Poly(phosphoric acid) (PPA)-Promoted 5-exo-Cyclization of Iminium Ions Generated In Situ: A Facile Access to Functionalized Indene Derivatives

Yi-Fan Zhu,a Xin-Le Geng,a Yong-Hong Guan,a Wei Teng,a Xiaohui Fan,b,c* aSchool of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China
bBeijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry, Peking University, Beijing 100871, China
cYMU-HKBU Joint Laboratory of Traditional Natural Medicine, Yunnan Minzu University, Kunming 650500, China
E-mail: fanxh@mail.lzjtu.cn

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General information
Reactions were monitored by analytical thin-layer chromatography (TLC) using ultraviolet light, phosphomolybdic acid or KMnO₄ for visualization. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh) and the purified compounds show a single spot by analytical TLC. ¹H NMR and ¹³C NMR spectra were recorded at 400 and 100 MHz respectively using CDCl₃ as the solvent with TMS as an internal standard. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (Hertz) respectively. High-resolution mass spectra (HRMS) were performed on an ITQ-Orbitrap Elite spectrometer. Melting points were measured on a micro melting apparatus and uncorrected.

General procedures for the synthesis of starting materials: 1a-1k

![Chemical reaction](attachment:image)

To a stirred solution of KOH (0.56g, 0.01 mol) in EtOH (25 mL, 95%) was added aldehyde A (0.01 mol), the mixture was cooled to 0 °C and aldehyde B (0.02 mol) was added slowly so that the reaction temperature did not exceed 10 °C. After being stirred for 6 h, the reaction was quenched by addition of HCl (25 mL, 3 M, aq.) and extraction with Et₂O (3×20 mL). The organic layer was dried over MgSO₄ and concentrated to give the crude product as a color residue. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9/1) to afford substituted cinnamyl aldehydes (1a-1k).

Synthesis of starting material: 1l

![Chemical reaction](attachment:image)

Step 1: To a stirred solution of anyhydrous ethanol (20 mL) at 20 °C was added sodium (0.46 g, 20.4 mmol, 1.2 equiv). The mixture was stirred at 30 °C until the metal dissolved. To the solution was then added triethyl 2-phosphonopropionate (4.45 g, 18.7 mmol, 1.1 equiv). The solution was stirred at 25 °C for 10 min and acetophenone (2 g, 17 mmol, 1 equiv) was added subsequently. The colorless solution was stirred at reflux for 24 h. The solution was cooled to 25 °C and the solvent was removed. The residue was diluted with water (20 mL) and extracted with EtOAc (2×25 mL). The combined organic layers were dried (MgSO4), filtered, concentrated and purified by flash
column chromatography (petroleum ether / EtOAc = 95/5) to afford (Z)- and (E)-isomer (major product), separately.

**Step 2**: To ethyl (2E)-3-phenylbut-2-enoate (2.8g, 14 mmol) diluted with THF (40 mL) and cooled to 0 ºC was added LiAlH₄ (1 M in THF; 23 mL, 23 mmol) and the reaction was stirred at RT for 2 h. Excess LiAlH₄ was quenched with water at 0 ºC; the product was extracted with Et₂O (3×30 mL) and dried with MgSO₄. After removal of the solvent under reduced pressure, the residue was diluted with CH₂Cl₂ and Dess-Martin periodinane (7.1 g, 16.8 mmol) was added. After stirring at RT for 0.5 h, the solvent was removed; the residue was extracted with pentane (5×30 mL) and filtered through Celite. After evaporation of the solvent, the obtained product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) to afford 2.0 g (89% yield) of aldehydes 1l.

**Synthesis of starting materials: 1m⁴**

To a stirred solution of benzophenone (3.60 g, 0.02 mol) and TiCl₄ (2.2 mL of 1:1 solution of TiCl₄/CH₂Cl₂, 0.08 mol) in anhydrous DCM (30 mL) under argon at 0 ºC was added Et₃N (8.10 g, 0.08 mol) slowly and stirred for 0.5 h at 0 ºC. After being further stirred at 25 ºC for 8 h, the reaction was quenched by addition of saturated aqueous NH₄Cl solution (20 mL) and stirred at rt for 0.5 h. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (2×25 mL). The combined organic was washed with brine (10 mL) and dried over MgSO₄, filtered and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the corresponding product 1m.

**General procedure for PPA-promoted cyclization reaction**

To a stirred solution of aldehyde 1 (0.20 mmol) in toluene (2 mL) was added 4-methylbenzenesulfonamide (0.24 mmol) and PPA (20 mol %). The resulting mixture was stirred at 40-80 ºC. After the aldehyde was completely consumed (monitored by TLC), the reaction was quenched by addition of saturated NaHCO₃ (3 mL) and then extracted with ethyl acetate (3×5 mL). The combined organic layer was washed with brine, dried over MgSO₄ and filtered. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc =10/1) to afford the corresponding product 3.
Transformation of 3a into corresponding indene-enamine 4a

**Condition A**: To a solution of 3a (21 mg, 0.07 mmol) in dry MeOH (1.5 mL) was added Mg powder (17 mg, 0.7 mmol). The suspension was sonicated for 2 h under argon and then added to 1M HCl (3.0 ml). The mixture was stirred for 5 minutes and neutralized with saturated aqueous sodium bicarbonate. The mixture was extracted twice with EtOAc, dried over MgSO₄, filtered and concentrated. The product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8/1) to afford the corresponding product 4a.

**Condition B**: A solution of 1M TBAF in THF (2.0 mL) was added to 3a (0.5 mmol), the resulted mixture was stirred at 40 ºC under argon for 2 h. The reaction mixture was cooled to room temperature and diluted with EtOAc. To this solution HCl (35% in H₂O, 2 mL) was added. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The combined organic was washed with brine and dried over Na₂SO₄, filtered and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the corresponding product 4a.

**General procedure for transformation of 3a and 3l into corresponding indanone 5a and 5l**

To a solution of SmI₂ (0.13 M, 2.1 mmol) in THF was added 3a (0.52 mmol) followed by water (15.6 mmol) and pyrrolidine (10.4 mmol) under an argon atmosphere. The reaction mixture immediately turned white upon addition of amine. After the mixture was stirred for 0.5 h at room temperature, the resulting mixture was diluted with EtOAc (6 mL) and treated with dilute hydrochloric acid (4 mL, 0.5 M). The aqueous phase was extracted with two portions of EtOAc. The combined organic was washed with brine and dried over Na₂SO₄, filtered and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to afford the corresponding products 5a (91%), and 5l (88%).
Characterization data

4-methyl-N-(2-methyl-1H-inden-1-yl)benzenesulfonamide (3a): 55 mg, 91%.
White solid; m.p. 130 - 132 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.37 - 7.33 (m, 2H), 7.18 - 7.16 (m, 2H), 7.07 (m, 1H), 6.96 (m, 1H), 6.32 (s, 1H), 4.70 (d, $J = 9.5$ Hz, 1H), 4.54 (d, $J = 9.5$ Hz, 1H), 2.47 (s, 3H), 1.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 145.9, 143.5, 143.3, 143.1, 138.4, 129.7, 128.3, 127.7, 127.1, 124.8, 123.2, 120.2, 62.3, 21.5, 13.7; HRMS (ESI, m/z) calcd for C$_{17}$H$_{21}$N$_2$O$_2$S [M+NH$_4$]$^+$: 317.1318. Found: 317.1315.

N-(2,6-dimethyl-1H-inden-1-yl)-4-methylbenzenesulfonamide (3b): 51 mg, 81%.
White solid; m.p. 145 - 147 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.3$ Hz, 2H), 6.95 (s, 2H), 6.39 (s, 1H), 6.28 (s, 1H), 4.65 (d, $J = 9.6$ Hz, 1H), 4.49 (d, $J = 8.9$ Hz, 1H), 2.49 (s, 3H), 2.16 (s, 3H), 1.86 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 144.7, 143.6, 140.4, 138.6, 134.5, 129.8, 128.7, 127.6, 127.3, 124.4, 119.9, 62.3, 21.5, 21.1, 13.8; HRMS (ESI, m/z) calcd for C$_{18}$H$_{19}$NNaO$_2$S [M+Na]$^+$: 336.1029. Found: 336.1036.

N-(2,4-dimethyl-1H-inden-1-yl)-4-methylbenzenesulfonamide (3c): 54 mg, 86%.
White solid; m.p. 147 - 148 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.38 - 7.34 (m, 2H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.86 (t, $J = 7.5$ Hz, 1H), 6.57 (d, $J = 7.4$ Hz, 1H), 6.45-6.41 (m, 1H), 4.69 (d, $J = 9.6$ Hz, 1H), 4.48 (d, $J = 9.6$ Hz, 1H), 2.48 (s, 3H), 2.28 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 145.4, 143.6, 143.2, 141.8, 138.5, 129.8, 129.6, 129.5, 127.2, 126.0, 124.9, 120.7, 62.7, 21.6, 18.0, 14.0; HRMS (APCI, m/z) calcd for C$_{18}$H$_{20}$NO$_2$S [M+H]$^+$: 314.1029. Found: 314.1216.

4-methyl-N-(2-phenyl-1H-inden-1-yl)benzenesulfonamide (3d): 72 mg, 99%.
White solid; m.p. 145 - 146 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.93 - 7.87 (m, 2H), 7.31 - 7.34 (m, 2H), 7.22 - 7.26 (m, 2H), 6.09 (m, 1H), 5.05 (d, $J = 9.7$ Hz, 1H), 4.58 (d, $J = 9.7$ Hz, 1H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.1, 144.2, 143.7, 141.9, 138.0, 134.4, 131.0, 129.9, 128.6, 128.3, 127.5, 127.3, 126.4, 124.1, 120.8, 59.4, 21.5; HRMS (ESI, m/z) calcd for C$_{22}$H$_{19}$NO$_2$S [M+H]$^+$: 384.1029. Found: 384.1034.

N-(6-methoxy-2-methyl-1H-inden-1-yl)-4-methylbenzenesulfonamide (3e): 52 mg, 79%.
White solid; m.p. 140 - 141 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.90 (d, \(J = 8.3\) Hz, 2H), 7.40 - 7.36 (m, 2H), 6.97 (d, \(J = 8.2\) Hz, 1H), 6.70 (dd, \(J = 8.1, 2.4\) Hz, 1H), 6.31 - 6.25 (m, 2H), 4.68 (d, \(J = 9.7\) Hz, 1H), 4.49 (d, \(J = 9.7\) Hz, 1H), 3.61 (s, 3H), 2.47 (s, 3H), 1.89 (d, \(J = 0.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.8, 145.1, 143.6, 138.8, 138.7, 135.8, 129.8, 127.2, 120.5, 113.9, 109.8, 62.4, 55.3, 21.5, 13.7; HRMS (ESI, \(m/z\)) calcd for C\(_{18}\)H\(_{19}\)NNaO\(_3\)S [M+Na]\(^+\): 352.0978. Found: 352.0982.

![Structure of NHTs](image1)

N-(4-methoxy-2-methyl-1H-inden-1-yl)-4-methylbenzenesulfonamide (3f): 59 mg, 90%.
White solid; m.p. 145 - 146 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.89 (d, \(J = 8.1\) Hz, 2H), 7.37 - 7.26 (m, 2H), 6.96 - 6.92 (m, 1H), 6.73 (d, \(J = 8.2\) Hz, 1H), 6.47 - 6.42 (m, 2H), 4.71 (d, \(J = 9.6\) Hz, 1H), 4.51 (d, \(J = 9.6\) Hz, 1H), 3.80 (s, 3H), 2.47 (s, 3H), 1.88 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 151.9, 145.2, 143.9, 143.4, 138.5, 131.1, 129.7, 127.1, 126.2, 123.7, 116.1, 110.9, 62.7, 55.4, 21.5, 13.8; HRMS (ESI, \(m/z\)) calcd for C\(_{18}\)H\(_{19}\)NNaO\(_3\)S [M+Na]\(^+\): 352.0978. Found: 352.0986.

![Structure of NHTs](image2)

4-methyl-N-(2-methyl-3H-cyclopenta[a]naphthalen-3-yl)benzenesulfonamide (3g): 63 mg, 90%.
White solid; m.p. 148 - 150 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.93 - 7.86 (m, 3H), 7.78 (d, \(J = 8.1\) Hz, 1H), 7.51 - 7.32 (m, 5H), 6.97 (d, \(J = 8.3\) Hz, 1H), 6.86 (s, 1H), 4.81 (d, \(J = 9.7\) Hz, 1H), 4.63 (d, \(J = 9.7\) Hz, 1H), 2.48 (s, 3H), 1.96 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 146.6, 143.7, 140.2, 139.5, 138.4, 133.7, 129.8, 128.4, 127.3, 126.8, 125.8, 125.7, 125.1, 125.0, 123.7, 121.2, 63.2, 21.6, 14.1; HRMS (ESI, \(m/z\)) calcd for C\(_{21}\)H\(_{19}\)NNaO\(_2\)S [M+Na]\(^+\): 372.1029. Found: 372.1040.

![Structure of NHTs](image3)

4-methyl-N-(2-methyl-1H-cyclopenta[a]naphthalen-1-yl)benzenesulfonamide (3h): 64 mg, 91%.
White solid; m.p. 181 - 182 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.94 - 7.86 (m, 3H), 7.78 (d, \(J = 8.1\) Hz, 1H), 7.52 - 7.32 (m, 5H), 6.97 (d, \(J = 8.3\) Hz, 1H), 6.86 (s, 1H), 4.81 (d, \(J = 9.7\) Hz, 1H), 4.63 (d, \(J = 9.7\) Hz, 1H), 2.48 (s, 3H), 1.96 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 146.6, 143.7, 140.2, 139.5, 138.4, 133.7, 129.8, 128.4, 127.3, 126.8, 125.8, 125.7, 125.1, 125.0, 123.7, 121.2, 63.2, 21.6, 14.1; HRMS (ESI, \(m/z\)) calcd for C\(_{21}\)H\(_{19}\)NNaO\(_2\)S [M+Na]\(^+\): 372.1029. Found: 372.1033.

![Structure of NHTs](image4)
4-methyl-N-(4-methyl-2-phenyl-1H-inden-1-yl)benzenesulfonamide (3i): 62 mg, 82%.  
White solid; m.p. 147 - 148 °C; 1H NMR (400 MHz, CDCl3): δ 7.83 (d, J = 8.2 Hz, 2H), 7.34 - 7.32 (m, 4H), 7.25 - 7.19 (m, 3H), 7.10 - 7.07 (m, 1H), 7.05 - 6.97 (m, 3H), 5.45 (d, J = 9.0 Hz, 1H), 4.47 (d, J = 9.0 Hz, 1H), 2.49 (s, 3H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 146.3, 144.2, 142.1, 138.5, 133.3, 129.0, 128.4, 127.8, 127.5, 126.9, 126.2, 124.7, 121.3, 59.6, 29.7, 21.6; HRMS (ESI, m/z) calcd for C23H21NNaO2S [M+Na]+: 398.1185. Found: 398.1184.

4-methyl-N-(6-methyl-2-phenyl-1H-inden-1-yl)benzenesulfonamide (3j): 55 mg, 73%.  
White solid; m.p. 168 - 170 °C; 1H NMR (400 MHz, CDCl3): δ 7.84 (d, J = 8.2 Hz, 2H), 7.36 - 7.33 (m, 4H), 7.12 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.96 (s, 1H), 6.71 (s, 1H), 5.41 (d, J = 9.2 Hz, 1H), 2.50 (s, 3H), 2.21 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 145.2, 144.3, 143.6, 139.4, 138.7, 136.1, 133.3, 129.8, 129.1, 128.5, 127.6, 126.7, 125.5, 120.9, 59.4, 21.5, 21.3; HRMS (ESI, m/z) calcd for C23H21NNaO2S [M+Na]+: 398.1185. Found: 398.1187.

N-(6-ethyl-2-methyl-1H-inden-1-yl)-4-methylbenzenesulfonamide (3k): 54 mg, 82%.  
White solid; m.p. 141 - 143 °C; 1H NMR (400 MHz, CDCl3): δ 7.90 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 6.98 (s, 2H), 6.31 (d, J = 16.9 Hz, 2H), 4.68 (d, J = 9.6 Hz, 1H), 4.49 (d, J = 9.7 Hz, 1H), 2.49 - 2.40 (m, 5H), 1.91 (s, 3H), 1.08 (t, J = 7.6 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 145.1, 143.9, 143.8, 141.3, 138.9, 130.1, 128.0, 127.8, 127.5, 123.2, 120.2, 62.6, 28.8, 21.7, 15.7, 14.0; HRMS (ESI, m/z) calcd for C19H21NNaO2S [M+Na]+: 350.1185. Found: 350.1191.

N-(2,3-dimethyl-1H-inden-1-yl)-4-methylbenzenesulfonamide (3l): 50 mg, 80%.  
White solid; m.p. 175 - 176 °C; 1H NMR (400 MHz, CDCl3): δ 7.89 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.18-7.28 (m, 1H), 7.08 (d, J = 7.4 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 7.3 Hz, 1H), 4.69 (d, J = 9.2 Hz, 1H), 4.44 (d, J = 9.2 Hz, 1H), 2.48 (s, 3H), 1.94 (s, 3H), 1.81 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 145.2, 143.5, 142.8, 138.7, 137.9, 134.0, 129.8, 128.3, 127.3, 125.0, 123.0, 118.3, 62.4, 21.6, 11.1, 10.3; HRMS (ESI, m/z) calcd for C18H19NNaO2S [M+Na]+: 336.1029. Found: 336.1035.

4-methyl-N-(3-phenyl-1H-inden-1-yl)benzenesulfonamide (3m): 54 mg, 75%.  
White solid; m.p. 115 - 117 °C; 1H NMR (400 MHz, CDCl3): δ 7.87 (d, J = 8.2 Hz, 2H), 7.46-7.33 (m, 8H), 7.32-7.29 (m, 2H), 7.26 - 7.22 (m, 1H), 6.08 (s, 1H), 5.05 (d, J = 9.7 Hz, 1H), 4.59 (d, J = 9.7 Hz, 1H), 2.47 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 146.1, 144.2, 143.7, 141.9, 138.0, 134.4,
131.0, 129.9, 128.6, 128.3, 127.5, 127.3, 126.4, 124.1, 120.8, 59.4, 21.5; HRMS (ESI, m/z) calcd for C_{22}H_{19}NNaO_{2}S [M+Na]^+: 384.1029. Found: 384.1037.

N-(6-chloro-2-methyl-1\textsubscript{H}-inden-1-yl)-4-methylbenzenesulfonamide (3n): 43 mg, 64%.
White solid; m.p. 175 - 176 °C; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \textit{\delta} 7.86 (d, \textit{J} = 8.1 Hz, 2H), 7.39 (d, \textit{J} = 8.0 Hz, 2H), 7.12 (d, \textit{J} = 7.9 Hz, 1H), 6.98 (d, \textit{J} = 7.9 Hz, 1H), 6.47 (s, 1H), 6.29 (s, 1H), 4.67 (d, \textit{J} = 9.4 Hz, 1H), 4.49 (d, \textit{J} = 9.7 Hz, 1H), 2.49 (s, 3H), 1.91 (s, 3H); \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \textit{\delta} 146.4, 145.0, 144.1, 138.3, 130.9, 130.0, 128.4, 127.2, 127.1, 121.0, 62.3, 21.6, 13.8; HRMS (ESI, m/z) calcd for C\textsubscript{17}H\textsubscript{17}ClNO\textsubscript{2}S [M+H]^+: 334.0663. Found: 334.0665.

N-(6-fluoro-2-methyl-1\textsubscript{H}-inden-1-yl)-4-methylbenzenesulfonamide (3o): 38 mg, 61%.
White solid; m.p. 116 - 118 °C; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \textit{\delta} 7.85 (dd, \textit{J} = 8.3, 1.8 Hz, 2H), 7.36 (d, \textit{J} = 8.0 Hz, 2H), 6.97 (dd, \textit{J} = 8.1, 5.0 Hz, 1H), 6.88 - 6.79 (m, 1H), 6.48 (d, \textit{J} = 8.4 Hz, 1H), 6.27 (s, 1H), 4.75 (d, \textit{J} = 9.8 Hz, 1H), 4.63 (d, \textit{J} = 9.5 Hz, 1H), 2.47 (s, 3H), 1.85 (s, 3H); \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \textit{\delta} 161.2 (d, \textit{J}_{C,F} = 244.6 Hz), 145.5 (d, \textit{J}_{C,F} = 3.0 Hz), 143.9, 138.8 (d, \textit{J}_{C,F} = 9.1 Hz), 114.7 (d, \textit{J}_{C,F} = 22.6 Hz), 111.7 (d, \textit{J}_{C,F} = 24.1 Hz), 62.3 (d, \textit{J}_{C,F} = 3.0 Hz), 21.5, 13.8.

N-(2-methyl-1\textsubscript{H}-inden-1-yl)benzenesulfonamide (3ab): 50 mg, 87%.
White solid; m.p. 137 - 139 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 7.97 (d, \textit{J} = 7.6 Hz, 2H), 7.60 (dt, \textit{J} = 15.1, 7.4 Hz, 3H), 7.17 - 7.01 (m, 2H), 6.91 (t, \textit{J} = 7.4 Hz, 1H), 6.68 (d, \textit{J} = 7.4 Hz, 1H), 6.30 (s, 1H), 4.68 (s, 2H), 1.87 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \textit{\delta} 145.8, 143.2, 141.4, 132.7, 129.2, 128.3, 127.8, 127.1, 124.9, 132.2, 120.2, 64.2, 13.7; HRMS (ESI, m/z) calcd for C\textsubscript{16}H\textsubscript{15}NNaO\textsubscript{2}S [M+Na]^+: 308.0716. Found: 308.0715.

4-chloro-N-(2-methyl-1\textsubscript{H}-inden-1-yl)benzenesulfonamide (3ac): 53 mg, 83%.
White solid; m.p. 125 - 126 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 7.86 (d, \textit{J} = 8.4 Hz, 2H), 7.50 (d, \textit{J} = 8.3 Hz, 2H), 7.05 (ddd, \textit{J} = 40.6, 14.7, 7.3 Hz, 3H), 6.81 (d, \textit{J} = 7.3 Hz, 1H), 6.30 (s, 1H), 4.79 (t, \textit{J} = 15.1 Hz, 1H), 4.64 (d, \textit{J} = 9.0 Hz, 1H), 1.86 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \textit{\delta} 145.5, 143.1, 140.0, 139.2, 129.4, 128.5, 128.1, 125.0, 123.2, 120.3, 62.4, 13.8; HRMS (ESI, m/z) calcd for C\textsubscript{16}H\textsubscript{14}NNaO\textsubscript{2}SCl [M+Na]^+: 342.0326. Found: 342.0327.
N-(2-methyl-1H-inden-1-yl)methanesulfonamide (3ag): 2 mg, 5%.
White solid; m.p. 98-99 °C; 'H NMR (400 MHz, CDCl3): δ 7.44 (d, J = 7.4 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.11 - 7.08 (m, 2H), 6.36 (s, 1H), 4.72 (d, J = 9.6 Hz, 1H), 4.58 (d, J = 9.6 Hz, 1H), 3.07 (s, 3H), 2.04 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 145.4, 143.4, 143.0, 128.4, 127.9, 124.9, 123.4, 120.3, 62.5, 42.3, 13.9; HRMS (ESI, m/z) calcd for C11H13NNaO2S [M+Na]+: 246.0559. Found: 246.0560.

N-(2-methyl-1H-inden-1-yl)benzamide (3ah): 7 mg, 15%.
White solid; m.p. 139 - 142 °C; 'H NMR (400 MHz, CDCl3): δ 7.83 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.44 (dd, J = 15.2, 7.6 Hz, 3H), 7.27 (t, J = 6.9 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.14 (t, J = 7.3 Hz, 1H), 6.48 (s, 1H), 6.28 (d, J = 8.9 Hz, 1H), 5.79 (d, J = 9.3 Hz, 1H), 2.07 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 168.1, 147.0, 144.3, 144.0, 134.2, 131.7, 128.6, 128.1, 127.07 (s), 124.9, 123.4, 120.3, 59.0, 14.3; HRMS (ESI, m/z) calcd for C17H15NNaO [M+Na]+: 272.1046. Found: 272.1050.

4-methyl-N-(2-methyl-1H-inden-3-yl)benzenesulfonamide (4a): 48 mg (80%, TBAF/THF), 59 mg (99%, Mg/MeOH).
White solid; m.p. 122 - 123 °C; 'H NMR (400 MHz, CDCl3): δ 7.66 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 6.9 Hz, 1H), 7.22 - 7.03 (m, 5H), 6.17 (s, 1H), 3.26 (s, 2H), 2.38 (s, 3H), 1.77 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 143.6, 142.3, 141.1, 140.3, 137.0, 130.7, 129.4, 127.2, 126.1, 124.5, 123.3, 118.4, 40.7, 21.4, 13.2.

2-methyl-2,3-dihydro-1H-inden-1-one (5a): 69 mg, 91%.
A yellow oil; 'H NMR (600 MHz, CDCl3): δ 7.76 (d, J = 7.7 Hz, 1H), 7.61 - 7.56 (m, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 3.44 - 3.36 (m, 1H), 3.07 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H); 13C NMR (151 MHz, CDCl3): δ 209.4, 153.4, 136.4, 134.6, 127.3, 126.5, 124.0, 42.0, 35.0, 16.3; HRMS (EI, m/z) calcd for C10H10O [M]+: 146.0726. Found: 146.0725.

2,3-dimethyl-2,3-dihydro-1H-inden-1-one (5l): 73 mg, 88%.
A yellow oil; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.73 (d, $J = 7.6$ Hz, 1H), 7.63 - 7.58 (m, 1H), 7.49 (d, $J = 7.7$ Hz, 1H), 7.37 (t, $J = 7.4$ Hz, 1H), 2.94 (dd, $J = 6.8$, 4.9 Hz, 1H), 2.24 (qd, $J = 7.3$, 4.7 Hz, 1H), 1.46 (d, $J = 7.1$ Hz, 3H), 1.32 (d, $J = 7.4$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 208.3, 157.7, 135.9, 134.7, 127.4, 124.8, 123.6, 51.4, 41.7, 19.1, 14.1; HRMS (EI, m/z) calcd for C$_{11}$H$_{12}$O [M$^+$]: 160.0883. Found: 160.0882.
X-ray Crystallographic data of 3h (CCDC: 965333, crystallographic data for 3h can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif)

Empirical formula $\text{C}_21\text{H}_{19}\text{NO}_2\text{S}$
Formula weight 349.43
Temperature/K 293.80(10)
Crystal system triclinic
Space group P-1

\begin{align*}
a/\text{Å} & = 8.5924(14) \\
b/\text{Å} & = 10.4758(18) \\
c/\text{Å} & = 10.797(2) \\
\alpha/^\circ & = 97.496(15) \\
\beta/^\circ & = 111.360(17) \\
\gamma/^\circ & = 90.383(14) \\
\text{Volume}/\text{Å}^3 & = 895.8(3) \\
Z & = 2 \\
\rho_{\text{calc}}, \text{mg/mm}^3 & = 1.295 \\
\text{m/mm}^1 & = 0.194 \\
F(000) & = 368.0 \\
\text{Crystal size/mm}^3 & = 0.36 \times 0.34 \times 0.28 \\
2\Theta \text{ range for data collection} & = 6.38 \text{ to } 52.02^\circ \\
\text{Index ranges} & = -10 \leq h \leq 10, -12 \leq k \leq 12, -13 \leq l \leq 12 \\
\text{Reflections collected} & = 5643 \\
\text{Independent reflections} & = 3519[R(\text{int}) = 0.0255] \\
\text{Data/restraints/parameters} & = 3519/42/232 \\
\text{Goodness-of-fit on } F^2 & = 1.104 \\
\text{Final R indexes} [I \geq 2\sigma (I)] & = R_1 = 0.0566, wR_2 = 0.1392 \\
\text{Final R indexes} [\text{all data}] & = R_1 = 0.0780, wR_2 = 0.1524 \\
\text{Largest diff. peak/hole } / \text{e Å}^{-3} & = 0.35/0.35
\end{align*}
References

$^1$H and $^{13}$C NMR Spectra

$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR

S17
$^{1}H$ NMR

$^{13}C$ NMR
$^1$H NMR

$^{13}$C NMR
$^{1}H$ NMR

$^{13}C$ NMR
$^1$H NMR

$^{13}$C NMR
\textbf{\textsuperscript{1}H NMR}

\begin{center}
\includegraphics[width=0.5\textwidth]{hnmr.png}
\end{center}

\textbf{\textsuperscript{13}C NMR}

\begin{center}
\includegraphics[width=0.5\textwidth]{cnmr.png}
\end{center}