Microwave-assisted catalyst-free synthesis of tetrasubstituted pyrroles using dialkyl acetylenedicarboxylates and monophenacylaniline

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Experimental Section

General Remarks:

All solvents were purchased from commercial sources and used without further purification. The melting points were measured in open capillary tubes and are uncorrected. A CEM Discover microwave synthesizer (Model No: 908010) operating at 180/264 V and 50/60 Hz with microwave power maximum level of 300 W and microwave frequency of 2455 MHz was employed for the microwave-assisted experiments. Nuclear Magnetic Resonance (^1H and ^{13}C NMR) spectra were recorded on a 300 MHz spectrometer in CDCl_3 using TMS as an internal standard. Chemical shifts are reported in parts per million (δ), coupling constants (J values) are reported in Hertz (Hz) and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quatret), sept (septet), m (multiplet). ^{13}C NMR spectra were routinely run with broadband decoupling. Elemental analyses were performed on a Perkin Elmer 2400Series II Elemental CHNS analyzer.

General procedure for the synthesis of Dimethyl 1,4-diphenyl-1*H*-pyrrole-2,3-dicarboxylate **3**

A mixture of substituted monophenacylaniline **1** (1 mmol), dialkyl acetylenedicarboxylate **2** (1.1 mmol) in DMF (1 mL) was sealed and subjected to microwave irradiation programmed at 110 °C and 110 W for 10 minutes. The completion of the reaction was monitored by TLC. The reaction mixture was extracted with ethyl acetate. The organic layer was washed with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuum. Crude product was purified by column chromatography using petroleum ether – ethyl acetate (5: 95) as the eluent to get **3**.

Characterization data for compounds (3a-3r)

Diethyl 1,4-bis(4-chlorophenyl)-1*H*-pyrrole-2,3-dicarboxylate (3c)

Yellow viscous liquid; IR (neat): 1728, 1698, 1590, 1453 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.44 - 7.34 (m, 6H), 7.31 - 7.27 (m, 2H), 6.94 (s, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 165.6, 159.7, 137.9, 134.5, 133.2, 131.6, 129.1, 129.1, 128.7, 127.5, 125.4, 124.0, 123.8, 122.1, 61.3, 61.0, 14.0, 13.9. Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{Cl}_2\text{NO}_4$: C, 61.13; H, 4.43; N, 3.24 %. Found: C, 61.08; H, 4.47; N, 3.30 %.

Diethyl 4-(4-chlorophenyl)-1-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (3d)

Yellow solid; mp 97 – 100 $^{\circ}\text{C}$; IR (neat): 1730, 1700, 1588, 1454 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.40 – 7.31 (m, 4H), 7.27 – 7.21 (m, 4H), 6.94 (s, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 2.41 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 165.9, 159.9, 138.5, 136.8, 132.9, 131.8, 129.4, 129.1, 128.6, 125.8, 125.5, 123.9, 123.5,

121.2, 61.3, 60.9, 21.1, 14.0, 13.9. Anal. Calcd for C₂₃H₂₂ClNO₄: C, 67.07; H, 5.38; N, 3.40 %.

Found: C, 67.09; H, 5.33; N, 3.43 %. ESI-MS m/z calcd [M+H]⁺ 412.12, found 412.11.

Diethyl 4-(4-bromophenyl)-1-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (3e)

Brown viscous liquid; IR (neat): 3123, 1731, 1703, 1592, 1446 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.21(m, 4H), 6.94 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 166.4, 160.2, 139.0, 137.2, 132.7, 131.9,* 129.9, 129.9, 126.3, 125.9, 123.8, 121.6, 121.5, 61.7, 61.3, 21.6, 14.5, 14.3. Anal. Calcd for C₂₃H₂₂BrNO₄: C, 60.54; H, 4.86; N, 3.07 %. Found: C, 60.51; H, 4.91; N, 3.05 %. *(Two carbon signals merged here)

Diethyl 1-(4-chlorophenyl)-4-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (3f)

White solid; mp 99 – 101 °C; IR (neat): 3130, 1730, 1701, 1511, 1418 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.94 (s, 1H), 4.2 (q, *J* = 7.1 Hz, 2H), 4.2 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 165.8, 159.7, 138.1, 136.9, 134.3, 129.9, 129.2, 129.0,

127.6, 127.5, 125.6, 124.9, 122.7, 122.6, 61.4, 60.8, 21.1, 14.0, 13.9. Anal. Calcd for $C_{23}H_{22}ClNO_4$: C, 67.07; H, 5.38; N, 3.40 %. Found: C, 67.09; H, 5.41; N, 3.36 %.

Diethyl 1-(4-chlorophenyl)-4-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dicarboxylate (3g)

Yellow viscous liquid; IR (neat): 1707, 1611, 1586, 1450 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.30 – 7.24 (m, 2H), 6.91 (m, 3H),* 4.32 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.83 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 159.6, 158.8, 138.0, 134.2, 128.9,* 128.8, 127.5, 125.3, 124.6, 122.7, 122.4, 113.9, 61.3, 60.8, 55.1, 14.0, 13.8. Anal. Calcd for $C_{23}H_{22}ClNO_5$: C, 64.56; H, 5.18; N, 3.27 %. Found: C, 64.60; H, 5.21; N, 3.23 %. *(Two carbon signals merged here).

Diethyl 4-(4-methoxyphenyl)-1-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (3h)

Pale brown solid; mp 62 – 64 $^{\circ}C$; IR (neat): 1706, 1608, 1579 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, $J = 8.7$ Hz, 2H), 7.21 - 7.24 (m, 4H), 6.92 – 6.89 (m, 3H), 4.31 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.83 (s, 3H), 2.41 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H). ^{13}C

NMR (75 MHz, CDCl₃) δ 166.3, 159.9, 158.7, 138.3, 137.0, 129.3, 128.9, 125.9, 125.7, 125.4, 124.3, 123.1, 121.5, 113.8, 61.2, 60.7, 55.2, 21.1, 14.0, 13.9. Anal. Calcd for C₂₄H₂₅NO₅ : C, 70.75; H, 6.18; N, 3.44 %. Found: C, 70.72; H, 6.23; N, 3.47 %.

Diethyl 4-(4-nitrophenyl)-1-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (3i)

Yellow solid; mp 109 – 112 °C; IR (neat): 1721, 1595, 1513, 1338, 1225 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.29 – 7.22 (m, 4H), 7.06 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 165.3, 159.9, 146.7, 140.3, 138.9, 136.6, 130.2, 129.6, 128.4, 125.9, 125.8, 123.7, 122.7, 120.7, 61.4, 61.1, 21.1, 14.0, 13.8. Anal. Calcd for C₂₃H₂₂N₂O₆ : C, 65.40; H, 5.25; N, 6.63 %. Found: C, 65.43; H, 5.20; N, 6.69 %.

Diethyl 1-(2-isopropylphenyl)-4-phenyl-1*H*-pyrrole-2,3-dicarboxylate (3j)

White solid; mp 71 – 73 °C; IR (neat): 3066, 2959, 1708, 1602, 1546 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.50 – 7.47 (m, 4H), 7.41 – 7.36 (m, 2H), 7.32 – 7.20 (m, 3H), 6.91 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.1, 1H), 4.09 (q, *J* = 7.1, 1H), 2.70 (sept, *J* = 6 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 6.0 Hz, 3H), 1.16 (d, *J* = 6.0 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). ¹³C NMR

(75 MHz, CDCl₃) δ 166.4, 159.4, 145.8, 137.6, 133.3, 129.3, 128.5, 127.6, 127.5, 126.9, 126.2, 125.9, 125.8, 124.4, 123.9, 121.6, 61.3, 60.5, 27.8, 24.7, 23.1, 14.0, 13.7. Anal. Calcd for C₂₅H₂₇NO₄ : C, 74.05; H, 6.71; N, 3.45 %. Found: C, 74.01; H, 6.76; N, 3.48

Diethyl 4-(4-chlorophenyl)-1-(3-methoxyphenyl)-1H-pyrrole-2,3-dicarboxylate (3k)

Brown viscous liquid; IR (neat): 1732, 1706, 1612, 1548 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.32 (m, 5H), 6.99 – 6.92 (m, 3H),* 6.89 (m, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 165.7, 159.9, 159.8, 140.3, 133.0, 131.7, 129.6, 129.2, 128.6, 125.3, 124.2, 123.7, 121.1, 118.2, 114.2, 111.9, 61.3, 61.0, 55.4, 14.0, 13.8. Anal. Calcd for C₂₃H₂₂ClNO₅ : C, 64.56; H, 5.18; N, 3.27%. Found: C, 64.61; H, 5.21; N, 3.23 %.

Diethyl 4-(4-chlorophenyl)-1-(naphthalen-1-yl)-1H-pyrrole-2,3-dicarboxylate (3l)

Brown viscous liquid; IR (neat): IR (neat): 1730, 1709, 1593, 1450 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.95 (m, 2H), 7.56 – 7.47 (m, 5H), 7.45 – 7.40 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.05 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.95 (q, *J* = 6Hz, 1H), 3.94 (q, *J* = 6Hz, 1H), 1.34 (d, *J* = 7.1 Hz,

3H), 0.85 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.1, 159.3, 136.5, 133.6, 133.2, 131.8, 130.6, 129.3, 129.0, 128.7, 128.1, 127.5, 126.7, 126.4, 125.1, 124.9, 124.6, 123.6, 122.5, 121.8, 61.4, 60.3, 14.1, 13.2. Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{ClNO}_4$: C, 69.72; H, 4.95; N, 3.13 %. Found: C, 69.76; H, 4.90; N, 3.10 %.

Diethyl 4-(naphthalen-2-yl)-1-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (3m)

Pale yellow solid; mp 89 – 92 °C; IR (neat): 1728, 1704, 1625, 1514 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.92 (s, 1H), 7.85 – 7.81 (m, 3H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.50 – 7.43 (m, 2H), 7.27 (s, 4H), 7.09 (s, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.42 (s, 3H), 1.29 (d, $J = 7.1$ Hz, 3H), 1.18 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.2, 159.8, 138.3, 136.9, 133.4, 132.3, 130.7, 129.3, 127.9, 127.8, 127.5, 126.2, 126.1, 126.0, 125.8, 125.6, 124.4, 121.8, 61.2, 60.7, 21.1, 14.0, 13.8. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_4$: C, 75.86; H, 5.89; N, 3.28 %. Found: C, 75.82; H, 5.86; N, 3.31 %.

Diethyl 1-(4-chlorophenyl)-4-(naphthalen-2-yl)-1*H*-pyrrole-2,3-dicarboxylate (3n)

White solid; mp 118 – 121 °C; IR (neat): 1724, 1707, 1626, 1516 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.91 (s, 1H), 7.86 – 7.80 (m, 4H), 7.60 – 7.56 (m, 1H), 7.49 – 7.47 (m, 1H), 7.46 – 7.42 (m, 2H), 7.35 – 7.33 (m, 1H), 7.32 – 7.30 (m, 1H), 7.08 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 166.1, 159.7, 138.1, 134.5, 133.5, 132.6, 130.5, 129.1, 128.1, 127.9, 127.6,* 126.25, 126.22, 126.20, 125.90, 125.86, 125.0, 123.4, 122.8, 61.4, 61.0, 14.1, 13.9. Anal. Calcd for C₂₆H₂₂ClNO₄ : C, 69.72; H, 4.95; N, 3.13 %. Found: C, 69.65; H, 4.90; N, 3.17 %. *(Two carbon signals merged here)

Diethyl 1-(4-bromophenyl)-4-(naphthalen-1-yl)-1*H*-pyrrole-2,3-dicarboxylate (3o)

White viscous solid; IR (neat): 1726, 1701, 1593, 1442 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.93 (m, 1H), 7.89 – 7.83 (m, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.48 – 7.44 (m, 4H), 7.31 (d, *J* = 8.7 Hz, 2H), 6.95 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 1.22 (d, *J* = 7.1 Hz, 3H), 0.82 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 164.8, 160.3, 138.3, 133.5, 132.6, 132.1, 131.1, 128.1, 127.9, 127.7, 127.5, 126.2, 125.9, 125.7,* 125.1, 124.3, 123.8, 123.1, 122.3, 61.3, 60.7, 13.9, 13.5. Anal. Calcd for : C₂₆H₂₂BrNO₄ C, 63.43; H, 4.50; N, 2.84 %. Found: C, 63.37; H, 4.46; N, 2.87 % (*Two carbon signals merged here).

Diethyl 1-(naphthalen-1-yl)-4-(naphthalen-2-yl)-1*H*-pyrrole-2,3-dicarboxylate (3p)

Pale brown solid; mp 216-218 °C; IR (neat): 1731, 1706, 1625, 1514 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.98 – 7.92 (m, 3H), 7.87 – 7.81 (m, 3H), 7.63 (dd, J = 8.5, 1.7 Hz, 1H), 7.56 – 7.45 (m, 7H), 7.19 (s, 1H), 4.40 (q, J = 7.1 Hz, 2H), 3.97 (q, J = 6Hz, 1H), 3.98 (q, J = 6Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.5, 159.3, 136.6, 133.7, 133.5, 132.4, 130.8, 130.7, 129.2, 128.1, 128.0, 127.9, 127.6, 127.4, 126.9, 126.7, 126.2, 126.1, 126.0, 125.7, 124.9, 124.6, 124.5, 124.5, 122.5, 122.3, 61.5, 60.5, 14.1, 13.5. Anal. Calcd for $\text{C}_{30}\text{H}_{25}\text{NO}_4$: C, 77.74; H, 5.44; N, 3.02 %. Found: C, 77.79; H, 5.41; N, 3.08 %. ESI-MS m/z calcd 463.18, found 463.39.

Diethyl 1-(4-methoxyphenyl)-4-(naphthalen-2-yl)-1H-pyrrole-2,3-dicarboxylate (3q)

White solid; mp 85 – 88 °C; IR (neat): 1708, 1628, 1598, 1458 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.92 (s, 1H), 7.83 (t, J = 7.2 Hz, 3H), 7.59 (dd, J = 8.5, 1.6 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.31 (d, J = 8.8 Hz, 2H), 7.07 (s, 1H), 6.97 (d, J = 8.9 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.2, 159.7, 159.3, 133.3, 132.2, 132.2, 130.6, 127.8, 127.7, 127.4, 127.2, 126.1, 126.1,

126.0, 125.9, 125.6, 124.1, 123.4, 121.7, 113.7, 61.1, 60.6, 55.3, 13.9, 13.8. Anal. Calcd for $C_{27}H_{25}NO_5$: C, 73.12; H, 5.68; N, 3.16 %. Found: C, 73.07; H, 5.71; N, 3.18 %. ESI-MS m/z calcd $[M+H]^+$ 444.17, found 444.07.

Dimethyl 1-(4-chlorophenyl)-4-phenyl-1*H*-pyrrole-2,3-dicarboxylate (3r)¹

Yellow solid; 1H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.41(m, 4H), 7.40 – 7.35 (m, 2H), 7.32 – 7.25 (m, 3H), 6.97 (s, 1H), 3.85 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 160.0, 137.8, 134.3, 132.7, 129.0, 128.5, 127.4, 127.4, 127.2, 125.8, 124.9, 122.7, 122.2, 52.4, 51.9.

Dimethyl 1-(4-bromophenyl)-4-phenyl-1*H*-pyrrole-2,3-dicarboxylate (3s)

Colourless viscous liquid; IR (neat):1707, 1600, 1436 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.7 Hz, 2H), 7.45 – 7.40 (m, 3H), 7.37 – 7.30 (m, 2H), 7.24 (d, J = 8.7 Hz, 2H), 6.98 (s, 1H), 3.85 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 160.2, 138.5, 132.9, 132.1, 128.6, 127.8, 127.7, 127.3, 125.8, 125.2, 123.0, 122.5, 122.4, 52.3, 51.9. Anal. Calcd for $C_{20}H_{16}BrNO_4$: C, 57.99; H, 3.89; N, 3.38 %. Found: C, 57.94; H, 3.92; N, 3.32 %.

Dimethyl 1-(4-chlorophenyl)-4-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (3t)

White solid; mp 101 – 121 °C; IR (neat): 1727, 1699, 1555, 1434 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.42 (d, J = 8.7 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 6.95 (s, 1H), 3.85 (s, 3H), 3.72 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.6, 160.1, 137.9, 137.0, 134.4, 129.8, 129.3,* 129.0, 127.5, 127.4, 125.7, 125.0, 122.3, 52.4, 51.9, 21.1. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{ClNO}_4$: C, 65.71; H, 4.73; N, 3.65 %. Found: C, 65.66; H, 4.77; N, 3.62 %. *(Two carbon signals merged here)

Dimethyl 1,4-bis(4-methoxyphenyl)-1H-pyrrole-2,3-dicarboxylate (3u)

Pale yellow solid; mp 91 – 93 °C; IR (neat): 1723, 1697, 1497 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.37 (d, J = 8.8 Hz, 2H), 7.28 – 7.25 (m, 2H), 6.96 (s, 1H), 6.93 – 6.90 (m, 4H), 3.85 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.7, 160.5, 159.5, 158.9, 132.4, 128.9, 127.3, 125.8, 125.7, 124.4, 123.3, 121.3, 114.0, 113.7, 55.5, 55.3, 52.2, 51.8. Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_6$: C, 66.83; H, 5.35; N, 3.54 %. Found: C, 66.87; H, 5.31; N, 3.57 %.

Fig.1. ¹H NMR spectrum of **3a**

Fig.2. ¹³C NMR spectrum **3a**

Fig.3. ¹H NMR spectrum of **3b**

Fig.4. ¹³C NMR spectrum **3b**

Fig.5. Mass spectrum of **3b**

Fig.6. ¹H NMR spectrum of **3c**

Fig.7. ^{13}C NMR spectrum **3c**

Fig.8. ¹H NMR spectrum of **3d**

Fig.9. ¹³C NMR spectrum **3d**

Fig.10. Mass spectrum of **3d**

Fig.11. ¹H NMR spectrum of **3e**

Fig.12. ¹³C NMR spectrum **3e**

Fig.13. ¹H NMR spectrum of **3f**

Fig.14. ¹³C NMR spectrum **3f**

Fig.15. ¹H NMR spectrum of **3g**

Fig.16. ¹³C NMR spectrum **3g**

Fig.17. ¹H NMR spectrum **3h**

Fig.18. ¹³C NMR spectrum **3h**

Fig.19. Mass spectrum of **3h**

Fig.20. ¹H NMR spectrum **3i**

Fig.21. ¹³C NMR spectrum **3i**

Fig.22. ^1H NMR spectrum **3j**

Fig.23. ¹³C NMR spectrum **3j**

Fig.24. ¹H NMR spectrum **3k**

Fig.25. ¹³C NMR spectrum **3k**

Fig.26. ¹H NMR spectrum **3l**

Fig.27. ^{13}C NMR spectrum **3l**

Fig.28. ¹H NMR spectrum **3m**

Fig.29. ^{13}C NMR spectrum **3m**

Fig.30. ¹H NMR spectrum **3n**

Fig.31. ¹³C NMR spectrum **3n**

Fig.32. ¹H NMR spectrum **30**

Fig.33. ¹³C NMR spectrum **3o**

Fig.34. ¹H NMR spectrum **3p**

Fig.35. ^{13}C NMR spectrum **3p**

Fig.36. Mass spectrum of **3p**

Fig.37. ¹H NMR spectrum **3q**

Fig.38. ^{13}C NMR spectrum **3q**

Fig.39. Mass spectrum of **3q**

Fig.40. ¹H NMR spectrum **3r**

Fig.41. ^{13}C NMR spectrum **3r**

Fig.42. ¹H NMR spectrum **3s**

Fig.43. ¹³C NMR spectrum 3s

Fig.44. ¹H NMR spectrum **3t**

Fig.45. ^{13}C NMR spectrum **3t**

Fig.46. ^1H NMR spectrum **3u**

Fig.47. ¹³C NMR spectrum **3u**

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