Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Supporting Information

# The effect of aryl hydrazono ester containing dipeptides (AHED) on mosquito egg-laying behaviour

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## Contents:

## Characterization of compounds

**Methyl 2-(4-aminobenzamido)-3-methylpentanoate (2).** White solid; Yield: 1.15 g; 60 %; m.p. 100-101 $^{o}$C; FT-IR (KBr, neat, cm$^{-1}$): 3453, 3360, 3239, 2964, 1732, 1603, 1527, 1370, 1317, 990, 842, 776; $^{1}$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 0.88-0.97 (6H, m), 1.21-1.28 (1H, m), 1.49-1.56 (1H, m), 1.95-2.01 (1H, m), 3.76 (3H, s), 4.03 (2NH, bs), 4.79 (1H, q, $J$ = 5.2 Hz), 6.52 (1NH, d, $J$ = 8.4 Hz), 6.65 (2H, d, $J$ = 8.4 Hz), 7.63 (2H, d, $J$ = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 11.6, 15.5, 25.4, 38.3, 52.1, 56.7, 114.1, 123.5, 128.9, 150.0, 167.0, 173.0; ESI-MS: *m/z* 287.5742 $[M+Na]^+$

**(E)-4-(2-(1-ethoxy-1,3-dioxobutan-2-ylidene)hydraz-inyl) benzoic acid (3a).** Yellow solid; Yield: 1.85 g; 90 %; m.p. 201-202 $^{o}$C; FT-IR (KBr, neat, cm$^{-1}$): 3445, 2985, 2668, 2548, 2361, 1687, 1608, 1529, 1295, 1224, 1162, 1082, 770; $^{1}$H NMR (400 MHz, DMSO-$d_6$: $\delta$ (ppm) 1.26-1.33 (3H, m), 2.41 (3H, s), 4.26-4.35 (2H, m), 7.53 (2H, dd, $J$ = 8.4 and 8.8 Hz), 7.95 (2H, t, $J$ = 8.0 and 8.4 Hz), 11.58 (1NH, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$: $\delta$ (ppm) 13.8, 14.1, 25.3, 30.4, 60.7, 61.3, 114.5, 115.6, 125.3, 126.5, 127.2, 131.0, 133.2, 145.4, 146.1, 162.3, 163.4, 166.9, 193.8, 195.4; ESI-MS: *m/z* 301.5674 $[M+Na]^+$

**(E)-4-(2-(1-methoxy-1,3-dioxobutan-2-ylidene) hyd-razin-yl)benzoic acid (3b).** Yellow solid; Yield: 1.68 g; 87 %; m.p. 232-233 $^{o}$C; FT-IR (KBr, neat, cm$^{-1}$): 3445, 2959, 2670, 2551, 2361, 1675, 1629, 1607, 1521, 1429, 1332, 1281, 1194, 1084, 983, 799, 768; $^{1}$H NMR (400 MHz, DMSO-$d_6$: $\delta$ (ppm) 2.41 (3H, s), 3.84 (3H, s), 7.52 (2H, dd, $J$ = 8.8 Hz), 7.95 (2H, t, $J$ = 8.4 and 6.8 Hz), 11.60 (NH) and 14.01(OH) (1H, s), 12.77 (1 COOH, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$: $\delta$ (ppm); 25.3, 30.5, 51.9, 52.2, 114.6, 115.7, 125.4, 127.2, 131.0, 132.9, 145.3, 146.0, 162.7, 164.4, 166.9, 193.7, 196.2; ESI-MS: *m/z* 287.0784 $[M+Na]^+$

**(E)-4-(2-(1-isobutoxy-1,3-dioxobutan-2-ylidene)hydrazinyl) benzoic acid (3c).** Yellow solid; Yield: 2.03 g; 91 %; m.p. 133-134 $^{o}$C; FT-IR (KBr, neat, cm$^{-1}$): 3434, 2962, 2668, 2547, 2361, 1690, 1528, 1430, 1293, 1224, 1193, 1162, 1090, 853, 768; $^{1}$H NMR (400 MHz, DMSO-$d_6$: $\delta$ (ppm) 0.94 (keto form) (6H, d, $J$ = 6.8 Hz), 0.98 (enol form) (6H, d, $J$ = 6.8 Hz), 1.94-2.00 (combined) (1H, s), 2.42 (3H, s), 4.02 (enol form) (2H, d, $J$ = 6.8 Hz), 4.07 (keto form) (2H, d, $J$ = 6.8 Hz), 7.49 (enol form) (2H, d, $J$ = 8.8 Hz), 7.85 (enol form) (2H, d, $J$ = 8.8 Hz), 7.95 (combined) (2H, dd, $J$ = 7.2 and 6.4 Hz), 11.61 (keto form) (1H, s, (NH)), 12.75 (combined)(1COOH, 1bs), 13.94 (enol form) (1H, s, (OH)); $^{13}$C NMR (100 MHz, DMSO-$d_6$: $\delta$ (ppm); 18.8, 18.9, 24.2, 25.3, 27.1, 27.4, 30.4, 36.2, 70.3, 70.9, 114.6, 115.5, 125.2, 126.7, 127.4, 130.9, 132.9, 145.5, 146.1, 162.3, 163.9, 166.7, 166.8, 193.7, 196.1; ESI-MS: *m/z* 329.5463 $[M+Na]^+$

**4-((Z)-((Z)-1-ethoxy-4,4,4-trifluoro-3-hydroxy-1-oxobut-2-en-2-yl) diazenyl)benzoic acid (3d).** Yellow solid; Yield: 2.18 g; 90 %; m.p. 211-212 $^{o}$C; FT-IR (KBr, neat, cm$^{-1}$): 3421, 2989, 2680, 2557, 2361, 1721, 1610, 1538, 1434, 1402, 1296, 1262, 1216, 1190, 1118, 1014, 905, 854, 801, 768, 724; $^{1}$H NMR (400 MHz, DMSO-$d_6$: $\delta$ (ppm) 1.32 (3H, t, $J$ = 6.8 and 7.2 Hz), 4.36 (2H, q, $J$ = 6.8 and 7.2 Hz), 7.62 (2H, d, $J$ = 8.4 Hz), 8.02 (2H, d, $J$ = 8.8 Hz), 12.86 (2H, bs, (1NH, 1COOH)); $^{13}$C NMR (100 MHz, DMSO-$d_6$: $\delta$ (ppm); 13.8, 61.7, 113.5, 116.3, 124.3, 127.7, 130.9, 131.1, 144.9, 160.8, 166.6; ESI-MS: *m/z* 355.5089 $[M+Na]^+$

**(E)-4-(2-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-ylidene) hydrazinyl)benzoic acid (3e).** Yellow solid; Yield: 2.21 g; 89 %; m.p. 214-215 $^{o}$C; FT-IR (KBr, neat, cm$^{-1}$): 3440, 3200, 3081, 2982, 2864, 2651, 2529, 1691, 1604, 1533, 1477, 1409, 1325, 1277, 1232, 1161, 902, 786, 771, 717, 692, 671; $^{1}$H NMR (400 MHz, DMSO-$d_6$: $\delta$ (ppm) 1.13 (keto form) (3H, t, $J$ = 6.8 and 7.2 Hz), 1.27 (enol form) (3H, t, $J$ = 7.2 Hz), 4.18 (keto form) (2H, q, $J$ = 6.8 and 7.2 Hz), 4.35 (enol form) (2H, q, $J$ = 6.8 and 7.2 Hz), 7.32 (2H, d, $J$ = 8.4Hz), 7.39 (1H, d, $J$ = 8.8 Hz), 7.54-7.60 (3H, m), 7.65-7.73 (2H, m), 7.82 (1H, d, $J$ = 7.2 Hz), 7.88-7.92 (5H, m), 11.52 (keto form) (1H, s, (NH)), 11.99 (enol form) (1H, s, (OH)), 12.70 (1COOH, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$: $\delta$ (ppm); 13.8, 13.9, 60.9, 61.4, 114.1, 114.6, 124.6, 125.7, 128.3, 128.4, 128.5, 129.0, 129.9, 130.6, 130.9, 131.0, 131.7, 132.8, 134.2, 135.7, 136.7, 146.0, 146.7, 162.1, 162.7, 166.8, 166.9, 188.8, 192.0; ESI-MS: *m/z* 363.1568 $[M+Na]^+$

**(E)-methyl 2-(4-(2-(1-ethoxy-1,3-dioxobutan-2-ylidene) hydrazineyl)benzamido)-3-methylpentanoate (1a).** Yellow solid; Yield: 0.19 g; 65 %; m.p. 111-112 $^{o}$C; FT-IR (KBr, neat, cm$^{-1}$): 3235, 2964, 2361, 1745, 1692, 1626, 1524, 1369, 1262, 1170, 1083, 855, 799; $^{1}$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 0.88-0.92 (6H, m), 1.16-1.24 (1H, m), 1.31-1.35 (3H, m), 1.44-1.49 (1H, m), 1.94-1.96 (1H, m), 2.43 (keto form) & 2.52 (enol form) (3H, s, $CH_3$), 3.71 (3H, s), 4.25-4.33 (2H, m), 4.71-4.76 (1H, m), 6.61 (1NH, d, $J$ = 8.0 Hz), 7.34 (2H, dd, $J$ = 8.4 Hz), 7.77 (2H, dd, $J$ = 4.4 Hz), 12.6 (keto form) & 14.56 (enol form) (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 10.6, 13.1, 13.3, 14.5, 24.5, 25.8, 29.7, 37.2, 51.1, 55.9, 60.1, 60.6, 114.1, 115.0, 126.2, 127.7, 127.7, 127.9, 129.0, 129.7, 143.4, 143.5, 162.5, 163.6, 165.2, 171.7, 171.7, 193.2, 196.2; ESI-MS: *m/z* 428.6332 $[M+Na]^+$

**(E)-methyl 2-(4-(2-(1-methoxy-1,3-dioxobutan-2-ylidene) hydrazinyl)benzamido)-3-methylpentanoate (1b).** Yellow solid; Yield: 0.17 g; 58 %; m.p. 115-116 $^{o}$C; FT-IR (KBr, neat, cm$^{-1}$): 3228, 3041, 2958, 2877, 2361, 1747, 1692, 1628, 1527, 1436, 1356, 1307, 1224, 1173, 949, 857, 772; $^{1}$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 0.92-1.00 (6H, m), 1.24-1.32 (1H, m), 1.52-1.58 (1H, m), 1.99-2.06 (1H, m), 2.51 (keto form) & 2.60 (enol form) (3H, s, $CH_3$), 3.78 (3H, s), 3.90 (3H, s), 4.79-4.83 (1H, m), 6.82 (1NH, d, $J$ = 8.4 Hz), 7.41 (2H, dd, $J$ = 8.4 Hz), 7.85 (2H, t, $J$ = 7.6 & 8.4 Hz), 12.73 (keto form) & 14.67 (enol form) (1H,

s); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 11.2, 15.2, 25.2, 26.4, 30.4, 37.0, 51.8, 51.8, 56.7, 114.8, 115.7, 126.4, 127.8, 128.5, 128.6, 129.8, 130.5, 143.9, 144.0, 163.5, 164.7, 166.1, 172.4, 172.4, 193.9, 196.8; ESI-MS: *m/z* 414.6075 $[M+Na]^+$

**(E)-methyl 2-(4-(2-(1-isobutoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benz-amido)-3-methylpentano-ate (1c).** Yellow brown semi solid; Yield: 0.17 g; 59 %; FT-IR (KBr, neat, $cm^{-1}$): 3306, 2963, 2930, 2876, 1742, 1693, 1638, 1610, 1524, 1306, 1268, 1223, 1085, 849; $^1$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 0.83-1.11 (12H, m), 1.21-1.33 (2H, m), 1.51-1.75 (2H, m), 1.98-2.13 (2H, m), 2.51 (keto form) & 2.61 (enol form) (3H, s, $CH_3$), 3.78 (3H, s), 4.09 (2H, q, *J* = 6.8 Hz), 4.82 (1H, q, *J* = 5.2 Hz), 6.66 (1NH, d, *J* = 8.4 Hz), 7.41 (2H, dd, *J* = 8.4 Hz), 7.85 (2H, dd, *J* = 3.2 & 3.6 Hz), 12.67 (keto form) & 14.63 (enol form) (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 10.6, 14.5, 18.1, 18.2, 24.4, 25.8, 26.7, 26.9, 29.7, 37.3, 51.2, 55.8, 70.1, 70.5, 114.1, 114.9, 126.1, 127.7, 127.8, 127.9, 129.0, 129.7, 143.4, 143.5, 162.5, 163.7, 165.2, 165.2, 171.7, 171.7, 193.1, 196.3; ESI-MS: *m/z* 456.5388 $[M+Na]^+$

**Methyl 2-(4-((E)-((E)-1-ethoxy-4,4,4-trifluoro-3-hydroxy-1-oxobut-2-en-2-yl)diazenyl)benzamido)-3-methylpentan-oate (1d).** Yellow solid; Yield: 0.17 g; 62 %; m.p. 100-101 $^oC$; FT-IR (KBr, neat, $cm^{-1}$): 3313, 3173, 2962, 2877, 2361, 1744, 1720, 1685, 1635, 1531, 1505, 1250, 1212, 1151, 1031, 908, 853, 808; $^1$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 0.92-0.99 (6H, m), 1.24-1.31 (1H, m), 1.43 (3H, t, *J* = 7.2 Hz), 1.50-1.57 (1H, m), 1.99-2.05 (1H, m), 3.78 (3H, s), 4.42 (2H, q, *J* = 7.2 Hz), 4.82 (1H, q, *J* = 4.8 Hz), 6.67 (1NH, d, *J* = 8.4 Hz), 7.46 (2H, d, *J* = 8.8 Hz), 7.89 (2H, d, *J* = 8.8 Hz), 13.42 (enol form) (1OH, s); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 10.6, 13.0, 14.5, 24.4, 37.2, 51.2, 55.9, 61.2, 114.5, 115.3, 117.4, 121.5, 128.0, 130.8, 142.4, 162.3, 164.3, 164.9, 171.6, 173.4, 173.8; ESI-MS: *m/z* 482.2170 $[M+Na]^+$ , *m/z* 492.0632 $[M+H+MeOH]^+$

**(E)-Methyl 2-(4-(2-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-ylidene)hydrazinyl)benz-amido)-3-methylpentanoate (1e).** Yellow brown semi solid; Yield: 0.18 g; 64 %; FT-IR (KBr, neat, $cm^{-1}$): 3350, 2965, 2877, 2361, 1741, 1657, 1610, 1528, 1328, 1303, 1230, 1174, 1017, 904, 850, 765, 717, 670; $^1$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 0.93-0.99 (6H, m), 1.25-1.27 (1H, m), 1.34 (3H, t, *J* = 7.2 Hz), 1.48-1.59 (1H, m), 1.99-2.00 (1H, m), 3.76 (3H, s), 4.36 (2H, q, *J* = 7.2 Hz), 4.79 (1H, q, *J* = 4.8 & 5.2 Hz), 6.69 (1NH, d, *J* = 8.4 Hz), 7.20 (2H, d, *J* = 8.4 Hz), 7.44-7.59 (3H, m), 7.58 (2H, d, *J* = 7.2 Hz), 7.93 (2H, t, *J* = 7.6 Hz), 12.67 (keto form) & 13.25 (enol form) (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 11.3, 13.8, 13.8, 15.3, 25.2, 37.9, 51.9, 56.7, 61.3, 61.4, 114.7, 114.9, 127.9, 127.9, 128.6, 129.3, 130.1, 132.5, 137.1, 137.6, 144.3, 144.4, 163.3, 164.2, 166.1, 172.5, 189.0, 191.2; ESI-MS: *m/z* 490.2157 $[M+Na]^+$

**(E)-Ethyl 2-(2-(4-(1-methoxy-1-oxo-3-phenylpropan-2-ylcarbamoyl)phenyl)hydraz-ono)-3-oxobutanoate (1f).** Yellow brown semi solid; Yield: 0.19 g; 60 %; FT-IR (KBr, neat, $cm^{-1}$): 3364, 2985, 2953, 2361, 1744, 1689, 1639, 1609, 1523, 1365, 1304, 1221, 1170, 1082, 1017, 851, 765, 701; $^1$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 1.37-1.42 (3H, m), 2.50 (keto form) and 2.59 (enol form) (3H, s), 3.20-3.32 (2H, m), 3.76 (3H, s), 4.32-4.40 (2H, m), 5.06-5.11 (1H, m), 6.65 (1NH, d, *J* = 7.2 Hz), 7.14 (2H, d, *J* = 6.4 Hz), 7.23-7.42 (5H, m), 7.76 (2H, dd, *J* = 5.2 & 5.6 Hz), 12.68 (keto form) & 14.61 (enol form) (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 14.0, 14.2, 26.7, 30.7, 37.8, 52.3, 53.5, 61.1, 61.6, 115.1, 115.9, 127.1, 128.5, 128.6, 128.6, 128.7, 129.2, 129.7, 130.4, 135.8, 144.3, 144.4, 163.4, 164.5, 165.9, 172.0, 172.0, 194.2, 197.2; ESI-MS: *m/z* 462.1385 $[M+Na]^+$

**(E)-Methyl 2-(2-(4-(1-methoxy-1-oxo-3-phenyl propan-2-ylcarbamoyl)phenyl)hydrazono)-3-oxobutanoate (1g).** Yellow brown semi solid; Yield: 0.19 g; 58 %; FT-IR (KBr, neat, $cm^{-1}$): 3364, 3028, 2953, 2361, 1736, 1688, 1639, 1610, 1510, 1436, 1360, 1307, 1222, 1170, 1086, 849, 751, 701; $^1$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 2.51 & 2.61 (3H, s), 3.24-3.29 (2H, m), 3.77 & 3.78 (3H, s), 3.89, 3.92 & 3.95 (3H, s), 5.07-5.10 (1H, m), 6.55 (1NH, d, *J* = 7.6 Hz), 7.13 (2H, d, *J* = 7.2 Hz), 7.24-7.45 (4H, m), 7.71-7.78 (2H, m), 12.74 (keto form) & 14.67 (enol form) (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 26.7, 30.7, 37.8, 52.1, 52.2, 52.4, 53.5, 114.2, 115.2, 116.1, 117.3, 126.8, 127.1, 128.1, 128.2, 128.6, 128.6, 128.7, 128.8, 129.2, 129.9, 130.5, 135.8, 135.9, 144.2, 144.3, 144.4, 159.8, 163.9, 165.0, 165.9, 166.1, 172.0, 172.1, 194.3; ESI-MS: *m/z* 448.1696 $[M+Na]^+$

**(E)-Isobutyl 2-(2-(4-(1-methoxy-1-oxo-3-phenylpropan-2-ylcarbamoyl)phenyl)hydrazono)-3-oxobutanoate (1h).** Yellow brown semi solid; Yield: 0.17 g; 55 %; FT-IR (KBr, neat, $cm^{-1}$): 3376, 3029, 2959, 2360, 1745, 1693, 1638, 1509, 1360, 1221, 1170, 1083, 849, 766, 700; $^1$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 1.03 (6H, q, *J* = 6.8 Hz), 2.04-2.10 (1H, m), 2.50 (keto) & 2.60 (enol) (3H, s), 3.20-3.32 (2H, m), 3.77 (3H, d, *J* = 1.6 Hz), 4.08 (2H, t, *J* = 6.8 Hz), 5.06-5.11 (1H, m), 6.61 (1NH, d, *J* = 7.6 Hz), 7.14 (2H, t, *J* = 4.4 & 2.4 Hz), 7.23-7.43 (5H, m), 7.76 (2H, dd, *J* = 2.4 & 2.0 Hz), 12.65 (keto form) & 14.60 (enol form) (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 14.1, 14.5, 17.2, 18.9, 19.1, 20.9, 23.3, 23.8, 24.6, 26.7, 27.6, 27.8, 28.4, 30.6, 36.6, 37.8, 52.3, 53.5, 60.2, 71.0, 71.4, 115.0, 115.8, 127.0, 127.1, 128.5, 128.6, 128.7, 129.2, 129.6, 130.3, 135.8, 144.3, 144.5, 163.3, 164.6, 165.9, 165.9, 171.0, 172.0, 172.1, 194.0, 197.1; ESI-MS: *m/z* 490.2568 $[M+Na]^+$

**(E)-Ethyl 4,4,4-trifluoro-3-hydroxy-2-((E)-(4-(1-methoxy-1-oxo-3-phenylpropan-2-ylcarbamoyl)phenyl)diazenyl)but-2-enoate (1i).** Yellow solid; Yield: 0.19 g; 65 %; m.p. 137-138 $^oC$; FT-IR (KBr, neat, $cm^{-1}$): 3316, 3166, 3032, 2361, 1753, 1719, 1635, 1530, 1251, 1173, 1155, 906, 855, 810, 771, 699; $^1$H NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 1.41 (3H, t, *J* = 7.2 Hz), 3.19-3.32 (2H, m), 3.77 (3H, s), 4.41 (2H, q, *J* = 6.8 & 7.2 Hz), 5.08 (1H, q, *J* = 6.0 Hz), 6.69 (1NH, d, *J* = 8.4 Hz), 7.14 (2H, d, *J* = 6.8 Hz), 7.24-7.43 (3H, m), 7.42 (2H, d, *J* = 8.4 Hz), 7.79 (2H, d, *J* = 8.8 Hz), 13.39 (enol form) (1OH, s); $^{13}$C NMR (100 MHz,

$CDCl_3$: $\delta$ (ppm) 13.8, 37.7, 52.3, 53.6, 62.0, 115.4, 116.2, 118.3, 122.4, 127.1, 128.5, 128.8, 129.2, 131.4, 135.8, 143.3, 163.1, 165.7, 172.0; ESI-MS: *m/z* 516.1593 $[M+Na]^+$ , *m/z* 526.1326 $[M+H+MeOH]^+$

**(E)-Ethyl 2-(2-(4-(1-methoxy-1-oxo-3-phenylpro-pan-2-ylcarbamoyl)phenyl)hydrazono)-3-oxo-3-phenylpropanoate (1j).** Yellow brown semi solid; Yield: 0.18 g; 61 %; FT-IR (KBr, neat, $cm^{-1}$): 3364, 3022, 2952, 2360, 1744, 1653, 1609, 1526, 1230, 1173, 1016, 904, 849, 764, 699; $^1H$ NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 1.33 (3H, t, *J* = 7.2 Hz), 3.17-3.29 (2H, m), 3.74 (3H, s), 4.35 (2H, q, *J* = 7.2 Hz), 5.05 (1H, q, J = 5.6 & 6.0 Hz), 6.61 (1NH, d, *J* = 7.2 Hz), 7.11-7.29 (8H, m), 7.41-7.76 (5H, m), 7.93 (2H, t, *J* = 8.8 Hz), 12.66 (keto form) & 13.26 (enol form) (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 13.9, 37.8, 52.3, 53.6, 61.6, 114.8, 127.1, 128.1, 128.1, 128.3, 128.5, 128.7, 129.2, 129.2, 130.2, 132.7, 136.0, 137.2, 144.6, 163.5, 166.0, 172.1, 189.2; ESI-MS: *m/z* 524.1378 $[M+Na]^+$

**(E)-dimethyl 2-(4-(2-(1-ethoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benzamido)succinate (1k).** Yellow solid; Yield: 0.2 g; 67 %; m.p. 117-118 $^oC$; FT-IR (KBr, neat, $cm^{-1}$): 3287, 3096, 2985, 2952, 2361, 1730, 1633, 1520, 1437, 1368, 1306, 1268, 1167, 1088, 1014, 850, 768, 679; $^1H$ NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 1.32 (3H, q, *J* = 6.8 Hz), 2.43 (keto) & 2.52 (enol) (3H, s), 2.88-3.09 (2H, m), 3.63 (3H, s), 3.72 (3H, s), 4.25-4.32 (2H, m), 4.99 (1H, t, *J* = 4.8 & 2.8 Hz), 7.22 (2H, q, *J* = 4.8 & 1.2 Hz), 7.30 (2H, d, *J* = 8.8 Hz), 7.37 (1H, d, *J* = 8.8 Hz), 7.72-780 (2H, m), 12.61 (keto) & 14.53 (enol form) (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 13.1, 13.2, 13.3, 25.8, 29.7, 35.1, 35.1, 48.0, 48.0, 51.1, 51.8, 51.9, 60.2, 60.6, 61.9, 113.2, 114.1, 115.0, 116.5, 126.2, 126.8, 127.7, 127.9, 127.9, 128.0, 128.5, 129.2, 143.5, 143.6, 143.8, 158.5, 162.4, 163.6, 165.1, 170.3, 170.4, 170.7, 193.3, 196.2; ESI-MS: *m/z* 444.2162 $[M+Na]^+$

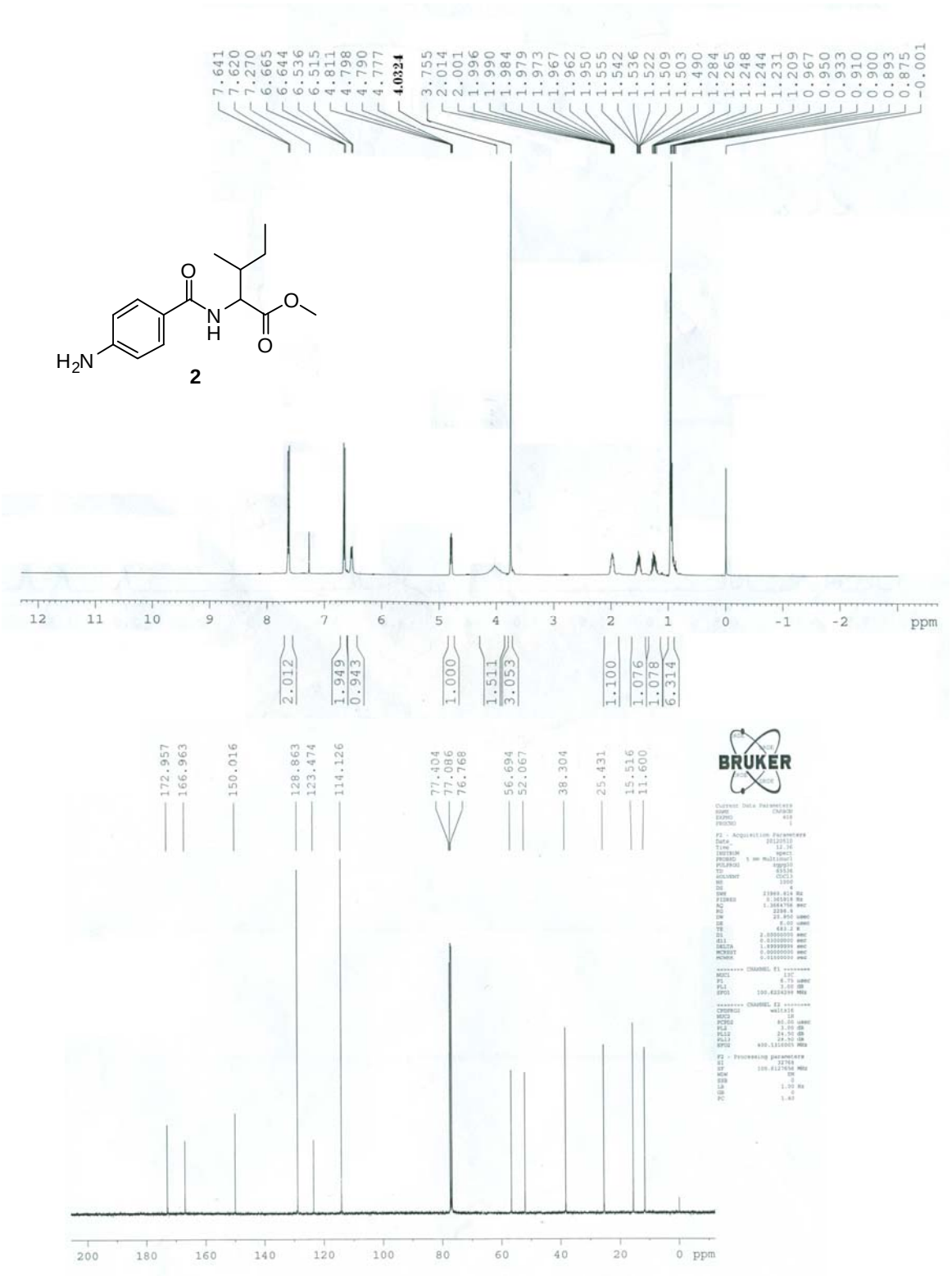
**(E)-Dimethyl 2-(4-(2-(1-methoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benzamido)succinate (1l).** Yellow semi solid; Yield: 0.19 g; 60 %; FT-IR (KBr, neat, $cm^{-1}$): 3284, 3002, 2954, 2361, 1739, 1639, 1525, 1436, 1333, 1305, 1205, 1169, 1083, 1009, 850, 767; $^1H$ NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 2.43 (keto) & 2.52 (enol) (3H, s), 2.88-3.08 (2H, m), 3.63 (3H, s), 3.72 (3H, s), 3.82 (3H, s), 4.97-5.00 (1H, m), 6.84 (1H, d, *J* = 8.0 Hz), 7.23-7.39 (3H, m), 7.78 (1H, t, *J* = 8.4 Hz), 12.65 (keto) & 14.58 (enol form) (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 25.7, 29.7, 35.1, 48.0, 51.0, 51.2, 51.2, 51.8, 51.9, 52.1, 52.6, 113.3, 114.3, 114.5, 115.1, 116.0, 123.8, 125.8, 126.7, 127.2, 127.9, 128.0, 128.2, 128.6, 129.2, 143.4, 143.5, 143.9, 159.0, 159.6, 162.8, 164.0, 165.2, 165.4, 165.8, 169.4, 170.3, 170.4, 170.5, 170.6, 170.6, 170.7, 193.4, 196.2; ESI-MS: *m/z* 430.1750 $[M+Na]^+$

**(E)-Dimethyl 2-(4-(2-(1-isobutoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benzamido)succinate (1m).** Yellow semi solid; Yield: 0.17 g; 59 %; FT-IR (KBr, neat, $cm^{-1}$): 3296, 2962, 2361, 1734, 1637, 1525, 1438, 1304, 1262, 1171, 1086, 1020, 850, 801, 766, 671; $^1H$ NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 0.92-0.97 (6H, m), 1.98-2.00 (1H, m), 2.42 (keto, d, *J* = 2.0 Hz) & 2.51 (enol, t, *J* = 2.4 Hz) (3H combined), 2.92 (1H, dd, *J* = 2.0 Hz), 3.04 (1H, dd, *J* = 3.6 Hz), 3.62 (3H, s), 3.71 (3H, s), 3.98-4.02 (2H, m), 4.98 (1H, t, *J* = 3.6 & 2.8 Hz), 7.28-7.37 (2H, m), 7.76-7.79 (2H, m), 12.55 (keto) & 14.51 (enol form) (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 18.0, 18.2, 25.7, 26.7, 26.9, 29.6, 35.1, 48.1, 51.0, 51.8, 70.1, 70.4, 114.1, 114.9, 126.1, 127.8, 127.9, 128.0, 128.4, 129.2, 143.5, 143.7, 162.4, 163.6, 165.1, 170.3, 170.3, 170.6, 193.0, 196.1; ESI-MS: *m/z* 472.3123 $[M+Na]^+$

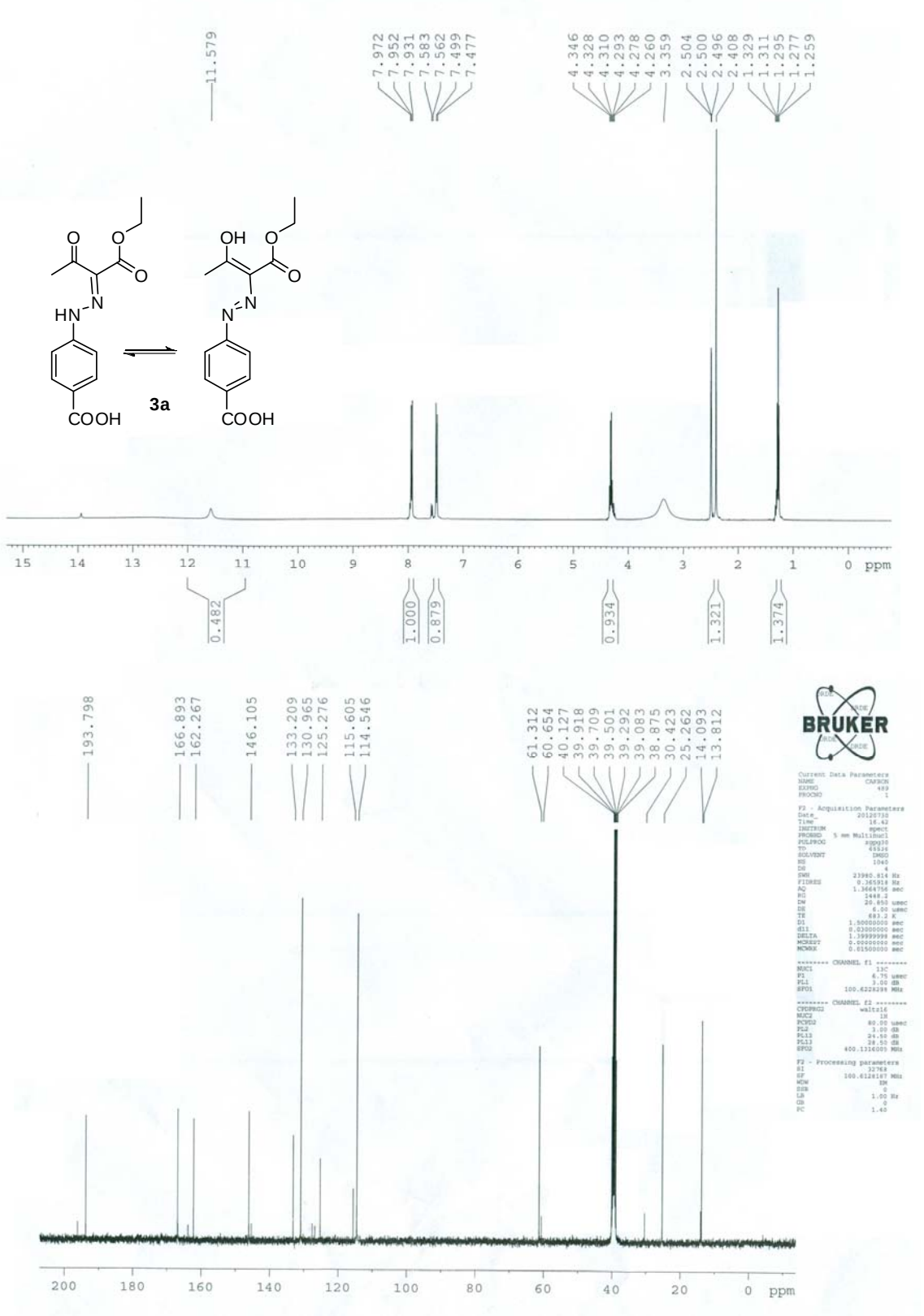
**Dimethyl 2-(4-((E)-((E)-1-ethoxy-4,4,4-trifluoro-3-hydroxy-1-oxobut-2-en-2-yl)diazenyl)benzamido)succinate (1n).** Yellow solid; Yield: 0.17 g; 58 %; m.p. 121-122 $^oC$; FT-IR (KBr, neat, $cm^{-1}$): 3331, 3164, 2960, 2360, 1743, 1642, 1527, 1443, 1353, 1247, 1050, 1018, 913, 855, 805, 768, 726, 640; $^1H$ NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 1.43 (3H, t, *J* = 6.8 & 7.2 Hz), 2.98 (1H, dd, *J* = 4.4 Hz), 3.15 (1H, dd, *J* = 4.4 Hz), 3.72 (3H, s), 3.81 (3H, s), 4.43 (2H, q, *J* = 7.2 Hz), 5.04-5.08 (1H, m), 7.23 (1NH, d, *J* = 7.6 Hz), 7.47 (2H, d, *J* = 8.8 Hz), 7.91 (2H, d, *J* = 8.8 Hz), 13.42 (enol form) (1OH, s); $^{13}C$ NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 14.1, 36.1, 49.1, 52.2, 53.0, 62.3, 116.4, 122.6, 129.2, 131.3, 143.6, 163.4, 165.9, 171.2, 171.8; ESI-MS: *m/z* 498.3548 $[M+Na]^+$ , *m/z* 508.2682 $[M+H+MeOH]^+$

**(E)-Dimethyl 2-(4-(2-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-ylidene)hydrazinyl)benzamido)succi-nate (1o).** Yellow brown semi solid; Yield: 0.18 g; 60 %; FT-IR (KBr, neat, $cm^{-1}$): 3381, 2954, 2926, 2360, 1741, 1659, 1609, 1529, 1439, 1231, 1174, 1017, 903, 851, 765, 718, 693, 669; $^1H$ NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 1.35 (3H, t, *J* = 7.2 Hz), 2.97 (1H, dd, *J* = 4.8 & 4.4 Hz), 3.13 (1H, dd, *J* = 4.0 & 4.4 Hz), 3.70 (3H, s), 3.79 (3H, s), 4.38 (2H, q, *J* = 7.2 Hz), 5.02-5.07 (1H, m), 7.15 (1NH, d, *J* = 8.0 Hz), 7.21 (2H, d, *J* = 8.8 Hz), 7.46-7.68 (3H, m), 7.78 (2H, d, *J* = 8.4 Hz), 7.94 (2H, d, *J* = 8.4 Hz), 12.68 (keto form) & 13.35 (enol form) (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$: $\delta$ (ppm) 13.9, 36.0, 48.9, 52.0, 52.8, 61.6, 114.9, 115.6, 127.8, 128.1, 128.1, 128.3, 128.9, 130.3, 132.7, 137.2, 144.8, 163.6, 166.0, 171.2, 171.7, 189.2, ; ESI-MS: *m/z* 506.4102 $[M+Na]^+$

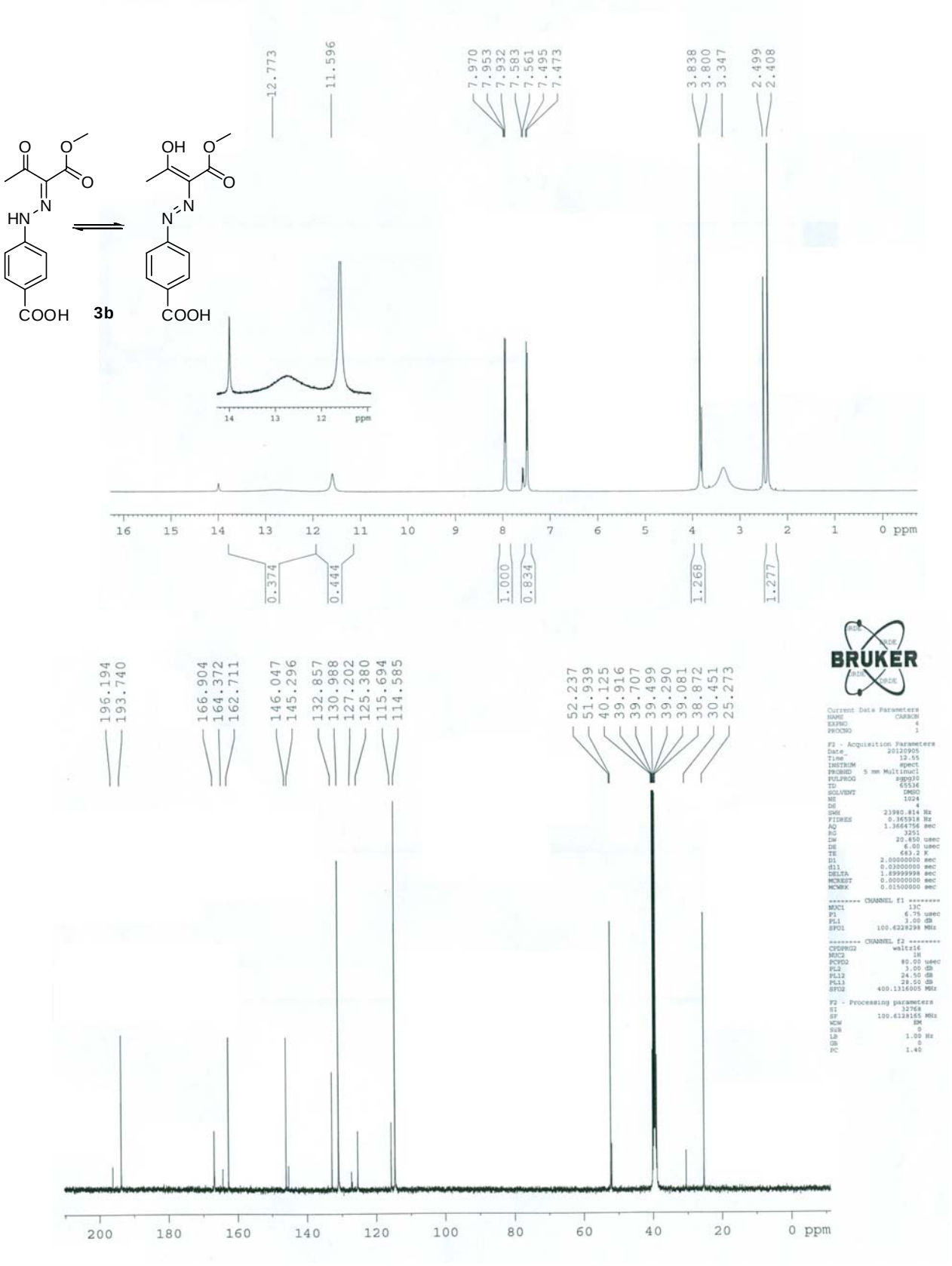
**$^{1}$H & $^{13}$C-NMR of Methyl 2-(4-aminobenzamido)-3-methylpentanoate (2):**



**$^{1}$H & $^{13}$C-NMR of (E)-4-(2-(1-ethoxy-1,3-dioxobutan-2-ylidene)hydrazinyl) benzoic acid (3a)**

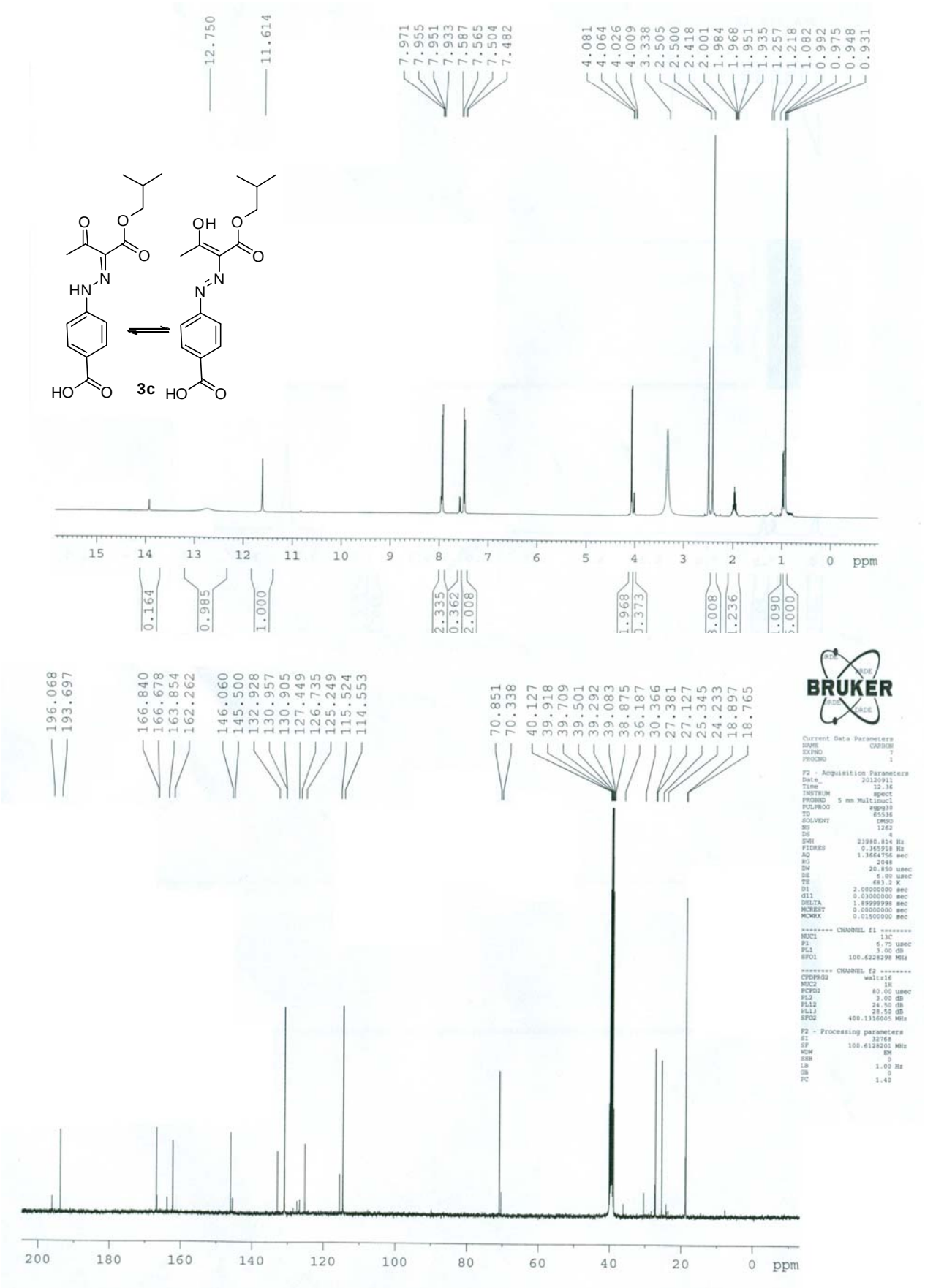


**$^{1}$H & $^{13}$C-NMR of (E)-4-(2-(1-methoxy-1,3-dioxobutan-2-ylidene) hydrazinyl)benzoic acid (3b)**

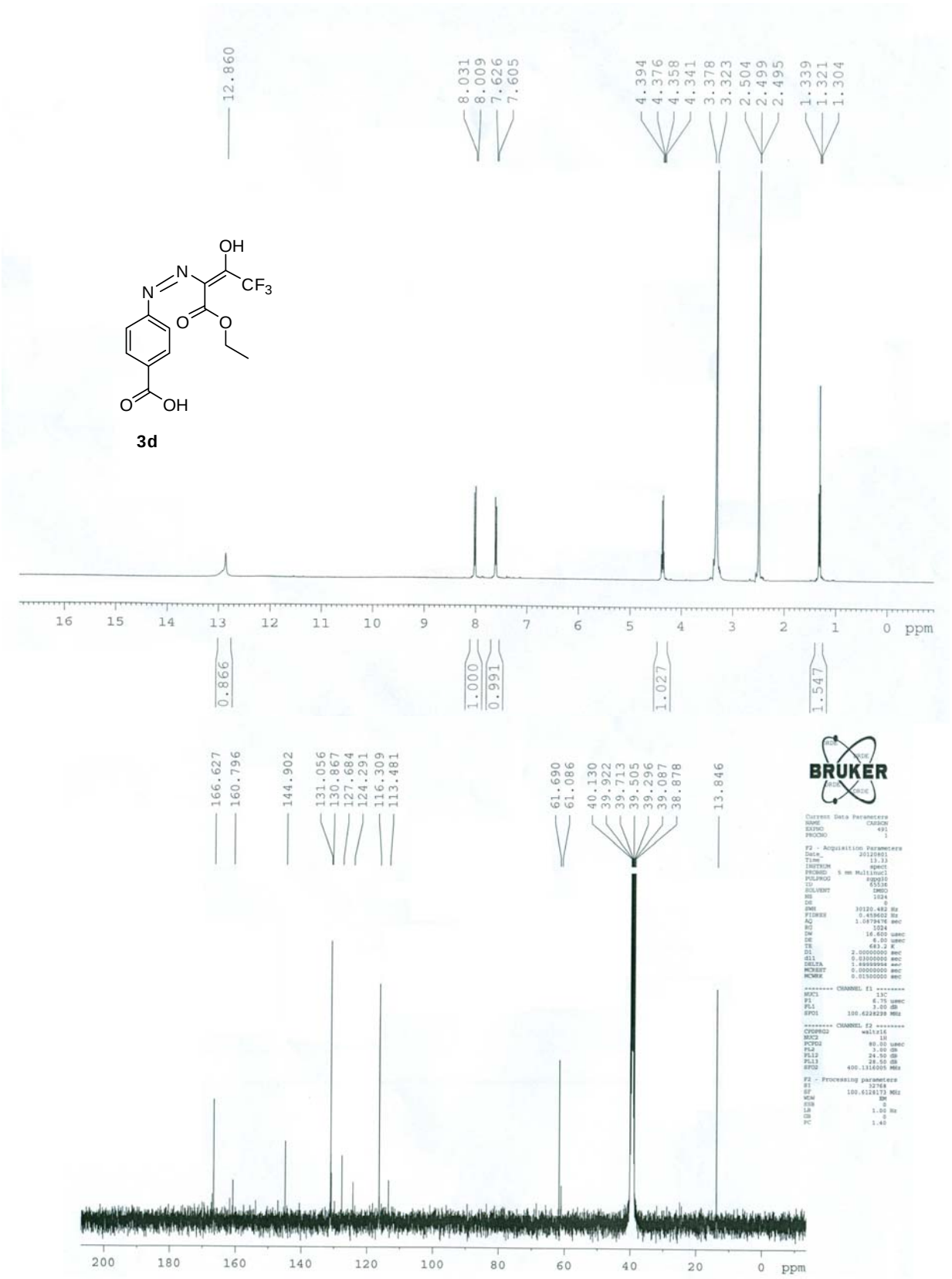



3b

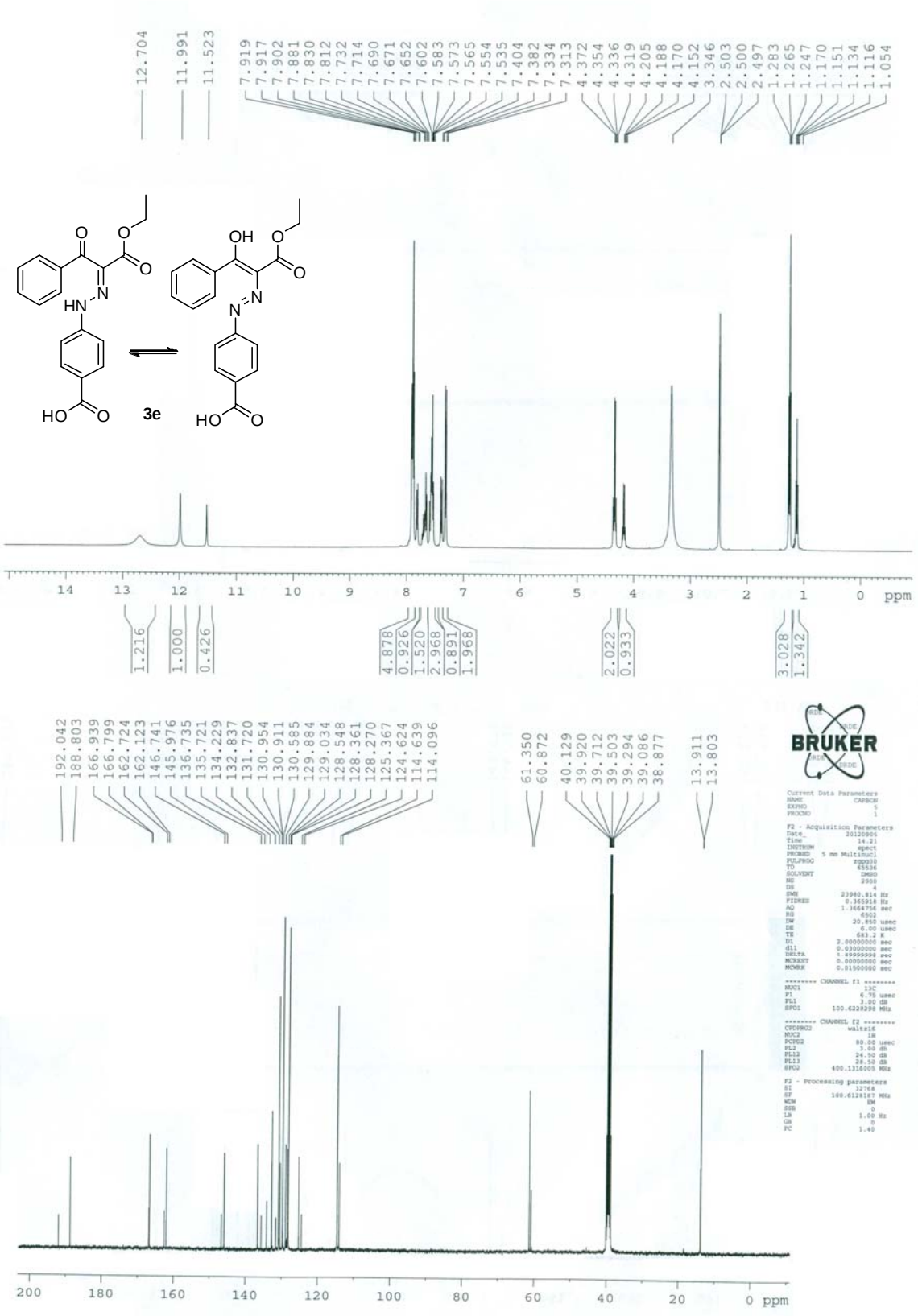
**$^{1}$H & $^{13}$C-NMR of (E)-4-(2-(1-isobutoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benzoic acid (3c)**



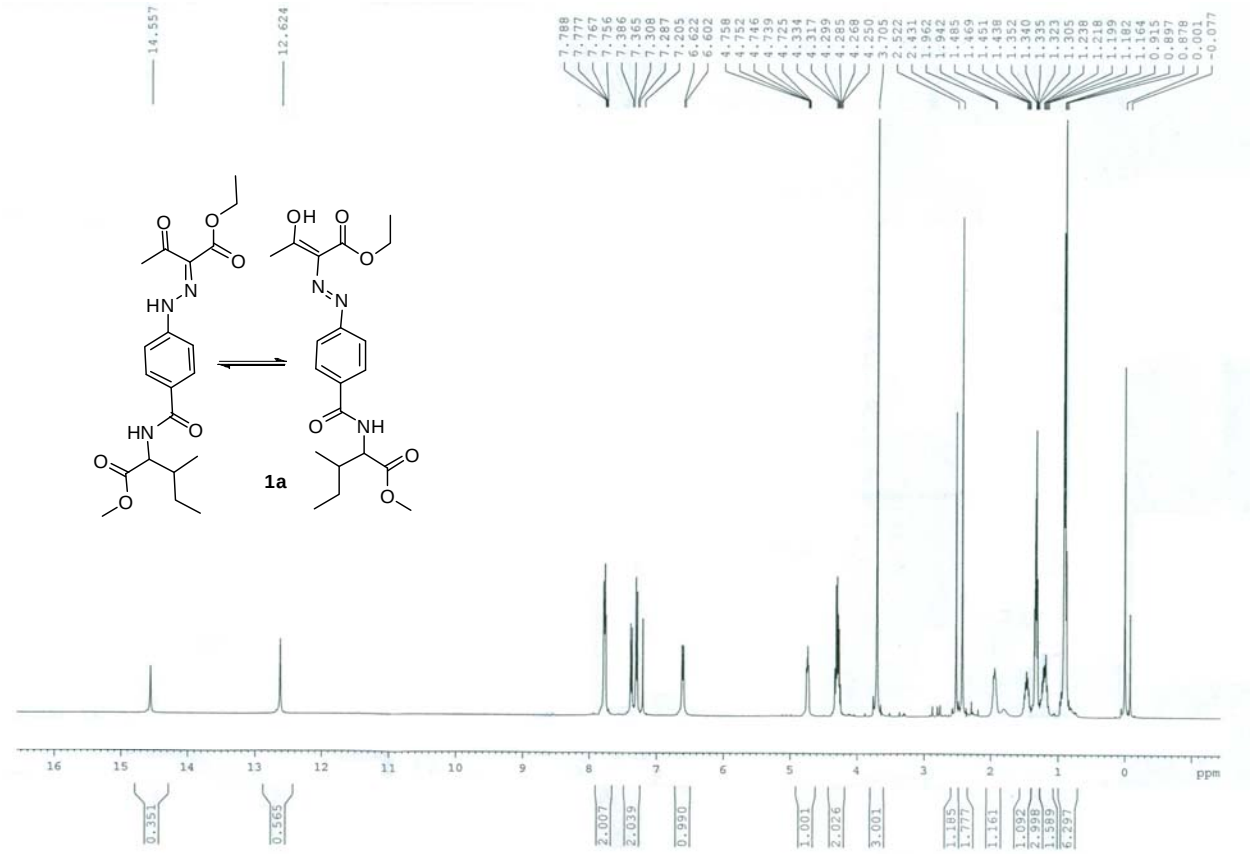
**$^{1}$H & $^{13}$C-NMR of 4-((Z)-((Z)-1-ethoxy-4,4,4-trifluoro-3-hydroxy-1-oxobut-2-en-2-yl) diazenyl)benzoic acid (3d)**

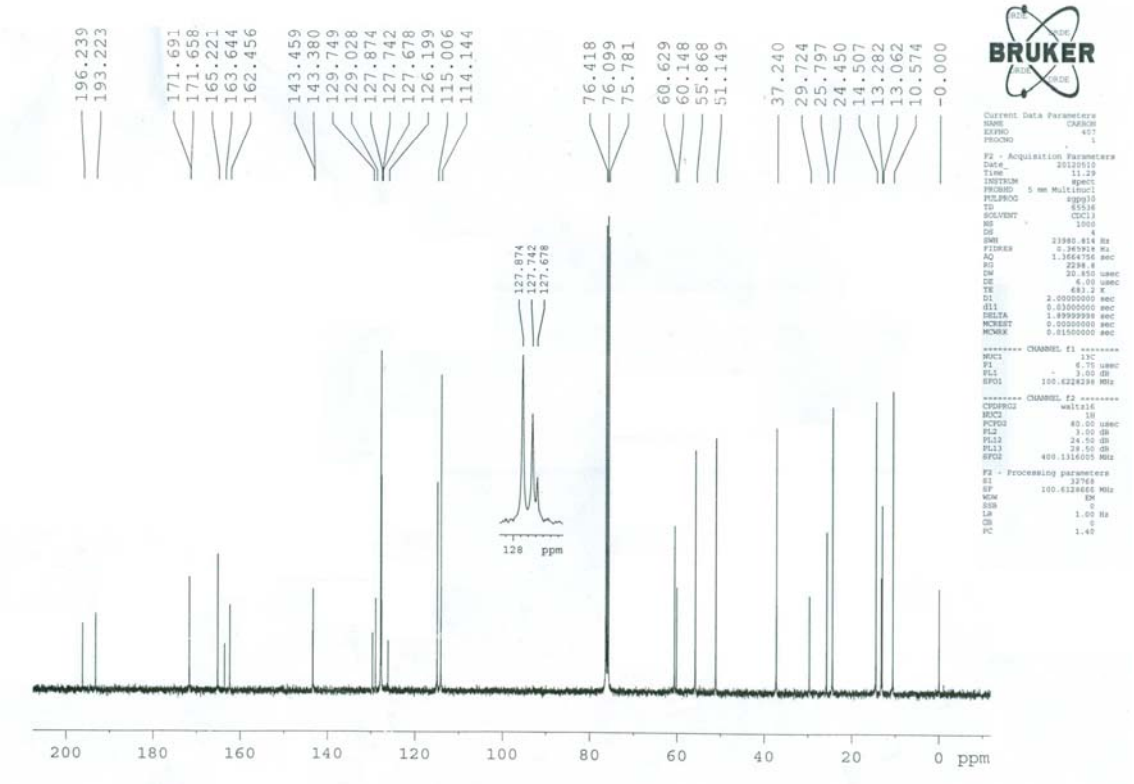


**(E)-4-(2-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-ylidene)hydrazinyl)benzoic acid (3e)**

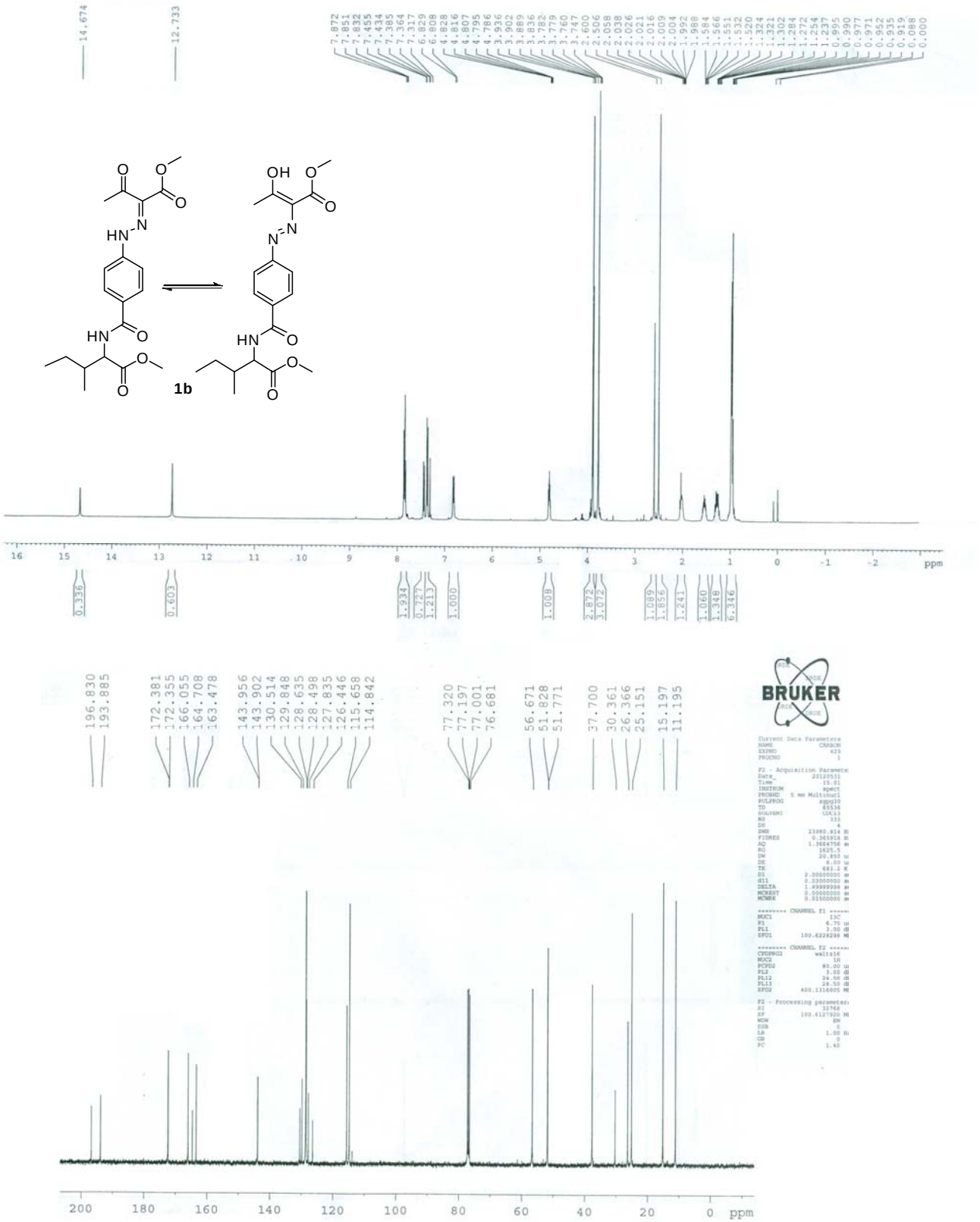


**(E)-Methyl 2-(4-(2-(1-ethoxy-1,3-dioxobut-an-2-ylidene)hydrazinyl)benzamido) -3-methylpentanoate (1a)**

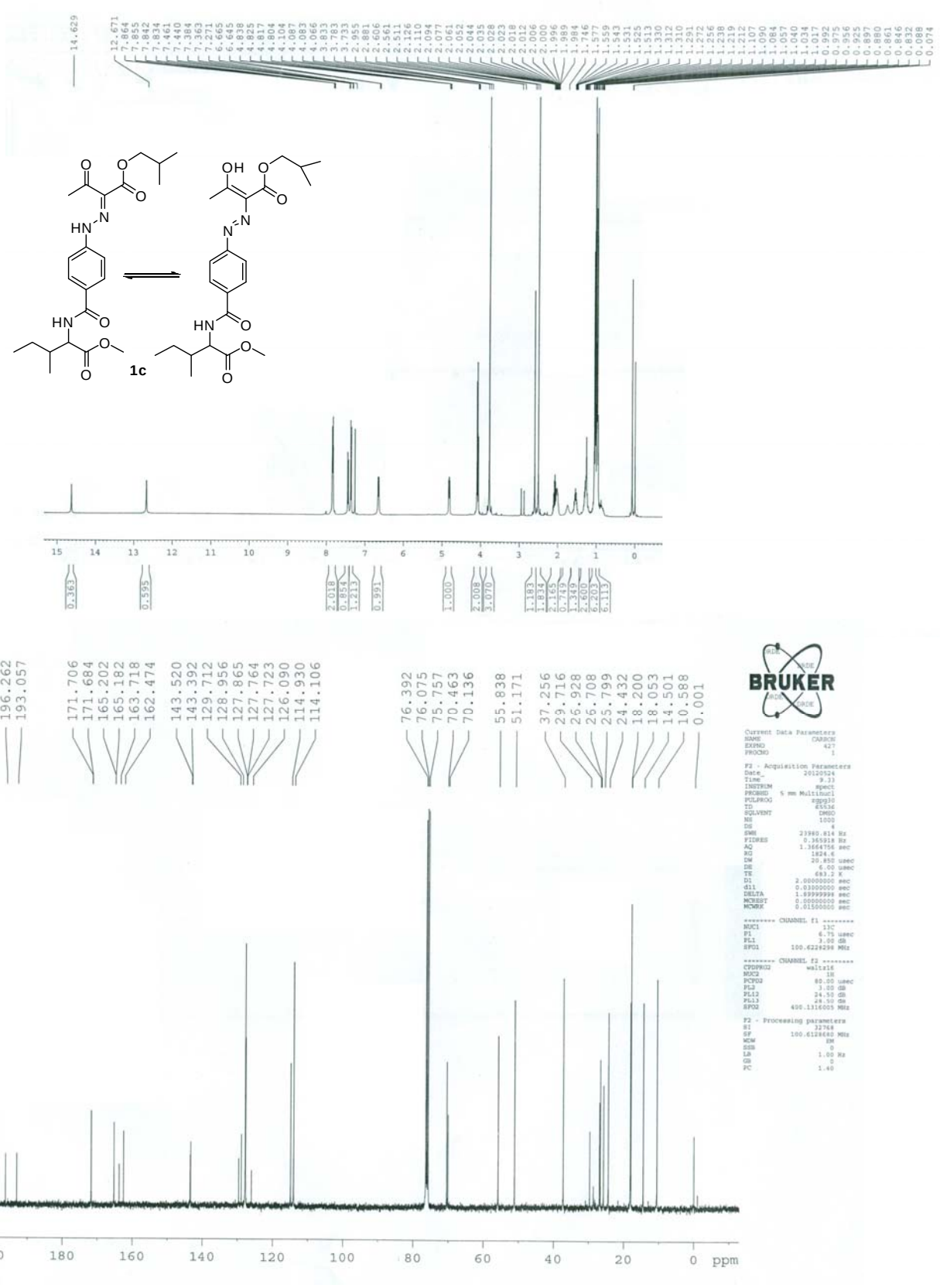


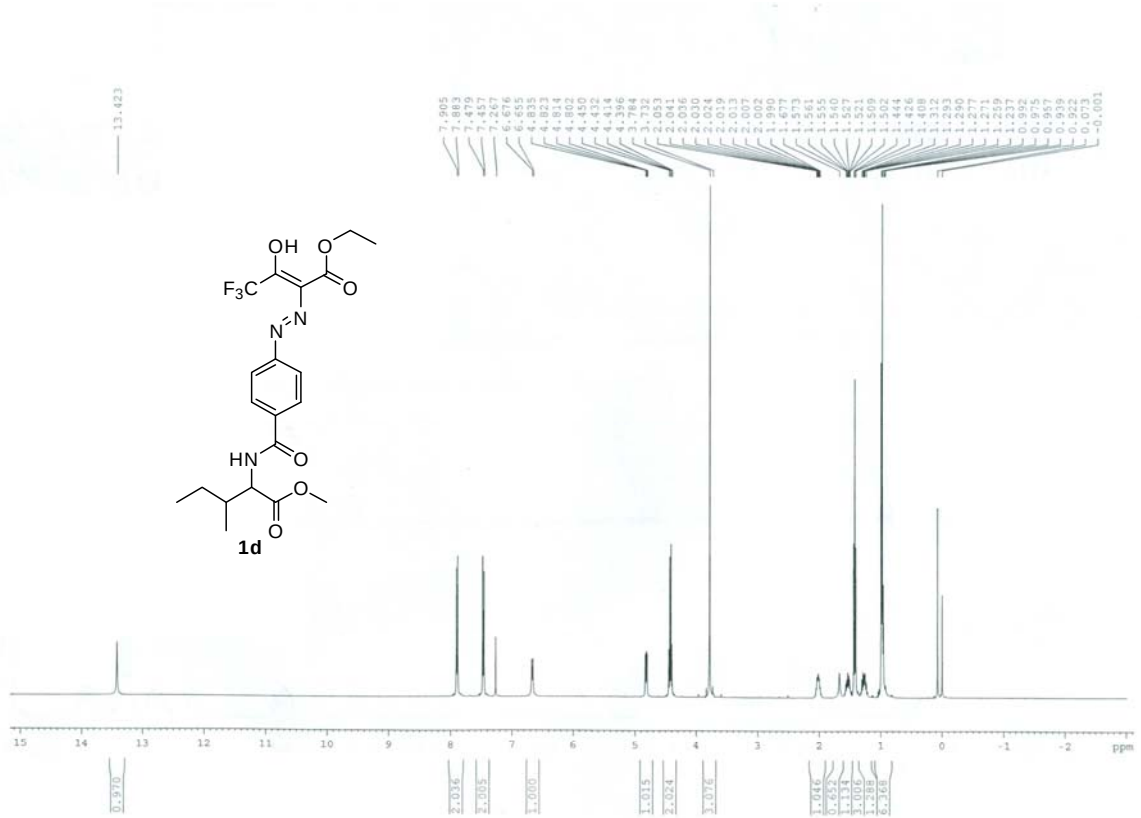
**(E)-Methyl 2-(4-(2-(1-methoxy-1,3-dioxobutan-2-ylidene)hydrazinyl) benzamido)-3-methylpentanoate (1b)**

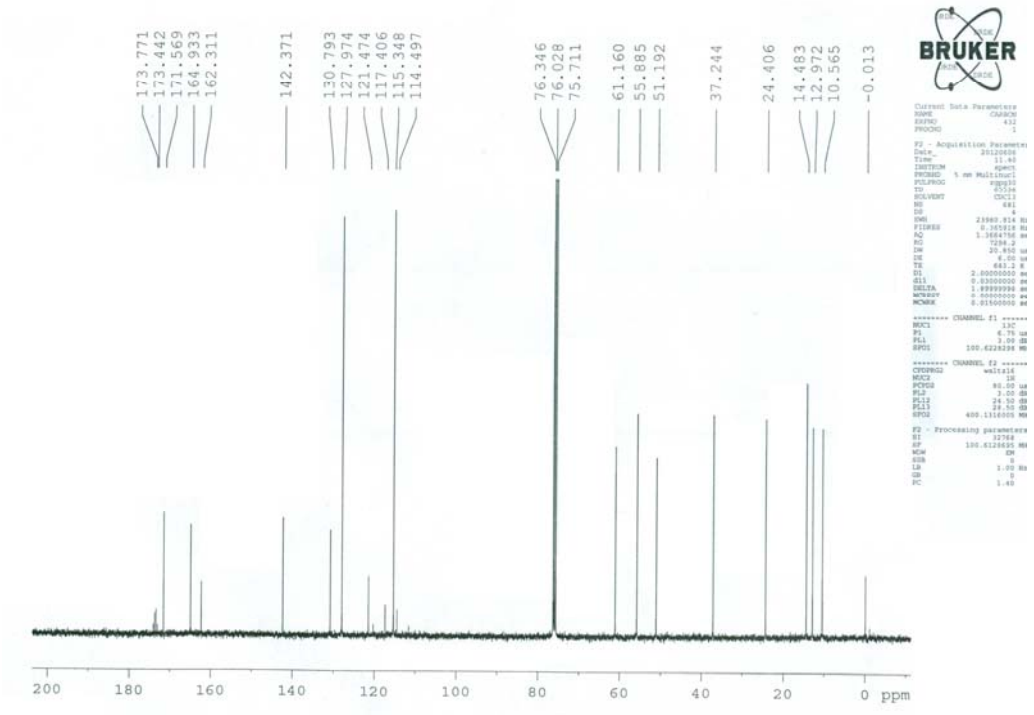


**(E)-Methyl 2-(4-(2-(1-isobutoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benzamido)-3-methylpentanoate (1c)**

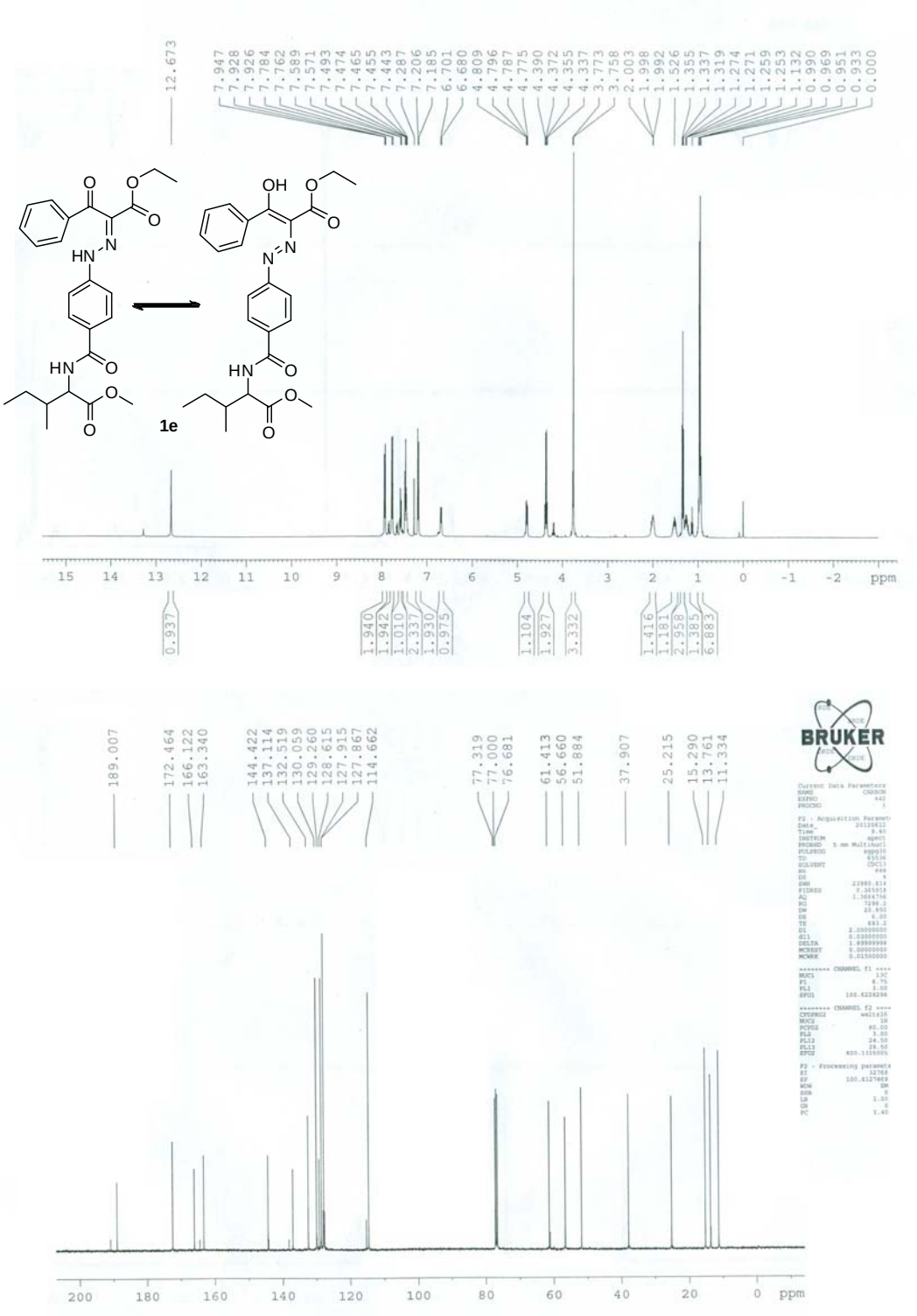


**Methyl 2-(4-((E)-((E)-1-ethoxy-4,4,4-trifluoro-3-hydroxy-1-oxobut-2-en-2-yl)diazenyl)benzamido)-3-methylpentanoate (1d)**

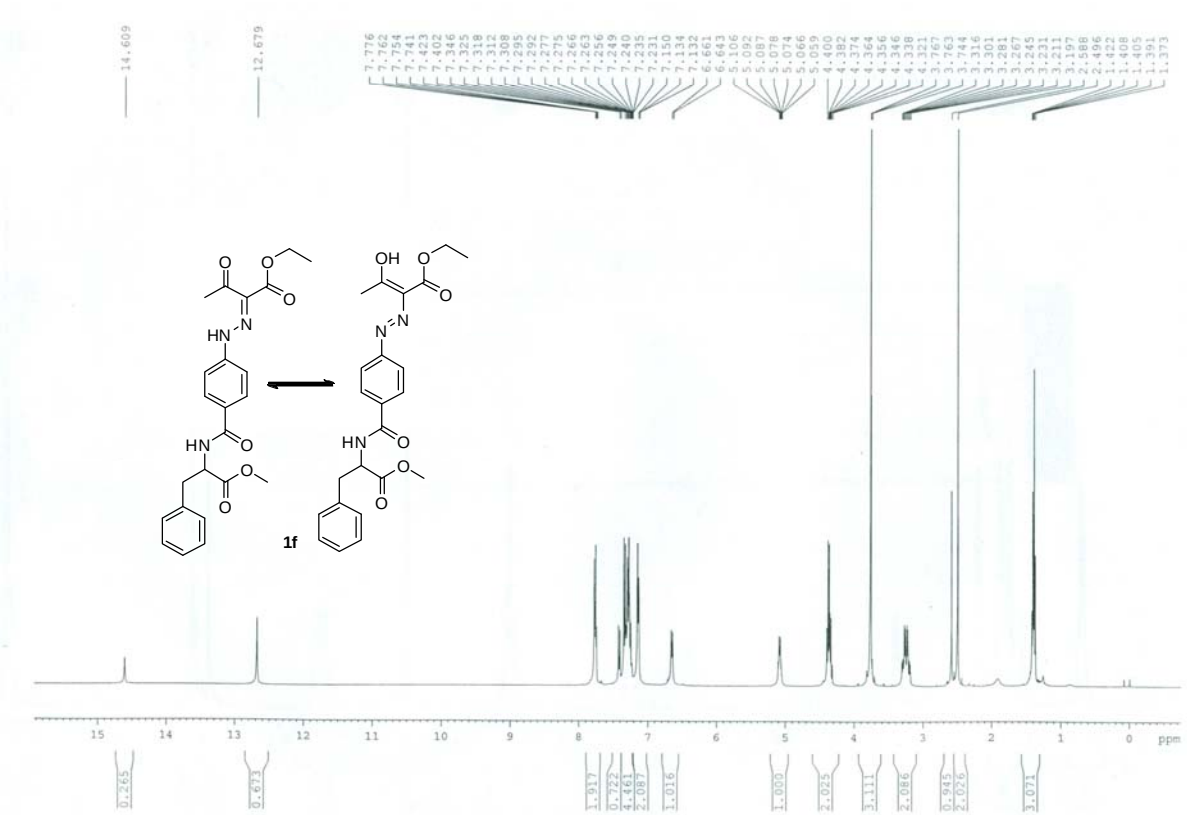


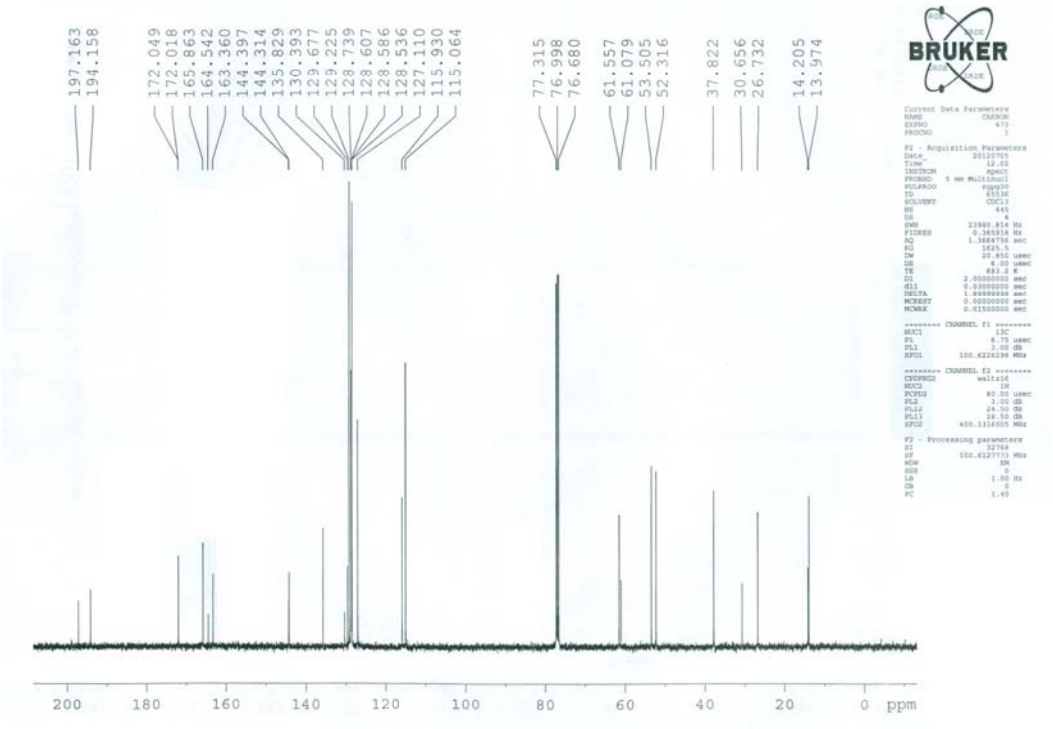



**(E)-Methyl 2-(4-(2-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-ylidene)hydrazinyl)benzamido)-3-methylpentanoate (1e)**

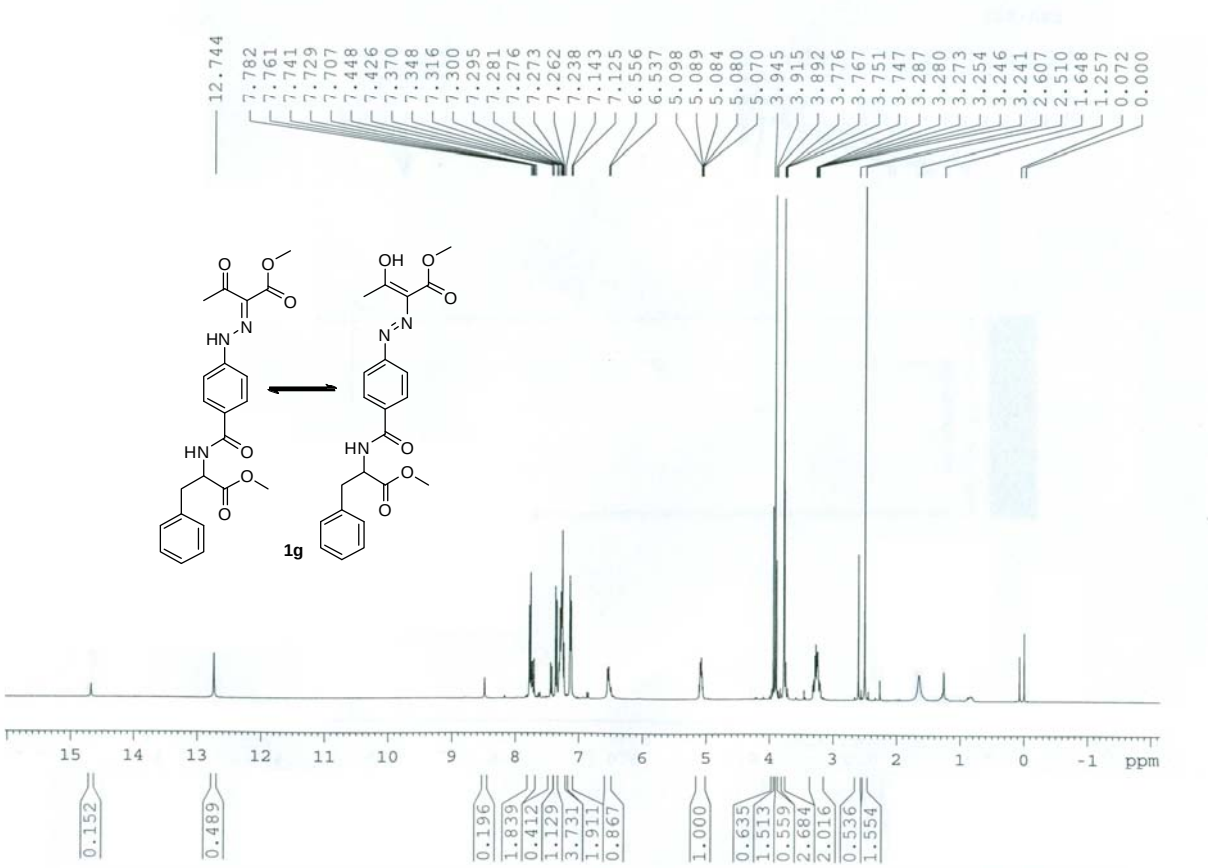


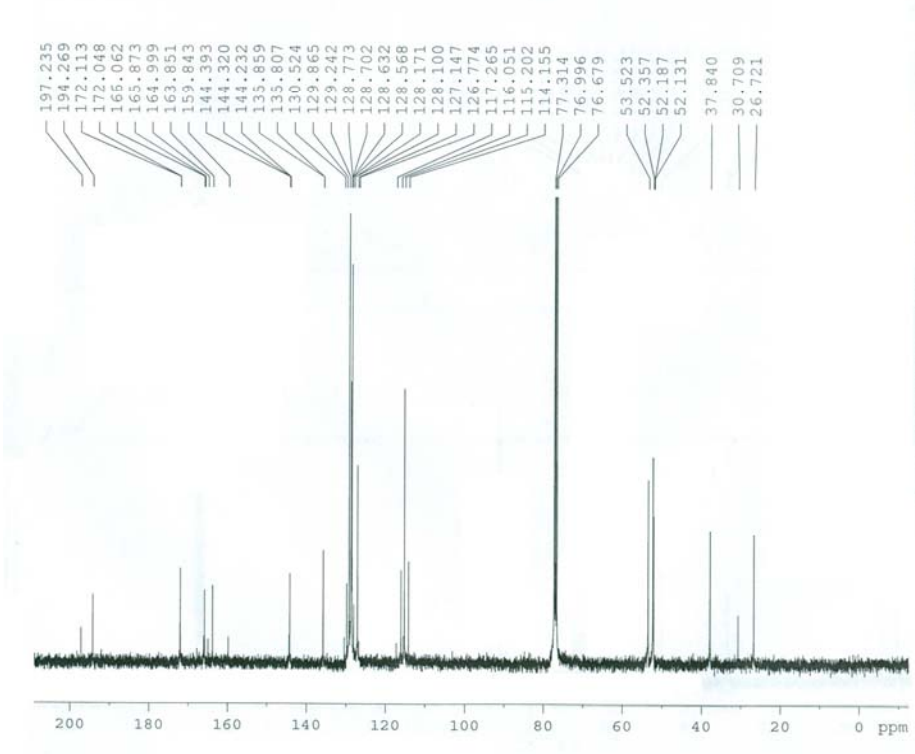
**(E)-Ethyl 2-(2-(4-(1-methoxy-1-oxo-3-phenylpropan-2-ylcarbamoyl)phenyl)hydrazono)-3-oxobutanoate (1f)**

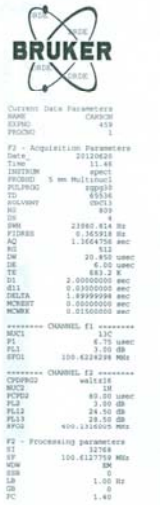


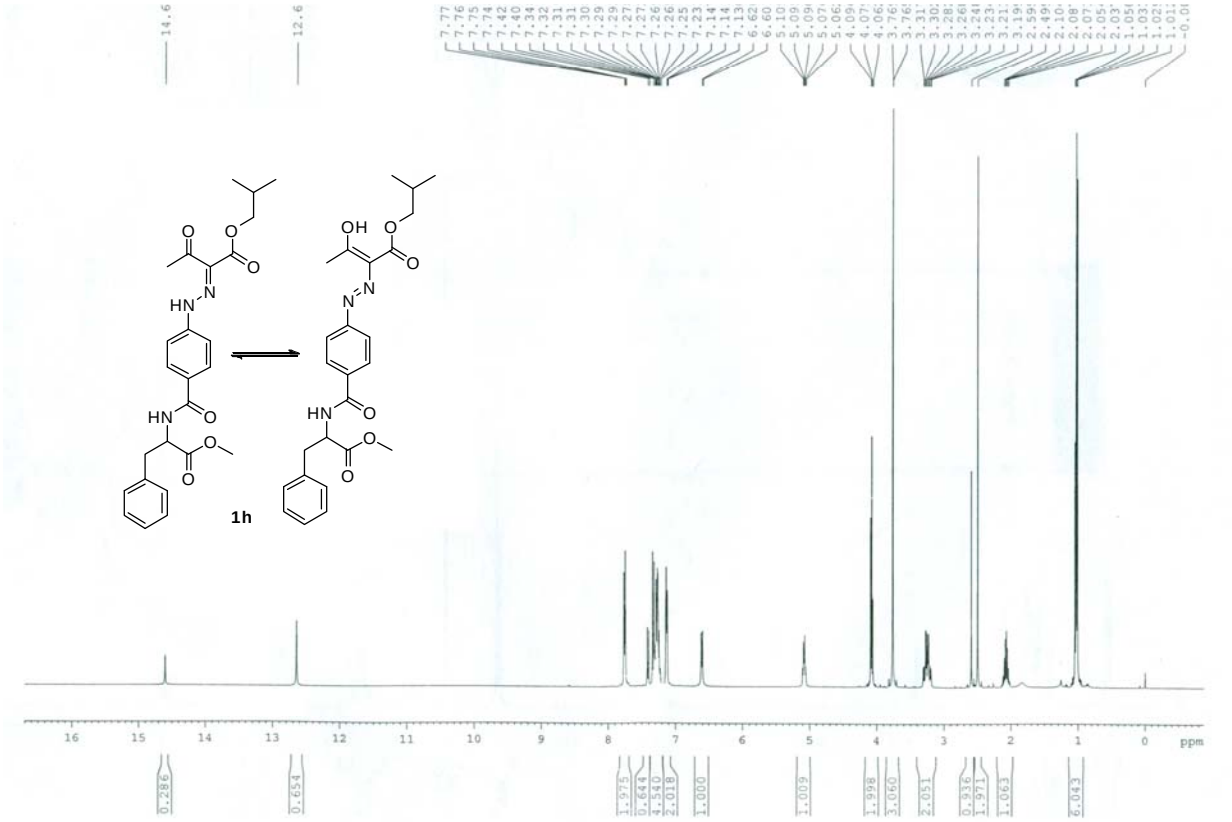
**(E)-Methyl 2-(2-(4-(1-methoxy-1-oxo-3-phenyl propan-2-ylcarbamoyl)phenyl)hydrazono)-3-oxobutanoate (1g)**

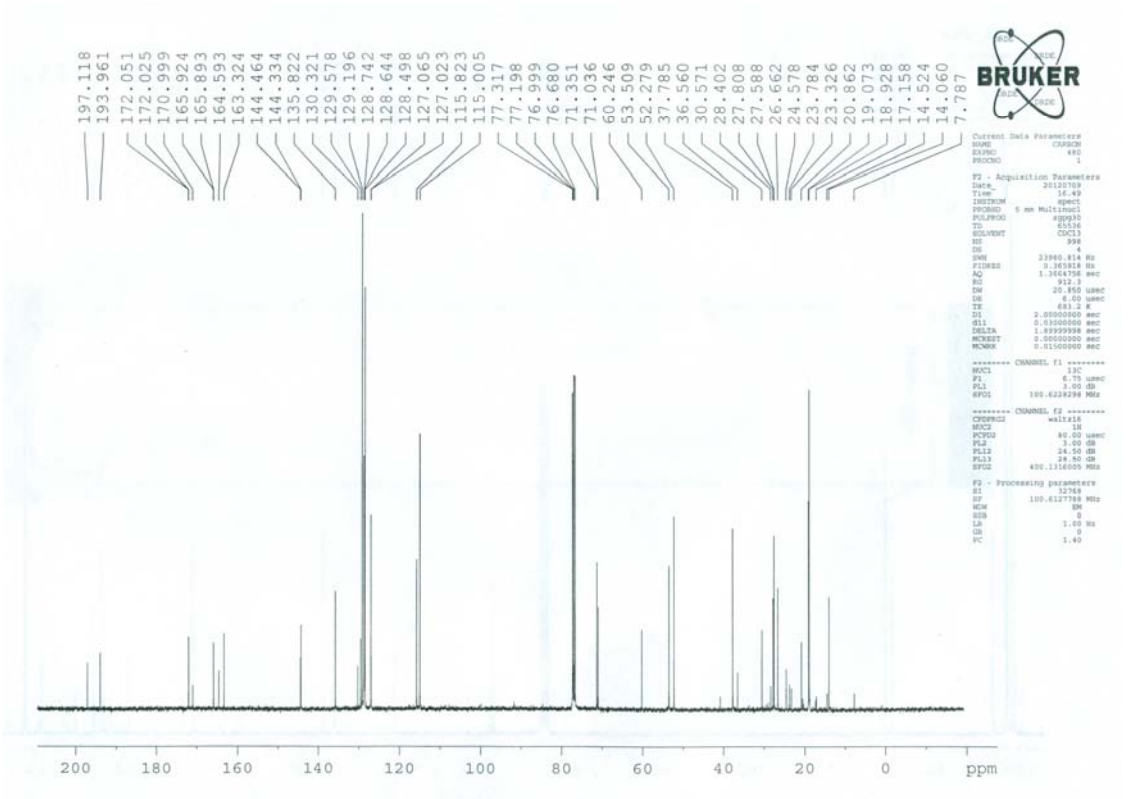


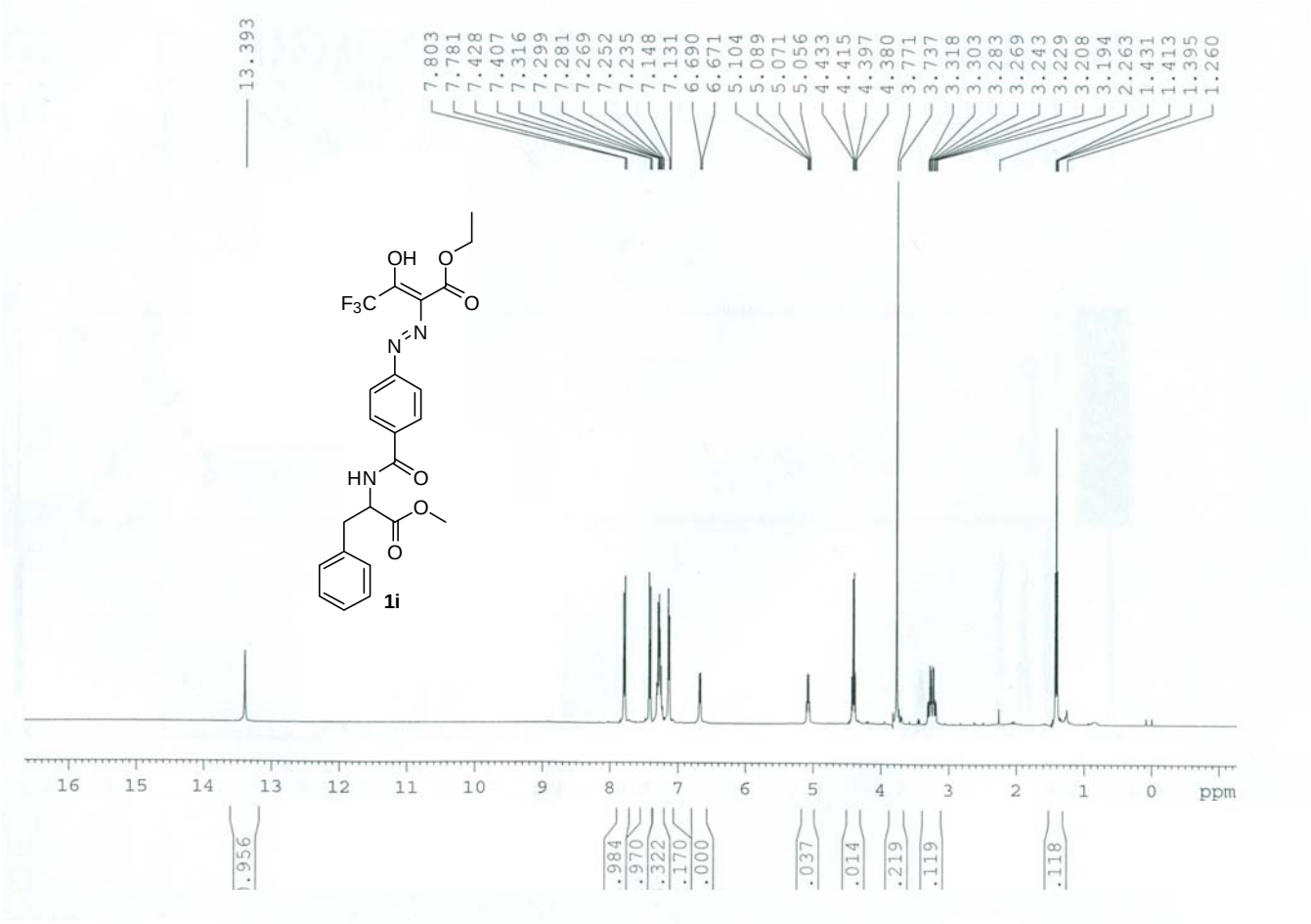



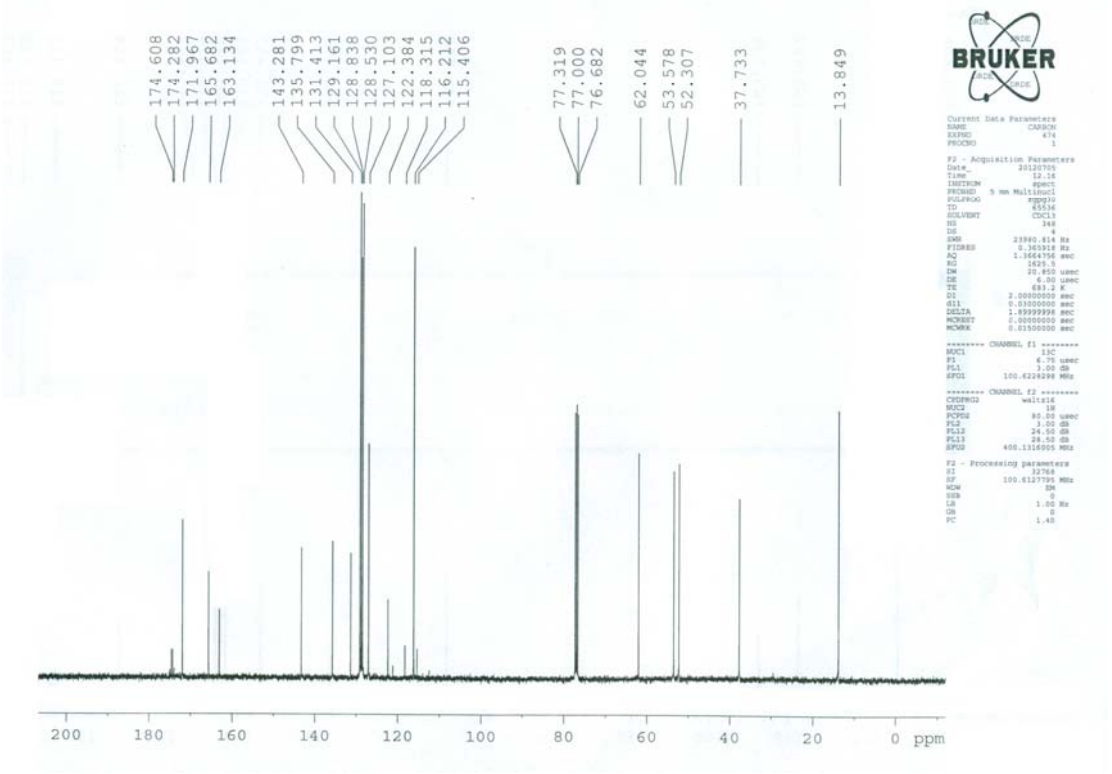
**(E)-Isobutyl 2-(2-(4-(1-methoxy-1-oxo-3-phenylpropan-2-ylcarbamoyl)phenyl)hydrazono)-3-oxobutanoate (1h)**



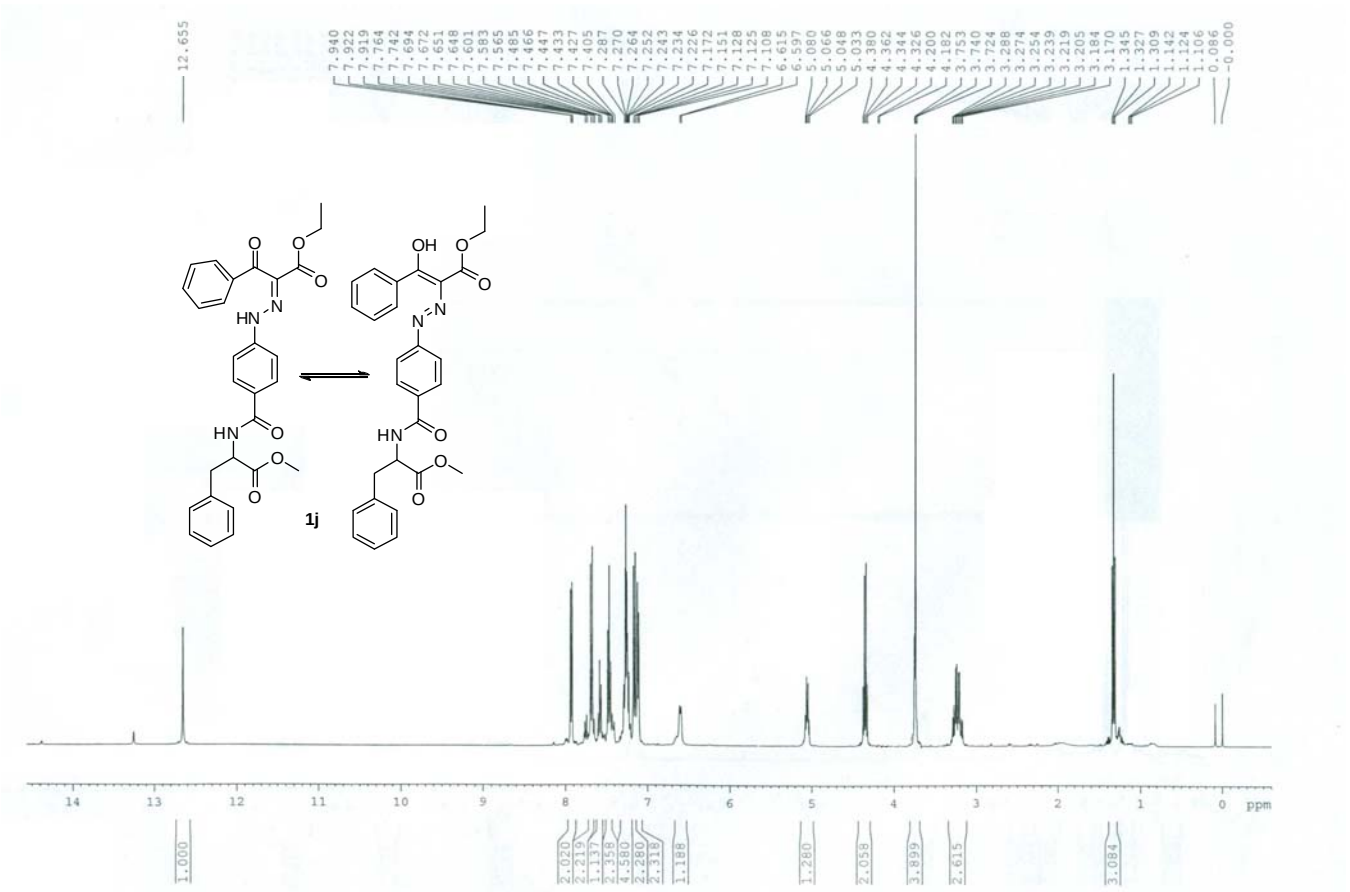



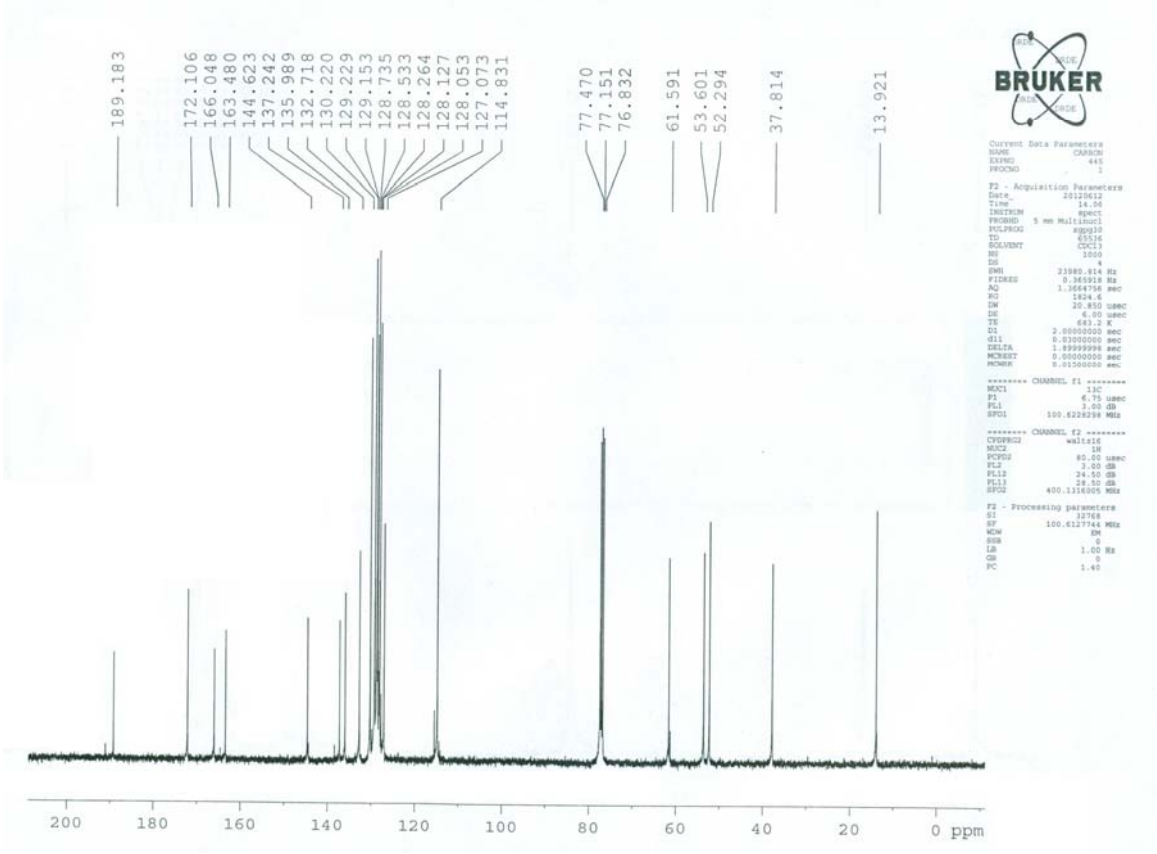
**(E)-Ethyl 4,4,4-trifluoro-3-hydroxy-2-((E)-(4-(1-methoxy-1-oxo-3-phenylpropan-2-ylcarbamoyl) phenyl)diazenyl)but-2-enoate (1i)**



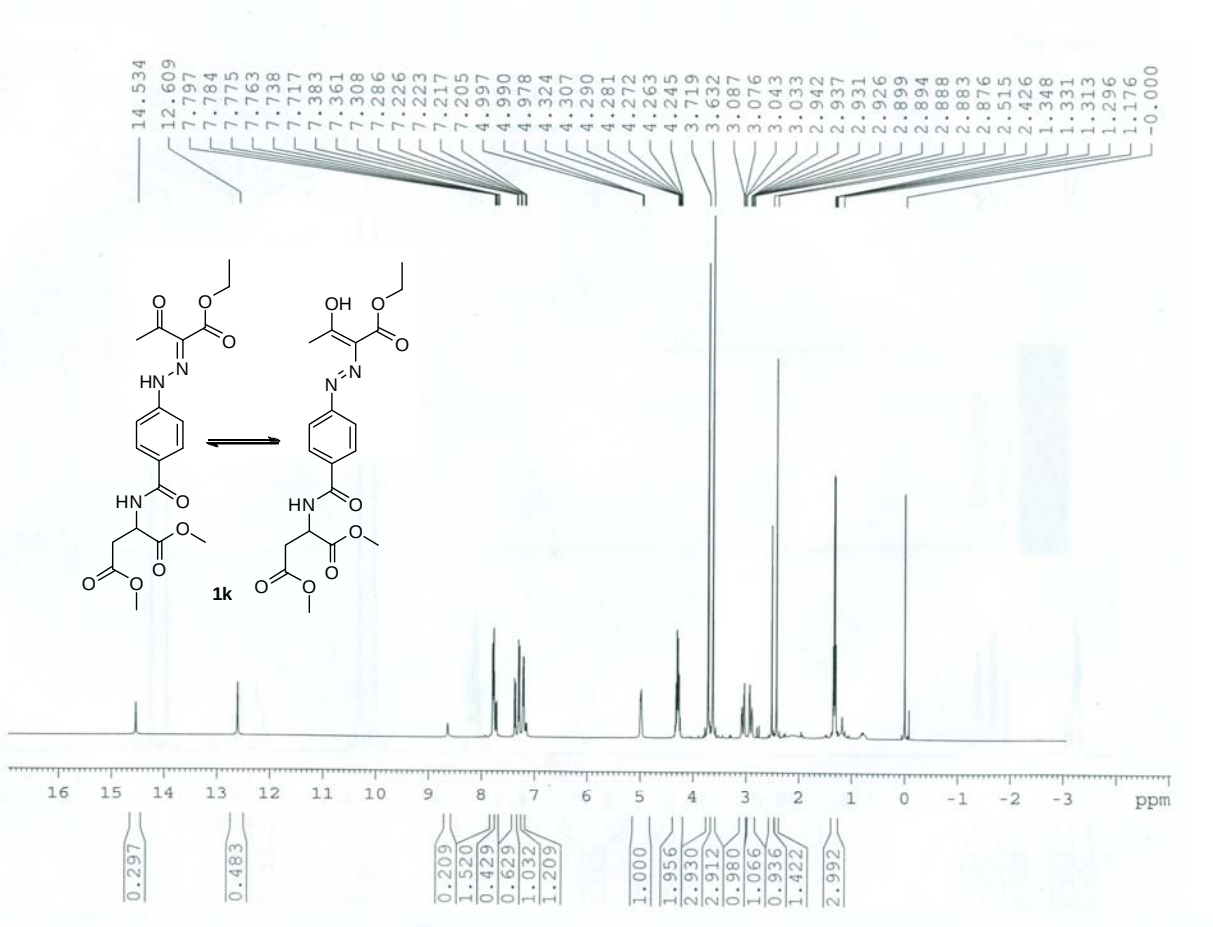



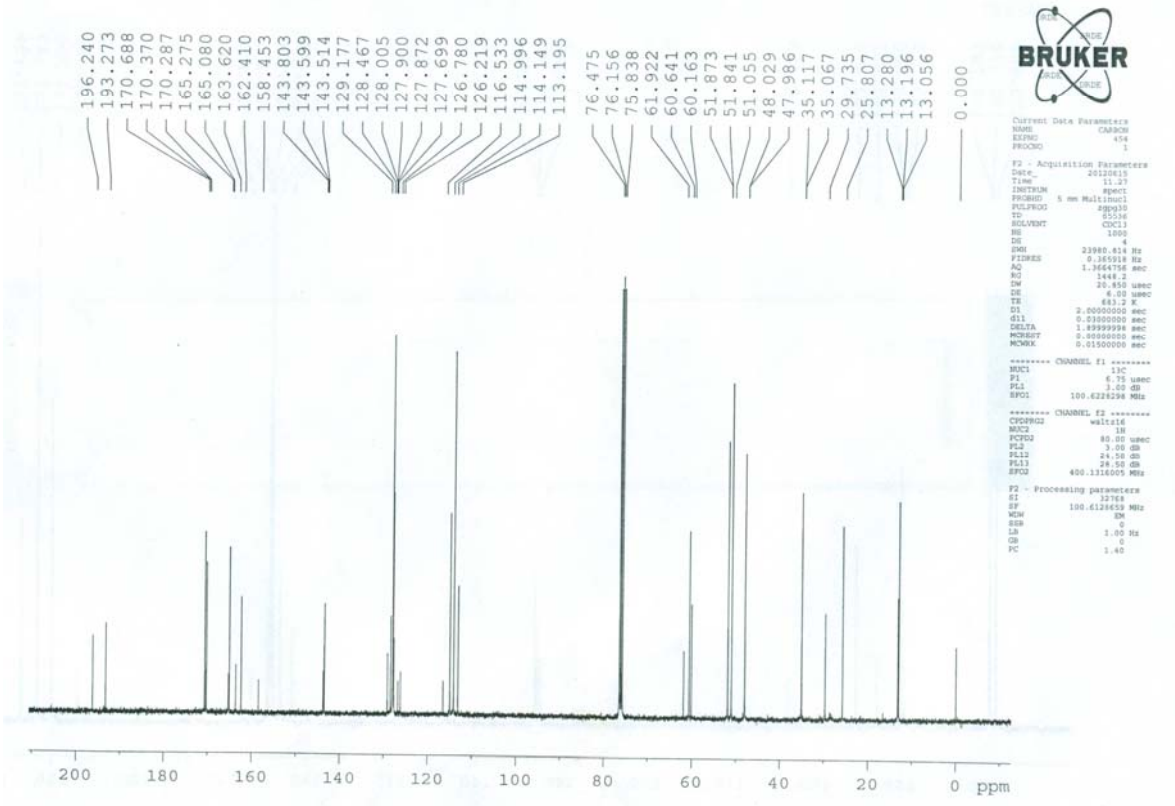
**(E)-Ethyl 2-(2-(4-(1-methoxy-1-oxo-3-phenylpro-pan-2-ylcarbamoyl)phenyl)hydrazono)-3-oxo-3-phenylpropanoate (1j)**



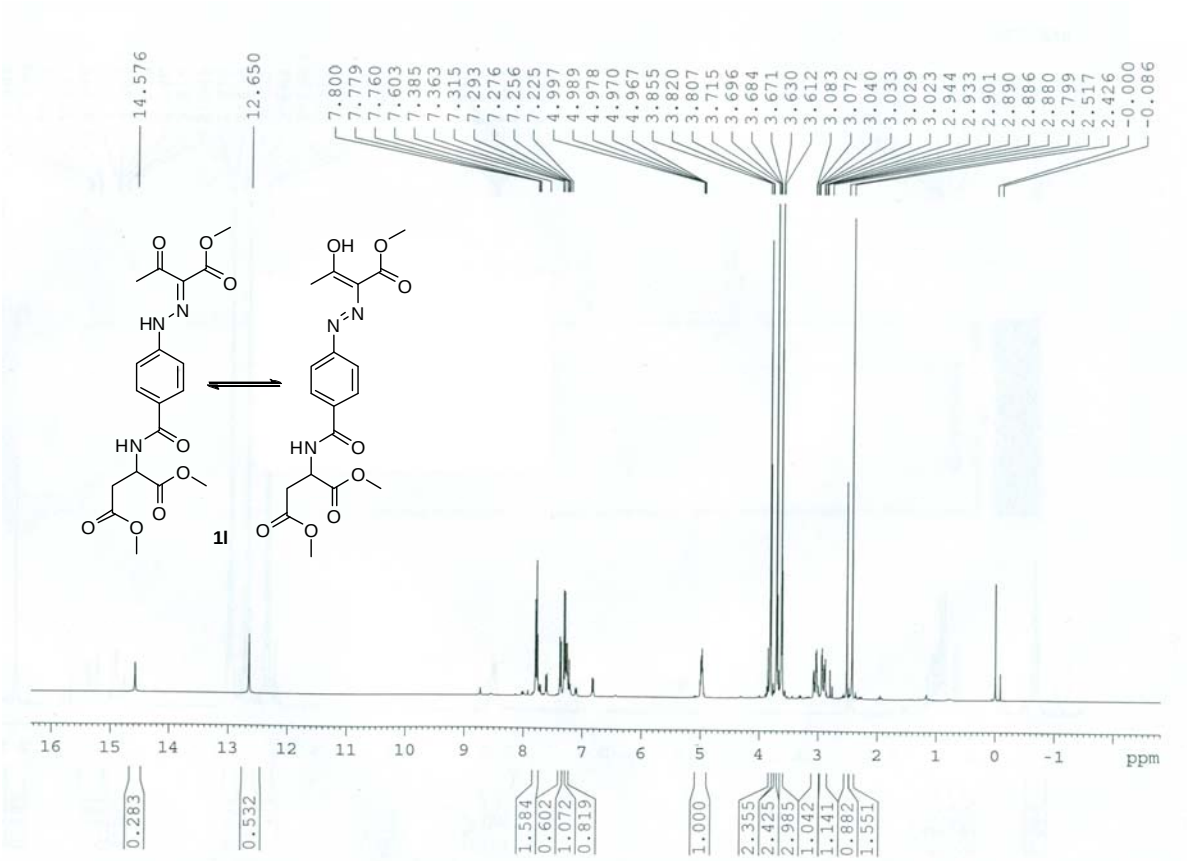



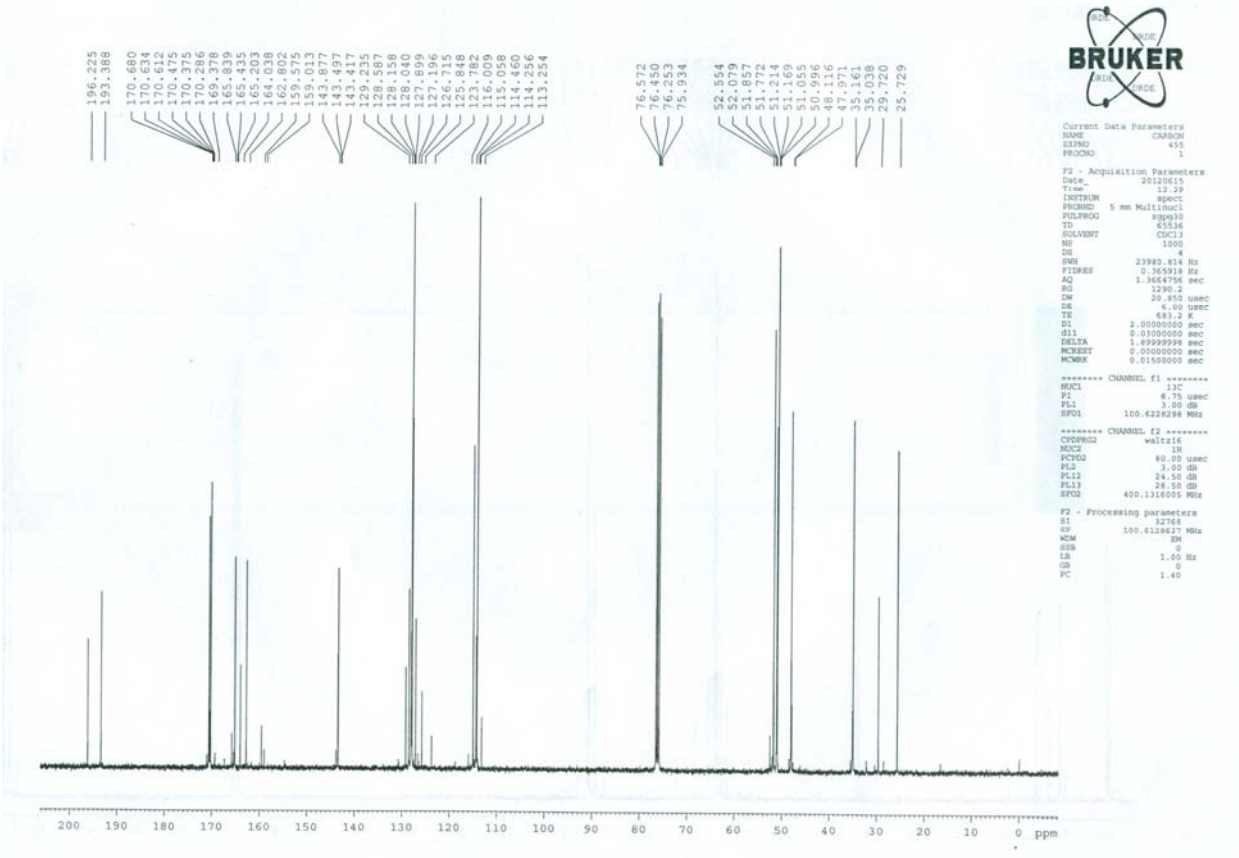
**(E)-dimethyl 2-(4-(2-(1-ethoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benzamido)succinate (1k)**



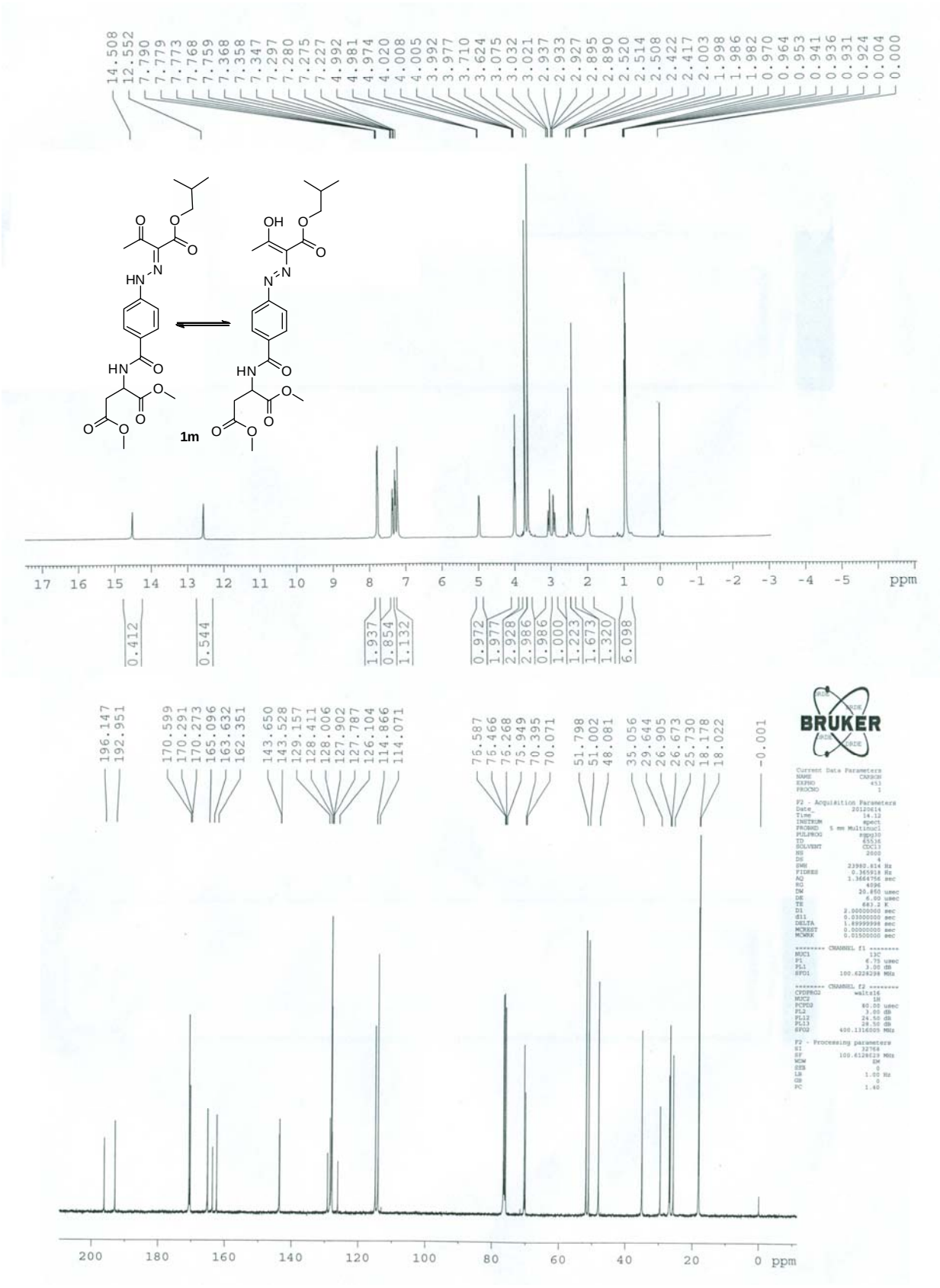



**(E)-Dimethyl 2-(4-(2-(1-methoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benzamido)succinate (1l)**

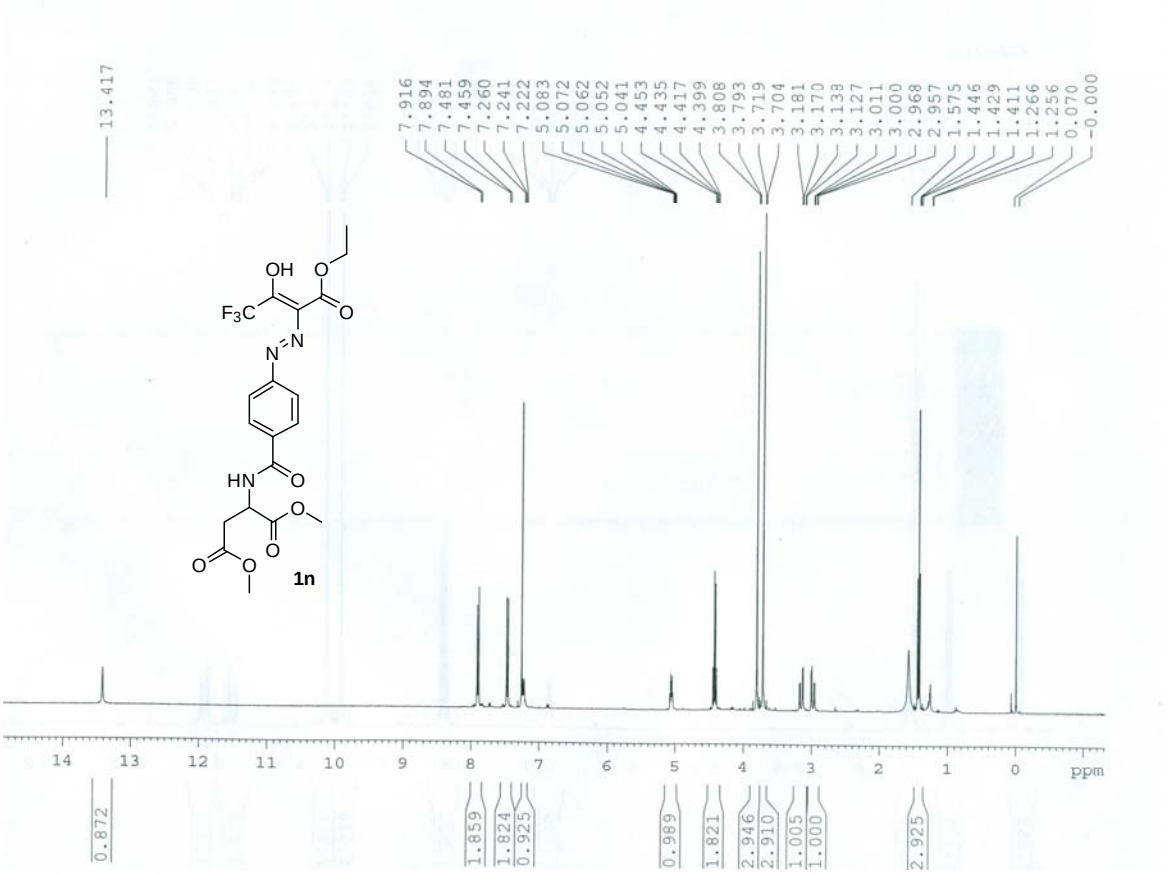


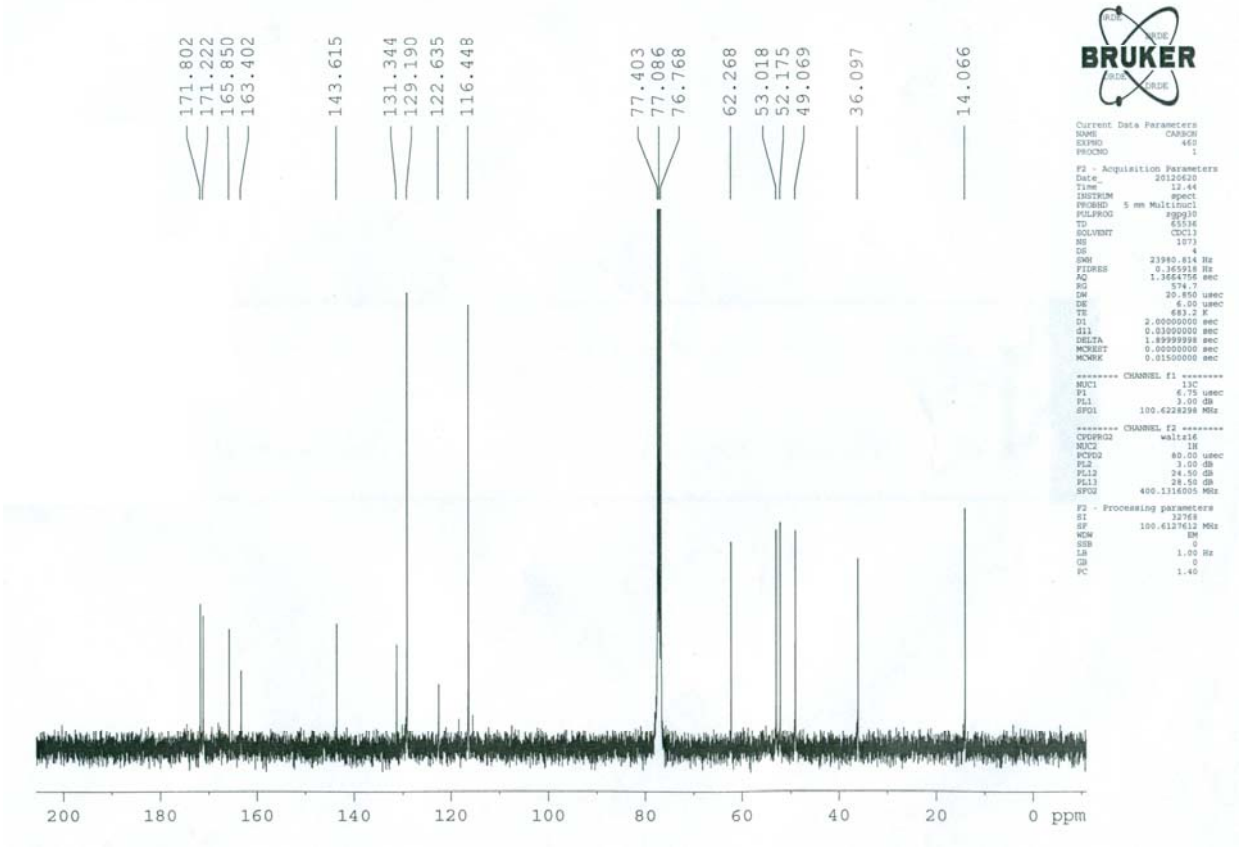



**(E)-Dimethyl 2-(4-(2-(1-isobutoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)benzamido)succinate (1m)**

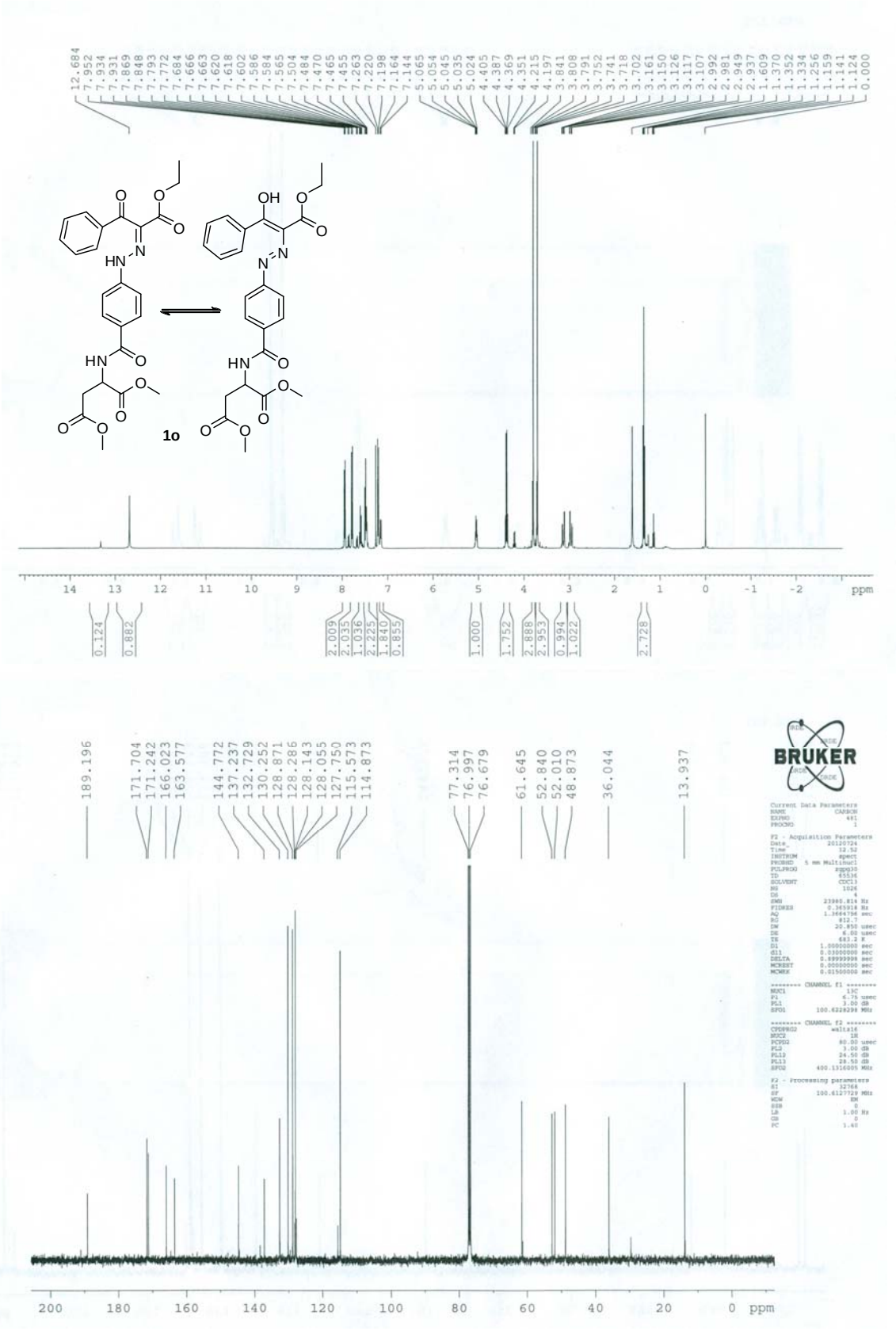


**Dimethyl 2-(4-((E)-((E)-1-ethoxy-4,4,4-trifluoro-3-hydroxy-1-oxobut-2-en-2-yl)diazenyl)benzamido) succinate (1n)**



**(E)-Dimethyl 2-(4-(2-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-ylidene)hydrazinyl)benzamido) succinate (1o)**



**$^{1}$H-NMR and ROESY spectrum of compound 1a to explain keto-enol tautomerism**