Iridium catalyzed acceptor/acceptor carbene insertion into the N−H bond in water medium

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Supporting Information

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**Figure S1.** Molecular structure of dimethyl 2-((4-nitrophenyl)amino)malonate (9b); thermal ellipsoids are set at 50% probability.

**X-ray data collection and refinement:**

X-ray data collections were performed on an OXFORD XCALIBUR diffractometer, equipped with a CCD area detector, using graphitemonochromated Mo Ka(I ¼0.71073Å) radiation. All calculations were executed using SHELXS-97 and SHELXL-97 respectively using Olex 2-1.1 software package. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F2). All nonhydrogen atoms were refined anisotropically. The crystallographic figures have been generated using Ortep3 software package (50% probability thermal ellipsoids).
### Crystallographic information

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Experimental section:

**General information:** Unless otherwise mentioned all the reactions were carried out under dinitrogen atmosphere. Distilled water was purged for 5 minutes with dinitrogen gas and used. Commercially available chemicals were obtained and used as received, unless otherwise mentioned. TLC was performed on pre coated silica gel 60 F$_{254}$ on aluminum plates and UV light (254 nm). Column chromatography was performed on silica gel 100-200 mesh size. $^1$H and $^{13}$C NMR were recorded on 400 MHz ($^1$H) and 100 MHz ($^{13}$C) instrument, Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references for $^1$H and $^{13}$C spectra, HR-MS was recorded on UHD Q-TOF mass spectrometer.

**General procedure for Ir catalyzed carbene insertion into N-H bond in water medium:**
A 20 mL glass tube was charged with aniline (1 mmol) and [(COD)IrCl]$_2$ catalyst (1 mol %), then 4 mL of water was added to the reaction mixture. Then diazo compound (1.1 mmol) was added to the reaction mixture. The reaction tube was closed with septum and reaction mixture was allowed to stir at room temperature for mentioned time. The progress of the reaction was monitored by TLC experiment for every 2 hours using appropriate mixture of hexane and ethyl acetate as eluent. After completion of reaction, the reaction mixture was extracted with 15 mL (5 mL X 3) of EtOAc. Then EtOAc was evaporated under reduced pressure and the crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate.
(Note: In case of 12 and 13 to increase the solubility of 10 and 11 in water, we have added 1 mmol of NaHCO$_3$, after completion of the reaction the reaction mixture was neutralized with 1 N HCl then extracted with EtOAc)

**Analytical data:**

**Diethyl 2-(phenylamino)malonate (5a):**
Off-White color solid (204 mg, 81% yield); mp 41–43 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.15 (m, 2H), 6.83 – 6.75 (m, 1H), 6.70 – 6.62 (m, 2H), 4.84 (s, 1H), 4.76 (s, 1H), 4.28 (qd, $J$ = 7.1, 0.6 Hz, 4H), 1.28 (t, $J$ = 7.1 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.84, 145.52, 129.48,
119.10, 113.63, 62.49, 60.91, 14.14; IR (Film): 3414, 2987, 1753, 1606, 1448, 1393, 1372, 1341, 1323, 1292, 1224, 1156, 1018, 877, 862, 753 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^{+}\) calculated (for C\(_{13}\)H\(_{18}\)NO\(_{4}\)) 252.1236, found 252.1238.

### Diethyl 2-(p-tolylamino)malonate (5b):

Off-White solid (235 mg, 88% yield); mp 51−53 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.00 (d, \(J = 8.2\) Hz, 2H), 6.58 (t, \(J = 5.5\) Hz, 2H), 4.73 (d, \(J = 7.2\) Hz, 2H), 4.31 – 4.23 (m, 4H), 2.23 (s, 3H), 1.28 (t, \(J = 7.1\) Hz, 6H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.98, 143.24, 129.98, 128.41, 113.85, 62.44, 61.29, 20.54, 14.17; IR (Film): 3380, 2992, 2919, 1756, 1731, 1621, 1525, 1370, 1335, 1285, 1259, 1173, 1115, 1017, 824, 804 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^{+}\) calculated (for C\(_{14}\)H\(_{20}\)NO\(_{4}\)) 266.1392, found 266.1397.

### Diethyl 2-((2,4-dimethylphenyl)amino)malonate (5c):

Yellow liquid (267 mg, 95% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.91 (d, \(J = 9.6\) Hz, 2H), 6.47 (d, \(J = 7.8\) Hz, 1H), 4.77 (d, \(J = 7.5\) Hz, 1H), 4.66 (d, \(J = 7.1\) Hz, 1H), 4.33 – 4.25 (m, 4H), 2.25 (s, 3H), 2.24 (s, 3H), 1.30 (td, \(J = 7.1, 1.3\) Hz, 6H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.12, 141.44, 131.43, 127.96, 127.43, 123.28, 111.01, 62.39, 61.35, 20.44, 17.41, 14.12; IR (Film): 3438, 2983, 2927, 1740, 1616, 1589, 1520, 1370, 1334, 1288, 1218, 1155, 1108, 1031 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^{+}\) calculated (for C\(_{15}\)H\(_{22}\)NO\(_{4}\)) 280.1549, found 280.1559.

### Diethyl 2-((2,6-diisopropylphenyl)amino)malonate (5d):

Light-yellow liquid (322 mg, 96% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.11 – 7.02 (m, 3H), 4.50 (d, \(J = 10.0\) Hz, 1H), 4.41 (d, \(J = 10.1\) Hz, 1H), 4.25 – 4.14 (m, 4H), 3.38 – 3.26 (m, 2H), 1.27 – 1.15 (m, 18H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.52, 142.12, 139.85, 124.20, 123.73, 66.02, 62.06, 27.74, 24.22, 14.05; IR (Film): 3396, 2965, 2871, 1757, 1739, 1463, 1367, 1308, 1258, 1221, 1151, 1027, 759 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^{+}\) calculated (for C\(_{19}\)H\(_{30}\)NO\(_{4}\)) 336.2175, found 336.2182.

### Diethyl 2-(mesitylamino)malonate (5e):

Light-yellow liquid (288 mg, 98% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.79 (s, 2H), 4.65 (d, \(J = 10.3\) Hz, 1H), 4.36 (d, \(J = 9.9\) Hz, 1H), 4.25 – 4.17 (m, 4H), 2.30 (s, 6H), 2.21 (s, 3H), 1.22 (t, \(J = 7.1\) Hz, 6H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.51, 140.30, 131.76, 129.65, 129.19, 63.74, 62.11,
20.60, 18.62, 14.06; IR (Film): 3388, 2981, 2934, 1757, 1738, 1488, 1446, 1369, 1303, 1220, 1159, 1031, 855 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^+\) calculated (for C\(_{16}\)H\(_{24}\)NO\(_4\)) 294.1705, found 294.1717.

**Diethyl 2-((3,4-dimethoxyphenyl)amino)malonate (5f):**
Brown solid (291 mg, 93% yield); mp 51−53 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.78 – 6.67 (m, 1H), 6.35 (t, \(J = 2.4\) Hz, 1H), 6.17 (dt, \(J = 8.5, 2.7\) Hz, 1H), 4.71 (d, \(J = 2.1\) Hz, 1H), 4.27 (qd, \(J = 7.2, 3.1\) Hz, 4H), 3.88 – 3.82 (m, 3H), 3.83 – 3.75 (m, 3H), 1.32 – 1.24 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.95, 150.02, 142.67, 140.14, 112.83, 104.34, 99.91, 62.43, 61.71, 56.53, 55.78, 14.14. IR (Film): 3371, 2983, 2936, 1741, 1722, 1618, 1516, 1464, 1441, 1280, 1233, 1188, 1140, 1026, 865, 788, 764 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^+\) calculated (for C\(_{15}\)H\(_{22}\)NO\(_6\)) 312.1447, found 312.1456.

**Diethyl 2-((4-fluorophenyl)amino)malonate (5g):**
4 White solid (257 mg, 95% yield); mp 62−64 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.48 – 7.39 (m, 2H), 6.48 – 6.41 (m, 2H), 4.88 (d, \(J = 7.1\) Hz, 1H), 4.69 (d, \(J = 7.5\) Hz, 1H), 4.31 – 4.22 (m, 4H), 1.28 (t, \(J = 7.1\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.46, 145.13, 138.11, 115.77, 80.23, 62.67, 60.55, 14.16; IR (Film): 3403, 2978, 2899, 1750, 1609, 1516, 1464, 1441, 1280, 1233, 1188, 1140, 1026, 865, 788, 764 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^+\) calculated (for C\(_{13}\)H\(_{17}\)FNO\(_4\)) 270.1142, found 270.1151.

**Diethyl 2-((4-bromophenyl)amino)malonate (5h):**
3 White solid (298 mg, 90% yield); mp 90−92 °C \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29 – 7.25 (m, 2H), 6.56 – 6.52 (m, 2H), 4.87 (d, \(J = 7.6\) Hz, 1H), 4.70 (d, \(J = 7.6\) Hz, 1H), 4.27 (qd, \(J = 7.1, 0.8\) Hz, 4H), 1.28 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.49, 144.54, 132.25, 115.23, 110.93, 62.65, 60.75, 14.16; IR (Film): 3401, 2981, 2907, 1753, 1732, 1595, 1505, 1369, 1339, 1318, 1288, 1257, 1229, 1174, 1022, 821 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^+\) calculated (for C\(_{13}\)H\(_{17}\)BrNO\(_4\)) 330.0341, found 330.0350.

**Diethyl 2-((4-iodophenyl)amino)malonate (5i):**
White solid (362 mg, 96% yield); mp 82−84 °C \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.95 – 6.85 (m, 1H), 6.61 (ddd, \(J = 6.7, 5.2, 3.0\) Hz, 1H), 4.71 (d, \(J = 12.9\) Hz, 1H), 4.32 – 4.23 (m, 2H), 1.28 (t, \(J = 7.1\) Hz, 6H). IR (Film): 3403, 2981, 2907, 1753, 1732, 1595, 1505, 1369, 1339, 1318, 1288, 1257, 1229, 1174, 1022, 821 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^+\) calculated (for C\(_{13}\)H\(_{17}\)I NO\(_4\)) 360.0441, found 360.0450.
= 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.75, 157.93, 155.57, 141.87, 141.85, 116.10, 115.87, 114.80, 114.73, 62.55, 61.50, 14.15; IR (Film): 3393, 2963, 2899, 1733, 1592, 1503, 1458, 1370, 1281, 1181, 1094, 1023, 815 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{13}$H$_{17}$NO$_4$) 378.0202, found 378.0222.

**Diethyl 2-((4-acetylphenyl)amino)malonate (5j):**
White solid (259 mg, 88% yield); mp 91−93 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.77 (m, 2H), 6.65 – 6.59 (m, 2H), 5.34 (d, $J$ = 7.2 Hz, 1H), 4.79 (d, $J$ = 7.2 Hz, 1H), 4.31 – 4.20 (m, 4H), 2.48 (s, 3H), 1.27 (t, $J$ = 7.1 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.47, 167.05, 149.39, 130.79, 128.35, 112.38, 62.78, 59.93, 26.15, 14.09; IR (Film): 3392, 2984, 2904, 1750, 1728, 1663, 1598, 1573, 1526, 1421, 1365, 1338, 1272, 1230, 1181, 1014, 956, 831 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{15}$H$_{20}$N$_2$O$_5$) 294.1341, found 294.1350.

**Diethyl 2-((2-(trifluoromethyl)phenyl)amino)malonate (5k):**
Colorless liquid (304 mg, 95% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J$ = 7.8 Hz, 1H), 7.36 (t, $J$ = 7.8 Hz, 1H), 6.81 (dd, $J$ = 11.3, 3.9 Hz, 1H), 6.65 (d, $J$ = 8.3 Hz, 1H), 5.61 (d, $J$ = 6.0 Hz, 1H), 4.79 (d, $J$ = 6.8 Hz, 1H), 4.34 – 4.24 (m, 4H), 1.28 (t, $J$ = 7.1 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.10, 143.16, 133.34, 127.09, 127.03, 126.98, 126.27, 123.56, 117.84, 114.99, 114.69, 112.51, 62.76, 60.50, 14.08; IR (Film): 3440, 2984, 2937, 1760, 1741, 1615, 1589, 1524, 1477, 1460, 1372, 1335, 1289, 1229, 1153, 1107, 1034, 754 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{14}$H$_{17}$F$_3$NO$_4$) 320.1110, found 320.1122.

**Diethyl 2-((4-cyanophenyl)amino)malonate (5l):**
White solid (250 mg, 90% yield); mp 135−137 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 – 7.37 (m, 2H), 6.69 – 6.59 (m, 2H), 5.34 (d, $J$ = 7.0 Hz, 1H), 4.75 (d, $J$ = 7.1 Hz, 1H), 4.36 – 4.21 (m, 4H), 1.28 (t, $J$ = 7.1 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.84, 148.71, 133.95, 119.91, 113.19, 101.12, 62.96, 59.79, 14.13; IR (Film): 3391, 2989, 2899, 2213, 1750, 1727, 1606, 1525, 1370, 1338, 1294, 1261, 1235, 1177, 1019, 838 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{14}$H$_{17}$N$_2$O$_4$) 277.1188, found 277.1199.

**Diethyl 2-((3-nitrophenyl)amino)malonate (5m):**
Yellow solid (261 mg, 88% yield); mp 86−88 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, $J = 8.1$ Hz, 1H), 7.47 (t, $J = 2.2$ Hz, 1H), 7.32 (td, $J = 8.1$, 0.9 Hz, 1H), 6.96 (dd, $J = 8.2$, 2.4 Hz, 1H), 5.28 (d, $J = 6.9$ Hz, 1H), 4.81 (d, $J = 7.4$ Hz, 1H), 4.35 − 4.28 (m, 4H), 1.31 (td, $J = 7.1$, 0.8 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.08, 149.38, 146.33, 130.12, 119.50, 113.61, 107.31, 62.90, 60.19, 14.11; IR (Film): 3392, 2984, 1731, 1622, 1528, 1355, 1296, 1266, 1224, 1167, 1025, 867, 813, 735 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{13}$H$_{17}$N$_2$O$_6$) 297.1087, found 297.1095.

**Diethyl 2-((2-nitrophenyl)amino)malonate (5n):**

Yellow solid (286 mg, 96% yield); mp 92−94 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.83 (s, 1H), 8.18 (dd, $J = 10.4$, 9.0 Hz, 1H), 7.44 (td, $J = 7.5$, 4.3 Hz, 1H), 6.75 (ddd, $J = 12.5$, 9.3, 6.3 Hz, 2H), 4.88 (dd, $J = 6.4$, 1.5 Hz, 1H), 4.34 − 4.26 (m, 4H), 1.32 − 1.26 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.30, 142.67, 136.41, 133.34, 127.11, 117.22, 113.95, 63.00, 60.07, 14.08; IR (Film): 3366, 3105, 2990, 2913, 1756, 1734, 1619, 1572, 1508, 1418, 1372, 1351, 1275, 1177, 1010, 855, 750 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{13}$H$_{17}$N$_2$O$_6$) 297.1087, found 297.1094.

**Diethyl 2-((2-bromo-4-methylphenyl)amino)malonate (5o):**

White solid (307 mg, 89% yield); mp 49−51 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, $J = 1.8$ Hz, 1H), 6.96 (dd, $J = 8.2$, 1.4 Hz, 1H), 6.49 (d, $J = 8.2$ Hz, 1H), 5.41 (d, $J = 7.3$ Hz, 1H), 4.73 (d, $J = 7.3$ Hz, 1H), 4.32 − 4.25 (m, 4H), 2.22 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.42, 153.14, 150.76, 142.43, 142.40, 121.55, 121.36, 117.26, 117.04, 115.01, 112.95, 62.60, 61.16, 20.17, 14.15; IR (Film): 3399, 3013, 2982, 2916, 1756, 1733, 1613, 1522, 1465, 1445, 1392, 1367, 1332, 1296, 1174, 1152, 1092, 1038, 1016, 881, 855, 809 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{14}$H$_{19}$BrNO$_4$) 344.0497, found 344.0507.

**Diethyl 2-((3-chloro-4-fluorophenyl)amino)malonate (5p):**

White solid (274 mg, 90% yield); mp 96−98 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.96 (t, $J = 8.8$ Hz, 1H), 6.67 (dd, $J = 6.0$, 2.9 Hz, 1H), 6.52 − 6.47 (m, 1H), 4.80 (d, $J = 7.5$ Hz, 1H), 4.65 (d, $J = 7.7$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 4H), 1.28 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.41, 153.14, 150.76, 142.43, 142.40, 121.55, 121.36, 117.26, 117.04, 115.01, 113.02, 112.95, 62.74,
61.03, 14.16; IR (Film): 3403, 2984, 2907, 1744, 1725, 1608, 1510, 1339, 1294, 1258, 1240, 1215, 1177, 1020, 865, 814 cm⁻¹; HRMS-ESI (m/z): [M+H]⁺ calculated (for C₁₃H₁₆ClFNO₄) 304.0752, found 304.0749.

**Diethyl 2-((2,4,5-trichlorophenyl)amino)malonate (5q):**
White solid (335 mg, 94% yield); mp 70–72 °C; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.36 (s, 1H), 6.67 (s, 1H), 5.56 (d, \(J = 6.8\) Hz, 1H), 4.68 (d, \(J = 7.0\) Hz, 1H), 4.34 – 4.27 (m, 4H), 1.30 (t, \(J = 7.1\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 166.68, 141.21, 131.77, 130.42, 121.28, 118.81, 112.87, 62.98, 60.22, 14.15; IR (Film): 3408, 2983, 2928, 1751, 1731, 1596, 1556, 1506, 1474, 1438, 1379, 1342, 1288, 1256, 1226, 1170, 1063, 882, 823 cm⁻¹; HRMS-ESI (m/z): [M+H]⁺ calculated (for C₁₃H₁₅ClNO₄) 354.0067, found 354.0080.

**Diethyl 2-((3-chlorophenyl)amino)malonate (5r):**
White solid (269 mg, 94% yield); mp 73–75 °C; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.09 (t, \(J = 8.1\) Hz, 1H), 6.78 – 6.70 (m, 1H), 6.65 (t, \(J = 2.1\) Hz, 1H), 6.53 (dd, \(J = 8.2, 2.0\) Hz, 1H), 4.96 (d, \(J = 6.5\) Hz, 1H), 4.72 (d, \(J = 7.5\) Hz, 1H), 4.28 (q, \(J = 7.1\) Hz, 4H), 1.29 (t, \(J = 7.1\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 167.41, 146.62, 135.17, 130.47, 118.95, 113.43, 111.79, 62.65, 60.47, 14.12; IR (Film): 3398, 2985, 2902, 1748, 1727, 1600, 1573, 1507, 1483, 1372, 1339, 1285, 1224, 1165, 1096, 1022, 858, 766 cm⁻¹; HRMS-ESI (m/z): [M+H]⁺ calculated (for C₁₃H₁₅ClNO₄) 286.0846, found 286.0853.

**Methyl 2-(4-methoxyphenyl)-2-(phenylamino)acetate (6):**
Light yellow semi solid (245 mg, 90% yield); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.42 – 7.37 (m, 2H), 7.11 (ddd, \(J = 8.9, 2.8, 1.2\) Hz, 2H), 6.89 – 6.85 (m, 2H), 6.69 (tt, \(J = 7.4, 1.0\) Hz, 1H), 6.55 (ddd, \(J = 6.8, 1.9, 1.0\) Hz, 2H), 5.02 (s, 1H), 3.77 (s, 4H), 3.71 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 172.71, 159.67, 146.09, 129.63, 129.33, 128.50, 118.15, 114.37, 113.49, 60.18, 55.37, 52.85; IR (Film): 3392, 2952, 2831, 1733, 1603, 1510, 1363, 1312, 1249, 1172, 1029, 750 cm⁻¹; HRMS-ESI (m/z): [M+H]⁺ calculated (for C₁₆H₁₈NO₃) 272.1287, found 272.1293.

**N-(bis(4-methoxyphenyl)methyl)aniline (7):**

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Colorless liquid (176 mg, 56% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.18 – 7.12 (m, 4H), 7.04 – 6.97 (m, 2H), 6.79 – 6.73 (m, 4H), 6.59 (t, $J = 7.3$ Hz, 1H), 6.49 – 6.39 (m, 2H), 5.32 (s, 1H), 4.08 (s, 1H), 3.68 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.84, 147.54, 135.50, 129.19, 128.59, 117.58, 114.14, 113.55, 61.80, 55.35; IR (Film): 3403, 2932, 1605, 1508, 1462, 1302, 1247, 1175, 1033, 813, 750 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{21}$H$_{22}$NO$_2$) 320.1651, found 320.1660.

**Diethyl 2-hydroxymalonate (8):**

Colorless liquid (136 mg, 77% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.68 (d, $J = 8.1$ Hz, 1H), 4.31 – 4.24 (m, 4H), 3.57 (d, $J = 8.2$ Hz, 1H), 1.29 (td, $J = 7.1$, 1.1 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.60, 71.61, 62.55, 14.03; IR (Film): 3486, 2985, 1743, 1604, 1468, 1447, 1369, 1238, 1185, 1123, 1025, 861, 774 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_7$H$_{12}$NaO$_5$) 199.0582, found 199.0583.

**Diethyl 2-((4-nitrophenyl)amino)malonate (9a):**

Off-White solid (244 mg, 82% yield); mp 122–124 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 – 8.08 (m, 2H), 6.66 – 6.61 (m, 2H), 5.60 (d, $J = 6.9$ Hz, 1H), 4.82 (d, $J = 7.0$ Hz, 1H), 4.35 – 4.28 (m, 4H), 1.31 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.61, 150.61, 139.64, 126.38, 112.20, 63.11, 59.77, 14.13; IR (Film): 3381, 2987, 2940, 1748, 1723, 1597, 1524, 1501, 1475, 1372, 1330, 1289, 1236, 1175, 1114, 1015, 846 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{13}$H$_{17}$N$_2$O$_6$) 297.1087, found 297.1095.

**Dimethyl 2-((4-nitrophenyl)amino)malonate (9b):**

Pale yellow color solid (192 mg, 71% yield); mp 154–156 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 9.1$ Hz, 2H), 6.62 (d, $J = 9.2$ Hz, 2H), 5.57 (d, $J = 6.9$ Hz, 1H), 4.85 (d, $J = 7.1$ Hz, 1H), 3.85 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.04, 150.46, 139.77, 126.42, 112.21, 59.46, 53.87; IR (Film): 3379, 2963, 2825, 1752, 1600, 1502, 1481, 1433, 1356, 1323, 1282, 1244, 1189, 1114, 843, 774 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{11}$H$_{13}$N$_2$O$_6$) 269.0774, found 269.0780.

**Ethyl 2-((4-nitrophenyl)amino)-3-oxobutanoate (9c):**


Yellow color semi-solid (210 mg, 79% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.50 (s, 0.9H), 8.26 – 7.96 (m, 3.5H), 6.62 – 6.51 (m, 3.5H), 5.79 (d, $J = 5.9$ Hz, 0.7H), 5.31 (s, 1H), 4.88 (d, $J = 6.3$ Hz, 0.7H), 4.31 (q, $J = 7.1$ Hz, 1.5H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.39 (s, 2.1H), 2.05 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 2H), 1.18 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.08, 176.76, 171.19, 166.81, 153.32, 150.54, 139.57, 126.50, 126.41, 112.14, 112.01, 102.58, 67.00, 63.25, 61.39, 26.98, 17.96, 14.30, 14.18. (More number of protons and carbon peaks are due to the keto-enol tautomerism (4:3)); IR (Film): 3343, 3078, 2987, 1731, 1712, 1599, 1561, 1508, 1345, 1314, 1177, 1112, 1014, 858, 751, 694 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{12}$H$_{15}$N$_2$O$_5$) 267.0981, found 267.0963.

3-((4-nitrophenyl)amino)pentane-2,4-dione (9d):
Yellow color solid (182 mg, 77% yield); mp 123–125 $^\circ$C $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 15.97 (s, 1H), 8.10 (d, $J = 9.3$ Hz, 2H), 6.62 (dd, $J = 6.9$, 2.1 Hz, 2H), 5.74 (s, 1H), 2.08 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.00, 152.84, 139.45, 126.79, 112.58, 22.01; IR (Film): 3349, 2807, 1597, 1476, 1300, 1180, 1108, 843, 752, 503 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{11}$H$_{13}$N$_2$O$_4$) 237.0875, found 237.0871.

Ethyl 2-((4-nitrophenyl)amino)-3-oxo-3-phenylpropanoate (9e):
Yellow color semi-solid (287 mg, 87% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 13.04 (s, 0.2H), 8.18 – 8.05 (m, 4.5H), 7.68 (tt, $J = 2.2$, 1.3 Hz, 1.5H), 7.58 – 7.51 (m, 2H), 7.34 (ddd, $J = 22.8$, 21.3, 10.8 Hz, 0.9H), 6.77 – 6.67 (m, 2H), 6.66 – 6.58 (m, 0.5H), 6.11 (d, $J = 6.9$ Hz, 0.9H), 5.73 (d, $J = 7.0$ Hz, 1H), 5.47 (s, 0.2H), 4.25 (d, $J = 7.1$ Hz, 0.5H), 4.16 (q, $J = 7.1$ Hz, 2H), 1.19 (t, $J = 7.1$ Hz, 0.8H), 1.10 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.39, 172.13, 171.88, 167.09, 153.48, 150.82, 139.56, 139.44, 134.98, 133.61, 132.80, 131.18, 129.39, 129.09, 128.37, 128.18, 126.43, 126.31, 112.37, 102.40, 62.99, 62.55, 61.77, 14.23, 13.92. (More number of proton and carbon peaks are due to the keto-enol tautomerism (4:1)); IR (Film): 3344, 3078, 2984, 2925, 1742, 1710, 1599, 1557, 1507, 1326, 1176, 1112, 1018, 858, 838 cm$^{-1}$; HRMS-ESI (m/z): [M+H]$^+$ calculated (for C$_{17}$H$_{17}$N$_2$O$_5$) 329.1137, found 329.1145.

Ethyl 2-(4-nitrophenyl)-2-((4-nitrophenyl)amino)acetate (9f):
Pale yellow color solid (257 mg, 77% yield); mp 141–143 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.32 – 8.18 (m, 2H), 8.03 (t, J = 6.1 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 6.52 – 6.43 (m, 2H), 5.93 (d, J = 5.0 Hz, 1H), 5.23 (d, J = 5.1 Hz, 1H), 4.34 – 4.14 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 169.40, 150.26, 148.34, 143.54, 139.48, 128.16, 126.37, 124.49, 112.41, 63.32, 59.63, 14.09; IR (Film): 3374, 3081, 2796, 1726, 1603, 1523, 1505, 1482, 1338, 1222, 1197, 1140, 1112, 1003, 855, 836 cm⁻¹; HRMS-ESI (m/z): [M+H]^+ calculated (for C₁₆H₁₆N₅O₆) 346.1039, found 346.1023.

4-((1,3-diethoxy-1,3-dioxopropan-2-yl)amino)benzoic acid (12):
White solid (232 mg, 78% yield); mp 168–170 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 5.36 (d, J = 7.1 Hz, 1H), 4.82 (d, J = 7.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 4H), 1.30 (t, J = 7.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.02, 167.15, 149.91, 132.51, 119.40, 112.49, 62.90, 60.01, 14.17; IR (Film): 3395, 2982, 2831, 2716, 1754, 1731, 1671, 1603, 1491, 1419, 1365, 1231, 1175, 1020, 847 cm⁻¹; HRMS-ESI (m/z): [M+H]^+ calculated (for C₁₄H₁₈NO₆) 296.1134, found 296.1129.

4-((1,3-diethoxy-1,3-dioxopropan-2-yl)amino)-2-hydroxybenzoic acid (13):
White solid (221 mg, 71% yield); mp 172–174 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.63 (s, 1H), 7.71 (d, J = 8.7 Hz, 1H), 6.22 (d, J = 7.6 Hz, 1H), 6.10 (s, 1H), 5.43 (d, J = 6.3 Hz, 1H), 4.78 (d, J = 6.2 Hz, 1H), 4.30 (dd, J = 13.9, 6.9 Hz, 4H), 1.30 (t, J = 7.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 174.59, 166.95, 164.52, 152.59, 132.70, 106.67, 102.32, 98.95, 62.99, 59.73, 14.16; IR (Film): 3388, 2984, 2831, 2542, 1754, 1729, 1628, 1523, 1458, 1365, 1328, 1273, 1210, 1172, 1020, 853 cm⁻¹; HRMS-ESI (m/z): [M+H]^+ calculated (for C₁₄H₁₈NO₇) 312.1083, found 312.1077.
References:

Diethyl 2-(phenylamino)malonate (5a):
Diethyl 2-\((p\text{-}tolylamino)\)malonate (5b):
Diethyl 2-((2,4-dimethylphenyl)amino)malonate (5c):
Diethyl 2-((2,6-diisopropylphenyl)amino)malonate (5d):
Diethyl 2-(mesitylamino)malonate (5c):
Diethyl 2-((3,4-dimethoxyphenyl)amino)malonate (5f):
Diethyl 2-((4-fluorophenyl)amino)malonate (5g):
Diethyl 2-((4-bromophenyl)amino)malonate (5h):
Diethyl 2-((4-iodophenyl)amino)malonate (5i):
Diethyl 2-((4-acetylphenyl)amino)malonate (5j):
Diethyl 2-((2-(trifluoromethyl)phenyl)amino)malonate (5k):
Diethyl 2-((4-cyanophenyl)amino)malonate (5l):
Diethyl 2-((3-nitropheryl)amino)malonate (5m):
Diethyl 2-((2-nitrophenyl)amino)malonate (5n):
Diethyl 2-((2-bromo-4-methylphenyl)amino)malonate (5o):
Diethyl 2-((3-chloro-4-fluorophenyl)amino)malonate (5p):
Diethyl 2-((2,4,5-trichlorophenyl)amino)malonate (5q):
Diethyl 2-((3-chlorophenyl)amino)malonate (5r):
Methyl 2-(4-methoxyphenyl)-2-(phenylamino)acetate (A/D) (6):

N-(bis(4-methoxyphenyl)methyl)aniline (D/D) (7):
Diethyl 2-hydroxymalonate (8):
Diethyl 2-((4-nitrophenyl)amino)malonate (9a):
Dimethyl 2-((4-nitrophenyl)amino)malonate (9b):
Ethyl 2-((4-nitrophenyl)amino)-3-oxobutanoate (9c):
3-((4-nitrophenyl)amino)pentane-2,4-dione (9d):
Ethyl 2-((4-nitrophenyl)amino)-3-oxo-3-phenylpropanoate (9e):
Ethyl 2-(4-nitrophenyl)-2-((4-nitrophenyl)amino)acetate (9f):
4-((1,3-diethoxy-1,3-dioxopropan-2-yl)amino)benzoic acid (12):
4-((1,3-diethoxy-1,3-dioxopropan-2-yl)amino)-2-hydroxybenzoic acid (13):