Supporting Information

Recyclable Amberlyst-15-catalyzed three-component reaction in water to synthesize diarylmethyl sulfones

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1. General Information

All reactions were carried out under air atmosphere in dried glassware. The glassware used was dried in an electric oven at 120 °C. Chemicals were purchased from Aladdin, Adamas, Aldrich, Alfa Aesar, and Kelong Chemical Co. and used as received. Petroleum ether refers to the fraction boiling in the 60–90 °C range. Unless otherwise stated, there is no further purification for the commercial supplier's chemicals.

Melting points were determined using a Shanghai Jingke SGW X-4 microscope melting point apparatus. $^1$H NMR (400 MHz), $^{13}$C NMR (101 MHz) and $^{31}$P NMR (162 MHz) spectra were determined on a Bruker Avance III 400 MHz instrument or on an Agilent Technologies 400MHz instrument. $^1$H NMR data are reported in δ units (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), DMSO (2.50 ppm) or acetone (2.05 ppm) in the deuterated solvent, unless otherwise stated. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. $^{13}$C NMR spectra were determined on a Bruker Avance III 101 MHz instrument. $^{13}$C NMR spectra are reported in (ppm) relative to deuterochloroform (77.2 ppm), DMSO-$d_6$ (39.5 ppm) or acetone-$d_6$ (206.7 ppm for C=O), and all were obtained with $^1$H decoupling. High-resolution mass spectra are recorded on a Shimadzu LCMS-IT-TOF instrument in the ESI mode.

2. General procedure for the synthesis of compounds 4

To a 25 mL glass test tube equipped a stir bar were added the corresponding aldehyde 1 (1.5 mmol), sulfinate 2 (1 mmol), Aryl-H 3 (1 mmol), Amberlyst-15 wet ion exchange resin (50% weight percentage according to 3) and 1 mL water. The test tube was stirred in an oil bath preheated at 60°C. After 6 hours, reaction progress was checked by TLC and confirmed reaction was completed. Then, the reaction mixture was cooled to room temperature. Then added water (10 mL) to reaction mixture, and the ion exchange resin was filtered and washed with ethyl acetate (5 mL) for three times. The filtrate was extracted with ethyl acetate (10 mL) for three times, and the combined organic layer was dried over anhydrous MgSO$_4$, and then adsorbed on some silica gel under reduced pressure on a rotary evaporator. The silica gel adsorbing the sample was transferred to a silica gel column. After purified by the silica gel column chromatography (Petroleum ether : Ethyl acetate = 5 : 1 used as eluents), the desired product 4 was obtained.
3. Spectral data of the synthesized compounds

1. 1,3,5-trimethoxy-2-(phenyl(phenylsulfonyl)methyl)benzene 4aaa

![4aaa]

Yield: 88%; white solid; Mp: 106-107°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.69-7.63 (m, 2H), 7.61-7.49 (m, 3H), 7.45-7.24 (m, 5H), 6.21 (s, 1H), 6.06 (s, 2H), 3.80 (s, 3H), 3.66 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.72, 141.02, 134.19, 132.64, 130.18, 128.67, 128.15, 127.91, 127.64, 104.12, 91.00, 67.77, 55.59, 55.30. HRMS (ESI): calculated for C$_{22}$H$_{22}$O$_5$SNa $[M + Na]^+$ = 421.1086, found C$_{22}$H$_{22}$O$_5$SNa$[M + Na]^+$ = 421.1079.

2. 2-((4-fluorophenyl)(phenylsulfonyl)methyl)-1,3,5-trimethoxybenzene 4baa

![4baa]

Yield: 90%; white solid; Mp: 87-88°C; $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 7.70 – 7.60 (m, 1H), 7.59 – 7.45 (m, 6H), 7.20 – 7.08 (m, 2H), 6.18 (s, 2H), 6.09 (s, 1H), 3.76 (s, 3H), 3.62 (s, 6H); $^{13}$C NMR (400 MHz, DMSO-d$_6$): $\delta$ 167.99, 166.74, 165.56, 145.29, 138.48, 137.31, 137.23, 135.31, 135.28, 133.86, 133.23, 120.07, 119.85, 108.10, 96.41, 71.66, 60.88, 60.50. HRMS (ESI): calculated for C$_{22}$H$_{21}$FO$_5$SNa $[M + Na]^+$ = 439.0991, found C$_{22}$H$_{21}$FO$_5$SNa $[M + Na]^+$ = 439.0992.

3. 2-((4-chlorophenyl)(phenylsulfonyl)methyl)-1,3,5-trimethoxybenzene 4caa
Yield: 91%; white solid; Mp: 118-119°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) : \( \delta = 7.71\text{-}7.62\) (m, 2H), 7.59\text{-}7.49 (m, 3H), 7.46\text{-}7.22 (m, 4H), 6.14 (s, 1H), 6.05 (s, 2H), 3.80 (s, 3H), 3.64 (s, 6H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta 161.91, 140.66, 133.51, 132.81, 131.54, 128.64, 128.26, 128.03, 103.50, 91.00, 66.83, 55.59, 55.31. \) HRMS (ESI): calculated for C\textsubscript{22}H\textsubscript{21}ClO\textsubscript{5}SNa [M + Na]\textsuperscript{+} = 455.0696, found C\textsubscript{22}H\textsubscript{21}ClO\textsubscript{5}SNa [M + Na]\textsuperscript{+} = 455.0696.

4. \textit{1,3,5-trimethoxy-2-\{(4-nitrophenyl)(phenylsulfonyl)methyl\}benzene 4daa}

Yield: 90%; white solid; Mp: 130-131°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) : \( \delta 8.06 \) (d, J = 8.9 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 6.14 (s, 1H), 5.93 (s, 2H), 3.71 (s, 3H), 3.51 (s, 6H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) : \( \delta 162.34, 146.96, 142.16, 140.09, 133.15, 130.79, 128.72, 128.35, 122.91, 102.55, 90.89, 66.33, 55.56, 55.34. \) HRMS (ESI): calculated for C\textsubscript{22}H\textsubscript{21}NO\textsubscript{7}SNa [M + Na]\textsuperscript{+} = 466.0936, found C\textsubscript{22}H\textsubscript{21}NO\textsubscript{7}SNa [M + Na]\textsuperscript{+} = 466.0911.

5. \textit{1,3,5-trimethoxy-2-\{(2-methoxyphenyl)(phenylsulfonyl)methyl\}benzene 4eaa}

4
Yield: 70%; white solid; Mp: 150-151°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.71 - 7.62 (m, 2H), 7.53 - 7.44 (m, 1H), 7.41 - 7.32 (m, 2H), 7.20 (ddd, $J = 8.2, 7.4, 1.7$ Hz, 1H), 6.96 (td, $J = 7.6, 1.2$ Hz, 1H), 6.70 (dd, $J = 8.3, 1.2$ Hz, 1H), 6.62 (s, 1H), 6.01 (s, 2H), 3.76 (s, 3H), 3.60 (s, 6H), 3.46 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): 161.50, 156.88, 141.53, 132.36, 132.32, 128.75, 128.73, 127.98, 122.59, 119.99, 110.25, 104.01, 91.22, 59.89, 55.72, 55.36, 55.22. HRMS (ESI): calculated for C$_{23}$H$_{24}$O$_6$SNa [M + Na]$^+$ m/z = 451.1191, found C$_{23}$H$_{24}$O$_6$SNa [M + Na]$^+$ m/z = 451.1193.

6. 2-((phenylsulfonyl)(2,4,6-trimethoxyphenyl)methyl)phenol 4faa

Yield: 75%; white solid; Mp: 116-117°C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.3 (bs, 1H), 8.06 (d, $J = 7.9$ Hz, 1H), 7.55 (td, $J = 21.3, 19.1, 7.4$ Hz, 4H), 7.32 (d, $J = 6.2$ Hz, 1H), 7.05 (t, $J = 7.7$ Hz, 1H), 6.77 (t, $J = 7.6$ Hz, 1H), 6.67 (d, $J = 8.0$ Hz, 1H), 6.53 (s, 1H), 6.11 (s, 2H), 3.73 (s, 3H), 3.52 (s, 6H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 161.70, 155.61, 148.72, 141.20, 133.42, 132.66, 128.90, 128.90, 128.86, 128.60, 128.11, 125.94, 120.57, 118.23, 115.05, 103.40, 91.75, 59.70, 56.10, 55.71. HRMS (ESI): calculated for C$_{23}$H$_{24}$O$_6$SNa [M + Na]$^+$ m/z = 437.1035, found C$_{23}$H$_{24}$O$_6$SNa [M + Na]$^+$ m/z = 437.1036.

7. 2-((phenylsulfonyl)(2,4,6-trimethoxyphenyl)methyl)pyridine 4gaa

Yield: 75%; white solid; Mp: 130-131°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.46 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 1H), 8.07 (dt, $J = 8.0, 1.1$ Hz, 1H), 7.75 - 7.62 (m, 3H), 7.56 - 7.46 (m, 1H), 7.38 (dd, $J = 8.4, 7.2$ Hz, 2H), 7.14 (dd, $J = 7.6, 4.9, 1.1$ Hz, 1H), 6.35 (s, 1H), 5.98 (s, 2H), 3.75 (s, 3H), 3.50 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.09, 154.76, 148.64, 140.75, 135.73, 132.81, 128.97,
128.11, 125.09, 122.18, 102.75, 90.98, 68.64, 55.54, 55.27. HRMS (ESI): calculated for C₂₁H₂₁NO₅SNa[M + Na]⁺ = 422.1038, found C₂₁H₂₁NO₅SNa [M + Na]⁺ = 422.1039.

8. 1,3,5-trimethoxy-2-(2-phenyl-1-(phenylsulfonfyl)ethy)benzene 4hhaa

![4hhaa](image)

Yield: 70%; color less liquid; ¹H NMR (400 MHz, CDCl₃) : δ 7.78 – 7.66 (m, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.20 – 7.01 (m, 5H), 6.00 (d, J = 2.3 Hz, 1H), 5.81 (d, J = 2.3 Hz, 1H), 5.27 (dd, J = 11.6, 4.7 Hz, 1H), 3.89 (dd, J = 13.6, 11.6 Hz, 1H), 3.7 (s, 3H), 3.67 (s, 4H), 3.38 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 161.59, 160.78, 159.85, 139.83, 138.45, 132.71, 128.93, 128.67, 128.11, 128.03, 126.06, 100.92, 91.02, 90.34, 63.97, 55.74, 55.26, 55.14, 31.65. HRMS (ESI): calculated for C₂₃H₂₄O₅SNa [M + Na]⁺ = 435.1242, found C₂₂H₂₁FO₅SNa [M + Na]⁺ = 435.1242.

9. 1,3,5-trimethoxy-2-((phenylsulfonfyl)methyl)benzene 4iiaa

![4iiaa](image)

Yield: 82%; white solid; ¹H NMR (400 MHz, CDCl₃) : δ 7.73 – 7.63 (m, 2H), 7.59 – 7.47 (m, 1H), 7.46 – 7.36 (m, 2H), 5.96 (s, 2H), 4.48 (s, 2H), 3.76 (s, 3H), 3.46 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 161.88, 159.58, 140.16, 132.80, 128.63, 128.19, 98.11, 90.16, 55.38, 55.29, 51.65. HRMS (ESI): calculated for C₁₆H₁₈O₅SNa [M + Na]⁺ = 345.0773, found C₁₆H₁₈O₅SNa [M + Na]⁺ = 345.0772.

10. 1,3,5-trimethoxy-2-(1-(phenylsulfonfyl)ethyl)benzene 4jaa
Yield: 79%; white solid; Mp: 123-124°C; ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.64 (m, 2H), 7.62 – 7.48 (m, 1H), 7.48 – 7.36 (m, 2H), 6.00 (dd, J = 36.1, 2.3 Hz, 2H), 5.06 (q, J = 7.3 Hz, 1H), 3.80 (s, 3H), 3.55 (d, J = 15.4 Hz, 6H), 1.84 (d, J = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 161.54, 161.15, 159.23, 139.50, 132.62, 129.06, 128.04, 103.04, 91.08, 90.17, 57.86, 55.62, 55.24, 12.81. HRMS (ESI): calculated for C₁₇H₂₀O₅SNa[M + Na]⁺ = 359.0929, found C₁₇H₂₀O₅SNa [M + Na]⁺ = 359.0921.

11. 2-(((4-chlorophenyl)sulfonyl)(phenyl)methyl)-1,3,5-trimethoxybenzene 4aba

Yield: 90%; white solid; Mp: 125-126°C; ¹H NMR (400 MHz, CDCl₃): δ 7.52 – 7.43 (m, 4H), 7.31 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 6.08 (s, 1H), 5.98 (s, 2H), 3.72 (s, 3H), 3.58 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 161.85, 139.54, 139.21, 133.89, 130.19, 130.15, 128.38, 128.00, 127.79, 103.82, 92.88, 91.02, 68.04, 55.57, 55.31. HRMS (ESI): calculated for C₂₂H₂₁ClO₅SNa [M + Na]⁺ = 455.0696, found C₂₂H₂₁ClO₅SNa [M + Na]⁺ = 455.0695.

12. 2-(((4-bromophenyl)sulfonyl)(phenyl)methyl)-1,3,5-trimethoxybenzene 4aca
Yield: 80%; white solid; Mp: 127-128°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 – 7.50 (m, 4H), 7.53 – 7.45 (m, 2H), 7.35 – 7.24 (m, 3H), 6.17 (s, 1H), 6.08 (s, 2H), 3.81 (s, 3H), 3.67 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.90, 159.63, 140.10, 134.49, 131.42, 130.34, 130.19, 129.76, 129.02, 128.06, 127.86, 103.80, 92.91, 91.05, 68.08, 55.61, 55.36. HRMS (ESI): calculated for C$_{22}$H$_{21}$BrO$_5$SNa [M + Na]$^+$ = 499.0191, found C$_{22}$H$_{21}$BrO$_5$SNa [M + Na]$^+$ = 499.0149.

13. 1,3,5-trimethoxy-2-(phenyl(tosyl)methyl)benzene 4ada$^2$

Yield: 79%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.61 – 7.50 (m, 4H), 7.33 – 7.25 (m, 3H), 7.20 (dd, $J$ = 7.4, 1.3 Hz, 2H), 6.18 (s, 1H), 6.08 (s, 2H), 3.80 (s, 3H), 3.67 (s, 6H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.64, 143.35, 138.21, 134.40, 130.21, 128.80, 128.68, 127.88, 127.58, 104.34, 91.05, 67.80, 55.61, 55.30, 21.51. HRMS (ESI): calculated for C$_{23}$H$_{24}$O$_5$SNa [M + Na]$^+$ = 435.1242, found C$_{23}$H$_{24}$O$_5$SNa [M + Na]$^+$ = 435.1228.

14. 1,3,5-trimethoxy-2-(((4-methoxyphenyl)sulfonyl)(phenyl)methyl)benzene 4aea

Yield: 75%; white solid; Mp: 120-121°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.65 – 7.53 (m, 4H), 7.33 – 7.22 (m, 3H), 6.90 – 6.83 (m, 2H), 6.17 (s, 1H), 6.08 (s, 2H), 3.83 (d, $J$ = 18.2 Hz, 6H), 3.68 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.95, 161.65, 161.53, 134.52, 134.50, 132.84, 130.83, 130.23, 129.76, 129.02, 127.91, 127.58, 113.36, 104.48, 92.91, 91.09, 67.94, 55.68, 55.57, 55.33. C$_{23}$H$_{24}$O$_6$SNa[M + Na]$^+$ = 451.1191, found C$_{23}$H$_{24}$O$_6$SNa [M + Na]$^+$ = 451.1187.

15. 2-(((4-(tert-butyl)phenyl)sulfonyl)(phenyl)methyl)-1,3,5-trimethoxybenzene 4afa
Yield: 76%; white solid; Mp: 115–116°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58 (ddt, $J$ = 9.0, 4.3, 2.7 Hz, 4H), 7.44 – 7.37 (m, 2H), 7.35 – 7.23 (m, 3H), 6.19 (s, 1H), 6.05 (s, 2H), 3.80 (s, 3H), 3.63 (s, 6H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.71, 156.38, 138.10, 134.50, 134.44, 130.17, 129.76, 129.01, 128.55, 128.45, 127.87, 127.53, 125.59, 125.15, 104.34, 92.91, 91.02, 67.59, 55.60, 55.34, 55.32, 35.11, 31.12, 29.71. HRMS (ESI): calculated for C$_{26}$H$_{30}$O$_5$SNa[M + Na]$^+$ = 477.1712, found C$_{26}$H$_{30}$O$_5$SNa[M + Na]$^+$ = 477.1705.

16. 2-((t-ert-butylsulfonyl)(phenyl)methyl)-1,3,5-trimethoxybenzene 4aga

Yield: 75%; white solid; Mp: 112–113°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 – 7.70 (m, 2H), 7.26 – 7.11 (m, 3H), 6.30 (s, 1H), 6.05 (t, $J$ = 1.9 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.70 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.35, 160.29, 157.84, 137.12, 130.36, 128.02, 127.51, 105.97, 91.71, 91.07, 62.36, 57.62, 56.18, 55.77, 55.31, 24.18. HRMS (ESI): calculated for C$_{20}$H$_{26}$O$_5$SNa [M + Na]$^+$ = 401.1399, found C$_{20}$H$_{26}$O$_5$SNa [M + Na]$^+$ = 401.1383.

17. 1,2,4-trimethoxy-5-(phenyl(phenylsulfonyl)methyl)benzene 4aab$^2$
Yield: 80%; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.70 – 7.57 (m, 5H), 7.56 – 7.50 (m, 1H), 7.42 – 7.29 (m, 5H), 6.32 (s, 1H), 6.03 (s, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.51 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 151.64, 149.97, 143.14, 138.84, 133.34, 133.16, 129.99, 128.86, 128.61, 128.34, 128.33, 113.25, 112.74, 96.78, 66.32, 56.61, 56.33, 55.95. HRMS (ESI): calculated for C$_{22}$H$_{22}$O$_5$SNa [M + Na]$^+$ = 421.1086, found C$_{22}$H$_{22}$O$_5$SNa [M + Na]$^+$ = 421.1091.

18. 2,4-dimethoxy-1-(phenyl(phenylsulfonyl)methyl)benzene 4aac

Yield: 69%; white solid; Mp: 111-112°C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.86 (d, $J = 8.7$ Hz, 1H), 7.59 – 7.52 (m, 2H), 7.53 – 7.47 (m, 2H), 7.47 – 7.40 (m, 1H), 7.34 – 7.21 (m, 4H), 7.19 (s, 1H), 6.49 (dd, $J = 8.7$, 2.5 Hz, 1H), 6.17 (d, $J = 2.5$ Hz, 1H), 5.90 (s, 1H), 3.71 (s, 3H), 3.41 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 160.95, 157.86, 138.92, 133.45, 133.09, 130.88, 130.10, 128.94, 128.53, 128.27, 128.25, 114.13, 109.99, 104.67, 98.24, 66.32, 55.37, 55.34.

19. 2-((4-chlorophenyl)(tosyl)methyl)-1,3,5-trimethoxybenzene 4cda

Yield: 81%; white solid; Mp: 108-109°C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.61 – 7.47 (m, 4H), 7.31 – 7.17 (m, 4H), 6.11 (s, 1H), 6.06 (s, 2H), 3.81 (s, 3H), 3.76 – 3.54 (s, 6H), 2.41 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 161.81, 143.59, 137.87, 133.46, 133.01, 131.55, 128.90, 128.66, 128.01, 103.76, 91.02, 66.86, 55.61, 55.31, 21.52. HRMS (ESI): calculated for C$_{23}$H$_{23}$ClO$_5$SNa [M + Na]$^+$ = 469.0852, found C$_{23}$H$_{23}$ClO$_5$SNa [M + Na]$^+$ = 469.0830.

20. 1,3,5-trimethoxy-2-((4-nitrophenyl)(tosyl)methyl)benzene 4dda
Yield: 86%; white solid; Mp: 133-134°C; ¹H NMR (400 MHz, CDCl₃): δ 8.09 – 8.01 (m, 2H), 7.76 – 7.65 (m, 2H), 7.50 – 7.40 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.11 (s, 1H), 5.94 (s, 2H), 3.71 (s, 3H), 3.52 (s, 6H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 162.25, 146.93, 144.03, 142.37, 137.25, 130.83, 128.99, 128.72, 122.88, 102.76, 90.95, 66.39, 55.58, 55.35, 21.54. HRMS (ESI): calculated for C₂₃H₂₃NOSNa [M + Na]⁺ = 480.1093, found C₂₃H₂₃NOSNa [M + Na]⁺ = 469.1061.

21. 2-(tosyl(2,4,6-trimethoxyphenyl)methyl)pyridine 4eda

Yield: 72%; white solid; Mp: 131-132°C; ¹H NMR (400 MHz, CDCl₃): δ 8.44 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H), 8.08 (dt, J = 8.1, 1.1 Hz, 1H), 7.66 (td, J = 7.8, 1.9 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.20 – 7.16 (m, 2H), 7.13 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 6.32 (s, 1H), 5.99 (s, 2H), 3.76 (s, 3H), 3.52 (s, 6H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 162.00, 154.92, 148.60, 143.55, 137.92, 135.72, 128.97, 128.76, 125.15, 122.14, 102.97, 91.02, 68.71, 55.55, 55.28, 21.51. HRMS (ESI): calculated for C₂₂H₂₃NO₅SNa [M + Na]⁺ = 436.1195, found C₂₂H₂₃NO₅SNa [M + Na]⁺ = 436.1194.

22. 2-((4-chlorophenyl)((4-chlorophenyl)sulfonyl)methyl)-1,3,5-trimethoxybenzene 4cba
Yield: 93%; white solid; Mp: 133-134°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52 – 7.40 (m, 4H), 7.33 – 7.25 (m, 2H), 7.21 – 7.14 (m, 2H), 6.01 (s, 1H), 5.96 (s, 2H), 3.71 (s, 3H), 3.56 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.03, 139.47, 139.15, 133.70, 132.48, 131.48, 130.16, 129.32, 128.50, 128.13, 127.19, 103.18, 90.97, 67.04, 55.58, 55.34. HRMS (ESI): calculated for C$_{22}$H$_{20}$Cl$_2$O$_5$SNa [M + Na]$^+$ m/z = 489.0306, found C$_{22}$H$_{20}$Cl$_2$O$_5$SNa[M + Na]$^+$ m/z = 489.0322.

23. 2-((2-bromo-5-methoxyphenyl)((4-chlorophenyl)sulfonyl)methyl)-1,3,5-trimethoxybenzene 4kba

Yield: 71%; white solid; Mp: 161-162°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (d, J = 3.1 Hz, 1H), 7.61 – 7.45 (m, 2H), 7.39 – 7.28 (m, 2H), 7.28 – 7.14 (m, 1H), 6.64 (dd, J = 8.8, 3.1 Hz, 1H), 6.27 (s, 1H), 5.96 (s, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 3.56 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.06, 158.11, 139.59, 139.04, 134.64, 132.83, 130.49, 128.59, 118.51, 115.97, 115.54, 102.34, 91.05, 66.20, 55.57, 55.47, 55.28. HRMS (ESI): calculated for C$_{23}$H$_{22}$BrClO$_6$SNa [M + Na]$^+$ m/z = 562.9907, found C$_{22}$H$_{20}$Cl$_2$O$_5$SNa[M + Na]$^+$ m/z = 562.9906.

24. 2-((4-chlorophenyl)(ethylsulfonyl)methyl)-1,3,5-trimethoxybenzene 4cha
Yield: 75%; white solid; Mp: 88-89°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.54 – 7.45 (m, 2H), 7.24 – 7.17 (m, 2H), 6.10 (s, 2H), 6.05 (s, 1H), 3.75 (s, 3H), 3.73 (s, 6H), 2.88 (ddq, $J = 45.8, 13.7, 7.5$ Hz, 2H), 1.22 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.91, 133.80, 132.53, 131.11, 128.37, 103.49, 91.36, 65.15, 55.78, 55.36, 46.70, 6.14. HRMS (ESI): calculated for C$_{18}$H$_{21}$ClO$_5$SNa [M + Na]$^+$ = 407.0696, found C$_{18}$H$_{21}$ClO$_5$SNa [M + Na]$^+$ = 407.0676.

25. 1,2,4-trimethoxy-5-(phenyl(tosyl)methyl)benzene 4adb

Yield: 80%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63 – 7.54 (m, 3H), 7.54 – 7.48 (m, 2H), 7.36 – 7.28 (m, 3H), 7.16 (d, $J = 7.9$ Hz, 2H), 6.33 (s, 1H), 5.98 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.52 (s, 3H), 2.37 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 151.66, 149.89, 144.00, 143.18, 135.98, 133.54, 130.01, 128.97, 128.88, 128.54, 128.25, 113.26, 97.03, 66.40, 56.61, 56.44, 55.97, 21.54. HRMS (ESI): calculated for C$_{23}$H$_{24}$O$_5$SNa [M + Na]$^+$ = 435.1242, found C$_{23}$H$_{24}$O$_5$SNa [M + Na]$^+$ = 435.1225.

26. 1,2,4-trimethoxy-5-((4-nitrophenyl)(phenylsulfonyl)methyl)benzene 4dab

Yield: 89%; white solid; Mp: 160-161°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.20 – 8.12 (m, 2H), 7.83 – 7.71 (m, 2H), 7.68 – 7.58 (m, 2H), 7.59 – 7.49 (m, 1H), 7.43 (s, 1H), 7.37 (t, $J = 7.8$ Hz, 2H), 6.27 (s, 1H), 6.08 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.45 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 151.66, 150.53, 147.60, 143.32, 140.85, 138.28, 133.65, 130.88, 128.82, 128.58, 123.64, 112.94, 111.31, 96.64, 65.69, 56.72, 56.15, 55.98. HRMS (ESI): calculated for C$_{22}$H$_{20}$NO$_7$S [M - H]$^+$ = 442.0955, found C$_{22}$H$_{20}$NO$_7$S[M - H]$^+$ = 442.0951.

27. 1,2,4-trimethoxy-5-((4-nitrophenyl)(tosyl)methyl)benzene 4ddb
Yield: 80%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.21 – 8.09 (m, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.53 – 7.48 (m, 2H), 7.47 (s, 1H), 7.21 – 7.13 (m, 2H), 6.30 (s, 1H), 6.04 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.49 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.67, 150.42, 147.57, 144.68, 143.33, 141.06, 135.39, 130.89, 129.24, 128.84, 123.60, 112.87, 111.63, 96.81, 65.79, 56.70, 56.25, 55.99, 21.59. HRMS (ESI): calculated for C$_{23}$H$_{22}$NO$_7$S [M - H]$^+$ = 456.1111, found C$_{22}$H$_{20}$NO$_7$S[M - H]$^+$ = 456.1114.

4. Trapping reaction intermediates C and D

Reaction Intermediate C

HRMS (ESI): calculated for C$_{16}$H$_{17}$O$_3$ [M]$^+$ = 257.1172, found C$_{16}$H$_{17}$O$_3$ [M]$^+$ = 257.1149.

Reaction Intermediate D$^2$
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.19 – 7.09 (m, 2H), 7.04 (dddd, J = 7.8, 3.8, 2.0, 1.2 Hz, 3H), 6.21 (s, 1H), 6.11 (s, 4H), 3.78 (s, 6H), 3.50 (s, 12H).

2,2’-(phenylmethylene)bis(1,3,5-trimethoxybenzene) D

5. Procedure for the synthesis of compound 6

The compounds 4caa (0.5 mmol) and 4-methylbenzenethiol 5 (0.55 mmol) were taken into DCM (2mL) solvent which was already added in 25mL dried glass reaction tube, then added FeCl$_3$(10 mol%) and stirred the reaction mixture for 1h at room temperature. The reaction was completed after 1h confirmed by the TLC. The reaction mixture was concentrated on a rotary evaporator. The
concentrated reaction mixture was extracted with ethyl acetate (3× 5 mL) and dried over anhydrous MgSO₄. Then organic layer was adsorbed on some silica gel under reduced pressure on a rotary evaporator. After purified by column chromatography (Petroleum ether : Ethyl acetate = 10 : 1 used as eluents), white solid of product 6 was obtained in 84% yield.

28. ((4-chlorophenyl)(2,4,6-trimethoxyphenyl)methyl)(p-tolyl)sulfane 6

![Chemical structure of product 6](image)

Yield: 84%; white solid; Mp: 120-121°C; ¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.33 (m, 2H), 7.20 – 7.07 (m, 5H), 6.95 (d, J = 7.7 Hz, 2H), 6.04 (s, 2H), 5.89 (s, 1H), 3.72 (s, 3H), 3.66 (s, 6H), 2.21 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 160.60, 141.30, 135.97, 134.86, 131.56, 130.29, 129.75, 129.44, 129.23, 128.52, 127.69, 111.85, 91.29, 55.82, 55.30, 47.10, 20.98. HRMS (ESI): calculated for C₂₃H₂₃ClKO₃S [M + K]⁺ = 453.0693, found C₂₃H₂₃ClNaO₃S [M + K]⁺ = 453.0917.
6. $^1$HNMR & $^{13}$CNMR spectra of the products 4 and 6

1. $^1$HNMR & $^{13}$CNMR spectra of 4aaa
2. $^1$HNMR & $^{13}$CNMR spectra of 4baa
3. $^1$HNMR & $^{13}$CNMR spectra of 4caa
4. $^1$HNMR & $^{13}$CNMR spectra of 4daa
5. $^1$HNMR & $^{13}$CNMR spectra of 4eaa
6. $^1$HNMR & $^{13}$CNMR spectra of 4faa
7. $^1$HNMR & $^{13}$CNMR spectra of 4gaa
8. $^1$HNMR & $^{13}$CNMR spectra of $4\text{haa}$
9. $^1$HNMR & $^{13}$CNMR spectra of 4iaa
10. $^1$HNMR & $^{13}$CNMR spectra of 4jaa
11. $^1$HNMR & $^{13}$CNMR spectra of 4aba
12. $^1$HNMR & $^{13}$CNMR spectra of 4aca
13. $^1$HNMR & $^{13}$CNMR spectra of 4ada
14. $^1$HNMR & $^{13}$CNR spectra of 4aea
15. $^1$HNMR & $^{13}$CNMR spectra of 4afa
16. $^1$HNMR & $^{13}$CNMR spectra of 4aga
17. $^1$HNMR & $^{13}$CNMR spectra of 4aab
18. $^1$HNMR & $^{13}$CNMR spectra of 4aac
19. $^1$HNMR & $^{13}$CNMR spectra of 4cda
20. $^1$HNMR & $^{13}$CNMR spectra of 4dda
21. $^1$H NMR & $^{13}$C NMR spectra of 4eda
22. $^1$HNMR & $^{13}$CNMR spectra of 4cba
23. $^1$HNMR & $^{13}$CNMR spectra of 4kba
24. $^1$HNMR & $^{13}$CNMR spectra of 4cha
25. $^1$HNMR & $^{13}$CNMR spectra of 4adb
26. $^1$HNMR & $^{13}$CNMR spectra of 4dab
27. $^1$HNMR & $^{13}$CNMR spectra of 4ddb
28. $^1$HNMR & $^{13}$CNMR spectra of 6
6. References