# Supporting Information

## Study on the Reactivity of the Alkene Component in Ruthenium-Catalyzed [2+2] Cycloadditions between an Alkene and an Alkyne: Part 1

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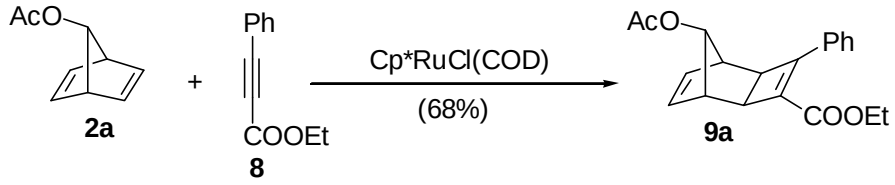
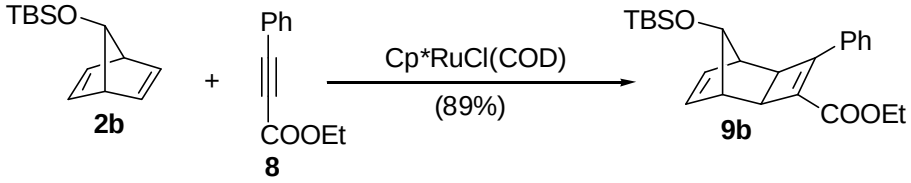
**General Information:** All reactions were carried out in an atmosphere of dry nitrogen at ambient temperature unless otherewise stated. Standard column chromatography was performed on 230-400 mesh silica gel (obtained from Silicycle) using flash column chromatography techniques.[18] Analytical thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 $F_{254}$ plates. All glassware was flame dried under an inert atmosphere of dry nitrogen. Infrared spectra were taken on a Bomem MB-100 FTIR spectrophotometer. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts for $^{1}H$ NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: $\delta$ 7.26 ppm). Chemical shifts for $^{13}C$ NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuterochloroform: $\delta$ 77.0 ppm). High resolution mass spectra were done by McMaster Regional Centre for Mass Spectrometry at McMaster University, Hamilton, Ontario. Elemental analyses were performed by Canadian Microanalytical Service Ltd., British Columbia or by Quantitative Technologies Inc., New Jersey.

**Reagents:** Unless stated otherwise, commercial reagents were used without purification. Solvents were purified by distillation under dry nitrogen: from $CaH_2$ ($Et_3N$, diglyme) and from potassium/benzophenone (THF). 7-substituted norbornadienes **2a-2f**,[13] Cp*RuCl(COD)[16] and alkyne **8**[14] were prepared according to literature procedures.

[18] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

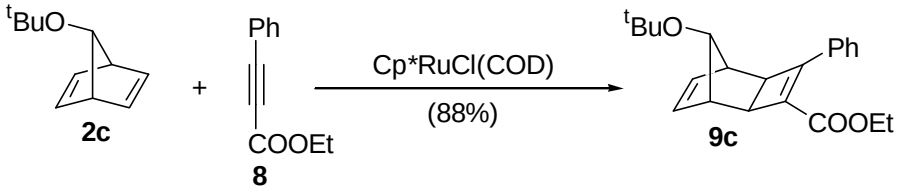



**9-Acetoxy-3-ethoxycarbonyl-4-phenyltricyclo[4.2.1.0$^{2,5}$]nona-3,7-diene (9a)**. A mixture of 7-OAc-norbornadiene **2a** (124 mg, 0.828 mmol) and acetylene **8** (28.8 mg, 0.166 mmol) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 4.40 mg, 0.012 mmol) under nitrogen. The oven-dried vial was rinsed with $Et_3N$ (0.44 mL). The reaction mixture was stirred in the dark at 95 °C for 90 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19, 1:9) to give the cycloadduct **9a** (36.3 mg, 0.112 mmol, 68%) as a white solid. $R_f$ 0.36 (EtOAc:hexanes=1:9); mp 103.5 – 104 °C; GC (HP-1 column): retention time=17.932 min.; IR ($CH_2Cl_2$) 3066 (m), 2985 (m), 2860 (m), 1737 (s), 1703 (s), 1616 (m), 1571 (w), 1492 (m), 1448 (m), 1366 (m), 1297 (m), 1251 (s), 1209 (s), 1128 (m), 1079 (m), 1040 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.07 (m, 2H), 7.39-7.44 (m, 3H), 6.21 (dd, 1H, *J* = 5.7, 2.8 Hz), 6.17 (dd, 1H, *J* = 5.7, 2.8 Hz), 4.77 (s, 1H), 4.29 ($m_{AB}$, 2H), 3.05 (d, 1H, *J* = 1.6 Hz), 3.02 (d, 1H, *J* = 1.6 Hz), 2.79 (dd, 1H, *J* = 4.2, 1.0 Hz), 2.70 (dd, 1H, *J* = 4.2, 1.0 Hz), 1.94 (s, 3H), 1.37 (t, 3H, *J* = 7.1 Hz); $^{13}$C NMR (APT, $CDCl_3$, 100 MHz) δ 171.1, 162.8, 155.9, 132.9, 132.0, 131.7, 130.4, 129.2, 128.9, 128.5, 85.6, 60.3, 42.53, 42.46, 42.40, 42.1, 21.2, 14.3. Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found C, 74.25; H, 6.48.

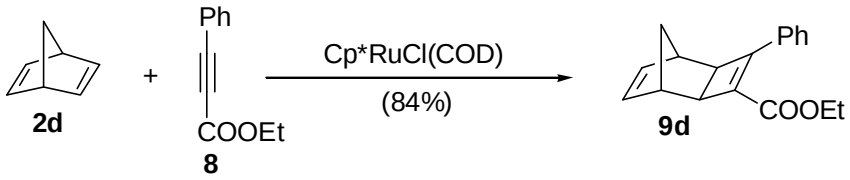



**9-*tert*-Butyldimethylsilyloxy-3-ethoxycarbonyl-4-phenyltricyclo[4.2.1.0$^{2,5}$]nona-3,7-diene (9b)**. A mixture of 7-OTBS-norbornadiene **2b** (56.7 mg, 0.255 mmol) and acetylene **8** (9.6 mg, 0.055 mmol) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 3.6 mg, 0.0095 mmol) under nitrogen. The oven-dried vial was rinsed with $Et_3N$ (0.15 mL). The reaction mixture was stirred in the dark at 80 °C for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:49, 1:19) followed by fractional recrystallization (hexanes at 0 °C) to give the cycloadduct **9b** (19.4 mg, 0.0489 mmol, 89%) as white crystals. $R_f$ 0.61 (EtOAc:hexanes=1:9); mp 71 - 72 °C; GC (HP-1 column): retention time=18.720 min.; IR ($CH_2Cl_2$) 3065 (m), 2955 (s), 2931 (s), 2856 (m), 1701 (s), 1619 (m), 1492 (m), 1463 (m),

1295 (m), 1266 (s), 1210 (s), 1182 (m), 1133 (s), 1084 (m), 1046 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, 1H, *J* = 2.1 Hz), 8.06 (d, 1H, *J* = 1.4 Hz), 7.39-7.45 (m, 3H), 6.17 (m, 2H), 4.33 (dq, 1H, *J* = 10.9, 7.1 Hz), 4.25 (dq, 1H, *J* = 10.9, 7.1 Hz), 4.08 (s, 1H), 2.77 (s, 1H), 2.73 (s, 1H), 2.72 (d, 1H, *J* = 3.8 Hz), 2.63 (d, 1H, *J* = 3.8 Hz), 1.36 (t, 3H, *J* = 7.1 Hz), 0.76 (s, 9H), -0.09 (s, 3H), -0.10 (s, 3H); $^{13}C$ NMR (APT, $CDCl_3$, 100 MHz) δ 163.0, 156.4, 132.7, 132.2, 131.6, 130.2, 129.3, 128.8, 128.4, 83.6, 60.1, 45.1, 44.8, 43.1, 42.6, 25.9, 18.3, 14.4, -4.78, -4.86. Anal. Calcd. for $C_{24}H_{32}SiO_3$: C, 72.68; H, 8.13. Found C, 72.20; H, 8.39.

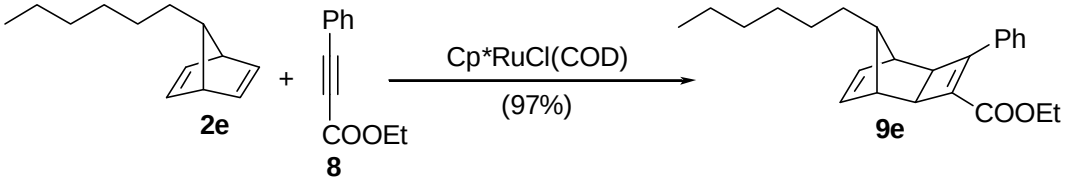



**9-*tert*-Butoxy-3-ethoxycarbonyl-4-phenyltricyclo[4.2.1.0$^{2,5}$]nona-3,7-diene (9c)**. A mixture of 7-O$^t$Bu-norbornadiene **2c** (155 mg, 0.943 mmol) and acetylene **8** (32.8 mg, 0.189 mmol) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 4.9 mg, 0.013 mmol) under nitrogen. The oven-dried vial was rinsed with $Et_3N$ (0.44 mL). The reaction mixture was stirred in the dark at 80 °C for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19, 1:9) to give the cycloadduct **9c** (56.0 mg, 0.166 mmol, 88%) as a white solid. $R_f$ 0.43 (EtOAc:hexanes=1:9); mp 106.5 – 107.5 °C; GC (HP-1 column): retention time=19.357 min.; IR ($CH_2Cl_2$) 3060 (m), 2980 (m), 1702 (s), 1616 (s), 1491 (m), 1364 (m), 1210 (s), 1182 (m), 1126 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 8.08 (m, 2H), 7.41 (m, 3H), 6.22 (m, 2H), 4.34 (dq, 1H, *J* = 10.8, 7.1 Hz), 4.26 (dq, 1H, *J* = 10.8, 7.1 Hz), 3.92 (s, 1H), 2.78 (s, 1H), 2.74 (s, 1H), 2.70 (d, 1H, *J* = 4.2 Hz), 2.62 (d, 1H, *J* = 4.2 Hz), 1.36 (t, 3H, *J* = 7.1 Hz), 1.02 (s, 9H); $^{13}C$ NMR (APT, $CDCl_3$, 100 MHz) δ 163.0, 156.4, 133.1, 132.2, 131.9, 130.2, 129.5, 128.7, 128.4, 83.1, 73.5, 60.1, 44.5, 44.3, 42.9, 42.5, 28.2, 14.4. Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found C, 78.00; H, 7.98.

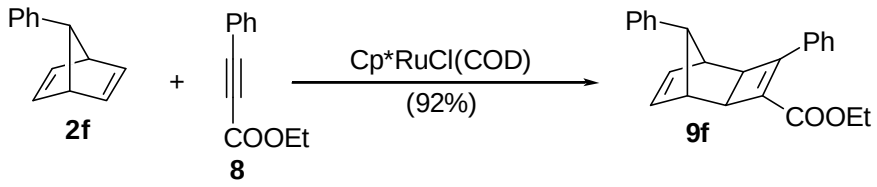



**3-Ethoxycarbonyl-4-phenyltricyclo[4.2.1.0$^{2,5}$]nona-3,7-diene (9d)**. A mixture of norbornadiene **2d** (92.2 mg, 1.00 mmol) and acetylene **8** (36.0 mg, 0.207 mmol) in an oven-dried vial was added via a

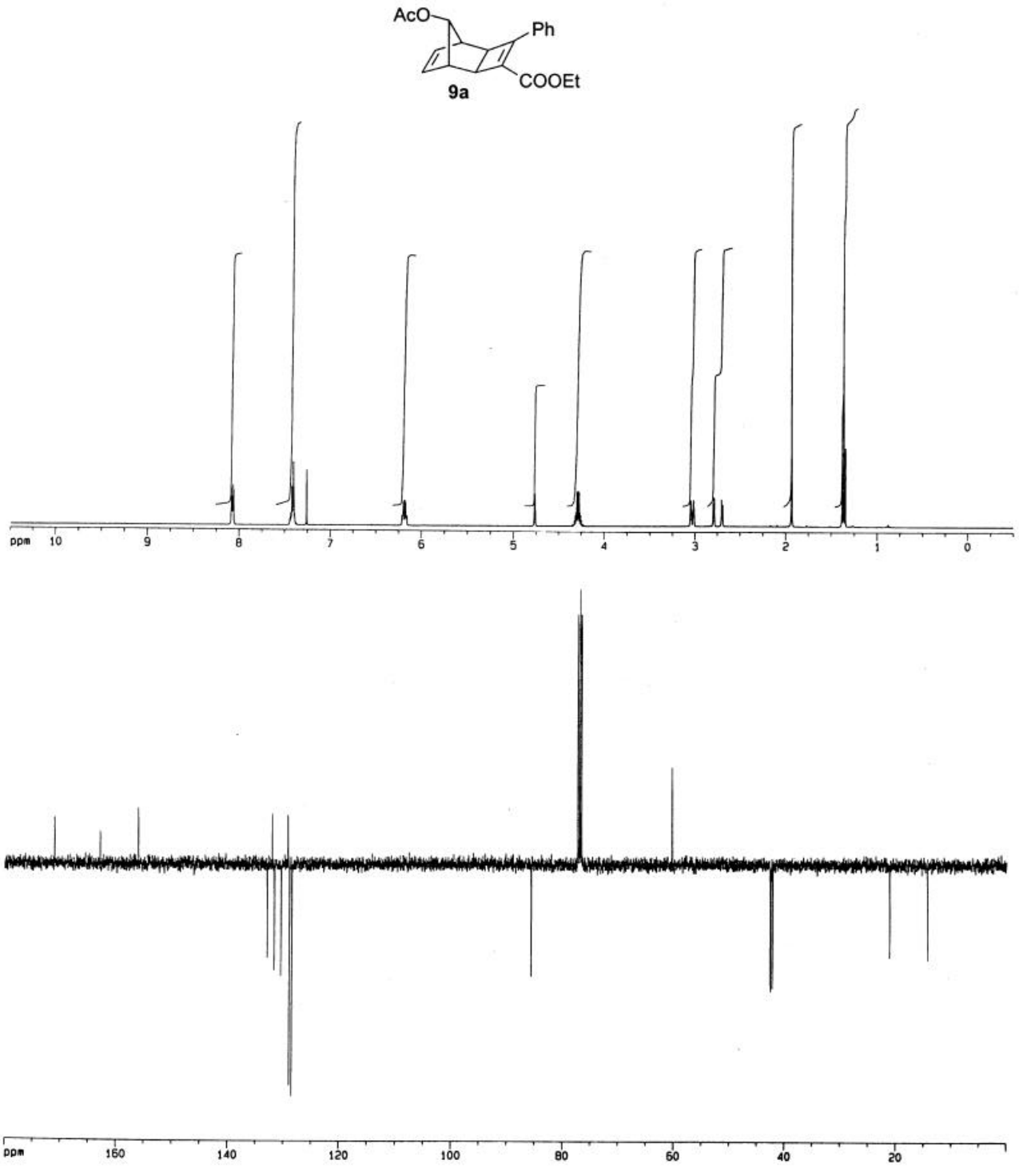
cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 4.8 mg, 0.013 mmol) under nitrogen. The oven-dried vial was rinsed with $Et_3N$ (0.40 mL). The reaction mixture was stirred in the dark at 80 °C for 48 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19) to give the cycloadduct **9d** (46.2 mg, 0.174 mmol, 84%) as a yellow oil. $R_f$ 0.51 (EtOAc:hexanes=1:19); GC (HP-1 column): retention time=15.380 min.; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.09 (m, 2H), 7.36-7.44 (m, 3H), 6.25 (dd, 1H, *J* = 5.5, 2.9 Hz), 6.22 (dd, 1H, *J* = 5.5, 2.9 Hz), 4.28 (q, 2H, *J* = 7.1 Hz), 2.75 (s, 1H), 2.73 (s, 1H), 2.69 (d, 1H, *J* = 3.8 Hz), 2.59 (d, 1H, *J* = 3.8 Hz), 1.37 (t, 3H, *J* = 7.1Hz), 1.34-1.41 (m, 2H); $^{13}$C NMR (APT, $CDCl_3$, 100 MHz) δ 163.2, 157.6, 136.6, 135.4, 132.5, 130.8, 130.0, 128.8, 128.4, 60.0, 43.2, 42.7, 39.8, 39.1, 38.9, 14.4. This is a known compound[6d].




**3-Ethoxycarbonyl-9-hexyl-4-phenyltricyclo[4.2.1.0$^{2,5}$]nona-3,7-diene (9e)**. A mixture of 7-hexyl-norbornadiene **2e** (162 mg, 0.918 mmol) and acetylene **8** (31.7 mg, 0.182 mmol) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 5.5 mg, 0.014 mmol) under nitrogen. The oven-dried vial was rinsed with $Et_3N$ (0.40 mL). The reaction mixture was stirred in the dark at 80 °C for 48 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:9) to give the cycloadduct **9e** (61.8 mg, 0.176 mmol, 97%) as a colourless liquid. $R_f$ 0.66 (EtOAc:hexanes=1:9); GC (HP-1 column): retention time=19.357 min.; IR (neat) 3062 (m), 2930 (s), 2855 (s), 1704 (s), 1615 (s), 1572 (m), 1492 (s), 1448 (m), 1366 (m), 1294 (m), 1206 (s), 1178 (s), 1126 (s), 1083 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.09 (m, 2H), 7.36-7.44 (m, 3H), 6.10 (dd, 1H, *J* = 5.5, 2.8 Hz), 6.07 (dd, 1H, *J* = 5.5, 2.8 Hz), 4.29 ($m_{AB}$, 2H), 2.68 (dd, 1H, *J* = 3.9, 0.8 Hz), 2.59 (s, 1H), 2.58 (d, 1H, *J* = 3.4 Hz), 2.57 (d, 1H, *J* = 1.4 Hz), 1.85 (t, 1H, *J* = 7.1 Hz), 1.36 (t, 3H, *J* = 7.1 Hz), 1.06-1.26 (m, 10H), 0.82 (t, 3H, *J* = 7.0 Hz); $^{13}$C NMR (APT, $CDCl_3$, 100 MHz) δ 163.2, 156.6, 133.9, 132.7, 132.6, 130.0, 129.8, 128.8, 128.4, 60.0, 49.8, 44.1, 43.6, 43.2, 42.8, 31.8, 29.5, 28.7, 26.3, 22.6, 14.4, 14.0. HRMS calcd. for $C_{24}H_{30}O_2$: m/z 350.2246, found m/z 350.2258.




**3-Ethoxycarbonyl-4,9-diphenyltricyclo[4.2.1.0$^{2,5}$]nona-3,7-diene (9f)**. A mixture of 7-Ph-norbornadiene **2f** (146 mg, 0.866 mmol) and acetylene **8** (29.9 mg, 0.172 mmol) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 3.90 mg, 0.010 mmol) under nitrogen. The oven-dried vial was rinsed with $Et_3N$ (0.40 mL). The reaction mixture was stirred in the dark at 80 °C for 48 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19) to give the cycloadduct **9f** (54.0 mg, 0.158 mmol, 92%) as a white crystal. $R_f$ 0.57 (EtOAc:hexanes=1:9); mp 71.5 – 72.5 °C; GC (HP-1 column): retention time=21.191 min.; IR ($CH_2Cl_2$) 3061 (m), 2975 (m), 2860 (m), 1699 (s), 1616 (s), 1572 (m), 1492 (s), 1448 (s), 1367 (m), 1207 (s), 1175 (s), 1127 (m), 1049 (m), 1022 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.16 (m, 2H), 7.42-7.48 (m, 3H), 7.21 (m, 2H), 7.06-7.14 (m, 3H), 6.15 (dd, 1H, *J* = 5.1, 2.9 Hz), 6.11 (dd, 1H, *J* = 5.1, 2.9 Hz), 4.33 (q, 2H, *J* = 7.1 Hz), 3.26 (s, 1H), 3.12 (s, 1H), 3.10 (s, 1H), 2.90 (d, 1H, *J* = 3.9 Hz), 2.81 (d, 1H, *J* = 3.9 Hz), 1.41 (t, 3H, *J* = 7.1 Hz); $^{13}$C NMR (APT, $CDCl_3$, 100 MHz) δ 163.1, 156.9, 140.5, 133.6, 132.3, 132.2, 130.2, 130.0, 128.9, 128.7, 128.5, 127.6, 125.5, 60.2, 53.7, 44.3, 43.9, 43.8, 43.6, 14.4. HRMS calcd. for $C_{24}H_{22}O_2$: m/z 342.1620, found m/z 342.1600.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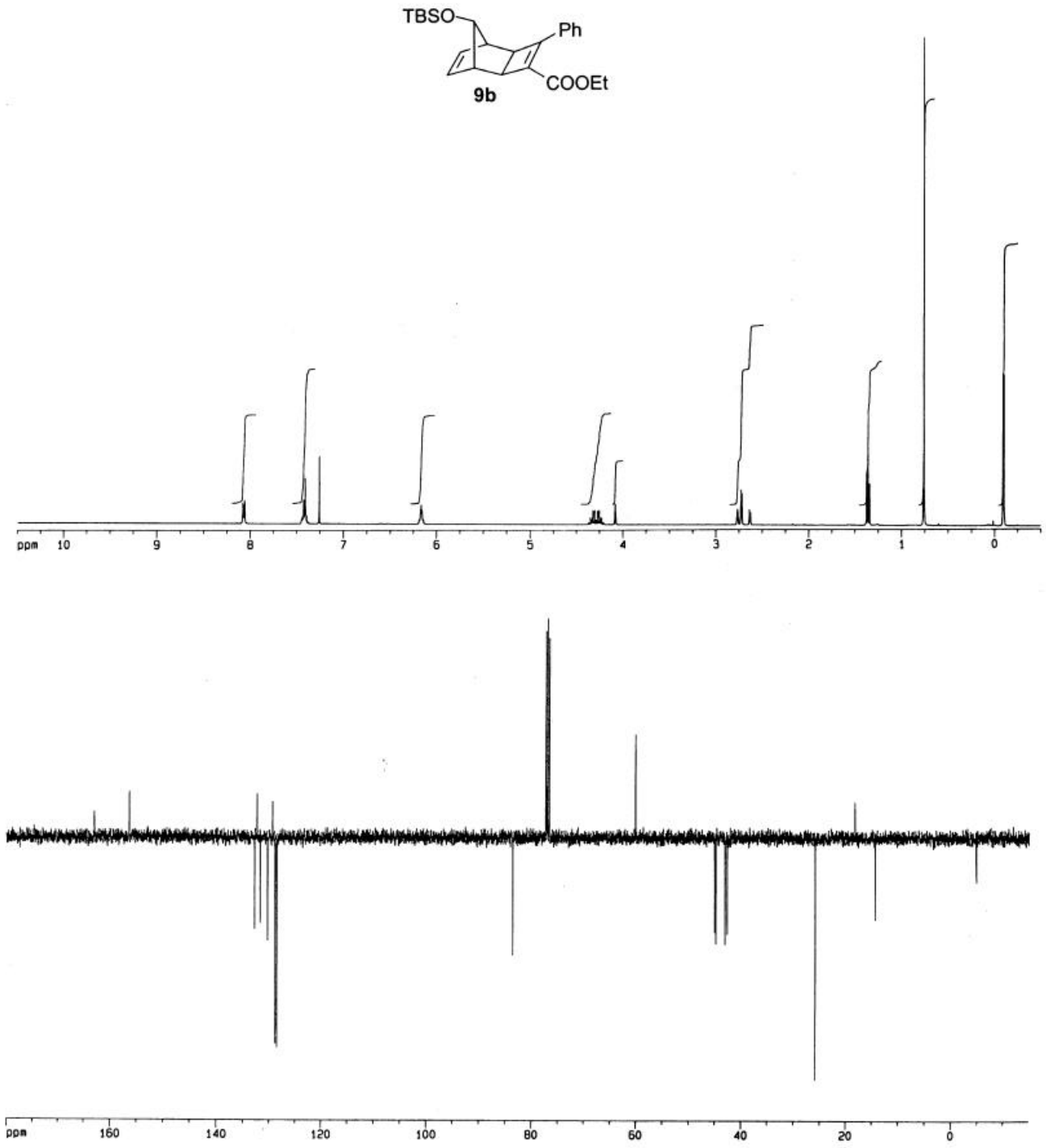
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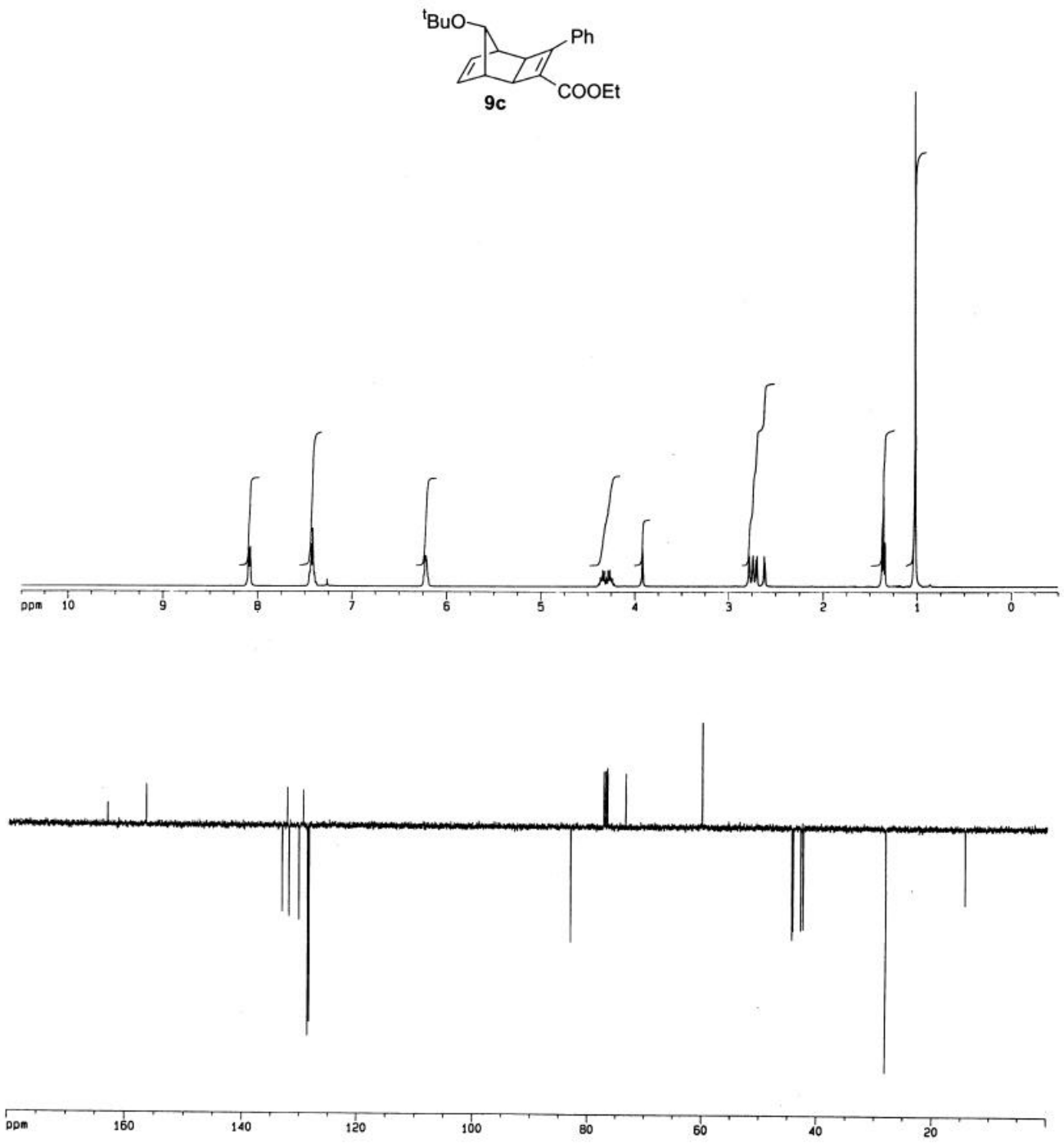
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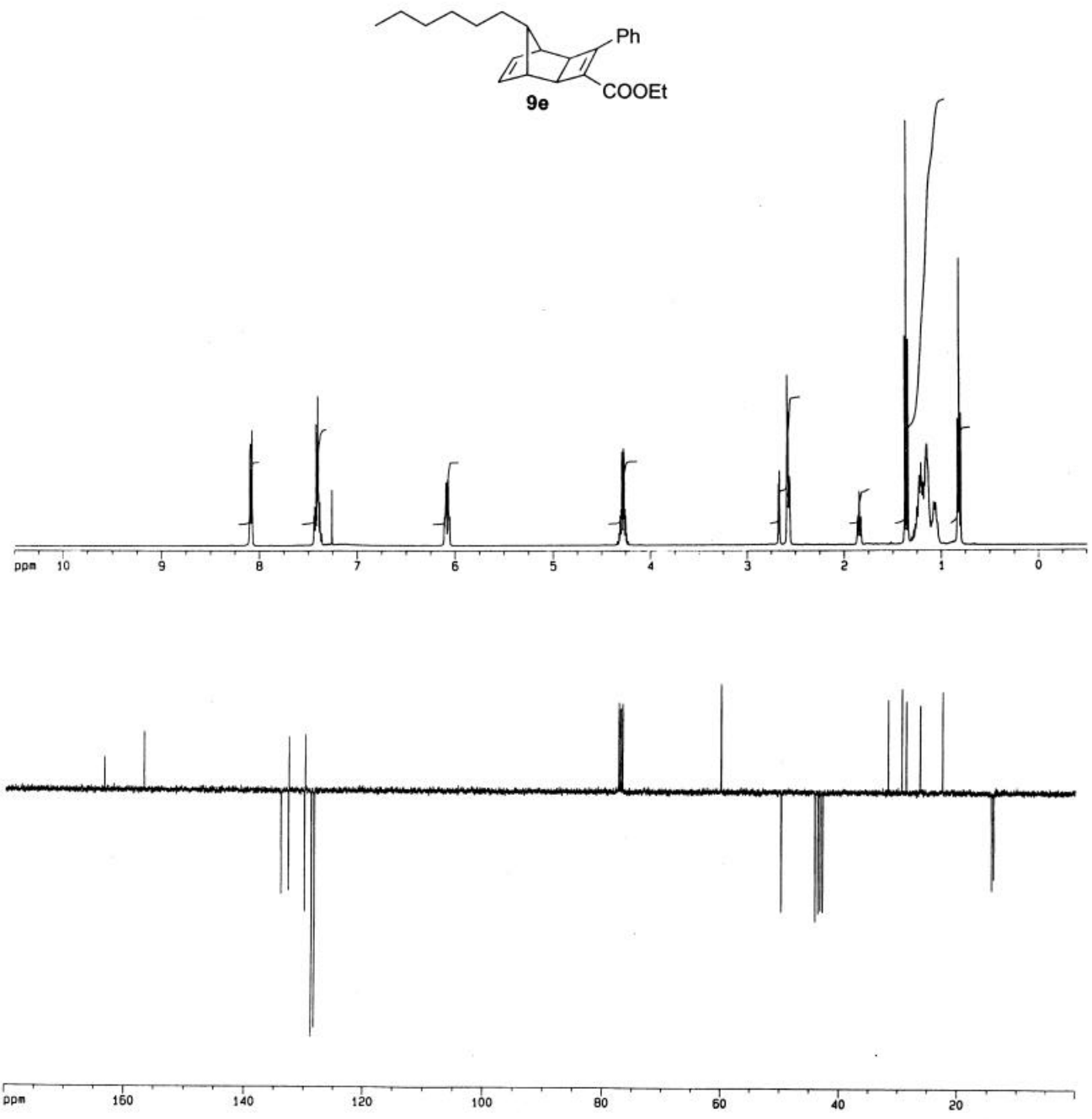
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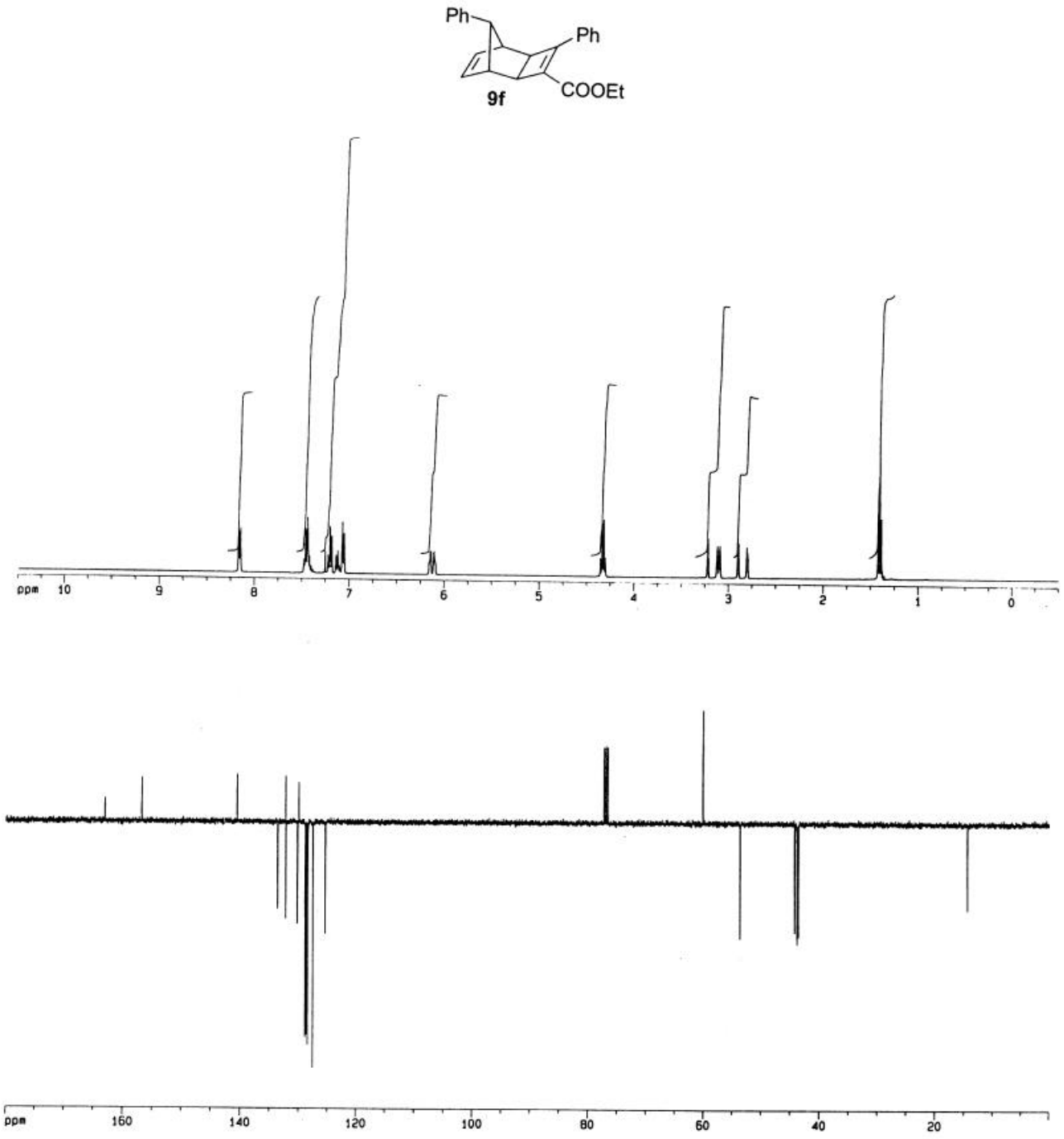
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