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Supporting Information to

Copper-catalyzed cascade annulation of unsaturated α-bromocarbonyls with enynals: a facile access to ketones from aldehydes

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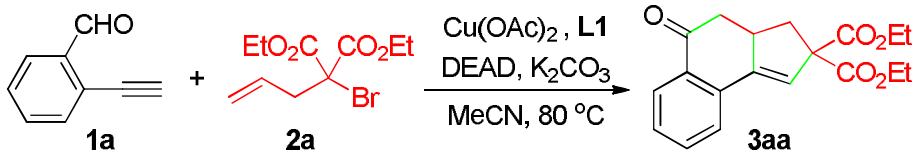
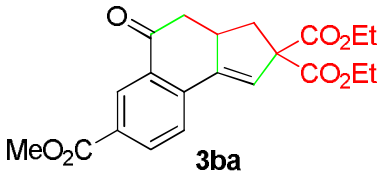
General. Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a 600 MHz or 400 MHz NMR spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analyses were carried out using a TOF MS instrument with APCI or ESI source. Column chromatography was performed using silica gel (100−200 mesh).

General Procedure for the Copper-Catalyzed Cascade Annulation of Unsaturated α-Bromocarbonyls with Enynals:

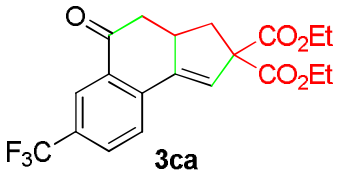


To a mixture of $Cu(OAc)_2$ (4.5 mg, 0.025 mmol), pentamethyldiethylenetriamine (**L1**) (8.7 mg, 0.050 mmol), DEAD (8.7 mg, 0.050 mmol) and K_2CO_3 (34.6 mg, 0.25 mmol) was added a solution of **1a** (32.5 mg, 0.25 mmol) and **2a** (83.4 mg, 0.30 mmol) in 3 mL of MeCN under a nitrogen atmosphere. After stirring at 80 ^{o}C for 10 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:10) gave 71 mg of **3aa** (yield: 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25−1.33 (m, 6H), 2.12 (dd, J = 8.4, 13.3 Hz, 1H), 2.50 (dd, J = 14.0, 15.6 Hz, 1H), 2.96−3.10 (m, 2H), 3.49−3.61 (m, 1H), 4.15−4.30 (m, 4H), 6.37 (d, J = 1.9 Hz, 1H), 7.38−7.45 (m, 1H), 7.53−7.59 (m, 1H), 7.67−7.71 (m, 1H), 7.90−8.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.0, 39.2, 42.3, 45.6, 61.8, 61.8, 66.3, 122.4, 125.5, 127.3, 129.0, 131.1, 133.7, 135.1, 143.7, 167.0, 171.0, 196.9; HRMS (ESI) calcd for $C_{19}H_{21}O_5$ $(M + H)^+$ 329.1389, found 329.1392.



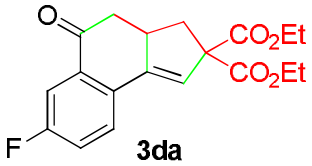
Compound ***3ba***. 76% yield (73 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.24−1.30 (m, 6H), 2.12 (dd, J = 8.4, 13.3 Hz, 1H), 2.49 (dd, J = 13.9, 15.8 Hz, 1H), 2.90−3.10 (m, 2H),

3.42−3.59 (m, 1H), 3.91 (s, 3H), 4.13−4.26 (m, 4H), 6.48 (d, J = 2.3 Hz, 1H), 7.72−7.80 (m, 1H), 8.14−8.18 (m, 1H), 8.58−8.61 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.9, 13.9, 39.1, 42.0, 45.3, 52.2, 61.8, 61.9, 66.3, 125.0, 125.7, 128.8, 130.5, 130.9, 133.9, 138.6, 142.8, 165.8, 169.5, 170.5, 195.8; HRMS (ESI) calcd for $C_{21}H_{23}O_7$ $(M + H)^+$ 387.1444, found 387.1437.



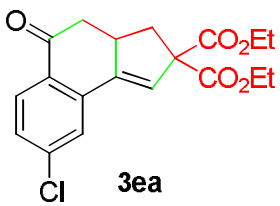
3ca

Compound ***3ca***.75% yield (74 mg); white solid, mp 97–99°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26−1.33 (m, 6H), 2.16 (dd, J = 8.3, 13.3 Hz, 1H), 2.53 (dd, J = 13.9, 15.9 Hz, 1H), 3.04–3.12 (m, 2H), 3.51–3.59 (m, 1H), 4.18–4.30 (m, 4H), 6.51 (d, J = 2.4 Hz, 1H), 7.75–7.85 (m, 2H), 8.28 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 39.1, 42.1, 45.3, 62.0,62.0, 66.4, 123.5 (q, J = 272.6 Hz), 124.7 (q, J = 3.9 Hz), 125.2, 126.2, 129.8 (q, J = 3.4 Hz), 131.1 (q, J = 33.2 Hz), 131.2, 138.0, 142.4, 169.6, 170.6, 195.5;^{19}F NMR (565 MHz, $CDCl_3$) δ –63.0;HRMS (ESI) calcd for $C_{20}H_{20}F_3O_5$ $(M + H)^+$ 397.1263, found 397.1255.



3da

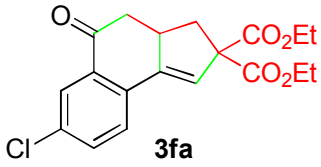
Compound ***3da***. 81% yield (70 mg); white solid, mp 96–98°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26−1.33 (m, 6H), 2.13 (dd, J = 8.4, 13.3 Hz, 1H), 2.50 (dd, J = 13.9, 15.8 Hz, 1H), 3.01−3.10 (m, 2H), 3.49−3.58 (m, 1H), 4.19−4.30 (m, 4H), 6.33 (d, J = 2.2 Hz, 1H), 7.26−7.30 (m, 1H), 7.60−7.74 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 39.1, 42.3, 45.3, 61.8, 61.9, 66.2, 113.3 (d, J = 22.4 Hz), 121.3 (d, J = 22.9 Hz), 122.2 (d, J = 2.1 Hz), 127.8 (d, J = 7.6 Hz), 131.5 (d, J = 3.2 Hz), 133.0 (d, J = 6.5 Hz), 142.6 (d, J = 1.0 Hz), 162.9 (d, J = 251.1 Hz),169.9, 170.9, 195.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ–110.2; HRMS (ESI) calcd for $C_{19}H_{20}FO_5$ $(M + H)^+$ 347.1295, found 347.1293.



3ea

Compound ***3ea***. 76% yield (69 mg); white solid, mp 141–143°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ

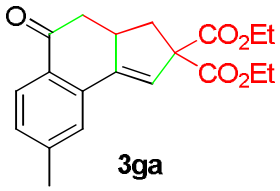
1.27−1.32 (m, 6H), 2.12 (dd, J = 8.3, 13.3 Hz, 1H), 2.48 (dd, J = 13.9, 15.8 Hz, 1H), 2.95−3.08 (m, 2H), 3.46−3.57 (m, 1H), 4.17−4.29 (m, 4H), 6.40 (d, J = 2.3 Hz, 1H), 7.37 (dd, J = 1.9, 8.4 Hz, 1H), 7.67 (d, J = 1.9 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 39.2, 42.3, 45.4, 61.9, 61.9, 66.3, 123.9, 125.3, 129.1, 129.3, 129.4, 136.5, 140.1, 142.6, 169.8, 170.7, 195.8; HRMS (ESI) calcd for $C_{19}H_{20}ClO_5$ $(M + H)^+$ 363.0999, found 363.0995.



3fa

Compound ***3fa***. 80% yield (73 mg); white solid, mp 136–138°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26−1.32 (m, 6H), 2.12 (dd, J = 8.4, 13.3 Hz, 1H), 2.48 (dd, J = 13.9, 15.8 Hz, 1H), 2.98−3.09 (m, 2H), 3.46−3.56 (m, 1H), 4.15−4.30 (m, 4H), 6.37 (d, J = 2.3 Hz, 1H), 7.51 (dd, J = 2.3, 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 2.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 39.1, 42.2, 45.3, 61.8, 61.9, 66.3, 123.1, 127.1, 127.1, 132.1, 133.4, 133.6, 135.3, 142.6, 169.8, 170.7, 195.6; HRMS (ESI) calcd for $C_{19}H_{20}ClO_5$ $(M + H)^+$ 363.0999, found 363.0988.

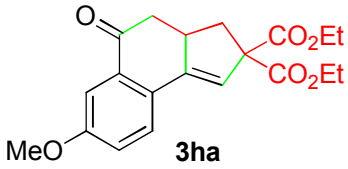
Crystal data for **3fa** ($C_{19}H_{19}ClO_5$, 362.79): triclinic, space group P–1, a = 7.9475(16) Å, b = 10.528(2) Å, c = 11.586(3) Å, U = 911.0(3) Å^3, Z = 2, T = 296(2) K, absorption coefficient 0.235 mm^{-1}, reflections collected 30570, independent reflections 3197 [R(int) = 0.047], refinement by full-matrix least-squares on F^2, data/restraints/parameters 4195/0/214, goodness-of-fit on F^2 = 1.042, final R indices [I>2σ(I)] R_1 = 0.0619, wR_2 = 0.1631, R indices (all data) R_1 = 0.0832, wR_2 = 0.1874, largest diff. peak and hole 0.376 and –0.358e· Å^{-3}. Crystallographic data for the structure **3fa** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC1439849.



3ga

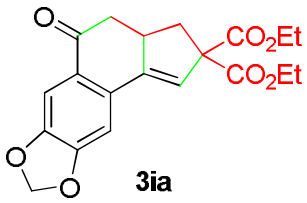
Compound ***3ga***. 81% yield (69 mg); white solid, mp 91–93°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26−1.33 (m, 6H), 2.11 (dd, J = 8.4, 13.3 Hz, 1H), 2.40−2.51 (m, 4H), 2.91−3.10 (m, 2H), 3.40−3.60 (m, 1H), 4.15−4.30 (m, 4H), 6.35 (d, J = 2.3 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.0, 21.7, 39.2, 42.4, 45.6,

61.7, 61.8, 66.2, 122.1, 125.7, 127.4, 128.9, 130.1, 135.1, 143.8, 144.5, 170.0, 171.0, 196.7; HRMS (ESI) calcd for $C_{20}H_{23}O_5$ $(M + H)^+$ 343.1545, found 343.1538.



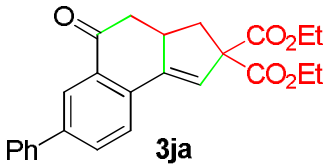
3ha

Compound ***3ha***.90% yield (81 mg); white solid, mp 101–103°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25−1.32 (m, 6H), 2.09 (dd, J = 8.6, 13.2 Hz, 1H), 2.48 (dd, J = 13.8, 15.7 Hz, 1H), 2.95−3.10 (m, 2H), 3.46−3.55 (m, 1H), 3.87 (s, 3H), 4.13−4.30 (m, 4H), 6.23 (d, J = 2.3 Hz, 1H), 7.13 (dd, J = 2.8, 8.6 Hz, 1H), 7.46 (d, J = 2.8 Hz, 1H), 7.62 (d, J = 8.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 39.2, 42.4, 45.5, 55.5, 61.7, 61.7, 66.2, 108.9, 120.3, 122.2, 127.1, 128.5, 132.3, 143.3, 160.2, 170.2, 171.1, 196.9; HRMS (ESI) calcd for $C_{20}H_{23}O_6$ $(M + H)^+$ 359.1495, found 359.1489.



3ia

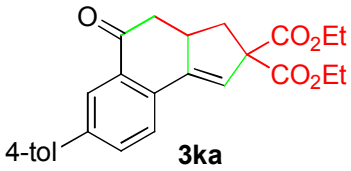
Compound ***3ia***. 84% yield (78 mg); white solid, mp 135–137°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24−1.31 (m, 6H), 2.08 (dd, J = 8.5, 13.3 Hz, 1H), 2.43 (dd, J = 13.7, 15.8 Hz, 1H), 2.90−3.10 (m, 2H), 3.40−3.53 (m, 1H), 4.15−4.30 (m, 4H), 6.04 (s, 2H), 6.22 (d, J = 2.3 Hz, 1H), 7.05 (s, 1H), 7.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.0, 39.2, 42.4, 45.2, 61.7, 61.8, 66.1, 101.9, 104.4, 106.2, 121.4, 127.0, 132.1, 143.7, 148.9, 152.3, 170.0, 171.0, 195.3; HRMS (ESI) calcd for $C_{20}H_{21}O_7$ $(M + H)^+$ 373.1287, found 373.1293.



3ja

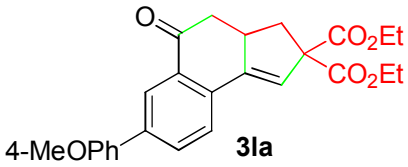
Compound ***3ja***. 73% yield (74 mg); white solid, mp 81–83°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26−1.33 (m, 6H), 2.14 (dd, J = 8.5, 13.2 Hz, 1H), 2.54 (dd, J = 14.0, 15.5 Hz, 1H), 3.02−3.10 (m, 2H), 3.52−3.59 (m, 1H), 4.19−4.29 (m, 4H), 6.41 (d, J = 2.3 Hz, 1H), 7.39 (d, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.64 (d, J = 7.4 Hz, 2H), 7.75−7.83 (m, 2H), 8.26 (d, J = 1.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 39.3, 42.3, 45.7, 61.8, 61.9, 66.3, 122.4, 125.6, 126.1,

127.0, 128.0, 128.9, 131.4, 132.2, 133.9, 139.5, 141.8, 143.4, 170.0, 171.0, 197.0; HRMS (ESI) calcd for $C_{25}H_{25}O_5$ $(M + H)^+$ 405.1702, found 405.1693.



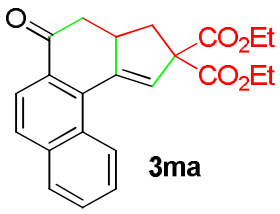
3ka

Compound ***3ka***. 79% yield (83 mg); white solid, mp 87–89°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26−1.33 (m, 6H), 2.13 (dd, J = 8.5, 13.2 Hz, 1H), 2.40 (s, 3H), 2.50−2.56 (m, 1H), 3.00−3.10 (m, 2H), 3.52−3.59 (m, 1H), 4.17−4.29 (m, 4H), 6.39 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 6.9 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.72−7.82 (m, 2H), 8.24 (d, J = 1.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 21.1, 39.2, 42.3, 45.7, 61.8, 61.8, 66.3, 122.2, 125.2, 126.1, 126.8, 129.6, 131.4, 131.9, 133.7, 136.6, 137.9, 141.7, 143.5, 170.0, 171.0, 197.0; HRMS (ESI) calcd for $C_{26}H_{27}O_5$ $(M + H)^+$ 419.1858, found 419.1850.



3la

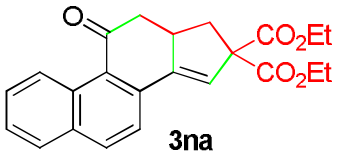
Compound ***3la***. 83% yield (90 mg); white solid, mp 99–101°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26−1.33 (m, 6H), 2.13 (dd, J = 8.5, 13.2 Hz, 1H), 2.53 (dd, J = 13.9, 15.6 Hz, 1H), 3.00−3.09 (m, 2H), 3.52−3.59 (m, 1H), 3.86 (s, 3H), 4.16−4.29 (m, 4H), 6.38 (d, J = 2.3 Hz, 1H), 6.90−7.01 (m, 2H), 7.57−7.60 (m, 2H), 7.70−7.80 (m, 2H), 8.20−8.22 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 39.3, 42.4, 45.7, 55.4, 61.8, 61.8, 66.3, 114.4, 122.1, 124.9, 126.1, 128.1, 131.4, 131.7, 132.0, 133.4, 141.5, 143.5, 159.7, 170.1, 171.0, 197.1; HRMS (ESI) calcd for $C_{26}H_{27}O_6$ $(M + H)^+$ 435.1808, found 435.1799.



3ma

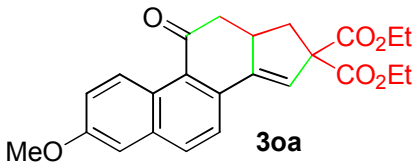
Compound ***3ma***. 72% yield (68 mg); white solid, mp 133–135°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H), 2.49 (dd, J = 4.3, 14.2 Hz, 1H), 2.72 (dd, J = 13.4, 16.5 Hz, 1H), 2.90 (dd, J = 8.7, 14.2 Hz, 1H), 3.15 (dd, J = 5.8, 16.5 Hz, 1H), 3.60−3.68 (m,

1H), 4.18−4.40 (m, 4H), 6.50 (d, J = 1.5 Hz, 1H), 7.60−7.65 (m, 2H), 7.80−7.89 (m, 2H), 8.00−8.10 (m, 1H), 8.56−8.60 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 36.4, 45.8, 47.4, 61.9, 62.0, 67.8, 122.7, 127.0, 127.4, 127.7, 128.6, 128.7, 128.9, 129.6, 129.6, 136.0, 136.3, 142.3, 170.8, 171.1, 197.0; HRMS (ESI) calcd for $C_{23}H_{23}O_5$ $(M + H)^+$ 379.1545, found 379.1547.



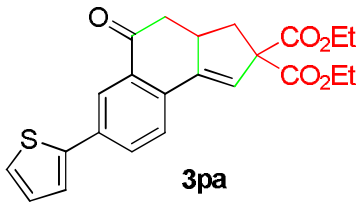
3na

Compound ***3na***. 74% yield (70 mg); white solid, mp 151–153°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27−1.33 (m, 6H), 2.16 (dd, J = 8.5, 13.1 Hz, 1H), 2.72 (t, J = 14.1 Hz, 1H), 3.01−3.10 (m, 2H), 3.60−3.70 (m, 1H), 4.15−4.30 (m, 4H), 6.48 (d, J = 2.2 Hz, 1H), 7.50−7.53 (m, 1H), 7.61−7.64 (m, 1H), 7.72−7.81 (m, 2H), 7.95−7.97 (m, 1H), 9.30−9.33 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 39.1, 42.8, 47.9, 61.8, 61.9, 66.3, 122.6, 123.7, 126.1, 126.8, 127.1, 128.3, 129.1, 130.7, 133.9, 134.4, 135.9, 145.1, 169.9, 170.9, 199.7; HRMS (ESI) calcd for $C_{23}H_{23}O_5$ $(M + H)^+$ 379.1545, found 379.1548.



3oa

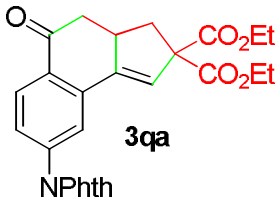
Compound ***3oa***. 78% yield (80 mg); white solid, mp 176–178°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27−1.33 (m, 6H), 2.14 (dd, J = 8.5, 13.1 Hz, 1H), 2.71 (t, J = 14.1 Hz, 1H), 3.00−3.08 (m, 2H), 3.60−3.67 (m, 1H), 3.93 (s, 3H), 4.17−4.29 (m, 4H), 6.42 (d, J = 2.2 Hz, 1H), 7.11 (d, J = 2.7 Hz, 1H), 7.26−7.29 (m, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H), 9.25 (d, J = 9.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 39.1, 42.8, 48.0, 55.2, 61.8, 61.8, 66.3, 106.9, 121.0, 122.6, 123.3, 125.9, 126.2, 128.8, 133.2, 133.8, 135.7, 145.1, 158.0, 170.0, 171.0, 199.9; HRMS (ESI) calcd for $C_{24}H_{25}O_6$ $(M + H)^+$ 409.1651, found 409.1642.



3pa

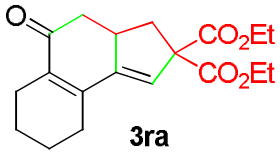
Compound ***3pa***. 68% yield (70 mg); white solid, mp 133–135°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26−1.33 (m, 6H), 2.12 (dd, J = 8.5, 13.2 Hz, 1H), 2.49−2.55 (m, 1H), 3.00−3.09 (m, 2H), 3.50−3.57 (m, 1H), 4.16−4.30 (m, 4H), 6.38 (d, J = 2.1 Hz, 1H), 7.11 (dd, J = 3.7, 5.0 Hz, 1H),

7.34 (d, J = 5.1 Hz, 1H), 7.42 (d, J = 3.6 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.79 (dd, J = 1.8, 8.2 Hz, 1H), 8.23 (d, J = 1.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 39.2, 42.3, 45.6, 61.8; 61.9, 66.3, 122.4, 124.0, 124.1, 125.8, 126.2, 128.3, 130.7, 131.4, 133.8, 135.2, 142.8, 143.3, 167.0, 171.0, 196.8; HRMS (ESI) calcd for $C_{23}H_{23}O_5S$ $(M + H)^+$ 411.1266, found 411.1258.



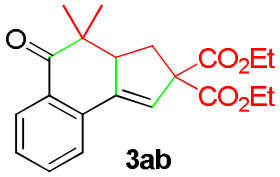
3qa

Compound ***3qa***. 64% yield (76 mg); white solid, mp 64–66°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26−1.34 (m, 6H), 2.16 (dd, J = 8.3, 13.3 Hz, 1H), 2.55 (dd, J = 13.9, 15.8 Hz, 1H), 2.99−3.13 (m, 2H), 3.54−3.62 (m, 1H), 4.16−4.31 (m, 4H), 6.44 (d, J = 2.3 Hz, 1H), 7.58 (dd, J = 2.0, 8.4 Hz, 1H), 7.86 (dd, J = 3.1, 5.3 Hz, 3H), 8.01 (dd, J = 3.0, 5.4 Hz, 2H), 8.17 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 39.2, 42.3, 45.5, 61.9, 61.9, 66.4, 122.9, 123.7, 124.0, 126.5, 128.5, 130.0, 131.5, 134.8, 136.1, 136.5, 142.9, 166.7, 169.8, 170.8, 196.0; HRMS (ESI) calcd for $C_{27}H_{24}NO_7$ $(M + H)^+$ 474.1553, found 474.1552.



3ra

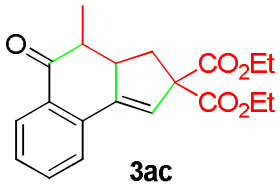
Compound ***3ra***. 80% yield (66 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.24−1.30 (m, 6H), 1.51−1.63 (m, 2H), 1.70−1.80 (m, 2H), 1.96 (dd, J = 9.2, 13.1 Hz, 1H), 2.16−2.21 (m, 1H), 2.28 (dd, J = 13.6, 15.7 Hz, 1H), 2.30−2.50 (m, 2H), 2.52−2.57 (m, 1H), 2.77 (dd, J = 5.9, 15.7 Hz, 1H), 2.93 (dd, J = 7.1, 13.1 Hz, 1H), 3.29−3.36 (m, 1H), 4.13−4.27 (m, 4H), 5.98 (d, J = 1.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 21.5, 21.6, 22.9, 26.9, 39.3, 41.6, 44.6, 61.7, 61.8, 66.0, 123.3, 135.5, 145.2, 145.7, 169.9, 171.0,198.1; HRMS (ESI) calcd for $C_{19}H_{25}O_5$ $(M + H)^+$ 333.1702, found 333.1697.



3ab

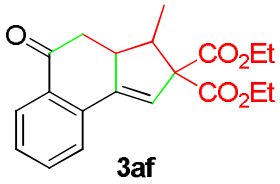
Compound ***3ab***. 92% yield (82 mg); white solid, mp 86–88°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.24 (s, 3H), 1.26−1.33 (m, 6H), 2.35 (dd, J = 8.2, 13.8 Hz, 1H), 2.80 (dd, J = 8.2, 13.8

Hz, 1H), 3.34−3.39 (m, 1H), 4.16−4.31 (m, 4H), 6.39 (d, *J* = 2.4 Hz, 1H), 7.38−7.44 (m, 1H), 7.51−7.56 (m, 1H), 7.66−7.70 (m, 1H), 7.97−8.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.0, 18.9, 21.8, 31.9, 45.9, 51.9, 61.7, 61.8, 66.3, 122.8, 125.0, 128.2, 129.2, 129.9, 133.1, 134.3, 142.4, 170.3, 171.0, 202.5; HRMS (ESI) calcd for $C_{21}H_{25}O_5$ $(M + H)^+$ 357.1702, found 357.1697.



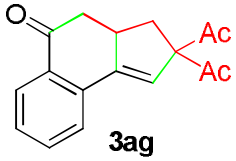
3ac

Compound ***3ac***. 80% yield (69 mg); colorless oil; dr = 88:12; ^{1}H NMR (600 MHz, $CDCl_3$) date of the major isomerδ 1.25−1.33 (m, 9H), 2.14 (dd, *J* = 8.5, 13.1 Hz, 1H), 2.44−2.52 (m, 1H), 3.07 (dd, *J* = 7.2, 13.1 Hz, 1H), 3.15−3,21 (m, 1H), 4.15−4.31 (m, 4H), 6.39 (d, *J* = 2.4 Hz, 1H), 7.38−7.44 (m, 1H), 7.53−7.56 (m, 1H), 7.67−7.71 (m, 1H), 7.97−8.01 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$)date of the major isomerδ 12.4, 14.0, 14.0, 38.5, 49.0, 49.1, 61.8, 61.8, 66.0, 122.2, 125.3, 127.5, 129.0, 131.3, 133.3, 134.7, 143.6, 170.0, 171.0, 199.1; HRMS (ESI) calcd for $C_{20}H_{23}O_5$ $(M + H)^+$ 343.1545, found 343.1540.



3af

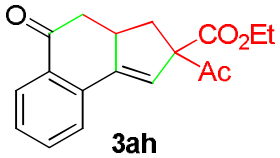
Compound ***3af***. 39% yield (33 mg); colorless oil; dr = 61:39; ^{1}H NMR (600 MHz, $CDCl_3$) date of the major isomerδ 1.22−1.36 (m, 9H), 2.45 (dd, *J* = 13.8, 15.4 Hz, 1H), 2.62−2.78 (m, 1H), 3.02 (dd, *J* = 5.5, 15.5 Hz, 1H), 3.08−3.17 (m, 1H), 4.13−4.35 (m, 4H), 6.40 (d, *J* = 2.2 Hz, 1H), 7.37−7.43 (m, 1H), 7.53−7.58 (m, 1H), 7.71 (t, *J* = 8.5 Hz, 1H), 7.96−8.01 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) date of the major isomer δ 13.9, 14.1, 14.2, 44.1, 47.9, 48.8, 61.6, 61.6, 69.5, 123.1, 125.2, 127.3, 129.0, 131.1, 133.7, 135.1, 143.4, 169.3, 170.5, 197.2; HRMS (ESI) calcd for $C_{20}H_{22}NaO_5$ $(M + Na)^+$ 365.1365, found 365.1358.



3ag

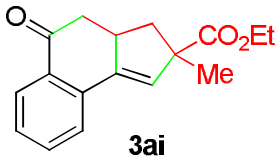
Compound ***3ag***.76% yield (51 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.92 (dd, *J* = 8.5, 13.0 Hz, 1H), 2.22 (s, 3H), 2.23 (s, 3H), 2.46 (dd, *J* = 13.8, 15.7 Hz, 1H), 3.02 (dd, *J* = 5.5, 15.7

Hz, 1H), 3.14 (dd, J = 7.3, 13.0 Hz, 1H), 3.37−3.44 (m, 1H), 6.56 (d, J = 2.4 Hz, 1H), 7.42−7.45 (m, 1H), 7.55−7.60 (m, 1H), 7.70 (d, J = 7.5 Hz, 1H), 8.02 (dd, J = 1.0, 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.0, 27.1, 37.1, 42.1, 45.7, 80.9, 122.0, 125.3, 127.5, 129.3, 131.2, 133.8, 134.8, 144.3, 196.6, 202.8, 205.2; HRMS (ESI) calcd for $C_{17}H_{17}O_3$ $(M + H)^+$ 269.1178, found 269.1172.



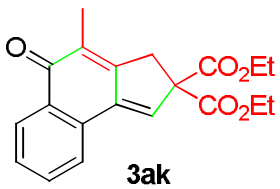
3ah

Compound ***3ah***. 78% yield (58 mg); colorless oil; dr = 55:45; ^{1}H NMR (600 MHz, $CDCl_3$) date of the major isomer δ 1.27−1.33 (m, 6H), 2.05−2.11 (m, 1H), 2.27 (s, 3H), 2.43−2.53 (m, 1H), 2.98−3.08 (m, 2H), 3.37−3,46 (m, 1H), 4.20−4.29 (m, 2H), 6.42 (d, J = 2.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) date of the major isomer δ 14.1, 26.6, 37.8, 42.2, 45.7, 61.9, 73.2, 122.2, 125.3, 127.4, 129.2, 131.1, 133.7, 135.0, 144.4, 170.4, 196.8, 201.3; HRMS (ESI) calcd for $C_{18}H_{19}O_4$ $(M + H)^+$ 299.1283, found 299.1277.



3ai

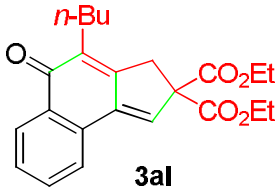
Compound ***3ai***. 80% yield (54 mg); colorless oil; dr = 60:40; ^{1}H NMR (600 MHz, $CDCl_3$) date of the major isomer δ 1.26 (t, J = 7.1 Hz, 3H), 1.53 (s, 3H), 2.21 (dd, J = 8.7, 12.8 Hz, 1H), 2.42−2.54 (m, 1H), 2.95−3.02 (m, 2H), 3.48−3.55 (m, 1H), 4.15 (q, J = 7.1 Hz, 2H), 6.20 (d, J = 2.3 Hz, 1H), 7.36−7.41 (m, 1H), 7.53−7.57 (m, 1H), 7.65−7.68 (m, 1H), 8.01 (d, J = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) date of the major isomer δ 14.1, 25.5, 42.8, 43.6, 46.3, 55.5, 60.8, 125.2, 127.2, 128.4, 129.1, 131.0, 133.5, 135.8, 140.8, 175.6, 197.6; HRMS (ESI) calcd for $C_{17}H_{19}O_3$ $(M + H)^+$ 271.1334, found 271.1327.



3ak

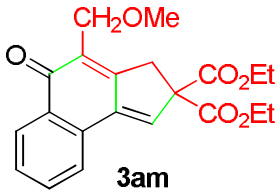
Compound ***3ak***.74% yield (63 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.32 (t, J = 7.1 Hz, 6H), 2.10 (s, 3H), 3.55 (s, 2H), 4.22−4.33 (m, 4H), 7.14 (s, 1H), 7.52−7.61 (m, 2H), 7.88 (d, J

= 7.6 Hz, 1H), 8.23 (d, J = 7.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 12.2, 14.0, 36.5, 62.5, 65.5, 124.3, 127.0, 128.7, 129.5, 130.4, 130.7, 131.4, 135.0, 138.4, 154.0, 169.1, 184.5; HRMS (ESI) calcd for $C_{20}H_{21}O_5(M + H)^+$ 341.1389, found 341.1383.



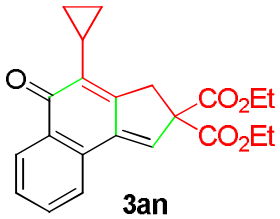
3al

Compound ***3al***.70% yield (67 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H), 1.33 (t, J = 7.1 Hz, 6H),1.38−1.46 (m, 2H), 1.49−1.56(m, 2H), 2.53−2.58 (m, 2H), 3.58 (s, 2H), 4.24−4.32 (m, 4H), 7.16 (s, 1H), 7.52−7.62 (m, 2H), 7.89 (d, J = 7.7 Hz, 1H), 8.23 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 22.9, 26.9, 30.6, 36.2, 62.4, 65.5, 124.3, 127.0, 129.5, 130.4, 130.9, 131.4, 133.3, 134.9, 138.6, 153.9, 169.1, 184.0; HRMS (ESI) calcd for $C_{23}H_{27}O_5$ $(M + H)^+$ 383.1858, found 383.1840.



3am

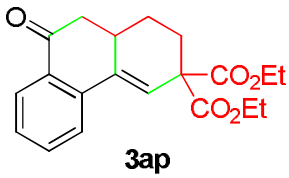
Compound ***3am***. 53% yield (49 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.31 (t, J = 7.1 Hz, 6H), 3.42 (s, 3H), 3.73 (s, 2H), 4.24− 4.30 (m, 4H), 4.52 (s, 2H), 7.26 (s, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.53−7.64 (m, 1H), 7.89 (d, J = 7.7 Hz, 1H), 8.24 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 36.4, 58.6, 62.5, 65.8, 66.3, 124.4, 127.2, 128.4, 129.7, 130.3, 130.6, 131.8, 137.2, 138.7, 158.0, 168.9, 183.5; HRMS (ESI) calcd for $C_{21}H_{23}O_6$ $(M + H)^+$ 371.1495, found 371.1486.



3an

Compound ***3an***. 35% yield (32 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.90−0.95 (m, 2H), 1.03−1.07 (m, 2H), 1.32 (t, J = 7.1 Hz, 6H), 1.65−1.71 (m, 1H), 3.68 (s, 2H), 4.24−4.32 (m, 4H), 7.13 (s, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 6.0, 10.5, 14.0, 36.5, 62.4, 65.5, 124.2, 126.8,

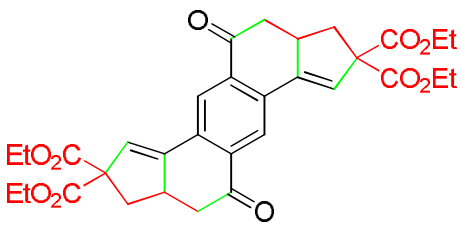
129.5, 130.1, 131.3, 131.3, 132.3, 134.5, 138.7, 154.9, 169.2, 184.3; HRMS (ESI) calcd for $C_{22}H_{22}O_5$ $(M + H)^+$ 367.1545, found 367.1537.



3ap

Compound ***3ap***. 81% yield (69 mg); white solid, mp 158–161°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27−1.34 (m, 6H), 1.61−1.69 (m, 1H), 1.88−1.94(m, 1H), 2.00−2.14 (m, 1H), 2.39−2.46(m, 1H), 2.52−2.56 (m, 1H), 2.80−2.89 (m, 2H), 4.16−4.32 (m, 4H), 6.69 (s, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.55−7.62 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 27.2, 27.2, 34.7, 45.4, 55.6, 61.8, 61.9, 121.8, 124.8, 126.9, 128.5, 131.3, 133.8, 138.0, 140.1, 170.0, 170.8, 197.0; HRMS (ESI) calcd for $C_{20}H_{23}O_5$ $(M + H)^+$ 343.1545, found 343.1542.

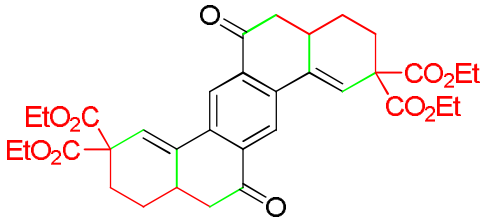
Crystal data for **3ap** ($C_{20}H_{22}O_5$, 342.38): triclinic, space group P–1, a = 8.1720(19) Å, b = 9.085(2) Å, c = 13.302(3) Å, U = 867.4(4) Å^3, Z = 2, T = 296(2) K, absorption coefficient mm^{-1}, reflections collected 5137, independent reflections 2385 [R(int) = 0.039], refinement by full-matrix least-squares on F^2, data/restraints/parameters 3166/13/238, goodness-of-fit on F^2 = 1.076, final R indices [I>2σ(I)] R_1 = 0.0687, wR_2 = 0.1835, R indices (all data) R_1 = 0.0787, wR_2 = 0.1891, largest diff. peak and hole 0.284 and –0.306e· Å^{-3}. Crystallographic data for the structure **3ap** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC1439850.



3sa

Compound ***3sa***. It was prepared from **1s** and **2a** in 47% yield (68 mg) using the general procedure except that 6 equivalents of K_2CO_3 was used; pale yellow solid, mp 59–61°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28−1.33 (m, 12H), 2.09−2.15 (m, 2H), 2.48−2.56 (m, 2H), 3.00−3.11 (m, 4H), 3.48−3.55 (m, 2H), 4.15−4.29 (m, 8H), 6.53 (dd, J = 2.3, 6.3 Hz, 2H), 8.32 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 14.4, 39.2, 39.2, 42.0, 42.0, 45.5, 45.6, 61.9, 61.9, 62.0, 62.0, 66.4,

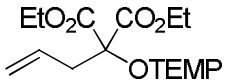
66.4, 124.4, 124.5, 125.0, 125.1, 133.9, 134.0, 135.0, 135.0, 142.4, 169.7, 169.7, 170.7, 170.7, 196.4, 196.4; HRMS (ESI) calcd for $C_{32}H_{35}O_{10}$ $(M + H)^+$ 579.2230, found 579.2249.



3sp

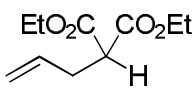
Compound ***3sp***. It was prepared from **1s** and **2p** in 38% yield (58 mg) using the general procedure except that 6 equivalents of K_2CO_3 was used; pale yellow solid, mp 66–68°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27−1.33 (m, 12H), 1.62−1.70 (m, 4H), 1.92−2.00 (m, 2H), 2.10−2.16 (m, 2H), 2.43−2.56 (m, 2H), 2.83−2.94 (m, 4H), 4.23 (d, J = 7.1 Hz, 2H), 4.30 (m, 6H), 6.75−2.86 (m, 2H), 8.42 (d, J = 5.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 14.4, 27.2, 27.2, 34.4, 34.4, 45.3, 45.4, 55.8, 55.9, 61.9, 61.9, 62.0, 62.3, 123.0, 123.1, 123.8, 123.9, 134.3, 134.3, 136.7, 136.9, 139.2, 139.4, 167.0, 167.0, 170.5, 170.5, 196.7, 196.7; HRMS (ESI) calcd for $C_{32}H_{39}O_{10}$ $(M + H)^+$ 607.2543, found 607.2540.

Experimental Procedure for the Synthesis of 4a from 1a and 2a:



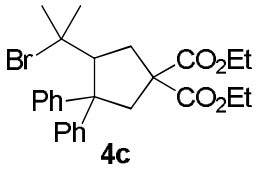
4a

*Compound **4a***. It was obtained from **1a** and **2a** under the reaction conditions in the presence of 2 equivalents of TEMPO in 51% yield (55 mg) as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.15 (d, J = 2.0 Hz, 6H), 1.21 (d, J = 1.9 Hz, 6H), 1.29 (td, J = 2.2, 7.1 Hz, 6H), 1.31−1.62 (m, 6H), 2.99 (d, J = 7.2 Hz, 2H), 4.16−4.25 (m, 4H), 5.05 (dd, J = 13.6, 22.2 Hz, 2H), 5.86−5.97 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.5, 13.5, 16.4, 20.2, 20.2, 32.7, 32.7, 38.3, 40.6, 40.6, 60.3, 60.6, 60.6, 88.1, 117.3, 132.8, 168.6; HRMS (ESI) calcd for $C_{19}H_{34}NO_5$ $(M + H)^+$ 356.2437, found 356.2433.



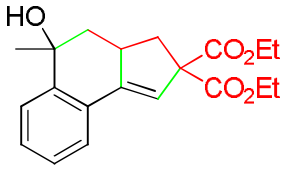
4b

Compound ***4b***[1]. It was obtained from **1a** and **2a** under the reaction conditions in the presence of 2 equivalents of BHT in 35% yield (18 mg) as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ1.27 (t, J = 7.1 Hz, 6H), 2.65 (t, J = 7.2 Hz, 2H), 3.43 (t, J = 7.6 Hz, 1H), 4.16−4.24 (m, 4H), 5.03−5.17 (m, 2H), 5.72−5.83 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 32.8, 51.6, 61.4, 117.5, 134.0, 168.9.



4c

Compound ***4c***. It was obtained from **1a** and **2b** under the reaction conditions in the presence of 2 equivalents of 1,1-diphenylethylene in 68% yield (83 mg) as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.78 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H), 1.25−1.32 (m, 6H), 2.05 (dd, J = 10.4, 13.3 Hz, 1H), 2.56 (dd, J = 7.6, 13.4 Hz, 1H), 2.95−3.01 (m, 2H), 3.21 (d, J = 14.7 Hz, 1H), 3.97 (q, J = 7.1 Hz, 2H), 4.23−4.33 (m, 2H), 7.08−7.38 (m, 10H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.9, 14.0, 23.9, 30.8, 37.8, 45.1, 50.5, 61.3, 61.4, 61.6, 62.7, 65.3, 123.0, 125.7, 126.6, 126.7, 127.0, 127.7, 128.0, 146.1, 148.8, 150.9, 171.3, 172.6; HRMS (ESI) calcd for $C_{26}H_{31}O_4$ $(M - Br)^+$ 407.2222, found 407.2222.

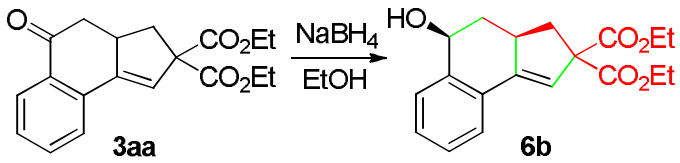


6a

Compound ***6a***. 62% yield (53 mg); colorless oil; dr = 68:32; ^{1}H NMR (600 MHz, $CDCl_3$) date of the major isomer δ 1.24−1.30 (m, 6H), 1.65 (s, 3H), 1.76 (m, 1H), 1.92−2.00 (m, 2H), 2.21−2.27 (m, 1H), 2.93−3.00 (m, 1H), 3.34−3.41 (m, 1H), 4.13−4.26 (m, 4H), 6.17−6.19 (d, J = 2.4 Hz, 1H), 7.25−7.34 (m, 2H), 7.55−7.59 (m, 1H), 7.62−7.66 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) date of the major isomer δ 14.0, 29.7, 38.5, 41.4, 45.2, 61.5, 65.8, 70.3, 119.6, 125.6, 126.2, 127.9, 129.1, 140.7, 146.3, 170.6, 171.6; HRMS (ESI) calcd for $C_{20}H_{25}O_5$ $(M + H)^+$ 345.1702, found 345.1697.

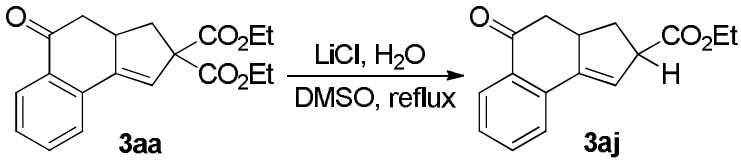
Experimental Procedure for the Preparation of 6b via Reduction of 3aa:

[1]K.-T. Yip, N.-Y. Zhu and D. Yang, *Org. Lett.*, 2009, **11**, 1911.



To a solution of **3aa** (164 mg, 0.5mmol) in 3 mL of EtOH was added $NaBH_4$ (28 mg, 0.75 mmol). After stirring at room temperature for 30 min, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:5) gave 145 mg of **6b** (yield: 88%) as a colorless oil; the stereochemistry of **6b** was determined by the NOE measurements. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25−1.32 (m, 6H), 1.48−1.56 (m, 1H), 1.96−2.07 (m, 2H), 2.46−2.50 (m, 1H), 2.96 (dd, J = 7.0, 12.8 Hz, 1H), 3.15−3.23 (m, 1H), 4.14−4.30 (m, 4H), 4.89−4.92 (m, 1H), 6.19 (d, J = 2.3 Hz, 1H), 7.24−7.29 (m, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.65 (dd, J = 7.7, 15.7 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.1, 39.0, 40.5, 41.6, 61.5, 61.6, 65.7, 69.5, 119.0, 125.0, 126.3, 127.4, 128.9, 129.3, 140.4, 145.9, 170.4, 171.5; HRMS (ESI) calcd for $C_{19}H_{22}NaO_5$ $(M + Na)^+$ 353.1365, found 353.1371.

Experimental Procedure for the Synthesis of 3aj from 3aa:[2]

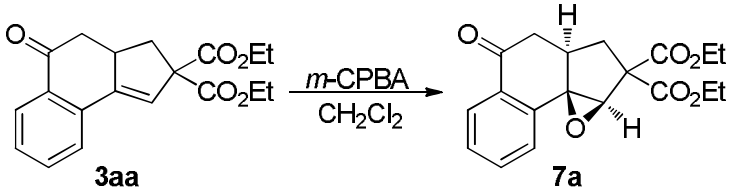


A mixture of **3aa** (164 mg, 0.5mmol), LiCl (63 mg, 1.5mmol), and H_2O (0.25 mL) in 1 mL of dimethyl sulfoxide was heated at reflux for 5 h. After cooling to room temperature, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:15) gave 103 mg of **3aj** (yield: 80%) as a colorless oil; dr = 54:46; ^{1}H NMR (600 MHz, $CDCl_3$) date of the major isomer δ 1.28−1.35 (m, 3H), 1.91−2.00 (m, 1H), 2.56 (dd, J = 13.8, 15.7 Hz, 1H), 2.62−2.69 (m, 1H), 3.00−3.05 (m, 1H), 3.32−3.39 (m, 1H), 3.79−3.84 (m, 1H), 4.20−4.26 (m, 2H), 6.32−6.36 (m, 1H), 7.40 (dd, J = 7.1, 14.3 Hz, 1H), 7.53−7.58 (m, 1H), 7.65−7.73 (m, 1H), 8.00−8.05 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) date of the major isomer δ 14.2, 34.6, 42.9, 46.0, 50.6, 61.0, 123.3, 125.0, 127.3, 128.5, 130.8, 133.6, 135.7, 141.6, 173.8, 197.6; HRMS (ESI)

[2]A. P. Krapcho, J. F. Weimaster, J. M. Eldridge, E. G. E. Jahngen, Jr., A. J. Lovey and W. P. Stephens, *J. Org. Chem.,*1978, **43**, 138.

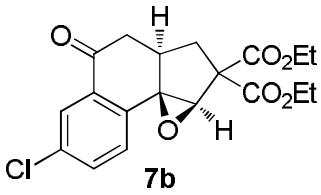
calcd for $C_{16}H_{17}O_3$ $(M + H)^+$ 257.1178, found 257.1174.

Experimental Procedure for the Epoxidation of Tricyclic Ketones:



3aa **7a**

To a mixture of **3aa** (164 mg, 0.5mmol) and $NaHCO_3$ (84 mg, 1.0 mmol) in 5 mL of DCM was added *m*-CPBA (172 mg, 1.0mmol) at 0°C. After stirring at 25°C for 24 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:15) gave 141 mg of **7a** (yield: 82%) as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.95−2.00 (m, 1H), 2.36−2.40 (m, 1H), 2.75−2.84 (m, 2H), 2.90−2.98 (m, 1H), 4.19−4.35 (m, 4H), 4.74 (s, 1H), 7.24−7.29 (m, 1H), 7.50−7.62 (m, 2H), 8.05−8.13 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.0, 14.0, 32.5, 36.2, 40.3, 60.9, 62.0, 62.1, 63.4, 64.9, 125.8, 127.9, 129.7, 134.0, 134.8, 135.7, 168.4, 168.8, 196.2; HRMS (ESI) calcd for $C_{19}H_{21}O_6$ $(M + H)^+$ 345.1338, found 345.1333.



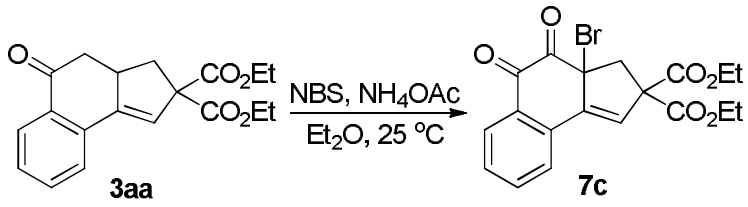
7b

Compound ***7b***. 76% yield (144 mg); white solid, mp 83–85°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.94−2.00 (m, 1H), 2.35−2.41 (m, 1H), 2.73−2.82 (m, 2H), 2.90−3.00 (m, 1H), 4.19−4.37 (m, 4H), 4.71 (s, 1H), 7.21 (d, J = 8.2 Hz, 1H), 7.56 (dd, J = 2.2, 8.2 Hz, 1H), 8.07 (d, J = 2.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.9, 14.0, 32.3, 36.0, 40.1, 60.8, 62.1, 62.1, 63.5, 64.3, 127.5, 127.9, 134.0, 134.0, 136.1, 136.3, 168.2, 168.7, 194.8; HRMS (ESI) calcd for $C_{19}H_{20}ClO_6$ $(M + H)^+$ 379.0948, found 379.0952.

Crystal data for **7b** ($C_{19}H_{19}ClO_6$, 378.79): triclinic, space group P–1, a = 9.9793(12) Å, b = 11.9540(15) Å, c = 15.515(2) Å, U = 1814.8(4) Å^3, Z = 4, T = 296(2) K, absorption coefficient 0.243mm^{-1}, reflections collected 8218, independent reflections 4660 [R(int) = 0.0639], refinement by full-matrix least-squares on F^2, data/restraints/parameters 8218/26/470, goodness-of-fit on F^2 =

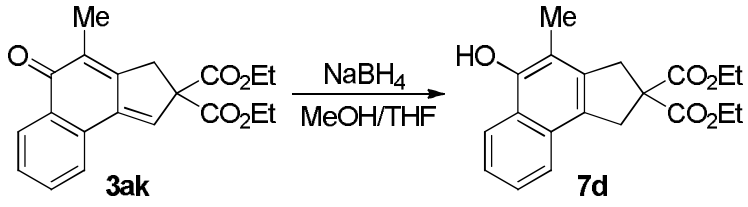
1.017, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0720$, $wR_2 = 0.1765$, R indices (all data) $R_1 = 0.1273$, $wR_2 = 0.2177$, largest diff. peak and hole 0.870 and –0.352 e·Å^{-3}. Crystallographic data for the structure **7b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC1439851.

Experimental Procedure for the Synthesis of α-BromoDiketone 7c:[3]



To a solution of **3aa** (82 mg, 0.25 mmol) in 1 mL of Et_2O was added NBS (445 mg, 2.5 mmol) and NH_4OAc (19 mg, 0.25 mmol). After stirring at room temperature for 1.5 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:15) gave 80 mg of **7c** (yield: 76%) as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.24−1.28 (m, 3H), 1.34−1.38 (m, 3H), 3.30 (d, J = 18.2 Hz, 1H), 3.72 (d, J = 18.2 Hz, 1H), 4.11−4.38 (m, 4H), 5.95 (s, 1H), 7.56 (t, J = 6.2 Hz, 2H), 7.73 (t, J = 7.1 Hz, 1H), 8.11−8.15 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 13.8, 14.0, 34.7, 51.8, 62.6, 62.9, 64.7, 126.6, 130.1, 130.8, 131.0, 131.4, 135.6, 135.7, 153.8, 166.2, 168.7, 178.2, 179.1; HRMS (ESI) calcd for $C_{19}H_{18}BrO_6$ $(M + H)^+$ 421.0287, found 421.0274.

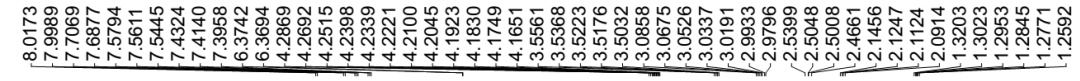
Experimental Procedure for the Preparation of 1-Naphthol 7d via Reduction of 3ak:



To a solution of **3ak** (170 mg, 0.5mmol) in 2 mL of MeOH/THF (v/v = 1:1) was added $NaBH_4$ (23 mg, 0.6 mmol). After stirring at 25°C for 30 min, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated.

[3]K. Tanemura, T. Suzuki, Y. Nishida, K. Satsumabayashi and T. Horaguchi, *Chem. Commun.,*2004, 470.

Column chromatography on silica gel (EtOAc/petroleum ether = 1:10) gave 154 mg of **7d** (yield: 92%) as a colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.1 Hz, 6H), 2.28 (s, 3H), 3.69 (s, 2H), 3.89 (s, 2H), 4.24 (q, J = 7.1 Hz, 4H), 5.23 (br,s, 1H), 7.40−7.46 (m, 2H), 7.66 (d, J = 7.6 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 12.3, 14.0, 39.2, 40.8, 59.6, 61.8, 113.5, 121.7, 123.9, 124.0, 124.5, 125.7, 126.8, 128.8, 137.5, 148.2, 172.0; HRMS (ESI) calcd for $C_{20}H_{23}O_5$ $(M + H)^+$ 343.1545, found 343.1535.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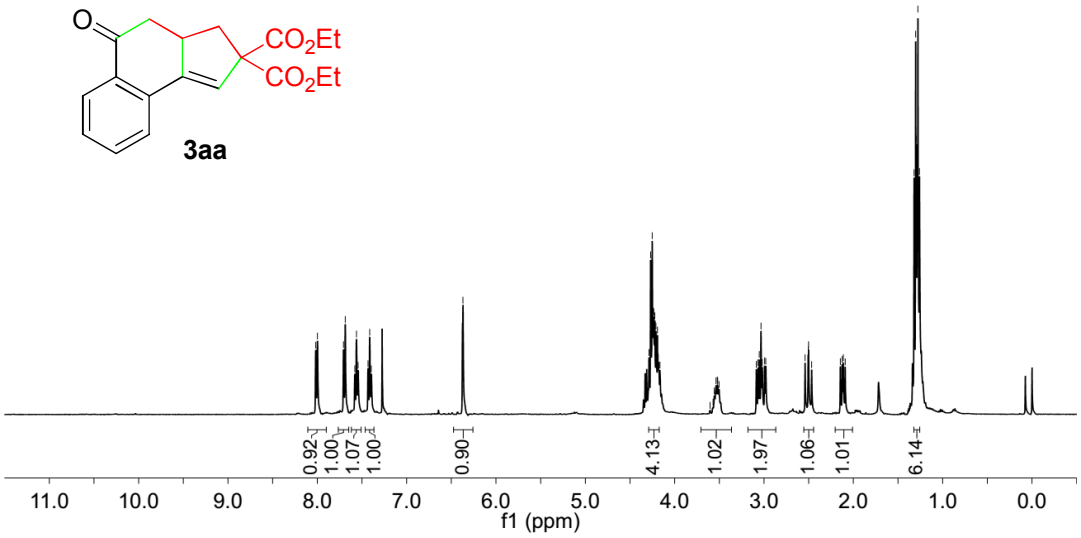
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f1 (ppm)


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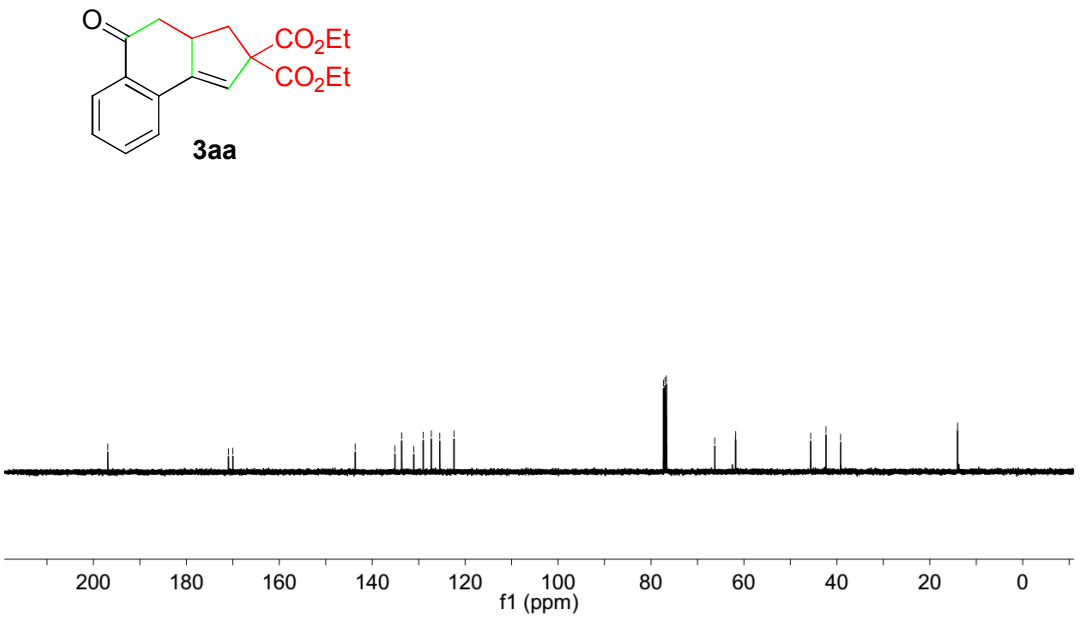
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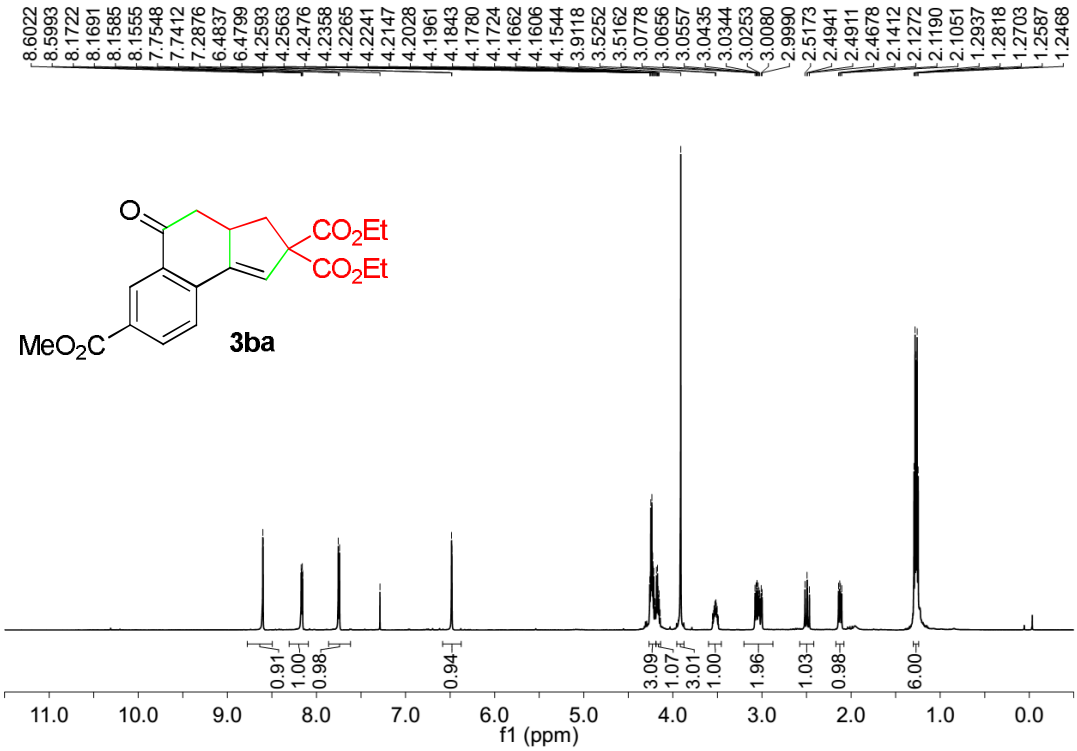
f1 (ppm)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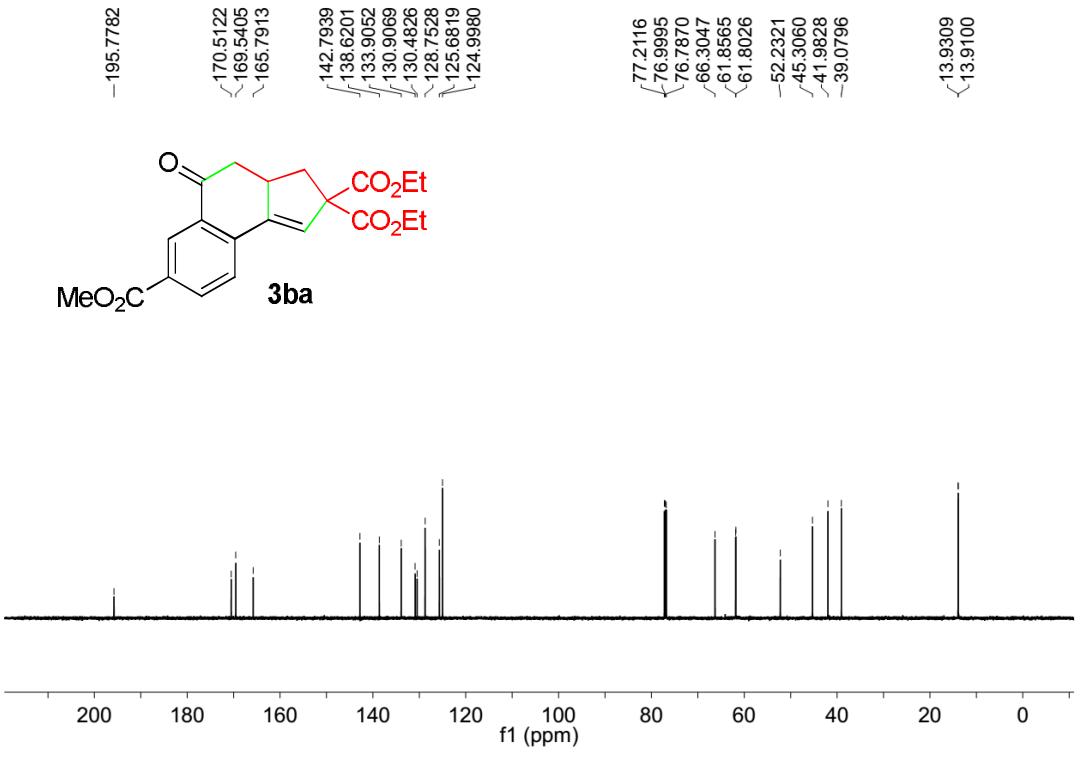
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3.5490
3.5453
3.1123
3.1000
3.0901
3.0845
3.0775
3.0580
3.0489
2.5526
2.5294
2.5262
2.5029
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2.1434
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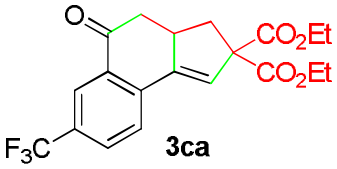
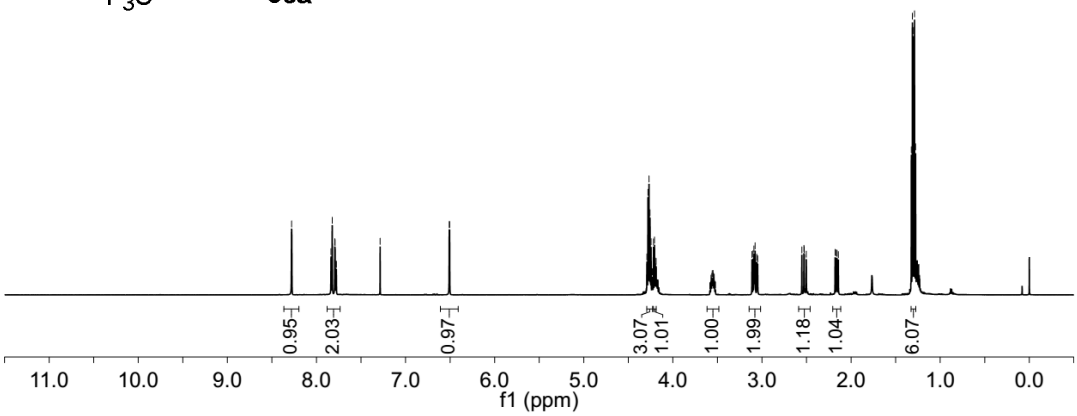
1.2881
1.2763


O
CO2Et
CO2Et
F3C

3ca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6.07
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


195.4856
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169.6100
142.3924
137.9968
131.1806
131.1310
130.9103
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129.7865
129.7627
126.2970
126.1747
125.1886
124.7087
124.6829
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124.3690
122.5637
77.2115
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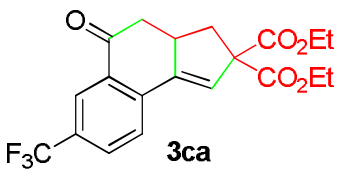
39.1037
13.9993
13.9791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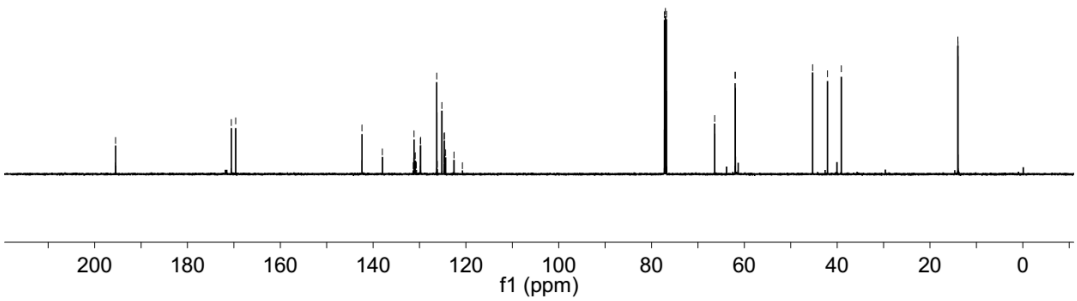
CO2Et
F3C

3ca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20
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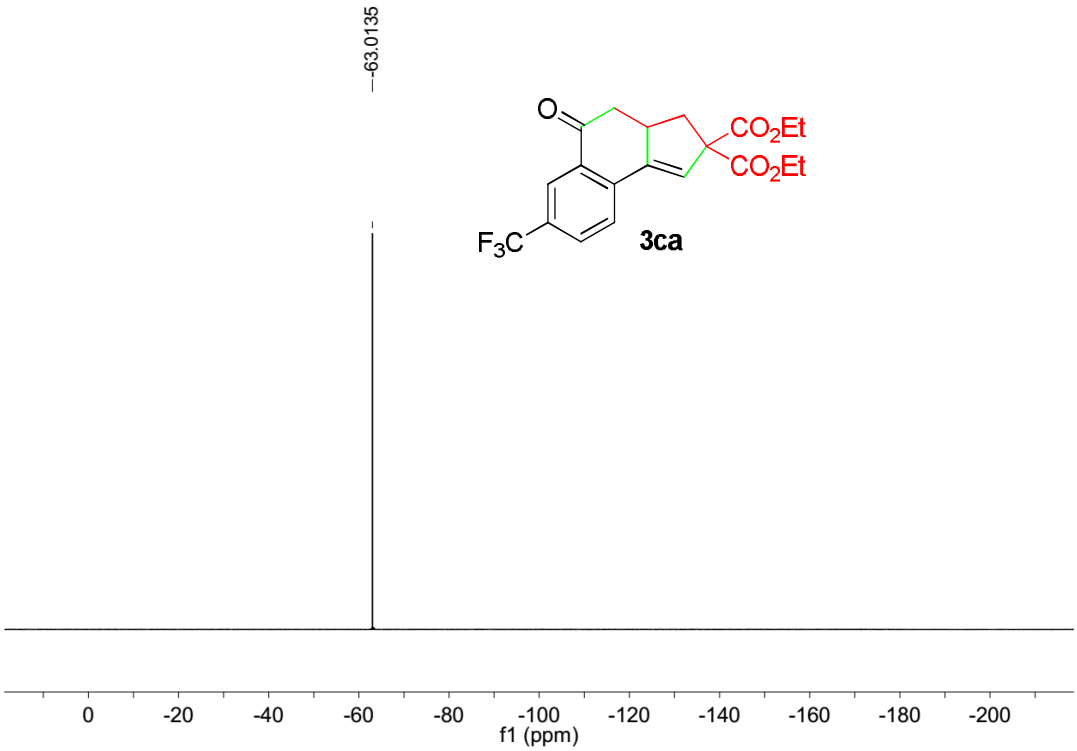
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CO2Et
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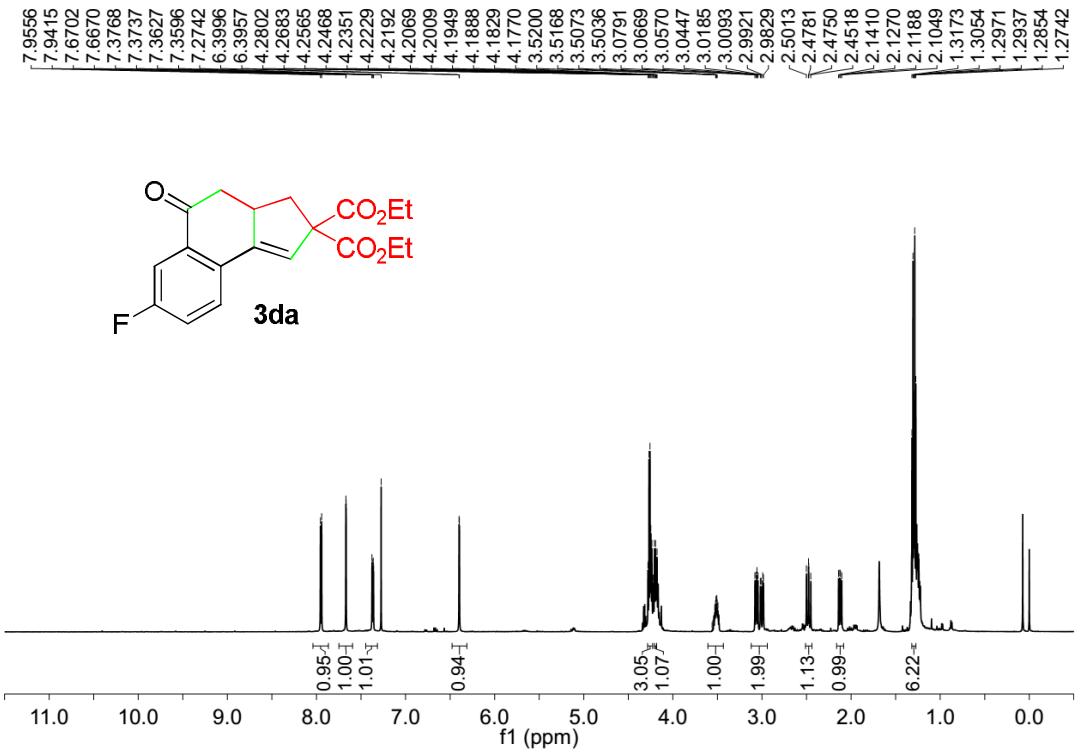
-160
-180
-200
f1 (ppm)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7.3627
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6.3957
4.2802
4.2683
4.2565
4.2468
4.2351
4.2229
4.2192
4.2069
4.2009
4.1949
4.1888
4.1829
4.1770
3.5200
3.5168
3.5073
3.5036
3.0791
3.0669
3.0570
3.0447
3.0185
3.0093
2.9921
2.9829
2.5013
2.4781
2.4750
2.4518
2.1410
2.1270
2.1188
2.1049
1.3173
1.3054
1.2971
1.2937
1.2854
1.2742
O
CO2Et
CO2Et
F
3da
0.95
1.00
1.01
0.94
3.05
1.07
1.00
1.99
1.13
0.99
6.22
11.0
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5.0
4.0
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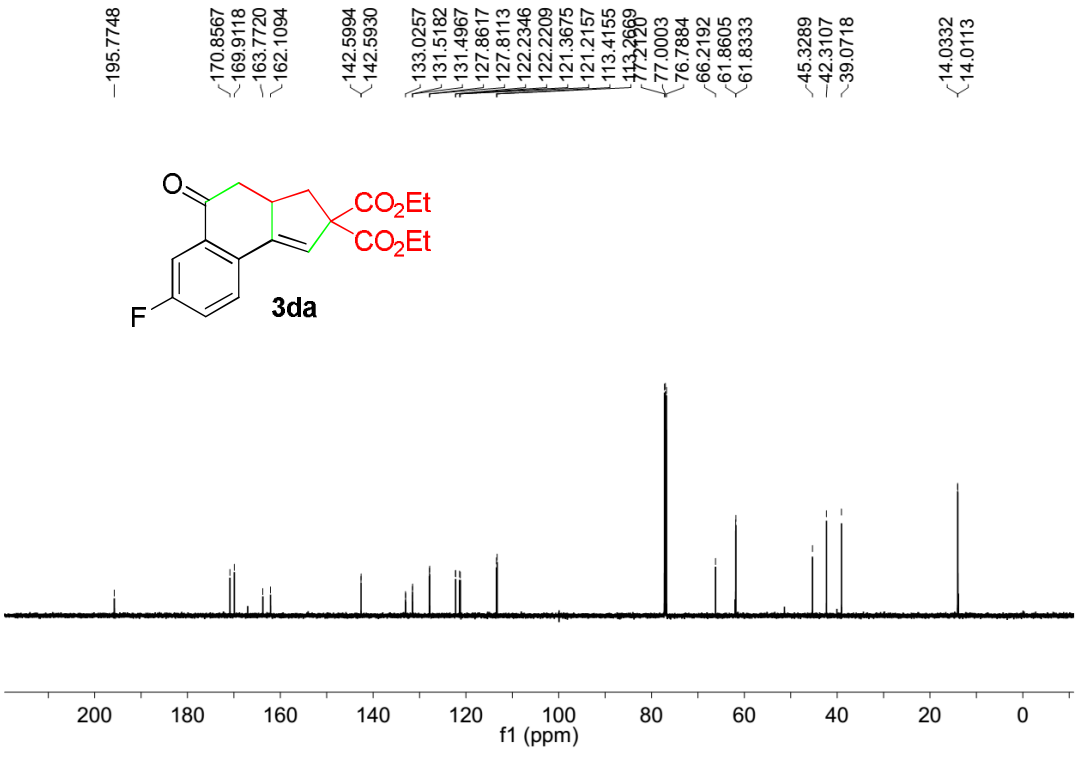
f1 (ppm)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127.8113
122.2346
122.2209
121.3675
121.2157
113.4155
113.2669
77.2120
77.0003
76.7884
66.2192
61.8605
61.8333
45.3289
42.3107
39.0718
14.0332
14.0113
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CO2Et
CO2Et
F
3da
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180
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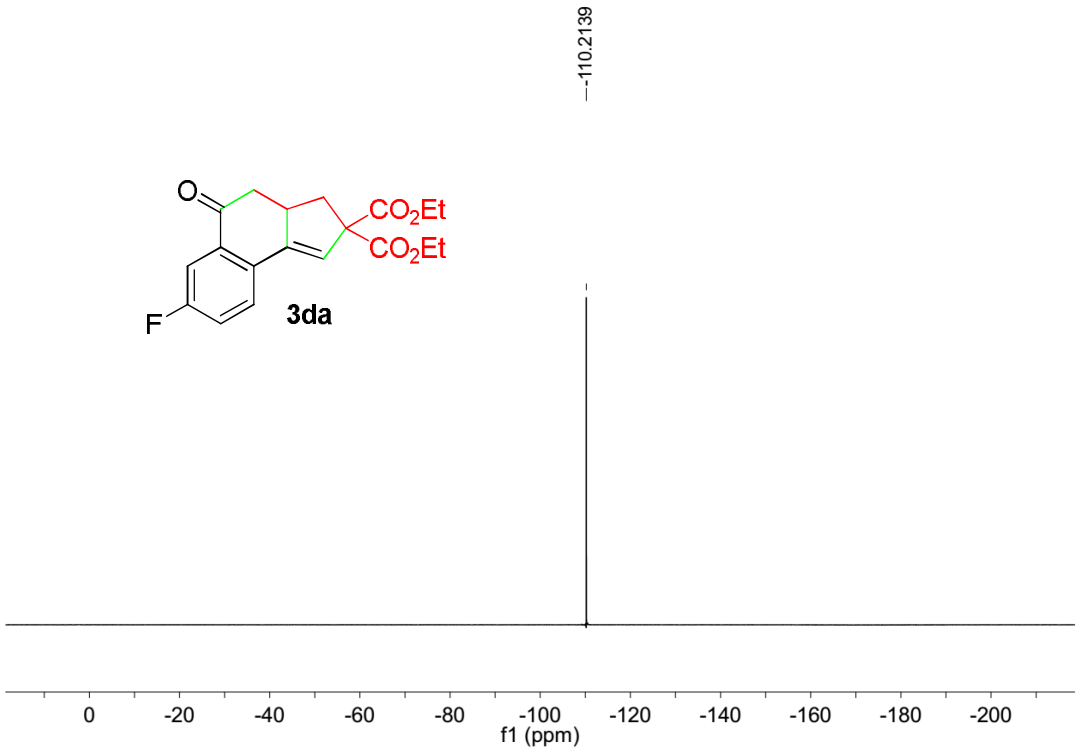
140
120
100
80
60
40
20
0
f1 (ppm)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CO2Et
F
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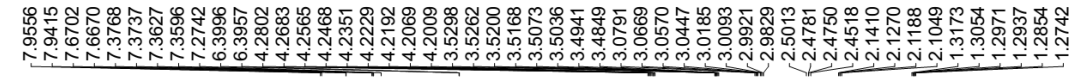
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)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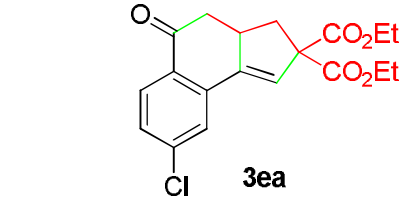
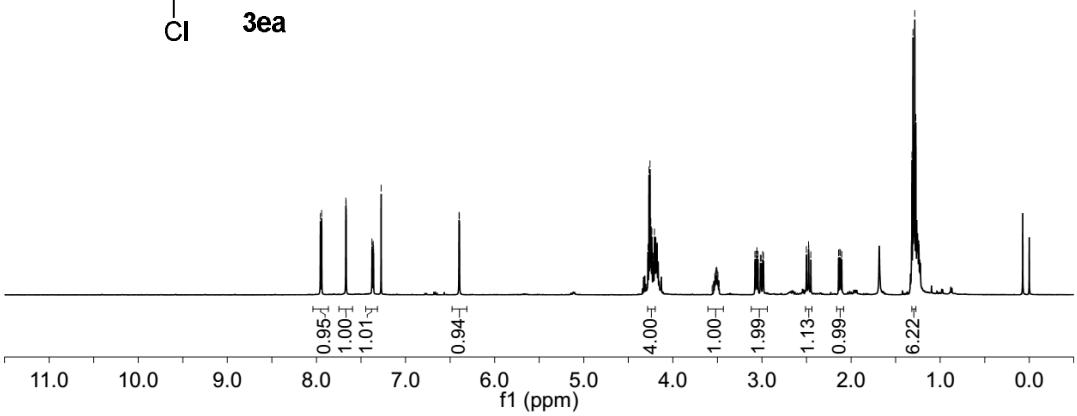
7.3737
7.3627
7.3596
7.2742
6.3996
6.3957
4.2802
4.2683
4.2565
4.2468
4.2351
4.2229
4.2192
4.2069
4.2009
3.5298
3.5262
3.5200
3.5168
3.5073
3.5036
3.4941
3.4849
3.0791
3.0669
3.0570
3.0447
3.0185
3.0093
2.9921
2.9829
2.5013
2.4781
2.4750
2.4518
2.1410
2.1270
2.1188
2.1049
1.3173
1.3054
1.2971
1.2937
1.2854
1.2742


O
CO2Et
CO2Et
Cl

3ea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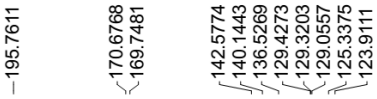
1.01
0.94
4.00
1.00
1.99
1.13
0.99
6.22
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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129.4273
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125.3375
123.9111
77.2115
76.9996
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66.3179
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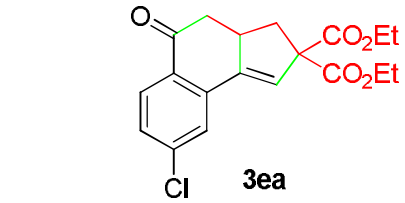
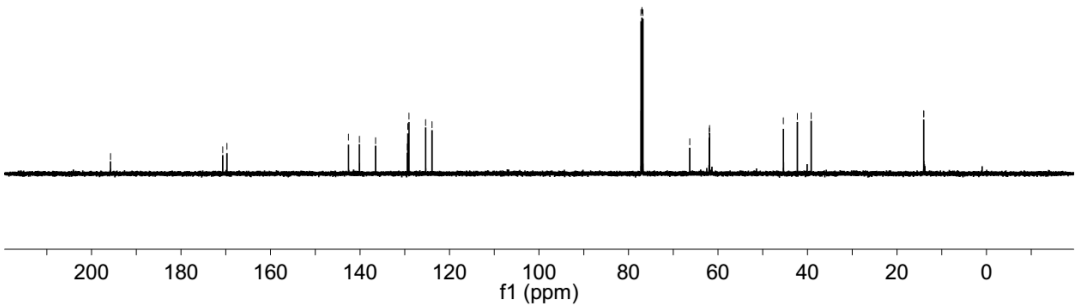
42.2656
39.1820
14.0393
14.0214


O
CO2Et
CO2Et
Cl

3ea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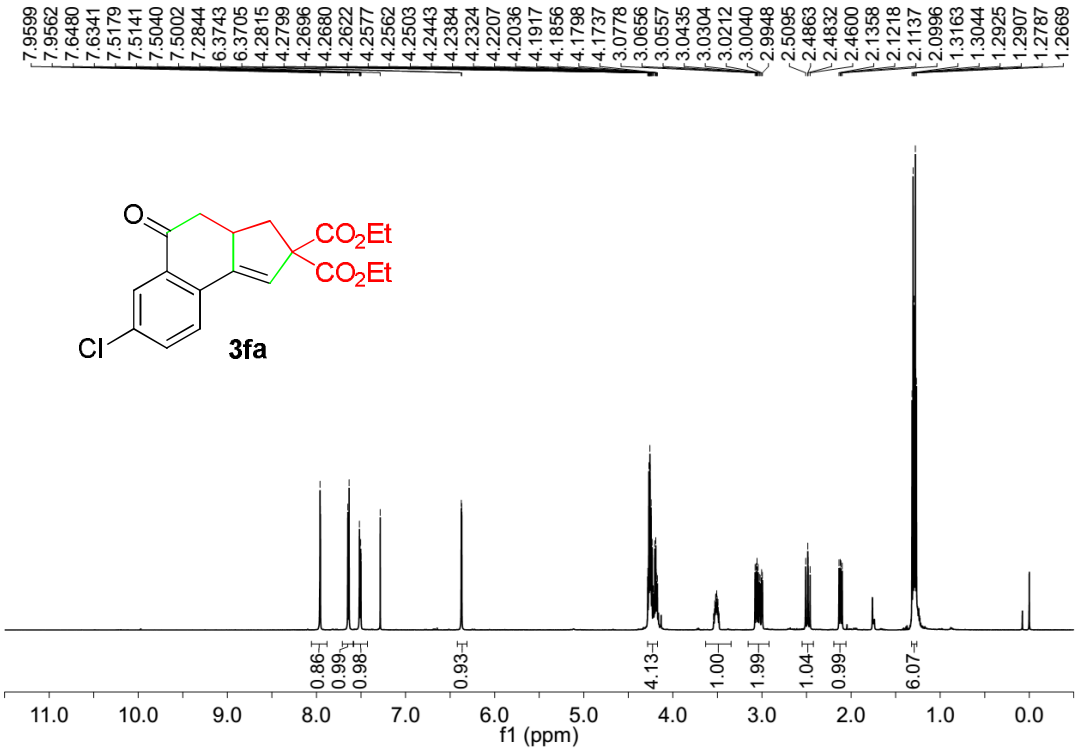
120
100
80
60
40
20
0
f1 (ppm)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7.5179
7.5141
7.5040
7.5002
7.2844
6.3743
6.3705
4.2815
4.2799
4.2696
4.2680
4.2622
4.2577
4.2562
4.2503
4.2443
4.2384
4.2324
4.2207
4.2036
4.1917
4.1856
4.1798
4.1737
3.0778
3.0656
3.0557
3.0435
3.0304
3.0212
3.0040
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2.5095
2.4863
2.4832
2.4600
2.1358
2.1218
2.1137
2.0996
1.3163
1.3044
1.2925
1.2907
1.2787
1.2669
O
CO2Et
CO2Et
Cl
3fa
0.86
0.99
0.98
0.93
4.13
1.00
1.99
1.04
0.99
6.07
11.0
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9.0
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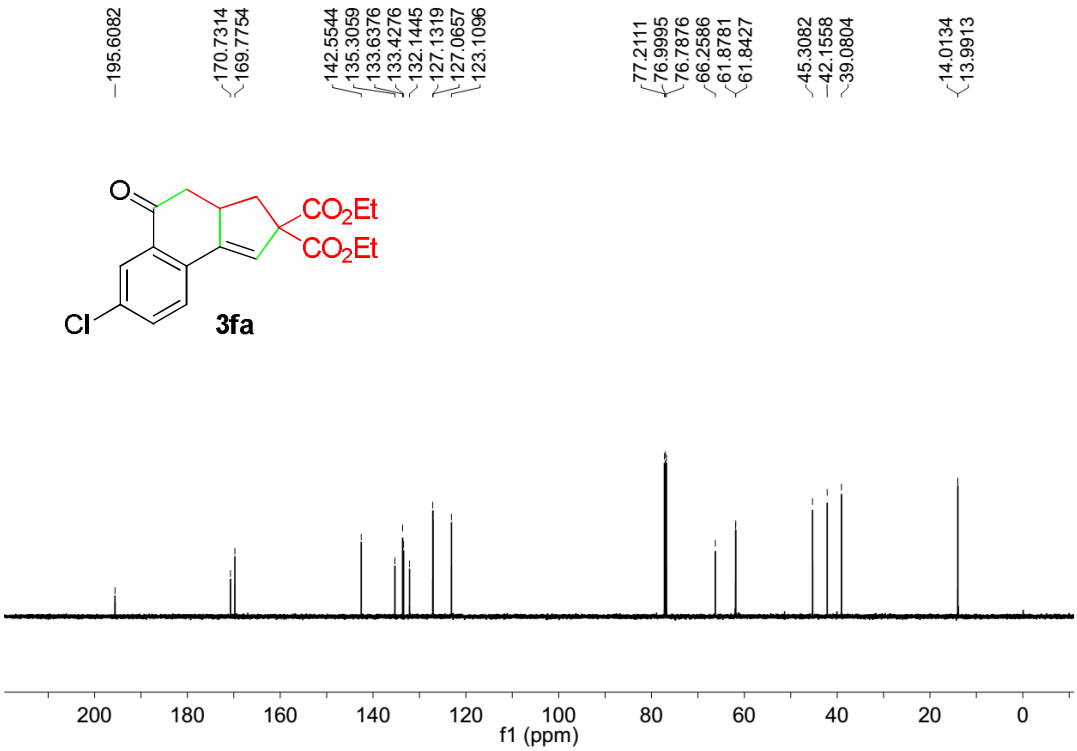
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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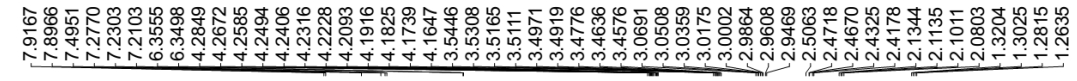
132.1445
127.1319
127.0657
123.1096
77.2111
76.9995
76.7876
66.2586
61.8781
61.8427
45.3082
42.1558
39.0804
14.0134
13.9913
O
CO2Et
CO2Et
Cl
3fa
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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4.2585
4.2494
4.2406
4.2316
4.2228
4.2093
4.1916
4.1825
4.1739
4.1647
3.5446
3.5308
3.5165
3.5111
3.4971
3.4919
3.4776
3.4636
3.4576
3.0691
3.0508
3.0359
3.0175
3.0002
2.9864
2.9608
2.9469
2.5063
2.4718
2.4670
2.4325
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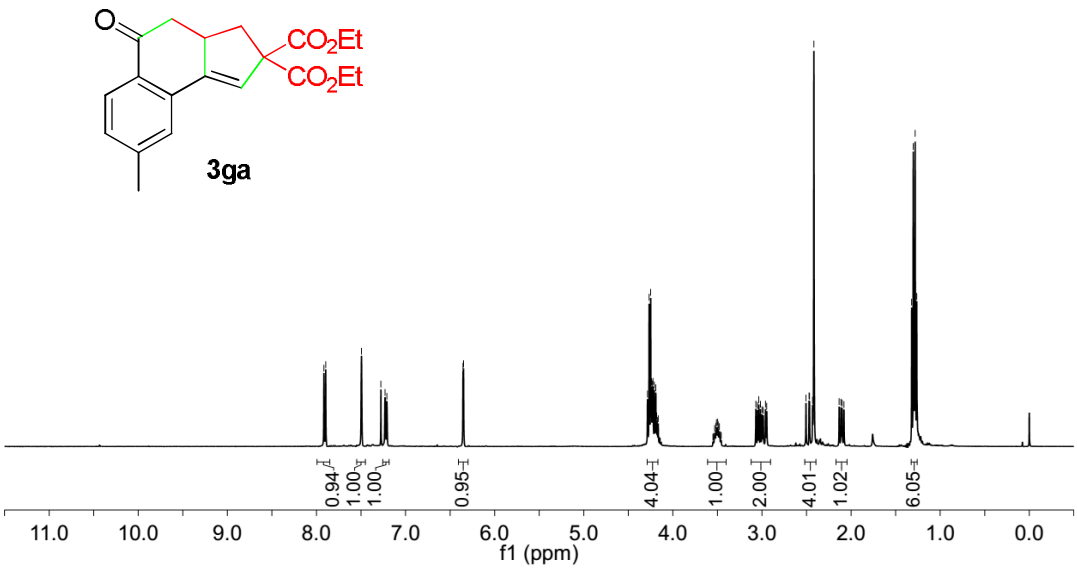
2.1344
2.1135
2.1011
2.0803
1.3204
1.3025
1.2815
1.2635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CO2Et
3ga
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1.00
0.95
4.04
1.00
2.00
4.01
1.02
6.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


196.6786
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144.4835
143.8314
135.0732
130.1035
128.8886
127.3742
125.6854
122.0638
77.3171
76.9996
76.6818
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45.6264
42.4006
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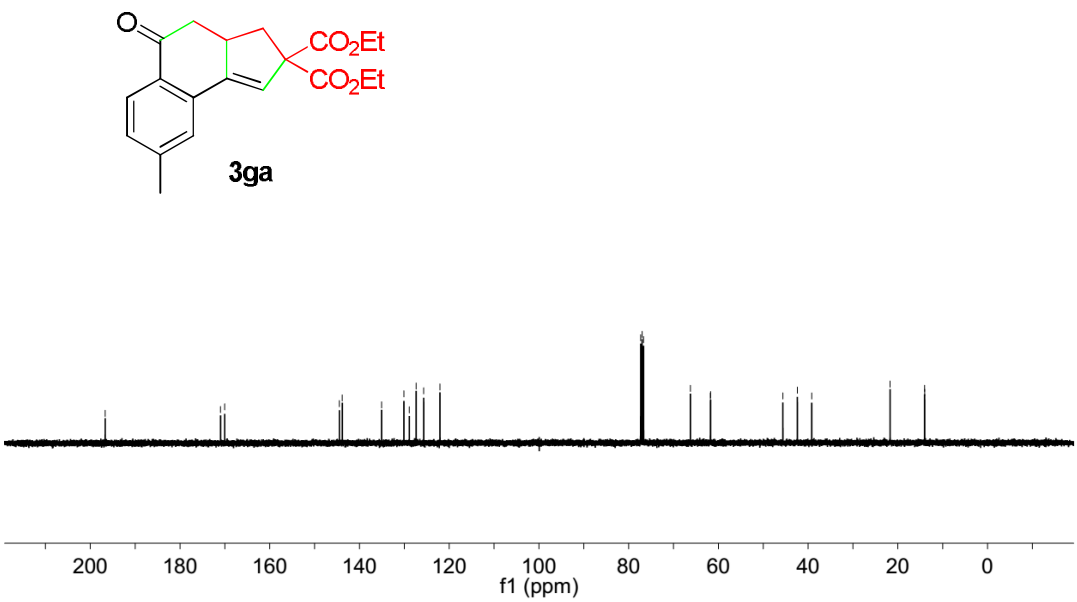
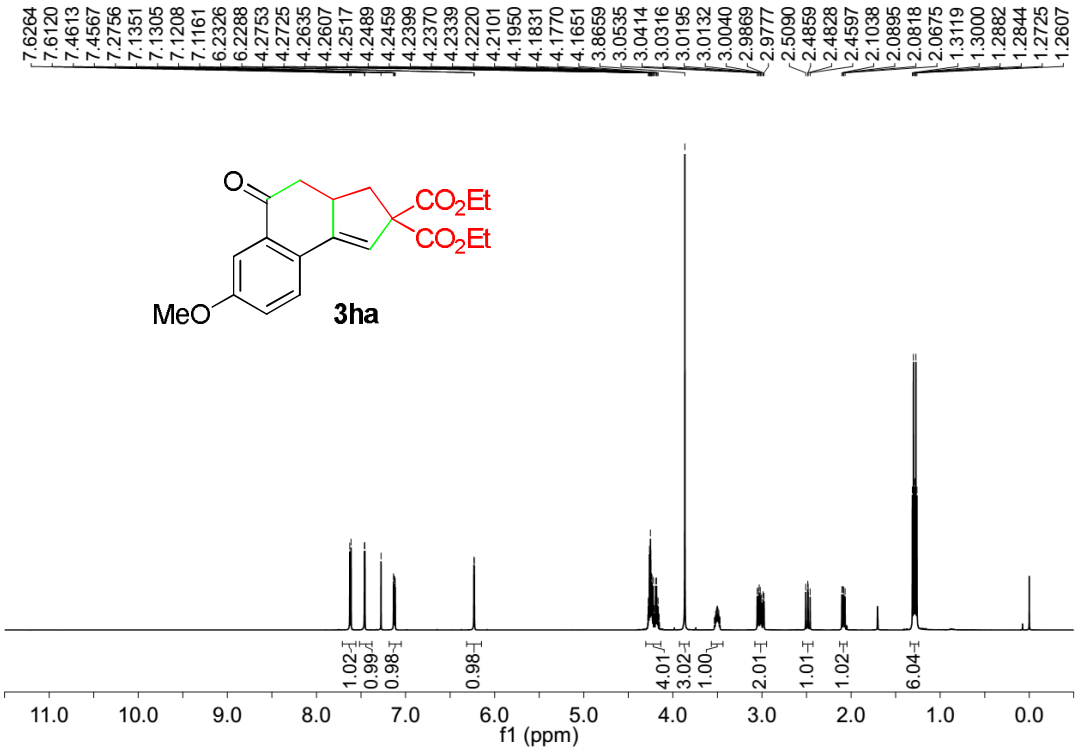
21.7265
14.0315
14.0139


O
CO2Et
CO2Et
3ga
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.1305
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7.1161
6.2326
6.2288
4.2753
4.2725
4.2635
4.2607
4.2517
4.2489
4.2459
4.2399
4.2370
4.2339
4.2220
4.2101
4.1950
4.1831
4.1770
4.1651
3.8659
3.0535
3.0414
3.0316
3.0195
3.0132
3.0040
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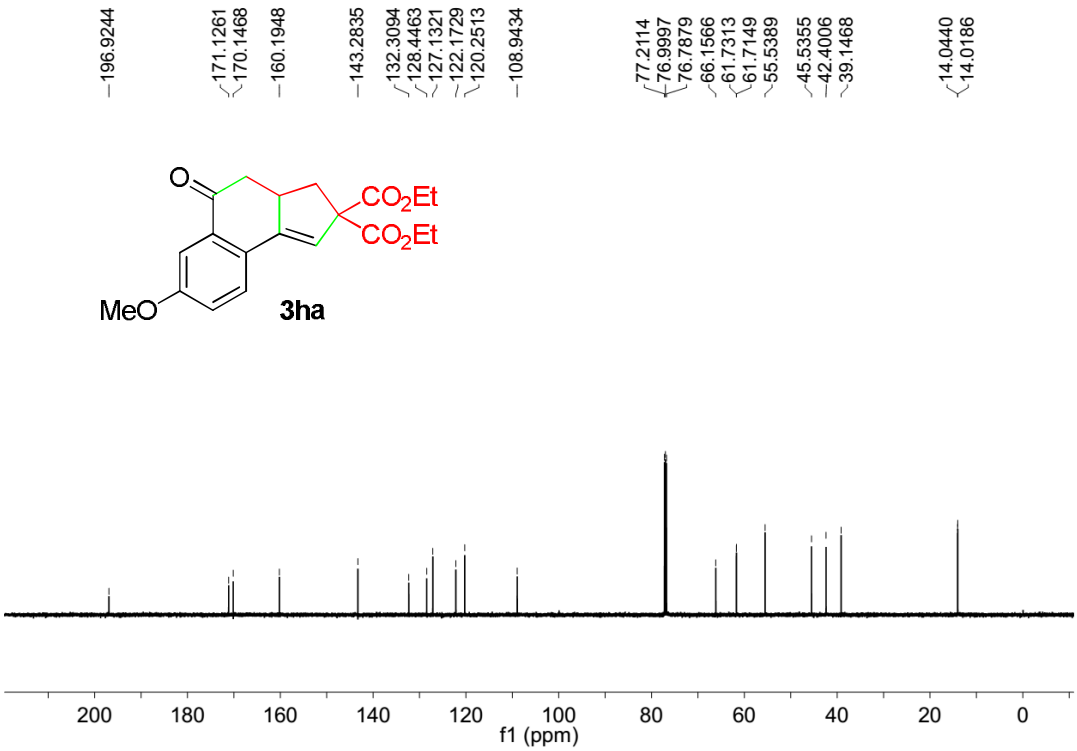
2.9777
2.5090
2.4859
2.4828
2.4597
2.1038
2.0895
2.0818
2.0675
1.3119
1.3000
1.2882
1.2844
1.2725
1.2607
O
CO2Et
CO2Et
MeO
3ha
1.02
0.99
0.98
0.98
4.01
3.02
1.00
2.01
1.01
1.02
6.04
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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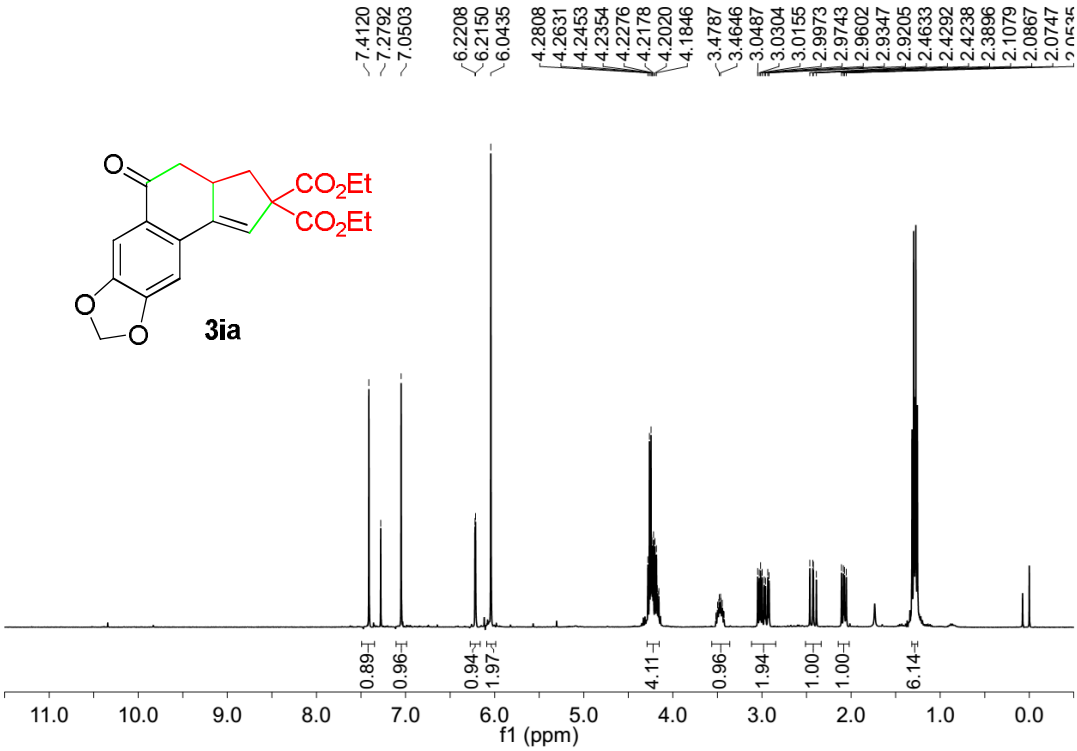
122.1729
120.2513
108.9434
77.2114
76.9997
76.7879
66.1566
61.7313
61.7149
55.5389
45.5355
42.4006
39.1468
14.0440
14.0186
O
CO2Et
CO2Et
MeO
3ha
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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6.0435
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4.2276
4.2178
4.2020
4.1846
3.4787
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3.0487
3.0304
3.0155
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2.9205
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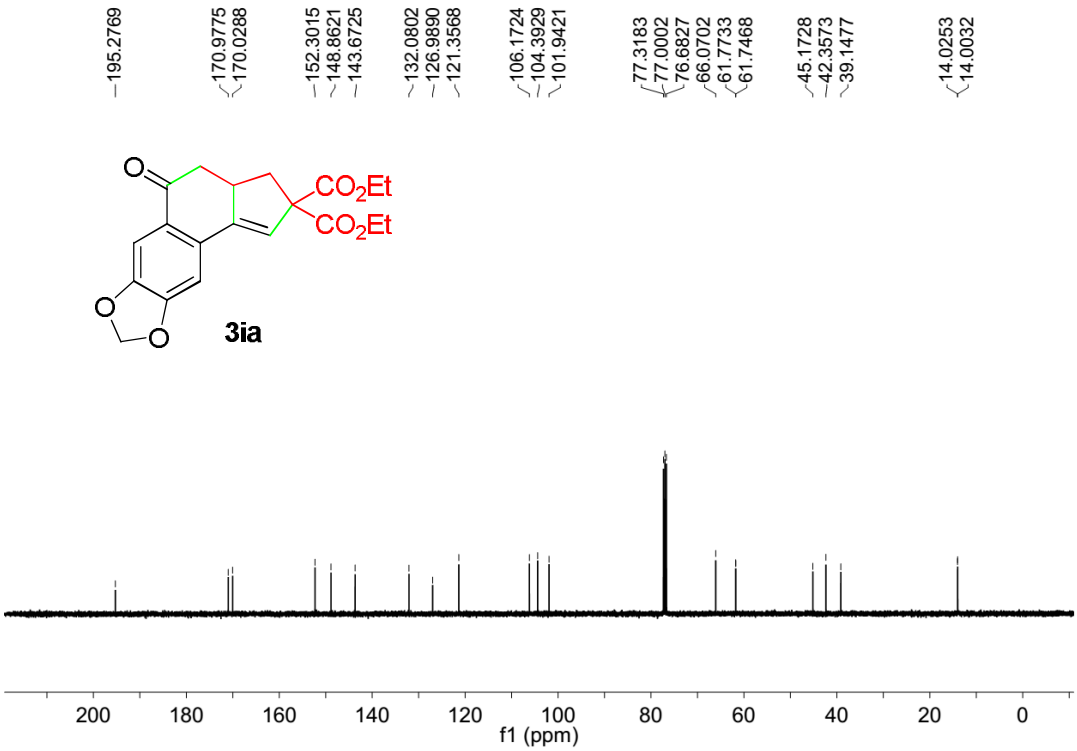
2.4292
2.4238
2.3896
2.1079
2.0867
2.0747
CO2Et
CO2Et
3ia
0.89
0.96
0.94
1.97
4.11
0.96
1.94
1.00
1.00
6.14
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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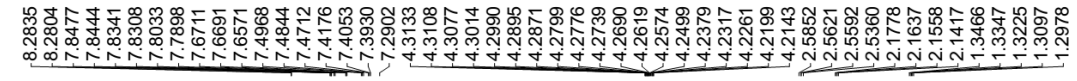
132.0802
126.9890
121.3568
106.1724
104.3929
101.9421
77.3183
77.0002
76.6827
66.0702
61.7733
61.7468
45.1728
42.3573
39.1477
14.0253
14.0032
CO2Et
CO2Et
3ia
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.8033
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7.6571
7.4968
7.4844
7.4712
7.4176
7.4053
7.3930
7.2902
4.3133
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4.3077
4.3014
4.2990
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4.2871
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4.2776
4.2739
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4.2619
4.2574
4.2499
4.2379
4.2317
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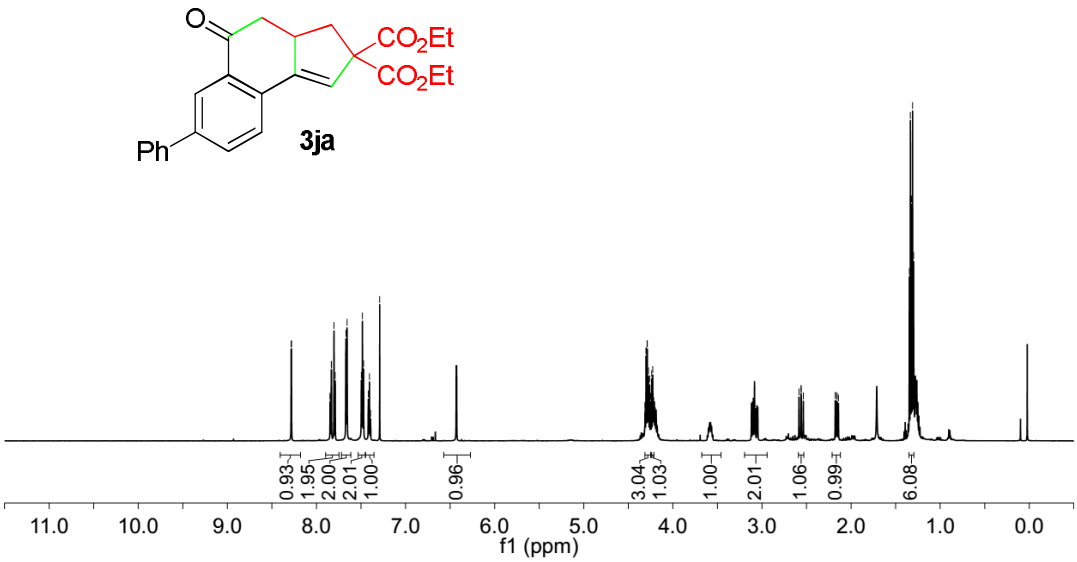
1.3347
1.3225
1.3097
1.2978


O
CO2Et
CO2Et
Ph
3ja
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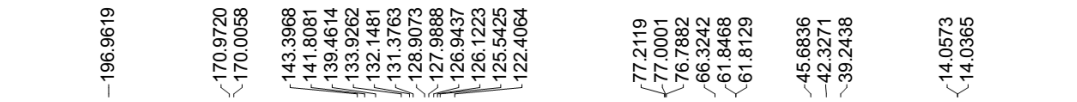
1.95
2.00
2.01
1.00
0.96
3.04
1.03
1.00
2.01
1.06
0.99
6.08
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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14.0365


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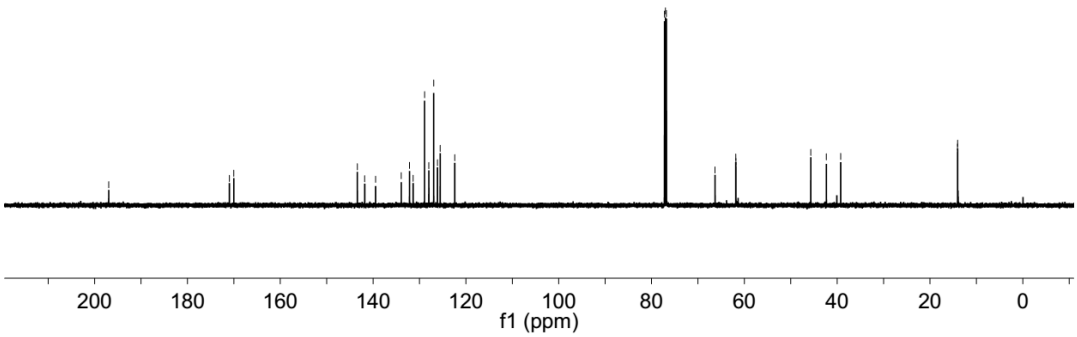
CO2Et
Ph
3ja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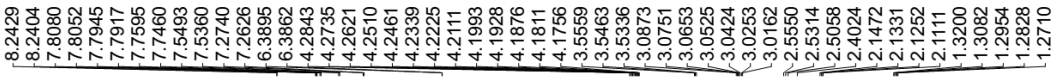
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3.5559
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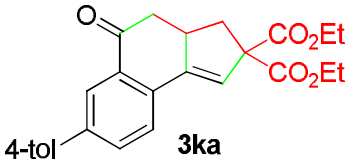
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CO2Et
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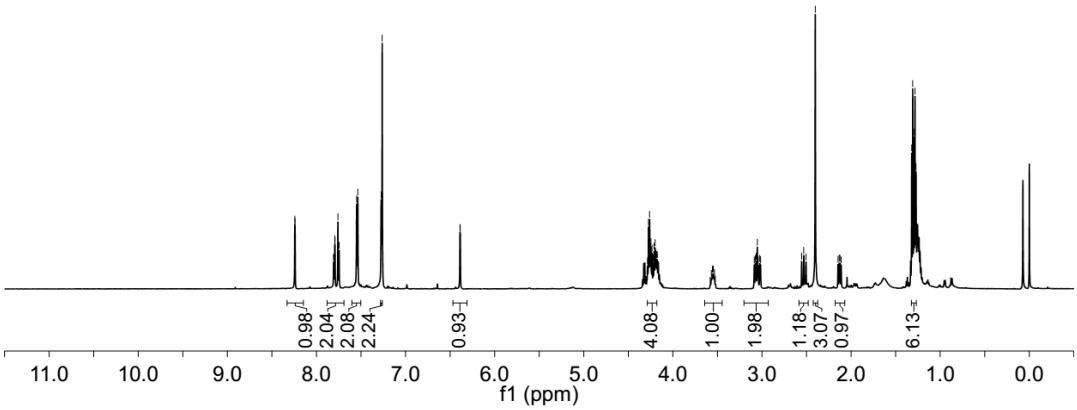
3ka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5.0
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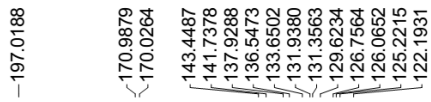
f1 (ppm)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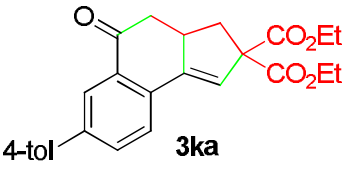
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CO2Et
4-tol
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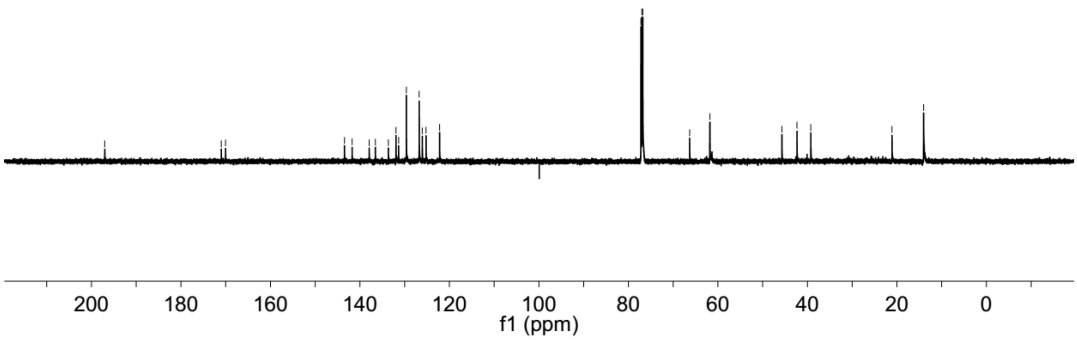
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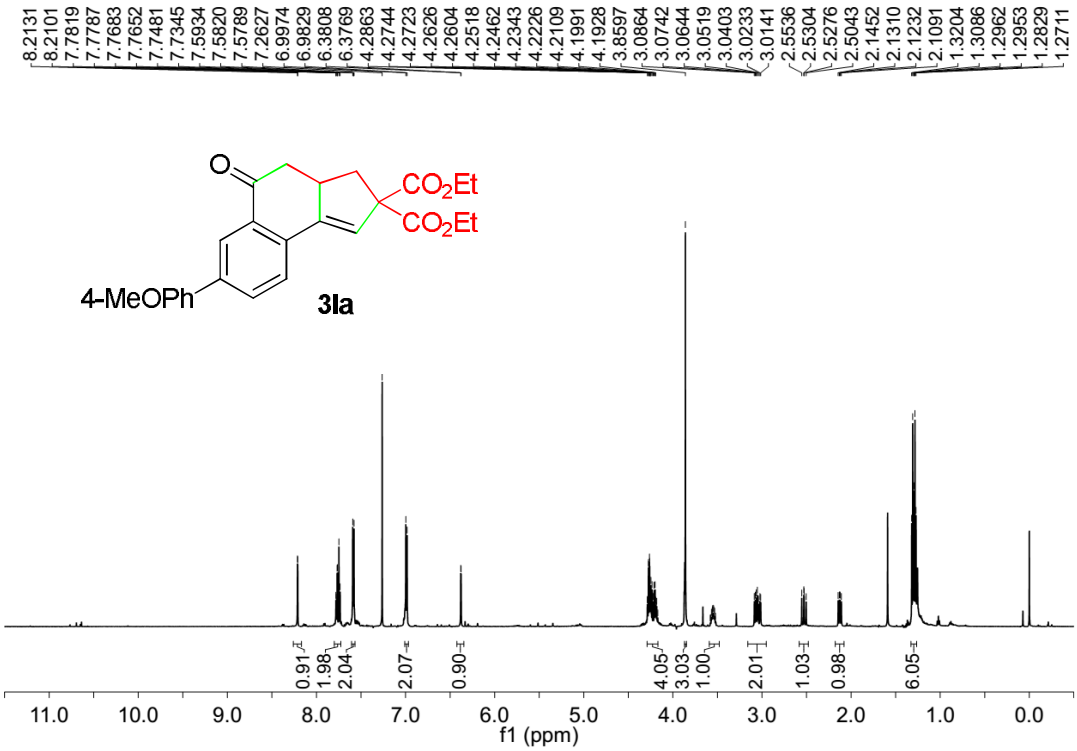
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7.2627
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6.9829
6.3808
6.3769
4.2863
4.2744
4.2723
4.2626
4.2604
4.2518
4.2462
4.2343
4.2226
4.2109
4.1991
4.1928
3.8597
3.0864
3.0742
3.0644
3.0519
3.0403
3.0233
3.0141
2.5536
2.5304
2.5276
2.5043
2.1452
2.1310
2.1232
2.1091
1.3204
1.3086
1.2962
1.2953
1.2829
1.2711
CO2Et
CO2Et
4-MeOPh
3la
0.91
1.98
2.04
2.07
0.90
4.05
3.03
1.00
2.01
1.03
0.98
6.05
11.0
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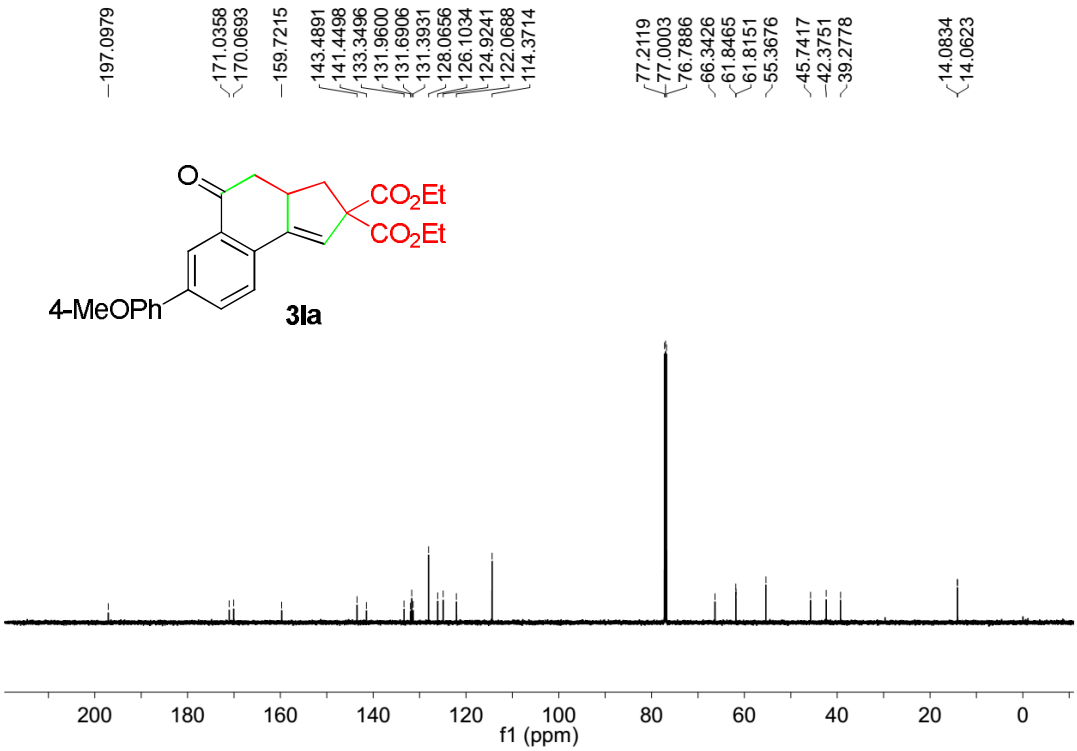
0.0
f1 (ppm)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77.0003
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61.8465
61.8151
55.3676
45.7417
42.3751
39.2778
14.0834
14.0623
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CO2Et
4-MeOPh
3la
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100
80
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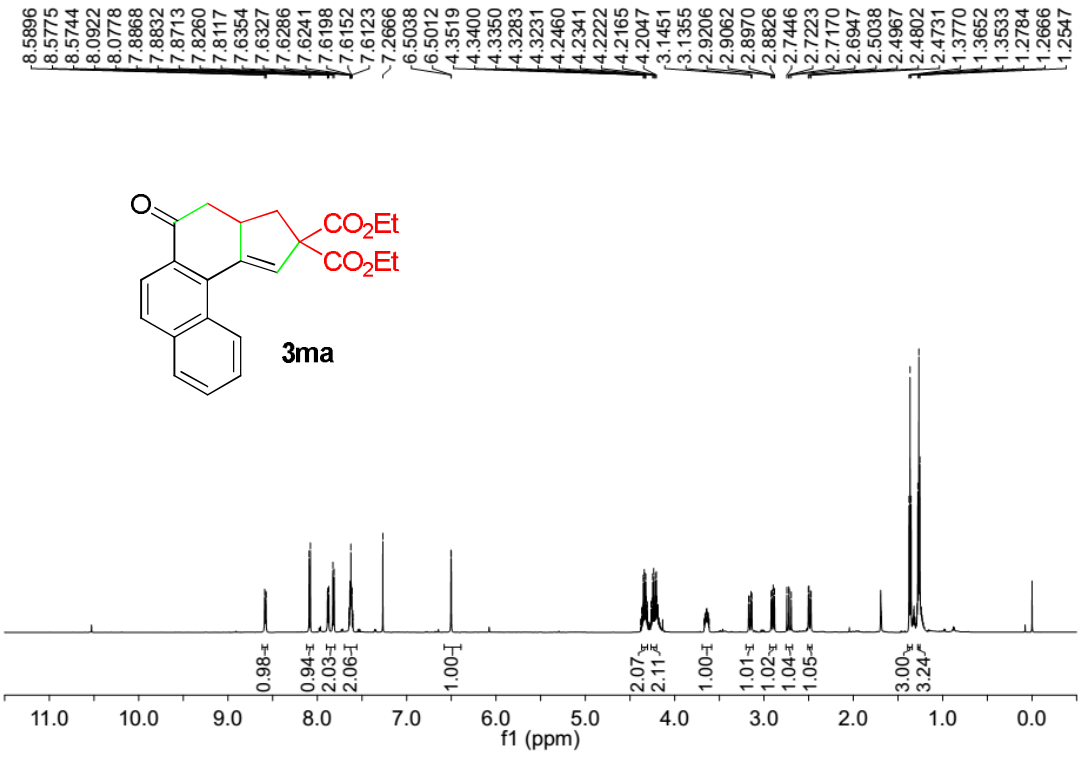
40
20
0
f1 (ppm)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7.6327
7.6286
7.6241
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7.6152
7.6123
7.2666
6.5038
6.5012
4.3519
4.3400
4.3350
4.3283
4.3231
4.2460
4.2341
4.2222
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4.2047
3.1451
3.1355
2.9206
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2.7446
2.7223
2.7170
2.6947
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2.4967
2.4802
2.4731
1.3770
1.3652
1.3533
1.2784
1.2666
1.2547
CO2Et
CO2Et
3ma
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0.94
2.03
2.06
1.00
2.07
2.11
1.00
1.01
1.02
1.04
1.05
3.00
3.24
11.0
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5.0
4.0
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2.0
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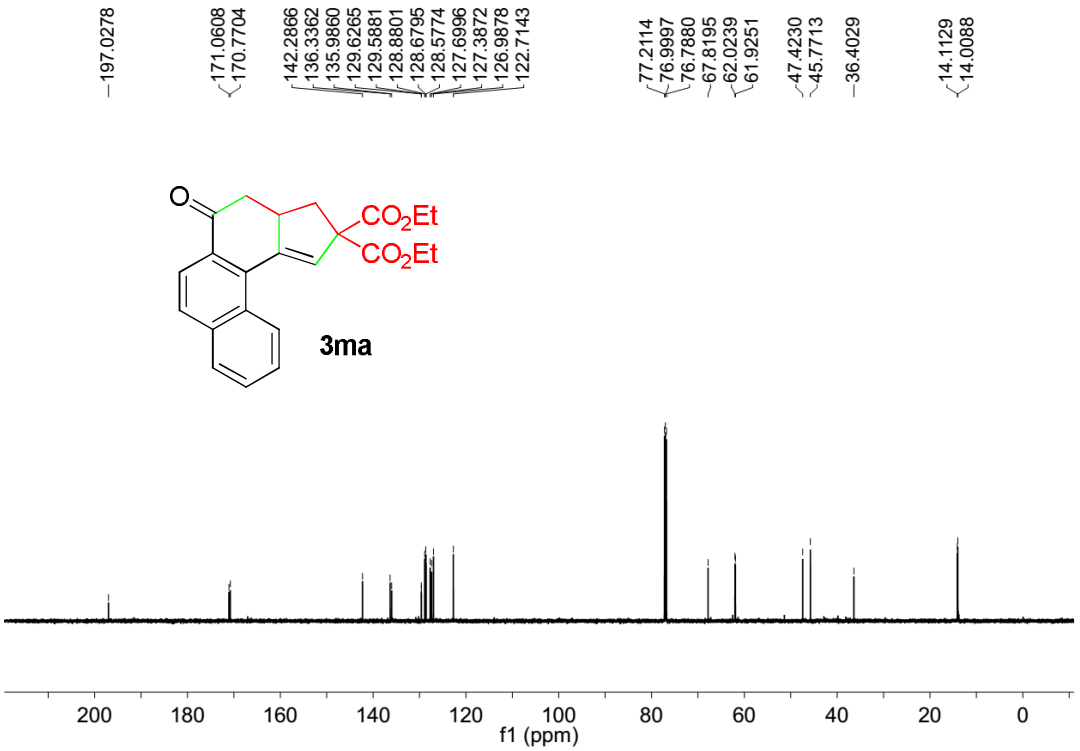
0.0
f1 (ppm)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62.0239
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47.4230
45.7713
36.4029
14.1129
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CO2Et
CO2Et
3ma
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120
100
80
60
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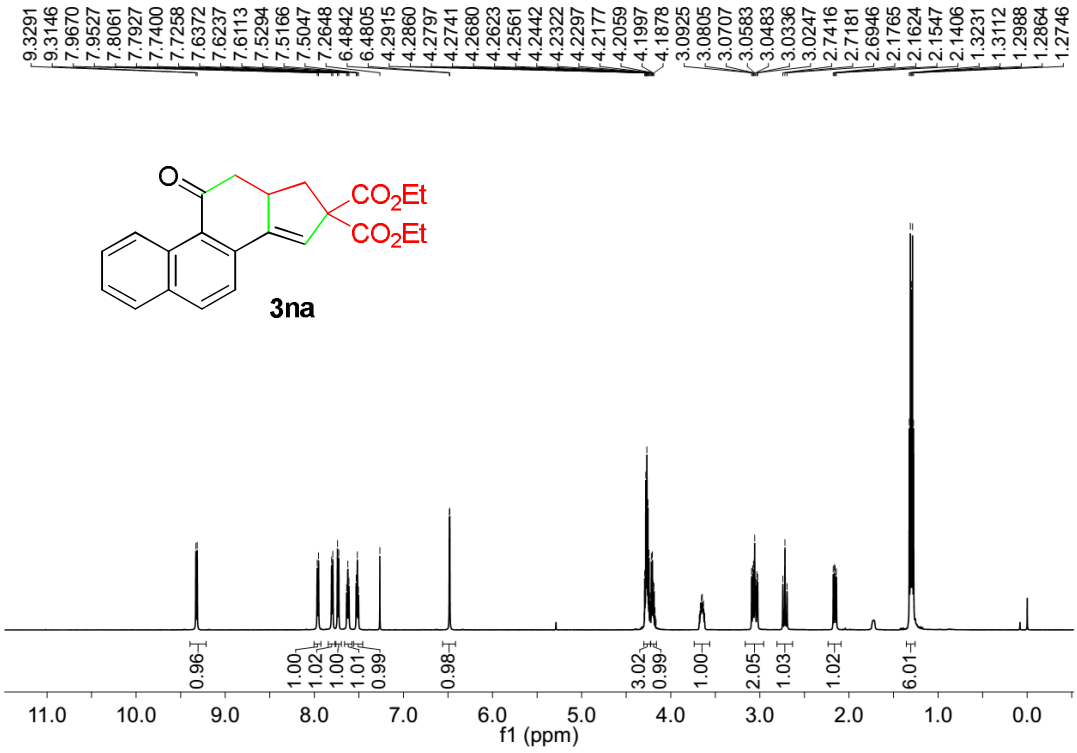
20
0
f1 (ppm)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7.5047
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6.4805
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4.2860
4.2797
4.2741
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4.2623
4.2561
4.2442
4.2322
4.2297
4.2177
4.2059
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3.0925
3.0805
3.0707
3.0583
3.0483
3.0336
3.0247
2.7416
2.7181
2.6946
2.1765
2.1624
2.1547
2.1406
1.3231
1.3112
1.2988
1.2864
1.2746
CO2Et
CO2Et
3na
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1.00
1.02
1.00
1.01
0.99
0.98
3.02
0.99
1.00
2.05
1.03
1.02
6.01
11.0
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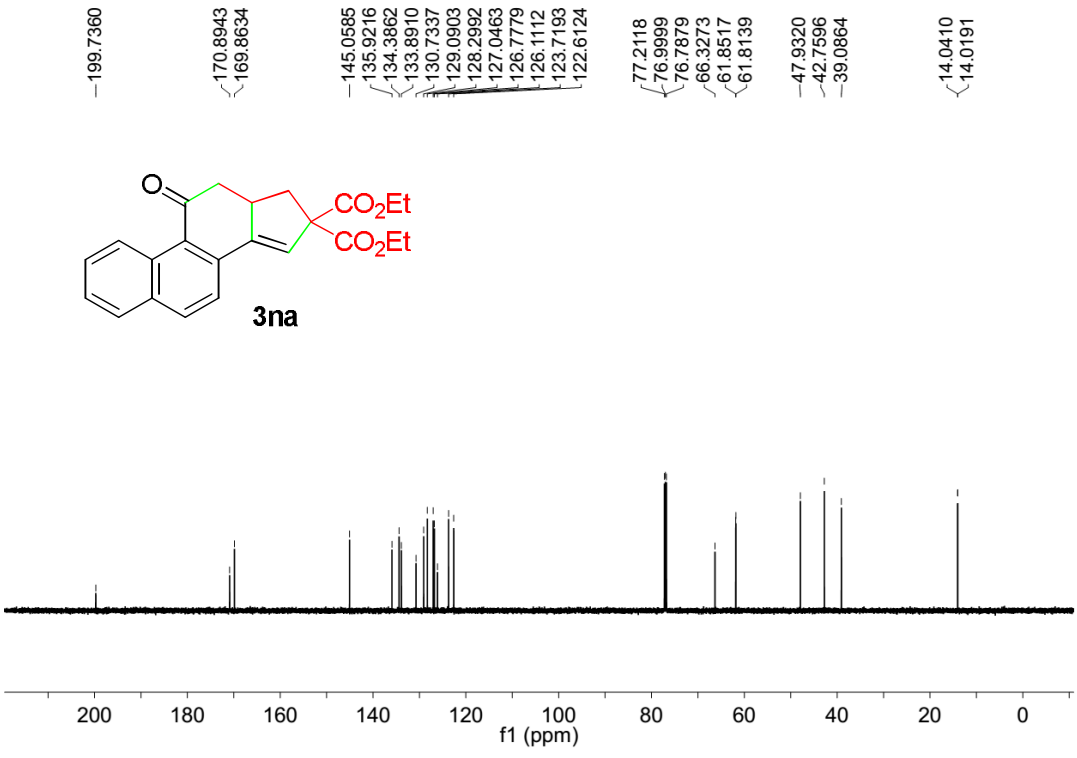
f1 (ppm)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126.1112
123.7193
122.6124
77.2118
76.9999
76.7879
66.3273
61.8517
61.8139
47.9320
42.7596
39.0864
14.0410
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CO2Et
CO2Et
3na
200
180
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140
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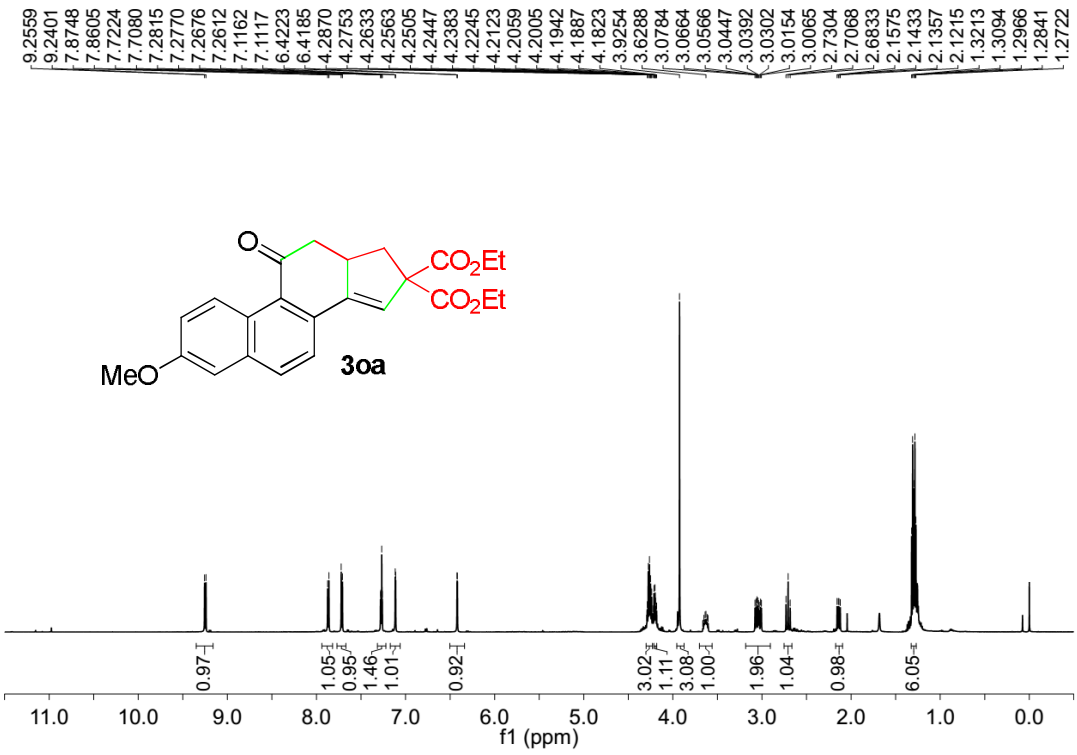
100
80
60
40
20
0
f1 (ppm)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6.4185
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4.2633
4.2563
4.2505
4.2447
4.2383
4.2245
4.2123
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3.0664
3.0566
3.0447
3.0392
3.0302
3.0154
3.0065
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2.6833
2.1575
2.1433
2.1357
2.1215
1.3213
1.3094
1.2966
1.2841
1.2722
CO2Et
CO2Et
MeO
3oa
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1.05
0.95
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1.01
0.92
3.02
1.11
3.08
1.00
1.96
1.04
0.98
6.05
11.0
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5.0
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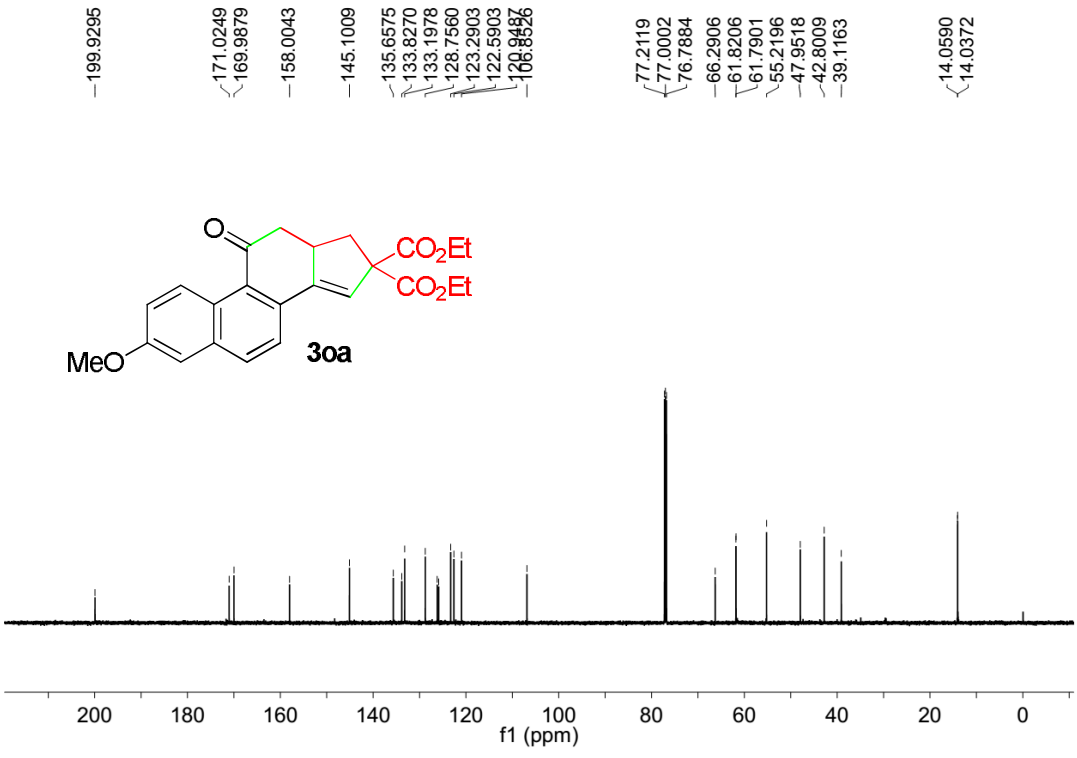
0.0
f1 (ppm)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55.2196
47.9518
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14.0590
14.0372
CO2Et
CO2Et
MeO
3oa
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140
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100
80
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20
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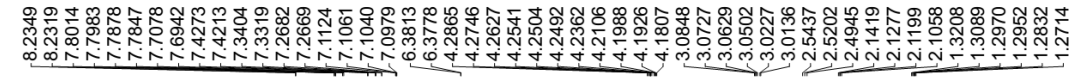
f1 (ppm)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7.2669
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7.1040
7.0979
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6.3778
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4.1807
3.0848
3.0727
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3.0227
3.0136
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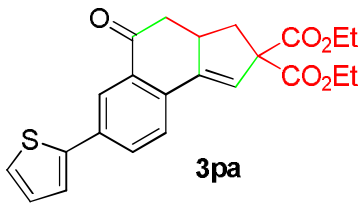
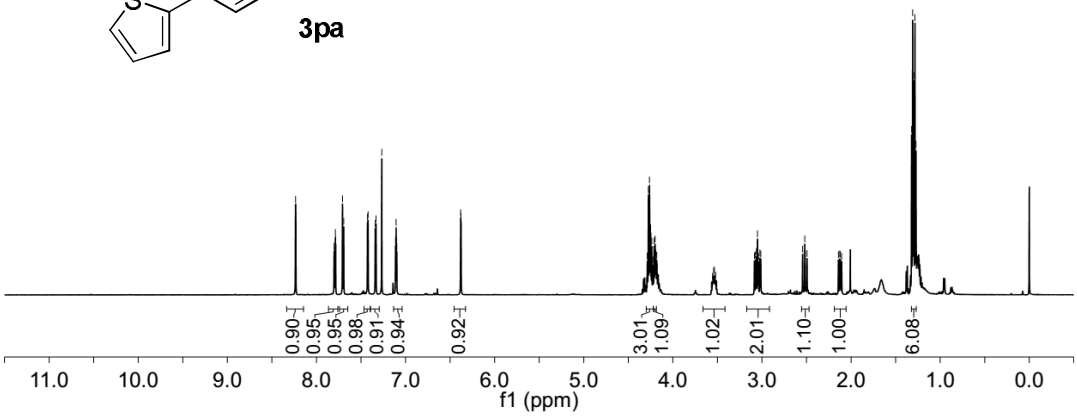
1.2832
1.2714


O
CO2Et
CO2Et
S

3pa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1.02
2.01
1.10
1.00
6.08
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


196.7690
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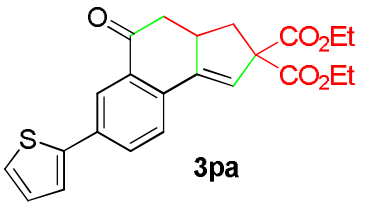
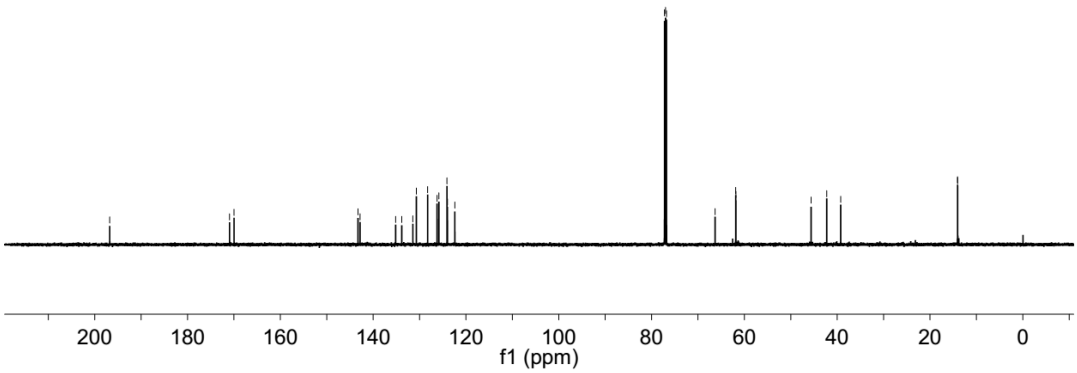

O
CO2Et
CO2Et
S

3pa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100
80
60
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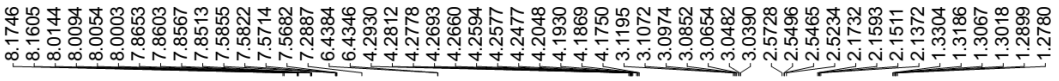
20
0
f1 (ppm)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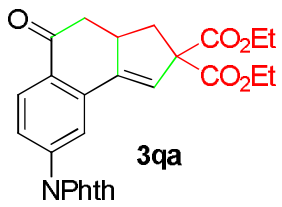
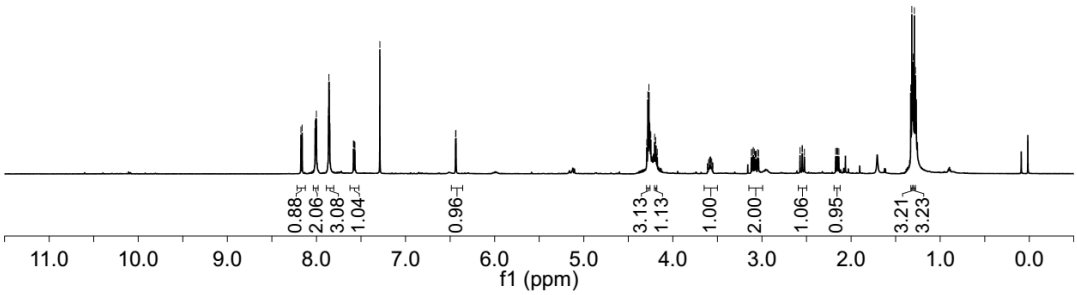

O
CO2Et
CO2Et
NPhth

3qa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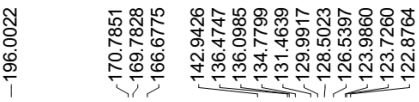
1.04
0.96
3.13
1.13
1.00
2.00
1.06
0.95
3.21
3.23
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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131.4639
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128.5023
126.5397
123.9860
123.7260
122.8764
77.2113
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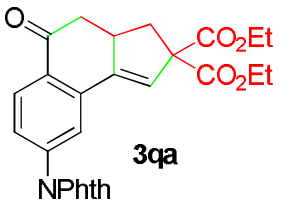
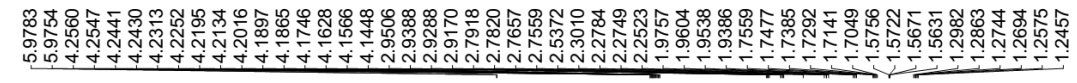
45.5369
42.3196
39.2037
14.0485
14.0150


O
CO2Et
CO2Et
NPhth

3qa

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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4.2134
4.2016
4.1897
4.1865
4.1746
4.1628
4.1566
4.1448
2.9506
2.9388
2.9288
2.9170
2.7918
2.7820
2.7657
2.7559
2.5372
2.3010
2.2784
2.2749
2.2523
1.9757
1.9604
1.9538
1.9386
1.7559
1.7477
1.7385
1.7292
1.7141
1.7049
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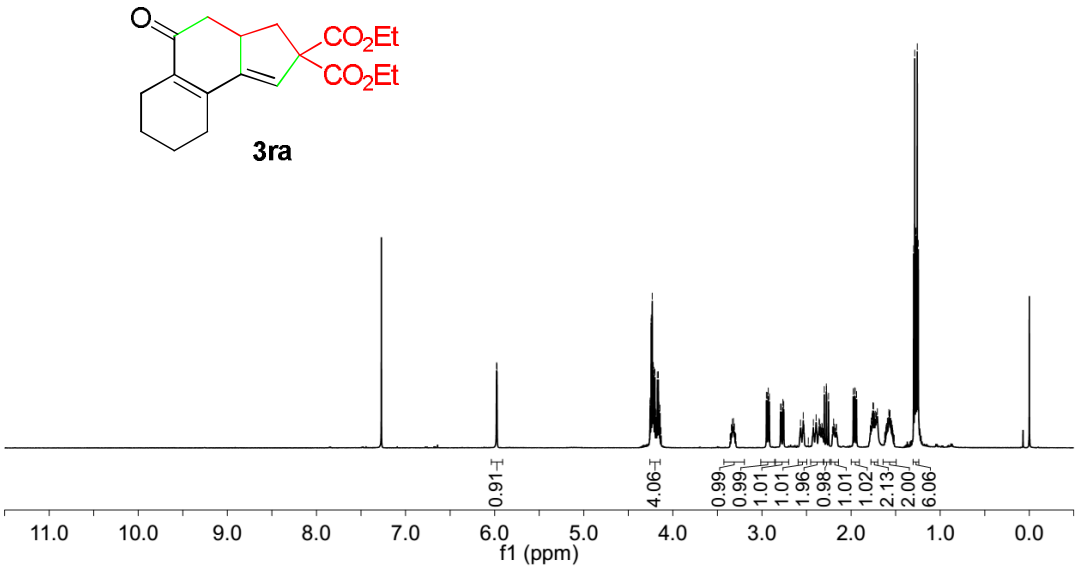
1.2982
1.2863
1.2744
1.2694
1.2575
1.2457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CO2Et
CO2Et
3ra
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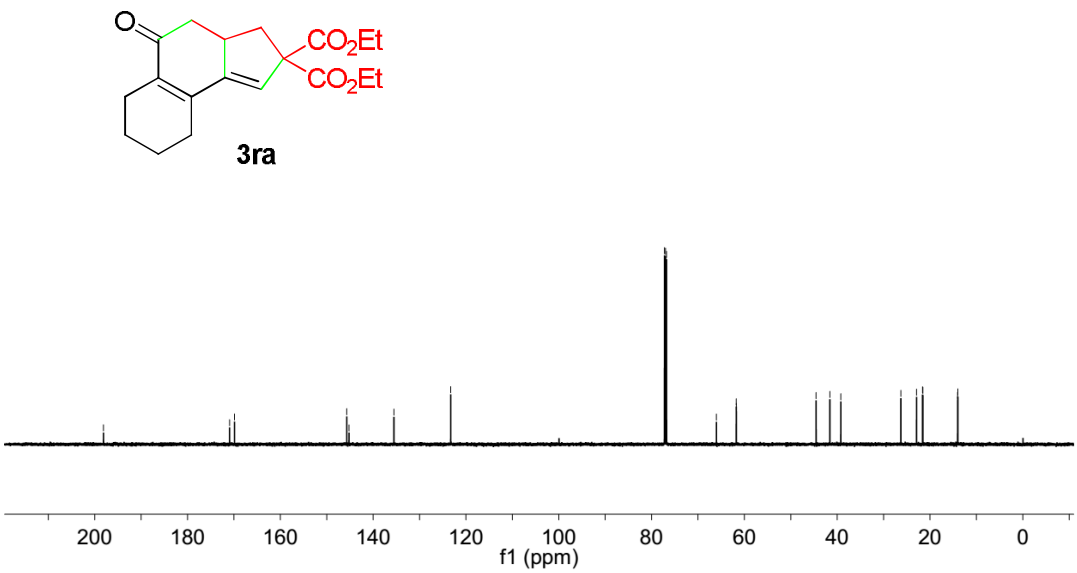
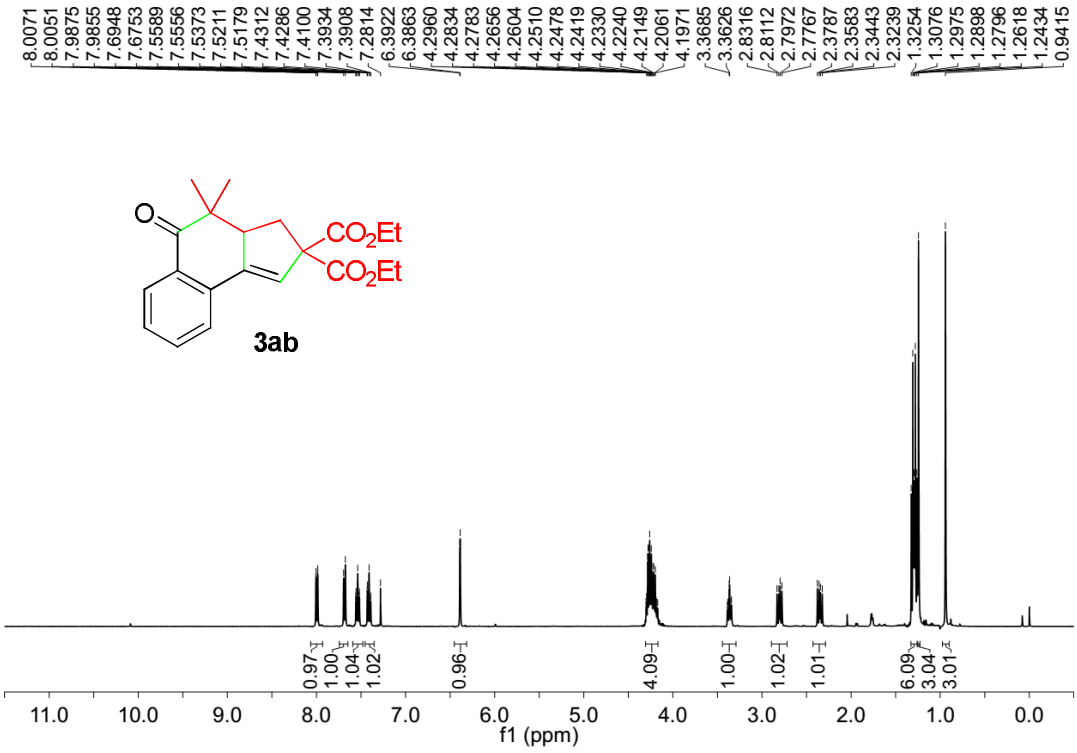
4.06
0.99
0.99
1.01
1.01
1.96
0.98
1.01
1.02
2.13
2.00
6.06
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


198.1119
170.9461
169.8882
145.6897
145.2024
135.5289
123.2882
77.2121
77.0005
76.7885
66.0297
61.7537
61.7413
44.5527
41.5843
39.2138
26.2816
22.8950
21.6039
21.5350
14.0396
14.0063


O
CO2Et
CO2Et
3ra
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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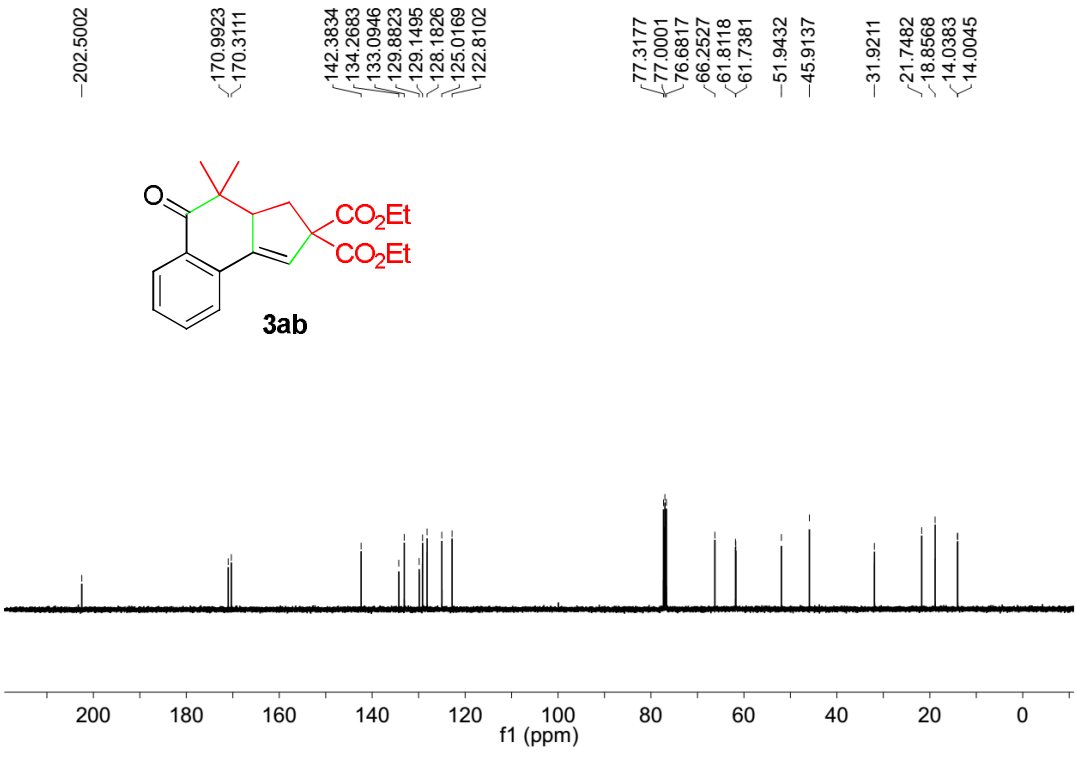
7.5373
7.5211
7.5179
7.4312
7.4286
7.4100
7.3934
7.3908
7.2814
6.3922
6.3863
4.2960
4.2834
4.2783
4.2656
4.2604
4.2510
4.2478
4.2419
4.2330
4.2240
4.2149
4.2061
4.1971
3.3685
3.3626
2.8316
2.8112
2.7972
2.7767
2.3787
2.3583
2.3443
2.3239
1.3254
1.3076
1.2975
1.2898
1.2796
1.2618
1.2434
1.2415
O
CO2Et
CO2Et
3ab
0.97
1.00
1.04
1.02
0.96
4.09
1.00
1.02
1.01
6.09
3.04
3.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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134.2683
133.0946
129.8823
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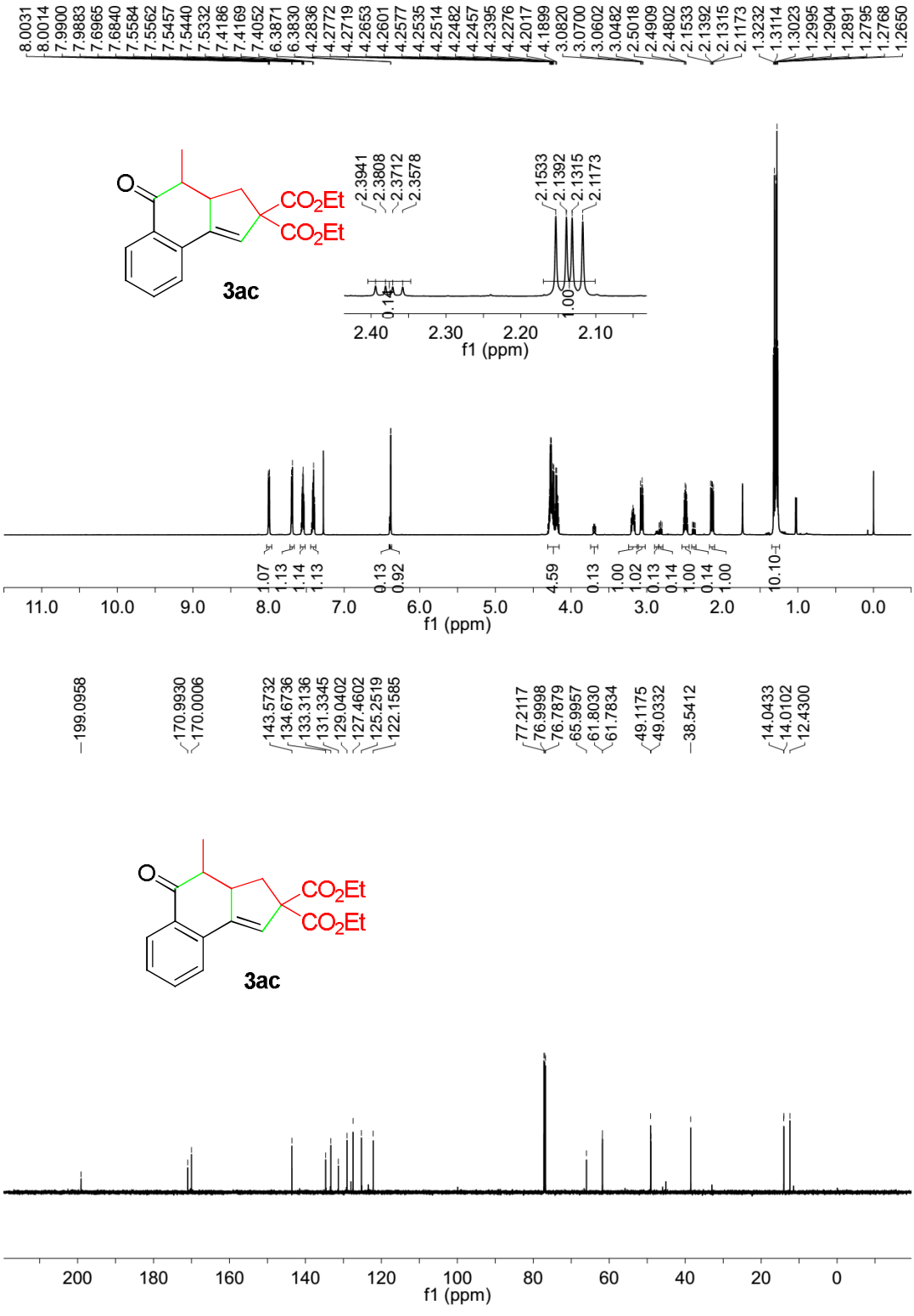
128.1826
125.0169
122.8102
77.3177
77.0001
76.6817
66.2527
61.8118
61.7381
51.9432
45.9137
31.9211
21.7482
18.8568
14.0383
14.0045
O
CO2Et
CO2Et
3ab
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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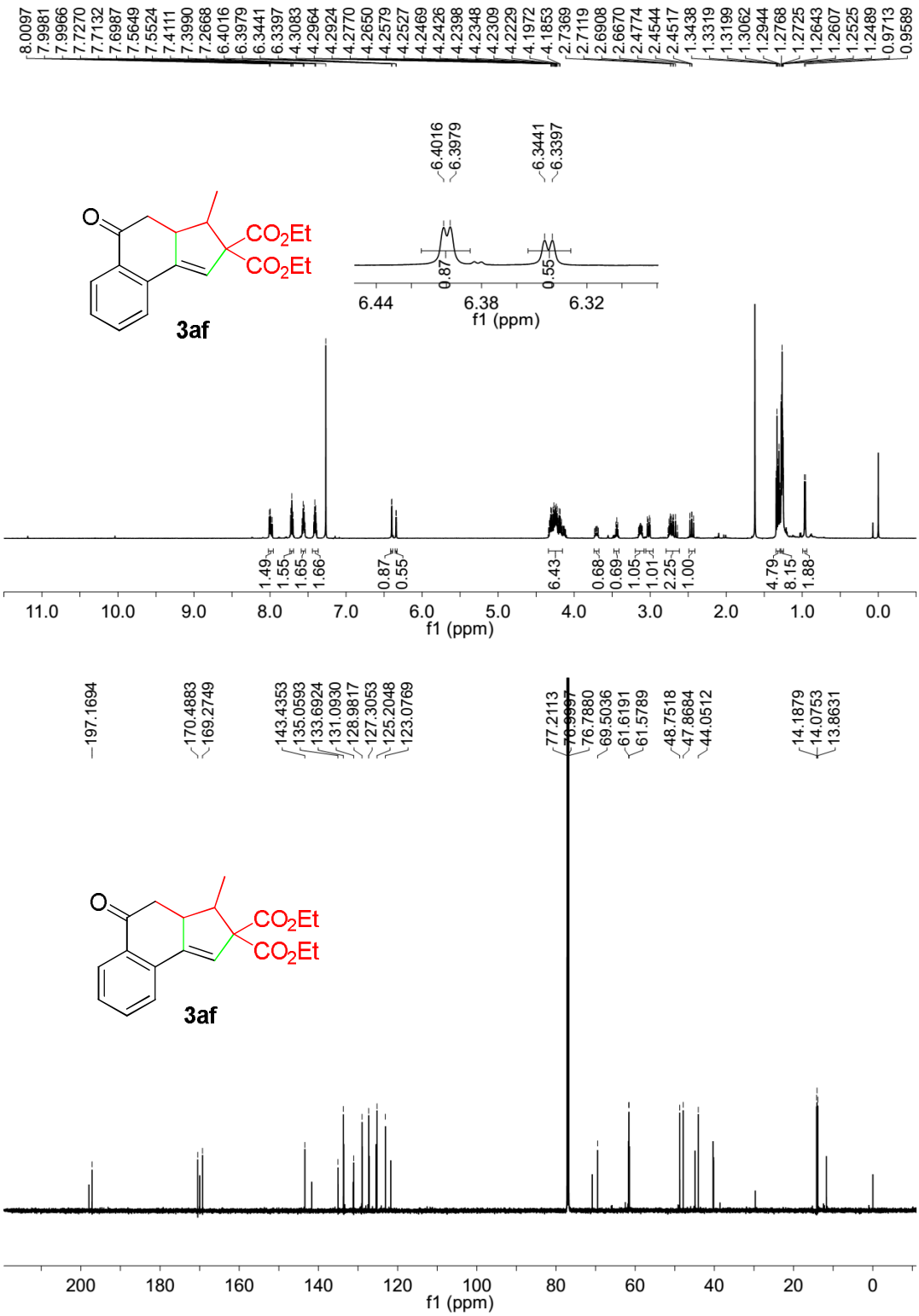
7.5584
7.5562
7.5457
7.5440
7.5332
7.4186
7.4169
7.4052
6.3871
6.3830
4.2836
4.2772
4.2719
4.2653
4.2601
4.2577
4.2535
4.2514
4.2482
4.2457
4.2395
4.2276
4.2017
4.1899
3.0820
3.0700
3.0602
3.0482
2.5018
2.4909
2.4802
2.1533
2.1392
2.1315
2.1173
1.3232
1.3114
1.3023
1.2995
1.2904
1.2891
1.2795
1.2768
1.2650
CO2Et
CO2Et
3ac
2.3941
2.3808
2.3712
2.3578
2.1533
2.1392
2.1315
2.1173
0.14
1.00
2.40
2.30
2.20
2.10
f1 (ppm)
1.07
1.13
1.14
1.13
0.13
0.92
4.59
0.13
1.00
1.02
0.13
0.14
1.00
0.14
1.00
10.10
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
199.0958
170.9930
170.0006
143.5732
134.6736
133.3136
131.3345
129.0402
127.4602
125.2519
122.1585
77.2117
76.9998
76.7879
65.9957
61.8030
61.7834
49.1175
49.0332
38.5412
14.0433
14.0102
12.4300
CO2Et
CO2Et
3ac
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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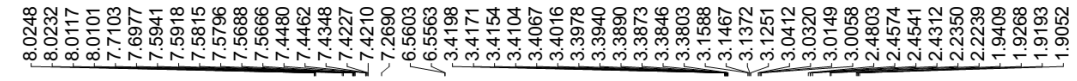
7.9981
7.9966
7.7270
7.7132
7.6987
7.5649
7.5524
7.4111
7.3990
7.2668
6.4016
6.3979
6.3441
6.3397
4.3083
4.2964
4.2924
4.2770
4.2650
4.2579
4.2527
4.2469
4.2426
4.2398
4.2348
4.2309
4.2229
4.1972
4.1853
2.7369
2.7119
2.6908
2.6670
2.4774
2.4544
2.4517
1.3438
1.3319
1.3199
1.3062
1.2944
1.2768
1.2725
1.2643
1.2607
1.2525
1.2489
0.9713
0.9589
CO2Et
CO2Et
3af
6.4016
6.3979
6.3441
6.3397
0.87
0.55
6.44
6.38
6.32
f1 (ppm)
1.49
1.55
1.65
1.66
0.87
0.55
6.43
0.68
0.69
1.05
1.01
2.25
1.00
4.79
8.15
1.88
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
197.1694
170.4883
169.2749
143.4353
135.0593
133.6924
131.0930
128.9817
127.3053
125.2048
123.0769
77.2113
76.9997
76.7880
69.5036
61.6191
61.5789
48.7518
47.8684
44.0512
14.1879
14.0753
13.8631
CO2Et
CO2Et
3af
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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8.0232
8.0117
8.0101
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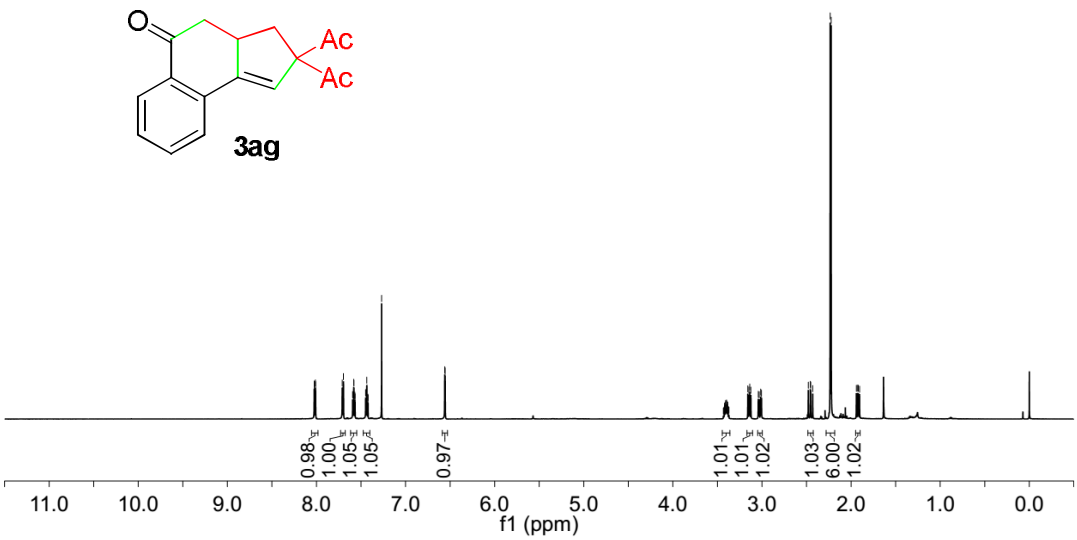
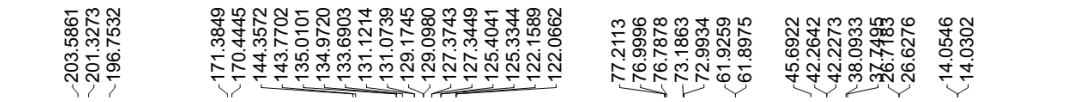
7.6977
7.5941
7.5918
7.5815
7.5796
7.5688
7.5666
7.4480
7.4462
7.4348
7.4227
7.4210
7.2690
6.5603
6.5563
3.4198
3.4171
3.4154
3.4104
3.4067
3.4016
3.3978
3.3940
3.3890
3.3873
3.3846
3.3803
3.1588
3.1467
3.1372
3.1251
3.0412
3.0320
3.0149
3.0058
2.4803
2.4574
2.4541
2.4312
2.2350
2.2239
1.9409
1.9268
1.9193
1.9052


Ac
Ac
3ag
0.98
1.00
1.05
1.05
0.97
1.01
1.01
1.02
1.03
6.00
1.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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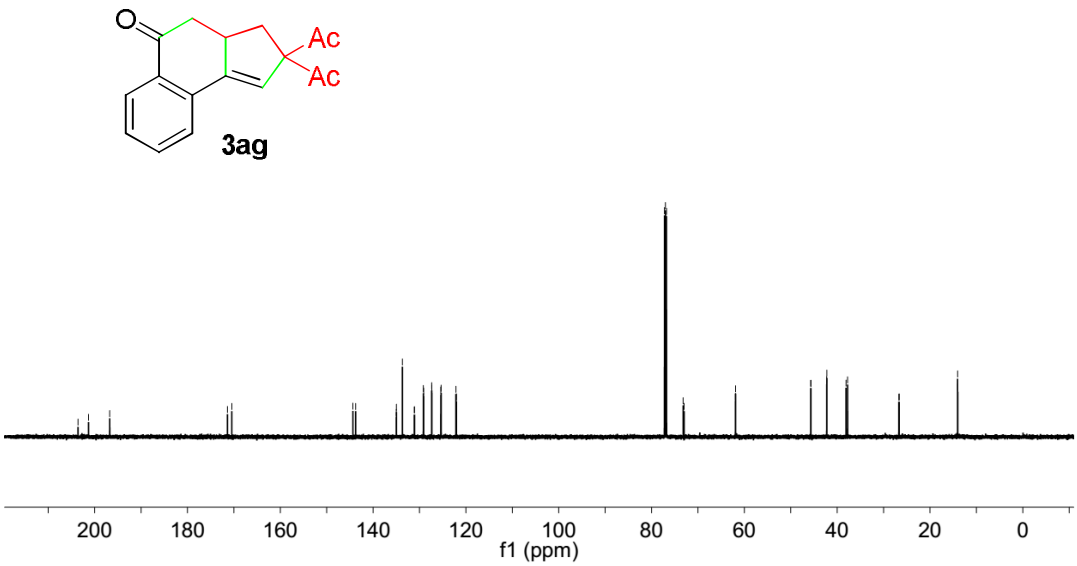
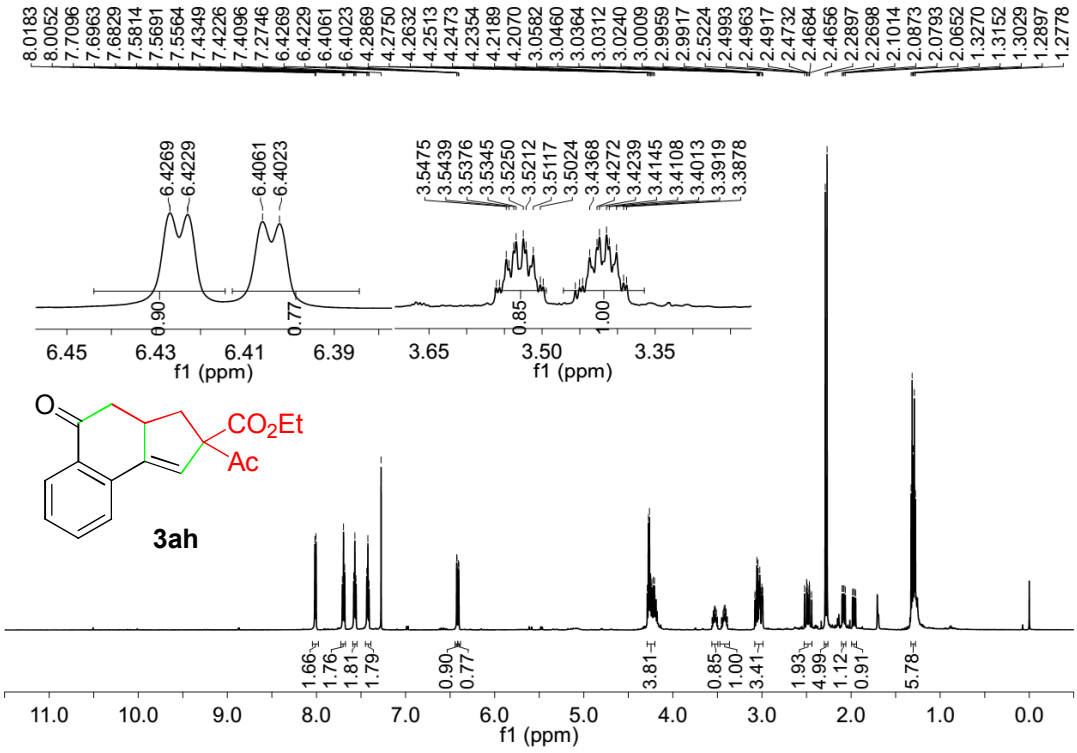
171.3849
170.4445
144.3572
143.7702
135.0101
134.9720
133.6903
131.1214
131.0739
129.1745
129.0980
127.3743
127.3449
125.4041
125.3344
122.1589
122.0662
77.2113
76.9996
76.7878
73.1863
72.9934
61.9259
61.8975
45.6922
42.2642
42.2273
38.0933
26.6276
14.0546
14.0302


Ac
Ac
3ag
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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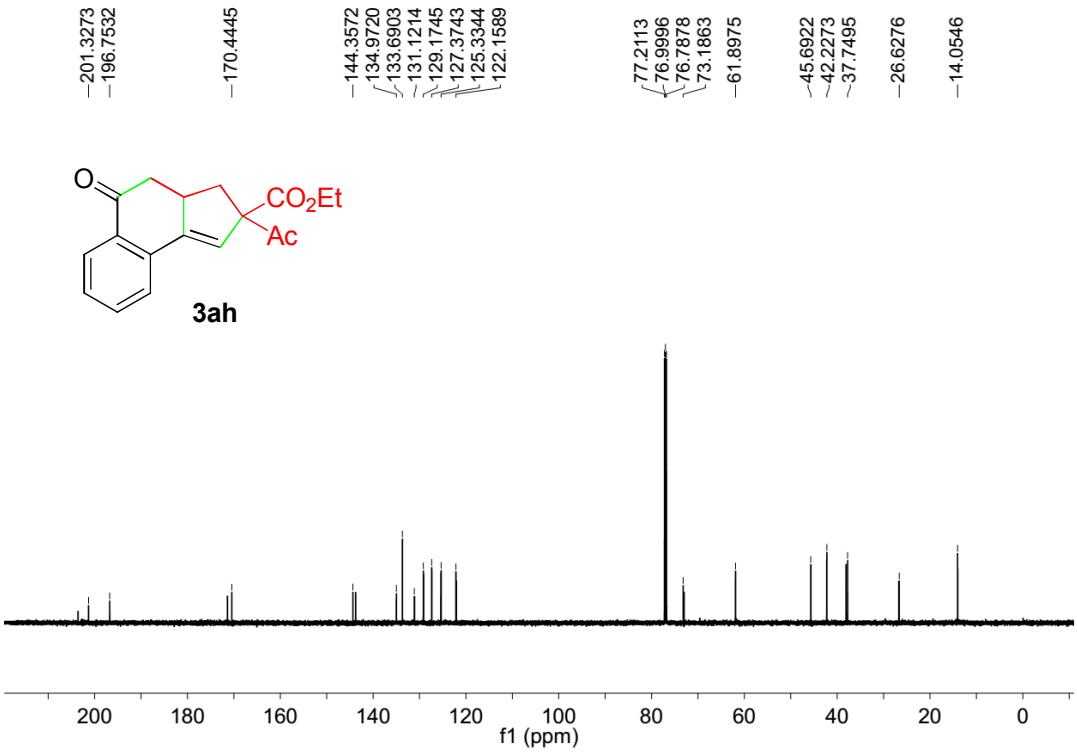
7.4349
7.4226
7.4096
7.2746
6.4269
6.4229
6.4061
6.4023
4.2869
4.2750
4.2632
4.2513
4.2473
4.2354
4.2189
4.2070
3.0582
3.0460
3.0364
3.0312
3.0240
3.0009
2.9959
2.9917
2.5224
2.4993
2.4963
2.4917
2.4732
2.4684
2.4656
2.2897
2.2698
2.1014
2.0873
2.0793
2.0652
1.3270
1.3152
1.3029
1.2897
1.2778
3.5475
3.5439
3.5376
3.5345
3.5250
3.5212
3.5117
3.5024
3.4368
3.4272
3.4239
3.4145
3.4108
3.4013
3.3919
3.3878
0.90
0.77
0.85
1.00
6.45
6.43
6.41
6.39
f1 (ppm)
3.65
3.50
3.35
f1 (ppm)
O
CO2Et
Ac
3ah
1.66
1.76
1.81
1.79
0.90
0.77
3.81
0.85
1.00
3.41
1.93
4.99
1.12
0.91
5.78
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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144.3572
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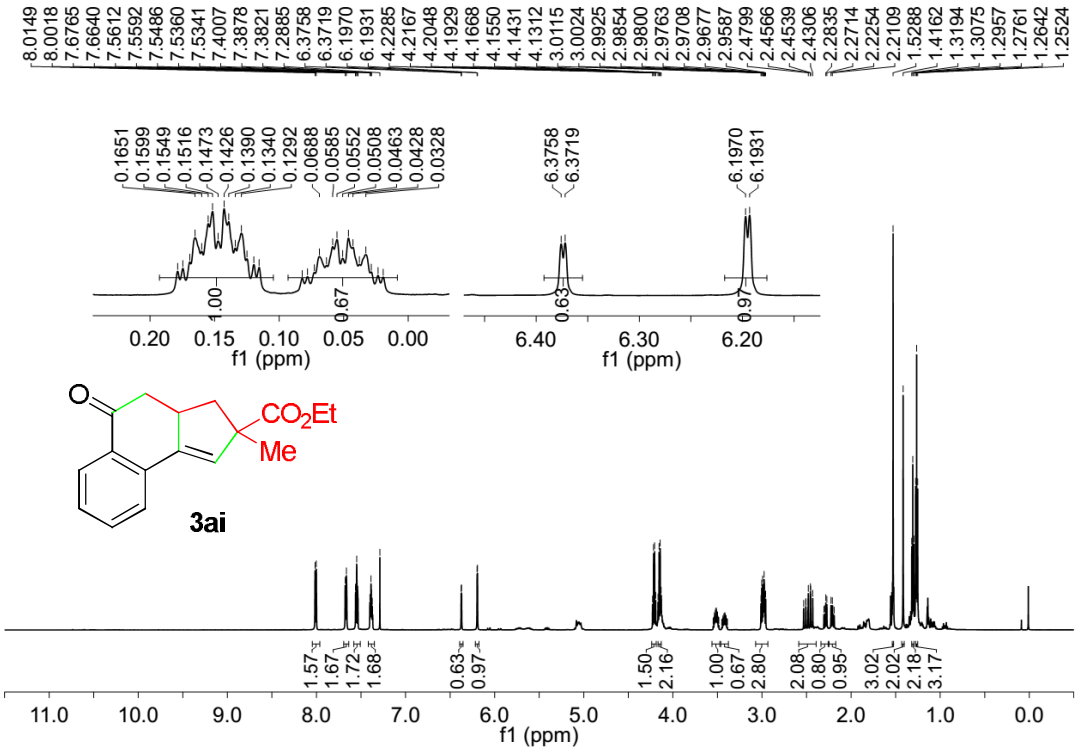
133.6903
131.1214
129.1745
127.3743
125.3344
122.1589
77.2113
76.9996
76.7878
73.1863
61.8975
45.6922
42.2273
37.7495
26.6276
14.0546
O
CO2Et
Ac
3ah
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.5341
7.4007
7.3878
7.3821
7.2885
6.3758
6.3719
6.1970
6.1931
4.2285
4.2167
4.2048
4.1929
4.1668
4.1550
4.1431
4.1312
3.0115
3.0024
2.9925
2.9854
2.9800
2.9763
2.9708
2.9677
2.9587
2.4799
2.4566
2.4539
2.4306
2.2835
2.2714
2.2254
2.2109
1.5288
1.4162
1.3194
1.3075
1.2957
1.2761
1.2642
1.2524
0.1651
0.1599
0.1549
0.1516
0.1473
0.1426
0.1390
0.1340
0.1292
0.0688
0.0585
0.0552
0.0508
0.0463
0.0428
0.0328
1.00
0.67
0.63
0.97
f1 (ppm)
CO2Et
Me
3ai
1.57
1.67
1.72
1.68
0.63
0.97
1.50
2.16
1.00
0.67
2.80
2.08
0.80
0.95
3.02
2.02
2.18
3.17
f1 (ppm)
197.5736
175.5683
140.7802
135.7477
133.5315
130.9792
129.0461
128.4317
127.2167
125.1635
77.2119
77.0000
76.7882
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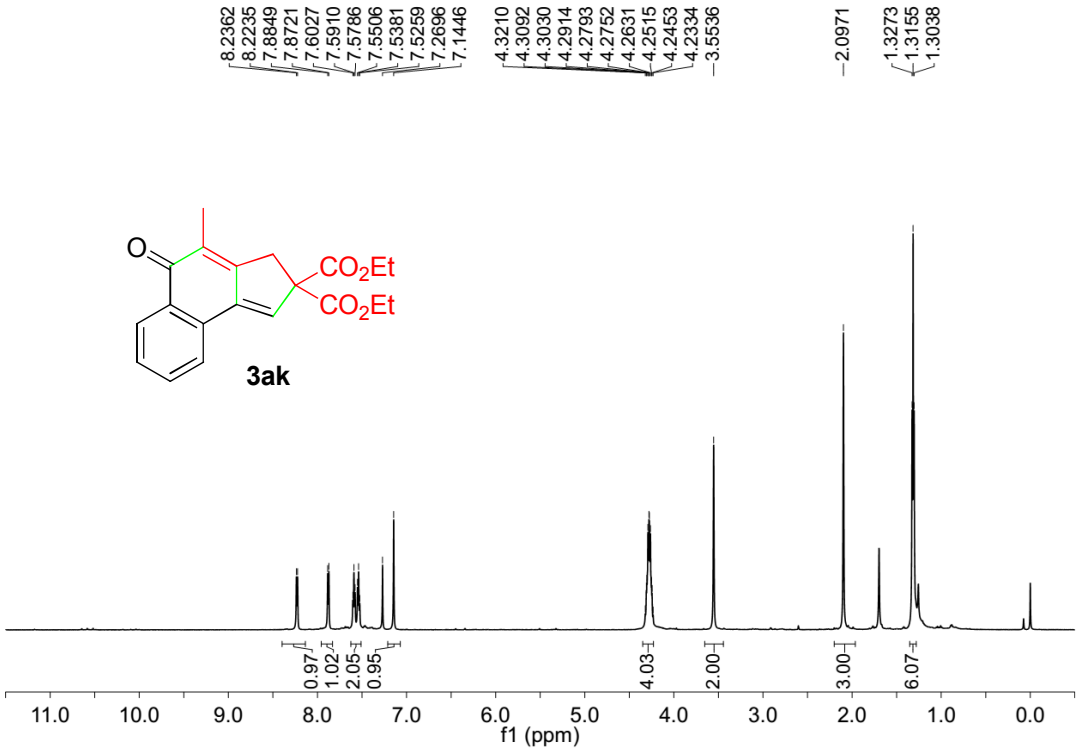
46.3072
43.6192
42.7970
25.4772
14.1312
CO2Et
Me
3ai
f1 (ppm)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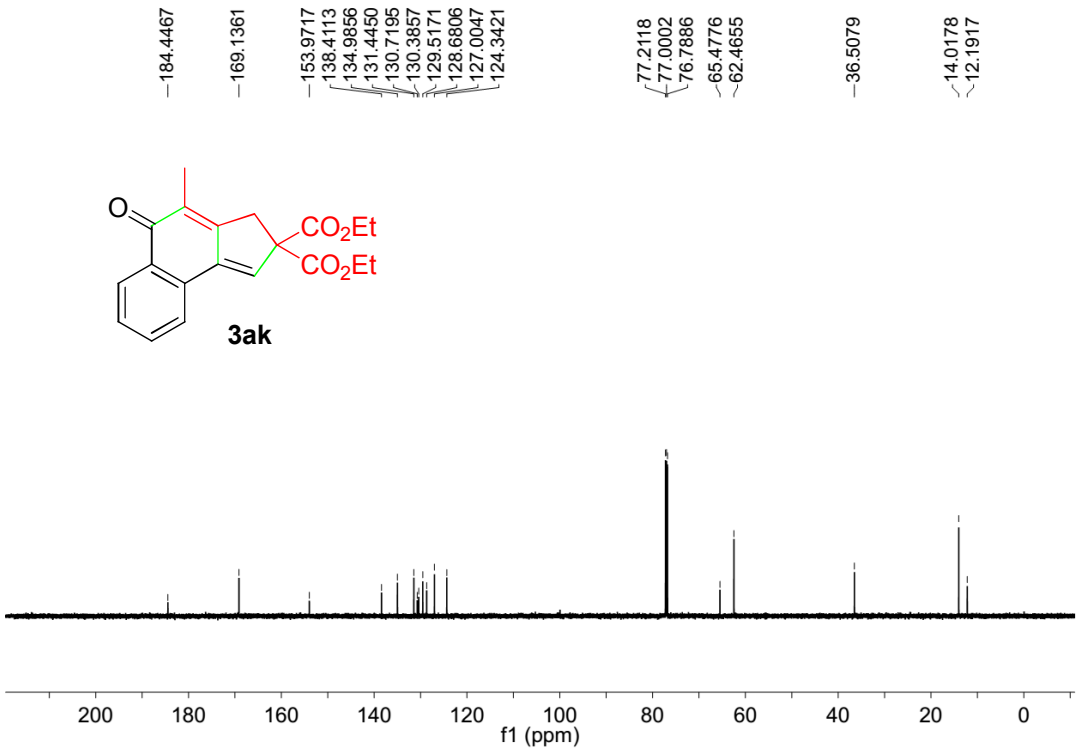
7.5786
7.5506
7.5381
7.5259
7.2696
7.1446
4.3210
4.3092
4.3030
4.2914
4.2793
4.2752
4.2631
4.2515
4.2453
4.2334
3.5536
2.0971
1.3273
1.3155
1.3038
O
CO2Et
CO2Et
3ak
0.97
1.02
2.05
0.95
4.03
2.00
3.00
6.07
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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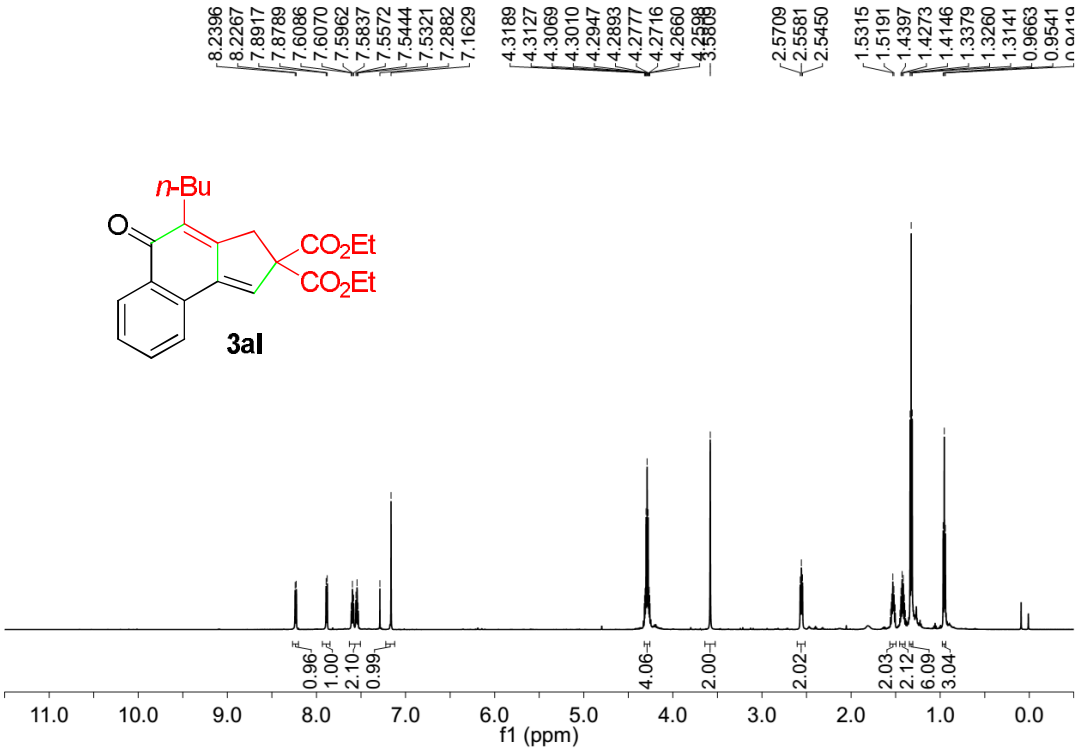
138.4113
134.9856
131.4450
130.7195
130.3857
129.5171
128.6806
127.0047
124.3421
77.2118
77.0002
76.7886
65.4776
62.4655
36.5079
14.0178
12.1917
O
CO2Et
CO2Et
3ak
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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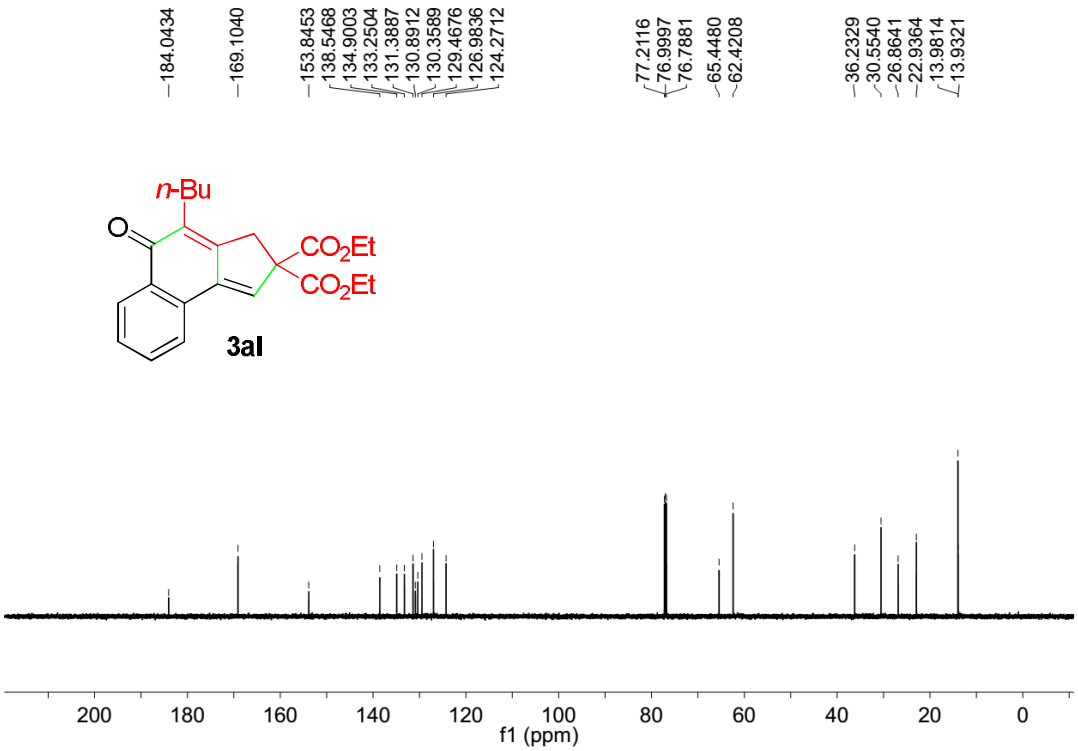
7.8789
7.6086
7.6070
7.5962
7.5837
7.5572
7.5444
7.5321
7.2882
7.1629
4.3189
4.3127
4.3069
4.3010
4.2947
4.2893
4.2777
4.2716
4.2660
3.5809
2.5709
2.5581
2.5450
1.5315
1.5191
1.4397
1.4273
1.4146
1.3379
1.3260
1.3141
0.9663
0.9541
n-Bu
CO2Et
CO2Et
3al
0.96
1.00
2.10
0.99
4.06
2.00
2.02
2.03
2.12
6.09
3.04
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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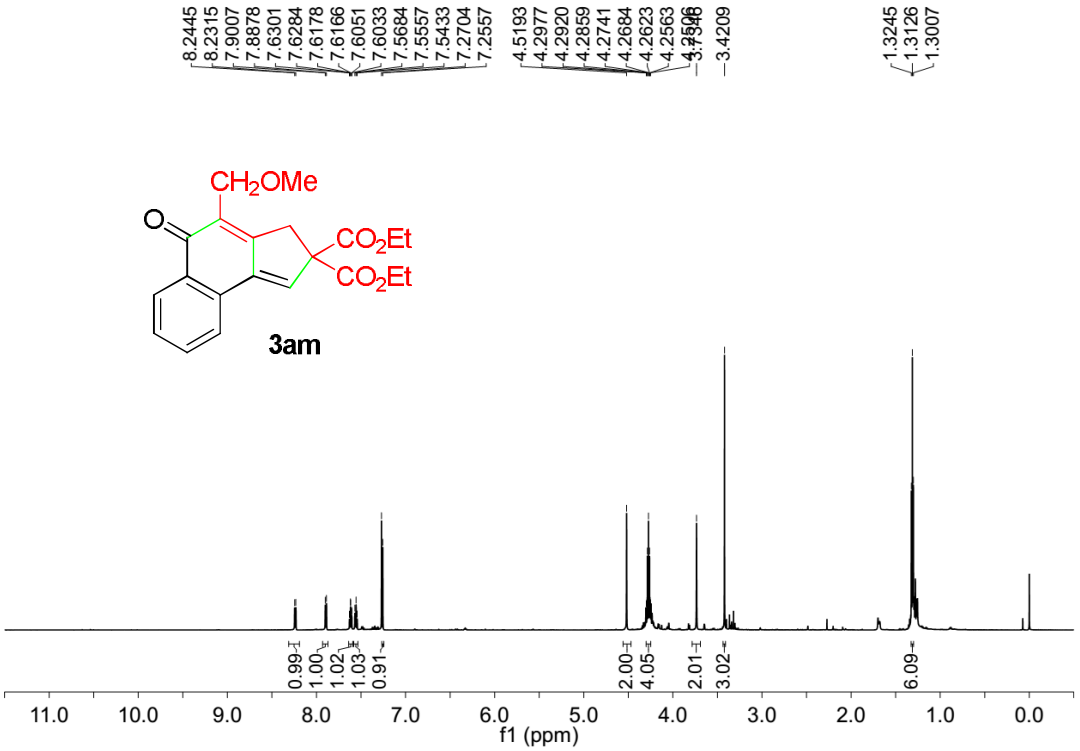
153.8453
138.5468
134.9003
133.2504
131.3887
130.8912
130.3589
129.4676
126.9836
124.2712
77.2116
76.9997
76.7881
65.4480
62.4208
36.2329
30.5540
26.8641
22.9364
13.9814
13.9321
n-Bu
CO2Et
CO2Et
3al
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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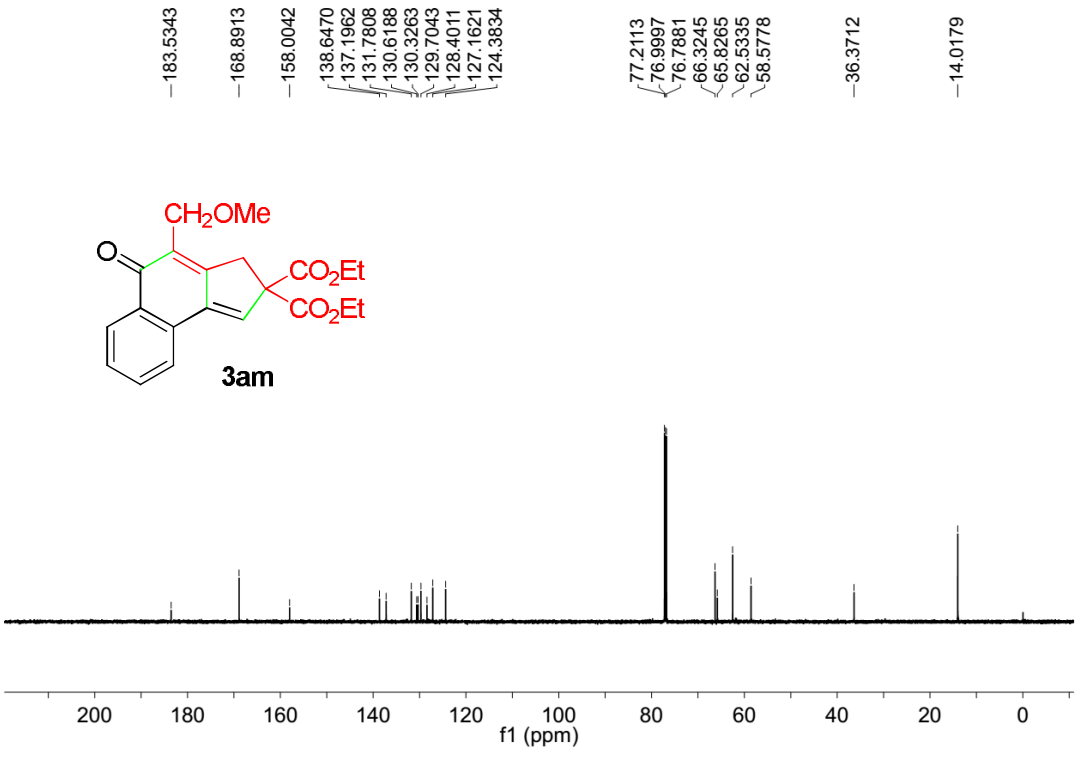
7.9007
7.8878
7.6301
7.6284
7.6178
7.6166
7.6051
7.6033
7.5684
7.5557
7.5433
7.2704
7.2557
4.5193
4.2977
4.2920
4.2859
4.2741
4.2684
4.2623
4.2563
3.4209
1.3245
1.3126
1.3007
CH2OMe
O
CO2Et
CO2Et
3am
0.99
1.00
1.02
1.03
0.91
2.00
4.05
2.01
3.02
6.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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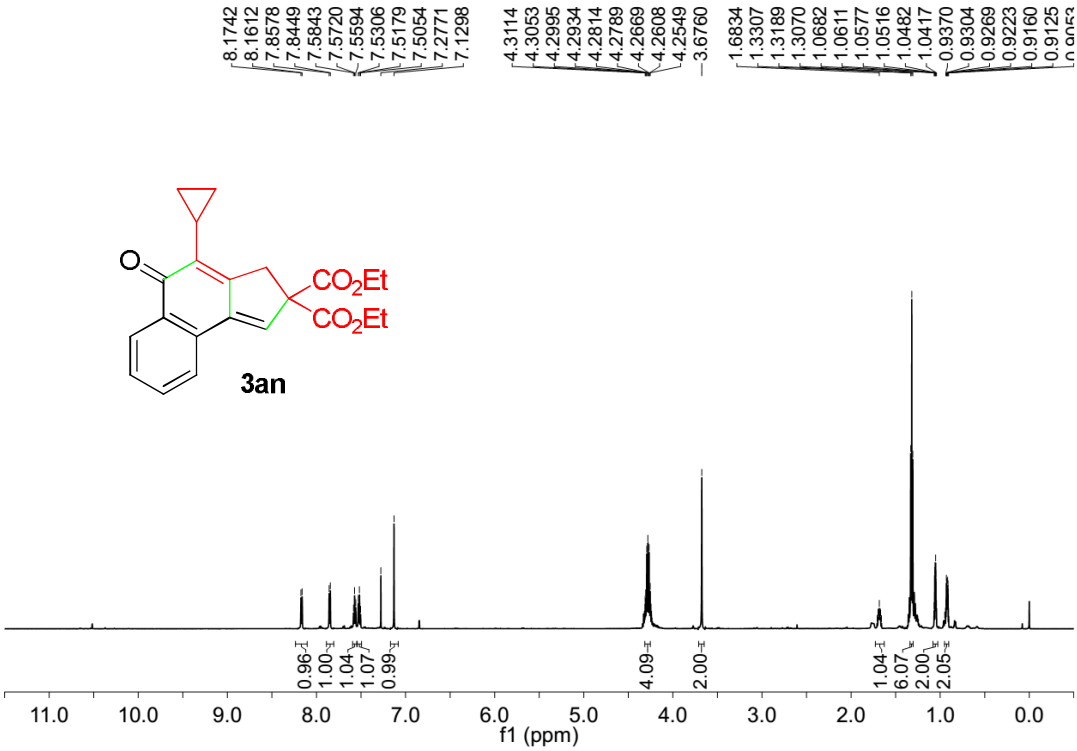
158.0042
138.6470
137.1962
131.7808
130.6188
130.3263
129.7043
128.4011
127.1621
124.3834
77.2113
76.9997
76.7881
66.3245
65.8265
62.5335
58.5778
36.3712
14.0179
CH2OMe
O
CO2Et
CO2Et
3am
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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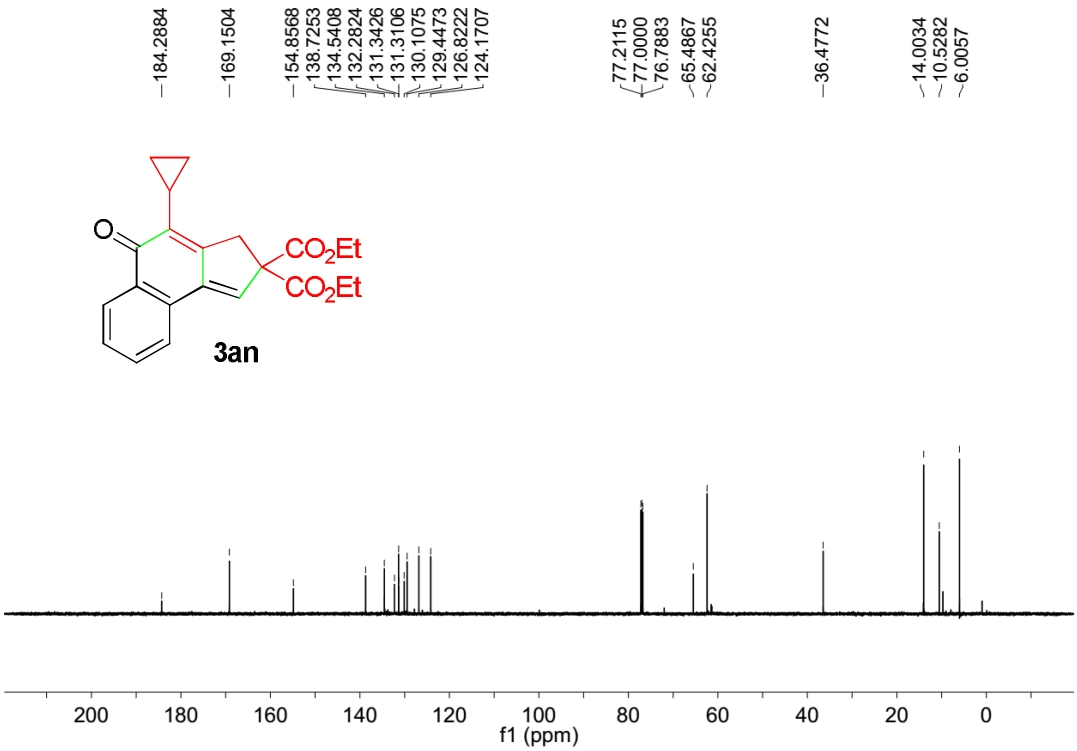
8.1612
7.8578
7.8449
7.5843
7.5720
7.5594
7.5306
7.5179
7.5054
7.2771
7.1298
4.3114
4.3053
4.2995
4.2934
4.2814
4.2789
4.2669
4.2608
4.2549
3.6760
1.6834
1.3307
1.3189
1.3070
1.0682
1.0611
1.0577
1.0516
1.0482
1.0417
0.9370
0.9304
0.9269
0.9223
0.9160
0.9125
O
CO2Et
CO2Et
3an
0.96
1.00
1.04
1.07
0.99
4.09
2.00
1.04
6.07
2.00
2.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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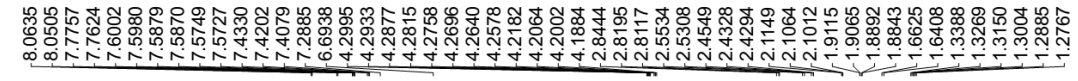
169.1504
154.8568
138.7253
134.5408
132.2824
131.3426
131.3106
130.1075
129.4473
126.8222
124.1707
77.2115
77.0000
76.7883
65.4867
62.4255
36.4772
14.0034
10.5282
6.0057
O
CO2Et
CO2Et
3an
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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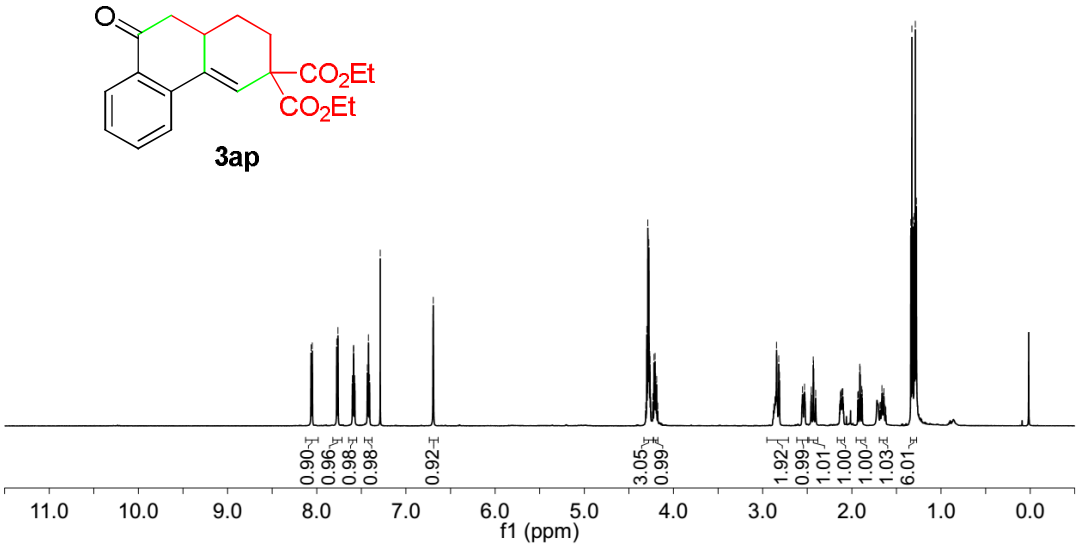
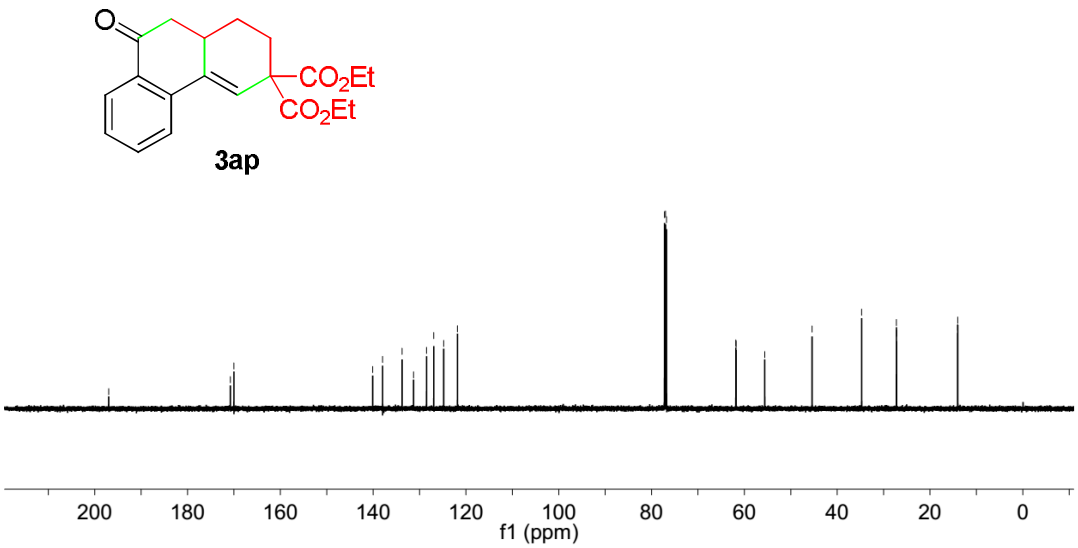
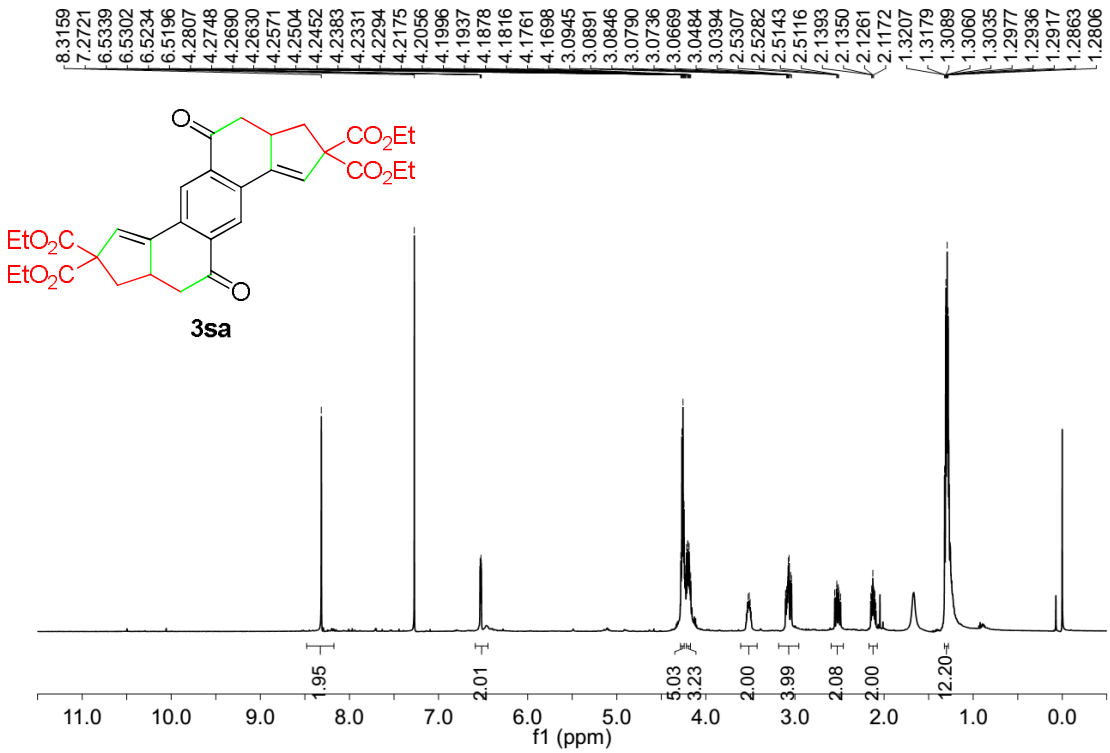
8.0505
7.7757
7.7624
7.6002
7.5980
7.5879
7.5870
7.5749
7.5727
7.4330
7.4202
7.4079
7.2885
6.6938
4.2995
4.2933
4.2877
4.2815
4.2758
4.2696
4.2640
4.2578
4.2182
4.2064
4.2002
4.1884
2.8444
2.8195
2.8117
2.5534
2.5308
2.4549
2.4328
2.4294
2.1149
2.1064
2.1012
1.9115
1.9065
1.8892
1.8843
1.6625
1.6408
1.3388
1.3269
1.3150
1.3004
1.2885
1.2767


O
CO2Et
CO2Et
3ap
0.90
0.96
0.98
0.98
0.92
3.05
0.99
1.92
0.99
1.01
1.00
1.00
1.03
6.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


196.9933
170.7752
170.0040
140.0990
137.9625
133.7645
131.2945
128.4864
126.9357
124.8016
121.8258
77.2118
77.0000
76.7882
61.8450
61.7876
55.6175
45.4134
34.7254
27.2407
27.1920
14.0487
14.0162


O
CO2Et
CO2Et
3ap
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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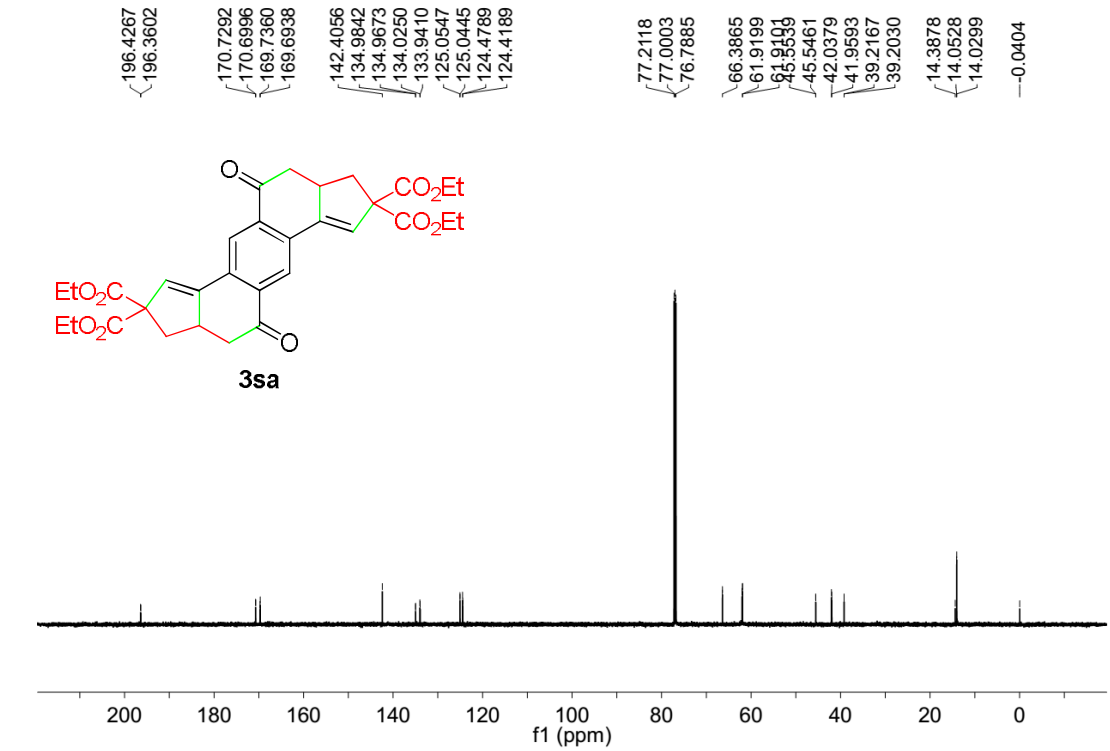
7.2721
6.5339
6.5302
6.5234
6.5196
4.2807
4.2748
4.2690
4.2630
4.2571
4.2504
4.2452
4.2383
4.2331
4.2294
4.2175
4.2056
4.1996
4.1937
4.1878
4.1816
4.1761
4.1698
3.0945
3.0891
3.0846
3.0790
3.0736
3.0669
3.0484
3.0394
2.5307
2.5282
2.5143
2.5116
2.1393
2.1350
2.1261
2.1172
1.3207
1.3179
1.3089
1.3060
1.3035
1.2977
1.2936
1.2917
1.2863
1.2806
CO2Et
CO2Et
EtO2C
EtO2C
3sa
1.95
2.01
5.03
3.23
2.00
3.99
2.08
2.00
12.20
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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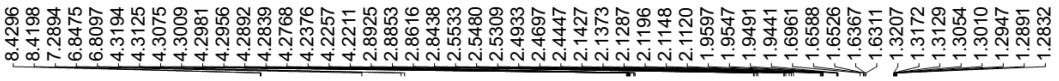
196.3602
170.7292
170.6996
169.7360
169.6938
142.4056
134.9842
134.9673
134.0250
133.9410
125.0547
125.0445
124.4789
124.4189
77.2118
77.0003
76.7885
66.3865
61.9199
61.9101
45.5539
45.5461
42.0379
41.9593
39.2167
39.2030
14.3878
14.0528
14.0299
-0.0404
CO2Et
CO2Et
EtO2C
EtO2C
3sa
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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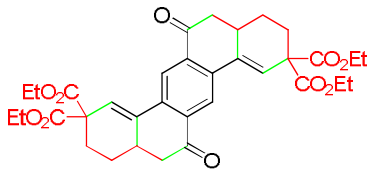
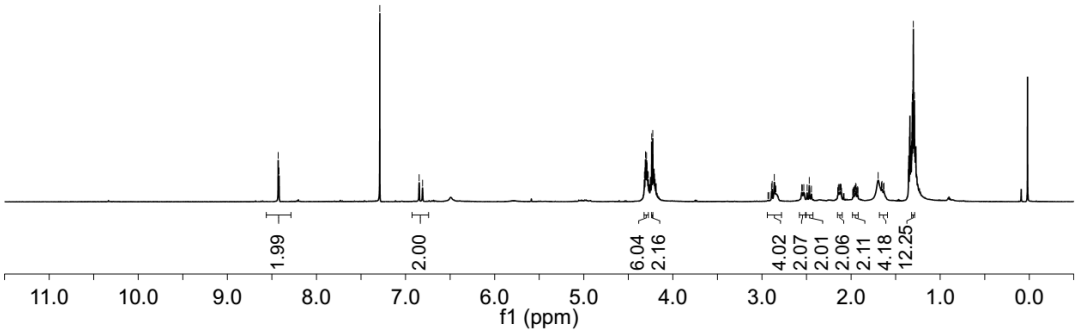
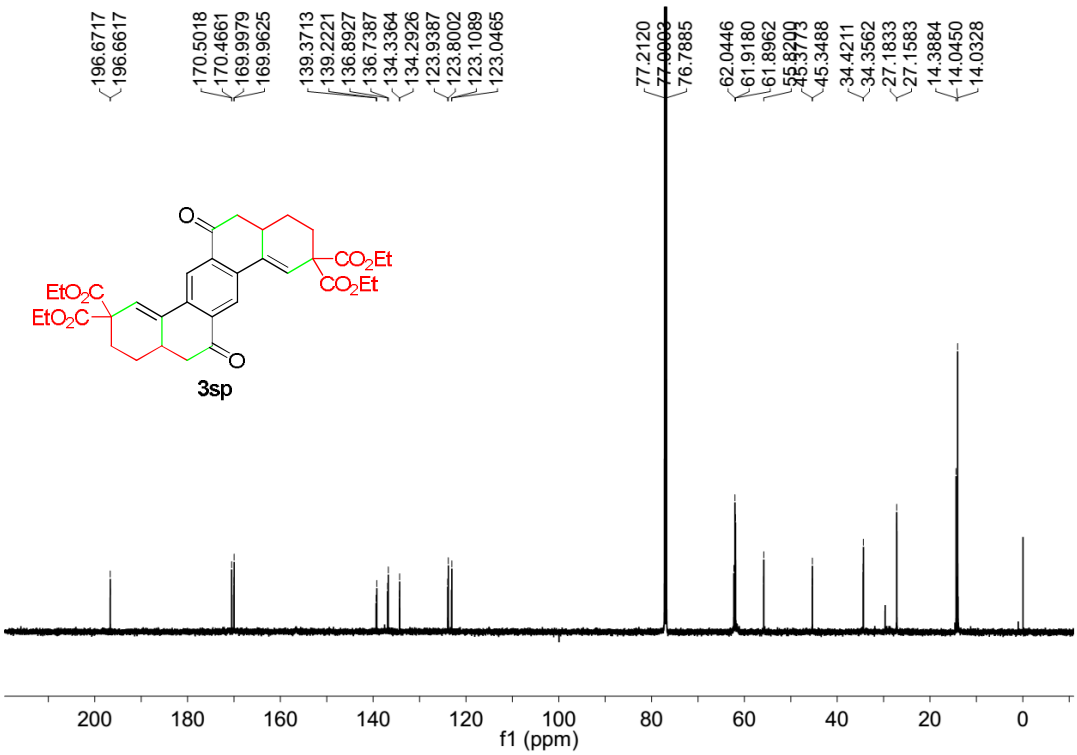
8.4198
7.2894
6.8475
6.8097
4.3194
4.3125
4.3075
4.3009
4.2981
4.2956
4.2892
4.2839
4.2768
4.2376
4.2257
4.2211
2.8925
2.8853
2.8616
2.8438
2.5533
2.5480
2.5309
2.4933
2.4697
2.4447
2.1427
2.1373
2.1287
2.1196
2.1148
2.1120
1.9597
1.9547
1.9491
1.9441
1.6961
1.6588
1.6526
1.6367
1.6311
1.3207
1.3172
1.3129
1.3054
1.3010
1.2947
1.2891
1.2832


O
CO2Et
CO2Et
EtO2C
EtO2C
O

3sp


1.99
2.00
6.04
2.16
4.02
2.07
2.01
2.06
2.11
4.18
12.25
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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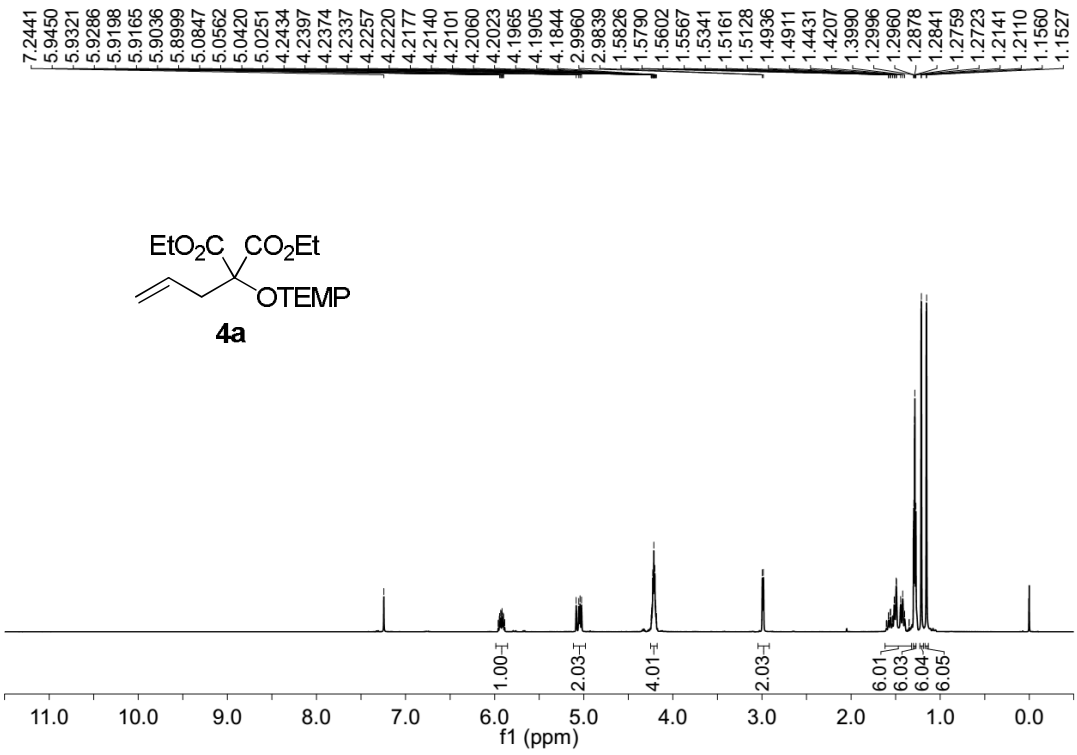
170.5018
170.4661
169.9979
169.9625
139.3713
139.2221
136.8927
136.7387
134.3364
134.2926
123.9387
123.8002
123.1089
123.0465
77.2120
77.0000
76.7885
62.0446
61.9180
61.8962
55.8200
45.3773
45.3488
34.4211
34.3562
27.1833
27.1583
14.3884
14.0450
14.0328
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

O
CO2Et
CO2Et
EtO2C
EtO2C
O

3sp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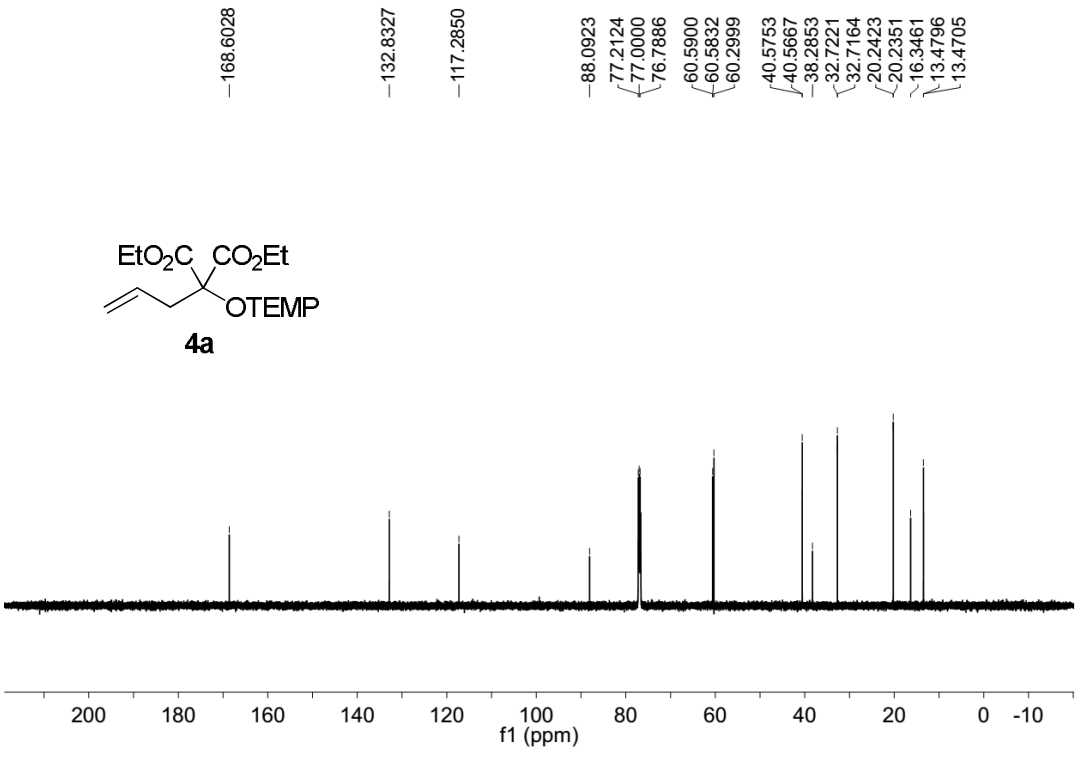
5.9450
5.9321
5.9286
5.9198
5.9165
5.9036
5.8999
5.0847
5.0562
5.0420
5.0251
4.2434
4.2397
4.2374
4.2337
4.2257
4.2220
4.2177
4.2140
4.2101
4.2060
4.2023
4.1965
4.1905
4.1844
2.9960
2.9839
1.5826
1.5790
1.5602
1.5567
1.5341
1.5161
1.5128
1.4936
1.4911
1.4431
1.4207
1.3990
1.2996
1.2960
1.2878
1.2841
1.2759
1.2723
1.2141
1.2110
1.1560
1.1527
EtO2C CO2Et
OTEMP
4a
1.00
2.03
4.01
2.03
6.01
6.03
6.04
6.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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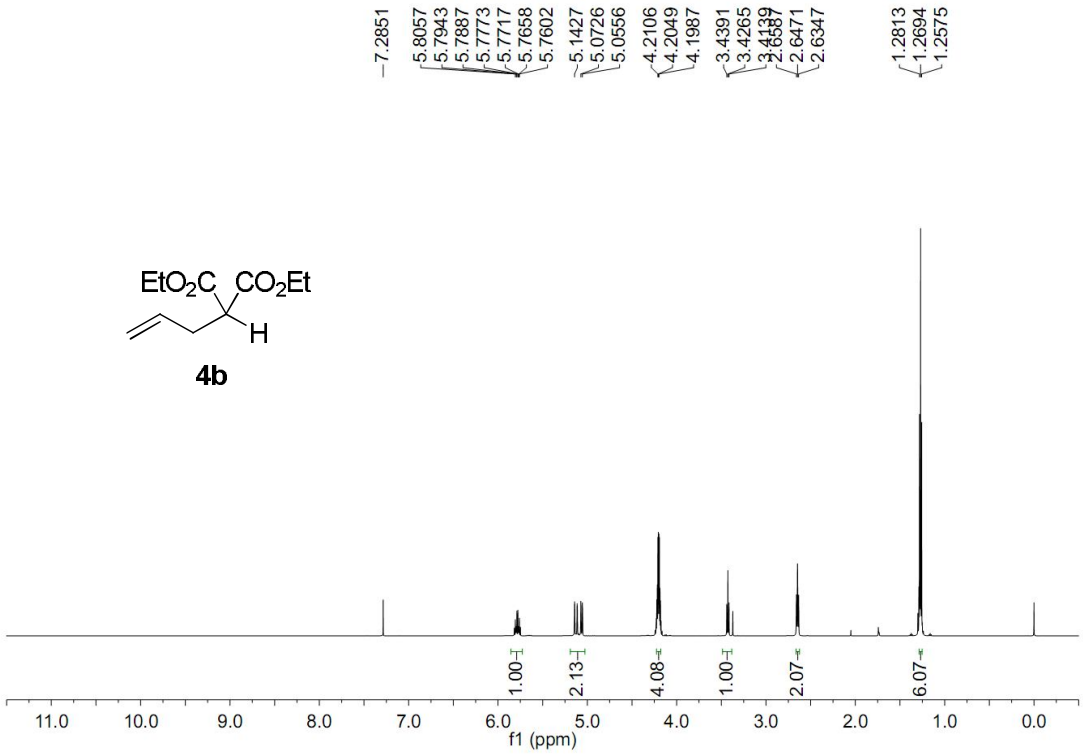
117.2850
88.0923
77.2124
77.0000
76.7886
60.5900
60.5832
60.2999
40.5753
40.5667
38.2853
32.7221
32.7164
20.2423
20.2351
16.3461
13.4796
13.4705
EtO2C CO2Et
OTEMP
4a
200
180
160
140
120
100
80
60
40
20
0
-10
f1 (ppm)


7.2851
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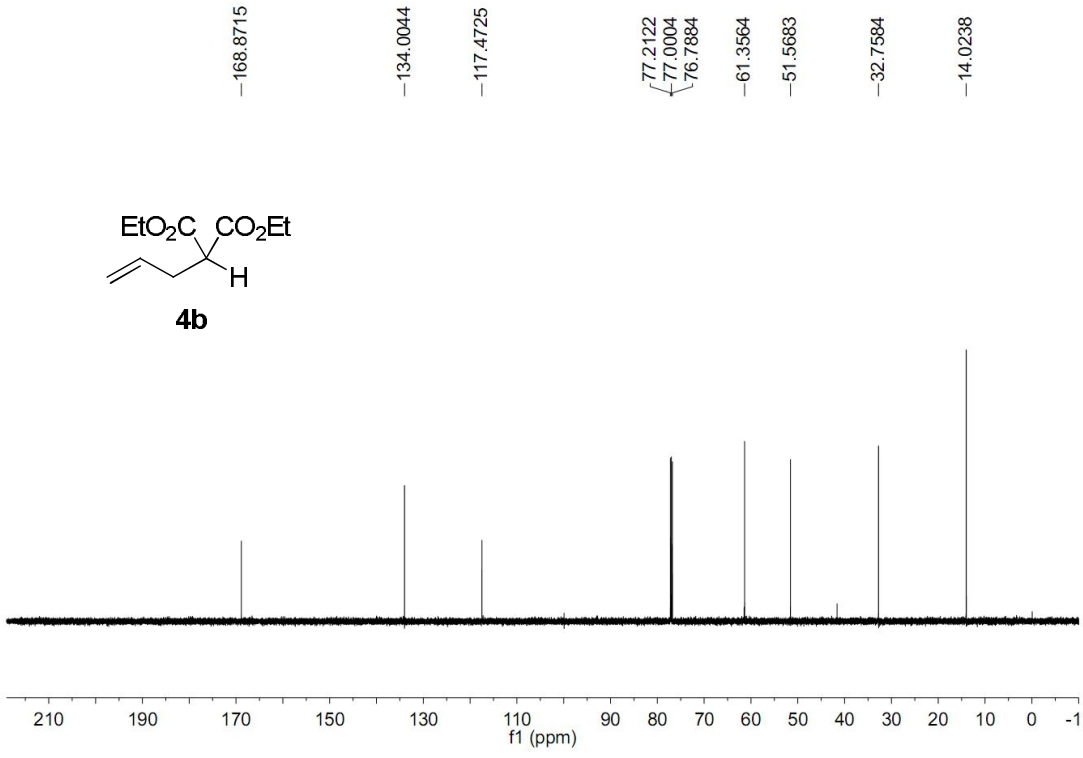
5.7943
5.7887
5.7773
5.7717
5.7658
5.7602
5.1427
5.0726
5.0556
4.2106
4.2049
4.1987
3.4391
3.4265
3.4139
2.6587
2.6471
2.6347
1.2813
1.2694
1.2575
EtO2C CO2Et
H
4b
1.00
2.13
4.08
1.00
2.07
6.07
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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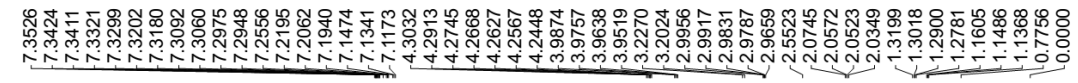
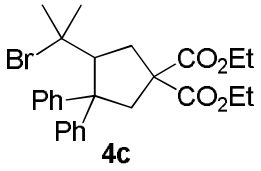
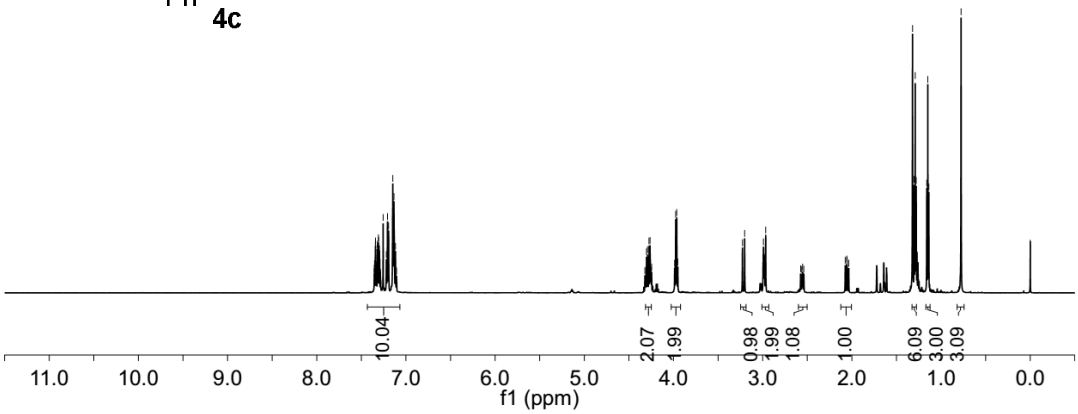
134.0044
117.4725
77.2122
77.0004
76.7884
61.3564
51.5683
32.7584
14.0238
EtO2C CO2Et
H
4b
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

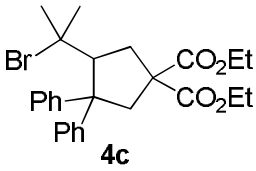

7.3526
7.3424
7.3411
7.3321
7.3299
7.3202
7.3180
7.3092
7.3060
7.2975
7.2948
7.2556
7.2195
7.2062
7.1940
7.1474
7.1341
7.1173
4.3032
4.2913
4.2745
4.2668
4.2627
4.2567
4.2448
3.9874
3.9757
3.9638
3.9519
3.2270
3.2024
2.9956
2.9917
2.9831
2.9787
2.9659
2.5523
2.0745
2.0572
2.0523
2.0349
1.3199
1.3018
1.2900
1.2781
1.1605
1.1486
1.1368
0.7756
0.0000


Br
CO2Et
CO2Et
Ph
Ph

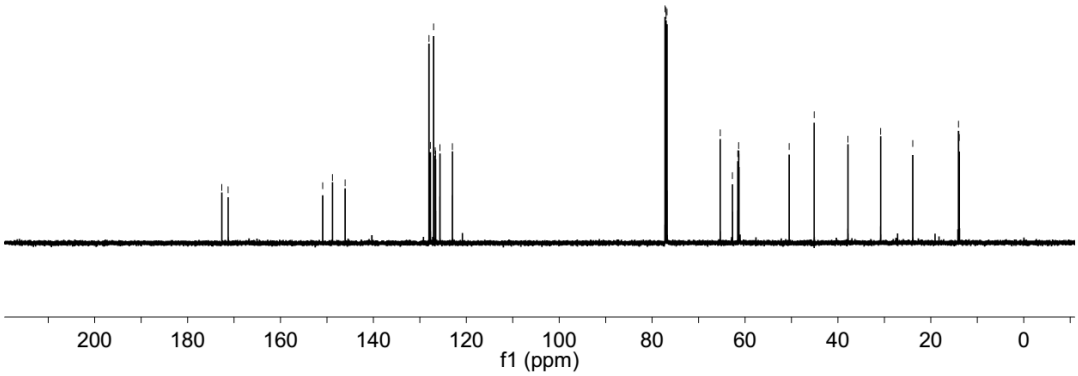
4c


10.04
2.07
1.99
0.98
1.99
1.08
1.00
6.09
3.00
3.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

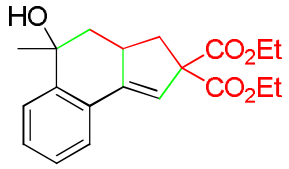

172.6293
171.2647
150.9122
148.8064
146.0907
128.0352
127.7295
127.0404
126.7008
126.6062
125.6718
122.9890
77.2118
77.0001
77.0000
76.7883
65.3384
61.5558
61.3708
50.4923
45.1140
37.8434
30.7952
23.8881
14.0425
13.8758


Br
CO2Et
CO2Et
Ph
Ph

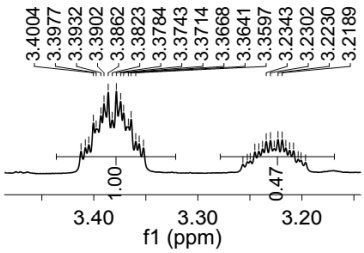
4c

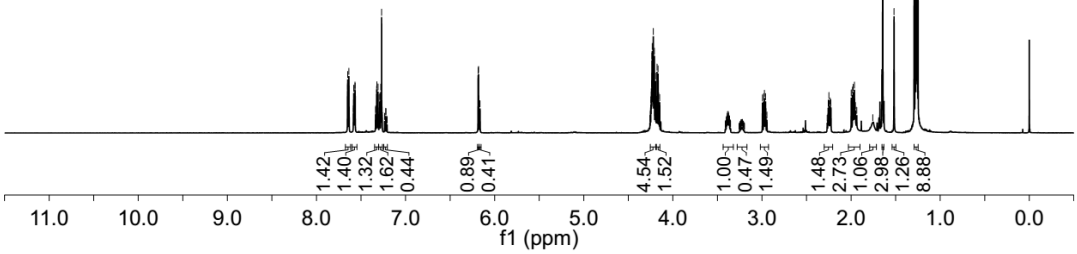

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

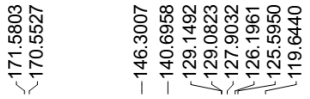

7.6509
7.6490
7.6382
7.6360
7.5810
7.5792
7.5679
7.5662
7.3244
7.3221
7.3092
7.2875
7.2770
7.2750
7.2693
6.1850
6.1809
4.2431
4.2392
4.2349
4.2313
4.2273
4.2256
4.2230
4.2195
4.2137
4.2111
4.2077
4.1958
4.1780
4.1662
4.1600
2.9822
2.9726
2.2486
1.9983
1.9839
1.9767
1.9622
1.6452
1.5180
1.2923
1.2805
1.2767
1.2716
1.2686
1.2648
1.2598
1.2530
1.2479

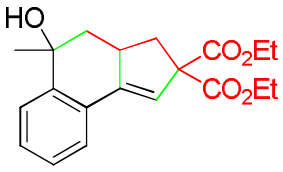

HO
CO2Et
CO2Et

6a

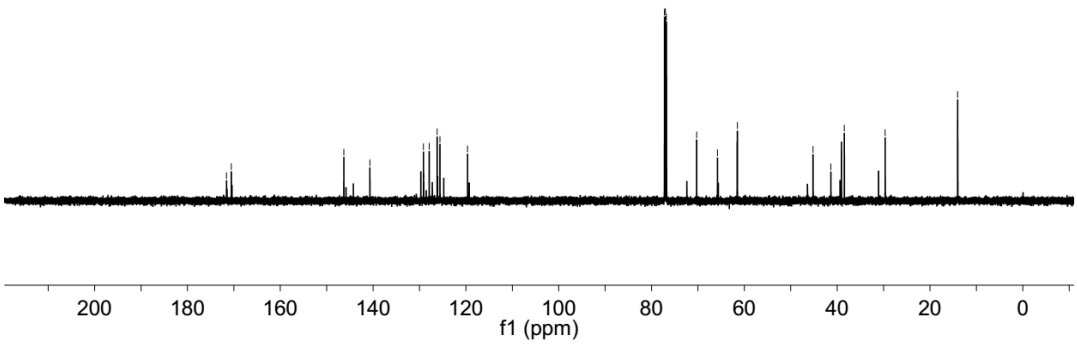

3.4004
3.3977
3.3932
3.3902
3.3862
3.3823
3.3784
3.3743
3.3714
3.3668
3.3641
3.3597
3.2343
3.2302
3.2230
3.2189
1.00
0.47
3.40
3.30
3.20
f1 (ppm)

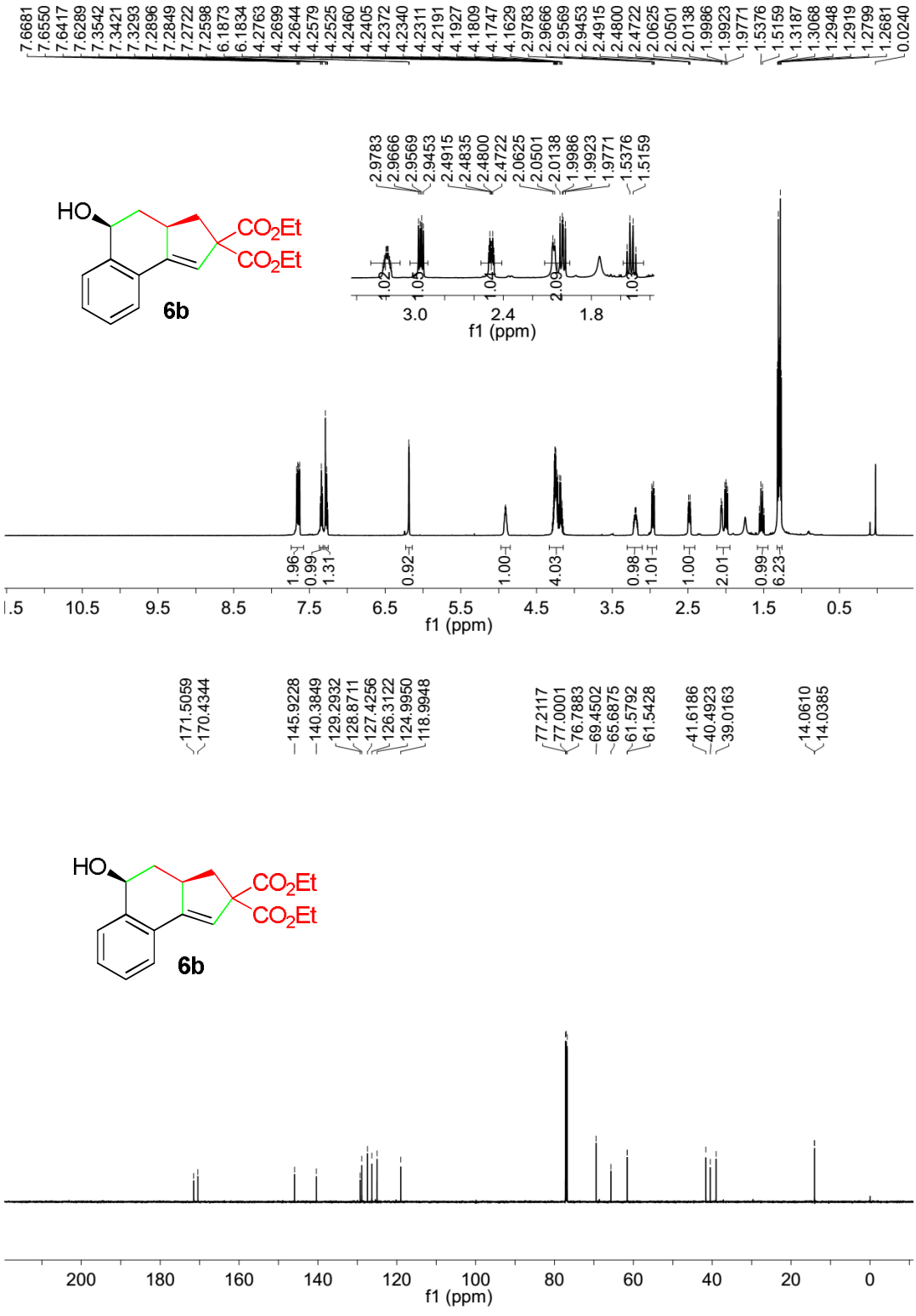

1.42
1.40
1.32
1.62
0.44
0.89
0.41
4.54
1.52
1.00
0.47
1.49
1.48
2.73
1.06
2.98
1.26
8.88
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


171.5803
170.5527
146.3007
140.6958
129.1492
129.0823
127.9032
126.1961
125.5950
119.6440
77.2113
76.9999
76.7879
70.2913
65.7921
61.5088
45.2080
41.3573
38.4646
29.6580
14.0390


HO
CO2Et
CO2Et

6a


200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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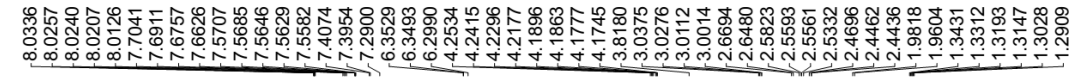
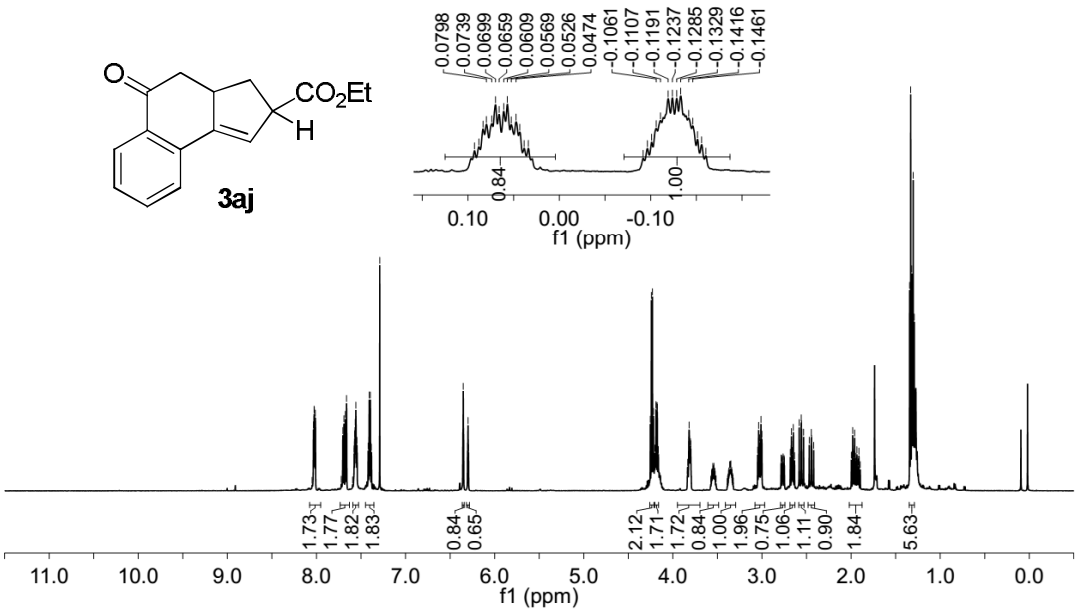
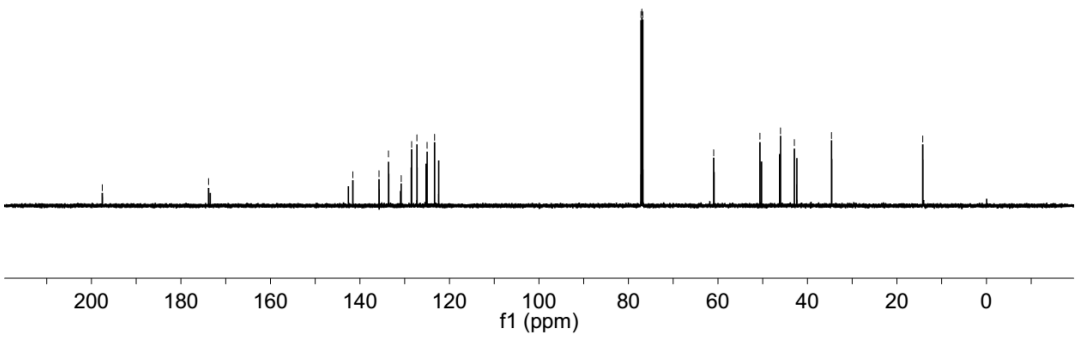
7.6550
7.6417
7.6289
7.3542
7.3421
7.3293
7.2896
7.2849
7.2722
7.2598
6.1873
6.1834
4.2763
4.2699
4.2644
4.2579
4.2525
4.2460
4.2405
4.2372
4.2340
4.2311
4.2191
4.1927
4.1809
4.1747
4.1629
2.9783
2.9666
2.9569
2.9453
2.4915
2.4835
2.4800
2.4722
2.0625
2.0501
2.0138
1.9986
1.9923
1.9771
1.5376
1.5159
1.3187
1.3068
1.2948
1.2919
1.2799
1.2681
0.0240
HO
CO2Et
CO2Et
6b
1.02
1.05
1.04
2.09
1.03
3.0
2.4
1.8
f1 (ppm)
1.96
0.99
1.31
0.92
1.00
4.03
0.98
1.01
1.00
2.01
0.99
6.23
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
171.5059
170.4344
145.9228
140.3849
129.2932
128.8711
127.4256
126.3122
124.9950
118.9948
77.2117
77.0001
76.7883
69.4502
65.6875
61.5792
61.5428
41.6186
40.4923
39.0163
14.0610
14.0385
HO
CO2Et
CO2Et
6b
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.0336
8.0257
8.0240
8.0207
8.0126
7.7041
7.6911
7.6757
7.6626
7.5707
7.5685
7.5646
7.5629
7.5582
7.4074
7.3954
7.2900
6.3529
6.3493
6.2990
4.2534
4.2415
4.2296
4.2177
4.1896
4.1863
4.1777
4.1745
3.8180
3.0375
3.0276
3.0112
3.0014
2.6694
2.6480
2.5823
2.5593
2.5561
2.5332
2.4696
2.4462
2.4436
1.9818
1.9604
1.3431
1.3312
1.3193
1.3147
1.3028
1.2909

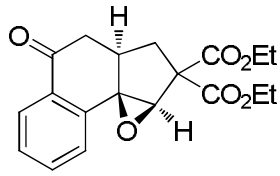

O
CO2Et
H
3aj
0.0798
0.0739
0.0699
0.0659
0.0609
0.0569
0.0526
0.0474
-0.1061
-0.1107
-0.1191
-0.1237
-0.1285
-0.1329
-0.1416
-0.1461
0.84
1.00
0.10
0.00
-0.10
f1 (ppm)
1.73
1.77
1.82
1.83
0.84
0.65
2.12
1.71
1.72
0.84
1.00
1.96
0.75
1.06
1.11
0.90
1.84
5.63
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


197.5820
173.8283
141.5949
135.7409
133.6160
130.7848
128.4479
127.2712
124.9926
123.3221
77.2112
76.9996
76.7878
60.9561
50.6266
46.0112
42.9224
34.6176
14.2320

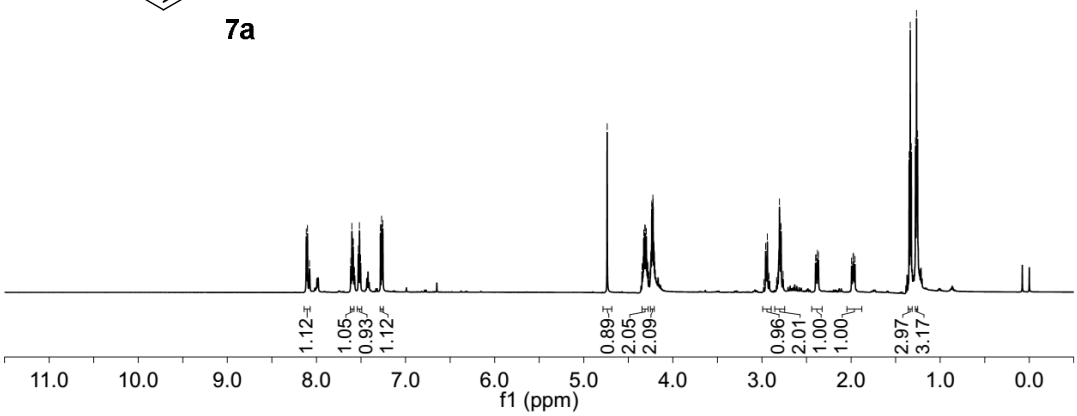

O
CO2Et
H
3aj


200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

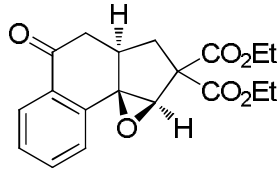

8.1144
8.1014
8.0775
7.6148
7.6023
7.5896
7.5881
7.5305
7.5177
7.5051
7.2821
7.2686
7.2559
4.7378
4.3328
4.3266
4.3216
4.3146
4.3099
4.3029
4.2980
4.2920
4.2486
4.2460
4.2369
4.2343
4.2250
4.2225
4.2134
4.2107
2.9594
2.9397
2.8114
2.8035
2.7918
2.7857
2.3986
2.3884
2.3775
2.3662
1.9945
1.9783
1.9731
1.9565
1.3482
1.3363
1.3245
1.2773
1.2654
1.2536


H
O
CO2Et
CO2Et
O
H

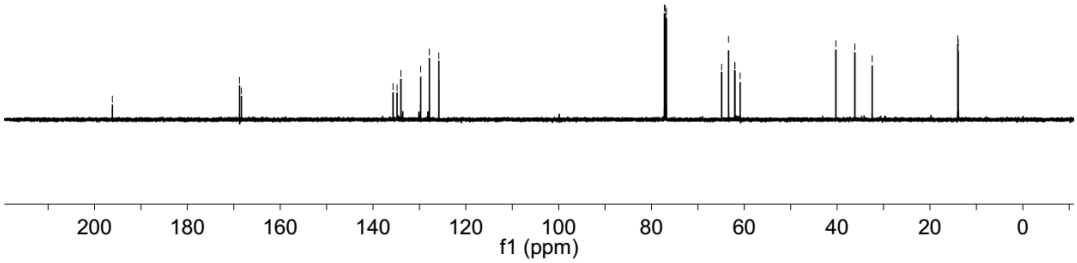
7a


1.12
1.05
0.93
1.12
0.89
2.05
2.09
0.96
2.01
1.00
1.00
2.97
3.17
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

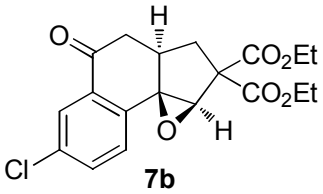

196.1544
168.7639
168.3480
135.6774
134.8270
133.9963
129.7312
127.8600
125.8209
77.2118
77.0000
76.7879
64.8923
63.3958
62.0740
62.0152
60.9024
40.2749
36.1829
32.4584
14.0116
13.9221


H
O
CO2Et
CO2Et
O
H

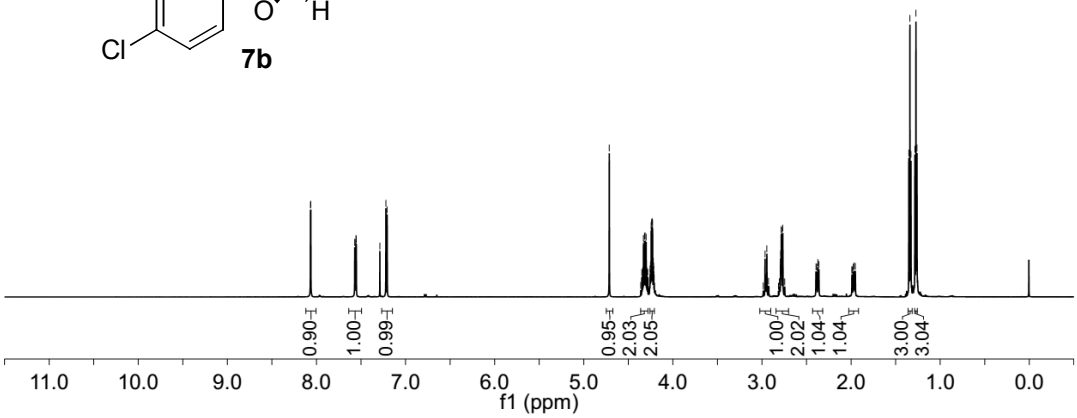
7a

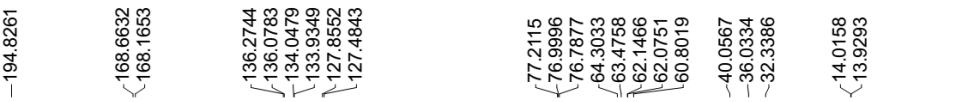

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

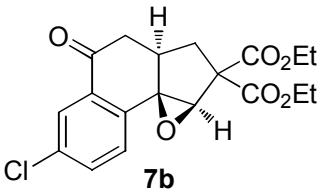

8.0673
8.0636
7.5704
7.5667
7.5567
7.5530
7.2887
7.2208
7.2071
4.7139
4.3482
4.3363
4.3302
4.3241
4.3183
4.3121
4.3063
4.3003
4.2942
4.2823
4.2555
4.2512
4.2436
4.2395
4.2317
4.2276
4.2200
4.2158
2.9657
2.9454
2.7900
2.7833
2.7809
2.7763
2.7668
2.3939
2.3839
2.3728
2.3615
1.9908
1.9879
1.9740
1.9688
1.9524
1.3519
1.3400
1.3282
1.2841
1.2722
1.2604


H
O
CO2Et
CO2Et
O
H
Cl

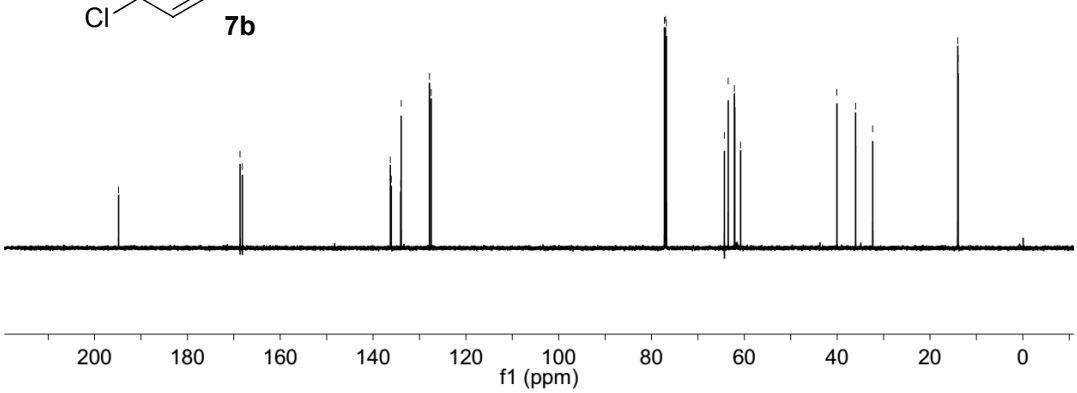
7b

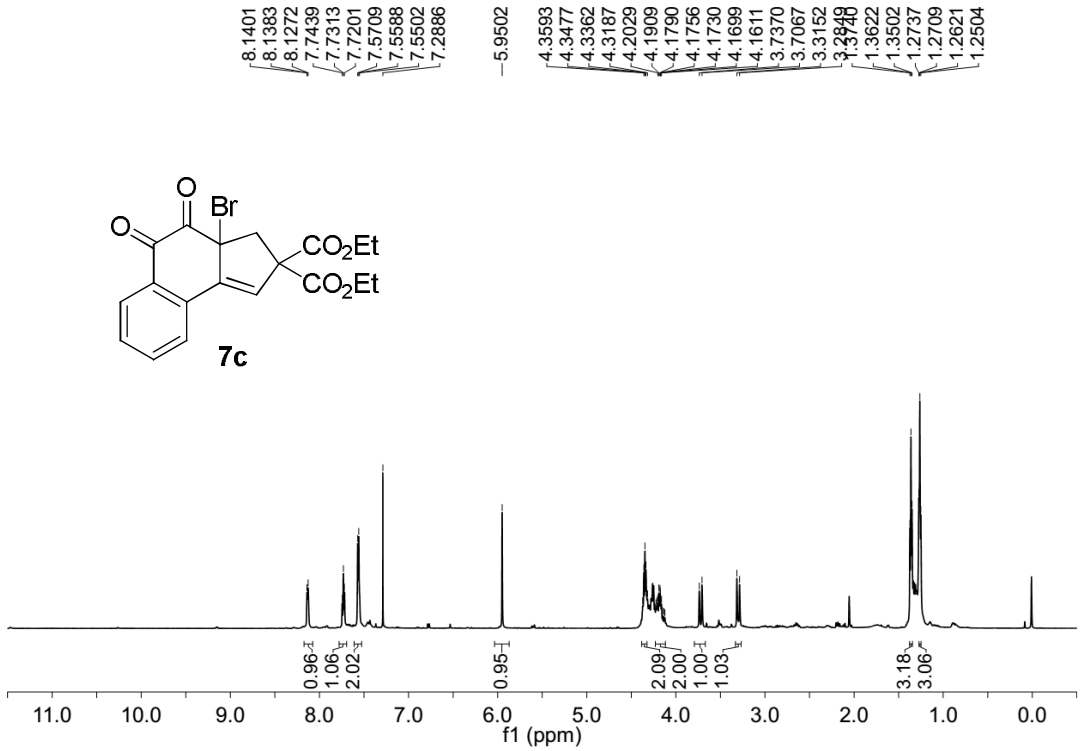

0.90
1.00
0.99
0.95
2.03
2.05
1.00
2.02
1.04
1.04
3.00
3.04
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

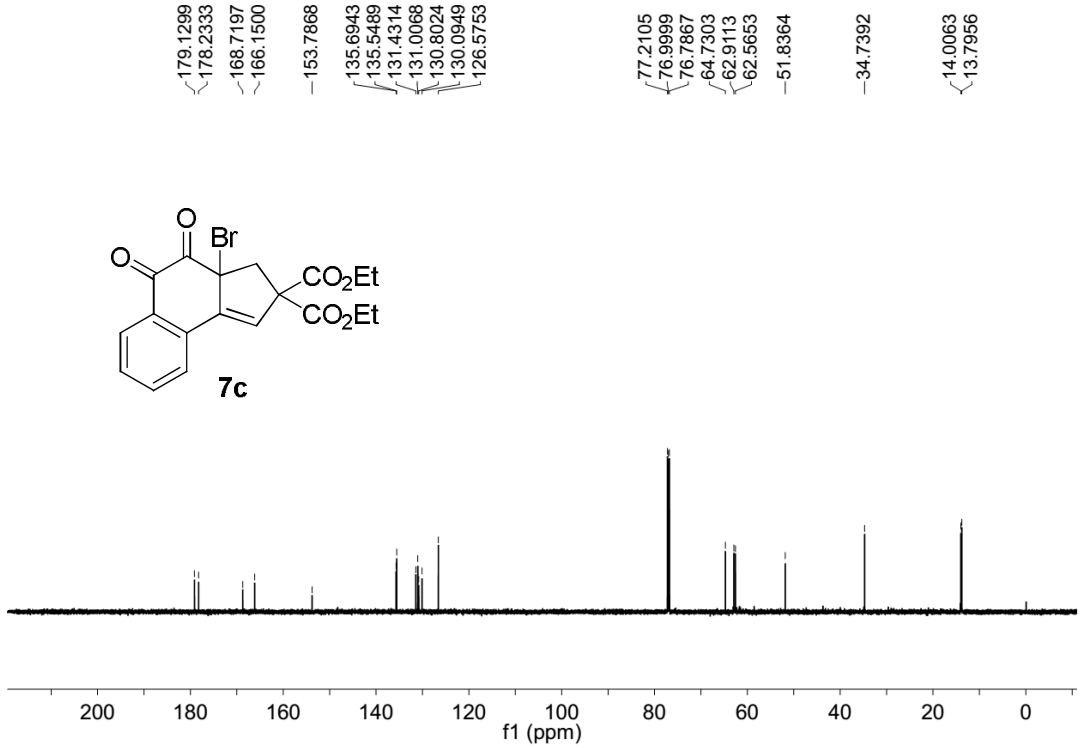

194.8261
168.6632
168.1653
136.2744
136.0783
134.0479
133.9349
127.8552
127.4843
77.2115
76.9996
76.7877
64.3033
63.4758
62.1466
62.0751
60.8019
40.0567
36.0334
32.3386
14.0158
13.9293

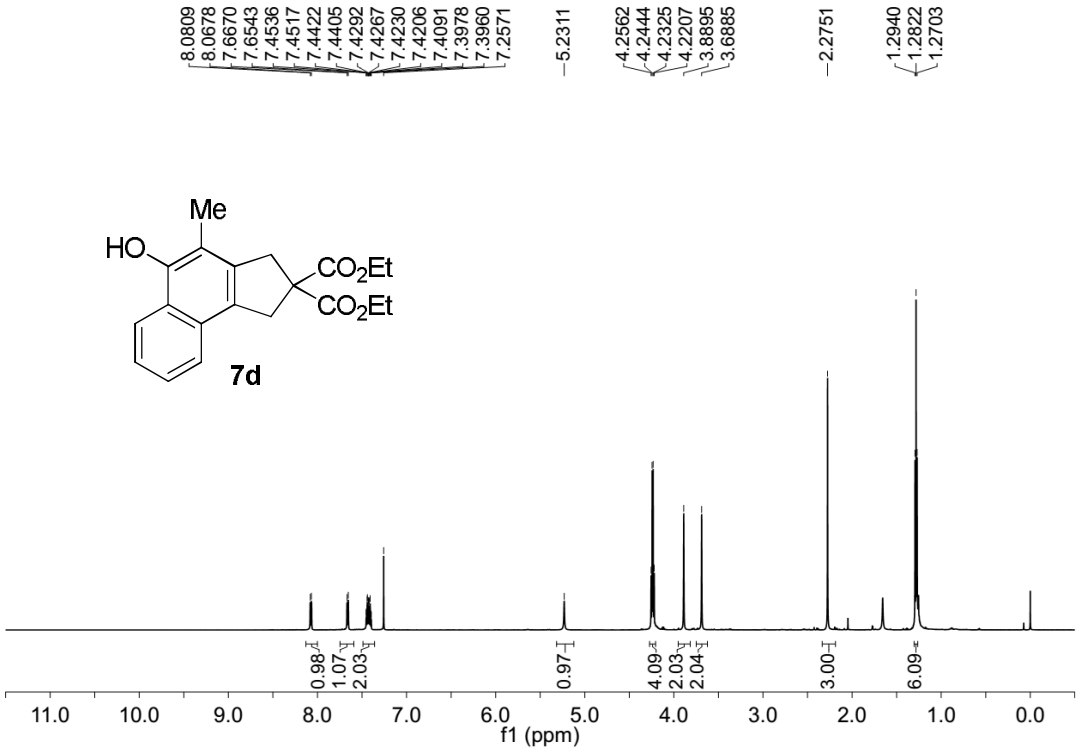

H
O
CO2Et
CO2Et
O
H
Cl

7b


200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.1401
8.1383
8.1272
7.7439
7.7313
7.7201
7.5709
7.5588
7.5502
7.2886
5.9502
4.3593
4.3477
4.3362
4.3187
4.2029
4.1909
4.1790
4.1756
4.1730
4.1699
4.1611
3.7370
3.7067
3.3152
1.3622
1.3502
1.2737
1.2709
1.2621
1.2504
O
Br
O
CO2Et
CO2Et
7c
0.96
1.06
2.02
0.95
2.09
2.00
1.00
1.03
3.18
3.06
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


179.1299
178.2333
168.7197
166.1500
153.7868
135.6943
135.5489
131.4314
131.0068
130.8024
130.0949
126.5753
77.2105
76.9999
76.7867
64.7303
62.9113
62.5653
51.8364
34.7392
14.0063
13.7956
O
Br
O
CO2Et
CO2Et
7c
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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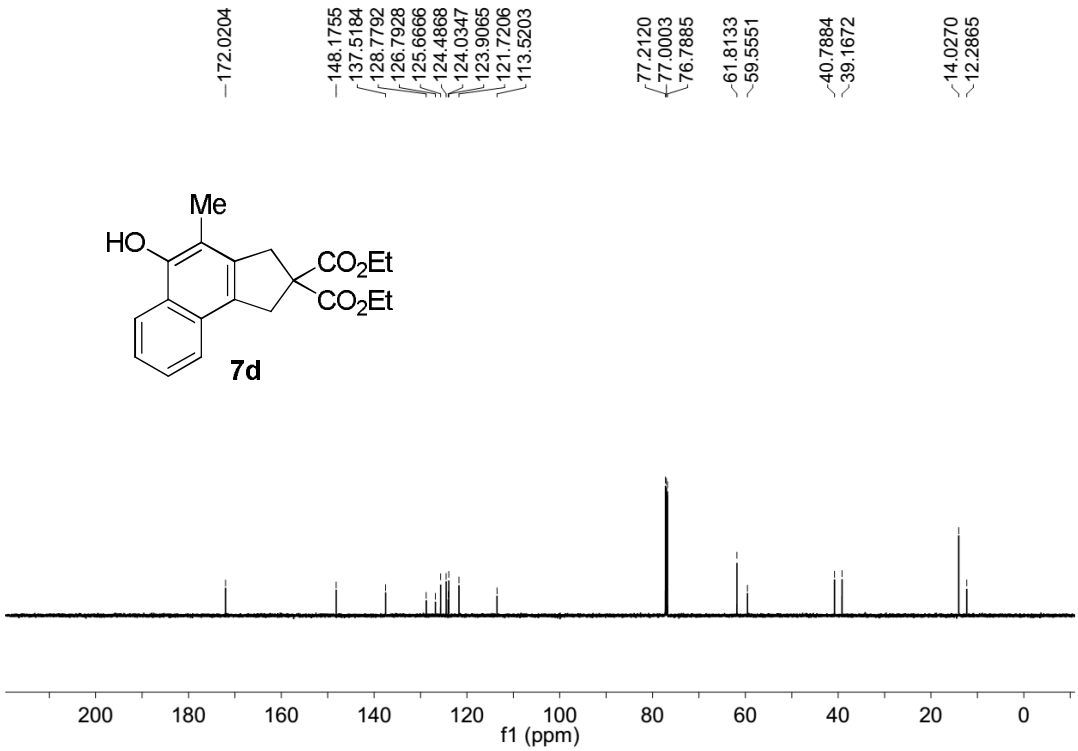
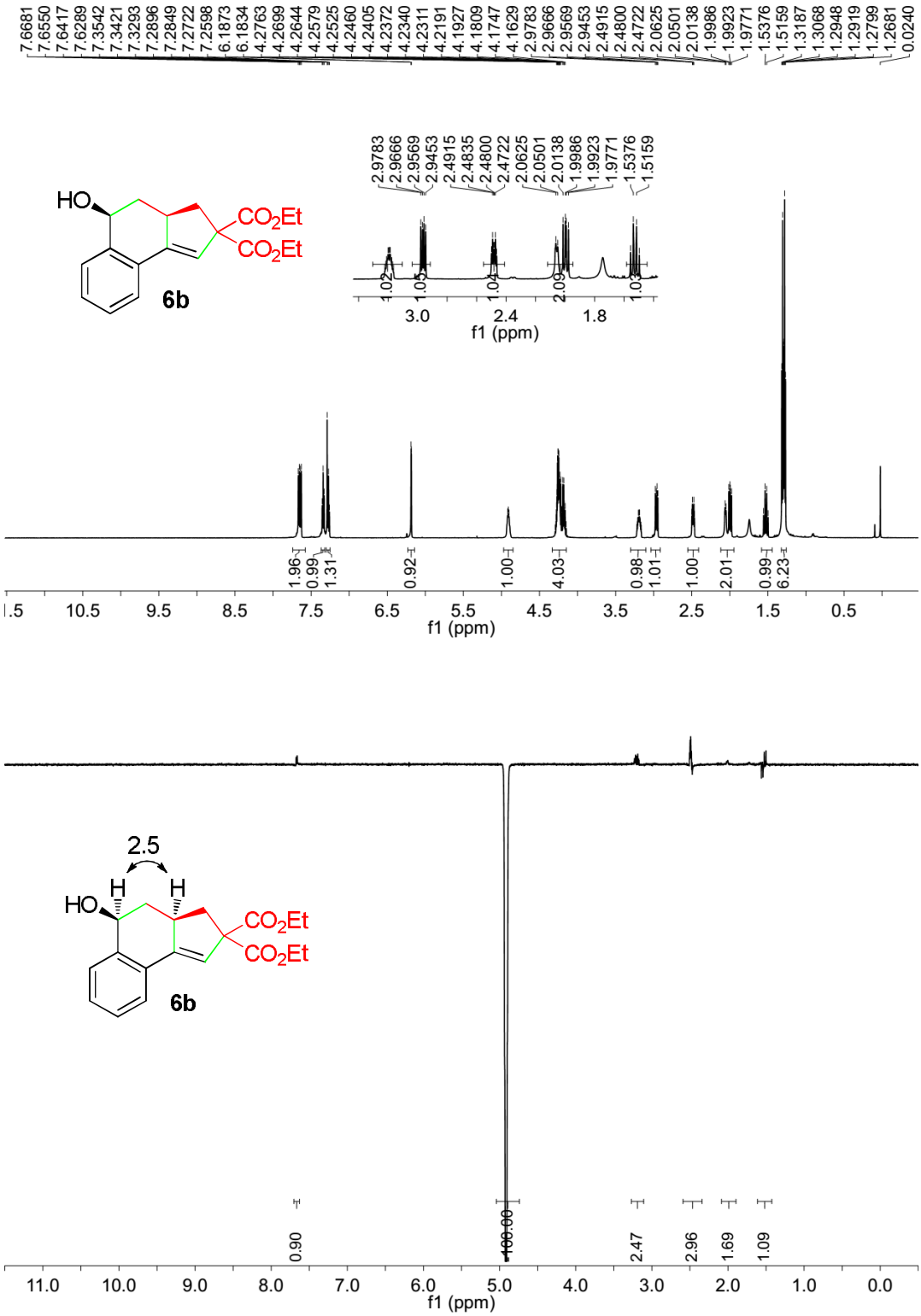
8.0678
7.6670
7.6543
7.4536
7.4517
7.4422
7.4405
7.4292
7.4267
7.4230
7.4206
7.4091
7.3978
7.3960
7.2571
5.2311
4.2562
4.2444
4.2325
4.2207
3.8895
3.6885
2.2751
1.2940
1.2822
1.2703
Me
HO
CO2Et
CO2Et
7d
0.98
1.07
2.03
0.97
4.09
2.03
2.04
3.00
6.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


172.0204
148.1755
137.5184
128.7792
126.7928
125.6666
124.4868
124.0347
123.9065
121.7206
113.5203
77.2120
77.0003
76.7885
61.8133
59.5551
40.7884
39.1672
14.0270
12.2865
Me
HO
CO2Et
CO2Et
7d
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.6681
7.6550
7.6417
7.6289
7.3542
7.3421
7.3293
7.2896
7.2849
7.2722
7.2598
6.1873
6.1834
4.2763
4.2699
4.2644
4.2579
4.2525
4.2460
4.2405
4.2372
4.2340
4.2311
4.2191
4.1927
4.1809
4.1747
4.1629
2.9783
2.9666
2.9569
2.9453
2.4915
2.4835
2.4800
2.4722
2.0625
2.0501
2.0138
1.9986
1.9923
1.9771
1.5376
1.5159
1.3187
1.3068
1.2948
1.2919
1.2799
1.2681
0.0240
HO
CO2Et
CO2Et
6b
1.02
1.05
1.04
2.09
1.03
3.0
2.4
1.8
f1 (ppm)
1.96
0.99
1.31
0.92
1.00
4.03
0.98
1.01
1.00
2.01
0.99
6.23
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
2.5
H
H
HO
CO2Et
CO2Et
6b
0.90
100.00
2.47
2.96
1.69
1.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)