CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Versatile Friedel–Crafts-type Alkylations of Benzenes Using Molybdenum Complex / *o*-Chloranil Catalytic System

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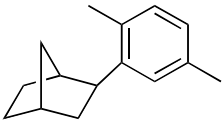
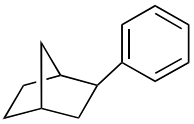
Supporting Information

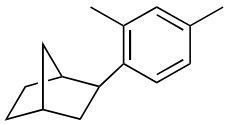
Characterization data for known products.



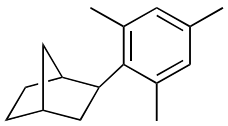
1a: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.20–1.40 (m, 3 H), 1.48–1.70 (m, 4 H), 1.79 (ddd, *J* = 12.3, 8.7, 2.1 Hz, 1 H), 2.26 (s, 3 H), 2.32 (s, 3 H), 2.33–2.39 (m, 2 H), 2.78 (dd, *J* = 8.4, 5.7 Hz, 1 H), 6.89 (d, *J* = 7.5 Hz, 1 H), 7.03 (d, *J* = 7.5 Hz, 1 H), 7.05 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 19.4, 21.2, 29.1, 30.5, 36.3, 36.9, 38.6, 41.4, 43.7, 125.7, 125.9, 130.2, 133.1, 135.0, 145.4.



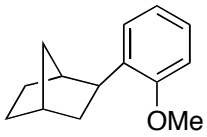
1b: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.17–1.40 (m, 3 H), 1.56–1.82 (m, 4 H), 1.78 (ddd, *J* = 12.6, 8.7, 2.1 Hz, 1 H), 2.37 (s, 2 H), 2.75 (dd, *J* = 8.7, 6.0 Hz, 1 H), 7.13–7.31 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 28.9, 30.6, 36.1, 36.8, 39.1, 42.9, 47.3, 125.3, 127.0, 128.2, 147.6.



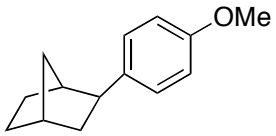
1c: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 1.19-1.40 (m, 3 H), 1.48-1.69 (m, 4 H), 1.78 (ddd, *J* = 12.3, 8.7, 2.1 Hz, 1 H), 2.27 (s, 3 H), 2.28 (s, 3 H), 2.29–2.37 (m, 2 H), 2.77 (dd, *J* = 8.7, 6.0 Hz, 1 H), 6.97 (d, *J* = 8.1 Hz, 1 H), 6.98 (s, 1 H), 7.13 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 19.8, 20.6, 29.1, 30.4, 36.2, 36.8, 38.7, 41.6, 43.5, 124.8, 126.3, 131.2, 134.6, 136.1, 142.6.



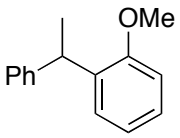
1d: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 1.28–1.38 (m, 3 H), 1.56–1.67 (m, 3 H), 1.84 (ddd, *J* = 11.4, 8.7, 2.1 Hz, 1 H), 2.23 (s, 3 H), 2.34 (s, 1 H), 2.40 (s, 6 H), 2.56 (s, 1 H), 3.00 (t, *J* = 8.4 Hz, 1 H), 6.81 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 20.4, 22.6, 28.4, 33.0, 36.4, 38.8, 39.6, 41.1, 45.4, 130.5, 134.4, 136.1, 139.7.



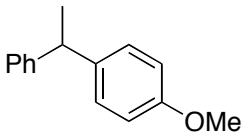
o-**1e**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 1.16–1.2 (m, 1 H), 1.25–1.32 (m, 1 H), 1.35–1.43 (m, 1 H), 1.41–1.65 (m, 4 H), 1.79 (ddd, *J* = 12.3, 9.0, 2.4 Hz, 1 H), 2.31 (s, 1 H), 2.35 (s, 1 H), 2.97 (dd, *J* = 8.4, 6.0 Hz, 1 H), 3.82 (s, 3 H), 6.84 (dd, *J* = 8.0, 0.9 Hz, 1 H), 6.90 (dt, *J* = 7.5, 0.9 Hz, 1 H), 7.15 (dt, *J* = 8.0, 1.5 Hz, 1 H), 7.22 (dd, *J* = 7.5, 1.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 29.0, 30.3, 36.2, 36.8, 38.6, 40.4, 41.0, 55.2, 110.2, 120.1, 125.8, 126.3, 136.0, 157.4.



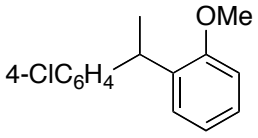
p-**1e**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.13–1.19 (m, 1 H), 1.20–1.29 (m, 1 H), 1.30–1.37 (m, 1 H), 1.74 (ddd, *J* = 12.6, 9.0, 2.4 Hz, 1 H), 2.30 (s, 1 H), 2.34 (s, 1 H), 2.69 (dd, *J* = 9.0, 5.4 Hz, 1 H), 3.79 (s, 3 H), 6.83 (d, *J* = 8.2 Hz, 1 H), 7.14 (d, *J* = 8.2, 1.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 28.8, 30.4, 35.9, 36.7, 39.1, 43.1, 46.5, 55.2, 113.6, 128.0, 139.9, 157.6.



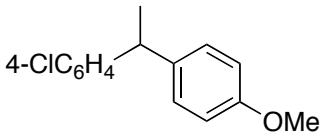
o-**3a**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.59 (d, *J* = 7.2 Hz, 3 H), 3.79 (s, 3 H), 4.59 (q, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 6.92 (dt, *J* = 7.5, 0.9 Hz, 1 H), 7.14–7.31 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.8, 37.3, 55.4, 110.7, 120.6, 125.7, 127.1, 127.8, 127.9, 128.2, 135.1, 146.5, 157.0.



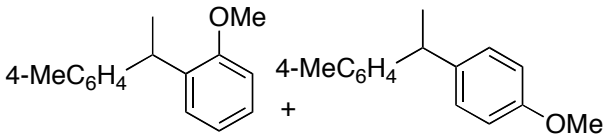
p-**3a**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.62 (d, *J* = 7.2 Hz, 3 H), 3.78 (s, 3 H), 4.11 (q, *J* = 7.2 Hz, 1 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 7.14 (d, *J* = 8.7 Hz, 2 H), 7.15–7.31 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.9, 43.9, 55.2, 113.8, 126.0, 127.6, 128.4, 128.6, 138.7, 146.9, 158.0.



o-**3b**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 1.55 (d, *J* = 7.5 Hz, 3 H), 3.76 (s, 3 H), 4.52 (q, *J* = 7.5 Hz, 1 H), 6.84 (dd, *J* = 8.1, 0.9 Hz, 1 H), 6.92 (dt, *J* = 7.5, 0.9 Hz, 1 H), 7.15 (d, *J* = 8.7 Hz, 2 H), 7.12–7.17 (m, 1 H), 7.18–7.22 (m, 1 H), 7.21 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 20.6, 36.9, 55.3, 110.7, 120.6, 127.4, 127.5, 128.2, 129.1, 131.4, 134.3, 145.1, 156.9.

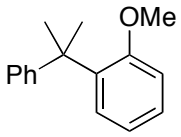


p-**3b**: colorless solid (mp. 54.5–55.5 ˚C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 1.59 (d, *J* = 7.2 Hz, 3 H), 3.78 (s, 3 H), 4.07 (q, *J* = 7.2 Hz, 1 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 8.7 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 21.8, 43.3, 55.1, 113.9, 128.5, 129.0, 131.7, 138.1, 145.4, 158.1.

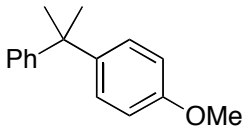


o- and *p*-**3c**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) *o*-**3c** δ 1.58 (d, *J* = 7.2 Hz, 3 H), 2.32 (s, 3 H), 3.80 (s, 3 H), 4.56 (q, *J* = 7.2 Hz, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 6.91 (dt, *J* = 7.5, 0.9 Hz, 1 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 7.10–7.21 (m, 3 H), *p*-**3c** δ 1.60 (d, *J* = 7.2 Hz, 3 H), 2.31 (s, 3 H), 3.78 (s, 3 H), 4.08 (q, *J* = 7.2 Hz, 1 H), 6.82 (d, *J* = 8.5 Hz, 2 H), 7.10 (s, 4 H), 7.14 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) *o*-**3c** δ 21.0, 22.1, 36.9, 55.4, 110.6, 120.5,

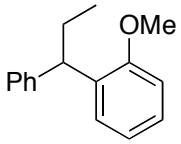
126.9, 127.6, 127.7, 128.8, 135.1, 135.2, 143.4, 156.8, *p*-**3c** δ 20.9, 22.1, 43.5, 55.1, 113.7, 127.3, 128.4, 129.0, 135.3, 138.7, 143.8, 157.8.



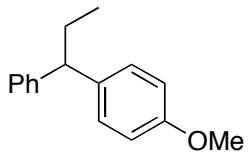
o-**3d**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.67 (s, 6 H), 3.32 (s, 3 H), 6.80 (dd, *J* = 7.8, 0.9 Hz, 1 H), 6.98 (dt, *J* = 7.8, 1.2 Hz, 1 H), 7.04–7.30 (m, 6 H), 7.46 (dd, *J* = 7.8, 1.5 Hz, 1 H).



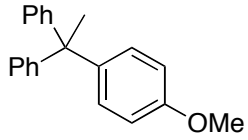
p-**3d**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.67 (s, 6 H), 3.79 (s, 3 H), 6.81 (d, *J* = 9.0 Hz, 2 H), 7.15 (d, *J* = 9.0 Hz, 2 H), 7.15–7.30 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 30.9, 42.3, 55.1, 113.3, 125.5, 126.7, 127.8, 127.9, 142.9, 150.9, 157.4.



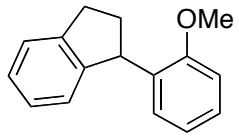
o-**3e**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.89 (t, *J* = 7.2 Hz, 3 H), 2.03 (quint, *J* = 7.2 Hz, 2 H), 3.77 (s, 3 H), 4.28 (t, *J* = 7.2 Hz, 1 H), 6.83 (d, *J* = 8.1 Hz, 1 H), 6.92 (dt, *J* = 7.5, 0.9 Hz, 1 H), 7.11–7.19 (m, 2 H), 7.21-7.28 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 12.6, 27.8, 45.0, 55.4, 110.8, 120.6, 125.7, 127.0, 127.7, 128.1, 128.3, 133.8, 145.3, 157.3.



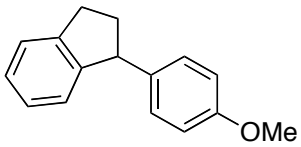
p-**3e**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 0.89 (t, *J* = 7.2 Hz, 3 H), 2.04 (quint, *J* = 7.2 Hz, 2 H), 3.74 (t, *J* = 7.2 Hz, 1 H), 3.77 (s, 3 H), 6.82 (d, *J* = 9.0 Hz, 2 H), 7.15 (d, *J* = 9.0 Hz, 2 H), 7.15–7.30 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 12.6, 28.6, 52.3, 55.1, 113.8, 126.0, 127.9, 128.4, 128.8, 137.4, 145.7, 158.0.



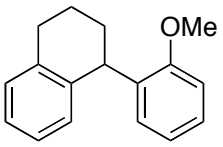
p-**3f**: colorless solid (mp. 85.0–85.8 ˚C, lit.[1] mp. 83–84 ˚C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 2.19 (s, 3 H), 3.81 (s, 3 H), 6.81 (d, *J* = 9.0 Hz, 2 H), 7.01 (d, *J* = 9.0 Hz, 2 H), 7.07-7.12 (m, 4 H), 7.17-7.30 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 30.5, 51.8, 55.1, 113.2, 126.0, 127.9, 128.8, 129.8, 141.3, 149.5, 157.8.



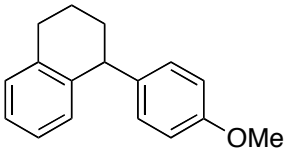
o-**3g**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 1.98 (ddd, *J* = 16.2, 12.6, 7.5 Hz, 1 H), 2.50-2.61 (m, 1 H), 2.92 (dd, *J* = 15.9, 7.5 Hz, 1 H), 2.97-3.07 (m, 1 H), 3.87 (s, 3 H), 4.81 (t, *J* = 7.8 Hz, 1 H), 6.86 (t, *J* = 7.5 Hz, 1 H), 6.92 (d, *J* = 7.5 Hz, 1 H), 6.90-6.93 (m, 1 H), 7.02 (d, *J* = 6.9 Hz, 1 H), 7.10–7.23 (m, 3 H), 7.29 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 31.6, 34.7, 44.0, 55.5, 110.5, 120.7, 124.4, 125.0, 126.3, 126.4, 127.2, 128.2, 133.9, 144.8, 146.7, 157.5.



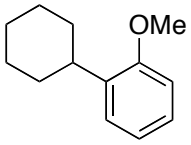
p-**3g**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.98 (ddd, *J* = 17.7, 12.3, 8.4 Hz, 1 H), 2.50–2.61 (m, 1 H), 2.92 (d, *J* = 15.9, 8.1 Hz, 1 H), 3.04 (ddd, *J* = 15.6, 8.4, 3.3 Hz, 1 H), 3.80 (s, 3 H), 4.29 (t, *J* = 8.1 Hz, 1 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 6.95 (d, *J* = 7.2 Hz, 1 H), 7.11 (d, *J* = 8.5 Hz, 2 H), 7.10–7.21 (m, 2 H), 7.29 (d, *J* = 7.2 Hz, 1 H) ; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 31.7, 36.7, 50.8, 55.2, 113.8, 124.3, 124.8, 126.3, 126.4, 129.0, 137.5, 144.2, 147.1, 158.1.



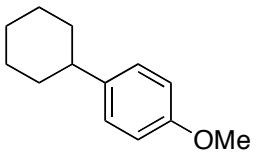
o-**3h**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.70–1.92 (m, 3 H), 2.01–2.11 (m, 1 H), 2.76–2.95 (m, 2 H), 3.85 (s, 3 H), 4.58 (t, *J* = 6.6 Hz, 1 H), 6.73 (dd, *J* = 7.2, 1.8 Hz, 1 H), 6.79–6.85 (m, 2 H), 6.90 (d, *J* = 7.5 Hz, 1 H), 6.99–7.20 (m, 4 H).



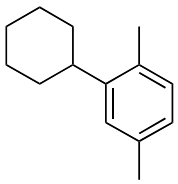
p-**3h**: colorless solid (mp. 64.5–65.5 °C, lit.[2] mp 65–67 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.70-1.94 (m, 3 H), 2.09-2.19 (m, 1 H), 2.77-2.97 (m, 2 H), 3.79 (s, 3 H), 4.07 (t, *J* = 6.6 Hz, 1 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 6.80-6.86 (m, 1 H), 7.02 (d, *J* = 9.0 Hz, 2 H), 7.04-7.14 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.8, 29.7, 33.2, 44.7, 55.1, 113.7, 125.7, 125.9, 129.0, 129.8, 130.2, 137.6, 139.8, 139.9, 158.0.



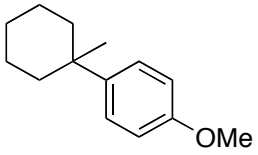
o-Cyclohexylanisole: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.20–1.50 (m, 5 H), 1.70–1.86 (m, 5 H), 2.90-3.01 (m, 1 H), 3.82 (s, 3 H), 6.85 (dd, *J* = 7.5, 1.2 Hz, 1 H), 6.92 (dt, *J* = 7.5, 1.2 Hz, 1 H), 7.16 (dt, *J* = 7.5, 1.8 Hz, 1 H), 7.20 (dd, *J* = 7.5, 1.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 26.3, 27.0, 33.1, 36.7, 55.3, 110.4, 120.6, 126.5, 126.6, 136.3, 156.9.



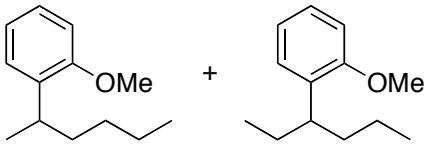
p-Cyclohexylanisole: colorless solid (mp. 55.5–56.5 °C, lit.[3] mp 57–59 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.20–1.49 (m, 5 H), 1.71–1.92 (m, 5 H), 2.41–2.52 (m, 1 H), 3.80 (s, 3 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 7.15 (dd, *J* = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 26.1, 26.9, 34.6, 43.6, 55.2, 113.7, 127.7, 140.5, 157.8.



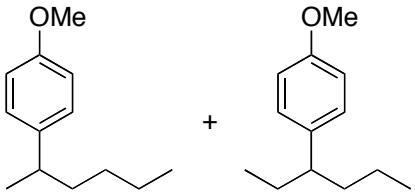
2-Cyclohexyl-1,4-dimethylbenzene: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.25–1.51 (m, 5 H), 1.72–1.90 (m, 5 H), 2.29 (s, 3 H), 2.31 (s, 3 H), 2.62–2.73 (m, 1 H), 6.85 (dd, *J* = 7.5, 1.2 Hz, 1 H), 6.90 (d, *J* = 7.2 Hz, 1 H), 7.02 (s, 1 H), 7.03 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 18.7, 21.1, 26.3, 27.1, 33.6, 40.0, 126.2, 126.3, 130.2, 132.0, 135.4, 145.8.



p-(1-Mehylcyclohexyl)anisole: colorless solid (mp. 40.0–40.7 °C, lit.[4] mp 40–41 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.16 (s, 3 H), 1.36–1.60 (m, 8 H), 1.92–2.00 (m, 2 H), 3.80 (s, 3 H), 6.86 (d, *J* = 9.0 Hz, 2 H), 7.29 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 22.5, 26.3, 30.5, 37.1, 38.0, 55.0, 113.6, 126.9, 142.2, 157.3.

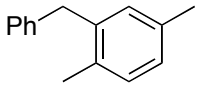


o-(2-hexyl)anisole (**A**) and *o*-(3-hexyl)anisole (**B**) (ca. 7:3): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.77 (t, *J* = 7.2 Hz, 0.9 H **B**), 0.84 (t, *J* = 7.2 Hz, 0.9 H **B**), 0.86 (t, *J* = 7.2 Hz, 2.1 H **A**), 1.18 (d, *J* = 7.2 Hz, 2.1 H **A**), 1.10–1.34 (m, 3 H **A**+**B**), 1.44–1.79 (m, 3 H **A**+**B**), 2.97–3.07 (m, 0.3 H **B**), 3.18 (sext, *J* = 7.2 Hz, 0.7 H **A**), 3.80 (s, 0.9 H **B**), 3.82 (s, 2.1 H **A**), 6.85 (d, *J* = 8.0 Hz, 1 H **A**+**B**), 6.89–6.96 (m, 1 H **A**+**B**), 7.10–7.17 (m, 1 H **A**+**B**), 7.17 (d, *J* = 8.0 Hz, 1 H **A**+**B**).

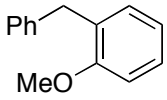


p-(2-hexyl)anisole (**A**) and *p*-(3-hexyl)anisole (**B**) (ca. 7:3): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.75 (t, *J* = 7.2 Hz, 0.9 H **B**), 0.83 (t, *J* = 7.2 Hz, 0.9 H **B**), 0.84 (t, *J* = 7.2 Hz, 2.1 H **A**), 1.20 (d, *J* = 7.2 Hz, 2.1 H **A**), 1.11–1.32 (m, 3 H **A**+**B**), 1.41–1.71 (m, 3 H **A**+**B**), 2.30–2.41 (m, 0.3 H **B**), 2.62 (sext, *J* = 7.2 Hz, 0.7 H **A**), 3.79 (s, 3 H **A**+**B**), 6.83 (d, *J* = 9.0 Hz,

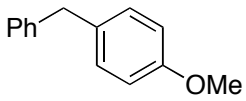
0.6 H **B**), 6.84 (d, *J* = 8.7 Hz, 1.4 H **A**), 7.05 (d, *J* = 9.0 Hz, 0.6 H **B**), 7.10 (d, *J* = 8.7 Hz, 1.4 H **A**).



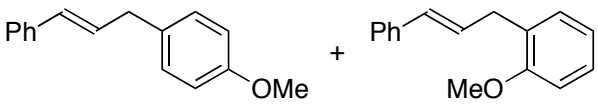
12a: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 2.20 (s, 3 H), 2.29 (s, 3 H), 3.96 (s, 2 H), 6.94 (s, 1 H), 6.97 (d, *J* = 7.5 Hz, 1 H), 7.06 (d, *J* = 7.5 Hz, 1 H), 7.11–7.30 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 19.1, 20.9, 39.4, 125.8, 127.1, 128.3, 128.7, 130.2, 130.7, 133.4, 135.3, 138.6, 140.5.



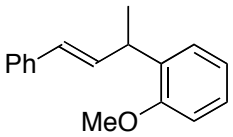
o-**12b**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 3.82 (s, 3 H), 3.98 (s, 2 H), 6.87 (d, *J* = 7.2 Hz, 1 H), 6.90 (dd, *J* = 5.1, 0.9 Hz, 1 H), 7.07 (dd, *J* = 7.5, 1.8 Hz, 1 H), 7.24 (d, *J* = 7.5 Hz, 1 H), 7.14–7.30 (m, 5 H) ; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 35.7, 55.2, 110.5, 120.5, 125.8, 127.5, 128.3, 129.0, 129.7, 130.4, 141.1, 157.5.



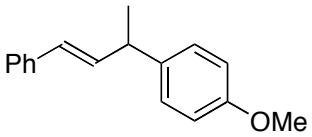
p-**12b**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 3.38 (s, 3 H), 3.93 (s, 2 H), 6.83 (d, *J* = 8.5 Hz, 2 H), 7.11 (d, *J* = 8.5 Hz, 2 H), 7.16–7.31 (m, 5 H) ; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 40.9, 55.1, 113.9, 126.0, 128.5, 128.9, 129.9, 133.3, 141.7, 158.1.



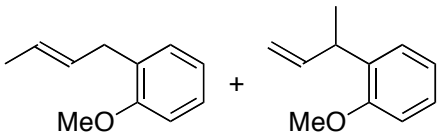
o-**14a** and *p*-**14a** (ca. 1:9): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) *p*-**14a** δ 3.50 (d, *J* = 6.0 Hz, 2 H), 3.80 (s, 3 H), 6.34 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.44 (d, *J* = 15.9 Hz, 1 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 7.16 (d, *J* = 8.8 Hz, 2 H), 7.19–7.38 (m, 5 H), *o*-**14a** δ 3.54 (d, *J* = 6.0 Hz, 2 H), 3.85 (s, 3 H), vinylic and aromatic protons were obscure due to the overlap with those of *p*-**14a**; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) *p*-**14a** δ 38.4, 55.3, 113.9, 126.1, 127.0, 128.5, 129.6, 129.7, 130.7, 132.2, 137.5, 158.1.



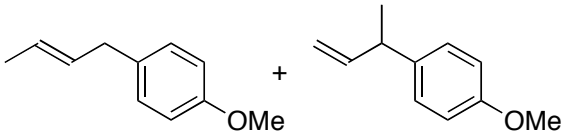
o-**14b**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) δ 1.42 (d, *J* = 7.2 Hz, 3 H), 3.86 (s, 3 H), 4.09 (dq, *J* = 7.2, 4.0 Hz, 1 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 6.45 (dd, *J* = 16.0, 4.0 Hz, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 6.93 (dt, *J* = 7.5, 1.0 Hz, 1 H), 7.16–7.37 (m, 7 H) ; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 20.0, 35.1, 55.5, 110.6, 120.7, 126.1, 126.8, 127.1, 127.5, 128.2, 128.4, 134.1, 135.0, 137.9, 156.8.



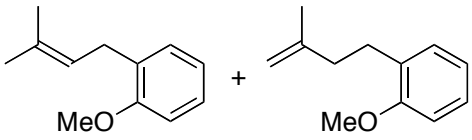
p-**14b**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) δ 1.44 (d, *J* = 7.2 Hz, 3 H), 3.60 (dq, *J* = 7.2, 4.8 Hz, 1 H), 3.80 (s, 3 H), 6.35 (dd, *J* = 16.0, 4.8 Hz, 1 H), 6.40 (d, *J* = 16.0 Hz, 1 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 7.19 (d, *J* = 8.8 Hz, 2 H), 7.16–7.37 (m, 5 H) ; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 21.3, 41.7, 55.2, 113.9, 126.1, 127.0, 128.2, 128.3, 128.4, 135.6, 137.6, 137.7, 158.0.



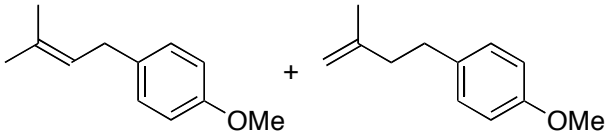
o-**14d** and *o*-**14d'** (ca. 9:1): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) *o*-**14d** δ 1.67 (ddd, *J* = 6.0, 3.0, 1.5 Hz, 3 H), 3.31 (d, *J* = 6.6 Hz, 2 H), 3.83 (s, 3 H), 5.40–5.54 (m, 1 H), 5.57-5.68 (m, 1 H), 6.85 (d, *J* = 7.8 Hz, 1 H), 6.90 (dt, *J* = 7.8, 0.9 Hz, 1 H), 7.12–7.22 (m, 2 H), *o*-**14d'** δ 1.31 (d, *J* = 6.6 Hz, 3 H), 3.37–3.40 (m, 1 H), 3.84 (s, 3 H), 5.03 (dt, *J* = 10.5, 1.5 Hz, 1 H), 5.05 (dt, *J* = 17.0, 1.5 Hz, 1 H), 6.05 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1 H), Aromatic protons are obscure due to the extensive overlap with those of *o*-**14d**.; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) *o*-**14d** δ 17.9, 32.9, 55.3, 110.3, 120.5, 125.9, 127.1, 129.4, 129.6, 142.9, 157.2.



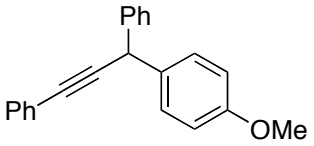
p-**14d** and *p*-**14d'** (ca. 9:1): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) *p*-**14d** δ 1.68 (dd, *J* = 6.0, 1.0 Hz, 3 H), 3.26 (d, *J* = 6.0 Hz, 2 H), 3.79 (s, 3 H), 5.42-5.64 (m, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 7.10 (d, *J* = 8.6 Hz, 2 H) *p*-**14d'** δ 1.34 (d, *J* = 7.2 Hz, 3 H), 3.30–3.44 (m, 1 H), 3.83 (s, 3 H), 5.01 (dt, *J* = 10.5, 1.5 Hz, 1 H), 5.03 (dt, *J* = 16.8, 1.5 Hz, 1 H), 5.99 (ddd, *J* = 16.8, 10.5, 6.6 Hz, 1 H), Aromatic protons are obscure due to the extensive overlap with those of *p*-**14d**.; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) *p*-**14d** δ 17.8, 38.1, 55.2, 113.8, 125.9, 129.3, 130.5, 133.1, 157.8.



o-**14e** + *o*-**14e'** (ca. 8:1): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) *o*-**14e** δ 1.71 (s, 3 H), 1.74 (d, *J* = 0.9 Hz, 3 H), 3.32 (d, *J* = 7.5 Hz, 2 H), 3.84 (s, 3 H), 5.31 (tquint, *J* = 7.5, 1.0 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 6.89 (dt, *J* = 7.5, 0.9 Hz, 1 H), 7.12–7.21 (m, 2 H), *o*-**14e'** δ 1.79 (s, 3 H), 2.28 (t, *J* = 7.5 Hz, 2 H), 2.76 (t, *J* = 7.5 Hz, 2 H), 3.84 (s, 3 H), 4.72 (br s, 2 H), Aromatic protons are obscure due to the extensive overlap with those of *o*-**14e**.; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) *o*-**14e** δ 17.7, 25.8, 28.4, 55.3, 110.2, 120.4, 122.5, 126.8, 129.3, 130.1, 132.4, 157.3.

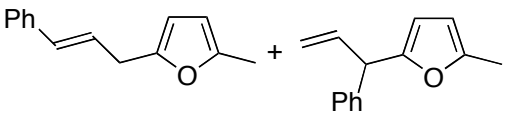


p-**14e** + *p*-**14e'** (ca. 8:1): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) *p*-**14e** δ 1.72 (s, 3 H), 1.74 (d, *J* = 0.9 Hz, 3 H), 3.28 (d, *J* = 7.2 Hz, 2 H), 3.79 (s, 3 H), 5.31 (tquint, *J* = 7.2, 1.0 Hz, 1 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 7.10 (d, *J* = 8.8 Hz, 2 H), *p*-**14e'** δ 1.77 (s, 3 H), 2.29 (t, *J* = 7.8 Hz, 2 H), 2.70 (t, *J* = 7.8 Hz, 2 H), 3.84 (s, 3 H), 4.71 (br s, 1 H), 4.74 (br s, 1 H), Aromatic protons are obscure due to the extensive overlap with those of *p*-**14e**.; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) *p*-**14e** δ 17.7, 25.7, 33.4, 55.2, 113.8, 123.6, 129.1, 132.1, 133.9, 157.7.

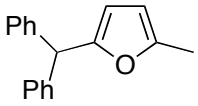


p-**16a**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C) δ 3.79 (s, 3 H), 5.17 (s, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 7.21–7.33 (m, 6 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 7.42–7.49 (m, 4 H); ^{13}C NMR

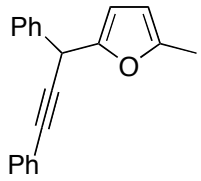
(75 MHz, $CDCl_3$, 25 ˚C) δ 42.9, 55.2, 84.7, 90.5, 114.0, 123.6, 126.8, 127.8, 127.9, 128.2, 128.6, 128.9, 131.7, 133.9, 142.1, 158.5.



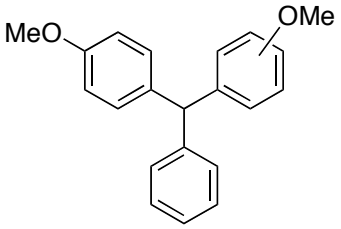
17a and **17b**: pale-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) **17a** δ 2.27 (d, *J* = 0.6 Hz, 3 H), 3.50 (d, *J* = 6.6 Hz, 2 H), 5.88 (dq, *J* = 3.0, 0.6 Hz, 1 H), 5.94 (d, *J* = 3.0 Hz, 1 H), 6.30 (dt, *J* = 15.9, 6.6 Hz, 1 H), 6.49 (d, *J* = 15.9 Hz, 1 H), 7.18–7.40 (m, 5 H), **17b** δ 2.25 (s, 3 H), 4.68 (d, *J* = 7.0 Hz, 1 H), 5.05 (dt, *J* = 17.2, 1.5 Hz, 1 H), 5.19 (dt, *J* = 10.2, 1.5 Hz, 1 H), 5.91 (d, *J* = 2.7 Hz, 1 H), 6.20 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1 H), other aromatic protons were obscure due to the overlap with those of **17a**; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) **17a** δ 13.5, 31.8, 106.0, 106.2, 126.0, 126.2, 127.2, 128.4, 131.7, 137.3, 150.8, 151.9, **17b** δ 13.5, 49.2, 105.9, 107.3, 116.2, 126.6, 128.2, 128.4, 138.4, 141.2, 151.2, 154.2.



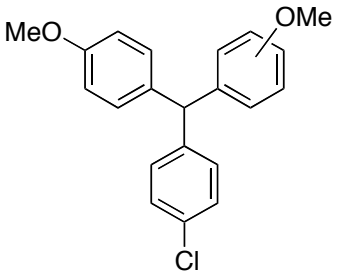
18: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) δ 2.25 (s, 3 H), 5.39 (s, 1 H), 5.75 (d, *J* = 3.0 Hz, 1 H), 5.88 (dd, *J* = 3.0, 0.9 Hz, 1 H), 7.16–7.33 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) δ 13.5, 50.9, 105.9, 109.0, 126.6, 128.3, 128.7, 142.0, 151.4, 154.8.



19: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.25 (s, 3 H), 5.21 (s, 1 H), 5.89 (dd, *J* = 3.0, 0.9 Hz, 1 H), 6.13 (d, *J* = 3.0 Hz, 1 H), 7.27–7.38 (m, 6 H), 7.46–7.51 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.6, 37.9, 83.7, 87.8, 106.2, 107.3, 123.3, 127.2, 127.8, 128.0, 128.2, 128.5, 131.7, 139.2, 151.9.

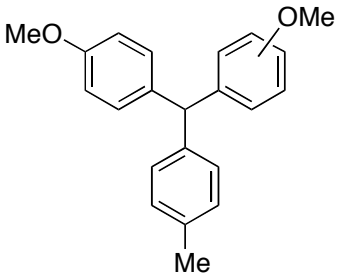


p,*p*- and *o*,*p*-**20a**: colorless solid (mp. 99–100 °C, lit.[5] mp. 99–101 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) *p*,*p*-**20a** δ 3.79 (s, 6 H), 5.46 (s, 1 H), 6.82 (d, *J* = 8.7 Hz, 4 H), 7.02 (d, *J* = 8.7 Hz, 4 H), 7.07–7.31 (m, 5 H), *o*,*p*-**20a** δ 3.72 (s, 6 H), 5.87 (s, 1 H), Aromatic protons are obscure due to the extensive overlap with those of *p*,*p*-**20a**.; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) *p*,*p*-**20a** δ 55.2, 113.6, 126.1, 128.2, 129.3, 130.3, 136.4, 144.6, 158.0.



p,*p*- and *o*,*p*-**20b**: colorless solid (mp. 64–65 °C, lit.[5] mp. 69–70 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) *p*,*p*-**20b** δ 3.79 (s, 6 H), 5.42 (s, 1 H), 6.82 (d, *J* = 8.6 Hz, 4 H), 6.99 (d, *J* = 8.6 Hz,

4 H), 7.03 (d, *J* = 8.2 Hz, 2 H), 7.24 (d, *J* = 8.2 Hz, 2 H), *o*,*p*-**20b** δ 3.72 (s, 6 H), 5.82 (s, 1 H), Aromatic protons are obscure due to the extensive overlap with those of *p*,*p*-**20b**.; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) *p*,*p*-**20b** δ 54.6, 55.2, 113.8, 128.4, 130.2, 130.6, 132.0, 135.9, 143.2, 158.1.



p,*p*- and *o*,*p*-**20c**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C) *p*,*p*-**20c** δ 2.32 (s, 3 H), 3.78 (s, 6 H), 5.41 (s, 1 H), 6.81 (d, *J* = 8.7 Hz, 4 H), 6.99 (d, *J* = 8.1 Hz, 2 H), 7.01 (d, *J* = 8.7 Hz, 4 H), 7.09 (d, *J* = 8.1 Hz, 2 H), *o*,*p*-**20c** δ 2.32 (s, 3 H), 3.72 (s, 6 H), 5.84 (s, 1 H), Aromatic protons are obscure due to the extensive overlap with those of *p*,*p*-**20c**.; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C) *p*,*p*-**20c** δ 21.0, 55.2, 113.6, 128.9, 129.1, 130.2, 135.6, 136.6, 141.6, 157.9.

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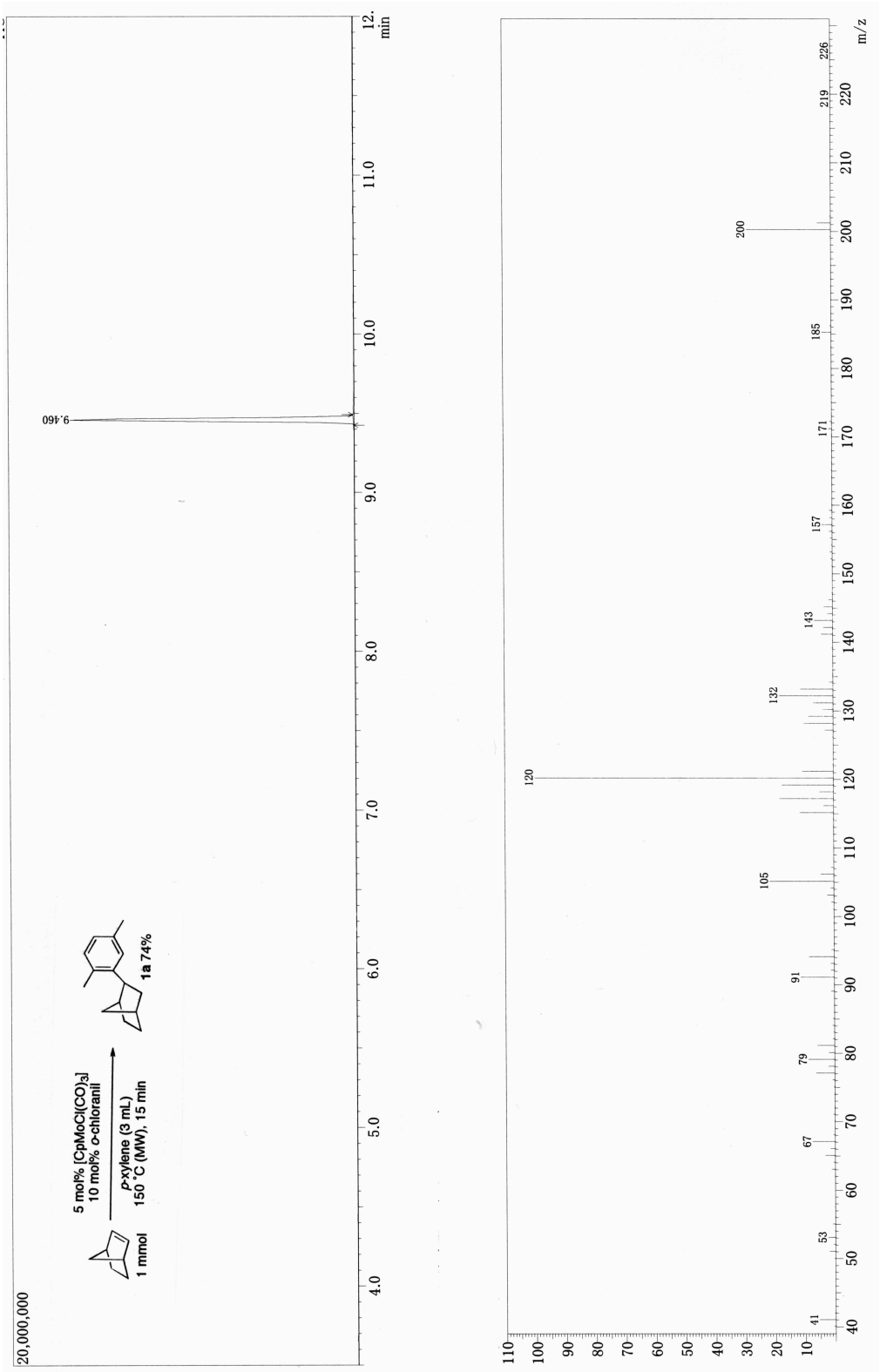

Figure S1. GC-MS chart of **1a**.

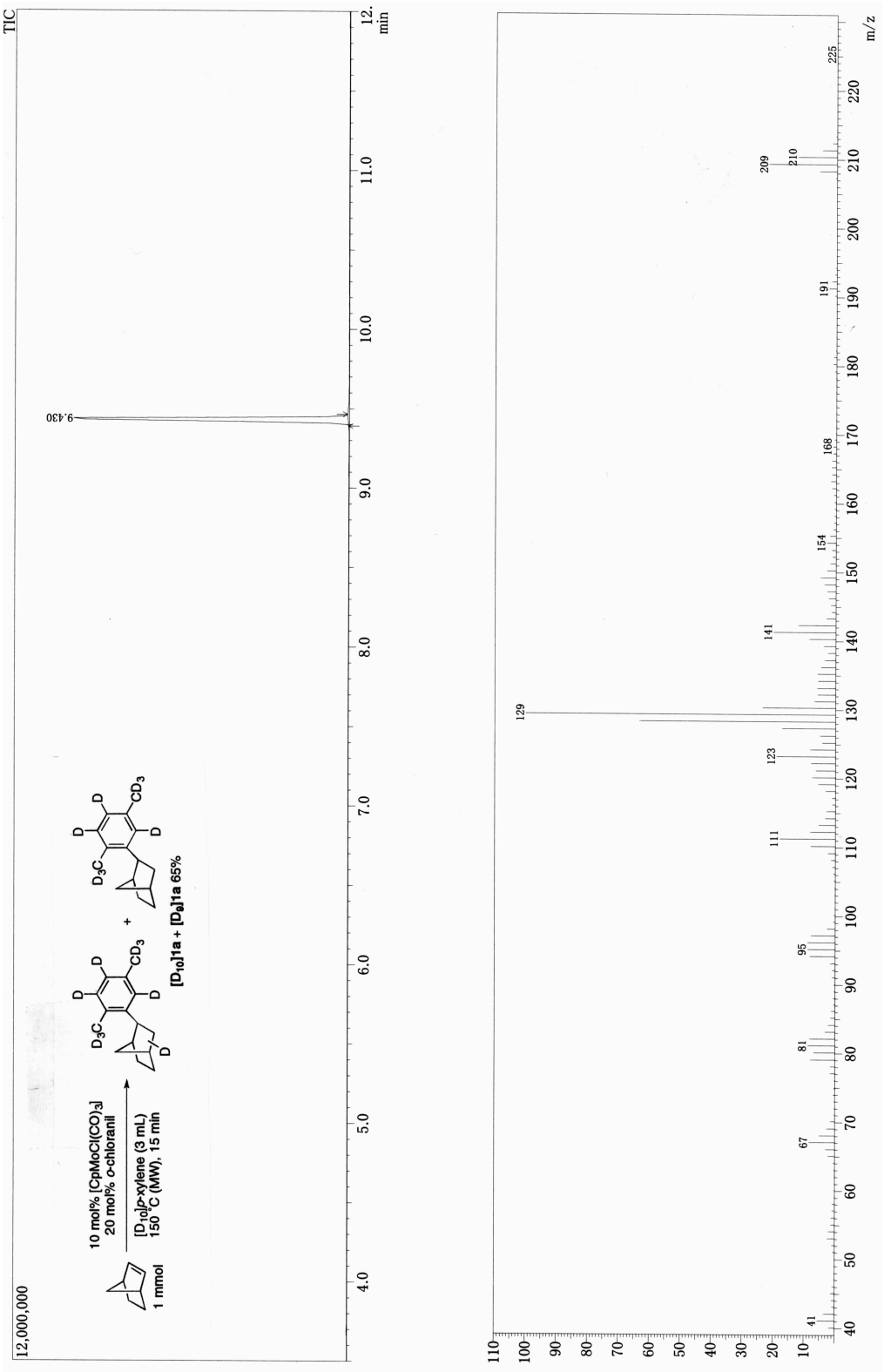

Figure S2. GC-MS chart of a mixture of $[D_{10}]$**1a** and $[D_9]$**1a**.