Novel Synthesis of Highly Functionalized Pyrazolines and Pyrazoles by Triphenylphosphine Mediated Reaction of Dialkyl Azodicarboxylate with Allenic Esters

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SUPPORTING INFORMATION

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General

All reactions were conducted in oven-dried glassware sealed with rubber septa under a positive pressure of deoxygenated argon from a manifold. Solvents used for the experiments were distilled or dried as specified. Diethyl azodicarboxylate (DEAD), and Diisopropyl azodicarboxylate (DIAD), were purchased from Alfa Aesar and used as received. The allenic esters used for the study are prepared by known procedures.¹ All other reagents were purchased from local suppliers and used without purification. All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (100-200 mesh).

Melting points were recorded on a Buchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 (¹H) and 75 (¹³C) MHz respectively on a Bruker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (¹H) or CDCl₃ (¹³C) as internal standards. IR spectra were recorded on Bomem MB series FT-IR spectrometer; absorbencies are reported in cm⁻¹. High resolution mass spectra were recorded under EI / HRMS (at 5000 resolution) using JOEL JMS 600 H Mass Spectrometer. Elemental analyses were performed on a Perkin Elmer-2400 elemental analyzer.

General Procedure for the Preparation of Functionalized Pyrazoles (7a-7e)

To a stirred solution of allenolate **6a-6e** (0.53mmol) in anhydrous THF (5 mL) under an atmosphere of Ar, was added diethyl azodicarboxylate (114mg, 0.64mmol) and the reaction mixture was stirred under reflux. To the refluxing solution was added triphenylphosphine (167 mg, 0.64mmol). The reaction mixture was kept stirring under reflux for 5 h. The reaction mixture cooled, Solvent was removed on a rotavap, residue column chromatographed on silica gel using 3% ethyl acetate-petroleum ether as eluent to afford the corresponding product (**7a-7e**)

Exocyclic pyrazole derivative **7a**

The colorless oil obtained after column chromatography is dissolved in dichloromethane and crystallized from Dichloromethane-Petroleum ether.

Colorless crys talline solid Mp 82-84°C

IR (KBr) ν_{max} : 2985, 1738, 1712, 1660, 1630, 1604, 1521, 1434, 1346, 1238, 1109 cm⁻¹.

¹H NMR δ : 1.28 (t, J = 7.2 Hz, 6H), 1.38 (t, J = 7.2 Hz, 3H), 3.30 (d, J = 13.5 Hz, 1H), 3.45 (d, J = 13.8 Hz, 1H), 4.14-4.36 (m, 6H), 4.77 (s, 1H), 5.73 (bs, 1H), 7.32 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.7 Hz, 2H),

¹³C NMR δ : 13.9, 14.2, 14.5, 40.1, 62.3, 62.4, 62.5, 66.1, 93.6, 123.3, 130.9, 142.1, 143.6, 147.4, 151.2, 160.9, 167.5.

Elemental Analysis: calcd. For C₁₉H₂₃N₃O₇, C, 56.29, H, 5.72, N, 10.37. Found C, 55.75, H, 5.91, N, 10.16.

Single crystal X-ray data: Crystal structure of compound **7a** has been deposited at the Cambridge Crystallographic Data Center and allocated the reference no. CCDC **298290**.

Single crystal X-ray structure of 7a **Packing diagram of 7a:**

Packing diagram viewed down b-axis showing the C-H...O interaction between the methyl and methylene hydrogens with oxygen of carboxy group creating two hydrogen bonded two dimensional networks (Figure 1).

Figure 1

It is interesting to note that oxygen atoms of carboethoxy group attached to the five membered ring is involved in strong intermolecular H-bonding interaction with the methylene hydrogen along c-axis and methyl hydrogen along a-axis creating a two dimensional hydrogen bonded supramolecular network along ac-plane. Close up view of this H-bonded assembly, involving four molecules engaged in H-bonding network is depicted in Figure 2. The various H-bonding network with symmetry code is as follows (C(13)-H(13B)...O(6): H13...O6= 2.56 Å; C13...O6= 3.505(9)Å ; < C(13)-H(13B)...O(6)= 168° symmetry code=1+x,y,z and C(19)-H(19B)...O(3): H(19B)...O(3)= 2.59 Å; C(19)...O(3)= 3.456(6) Å ; < C(19)-H(19B)...O(3)= 155°, symmetry code=-x,-y,-z

Close up view of hydrogen bonding pattern in 7a

Exocyclic pyrazole derivative **7b**

Colorless Oil

IR (film) ν_{max} : 2987, 2934, 1747, 1713, 1664, 1630, 1494, 1435, 1382, 1343, 1309, 1241, 1177, 1100 cm^{-1} .

^1H NMR δ : 1.27 (t, J = 7.2 Hz, 6H), 1.36 (t, J = 6.9 Hz, 3H), 3.16 (d, J = 13.8 Hz, 1H), 3.31 (d, J = 13.8 Hz, 1H), 4.12-4.26 (m, 6H), 4.74 (s, 1H), 5.70 (bs, 1H), 7.07 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H),

^{13}C NMR δ : 13.9, 14.2, 14.5, 39.8, 62.1, 62.3, 62.6, 65.8, 93.4, 128.4, 131.3, 132.0, 132.9, 133.4, 143.9, 151.3, 161.5, 167.9.

HRMS for $\text{C}_{19}\text{H}_{23}\text{ClN}_2\text{O}_5$: calcd. (M^+): 394.1295, found: 394.1280.

Exocyclic pyrazole derivative **7c**

Colorless Oil

IR (film) ν_{max} : 2988, 2365, 1741, 1722, 1631, 1511, 1439, 1382, 1348, 1286, 1224 cm^{-1} .

^1H NMR δ : 1.24-1.29 (m, 6H), 1.36 (t, J = 6.9 Hz, 3H), 3.17 (d, J = 13.8 Hz, 1H), 3.32 (d, J = 13.8 Hz, 1H), 4.12-4.33 (m, 6H), 4.74 (s, 1H), 5.70 (bs, 1H), 6.89 (d, J = 8.7 Hz, 2H), 7.08-7.13 (m, 2H).

^{13}C NMR δ : 13.9, 14.2, 14.5, 39.7, 62.1, 62.2, 65.7, 93.3, 114.9, 115.2, 130.1, 131.4, 131.5, 143.9, 151.5, 161.5, 167.7.

HRMS for $\text{C}_{19}\text{H}_{23}\text{FN}_2\text{O}_5$: calcd. (M^+): 378.1591, found: 378.1598.

Exocyclic pyrazole derivative **7d**

Colorless Oil

IR (film) ν_{max} : 2987, 1815, 1747, 1717, 1664, 1615, 1518, 1445, 1377, 1333, 1250, 1177, 1109 cm^{-1} .

^1H NMR δ : 1.26-1.39 (m, 9H), 3.15 (d, $J = 13.8$ Hz, 1H), 3.28 (d, $J = 14.1$ Hz, 1H), 3.75 (s, 3H), 4.17-4.31 (m, 6H), 4.74 (s, 1H), 5.69 (bs, 1H), 6.72 (d, $J = 8.4$ Hz, 2H), 7.05 (d, $J = 8.7$ Hz, 2H),

^{13}C NMR δ : 13.4, 13.9, 14.3, 39.8, 55.0, 62.1, 62.7, 64.1, 65.7, 93.3, 113.6, 126.4, 131.0, 145.5, 150.1, 158.8, 168.8.

HRMS for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_6$: calcd. (M^+): 390.1791, found: 390.1790

Exocyclic pyrazole derivative **7e**

Colorless Oil

IR (film) ν_{max} : 3018, 2983, 2401, 1737, 1708, 1658, 1629, 1516, 1469, 1379, 1309, 1226, 1132, 1045 cm^{-1} .

^1H NMR δ : 1.24-1.29 (m, 6H), 1.36 (t, $J = 7.1$ Hz, 3H), 3.20 (d, $J = 13.7$ Hz, 1H), 3.34 (d, $J = 13.7$ Hz, 1H), 4.08-4.34 (m, 6H), 4.76 (s, 1H), 5.70 (bs, 1H), 7.11-7.21 (m, 5H).

^{13}C NMR δ : 13.9, 14.1, 14.5, 39.2, 62.1, 62.8, 63.4, 65.7, 93.3, 127.3, 128.1, 129.5, 130.5, 134.4, 144.0, 151.3, 161.8, 168.1.

HRMS for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_5$: calcd. (M^+): 360.1685, found: 360.1684.

General Procedure for the Preparation of Functionalized Pyrazoles (**7f-7n**)

To a stirred solution of allenolate **6a-6i** (0.53mmol) in anhydrous THF (5 mL) under an atmosphere of Ar, was added diisopropyl azodicarboxylate (136mg, 0.64mmol) and the reaction mixture was stirred under reflux. To the refluxing solution was added triphenylphosphine (167 mg, 0.64mmol). The reaction mixture was kept stirring under reflux for 5 h. The reaction mixture cooled, Solvent was removed on a rotavap, residue column chromatographed on silica gel using 3% ethyl acetate-petroleum ether as eluent to afford the corresponding product (**7f-7n**)

Exocyclic pyrazole derivative **7f**

Colorless oil

IR (film) ν_{max} : 2985, 1738, 1712, 1655, 1624, 1604, 1521, 1429, 1341, 1243, 1176, 1104 cm^{-1} .

^1H NMR δ : 1.23-1.33 (m, 15H), 3.27 (d, $J = 13.5$ Hz, 1H), 3.42 (d, $J = 13.8$ Hz, 1H), 4.18 (m, 1H), 4.31 (m, 1H), 4.73 (s, 1H), 4.92-5.10 (m, 2H), 5.64 (bs, 1H), 7.35 (d, $J = 7.8$ Hz, 2H), 8.09 (d, $J = 8.4$ Hz, 2H),

^{13}C NMR δ : 13.9, 21.3, 21.5, 21.9, 22.0, 40.3, 62.4, 65.9, 70.1, 73.6, 93.3, 123.2, 131.0, 142.2, 143.8, 147.4, 150.9, 160.8, 167.1.

HRMS for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_7$: calcd. (M^+): 433.1849, found: 433.1835.

Exocyclic pyrazole derivative **7g**

Colorless oil

IR (film) ν_{max} : 2982, 2934, 1737, 1703, 1654, 1630, 1494, 1426, 1372, 1338, 1250, 1105 cm^{-1} .

^1H NMR δ : 1.29-1.39 (m, 15H), 3.17 (d, $J = 13.8$ Hz, 1H), 3.28 (d, $J = 13.5$ Hz, 1H), 4.15 (m, 1H), 4.30 (m, 1H), 4.70 (s, 1H), 4.92-5.11 (m, 2H), 5.60 (bs, 1H), 7.09 (d, $J = 7.8$ Hz, 2H), 7.16 (d, $J = 8.1$ Hz, 2H),

^{13}C NMR δ : 13.9, 21.2, 21.4, 21.8, 21.9, 39.9, 62.1, 65.6, 69.8, 73.2, 93.1, 128.1, 128.2, 131.3, 131.5, 132.9, 133.2, 143.9, 144.2, 151.0, 167.4, 168.1.

HRMS for $\text{C}_{21}\text{H}_{27}\text{ClN}_2\text{O}_5$: calcd. (M^+): 422.1608, found: 422.1613

Exocyclic pyrazole derivative **7h**

Colorless oil

IR (film) ν_{max} : 2981, 2360, 1737, 1712, 1666, 1629, 1512, 1448, 1429, 1377, 1311, 1244, 1180, 1105 cm^{-1} .

^1H NMR δ : 1.22-1.35 (m, 15H), 3.14 (d, $J = 13.8$ Hz, 1H), 3.27 (d, $J = 13.9$ Hz, 1H), 4.15-4.18 (m, 1H), 4.27-4.29 (m, 1H), 4.70 (s, 1H), 4.93-5.07 (m, 2H), 5.60 (bs, 1H), 6.86-6.91 (m, 2H), 7.08-7.13 (m, 2H).

^{13}C NMR δ : 14.3, 21.3, 21.5, 21.8, 22.0, 39.9, 62.1, 65.6, 69.8, 73.2, 93.1, 114.7, 114.8, 115.0, 130.2, 131.6, 131.8, 143.5, 150.8, 160.6, 167.5.

HRMS for $\text{C}_{21}\text{H}_{27}\text{FN}_2\text{O}_5$: calcd. (M^+): 406.1904, found: 406.1872

Exocyclic pyrazole derivative **7i**

Colorless oil

IR (film) $\tilde{\nu}_{\text{max}}$: 2982, 2939, 1810, 1742, 1703, 1654, 1615, 1513, 1426, 1372, 1304, 1245, 1177, 1095 cm^{-1} .

^1H NMR δ : 1.26-1.44 (m, 15H), 3.15 (d, $J = 13.8$ Hz, 1H), 3.25 (d, $J = 13.8$ Hz, 1H), 3.74 (s, 3H), 4.16 (m, 1H), 4.27 (m, 1H), 4.70 (s, 1H), 4.94-5.01 (m, 2H), 5.58 (bs, 1H), 6.71 (d, $J = 8.4$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 2H),

^{13}C NMR δ : 13.9, 21.1, 21.4, 21.7, 21.9, 39.4, 54.9, 61.9, 65.5, 69.7, 72.4, 92.9, 113.3, 113.4, 126.4, 130.9, 131.1, 145.7, 150.3, 158.7, 167.8.

HRMS for $\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_6$: calcd. (M^+): 418.2104, found: 418.2107

Exocyclic pyrazole derivative **7j**

Colorless oil

IR (film) ν_{max} : 2988, 2940, 2360, 1751, 1722, 1631, 1511, 1454, 1382, 1276, 1104 cm^{-1} .

^1H NMR δ : 1.26-1.37 (m, 15H), 3.20 (d, $J = 13.8$ Hz, 1H), 3.33 (d, $J = 13.8$ Hz, 1H), 4.15 (m, 1H), 4.29 (m, 1H), 4.70 (s, 1H), 4.90-5.05 (m, 2H), 5.59 (bs, 1H), 7.13-7.18 (m, 5H).

^{13}C NMR δ : 14.2, 21.3, 21.5, 21.8, 22.0, 40.7, 62.6, 65.5, 69.7, 72.6, 93.0, 127.2, 127.9, 128.1, 129.9, 130.2, 148.3, 161.5, 167.4.

HRMS for $\text{C}_{21}\text{H}_{28}\text{N}_2\text{O}_5$: calcd. (M^+): 388.1998, found: 388.2022.

Exocyclic pyrazole derivative **7k**

The colorless oil obtained after column chromatography after crystallization using n-decane afforded the colorless crystalline compound.

Colorless crystalline compound Mp 70-72°C

IR (film) ν_{max} : 3020, 2981, 2401, 1734, 1708, 1658, 1627, 1516, 1467, 1427, 1381, 1309, 1219, 1143, 1074 cm^{-1} .

^1H NMR δ : 1.22-1.37 (m, 15H), 3.37 (d, $J = 13.7$ Hz, 1H), 3.47 (d, $J = 13.9$ Hz, 1H), 4.21-4.24 (m, 1H), 4.25-4.29 (m, 1H), 4.81 (s, 1H), 4.85-5.09 (m, 2H), 5.72 (bs, 1H), 7.29 (m, 1H), 7.39-7.41 (m, 2H), 7.60-7.76 (m, 4H).

^{13}C NMR δ : 14.3, 21.1, 21.4, 21.8, 40.7, 62.0, 65.5, 69.7, 73.1, 93.1, 125.6, 126.1, 127.5, 127.8, 128.2, 128.9, 129.2, 132.1, 132.6, 133.1, 144.5, 151.1, 161.7, 167.6.

HRMS for $\text{C}_{25}\text{H}_{30}\text{N}_2\text{O}_5$: calcd. (M^+): 438.2155, found: 438.2147.

Single crystal X-ray data: Crystal structure of compound **7k** has been deposited at the Cambridge Crystallographic Data Center and allocated the reference no. CCDC **298292**. The H atoms and disordered positions of C_{19} and C_{20} are omitted for clarity.

Figure 3. Single crystal X-ray structure of 7k

Exocyclic pyrazole derivative **7m**

Colorless oil

IR (film) ν_{max} : 2988, 2935, 1747, 1718, 1660, 1631, 1531, 1430, 1377, 1353, 1248, 1100 cm^{-1} .

^1H NMR δ : 1.26-1.36 (m, 15H), 3.26 (d, $J = 13.7$ Hz, 1H), 3.44 (d, $J = 13.7$ Hz, 1H), 4.21 (m, 1H), 4.29 (m, 1H), 4.75 (s, 1H), 4.94-5.09 (m, 2H), 5.72 (bs, 1H), 7.40-7.51 (m, 2H), 8.03-8.11 (m, 2H).

^{13}C NMR δ : 14.2, 21.2, 21.5, 21.8, 21.9, 40.2, 62.8, 66.0, 70.2, 73.8, 93.3, 122.4, 124.9, 125.1, 128.9, 136.3, 136.7, 143.8, 148.0, 161.0, 167.1.

HRMS for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_7$: calcd. (M^+): 433.1849, found: 433.1854.

Exocyclic pyrazole derivative **7n**

Colorless oil

IR (film) ν_{max} : 2981, 1741, 1710, 1662, 1629, 1467, 1429, 1373, 1340, 1311, 1282, 1209, 1105 cm^{-1} .

^1H NMR δ : 1.24-1.39 (m, 15H), 3.12 (d, $J = 13.7$ Hz, 1H), 3.27 (d, $J = 13.7$ Hz, 1H), 4.16-4.21 (m, 1H), 4.27-4.30 (m, 1H), 4.71 (s, 1H), 4.96-5.07 (m, 2H), 5.68 (bs, 1H), 6.97-7.04 (m, 1H), 7.25-7.29 (m, 2H),

^{13}C NMR δ : 14.3, 21.2, 21.4, 21.8, 22.0, 39.8, 62.3, 65.8, 70.1, 73.5, 93.2, 129.3, 129.9, 130.1, 131.5, 132.2, 134.8, 144.0, 151.0, 161.2, 167.2.

HRMS for $\text{C}_{21}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_5$: calcd. (M^+): 456.1219, found: 456.0896

General Procedure for the Preparation of Fully Substituted Pyrazoles (**12a-12f**)

To a stirred solution of allenoate **11** (0.53mmol) in anhydrous DME (5 mL) under an atmosphere of Ar, was added DEAD / DIAD (111mg / 136mg, 0.64mmol) followed by the addition of triphenylphosphine (167 mg, 0.64mmol). The reaction mixture was kept stirring at rt for 3 h. Solvent was removed on a rotavap, residue column chromatographed on silica gel using 5% ethyl acetate-petroleum ether as eluent to afford the corresponding product (**12a-12f**)

Fully substituted pyrazole derivative **12a**

White crystalline solid Mp. 100-102 °C

IR (KBr) ν_{max} : 2985, 1753, 1702, 1588, 1511, 1459, 1382, 1264, 1104 cm^{-1} .

^1H NMR δ : 1.28 (d, $J = 6.3$ Hz, 12H), 1.41 (t, $J = 6.3$ Hz, 3H), 4.39. (q, $J = 7.2$ Hz, 2H), 4.74 (s, 2H), 5.07-5.18 (m, 2H), 7.09-7.23 (m, 5H).

^{13}C NMR δ : 14.5, 21.5, 21.8, 22.0, 31.8, 65.0, 67.9, 72.8, 105.6, 126.2, 128.0, 128.1, 128.3, 137.5, 149.1, 150.9, 161.9, 162.3.

Elemental Analysis: calcd. For $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_5$, C, 64.15, H, 7.00, N, 7.48. Found C, 64.30, H, 7.13, N, 7.52.

Single crystal X-ray data: Crystal structure of compound **12a** has been deposited at the Cambridge Crystallographic Data Center and allocated the reference no. CCDC **298291**.

Single crystal X-ray structure of **12a**

Fully substituted pyrazole derivative **12b**

Colorless crystalline solid Mp. 82-84 °C.

IR (KBr) ν_{max} : 2985, 1753, 1702, 1583, 1511, 1454, 1377, 1269, 1182, 1089, 1027 cm^{-1} .

^1H NMR δ : 1.29-1.34 (m, 6H), 1.45 (t, $J = 7.1$ Hz, 3H), 4.20-4.43 (m, 6H), 4.76 (s, 2H), 7.14-7.49 (m, 5H).

^{13}C NMR δ : 14.0, 14.2, 14.5, 31.6, 60.3, 64.2, 65.0, 104.6, 126.2, 127.9, 128.2, 128.3, 137.2, 149.4, 151.9, 162.1, 162.3

HRMS for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_5$: calcd. (M^+): 346.1529, found: 346.1526.

Fully substituted pyrazole derivative **12c**

Colorless crystalline solid Mp. 55-57°C

IR (KBr) ν_{max} : 2979, 1753, 1707, 1588, 1511, 1465, 1382, 1284, 1243, 1197, 1094, 1022 cm^{-1} .

^1H NMR δ : 1.24 (t, $J = 7.3$ Hz, 3H), 1.34-1.46 (m, 9H), 3.32 (q, $J = 7.3$ Hz, 2H), 4.27-4.40 (m, 4H), 4.47 (q, $J = 7.1$ Hz, 2H).

^{13}C NMR δ : 13.2, 14.2, 14.5, 20.2, 60.1, 64.2, 64.9, 118.8, 149.7, 156.4, 162.2, 162.3.

HRMS for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_5$: calcd. (M^+): 284.1372, found: 284.1372.

Fully substituted pyrazole derivative **12d**

Colorless crystalline solid Mp. 64-66 °C

IR (KBr) ν_{max} : 2979, 2835, 1753, 1707, 1583, 1506, 1459, 1377, 1269, 1176, 1089, 1032 cm^{-1} .

^1H NMR δ : 1.28-1.37 (m, 6H), 1.45 (t, $J = 6.9$ Hz, 3H), 3.75 (m, 3H), 4.23-4.42 (m, 6H), 4.68 (s, 2H), 6.76 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H),

^{13}C NMR δ : 14.1, 14.2, 14.6, 30.7, 55.1, 60.4, 64.3, 65.1, 114.1, 127.7, 129.3, 130.3, 149.6, 152.5, 158.1, 162.2, 162.5.

HRMS for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_6$: calcd. (M^+): 376.1634, found: 376.1693.

Fully substituted pyrazole derivative **12e**

viscous oil

IR (KBr) ν_{max} : 2979, 1748, 1702, 1588, 1511, 1470, 1382, 1279, 1238, 1197, 1094 cm^{-1} .

^1H NMR δ : 1.24 (t, $J = 7.2$ Hz, 3H), 1.33 (d, $J = 6.2$ Hz, 6H), 1.40-1.46 (m, 9H), 3.29 (q, $J = 7.2$ Hz, 2H), 4.36 (q, $J = 6.9$ Hz, 2H), 5.13-5.25 (m, 2H).

^{13}C NMR δ : 13.6, 14.8, 20.6, 21.8, 22.0, 22.2, 65.1, 70.2, 72.7, 118.4, 149.5, 155.8, 162.1, 162.5.

HRMS for $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_5$: calcd. (M^+): 312.1685, found: 312.1696.

Fully substituted pyrazole derivative **12f**

White crystalline solid Mp. 104-106 °C

IR (KBr) $\tilde{\nu}_{\text{max}}$: 2976, 1748, 1702, 1583, 1511, 1454, 1377, 1274, 1176, 1099, 1017 cm^{-1} .

^1H NMR δ : 1.27-1.32 (m, 12H), 1.45 (t, $J = 6.9$ Hz, 3H), 4.38 (q, $J = 7.2$ Hz, 2H), 4.69. (s, 2H), 5.06-5.21 (m, 2H), 7.08 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H),

^{13}C NMR δ : 14.5, 21.5, 21.8, 31.1, 65.0, 68.1, 72.9, 104.9, 128.3, 129.4, 135.8, 149.0, 150.5, 161.8, 162.2.

HRMS for $\text{C}_{20}\text{H}_{25}\text{ClN}_2\text{O}_5$: calcd. (M^+):408.1454, found: 408.1463.

References

1. (a) Zhu, X. F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716. (b) Lang, R. W., Hansen, H. J. *Organic Synthesis Coll. Vol. 7*, p.232.

Current Data Parameters
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 PROCNO 1

F2 - Acquisition Parameters
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 RG 2048
 DW 27.600 usec
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===== CHANNEL f2 =====
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 PL12 17.23 dB
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F2 - Processing parameters
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Current Data Parameters
 NAME saumini
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date 20051025
 Time 17.07
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zg30
 TD 22468
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 7812.500 Hz
 FIDRES 0.347717 Hz
 AQ 1.4380020 sec
 RG 90.5
 DW 64.000 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 11.00 usec
 PL1 0.00 dB
 SFO1 300.1318008 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300055 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

Current Data Parameters
 NAME sauminil3C
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date 20051028
 Time 10.24
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zgdc
 TD 32768
 SOLVENT CDCl3
 NS 162
 DS 0
 SWH 18115.941 Hz
 FIDRES 0.552855 Hz
 AQ 0.9044468 sec
 RG 2896.3
 DW 27.600 usec
 DE 9.00 usec
 TE 0.0 K
 D1 3.00000000 sec
 d11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWRRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 12.50 usec
 PL1 -6.00 dB
 SFO1 75.4760204 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 17.23 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677497 MHz
 WDW EM
 SSB 0

Current Data Parameters
 NAME saumini
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050903
 Time_ 16.29
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zg30
 TD 22468
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 7812.500 Hz
 FIDRES 0.347717 Hz
 AQ 1.4380020 sec
 RG 90.5
 DW 64.000 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 11.00 usec
 PL1 0.00 dB
 SFO1 300.1318008 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300055 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 5.00

Current Data Parameters
 NAME sauminil3C
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050906
 Time_ 10.30
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zgdc
 TD 32768
 SOLVENT cdcl3
 NS 305
 DS 0
 SWH 18115.941 Hz
 FIDRES 0.552855 Hz
 AQ 0.9044468 sec
 RG 6502
 DW 27.600 usec
 DE 9.00 usec
 TE 0.0 K
 D1 3.00000000 sec
 d11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 12.50 usec
 PL1 -6.00 dB
 SFO1 75.4760204 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 17.23 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677475 MHz
 WDW EM
 SSB 0
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Current Data Parameters
 NAME saumini
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050928
 Time 17.08
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zg30
 TD 22468
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 7812.500 Hz
 FIDRES 0.347717 Hz
 AQ 1.4380020 sec
 RG 64
 DW 64.000 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 11.00 usec
 PL1 0.00 dB
 SFO1 300.1318008 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300045 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

Current Data Parameters
 NAME saumini13C
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051020
 Time_ 12.42
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zgdc
 TD 32768
 SOLVENT CDC13
 NS 200
 DS 0
 SWH 18115.941 Hz
 FIDRES 0.552855 Hz
 AQ 0.9044468 sec
 RG 2298.8
 DW 27.600 usec
 DE 9.00 usec
 TE 0.0 K
 D1 3.00000000 sec
 d11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 12.50 usec
 PL1 -6.00 dB
 SFO1 75.4760204 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 17.23 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677492 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

Current Data Parameters
 NAME saumini
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051018
 Time_ 12.20
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zg30
 TD 22468
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 7812.500 Hz
 FIDRES 0.347717 Hz
 AQ 1.4380020 sec
 RG 143.7
 DW 64.000 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 11.00 usec
 PL1 0.00 dB
 SFO1 300.1318008 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300083 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 5.00

S45

Current Data Parameters
 NAME Instrumalai13c
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050623
 Time 16.20
 INSTRUM dpx300
 PTD80 5 mm Multinu
 PULPROG zgpg
 TD 32768
 SOLVENT CDCl3
 NS 164
 DS 0
 SWH 18115.941 Hz
 FIDRES 0.552895 Hz
 AQ 0.9044468 sec
 RG 1149.4
 DW 27.600 usec
 DE 9.43 usec
 TE 300.0 K
 D11 0.03000000 sec
 PL12 17.20 dB
 CPOPRG2 waltz16
 PCPD2 80.00 usec
 SF02 300.1312700 MHz
 NUC2 1H
 PL2 120.00 dB
 D1 10.00000000 sec
 P1 12.50 usec
 SF01 75.4760204 MHz
 NUC1 13C
 PL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 75.4677470 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 208.509 ppm
 F1 15735.70 Hz
 F2P -4.488 ppm
 F2 -336.68 Hz
 FWHM 10.64983 ppm/cm
 HZCM 803.71899 Hz/cm

Current Data Parameters
 NAME Thirumalai13C
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050630
 Time 12.53
 INSTRUM dpv300
 PROBHD 5 mm Multinu
 PULPROG zgpgc
 TO 32768
 SOLVENT CDCl3
 NS 829
 DS 0
 SMH 18115.941 Hz
 FIDRES 0.562855 Hz
 AQ 0.9044468 sec
 RG 2580.3
 DW 27.600 usec
 DE 9.43 usec
 TE 300.0 K
 D11 0.03000000 sec
 PL12 17.20 dB
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 SF02 300.1312700 MHz
 NUC2 1H
 PL2 120.00 dB
 D1 3.00000000 sec
 P1 12.50 usec
 SF01 75.4760204 MHz
 NUC1 13C
 PL1 -6.00 dB

F2 - Processing parameters
 SI 16384
 SF 75.4677531 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

3D NMR plot parameters
 CX 20.00 cm
 F1P 229.573 ppm
 F1 17320.35 Hz
 F2P -10.476 ppm
 F2 -790.59 Hz
 PPMM 12.00244 ppm/cm
 HZCM 905.79712 Hz/cm

Current Data Parameters
 NAME saumini13C
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050922
 Time_ 8.38
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zgdc
 TD 32768
 SOLVENT CDCl3
 NS 10965
 DS 0
 SWH 18115.941 Hz
 FIDRES 0.552855 Hz
 AQ 0.9044468 sec
 RG 2048
 DW 27.600 usec
 DE 9.00 usec
 TE 0.0 K
 D1 3.00000000 sec
 d11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 12.50 usec
 PL1 -6.00 dB
 SFO1 75.4760204 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 17.23 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677313 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1 50

Current Data Parameters
 NAME Thirumalai13C
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051103
 Time_ 10.41
 INSTRUM spect
 PROBHD 5 mm Dual 13C/
 PULPROG zgdc
 TD 32768
 SOLVENT CDC13
 NS 891
 DS 0
 SWH 18115.941 Hz
 FIDRES 0.552855 Hz
 AQ 0.9044468 sec
 RG 3649.1
 DW 27.600 usec
 DE 9.00 usec
 TE 0.0 K
 D1 3.00000000 sec
 d11 0.03000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 12.50 usec
 PL1 -6.00 dB
 SFO1 75.4760204 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 17.23 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677541 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00