Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Gold Catalyzed Heck-Coupling of Arenediazonium *o*-Benzenedisulfonimides

Margherita Barbero and Stefano Dughera

Supplementary Information

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Physical and spectroscopical data of compounds 4–8

(*E*)-4-Nitrocinnamaldehyde (4a): white solid (150 mg, 84% yield); mp 140–141 °C (from EtOH; lit[1] 138–139 °C). R_f =0.35 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 9.70 (d, J = 7.4 Hz, 1H), 8.21 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 16.0 Hz, 1H), 6.73 (dd, J^1 = 16.0 Hz, J^2 = 7.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 193.3, 149.4, 149.2, 140.1, 131.9, 129.3, 124.3. MS (*m/z,* EI): 177 [M^+] (25), 176 (10), 160 (100), 130 (85). IR (neat) ν (cm^{-1}): 2842, 2773, 1688, 1613, 1535, 1428, 1358, 1225, 1210, 1115, 825.

(*E*)-Ethyl 4-nitrocinnamate (5a); white solid (193 mg, 87% yield); mp 137–138 °C (from EtOH; lit[2] 138–140 °C). R_f =0.45 (petroleum ether/diethyl ether 4:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 8.13 (d, J = 8.6 Hz, 2H), 7.64–7.55 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.2, 148.6, 141.8, 140.7, 128.8, 124.3, 122.7, 60.9,14.4. MS (*m/z,* EI): 221 [M^+] (15), 193 (35), 176 (100), 130 (25). IR (neat) ν (cm^{-1}): 2900, 2851, 1689, 1613, 1555, 1501, 1307, 1235,1119, 1025, 918, 843.

(*E*)-4-Nitrostilbene (6a); white solid (206 mg, 91% yield); mp 156–157 °C (from EtOH; lit[3] 156–157 °C). R_f =0.68 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 8.16 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 9.0 Hz, 2H), 7.52–7.47 (m, 2H), 7.39–7.26 (m, 3H), 7.20–7.11 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.9, 144.0, 136.4, 133.5, 129.1, 127.2, 127.0, 126.4, 124.3, 123.8. MS (*m/z,* EI): 225 [M^+] (75), 178 (100), 152 (20). IR (neat) ν (cm^{-1}):. 2915, 1600, 1513, 1326, 956, 813, 785, 740.

1-(4-Nitrophenyl)cyclopentene (7a); grey solid (127 mg, 67% yield); mp 99–100 °C (from EtOH; lit[4] 99–100 °C). R_f =0.57 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 8.06 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 6.34–6.33 (m, 1H), 2.64–2.60 (m, 2H), 2.54–2.47 (m, 2H), 2.05–1.91 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.4, 143.3, 141.1, 140.7, 132.0, 126.1, 33.9, 33.2, 23.4. MS (*m/z,* EI): 189 [M^+] (100), 172 (10), 142 (80), 128 (90), 115 (55). IR (neat) ν (cm^{-1}): 2984, 2914, 2853, 1603,1553, 1418, 1275, 999, 823

(*E*)-3-(4-Nitrophenyl)but-2-enale (8a): brown solid (150 mg, 78% yield); mp 111–112 °C (from EtOH; lit[5] 110–114 °C). R_f =0.38 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 10.14 (d, J = 7.6 Hz, 1H), 8.21 (d, J = 9.0 Hz, 2H), 7.62 (d, J = 9.0 Hz, 2H), 6.34 (dq, J^1 = 7.6 Hz, J^2 = 1.2 Hz, 1H), 2.54 (d, J = 1.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 191.2, 155.1, 148.6, 147.2, 129.4, 127.4, 124.1, 16.7. MS (*m/z,* EI): 191 [M^+] (15), 190 (20), 174 (100), 144 (85), 115 (100). IR (neat) ν (cm^{-1}): 2912, 2810, 2779, 1667, 1605, 1515, 1410, 1200, 840.

(*E*)-4-Methylcinnamaldehyde (4b): white solid (105 mg, 72% yield); mp 44–45 °C (from EtOH; lit[1] 45–47 °C). R_f=0.45 (petroleum ether/diethyl ether 9.8:0.2). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 9.58 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.19–7.13 (m, 3H), 6.59 (dd, J^1 = 16.0 Hz, J^2 = 7.8 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 194.3, 153.2, 142.2, 131.5, 130.0, 128.7, 127.8, 21.8. MS (*m/z,* EI): 146 [M^+] (25), 145 (25), 131 (100), 115 (40). IR (neat) ν (cm^{-1}): 3000, 2925, 2832, 2777, 1648, 1597, 1435, 1221, 1135, 944, 824.

(*E*)-Ethyl 4-methylcinnamate (5b); viscous oil (131 mg, 68% yield). R_f =0.44 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ =7.54 (d, J = 16.0 Hz, 1H), 7.25 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.26 (d, J = 16.0 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 2.21 (s, 3H),1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.1, 144.7, 140.6, 131.9, 129.7, 128.1, 117.2, 60.4, 21.5, 14.5. MS (*m/z,* EI): 190 [M^+] (45), 145 (100), 115 (35), 91 (15). IR (neat) ν (cm^{-1}): 2975, 2961, 1700, 1603, 1310, 1163, 975, 831.

(*E*)-4-Methylstilbene (6b); white solid (145 mg, 75% yield); mp 117–118 °C (from EtOH; lit[3] 119–120 °C). R_f=0.61 (petroleum ether/diethyl ether 9.8:0.2). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.50–7.05 (m, 11H), 2.33 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.8, 137.7, 134.9, 129.7, 128.9, 128.0, 127.7,126.8, 126.7 21.6. MS (*m/z,* EI): 194 [M^+] (95), 179 (100), 178 (85), 152 (10). IR (neat) ν (cm^{-1}):. 2995, 2935, 1605, 1421, 899, 840, 735, 700.

1-(4-Tolyl)cyclopentene (7b); pale brown solid (99 mg, 63% yield); mp 52–53 °C (from EtOH; lit[6] 54–57 °C). R_f=0.64 (petroleum ether/diethyl ether 9.8:0.2). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.45 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 6.25–6.24 (m, 1H), 2.85–2.82 (m, 2H), 2.78–2.65 (m, 2H), 2.45 (s, 3H), 2.20–2.09 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.7, 136.8, 134.4, 129.3, 125.8, 125.2, 33.7, 33.6, 23.7, 21.5. MS (*m/z,* EI): 158 [M^+] (70), 143 (100), 128 (25), 115 (20). IR (neat) ν (cm^{-1}): 2930, 2845, 1615, 1445, 1215, 1015, 823.

(*E*)-3-(4-Tolyl)but-2-enale (8b): viscous oil (59 mg, 37% yield); R_f =0.43 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 10.14 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.34 (dq, J^1 = 7.6 Hz, J^2 = 1.2 Hz, 1H), 2.54 (d, J = 1.2 Hz, 3H), 2.29 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 187.9, 158.4, 137.8, 137.1, 128.8, 128.4, 126.8, 21.1,16.5. MS (*m/z,* EI): 160 [M^+] (5), 159 (85), 158 (100), 144 (65), 91 (60). IR (neat) ν (cm^{-1}): 2900, 2858, 2799, 1657, 1605, 1400, 830.

(*E*)-4-Bromocinnamaldehyde (4c): white solid (172 mg, 81% yield); mp 79–80 °C (from EtOH; lit[7] 78–79 °C). R_f =0.41 (petroleum ether). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 9.62 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 8.6 Hz, 2H), 7.38–7.30 (m, 3H), 6.61(dd, J^1 = 16.2 Hz, J^2 = 7.6 Hz, 1H); ^{13}C NMR (50

MHz, $CDCl_3$): δ = 193.6, 151.3, 133.1, 132.6,129.9, 129.2, 125.8. MS (*m/z,* EI): 212 (25), 211 (20), 210 [M^+] (25), 209 (20),), 131 (100), 103 (40). IR (neat) ν (cm^{-1}): 3054, 3018, 2803, 2719, 1652, 1600, 1551, 1418, 961, 818.

(*E*)-Ethyl 4-bromocinnamate (5c); viscous oil (229 mg, 90% yield). R_f=0.34 (petroleum ether). ^1H NMR (200 MHz,$CDCl_3$): δ = 7.44 (d, *J* = 16.0 Hz, 1H), 7.33 (d, *J* = 6.8 Hz, 2H), 7.19 (d, *J* = 6.8 Hz, 2H), 6.15 (d, *J* = 16.0 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.7, 143.2, 133.5, 132.2, 129.5, 124.5, 119.1, 60.7,14.5. MS (*m/z,* EI): 256 (45), 254 [M^+] (45), 211 (100), 209 (100), 182 (25), 130 (25), 102 (75). IR (neat) ν (cm^{-1}): 2985, 1700, 1625, 1495, 1222, 995, 831.

(*E*)-4-Bromostilbene (6c); white solid (212 mg, 82% yield); mp 137–138 °C (from EtOH; lit[3] 139–140 °C). R_f=0.41 (petroleum ether). ^1H NMR (200 MHz,$CDCl_3$): δ = 7.47–7.40 (m, 4H), 7.34–7.40 (m, 5H), 7.00 (d, *J* = 3.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.2, 136.5, 132.0, 129.6, 128.9, 128.2, 128.1, 127.6, 126.8, 121.5. MS (*m/z,* EI): 260 (55), 258 [M^+] (55), 179 (80), 178 (100), 152 (10). IR (neat) ν (cm^{-1}): 2991, 1615, 915, 833, 739, 695.

1-(4-Bromophenyl)cyclopentene (7c); pale brown solid (176 mg, 79% yield); mp 95–96 °C (from EtOH; lit[6] 89–97 °C). R_f=0.37 (petroleum ether). ^1H NMR (200 MHz,$CDCl_3$): δ = 7.36 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.15–6.11 (m, 1H), 2.66–2.57 (m, 2H), 2.51–2.42 (m, 2H), 2.04–1.89 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.6, 135.9, 131.3, 127.3, 127.2, 121.1, 33.6, 33.3, 23.5. MS (*m/z,* EI): 224 (45), 222 [M^+] (45), 143 (100), 128 (75), 115 (20). IR (neat) ν (cm^{-1}): 3015, 2911, 1612, 1435, 1398, 958, 818.

(*E*)-3-(4-Bromophenyl)but-2-enale (8c): waxy solid (140 mg, 62% yield); R_f =0.52 (petroleum ether/diethyl ether 9.5:0.5). ^1H NMR (200 MHz,$CDCl_3$): δ = 10.14 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.33 (dq, J^1 = 7.6 Hz, J^2 = 1.2 Hz, 1H), 2.55 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 187.9, 158.4, 138.9, 131.0, 128.8, 127.4, 120.9, 16.3. MS (*m/z,* EI): 226 (15), 225 (20), 224 [M^+] (15), 223 (20) , 145 (100), 115 (75). IR (neat) ν (cm^{-1}): 2998, 2790, 2762, 1661, 1600, 835.

(*E*)-4-Methoxycinnamaldehyde (4d): pale yellow solid (125 mg, 77% yield); mp 59–60 °C (from EtOH; lit[8] 58–60 °C). R_f=0.38 (petroleum ether/diethyl ether 9.8:0.2). ^1H NMR (200 MHz,$CDCl_3$): δ = 9.59 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 16.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.54 (dd, J^1 = 16.0 Hz, J^2 = 7.8 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 194.0, 162.4, 153.1, 130.6, 126.9, 126.6, 114.8, 55.6. MS (*m/z,* EI): 162 [M^+] (100), 161 (75), 147 (15), 131 (60), 119 (30). IR (neat) ν (cm^{-1}): 3012, 2935, 2842, 2778, 1672, 1600, 1375, 1135, 834.

(*E*)-Ethyl 4-methoxycinnamate (5d); waxy solid (188 mg, 91% yield). R_f =0.41 (petroleum ether/diethyl ether 9.5: 0.5). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.65 (d, J = 16.0 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H), 6.83 (d, J =8.8 Hz, 2H), 6.24 (d, J = 16.0 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.77 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.6, 161.5, 144.5, 129.9, 127.3, 115.9, 114.5, 60.5, 55.5, 14.5. MS (*m/z,* EI): 206 [M^+] (85), 178 (10), 161 (100), 134 (35). IR (neat) ν (cm^{-1}): 2980, 2910, 1710, 1633, 1512, 1243, 839.

(*E*)-4-Methoxystilbene (6d); pale grey solid (187 mg, 89% yield); mp 134–135 °C (from EtOH; lit[3] 136 °C). R_f =0.49 (petroleum ether/diethyl ether 9.8:0.2). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.51–7.20 (m, 7H), 7.02 (d, J = 8.8 Hz, 2H); 6.89 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.6, 137.9, 130.4, 128.9, 128.5, 128.0, 127.5, 126.8, 126.5, 114.4, 55.5. MS (*m/z,* EI): 210 [M^+] (100), 195 (15) 179 (10), 165 (20), 152 (15). IR (neat) ν (cm^{-1}): 2991, 1600, 1443, 1294, 1115, 945, 835, 748, 691.

1-(4-Methoxyphenyl)cyclopentene (7d); pale brown solid (141 mg, 81% yield); mp 84–85 °C (from EtOH; lit[6] 84–89 °C). R_f =0.42 (petroleum ether/diethyl ether 9.8: 0.2). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.32 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.01–5.97 (m, 1H), 3.75 (s, 3H), 2.67–2.57 (m, 2H), 2.51–2.41 (m, 2H), 2.02–1.87 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.3, 129.9, 129.4, 126.9, 124.1, 113.9, 55.4, 33.5, 33.2, 23.6. MS (*m/z,* EI): 174 [M^+] (100), 173 (60), 159 (25), 143 (35). IR (neat) ν (cm^{-1}): 3000, 2894, 1621, 1502, 1415, 928, 835.

(*E*)-3-Nitrocinnamaldehyde (4e): white solid (145 mg, 82% yield); mp 117–118 °C (from EtOH; lit[9] 78–79 °C). R_f = 0.32 (petroleum ether/diethyl ether 9:1).^{1}H NMR (200 MHz,$CDCl_3$): δ = 9.70 (d, J = 7.4 Hz, 1H), 8.37–8.36 (m, 1H), 8.26–8.21 (m, 1H), 7.86–7.82 (m, 1H), 7.63–7.44 (m, 2H), 6.75 (dd, J^1 = 16.0 Hz, J^2 = 7.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 193.2, 149.4, 148.9, 135.9, 133.9, 130.9, 130.4, 125.5, 123.1. MS (*m/z,* EI): 177 [M^+] (25), 160 (100), 130 (50), 102 (40); IR (neat) ν (cm^{-1}): 2852, 2741, 1668, 1600, 1514, 1339, 1215, 1201, 1112, 827.

(*E*)-Ethyl 3-nitrocinnamate (5e); white solid (193 mg, 87% yield); mp 74–75 °C (from EtOH; lit[10] 73–74 °C). R_f =0.40 (petroleum ether/diethyl ether 4:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 8.33–8.31 (m, 1H), 8.19–8.14 (m, 1H), 7.78–7.48 (m, 3H), 6.51 (d, J = 16.0 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.2, 148.8, 141.8, 136.3, 133.8, 130.1, 124.6, 122.5, 121.6, 61.0, 14.4. MS (*m/z,* EI): 221 [M^+] (15), 193 (35), 176 (100), 160 (15). IR (neat) ν (cm^{-1}): 2918, 2862, 1700, 1631, 1592, 1498, 1343, 1181, 1064, 920, 763.

(*E*)-3-Nitrostilbene (6e); white solid (202 mg, 90% yield); mp 106–107 °C (from EtOH; lit[11] 104–106 °C). R_f =0.62 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 8.31–8.29 (m,

1H), 8.06–8.00 (m, 1H), 7.75–7.71 (m, 1H), 7.51–7.09 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.9, 139.3, 136.4, 132.4, 131.9, 129.7, 129.0, 128.7, 127.1, 126.2, 122.2, 121.0. MS (*m/z,* EI): 225 [M^+] (80), 178 (100), 152 (20). IR (neat) ν (cm^{-1}): 3026, 1610, 1520, 1490, 1330, 928, 798, 753, 720.

1-(3-Nitrophenyl)cyclopentene (7e); grey solid (130 mg, 69% yield); mp 77–78°C (from EtOH). Calcd for $C_{11}H_{11}NO_2$: C 69.83%; H 5.86%; N 7.40%; found: C 69.91%; H 5.88%; N 7.34%. R_f=0.59 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 8.18–8.16 (m, 1H), 8.01–7.98 (m, 1H), 7.69–7.65 (m, 1H), 7.44–7.36 (m, 1H), 6.31–6.27 (m, 1H), 2.72–2.64 (m, 2H), 2.57–2.47 (m, 2H), 2.08–1.93 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.5, 140.6, 138.5, 131.5, 129.7, 129.2, 121,4, 120.2, 33.7, 33.2, 23.4. MS (*m/z,* EI): 189 [M^+] (100), 172 (25), 142 (90), 128 (95), 115 (65). IR (neat) ν (cm^{-1}): 2981, 2904, 1614, 1512, 1437, 1252, 1100, 982, 784.

(*E*)-3-(3-Nitrophenyl)but-2-enale (8e): pale brown solid (150 mg, 76% yield); mp 98–99 °C (from EtOH.). R_f =0.40 (petroleum ether/diethyl ether 9:1). Calcd for $C_{10}H_9NO_3$: C 62.82%; H 4.74%; N 7.33%; found: C 62.86%; H 4.76%; S 7.28%. ^{1}H NMR (200 MHz,$CDCl_3$): δ = 10.14 (d, J = 7.6 Hz, 1H), 8.35–8.32 (m, 1H), 8.25–8.19 (m, 1H), 7.83–7.79 (m, 1H), 7.60–7.52 (m, 2H), 6.35 (dq, J^1 = 7.6 Hz, J^2 = 1.2 Hz, 1H), 2.56 (d, J = 1.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 191.1, 148.6, 142.4, 134.5, 132.3, 130.1, 128.8, 124.6, 121.4, 16.6. MS (*m/z,* EI): 191 [M^+] (25), 190 (20), 174 (100), 144 (85), 115 (100). IR (neat) ν (cm^{-1}): 2900, 2842, 2777, 1664, 1600, 1535, 1220, 832.

(*E*)-Ethyl 2-nitrocinnamate (5f); white solid (202 mg, 90% yield); mp 43–44 °C (from EtOH; lit[4] 42–43 °C). R_f =0.40 (petroleum ether/diethyl ether 4:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.95–7.82 (m, 1H), 7.91 (d, J = 16.0 Hz, 1H), 7.51–7.34 (m, 3H), 6.21 (d, J = 16.0 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.9, 148.4, 139.9, 133.7, 130.5, 129.2, 124.9, 123.3, 119.4, 61.0, 19.9, 14.3. MS (*m/z,* EI): 176 [M^+] (70), 147 (60), 130(100), 120 (55), 102 (45), 92 (70). IR (neat) ν (cm^{-1}) 2986, 1715, 1601, 1552, 1424, 1365, 1243, 1141, 997, 754.

(*E*)-Ethyl 2-methylcinnamate (5g); viscous oil (67 mg, 35% yield); R_f =0.54 (petroleum ether/diethyl ether 9:1). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.92 (d, J = 16.0 Hz, 1H), 7.51–7.46 (m, 1H), 7.25–7.12 (m, 3H), 6.31 (d, J = 16.0 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 162.2, 142.5, 137.8, 133.6, 130.9, 130.1, 126.6, 126.5, 119.4, 60.7, 19.9, 14.5. MS (*m/z,* EI): 176 [M^+] (20), 145 (100), 115 (75). IR (neat) ν (cm^{-1}) 2924, 1700, 1612, 1444, 1112, 787.

(*E*)-Ethyl 2-iodocinnamate (5h); viscous oil (86 mg, 28% yield); R_f =0.42 (petroleum ether). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.86–7.78 (m, 2H), 7.50–7.45 (m, 1H), 7.33–7.23 (m, 1H), 7.00–6.92 (m, 1H), 6.23 (d, *J* = 16.0 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.4, 147.8, 140.2, 137.9, 131.4, 128.7, 127.5, 120.9, 101.4, 60.8, 14.5. MS (*m/z,* EI): 302 [M^+] (5), 257 (20), 175 (45), 147 (100), 130 (35), 102 (35). IR (neat) ν (cm^{-1}) 2900, 1711, 1602, 1399, 1114, 753.

***(E)*-3-(2-Methoxycarbonyl-3-thienyl)prop-2-enale (4i);** white solid (165 mg, 86% yield); mp 91–92°C (from EtOH); R_f =0.51 (petroleum ether/diethyl ether 9.5:0.5). Calcd for $C_9H_8O_3S$: C 55.09%; H 4.11%; S 16.34%; found: C 55.21%; H 4.06%; S 16.31%. ^{1}H NMR (200 MHz,$CDCl_3$): δ = 9.70 (d, *J* = 7.8 Hz, 1H), 8.39 (d, *J* = 16.0 Hz, 1H), 7.46 (d, *J* = 5.4 Hz, 1H), 7.32 (d, *J* = 5.4 Hz, 1H), , 6.55 (dd, J^1 = 16.0 Hz, J^2 = 7.8 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 194.5, 162.3, 144.1, 141.9, 131.9, 131.7, 131.3, 126.8, 52.6. MS (*m/z,* EI): 167 [M^+-29] (100), 152 (12), 137 (45), 109 (15). IR (neat) ν (cm^{-1}): 3001, 2995, 2815, 2777, 1710, 1665, 1512, 987.

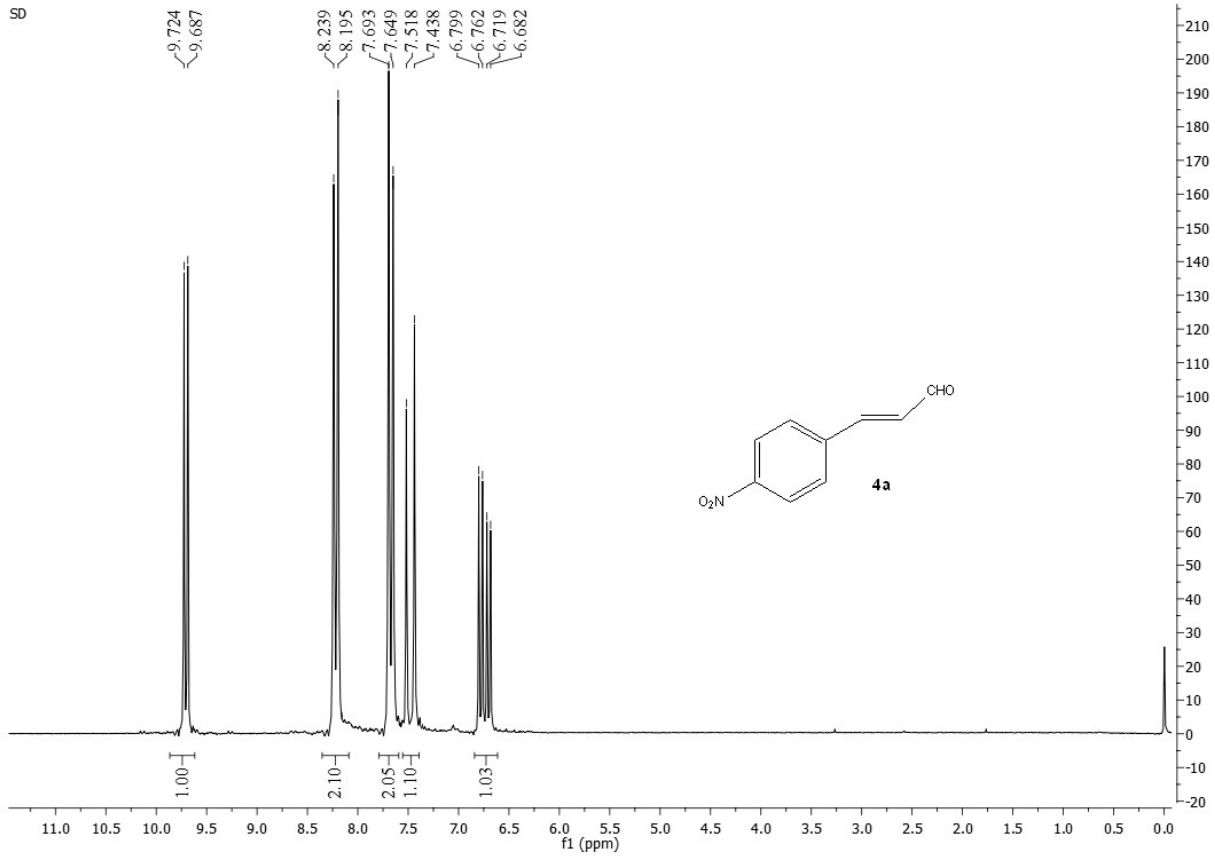
(*E*)-Ethyl (2-methoxycarbonyl-3-thienyl)acrilate (5i); pale orange solid (219 mg, 91% yield); mp 66–67 °C (from EtOH; lit[4] 65–66 °C); R_f =0.38 (petroleum ether/diethyl ether 9.5:0.5). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 8.42 (d, *J* = 16 Hz, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.26 (d, *J* = 5.2 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.84 (s,3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.8, 166.2, 141.9, 136.5, 131.0, 126.7, 122.1, 60.7, 52.3, 14.4. MS (*m/z,* EI): 240 [M^+] (5), 195 (15), 167(100). IR (neat) ν (cm^{-1}): 2974, 2854, 1701, 1695, 1555, 1445, 922.

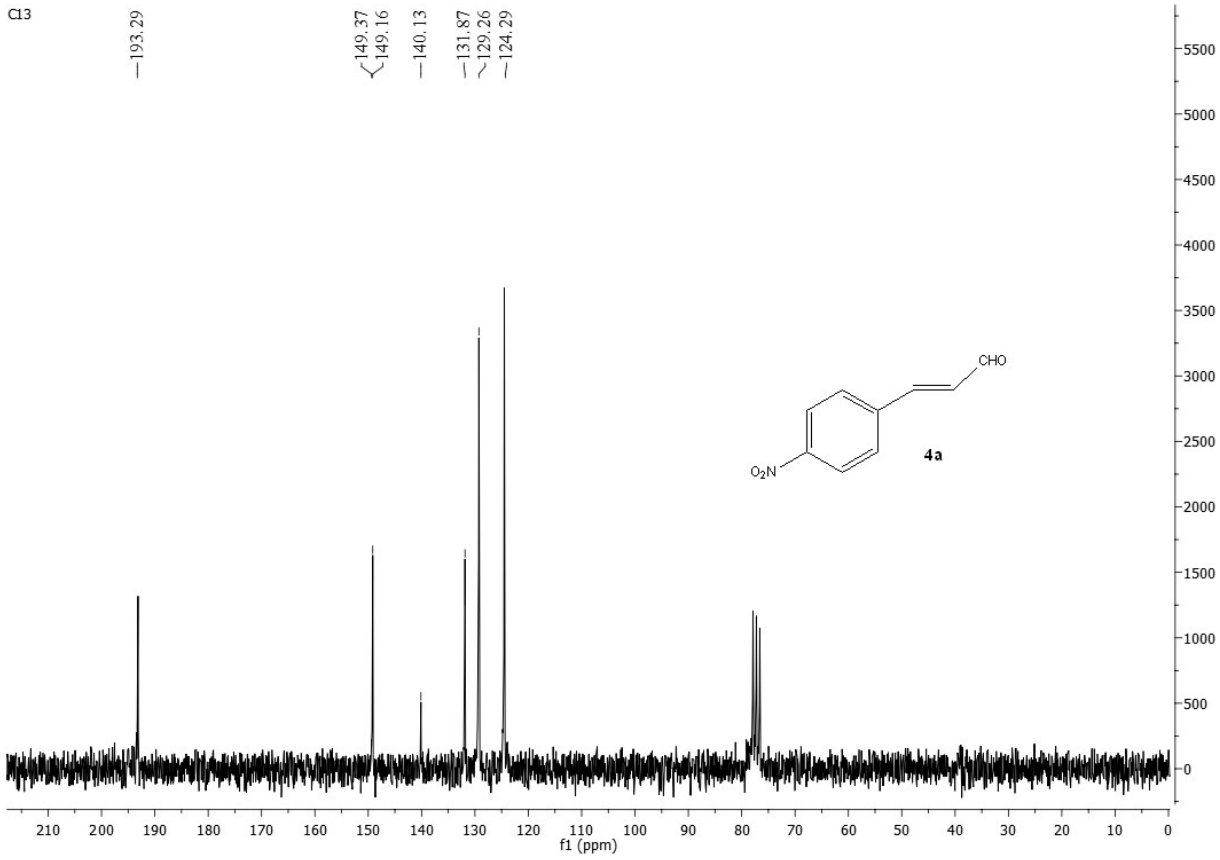
***(E)*-Methyl 3-styrylthiophene-2-carboxylate (6i);** pale brown solid (206 mg, 84% yield); mp 81–82°C (from EtOH; ; lit[12] 83–84 °C); R_f =0.45 (petroleum ether/diethyl ether 9.5:0.5) . ^{1}H NMR (200 MHz,$CDCl_3$): δ = 8.11 (d, *J* = 16.6 Hz, 1H), 7.55–7.51 (m, 2H), 7.40–7.20 (m, 5H), 7.05 (d, *J* = 16.6 Hz, 1H) 3.85 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.2, 145.8, 137.2, 133.1, 130.7, 128.9, 128.5, 127.2, 126.5, 126.3, 122.1, 52.2. MS (*m/z,* EI): 244 [M^+] (90), 211 (20), 185 (100), 184 (85). IR (neat) ν (cm^{-1}): 3012, 2991, 1704, 1612, 1225, 987, 734, 699.

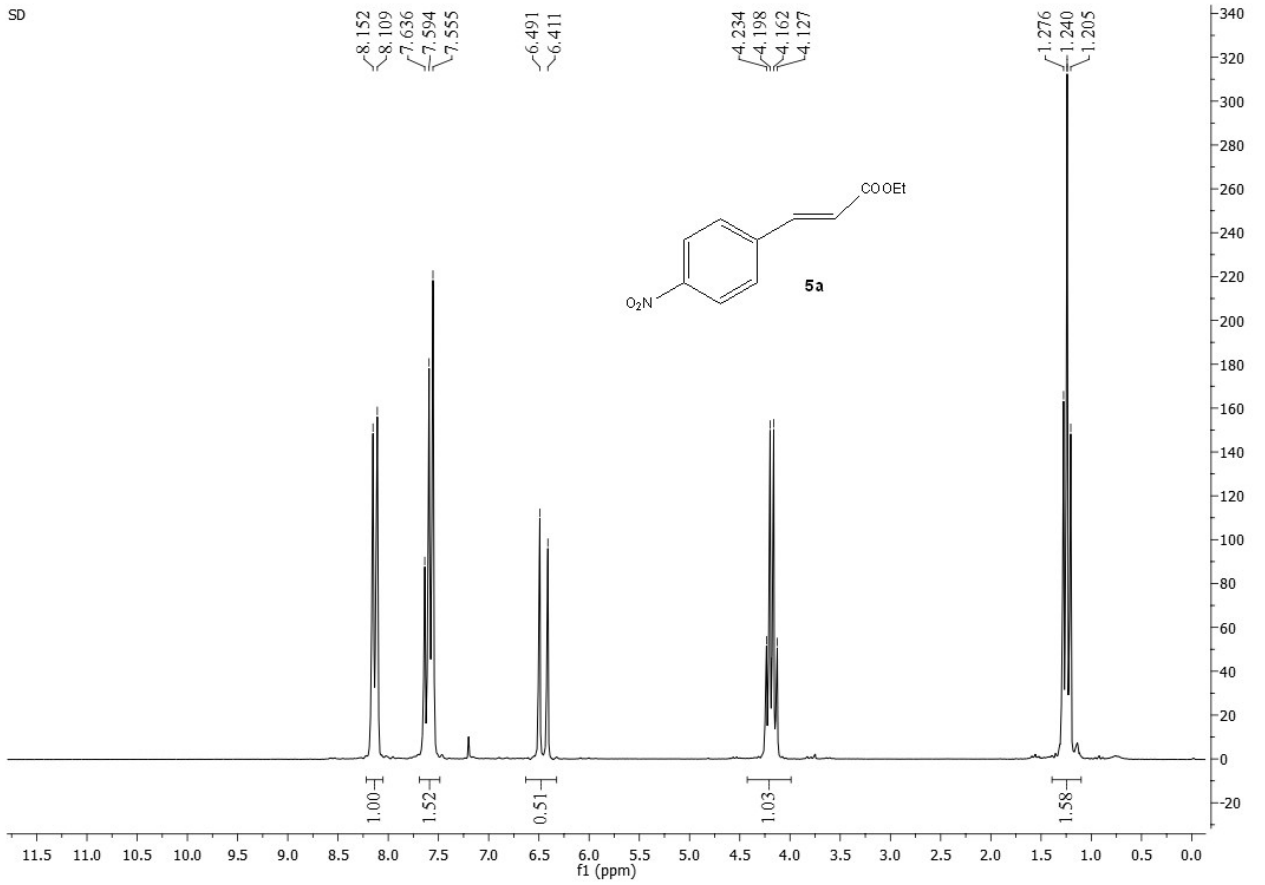
Methyl 3-(cyclopent-1-enyl)thiophene-2-carboxylate (7i); waxy solid (133 mg, 64% yield); R_f =0.58 (petroleum ether/diethyl ether 9.5:0.5). ^{1}H NMR (200 MHz,$CDCl_3$): δ = 7.31 (d, *J* = 5.2 Hz, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 6.11–6.06 (m, 1H),3.74 (s, 3H), 2.71–2.62 (m, 2H), 2.50–2.36 (m, 2H), 2.01–1.87 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 162.8, 145.6, 138.3, 132.3, 130.7, 129.9, 128.7, 52.0, 33.6, 32.5, 24.0. MS (*m/z,* EI): 208 [M^+] (85), 176 (85), 185 (100), 148 (45), 147 (50). IR (neat) ν (cm^{-1}): 3000, 2941, 1712, 1442, 1312, 1054, 991.

***(E)*-3-(2-Methoxycarbonyl-3-thienyl)but-2-enale (8i);** white solid (165 mg, 78% yield); mp 87–88°C (from EtOH); R_f=0.47 (petroleum ether/diethyl ether 9.5:0.5). Calcd for $C_{10}H_{10}O_3S$: C 57.13%; H 4.79%; S 22.83%; found: C 57.08%; H 4.82%; S 22.81%. ^{1}H NMR (200 MHz,$CDCl_3$): δ = 10.07 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 5.4 Hz, 1H), 6.85 (d, J = 5.4 Hz, 1H), 5.91 (dq, J^1 = 8.0 Hz, J^2 = 1.4 Hz, 1H), 3.77 (s, 3H), 2.43 (d, J = 1.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 191.1, 161.9, 131.8, 131.5, 130.2, 130.1, 129.8, 129.4, 52.5, 16.6. MS (*m/z,* EI): 181 [M^+ - 29] (100), 151 (75), 121 (15), IR (neat) ν (cm^{-1}): 3000, 2956, 2845, 2792, 1700, 1645, 1500, 983.

NMR spectra of compounds 4–8



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5a
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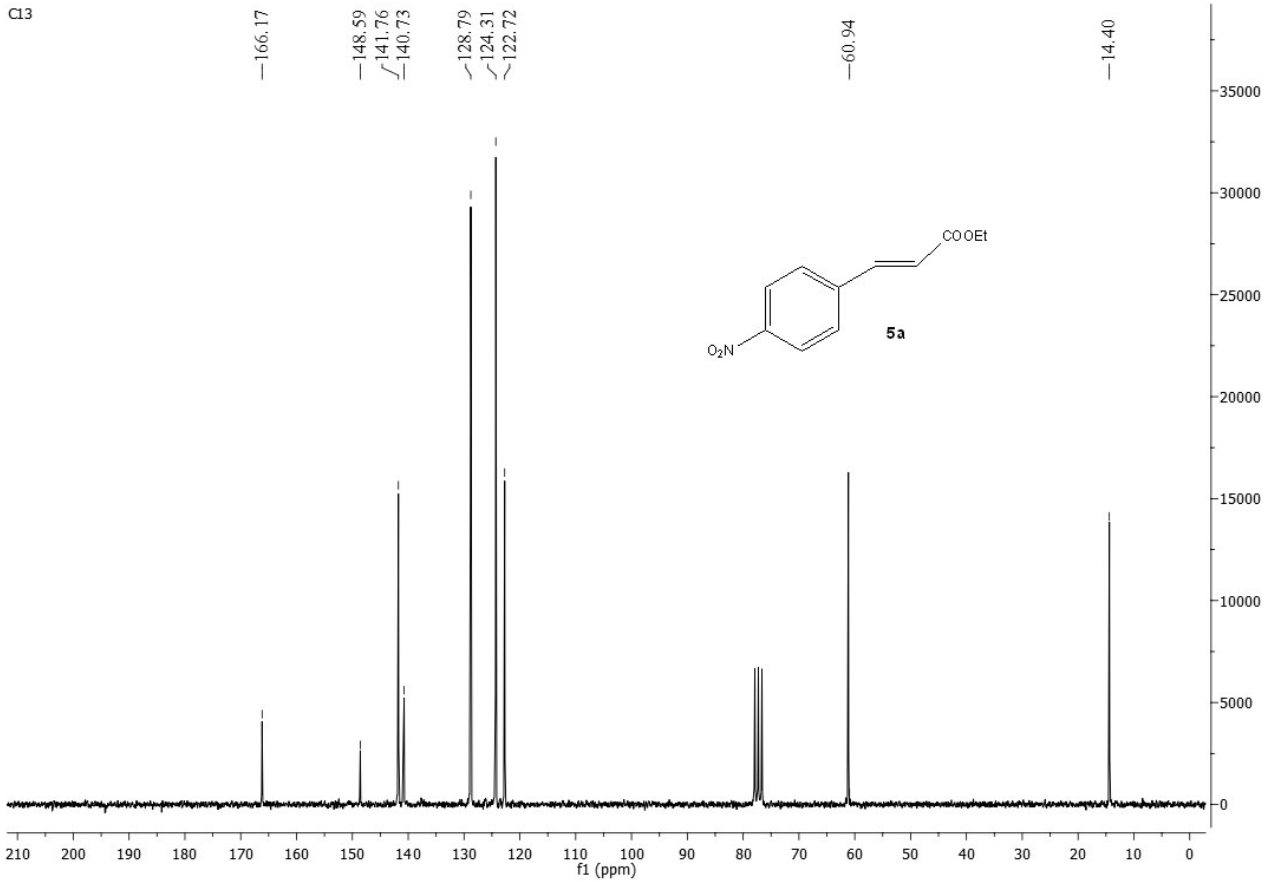
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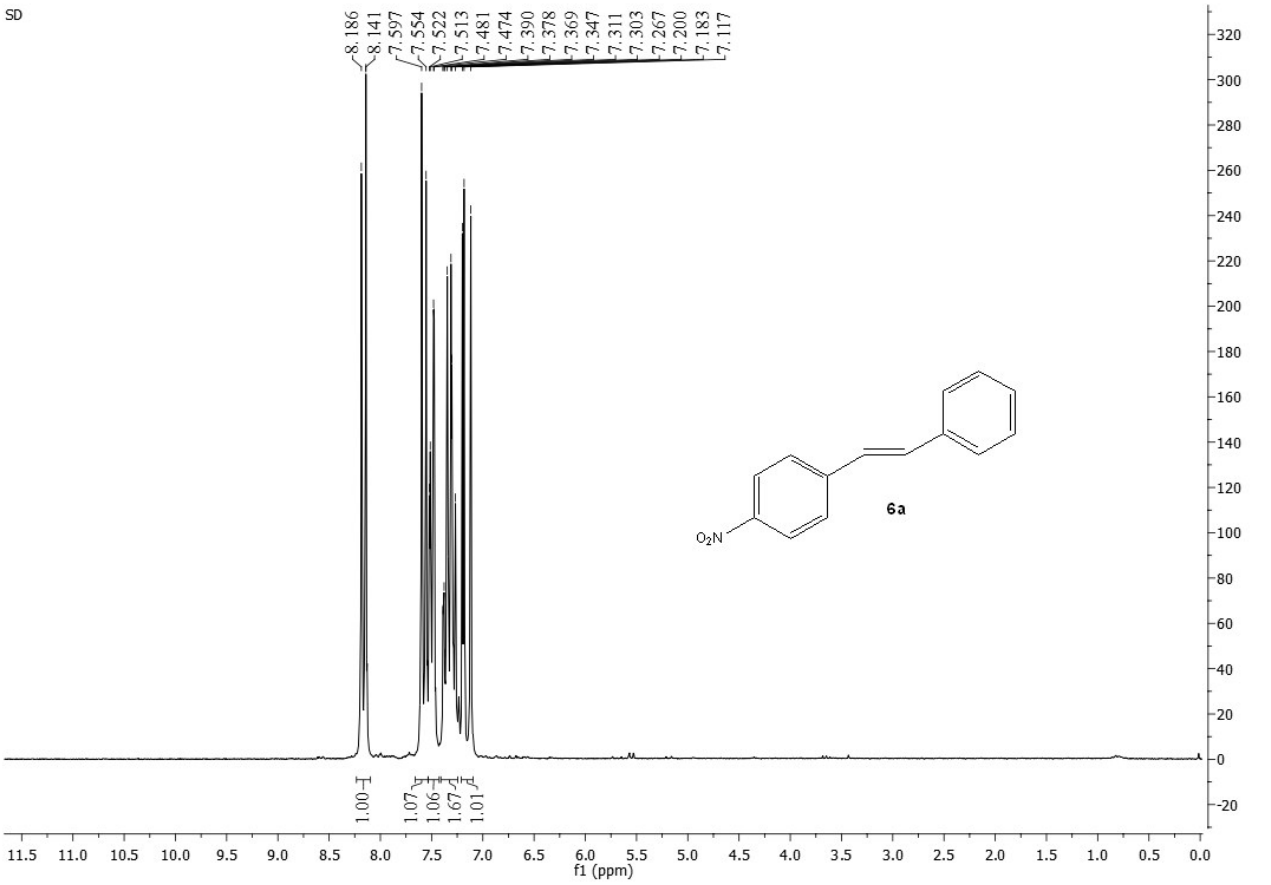
f1 (ppm)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7.303
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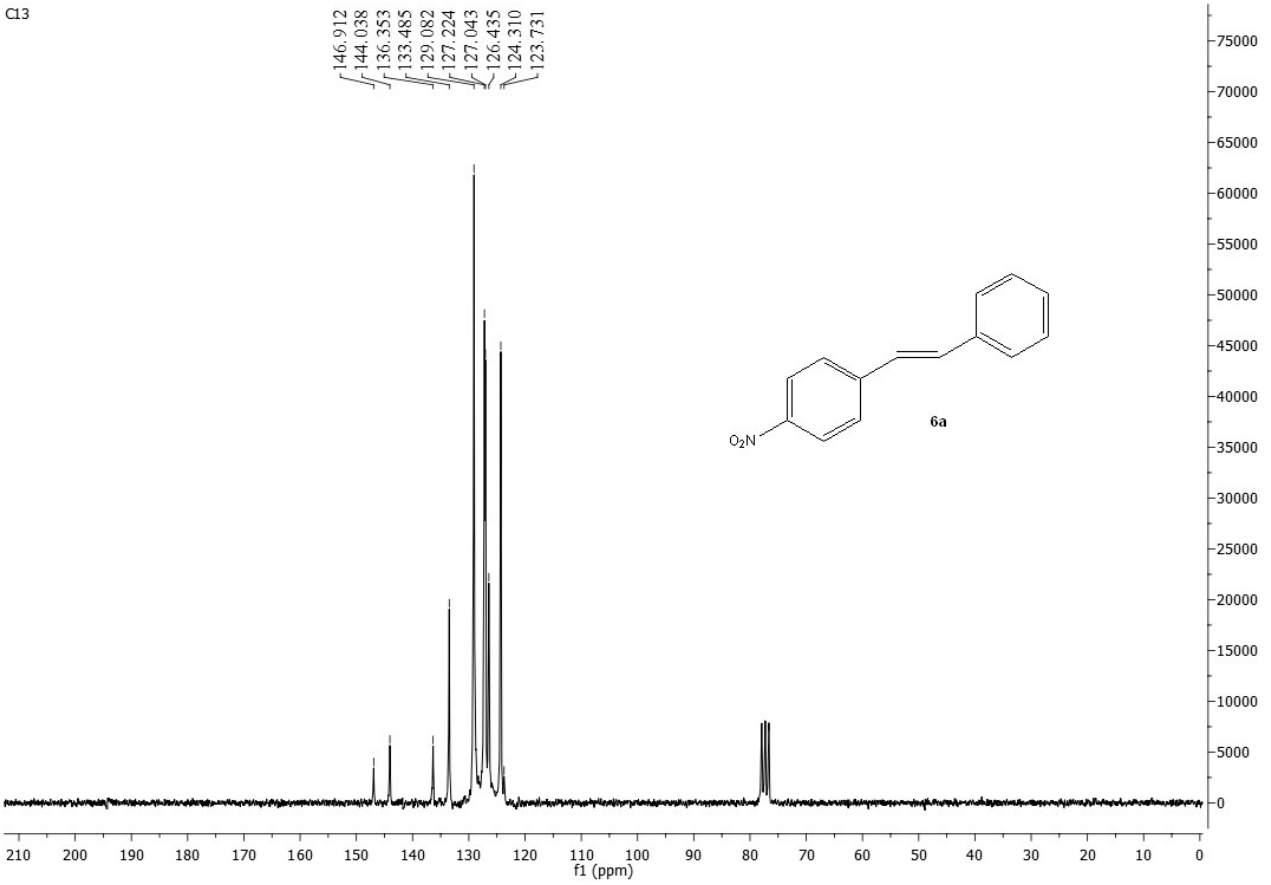
1.07
1.06
1.67
1.01
6a
O2N
f1 (ppm)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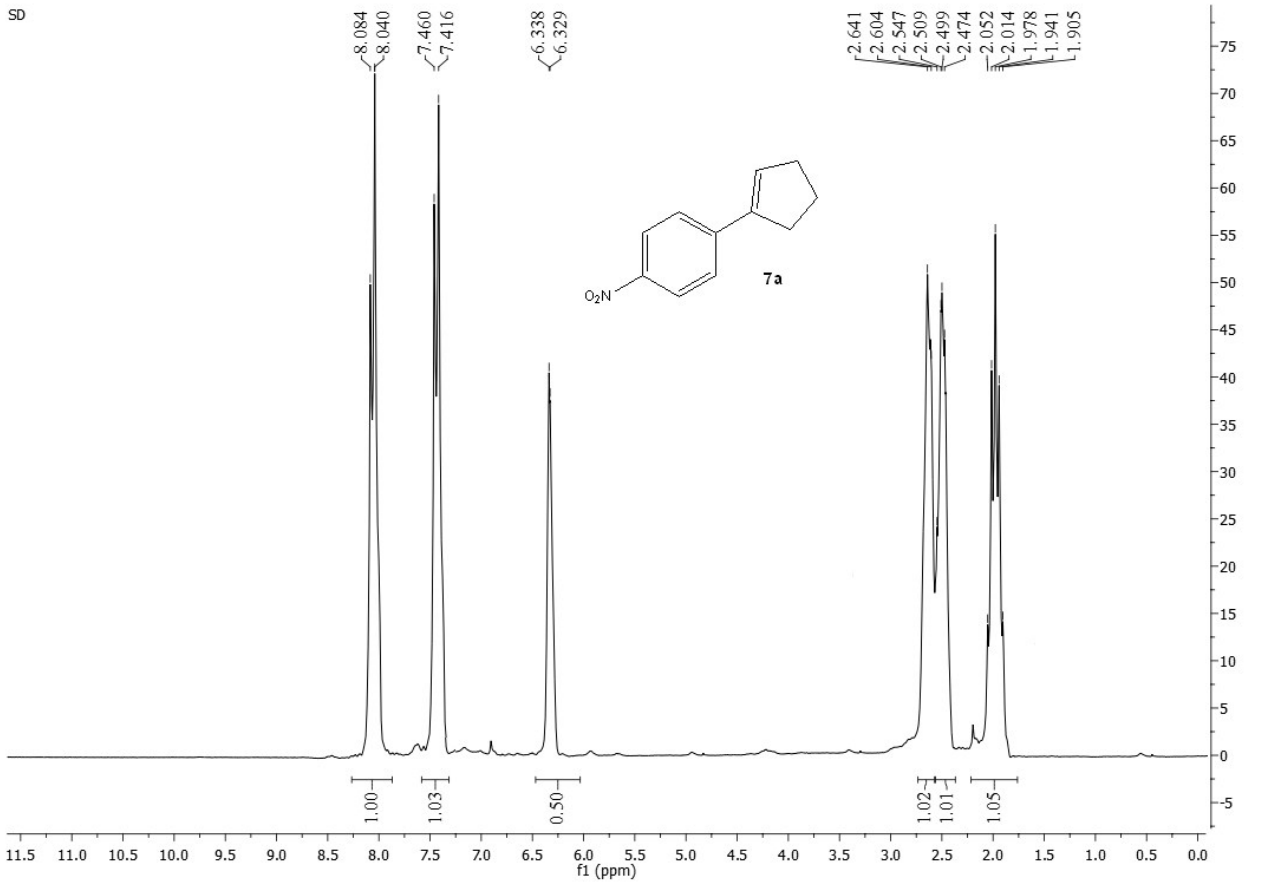
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2.474
2.052
2.014
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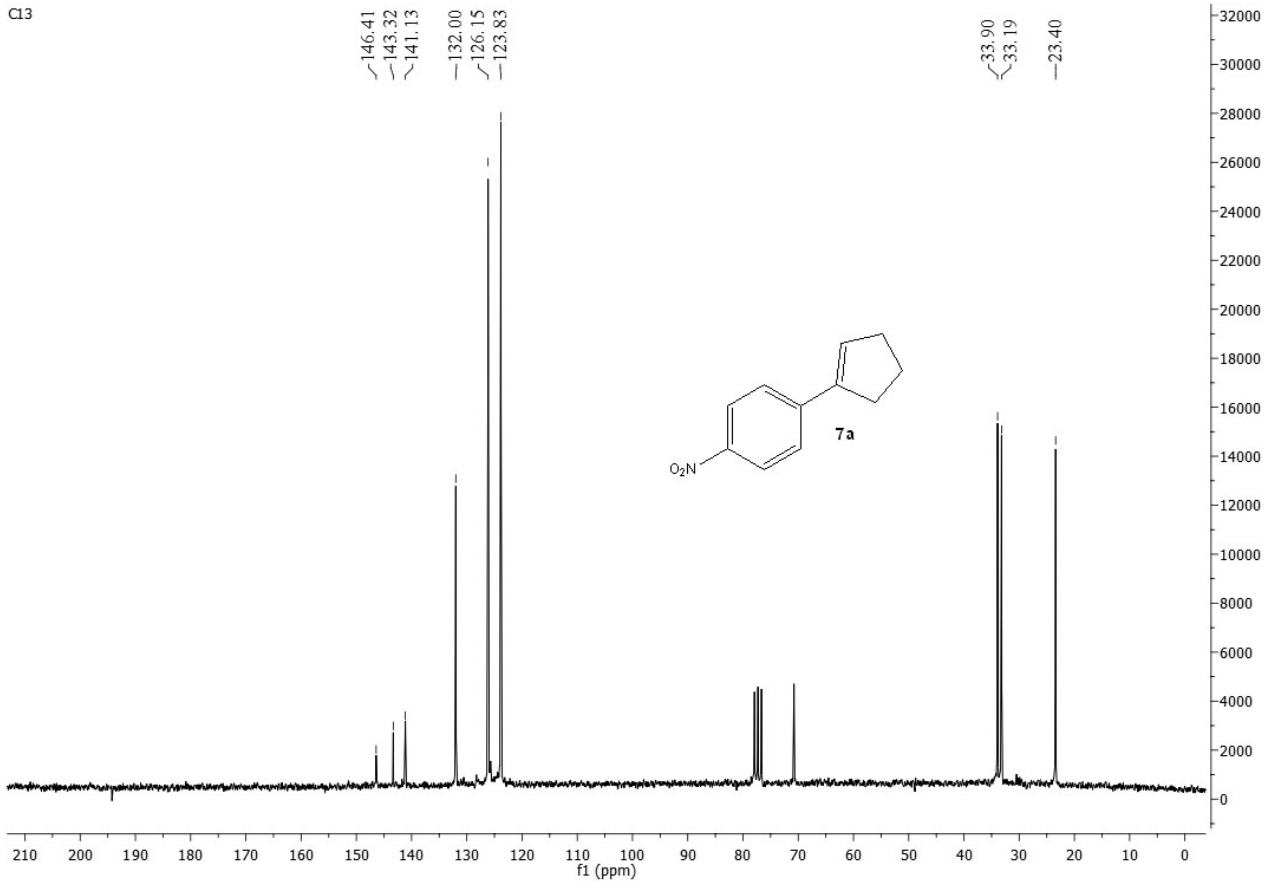
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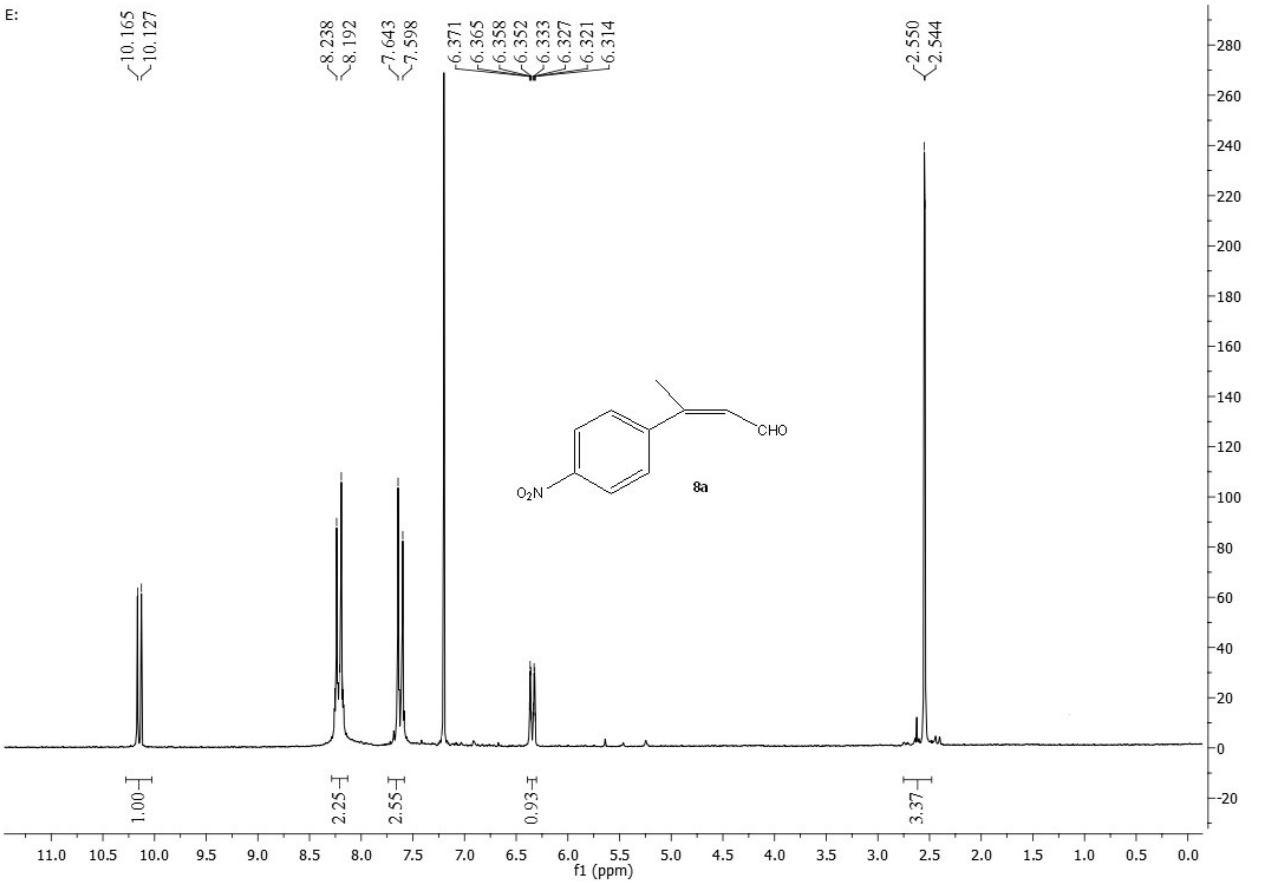
f1 (ppm)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6.321
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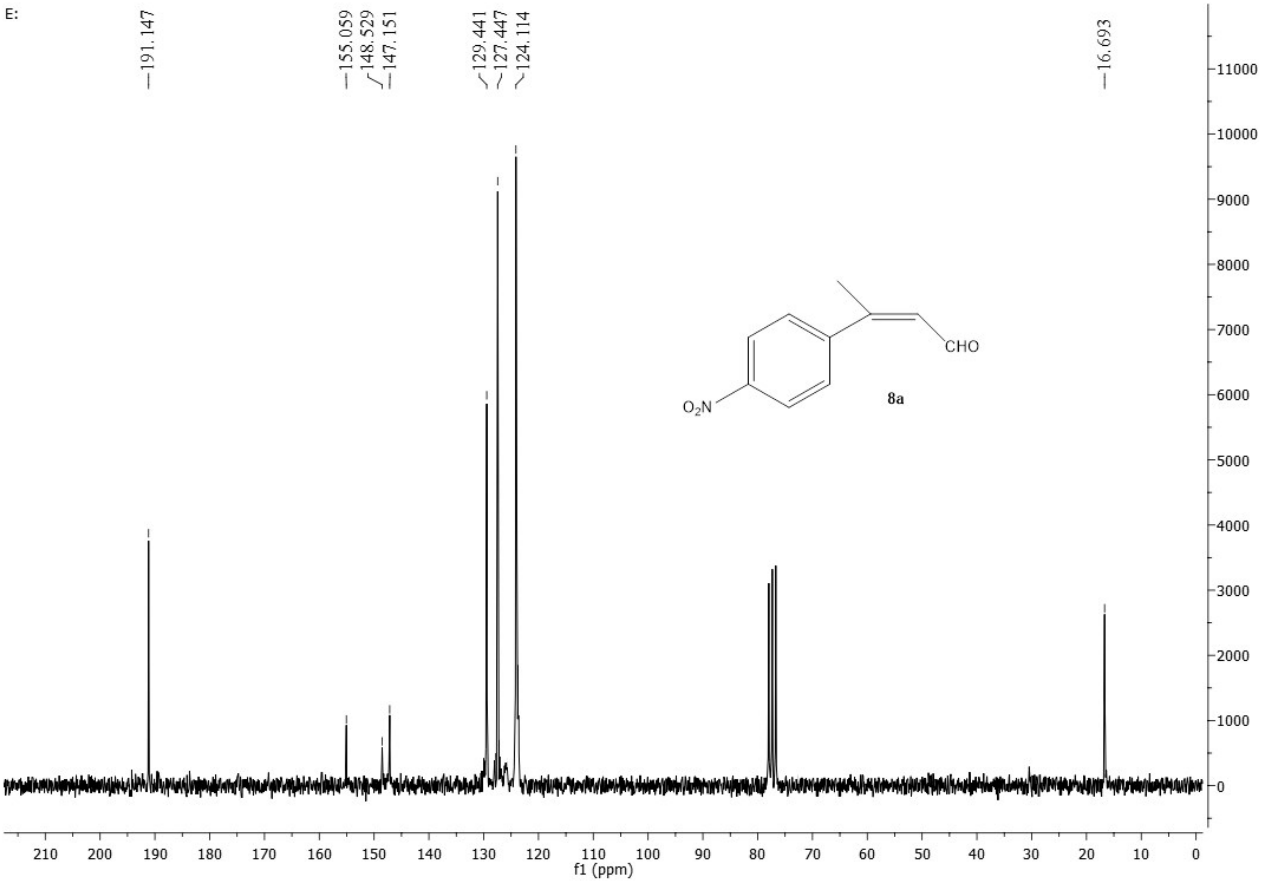
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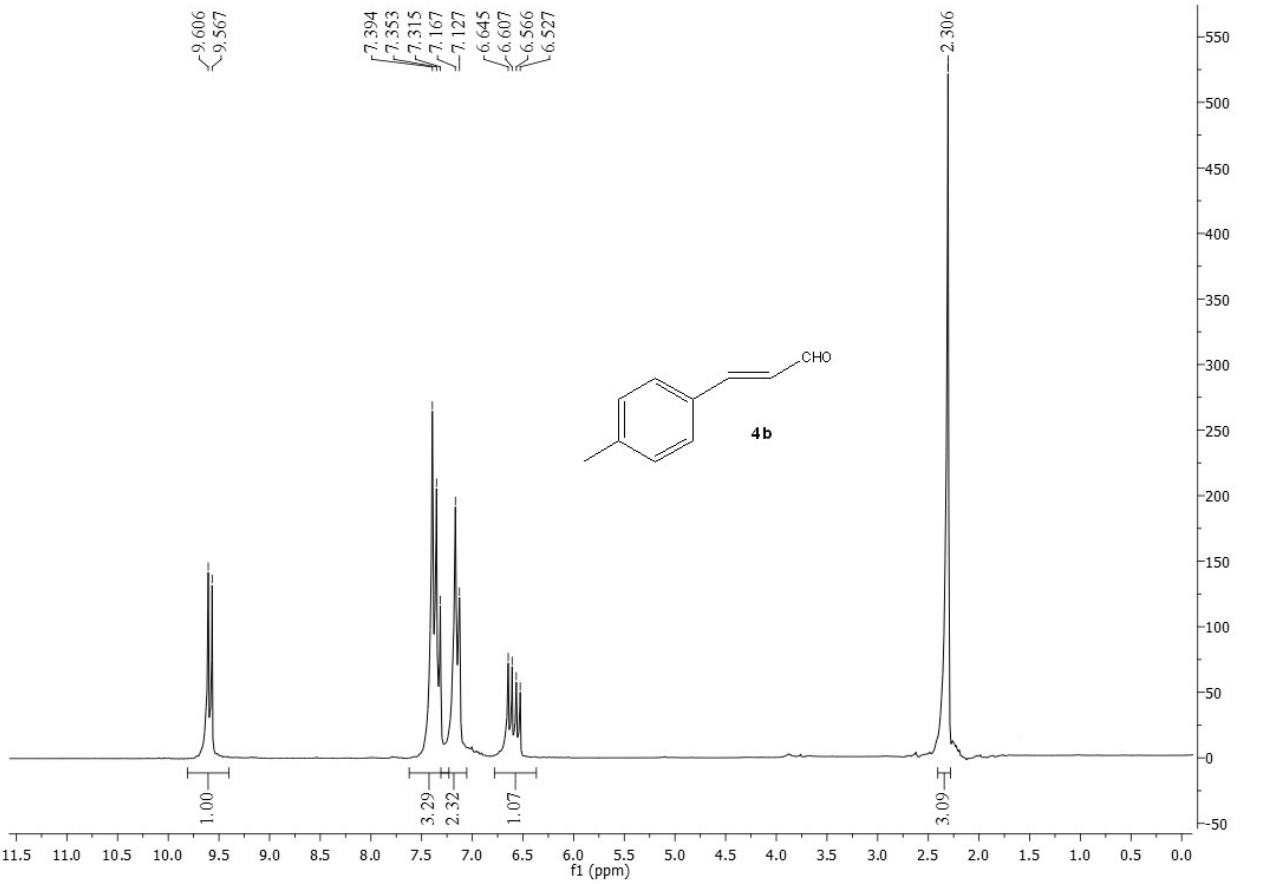
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7.167
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4b
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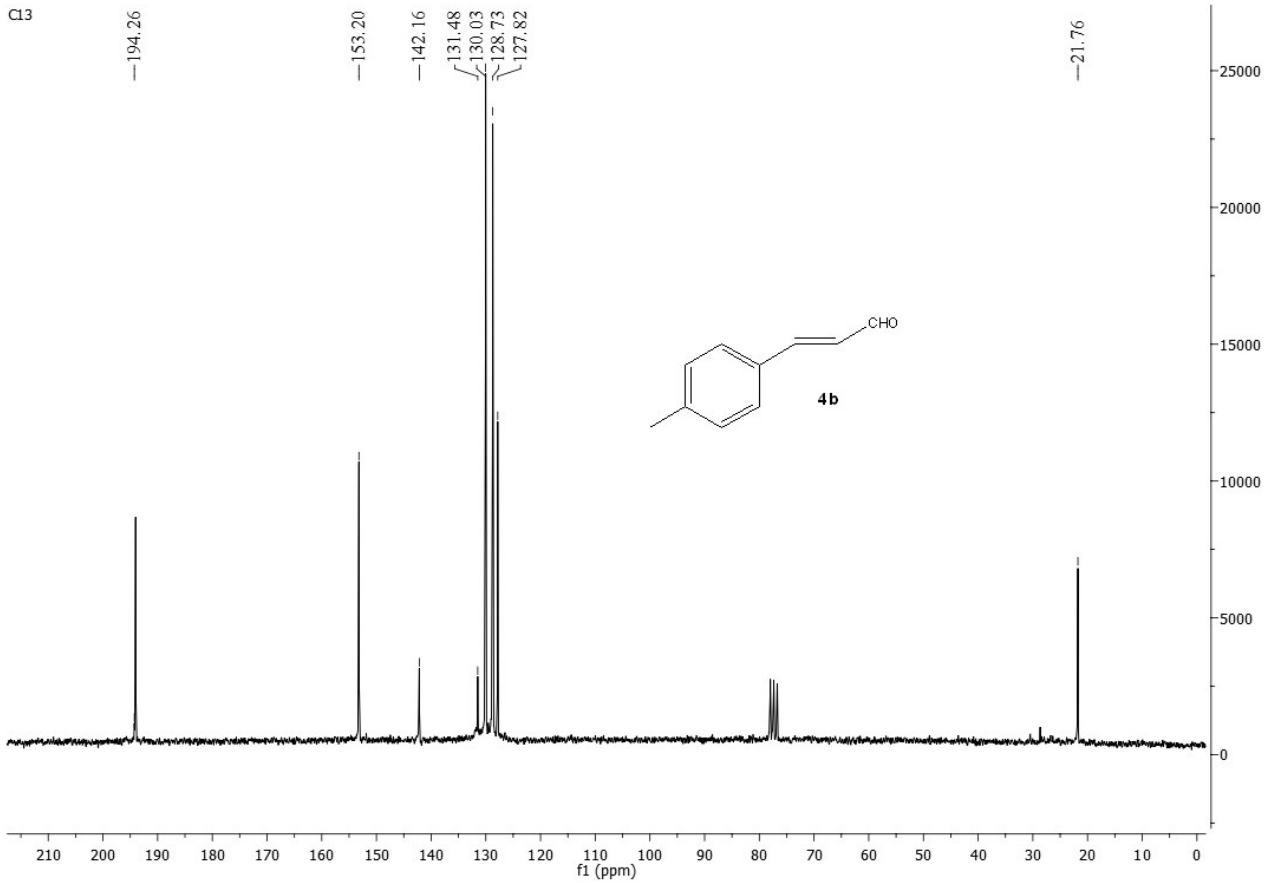
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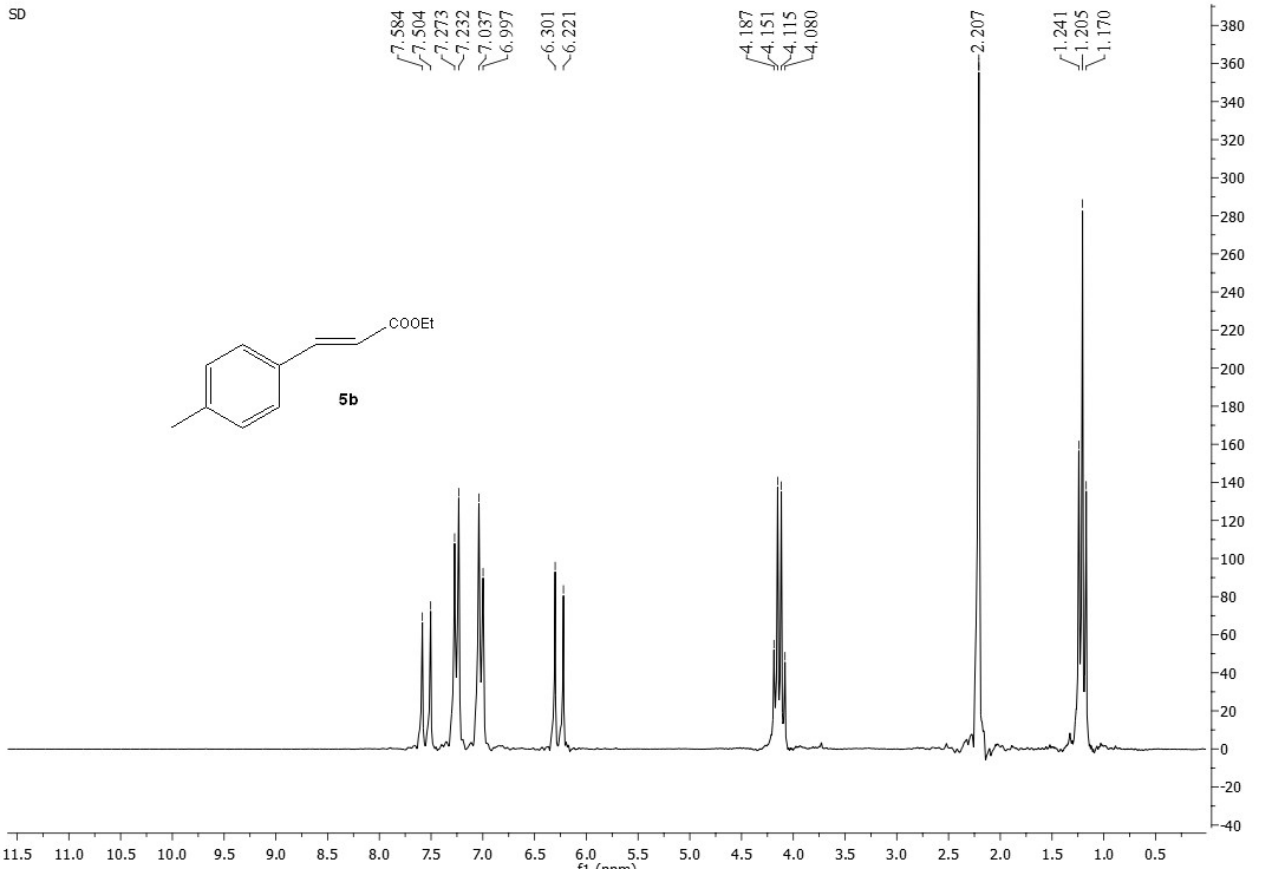
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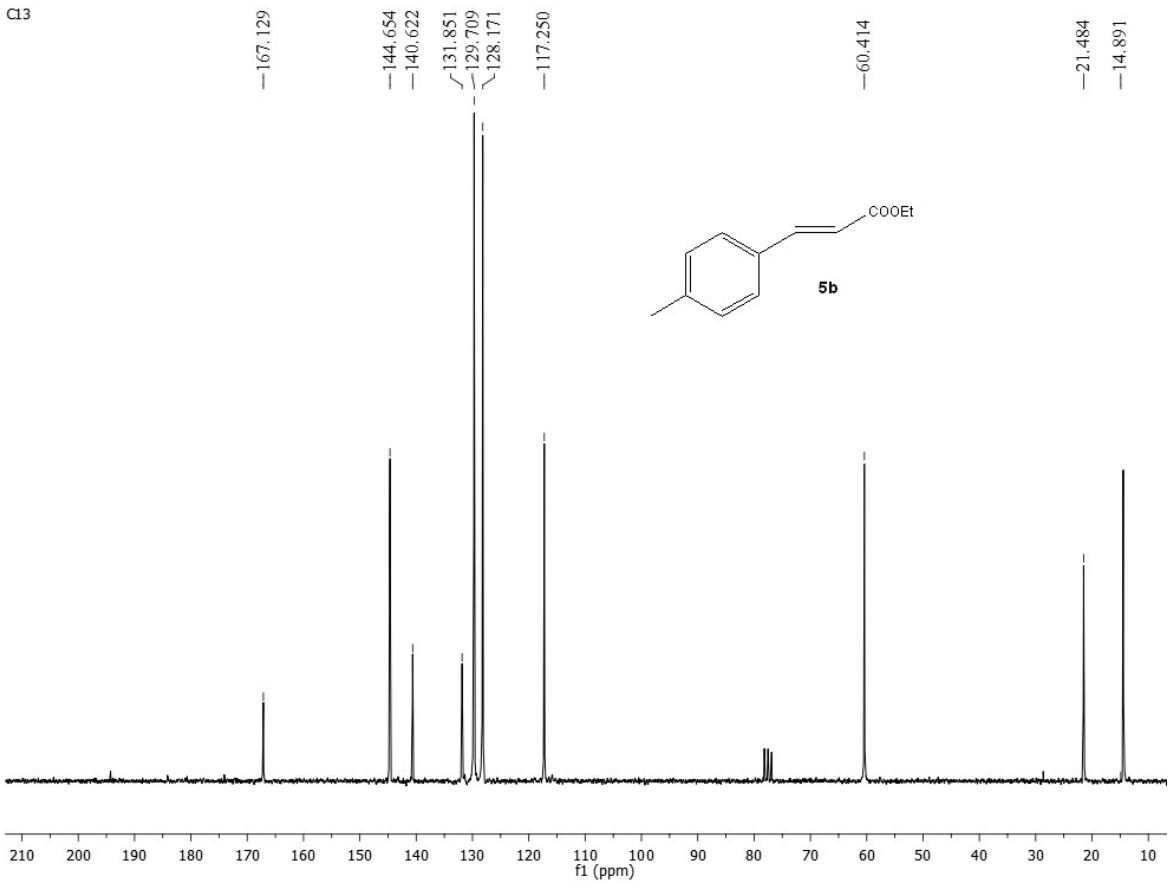
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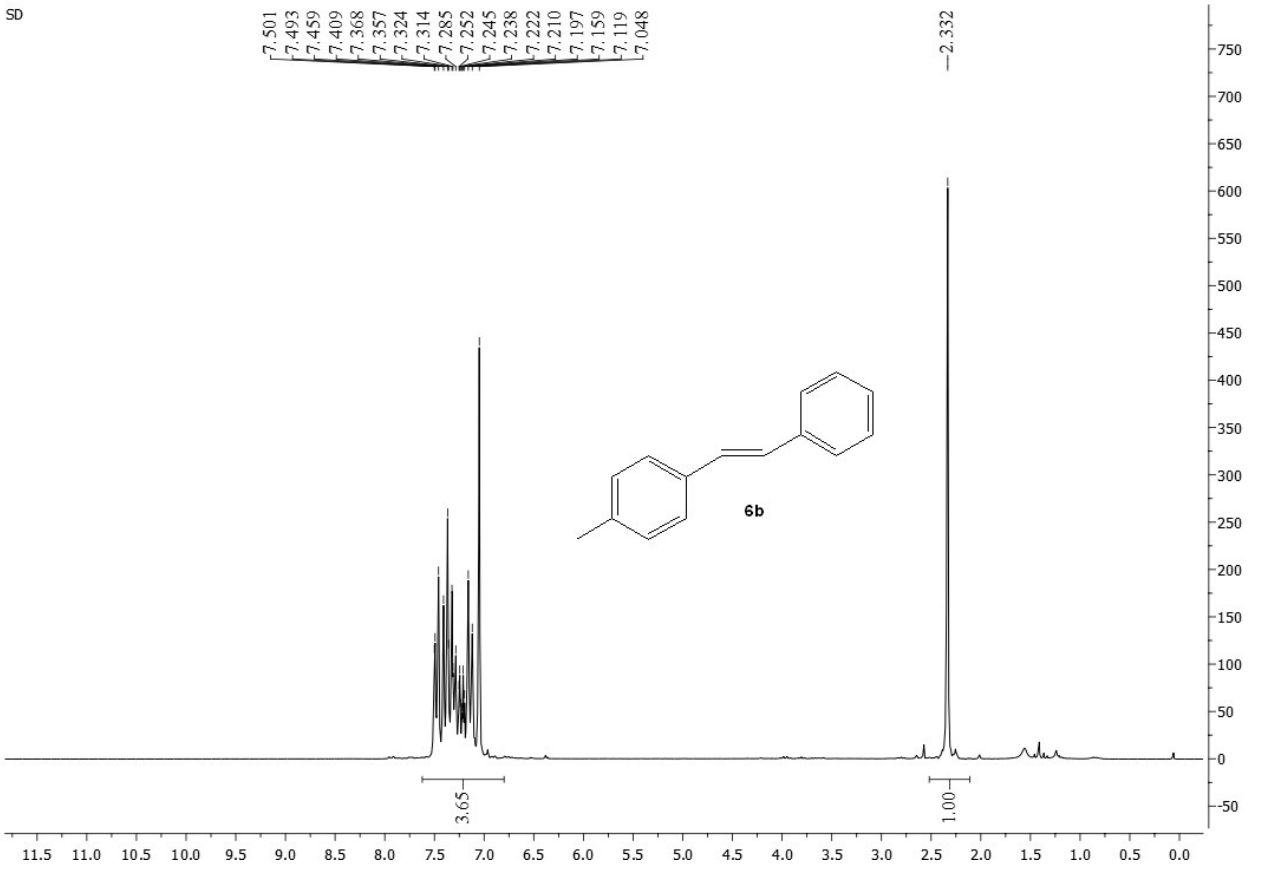
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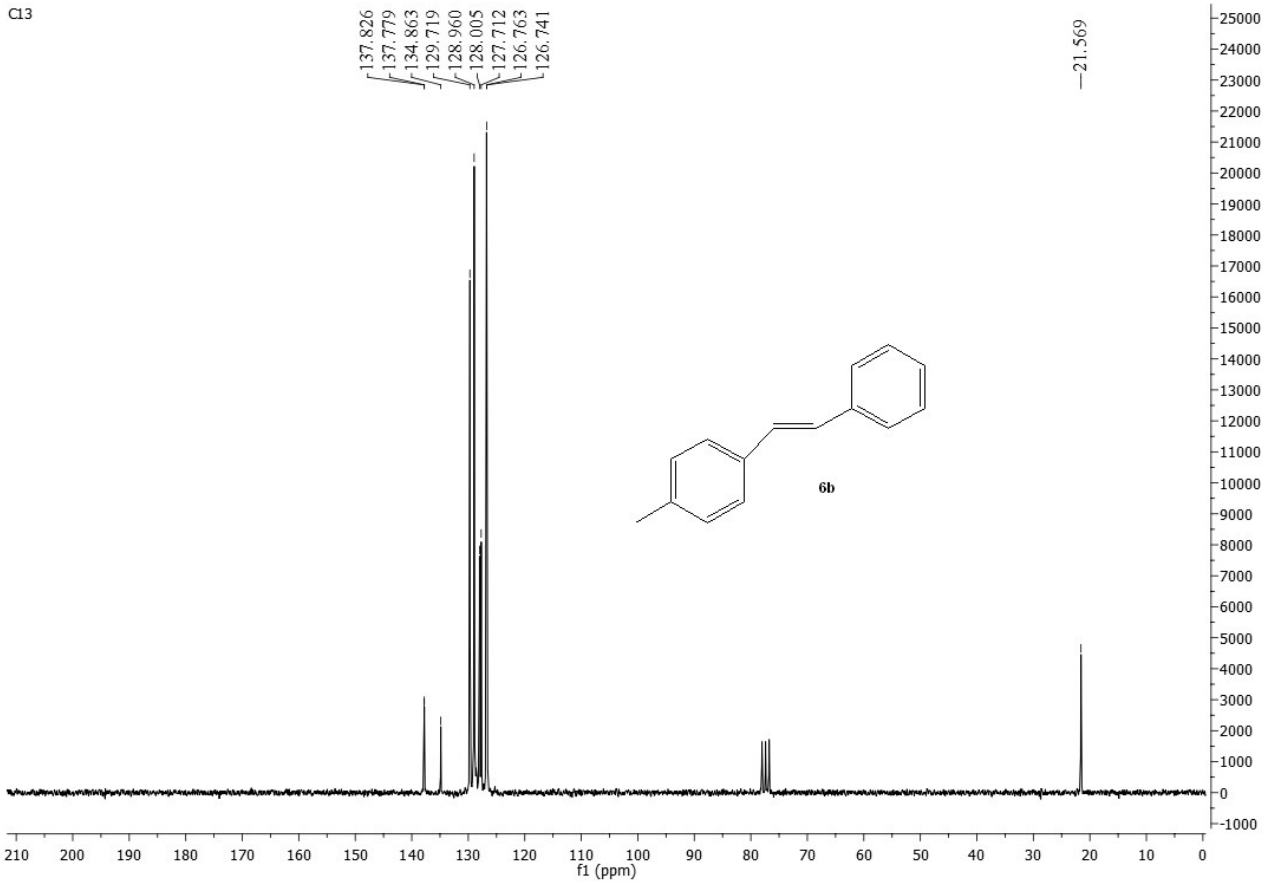
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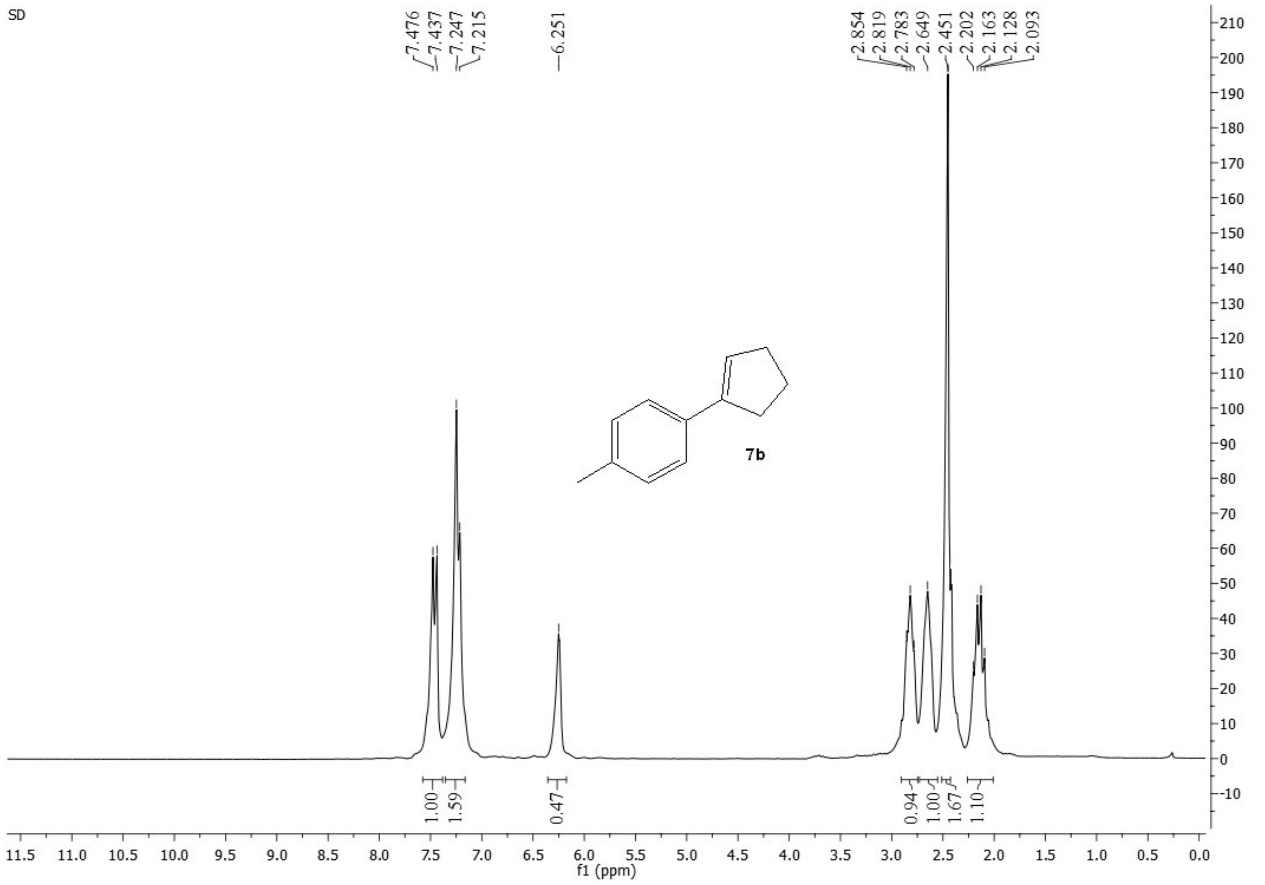
f1 (ppm)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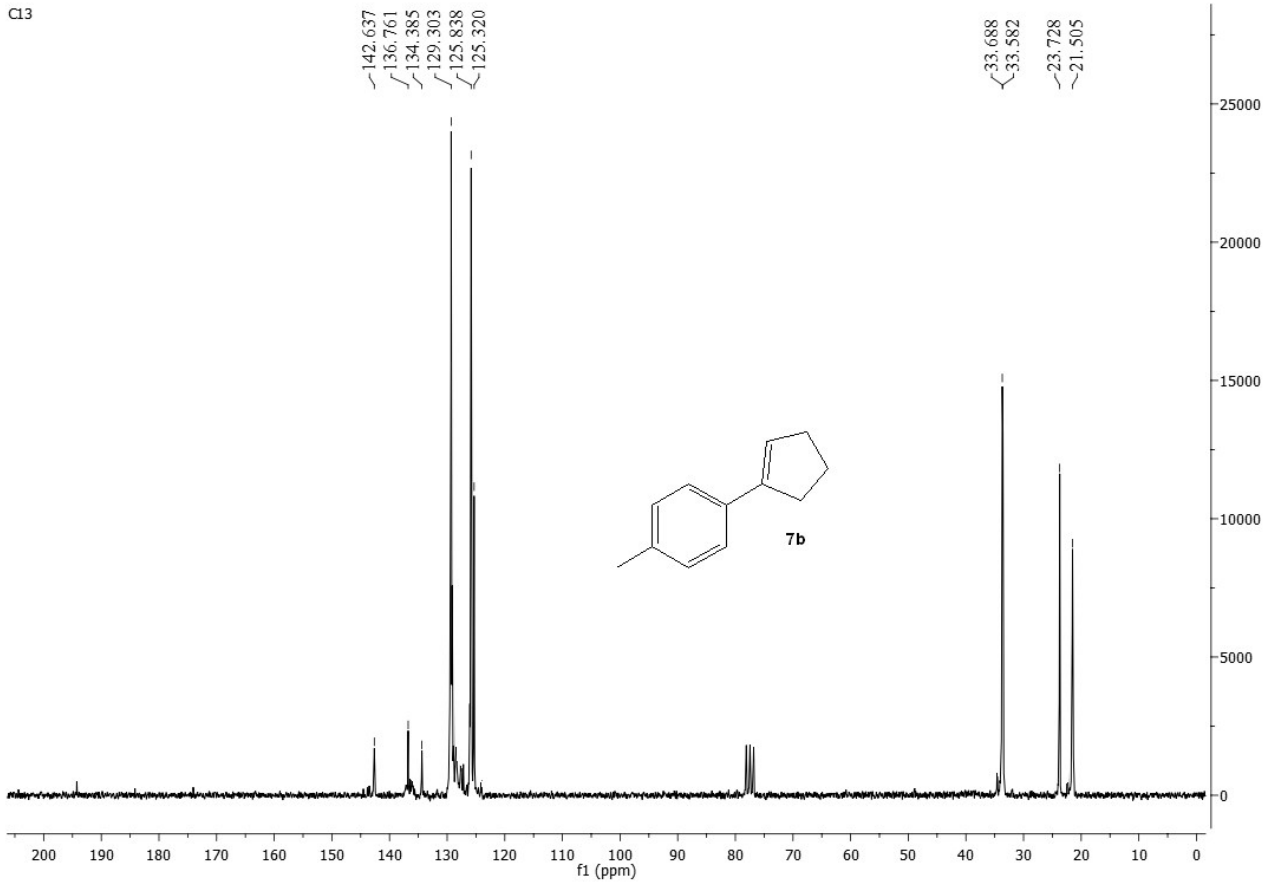
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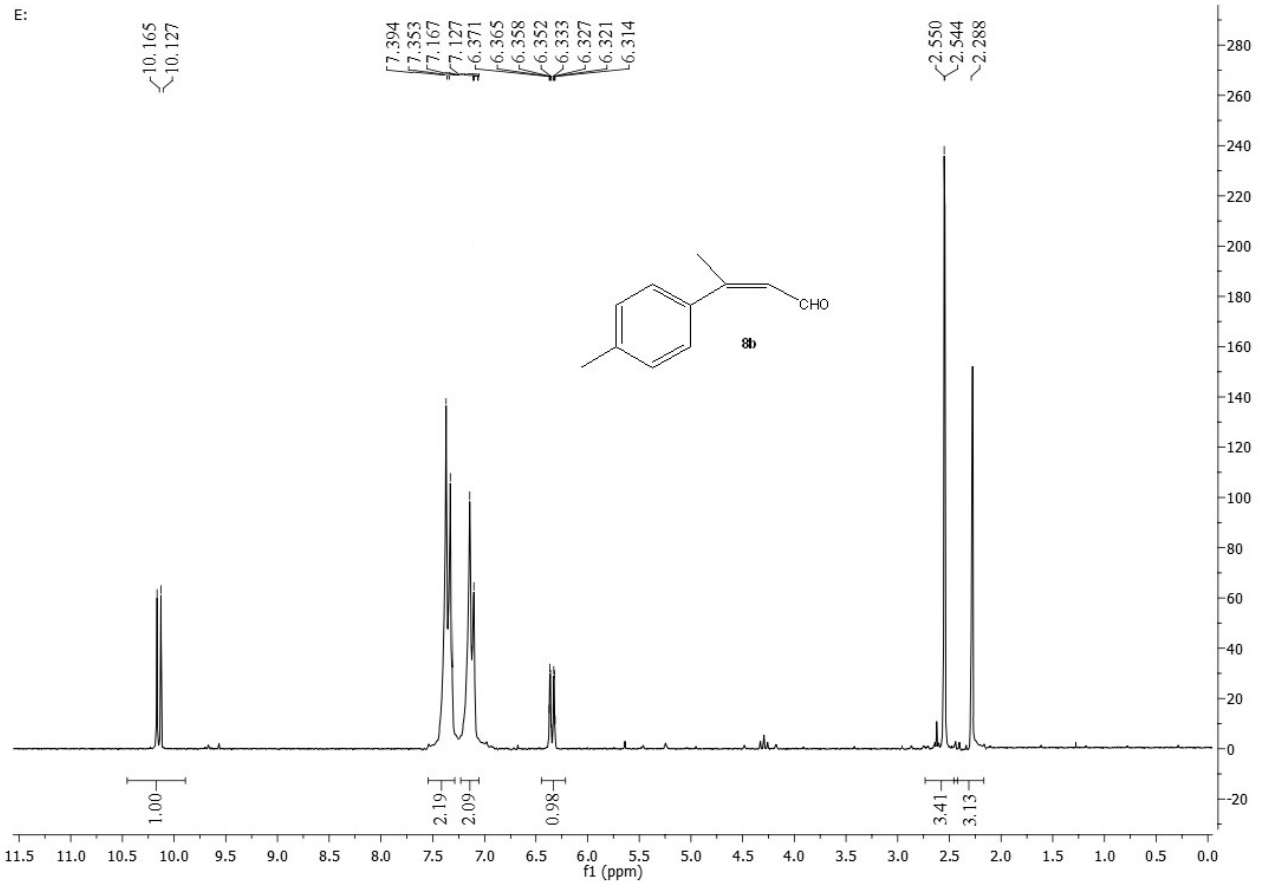
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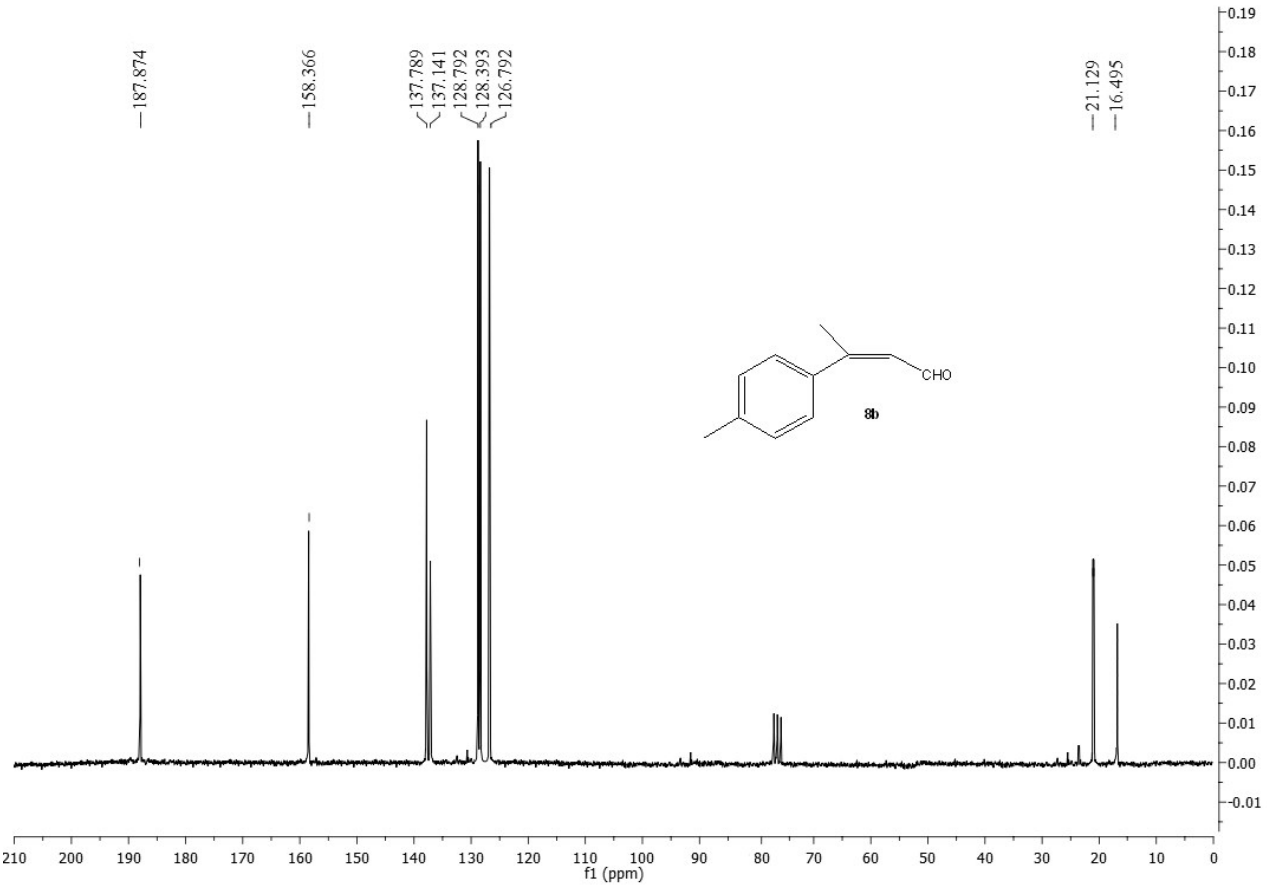
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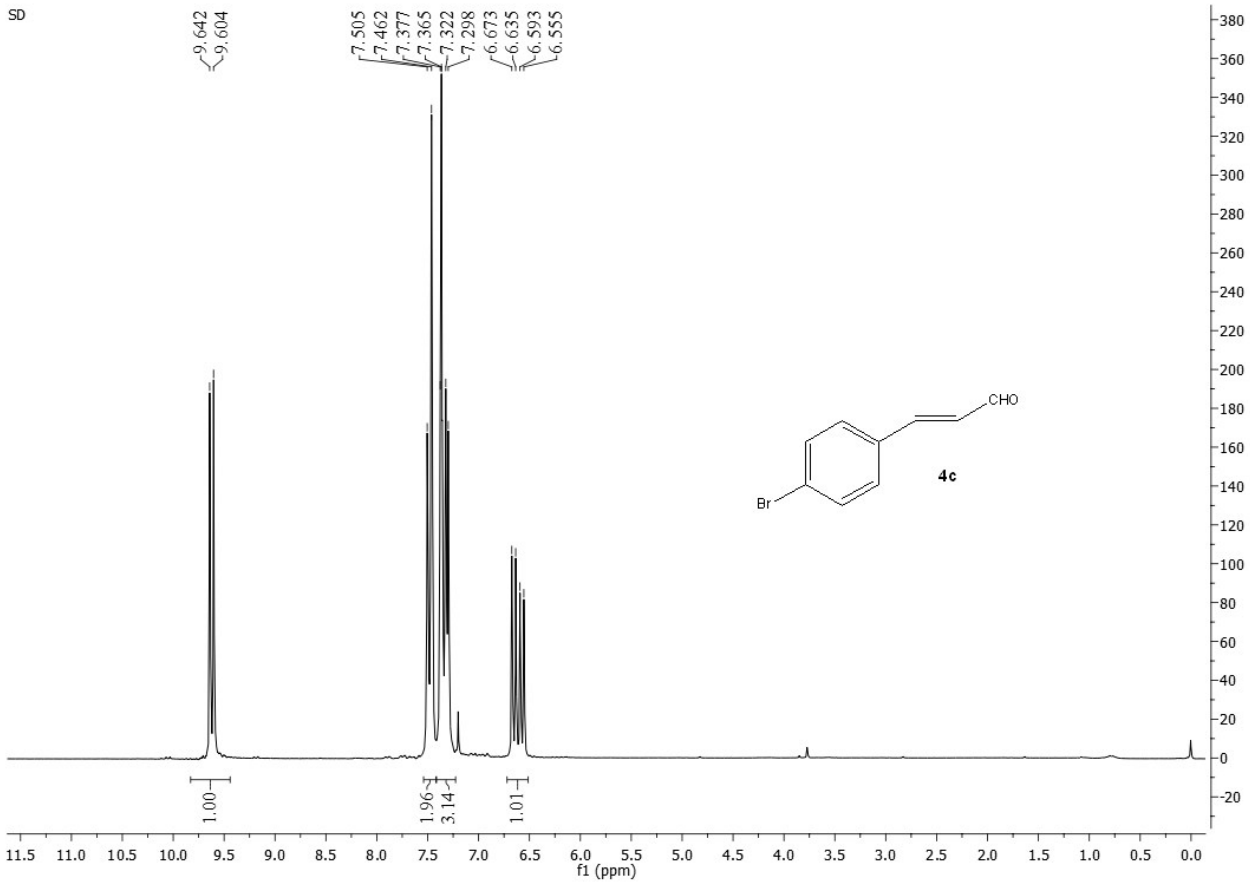
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Br
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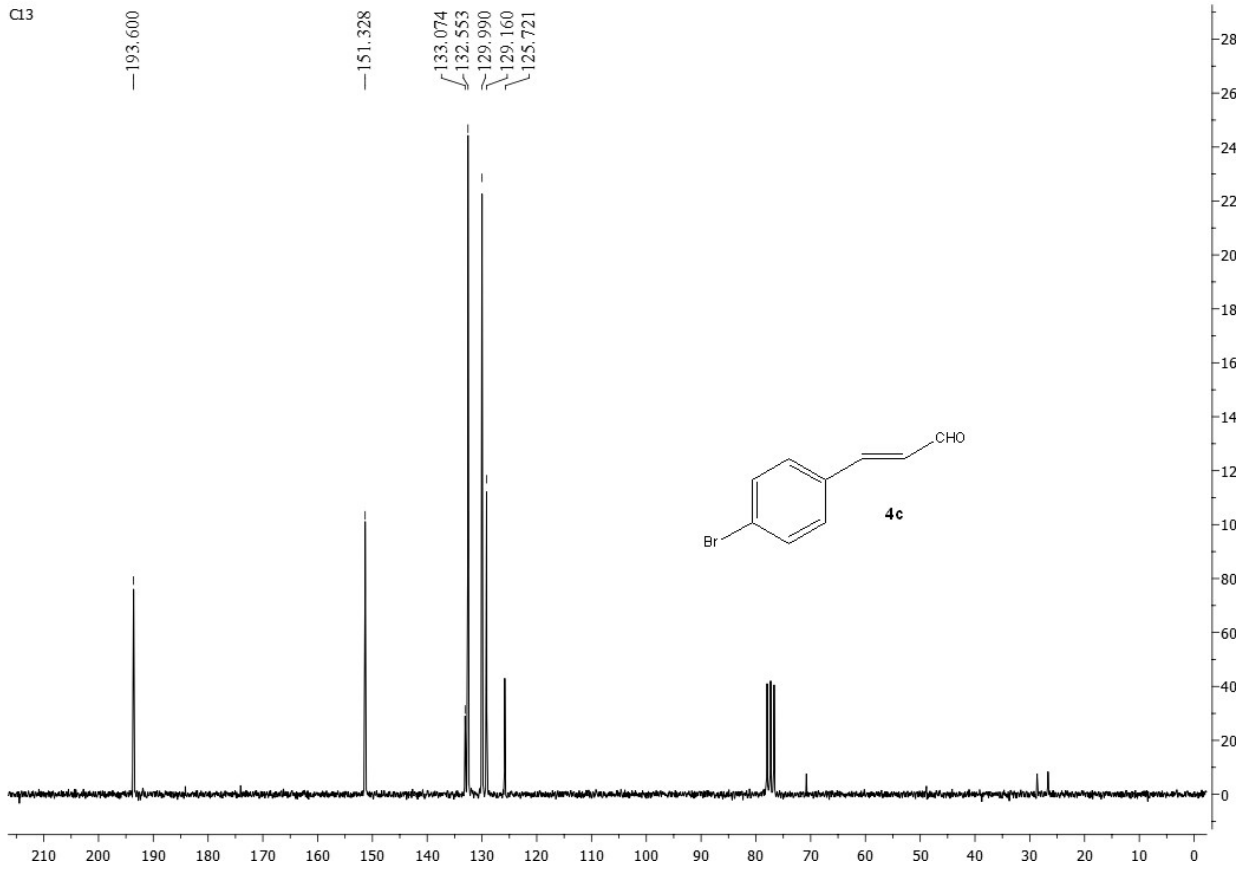
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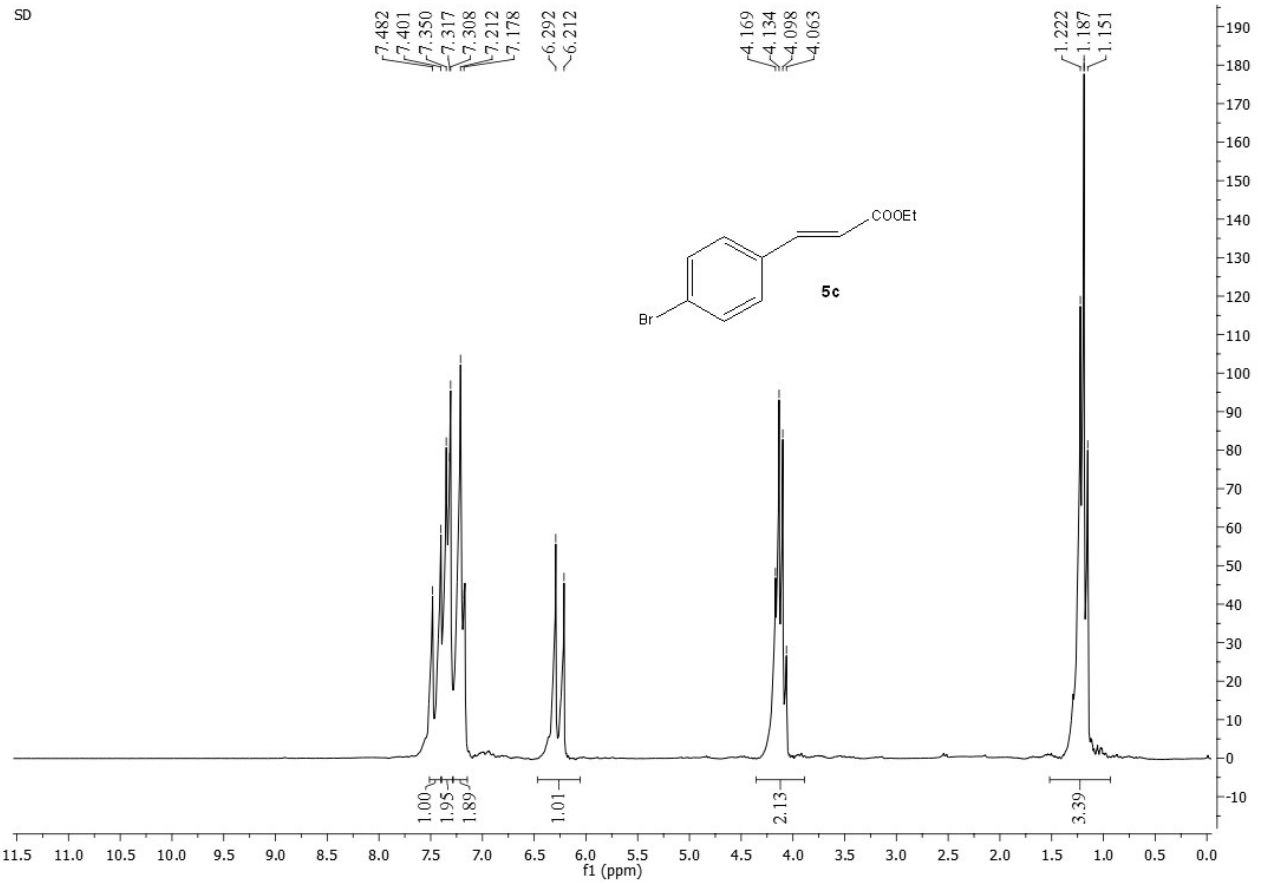
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6.212
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4.098
4.063
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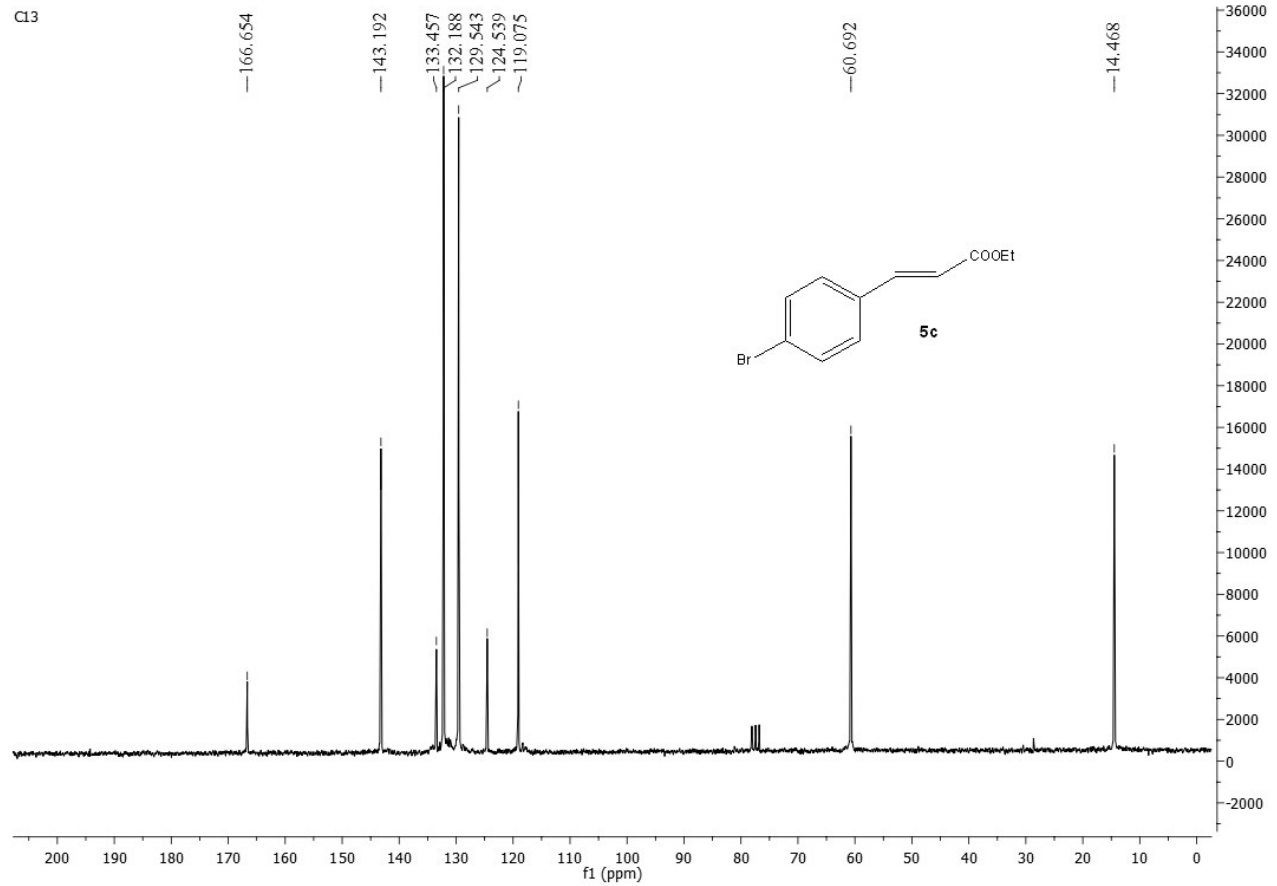
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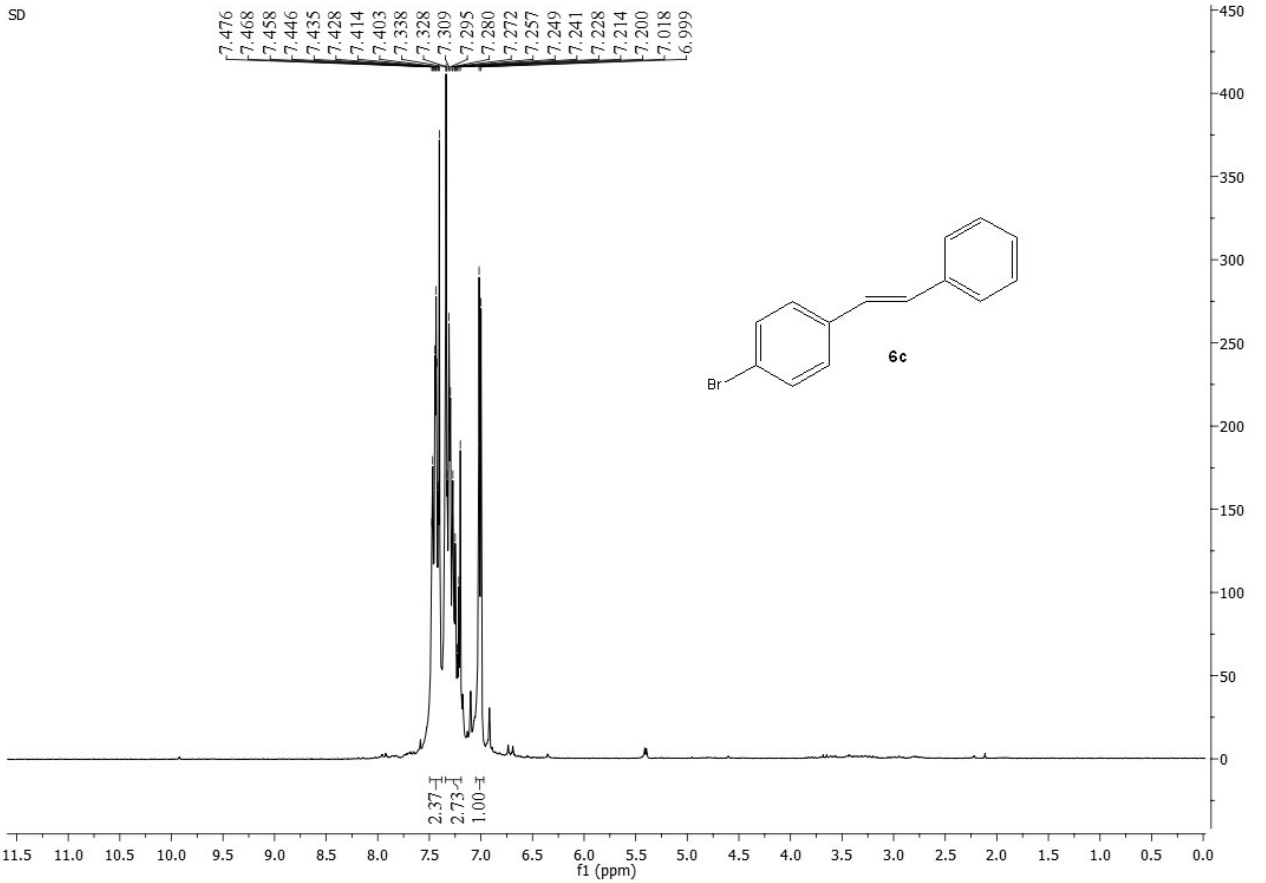
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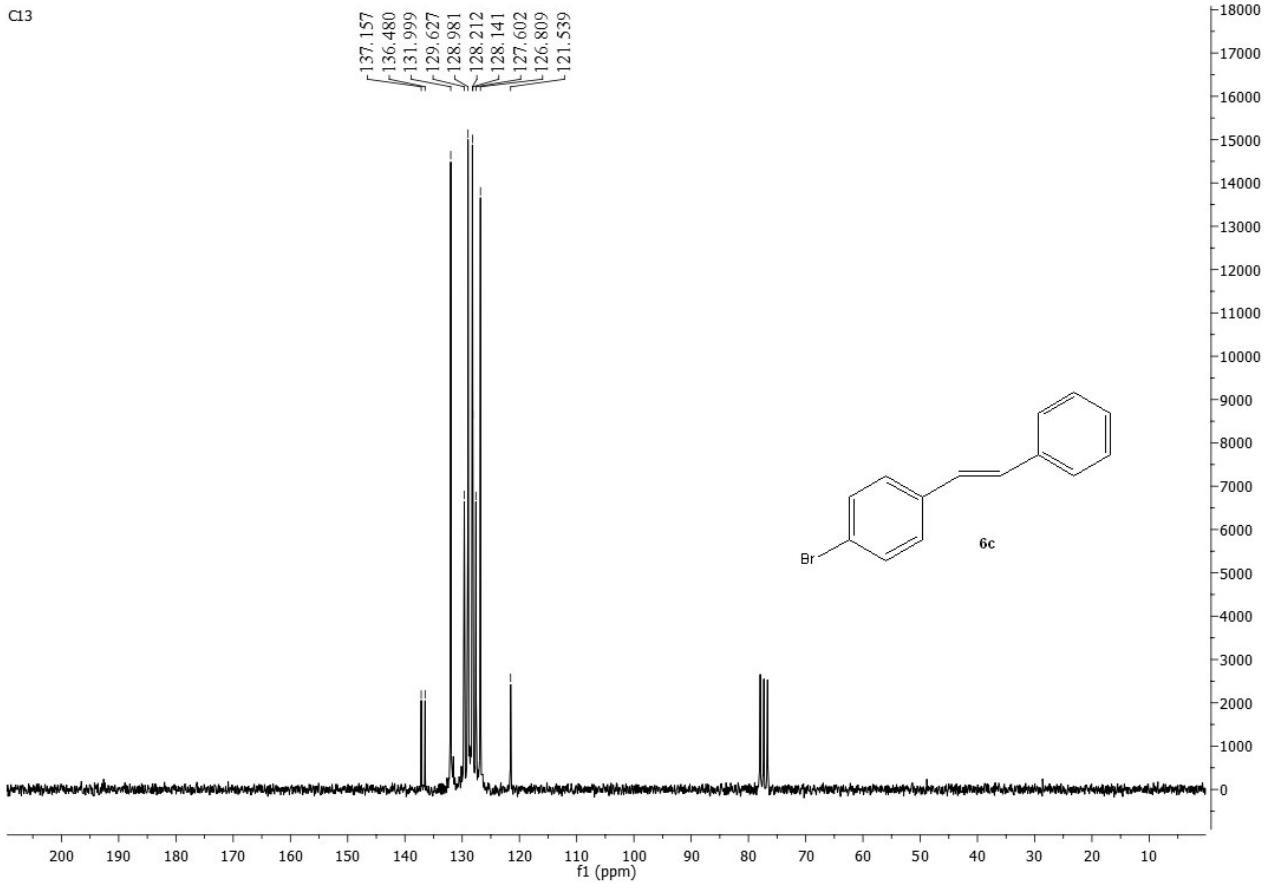
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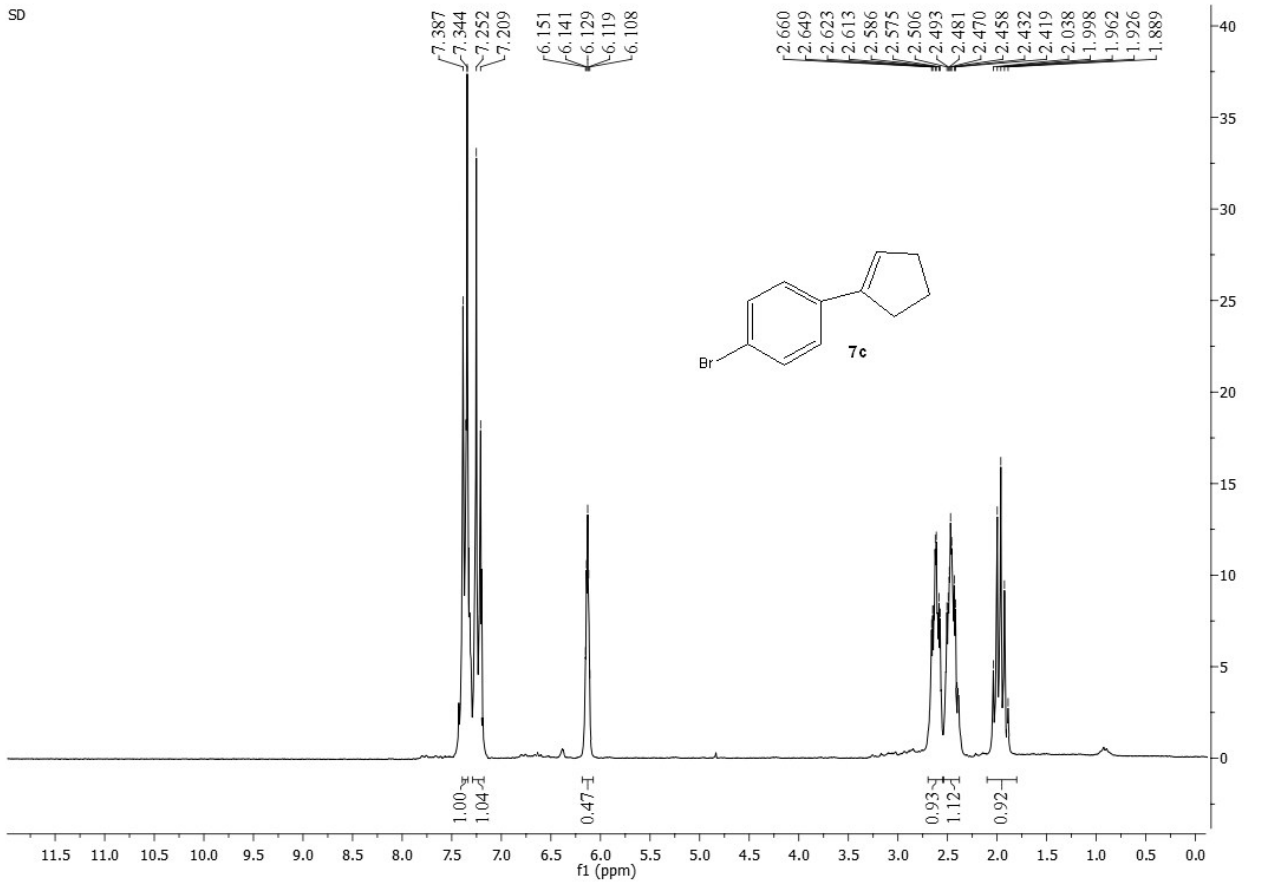
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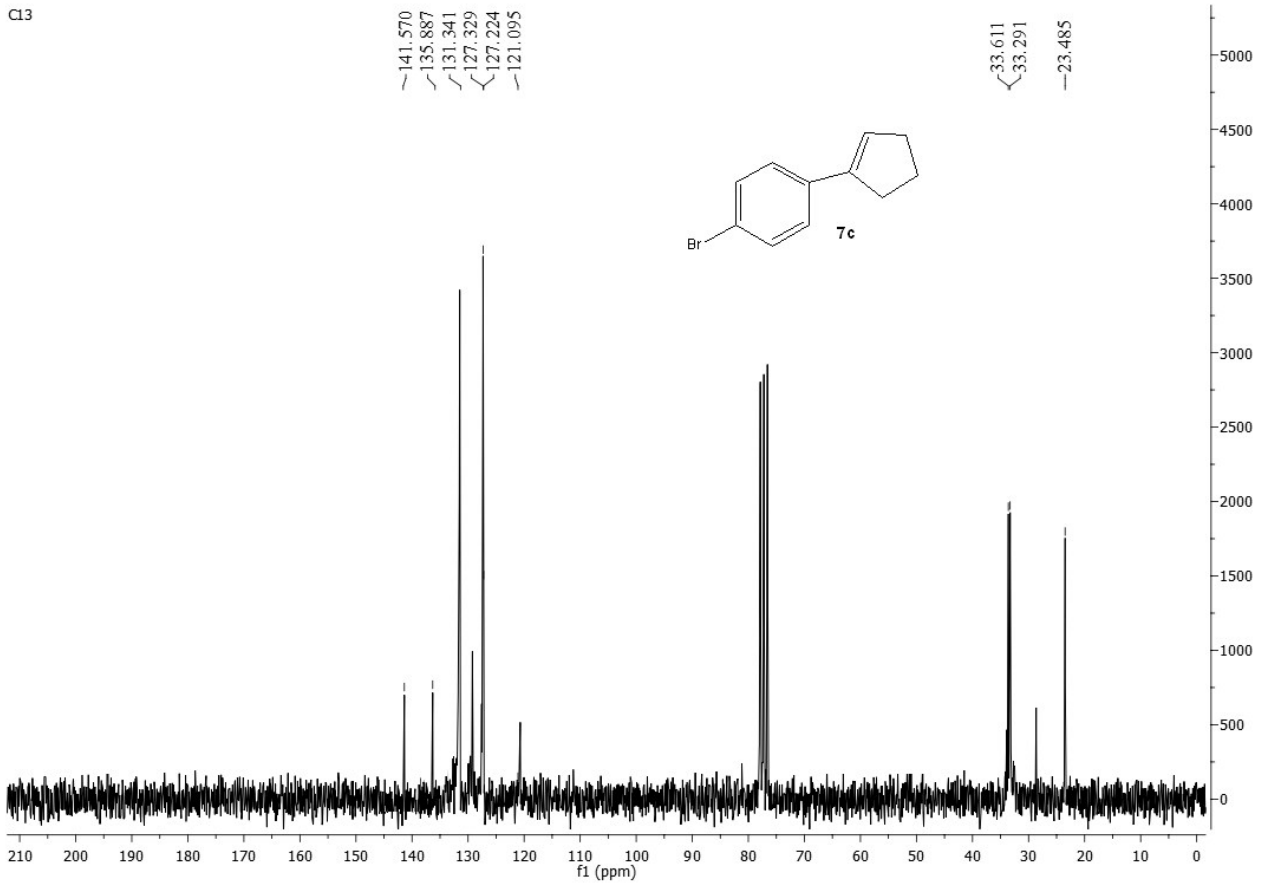
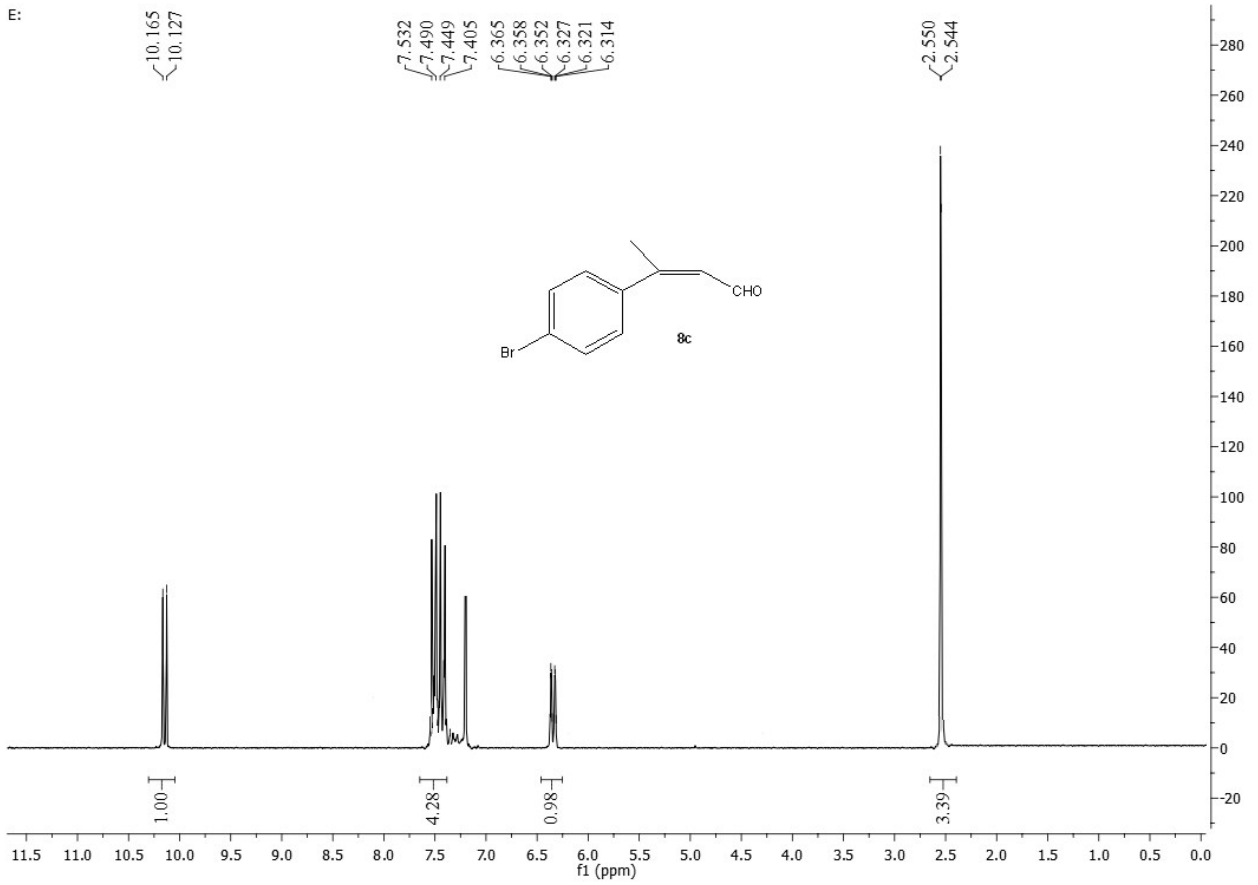
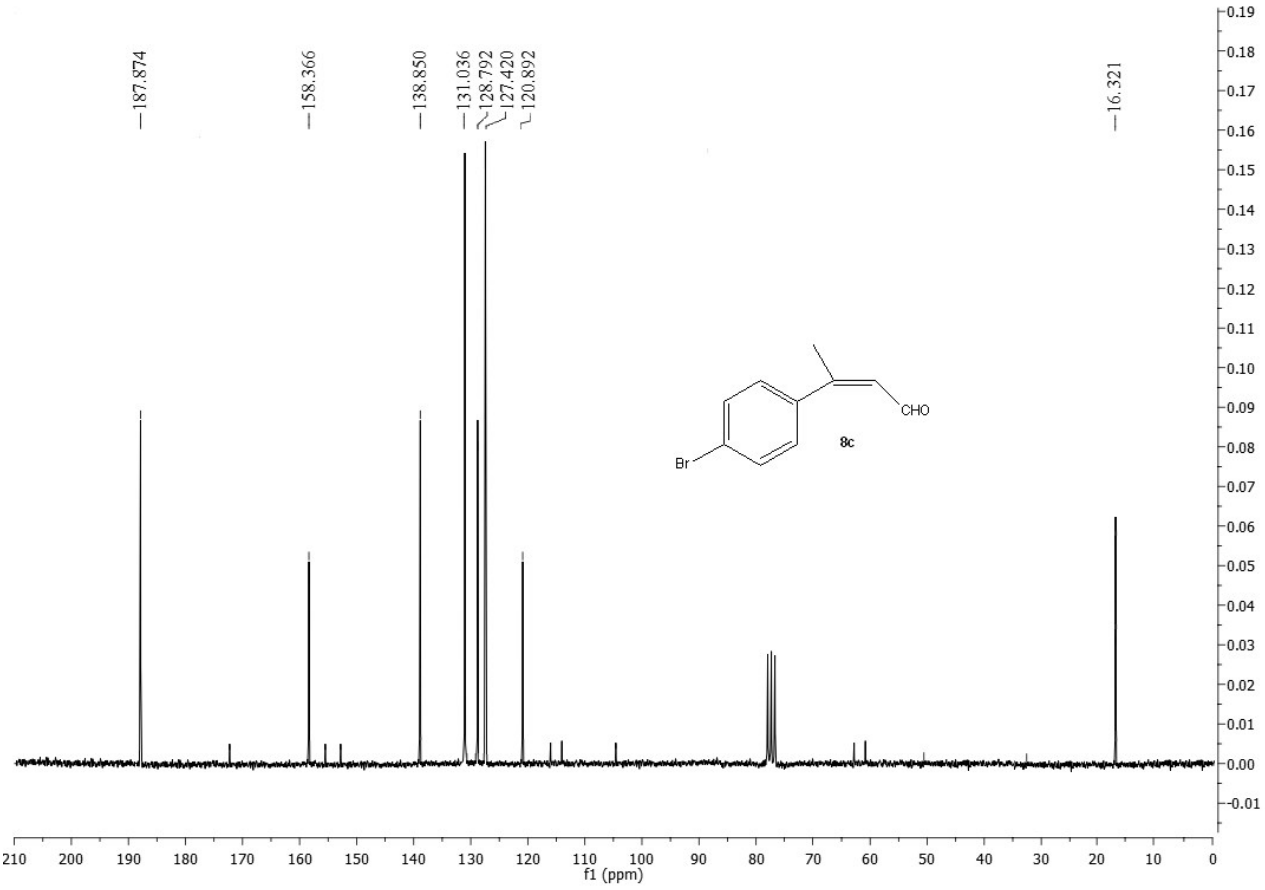
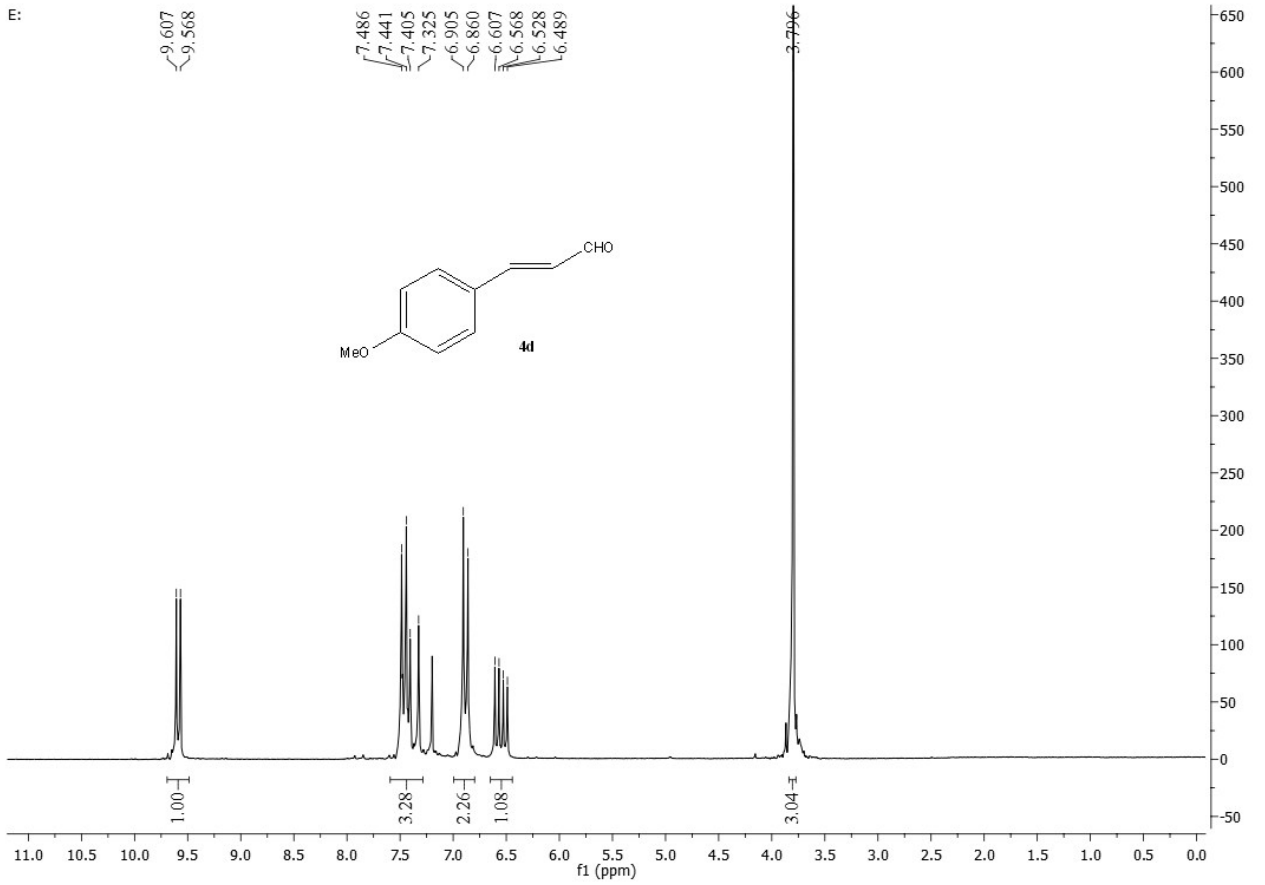
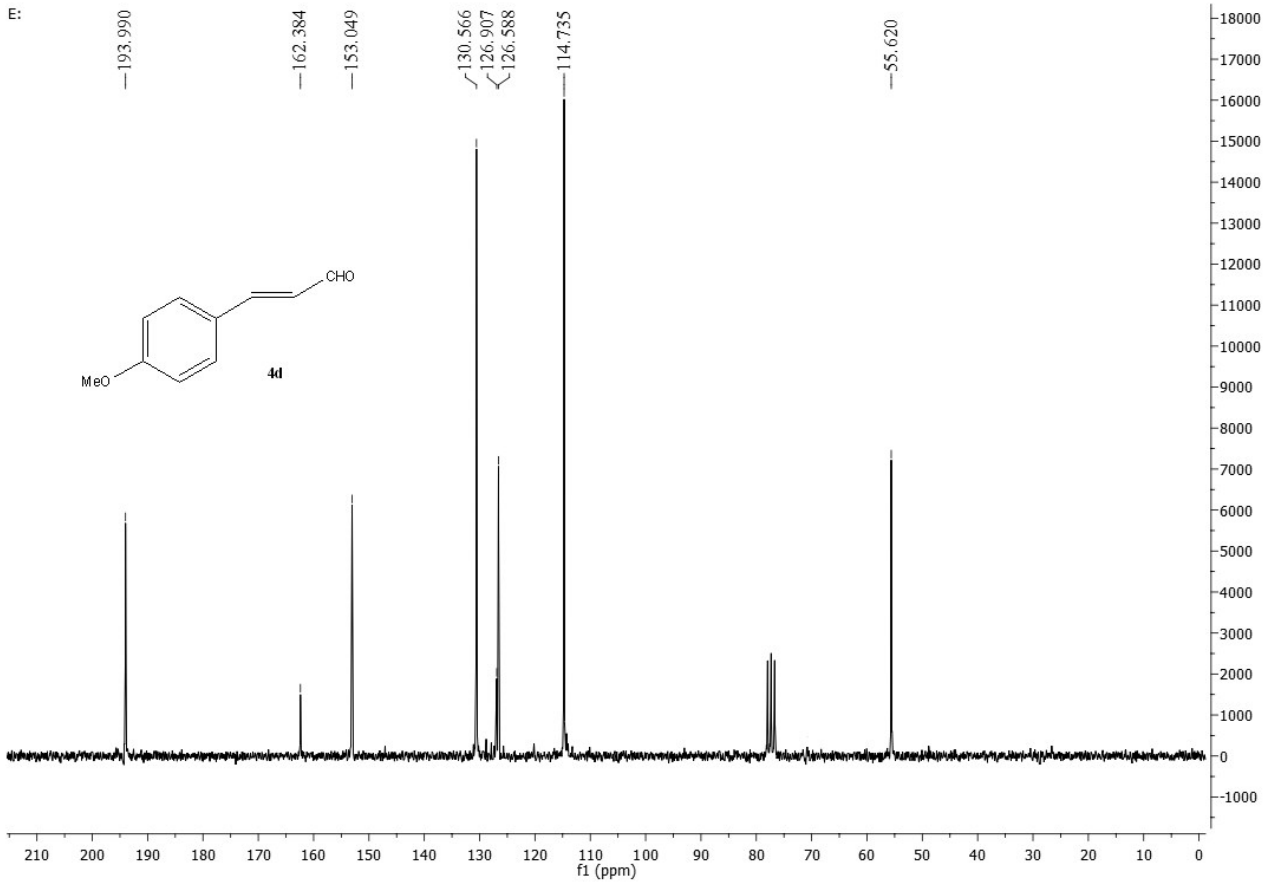
1.962
1.926
1.889
Br
7c
1.00
1.04
0.47
0.93
1.12
0.92
f1 (ppm)

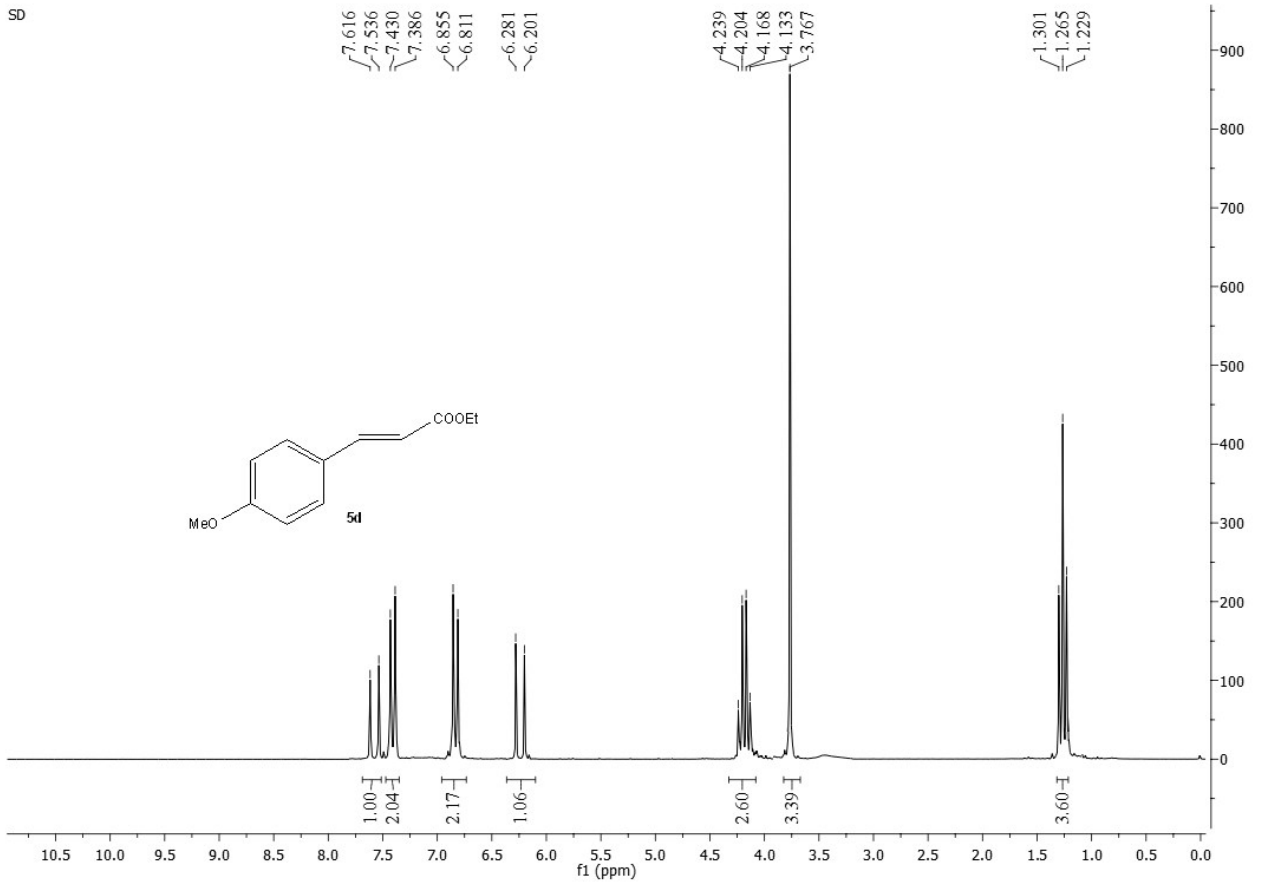

C13
141.570
135.887
131.341
127.329
127.224
121.095
33.611
33.291
23.485
Br
7c
f1 (ppm)

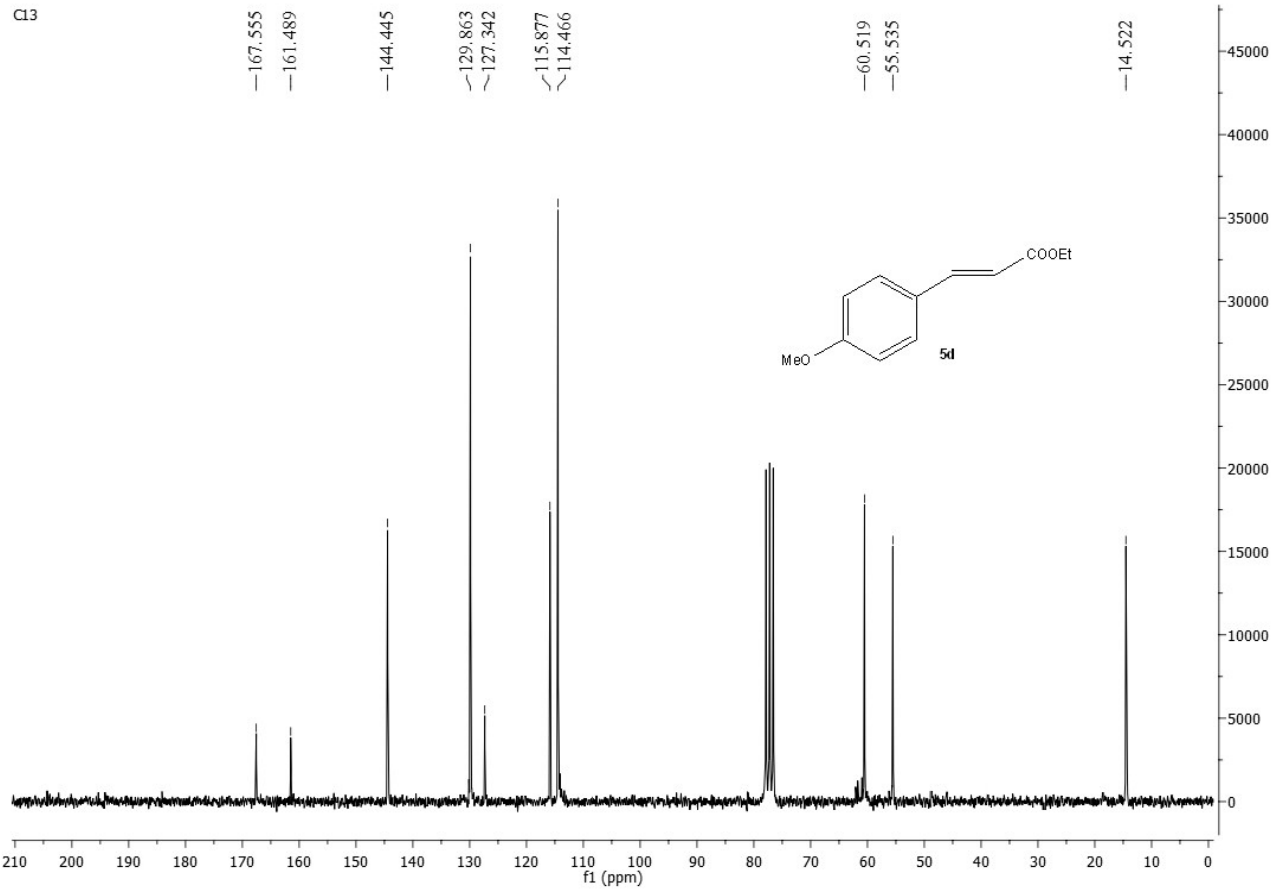

E:
10.165
10.127
7.532
7.490
7.449
7.405
6.365
6.358
6.352
6.327
6.321
6.314
2.550
2.544
CHO
Br
8c
1.00
4.28
0.98
3.39
f1 (ppm)

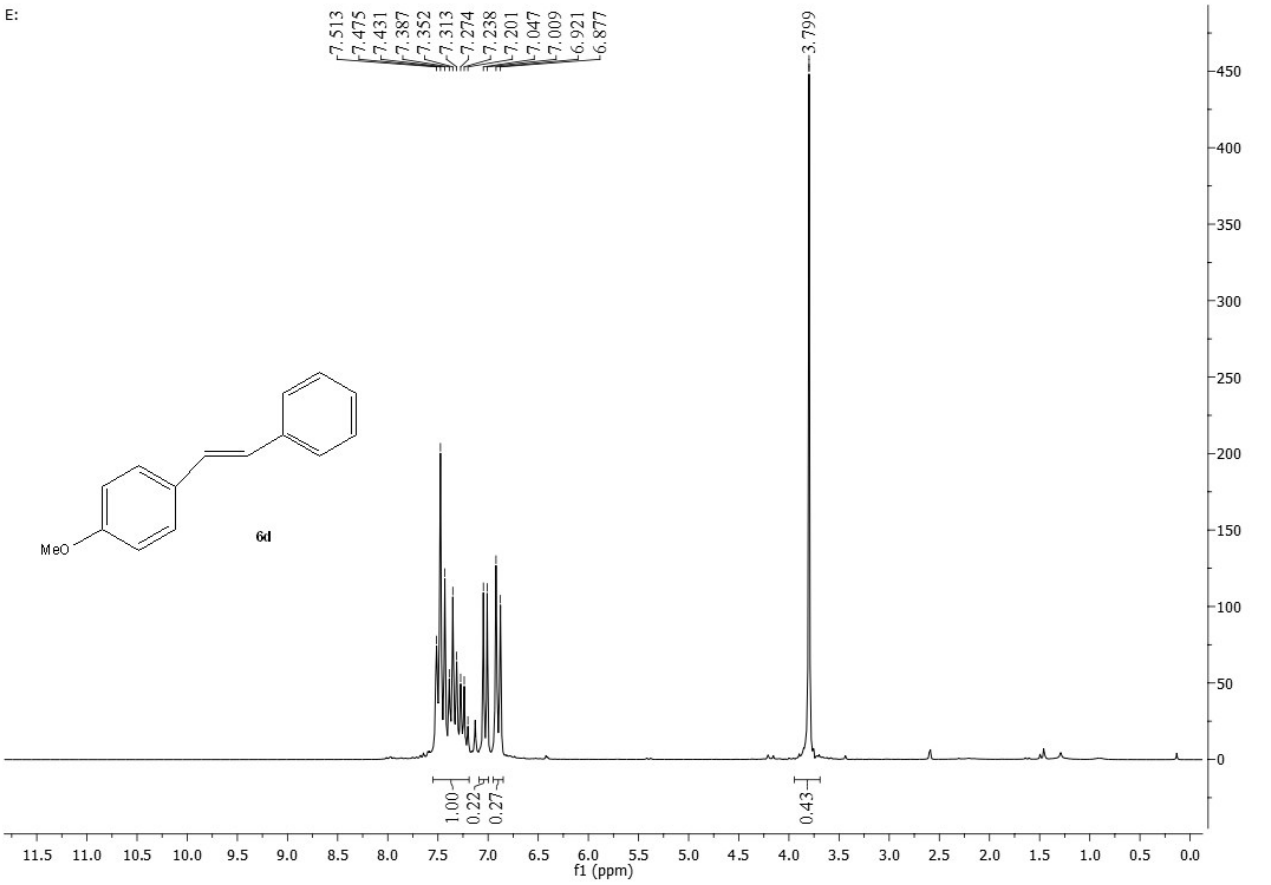

187.874
158.366
138.850
131.036
128.792
127.420
120.892
16.321
CHO
Br
8c
f1 (ppm)

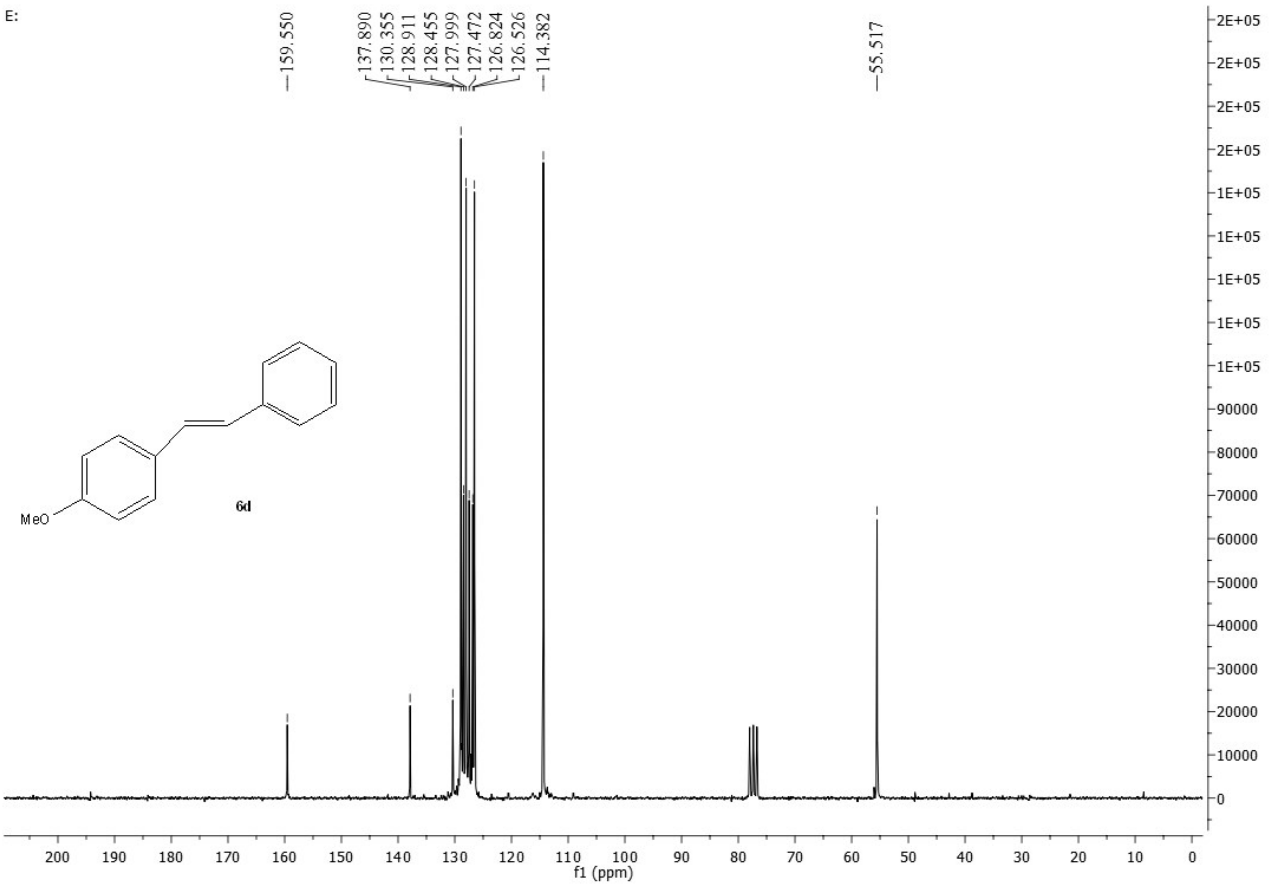

E:
9.607
9.568
7.486
7.441
7.405
7.325
6.905
6.860
6.607
6.568
6.528
6.489
3.796
CHO
MeO
4d
1.00
3.28
2.26
1.08
3.04
f1 (ppm)

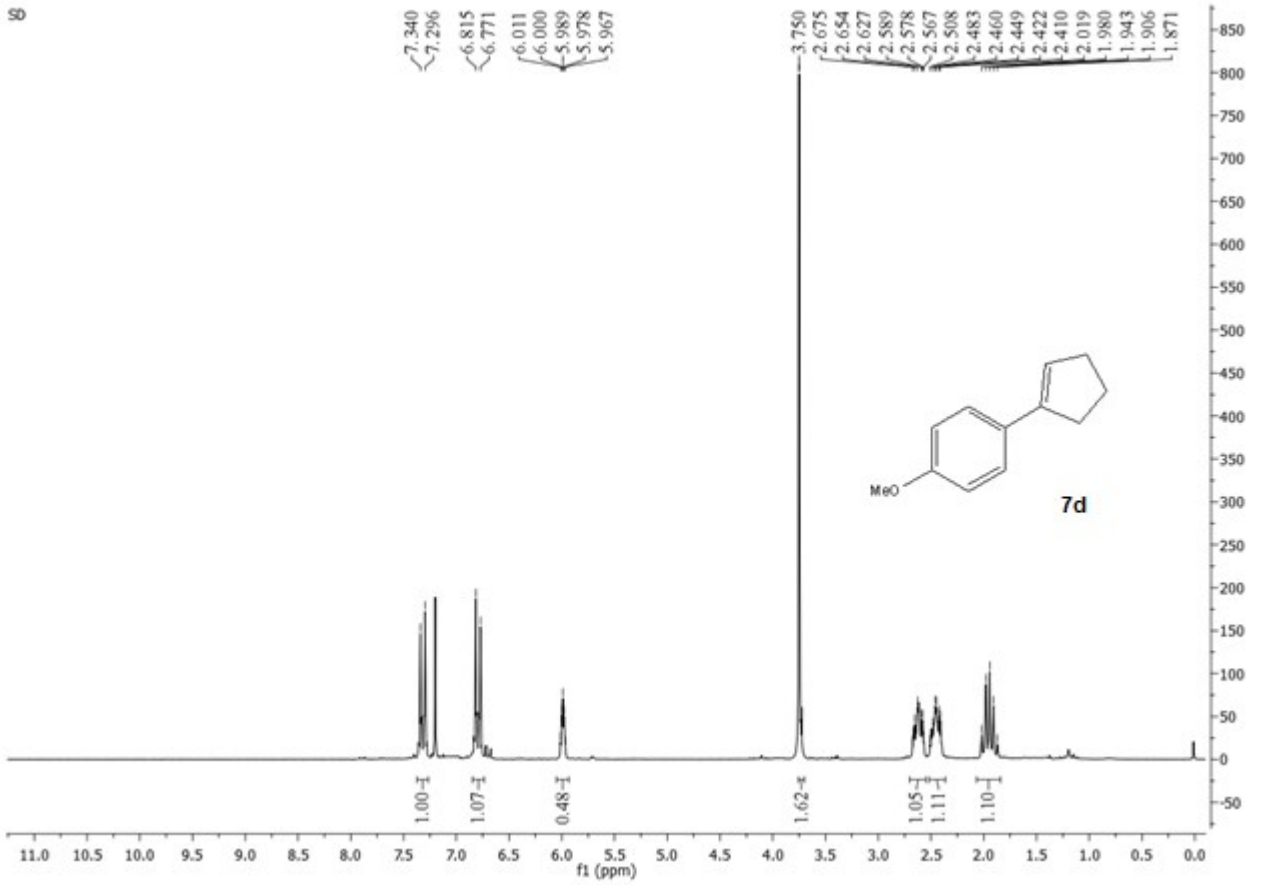

E:
193.990
162.384
153.049
130.566
126.907
126.588
114.735
55.620
CHO
MeO
4d
f1 (ppm)

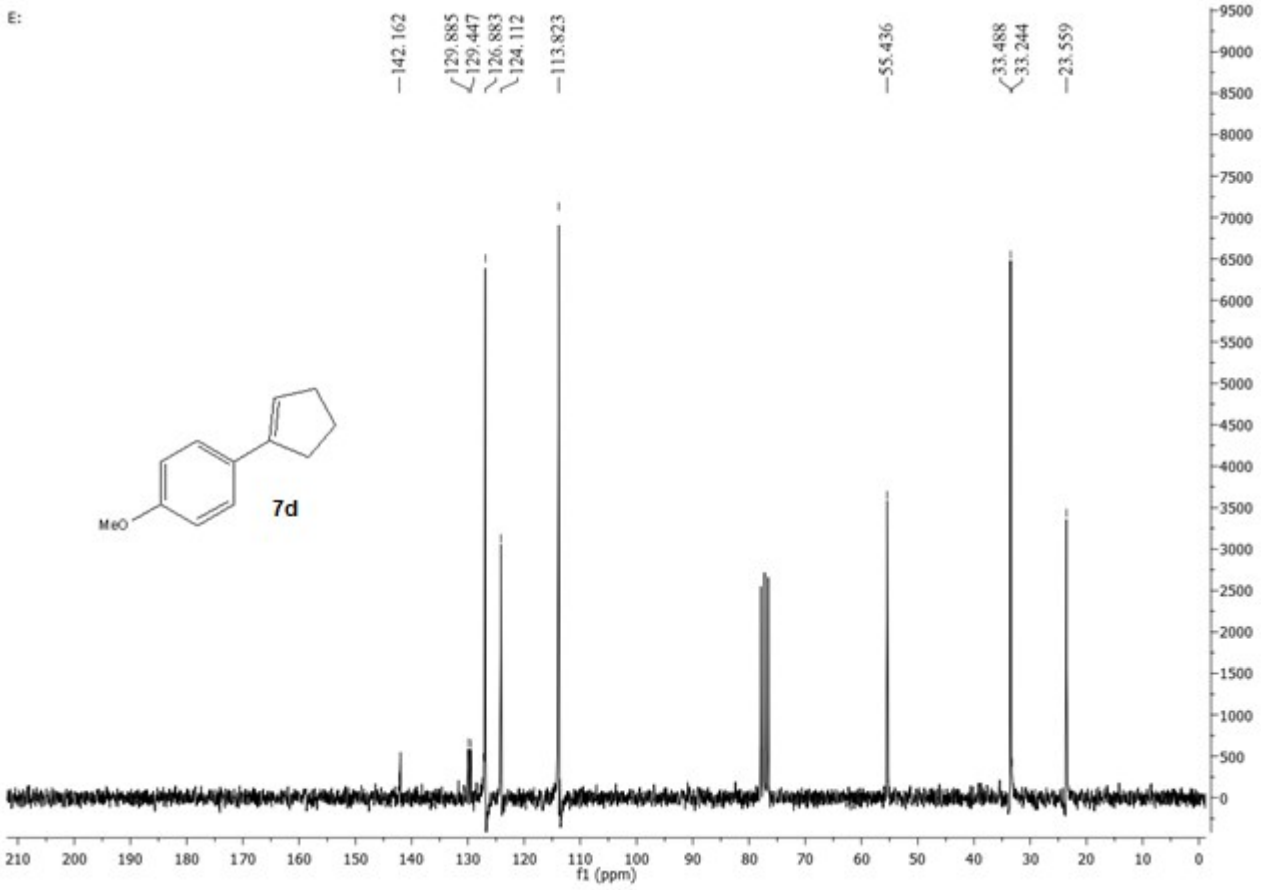

SD
7.616
7.536
7.430
7.386
6.855
6.811
6.281
6.201
4.239
4.204
4.168
4.133
3.767
1.301
1.265
1.229
COOEt
MeO
5d
1.00
2.04
2.17
1.06
2.60
3.39
3.60
f1 (ppm)

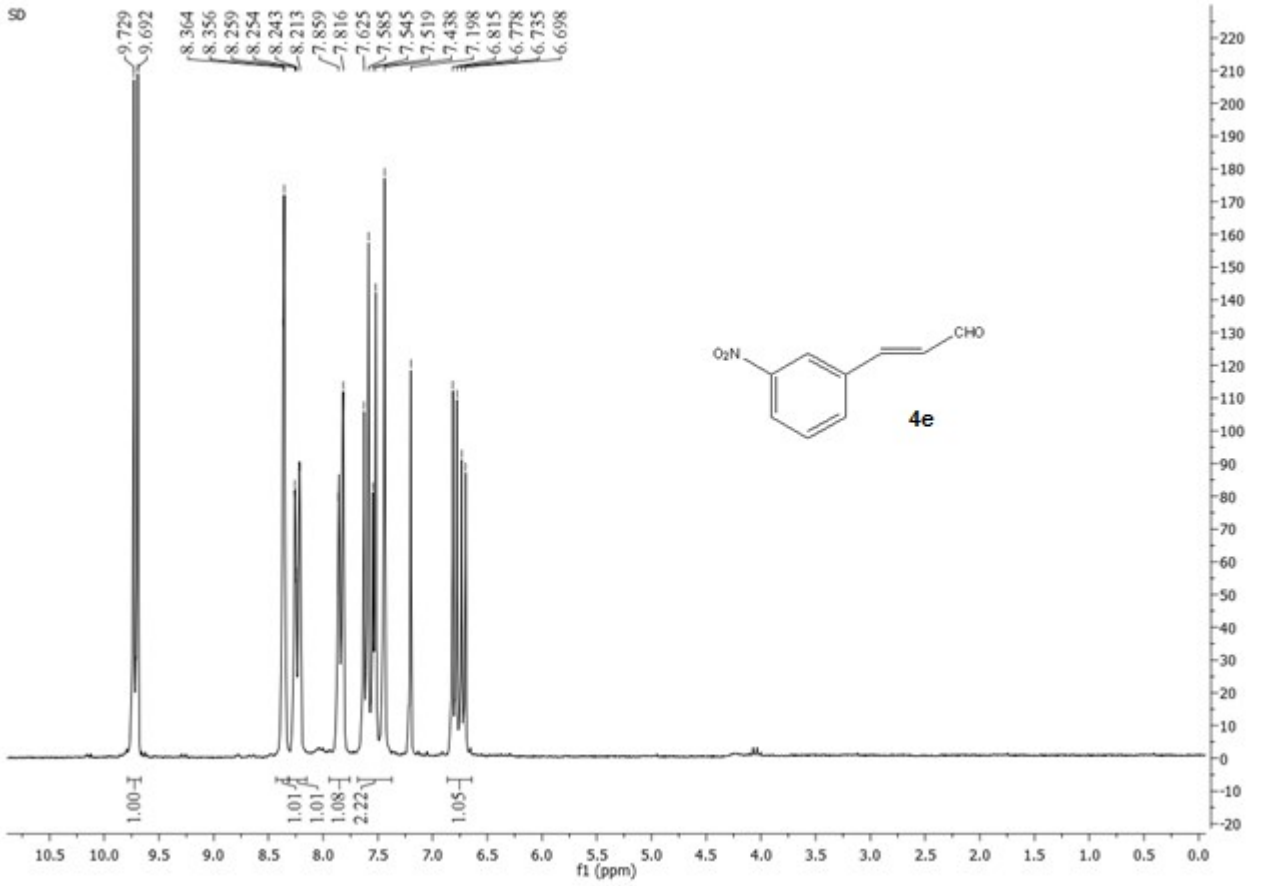

C13
167.555
161.489
144.445
129.863
127.342
115.877
114.466
60.519
55.535
14.522
COOEt
MeO
5d
f1 (ppm)

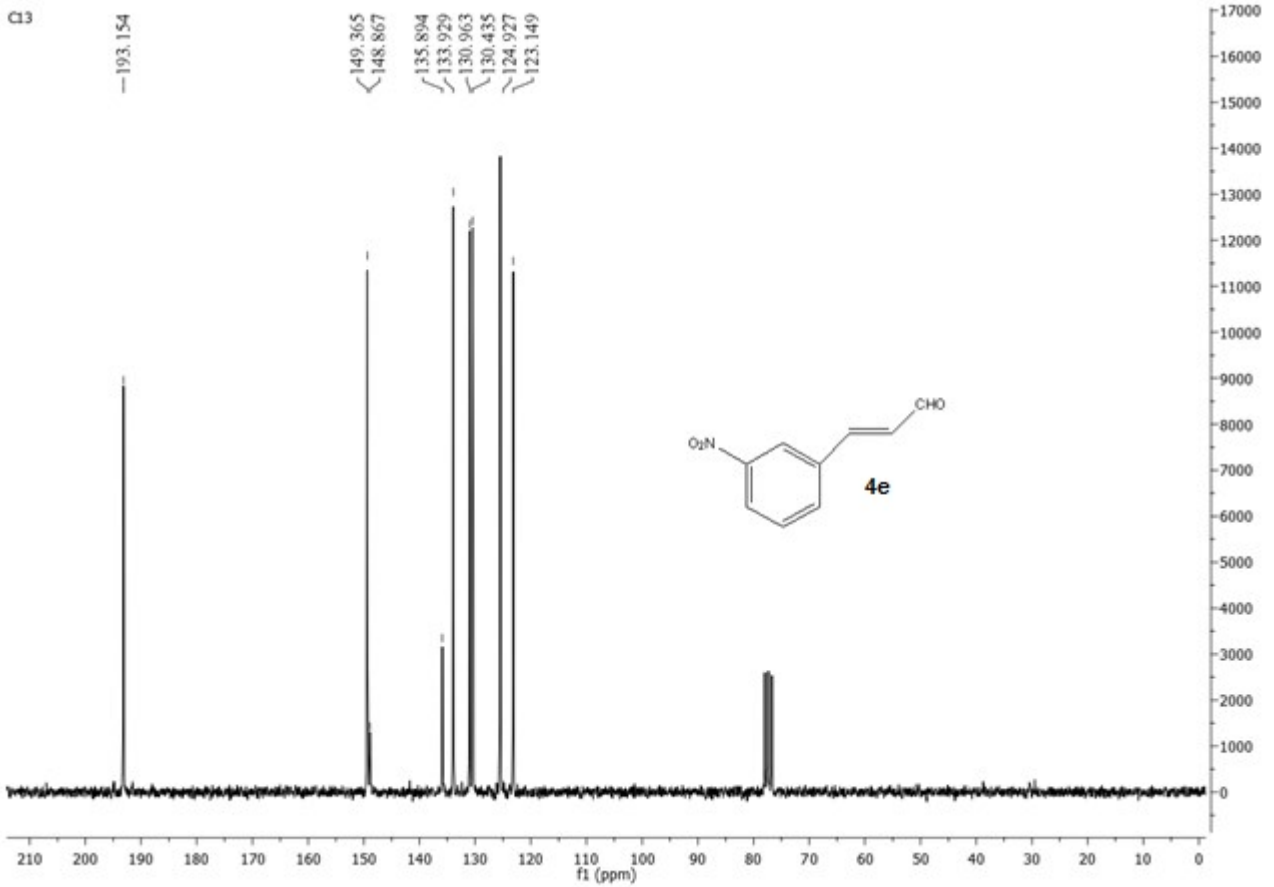

E:
7.513
7.475
7.431
7.387
7.352
7.313
7.274
7.238
7.201
7.047
7.009
6.921
6.877
3.799
MeO
6d
1.00
0.22
0.27
0.43
f1 (ppm)

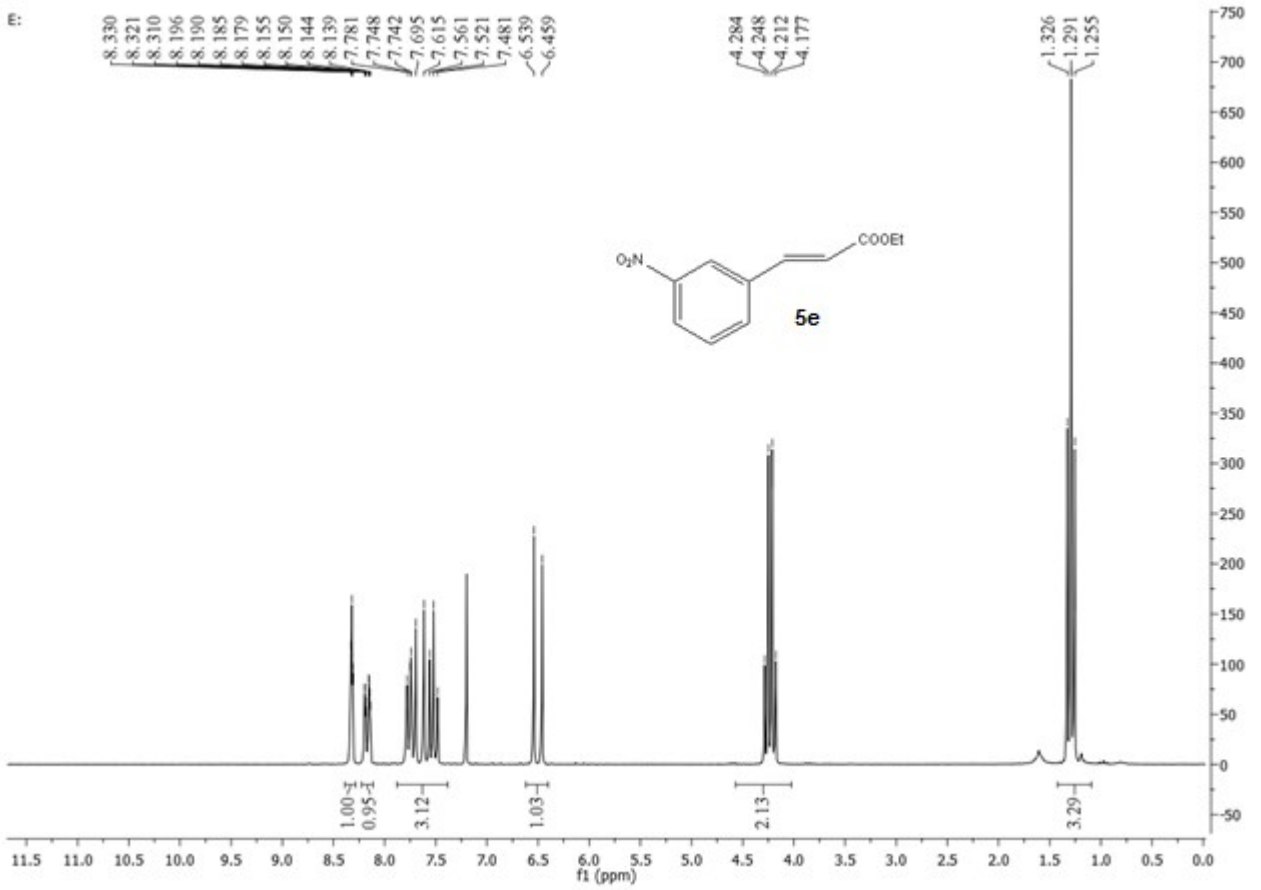

E:
159.550
137.890
130.355
128.911
128.455
127.999
127.472
126.824
126.526
114.382
55.517
MeO
6d
f1 (ppm)

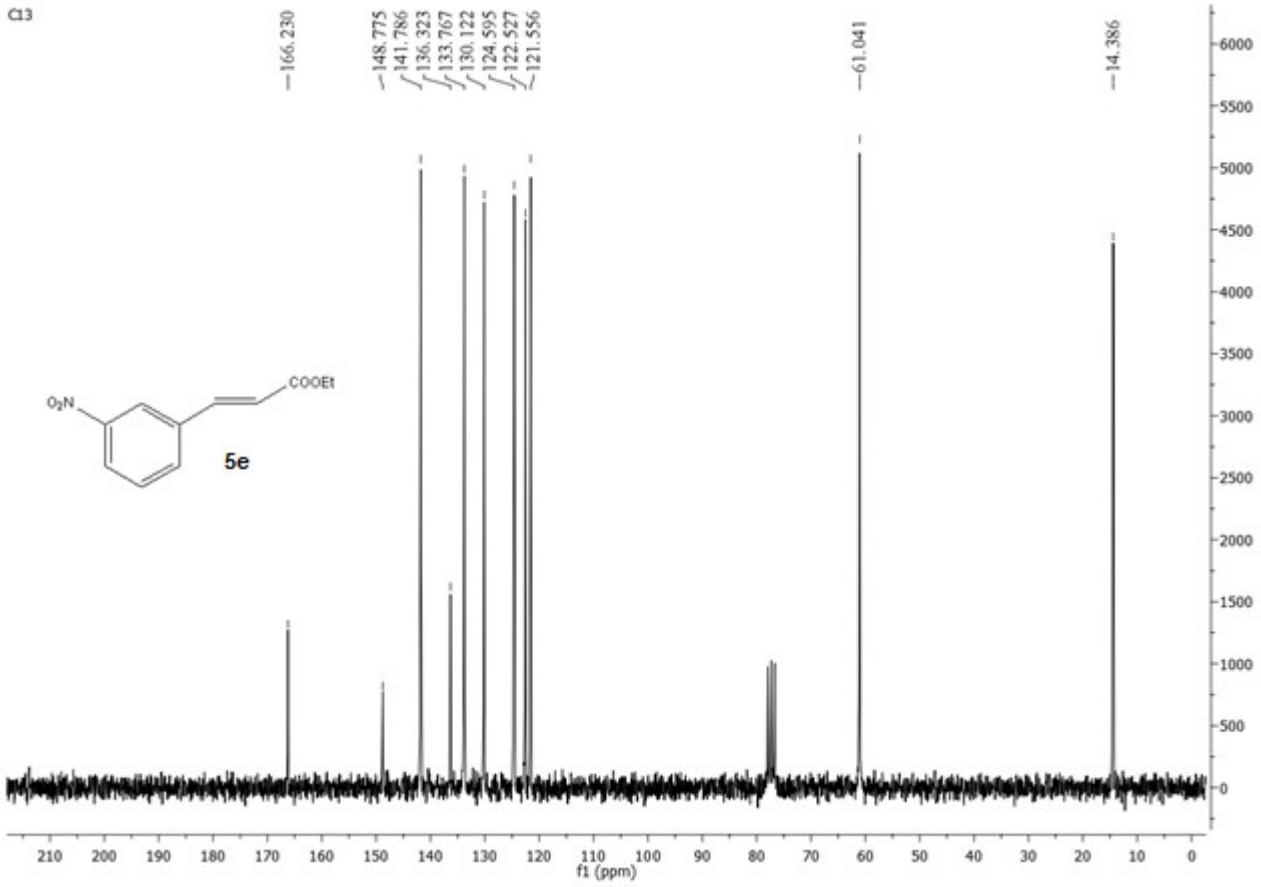

SD
7.340
7.296
6.815
6.771
6.011
6.000
5.989
5.978
5.967
3.750
2.675
2.654
2.627
2.589
2.578
2.567
2.508
2.483
2.460
2.449
2.422
2.410
2.019
1.980
1.943
1.906
1.871
MeO
7d
1.00
1.07
0.48
1.62
1.05
1.11
1.10
f1 (ppm)

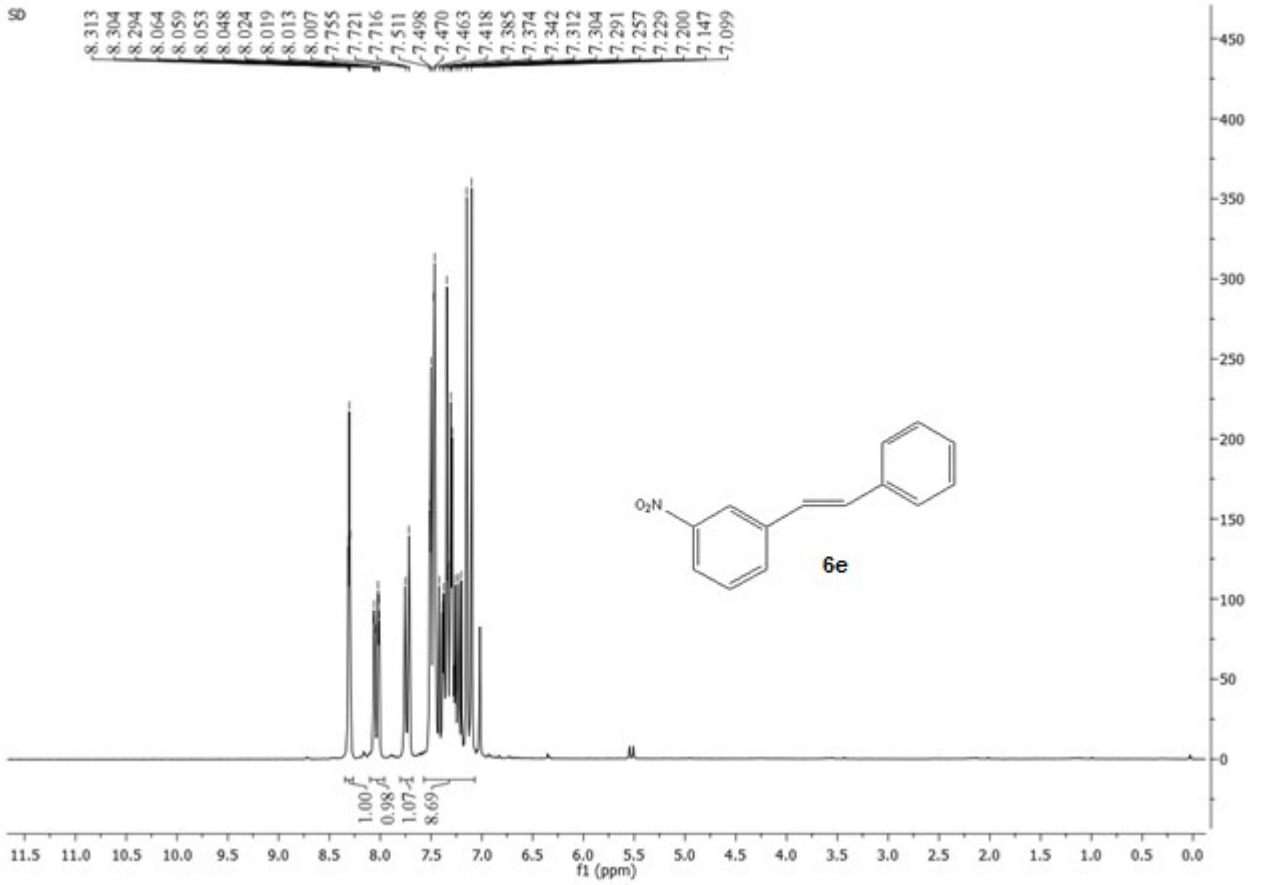

E:
142.162
129.885
129.447
126.883
124.112
113.823
55.436
33.488
33.244
23.559
MeO
7d
f1 (ppm)

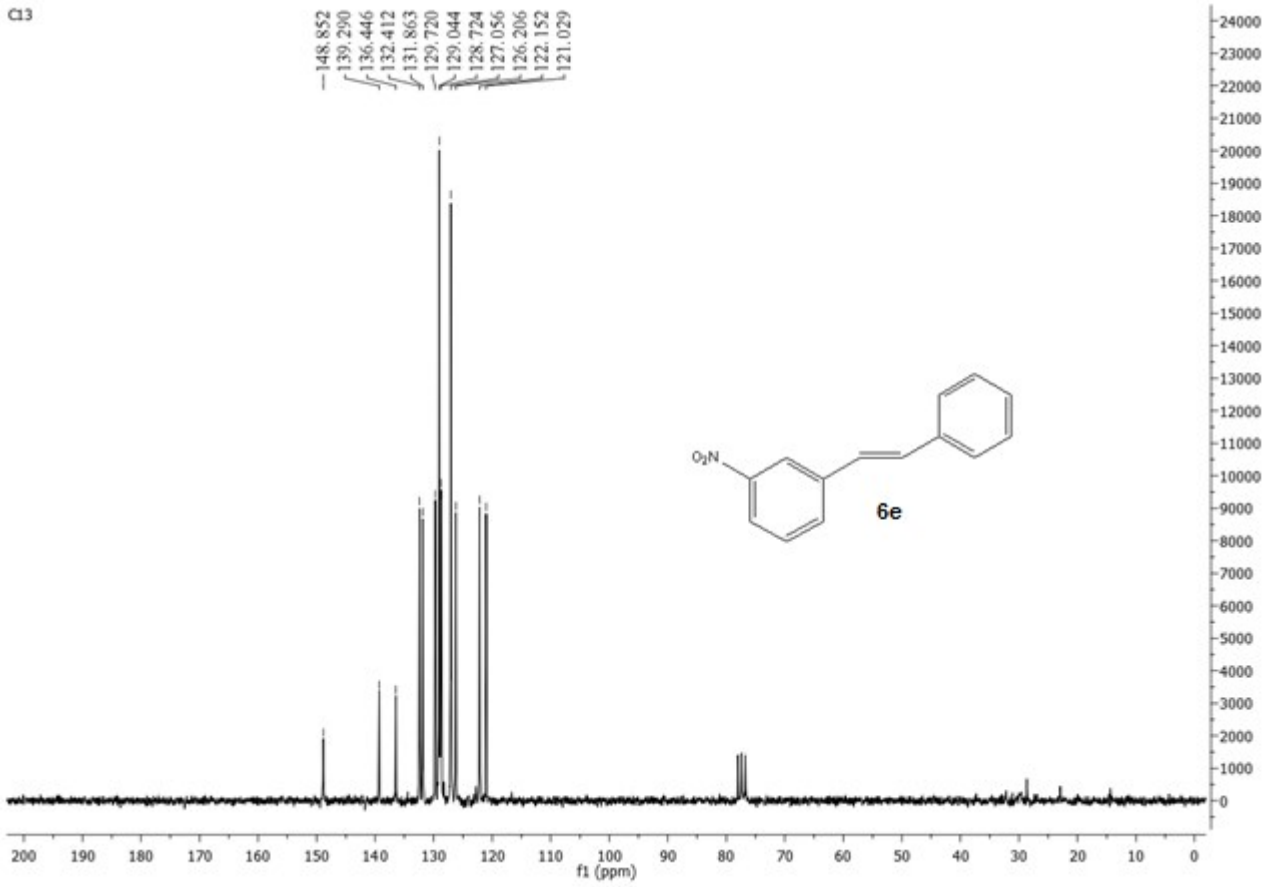

1H
9.729
9.692
8.364
8.356
8.259
8.254
8.243
8.213
7.859
7.816
7.625
7.585
7.545
7.519
7.438
7.198
6.815
6.778
6.735
6.698
1.00
1.01
1.01
1.08
2.22
1.05
O2N
CHO
4e
f1 (ppm)

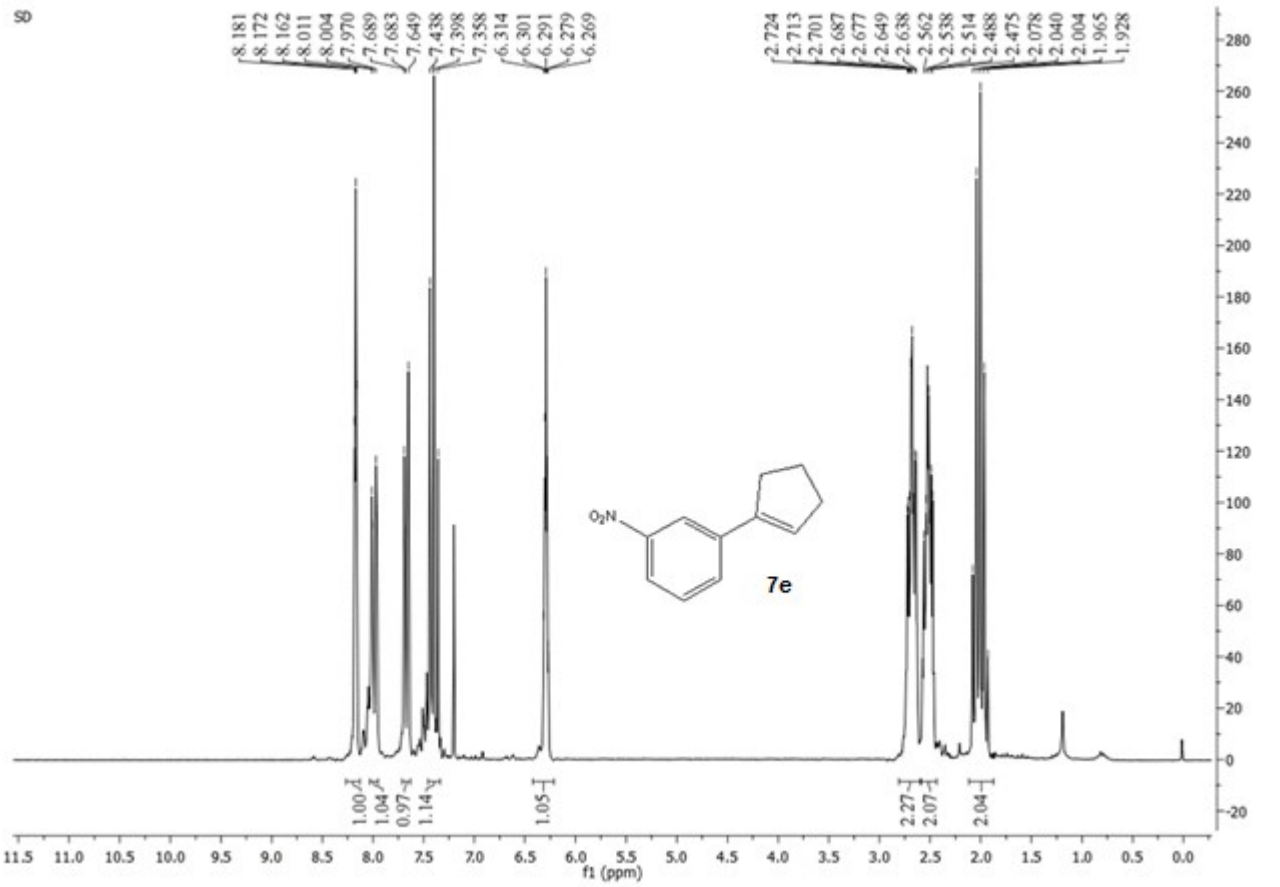

13C
193.154
149.365
148.867
135.894
133.929
130.963
130.435
124.927
123.149
O2N
CHO
4e
f1 (ppm)

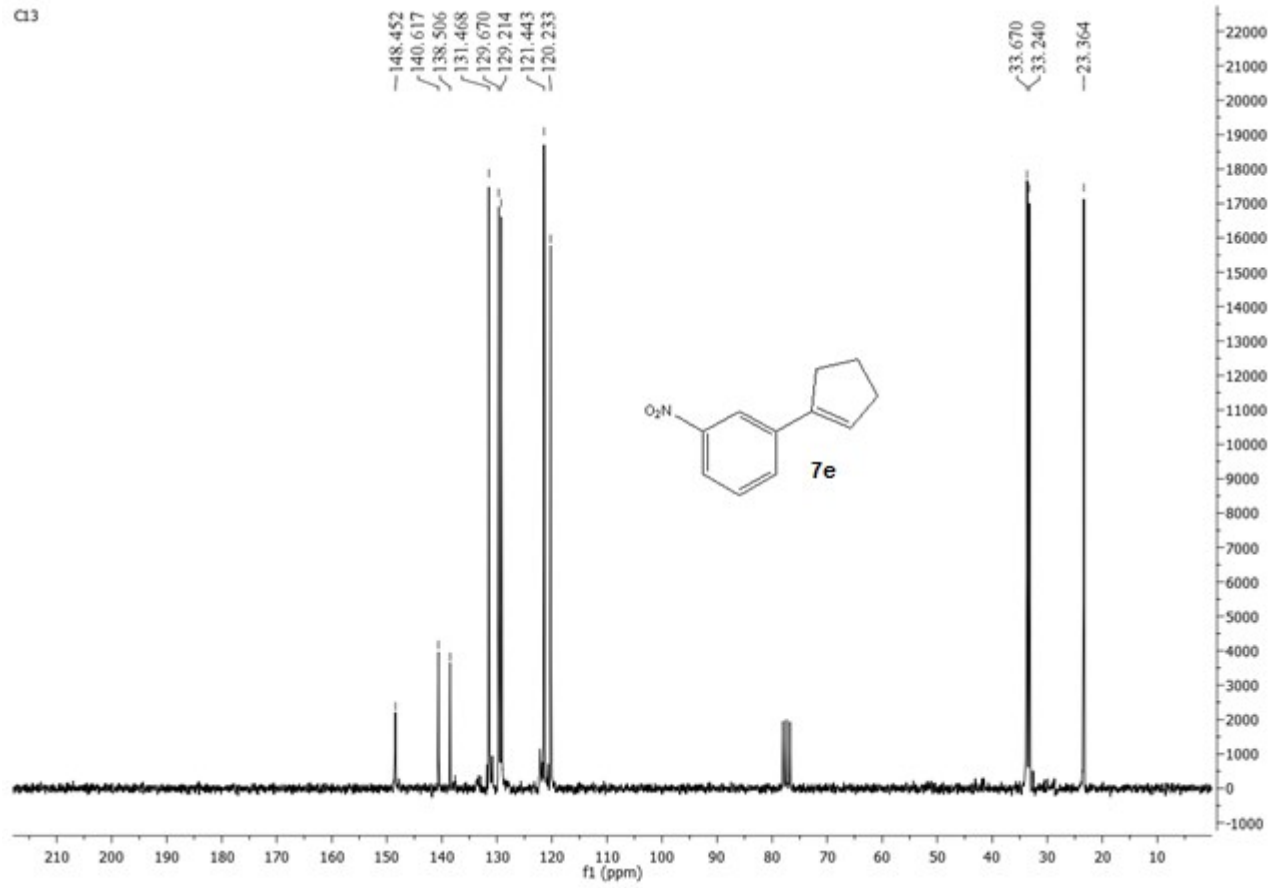

8.330
8.321
8.310
8.196
8.190
8.185
8.179
8.155
8.150
8.144
8.139
7.781
7.748
7.742
7.695
7.615
7.561
7.521
7.481
6.539
6.459
4.284
4.248
4.212
4.177
1.326
1.291
1.255
O2N
COOEt
5e
1.00
0.95
3.12
1.03
2.13
3.29
f1 (ppm)

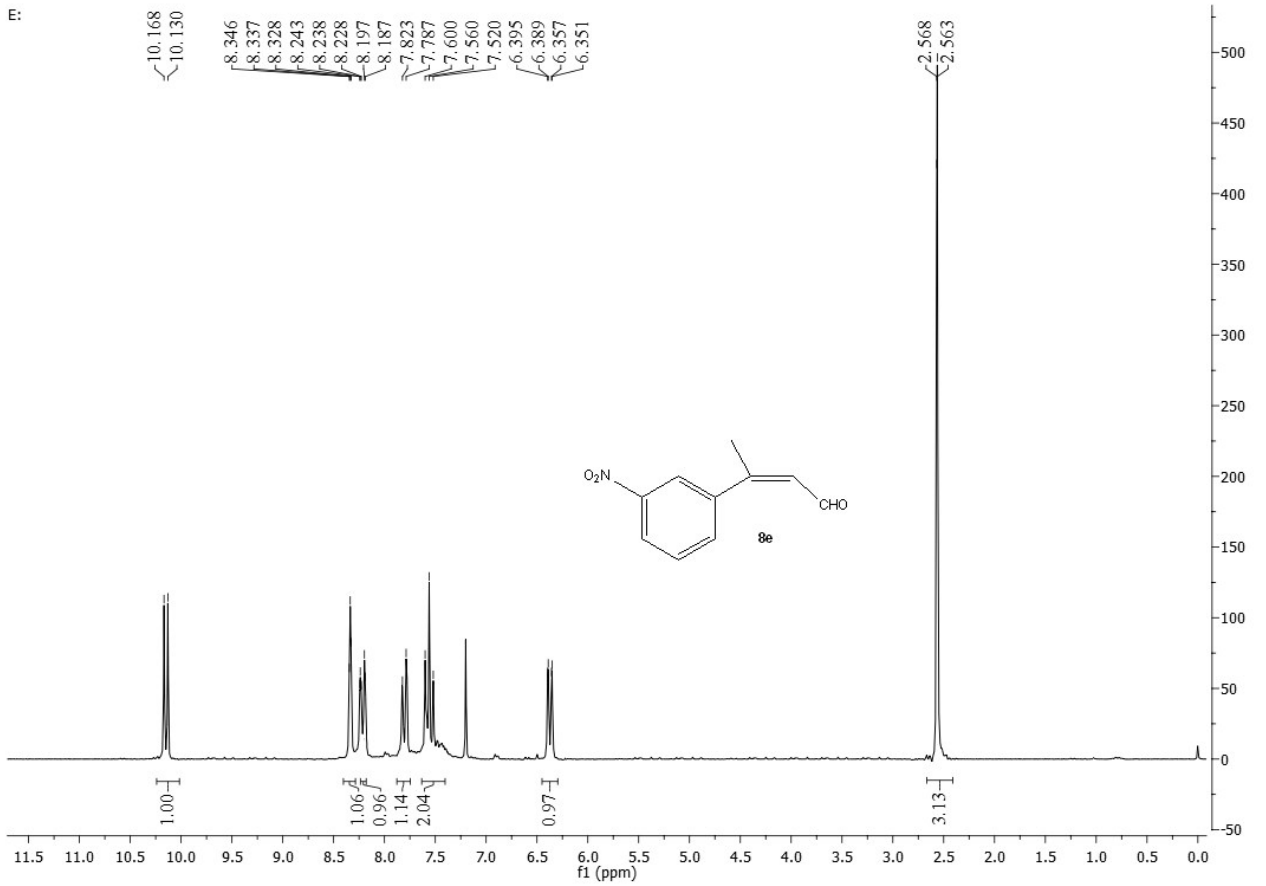

C13
166.230
148.775
141.786
136.323
133.767
130.122
124.595
122.527
121.556
61.041
14.386
O2N
COOEt
5e
f1 (ppm)

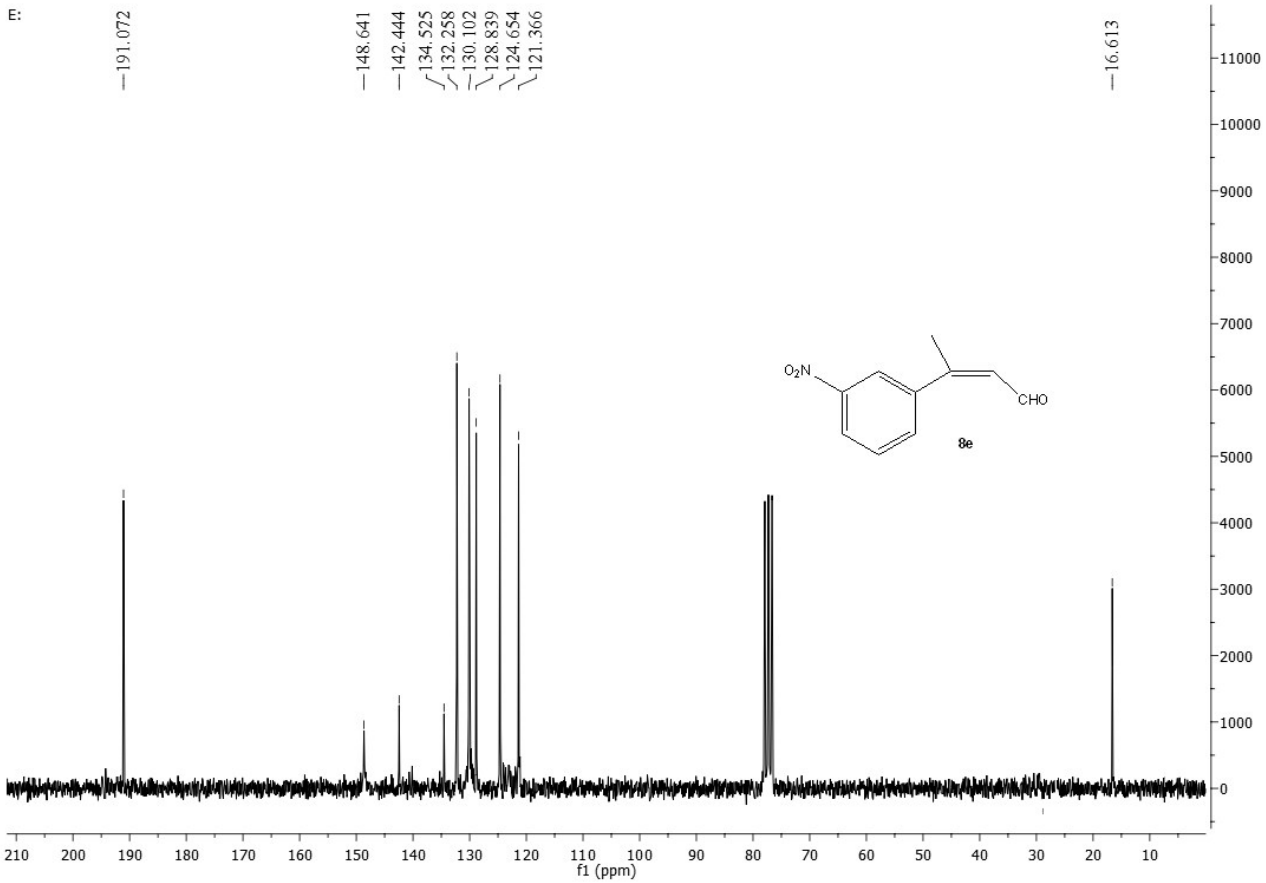

S0
8.313
8.304
8.294
8.064
8.059
8.053
8.048
8.024
8.019
8.013
8.007
7.755
7.721
7.716
7.511
7.498
7.470
7.463
7.418
7.385
7.374
7.342
7.312
7.304
7.291
7.257
7.229
7.200
7.147
7.099
1.00
0.98
1.07
8.69
O2N
6e
f1 (ppm)

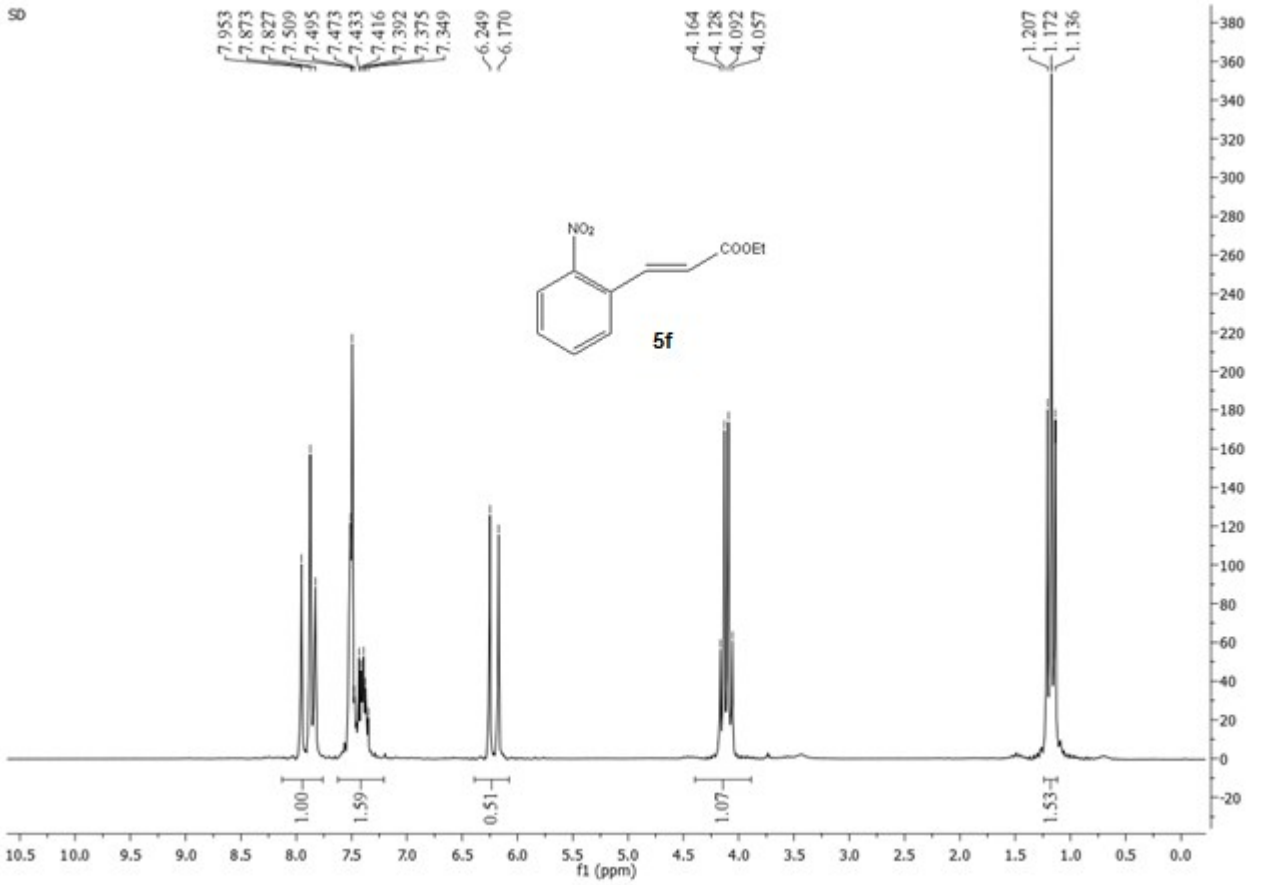

C13
148.852
139.290
136.446
132.412
131.863
129.720
129.044
128.724
127.056
126.206
122.152
121.029
O2N
6e
f1 (ppm)

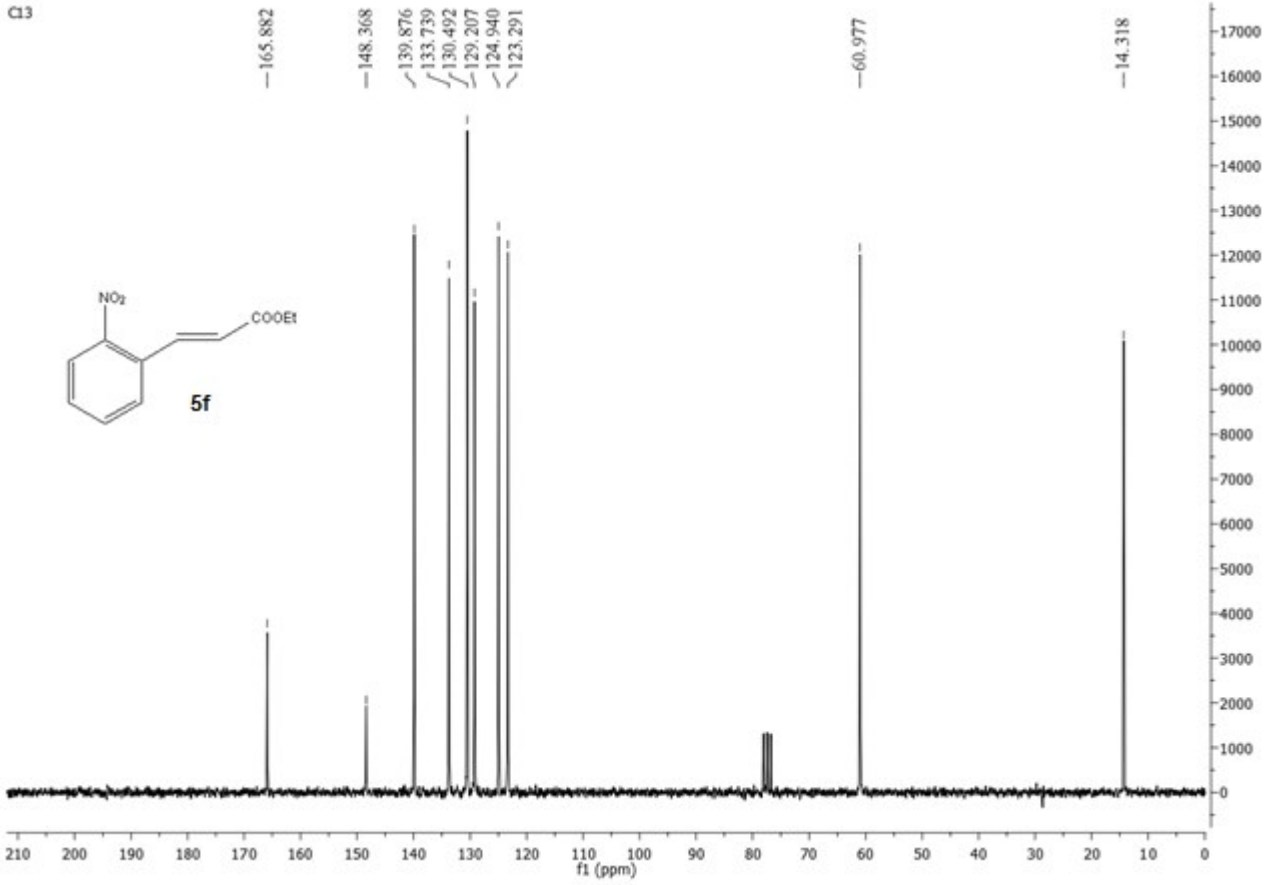

S0
8.181
8.172
8.162
8.011
8.004
7.970
7.689
7.683
7.649
7.438
7.398
7.358
6.314
6.301
6.291
6.279
6.269
2.724
2.713
2.701
2.687
2.677
2.649
2.638
2.562
2.538
2.514
2.488
2.475
2.078
2.040
2.004
1.965
1.928
1.00
1.04
0.97
1.14
1.05
2.27
2.07
2.04
O2N
7e
f1 (ppm)

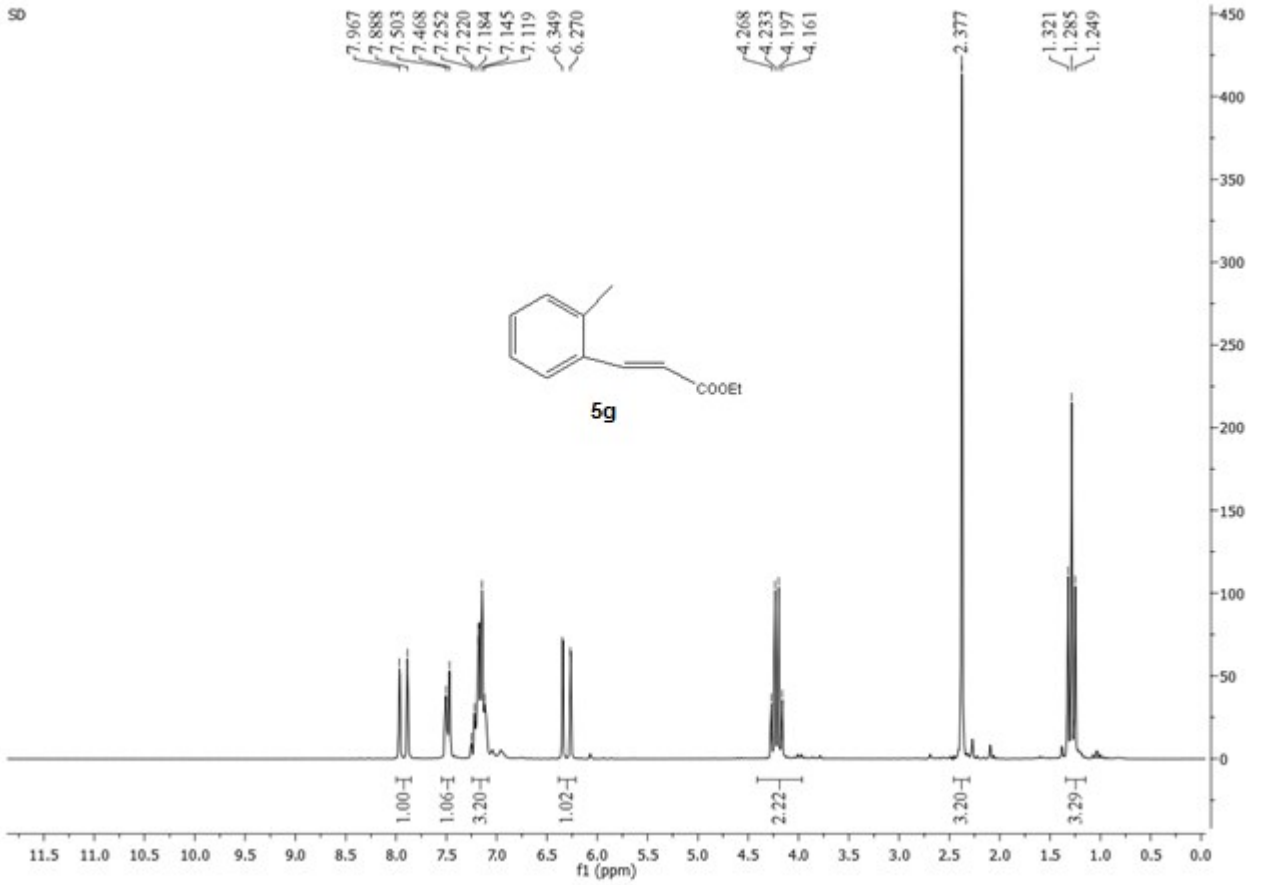

C13
148.452
140.617
138.506
131.468
129.670
129.214
121.443
120.233
33.670
33.240
23.364
O2N
7e
f1 (ppm)

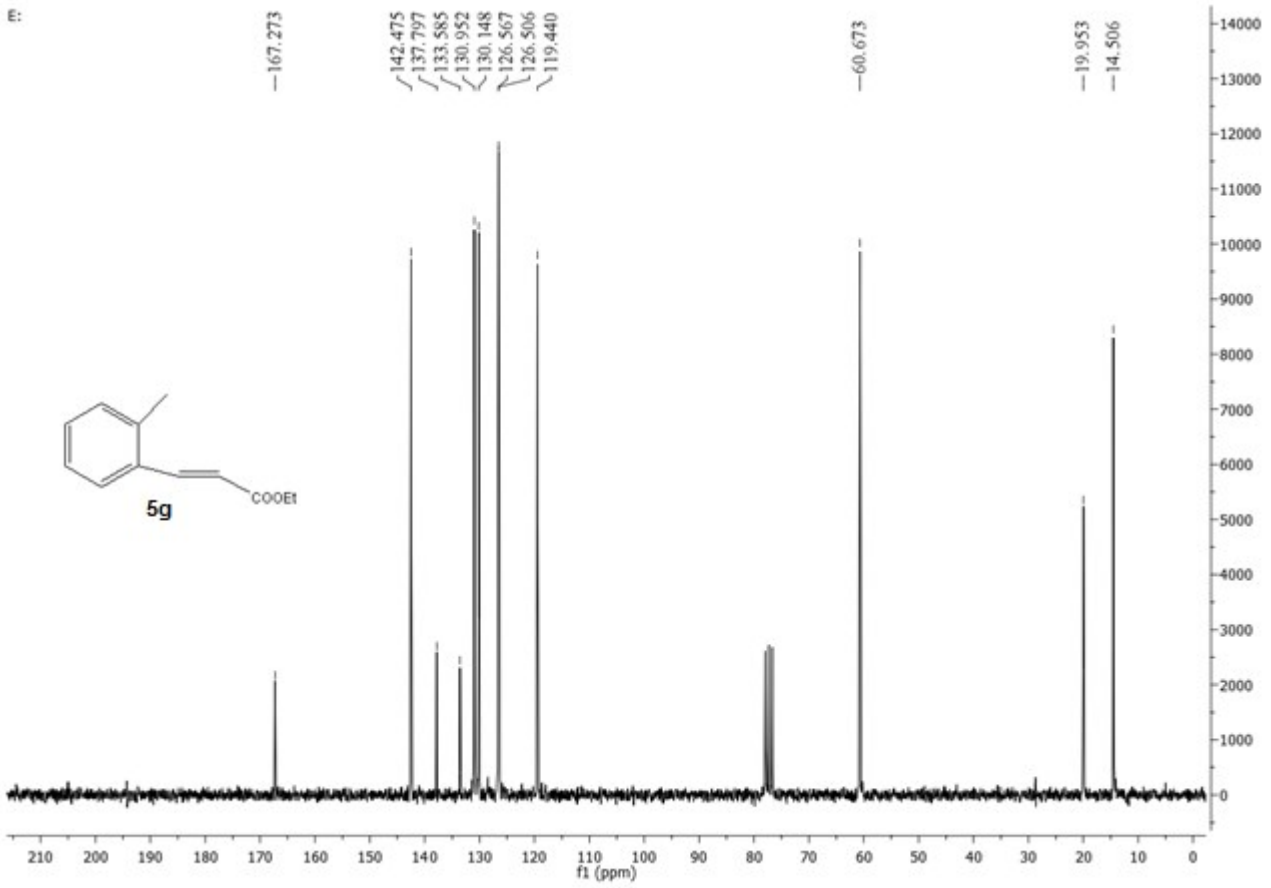

E:
10.168
10.130
8.346
8.337
8.328
8.243
8.238
8.228
8.197
8.187
7.823
7.787
7.600
7.560
7.520
6.395
6.389
6.357
6.351
2.568
2.563
O2N
CHO
8e
1.00
1.06
0.96
1.14
2.04
0.97
3.13
f1 (ppm)

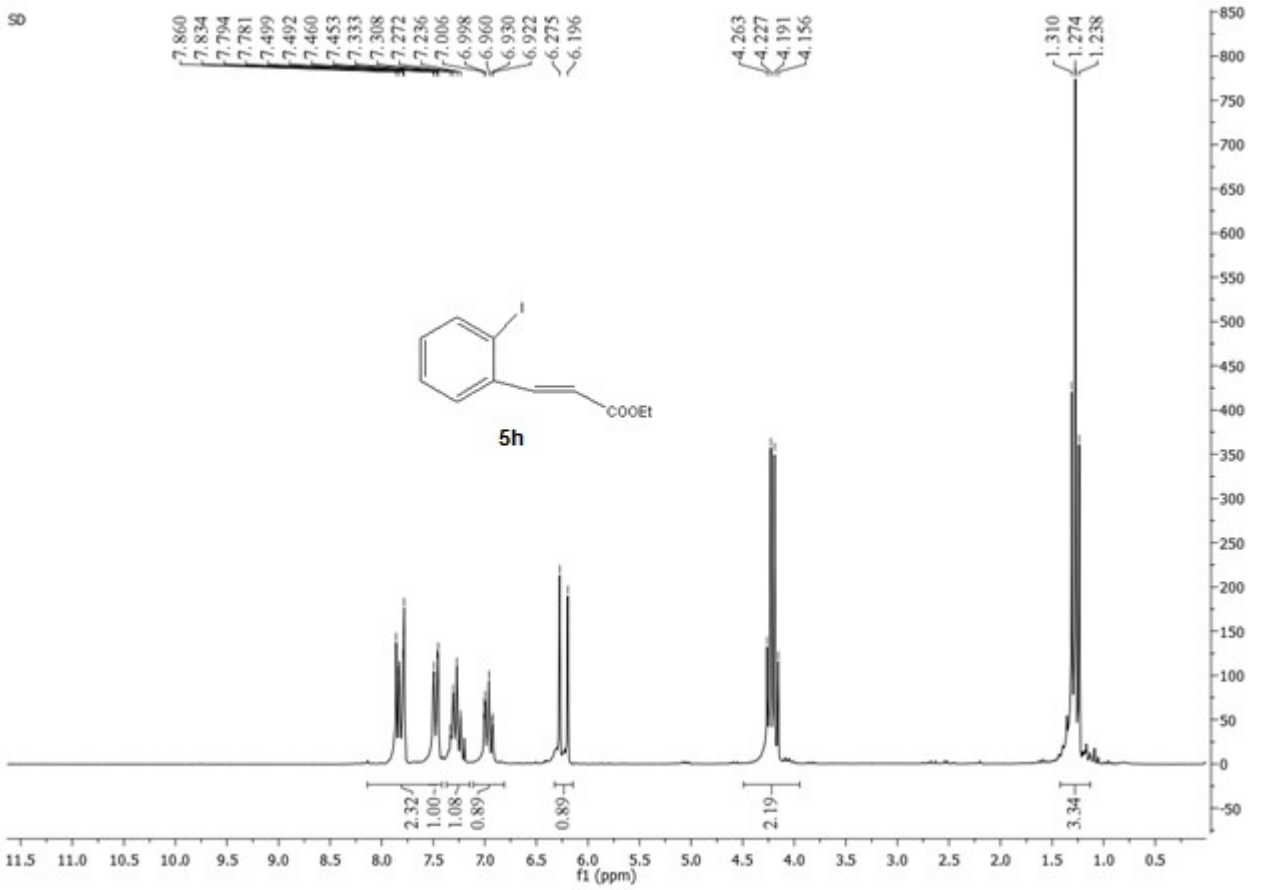

E:
191.072
148.641
142.444
134.525
132.258
130.102
128.839
124.654
121.366
16.613
O2N
CHO
8e
f1 (ppm)

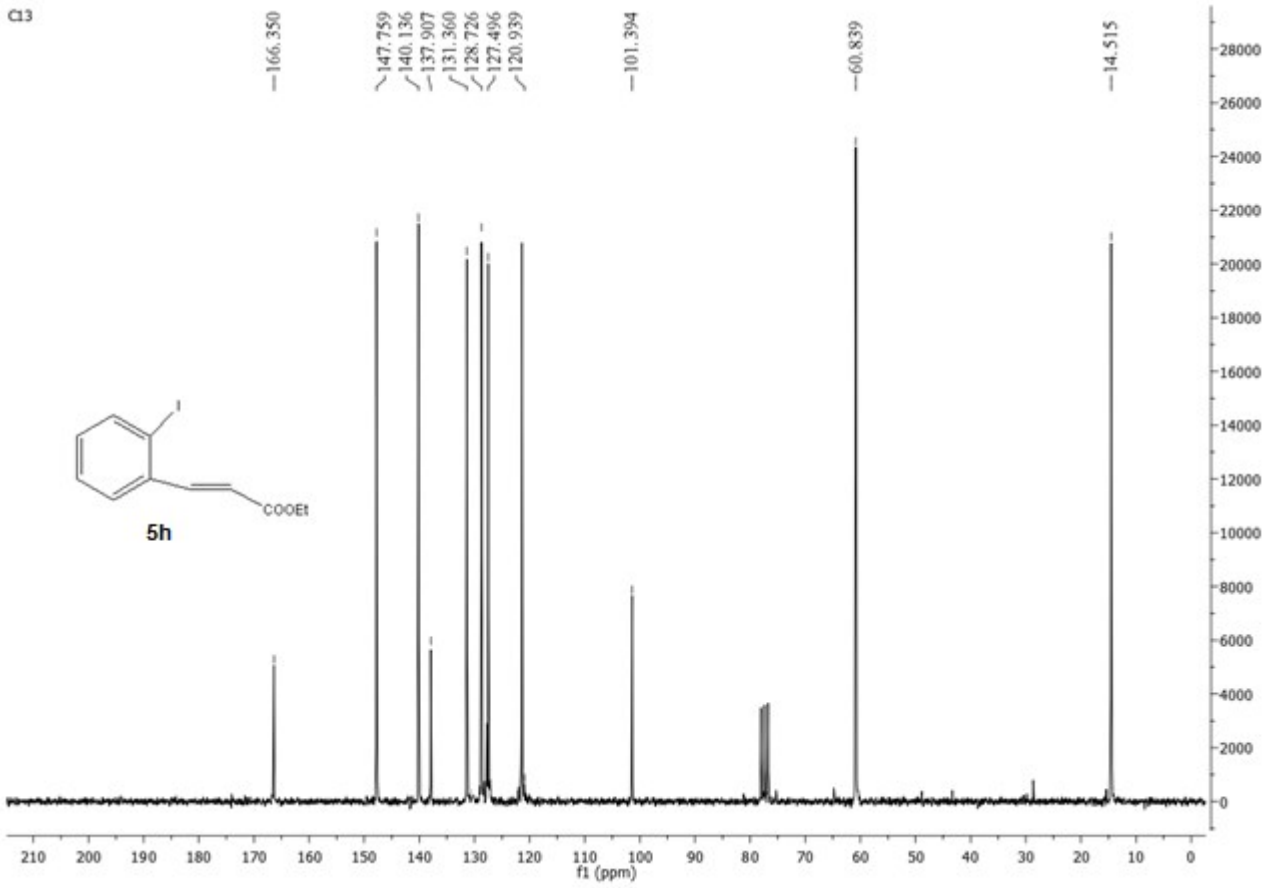

S0
7.953
7.873
7.827
7.509
7.495
7.473
7.433
7.416
7.392
7.375
7.349
6.249
6.170
4.164
4.128
4.092
4.057
1.207
1.172
1.136
NO2
COOEt
5f
1.00
1.59
0.51
1.07
1.53
f1 (ppm)

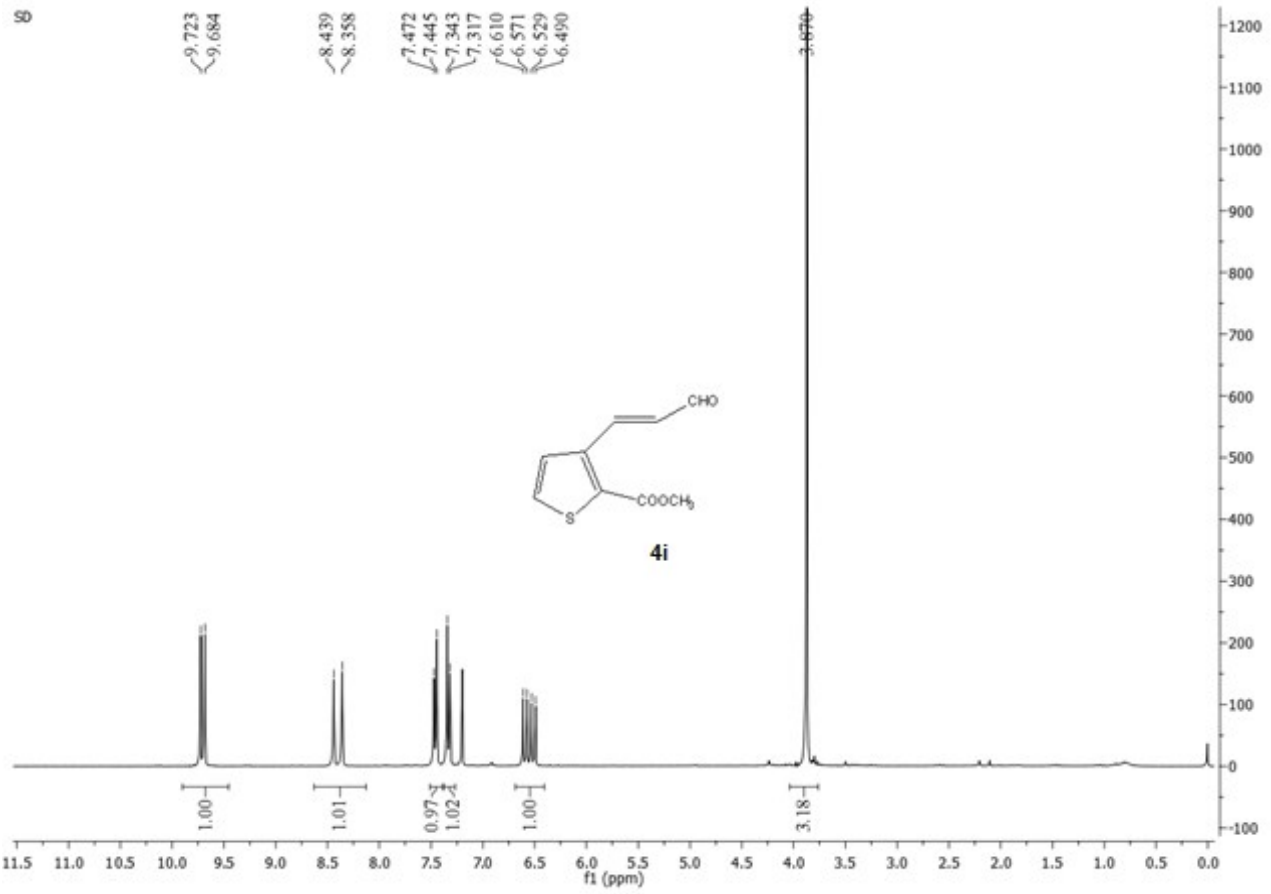

C13
165.882
148.368
139.876
133.739
130.492
129.207
124.940
123.291
60.977
14.318
NO2
COOEt
5f
f1 (ppm)

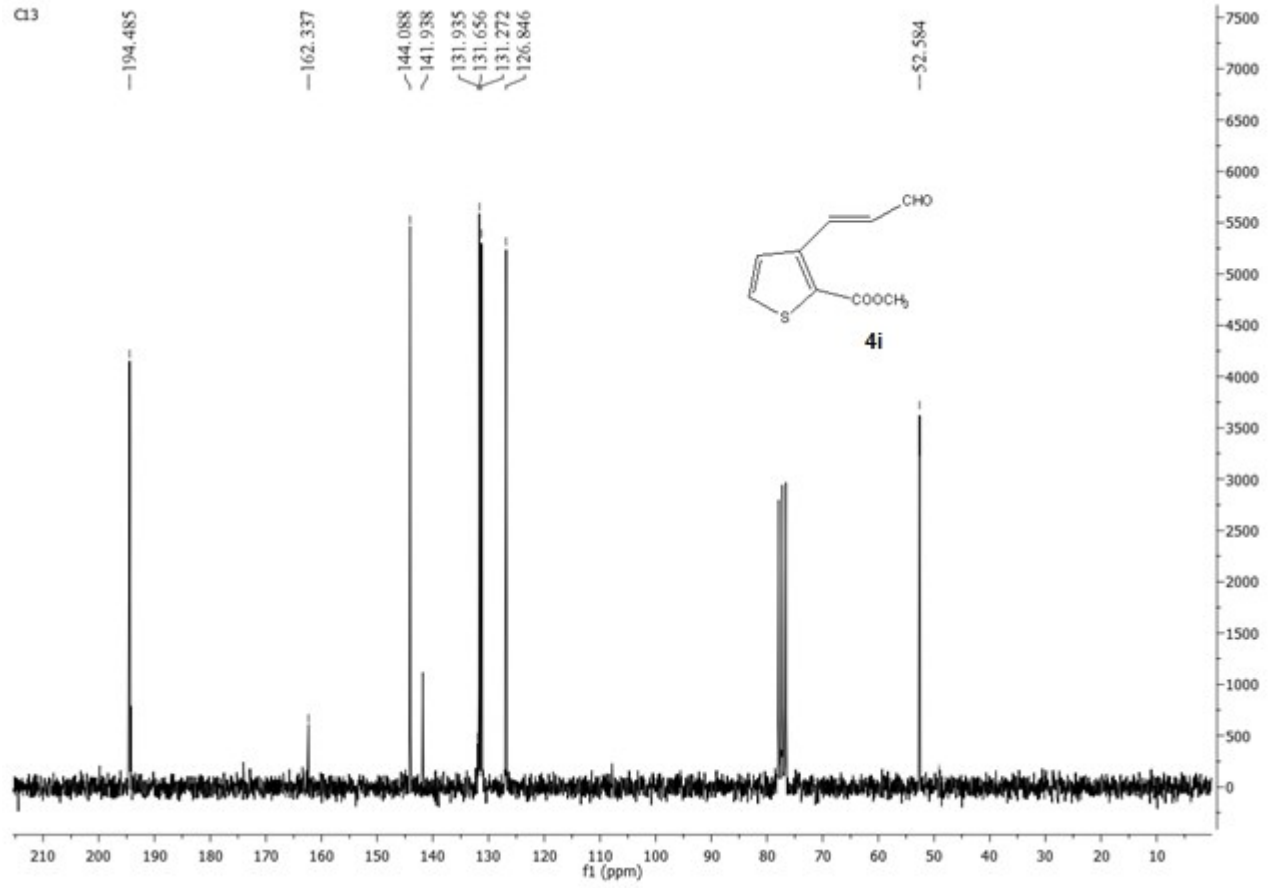

7.967
7.888
7.503
7.468
7.252
7.220
7.184
7.145
7.119
6.349
6.270
4.268
4.233
4.197
4.161
2.377
1.321
1.285
1.249
1.00
1.06
3.20
1.02
2.22
3.20
3.29
COOEt
5g
f1 (ppm)

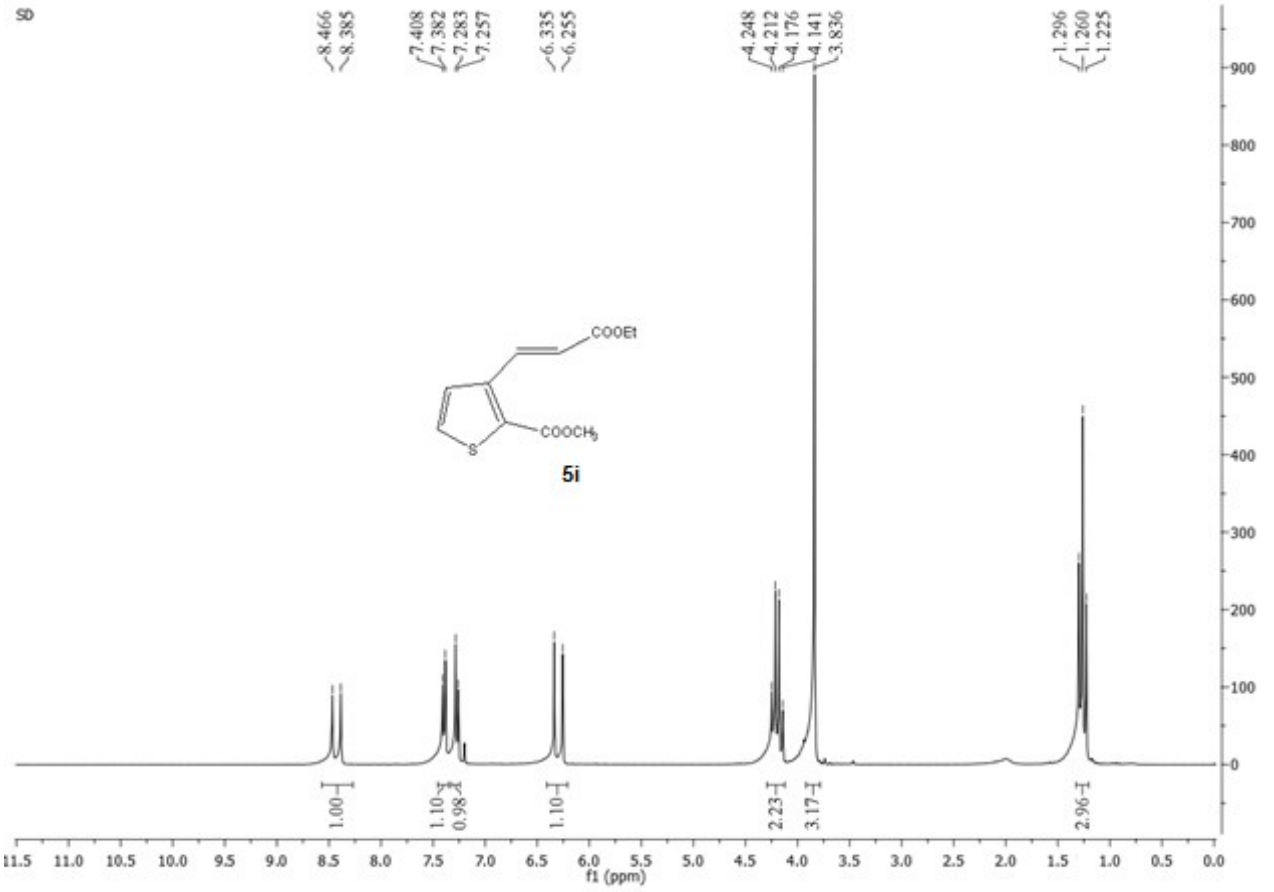

167.273
142.475
137.797
133.585
130.952
130.148
126.567
126.506
119.440
60.673
19.953
14.506
COOEt
5g
f1 (ppm)

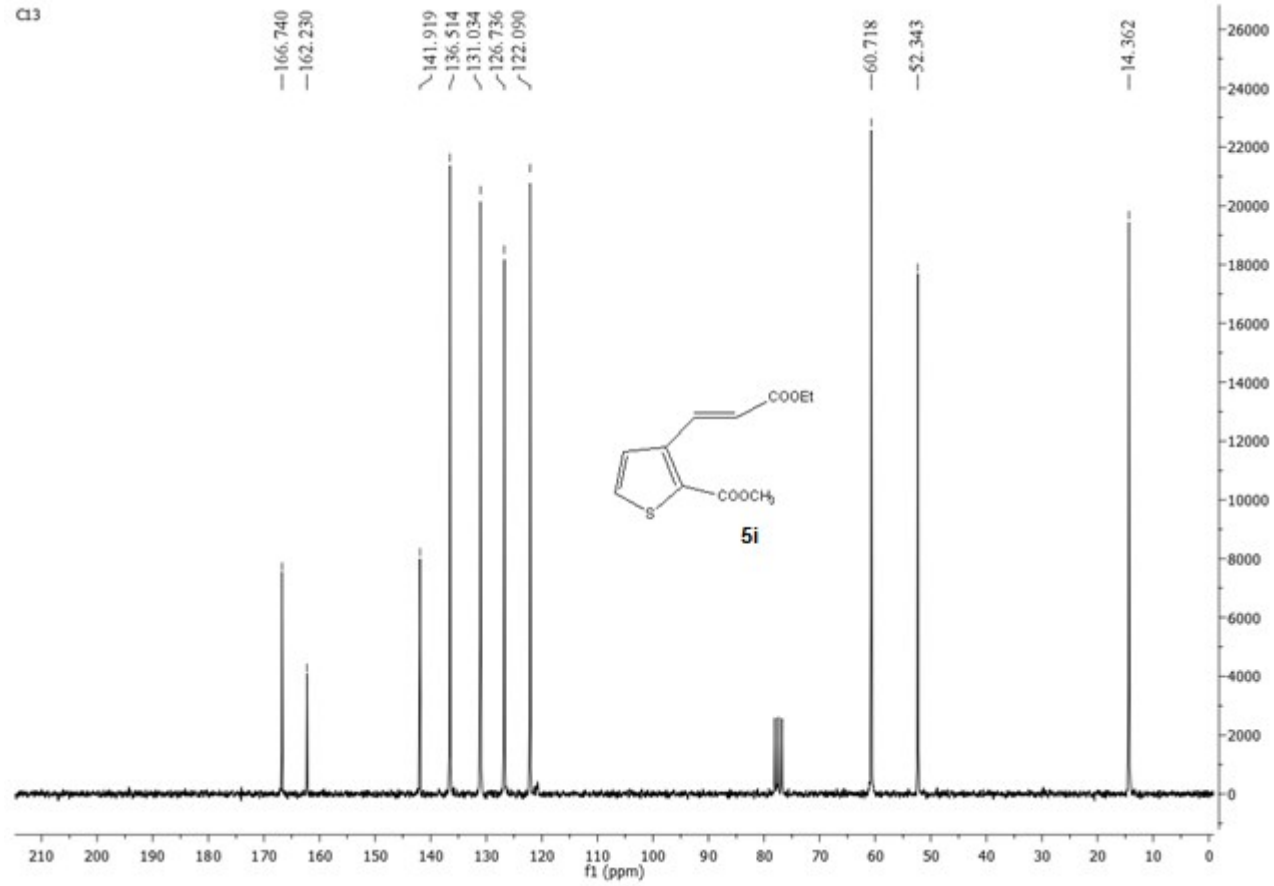

1H
7.860
7.834
7.794
7.781
7.499
7.492
7.460
7.453
7.333
7.308
7.272
7.236
7.006
6.998
6.960
6.930
6.922
6.275
6.196
4.263
4.227
4.191
4.156
1.310
1.274
1.238
I
COOEt
5h
2.32
1.00
1.08
0.89
0.89
2.19
3.34
f1 (ppm)

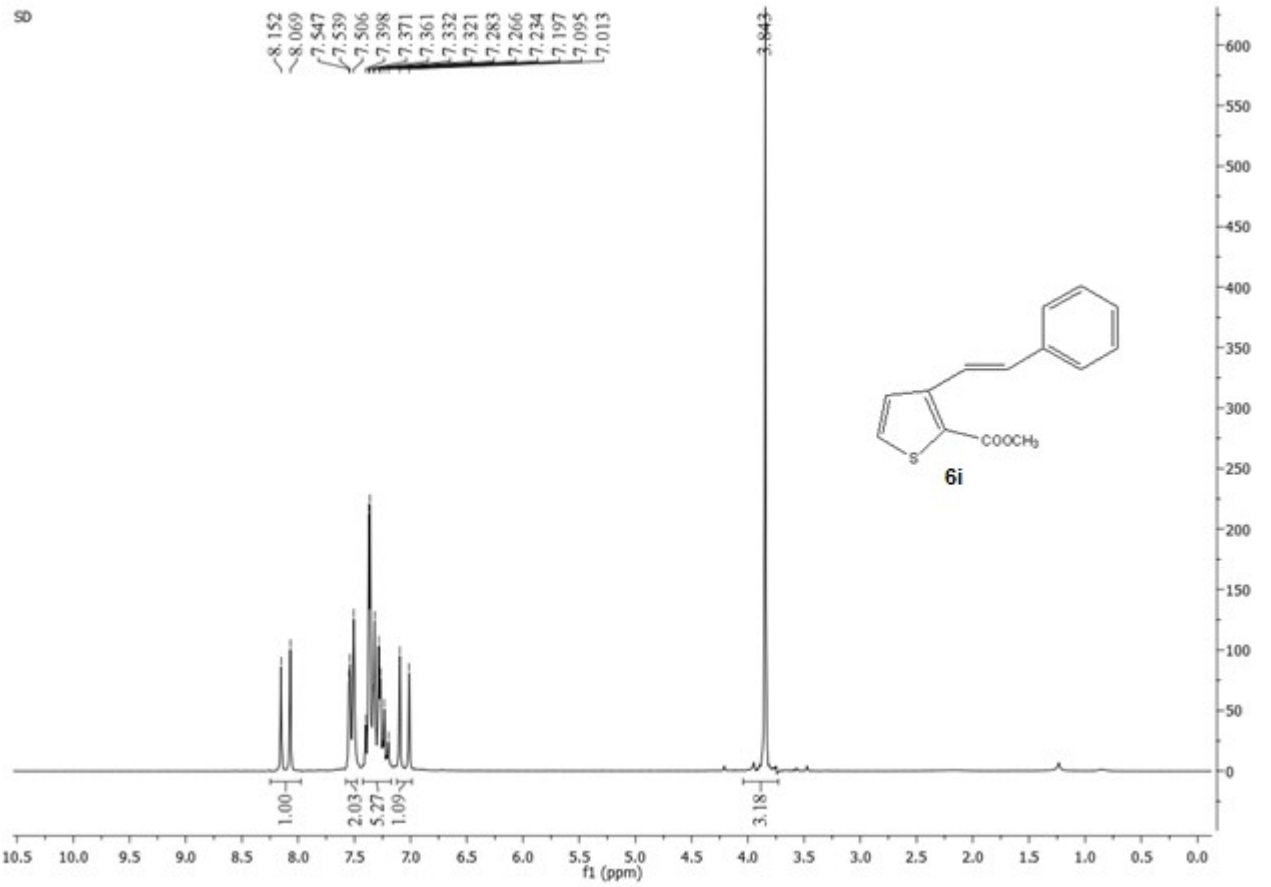

13C
166.350
147.759
140.136
137.907
131.360
128.726
127.496
120.939
101.394
60.839
14.515
I
COOEt
5h
f1 (ppm)

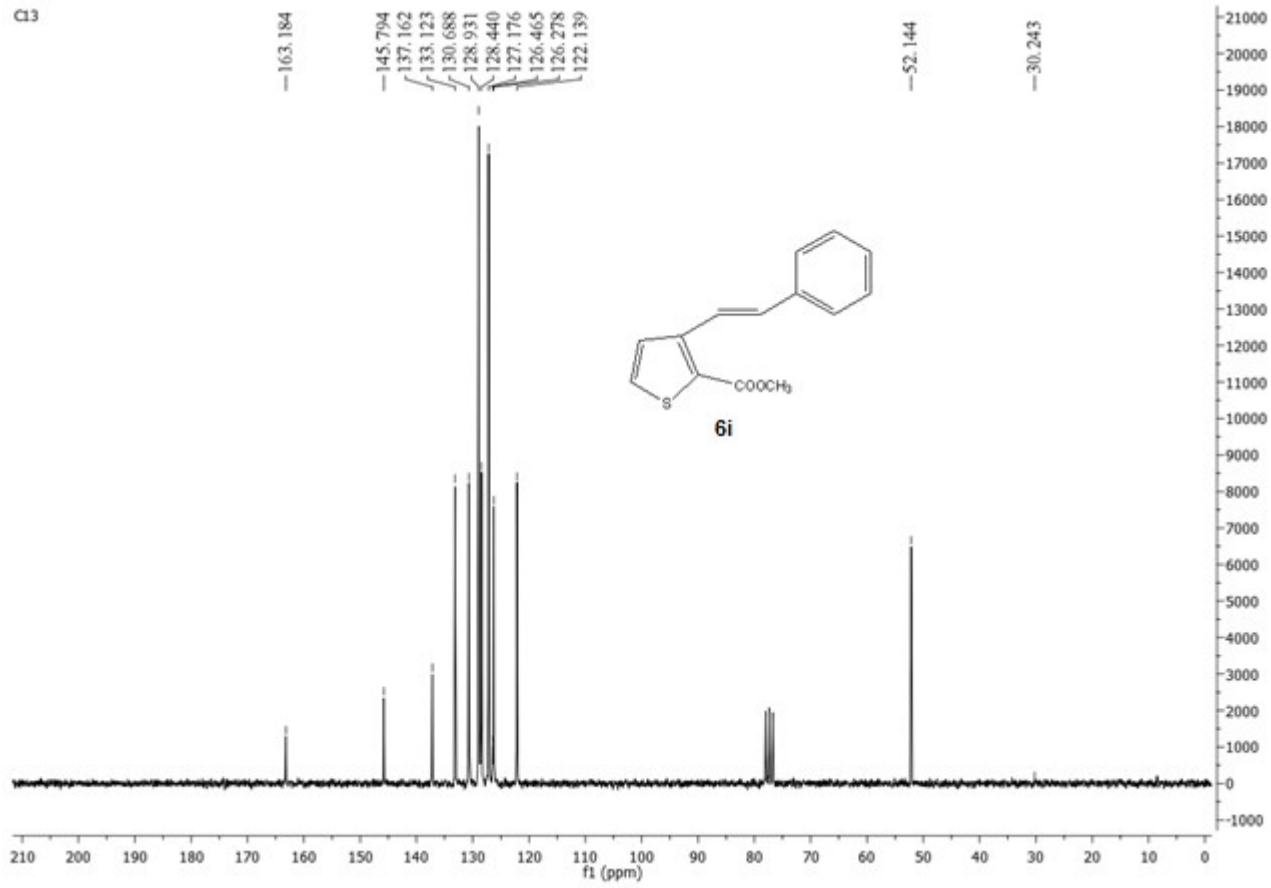

S0
9.723
9.684
8.439
8.358
7.472
7.445
7.343
7.317
6.610
6.571
6.529
6.490
3.870
1.00
1.01
0.97
1.02
1.00
3.18
CHO
COOCH3
S
4i
f1 (ppm)

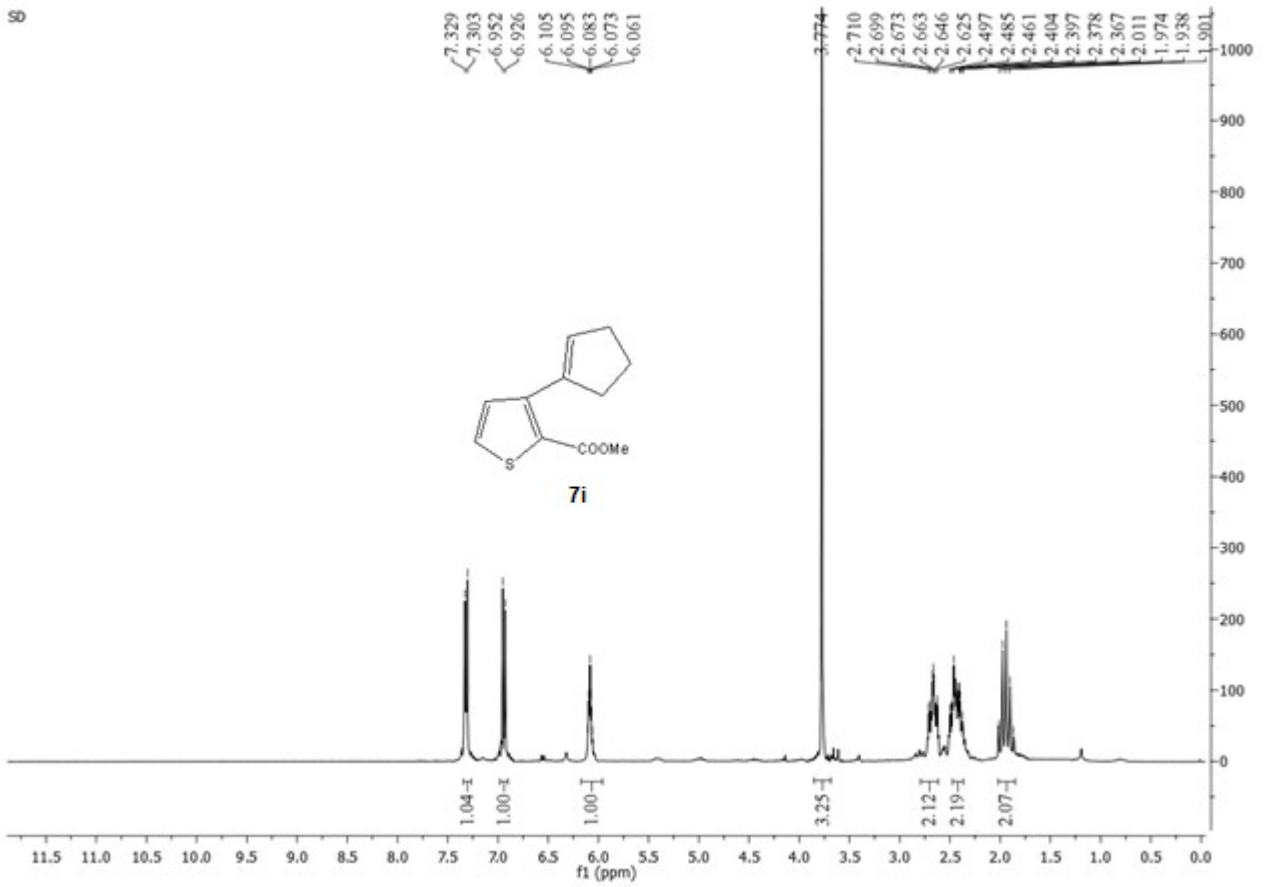

C13
194.485
162.337
144.088
141.938
131.935
131.656
131.272
126.846
52.584
CHO
COOCH3
S
4i
f1 (ppm)

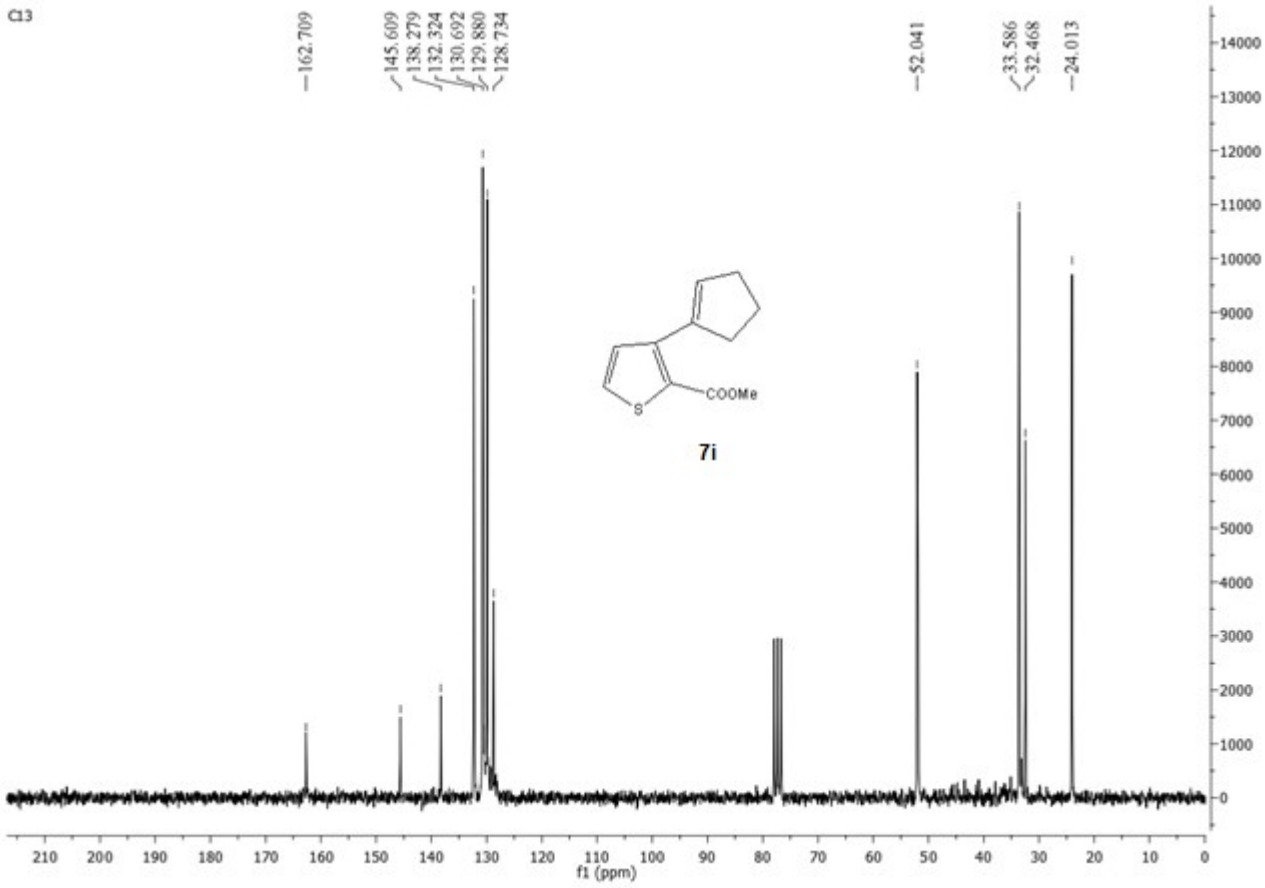

8.466
8.385
7.408
7.382
7.283
7.257
6.335
6.255
4.248
4.212
4.176
4.141
3.836
1.296
1.260
1.225
COOEt
COOCH3
S
5i
1.00
1.10
0.98
1.10
2.23
3.17
2.96
f1 (ppm)

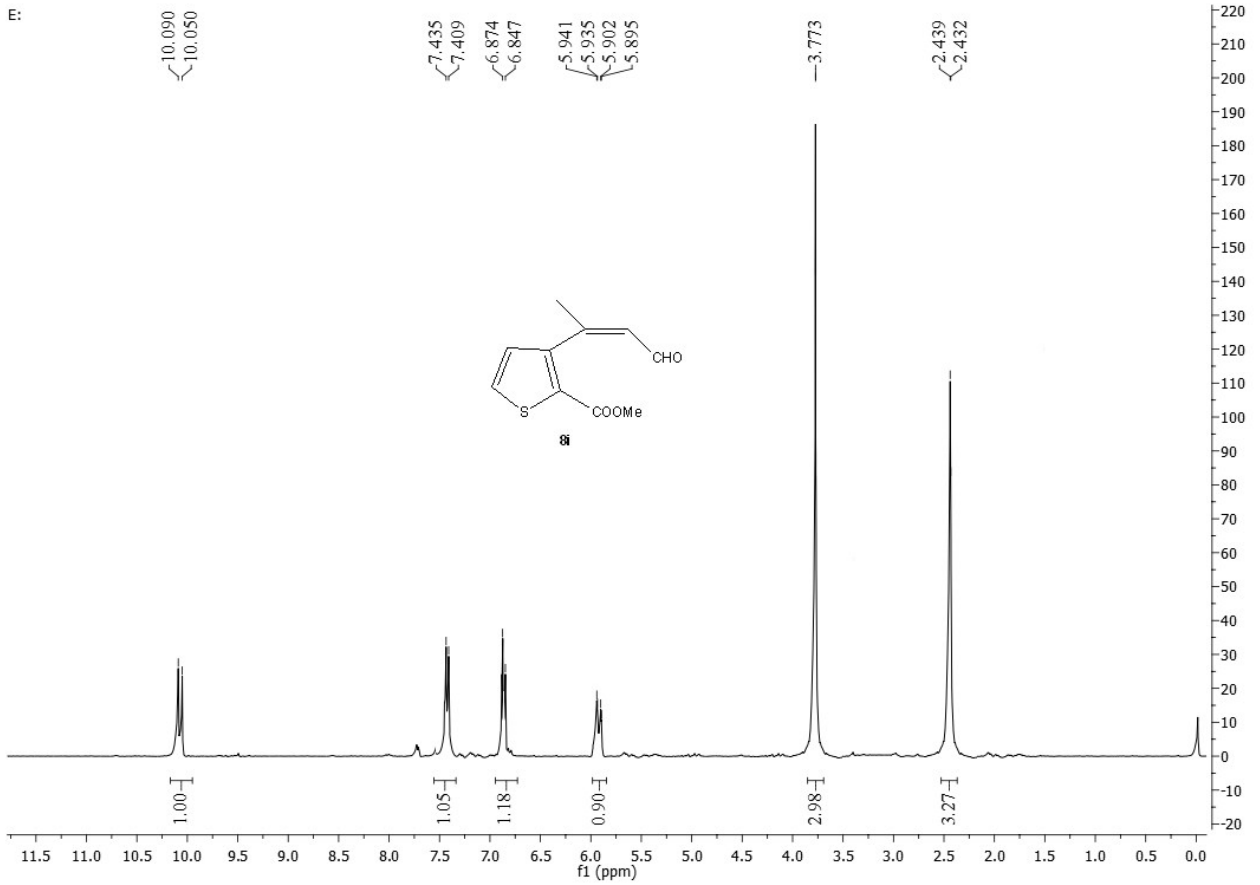

166.740
162.230
141.919
136.514
131.034
126.736
122.090
60.718
52.343
14.362
COOEt
COOCH3
S
5i
f1 (ppm)

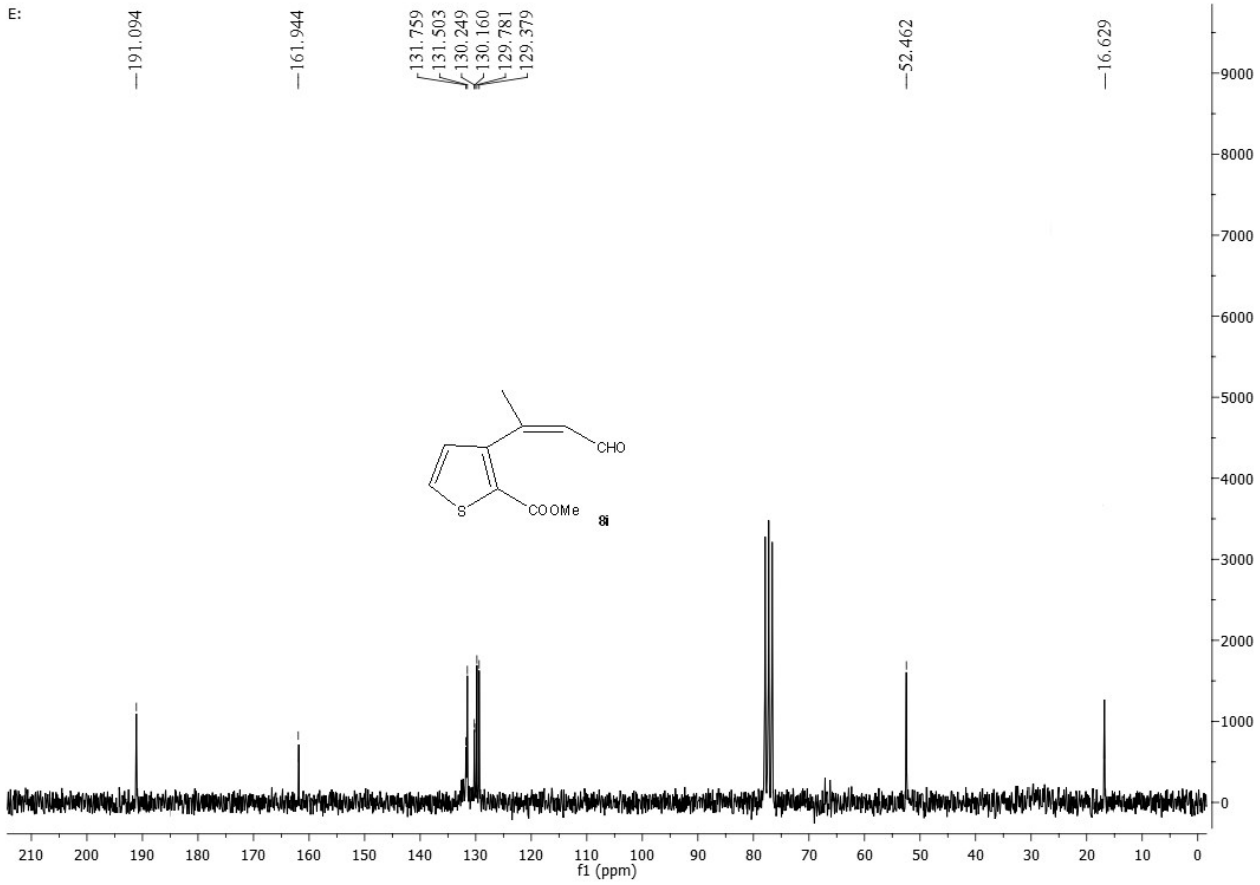

S0
8.152
8.069
7.547
7.539
7.506
7.398
7.371
7.361
7.332
7.321
7.283
7.266
7.234
7.197
7.095
7.013
3.843
1.00
2.03
5.27
1.09
3.18
f1 (ppm)
COOCH3
S
6i


C13
163.184
145.794
137.162
133.123
130.688
128.931
128.440
127.176
126.465
126.278
122.139
52.144
30.243
f1 (ppm)
COOCH3
S
6i


S0
7.329
7.303
6.952
6.926
6.105
6.095
6.083
6.073
6.061
3.774
2.710
2.699
2.673
2.663
2.646
2.625
2.497
2.485
2.461
2.404
2.397
2.378
2.367
2.011
1.974
1.938
1.901
COOMe
S
7i
1.04
1.00
1.00
3.25
2.12
2.19
2.07
f1 (ppm)


C13
162.709
145.609
138.279
132.324
130.692
129.880
128.734
52.041
33.586
32.468
24.013
COOMe
S
7i
f1 (ppm)


E:
10.090
10.050
7.435
7.409
6.874
6.847
5.941
5.935
5.902
5.895
3.773
2.439
2.432
CHO
S
COOMe
8i
1.00
1.05
1.18
0.90
2.98
3.27
f1 (ppm)


E:
191.094
161.944
131.759
131.503
130.249
130.160
129.781
129.379
52.462
16.629
CHO
S
COOMe
8i
f1 (ppm)

References

1. J. Liu, J. Zhu, H. Jiang, W. Wang and J. Li, *Chem. Comm.*, 2010, **46**, 415.
2. J. L. Nallavasim and R. A. Fernandes, *Eur. J. Org. Chem.,* 2015, **16**, 3558.
3. R. Kusy and K. Grela, *Org. Lett.*, 2016, **18**, 6196.
4. E. Artuso, M. Barbero, I. Degani, S. Dughera and R. Fochi, *Tetrahedron,* 2006, **62**, 3146.
5. T. K. Johansen, C. Villegas Gómez, J. R. Bak, R. L. Davis and K. A. Jørgensen, *Chem. Eur. J.,* 2013, **19**, 16518.
6. K.Kikukawa, K. Nagira, F. Wada and T. Matsuda, *Tetrahedron,* 1981, **37**, 31.
7. L.Yang and Q. Zeng, *Synthesis*, 2017, **49**, 3149.
8. P. M. Killoran, S. B. Rossington, J. A. Wilkinson and J. A. Hadfield, *Tetrahedron Lett.,* 2016, **57**, 3954.
9. G.Cignarella, E. Occelli and E. Testa, *J. Med. Chem.,* 1965, **8**, 326.
10. B. China Raju and P. Suman, *Chem. Eur. J.,* 2010, **16**, 11840.
11. F.-L. Yang, X.-T. Ma and S.-K. Tian, *Chem. Eur. J.,* 2012, **18**, 1582.
12. T. Iitsuka, P. Schaal, K. Hirano, T. Satoh, C. Bolm, Carsten and M. Miura, *J. Org. Chem.,* 2013, **78**, 7216.