METSULFURON-METHYL-BASED HERBICIDAL IONIC LIQUIDS

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Electronic Supporting Information (ESI)

*Bis(2-hydroxyethyl)methyloleylammonium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**3**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 0.89 (t, *J*= 6.9 Hz, 3H); 1.27 (m, 22H); 1.70 (s, 2H); 2.01 (m, 4H); 2.29 (s, 3H); 3.31 (s, 3H); 3.59 (m, 2H); 3.70 (m, 4H); 3.71 (s, 3H); 3.89 (s, 3H); 4.11 (m, 4H); 5.41 (m, 2H); 5.56 (s, 2H); 7.36 (d, *J* = 6.8 Hz 1H); 7.51 (m, 2H); 8.01 (d, *J* = 6.9 Hz, 1H); 8.80 (s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.7, 170.6, 169.0, 165.4, 154.4, 142.7, 131.8, 129.9, 129.6, 129.3, 129.0, 128.9, 127.1, 64.2, 63.9, 55.5, 54.1, 52.5, 50.1, 32.7, 31.9, 29.6, 29.7, 29.5, 29.3, 29.2, 29.1, 27.1, 26.5, 25.4, 22.2, 16.2, 14.0. Purity assayed by EN ISO 2871-1:2010: 97%.

*2-Hydroxyethyltrimethyl ammonium(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**4**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 2.30 (s, 3H); 3.09 (s, 9H); 3.39 (t, *J* = 5.0 Hz, 3H); 3.76 (s, 3H); 3.80 (m, 2H); 3.84 (s, 3H); 7.36 (d, *J* = 7.4 Hz, 1H); 7.51 (m, 2H); 7.99 (d, *J* = 7.8 Hz, 1H); 8.97 (s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.5, 170.7, 168.8, 165.7, 154.9, 143.3, 131.9, 129.7, 129.2, 128.7, 127.0, 66.9, 62.1, 54.2, 53.2, 52.3, 25.1. Elemental analysis calculated for $C_{19}H_{28}N_6O_7S$ (MW = 484.5 g/ mol) (%): C = 47.10, H = 5.82, N = 17.34; found: C = 47.27, H = 5.98, N = 17.26.

*1-Dodecylpyridinium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**5**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 0.85 (t, *J* = 6.8 Hz, 3H); 1.22 (m, 18H); 1.89 (m, 2H); 2.32 (s, 3H); 3.77 (s, 3H); 3.86 (s, 3H); 4.61 (t, *J* = 7.7 Hz, 2H); 7.41 (m, 1H), 7.54 (m, 2H); 8.03 (d, *J* = 9.0 Hz, 1H); 8.16 (t, *J* = 6.9 Hz, 2H); 8.61 (t, *J* = 7.8 Hz, 1H); 9.16 (d, *J* = 5.7 Hz, 2H); 9.37 (s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.5, 170.5, 168.4, 165.3, 145.4, 144.8, 131.8, 129.4, 129.2, 128.0, 127.5, 127.3, 60.7, 54.2, 52.3, 31.3, 30.7, 29.0,

28.9, 28.8, 28.7, 28.4, 25.4, 25.0, 22.1, 13.9. Elemental analysis calculated for $C_{31}H_{44}N_6O_6S$ (MW = 628.8 g/ mol) (%): C = 59.20, H = 7.05, N = 13.37; found: C = 59.49, H = 7.34, N = 13.20. Purity assayed by EN ISO 2871-1:2010: 98%.

*1-Methyl-1-propylpiperidinium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**6**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 0.87 (t, *J* = 7.2 Hz, 3H); 1.49 (m, 2H); 1.66 (m, 2H); 1.73 (m, 4H); 2.30 (s, 3H); 2.96 (s, 3H); 3.27 (m, 4H); 3.38 (m, 2H); 3.77 (s, 3H); 3.84 (s, 3H); 7.38 (d, *J* = 7.8 Hz 1H); 7.52 (m, 2H); 8.02 (d, *J* = 7.5 Hz, 1H); 9.15(s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.5, 170.6, 168.9, 165.6, 154.5, 142.9, 131.7, 129.9, 129.2, 129.0, 128.9, 127.0, 63.7, 59.9, 54.2, 52.3, 47.0, 25.0, 20.6, 19.2, 14.6, 10.5. Elemental analysis calculated for $C_{23}H_{34}N_6O_6S$ (MW = 522.6 g/ mol) (%): C = 52.86, H = 6.56, N = 16.08; found: C = 52.55, H = 6.86, N = 16.25.

*1-Allyl-3-methylimidazolium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**7**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 2.28 (s, 3H); 3.74 (s, 3H); 3.82 (s, 3H); 3.84 (s, 3H); 4.82 (d, *J* = 5.7 Hz, 2H); 5.30 (t, J_1= 11.4 Hz, J_2= 17.1 Hz, 2H); 6,00 (m, 1H); 7.33 (d, *J* = 6.9 Hz, 1H); 7.48 (m, 2H); 7.70 (d, *J* = 7.2 Hz 2H); 7.97 (d, *J* = 6.9 Hz, 1H); 9.01 (s, 1H); 9.19(s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.4, 170.6, 168.8, 165.7, 154.8, 143.3, 136.9, 131.8, 129.6, 129.1, 128.7, 126.9, 123.7, 122.2, 120.0, 54.1, 52.2, 50.7, 35.7, 25.1. Elemental analysis calculated for $C_{21}H_{25}N_7O_6S$ (MW = 503.5 g/ mol) (%): C = 50.09, H = 5.00, N = 19.47; found: C = 49.77, H = 5.31, N = 19.21.

*1-Butyl-3-methylimidazolium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**8**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 0.85 (t, *J* = 7.5 Hz, 3H); 1.21 (m, *J* = 7.8 Hz, 2H); 1.72 (m, *J* = 7.4 Hz, 2H); 2.28 (s, 3H); 3.75 (s, 3H); 3.82 (s, 6H); 4.14 (t, *J* = 7.2 Hz, 2H); 7.35 (d, *J* = 6.9 Hz, 1H), 7.49 (m, 2H); 7.69 (t, *J* = 1.8 Hz, 1H); 7.75 (t, *J* = 1.8 Hz,1H); 7.99 (d, *J* = 7.2 Hz, 1H); 9.05 (s, 1H); 9.20(s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.4, 170.6, 168.8, 165.6, 154.7, 143.2, 136.7, 131.8, 129.6, 129.1, 128.7, 126.9, 123.5, 122.2, 54.1, 52.2, 48.4, 35.6, 31.4, 25.0, 18.7, 13.2. Elemental analysis calculated for $C_{22}H_{29}N_7O_6S$ (MW = 519.6 g/ mol) (%): C = 50.86, H = 5.63, N = 18.87; found: C = 50.99, H = 5.41, N = 19.11.

*1-Butyl-1-methylpyrrolidinium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**9**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 0.90 (t, *J* = 7.4 Hz, 3H); 1.27 (m, *J* = 7.5 Hz, 2H); 1.64 (m, 2H); 2.04 (s, 4H); 2.30 (s, 3H); 2.96 (s, 3H); 3.28 (t, *J* = 8.3 Hz, 2H); 3.42 (m, 4H); 3.77 (s, 3H); 3.84 (s, 3H); 7.38 (d, *J* = 6.9 Hz 1H), 7.52 (m, 2H); 8.01 (d, *J* = 7.2 Hz, 1H); 9.11(s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.4, 170.6, 168.8, 165.6, 154.5, 142.9, 131.7, 129.8, 129.2, 128.9, 127.0, 63.3, 62.8, 54.2, 52.3, 47.4, 25.0, 24.9, 21.0, 19.2, 13.4. Elemental analysis calculated for $C_{23}H_{34}N_6O_6S$ (MW = 522.6 g/ mol) (%): C = 52.86, H = 6.56, N = 16.08; found: C = 53.05, H = 6.79, N = 15.82.

*4-Decyl-4-methylmorpholinium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**10**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 0.86 (t, *J* = 6.6 Hz, 3H); 1.25 (s, 14H); 1.65 (m, 2H); 2.30 (s, 3H); 3.13 (s, 3H); 3.41 (m, 6H); 3.77 (s, 3H); 3.84 (s, 3H); 3.91 (s, 4H); 7.38 (d, *J* = 7.2 Hz 1H), 7.52 (m, 2H); 8.01 (d, *J* = 6.9 Hz, 1H); 9.15 (s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.4, 170.6, 168.9, 165.6, 154.5, 142.9, 131.6, 129.9, 129.2,

129.0, 127.0, 63.7, 59.8, 58.9, 54.2, 52.3, 45.9, 31.3, 28.9, 28.8, 28.6, 28.5, 25.7, 25.0, 22.1, 20.7, 13.9. Elemental analysis calculated for $C_{29}H_{46}N_6O_7S$ (MW = 622.8 g/ mol) (%): C = 55.93, H = 7.44, N = 13.49; found: C = 55.80, H = 7.79, N = 13.22.

*Trihexyltetradecylphosphonium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**11**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 0.87 (m, 12H); 1.27 (m, 48H); 2.19 (m, 8H); 2.29 (s, 3H); 3.75 (s, 3H); 3.84 (s, 3H); 7.34 (d, *J* = 6.9 Hz 1H); 7.48 (m, 2H); 8.00 (d, *J* = 6.9 Hz, 1H); 8.87 (s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.3, 170.6, 168.7, 165.6, 154.2, 143.4, 131.8, 129.4, 128.9, 126.8, 54.0, 52.1, 31.3, 30.6, 30.4, 30.0, 29.8, 29.6, 29.0, 28.7, 28.6, 28.1, 25.0, 22.1, 21.8, 20.6, 20.5, 17.8, 17.2, 13.8; ^{31}P NMR (DMSO-d_6) δ [ppm] = 34.2. Elemental analysis calculated for $C_{46}H_{82}N_5O_6PS$ (MW = 864.2 g/ mol) (%): C = 63.93, H = 9.56, N = 8.10; found: C = 63.71, H = 9.76, N = 8.37. Purity assayed by EN ISO 2871-1:2010: 97%.

*Tetrabutylphosphonium (4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoyl)(2-(methoxycarbonyl)phenylsulfonyl)amidate (**12**).* ^{1}H NMR (DMSO-d_6) δ [ppm] = 0.91 (t, J = 7.1 Hz, 12H); 1.43 (m, 16H); 2.21 (m, 8H); 2.28 (s, 3H); 3.74 (s, 3H); 3.83 (s, 3H); 7.33 (d, *J* = 7.1 Hz, 1H); 7.48 (m, 2H); 7.98 (d, *J* = 7.1 Hz, 1H); 8.83 (s, 1H); ^{13}C NMR (DMSO-d_6) δ [ppm] = 177.3, 170.6, 168.7, 165.6, 154.2, 143.5, 131.8, 129.4, 128.9, 128.8, 126.8, 54.0, 52.1, 25.0, 23.4, 23.2, 22.6, 17.6, 17.0 13.2. Elemental analysis calculated for $C_{30}H_{50}N_5O_6PS$ (MW = 639.8 g/ mol) (%): C = 56.32, H = 7.88, N = 10.95; found: C = 56.04, H = 7.52, N = 10.70.

Figure S1. ^{13}C spectrum of compound **3**.

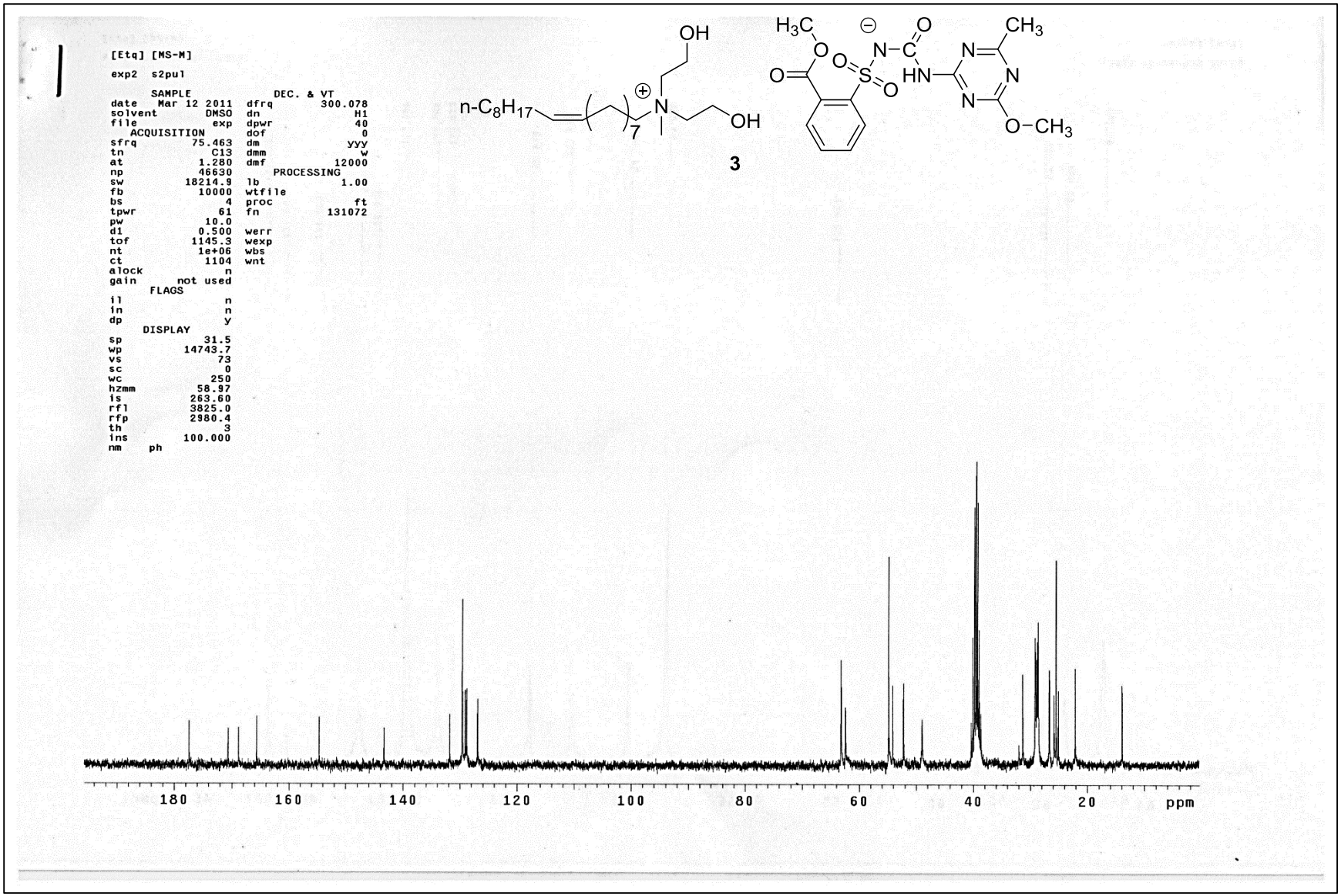

Figure S2. ^{1}H spectrum of compound **3**.

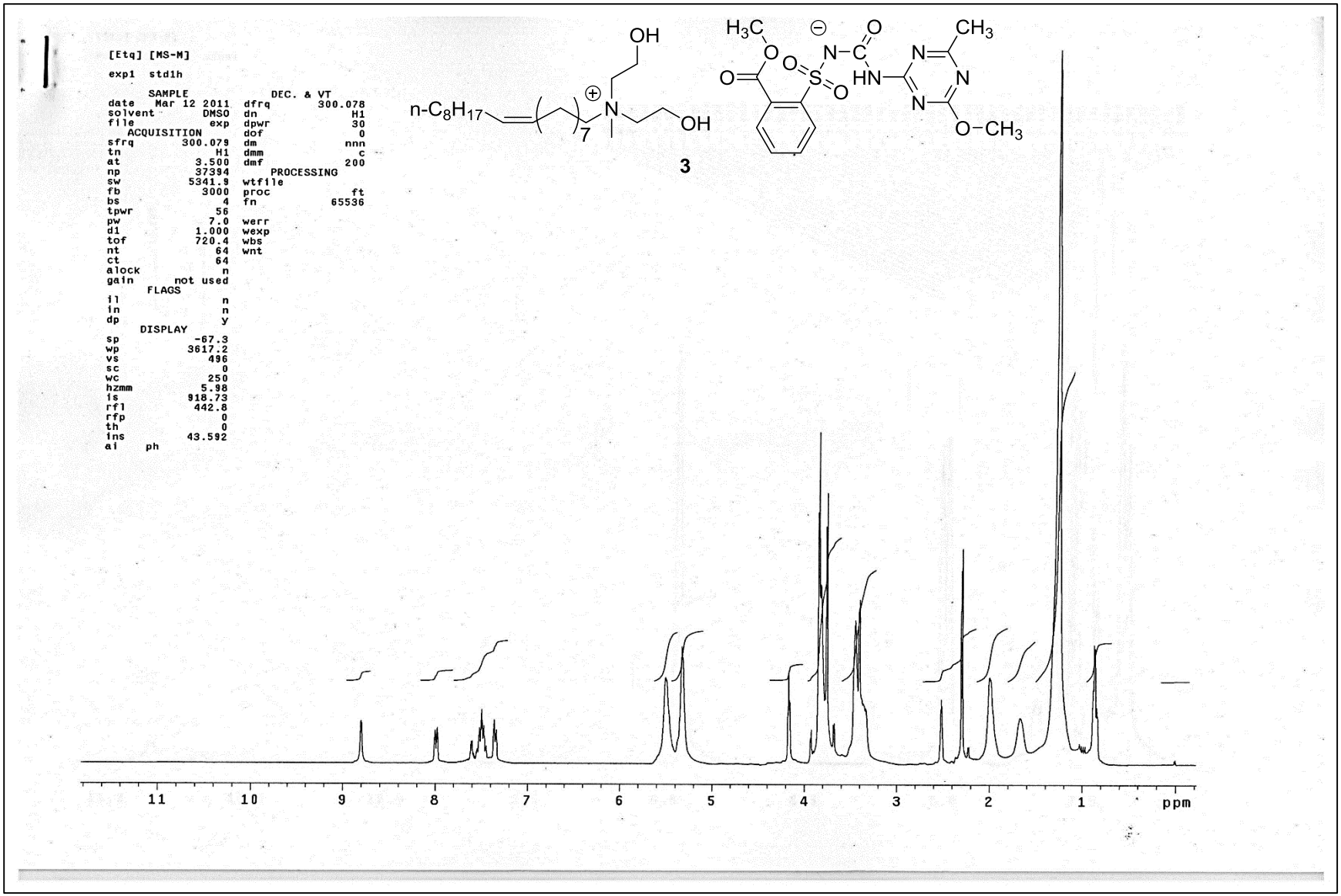

Figure S3. ^{13}C spectrum of compound **4**.

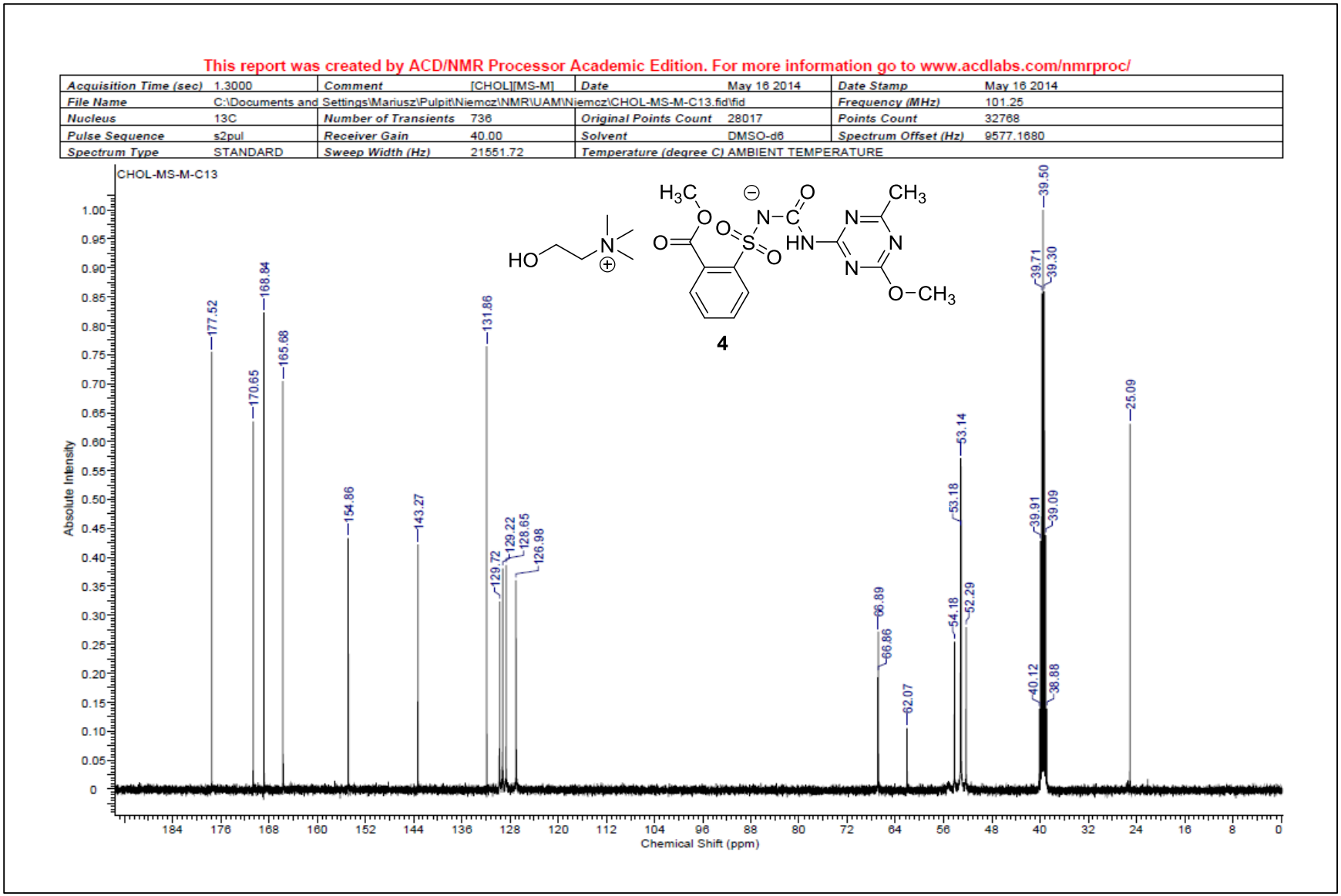

Figure S4. ^{1}H spectrum of compound **4**.

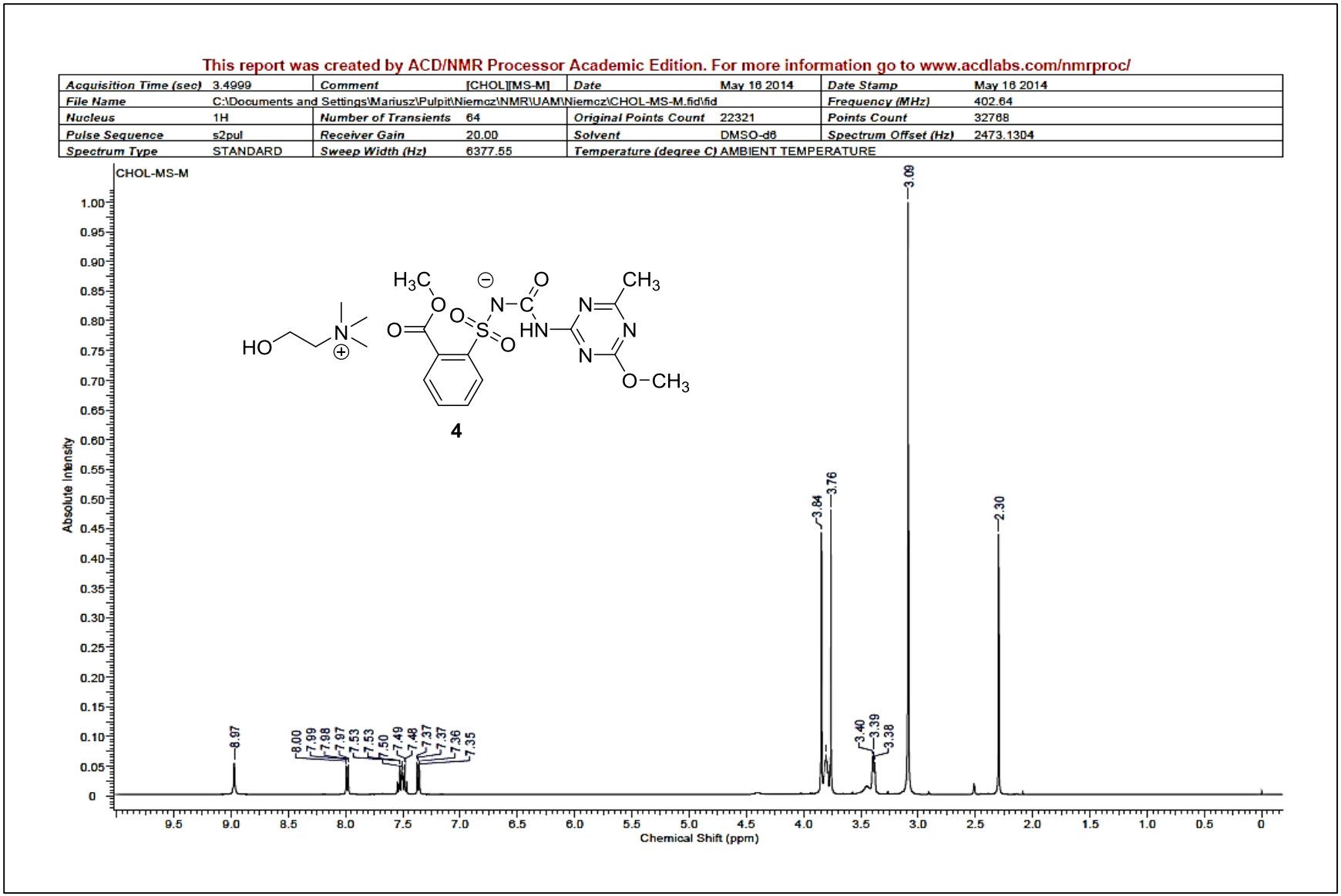

Figure S5. ^{13}C spectrum of compound **5**.

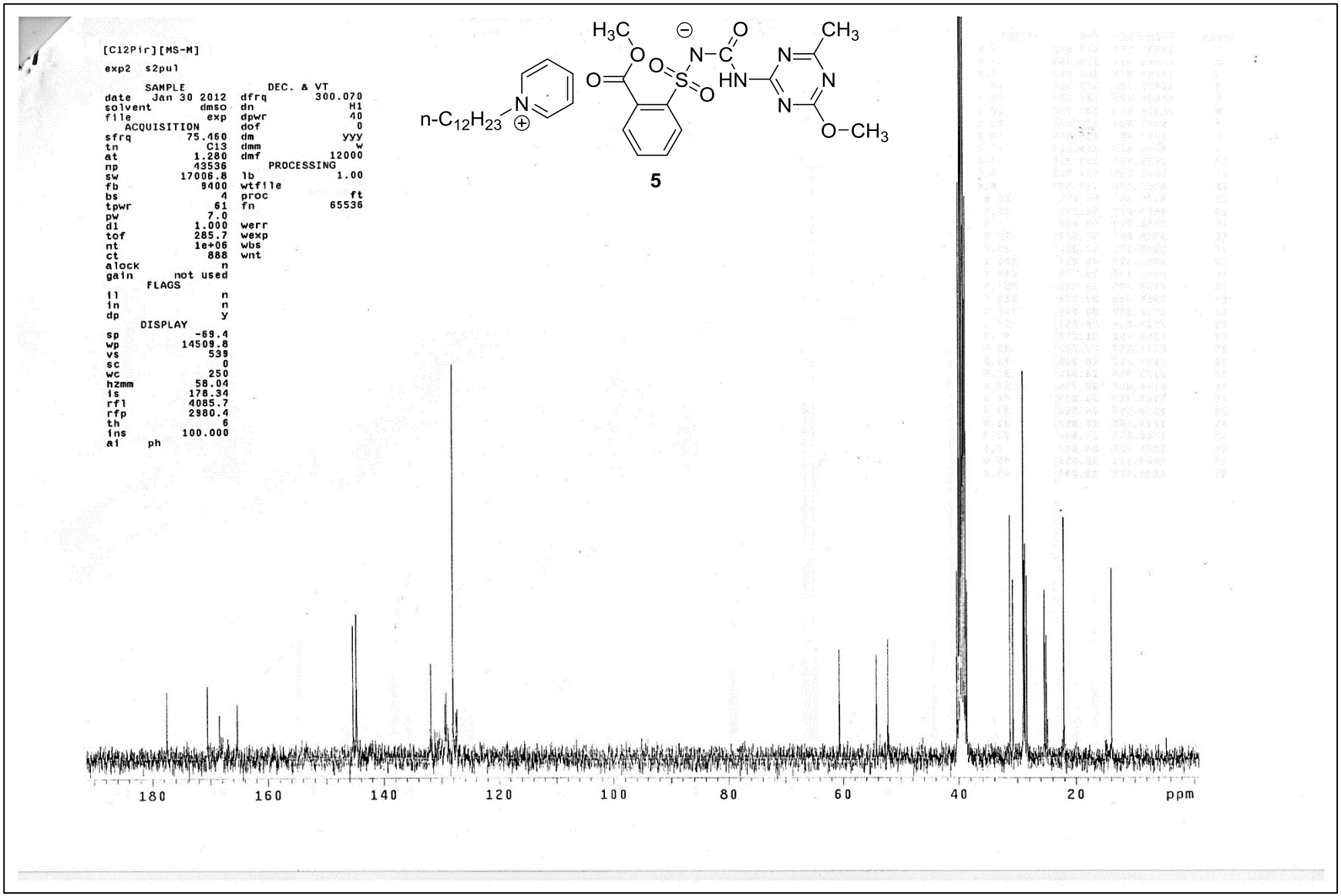

Figure S6. ^{1}H spectrum of compound **5**.

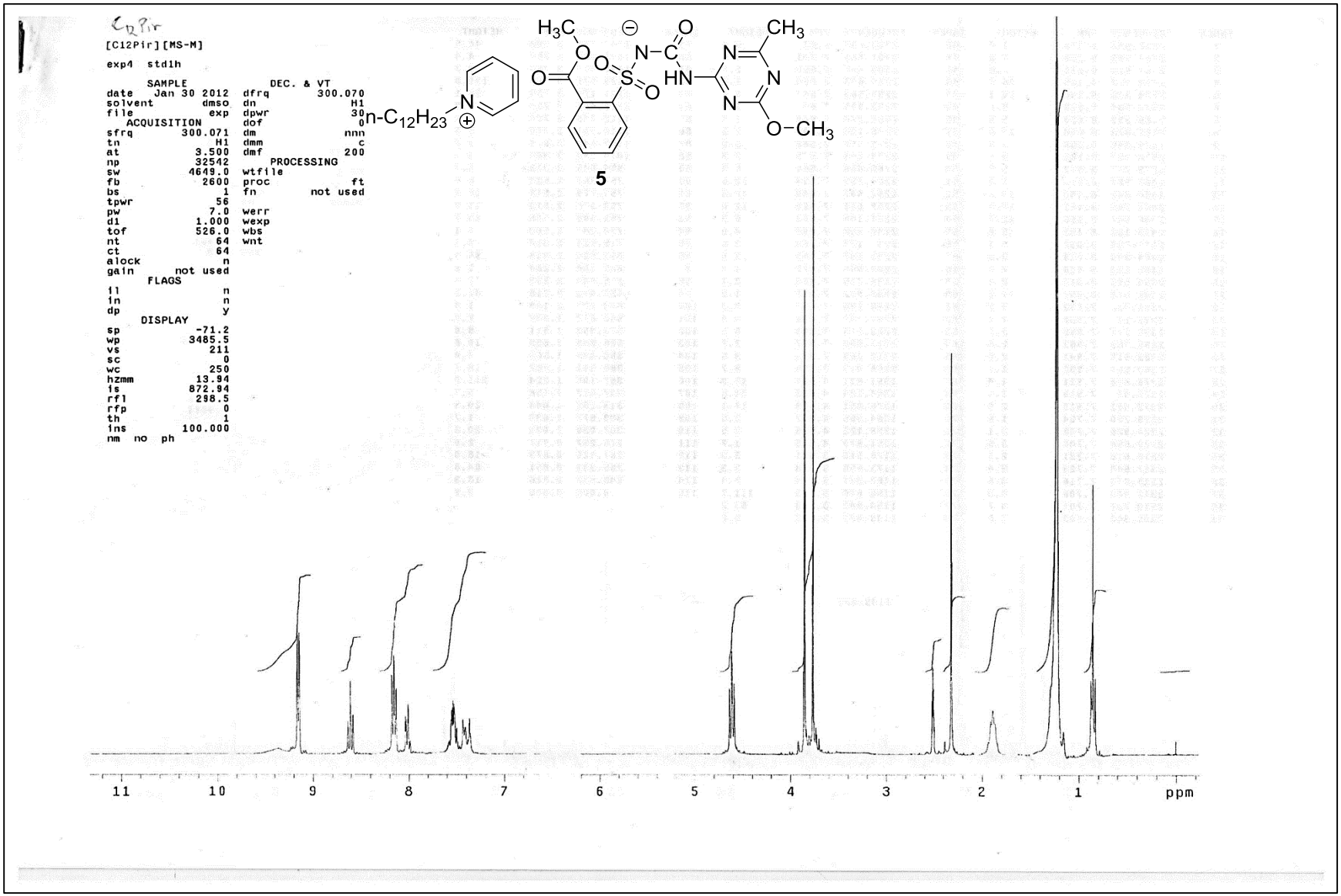

Figure S7. ^{13}C spectrum of compound **6**.

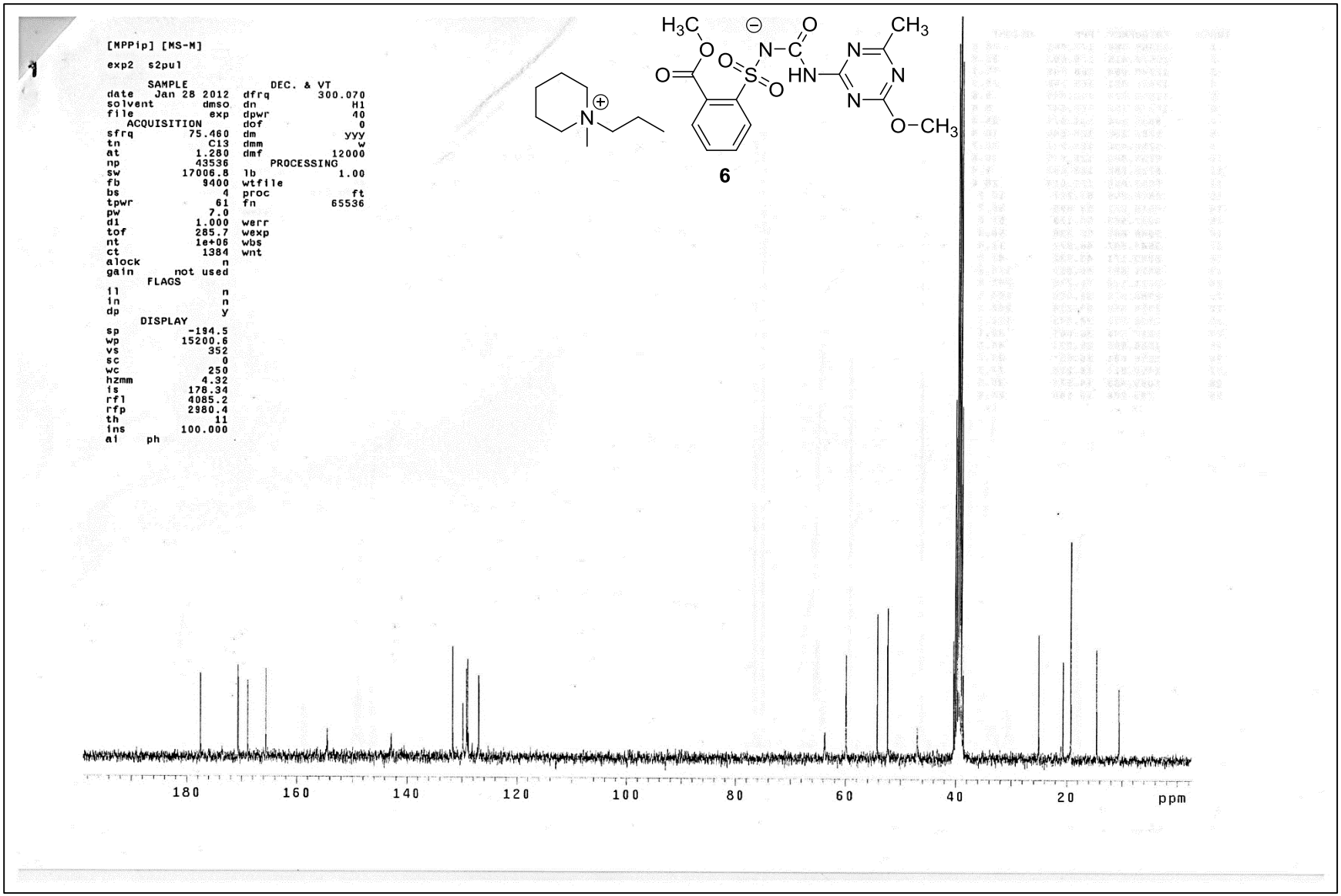

Figure S8. ^{1}H spectrum of compound **6**.

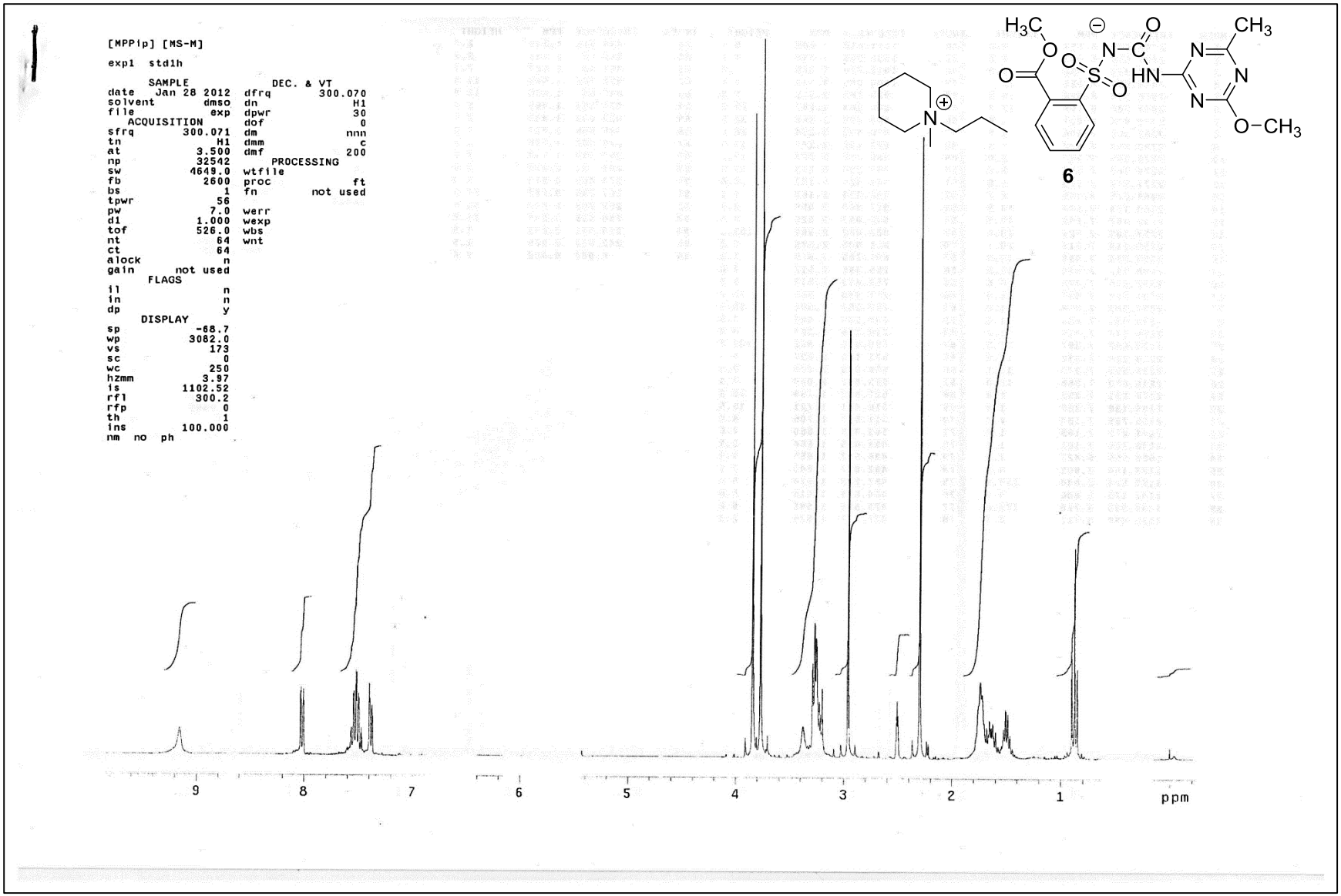

Figure S9. ^{13}C spectrum of compound **7**.

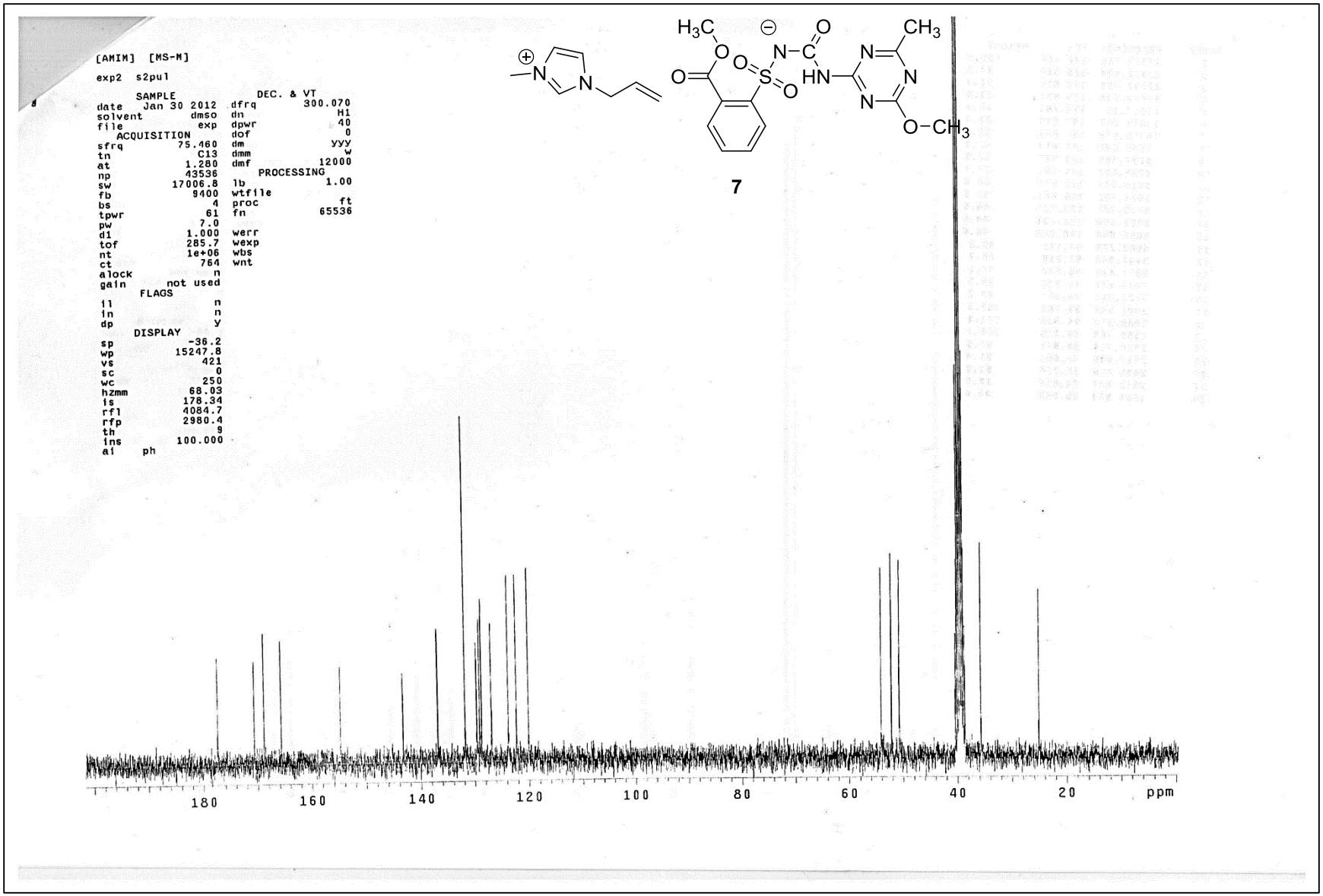

Figure S10. ^{1}H spectrum of compound **7**.

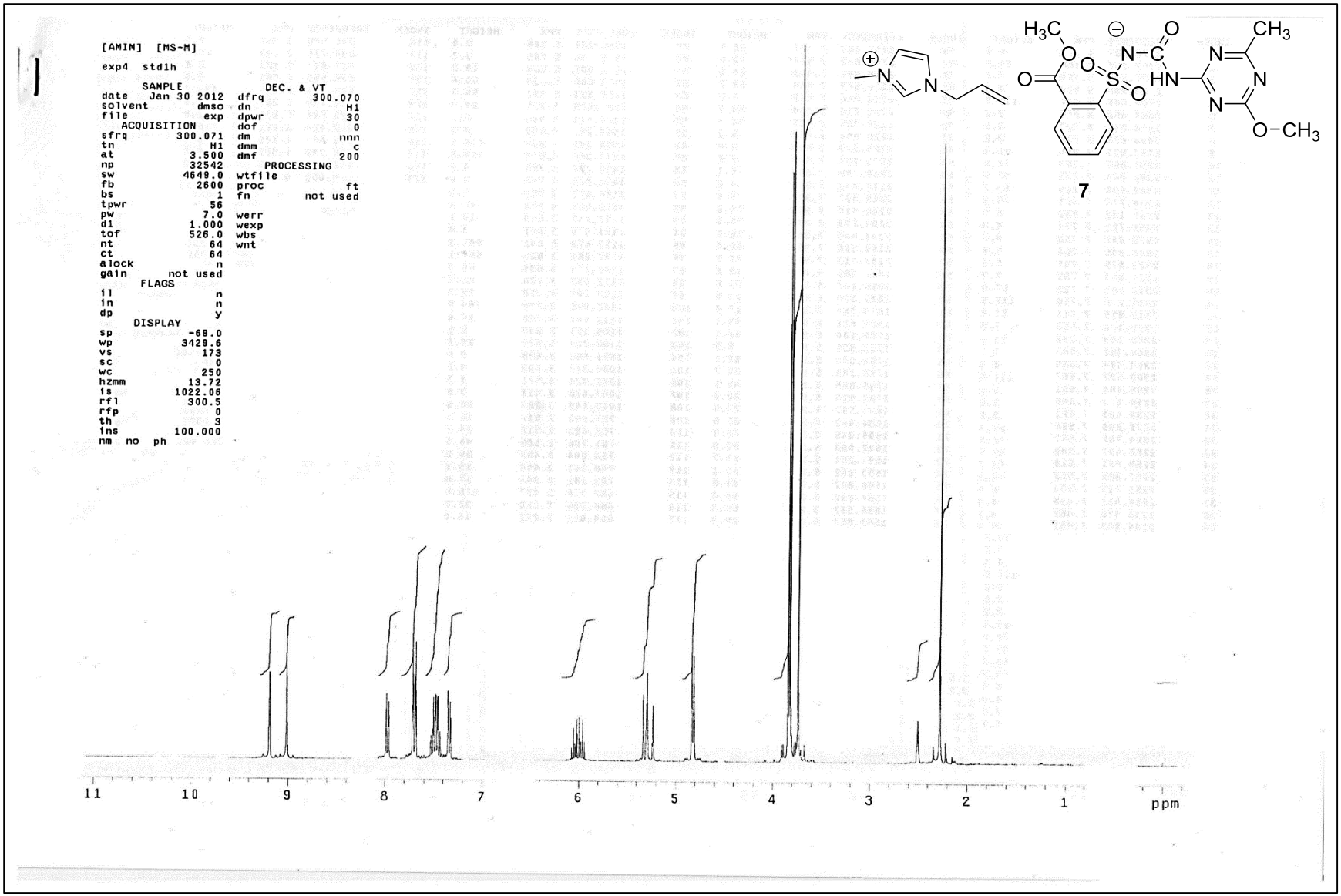

Figure S11. ^{13}C spectrum of compound **8**.

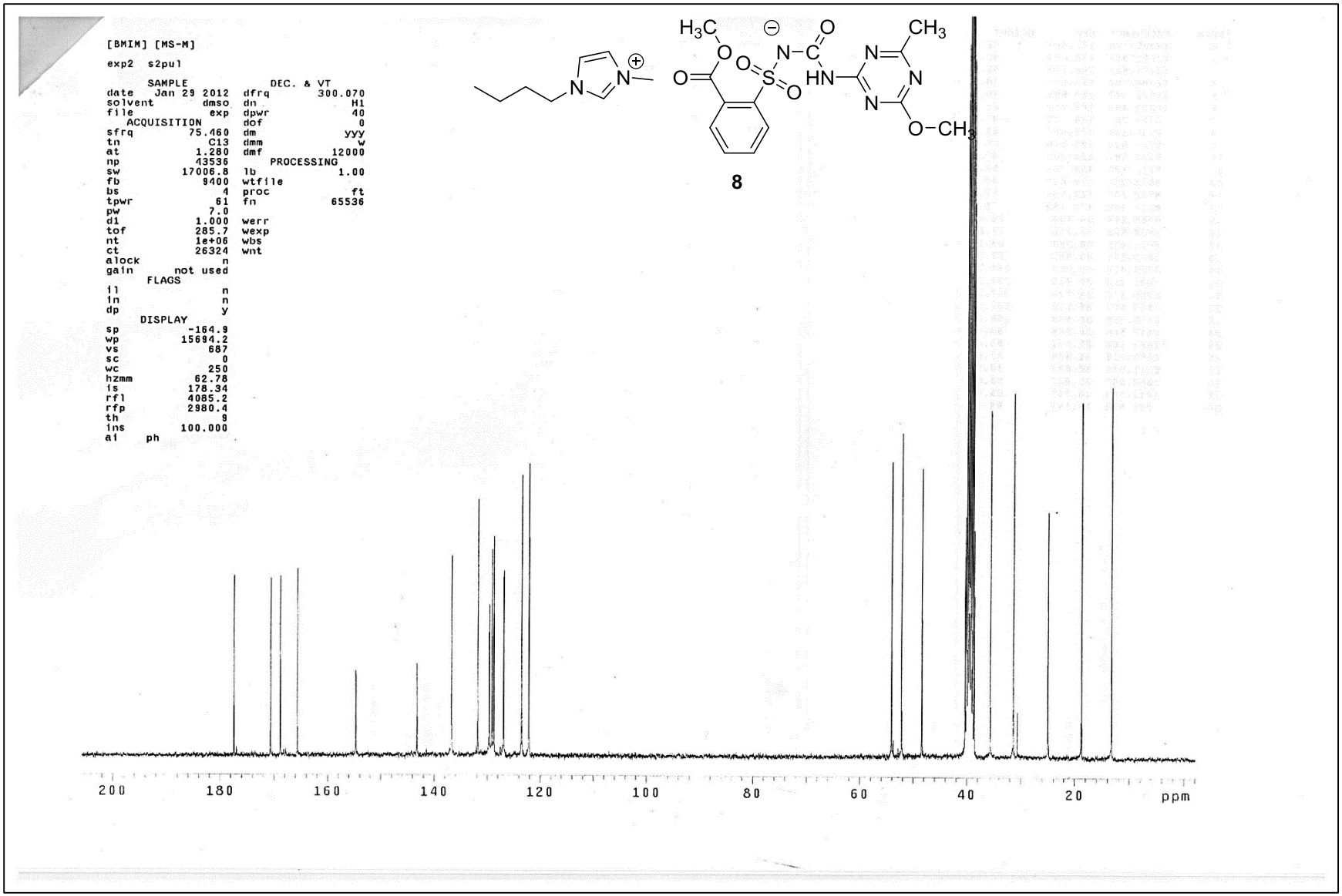

Figure S12. ^{1}H spectrum of compound **8**.

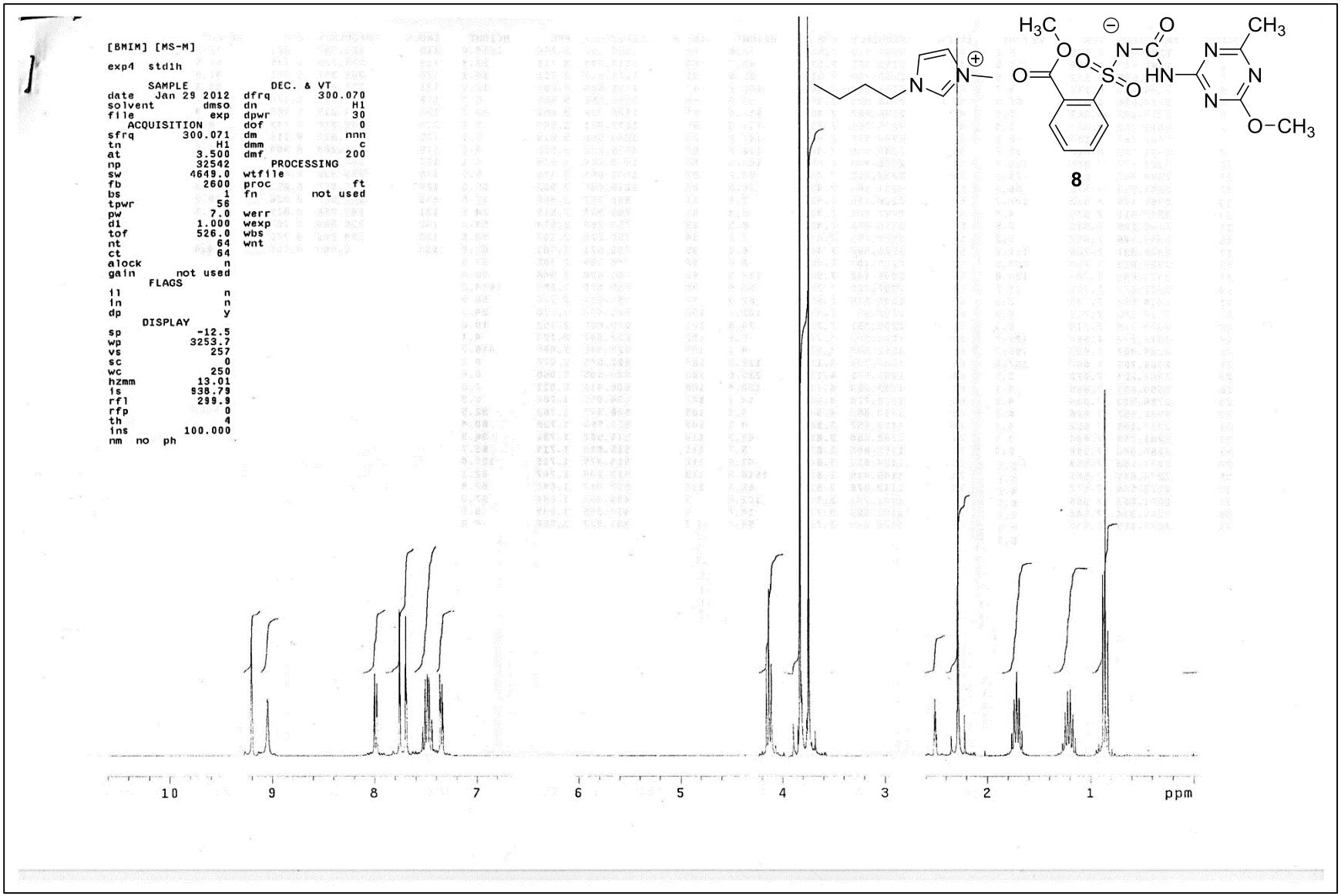

Figure S13. ^{13}C spectrum of compound **9**.

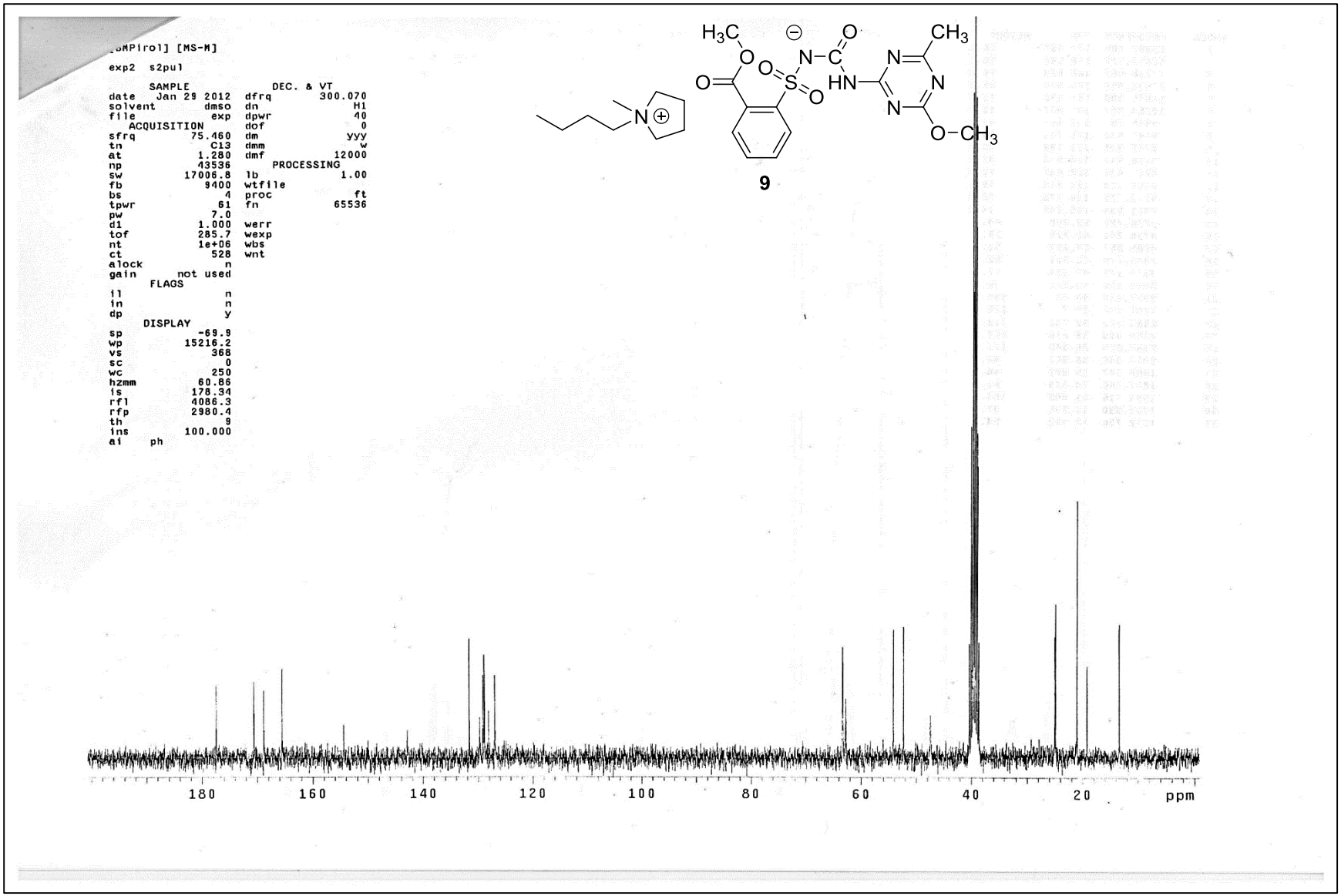

Figure S14. ^{1}H spectrum of compound **9**.

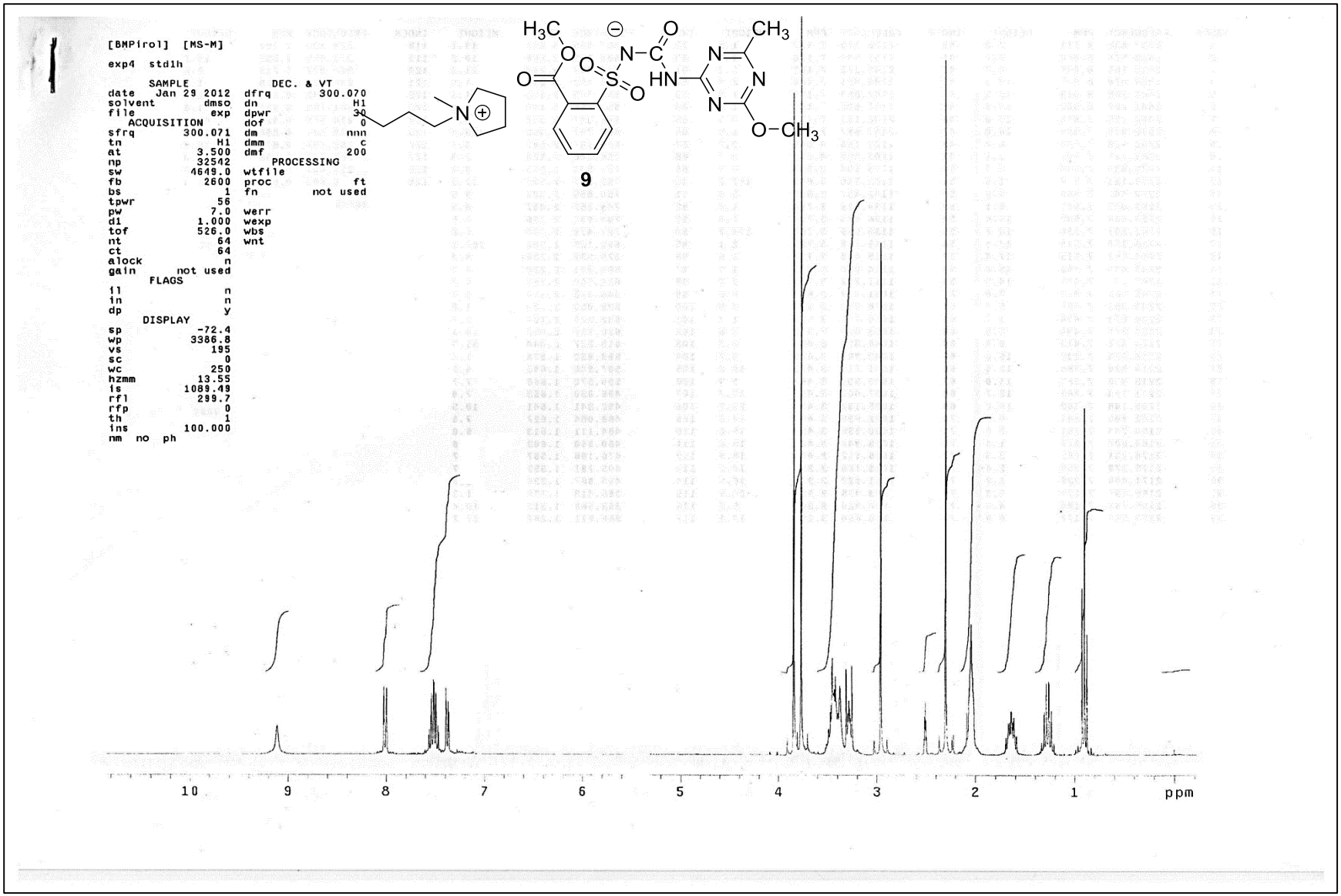

Figure S15. ^{13}C spectrum of compound **10**.

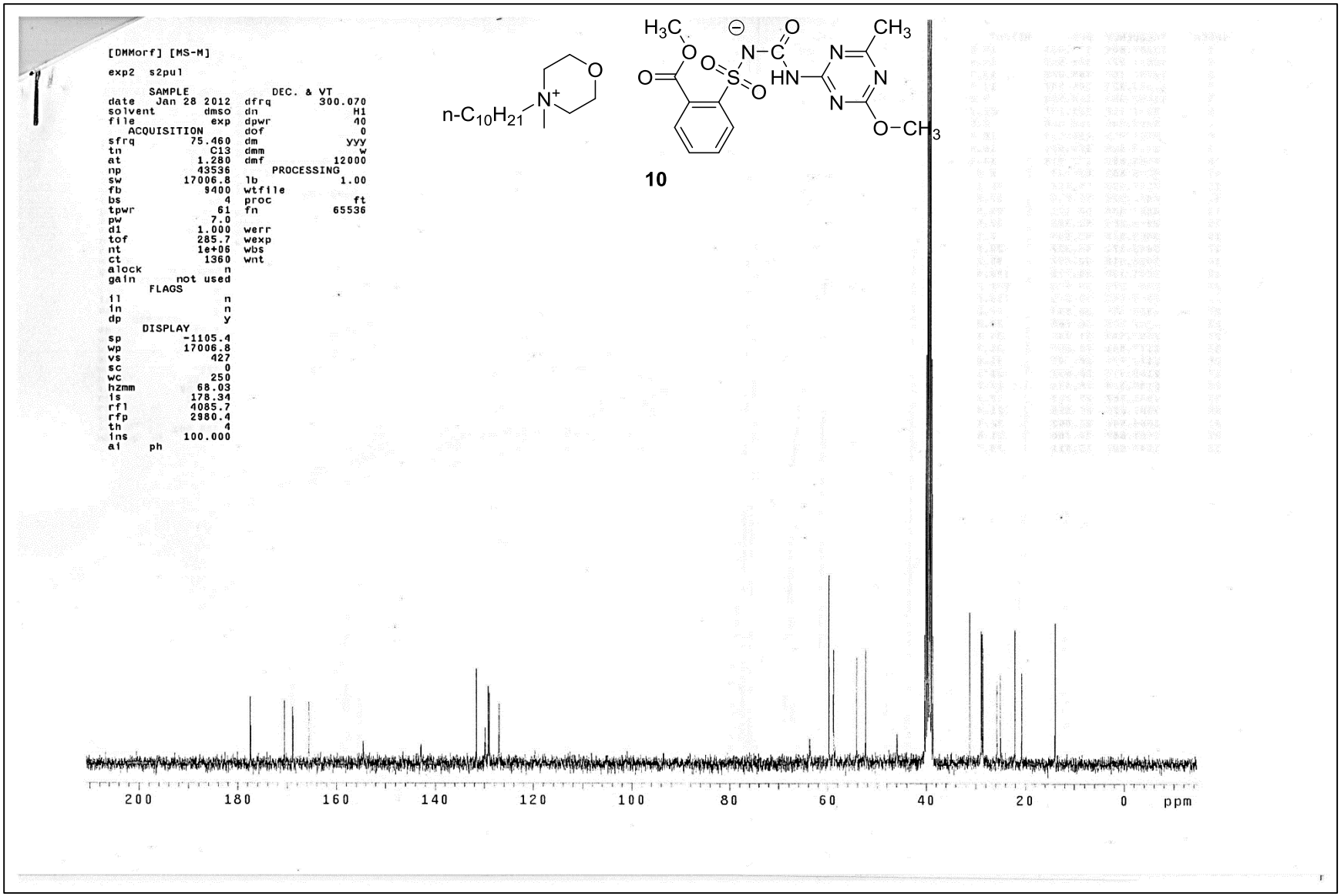

Figure S16. ^{1}H spectrum of compound **10**.

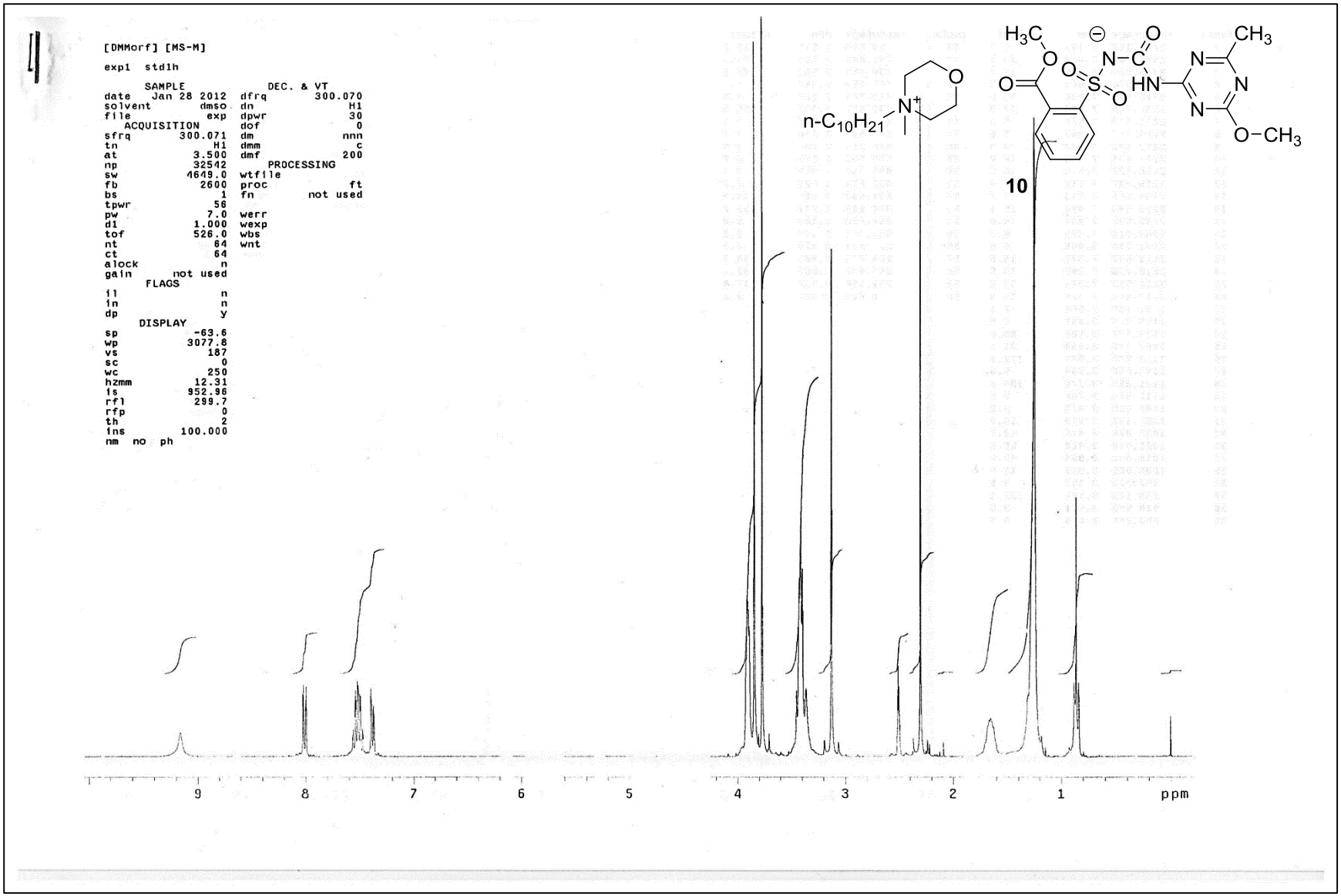

Figure S17. ^{13}C spectrum of compound **11**.

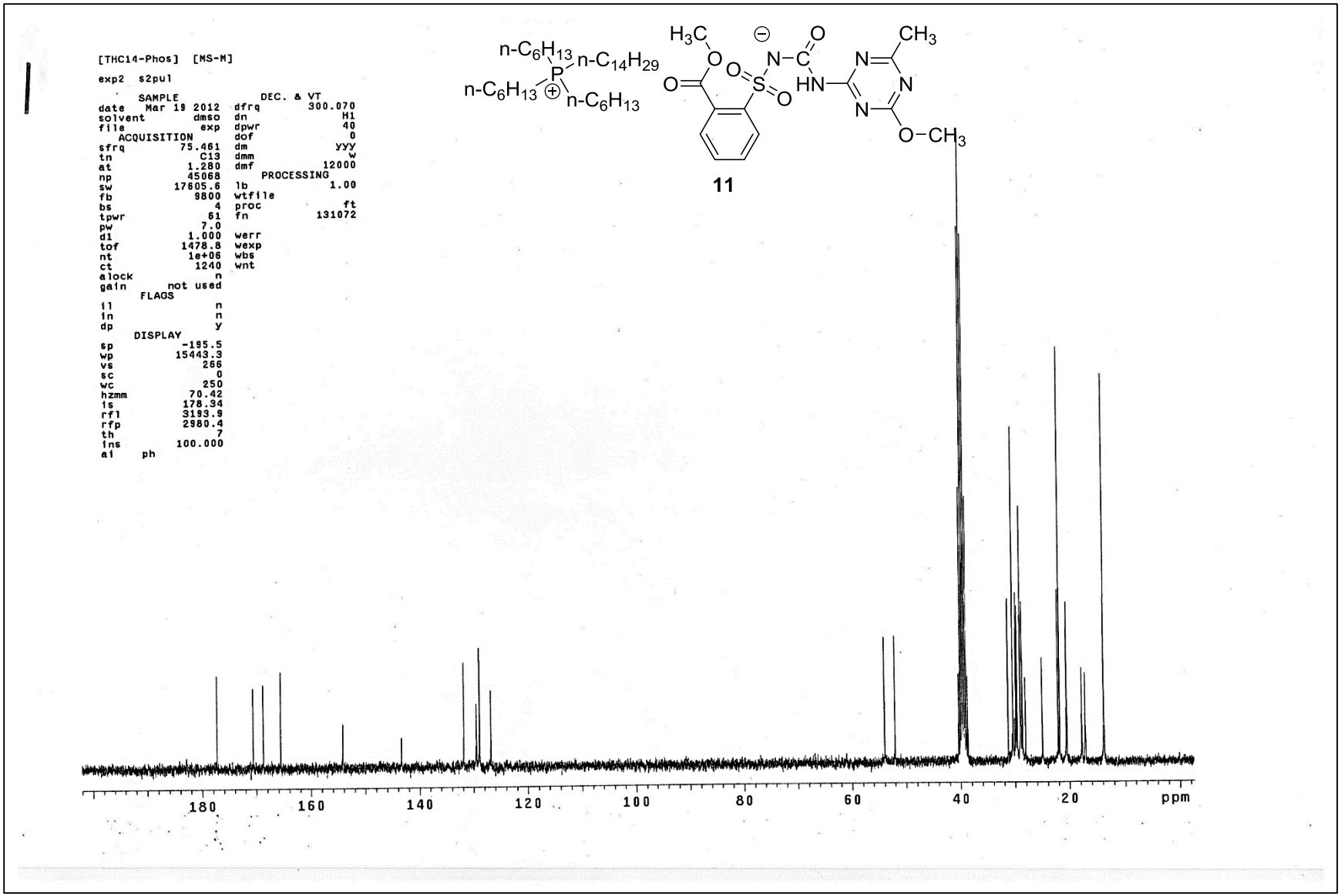

Figure S18. ^{1}H spectrum of compound **11**.

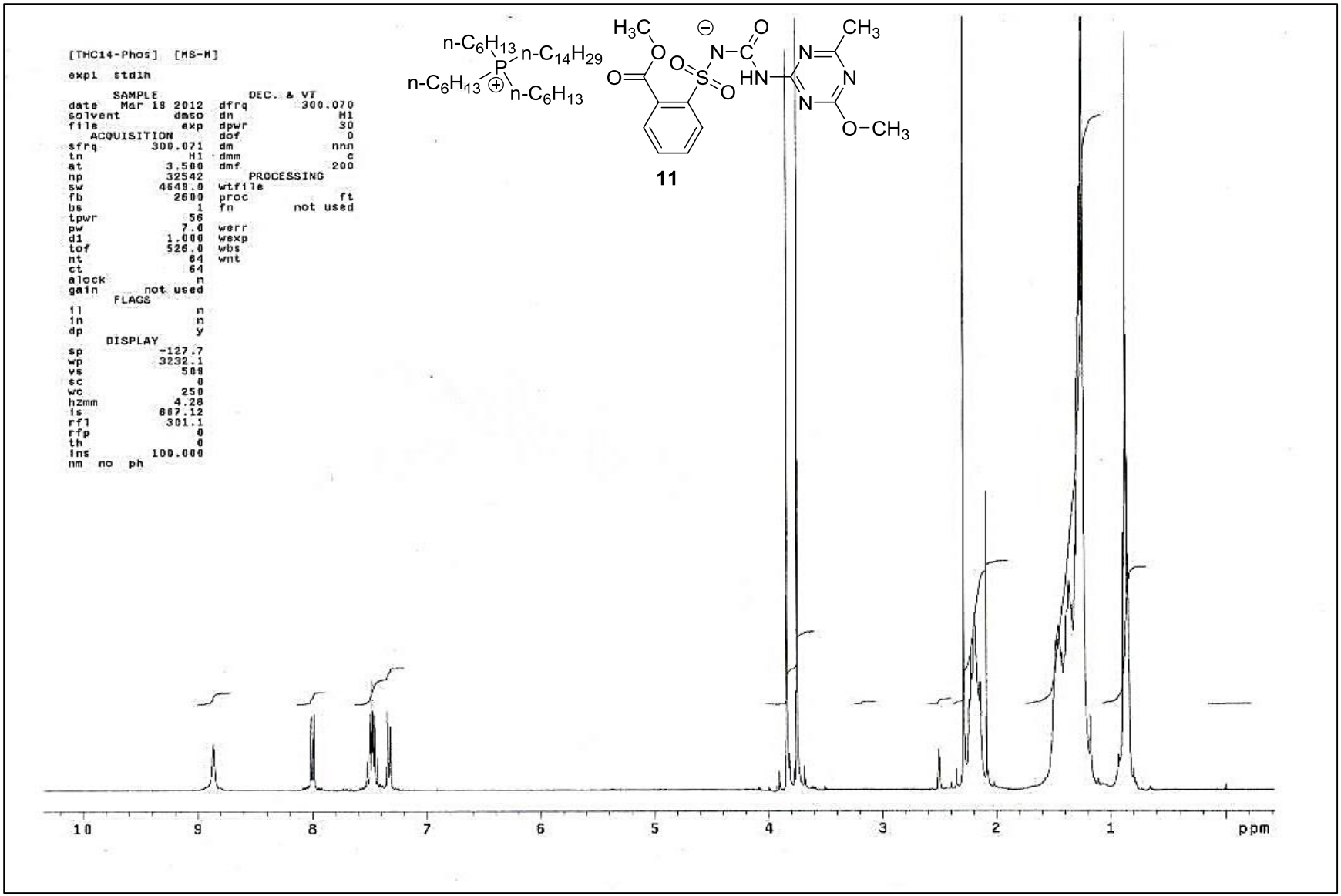

Figure S19. ^{31}P spectrum of compound **11**.

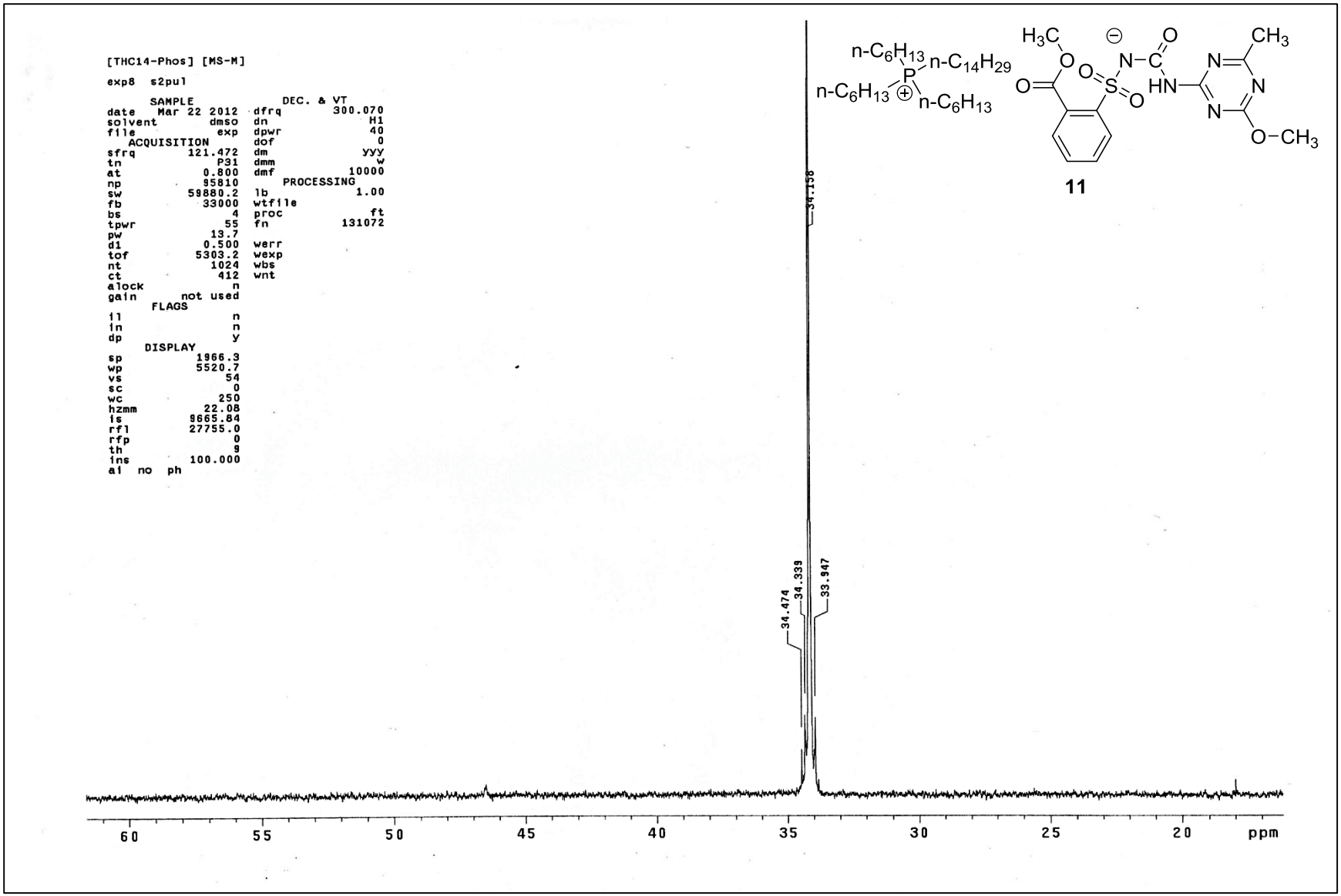

Figure S20. ^{13}C spectrum of compound **12**.

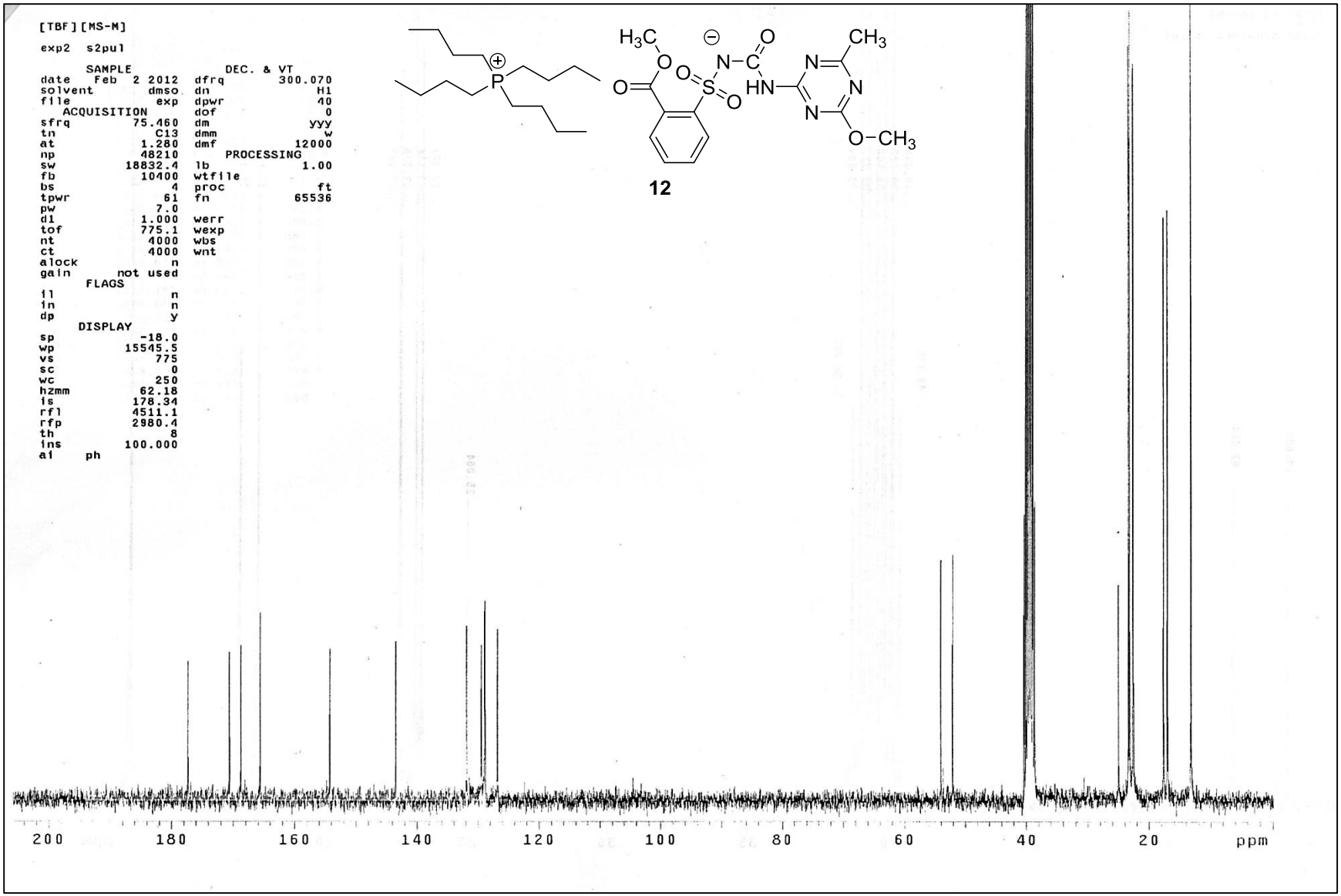

Figure S21. ^{1}H spectrum of compound **12**.