

**Synthesis of Ferrocenyl Alkenes, Dienes and Enynes via Samarium Diiodide Promoted
Tandem Addition and Dehydration of Ferrocenyl Carbonyls with Halides**

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Supporting Information:

Additional experimental procedures and spectra of new compounds (14 pages).

1-Ferrocenyl-2-phenylethene (3a).^{3c} According to the representative procedure, the SmI₂ promoted condensation of ferrocenylcarboxaldehyde (257 mg, 1.2 mmol) and benzyl bromide (342 mg, 2.0 mmol) gave the title compound (343 mg, 95% yield). Red solid, mp 118 °C; IR (KBr) 1636, 1597 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.16 (5 H, s), 4.30 (2 H, t, *J* = 1.7 Hz), 4.49 (2 H, t, *J* = 1.7 Hz), 6.72 (1 H, d, *J* = 16.2 Hz), 6.90 (1 H, d, *J* = 16.2 Hz), 7.22–7.47 (5 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 66.9 (2 ×), 69.0 (2 ×), 69.2 (5 ×), 83.3, 125.8, 126.0, 126.7, 127.0, 128.6, 131.9; FAB-MS *m/z* 288 (M⁺); HRMS Calcd for C₁₈H₁₆Fe: 288.0601. Found: 288.0628.

1-Ferrocenyl-2-(4-cyanophenyl)ethene (3b). According to the representative procedure, the SmI₂ promoted condensation of ferrocenylcarboxaldehyde (257 mg, 1.2 mmol) and 4-cyanobenzyl bromide (394 mg, 2.0 mmol) gave the title compound (360 mg, 95% yield). Red solid, mp 182–184 °C; IR (KBr) 2223, 1635, 1599 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.13 (5 H, s), 4.34 (2 H, t, *J* = 1.5 Hz), 4.47 (2 H, t, *J* = 1.5 Hz), 6.65 (1 H, d, *J* = 16.1 Hz), 7.00 (1 H, d, *J* = 16.1 Hz), 7.46 (1 H, d, *J* = 8.3 Hz), 7.56 (1 H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 67.3 (2 ×), 69.3 (5 ×), 69.8 (2 ×), 81.9, 109.4, 119.3, 123.9, 126.0, 131.6, 132.4, 142.3, 149.9; FAB-MS *m/z* 313 (M⁺); HRMS Calcd for C₁₉H₁₅FeN: 313.0554. Found: 313.0548.

1-Ferrocenyl-2-(3-methoxyphenyl)ethene (3c). According to the representative procedure, the SmI₂ promoted condensation of ferrocenylcarboxaldehyde (257 mg, 1.2 mmol) and 3-methoxybenzyl bromide (402 mg, 2.0 mmol) gave the title compound (343 mg, 90% yield). Red solid, mp 99–101 °C; IR (KBr) 1604, 1597 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.84 (3 H, s, OMe), 4.14 (5 H, s), 4.29 (2 H, s), 4.47 (2 H, s), 6.65 (1 H, d, *J* = 16.1 Hz), 6.78 (1 H, m), 6.85 (1 H, d, *J* = 16.1 Hz), 6.96 (1 H, s), 7.02 (1 H, *J* = 7.8 Hz), 7.24 (1 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 55.2 (OMe), 66.9 (2 ×), 69.1 (2 ×), 69.3 (5 ×), 83.3, 111.1, 112.4, 118.5, 125.9, 129.3, 129.6, 139.4, 159.9; FAB-MS *m/z* 318 (M⁺); HRMS Calcd for C₁₇H₁₉FeO: 318.0707. Found:

318.0718.

1-Ferrocenyl-2-(2-naphthyl)ethene (3d). According to the representative procedure, the SmI₂ promoted condensation of ferrocenylcarboxaldehyde (257 mg, 1.2 mmol) and 2-(bromomethyl)naphthalene (442 mg, 2.0 mmol) gave the title compound (305 mg, 75% yield). Red-brown solid, mp 143–145 °C; IR (KBr) 1626 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.15 (5 H, s), 4.30 (2 H, t, *J* = 1.7 Hz), 4.50 (2 H, t, *J* = 1.7 Hz), 6.85 (1 H, d, *J* = 16.1 Hz), 7.00 (1 H, d, *J* = 16.1 Hz), 7.40–7.46 (2 H, m), 7.63–7.81 (5 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 66.9 (2 ×), 69.1 (2 ×), 69.2 (5 ×), 83.4, 123.3, 125.2, 125.5, 126.1, 126.3, 127.4, 127.7, 127.8, 128.2, 132.6, 133.9, 135.4; FAB-MS *m/z* 338 (M⁺); HRMS Calcd for C₂₂H₁₈Fe: 338.0758. Found: 338.0769.

2-Ferrocenyl-1-phenylpropene (3e). According to the representative procedure, the SmI₂ promoted condensation of acetylferrocene (274 mg, 1.2 mmol) and benzyl bromide (342 mg, 2.0 mmol) gave the title compound (355 mg, 98% yield). Red-brown solid, mp 64–66 °C; IR (KBr) 1627 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.28 (3 H, s), 4.18 (5 H, s), 4.32 (2 H, s), 4.54 (2 H, s), 6.79 (1 H, s), 7.24–7.44 (5 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 17.1, 65.7 (2 ×), 68.7 (2 ×), 69.1 (5 ×), 89.1, 123.1, 125.9 (2 ×), 128.1 (2 ×), 129.0, 134.9, 138.4; FAB-MS *m/z* 302 (M⁺); HRMS Calcd for C₁₉H₁₈Fe: 302.0758. Found: 302.0767.

2-Ferrocenyl-1-(4-cyanophenyl)propene (3f). According to the representative procedure, the SmI₂ promoted condensation of acetylferrocene (274 mg, 1.2 mmol) and 4-cyanobenzyl bromide (392 mg, 2.0 mmol) gave the title compound (390 mg, 98% yield). Red solid, mp 113–115 °C; IR (KBr) 2225, 1627, 1605 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.22 (3 H, s), 4.14 (5H, s), 4.31 (2 H, t, *J* = 1.9 Hz), 4.49 (2 H, t, *J* = 1.9 Hz), 6.67 (1 H, s), 7.38 (2 H, d, *J* = 8.4 Hz), 7.59 (2 H, d, *J* = 8.4 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 17.3, 65.9 (2 ×), 69.2 (7 ×), 87.8, 108.8, 119.1, 121.2, 129.2 (2 ×), 131.8 (2 ×), 139.2, 142.9; FAB-MS *m/z* 327 (M⁺); HRMS Calcd for C₂₀H₁₇FeN: 327.0710. Found: 327.0697.

2-Ferrocenyl-1-(4-trifluoromethylphenyl)propene (3g). According to the representative procedure, the SmI₂ promoted condensation of acetylferrocene (274 mg, 1.2 mmol) and 4-(trifluoromethyl)benzyl bromide (478 mg, 2.0 mmol) gave the title compound (436 mg, 98% yield). Red-brown solid, mp 132–134 °C (from CHCl₃/hexane); IR (KBr) 1615 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 2.22 (3 H, s), 4.15 (5 H, s), 4.30 (2 H, t, *J* = 1.9 Hz), 4.49 (2 H, t, *J* = 1.9 Hz), 6.72 (1 H, s), 7.40 (2 H, d, *J* = 8.1 Hz), 7.59 (2 H, d, *J* = 8.1 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 65.9 (2 ×), 69.1 (2 ×), 69.2 (5 ×), 88.3, 121.7, 125.0, 129.0, 137.7, 142.0; FAB-MS *m/z* 370 (M⁺); HRMS Calcd for C₂₀H₁₇F₃Fe: 370.0632. Found: 370.0619. The structure was confirmed by an X-ray diffraction analysis, and the crystal structure has been deposited at the Cambridge Crystallographic Data Center.

1,2-Diphenyl-1-ferrocenylethene (3h). According to the representative procedure, the SmI₂ promoted condensation of benzoylferrocene (348 mg, 1.2 mmol) and benzyl bromide (342 mg, 2.0 mmol) gave the title compound (431 mg, 98% yield). Red solid, mp 102–104 °C; IR (KBr) 1597 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.12 (5 H, s), 4.22 (2 H, t, *J* = 1.6 Hz), 4.27 (2 H, t, *J* = 1.6 Hz), 6.88–7.39 (11 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 66.8 (2 ×), 68.9 (2 ×), 69.4 (5 ×), 88.0, 124.1, 126.0, 127.1, 127.9, 128.5, 128.9, 129.4, 137.3, 140.1, 140.7; FAB-MS *m/z* 364 (M⁺); HRMS Calcd for C₂₄H₂₀Fe: 364.0914. Found: 364.0924.

1-Ferrocenyl-1-phenyl-2-(4-cyanophenyl)ethene (3i). According to the representative procedure, the SmI₂ promoted condensation of benzoylferrocene (348 mg, 1.2 mmol) and 4-cyanobenzyl bromide (392 mg, 2.0 mmol) gave the title compound (463 mg, 99% yield). Red solid, mp 175–177 °C (from CHCl₃/hexane); IR (KBr) 2224, 1599 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 4.14 (5 H, m), 4.30 (4 H, m), 6.86 (1 H, s), 6.92 (2 H, *J* = 8.4 Hz), 7.23–7.42 (7 H, m); ¹³C NMR (CDCl₃, 50 MHz) δ 67.2 (2 ×), 69.5 (7 ×), 86.5, 108.7, 119.1, 121.9, 127.7, 128.7,

129.0, 129.1, 131.6, 139.1, 142.0, 145.5; FAB-MS m/z 389 (M^+); HRMS Calcd for $C_{25}H_{19}FeN$: 389.0867. Found: 389.0876. The structure was confirmed by an X-ray diffraction analysis, and the crystal structure has been deposited at the Cambridge Crystallographic Data Center.

1-Ferrocenyl-1-phenyl-2-(3-methoxyphenyl) ethene (3j). According to the representative procedure, the SmI_2 promoted condensation of benzoylferrocene (348 mg, 1.2 mmol) and 3-methoxybenzyl bromide (402 mg, 2.0 mmol) gave the title compound (434 mg, 92% yield). Red solid, mp 109–111 °C; IR (KBr) 1597, 1578 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 3.47 (3 H, s, OMe), 4.16 (5 H, s), 4.27–4.29 (4 H, m), 6.39 (1 H, s), 6.60–6.65 (2 H, m), 6.89 (1 H, s), 7.04 (1 H, t, $J = 7.7$ Hz), 7.33–7.45 (5 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 54.7, 66.8 (2 $\times$), 69.0 (2 $\times$), 69.4 (5 $\times$), 87.9, 113.0 (2 $\times$), 122.0, 123.9, 127.2, 128.6 (2 $\times$), 128.9, 129.5 (2 $\times$), 138.6, 140.3, 141.0, 159.1; FAB-MS m/z 394 (M^+); HRMS Calcd for $C_{25}H_{23}FeO$: 394.1020. Found: 394.1028.

1-Ferrocenyl-1-phenyl-2-(2-naphthyl)ethene (3k). According to the representative procedure, the SmI_2 promoted condensation of benzoylferrocene (348 mg, 1.2 mmol) and 2-(bromomethyl)naphthalene (442 mg, 2.0 mmol) gave the title compound (435 mg, 88% yield). Red solid, mp 145–147 °C; IR (KBr) 1612 cm^{-1} ; 1H NMR ($CDCl_3$, 200 MHz) δ 4.19 (5 H, s), 4.30 (2 H, t, $J = 2.0$ Hz), 4.36 (2 H, t, $J = 2.0$ Hz), 6.96 (1 H, dd, $J = 8.6, 1.8$ Hz), 7.10 (1 H, s), 7.70–7.35 (11 H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 66.9 (2 $\times$), 69.5 (5 $\times$), 87.9, 124.2, 125.5, 125.9, 127.0, 127.1, 127.4, 127.8, 128.1, 128.6, 128.6 (2 $\times$), 129.6 (2 $\times$), 131.9, 133.4, 135.1, 140.1, 141.3; FAB-MS m/z 414 (M^+); HRMS Calcd for $C_{28}H_{22}Fe$: 414.1071. Found: 414.1060.

1-Ferrocenyl-1,3-butadiene (5a).^{4a, b} According to the representative procedure, the SmI_2 promoted condensation of ferrocenylcarboxaldehyde (257 mg, 1.2 mmol) and allyl bromide (242 mg, 2.0 mmol) gave the title compound (280 mg, 98% yield). Orange solid, mp 87–88 °C; 1H NMR ($CDCl_3$, 300 MHz) δ 4.11 (5 H, s, Fc), 4.23 (2 H, t, $J = 1.3$ Hz, Fc), 4.34 (2 H, t, $J = 1.3$

Hz), 5.01–5.05 (1 H, m, H-4), 5.14– 5.20 (1 H, m, H-4), 6.32–6.43 (3 H, m, H-1, 2, 3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 66.8 (2 $\times$), 68.9 (2 $\times$), 69.2 (5 $\times$), 83.1, 114.7, 127.4, 131.2, 137.5; FAB-MS m/z 238 (M^+); HR-FABMS: Calcd. for $\text{C}_{14}\text{H}_{14}\text{Fe}$: 238.0445. Found: 238.0437.

1-Ferrocenyl-1-phenyl-1,3-butadiene (5c). According to the representative procedure, the SmI_2 promoted condensation of benzoylferrocene (348 mg, 1.2 mmol) and allyl bromide (242 mg, 2.0 mmol) gave the title compound (373 mg, 99 % yield). Brown oil, ^1H NMR (CDCl_3 , 300 MHz) δ 4.14 (5 H, s, Fc), 4.23 (4 H, m, Fc), 5.02 (1 H, d, J = 9.7 Hz, H-4), 5.29 (1 H, d, J = 17.2 Hz, H-4), 6.25 (1 H, ddd, J = 9.7, 11.1, 17.2 Hz, H-3), 6.63 (1 H, d, J = 11.1 Hz, H-2), 7.31–7.46 (5 H, m, Ph); ^{13}C NMR (CDCl_3 , 75 MHz) δ 66.8 (2 $\times$), 68.9 (2 $\times$), 69.4 (5 $\times$), 86.3, 115.7, 125.1, 127.1, 127.9 (2 $\times$), 129.6 (2 $\times$), 134.8, 139.3, 141.9; FAB-MS m/z 314 (M^+); HR-FABMS Calcd for $\text{C}_{20}\text{H}_{18}\text{Fe}$: 314.0758. Found: 314.0745.

2-Ferrocenyl-2-penten-4-yne (7a). According to the representative procedure, the SmI_2 promoted condensation of acetylferrocene (274 mg, 1.2 mmol) and propargyl bromide (238 mg, 2.0 mmol) gave the title compound (292 mg, 98 % yield) as a mixture of (*E*)- and (*Z*)-isomers (90:10) after chromatography on neutral Al_2O_3 . Red-brown oil; IR (KBr) 2090, 1600 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz, *E/Z* = 90:10) δ 2.22 (3 H, s)/2.16, 3.20 (1 H, d, J = 2.4 Hz), 4.11 (5 H, s), 4.28 (2 H, m), 4.40 (2 H, m)/4.94, 5.64 (1 H, m)/5.42; ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.3, 65.9 (2 $\times$), 69.3 (5 $\times$), 69.5 (2 $\times$), 81.1, 82.8, 85.2, 100.6, 149.9; FAB-MS m/z 250 (M^+); HRMS Calcd for $\text{C}_{15}\text{H}_{14}\text{Fe}$: 250.0445, Found: 250.0450.

1-Ferrocenyl-1-phenyl-1-buten-3-yne (7b). According to the representative procedure, the SmI_2 promoted condensation of benzoylferrocene (348 mg, 1.2 mmol) and propargyl bromide (238 mg, 2.0 mmol) gave the title compound (258 mg, 96 % yield) as a mixture of (*E*)- and (*Z*)-isomers (82:18) after chromatography on neutral Al_2O_3 . Red-brown oil; IR (KBr) 2084, 1588

cm⁻¹; ¹H NMR (CDCl₃, 300 MHz, *E/Z* = 82:18) δ 2.94/3.55(1 H, d, *J* = 2.2 Hz), 4.12 (5 H, s)/4.16, 4.29 (4 H, br s)/4.86, 6.00 (1H, d, *J* = 2.2 Hz)/5.58, 7.35–7.48 (5 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 67.5, 69.3, 69.7, 69.8, 70.0, 79.6, 80.8, 82.8, 84.1, 102.1, 103.5, 127.8, 127.9, 128.2, 128.9, 138.8, 150.9, 151.0, 154.4; FAB-MS *m/z* 312 (M⁺); HRMS Calcd for C₂₀H₁₆Fe: 312.0601, Found: 312.0595.

1-Ferrocenyl-3-buten-1-ol (8a).^{2a, 5a} Under an atmosphere of argon, a solution of allyl bromide (242 mg, 2.0 mmol) in THF (10 mL) was added to a freshly prepared SmI₂ solution (0.1 M) in THF (20 mL). After which, a solution of ferrocenecarboxaldehyde (257 mg, 1.2 mmol) in THF (10 mL) was added. The mixture was stirred for 30 min at room temperature, and quenched by addition of water (1 mL). The mixture was filtered through a short silica gel column, and eluted by EtOAc/hexane (1:1) to give the title compound (298 mg, 97% yield). Orange oil; ¹H NMR (CDCl₃, 300 MHz) δ 2.05 (1 H, d, *J* = 2.9 Hz), 2.42 (2 H, m), 4.14–4.25 (9 H, m), 4.40 (1 H, m), 4.51 (2 H, m), 5.86 (1 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 42.7, 65.5, 66.9, 67.7, 67.8, 69.1, 93.3, 117.3, 134.9; FAB-MS *m/z* 256 (M⁺); HRMS Calcd for C₁₄H₁₆FeO: 256.0551. Found: 256.0540.

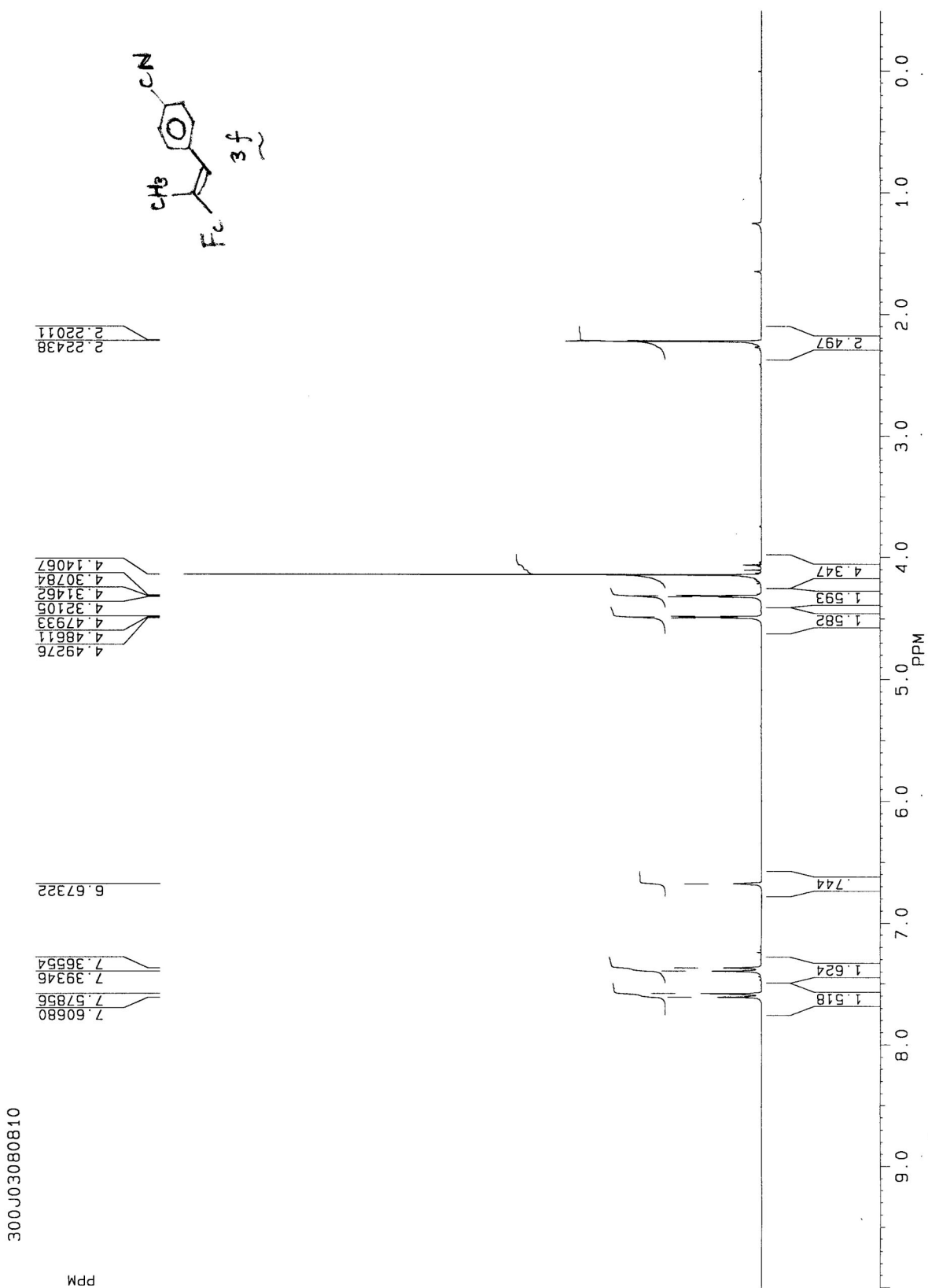
1-Ferrocenyl-1-phenyl-3-buten-1-ol (8c). The SmI₂ promoted addition reaction of allyl bromide (242 mg, 2.0 mmol) to benzoylferrocene (348 mg, 1.2 mmol), by a procedure similar to that for **8a**, gave the title compound (390 mg, 98% yield). Orange oil; ¹H NMR (CDCl₃, 300 MHz) δ 2.73 (1 H, s), 2.87 (2 H, m), 3.99–4.34 (9 H, m), 5.04 (2 H, m), 5.69 (1 H, m), 7.14–7.40 (5 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 48.2, 66.6 (2 ×), 67.7, 68.0, 68.4 (5 ×), 73.9, 100.0, 118.1, 125.5 (2 ×), 126.3, 127.6 (2 ×), 133.9, 145.6.

4-Ferrocenyl-1-butene (9a).^{11a} Under an atmosphere of nitrogen, a SmI₂ solution (0.1 M) in THF (40 mL) was prepared. A mixture of alcohol **8a** (256 mg, 1.0 mmol) and water (99 mg, 5.5 mmol) in THF (10 mL) was added. The reaction mixture was refluxed at 68 °C for 2 h, cooled,

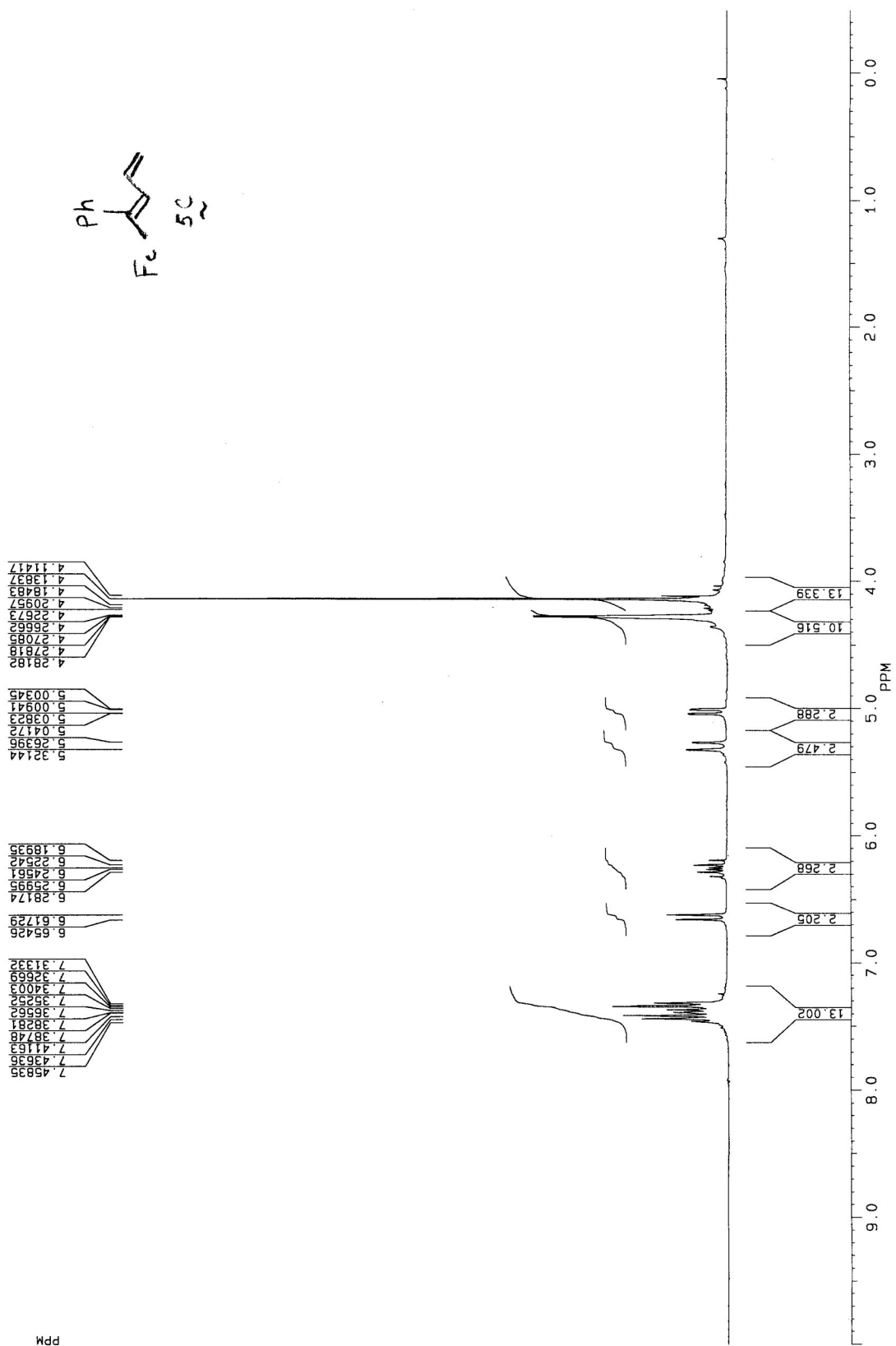
and filtered through a short silica gel column by elution with EtOAc/hexane (1:1) to give the title compound (231 mg, 96% yield). Brown oil; ^1H NMR (CDCl_3 , 200 MHz) δ 2.32 (2 H, m), 2.45 (2 H, m), 4.13 (9 H, m), 4.98–5.14 (2 H, m), 5.81–5.98 (1 H, m); ^{13}C NMR (CDCl_3 , 50 MHz) δ 29.0, 35.2, 67.0 (2 $\times$), 68.0 (2 $\times$), 68.4 (5 $\times$), 88.6, 114.5, 138.5; Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{Fe}$: C, 70.03; H, 6.72. Found: C, 70.15; H, 6.55.

4-Ferrocenyl-4-phenyl-1-butene (9c).^{11b} Reduction of alcohol **8c** (332 mg, 1.0 mmol), by a procedure similar to that for **9a**, gave the title compound (313 mg, 99% yield). ^1H NMR (CDCl_3 , 300 MHz) δ 2.60 (1 H, m), 2.81 (1 H, m), 3.68 (1 H, dd, $J = 10.3, 4.7$ Hz), 3.94–4.18 (9 H, m), 4.90–5.02 (2 H, m), 5.62–5.76 (1 H, m), 7.14–7.29 (5 H, m); ^{13}C NMR (CDCl_3 , 75 MHz) δ 41.5, 46.2, 66.9 (2 $\times$), 67.5, 67.6, 68.6 (5 $\times$), 93.7, 115.8, 126.1, 127.9 (2 $\times$), 128.1 (2 $\times$), 137.1, 144.8; FAB-MS m/z 316 (M^+); HRMS Calcd for $\text{C}_{20}\text{H}_{20}\text{Fe}$: 316.0914. Found: 316.0893.

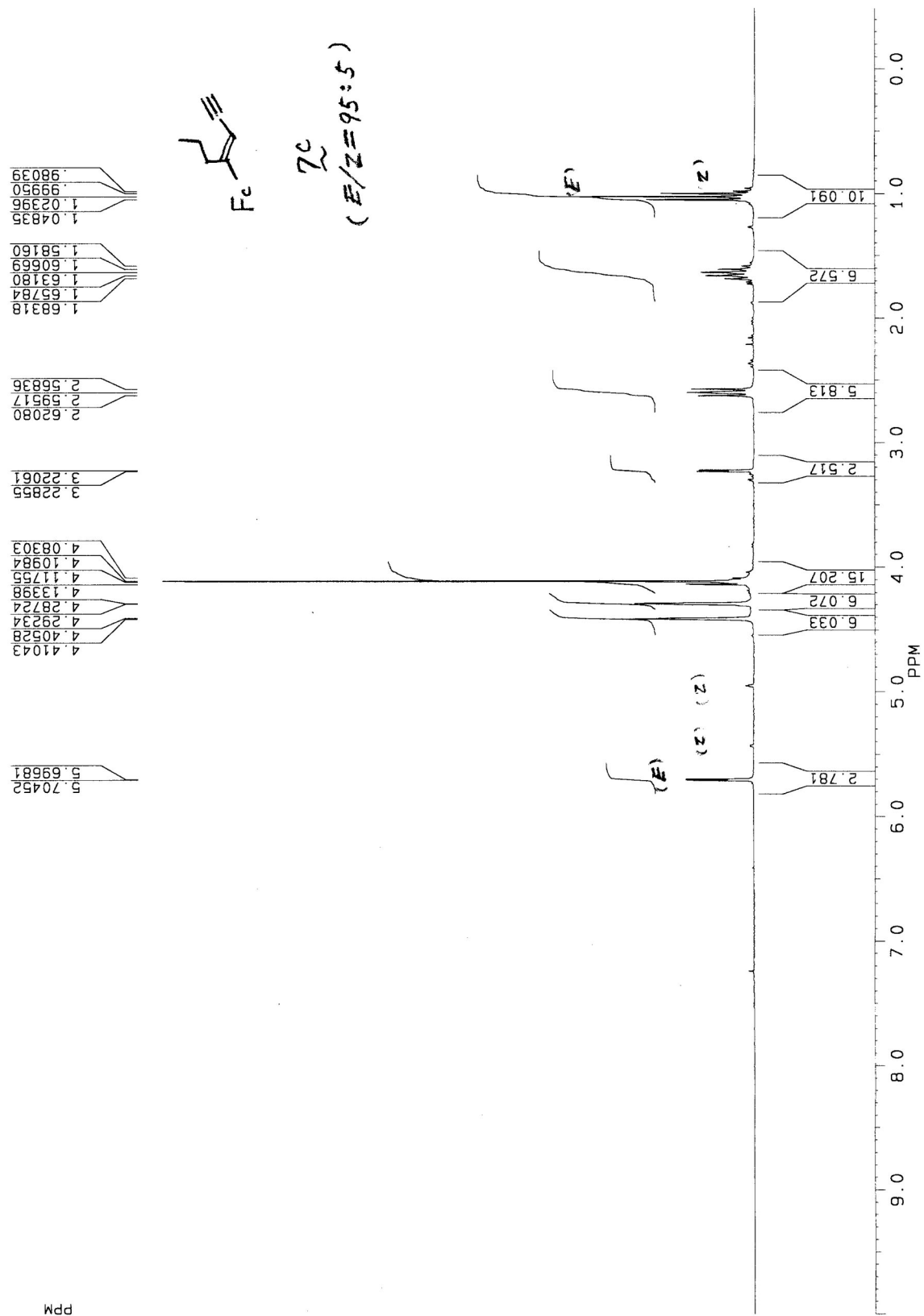
2-Ferrocenyl-3-phenyl-2-propanol (15). Under an atmosphere of argon, Mg powders (72 mg, 3 mmol) were placed in a round-bottomed flask. A freshly prepared SmI_2 solution (0.1 M) in anhydrous THF (2 mL) was added. A mixture of acetylferrocene (229 mg, 1 mmol) and benzyl bromide (182 mg, 1.5 mmol) in THF (20 mL) was added. The deep blue color of SmI_2 discharged. After stirring for 1 h, the light blue color resumed, and the reaction mixture was quenched by addition of water (1 mL). The mixture was chromatographed on a short silica gel column by elution with EtOAc/hexane (1:1) to give the title compound (318 mg, 99%). Red-brown oil; IR (KBr) 3454 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 1.46 (3 H, s), 2.23 (1 H, s), 2.90 (1 H, d, $J = 13.0$ Hz), 3.00 (1 H, d, $J = 13.0$ Hz), 3.96–4.26 (9 H, m), 6.98–7.03 (2 H, m), 7.19–7.24 (3 H, m); ^{13}C NMR (CDCl_3 , 50 MHz) δ 27.9, 50.0, 65.3, 67.2, 67.5, 67.8, 68.1 (5 $\times$), 71.2, 99.0, 126.1, 127.5 (2 $\times$), 130.6 (2 $\times$), 137.5; FAB-MS m/z 320 (M^+); HRMS Calcd for $\text{C}_{19}\text{H}_{20}\text{FeO}$: 320.0864. Found: 320.0853.

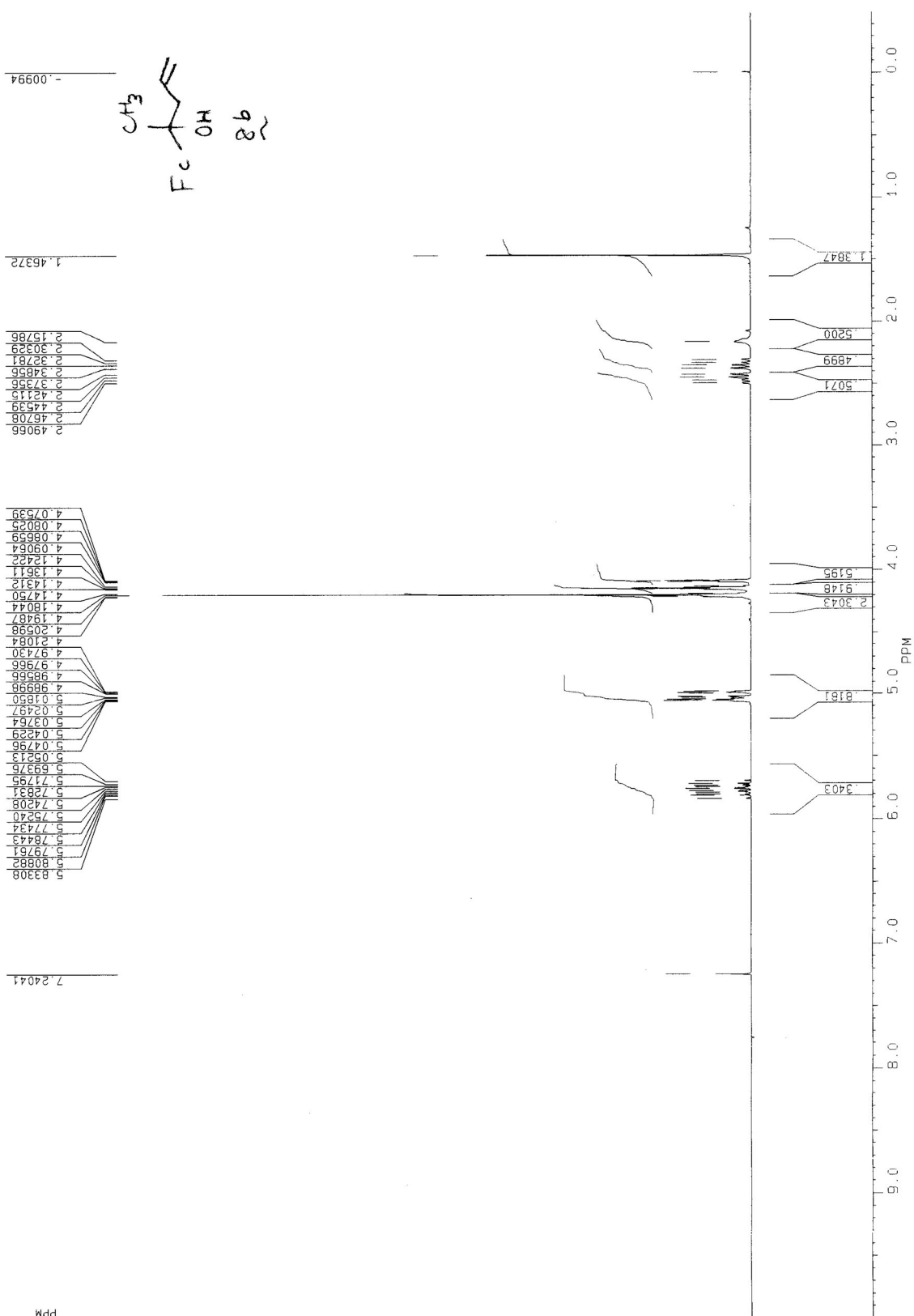


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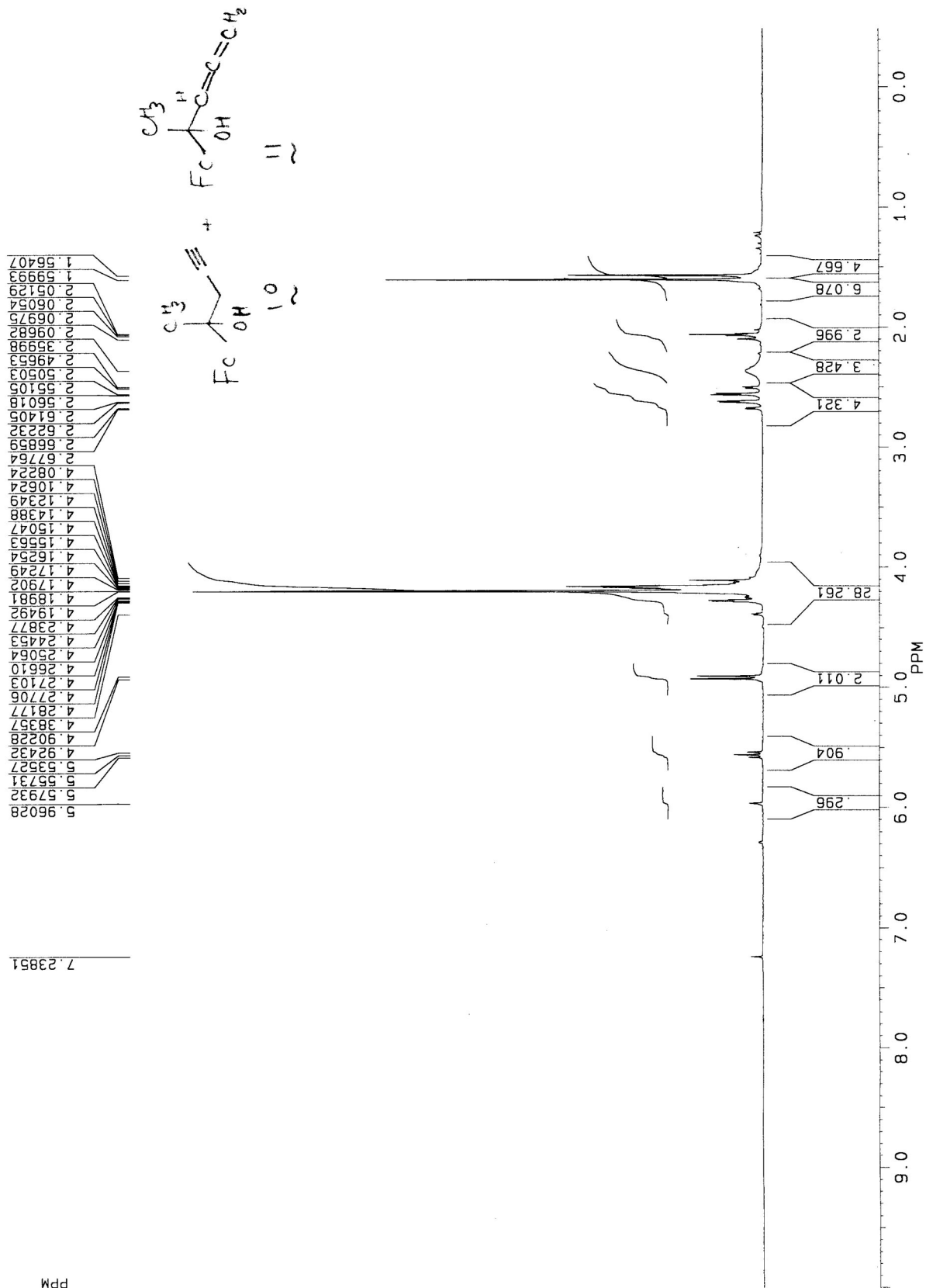


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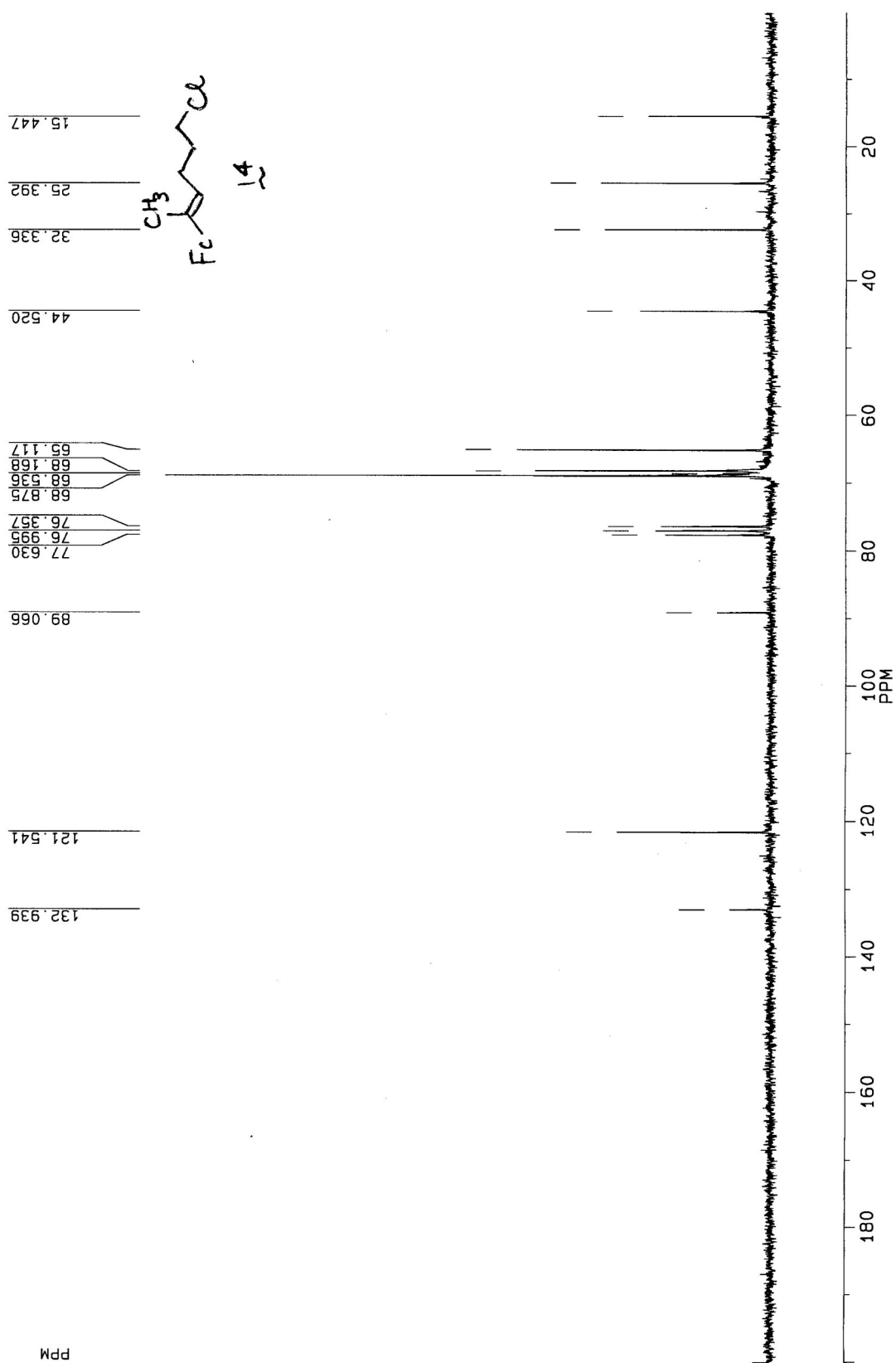




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