Supporting Information

Unexpected ring opening of pyrazolines with activated alkynes: Synthesis of 1*H*-pyrazole-4,5-dicarboxylates and chromenopyrazolecarboxylates†

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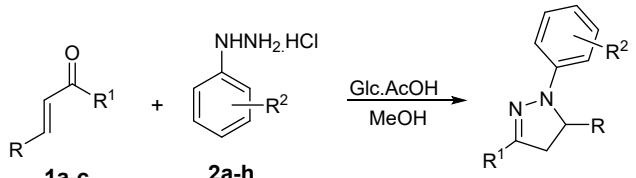
1. General information

Salicylaldehydes, alkynes and TBHP were procured from Sigma-Aldrich. Benzaldehydes, acetophenones, phenylhydrazines, acetic acid, $Cu(OAc)_2$ and solvents were procured from the local suppliers. All the reactions were monitored by thin layer chromatography (TLC) on pre-coated silica gel 60 F254 (mesh); spots were visualized under UV light. Melting points were determined in open glass capillary tubes on a Stuart melting point apparatus and are uncorrected. Merck silica gel (60-120 mesh) was used for column chromatography. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on an Avance 300, 400, 500 MHz spectrometers in $CDCl_3$, DMSO-d_6 using TMS as internal standard. FT-IR spectra were recorded on Nicollet Nexus 670 FT spectrometer. ESI-MS obtained on quarto micro spectrometer. HRMS were measured on Agilent Technologies 6510, Q-TOFLC/MS ESI-Technique.

2. General procedure for the preparation of pyrazolines (3a-o): Glacial acetic acid (0.12 mL, 1.0 equiv.) was added to a stirred solution of (*E*)-4-phenylbut-3-en-2-one (**1a**, 0.300 g, 1.0 equiv.) and phenylhydrazine hydrochloride (**2a**, 0.355 g, 1.2 equiv.) in anhydrous methanol (5 mL) at room temperature. The reaction mixture was stirred at 60 ^{o}C (Oil bath) and monitored by TLC. After completion of the reaction (TLC, 3 h), the solvent was removed under reduced pressure and the reaction mixture was subjected for the column chromatography purification using silica gel (60:120, ethyl acetate/hexane 2:98) afforded the 3-methyl-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole **3a** (0.46 g) as pale yellow solid in 90% yield. The pyrazolines **3b-e** were prepared from 4-phenylbut-3-en-2-one **1a** with substituted phenylhydrazine hydrochlorides **2a-e** under above optimized conditions.

Another set of pyrazoline compounds **3f-o** were prepared from but-3-en-2-one **1b,** chalcone **1c**, with substituted phenylhydrazine hydrochlorides **2a-h** under above optimized conditions. The prepared pyrazolines **3a-o** are known and compared with the literature data.[1]

Structures of pyrazolines (3a-o):[1]



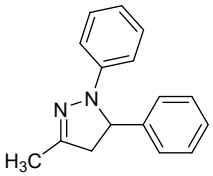
1a-c

1a R = Ph, R^1 = CH_3
1b R = H, R^1 = CH_3
1c R = Ph, R^1 = Ph

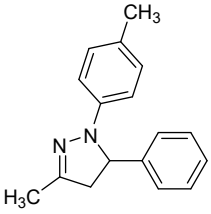
2a-h

2a R^2= H
2b R^2 = 4-CH_3
2c R^2 = 4-OCH_3
2d R^2 = 4-Cl
2e R^2 = 4-Br
2f R^2 = 2-CH_3
2g R^2 = 3-Cl
2h R^2 = 3-Br

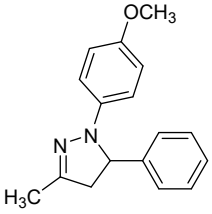
3a-o



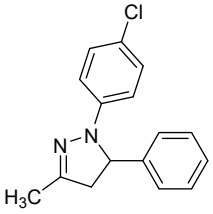
3a, 91%



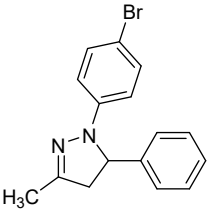
3b, 92%



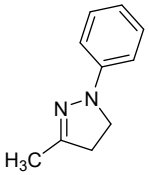
3c, 94%



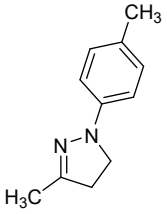
3d, 93%



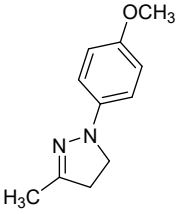
3e, 86%



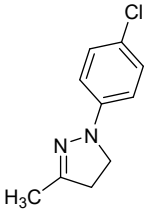
3f, 68%



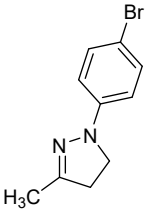
3g, 70%



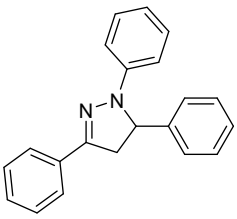
3h, 71%



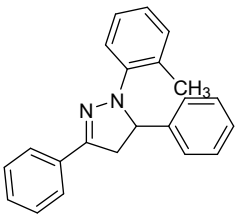
3i, 83%



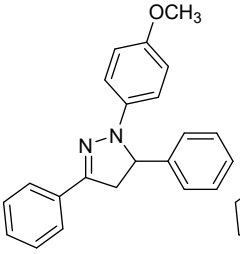
3j, 74%



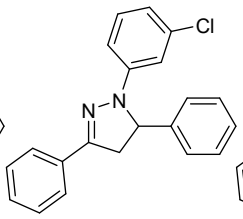
3k, 90%



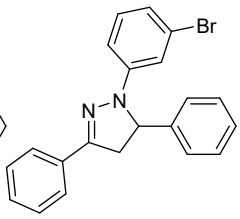
3l, 92%



3m, 72%



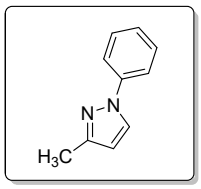
3n, 69%



3o, 76%

3. General procedure for the preparation of 1*H*-pyrazole (3fa):[1] $Cu(OAc)_2$ (0.011 g, 10 mol%) was added to a stirred solution of 4,5-dihydro-1*H*-pyrazole (**3f**, 0.1 g, 1.0 equiv.) in acetonitrile (4 mL) at room temperature. TBHP (70% solution, 0.28 mL, 5.0 equiv.) was added to the reaction mixture simultaneously. The reaction mixture was monitored by TLC and after completion of the reaction (TLC, 10 min), the solvent was removed under reduced pressure. The product was purified by column chromatography using silica gel (60:120, ethyl acetate/hexane 2:98) afforded 1*H*-pyrazole **3fa** (0.09 g) as colourless solid in 95% yield.

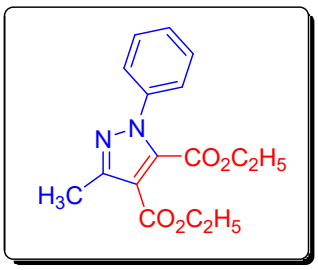
3-Methyl-1-phenyl-1*H*-pyrazole (3fa):



^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 2.2 Hz, 1H, aromatic), 7.57 (dd, J = 8.6, 1.0 Hz, 2H, aromatic), 7.35 (dd, J = 8.4, 7.6 Hz, 2H, aromatic), 7.18 (d, J = 8.3 Hz, 1H, aromatic), 6.17 (d, J = 2.2 Hz, 1H, aromatic), 2.31 (s, 3H, CH_3) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ 150.95, 138.79, 131.29, 129.46, 127.32, 119.89, 107.97, 13.77 ppm.

4. General procedure for the preparation of 1*H*-pyrazole-4,5-dicarboxylates (5a-t): 3-Methyl-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3a**, 0.100 g, 1.0 equiv.) and diethyl but-2-ynedioate (**4a**, 0.075 g, 1.0 equiv.) were heated at 120 °C. The reaction mixture was monitored by TLC and after completion of reaction (TLC, 28 h), the residue was purified by column chromatography by using silica gel (60:120, ethyl acetate/hexane 3:97) afforded diethyl 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dicarboxylate **5a** (0.087 g) as pale yellow solid in 69% yield. The other pyrazoledicarboxylates **5b-t** were prepared from pyrazolines **3b-o** with activated alkynes **4a-b** under above optimized conditions.

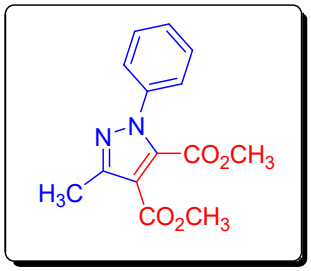
Diethyl 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dicarboxylate (5a):



Yield: 69% (89 mg), pale yellow solid; M.P: 216-218 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J = 7.2 Hz, 2H, aromatic), 7.47-7.38 (m, 3H, aromatic), 4.34-4.27 (m, 4H, $2OCH_2$), 2.53 (s, 3H, CH_3), 1.34 (t, J = 7.1 Hz, 3H, CH_3), 1.23 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.46, 161.11, 151.09, 138.82, 137.85, 129.13, 128.63, 123.79,

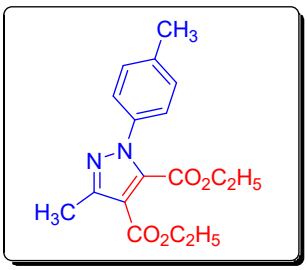
113.01, 62.44, 60.40, 14.09, 13.65, 13.33 ppm. FT-IR (KBr): 2952, 1733, 1499, 1266 cm^{-1}. MS-ESI: (*m/z*) 303 $[M+H]^+$; HRMS-ESI: calcd for $C_{16}H_{19}N_2O_4$ $[M+H]^+$ 303.1345; found 303.1347.

Dimethyl 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dicarboxylate (5b):



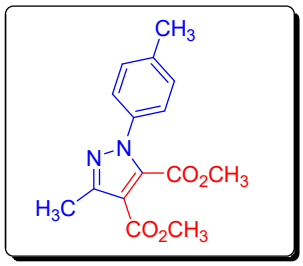
Yield: 86% (100 mg), pale yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 6.8 Hz, 2H, aromatic), 7.46-7.39 (m, 3H, aromatic), 3.85 (s, 6H, $2OCH_3$), 2.53 (s, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.98, 161.68, 151.15, 138.81, 137.63, 129.28, 128.74, 123.68, 113.10, 53.25, 51.69, 13.42 ppm. FT-IR (KBr): 1777, 1714, 1304, 1215 cm^{-1}. MS-ESI: (*m/z*) 275 $[M+H]^+$; HRMS-ESI: calcd for $C_{14}H_{15}N_2O_4$ $[M+H]^+$ 275.1032; found 275.1032.

Diethyl 3-methyl-1-*p*-tolyl-1*H*-pyrazole-4,5-dicarboxylate (5c):



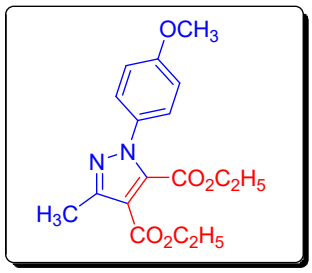
Yield: 78% (99 mg), pale yellow solid; M.P: 251-253 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.4 Hz, 2H, aromatic), 7.23 (d, J = 8.1 Hz, 2H, aromatic), 4.31 (qd, J = 7.1, 2.1 Hz, 4H, $2OCH_2$), 2.52 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 1.34 (t, J = 7.1 Hz, 3H, CH_3), 1.24 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.47, 161.17, 150.86, 138.66, 137.77, 136.37, 129.63, 123.60, 112.71, 62.35, 60.31, 20.97, 14.07, 13.66, 13.29 ppm. FT-IR (KBr): 2959, 1734, 1501, 1266 cm^{-1}. MS-ESI: (*m/z*) 317 $[M+H]^+$; HRMS-ESI: calcd for $C_{17}H_{21}N_2O_4$ $[M+H]^+$ 317.1501; found 317.1502.

Dimethyl 3-methyl-1-*p*-tolyl-1*H*-pyrazole-4,5-dicarboxylate (5d):



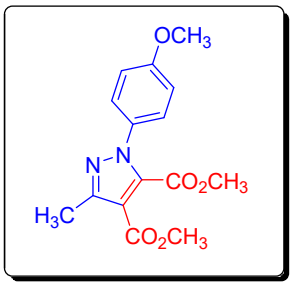
Yield: 84% (97 mg), pale yellow solid; M.P: 179-182 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 8.4 Hz, 2H, aromatic), 7.24 (d, J = 8.0 Hz, 2H, aromatic), 3.85 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 2.52 (s, 3H, CH_3), 2.39 (s, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.06, 161.80, 151.00, 138.89, 137.64, 136.44, 129.87, 123.58, 112.89, 53.26, 51.69, 21.12, 13.45 ppm. FT-IR (KBr): 2983, 1764, 1717, 1254, 1221, 1100, 762 cm^{-1}. MS-ESI: (*m/z*) 289 $[M+H]^+$; HRMS-ESI: calcd for $C_{15}H_{17}N_2O_4$ $[M+H]^+$ 289.1188; found 289.1190.

Diethyl 1-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylate (5e):



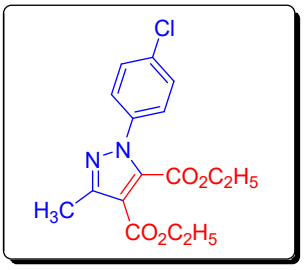
Yield: 75% (94 mg), pale yellow solid; M.P: 278-280 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, J = 8.9 Hz, 2H, aromatic), 6.94 (d, J = 8.9 Hz, 2H, aromatic), 4.30 (qd, J = 7.1, 3.3 Hz, 4H, $2OCH_2$), 3.84 (s, 3H, OCH_3), 2.52 (s, 3H, CH_3), 1.34 (t, J = 7.1 Hz, 3H, CH_3), 1.24 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ 162.63, 161.24, 159.80, 150.87, 138.03, 132.02, 125.54, 114.29, 112.66, 62.47, 60.45, 55.54, 14.22, 13.84, 13.40 ppm. FT-IR (KBr): 2962, 1739, 1699, 1266, 1213 cm^{-1}. MS-ESI: (*m/z*) 333 $[M+H]^+$; HRMS-ESI: calcd for $C_{17}H_{21}N_2O_5$ $[M+H]^+$ 333.1450; found 333.1455.

Dimethyl 1-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylate (5f):



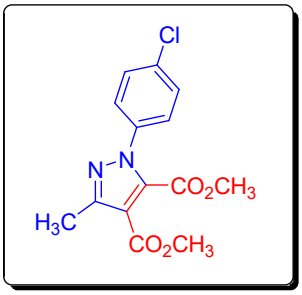
Yield: 78% (89 mg), pale yellow solid; M.P: 206-208 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 9.0 Hz, 2H, aromatic), 6.86 (d, J = 9.0 Hz, 2H, aromatic), 3.76 (s, 6H, $2OCH_3$), 3.75 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.09, 161.73, 159.82, 150.87, 137.74, 131.94, 125.39, 114.38, 112.70, 55.54, 53.25, 51.69, 13.43 ppm. FT-IR (KBr): 2983, 1778, 1717, 1254, 1221, 1210, 1100, 762 cm^{-1}. MS-ESI: (*m/z*) 305 $[M+H]^+$; HRMS-ESI: calcd for $C_{15}H_{17}N_2O_5$ $[M+H]^+$ 305.1137; found 305.1142.

Diethyl 1-(4-chlorophenyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylate (5g):



Yield: 71% (88 mg), pale yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.8 Hz, 2H, aromatic), 7.30 (d, J = 8.8 Hz, 2H, aromatic), 4.27-4.21 (m, 4H, $2OCH_2$), 2.44 (s, 3H, CH_3), 1.26 (t, J = 7.1 Hz, 3H, CH_3), 1.19 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.44, 161.08, 151.44, 137.87, 137.45, 134.60, 129.43, 125.14, 113.56, 62.74, 60.63, 14.22, 13.84, 13.42 ppm. FT-IR (KBr): 2862, 1785, 1491, 1268 cm^{-1}. MS-ESI: (*m/z*) 337 $[M+H]^+$; HRMS-ESI: calcd for $C_{16}H_{18}N_2O_4Cl$ $[M+H]^+$ 337.0955; found 337.0958.

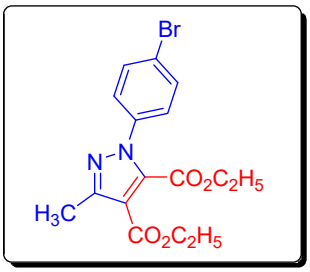
Dimethyl 1-(4-chlorophenyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylate (5h):



Yield: 79% (90 mg), pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 4H, aromatic), 3.87 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 2.51 (s, 3H, CH_3) ppm. ^{13}C NMR (101

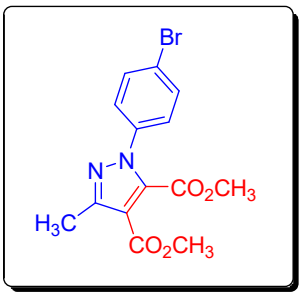
MHz, $CDCl_3$): δ 162.79, 161.45, 151.33, 137.52, 137.28, 134.57, 129.43, 124.92, 113.49, 53.33, 51.73, 13.36 ppm. FT-IR (KBr): 1751, 1725, 1712, 1223, 1100, 763 cm^{-1}. MS-ESI: (*m/z*) 309 $[M+H]^+$; HRMS-ESI: calcd for $C_{14}H_{14}N_2O_4Cl$ $[M+H]^+$ 309.0642; found 309.0645.

Diethyl 1-(4-bromophenyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylate (5i):



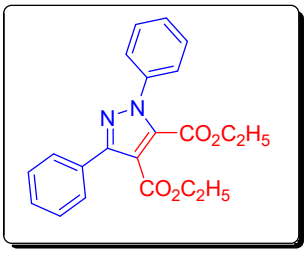
Yield: 79% (96 mg), pale yellow solid; M.P: 196-198 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.8 Hz, 2H, aromatic), 7.30 (d, J = 8.8 Hz, 2H, aromatic), 4.27-4.21 (m, 4H, $2OCH_2$), 2.44 (s, 3H, CH_3), 1.26 (t, J = 7.1 Hz, 3H, CH_3), 1.19 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.40, 161.07, 151.46, 137.94, 137.81, 132.40, 125.35, 122.53, 113.60, 62.75, 60.63, 14.22, 13.84, 13.42 ppm. FT-IR (KBr): 2960, 1734, 1489, 1279 cm^{-1}. MS-ESI: (*m/z*) 381 $[M+H]^+$; HRMS-ESI: calcd for $C_{16}H_{18}N_2O_4Br$ $[M+H]^+$ 381.0450; found 381.0451.

Dimethyl 1-(4-bromophenyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylate (5j):



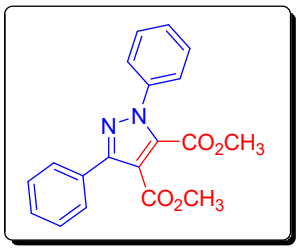
Yield: 69% (78 mg), pale yellow solid; M.P: 136-138 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 8.8 Hz, 2H, aromatic), 7.36 (d, J = 8.8 Hz, 2H, aromatic), 3.87 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 2.51 (s, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.84, 161.51, 151.43, 137.82, 137.53, 32.46, 125.20, 122.60, 113.59, 53.40, 51.79, 13.41 ppm. FT-IR (KBr): 2952, 1769, 1743, 1496, 1263, 1041 cm^{-1}. MS-ESI: (*m/z*) 353 $[M+H]^+$; HRMS-ESI: calcd for $C_{14}H_{14}N_2O_4Br$ $[M+H]^+$ 353.0137; found 353.0138.

Diethyl 1,3-diphenyl-1*H*-pyrazole-4,5-dicarboxylate (5k):



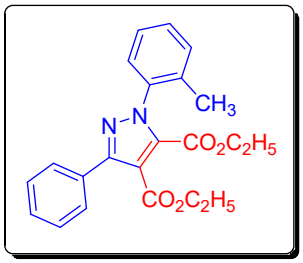
Yield: 72% (88 mg), pale yellow solid; M.P: 52-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 1.7 Hz, 2H, aromatic), 7.53 (d, J = 1.5 Hz, 2H, aromatic), 7.50-7.39 (m, 6H, aromatic), 4.30 (qd, J = 7.1, 3.3 Hz, 4H, $2OCH_2$), 1.27 (t, J = 7.1 Hz, 3H, CH_3), 1.24 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.98, 160.19, 151.99, 139.20, 137.11, 131.50, 129.18, 129.12, 128.89, 128.74, 128.15, 124.79, 114.37, 62.45, 61.19, 14.02, 13.82 ppm. FT-IR (KBr): 1716, 1702, 1523, 1489, 1440, 1261, 1227, 1143, 1099, 1011 cm^{-1}. MS-ESI: (*m/z*) 365 $[M+H]^+$; HRMS-ESI: calcd for $C_{21}H_{21}N_2O_4$ $[M+H]^+$ 365.1501; found 365.1498.

Dimethyl 1,3-diphenyl-1*H*-pyrazole-4,5-dicarboxylate (5l):



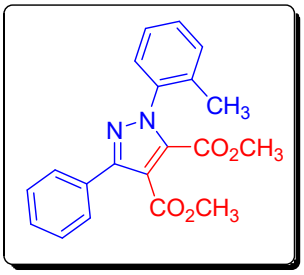
Yield: 74% (83 mg), Colourless solid; M.P: 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H, aromatic), 7.53 (d, J = 1.5 Hz, 2H, aromatic), 7.51-7.45 (m, 3H, aromatic), 7.45- 7.39 (m, 3H, aromatic), 3.86 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.16, 169.27, 143.66, 143.54, 131.09, 129.23, 129.03, 128.58, 126.31, 120.33, 113.30, 65.82, 55.67, 53.23, 53.11 ppm. FT-IR (KBr): 1728, 1725, 1522, 1489, 1442, 1265, 1227, 1150, 1098, 1019 cm^{-1}. MS-ESI: (*m/z*) 337 $[M+H]^+$; HRMS-ESI: calcd for $C_{19}H_{17}N_2O_4$ $[M+H]^+$ 337.1188; found 337.1186.

Diethyl 2-phenyl-1-(*o*-tolyl)-1*H*-pyrazole-4,5-dicarboxylate (5m):



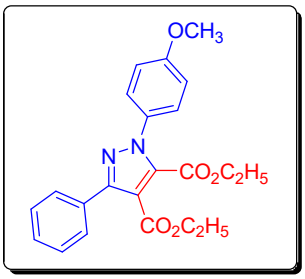
Yield: 82% (100 mg), pale yellow solid; M.P: 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 1.5 Hz, 2H, aromatic), 7.40 (ddd, J = 10.1, 7.0, 3.9 Hz, 4H, aromatic), 7.34 (s, 1H, aromatic), 7.32-7.27 (m, 2H, aromatic), 4.34 (q, J = 7.1 Hz, 2H, OCH_2), 4.19 (q, J = 7.1 Hz, 2H, OCH_2), 2.17 (s, 3H, CH_3), 1.30 (t, J = 7.1 Hz, 3H, CH_3), 1.12 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.61, 159.12, 151.10, 138.53, 137.04, 135.82, 131.53, 130.85, 129.93, 128.81, 128.51, 128.26, 127.35, 126.39, 114.34, 61.98, 61.39, 17.42, 14.04, 13.71 ppm. FT-IR (KBr): 1714, 1705, 1587, 1479, 1450, 1211, 1237, 1150, 1098, 1012, cm^{-1}. MS-ESI: (*m/z*) 379 $[M+H]^+$; HRMS-ESI: calcd for $C_{22}H_{23}N_2O_4$ $[M+H]^+$ 379.1658; found 379.1653.

Dimethyl 2-methyl-1-*o*-tolyl-1*H*-pyrazole-4,5-dicarboxylate (5n):



Yield: 75% (84 mg), pale yellow solid; M.P: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.9 Hz, 2H, aromatic), 7.46-7.36 (m, 4H, aromatic), 7.34 (s, 1H, aromatic), 7.30 (d, J = 0.7 Hz, 2H, aromatic), 3.86 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 2.16 (s, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.13, 159.55, 151.03, 138.33, 136.53, 135.67, 131.33, 130.92, 129.98, 128.88, 128.74, 128.36, 127.19, 126.44, 114.14, 52.88, 52.42, 17.40 ppm. FT-IR (KBr): 1730, 1725, 1532, 1499, 1432, 1256, 1232, 1148, 1088, 1020 cm^{-1}. MS-ESI: (*m/z*) 351 $[M+H]^+$; HRMS-ESI: calcd for $C_{20}H_{19}N_2O_4$ $[M+H]^+$ 351.1345; found 351.1344.

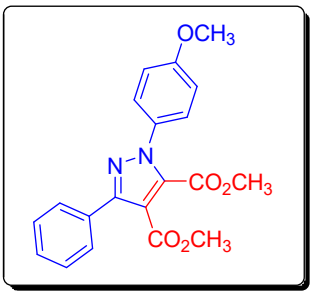
Diethyl 1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazole-4,5-dicarboxylate (5o):



Yield: 69% (83 mg), pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H, aromatic), 7.45 (d, J = 9.0 Hz, 2H, aromatic), 7.44-7.38 (m, 3H, aromatic), 6.97 (d, J = 9.0 Hz, 2H, aromatic), 4.30 (qd, J = 7.1, 3.2 Hz, 4H, $2OCH_2$), 3.85 (s, 3H, OCH_3), 1.29-1.23 (t, 6H, $2CH_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.09, 160.17, 160.03, 151.63, 137.05,

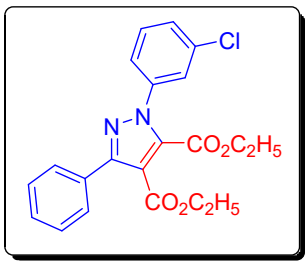
132.25, 131.57, 128.84, 128.78, 128.13, 126.33, 114.20, 114.04, 62.35, 61.14 55.61, 14.02, 13.89 ppm. FT-IR (KBr): 2925, 1775, 1358, 1275, 1223, 1210, 1156, 780 cm^{-1}. MS-ESI: (*m/z*) 395 $[M+H]^+$; HRMS-ESI: calcd for $C_{22}H_{23}N_2O_5$ $[M+H]^+$ 395.1600; found 395.1600.

Dimethyl 1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazole-4,5-dicarboxylate (5p):



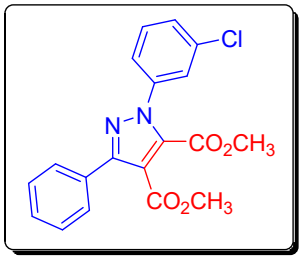
Yield: 73% (82 mg), pale yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 5.9 Hz, 2H, aromatic), 7.43 (s, 2H, aromatic), 7.41 (m, 3H, aromatic), 6.97 (d, J = 8.9 Hz, 2H, aromatic), 3.84 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.56, 160.69, 160.06, 151.71, 136.86, 132.13, 131.47, 128.88, 128.79, 128.22, 126.16, 114.29, 113.89, 55.60, 53.14, 52.19 ppm. FT-IR (KBr): 2935, 1780, 1305, 1254, 1265, 1290, 1145 cm^{-1}. MS-ESI: (*m/z*) 367 $[M+H]^+$; HRMS-ESI: calcd for $C_{20}H_{19}N_2O_5$ $[M+H]^+$ 367.1325; found 367.1324.

Diethyl 1-(3-chlorophenyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylate (5q):



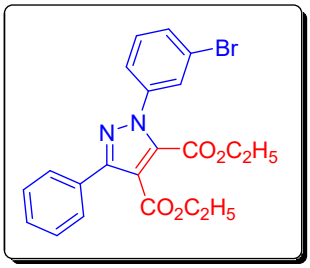
Yield: 70% (85 mg), pale yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (ddd, J = 8.2, 5.5, 3.0 Hz, 2H, aromatic), 7.60 (dd, J = 2.5, 1.4 Hz, 1H, aromatic), 7.45-7.40 (m, 6H, aromatic), 4.35 (q, J = 7.1 Hz, 2H, OCH_2), 4.30 (q, J = 7.1 Hz, 2H, OCH_2), 1.29 (t, J = 7.1 Hz, 3H, CH_3), 1.27 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.84, 159.90, 152.22, 140.07, 136.95, 134.84, 131.23, 130.12, 129.20, 129.04, 128.81, 128.23, 125.13, 122.86, 115.00, 62.65, 61.33, 14.01, 13.87 ppm. FT-IR (KBr): 1715, 1744, 1568, 1470, 1340, 1311, 1247, 1120, 1078, 1024, 749, 692 cm^{-1}. MS-ESI: (*m/z*) 399 $[M+H]^+$; HRMS-ESI: calcd for $C_{21}H_{20}N_2O_4Cl$ $[M+H]^+$ 399.1112; found 399.1109.

Dimethyl 1-(3-chlorophenyl)-3-phenyl-1*H*-pyrazole-4,5-dicarboxylate (5r):



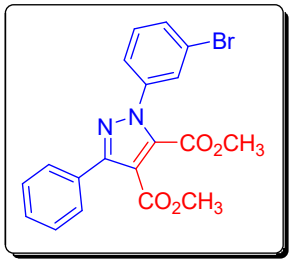
Yield: 64% (71 mg), pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 1.8 Hz, 2H, aromatic), 7.60 (d, J = 0.9 Hz, 1H, aromatic), 7.45-7.40 (m, 6H, aromatic), 3.89 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.31, 160.38, 152.25, 139.96, 136.67, 134.97, 131.10, 130.13, 129.29, 129.11, 128.73, 128.30, 125.10, 122.67, 114.81, 53.31, 52.31 ppm. FT-IR (KBr): 1736, 1719, 1529, 1479, 1453, 1268, 1223, 1156, 1098, 1019, 789, 757, 688 cm^{-1}. MS-ESI: (*m/z*) 371 $[M+H]^+$; HRMS-ESI: calcd for $C_{19}H_{16}N_2O_4Cl$ $[M+H]^+$ 371.0799; found 371.0795.

Diethyl 1-(3-bromophenyl)-3-phenyl-1*H*-pyrazole-4,5-dicarboxylate (5s):



Yield: 65% (76 mg), pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 1.9 Hz, 2H, aromatic), 7.73 (s, 1H, aromatic), 7.58 (ddd, J = 8.0, 1.7, 0.9 Hz, 1H, aromatic), 7.49 (ddd, J = 8.1, 2.0, 0.9 Hz, 1H, aromatic), 7.42 (dt, J = 6.9, 2.0 Hz, 3H, aromatic), 7.34 (t, J = 8.0 Hz, 1H, aromatic), 4.35 (q, J = 7.1 Hz, 2H, OCH_2), 4.30 (q, J = 7.1 Hz, 2H, OCH_2), 1.30 (t, J = 7.1 Hz, 3H, CH_3), 1.27 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.79, 158.83, 151.18, 139.09, 135.88, 131.07, 130.15, 129.30, 127.99, 127.75, 127.18, 126.90, 122.29, 121.49, 113.95, 61.61, 60.28, 12.96, 12.84 ppm. FT-IR (KBr): 1720, 1709, 1577, 1468, 1444, 1221, 1247, 1152, 1091, 1055 cm^{-1}. MS-ESI: (*m/z*) 443 $[M+H]^+$; HRMS-ESI: calcd for $C_{21}H_{20}N_2O_4Br$ $[M+H]^+$ 443.0606; found 443.0602.

Dimethyl 1-(3-bromophenyl)-3-phenyl-1*H*-pyrazole-4,5-dicarboxylate (5t):



Yield: 80% (88 mg), pale yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 3.8 Hz, 2H, aromatic), 7.72 (d, J = 1.7 Hz, 1H, aromatic), 7.59 (ddd, J = 8.0, 1.8, 1.0 Hz, 1H, aromatic), 7.49-7.40 (m, 4H, aromatic), 7.35 (t, J = 8.0 Hz, 1H, aromatic), 3.89 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.30, 160.36, 152.25, 140.03, 136.65, 132.20, 131.08, 130.35, 129.11, 128.72, 128.30, 127.93, 123.13, 122.66, 114.81, 53.30, 52.31 ppm. FT-IR (KBr): 1721, 1730, 1529, 1496, 1451, 1266, 1268, 1152, 1099, 1010, 786, 758, 689 cm^{-1}. MS-ESI: (*m/z*) 415 $[M+H]^+$; HRMS-ESI: calcd for $C_{19}H_{16}N_2O_4Br$ $[M+H]^+$ 415.0293; found 415.0291.

5. Gram-scale synthesis of pyrazoledicarboxylates (5b, 5m & 5t):

a) Preparation of 5b: 3-Methyl-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (**3a**, 1.0 g, 1.0 equiv.) and dimethyl but-2-ynedioate (**4b**, 0.600 g, 1.0 equiv.) were heated at 120 °C. The column chromatography purification afforded dimethyl 3-methyl-1-phenyl-1*H*-pyrazole-4,5-dicarboxylate **5a** (0.96 g) as pale yellow liquid in 82% yield.

b) Preparation of 5m: 3,5-Diphenyl-1-*o*-tolyl-4,5-dihydro-1*H*-pyrazole (**3l**, 1.0 g, 1.0 equiv.) and diethyl but-2-ynedioate (**4a**, 0.544 g, 1.0 equiv.) were heated at 120 °C. The column chromatography purification afforded diethyl 3-phenyl-1-*o*-tolyl-1*H*-pyrazole-4,5-dicarboxylate **5m** (0.97 g) as pale yellow solid in 80% yield.

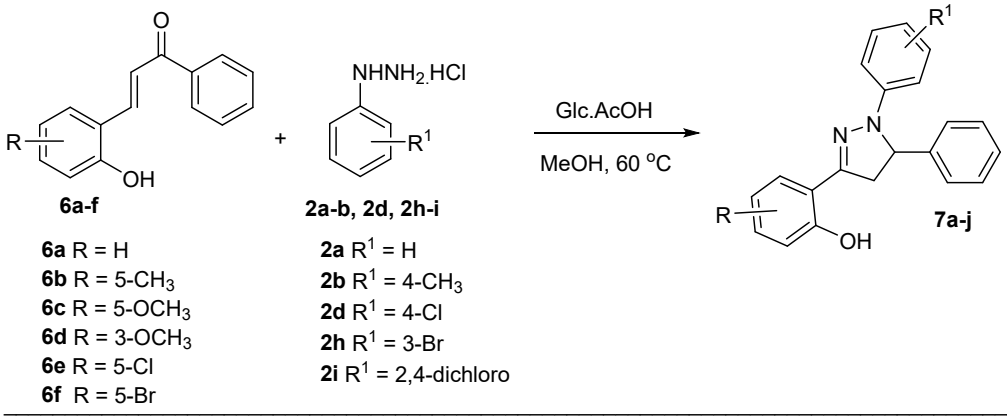
c) Preparation of 5t: 1-(3-bromophenyl)-3,5-Diphenyl-4,5-dihydro-1*H*-pyrazole (**3o**, 1.0 g, 1.0 equiv.) and dimethyl but-2-ynedioate (**4b**, 0.376 g, 1.0 equiv.) were heated at 120 °C. The column chromatography purification afforded dimethyl 1-(3-bromophenyl)-3-phenyl-1*H*-pyrazole-4,5-dicarboxylate **5t** (0.84 g) as pale yellow liquid in 78% yield.

6. General procedure for the preparation of 2-(1,5-diphenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenol (7a-j): Glacial acetic acid (0.12 mL, 1.0 equiv.) was added to a stirred solution of (*E*)-3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one (**6a**, 0.200 g, 1.0 equiv.) and phenylhydrazine hydrochloride (**2a**, 0.154 g, 1.2 equiv.) in anhydrous methanol (5 mL) at room temperature. The reaction mixture was stirred at 60 °C (Oil bath) and the reaction was monitored by TLC. After completion of the reaction (5 h), the solvent was removed under

reduced pressure and the reaction mixture was subjected for the column chromatography purification using silica gel (60:120, ethyl acetate/hexane 2:98) afforded the 2-(1,5-diphenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenol **7a** (0.205 g) as colourless solid in 73% yield.

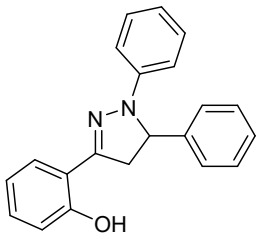
The compounds **7b-j** were prepared from substituted 2-hydroxychalcones **6a-f** with **2a** and **6a** with **2b**, **2d**, **2h-i** under above optimized conditions. The known pyrazolines **7a-e**, **7g** are compared with the reported data and unknown compounds **7f**, **7h-j** are characterized by spectral data and depicted below.

Structures of substituted 2-(1,5-diphenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenols (7a-e, 7g):

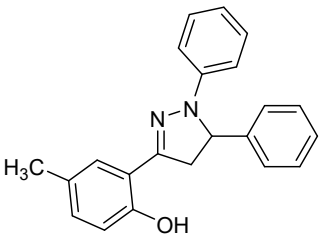


6a R = H
6b R = 5-CH_3
6c R = 5-OCH_3
6d R = 3-OCH_3
6e R = 5-Cl
6f R = 5-Br

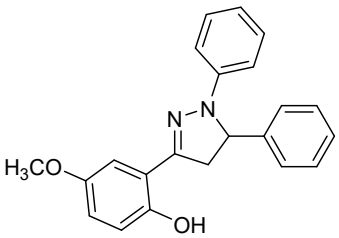
2a R^1 = H
2b R^1 = 4-CH_3
2d R^1 = 4-Cl
2h R^1 = 3-Br
2i R^1 = 2,4-dichloro



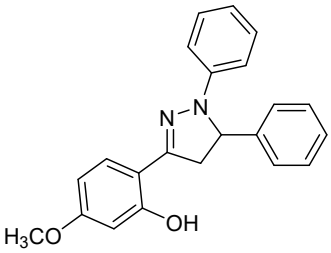
(**7a**, 73%)[2]



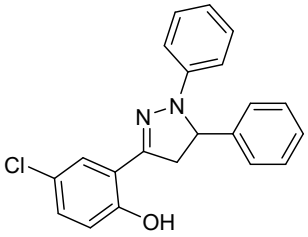
(**7b**, 67%)[3]



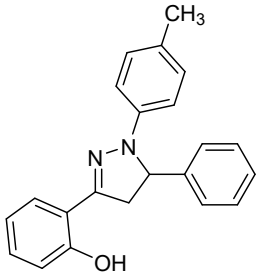
(**7c**, 67%)[5]



(**7d**, 71%)[3]

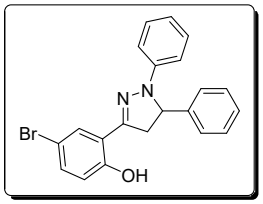


(**7e**, 79%)[3]



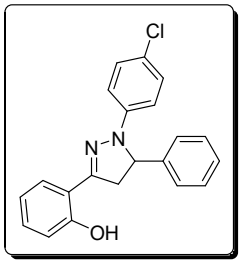
(**7g**, 71%)[4]

4-Bromo-2-(1,5-diphenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenol (7f):



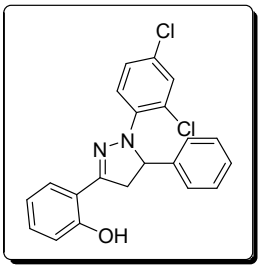
Yield: 71% (180 mg), pale yellow solid; M.P: 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, J = 7.9, 1.7 Hz, 2H, aromatic), 7.44-7.39 (m, 2H, aromatic), 7.39 (s, 1H, aromatic), 7.19 (ddd, J = 9.5, 7.2, 5.4 Hz, 2H, aromatic), 7.14 (d, J = 7.2 Hz, 2H, aromatic), 7.11 (d, J = 9.1 Hz, 2H, aromatic), 6.93-6.85 (m, 2H, aromatic), 5.18 (t, J = 10.8 Hz, 1H, CH), 3.81 (dd, J = 17.1, 11.6 Hz, 1H, CH), 3.25 (dd, J = 17.1, 10.1 Hz, 1H, CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.57, 141.08, 131.31, 130.19, 129.36, 129.14, 128.71, 128.26, 126.98, 125.91, 123.62, 123.12, 119.98, 116.98, 67.01, 40.73 ppm. FT-IR (KBr): 3452, 2380, 1724, 1588, 1495, 1318, 1099, 1033, 984, 758 cm^{-1}. MS-ESI: (*m/z*) 393 $[M+H]^+$; HRMS-ESI: calcd for $C_{21}H_{18}BrN_2O$ $[M+H]^+$ 393.0132; found 393.0129.

2-(1,5-diphenyl-4,5-dihydro-1*H*-pyrazol-3-yl)-5-Methoxyphenol (7h):



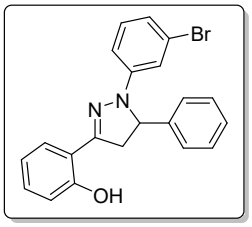
Yield: 79% (213 mg), pale yellow solid; M.P: 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 2H, aromatic), 7.45-7.38 (m, 3H, aromatic), 7.21 (ddd, J = 9.5, 7.2, 5.4 Hz, 2H, aromatic), 7.16 (d, J = 7.2 Hz, 2H, aromatic), 7.13 (d, J = 9.1 Hz, 2H, aromatic), 6.95-6.87 (m, 2H, aromatic), 5.20 (t, J = 10.8 Hz, 1H, CH), 3.83 (dd, J = 17.1, 11.6 Hz, 1H, CH), 3.27 (dd, J = 17.1, 10.1 Hz, 1H, CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.30, 140.76, 130.97, 130.35, 129.89, 129.05, 127.93, 126.66, 125.59, 123.33, 122.70, 119.65, 116.72, 115.34, 103.97, 66.87, 40.40 ppm. FT-IR (KBr): 3466, 2395, 1724, 1588, 1495, 1318, 1243, 1033, 984, 757 cm^{-1}. MS-ESI: (*m/z*) 349 $[M+H]^+$; HRMS-ESI: calcd for $C_{21}H_{18}ClN_2O$ $[M+H]^+$ 349.1106; found 349.1102.

2-(1-(2,4-dichlorophenyl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)Phenol (7i):



Yield: 62% (212 mg), colourless solid; M.P: 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.69 (m, 2H, aromatic), 7.41 (dd, J = 5.1, 1.8 Hz, 3H, aromatic), 7.37 (d, J = 2.3 Hz, 1H, aromatic), 7.24 (d, J = 8.7 Hz, 1H, aromatic), 7.16 (ddd, J = 11.0, 8.3, 2.0 Hz, 2H, aromatic), 7.08 (dd, J = 7.5, 1.6 Hz, 1H, aromatic), 6.87-6.79 (m, 2H, aromatic), 5.36 (t, J = 11.1 Hz, 1H, CH), 3.67 (dd, J = 16.6, 10.6 Hz, 1H, CH), 3.42 (dd, J = 16.6, 11.6 Hz, 1H, CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.01, 141.53, 131.75, 131.02, 130.63, 130.14, 130.07, 129.80, 129.58, 129.16, 128.70, 127.42, 126.35, 124.07, 123.57, 120.4, 117.42, 67.45, 41.17 ppm. FT-IR (KBr): 3478, 2380, 1711, 1589, 1478, 1311, 1243, 1033, 985, 758 cm^{-1}. MS-ESI: (*m/z*) 383 $[M+H]^+$; HRMS-ESI: calcd for $C_{21}H_{17}Cl_2N_2O$ $[M+H]^+$ 383.0717; found 383.0713.

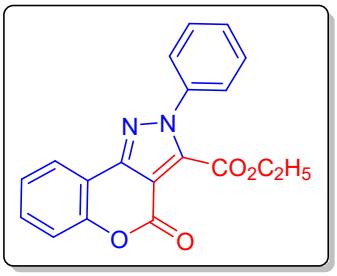
2-(1-(3-bromophenyl)-5-Phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenol (7j):



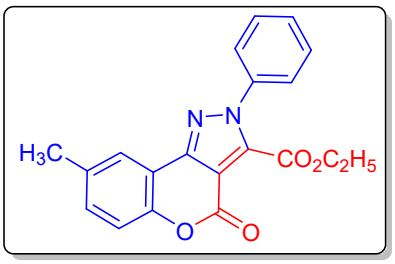
Yield: 74% (260 mg), pale yellow solid; M.P: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, J = 6.6, 3.0 Hz, 2H, aromatic), 7.44-7.38 (m, 3H, aromatic), 7.37 (d, J = 2.3 Hz, 1H, aromatic), 7.29 (s, 1H, aromatic), 7.25 (s, 1H, aromatic), 7.15 (ddd, J = 10.9, 8.8, 1.9 Hz, 2H, aromatic), 7.07 (dd, J = 7.5, 1.4 Hz, 1H, aromatic), 6.82 (dd, J = 13.5, 7.4 Hz, 2H, aromatic), 5.36 (t, J = 11.0 Hz, 1H, CH), 3.67 (dd, J = 16.6, 10.6 Hz, 1H, CH), 3.42 (dd, J = 16.6, 11.5 Hz, 1H, CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.98, 141.54, 131.77, 131.48, 130.97, 130.62, 129.98, 129.89, 129.58, 129.15, 128.71, 127.42, 126.36, 124.06, 123.64, 120.43, 117.39, 67.34, 41.19 ppm. FT-IR (KBr): 3426, 2377, 1724, 1495, 1318, 1243, 1033, 978, 751 cm^{-1}. MS-ESI: (*m/z*) 393 $[M+H]^+$; HRMS-ESI: calcd for $C_{21}H_{18}BrN_2O$ $[M+H]^+$ 393.0185; found 393.0181.

7. General procedure for the preparation of chromenopyrazolecarboxylates (8a-j): 2-(1,5-diphenyl-4,5-dihydro-1*H*-pyrazol-3-yl) Phenol (**7a**, 0.100 g, 1.0 equiv.) and diethyl but-2-ynedioate (**4a**, 0.055 g, 1.0 equiv.) were heated at 120 °C. The reaction was monitored by TLC and after completion of reaction (TLC, 22 h), the residue was purified by column chromatography by using silica gel (60:120, ethyl acetate/hexane 2:98) afforded diethyl ethyl 4-oxo-2-phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate **8a** (0.074 g) as colourless solid in 70% yield. The other chromenopyrazolecarboxylates **8b-j** were prepared from pyrazolines **7a-j** with diethyl but-2-ynedioate **4a** under above optimized conditions. The known chromenopyrazolecarboxylates **(8a-b**, **8d-h)**[6] are compared with the reported data and unknown compounds **8c**, **8i-j** are characterized by spectral data and depicted below.

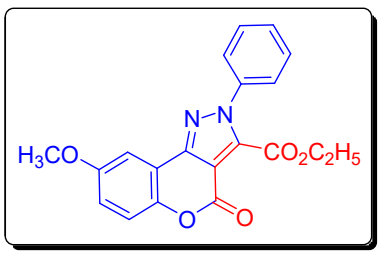
Compound 8a: The compound ethyl 4-oxo-2-phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate was prepared from **7a** with **4a.** The product yield: 72% (72 mg), Ref: 6



Compound 8b: The compound ethyl 8-methyl-4-oxo-2-phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate was prepared from **7b** with **4a.** The product yield: 74% (79 mg), Ref: 6

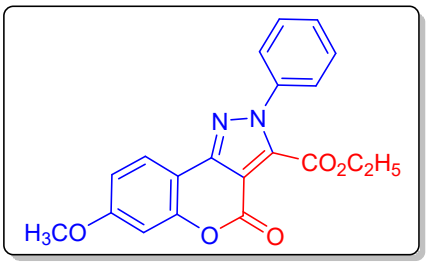


Ethyl 8-methoxy-4-oxo-2-phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate (8c):

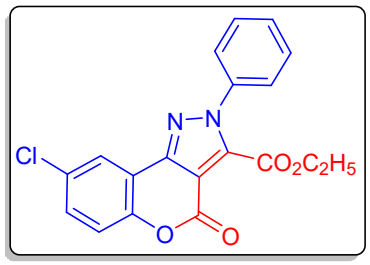


Yield: 58% (84 mg), colourless solid; M.P: 204-206 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J = 9.3 Hz, 1H, aromatic), 7.58-7.52 (m, 5H, aromatic), 6.91 (dd, J = 4.5, 2.3 Hz, 2H, aromatic), 4.40 (q, J = 7.1 Hz, 2H, OCH_2), 3.89 (s, 3H, CH_3), 1.27 (t, J = 6.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.97, 156.30, 151.18, 149.17, 139.06, 134.47, 131.95, 129.82, 129.40, 124.89, 122.84, 120.46, 117.27, 113.60, 63.14, 20.87, 13.75 ppm. FT-IR (KBr): 3428, 2924, 2851, 1755, 1721, 1627, 1594, 1462, 1319, 1206, 1031, 982, 772 cm^{-1}. MS-ESI: (*m/z*) 365 $[M+H]^+$; HRMS-ESI: calcd for $C_{20}H_{17}N_2O_5$ $[M+H]^+$ 365.1147; found 365.1143.

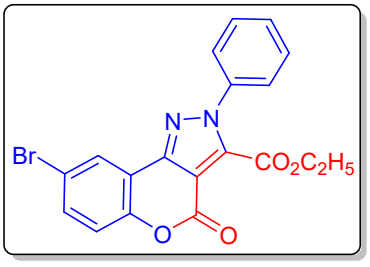
Compound 8d: The compound ethyl 7-methoxy-4-oxo-2-phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate was prepared from **7d** with **4a.** The product yield: 55% (58 mg), Ref: 6



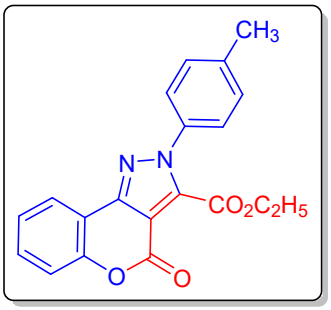
Compound 8e: The compound ethyl 8-chloro-4-oxo-2-phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate was prepared from **7e** with **4a.** The product yield: 75% (79 mg), Ref: 6



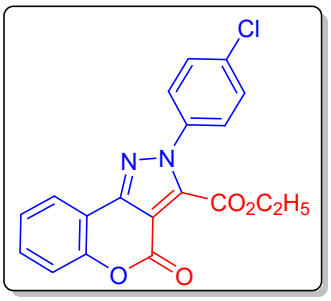
Compound 8f: This compound ethyl 8-bromo-4-oxo-2-phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate was prepared from **7f** with **4a.** The product yield: 69% (73 mg), Ref: 6



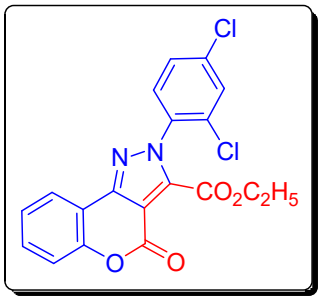
Compound 8g: The compound ethyl 4-oxo-2-(*p*-tolyl)-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate was prepared from **7g** with **4a.** The product yield: 71% (75 mg), Ref: 6



Compound 8h: The compound ethyl 2-(4-chlorophenyl)-4-oxo-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate was prepared from **7h** with **4a.** The product yield: 61% (65 mg), Ref: 6

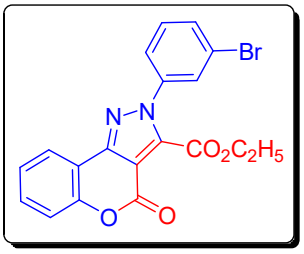


Ethyl 2-(2,4-dichlorophenyl)-4-oxo-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate (8i):



Yield: 76% (115 mg), colourless solid; M.P: 156-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, J = 7.8, 1.5 Hz, 1H, aromatic), 7.60 (d, J = 2.0 Hz, 1H, aromatic), 7.56-7.52 (m, 1H, aromatic), 7.51 (d, J = 5.2 Hz, 1H, aromatic), 7.49-7.46 (m, 1H, aromatic), 7.41 (d, J = 7.7 Hz, 1H, aromatic), 7.34 (td, J = 7.8, 1.1 Hz, 1H, aromatic), 4.38 (q, J = 7.1 Hz, 2H, OCH_2), 1.30 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.65, 155.40, 153.08, 149.77, 137.26, 136.96, 136.14, 132.25, 131.32, 130.09, 129.56, 128.08, 124.71, 123.01, 117.50, 113.72, 108.15, 62.96, 13.78 ppm. FT-IR (KBr): 3109, 3061, 2923, 2860, 1780, 1737, 1618, 1596, 1433, 1317, 1249, 1107, 1018, 985, 758 cm^{-1}. MS-ESI: (*m/z*) 403 $[M+H]^+$; HRMS-ESI: calcd for $C_{19}H_{13}Cl_2N_2O_4$ $[M+H]^+$ 403.0253; found 403.0250.

Ethyl 2-(3-bromophenyl)-4-oxo-2,4-dihydrochromeno[4,3-*c*]pyrazole-3-carboxylate (8j):



Yield: 63% (67 mg), colourless solid; M.P: 182-184 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 2.5 Hz, 1H, aromatic), 7.59-7.53 (m, 5H, aromatic), 7.46 (dd, J = 8.9, 2.5 Hz, 1H, aromatic), 7.35 (d, J = 8.9 Hz, 1H, aromatic), 4.41 (q, J = 7.1 Hz, 2H, OCH_2), 1.27 (t, J = 7.2 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.60, 154.35, 152.04, 148.73, 136.21, 135.91, 135.10, 131.21, 130.28, 129.04, 128.51, 127.04, 123.66, 121.97, 116.45, 112.68, 107.11, 61.92, 12.73 ppm. FT-IR (KBr): 3428, 2329, 2860, 1724, 1359, 1588, 1495, 1463, 1318, 1243, 1099, 1033, 984, 757 cm^{-1}. MS-ESI: (*m/z*) 413 $[M+H]^+$; HRMS-ESI: calcd for $C_{19}H_{14}BrN_2O_4$ $[M+H]^+$ 413.0138; found 413.0134.

8. References:

1. K. S. Teja, S. Ramya and B. C. Raju, *Synth. Commun*., 2021, **51**, 1425-1432.
2. (*a*) A. S. Al-Bogami, H. Z. Alkhathlan and T. S. Saleh, *Asian J. Chem*., 2013, **25**, 6427-6433; (*b*) X. Wang, P. Ying-Ming; H. Xiao-Chao; M. Zhong-Yuan, W. Heng-Shan, *Org. Biomol. Chem*., 2014, **12**, 2028-2032.
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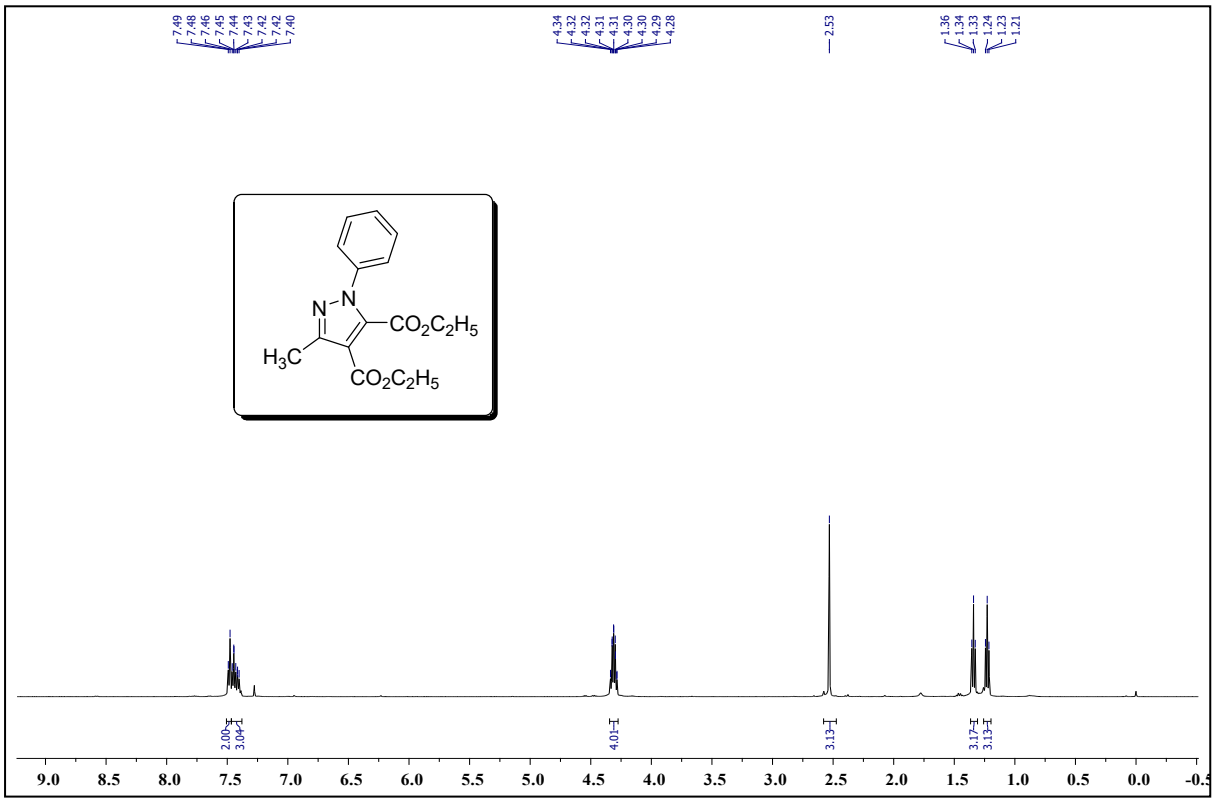
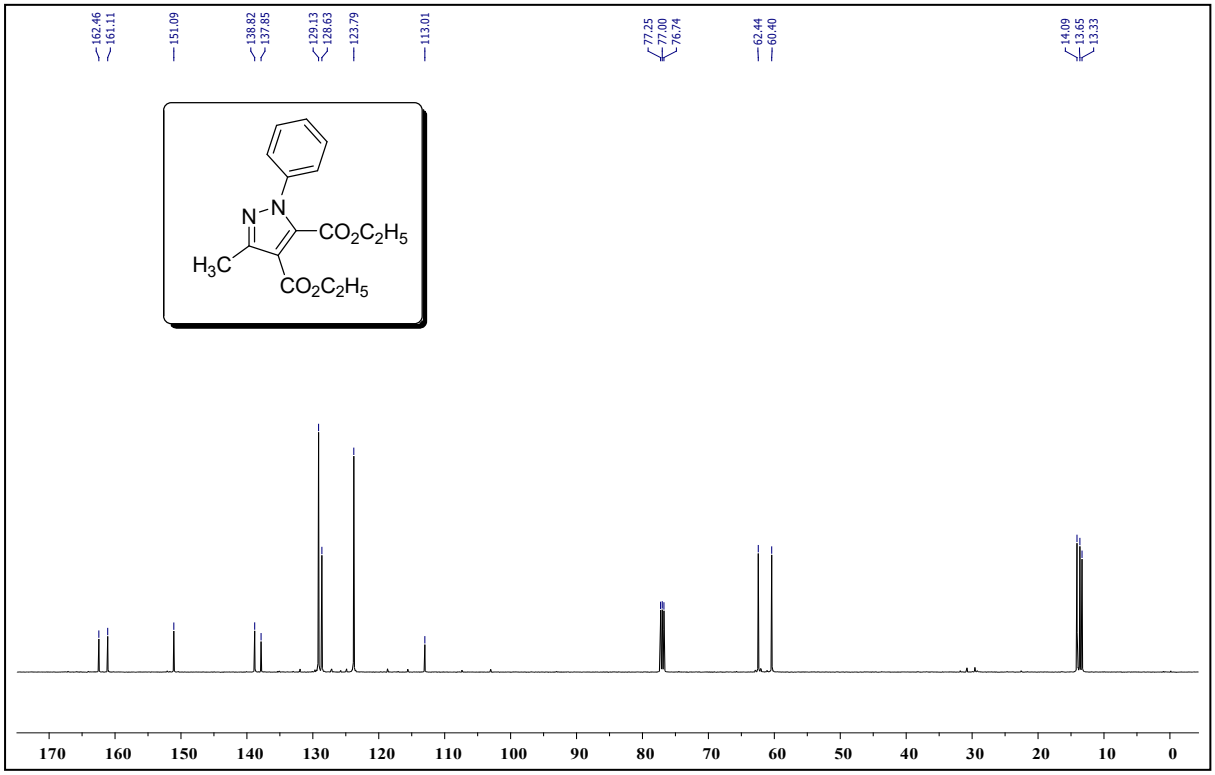
6. K. S. Hariprasad, K. V. Prasad and B. C. Raju, *RSC Adv*., 2016, **6**, 108654-108661.
7. (*a*) Jones, *J. Chem. Soc*., 1951, 48-51. (*b*) M. Lautens and T. Marquardt, *J. Org. Chem*., 2004, **69**, 4607-4614. (*c*) M. Kobayashi and K. Tanaka, *Chem. Eur. J*., 2012, **18**, 9225-9229. (*d*) S. K. Rodrigo, I. V. Powell, M. G. Coleman, J. A. Krausea and H. Guan, *Org. Biomol. Chem*., 2013, **11**, 7653-7657.

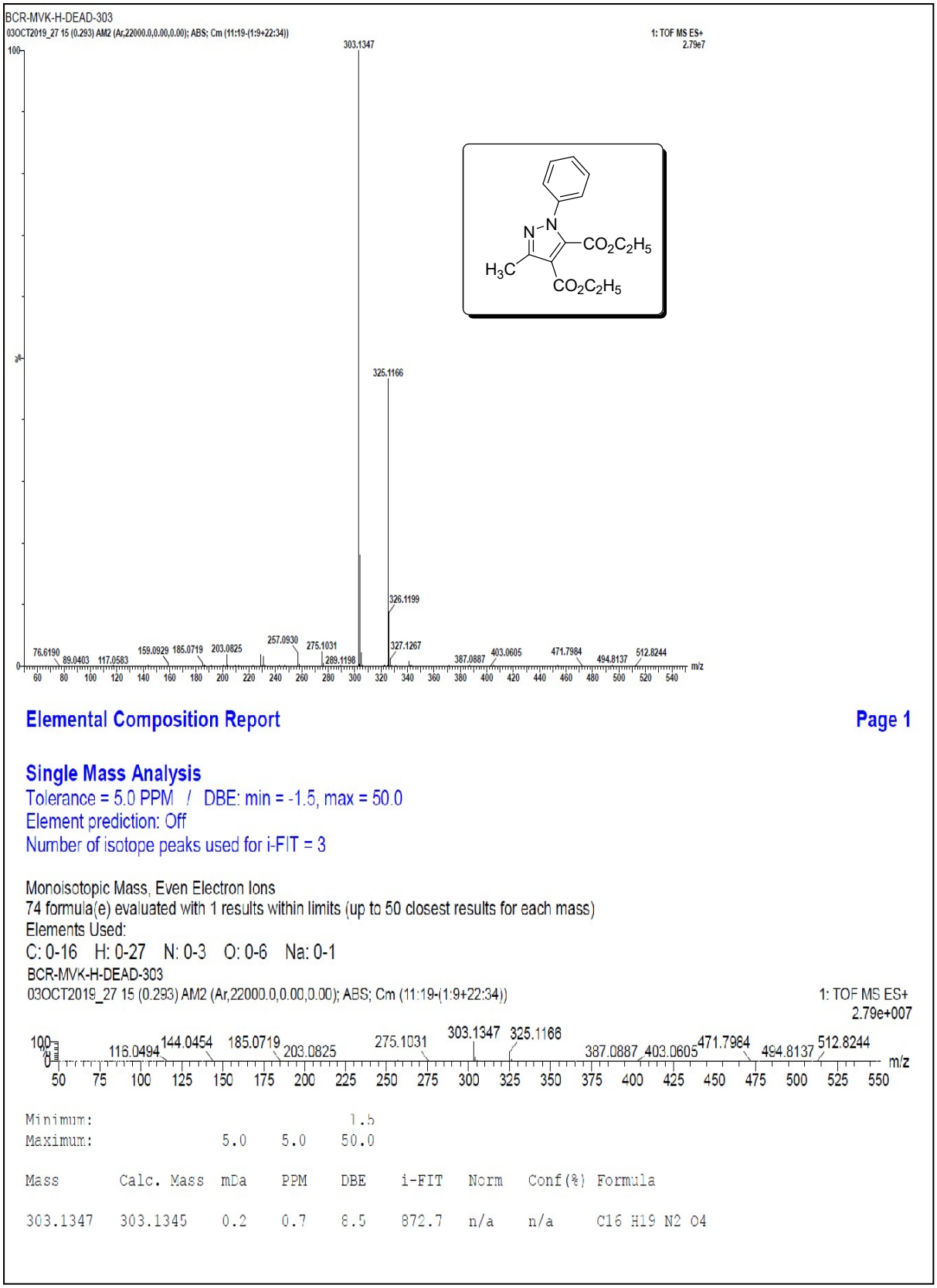
9. Copies of ^{1}H-NMR, ^{13}C-NMR and HRMS Spectrums (5a-t):



^{1}H NMR spectrum of compound **5a**

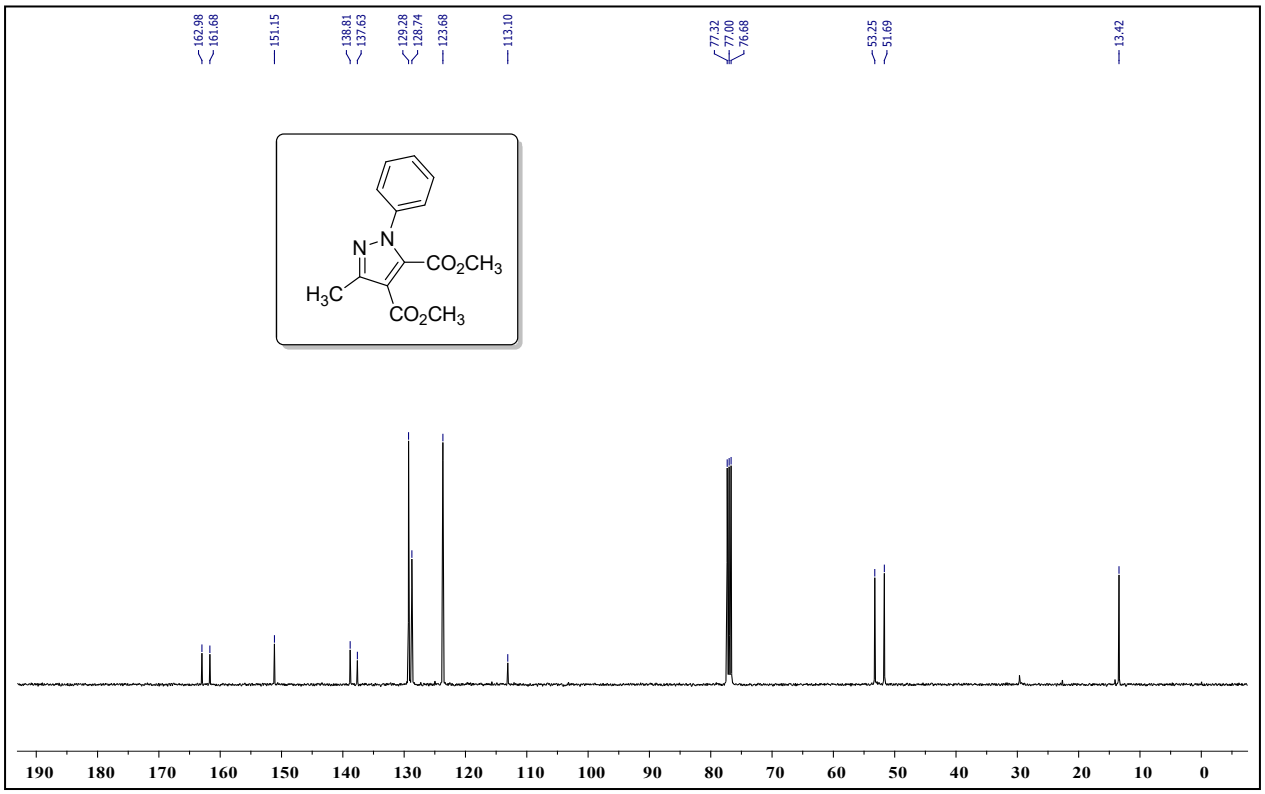


^{13}C NMR spectrum of compound **5a**

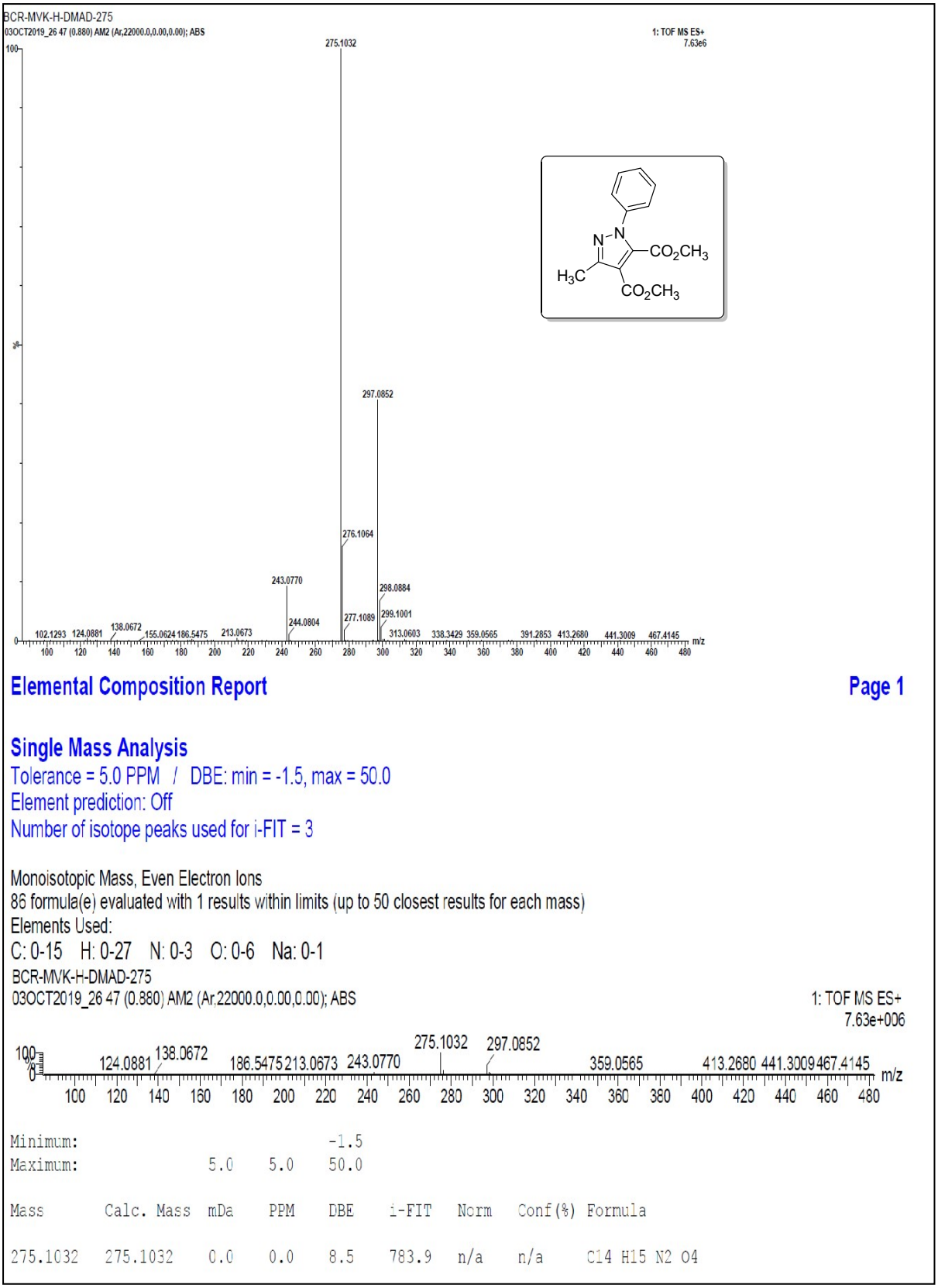


HRMS spectrum of compound **5a**

^{1}H NMR spectrum of compound **5b**



^{13}C NMR spectrum of compound **5b**



Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

86 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-15 H: 0-27 N: 0-3 O: 0-6 Na: 0-1

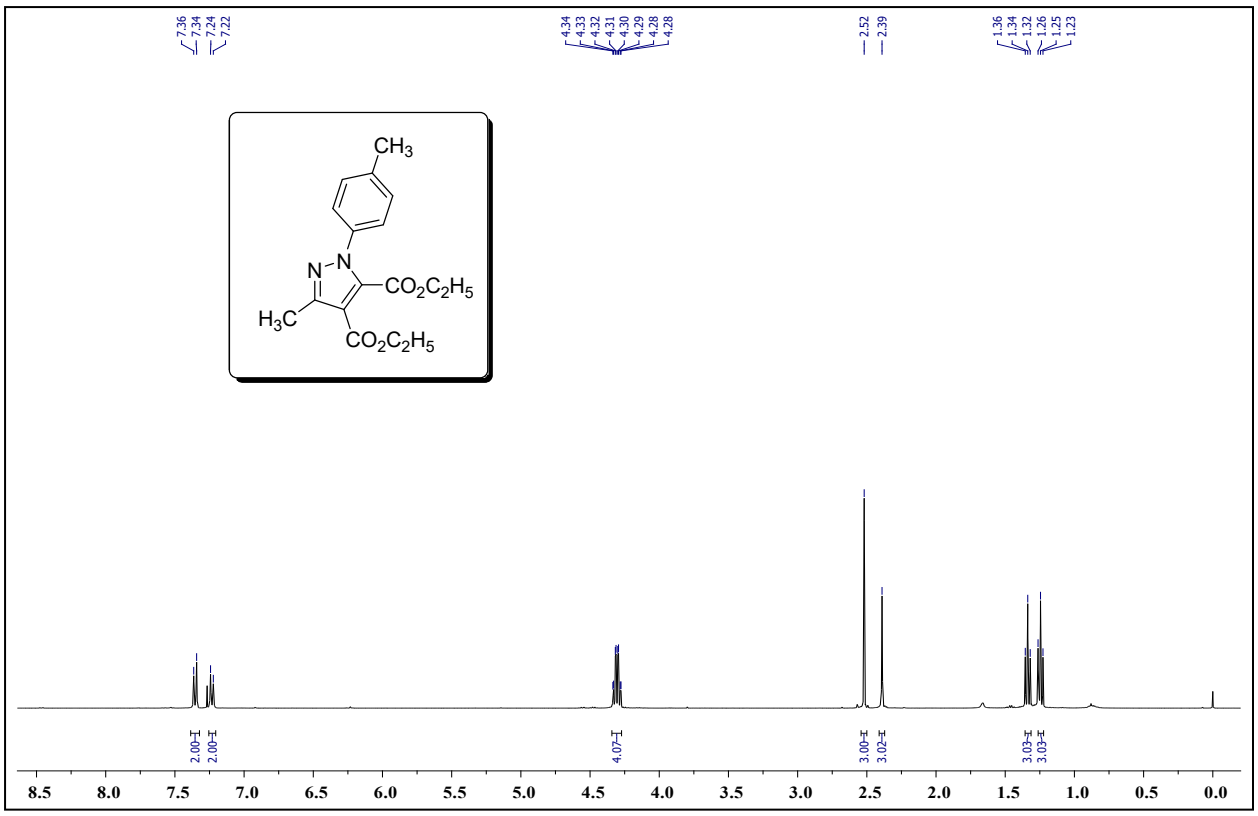
BCR-MVK-H-DMAD-275

03OCT2019_26 47 (0.880) AM2 (Ar,22000.0,0.00,0.00); ABS

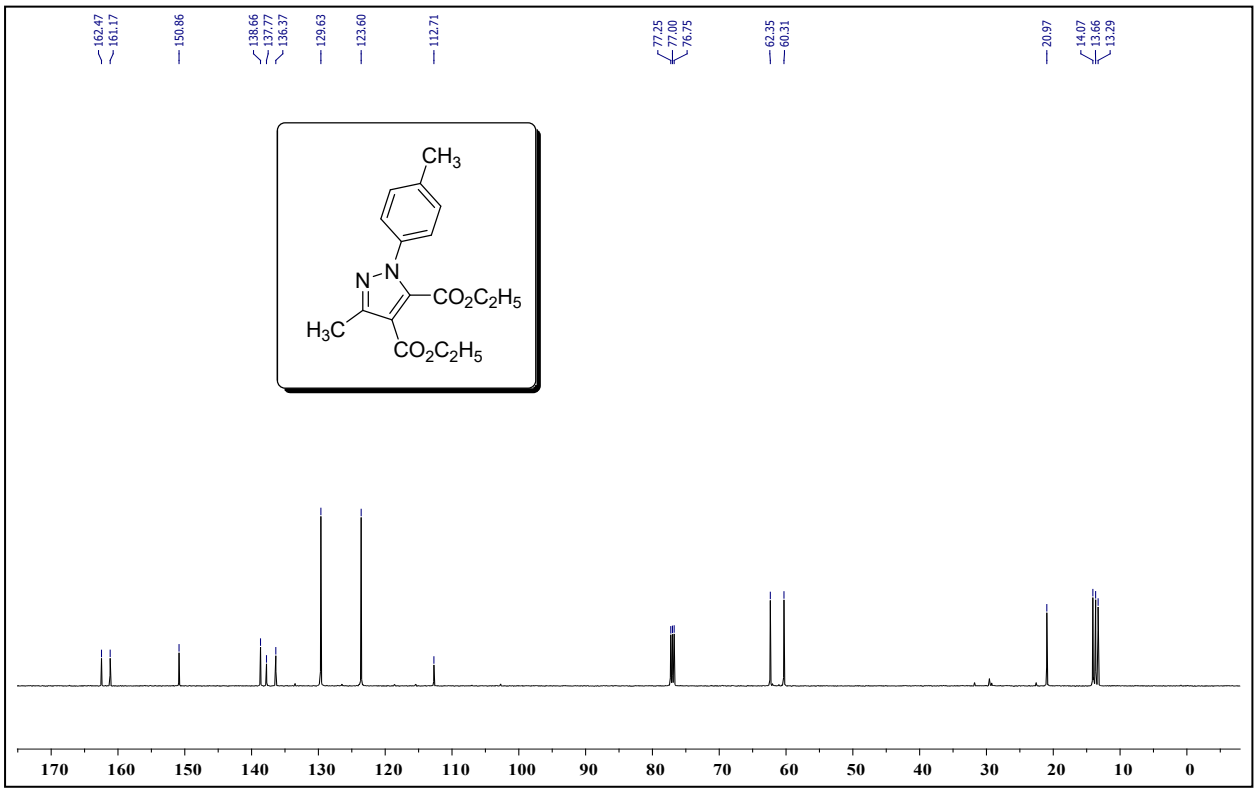
1: TOF MS ES+
7.63e+006

Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
275.1032	275.1032	0.0	0.0	8.5	783.9	n/a	n/a	C14 H15 N2 O4

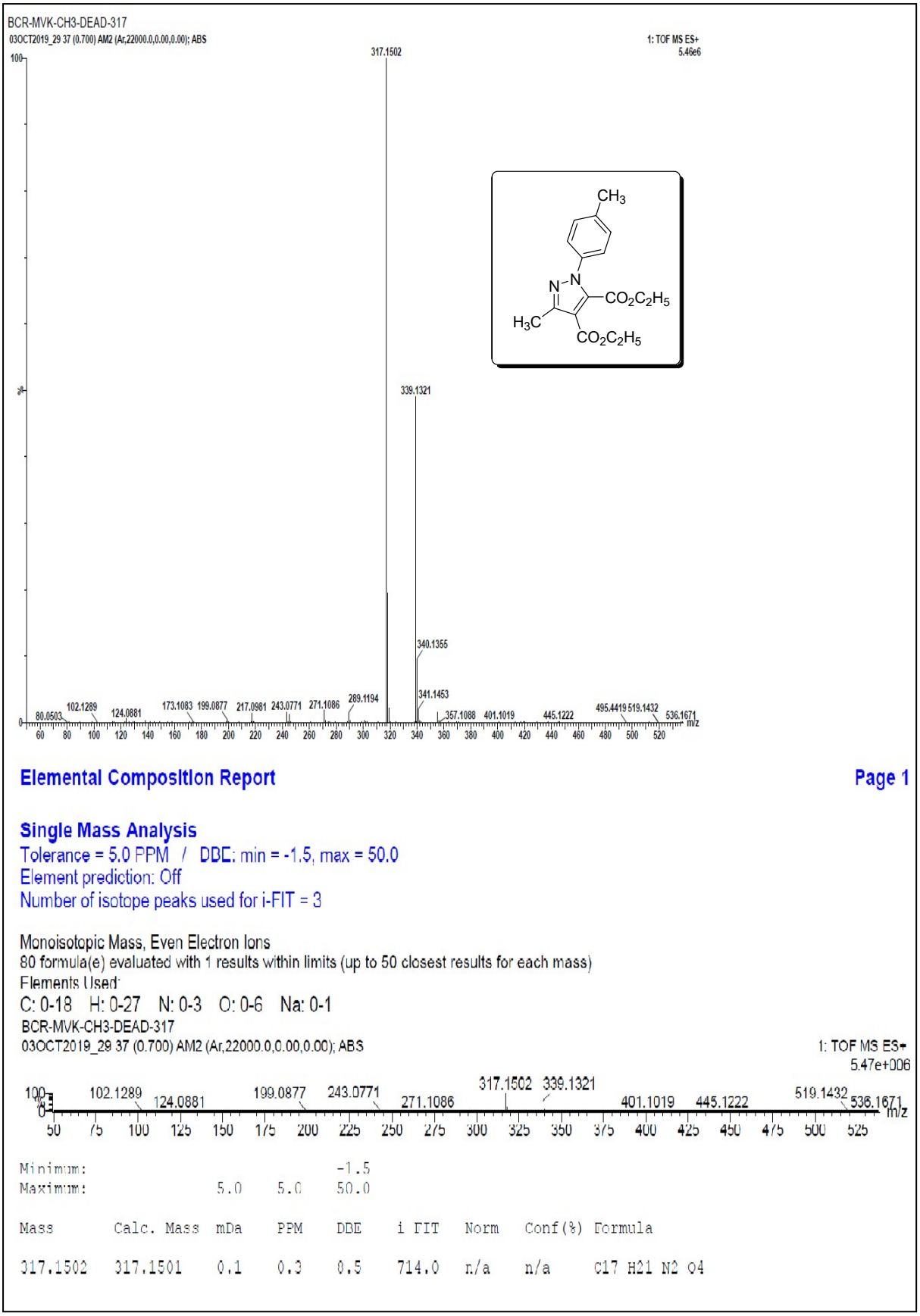
HRMS spectrum of compound **5b**



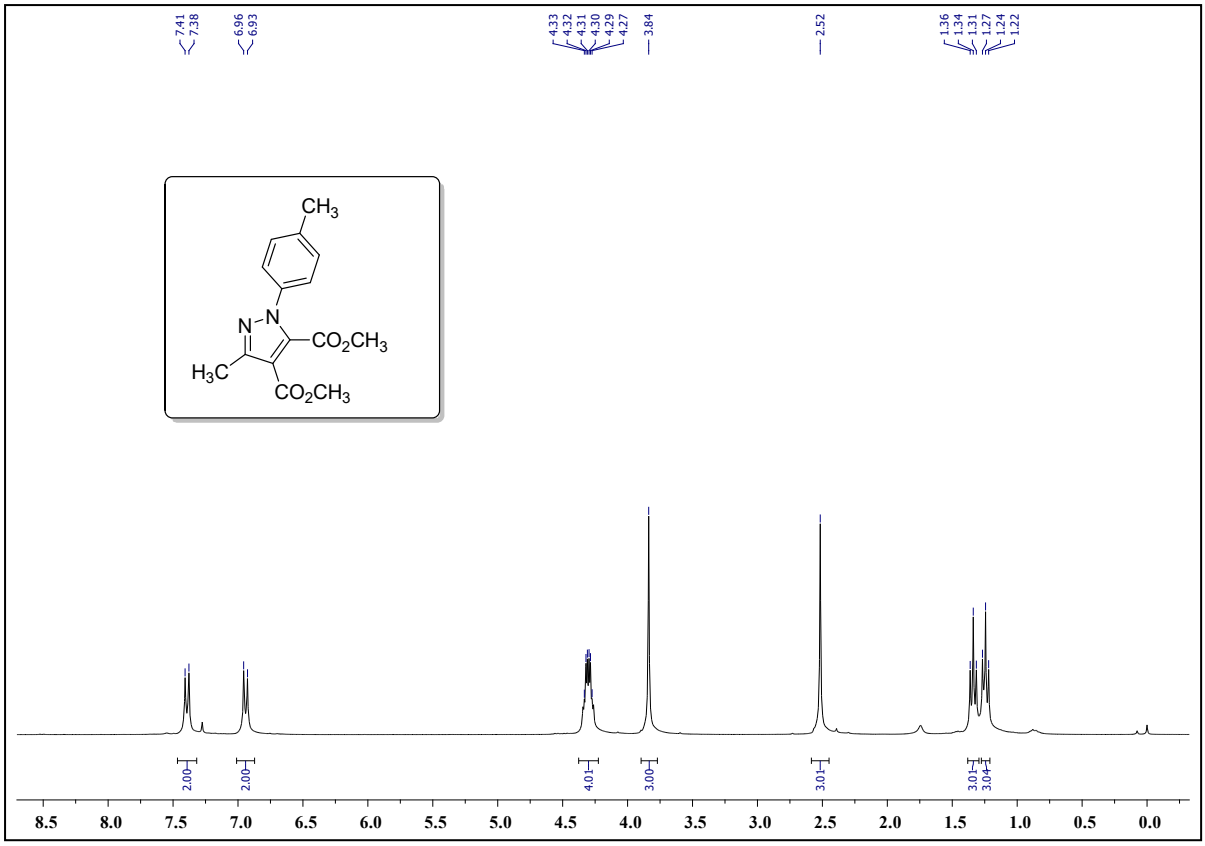
^{1}H NMR spectrum of compound **5c**



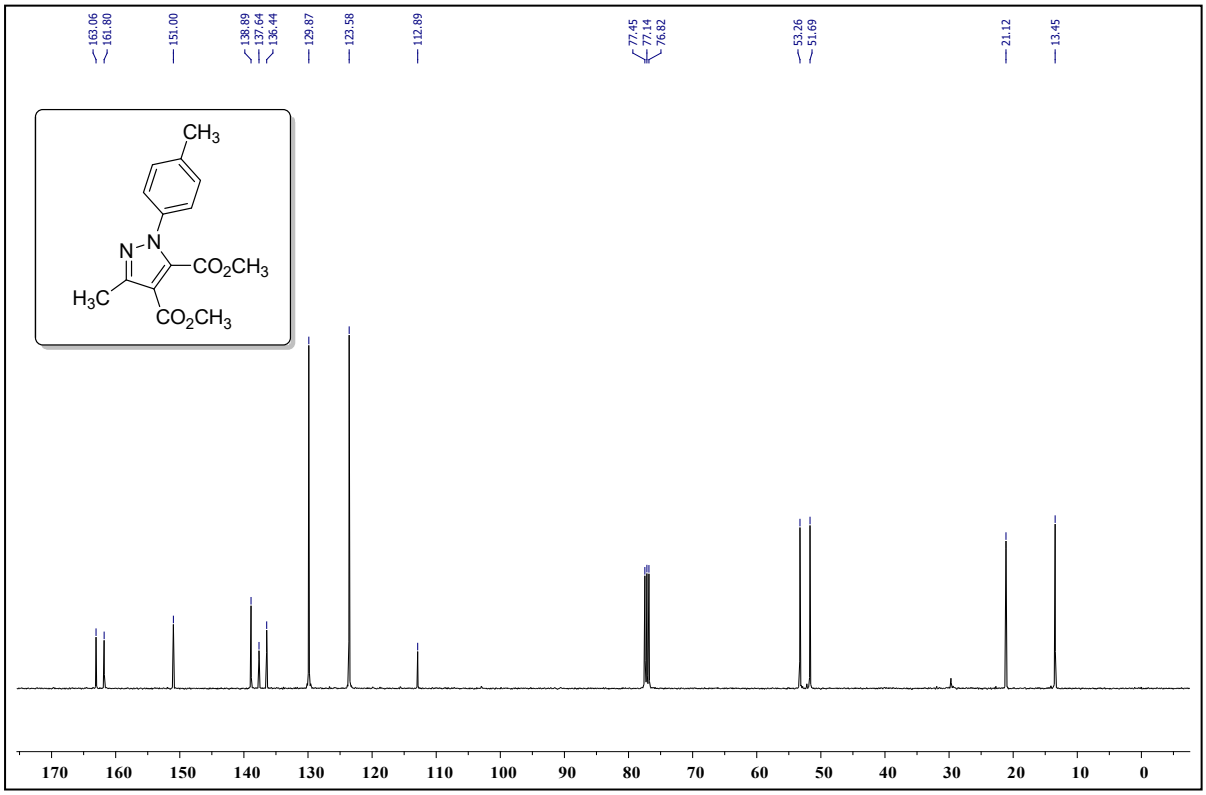
^{13}C NMR spectrum of compound **5c**



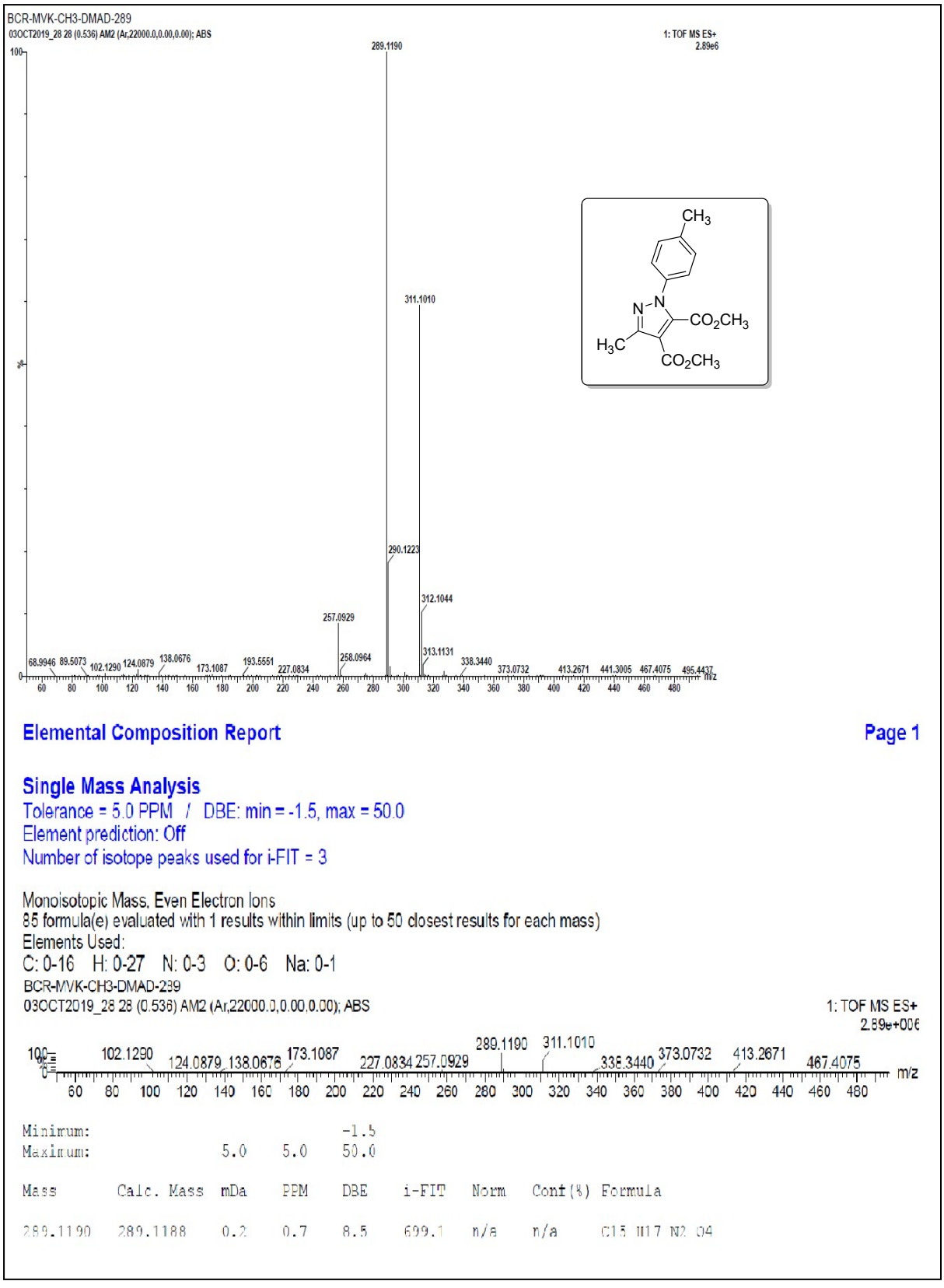
HRMS spectrum of compound **5c**



^{1}H NMR spectrum of compound **5d**

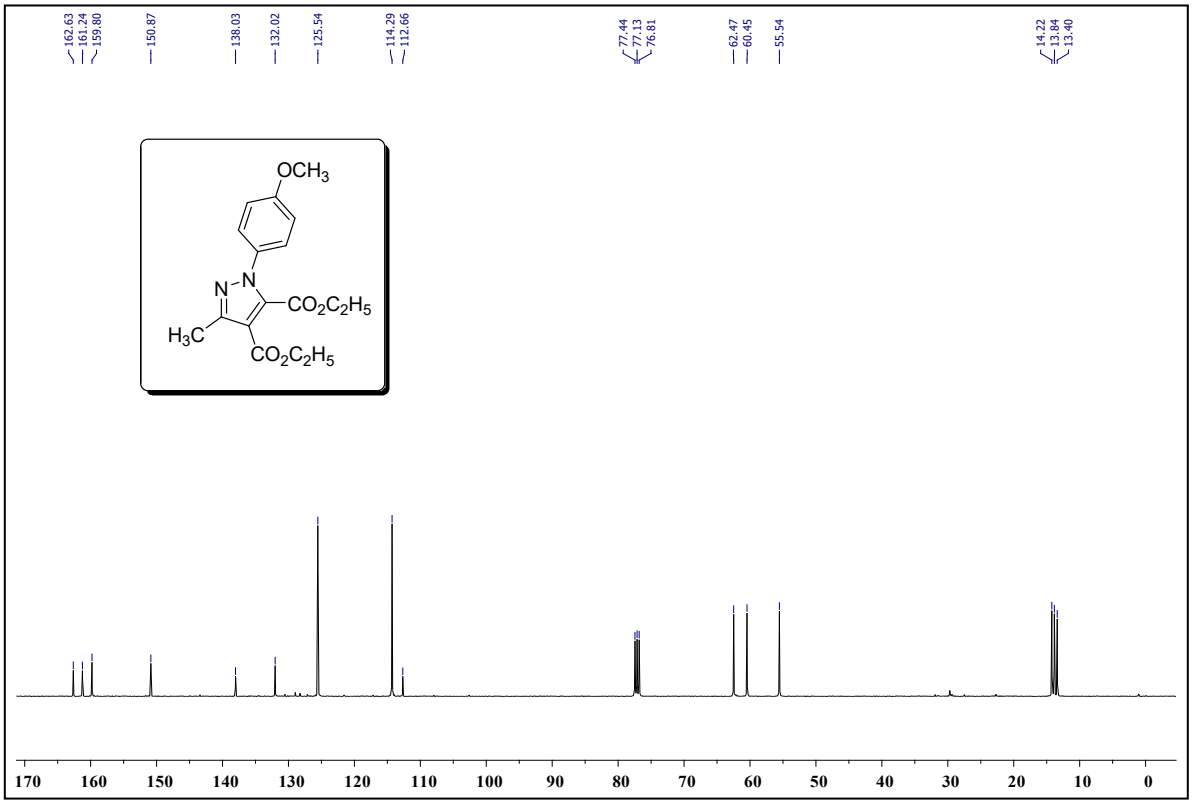


^{13}C NMR spectrum of compound **5d**

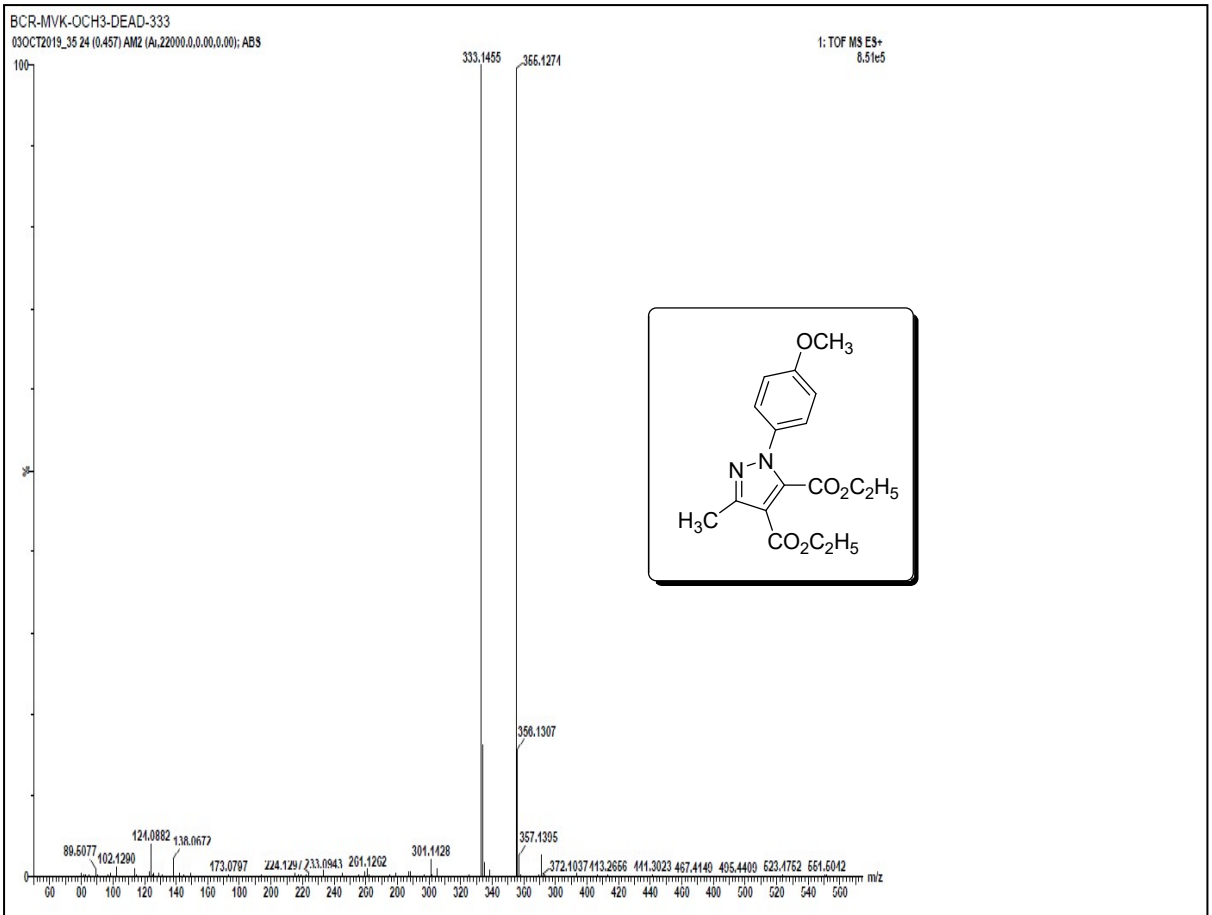


HRMS spectrum of compound **5d**

^{1}H NMR spectrum of compound **5e**



^{13}C NMR spectrum of compound **5e**



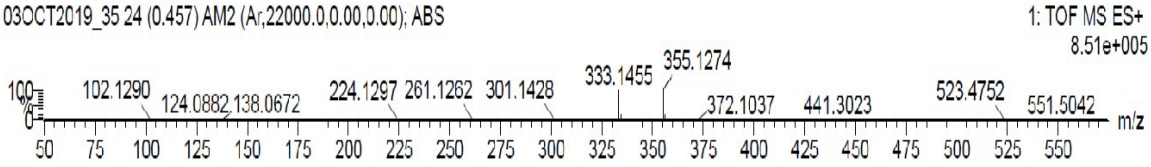
Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

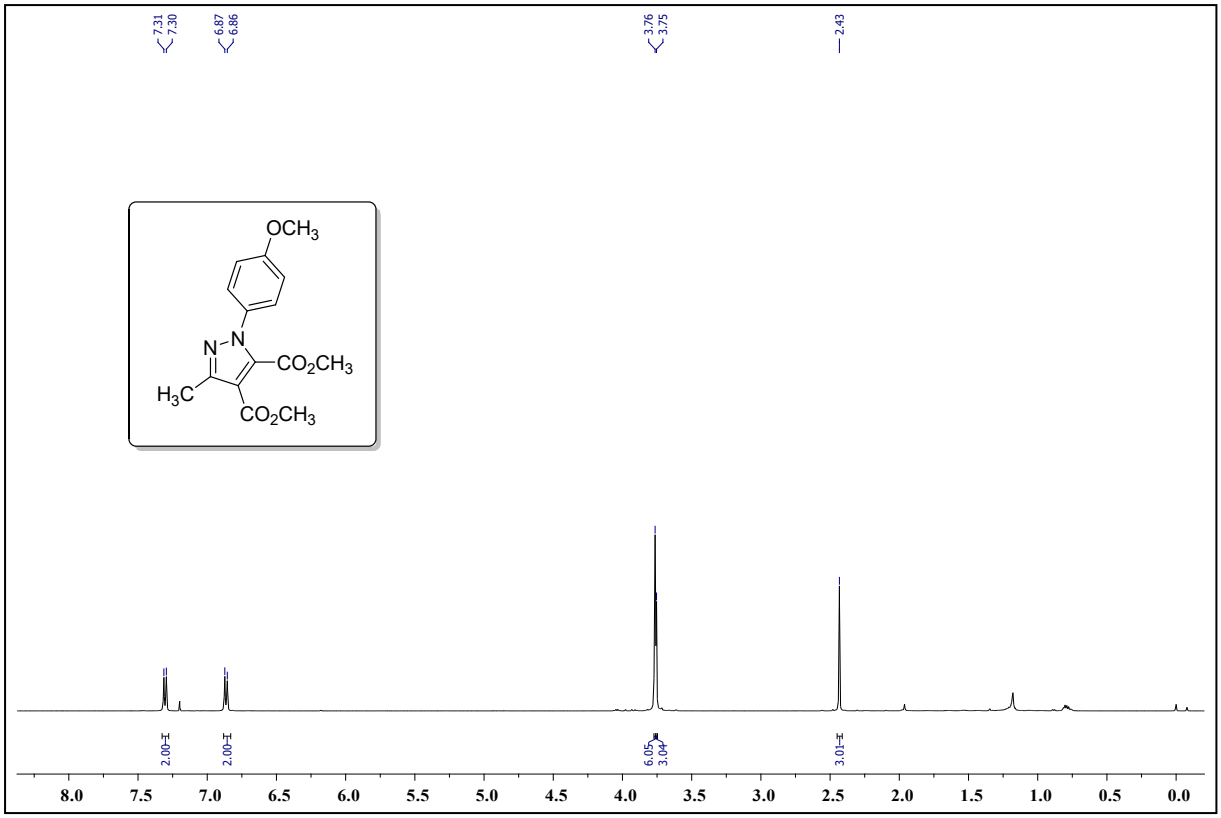
Monoisotopic Mass, Even Electron Ions
217 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-17 H: 0-22 N: 0-3 O: 0-6 Na: 0-1 Cl: 0-2

BCR-MVK-OCH3-DEAD-333
03OCT2019_35 24 (0.457) AM2 (Ar,22000.0,0.00,0.00); ABS

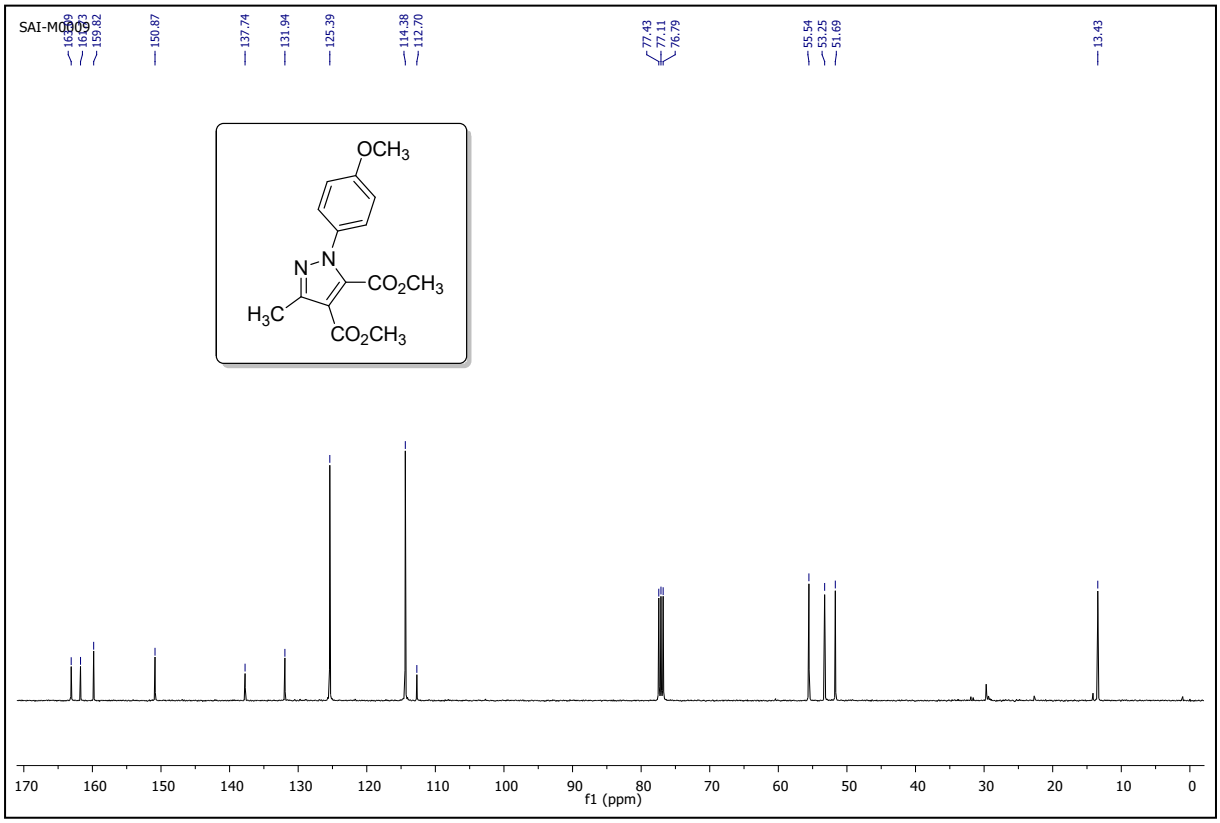


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
333.1455	333.1450	0.5	1.5	8.5	529.3	n/a	n/a	C17 H21 N2 O5

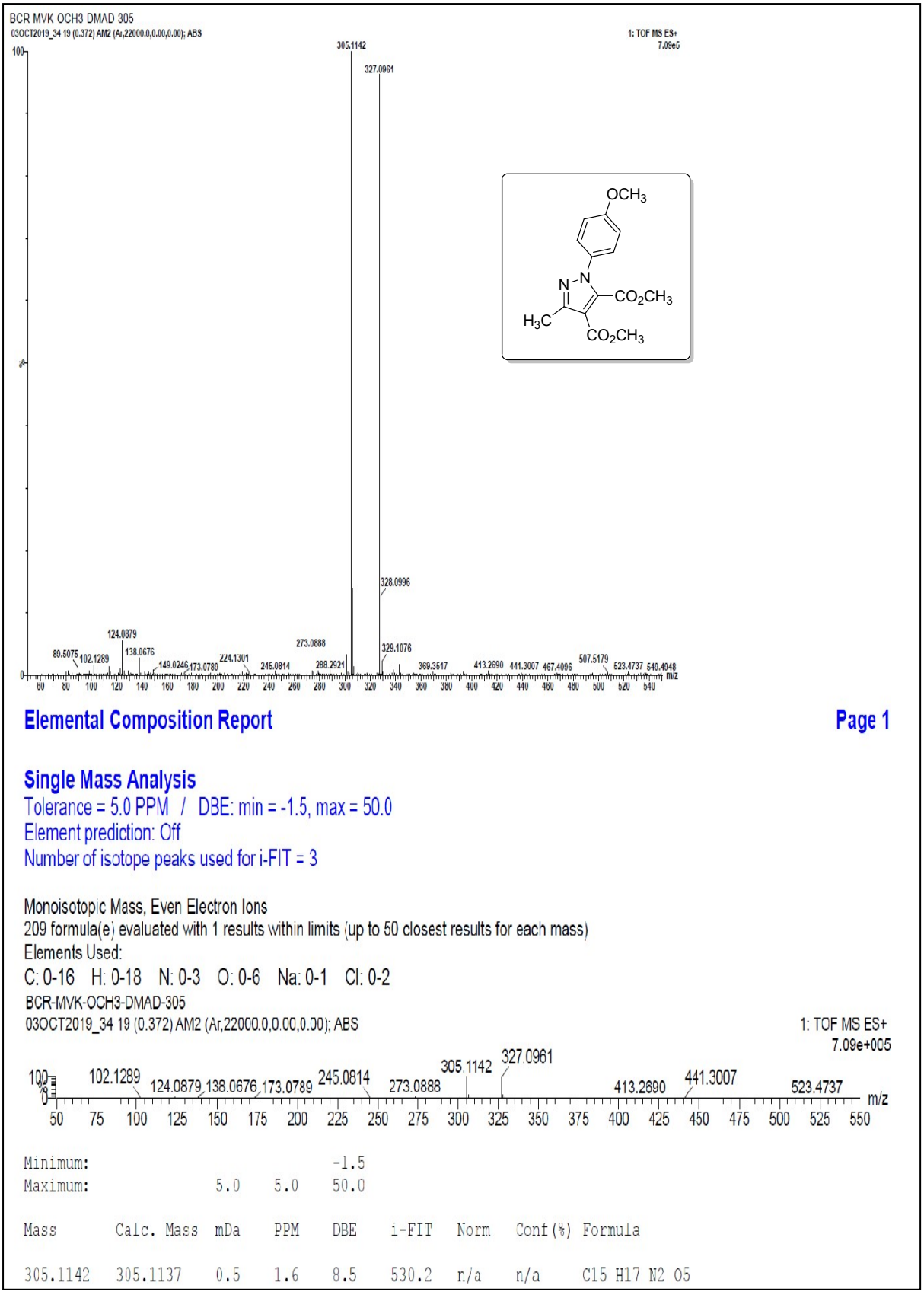
HRMS spectrum of compound **5e**



^{1}H NMR spectrum of compound **5f**



^{13}C NMR spectrum of compound **5f**



Elemental Composition Report

Page 1

Single Mass Analysis

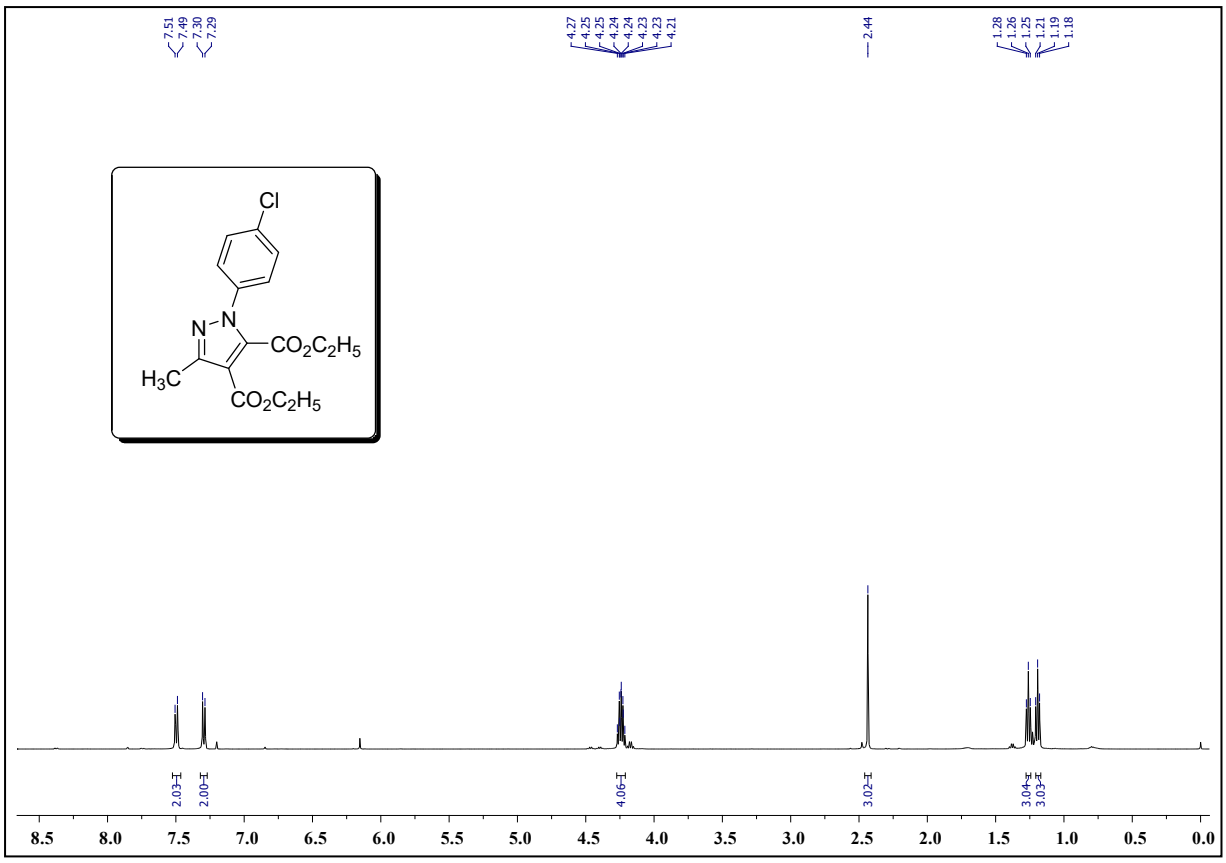
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
209 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 0-18 N: 0-3 O: 0-6 Na: 0-1 Cl: 0-2

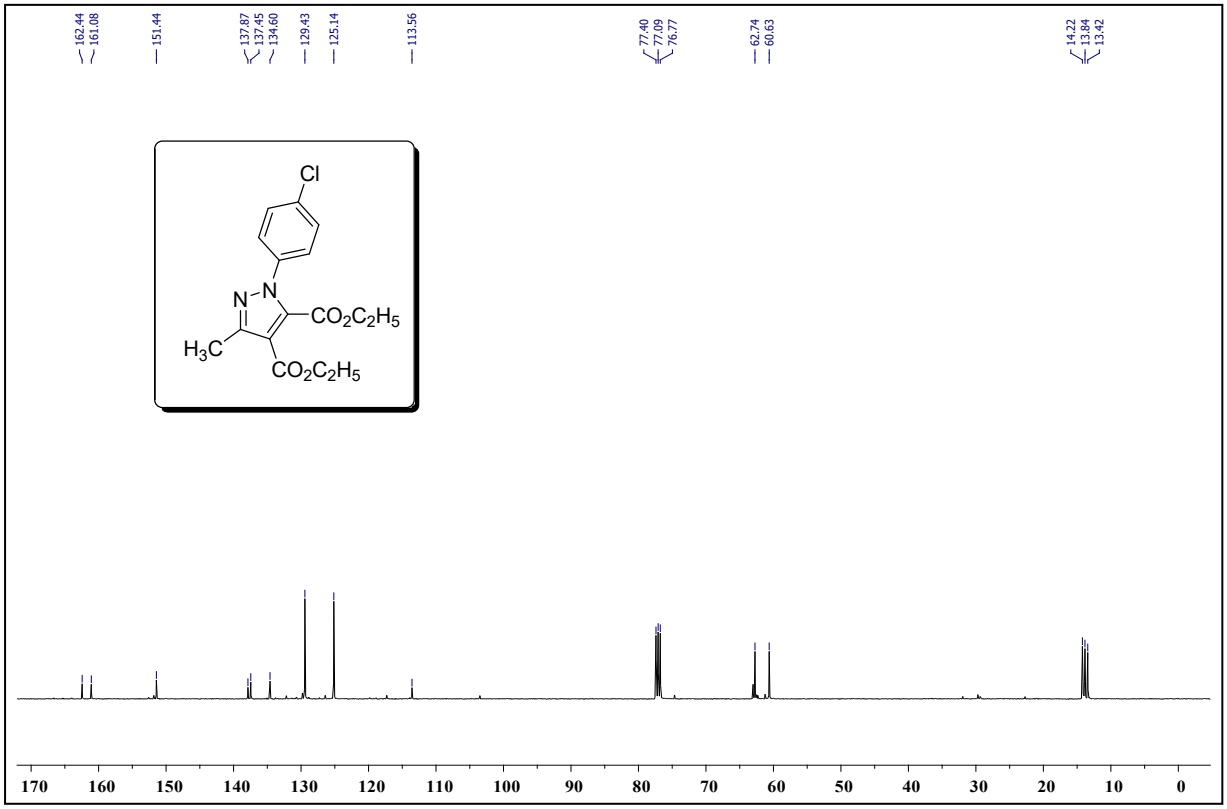
BCR-MVK-OCH3-DMAD-305
03OCT2019_34 19 (0.372) AM2 (Ar,22000.0,0.00,0.00); ABS

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
305.1142	305.1137	0.5	1.6	8.5	530.2	n/a	n/a	C15 H17 N2 O5

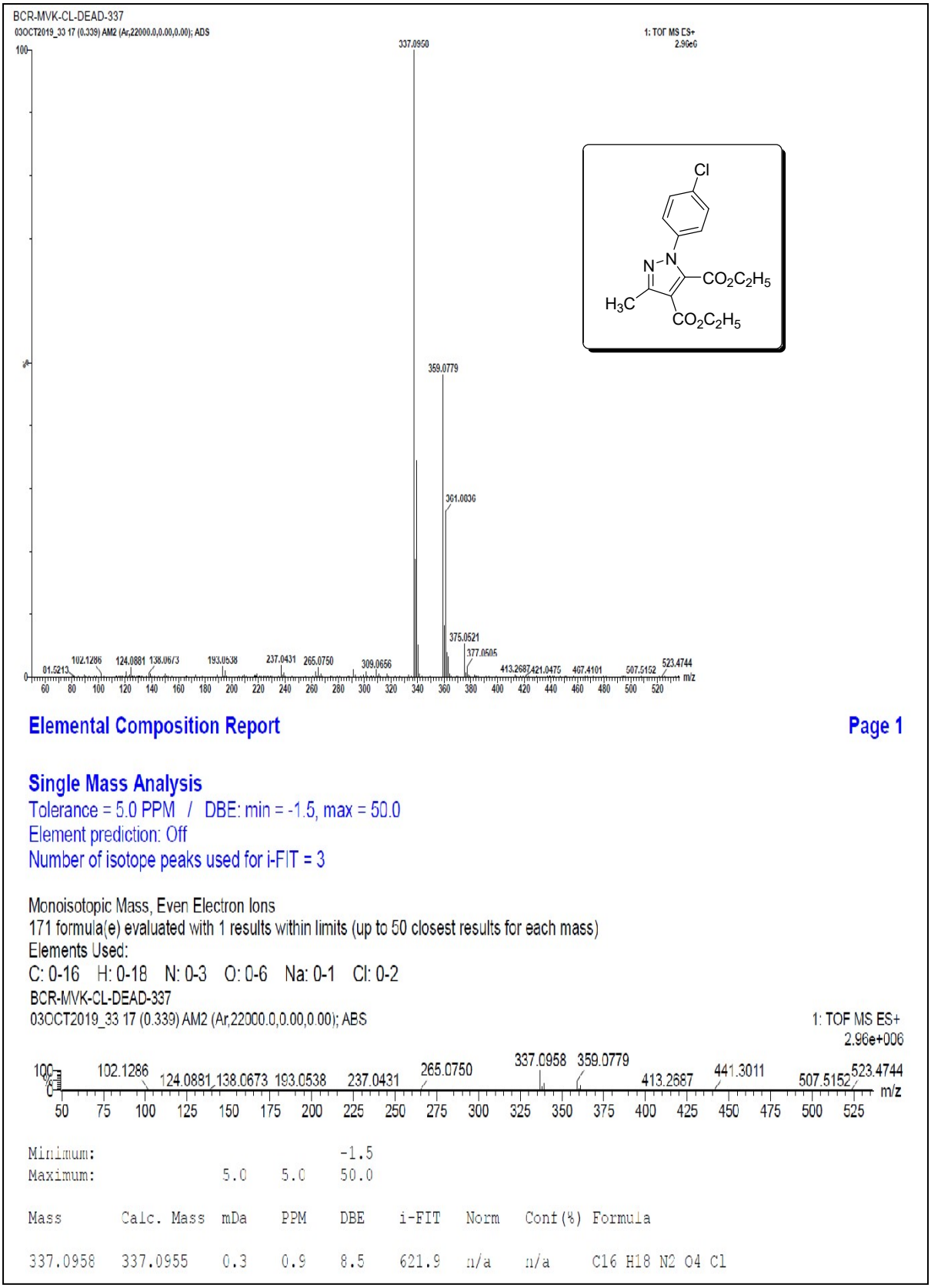
HRMS spectrum of compound **5f**



^{1}H NMR spectrum of compound **5g**



^{13}C NMR spectrum of compound **5g**



Elemental Composition Report **Page 1**

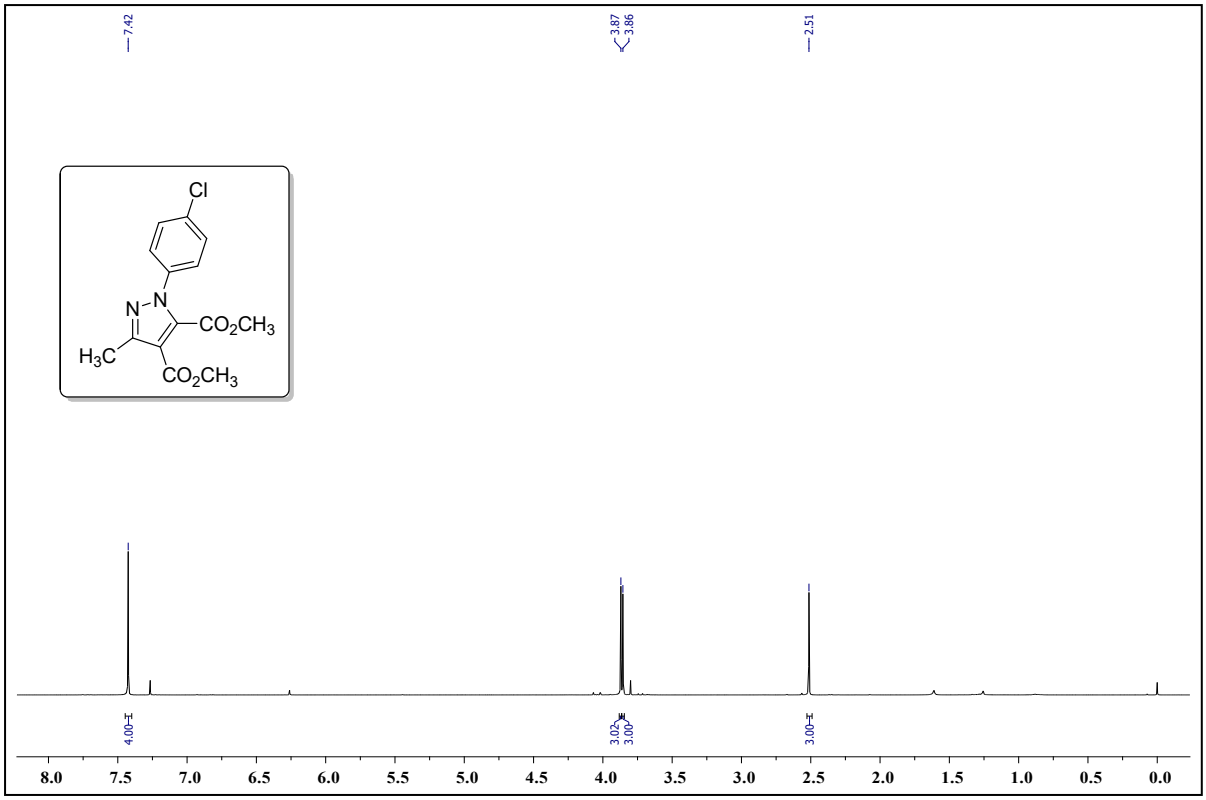
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
171 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 0-18 N: 0-3 O: 0-6 Na: 0-1 Cl: 0-2

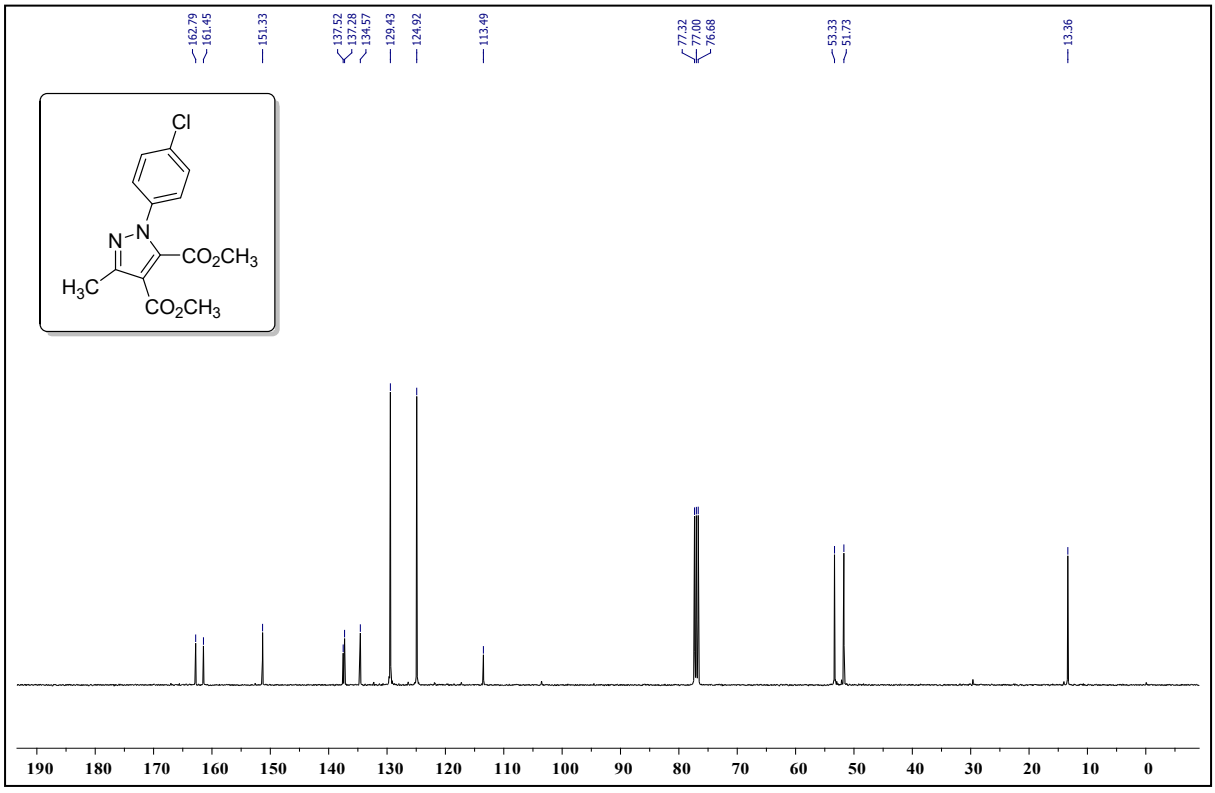
BCR-MVK-CL-DEAD-337
03OCT2019_33 17 (0.339) AM2 (Ar,22000.0,0.00,0.00); ABS
1: TOF MS ES+
2.96e+006

Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
337.0958	337.0955	0.3	0.9	8.5	621.9	n/a	n/a	C16 H18 N2 O4 Cl

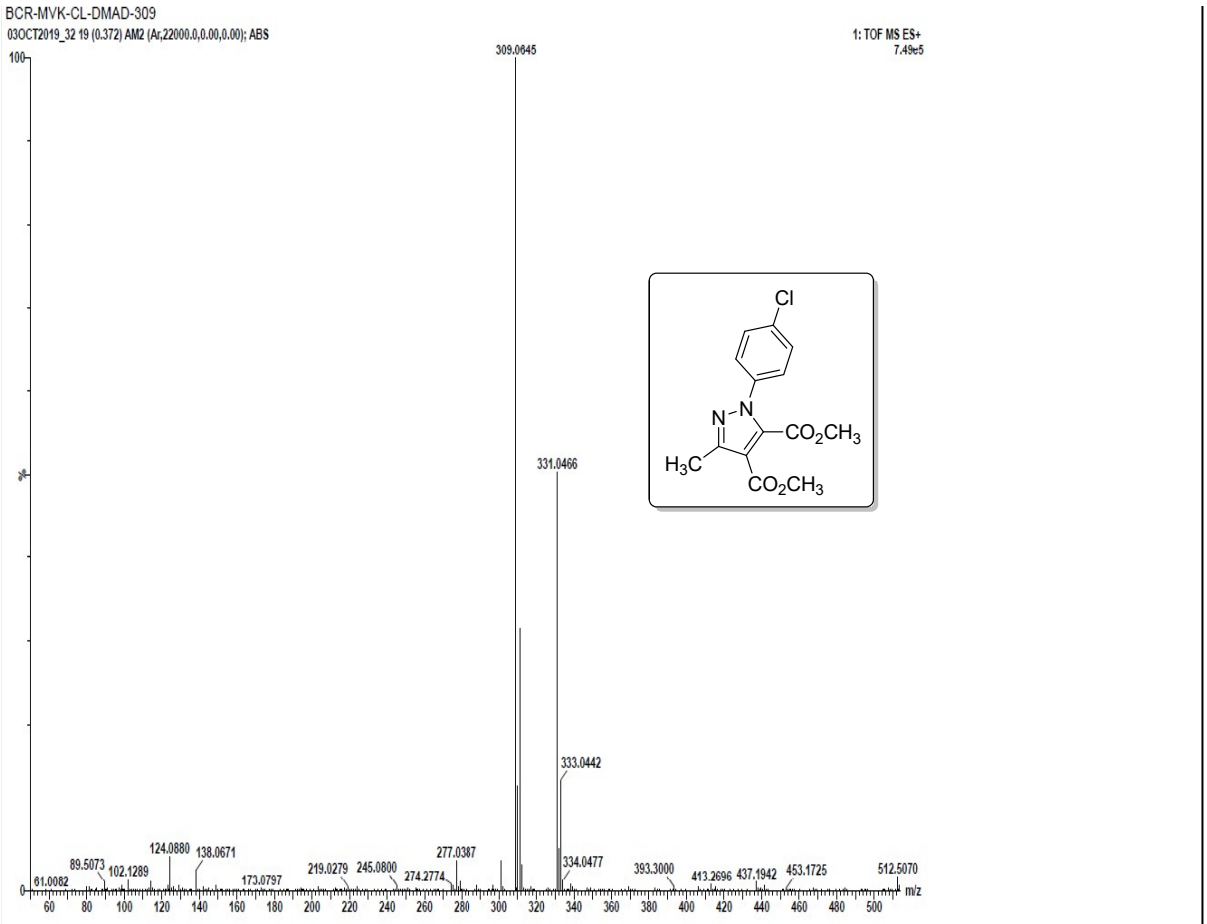
HRMS spectrum of compound **5g**



^{1}H NMR spectrum of compound **5h**



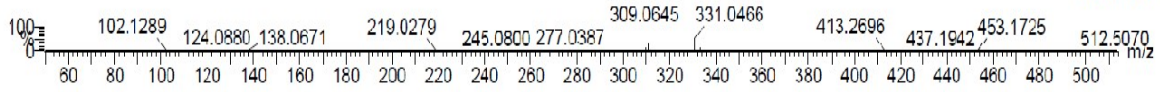
^{13}C NMR spectrum of compound **5h**



Elemental Composition Report **Page 1**

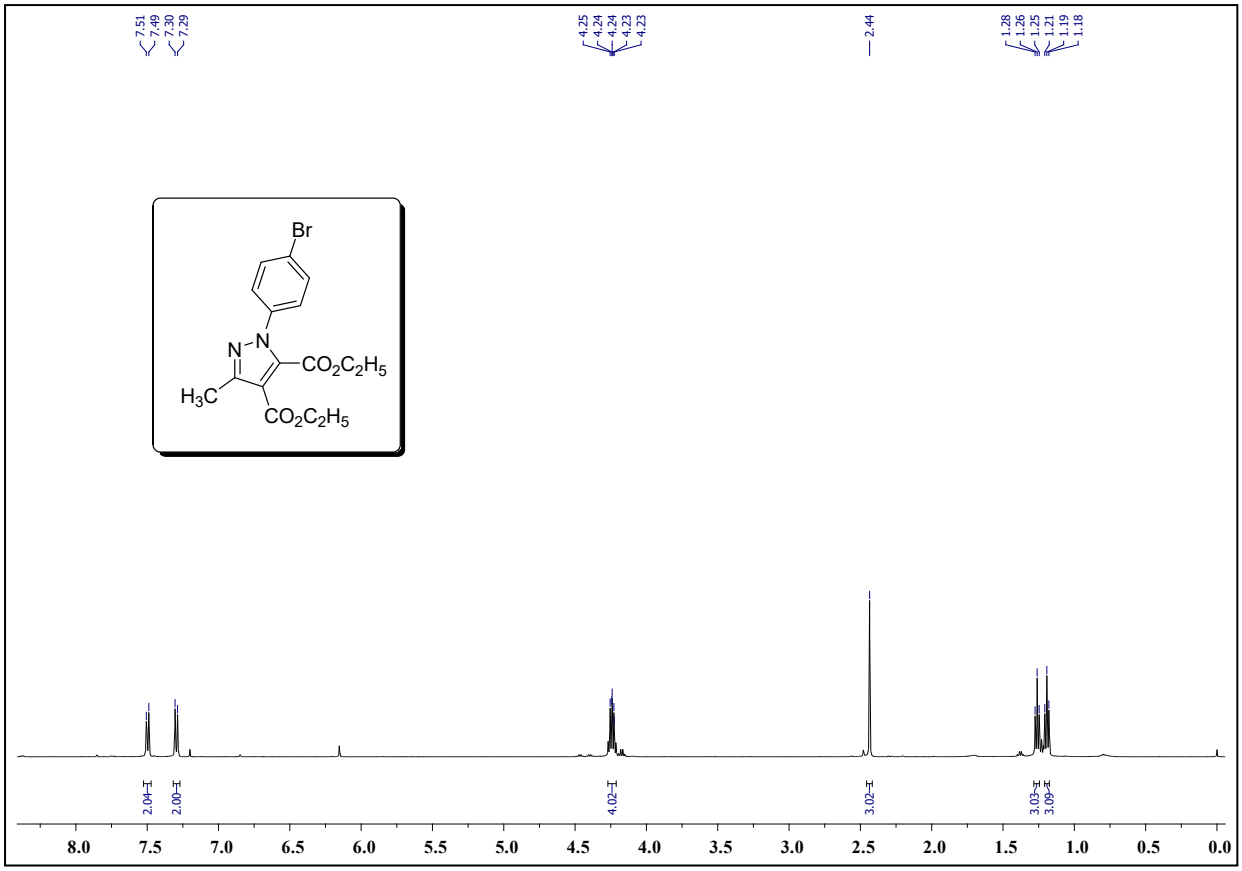
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
171 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 0-15 N: 0-3 O: 0-6 Na: 0-1 Cl: 0-2
BCR-MVK-CL-DMAD-309
03OCT2019_32 19 (0.372) AM2 (Ar,22000.0,0.00,0.00); ABS
1: TOF MS ES+
7.49e+005

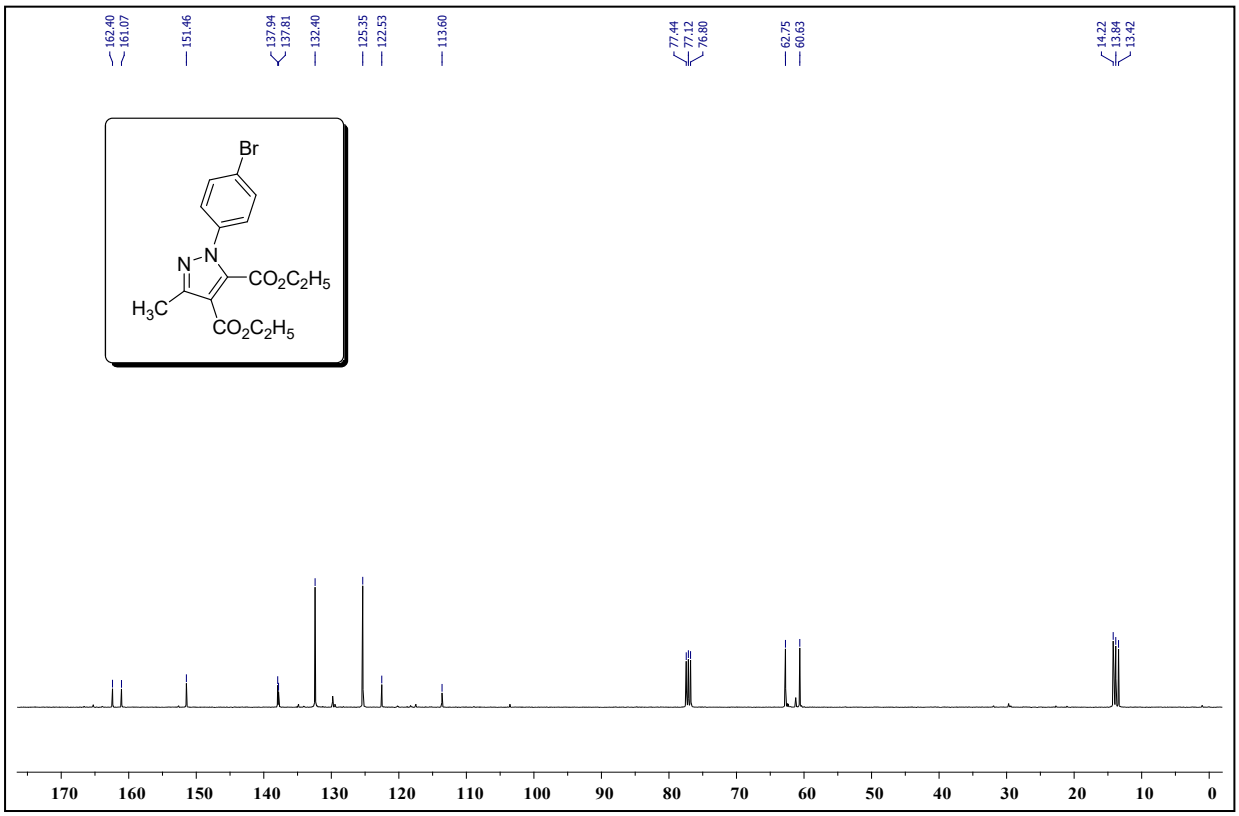


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
309.0645	309.0642	0.3	1.0	8.5	520.9	n/a	n/a	C14 H14 N2 O4 Cl

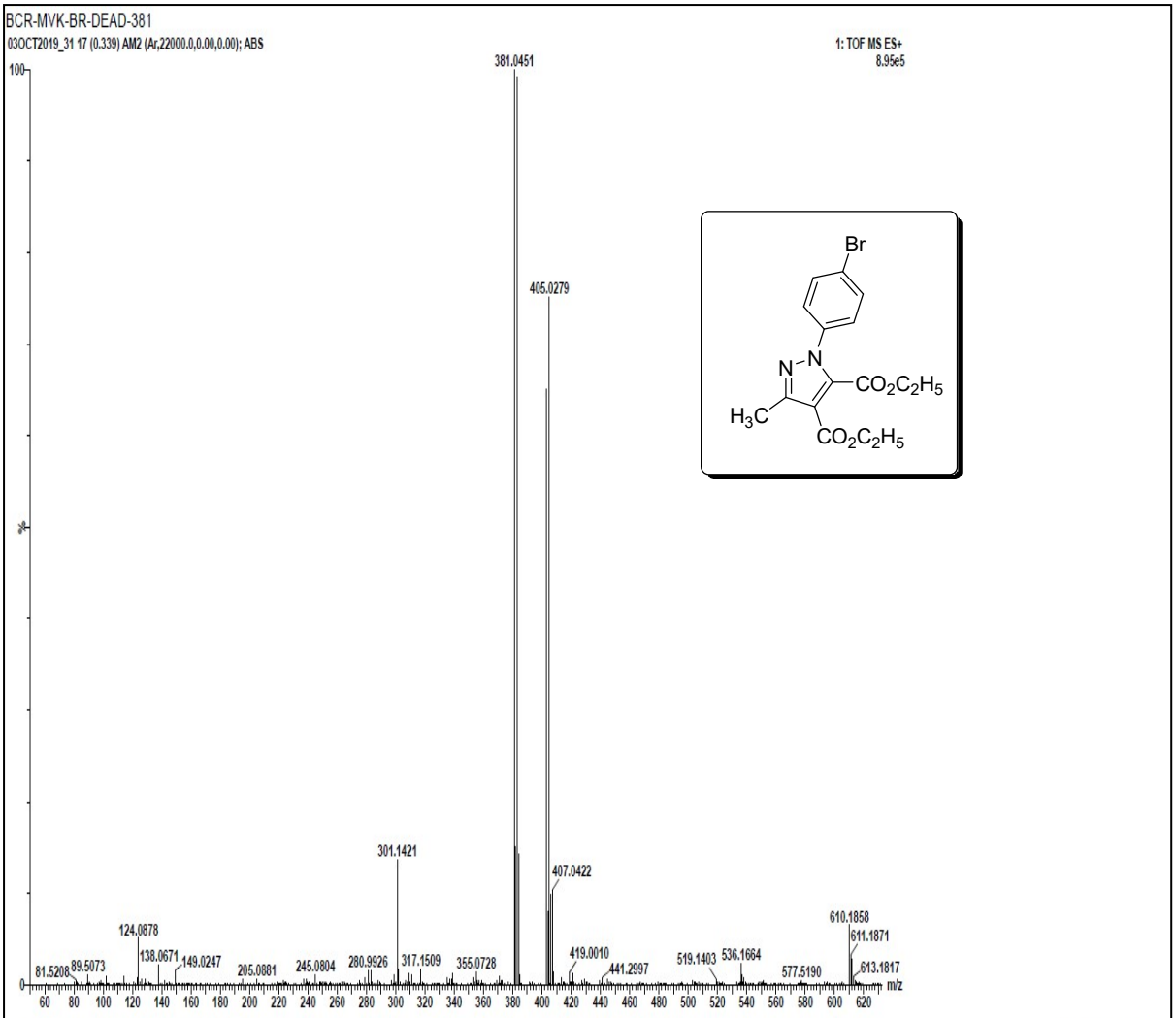
HRMS spectrum of compound **5h**



^{1}H NMR spectrum of compound **5i**



^{13}C NMR spectrum of compound **5i**

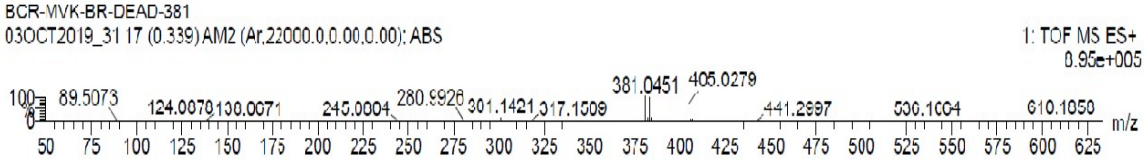


Elemental Composition Report **Page 1**

Single Mass Analysis

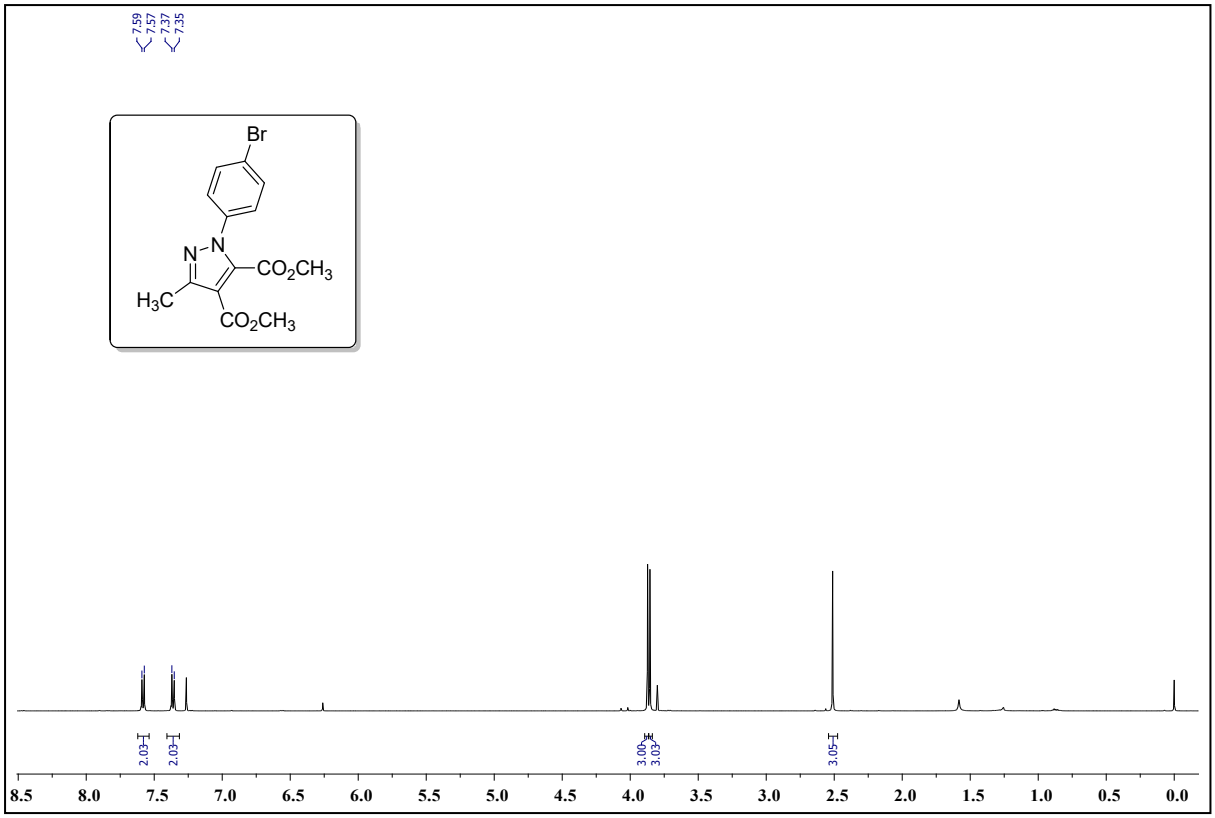
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
129 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 0-27 N: 0-3 O: 0-6 Na: 0-1 Br: 0-1

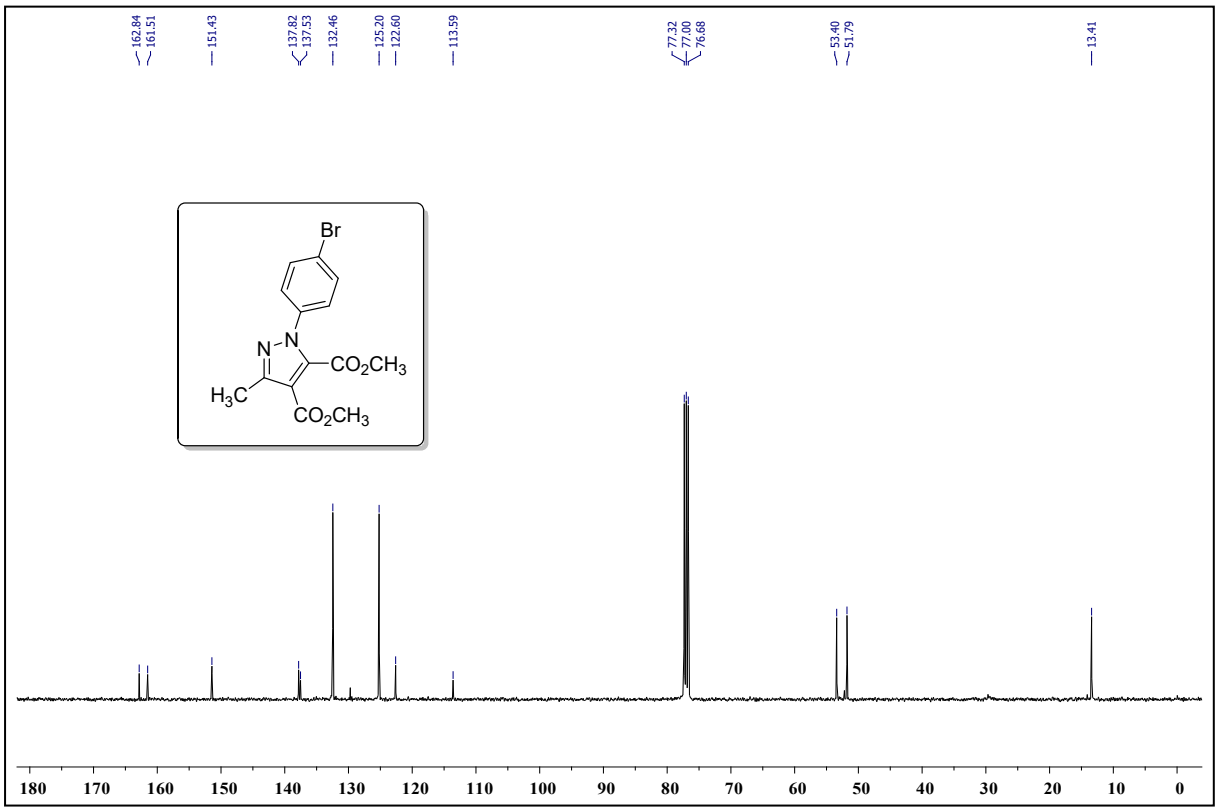


Minimum:				1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%) Formula
381.0451	381.0450	0.1	0.3	8.5	510.9	n/a	n/a C15 H18 N2 O4 Br

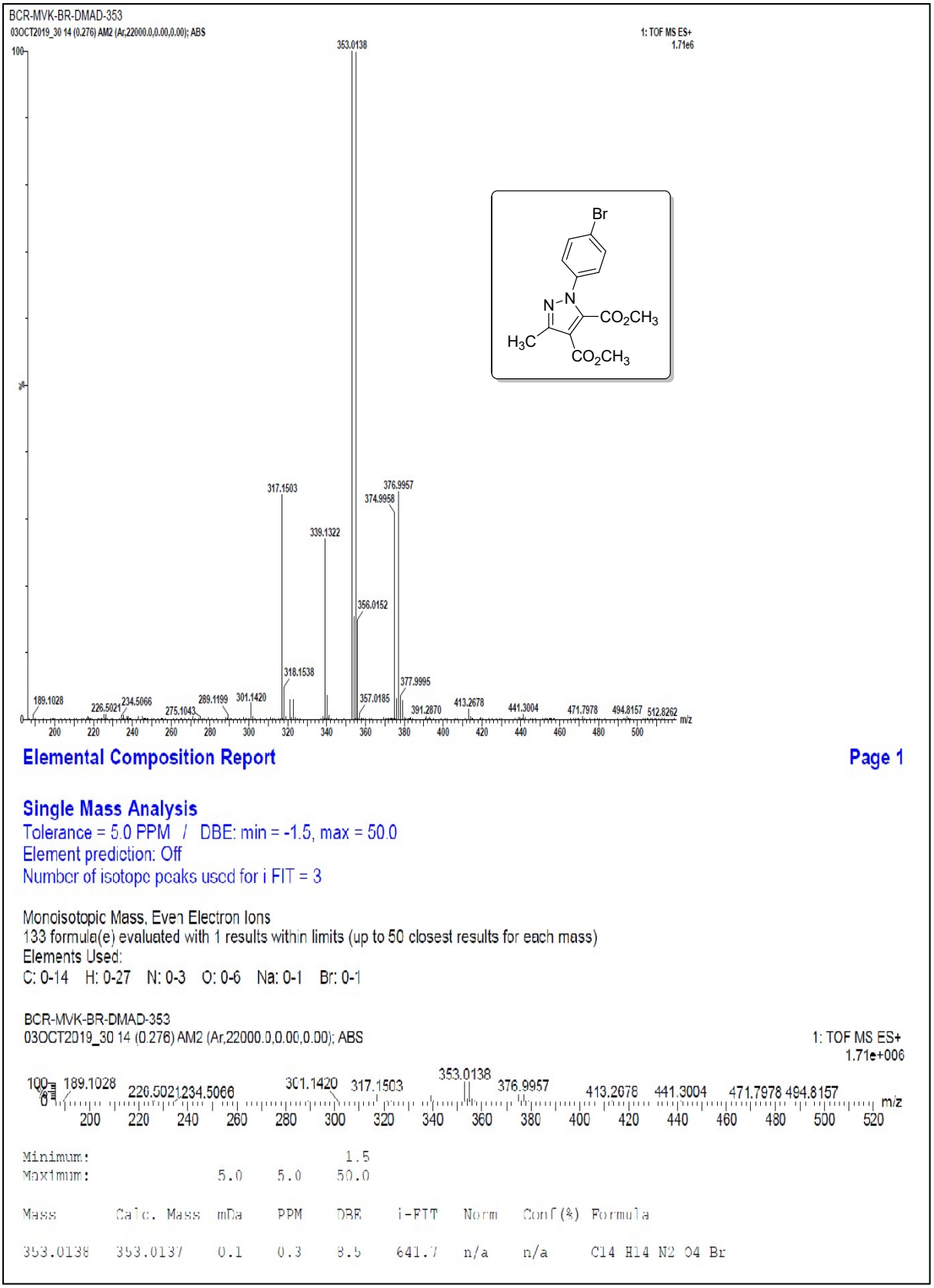
HRMS spectrum of compound **5i**



^{1}H NMR spectrum of compound **5j**



^{13}C NMR spectrum of compound **5j**



Elemental Composition Report **Page 1**

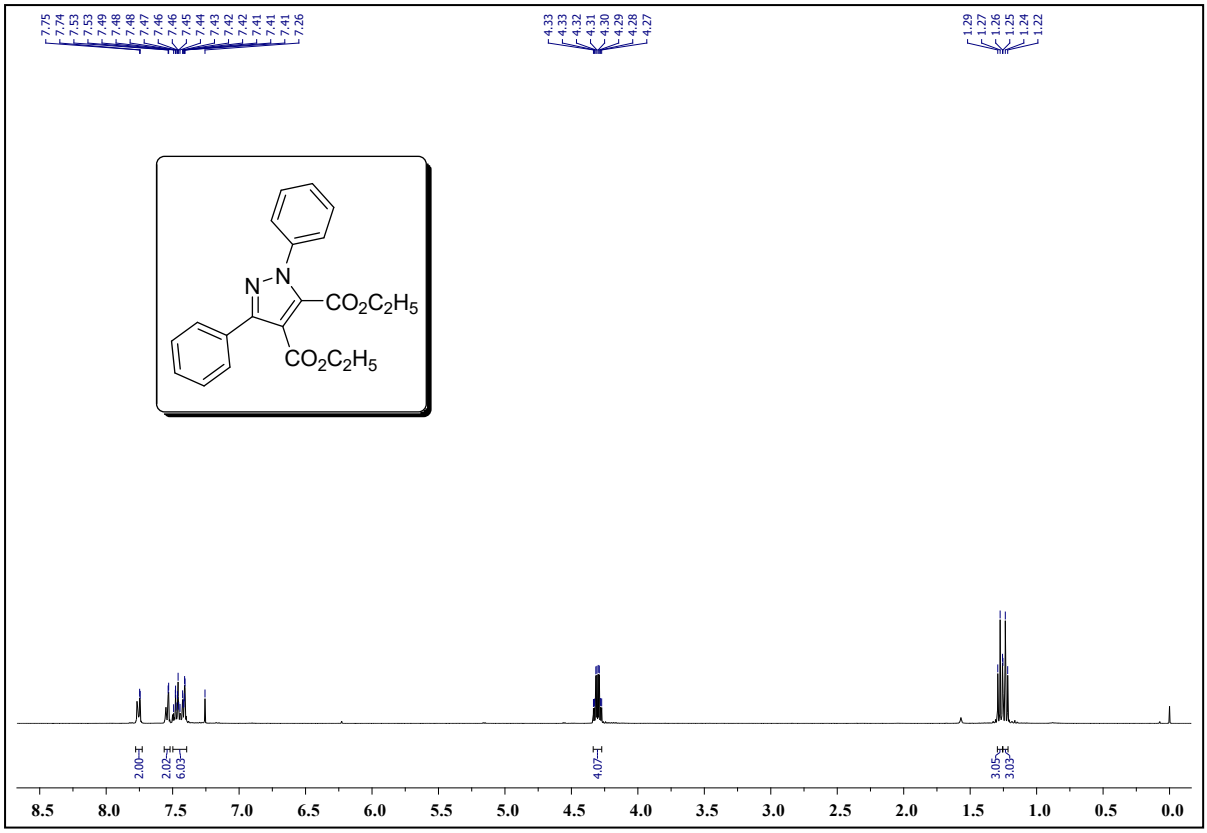
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i FIT = 3

Monoisotopic Mass, Even Electron Ions
133 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-14 H: 0-27 N: 0-3 O: 0-6 Na: 0-1 Br: 0-1

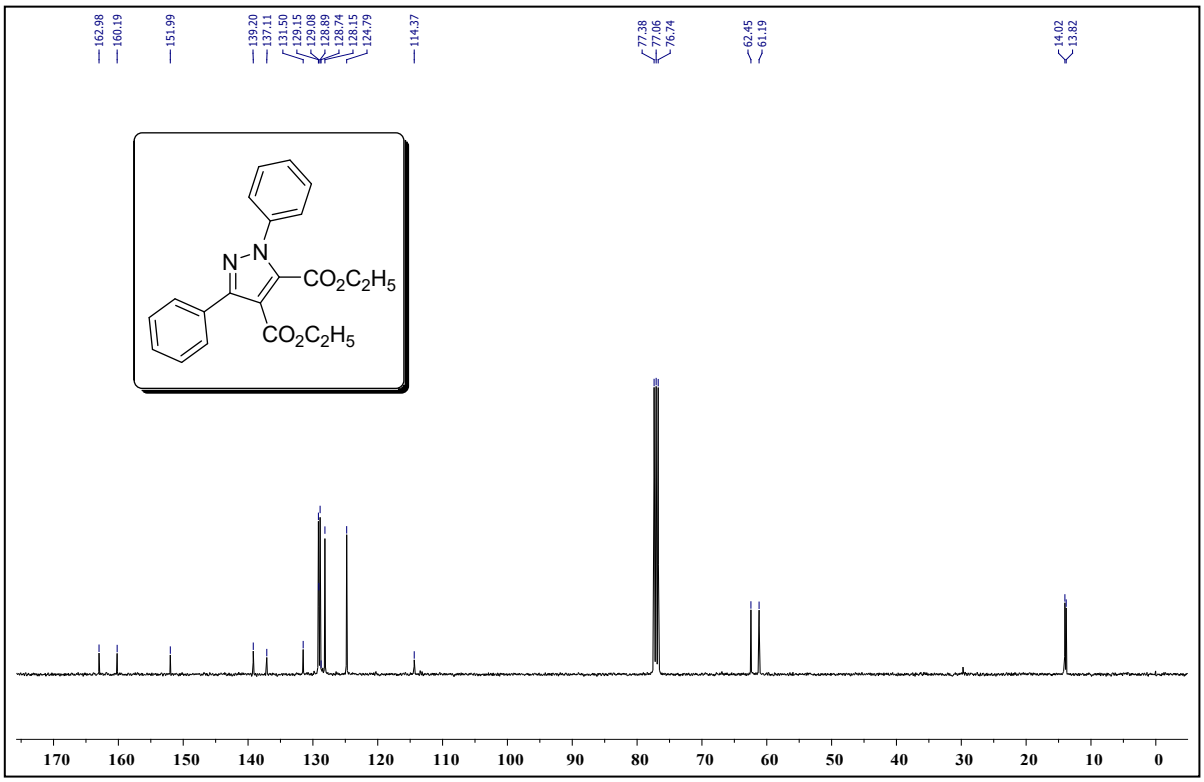
BCR-MVK-BR-DMAD-353
03OCT2019_30 14 (0.276) AM2 (Ar,22000.0,0.00,0.00); ABS
1: TOF MS ES+
1.71e+006

Minimum:				1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
353.0138	353.0137	0.1	0.3	8.5	641.7	n/a	n/a	C14 H14 N2 O4 Br

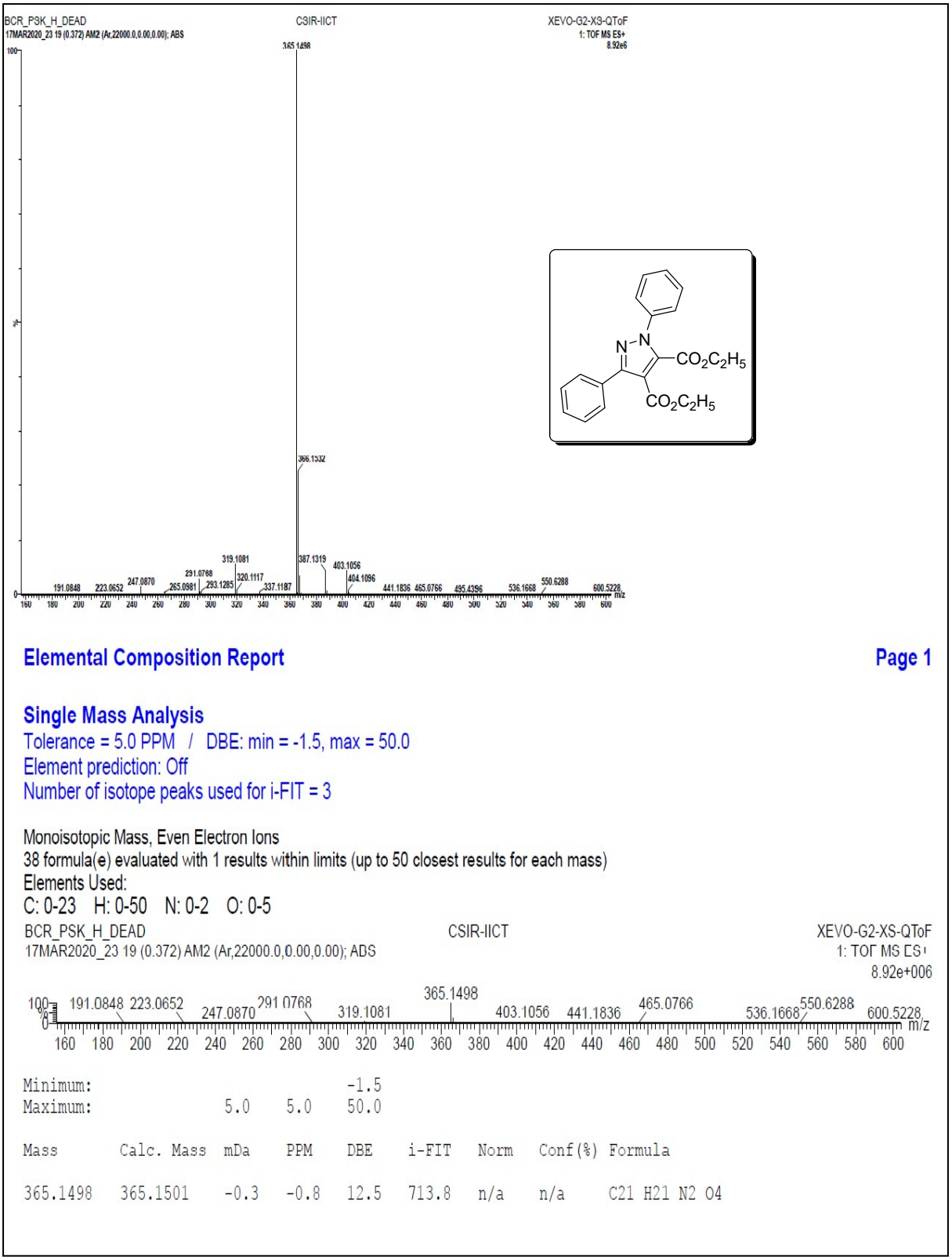
HRMS spectrum of compound **5j**



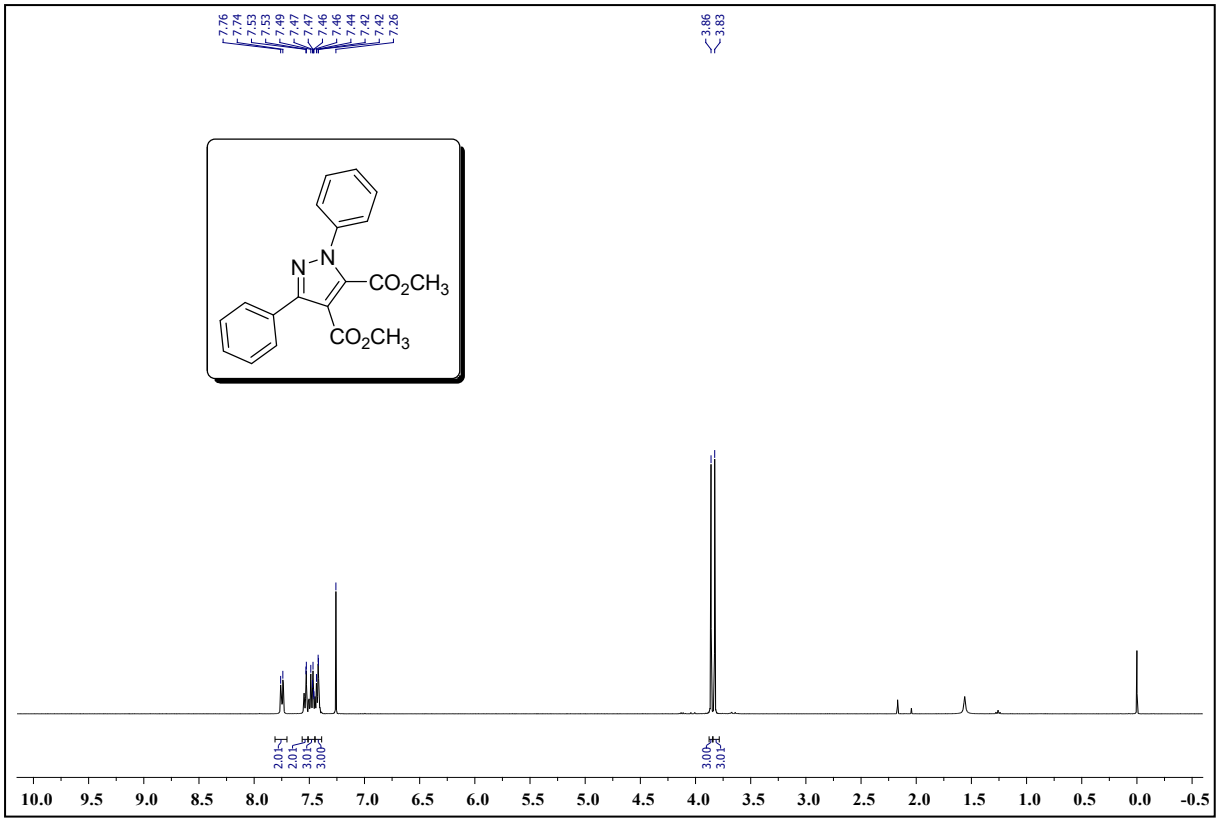
^{1}H NMR spectrum of compound **5k**



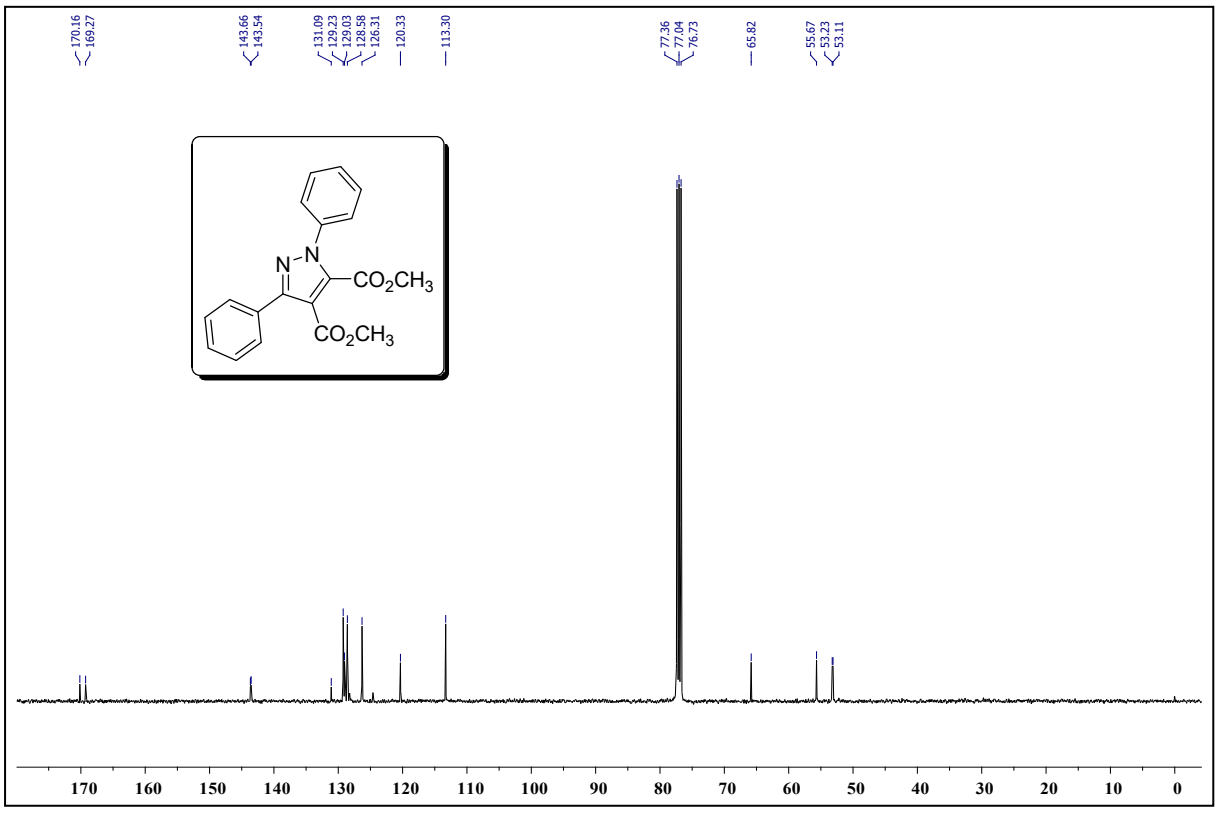
^{13}C NMR spectrum of compound **5k**



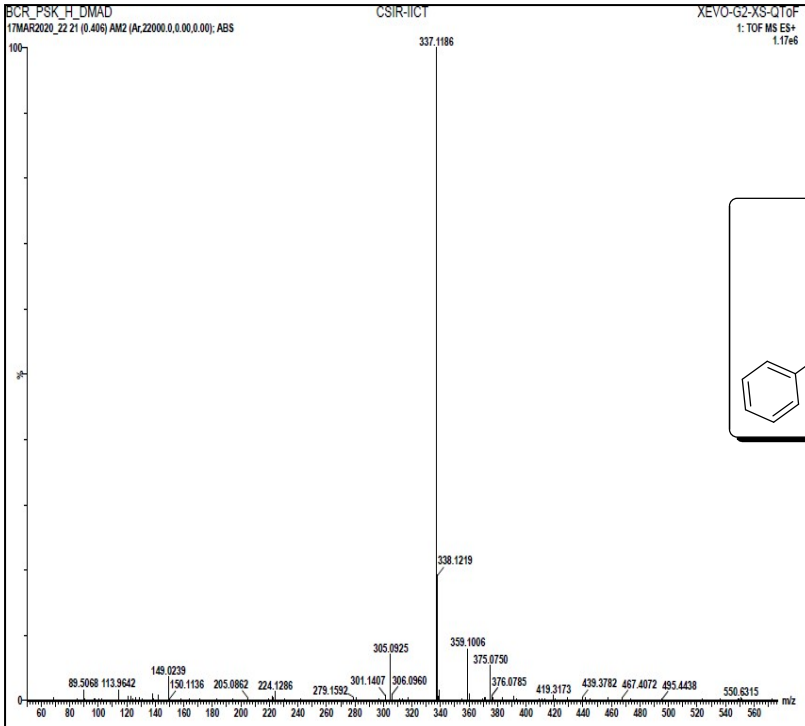
HRMS spectrum of compound **5k**

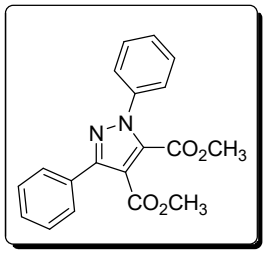


^{1}H NMR spectrum of compound **5l**



^{13}C NMR spectrum of compound **5l**



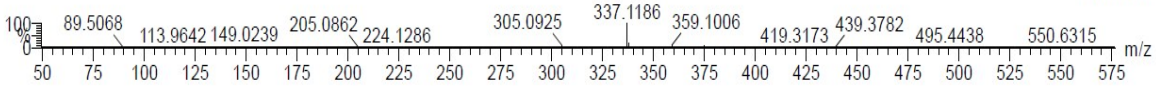


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

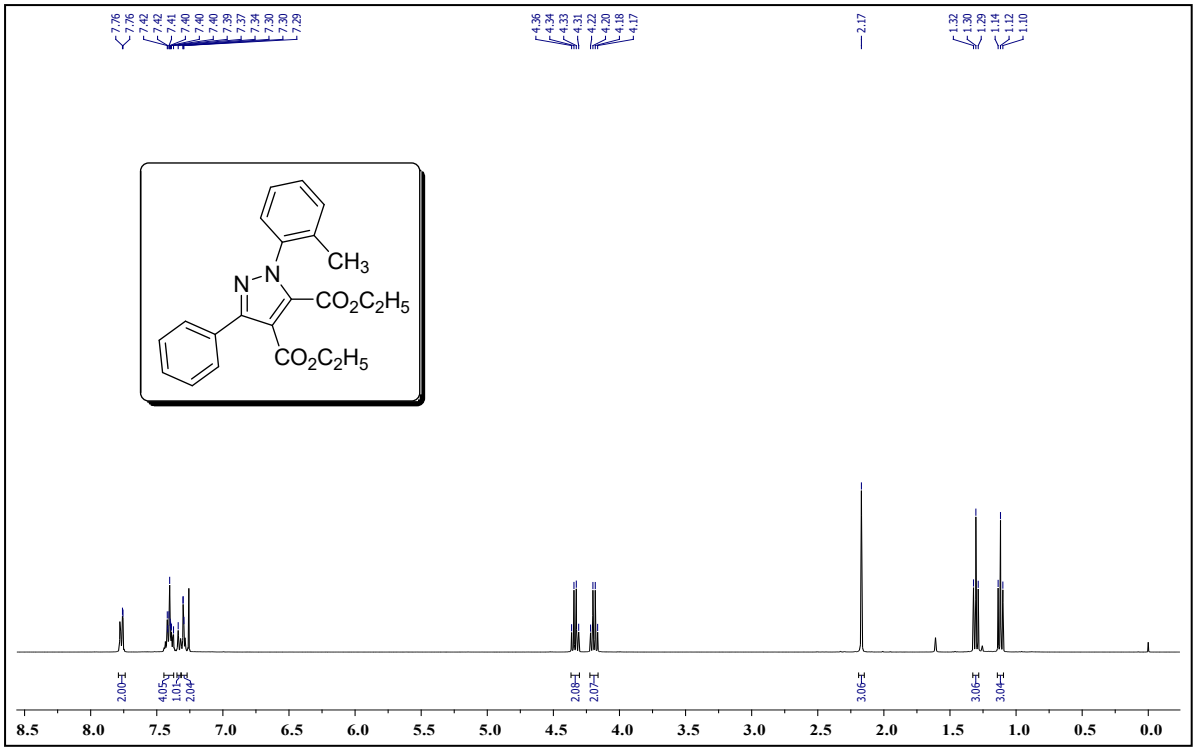
Monoisotopic Mass, Even Electron Ions
57 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-50 N: 0-2 O: 0-5

BCR_PSK_H_DMAD
17MAR2020_22 21 (0.406) AM2 (Ar,22000.0,0.00,0.00); ABS
CSIR-IICT
XEVO-G2-XS-QToF
1: TOF MS ES+
1.17e+006

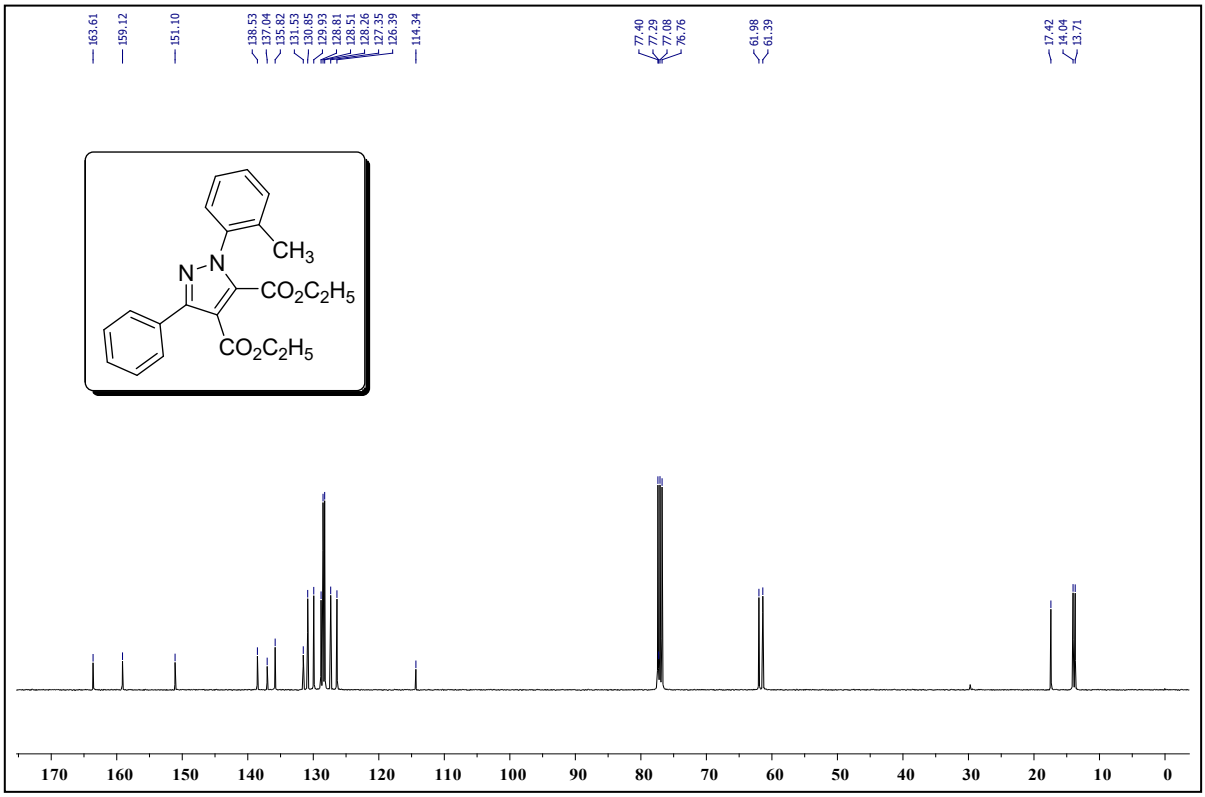


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
337.1186	337.1188	-0.2	-0.6	12.5	501.9	n/a	n/a	C19 H17 N2 O4

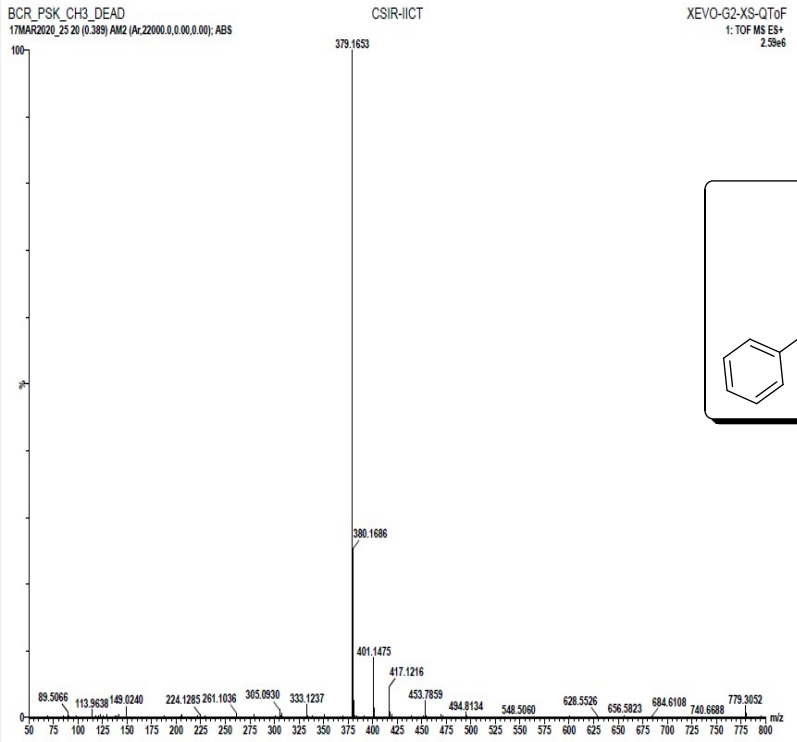
HRMS spectrum of compound **5l**



^{1}H NMR spectrum of compound **5m**



^{13}C NMR spectrum of compound **5m**



Elemental Composition Report

Single Mass Analysis

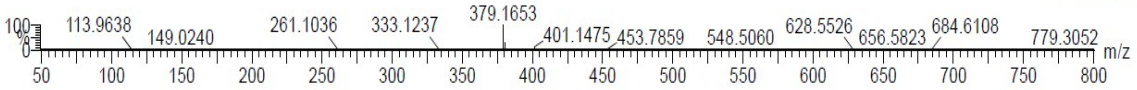
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
29 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-50 N: 0-2 O: 0-5

BCR_PSK_CH3_DEAD
17MAR2020_25 20 (0.389) AM2 (Ar,22000.0,0.00,0.00); ABS

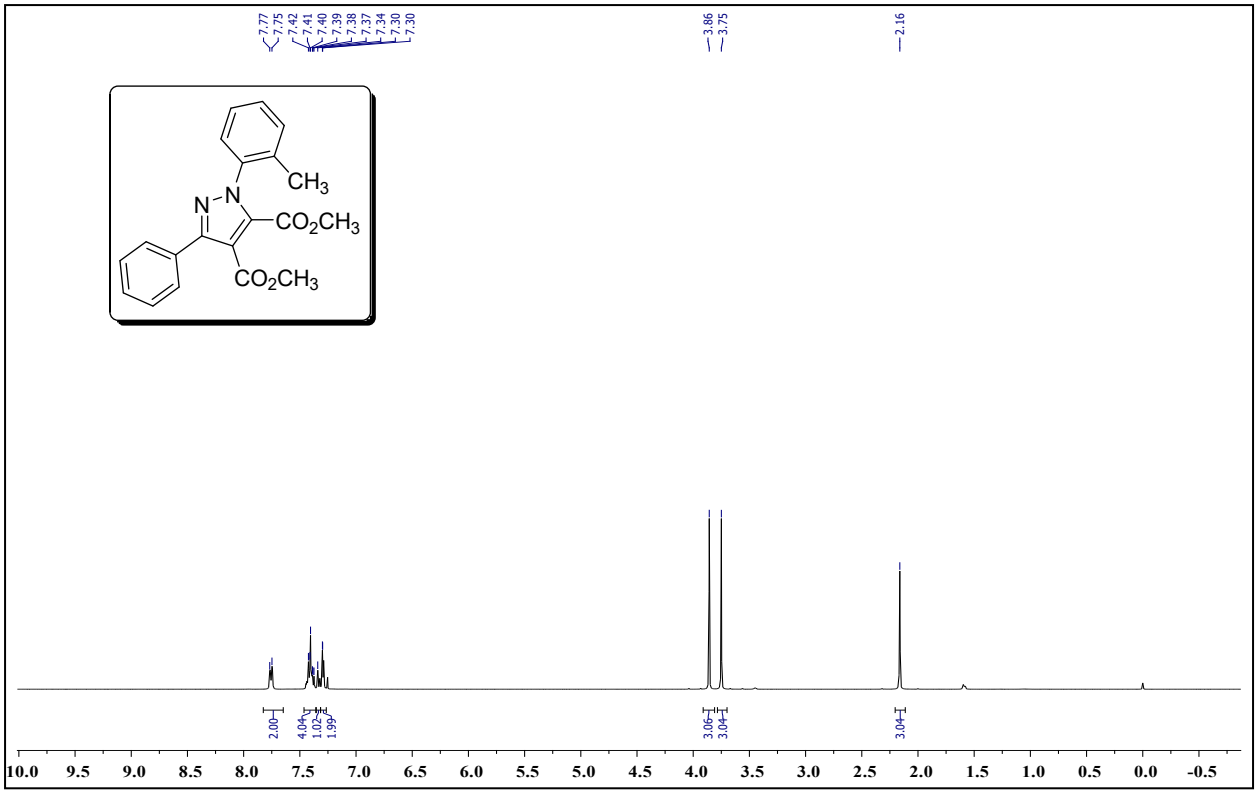
CSIR-IICT

XEVO-G2-XS-QToF
1: TOF MS ES+
2.59e+006

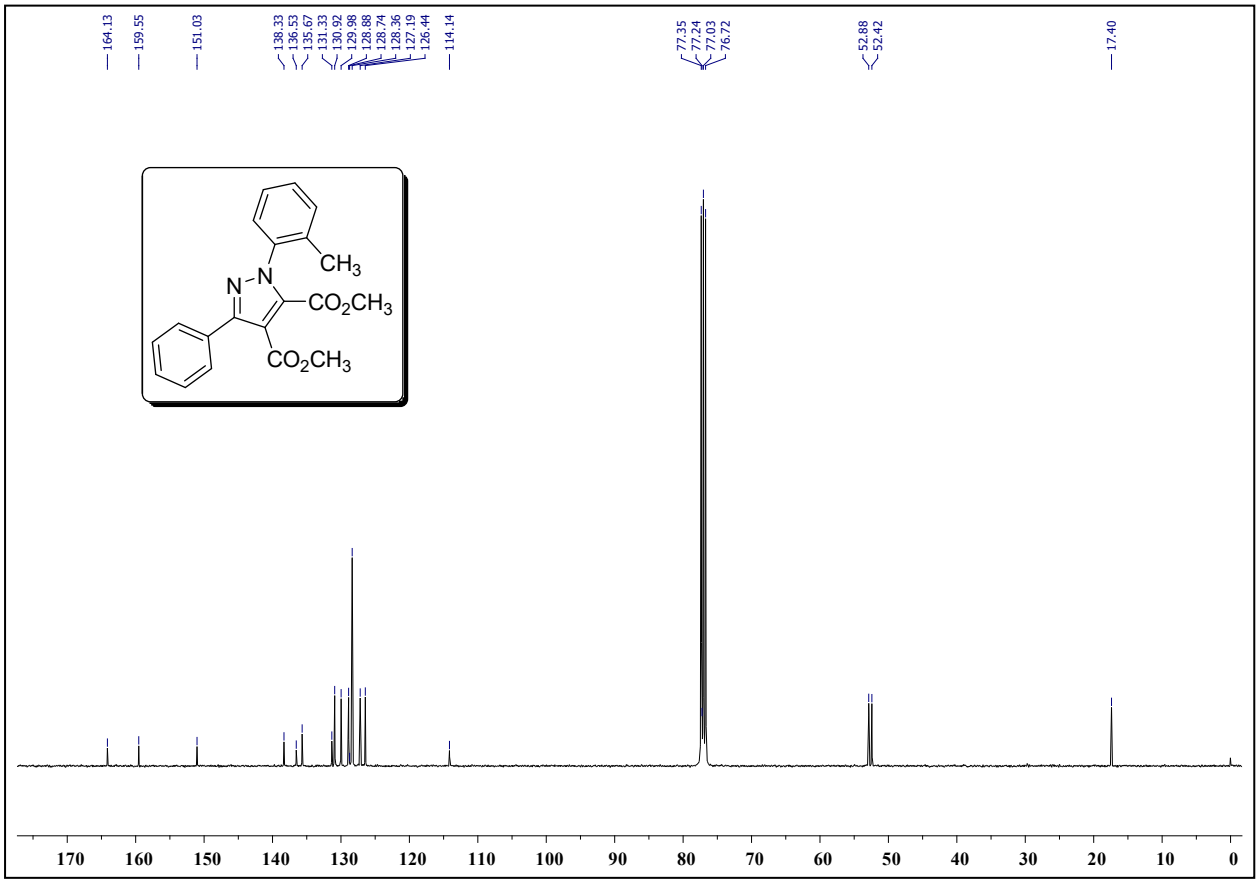


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
379.1653	379.1658	-0.5	-1.3	12.5	596.5	n/a	n/a	C22 H23 N2 O4

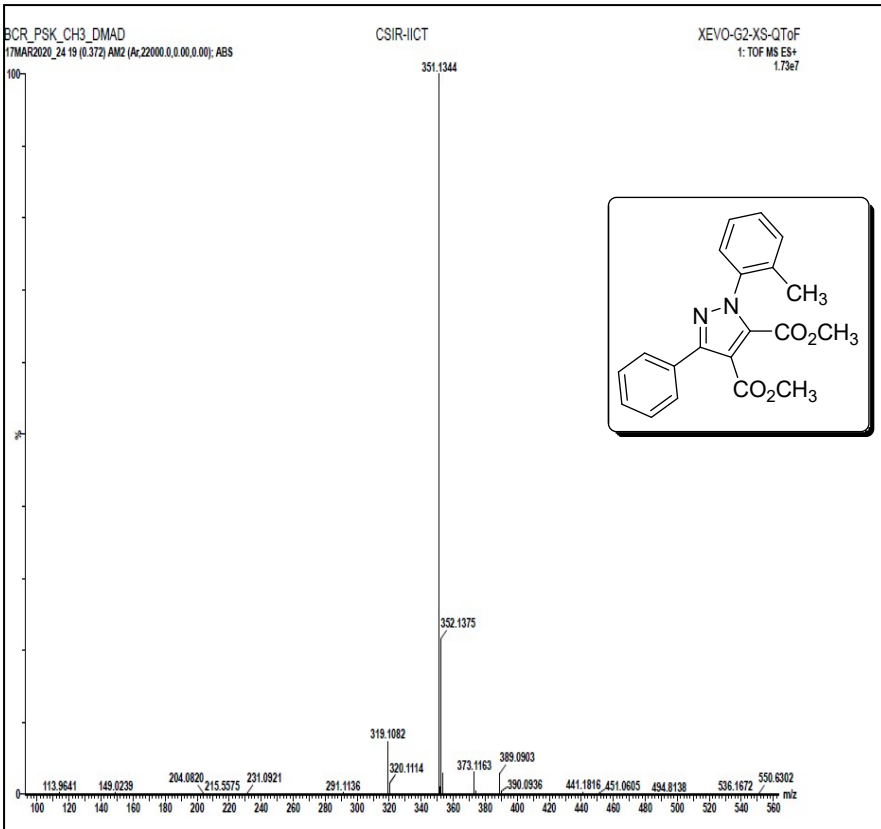
HRMS spectrum of compound **5m**



^{1}H NMR spectrum of compound **5n**



^{13}C NMR spectrum of compound **5n**



Elemental Composition Report

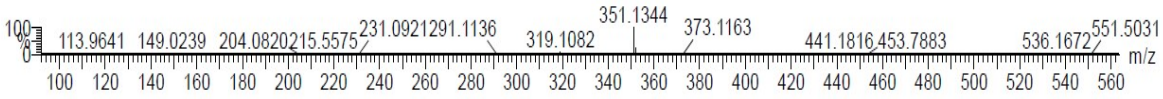
Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

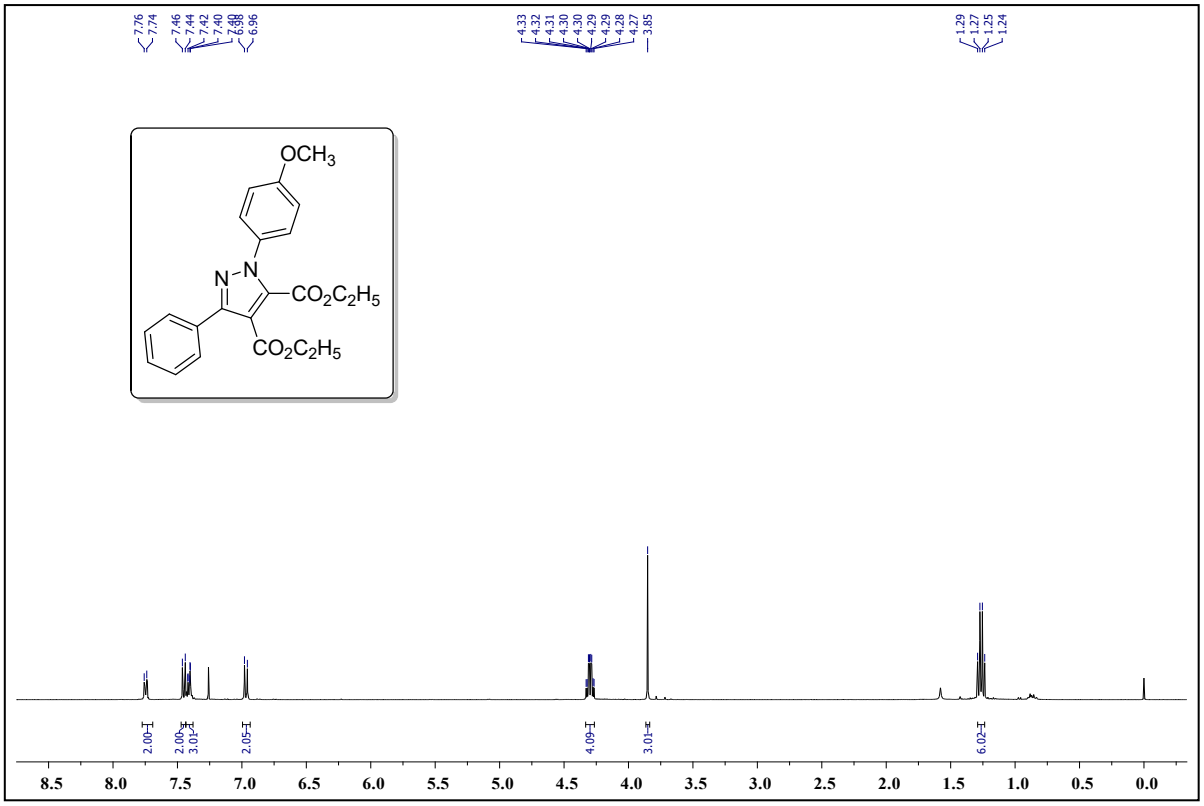
Monoisotopic Mass, Even Electron Ions
48 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-50 N: 0-2 O: 0-5

BCR_PSK_CH3_DMAD
17MAR2020_24 19 (0.372) AM2 (Ar,22000.0,0.00,0.00); ABS
CSIR-IICT
XEVO-G2-XS-QToF
1: TOF MS ES+
1.73e+007

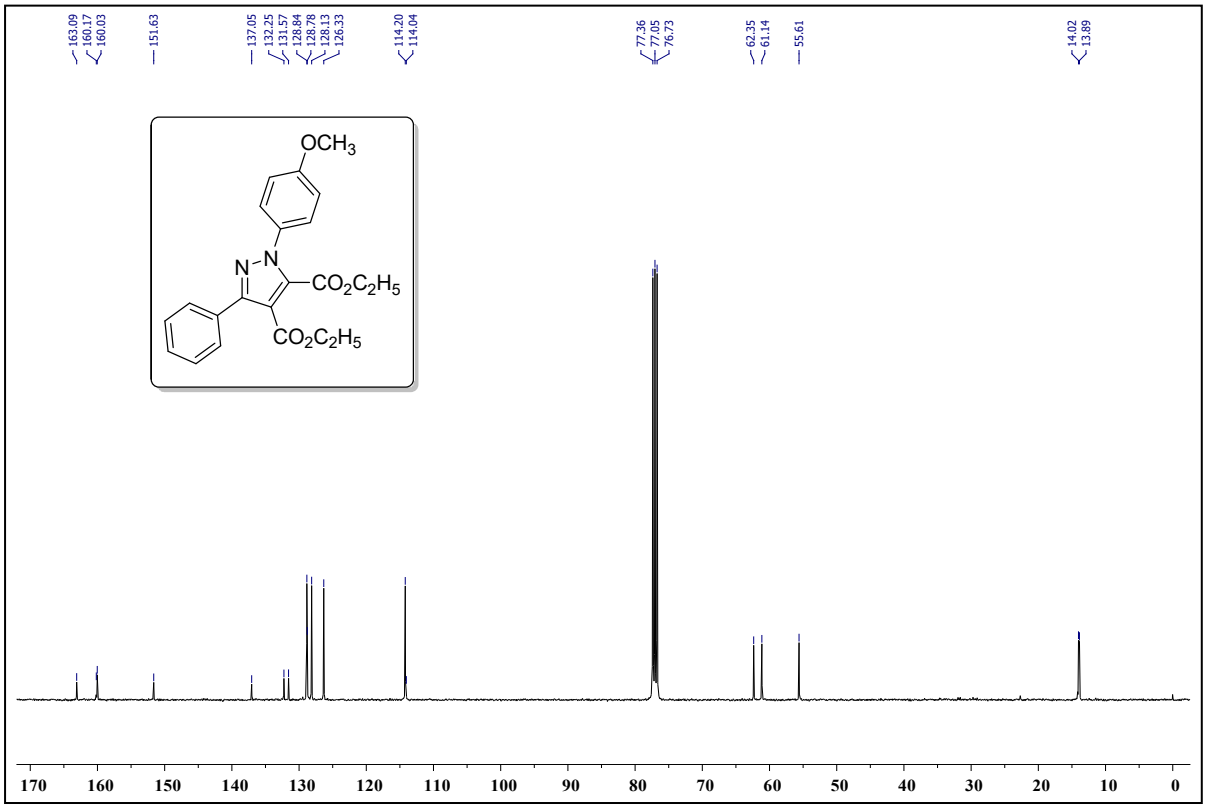


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
351.1344	351.1345	-0.1	-0.3	12.5	749.3	n/a	n/a	C20 H19 N2 O4

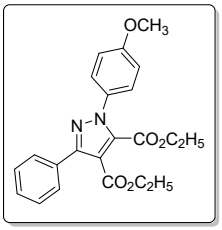
HRMS spectrum of compound **5n**



^{1}H NMR spectrum of compound **5o**



^{13}C NMR spectrum of compound **5o**



Created by: Administrator, UNIFI

Created on: Aug 24, 2020

Item name: 20200728_Elemental Compostion Aug 24, 2020 09:39:44 India Standard Time

Created time: 14:26:09 India Standard Time

Item name: BCR_PSKOCH3DEAD_395

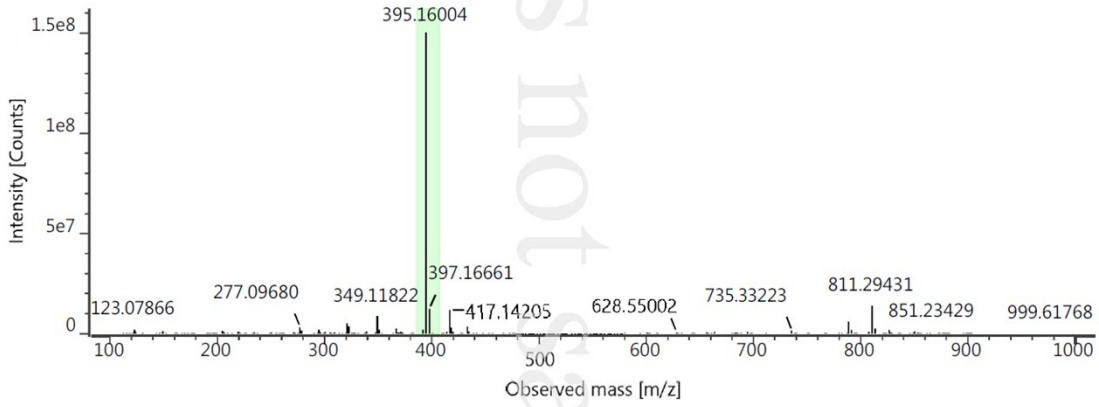
Item name: BCR_PSKOCH3DEAD_395, Sample position: 1:A,6, Replicate number: 1

.	Component name	Observed neutral mass (Da)	Neutral mass (Da)	Observed m/z	Mass error (ppm)	Adducts
1	C22H23N2O5	394.1528	372.16852	395.1600	58911.2	+H

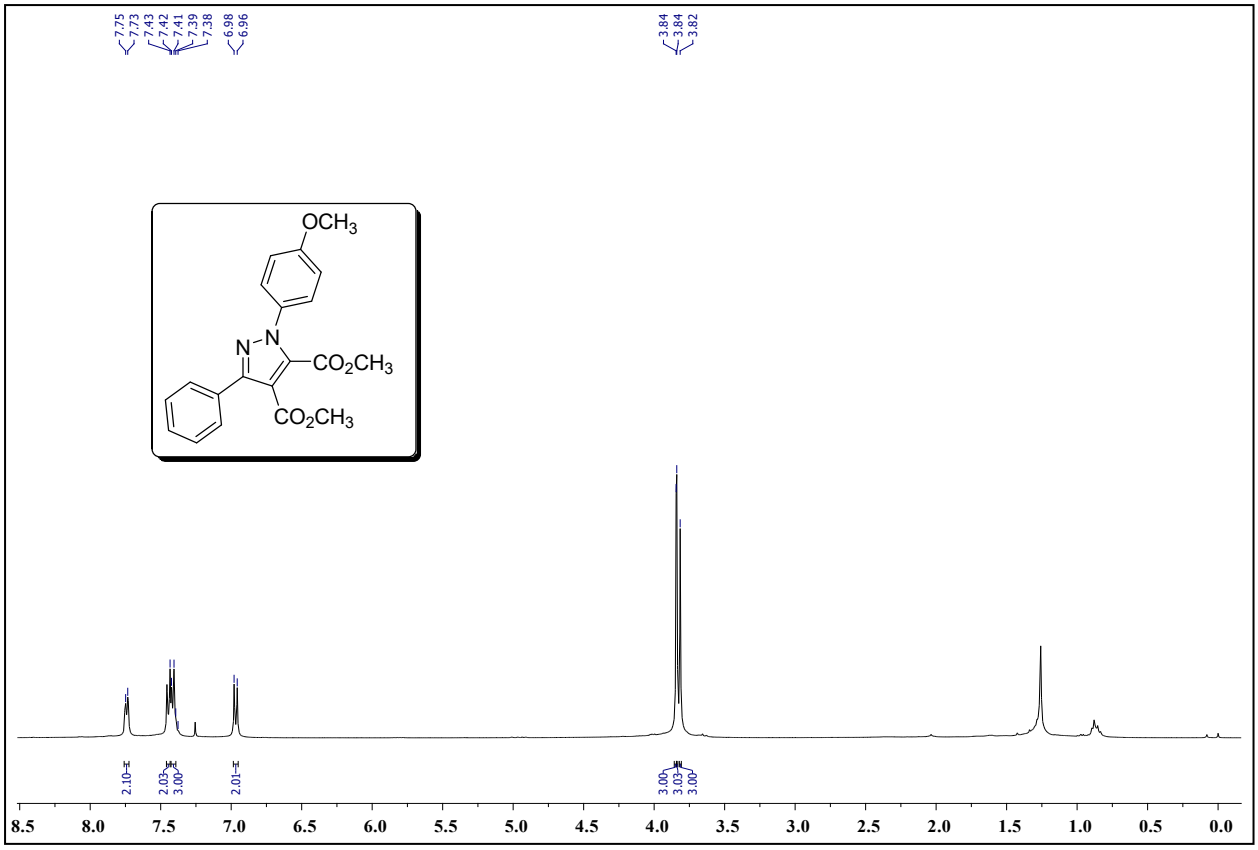
Component name: C22H23N2O5

Item name: BCR_PSKOCH3DEAD_395
Item description:

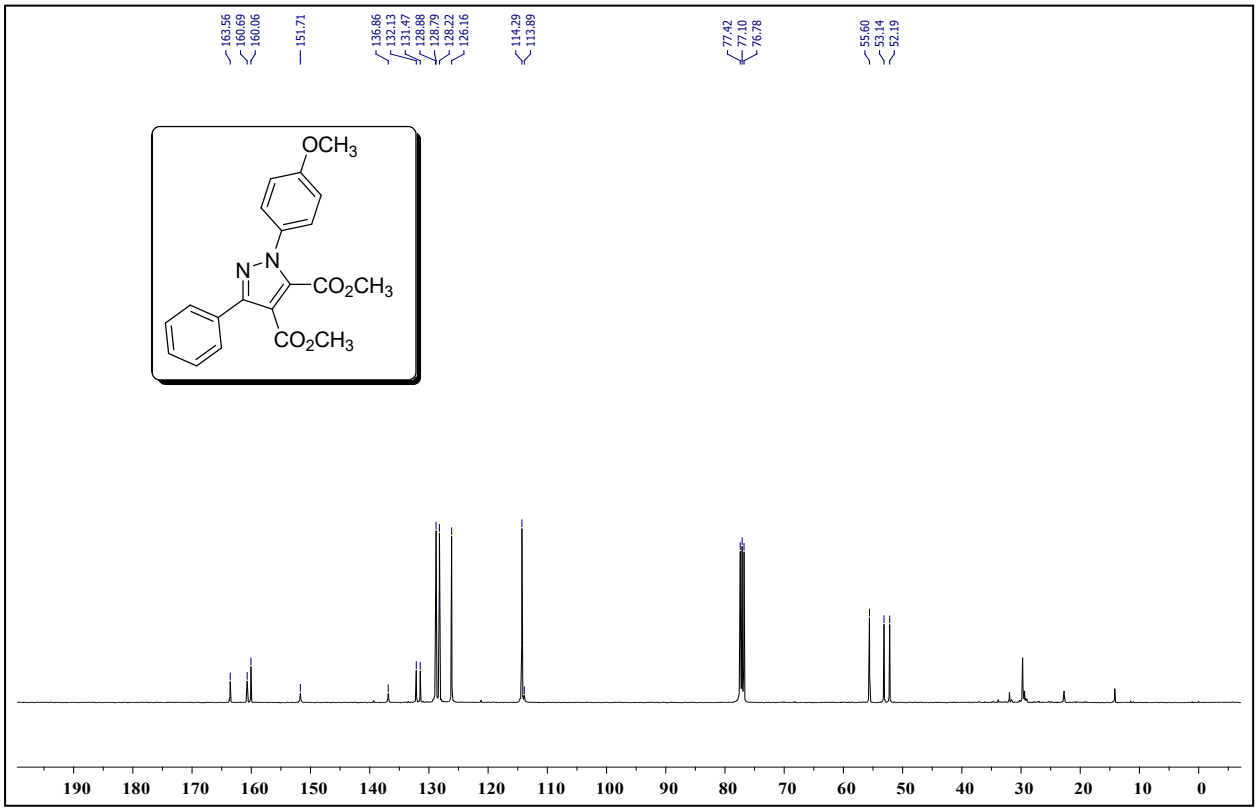
Channel name: Low energy : Time 0.3561 +/- 0.1838 minutes



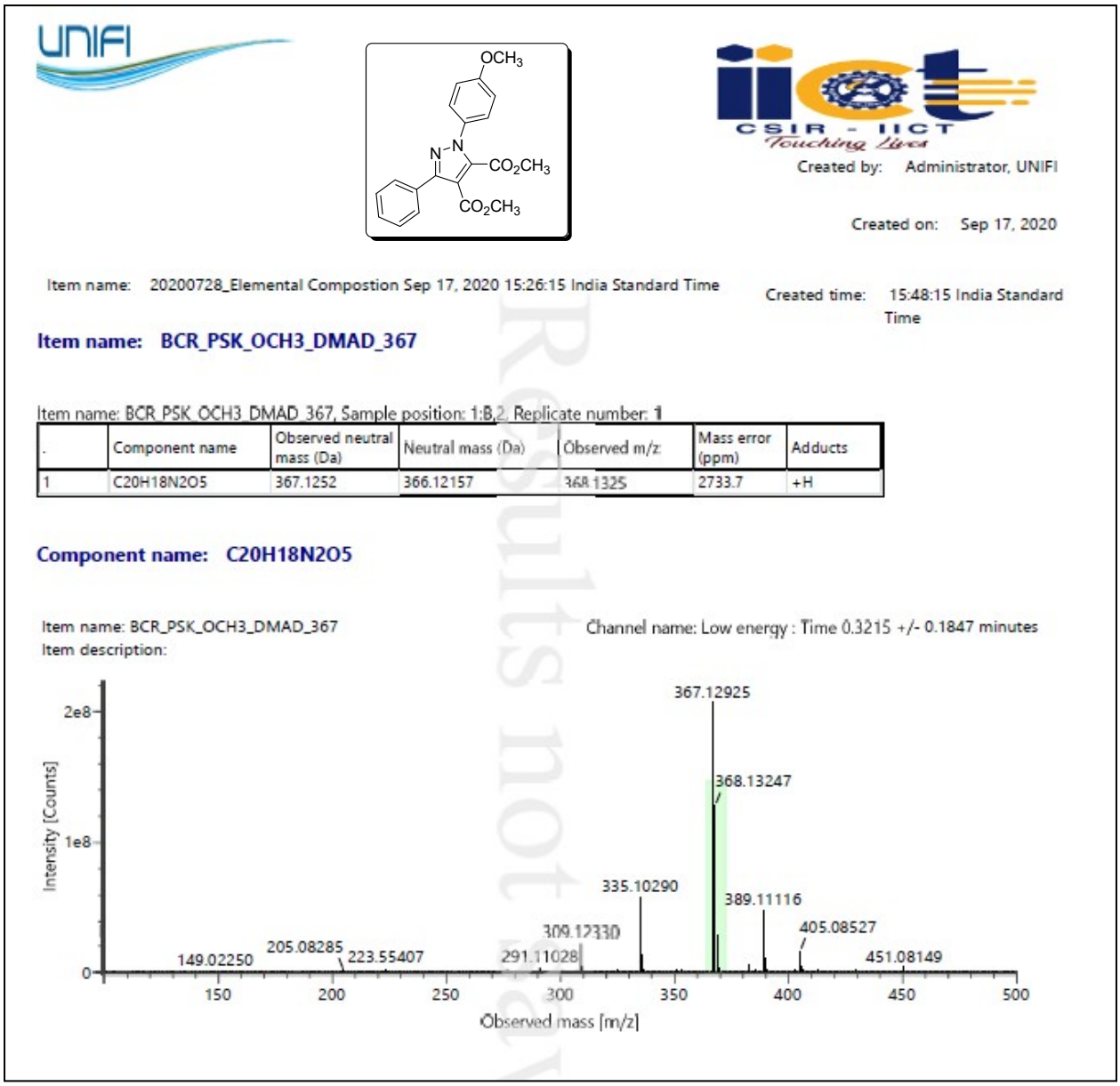
HRMS spectrum of compound **5o**



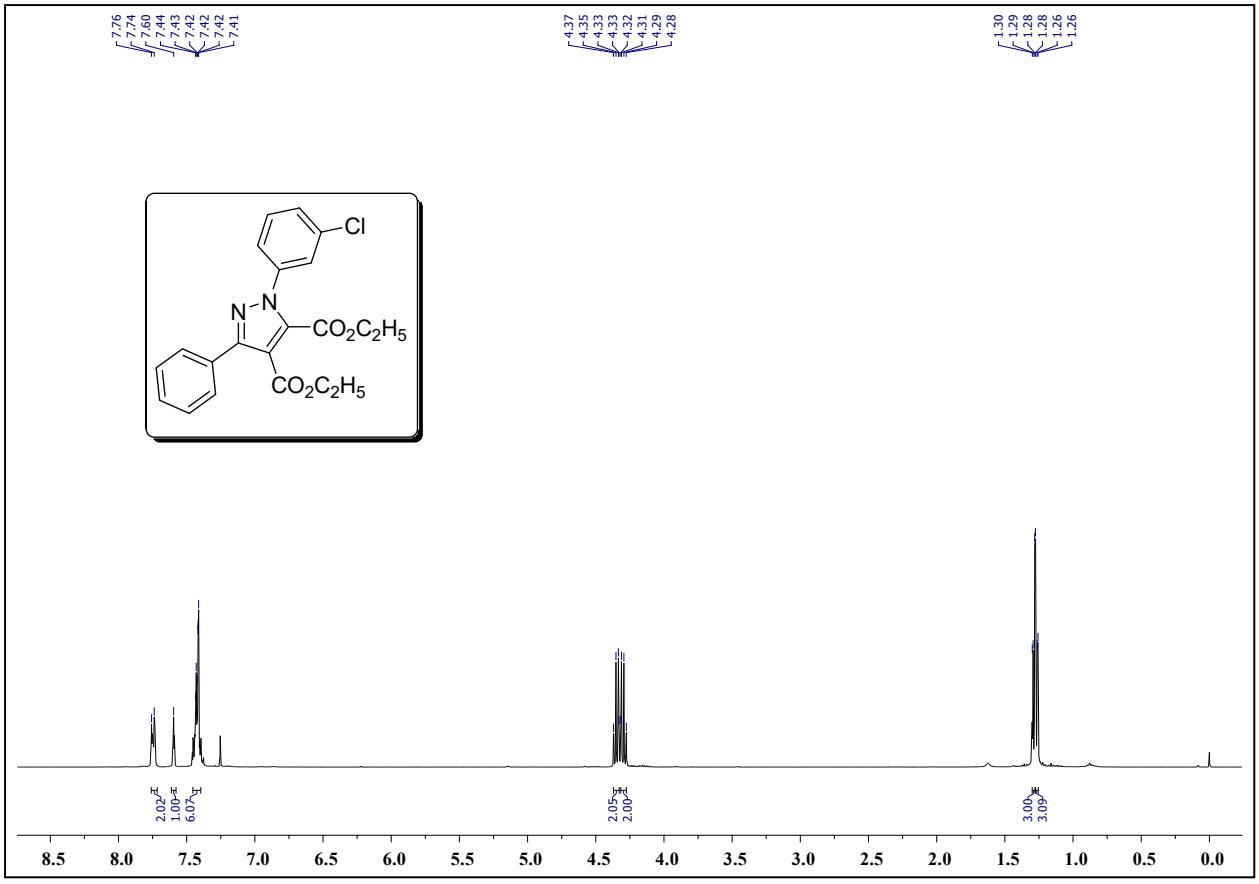
^{1}H NMR spectrum of compound **5p**



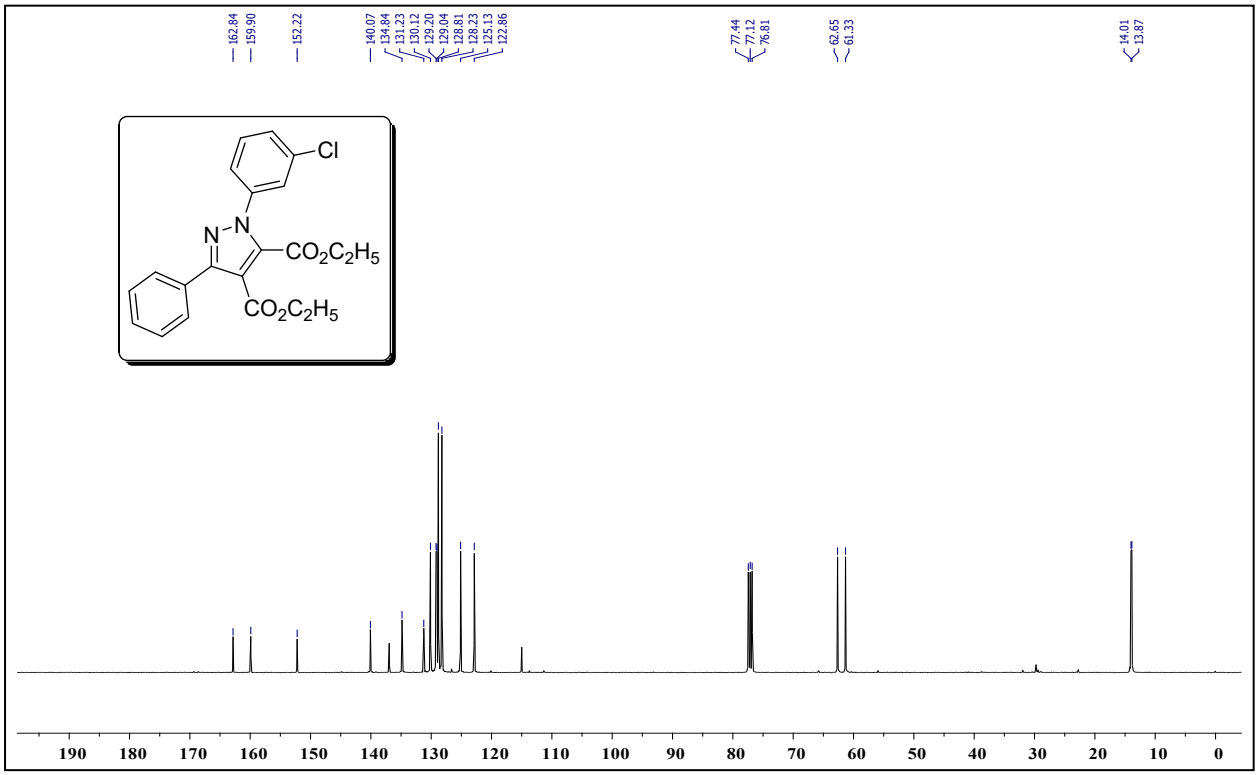
^{13}C NMR spectrum of compound **5p**



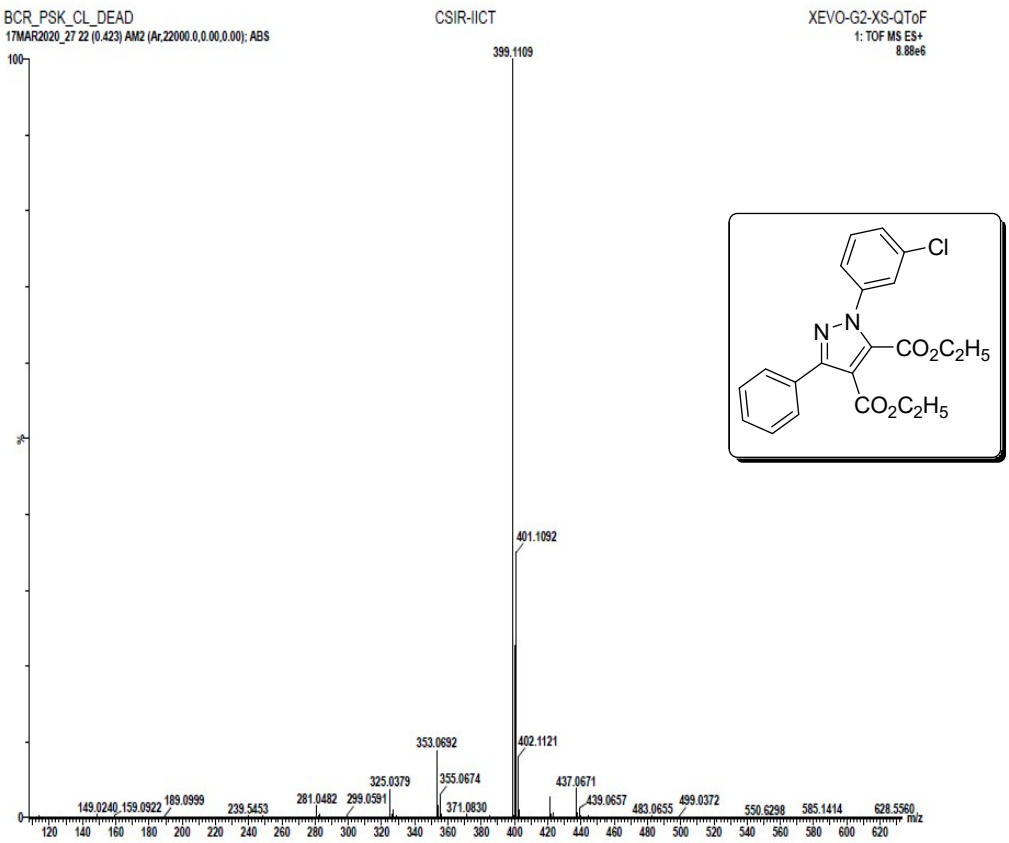
HRMS spectrum of compound **5p**



^{1}H NMR spectrum of compound **5q**



^{13}C NMR spectrum of compound **5q**



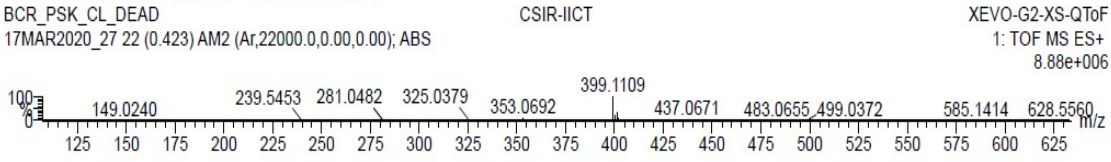
Elemental Composition Report

Page 1

Single Mass Analysis

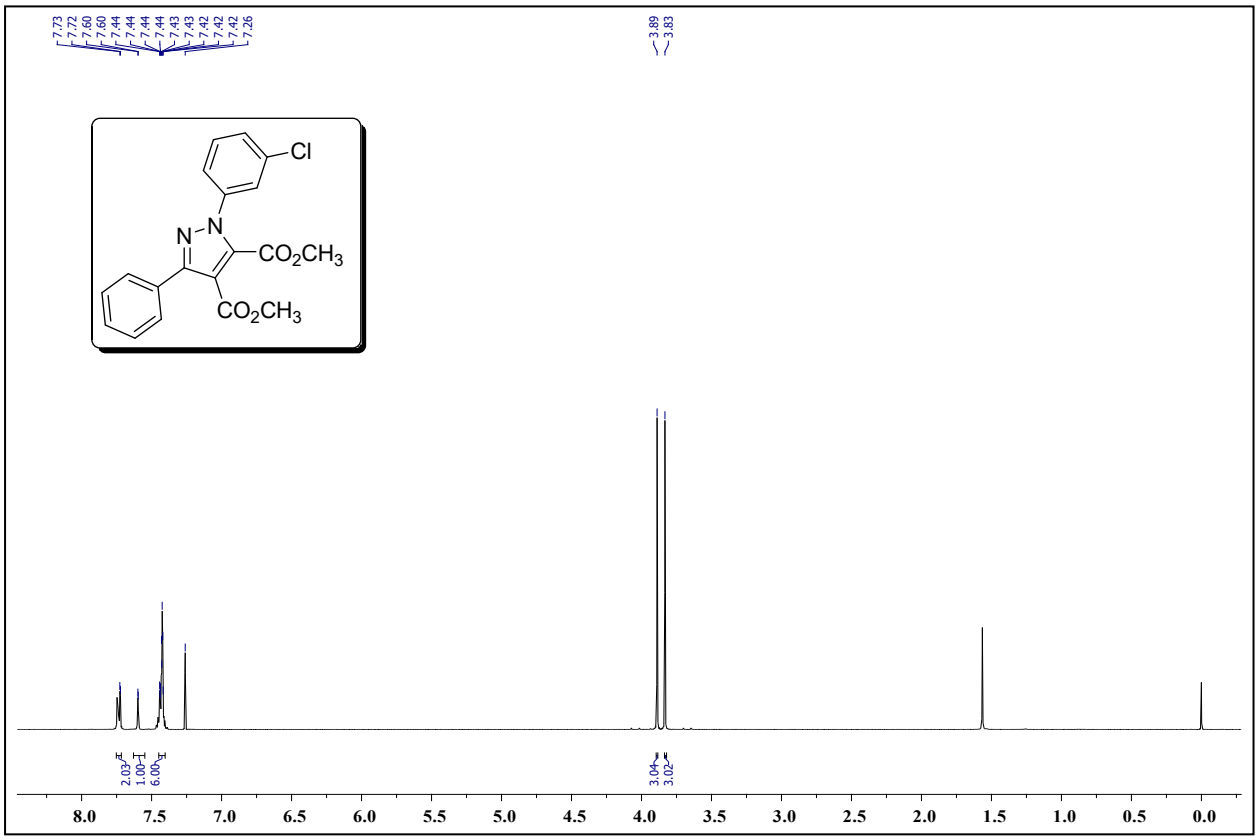
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
61 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-50 N: 0-2 O: 0-5 Cl: 0-1

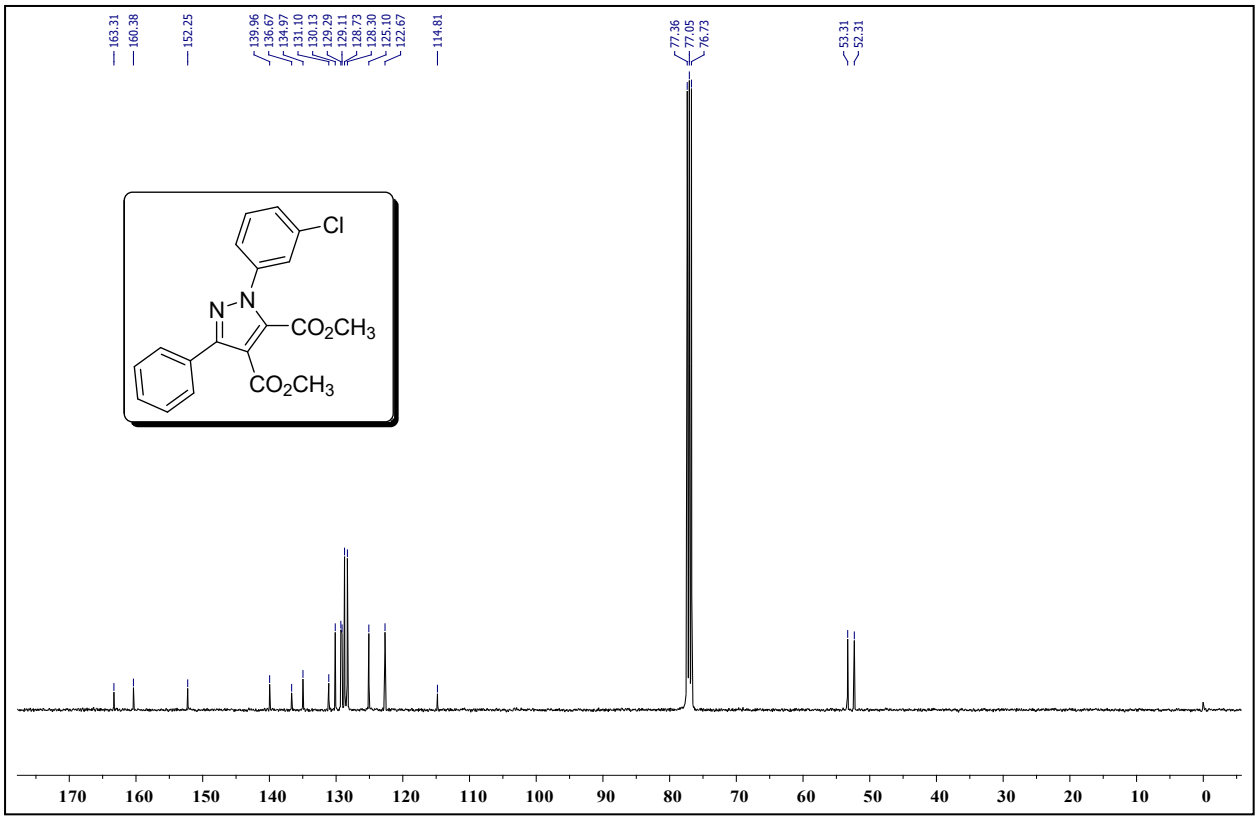


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
399.1109	399.1112	-0.3	-0.8	12.5	734.4	n/a	n/a	C21 H20 N2 O4 Cl

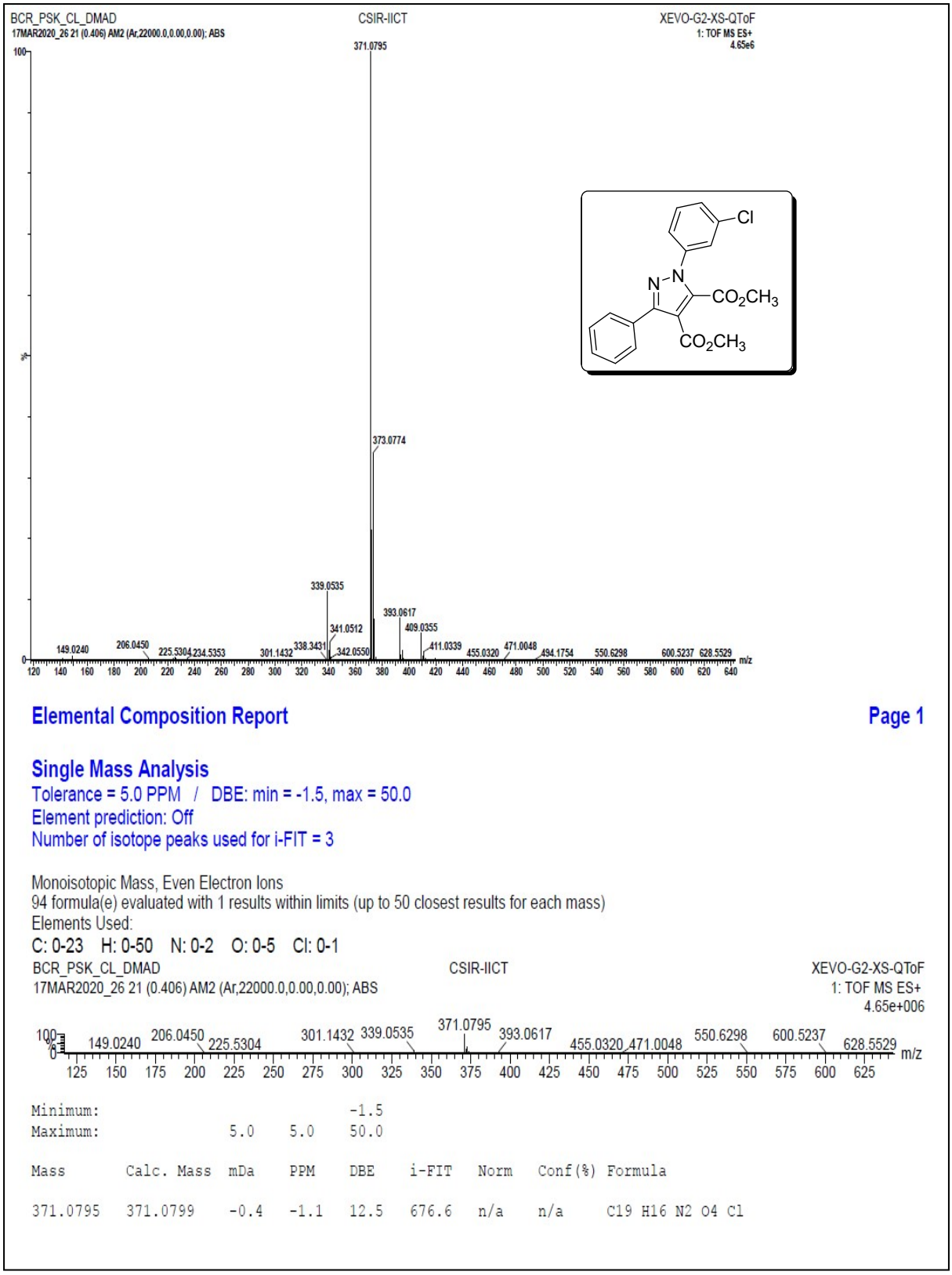
HRMS spectrum of compound **5q**



^{1}H NMR spectrum of compound **5r**

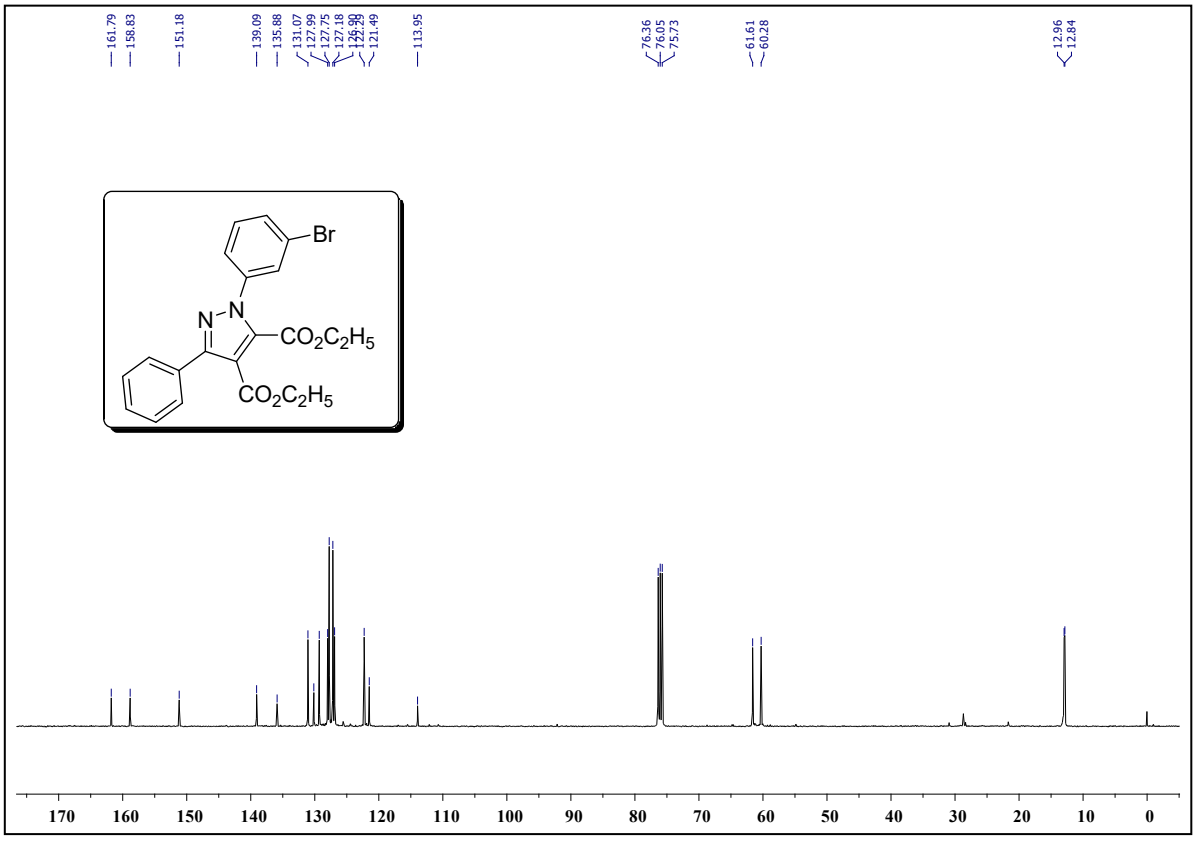


^{13}C NMR spectrum of compound **5r**

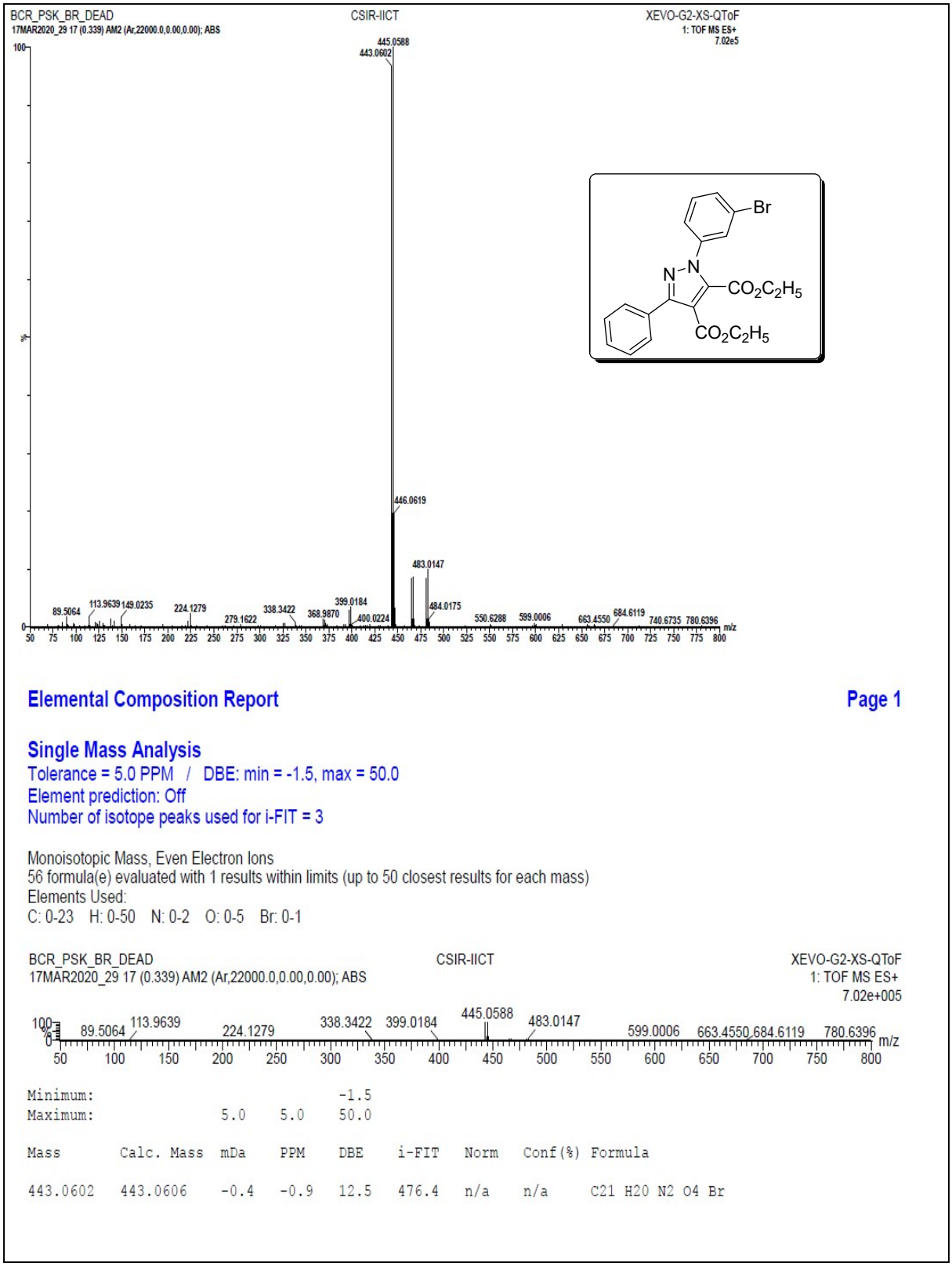


HRMS spectrum of compound **5r**

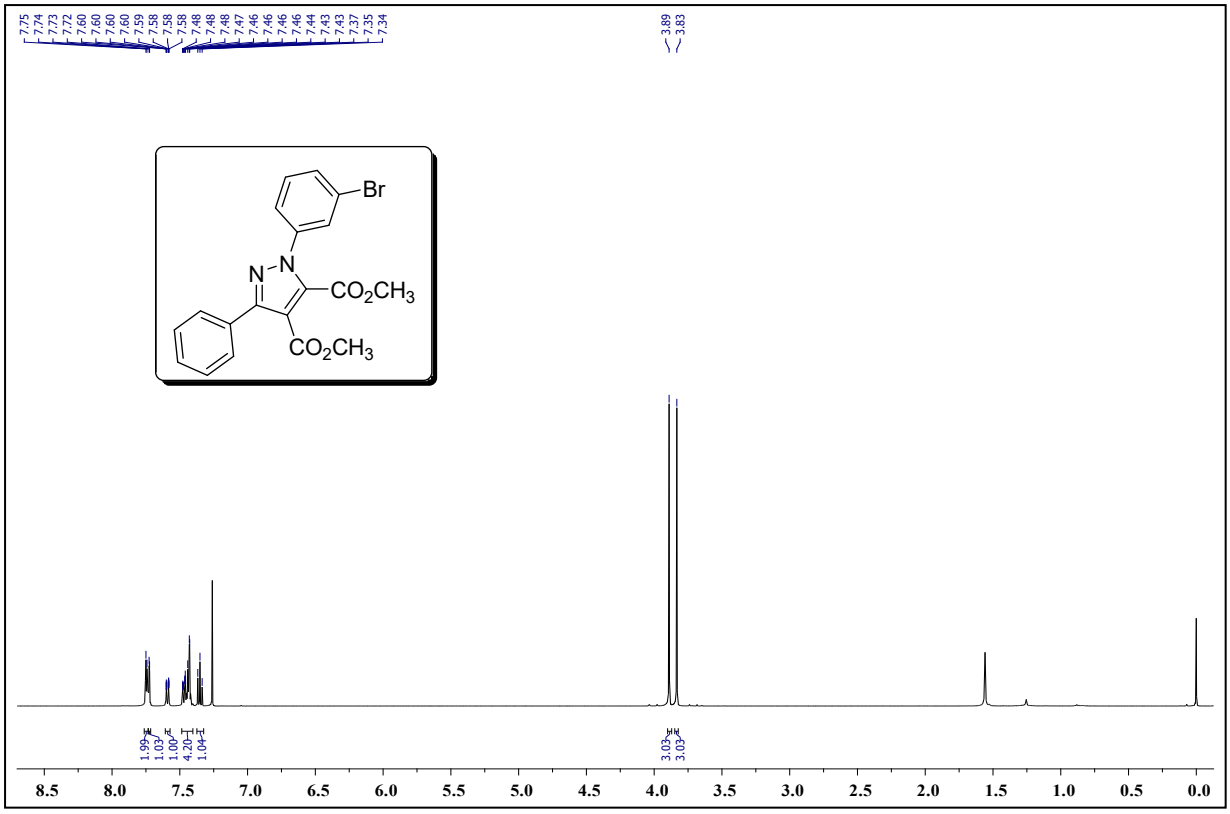
^{1}H NMR spectrum of compound **5s**



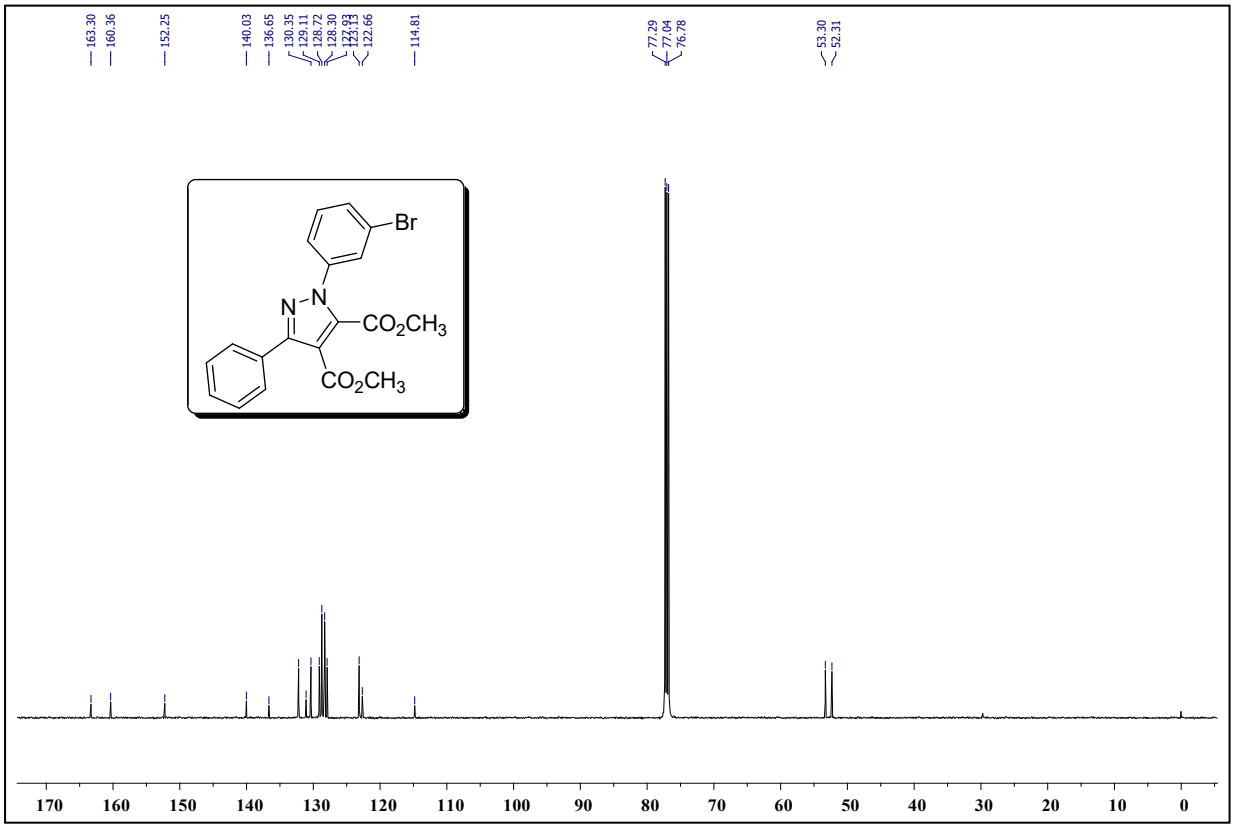
^{13}C NMR spectrum of compound **5s**



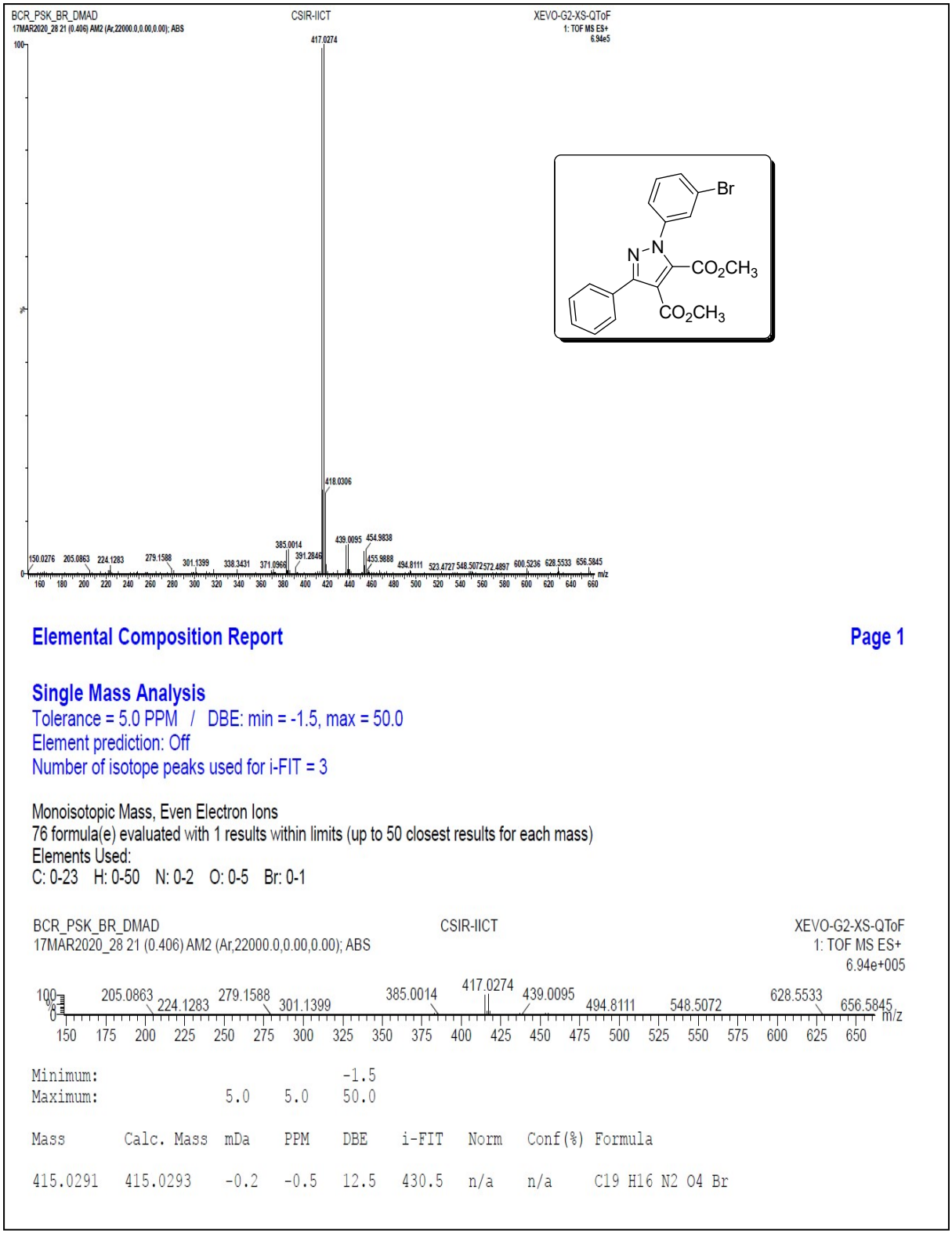
HRMS spectrum of compound **5s**



^{1}H NMR spectrum of compound **5t**

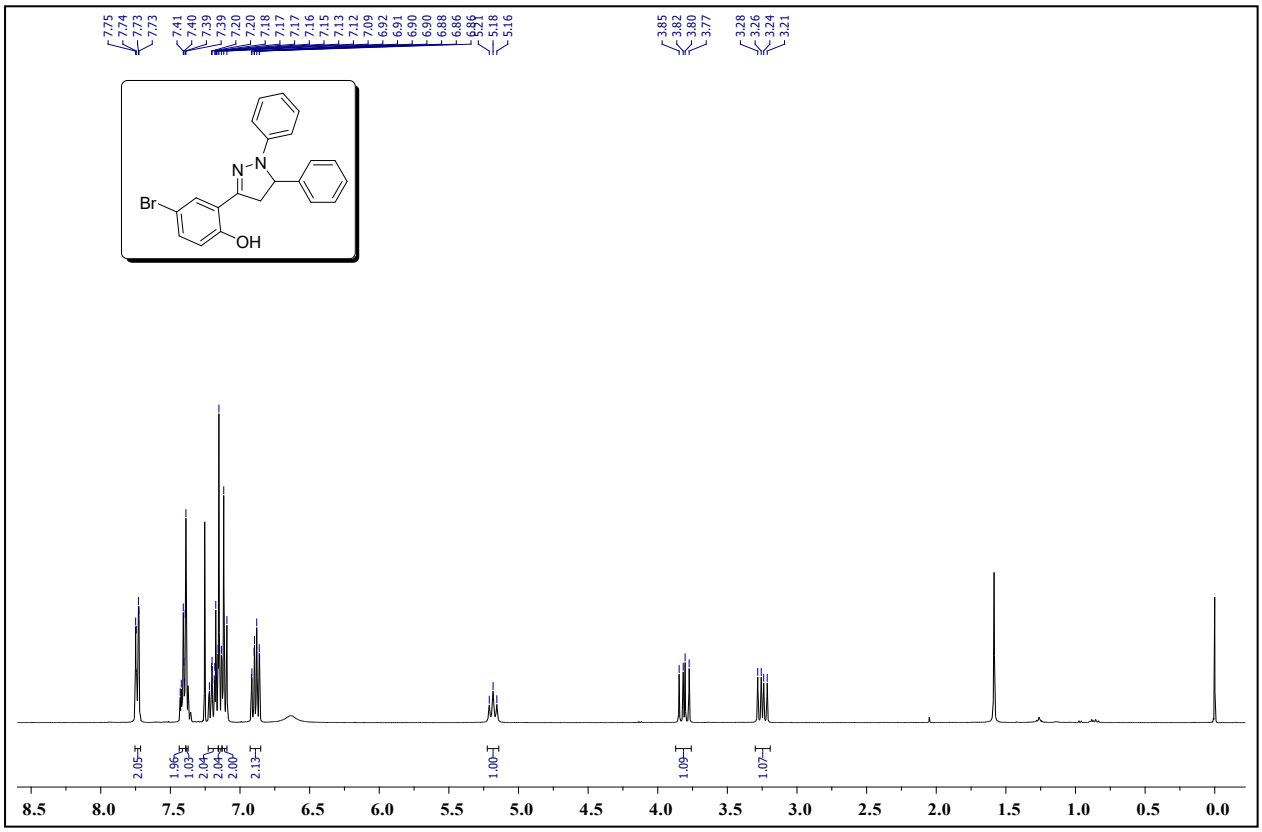


^{13}C NMR spectrum of compound **5t**

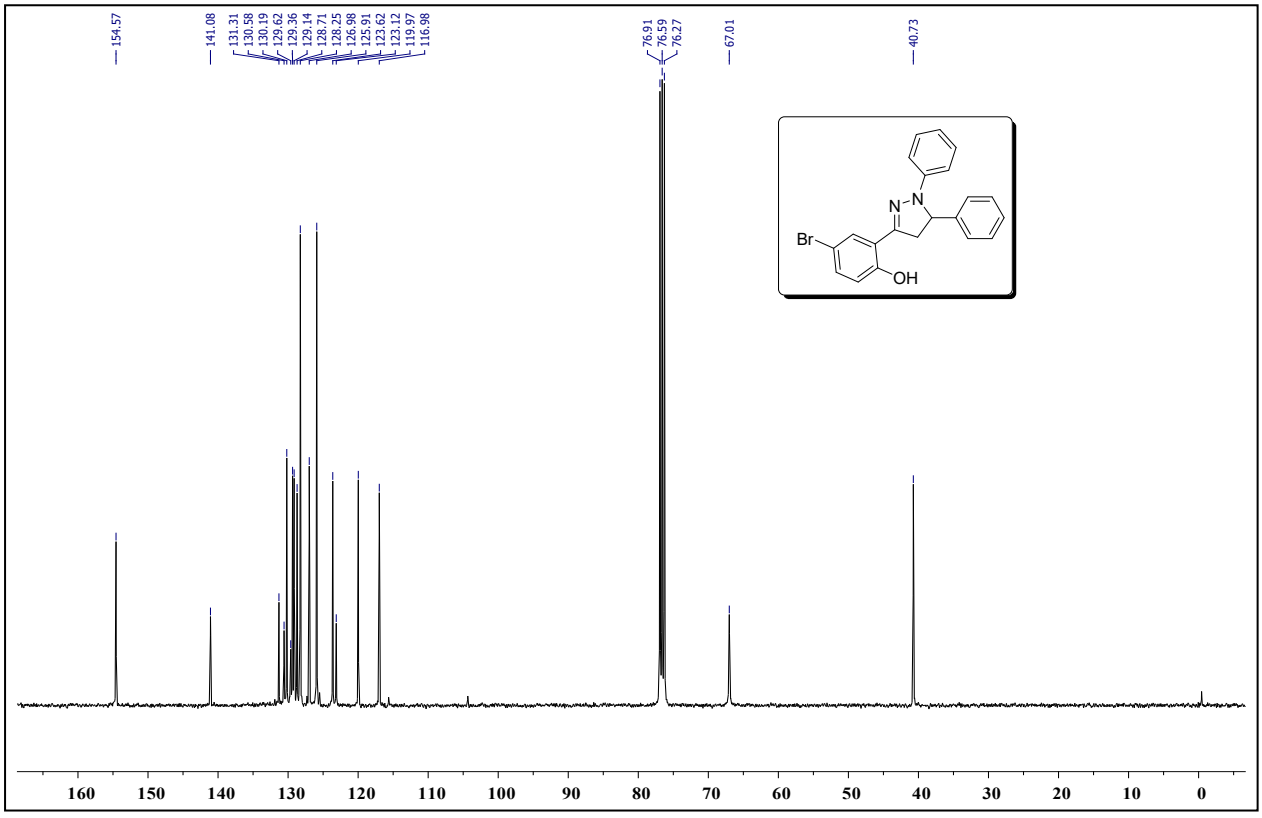


HRMS spectrum of compound **5t**

10. Copies of ^{1}H NMR, ^{13}C NMR and HRMS Spectrums (7f, 7h-j):



^{1}H NMR Spectrum of compound **7f**

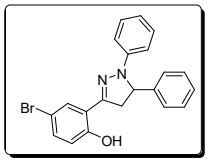


^{13}C NMR Spectrum of compound **7f**

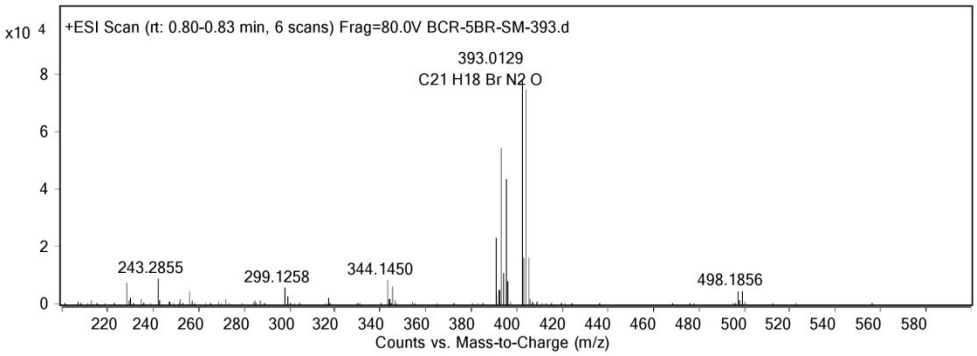
Qualitative Analysis Report

Data File	BCR-5BR-SM-393.d	**Sample Name**	
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	CSIR-IICT\Analyst
Acq Method	hrms-pos-method.m	**Acquired Time**	29-06-2021 12:07:35
IRM Calibration Status	Success	**DA Method**	11.m
Comment			
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

User Spectra



Fragmentor Voltage	Collision Energy	Ionization Mode
80	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
393.0129	1	56824.26	C21 H18 Br N2 O	M+

Formula Calculator Element Limits

Element	Min	Max
C	0	25
H	0	50
O	0	5
N	0	5
Cl	0	0
Br	0	1

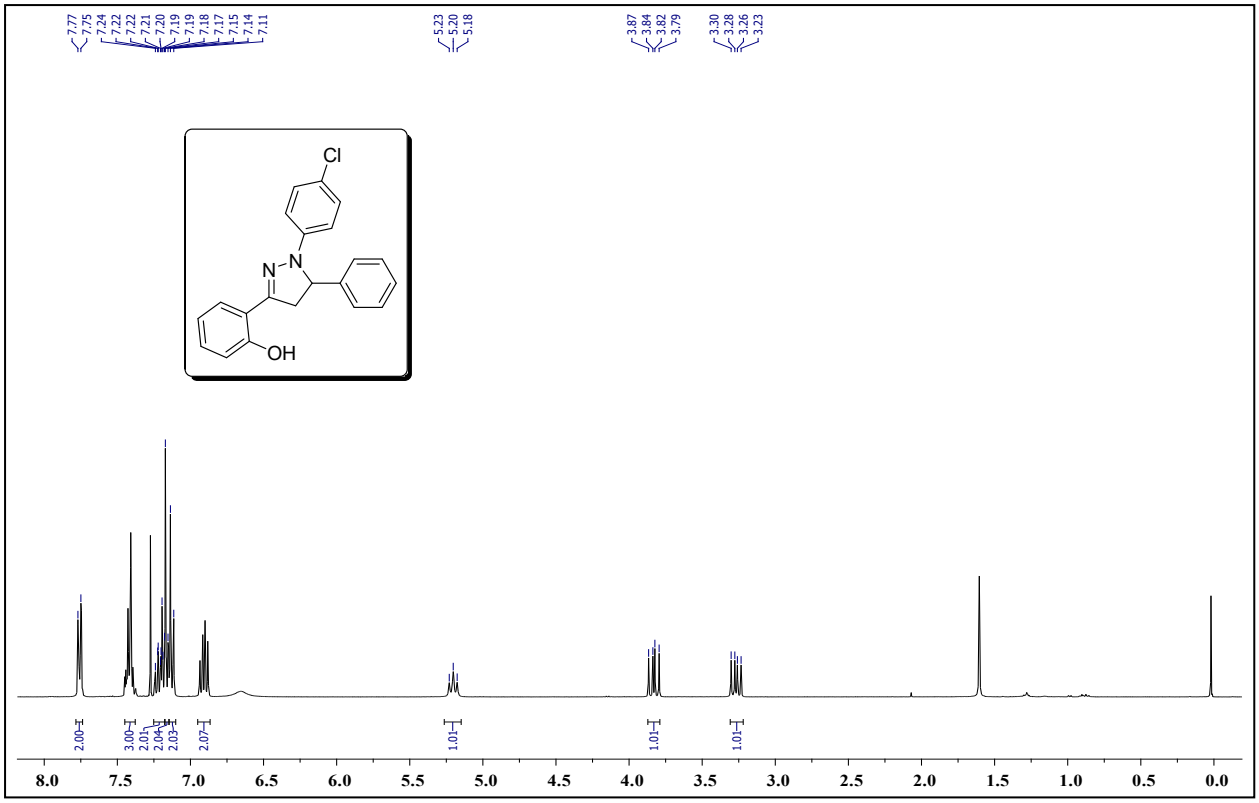
Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C21 H18 Br N2O	True	393.0132	393.0134	5.57	C21 H18 Br N2O	89.69
C21 H17 Br N2O	True	392.1210	392.1213	5.57	C21 H17 Br N2O	89.69

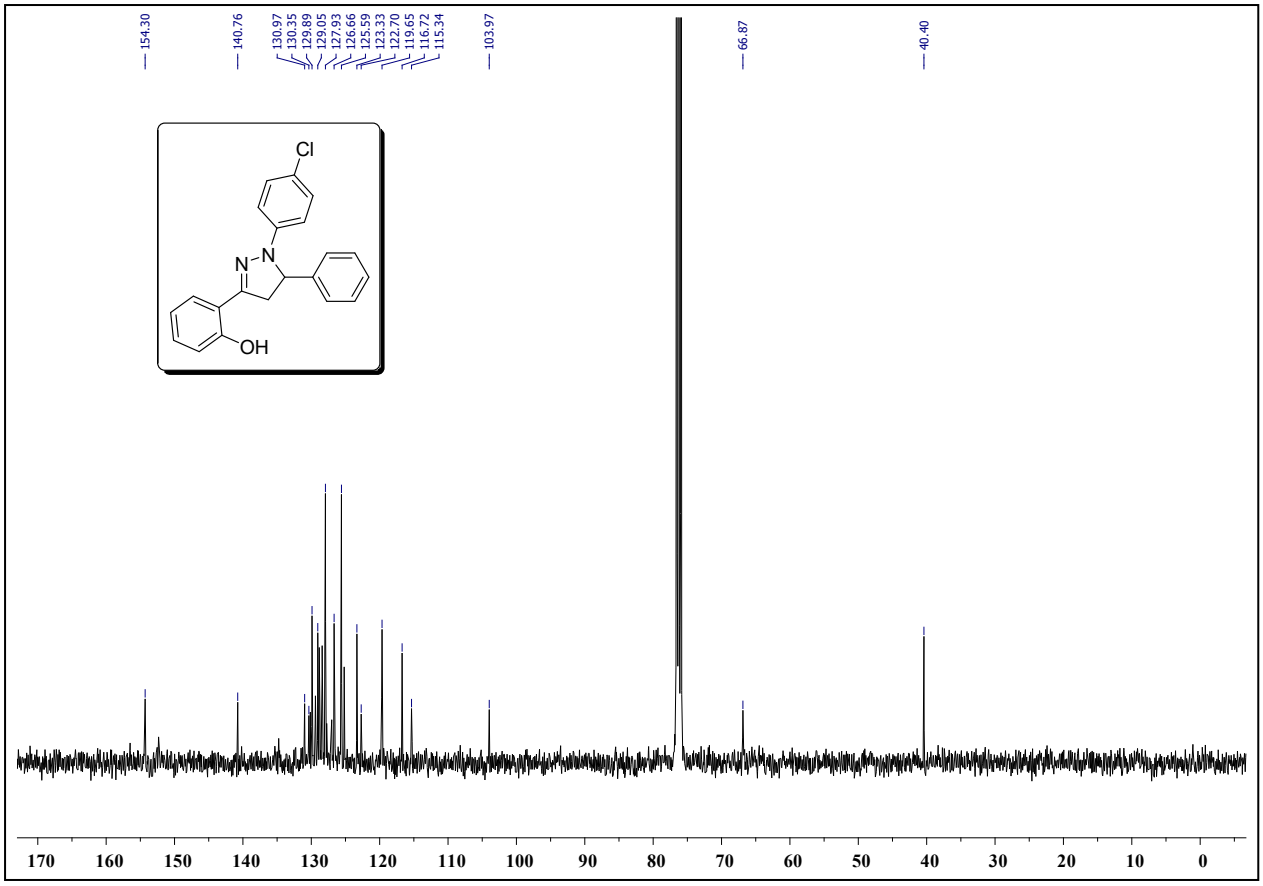
Printed at 12:07 PM on 29-Jun-2021

Agilent Technologies

HRMS Spectrum of compound **7f**



^{1}H NMR Spectrum of compound **7h**

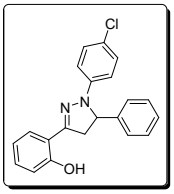


^{13}C NMR Spectrum of compound **7h**

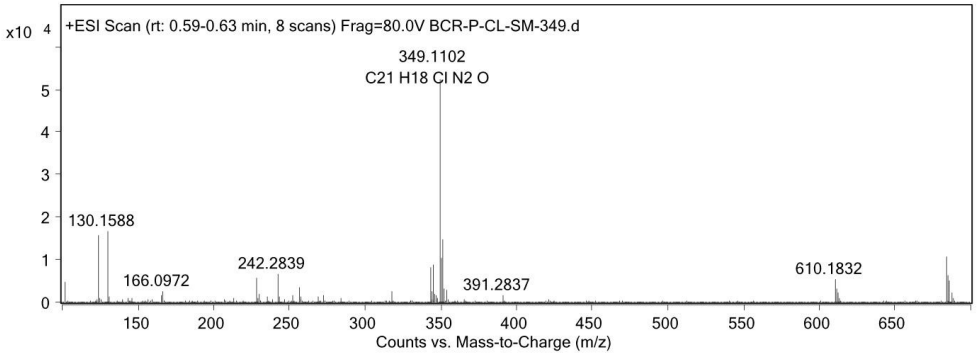
Qualitative Analysis Report

Data File	BCR-P-CL-SM-349.d	**Sample Name**	
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	CSIR-IICT\Analyst
Acq Method	hrms-pos-method.m	**Acquired Time**	29-06-2021 11:54:51
IRM Calibration Status	Success	**DA Method**	11.m
Comment			
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

User Spectra



Fragmentor Voltage	Collision Energy	Ionization Mode
80	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
349.1102	1	52428.91	C21 H18 Cl N2 O	M+

Formula Calculator Element Limits

Element	Min	Max
C	0	25
H	0	50
O	0	5
N	0	5
Cl	0	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C21 H18 Cl N2 O	True	349.1106	349.1108	0.51	C21 H18 Cl N2 O	88.91
C21 H17 Cl N2 O	True	348.1028	348.1029	0.51	C21 H18 Cl N2 O	88.91

Printed at 11:57 AM on 29-Jun-2021

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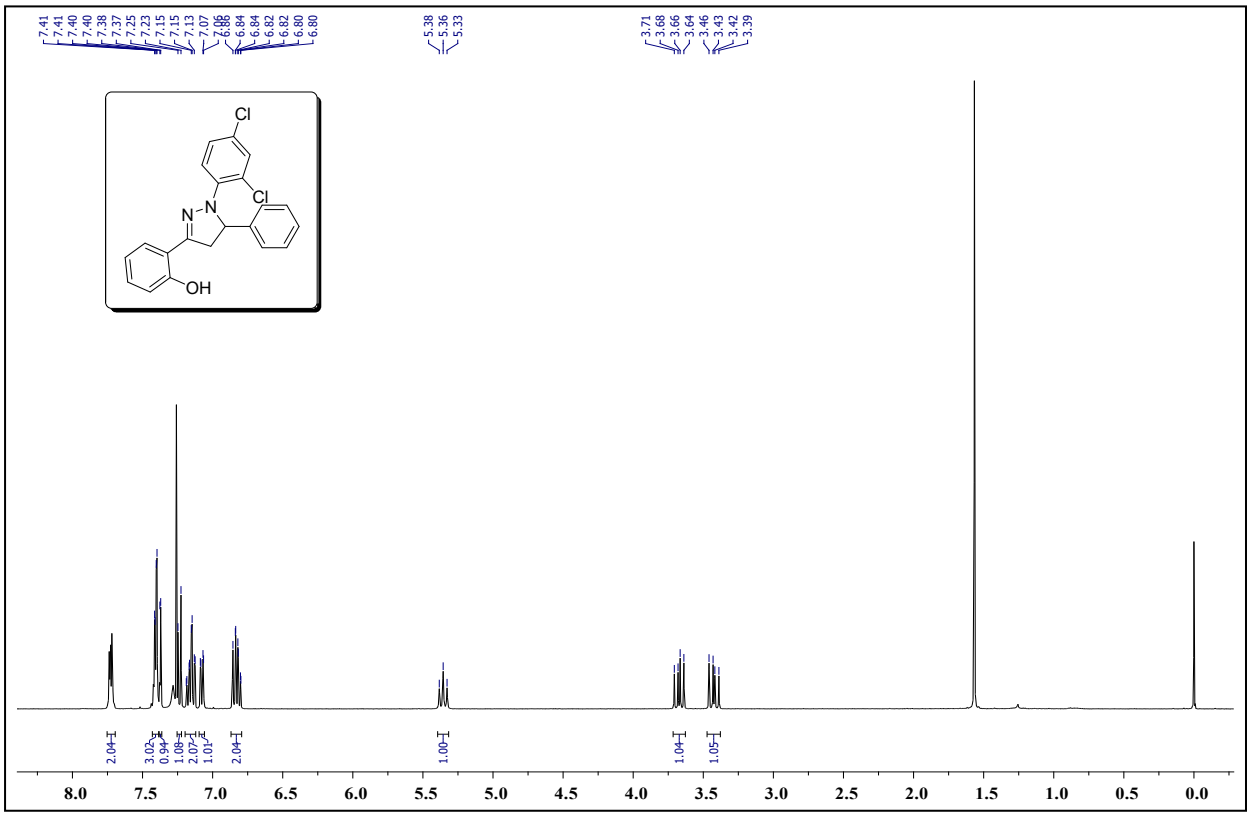
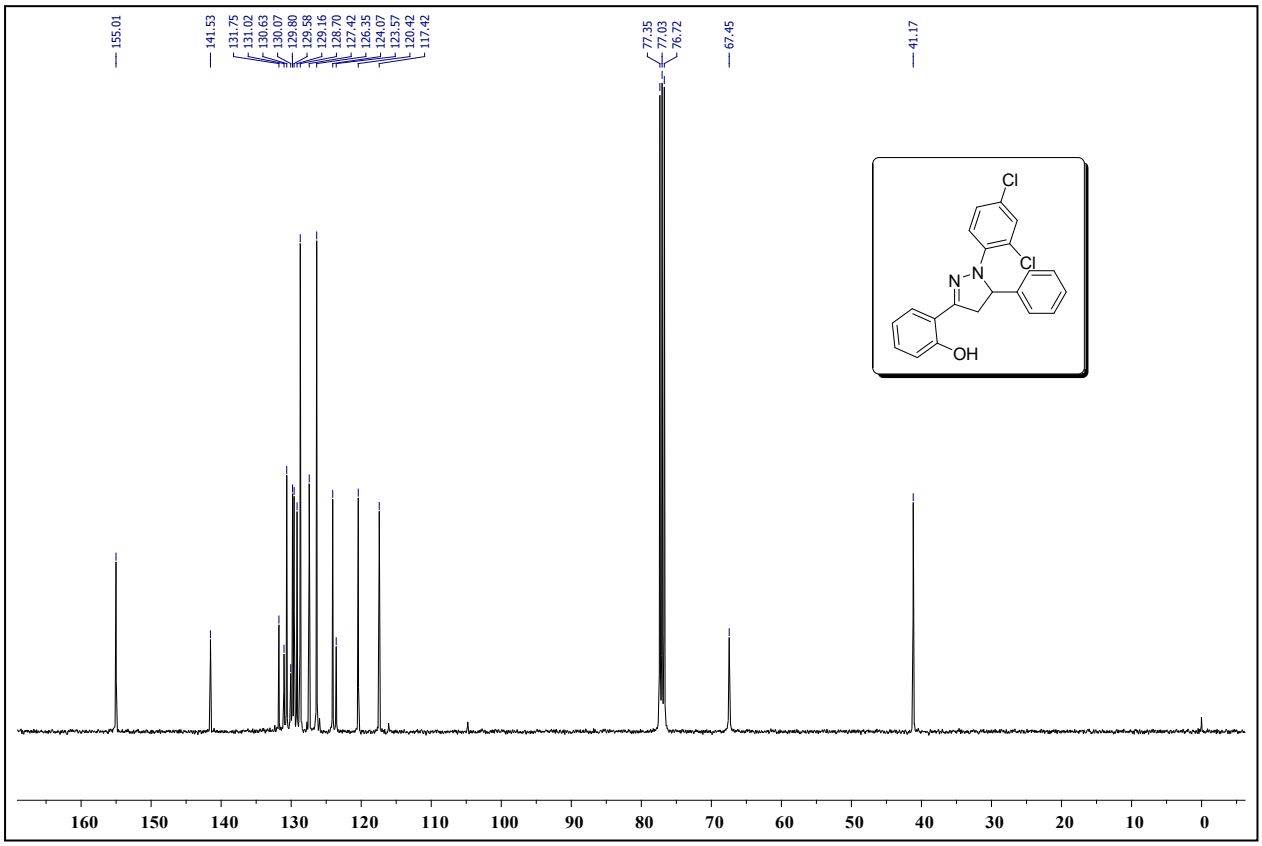
HRMS Spectrum of compound **7h**



^{1}H NMR Spectrum of compound **7i**

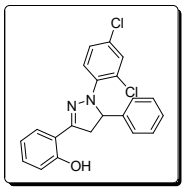


^{13}C NMR Spectrum of compound **7i**

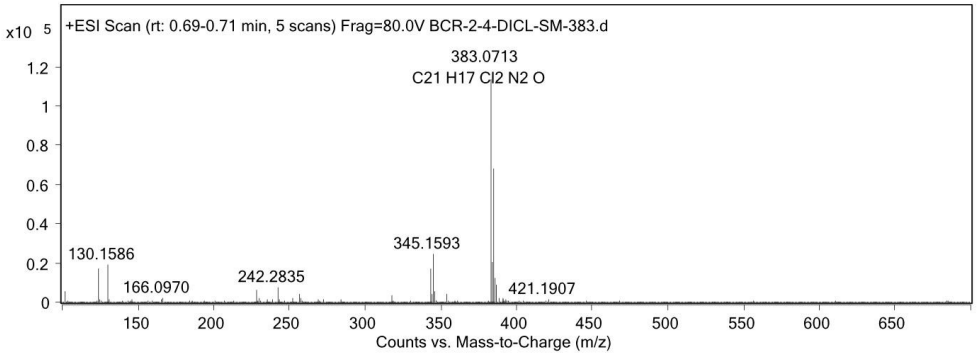
Qualitative Analysis Report

Data File	BCR-2-4-DICL-SM-383.d	**Sample Name**	
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	CSIR-IICT\Analyst
Acq Method	hrms-pos-method.m	**Acquired Time**	29-06-2021 12:01:35
IRM Calibration Status	Success	**DA Method**	11.m
Comment			
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

User Spectra



Fragmentor Voltage	Collision Energy	Ionization Mode
80	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
383.0713	1	113774.95	C21 H17 Cl2 N2 O	M+

Formula Calculator Element Limits

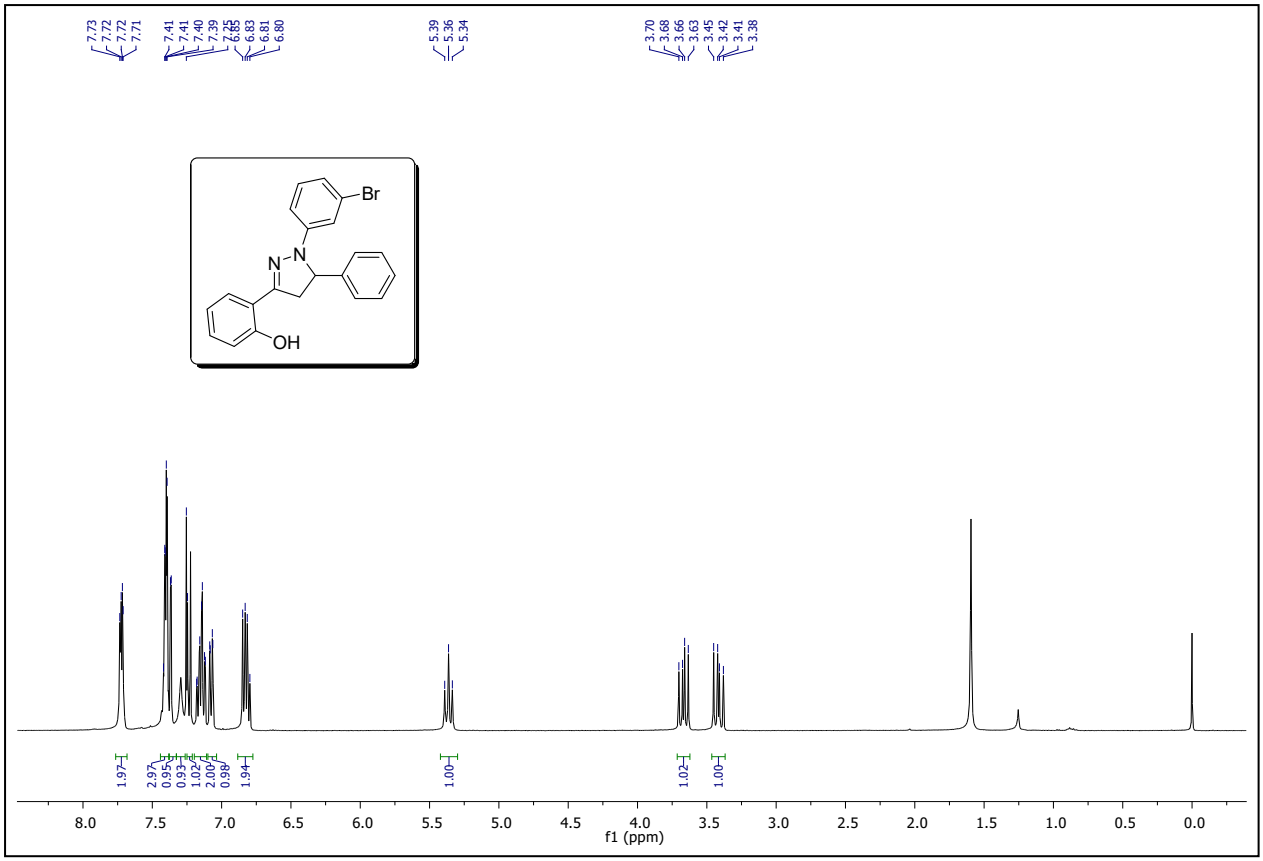
Element	Min	Max
C	0	25
H	0	50
O	0	5
N	0	5
Cl	0	2
Br	0	0

Formula Calculator Results

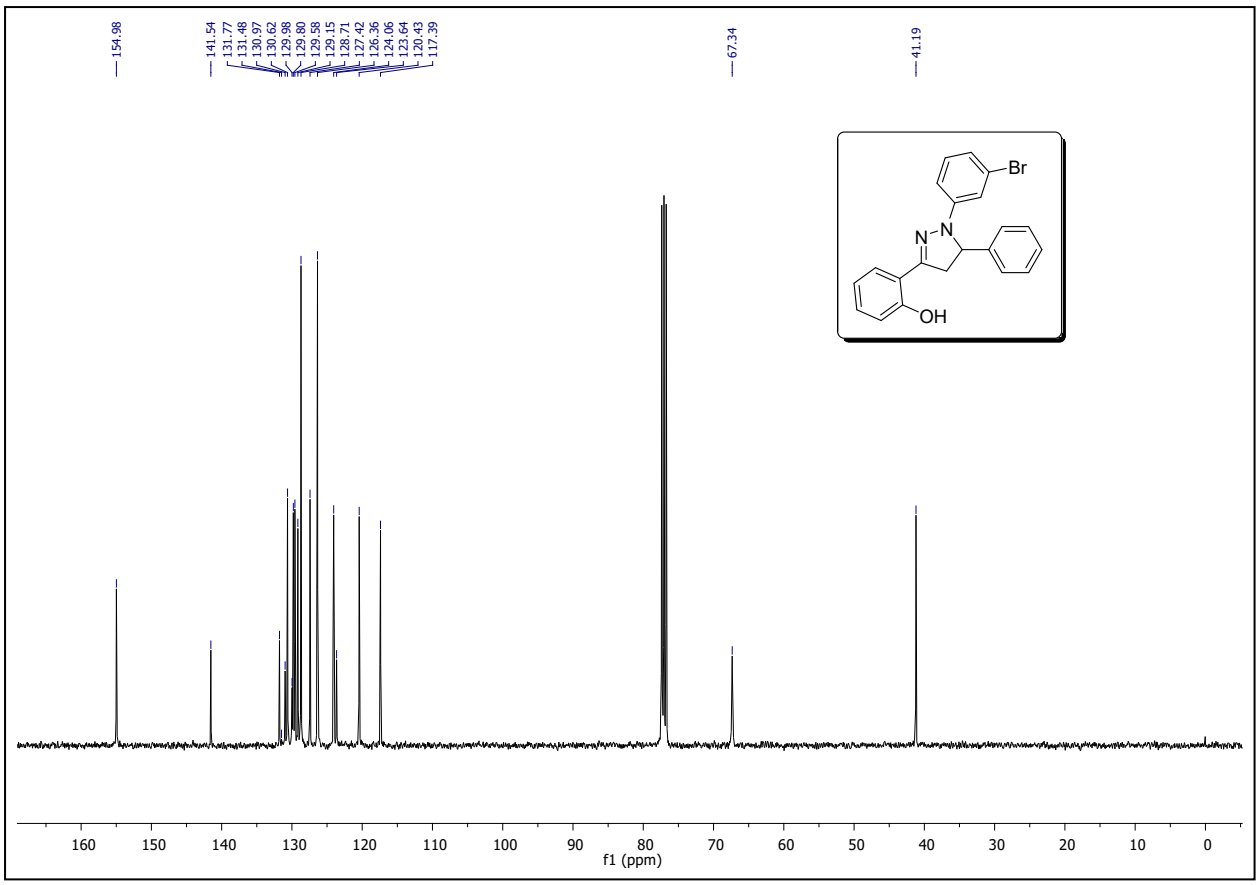
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C21 H17 Cl2 N2 O	True	383.0717	383.0718	0.33	C21 H17 Cl2 N2 O	96.01
C21 H16 Cl2 N2 O	True	382.0638	382.064	0.33	C21 H17 Cl2 N2 O	96.01

Agilent Technologies

HRMS Spectrum of compound **7i**



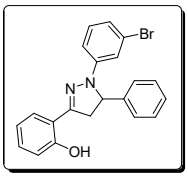
^{1}H NMR Spectrum of compound **7j**



^{13}C NMR Spectrum of compound **7j**

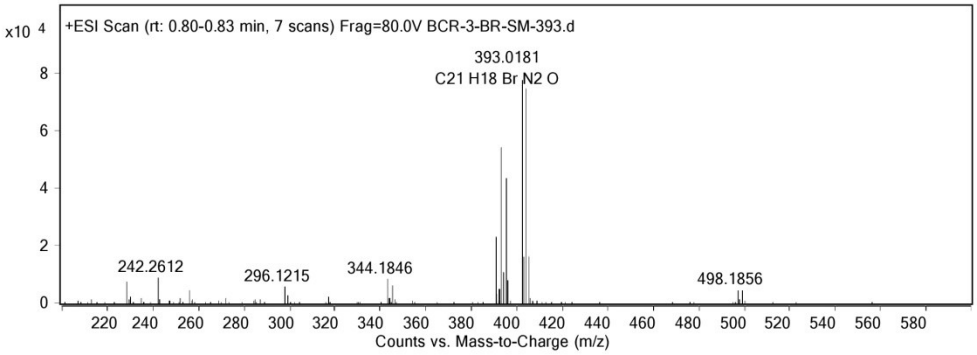
Qualitative Analysis Report

Data File	BCR-3BR-SM-393.d	**Sample Name**	
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	CSIR-IICT\Analyst
Acq Method	hrms-pos-method.m	**Acquired Time**	29-06-2021 12:25:51
IRM Calibration Status	Success	**DA Method**	11.m
Comment			
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
80	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
393.0181	1	57812.55	C21 H18 Br N2 O	M+

Formula Calculator Element Limits

Element	Min	Max
C	0	25
H	0	50
O	0	5
N	0	5
Cl	0	0
Br	0	1

Formula Calculator Results

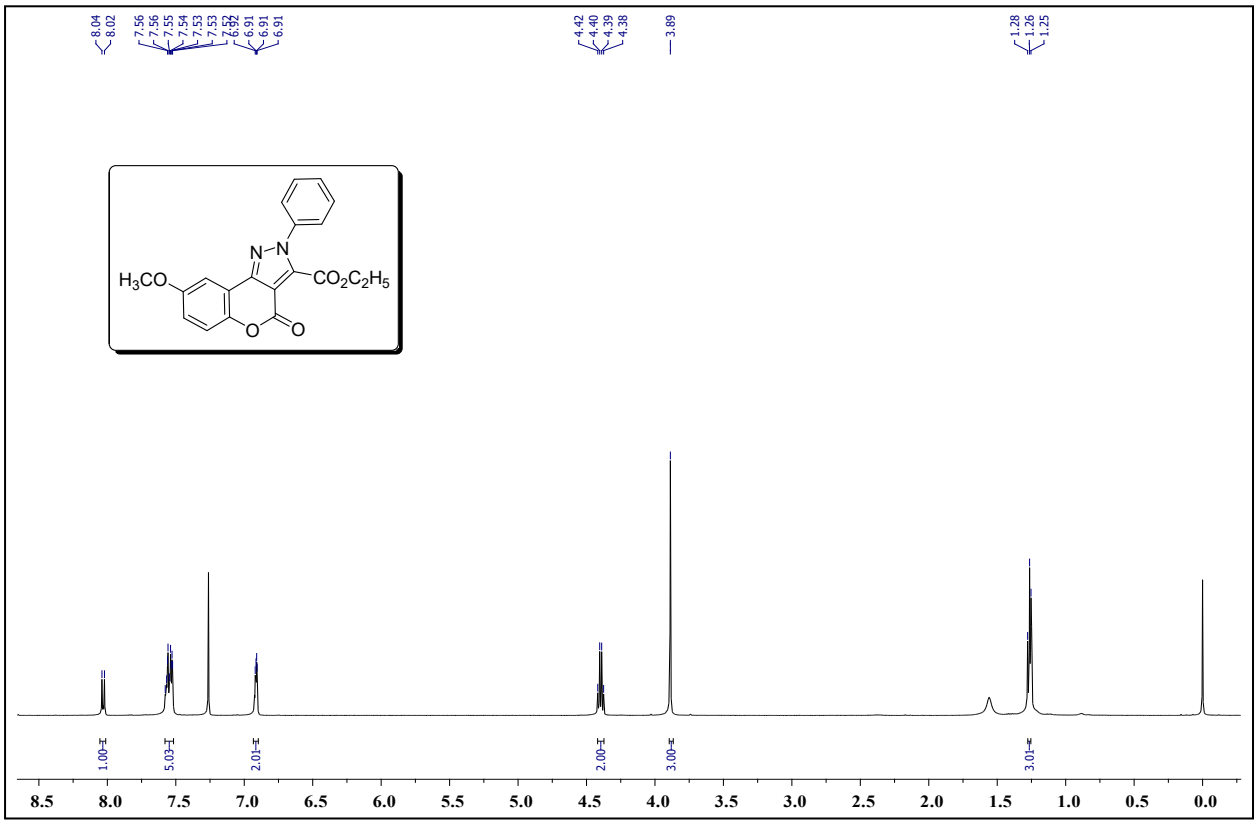
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C21 H18 Br N2O	True	393.0185	393.0187	5.57	C21 H18 Br N2O	90.06
C21 H17 Br N2O	True	392.1218	392.1221	5.57	C21 H17 Br N2O	90.06

Printed at 12:25 PM on 29-Jun-2021

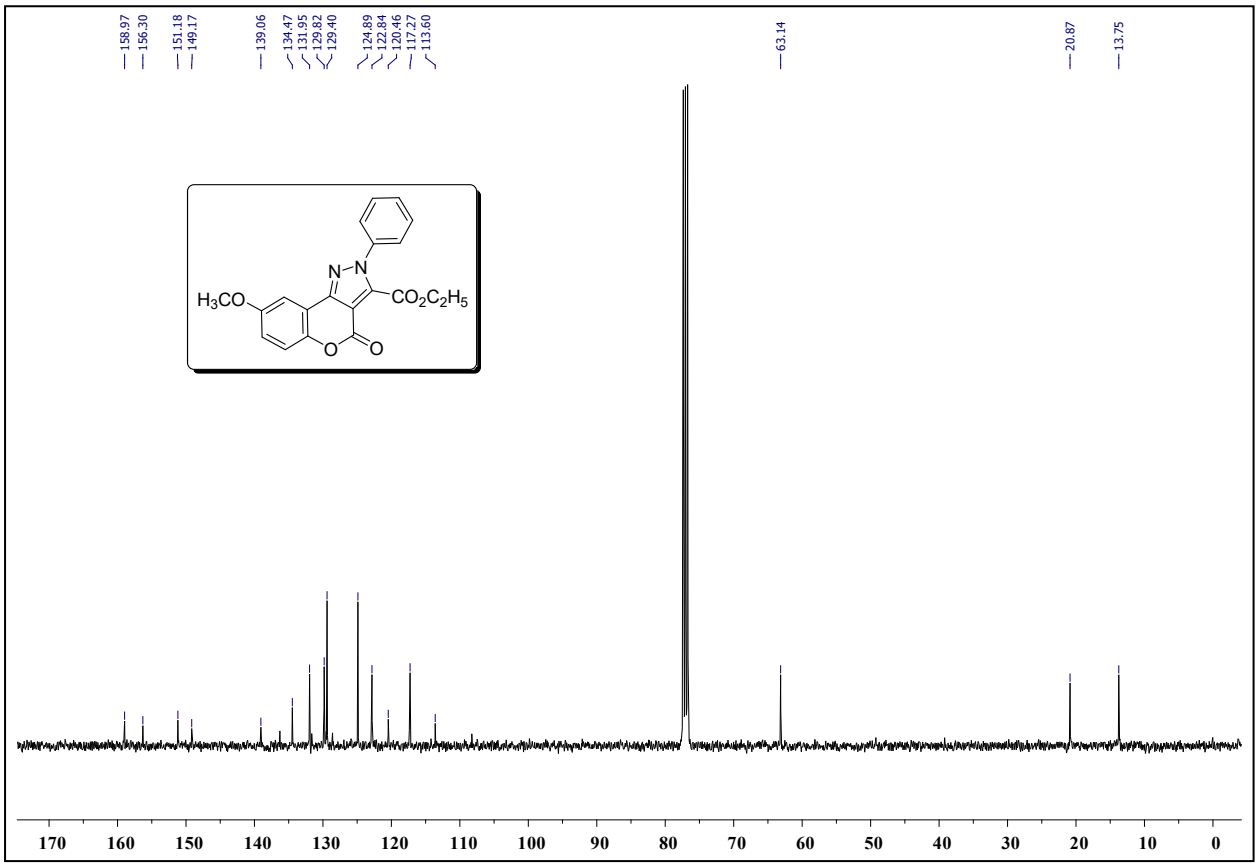
Agilent Technologies

HRMS Spectrum of compound **7j**

11. Copies of ^{1}H NMR, ^{13}C NMR and HRMS Spectrums (8c, 8i-j):



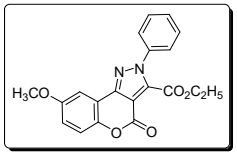
^{1}H NMR Spectrum of compound **8c**



^{13}C NMR Spectrum of compound **8c**

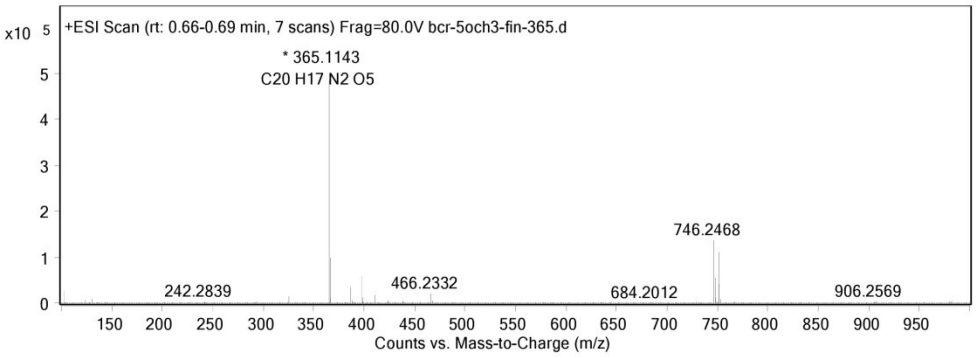
Qualitative Analysis Report

Data File	bcr-5och3-fin-365.d	**Sample Name**	
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	CSIR-IICT\Analyst
Acq Method	hrms-pos-method.m	**Acquired Time**	29-06-2021 11:50:32
IRM Calibration Status	Success	**DA Method**	11.m
Comment			
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
80	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
365.1143	1	486150.75	C20 H17 N2 O5	M+

Formula Calculator Element Limits

Element	Min	Max
C	0	25
H	0	50
O	0	5
N	0	5
Cl	0	0
S	0	0
B	0	0
Se	0	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H17 N2 O5	True	365.1147	365.1137	-2.53	C20 H17 N2 O5	95.57
C20 H16 N2 O5	True	364.1068	364.1059	-2.54	C20 H17 N2 O5	95.57

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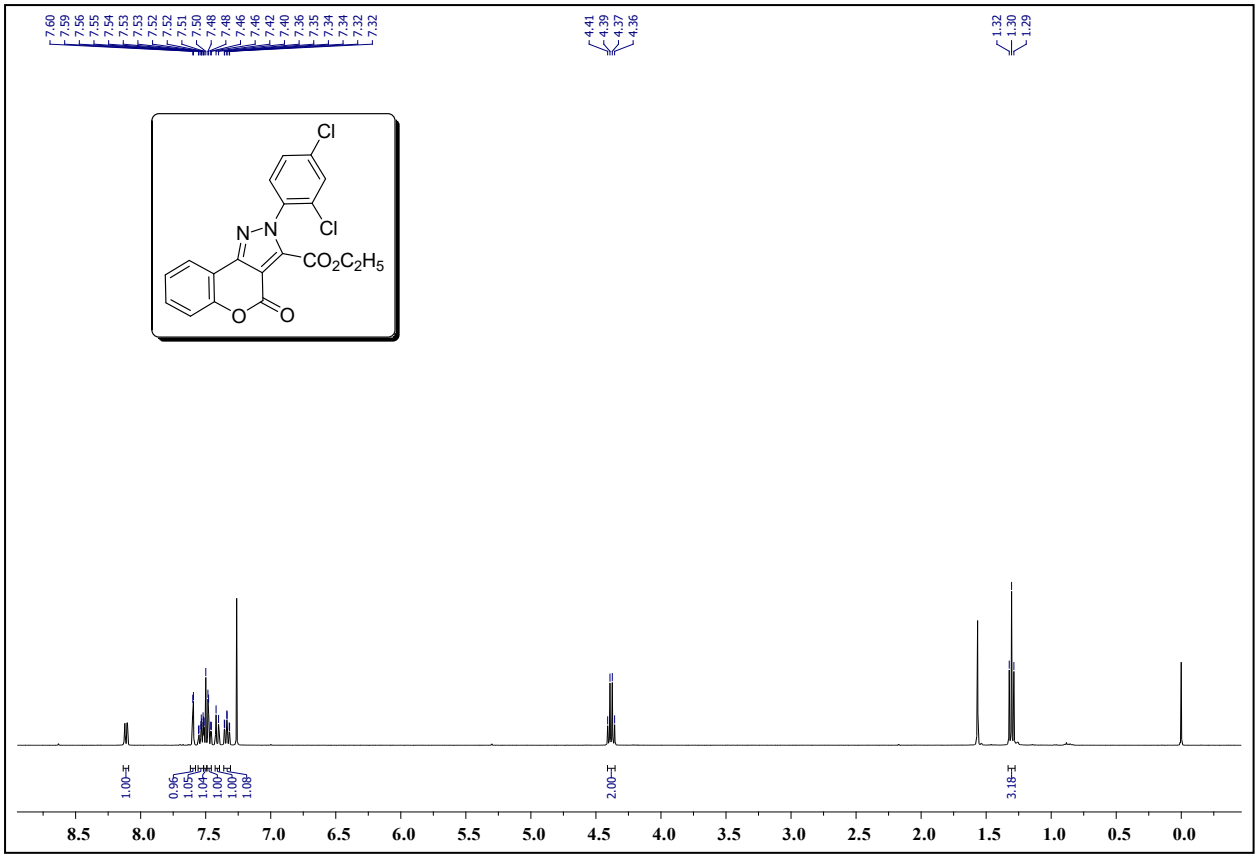
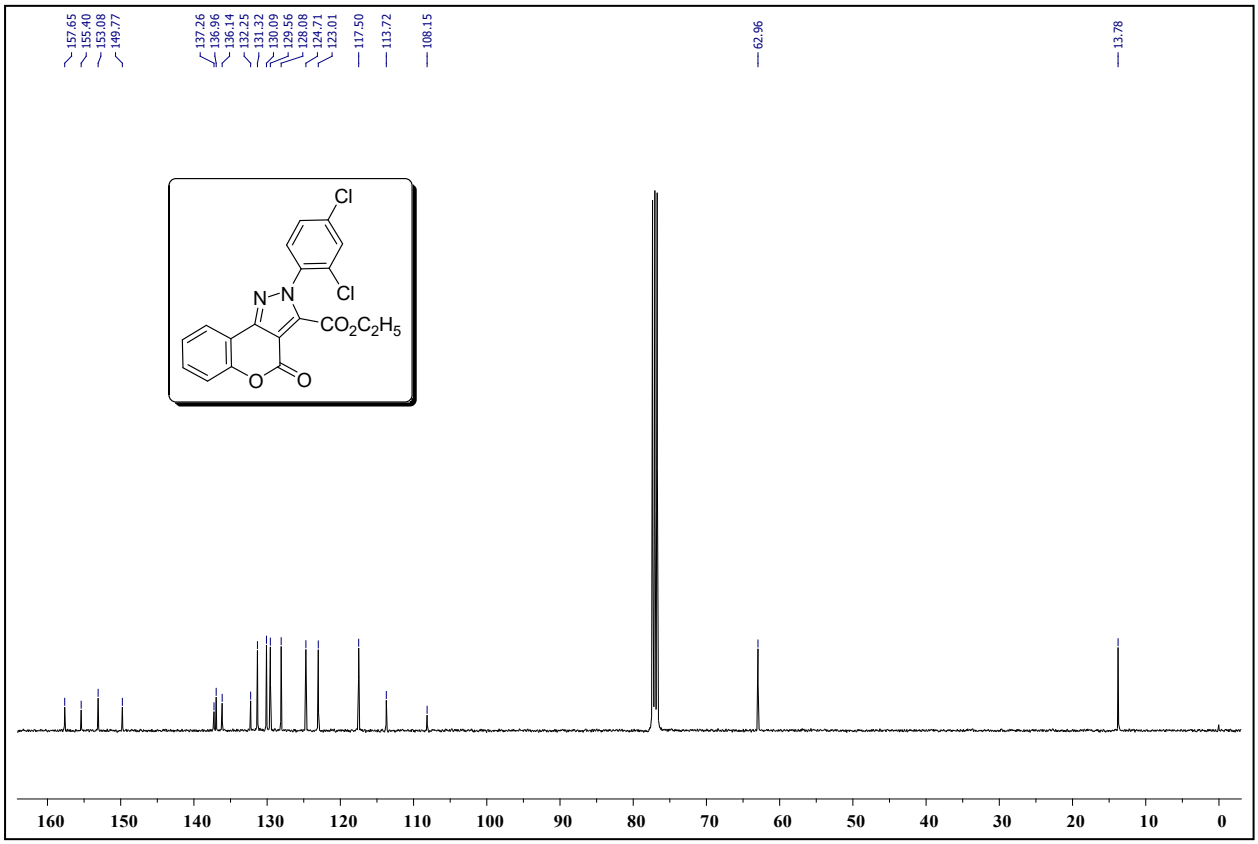
HRMS Spectrum of compound **8c**



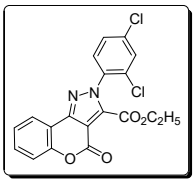
^{1}H NMR Spectrum of compound **8i**



^{13}C NMR Spectrum of compound **8i**

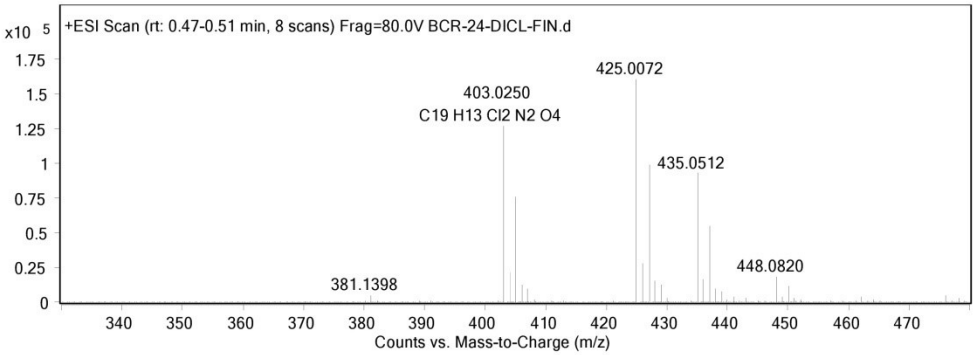
Qualitative Analysis Report

Data File	BCR-24-DICL-FIN.d	**Sample Name**	
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	CSIR-IICT\Analyst
Acq Method	hrms-pos-method.m	**Acquired Time**	29-06-2021 11:43:09
IRM Calibration Status	Success	**DA Method**	11.m
Comment			
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
80	0	ESI



Peak List

m/z	z	Abund
829.0238	1	267065.28

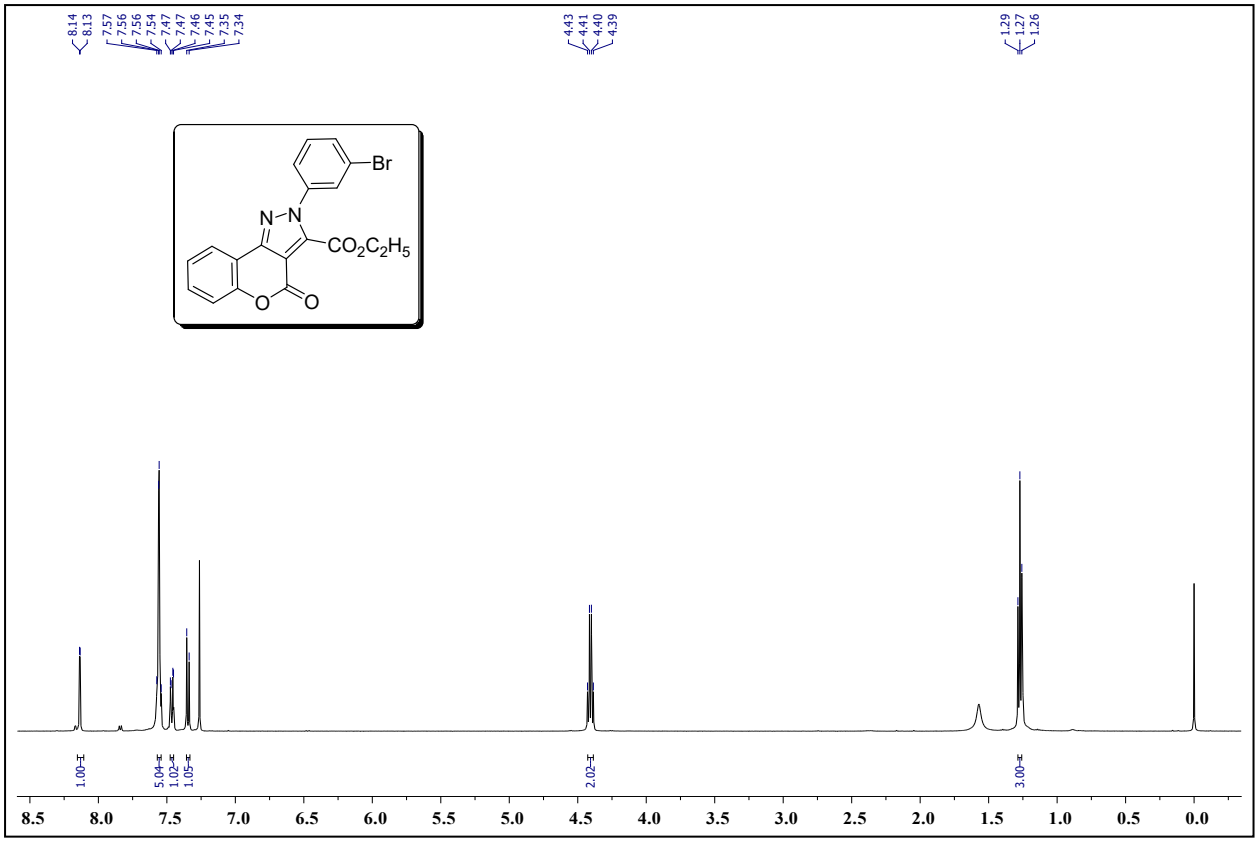
Formula Calculator Element Limits

Element	Min	Max
C	0	25
H	0	50
O	0	5
N	0	5
F	0	0
Br	0	0
Cl	0	2
S	0	1
B	0	1

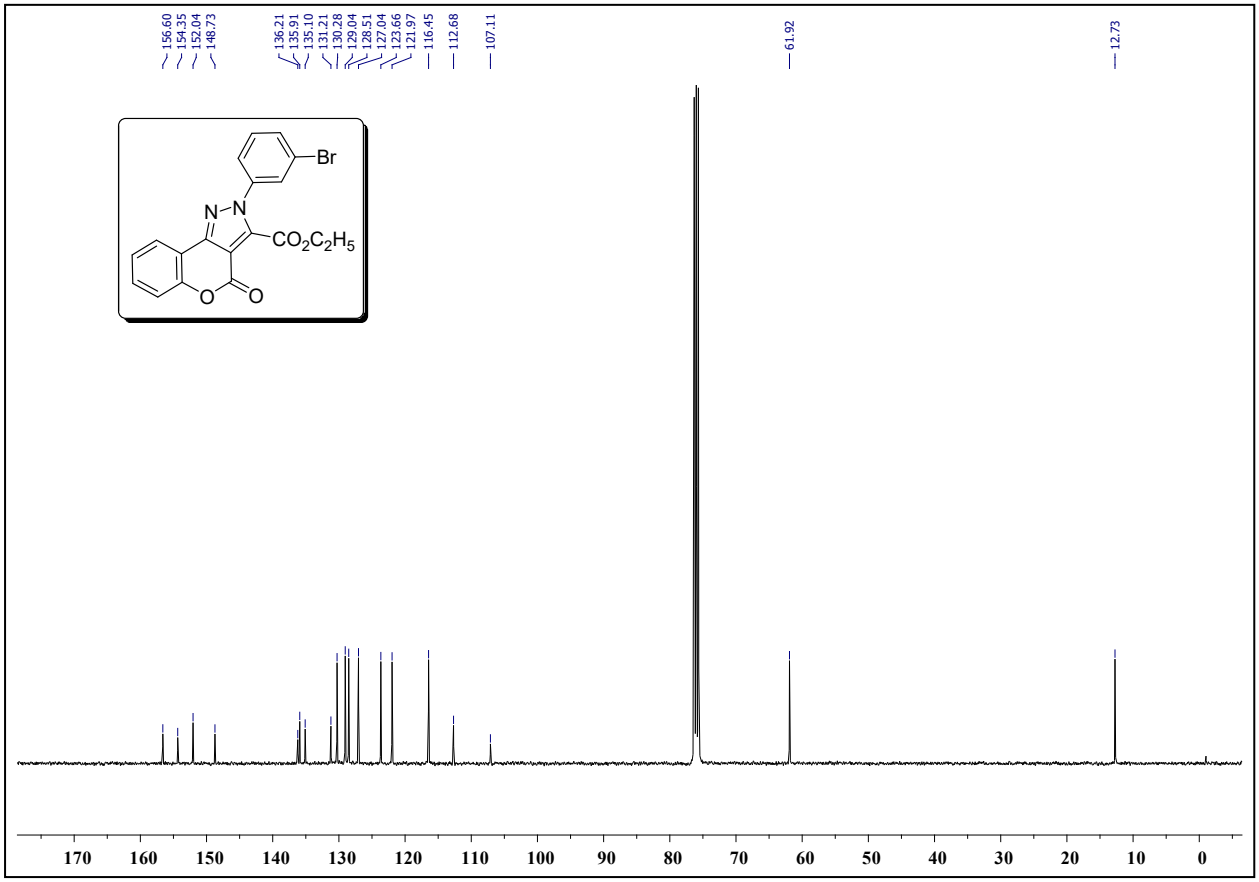
Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C19 H13 Cl2 N2 O4	True	403.0253	403.0252	-0.21	C19 H13 Cl2 N2 O4	95.95

HRMS Spectrum of compound **8i**



^{1}H NMR Spectrum of compound **8j**

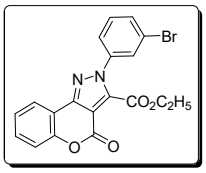


^{13}C NMR Spectrum of compound **8j**

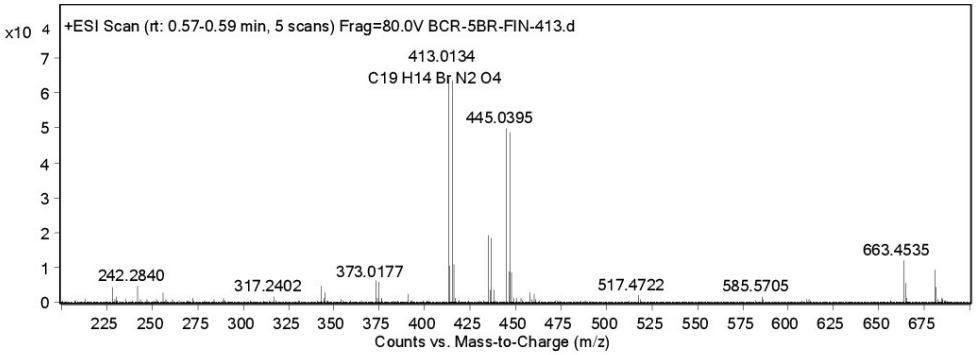
Qualitative Analysis Report

Data File	BCR-5BR-FIN-413.d	**Sample Name**	
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	CSIR-IICT\Analyst
Acq Method	hrms-pos-method.m	**Acquired Time**	29-06-2021 12:03:42
IRM Calibration Status	Success	**DA Method**	11.m
Comment			
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

User Spectra



Fragmentor Voltage	Collision Energy	Ionization Mode
80	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
413.0134	1	63994	C19 H14 Br N2 O4	M+

Formula Calculator Element Limits

Element	Min	Max
C	0	25
H	0	50
O	0	5
N	0	5
Cl	0	0
Br	0	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C19 H14 Br N2 O4	True	413.0138	413.0137	-0.28	C19 H14 Br N2 O4	94.9
C19 H13 Br N2 O4	True	412.006	412.0059	-0.28	C19 H14 Br N2 O4	94.9

Printed at 12:06 PM on 29-Jun-2021

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HRMS Spectrum of compound **8j**

12. **GC-MS analysis data**: The pyrazoline 3a, pyrazoledicarboxylate 5a, 1H-pyrazole 3aa, and reaction mixture of pyrazoline 3a with ethyl acetylenedicarboxylate 4a have been analysed by GC-MS using Simadzu-GCMS-QP2010 instrument. We have analyzed styrene (bottle grade chemical) and compared with the reaction mixture. The results were depicted in next page and analysis parameters were given below:

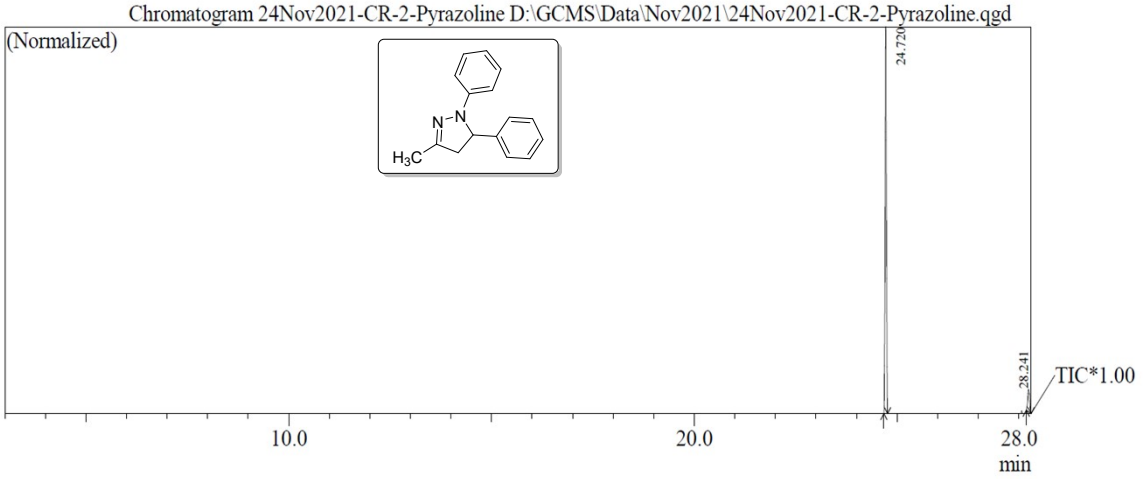
The Column Name: ZB-5MS; Column Length: 30.0 mm; Column Thickness: 0.25 um; Column Diameter: 0.25 mm; Oven Temperature: 60.0 ^{o}C; Injection Temperature: 250.0 ^{o}C; Injection Mode: Split; Carrier Gas: Helium; Prim. Pressure: 500-900; Pressure: 50.0 kPa; Total Flow: 8.5 mL/min; Column Flow: 0.91 mL/min; Linear Velocity: 34.8 cm/sec; Purge Flow: 3.0 mL/min; Split Ratio: 5.0.

GC MS REPORT
BIOTRANSFORMATION LAB

Sample Information

Analyzed : 24-Nov-21 1:22:33 PM
Sample Name : 24Nov2021-CR-2-Pyrazoline
Sample ID : 24Nov2021-CR-2-Pyrazoline
Data File : D:\GCMS\Data\Nov2021\24Nov2021-CR-2-Pyrazoline.qgd
Method File : D:\GCMS\Data\Nov2021\GC-Gen2021-CR.qgm
Tuning File : D:\GCMS\Data\Dec2019\11-03-2020 with column.qgt
24Nov2021-CR-2-Pyrazoline

Chromatogram 24Nov2021-CR-2-Pyrazoline D:\GCMS\Data\Nov2021\24Nov2021-CR-2-Pyrazoline.qgd

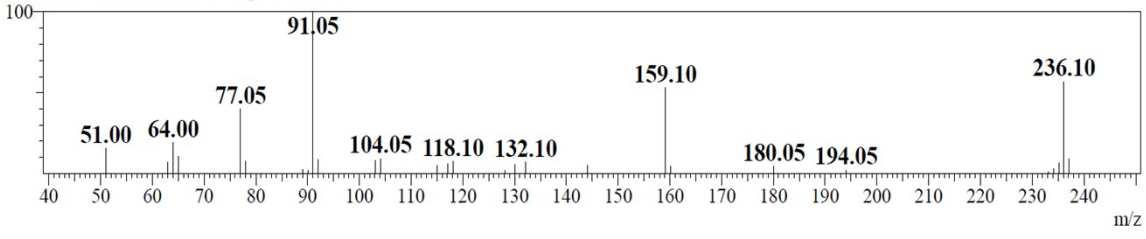


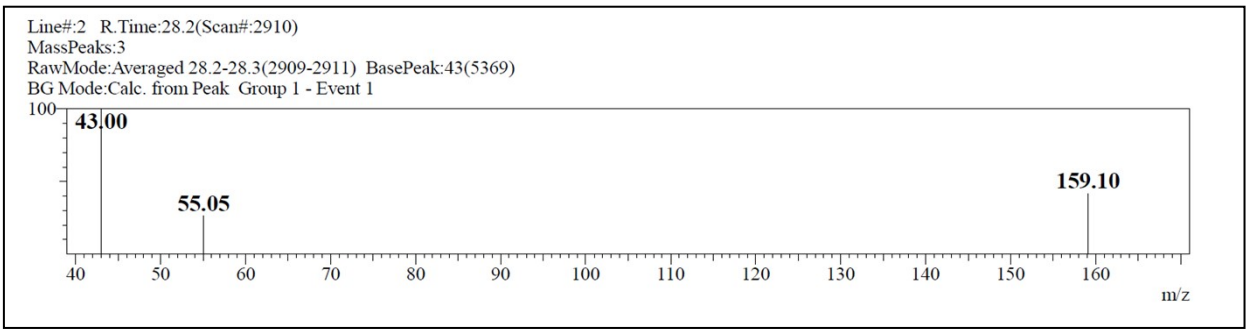
Peak Report TIC

Peak#	R.Time	Area	Area%
1	24.720	353052	92.18
2	28.241	29967	7.82
		383019	100.00

Spectrum

Line#:1 R.Time:24.7(Scan#:2487)
MassPeaks:28
RawMode:Averaged 24.7-24.7(2486-2488) BasePeak:91(35107)
BG Mode:Calc. from Peak Group 1 - Event 1





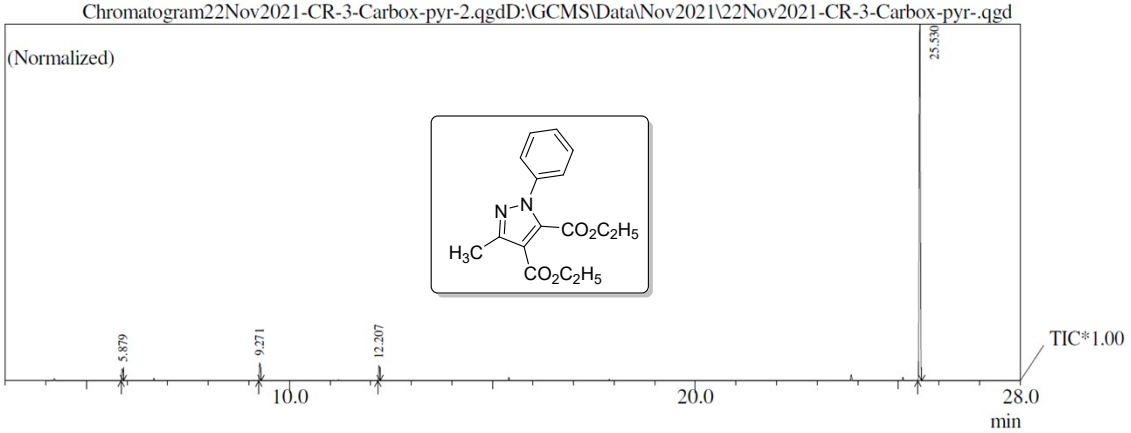
GC-MS spectra of compound **3a**

GCMSREPORTBIOTRANSFO RMATIONLAB

Sample Information

Analyzed :22-Nov-214:14:43PM
SampleName :22 Nov2021-CR-3-Carbox-pyr-2.qgd
Sample ID :22 Nov2021-CR-3-Carbox-pyr
DataFile :D:\GCMS\Data\Nov2021\22Nov2021-CR-3-Carbox-pyr-2.qgd
Method :D:\GCMS\Data\Nov2021\GC-Gen2021-CR.qgm
FileTuning F ile :D:\GCMS\Data\Dec2019\11-03-2020withcolumn.qgt
22Nov2021-CR-3-Carbox-pyr-2.qgd

Chromatogram22Nov2021-CR-3-Carbox-pyr-2.qgdD:\GCMS\Data\Nov2021\22Nov2021-CR-3-Carbox-pyr-.qgd

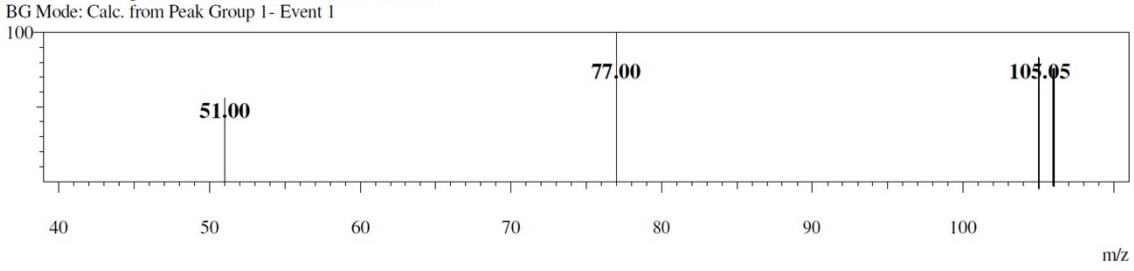


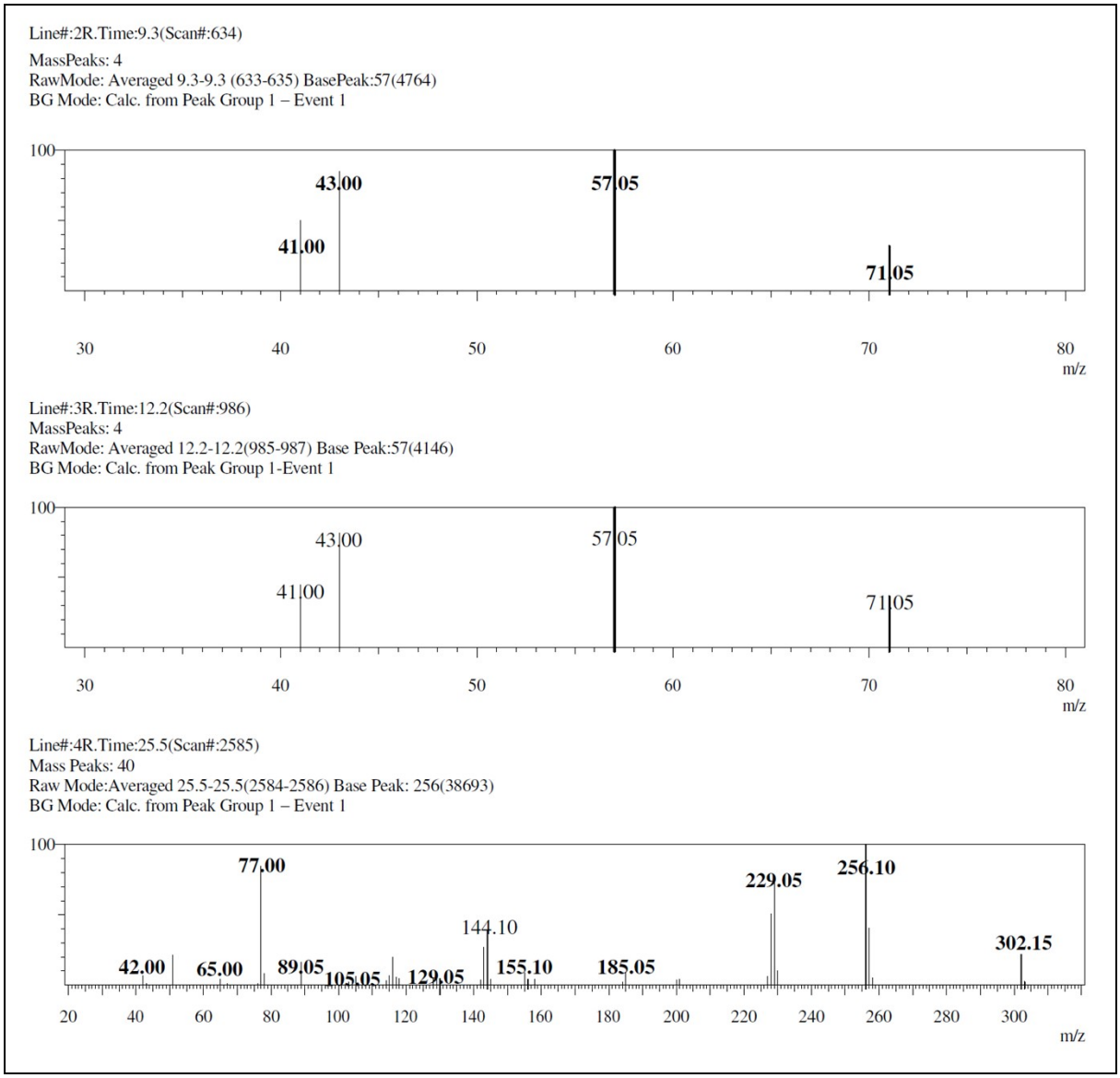
Peak Report TIC

Peak#	R.Time	Area	Area%
1	5.879	21127	1.69
2	9.271	28460	0.92
3	12.207	22224	2.68
4	25.530	585333	94.70
		657144	100.00

Spectrum

Line#:1R.Time:5.9(Scan#:226)]
MassPeaks: 4
RawMode:Averaged 5.9-5.9(225-227) BasePeak: 77(2816)
BG Mode: Calc. from Peak Group 1- Event 1





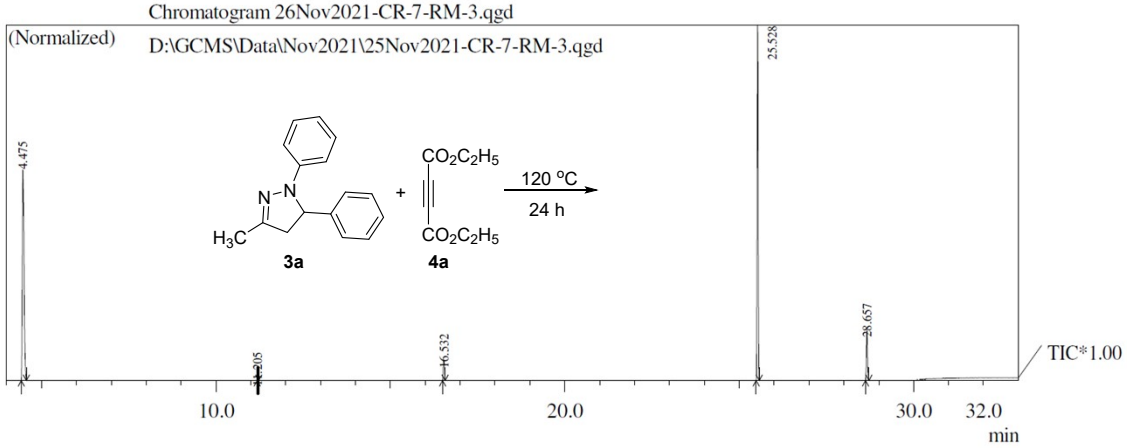
GC-MS spectrum of isolated compound **5a**

GCMSREPORTBIOTRANSFORMATIONLAB

SampleInformation

Analyzed : 25-Nov-21 2:30:16 PM
SampleName : 25Nov2021-CR-7-RM-3.qgd
SampleID : 25Nov2021-CR-7-RM-3
DataFile : D:\GCMS\Data\Nov2021\22Nov2021-CR-7-RM-3.qgd
MethodFile : D:\GCMS\Data\Nov2021\GC-Gen 2021-CR.qgm
TuningFile : D:\GCMS\Data\Dec2019\11-03-2020 withcolumn.qgt
25Nov2021-CR-7-RM-3.qgd

Chromatogram 26Nov2021-CR-7-RM-3.qgd

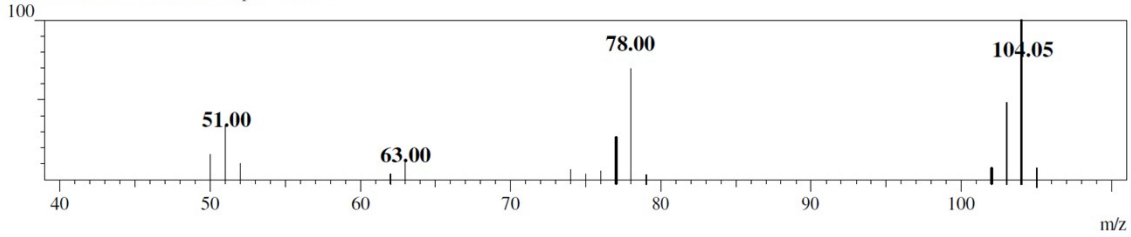


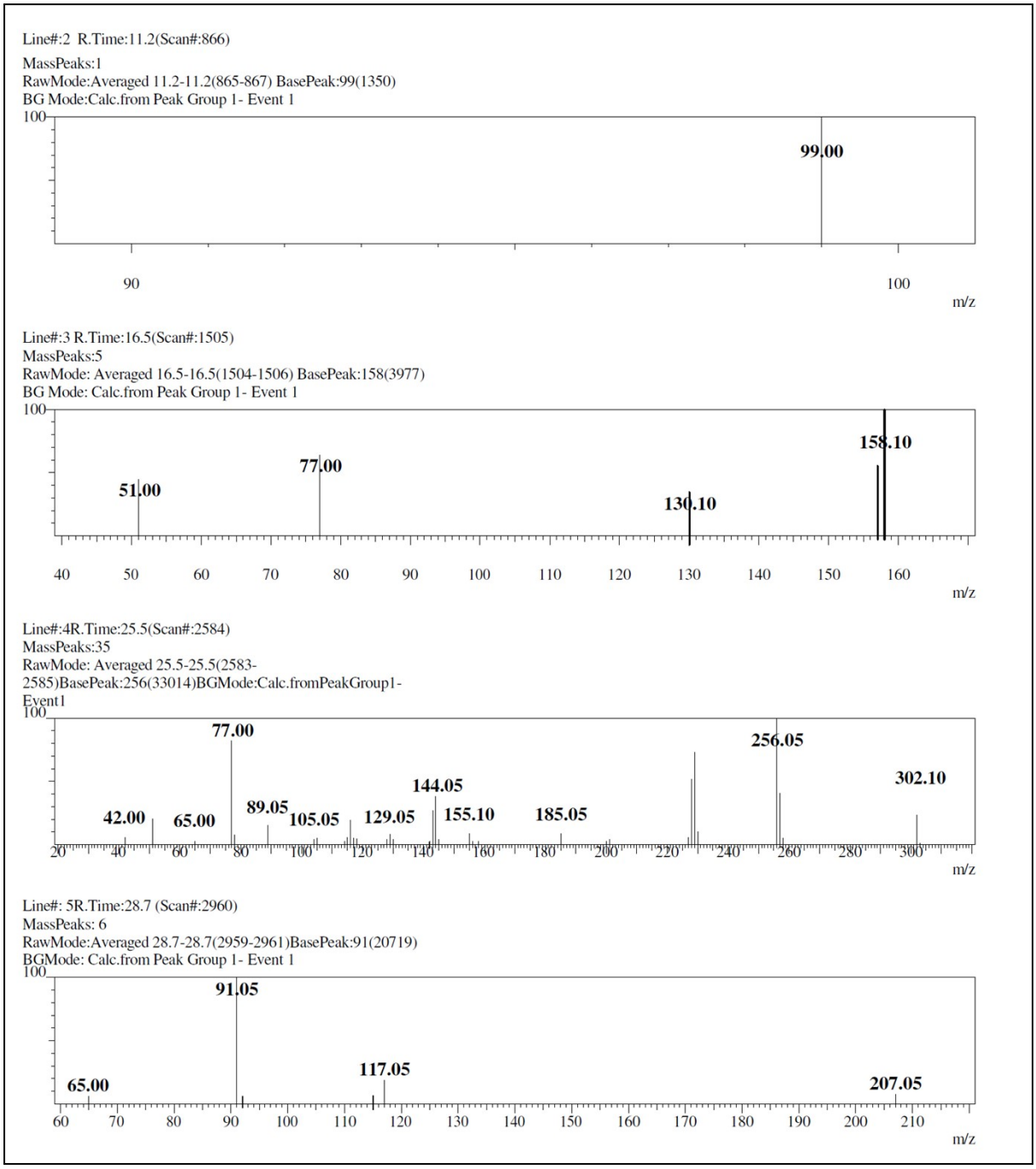
Peak Report TIC

Peak#	R.Time	Area	Aea%
1	4.475	410066	8.25
2	11.205	2579	0.26
3	16.532	26472	2.68
4	25.528	472314	81.11
5	28.657	76032	7.70
		987463	100.00

Spectrum

Line#: 1R.Time:4.5(Scan#:58)
MassPeaks:15
RawMode:Averaged 4.5-4.5(57-59) BasePeak:104(35818)
BG Mode: Calc. fromPeak Group 1 - Event 1





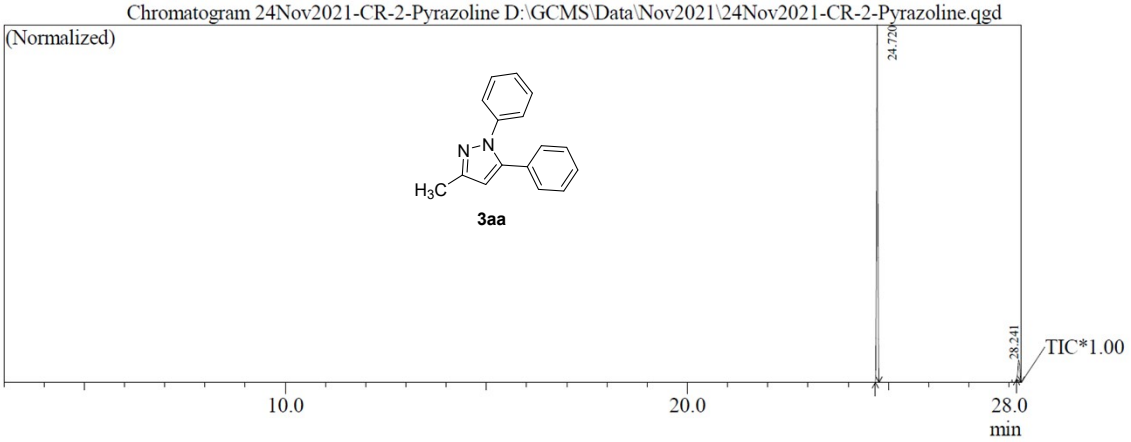
GC-MS spectrum of reaction mixture (compound **5a** and by-product **styrene**)

GC MS REPORT
BIOTRANSFORMATION LAB

Sample Information

Analyzed : 24-Nov-21 1:22:33 PM
Sample Name : 24Nov2021-CR-2-Pyrazoline
Sample ID : 24Nov2021-CR-2-Pyrazoline
Data File : D:\GCMS\Data\Nov2021\24Nov2021-CR-2-Pyrazoline.qgd
Method File : D:\GCMS\Data\Nov2021\GC-Gen2021-CR.qgm
Tuning File : D:\GCMS\Data\Dec2019\11-03-2020 with column.qgt
24Nov2021-CR-2-Pyrazoline

Chromatogram 24Nov2021-CR-2-Pyrazoline D:\GCMS\Data\Nov2021\24Nov2021-CR-2-Pyrazoline.qgd



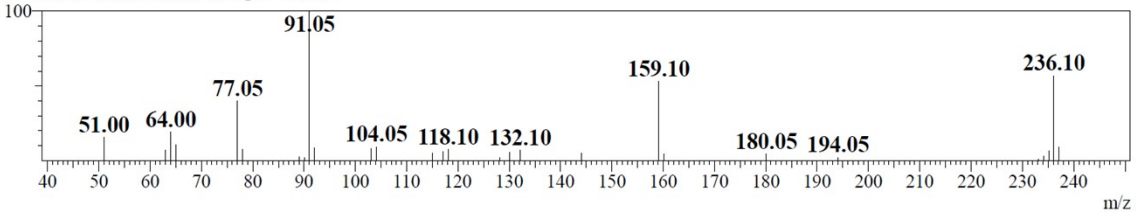
3aa

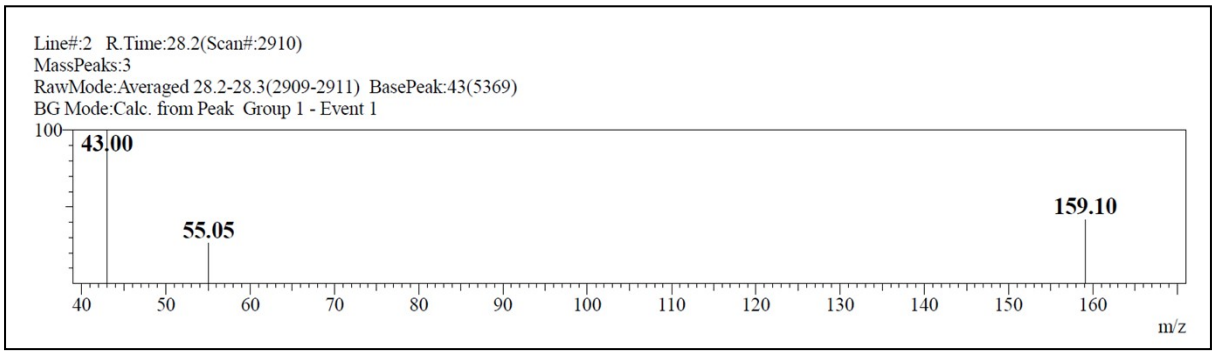
Peak Report TIC

Peak#	R.Time	Area	Area%
1	24.720	353052	92.18
2	28.241	29967	7.82
		383019	100.00

Spectrum

Line#:1 R.Time:24.7(Scan#:2487)
MassPeaks:28
RawMode:Averaged 24.7-24.7(2486-2488) BasePeak:91(35107)
BG Mode:Calc. from Peak Group 1 - Event 1





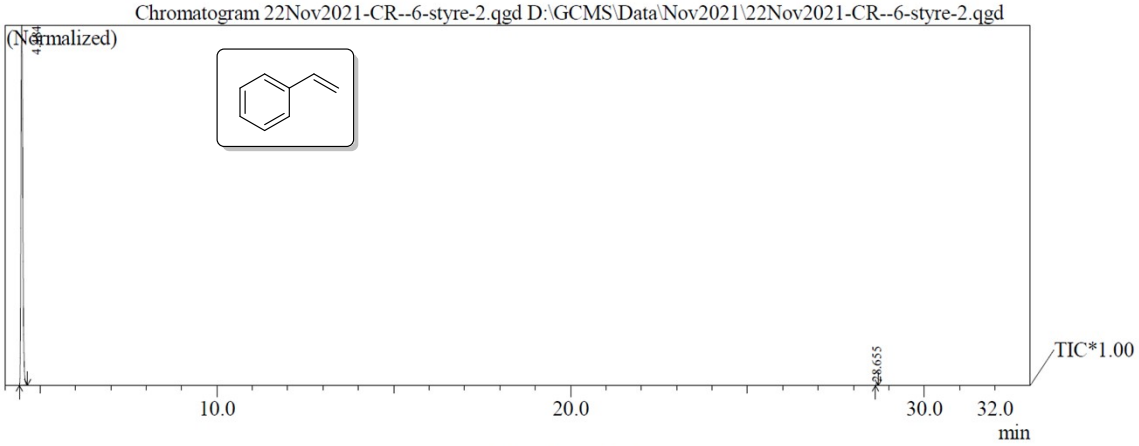
GC-MS spectrum of compound **3aa**

GC MS REPORT
BIOTRANSFORMATION LAB

Sample Information

Analyzed : 22-Nov-21 5:37:07 PM
Sample Name : 22Nov2021-CR--6-styre-2.qgd
Sample ID : 22Nov2021-CR--6-styre
Data File : D:\GCMS\Data\Nov2021\22Nov2021-CR--6-styre-2.qgd
Method File : D:\GCMS\Data\Nov2021\GC-Gen2021-CR.qgm
Tuning File : D:\GCMS\Data\Dec2019\11-03-2020 with column.qgt
22Nov2021-CR--6-styre-2.qgd

Chromatogram 22Nov2021-CR--6-styre-2.qgd D:\GCMS\Data\Nov2021\22Nov2021-CR--6-styre-2.qgd

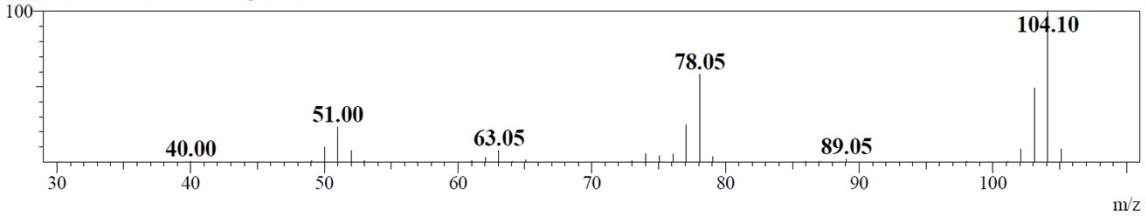


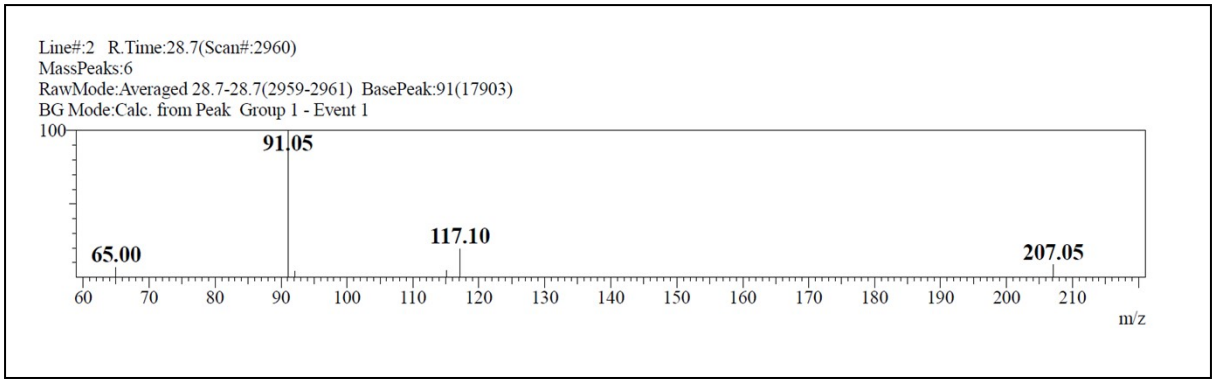
Peak Report TIC

Peak#	R.Time	Area	Area%
1	4.484	10956962	99.44
2	28.655	62062	0.56
		11019024	100.00

Spectrum

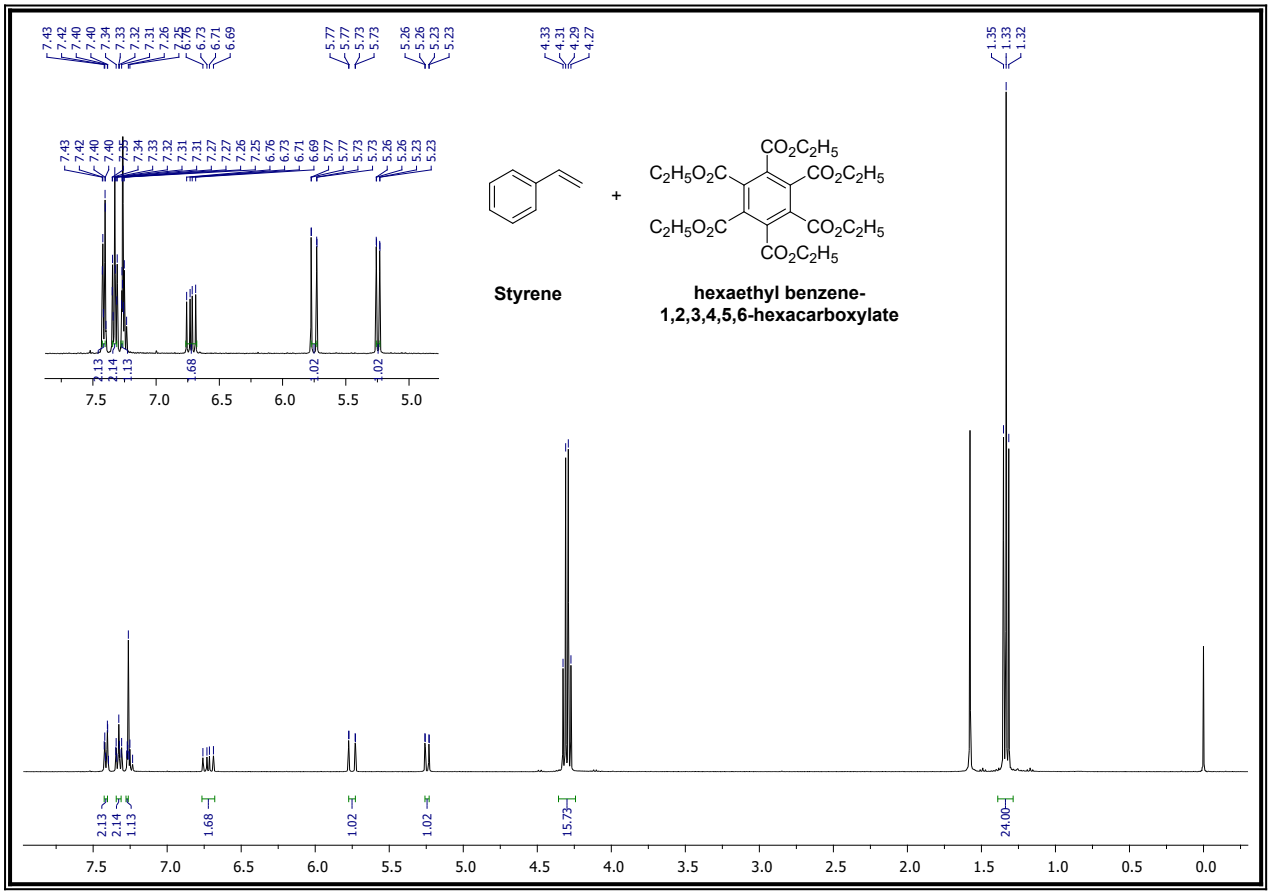
Line#:1 R.Time:4.5(Scan#:59)
MassPeaks:33
RawMode:Averaged 4.5-4.5(58-60) BasePeak:104(961717)
BG Mode:Calc. from Peak Group 1 - Event 1





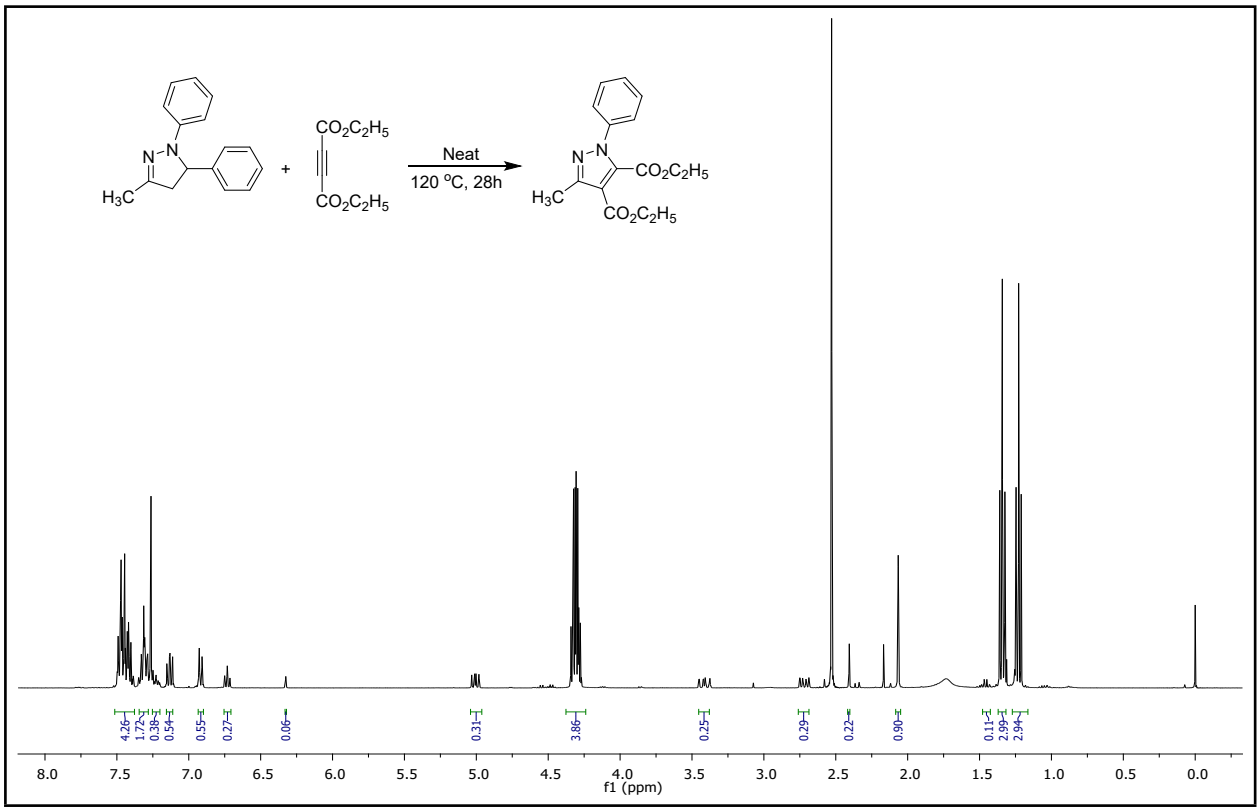
GC-MS sample of **Styrene (Bottle grade sample)**

13. ^{1}H-NMR spectrum (Isolated styrene and hexaethyl benzene-1,2,3,4,5,6-hexacarboxylate[7]):

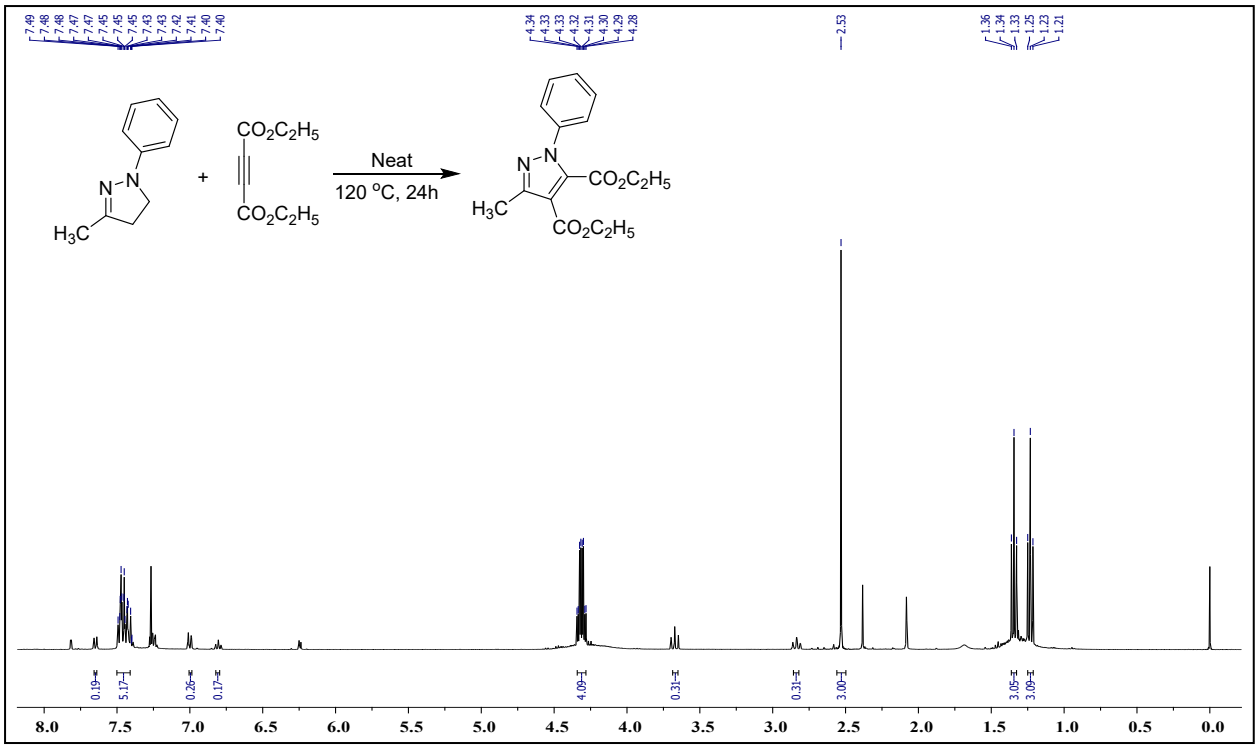


^{1}H-NMR spectrum

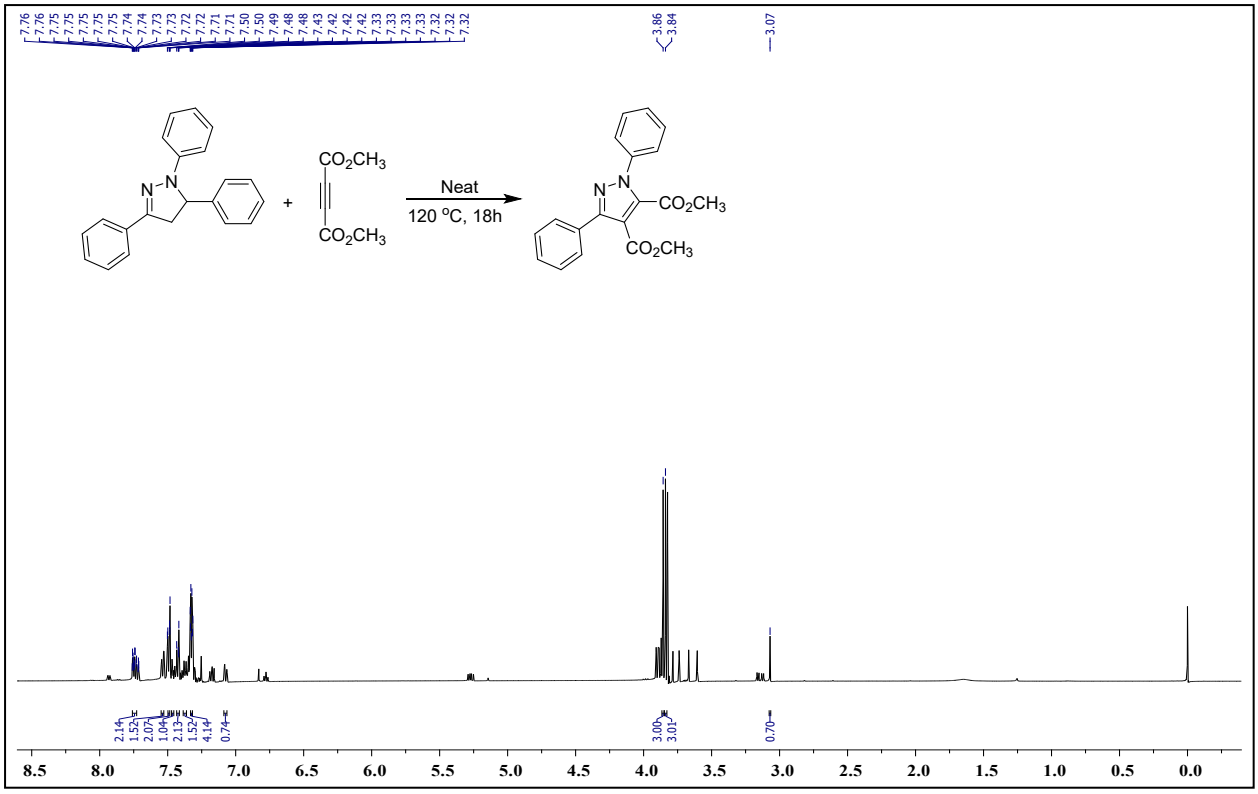
14. Copies of ^{1}H-NMR Spectrums of crude reaction mixture **(5a, 5l, 5s & 8a, 8h)**:



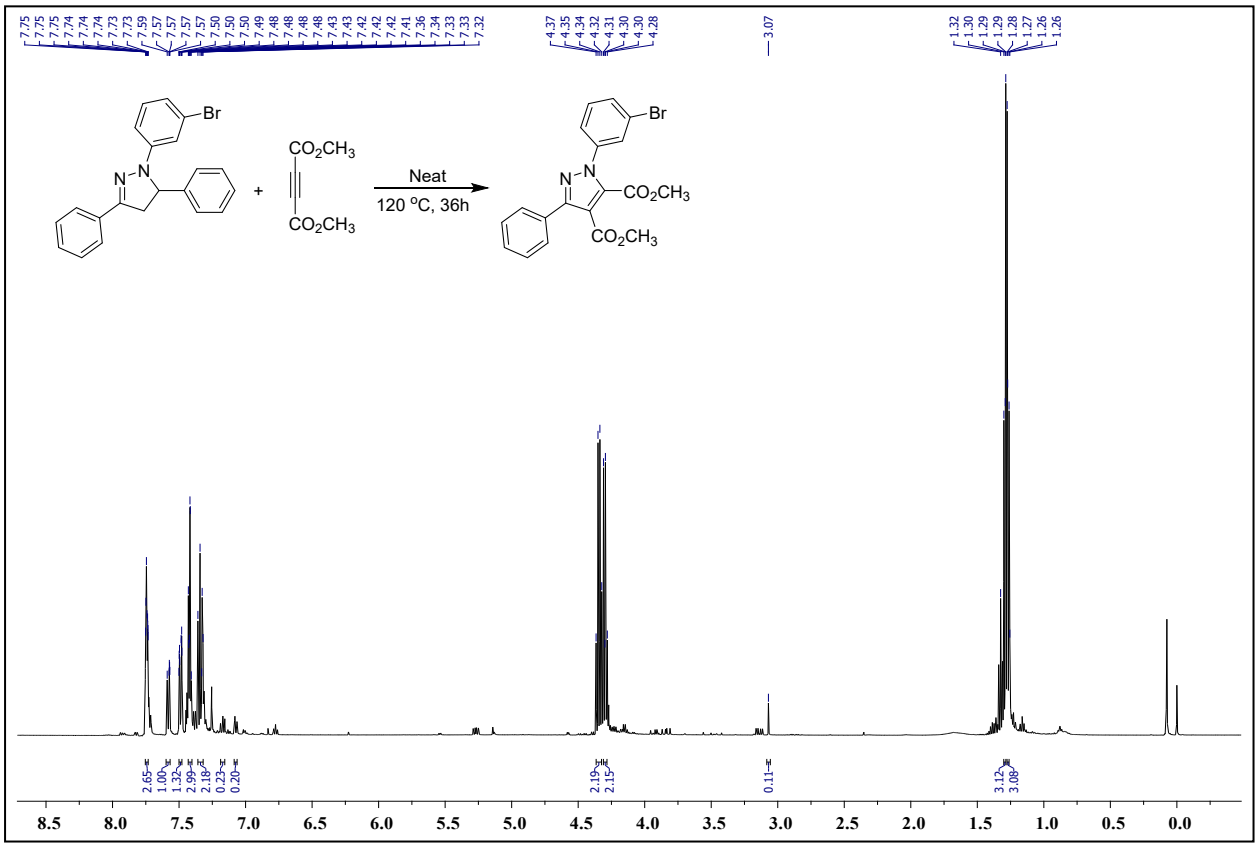
NMR tube reaction crude ^{1}H-NMR spectrum of compound **5a** after 28 hours



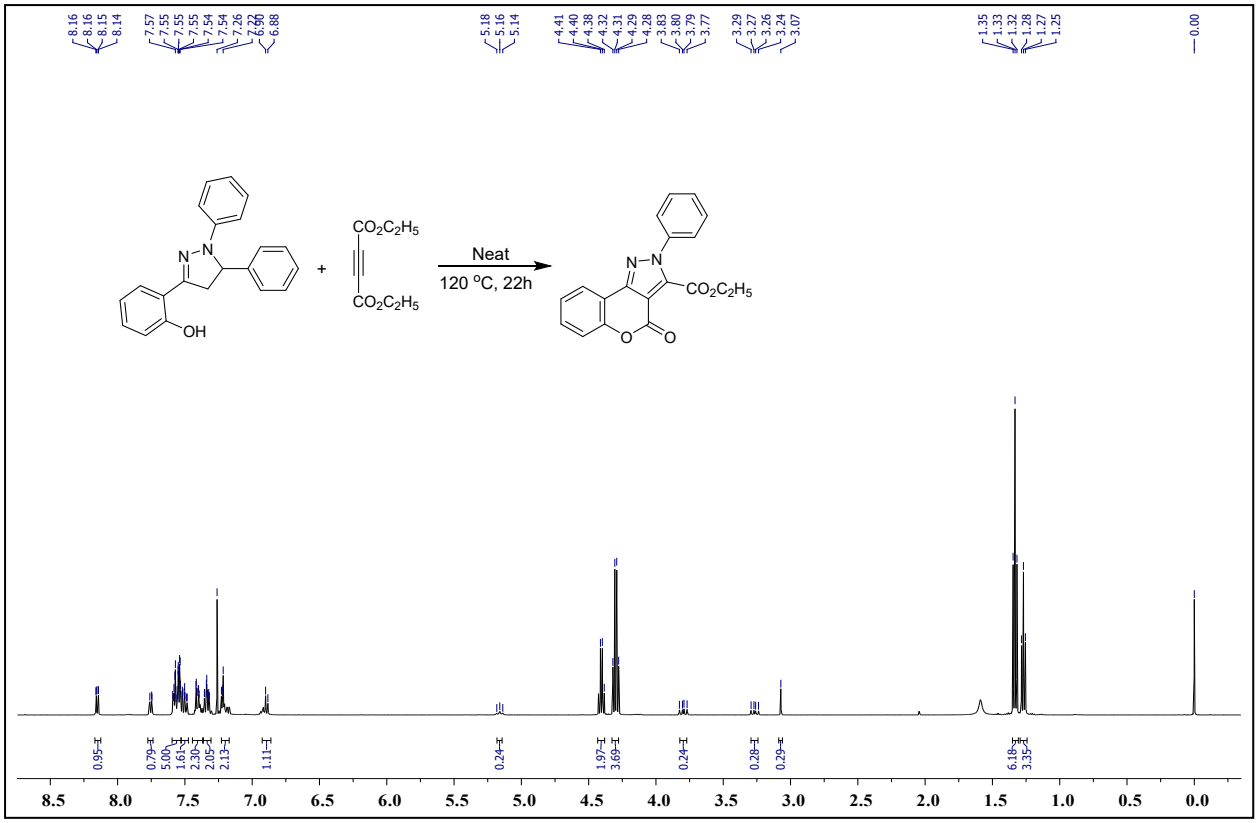
NMR tube reaction crude ^{1}H-NMR spectrum of compound **5a** after 24 hours



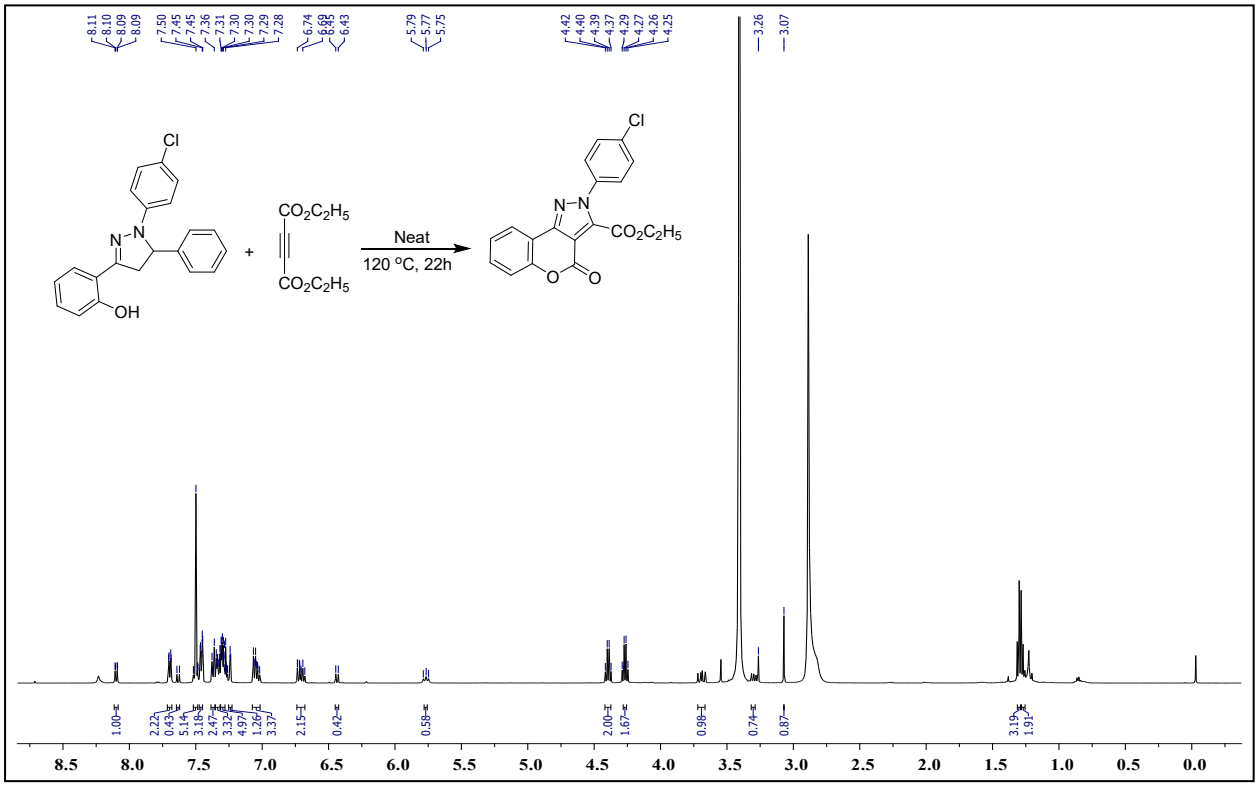
NMR tube reaction crude ^{1}H-NMR spectrum of compound **5l** after 18 hours



NMR tube reaction crude ^{1}H-NMR spectrum of compound **5s** after 36 hours



NMR tube reaction crude ^{1}H-NMR spectrum of compound **8a** after 22 hours



NMR tube reaction crude ^{1}H-NMR spectrum of compound **8h** after 22 hours

15. X-ray crystallography data of compounds (5e & 5n): X-ray data for the compounds **5e** & **5n** was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for other H atoms].

Crystal structure determination of 5e:

Crystal Data for $C_{17}H_{20}N_2O_5$ (*M* =332.35 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 5.6344(3) Å, *b* = 34.6710(19) Å, *c* = 8.8274(5) Å, *β* = 92.1715(18)°, *V* = 1723.20(16) Å^3, *Z* = 4, *T* = 294.15 K, μ(MoKα) = 0.095 mm^{-1}, *Dcalc* = 1.281 g/cm^3, 23948 reflections measured (4.7° ≤ 2Θ ≤ 52.768°), 3501 unique (R_{int} = 0.0309, R_{sigma} = 0.0185) which were used in all calculations. The final R_1 was 0.0433 (I > 2σ(I)) and wR_2 was 0.1120 (all data). CCDC 2070275 contains supplementary Crystallographic data for the structure.

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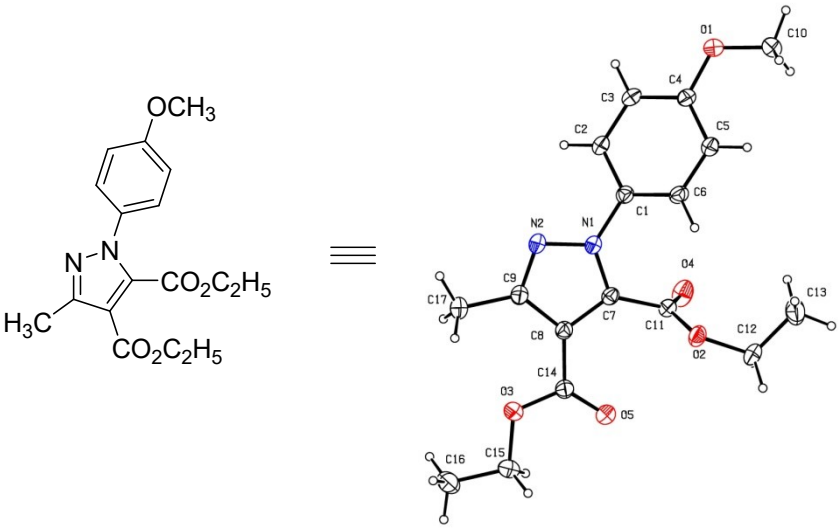

Figure SI. A view of **5e**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Crystal structure determination of 5n:

Crystal Data for $C_{20}H_{18}N_2O_4$ (M =350.36 g/mol): triclinic, space group P-1 (no. 2), a = 8.9944(19) Å, b = 10.698(2) Å, c = 11.488(2) Å, α = 116.186(6)°, β = 111.602(6)°, γ = 90.504(7)°, V = 902.6(3) Å^3, Z = 2, T = 294.15 K, μ(MoKα) = 0.091 mm^{-1}, *Dcalc* = 1.289 g/cm^3, 23581 reflections measured (4.336° ≤ 2Θ ≤ 56.91°), 4518 unique (R_{int} = 0.0685, R_{sigma} = 0.0492) which were used in all calculations. The final R_1 was 0.0574 (I > 2σ(I)) and wR_2 was 0.1727 (all data). CCDC 2070274 contains supplementary Crystallographic data for the structure.

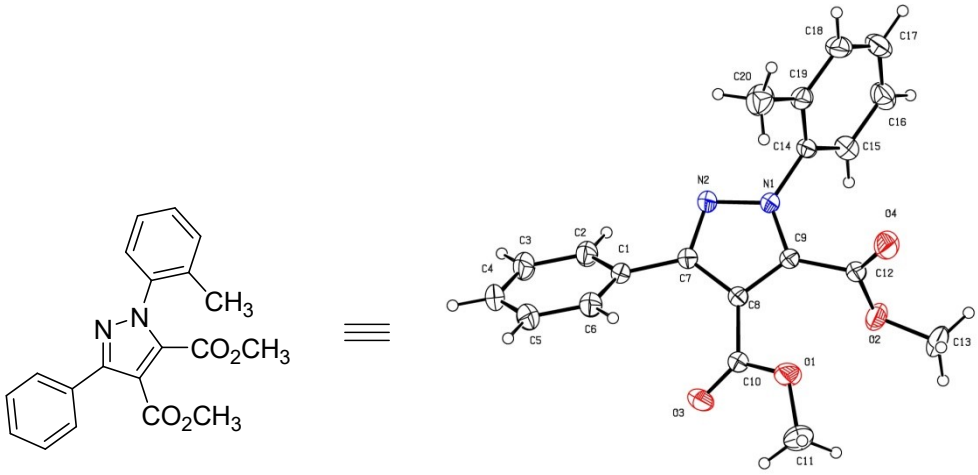

Figure SII. A view of **5n**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** Acta Crystallogr C71: 3-8.