

Supporting Information

A novel iodine-mediated tandem cyclization-cycloaddition reactions leading to polyoxacyclic ring systems

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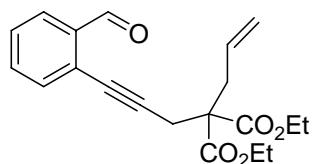
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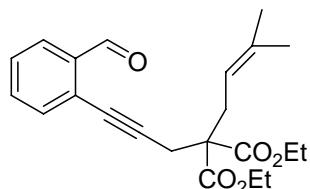
General Remarks

Column chromatography was carried out on silica gel (200–300 mesh). ^1H NMR spectra were recorded at 400 MHz in CDCl_3 by using TMS as an internal standard. Data for ^1H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz) and integration. ^{13}C NMR spectra were recorded at 100 MHz in CDCl_3 and ^{13}C NMR data are reported in terms of chemical shift in ppm with CDCl_3 as an internal standard. IR spectra were recorded with an FT-IR spectrometer and only major peaks are reported. Melting points were determined with a microscopic apparatus and are uncorrected. All compounds were further characterized by HRMS. Commercially available reagents and solvents were used without further purification.

The substrates **1a**-**15a** were prepared according to the methods in the literatures.¹

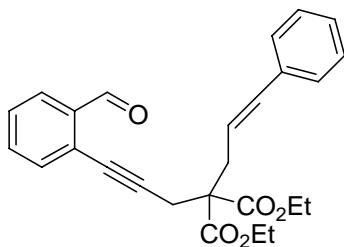


(1a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.25-1.29 (t, J = 7.0 Hz, 6 H), 2.87-2.88 (d, J = 7.6 Hz, 2 H), 3.11 (s, 2 H), 4.22-4.27 (q, J = 7.2 Hz, 4 H), 5.15-5.24 (m, 2 H), 5.66-5.73 (m, 1 H), 7.39-7.43 (m, 1 H), 7.48-7.55 (m, 2 H), 7.87-7.89 (t, J = 4.0 Hz, 1 H), 10.46 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.5, 169.5, 136.1, 133.5, 133.4, 131.5, 128.2, 126.8, 126.6, 119.8, 91.9, 79.0, 61.6, 56.7, 36.7, 23.7, 13.9. IR (neat): 3376, 2982, 1733, 1293, 1216, 1194, 765 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5$ ($\text{M}+\text{NH}_4$): 360.1805, found ($\text{M}+\text{NH}_4$): 360.1810.

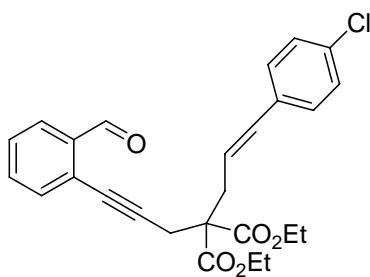


(2a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.24-1.28 (q, J = 7.2 Hz, 6 H), 1.67 (s, 3 H), 1.72 (s, 3 H), 2.82-2.84 (d, J = 7.6 Hz, 2 H), 3.08 (s, 2 H), 4.19-4.27 (m, 4 H), 4.96-

5.00 (t, J = 7.2 Hz, 1 H), 7.38-7.42 (t, J = 7.4 Hz, 1 H), 7.47-7.54 (m, 2 H), 7.87-7.89 (d, J = 7.6 Hz, 1 H), 10.46 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.7, 169.9, 136.7, 136.0, 133.5, 133.4, 128.2, 126.8, 116.9, 92.5, 78.8, 61.5, 57.1, 30.9, 25.9, 23.5, 17.9, 14.0. IR (neat): 3525, 2981, 1779, 1732, 1594, 1472, 1193, 766 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_5$ ($\text{M}+\text{NH}_4^+$): 388.2118, found ($\text{M}+\text{NH}_4^+$): 388.2112.

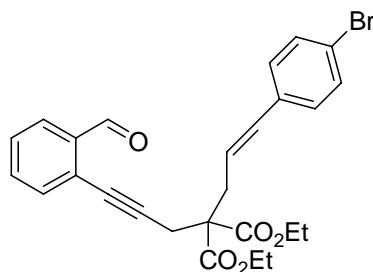


(3a): Yellow solid. mp 60-62 °C; ^1H NMR (400 MHz, CDCl_3): δ 1.25-1.28 (t, J = 7.0 Hz, 6 H), 3.01-3.04 (q, J = 0.8 Hz, 2 H), 3.15 (s, 2 H), 4.22-4.28 (q, J = 7.2 Hz, 4 H), 6.05-6.12 (m, 1 H), 6.52-6.56 (d, J = 15.6 Hz, 1 H), 7.19-7.23 (m, 1 H), 7.25-7.30 (m, 4 H), 7.33-7.36 (m, 1 H), 7.38-7.54 (m, 2 H), 7.88-7.90 (d, J = 7.6 Hz, 1 H), 10.49 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.5, 169.5, 136.7, 136.0, 134.6, 133.5, 133.4, 128.4, 128.3, 127.4, 126.9, 126.6, 126.1, 123.0, 92.0, 79.2, 61.7, 57.1, 36.1, 24.0, 14.0. IR (KBr): 3466, 2981, 1732, 1696, 1194, 1095, 765, 694 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_5(\text{M}+\text{Na})$: 441.1672, found ($\text{M}+\text{Na}$): 441.1666.

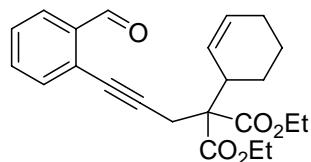


(4a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.25-1.28 (t, $J = 7.2$ Hz, 6 H), 3.00-3.02 (d, $J = 7.2$ Hz, 2 H), 3.14 (s, 2 H), 4.23-4.28 (q, $J = 7.2$ Hz, 4 H), 6.06-6.10 (t, $J = 8.0$ Hz, 1 H), 6.47-6.51 (d, $J = 16.0$ Hz, 1H), 7.24-7.27 (d, $J = 10.8$ Hz, 4 H), 7.41-7.43 (t, $J = 4.0$ Hz, 1 H), 7.50-7.52 (m, 2 H), 7.88-7.90 (d, $J = 7.6$ Hz, 1H), 10.48 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.5, 169.5, 136.0, 135.2, 133.5, 133.4, 133.3, 133.0, 128.5, 128.3, 127.3, 127.0, 126.5, 123.9, 91.9, 79.3, 61.7, 57.1, 36.2, 24.1, 14.0. IR (neat):

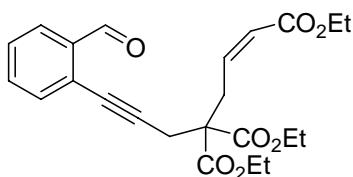
3465, 2982, 1731, 1696, 1486, 1193, 765, 492 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{25}\text{ClO}_5$ ($\text{M}+\text{Na}$): 475.1283, found ($\text{M}+\text{Na}$): 475.1287.



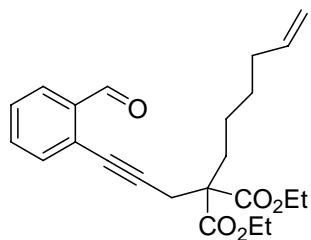
(5a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.26 (s, 6 H), 2.99-3.01 (d, $J = 7.6$ Hz, 2 H), 3.13 (s, 2 H), 4.22-4.28 (q, $J = 7.2$ Hz, 4 H), 6.06-6.12 (q, $J = 7.6$ Hz, 1 H), 6.45-6.49 (d, $J = 15.6$ Hz, 1 H), 7.18-7.20 (d, $J = 8.4$ Hz, 2 H), 7.39-7.44 (m, 3 H), 7.48-7.53 (m, 2 H), 7.89-7.90 (d, $J = 7.6$ Hz, 1 H), 10.47 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.6, 169.6, 136.1, 135.7, 133.6, 133.5, 133.4, 131.5, 128.4, 127.7, 127.1, 126.6, 124.1, 121.2, 91.9, 79.4, 61.8, 57.1, 36.3, 24.2, 14.1. IR (neat): 3458, 2978, 1730, 1698, 1190, 1093, 764 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{25}\text{BrO}_5$ ($\text{M}+\text{Na}$): 496.0885, found ($\text{M}+\text{Na}$): 496.0881.



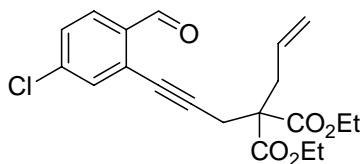
(6a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.45-1.48 (t, $J = 6.4$ Hz, 6 H), 1.54-1.61 (m, 1 H), 1.74 (s, 1 H), 1.81-1.91 (m, 2 H), 1.95-1.99 (m, 2 H), 3.07-3.21 (m, 3 H), 4.18-4.27 (m, 4 H), 5.76 (s, 2 H), 7.38-7.41 (t, $J = 7.4$ Hz, 1 H), 7.46-7.53 (m, 2 H), 7.87-7.89 (d, $J = 7.6$ Hz, 1 H), 10.46 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.9, 169.7, 169.5, 136.1, 133.6, 133.3, 129.0, 128.2, 127.4, 127.0, 126.8, 93.0, 78.8, 61.4, 61.3, 60.2, 39.0, 24.8, 24.3, 23.3, 22.2, 14.1, 14.0. IR (neat): 3458, 2934, 1729, 1473, 1228, 1095, 766, 725 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{26}\text{O}_5$ ($\text{M}+\text{NH}_4$): 400.2118, found ($\text{M}+\text{NH}_4$): 400.2125.



(7a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.26-1.29 (t, $J = 7.2$ Hz, 9 H), 2.99-3.02 (q, $J = 4.0$ Hz, 2 H), 3.11 (s, 2 H), 4.15-4.20 (m, 2 H), 4.23-4.28 (q, $J = 7.0$ Hz, 4 H), 5.87-5.98 (q, $J = 15.6$ Hz, 1 H), 6.75-6.87 (m, 1 H), 7.41-7.45 (m, 1 H), 7.49-7.56 (m, 2 H), 7.88-7.90 (m, 1 H), 10.44 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.4, 169.5, 169.1, 165.6, 141.7, 141.5, 136.0, 133.6, 133.5, 128.5, 127.1, 126.3, 125.7, 125.4, 91.2, 79.6, 62.0, 60.4, 56.5, 35.2, 24.2, 14.1, 14.0. IR (neat): 3466, 2983, 1730, 1656, 1273, 1096, 767, 638 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{26}\text{O}_7$ ($\text{M}+\text{NH}_4$): 432.2017, found ($\text{M}+\text{NH}_4$): 432.2016.

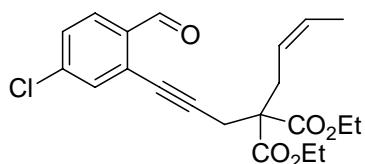


(8a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.24-1.30 (m, 8 H), 1.43-1.47 (t, $J = 7.40$ Hz, 2 H), 2.04-2.12 (m, 4 H), 3.11 (s, 2 H), 4.20-4.25 (m, 4 H), 4.92-5.01 (m, 2 H), 5.74-5.78 (t, $J = 8.6$ Hz, 1 H), 7.40-7.42 (d, $J = 7.6$ Hz, 1 H), 7.47-7.52 (m, 2 H), 7.88-7.89 (d, $J = 7.6$ Hz, 1 H), 10.45 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.7, 170.2, 138.4, 136.1, 133.6, 133.4, 128.3, 126.9, 126.8, 114.6, 92.2, 78.9, 61.6, 57.0, 33.3, 32.0, 28.8, 23.9, 23.3, 14.0. IR (neat): 3372, 2848, 1698, 1586, 1554, 1394, 1239, 1086, 984, 839, 775, 461 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_5$ ($\text{M}+\text{Na}$): 407.1829, found ($\text{M}+\text{Na}$): 407.1835.

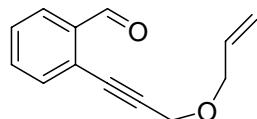


(9a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.25-1.29 (t, $J = 7.0$ Hz, 6 H), 2.84-2.86 (d, $J = 7.6$ Hz, 2 H), 3.10 (s, 2 H), 4.21-4.27 (q, $J = 7.2$ Hz, 4 H), 5.16-5.23 (q, $J =$

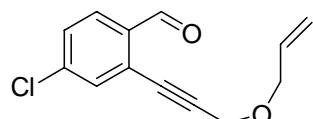
9.0 Hz, 2 H), 5.62-5.73 (m, 1 H), 7.37-7.39 (q, $J = 4.2$ Hz, 1 H), 7.47-7.48 (d, $J = 7.2$ Hz, 1 H), 7.81-7.83 (d, $J = 8.4$ Hz, 1 H), 10.38 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.3, 169.5, 140.0, 134.4, 133.1, 131.4, 128.9, 128.3, 128.1, 120.1, 93.5, 77.9, 61.7, 56.7, 36.8, 23.7, 14.0. IR (neat): 3459, 2982, 1733, 1588, 1293, 1216, 1090, 1011, 842, 777 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{21}\text{O}_5(\text{M}+\text{NH}_4)$: 394.1416, found ($\text{M}+\text{NH}_4$): 394.1421.



(10a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.25-1.28 (t, $J = 7.0$ Hz, 6 H), 1.66-1.70 (t, $J = 8.0$ Hz, 3 H), 2.76-2.78 (d, $J = 7.2$ Hz, 2 H), 3.07 (s, 1 H), 4.20-4.26 (q, $J = 7.0$ Hz, 4 H), 5.25-5.30 (m, 1 H), 5.59-5.64 (m, 1 H), 7.27-7.39 (m, 1 H), 7.47-7.48 (d, $J = 2.0$ Hz, 1 H), 7.81-7.83 (m, 1 H), 10.39 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.4, 169.7, 140.0, 134.4, 133.1, 130.8, 128.8, 128.3, 128.2, 123.7, 93.7, 77.8, 61.7, 56.9, 35.6, 23.6, 18.0, 14.0. IR (neat): 3376, 2923, 1734, 1698, 1587, 1203, 839 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{23}\text{O}_5\text{Cl}(\text{M}+\text{H})$: 391.1307, found ($\text{M}+\text{H}$): 391.1308.

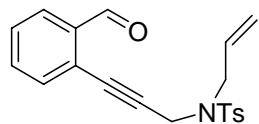


(11a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 4.14-4.16 (m, 2 H), 4.44 (s, 2 H), 5.24-5.27 (m, 1 H), 5.33-5.38 (m, 1 H), 5.90-5.98 (m, 1 H), 7.41-7.52 (m, 1 H), 7.53-7.57 (m, 2 H), 7.89-7.91 (m, 1 H), 10.51 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.1, 135.9, 133.6, 133.5, 133.3, 128.6, 127.0, 125.8, 117.8, 92.2, 81.6, 70.7, 57.6. IR (neat): 3378, 2847, 1697, 1594, 1083, 929, 765, 639 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2(\text{M}+\text{Na})$: 223.0730, found ($\text{M}+\text{Na}$): 223.0730.

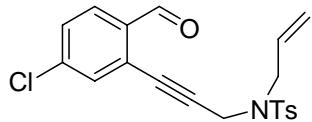


(12a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 4.14-4.15 (d, $J = 5.6$ Hz, 2 H), 4.44 (s,

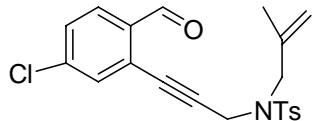
2 H), 5.25-5.38 (m, 2 H), 5.90-5.98 (m, 1 H), 7.39-7.42 (q, $J = 4.2$ Hz, 1 H), 7.52-7.53 (d, 1 H), 7.82-7.84 (d, 1 H), 10.43 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 189.8, 139.9, 134.2, 133.5, 132.9, 129.1, 128.4, 127.2, 118.0, 93.6, 80.3, 70.8, 57.4. IR (neat): 3393, 2923, 1734, 1190, 763 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{11}\text{O}_2\text{Cl}$ ($\text{M}+\text{NH}_4$): 252.0786, found ($\text{M}+\text{NH}_4$): 252.0781.



(13a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 2.26 (s, 3 H), 3.91-3.93 (d, $J = 6.4$ Hz 2 H), 4.39 (s, 2 H), 5.27-5.36 (m, 2 H), 5.77-5.84 (m, 1 H), 7.20-7.24 (t, $J = 8.2$ Hz, 3 H), 7.39-7.43 (t, $J = 7.4$ Hz, 1 H), 7.48-7.52 (m, 1 H), 7.74-7.76 (d, $J = 8.4$ Hz, 2 H), 7.82-7.84 (d, $J = 8.0$ Hz, 1 H), 9.92 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.5, 143.7, 135.6, 133.4, 133.2, 131.8, 129.5, 128.7, 127.5, 126.9, 125.4, 119.9, 88.9, 81.2, 49.4, 36.5, 21.1. IR (neat): 3555, 2962, 1696, 1594, 1349, 1161, 895, 763, 586, 544 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_3\text{SN}$ ($\text{M}+\text{NH}_4$): 371.1424, found ($\text{M}+\text{NH}_4$): 371.1417.



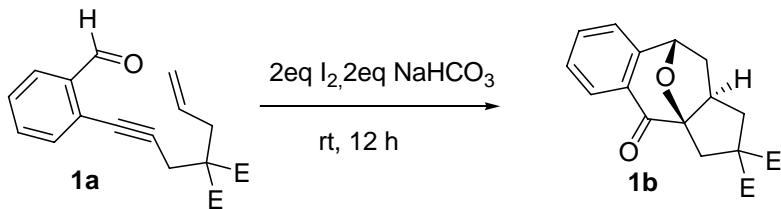
(14a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 2.32 (s, 3 H), 3.90-3.92 (d, $J = 6.4$ Hz, 2 H), 4.39 (s, 2 H), 5.28-5.35 (t, $J = 13.2$ Hz, 2 H), 5.78-5.84 (m, 1 H), 7.10-7.11 (d, $J = 1.6$ Hz, 1 H), 7.24-7.26 (d, $J = 8.0$ Hz, 2 H), 7.37-7.39 (m, 1 H), 7.75-7.78 (m, 3 H), 9.89 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 189.3, 143.9, 139.8, 135.6, 134.0, 132.9, 131.7, 129.5, 129.2, 128.4, 127.5, 126.7, 120.1, 90.2, 80.0, 49.5, 36.4, 21.2. IR (neat): 3371, 2850, 1698, 1350, 1162, 1089, 839, 664, 544 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_3\text{SNCI}$ ($\text{M}+\text{NH}_4$): 405.1034, found ($\text{M}+\text{NH}_4$): 405.1036.



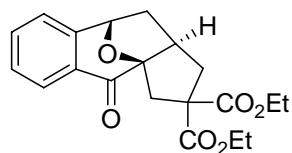
(15a): Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.70-1.72 (m, 3 H), 2.31-2.32 (d, $J = 6.0$ Hz, 3 H), 3.83-3.85 (d, $J = 6.8$ Hz, 2 H), 4.37 (s, 2 H), 5.42-5.48 (m, 1 H), 5.71-5.77

(m, 1 H), 7.10-7.11 (d, J = 2.0 Hz, 1 H), 7.23-7.30 (t, J = 14.4 Hz, 2 H), 7.36-7.39 (m, 1 H), 7.74-7.78 (t, J = 8.6 Hz, 3 H), 9.89 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 189.2, 143.7, 139.7, 135.7, 133.9, 132.8, 131.7, 129.4, 129.1, 128.3, 127.5, 126.8, 124.3, 90.5, 79.8, 48.8, 36.1, 21.2, 17.6. IR (neat): 3371, 2921, 1698, 1587, 1349, 1162, 1088, 906, 839, 732, 659, 552 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3\text{SNCI}$ ($\text{M}+\text{NH}_4$): 419.1191, found ($\text{M}+\text{NH}_4$): 419.1192.

General procedure for the iodo-catalyzed cyclization of enynebenzaldehyde

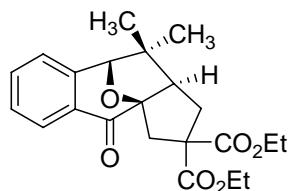


To a stirred solution of enynebenzaldehyde **1a** (0.2 mmol) in CH_2Cl_2 (3.0 mL) was added NaHCO_3 (33.6 mg, 0.40 mmol) and I_2 (101.6 mg, 0.4 mmol) at room temperature. When the reaction was considered complete as determined by TLC analysis, diethyl ether (15 mL) was added to the reaction, then, washed with 5% $\text{Na}_2\text{S}_2\text{O}_3$ solution and extracted with CH_2Cl_2 (3×15 mL). The organic layer was washed with saturated NaCl solution (2×10 mL), dried with Na_2SO_4 and the solvent was evaporated and the residue was purified by column chromatography, eluting with hexane\EtOAc (20:1) to give the pure **1b**. Other compounds **2b-15b** were synthesized by similar method.

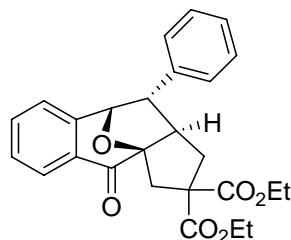


(1b): Yield 95 %, yellow solid, mp 82-84 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 1.25-1.30 (m, 6 H), 2.12-2.17 (m, 1 H), 2.37-2.43 (m, 2 H), 2.50-2.52 (d, J = 4.0 Hz, 1 H), 2.66-2.72 (t, J = 11.0 Hz, 2 H), 3.26-3.29 (d, J = 14.4 Hz, 1 H), 4.17-4.25 (m, 4 H), 5.29-5.31 (d, J = 6.8 Hz, 1 H), 7.16-7.18 (d, J = 7.6 Hz, 1 H), 7.35-7.39 (m, 1 H), 7.49-7.53 (m, 1 H), 7.99-8.01 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.7, 171.0, 170.9, 146.8, 133.7, 128.3, 127.8, 127.1, 123.8, 96.9, 79.8, 62.1, 61.7, 61.5, 43.8, 39.5, 39.3, 37.4, 14.0, 13.9. IR (KBr): 3383, 2980, 1731, 1248, 1091, 771, 565 cm^{-1} . HRMS (ESI)

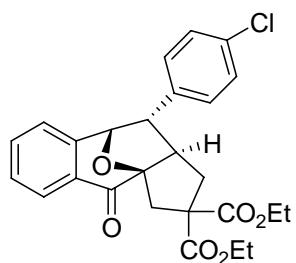
Calcd for C₂₀H₂₂O₆(M+H): 359.1489, found (M+H): 359.1492.



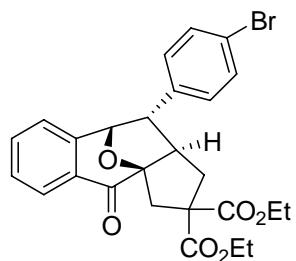
(2b): Yield 33%, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 0.79 (s, 3 H), 1.25-1.28 (q, J = 6.0 Hz, 3 H), 1.30-1.35 (q, J = 7.2 Hz, 6 H), 2.08-2.14 (q, J = 6.2 Hz, 1 H), 2.45-2.62 (m, 3 H), 3.19-3.23 (d, J = 14.4 Hz, 1 H), 4.16-4.30 (m, 4 H), 4.77 (s, 1 H), 7.14-7.16 (d, J = 7.2 Hz, 1 H), 7.37-7.41 (t, J = 7.6 Hz, 1 H), 7.49-7.53 (t, J = 7.6 Hz, 1 H), 8.00-8.01 (d, J = 7.6 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 194.4, 171.1, 170.5, 144.0, 133.1, 128.4, 128.0, 127.1, 125.8, 97.5, 91.9, 64.3, 61.7, 61.5, 54.9, 43.2, 38.0, 34.0, 26.7, 26.6, 13.9. IR (neat): 3463, 2962, 1732, 1602, 1462, 1249, 1094, 1022, 765, 439 cm⁻¹. HRMS (ESI) Calcd for C₂₂H₂₆O₆(M+H): 387.1802, found (M+H): 387.1795.



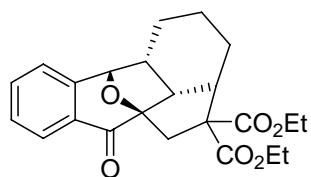
(3b): Yield 51%, yellow solid, mp 100-102 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.26-1.32 (m, 6 H), 2.32-2.38 (q, J = 6.8 Hz, 1 H), 2.70-2.75 (m, 2 H), 2.85-2.89 (m, 1 H), 4.04-4.09 (m, 1 H), 4.18-4.30 (m, 4 H), 6.46-6.47 (d, J = 7.6 Hz, 1 H), 6.66-6.67 (d, J = 6.4 Hz, 2 H), 7.06-7.12 (m, 3 H), 7.21-7.26 (m, 1 H), 7.33-7.37 (m, 1 H), 8.08-8.09 (d, J = 7.2 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 171.1, 170.8, 142.9, 137.0, 132.9, 129.2, 128.3, 128.1, 128.0, 127.0, 126.8, 126.5, 97.5, 84.5, 61.9, 61.8, 61.6, 57.3, 50.8, 38.4, 37.5, 14.0. IR (KBr): 3732, 2977, 1733, 1697, 1692, 1246, 1103, 700, 566 cm⁻¹. HRMS (ESI) Calcd for C₂₆H₂₆O₆(M+H): 435.1802, found (M+H): 435.1811.



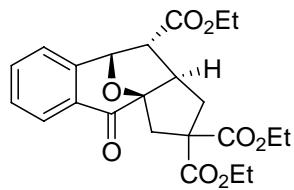
(4b): Yield 55%, yellow solid, mp 181-182 °C; ^1H NMR (400 MHz, CDCl_3): δ 1.26-1.32 (m, 6 H), 2.32-2.38 (q, J = 6.8 Hz, 1 H), 2.70-2.75 (m, 2 H), 2.85-2.89 (m, 1 H), 4.04-4.09 (m, 1 H), 4.18-4.30 (m, 4 H), 6.46-6.47 (d, J = 7.6 Hz, 1 H), 6.66-6.67 (d, J = 6.4 Hz, 2 H), 7.06-7.12 (m, 3 H), 7.21-7.26 (m, 1 H), 7.33-7.37 (m, 1 H), 8.08-8.09 (d, J = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.3, 171.1, 170.7, 142.5, 135.6, 133.1, 132.8, 129.6, 129.2, 128.3, 128.2, 126.9, 126.5, 97.4, 84.2, 61.9, 61.8, 61.7, 56.6, 51.1, 38.3, 37.5, 14.0. IR (KBr): 3404, 2924, 1729, 1248, 1092, 761, 517 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{25}\text{ClO}_6$ ($\text{M}+\text{H}$): 469.1412, found ($\text{M}+\text{H}$): 469.1405.



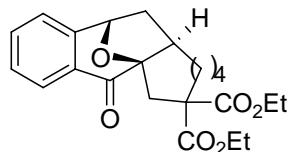
(5b): Yield 54%, yellow solid, mp 160-162 °C; ^1H NMR (400 MHz, CDCl_3): δ 1.28-1.30 (d, J = 7.6 Hz, 6 H), 2.30-2.36 (q, J = 6.6 Hz, 1 H), 2.68-2.78 (m, 3 H), 3.30-3.34 (d, J = 14.8 Hz, 1 H), 4.01 (s, 1 H), 4.20-4.30 (m, 4 H), 5.20-5.22 (s, J = 6.4 Hz, 1 H), 6.48-6.53 (m, 3 H), 7.20-7.22 (d, J = 8.4 Hz, 2 H), 7.26-7.30 (t, J = 8.6 Hz, 1 H), 7.36-7.40 (t, J = 7.4 Hz, 1 H), 8.08-8.10 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.3, 171.1, 170.7, 142.4, 136.1, 133.1, 131.2, 130.0, 129.2, 128.4, 127.0, 126.5, 121.0, 97.5, 84.2, 61.9, 61.8, 61.7, 56.7, 51.1, 38.3, 37.5, 14.0. IR (KBr): 3411, 2919, 1728, 1247, 1072, 513 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{25}\text{BrO}_6$ ($\text{M}+\text{Na}$): 535.0727, found ($\text{M}+\text{Na}$): 535.0724.



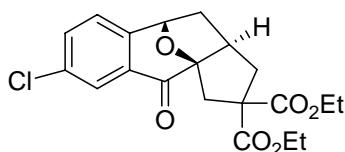
(6b): Yield 65%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 1.00-1.11 (m, 2 H), 1.26 (s, 3 H), 1.34 (s, 3 H), 1.65-1.67 (m, 1 H), 1.73-1.76 (d, $J = 13.2$ Hz, 1 H), 2.23-2.30 (m, 2 H), 2.65-2.69 (d, $J = 14.4$ Hz, 1 H), 2.84-2.91 (m, 2 H), 3.10-3.14 (d, $J = 14$ Hz, 1 H), 4.13-4.17 (m, 1 H), 4.18-4.31 (m, 3 H), 5.02 (s, 1 H), 7.18-7.20 (d, $J = 7.6$ Hz, 1 H), 7.33-7.37 (t, $J = 7.6$ Hz, 1 H), 7.48-7.51 (t, $J = 7.2$ Hz, 1 H), 7.94-7.96 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 194.1, 171.2, 168.9, 144.9, 133.5, 128.1, 127.8, 127.1, 123.9, 95.1, 89.2, 69.3, 61.8, 61.2, 45.2, 41.2, 40.6, 34.8, 30.0, 24.8, 22.1, 14.1, 14.0. IR (neat): 3464, 2938, 1731, 1258, 1091, 995, 762, 654, 549 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_6$ ($\text{M}+\text{H}$): 399.1705, found ($\text{M}+\text{H}$): 399.1701.



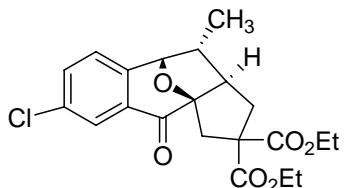
(7b): Yield 72%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 1.13-1.17 (t, $J = 7.2$ Hz, 3 H), 1.25-1.29 (m, 6 H), 2.33-2.36 (t, $J = 6.8$ Hz, 1 H), 2.62-2.66 (d, $J = 14$ Hz, 2 H), 3.11-3.16 (m, 1 H), 3.25-3.28 (d, $J = 7.4$ Hz, 1 H), 3.82-3.85 (t, $J = 6.4$ Hz 1 H), 3.82-3.98 (m, 2 H), 4.17-4.26 (m, 4 H), 5.42-5.44 (d, $J = 6.8$ Hz, 1 H), 7.13-7.14 (d, $J = 7.2$ Hz, 1 H), 7.40-7.43 (m, 1 H), 7.46-7.48 (m, 1 H), 8.01-8.03 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.7, 171.0, 170.5, 169.6, 142.1, 133.2, 129.0, 128.7, 127.1, 125.4, 97.4, 80.4, 61.8, 61.6, 61.5, 60.9, 56.6, 45.8, 37.9, 37.4, 14.1, 14.0, 13.9, 13.9. IR (neat): 3456, 2982, 1733, 1267, 1187, 1106, 646 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{26}\text{O}_8$ ($\text{M}+\text{H}$): 431.1700, found ($\text{M}+\text{H}$): 431.1704.



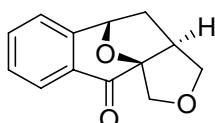
(8b): Yield 0%.



(9b): Yield 84%, yellow solid, mp 130-132 °C; ^1H NMR (400 MHz, CDCl_3): δ 1.24-1.30 (m, 6 H), 2.10-2.15 (q, J = 6.2 Hz, 1 H), 2.36-2.44 (m, 2 H), 2.50-2.55 (t, J = 8.8 Hz, 1 H), 2.65-2.71 (m, 2 H), 3.24-3.27 (d, J = 14.8 Hz, 1 H), 4.19-4.25 (m, 4 H), 5.28-5.30 (d, J = 6.8 Hz, 1 H), 7.13-7.15 (d, J = 8.0 Hz, 1 H), 7.45-7.48 (m, 1 H), 7.96-7.97 (d, J = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.5, 170.8, 145.0, 134.1, 133.6, 129.8, 127.0, 125.5, 96.7, 79.4, 62.0, 61.8, 61.6, 43.7, 39.4, 39.2, 37.3, 14.0, 13.9. IR (KBr): 3379, 2926, 1728, 1699, 1255, 1179, 1101, 1019, 838, 549 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{21}\text{ClO}_6$ ($\text{M}+\text{H}$): 393.1099, found ($\text{M}+\text{H}$): 393.1093.

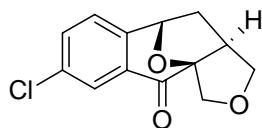


(10b): Yield 56%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 0.76-0.78 (d, J = 6.8 Hz, 3 H), 1.25-1.28 (t, J = 5.2 Hz, 6 H), 2.09-2.13 (m, 1 H), 2.30-2.35 (m, 1 H), 2.60-2.66 (m, 2 H), 2.77-2.82 (q, J = 6.8 Hz, 1 H), 3.18-3.22 (d, J = 14.8 Hz, 1 H), 4.21-4.23 (d, J = 7.2 Hz, 4 H), 5.04-5.06 (d, J = 6.4 Hz, 1 H), 7.07-7.09 (d, J = 8.0 Hz, 1 H), 7.46-7.48 (q, J = 4.2 Hz, 1 H), 8.00-8.01 (d, J = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.6, 170.9, 170.8, 141.5, 134.2, 133.0, 130.4, 127.3, 127.1, 96.8, 83.0, 61.9, 61.8, 61.6, 51.8, 44.6, 37.9, 37.3, 31.9, 22.6, 15.7, 14.1, 14.0, 13.9. IR (neat): 3462, 2924, 1733, 1460, 1732, 1251, 862, 734, 474 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{23}\text{ClO}_6$ ($\text{M}+\text{H}$): 407.1256, found ($\text{M}+\text{H}$): 407.1262.

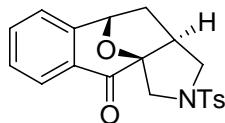


(11b): Yield 63%, yellow solid, mp 121-123 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.17-2.28 (m, 2 H), 2.77-2.80 (q, J = 4.0 Hz, 1 H), 3.78-3.82 (m, 1 H), 3.98-4.02 (q, J = 5.2 Hz, 1 H), 4.10-4.15 (q, J = 7.4 Hz, 1 H), 4.53-4.56 (q, J = 5.2 Hz, 1 H), 5.50-5.52 (d, J = 6.0 Hz, 1 H), 7.23-7.28 (q, J = 9.4 Hz, 1 H), 7.39-7.43 (m, 1 H), 7.53-7.57 (m, 1 H), 8.01-

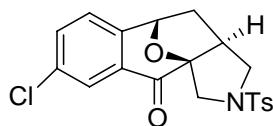
8.03 (q, $J = 3.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.8, 146.4, 133.9, 128.7, 128.0, 126.9, 124.0, 97.5, 81.2, 74.1, 70.6, 46.7, 37.3. IR (KBr): 3381, 2865, 1698, 1601, 1288, 1077, 920, 755, 558 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_3$ ($\text{M}+\text{NH}_4$): 234.1125, found ($\text{M}+\text{NH}_4$): 234.1123.



(12b): Yield 76%, yellow solid, mp 158-160 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.16-2.30 (m, 2 H), 2.74-2.81 (m, 1 H), 3.79-3.83 (q, $J = 4.4$ Hz, 1 H), 3.99-4.02 (d, $J = 10.4$ Hz, 1 H), 4.11-4.15 (t, $J = 8.4$ Hz, 1 H), 4.51-4.53 (d, $J = 10.8$ Hz, 1 H), 5.49-5.51 (d, $J = 6.4$ Hz, 1 H), 7.19-7.26 (t, $J = 14.6$ Hz, 1 H), 7.49-7.52 (q, $J = 4.0$ Hz, 1 H), 7.98-7.99 (d, $J = 2.0$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.6, 144.6, 134.3, 133.8, 130.2, 126.9, 125.7, 97.4, 80.8, 74.1, 70.6, 46.7, 37.3. IR (KBr): 3739, 2923, 1704, 1281, 1072, 833, 479 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{11}\text{ClO}_3$ ($\text{M}+\text{NH}_4$): 268.0735, found ($\text{M}+\text{NH}_4$): 268.0733.

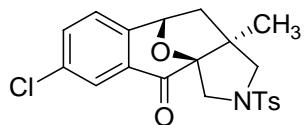


(13b): Yield 61%, yellow solid, Yellow solid. mp 181-183 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.15-2.21 (m, 2 H), 2.44 (s, 3 H), 2.62 (s, 1 H), 3.23-3.26 (q, $J = 5.0$ Hz, 1 H), 3.47-3.53 (m, 2 H), 4.01-4.04 (d, $J = 11.2$ Hz, 1 H), 5.39-5.40 (d, $J = 6.4$ Hz, 1 H), 7.19-7.20 (d, $J = 7.6$ Hz, 1 H), 7.35-7.40 (m, 3 H), 7.51-7.53 (q, $J = 3.8$ Hz, 1 H), 7.74-7.76 (d, $J = 8.4$ Hz, 2 H), 7.95-7.97 (d, $J = 8.0$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.6, 146.2, 143.8, 134.2, 132.3, 129.7, 128.2, 128.0, 127.9, 127.2, 123.9, 95.3, 80.3, 53.8, 51.3, 44.0, 38.0, 21.5. IR (KBr): 3403, 2924, 1700, 1343, 1160, 1092, 1008, 663, 548 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{19}\text{NSO}_4$ ($\text{M}+\text{H}$): 370.1108, found ($\text{M}+\text{H}$): 370.1111.



(14b): Yield 83%, yellow solid, mp 170-172 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.11-

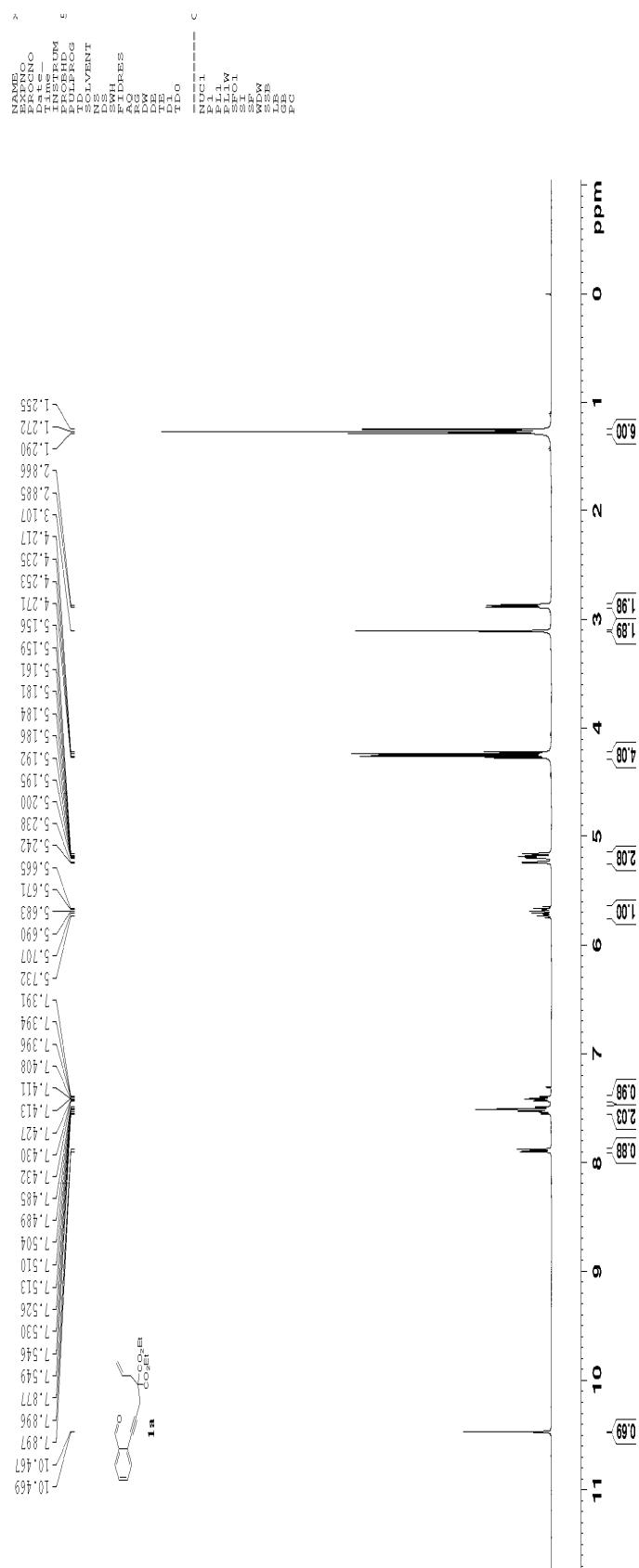
2.24 (m, 2 H), 2.45 (s, 3 H), 2.57-2.64 (m, 1 H), 3.22-3.26 (q, $J = 5.0$ Hz, 1 H), 3.45-3.52 (m, 2 H), 3.96-3.99 (d, $J = 5.8$ Hz, 1 H), 5.38-5.40 (d, $J = 6.4$ Hz, 1 H), 7.16-7.18 (d, $J = 8.0$ Hz, 1 H), 7.35-7.37 (d, $J = 8.0$ Hz, 2 H), 7.47-7.50 (q, $J = 4.2$ Hz, 1 H), 7.73-7.75 (d, $J = 4.2$ Hz, 2 H), 7.90-7.91 (d, $J = 2.4$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.4, 144.4, 143.9, 134.3, 134.0, 132.1, 129.7, 129.5, 127.9, 127.1, 125.6, 95.1, 79.9, 53.7, 51.2, 43.9, 37.8, 21.5. IR (KBr): 3403, 2924, 2856, 1706, 1596, 1345, 1162, 1014, 664, 549 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{18}\text{ClNSO}_4$ ($\text{M}+\text{H}$): 404.0718, found ($\text{M}+\text{H}$): 404.0728.

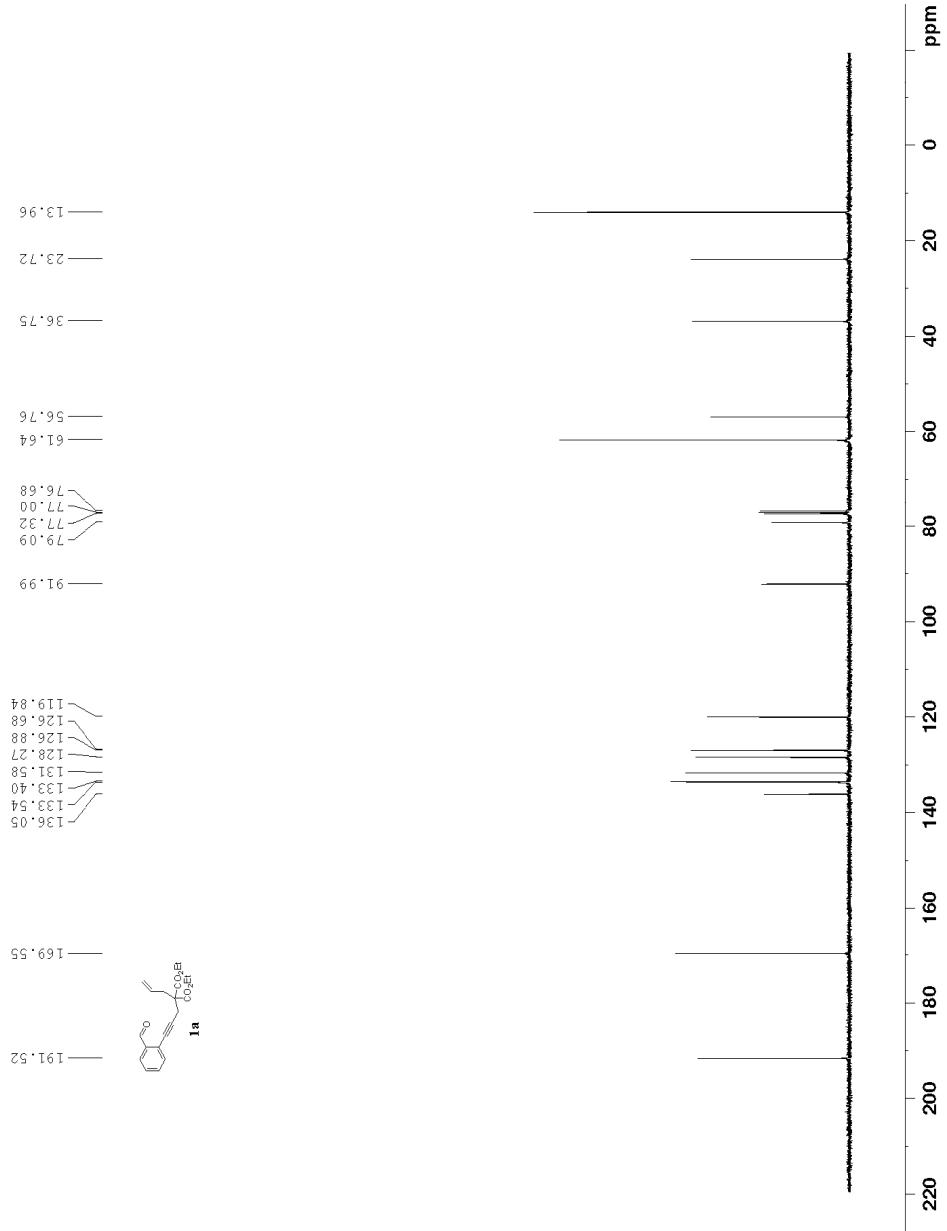


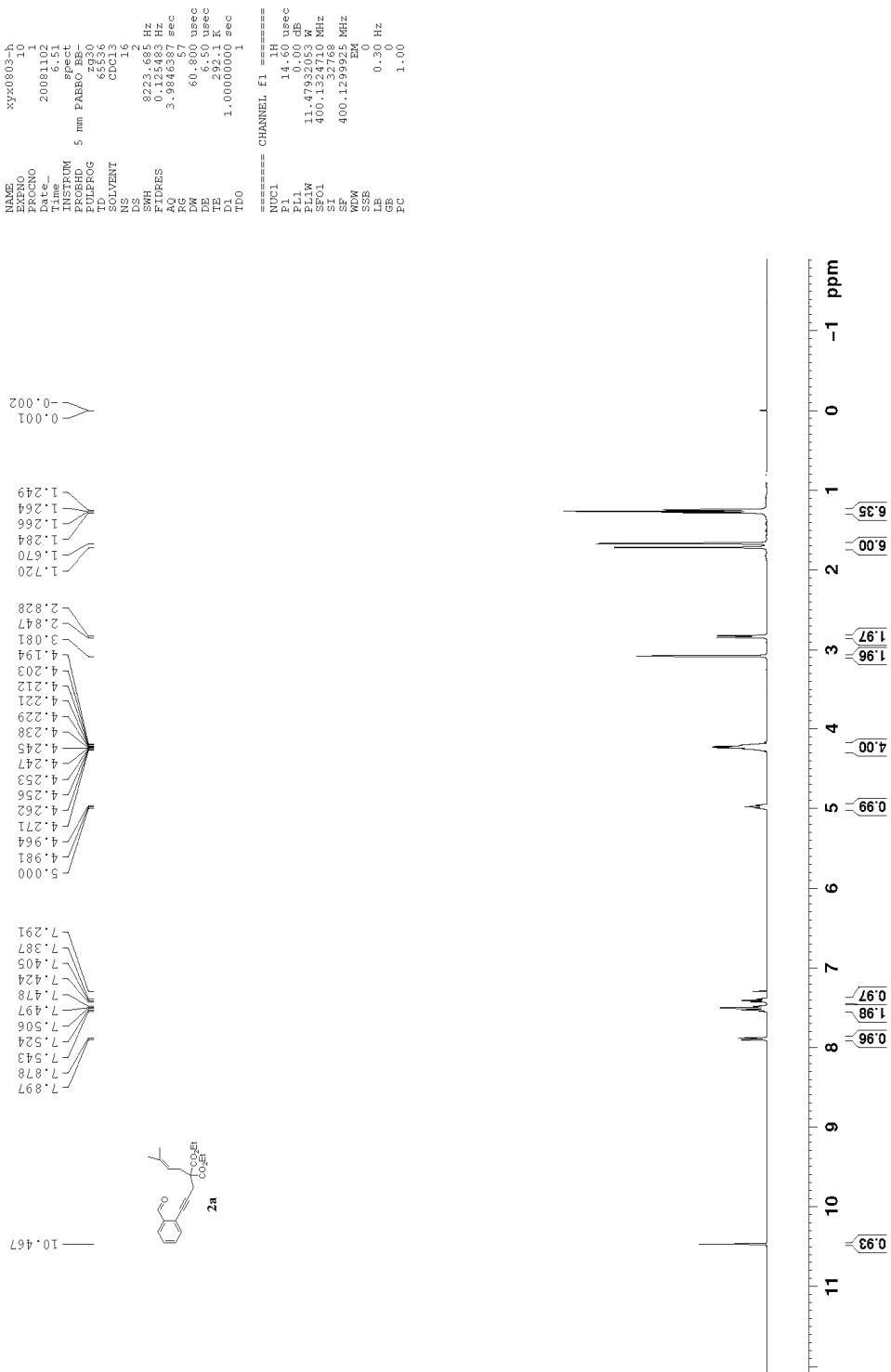
(15b): Yield 75%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 0.87 (s, 3 H), 1.47-1.50 (d, $J = 12.4$ Hz, 1 H), 2.47 (s, 3 H), 3.02-3.05 (d, $J = 12.4$ Hz, 1 H), 3.56-3.59 (q, $J = 6.2$ Hz, 1 H), 4.03-4.06 (d, $J = 12.4$ Hz, 1 H), 4.76-4.79 (q, $J = 6.4$ Hz, 1 H), 7.19-7.23 (d, $J = 8.0$ Hz, 1 H), 7.37-7.44 (m, 3 H), 7.70-7.72 (d, $J = 8.4$ Hz, 2 H), 7.77-7.78 (d, $J = 1.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.5, 143.87, 140.07, 134.84, 134.75, 132.71, 131.52, 129.97, 129.36, 127.05, 124.03, 91.09, 72.84, 72.19, 58.19, 54.14, 40.35, 38.72, 31.36, 21.61. IR (neat): 3395, 2924, 1708, 1459, 1162, 1015, 664, 549 cm^{-1} . HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{20}\text{ClNSO}_4$ ($\text{M}+\text{H}$): 418.0874, found ($\text{M}+\text{H}$): 418.0872.

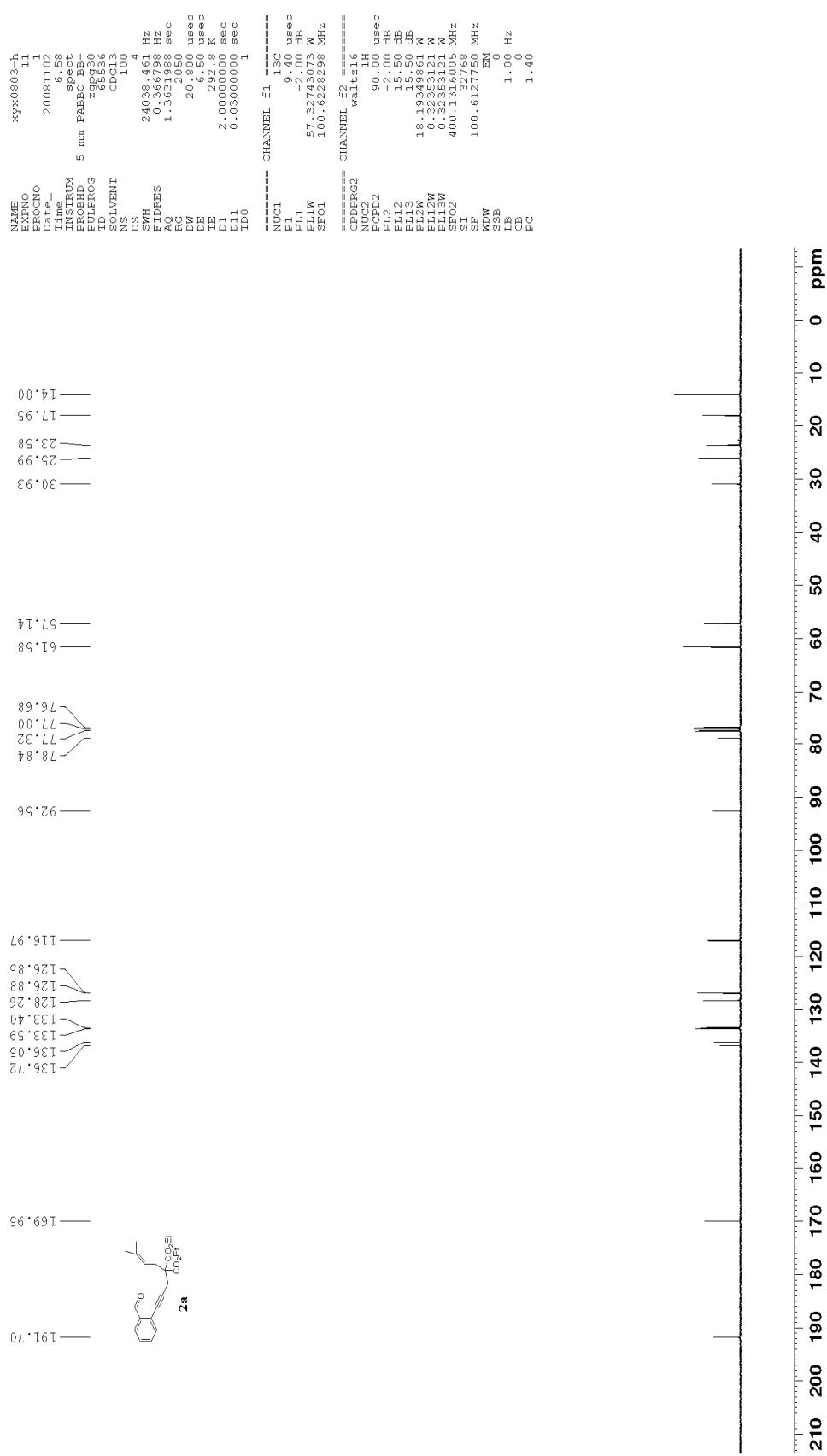
Reference

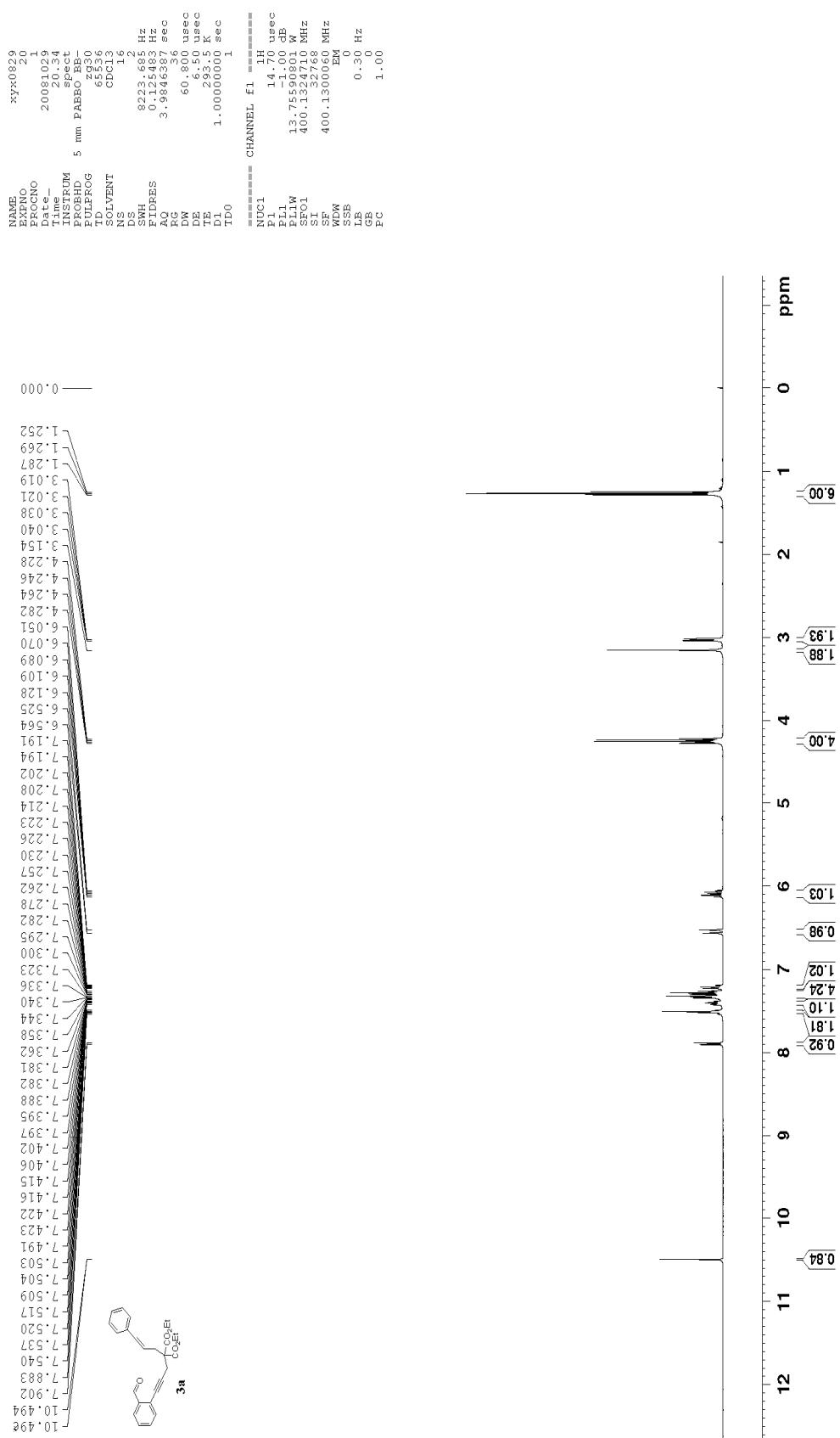
- 1 (a) G. Dyker, D.Hildebrandt, *J. Org. Chem.* **2005**, *70*, 6093-6096.

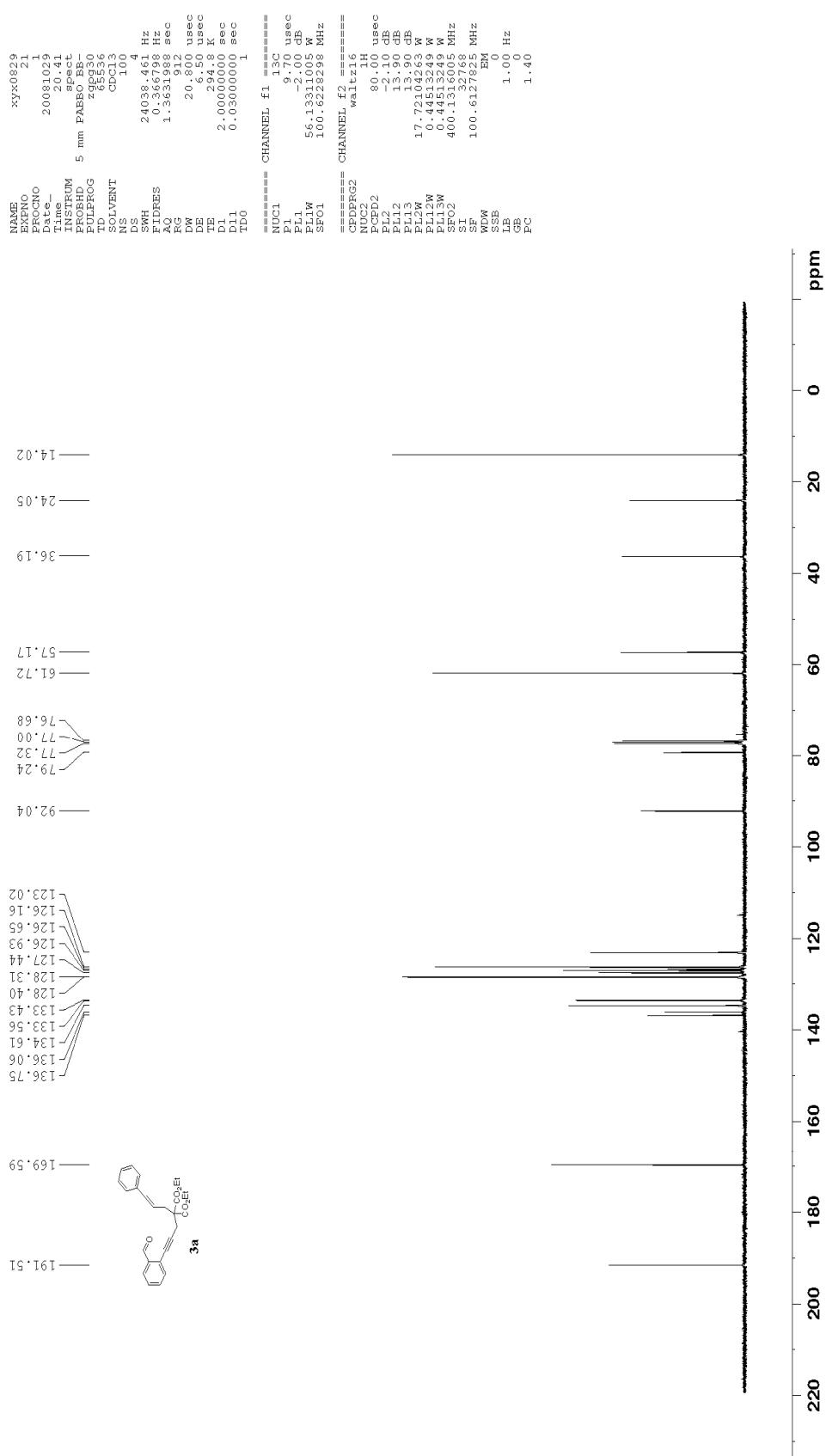


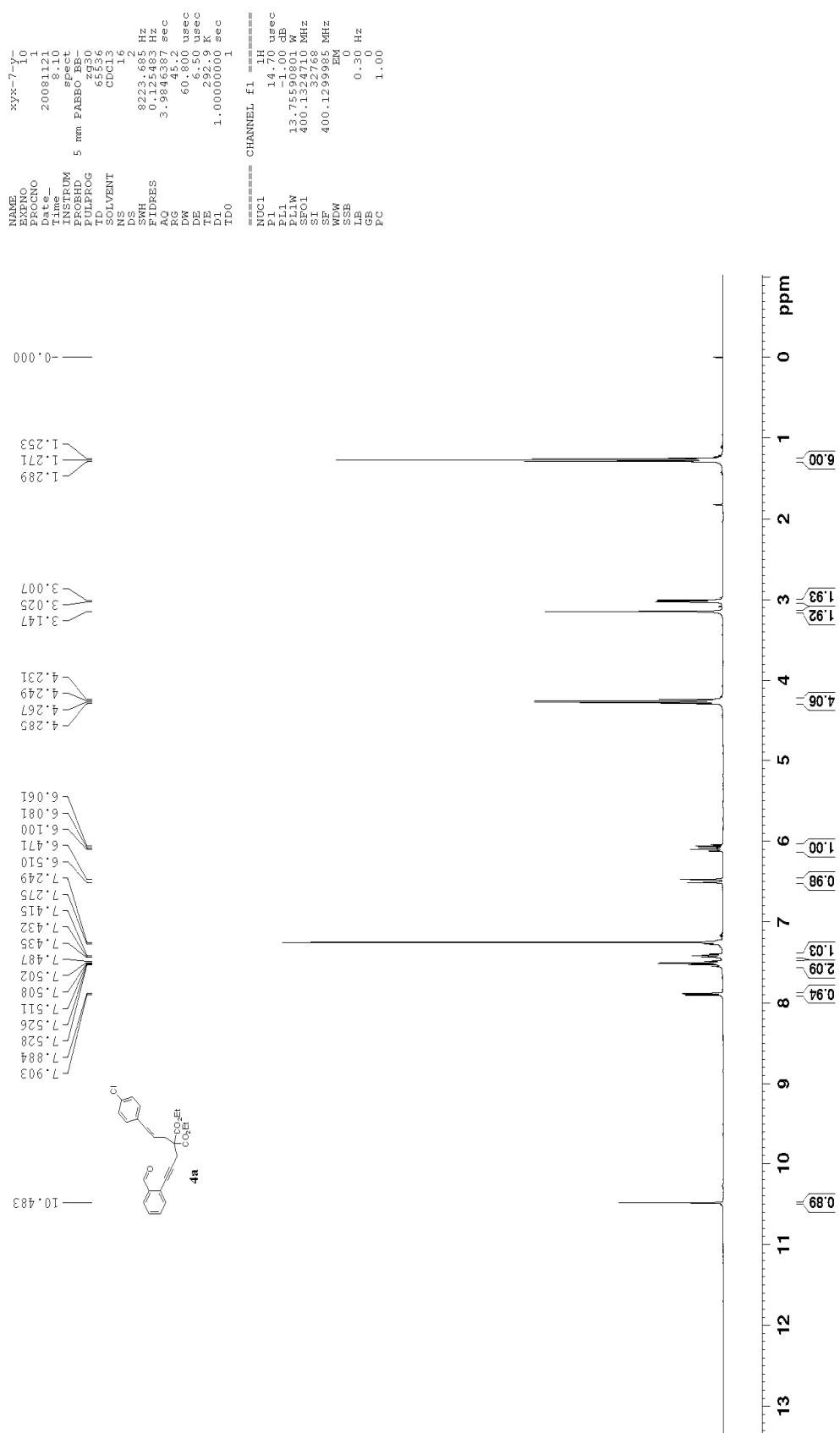


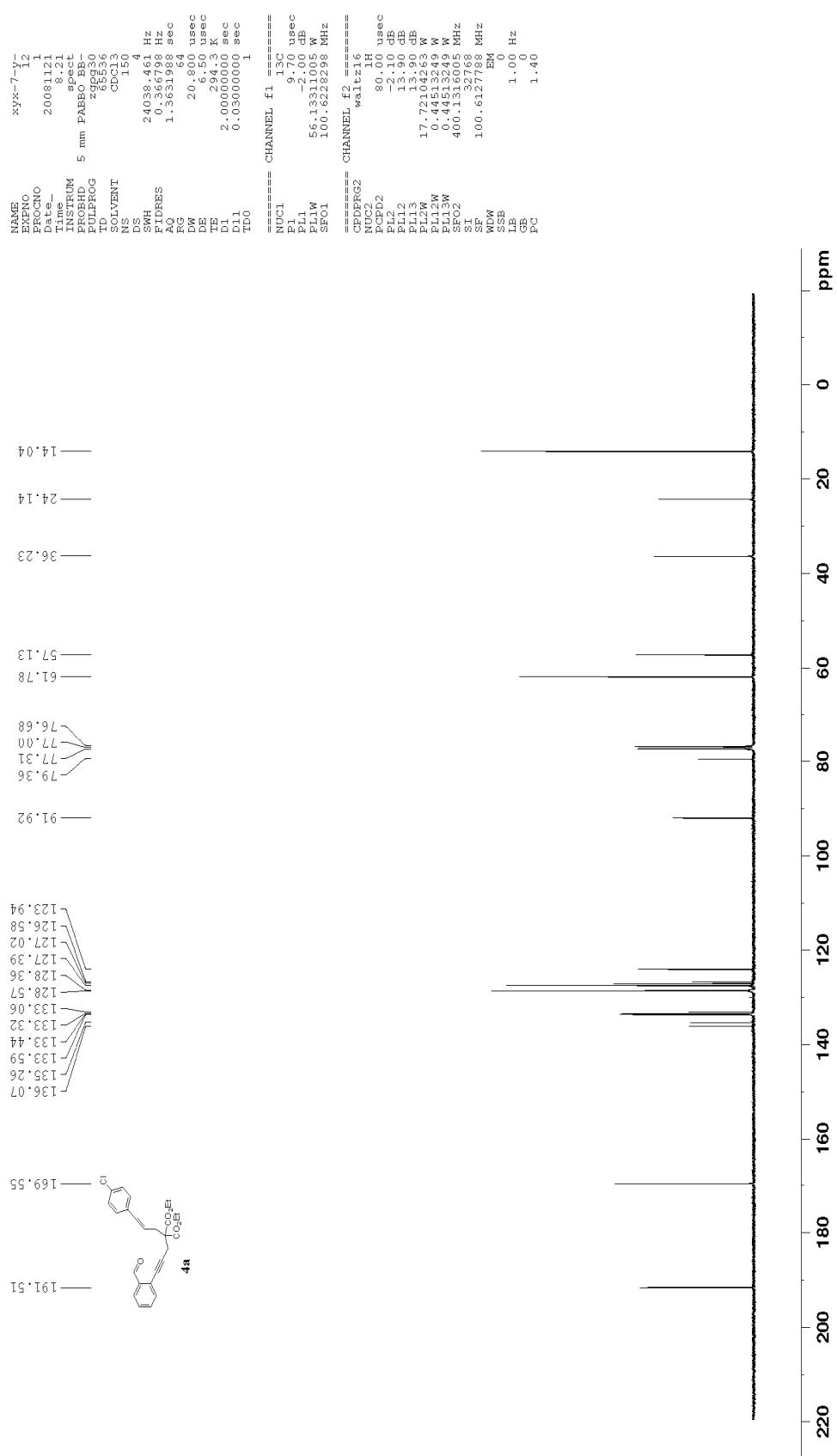


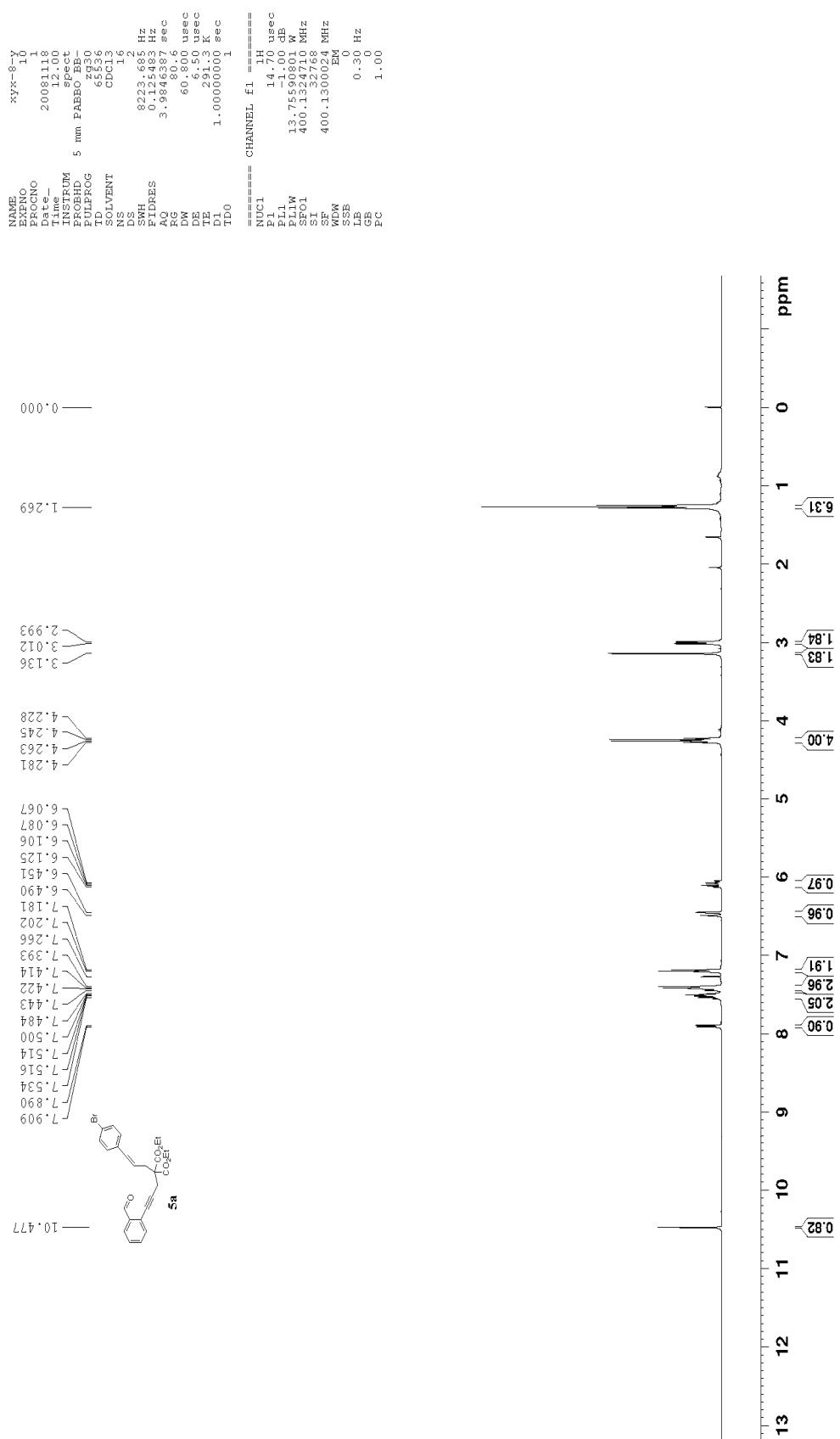


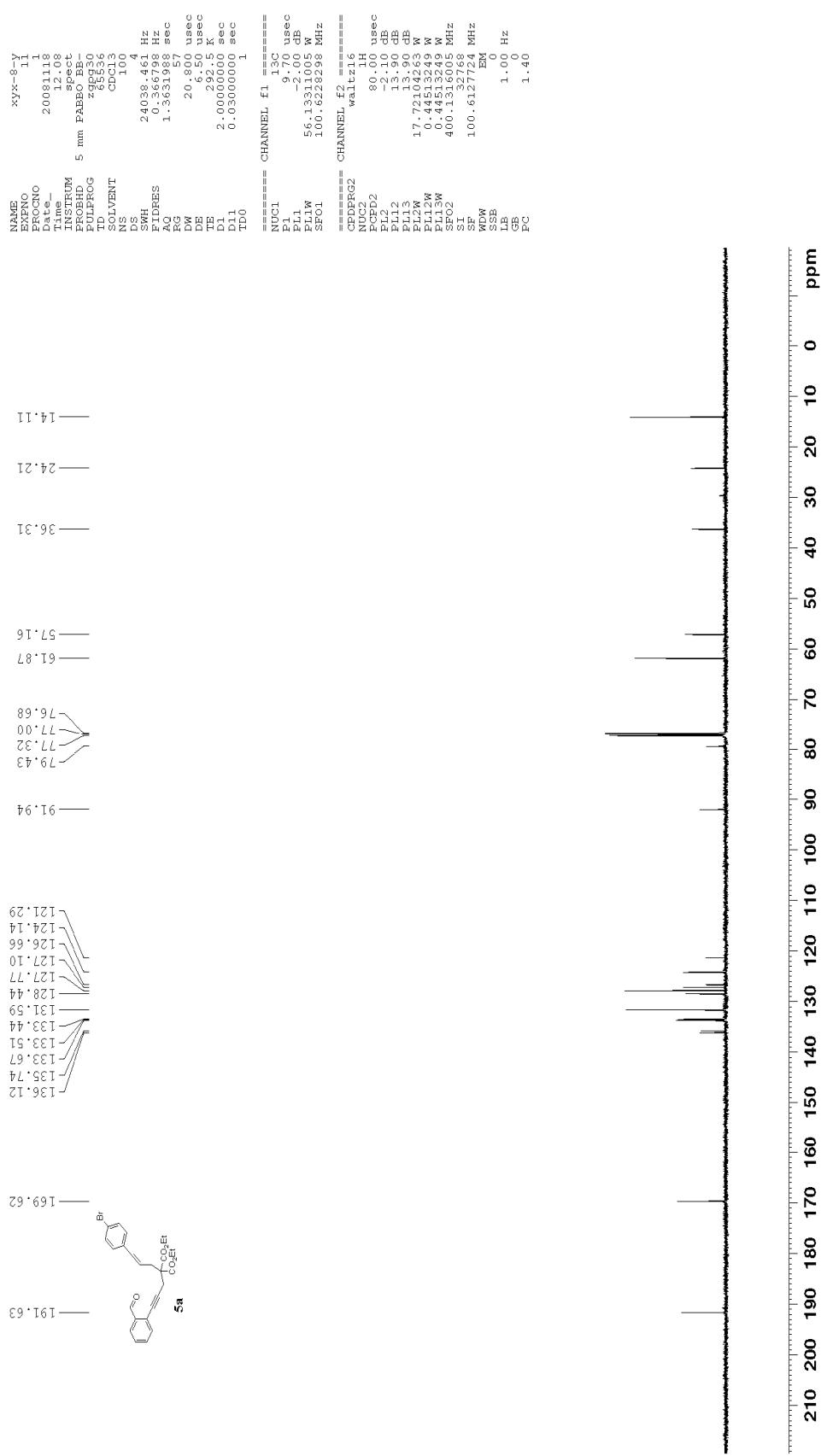


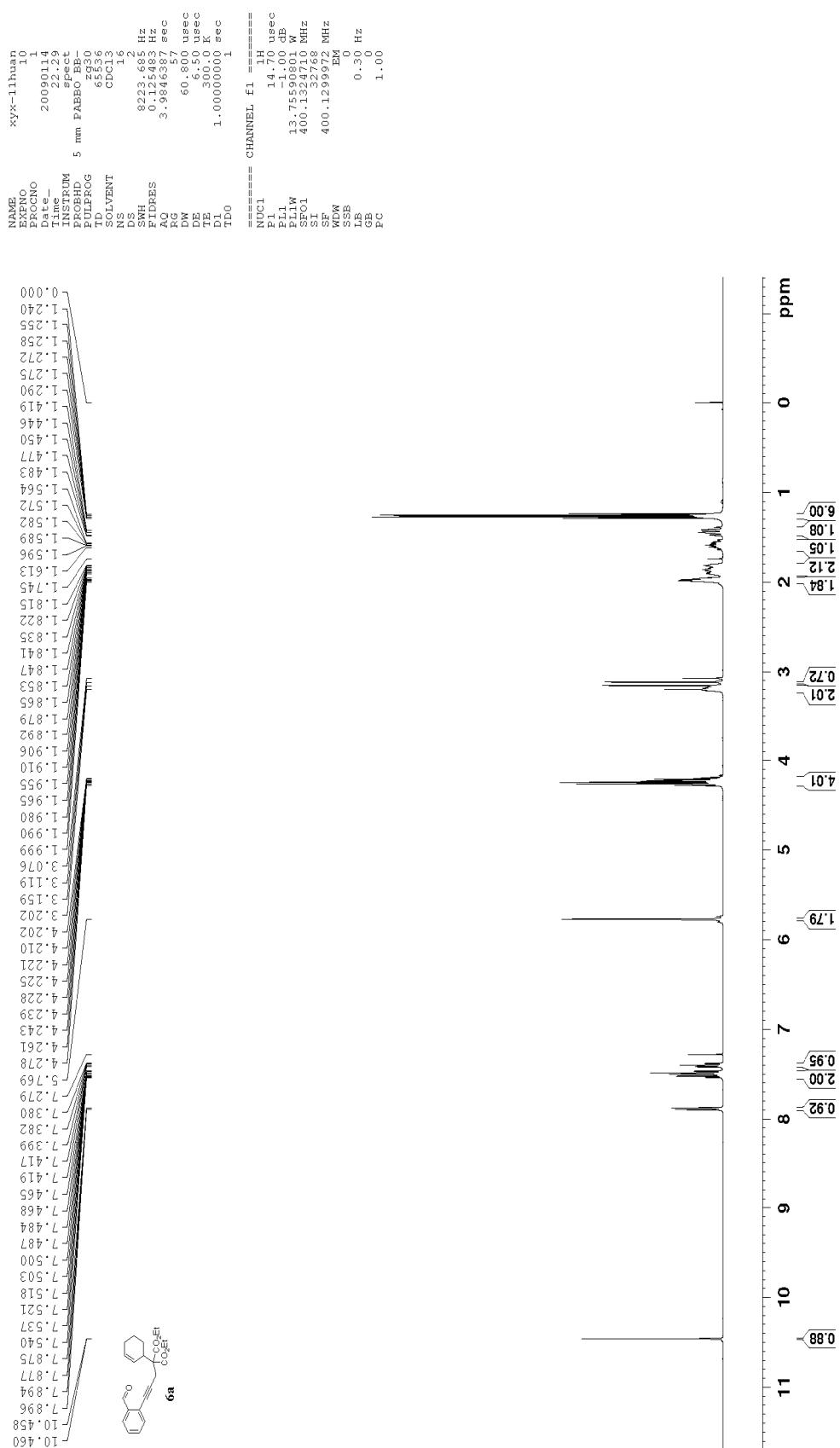


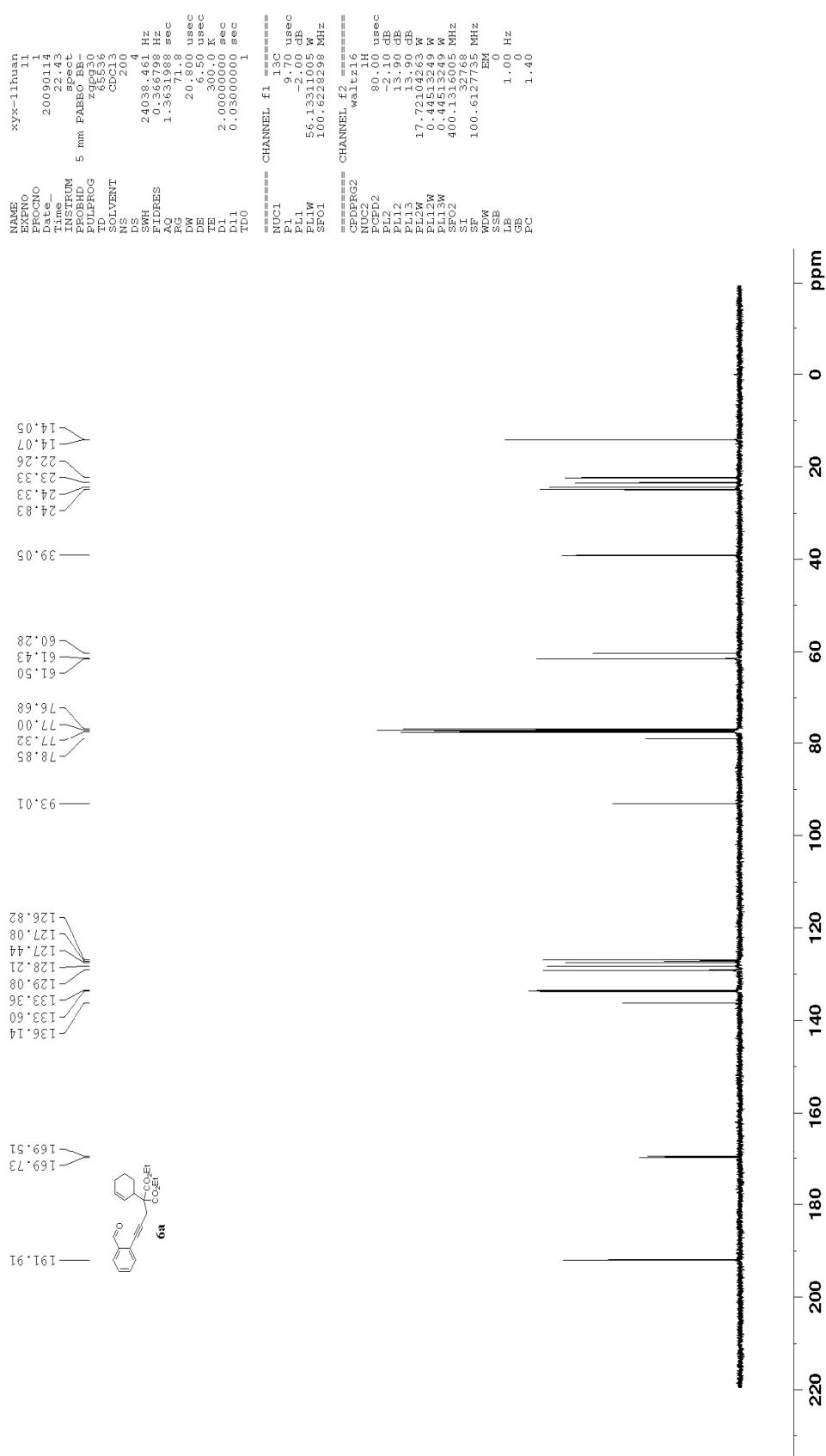


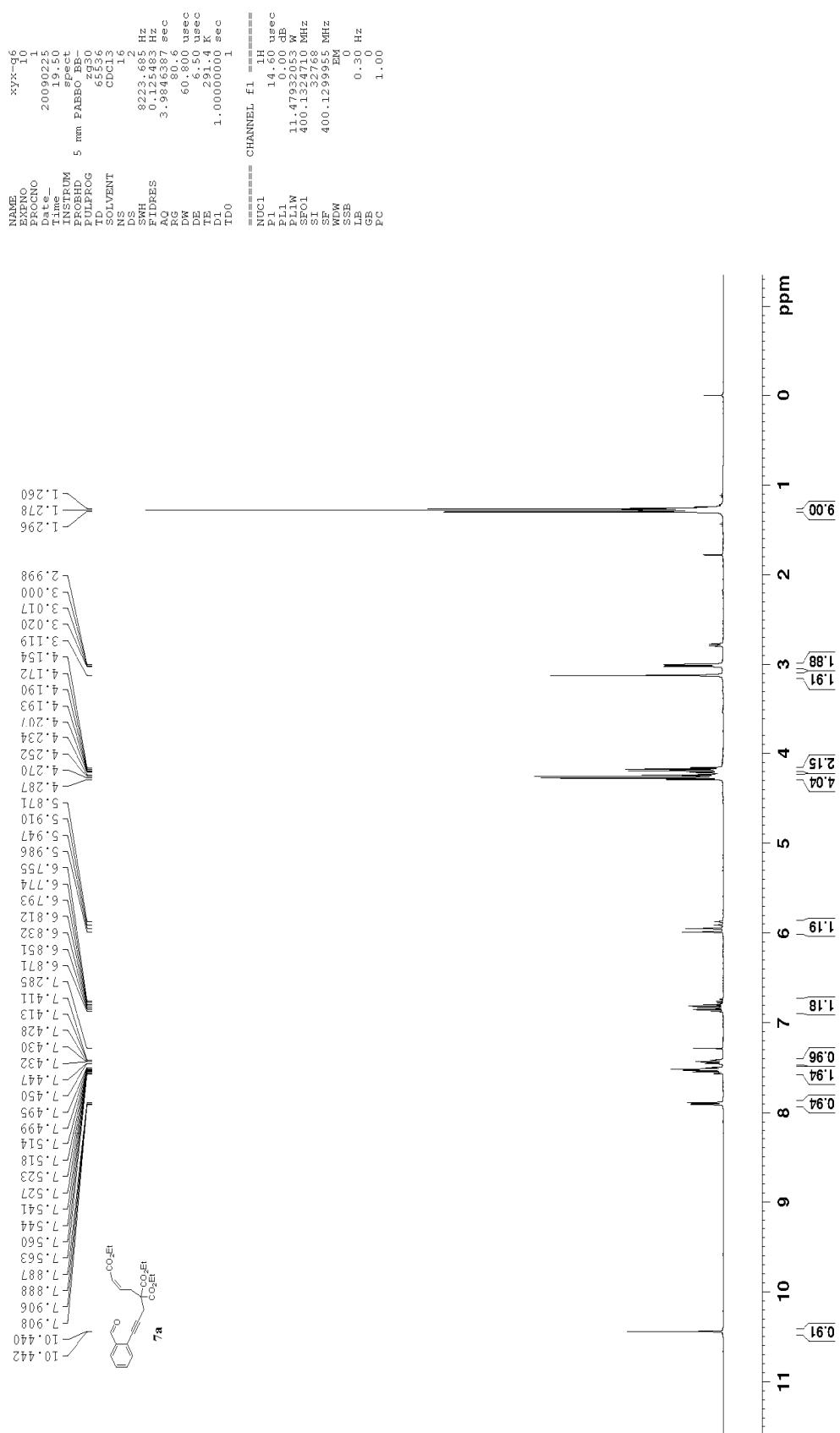


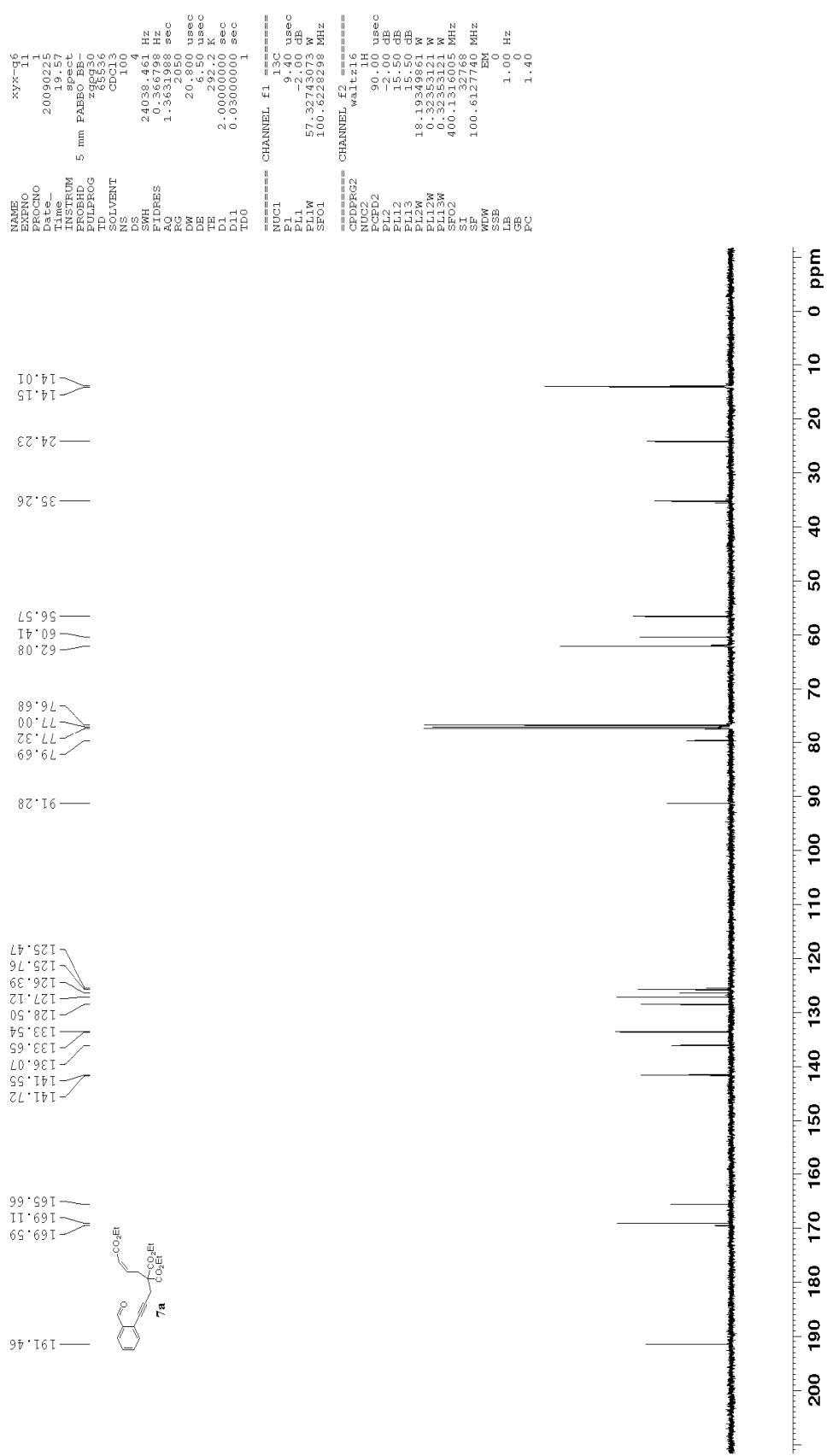










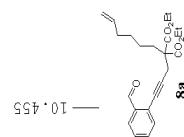
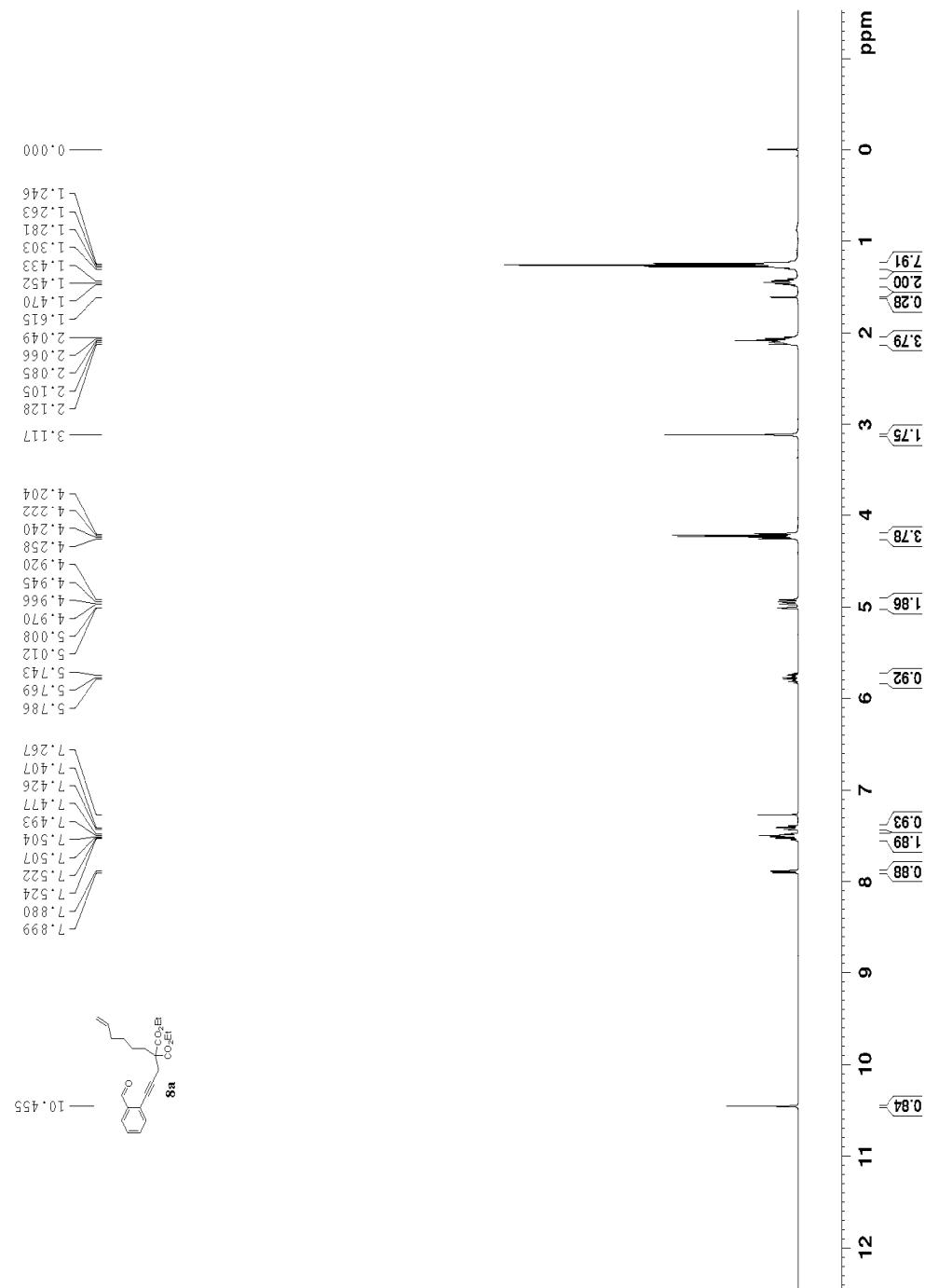


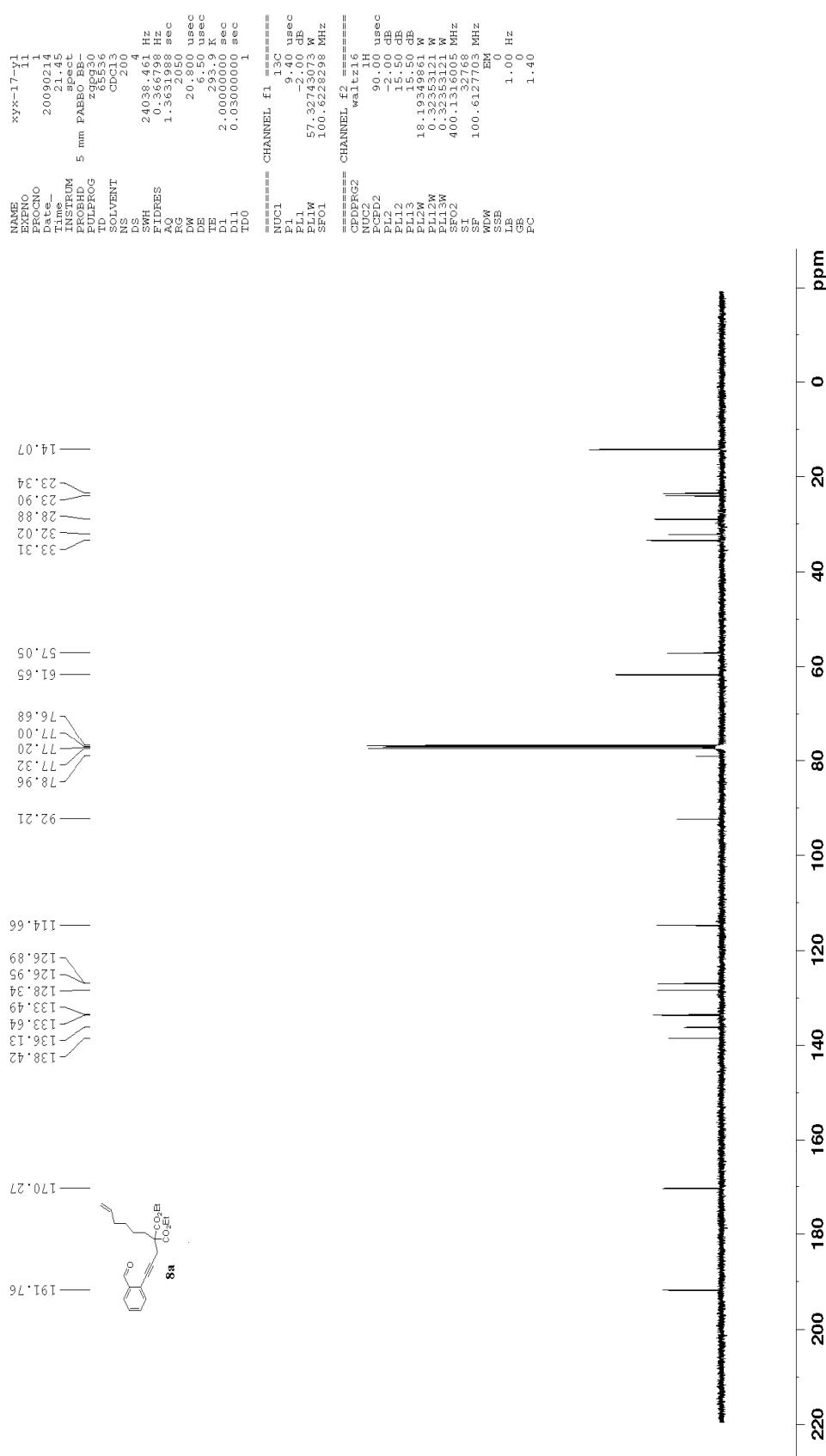
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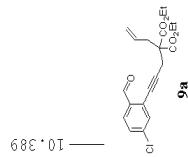
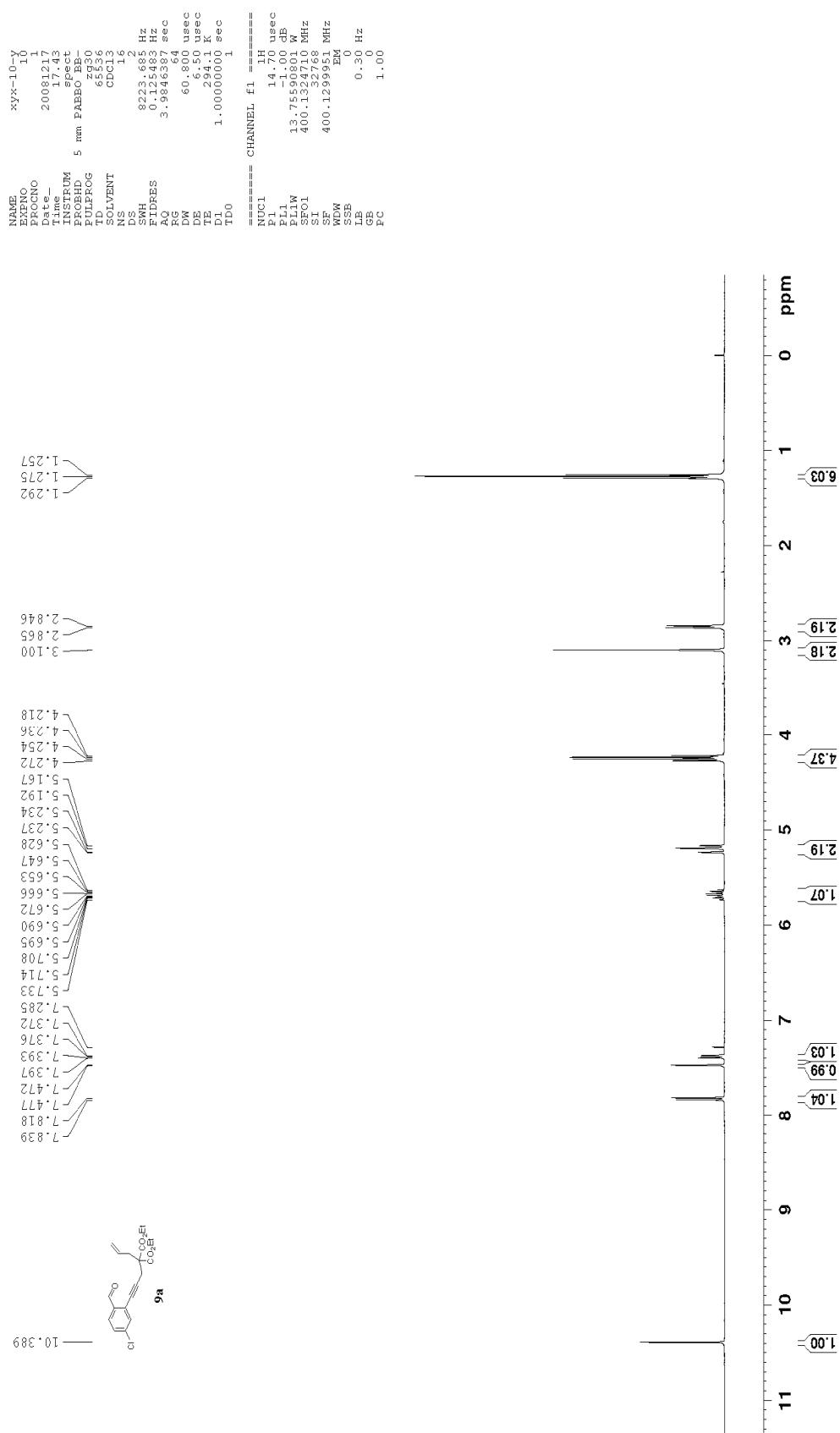
      XYX-17 Y1
      10
      20090214
      21.32
      PABBO BB-
      2920
      65536
      CDC3.3
      16
      8223.655 Hz
      0.15453 Hz
      3.9846377 sec
      228
      60.800 usec
      6.950 usec
      293.1 K
      1.0000000 sec
      1

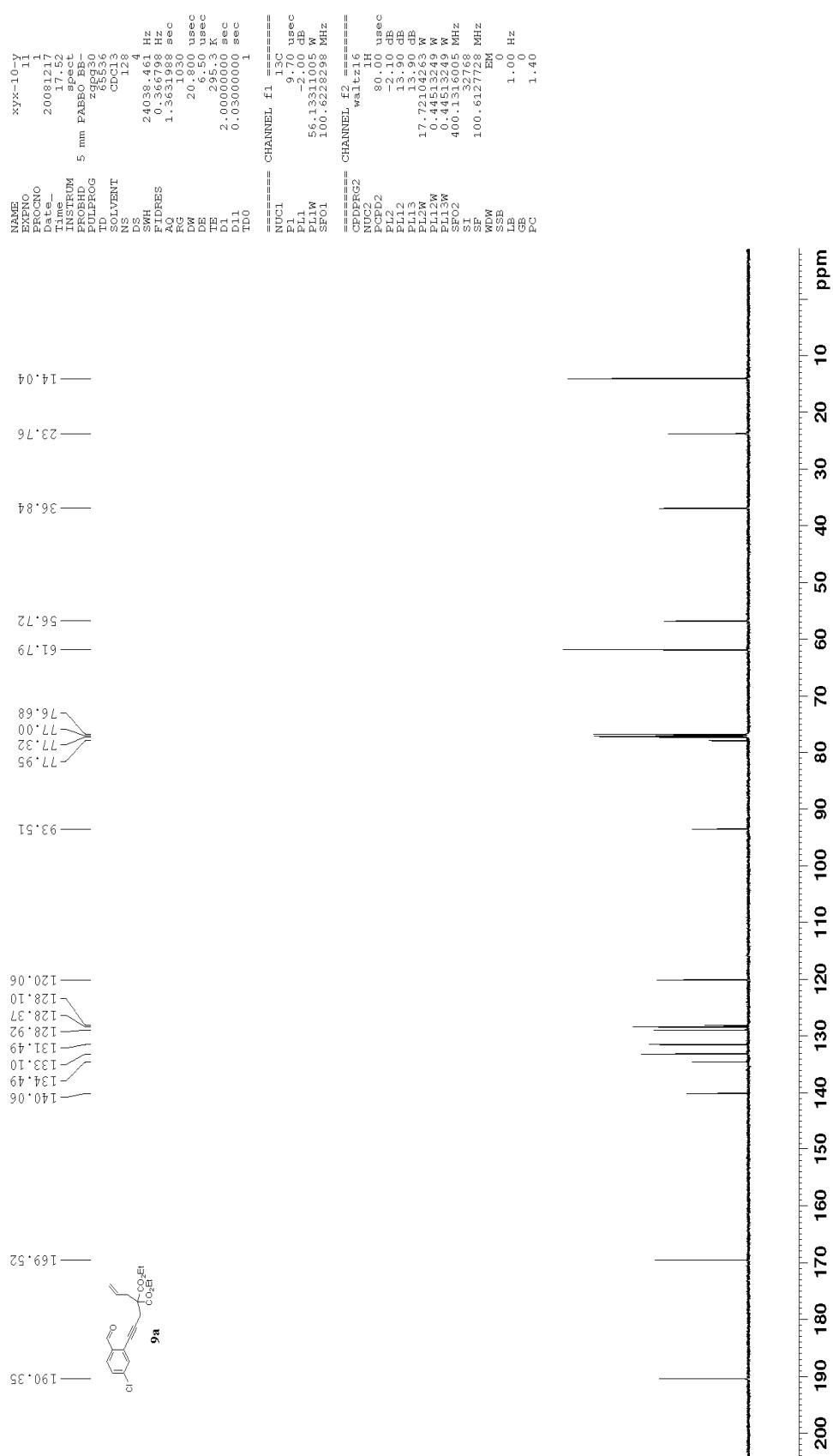
      ===== CHANNEL f1 =====
      C1C1
      L 1H 14.60 usec
      L 0.00 dB
      11.4792203 W
      400.134710 MHz
      127.98 MHz
      400.130000 MHz
      EM 0
      0.30 Hz
      1.00

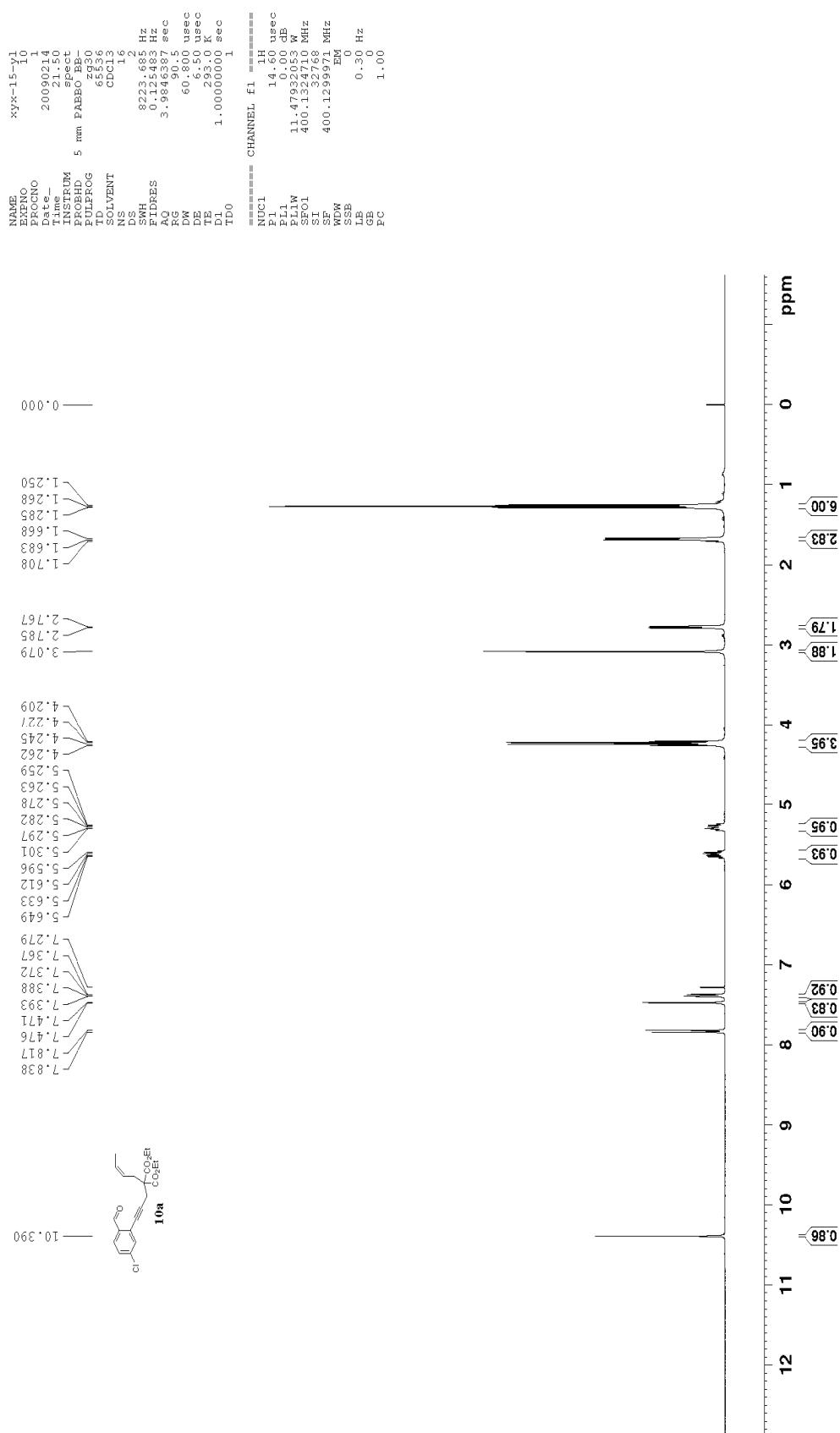
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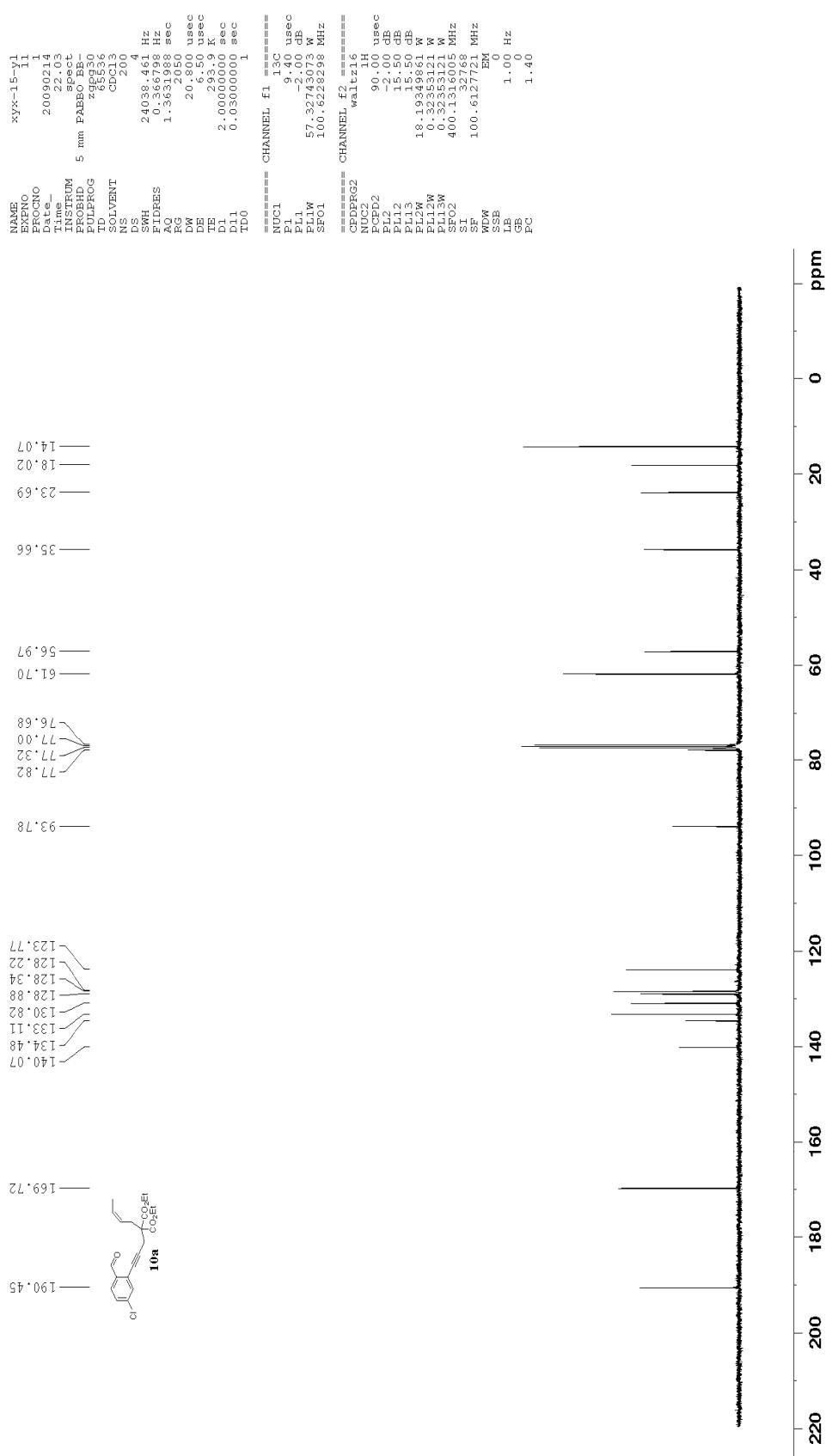


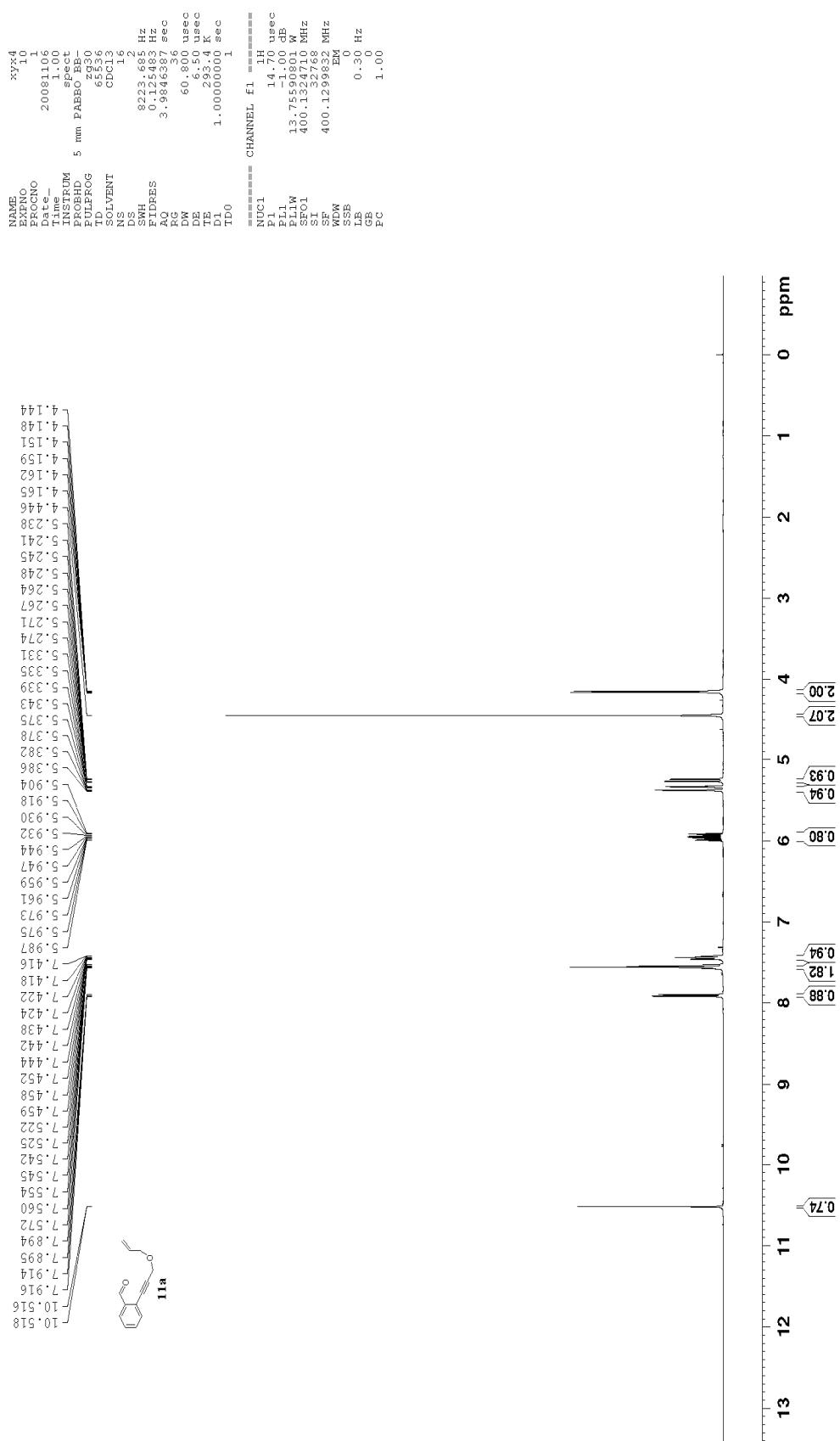


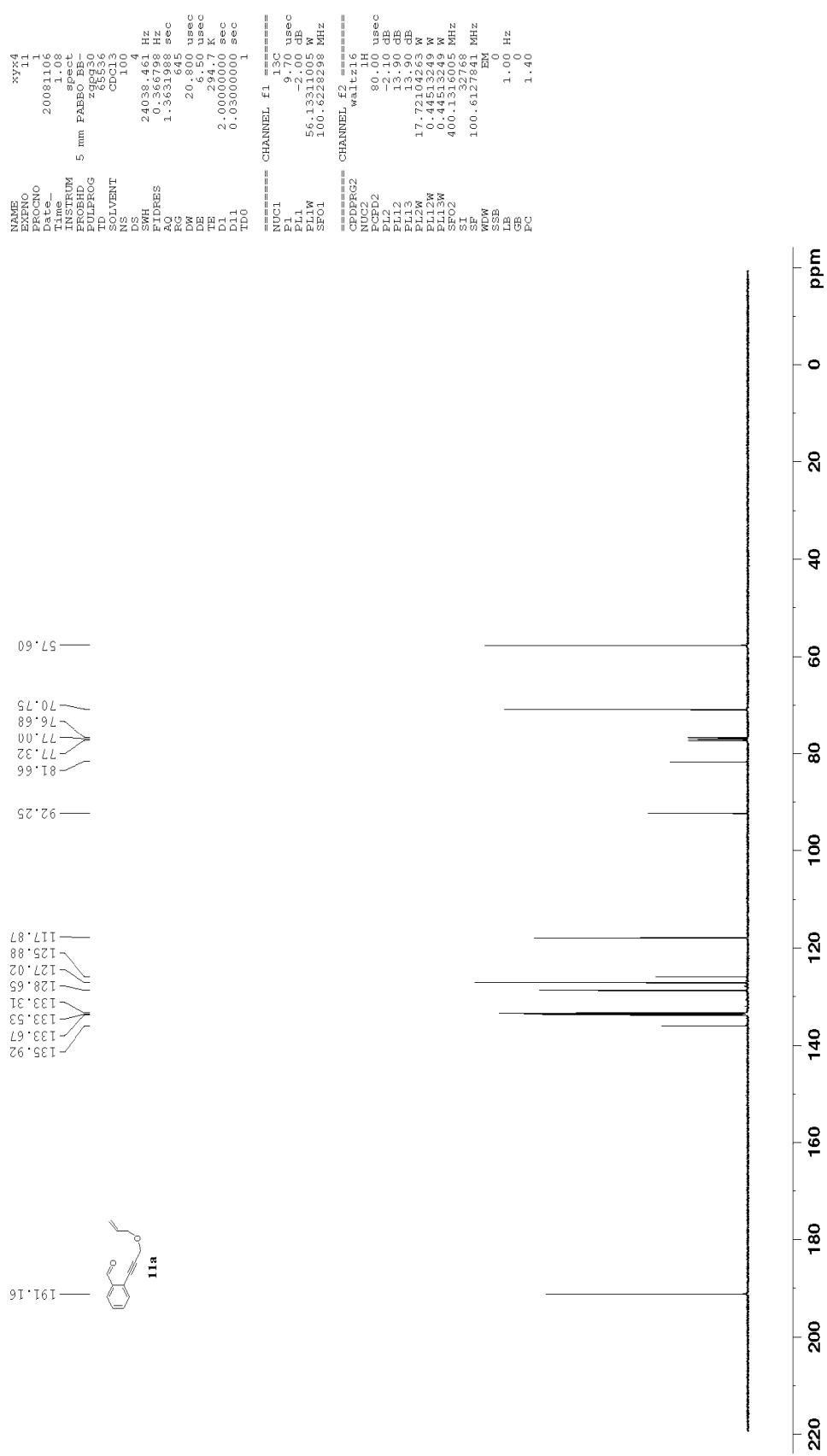












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NAME: xyx-9-y1
EXPER: 1.0
PROFCNO: 1
Date: 20081231
Time: 6.45
INSTRUM: 5 run FABIO-BB-
FROBIDP-G
TD: 652940
SOLVENT: CDD13
IS: 1.6
DS: 1.6
SMR: 8223.685 Hz
FIDRES: 0.125833 Hz
DW: 3.94646387 sec
RG: 36
TE: 60.000 usec
DE: 6.600 usec
TM: 291.0 sec
D1: 1.0000000 sec
TQD: 1

=====
CHANNEL f1 =====
NUC1: 1H
F1: 14.70 usec
PL1: -1.00 dB
PL1W: 13.7595001 W
SF1: 400.124710 MHz
SL1: 32.68 MHz
MDW: 400.1299422 MHz
SSB: 0.0 MHz
PC: 0.30 Hz
GC: 1.00

```

