

## Supplementary Material

### Synthesis of Sulfonyldiazomethanes and Acetylazomethanes via an Alumina-Mediated Decarboxylation Strategy

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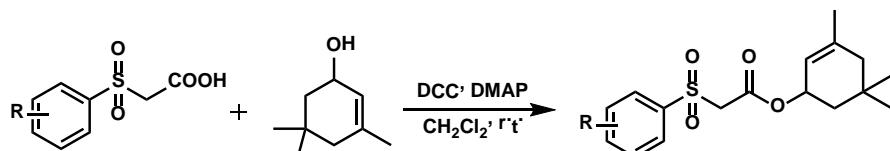
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### 1. General

All chemicals (reagent grade) used were commercially available. All the <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded with tetramethylsilane as the internal standard on a Bruker DPX 500 or DPX 300 model Spectrometer in CDCl<sub>3</sub>-d<sup>6</sup> and Chemical shifts were reported in ppm ( $\delta$ ). ESI-MS spectra were recorded on a Mariner System 5304 Mass spectrometer. TLC was performed on the glass-backed silica gel sheets (silica gel HG/T2354-92 GF254) and visualized in UV light (254 nm). Column chromatography was performed using silica gel (200-300mesh) eluting with ethyl acetate and petroleum ether. All solvents were purified and dried according to standard methods prior to use.

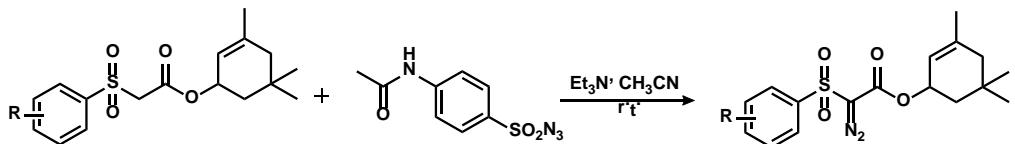
### 2. Standard procedure for preparation of sulfonyl acetates



To a solution of alcohol (6 mmol, 1.0 equiv) in dichloromethane (10 mL) was added 4-(dimethylamino)-pyridine (0.6 mmol, 0.1 equiv) followed by a solution of 1,3-dicyclohexylcarbodiimide (6.6 mmol, 1.1 equiv) in dichloromethane (6 mL). After 5 min sulfonyl acetic acid (6.6 mmol, 1.1 equiv) was added and the reaction stirred at rt for 12 h. The crude mixture was filtered, and the precipitate washed with EtOAc (20 mL). The solution was then washed with aqueous KHSO<sub>4</sub> (1 M; 10 mL), saturated aqueous NaHCO<sub>3</sub> (10 mL), brine (10 mL) and dried (MgSO<sub>4</sub>).

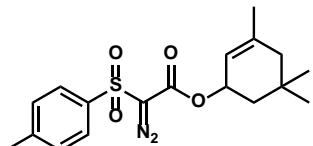
Concentration under reduced pressure and column chromatography (Ethyl acetate/Petroleum ether) yielded sulfonyl acetates.

### 3. Standard procedure for preparation of diazo sulfonyl acetates



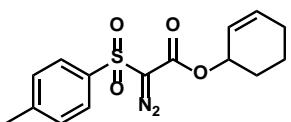
To a solution of sulfonyl acetate (4 mmol) in CH<sub>3</sub>CN (10 mL) was added triethylamine (1.3mL, 9.6mmol) at 0 °C and then a solution of 4-acetamidobenzenesulfonyl azide (4.8 mmol) in CH<sub>3</sub>CN (5 mL ×2) via a cannula. The reaction mixture was stirred at room temperature for 8 h. The solution was concentrated under vacuum and diluted with ether (40 mL). This solution was washed with saturated NH<sub>4</sub>Cl solution (10 mL), brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The residue was purified by silicon gel chromatography (Ethyl acetate/Petroleum ether) to afford diazo sulfonyl acetate as a yellow solid or oil.

#### 3.1. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl 2-diazo-2-tosylacetate



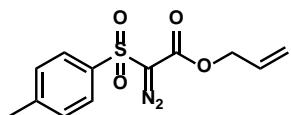
Yield: 74%. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, 303K) δ 7.91(d, *J*=8.4Hz, 2H), 7.35(d, *J*=8.1Hz, 2H), 5.37(m, 1H), 5.31(m, 1H), 2.45(s, 3H), 1.85(d, *J*=17.7Hz, 1H), 1.73-1.65(m, 5H), 1.39(dd, *J*=13.2, 7.5Hz, 1H), 0.96(s, 3H), 0.90(s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 303K) δ 159.6, 145.1, 139.5, 129.7, 127.5, 118.2, 72.6, 43.9, 40.5, 29.8, 27.2, 23.6, 21.7; IR (neat, cm<sup>-1</sup>): 3075, 2955, 2133, 1708, 1595, 1344, 1159, 1068, 814, 736, 666; MS(ESI) [M+Na]<sup>+</sup>, 385.

#### 3.2. Spectroscopic data for cyclohex-2-enyl 2-diazo-2-tosylacetate



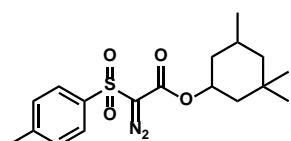
Yield: 86%. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, 303K) δ 7.91(d, *J*=8.4Hz, 2H), 7.35(d, *J*=8.1Hz, 2H), 6.0-5.95(m, 1H), 5.66-5.60(m, 1H), 5.30-5.28(m, 1H), 2.45(s, 3H), 2.12-1.99(m, 2H), 1.87-1.72(m, 2H), 1.70-1.58(m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 303K) δ 159.4, 145.1, 138.8, 133.8, 129.6, 127.9, 124.5, 70.38, 28.1, 24.7, 21.6, 18.4; IR (neat, cm<sup>-1</sup>): 3032, 2951, 2127, 1715, 1597, 1346, 1288, 1155, 1059, 903, 737, 669; MS(ESI) [M+Na]<sup>+</sup>, 343.

### 3.3. Spectroscopic data for allyl 2-diazo-2-tosylacetate



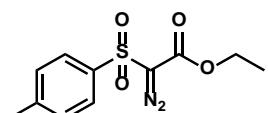
Yield: 88%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.90(d,  $J=8.4\text{Hz}$ , 2H), 7.35(d,  $J=8.1\text{Hz}$ , 2H), 5.91-5.78(m, 2H), 5.32-5.22(m, 2H), 4.64(dt,  $J=6, 1.5\text{Hz}$ , 2H), 2.44(s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  159.3, 145.2, 138.7, 130.9, 129.6, 127.8, 119.3, 66.4, 21.5; IR (neat,  $\text{cm}^{-1}$ ): 3069, 2952, 2129, 1717, 1596, 1342, 1157, 1069, 815, 739, 669; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 303.

### 3.4. Spectroscopic data for 3,3,5-trimethylcyclohexyl 2-diazo-2-tosylacetate



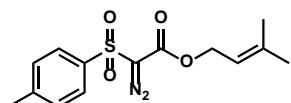
Yield: 77%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.90(d,  $J=7.9\text{Hz}$ , 2H), 7.35(d,  $J=7.9\text{Hz}$ , 2H), 5.15-4.92(m, 1H), 2.45(s, 3H), 1.94(m, 1H), 1.82-1.20(m, 6H), 0.93(d,  $J=2.4\text{Hz}$ , 3H), 0.88(s, 3H), 0.87(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  145.1, 138.9, 129.7, 127.9, 74.0, 47.7, 43.8, 41.3, 40.3, 38.2, 33.7, 32.9, 27.0, 25.4, 23.2, 22.3, 22.2, 21.7; IR (neat,  $\text{cm}^{-1}$ ): 3068, 2952, 2124, 1716, 1597, 1344, 1158, 1066, 814, 740, 668; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 387.

### 3.5. Spectroscopic data for ethyl 2-diazo-2-tosylacetate



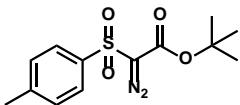
Yield: 79%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.90(d,  $J=8.7\text{Hz}$ , 2H), 7.35(d,  $J=8.1\text{Hz}$ , 2H), 4.22(q,  $J=7.5\text{Hz}$ , 2H), 2.45(s, 3H), 1.25(t,  $J=7.2\text{Hz}$ , 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  159.7, 145.2, 138.8, 129.7, 127.9, 62.3, 21.7, 14.2; IR (neat,  $\text{cm}^{-1}$ ): 3092, 2989, 2132, 1712, 1598, 1341, 1157, 1071, 813, 741, 667; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 291.

### 3.6. Spectroscopic data for 3-methylbut-2-enyl 2-diazo-2-tosylacetate



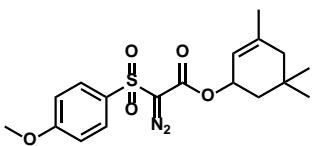
Yield: 78%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.89(d,  $J=8.4\text{Hz}$ , 2H), 7.33(d,  $J=8.0\text{Hz}$ , 2H), 5.26(t,  $J=7.3\text{Hz}$ , 1H), 4.64(d,  $J=7.3\text{Hz}$ , 2H), 2.44(s, 3H), 1.73(s, 3H), 1.66(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  159.7, 145.1, 140.5, 138.8, 129.6, 127.9, 117.5, 62.8, 25.7, 21.6, 18; IR (neat,  $\text{cm}^{-1}$ ): 3030, 2926, 2125, 1717, 1596, 1344, 1157, 1064, 814, 739, 669; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 331.

### 3.7. Spectroscopic data for tert-butyl 2-diazo-2-tosylacetate



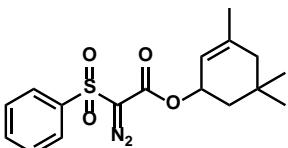
Yield: 30%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.88(d,  $J=8.4\text{Hz}$ , 2H), 7.35(d,  $J=8\text{Hz}$ , 2H), 2.46(s, 3H), 1.43(s, 9H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  158.5, 144.70, 138.8, 129.4, 127.6, 84.3, 27.9, 21.4; IR (neat,  $\text{cm}^{-1}$ ): 3048, 2925, 2124, 1709, 1596, 1338, 1156, 1066, 813, 723, 669; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 319.

### 3.8. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl-2-diazo-2-(4-methoxyphenylsulfonyl)acetate



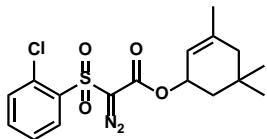
Yield: 60%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.93(d,  $J=9\text{Hz}$ , 2H), 7.49(d,  $J=9\text{Hz}$ , 2H), 5.35(m, 1H), 5.31(m, 1H), 3.89(s, 3H), 1.85(d,  $J=18\text{Hz}$ , 1H), 1.73-1.65(m, 5H), 1.39(dd,  $J=13.2, 7.5\text{Hz}$ , 1H), 0.96(s, 3H), 0.90(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  163.9, 159.6, 139.5, 133.2, 130.2, 118.1, 114.1, 72.4, 55.6, 43.8, 40.4, 29.8, 27.2, 23.5; IR (neat,  $\text{cm}^{-1}$ ): 3078, 2952, 2124, 1711, 1595, 1341, 1264, 1153, 1024, 805, 674, 596; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 401.

### 3.9. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl-2-diazo-2-(phenylsulfonyl)acetate



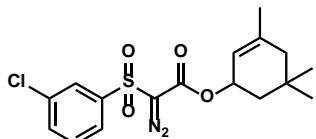
Yield: 69%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  8.04(d,  $J=7.5\text{Hz}$ , 2H), 7.67(tt,  $J=7.8, 1.5\text{Hz}$ , 1H), 7.57(tt,  $J=7.8, 1.8\text{Hz}$ , 2H), 5.39(m, 1H), 5.31(m, 1H), 1.86(d,  $J=17.7\text{Hz}$ , 1H), 1.74-1.66(m, 5H), 1.40(dd,  $J=13.2, 7.5\text{Hz}$ , 1H), 0.97(s, 3H), 0.91(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  159.4, 141.7, 139.6, 133.9, 129, 127.9, 118, 72.6, 43.9, 40.4, 29.8, 27.2, 23.6; IR (neat,  $\text{cm}^{-1}$ ): 3090, 2927, 2139, 1703, 1349, 1221, 1037, 608; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 371.

**3.10. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl  
2-(2-chlorophenylsulfonyl)-2-diazoacetate**



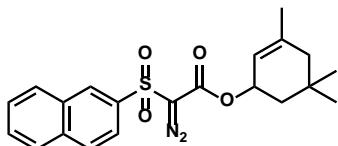
Yield: 63%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  8.25(d,  $J=7.5\text{Hz}$ , 2H), 7.58(d,  $J=3.6\text{Hz}$ , 2H), 7.52-7.45(m, 1H), 5.32(m, 1H), 5.23(m, 1H), 1.82(d,  $J=17.7\text{Hz}$ , 1H), 1.69-1.62(m, 5H), 1.33(dd,  $J=13.2, 7.5\text{Hz}$ , 1H), 0.94(s, 3H), 0.88(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  159.1, 139.5, 137.9, 134.6, 132.8, 131.7, 127.1, 117.9, 72.7, 43.8, 40.3, 29.7, 27.2, 23.5; IR (neat,  $\text{cm}^{-1}$ ): 3090, 2958, 2139, 1703, 1572, 1348, 1221, 1074, 765, 608; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 405.

**3.11. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl  
2-(3-chlorophenylsulfonyl)-2-diazoacetate**



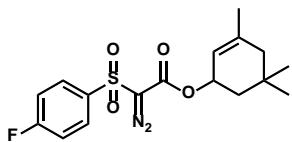
Yield: 62%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  8.01(d,  $J=7.7\text{Hz}$ , 1H), 7.92(d,  $J=7.7\text{Hz}$ , 1H), 7.63(d,  $J=8.1\text{Hz}$ , 1H), 7.51(t,  $J=7.8\text{Hz}$ , 1H), 5.39(m, 1H), 5.31(m, 1H), 1.87(d,  $J=17.4\text{Hz}$ , 1H), 1.75-1.66(m, 5H), 1.41(dd,  $J=13.5, 6\text{Hz}$ , 1H), 0.97(s, 3H), 0.91(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  159.3, 143.1, 139.9, 135.2, 134.0, 130.4, 128.1, 126, 117.9, 73, 43.9, 40.5, 29.9, 27.1, 23.6; IR (neat,  $\text{cm}^{-1}$ ): 3085, 2949, 2132, 1711, 1579, 1335, 1156, 1069, 793, 678; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 405.

**3.12. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl  
2-diazo-2-(naphthalen-2-ylsulfonyl)acetate**



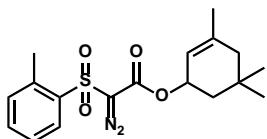
Yield: 75%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  8.6(d,  $J=1.2\text{Hz}$ , 1H), 8.01-7.91(m, 4H), 7.71-7.60(m, 2H), 5.34(m, 1H), 5.24(m, 1H), 1.80(d,  $J=17.4\text{Hz}$ , 1H), 1.68-1.61(m, 5H), 1.34(dd,  $J=13, 7.5\text{Hz}$ , 1H), 0.92(s, 3H), 0.86(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  159.5, 139.6, 138.4, 135.4, 131.9, 130.1, 129.6, 129.5, 129.4, 127.9, 127.7, 122.4, 118.0, 72.7, 43.8, 40.4, 29.8, 27.1, 23.6; IR (neat,  $\text{cm}^{-1}$ ): 3058, 2954, 2127, 1711, 1590, 1339, 1154, 1063, 816, 739, 666; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 421.

**3.13. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl  
2-diazo-2-(4-fluorophenylsulfonyl)acetate**



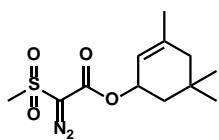
Yield: 60%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  8.09-8.03(m, 2H), 7.27-7.20(m, 2H), 5.38(m, 1H), 5.31(m, 1H), 1.85(d,  $J=18.3\text{Hz}$ , 1H), 1.74-1.62(m, 5H); 1.39(dd,  $J=13.2, 7.2\text{Hz}$ , 1H); 0.96(s, 3H); 0.91(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  167.6, 164.1, 159.3, 139.8, 130.9, 118, 116.2, 72.8, 43.9, 40.5, 29.8, 27.2, 23.6; IR (neat,  $\text{cm}^{-1}$ ): 3079, 2955, 2127, 1712, 1590, 1344, 1292, 1154, 1067, 838, 673; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 389.

**3.14. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl  
2-diazo-2-(o-tolylsulfonyl)acetate**



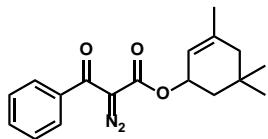
Yield: 47%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  8.12(dd,  $J=7.8, 1.2\text{Hz}$ , 1H), 7.52(td,  $J=7.7, 1.5\text{Hz}$ , 1H), 7.40-7.32(m, 2H), 5.31(m, 1H), 5.22(m, 1H), 2.63(s, 3H), 1.82(d,  $J=18\text{Hz}$ , 1H), 1.67-1.59(m, 5H), 1.31(dd,  $J=12.6, 7.5\text{Hz}$ , 1H), 0.93(s, 3H), 0.87(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  159.4, 139.4, 139.1, 137.3, 133.9, 132.6, 131.4, 126.3, 118, 72.7, 43.8, 40.3, 29.8, 27.1, 23.6, 20.2; IR (neat,  $\text{cm}^{-1}$ ): 3065, 2954, 2126, 1711, 1596, 1461, 1336, 1159, 1056, 707, 612; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 385.

**3.15. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl  
2-diazo-2-(methylsulfonyl)acetate**



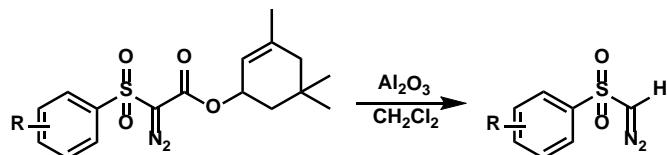
Yield: 68%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  5.50(m, 1H), 5.43(m, 1H), 3.31(s, 3H), 1.88(d,  $J=17.7\text{Hz}$ , 1H), 1.82-1.71(m, 5H), 1.5(dd,  $J=12.9, 7.2\text{Hz}$ , 1H), 1.0(s, 3H), 0.96(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  159.9, 140, 117.9, 72.9, 44.8, 43.9, 40.5, 29.6, 27.4, 23.6; IR (neat,  $\text{cm}^{-1}$ ): 2951, 2132, 1707, 1456, 1337, 1153, 1092, 764, 564; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 309.

**3.16. Spectroscopic data for 3,5,5-trimethylcyclohex-2-enyl 2-diazo-3-oxo-3-phenylpropanoate**



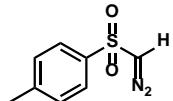
Yield: 79%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.63(d,  $J=8.1\text{Hz}$ , 2H), 7.51(t,  $J=7.5\text{Hz}$ , 1H), 7.41(t,  $J=8.0\text{Hz}$ , 2H), 5.41(m, 1H), 5.40(m, 1H), 1.83(d, 17.4Hz, 1H), 1.76-1.66(m, 5H), 1.41(dd,  $J=13.2, 7.1\text{Hz}$ , 1H), 0.93(s, 3H), 0.92(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  187.1, 160.8, 139.3, 137.2, 132.2, 128.4, 127.8, 118.4, 71.6, 44.0, 40.5, 29.6, 27.6, 23.7; IR (neat,  $\text{cm}^{-1}$ ): 3061, 2954, 2106, 1717, 1627, 1577, 1365, 1115, 1013, 942, 701, 670; MS(ESI)  $[\text{M}+\text{Na}]^+$ , 335.

**4. Procedure for the decarbonylation by neutral  $\text{Al}_2\text{O}_3$ .**



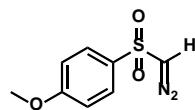
To the white solid of 5g  $\text{Al}_2\text{O}_3$  in the schlenk tube was added the anhydrous dichloromethane (15 mL) under the protection of nitrogen and stirred the suspension at 0 °C. The schlenk tube was covered by aluminum foil in order to be protected from light. Then diazo acetate was added to the tube under 0 °C, and reacted at the room temperature. The reaction was monitored by TLC under diazo acetate was consumed. The reaction mixture was filtrated and washed by dichloromethane to ensure all the product was washed out. The yellow filtrate was concentrated by rotary evaporation at room temperature to get yellow oil or solid. The raw product was purified by chromatography column (Ethyl acetate/Petroleum ether). The product was stored well at -20°C in the dark.

**4.1. Spectroscopic data for 1-(diazenylsulfonyl)-4-methylbenzene(2a)**



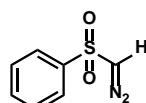
Yield: 98%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.77(d,  $J=8.1\text{Hz}$ , 2H), 7.35(d,  $J=8.1\text{Hz}$ , 2H), 5.25(s, 1H), 2.45(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  144.2, 141.3, 129.9, 126.2, 57.7, 21.5; IR (neat,  $\text{cm}^{-1}$ ): 3085, 2106, 1597, 1332, 1154, 665; MS(EI)  $m/z$  196.

#### 4.2. Spectroscopic data for 1-(diazomethylsulfonyl)-4-methoxybenzene(2b)



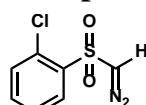
Yield: 73%.  $^1\text{H}$  NMR (300MHz, CDCl<sub>3</sub>, 303K)  $\delta$  7.81(dd,  $J=6.9$ , 2.1Hz, 2H), 7.00(dd,  $J=6.9$ , 2.1Hz, 2H), 5.28(s, 1H), 3.88(s, 3H);  $^{13}\text{C}$  NMR (75MHz, CDCl<sub>3</sub>, 300K)  $\delta$  163.4, 136.1, 128.4, 114.4, 57.9, 55.6; IR (neat, cm<sup>-1</sup>): 3070, 2128, 1329, 1141, 668; MS(EI)  $m/z$  212.

#### 4.3. Spectroscopic data for (diazomethylsulfonyl)benzene(2c)



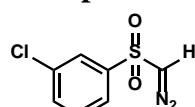
Yield: 99%.  $^1\text{H}$  NMR (300MHz, CDCl<sub>3</sub>, 303K)  $\delta$  7.9-7.87(m, 2H), 7.65-7.60(m, 1H), 7.58-7.52(m, 2H), 5.30(s, 1H);  $^{13}\text{C}$  NMR (75MHz, CDCl<sub>3</sub>, 300K)  $\delta$  144.1, 133.3, 129.4, 126.2, 57.6; IR(neat, cm<sup>-1</sup>): 3067, 1901, 1585, 1333, 1155, 687; MS(EI)  $m/z$  182.

#### 4.4. Spectroscopic data for 1-chloro-2-(diazomethylsulfonyl)benzene(2d)



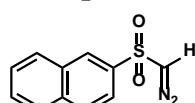
Yield: 98%.  $^1\text{H}$  NMR (300MHz, CDCl<sub>3</sub>, 303K)  $\delta$  8.1(dd,  $J=7.5$ , 1.5Hz, 1H), 7.58-7.5(m, 2H), 7.47-7.41(m, 1H), 5.44(s, 1H);  $^{13}\text{C}$  NMR (75MHz, CDCl<sub>3</sub>, 300K)  $\delta$  140.7, 134, 132, 131.8, 129.8, 127.3, 56.7; IR (neat, cm<sup>-1</sup>): 3083, 2113, 1332, 1153, 1040, 761, 604; MS(EI)  $m/z$  216.

#### 4.5. Spectroscopic data for 1-chloro-3-(diazomethylsulfonyl)benzene(2e)



Yield: 77%.  $^1\text{H}$  NMR (300MHz, CDCl<sub>3</sub>, 303K)  $\delta$  7.87(d,  $J=1.5\text{Hz}$ , 1H), 7.79-7.75(m, 1H), 7.61-7.54(m, 1H), 7.49(t,  $J=8.1\text{Hz}$ , 1H), 5.30(s, 1H);  $^{13}\text{C}$  NMR (75MHz, CDCl<sub>3</sub>, 300K)  $\delta$  145.6, 135.8, 133.4, 130.7, 126.4, 124.3, 57.6; IR (neat, cm<sup>-1</sup>): 3090, 2111, 1579, 1338, 1157, 1023, 791, 676; MS(EI)  $m/z$  216.

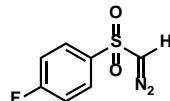
#### 4.6. Spectroscopic data for 2-(diazomethylsulfonyl)naphthalene(2f)



Yield: 96%.  $^1\text{H}$  NMR (300MHz, CDCl<sub>3</sub>, 303K)  $\delta$  8.45(d,  $J=1.8\text{Hz}$ , 1H), 8.01-7.97(m, 2H), 7.92(dd,  $J=8.1$ , 1.8Hz, 1H), 7.84(dd,  $J=8.7$ , 2.1Hz, 1H), 7.70-7.60(m, 2H), 5.34(s, 1H);  $^{13}\text{C}$  NMR (75MHz, CDCl<sub>3</sub>, 300K)  $\delta$  141, 135.1, 132.2, 130, 129.5, 129.2, 128, 127.8, 127.6, 121.4, 57.7; IR (neat, cm<sup>-1</sup>): 3073, 2104, 1589, 1327, 1127, 659; MS(EI)

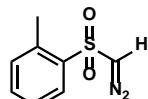
*m/z* 232.

#### 4.7. Spectroscopic data for 1-(diazomethylsulfonyl)-4-fluorobenzene(2g)



Yield: 90%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.94-7.87(m, 2H), 7.26-7.18(m, 2H), 5.29(s, 1H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  167.3, 163.7, 129.2, 116.5, 57.8; IR (neat,  $\text{cm}^{-1}$ ): 3108, 1906, 1592, 1338, 1235, 1152, 840; MS(EI) *m/z* 200.

#### 4.8. Spectroscopic data for 1-(diazomethylsulfonyl)-2-methylbenzene(2h)



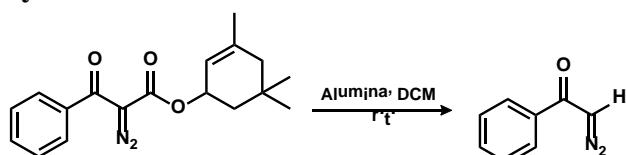
Yield: 70%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.98(d,  $J=7.8\text{Hz}$ , 1H), 7.49(t,  $J=7.5\text{Hz}$ , 2H), 7.35(t,  $J=7.8\text{Hz}$ , 1H), 5.32(s, 1H), 2.63(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  141.7, 136.7, 133.3, 132.7, 128.3, 126.4, 56.7, 20.2; IR (neat,  $\text{cm}^{-1}$ ): 3084, 2107, 1595, 1327, 1155, 760; MS(EI) *m/z* 196.

#### 4.9. Spectroscopic data for diazo(methylsulfonyl)methane(2i)

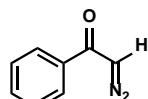


Yield: 64%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  5.24(s, 1H), 3.20(s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  39.3, 29.6; IR (neat,  $\text{cm}^{-1}$ ): 2956, 2920, 2103, 1465, 1151; MS(EI) *m/z* 120.

### 5. Synthesis of acetyl diazomethane



#### 5.1. Spectroscopic data for 2-diazo-1-phenylethanone(2j)



Yield: 60%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ , 303K)  $\delta$  7.87(dd,  $J=7.8, 1.8\text{Hz}$ , 2H), 7.54(m, 1H), 7.44(t,  $J=7.8\text{Hz}$ , 1H), 5.91(s, 1H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ , 300K)  $\delta$  173.7, 134.9, 132.6, 128.6, 126.6, 54; IR (neat,  $\text{cm}^{-1}$ ): 3063, 2107, 1605, 1573, 697; MS(EI) *m/z* 146.