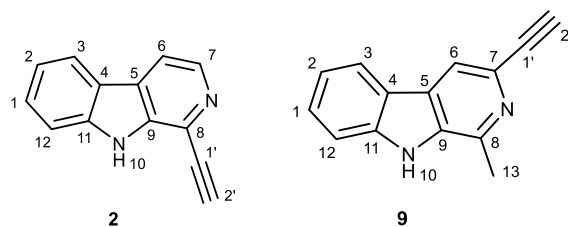
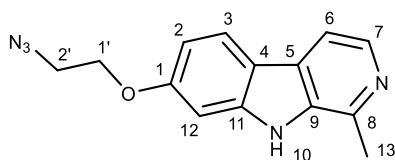


Table S1. IR, ^1H and ^{13}C NMR spectroscopic data for alkynes **2** and **9**



Compd.	IR (ATR, νcm^{-1})	^1H NMR (DMSO- d_6 , δ ppm)	^{13}C NMR (DMSO- d_6 , δ ppm)
2	3289, 3154, 3061, 2111, 1626, 1562, 1498, 1452, 1424, 1387, 1321, 1273, 1246, 1151, 1081, 1066, 939, 874, 856, 837, 783, 748, 684, 631, 569, 513	11.79 (s, 1H, 10), 8.34 (d, 1H, 7, $J = 5.2$ Hz), 8.26 (d, 1H, 3, $J = 7.9$ Hz), 8.17 (d, 1H, 6, $J = 5.2$ Hz), 7.64 (d, 1H, 12, $J = 8.2$ Hz), 7.60–7.56 (m, 1H, 1), 7.30–7.26 (m, 1H, 2), 4.77 (s, 1H, 2')	140.83 (8), 138.66 (7), 137.67 (11), 128.67 (1), 128.14 (9), 125.42 (5), 122.02 (3), 120.69 (4), 119.81 (2), 115.32 (6), 112.33 (12), 84.94 (1'), 30.68 (2')
9	3306, 3143, 2104, 1622, 1597, 1563, 1499, 1446, 1375, 1338, 1315, 1281, 1247, 1178, 1147, 1014, 961, 899, 877, 776, 740, 654, 625, 587, 504, 457	11.83 (s, 1H, 10), 8.25–8.22 (m, 1H, 3), 8.21 (s, 1H, 6), 7.62–7.59 (m, 1H, 12), 7.57–7.53 (m, 1H, 1), 7.27–7.23 (m, 1H, 2), 4.03 (s, 1H, 2'), 2.74 (s, 3H, 13)	142.83 (7), 140.70 (8), 134.06 (11), 129.54 (9), 128.30 (1), 127.01 (5), 122.05 (3), 120.72 (4), 119.78 (2), 117.22 (6), 112.15 (12), 84.85 (1'), 76.72 (2'), 20.33 (13)

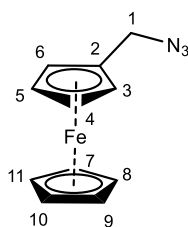
Table S2. ^1H and ^{13}C NMR spectroscopic data for azide **15**



15

Compd.	^1H NMR (DMSO- d_6 , δ ppm)	^{13}C NMR (DMSO- d_6 , δ ppm)
15	11.44 (s, 1H, 10), 8.16 (d, 1H, 7, $J = 5.3$ Hz), 8.08 (d, 1H, 3, $J = 5.2$ Hz), 7.82 (d, 1H, 6, $J = 5.2$ Hz), 7.04 (d, 1H, 12, $J = 2.2$ Hz), 6.87 (dd, 1H, 2, $J = 8.6, 2.2$ Hz), 4.30 (t, 2H, 1', $J = 4.8$ Hz), 3.72 (t, 2H, 2', $J = 4.8$ Hz), 2.73 (s, 3H, 13)	158.70 (1), 141.77 (8), 141.35 (11), 137.78 (7), 134.60 (9), 127.12 (5), 122.75 (3), 115.26 (4), 111.99 (6), 109.14 (2), 95.62 (12), 67.14 (1'), 49.64 (2'), 20.33 (13)

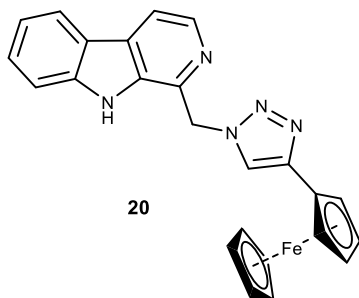
Table S3. ^1H and ^{13}C NMR spectroscopic data for ferrocene azide **19**



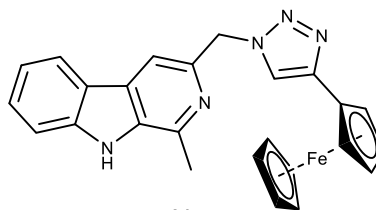
19

Compd.	^1H NMR (DMSO- d_6 , δ ppm)	^{13}C NMR (DMSO- d_6 , δ ppm)
19	4.29 (t, 2H, 3, 6, $J = 1.8$ Hz), 4.21 (t, 2H, 4, 5, $J = 1.9$ Hz), 4.20 (s, 2H, 1), 4.20 (s, 5H, 7–11)	81.78 (2), 68.62 (3, 6), 68.58 (7–11), 68.44 (4, 5), 50.02 (1)

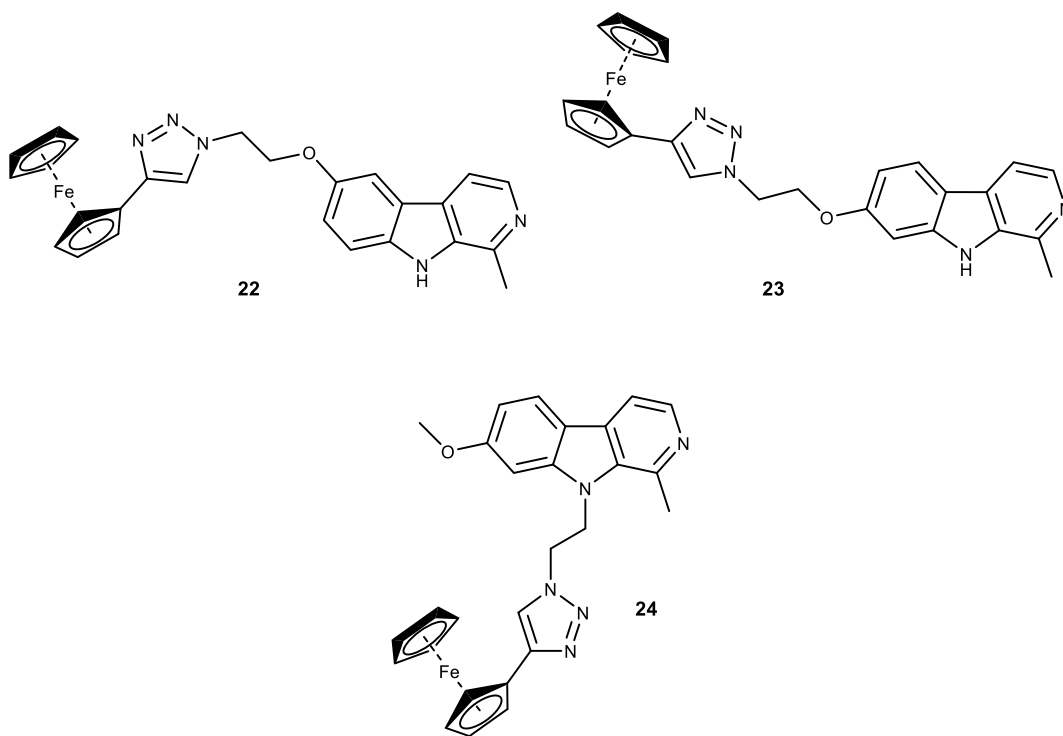
Table S4. Analytical and MS data for harmicenes **20–24**



20

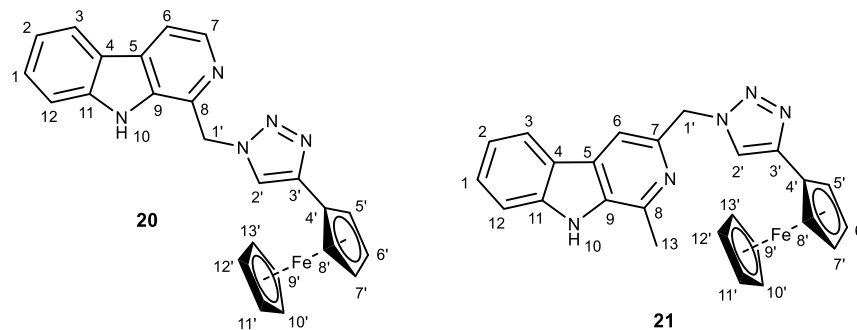


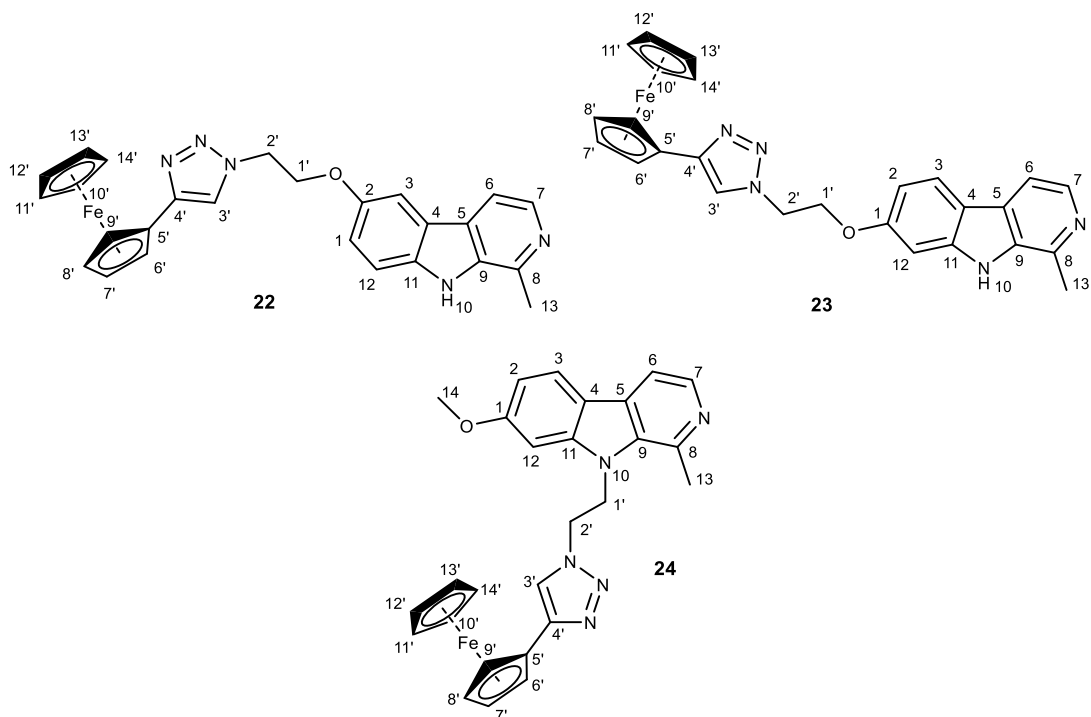
21



Compd.	Yield (%)	<i>t_f</i> (°C)	Molecular formula	<i>M_r</i>	MS (<i>m/z</i>)	CHN
20	78	252–255.5	C ₂₄ H ₁₉ FeN ₅	433.30	434.9 (M+1) ⁺	C, 66.53; H, 4.42; N, 16.16
21	62	242.5–244	C ₂₅ H ₂₁ FeN ₅	447.32	448.9 (M+1) ⁺	C, 67.13; H, 4.73; N, 15.66
22	37	201.5–204	C ₂₆ H ₂₃ FeN ₅ O	477.35	477.9 (M+1) ⁺	C, 65.42; H, 4.86; N, 14.67
23	77	228–229.5	C ₂₆ H ₂₃ FeN ₅ O	477.35	477.9 (M+1) ⁺	C, 65.42; H, 4.86; N, 14.67
24	63	218–220	C ₂₇ H ₂₅ FeN ₅ O	491.38	491.9 (M+1) ⁺	C, 66.00; H, 5.13; N, 14.25

Table S5. IR, ¹H and ¹³C NMR spectroscopic data for harmicenes **20–24**

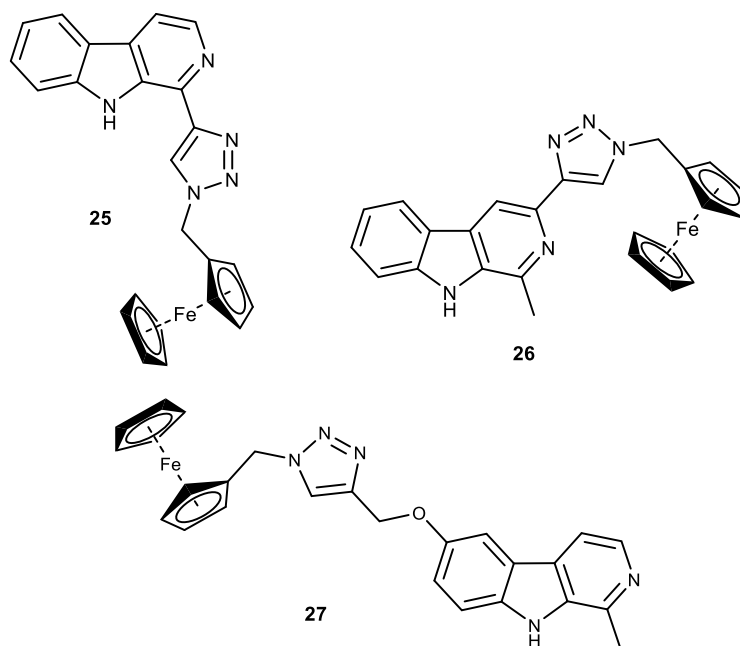


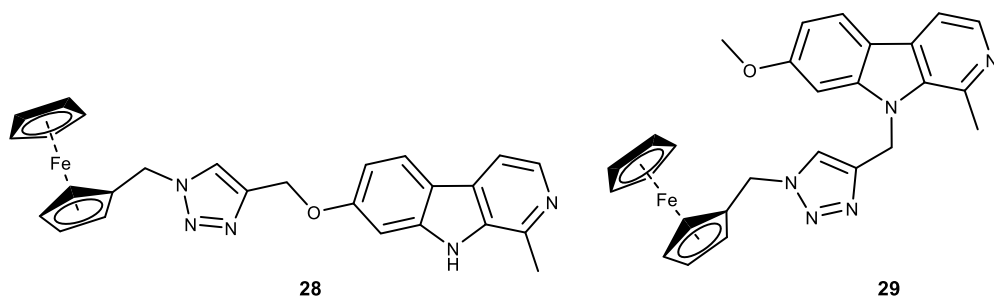


Compd.	IR (ATR, ν/cm^{-1})	^1H NMR (DMSO- d_6 , δ ppm)	^{13}C NMR (DMSO- d_6 , δ ppm)
20	3249, 3138, 3094, 2987, 2953, 1625, 1585, 1567, 1497, 1455, 1430, 1389, 1321, 1236, 1212, 1189, 1094, 1058, 998, 875, 816, 794, 750, 730, 622, 592, 500	11.95 (s, 1H, 10), 8.31 (d, 1H, 7, $J = 5.2$ Hz), 8.28–8.26 (m, 2H, 3, 2'), 8.13 (d, 1H, 6, $J = 5.1$ Hz), 7.70–7.68 (m, 1H, 12), 7.61–7.59 (m, 1H, 1), 7.30–7.27 (m, 1H, 2), 6.08 (s, 2H, 1'), 4.73 (t, 2H, 5', 8', $J = 1.9$ Hz), 4.28 (t, 2H, 6', 7', $J = 1.8$ Hz), 4.03 (s, 5H, 9'–13')	145.22 (8), 140.71 (11), 138.17 (3'), 137.86 (7), 133.85 (9), 128.71 (5), 128.54 (2'), 121.91 (3), 121.57 (1), 120.76 (4), 119.64 (2), 114.82 (6), 112.09 (12), 76.04 (4'), 69.23 (9'–13'), 68.21 (5', 8'), 66.34 (6', 7'), 51.24 (1')
21	3148, 3101, 2993, 2891, 1737, 1627, 1566, 1506, 1456, 1443, 1351, 1328, 1251, 1219, 1086, 1057, 1019, 1000, 874, 815, 729, 680, 587, 506, 487	11.66 (s, 1H, 10), 8.23 (s, 1H, 6), 8.16 (d, 1H, 3, $J = 7.9$ Hz), 7.90 (s, 1H, 2'), 7.60–7.59 (m, 1H, 12), 7.55–7.52 (m, 1H, 1), 7.24–7.21 (m, 1H, 2), 5.76 (s, 2H, 1'), 4.74 (t, 2H, 5', 8', $J = 1.9$ Hz), 4.29 (t, 2H, 6', 7', $J = 1.9$ Hz), 4.03 (s, 5H, 9'–13'), 2.76 (s, 3H, 13)	145.37 (8), 142.95 (7), 142.05 (11), 140.77 (3'), 133.94 (9), 128.08 (2'), 127.63 (5), 121.64 (3), 121.06 (1), 120.91 (4), 119.44 (2), 112.09 (6), 111.42 (12), 76.09 (4'), 69.26 (9'–13'), 68.21 (5', 8'), 66.32 (6', 7'), 55.10 (1'), 20.38 (13)
22	3133, 2949, 2872, 1583, 1568, 1497, 1458, 1286, 1210, 1105, 1041, 988, 878, 818, 705, 621, 504	11.39 (s, 1H, 10), 8.29 (s, 1H, 3'), 8.15 (d, 1H, 7, $J = 5.3$ Hz), 7.87 (d, 1H, 6, $J = 5.3$ Hz), 7.78 (d, 1H, 12, $J = 2.5$ Hz), 7.48 (d, 1H, 12, $J = 8.8$ Hz), 7.16 (dd, 1H, 1, $J = 8.8, 2.5$ Hz), 4.82 (t, 2H, 1', $J = 5.1$ Hz), 4.73 (t, 2H, 6', 9', $J = 1.9$ Hz), 4.53 (t, 2H, 2', $J = 5.2$	151.85 (2), 145.24 (8), 142.24 (4'), 136.98 (7), 135.52 (11), 135.10 (9), 126.63 (4), 121.35 (5), 121.28 (3'), 118.14 (1), 112.77 (6), 112.64 (12), 105.13 (3), 76.05 (5'), 69.22 (10'–14'), 68.21 (6', 9'), 67.14 (1'), 66.34 (7', 8'), 49.24 (2'), 20.40 (13)

			Hz), 4.30 (t, 2H, 7', 8', $J = 1.8$ Hz), 4.01 (s, 5H, 10'–14'), 2.72 (s, 3H, 13)
23	3125, 3077, 2959, 2850, 2772, 1623, 1566, 1443, 1426, 1301, 1278, 1240, 1185, 1108, 1053, 1042, 977, 874, 822, 810, 743, 720, 693, 638, 587, 570, 522, 513, 495, 483	11.44 (s, 1H, 10), 8.30 (s, 1H, 3'), 8.14 (d, 1H, 7, $J = 5.3$ Hz), 8.05 (d, 1H, 3, $J = 8.6$ Hz), 7.79 (d, 1H, 6, $J = 5.3$ Hz), 7.03 (d, 1H, 12, $J = 2.2$ Hz), 6.85 (dd, 1H, 2, $J = 8.6, 2.2$ Hz), 4.83 (t, 2H, 1', $J = 5.1$ Hz), 4.73 (t, 2H, 6', 9', $J = 1.9$ Hz), 4.55 (t, 2H, 2', $J = 5.1$ Hz), 4.30 (t, 2H, 7', 8', $J = 1.8$ Hz), 4.01 (s, 5H, 10'–14'), 2.72 (s, 3H, 13)	158.62 (1), 145.25 (8), 141.72 (4'), 141.35 (11), 137.76 (7), 134.59 (9), 127.07 (5), 122.71 (3'), 121.34 (3), 115.33 (4), 111.98 (6), 109.17 (2), 95.73 (12), 76.01 (5'), 69.23 (10'–14'), 68.22 (6', 9'), 66.57 (1'), 66.35 (7', 8'), 49.09 (2'), 20.36 (13)
24	2968, 1621, 1565, 1445, 1404, 1339, 1253, 1222, 1158, 1182, 1136, 1096, 1041, 1021, 970, 929, 877, 821, 807, 641, 590, 545, 501, 475	8.17 (d, 1H, 7, $J = 5.2$ Hz), 8.04 (d, 1H, 3, $J = 8.5$ Hz), 7.88 (d, 1H, 6, $J = 5.2$ Hz), 7.80 (s, 1H, 3'), 6.84–6.78 (m, 2H, 2, 12), 5.08 (t, 2H, 1', $J = 5.6$ Hz), 4.88 (t, 2H, 2', $J = 5.6$ Hz), 4.49 (t, 2H, 6', 9', $J = 1.9$ Hz), 4.22 (t, 2H, 7', 8', $J = 1.9$ Hz), 3.86–3.85 (m, 8H, 14, 10'–14'), 2.90 (s, 3H, 13)	160.51 (1), 145.15 (4'), 142.76 (8), 140.67 (11), 138.12 (7), 134.68 (9), 128.73 (5), 122.23 (3'), 121.79 (3), 114.10 (4), 112.26 (6), 109.81 (2), 92.93 (12), 75.78 (5'), 68.09 (10'–14'), 68.06 (6', 9'), 66.26 (7', 8'), 55.37 (14), 49.71 (1'), 44.47 (2'), 23.18 (13)

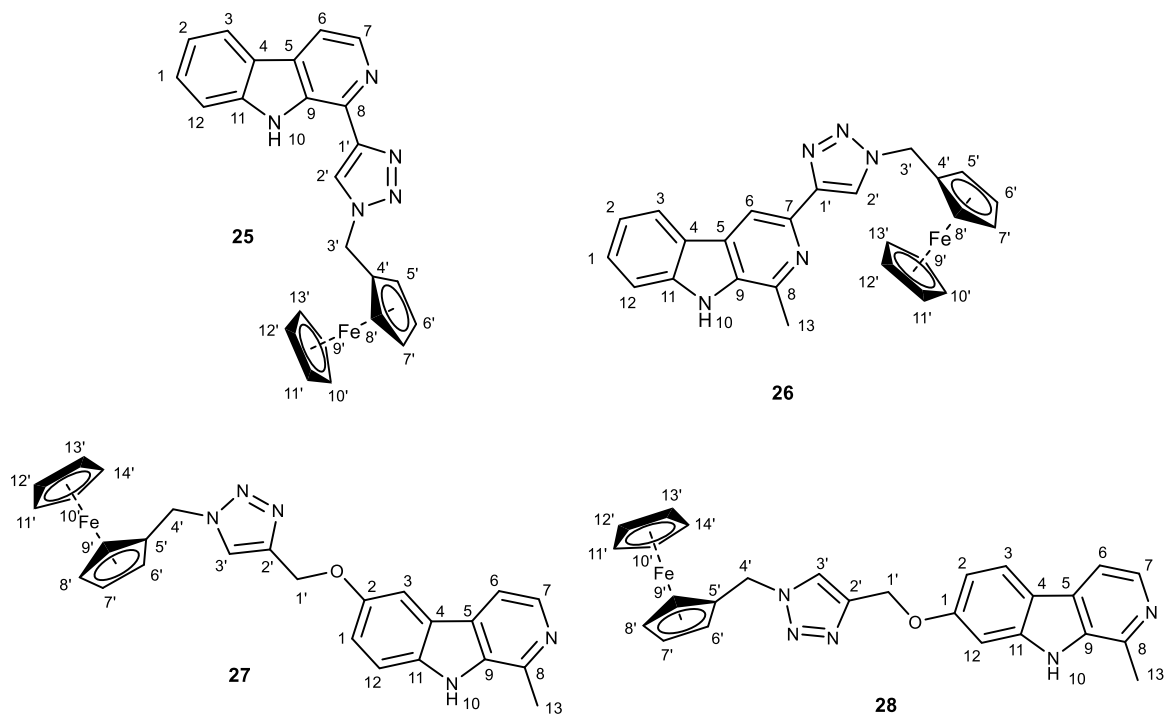
Table S6. Analytical and MS data for harmicenes **25–29**

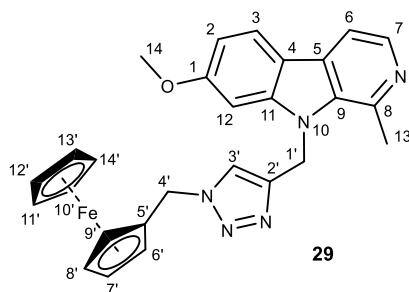




Compd.	Yield (%)	<i>t</i> _f (°C)	Molecular formula	<i>M</i> _r	MS (<i>m/z</i>)	CHN
25	51	229–230	C ₂₄ H ₁₉ FeN ₅	433.30	434.1 (M+1) ⁺	C, 66.53; H, 4.42; N, 16.16
26	45	183–186	C ₂₅ H ₂₁ FeN ₅	447.32	447.9 (M+1) ⁺	C, 67.13; H, 4.73; N, 15.66
27	68	244.5–248	C ₂₆ H ₂₃ FeN ₅ O	477.35	478.1 (M+1) ⁺	C, 65.42; H, 4.86; N, 14.67
28	60	242–244	C ₂₆ H ₂₃ FeN ₅ O	477.35	478.1 (M+1) ⁺	C, 65.42; H, 4.86; N, 14.67
29	30	187–190	C ₂₇ H ₂₅ FeN ₅ O	491.38	492.1 (M+1) ⁺	C, 66.00; H, 5.13; N, 14.25

Table S7. IR, ¹H and ¹³C NMR spectroscopic data for harmicenes **25–29**

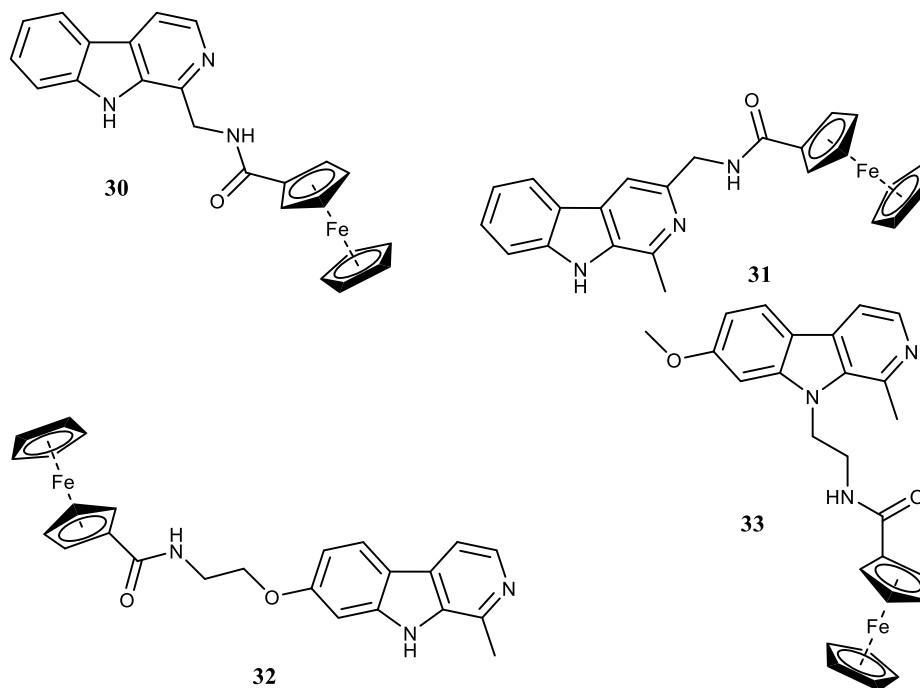




Compd.	IR (ATR, ν/cm^{-1})	^1H NMR (DMSO- d_6 , δ ppm)	^{13}C NMR (DMSO- d_6 , δ ppm)
25	3385, 3172, 3105, 3065, 2991, 1625, 1576, 1489, 1452, 1437, 1419, 1351, 1314, 1282, 1254, 1239, 1152, 1103, 1000, 829, 807, 749, 629, 591, 548, 499, 479	11.53 (s, 1H, 10), 8.78 (s, 1H, 2'), 8.38 (d, 1H, 7, $J = 5.2$ Hz), 8.26–8.24 (m, 1H, 3), 8.11 (d, 1H, 6, $J = 5.1$ Hz), 7.91–7.90 (m, 1H, 12), 7.57–7.54 (m, 1H, 1), 7.27–7.25 (m, 1H, 2), 5.49 (s, 2H, 3'), 4.46 (t, 2H, 5', 8', $J = 1.9$ Hz), 4.24 (s, 5H, 9'–13'), 4.22 (t, 2H, 6', 7', $J = 1.9$ Hz)	147.60 (8), 141.15 (11), 137.83 (7), 133.68 (9), 131.74 (1'), 129.05 (4), 128.18 (2'), 122.94 (1), 121.47 (3), 120.40 (5), 119.51 (2), 114.11 (6), 113.23 (12), 82.36 (4'), 68.74 (5', 8'), 68.69 (9'–13'), 68.48 (6', 7'), 49.33 (3')
26	3361, 2920, 2851, 1734, 1626, 1574, 1496, 1455, 1431, 1373, 1338, 1303, 1277, 1234, 1172, 1104, 1049, 1024, 1000, 924, 889, 818, 788, 775, 704, 631, 558, 584, 503, 478	11.69 (s, 1H, 10), 8.58 (s, 1H, 2'), 8.41 (s, 1H, 6), 8.29 (d, 1H, 3, $J = 7.9$ Hz), 7.60 (d, 1H, 12, $J = 8.1$ Hz), 7.54 (t, 1H, 1, $J = 7.6$ Hz), 7.24 (t, 1H, 2, $J = 7.4$ Hz), 5.39 (s, 2H, 3'), 4.45 (t, 2H, 5', 8', $J = 1.9$ Hz), 4.23 (s, 5H, 9'–13'), 4.21 (t, 2H, 6', 7', $J = 1.9$ Hz), 2.80 (s, 3H, 13)	148.61 (7), 141.93 (11), 140.82 (8), 139.95 (9), 133.96 (1'), 128.02 (2'), 127.73 (4), 121.97 (1), 121.27 (5), 121.25 (3), 119.36 (2), 112.01 (6), 108.31 (12), 82.45 (4'), 68.86 (5', 8'), 68.68 (9'–13'), 68.44 (6', 7'), 49.05 (3'), 20.48 (13)
27	3631, 3137, 3081, 2950, 1637, 1603, 1583, 1567, 1499, 1480, 1451, 1411, 1283, 1211, 1107, 1069, 1054, 1040, 1027, 849, 821, 765, 620, 504	11.37 (s, 1H, 10), 8.24 (s, 1H, 3'), 8.16 (d, 1H, 7, $J = 5.3$ Hz), 7.89–7.88 (m, 2H, 3, 6), 7.49 (d, 1H, 12, $J = 8.8$ Hz), 7.21 (dd, 1H, 1, $J = 8.9, 2.5$ Hz), 5.32 (s, 2H, 1'), 5.21 (s, 2H, 4'), 4.32 (t, 2H, 6', 9', $J = 1.8$ Hz), 4.16–4.14 (m, 7H, 7', 8', 10'–14'), 2.73 (s, 3H, 13)	151.88 (2), 142.95 (2'), 142.19 (8), 136.96 (7), 135.42 (11), 135.08 (9), 126.69 (4), 124.09 (3'), 121.34 (5), 118.39 (1), 112.73 (6), 112.67 (12), 105.20 (3), 82.49 (5'), 68.62 (10'–14'), 68.59 (6', 9'), 68.31 (7', 8'), 61.88 (1'), 48.92 (4'), 20.40 (13)
28	3344, 3072, 2869, 2785, 1738, 1626, 1567, 1488, 1444, 1377, 1325, 1305, 1290, 1278, 1177, 1142, 1110, 1058, 1142, 1011, 965, 828, 813, 781, 661, 639, 598, 572, 505, 480	11.45 (s, 1H, 10), 8.23 (s, 1H, 3'), 8.15 (d, 1H, 7, $J = 5.2$ Hz), 8.05 (d, 1H, 3, $J = 8.6$ Hz), 7.80 (d, 1H, 6, $J = 5.3$ Hz), 7.16 (d, 1H, 12, $J = 2.2$ Hz), 6.89 (dd, 1H, 2, $J = 8.7, 2.3$ Hz), 5.33 (s, 2H, 1'), 5.25 (s, 2H, 4'), 4.34 (t, 2H, 6', 9', $J = 1.9$ Hz), 4.18–4.16 (m, 7H, 7', 8', 10'–14'), 2.72 (s, 3H, 13)	158.74 (1), 142.71 (8), 141.76 (2'), 141.33 (11), 137.74 (7), 134.58 (9), 127.13 (5), 124.15 (3'), 122.63 (3), 115.11 (4), 111.95 (6), 109.46 (2), 95.86 (12), 82.41 (5'), 68.66 (6', 9'), 68.64 (10'–14'), 68.36 (7', 8'), 61.45 (1'), 48.98 (4'), 20.32 (13)

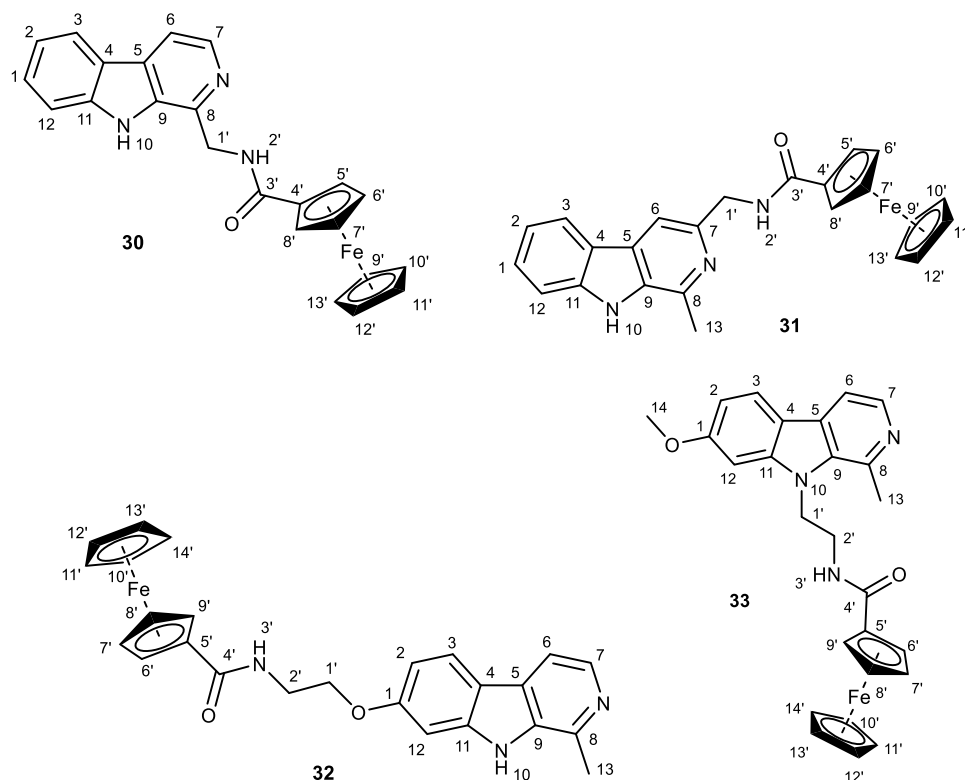
29	3135, 3090, 2929, 1709, 1623, 1564, 1499, 1449, 1408, 1325, 1252, 1227, 1193, 1174, 1106, 1042, 1000, 913, 815, 764, 732, 638, 596, 550, 481	8.16 (d, 1H, 7, $J = 5.2$ Hz), 8.07 (d, 1H, 3, $J = 8.5$ Hz), 7.98 (s, 1H, 3'), 7.86 (d, 1H, 6, $J = 5.2$ Hz), 7.32 (d, 1H, 12, $J = 2.2$ Hz), 6.87 (dd, 1H, 2, $J = 8.5, 2.2$ Hz), 5.86 (s, 2H, 1'), 5.21 (s, 2H, 4'), 4.23 (t, 2H, 6', 9', $J = 1.8$ Hz), 4.12 (t, 2H, 7', 8', $J = 1.8$ Hz), 4.06 (s, 5H, 10'-14'), 3.88 (s, 3H, 14), 3.03 (s, 3H, 13)	160.55 (1), 143.81 (2'), 142.67 (8), 141.13 (11), 138.05 (7), 134.66 (9), 128.54 (5), 122.55 (3'), 122.38 (3), 114.46 (4), 112.26 (6), 109.46 (2), 94.05 (12), 82.59 (5'), 68.54 (10'-14'), 68.44 (6', 9'), 68.21 (7', 8'), 55.62 (14), 48.77 (4'), 23.24 (13)

Table S8. Analytical and MS data for harmicenes **30–33**



Compd.	Yield (%)	t_f (°C)	Molecular formula	M_r	MS (m/z)	CHN
30	48	210–213	C ₂₃ H ₁₉ FeN ₃ O	409.27	410.0 (M+1) ⁺	C, 67.50; H, 4.68; N, 10.27
31	39	240.5–243	C ₂₄ H ₂₁ FeN ₃ O	423.30	424.0 (M+1) ⁺	C, 68.10; H, 5.00; N, 9.93
32	42	243–245.5	C ₂₅ H ₂₃ FeN ₃ O ₂	453.32	454.0 (M+1) ⁺	C, 66.24; H, 5.11; N, 9.27
33	50	225–227	C ₂₆ H ₂₅ FeN ₃ O ₂	467.35	468.1 (M+1) ⁺	C, 66.82; H, 5.39; N, 8.99

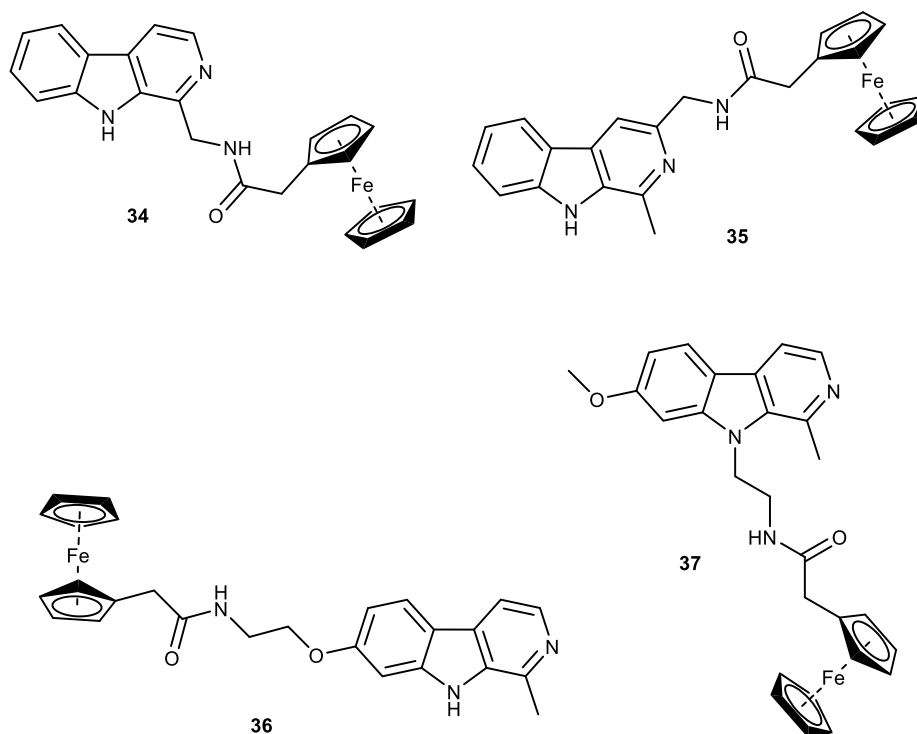
Table S9. IR, ^1H and ^{13}C NMR spectroscopic data for harmicenes **30–33**



Compd.	IR (ATR, ν/cm^{-1})	^1H NMR (DMSO- d_6 , δ ppm)	^{13}C NMR (DMSO- d_6 , δ ppm)
30	3623, 3467, 3085, 3050, 2962, 2928, 1711, 1649, 1622, 1531, 1503, 1444, 1408, 1375, 1340, 1300, 1249, 1229, 1195, 138, 1123, 1106, 1041, 1017, 914, 819, 801, 634, 598, 558	11.49 (s, 1H, 10), 8.58 (t, 1H, 2', $J = 6.0$ Hz), 8.31 (d, 1H, 7, $J = 5.2$ Hz), 8.23 (d, 1H, 3, $J = 7.8$ Hz), 8.05 (d, 1H, 6, $J = 5.2$ Hz), 7.68 (d, 1H, 12, $J = 8.2$ Hz), 7.56 (t, 1H, 1, $J = 7.6$ Hz), 7.25 (t, 1H, 2, $J = 7.5$ Hz), 4.88–4.87 (m, 4H, 1', 5', 8'), 4.35 (t, 2H, 6', 7', $J = 1.9$ Hz), 4.07 (s, 5H, 9'–13')	169.83 (3'), 142.64 (8), 140.17 (11), 137.35 (7), 133.55 (9), 128.10 (3), 127.74 (5), 121.74 (1), 120.93 (4), 119.37 (2), 113.86 (6), 111.99 (12), 76.11 (4'), 70.10 (5', 8'), 69.31 (9'–13'), 68.30 (6', 7'), 41.73 (1')
31	3324, 3226, 1634, 1574, 1532, 1498, 1447, 1380, 1348, 1297, 1248, 1104, 1026, 901, 814, 755, 738, 629, 528, 482	11.51 (s, 1H, 10), 8.47 (t, 1H, 2', $J = 6.1$ Hz), 8.12 (d, 1H, 3, $J = 7.9$ Hz), 7.89 (s, 1H, 6), 7.57 (d, 1H, 12, $J = 8.2$ Hz), 7.52–7.48 (m, 1H, 1), 7.21–7.17 (m, 1H, 2), 4.90 (t, 2H, 5', 8', $J = 1.9$ Hz), 4.60 (d, 2H, 1', $J = 6.0$ Hz), 4.37 (t, 2H, 6', 7', $J = 1.9$ Hz), 4.20 (s, 5H, 9'–13'), 2.78 (s, 3H, 13)	168.94 (3'), 147.17 (7), 141.14 (8), 140.76 (11), 133.49 (9), 127.78 (3), 127.66 (5), 121.35 (1), 120.95 (4), 119.16 (2), 111.98 (12), 109.47 (6), 76.73 (4'), 69.96 (5', 8'), 69.25 (9'–13'), 68.28 (6', 7'), 44.31 (1'), 20.27 (13)

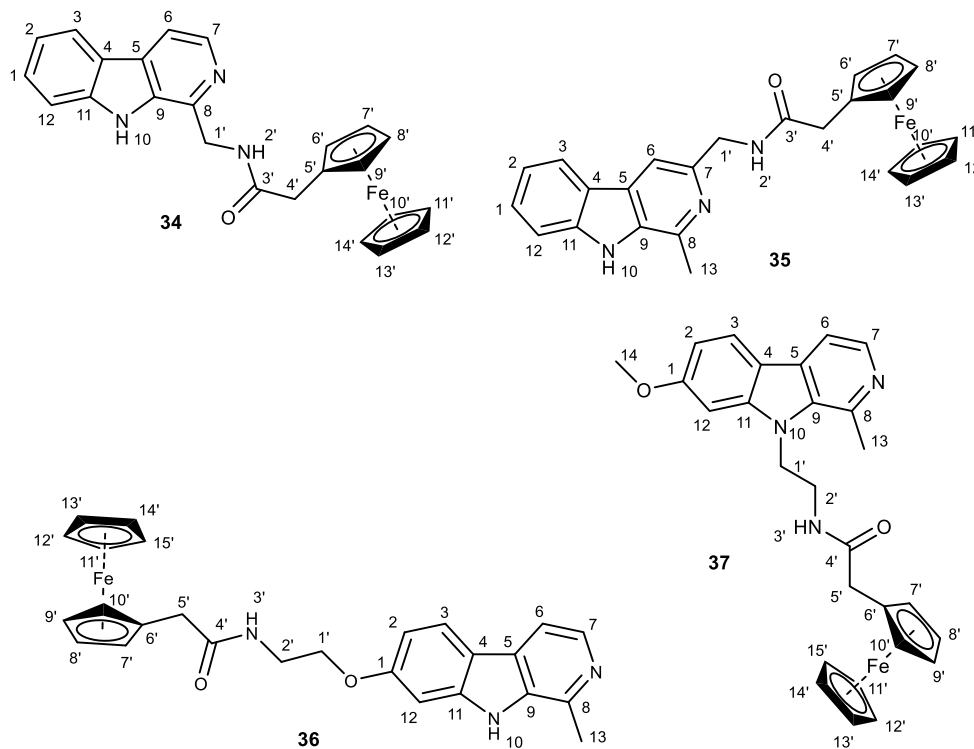
32	3216, 1716, 1622, 1551, 1451, 1422, 1376, 1312, 1278, 1236, 1217, 1105, 960, 842, 801, 741, 641, 605, 505, 476	11.41 (s, 1H, 10), 8.14 (d, 1H, 7, $J = 5.3$ Hz), 8.07–8.05 (m, 2H, 3', 3), 7.79 (d, 1H, 6, $J = 5.3$ Hz), 7.07 (d, 1H, 12, $J = 2.4$ Hz), 6.90 (dd, 1H, 2, $J = 8.7, 2.2$ Hz), 4.83 (t, 2H, 6', 9', $J = 2.0$ Hz), 4.35 (t, 2H, 7', 8', $J = 1.9$ Hz), 4.23 (t, 2H, 1', $J = 5.7$ Hz), 4.13 (s, 5H, 10'–14'), 3.63 (q, 2H, 2', $J = 5.7$ Hz), 2.71 (s, 3H, 13)	169.36 (4'), 159.31 (1), 141.89 (8), 141.28 (11), 137.74 (7), 134.55 (9), 127.17 (5), 122.69 (3), 114.98 (4), 111.93 (6), 109.22 (2), 95.38 (12), 76.31 (5'), 70.01 (6', 9'), 69.40 (10'–14'), 68.22 (7', 8'), 66.40 (1'), 38.49 (2'), 20.33 (13)
33	3623, 3467, 3085, 3050, 2962, 2928, 1711, 1649, 1622, 1531, 1503, 1444, 1408, 1375, 1340, 1300, 1249, 1229, 1195, 1177, 1138, 1123, 1107, 1041, 1016, 914, 819, 801, 634, 598, 558	8.17 (d, 1H, 7, $J = 5.1$ Hz), 8.10–8.07 (m, 2H, 3, 3'), 7.88 (d, 1H, 6, $J = 5.1$ Hz), 7.32 (d, 1H, 12, $J = 2.2$ Hz), 6.88 (dd, 1H, 2, $J = 8.5, 2.1$ Hz), 4.69 (t, 2H, 6', 9', $J = 1.9$ Hz), 4.66 (t, 2H, 1', $J = 7.1$ Hz), 4.34 (t, 2H, 7', 8', $J = 1.9$ Hz), 4.07 (s, 5H, 10'–14'), 3.91 (s, 3H, 14), 3.60 (q, 2H, 2', $J = 6.7$ Hz), 3.04 (s, 3H, 13)	169.75 (4'), 160.52(1), 143.00 (8), 140.66 (11), 137.82 (7), 134.67 (9), 128.43 (5), 122.39 (3), 114.28 (4), 112.26 (6), 109.20 (2), 93.78 (12), 76.40 (5'), 69.93 (6', 9'), 69.32 (10'–14'), 68.08 (7', 8'), 55.50 (14), 43.56 (1'), 39.10 (2'), 23.14 (13)

Table S10. Analytical and MS data for harmicenes **34–37**



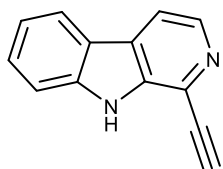
Compd.	Yield (%)	<i>t</i> _f (°C)	Molecular formula	<i>M</i> _r	MS (<i>m/z</i>)	CHN
34	34	222–224.5	C ₂₄ H ₂₁ FeN ₃ O	423.30	424.1 (M+1) ⁺	C, 68.10; H, 5.00; N, 9.93
35	39	247.5–250	C ₂₅ H ₂₃ FeN ₃ O	437.32	438.0 (M+1) ⁺	C, 68.66; H, 5.30; N, 9.61
36	58	176–177.5	C ₂₆ H ₂₅ FeN ₃ O ₂	467.35	468.1 (M+1) ⁺	C, 66.82; H, 5.39; N, 8.99
37	69	170.5–172	C ₂₇ H ₂₇ FeN ₃ O ₂	481.38	482.2 (M+1) ⁺	C, 67.37; H, 5.65; N, 8.73

Table S11. IR, ¹H and ¹³C NMR spectroscopic data for harmicenes **34–37**

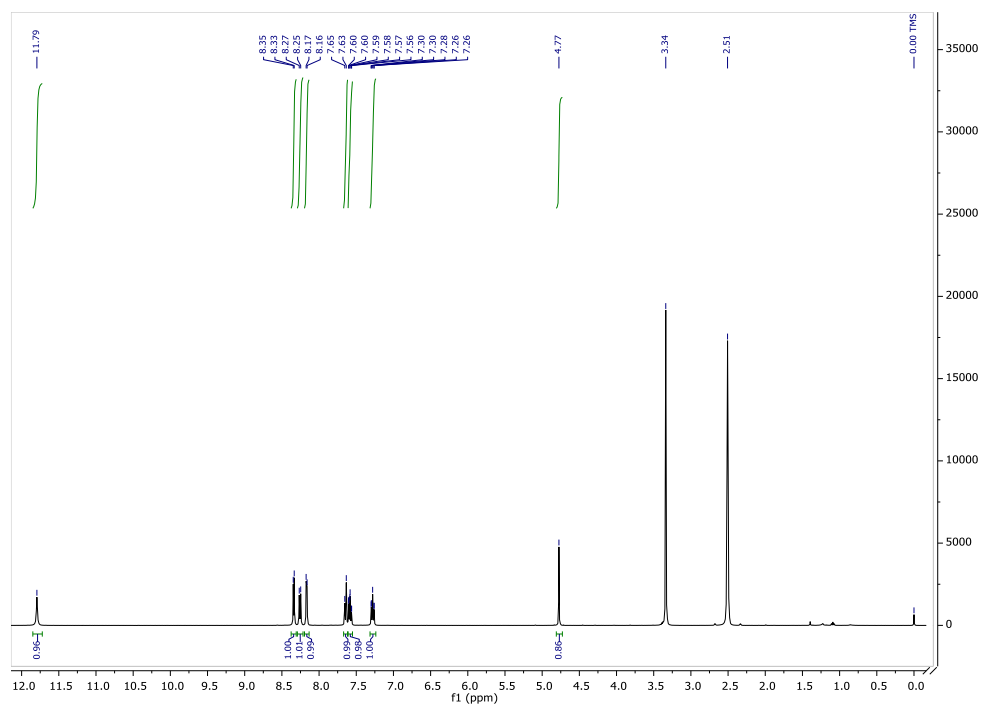
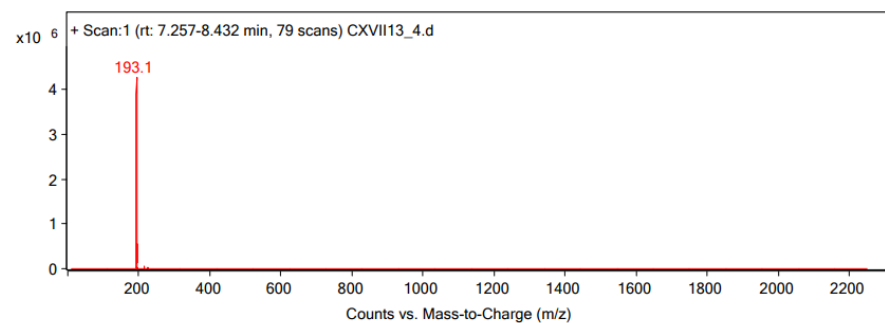
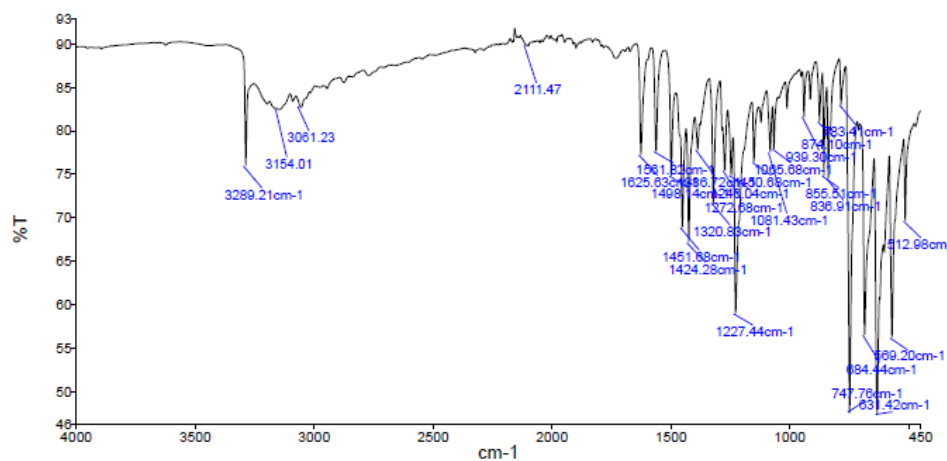


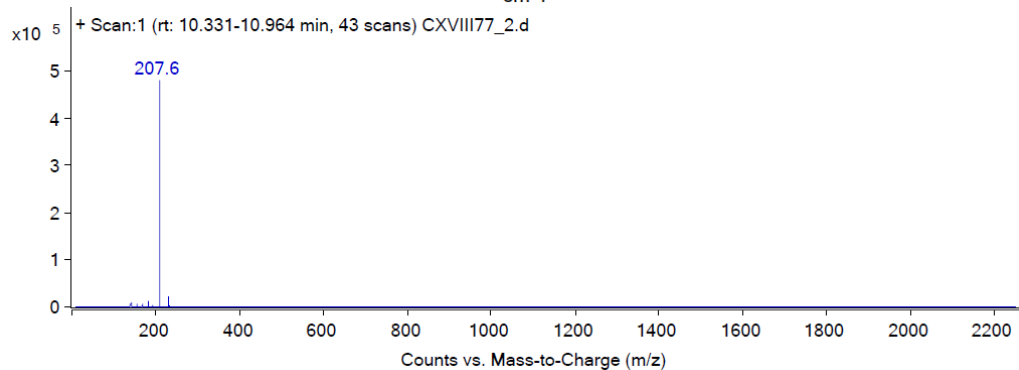
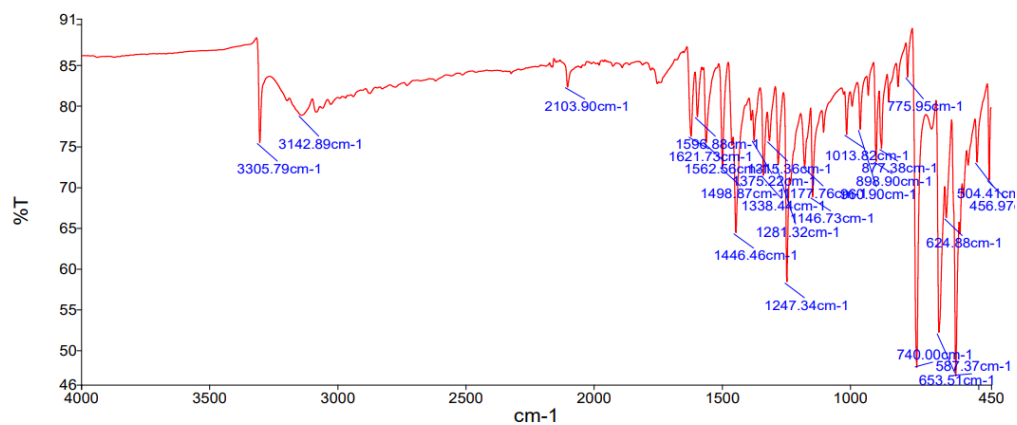
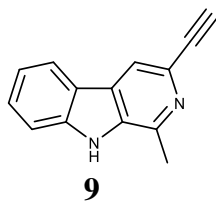
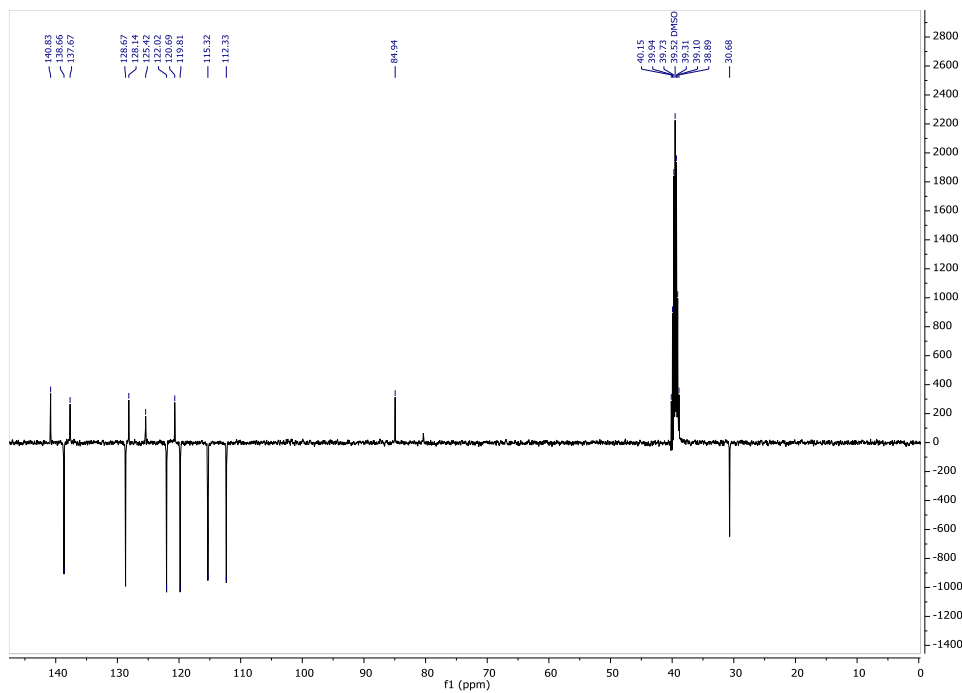
Compd.	IR (ATR, ν cm ⁻¹)	¹ H NMR (DMSO- <i>d</i> ₆ , δ ppm)	¹³ C NMR (DMSO- <i>d</i> ₆ , δ ppm)
34	3333, 3219, 3168, 3099, 2995, 2898, 1651, 1568, 1521, 1502, 1445, 1436, 1413, 1361, 1321, 1285, 1248, 1151, 1106, 1045, 1026, 999, 878, 820, 740, 677, 595, 564, 504	11.50 (s, 1H, 10), 8.55 (t, 1H, 2', <i>J</i> = 5.4 Hz), 8.29 (d, 1H, 7, <i>J</i> = 5.2 Hz), 8.22 (d, 1H, 3, <i>J</i> = 7.8 Hz), 8.04 (d, 1H, 6, <i>J</i> = 5.2 Hz), 7.63 (d, 1H, 12, <i>J</i> = 8.2 Hz), 7.55 (t, 1H, 1, <i>J</i> = 7.6 Hz), 7.25 (t, 1H, 2, <i>J</i> = 7.4 Hz), 4.76 (d, 2H, 1', <i>J</i> = 5.4 Hz), 4.22 (t, 2H, 6', 9', <i>J</i> = 1.9 Hz), 4.05 (m, 7H, 7', 8', 10'–14'), 3.26 (s, 2H, 4')	170.47 (3'), 141.60 (8), 140.36 (11), 137.36 (7), 133.50 (9), 128.12 (3), 127.74 (5), 121.73 (1), 120.87 (4), 119.39 (2), 113.89 (6), 112.05 (12), 82.66 (5'), 68.58 (6', 9'), 68.41 (10'–14'), 67.11 (7', 8'), 41.52 (1'), 36.33 (4')

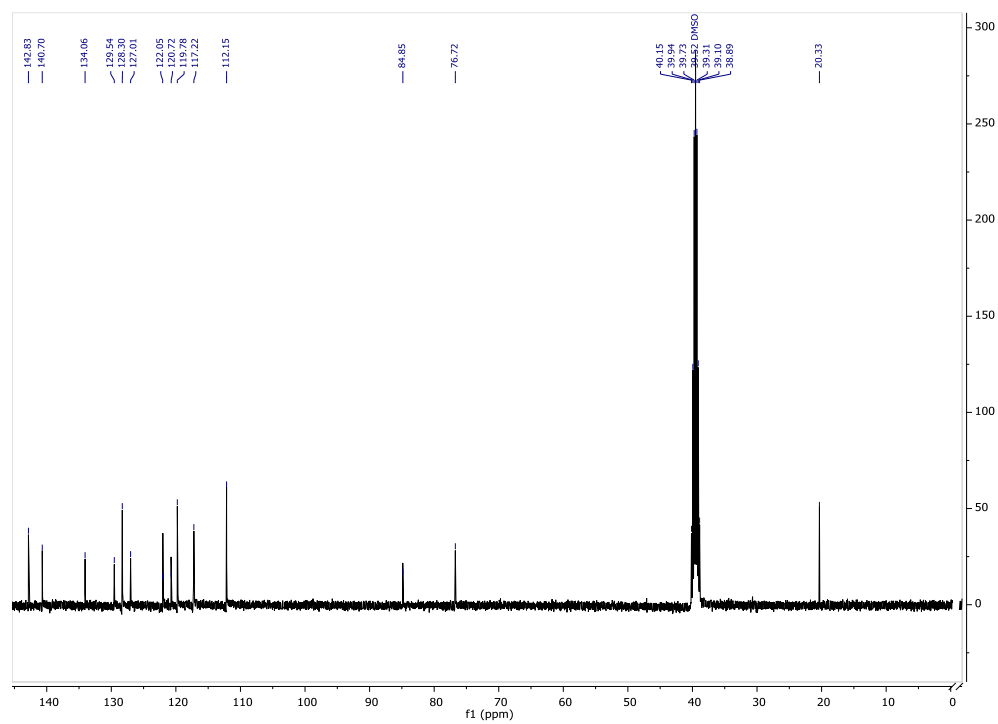
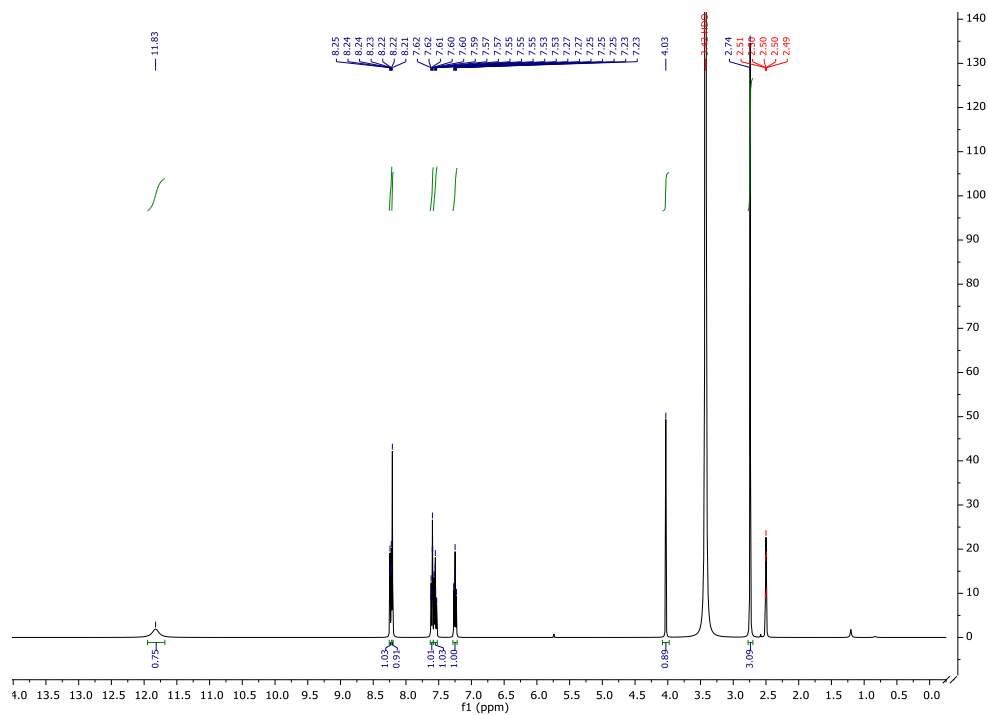
35	3404, 3191, 3081, 2944, 1649, 1621, 1570, 1522, 1471, 1455, 1421, 1312, 1247, 1267, 1136, 1103, 1038, 1023, 997, 925, 826, 803, 753, 741, 693, 621, 584, 543, 500, 482	11.48 (s, 1H, 10), 8.42 (t, 1H, 2', $J = 5.9$ Hz), 8.10 (d, 1H, 3, $J =$ 7.8 Hz), 7.73 (s, 1H, 6), 7.56 (d, 1H, 12, $J = 8.2$ Hz), 7.52–7.50 (m, 1H, 1), 7.21 (t, 1H, 2, $J = 7.4$ Hz), 4.46 (d, 2H, 1', $J = 5.8$ Hz), 4.27 (t, 2H, 6', 9', $J = 1.9$ Hz), 4.12 (s, 5H, 10'–14'), 4.10 (t, 2H, 7', 8', $J = 1.9$ Hz), 3.24 (s, 2H, 4'), 2.73 (s, 3H, 13)	169.93 (3'), 146.33 (7), 141.16 (8), 140.71 (11), 133.44 (9), 127.78 (3), 127.66 (5), 121.49 (1), 120.98 (4), 119.11 (2), 111.94 (12), 109.54 (6), 83.05 (5'), 68.63 (6', 9'), 68.45 (10'– 14'), 67.15 (7', 8'), 44.28 (1'), 36.72 (4'), 20.28 (13)
36	3222, 3055, 2875, 1656, 1630, 1539, 1484, 1434, 1378, 1324, 1299, 1273, 1238, 1174, 1134, 1106, 1073, 1037, 1023, 1002, 961, 924, 871, 814, 776, 738, 661, 634, 590, 567, 484	11.40 (s, 1H, 10), 8.19 (t, 1H, 3', $J = 5.5$ Hz), 8.14 (d, 1H, 7, $J =$ 5.3 Hz), 8.05 (d, 1H, 3, $J = 8.6$ Hz), 7.80 (d, 1H, 6, $J = 5.3$ Hz), 7.02 (d, 1H, 12, $J = 2.2$ Hz), 6.85 (dd, 1H, 2, $J = 8.6, 2.2$ Hz), 4.20 (t, 2H, 7', 10', $J = 1.9$ Hz), 4.13 (t, 2H, 1', $J = 5.5$ Hz), 4.11 (s, 5H, 11'–15'), 4.05 (t, 2H, 8', 9', J $= 1.9$ Hz), 3.51 (q, 2H, 2', $J = 5.6$ Hz), 3.16 (s, 2H, 5'), 2.72 (s, 3H, 13)	170.25 (4'), 159.17 (1), 141.84 (8), 141.29 (11), 137.75 (7), 134.56 (9), 127.16 (5), 122.63 (3), 115.00 (4), 111.93 (6), 109.30 (2), 95.40 (12), 82.72 (6'), 68.50 (7', 10'), 68.43 (11'– 15'), 67.08 (8', 9'), 66.55 (1'), 38.40 (2'), 36.37 (5'), 20.35 (13)
37	3341, 2931, 1655, 1624, 1566, 1503, 1451, 1439, 1410, 1347, 1330, 1300, 1251, 1195, 1172, 1141, 1104, 1048, 1024, 929, 835, 813, 794, 639, 567, 496, 482	8.17 (d, 1H, 7, $J = 5.1$ Hz), 8.09 (d, 1H, 3, $J = 8.6$ Hz), 8.01 (t, 1H, 3', $J = 6.0$ Hz), 7.88 (d, 1H, 6, J $= 5.1$ Hz), 7.27 (d, 1H, 12, $J = 2.2$ Hz), 6.89 (dd, 1H, 2, $J = 8.6, 2.2$ Hz), 4.57 (t, 2H, 1', $J = 7.1$ Hz), 4.13 (t, 2H, 7', 10', $J = 1.9$ Hz), 4.11 (s, 5H, 11'–15'), 4.05 (t, 2H, 8', 9', $J = 1.8$ Hz), 3.92 (s, 3H, 14), 3.45 (q, 2H, 2', $J = 6.7$ Hz), 3.07 (s, 2H, 5'), 2.95 (s, 3H, 13)	170.58 (4'), 160.52 (1), 142.86 (8), 140.61 (11), 137.80 (7), 134.64 (9), 128.43 (5), 122.40 (3), 114.31 (4), 112.25 (6), 109.24 (2), 93.64 (12), 82.12 (6'), 68.72 (7', 10'), 68.46 (11'– 15'), 67.21 (8', 9'), 55.52 (14), 43.37 (1'), 38.73 (2'), 36.65 (5'), 23.08 (13)

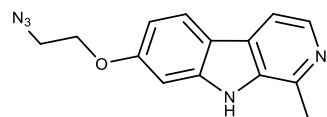


2

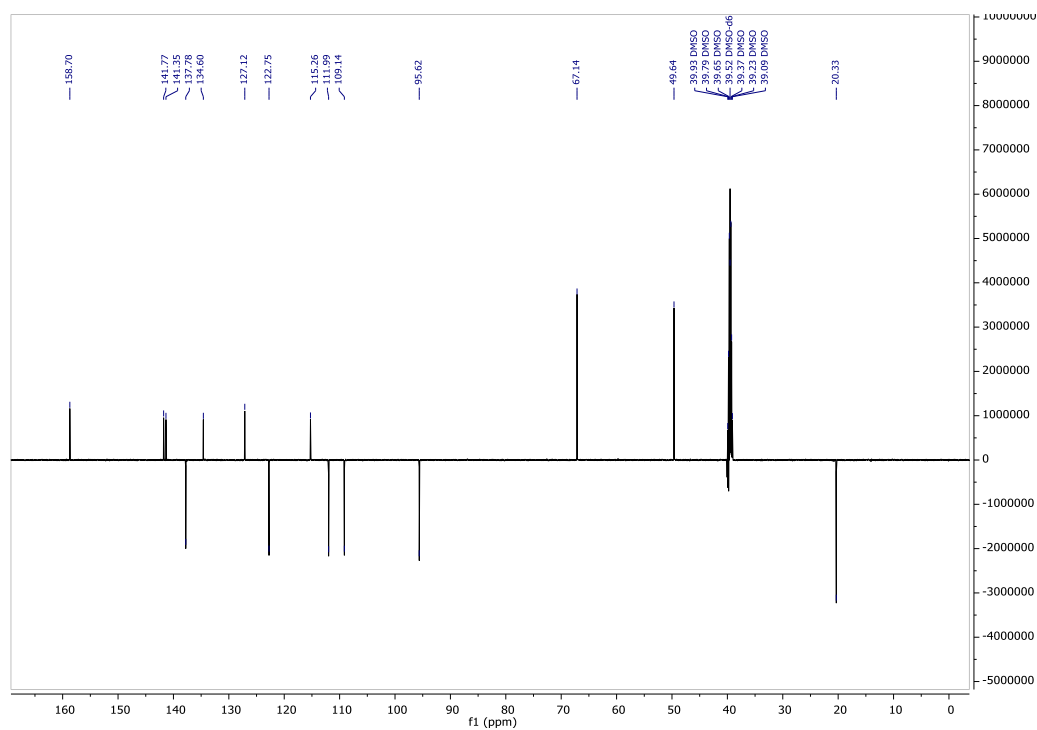
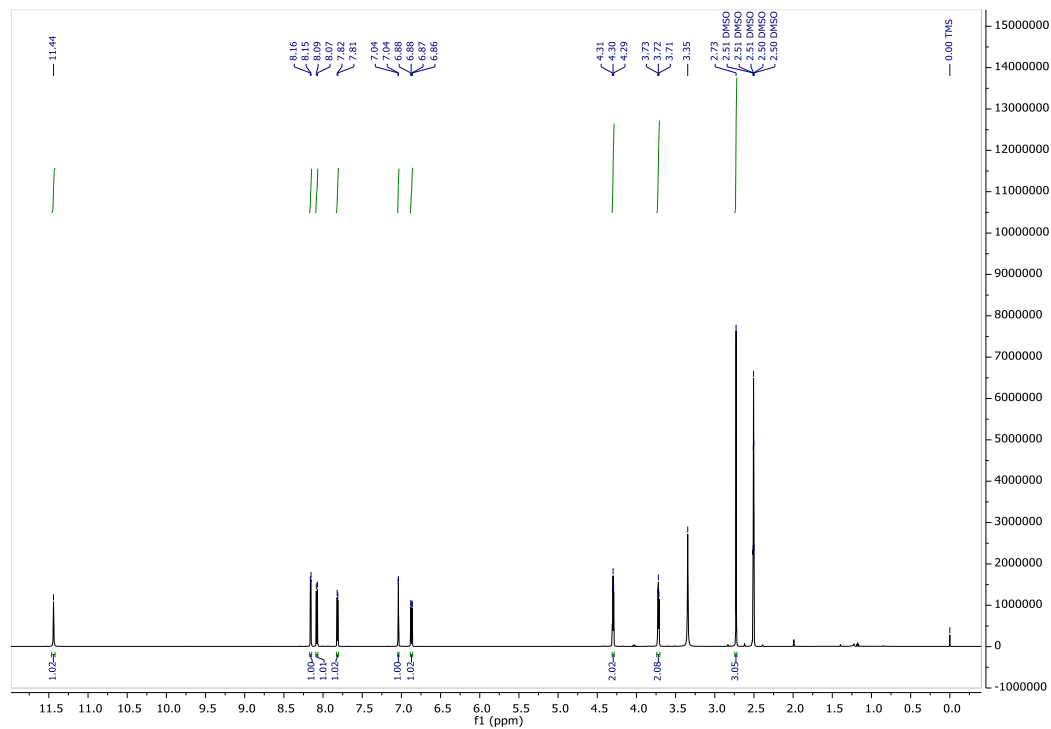


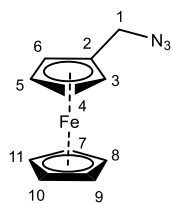




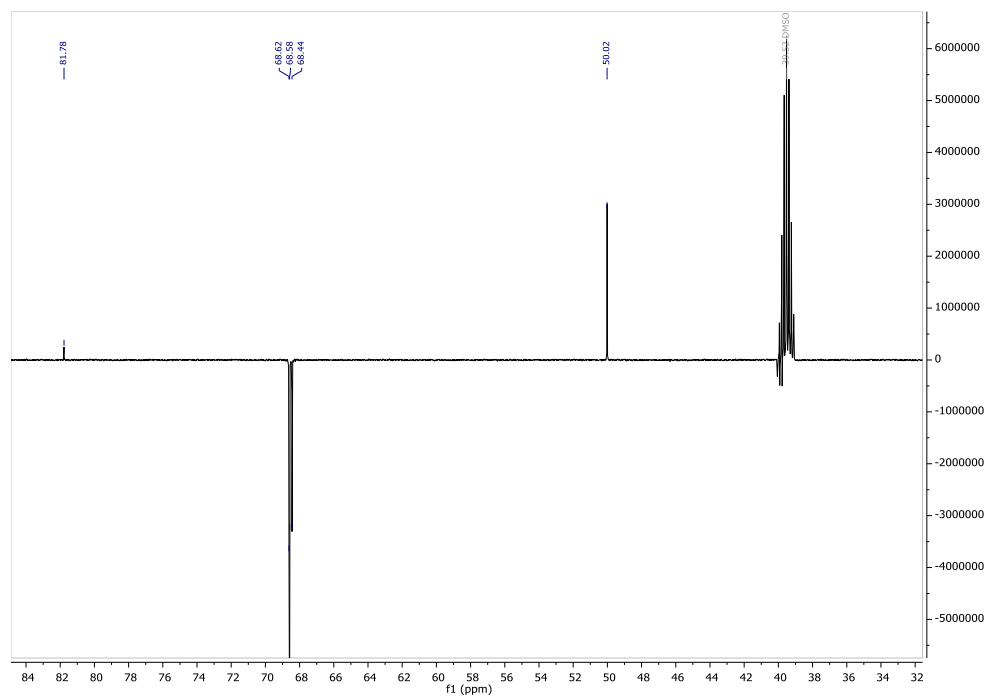
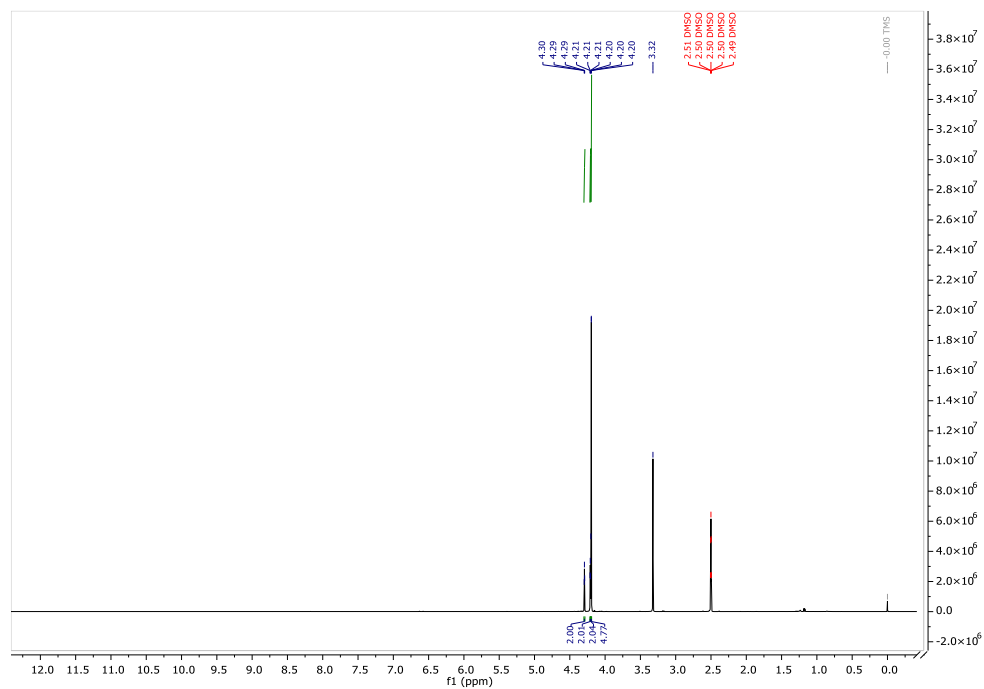


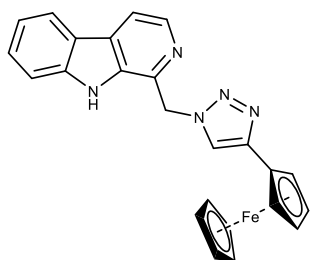
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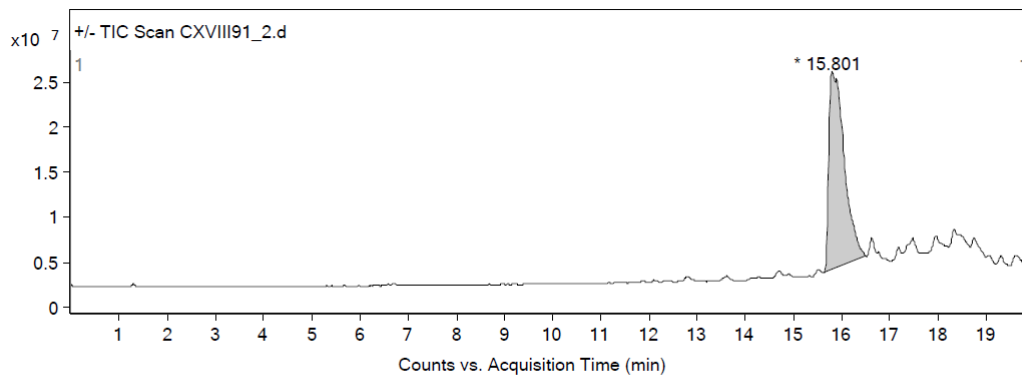
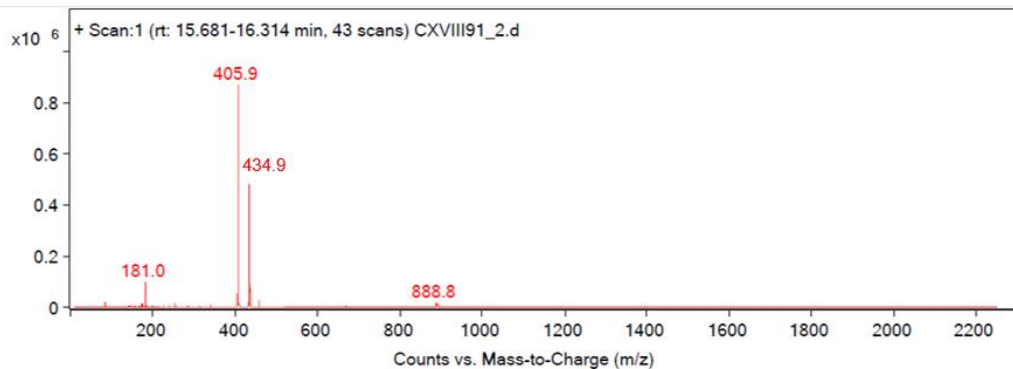
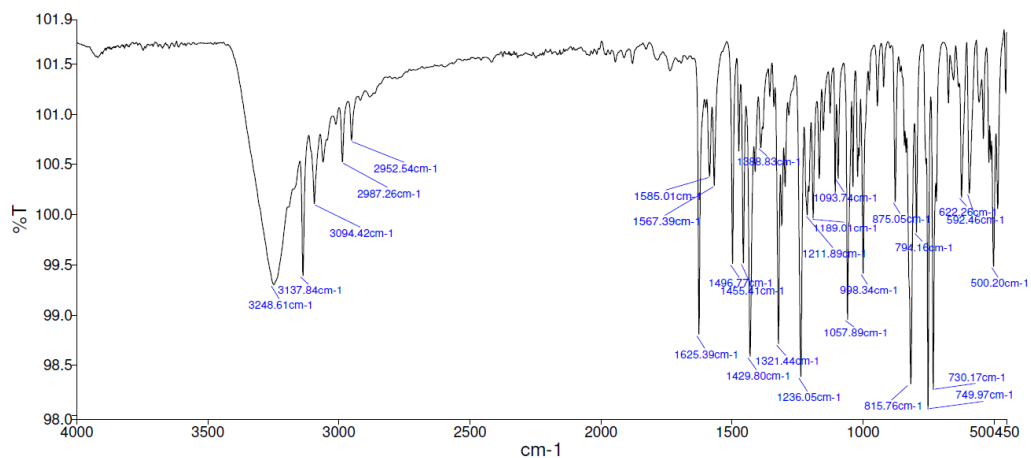


19



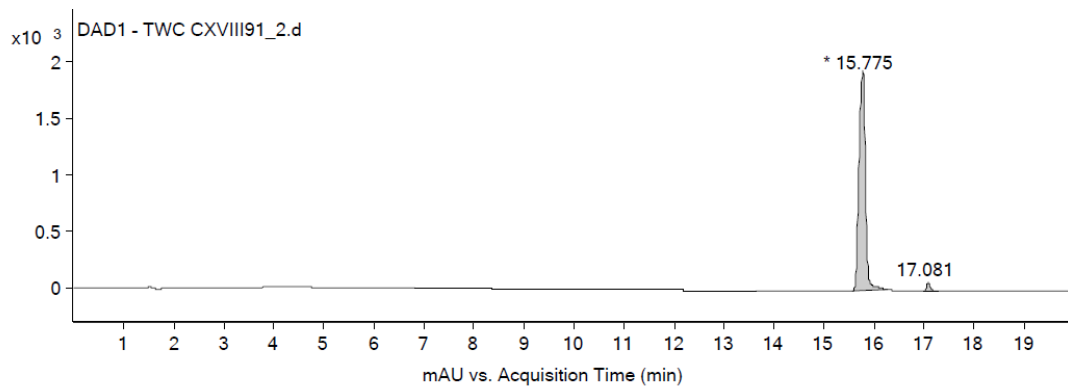


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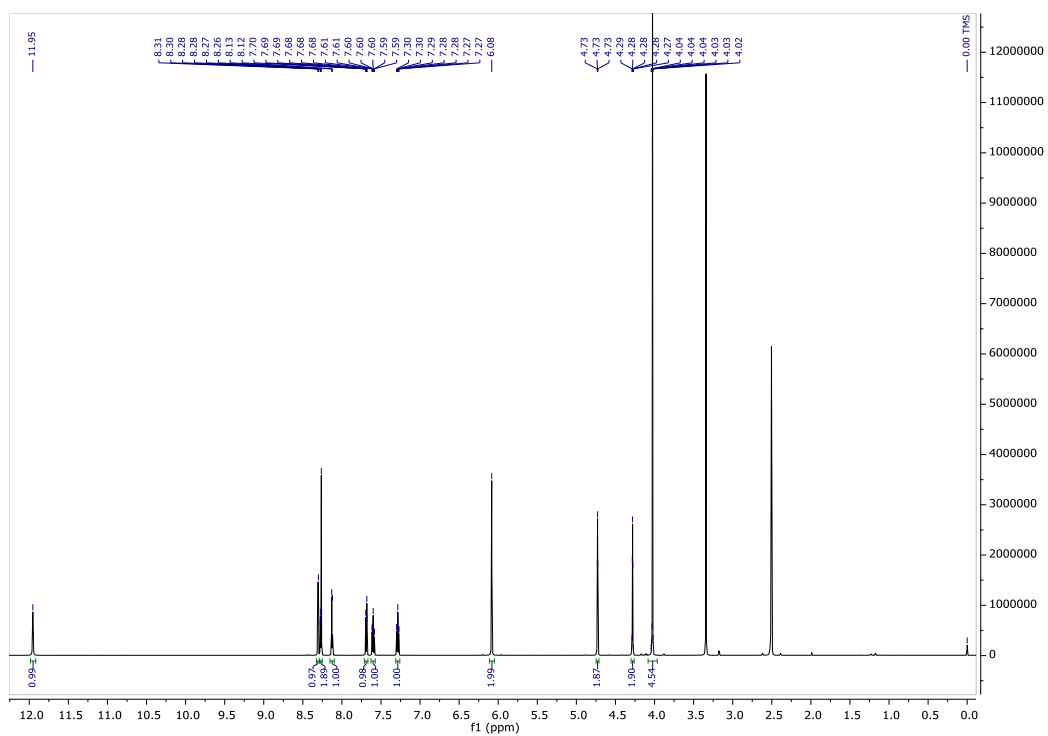
Integration Peak List

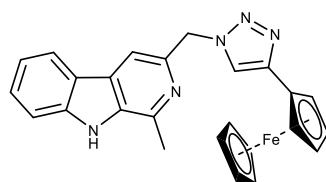
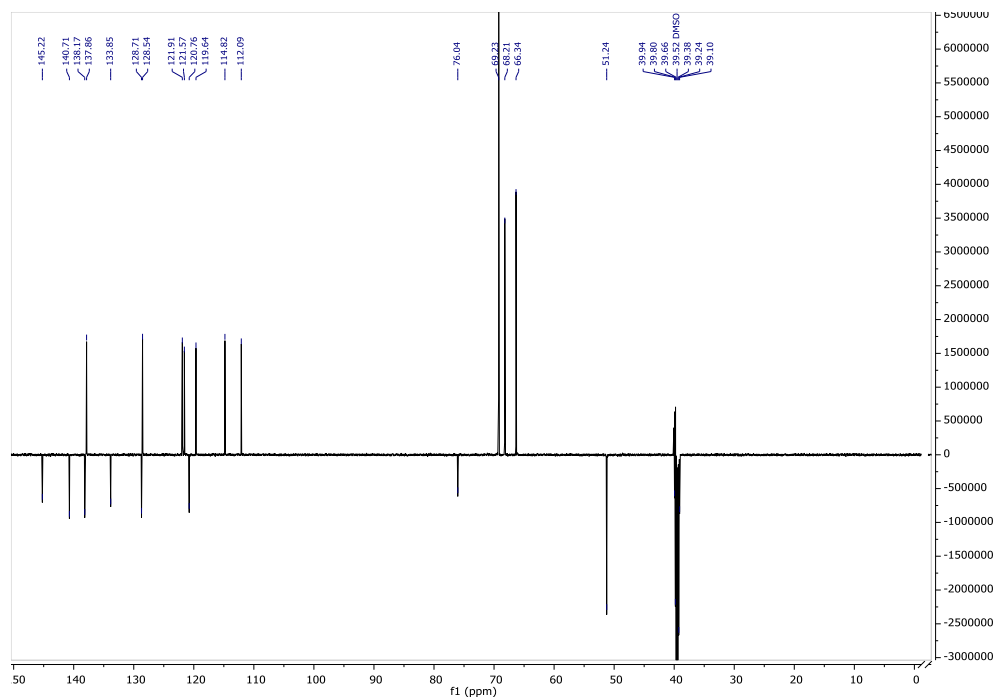
Peak	Start	RT	End	Height	Area	Area %
1	15.62	15.801	16.495	21919671.61	489627897.53	100



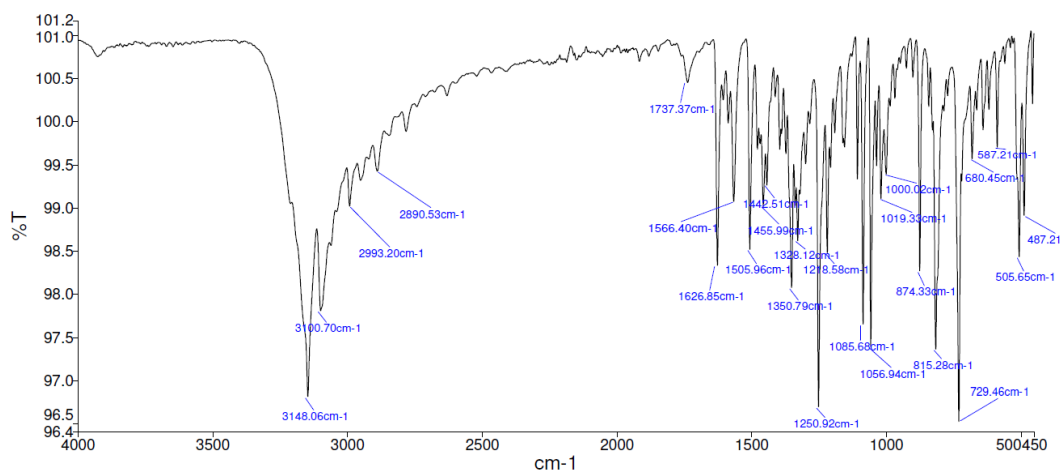
Integration Peak List

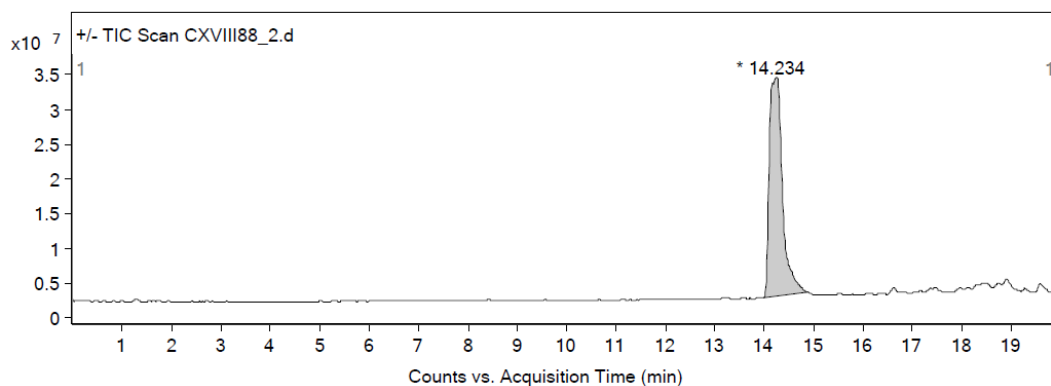
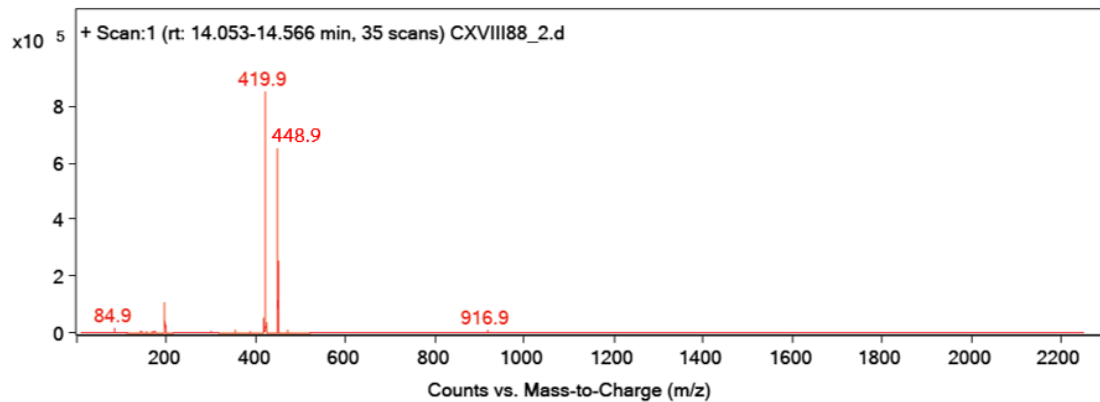
Peak	Start	RT	End	Height	Area	Area %
1	15.568	15.775	16.281	1945.65	17575.54	100
2	17.002	17.081	17.281	69.71	327.96	1.87





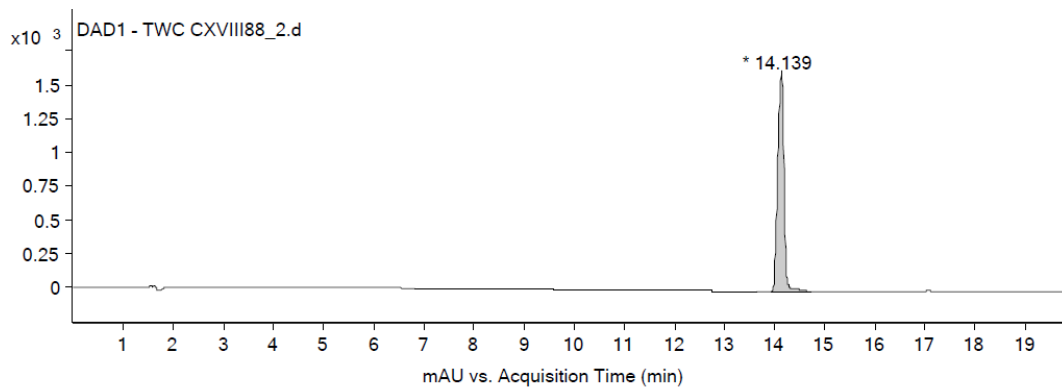
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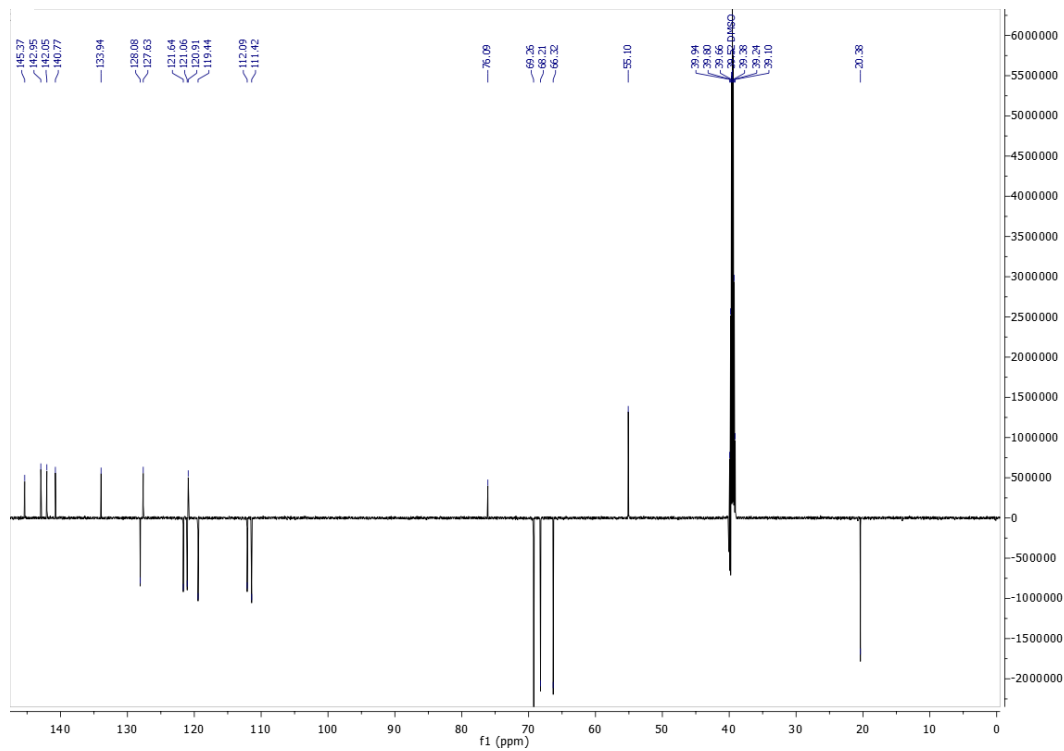
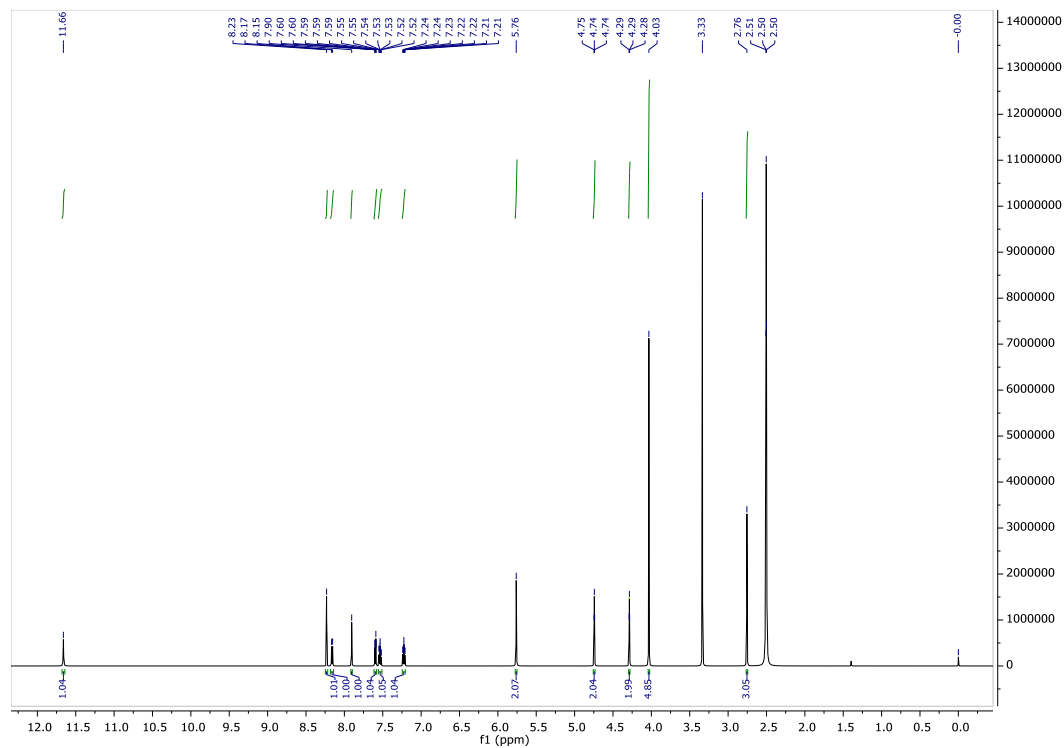
Integration Peak List

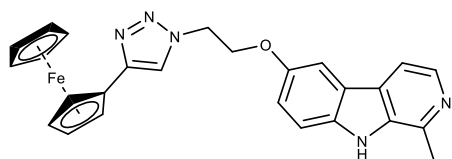
Peak	Start	RT	End	Height	Area	Area %
1	13.978	14.234	14.897	31661829.12	575842089.03	100



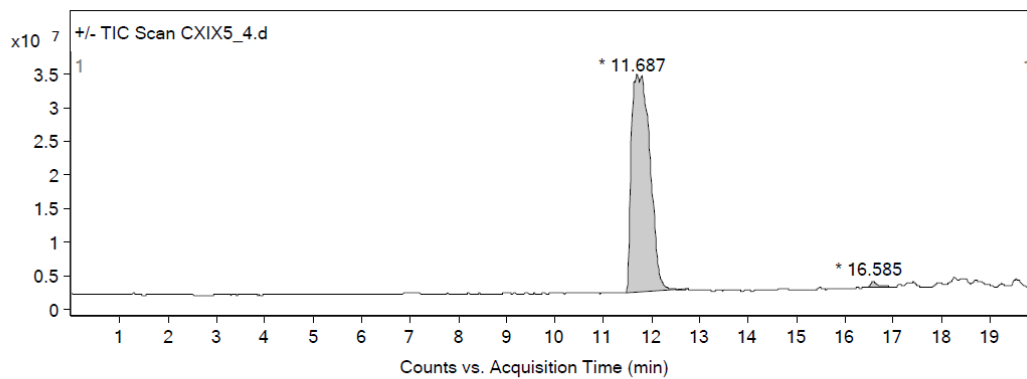
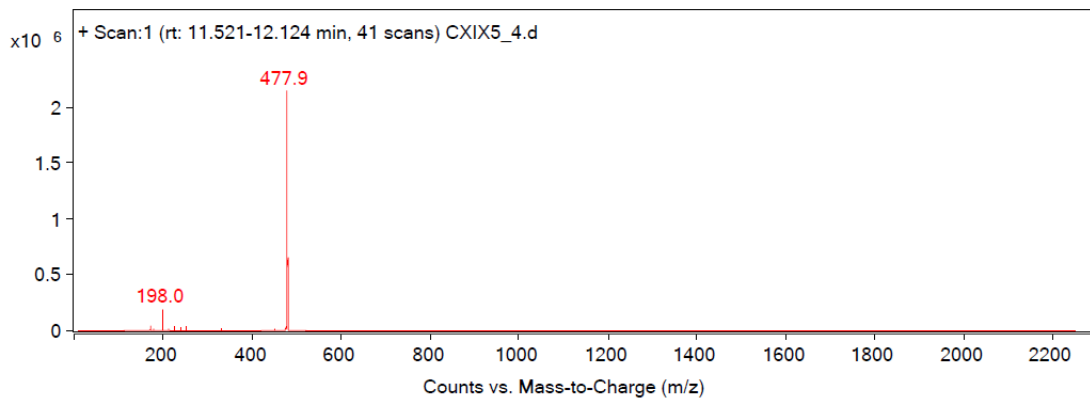
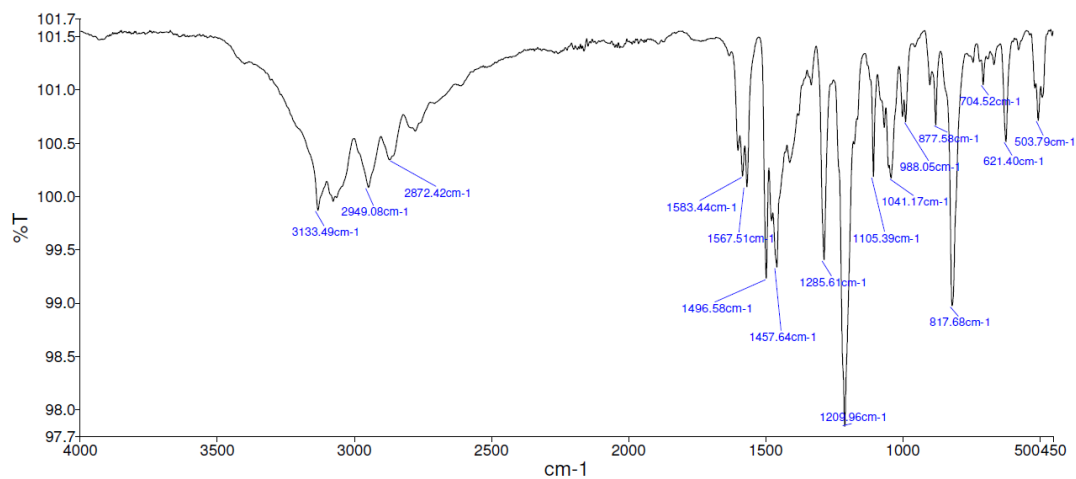
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	13.936	14.139	14.726	1625.52	14001.55	100



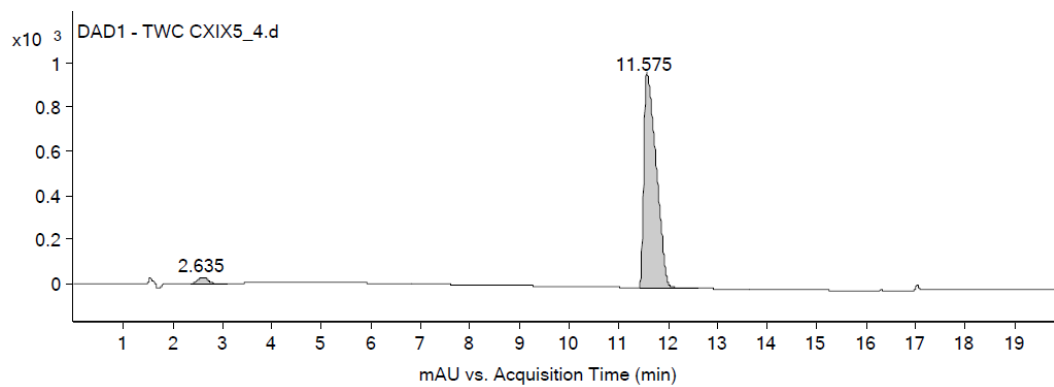


22



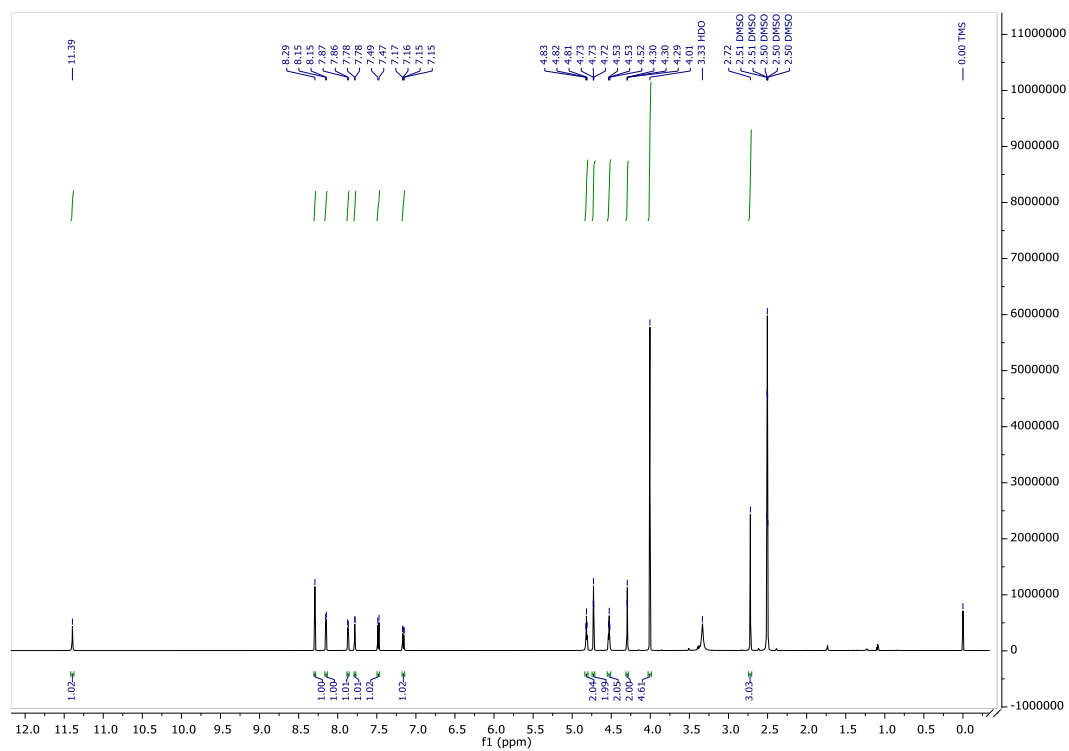
Integration Peak List

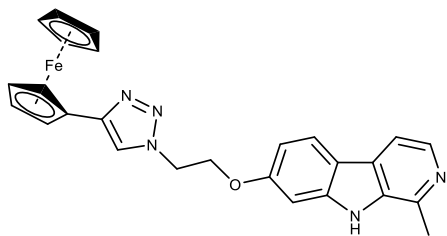
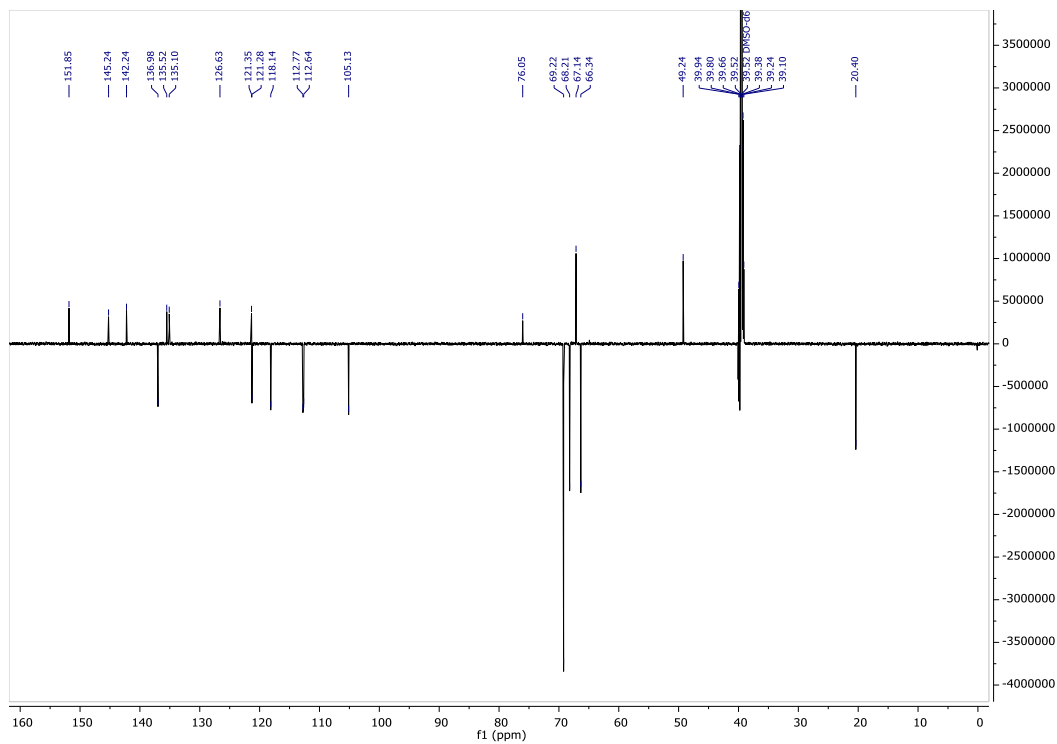
Peak	Start	RT	End	Height	Area	Area %
1	11.476	11.687	12.757	32331990.89	849627736.64	100
2	16.434	16.585	16.947	911139.02	10049820.27	1.18



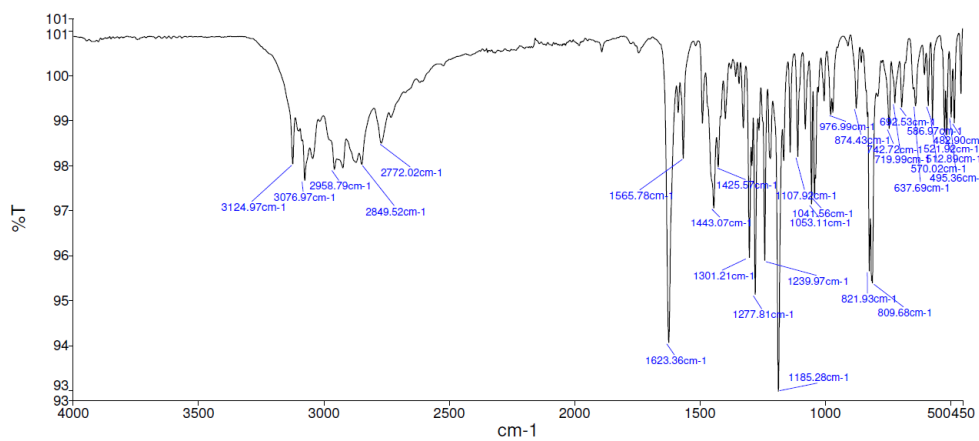
Integration Peak List

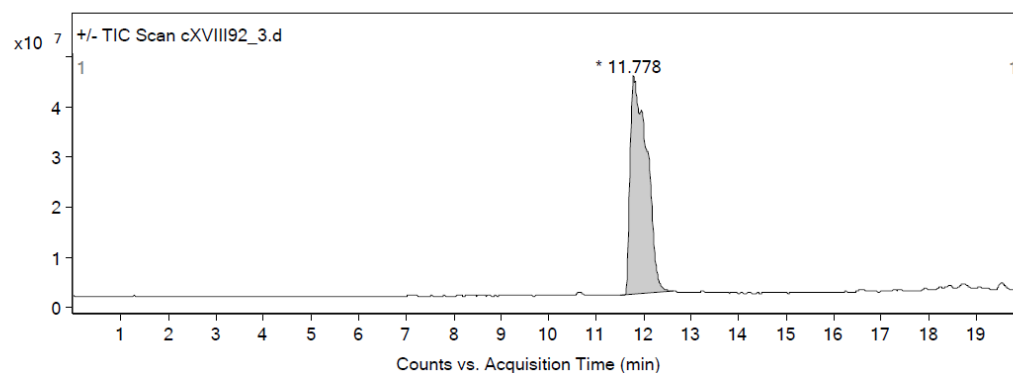
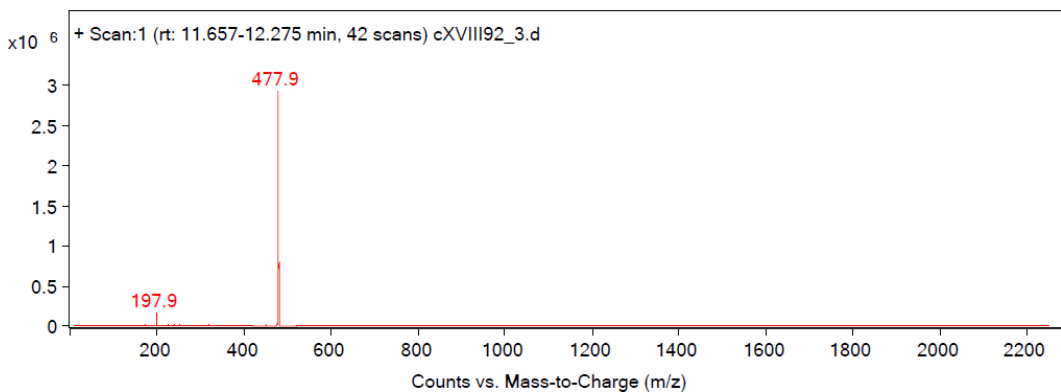
Peak	Start	RT	End	Height	Area	Area %
1	2.369	2.635	3.081	26.47	374.29	2.22
2	11.416	11.575	12.586	977.51	16897.38	100





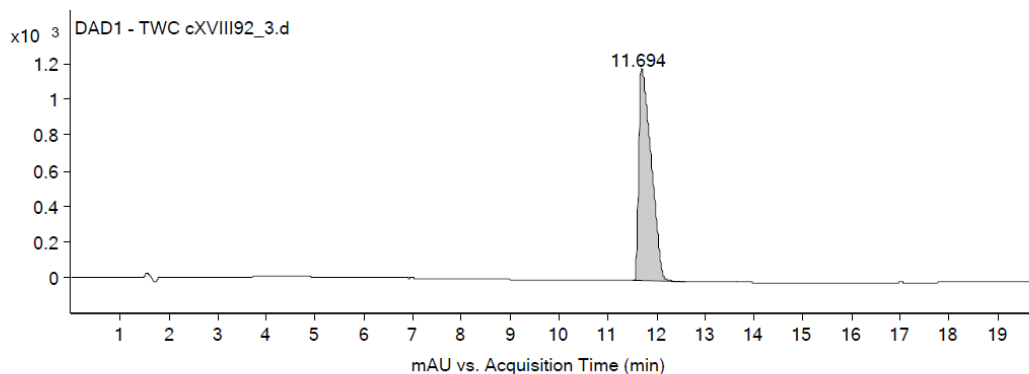
23





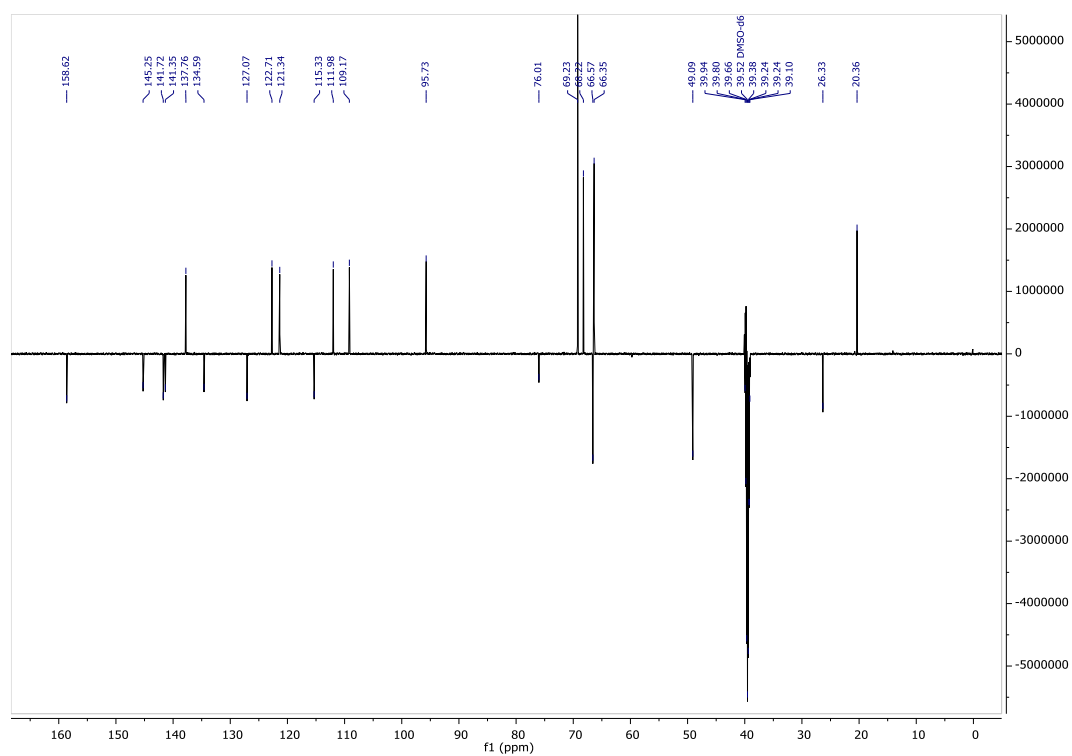
Integration Peak List

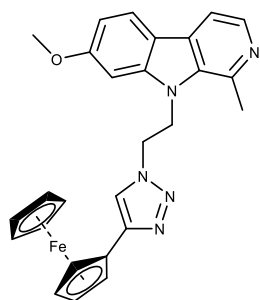
Peak	Start	RT	End	Height	Area	Area %
1	11.521	11.778	12.621	43527887.01	1069966983.92	100



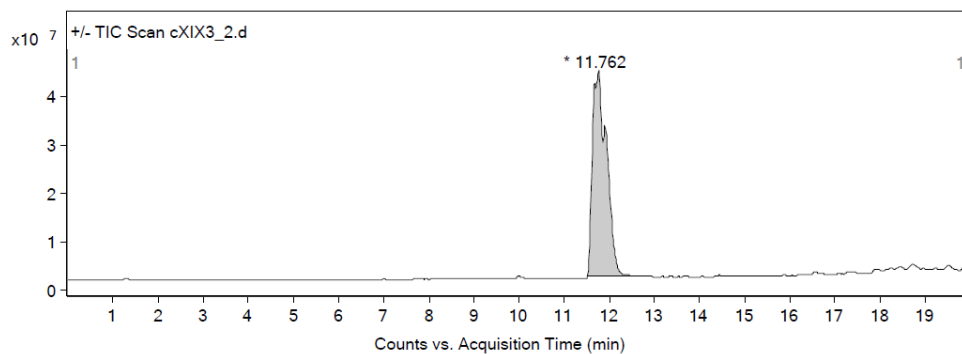
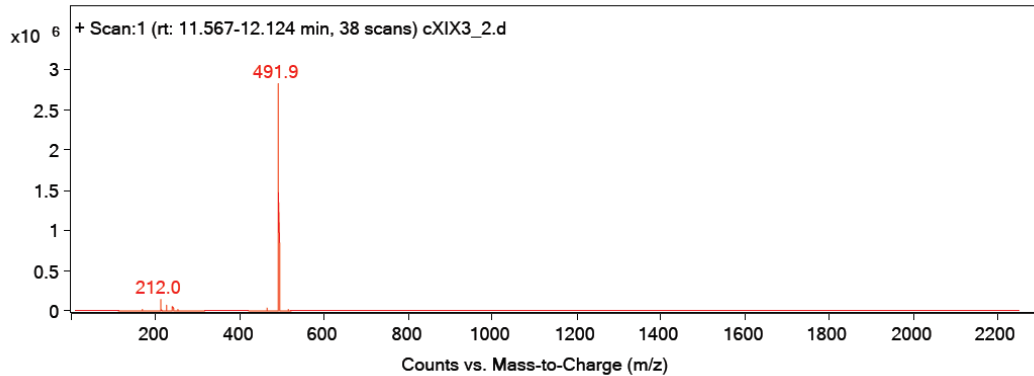
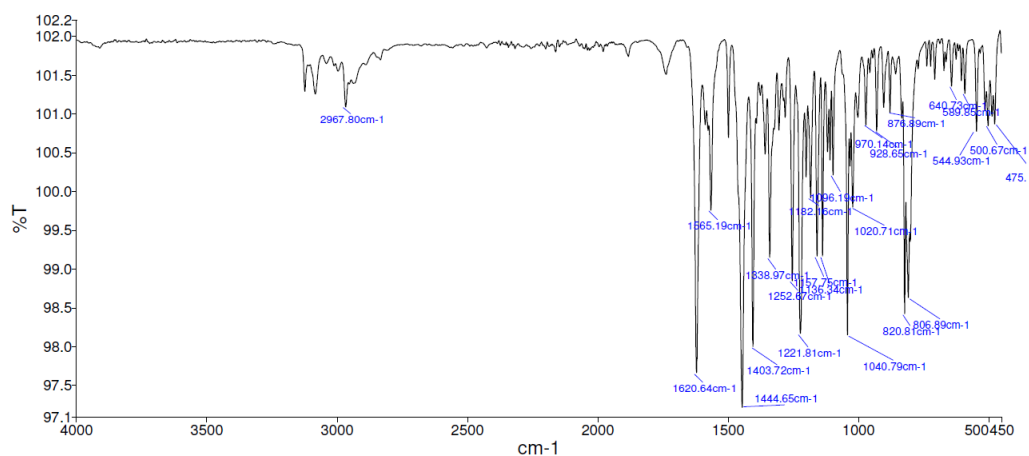
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	11.527	11.694	12.601	1194.83	21125.4	100



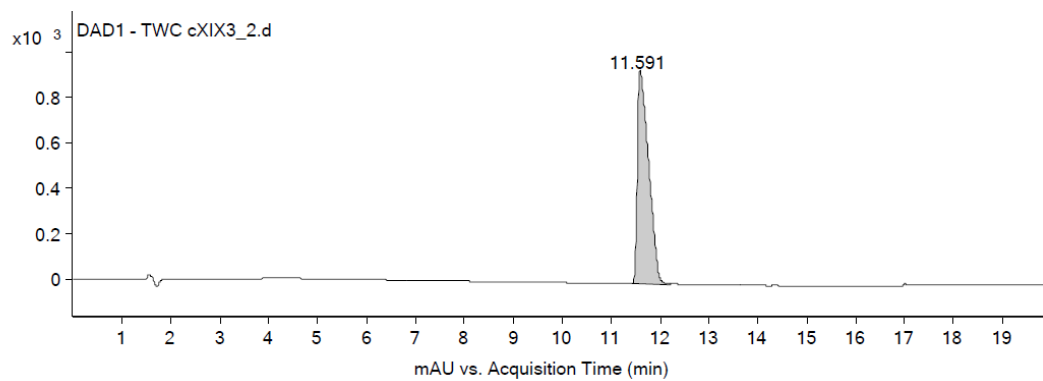


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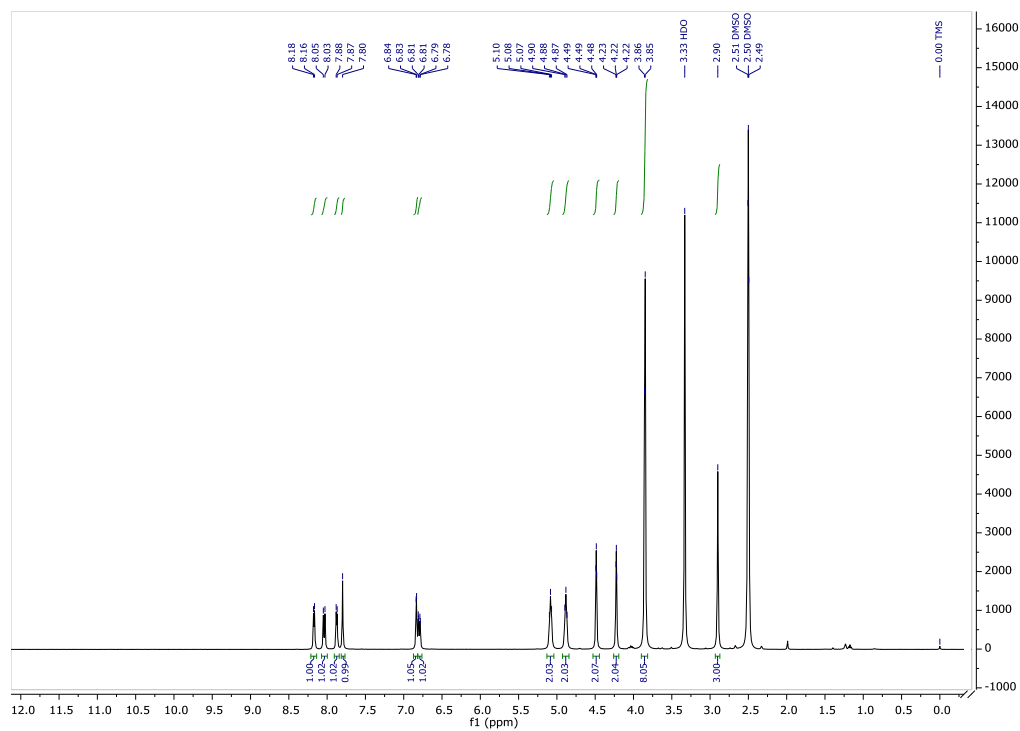
Integration Peak List

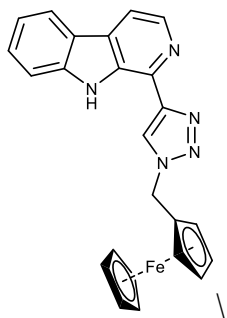
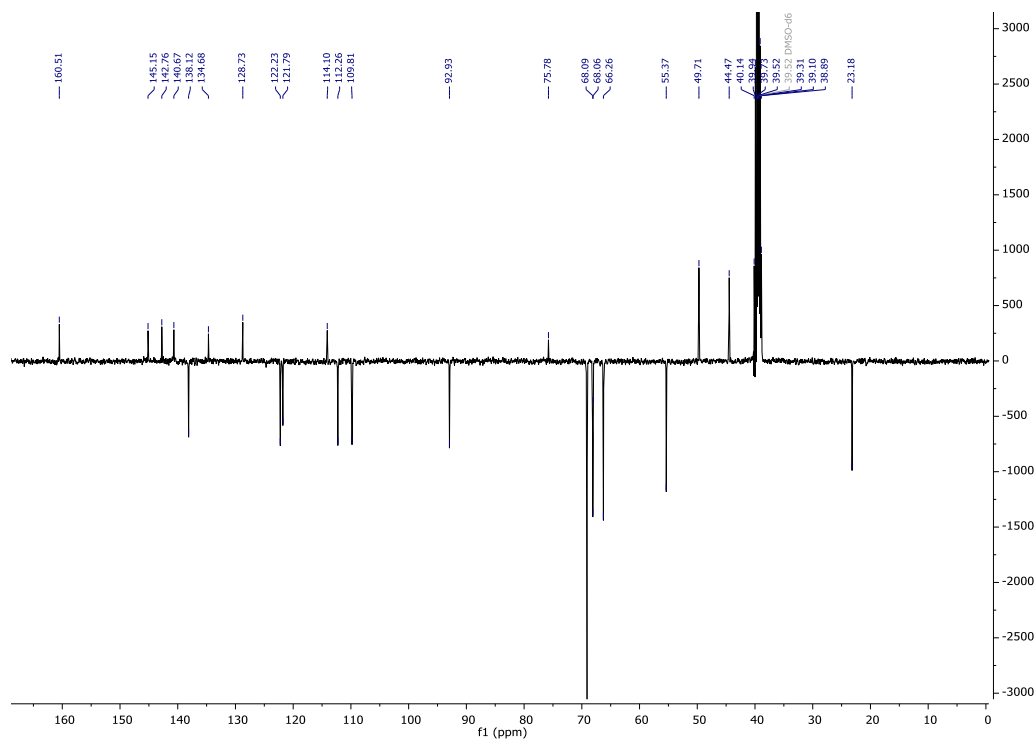
Peak	Start	RT	End	Height	Area	Area %
1	11.521	11.762	12.456	42407508.75	919756502.02	100



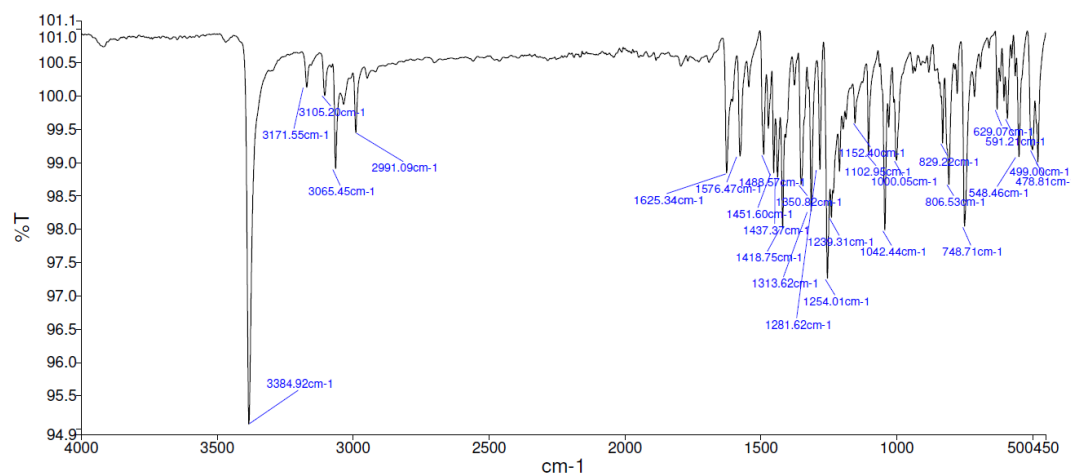
Integration Peak List

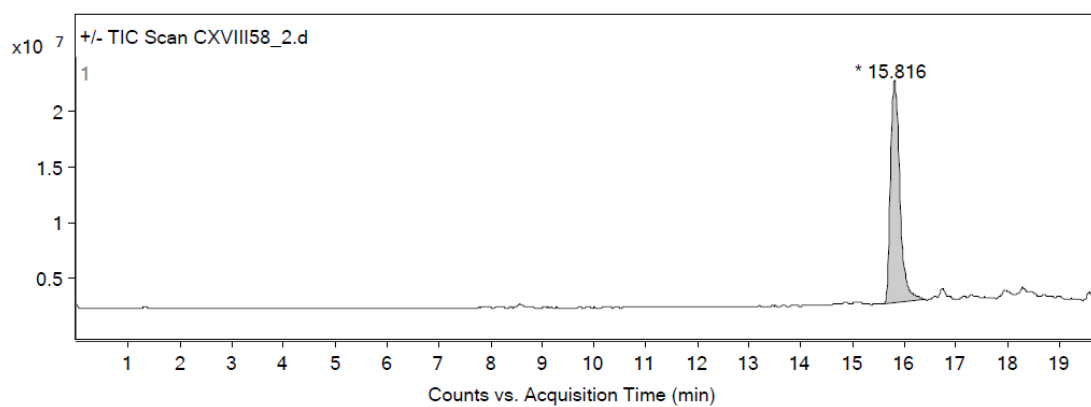
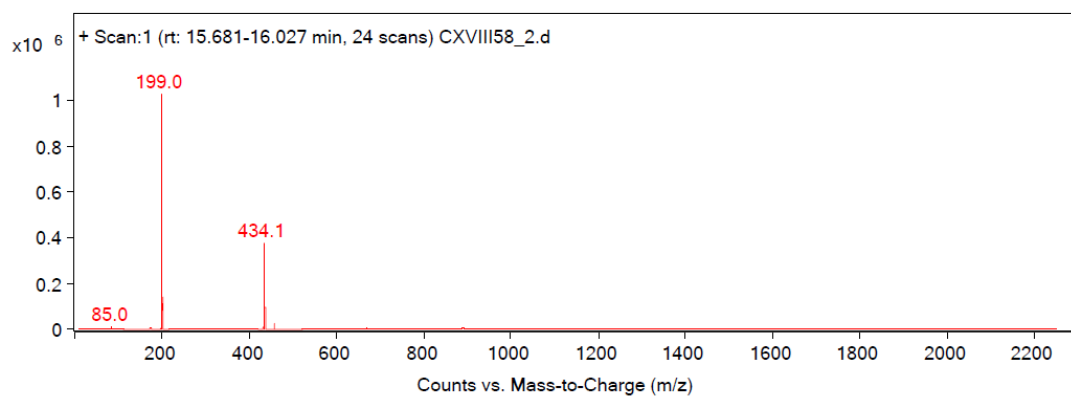
Peak	Start	RT	End	Height	Area	Area %
1	11.431	11.591	12.218	933.81	14867.52	100





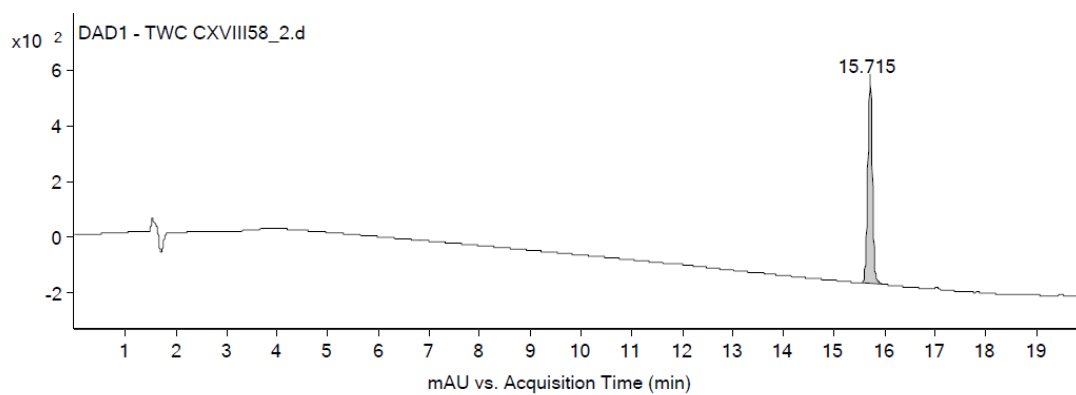
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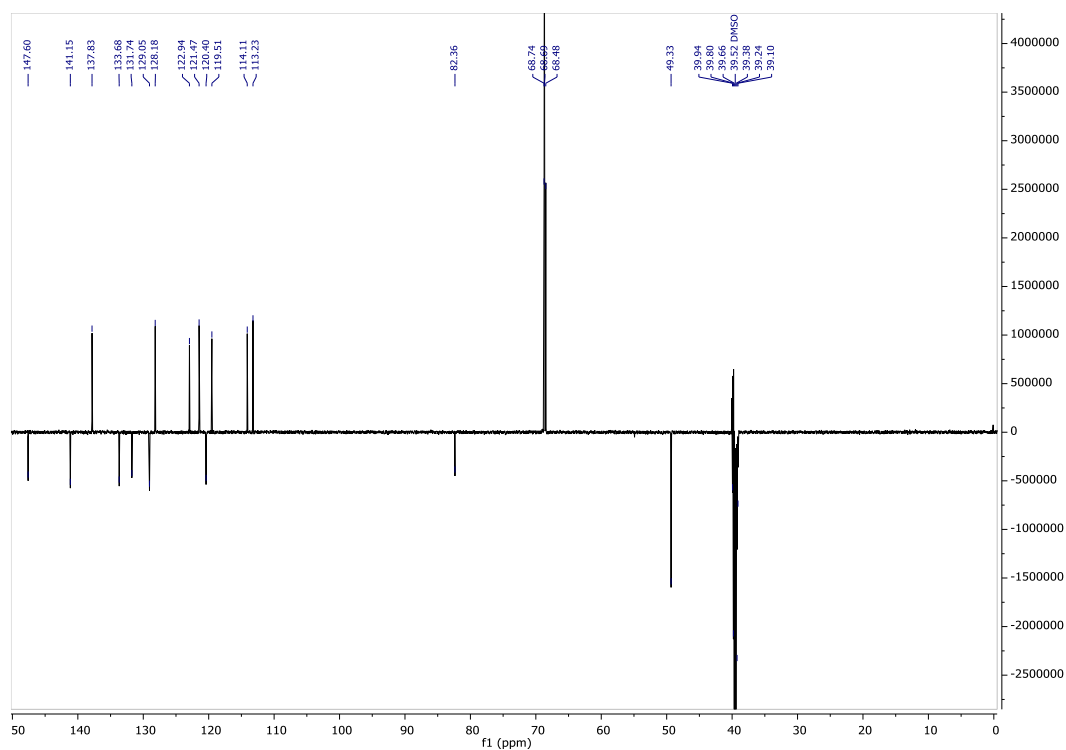
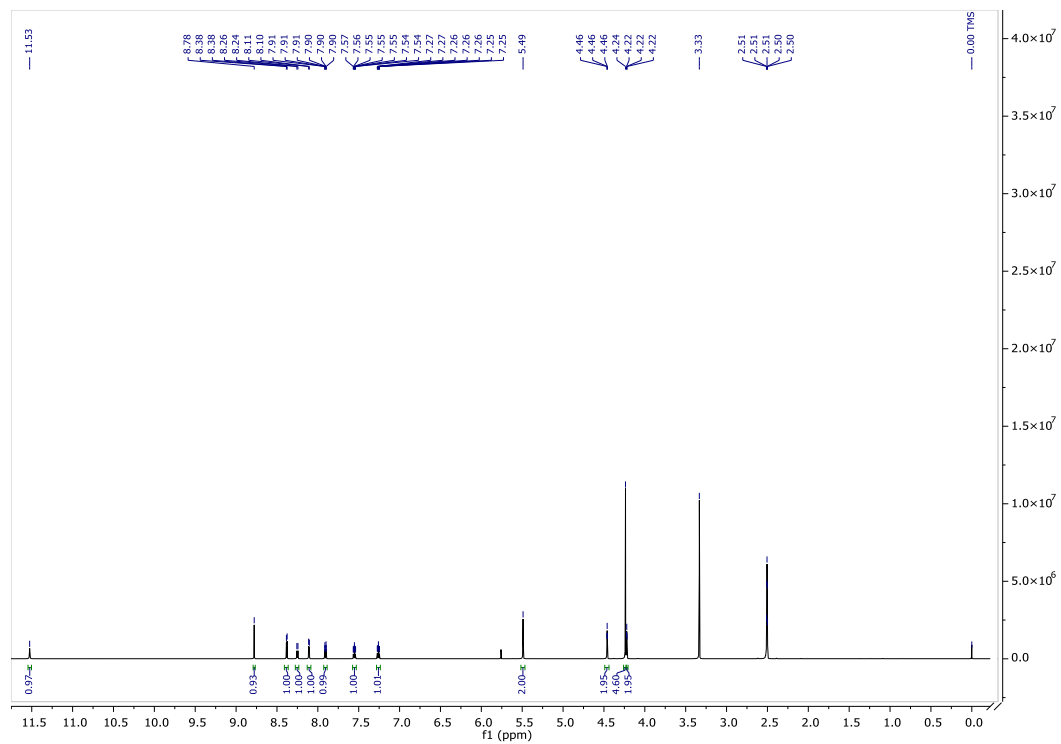
Integration Peak List

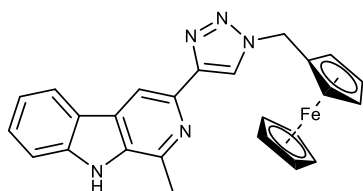
Peak	Start	RT	End	Height	Area	Area %
1	15.605	15.816	16.404	19997711.6	259614271.16	100



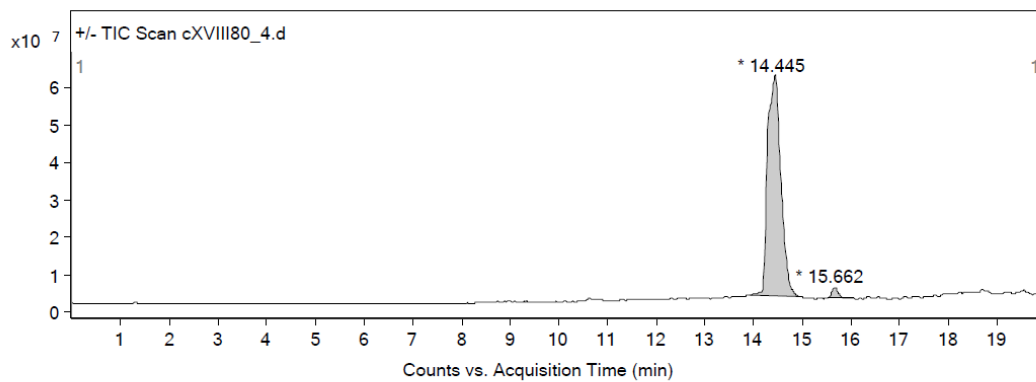
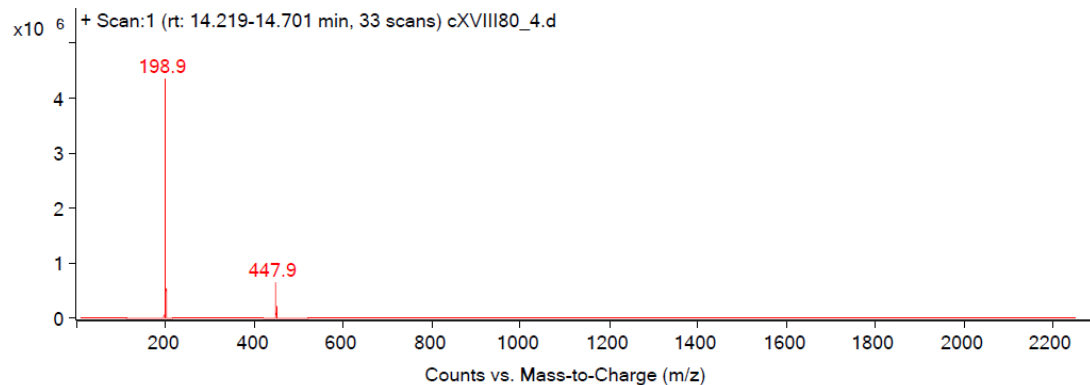
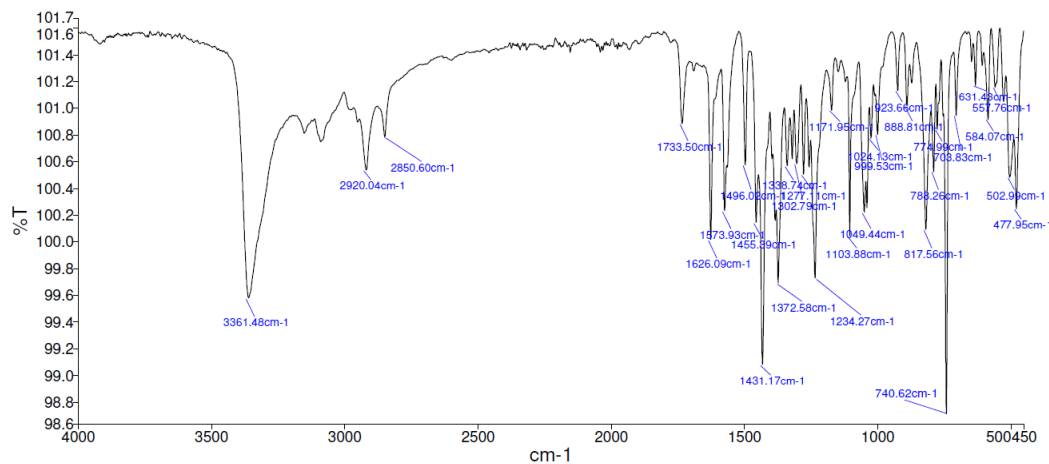
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	15.555	15.715	16.002	747.4	4724.58	100



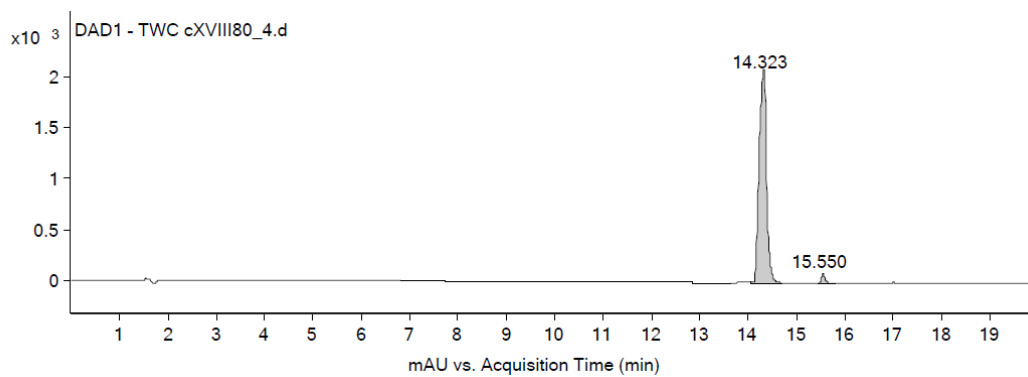


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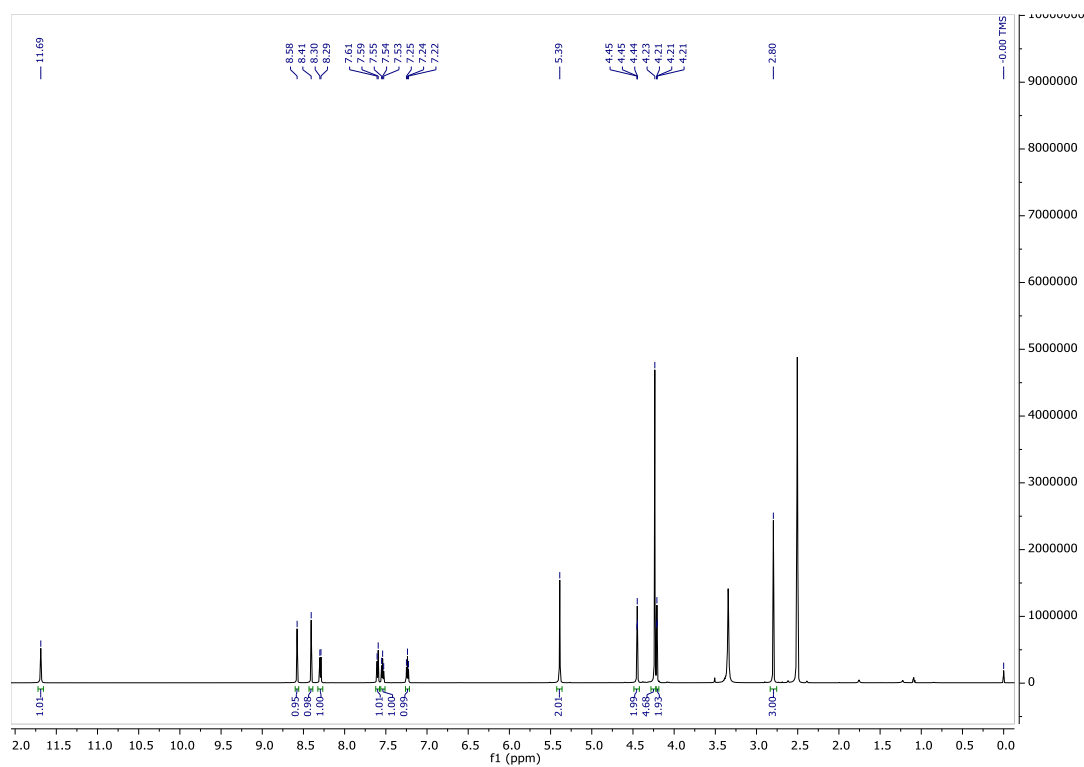
Integration Peak List

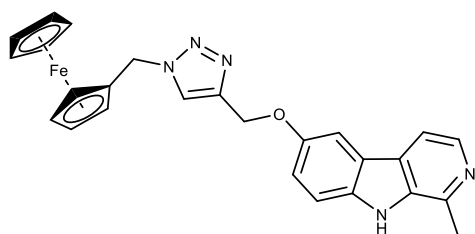
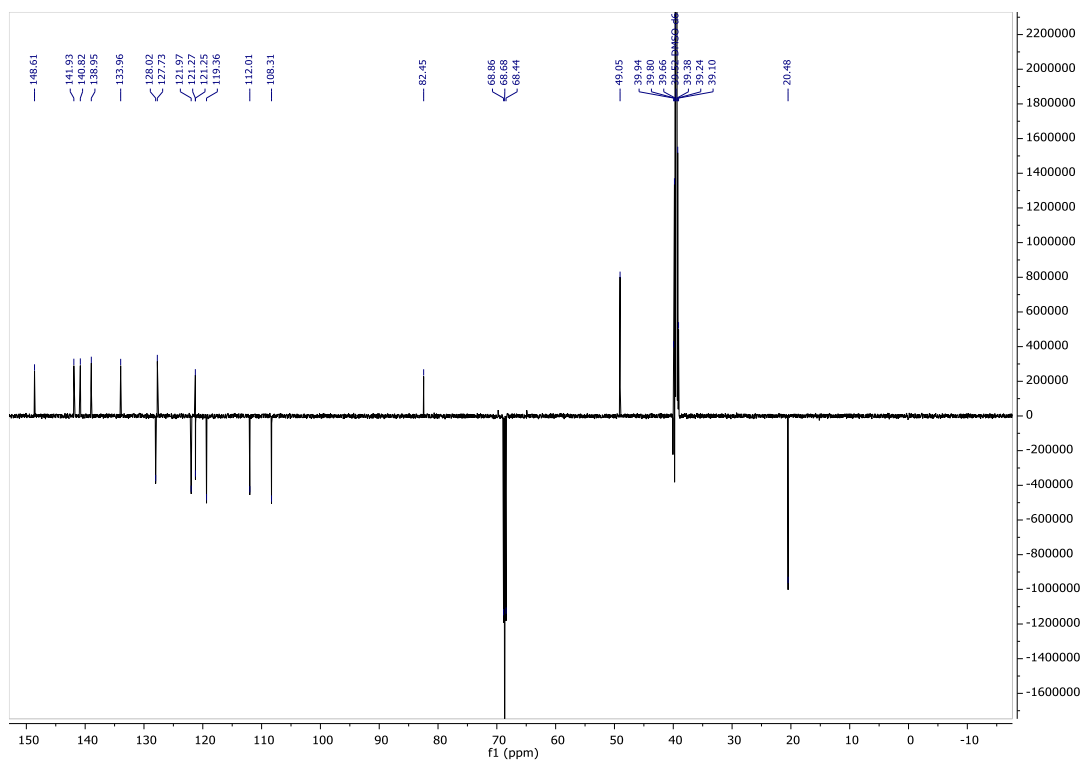
Peak	Start	RT	End	Height	Area	Area %
1	13.918	14.445	14.957	59020670.24	1134308297.78	100
2	15.545	15.662	16.057	2695116.31	25830575.15	2.28



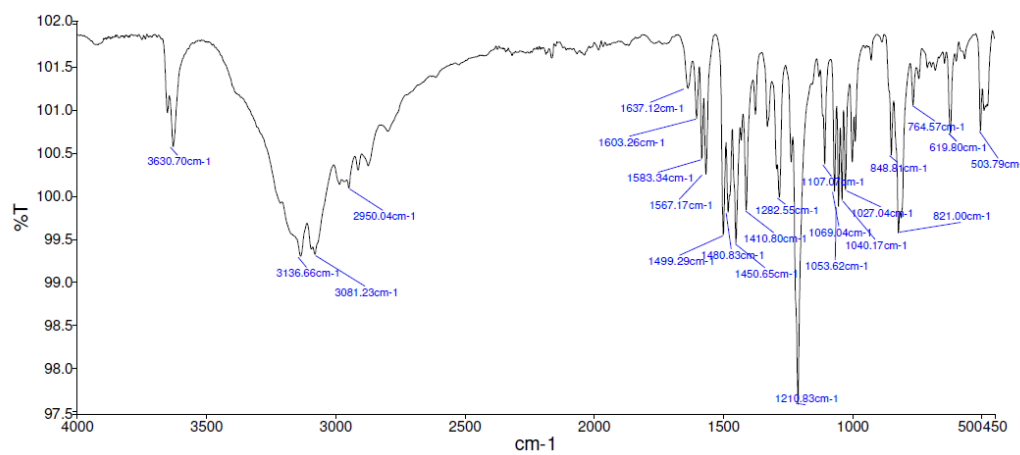
Integration Peak List

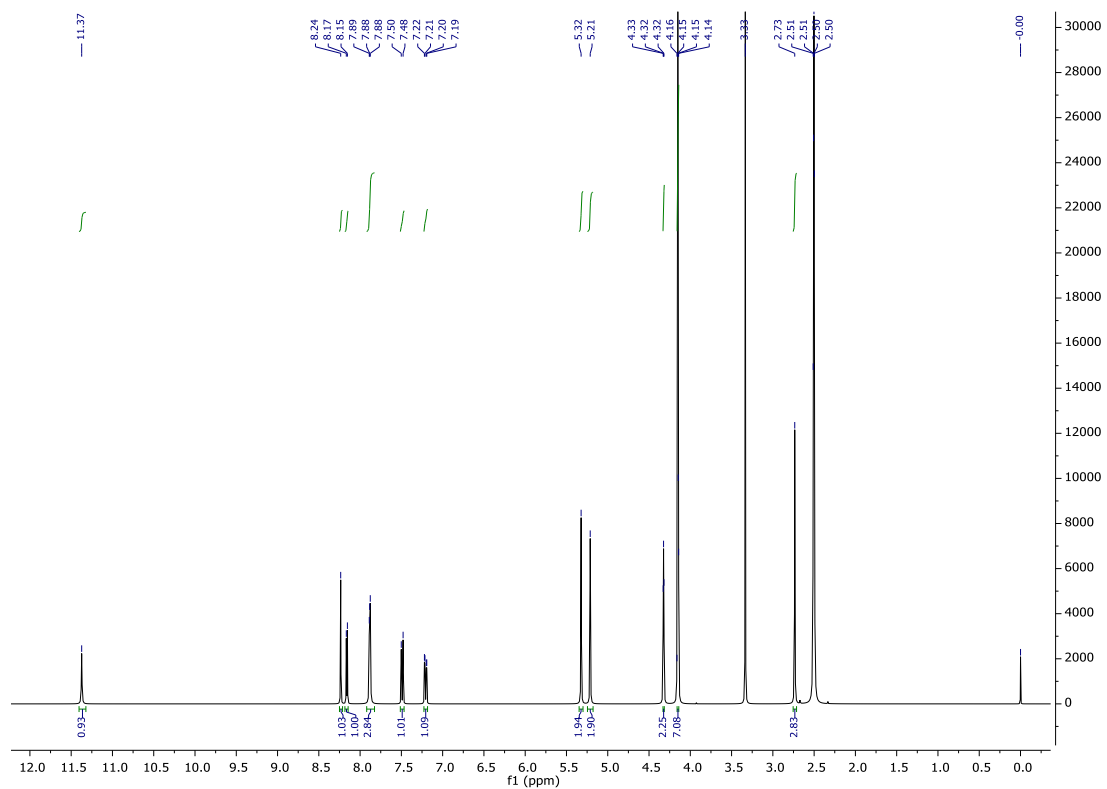
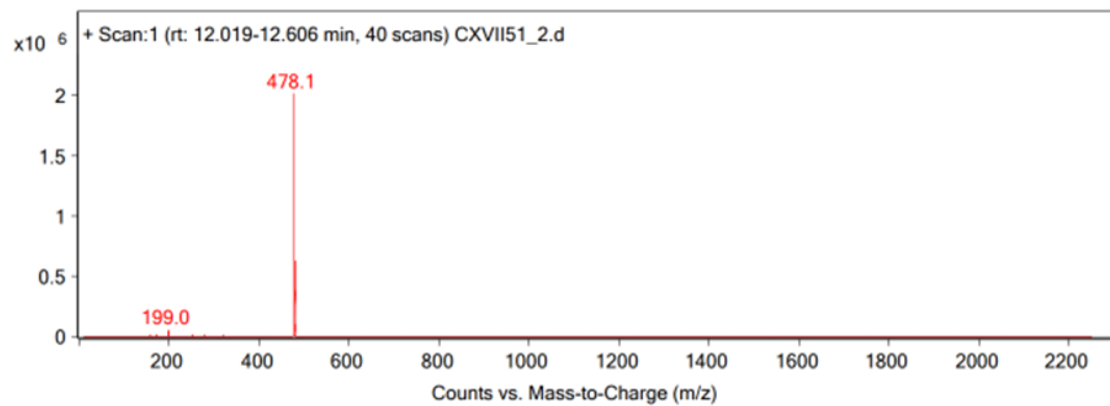
Peak	Start	RT	End	Height	Area	Area %
1	14.036	14.323	14.69	2083.3	22246.88	100
2	15.445	15.55	15.796	96.9	477.93	2.15

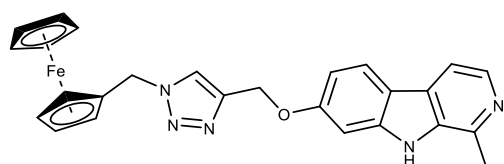
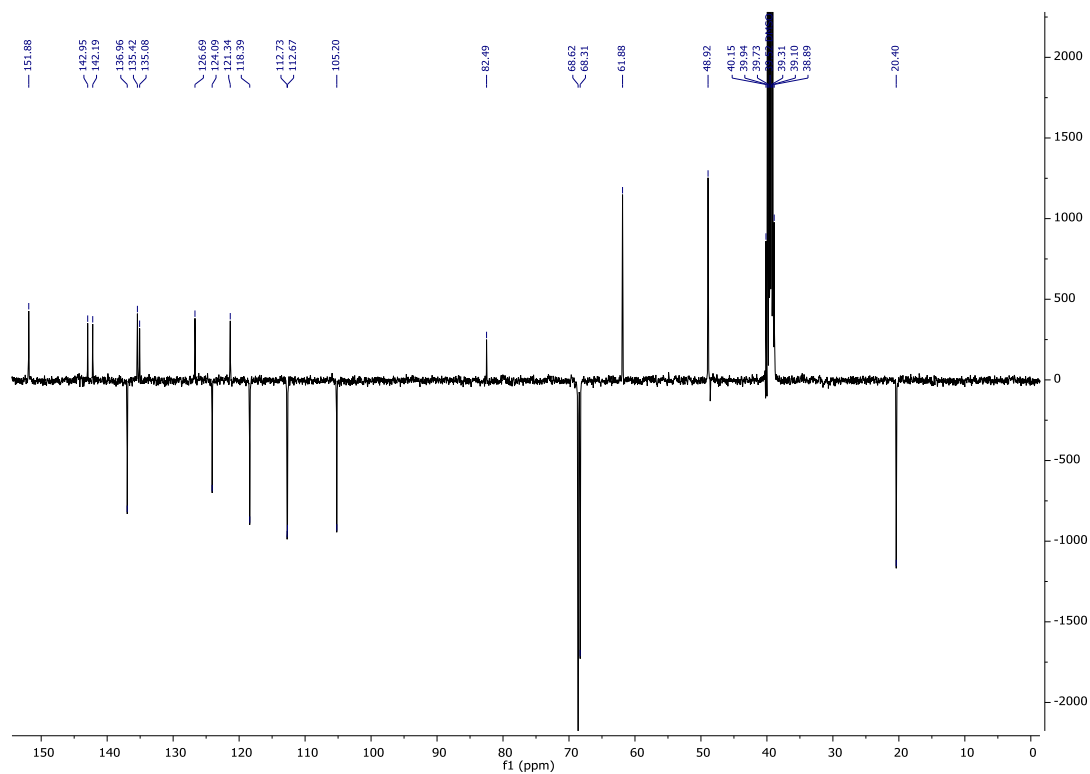




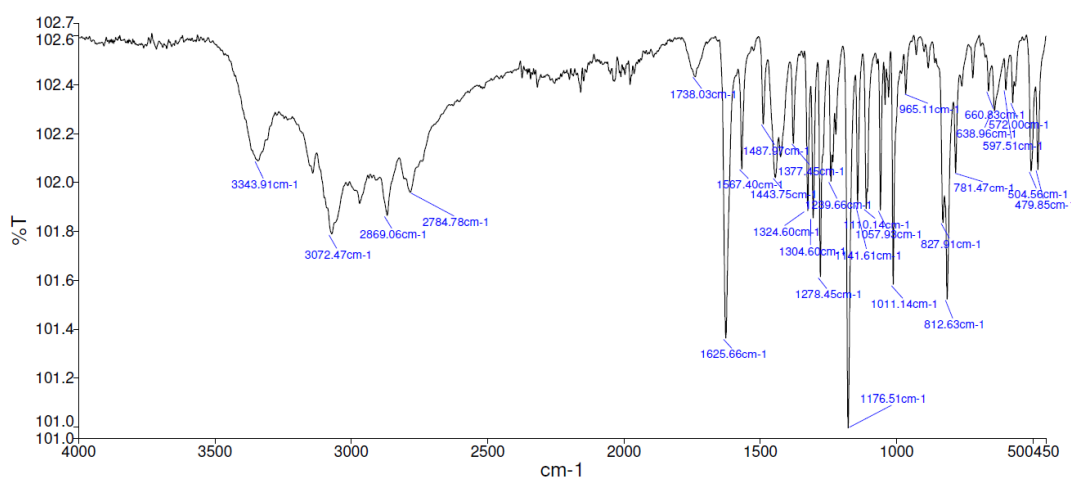
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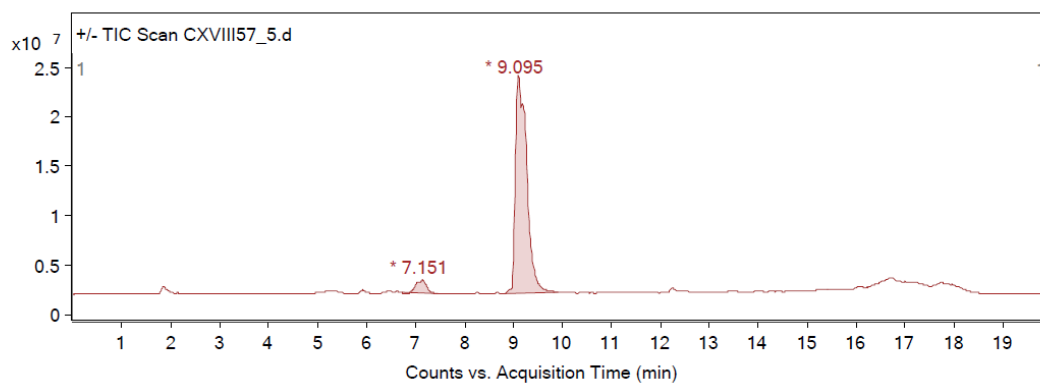
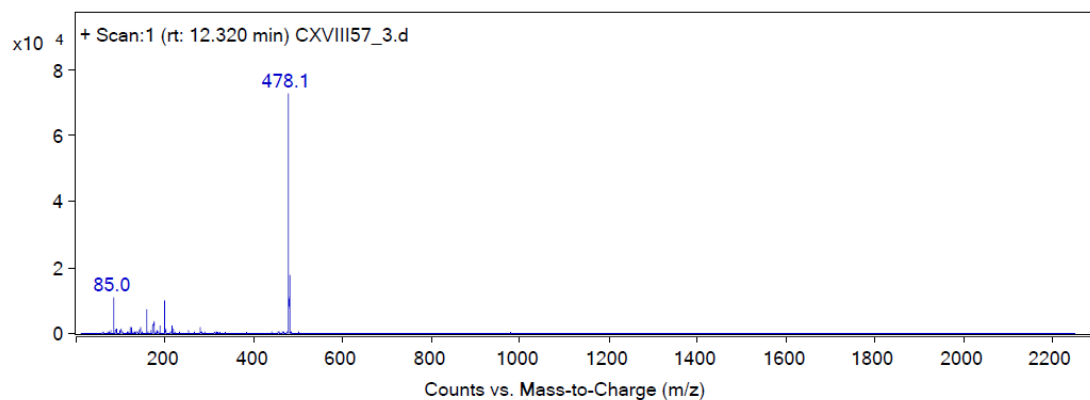






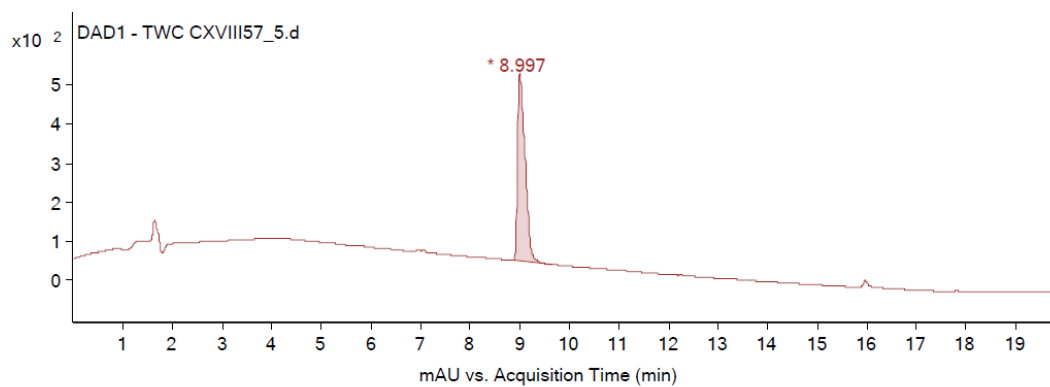
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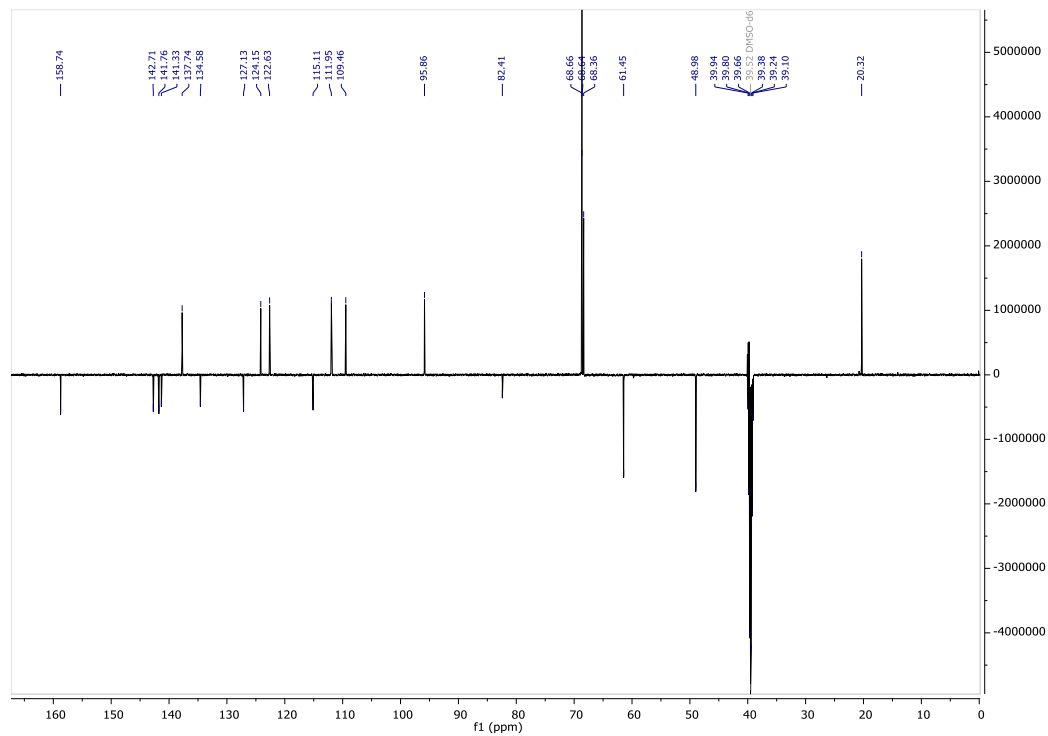
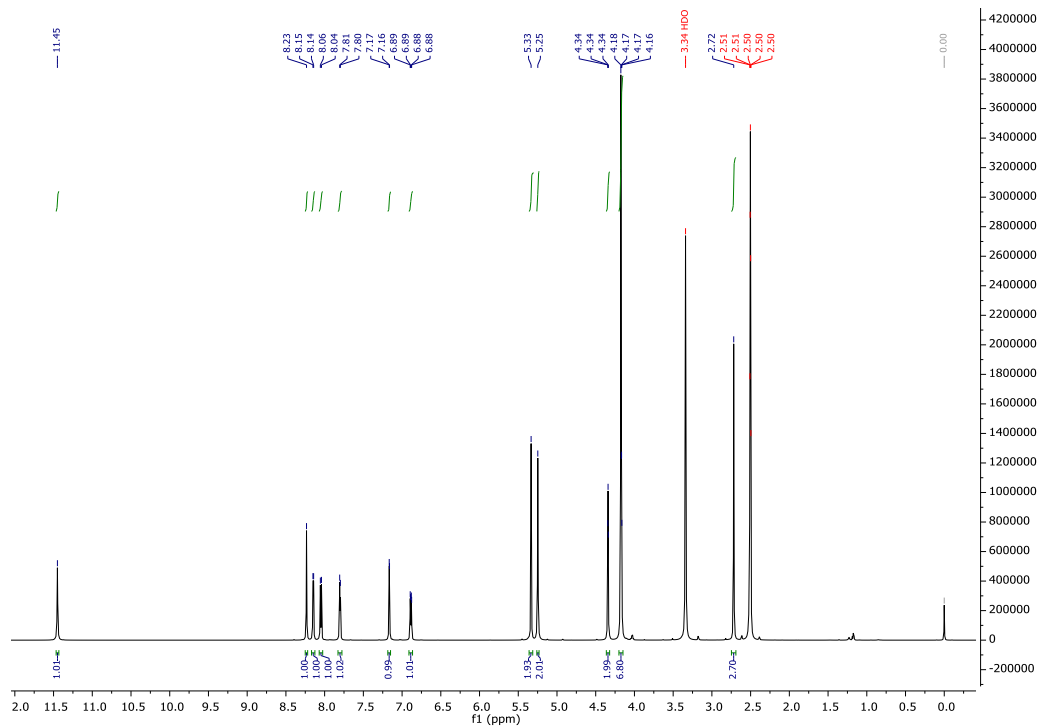
Integration Peak List

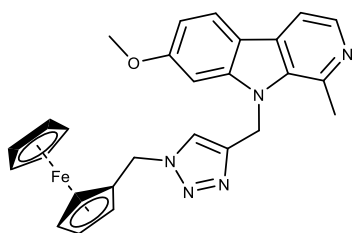
Peak	Start	RT	End	Height	Area	Area %
1	6.729	7.151	7.483	1334525.72	19487940.07	5.34
2	8.794	9.095	9.909	21941635.24	364759531.81	100



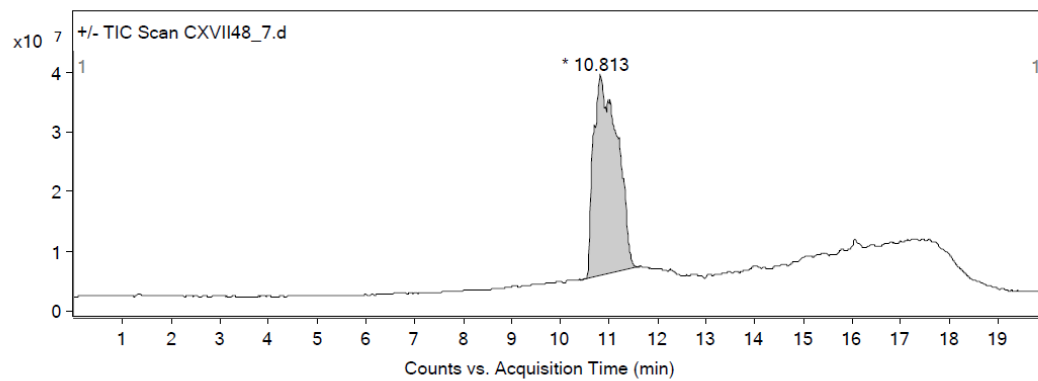
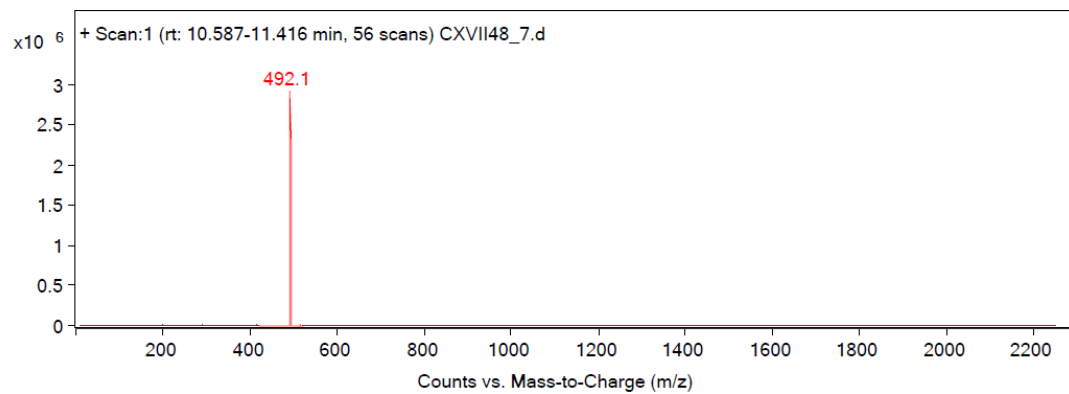
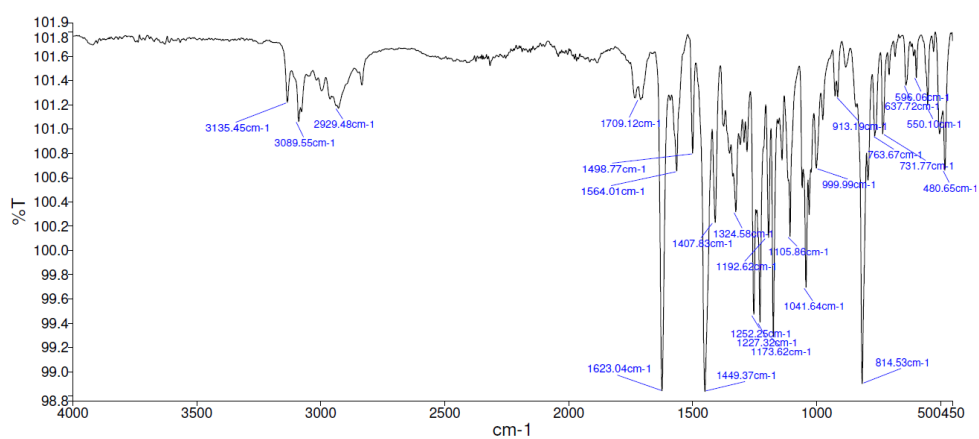
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	8.864	8.997	9.644	479.79	5004.85	100



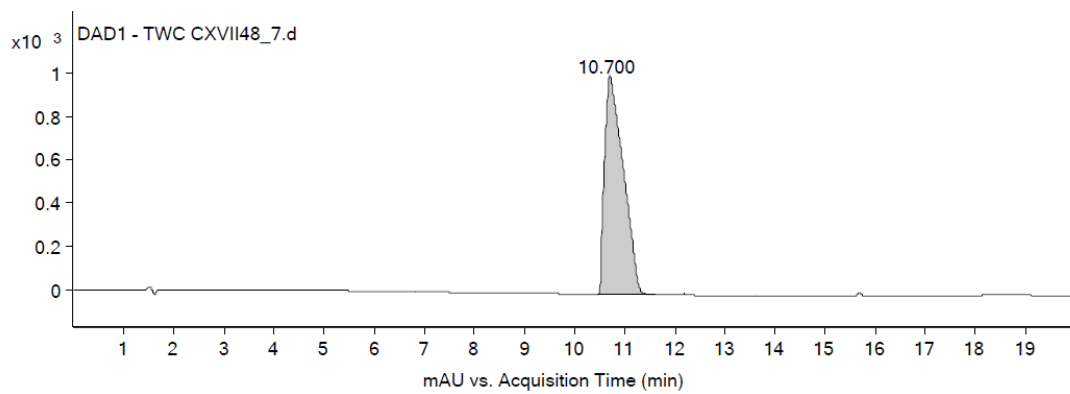


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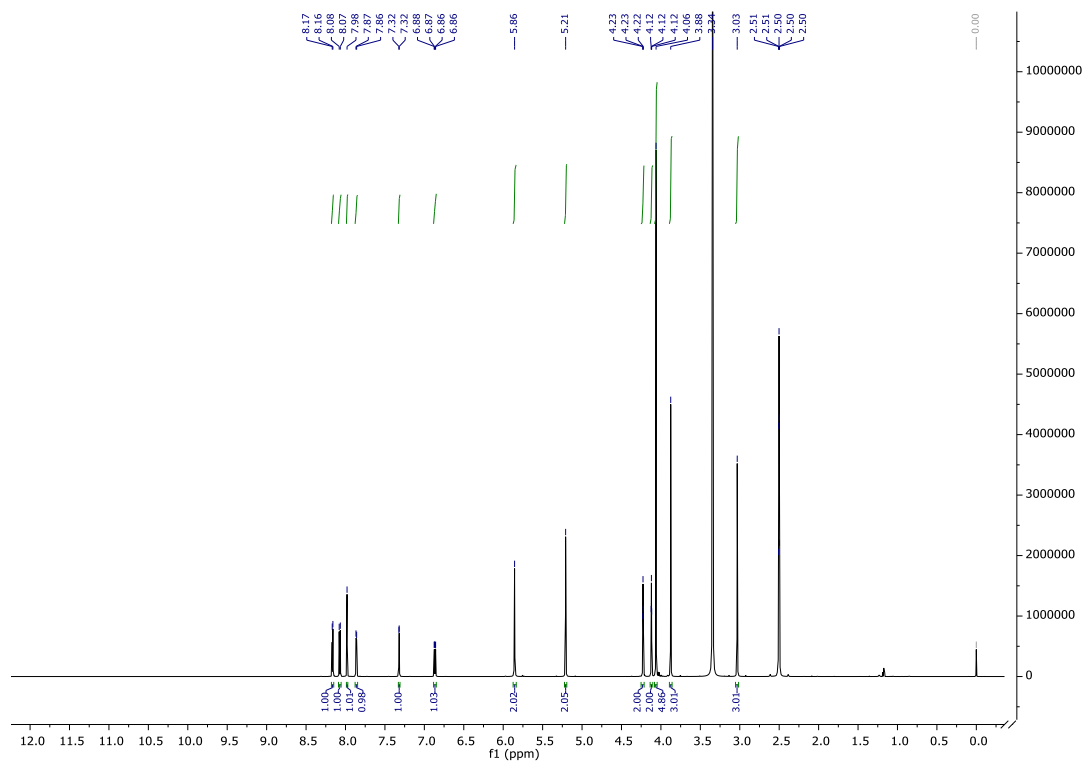
Integration Peak List

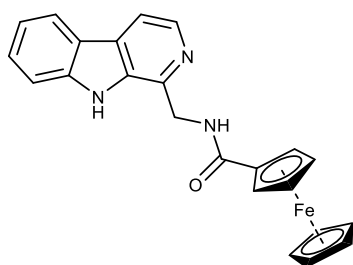
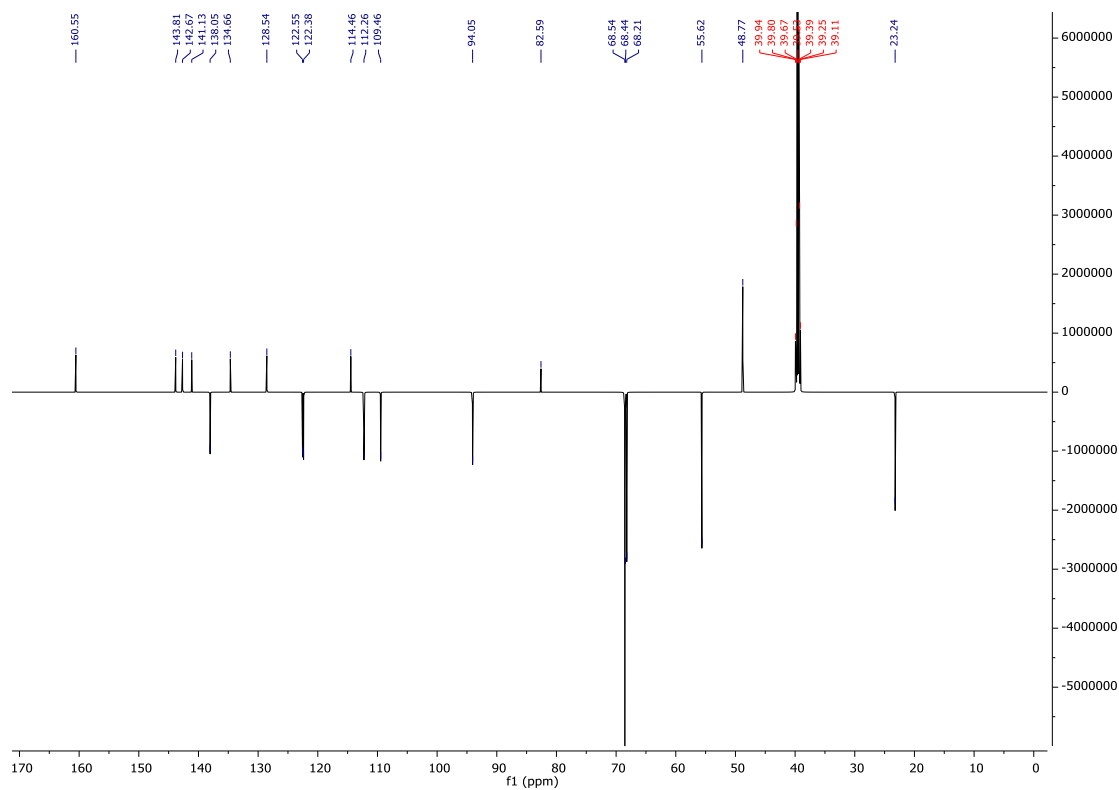
Peak	Start	RT	End	Height	Area	Area %
1	10.406	10.813	11.642	33720931.72	1130409678.26	100



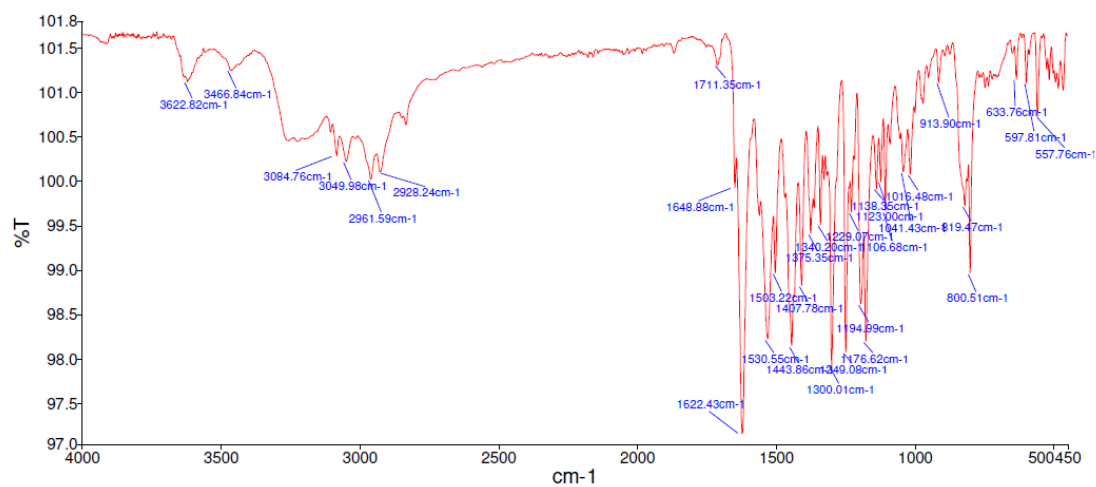
Integration Peak List

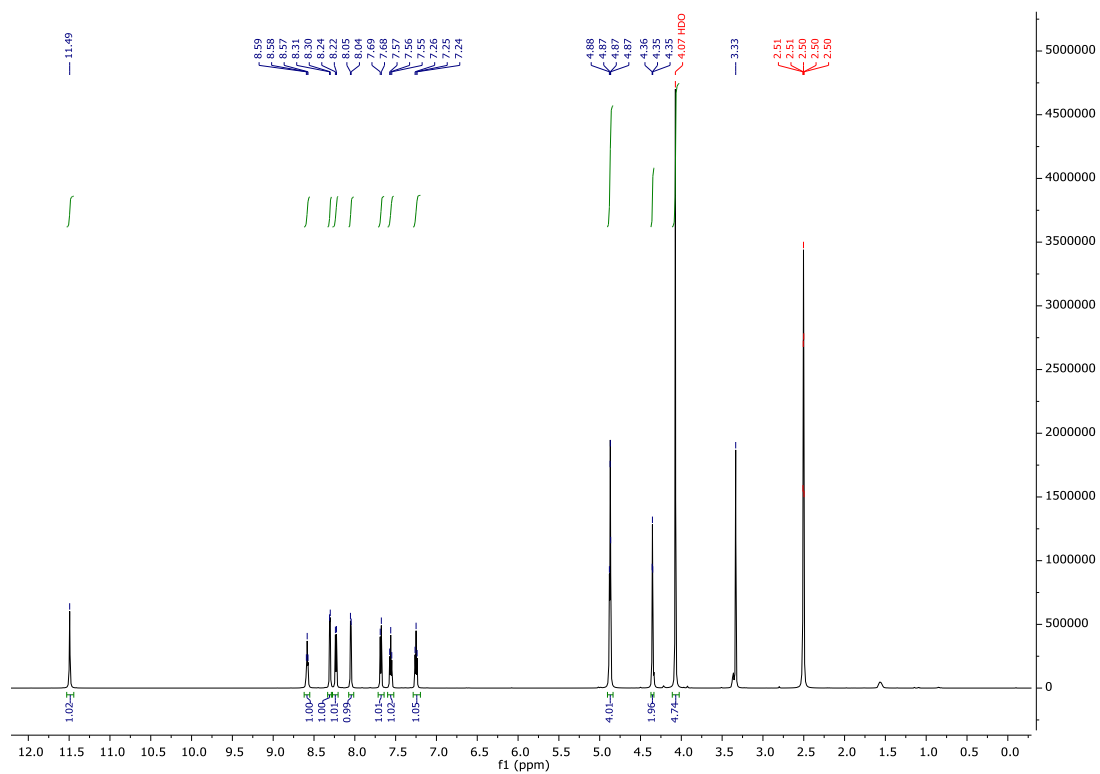
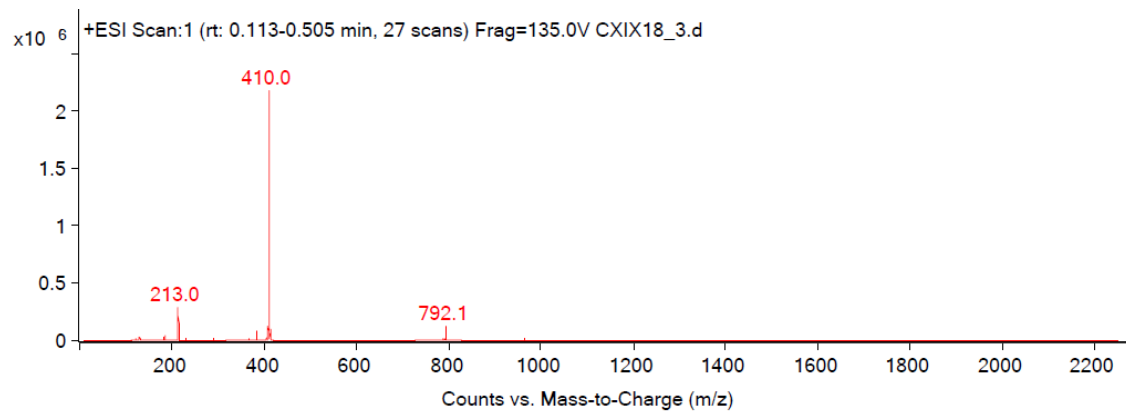
Peak	Start	RT	End	Height	Area	Area %
1	10.466	10.7	11.606	1011.94	26136.72	100

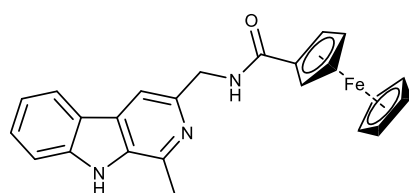
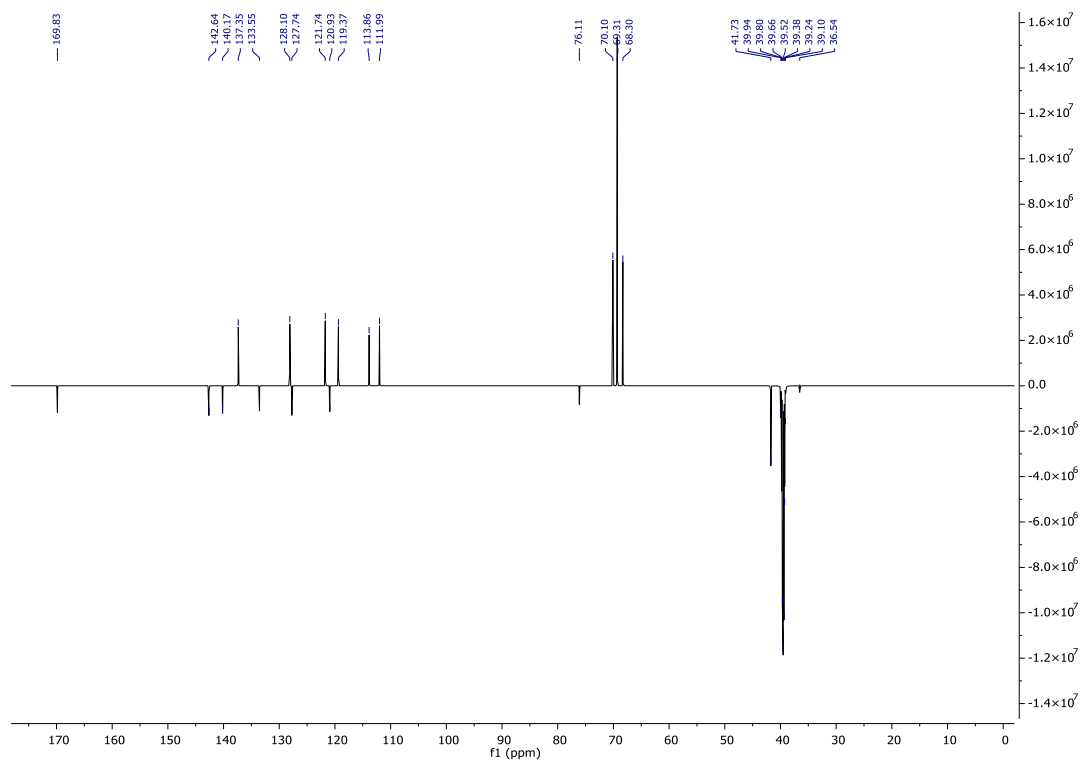




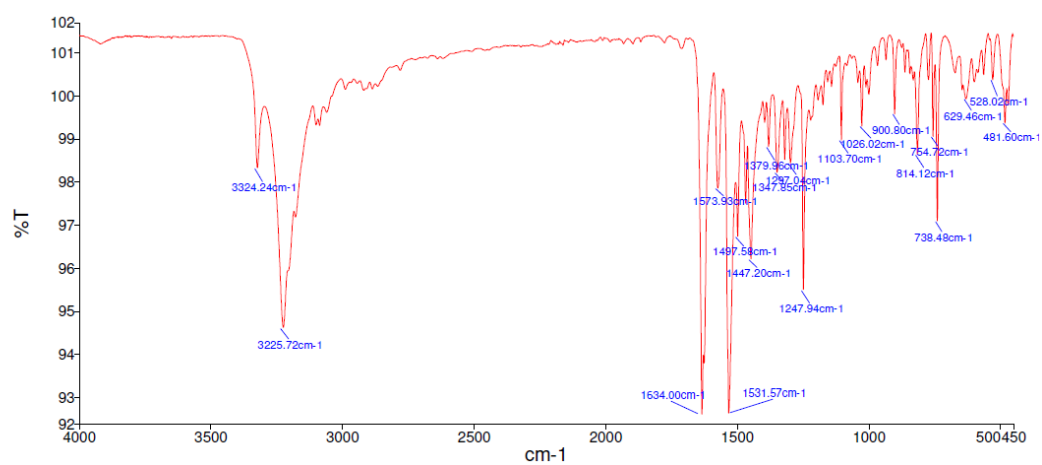
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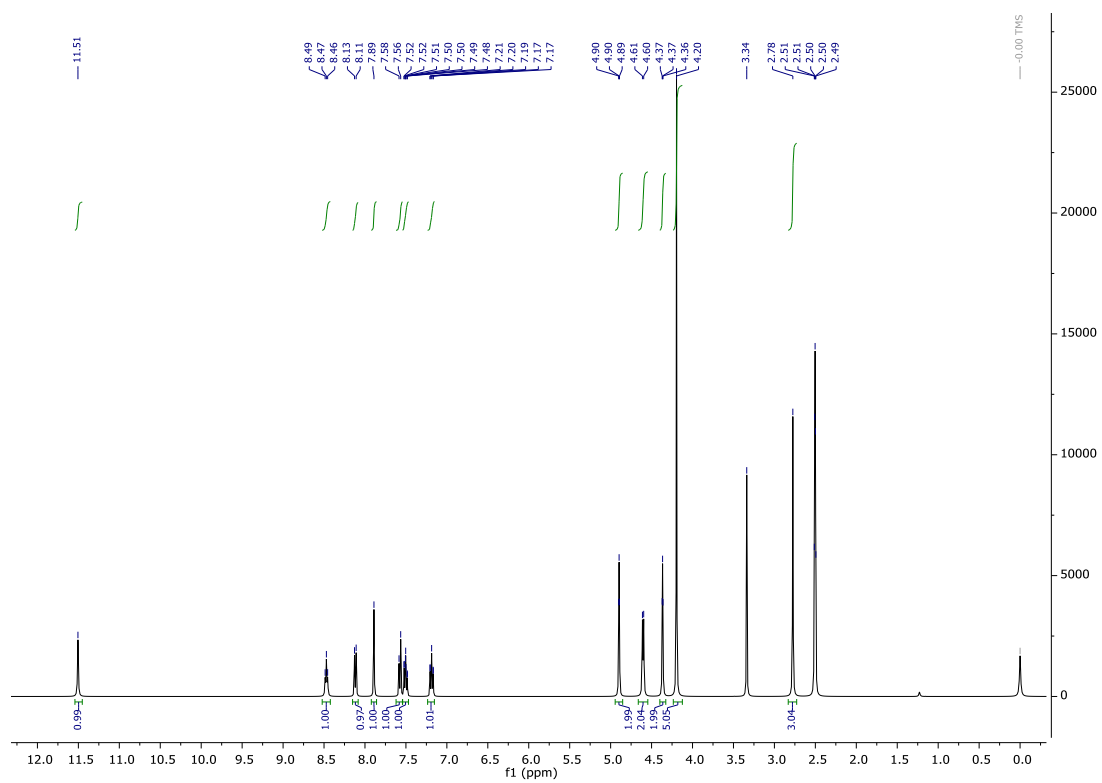
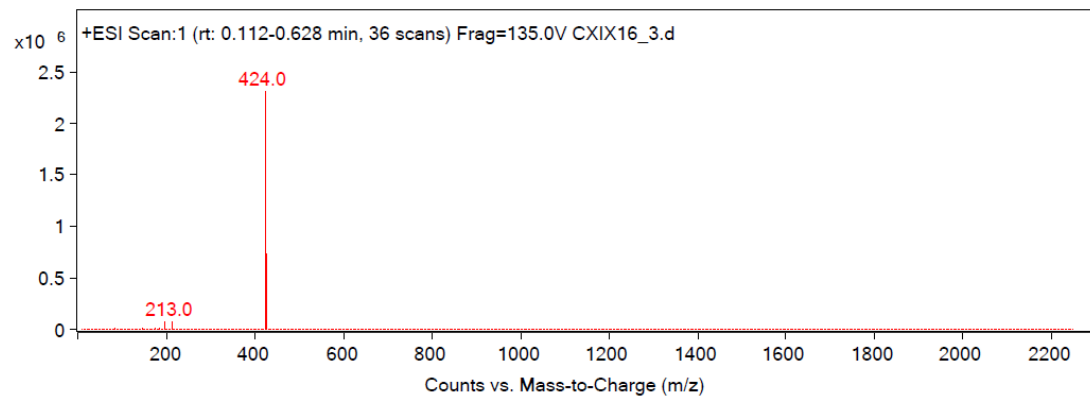


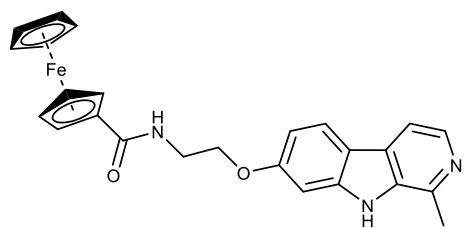
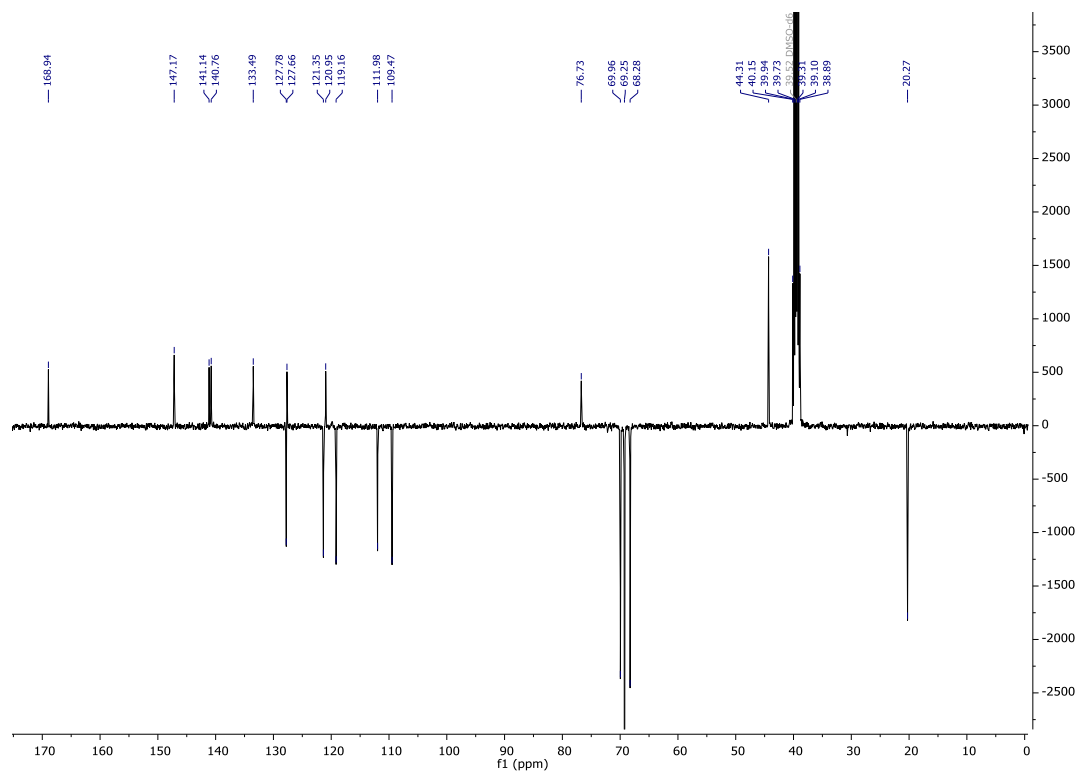




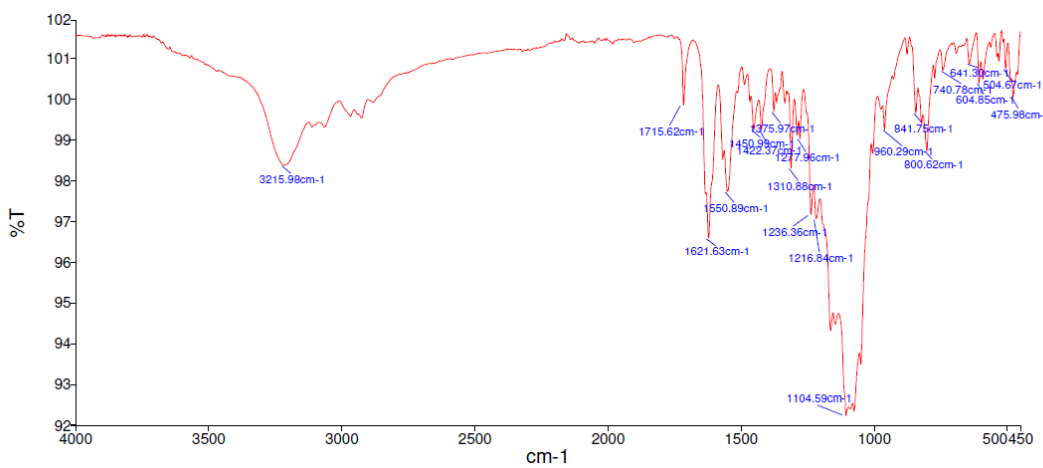
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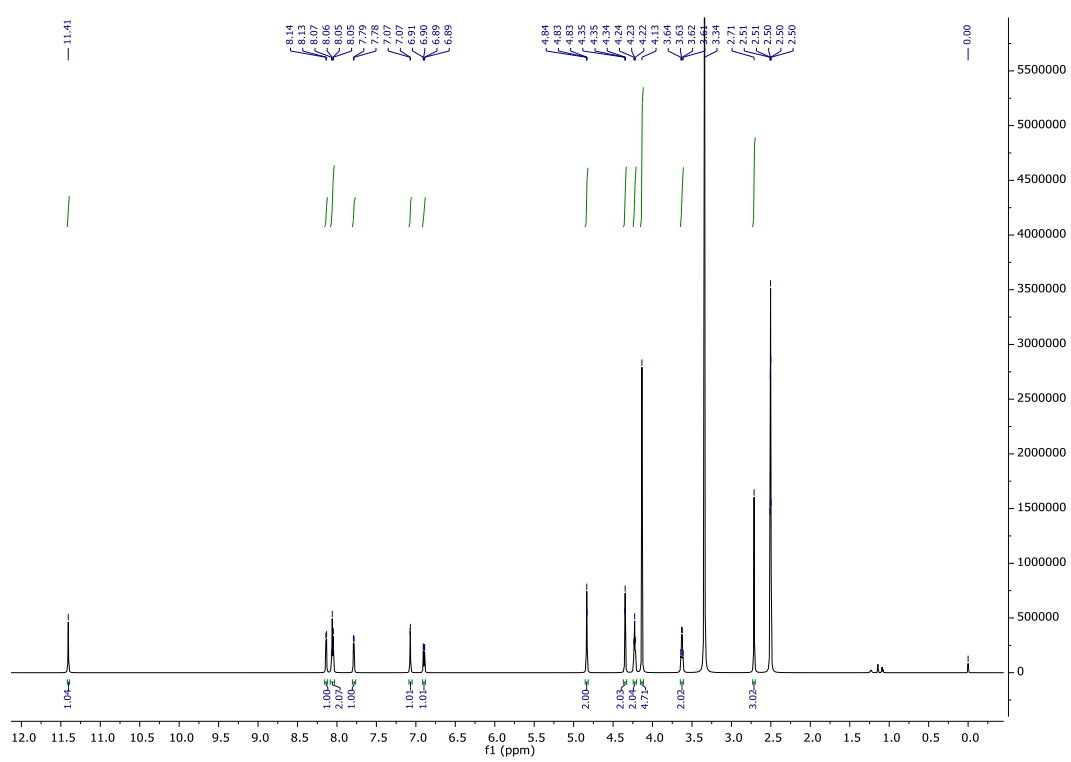
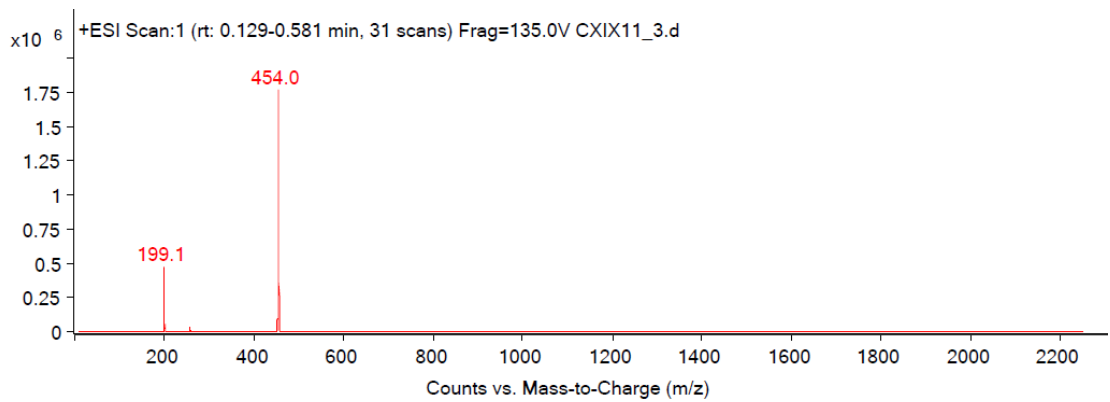


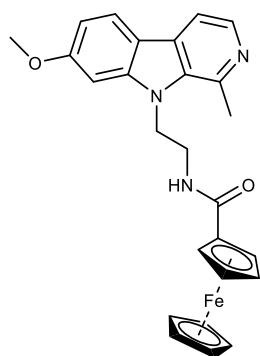
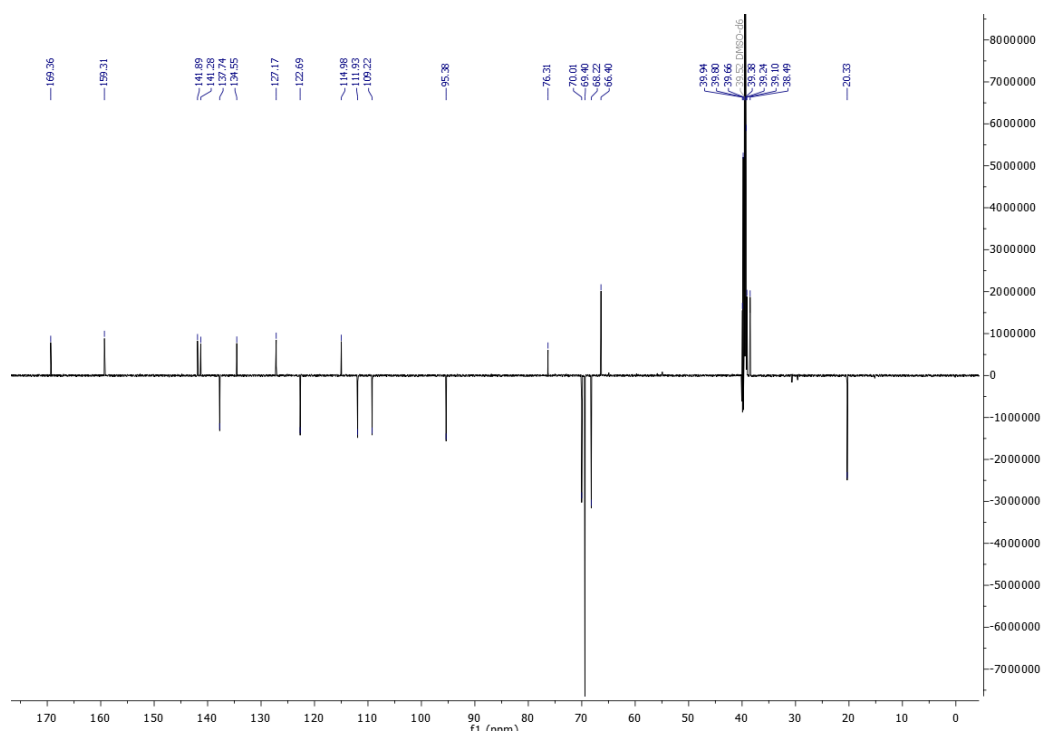




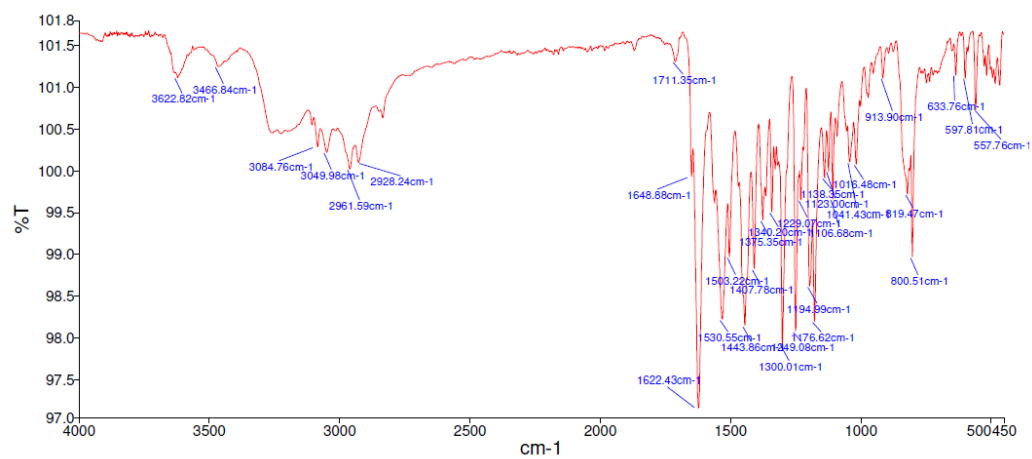
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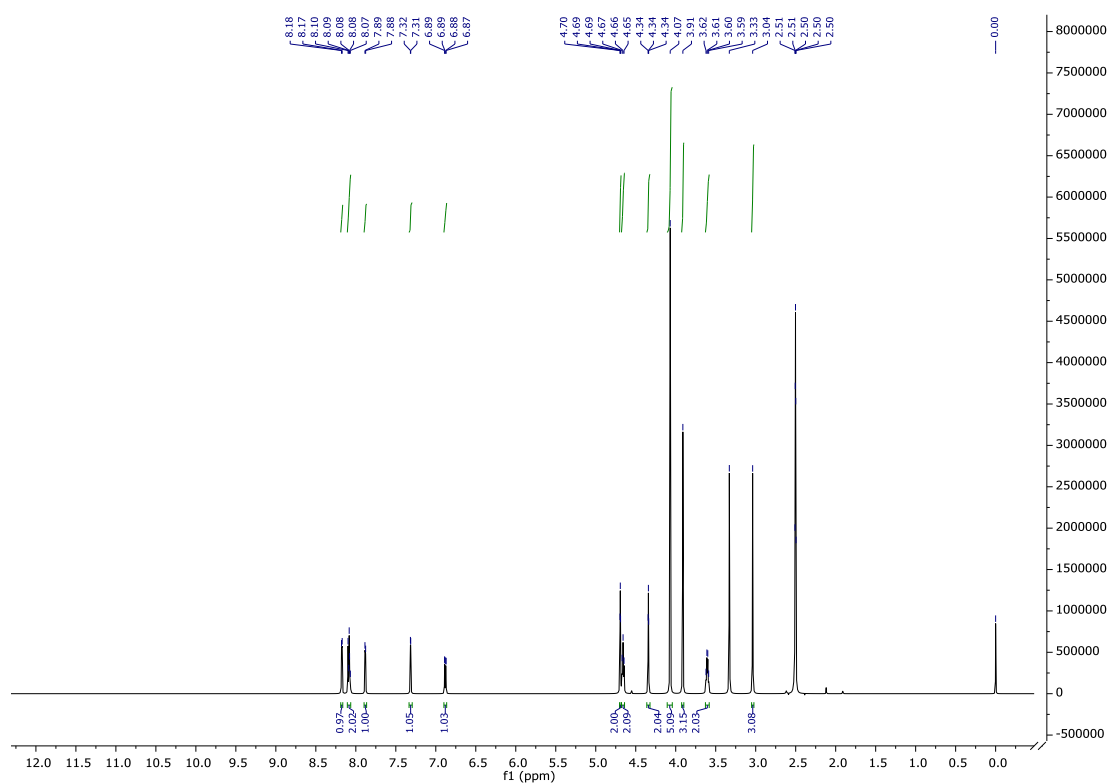
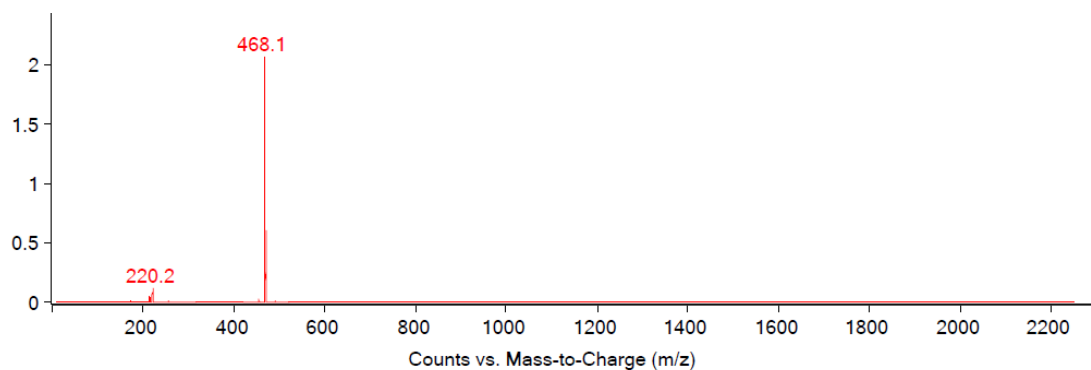


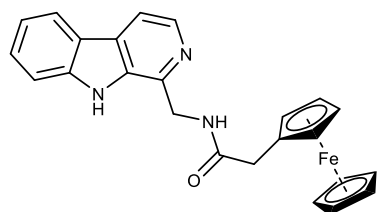
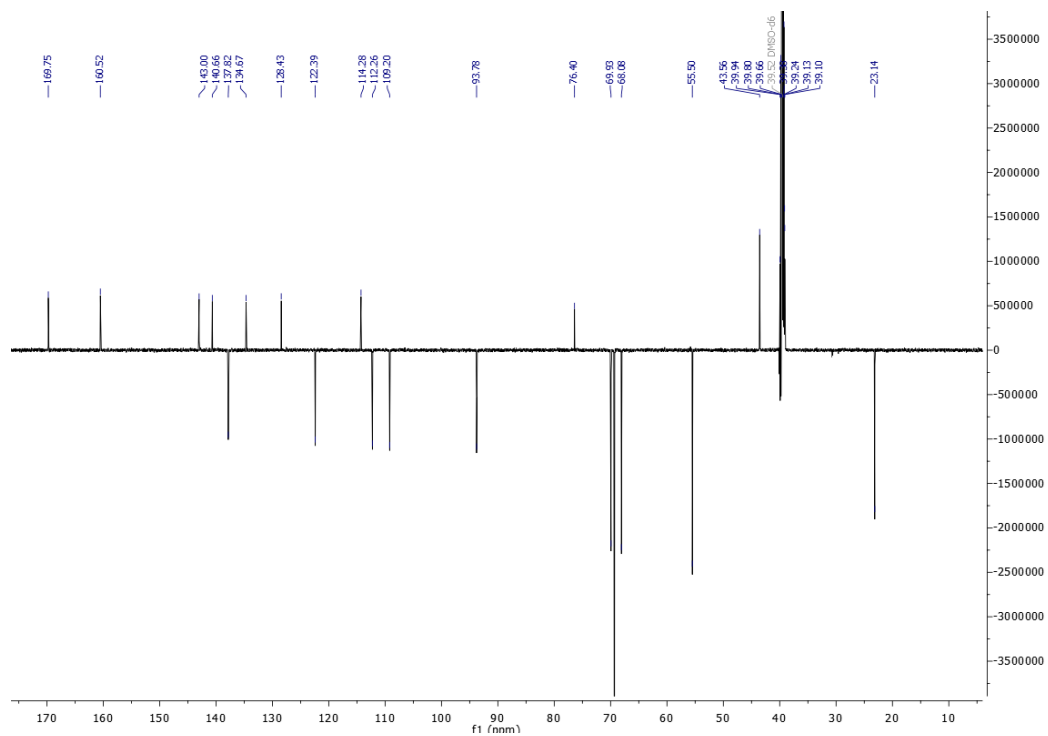




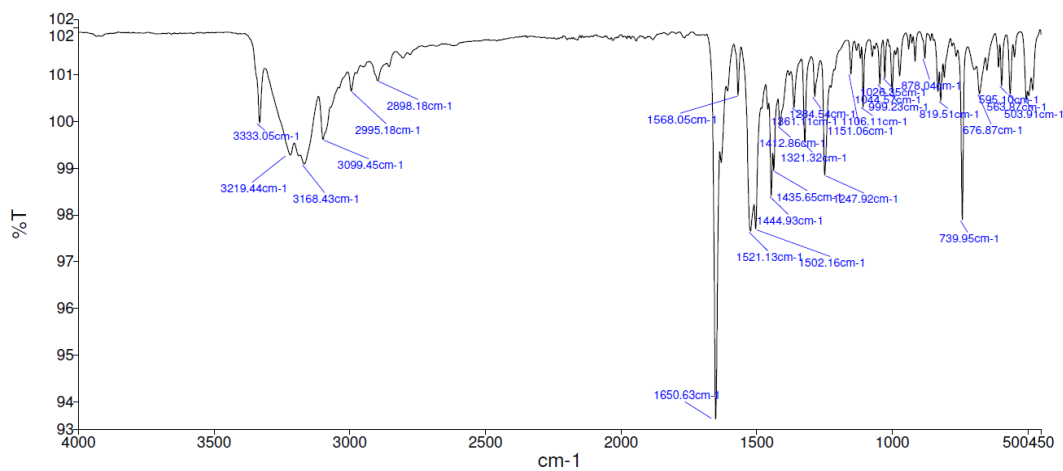
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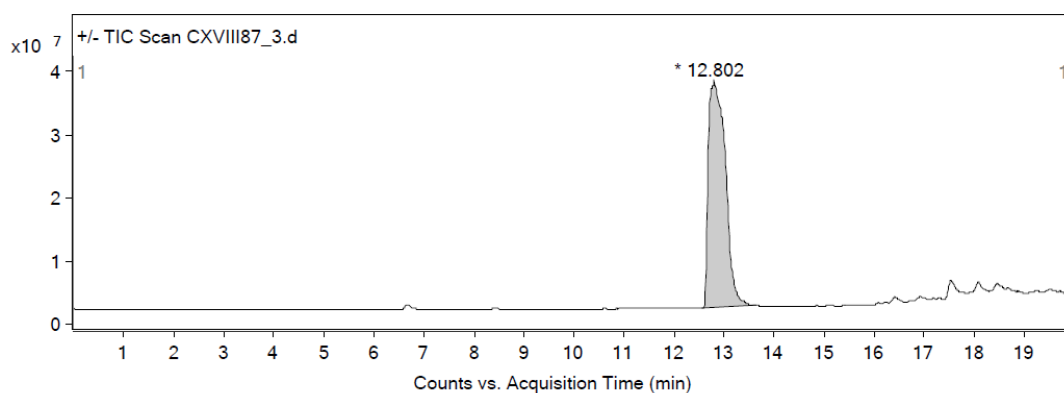
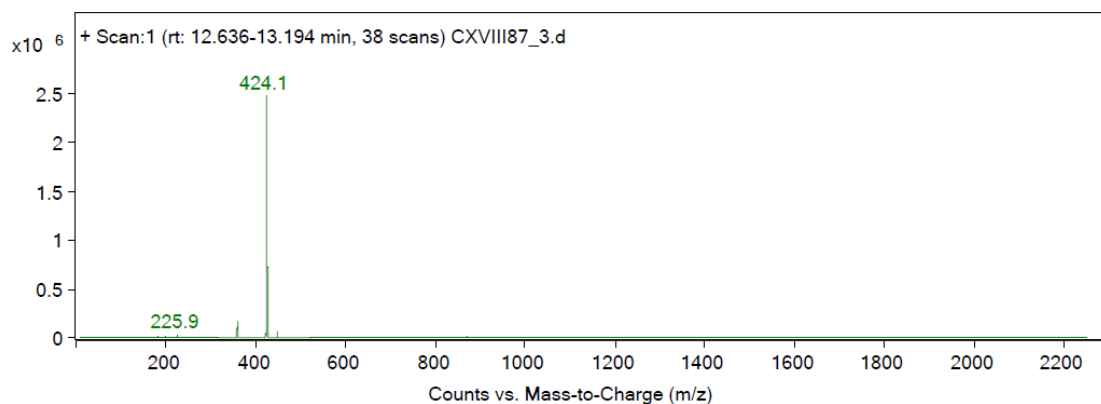






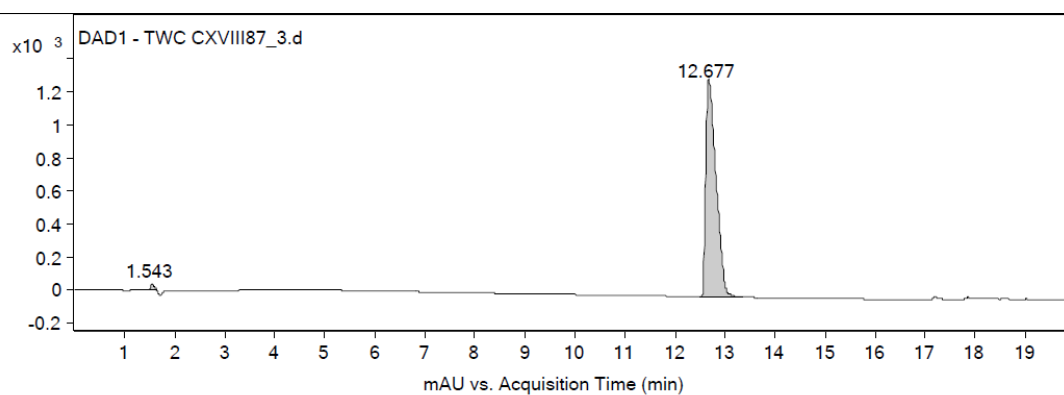
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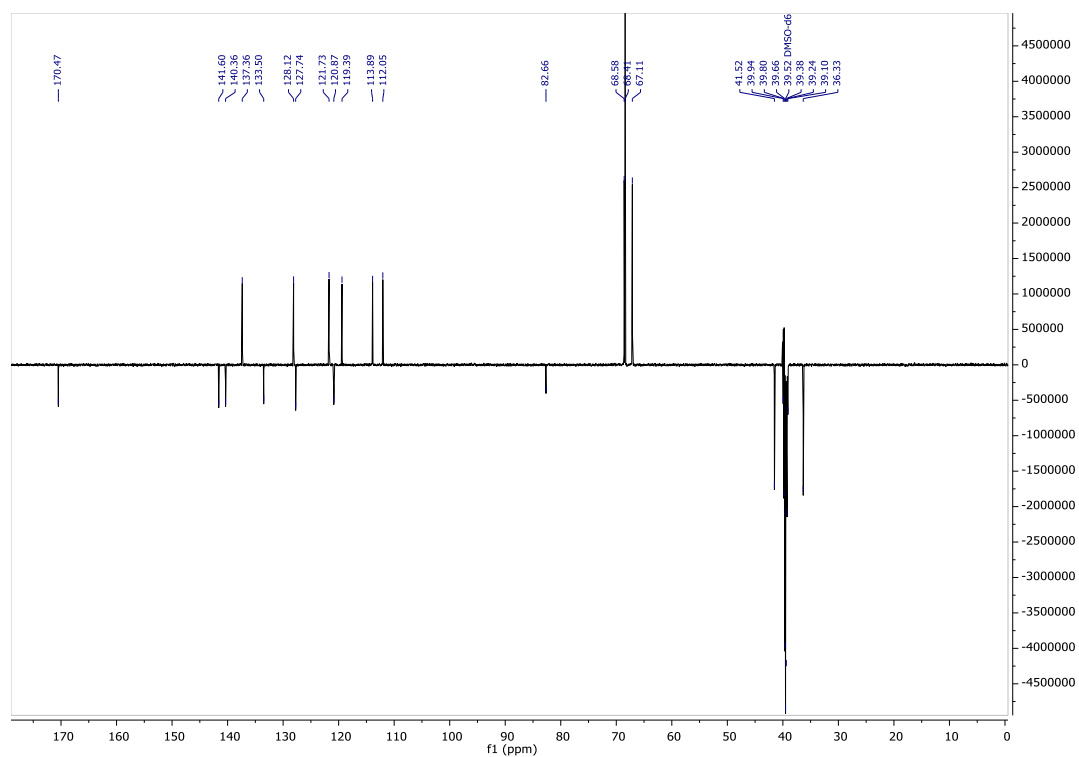
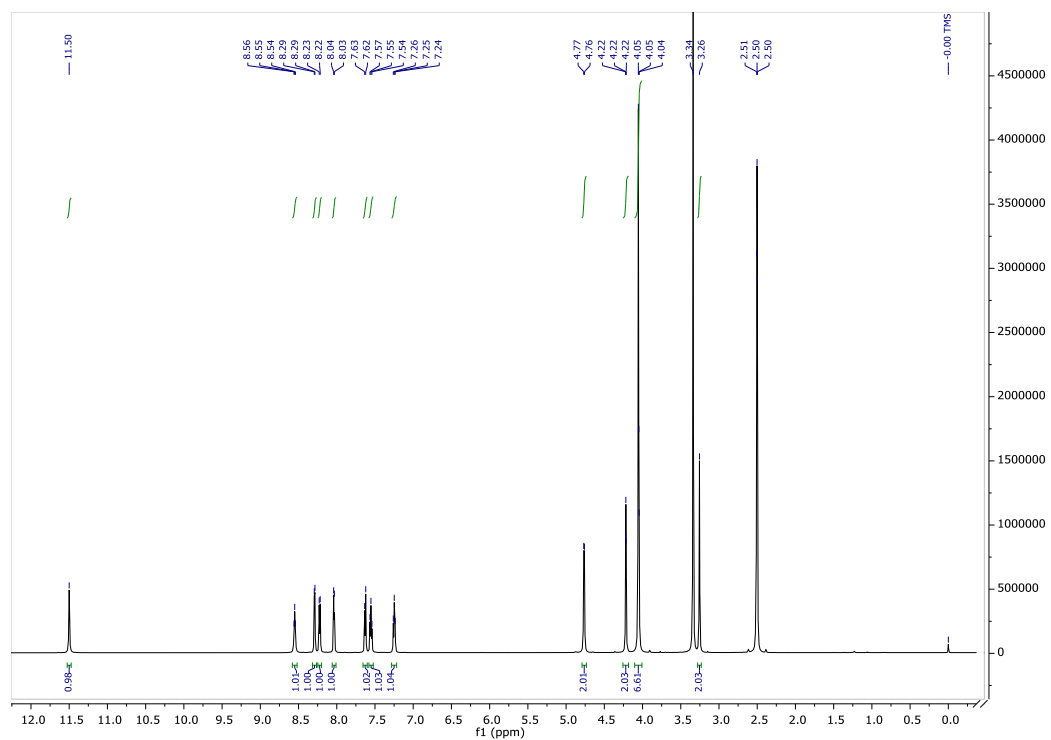
Integration Peak List

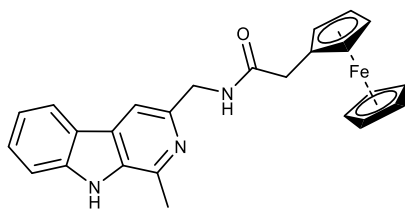
Peak	Start	RT	End	Height	Area	Area %
1	12.546	12.802	13.631	36091192.23	844377614.54	100



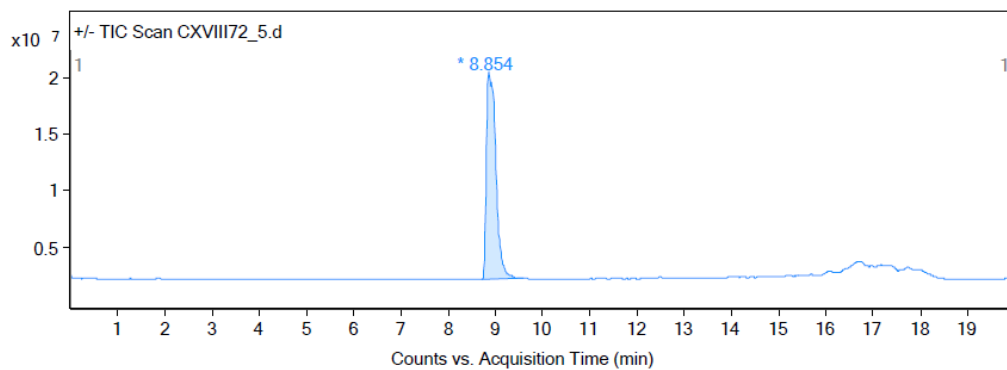
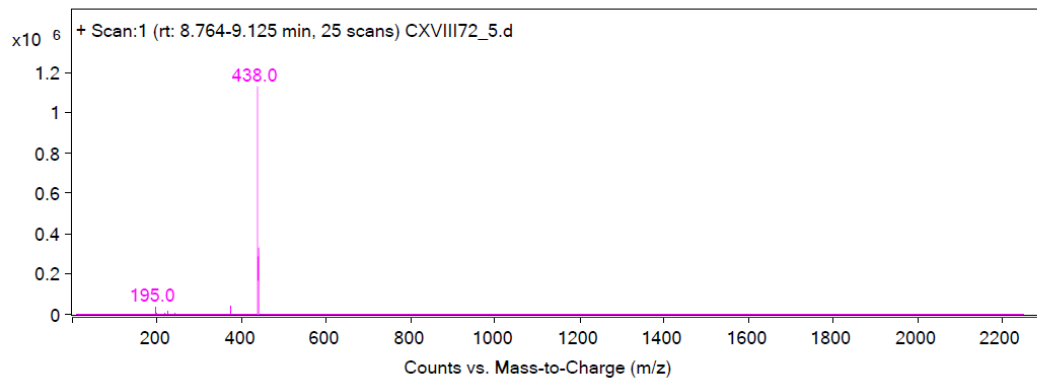
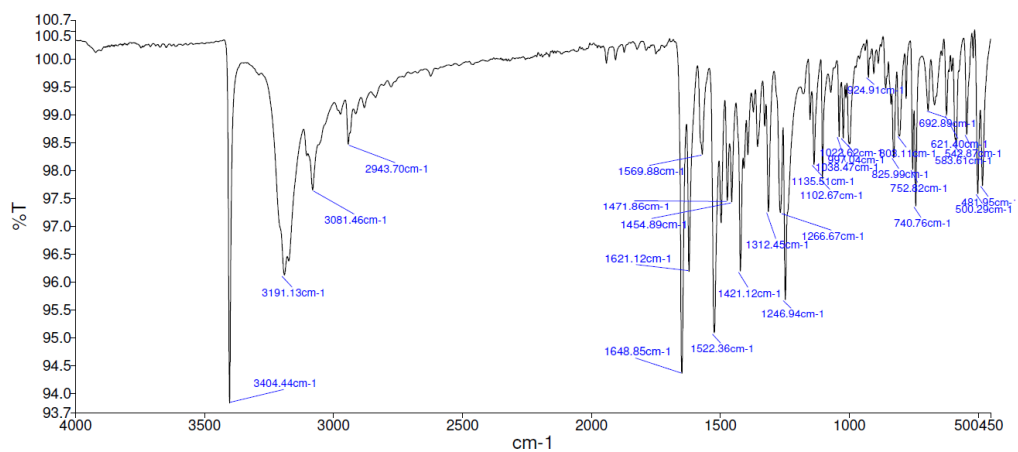
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	1.45	1.543	1.639	38.73	190.72	1.01
2	12.517	12.677	13.358	1319.93	18842.47	100



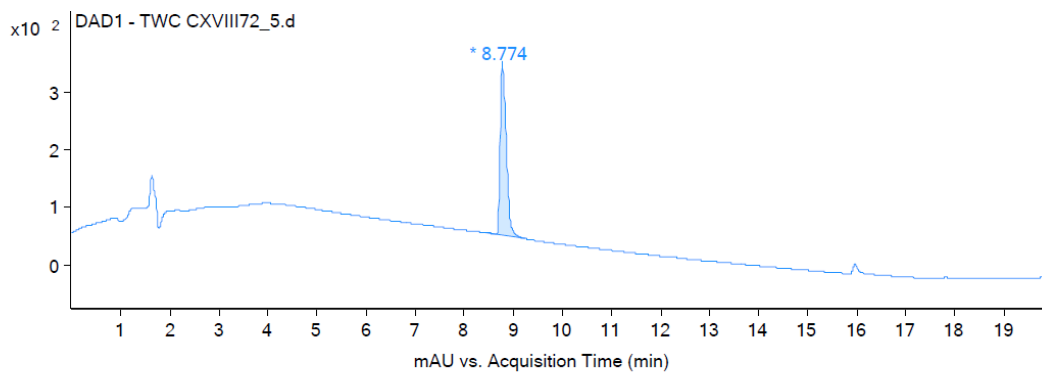


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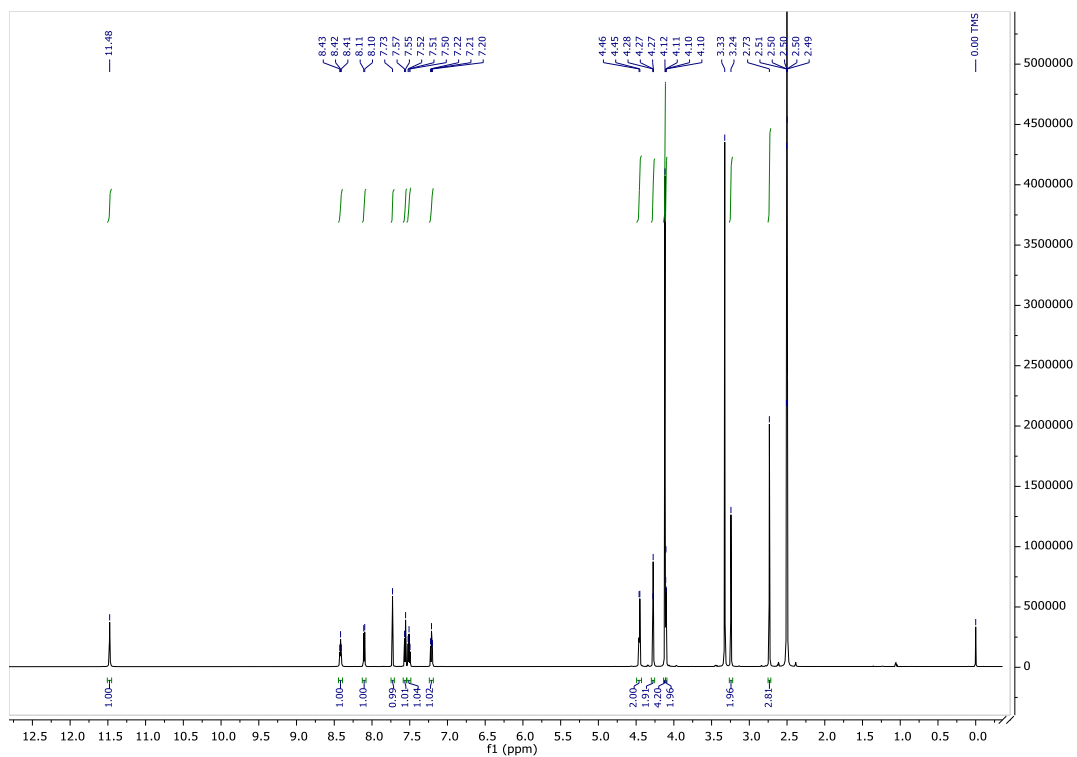
Integration Peak List

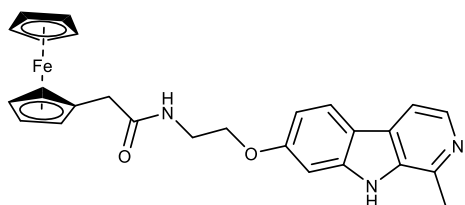
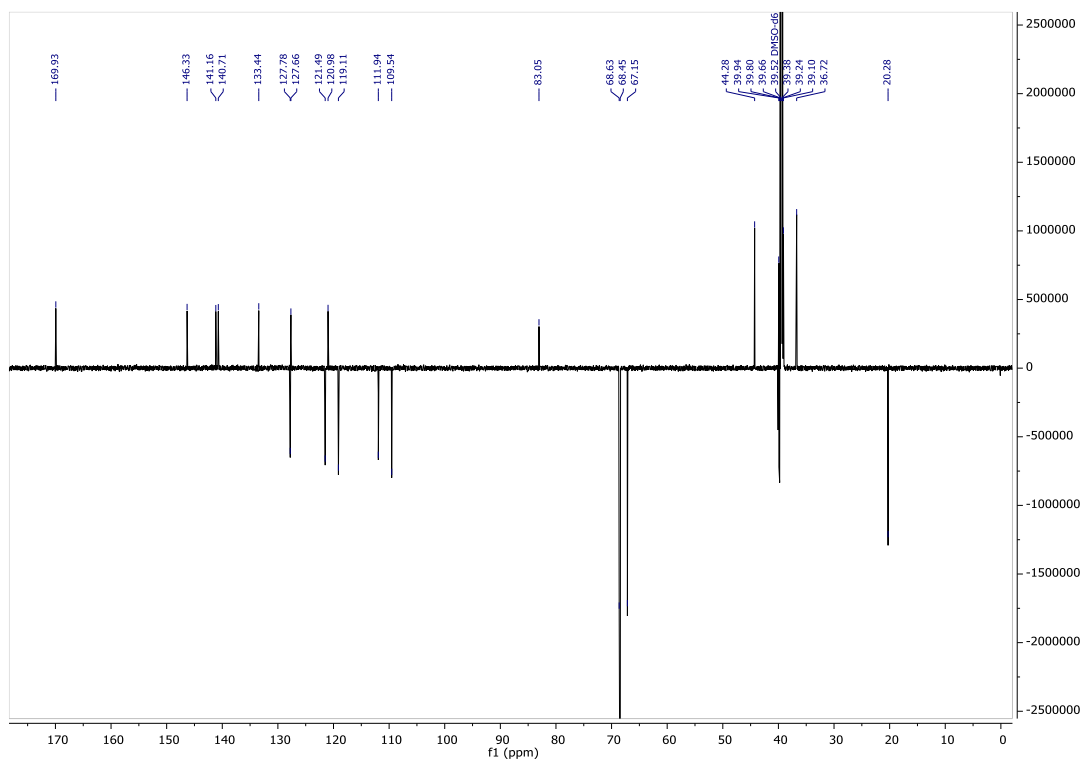
Peak	Start	RT	End	Height	Area	Area %
1	8.703	8.854	9.577	18358298.28	248380233.19	100



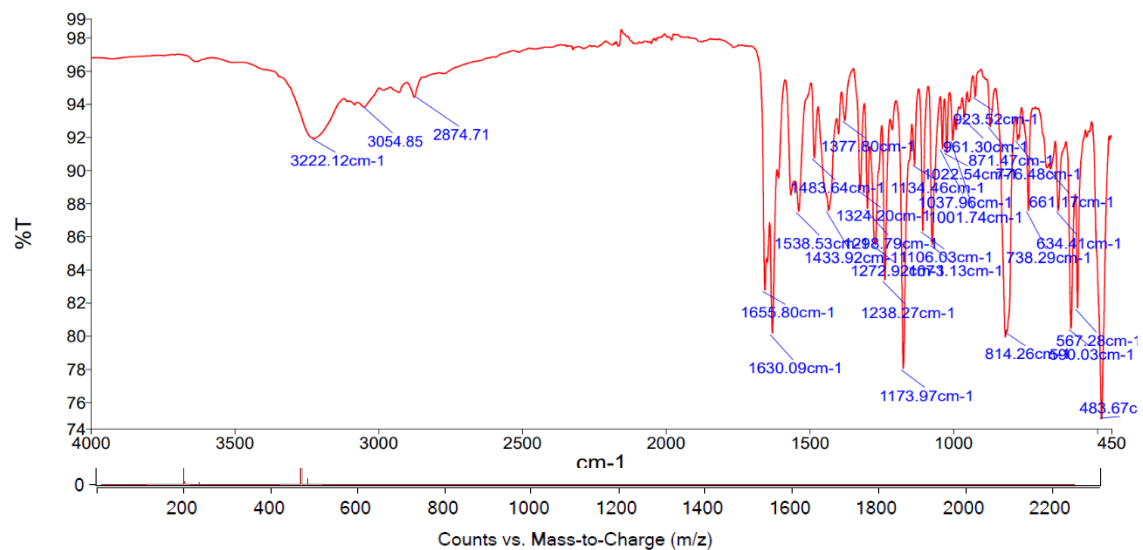
Integration Peak List

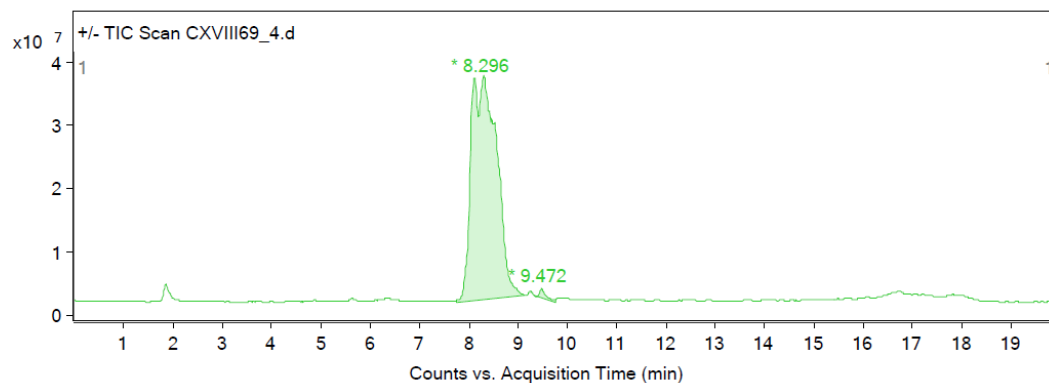
Peak	Start	RT	End	Height	Area	Area %
1	8.42	8.774	9.234	301.5	2556	100





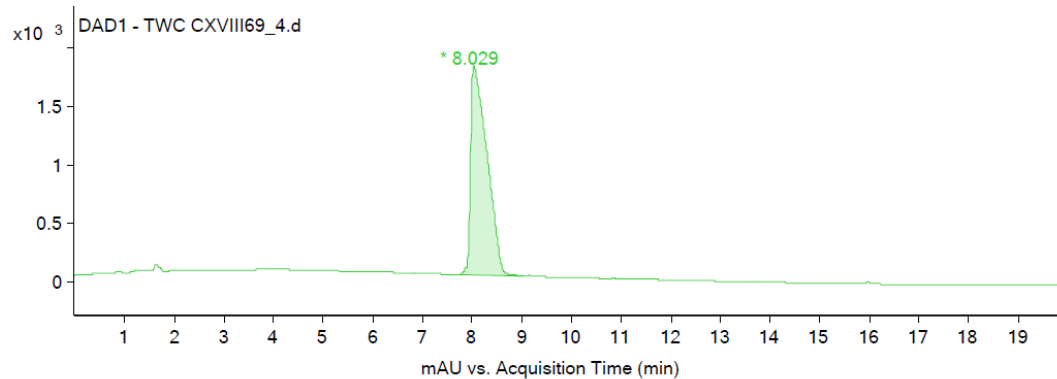
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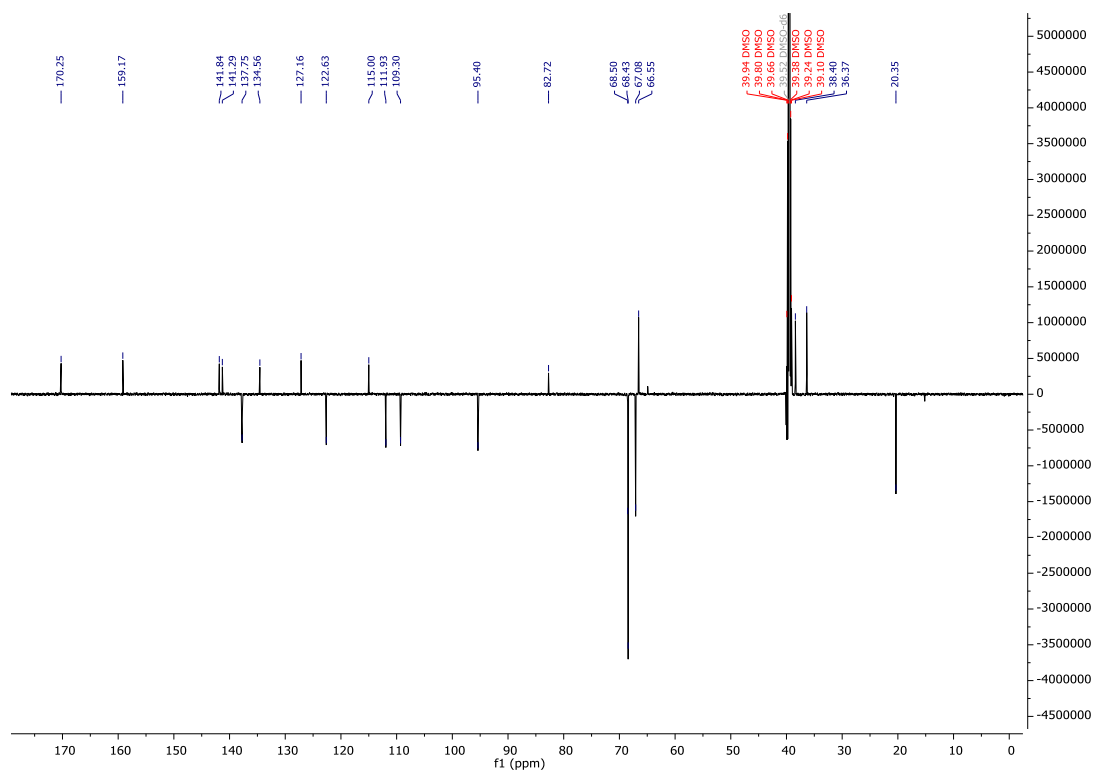
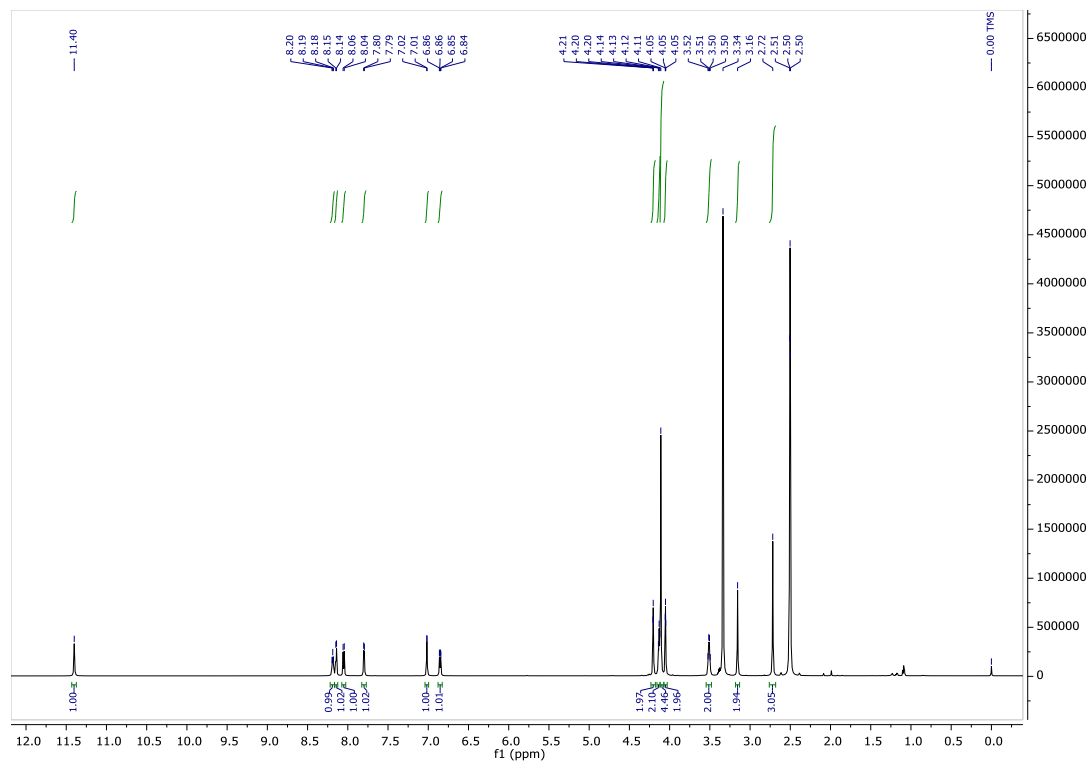
Integration Peak List

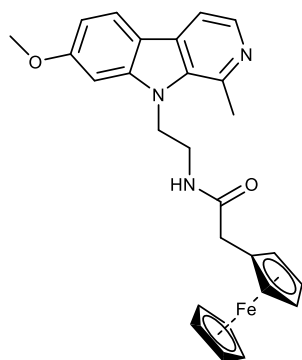
Peak	Start	RT	End	Height	Area	Area %
1	7.739	8.296	9.125	35456743.85	1278789928.72	100
2	9.336	9.472	9.773	1420821.54	13300609.58	1.04



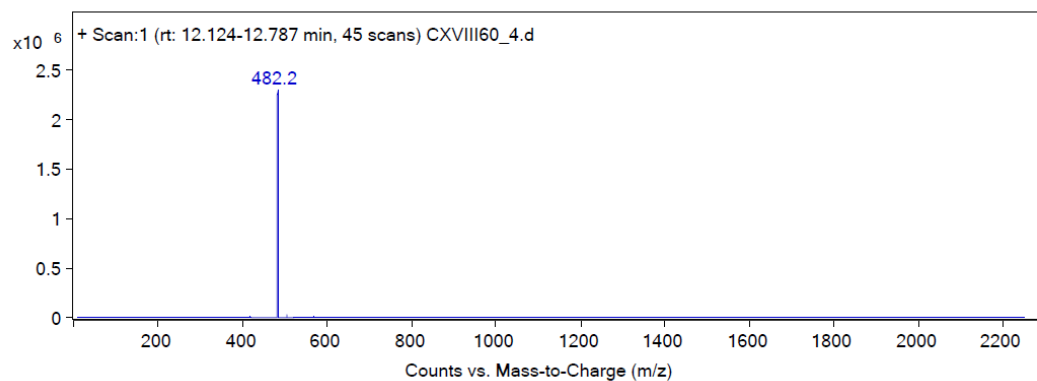
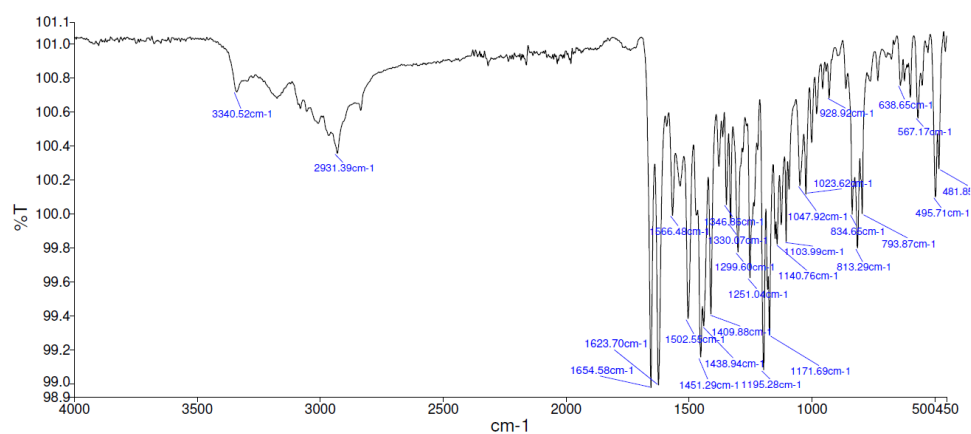
Integration Peak List

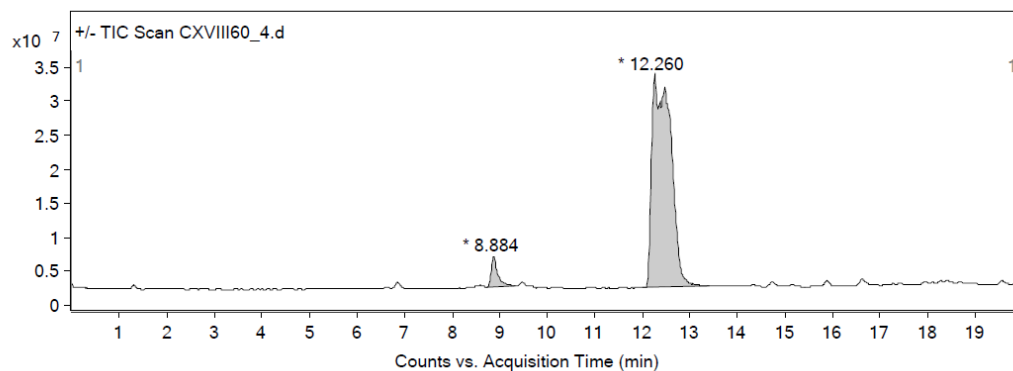
Peak	Start	RT	End	Height	Area	Area %
1	7.722	8.029	9.029	1782.73	41115.7	100





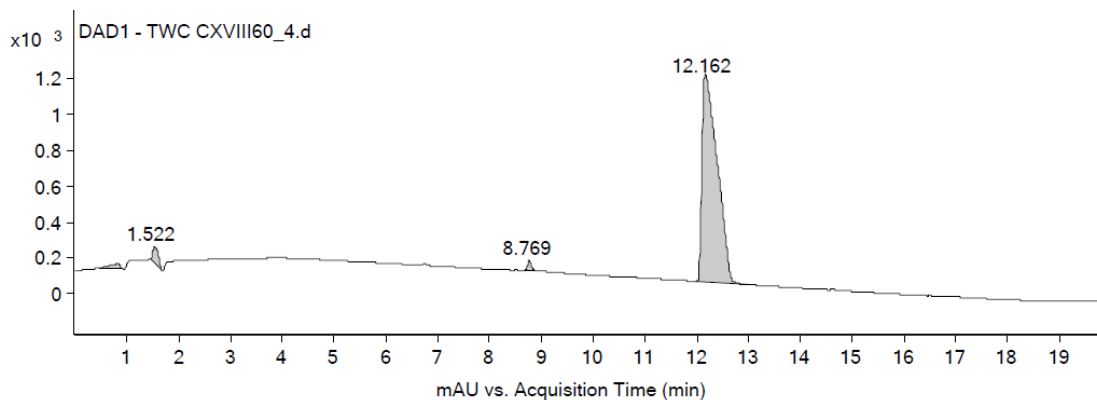
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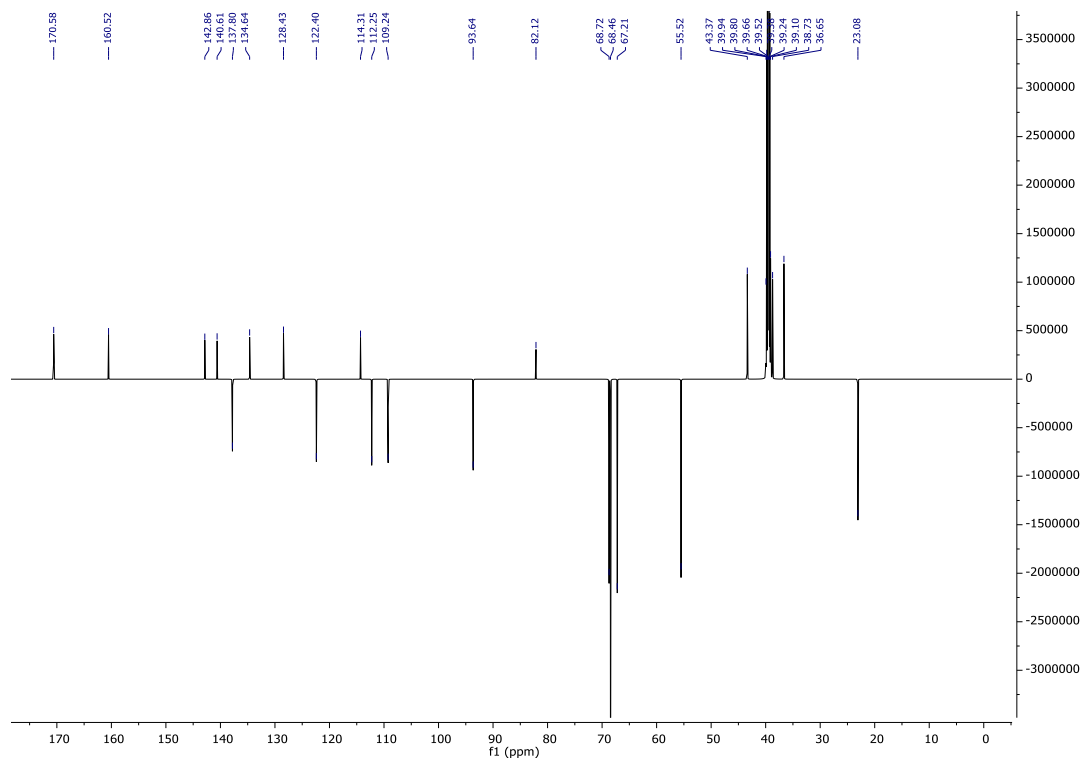
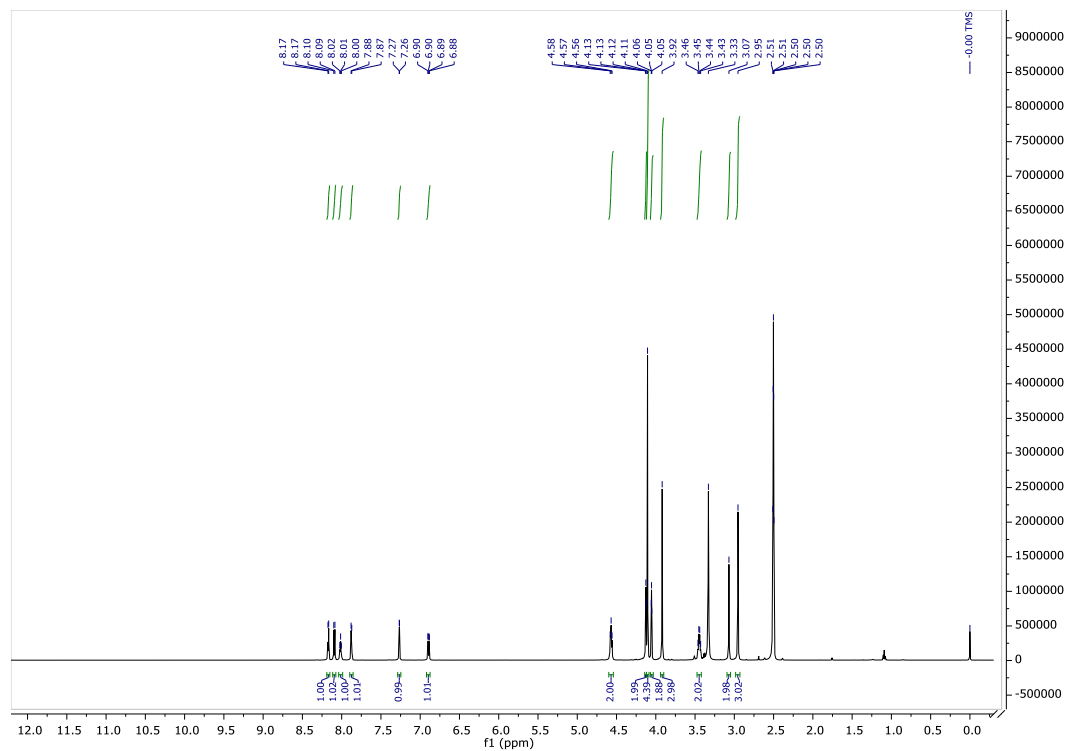
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	8.718	8.884	9.336	4479840.71	44307179.08	5.08
2	12.019	12.26	13.39	31597336.17	871523549.01	100



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	0.475	0.822	0.909	24.56	351.74	1.49
2	1.455	1.522	1.662	87.27	731.86	3.1
3	8.694	8.769	8.875	58.9	287.3	1.22
4	11.975	12.162	13.029	1153.28	23574.59	100



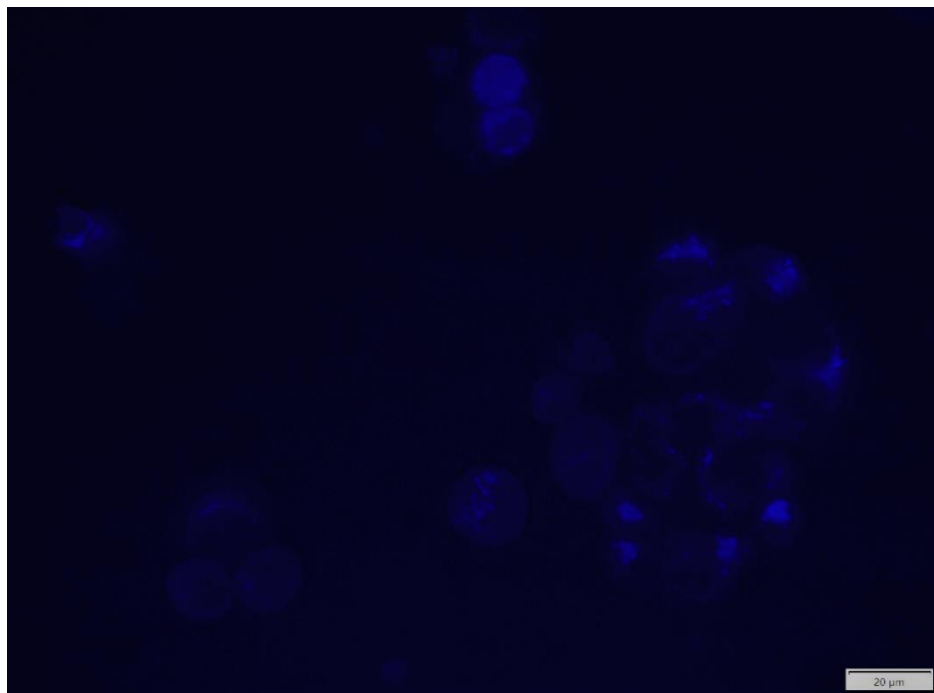


Figure S1. Fluorescent microscopy image (400 × magnification) of MCF-7 cells incubated with 5 μM concentration of compound **23** for 30 min. The scale bar is 20 μm.