

Supporting Information to

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

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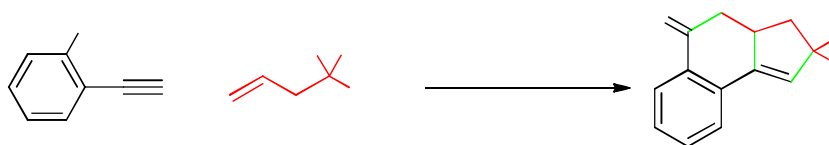
gangguo@zjnu.cn

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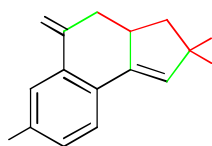
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General. Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. ^1H , ^{13}C , and ^{19}F NMR spectra were measured on a 600 MHz or 400 MHz NMR spectrometer using CDCl_3 as the solvent 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:

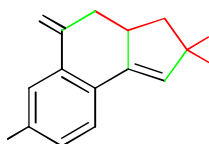


To a mixture of $\text{Cu}(\text{OAc})_2$ (4.5 mg, 0.025 mmol), pentamethyldiethylenetriamine (**L1**) (8.7 mg, 0.050 mmol), DEAD (8.7 mg, 0.050 mmol) and K_2CO_3 (34.6 mg, 0.25 mmol) was added a solution of **1a** (32.5 mg, 0.25 mmol) and **2a** (83.4 mg, 0.30 mmol) in 3 mL of MeCN under a nitrogen atmosphere. After stirring at 80 °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. ^1H 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 $\text{C}_{19}\text{H}_{21}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 329.1389, found 329.1392.

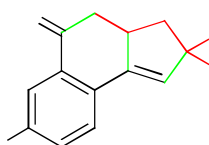


Compound **3ba**. 76% yield (73 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 1.24–1.30 (m, 6H), 2.12 (dd, $J = 8.4, 13.3$ Hz, 1H), 2.49 (dd, $J = 13.9, 15.8$ Hz, 1H), 2.90–3.10 (m, 2H),

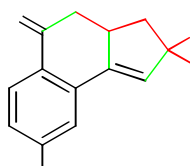
3.42–3.59 (m, 1H), 3.91 (s, 3H), 4.13–4.26 (m, 4H), 6.48 (d, $J = 2.3$ Hz, 1H), 7.72–7.80 (m, 1H), 8.14–8.18 (m, 1H), 8.58–8.61 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 13.9, 13.9, 39.1, 42.0, 45.3, 52.2, 61.8, 61.9, 66.3, 125.0, 125.7, 128.8, 130.5, 130.9, 133.9, 138.6, 142.8, 165.8, 169.5, 170.5, 195.8; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{O}_7$ ($\text{M} + \text{H}$) $^+$ 387.1444, found 387.1437.



Compound **3ca**. 75% yield (74 mg); white solid, mp 97–99°C; ^1H 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 $\text{C}_{20}\text{H}_{20}\text{F}_3\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 397.1263, found 397.1255.

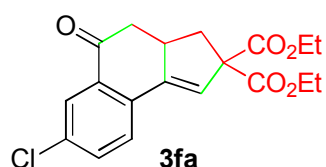


Compound **3da**. 81% yield (70 mg); white solid, mp 96–98°C; ^1H NMR (600 MHz, CDCl_3) δ 1.26–1.33 (m, 6H), 2.13 (dd, $J = 8.4, 13.3$ Hz, 1H), 2.50 (dd, $J = 13.9, 15.8$ Hz, 1H), 3.01–3.10 (m, 2H), 3.49–3.58 (m, 1H), 4.19–4.30 (m, 4H), 6.33 (d, $J = 2.2$ Hz, 1H), 7.26–7.30 (m, 1H), 7.60–7.74 (m, 2H); ^{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 $\text{C}_{19}\text{H}_{20}\text{FO}_5$ ($\text{M} + \text{H}$) $^+$ 347.1295, found 347.1293.



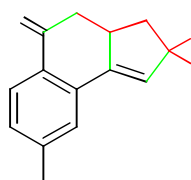
Compound **3ea**. 76% yield (69 mg); white solid, mp 141–143°C; ^1H NMR (600 MHz, CDCl_3) δ

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 $\text{C}_{19}\text{H}_{20}\text{ClO}_5$ ($\text{M} + \text{H}$) $^+$ 363.0999, found 363.0995.



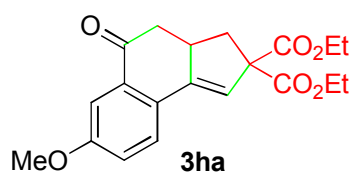
Compound **3fa**. 80% yield (73 mg); white solid, mp 136–138°C; ^1H NMR (600 MHz, CDCl_3) δ 1.26–1.32 (m, 6H), 2.12 (dd, $J = 8.4, 13.3$ Hz, 1H), 2.48 (dd, $J = 13.9, 15.8$ Hz, 1H), 2.98–3.09 (m, 2H), 3.46–3.56 (m, 1H), 4.15–4.30 (m, 4H), 6.37 (d, $J = 2.3$ Hz, 1H), 7.51 (dd, $J = 2.3, 8.4$ Hz, 1H), 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 $\text{C}_{19}\text{H}_{20}\text{ClO}_5$ ($\text{M} + \text{H}$) $^+$ 363.0999, found 363.0988.

Crystal data for **3fa** ($\text{C}_{19}\text{H}_{19}\text{ClO}_5$, 362.79): triclinic, space group $P\bar{1}$, $a = 7.9475(16)$ 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 [$R(\text{int}) = 0.047$], 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 [$I > 2\sigma(I)$] $R_1 = 0.0619$, $wR_2 = 0.1631$, R indices (all data) $R_1 = 0.0832$, $wR_2 = 0.1874$, largest diff. peak and hole 0.376 and -0.358e^{-3} Å $^{-3}$. Crystallographic data for the structure **3fa** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC1439849.

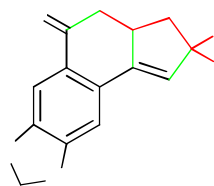


Compound **3ga**. 81% yield (69 mg); white solid, mp 91–93°C; ^1H NMR (400 MHz, CDCl_3) δ 1.26–1.33 (m, 6H), 2.11 (dd, $J = 8.4, 13.3$ Hz, 1H), 2.40–2.51 (m, 4H), 2.91–3.10 (m, 2H), 3.40–3.60 (m, 1H), 4.15–4.30 (m, 4H), 6.35 (d, $J = 2.3$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.50 (s, 1H), 7.91 (d, $J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

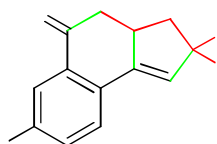
61.7, 61.8, 66.2, 122.1, 125.7, 127.4, 128.9, 130.1, 135.1, 143.8, 144.5, 170.0, 171.0, 196.7;
HRMS (ESI) calcd for C₂₀H₂₃O₅ (M + H)⁺ 343.1545, found 343.1538.



Compound **3ha**. 90% yield (81 mg); white solid, mp 101–103°C; ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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 C₂₀H₂₃O₆ (M + H)⁺ 359.1495, found 359.1489.

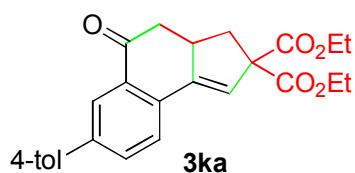


Compound **3ia**. 84% yield (78 mg); white solid, mp 135–137°C; ¹H NMR (400 MHz, CDCl₃) δ 1.24–1.31 (m, 6H), 2.08 (dd, *J* = 8.5, 13.3 Hz, 1H), 2.43 (dd, *J* = 13.7, 15.8 Hz, 1H), 2.90–3.10 (m, 2H), 3.40–3.53 (m, 1H), 4.15–4.30 (m, 4H), 6.04 (s, 2H), 6.22 (d, *J* = 2.3 Hz, 1H), 7.05 (s, 1H), 7.41 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) 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 C₂₀H₂₁O₇ (M + H)⁺ 373.1287, found 373.1293.

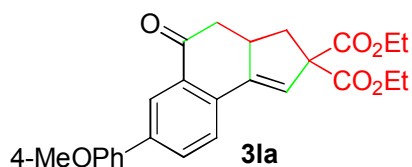


Compound **3ja**. 73% yield (74 mg); white solid, mp 81–83°C; ¹H NMR (600 MHz, CDCl₃) δ 1.26–1.33 (m, 6H), 2.14 (dd, *J* = 8.5, 13.2 Hz, 1H), 2.54 (dd, *J* = 14.0, 15.5 Hz, 1H), 3.02–3.10 (m, 2H), 3.52–3.59 (m, 1H), 4.19–4.29 (m, 4H), 6.41 (d, *J* = 2.3 Hz, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 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); ¹³C NMR (151 MHz, CDCl₃) δ 14.0, 14.1, 39.3, 42.3, 45.7, 61.8, 61.9, 66.3, 122.4, 125.6, 126.1,

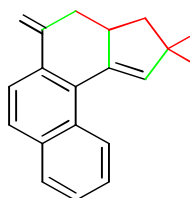
127.0, 128.0, 128.9, 131.4, 132.2, 133.9, 139.5, 141.8, 143.4, 170.0, 171.0, 197.0; HRMS (ESI) calcd for C₂₅H₂₅O₅ (M + H)⁺ 405.1702, found 405.1693.



Compound **3ka**. 79% yield (83 mg); white solid, mp 87–89°C; ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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 C₂₆H₂₇O₅ (M + H)⁺ 419.1858, found 419.1850.

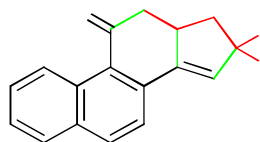


Compound **3la**. 83% yield (90 mg); white solid, mp 99–101°C; ¹H NMR (600 MHz, CDCl₃) δ 1.26–1.33 (m, 6H), 2.13 (dd, *J* = 8.5, 13.2 Hz, 1H), 2.53 (dd, *J* = 13.9, 15.6 Hz, 1H), 3.00–3.09 (m, 2H), 3.52–3.59 (m, 1H), 3.86 (s, 3H), 4.16–4.29 (m, 4H), 6.38 (d, *J* = 2.3 Hz, 1H), 6.90–7.01 (m, 2H), 7.57–7.60 (m, 2H), 7.70–7.80 (m, 2H), 8.20–8.22 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) 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 C₂₆H₂₇O₆ (M + H)⁺ 435.1808, found 435.1799.

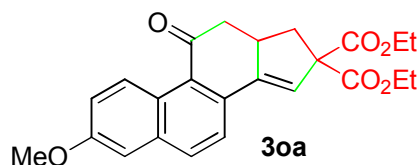


Compound **3ma**. 72% yield (68 mg); white solid, mp 133–135°C; ¹H NMR (600 MHz, CDCl₃) δ 1.27 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 2.49 (dd, *J* = 4.3, 14.2 Hz, 1H), 2.72 (dd, *J* = 13.4, 16.5 Hz, 1H), 2.90 (dd, *J* = 8.7, 14.2 Hz, 1H), 3.15 (dd, *J* = 5.8, 16.5 Hz, 1H), 3.60–3.68 (m,

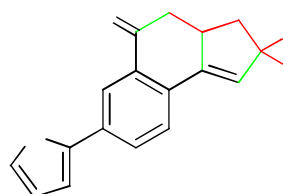
1H), 4.18–4.40 (m, 4H), 6.50 (d, $J = 1.5$ Hz, 1H), 7.60–7.65 (m, 2H), 7.80–7.89 (m, 2H), 8.00–8.10 (m, 1H), 8.56–8.60 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 14.0, 14.1, 36.4, 45.8, 47.4, 61.9, 62.0, 67.8, 122.7, 127.0, 127.4, 127.7, 128.6, 128.7, 128.9, 129.6, 129.6, 136.0, 136.3, 142.3, 170.8, 171.1, 197.0; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 379.1545, found 379.1547.



Compound **3na**. 74% yield (70 mg); white solid, mp 151–153°C; ^1H 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 $\text{C}_{23}\text{H}_{23}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 379.1545, found 379.1548.

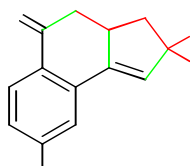


Compound **3oa**. 78% yield (80 mg); white solid, mp 176–178°C; ^1H NMR (600 MHz, CDCl_3) δ 1.27–1.33 (m, 6H), 2.14 (dd, $J = 8.5, 13.1$ Hz, 1H), 2.71 (t, $J = 14.1$ Hz, 1H), 3.00–3.08 (m, 2H), 3.60–3.67 (m, 1H), 3.93 (s, 3H), 4.17–4.29 (m, 4H), 6.42 (d, $J = 2.2$ Hz, 1H), 7.11 (d, $J = 2.7$ Hz, 1H), 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 $\text{C}_{24}\text{H}_{25}\text{O}_6$ ($\text{M} + \text{H}$) $^+$ 409.1651, found 409.1642.

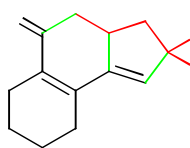


Compound **3pa**. 68% yield (70 mg); white solid, mp 133–135°C; ^1H NMR (600 MHz, CDCl_3) δ 1.26–1.33 (m, 6H), 2.12 (dd, $J = 8.5, 13.2$ Hz, 1H), 2.49–2.55 (m, 1H), 3.00–3.09 (m, 2H), 3.50–3.57 (m, 1H), 4.16–4.30 (m, 4H), 6.38 (d, $J = 2.1$ Hz, 1H), 7.11 (dd, $J = 3.7, 5.0$ Hz, 1H),

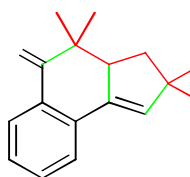
7.34 (d, $J = 5.1$ Hz, 1H), 7.42 (d, $J = 3.6$ Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.79 (dd, $J = 1.8, 8.2$ Hz, 1H), 8.23 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 14.0, 14.1, 39.2, 42.3, 45.6, 61.8; 61.9, 66.3, 122.4, 124.0, 124.1, 125.8, 126.2, 128.3, 130.7, 131.4, 133.8, 135.2, 142.8, 143.3, 167.0, 171.0, 196.8; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{O}_5\text{S}$ ($\text{M} + \text{H}$) $^+$ 411.1266, found 411.1258.



Compound **3qa**. 64% yield (76 mg); white solid, mp 64–66°C; ^1H 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 $\text{C}_{27}\text{H}_{24}\text{NO}_7$ ($\text{M} + \text{H}$) $^+$ 474.1553, found 474.1552.

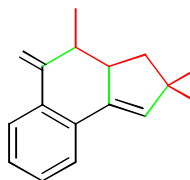


Compound **3ra**. 80% yield (66 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 1.24–1.30 (m, 6H), 1.51–1.63 (m, 2H), 1.70–1.80 (m, 2H), 1.96 (dd, $J = 9.2, 13.1$ Hz, 1H), 2.16–2.21 (m, 1H), 2.28 (dd, $J = 13.6, 15.7$ Hz, 1H), 2.30–2.50 (m, 2H), 2.52–2.57 (m, 1H), 2.77 (dd, $J = 5.9, 15.7$ Hz, 1H), 2.93 (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 $\text{C}_{19}\text{H}_{25}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 333.1702, found 333.1697.

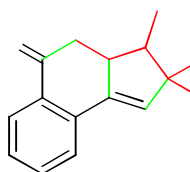


Compound **3ab**. 92% yield (82 mg); white solid, mp 86–88°C; ^1H NMR (400 MHz, CDCl_3) δ 0.94 (s, 3H), 1.24 (s, 3H), 1.26–1.33 (m, 6H), 2.35 (dd, $J = 8.2, 13.8$ Hz, 1H), 2.80 (dd, $J = 8.2, 13.8$

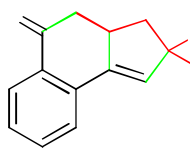
Hz, 1H), 3.34–3.39 (m, 1H), 4.16–4.31 (m, 4H), 6.39 (d, $J = 2.4$ Hz, 1H), 7.38–7.44 (m, 1H), 7.51–7.56 (m, 1H), 7.66–7.70 (m, 1H), 7.97–8.01 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 14.0, 18.9, 21.8, 31.9, 45.9, 51.9, 61.7, 61.8, 66.3, 122.8, 125.0, 128.2, 129.2, 129.9, 133.1, 134.3, 142.4, 170.3, 171.0, 202.5; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 357.1702, found 357.1697.



Compound **3ac**. 80% yield (69 mg); colorless oil; dr = 88:12; ^1H NMR (600 MHz, CDCl_3) date of the major isomer δ 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 isomer δ 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 $\text{C}_{20}\text{H}_{23}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 343.1545, found 343.1540.

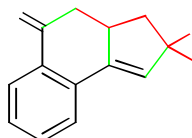


Compound **3af**. 39% yield (33 mg); colorless oil; dr = 61:39; ^1H NMR (600 MHz, CDCl_3) date of the major isomer δ 1.22–1.36 (m, 9H), 2.45 (dd, $J = 13.8, 15.4$ Hz, 1H), 2.62–2.78 (m, 1H), 3.02 (dd, $J = 5.5, 15.5$ Hz, 1H), 3.08–3.17 (m, 1H), 4.13–4.35 (m, 4H), 6.40 (d, $J = 2.2$ Hz, 1H), 7.37–7.43 (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 $\text{C}_{20}\text{H}_{22}\text{NaO}_5$ ($\text{M} + \text{Na}$) $^+$ 365.1365, found 365.1358.

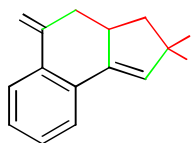


Compound **3ag**. 76% yield (51 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 1.92 (dd, $J = 8.5, 13.0$ Hz, 1H), 2.22 (s, 3H), 2.23 (s, 3H), 2.46 (dd, $J = 13.8, 15.7$ Hz, 1H), 3.02 (dd, $J = 5.5, 15.7$

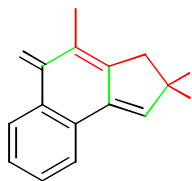
Hz, 1H), 3.14 (dd, $J = 7.3, 13.0$ Hz, 1H), 3.37–3.44 (m, 1H), 6.56 (d, $J = 2.4$ Hz, 1H), 7.42–7.45 (m, 1H), 7.55–7.60 (m, 1H), 7.70 (d, $J = 7.5$ Hz, 1H), 8.02 (dd, $J = 1.0, 7.9$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 27.0, 27.1, 37.1, 42.1, 45.7, 80.9, 122.0, 125.3, 127.5, 129.3, 131.2, 133.8, 134.8, 144.3, 196.6, 202.8, 205.2; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_3$ ($\text{M} + \text{H}$) $^+$ 269.1178, found 269.1172.



Compound **3ah**. 78% yield (58 mg); colorless oil; dr = 55:45; ^1H NMR (600 MHz, CDCl_3) data 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) data 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 $\text{C}_{18}\text{H}_{19}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 299.1283, found 299.1277.

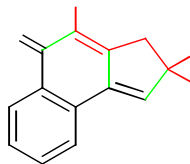


Compound **3ai**. 80% yield (54 mg); colorless oil; dr = 60:40; ^1H NMR (600 MHz, CDCl_3) data of the major isomer δ 1.26 (t, $J = 7.1$ Hz, 3H), 1.53 (s, 3H), 2.21 (dd, $J = 8.7, 12.8$ Hz, 1H), 2.42–2.54 (m, 1H), 2.95–3.02 (m, 2H), 3.48–3.55 (m, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 6.20 (d, $J = 2.3$ Hz, 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) data 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 $\text{C}_{17}\text{H}_{19}\text{O}_3$ ($\text{M} + \text{H}$) $^+$ 271.1334, found 271.1327.

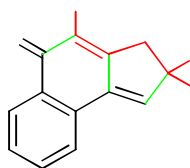


Compound **3ak**. 74% yield (63 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 1.32 (t, $J = 7.1$ Hz, 6H), 2.10 (s, 3H), 3.55 (s, 2H), 4.22–4.33 (m, 4H), 7.14 (s, 1H), 7.52–7.61 (m, 2H), 7.88 (d, J

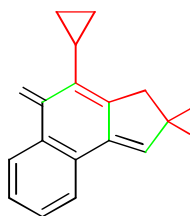
= 7.6 Hz, 1H), 8.23 (d, $J = 7.7$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 12.2, 14.0, 36.5, 62.5, 65.5, 124.3, 127.0, 128.7, 129.5, 130.4, 130.7, 131.4, 135.0, 138.4, 154.0, 169.1, 184.5; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{O}_5(\text{M} + \text{H})^+$ 341.1389, found 341.1383.



Compound **3al**. 70% yield (67 mg); colorless oil; ^1H 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 $\text{C}_{23}\text{H}_{27}\text{O}_5(\text{M} + \text{H})^+$ 383.1858, found 383.1840.

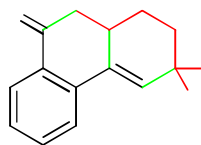


Compound **3am**. 53% yield (49 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 1.31 (t, $J = 7.1$ Hz, 6H), 3.42 (s, 3H), 3.73 (s, 2H), 4.24–4.30 (m, 4H), 4.52 (s, 2H), 7.26 (s, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.53–7.64 (m, 1H), 7.89 (d, $J = 7.7$ Hz, 1H), 8.24 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (151 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 $\text{C}_{21}\text{H}_{23}\text{O}_6(\text{M} + \text{H})^+$ 371.1495, found 371.1486.



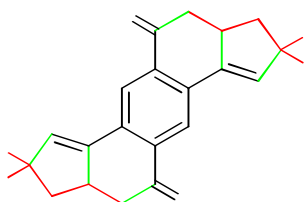
Compound **3an**. 35% yield (32 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 0.90–0.95 (m, 2H), 1.03–1.07 (m, 2H), 1.32 (t, $J = 7.1$ Hz, 6H), 1.65–1.71 (m, 1H), 3.68 (s, 2H), 4.24–4.32 (m, 4H), 7.13 (s, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.85 (d, $J = 7.7$ Hz, 1H), 8.17 (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.



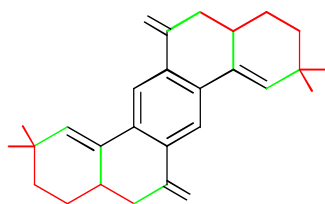
Compound **3ap**. 81% yield (69 mg); white solid, mp 158–161°C; ¹H NMR (600 MHz, CDCl₃) δ 1.27–1.34 (m, 6H), 1.61–1.69 (m, 1H), 1.88–1.94(m, 1H), 2.00–2.14 (m, 1H), 2.39–2.46(m, 1H), 2.52–2.56 (m, 1H), 2.80–2.89 (m, 2H), 4.16–4.32 (m, 4H), 6.69 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.55–7.62 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) 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) Å³, *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 -0.306 e Å⁻³. Crystallographic data for the structure **3ap** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC1439850.



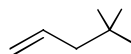
Compound **3sa**. It was prepared from **1s** and **2a** in 47% yield (68 mg) using the general procedure except that 6 equivalents of K₂CO₃ was used; pale yellow solid, mp 59–61°C; ¹H NMR (600 MHz, CDCl₃) δ 1.28–1.33 (m, 12H), 2.09–2.15 (m, 2H), 2.48–2.56 (m, 2H), 3.00–3.11 (m, 4H), 3.48–3.55 (m, 2H), 4.15–4.29 (m, 8H), 6.53 (dd, *J* = 2.3, 6.3 Hz, 2H), 8.32 (s, 2H); ¹³C NMR (151 MHz, CDCl₃) 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 C₃₂H₃₅O₁₀ (M + H)⁺ 579.2230, found 579.2249.

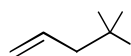


Compound **3sp**. It was prepared from **1s** and **2p** in 38% yield (58 mg) using the general procedure except that 6 equivalents of K₂CO₃ was used; pale yellow solid, mp 66–68°C; ¹H NMR (600 MHz, CDCl₃) δ 1.27–1.33 (m, 12H), 1.62–1.70 (m, 4H), 1.92–2.00 (m, 2H), 2.10–2.16 (m, 2H), 2.43–2.56 (m, 2H), 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); ¹³C NMR (151 MHz, CDCl₃) 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 C₃₂H₃₉O₁₀ (M + H)⁺ 607.2543, found 607.2540.

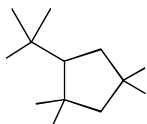
Experimental Procedure for the Synthesis of **4a** from **1a** and **2a**:



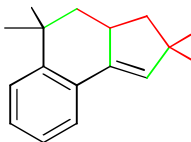
Compound **4a**. It was obtained from **1a** and **2a** under the reaction conditions in the presence of 2 equivalents of TEMPO in 51% yield (55 mg) as a colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 1.15 (d, *J* = 2.0 Hz, 6H), 1.21 (d, *J* = 1.9 Hz, 6H), 1.29 (td, *J* = 2.2, 7.1 Hz, 6H), 1.31–1.62 (m, 6H), 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); ¹³C NMR (151 MHz, CDCl₃) 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 C₁₉H₃₄NO₅ (M + H)⁺ 356.2437, found 356.2433.



Compound 4b¹. 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; ¹H NMR (600 MHz, CDCl₃) δ 1.27 (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); ¹³C NMR (151 MHz, CDCl₃) δ 14.0, 32.8, 51.6, 61.4, 117.5, 134.0, 168.9.



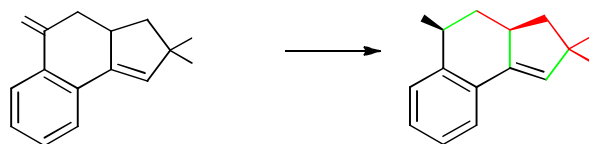
Compound 4c. It was obtained from **1a** and **2b** under the reaction conditions in the presence of 2 equivalents of 1,1-diphenylethylene in 68% yield (83 mg) as a colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 0.78 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.25–1.32 (m, 6H), 2.05 (dd, *J* = 10.4, 13.3 Hz, 1H), 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); ¹³C NMR (151 MHz, CDCl₃) 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 C₂₆H₃₁O₄ (M – Br)⁺ 407.2222, found 407.2222.



Compound 6a. 62% yield (53 mg); colorless oil; dr = 68:32; ¹H NMR (600 MHz, CDCl₃) data 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); ¹³C NMR (151 MHz, CDCl₃) data 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 C₂₀H₂₅O₅ (M + H)⁺ 345.1702, found 345.1697.

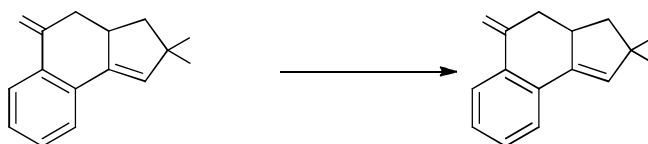
Experimental Procedure for the Preparation of **6b** via Reduction of **3aa**:

¹K.-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 NaBH₄ (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 Na₂SO₄, 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. ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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 C₁₉H₂₂NaO₅ (M + Na)⁺ 353.1365, found 353.1371.

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

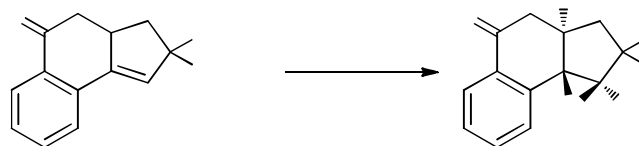


A mixture of **3aa** (164 mg, 0.5mmol), LiCl (63 mg, 1.5mmol), and H₂O (0.25 mL) in 1 mL of dimethyl sulfoxide was heated at reflux for 5 h. After cooling to room temperature, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:15) gave 103 mg of **3aj** (yield: 80%) as a colorless oil; dr = 54:46; ¹H NMR (600 MHz, CDCl₃) data 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); ¹³C NMR (151 MHz, CDCl₃) data 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)

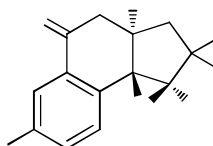
²A. P. Krapcho, J. F. Weimaster, J. M. Eldridge, E. G. E. Jahngen, Jr., A. J. Lovey and W. P. Stephens, *J. Org. Chem.*, 1978, **43**, 138.

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

Experimental Procedure for the Epoxidation of Tricyclic Ketones:



To a mixture of **3aa** (164 mg, 0.5 mmol) and $NaHCO_3$ (84 mg, 1.0 mmol) in 5 mL of DCM was added *m*-CPBA (172 mg, 1.0 mmol) 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; 1H 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.

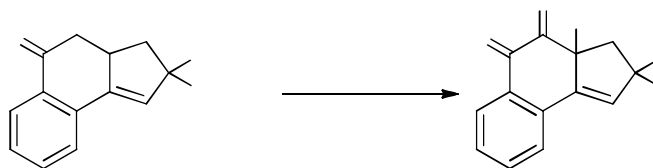


Compound **7b**. 76% yield (144 mg); white solid, mp 83–85°C; 1H NMR (600 MHz, $CDCl_3$) δ 1.27 (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.94–2.00 (m, 1H), 2.35–2.41 (m, 1H), 2.73–2.82 (m, 2H), 2.90–3.00 (m, 1H), 4.19–4.37 (m, 4H), 4.71 (s, 1H), 7.21 (d, $J = 8.2$ Hz, 1H), 7.56 (dd, $J = 2.2, 8.2$ 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, $U = 1814.8(4)$ Å³, $Z = 4$, $T = 296(2)$ K, absorption coefficient 0.243mm^{-1} , reflections collected 8218, independent reflections 4660 [$R(\text{int}) = 0.0639$], refinement by full-matrix least-squares on F^2 , data/restraints/parameters 8218/26/470, goodness-of-fit on $F^2 =$

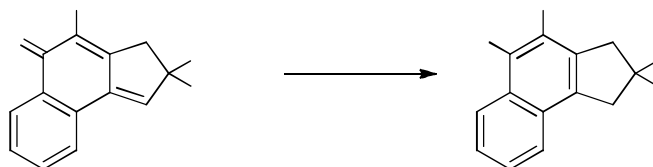
1.017, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0720$, $wR_2 = 0.1765$, R indices (all data) $R_1 = 0.1273$, $wR_2 = 0.2177$, largest diff. peak and hole 0.870 and $-0.352 \text{ e} \cdot \text{\AA}^{-3}$. Crystallographic data for the structure **7b** have been deposited with the Cambridge Crystallographic 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 Et₂O was added NBS (445 mg, 2.5 mmol) and NH₄OAc (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 Na₂SO₄, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:15) gave 80 mg of **7c** (yield: 76%) as a colorless oil; ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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 C₁₉H₁₈BrO₆ (M + H)⁺ 421.0287, found 421.0274.

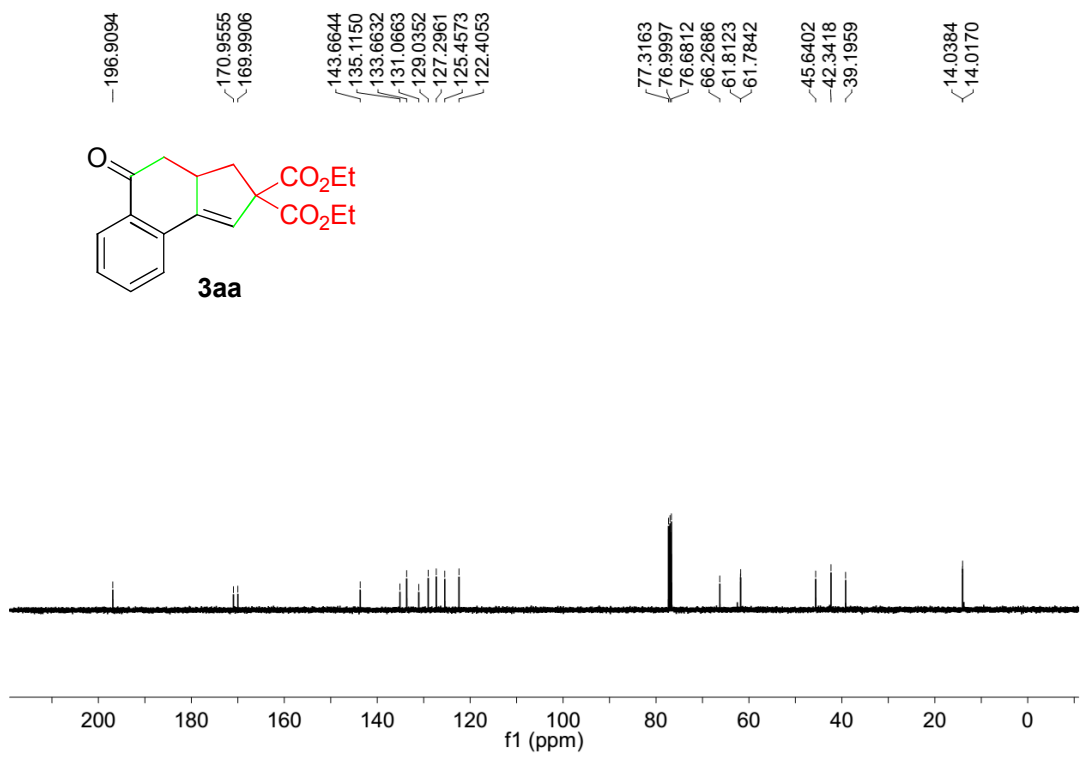
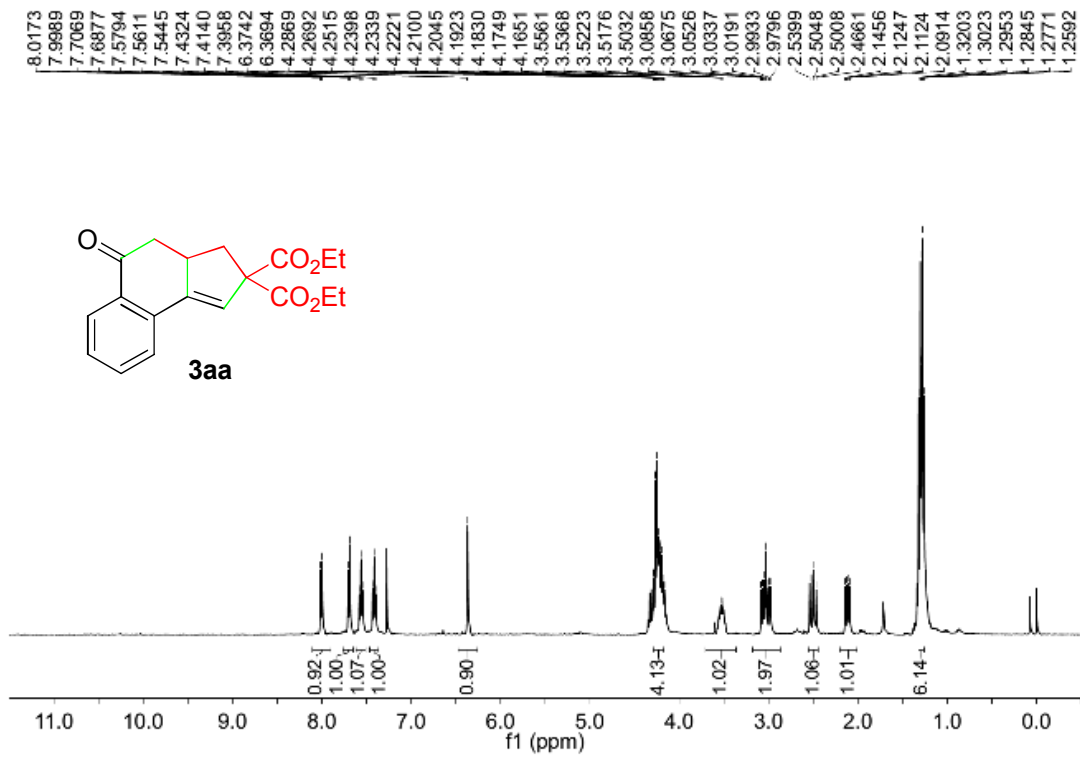
Experimental Procedure for the Preparation of 1-Naphthol **7d** via Reduction of **3ak**:

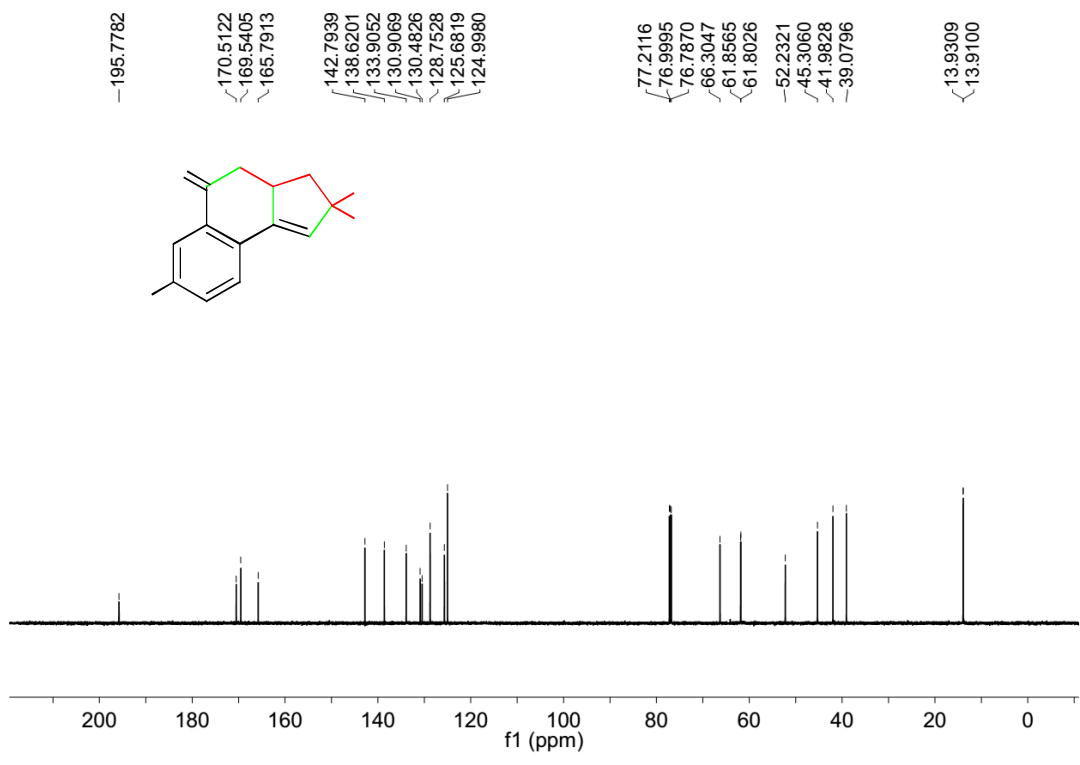
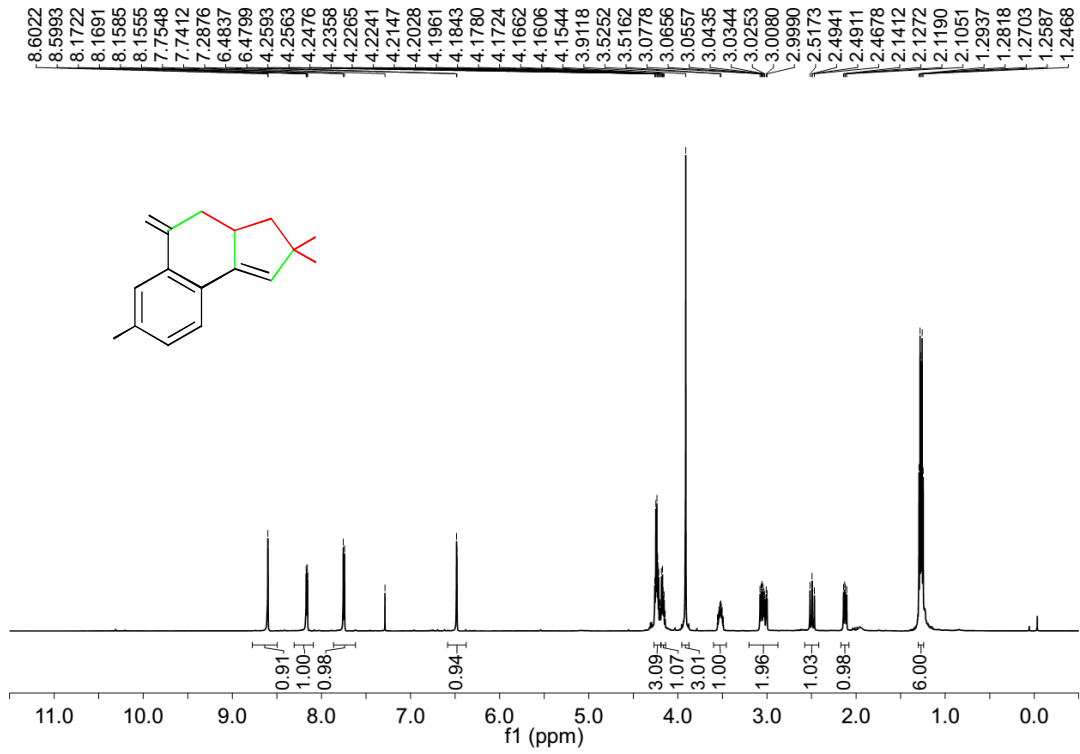


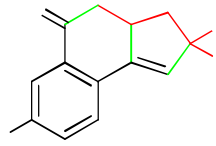
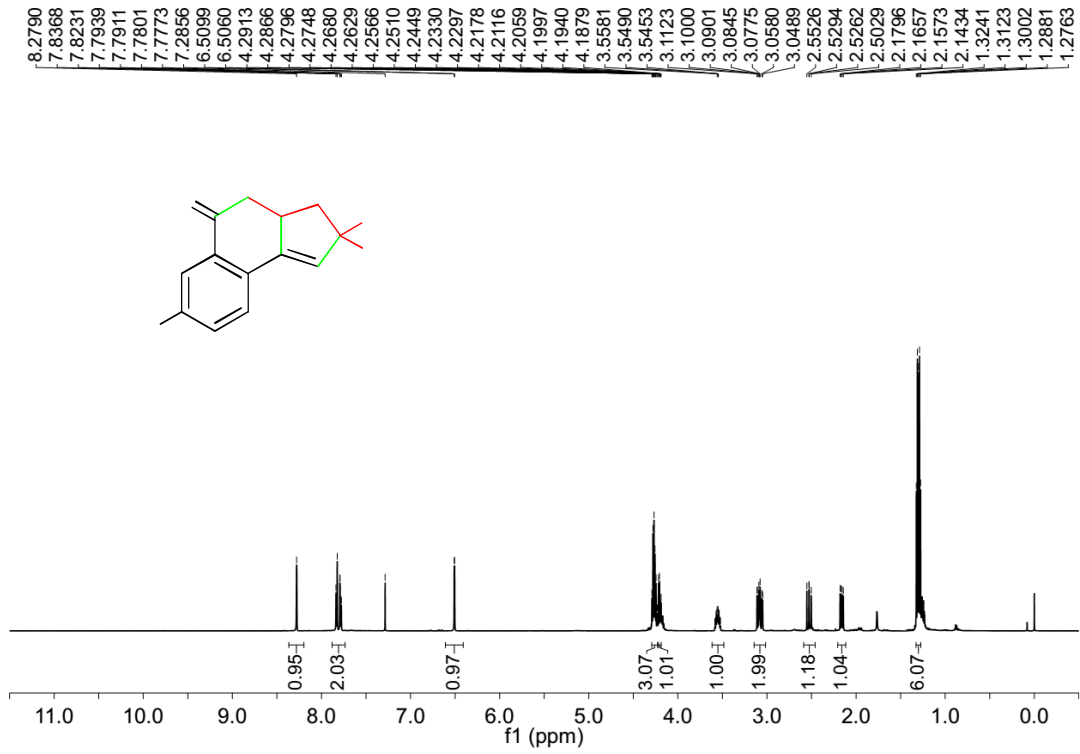
To a solution of **3ak** (170 mg, 0.5 mmol) in 2 mL of MeOH/THF (v/v = 1:1) was added NaBH₄ (23 mg, 0.6 mmol). After stirring at 25°C for 30 min, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated.

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

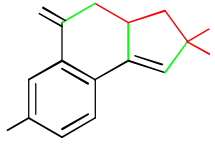
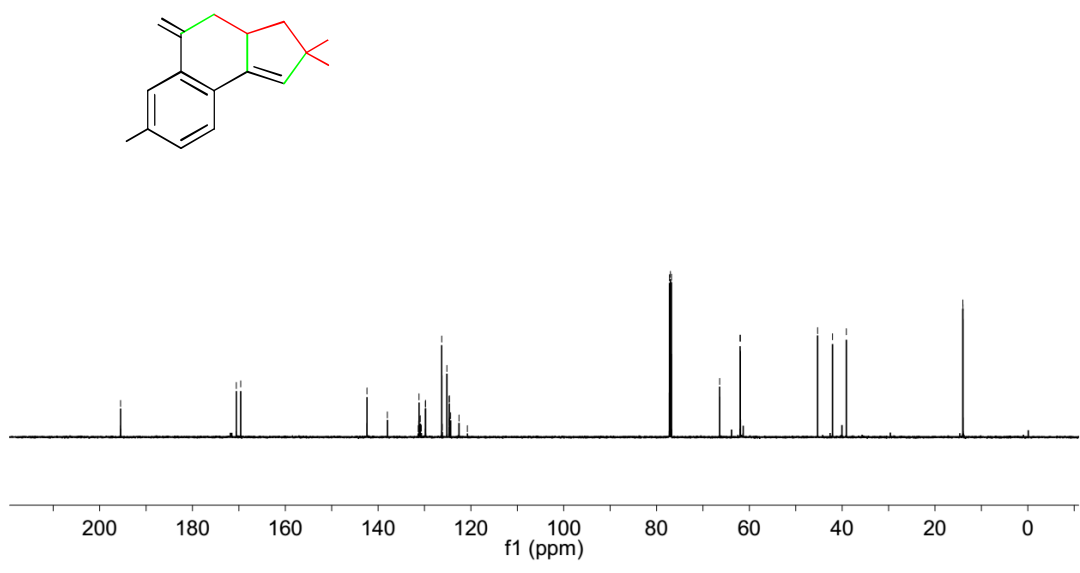
Column chromatography on silica gel (EtOAc/petroleum ether = 1:10) gave 154 mg of **7d** (yield: 92%) as a colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 1.28 (t, $J = 7.1$ Hz, 6H), 2.28 (s, 3H), 3.69 (s, 2H), 3.89 (s, 2H), 4.24 (q, $J = 7.1$ Hz, 4H), 5.23 (br,s, 1H), 7.40–7.46 (m, 2H), 7.66 (d, $J = 7.6$ 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 $\text{C}_{20}\text{H}_{23}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 343.1545, found 343.1535.

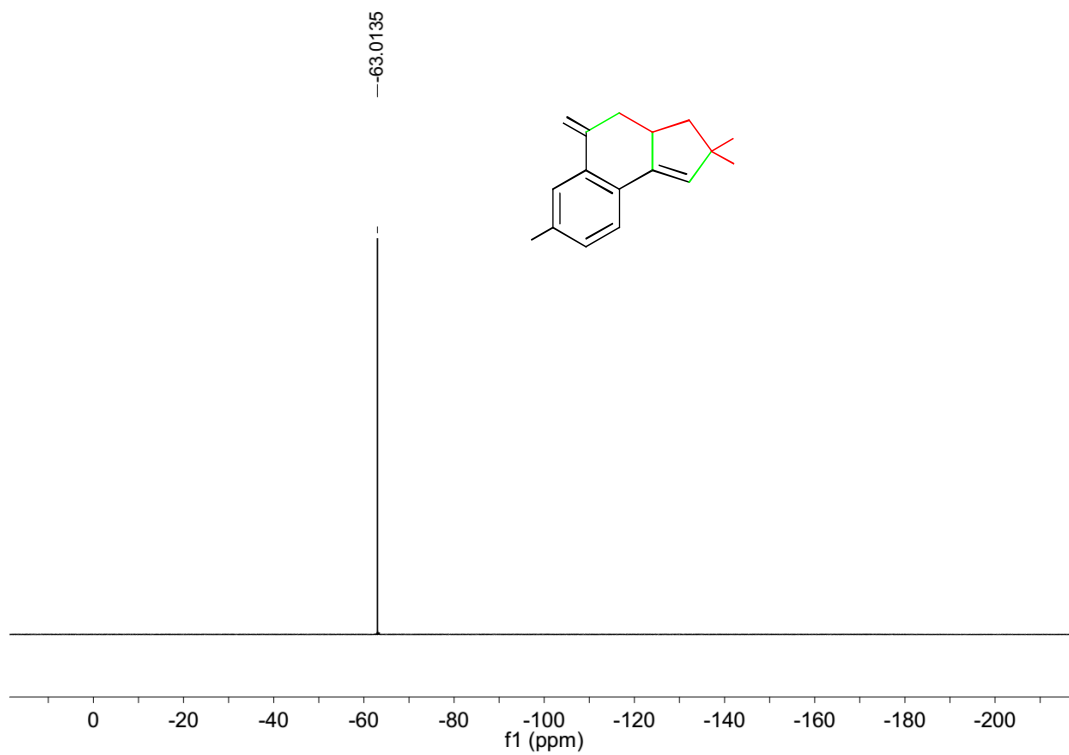


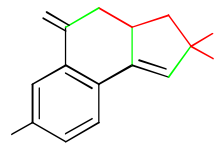
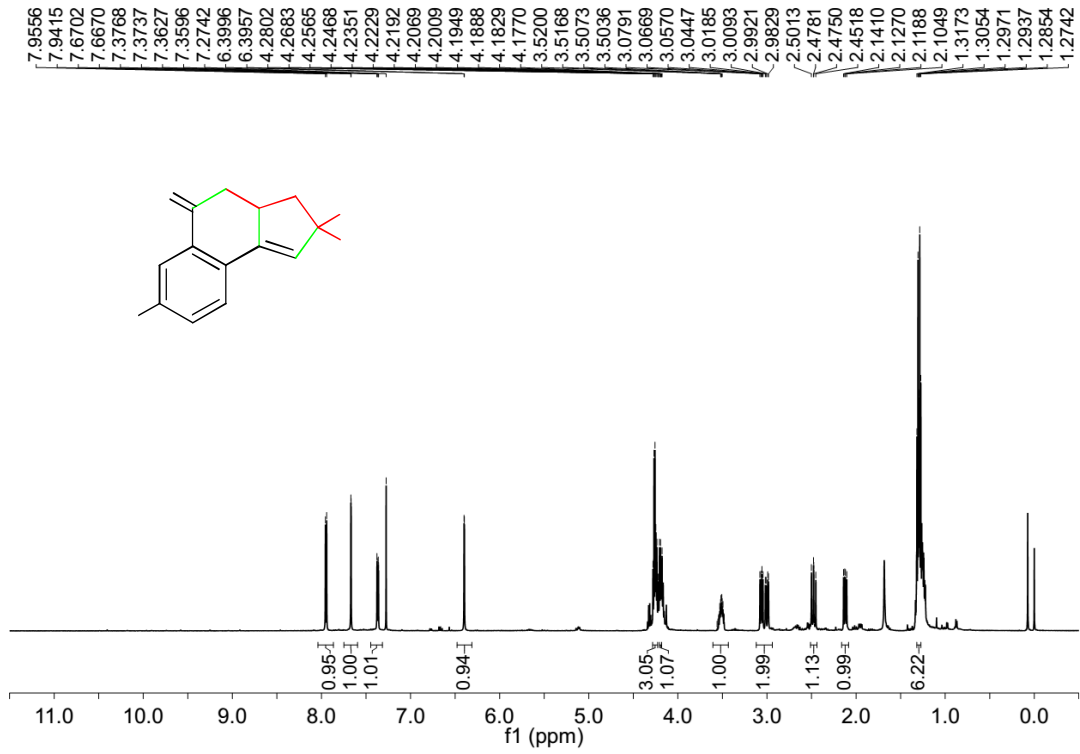




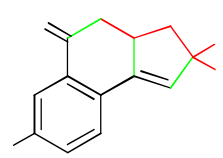
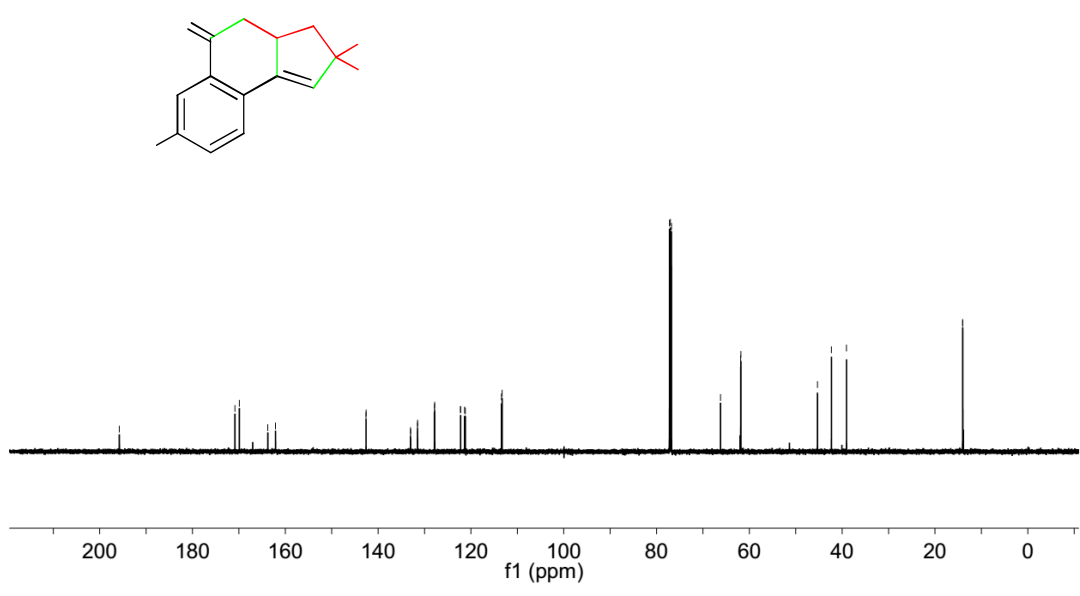
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- 124.6311
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- 13.9791

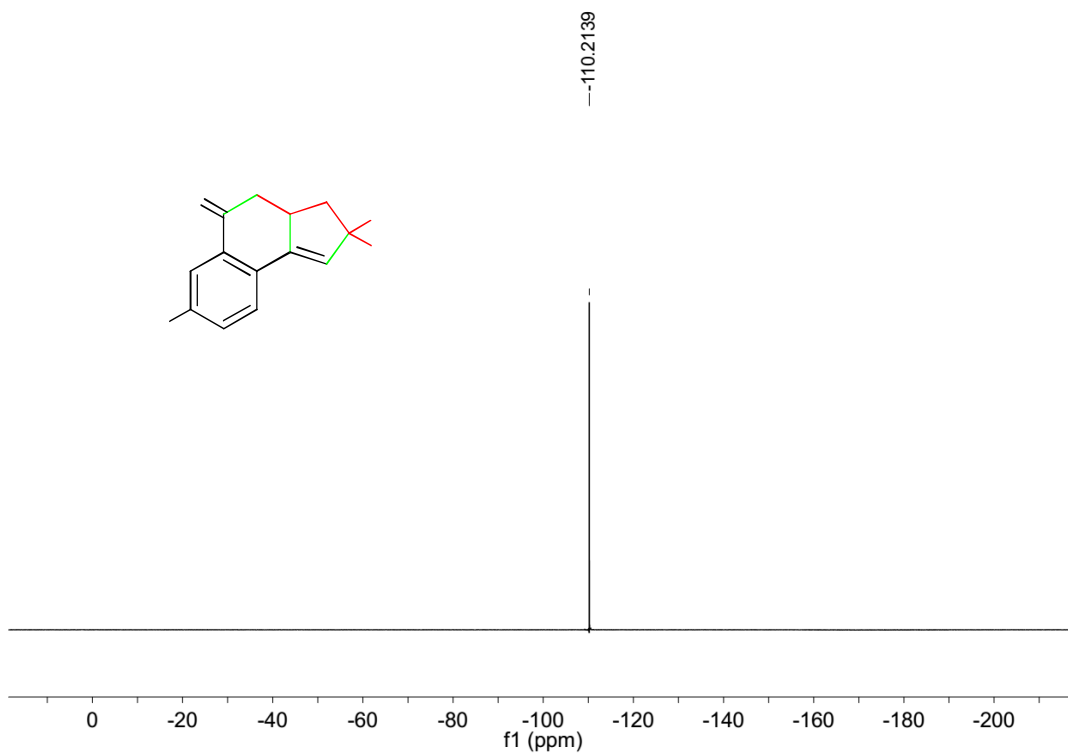


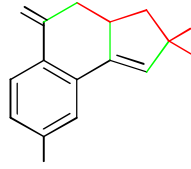
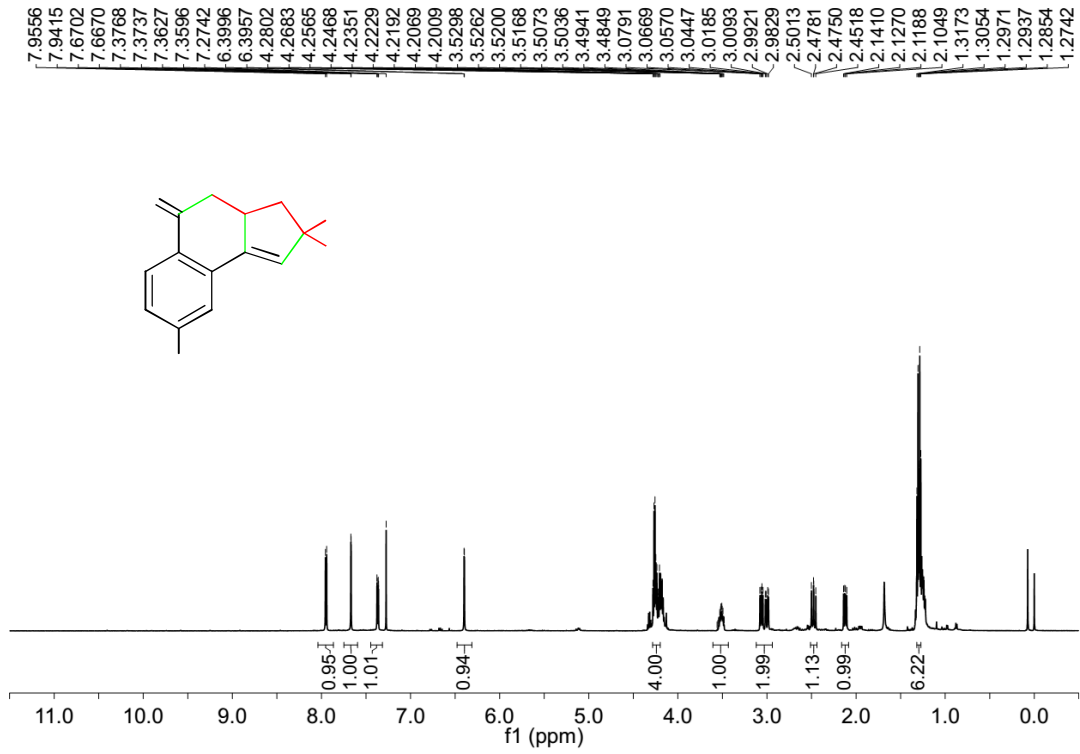




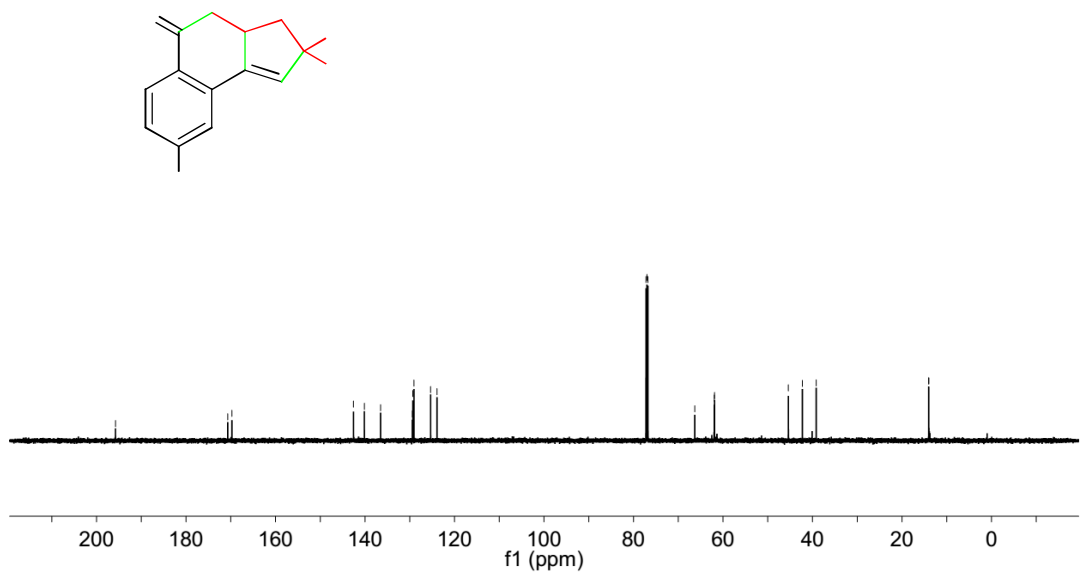
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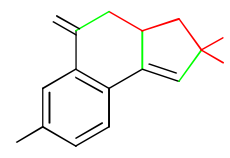
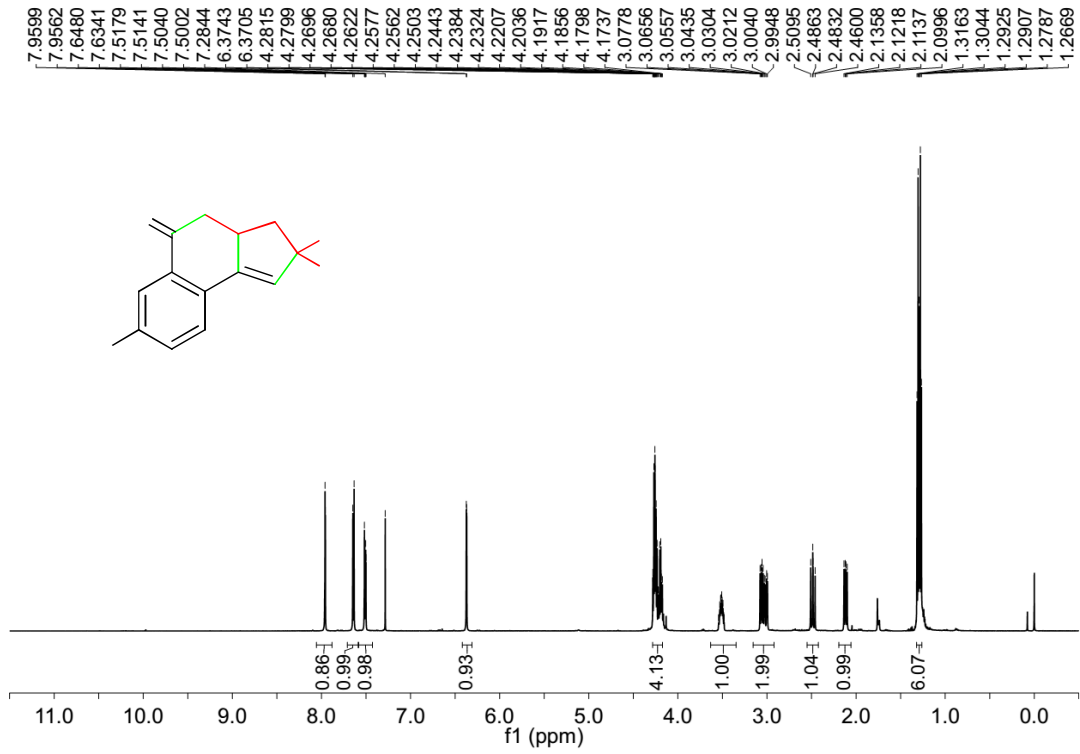




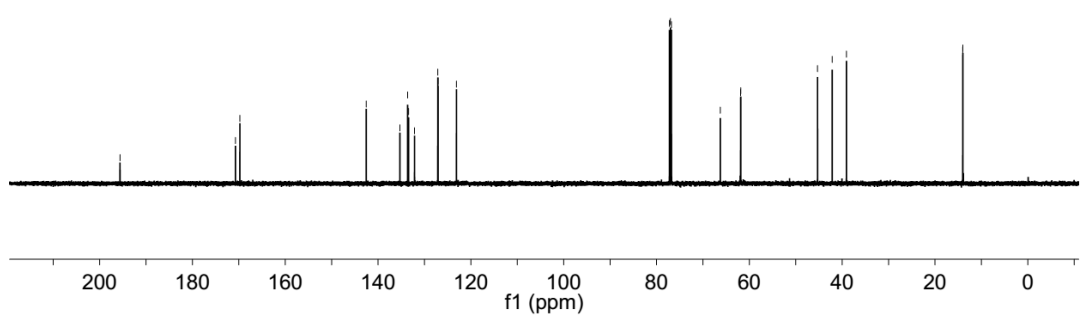
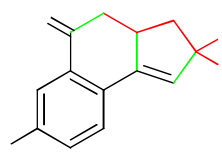


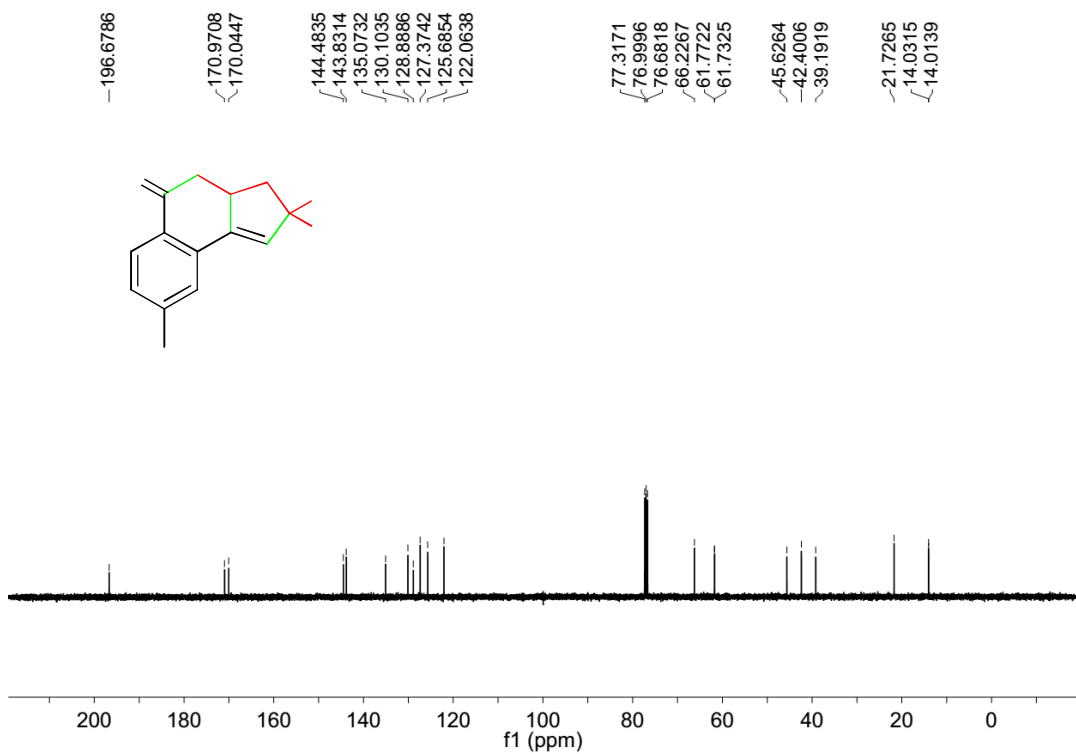
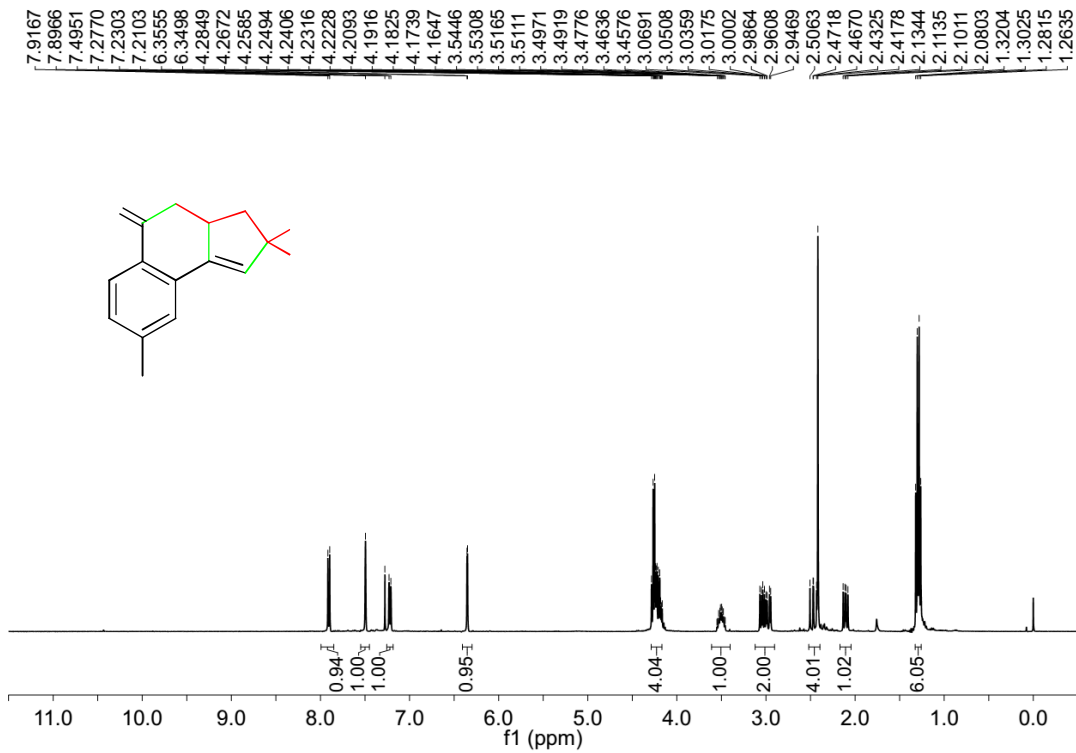
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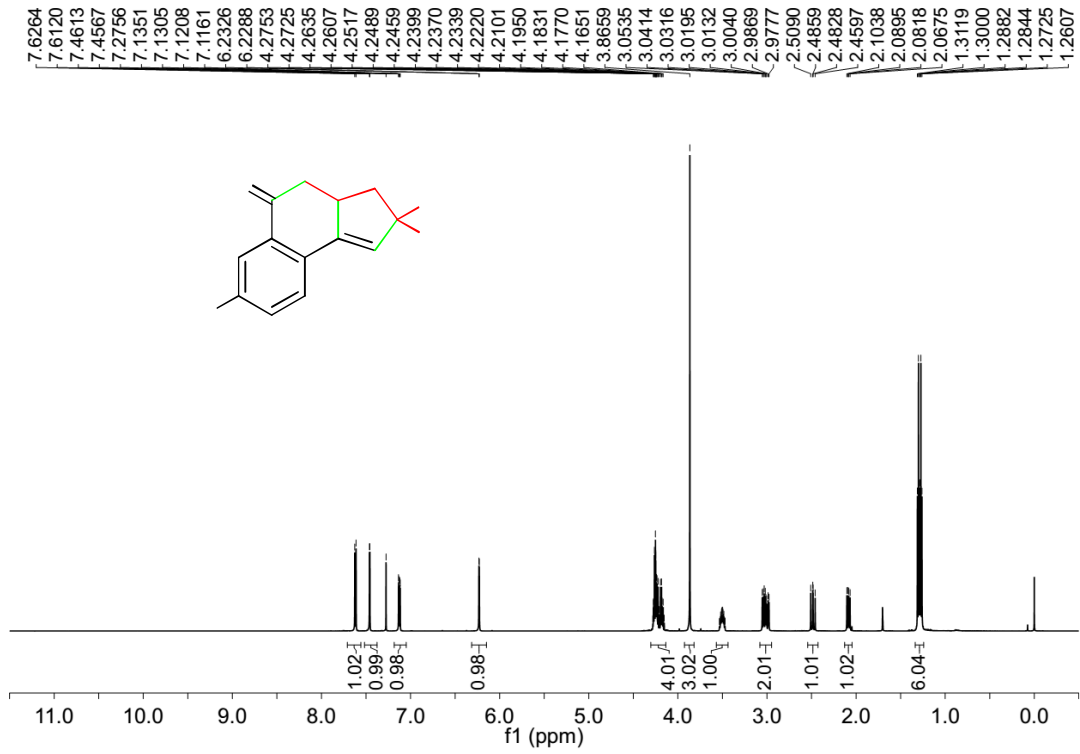




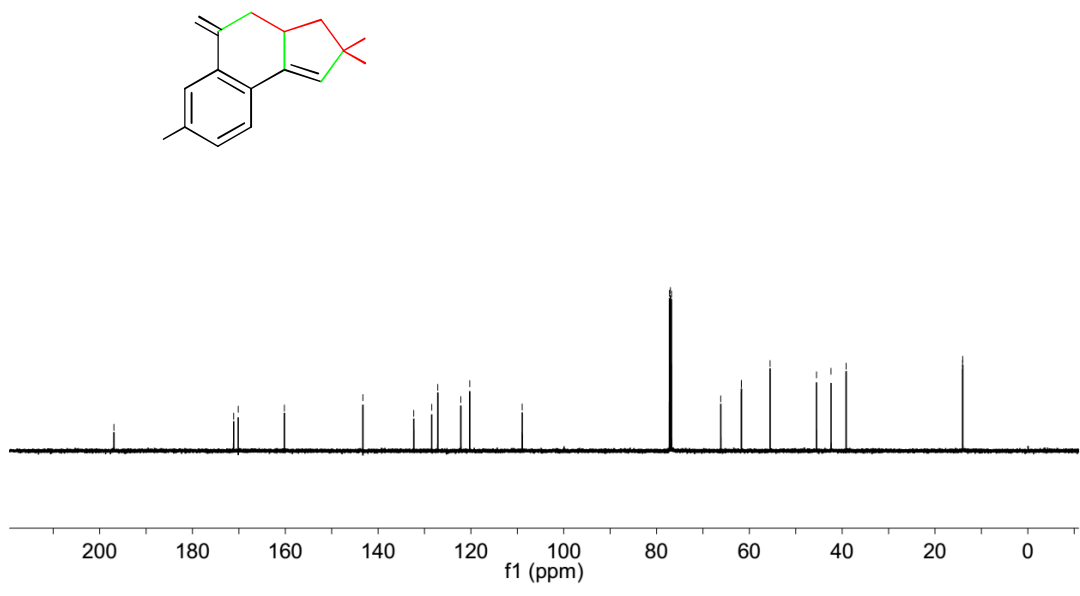
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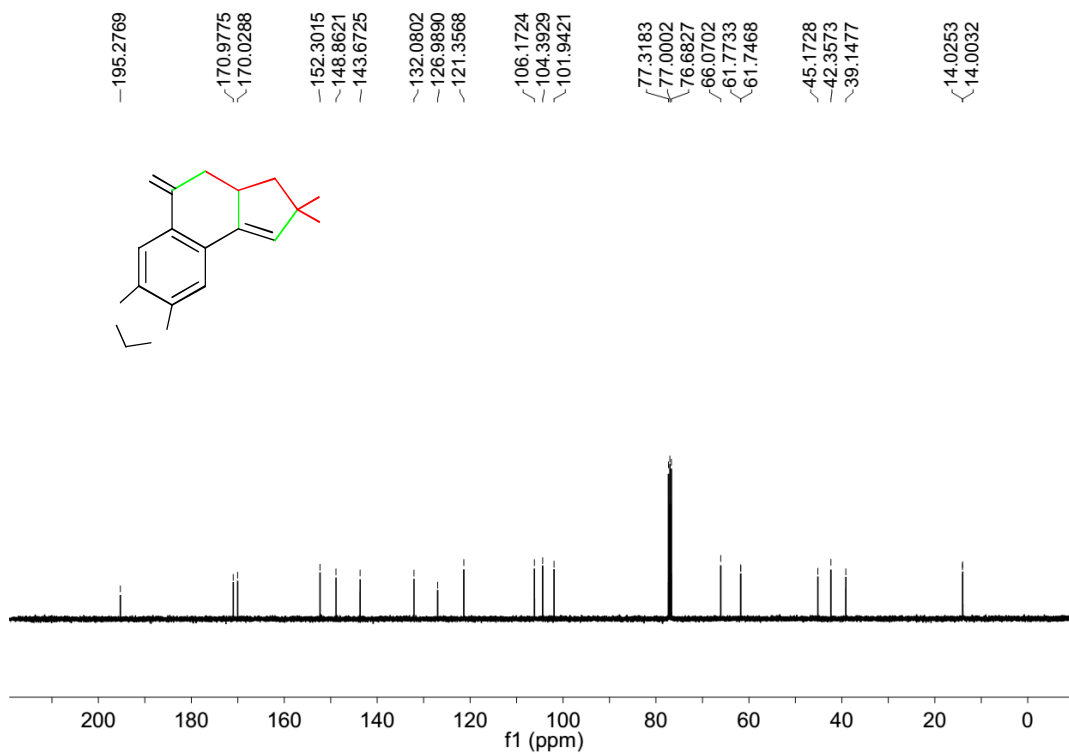
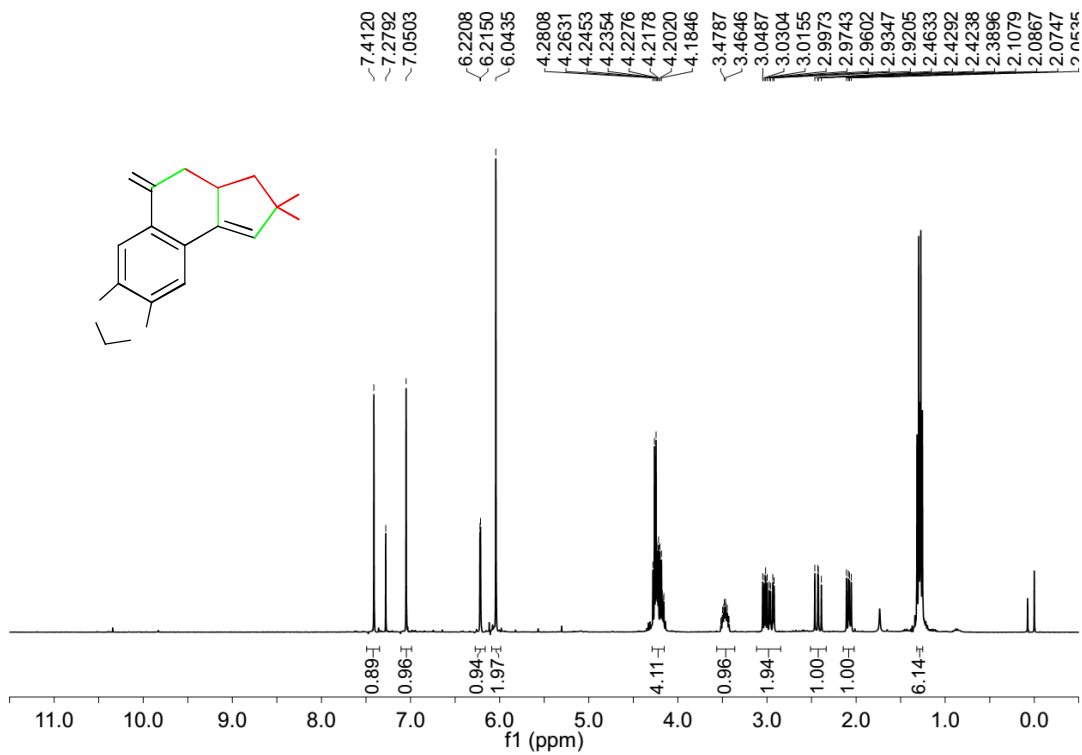


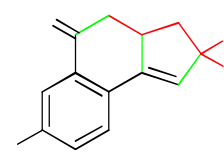
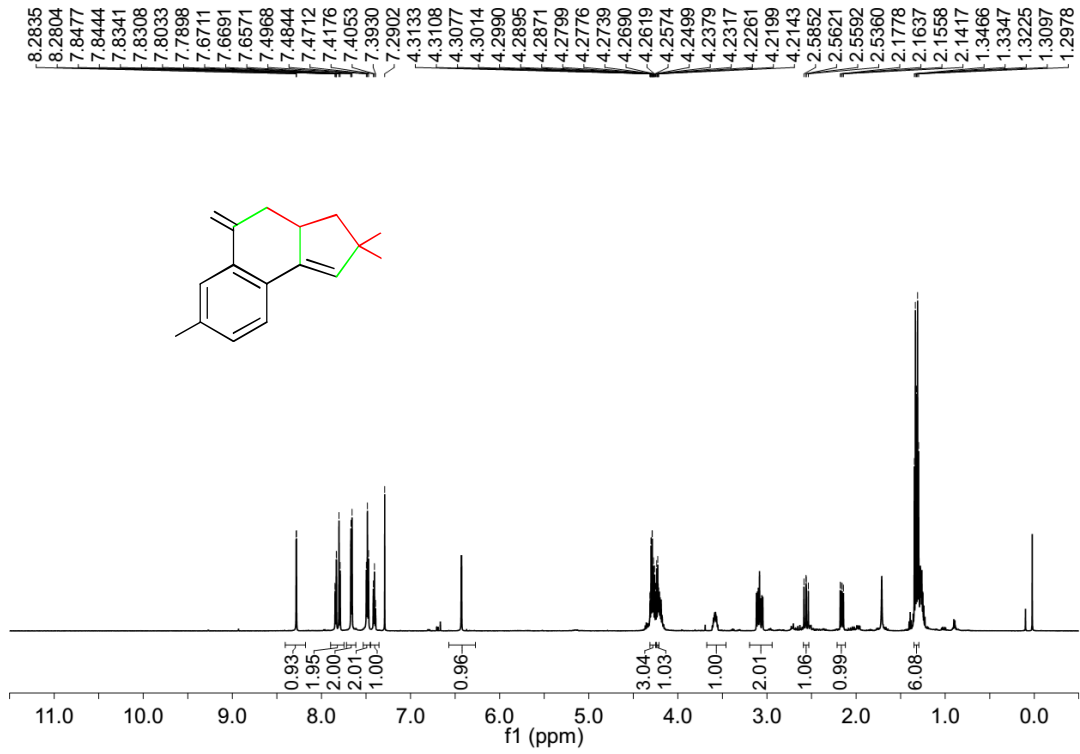




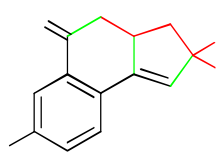
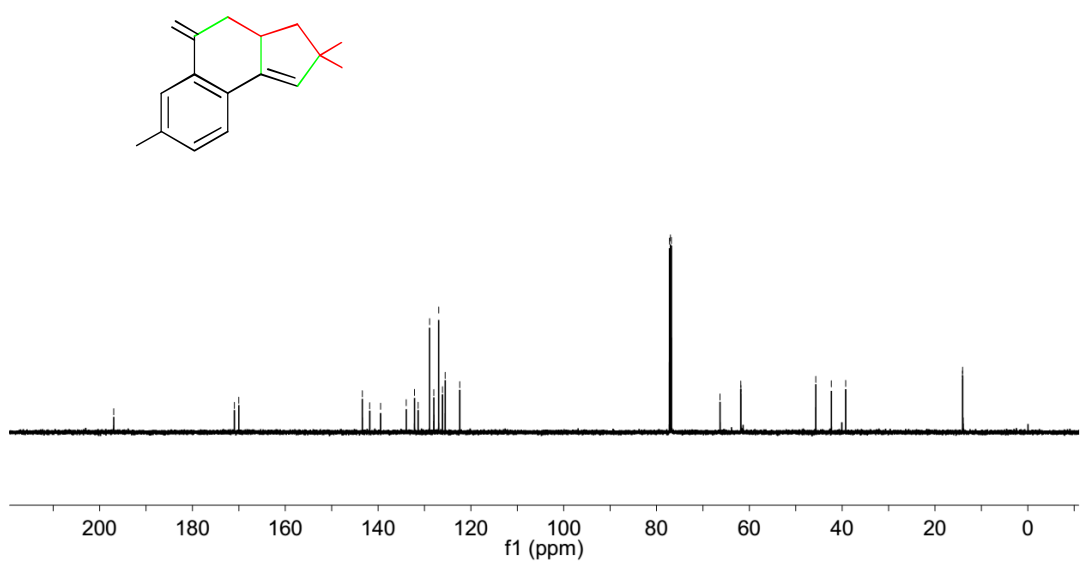
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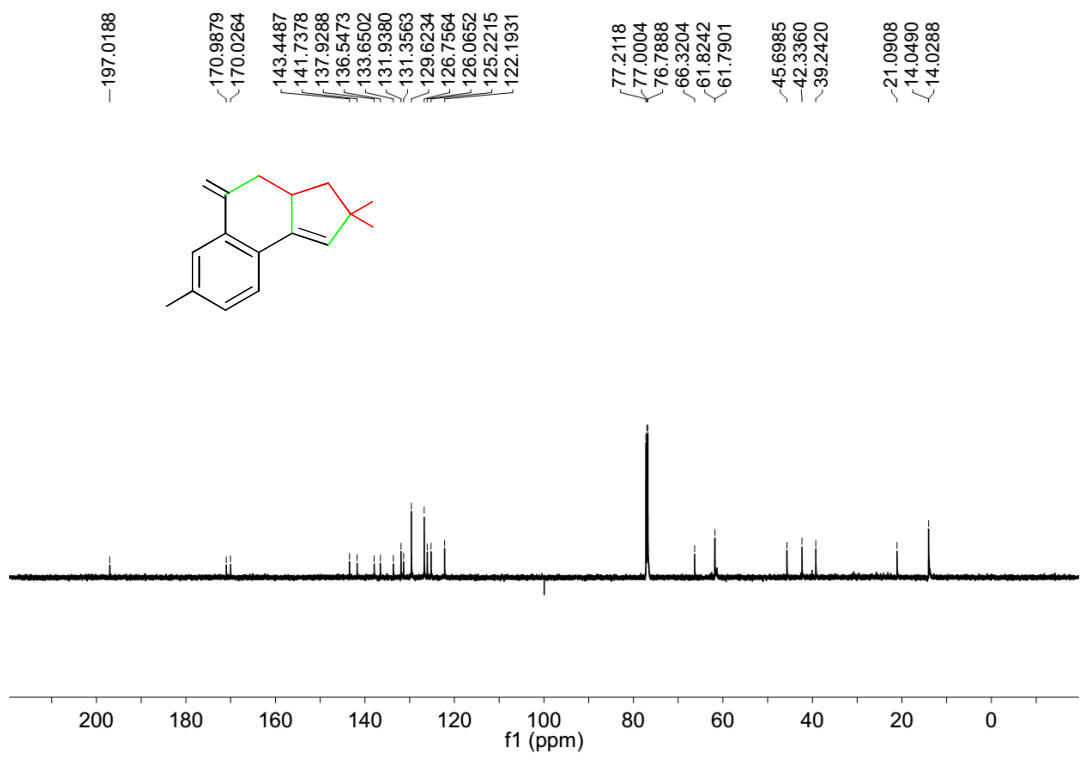
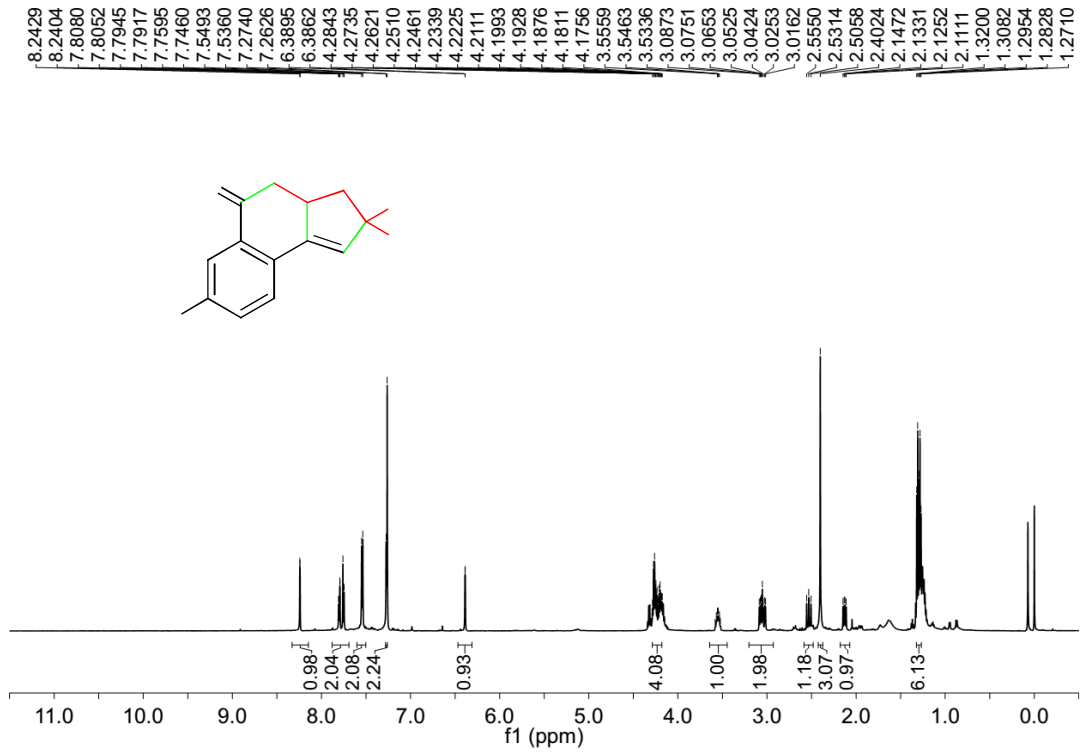


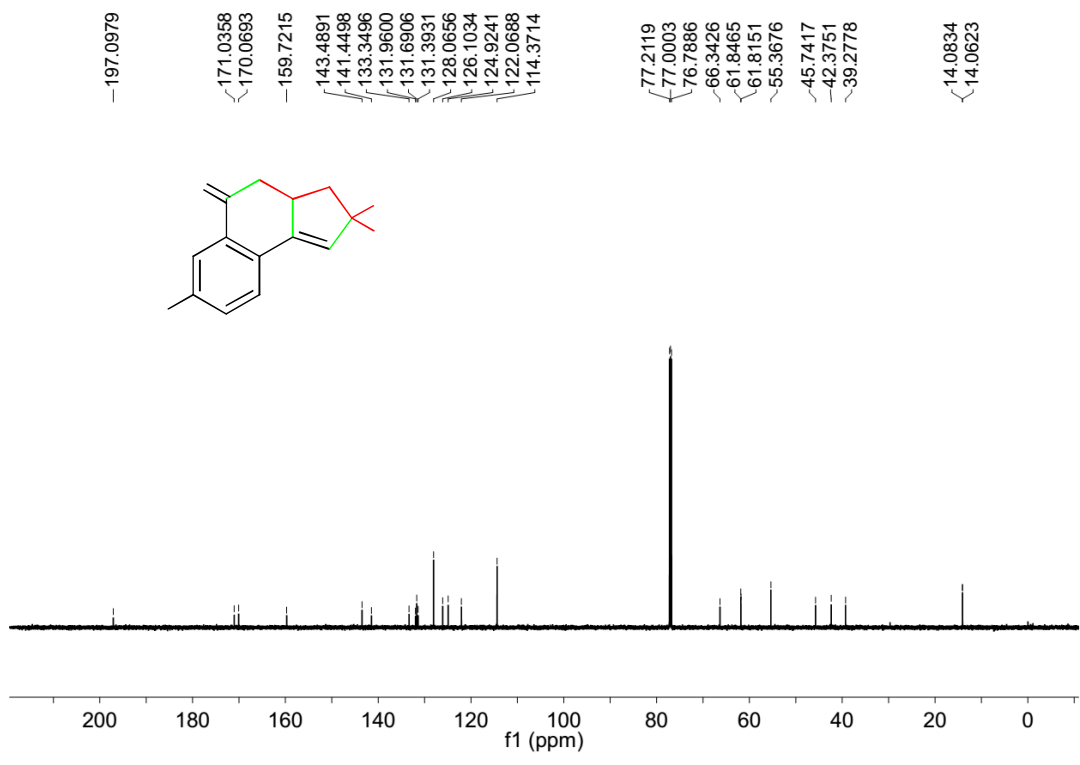
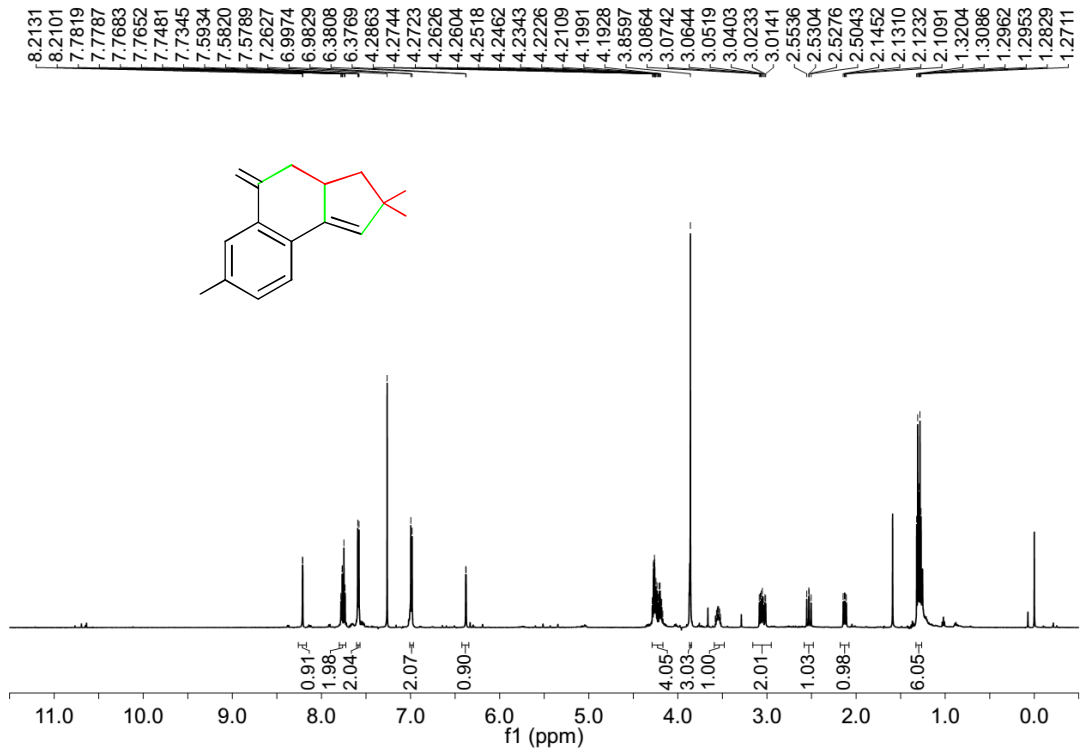


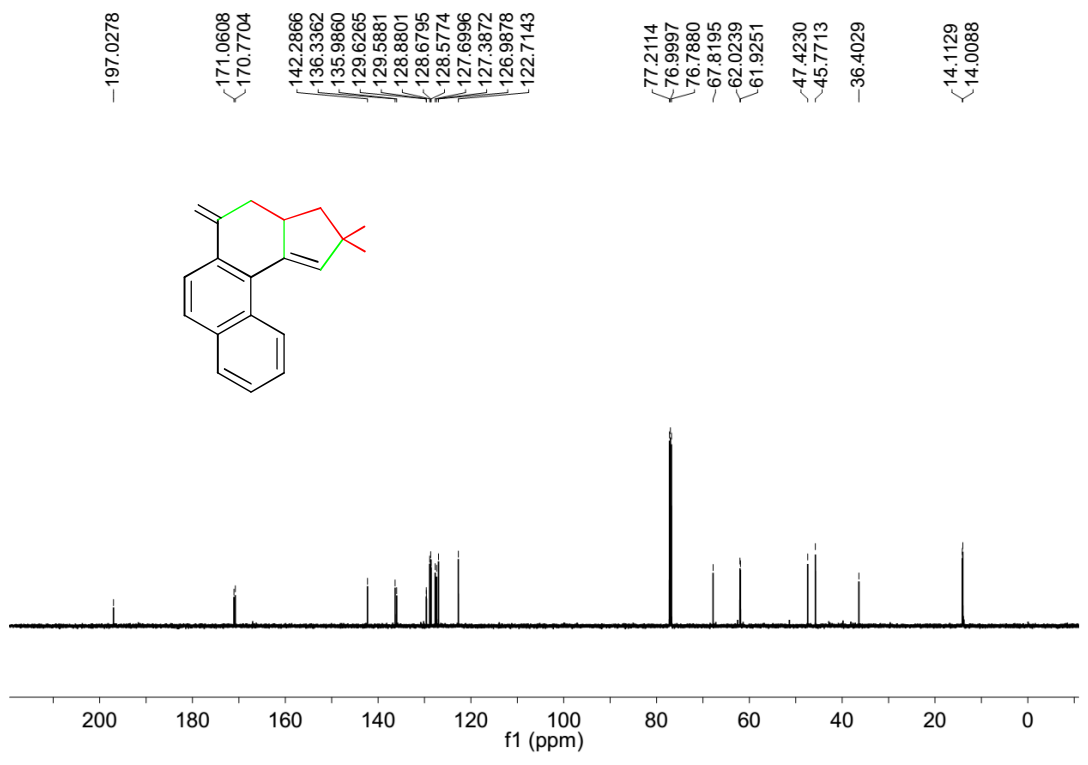
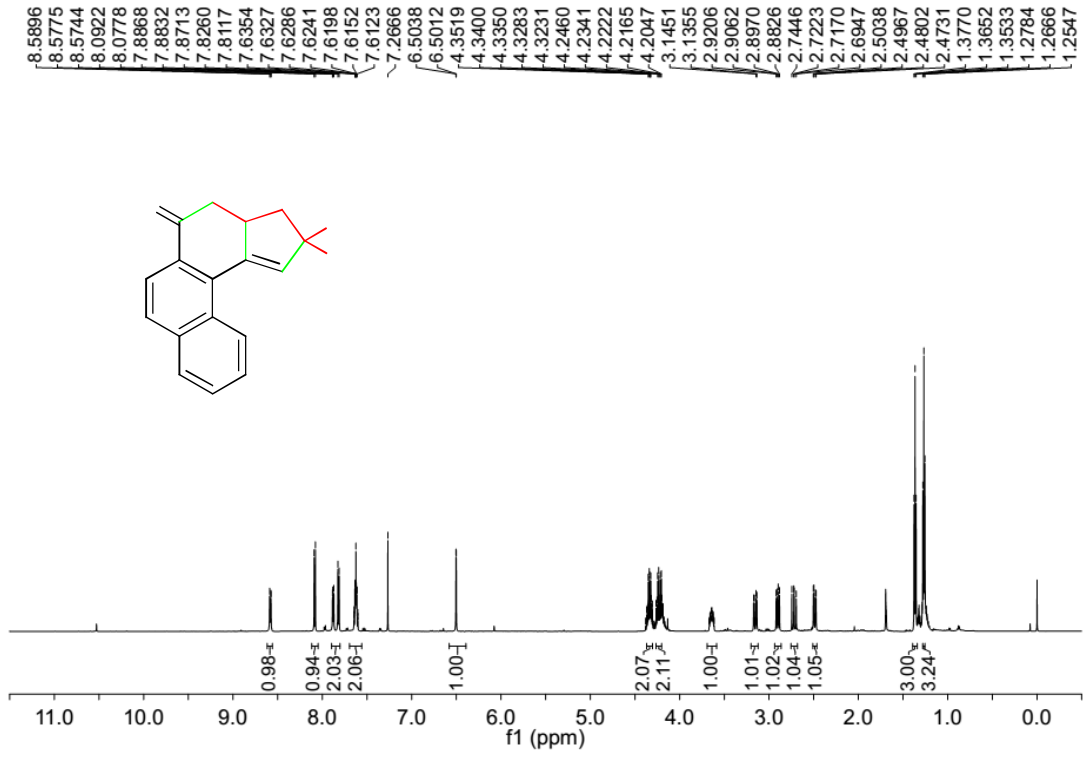


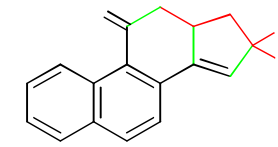
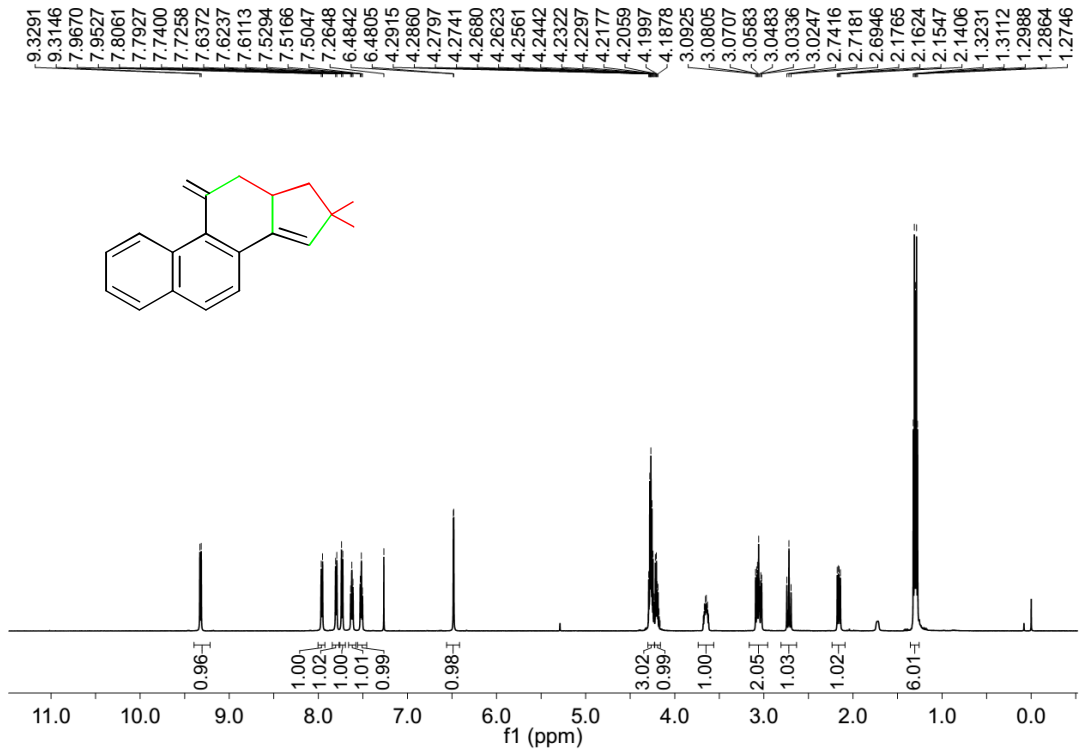
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- 127.9888
- 126.9437
- 126.1223
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- 122.4064
- 77.2119
- 77.0001
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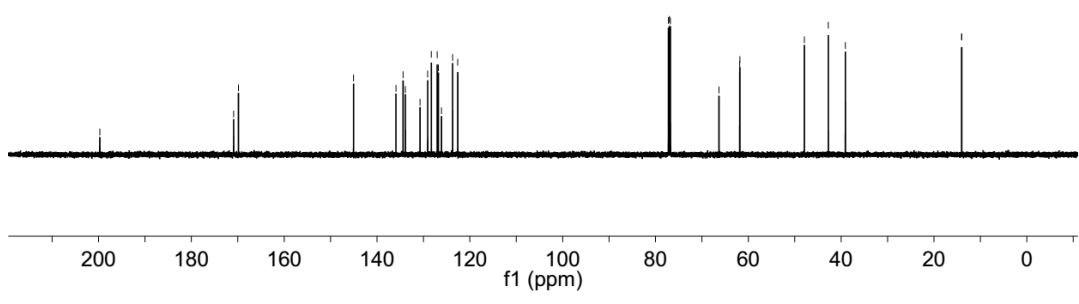
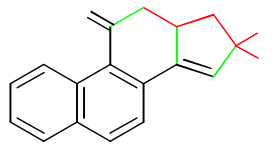


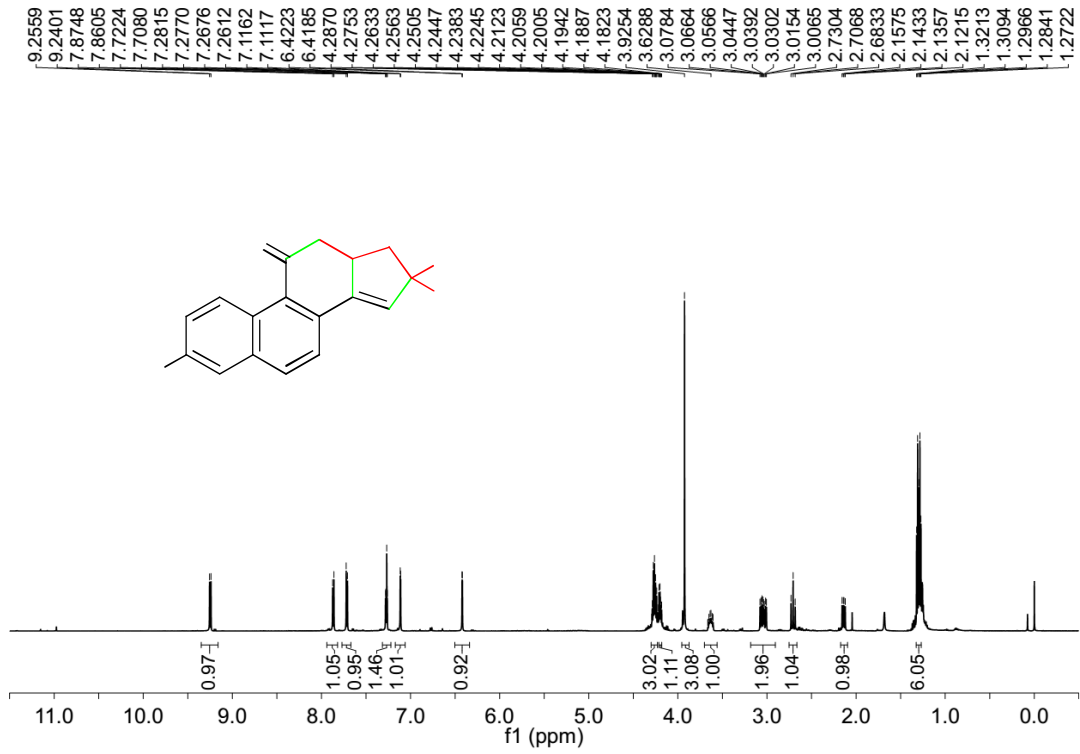




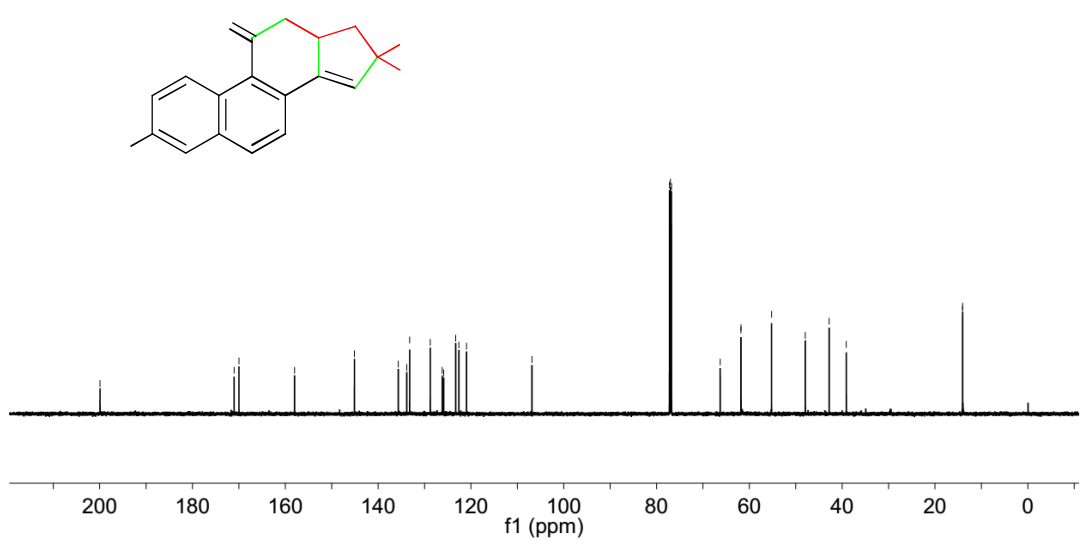


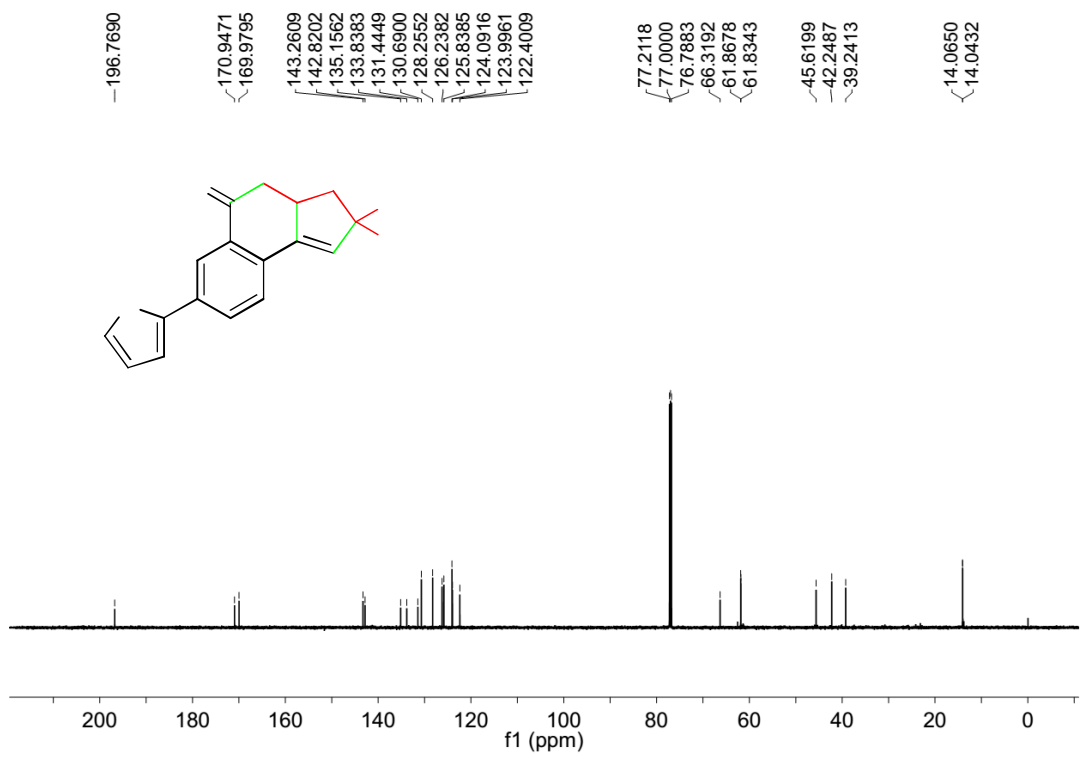
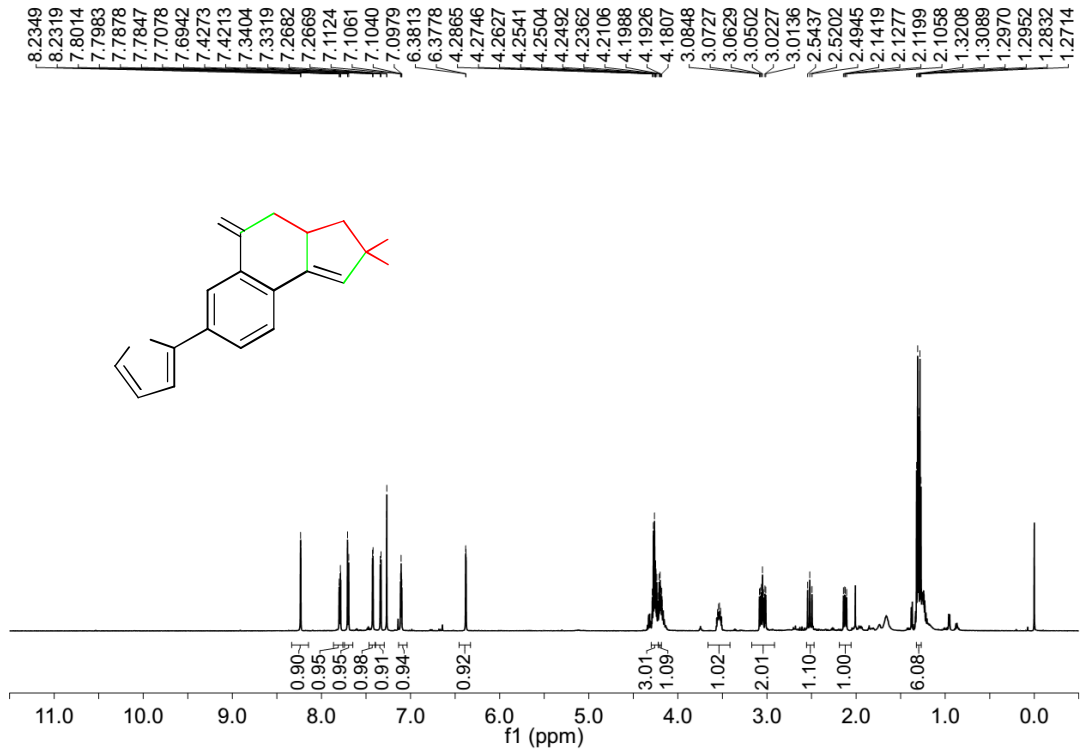
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- 128.2992
- 127.0463
- 126.7779
- 126.1112
- 123.7193
- 122.6124
- 77.2118
- 76.9999
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- 14.0191

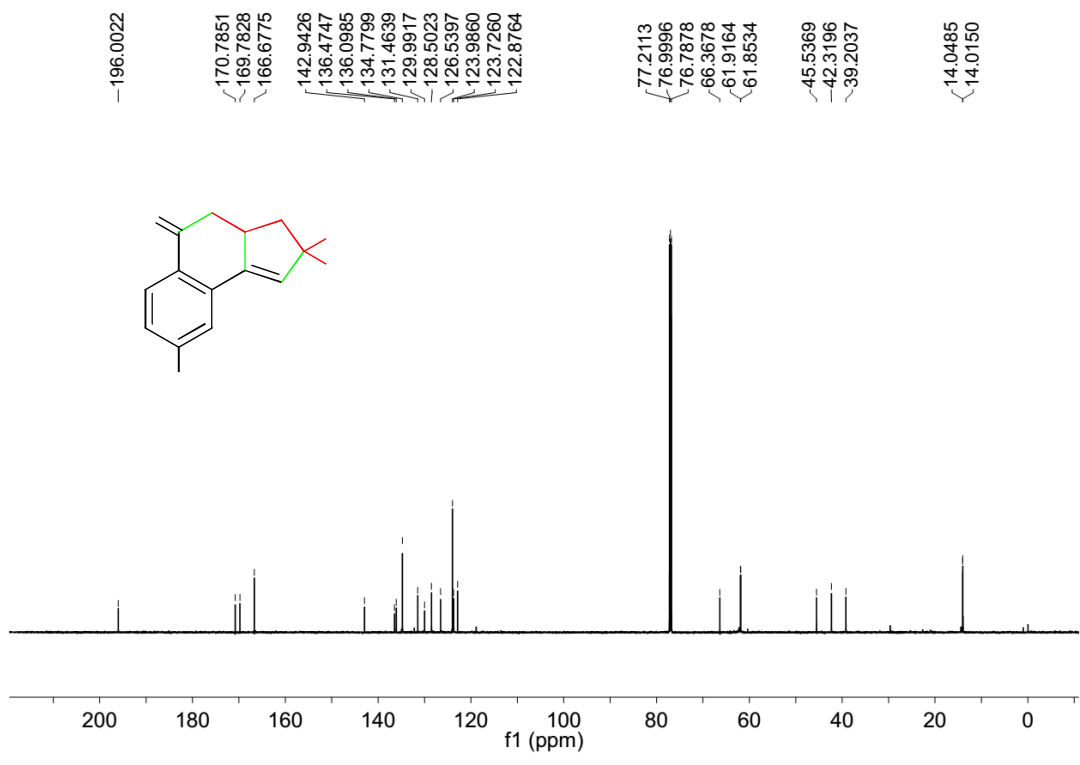
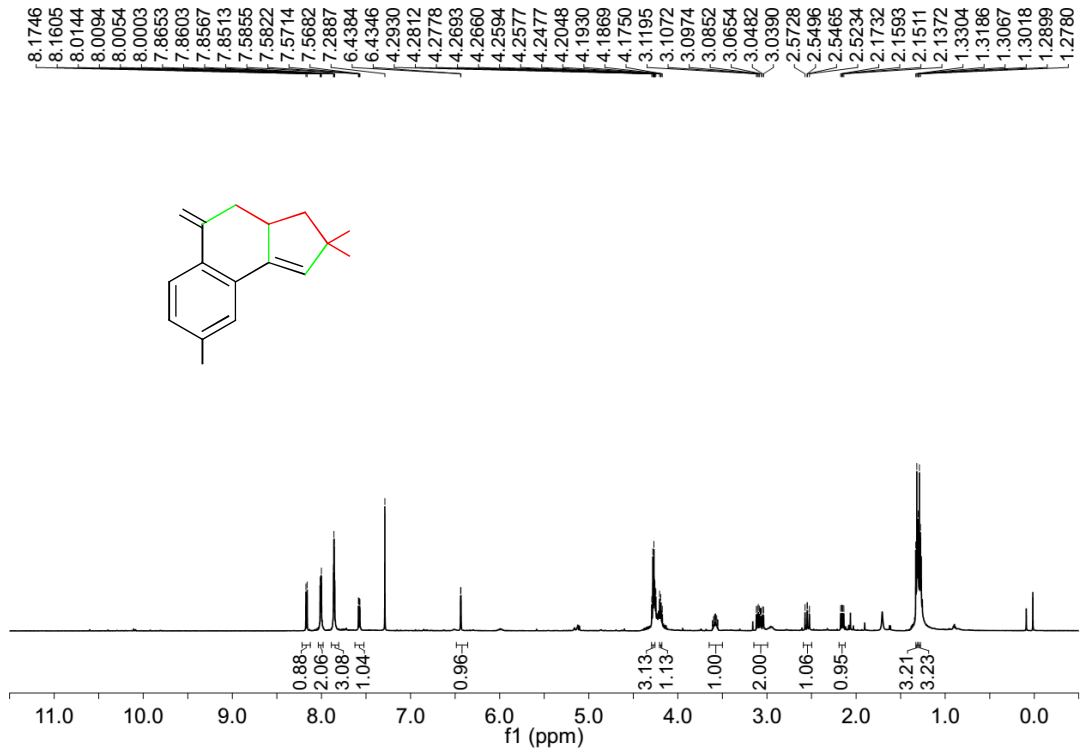


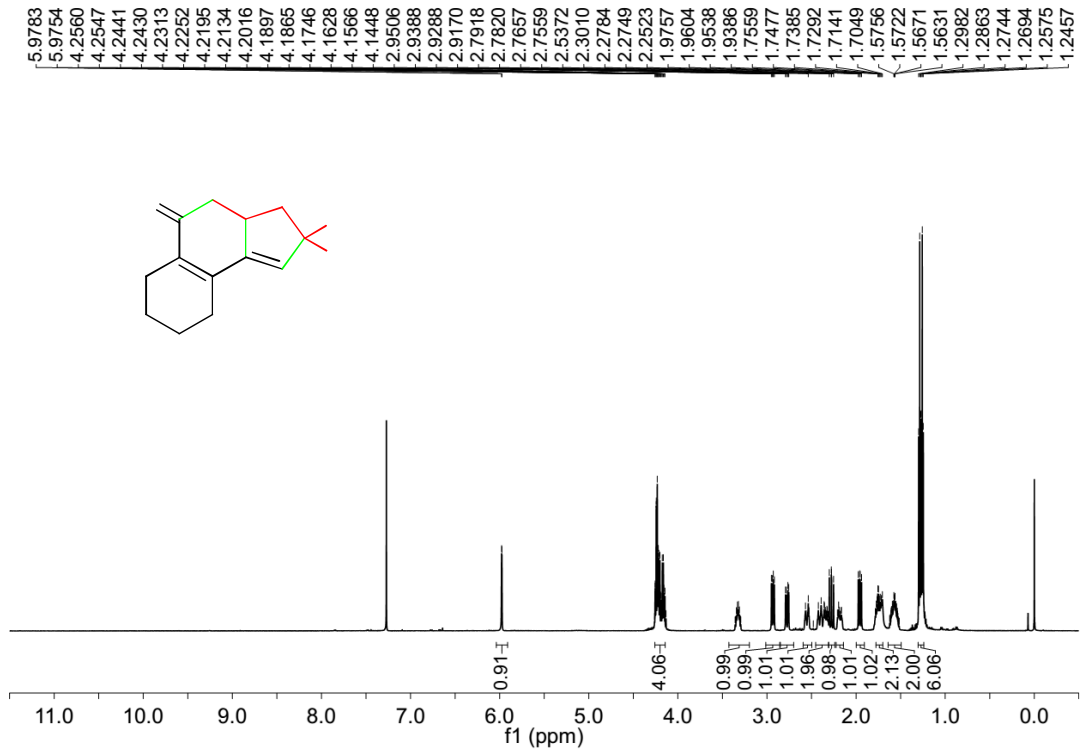


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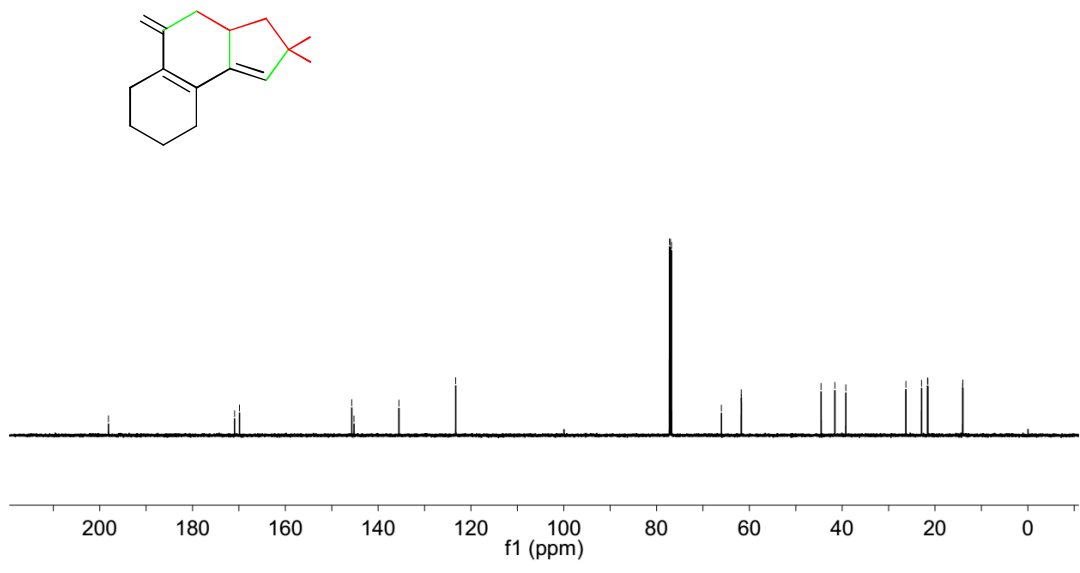


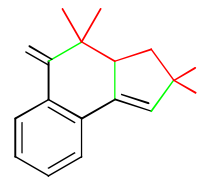
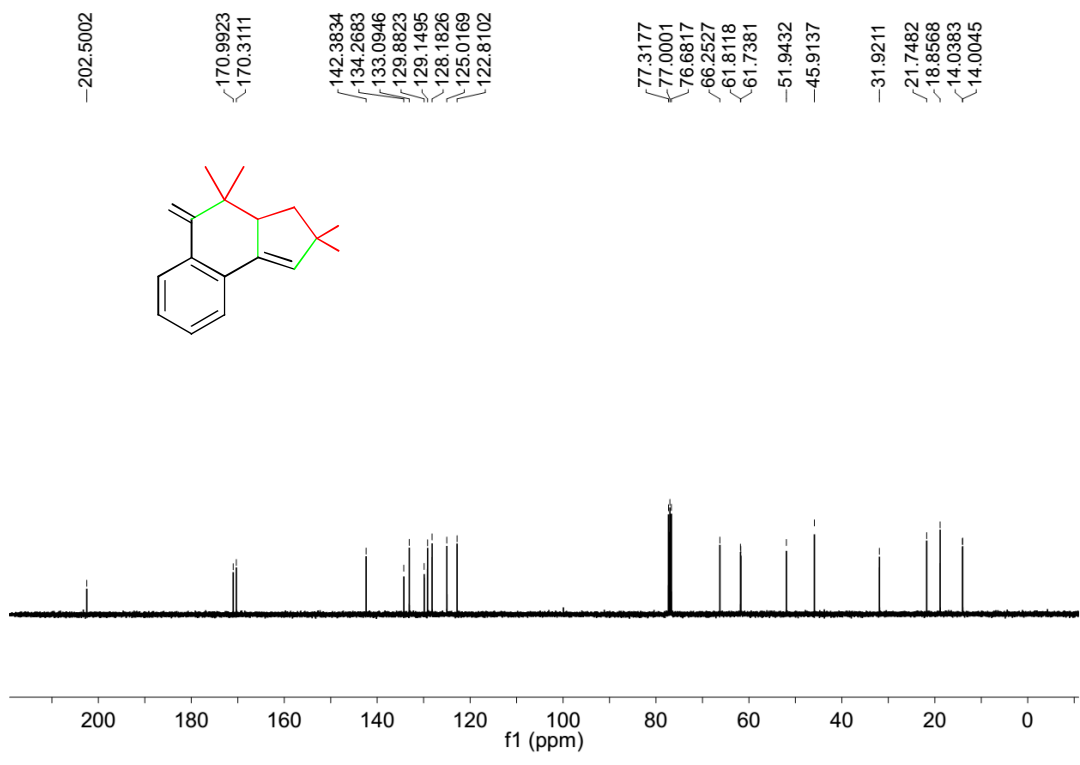
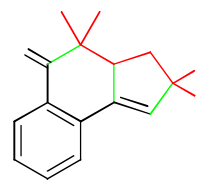
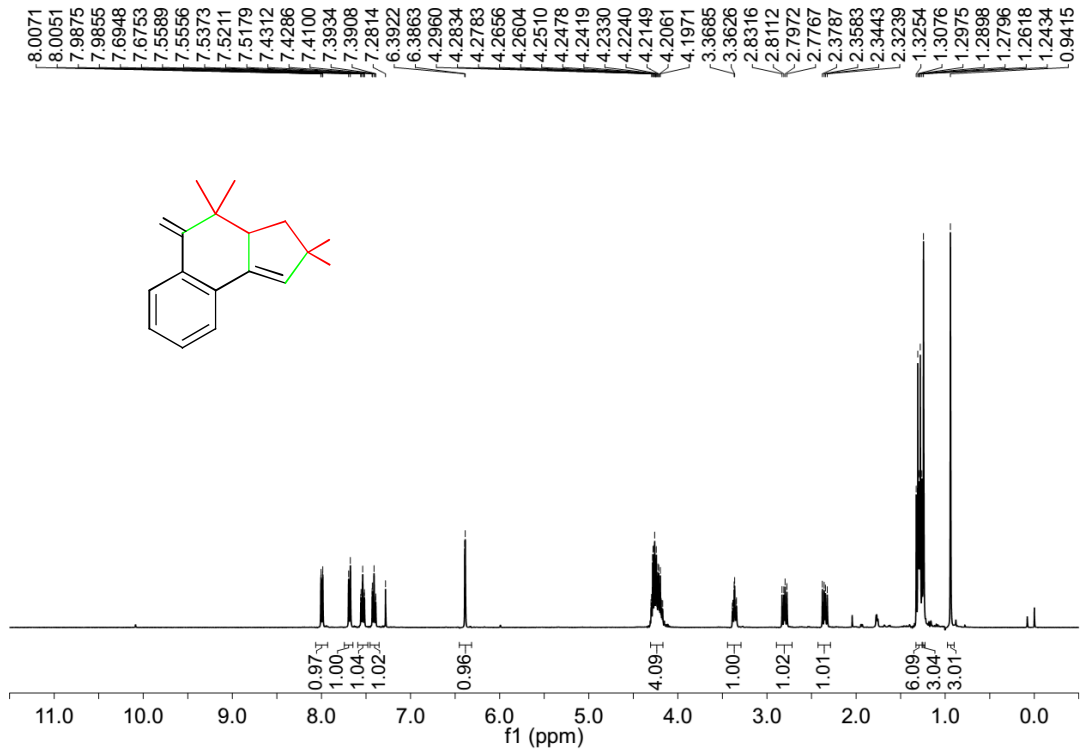


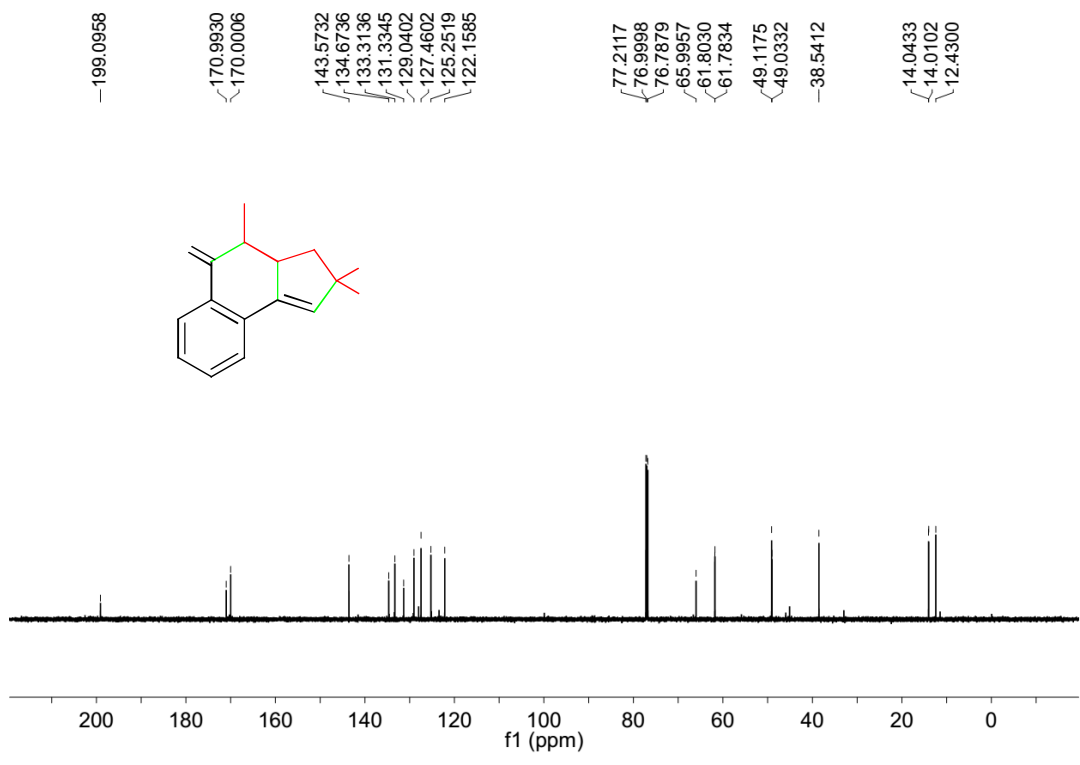
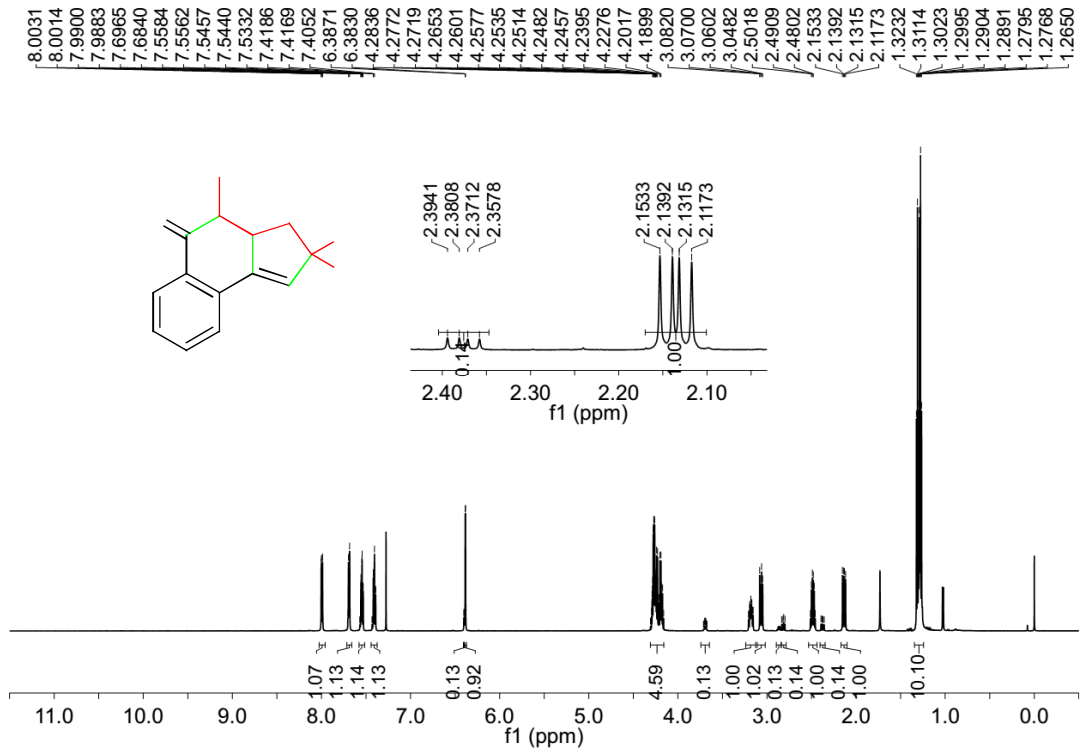


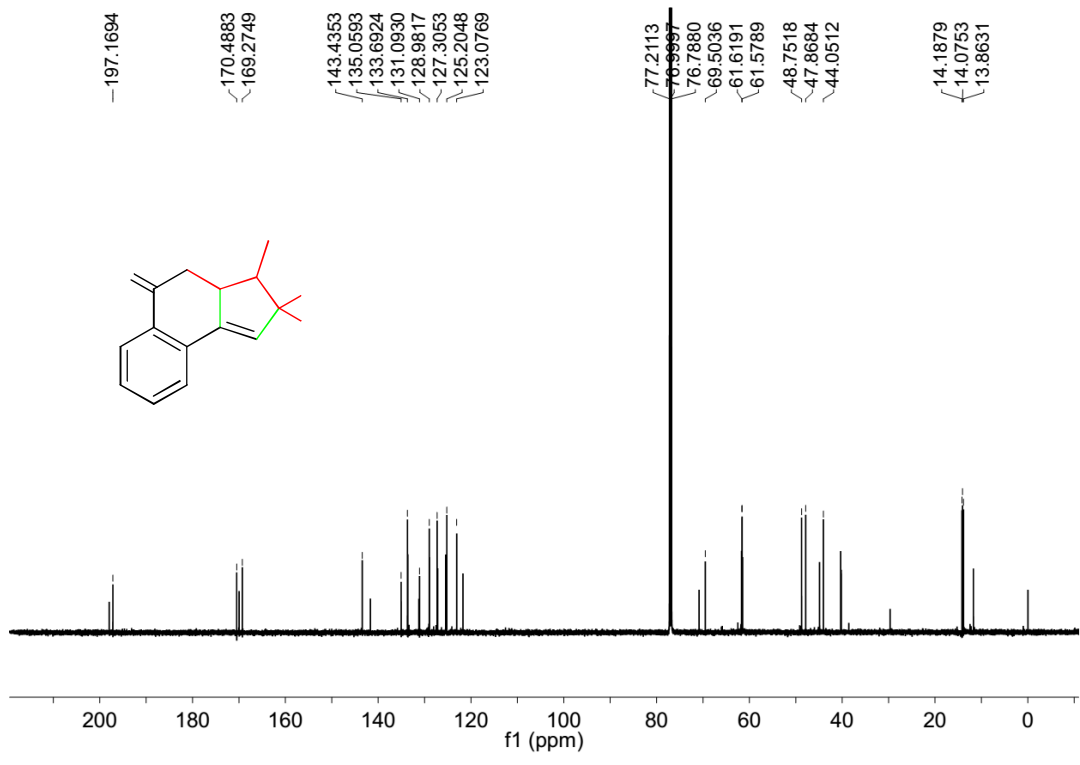
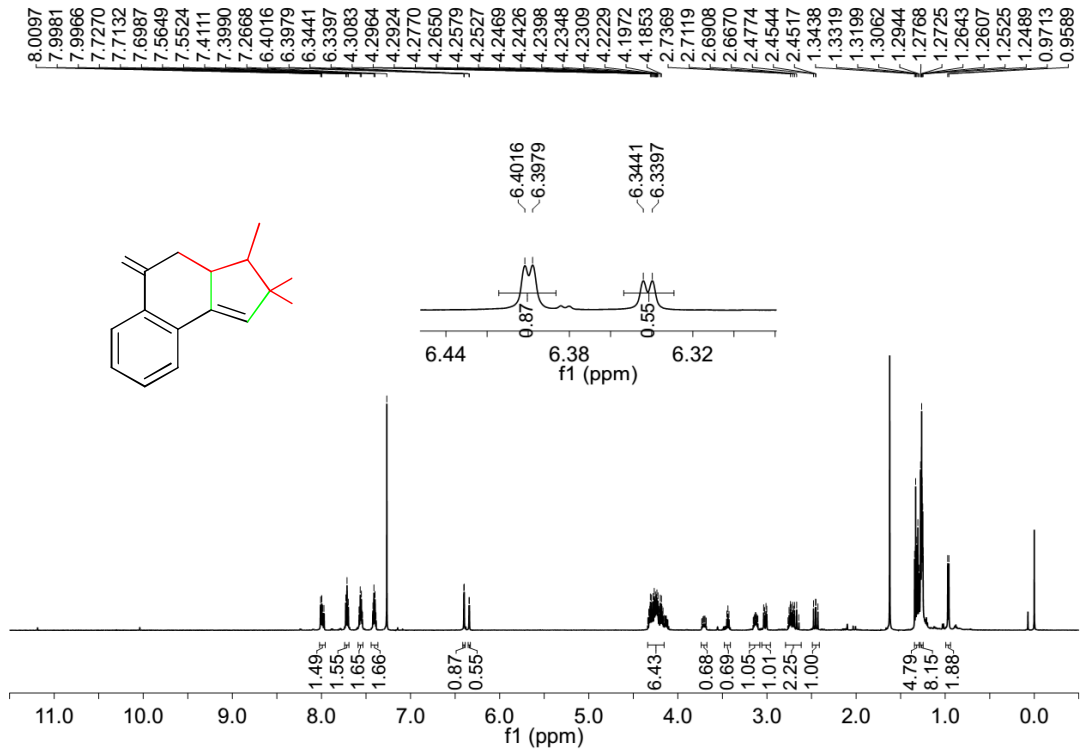


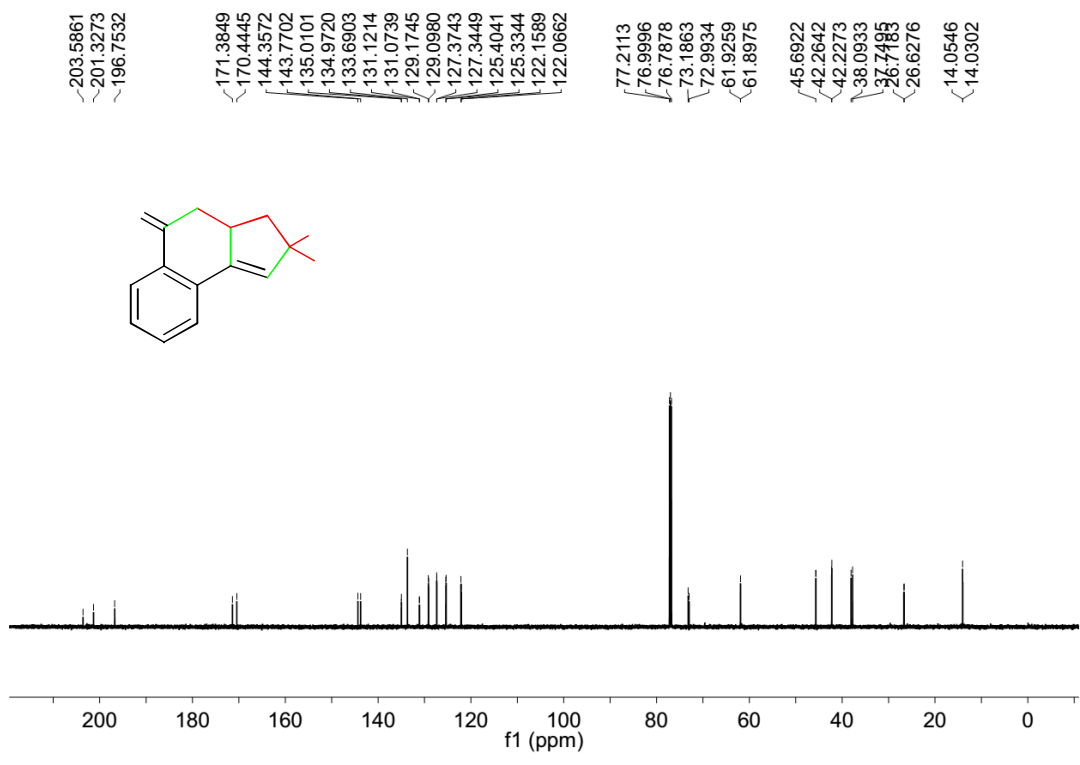
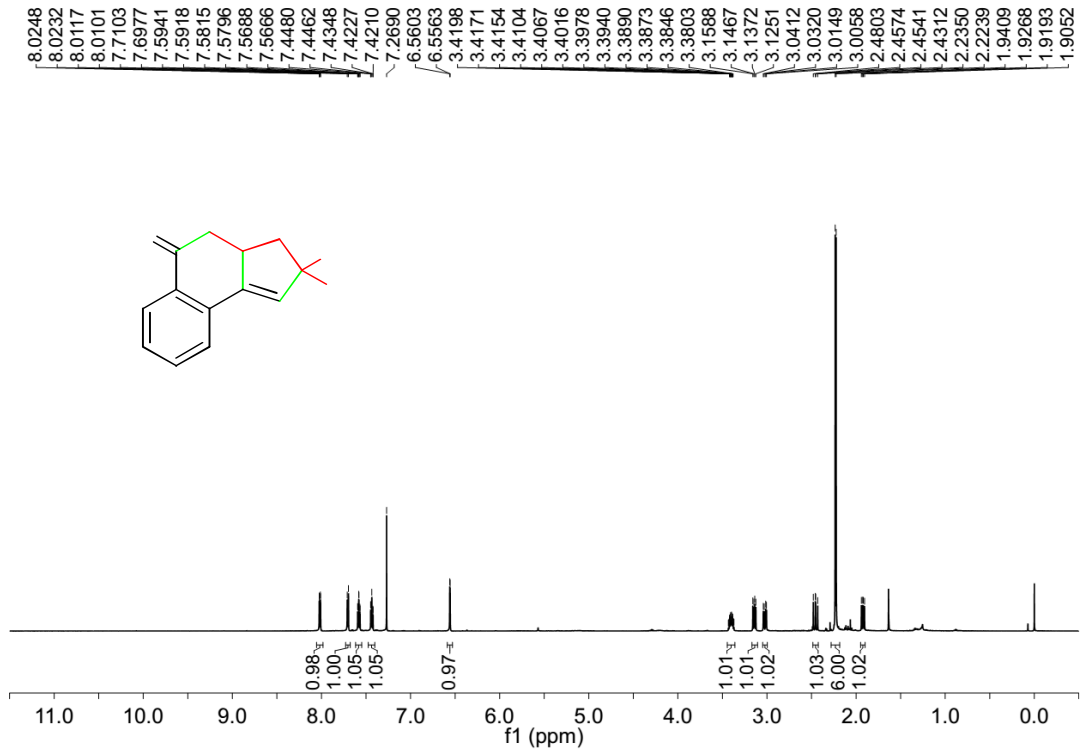
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- 76.7885
- 66.0297
- 61.7537
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- 44.5527
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- 14.0063

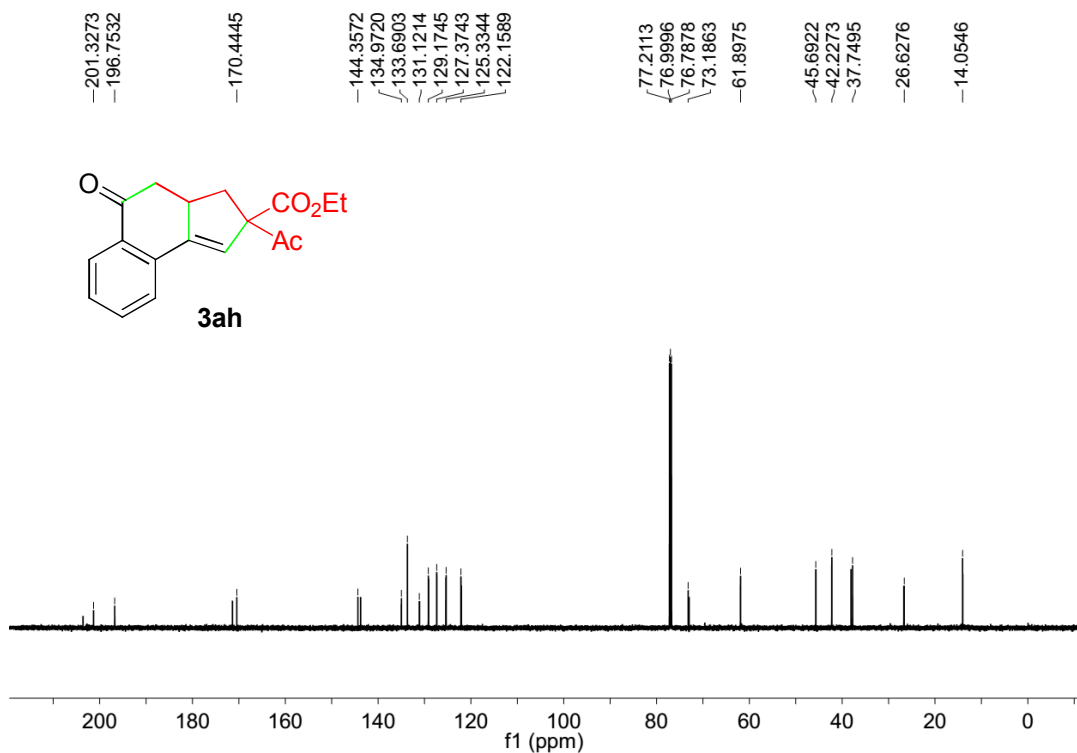
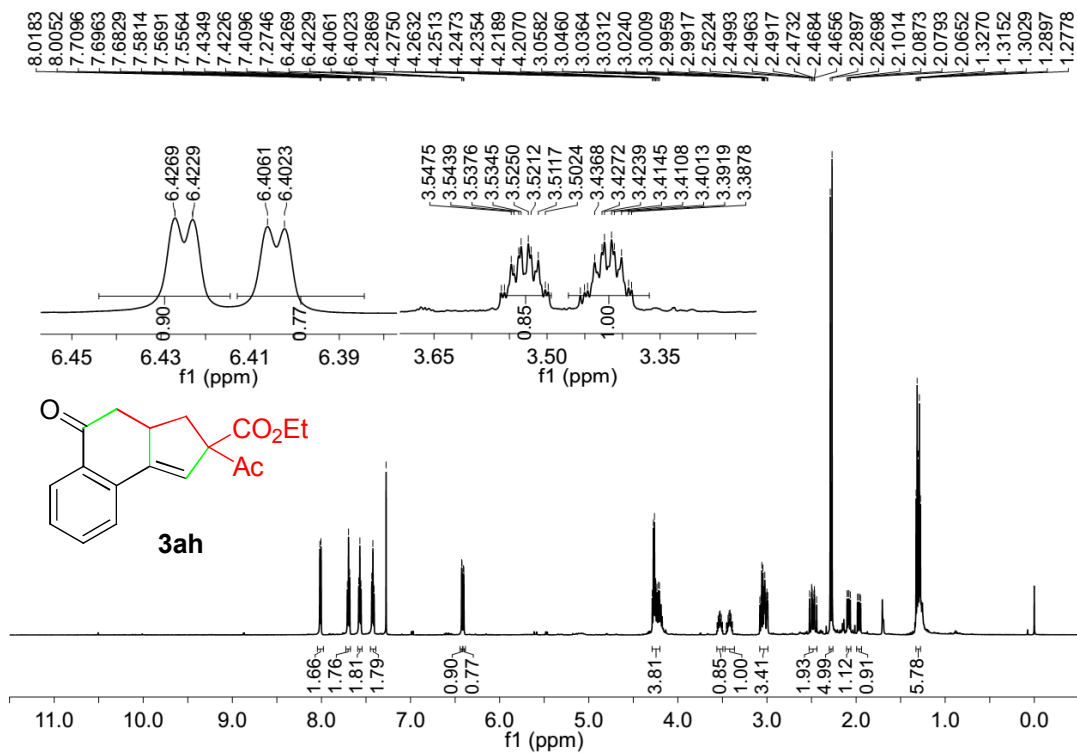


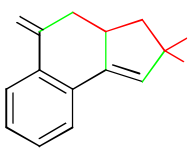
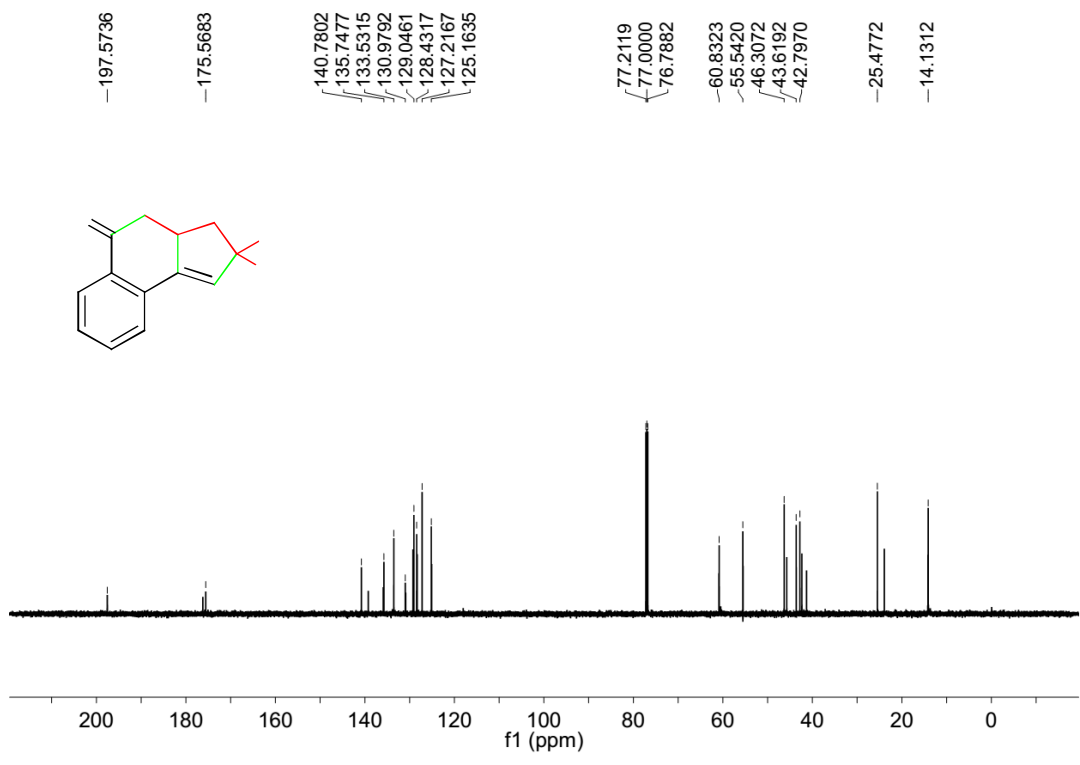
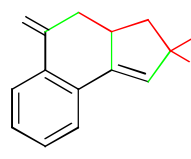
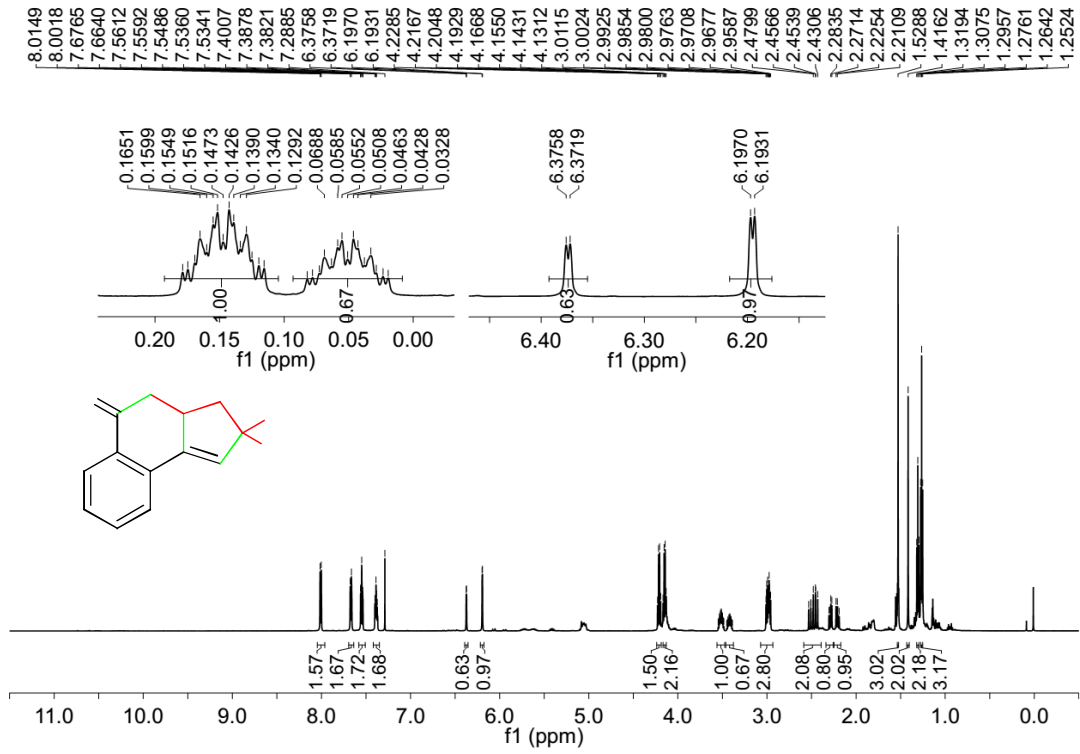


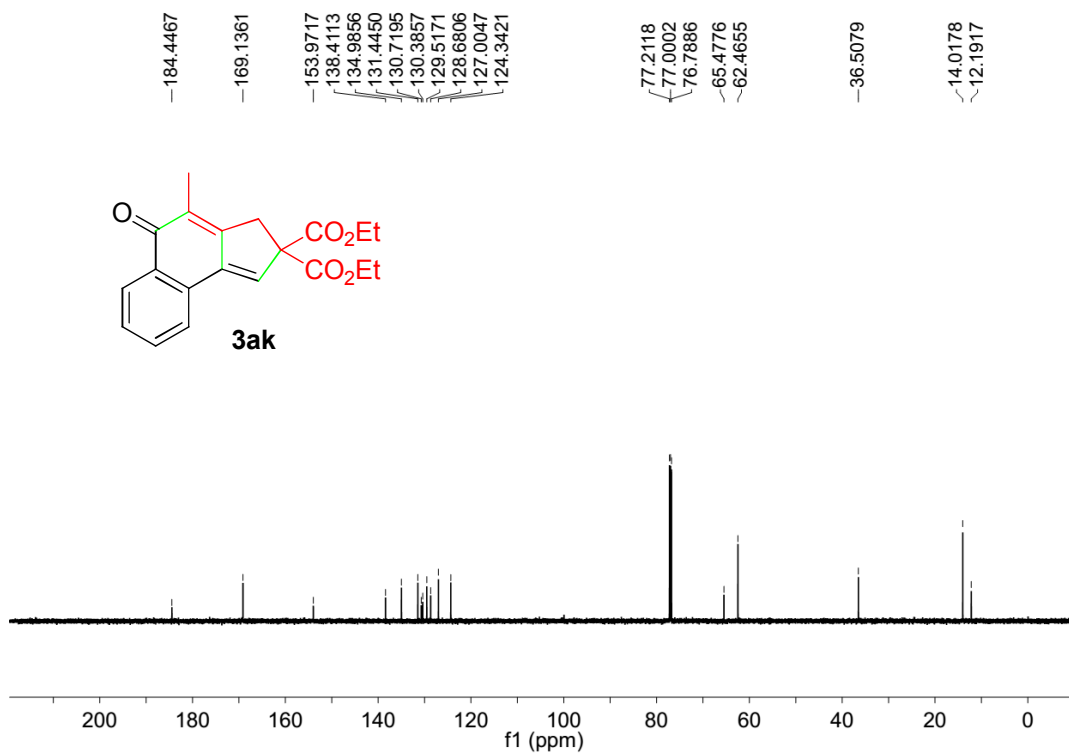
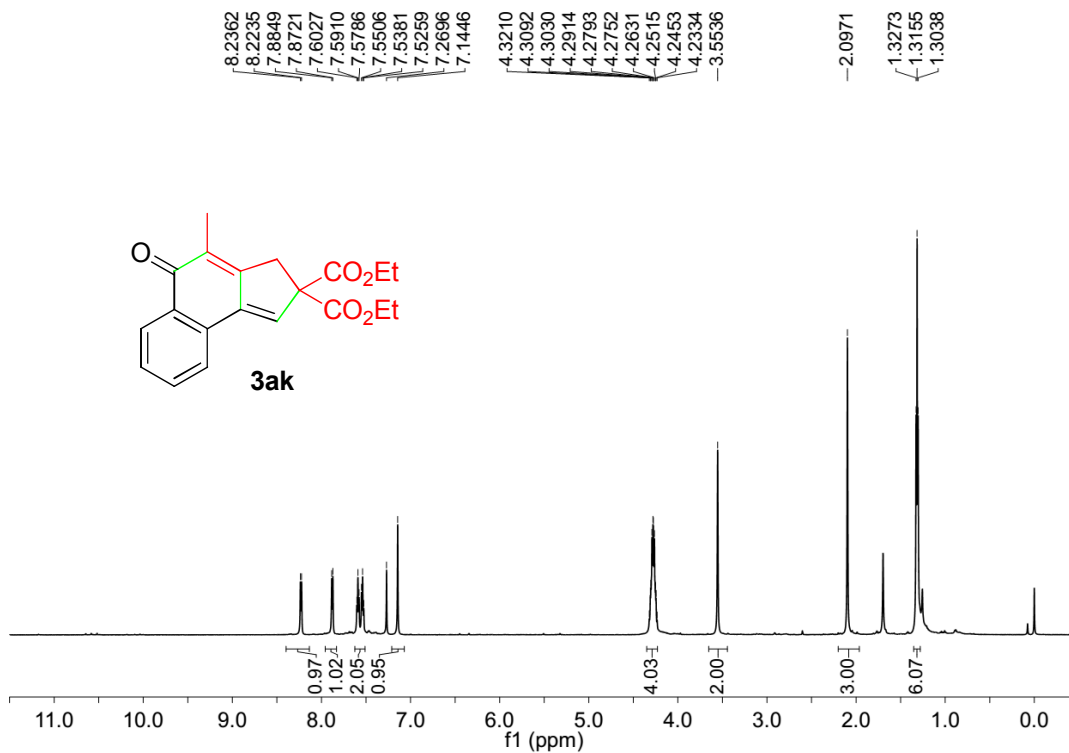


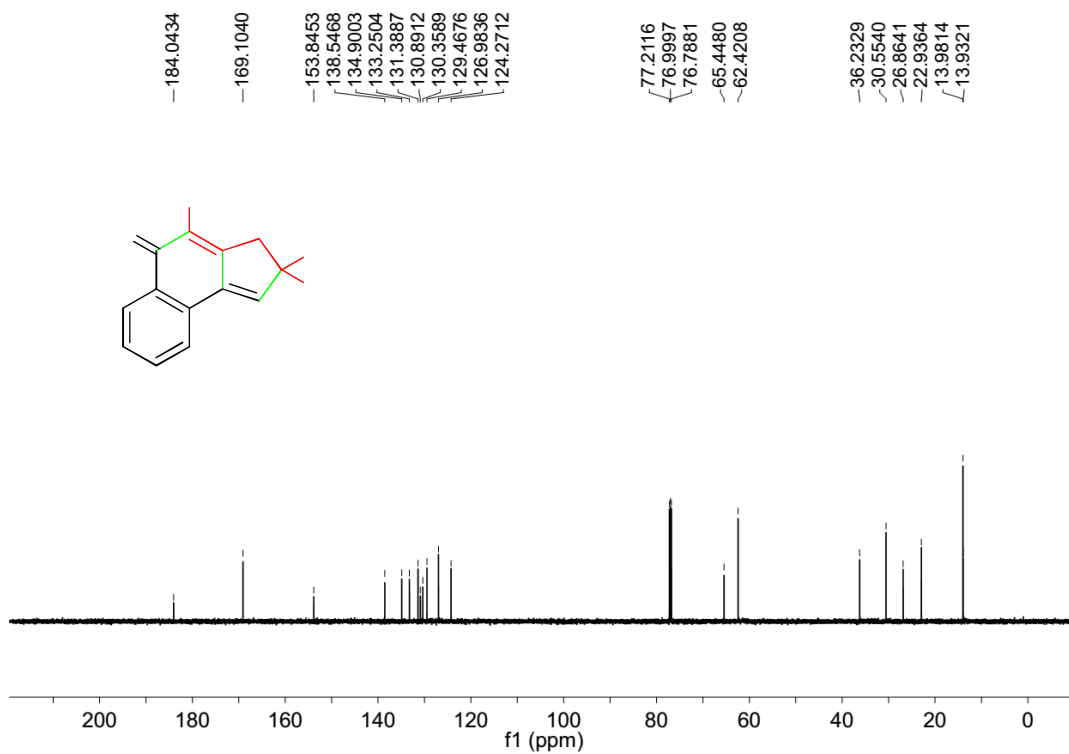
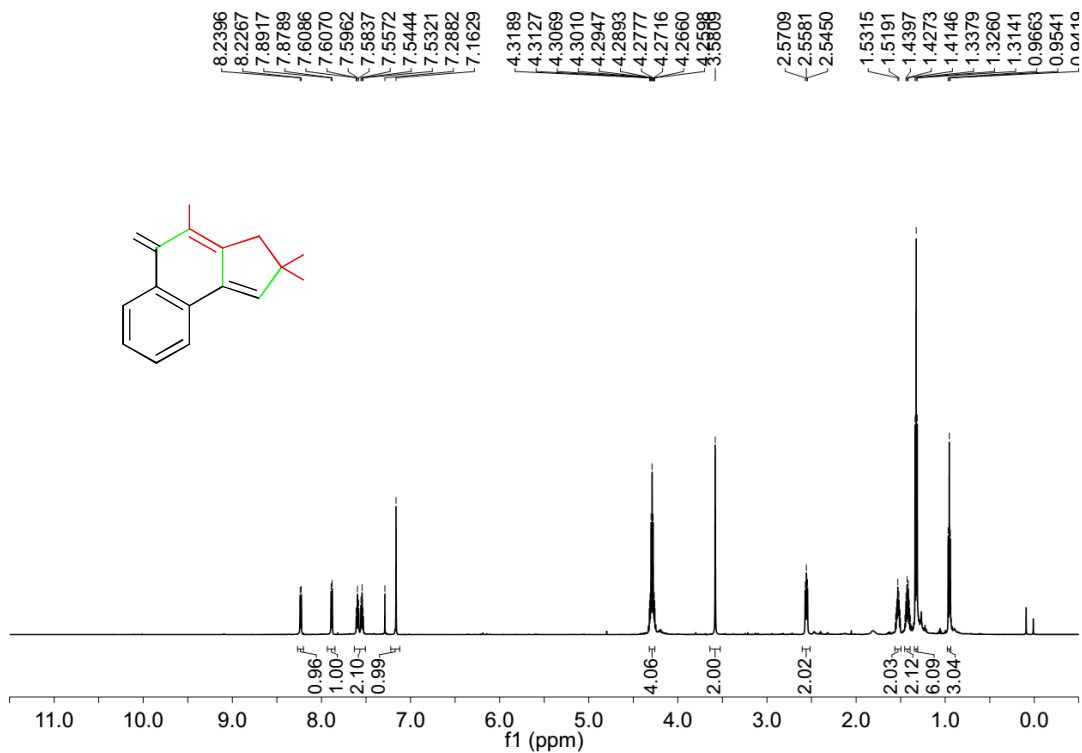


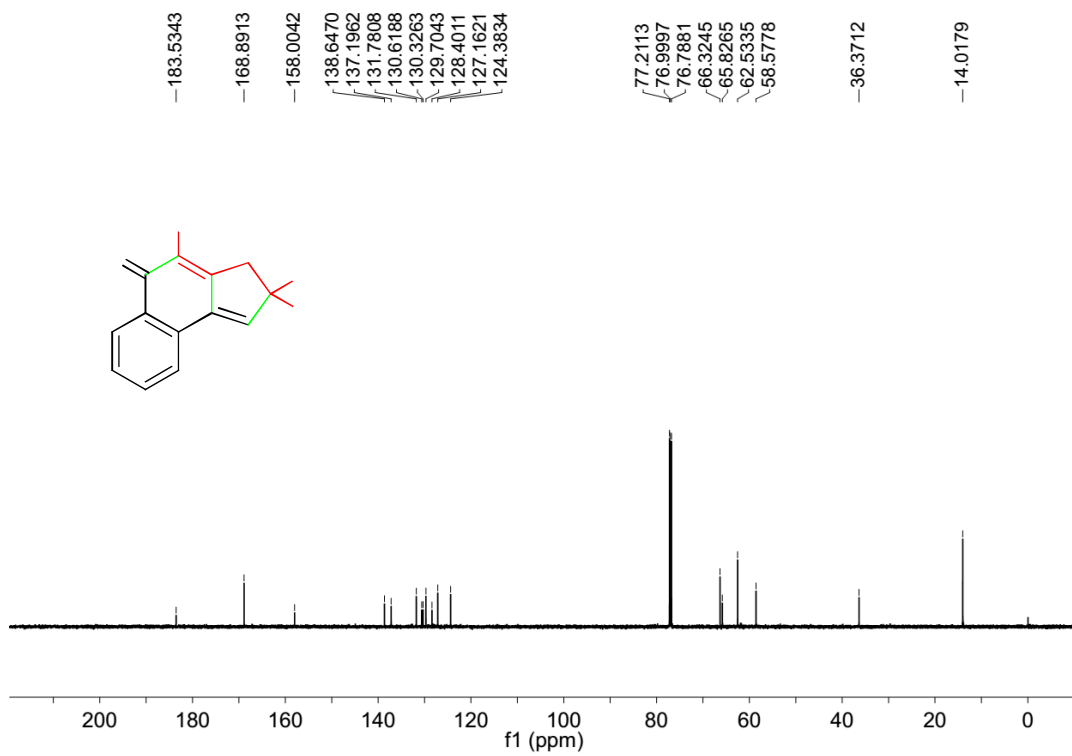
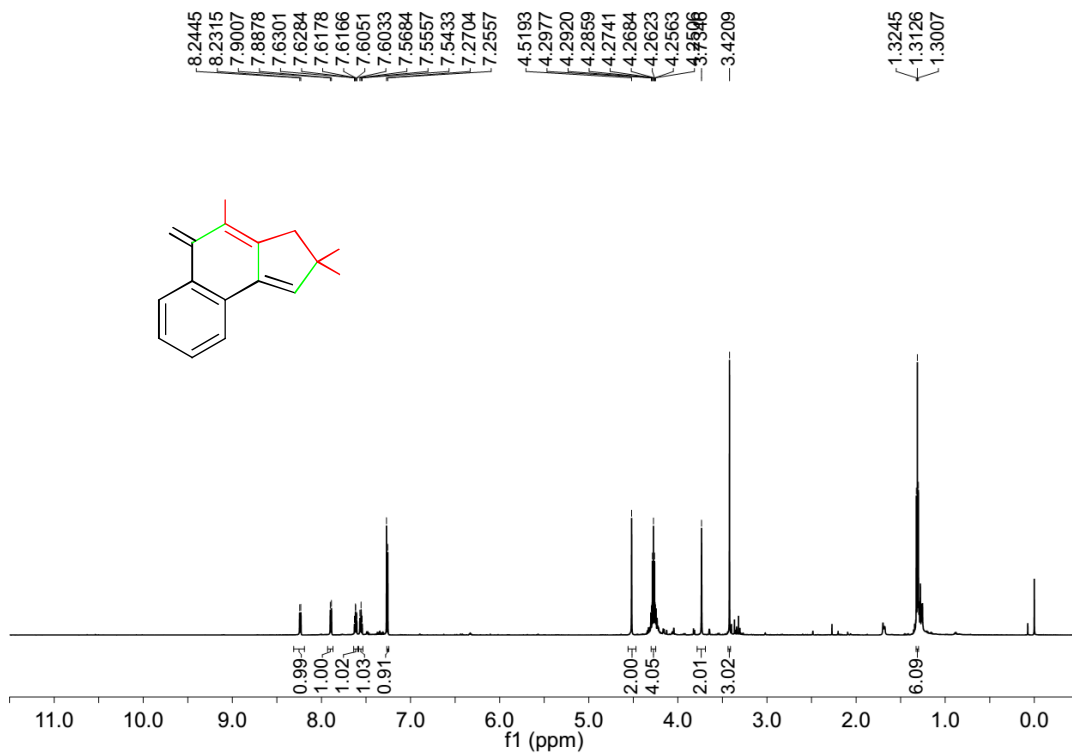


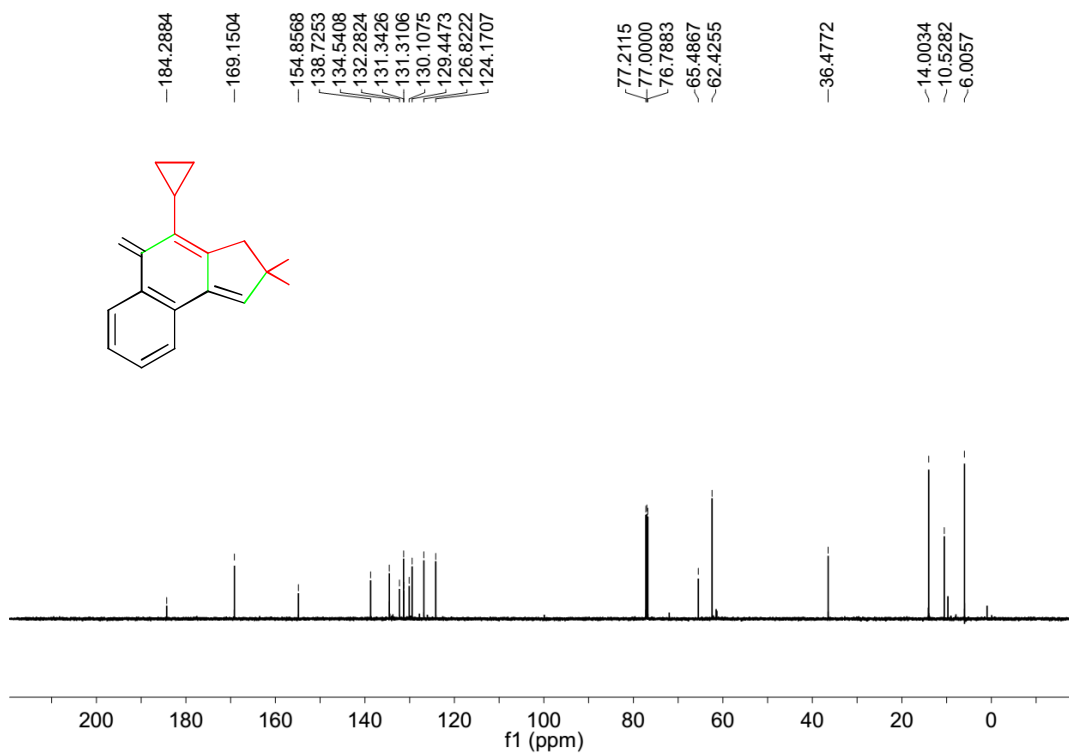
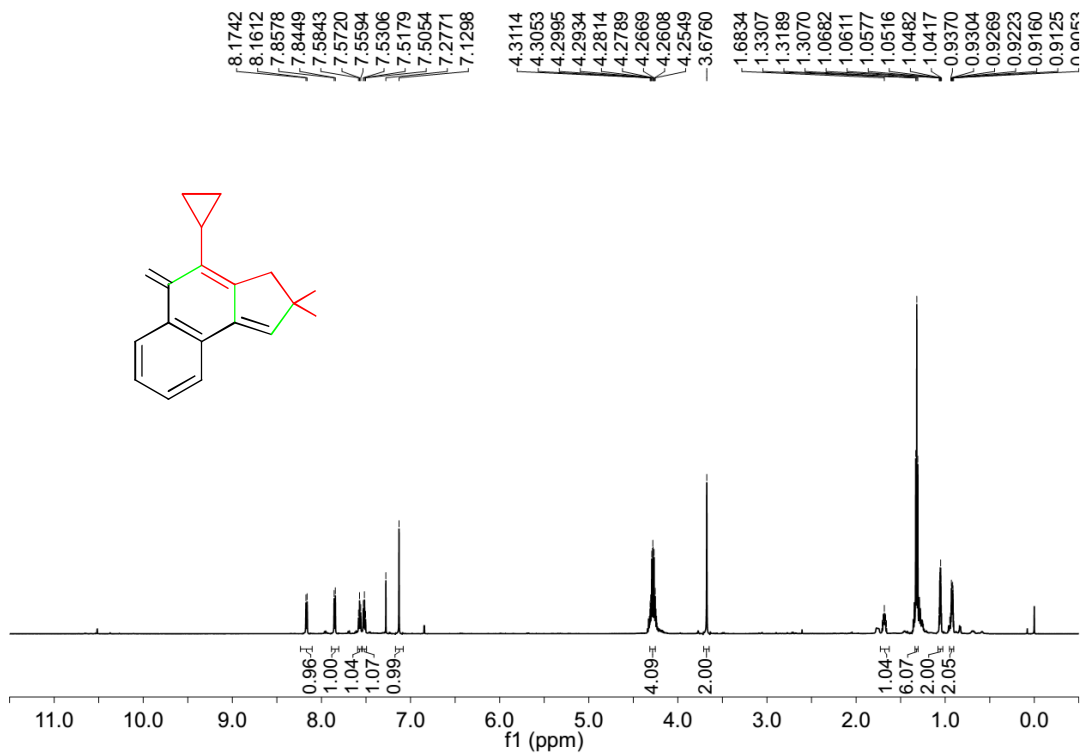


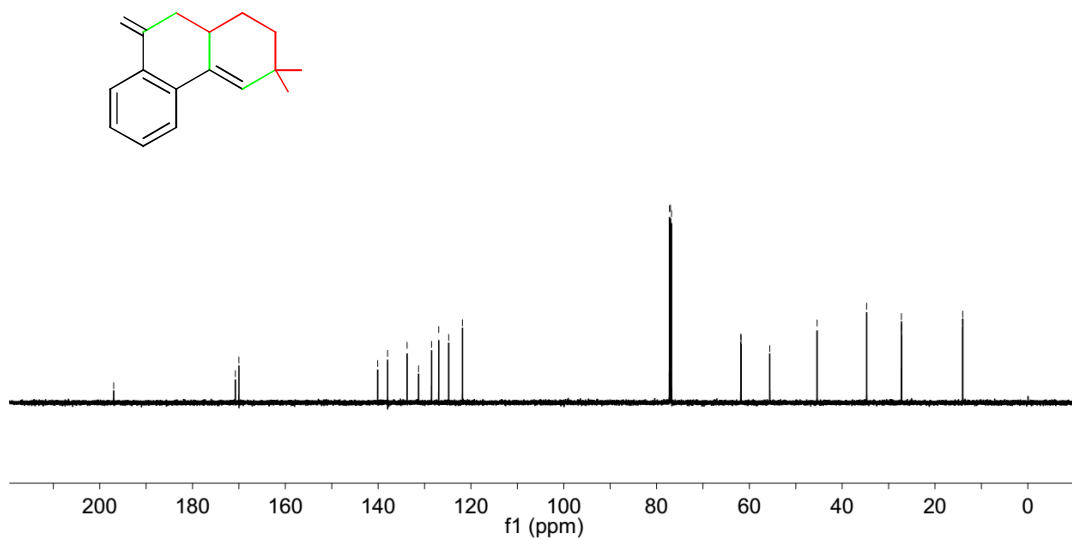
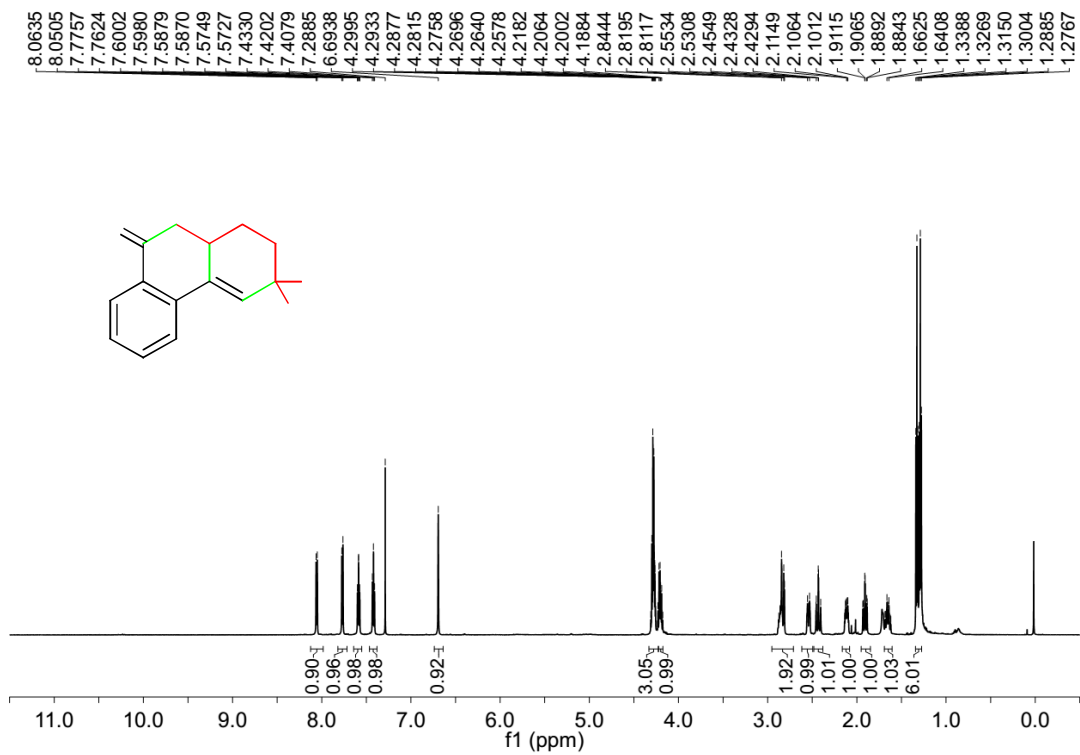


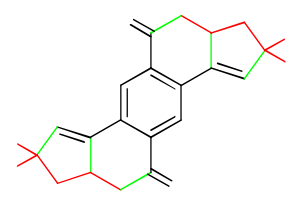
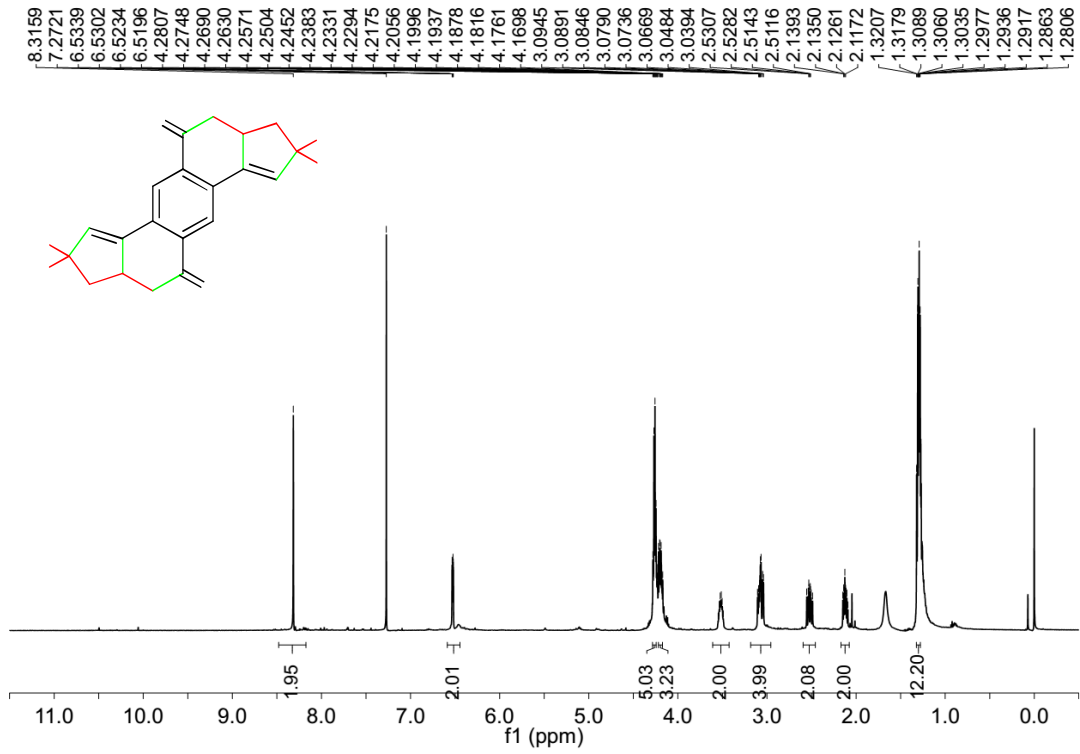




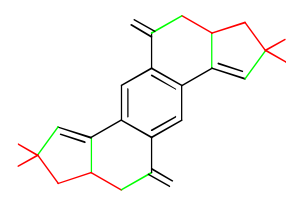
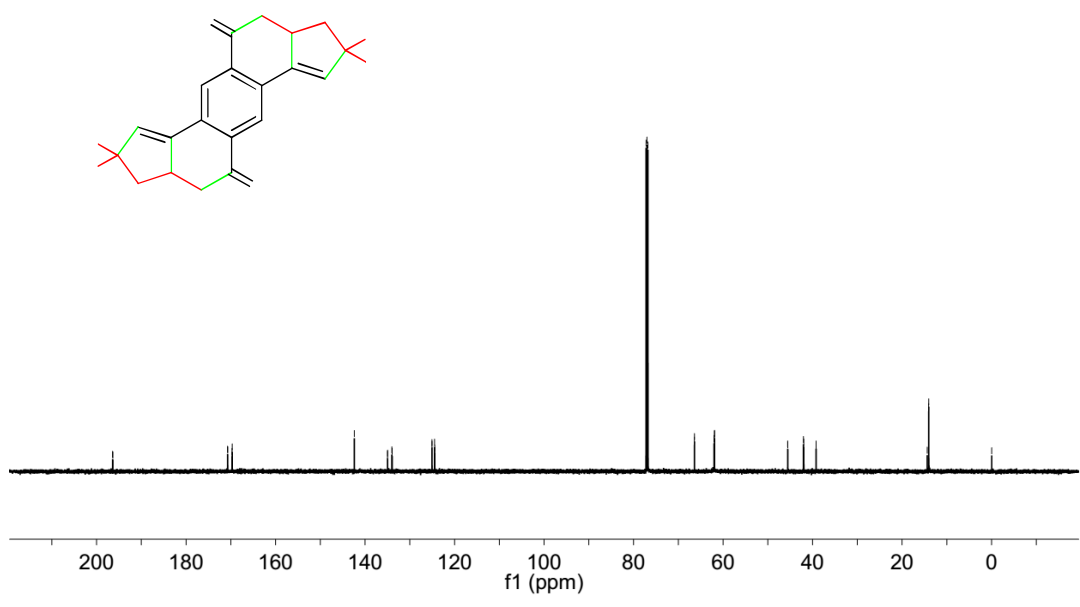


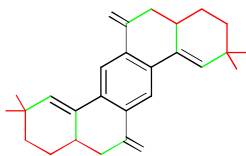
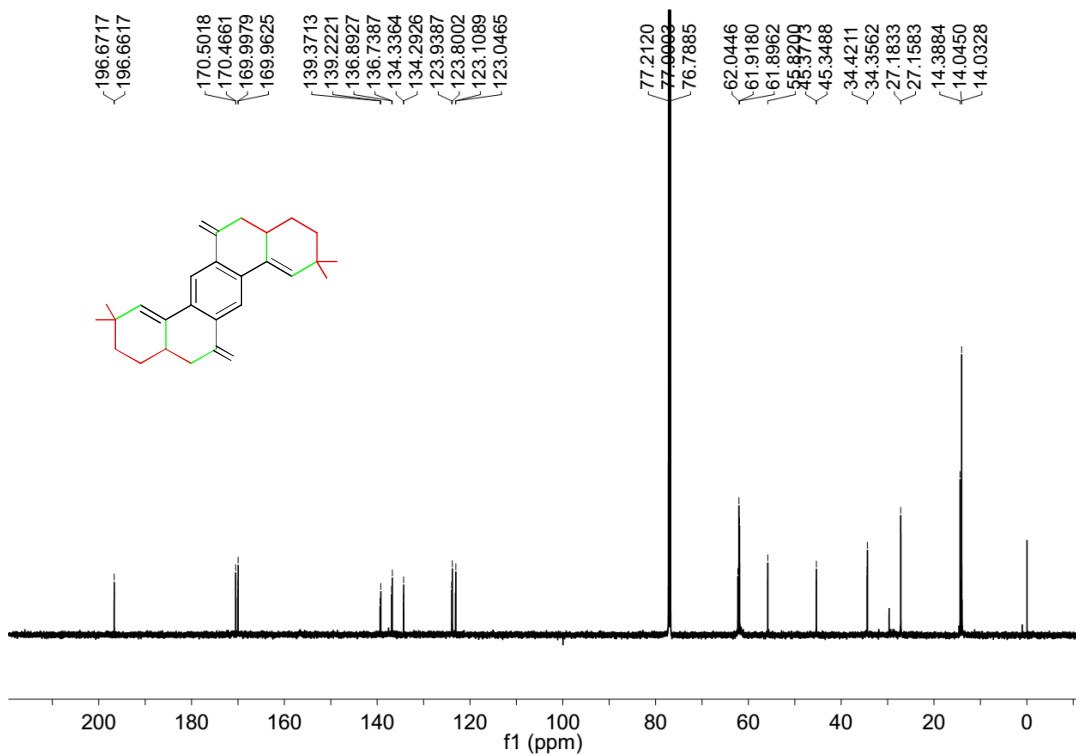
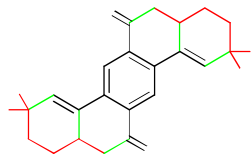
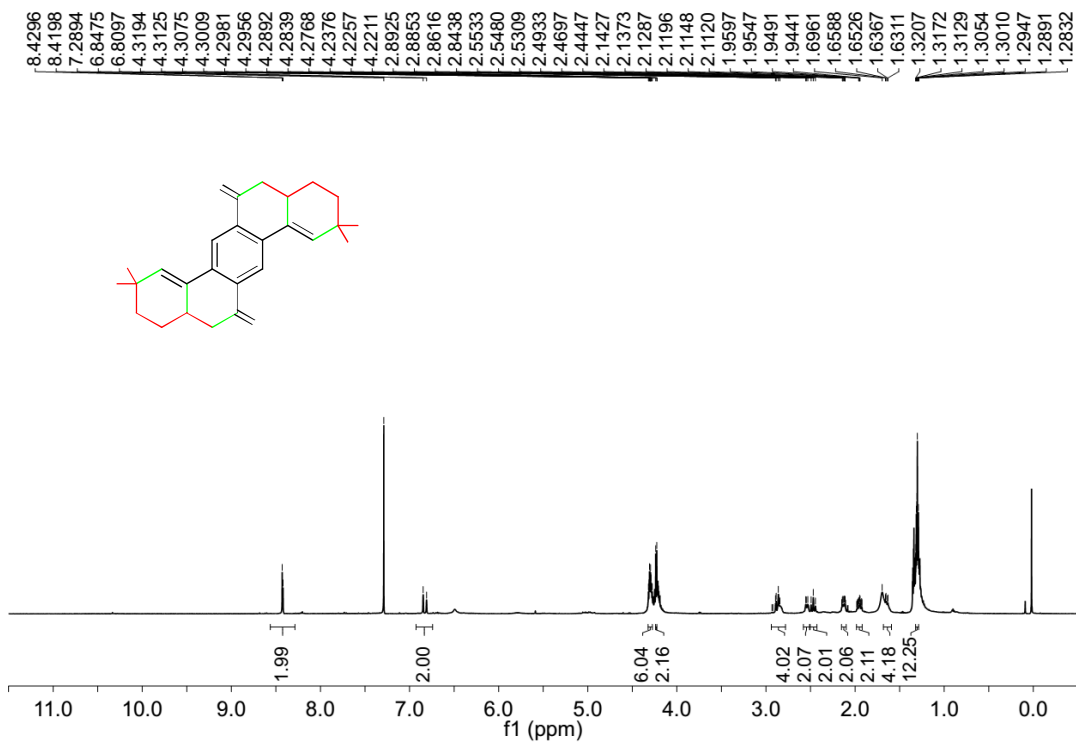


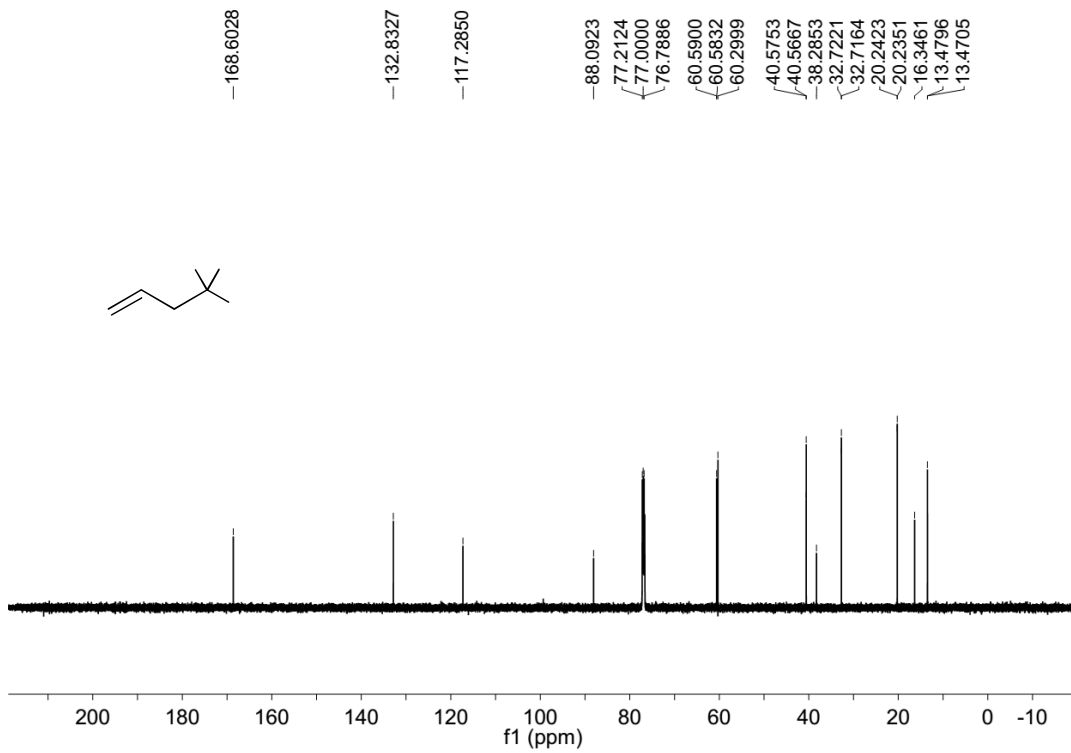
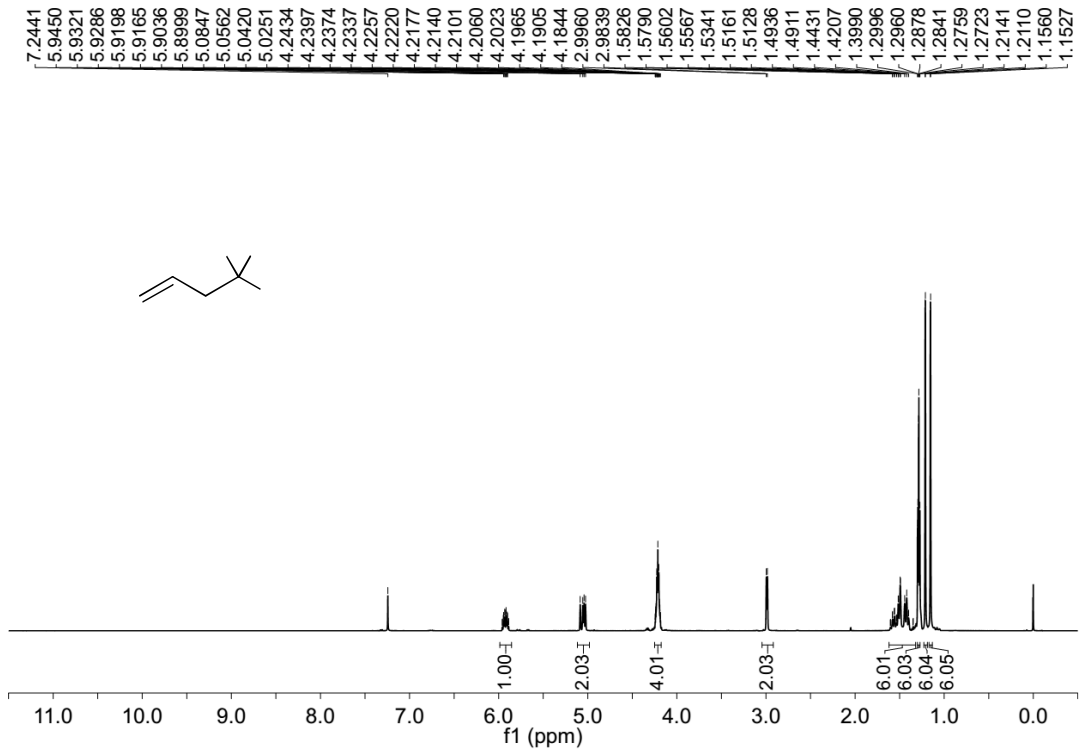


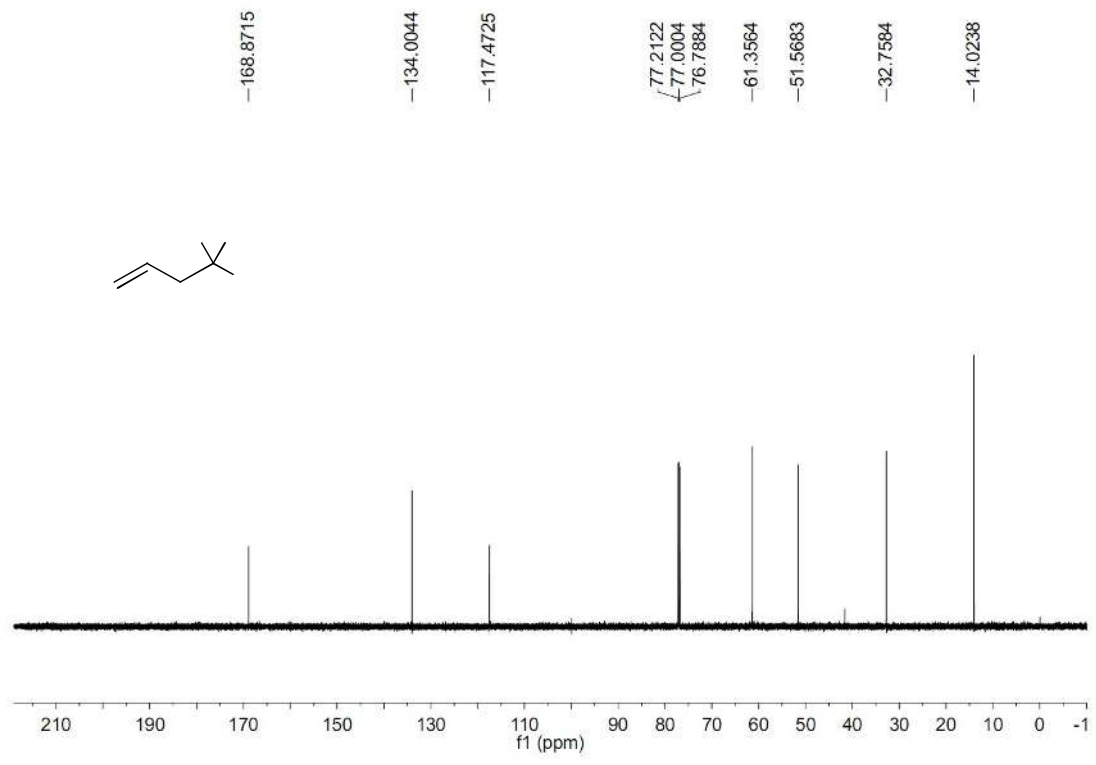
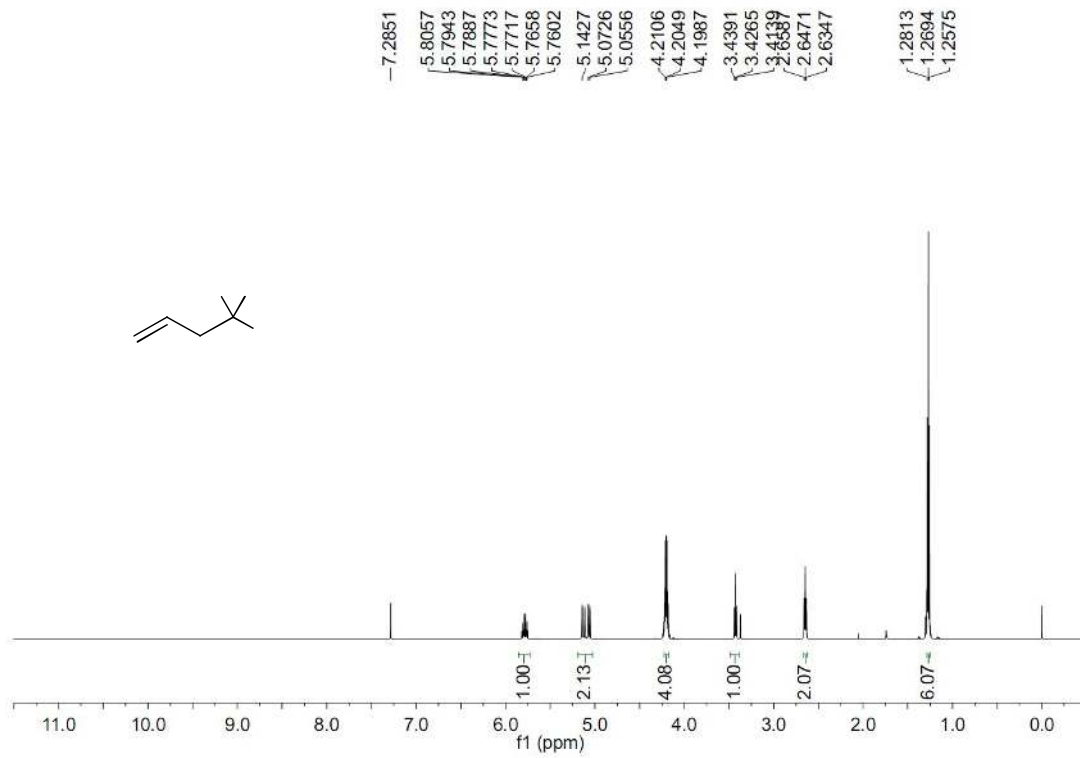


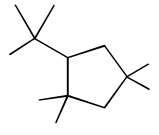
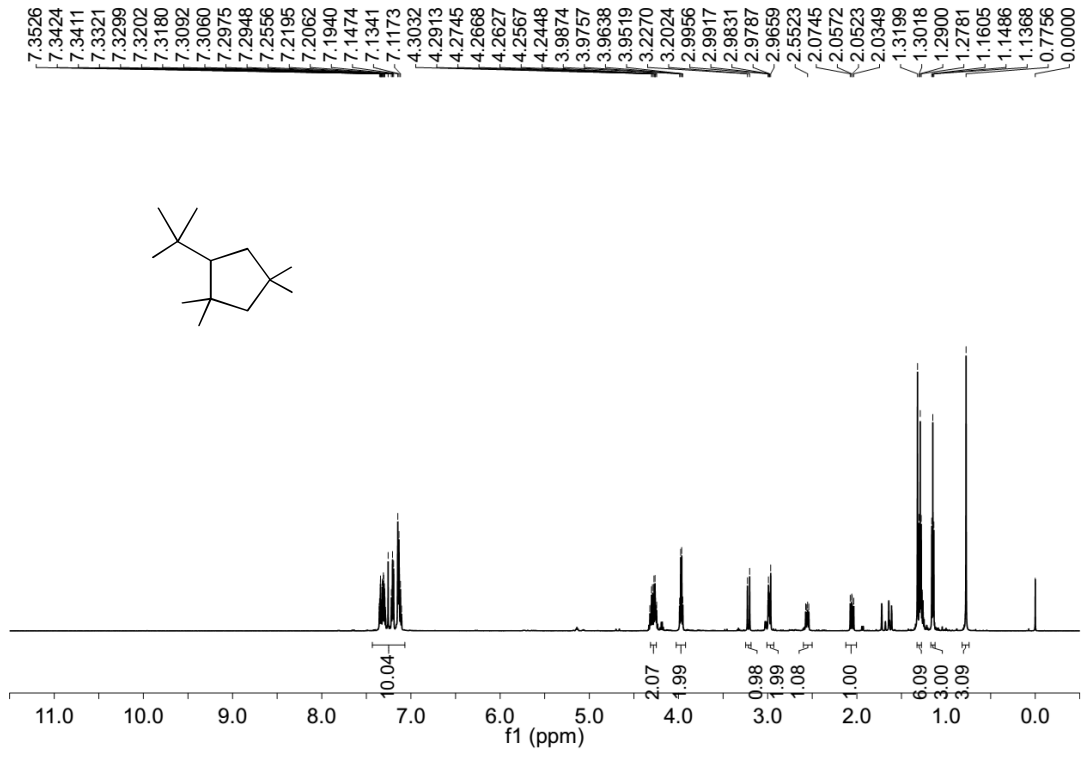
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- 61.9199
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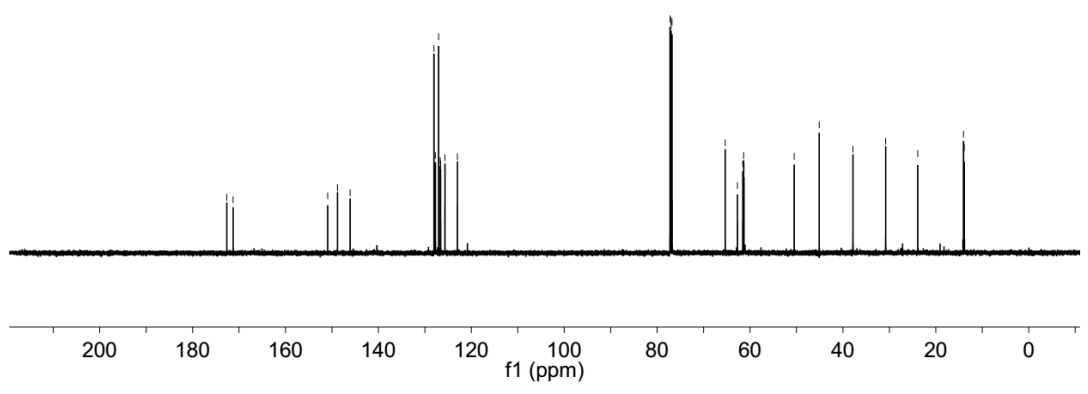
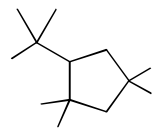


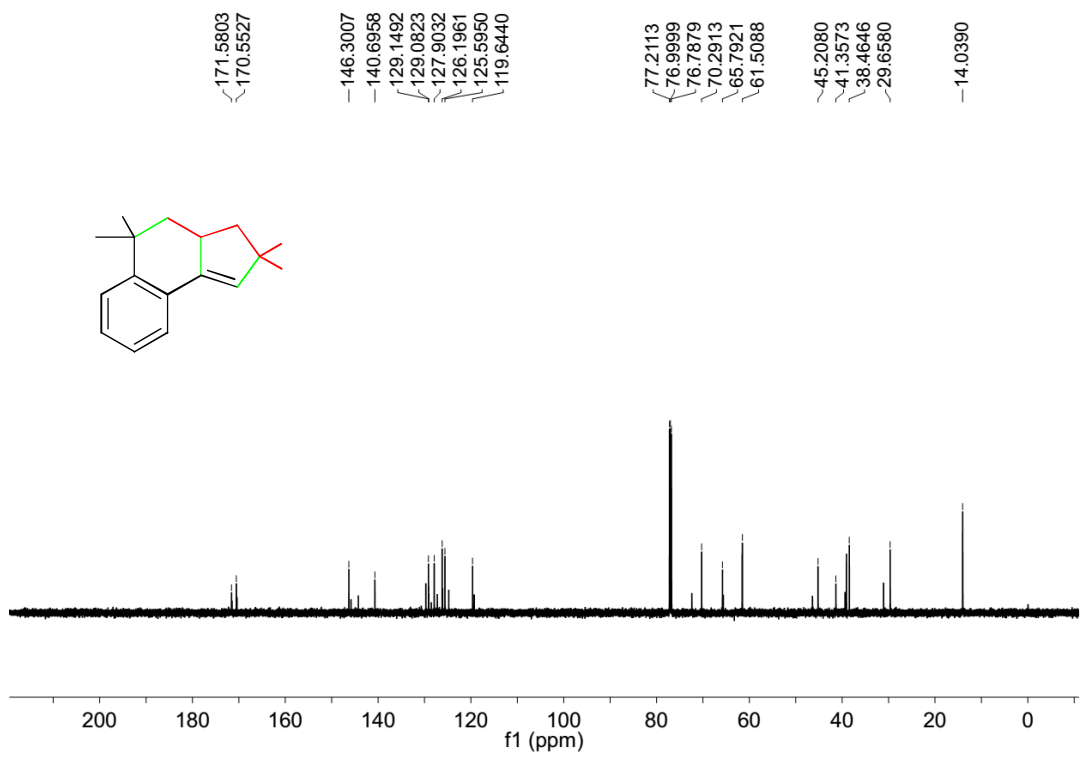
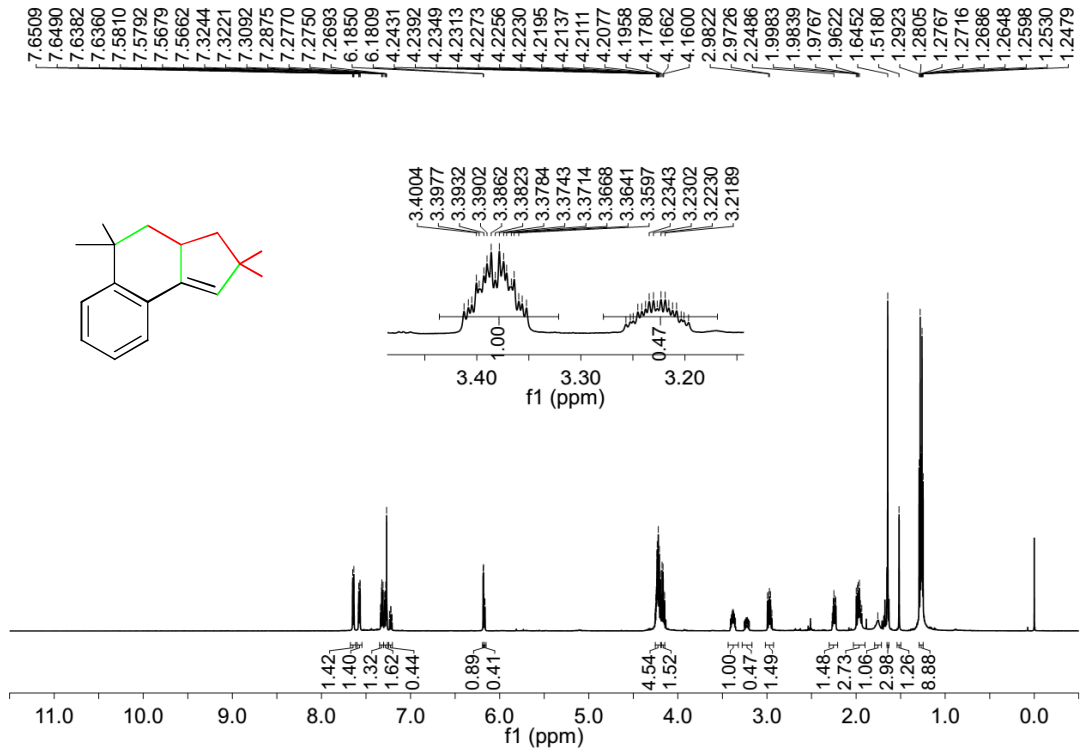


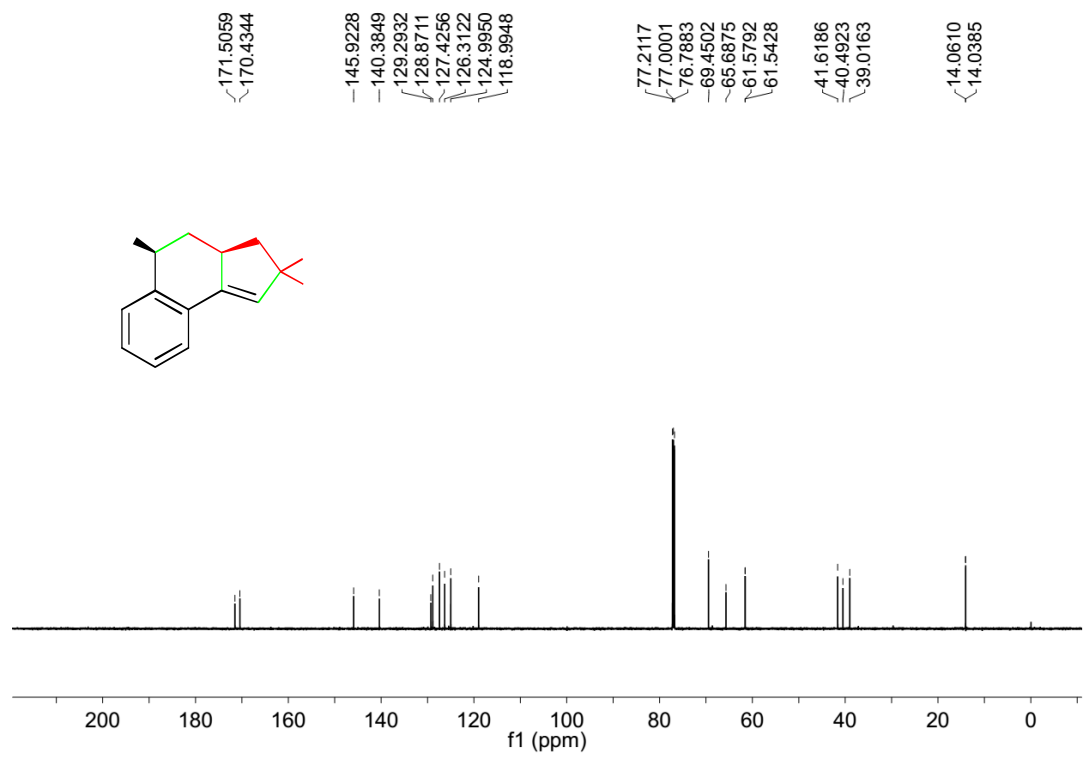
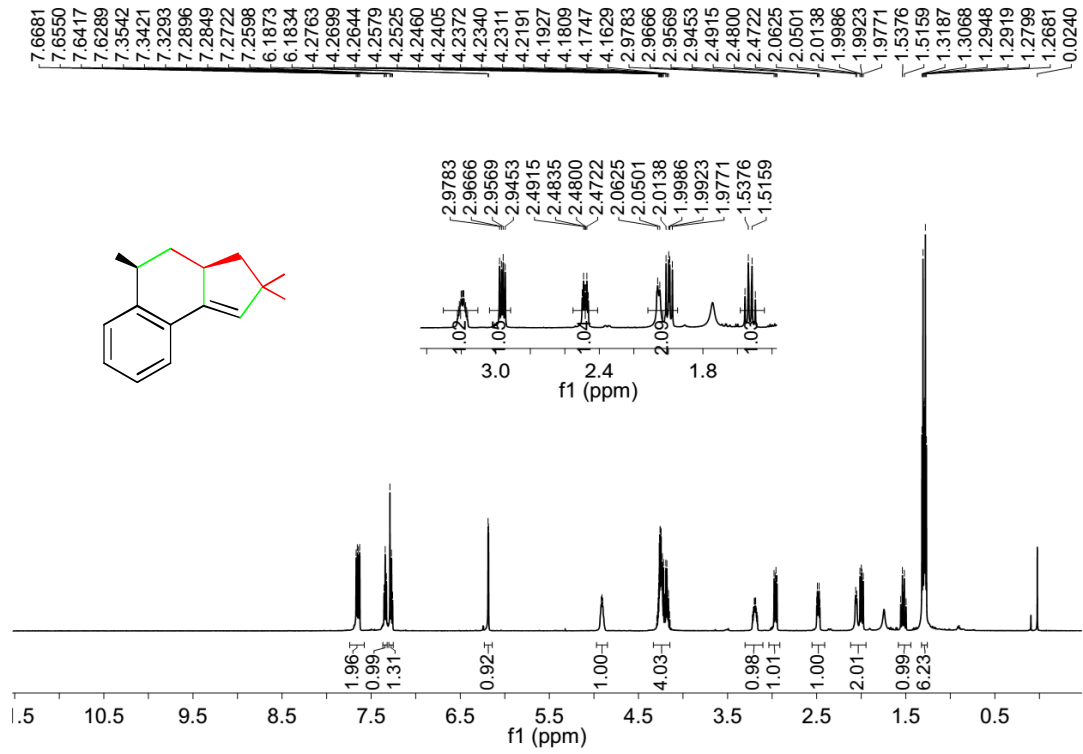


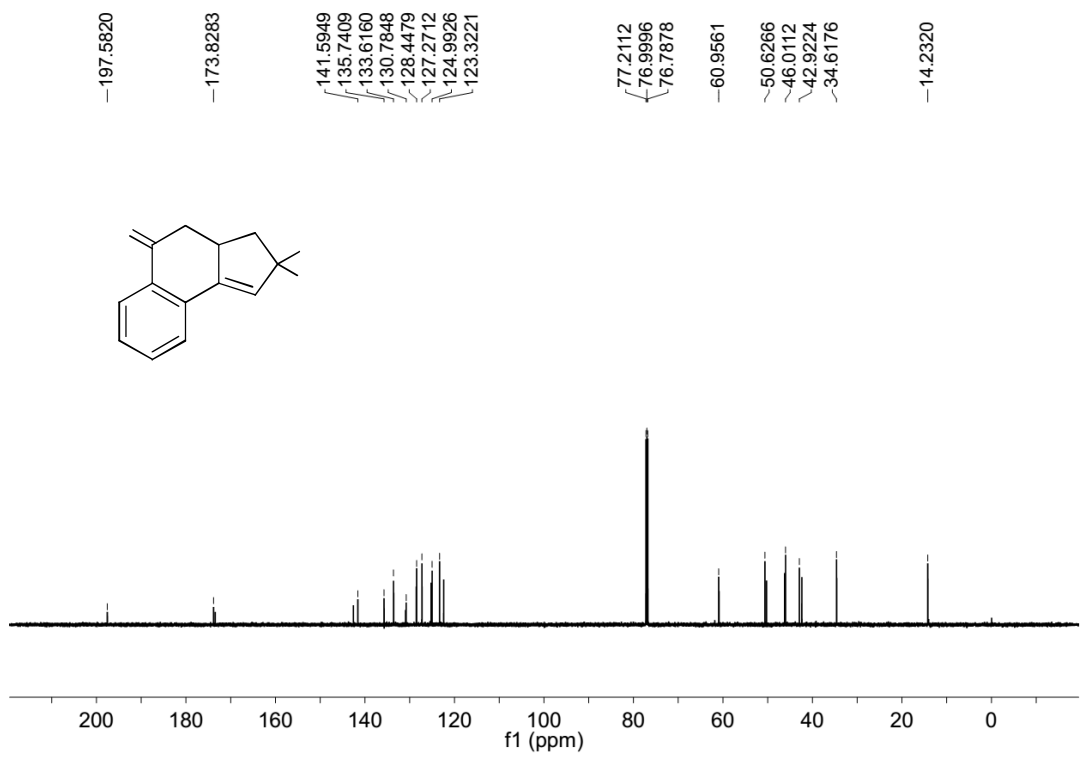
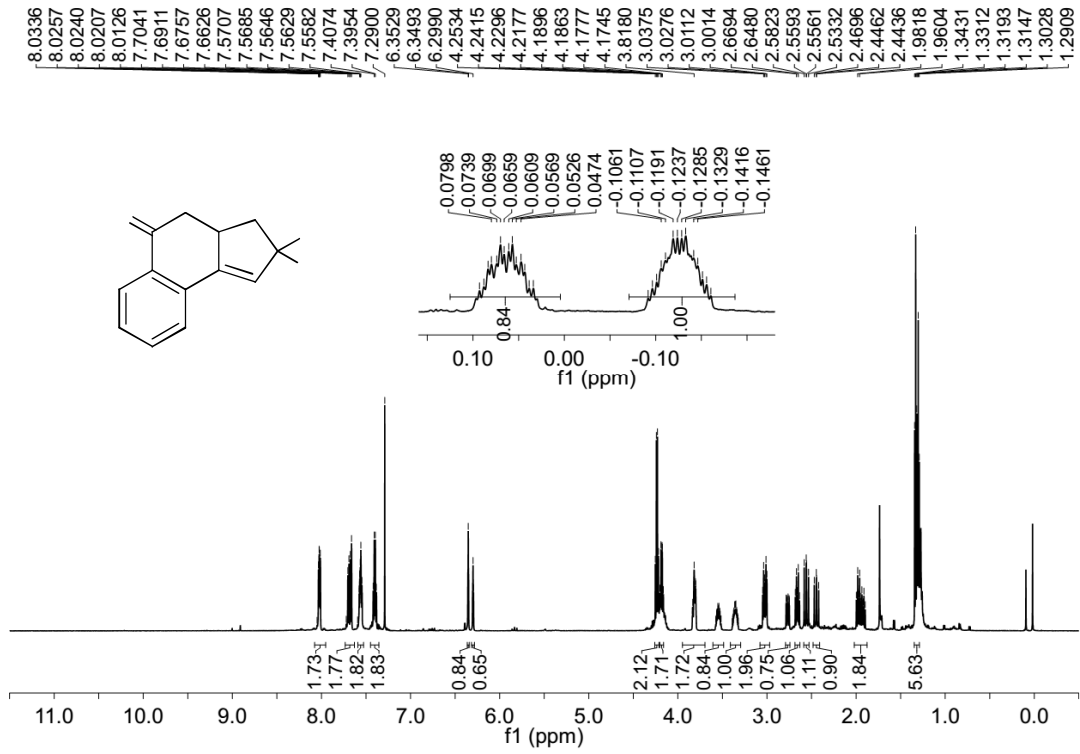


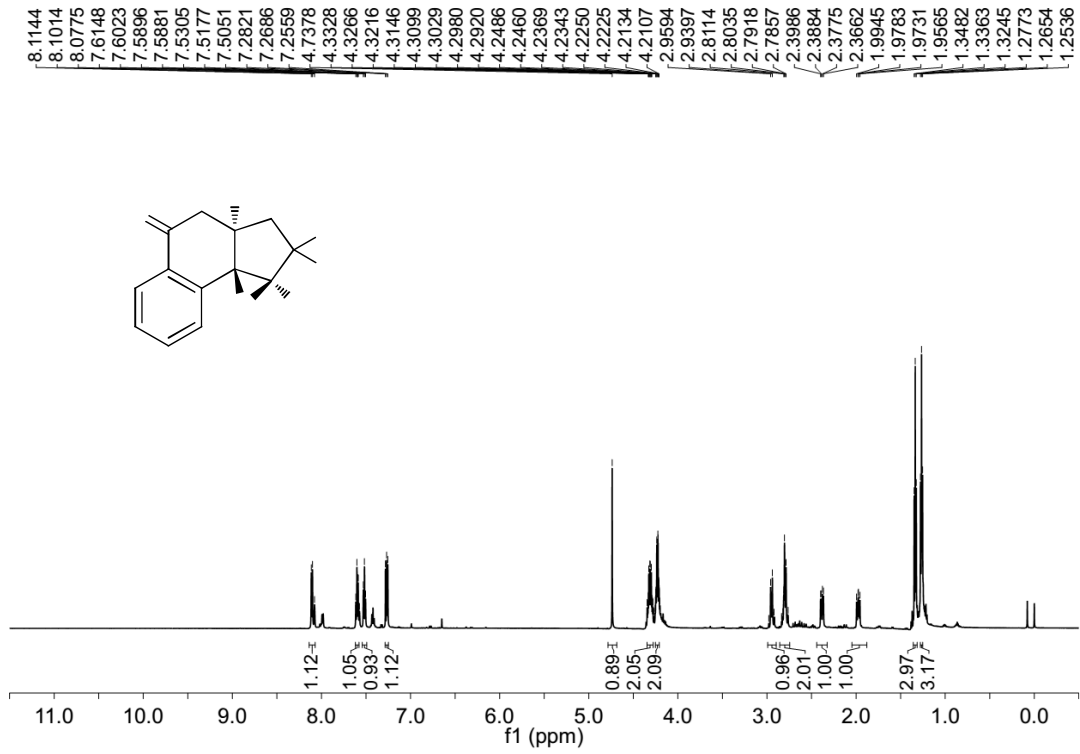
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- 23.8881
- 14.0425
- 13.8758











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