Efficient Access to Triarylmethanes through Decarboxylation

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Supporting Information

EXPERIMENTAL SECTION

General. All the reactions were carried out in oven-dried glassware under Argon atmosphere. Carboxylic acids were purchased from Sigma Aldrich. Palladium catalysts were purchased from Sigma Aldrich. Phosphine ligands were bought from Sigma-Aldrich or Alfa Aesar and used as such. DMSO and DMF was dried according to standard procedure and stored on molecular sieves 4 Å. All the other reagents and solvents mentioned in this text were bought from Sigma Aldrich or Alfa Aesar or spectrochem and purified if necessary. NMR spectra were recorded on 300, 400 or 500 MHz spectrometer for $^1$H NMR, 75 or 100 or 125 MHz for $^{13}$C NMR spectroscopy. Chemical shifts are reported in parts per million ($\delta$) downfield relative to the residual signals of tetramethylsilane in CDCl$_3$. Spin multiplicities are indicated by the following symbol: s (singlet), d (doublet), t (triplet) and m (multiplet).

General procedure for synthesis of Diphenyl carbinols

A 100 ml double-necked round bottom flask was charged with magnesium (2 equiv), pinch of iodine and after flushing with nitrogen, dried THF was added and stirred. Then corresponding bromoarene (1.5equiv) was added, the colour of iodine disappeared slowly on time, indicating the generation of Grignard reagent. It was stirred for one hour followed by addition of corresponding carbaldehyde (1 equiv). Completion of reaction was determined by TLC. Reaction was quenched by NH$_4$Cl solution. Organic layer was extracted thrice with ethyl acetate and concentrated in vacuo. Compound was purified by column chromatography.

General procedure for synthesis of Diphenyl methyl iodide

To oven dried round bottom flask under nitrogen, the alcohol (1 equiv) and KI (1 equiv) were added and dissolved in dry 1,4-dioxane and stirred for 5 min. Then BF$_3$.Et$_2$O (1equiv) was added and...
stirred at room temperature. Completion of reaction was monitored by TLC. The reaction mixture was poured in cold water and extracted with dichloromethane. The organic layer was washed with water and dried by sodium sulphate; solvent was evaporated under reduced pressure. The crude was purified by quickly passing through short pad of silica using hexane /ethyl acetate (8:2) as eluent to obtain diphenylmethyl iodides and should be used immediately.

**General procedure A for synthesis of various substituted triarylmethanes by Decarboxylative Cross Coupling**

To the oven dried round bottom flask was charged with aryl carboxylic acid (1equiv), Ag$_2$CO$_3$ (1.5 equiv), PdCl$_2$ (0.1 equiv), Xantphos (0.2 equiv), diphenyl methyl iodides (1 equiv) were dissolved in DMSO. The reaction mixture was degassed with argon thrice and stirred in preheated oil bath. Reaction as monitored by TLC after completion, the reaction mixture was cooled to room temperature and filtered through celite bed. The organic layer was washed with NH$_4$Cl solution and dried on sodium sulphate and concentrated under reduced pressure. It was later purified by column chromatography on silica gel to obtain corresponding triarylmethanes.

**General procedure B for synthesis of substituted triarylmethanes by Decarboxylative Cross Coupling**

To the oven dried round bottom flask was charged with aryl carboxylic acid (1equiv), Ag$_2$CO$_3$ (1.5 equiv), PdCl$_2$ (0.2 equiv), Xantphos (0.4 equiv), diphenyl methyl iodides (1 equiv) were dissolved in DMSO:DMF 90:10. The reaction mixture was degassed with argon thrice and stirred in preheated oil bath at requisite temperature and was monitored by TLC. After the completion of reaction, mixture was cooled to room temperature and filtered through a bed celite with ethyl acetate. The organic layer was washed with NH$_4$Cl solution and dried on sodium sulphate and concentrated *in vacuo*. It was later purified by column chromatography on silica gel to obtain corresponding triarylmethanes.

**Spectroscopic data of synthesized compounds**

((2,6-dimethoxyphenyl)methylene)dibenzene (3aa)

![3aa](image)

Prepared following the general procedure A. Rf: 0.35 (2% EtOAc in Hex). Isolated as pale brown, oily liquid (yield: 68%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.27-7.06 (m, 10H), 6.73-6.71 (m, 1H), 6.46-6.37 (m, 2H), 5.82 (s,
1H), 3.78 (s, 3H), 3.68 (s, 3H) ppm. 13C NMR (100 MHz, CDCl3): 158.2 (2C), 143.0 (2C), 129.5 (4C), 128.1 (4C), 126.8 (2C), 124.6, 102.5 (2C), 97.4, 54.3, 54.0, 47.9 ppm. IR (film, cm⁻¹): 2817, 1726, 1582, 1231, 814, 770, 637. MS (ESI): m/z 305 (M+H)⁺. HRMS (ESI): m/z calcd for C21H21O2 [M+H]⁺ 305.1536, found 305.1542.

1,3-dimethoxy-2-(phenyl(o-tolyl)methyl)benzene (3ab)

![Chemical structure of 3ab]

Prepared following the general procedure A. Rf: 0.4 (2% EtOAc in Hex). Isolated as yellow oily liquid (yield: 70%). 1H NMR (400 MHz, CDCl3): δ 7.22-7.02 (m, 8H), 6.79-6.35 (m, 4H), 5.89 (s, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 2.18 (s, 3H) ppm. 13C NMR (100 MHz, CDCl3): 159.3, 158.0, 143.6, 142.6, 136.7, 130.6, 130.1, 129.5 (2C), 128.9, 128.0 (2C), 126.0, 125.8, 125.4, 124.7, 103.7, 98.6, 55.6, 55.2, 45.9, 19.6 ppm. IR (film, cm⁻¹): 2828, 1631, 1536, 1483, 1284, 1171, 823, 772, 656. MS (ESI): m/z 319 (M+H)⁺. HRMS (ESI): m/z calcd for C22H23O2 [M+H]⁺ 319.1693, found 319.1691.

1-methoxy-2-(phenyl(p-tolyl)methyl)benzene (3bf)

![Chemical structure of 3bf]

Prepared following the general procedure A. Rf: 0.6 (1.5% EtOAc in Hex). Yield: 72%. 1H NMR (400 MHz, CDCl3): δ 7.23-6.80 (m, 11H), 6.43-6.34 (m, 2H), 5.69 (s, 1H), 3.70 (s, 3H), 2.27 (s, 3H) ppm. 13C NMR (100 MHz, CDCl3): 156.2, 144.4, 141.1, 141.0, 135.1, 135.0, 132.7, 132.6, 129.1, 129.0, 129.0, 128.6, 127.8, 125.6, 125.5, 124.1, 103.7, 98.6, 55.8, 48.6, 21.0 ppm. IR (film, cm⁻¹): 1689, 1276, 948, 879, 847, 716. MS (ESI): m/z 289 (M+H)⁺. HRMS (ESI): m/z calcd for C21H21O [M+H]⁺ 289.1587, found 289.1594.

1,3-dimethoxy-2-(phenyl(4-propylphenyl)methyl)benzene (3ac)

![Chemical structure of 3ac]
Prepared following the general procedure A. Rf: 0.3 (2% EtOAc in Hex). Yield: 80%, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.25-6.96 (m, 9H), 6.75-6.73 (m, 1H), 6.45-6.37 (m, 2H), 5.79 (s, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 2.54 (t, 2H, $J=7.83$Hz), 1.64-1.59 (m, 2H), 0.92 (t, 3H, $J=7.32$Hz) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 159.3, 157.9, 144.5, 141.3, 140.1, 130.7, 129.3 (2C), 129.1 (2C), 128.1 (2C), 128.0 (2C), 125.8, 125.5, 103.7, 98.6, 55.5, 55.2, 48.6, 37.6, 24.4, 13.9 ppm. IR (film, cm$^{-1}$): 3248, 1692, 1452, 1268, 910, 880, 730, 633. MS (ESI): m/z 347 (M+H)$^+$. HRMS (ESI): m/z calcd for C$_{24}$H$_{27}$O$_2$ (M+H)$^+$ 347.2006, found 347.2003.

1,3-dimethoxy-2-((4-methoxyphenyl)(phenyl)methyl)benzene (3 ad):

![3ad]

Prepared following the general procedure A. Rf: 0.2 (3% EtOAc in Hex). Yield: 74%, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-6.36 (m, 12H), 5.76 (s, 1H), 3.76 (s, 3H), 3.76 (s, 3H), 3.67 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 159.3, 158.9, 157.9, 144.6, 136.3, 130.6, 130.3, 129.3, 128.5, 128.3, 128.0, 127.1, 127.0, 125.8, 125.5, 113.4, 103.7, 98.6, 55.6, 55.2, 55.2, 48.3 ppm. IR (film, cm$^{-1}$): 2802, 1664, 1596, 1327, 932, 815, 804, 730, 623. MS (ESI): m/z 335 (M+H)$^+$. HRMS (ESI): m/z calcd for C$_{22}$H$_{23}$O$_3$ (M+H)$^+$ 335.1642, found 335.1632.

1,3-dimethoxy-2-((4-methoxyphenyl)(o-tolyl)methyl)benzene (3 ae)

![3ae]

Prepared following the general procedure A. Rf: 0.3 (4% EtOAc in Hex). Yield: 72%, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.17-6.28 (m, 11H), 5.76 (s, 1H), 3.70 (s, 6H), 3.60 (s, 3H), 2.10 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 159.3, 157.9, 157.7, 143.0, 136.6, 135.6, 130.5, 130.3, 130.1 (2C), 128.7 (2C), 125.9, 125.4, 125.0, 113.4, 103.7, 98.6, 55.6, 55.2, 55.1, 45.1, 19.5 ppm. IR (film, cm$^{-1}$): 2902, 1685, 1536, 1347, 911, 776. MS (ESI): m/z 349 (M+H)$^+$. HRMS (ESI): m/z calcd for C$_{23}$H$_{25}$O$_3$ (M+H)$^+$ 349.1798, found 349.1810.
1-((4-ethoxyphenyl)(phenyl)methyl)-2-methoxybenzene (3bg):

Prepared following the general procedure A. Rf: 0.3 (2 % EtOAc in Hex). Yield: 68%, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.08-6.29 (m, 13H), 5.62 (s, 1H), 3.90 (m, 2H), 3.62 (s, 3H), 1.31 (t, 3H, J=5.4 Hz) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 157.0, 156.2, 144.6, 136.2, 136.1, 132.6, 132.5, 130.0 (2C), 129.1 (3C), 127.9 (2C), 125.6, 124.3, 113.9, 95.6, 63.3, 55.8, 48.2, 14.9 ppm. IR (film, cm$^{-1}$): 2815, 1664, 1592, 1585, 1320, 1104, 932, 812, 730, 623. MS (ESI): m/z 319 (M+H)$^+$. HRMS (ESI): m/z calcd for C$_{22}$H$_{23}$O$_2$ [M+H]$^+$ 319.1693, found 319.1693.

2-((3,4-dimethoxyphenyl)(phenyl)methyl)-1,3-dimethoxybenzene (3ah):

Prepared following the general procedure A. Rf: 0.3 (5% EtOAc in Hex). Yield: 79%, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18-6.29 (m, 11H), 5.68 (s, 1H), 3.76 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.61 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 158.2, 156.8, 147.4, 146.0, 143.3, 135.6, 129.4 (2C), 128.1 (2C), 126.8, 124.7, 124.2, 120.1, 111.7, 109.5, 102.6, 97.5, 54.6, 54.6, 54.4, 54.1, 47.5 ppm. IR (film, cm$^{-1}$): 2805, 1664, 1587, 1523, 1320, 1104, 897, 816. MS (ESI): m/z 365 (M+H)$^+$. HRMS (ESI): m/z calcd for C$_{23}$H$_{25}$O$_3$ [M+H]$^+$ 365.1747, found 365.1756.

((2-methoxyphenyl)methylene)dibenzene (3ba):

Prepared following the general procedure A. Rf: 0.5 (1% EtOAc in Hex). Yield: 71%, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.27-6.79 (m, 14H), 5.48 (s, 1H), 3.75 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 158.0, 144.3 (2C), 136.1, 130.4 (2C), 129.4 (5C), 128.3 (4C), 126.2 9(2C), 113.7, 56.0, 55.2 ppm. IR (film, cm$^{-1}$): 2943, 1685,
Triphenylmethane (3ca):

![Triphenylmethane (3ca)](#)

Prepared following the general procedure A. Rf: 0.5 (1% EtOAc in Hex). Yield: 67%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33-7.09 (m, 15H), 5.54 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 143.9 (3C), 129.5, 128.3 (6C), 128.3 (6C), 128.2, 126.3, 56.9 ppm. IR (film, cm$^{-1}$): 2987, 1642, 1586, 1572, 1121. MS (ESI): m/z 275 (M+H)$^+$. HRMS (ESI): m/z calcd for C$_{20}$H$_{19}$O [M+H]$^+$ 275.1430, found 275.1439.

1-((4-chlorophenyl)(phenyl)methyl)-2-methoxybenzene (3bi):

![1-((4-chlorophenyl)(phenyl)methyl)-2-methoxybenzene (3bi)](#)

Prepared following the general procedure A. Rf: 0.3 (2% EtOAc in Hex). Yield: 62%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.25-7.19 (m, 6H), 7.07-6.99 (m, 4H), 6.87-6.79 (m, 3H), 5.87 (s, 1H), 3.69 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 157.0, 143.3, 142.5, 132.1, 131.8, 130.7, 130.2, 129.4 (2C), 128.2 (5C), 127.8, 126.2, 120.3, 110.7, 55.5, 49.0 ppm. IR (film, cm$^{-1}$): 2763, 1675, 1297, 981, 824, 747, 615. MS (ESI): m/z 309 (M+H)$^+$. HRMS (ESI): m/z calcd for C$_{20}$H$_{18}$ClO [M+H]$^+$ 309.1041, found 309.1050.

((4-(trifluoromethyl)phenyl)methylene)dibenzene (3cj):

![((4-(trifluoromethyl)phenyl)methylene)dibenzene (3cj)](#)

Prepared following the general procedure A. Rf: 0.5 (1 % EtOAc in Hex). Yield: 56%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.54-7.52 (m, 2H), 7.31-7.21 (m, 8H), 7.10-7.08 (m, 4H), 5.59 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 148.0, 142.9 (2C), 129.7, 129.3 (6C), 128.5 (6C), 126.6, 125.2, 125.2, 56.6. IR (film, cm$^{-1}$): 2812,
1664, 1543, 1320, 932, 815. MS (ESI): m/z 313 (M+H)+. HRMS (ESI): m/z calcd for C_{20}H_{18}F_{3} [M+H]^+ 313.1199, found 313.1198.

4-((2-fluoro-5-nitrophenyl)(phenyl)methyl)-1,1′-biphenyl (3dk):

![Chemical structure of 3dk]

Prepared following the general procedure B. Rf: 0.5 (3% EtOAc in Hex). Yield: 42%. 1H NMR (400 MHz, CDCl₃): δ 7.58-7.54 (m, 4H), 7.45-7.32 (m, 6H), 7.29-7.25 (m, 7H), 5.48 (s, 1H) ppm. 13C NMR (100 MHz, CDCl₃): 145.2, 142.1, 140.8, 140.0, 137.8, 132.3, 130.7, 130.0, 128.9, 128.7, 128.4, 128.3 (4C), 128.1(2C), 127.6 (2C), 127.3, 127.2, 127.1, 127.0, 126.9, 79.8. IR (film, cm⁻¹): 2883, 1904, 1684, 1892, 1543, 871, 810, 742, 613. MS (ESI): m/z 384 (M+H)+. HRMS (ESI): m/z calcd for C_{25}H_{19}FNO₂ [M+H]^+ 384.1394, found 384.1402.

2-((4-methoxyphenyl)(o-tolyl)methyl)-1,3-dimethylbenzene (3ef):

![Chemical structure of 3ef]

Prepared following the general procedure A. Rf: 0.5 (2 % EtOAc in Hex). Yield: 74%. 1H NMR (400 MHz, CDCl₃): δ 7.42-7.40 (m, 1H), 7.31-7.12 (m, 10H), 5.40 (s, 1H), 3.38 (s, 3H), 2.26 (s, 9H) ppm. 13C NMR (100 MHz, CDCl₃): 144.6, 141.8, 141.4, 141.0, 139.9, 139.6, 136.4, 136.0, 130.6, 130.5, 128.3, 128.2, 127.9, 127.6, 127.4, 126.2, 126.1 (2C), 57.1, 47.4, 19.5 (2C), 19.3 ppm. IR (film, cm⁻¹): 2984, 1683, 1317, 981, 823, 728, 604. HRMS (ESI): m/z calcd for C_{23}H_{25}O [M+H]^+ 317.1900, found 317.1898.

4-((2-nitrophenyl)(phenyl)methyl)-1,1′-biphenyl (3fk):

![Chemical structure of 3fk]
1-((4-methoxyphenyl)(3-(trifluoromethyl)phenyl)methyl)-3-nitrobenzene (3gl):

\[
\text{\begin{center}
\begin{tikzpicture}
\begin{scope}
\node (A) at (0,0) {\text{NO}_2};
\node (B) at (-1,0) {\text{CF}_3};
\node (C) at (-2,0) {\text{O}};
\node (D) at (1,0) {\text{CF}_3};
\node (E) at (2,0) {\text{O}};
\end{scope}
\end{tikzpicture}
\end{center}
\]
\]

Prepared following the general procedure B. Rf: 0.4 (3% EtOAc in Hex). Yield: 51%. \( ^1\text{H} \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.85-7.79 (m, 1H), 7.56-7.51 (m, 2H), 7.42-7.36 (m, 3H), 7.09-7.06 (m, 2H), 7.01-7.00 (m, 2H), 6.85-6.82 (m, 2H), 5.85 (s, 1H), 3.80 (S, 3H) ppm. IR (film, cm\textsuperscript{-1}): 2907, 1886, 1673, 1584, 1543, 1281, 942, 881, 634. HRMS (ESI): m/z calcd for C\textsubscript{21}H\textsubscript{17}F\textsubscript{3}NO\textsubscript{3} [M+H]\textsuperscript{+} 388.1155, found 388.1149.

1-chloro-3-((4-methoxyphenyl)(3-(trifluoromethyl)phenyl)methyl)benzene (3hl):

\[
\text{\begin{center}
\begin{tikzpicture}
\begin{scope}
\node (A) at (0,0) {\text{Cl}};
\node (B) at (-1,0) {\text{CF}_3};
\node (C) at (-2,0) {\text{O}};
\node (D) at (1,0) {\text{CF}_3};
\node (E) at (2,0) {\text{O}};
\end{scope}
\end{tikzpicture}
\end{center}
\]
\]

Prepared following the general procedure B. Rf: 0.2 (2% EtOAc in Hex). Yield: 56%. \( ^1\text{H} \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.24-7.22 (m, 1H), 7.04-6.98 (m, 2H), 6.95-6.93 (m, 3H), 6.89-6.88 (m, 2H), 6.85-6.84 (m, 1H), 6.82-6.79 (m, 2H), 6.63-6.62 (m, 1H), 5.82 (s, 1H), 3.78 (S, 3H) ppm. IR (film, cm\textsuperscript{-1}): 2928, 1691, 1564, 1298, 911, 828, 804. HRMS (ESI): m/z calcd for C\textsubscript{21}H\textsubscript{17}ClF\textsubscript{3}O [M+H]\textsuperscript{+} 377.0915, found 377.0919.

2-benzhydrylthiophene (5):

\[
\text{\begin{center}
\begin{tikzpicture}
\begin{scope}
\node (A) at (0,0) {S};
\node (B) at (-1,0) {\text{CF}_3};
\node (C) at (-2,0) {\text{O}};
\node (D) at (1,0) {\text{CF}_3};
\node (E) at (2,0) {\text{O}};
\end{scope}
\end{tikzpicture}
\end{center}
\]
\]

Prepared following the general procedure A. Rf: 0.6 (1% EtOAc in Hex). Yield: 50%. \( ^1\text{H} \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.30-7.17 (m, 11H), 6.92 (m, 1H), 6.68 (m, 1H), 5.67 (s, 1H) ppm. \( ^{13}\text{C} \) NMR (100 MHz, CDCl\textsubscript{3}): 147.9, 143.8 (2C), 128.8 (4C), 128.4 (4C), 126.7, 126.6, 126.4 (2C), 124.5, 52.1. IR (film, cm\textsuperscript{-1}): 1592, 1585,
1365, 623. MS (ESI): m/z 251 (M+H)⁺. HRMS (ESI): m/z calcd for C_{17}H_{15}S [M+H]⁺ 251.0889, found 251.0892.

Figure 1. ¹H spectrum of compound 3aa.
Figure 2. $^{13}$C spectrum of compound 3aa.
Figure 3. $^1$H spectrum of compound 3ab
Figure 4. $^{13}$C spectrum of compound 3ab.
Figure 5. $^1$H spectrum of compound 3bf.
Figure 6. $^{13}$C spectrum of compound 3bf
Figure 7. $^1$H spectrum of compound 3ac
Figure 8: $^{13}$C spectrum of compound 3ac
Figure 9. $^1$H spectrum of compound 3ad

Figure 10. $^{13}$C spectrum of compound 3ad
Figure 11. $^1$H spectrum of compound 3ae
Figure 12. $^{13}$C spectrum of compound \(3ae\)
Figure 13. $^1$H spectrum of compound 3bg
Figure 14. $^{13}$C spectrum of compound 3bg
Figure 15. $^1$H spectrum of compound 3ah
Figure 16. $^{13}$C spectrum of compound 3ah
Figure 17. $^1$H spectrum of compound 3ba
Figure 18. $^{13}$C spectrum of compound 3ba
Figure 19. $^1$H spectrum of compound 3ca
Figure 20. $^{13}$C spectrum of compound 3ca
Figure 21. $^1$H spectrum of compound 3bi
Figure 22. $^{13}$C spectrum of compound 3bi
Figure 23. $^1$H spectrum of compound 3cJ
Figure 24. $^{13}$C spectrum of compound $3cj$
Figure 25. $^1$H spectrum of compound 3dk
Figure 26. $^{13}$C spectrum of compound 3dk
Figure 27. $^1$H spectrum of compound 3ef
Figure 28. $^{13}$C spectrum of compound 3ef
Figure 29. $^1$H spectrum of compound 3fk
Figure 30. $^1$H spectrum of compound 3hl
Figure 31. $^1$H spectrum of compound 3gl
Figure 32. $^1$H spectrum of compound 5
Figure 33. $^{13}$C spectrum of compound 5