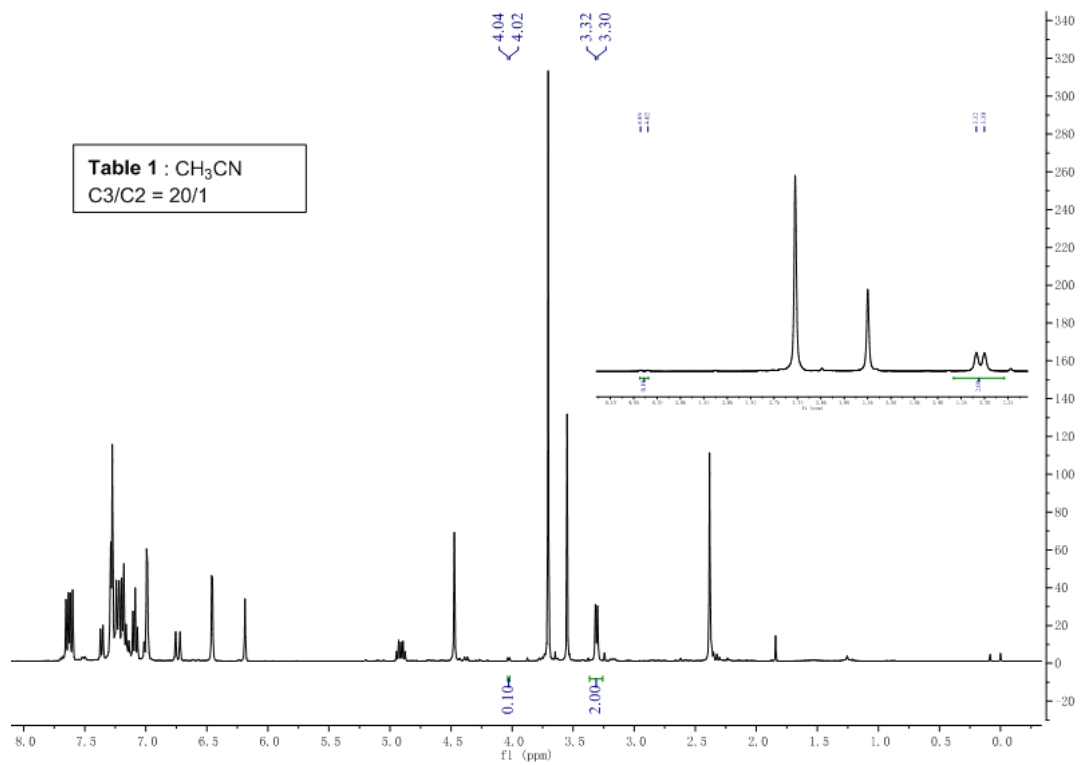
General procedure for catalyst-free intermolecular addition of allenamide 1a with N-Methylindole 2a.

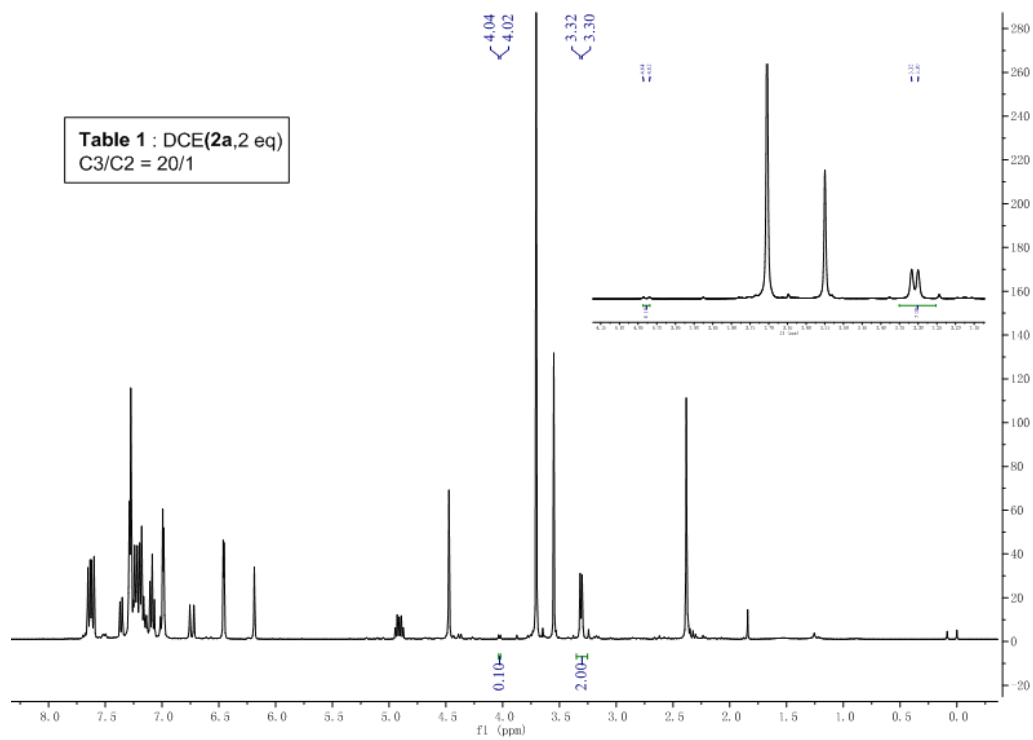
To a Schlenk tube charged with nitrogen were added allenamide **1a** (0.1 mmol), N-Methylindole **2a** (3.0 eq) and DCE (anhydrous, 3 mL). Then the reaction mixture was stirred at 80 °C for 5 h until complete consumption of starting material as monitored by TLC. Concentration of the reaction mixture in vacuo followed by purification through flash chromatography on silica gel column (hexane/EtOAc=30/1 as the eluent) afforded **3a** (39.5 mg, 92% yield) as a white solid.

2. The ratio of C3/C2 in the NMR spectra

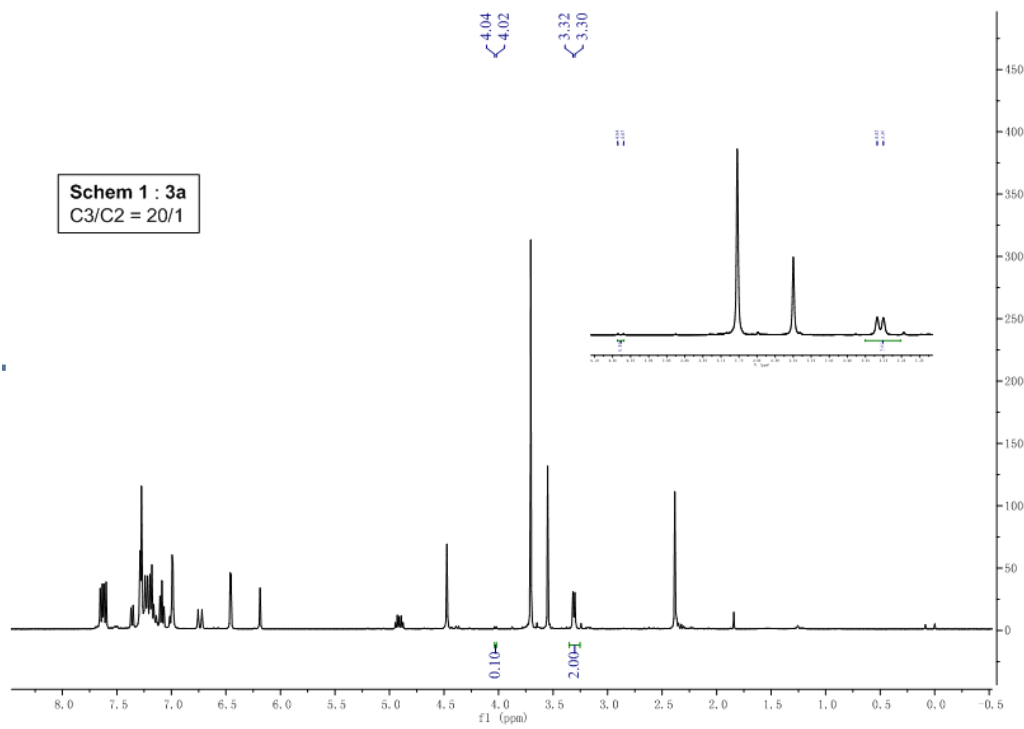
(1) The NMR spectra of **table 1**.

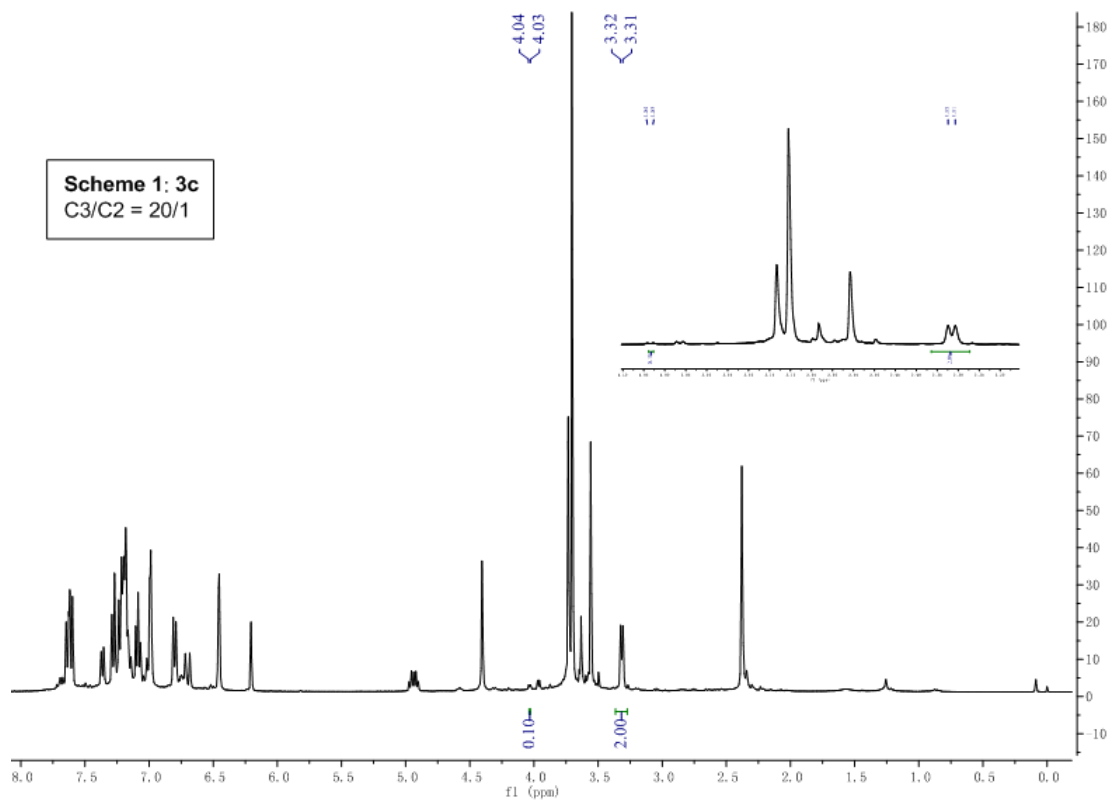
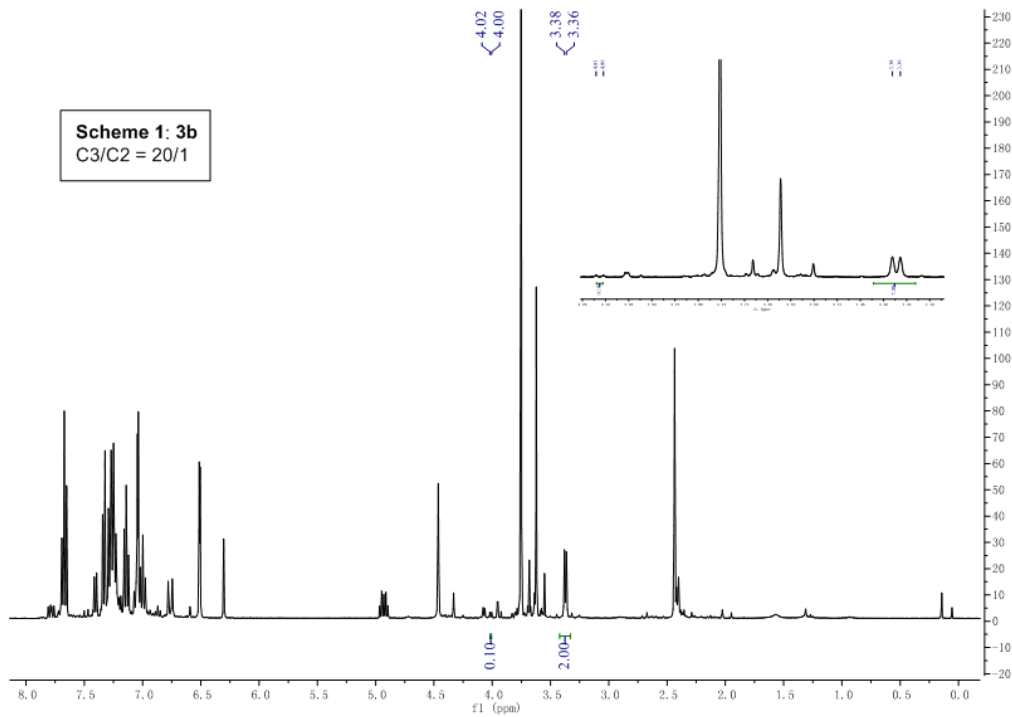


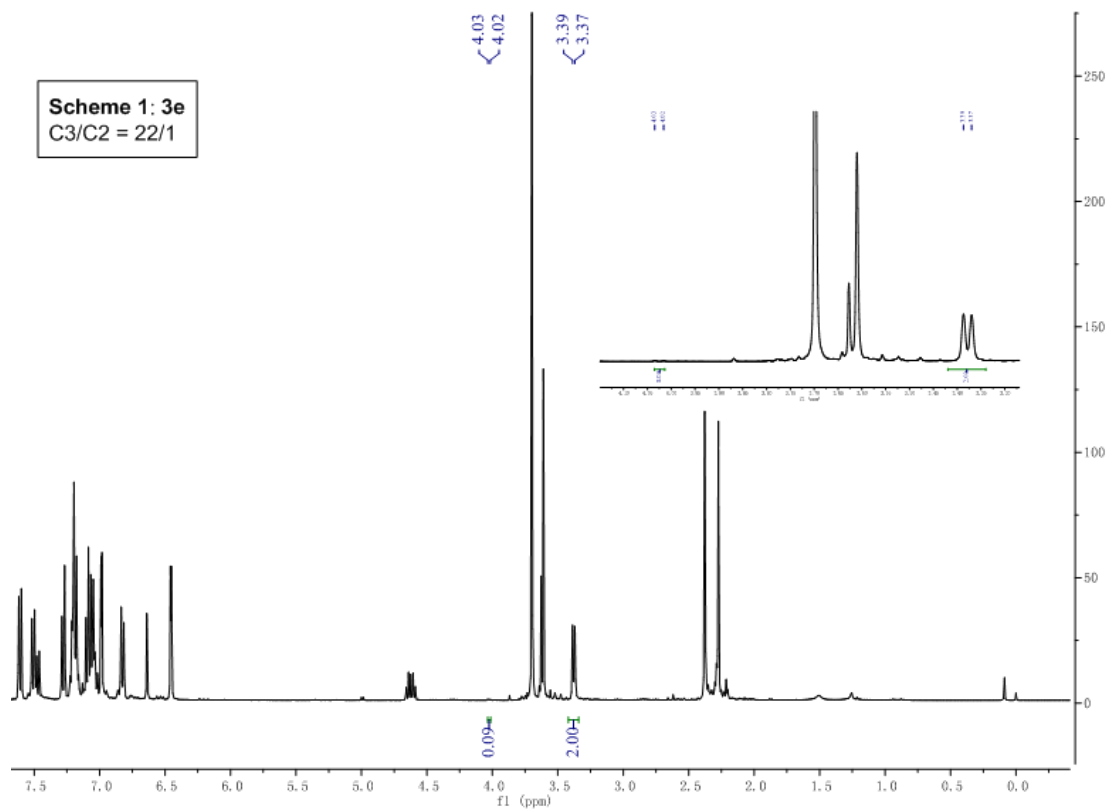
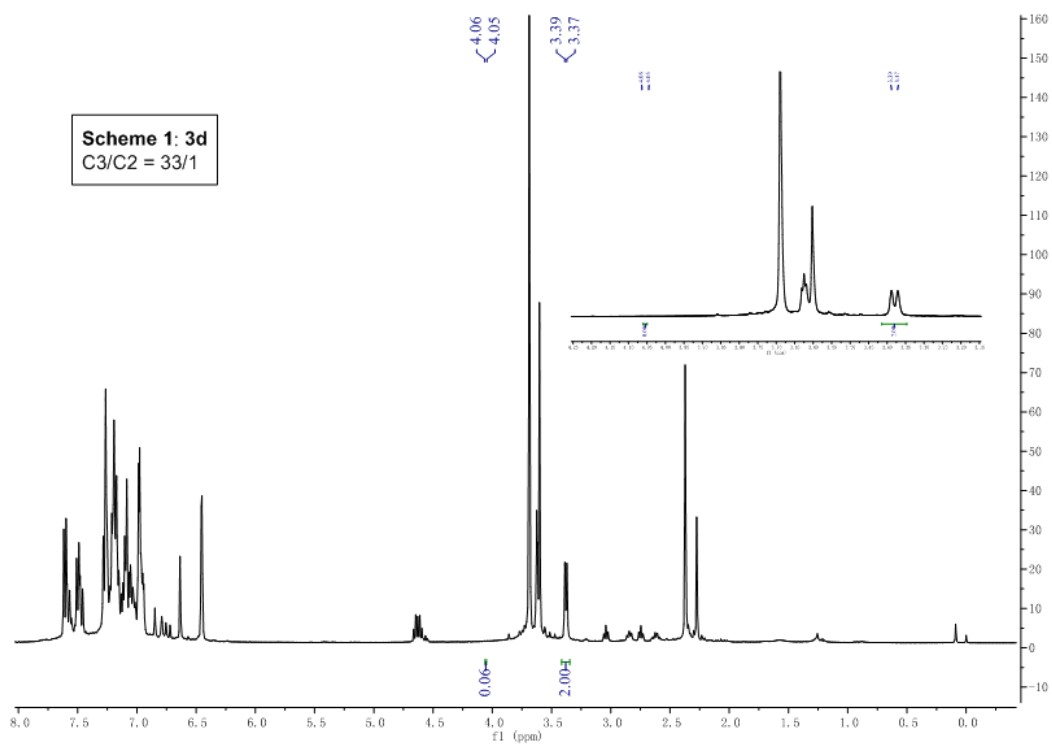


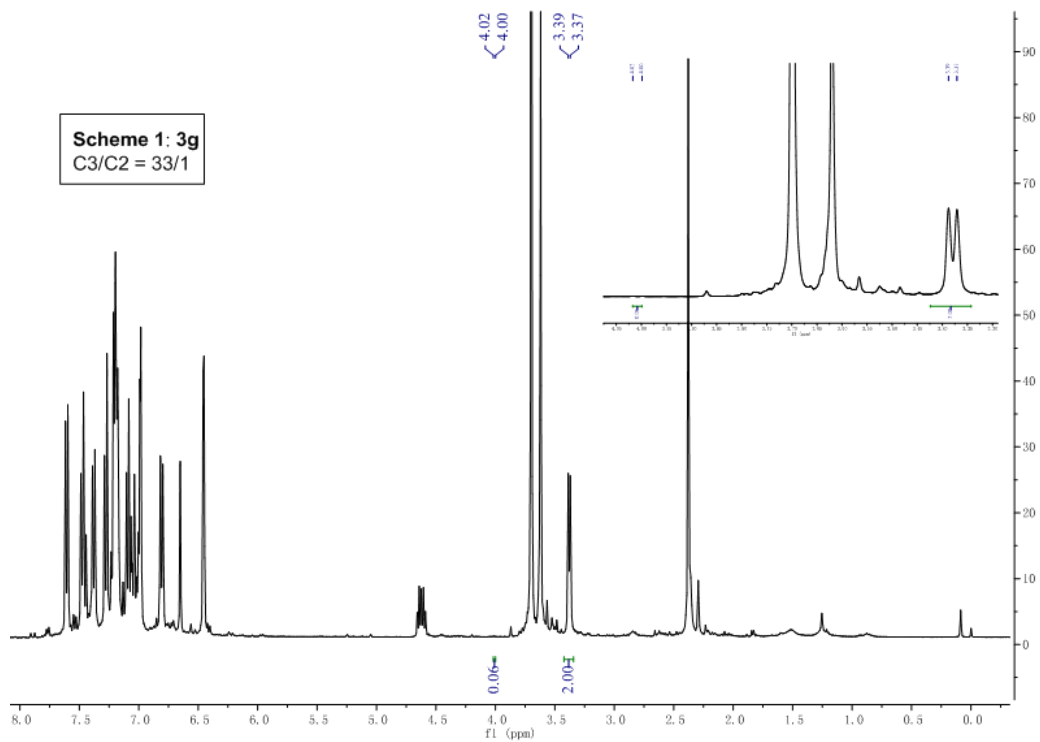
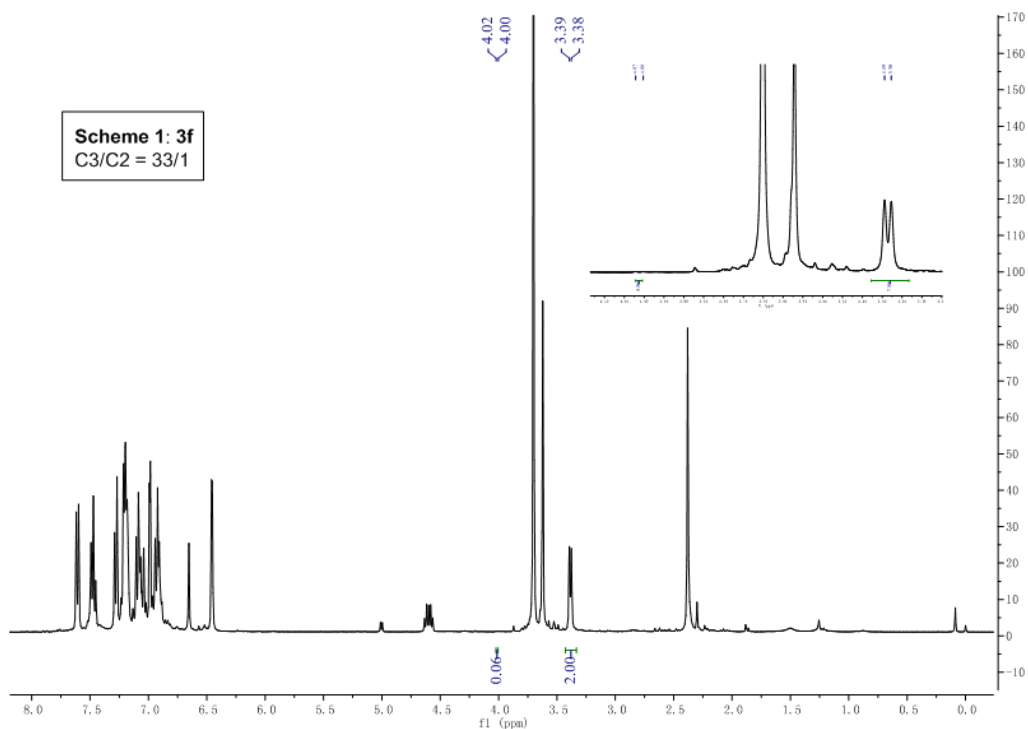


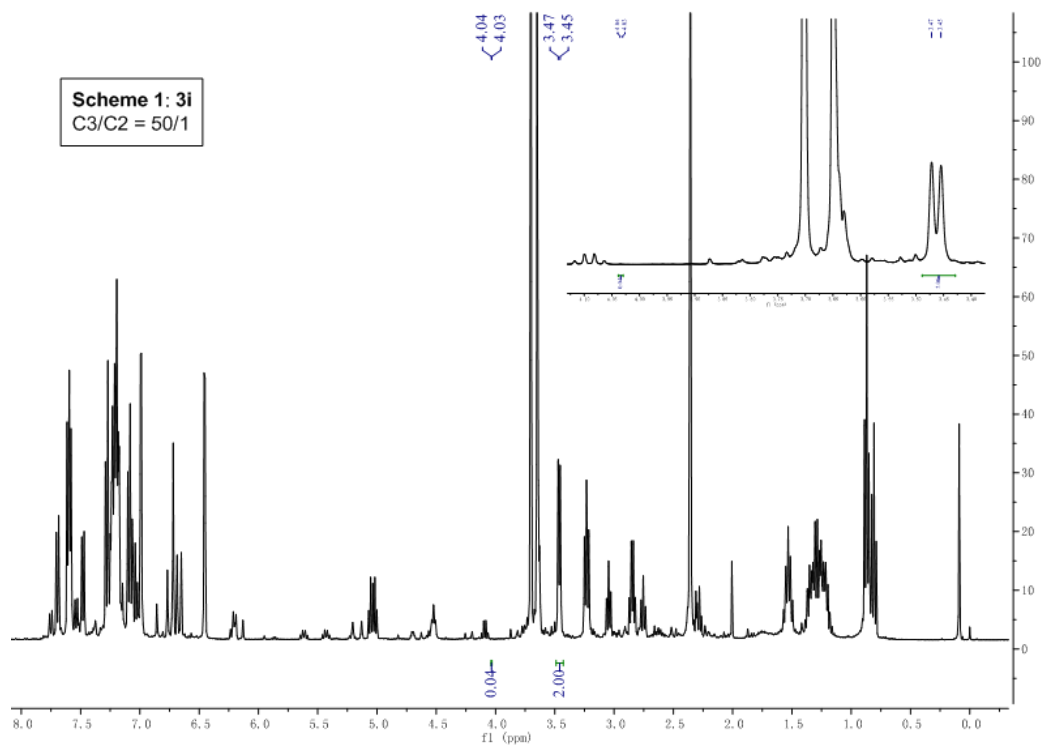
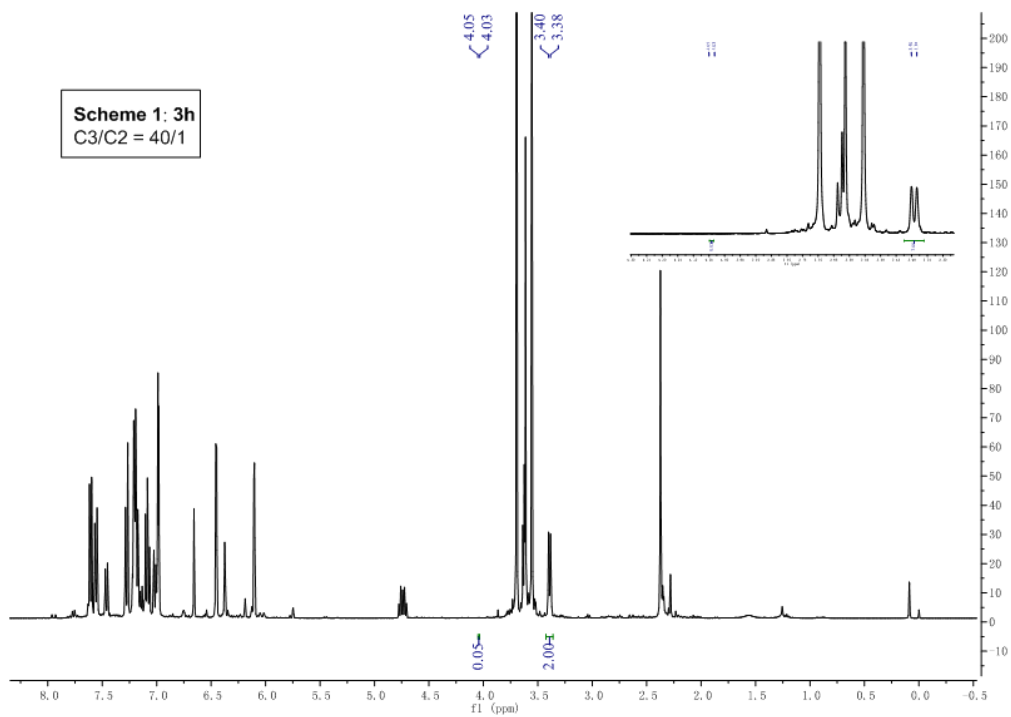
(2) The NMR spectra of **Scheme 1**.

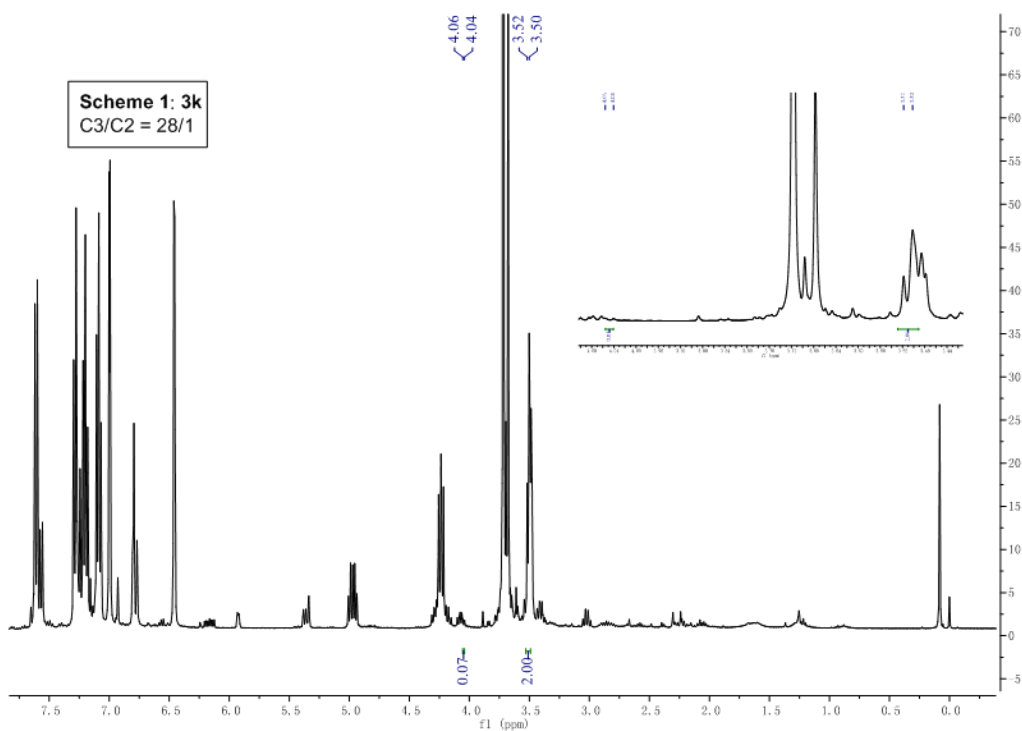
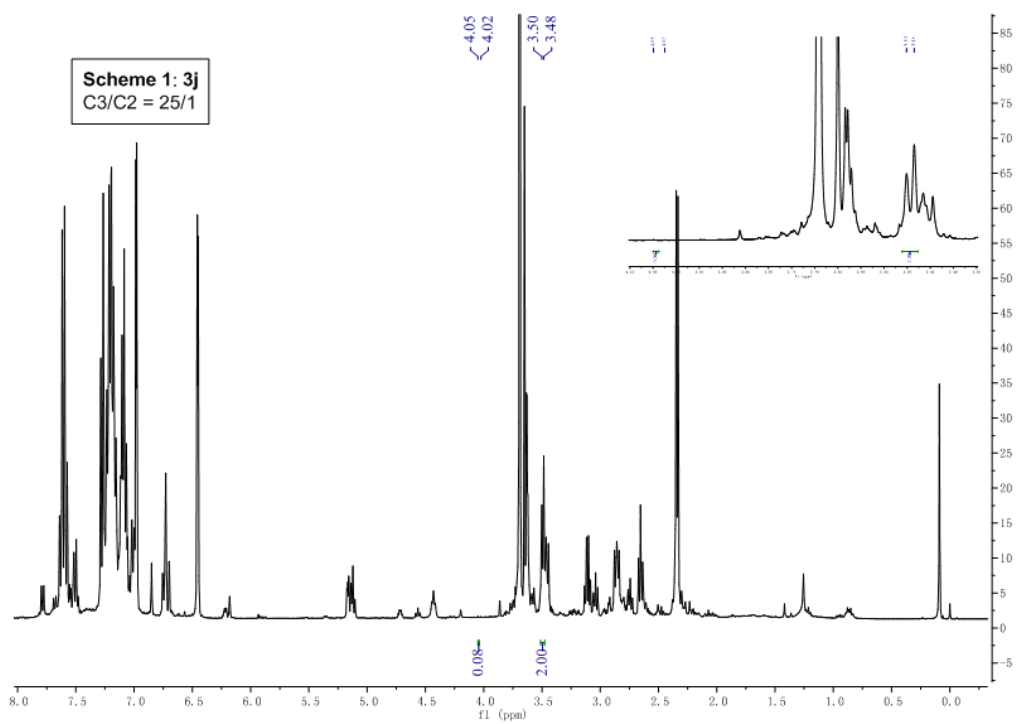


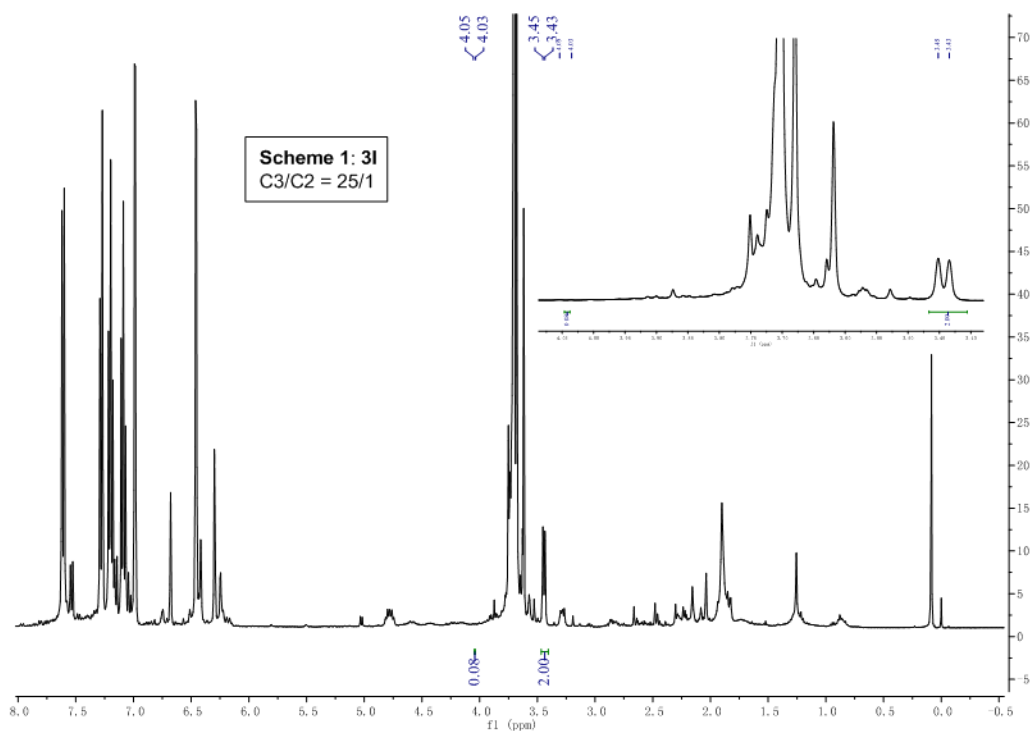




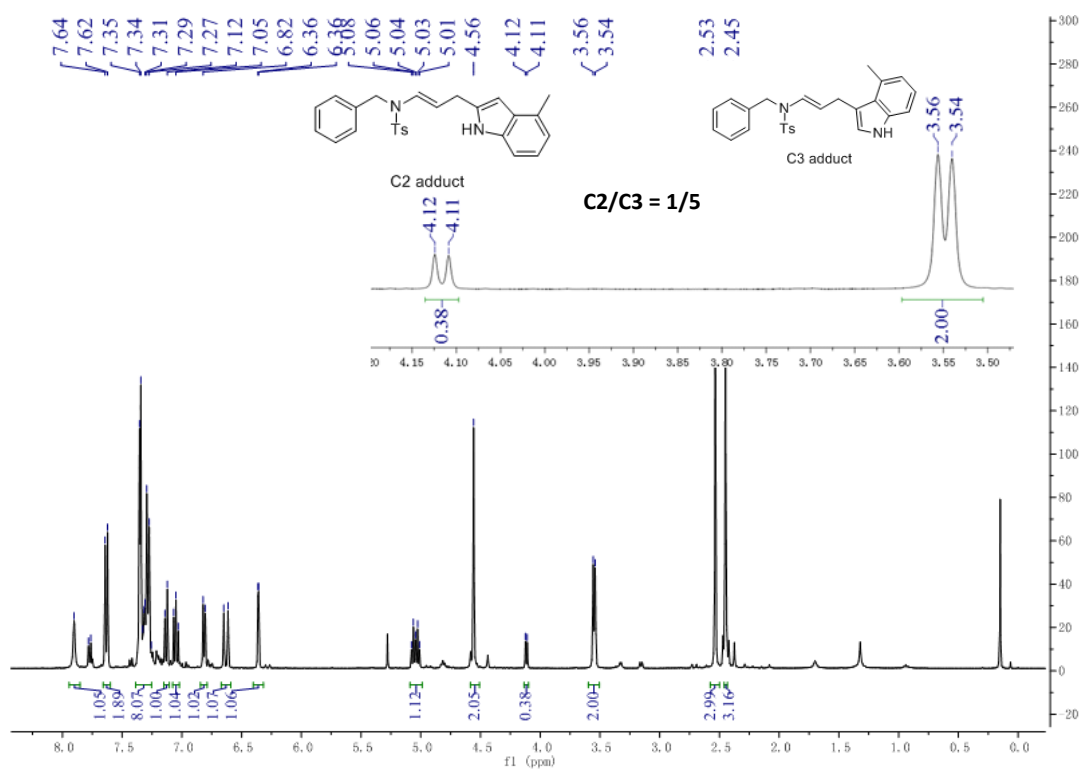




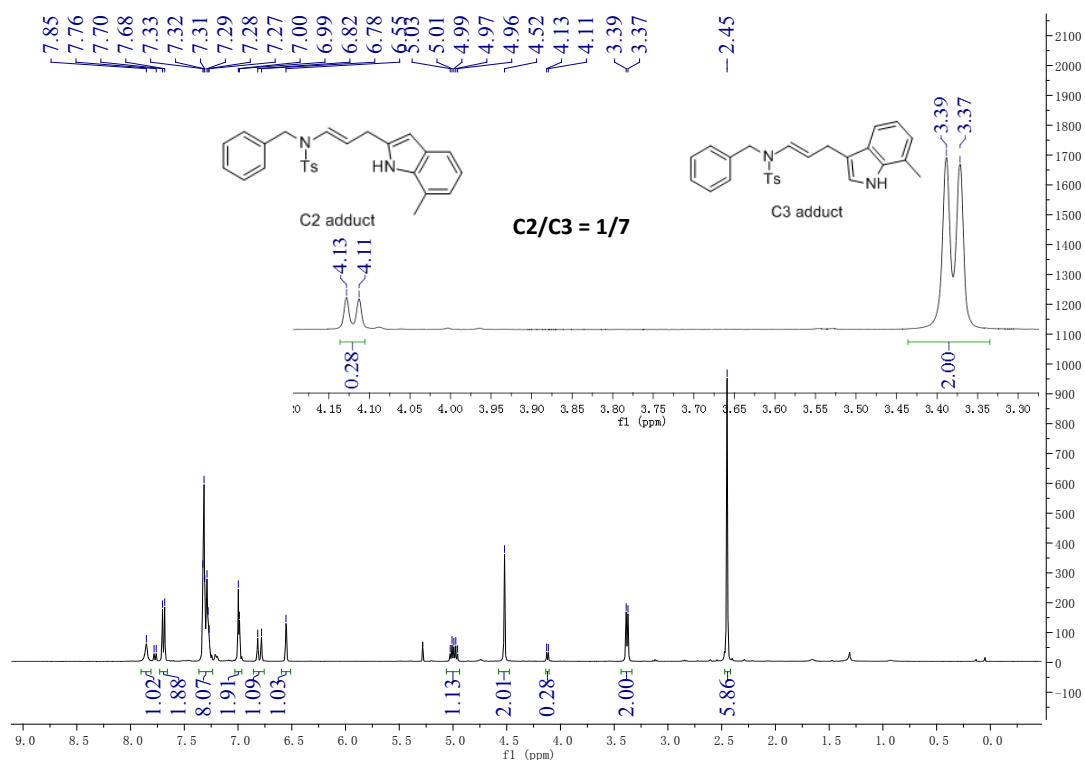




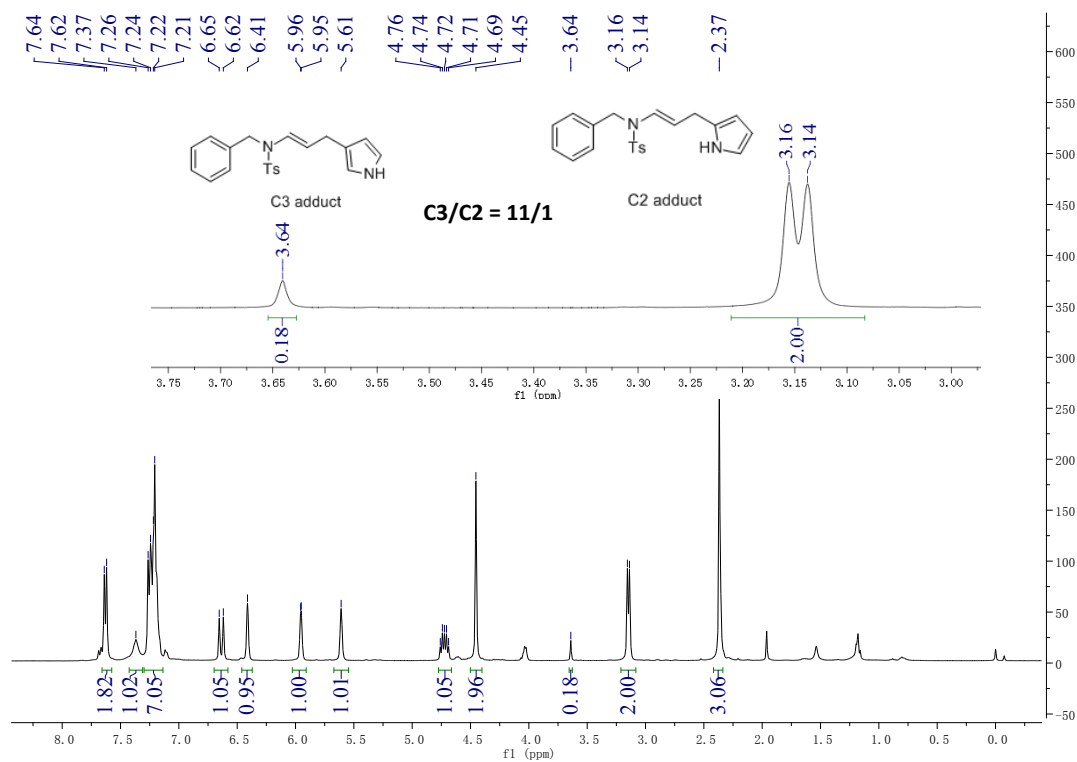
(3) The ratio of C3/C2 adducts of 4-Methylindole in the NMR spectra is 5/1(2/0.38).



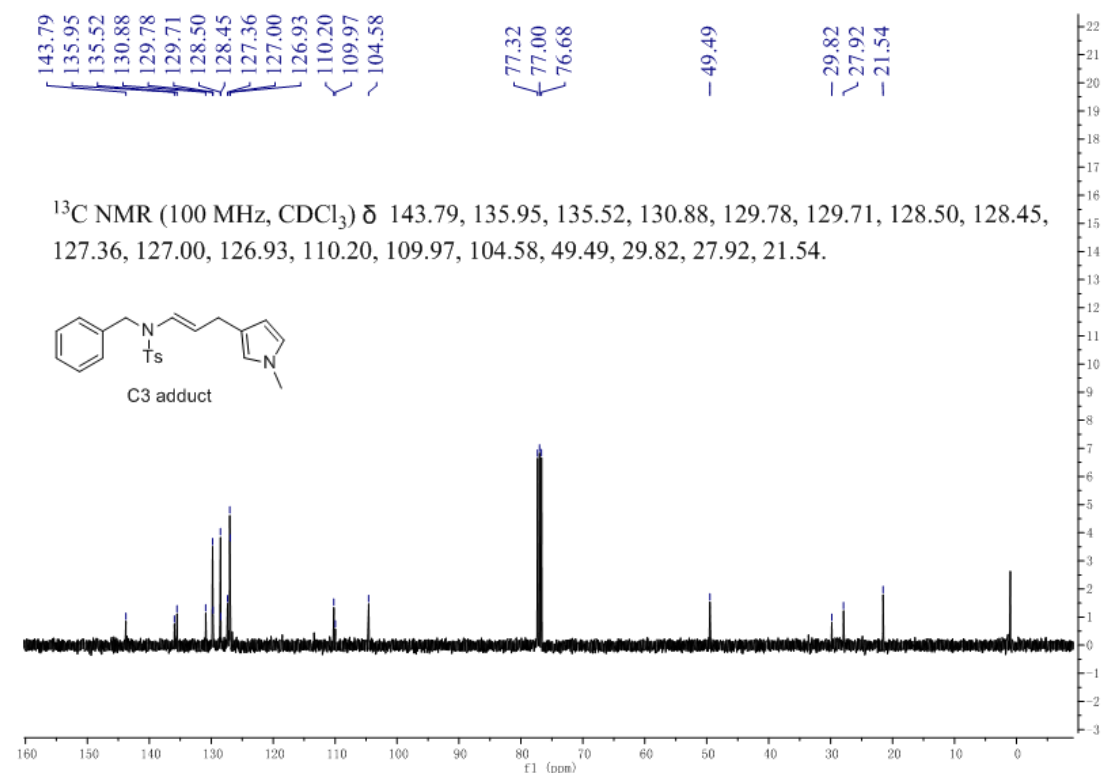
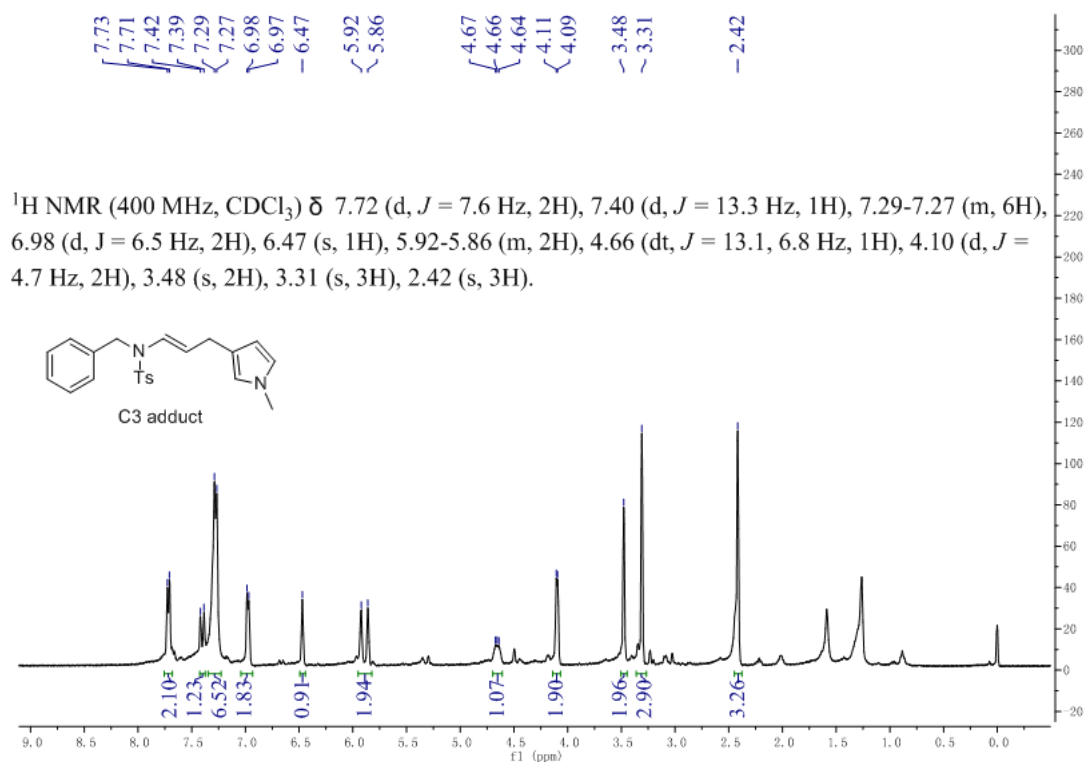
(4) The ratio of C3/C2 adducts of 7-Methylindole in the NMR spectra is 7/1(2/0.28).



(5) The ratio of C2/C3 adducts of pyrrole in the NMR spectra is 11/1(2/0.18).



3. NMR spectra of C3-addition product of N-Methylpyrrole

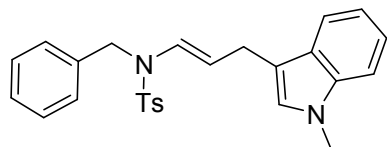


Colourless oil liquid; yield 15%;

IR (neat): 3038, 2934, 1602, 1493, 1454, 753, 542 cm⁻¹ ;

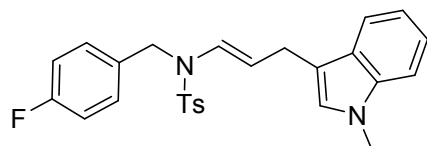
HRMS (ESI) calcd for C₂₂H₂₄N₂NaO₂S [M+Na]⁺ 403.1456; found, 403.1451.

4. Analytical Data



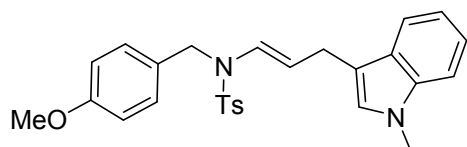
(E)-N-benzyl-4-methyl-N-(3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide(3a)

White solid; yield, 92%; mp 112.8-113.9°C; IR (neat) 3038, 2934, 1499, 1457, 758, 702, 540 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.14 (m, 9H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 14.1 Hz, 1H), 6.24 (s, 1H), 4.93 (dt, *J* = 13.9, 6.9 Hz, 1H), 4.51 (s, 2H), 3.62 (s, 3H), 3.34 (d, *J* = 6.8 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.62, 137.03, 135.91, 135.87, 129.77, 128.52, 127.30, 127.18, 126.99, 126.33, 126.21, 121.43, 118.87, 118.52, 113.35, 112.80, 109.97, 109.08, 49.46, 32.44, 26.03, 21.56; HRMS (ESI) calcd for C₂₆H₂₆N₂NaO₂S [M+Na]⁺ 453.1613; found, 453.1608.



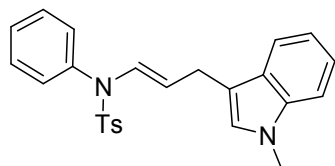
(E)-N-(4-fluorobenzyl)-4-methyl-N-(3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide(3b)

White solid; yield, 95%; mp 123.5-124.3°C; IR (neat) 3038, 2934, 1496, 1454, 758, 702, 540 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.23 (m, 5H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.03-6.97 (m, 3H), 6.72 (d, *J* = 14.1 Hz, 1H), 6.31 (s, 1H), 4.91 (dt, *J* = 14.0, 6.9 Hz, 1H), 4.46 (s, 2H), 3.65 (s, 3H), 3.35 (d, *J* = 6.8 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.34, 160.62, 143.74, 137.08, 131.55, 129.81, 128.93, 128.85, 127.34, 126.99, 126.30, 126.07, 121.52, 118.87, 118.57, 115.51, 115.29, 113.24, 113.11, 109.98, 109.15, 48.82, 32.46, 26.05, 21.58; HRMS (ESI) calcd for C₂₆H₂₅FN₂NaO₂S [M+Na]⁺ 471.1518; found, 471.1521.

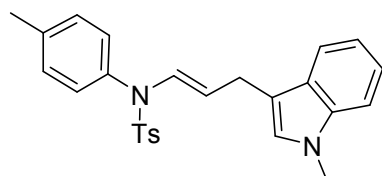


(E)-N-(4-methoxybenzyl)-4-methyl-N-(3-(1-methyl-1H-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide(3c)

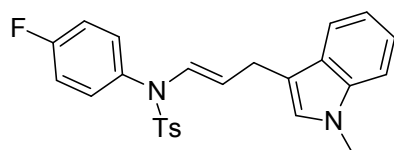
White solid; yield, 72%; mp 128.9-131.9°C; IR (neat) 2937, 1661, 1515, 1471, 1356, 742 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.24-7.21 (m, 3H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 14.2 Hz, 1H), 6.25 (s, 1H), 4.95 (dt, *J* = 14.0, 6.9 Hz, 1H), 4.43 (s, 2H), 3.79 (s, 3H), 3.62 (s, 3H), 3.34 (d, *J* = 6.9 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.84, 143.55, 137.03, 135.92, 129.73, 128.53, 127.77, 127.35, 126.96, 126.36, 126.12, 121.42, 118.88, 118.50, 113.86, 113.37, 113.02, 109.07, 55.21, 48.94, 32.37, 26.07, 21.55; HRMS (ESI) calcd for C₂₇H₂₈N₂NaO₃S [M+Na]⁺ 483.1718; found, 483.1721.



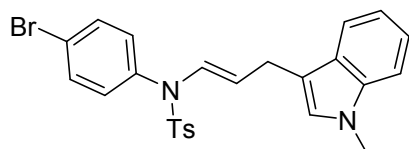
(*E*)-4-methyl-*N*-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)-*N*-phenylbenzenesulfonamide (**3d**)
 White solid; yield, 77%; mp 90.2-91.1 °C; IR (neat) 3038, 2934, 1501, 1457, 756, 702, 537 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.24 (m, 6H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.06 (dd, *J* = 14.3, 6.5 Hz, 2H), 7.01 – 6.93 (m, 2H), 6.71 (s, 1H), 4.63 (dt, *J* = 13.7, 6.8 Hz, 1H), 3.71 (s, 3H), 3.41 (d, *J* = 6.8 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.64, 137.09, 136.93, 135.89, 130.08, 129.51, 129.39, 129.33, 128.73, 127.50, 126.43, 121.46, 119.08, 118.56, 113.10, 111.82, 109.98, 109.15, 32.56, 25.79, 21.60; HRMS (ESI) calcd for C₂₅H₂₄N₂NaO₂S [M+Na]⁺ 439.1456; found, 439.1463.



(*E*)-4-methyl-*N*-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)-*N*-(*p*-tolyl)benzenesulfonamide (**3e**)
 Colourless oil liquid; yield, 82%; IR (neat) 2937, 1661, 1515, 1471, 1356, 742 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.27-7.19 (m, 4H), 7.11 – 7.03 (m, 4H), 6.83 (d, *J* = 8.1 Hz, 2H), 6.70 (s, 1H), 4.62 (dt, *J* = 13.8, 6.8 Hz, 1H), 3.70 (s, 3H), 3.40 (d, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.54, 138.76, 137.07, 135.96, 134.09, 130.01, 129.75, 129.48, 129.43, 127.54, 127.48, 126.42, 121.42, 119.08, 118.52, 113.16, 111.48, 109.13, 32.55, 25.76, 21.59, 21.17; HRMS (ESI) calcd for C₂₆H₂₆N₂NaO₂S [M+Na]⁺ 453.1613; found, 453.1609.

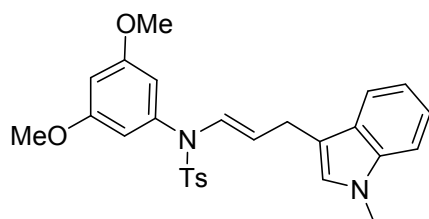


(*E*)-*N*-(4-fluorophenyl)-4-methyl-*N*-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide (**3f**)
 Colourless oil liquid; yield, 92%; IR (neat) 3070, 2937, 1509, 1356, 1167, 748 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 3H), 7.23 – 7.18 (m, 1H), 7.10 – 7.03 (m, 2H), 7.00-6.91 (m, 4H), 6.71 (s, 1H), 4.60 (dt, *J* = 13.8, 6.8 Hz, 1H), 3.70 (s, 3H), 3.41 (d, *J* = 6.8 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.37 (d, *J* = 247.5 Hz), 143.85, 137.10, 135.54, 132.70, 132.67, 131.95, 131.87, 129.59, 129.29, 127.48 (d, *J* = 4.4 Hz), 126.41, 121.49, 119.01, 118.58, 116.35 (d, *J* = 22.6 Hz), 112.95, 111.85, 109.19, 32.54, 25.76, 21.59; HRMS (ESI) calcd for C₂₅H₂₃FN₂NaO₂S [M+Na]⁺ 457.1362; found, 457.1356.



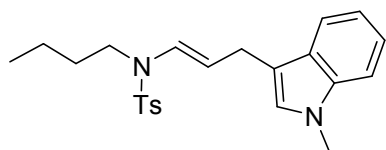
(*E*)-*N*-(4-bromophenyl)-4-methyl-*N*-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide (**3g**)

Colourless oil liquid; yield, 90%; IR (neat) 3069, 2940, 1726, 1339, 1163, 749 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.1$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.26-7.18 (m, 4H), 7.04 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 14.4$ Hz, 1H), 6.83 (d, $J = 8.4$ Hz, 2H), 6.69 (s, 1H), 4.63 (dt, $J = 13.8, 6.8$ Hz, 1H), 3.68 (s, 3H), 3.40 (d, $J = 6.8$ Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.94, 137.13, 136.05, 135.52, 132.65, 131.74, 129.65, 129.05, 127.48, 126.44, 122.86, 121.52, 119.01, 118.61, 112.87, 112.36, 110.00, 109.21, 32.57, 25.79, 21.61; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{23}\text{BrN}_2\text{NaO}_2\text{S}$ [$\text{M}+\text{Na}$] $^+$ 517.0561; found, 517.0497.



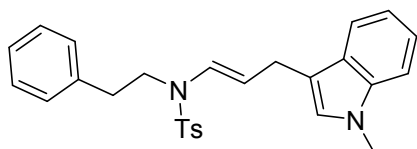
(*E*)-*N*-(3,5-dimethoxyphenyl)-4-methyl-*N*-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide (**3h**)

White solid; yield, 62%; mp 132.5-133.5 $^{\circ}\text{C}$; IR (neat) 2937, 1608, 1471, 1361, 1172, 742 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 8.2$ Hz, 2H), 7.48 (d, $J = 7.9$ Hz, 1H), 7.26 (d, $J = 8.6$ Hz, 3H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.02 (dd, $J = 14.3, 6.9$ Hz, 2H), 6.72 (s, 1H), 6.39 (t, $J = 2.1$ Hz, 1H), 6.11 (d, $J = 2.2$ Hz, 2H), 4.74 (dt, $J = 13.8, 6.8$ Hz, 1H), 3.70 (s, 3H), 3.61 (s, 6H), 3.41 (d, $J = 6.8$ Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.84, 143.68, 138.68, 137.10, 135.91, 129.47, 129.06, 127.59, 127.52, 126.45, 121.43, 119.09, 118.50, 112.99, 112.44, 109.16, 107.87, 101.23, 55.29, 32.54, 25.81, 21.58; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{NaO}_4\text{S}$ [$\text{M}+\text{Na}$] $^+$ 499.1667; found, 499.1672.



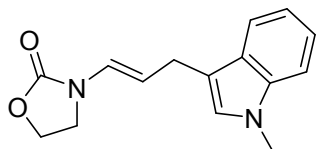
(*E*)-*N*-butyl-4-methyl-*N*-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide (**3i**)

Colourless oil liquid; yield, 96%; IR (neat) 2931, 1661, 1653, 1468, 739, 663 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 7.9$ Hz, 1H), 7.31 – 7.21 (m, 4H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.79 (s, 1H), 6.70 (d, $J = 14.2$ Hz, 1H), 5.06 (dt, $J = 13.9, 6.8$ Hz, 1H), 3.73 (s, 3H), 3.51 (d, $J = 6.8$ Hz, 2H), 3.27 (t, $J = 7.3$ Hz, 2H), 2.42 (s, 3H), 1.61-1.52 (m, 2H), 1.36-1.27 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.25, 137.10, 136.09, 129.58, 127.48, 126.84, 126.45, 126.40, 121.49, 119.03, 118.56, 113.29, 111.55, 109.15, 45.49, 32.53, 29.07, 26.19, 21.48, 19.89, 13.63; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{NaO}_2\text{S}$ [$\text{M}+\text{Na}$] $^+$ 419.1769; found, 419.1770.



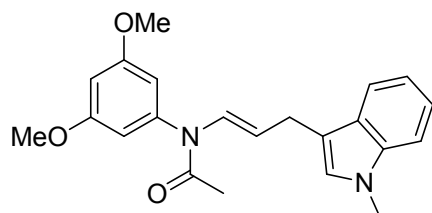
(*E*)-4-methyl-*N*-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)-*N*-phenethylbenzenesulfonamide(**3j**)

Colourless oil liquid; yield, 93%; IR (neat) 3047, 2940, 1726, 1339, 1163, 749 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 7.9$ Hz, 1H), 7.29 (d, $J = 8.2$ Hz, 1H), 7.26 – 7.16 (m, 6H), 7.13 (d, $J = 7.0$ Hz, 2H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.79 (s, 1H), 6.73 (d, $J = 14.2$ Hz, 1H), 5.16 (dt, $J = 13.9$, 6.8 Hz, 1H), 3.73 (s, 3H), 3.52 (d, $J = 6.8$ Hz, 2H), 3.50-3.46 (m, 2H), 2.90-2.86 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.44, 138.26, 137.17, 136.09, 129.67, 128.70, 128.52, 127.49, 126.89, 126.51, 126.43, 126.33, 121.57, 119.02, 118.65, 113.27, 111.45, 109.21, 47.24, 33.82, 32.58, 26.22, 21.50; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{28}\text{N}_2\text{NaO}_2\text{S}$ [$\text{M}+\text{Na}$] $^+$ 467.1769; found, 467.1773.



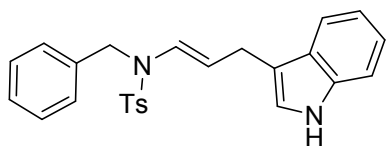
(*E*)-3-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)oxazolidin-2-one(**3k**)

Colourless oil liquid; yield, 80%; IR (neat) 2931, 1757, 1672, 1482, 1417, 739 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.9$ Hz, 1H), 7.27 (d, $J = 8.2$ Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.09 (t, $J = 7.4$ Hz, 1H), 6.83 (s, 1H), 6.80 (d, $J = 14.6$ Hz, 1H), 5.02 (dt, $J = 14.1$, 6.9 Hz, 1H), 4.36 – 4.30 (m, 2H), 3.72 (s, 3H), 3.63 – 3.58 (m, 2H), 3.51 (d, $J = 6.9$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.44, 137.14, 127.50, 126.47, 124.22, 121.64, 118.95, 118.78, 113.24, 110.39, 109.26, 62.12, 42.60, 32.59, 25.74; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{NaO}_2\text{S}$ [$\text{M}+\text{Na}$] $^+$ 279.1109; found, 279.1158.



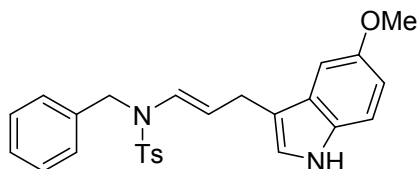
(*E*)-*N*-(3,5-dimethoxyphenyl)-*N*-(3-(1-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)acetamide(**3l**)

Colourless oil liquid; yield, 50%; IR (neat) 2942, 2844, 1681, 1605, 1471, 1058, 742 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 13.8$ Hz, 1H), 7.46 (d, $J = 7.9$ Hz, 1H), 7.15 (d, $J = 8.1$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.97 (t, $J = 7.4$ Hz, 1H), 6.63 (s, 1H), 6.36 (s, 1H), 6.23 (d, $J = 2.0$ Hz, 2H), 4.70 (dt, $J = 14.0$, 6.9 Hz, 1H), 3.64 (s, 6H), 3.59 (s, 3H), 3.37 (d, $J = 7.1$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.22, 161.46, 141.64, 136.97, 128.14, 127.56, 126.28, 121.34, 119.02, 118.49, 113.53, 113.37, 108.98, 106.88, 100.24, 55.37, 32.42, 25.88, 22.88. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaO}_3$ [$\text{M}+\text{Na}$] $^+$ 387.1685; found, 387.1690.



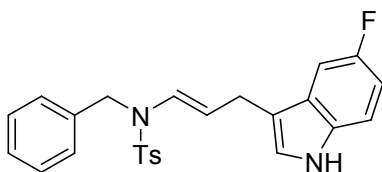
(E)-N-(3-(1H-indol-3-yl)prop-1-en-1-yl)-N-benzyl-4-methylbenzenesulfonamide(4b)

White solid; yield, 97%; mp 52-52.8 °C; IR (neat) 3444, 2934, 2861, 1661, 1630, 672 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.20 (m, 7H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 14.1 Hz, 1H), 6.48 (s, 1H), 4.94 (dt, *J* = 13.9, 6.8 Hz, 1H), 4.47 (s, 2H), 3.33 (d, *J* = 6.7 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.64, 136.30, 135.78, 135.73, 129.73, 128.46, 127.27, 127.01, 126.94, 126.89, 126.36, 121.76, 121.52, 118.97, 118.74, 114.59, 112.60, 111.05, 49.48, 26.07, 21.48. HRMS (ESI) calcd for C₁₅H₁₆N₂NaO₂S [M+Na]⁺ 439.1456; found, 439.1452.



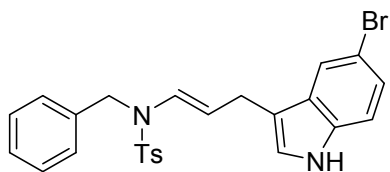
(E)-N-benzyl-N-(3-(5-methoxy-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide(4c)

Colourless oil liquid; yield, 90%; IR (neat) 3412, 2923, 1656, 1485, 1454, 1162, 736 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.18 (m, 7H), 7.19 (d, *J* = 8.6 Hz, 1H), 6.85 – 6.81 (m, 2H), 6.72 (d, *J* = 14.1 Hz, 1H), 6.49 (s, 1H), 4.94 (dt, *J* = 14.1, 6.7 Hz, 1H), 4.50 (s, 2H), 3.77 (s, 3H), 3.32 (d, *J* = 6.7 Hz, 2H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.71, 143.62, 135.79, 131.45, 129.75, 128.65, 128.49, 127.33, 127.29, 127.13, 127.03, 126.91, 126.48, 122.38, 114.45, 112.15, 111.98, 111.76, 100.63, 55.72, 49.51, 25.98, 21.52; HRMS (ESI) calcd for C₂₆H₂₆N₂NaO₃S [M+Na]⁺ 469.1562; found, 469.1561.



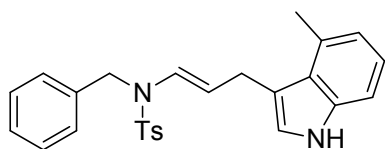
(E)-N-benzyl-N-(3-(5-fluoro-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide(4d)

Colourless oil liquid; yield, 95%; IR (neat) 3429, 2934, 1460, 1262, 911, 748 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.18 (m, 8H), 7.00 (dd, *J* = 9.6, 2.3 Hz, 1H), 6.90 (td, *J* = 9.1, 2.4 Hz, 1H), 6.71 (d, *J* = 14.2 Hz, 1H), 6.61 (s, 1H), 4.89 (dt, *J* = 14.1, 6.6 Hz, 1H), 4.49 (s, 2H), 3.30 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.63(d, *J* = 232.9 Hz), 143.85, 135.73, 135.71, 132.86, 129.86, 128.54, 127.35, 127.02, 126.88, 126.60, 123.50, 114.75(d, *J* = 14.0 Hz), 111.88, 111.73, 111.64, 110.37, 110.10, 103.8(d, *J* = 4.9 Hz), 49.50, 26.07, 21.55; HRMS (ESI) calcd for C₂₅H₂₃FN₂NaO₂S [M+Na]⁺ 457.1362; found, 457.1362.



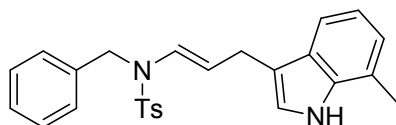
(*E*)-*N*-benzyl-*N*-(3-(5-bromo-1*H*-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide(**4e**)

Colourless oil liquid; yield, 61%; IR (neat) 3458, 2934, 1640, 911, 733, 646 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.51 (s, 1H), 7.30 – 7.19 (m, 8H), 7.14 (d, $J = 8.6$ Hz, 1H), 6.68 (d, $J = 14.2$ Hz, 1H), 6.53 (s, 1H), 4.89 (dt, $J = 14.1, 6.6$ Hz, 1H), 4.47 (s, 2H), 3.27 (d, $J = 6.5$ Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.99, 137.16, 136.08, 135.52, 132.68, 131.77, 129.69, 129.08, 127.54, 127.49, 126.49, 122.89, 121.55, 119.04, 118.64, 112.86, 112.41, 32.59, 25.83, 21.65; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{23}\text{BrN}_2\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 517.0561; found, 519.0565.



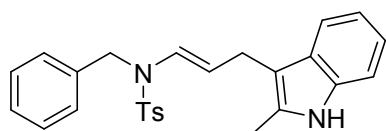
(*E*)-*N*-benzyl-4-methyl-*N*-(3-(4-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide(**4f**)

(major product); Light yellow oil liquid; yield 75%; IR (neat) 3464, 2937, 1661, 1642, 1328, 742 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (s, 1H), 7.48 (d, $J = 8.2$ Hz, 2H), 7.20-7.19 (m, 4H), 7.13 (d, $J = 8.0$ Hz, 3H), 6.98 (d, $J = 8.1$ Hz, 1H), 6.90 (t, $J = 7.6$ Hz, 1H), 6.66 (d, $J = 7.0$ Hz, 1H), 6.48 (d, $J = 14.2$ Hz, 1H), 6.21 (d, $J = 1.2$ Hz, 1H), 4.89 (dt, $J = 14.2, 6.4$ Hz, 1H), 4.41 (s, 2H), 3.40 (d, $J = 6.4$ Hz, 2H), 2.38 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.62, 135.87, 135.81, 135.75, 129.73, 128.46, 127.28, 127.01, 126.90, 126.51, 126.33, 122.33, 121.23, 120.20, 119.24, 116.50, 115.12, 112.60, 49.48, 26.23, 21.48, 16.48. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 453.1613; found, 453.1618.



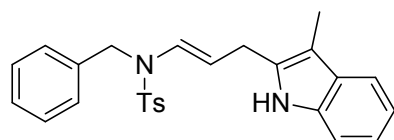
(*E*)-*N*-benzyl-4-methyl-*N*-(3-(7-methyl-1*H*-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide(**4g**)

(major product); colourless oil liquid; yield 69%; IR (neat) 3428, 3066; 2934, 1664, 1445, 1165, 742 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (s, 1H), 7.64 (d, $J = 8.1$ Hz, 2H), 7.28-7.22 (m, 8H), 6.94 (d, $J = 4.3$ Hz, 2H), 6.75 (d, $J = 14.1$ Hz, 1H), 6.50 (s, 1H), 4.94 (dt, $J = 13.9, 6.8$ Hz, 1H), 4.47 (s, 2H), 3.33 (d, $J = 6.7$ Hz, 2H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.62, 135.87, 135.81, 135.75, 129.73, 128.46, 127.28, 127.01, 126.90, 126.51, 126.33, 122.33, 121.23, 120.20, 119.24, 116.50, 115.12, 112.60, 49.48, 26.23, 21.48, 16.48; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 453.1613; found, 453.1617.



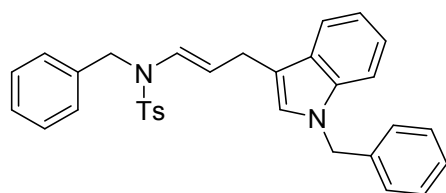
(E)-N-benzyl-4-methyl-N-(3-(2-methyl-1H-indol-3-yl)prop-1-en-1-yl)benzenesulfonamide(4h)

White solid; yield, 75%; mp 143.5-144.6 °C; IR (neat) 3414, 2934, 1661, 1456, 1342, 742 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (br, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.26-7.21 (m, 9H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 14.1 Hz, 1H), 4.88 (dt, *J* = 14.1, 6.4 Hz, 1H), 4.42 (s, 2H), 3.31 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 2.20 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.53, 135.79, 135.11, 131.17, 129.70, 128.43, 128.33, 127.27, 127.15, 127.00, 126.93, 126.12, 120.84, 118.97, 118.10, 112.78, 110.12, 109.27, 49.49, 24.95, 21.54, 11.52; HRMS (ESI) calcd for C₂₆H₂₆N₂NaO₂S [M+Na]⁺ 453.1613; found, 453.1613.



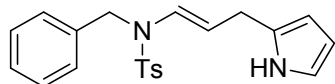
(E)-N-benzyl-4-methyl-N-(3-(3-methyl-1H-indol-2-yl)prop-1-en-1-yl)benzenesulfonamide(4i)

White solid; yield, 70%; mp 75.8-76.5 °C; IR (neat) 3464, 2937, 1661, 1642, 1328, 742 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.26 (m, 7H), 7.08-7.01 (m, 4H), 6.76 (d, *J* = 14.1 Hz, 1H), 4.78 (dt, *J* = 14.3, 7.2 Hz, 1H), 4.54 (s, 2H), 3.34 (d, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 2.11 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.00, 135.79, 135.45, 134.91, 132.27, 129.91, 128.74, 127.77, 127.73, 127.15, 126.97, 120.98, 118.95, 117.98, 110.22, 110.19, 109.98, 106.68, 49.54, 27.08, 21.58, 8.26. HRMS (ESI) calcd for C₂₆H₂₆N₂NaO₂S [M+Na]⁺ 453.1613; found, 453.1614.



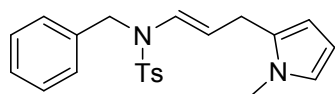
(E)-N-benzyl-N-(3-(1-benzyl-1H-indol-3-yl)prop-1-en-1-yl)-4-methylbenzenesulfonamide(4j)

colourless oil liquid; yield, 71%; IR (neat) 3033, 2928, 1729, 1462, 1366, 727 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.29-7.21 (m, 9H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.01 (m, 3H), 6.75 (d, *J* = 14.1 Hz, 1H), 6.31 (s, 1H), 5.13 (s, 2H), 4.94 (dt, *J* = 13.9, 6.9 Hz, 1H), 4.50 (s, 2H), 3.35 (d, *J* = 6.8 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.68, 137.76, 136.71, 135.90, 135.85, 129.82, 128.71, 128.54, 127.67, 127.49, 127.36, 127.17, 127.00, 126.59, 126.37, 125.84, 121.71, 119.01, 118.85, 114.14, 112.60, 109.64, 49.76, 49.48, 26.11, 21.60; HRMS (ESI) calcd for C₃₂H₃₀N₂NaO₂S [M+Na]⁺ 529.1926; found, 529.1922.



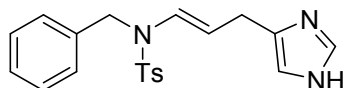
(E)-N-(3-(1H-pyrrol-2-yl)prop-1-en-1-yl)-N-benzyl-4-methylbenzenesulfonamide(4k)

(major product); White solid; yield, 82%; mp 83.8-84.3 °C; IR (neat) 3460, 2934, 1662, 1346, 1165, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.0 Hz, 2H), 7.33-7.28 (m, 7H), 6.71 (d, J = 14.1 Hz, 1H), 6.49 (s, 1H), 6.03 (s, 1H), 5.68 (s, 1H), 4.80 (dt, J = 14.2, 7.2 Hz, 1H), 4.53 (s, 2H), 3.22 (d, J = 7.1 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.91, 135.80, 135.47, 129.97, 129.90, 129.85, 128.63, 127.48, 127.33, 127.06, 126.94, 116.49, 110.75, 108.27, 105.11, 49.57, 28.57, 21.58; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 389.1300; found, 389.1304.



(E)-N-benzyl-4-methyl-N-(3-(1-methyl-1H-pyrrol-2-yl)prop-1-en-1-yl)benzenesulfonamide(4l)

(major product); White solid; yield, 80%; mp 86.6-87.5 °C; IR (neat) 2934, 2861, 1664, 1356, 913, 744, 548 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.2 Hz, 2H), 7.28 (m, 7H), 6.69 (d, J = 14.1 Hz, 1H), 6.48 (s, 1H), 5.95 (s, 1H), 5.51 (s, 1H), 4.80 (dt, J = 13.9, 6.8 Hz, 1H), 4.51 (s, 2H), 3.34 (s, 3H), 3.17 (d, J = 6.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.80, 135.90, 135.49, 131.07, 129.80, 128.54, 127.85, 127.42, 127.05, 126.98, 126.95, 121.58, 110.25, 109.99, 106.42, 106.18, 49.49, 33.44, 27.53, 21.56; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 403.1456; found, 403.1458.



(E)-N-(3-(1H-imidazol-4-yl)prop-1-en-1-yl)-N-benzyl-4-methylbenzenesulfonamide(4m)

White solid; yield, 81%; mp 127.8-128.6 °C; IR (neat) 3360, 2917, 1667, 1634, 1512, 664 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.31-7.28 (m, 3H), 7.24 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 14.0 Hz, 1H), 6.99 (s, 1H), 6.66 (s, 1H), 4.74 (dt, J = 14.2, 7.1 Hz, 1H), 4.54 (s, 2H), 4.42 (d, J = 7.1 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.47, 135.60, 134.61, 130.95, 130.09, 128.78, 127.79, 126.91, 126.72, 118.39, 113.24, 110.00, 104.88, 49.50, 47.30, 21.61; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 390.1252; found, 390.1251.

5. References

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3. J. M. Chapman, J. G. H. Cocolas and I. H. Hall, *J. Med. Chem.*, 1983, **26**, 243-246.
4. M. C. Kimber, *Org. Lett.*, 2010, **12**, 1128-1131.

6. NMR Spectra

