Parallel Synthesis of Bis-heterocyclic Isoxazolylmethyl- and Isoxazolinylmethyl Pyrazoles

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Experimental Procedures for Intermediates and Representative Library Compounds

General Procedures. All chemicals were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography was carried out on pre-coated plates (silica gel $60F_{254}$, 250 μm thickness) and visualized with UV light. Flash chromatography was performed with silica gel 60 (230-400 mesh) or using Combi-Flash on SiO_2. Preparative HPLC was accomplished with an Xterra® MS C_{18} column (19 × 100 mm). Mobile phases were 99.9% CH_3CN with 0.1% TFA (B) and 99.9% water with 0.1%TFA (A). The separation gradient was 0-1 min, 90% A; 1-13 min, 90% to 40% A; 13-20 min, 40% to 0% A; 20-22.5 min, 0% A; 22.5-23.5 min, 0% to 90% A, 23.5-25 min, 90% A. Samples were eluted at a constant flow rate of 15 mL/min and a temperature of 25°C. ^1H NMR spectra were recorded at 400 MHz or 600 MHz at ambient temperature. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz at ambient temperature. Chemical shifts are reported in parts per million relative to CDCl3 (^1H, δ 7.26; ^{13}C, δ 77.26), CD_3OD (^1H, δ 3.31; ^{13}C, δ 49.00) or $(CD_3)_2SO$ (^1H, δ 2.50; ^{13}C, δ 39.52). Infrared spectra were recorded on a FTIR spectrophotometer (Mattson Genesis II). Melting points were determined with an EZMelt Automated Melting Point Apparatus (Stanford Research Systems). The specifications of the LC/MS are as follows: electrospray (+) ionization, mass range 150 - 1500 Da, 20 V cone voltage, and Xterra® MS C_{18} column (2.1 mm × 50 mm × 3.5 μm). Mobile phases were 99.9% CH_3CN with 0.1% TFA (B) and 99.9% water with 0.1%TFA (A). The inlet gradient was 0-5 min, 100% A; 5-25 min, 100% to 0% A; 25-30 min, 0% to 100% A; 30-35 min, 100% A. In microwave mediated reactions, the temperature was maintained using Personal Chemistry Emrys Optimizer EXP microwave reactor, which heated the sealed samples to 80°C in 25 sec, and then maintained that temperature for the duration of the 45 min reaction.

Concentration refers to rotary evaporation under reduced pressure. All yields reported refer to isolated material judged to be homogeneous by TLC and NMR spectroscopy.

All aldoximes used in the syntheses are known compounds. 3-Nitrobenzaldoxime and 3-pyridinealdoxime were commercially available. All other oximes were prepared from reaction of the corresponding aldehyde with hydroxylamine hydrochloride using standard published procedures.[1] All aromatic hydroximoyl chlorides were prepared according to published method.[1b] Dry solvents were used where indicated. Rink Amide-MBHA resin (0.59 mmol/g loading, 100-200 mesh) was purchased from Tianjin Nankai Hecheng Sci & Tech. Co., Ltd, (batch number GRMH0808). After each solid-phase step, the resin was washed by sequential treatment with the following solvents: DMF (2 × 5 mL), H_2O (2 × 5 mL), CH_3OH (3 × 5 mL), and CH_2Cl_2 (5 × 5 mL).

General Procedure for Pyrazole Synthesis: Ethyl 3-phenyl-1*H*-pyrazole-5-carboxylate (3{*1*}). Anhydrous ethanol (400 ml) was added to a 1 L round-bottomed flask, and sodium (7.08g, 308 mmol) was added rapidly. The mixture was stirred until all the sodium had dissolved. After the mixture was cooled to room temperature, diethyl oxalate (24 mL, 177 mmol) was added and the mixture was stirred for 10 min. Acetophenone (16.82 g, 140 mmol) dissolved in anhydrous ethanol (200 ml) was added slowly (about 1.5 h for addition). After the mixture had been stirred continuously for 1 h, acetic acid (20 mL) was added. After 30 min, 85% hydrazine hydrate (11 mL) was added. The reaction mixture was stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in water (200 ml) and then extracted with ethyl acetate. The organic phase was dried over anhydrous magnesium sulfate, filtered and

[1](a) O¨ hler, E.; El-Badawi, M.; Zbiral, E. *Chem. Ber.* **1985**, *118*, 4099–4130. (b) For a related transformation, see: Dixon, S. M.; Milinkevich, K. A.; Fujii, J.; Liu, R.; Yao, N.; Lam, K. S.; Kurth, M. J. *J. Comb. Chem.* **2007**, *9*, 143–157.

concentrated under reduced pressure. The product **3**{*1*} was obtained by flash column chromatography on silica gel with hexane/EtOAc 1:1 as eluent (yellow solid, 25.8 g, 85% yield). The analytical data are in accord with literature values.[2]

Ethyl 3-*o*-tolyl-1*H*-pyrazole-5-carboxylate (3{*2*}). Following the General Procedure for Pyrazole Synthesis using 1-*o*-tolylethanone gave **3**{*2*} (orange solid, 28.0 g, 87% yield): mp 85-86^{o}C; IR (neat) 3139, 3068, 2977, 2861, 1718, 1568, 1488, 1467, 1411, 1239, 1194, 1146, 1111, 1025, 1003, 963, 762, 724 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.45 (m, 1H), 7.24 –7.28 (m, 2H), 7.17-7.21 (m, 1H), 6.89 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 146.4, 141.3, 136.2, 131.2, 129.8, 129.1, 128.9, 126.3, 108.4, 61.2, 21.1, 14.3; ESIMS *m*/*z* 231.12 $(M + H)^+$; Purity was determined to be 86% by HPLC analysis on the basis of absorption at 214 nm.

General Procedure for *N*-Alkylation in NaH/THF System: Ethyl 1-allyl-5-phenyl-1*H*-pyrazole-3-carboxylate (4{*1*}) and ethyl 1-allyl-3-phenyl-1*H*-pyrazole-5-carboxylate (5{*1*}). Ethyl 3-phenyl-1*H*-pyrazole-5-carboxylate **3**{*1*} (638 mg, 2.95 mmol) was added to NaH (60% dispersion in mineral oil; 144 mg, 3.54 mmol) in anhydrous THF (70 mL) and refluxed for 30 min. Allyl bromide (535 mg, 4.43 mmol) was added and the resulting solution refluxed for a further 6 h. The reaction was monitored by TLC and was determined to be completely converted to product. The mixture was cooled to room temperature and water (100 mL) was added. The product was extracted with Et_2O (2 × 75 mL), dried ($MgSO_4$), filtered, and evaporated to dryness. The crude oil was purified by CombiFlash on silica gel with eluent hexane/EtOAc, 2:1. The first eluted is ethyl 1-allyl-3-phenyl-1*H*-pyrazole-5-carboxylate (**5**{*1*})(pale-yellow oil, 75 mg, 10% yield): IR (neat) 3063, 2942, 2984, 1719, 1607, 1539, 1505, 1450, 1431, 1368, 1253,

[2] Dang T. T.; Dang, T. T.; Fischer, C.; Goerls, H.; Langer, P. *Tetrahedron*, **2008**, *64*, 2207-2215.

1204, 1084, 990, 917, 759, 692 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.81-7.83 (m, 2H), 7.40-7.42 (m, 2H), 7.31-7.34 (m, 1H), 7.16 (s, 1H), 6.04-6.11 (m, 1H), 5.23-5.24 (m, 2H), 5.20 (dq, *J* = 10.2, 1.2 Hz, 1H), 5.13 (dq, *J* = 17.4, 1.2 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 150.4, 133.7, 133.6, 132.8, 128.9, 128.3, 125.9, 117.6, 108.5, 61.3, 54.4, 14.5; ESIMS *m*/*z* 257.13 $(M + H)^+$; Purity was determined to be 97% by HPLC analysis on the basis of absorption at 214 nm. The second eluted is ethyl 1-allyl-5-phenyl-1*H*-pyrazole-3-carboxylate (**4**{*1*}) (pale-yellow oil, 651 mg, 86% yield). IR (neat) 3134, 3063, 2983, 2937, 1714, 1606, 1469, 1446, 1424, 1380, 1243, 1204, 1100, 1027, 992, 922, 761, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.24-7.29 (m,5H), 6.69 (s, 1H), 5.80-5.86 (m, 1H), 5.03 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.81(dd, *J* = 17.4, 1.2 Hz, 1H), 4.65-4.67 (m, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.7, 145.4, 143.4, 133.2, 129.8, 129.3, 129.1, 129.0, 118.2, 109.2, 61.2, 53.0, 14.7; ESIMS *m*/*z* 257.13 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-allyl-5-*o*-tolyl-1*H*-pyrazole-3-carboxylate (4{*2*}) and ethyl 1-allyl-3-*o*-tolyl-1*H*-pyrazole-5-carboxylate (5{*2*}). Following the General Procedure for *N*-Alkylation in NaH/THF System using ethyl 3-*o*-tolyl-1*H*-pyrazole-5-carboxylate **3**{*2*} gave the first eluted **5**{*2*}(pale-yellow oil, 24 mg, 3% yield): IR (neat) 3139, 3063, 2983, 2937, 1719, 1534, 1453, 1417, 1368, 1252, 1201, 1084, 990, 958, 917, 760, 725 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.54-7.56 (m, 1H), 7.20-7.24 (m, 3H), 7.01 (s, 1H), 6.04-6.10 (m, 1H), 5.23-5.24 (m, 2H), 5.17-5.19 (m, 1H), 5.10-5.14 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 150.8, 136.3, 133.8, 132.8, 132.5, 131.1, 129.5, 128.2, 126.1, 117.6, 111.4, 61.3, 54.3, 21.4, 14.5; ESIMS *m*/*z* 271.18 $(M + H)^+$; Purity was determined to be 88% by HPLC analysis on the basis of absorption at 214 nm; and gave the second eluted **6**{*2*}(pale-

yellow oil, 718 mg, 90% yield): IR (neat) 3134, 3063, 2983, 2932, 1715, 1458, 1422, 1379, 1240, 1203, 1097, 1026, 990, 923, 758, 726 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34-7.38 (m, 1H), 7.29-7.31 (m, 1H), 7.24-7.26 (m, 1H), 7.19-7.21 (m, 1H), 6.78 (s, 1H), 5.85-5.91 (m, 1H), 5.09-5.11 (m, 1H), 4.86-4.89 (m, 1H), 4.61-4.62 (m, 2H), 4.43 (q, J = 7.2 Hz, 2H), 2.16 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6, 143.8, 143.2, 137.6, 132.6, 130.5, 130.4, 129.8, 129.3, 126.0, 118.4, 109.6, 61.0, 52.8, 20.0, 14.6; ESIMS m/z 271.18 $(M + H)^+$; Purity was determined to be 87% by HPLC analysis on the basis of absorption at 214 nm;

General Procedure for *N*-Alkylation in K_2CO_3/MeCOMe System: Ethyl 5-phenyl-1-(prop-2-ynyl)-1*H*-pyrazole-3-carboxylate (6{*1*}) and ethyl 3-phenyl-1-(prop-2-ynyl)-1*H*-pyrazole-5-carboxylate (7{*1*}). To a solution of ethyl 3-phenyl-1*H*-pyrazole-5-carboxylate **3**{*1*} (3.9 g, 18 mmol) in acetone (75 mL) was added K_2CO_3 (7.6 g, 54 mmol) and propargyl bromide solution (80% wt in toluene) (5.4 g, 36 mmol). The reaction mixture was heated to 70°C for 6.5 h. The reaction mixture was cooled and the solvent was removed to give a crude residue. The residue was taken into EtOAc, and filtered. The filtrate was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by CombiFlash on silica gel with eluent hexane/EtOAc, 2:1. The first eluted is ethyl 3-phenyl-1-(prop-2-ynyl)-1*H*-pyrazole-5-carboxylate (**7**{*1*}) (off-white solid, 3.7 g, 81% yield): mp 83-84°C; IR (neat) 3216, 3134, 3063, 2990, 2942, 2119, 1717, 1542, 1507, 1470, 1454, 1430, 1369, 1317, 1294, 1262, 1204, 1094, 959, 943, 773, 756, 695 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.79-7.80 (m, 2H), 7.34-7.37 (m, 2H), 7.26-7.28 (m, 1H), 7.11 (s, 1H), 5.35 (d, J = 3.0 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 2.42 (t, J = 3.0 Hz, 1H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 150.8, 133.5, 132.4, 128.9, 128.5, 125.8, 108.7, 78.2, 73.6, 61.5, 41.8, 14.4; ESIMS m/z 255.10 $(M + H)^+$; Purity was determined to be

100% by HPLC analysis on the basis of absorption at 214 nm. The second eluted is ethyl 5-phenyl-1-(prop-2-ynyl)-1*H*-pyrazole-3-carboxylate (**6**{*1*}) (off-white solid, 754 mg, 17% yield): mp 102-103^{o}C; IR (neat) 3227, 3149, 3069, 2984, 2941, 2119, 1711, 1475, 1449, 1419, 1372, 1341, 1312, 1256, 1218, 1167, 1109, 1026, 1000, 946, 838, 822, 781, 755, 721, 686 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24-7.34 (m, 5H), 6.65 (s, 1H), 4.76 (d, J = 2.4 Hz, 2H), 4.19 (q, J = 7.2 Hz, 2H), 2.34 (t, J = 2.4 Hz, 1H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ162.1, 145.2, 143.6, 129.4, 129.1, 129.0, 128.8, 109.1, 77.6, 74.8, 61.1, 40.7, 14.5; ESIMS *m*/*z* 255.10 $(M + H)^+$; Purity was determined to be 94% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-(prop-2-ynyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxylate (6{*2*}) and ethyl 1-(prop-2-ynyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxylate (7{*2*}). Following the General Procedure for *N*-Alkylation in K_2CO_3/MeCOMe System using ethyl 3-*o*-tolyl-1*H*-pyrazole-5-carboxylate **3**{*2*} gave the first eluted **7**{*2*}(pale-yellow oil, 3.4 g, 70% yield): IR (neat) 3291, 3048, 2983, 2871, 2127, 1717, 1536, 1502, 1452, 1416, 1368, 1254, 1196, 1088, 957, 759, 725 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56-7.57 (m, 1H), 7.23-7.26 (m, 3H), 7.03 (s, 1H), 5.42 (d, J = 3.0 Hz, 2H), 4.40 (q, J = 7.2 Hz, 2H), 2.49 (s, 3H), 2.38 (t, J = 3.0 Hz, 1H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 151.3, 136.3, 132.7, 132.2, 131.1, 129.5, 128.4, 126.1, 111.9, 78.0, 73.3, 61.6, 41.8, 21.4, 14.5; ESIMS *m*/*z* 269.15 $(M + H)^+$; Purity was determined to be 95% by HPLC analysis on the basis of absorption at 214 nm. The second eluted is ethyl 1-(prop-2-ynyl)-3-o-tolyl-1*H*-pyrazole-5-carboxylate (**6**{*2*}) (pale-yellow oil, 1.3 g, 26% yield). IR (neat) 3274, 3058, 2981, 2871, 2127, 1715, 1459, 1426, 1376, 1239, 1206, 1173, 1102, 1025, 996, 769, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.41 (m, 1H), 7.28-7.33 (m, 3H), 6.78 (s, 1H), 4.76 (d, J = 2.8 Hz, 2H), 4.43 (q, J = 7.2 Hz, 2H), 2.31 (t, J = 2.8 Hz, 1H), 2.20 (s, 3H), 1.42 (t, J = 7.2

Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ162.5, 144.1, 143.9, 138.1, 130.7, 130.5, 130.1, 128.8, 126.2, 110.0, 77.1, 74.1, 61.3, 40.2, 20.2, 14.6; ESIMS *m*/*z* 269.15 $(M + H)^+$; Purity was determined to be 93% by HPLC analysis on the basis of absorption at 214 nm.

General Procedure for Isoxazoline Synthesis (Strategy 1): Ethyl 1-((3-(4-chlorophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxylate (9{*1,1*}). Compound **4**{*1*} (1.2 g, 4.7 mmol) and 4-chlorobenzaldehyde oxime (2.2 g, 14.1 mmol) were dissolved in dichloromethane (30 mL) and cooled in an ice bath. Bleach (laboratory grade, 5.65%, 31.7 mL) was added dropwise and the reaction mixture was stirred overnight. The water layer was extracted with dichloromethane (2 × 40 mL). The combined organic layer was dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by Combiflash on silica gel with hexane/EtOAc in gradient gave some pure product 9{*1,1*} and the mixture of 9{*1,1*} with its byproduct ethyl 1-((3-(4-chlorophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-4-chloro-5-phenyl-1*H*-pyrazole-3-carboxylate, which was subjected to preparative HPLC. After twice separation, pure **9**{*1,1*} was obtained (white solid, 1.2 g, 62% yield): mp 114-115ºC; IR (neat) 3068, 2985, 2938, 1738, 1598, 1495, 1442, 1391, 1355, 1241, 1205, 1091, 1039, 894, 869, 786 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.53 (m, 2H), 7.42-7.49 (m, 5H), 7.33-7.36 (m, 2H), 6.82 (s, 1H), 5.22-5.26 (m, 1H), 4.37-4.43 (m, 3H), 4.29-4.32 (m, 1H), 3.29-3.42 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 156.0, 146.6, 143.9, 136.5, 129.6, 129.5, 129.5, 129.2, 129.1, 128.4, 127.7, 109.4, 79.5, 61.3, 52.5, 38.4, 14.6; ESIMS *m*/*z* 410.12 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(3-nitrophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxylate (9{*1,3*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 1)

using compound **4**{*1*} and 3-Nitrobenzaldoxime gave **9**{*1,3*} (white solid, 1.0 g, 51% yield): mp 108-109ºC; IR (neat) 3073, 2995, 2938, 2162, 1733, 1526, 1479, 1458, 1443, 1391, 1350, 1246, 1205, 1112, 1034, 923, 889, 760, 739 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (t, J = 1.8 Hz, 1H), 8.24-8.26 (m, 1H), 7.96-7.98 (m, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.43-7.49 (m, 5H), 6.83 (s, 1H), 5.26-5.31 (m, 1H), 4.37 (q, J = 7.2 Hz, 2H), 4.35-4.46 (m, 2H), 3.40-3.49 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 155.3, 148.6, 146.7, 143.9, 132.5, 131.0, 130.0, 129.7, 129.6, 129.4, 129.2, 125.0, 121.9, 109.5, 80.0, 61.4, 52.4, 38.1, 14.6; ESIMS *m*/*z* 421.18 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

By-product ethyl 1-((3-(3-nitrophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-4-chloro-5-phenyl-1*H*-pyrazole-3-carboxylate (white solid, 107 mg, 5%): mp 107-108ºC; IR (neat) 3084, 2984, 2937, 1720, 1529, 1478, 1445, 1350, 1245, 1221, 1153, 1061, 912, 784, 736, 700, 676 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (t, J = 1.2 Hz, 1H), 8.25-8.27 (m, 1H), 7.97 (dt, J = 7.8, 1.2 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.46-7.54 (m, 5H), 5.21-5.26 (m, 1H), 4.41 (q, J = 7.2 Hz, 2H), 4.30-4.38 (m, 2H), 3.34-3.51 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 155.3, 148.6, 143.8, 139.6, 132.5, 130.8, 130.5, 130.3, 130.1, 129.3, 126.7, 125.1, 121.9, 112.5, 79.7, 61.8, 53.2, 38.0, 14.4; ESIMS *m*/*z* 455.19 $(M + H)^+$; Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(3-pyridinyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxylate (9{*1,4*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 1) using compound **4**{*1*} and 3-pyridinealdoxime gave **9**{*1,4*} (white solid, 1.0 g, 58% yield): mp 111-112ºC; IR (neat) 3131, 3048, 2923, 2851, 1723, 1599, 1458, 1423, 1391, 1358, 1245, 1207, 1031, 914, 897, 785, 756, 696 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74-8.75 (m, 1H), 8.62-8.63

(m, 1H), 7.94 (dt, *J* = 8.4, 1.8 Hz, 1H); 7.42-7.49 (m, 5H), 7.30-7.33 (m, 1H), 6.82 (s, 1H), 5.24-5.29 (m, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 4.32-4.44 (m, 2H), 3.35-3.45 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 154.6, 151.4, 148.1, 146.6, 143.9, 134.0, 129.6, 129.5, 129.5, 129.1, 125.4, 123.8, 109.5, 79.6, 61.3, 52.4, 37.9, 14.6; ESIMS *m*/*z* 377.18 $(M + H)^+$; Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(3-pyridinyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxylate (9{*2,4*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 1) using compound **4**{*2*} and 3-pyridinealdoxime gave **9**{*2,4*} (pale-yellow oil, 973 g, 53% yield): IR (neat) 3068, 2985, 2851, 1720, 1462, 1430, 1386, 1242, 1178, 1133, 1027, 923, 765, 719, 705, 681 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73-8.74 (m, 1H), 8.62-8.63 (m, 1H), 7.93 (dt, *J* = 7.8, 1.8 Hz, 1H); 7.26-7.37 (m, 5H), 6.77 (s, 1H), 5.14-5.19 (m, 1H), 4.40 (q, *J* = 7.2 Hz, 2H); 4.10-4.24 (m, 2H), 3.33-3.42 (m, 2H), 2.19 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 154.4, 151.4, 148.0, 145.2, 143.9, 137.9, 134.0, 131.0, 130.7, 130.0, 128.9, 126.2, 125.5, 123.8, 109.8, 79.4, 61.3, 52.1, 37.9, 20.0, 14.6; ESIMS *m*/*z* 391.20 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(3-nitrophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (10{*1,3*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 1) using compound **5**{*1*} and 3-nitrobenzaldoxime gave **10**{*1,3*} (white solid, 1.3 g, 67% yield): mp 137-138ºC; IR (neat) 3089, 2984, 2253, 1718, 1531, 1449, 1349, 1261, 1094, 909, 763, 734 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (t, *J* = 1.8 Hz, 1H), 8.20 –8.22 (m, 1H), 8.01 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.73-7.74 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.36-7.39 (m, 2H), 7.30-7.33 (m, 1H), 7.15 (s, 1H), 5.32-5.36 (m, 1H), 4.86-4.92 (m, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.53 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.44 (dd, *J* = 16.8, 10.2 Hz, 1H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$)

δ 159.8, 154.9, 150.8, 148.3, 134.6, 132.3, 132.1, 131.1, 129.7, 128.7, 128.3, 125.5, 124.6, 121.7, 108.4, 79.9, 61.4, 53.3, 37.7, 14.2; ESIMS *m*/*z* 421.07 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(3-pyridinyl)-4,5-dihydroisoxazol-5-yl)methyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (10{*1,4*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 1) using compound **5**{*1*} and 3-pyridinealdoxime gave **10**{*1,4*} (pale-yellow solid, 920 mg, 52% yield): mp 137-138ºC; IR (neat) 3096, 2982, 1718, 1450, 1268, 1183, 1125, 1100, 922, 805, 795, 763, 719, 685 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.79-8.80 (m, 1H), 8.61-8.62 (m, 1H), 8.00 (dt, *J* = 8.4, 1.8 Hz, 1H); 7.75-7.77 (m, 2H), 7.38-7.40 (m, 2H), 7.29-7.34 (m, 2H), 7.15 (s, 1H), 5.28-5.32 (m, 1H), 4.92-4.96 (m, 1H), 4.77-4.80 (m, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.38-3.48 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 154.4, 151.3, 151.0, 148.1, 134.7, 134.0, 132.4, 128.9, 128.5, 125.8, 125.7, 123.8, 108.7, 79.8, 61.6, 53.6, 37.8, 14.4; ESIMS *m*/*z* 377.20 $(M + H)^+$; Purity was determined to be 91% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(3-pyridinyl)-4,5-dihydroisoxazol-5-yl)methyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxylate (10{*2,4*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 1) using compound **5**{*2*} and 3-pyridinealdoxime gave **10**{*2,4*} (white solid, 1.25 g, 68% yield): mp 114-115ºC; IR (neat) 3094, 2966, 1715, 1452, 1273, 1184, 1120, 1105, 918, 804, 797, 763, 716, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.90-8.92 (m, 1H), 8.75-8.77 (m, 1H), 8.50-8.23 (m, 1H), 7.71-7.75 (m, 1H), 7.43-7.45 (m, 1H), 7.20-7.27 (m, 3H), 7.00 (s, 1H), 5.39-5.45 (m, 1H), 4.86-4.96 (m, 2H), 4.89 (q, *J* = 7.2 Hz, 2H), 3.41-3.58 (m, 2H), 2.41 (s, 1H), 1.41 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 152.5, 151.5, 144.6, 141.9, 139.9, 136.1, 134.0, 131.8, 131.2, 1129.2, 129.0, 128.5, 126.2, 126.2, 111.7, 80.9, 61.7, 53.2, 37.0, 21.4, 14.2; ESIMS

m/*z* 391.13 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

General Procedure for Isoxazoline Synthesis (Strategy 2A): Ethyl 1-((3-(4-methoxyphenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxylate (9{*1,2*}). Compound **4**{*1*} (1.2 g, 4.7 mmol) and *N*-hydroxy-4-methoxybenzimidoyl chloride (crude, 1.31 g, 7.05 mmol) were dissolved in DCM (15 mL) in 25-mL round-bottom flask, and the reaction mixture was cooled to 0^oC and placed under nitrogen. Triethylamine (1.96 mL, 14.1 mmol) was added to the reaction mixture via syringe. Then the reaction mixture was allowed to warm to room temperature and vigorously stirred overnight. After washing with water, the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by Combiflash on silica gel with eluent hexane/EtOAc in gradient to give the product **9**{*1,2*} as pale-yellow solid (989 mg, 52% yield): mp 117-118ºC; IR (neat) 3152, 3058, 2983, 1718, 1605, 1515, 1458, 1440, 1422, 1350, 1254, 1246, 1215, 1179, 1039, 835, 823, 764, 702 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.51-7.53 (m, 2H), 7.47-7.49 (m, 2H), 7.39-7.45 (m, 3H), 6.87-6.88 (m, 2H), 6.81 (s, 1H), 5.19-5.24 (m, 1H), 4.38-4.42 (m, 3H), 4.25-4.28 (m, 1H), 3.81 (s, 1H), 3.36-3.41 (m, 1H), 3.23-3.26 (m, 1H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 161.4, 156.4, 146.5, 143.8, 129.7, 129.6, 129.4, 129.1, 128.5, 121.8, 114.3, 109.3, 79.1, 61.2, 55.6, 52.7, 38.7, 14.6; ESIMS *m*/*z* 406.14 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

General Procedure for Isoxazoline Synthesis (Strategy 2B): Ethyl 1-((3-(3-nitrophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxylate (9{*1,3*}). Compound **4**{*1*}

(317 mg, 1.24 mmol) and *N*-hydroxy-3-nitrobenzimidoyl chloride (purified via flash chromatography with 20% EtOAc in hexane, 372 mg, 1.85 mmol) were dissolved in DCM (5 mL) in 25-mL round-bottom flask, and the reaction mixture was cooled to 0^{o}C and placed under nitrogen. Triethylamine (513 μL, 3.72 mmol) was added to the reaction mixture via syringe. Then the reaction mixture was allowed to warm to room temperature and vigorously stirred overnight. After washing with water, the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by Combiflash on silica gel with eluent hexane/EtOAc in gradient to give the product **9**{*1,3*} as pale-yellow solid (461 mg, 89% yield). The spectra data see aforementioned.

Ethyl 1-((3-(4-methoxyphenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxylate (9{*2,2*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 2B) using compound **4**{*2*} and *N*-hydroxy-4-methoxybenzimidoyl chloride (purified via flash chromatography with 10% EtOAc in hexane) gave **9**{*2,2*} (white oil, 375 mg, 72%): IR (neat) 3134, 3058, 2972, 2839, 1718, 1608, 1516, 1423, 1357, 1244, 1207, 1176, 1103, 1022, 831, 762, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.47 (m, 2H), 7.19-7.32 (m, 4H), 6.82-6.84 (m, 2H), 6.73 (s, 1H), 5.03-5.10 (m, 1H), 4.37 (q, J = 7.2 Hz, 2H), 4.04-4.18 (m, 2H), 3.77 (s, 3H), 3.27-3.34 (m, 1H), 3.15-3.21 (m, 1H), 2.14 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6, 161.3, 156.2, 145.1, 143.7, 137.9, 131.0, 130.7, 129.9, 128.9, 128.5, 126.2, 121.8, 114.3, 109.8, 78.9, 61.2, 55.6, 52.4, 38.6, 20.1, 14.6; ESIMS m/z 420.16 $(M + H)^+$; Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(3-nitrophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxylate (9{*2,3*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 2B) using compound **4**{*2*} and *N*-hydroxy-3-nitrobenzimidoyl chloride (purified via flash

chromatography with 20% EtOAc in hexane) gave **9**{*2,3*} (white solid, 421 mg, 78%): mp 74-75ºC; IR (neat) 3134, 3078, 2979, 1719, 1530, 1430, 1348, 1239, 1208, 1103, 1026, 914, 765, 727, 736, 676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (t, J = 2.0 Hz, 1H), 8.23 –8.26 (m, 1H), 7.96 (dt, J = 8.0, 1.2 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.26-7.39 (m, 4H), 6.77 (s, 1H), 5.15-5.23 (m, 1H), 4.38 (q, J = 7.2 Hz, 2H), 4.16-4.27 (m, 2H), 3.39-3.48 (m, 2H), 2.19 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 155.1, 148.6, 145.2, 143.9, 137.9, 131.1, 131.0, 130.8, 130.0, 130.0, 128.8, 126.3, 124.9, 121.8, 109.9, 79.9, 61.3, 52.1, 38.0, 20.1, 14.6; ESIMS m/z 435.06 $(M + H)^+$; Purity was determined to be 94% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(4-methoxyphenyl)-4,5-dihydroisoxazol-5-yl)methyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (10{*1,2*}). Following the General Procedure for Isoxazoline Synthesis (Strategy 2B) using compound **5**{*1*} and *N*-hydroxy-4-methoxybenzimidoyl chloride (purified via flash chromatography with 10% EtOAc in hexane) gave **10**{*1,2*} (white solid, 383 mg, 76% yield): mp 95-96ºC; IR (neat) 3129, 3053, 2963, 2841, 1726, 1607, 1517, 1439, 1355, 1252, 1177, 1082, 1020, 903, 831, 758, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.78 (m, 2H), 7.54-7.56 (m, 2H), 7.36-7.39 (m, 2H), 7.28-7.32 (m, 1H), 7.15 (s, 1H), 6.84-6.86 (m 2H), 5.15-5.24 (m, 1H), 4.92 (dd, J = 13.6, 6.0 Hz,1H), 4.68 (dd, J = 13.6, 6.4 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 3.77 (s, 3H), 3.31-3.33 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 159.9, 156.2, 150.8, 134.7, 132.6, 128.9, 128.6, 128.4, 125.9, 122.1, 114.3, 108.6, 79.2, 61.6, 55.5, 53.9, 38.6, 14.5; ESIMS m/z 406.10 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-(4-methoxyphenyl)-4,5-dihydroisoxazol-5-yl)methyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxylate (10{*2,2*}). Following the General Procedure for Isoxazoline Synthesis (Strategy

2B) using compound **5**{*2*} and *N*-hydroxy-4-methoxybenzimidoyl chloride (purified via flash chromatography with 10% EtOAc in hexane) gave **10**{*2,2*} (white solid, 417 mg, 80% yield): mp 101-102ºC; IR (neat) 3128, 2966, 2835, 1717, 1608, 1516, 1457, 1419, 1356, 1250, 1177, 1091, 832, 762, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.56 (m, 3H), 7.18-7.23 (m, 3H), 7.02 (s, 1H), 6.84-6.86 (m 2H), 5.15-5.22 (m, 1H), 4.94 (dd, J = 13.6, 6.0 Hz, 1H), 4.71 (dd, J = 13.6, 6.4 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 3.76 (s, 3H), 3.27-3.39 (m, 2H), 2.26 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 160.0, 156.2, 151.2, 136.3, 133.9, 132.3, 131.1, 129.4, 128.6, 128.3, 126.1, 122.1, 114.3, 111.6, 79.2, 61.5, 55.6, 53.4, 38.6, 21.4, 14.5; ESIMS m/z 420.09 $(M + H)^+$; Purity was determined to be 99% by HPLC analysis on the basis of absorption at 214 nm.

General Procedure for Isoxazol(in)e Synthesis (Strategy 3): Ethyl 1-((3-methylisoxazol-5-yl)methyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (12{*1,5*}). 1,4-Phenylene diisocyanate (1.92 g, 12 mmol) was added to **7**{*1*} (1.02 g, 4 mmol) in dry THF (53 mL). Triethylamine (1.67 mL, 12 mmol) was added to the reaction mixture and this was heated to 45°C. Nitroethane (862 µL, 12 mmol) was added in syringe pump over a period of 6-8 h, and then the reaction was heated an additional 2 h. The reaction was quenched with water (24 mL) and allowed to stir at room temperature for 1 h. 1,4-Phenylene diisocyanate was removed by filtration over celite (washing several times with ethyl acetate), and the filtrate was then concentrated and subjected to flash chromatography (Combiflash, silica gel, hexane/EtOAc in gradient) to afford **12**{*1,5*} as white solid (1.02 g, 82% yield): mp 66-67ºC; IR (neat) 3124, 3058, 2900, 2937, 2901, 1711, 1610, 1544, 1509, 1471, 1454, 1432, 1385, 1360, 1324, 1269, 1205, 1094, 1018, 1004, 957, 886, 828, 797, 782, 760, 747, 689 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.79-7.81 (m, 2H), 7.39 –7.41 (m,

2H), 7.31-7.34 (m, 1H), 7.18 (s, 1H), 5.92 (s, 1H), 5.89 (s, 2H), 4.36 (q, J = 7.2 Hz, 2H), 2.23 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.5, 160.1, 159.6, 151.3, 134.0, 132.3, 128.9, 128.6, 125.9, 109.0, 103.7, 61.7, 47.4, 14.4, 11.6; ESIMS m/z 312.12 $(M + H)^+$; Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-methyl-4,5-dihydroisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxylate (9{*1,5*}). Following the General Procedure for Isoxazol(in)e Synthesis (Strategy 3) using compound **4**{*1*} and nitroethane gave **9**{*1,5*} (pale-yellow oil, 1.2 g, 95% yield): IR (neat) 3063, 2984, 2932, 2248, 1721, 1438, 1386, 1244, 1212, 1027, 907, 724, 700 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.38 (m, 5H), 6.69 (s, 1H), 4.90-4.95 (m, 1H), 4.29 (q, J = 7.2 Hz, 2H), 4.20 (dd, J = 13.8, 6.0 Hz, 1H), 4.08 (dd, J = 13.8, 5.4 Hz, 1H), 2.92 (ddd, J = 17.4, 10.2, 1.2 Hz, 1H), 2.78 (ddd, J = 17.4, 6.0, 0.6 Hz, 1H), 1.79 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 155.7, 146.3, 143.5, 129.5, 129.4, 129.3, 129.0, 109.2, 78.1, 61.1, 52.6, 42.0, 14.6, 13.1; ESIMS m/z 314.12 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-methylisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxylate (11{*1,5*}). Following the General Procedure for Isoxazol(in)e Synthesis (Strategy 3) using compound **6**{*1*} and nitroethane gave **11**{*1,5*} (pale-yellow oil, 1.21 g, 97% yield): IR (neat) 3135, 3063, 2983, 2935, 2007, 1895, 1720, 1613, 1505, 1469, 1449, 1425, 1381, 1234, 1210, 1102, 1027, 1007, 784, 768, 704 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.41 (m, 3H), 7.33 –7.34 (m, 2H), 6.82 (s, 1H), 5.90 (s, 1H), 5.37 (s, 2H), 4.36 (q, J = 7.2 Hz, 2H), 2.18 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 162.3, 160.2, 146.0, 144.3, 129.7, 129.3, 129.1, 129.0, 109.4, 104.4, 61.3, 46.2, 14.6, 11.6; ESIMS m/z 312.05 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-ethylisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxylate (11{*1,6*}). Following the General Procedure for Isoxazol(in)e Synthesis (Strategy 3) using compound **6**{*1*} and 1-nitropropane gave **11**{*1,6*} (pale-yellow oil, 989 mg, 76% yield): IR (neat) 3129, 3058, 2979, 2937, 1720, 1609, 1446, 1425, 1380, 1206, 1101, 1026, 1006, 752, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.48 (m, 3H), 7.39 –7.41 (m, 2H), 6.89 (s, 1H), 5.98 (s, 1H), 5.44 (s, 2H), 4.43 (q, J = 7.2 Hz, 2H), 2.65 (q, J = 7.6 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 165.6, 162.3, 146.0, 144.3, 129.8, 129.3, 129.2, 129.1, 109.4, 103.2, 61.4, 46.3, 19.7, 14.6, 12.6; ESIMS m/z 326.07 $(M + H)^+$; Purity was determined to be 91% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-methylisoxazol-5-yl)methyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxylate (11{*2,5*}). Following the General Procedure for Isoxazol(in)e Synthesis (Strategy 3) using compound **6**{*2*} and nitroethane gave **11**{*2,5*} (yellow solid, 950 mg, 73% yield): mp 87-88ºC; IR (neat) 3133, 2998, 2947, 1712, 1614, 1475, 1423, 1367, 1266, 1244, 1210, 1023, 996, 774, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.41 (m, 3H), 7.17 –7.19 (m, 1H), 6.81 (s, 1H), 5.90 (s, 1H), 5.23 (s, 2H), 4.40 (q, J = 7.2 Hz, 2H), 2.23 (s, 3H), 2.13 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 162.5, 160.2, 144.7, 144.2, 138.0, 130.8, 130.5, 130.2, 128.5, 126.3, 110.1, 104.4, 61.4, 45.7, 20.0, 14.6, 11.6; ESIMS m/z 326.14 $(M + H)^+$; Purity was determined to be 99% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-ethylisoxazol-5-yl)methyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxylate (11{*2,6*}). Following the General Procedure for Isoxazol(in)e Synthesis (Strategy 3) using compound **6**{*2*} and 1-nitropropane gave **11**{*2,6*} (yellow oil, 829 mg, 61% yield): IR (neat) 3129, 2978, 2932, 1718, 1609, 1460, 1424, 1380, 1234, 1220, 1100, 1026, 777, 765, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.37 (m, 4H), 6.80 (s, 1H), 5.92 (s, 1H), 5.29 (s, 2H), 4.40 (q, J = 7.2 Hz, 2H),

2.59 (q, J = 7.6 Hz, 2H), 2.13 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.1, 162.2, 144.4, 143.9, 137.8, 130.6, 130.3, 130.0, 128.4, 126.1, 109.8, 102.9, 61.0, 45.7, 19.8, 19.5, 14.4, 12.5; ESIMS m/z 340.13 $(M + H)^+$; Purity was determined to be 96% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-ethylisoxazol-5-yl)methyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (12{*1,6*}). Following the General Procedure for Isoxazol(in)e Synthesis (Strategy 3) using compound **7**{*1*} and 1-nitropropane gave **12**{*1,6*} (colorless oil, 965 mg, 74% yield): IR (neat) 3129, 3063, 2978, 2937, 1718, 1608, 1451, 1430, 1259, 1196, 1087, 957, 758, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.90 (m, 2H), 7.43 –7.47 (m, 2H), 7.35-7.39 (m, 1H), 7.26 (s, 1H), 6.05 (s, 1H), 5.95 (s, 2H), 4.40 (q, J = 7.2 Hz, 2H), 2.67 (q, J = 7.6 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.3, 159.5, 151.1, 133.9, 132.3, 128.9, 128.5, 125.8, 108.8, 102.3, 61.6, 47.3, 19.7, 14.3, 12.6; ESIMS m/z 326.18 $(M + H)^+$; Purity was determined to be 93% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-methylisoxazol-5-yl)methyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxylate (12{*2,5*}). Following the General Procedure for Isoxazol(in)e Synthesis (Strategy 3) using compound **7**{*2*} and nitroethane gave **12**{*2,5*} (colorless oil, 963 mg, 74% yield): IR (neat) 3134, 3058, 2982, 2927, 1717, 1610, 1451, 1416, 1257, 1189, 1087, 958, 759, 726 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.55 (m, 1H), 7.19 –7.25 (m, 3H), 7.04 (s, 1H), 5.94 (s, 1H), 5.89 (s, 2H), 4.35 (q, J = 7.2 Hz, 2H), 2.46 (s, 3H), 2.23 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 160.1, 159.8, 151.7, 136.3, 133.1, 132.0, 131.2, 129.4, 128.5, 126.2, 111.9, 103.7, 61.6, 47.3, 21.4, 14.4, 11.6; ESIMS m/z 326.14 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

Ethyl 1-((3-ethylisoxazol-5-yl)methyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxylate (12{*2,6*}). Following the General Procedure for Isoxazol(in)e Synthesis (Strategy 3) using compound **7**{*2*} and 1-nitropropane gave **12**{*2,6*} (colorless oil, 856 mg, 63% yield): IR (neat) 3129, 3053, 2977, 2932, 1718, 1608, 1458, 1417, 1257, 1189, 1087, 957, 760, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.55 (m, 1H), 7.21 –7.27 (m, 3H), 7.05 (s, 1H), 6.00 (s, 1H), 5.92 (s, 2H), 4.37 (q, J = 7.2 Hz, 2H), 2.65 (q, J = 7.6 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.5, 159.8, 151.7, 136.3, 133.2, 131.9, 131.2, 129.4, 128.6, 126.2, 112.0, 102.5, 61.7, 47.2, 21.4, 19.8, 14.4, 12.7; ESIMS m/z 340.13 $(M + H)^+$; Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides: *N*-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-1-((3-(4-methoxyphenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxamide (17{*1,2,4*}). To a solution of Compound **9**{*1,2*}(989 mg, 2.44 mmol) in THF/water (1:1, 20 mL), 5M NaOH (1 mL) was added. The reaction mixture was stirred at 50°C for 6 h. The reaction mixture was allowed to cool to room temperature. After removing THF by rotary evaporation, the remaining aqueous layer was acidified by 2M HCl to pH 2. The precipitate formed was filtered, washed with water and pentane, and dried in vacuum to give **13**{*1,2*} as white solid (918 mg, 99% yield): mp 196-197°C; IR (neat) 2946, 2367, 1725, 1607, 1515, 1445, 1424, 1359, 1253, 1176, 1042, 1013, 826, 786, 766, 698 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.52-7.55 (m, 4H), 7.41-7.47 (m, 3H), 6.92-6.94 (m, 2H), 6.74 (s, 1H), 5.14-5.18 (m, 1H), 4.35 (dd, J = 14.4, 7.2 Hz, 1H), 4.25 (dd, J = 14.4, 5.4 Hz, 1H), 3.82 (s, 3H), 3.47 (dd, J = 16.8, 10.2 Hz, 1H), 3.35 (dd, J = 16.8, 5.4 Hz, 1H); ^{13}C NMR (150 MHz, $(CD_3)_2SO$) δ 164.2, 161.4, 157.1, 145.7, 130.2, 129.8, 129.5, 129.4, 128.9, 122.1, 114.9, 108.9, 105.0, 79.3,

56.0, 52.9, 38.6; ESIMS *m*/*z* 378.20 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

The above-obtained free acid (65 mg, 0.17 mmol) was dissolved in DMF (0.7 mL) and THF (1.5 mL). *N*-hydroxybenzotriazole (35 mg, 0.26 mmol), triethylamine (36.4 μL, 0.26 mmol) and *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (50 mg**,** 0.66 mmol) were added. After the solution was stirred at room temperature for 30 min, Benzo[*d*][1,3]dioxol-5-ylmethanamine (79 mg, 0.52 mmol) was added and the reaction was stirring for 24 h. The resulting reaction mixture was diluted with water (15 mL) and extracted with EtOAc (3 × 20 mL). The combined organics were washed with aq. sodium bicarbonate, water, 1 M aq. HCl, and brine, dried over sodium sulfate, filtered, and concentrated to give the crude material. Purification by preparative HPLC delivered **17**{*1,2,4*} as white solid (64 mg, 74% yield): mp 103-104^{o}C; IR (neat) 3409, 3316, 3063, 2921, 2835, 1661, 1608, 1536, 1516, 1502, 1487, 1442, 1358, 1250, 1177, 1039, 910, 867, 831, 764, 730, 701 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.50-7.53 (m, 2H), 7.40-7.49 (m, 5H), 7.10 (brs, NH, 1H), 6.88-6.90 (m, 3H), 6.86 (s, 1H), 6.77-6.82 (m, 2H), 5.95 (s, 2H), 5.13-5.17 (m, 1H), 4.54 (dd, *J* = 14.4, 6.0 Hz, 1H), 4.48 (dd, *J* = 14.4, 5.4 Hz, 1H), 4.35 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.16 (dd, *J* = 13.8, 6.0 Hz, 1H), 3.83 (s, 3H), 3.37 (dd, *J* = 16.2, 10.2 Hz, 1H), 3.17 (dd, *J* = 16.2, 6.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.0, 161.5, 156.3, 148.1, 147.2, 146.9, 146.4, 132.5, 129.7, 129.5, 129.4, 129.2, 128.5, 121.7, 121.4, 114.4, 108.7, 108.5, 107.4, 101.3, 78.7, 55.6, 52.4, 43.2, 38.8; ESIMS *m*/*z* 511.25 $(M + H)^+$; Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(2-Methoxybenzyl)-1-((3-(3-nitrophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxamide (17{*1,3,1*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **9**{*1,3*} and 2-methoxybenzylamine

gave **17**{*1,3,1*} (off-white solid, 74 mg, 85% yield): mp 69-70°C; IR (neat) 3408, 3073, 2942, 2835, 1774, 1662, 1602, 1530, 1486, 1459, 1348, 1244, 1160, 1026, 915, 809, 755, 736, 698, 675 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.31 (t, J = 1.8 Hz, 1H), 8.23-8.24 (m, 1H), 7.94-7.96 (m, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.41-7.46 (m, 6H), 7.28-7.32 (m, 2H), 6.90-6.95 (m, 2H), 6.85 (s, 1H), 5.21-5.26 (m, 1H), 4.63 (dd, J = 14.4, 6.0 Hz, 1H), 4.59 (dd, J = 14.4, 6.0 Hz, 1H), 4.40 (dd, J = 14.4, 6.0 Hz, 1H), 4.27 (dd, J = 14.4, 6.0 Hz, 1H), 3.89 (s, 3H), 3.45 (dd, J = 16.8, 10.2 Hz, 1H), 3.25 (dd, J = 16.8, 6.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.7, 157.8, 155.2, 148.6, 147.1, 145.9, 132.4, 130.9, 130.2, 130.0, 129.7, 129.5, 129.4, 129.3, 129.2, 125.6, 125.1, 121.7, 121.0, 110.7, 107.7, 79.8, 55.7, 52.3, 39.5, 38.2; ESIMS m/z 512.15 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(3-Bromobenzyl)-5-phenyl-1-((3-(pyridin-3-yl)-4,5-dihydroisoxazol-5-yl) methyl)-1*H*-pyrazole-3-carboxamide (17{*1,4,2*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **9**{*1,4*} and 3-bromobenzylamine gave **17**{*1,4,2*} (white solid, 79 mg, 90% yield): mp 40-41°C; IR (neat) 3300, 3072, 2933, 1655, 1541, 1483, 1455, 1428, 1261, 1180, 1132, 926, 812, 797, 764, 719, 701 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.90 (brs, 1H), 8.66-8.67 (m, 1H), 8.43-8.44 (m, 1H), 7.69-7.71 (m, 1H), 7.35-7.46 (m, 8H), 7.22-7.23 (m, 1H), 7.15-7.18 (m, 1H), 6.81 (s, 1H), 5.24-5.28 (m, 1H), 4.48-4.55 (m, 2H), 4.28-4.35 (m, 2H), 3.44 (d, J = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 152.7, 147.3, 146.2, 144.9, 142.0, 140.9, 139.7, 130.9, 130.8, 130.5, 129.7, 129.5, 129.4, 129.2, 128.7, 126.7, 126.3, 122.9, 107.7, 80.5, 52.1, 42.7, 37.2; ESIMS m/z 517.04 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-(4-Methoxyphenyl)-4,5-dihydroisoxazol-5-yl)methyl)-*N*-(thiophen-2-ylmethyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxamide (17{*2,2,5*}). Following the General Procedure for Solution-

Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **9**{*2,2*} and thiophen-2-ylmethanamine gave **17**{*2,2,5*} (white solid, 71 mg, 85% yield): mp 61-62°C; IR (neat) 3404, 3311, 2935, 2841, 2243, 1777, 1662, 1608, 1539, 1516, 1357, 1252, 1212, 1172, 1042, 908, 830, 766, 726, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.49-7.51 (m, 2H), 7.32-7.36 (m, 2H), 7.29-7.30 (m, 2H), 7.23-7.26 (m, 2H), 7.05-7.06 (m, 1H), 6.98-6.99 (m, 1H), 6.88-6.90 (m, 2H), 6.80 (s, 1H), 5.00-5.05 (m, 1H), 4.82 (dd, *J* = 15.0, 6.0 Hz, 1H), 4.75 (dd, *J* = 15.0, 5.4 Hz, 1H), 4.13 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.00 (dd, *J* = 13.8, 6.0 Hz, 1H), 3.83 (s, 3H), 3.34 (dd, *J* = 16.8, 10.2 Hz, 1H), 3.14 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 161.5, 156.2, 145.6, 145.6, 140.6, 137.9, 130.9, 130.8, 130.1, 128.9, 128.5, 127.2, 126.6, 126.3, 125.6, 121.6, 114.4, 108.0, 78.5, 55.6, 52.2, 38.8, 38.3, 20.1; ESIMS *m/z* 487.12 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(2-Methoxyethyl)-1-((3-(3-nitrophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxamide (17{*2,3,9*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **9**{*2,3*} and 2-methoxyethanamine gave **17**{*2,3,9*} (colorless oil, 71 mg, 91% yield): IR (neat) 3413, 3078, 2931, 2881, 2248, 1778, 1660, 1531, 1483, 1438, 1349, 1209, 1163, 1118, 910, 766, 728, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (t, *J* = 2.0 Hz, 1H), 8.25-8.27 (m, 1H), 7.97-7.99 (m, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.26-7.38 (m, 5H), 6.78 (s, 1H), 5.14-5.21 (m, 1H), 4.19 (dd, *J* = 14.0, 5.6 Hz, 1H), 4.10 (dd, *J* = 14.0, 6.4 Hz, 1H), 3.55-3.69 (m, 4H), 3.46 (dd, *J* = 17.2, 10.8 Hz, 1H), 3.41 (s, 3H), 3.30 (dd, *J* = 17.2, 6.4 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 155.1, 148.6, 145.9, 145.7, 137.9, 132.4, 131.0, 130.8, 130.1, 130.0, 128.8, 126.3, 125.0, 121.7, 108.0, 79.7, 71.3, 59.1, 52.0, 39.3, 38.1, 20.0; ESIMS *m/z* 464.10 $(M + H)^+$; Purity was determined to be 92% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(3-Bromobenzyl)-1-((3-(pyridin-3-yl)-4,5-dihydroisoxazol-5-yl)methyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxamide (17{*2,4,2*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **9**{*2,4*} and 3-bromobenzylamine gave **17**{*2,4,2*} (syrup, 78 mg, 87% yield): IR (neat) 3408, 3316, 3063, 2937, 2248, 1737, 1660, 1539, 1480, 1430, 1184, 1139, 910, 812, 766, 722, 705, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.70 (d, J = 4.8 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 7.72 (dd, J = 8.0, 5.2 Hz, 1H), 7.19-7.48 (m, 9H), 6.79 (s, 1H), 5.15-5.22 (m, 1H), 4.56 (d, J = 6.4 Hz, 2H), 4.10-4.19 (m, 2H), 3.44 (d, J = 8.4 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 152.5, 146.1, 145.9, 145.2, 142.3, 140.8, 139.4, 137.9, 131.0, 130.9, 130.8, 130.5, 130.1, 128.8, 128.6, 126.8, 126.3, 126.2, 122.9, 108.2, 80.3, 51.8, 42.8, 37.2, 20.1; ESIMS m/z 531.12 $(M + H)^+$; Purity was determined to be 92% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(Cyclopropylmethyl)-1-((3-(4-methoxyphenyl)-4,5-dihydroisoxazol-5-yl)methyl)-3-phenyl-1*H*-pyrazole-5-carboxamide (18{*1,2,10*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **10**{*1,2*} and cyclopropylmethanamine gave **18**{*1,2,10*} (white solid, 63 mg, 86% yield): mp 150-151^oC; IR (neat) 3337, 3078, 3006, 2935, 2841, 2243, 1653, 1608, 1549, 1516, 1461, 1444, 1255, 1177, 909, 831, 731, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71-7.74 (m, 2H), 7.54-7.57 (m, 2H), 7.29-7.40 (m, 3H), 6.85-6.88 (m, 2H), 6.82 (s, 1H), 6.51 (brs, NH, 1H), 5.21-5.28 (m, 1H), 4.70-4.82 (m, 2H), 3.82 (s, 3H), 3.36-3.49 (m, 2H), 3.29 (dd, J = 7.2, 5.6 Hz, 2H), 1.03-1.13 (m, 1H), 0.51-0.60 (m, 2H), 0.24-0.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 160.0, 156.3, 150.6, 138.5, 132.5, 128.6, 128.4, 128.1, 125.7, 121.8, 114.1, 103.8, 79.2, 55.3, 53.5, 44.6, 38.3, 10.6, 3.61, 3.59; ESIMS m/z 431.14 $(M + H)^+$; Purity was determined to be 97% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(Furan-2-ylmethyl)-1-((3-(3-nitrophenyl)-4,5-dihydroisoxazol-5-yl)methyl)-3-phenyl-1H-pyrazole-5-carboxamide (18{*1,3,6*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **10**{*1,3*} and furan-2-ylmethanamine gave **18**{*1,3,6*} (off-white solid, 59 mg, 74% yield): mp 143-144°C; IR (neat) 3329, 3084, 2957, 2250, 1658, 1528, 1446, 1348, 1280, 909, 731, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (t, J = 2.0 Hz, 1H), 8.17-8.19 (m, 1H), 7.94-7.97 (m, 1H), 7.64-7.67 (m, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.39-7.41 (m, 1H), 7.27-7.36 (m, 3H), 6.80 (s, 1H), 6.58 (t, J = 5.6 Hz, NH, 1H), 6.35-6.37 (m, 2H), 5.31-5.37 (m, 1H), 4.92 (dd, J = 14.0, 5.6 Hz, 1H), 4.78 (dd, J = 14.0, 5.6 Hz, 1H), 4.63 (d, J = 5.6 Hz, 2H), 3.59 (dd, J = 16.8, 5.6 Hz, 1H), 3.59 (dd, J = 16.8, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 155.4, 151.1, 150.6, 148.5, 142.8, 138.0, 132.5, 132.2, 131.2, 129.9, 128.9, 128.5, 125.7, 124.7, 121.9, 110.8, 108.3, 104.2, 80.3, 53.4, 37.9, 36.9; ESIMS m/z 472.14 $(M + H)^+$; Purity was determined to be 93% by HPLC analysis on the basis of absorption at 214 nm.

Morpholino(3-phenyl-1-((3-(pyridin-3-yl)-4,5-dihydroisoxazol-5-yl)methyl)-1*H*-pyrazol-5-yl)methanone (18{*1,4,11*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **10**{*1,4*} and morpholine gave **18**{*1,4,11*} (white solid, 62 mg, 87% yield): mp 65-66°C; IR (neat) 3068, 2962, 2922, 2861, 2243, 1631, 1447, 1254, 1187, 1136, 1114, 918, 814, 771, 721, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 8.60-8.61 (m, 1H), 8.18-8.20 (m, 1H), 7.59-7.61 (m, 2H), 7.49-7.53 (m, 1H), 7.29-7.35 (m, 3H), 6.55 (s, 1H), 5.22-5.29 (m, 1H), 4.78 (dd, J = 14.4, 4.4 Hz, 1H), 4.51 (dd, J = 14.4, 4.4 Hz, 1H), 3.74-3.90 (m, 8H), 3.67 (dd, J = 16.4, 5.2 Hz, 1H), 3.48 (dd, J = 16.4, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 153.1, 150.6, 145.6, 143.1, 138.0, 137.9, 132.0, 128.7, 128.3,

127.7, 125.4, 125.3, 104.0, 80.1, 77.2, 66.8, 52.6, 48.4, 42.6, 37.0; ESIMS *m*/*z* 418.20 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-(4-Methoxyphenyl)-4,5-dihydroisoxazol-5-yl)methyl)-*N*-(4-methylbenzyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxamide (18{*2,2,3*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **10**{*2,2*} and 4-methylbenzylamine gave **18**{*2,2,3*} (white solid, 72 mg, 85% yield): mp 156-157°C; IR (neat) 3360, 3017, 2939, 2253, 1656, 1607, 1552, 1515, 1452, 1358, 1284, 1254, 1174, 1020, 918, 870, 833, 760, 720 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.53-7.58 (m, 2H), 7.37-7.38 (m, 1H), 7.16-7.29 (m, 7H), 6.86-6.88 (m, 2H), 6.63-6.64 (m, 1H), 6.61 (s, 1H), 5.21-5.25 (m, 1H), 4.77-4.84 (m, 2H), 4.55-4.62 (m, 2H), 3.82 (s, 3H), 3.46 (dd, J = 16.8, 6.6 Hz, 1H), 3.39 (dd, J = 16.8, 10.8 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 165.4, 159.7, 151.1, 136.7, 132.4, 129.0, 128.6, 125.9, 104.1, 102.4, 71.1, 59.1, 47.0, 39.5, 19.8, 12.7; ESIMS *m*/*z* 495.17 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-(Pyridin-3-yl)-4,5-dihydroisoxazol-5-yl)methyl)-3-*o*-tolyl-*N*-(4-(trifluoromethoxy) benzyl)-1*H*-pyrazole-5-carboxamide (18{*2,4,7*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **10**{*2,4*} and 4-(trifluoromethoxy)benzylamine gave **18**{*2,4,7*} (white solid, 81 mg, 89% yield): mp 98-99°C; IR (neat) 3314, 3063, 2962, 2248, 1659, 1550, 1509, 1451, 1259, 1219, 1191, 1166, 916, 813, 766, 720, 683 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.90 (dd, J = 1.2 Hz, 1H), 8.65-8.66 (m, 1H), 8.33-8.35 (m, 1H), 7.61-7.63 (m, 1H), 7.41-7.43 (m, 2H), 7.32-7.33 (m, 1H), 7.14-7.23 (m, 5H), 6.88 (t, J = 6.0 Hz, NH, 1H), 6.68 (s, 1H), 5.36-5.41 (m, 1H), 5.02 (dd, J = 14.4, 5.4 Hz, 1H), 4.78 (dd, J = 14.4, 4.8 Hz, 1H), 4.63 (d, J = 6.0 Hz, 2H), 3.59 (dd, J = 16.8, 5.4 Hz, 1H), 3.42 (dd, J = 16.8, 10.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 152.6, 151.2, 148.7,

144.4, 142.1, 139.2, 137.1, 136.4, 135.8, 131.5, 131.0, 129.2, 128.9, 128.5, 128.3, 125.9, 125.8, 121.3, 119.6, 116.7, 114.8, 107.0, 80.8, 52.9, 42.9, 36.7, 21.1; ESIMS *m*/*z* 536.17 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(3-bromobenzyl)-1-((3-methylisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxamide (19{*1,5,2*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **11**{*1,5*} and 3-bromobenzylamine gave **19**{*1,5,2*} (colorless oil, 61 mg, 79% yield): IR (neat) 3404, 3300, 3140, 3057, 2933, 1776, 1660, 1613, 1573, 1541, 1481, 1461, 1425, 1377, 1354, 1258, 1214, 1166, 1975, 1007, 963, 891, 808, 764, 704 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.45-7.49 (m, 4H), 7.36-7.41 (m, 4H), 7.27-7.28 (m, 1H), 7.20 (t, J = 7.8 Hz, 1H), 6.90 (s, 1H), 5.90 (s, 1H), 5.32 (s, 2H), 4.60 (d, J = 6.6 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 162.6, 160.4, 146.8, 146.1, 140.3, 131.0, 130.9, 130.5, 129.9, 129.4, 129.1, 129.0, 126.7, 123.0, 107.7, 104.4, 45.9, 43.0, 11.5; ESIMS *m*/*z* 452.95 $(M + H)^+$; Purity was determined to be 96% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(2-methoxyethyl)-1-((3-methylisoxazol-5-yl)methyl)-5-phenyl-1*H*-pyrazole-3-carboxamide (19{*1,5,9*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **11**{*1,5*} and 2-methoxyethanamine gave **19**{*1,5,9*} (colorless oil, 45 mg, 78% yield): IR (neat) 3418, 3323, 2932, 2886, 1776, 1659, 1611, 1538, 1484, 1455, 1423, 1197, 1166, 1120, 1005, 764, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.42-7.45 (m, 3H), 7.35-7.36 (m, 2H), 7.26 (brs, NH, 1H), 6.84 (s, 1H), 5.88 (s, 1H), 5.32 (s, 2H), 3.60-3.63 (m, 2H), 3.55 (t, J = 5.4 Hz, 2H), 3.37 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.9, 162.4, 160.3, 146.8, 146.4, 129.7, 129.3, 129.2, 129.1, 107.4, 104.3, 71.4, 59.0,

45.9, 39.3, 11.5; ESIMS *m*/*z* 341.15 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-Ethylisoxazol-5-yl)methyl)-5-phenyl-*N*-(thiophen-2-ylmethyl)-1*H*-pyrazole-3-carboxamide (19{*1,6,5*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **11**{*1,6*} and thiophen-2-ylmethanamine gave **19**{*1,6,5*} (colorless oil, 55 mg, 82% yield): IR (neat) 3417, 3318, 2975, 2936, 2238, 1663, 1609, 1534, 1484, 1457, 1426, 1214, 765, 701 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.45-7.48 (m, 3H), 7.38-7.40 (m, 2H), 7.24-7.26 (m, 2H), 7.05-7.06 (m, 1H), 6.96-6.98 (m, 1H), 6.91 (s, 1H), 5.90 (s, 1H), 5.33 (s, 2H), 4.81 (d, J = 6.0 Hz, 2H), 2.65 (q, J = 7.8 Hz, 2H), 1.24 (t, J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 165.6, 161.5, 146.7, 146.3, 141.0, 129.6, 129.2, 129.1, 129.0, 127.0, 126.3, 125.4, 107.5, 102.9, 45.9, 38.0, 19.7, 12.6; ESIMS *m*/*z* 393.15 $(M + H)^+$; Purity was determined to be 95% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-Methylisoxazol-5-yl)methyl)-5-*o*-tolyl-*N*-(3-(trifluoromethyl)benzyl)-1*H*-pyrazole-3-carboxamide (19{*2,5,8*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **11**{*2,5*} and (3-(trifluoromethyl)phenyl) methanamine gave **19**{*2,5,8*} (colorless oil, 76 mg, 98% yield): IR (neat) 3413, 3312, 2935, 2248, 1779, 1661, 1612, 1540, 1484, 1434, 1328, 1161, 1125, 1073, 768, 727, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.61 (m, 5H), 7.37-7.41 (m, 1H), 7.25-7.33 (m, 2H), 7.17-7.19 (m, 1H), 6.85 (s, 1H), 5.84 (s, 1H), 5.14 (s, 2H), 4.70 (d, J = 6.4 Hz, 2H), 2.24 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 162.7, 160.3, 146.0, 145.4, 139.2, 138.0, 131.5, 131.2 (q, J = 32.3 Hz, CF_3), 130.9, 130.4, 130.3, 129.5, 128.4, 126.4, 125.6, 124.7, 122.9, 108.3, 104.4, 45.3, 43.1, 20.0, 11.5; ESIMS *m*/*z* 455.07 $(M + H)^+$; Purity was determined to be 97% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-Ethylisoxazol-5-yl)methyl)-*N*-(4-methylbenzyl)-5-*o*-tolyl-1*H*-pyrazole-3-carboxamide (19{*2,6,3*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **11**{*2,6*} and 4-methylbenzylamine gave **19**{*2,6,3*} (yellow oil, 69 mg, 98% yield): IR (neat) 3415, 3310, 2977, 2927, 1778, 1662, 1609, 1539, 1483, 1430, 1251, 1210, 1163, 812, 769, 725, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.40 (m, 6H), 7.16-7.18 (m, 3H), 6.84 (s, 1H), 5.81 (s, 1H), 5.13 (s, 2H), 4.61 (d, J = 6.0 Hz, 2H), 2.62 (q, J = 7.6 Hz, 2H), 2.35 (s, 3H), 2.12 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.6, 162.6, 146.2, 145.2, 138.0, 137.6, 134.9, 130.9, 130.4, 130.2, 129.7, 128.5, 128.3, 126.4, 108.3, 103.0, 45.5, 43.5, 21.3, 20.0, 19.7, 12.7; ESIMS *m*/*z* 415.19 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-Methylisoxazol-5-yl)methyl)-3-phenyl-*N*-(thiophen-2-ylmethyl)-1*H*-pyrazole-5-carboxamide (20{*1,5,5*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **12**{*1,5*} and thiophen-2-ylmethanamine gave **20**{*1,5,5*} (white solid, 48 mg, 75% yield): mp 154-155^oC; IR (neat) 3296, 3104, 2997, 2928, 1660, 1606, 1554, 1527, 1465, 1451, 1425, 1287, 1219, 1115, 961, 815, 754, 686 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.74-7.75 (m, 2H), 7.37-7.39 (m, 2H), 7.30-7.33 (m, 1H), 7.25-7.26 (m, 1H), 7.02-7.03 (m, 1H), 6.97-6.98 (m, 1H), 6.81 (s, 1H), 6.43 (brs, NH, 1H), 5.98 (s, 1H), 5.93 (s, 2H), 4.76 (d, J = 6.6 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 160.1, 159.3, 151.1, 140.1, 136.3, 132.3, 128.9, 128.6, 127.3, 126.8, 125.9, 125.9, 104.1, 103.9, 47.0, 38.6, 11.6; ESIMS *m*/*z* 379.06 $(M + H)^+$; Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-Ethylisoxazol-5-yl)methyl)-*N*-(2-methoxyethyl)-3-phenyl-1*H*-pyrazole-5-carboxamide (20{*1,6,9*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **12**{*1,6*} and 2-methoxyethanamine gave **20**{*1,6,9*} (white solid, 53 mg, 88% yield): mp 107-108°C; IR (neat) 3324, 3129, 2977, 2935, 2246, 1656, 1608, 1551, 1525, 1461, 1447, 1426, 1281, 1197, 1115, 1095, 958, 910, 757, 725 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.78-7.79 (m, 2H), 7.40-7.42 (m, 2H), 7.32-7.35 (m, 1H), 6.85 (s, 1H), 6.50 (brs, NH, 1H), 6.00 (s, 1H), 5.93 (s, 2H), 3.61-3.63 (m, 2H), 3.55-3.56 (m, 2H), 3.40 (s, 3H), 2.63 (q, J = 7.8 Hz, 2H), 1.22 (t, J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 165.4, 159.7, 151.1, 136.7, 132.4, 129.0, 128.6, 125.9, 104.1, 102.4, 71.1, 59.1, 47.0, 39.5, 19.8, 12.7; ESIMS m/z 355.21 $(M + H)^+$; Purity was determined to be 100% by HPLC analysis on the basis of absorption at 214 nm.

***N*-(2-methoxybenzyl)-1-((3-methylisoxazol-5-yl)methyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxamide (20{*2,5,1*}).** Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **12**{*2,5*} and 2-methoxybenzylamine gave **20**{*2,5,1*} (yellow syrup, 64 mg, 90% yield): IR (neat) 3313, 3129, 2946, 2898, 2247, 1779, 1652, 1605, 1550, 1493, 1448, 1244, 1165, 908, 752, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.46 (m, 1H), 7.18-7.31 (m, 5H), 6.89-6.96 (m, 2H), 6.80 (brs, NH, 1H), 6.64 (s, 1H), 5.99 (s, 1H), 5.92 (s, 2H), 4.59 (d, J = 5.6 Hz, 2H), 3.86 (s, 3H), 2.41 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 160.2, 159.5, 157.8, 151.5, 136.4, 136.1, 132.0, 131.1, 130.1, 129.6, 129.5, 128.6, 126.1, 125.5, 121.0, 110.7, 107.1, 104.1, 55.7, 46.7, 40.0, 21.3, 11.6; ESIMS m/z 417.15 $(M + H)^+$; Purity was determined to be 97% by HPLC analysis on the basis of absorption at 214 nm.

1-((3-Ethylisoxazol-5-yl)methyl)-*N*-(thiophen-2-ylmethyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxamide (20{*2,6,5*}). Following the General Procedure for Solution-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound **12**{*2,6*} and thiophen-2-ylmethanamine gave **20**{*2,6,5*} (pale-yellow oil, 64 mg, 90% yield): IR (neat) 3307, 3124, 2976, 2932, 2248, 1779, 1652, 1608, 1549, 1521, 1452, 1427, 1272, 1211, 1162, 760, 726, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.45 (m, 1H), 7.17-7.26 (m, 4H), 6.93-7.00 (m, 2H), 6.82 (t, J = 5.6 Hz, NH, 1H), 6.70 (s, 1H), 6.07 (s, 1H), 5.94 (s, 2H), 4.73 (d, J = 6.0 Hz, 2H), 2.62 (q, J = 7.6 Hz, 2H), 2.39 (s, 3H), 1.20 (t, = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 165.6, 159.5, 151.6, 140.1, 136.3, 135.6, 131.8, 131.2, 129.4, 128.6, 127.3, 126.8, 126.2, 125.9, 107.5, 102.9, 46.7, 38.6, 21.2, 19.7, 12.7; ESIMS m/z 407.08 $(M + H)^+$; Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

General Procedure for Solid-Phase Synthesis of Isoxazoline-Pyrazole Amide: 1-((3-Methyl-4,5-dihydroisoxazol-5-yl)methyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxamide (21{*2,5*}) and 1-((3-ethyl-4,5-dihydroisoxazol-5-yl)methyl)-3-*o*-tolyl-1*H*-pyrazole-5-carboxamide (21{*2,6*}).
Rink amide resin (375 mg, 0.19 mmol) was swollen in DMF (5 mL) for 3 h, followed by treatment with 20% piperidine in DMF (5 mL) for 20 min. After washing and a positive Kaiser test, 1-allyl-3-*o*-tolyl-1*H*-pyrazole-5-carboxylic acid (137 mg, 0.57 mmol) was coupled using 2-(1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (215 mg, 0.57 mmol), *N*-hydroxybenzotriazole hydrate (76 mg, 0.57 mmol), and diisopropylethyl-amine (98 μL, 0.57 mmol) in DMF (5 mL). After shaking for 10 h, the resin was washed, followed by a negative Kaiser test. The resin was split into two pyrex vessels (~188 mg each) with one of the pyrex vessel receiving nitroethane (103.2 μL, 1.44 mmol), phenyl isocyanate (313.2 μL, 2.88 mmol),

and triethylamine (7.2 μL) in THF (2 mL). The reaction mixture was submitted to microwave irradiation at 80°C for 45 min. The resin was then washed with DMF, THF, and ether, vacuum-dried, and cleaved with 5 mL of TFA/triisopropylsilane/H_2O (95%/2.5%/2.5%) for 2 h. After this crude reaction product was drained and collected, the cleavage was repeated for an additional 2 h with fresh cleavage reagents. The combined crude cleavages were concentrated to a minimal volume to afford crude **21**{*2,5*}. After purified by preparative HPLC, **21**{*2,5*} was obtained as a white solid (24 mg, 85% overall yield from Rink resin): mp 44-45°C; IR (neat) 3335, 3190, 2952, 2922, 1673, 1611, 1535, 1502, 1455, 1434, 1385, 1331, 1169, 959, 764, 729 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.50-7.51 (m, 1H), 7.23-7.28 (m, 3H), 6.73 (s, 1H), 6.42 (brs, NH_2, 1H), 5.88 (brs, NH_2, 1H), 5.05-5.09 (m, 1H), 4.69-4.75 (m, 2H), 3.06-3.07 (m, 2H), 2.47 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.0, 155.8, 151.1, 136.5, 136.0, 132.0, 130.9, 129.1, 128.2, 126.0, 108.0, 78.4, 53.3, 41.6, 21.2, 13.0; ESI-MS *m/z* 299.08 $(M + H)^+$. Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

The other pyrex vessel received nitropropane (128.4 μL, 1.44 mmol), phenyl isocyanate (313.2 μL, 2.88 mmol), and triethylamine (7.2 μL) in THF (2 mL). Following the general procedure, **21**{*2,6*} was obtained as a white solid (25 mg, 83% overall yield from Rink resin): mp 164-165°C; IR (neat) 3347, 3190, 2962, 2927, 1674, 1611, 1532, 1499, 1454, 1419, 1378, 1345, 1158, 958, 761, 726, 683 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.51-7.52 (m, 1H), 7.23-7.28 (m, 3H), 6.73 (s, 1H), 6.36 (brs, NH_2, 1H), 5.69 (brs, NH_2, 1H), 5.05-5.09 (m, 1H), 4.68-4.75 (m, 2H), 3.02-3.08 (m, 2H), 2.47 (s, 3H), 2.32 (q, J = 7.8 Hz, 2H), 1.12 (t, J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 160.3, 151.0, 136.5, 136.0, 132.0, 130.9, 129.1, 128.2, 125.9, 107.9, 78.2, 77.4, 53.2, 39.9, 21.2, 10.8; ESI-MS *m/z* 313.14 $(M + H)^+$. Purity was determined to be 99% by HPLC analysis on the basis of absorption at 214 nm.

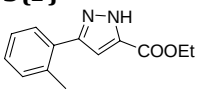
1-((3-Methyl-4,5-dihydroisoxazol-5-yl)methyl)-3–phenyl-1*H*–pyrazole–5-carboxamide (21{*1,5*}) and 1-((3-ethyl-4,5-dihydroisoxazol-5-yl)methyl)-3-phenyl-1*H*-pyrazole-5-carboxamide (21{*1,6*}). Following the General Procedure for Solid-Phase Synthesis of Isoxazol(in)e-Pyrazole Amides using compound 1-allyl-3-phenyl-1*H*-pyrazole-5-carboxylic acid (130 mg, 0.57 mmol), and nitroethane (103.2 μL, 1.44 mmol) or nitropropane (128.4 μL, 1.44 mmol) gave **21**{*1,5*} or **21**{*1,6*}, respectively.

21{*1,5*} (white solid, 24 mg, 88% overall yield from Rink resin): mp 150-151^{o}C; IR (neat) 3339, 3190, 2962, 2922, 1675, 1611, 1540, 1504, 1452, 1434, 1383, 1328, 1166, 956, 764, 731, 696 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.78 (m, 2H), 7.40-7.43 (m, 2H), 7.33-7.36 (m, 1H), 6.89 (s, 1H), 6.50 (brs, NH_2, 1H), 6.03 (brs, NH_2, 1H), 5.04-5.08 (m, 1H), 4.67-4.74 (m, 2H), 3.06-3.08 (m, 2H), 1.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 156.1, 150.9, 137.5, 132.5, 129.0, 128.5, 125.8, 105.3, 78.6, 53.6, 41.9, 13.2; ESI-MS *m*/*z* 285.09 $(M + H)^+$. Purity was determined to be 98% by HPLC analysis on the basis of absorption at 214 nm.

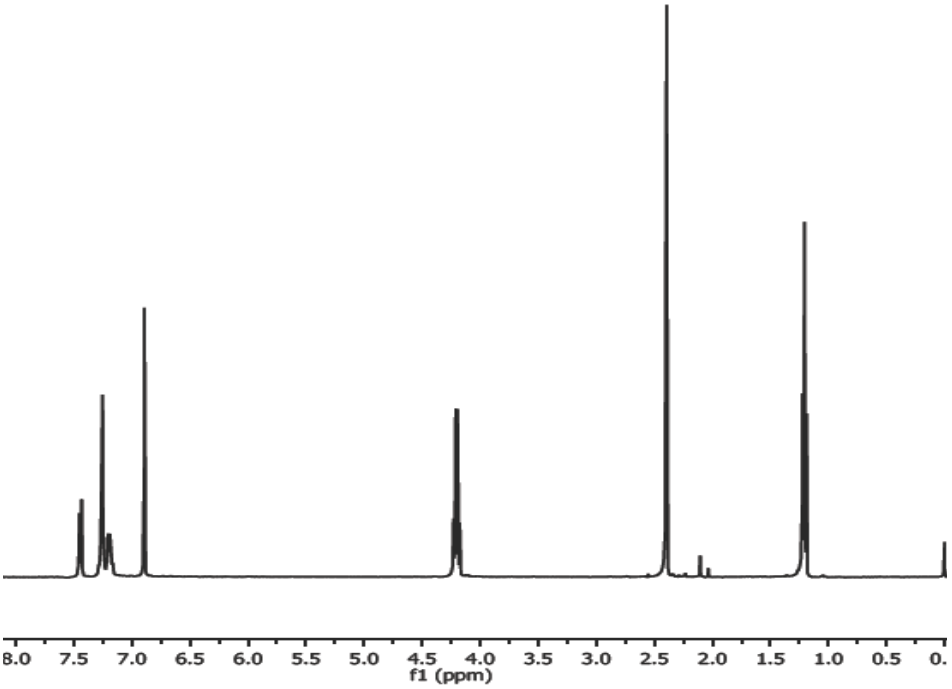
21{*1,6*} (white solid, 26 mg, 92% overall yield from Rink resin): mp 77-78^{o}C; IR (neat) 3338, 3190, 2972, 2942, 1675, 1611, 1540, 1504, 1452, 1434, 1378, 1350, 1163, 958, 764, 695 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75-7.77 (m, 2H), 7.40-7.42 (m, 2H), 7.32-7.35 (m, 1H), 6.90 (s, 1H), 6.57 (brs, NH_2, 1H), 6.13 (brs, NH_2, 1H), 5.04-5.08 (m, 1H), 4.66-4.74 (m, 2H), 3.03-3.11 (m, 2H), 2.29 (q, J = 7.2 Hz, 2H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 160.8, 150.9, 137.5, 132.4, 129.0, 128.5, 125.8, 105.4, 78.3, 53.6, 40.1, 21.4, 11.0; ESI-MS *m*/*z* 299.08 $(M + H)^+$. Purity was determined to be 96% by HPLC analysis on the basis of absorption at 214 nm.

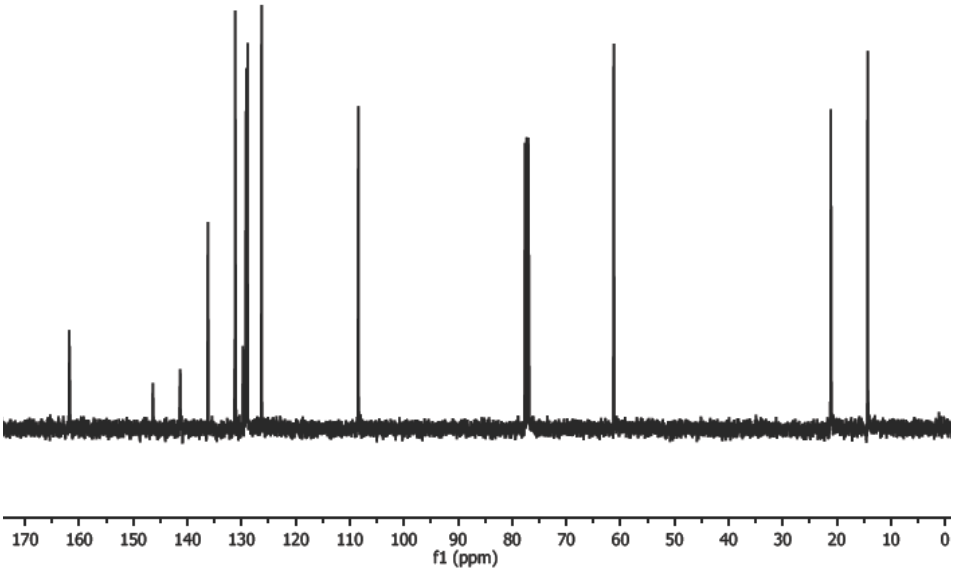
^{1}H NMR, ^{13}C NMR, LC/MS Spectra of Intermediates and Representative Library Compounds:

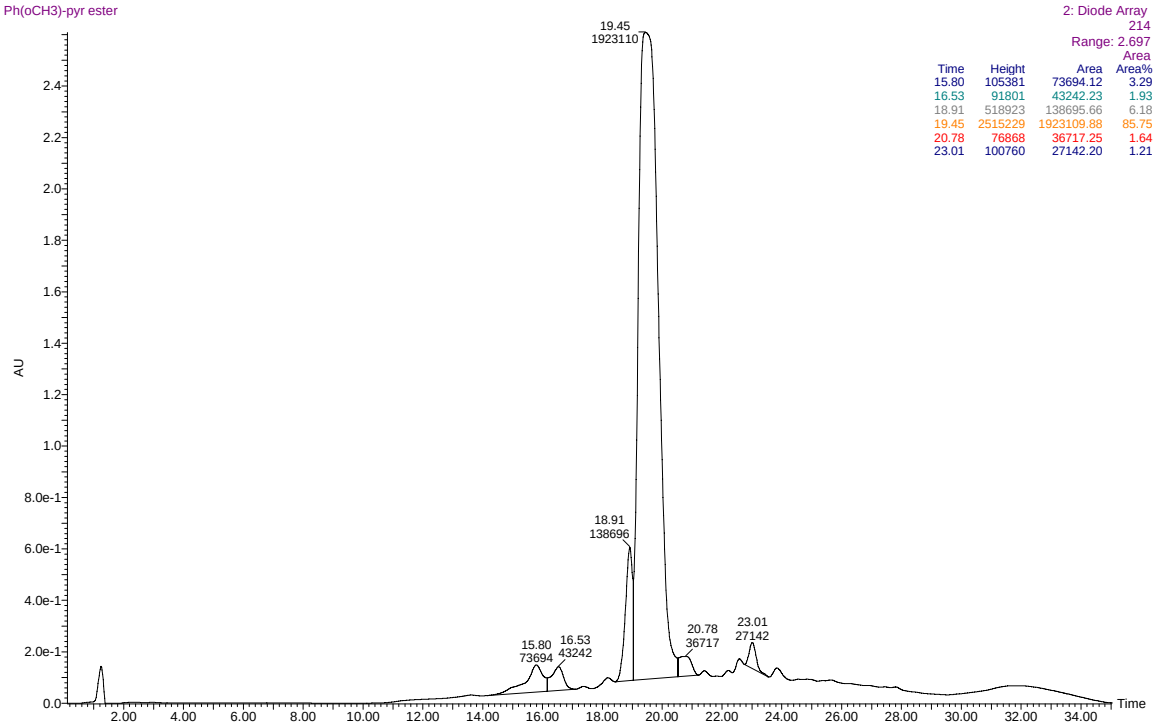
3{*2*}

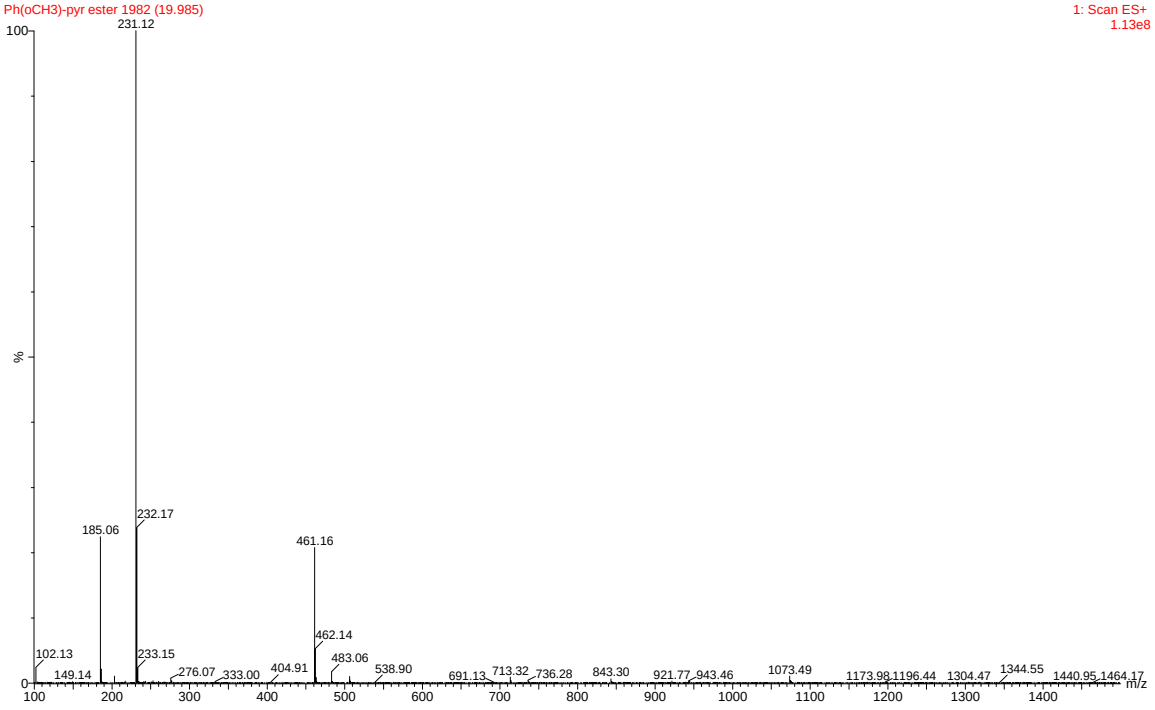


$C_{13}H_{14}N_2O_2$
Mol. Wt.: 230.26

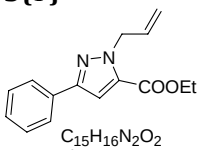




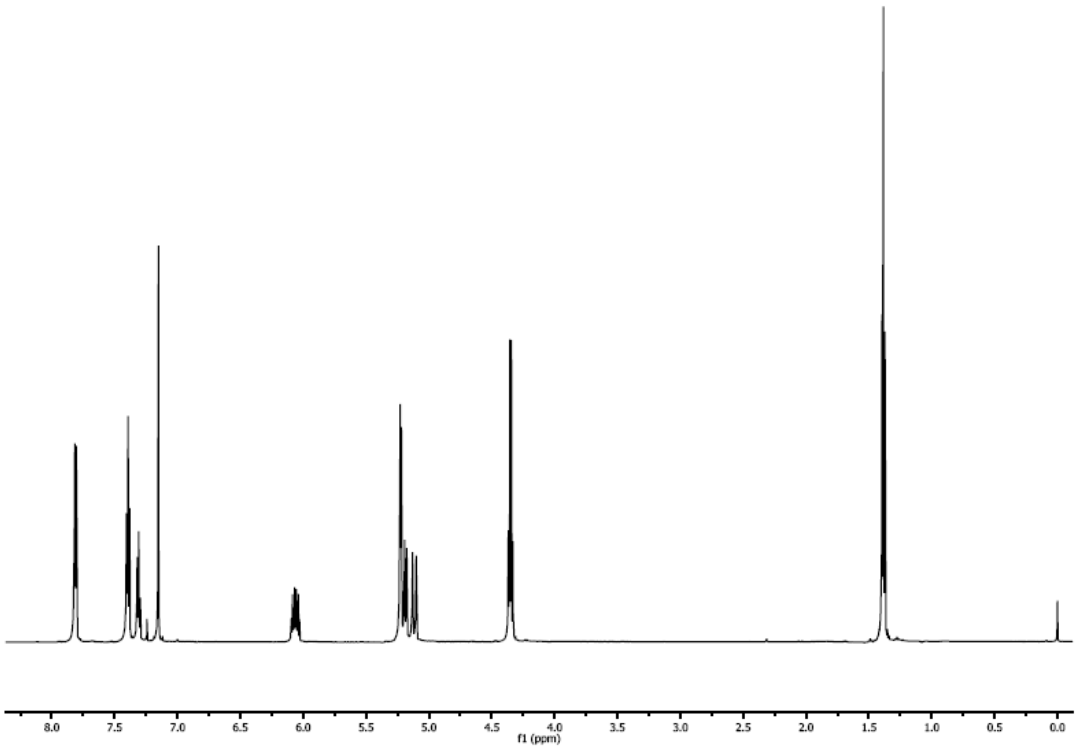

Ph(oCH3)-pyr ester
2: Diode Array
214
Range: 2.697
Area
Time Height Area Area%
15.80 105381 73694.12 3.29
16.53 91801 43242.23 1.93
18.91 518923 138695.66 6.18
19.45 2515229 1923109.88 85.75
20.78 76868 36717.25 1.64
23.01 100760 27142.20 1.21
19.45
1923110
18.91
138696
15.80
73694
16.53
43242
20.78
36717
23.01
27142
AU
Time

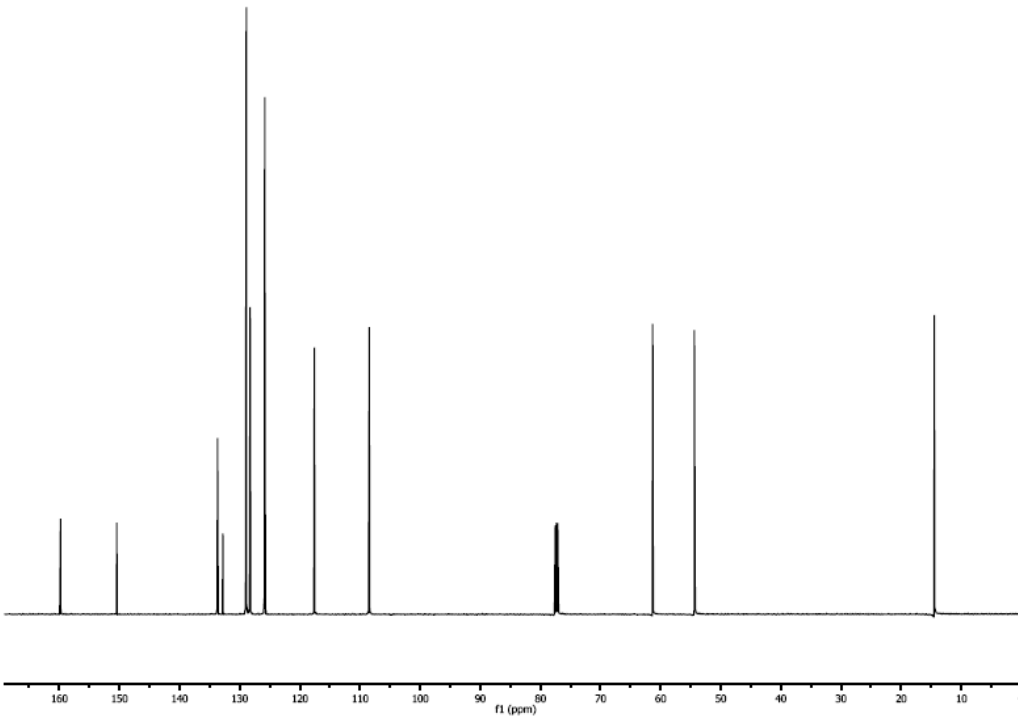

Ph(oCH3)-pyr ester 1982 (19.985)
1: Scan ES+
1.13e8
231.12
232.17
185.06
461.16
462.14
102.13
233.15
483.06
149.14
276.07
333.00
404.91
538.90
691.13
713.32
736.28
843.30
921.77
943.46
1073.49
1173.98
1196.44
1304.47
1344.55
1440.95
1464.17
%
m/z

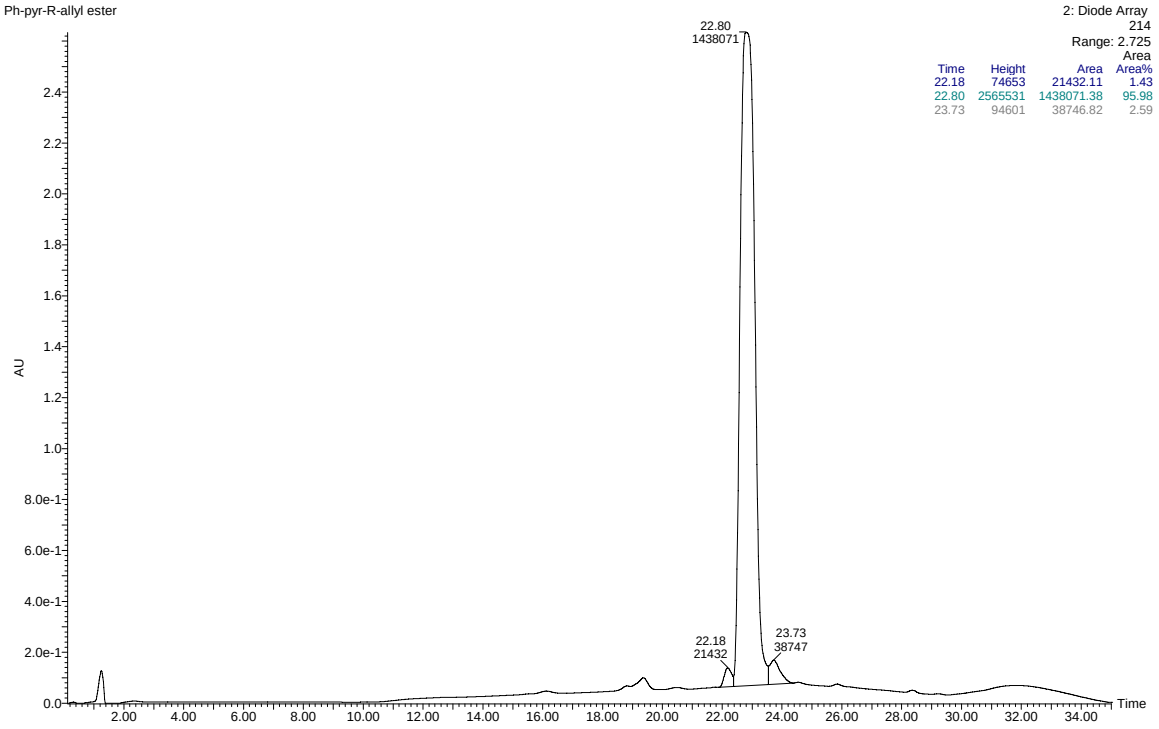
5{*l*}

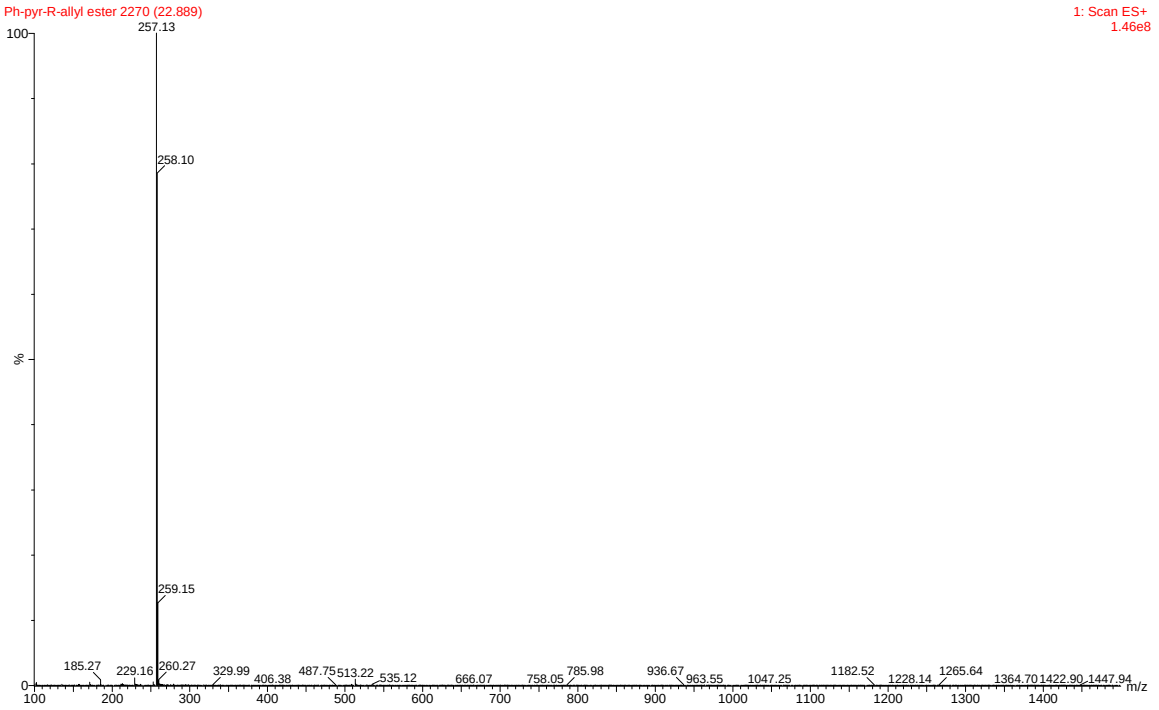


$C_{15}H_{16}N_2O_2$
Mol. Wt.: 256.30

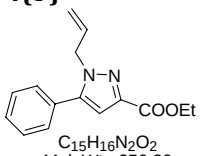




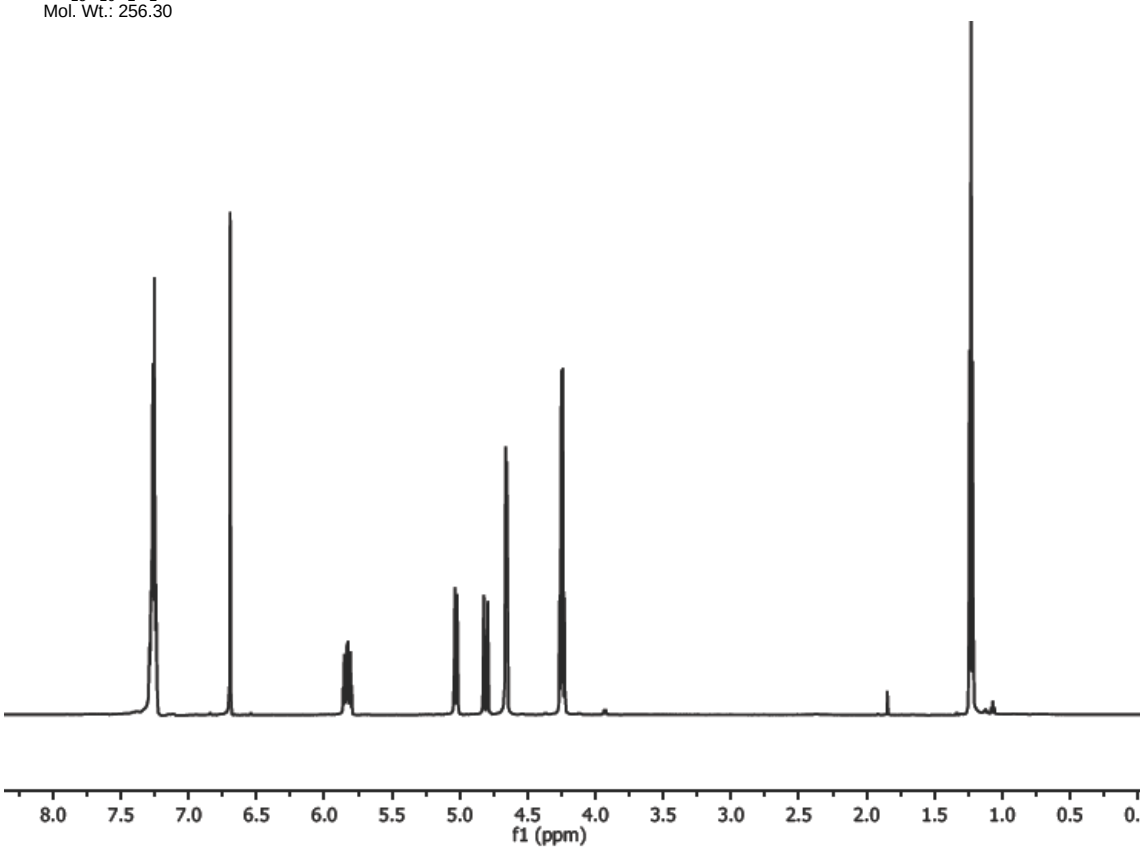

Ph-pyr-R-allyl ester
2: Diode Array
214
Range: 2.725
Area
Time Height Area Area%
22.18 74653 21432.11 1.43
22.80 2565531 1438071.38 95.98
23.73 94601 38746.82 2.59
22.80
1438071
22.18
21432
23.73
38747
AU
Time

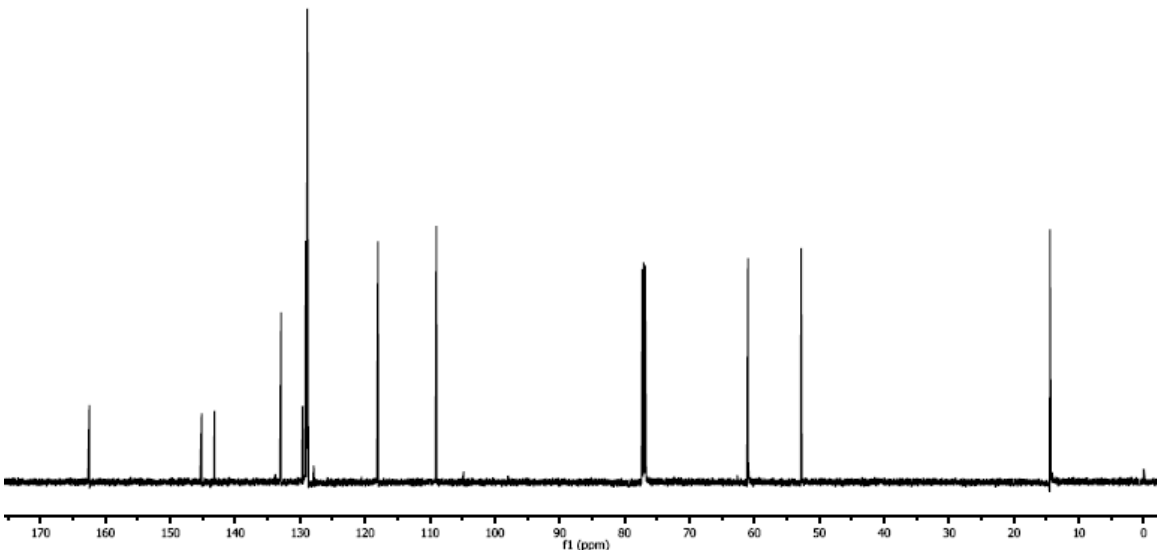

Ph-pyr-R-allyl ester 2270 (22.889)
1: Scan ES+
1.46e8
257.13
258.10
259.15
%
m/z

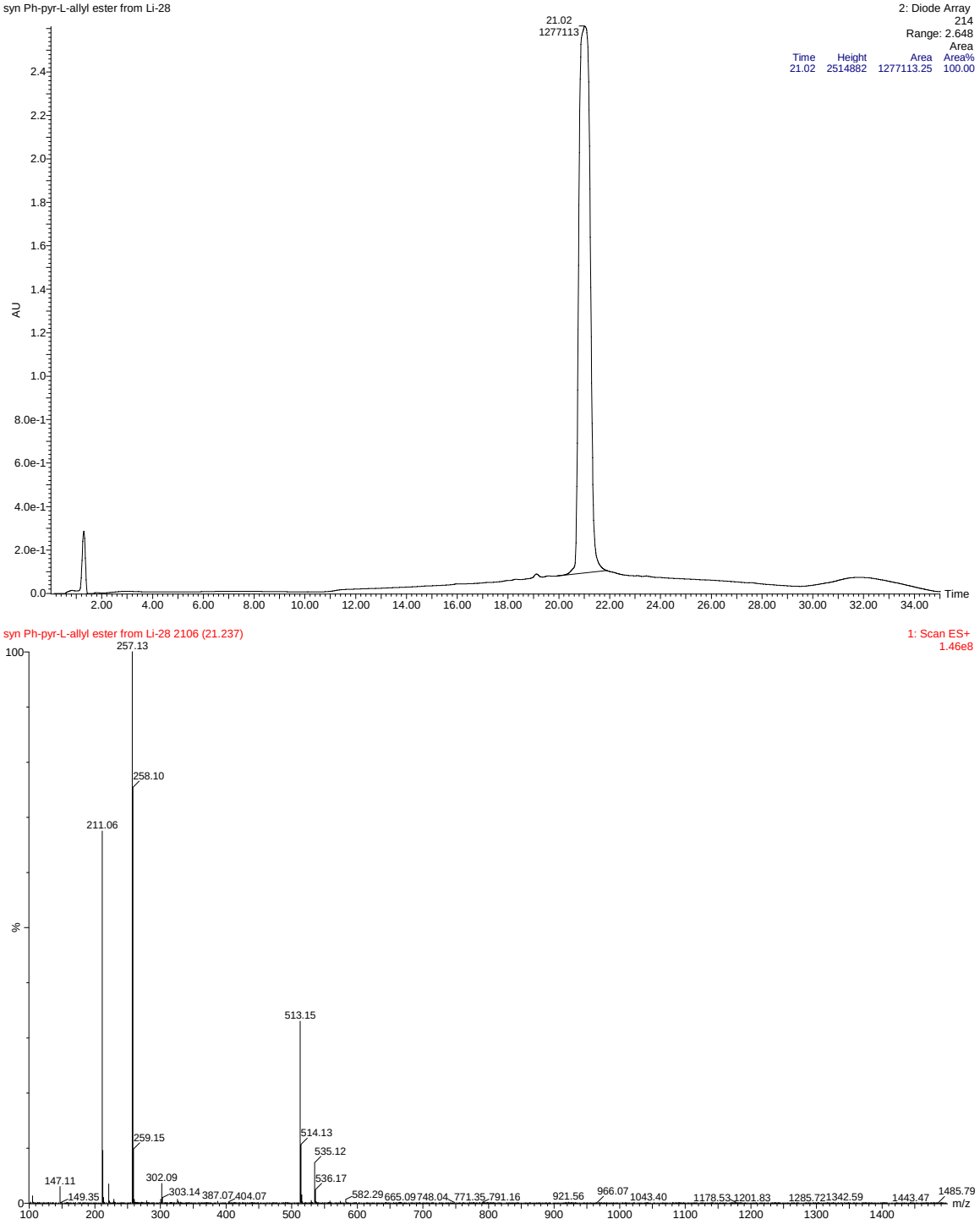
4{*l*}



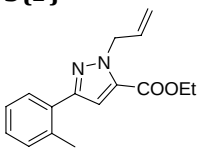
$C_{15}H_{16}N_2O_2$
Mol. Wt.: 256.30



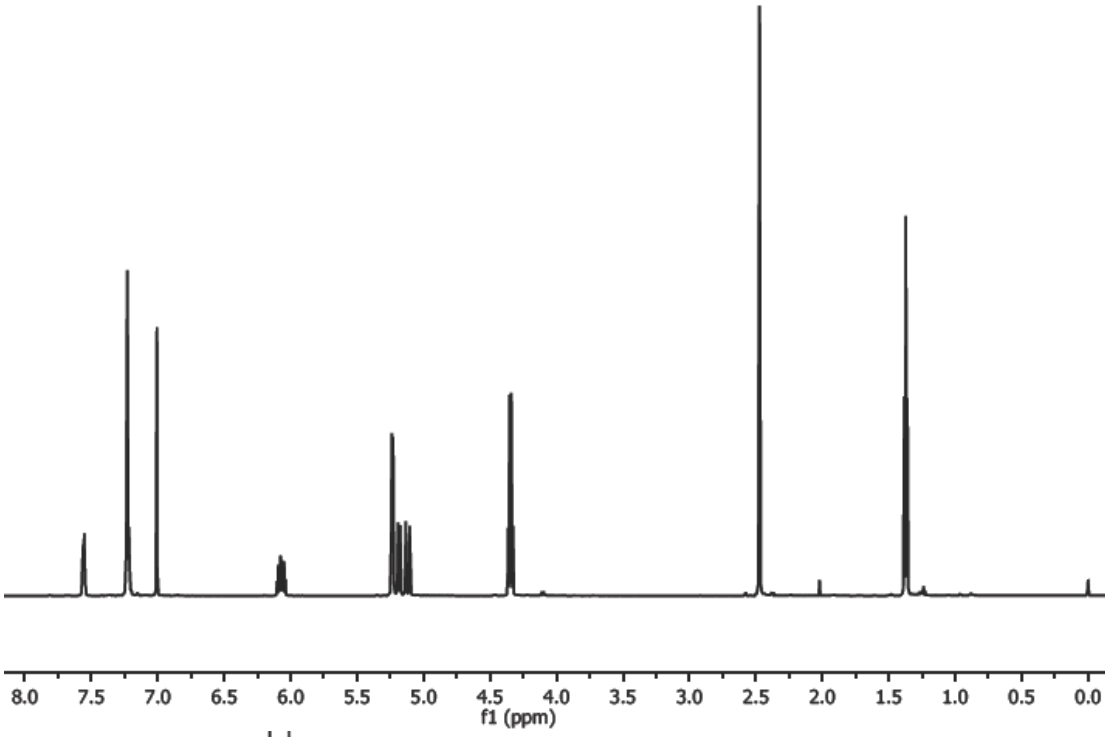


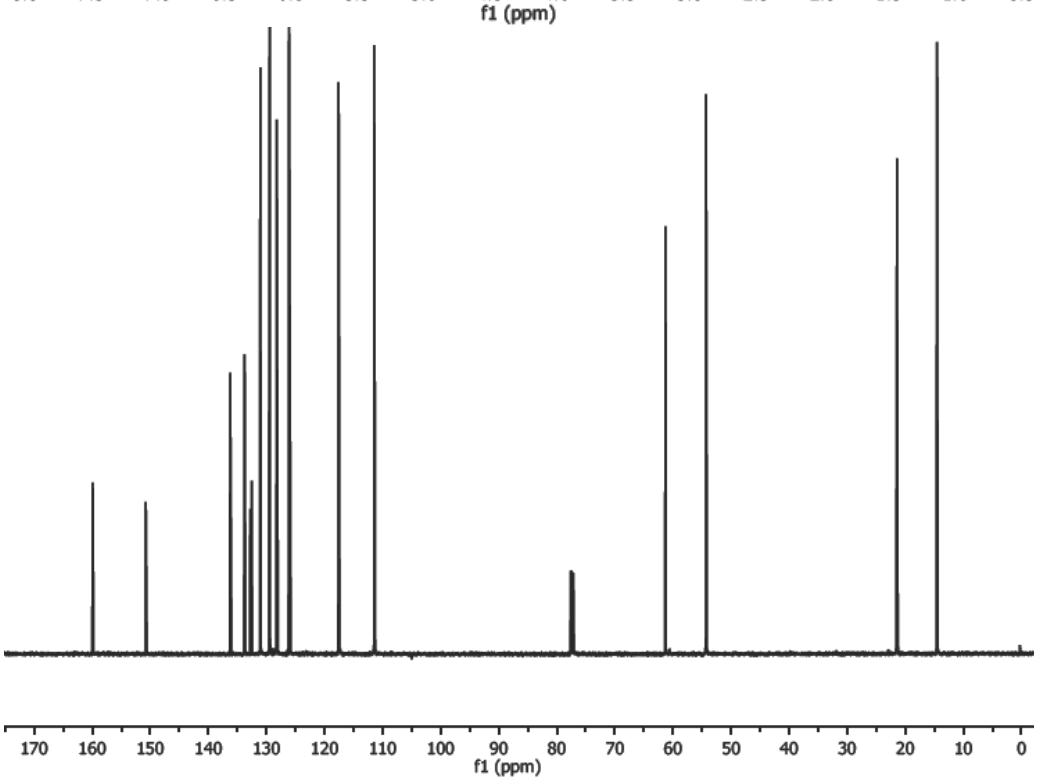

syn Ph-pyr-L-allyl ester from Li-28
2: Diode Array
214
Range: 2.648
Area
Time Height Area Area%
21.02 2514882 1277113.25 100.00
21.02
1277113
AU
Time
syn Ph-pyr-L-allyl ester from Li-28 2106 (21.237)
1: Scan ES+
1.46e8
257.13
258.10
211.06
513.15
514.13
535.12
536.17
259.15
302.09
147.11
149.35
303.14
387.07
404.07
582.29
665.09
748.04
771.35
791.16
921.56
966.07
1043.40
1178.53
1201.83
1285.72
1342.59
1443.47
1485.79
%
m/z

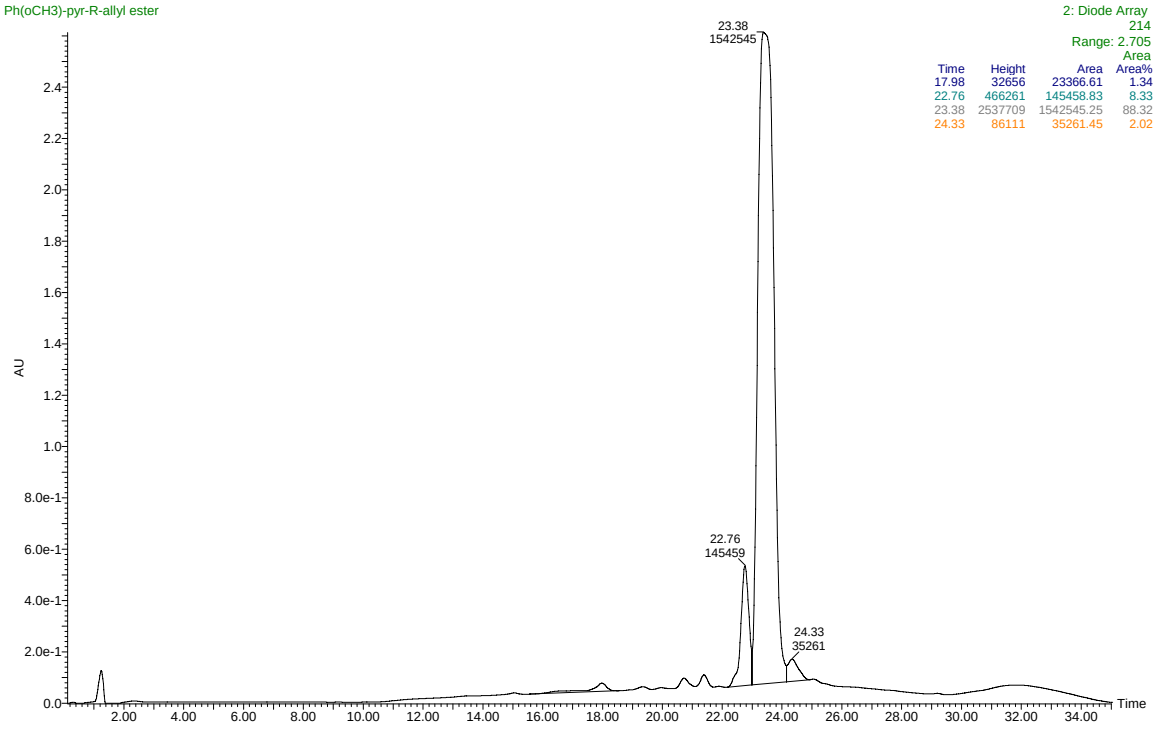
5{*2*}

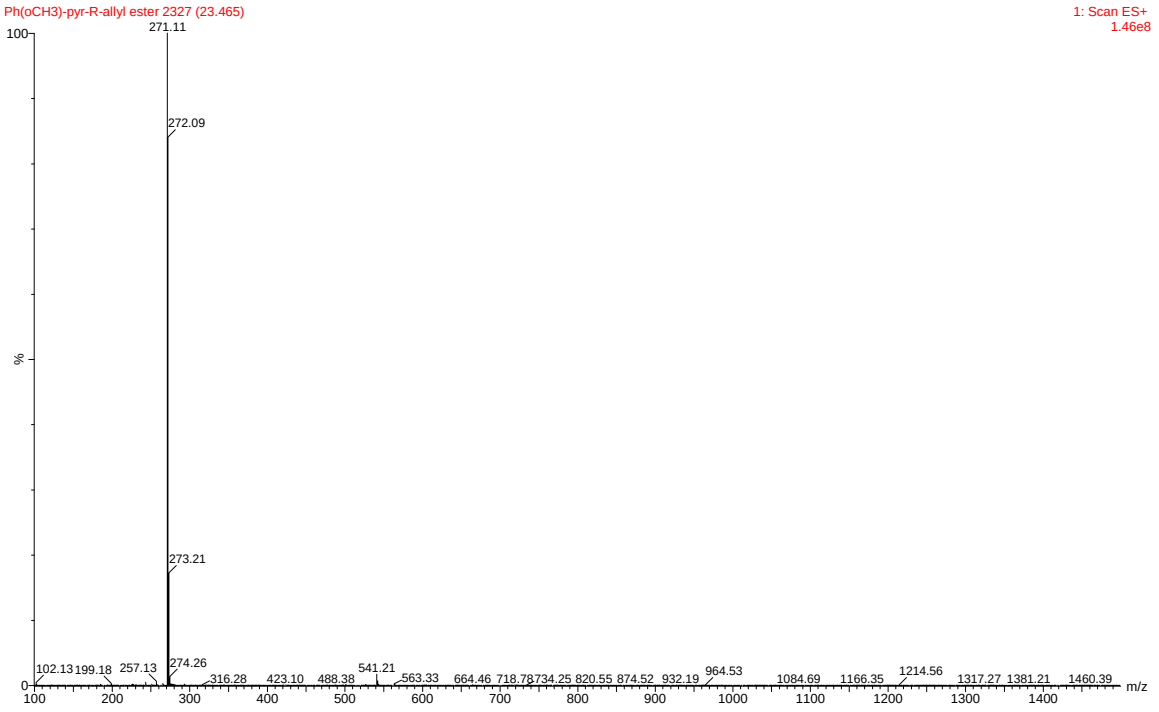


$C_{16}H_{18}N_2O_2$
Mol. Wt.: 270.33

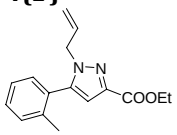




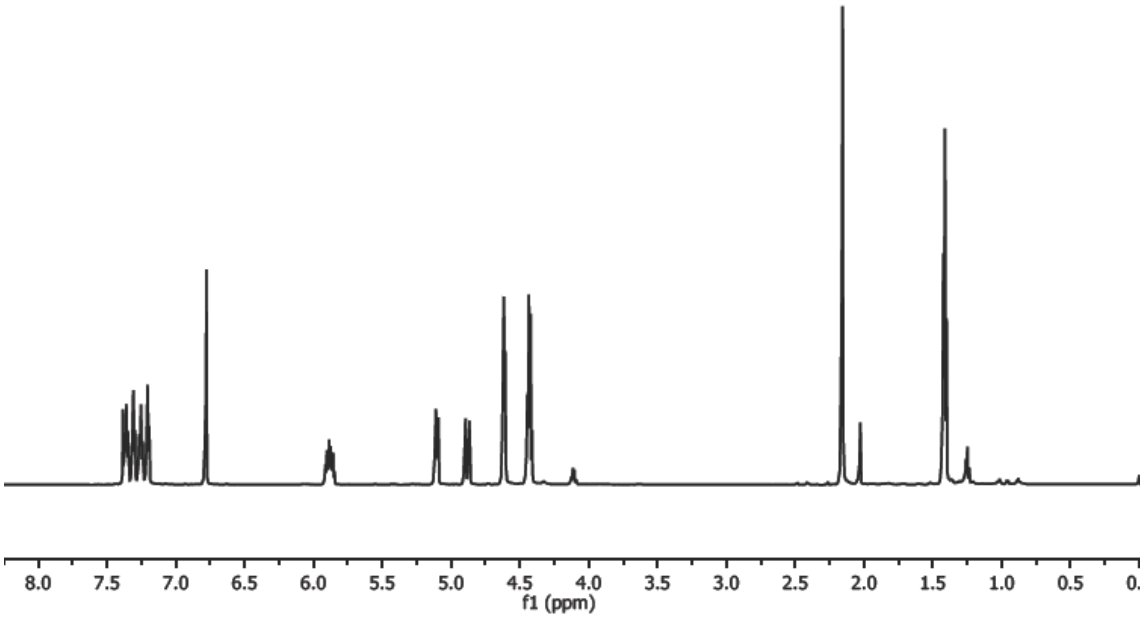

Ph(oCH3)-pyr-R-allyl ester
2: Diode Array
214
Range: 2.705
Area
Time Height Area Area%
17.98 32656 23366.61 1.34
22.76 466261 145458.83 8.33
23.38 2537709 1542545.25 88.32
24.33 86111 35261.45 2.02
23.38
1542545
22.76
145459
24.33
35261
AU
Time

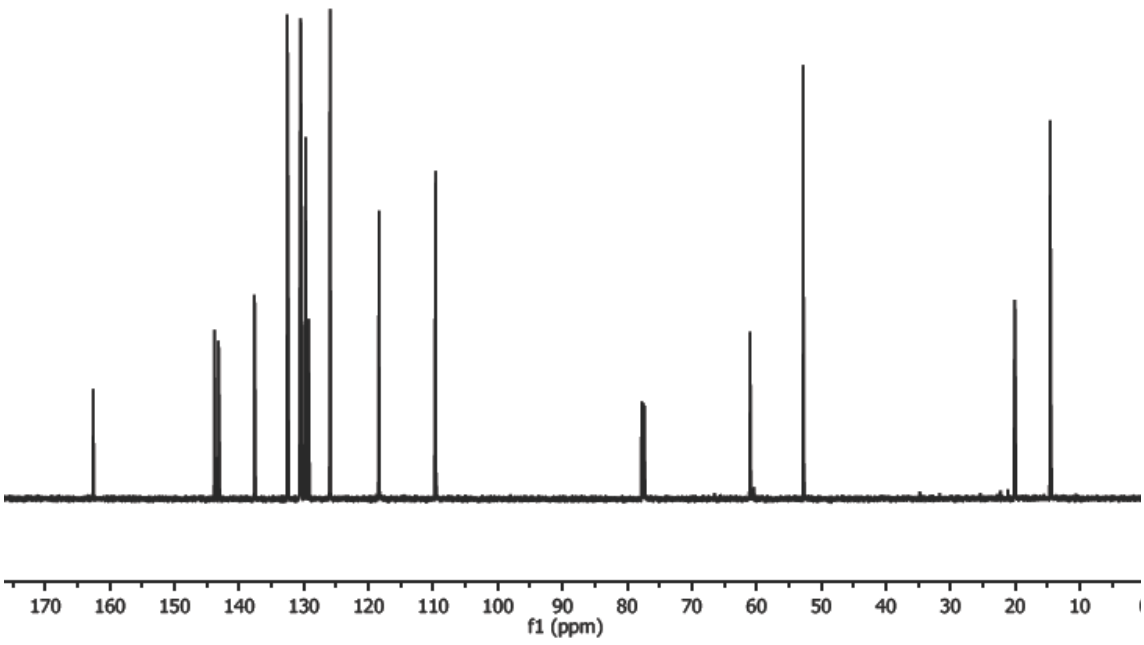

Ph(oCH3)-pyr-R-allyl ester 2327 (23.465)
1: Scan ES+
1.46e8
271.11
272.09
273.21
274.26
%
m/z

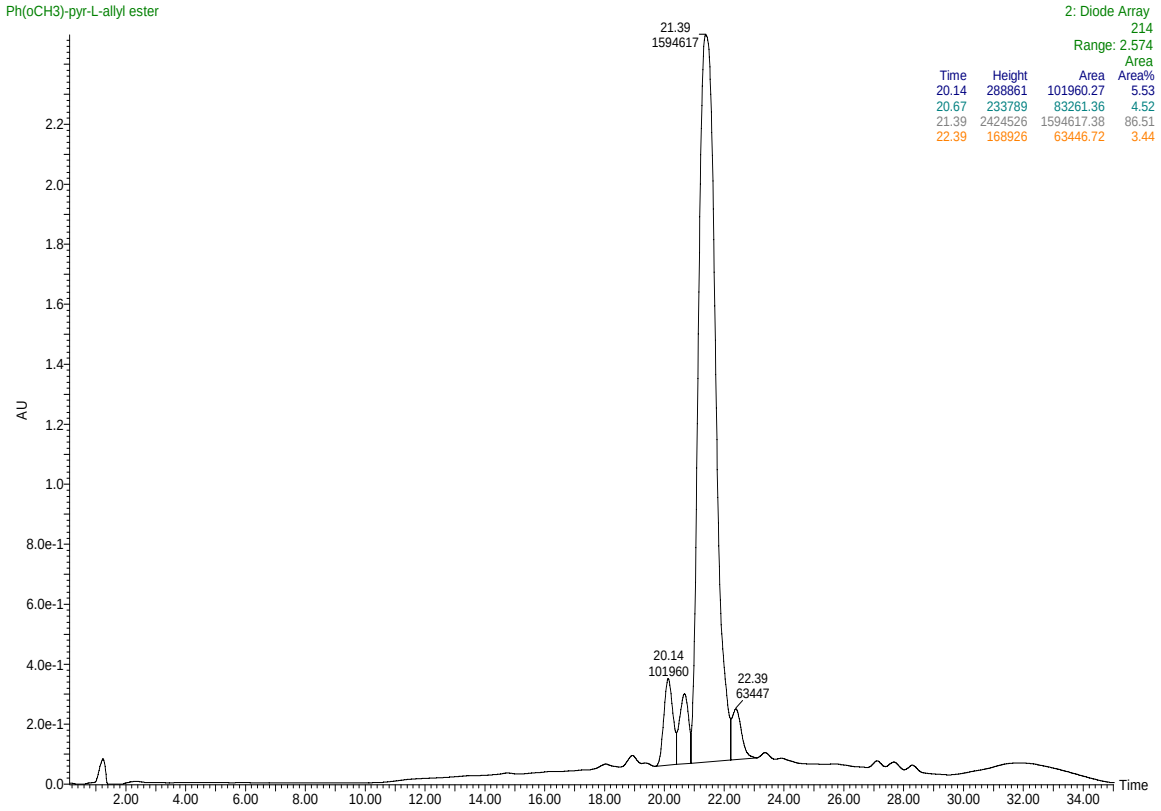
4{*2*}

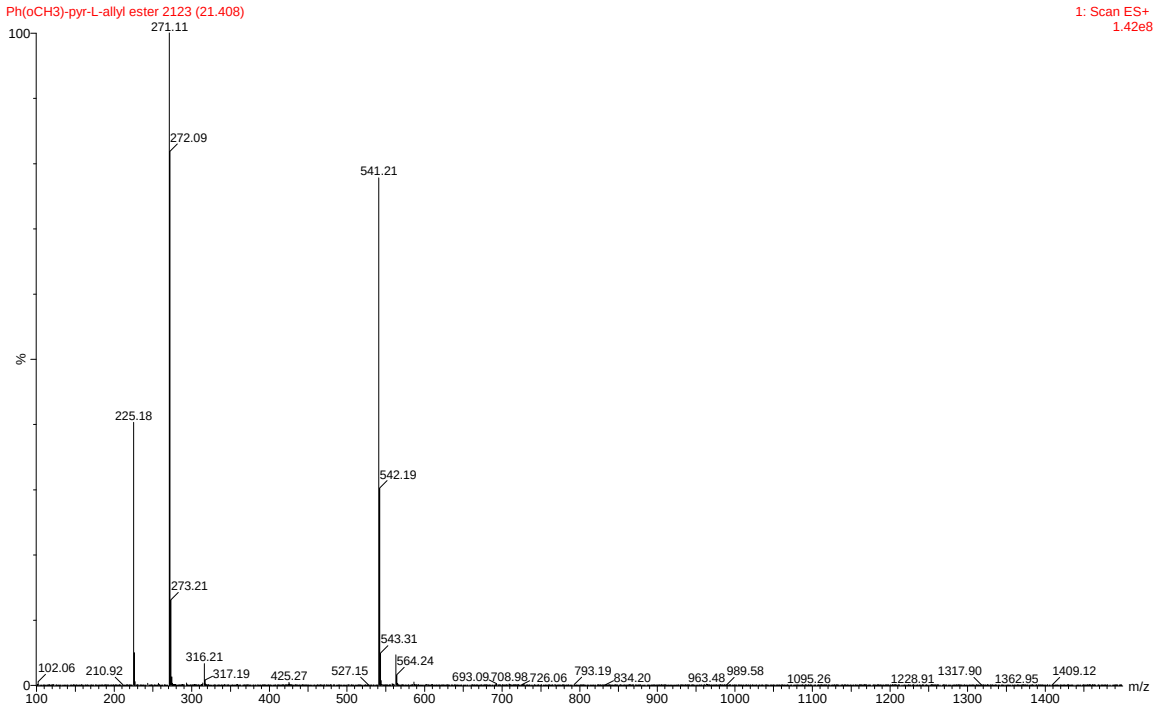


$C_{16}H_{18}N_2O_2$
Mol. Wt.: 270.33

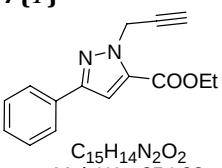




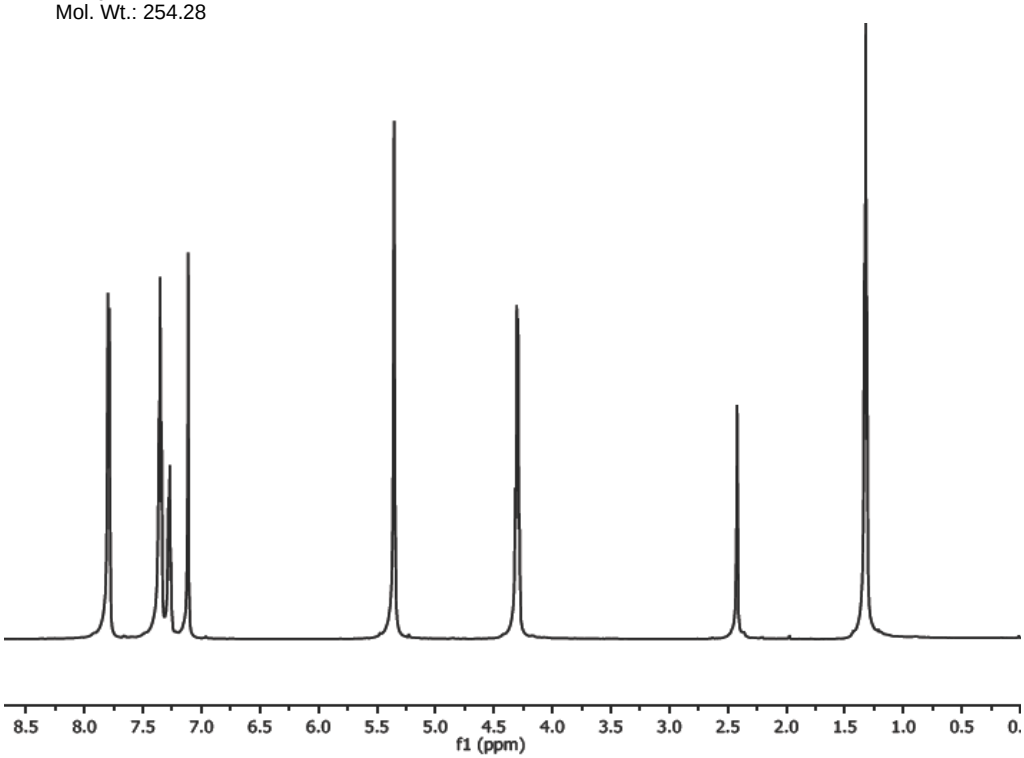

Ph(oCH3)-pyr-L-allyl ester
2: Diode Array
214
Range: 2.574
Area
Time Height Area Area%
20.14 288861 101960.27 5.53
20.67 233789 83261.36 4.52
21.39 2424526 1594617.38 86.51
22.39 168926 63446.72 3.44
21.39
1594617
20.14
101960
22.39
63447
AU
Time

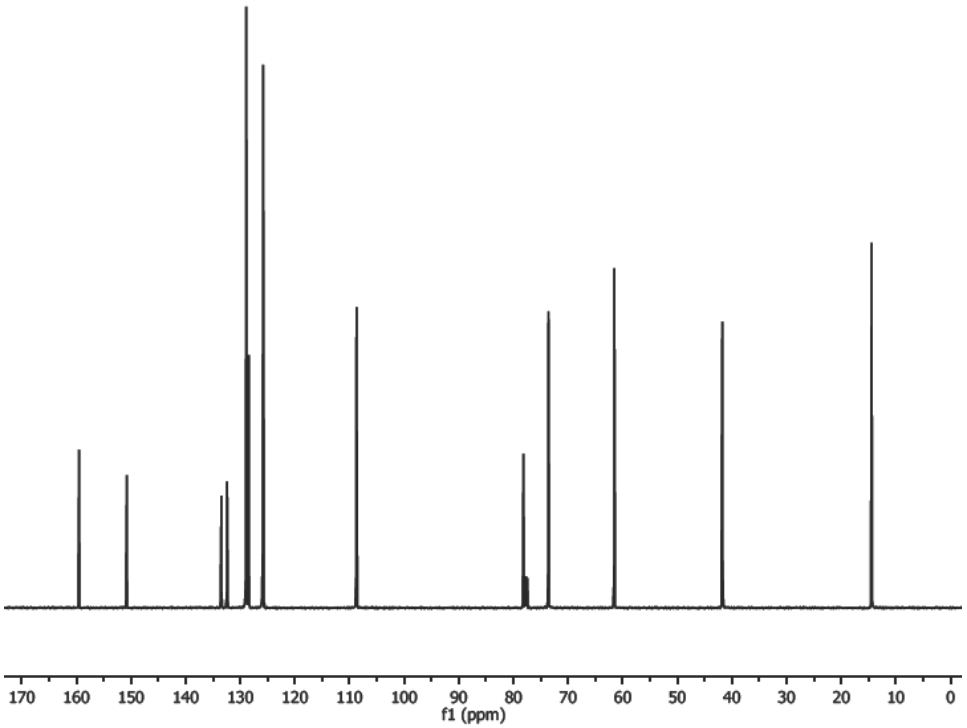

Ph(oCH3)-pyr-L-allyl ester 2123 (21.408)
1: Scan ES+
1.42e8
271.11
272.09
541.21
225.18
542.19
273.21
543.31
316.21
102.06
210.92
317.19
425.27
527.15
564.24
693.09
708.98
726.06
793.19
834.20
963.48
989.58
1095.26
1228.91
1317.90
1362.95
1409.12
%
m/z

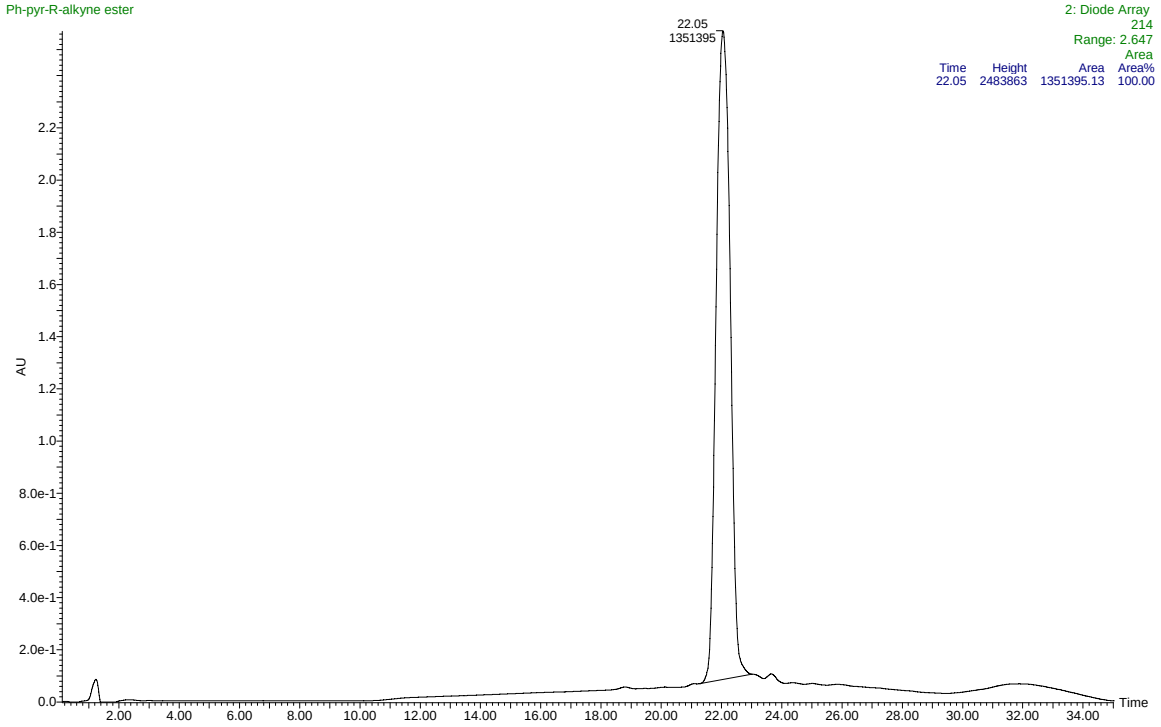
7{*l*}

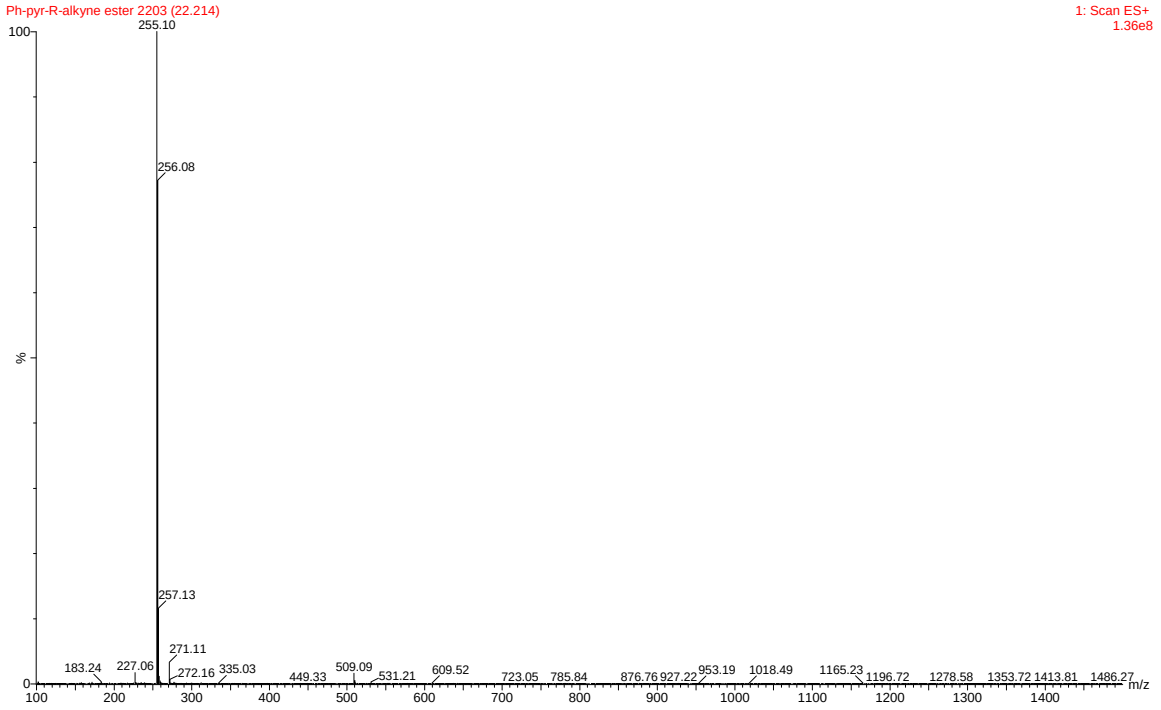


$C_{15}H_{14}N_2O_2$
Mol. Wt.: 254.28

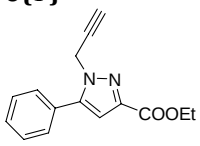




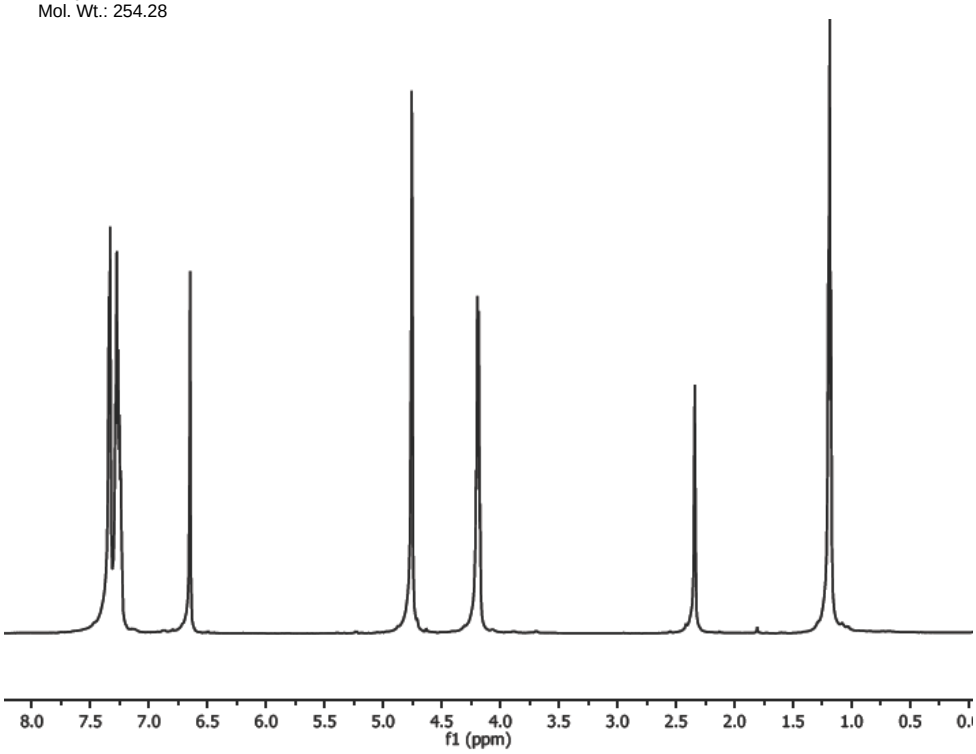

Ph-pyr-R-alkyne ester
2: Diode Array
214
Range: 2.647
Area
Time Height Area Area%
22.05 2483863 1351395.13 100.00
22.05
1351395
AU
Time

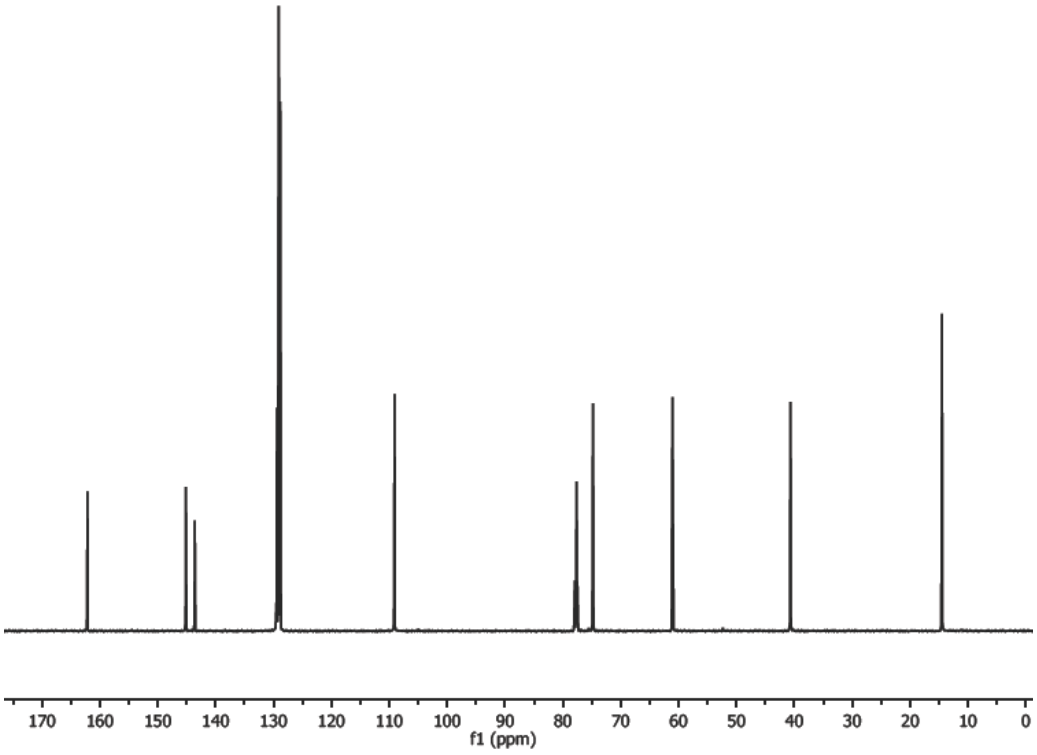

Ph-pyr-R-alkyne ester 2203 (22.214)
1: Scan ES+
1.36e8
255.10
256.08
257.13
271.11
%
m/z

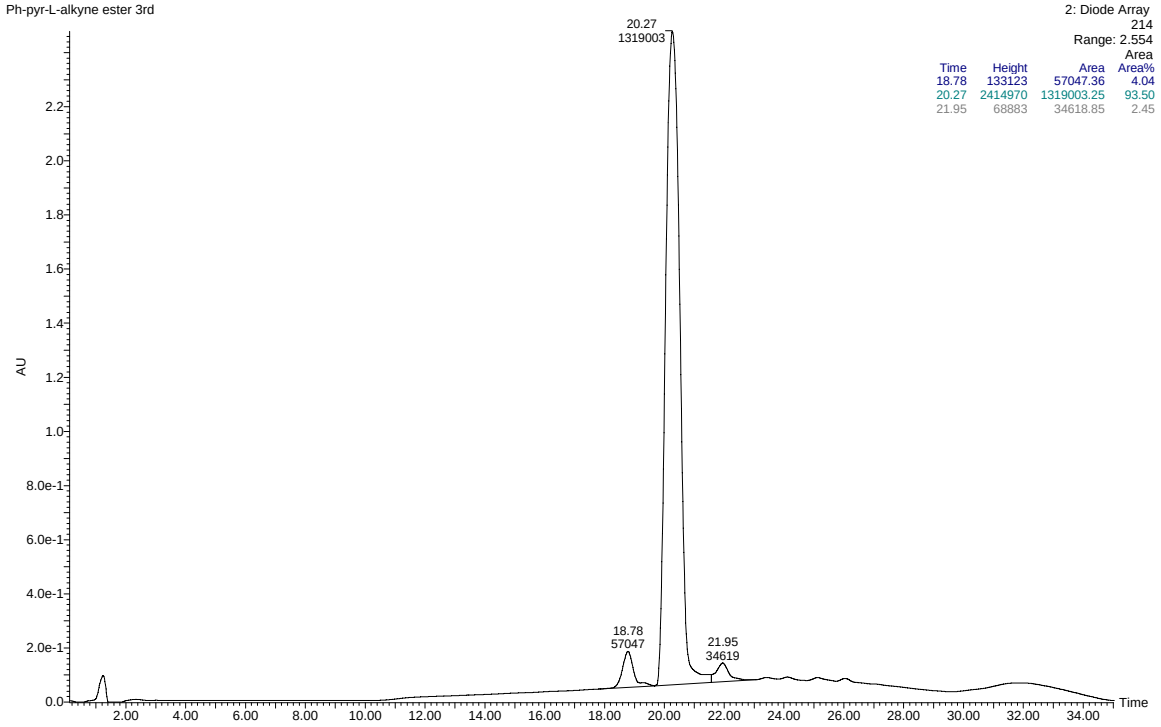
6{*l*}

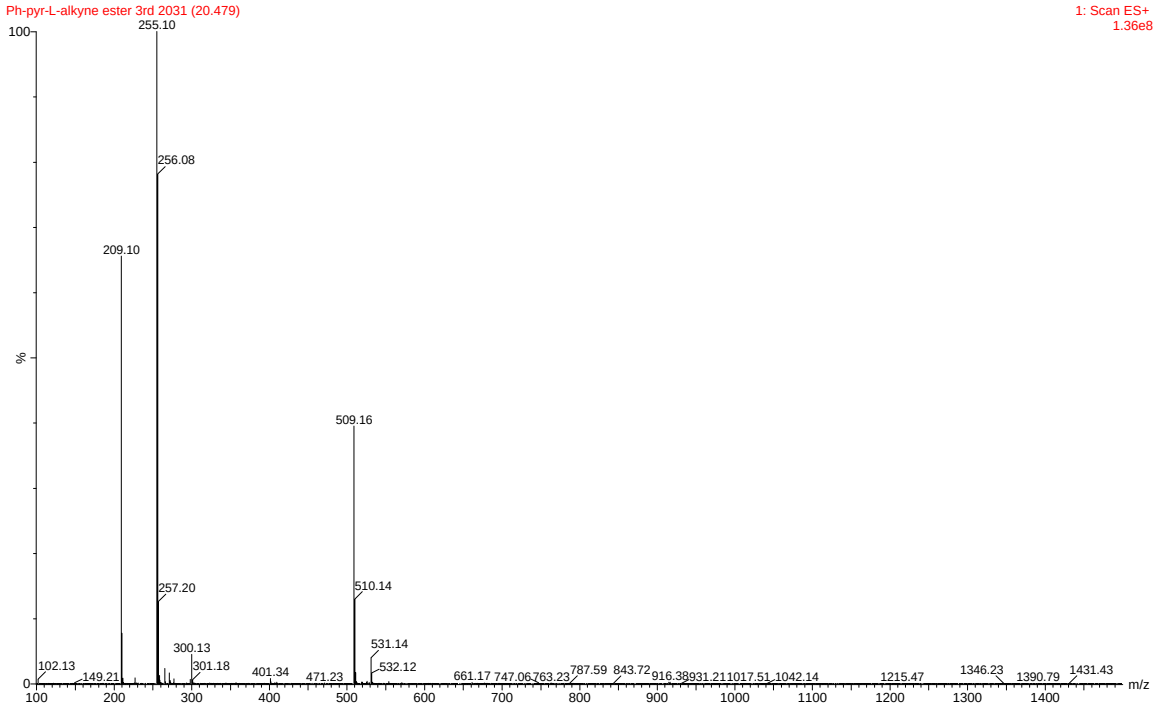


$C_{15}H_{14}N_2O_2$
Mol. Wt.: 254.28

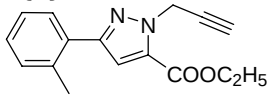




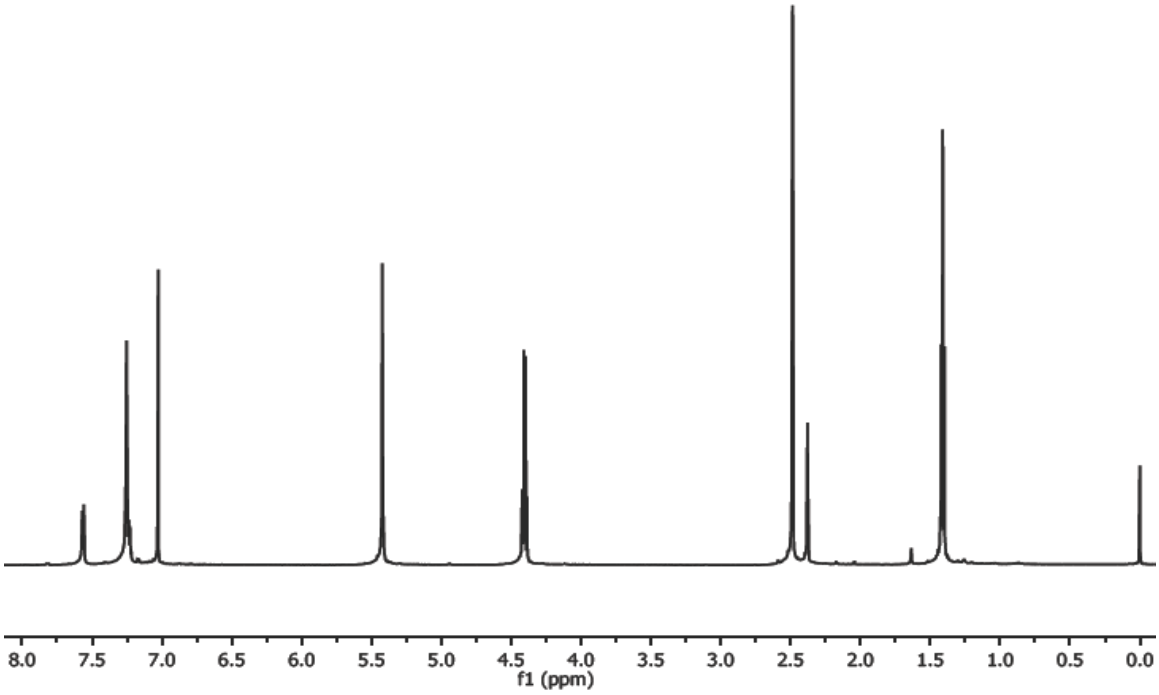

Ph-pyr-L-alkyne ester 3rd
2: Diode Array
214
Range: 2.554
Area
Time Height Area Area%
18.78 133123 57047.36 4.04
20.27 2414970 1319003.25 93.50
21.95 68883 34618.85 2.45
20.27
1319003
18.78
57047
21.95
34619
AU
Time

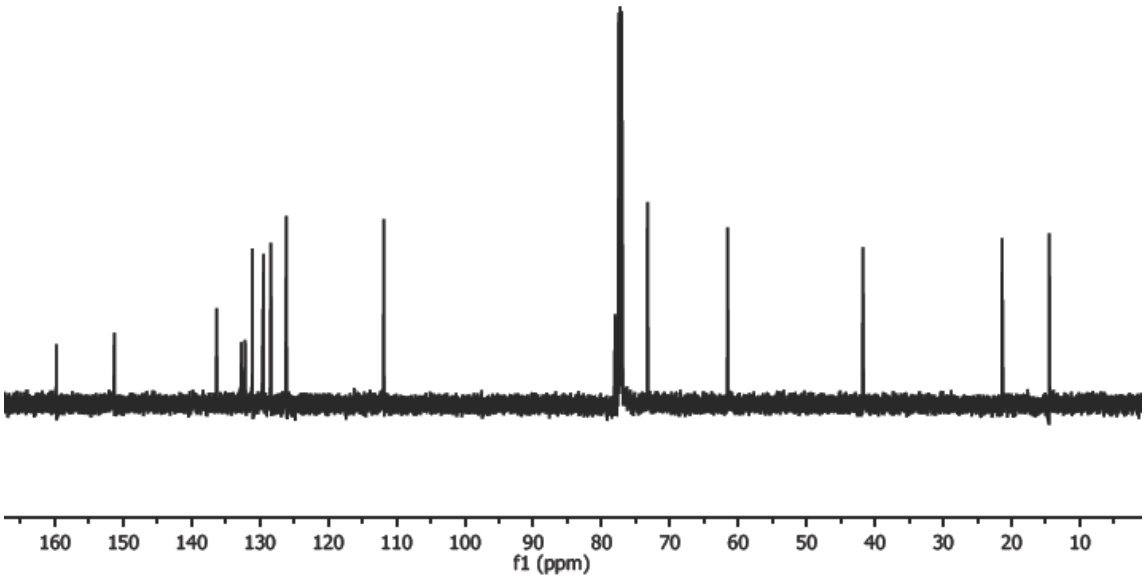

Ph-pyr-L-alkyne ester 3rd 2031 (20.479)
1: Scan ES+
1.36e8
255.10
256.08
209.10
509.16
257.20
510.14
300.13
531.14
301.18
532.12
102.13
149.21
401.34
471.23
661.17
747.06
763.23
787.59
843.72
916.38
931.21
1017.51
1042.14
1215.47
1346.23
1390.79
1431.43
%
m/z

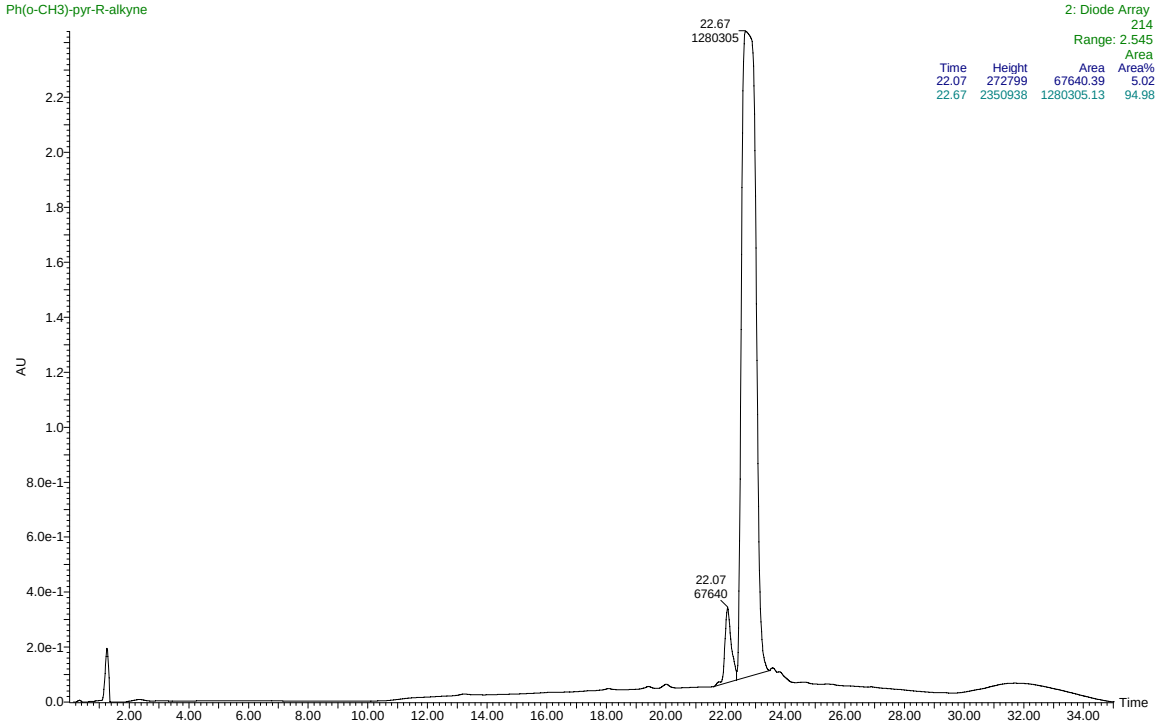
7{*2*}

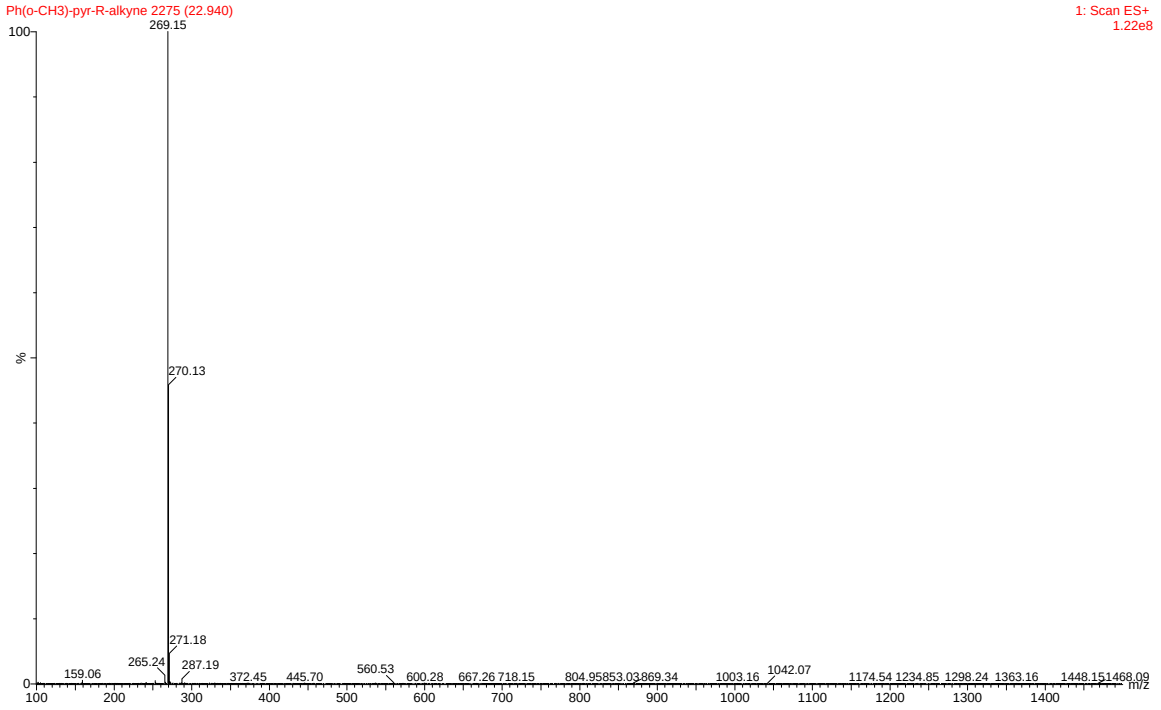


$C_{16}H_{16}N_2O_2$
Mol. Wt.: 268.31

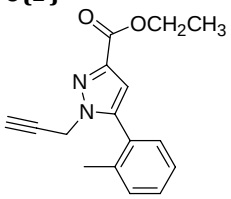




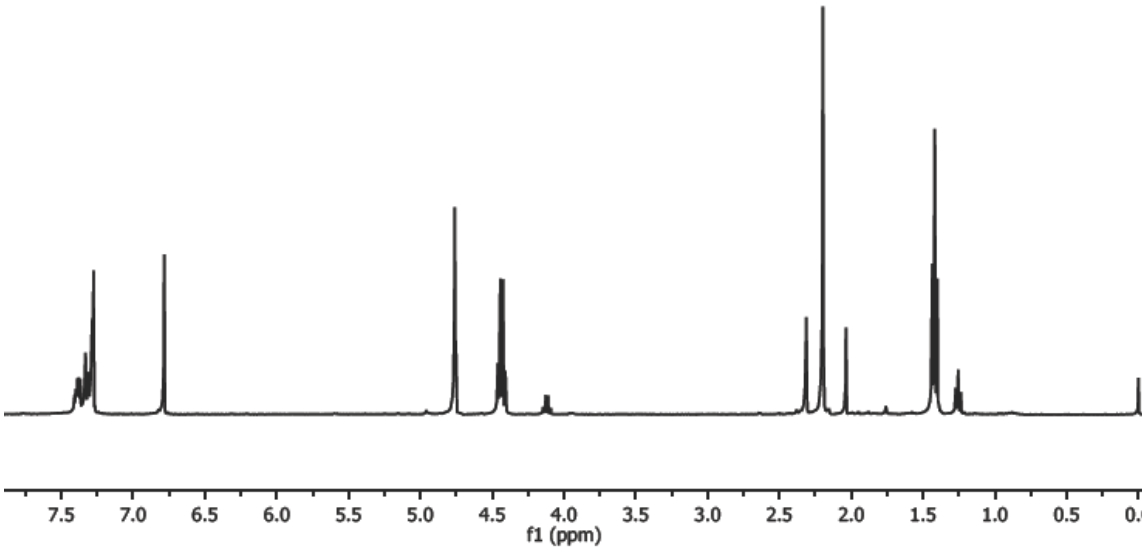

Ph(o-CH3)-pyr-R-alkyne
2: Diode Array
214
Range: 2.545
Area
Time Height Area Area%
22.07 272799 67640.39 5.02
22.67 2350938 1280305.13 94.98
22.67
1280305
22.07
67640
AU
Time

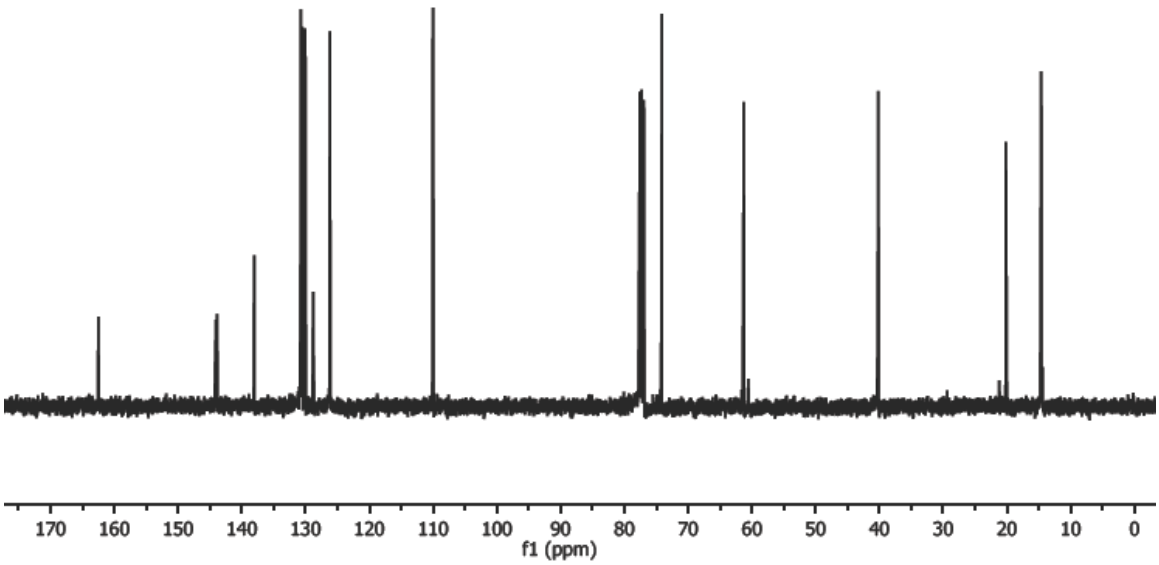

Ph(o-CH3)-pyr-R-alkyne 2275 (22.940)
1: Scan ES+
1.22e8
269.15
270.13
271.18
265.24
287.19
159.06
%
m/z

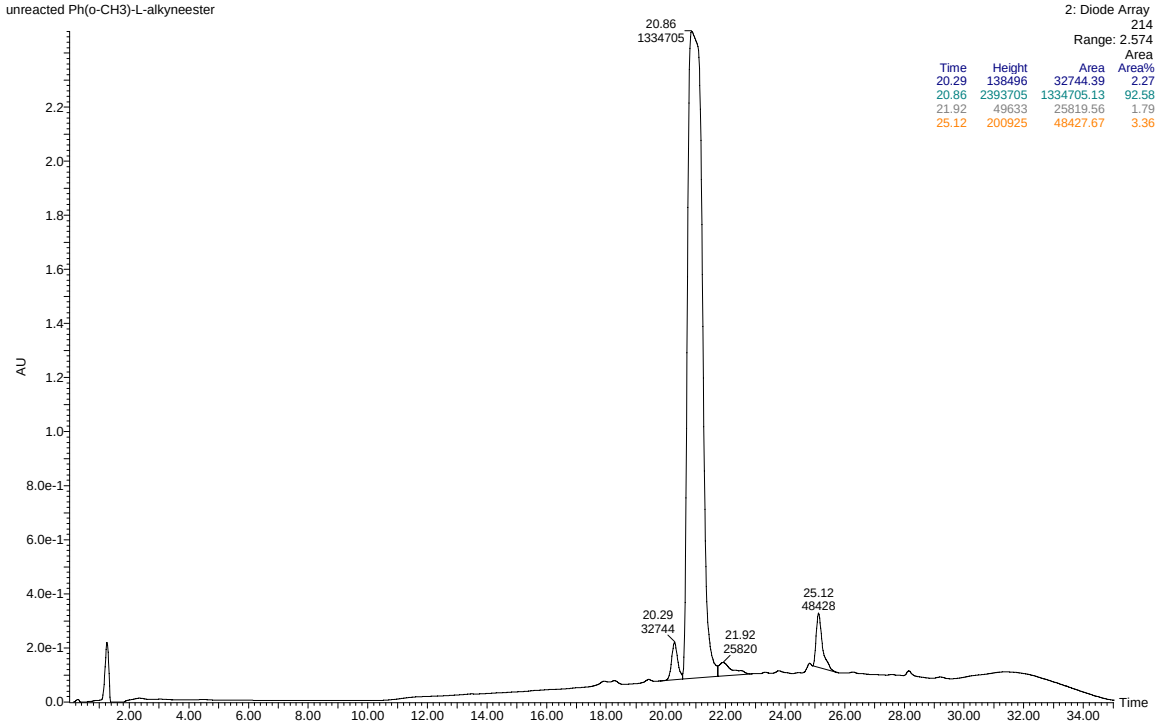
6{*2*}

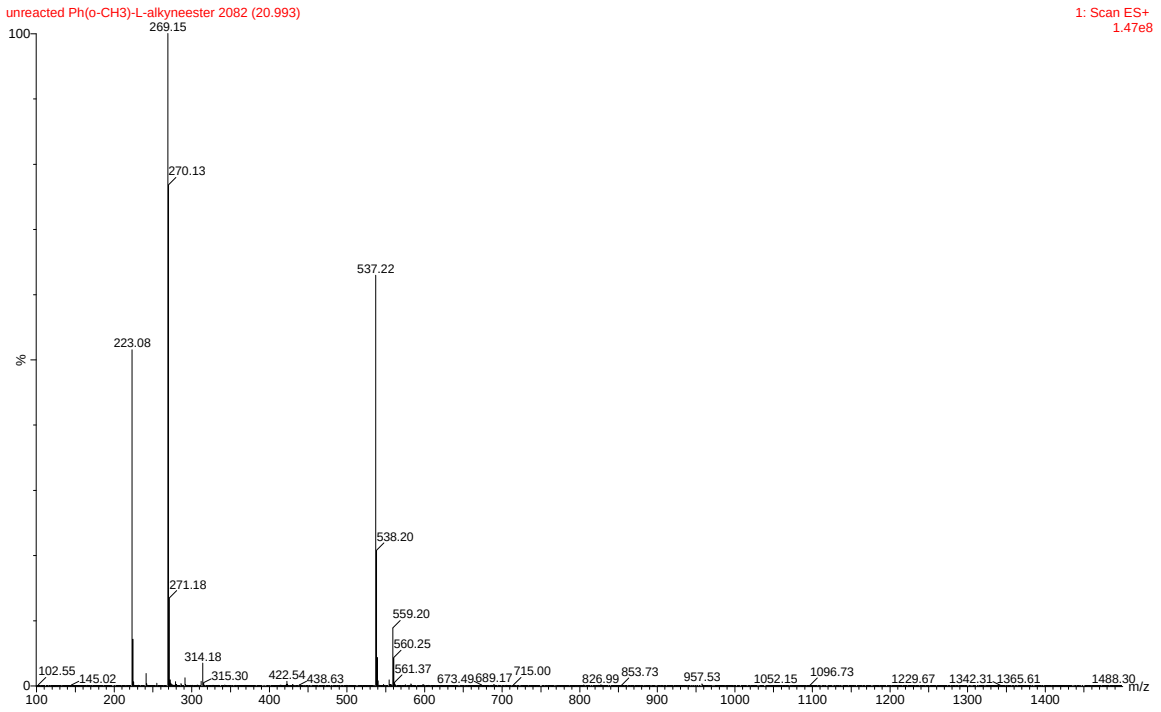


$C_{16}H_{16}N_2O_2$
Mol. Wt.: 268.31

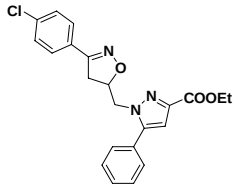




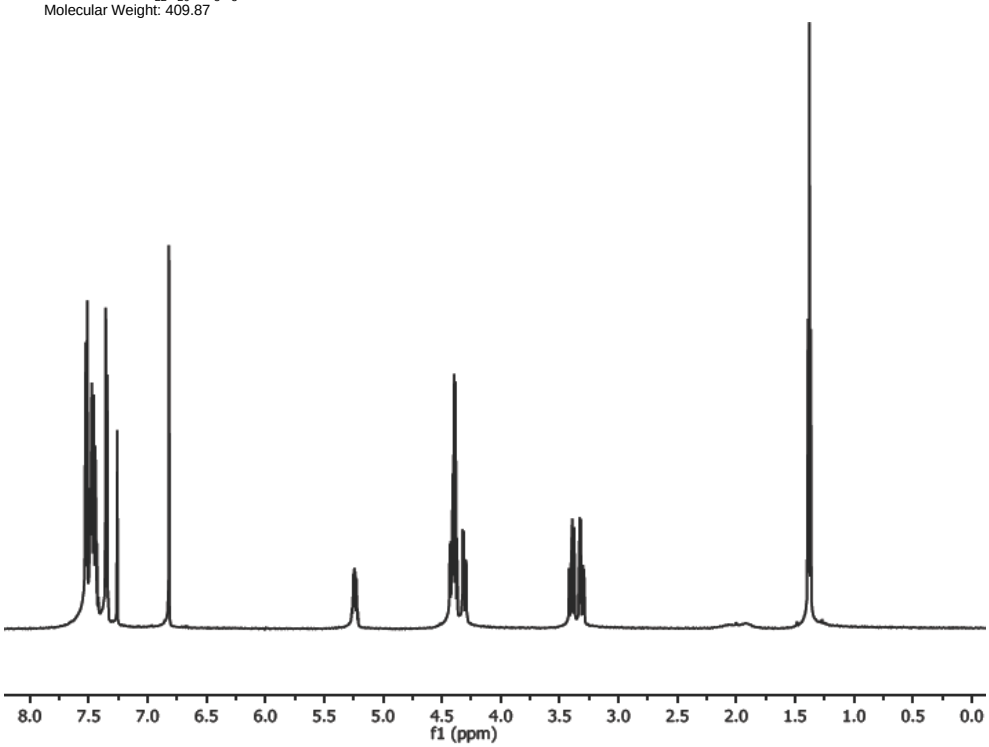

unreacted Ph(o-CH3)-L-alkyneester
2: Diode Array
214
Range: 2.574
Area
Time Height Area Area%
20.29 138496 32744.39 2.27
20.86 2393705 1334705.13 92.58
21.92 49633 25819.56 1.79
25.12 200925 48427.67 3.36
20.86
1334705
20.29
32744
21.92
25820
25.12
48428
AU
Time

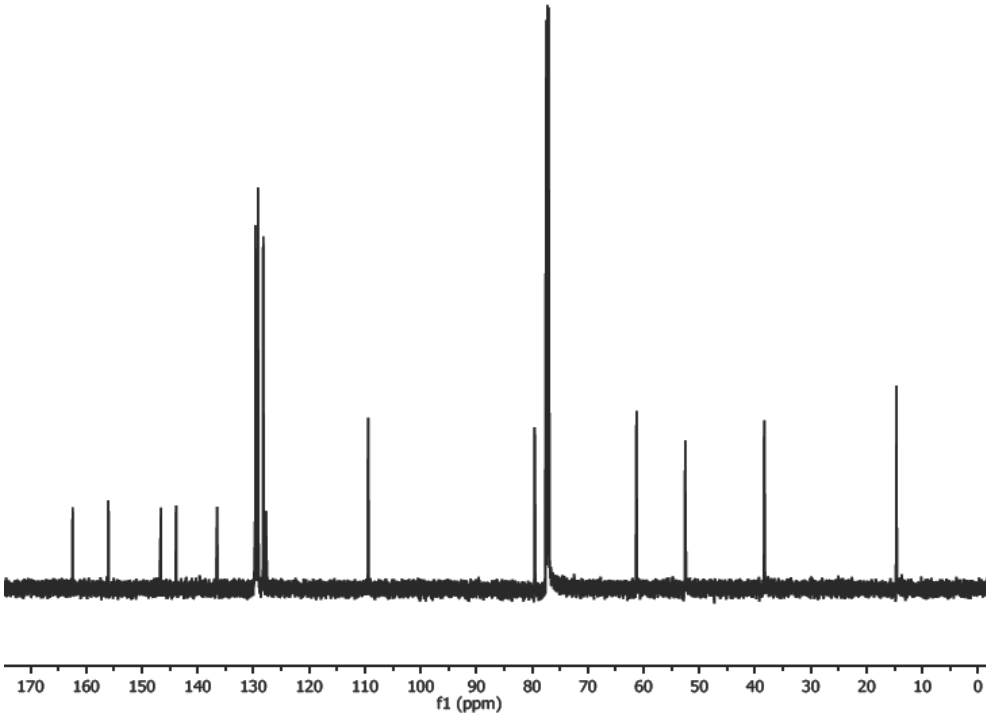

unreacted Ph(o-CH3)-L-alkyneester 2082 (20.993)
1: Scan ES+
1.47e8
269.15
270.13
537.22
223.08
538.20
271.18
559.20
560.25
314.18
561.37
102.55
145.02
315.30
422.54
438.63
673.49
689.17
715.00
826.99
853.73
957.53
1052.15
1096.73
1229.67
1342.31
1365.61
1488.30
%
m/z

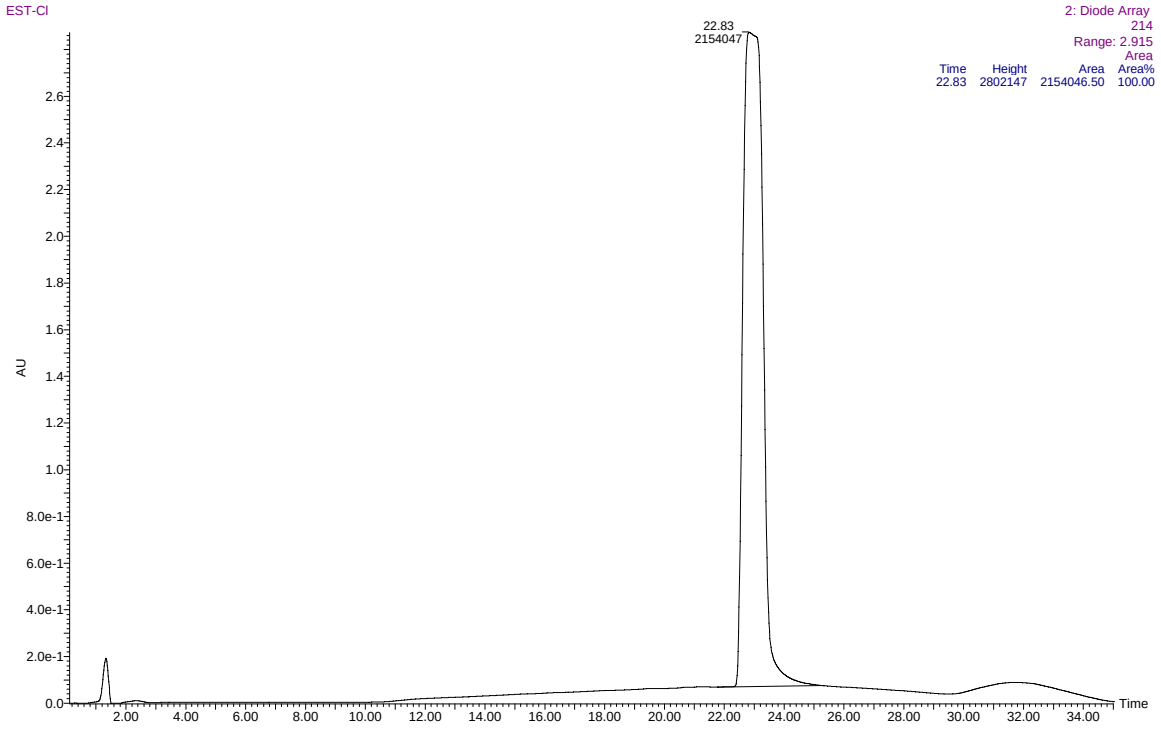
9{*1,1*}

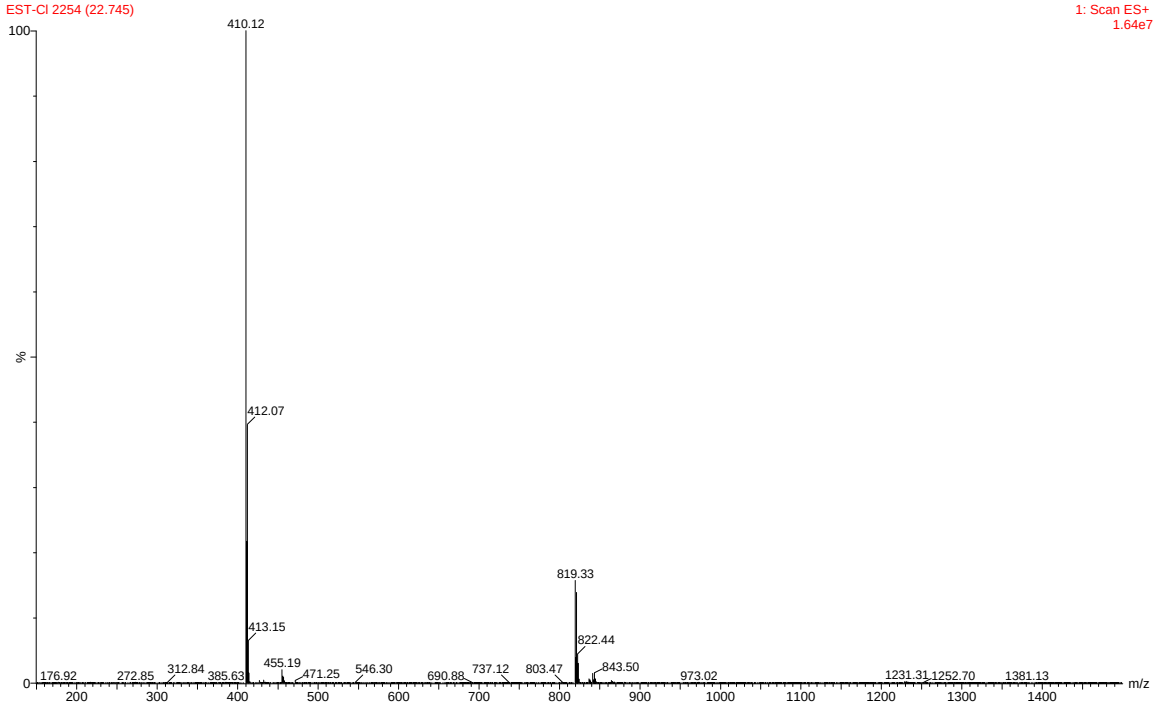


Chemical Formula: $C_{22}H_{20}ClN_3O_3$
Molecular Weight: 409.87

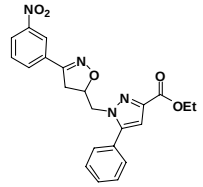




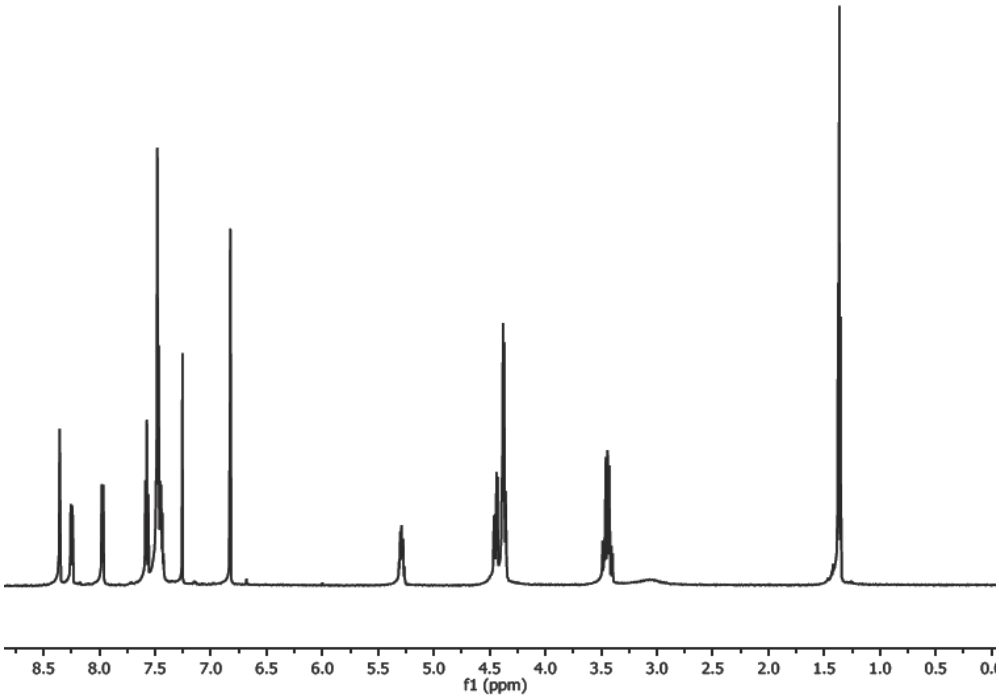

EST-Cl
2: Diode Array
214
Range: 2.915
Area
Time Height Area Area%
22.83 2802147 2154046.50 100.00
22.83
2154047
AU
Time

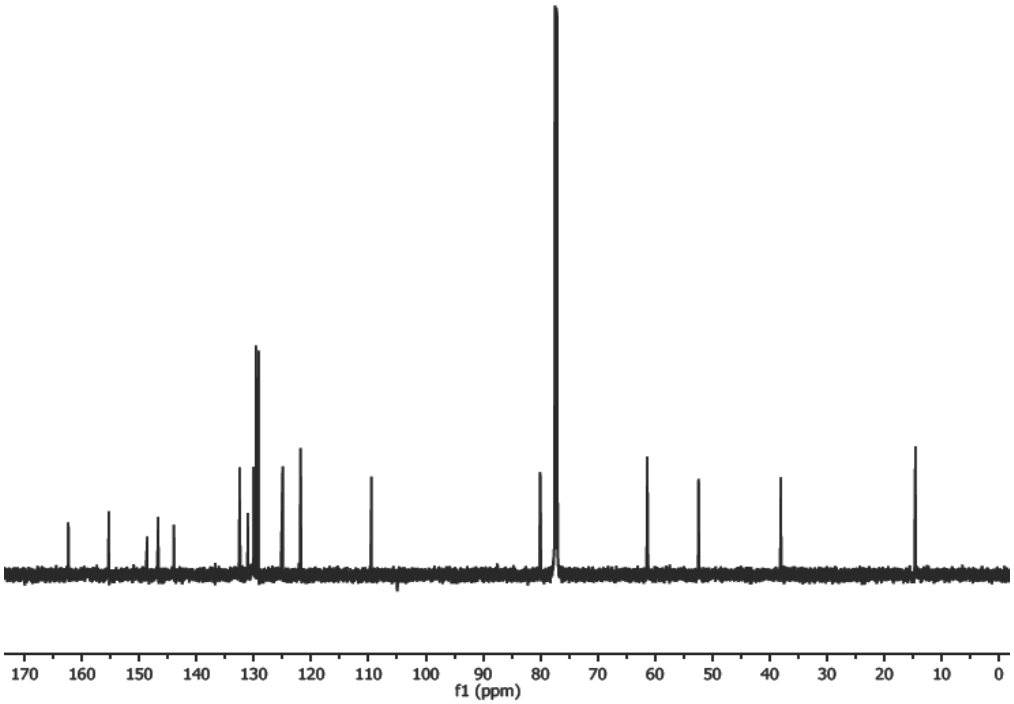

EST-Cl 2254 (22.745)
1: Scan ES+
1.64e7
410.12
412.07
819.33
413.15
822.44
455.19
843.50
176.92
272.85
312.84
385.63
471.25
546.30
690.88
737.12
803.47
973.02
1231.31
1252.70
1381.13
%
m/z

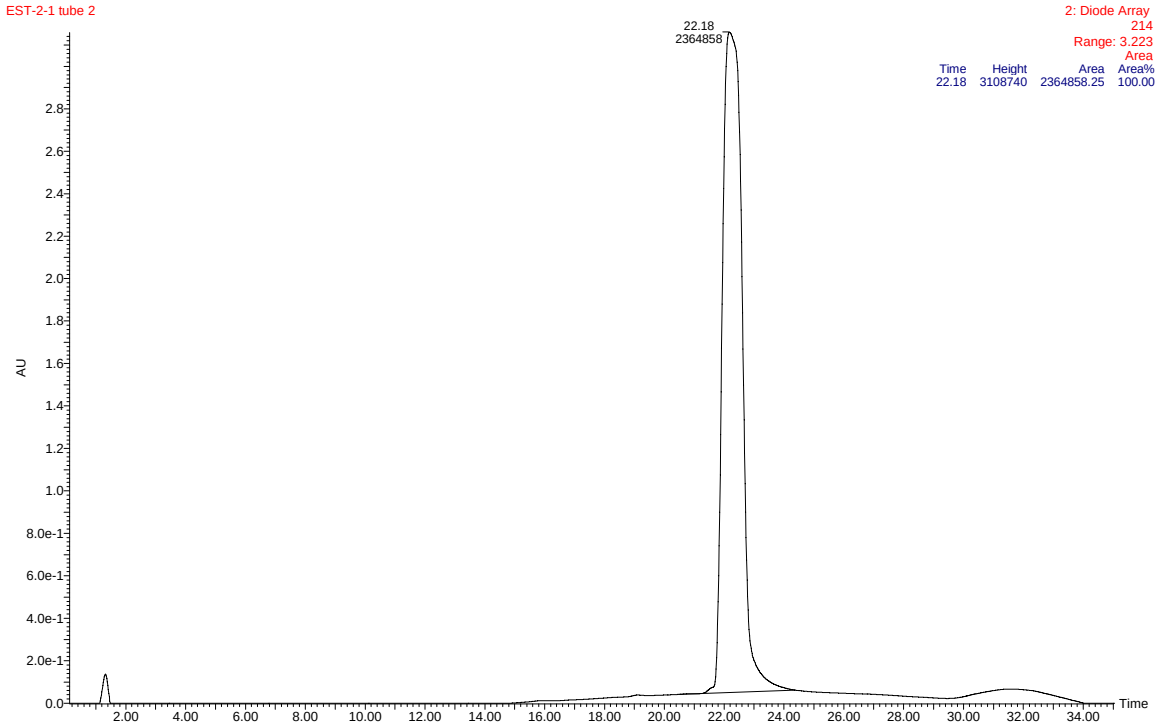
9{*1,3*}

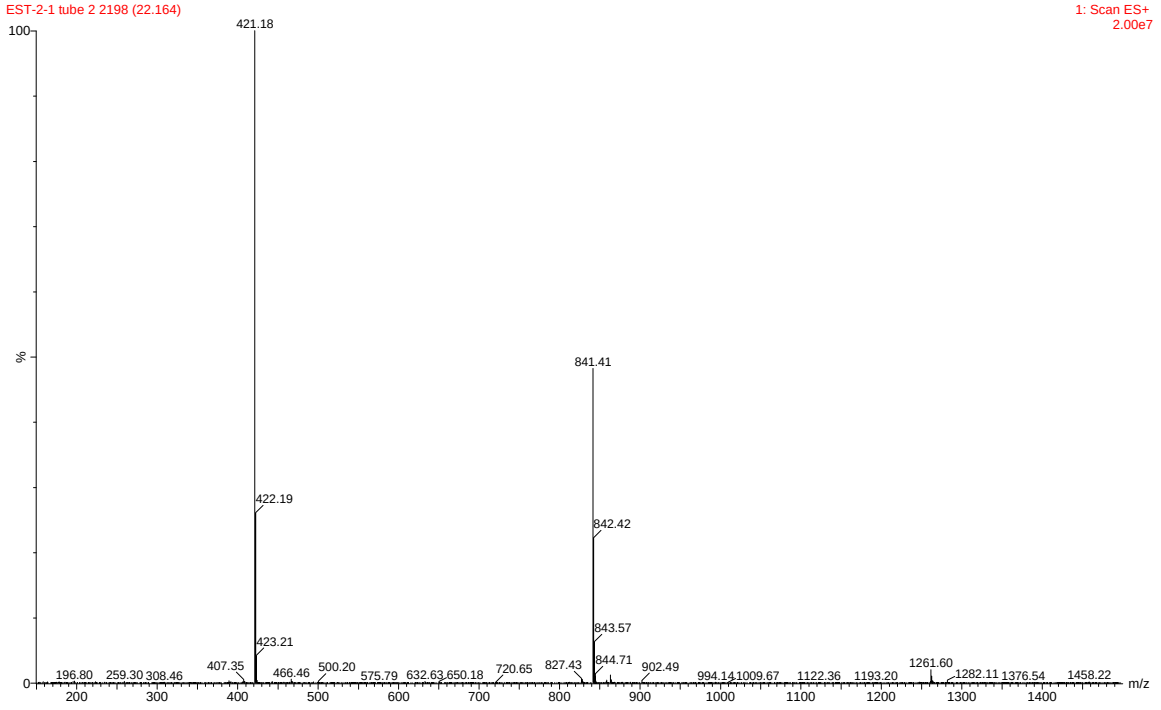


Chemical Formula: $C_{22}H_{20}N_4O_5$
Molecular Weight: 420.42

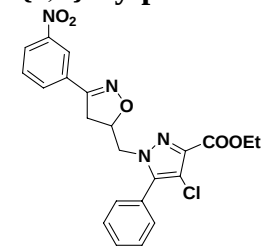




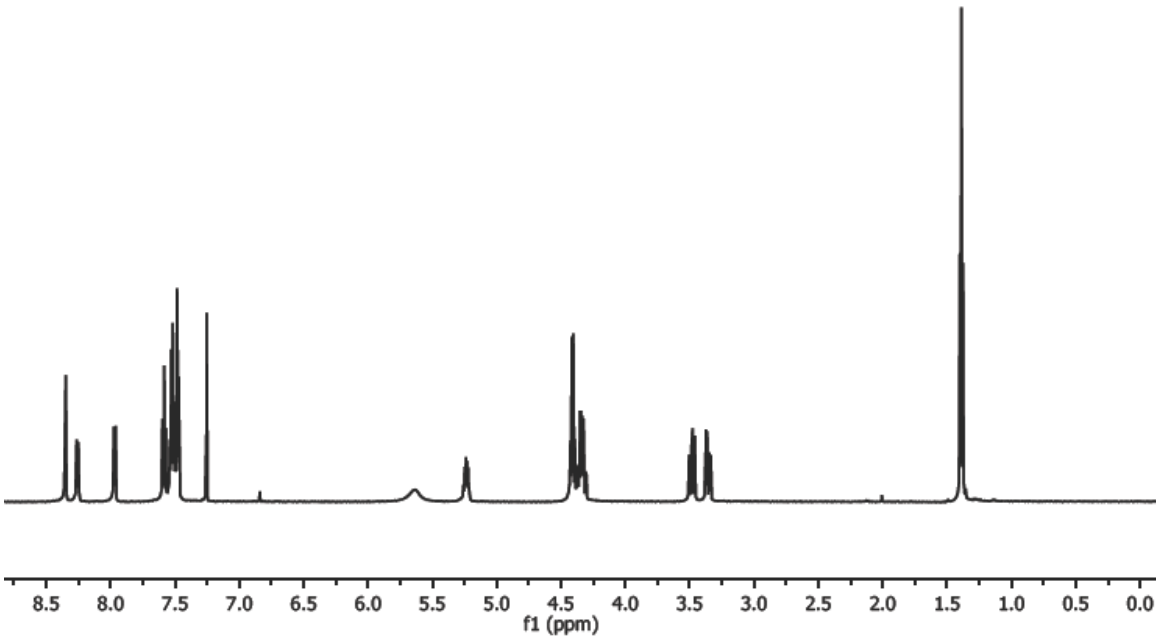

EST-2-1 tube 2
2: Diode Array
214
Range: 3.223
Area
Time Height Area Area%
22.18 3108740 2364858.25 100.00
22.18
2364858
AU
Time

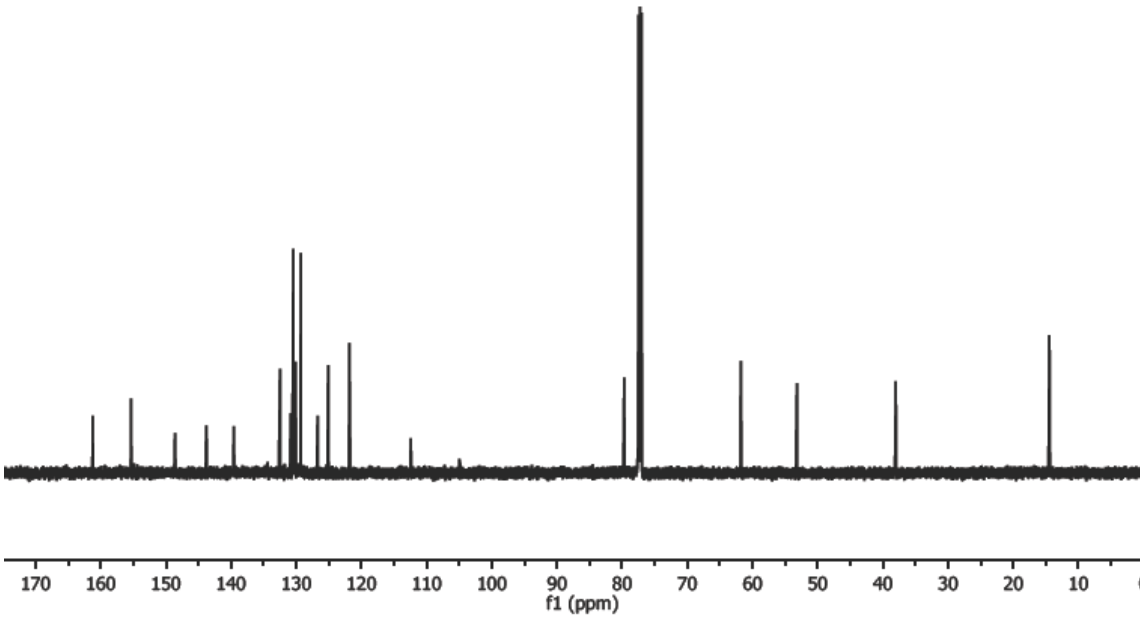

EST-2-1 tube 2 2198 (22.164)
1: Scan ES+
2.00e7
421.18
841.41
422.19
842.42
843.57
423.21
844.71
%
m/z

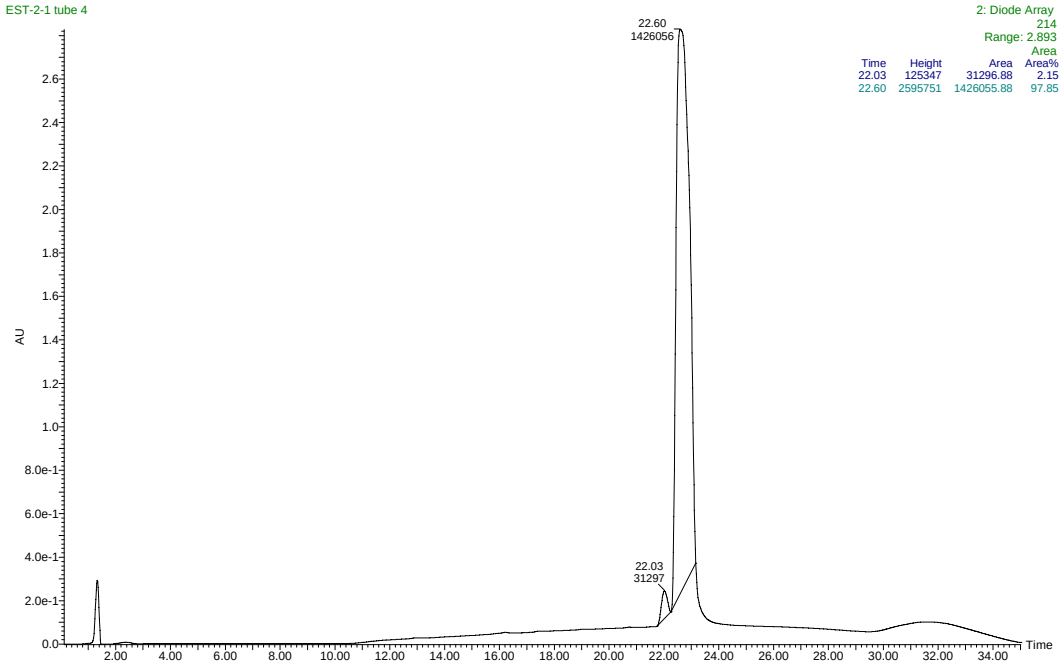
9{*1,3*} By-product

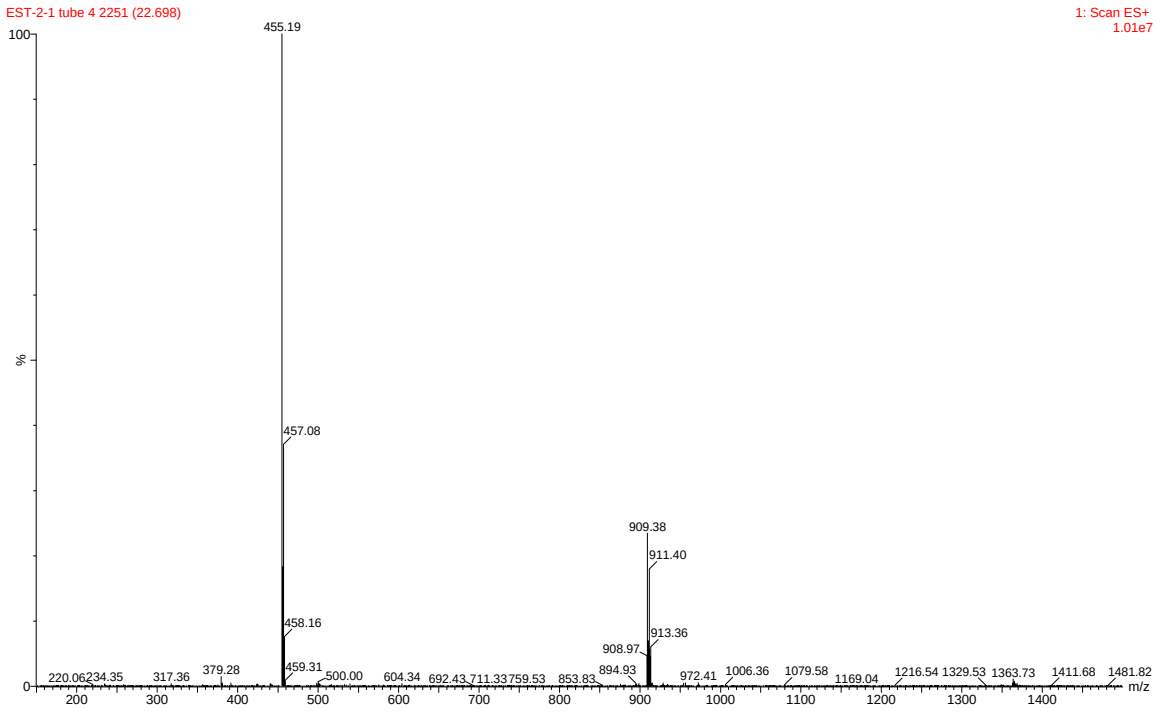


Chemical Formula: $C_{22}H_{19}ClN_4O_5$
Molecular Weight: 454.86

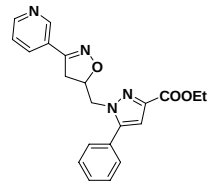




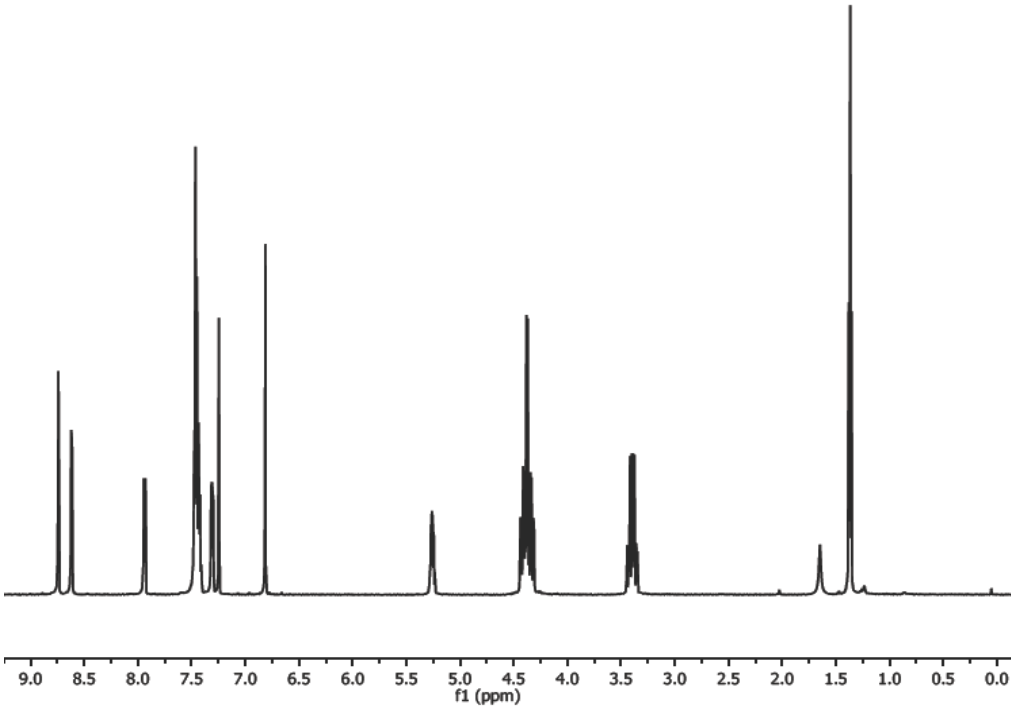

EST-2-1 tube 4
2: Diode Array
214
Range: 2.893
Area
Time Height Area Area%
22.03 125347 31296.88 2.15
22.60 2595751 1426055.88 97.85
22.60
1426056
22.03
31297
AU
Time

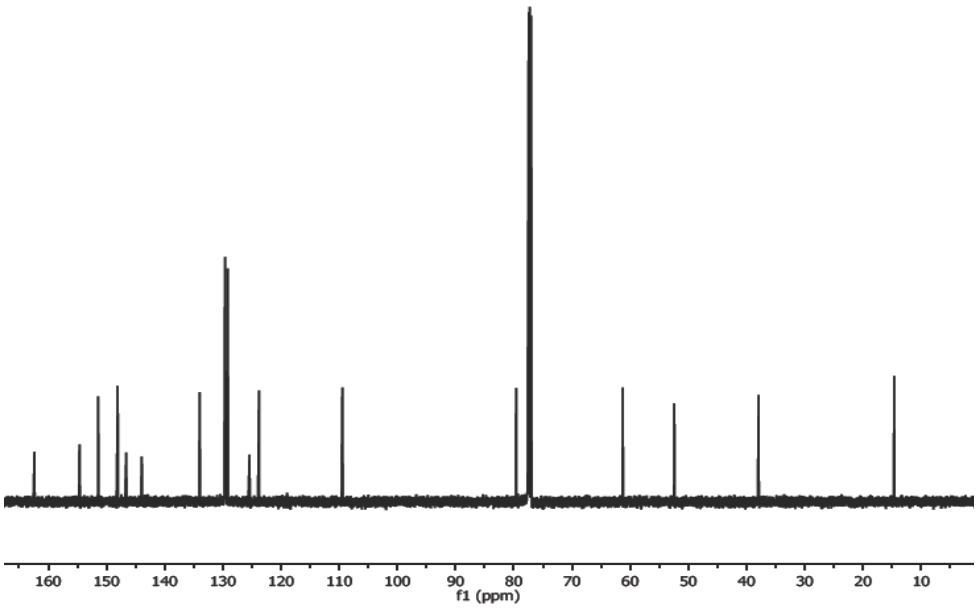

EST-2-1 tube 4 2251 (22.698)
1: Scan ES+
1.01e7
455.19
457.08
909.38
911.40
458.16
913.36
908.97
459.31
%
m/z

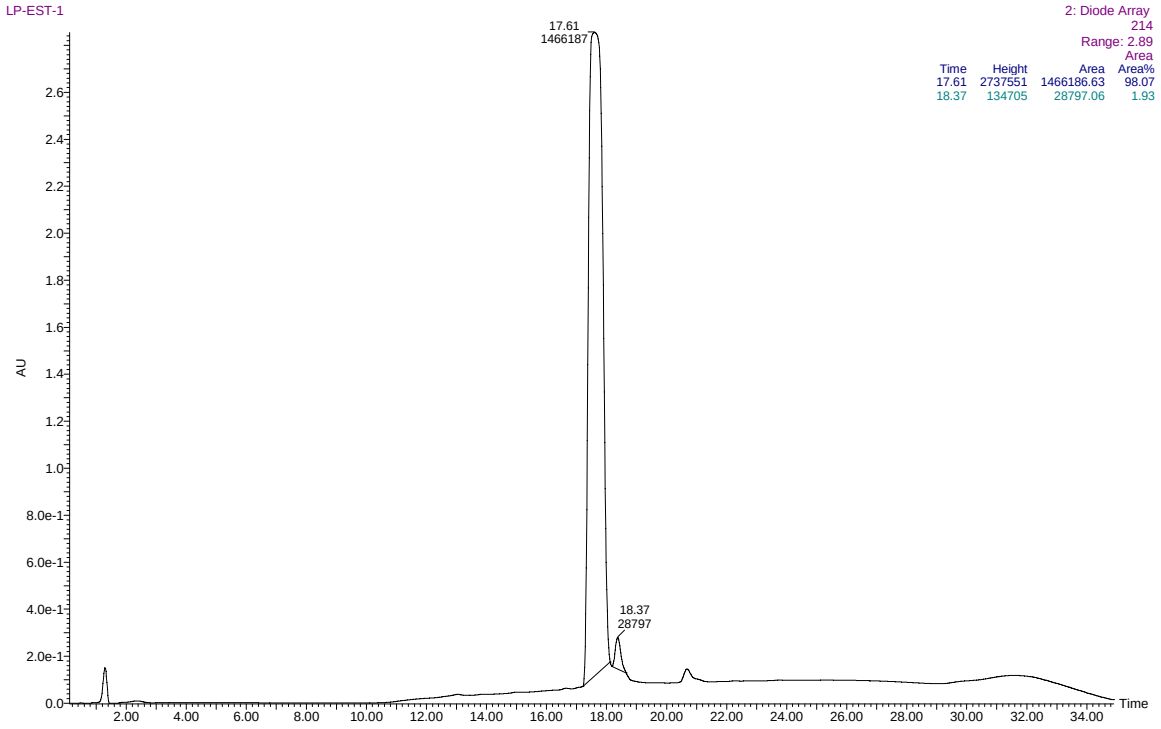
9{*1,4*}

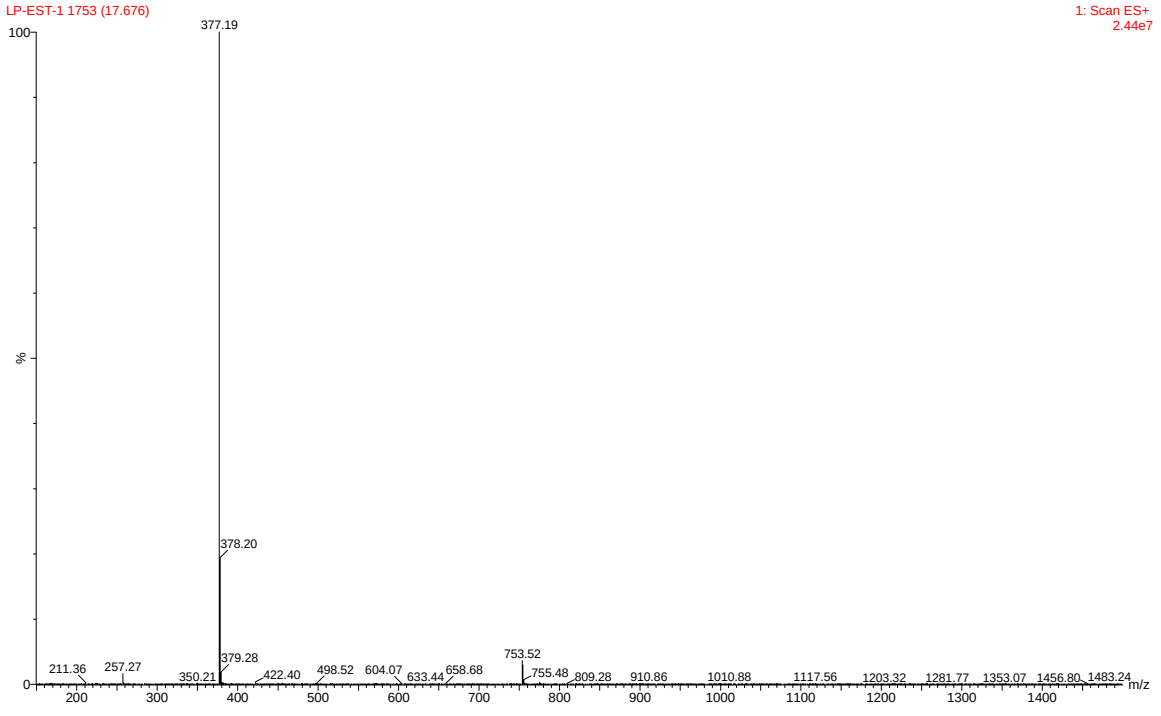


Chemical Formula: $C_{21}H_{20}N_4O_3$
Molecular Weight: 376.41

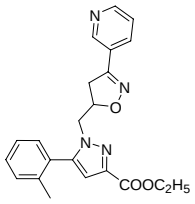




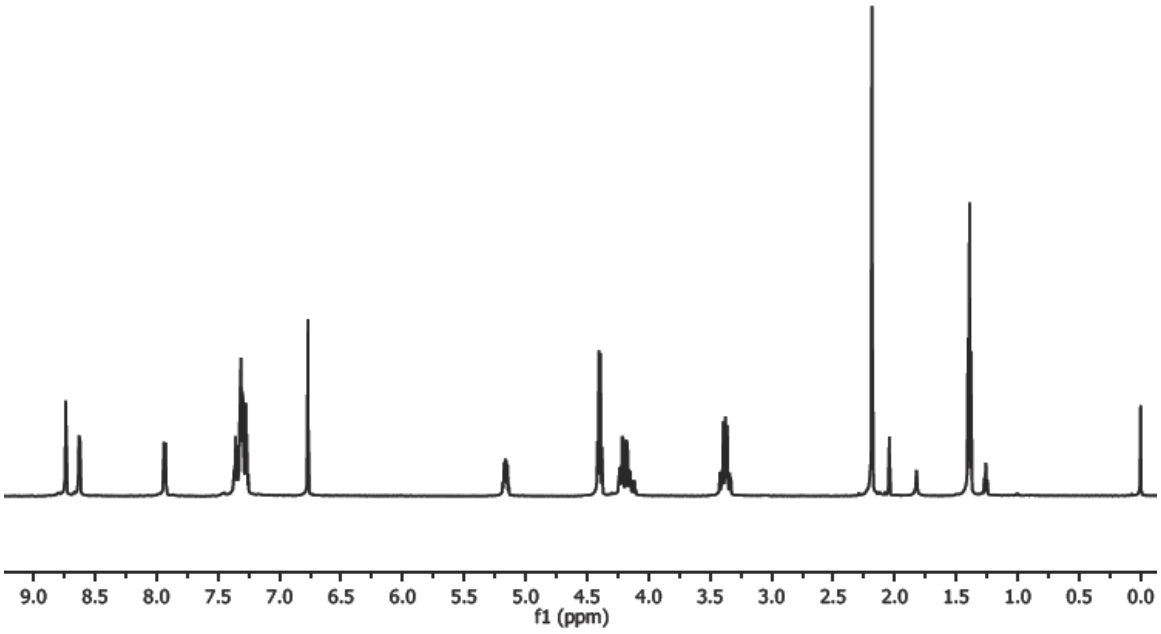

LP-EST-1
2: Diode Array
214
Range: 2.89
Area
Time Height Area Area%
17.61 2737551 1466186.63 98.07
18.37 134705 28797.06 1.93
17.61
1466187
18.37
28797
AU
Time

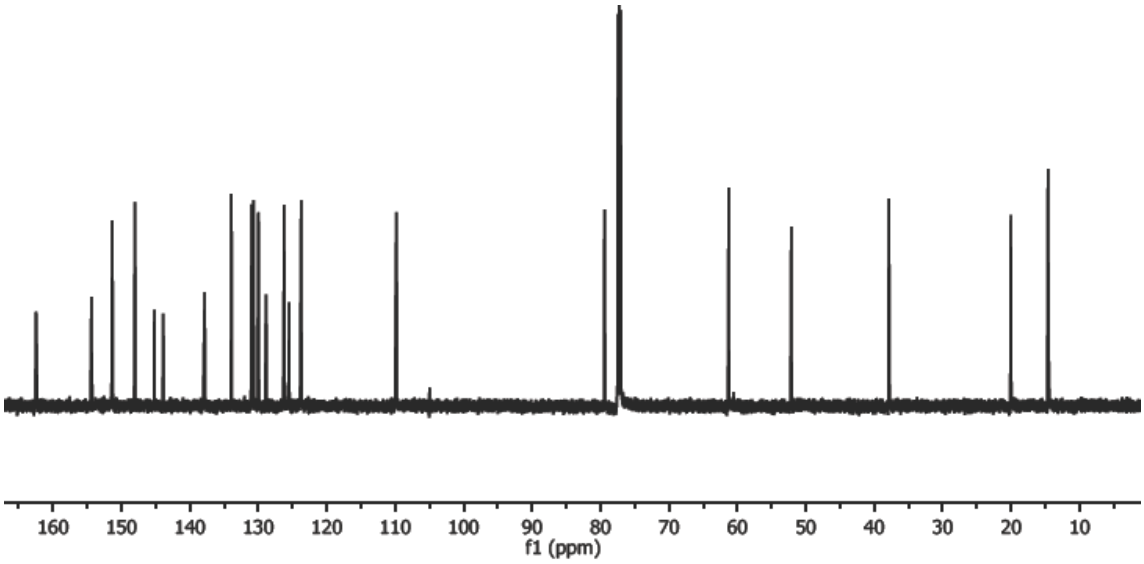

LP-EST-1 1753 (17.676)
1: Scan ES+
2.44e7
377.19
378.20
379.28
753.52
%
m/z

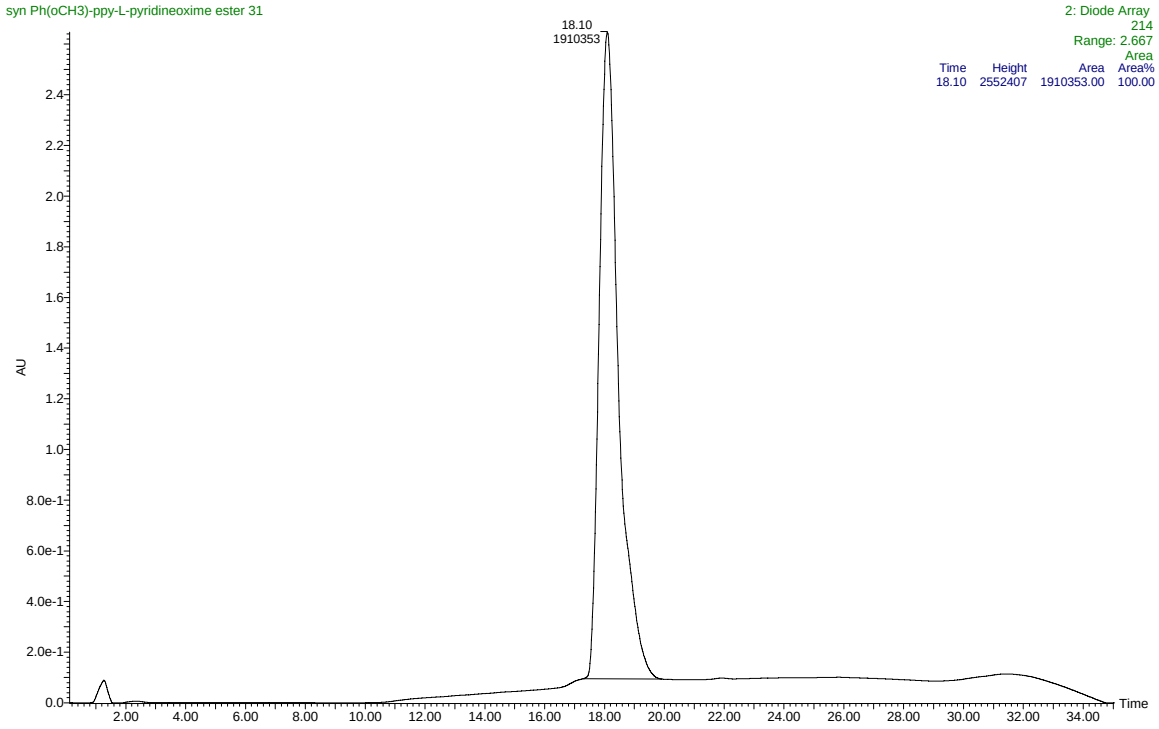
9{*2,4*}

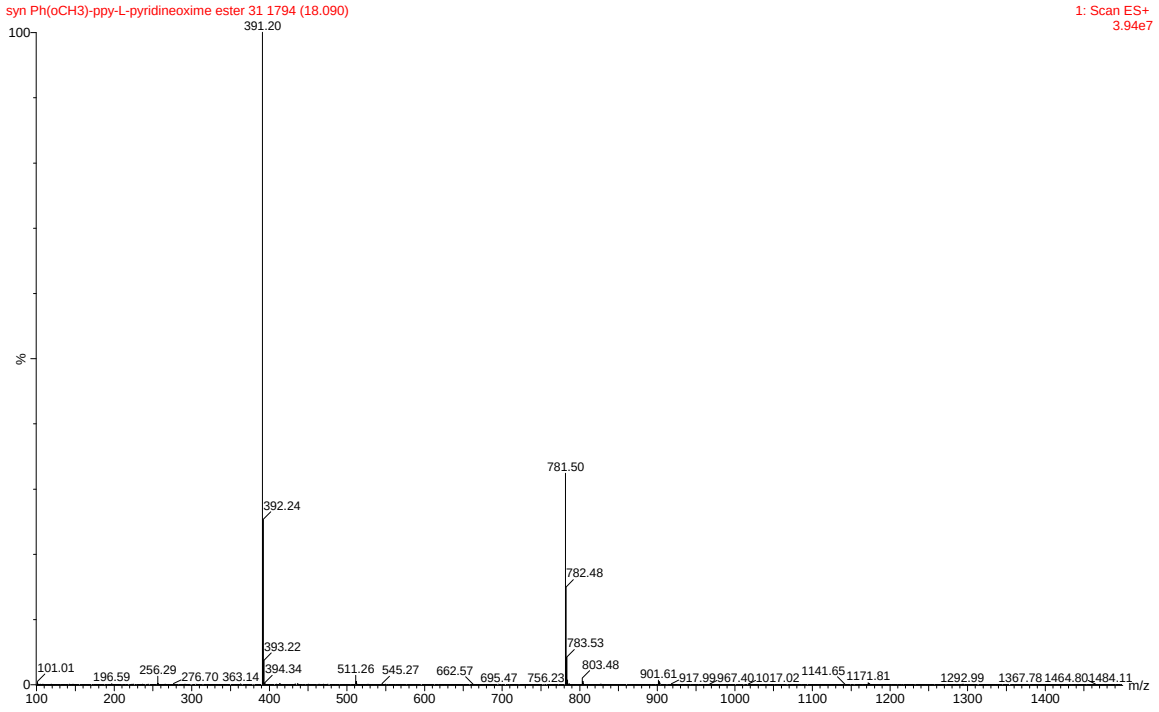


$C_{22}H_{22}N_4O_3$
Mol. Wt.: 390.44

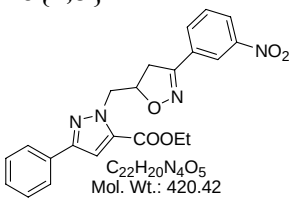




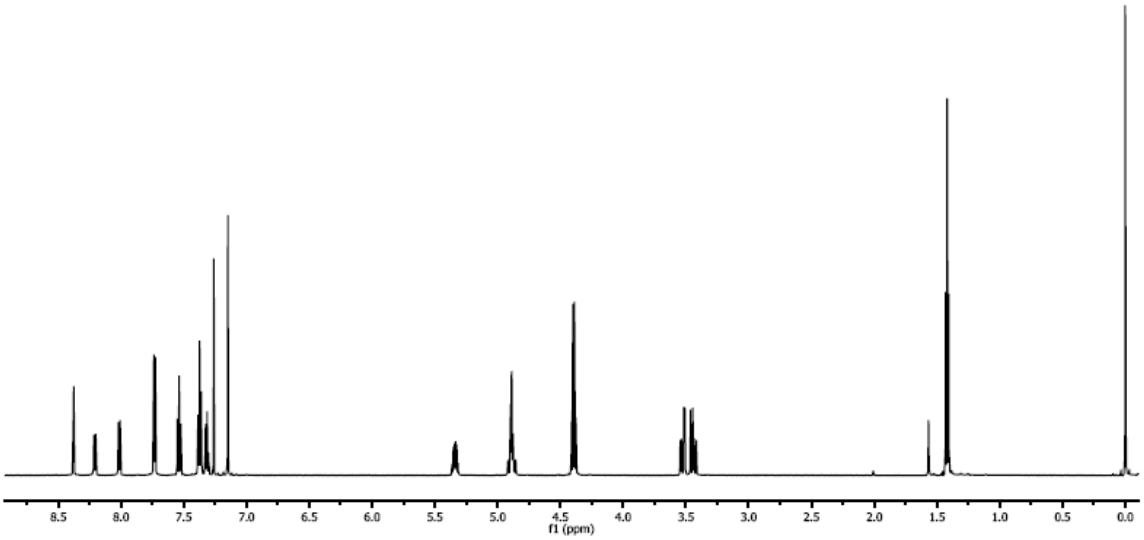

syn Ph(oCH3)-ppy-L-pyridineoxime ester 31
2: Diode Array
214
Range: 2.667
Area
Time Height Area Area%
18.10 2552407 1910353.00 100.00
18.10
1910353
AU
Time

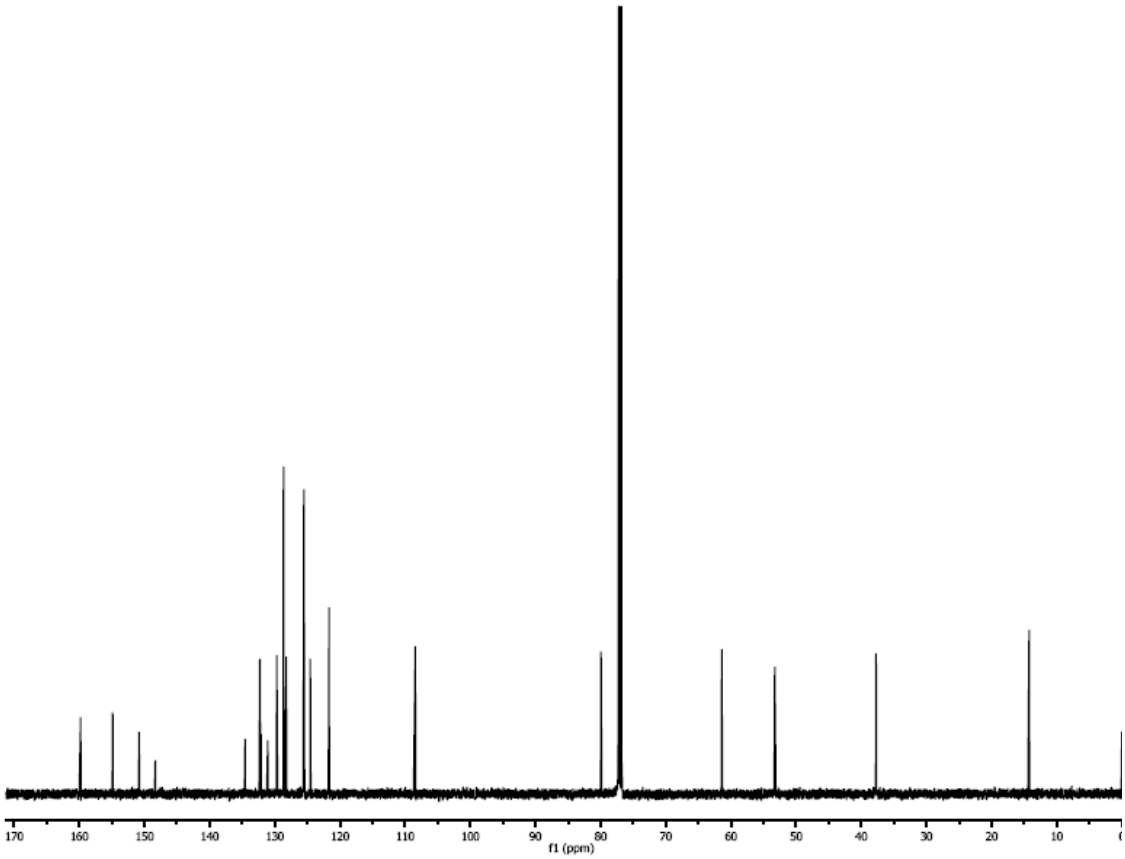

syn Ph(oCH3)-ppy-L-pyridineoxime ester 31 1794 (18.090)
1: Scan ES+
3.94e7
391.20
392.24
781.50
782.48
393.22
783.53
394.34
803.48
%
m/z

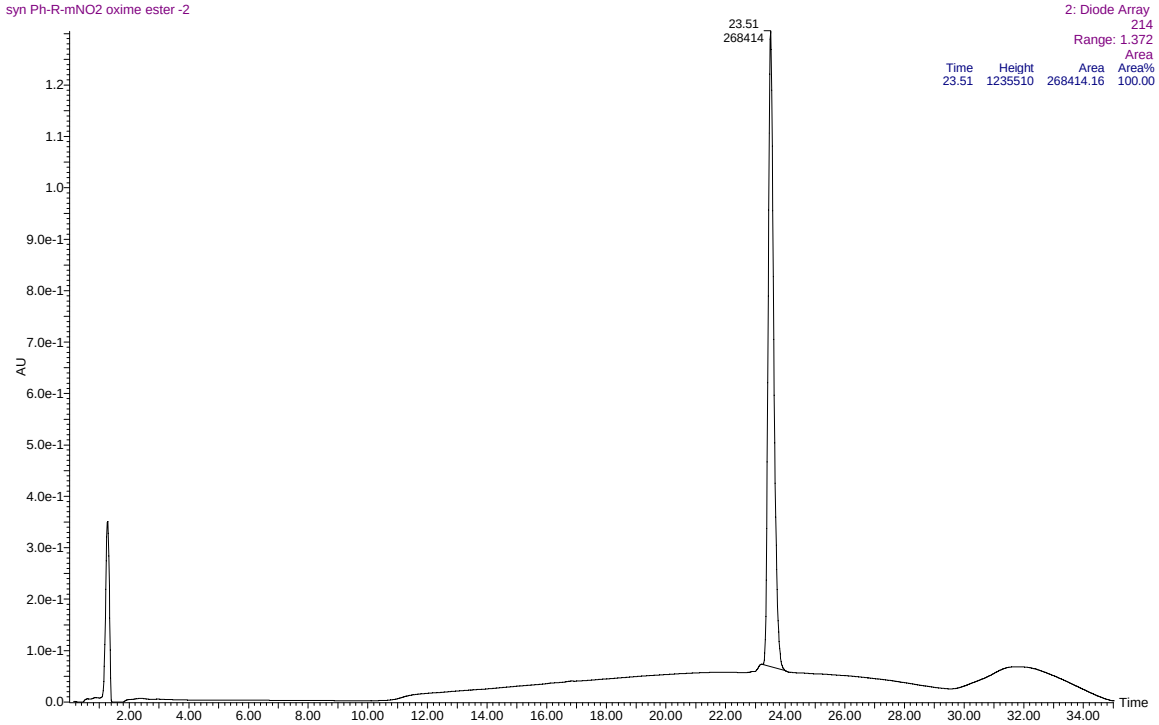
10{*1,3*}

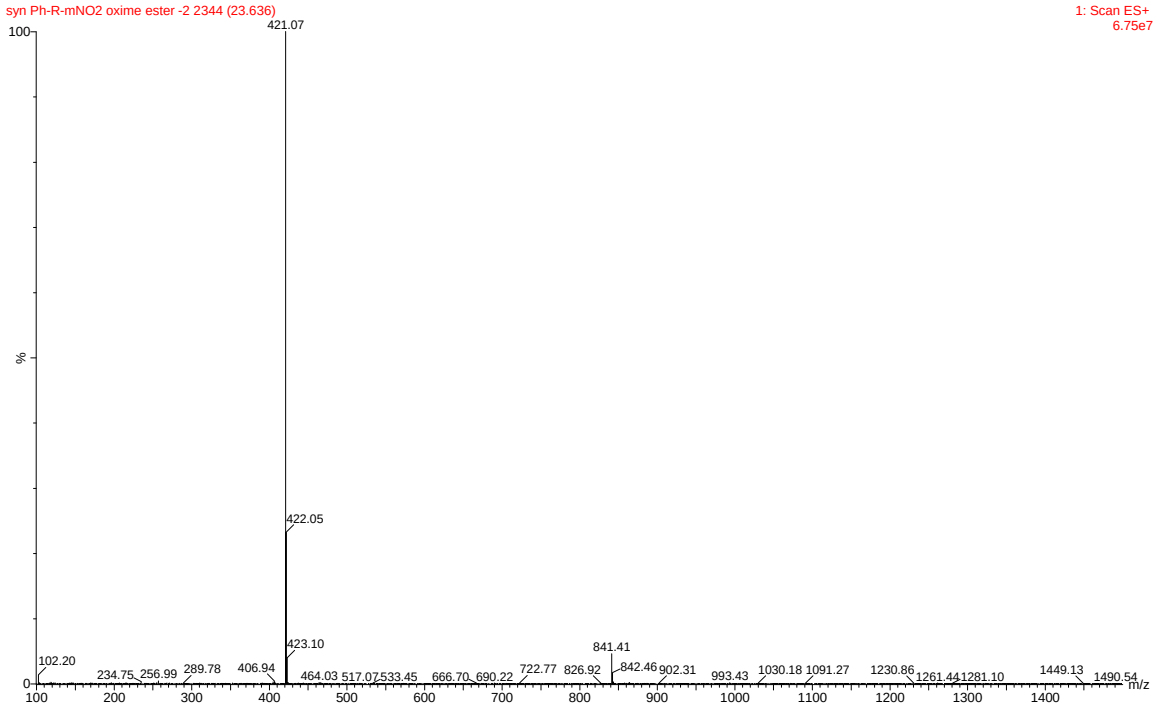


$C_{22}H_{20}N_4O_5$
Mol. Wt.: 420.42

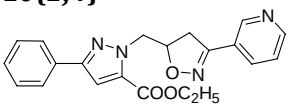




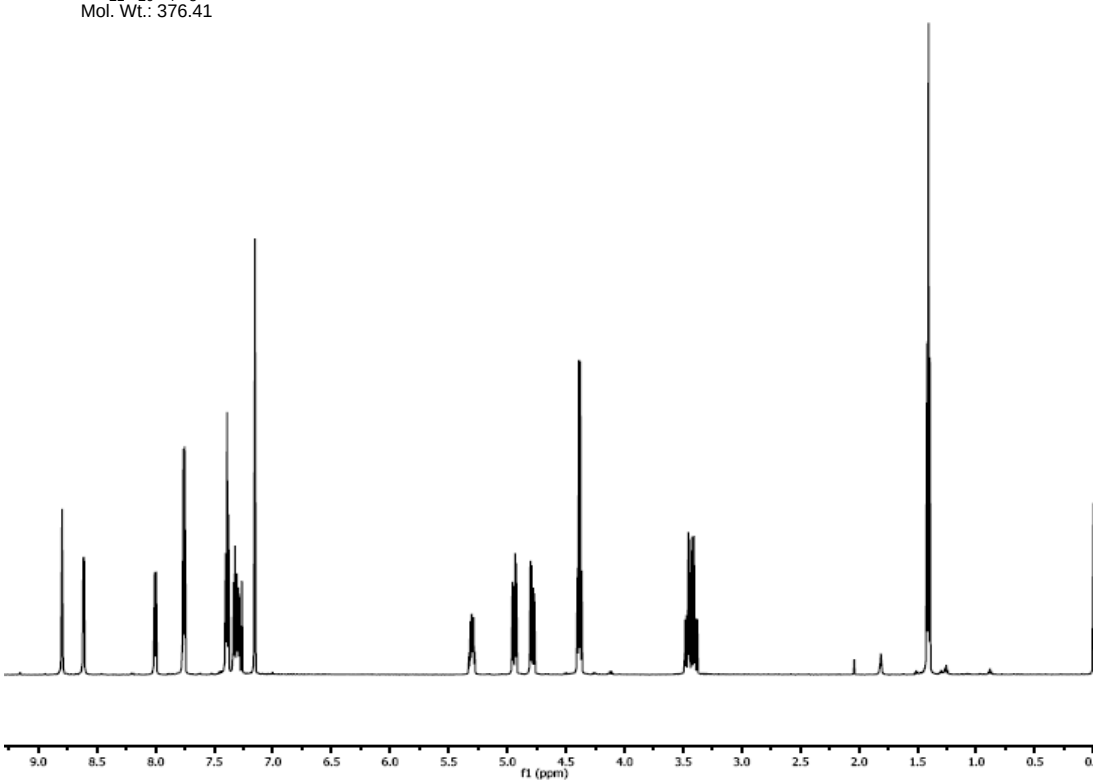

syn Ph-R-mNO2 oxime ester -2
2: Diode Array
214
Range: 1.372
Area
Time Height Area Area%
23.51 1235510 268414.16 100.00
23.51
268414
AU
Time

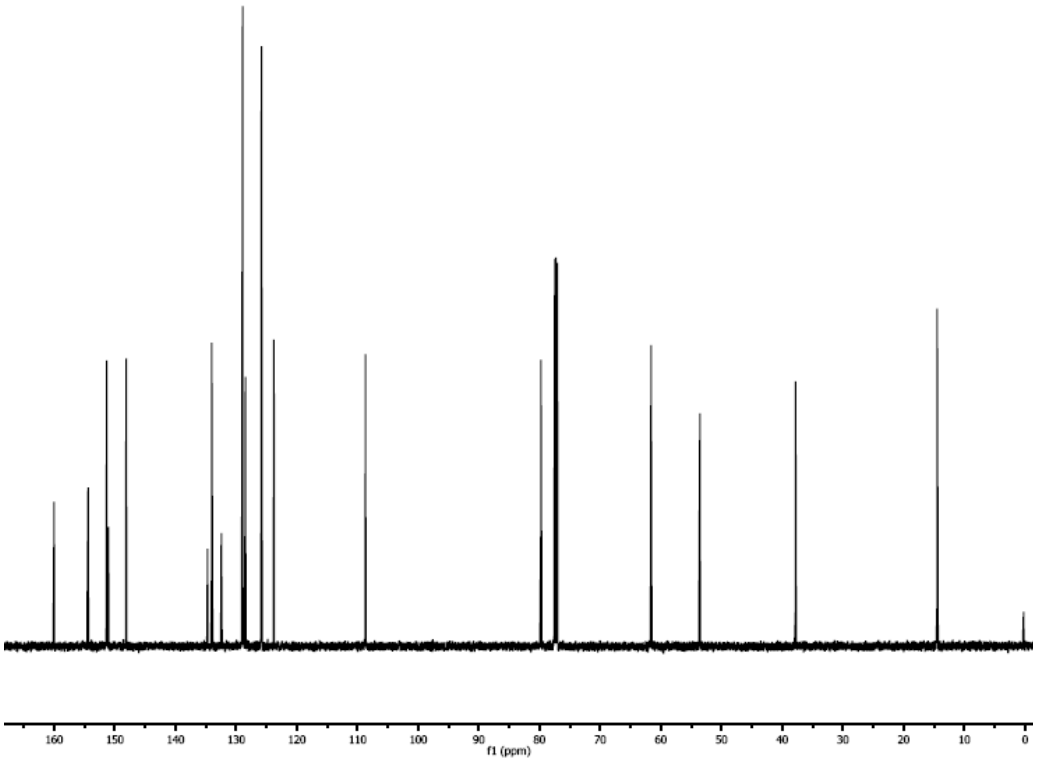

syn Ph-R-mNO2 oxime ester -2 2344 (23.636)
1: Scan ES+
6.75e7
421.07
422.05
423.10
102.20
841.41
%
m/z

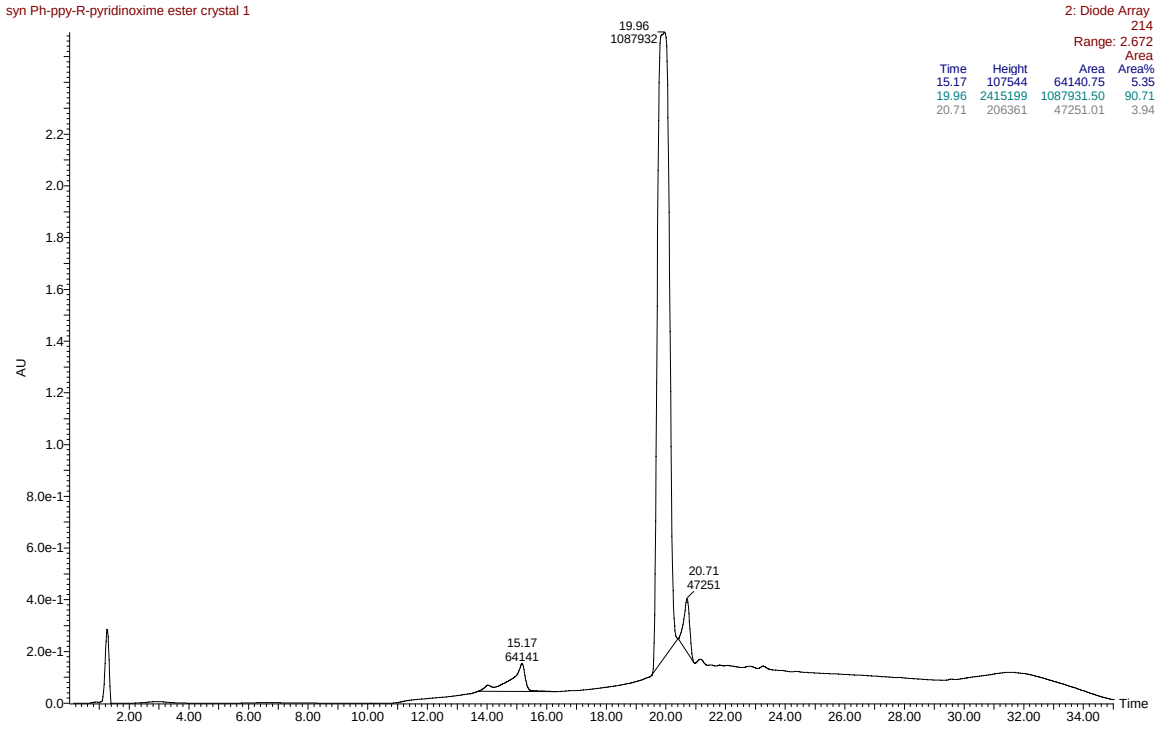
10{*1,4*}

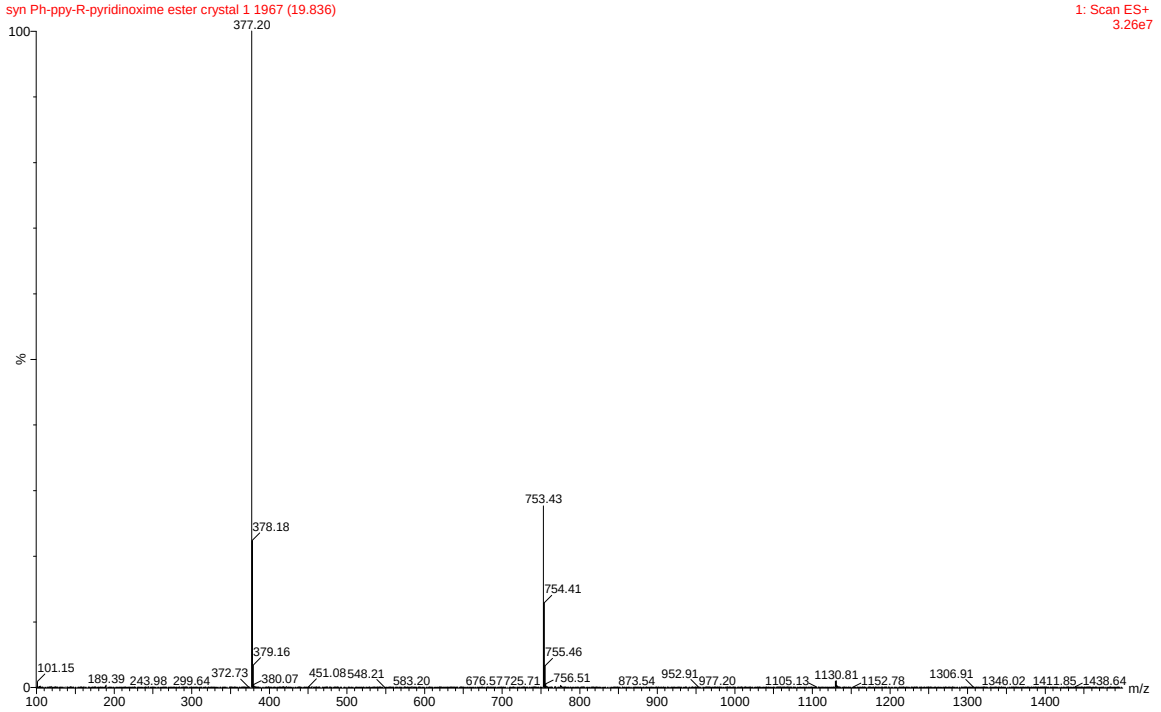


$C_{21}H_{20}N_4O_3$
Mol. Wt.: 376.41

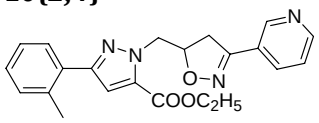




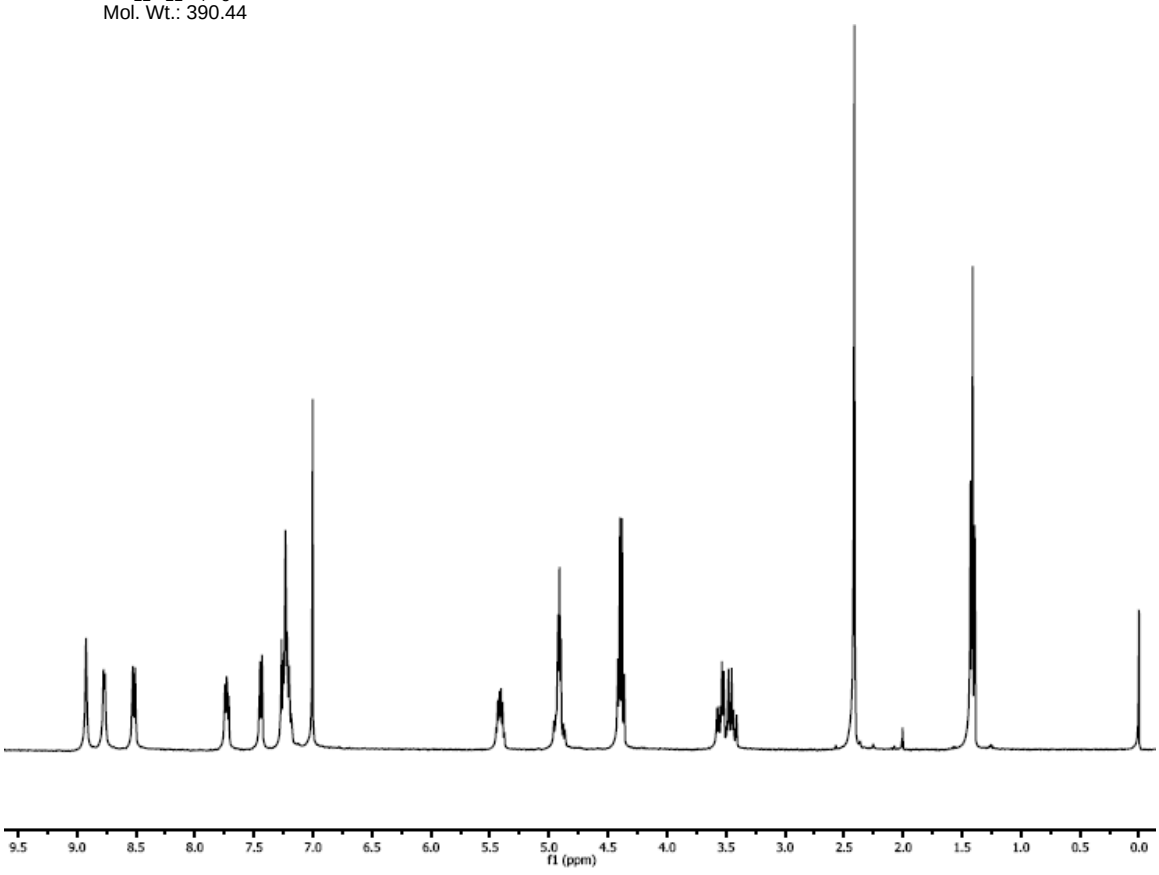

syn Ph-ppy-R-pyridinoxime ester crystal 1
2: Diode Array
214
Range: 2.672
Area
Time Height Area Area%
15.17 107544 64140.75 5.35
19.96 2415199 1087931.50 90.71
20.71 206361 47251.01 3.94
19.96
1087932
20.71
47251
15.17
64141
AU
Time

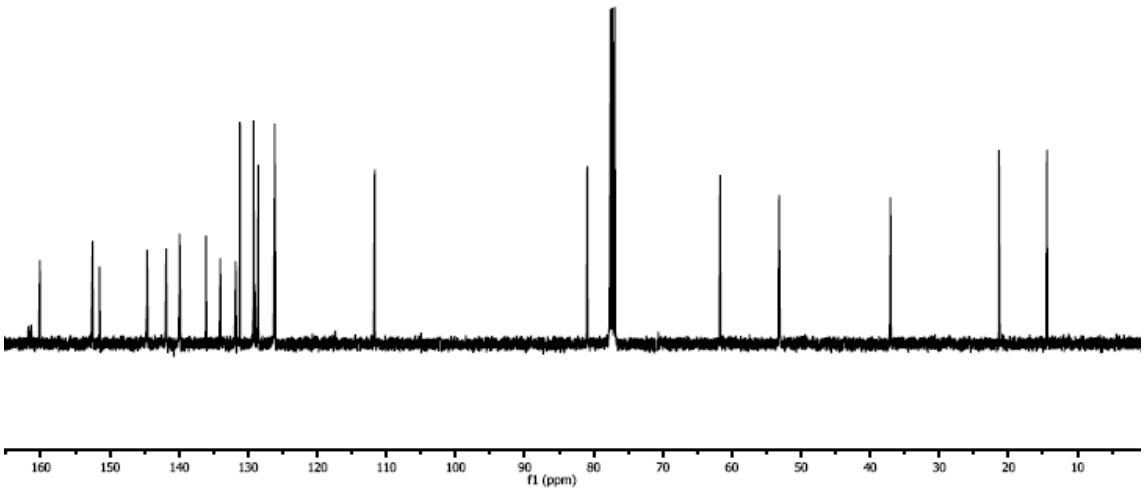

syn Ph-ppy-R-pyridinoxime ester crystal 1 1967 (19.836)
1: Scan ES+
3.26e7
377.20
753.43
378.18
754.41
379.16
755.46
101.15
%
m/z

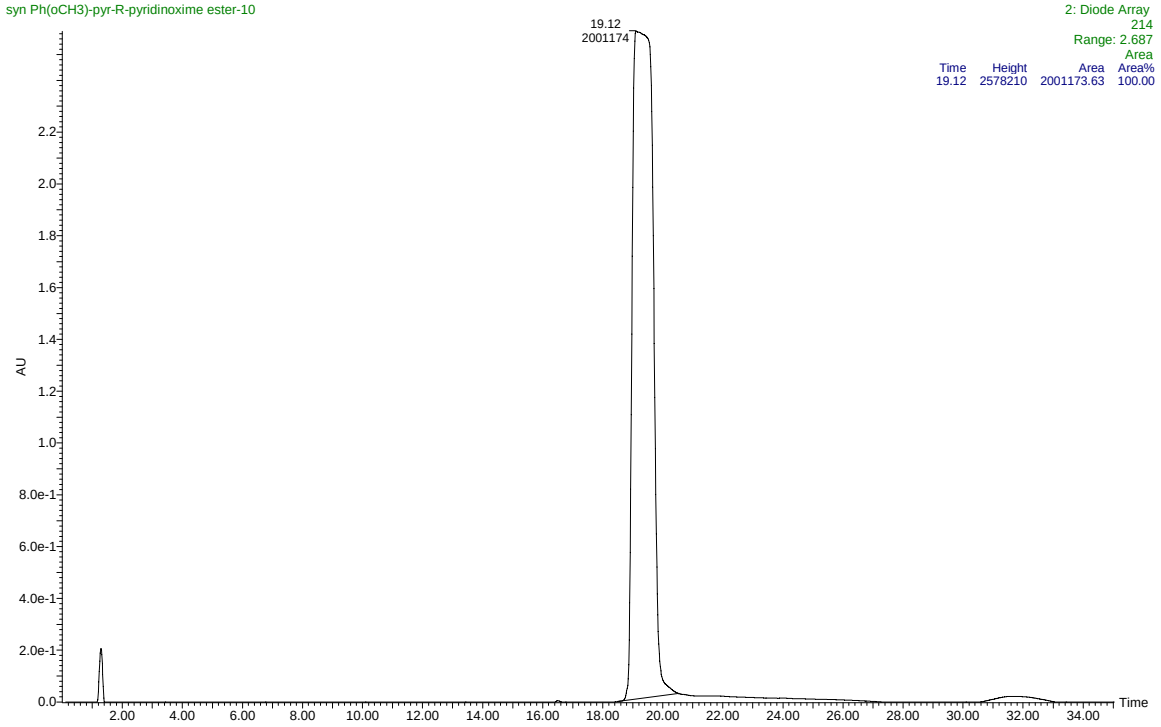
10{*2,4*}

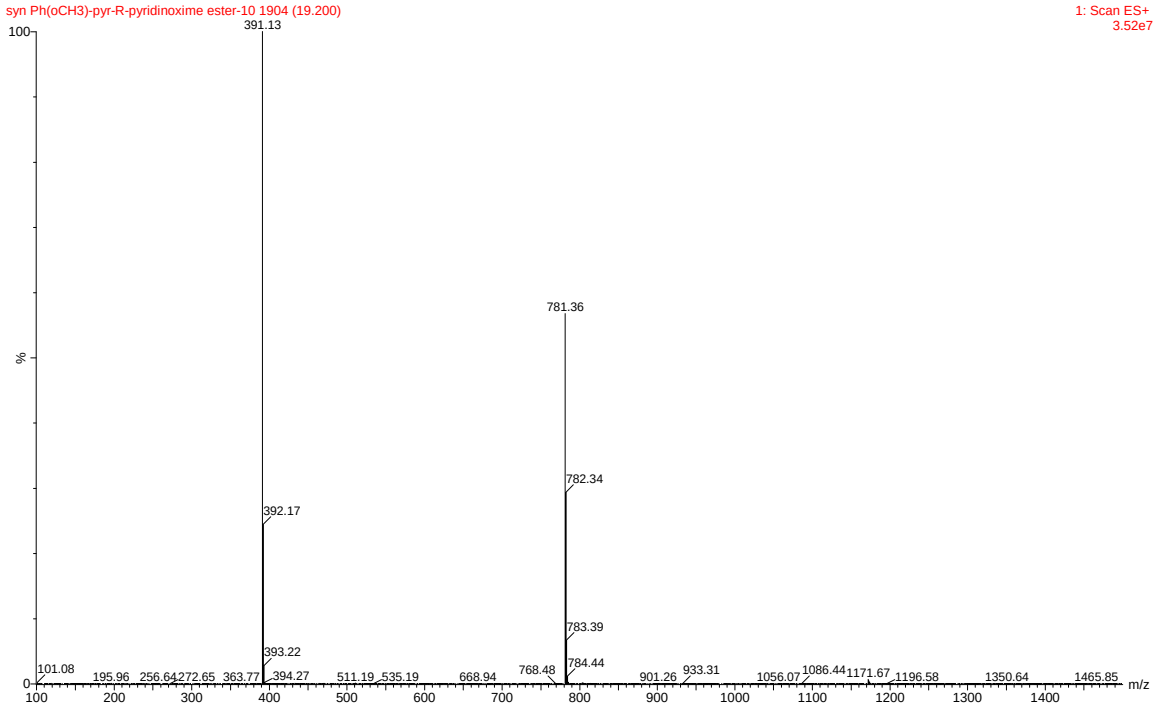


$C_{22}H_{22}N_4O_3$
Mol. Wt.: 390.44

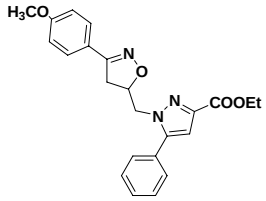




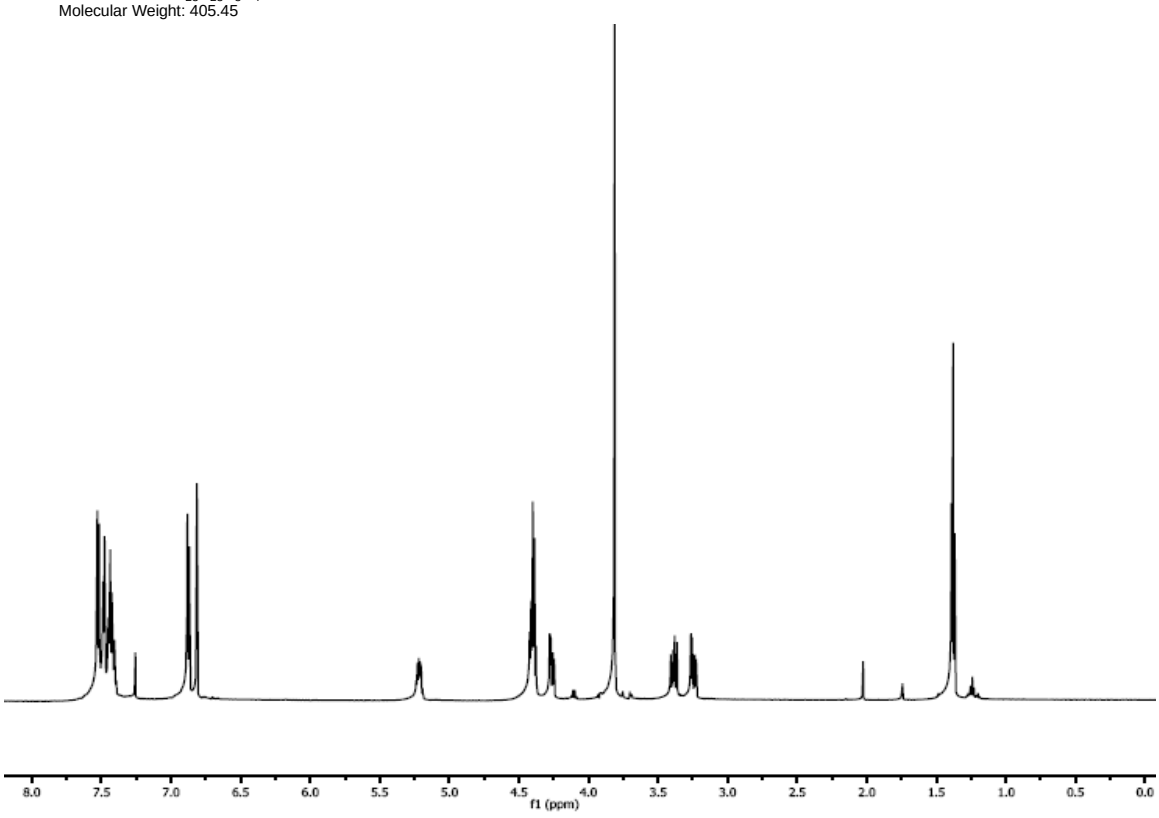

syn Ph(oCH3)-pyr-R-pyridinoxime ester-10
2: Diode Array
214
Range: 2.687
Area
Time Height Area Area%
19.12 2578210 2001173.63 100.00
19.12
2001174
AU
Time

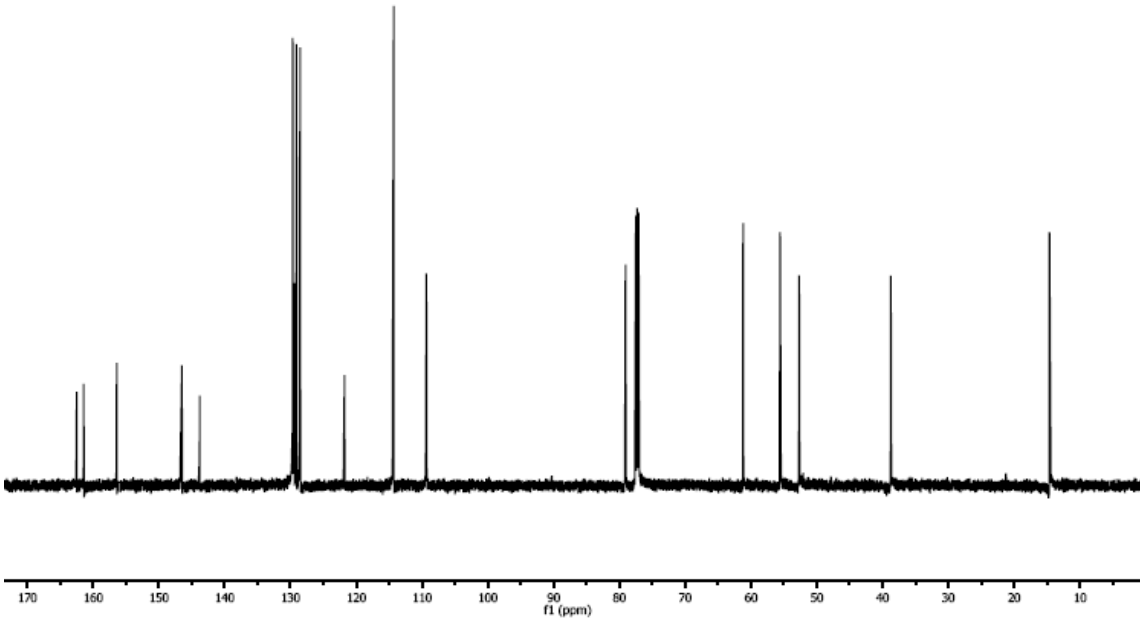

syn Ph(oCH3)-pyr-R-pyridinoxime ester-10 1904 (19.200)
1: Scan ES+
3.52e7
391.13
781.36
782.34
392.17
783.39
393.22
784.44
%
m/z

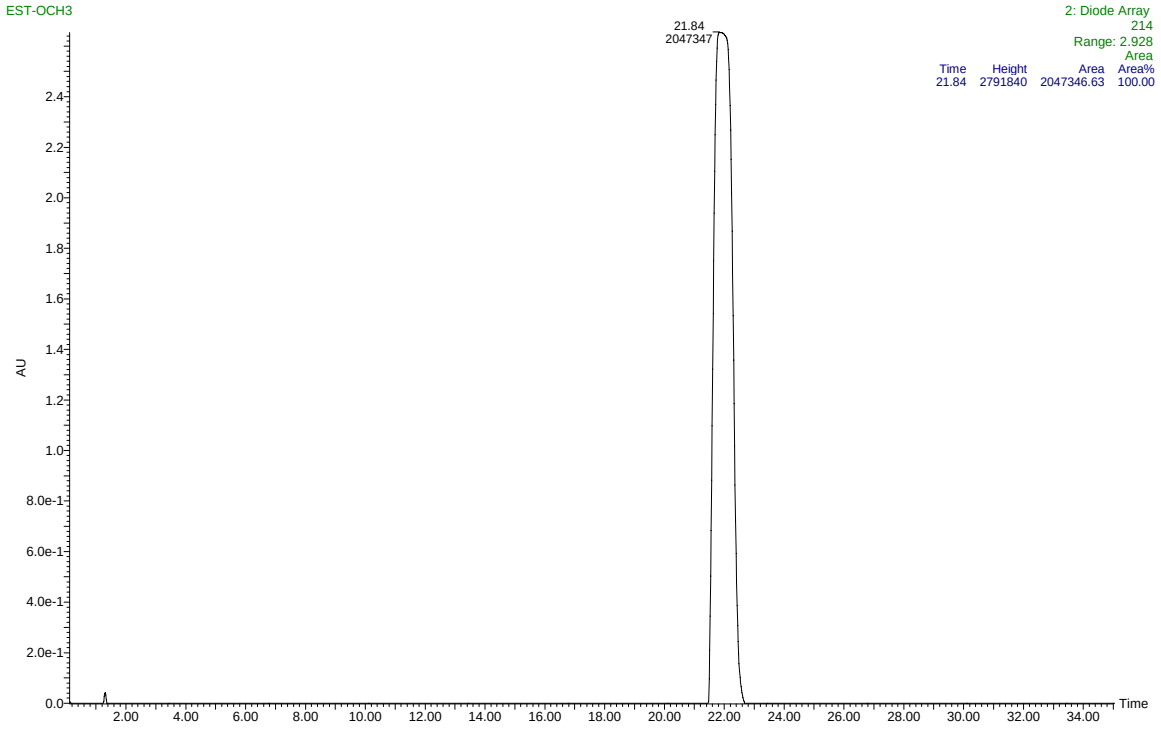
9{*1,2*}

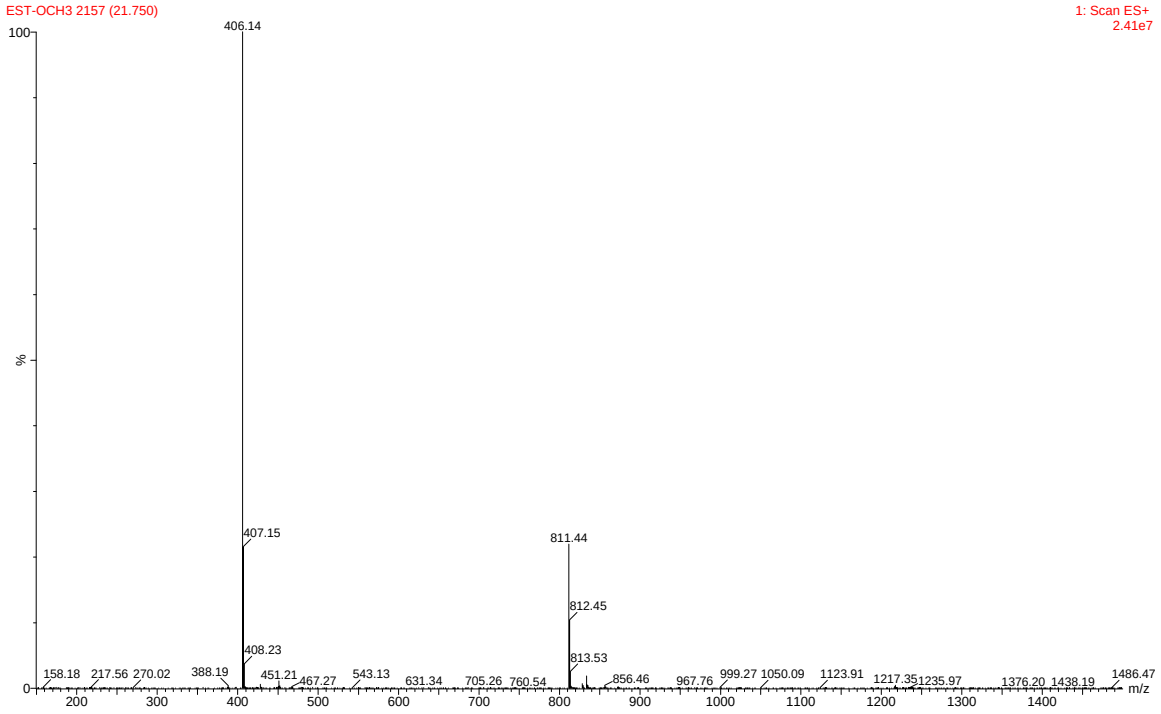


Chemical Formula: $C_{23}H_{23}N_3O_4$
Molecular Weight: 405.45

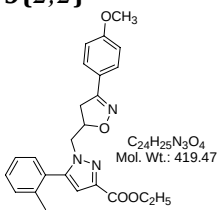




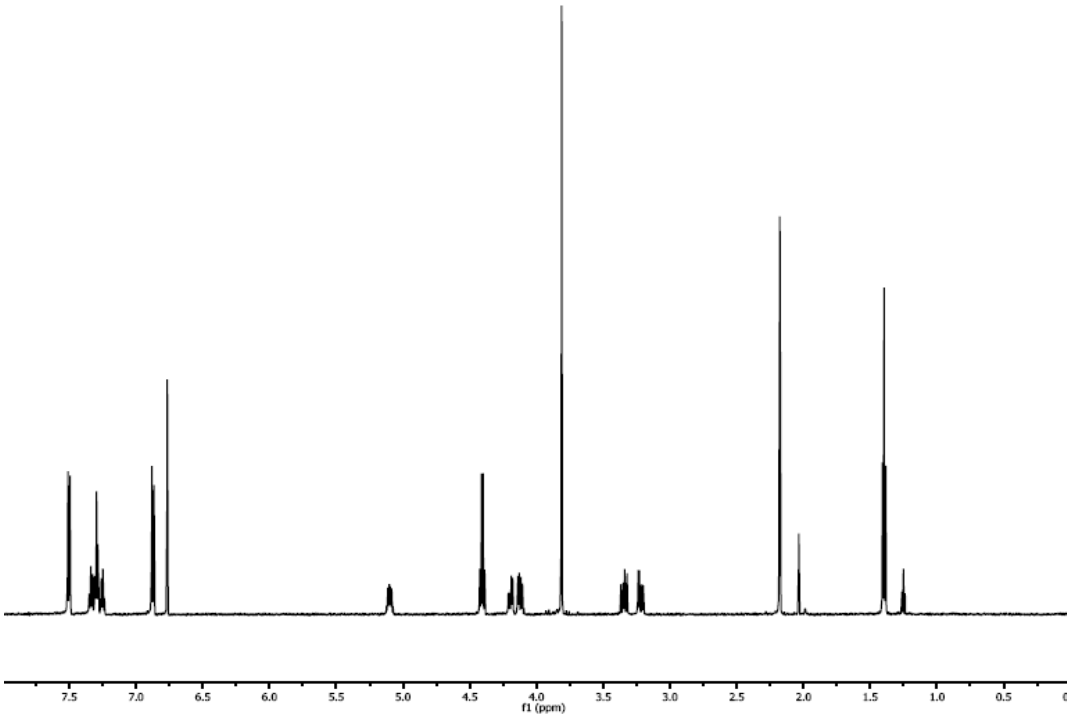

EST-OCH3
2: Diode Array
214
Range: 2.928
Area
Time Height Area Area%
21.84 2791840 2047346.63 100.00
21.84
2047347
AU
Time

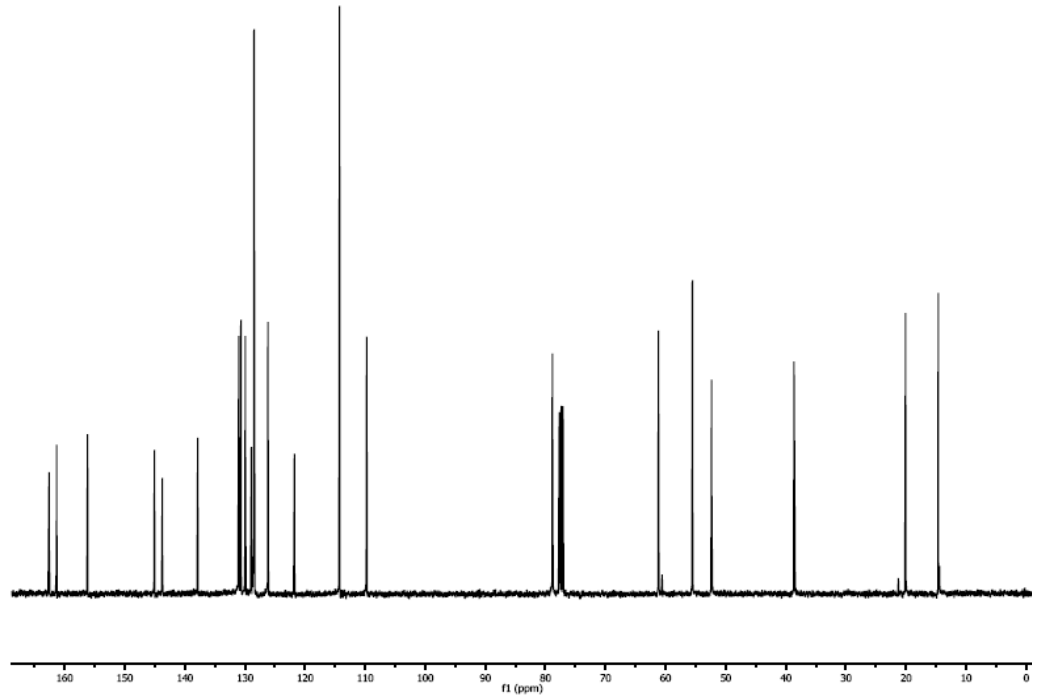

EST-OCH3 2157 (21.750)
1: Scan ES+
2.41e7
406.14
407.15
408.23
811.44
812.45
813.53
%
m/z

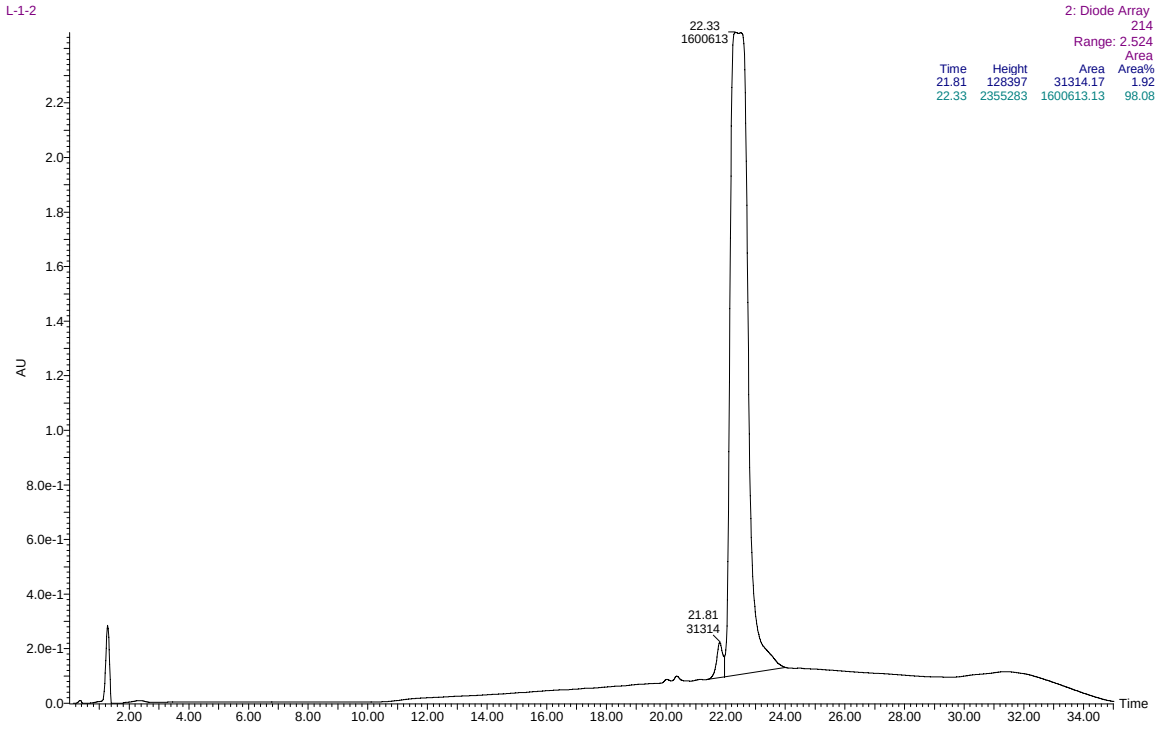
9{*2,2*}

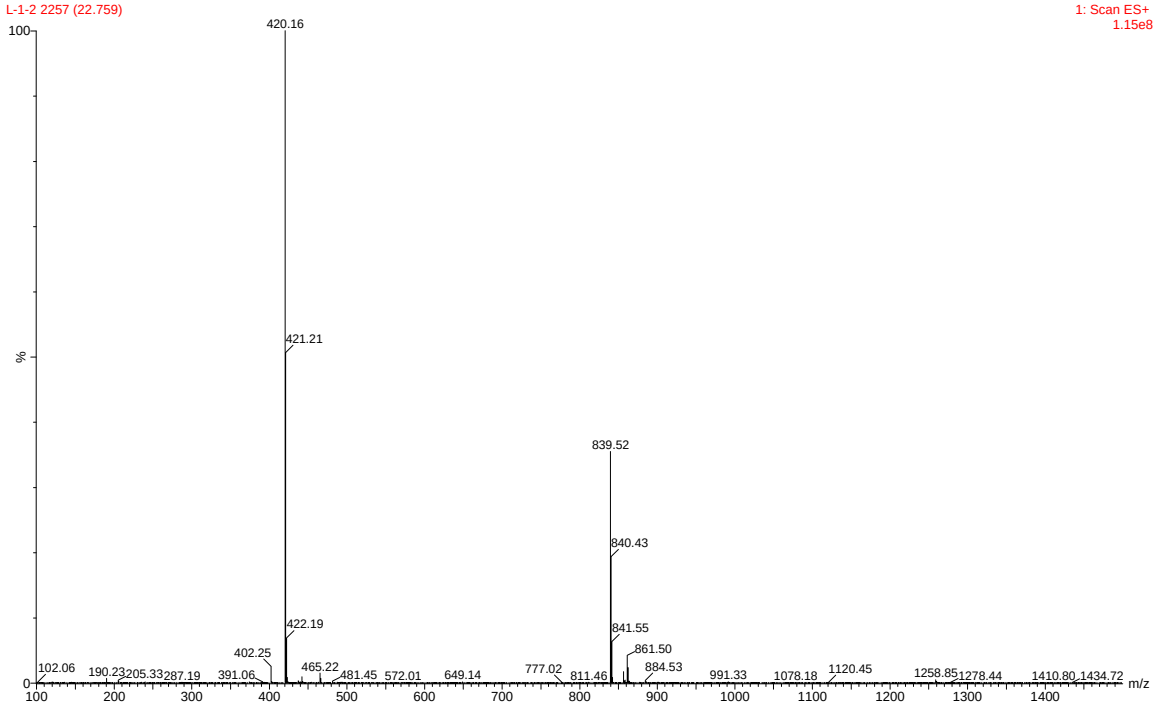


$C_{24}H_{25}N_3O_4$
Mol. Wt.: 419.47

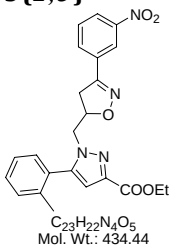




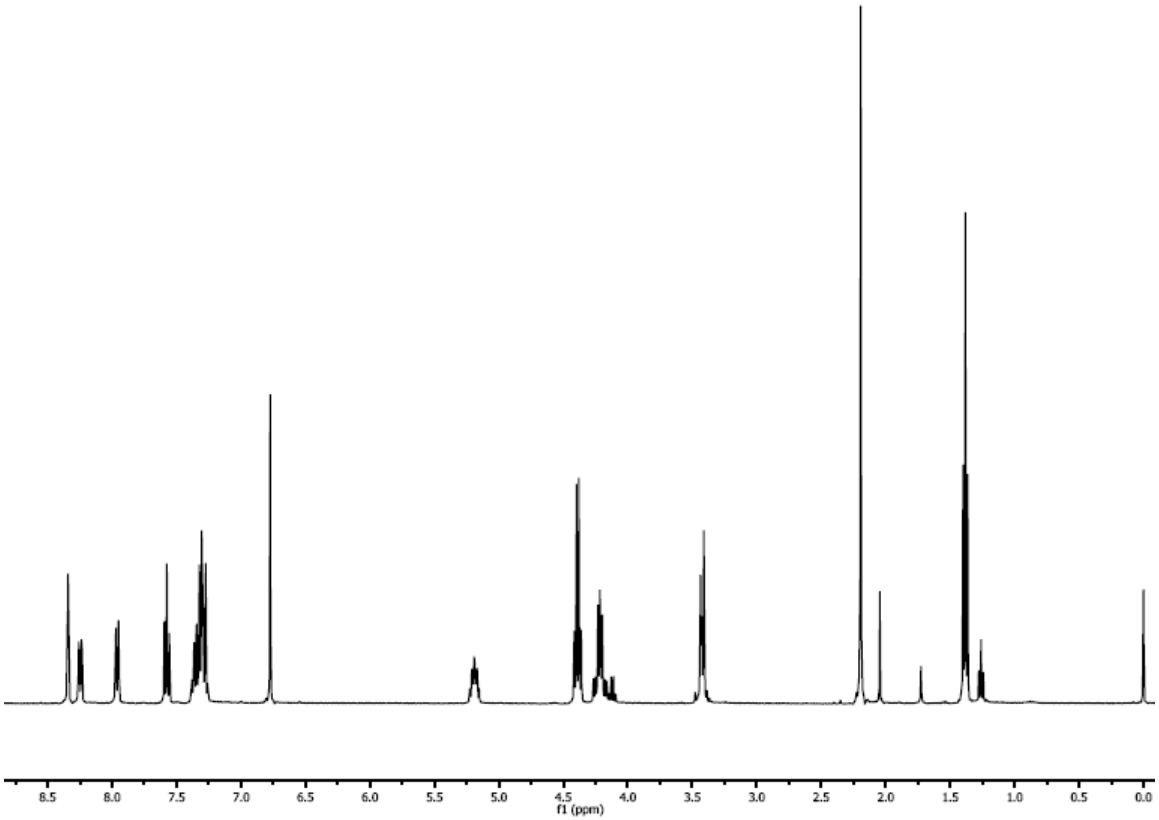

L-1-2
2: Diode Array
214
Range: 2.524
Area
Time Height Area Area%
21.81 128397 31314.17 1.92
22.33 2355283 1600613.13 98.08
22.33
1600613
21.81
31314
AU
Time

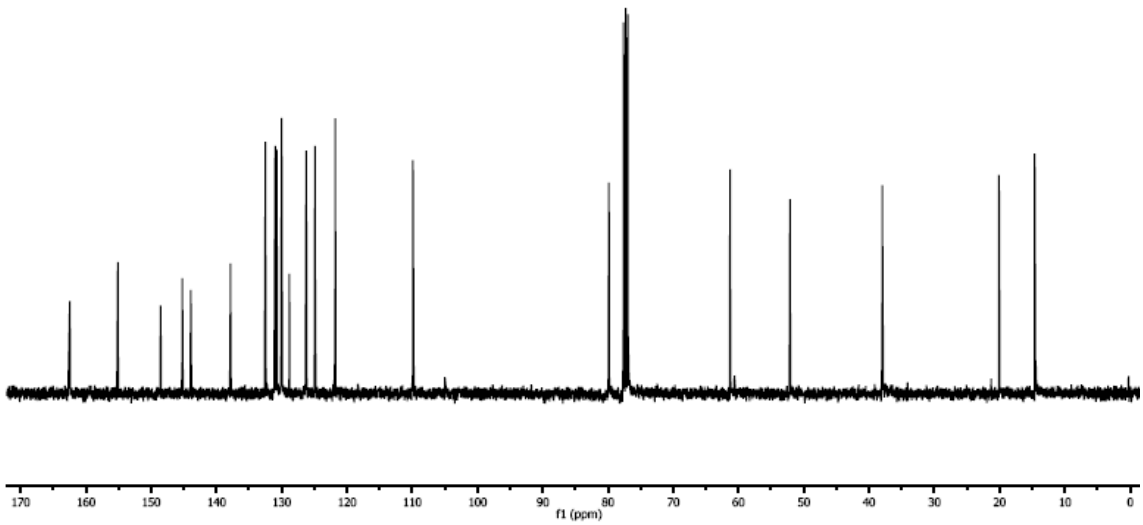

L-1-2 2257 (22.759)
1: Scan ES+
1.15e8
420.16
421.21
839.52
840.43
422.19
841.55
861.50
402.25
884.53
102.06
190.23
205.33
287.19
391.06
465.22
481.45
572.01
649.14
777.02
811.46
991.33
1078.18
1120.45
1258.85
1278.44
1410.80
1434.72
%
m/z

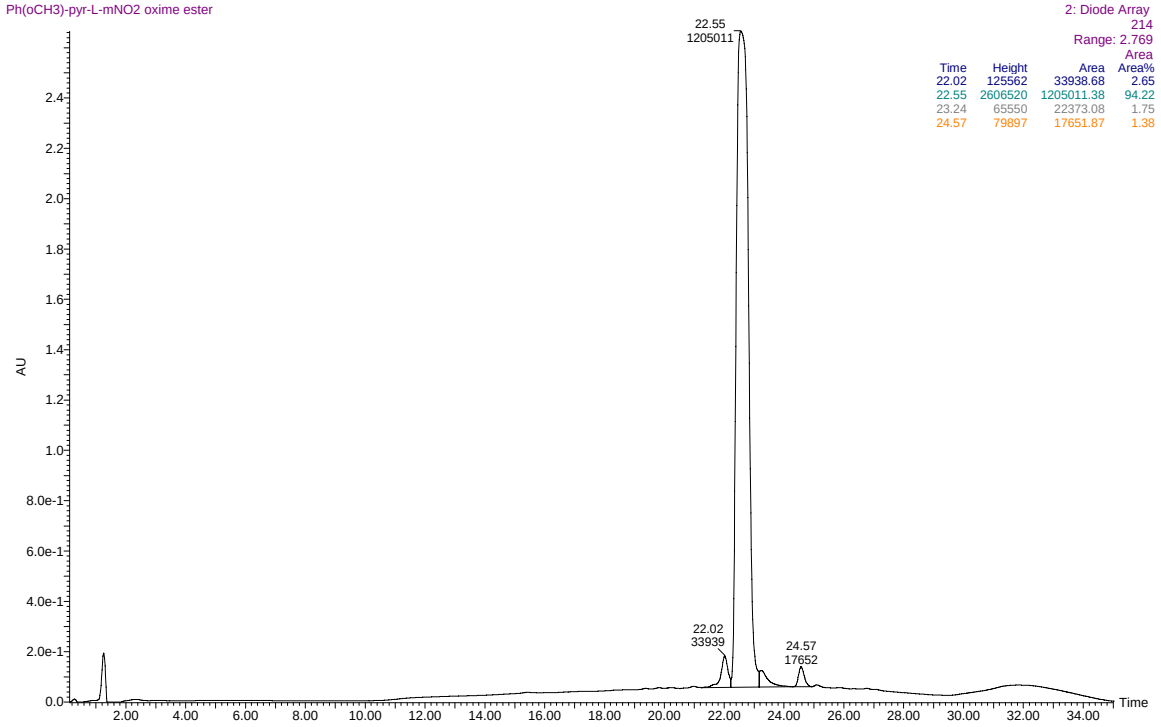
9{*2,3*}

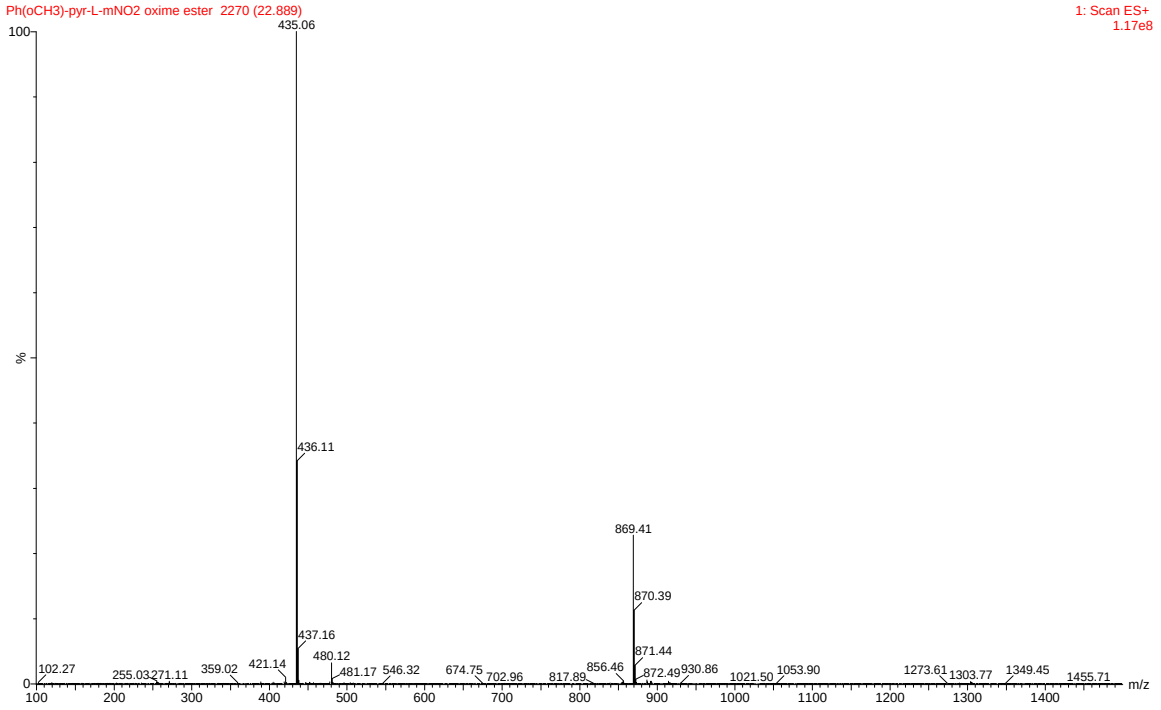


$C_{23}H_{22}N_4O_5$
Mol. Wt.: 434.44

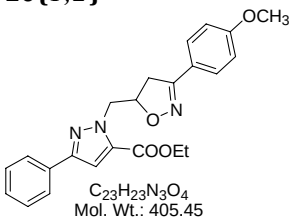




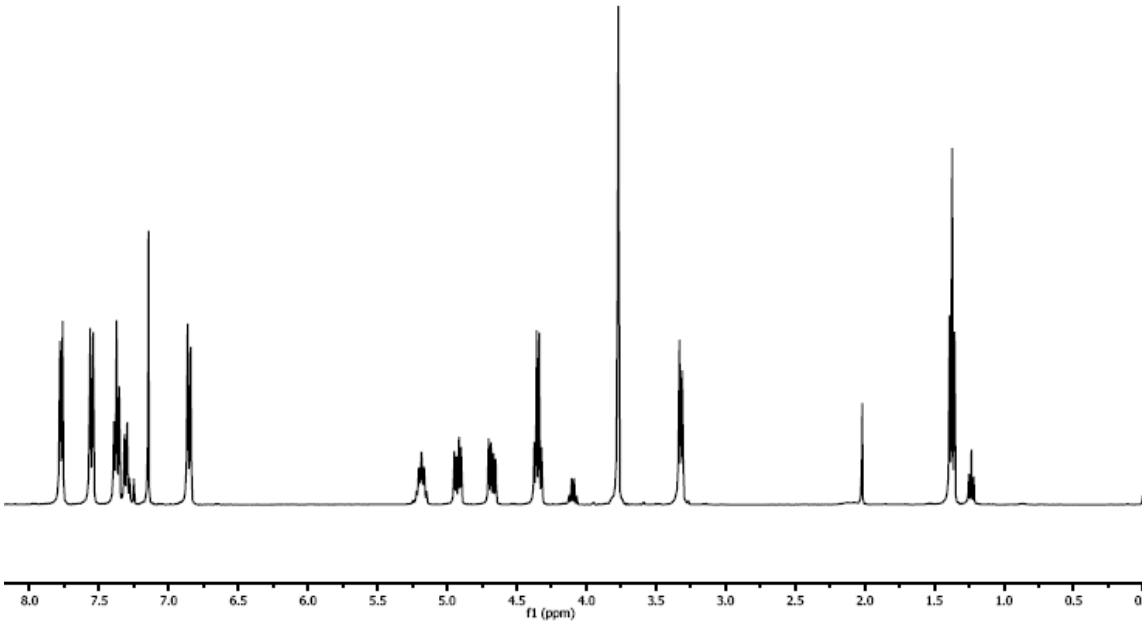

Ph(oCH3)-pyr-L-mNO2 oxime ester
2: Diode Array
214
Range: 2.769
Area
Time Height Area Area%
22.02 125562 33938.68 2.65
22.55 2606520 1205011.38 94.22
23.24 65550 22373.08 1.75
24.57 79897 17651.87 1.38
22.55
1205011
22.02
33939
24.57
17652
AU
Time

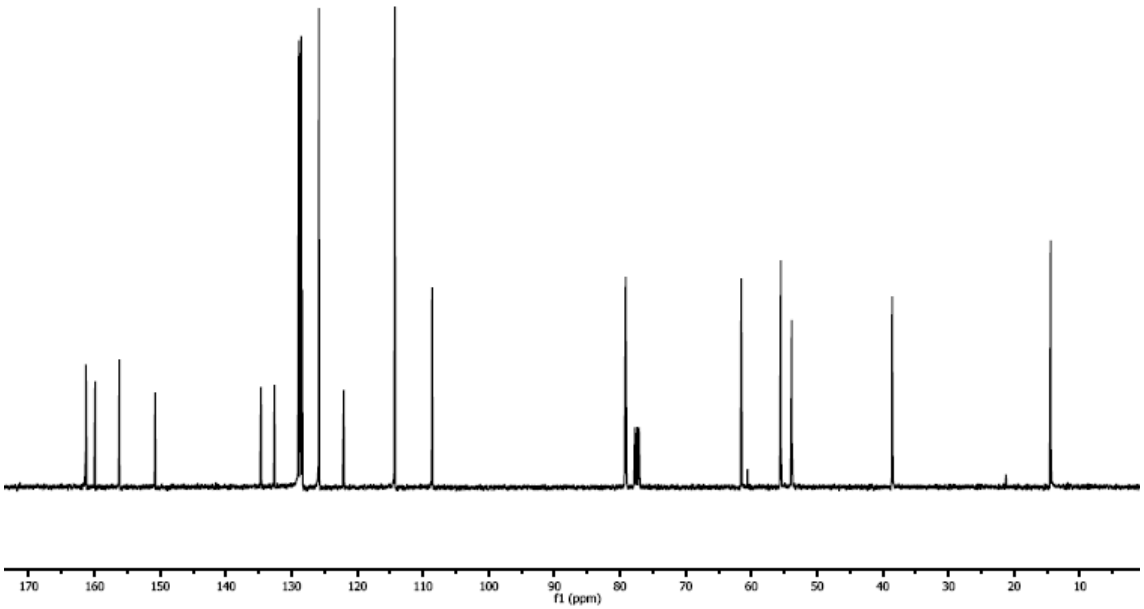

Ph(oCH3)-pyr-L-mNO2 oxime ester 2270 (22.889)
1: Scan ES+
1.17e8
435.06
436.11
869.41
870.39
437.16
480.12
871.44
102.27
255.03
271.11
359.02
421.14
481.17
546.32
674.75
702.96
817.89
856.46
872.49
930.86
1021.50
1053.90
1273.61
1303.77
1349.45
1455.71
%
m/z

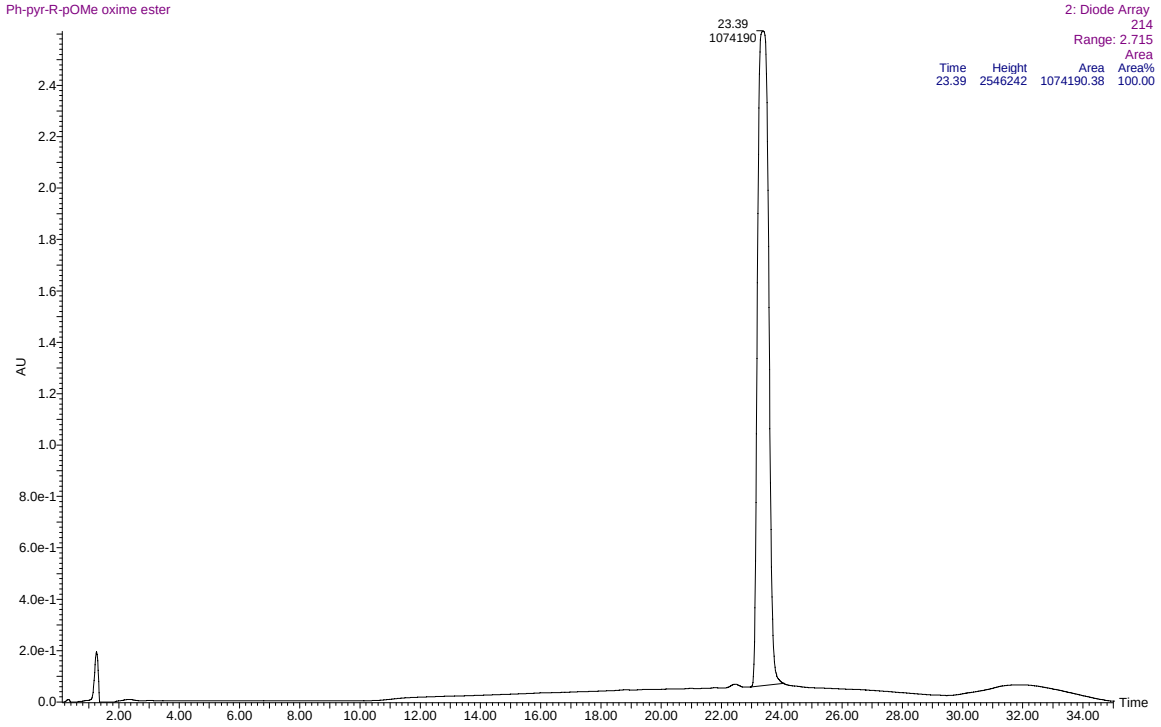
10{*1,2*}

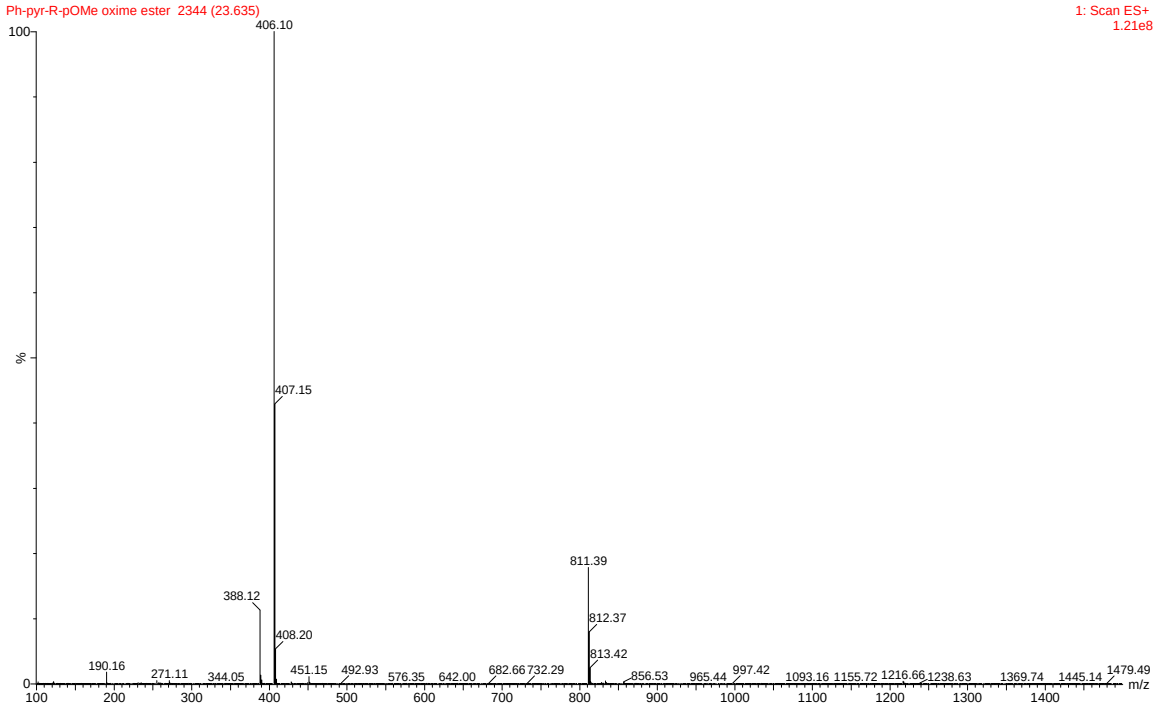


$C_{23}H_{23}N_3O_4$
Mol. Wt.: 405.45

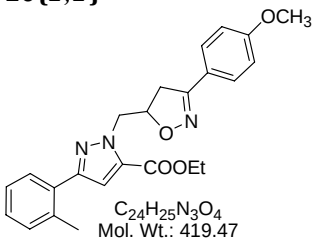




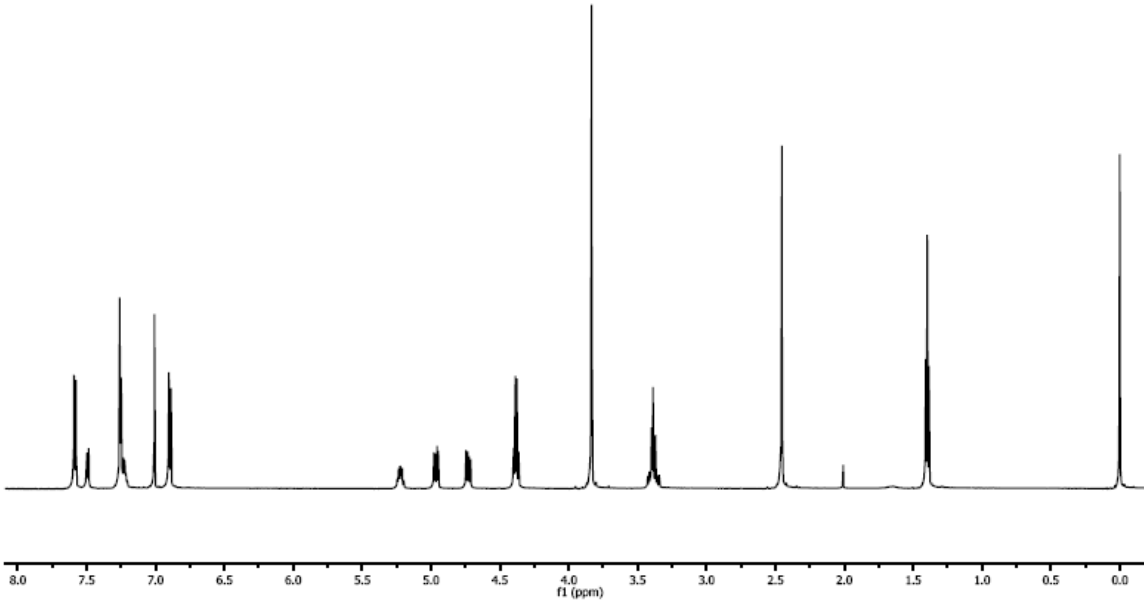

Ph-pyr-R-pOMe oxime ester
2: Diode Array
214
Range: 2.715
Area
Time Height Area Area%
23.39 2546242 1074190.38 100.00
23.39
1074190
AU
Time

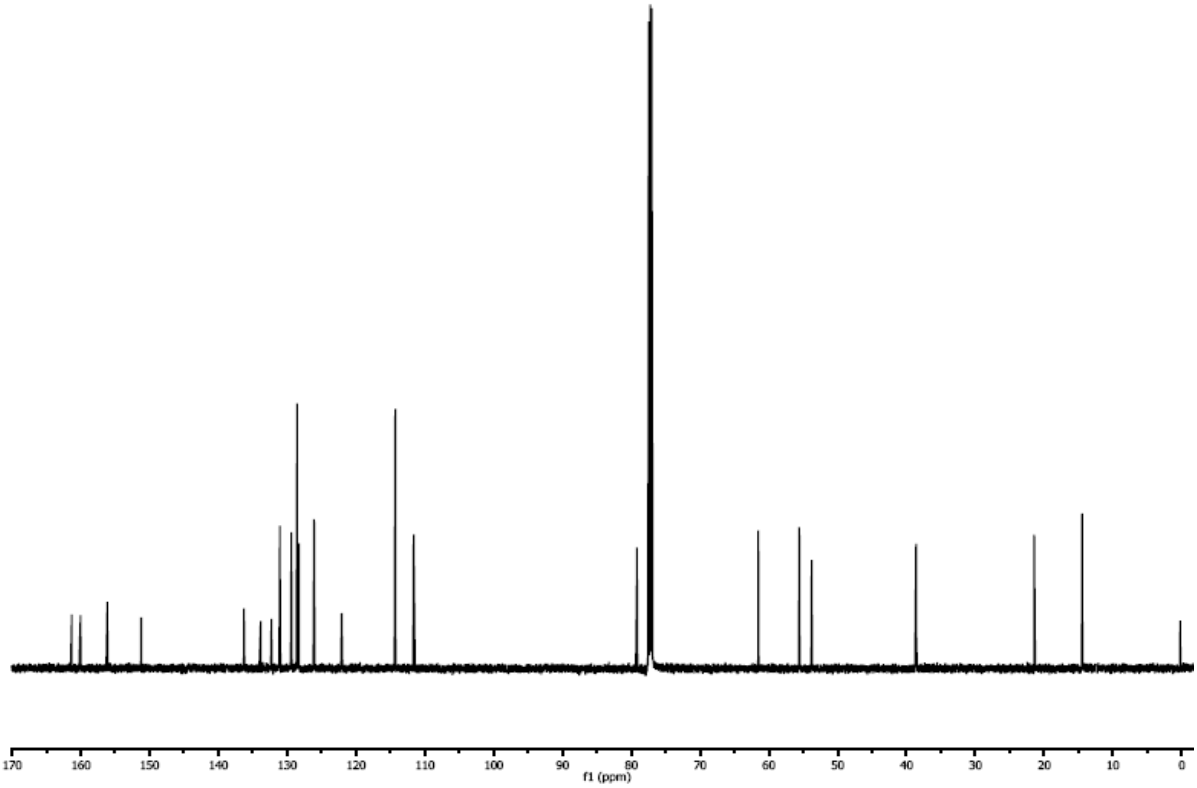

Ph-pyr-R-pOMe oxime ester 2344 (23.635)
1: Scan ES+
1.21e8
406.10
407.15
811.39
388.12
812.37
408.20
813.42
190.16
271.11
344.05
451.15
492.93
576.35
642.00
682.66
732.29
856.53
965.44
997.42
1093.16
1155.72
1216.66
1238.63
1369.74
1445.14
1479.49
%
m/z

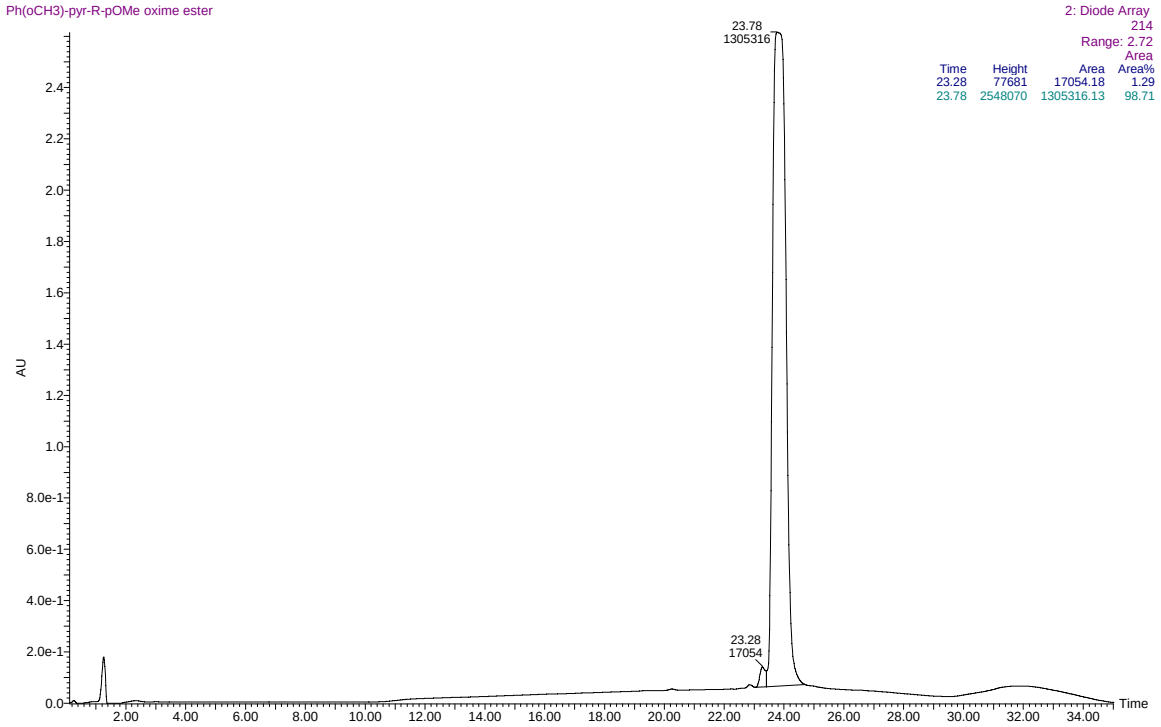
10{*2,2*}

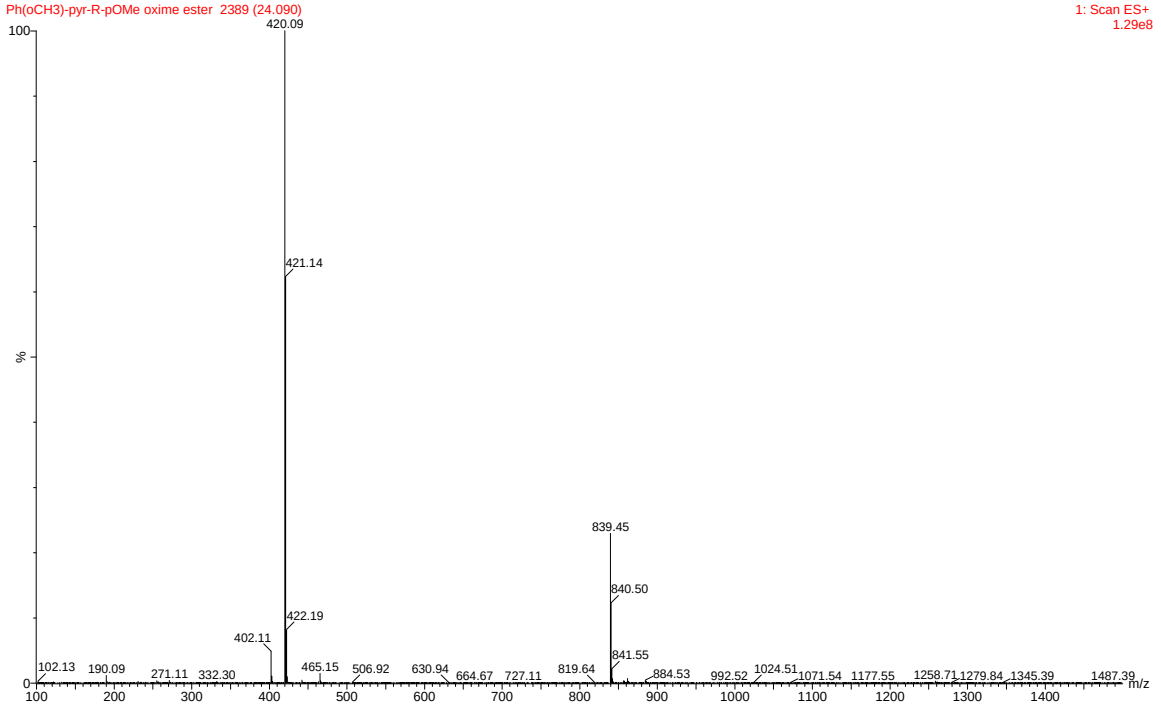


$C_{24}H_{25}N_3O_4$
Mol. Wt.: 419.47

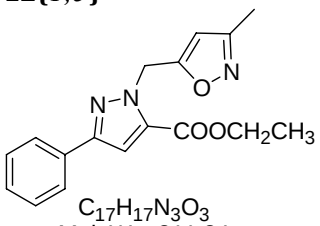




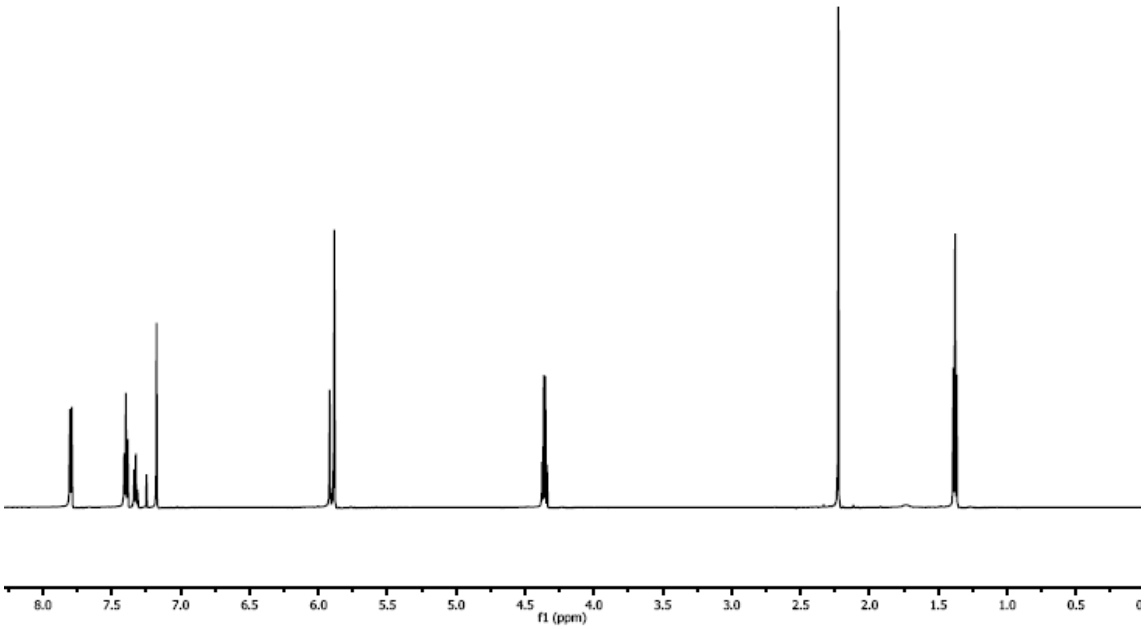

Ph(oCH3)-pyr-R-pOMe oxime ester
2: Diode Array
214
Range: 2.72
Area
Time Height Area Area%
23.28 77681 17054.18 1.29
23.78 2548070 1305316.13 98.71
23.78
1305316
23.28
17054
AU
Time

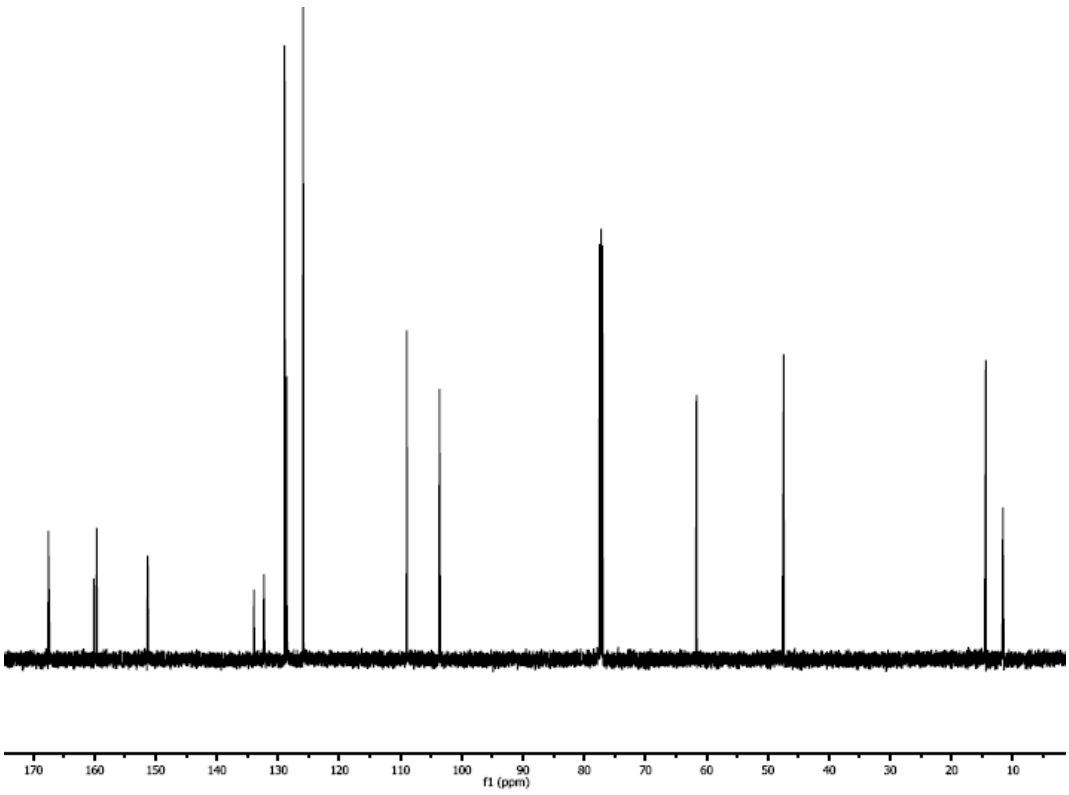

Ph(oCH3)-pyr-R-pOMe oxime ester 2389 (24.090)
1: Scan ES+
1.29e8
420.09
421.14
422.19
402.11
839.45
840.50
841.55
%
m/z

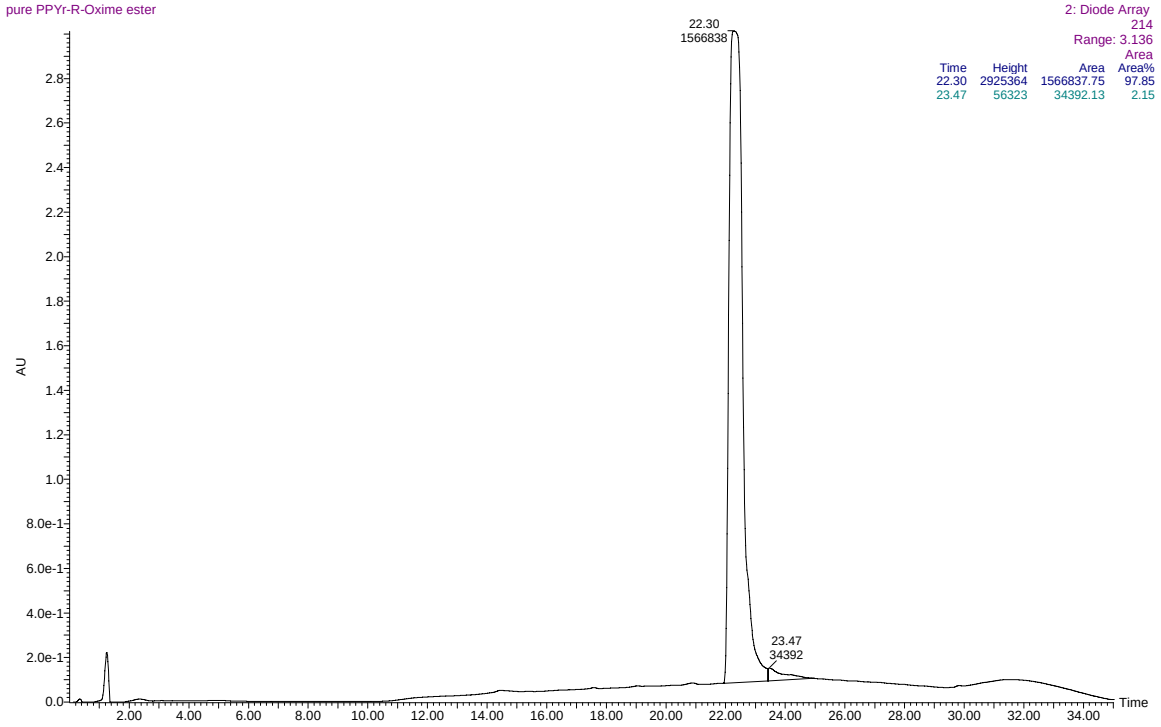
12{*1,5*}

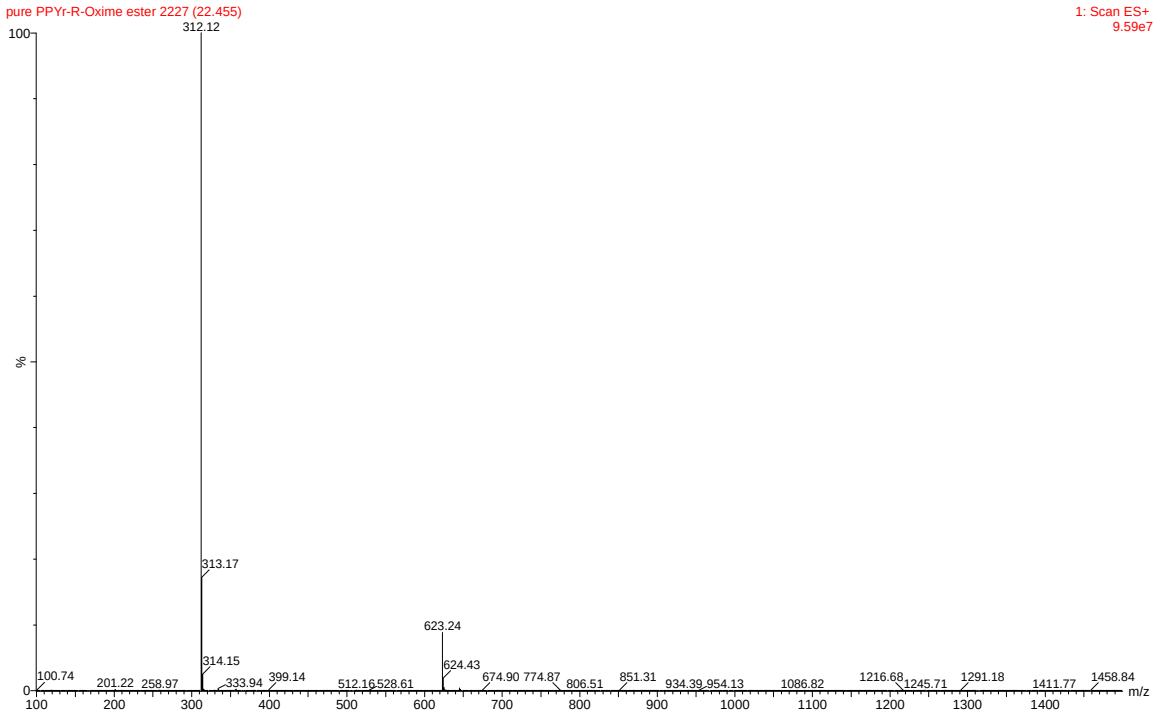


$C_{17}H_{17}N_3O_3$
Mol. Wt.: 311.34

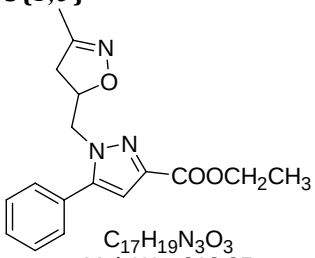




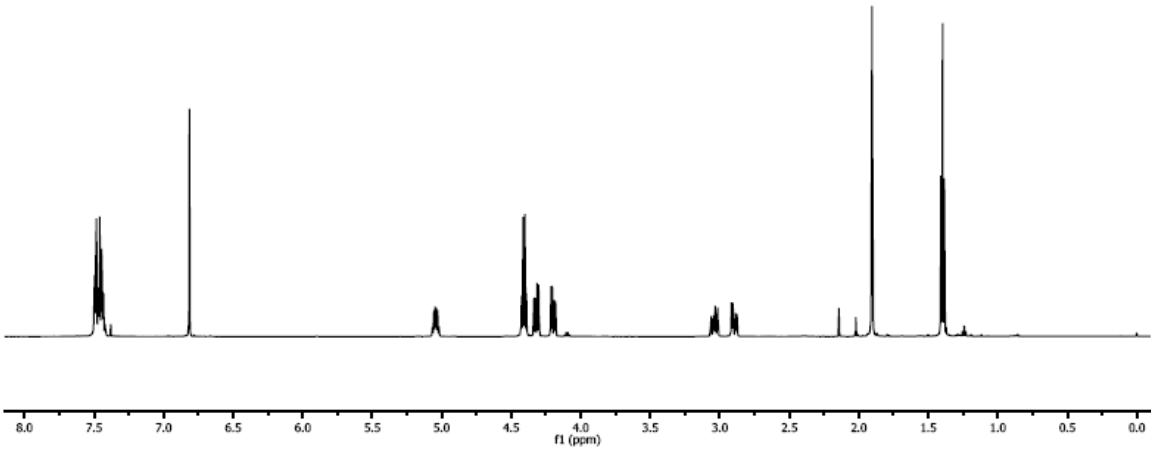

pure PPYr-R-Oxime ester
2: Diode Array
214
Range: 3.136
Area
Time Height Area Area%
22.30 2925364 1566837.75 97.85
23.47 56323 34392.13 2.15
22.30
1566838
23.47
34392
AU
Time

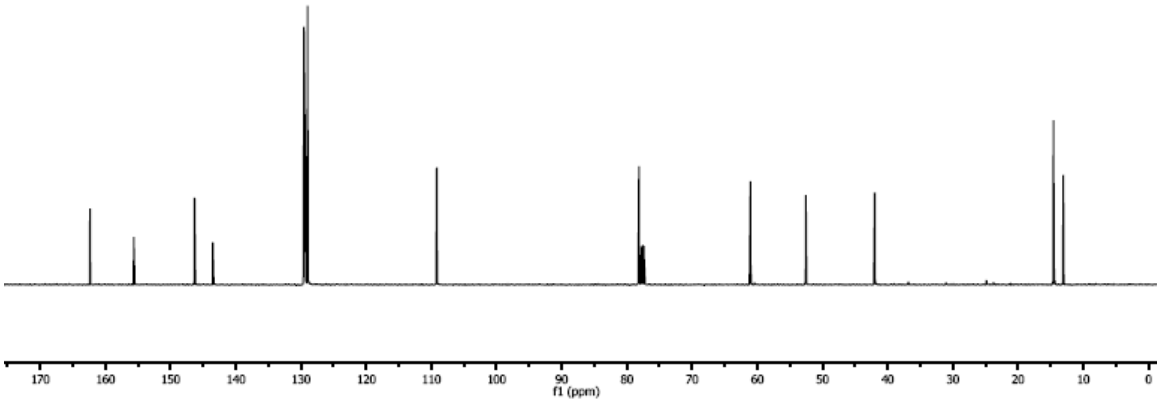

pure PPYr-R-Oxime ester 2227 (22.455)
1: Scan ES+
9.59e7
312.12
313.17
314.15
623.24
624.43
%
m/z

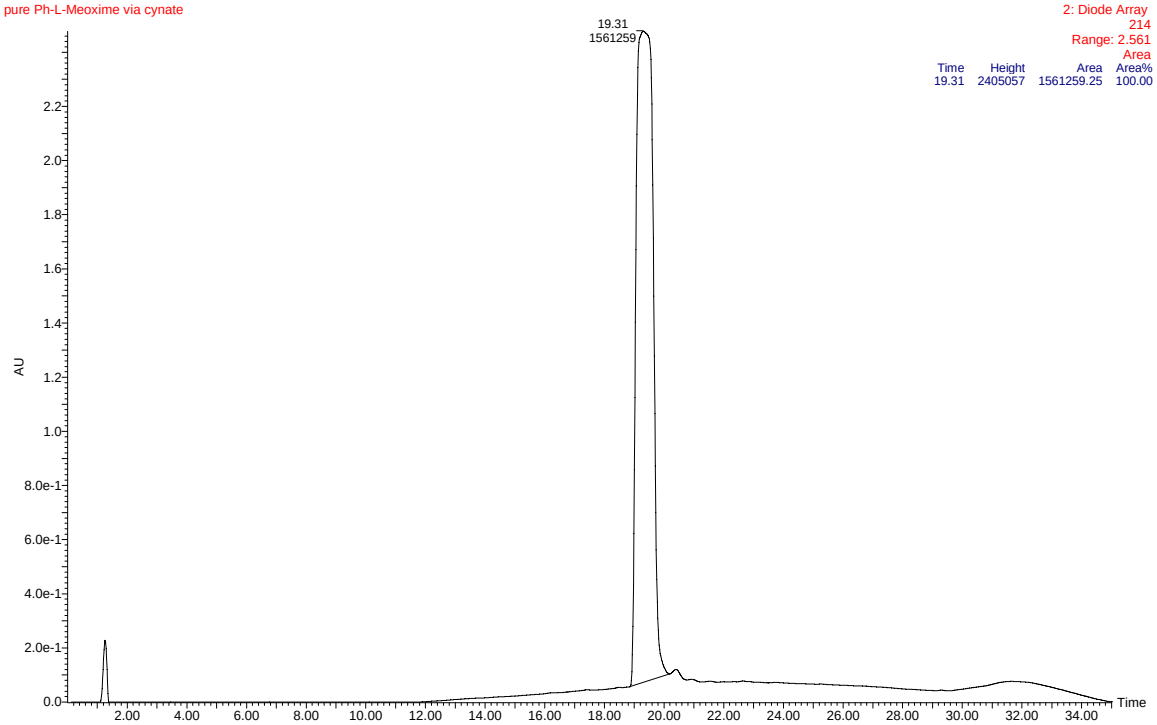
9{*1,5*}

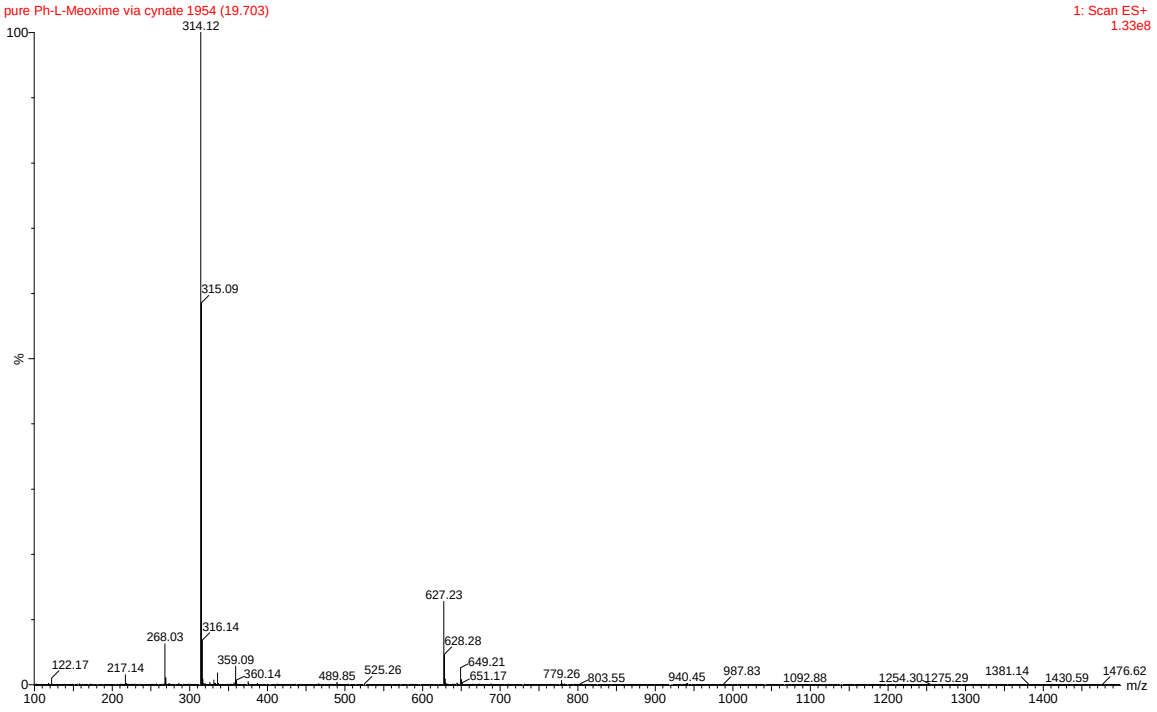


$C_{17}H_{19}N_3O_3$
Mol. Wt.: 313.35

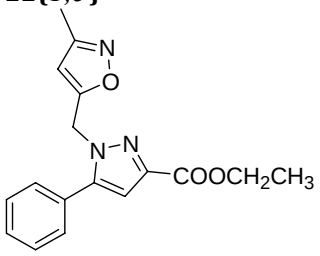




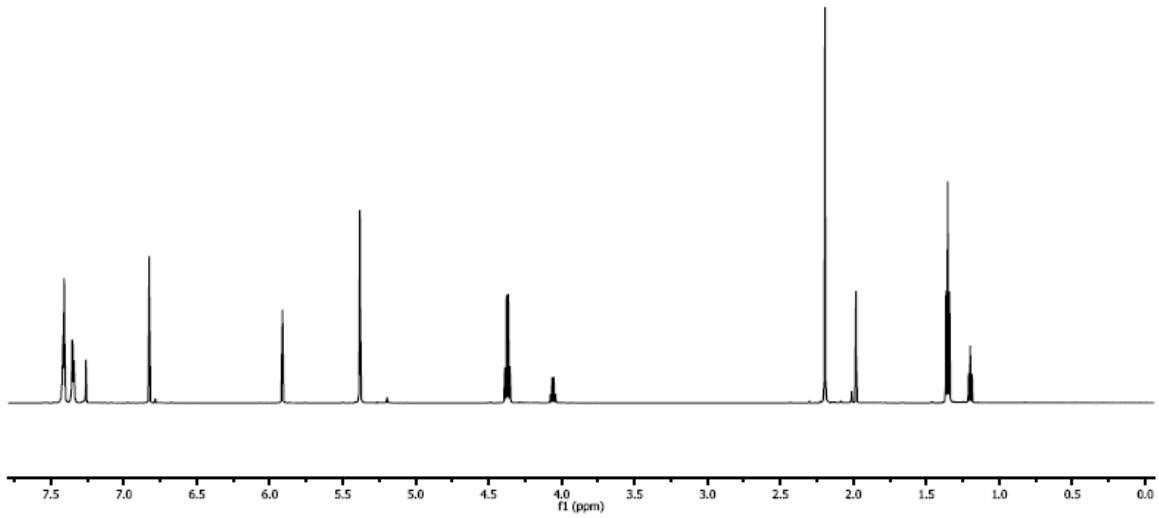

pure Ph-L-Meoxime via cynate
2: Diode Array
214
Range: 2.561
Area
Time Height Area Area%
19.31 2405057 1561259.25 100.00
19.31
1561259
AU
Time

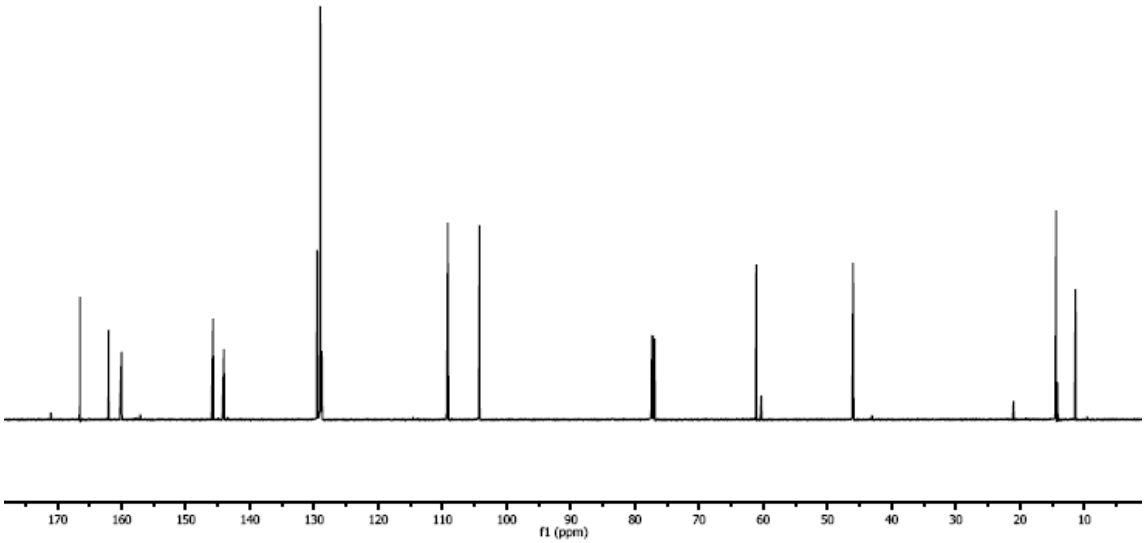

pure Ph-L-Meoxime via cynate 1954 (19.703)
1: Scan ES+
1.33e8
%
m/z
314.12
315.09
316.14
627.23
628.28
268.03
122.17
217.14
359.09
360.14
649.21
651.17
489.85
525.26
779.26
803.55
940.45
987.83
1092.88
1254.30
1275.29
1381.14
1430.59
1476.62

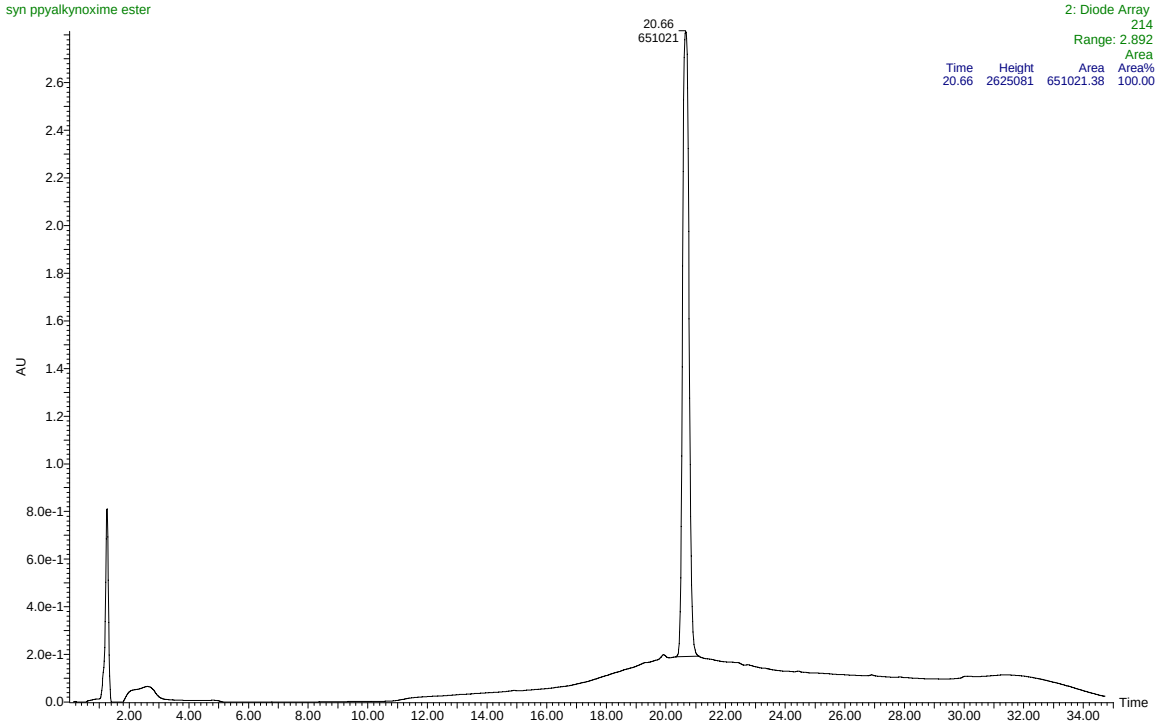
11{*1,5*}

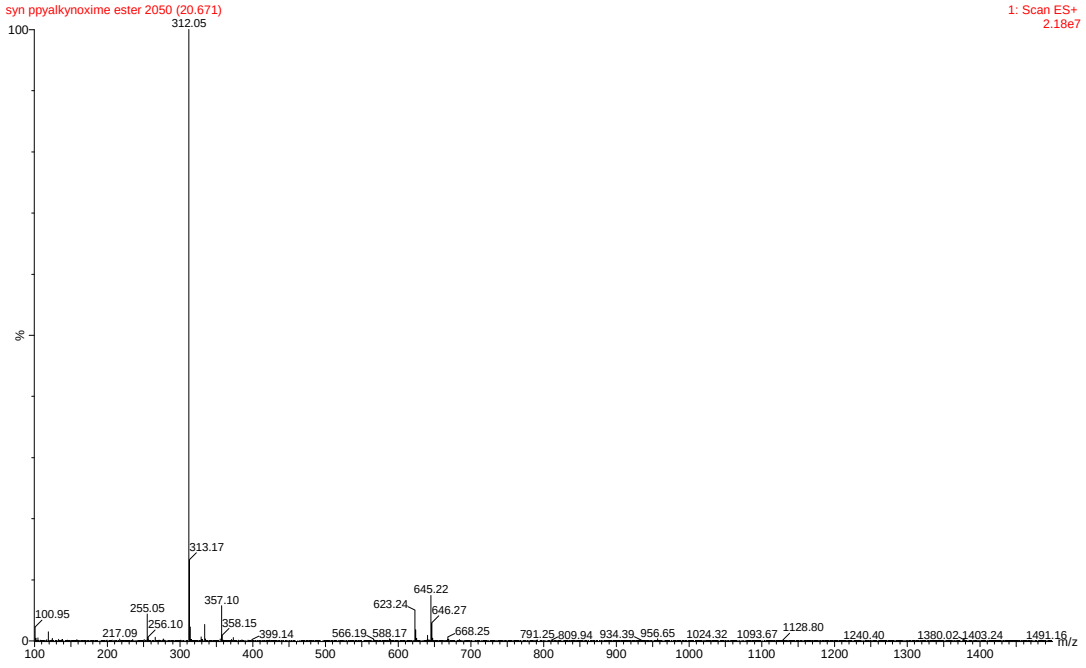


$C_{17}H_{17}N_3O_3$
Mol. Wt.: 311.34

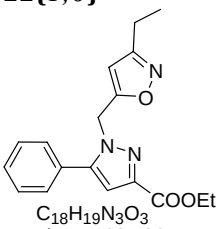




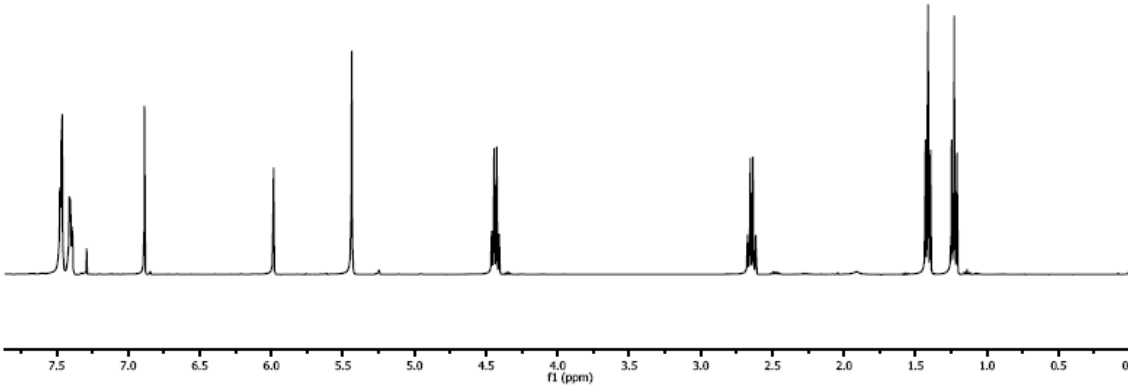

syn ppyalkynoxime ester
2: Diode Array
214
Range: 2.892
Area
Time Height Area Area%
20.66 2625081 651021.38 100.00
20.66
651021
AU
Time

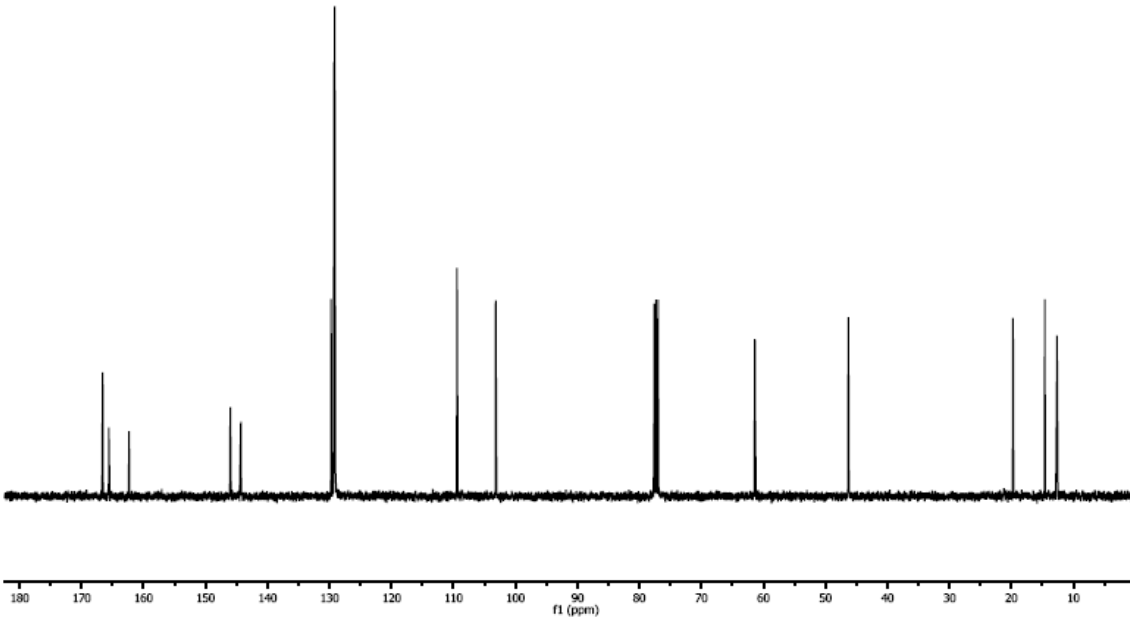

syn ppyalkynoxime ester 2050 (20.671)
1: Scan ES+
2.18e7
312.05
313.17
645.22
623.24
646.27
357.10
255.05
100.95
256.10
358.15
217.09
399.14
566.19
588.17
668.25
791.25
809.94
934.39
956.65
1024.32
1093.67
1128.80
1240.40
1380.02
1403.24
1491.16
%
m/z

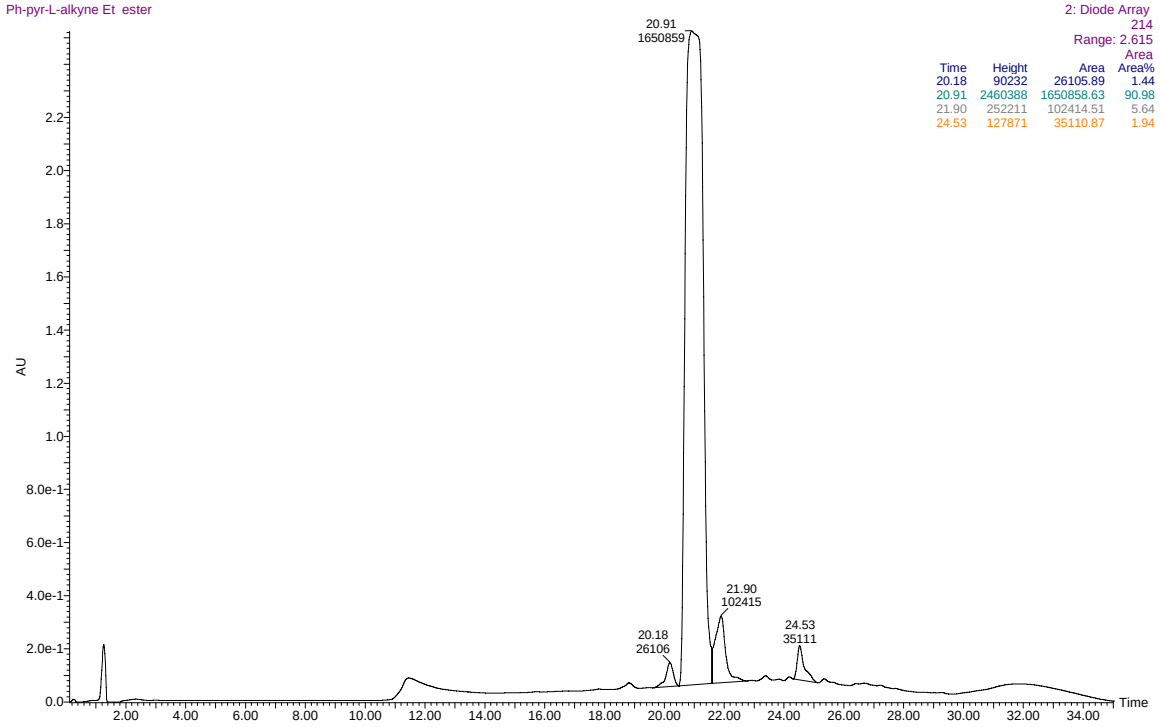
11{*1,6*}

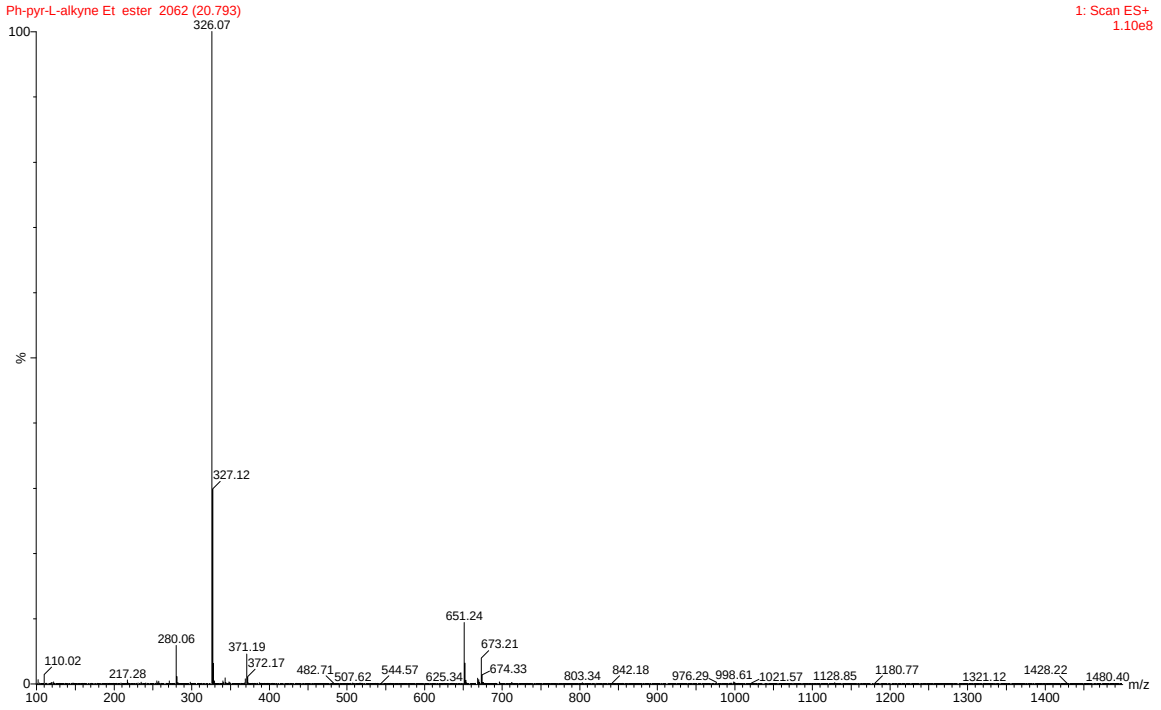


$C_{18}H_{19}N_3O_3$
Mol. Wt.: 325.36

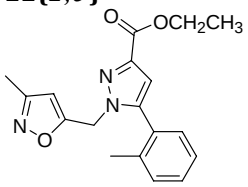




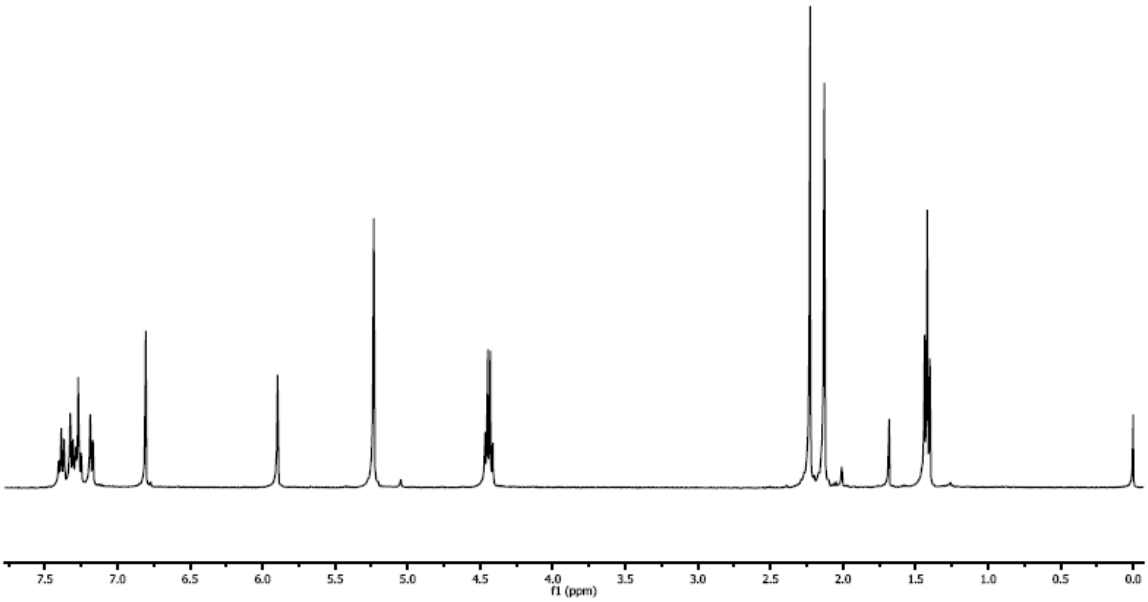

Ph-pyr-L-alkyne Et ester
2: Diode Array
214
Range: 2.615
Area
Time Height Area Area%
20.18 90232 26105.89 1.44
20.91 2460388 1650858.63 90.98
21.90 252211 102414.51 5.64
24.53 127871 35110.87 1.94
20.91
1650859
21.90
102415
24.53
35111
20.18
26106
AU
Time

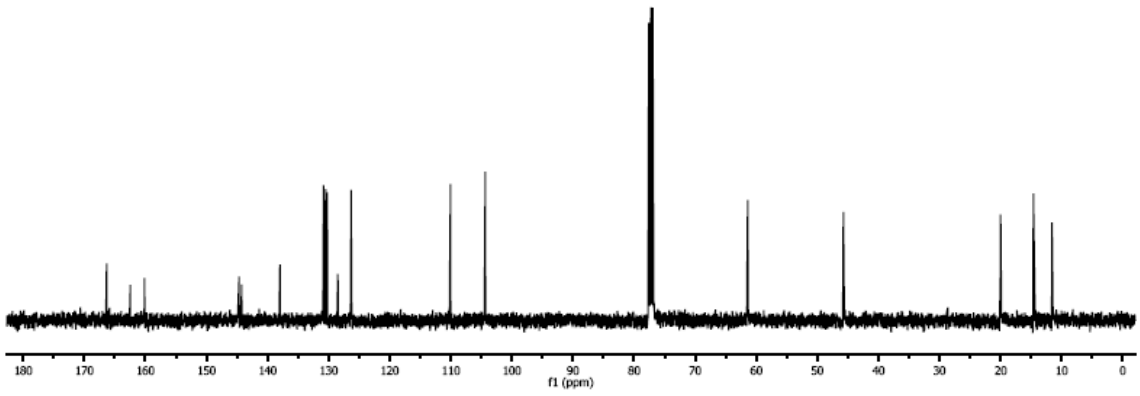

Ph-pyr-L-alkyne Et ester 2062 (20.793)
1: Scan ES+
1.10e8
326.07
327.12
651.24
280.06
673.21
371.19
372.17
110.02
217.28
482.71
507.62
544.57
625.34
674.33
803.34
842.18
976.29
998.61
1021.57
1128.85
1180.77
1321.12
1428.22
1480.40
%
m/z

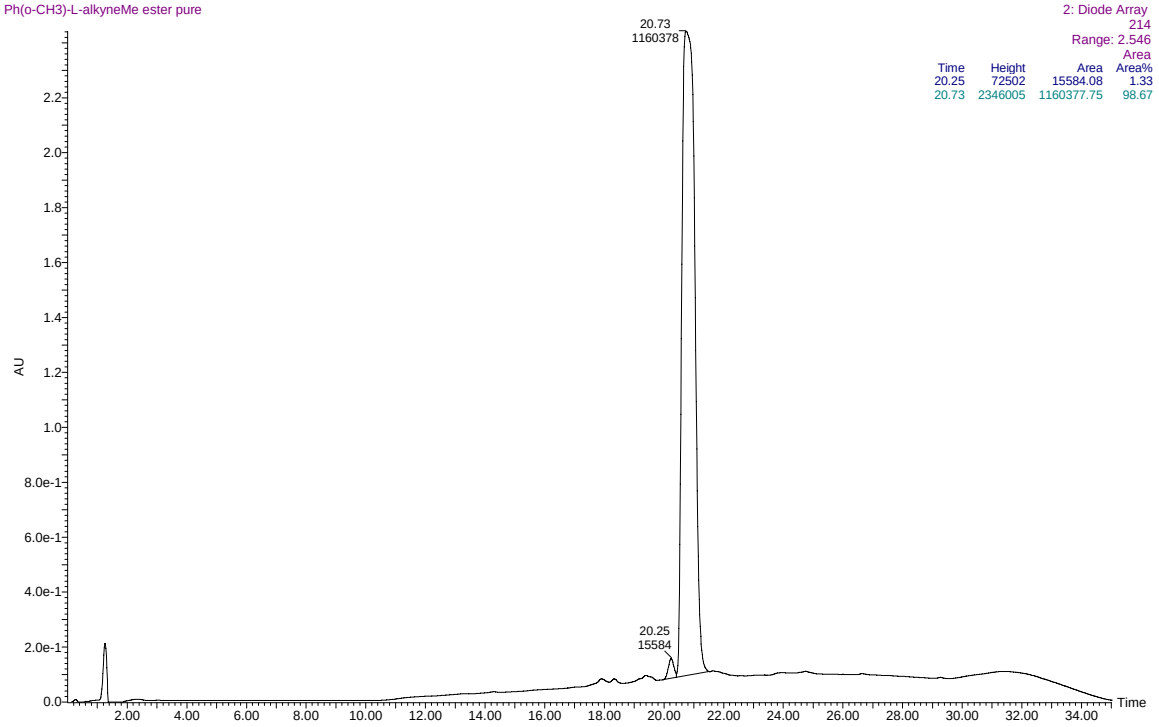
11{*2,5*}

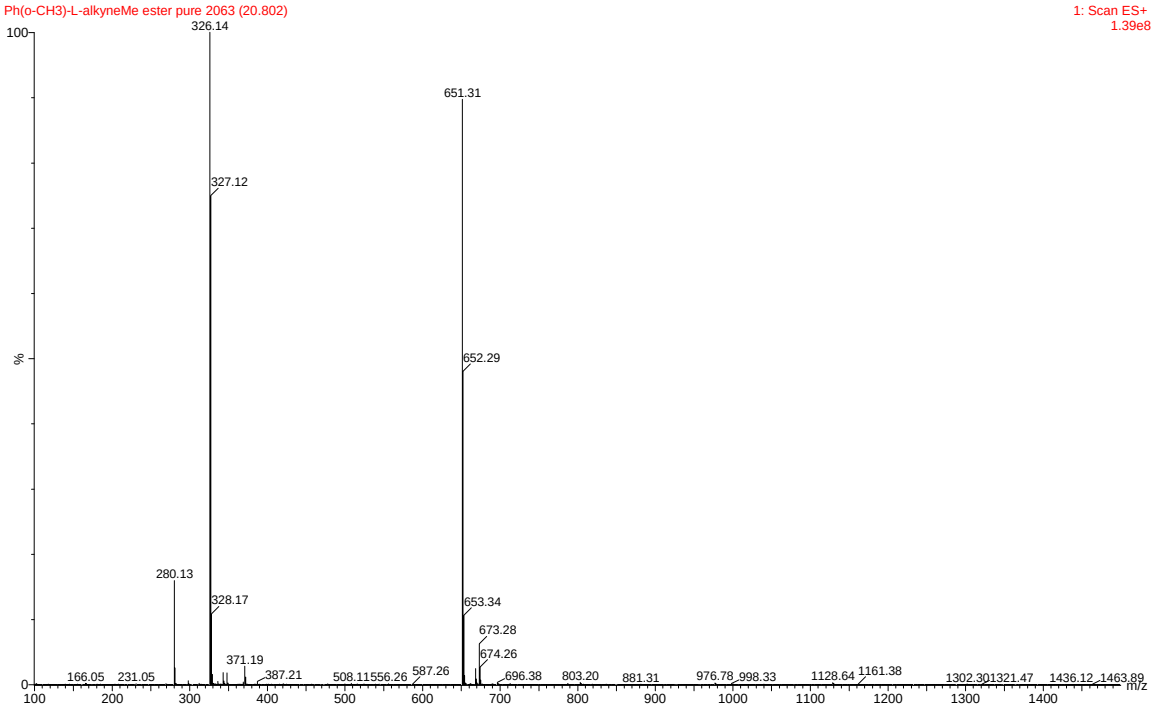


$C_{18}H_{19}N_3O_3$
Mol. Wt.: 325.36

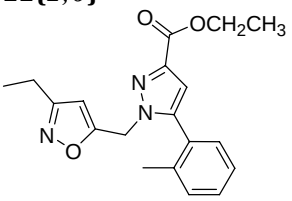




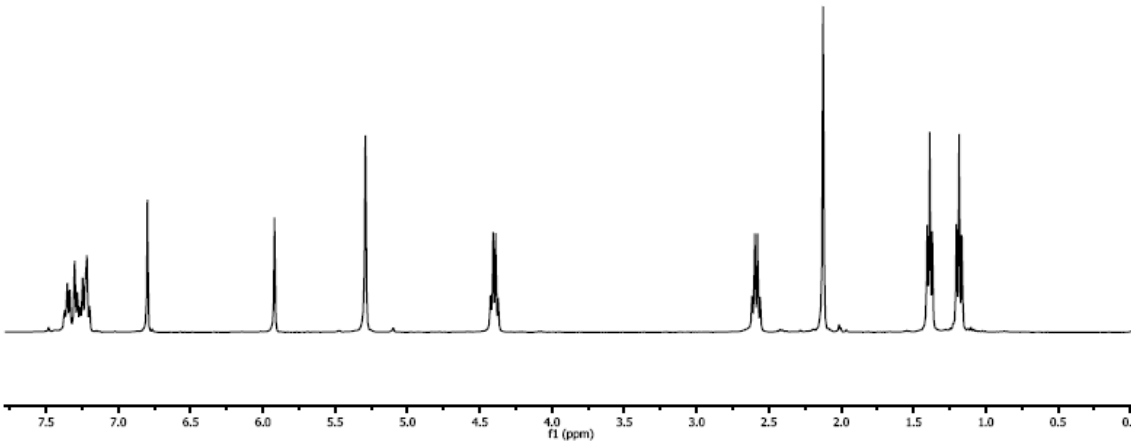

Ph(o-CH3)-L-alkyneMe ester pure
2: Diode Array
214
Range: 2.546
Area
Time Height Area Area%
20.25 72502 15584.08 1.33
20.73 2346005 1160377.75 98.67
20.73
1160378
20.25
15584
AU
Time

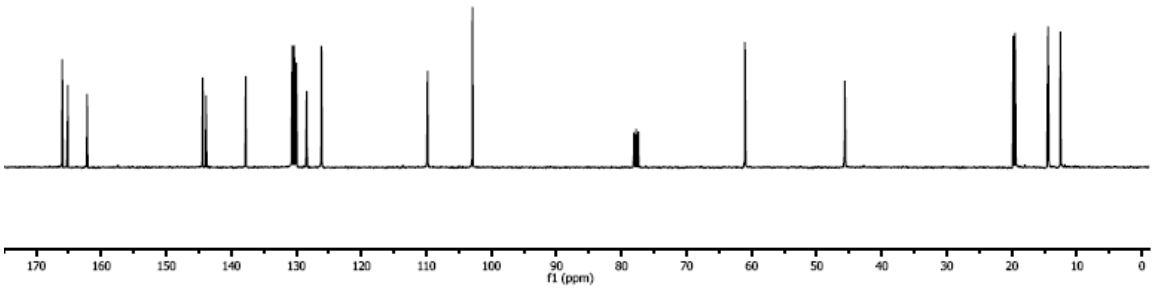

Ph(o-CH3)-L-alkyneMe ester pure 2063 (20.802)
1: Scan ES+
1.39e8
326.14
651.31
327.12
652.29
280.13
328.17
653.34
673.28
674.26
371.19
%
m/z

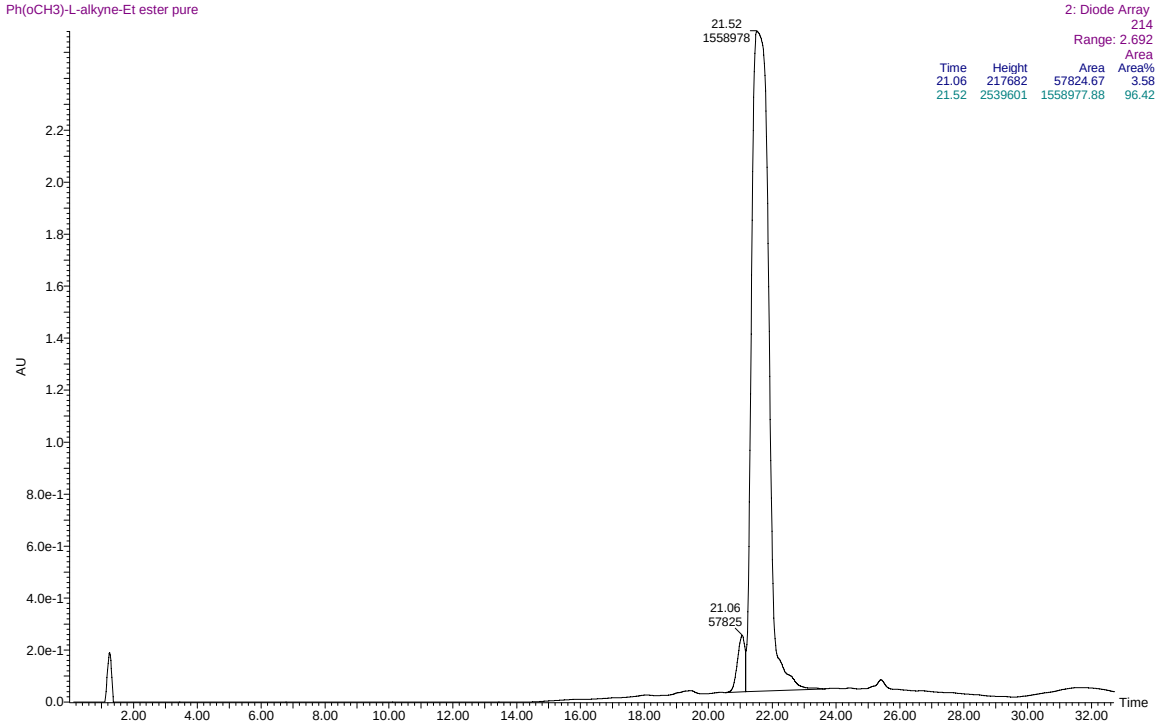
11{*2,6*}

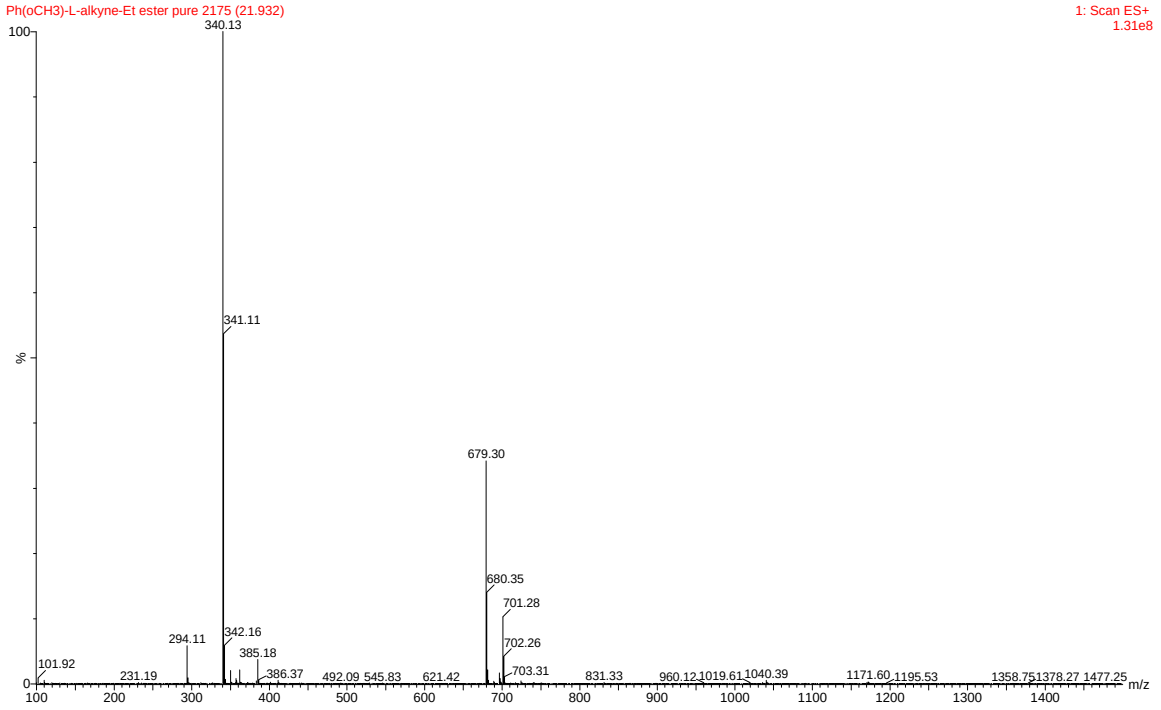


$C_{19}H_{21}N_3O_3$
Mol. Wt.: 339.39

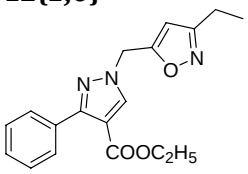




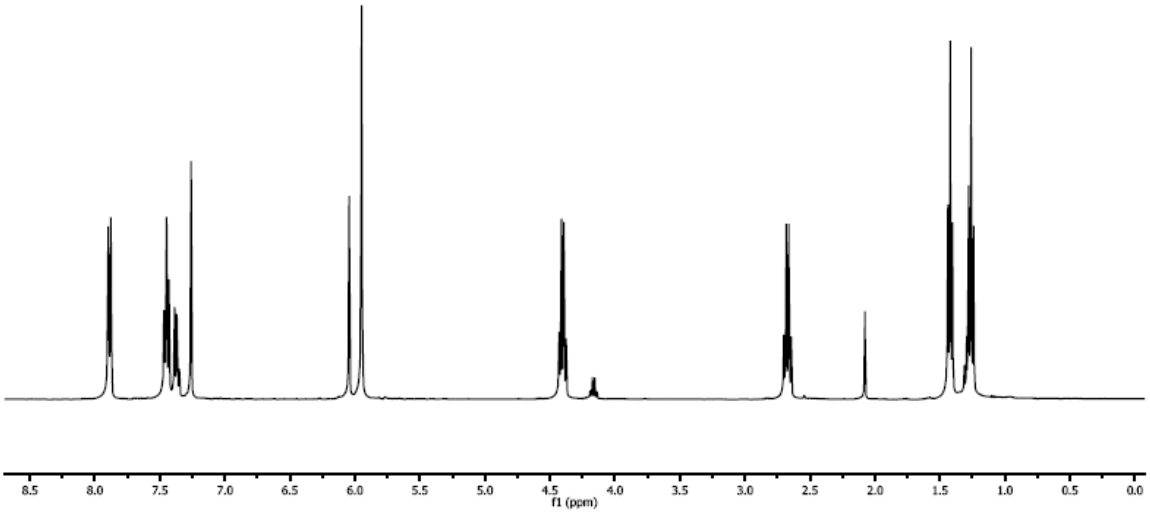

Ph(oCH3)-L-alkyne-Et ester pure
2: Diode Array
214
Range: 2.692
Area
Time Height Area Area%
21.06 217682 57824.67 3.58
21.52 2539601 1558977.88 96.42
21.52
1558978
21.06
57825
AU
Time

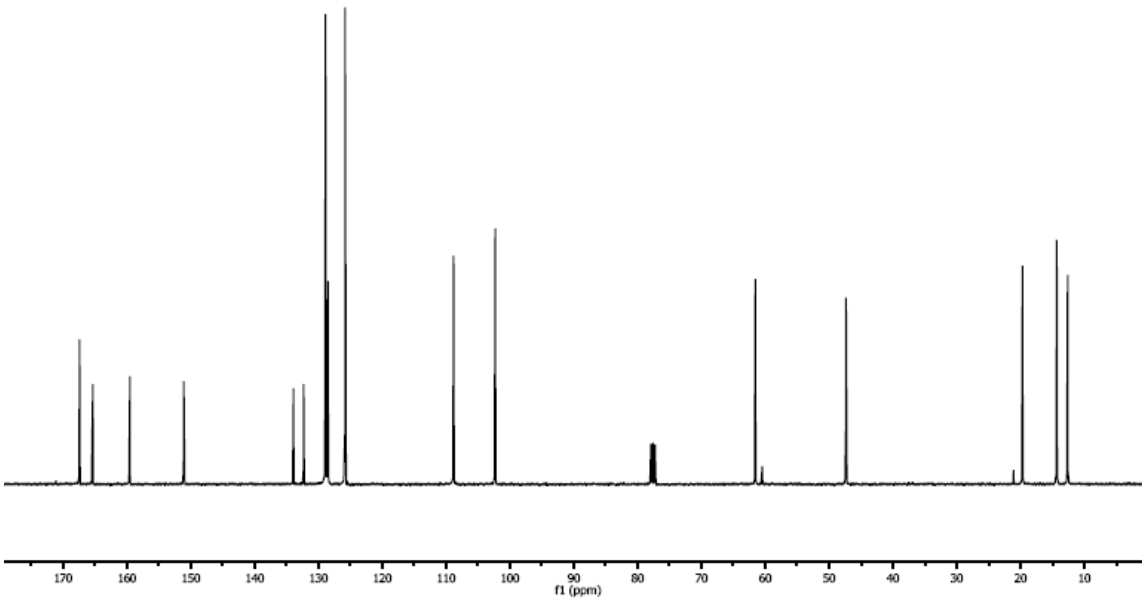

Ph(oCH3)-L-alkyne-Et ester pure 2175 (21.932)
1: Scan ES+
1.31e8
340.13
341.11
679.30
680.35
701.28
702.26
703.31
294.11
342.16
385.18
101.92
231.19
386.37
492.09
545.83
621.42
831.33
960.12
1019.61
1040.39
1171.60
1195.53
1358.75
1378.27
1477.25
%
m/z

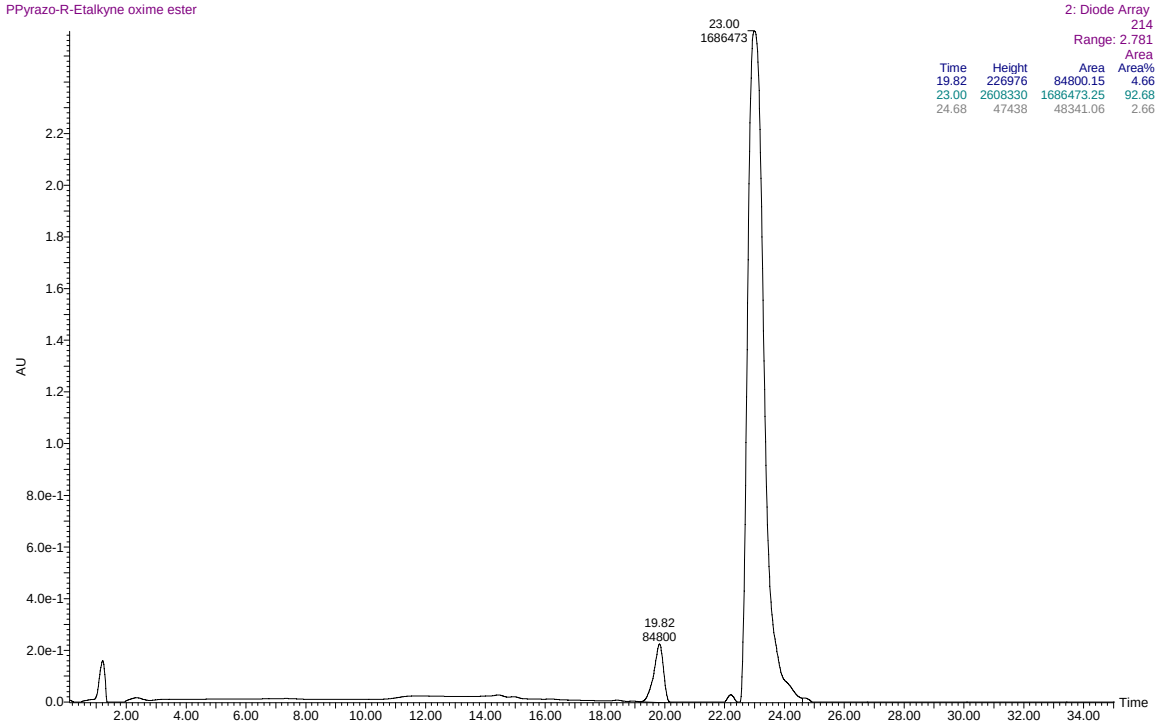
12{*1,6*}

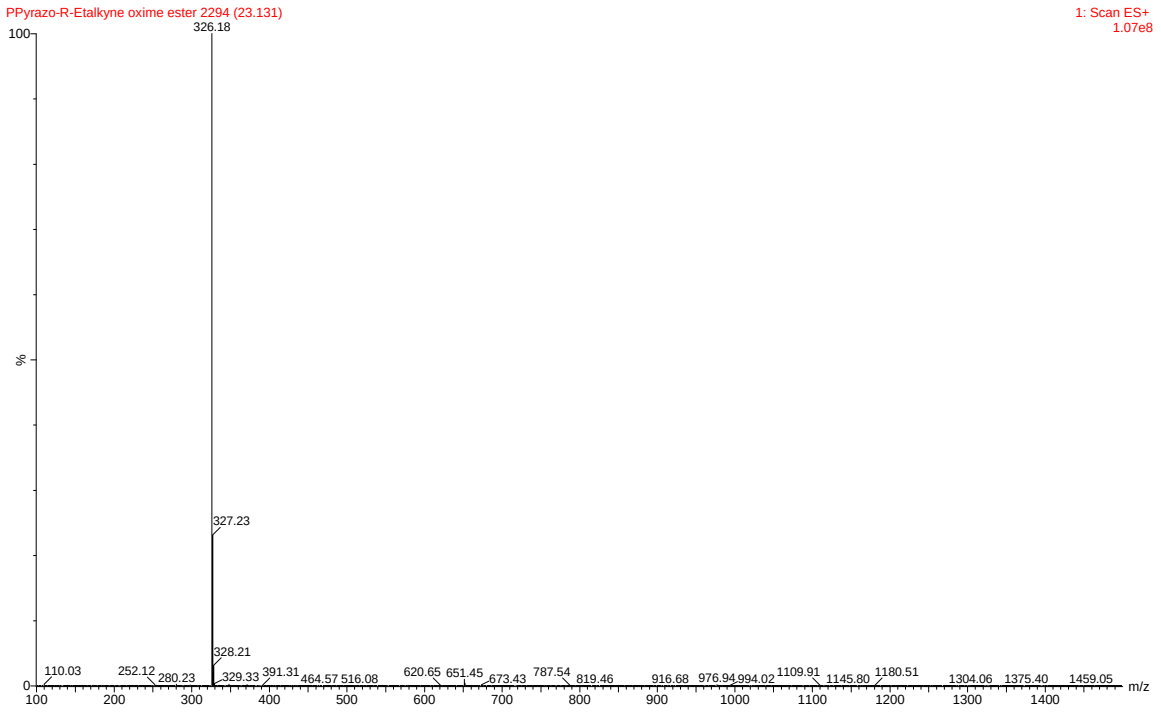


$C_{18}H_{19}N_3O_3$
Mol. Wt.: 325.36

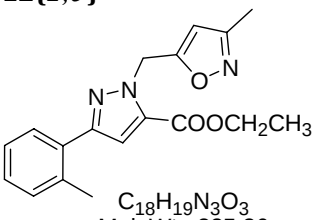




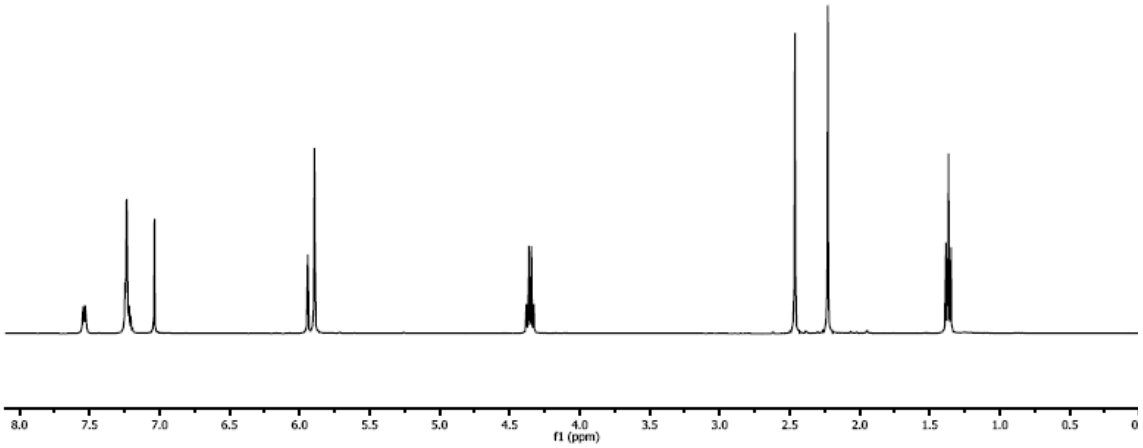

PPyrazo-R-Etalkyne oxime ester
2: Diode Array
214
Range: 2.781
Area
Time Height Area Area%
19.82 226976 84800.15 4.66
23.00 2608330 1686473.25 92.68
24.68 47438 48341.06 2.66
23.00
1686473
19.82
84800
AU
Time

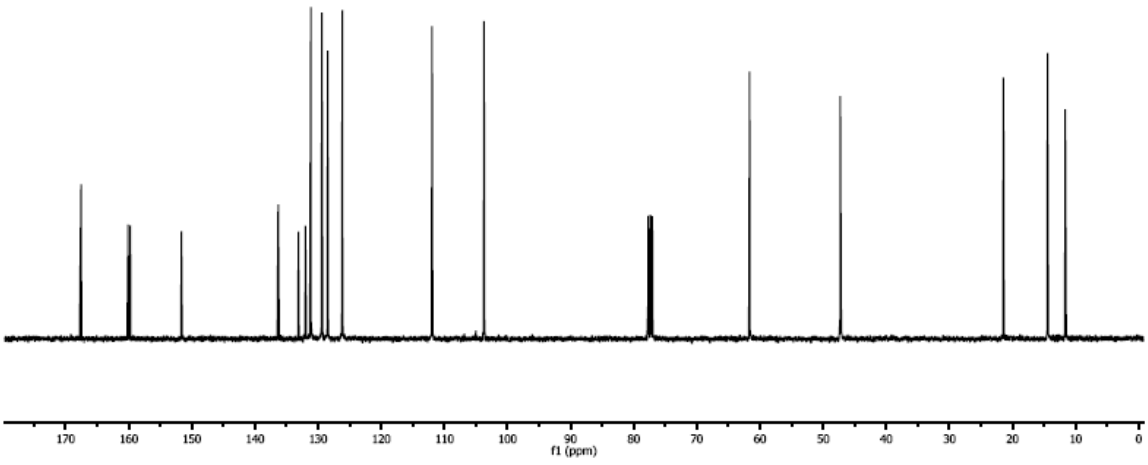

PPyrazo-R-Etalkyne oxime ester 2294 (23.131)
1: Scan ES+
1.07e8
326.18
327.23
328.21
%
m/z

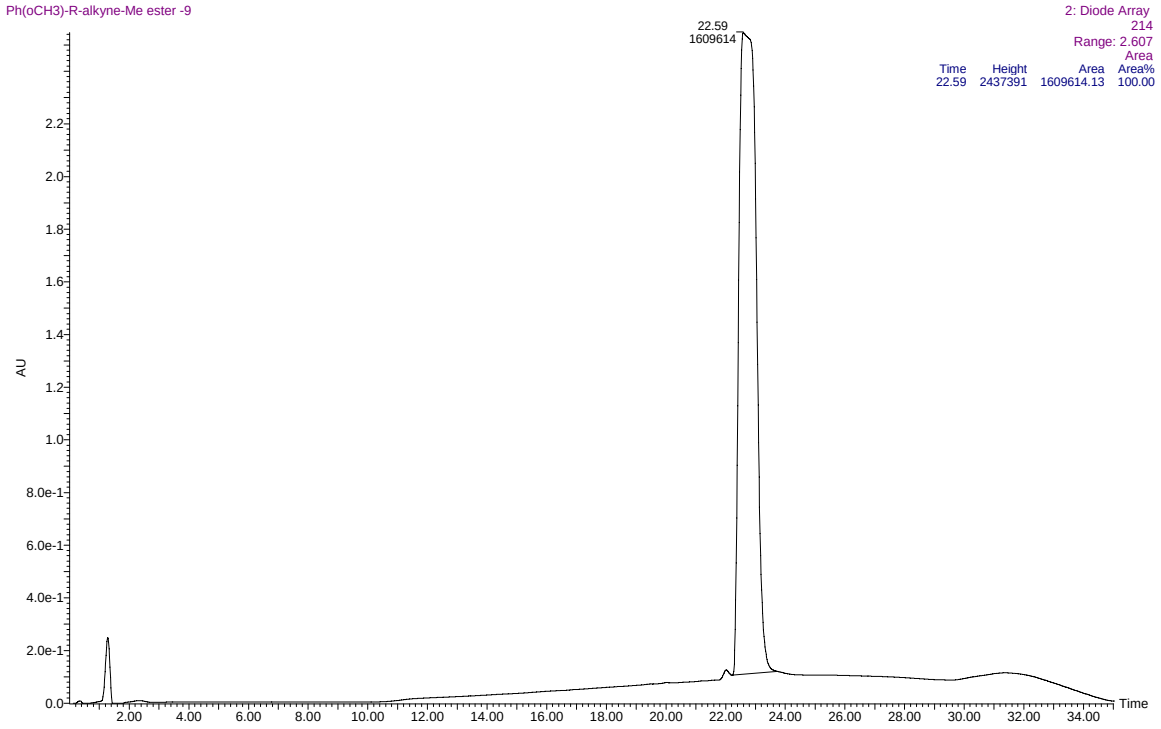
12{*2,5*}

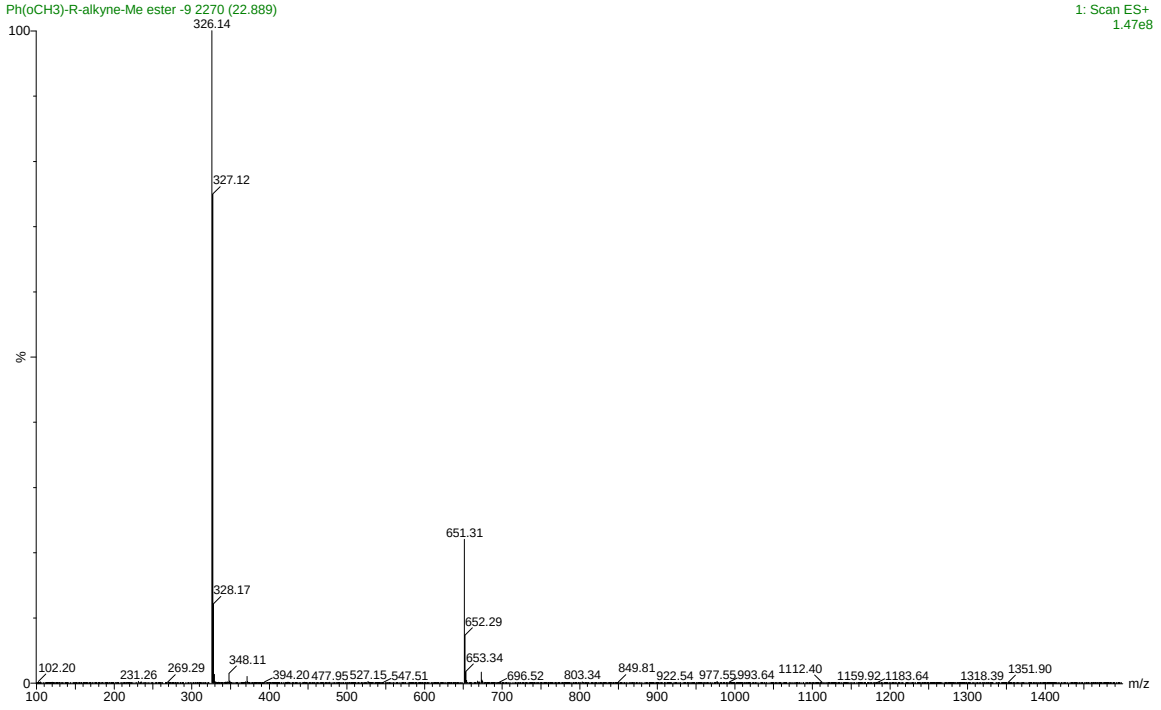


$C_{18}H_{19}N_3O_3$
Mol. Wt.: 325.36

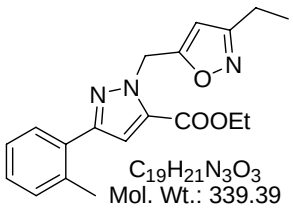




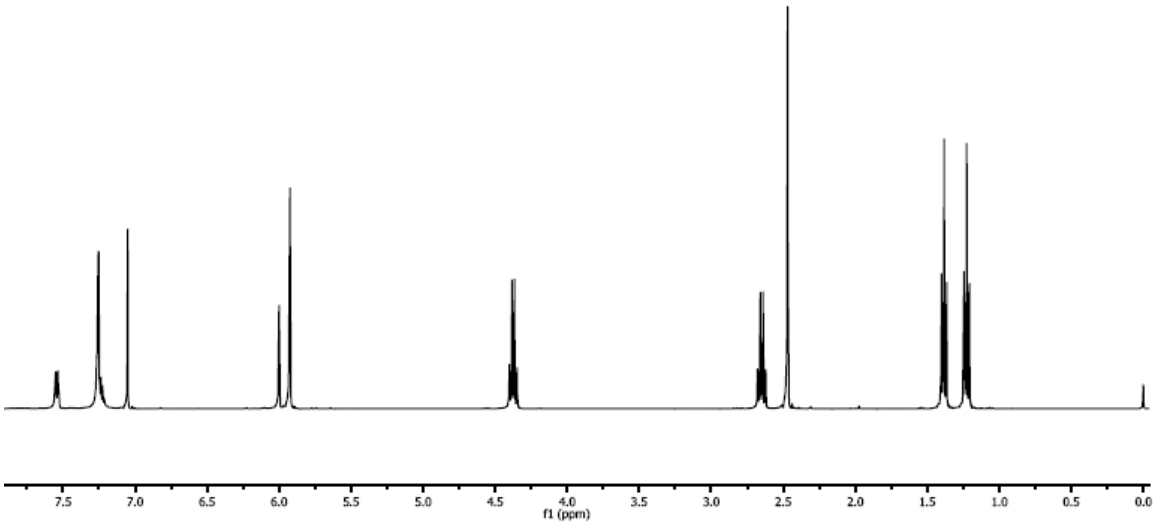

Ph(oCH3)-R-alkyne-Me ester -9
2: Diode Array
214
Range: 2.607
Area
Time Height Area Area%
22.59 2437391 1609614.13 100.00
22.59
1609614
AU
Time

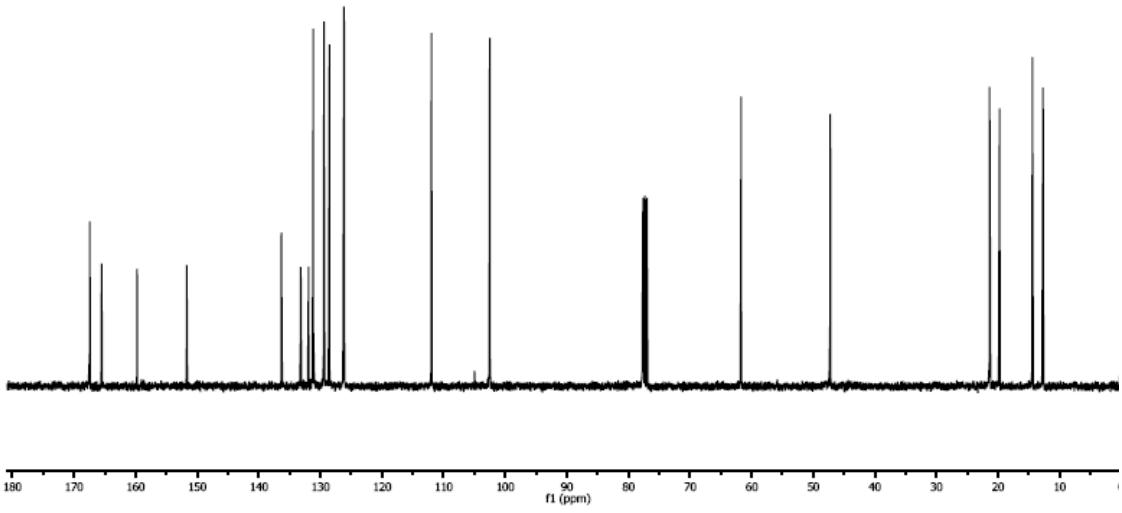

Ph(oCH3)-R-alkyne-Me ester -9 2270 (22.889)
1: Scan ES+
1.47e8
326.14
327.12
651.31
328.17
652.29
653.34
%
m/z

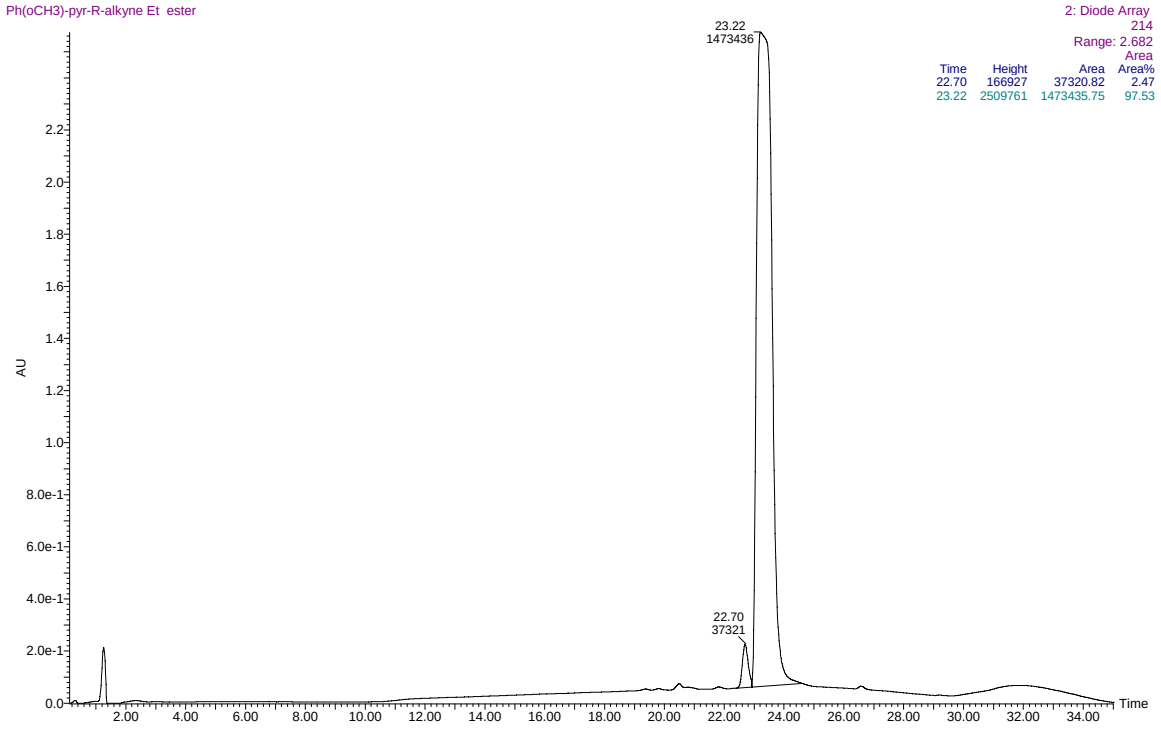
12{*2,6*}

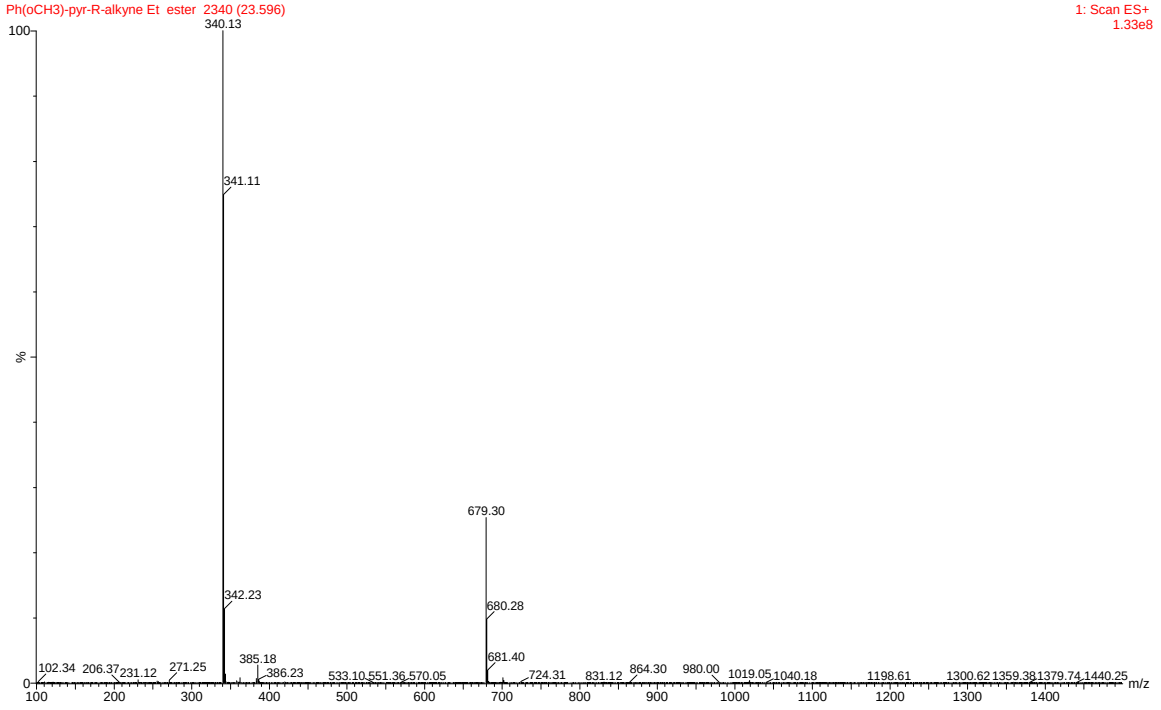


$C_{19}H_{21}N_3O_3$
Mol. Wt.: 339.39

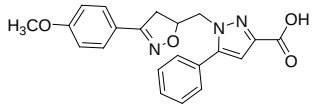




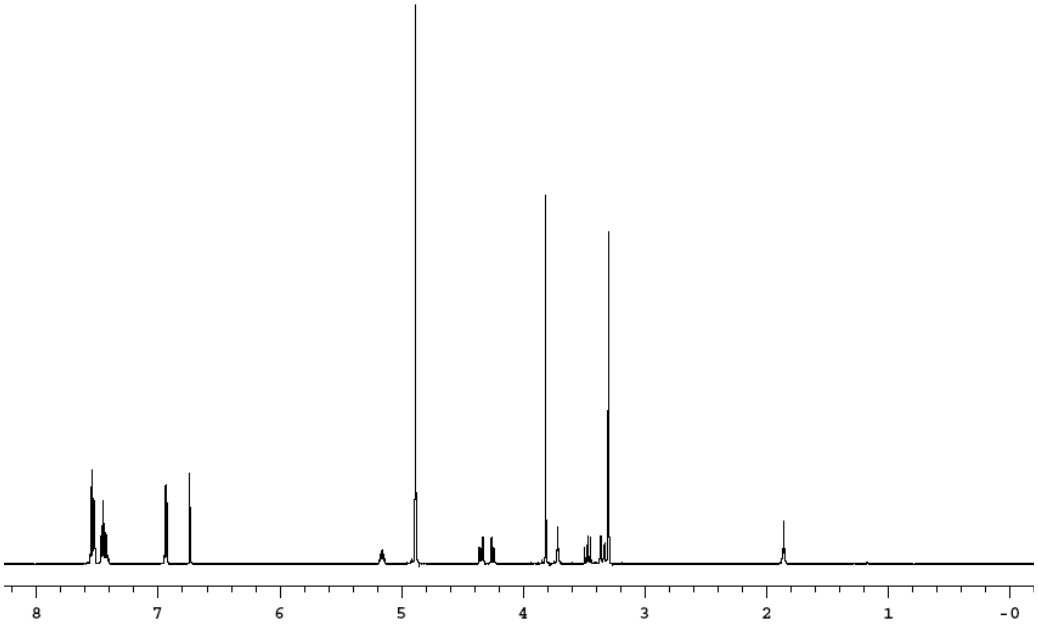

Ph(oCH3)-pyr-R-alkyne Et ester
2: Diode Array
214
Range: 2.682
Area
Time Height Area Area%
22.70 166927 37320.82 2.47
23.22 2509761 1473435.75 97.53
23.22
1473436
22.70
37321
AU
Time

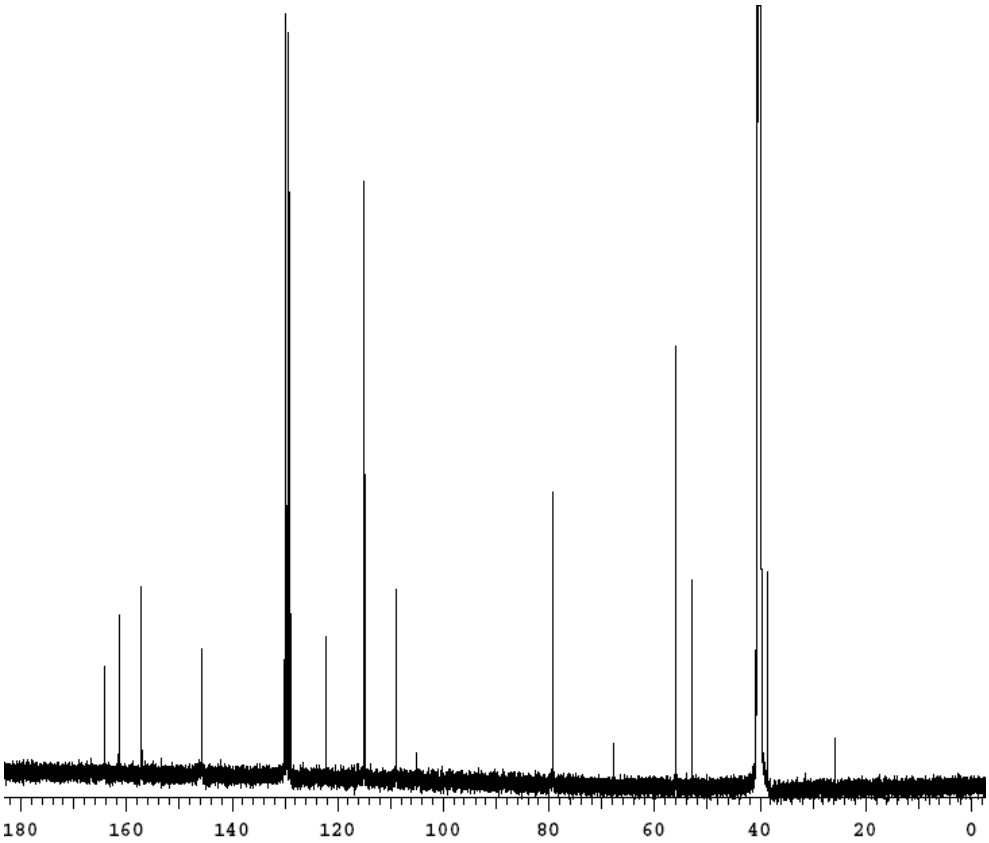

Ph(oCH3)-pyr-R-alkyne Et ester 2340 (23.596)
1: Scan ES+
1.33e8
340.13
341.11
679.30
342.23
680.28
681.40
%
m/z

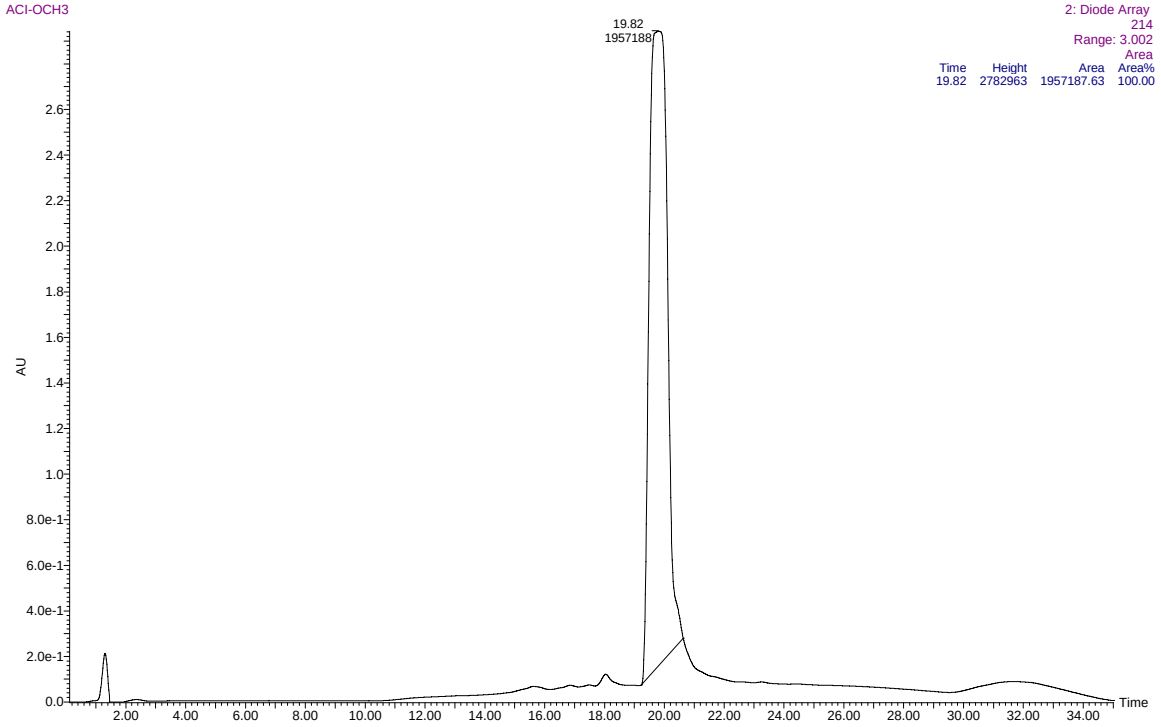
13{*1,2*}

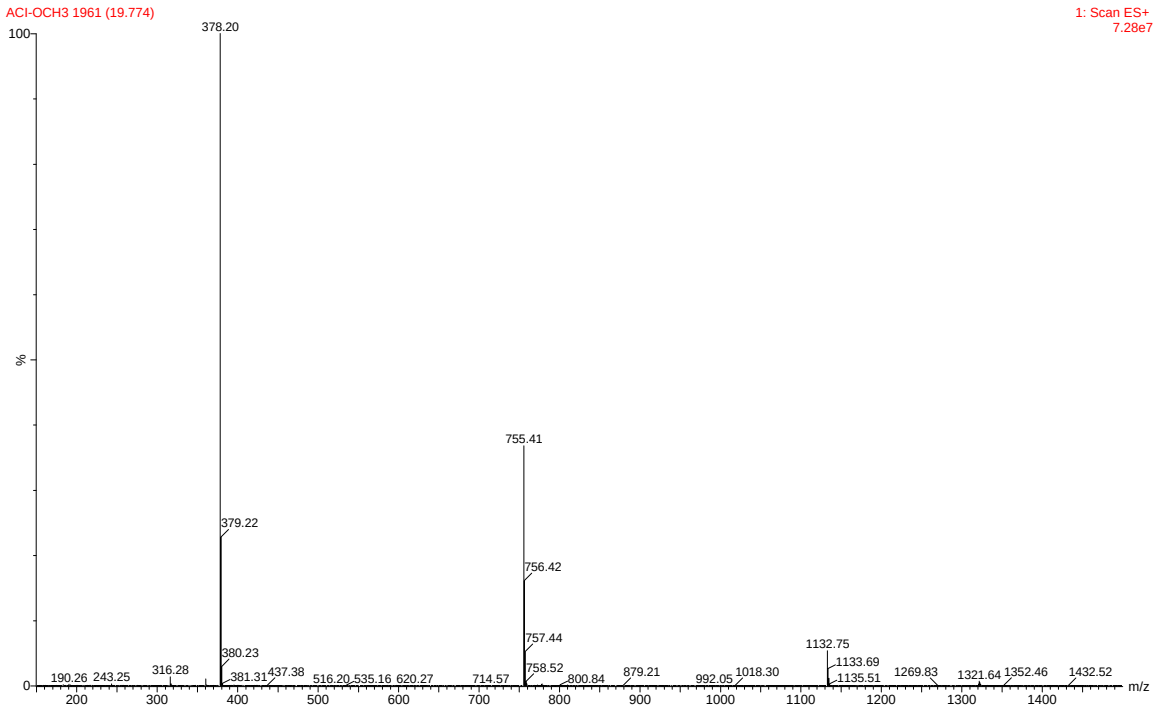


Chemical Formula: $C_{21}H_{19}N_3O_4$
Molecular Weight: 377.39

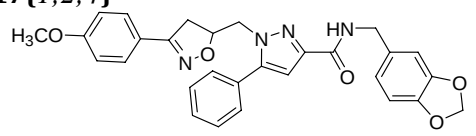




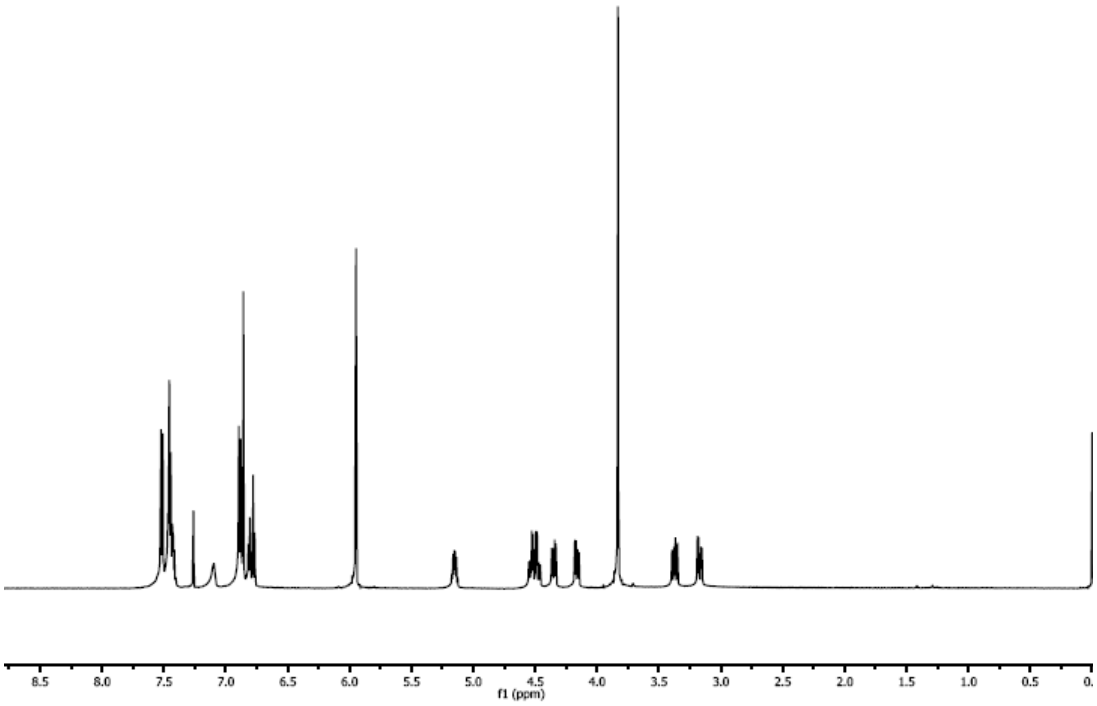

ACI-OCH3
2: Diode Array
214
Range: 3.002
Area
Time Height Area Area%
19.82 2782963 1957187.63 100.00
19.82
1957188
AU
Time

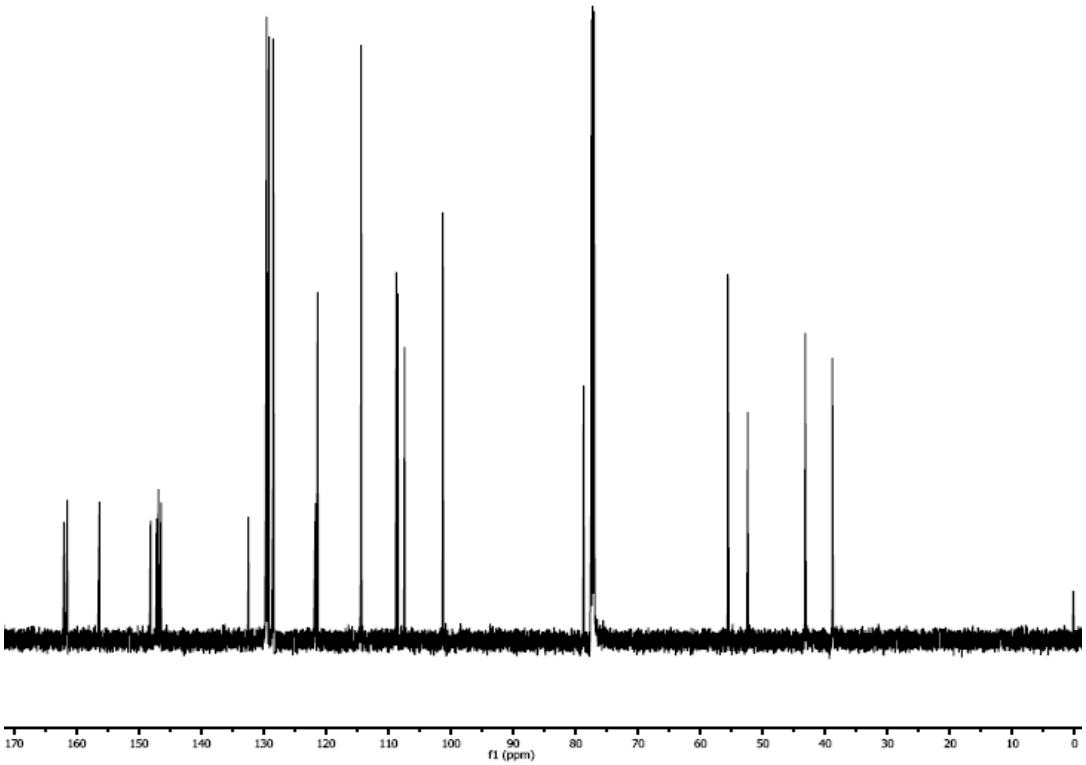

ACI-OCH3 1961 (19.774)
1: Scan ES+
7.28e7
%
m/z
378.20
379.22
380.23
755.41
756.42
757.44
758.52
1132.75
1133.69
1135.51

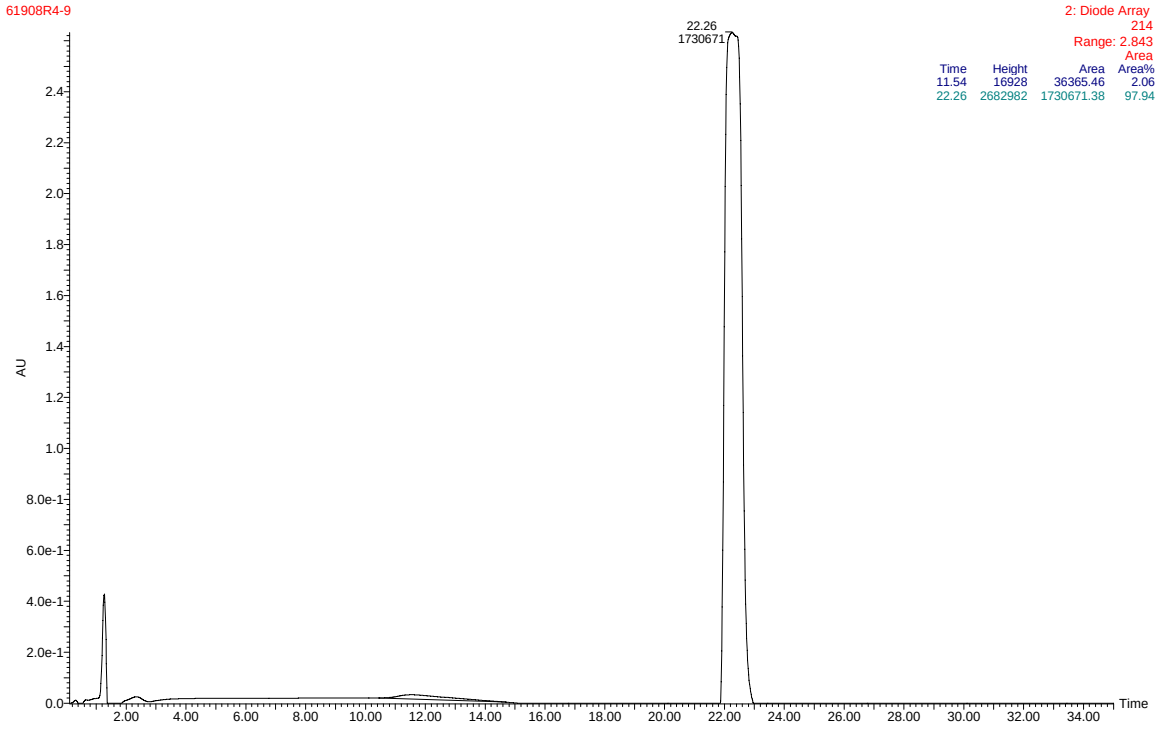
17{*1,2,4*}

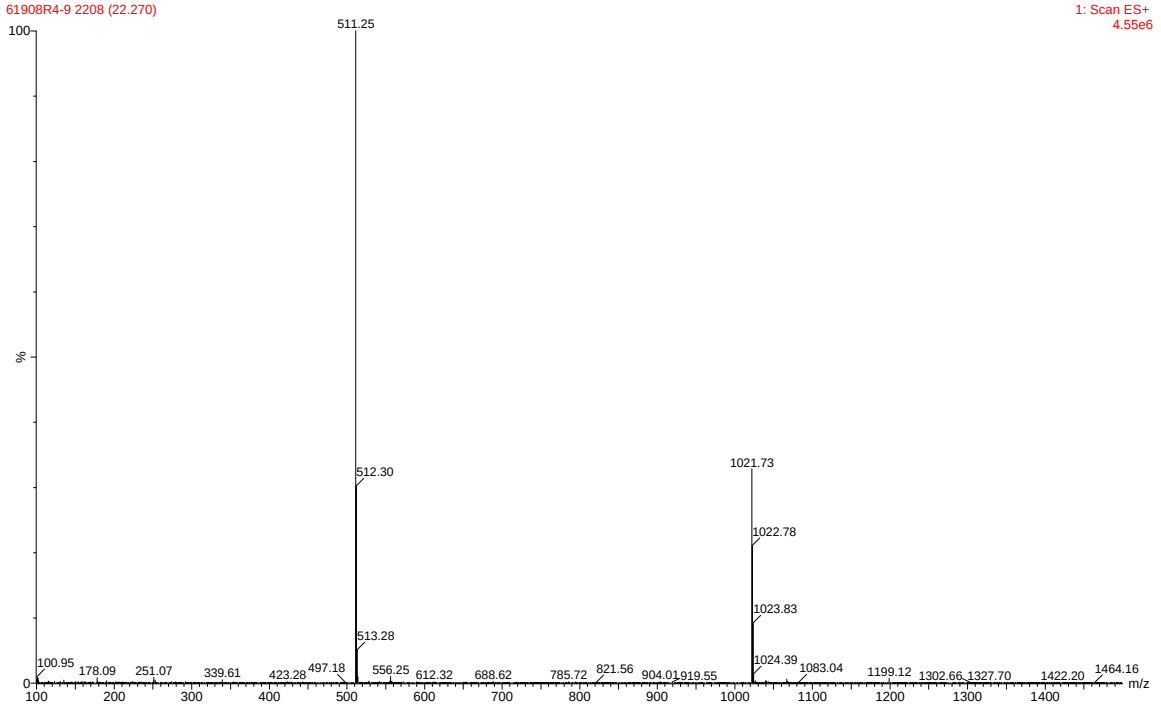


$C_{29}H_{26}N_4O_5$
Mol. Wt.: 510.54

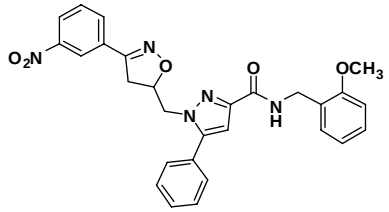




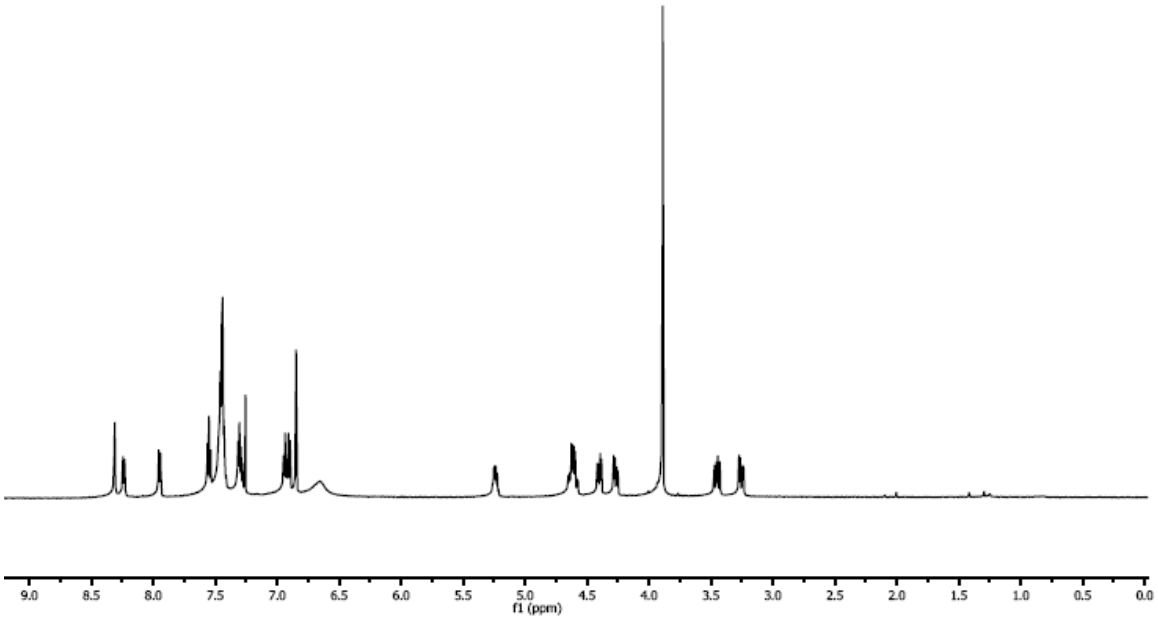

61908R4-9
2: Diode Array
214
Range: 2.843
Area
Time Height Area Area%
11.54 16928 36365.46 2.06
22.26 2682982 1730671.38 97.94
22.26
1730671
AU
Time

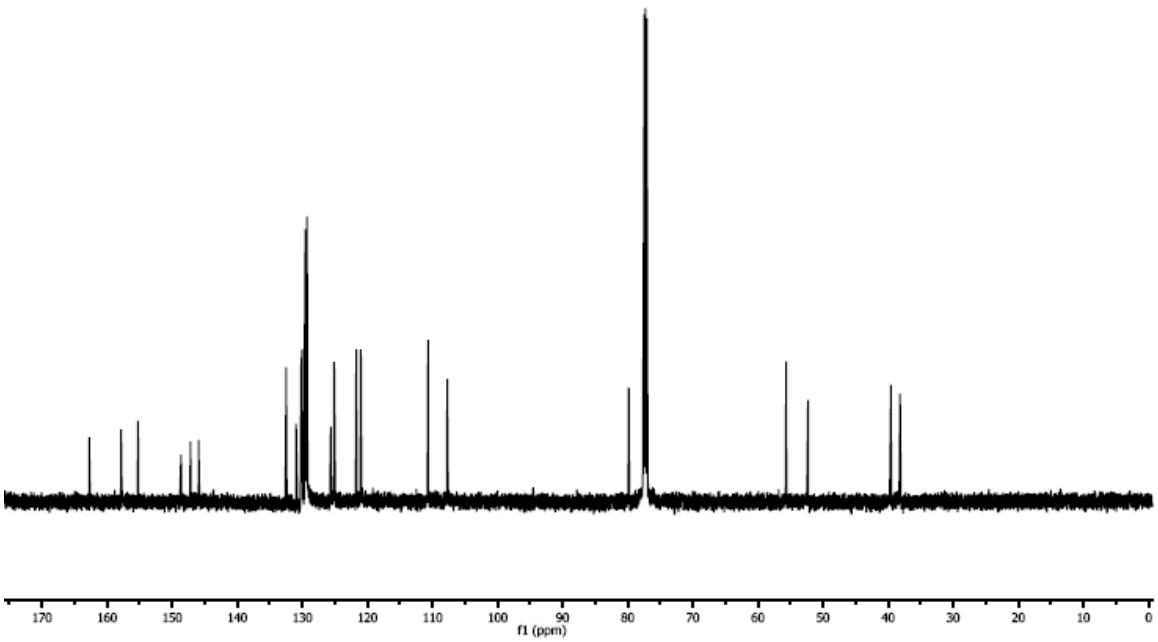

61908R4-9 2208 (22.270)
1: Scan ES+
4.55e6
%
m/z
511.25
512.30
513.28
1021.73
1022.78
1023.83
1024.39

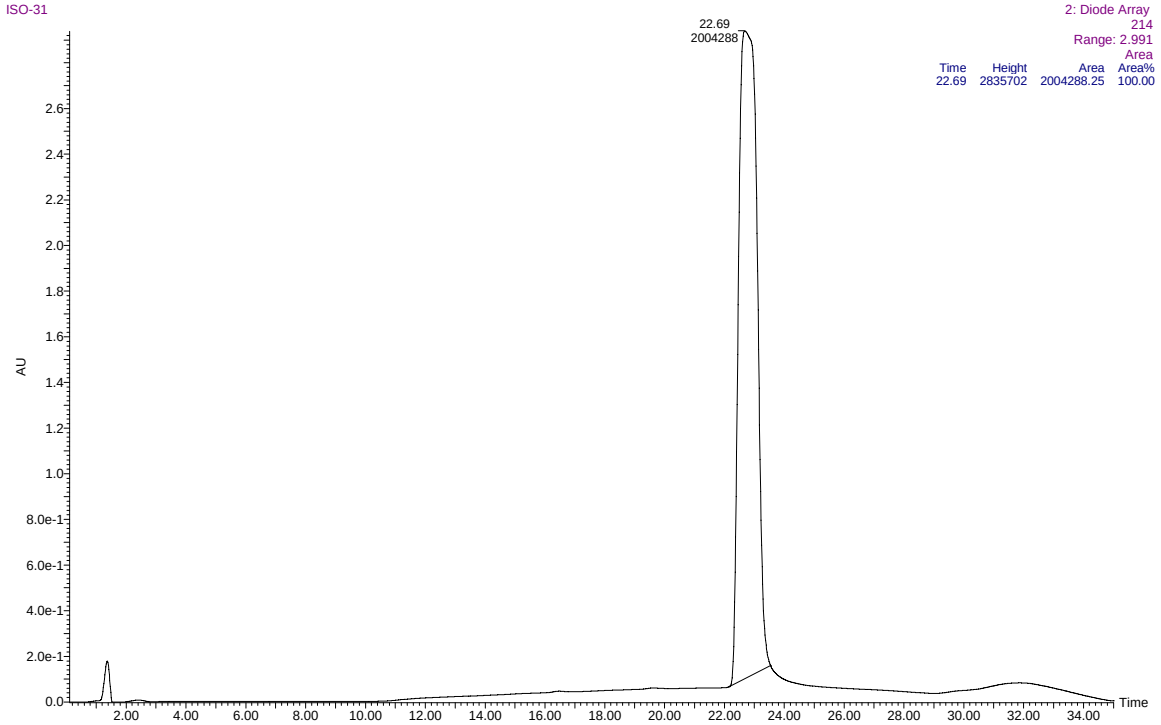
17{*1,3,1*}

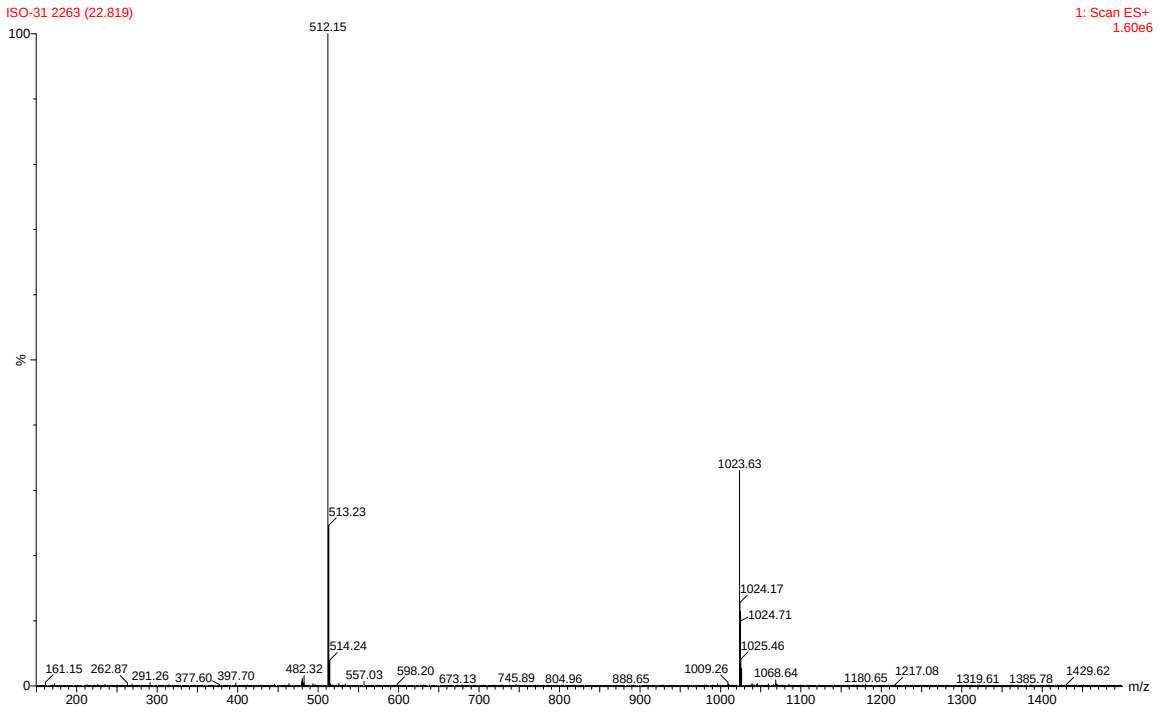


Chemical Formula: $C_{28}H_{25}N_5O_5$
Molecular Weight: 511.53

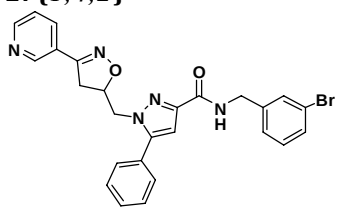




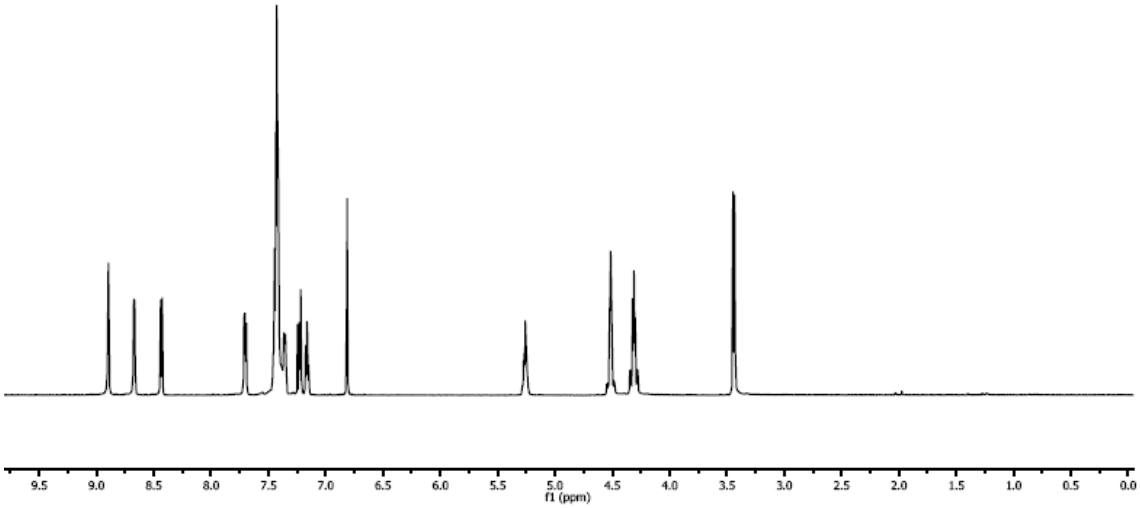

ISO-31
2: Diode Array
214
Range: 2.991
Area
Time Height Area Area%
22.69 2835702 2004288.25 100.00
22.69
2004288
AU
Time

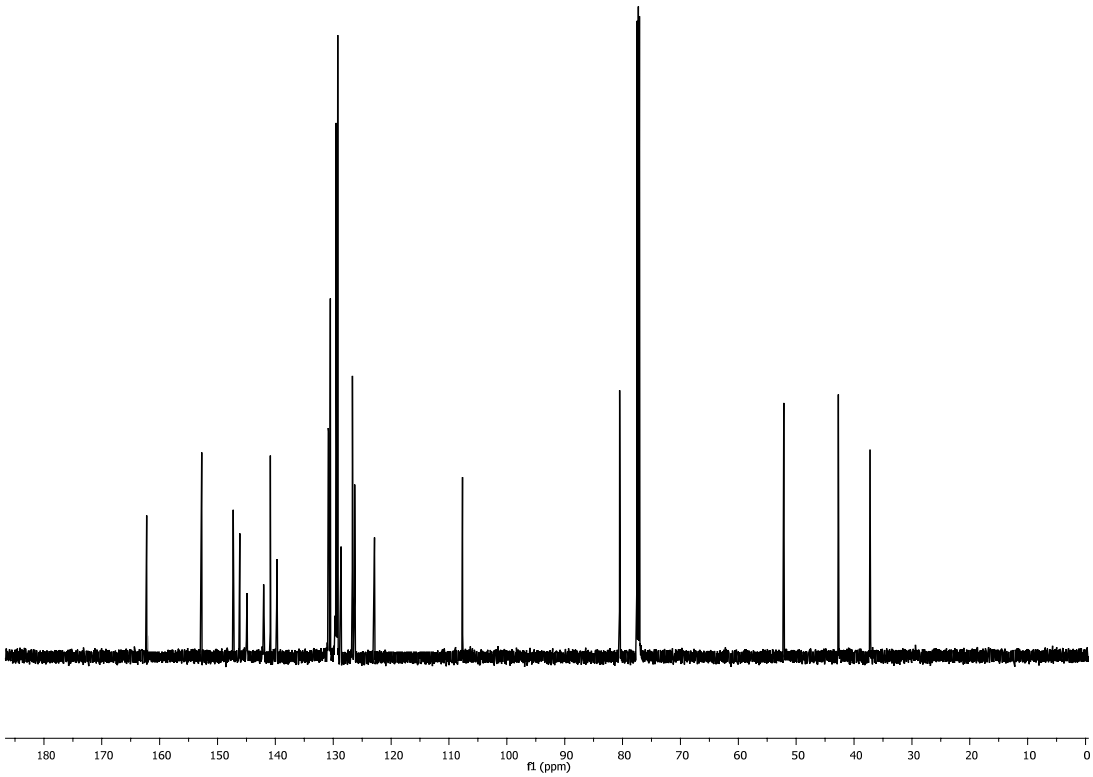

ISO-31 2263 (22.819)
1: Scan ES+
1.60e6
512.15
1023.63
513.23
1024.17
1024.71
514.24
1025.46
%
m/z

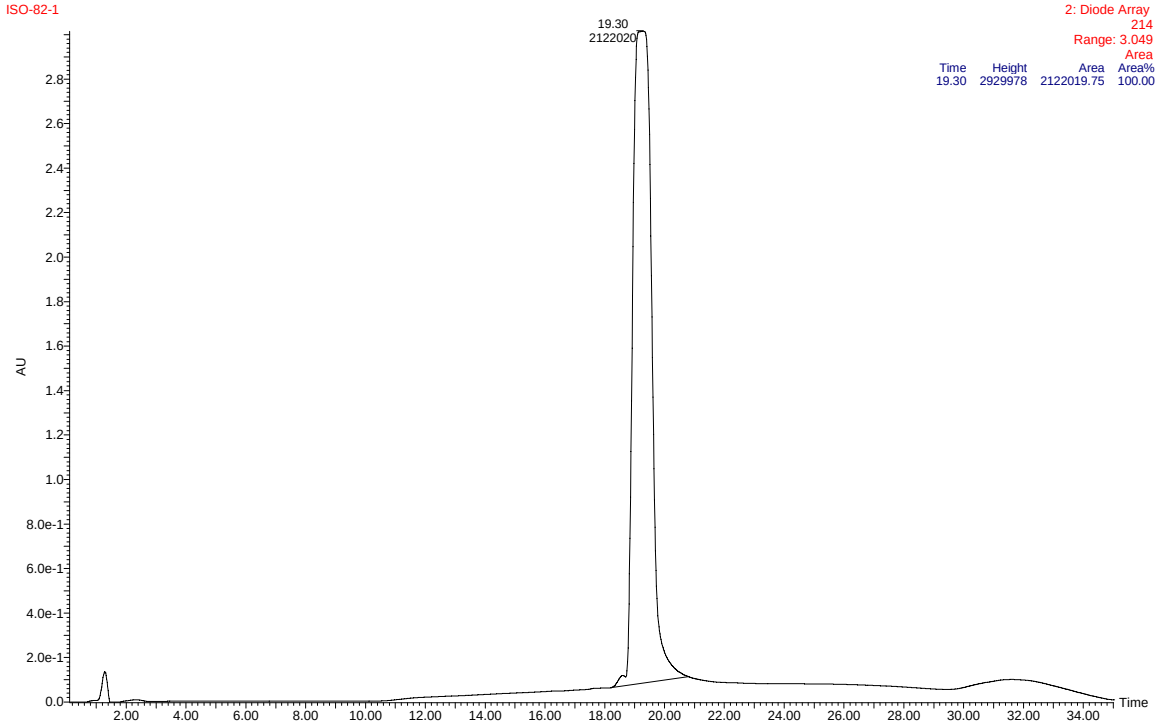
17{*1,4,2*}

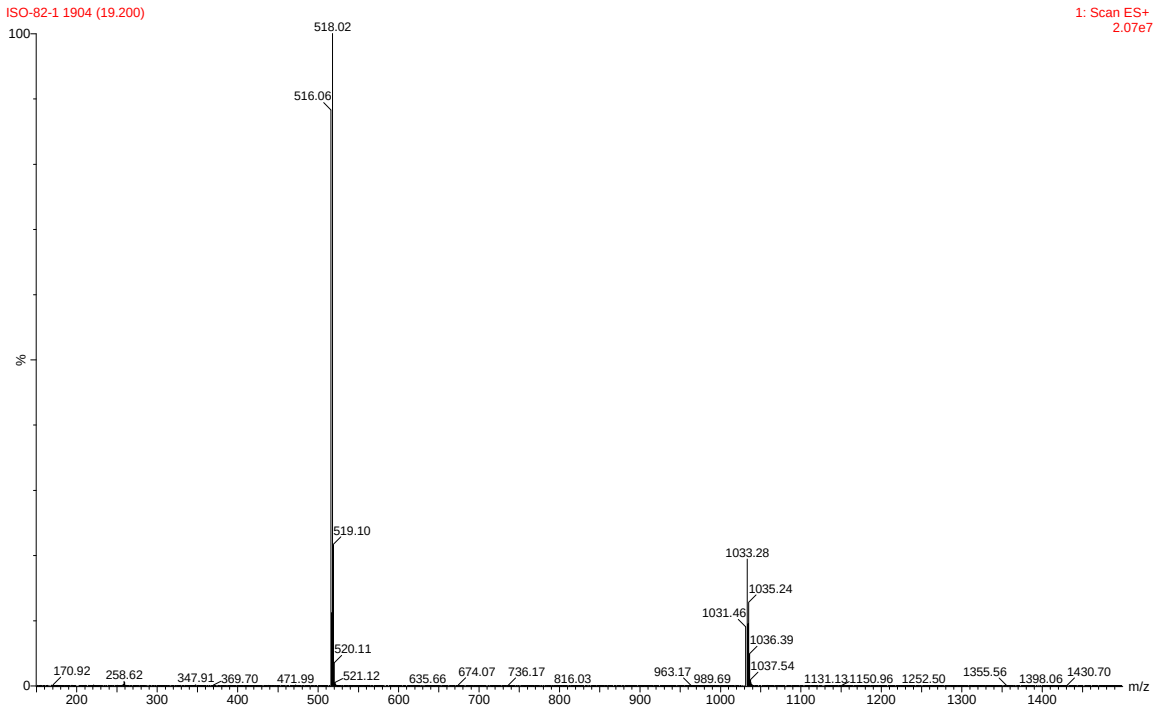


Chemical Formula: $C_{26}H_{22}BrN_5O_2$
Molecular Weight: 516.39

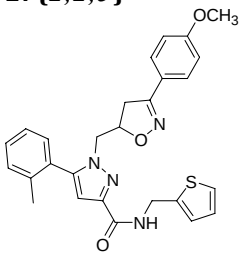




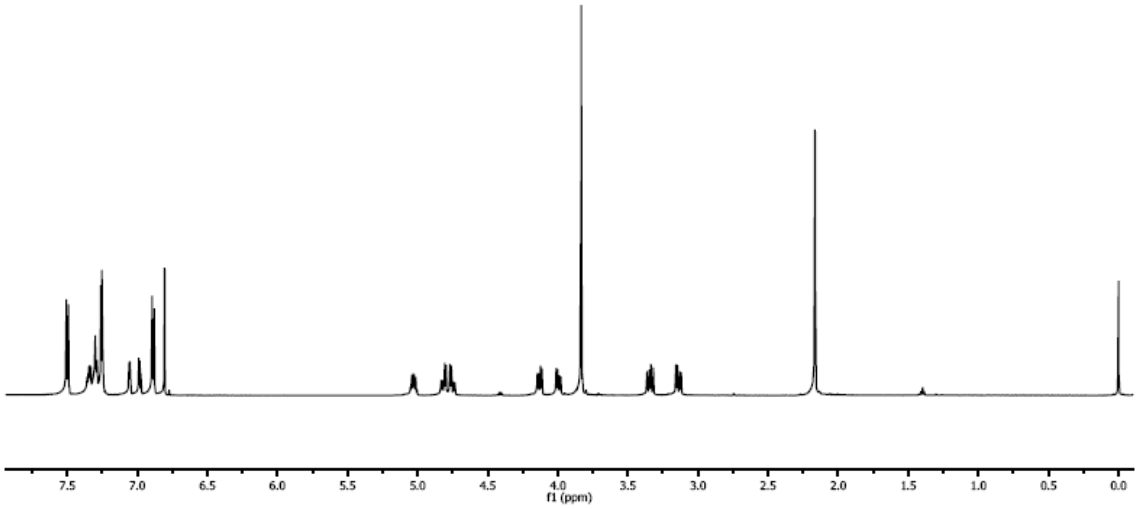

ISO-82-1
2: Diode Array
214
Range: 3.049
Area
Time Height Area Area%
19.30 2929978 2122019.75 100.00
19.30
2122020
AU
Time

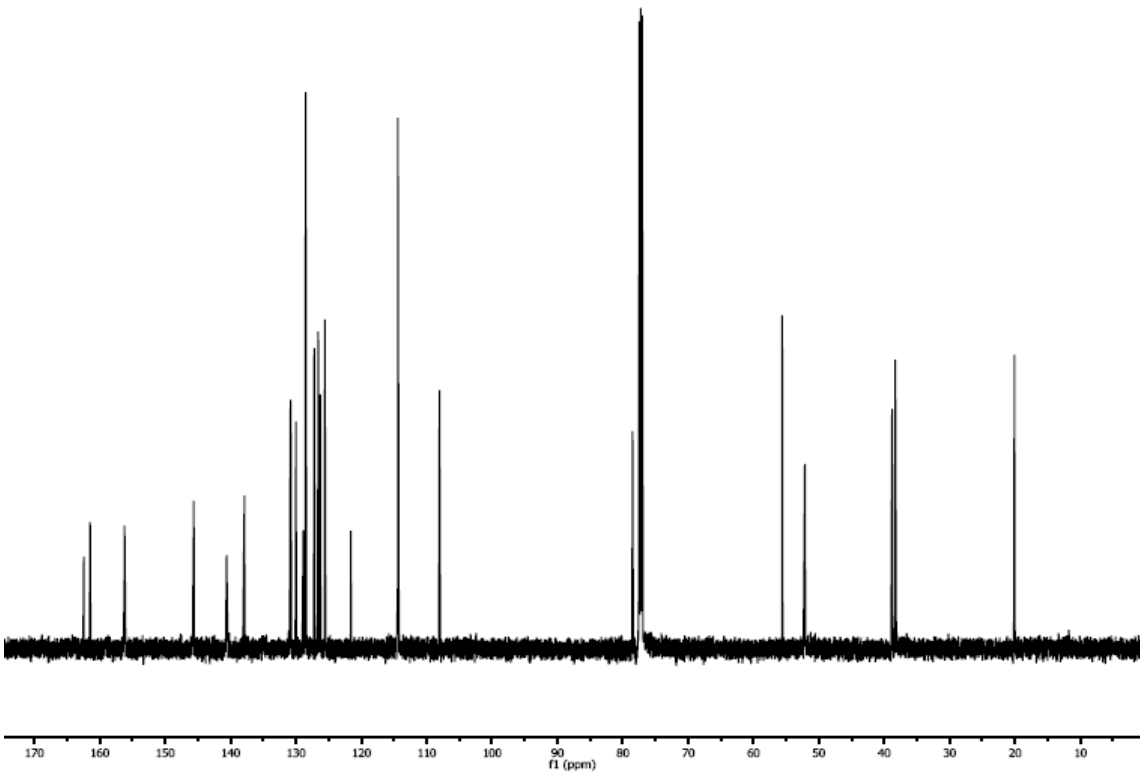

ISO-82-1 1904 (19.200)
1: Scan ES+
2.07e7
%
m/z
518.02
516.06
519.10
520.11
521.12
1033.28
1035.24
1031.46
1036.39
1037.54
170.92
258.62
347.91
369.70
471.99
635.66
674.07
736.17
816.03
963.17
989.69
1131.13
1150.96
1252.50
1355.56
1398.06
1430.70

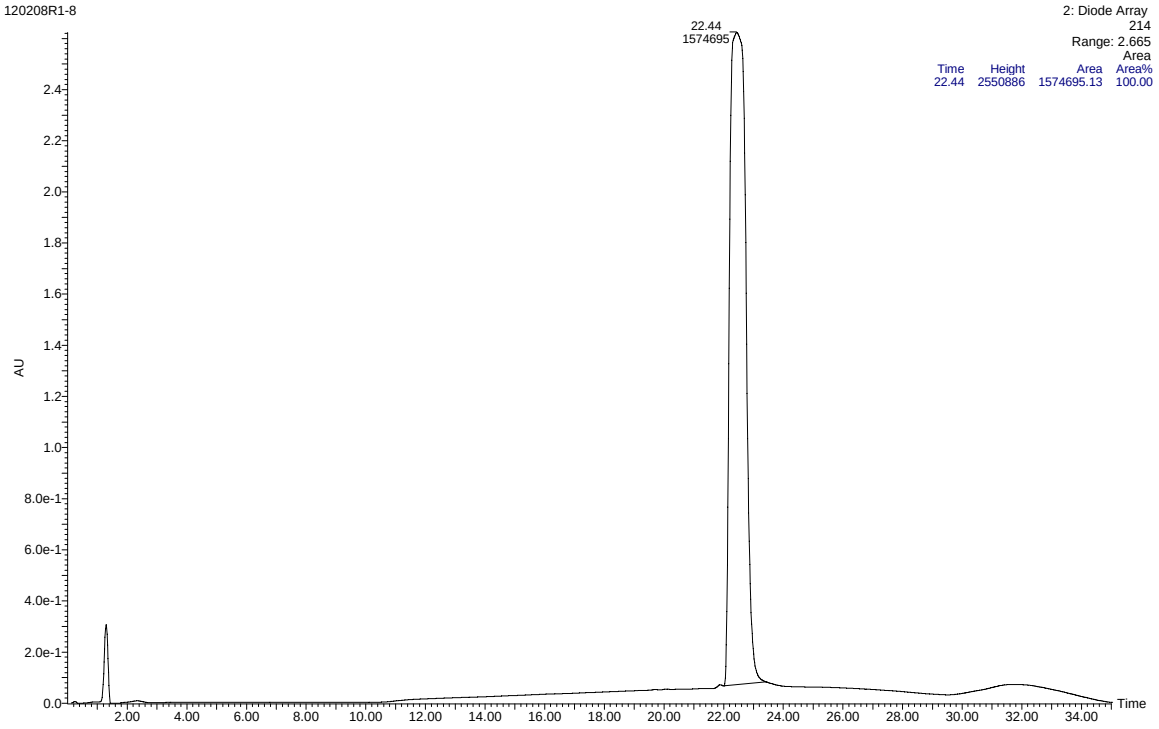
17{*2,2,5*}

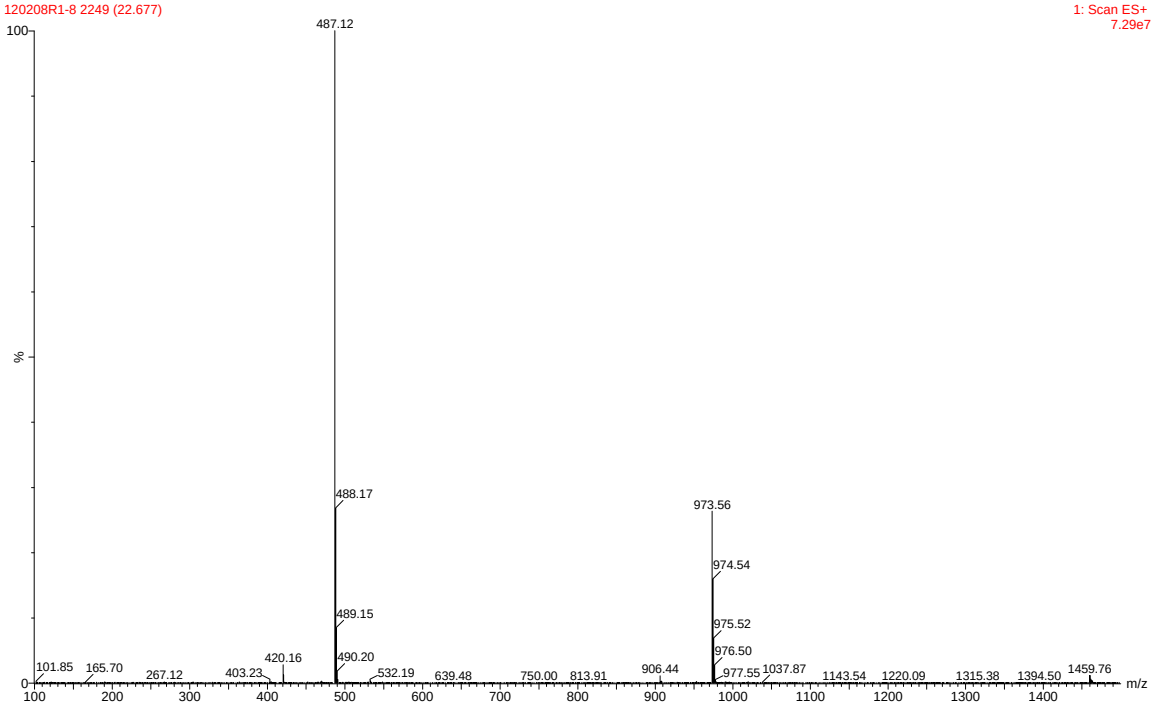


$C_{27}H_{26}N_4O_3S$
Mol. Wt.: 486.59

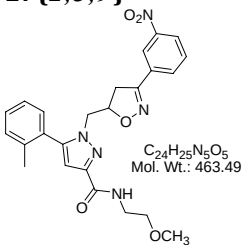




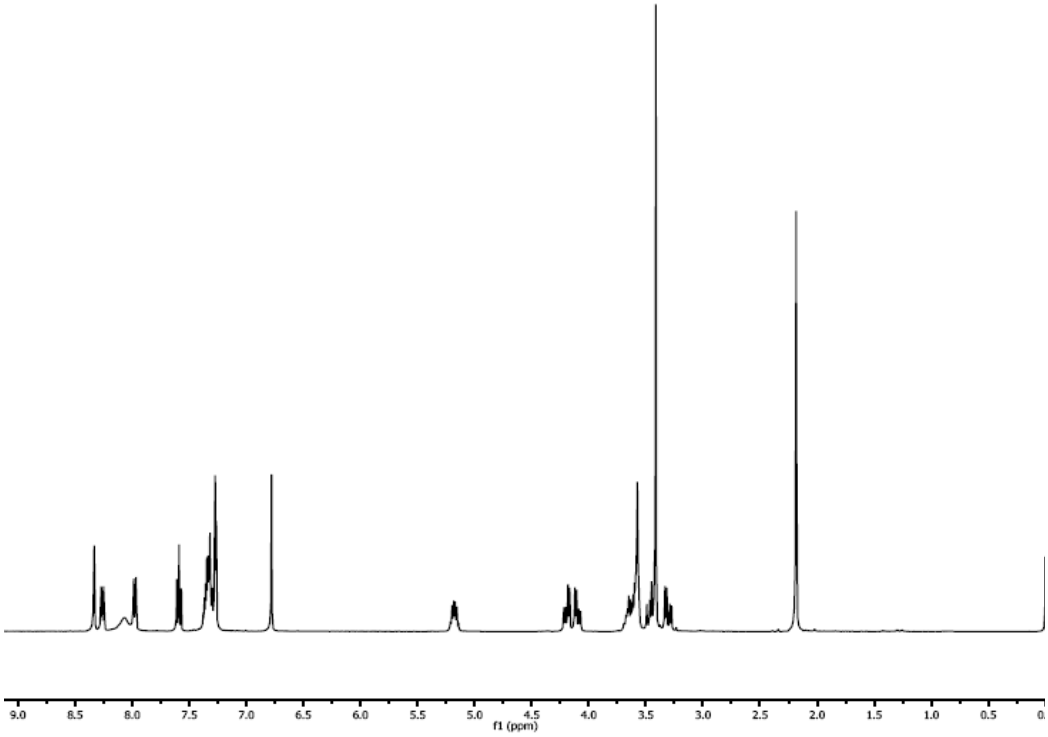

120208R1-8
2: Diode Array
214
Range: 2.665
Area
Time Height Area Area%
22.44 2550886 1574695.13 100.00
22.44
1574695
AU
Time

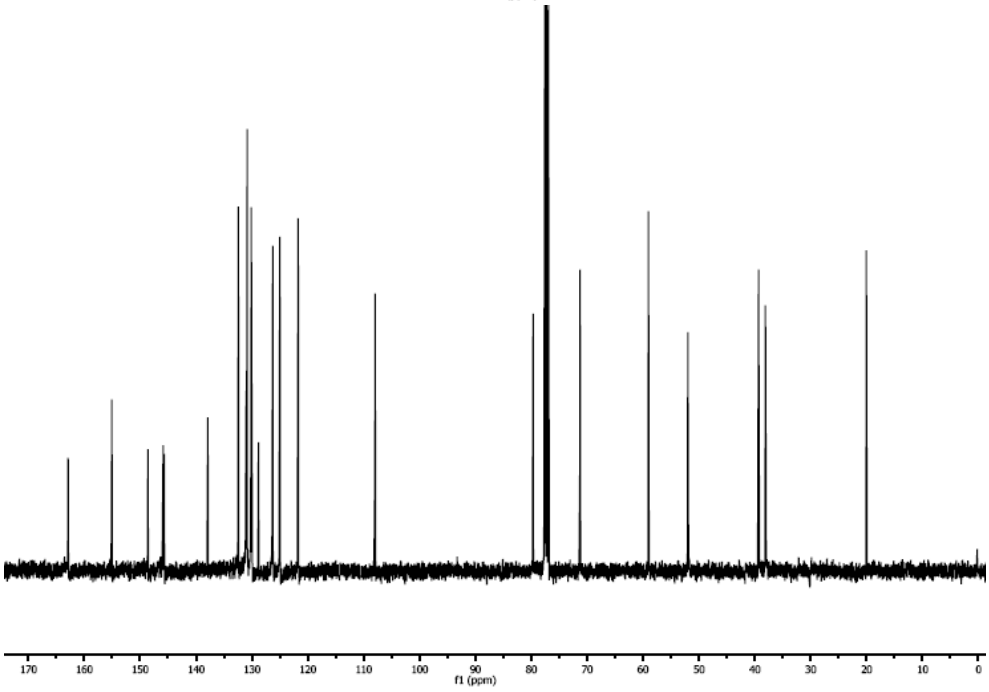

120208R1-8 2249 (22.677)
1: Scan ES+
7.29e7
%
m/z
487.12
488.17
489.15
490.20
973.56
974.54
975.52
976.50
977.55

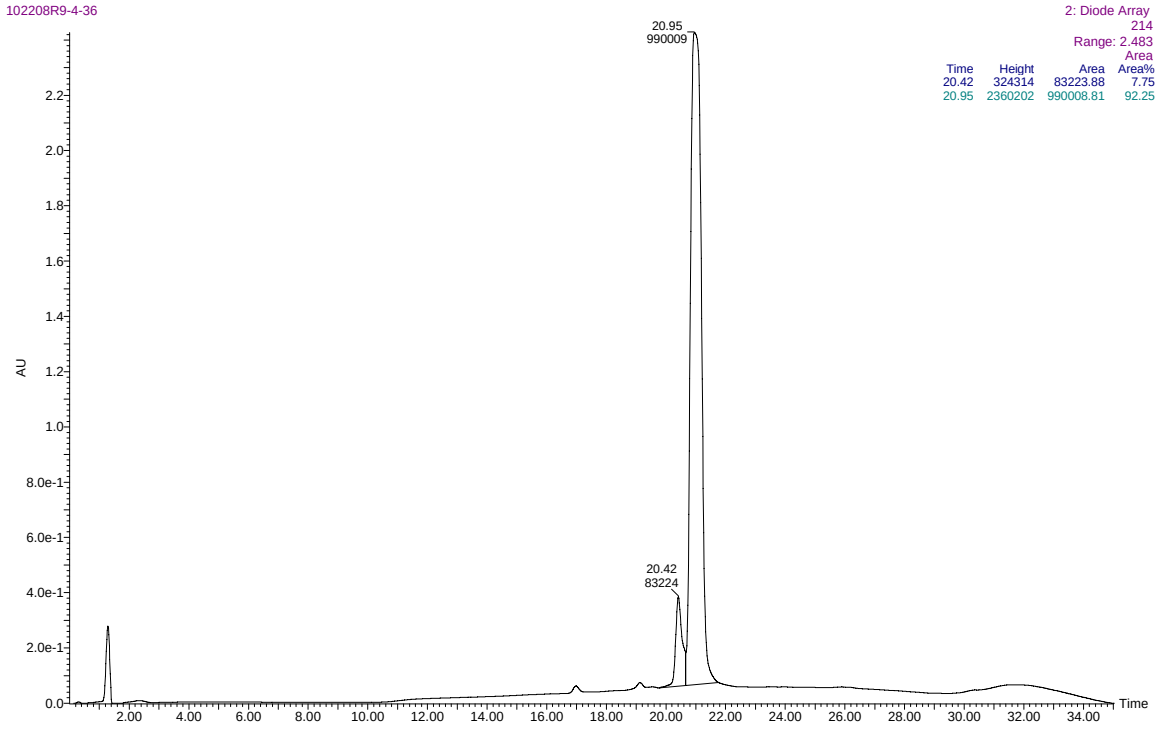
17{*2,3,9*}

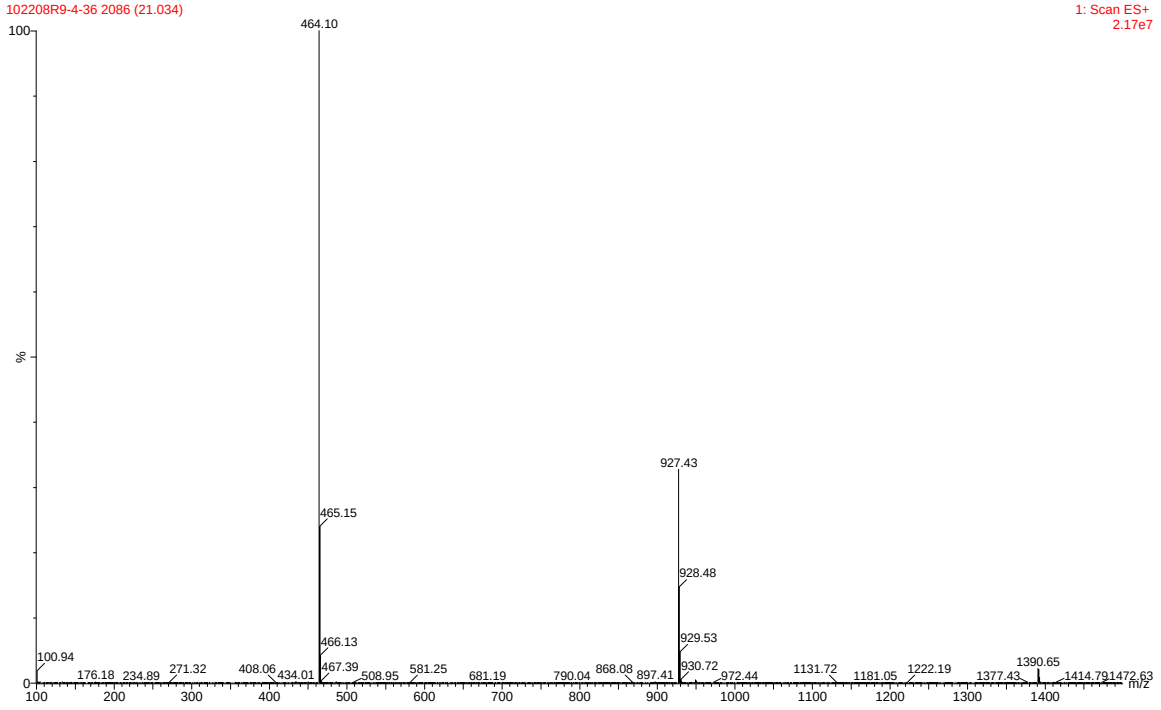


$C_{24}H_{25}N_5O_5$
Mol. Wt.: 463.49

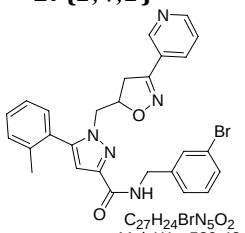




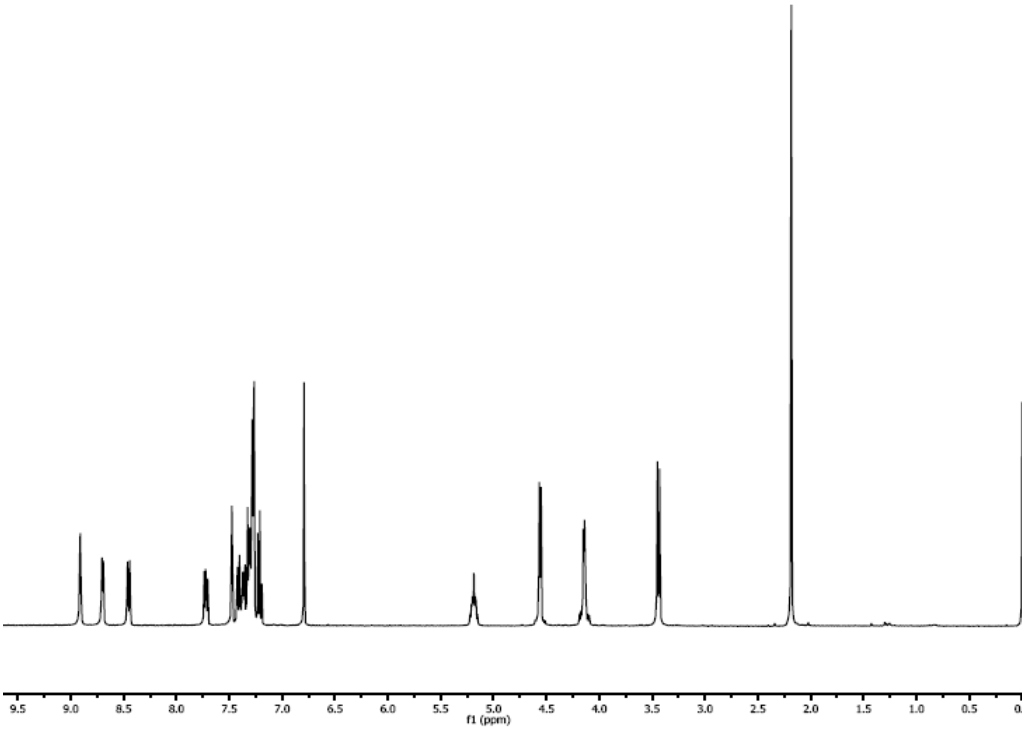

102208R9-4-36
2: Diode Array
214
Range: 2.483
Area
Time Height Area Area%
20.42 324314 83223.88 7.75
20.95 2360202 990008.81 92.25
20.95
990009
20.42
83224
AU
Time

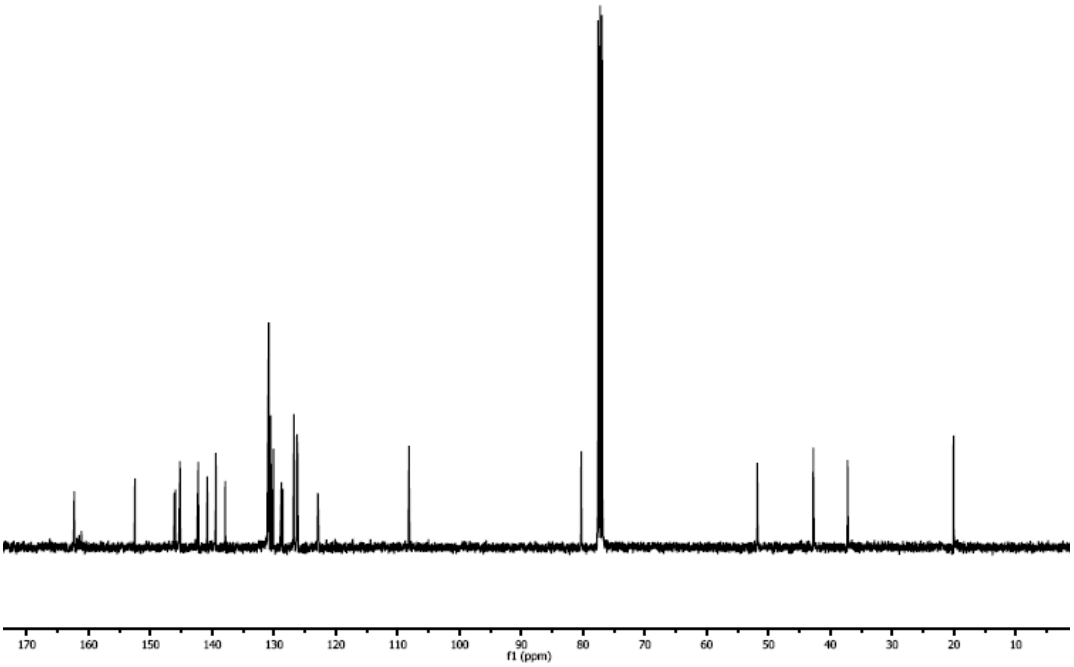

102208R9-4-36 2086 (21.034)
1: Scan ES+
2.17e7
464.10
927.43
465.15
928.48
466.13
929.53
467.39
930.72
100.94
176.18
234.89
271.32
408.06
434.01
508.95
581.25
681.19
790.04
868.08
897.41
972.44
1131.72
1181.05
1222.19
1377.43
1390.65
1414.79
1472.63
%
m/z

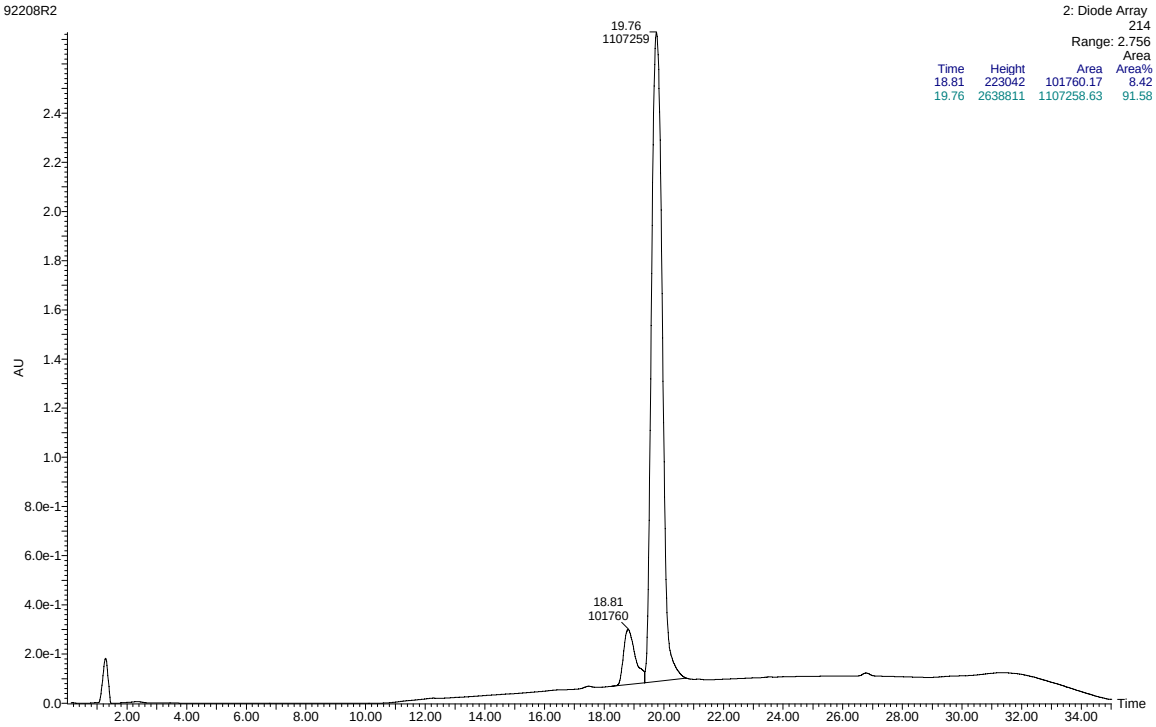
17{*2,4,2*}

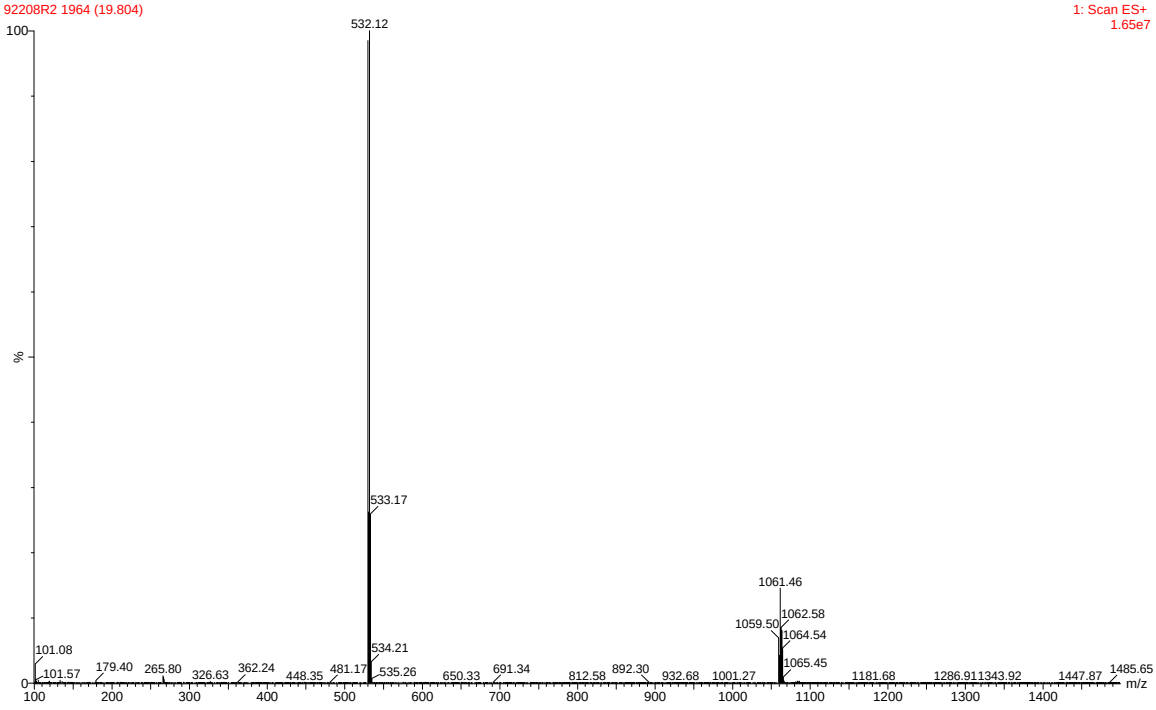


$C_{27}H_{24}BrN_5O_2$
Mol. Wt.: 530.42

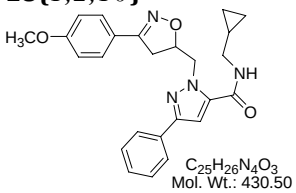




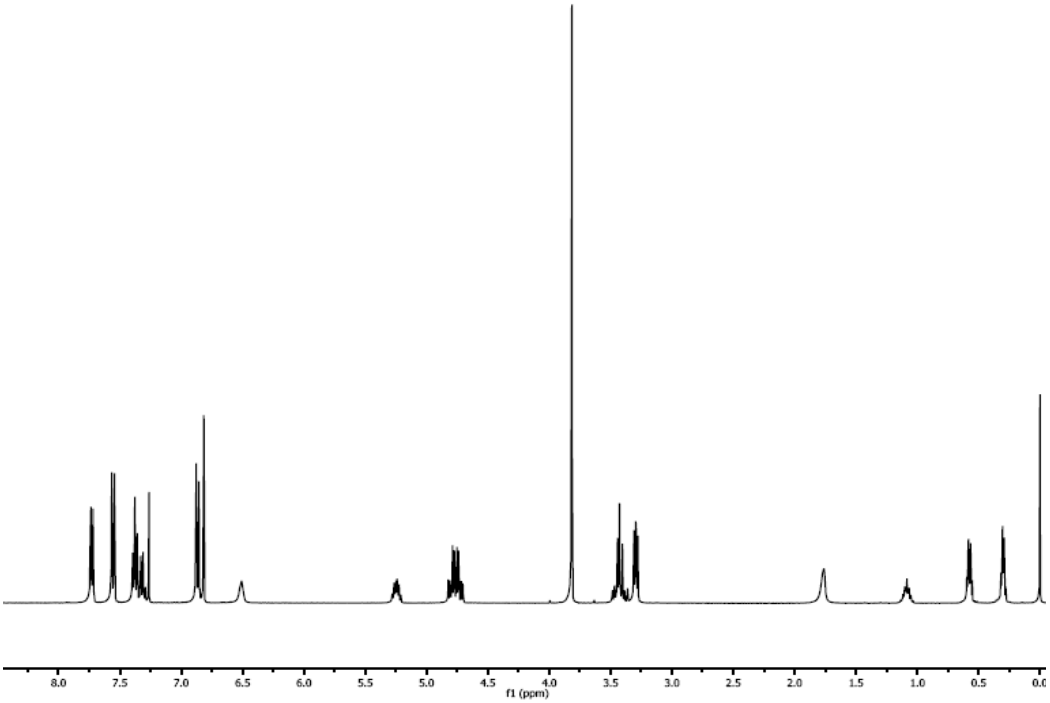

92208R2
2: Diode Array
214
Range: 2.756
Area
Time Height Area Area%
18.81 223042 101760.17 8.42
19.76 2638811 1107258.63 91.58
19.76
1107259
18.81
101760
AU
Time

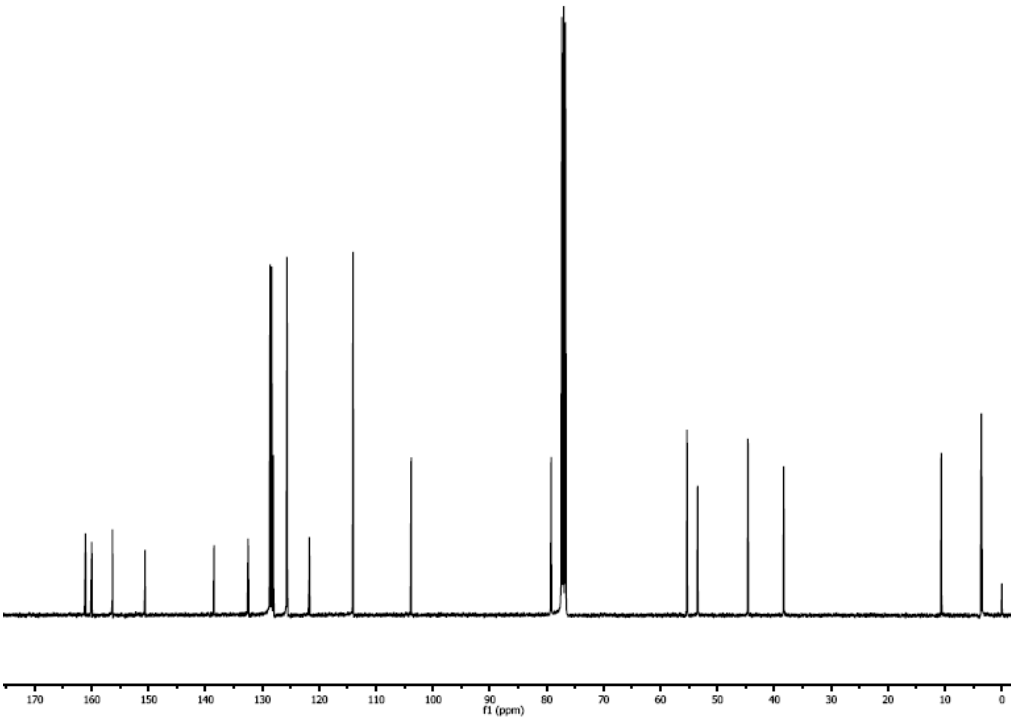

92208R2 1964 (19.804)
1: Scan ES+
1.65e7
532.12
533.17
534.21
1061.46
1062.58
1064.54
1065.45
1059.50
101.08
101.57
179.40
265.80
326.63
362.24
448.35
481.17
535.26
650.33
691.34
812.58
892.30
932.68
1001.27
1181.68
1286.91
1343.92
1447.87
1485.65
%
m/z

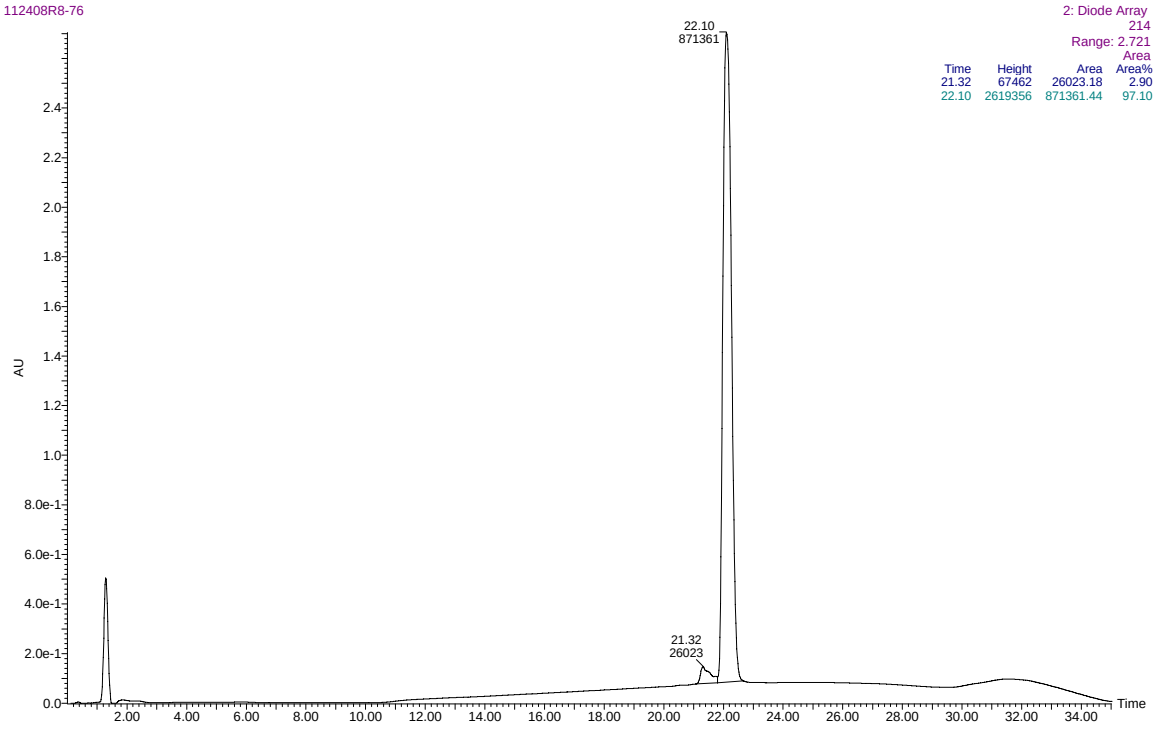
18{*1,2,10*}

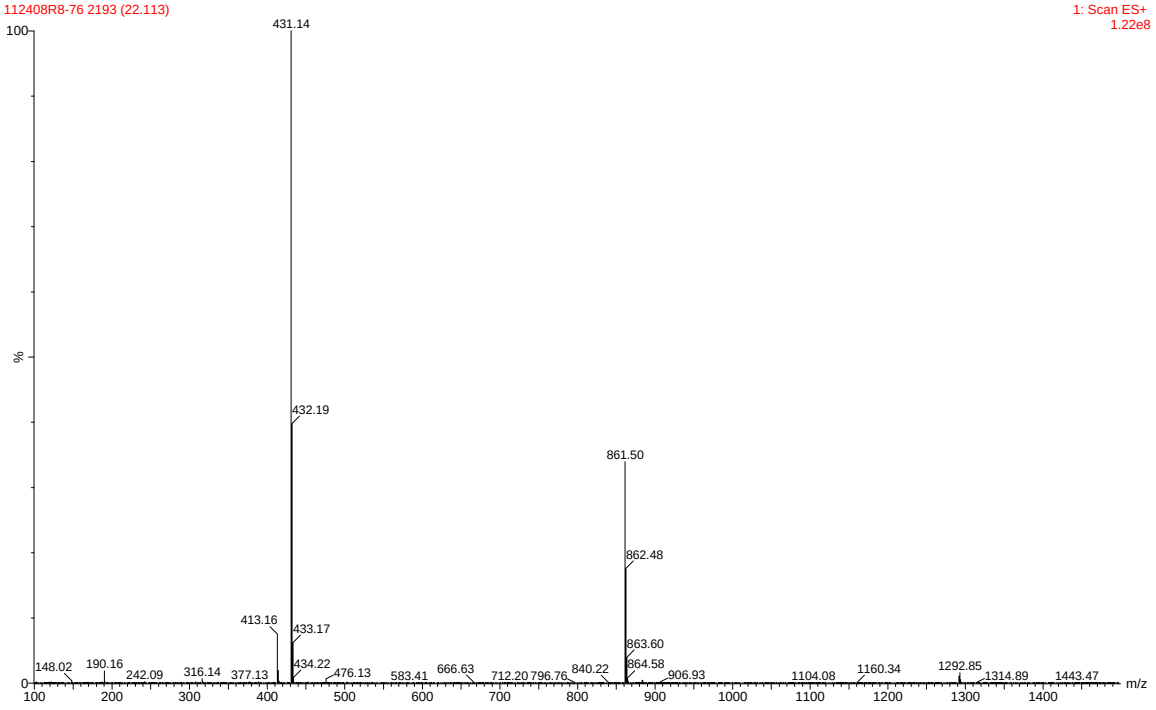


$C_{25}H_{26}N_4O_3$
Mol. Wt.: 430.50

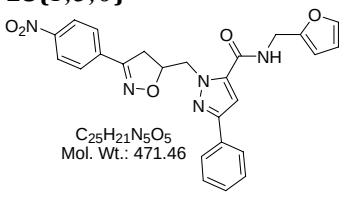




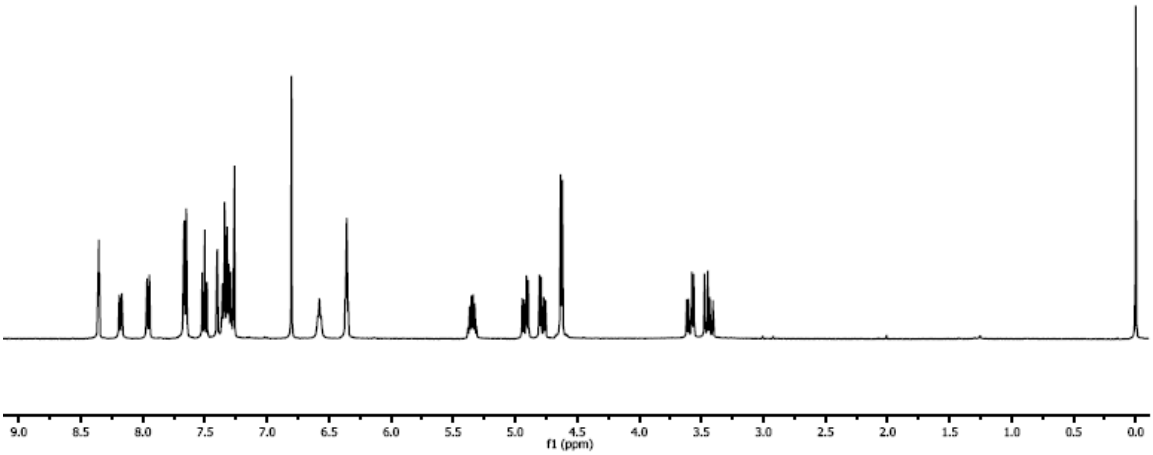

112408R8-76
2: Diode Array
214
Range: 2.721
Area
Time Height Area Area%
21.32 67462 26023.18 2.90
22.10 2619356 871361.44 97.10
22.10
871361
21.32
26023
AU
Time

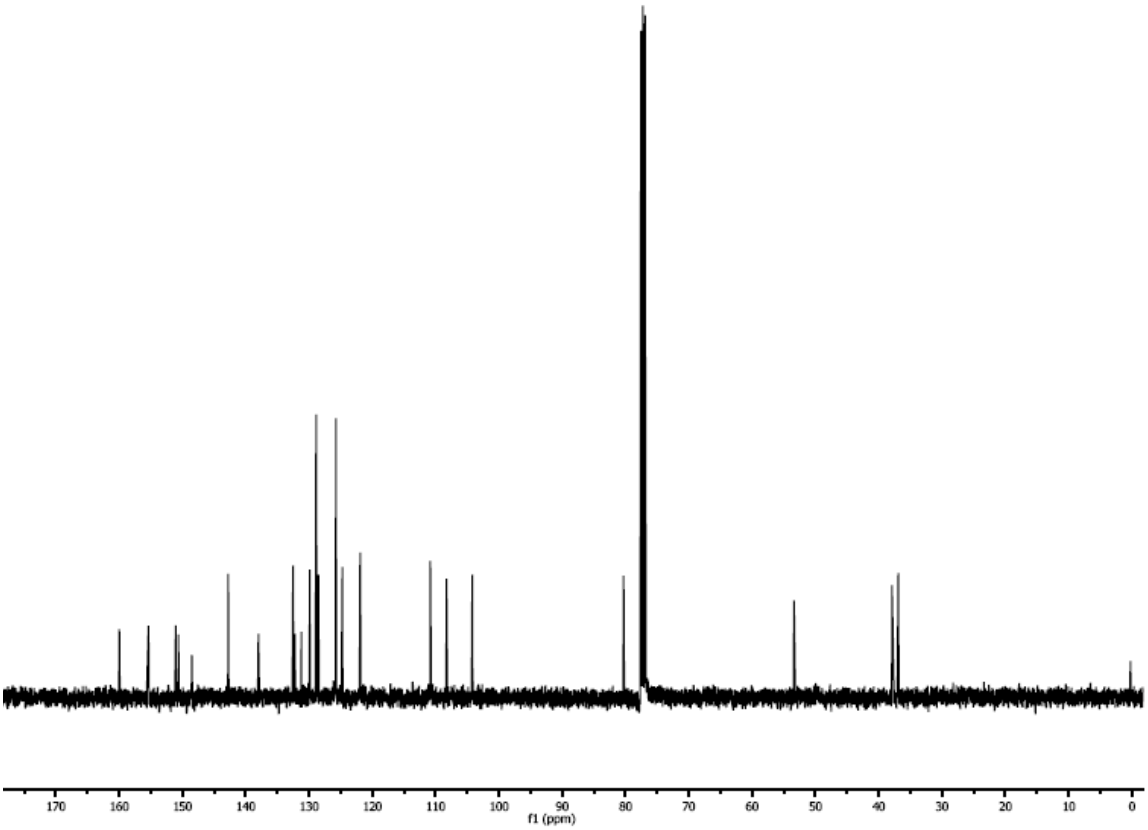

112408R8-76 2193 (22.113)
1: Scan ES+
1.22e8
431.14
432.19
861.50
862.48
413.16
433.17
863.60
864.58
%
m/z

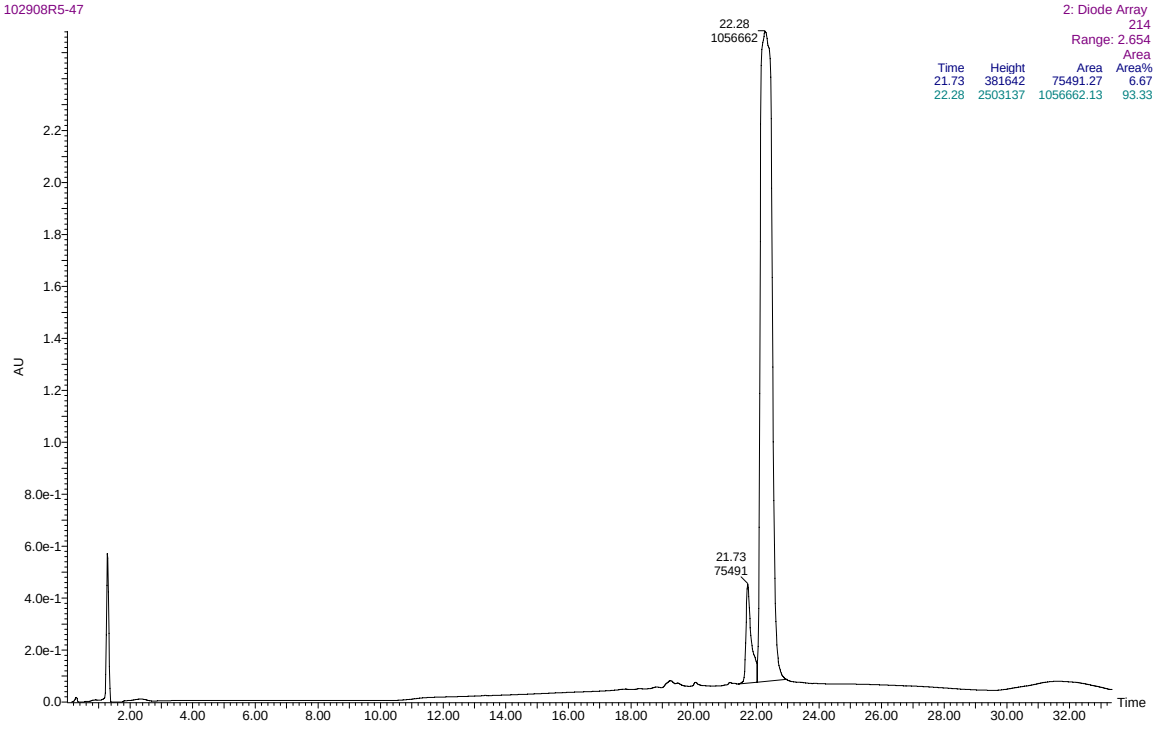
18{*1,3,6*}

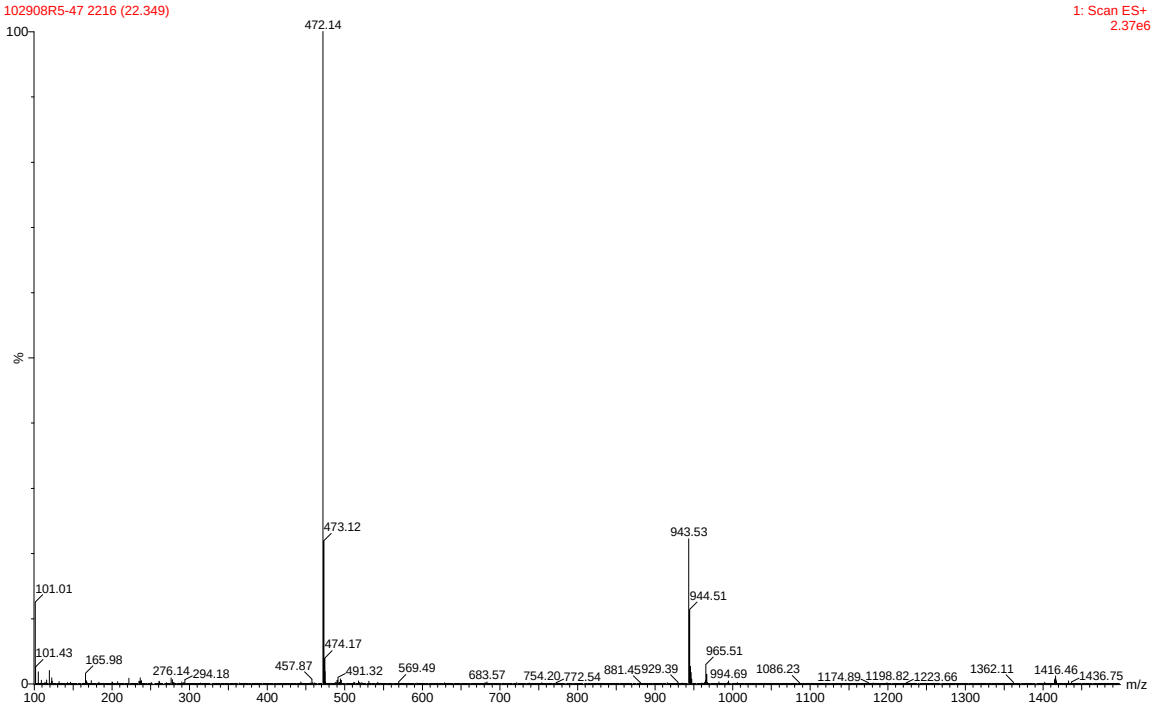


$C_{25}H_{21}N_5O_5$
Mol. Wt.: 471.46

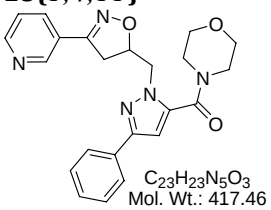




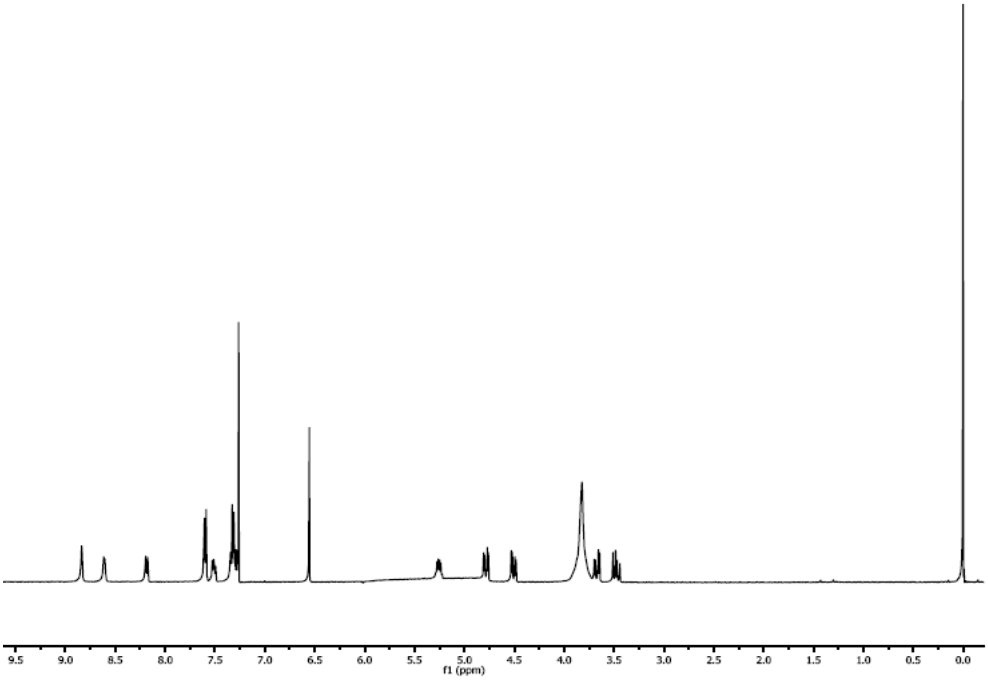

102908R5-47
2: Diode Array
214
Range: 2.654
Area
Time Height Area Area%
21.73 381642 75491.27 6.67
22.28 2503137 1056662.13 93.33
22.28
1056662
21.73
75491
AU
Time

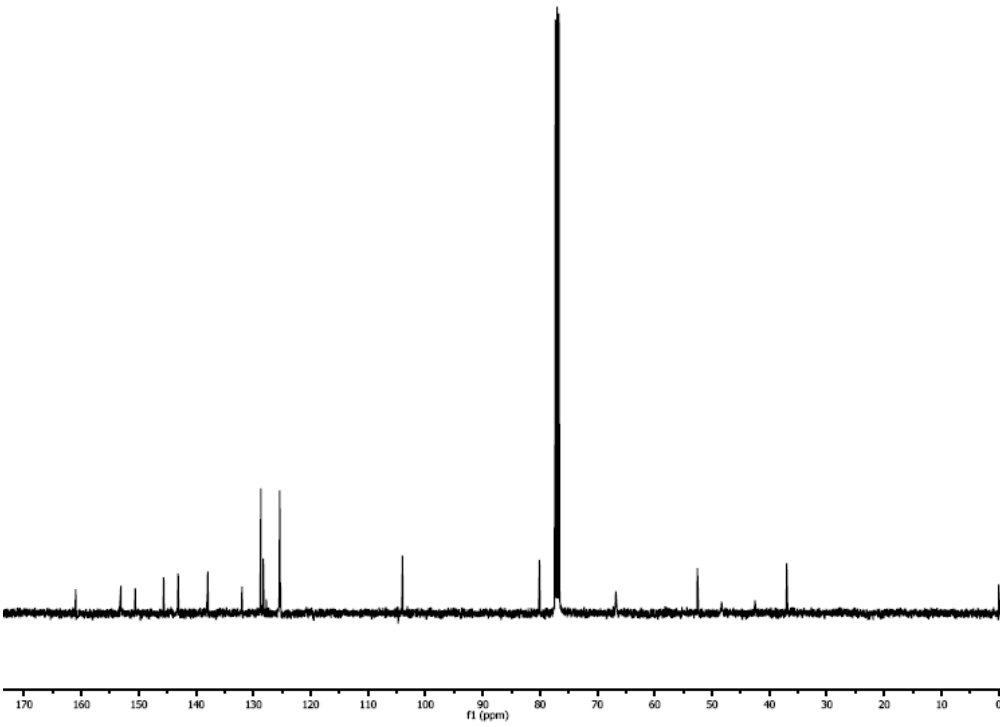

102908R5-47 2216 (22.349)
1: Scan ES+
2.37e6
472.14
473.12
943.53
944.51
101.01
101.43
165.98
276.14
294.18
457.87
474.17
491.32
569.49
683.57
754.20
772.54
881.45
929.39
965.51
994.69
1086.23
1174.89
1198.82
1223.66
1362.11
1416.46
1436.75
%
m/z

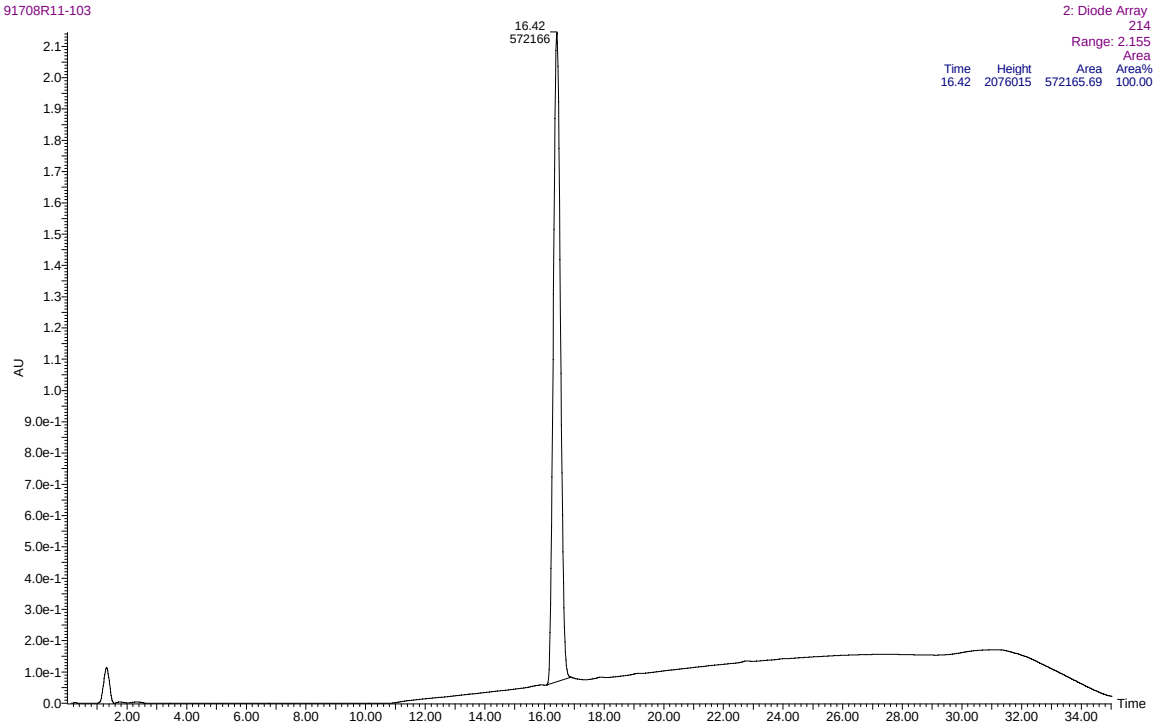
18{*1,4,11*}

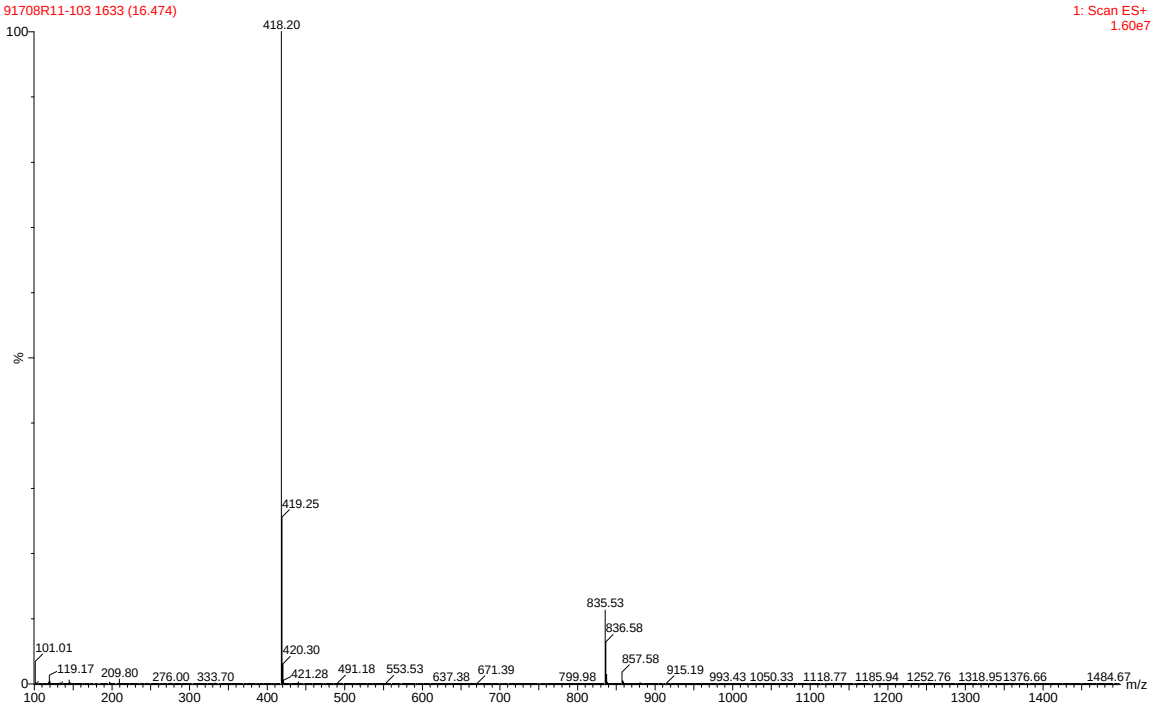


$C_{23}H_{23}N_5O_3$
Mol. Wt.: 417.46

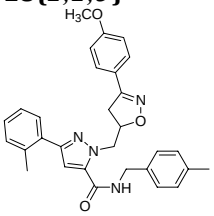




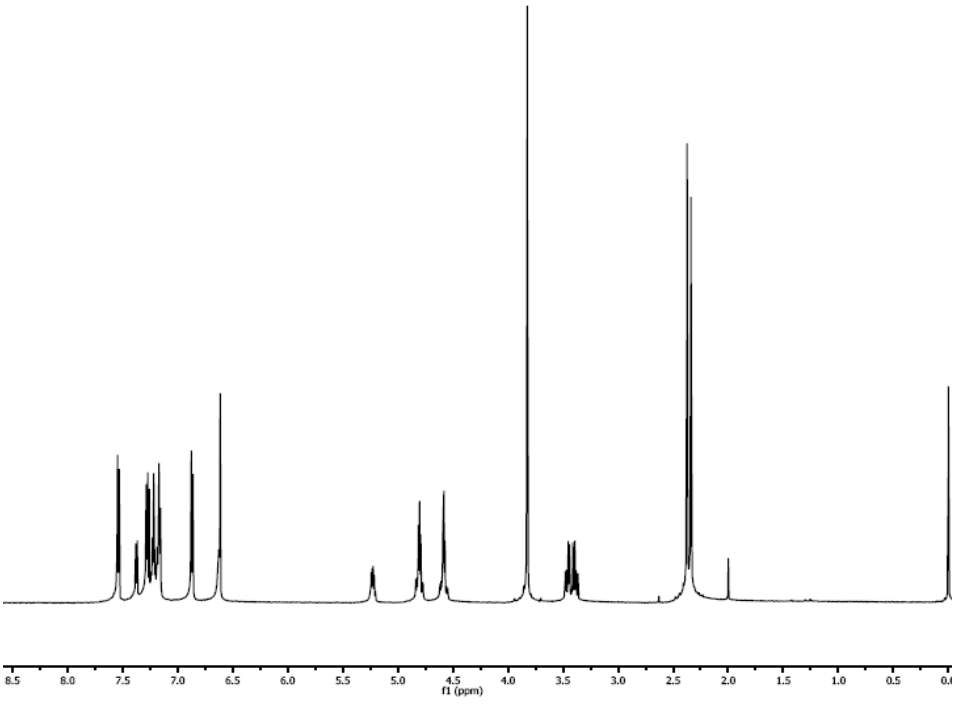

91708R11-103
2: Diode Array
214
Range: 2.155
Area
Time Height Area Area%
16.42 2076015 572165.69 100.00
16.42
572166
AU
Time

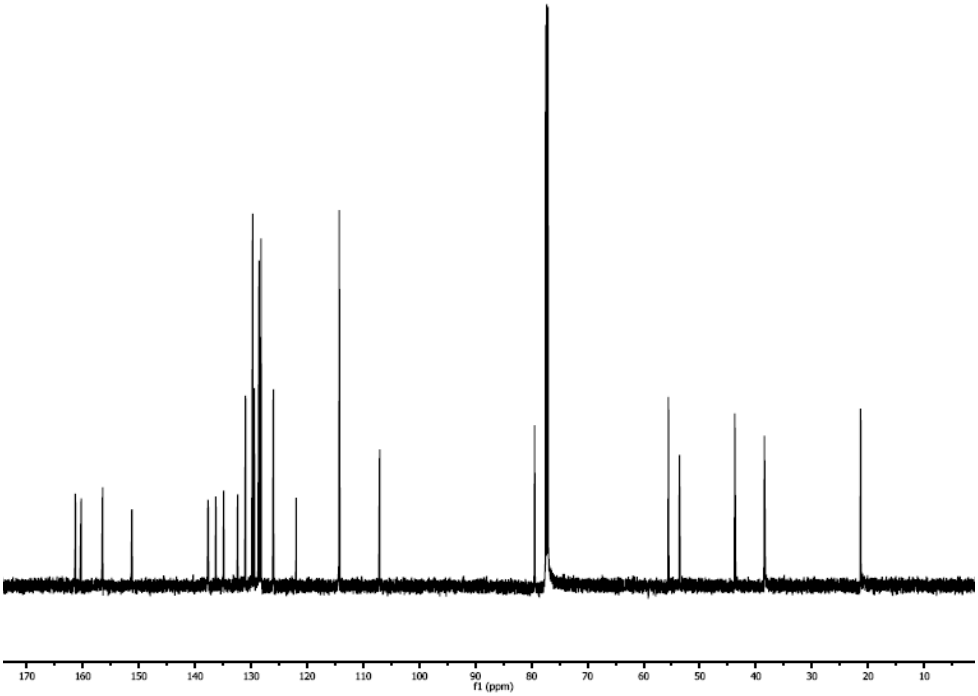

91708R11-103 1633 (16.474)
1: Scan ES+
1.60e7
418.20
419.25
835.53
836.58
857.58
101.01
119.17
209.80
276.00
333.70
420.30
421.28
491.18
553.53
637.38
671.39
799.98
915.19
993.43
1050.33
1118.77
1185.94
1252.76
1318.95
1376.66
1484.67
%
m/z

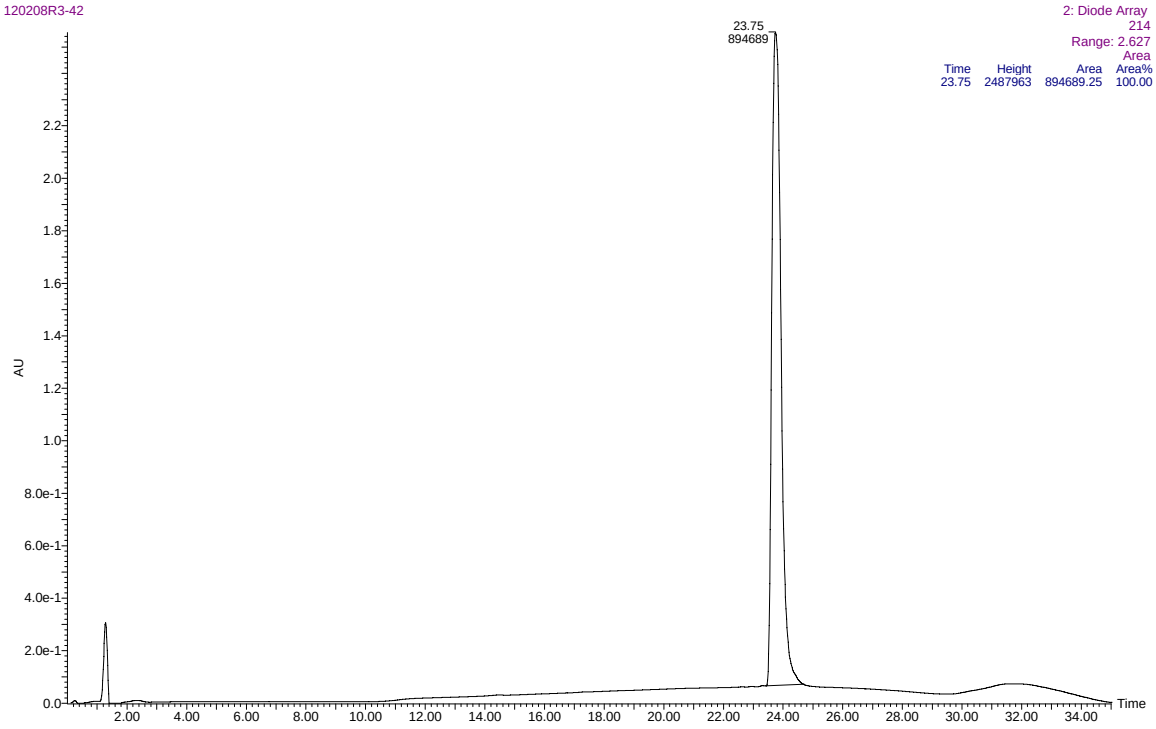
18{*2,2,3*}

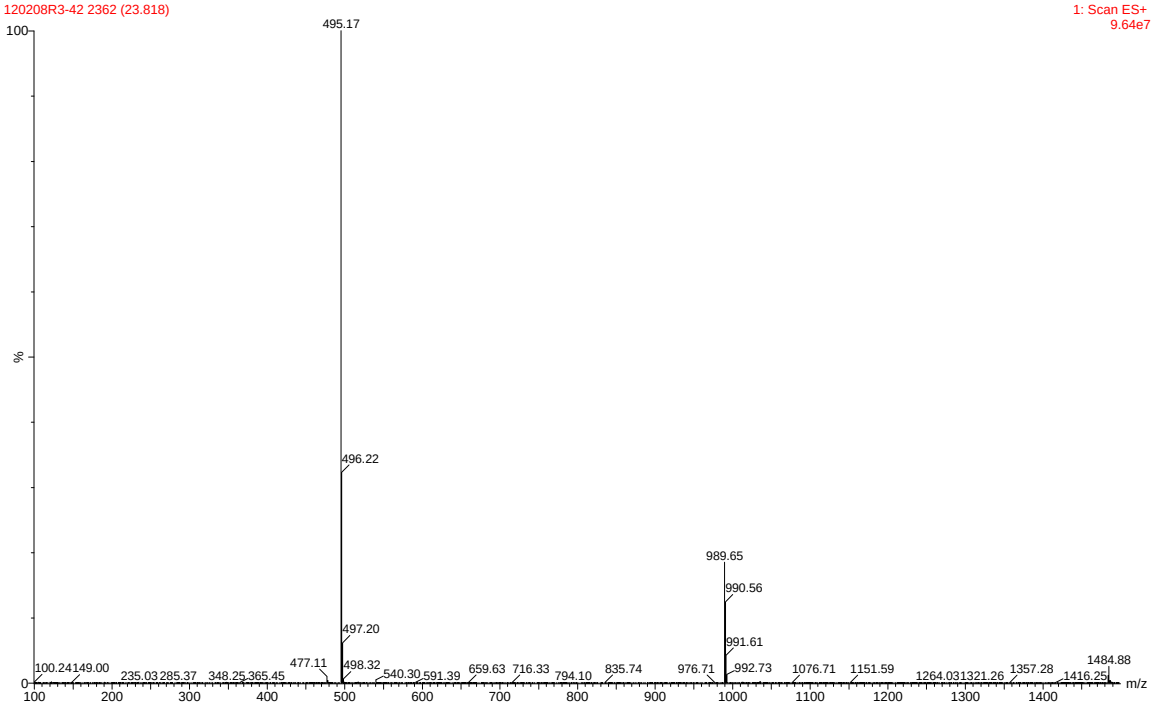


$C_{30}H_{30}N_4O_3$
Mol. Wt.: 494.58

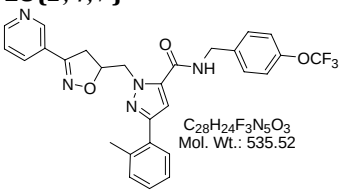




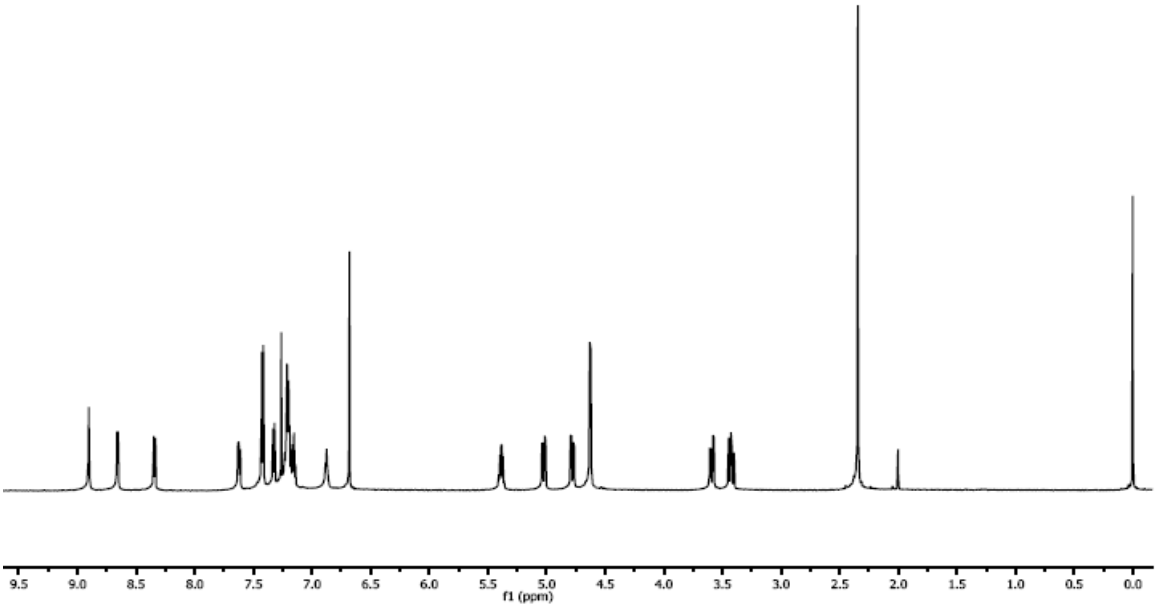

120208R3-42
2: Diode Array
214
Range: 2.627
Area
Time Height Area Area%
23.75 2487963 894689.25 100.00
23.75
894689
AU
Time

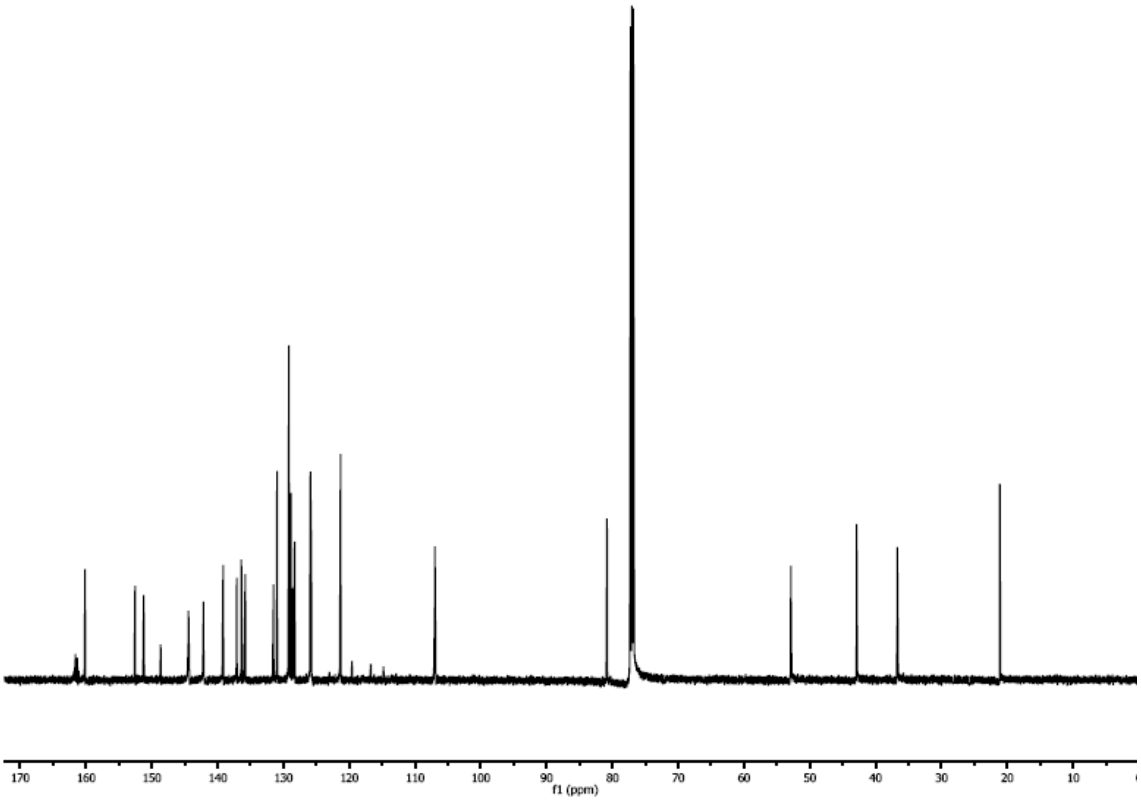

120208R3-42 2362 (23.818)
1: Scan ES+
9.64e7
%
m/z
495.17
496.22
497.20
989.65
990.56
991.61

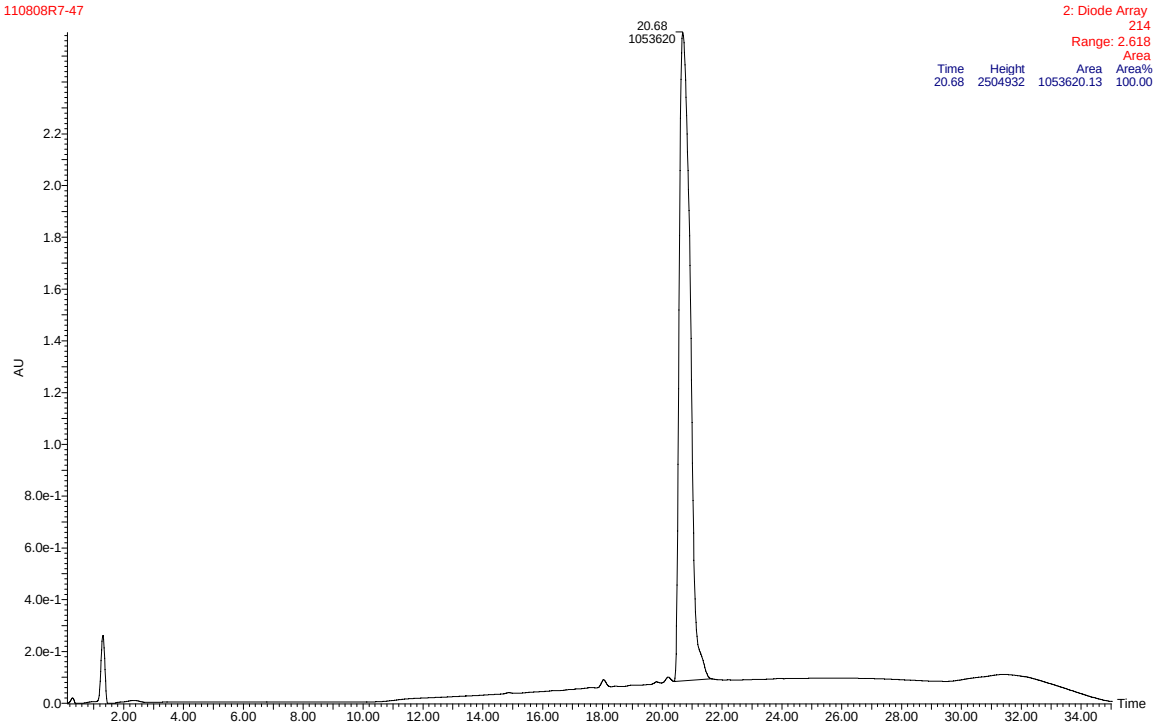
18{*2,4,7*}

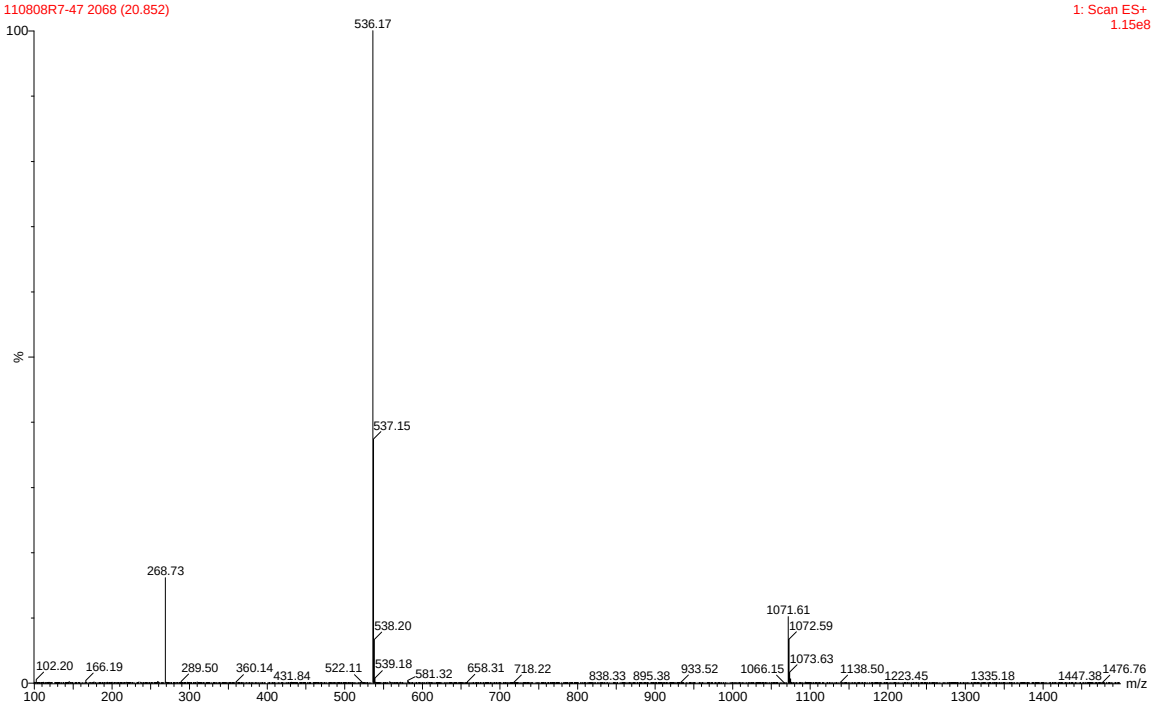


$C_{28}H_{24}F_3N_5O_3$
Mol. Wt.: 535.52

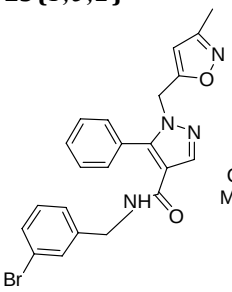




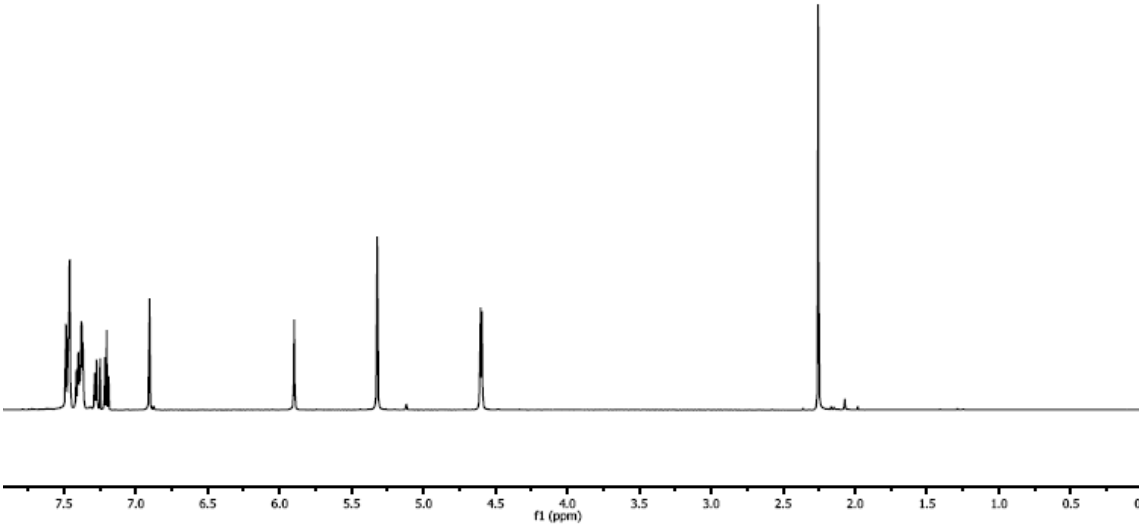

110808R7-47
2: Diode Array
214
Range: 2.618
Area
Time Height Area Area%
20.68 2504932 1053620.13 100.00
20.68
1053620
AU
Time

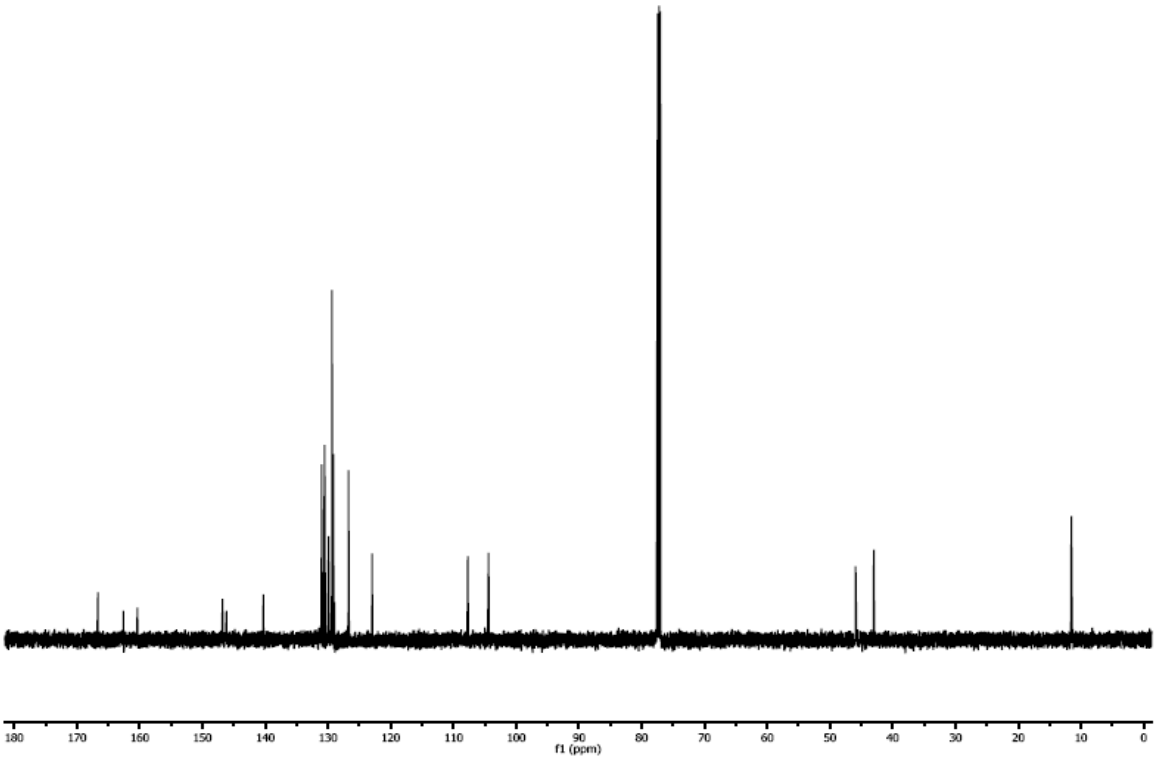

110808R7-47 2068 (20.852)
1: Scan ES+
1.15e8
%
m/z
536.17
537.15
538.20
539.18
268.73
1071.61
1072.59
1073.63
102.20
166.19
289.50
360.14
431.84
522.11
581.32
658.31
718.22
838.33
895.38
933.52
1066.15
1138.50
1223.45
1335.18
1447.38
1476.76

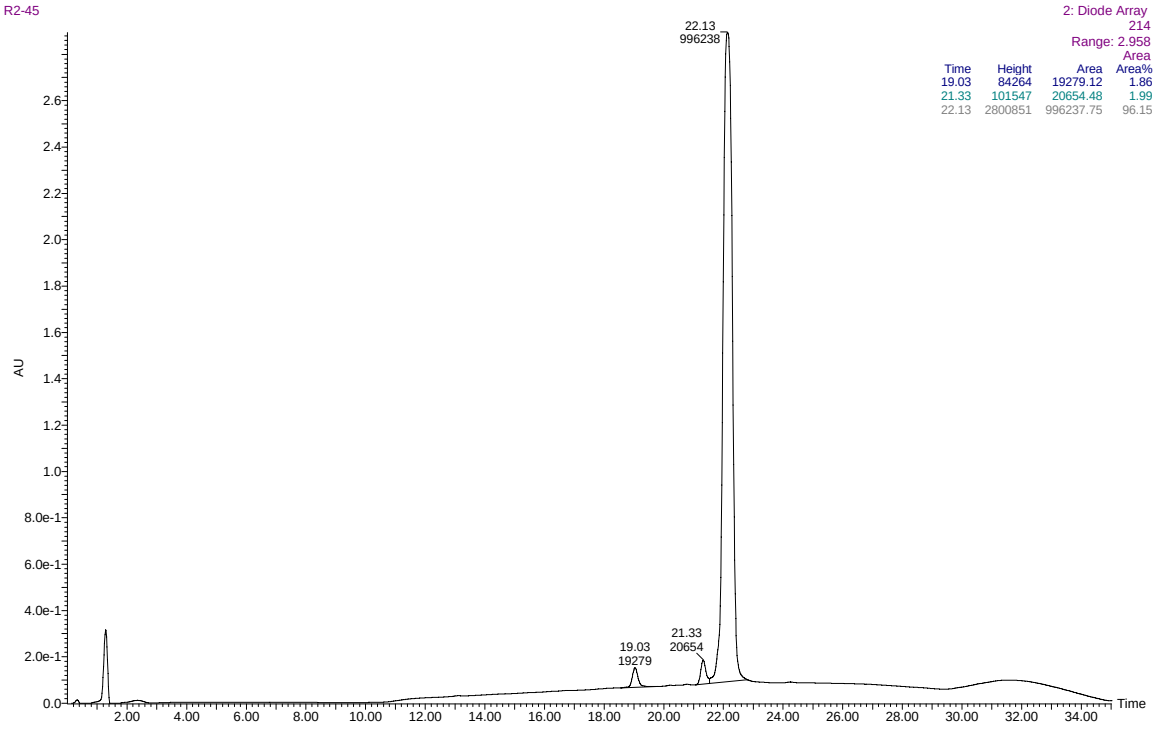
19{*1,5,2*}

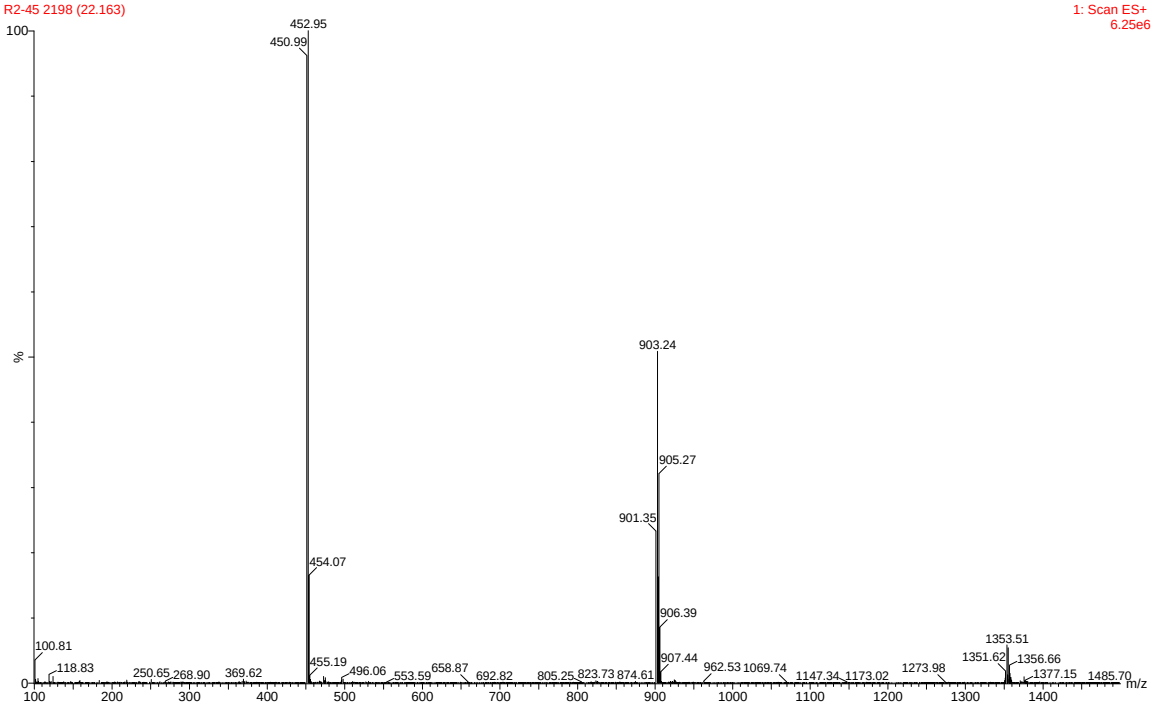


$C_{22}H_{19}BrN_4O_2$
Mol. Wt.: 451.32

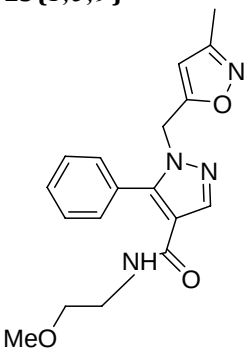




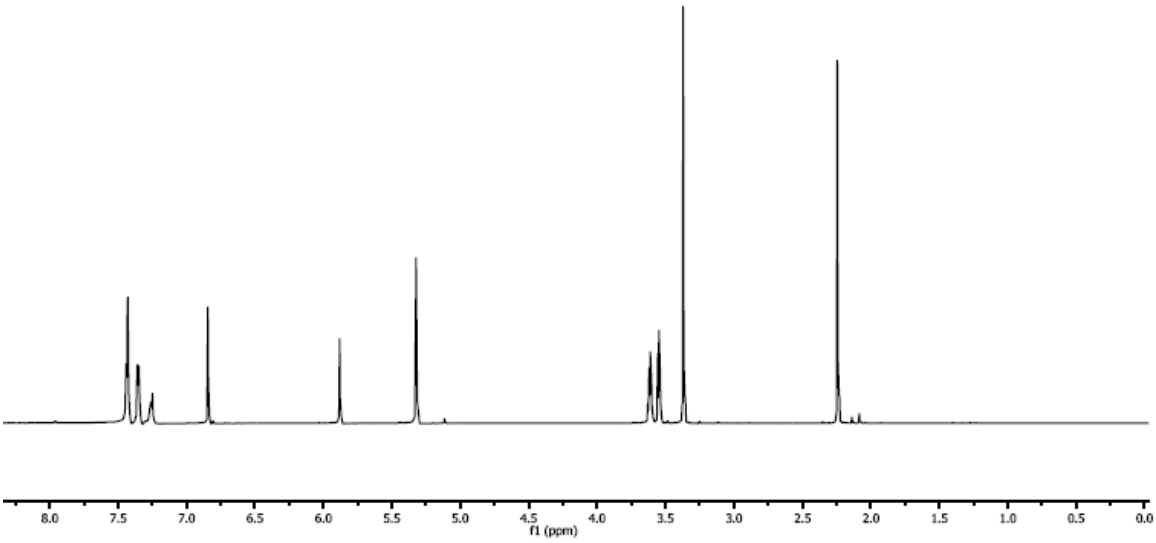

R2-45
2: Diode Array
214
Range: 2.958
Area
Time Height Area Area%
19.03 84264 19279.12 1.86
21.33 101547 20654.48 1.99
22.13 2800851 996237.75 96.15
22.13
996238
19.03
19279
21.33
20654
AU
Time

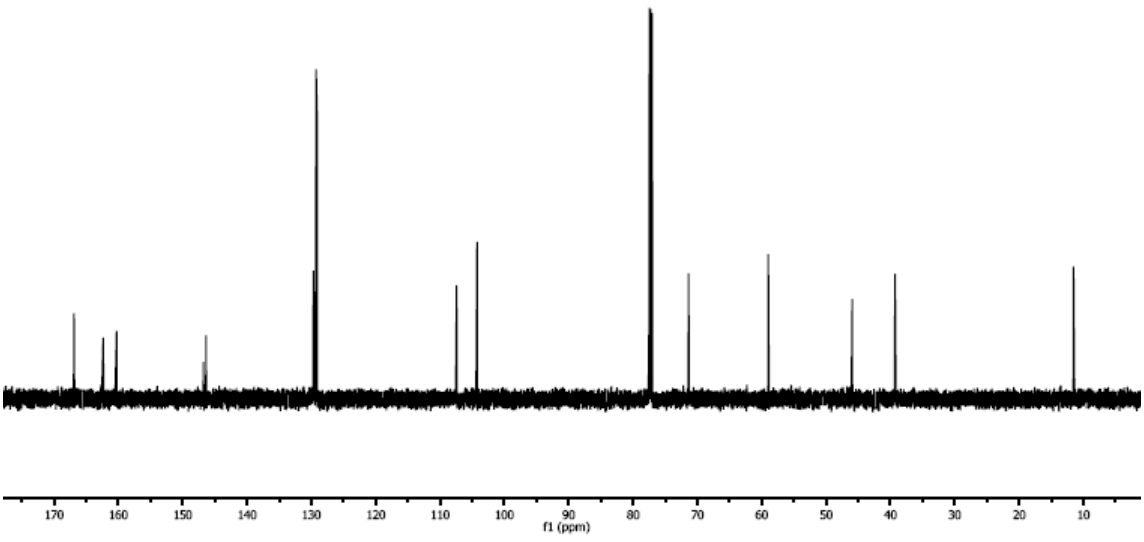

R2-45 2198 (22.163)
1: Scan ES+
6.25e6
452.95
450.99
903.24
905.27
901.35
454.07
906.39
907.44
100.81
118.83
250.65
268.90
369.62
455.19
496.06
553.59
658.87
692.82
805.25
823.73
874.61
962.53
1069.74
1147.34
1173.02
1273.98
1353.51
1351.62
1356.66
1377.15
1485.70
%
m/z

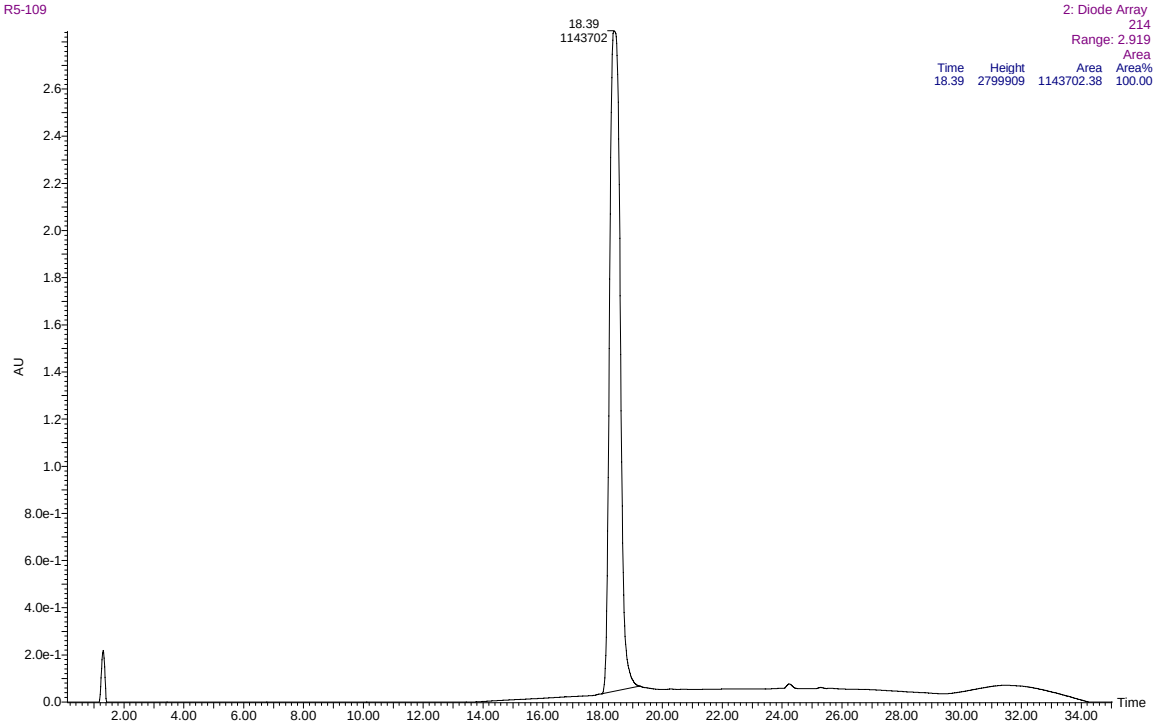
19{*1,5,9*}

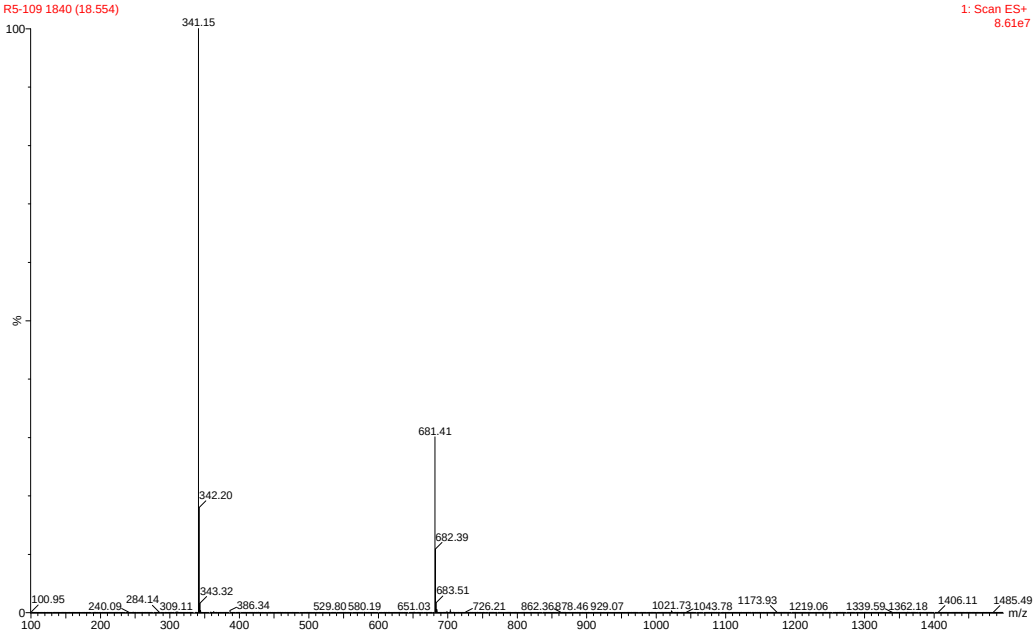


$C_{18}H_{20}N_4O_3$
Mol. Wt.: 340.38

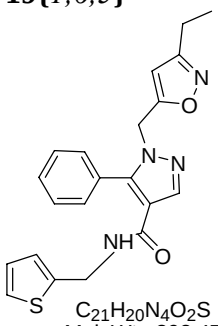




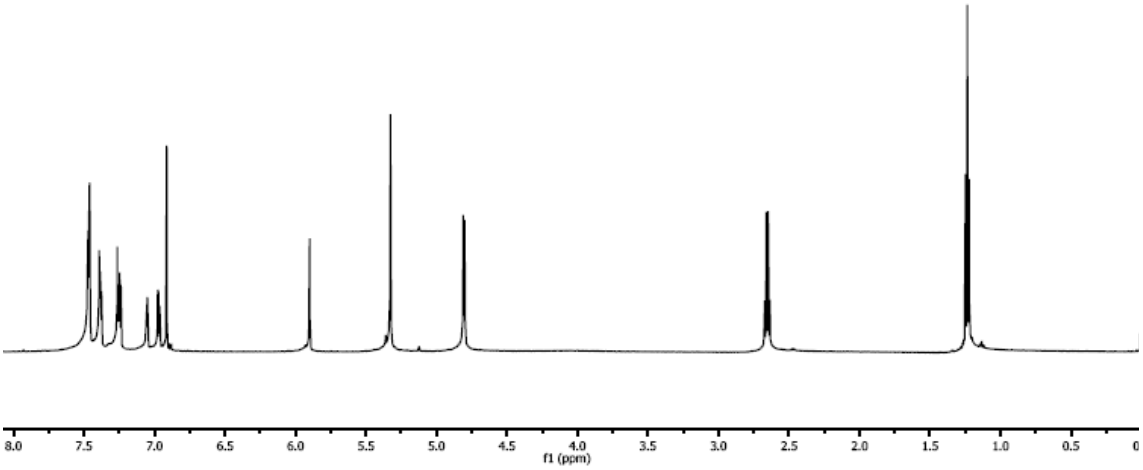

R5-109
2: Diode Array
214
Range: 2.919
Area
Time Height Area Area%
18.39 2799909 1143702.38 100.00
18.39
1143702
AU
Time

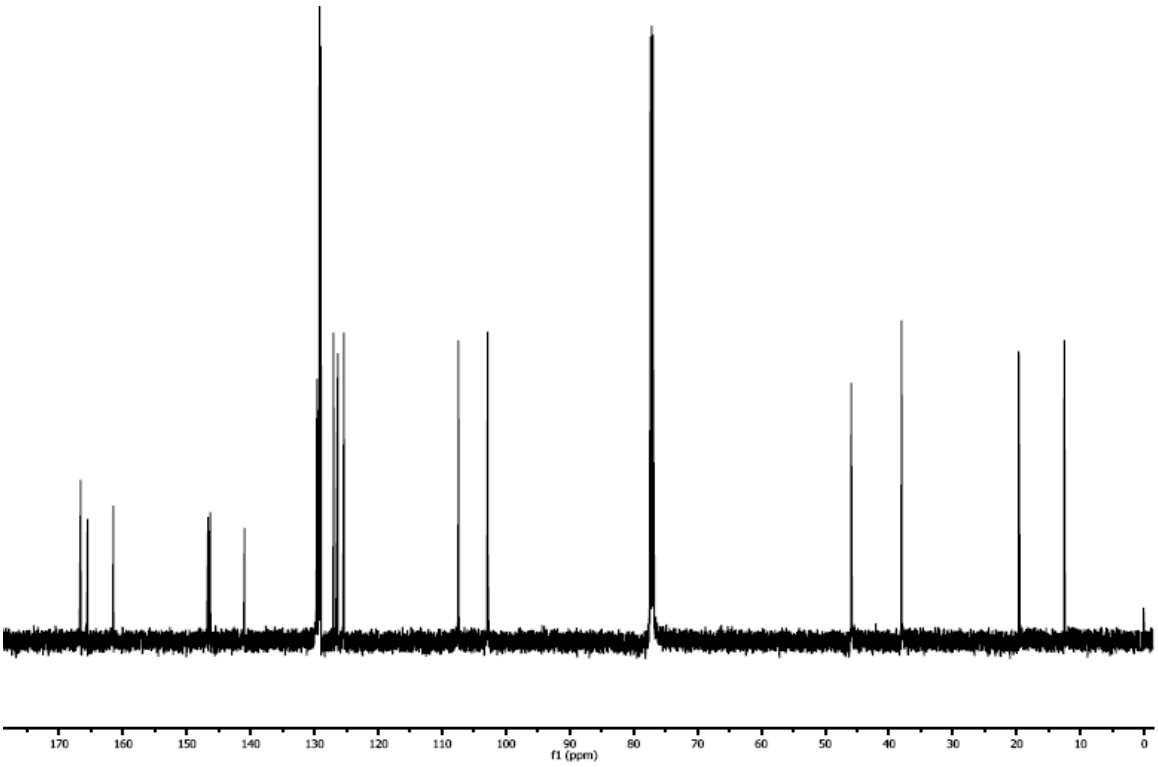

R5-109 1840 (18.554)
1: Scan ES+
8.61e7
%
m/z
341.15
681.41
342.20
682.39
683.51
343.32

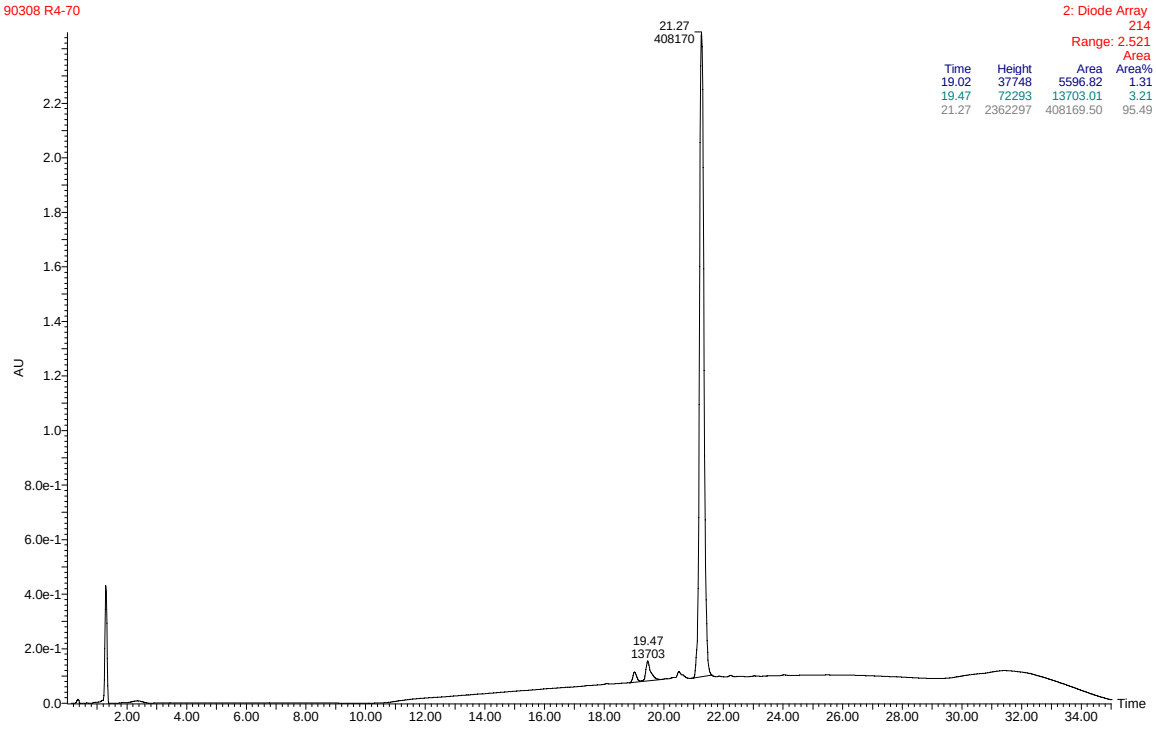
19{*1,6,5*}

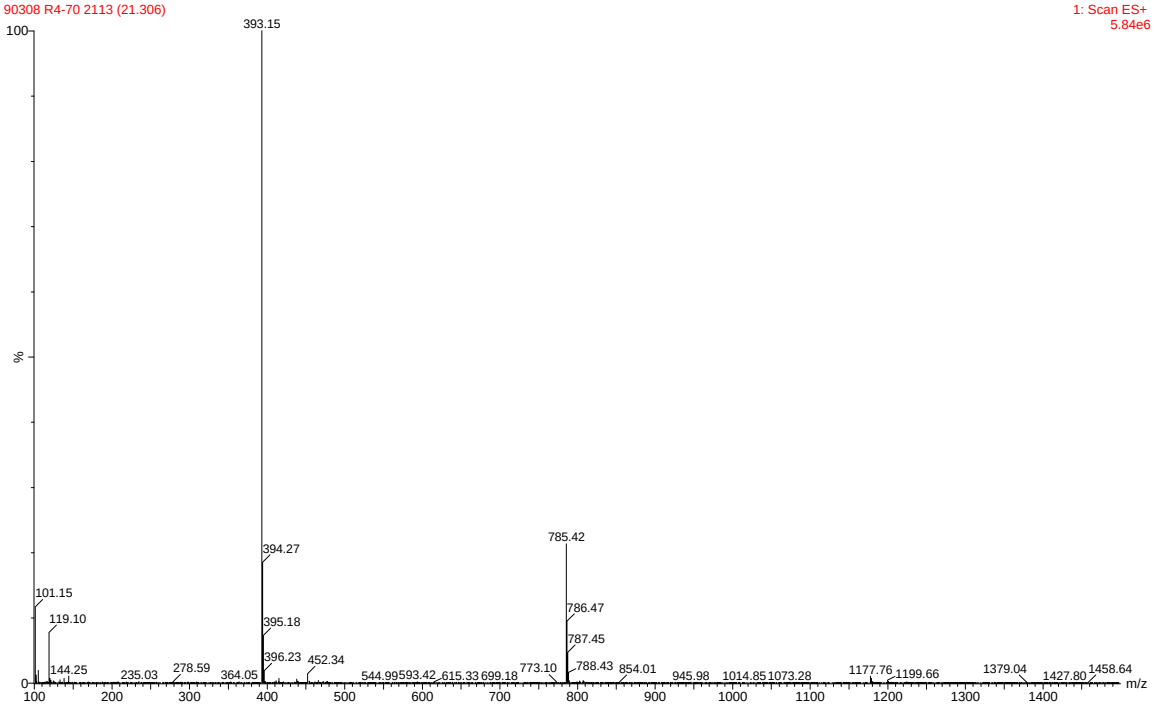


$C_{21}H_{20}N_4O_2S$
Mol. Wt.: 392.47

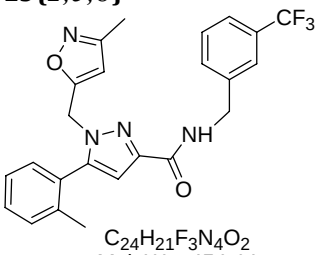




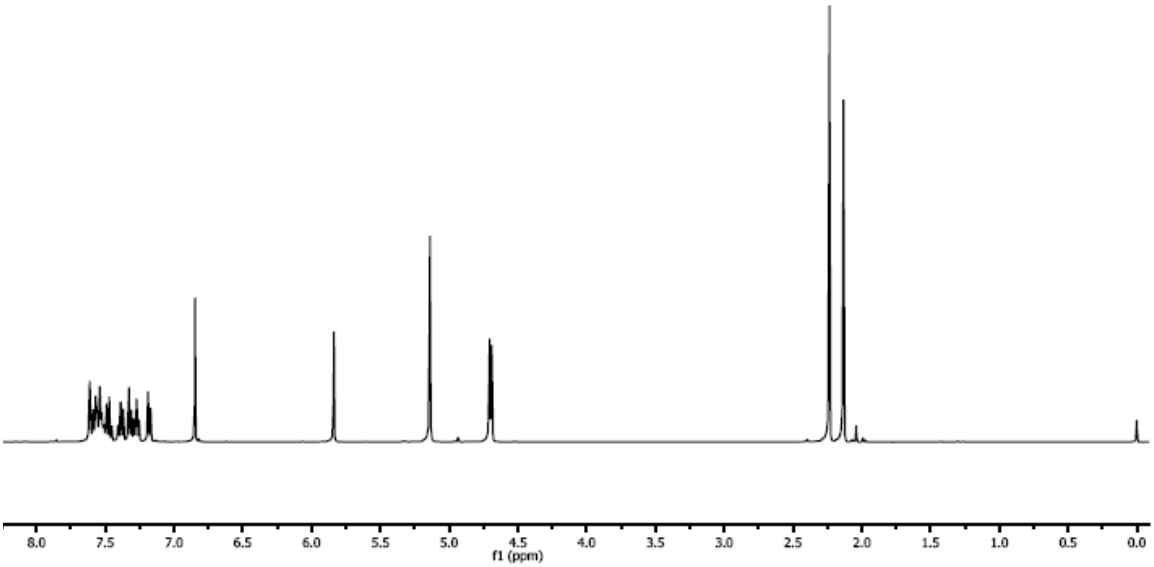

90308 R4-70
2: Diode Array
214
Range: 2.521
Area
Time Height Area Area%
19.02 37748 5596.82 1.31
19.47 72293 13703.01 3.21
21.27 2362297 408169.50 95.49
21.27
408170
19.47
13703
AU
Time

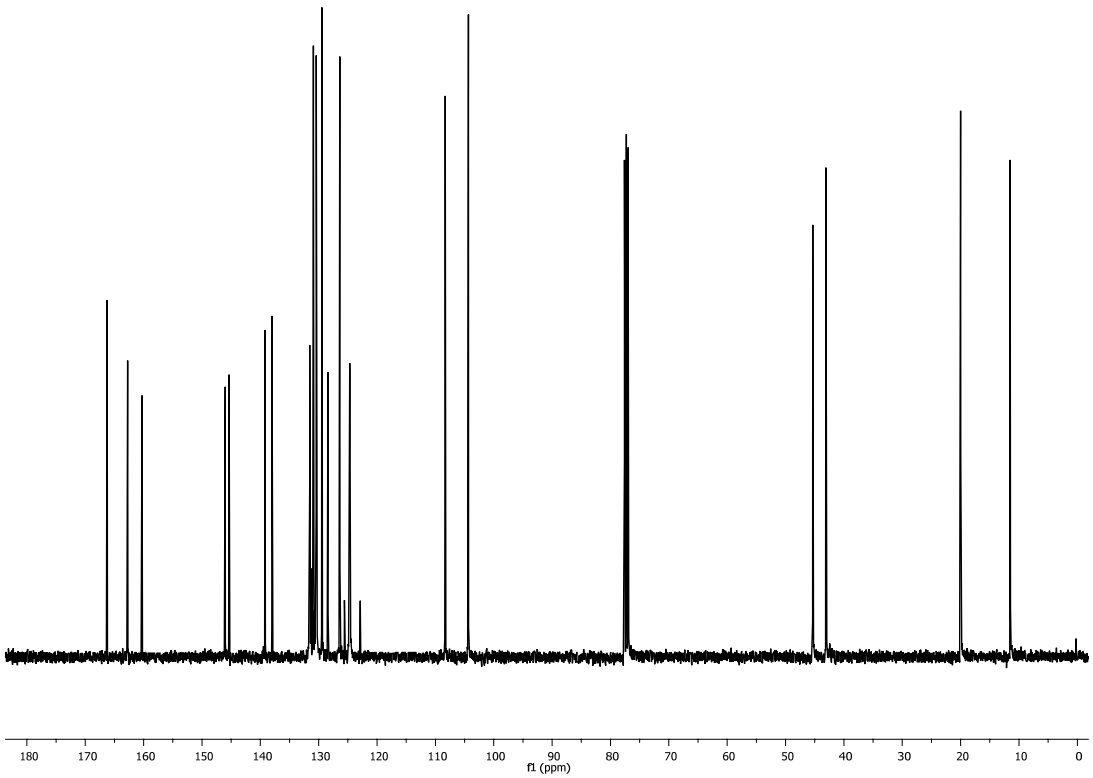

90308 R4-70 2113 (21.306)
1: Scan ES+
5.84e6
393.15
394.27
785.42
786.47
787.45
101.15
119.10
395.18
396.23
452.34
144.25
235.03
278.59
364.05
544.99
593.42
615.33
699.18
773.10
788.43
854.01
945.98
1014.85
1073.28
1177.76
1199.66
1379.04
1427.80
1458.64
%
m/z

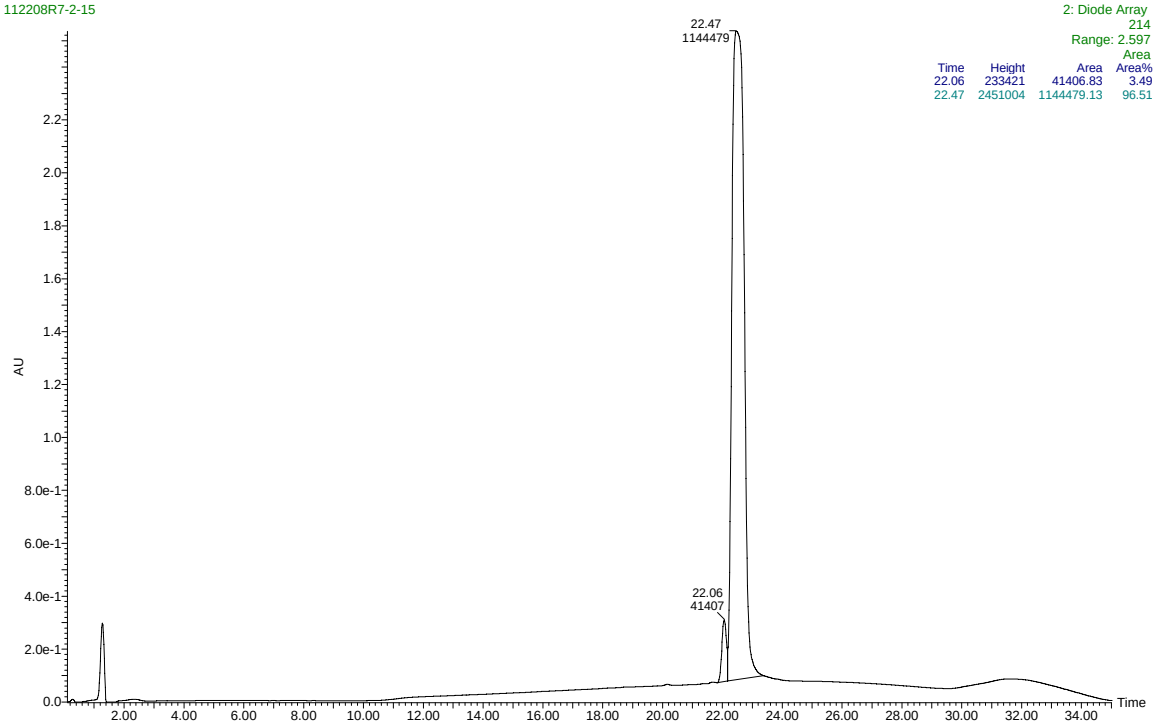
19{*2,5,8*}

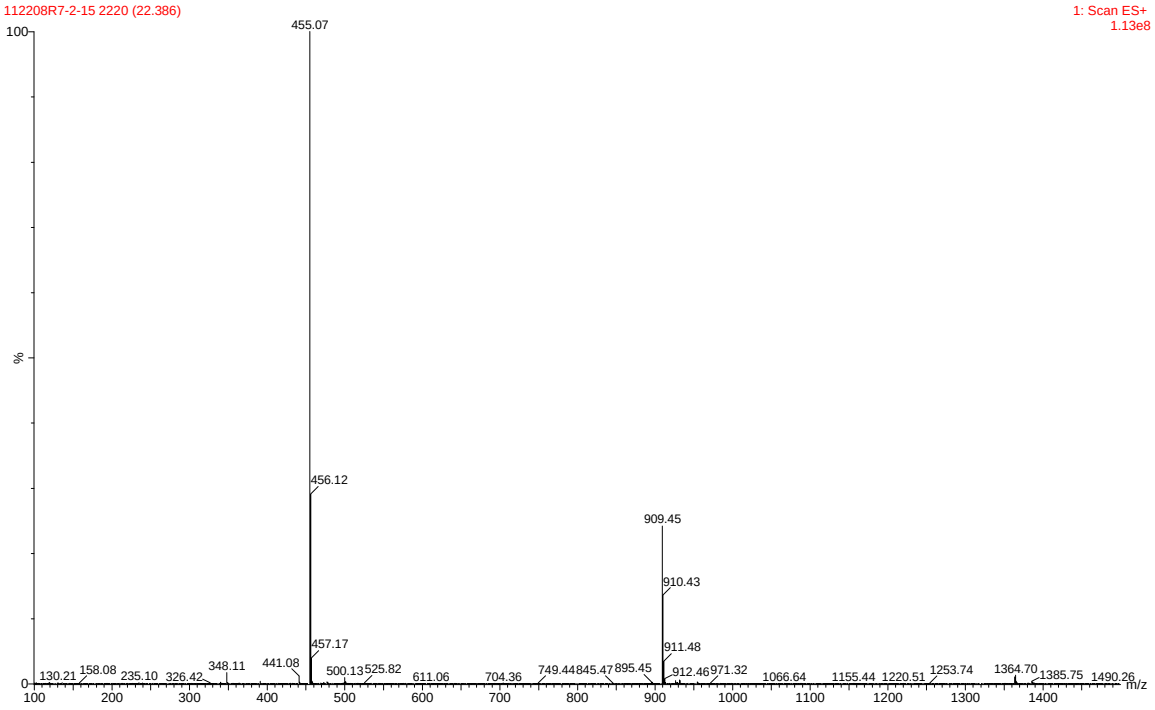


$C_{24}H_{21}F_3N_4O_2$
Mol. Wt.: 454.44

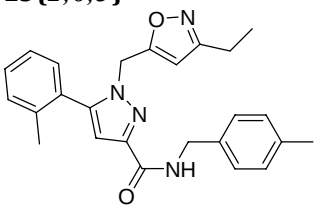




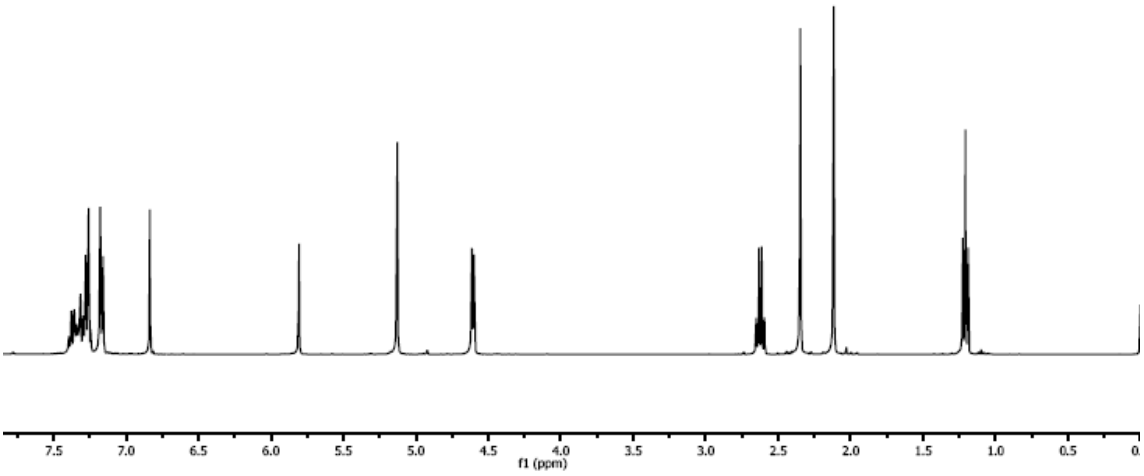

112208R7-2-15
2: Diode Array
214
Range: 2.597
Area
Time Height Area Area%
22.06 233421 41406.83 3.49
22.47 2451004 1144479.13 96.51
22.47
1144479
22.06
41407
AU
Time

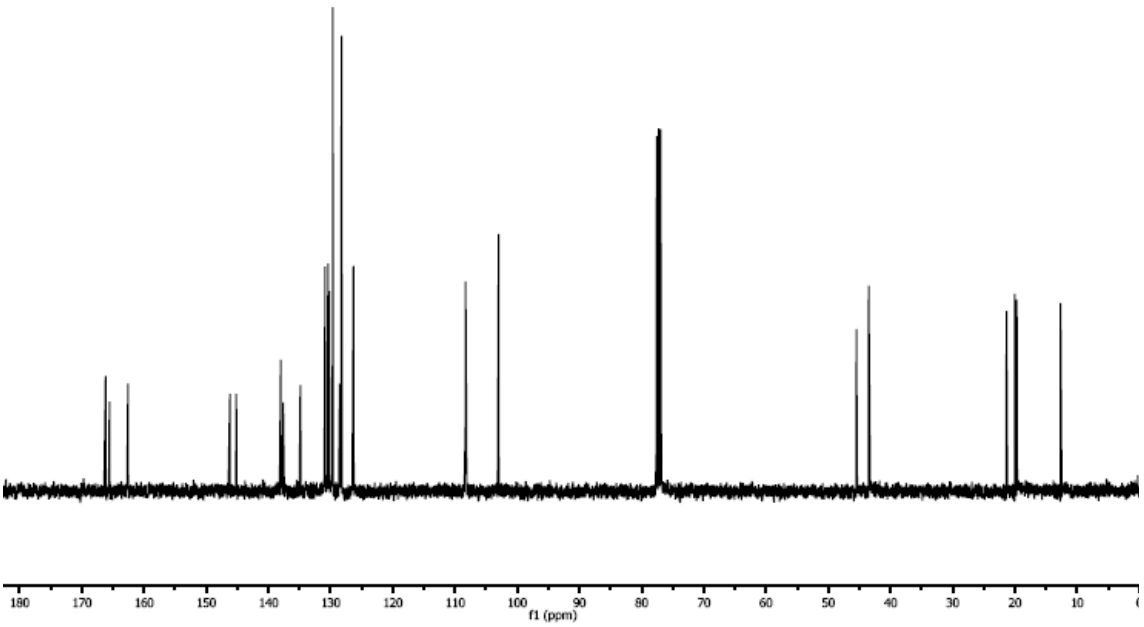

112208R7-2-15 2220 (22.386)
1: Scan ES+
1.13e8
455.07
456.12
909.45
910.43
457.17
911.48
%
m/z

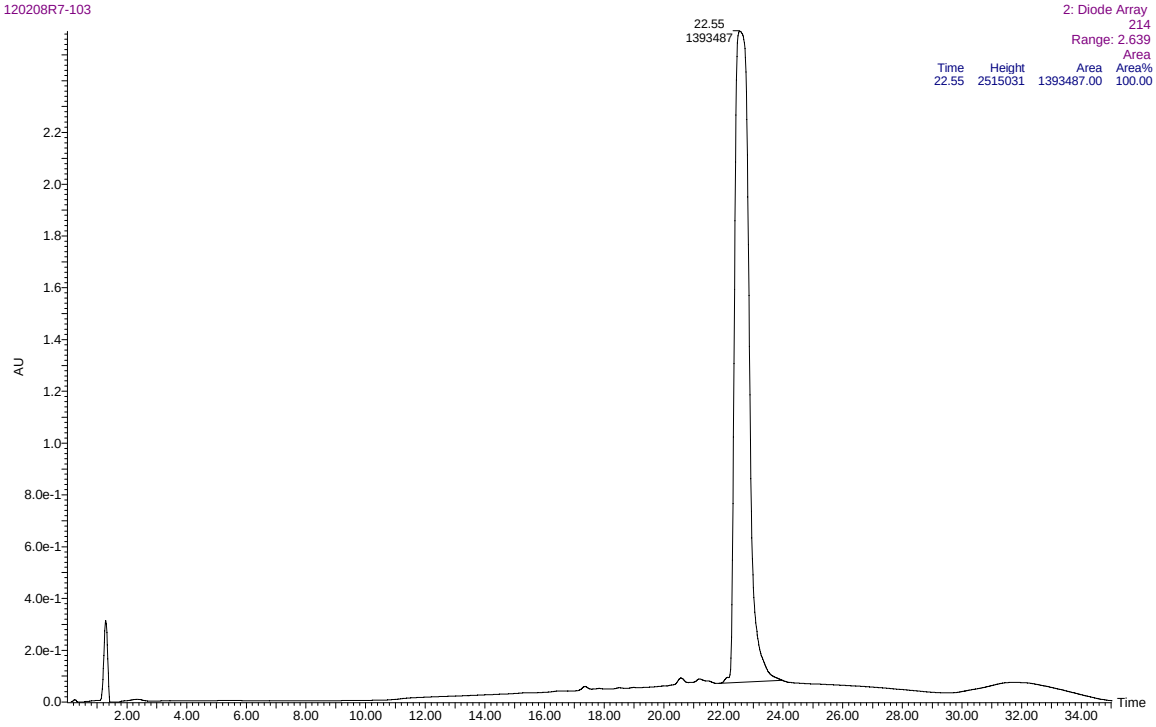
19{*2,6,3*}

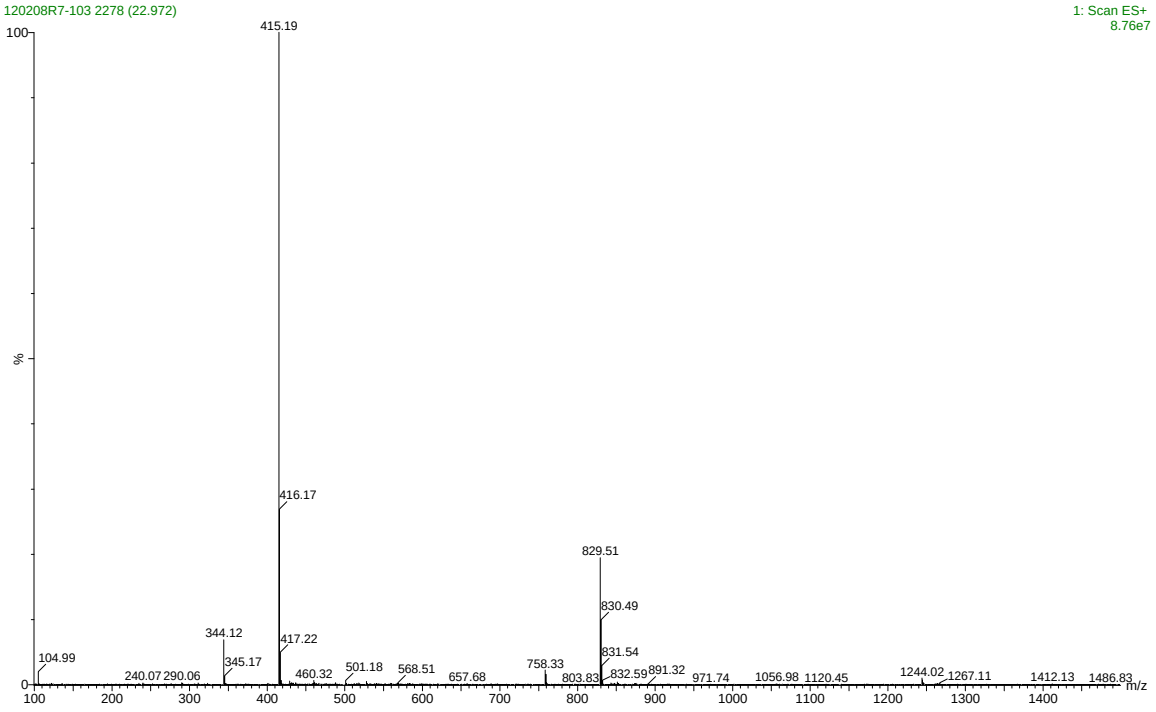


$C_{25}H_{26}N_4O_2$
Mol. Wt.: 414.50

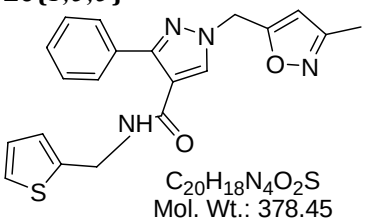




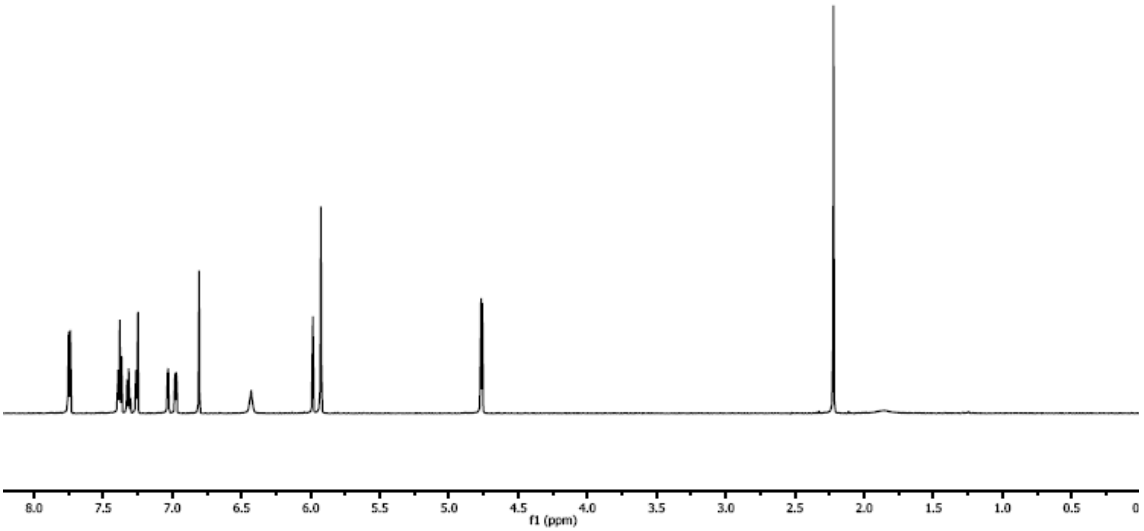

120208R7-103
2: Diode Array
214
Range: 2.639
Area
Time Height Area Area%
22.55 2515031 1393487.00 100.00
22.55
1393487
AU
Time

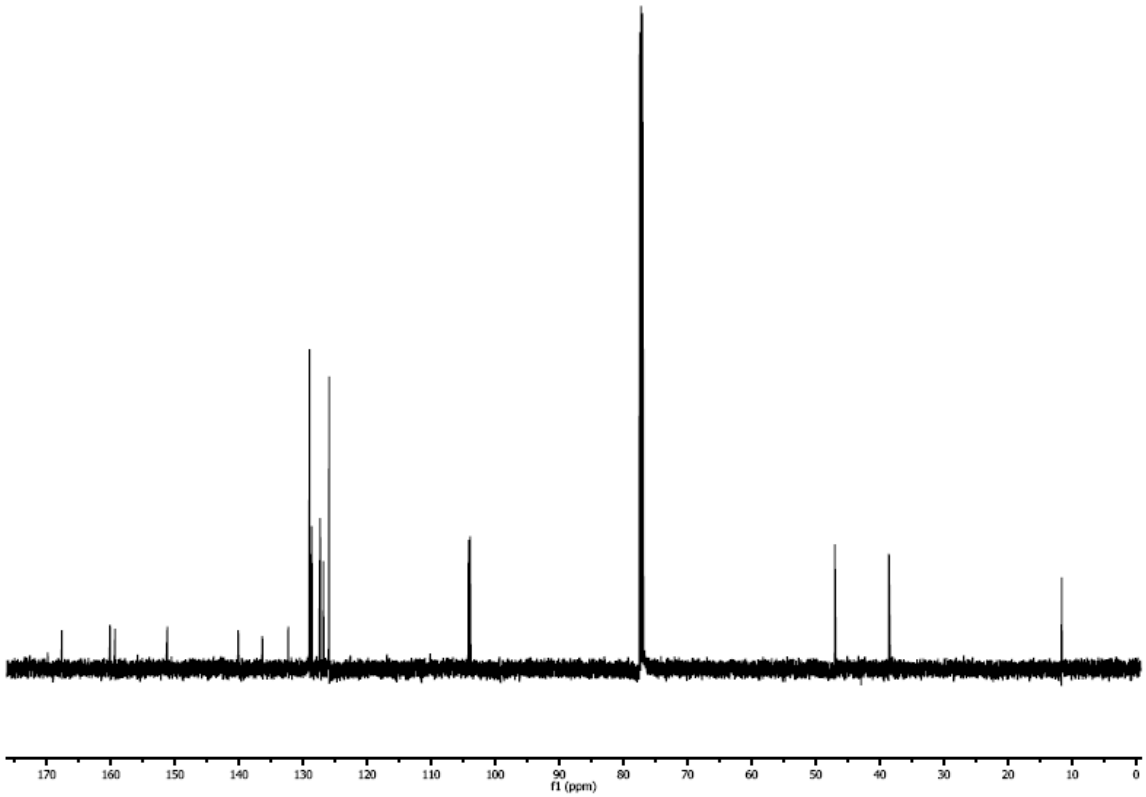

120208R7-103 2278 (22.972)
1: Scan ES+
8.76e7
%
m/z
415.19
416.17
829.51
830.49
831.54
344.12
417.22
104.99
345.17
240.07
290.06
460.32
501.18
568.51
657.68
758.33
803.83
832.59
891.32
971.74
1056.98
1120.45
1244.02
1267.11
1412.13
1486.83

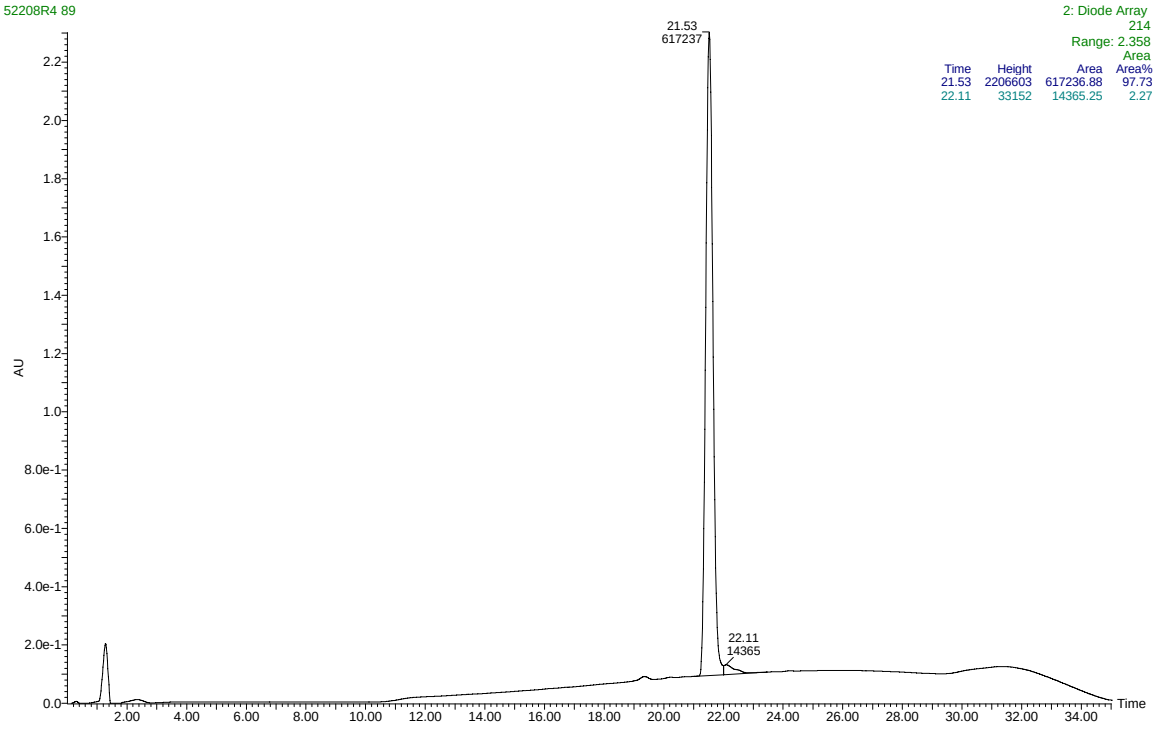
20{*1,5,5*}

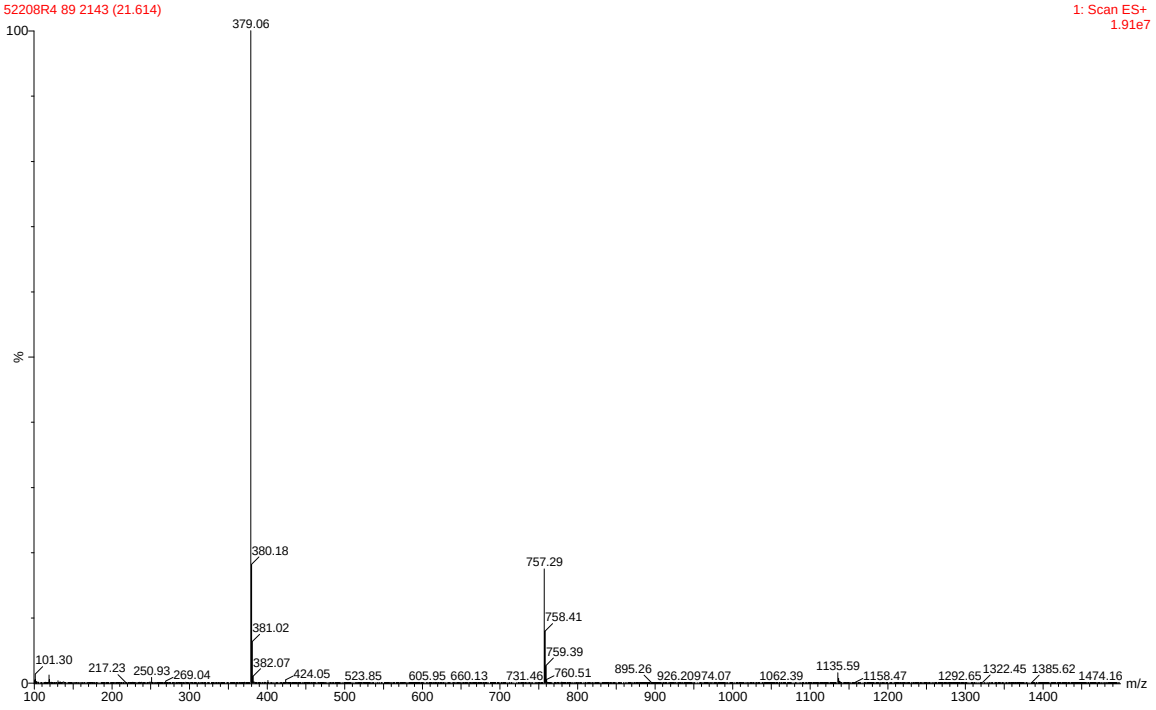


$C_{20}H_{18}N_4O_2S$
Mol. Wt.: 378.45

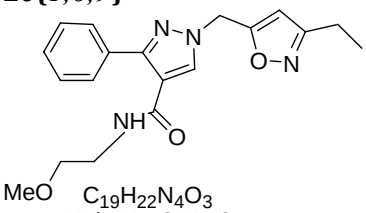




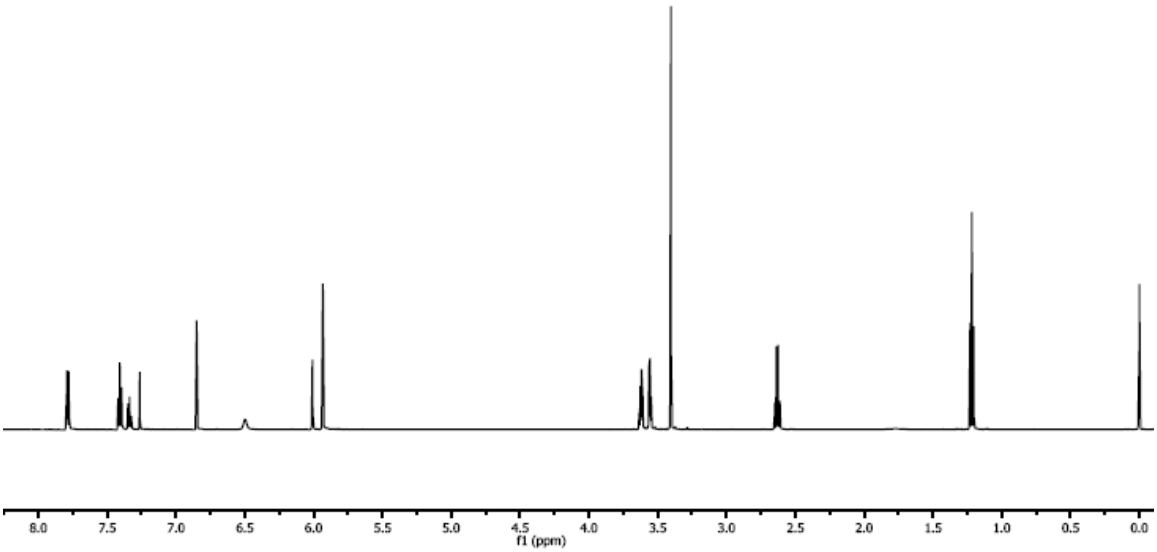

52208R4 89
2: Diode Array
214
Range: 2.358
Area
Time Height Area Area%
21.53 2206603 617236.88 97.73
22.11 33152 14365.25 2.27
21.53
617237
22.11
14365
AU
Time

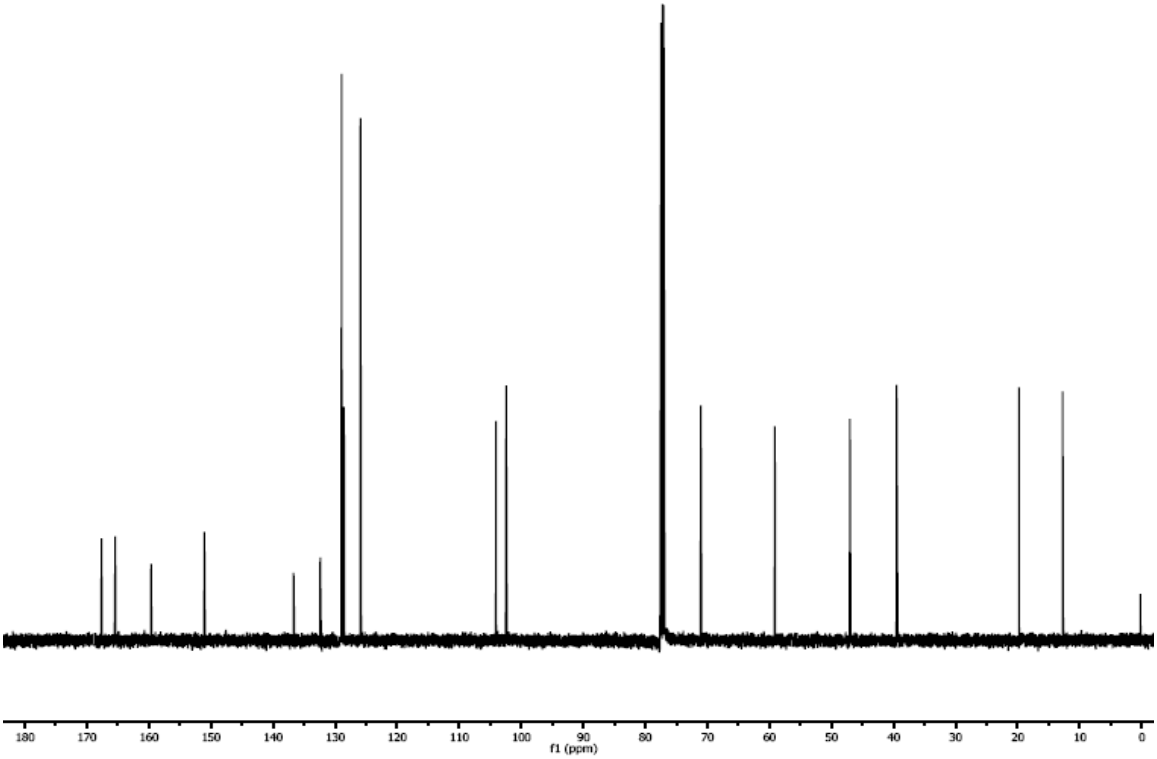

52208R4 89 2143 (21.614)
1: Scan ES+
1.91e7
379.06
380.18
381.02
382.07
757.29
758.41
759.39
760.51
%
m/z

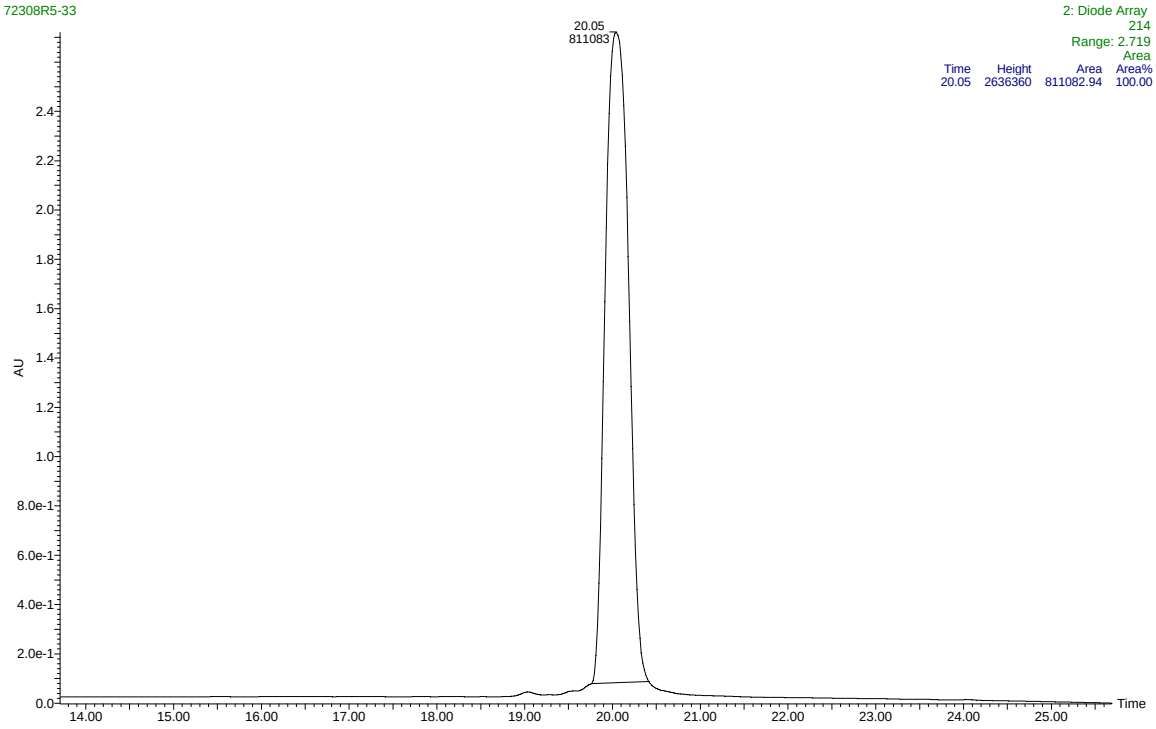
20{*1,6,9*}

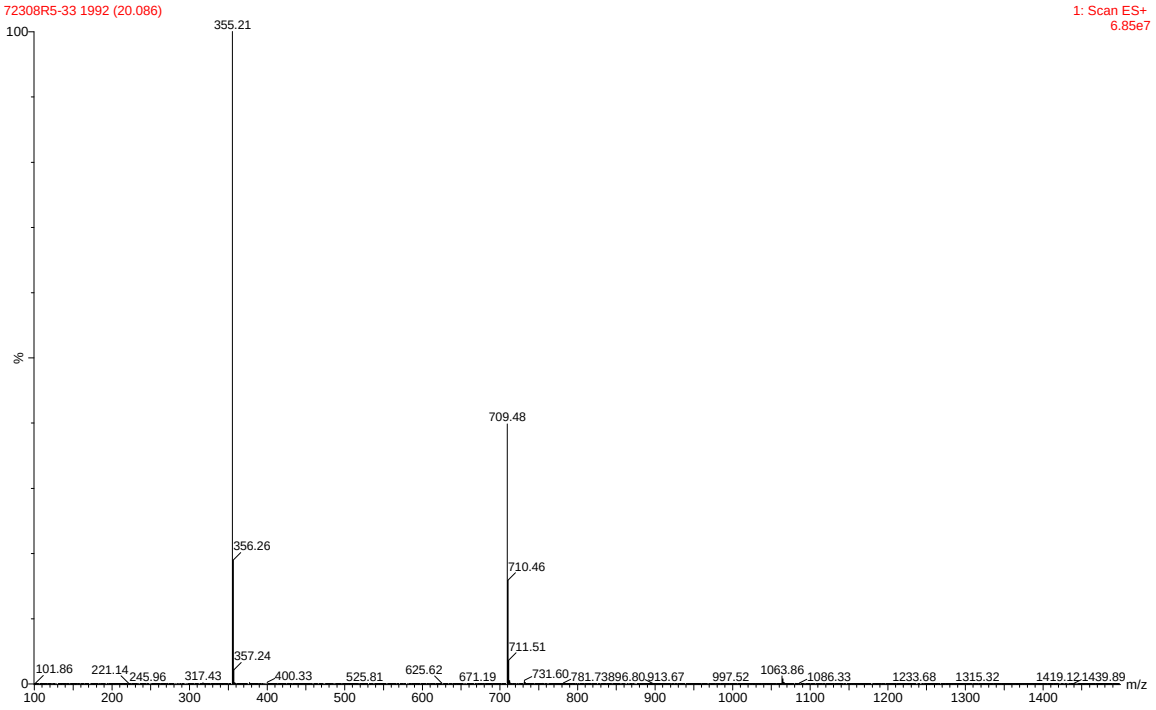


$C_{19}H_{22}N_4O_3$
Mol. Wt.: 354.40

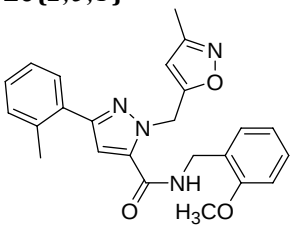




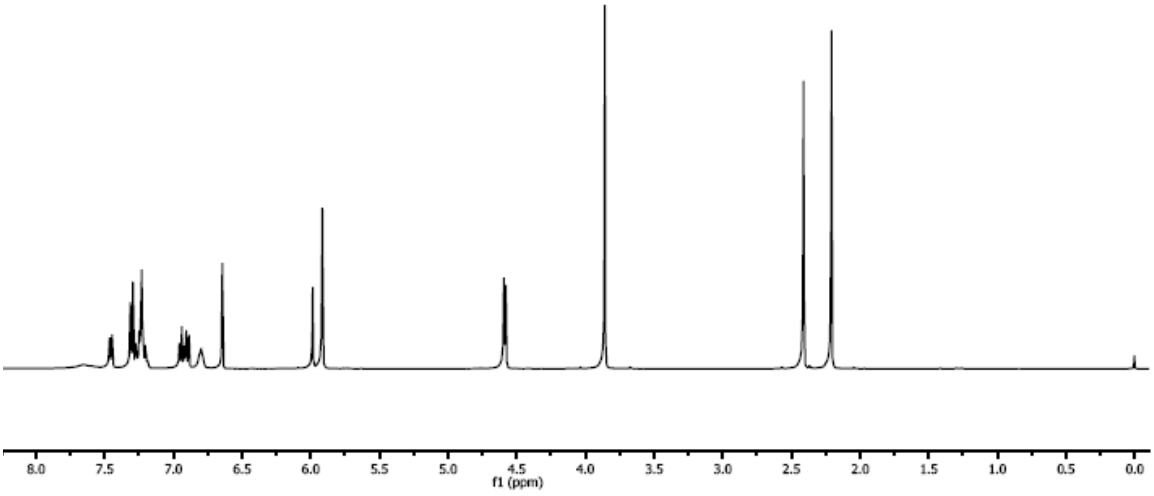

72308R5-33
2: Diode Array
214
Range: 2.719
Area
Time Height Area Area%
20.05 2636360 811082.94 100.00
20.05
811083
AU
Time

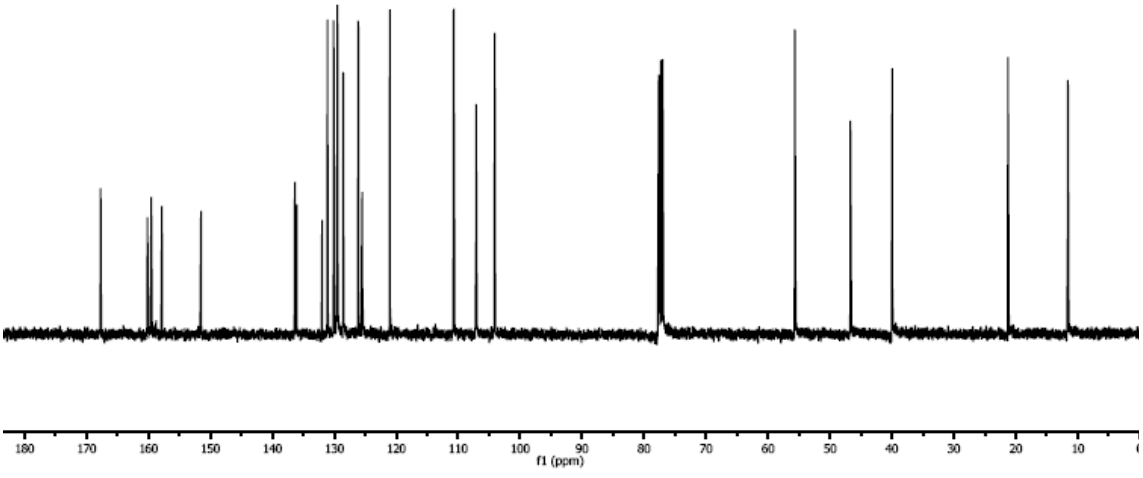

72308R5-33 1992 (20.086)
1: Scan ES+
6.85e7
355.21
709.48
356.26
710.46
357.24
711.51
%
m/z

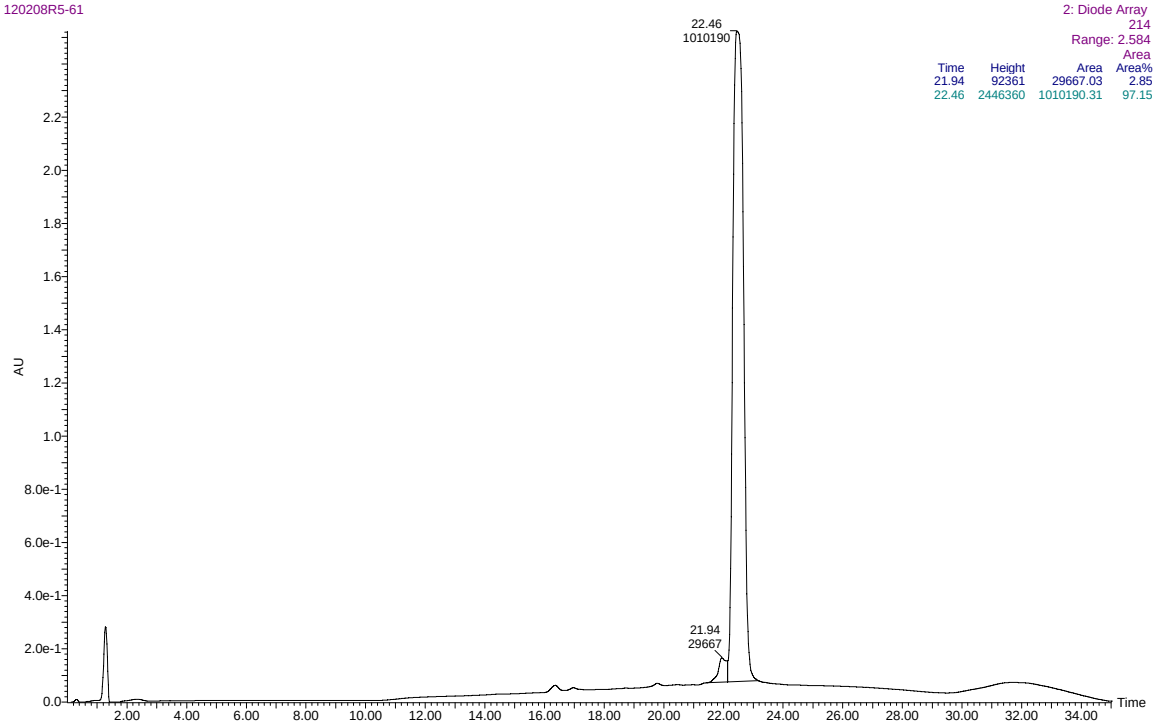
20{*2,5,1*}

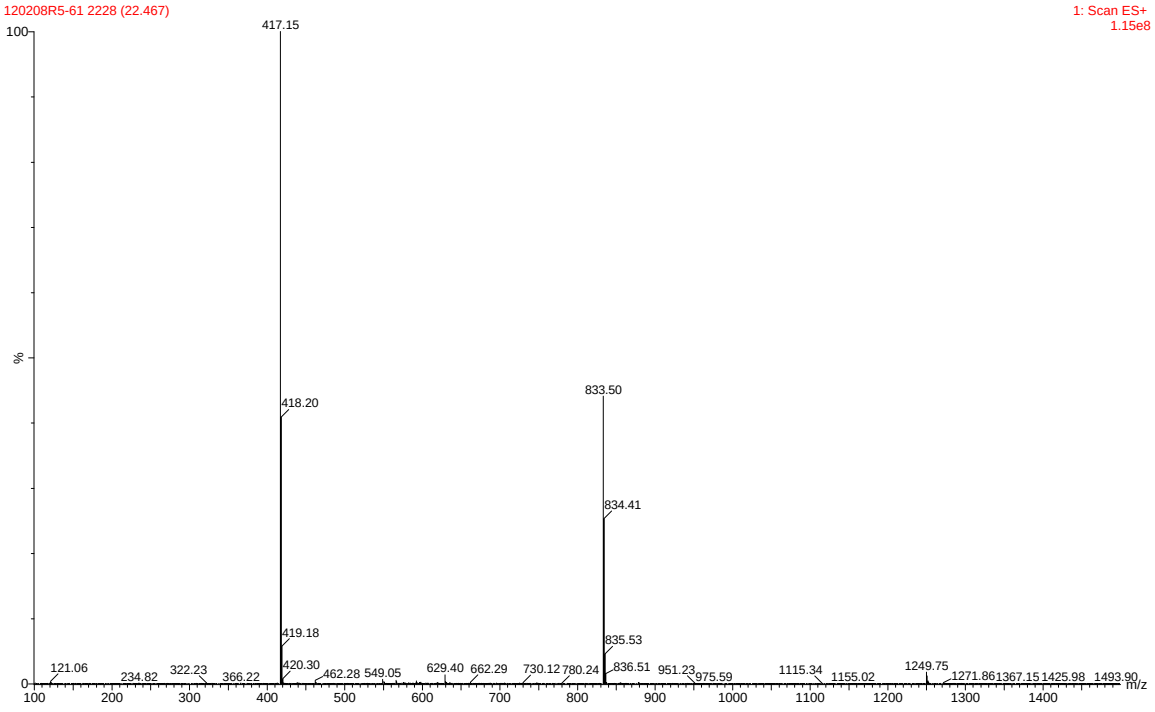


$C_{24}H_{24}N_4O_3$
Mol. Wt.: 416.47

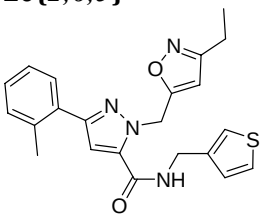




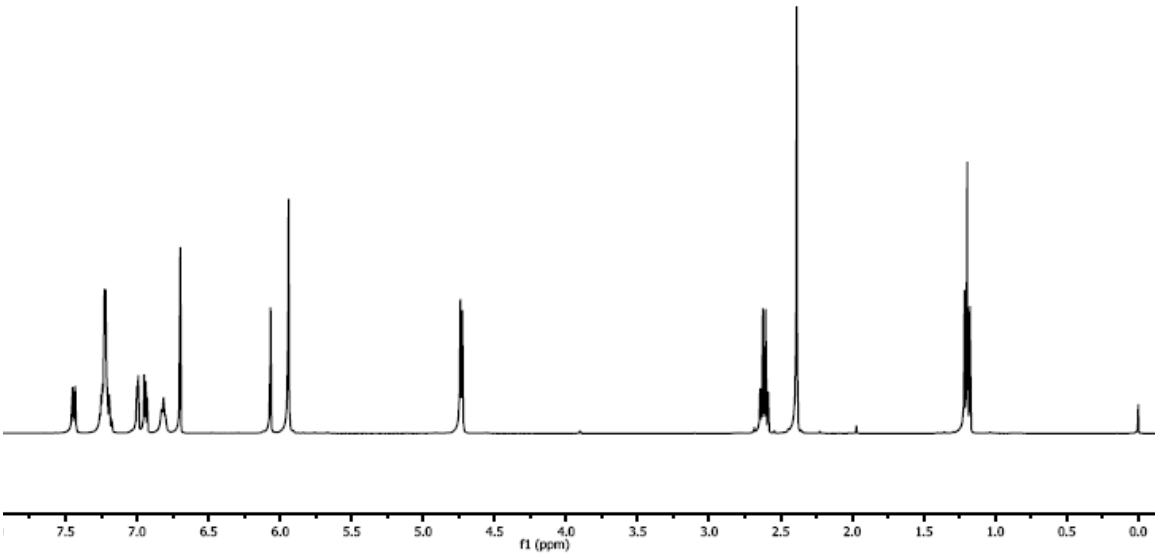

120208R5-61
2: Diode Array
214
Range: 2.584
Area
Time Height Area Area%
21.94 92361 29667.03 2.85
22.46 2446360 1010190.31 97.15
22.46
1010190
21.94
29667
AU
Time

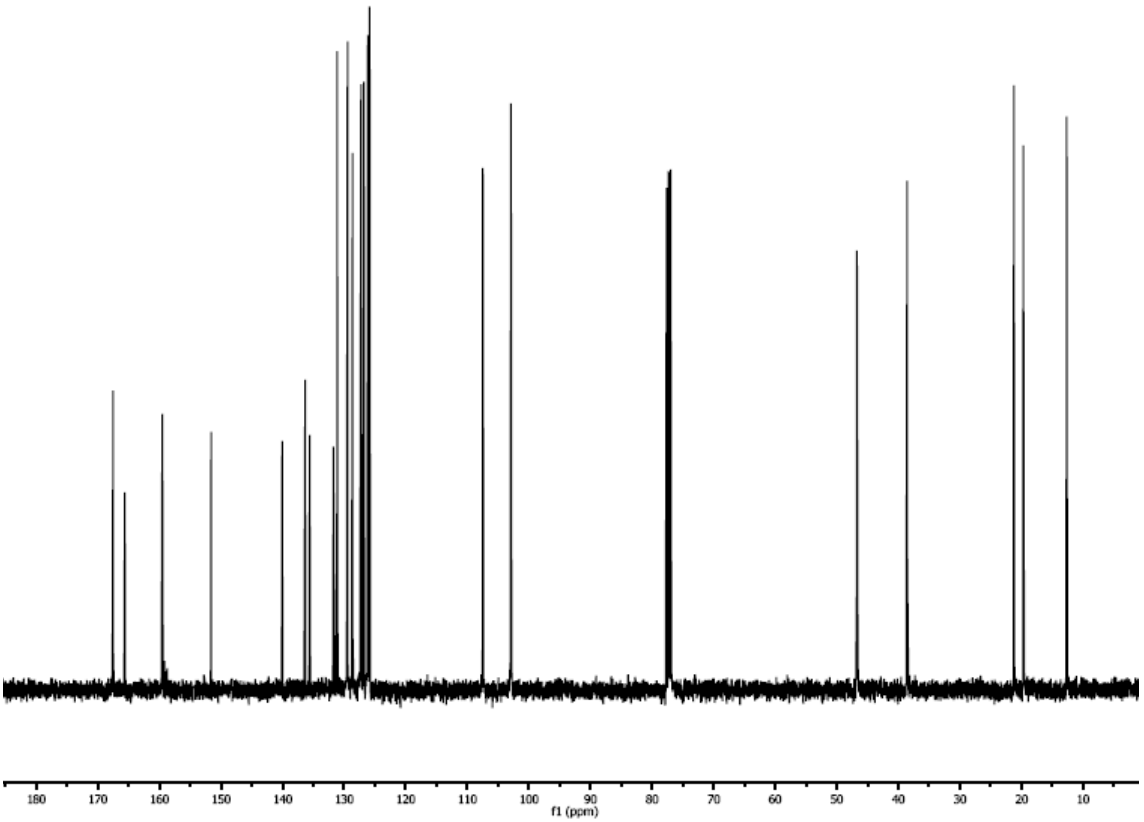

120208R5-61 2228 (22.467)
1: Scan ES+
1.15e8
%
m/z
417.15
418.20
833.50
834.41
419.18
835.53
420.30
836.51
121.06
234.82
322.23
366.22
462.28
549.05
629.40
662.29
730.12
780.24
951.23
975.59
1115.34
1155.02
1249.75
1271.86
1367.15
1425.98
1493.90

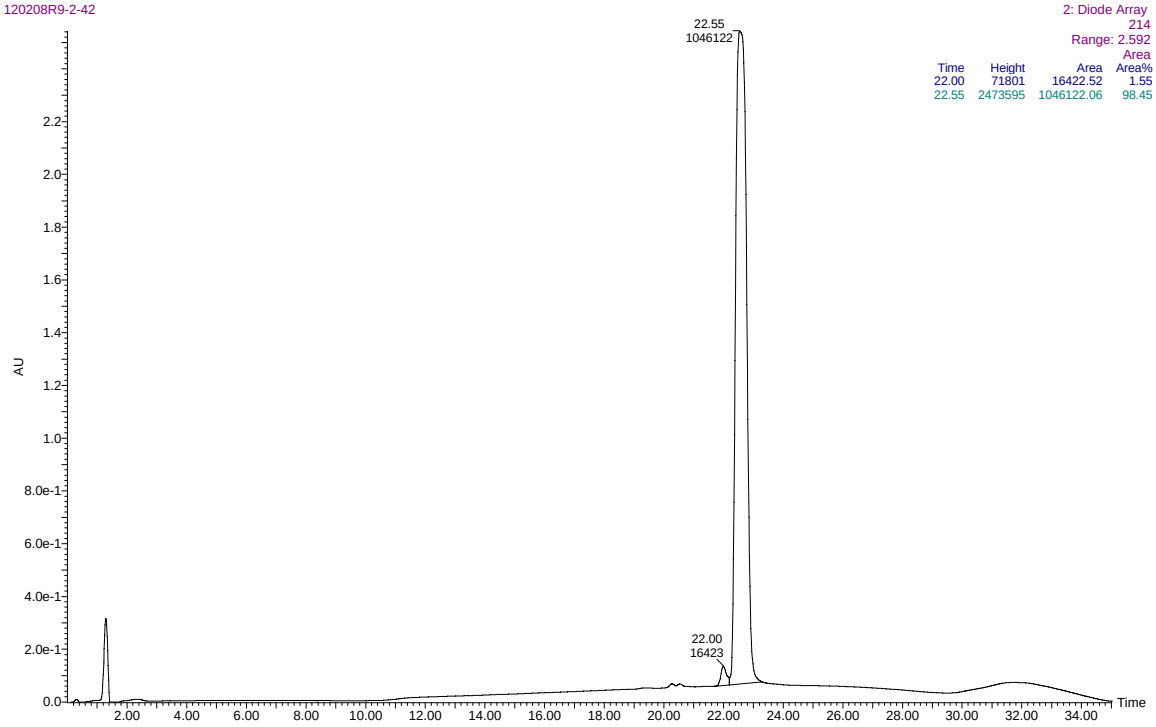
20{*2,6,5*}

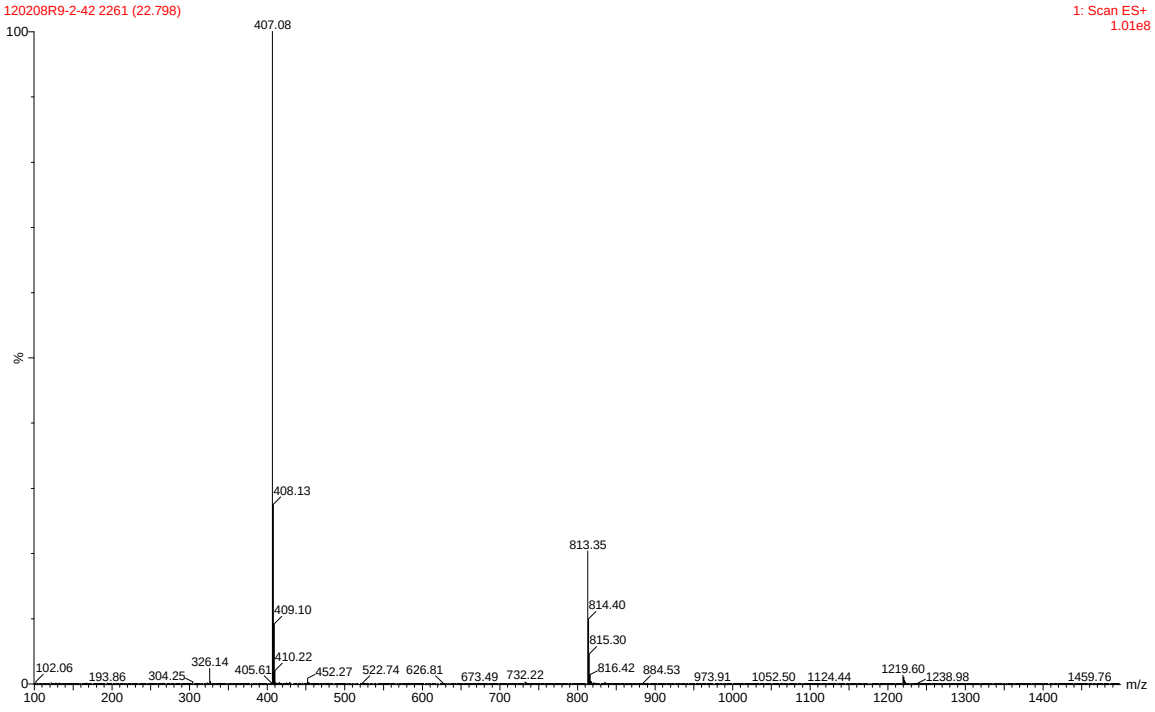


$C_{22}H_{22}N_4O_2S$
Mol. Wt.: 406.50

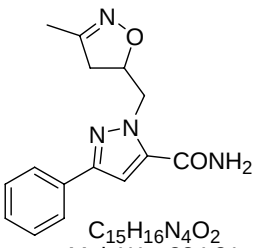




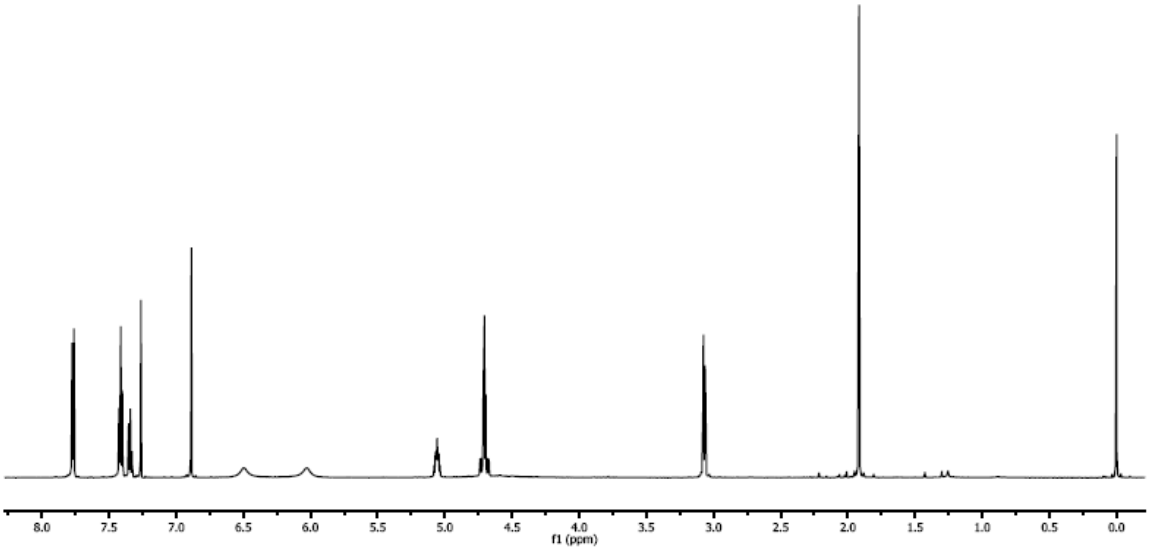

120208R9-2-42
2: Diode Array
214
Range: 2.592
Area
Time Height Area Area%
22.00 71801 16422.52 1.55
22.55 2473595 1046122.06 98.45
22.55
1046122
22.00
16423
AU
Time

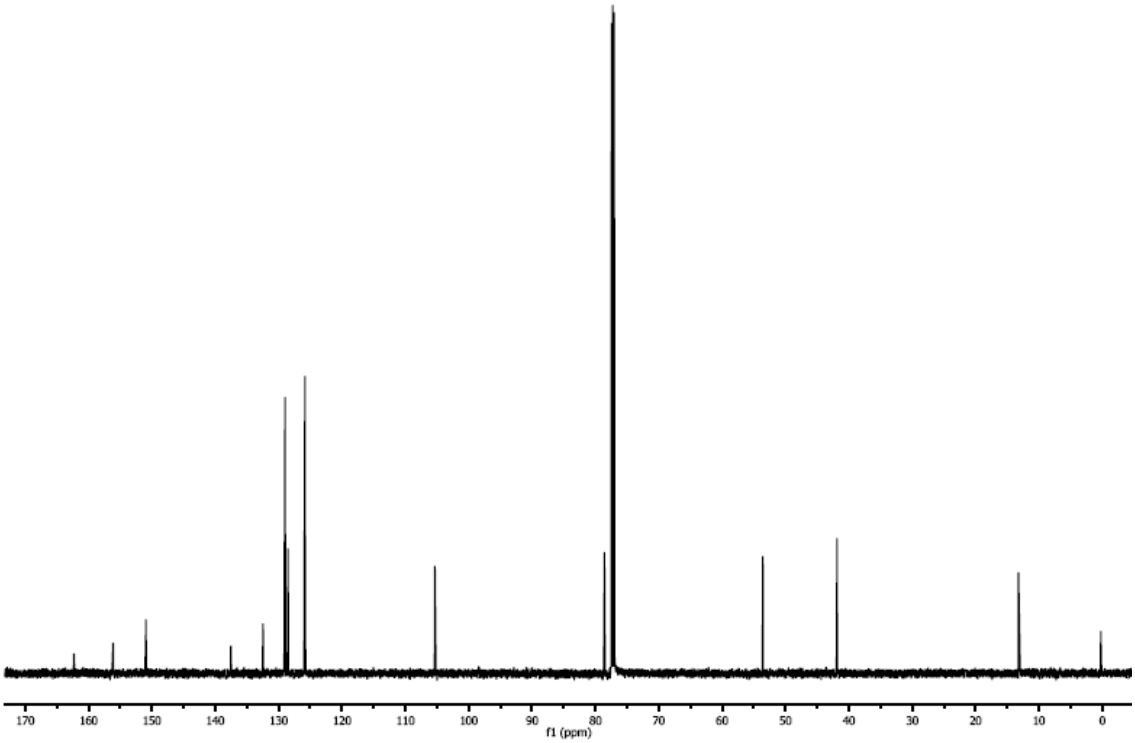

120208R9-2-42 2261 (22.798)
1: Scan ES+
1.01e8
407.08
408.13
813.35
409.10
814.40
815.30
410.22
816.42
102.06
193.86
304.25
326.14
405.61
452.27
522.74
626.81
673.49
732.22
884.53
973.91
1052.50
1124.44
1219.60
1238.98
1459.76
%
m/z

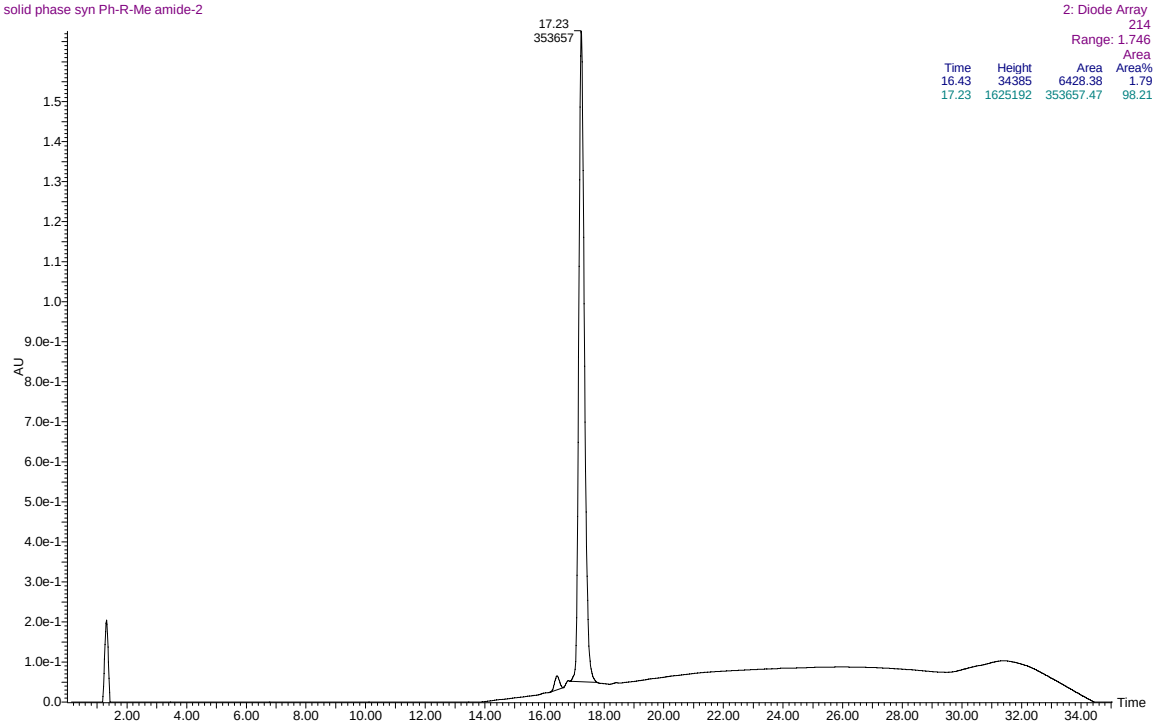
21 {*1,5*}

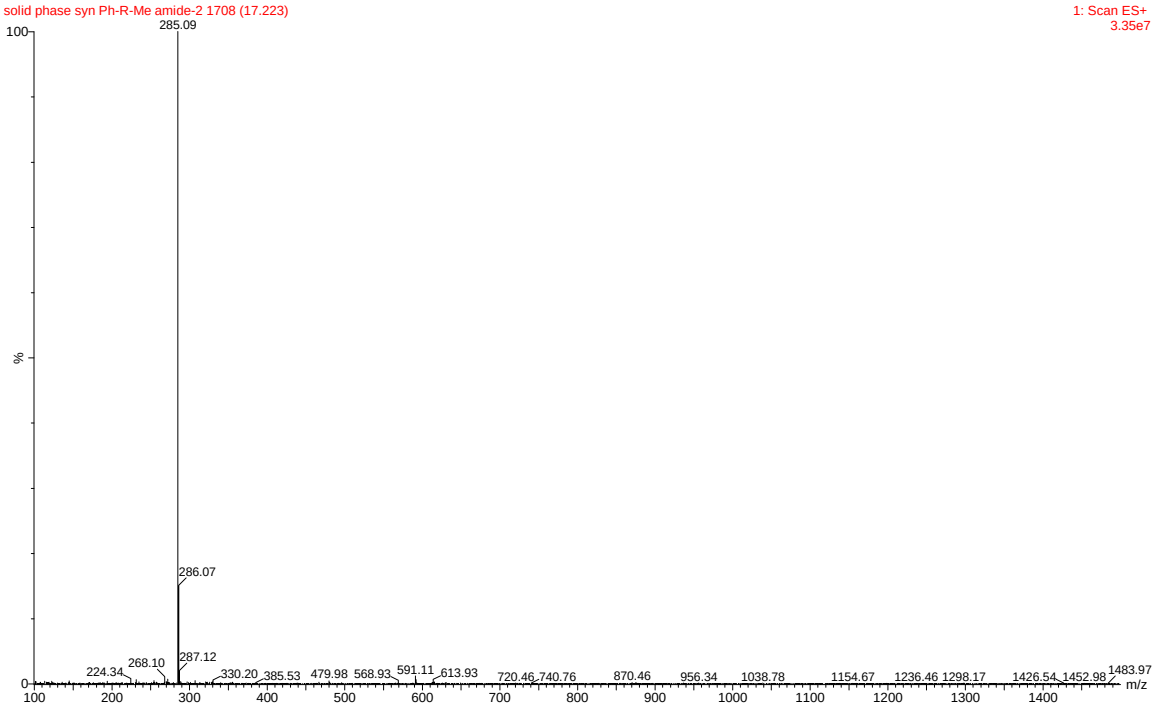


$C_{15}H_{16}N_4O_2$
Mol. Wt.: 284.31

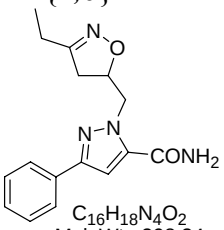




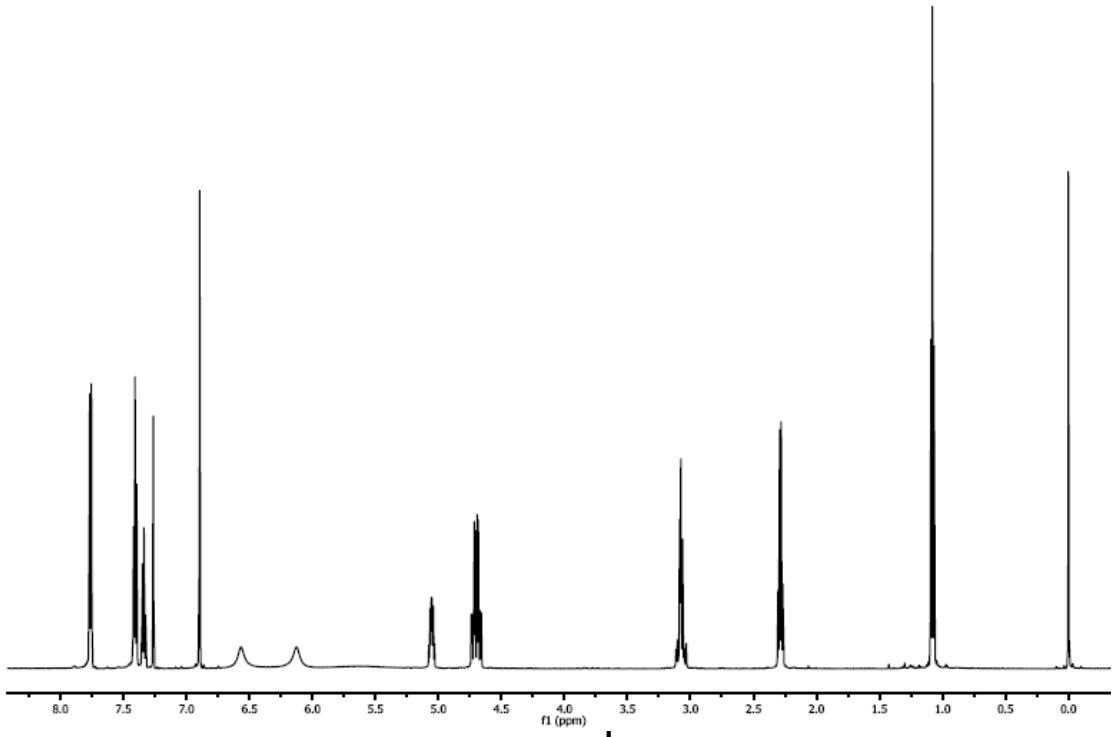

solid phase syn Ph-R-Me amide-2
2: Diode Array
214
Range: 1.746
Area
Time Height Area Area%
16.43 34385 6428.38 1.79
17.23 1625192 353657.47 98.21
17.23
353657
AU
Time

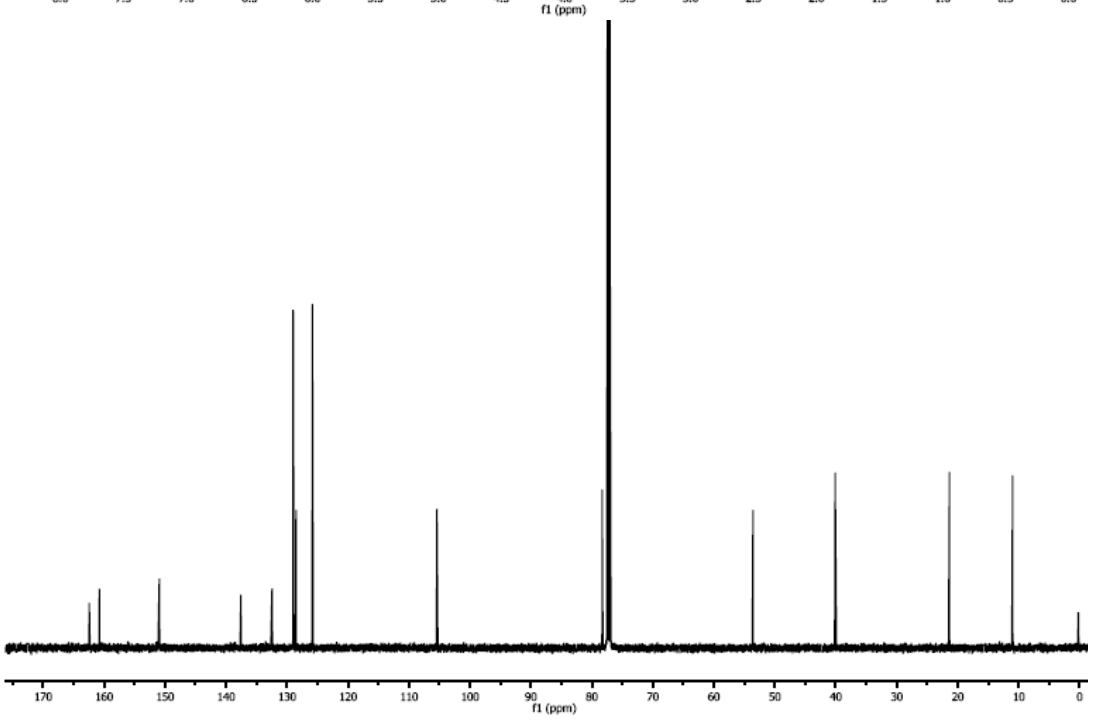

solid phase syn Ph-R-Me amide-2 1708 (17.223)
1: Scan ES+
3.35e7
285.09
286.07
287.12
268.10
224.34
%
m/z

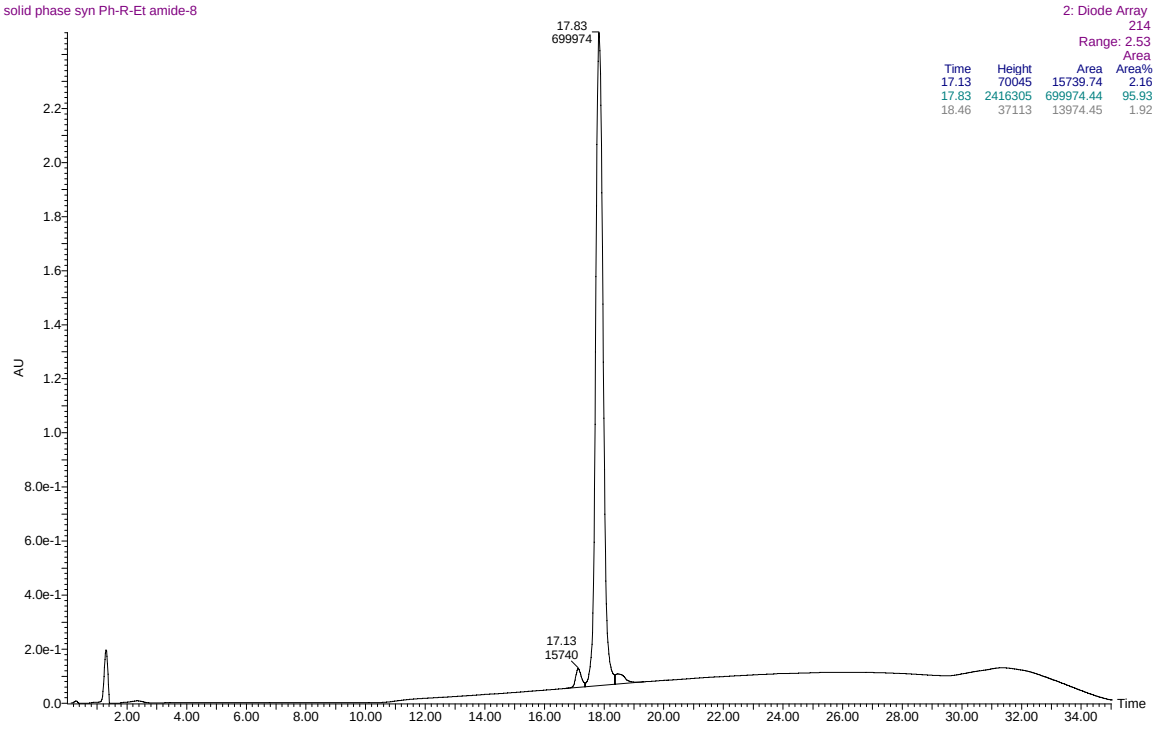
21 {*1,6*}

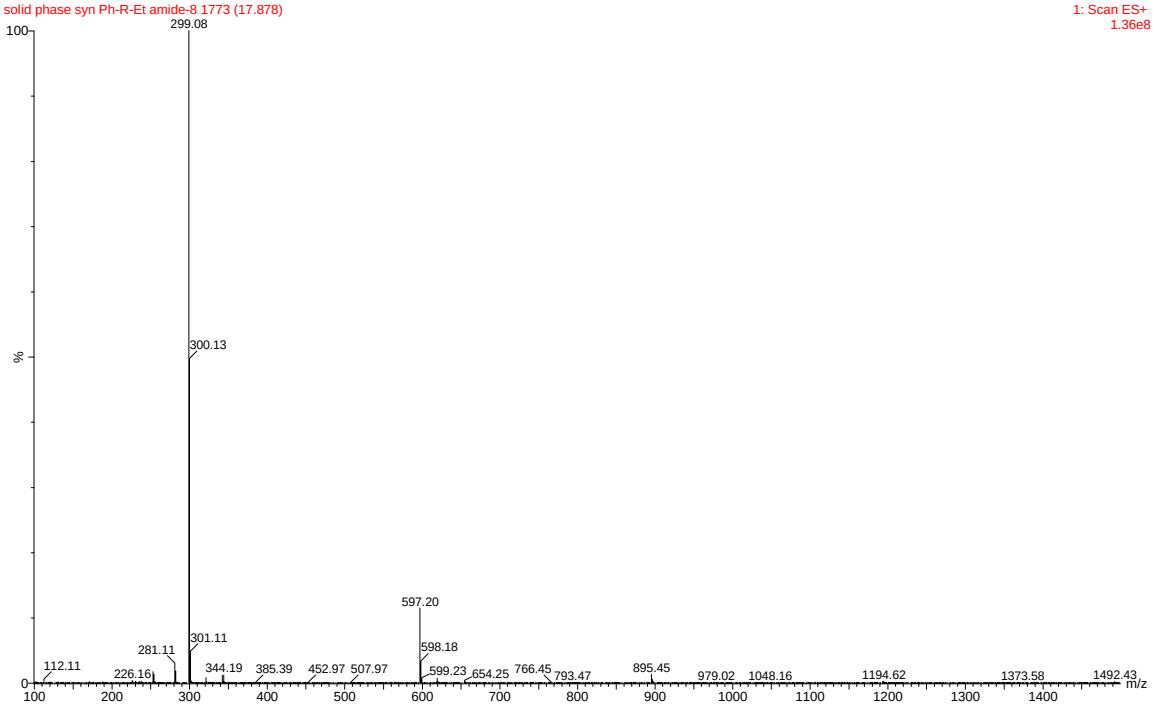


$C_{16}H_{18}N_4O_2$
Mol. Wt.: 298.34

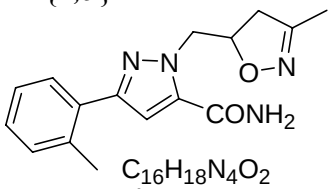




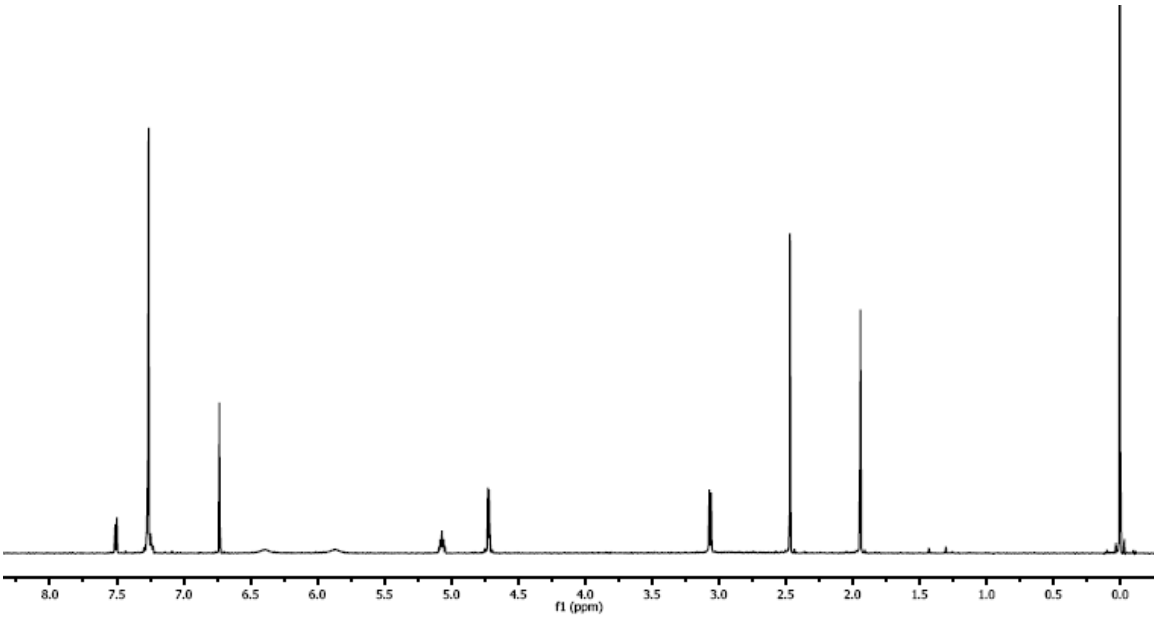

solid phase syn Ph-R-Et amide-8
2: Diode Array
214
Range: 2.53
Area
Time Height Area Area%
17.13 70045 15739.74 2.16
17.83 2416305 699974.44 95.93
18.46 37113 13974.45 1.92
17.83
699974
17.13
15740
AU
Time

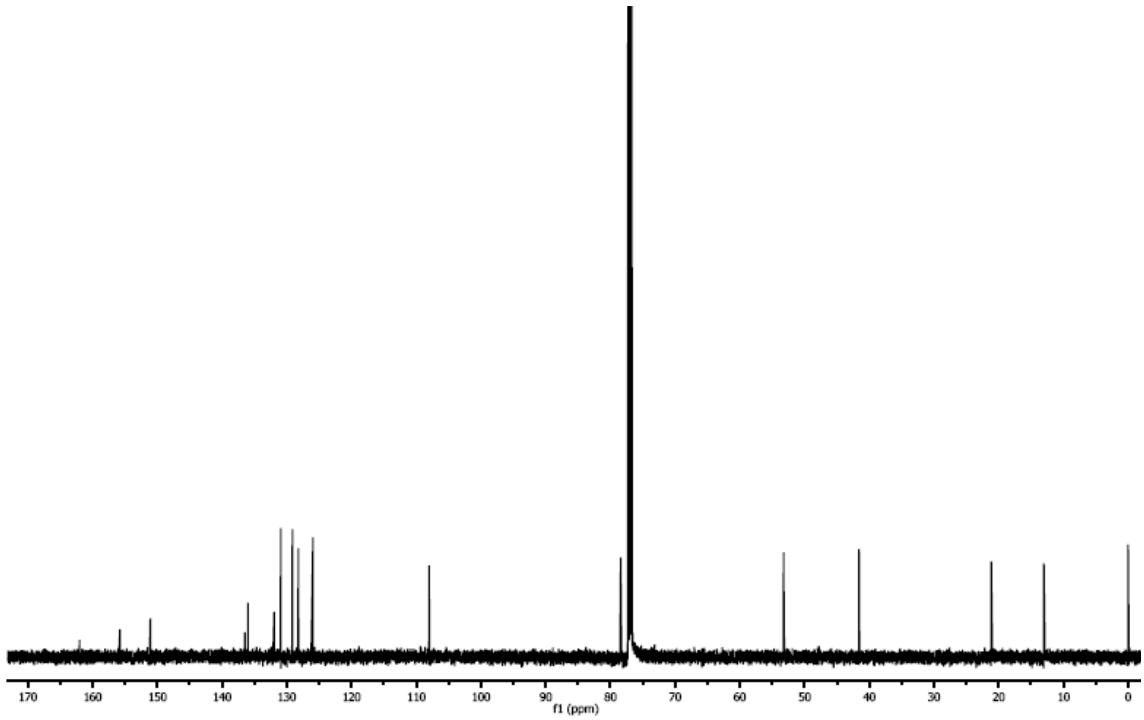

solid phase syn Ph-R-Et amide-8 1773 (17.878)
1: Scan ES+
1.36e8
299.08
300.13
597.20
598.18
301.11
281.11
112.11
226.16
344.19
385.39
452.97
507.97
599.23
654.25
766.45
793.47
895.45
979.02
1048.16
1194.62
1373.58
1492.43
%
m/z

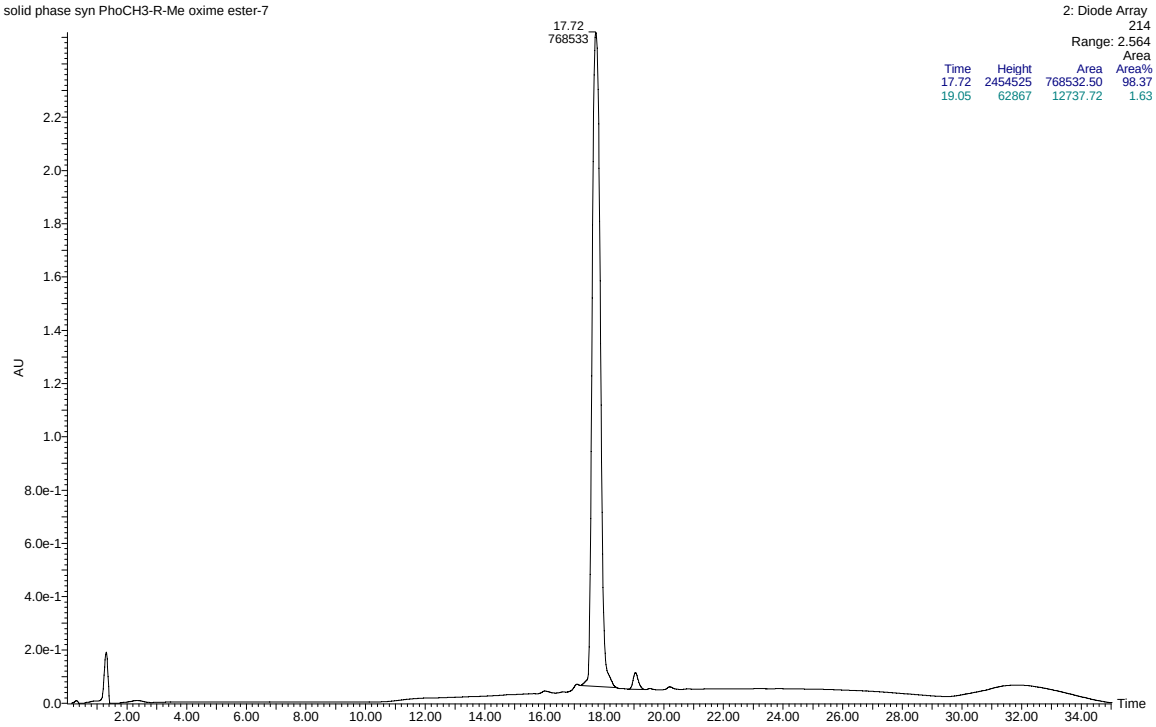
21 {*2,5*}

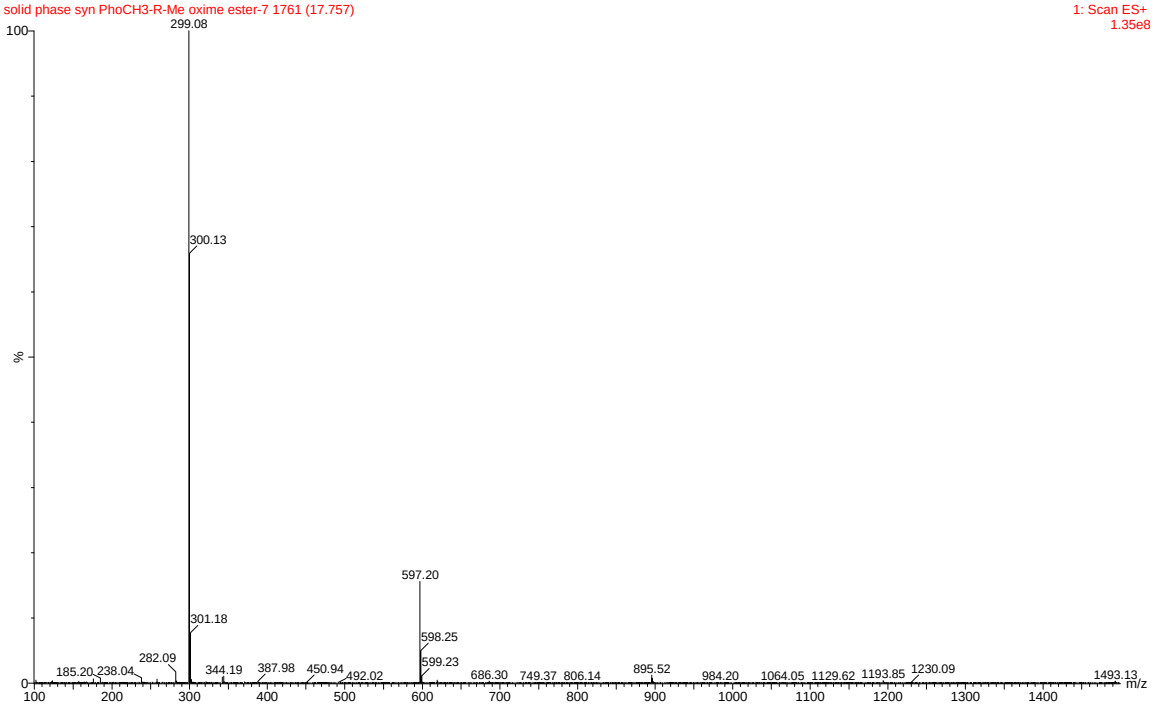


$C_{16}H_{18}N_4O_2$
Mol. Wt.: 298.34

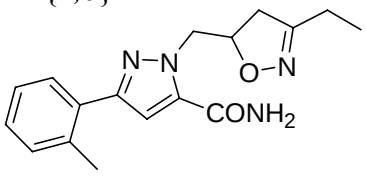




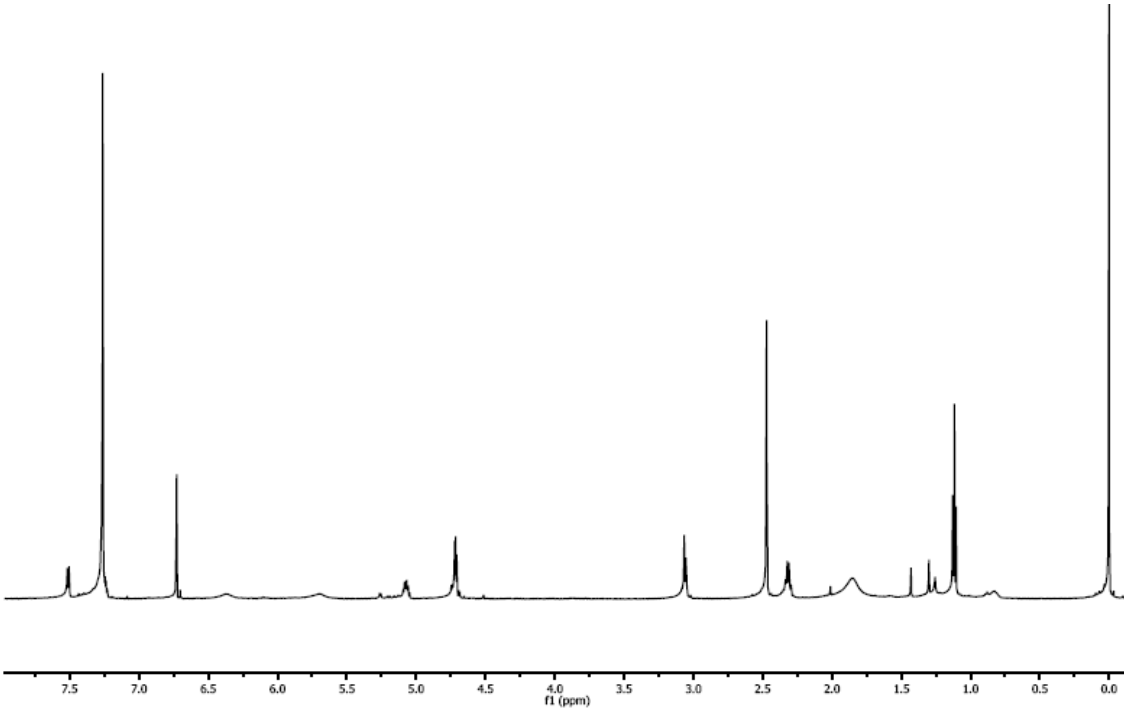

solid phase syn PhoCH3-R-Me oxime ester-7
2: Diode Array
214
Range: 2.564
Area
Time Height Area Area%
17.72 2454525 768532.50 98.37
19.05 62867 12737.72 1.63
17.72
768533
AU
Time

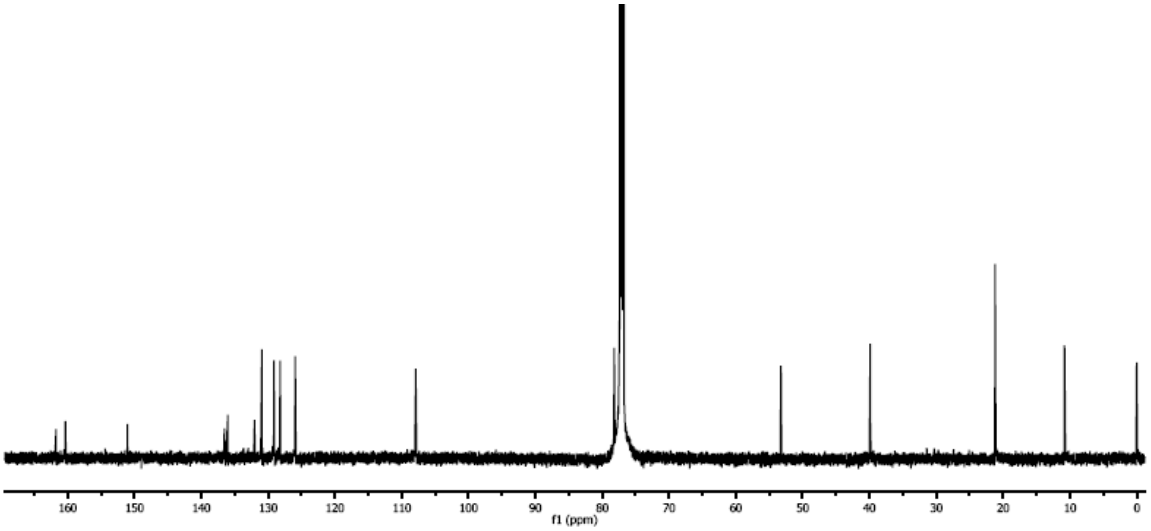

solid phase syn PhoCH3-R-Me oxime ester-7 1761 (17.757)
1: Scan ES+
1.35e8
299.08
300.13
301.18
597.20
598.25
599.23
%
m/z

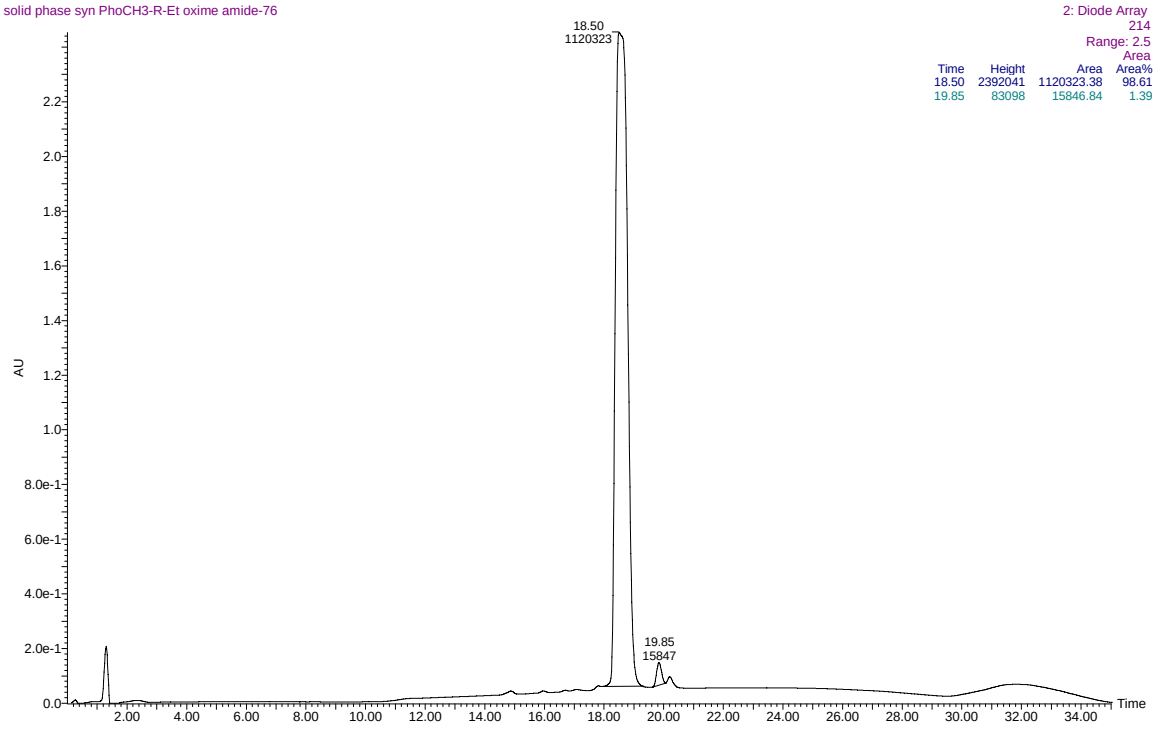
21 {*2,6*}

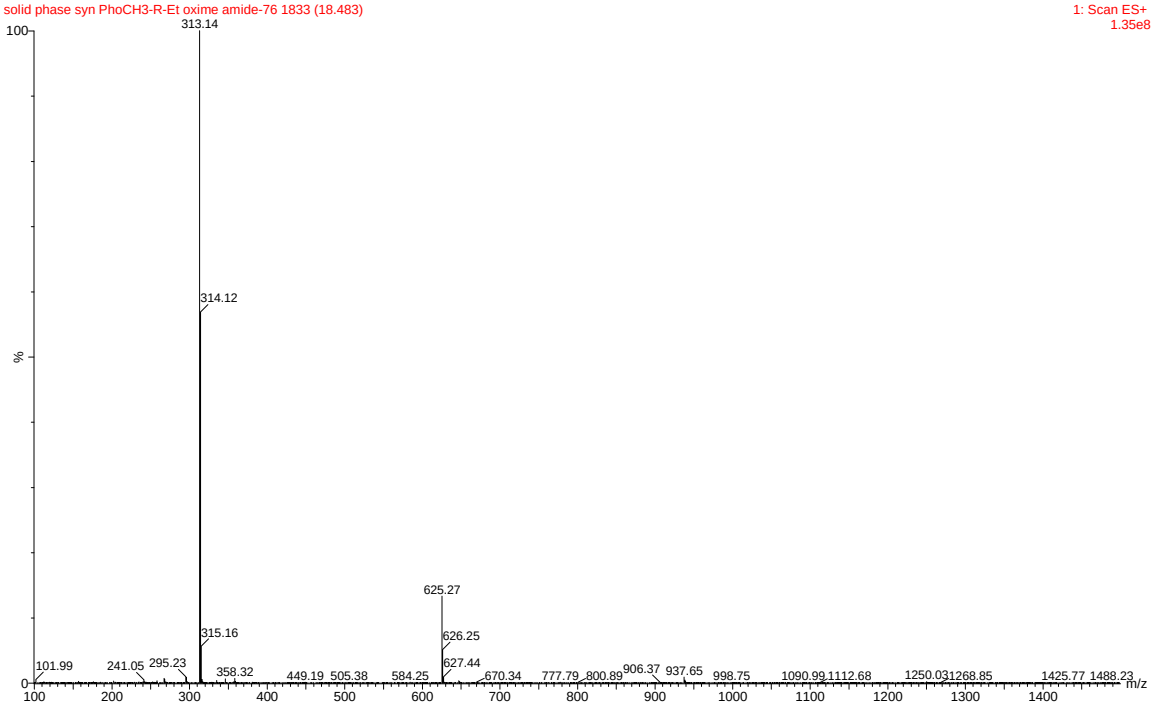


$C_{17}H_{20}N_4O_2$
Mol. Wt.: 312.37





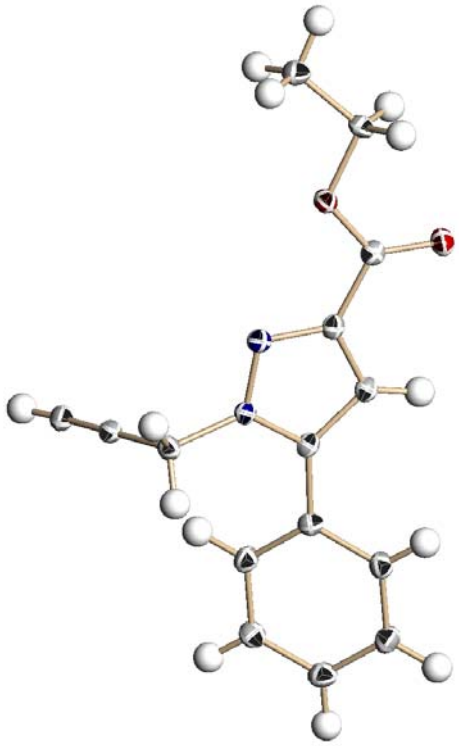

solid phase syn PhoCH3-R-Et oxime amide-76
2: Diode Array
214
Range: 2.5
Area
Time Height Area Area%
18.50 2392041 1120323.38 98.61
19.85 83098 15846.84 1.39
18.50
1120323
19.85
15847
AU
Time


solid phase syn PhoCH3-R-Et oxime amide-76 1833 (18.483)
1: Scan ES+
1.35e8
313.14
314.12
625.27
626.25
315.16
627.44
%
m/z

Crystallographic Methods and Data

6{*1*}

A colorless block with approximate orthogonal dimensions 0.50 x 0.17 x 0.08mm^3 was placed and optically centered on the Bruker SMART1000[1] CCD system at –183°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Four ω-scan data frame series were collected [MoKα] with 0.3° wide scans, 20 seconds per frame and 606 frames collected per series at varying φ angles (φ=0°, 90°, 180°, 270°). The crystal to detector distance was 4.287cm, thus providing a complete sphere of data to $2\theta_{max}$=60.07°.



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 3.20GHz processor and 1GB of extended memory. A total of 15484 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[2, 3] with 2992 unique for point group 222. The SHELXTL[4] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences, and intensity statistics indicated the non-centrosymmetric orthorhombic space group $P2_12_12_1$ (no. 19). The structure was determined by direct methods with the successful location of the molecule using the program XS[5]. The structure was refined with XL[5]. The 15484 data collected were merged, based upon identical indices yielding 11081 [R(int)=0.0147], truncated to 2ThetaMax=55.00° and finally merged during least-squares refinement to 2962 unique data [R(int)=0.0178]. A single Least-squares difference-Fourier cycle was required to locate the remaining hydrogen atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were allowed to refine freely, xyzU, throughout the final refinement stages. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=2.97%, wR(F^2)=6.87%, GOF=1.061 for all 2962 unique reflections [R(F)=2.76%, wR(F^2)=6.69% for those 2826 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. An empirical correction for extinction was also attempted but found to be negative and therefore not applied. The absolute structure parameter, Flack(x)[6], was refined and found to be 0.1(9) indicating that the correct absolute configuration cannot be conclusively determined.

References:

1. Bruker (2004) SMART (Version 5.054) and SAINT (Version 7.23A). Bruker AXS Inc., Madison, Wisconsin, USA.

2. An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). Acta Cryst., A51, 33-38.

3. Sheldrick, G.M., SADABS (2003) Version 2.10, 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany.

4. Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.

5. Sheldrick, G. M., (1997). SHELXS97 and SHELXL97. Universität Göttingen: Göttingen, Germany.

6. On Enantiomorph-Polarity Estimation, Flack, H.D. (1983). Acta Cryst., A39, 876-881.

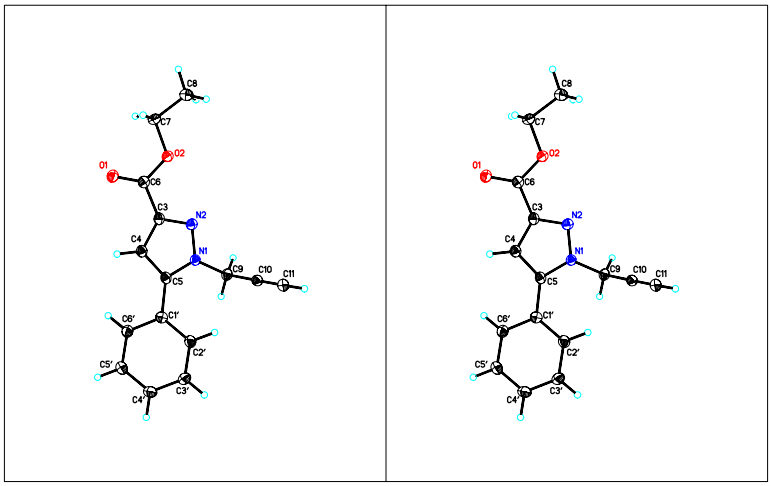


Table 1. Crystal data and structure refinement for **6**{*1*}.

Identification code	jf1605ffmi	
Empirical formula	C15 H14 N2 O2	
Formula weight	254.28	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2(1)2(1)2(1)	
Unit cell dimensions	a = 4.0329(2) Å	α= 90°.
	b = 14.8431(8) Å	β= 90°.
	c = 21.5968(12) Å	γ = 90°.
Volume	1292.80(12) $Å^3$	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	536	
Crystal size	0.50 x 0.17 x 0.08 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Bruker SMART1000	
Theta range for data collection	1.66 to 27.49°.	
Index ranges	-5<=h<=5, -19<=k<=19, -27<=l<=28	
Reflections collected	11027	
Independent reflections	2962 [R(int) = 0.0178]	
Observed reflections (I > 2sigma(I))	2826	
Completeness to theta = 27.49°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9933 and 0.9570	
Solution method	SHELXS-97 (Sheldrick, 1990)	
Refinement method	SHELXL-97 (Sheldrick, 1997) Full-matrix least-squares on F^2	
Data / restraints / parameters	2962 / 0 / 228	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0669	
R indices (all data)	R1 = 0.0297, wR2 = 0.0687	
Absolute structure parameter	0.1(9)	
Largest diff. peak and hole	0.216 and -0.160 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6**{*1*}. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5102(2)	1336(1)	2408(1)	16(1)
N(2)	6401(2)	1161(1)	1845(1)	17(1)
O(1)	11131(2)	2717(1)	947(1)	22(1)
O(2)	9904(2)	1258(1)	774(1)	19(1)
C(3)	8061(3)	1914(1)	1702(1)	17(1)
C(4)	7826(3)	2564(1)	2169(1)	18(1)
C(5)	5892(3)	2178(1)	2625(1)	17(1)
C(6)	9858(3)	2016(1)	1108(1)	17(1)
C(7)	11709(3)	1313(1)	189(1)	20(1)
C(8)	11921(4)	369(1)	-65(1)	25(1)
C(9)	2938(3)	652(1)	2683(1)	18(1)
C(10)	4753(3)	6(1)	3073(1)	18(1)
C(11)	6164(3)	-531(1)	3383(1)	21(1)
C(1')	4709(3)	2563(1)	3214(1)	18(1)
C(2')	4263(3)	2054(1)	3752(1)	21(1)
C(3')	3083(3)	2459(1)	4289(1)	23(1)
C(4')	2421(3)	3375(1)	4301(1)	24(1)
C(5')	2930(3)	3894(1)	3774(1)	24(1)
C(6')	4047(3)	3489(1)	3236(1)	21(1)

Table 3. Bond lengths [Å] and angles [°] for **6**{*I*}.

N(1)-N(2)	1.3480(13)		
N(1)-C(5)	1.3727(14)	N(2)-N(1)-C(5)	113.21(9)
N(1)-C(9)	1.4654(14)	N(2)-N(1)-C(9)	117.61(9)
N(2)-C(3)	1.3397(14)	C(5)-N(1)-C(9)	129.07(9)
O(1)-C(6)	1.2125(14)	C(3)-N(2)-N(1)	103.91(9)
O(2)-C(6)	1.3361(13)	C(6)-O(2)-C(7)	115.32(9)
O(2)-C(7)	1.4614(13)	N(2)-C(3)-C(4)	112.07(10)
C(3)-C(4)	1.3993(15)	N(2)-C(3)-C(6)	121.96(10)
C(3)-C(6)	1.4810(15)	C(4)-C(3)-C(6)	125.97(10)
C(4)-C(5)	1.3803(16)	C(5)-C(4)-C(3)	105.42(10)
C(4)-H(4)	0.985(15)	C(5)-C(4)-H(4)	128.0(8)
C(5)-C(1')	1.4744(15)	C(3)-C(4)-H(4)	126.5(8)
C(7)-C(8)	1.5062(17)	N(1)-C(5)-C(4)	105.38(9)
C(7)-H(7A)	1.008(15)	N(1)-C(5)-C(1')	124.97(10)
C(7)-H(7B)	0.996(16)	C(4)-C(5)-C(1')	129.60(10)
C(8)-H(8A)	0.991(16)	O(1)-C(6)-O(2)	124.16(10)
C(8)-H(8B)	1.010(17)	O(1)-C(6)-C(3)	122.97(10)
C(8)-H(8C)	0.978(18)	O(2)-C(6)-C(3)	112.87(9)
C(9)-C(10)	1.4713(15)	O(2)-C(7)-C(8)	106.98(9)
C(9)-H(9A)	0.969(14)	O(2)-C(7)-H(7A)	108.7(9)
C(9)-H(9B)	0.971(14)	C(8)-C(7)-H(7A)	112.9(8)
C(10)-C(11)	1.1855(17)	O(2)-C(7)-H(7B)	108.4(8)
C(11)-H(11)	0.903(16)	C(8)-C(7)-H(7B)	111.8(8)
C(1')-C(2')	1.3981(15)	H(7A)-C(7)-H(7B)	108.0(12)
C(1')-C(6')	1.4007(15)	C(7)-C(8)-H(8A)	108.7(9)
C(2')-C(3')	1.3892(16)	C(7)-C(8)-H(8B)	110.3(9)
C(2')-H(2')	0.970(14)	H(8A)-C(8)-H(8B)	108.7(13)
C(3')-C(4')	1.3854(17)	C(7)-C(8)-H(8C)	110.1(10)
C(3')-H(3')	0.943(14)	H(8A)-C(8)-H(8C)	110.7(13)
C(4')-C(5')	1.3903(17)	H(8B)-C(8)-H(8C)	108.5(14)
C(4')-H(4')	0.951(14)	N(1)-C(9)-C(10)	112.84(9)
C(5')-C(6')	1.3839(16)	N(1)-C(9)-H(9A)	105.5(8)
C(5')-H(5')	0.978(14)	C(10)-C(9)-H(9A)	111.2(8)
C(6')-H(6')	0.945(14)	N(1)-C(9)-H(9B)	109.5(8)

C(10)-C(9)-H(9B)	109.4(8)	C(4')-C(3')-H(3')	120.5(8)
H(9A)-C(9)-H(9B)	108.2(11)	C(2')-C(3')-H(3')	119.0(8)
C(11)-C(10)-C(9)	178.44(12)	C(3')-C(4')-C(5')	119.94(11)
C(10)-C(11)-H(11)	175.7(10)	C(3')-C(4')-H(4')	119.7(8)
C(2')-C(1')-C(6')	118.63(10)	C(5')-C(4')-H(4')	120.4(8)
C(2')-C(1')-C(5)	123.32(10)	C(6')-C(5')-C(4')	119.75(11)
C(6')-C(1')-C(5)	118.05(10)	C(6')-C(5')-H(5')	120.2(8)
C(3')-C(2')-C(1')	120.20(10)	C(4')-C(5')-H(5')	120.0(8)
C(3')-C(2')-H(2')	119.6(8)	C(5')-C(6')-C(1')	120.99(11)
C(1')-C(2')-H(2')	120.2(8)	C(5')-C(6')-H(6')	119.0(8)
C(4')-C(3')-C(2')	120.46(11)	C(1')-C(6')-H(6')	120.0(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6**{*1*}. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

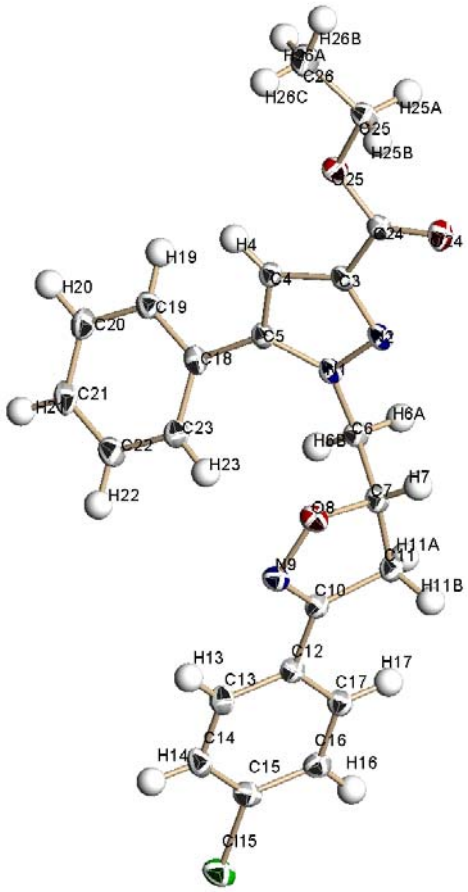
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	17(1)	15(1)	16(1)	2(1)	0(1)	2(1)
N(2)	16(1)	19(1)	16(1)	1(1)	-1(1)	2(1)
O(1)	28(1)	19(1)	20(1)	1(1)	1(1)	-5(1)
O(2)	21(1)	19(1)	17(1)	0(1)	2(1)	-2(1)
C(3)	16(1)	16(1)	19(1)	2(1)	-3(1)	1(1)
C(4)	19(1)	16(1)	18(1)	1(1)	-2(1)	1(1)
C(5)	17(1)	15(1)	18(1)	1(1)	-3(1)	2(1)
C(6)	17(1)	18(1)	17(1)	1(1)	-4(1)	2(1)
C(7)	20(1)	24(1)	16(1)	1(1)	3(1)	-1(1)
C(8)	29(1)	24(1)	21(1)	-2(1)	4(1)	2(1)
C(9)	16(1)	18(1)	20(1)	1(1)	0(1)	-1(1)
C(10)	19(1)	17(1)	19(1)	-2(1)	2(1)	-2(1)
C(11)	25(1)	17(1)	21(1)	1(1)	1(1)	1(1)
C(1')	16(1)	20(1)	18(1)	-1(1)	-1(1)	1(1)
C(2')	24(1)	18(1)	20(1)	1(1)	-1(1)	3(1)
C(3')	29(1)	24(1)	17(1)	3(1)	1(1)	2(1)
C(4')	28(1)	25(1)	19(1)	-4(1)	2(1)	2(1)
C(5')	29(1)	18(1)	25(1)	-2(1)	1(1)	1(1)
C(6')	24(1)	19(1)	20(1)	2(1)	-1(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6**{*1*}.

	x	y	z	U(eq)
H(4)	8870(40)	3164(9)	2170(6)	25(4)
H(7A)	10500(40)	1739(10)	-96(7)	27(4)
H(7B)	13940(40)	1570(9)	272(6)	23(4)
H(8A)	13230(40)	382(10)	-453(7)	31(4)
H(8B)	13070(50)	-40(11)	240(7)	38(4)
H(8C)	9690(50)	132(11)	-141(7)	35(4)
H(9A)	1880(40)	353(9)	2337(6)	20(3)
H(9B)	1230(40)	945(9)	2928(6)	18(3)
H(11)	7110(40)	-968(10)	3613(7)	30(4)
H(2')	4780(40)	1415(9)	3754(6)	19(3)
H(3')	2800(40)	2105(9)	4647(6)	24(4)
H(4')	1710(40)	3649(9)	4677(6)	25(4)
H(5')	2480(40)	4541(10)	3783(6)	25(4)
H(6')	4310(40)	3844(9)	2876(6)	23(3)

9{*1,1*}

A colorless block with approximate orthogonal dimensions 0.28 x 0.38 x 0.57mm^3 was placed and optically centered on the Bruker SMART 1000[1] CCD system at 90(2)K. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Four ω-scan data frame series were collected [MoKα] with 0.3° wide scans, 30 seconds per frame and 606 frames were collected, at varying phi angles (phi=0°, 72°, 144°, 216°, 288°), for each series. The crystal to detector distance was 4.23cm, thus providing a complete sphere of data with processing to $2\theta_{max}$=55.16°.



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 3.20GHz processor and 1GB of extended memory. A total of 15173 reflections were collected and corrected for Lorentz and polarization effects and numerical, face based, absorption using Blessing's method as incorporated into the program SADABS[2, 3] with 4470 unique. The SHELXTL[4] program package was implemented to determine the probable space group and set up the initial files. System symmetry, lack of systematic absences and intensity statistics indicated the centrosymmetric triclinic space group P-1 (no. 2). The structure was determined by direct methods with the successful location of a majority of the molecule using the program XS[5]. The structure was refined with XL[5]. The data collected were merged based upon identical indices yielding 8857 data [R(int)=0.0236] that were merged in least-squares refinement to 4470 unique data [R(int)=0.0221]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located directly from difference-Fourier maps and allowed to refine freely throughout the final convergence process (xyzU) except for a minor disorder at C(4) with H(4):Cl(4) 0.97:0.03. Although H(4) refined freely it was deemed appropriate to have it ride on C(4) with AFIX. The final structure was refined to convergence with R(F)=5.96%, wR(F^2)=10.30%, GOF=1.042 for all 4470 unique reflections [R(F)=3.61%, wR(F^2)=9.07% for those 3232 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

References:

1. Bruker (2004) SMART (Version 5.054) and (2007) SAINT (Version 7.46a). Bruker AXS Inc., Madison, Wisconsin, USA.

2. An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). Acta Cryst., A51, 33-38.

3. Sheldrick, G.M., SADABS (2006) Version 2006/1, 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany.

4. Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.

5. Sheldrick, G. M., (1997). SHELXS97 and SHELXL97. Universität Göttingen: Göttingen, Germany.

Table 1. Crystal data and structure refinement for **9**{*1,1*}.

Identification code	jf1613fmi	
Empirical formula	C22 H19.97 Cl1.03 N3 O3	
Formula weight	410.89	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 4.6206(5) Å	α= 62.652(2)°.
	b = 15.1053(17) Å	β= 83.235(2)°.
	c = 15.9777(18) Å	γ = 82.671(2)°.
Volume	980.22(19) $Å^3$	
Z	2	
Density (calculated)	1.392 Mg/m^3	
Absorption coefficient	0.229 mm^{-1}	
F(000)	429	
Crystal size	0.34 x 0.196 x 0.108 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	Bruker SMART1000	
Theta range for data collection	1.44 to 27.53°.	
Index ranges	-6<=h<=6, -19<=k<=19, -20<=l<=20	
Reflections collected	8857	
Independent reflections	4470 [R(int) = 0.0221]	
Observed reflections (I > 2sigma(I))	3232	
Completeness to theta = 27.53°	99.8 %	
Absorption correction	Numerical	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008) Full-matrix least-squares on F^2	
Data / restraints / parameters	4470 / 0 / 343	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0907	
R indices (all data)	R1 = 0.0596, wR2 = 0.1030	
Largest diff. peak and hole	0.298 and -0.221 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9**{*1,1*}. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	4148(3)	1014(1)	6015(1)	20(1)
N(2)	2459(3)	251(1)	6286(1)	21(1)
C(3)	1280(3)	109(1)	7143(1)	20(1)
C(4)	2235(3)	772(1)	7417(1)	21(1)
Cl(4)	1500(30)	776(10)	8576(9)	26(3)
C(5)	4050(3)	1363(1)	6674(1)	20(1)
C(6)	5963(3)	1284(1)	5136(1)	21(1)
C(7)	4135(3)	1713(1)	4283(1)	22(1)
O(8)	2190(2)	2558(1)	4275(1)	24(1)
N(9)	3522(3)	3451(1)	3651(1)	23(1)
C(10)	5639(3)	3241(1)	3162(1)	20(1)
C(11)	6026(3)	2159(1)	3368(1)	22(1)
C(12)	7368(3)	4028(1)	2434(1)	20(1)
C(13)	6841(4)	5013(1)	2305(1)	25(1)
C(14)	8408(4)	5762(1)	1602(1)	27(1)
C(15)	10513(3)	5525(1)	1034(1)	24(1)
Cl(15)	12452(1)	6474(1)	143(1)	32(1)
C(16)	11113(4)	4557(1)	1150(1)	24(1)
C(17)	9523(3)	3809(1)	1856(1)	23(1)
C(18)	5549(3)	2211(1)	6586(1)	22(1)
C(19)	6430(3)	2168(1)	7409(1)	24(1)
C(20)	7791(4)	2952(1)	7381(1)	28(1)
C(21)	8324(4)	3781(1)	6532(1)	29(1)
C(22)	7408(4)	3838(1)	5717(1)	30(1)
C(23)	5986(4)	3067(1)	5739(1)	26(1)
C(24)	-790(3)	-664(1)	7664(1)	20(1)
O(24)	-1714(2)	-1174(1)	7374(1)	26(1)
C(25)	-3568(4)	-1464(1)	9113(1)	26(1)
O(25)	-1518(2)	-731(1)	8531(1)	25(1)
C(26)	-4272(6)	-1360(2)	9999(2)	45(1)

Table 3. Bond lengths [Å] and angles [°] for **9**{*1,1*}.

N(1)-N(2)	1.3472(16)	C(18)-C(19)	1.393(2)
N(1)-C(5)	1.3712(19)	C(19)-C(20)	1.390(2)
N(1)-C(6)	1.4582(19)	C(19)-H(19)	0.983(17)
N(2)-C(3)	1.342(2)	C(20)-C(21)	1.382(2)
C(3)-C(4)	1.397(2)	C(20)-H(20)	0.99(2)
C(3)-C(24)	1.475(2)	C(21)-C(22)	1.378(2)
C(4)-C(5)	1.375(2)	C(21)-H(21)	0.95(2)
C(4)-Cl(4)	1.846(13)	C(22)-C(23)	1.394(2)
C(4)-H(4)	0.9500	C(22)-H(22)	0.99(2)
C(5)-C(18)	1.476(2)	C(23)-H(23)	0.948(19)
C(6)-C(7)	1.520(2)	C(24)-O(24)	1.2049(18)
C(6)-H(6A)	0.996(17)	C(24)-O(25)	1.3450(19)
C(6)-H(6B)	0.969(18)	C(25)-O(25)	1.4493(18)
C(7)-O(8)	1.4602(19)	C(25)-C(26)	1.490(3)
C(7)-C(11)	1.517(2)	C(25)-H(25A)	0.960(18)
C(7)-H(7)	0.991(17)	C(25)-H(25B)	0.961(18)
O(8)-N(9)	1.4217(16)	C(26)-H(26A)	1.01(3)
N(9)-C(10)	1.279(2)	C(26)-H(26B)	0.99(2)
C(10)-C(12)	1.469(2)	C(26)-H(26C)	0.90(2)
C(10)-C(11)	1.502(2)		
C(11)-H(11A)	0.987(19)	N(2)-N(1)-C(5)	112.75(12)
C(11)-H(11B)	0.993(18)	N(2)-N(1)-C(6)	117.27(12)
C(12)-C(17)	1.391(2)	C(5)-N(1)-C(6)	129.73(12)
C(12)-C(13)	1.399(2)	C(3)-N(2)-N(1)	104.25(12)
C(13)-C(14)	1.384(2)	N(2)-C(3)-C(4)	111.68(13)
C(13)-H(13)	0.967(18)	N(2)-C(3)-C(24)	120.22(13)
C(14)-C(15)	1.378(2)	C(4)-C(3)-C(24)	128.10(14)
C(14)-H(14)	0.95(2)	C(5)-C(4)-C(3)	105.59(13)
C(15)-C(16)	1.381(2)	C(5)-C(4)-Cl(4)	127.0(4)
C(15)-Cl(15)	1.7427(16)	C(3)-C(4)-Cl(4)	127.2(4)
C(16)-C(17)	1.391(2)	C(5)-C(4)-H(4)	127.2
C(16)-H(16)	0.988(18)	C(3)-C(4)-H(4)	127.2
C(17)-H(17)	0.976(18)	Cl(4)-C(4)-H(4)	4.2
C(18)-C(23)	1.392(2)	N(1)-C(5)-C(4)	105.71(12)

N(1)-C(5)-C(18)	126.62(13)	C(16)-C(15)-Cl(15)	119.30(13)
C(4)-C(5)-C(18)	127.66(14)	C(15)-C(16)-C(17)	118.72(15)
N(1)-C(6)-C(7)	111.92(12)	C(15)-C(16)-H(16)	120.4(10)
N(1)-C(6)-H(6A)	108.2(9)	C(17)-C(16)-H(16)	120.8(10)
C(7)-C(6)-H(6A)	110.0(9)	C(16)-C(17)-C(12)	120.81(15)
N(1)-C(6)-H(6B)	106.5(10)	C(16)-C(17)-H(17)	117.7(10)
C(7)-C(6)-H(6B)	111.3(10)	C(12)-C(17)-H(17)	121.5(10)
H(6A)-C(6)-H(6B)	108.7(14)	C(23)-C(18)-C(19)	118.61(14)
O(8)-C(7)-C(11)	104.36(12)	C(23)-C(18)-C(5)	123.68(14)
O(8)-C(7)-C(6)	109.31(12)	C(19)-C(18)-C(5)	117.62(14)
C(11)-C(7)-C(6)	111.35(12)	C(20)-C(19)-C(18)	120.70(15)
O(8)-C(7)-H(7)	105.9(9)	C(20)-C(19)-H(19)	118.1(10)
C(11)-C(7)-H(7)	114.5(9)	C(18)-C(19)-H(19)	121.1(10)
C(6)-C(7)-H(7)	110.9(9)	C(21)-C(20)-C(19)	120.34(16)
N(9)-O(8)-C(7)	107.92(10)	C(21)-C(20)-H(20)	120.3(11)
C(10)-N(9)-O(8)	108.81(12)	C(19)-C(20)-H(20)	119.3(11)
N(9)-C(10)-C(12)	120.88(14)	C(22)-C(21)-C(20)	119.31(15)
N(9)-C(10)-C(11)	114.14(13)	C(22)-C(21)-H(21)	119.3(12)
C(12)-C(10)-C(11)	124.89(14)	C(20)-C(21)-H(21)	121.4(12)
C(10)-C(11)-C(7)	99.80(12)	C(21)-C(22)-C(23)	120.88(16)
C(10)-C(11)-H(11A)	113.2(10)	C(21)-C(22)-H(22)	119.5(12)
C(7)-C(11)-H(11A)	112.2(10)	C(23)-C(22)-H(22)	119.6(12)
C(10)-C(11)-H(11B)	109.7(10)	C(18)-C(23)-C(22)	120.09(16)
C(7)-C(11)-H(11B)	113.5(10)	C(18)-C(23)-H(23)	121.0(11)
H(11A)-C(11)-H(11B)	108.3(14)	C(22)-C(23)-H(23)	118.9(11)
C(17)-C(12)-C(13)	119.01(14)	O(24)-C(24)-O(25)	123.77(14)
C(17)-C(12)-C(10)	120.70(14)	O(24)-C(24)-C(3)	125.95(14)
C(13)-C(12)-C(10)	120.28(14)	O(25)-C(24)-C(3)	110.28(12)
C(14)-C(13)-C(12)	120.41(16)	O(25)-C(25)-C(26)	107.03(14)
C(14)-C(13)-H(13)	119.9(10)	O(25)-C(25)-H(25A)	108.2(10)
C(12)-C(13)-H(13)	119.7(10)	C(26)-C(25)-H(25A)	111.9(10)
C(15)-C(14)-C(13)	119.34(15)	O(25)-C(25)-H(25B)	107.6(10)
C(15)-C(14)-H(14)	122.4(12)	C(26)-C(25)-H(25B)	111.7(11)
C(13)-C(14)-H(14)	118.3(12)	H(25A)-C(25)-H(25B)	110.3(15)
C(14)-C(15)-C(16)	121.71(15)	C(24)-O(25)-C(25)	115.53(12)
C(14)-C(15)-Cl(15)	118.99(12)	C(25)-C(26)-H(26A)	113.2(15)

C(25)-C(26)-H(26B)	110.8(13)	H(26A)-C(26)-H(26C)	104(2)
H(26A)-C(26)-H(26B)	108.9(19)	H(26B)-C(26)-H(26C)	110(2)
C(25)-C(26)-H(26C)	109.9(15)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9**{*1,1*} . The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	19(1)	18(1)	24(1)	-9(1)	-1(1)	-6(1)
N(2)	18(1)	19(1)	26(1)	-9(1)	-2(1)	-5(1)
C(3)	18(1)	19(1)	24(1)	-9(1)	-3(1)	-2(1)
C(4)	20(1)	21(1)	22(1)	-10(1)	0(1)	-4(1)
C(5)	19(1)	19(1)	23(1)	-10(1)	-3(1)	-2(1)
C(6)	19(1)	22(1)	23(1)	-10(1)	2(1)	-6(1)
C(7)	20(1)	23(1)	26(1)	-12(1)	0(1)	-7(1)
O(8)	19(1)	23(1)	27(1)	-9(1)	1(1)	-5(1)
N(9)	22(1)	23(1)	22(1)	-8(1)	-2(1)	-6(1)
C(10)	19(1)	23(1)	22(1)	-11(1)	-5(1)	-3(1)
C(11)	22(1)	23(1)	25(1)	-12(1)	-1(1)	-6(1)
C(12)	18(1)	22(1)	23(1)	-10(1)	-6(1)	-4(1)
C(13)	24(1)	24(1)	30(1)	-15(1)	-3(1)	-4(1)
C(14)	29(1)	22(1)	33(1)	-13(1)	-7(1)	-5(1)
C(15)	23(1)	24(1)	24(1)	-6(1)	-6(1)	-9(1)
Cl(15)	32(1)	28(1)	31(1)	-7(1)	-2(1)	-13(1)
C(16)	24(1)	28(1)	22(1)	-10(1)	0(1)	-6(1)
C(17)	24(1)	22(1)	24(1)	-10(1)	-4(1)	-4(1)
C(18)	16(1)	21(1)	29(1)	-13(1)	1(1)	-4(1)
C(19)	26(1)	22(1)	26(1)	-12(1)	1(1)	-6(1)
C(20)	30(1)	31(1)	32(1)	-20(1)	0(1)	-8(1)
C(21)	28(1)	28(1)	39(1)	-22(1)	5(1)	-10(1)
C(22)	34(1)	25(1)	32(1)	-12(1)	4(1)	-12(1)
C(23)	30(1)	26(1)	27(1)	-13(1)	-2(1)	-7(1)
C(24)	18(1)	19(1)	23(1)	-9(1)	-1(1)	-2(1)
O(24)	23(1)	28(1)	32(1)	-17(1)	2(1)	-10(1)
C(25)	27(1)	22(1)	26(1)	-8(1)	3(1)	-10(1)
O(25)	28(1)	24(1)	23(1)	-10(1)	2(1)	-11(1)
C(26)	68(2)	36(1)	35(1)	-19(1)	20(1)	-28(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **9**{*1,1*}.

	x	y	z	U(eq)
H(4)	1736	808	7995	25(5)
H(6A)	7180(40)	673(13)	5178(11)	19(4)
H(6B)	7240(40)	1765(13)	5098(11)	23(4)
H(7)	2850(40)	1216(12)	4325(11)	19(4)
H(11A)	8080(40)	1875(13)	3446(12)	29(5)
H(11B)	5300(40)	2081(13)	2846(12)	28(5)
H(13)	5360(40)	5173(13)	2706(12)	26(5)
H(14)	7990(40)	6427(15)	1530(13)	38(5)
H(16)	12590(40)	4407(13)	724(12)	27(5)
H(17)	10030(40)	3125(14)	1947(12)	30(5)
H(19)	6170(40)	1576(13)	8021(12)	27(5)
H(20)	8350(40)	2913(14)	7976(13)	37(5)
H(21)	9230(40)	4328(15)	6502(14)	41(5)
H(22)	7730(40)	4442(15)	5108(15)	44(6)
H(23)	5300(40)	3142(14)	5172(13)	33(5)
H(25A)	-2660(40)	-2115(14)	9233(12)	23(4)
H(25B)	-5270(40)	-1317(13)	8764(12)	27(5)
H(26A)	-2470(60)	-1406(19)	10329(18)	72(8)
H(26B)	-5570(50)	-1871(17)	10444(15)	51(6)
H(26C)	-5120(50)	-741(19)	9865(16)	56(7)